

Boosting Charge Separation in Conjugated Microporous Polymers via Fluorination for Enhancing Photocatalysis

Penghao Sun^a, Peigen Wang^a, Dong Yan^{a,c}, Qian Liu^a, Weijie Zhang^{a*}, Jiyong Deng^{a*}, Qingquan Liu^{b*}

^a Hunan Provincial Key Laboratory of Environmental Catalysis & Waste Recycling, School of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China.

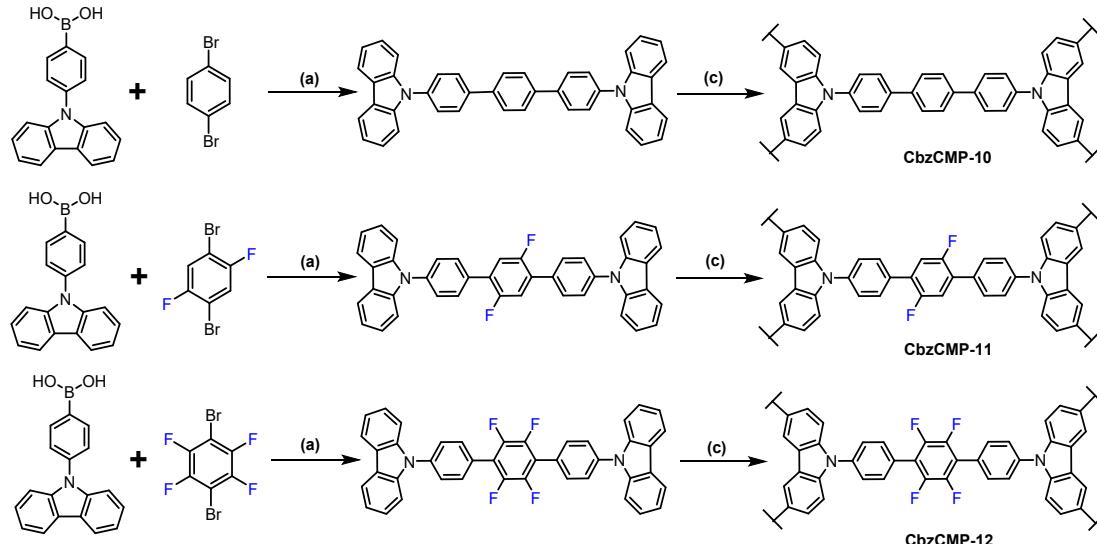
^b Hunan Provincial Key Lab of Advanced Materials for New Energy Storage and Conversion, Hunan University of Science and Technology, Xiangtan 411201, China.

^c College of Materials Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, China.

E-mail: weijie_zhang@hnie.edu.cn; djyong@yeah.net; qqliu@hnust.edu.cn.

1.procedures

1.1 Synthesis of intermediates, CbzCMP-10, CbzCMP-11, and CbzCMP-12



Scheme S1. Synthesis routes of CbzCMP-10, CbzCMP-11 and CbzCMP-12

1.1.1 Preparation of 4,4"-di(9H-carbazol-9-yl)-1,1':4',1"-terphenyl (DCT)

A mixture of (4-(9H-carbazol-9-yl)phenyl)boronic acid (2.76 g, 9.6 mmol), K₂CO₃ (2.76 g, 0.02 mol), 1,4-dibromobenzene (0.94 g, 4 mmol) and Pd(PPh₃)₄ (462.24 mg, 0.4 mmol) in DMF (50 mL) was heated to 150°C under N₂ for 24 h. After cooling to room temperature, the reaction mixture was concentrated to remove the solvent and the residue was purified by flash column chromatography to obtain as a white solid in 96% yield.

1.1.2 Preparation of 9,9'-(2',5'-difluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole) (DCT-2F)

A mixture of (4-(9H-carbazol-9-yl)phenyl)boronic acid (2.76 g, 9.6 mmol), K₂CO₃ (2.76 g, 0.02

mol) , 1,4-dibromo-2,5-difluorobenzene (1.09 g, 4 mmol) and Pd(PPh₃)₄ (462.24 mg, 0.4 mmol) in DMF (50 mL) was heated to 150°C under N₂ for 24 h. After cooling to room temperature, the reaction mixture was concentrated to remove the solvent and the residue was purified by flash column chromatography to obtain as a white solid in 91% yield.

1.1.3 Preparation of 9,9'-(2',3',5',6'-tetrafluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole) (DCT-4F)

A mixture of (4-(9H-carbazol-9-yl)phenyl)boronic acid (2.76 g, 9.6 mmol), K₂CO₃ (2.76 g, 0.02 mol) , 1,4-dibromo-2,3,5,6-tetrafluorobenzene (1.23 g, 4 mmol) and Pd(PPh₃)₄ (462.24 mg, 0.4 mmol) in DMF (50 mL) was heated to 150°C under N₂ for 24 h. After cooling to room temperature, the reaction mixture was concentrated to remove the solvent and the residue was purified by flash column chromatography to obtain as a white solid in 71% yield.

2. Photocatalyst Characterizations

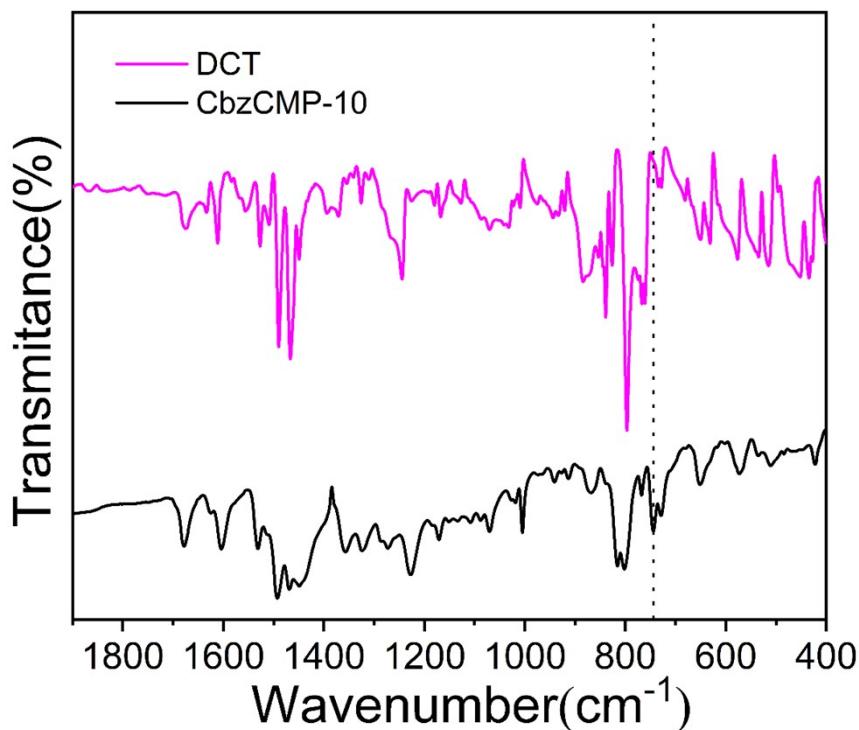


Figure S1. FT-IR of DCT and CbzCMP-10

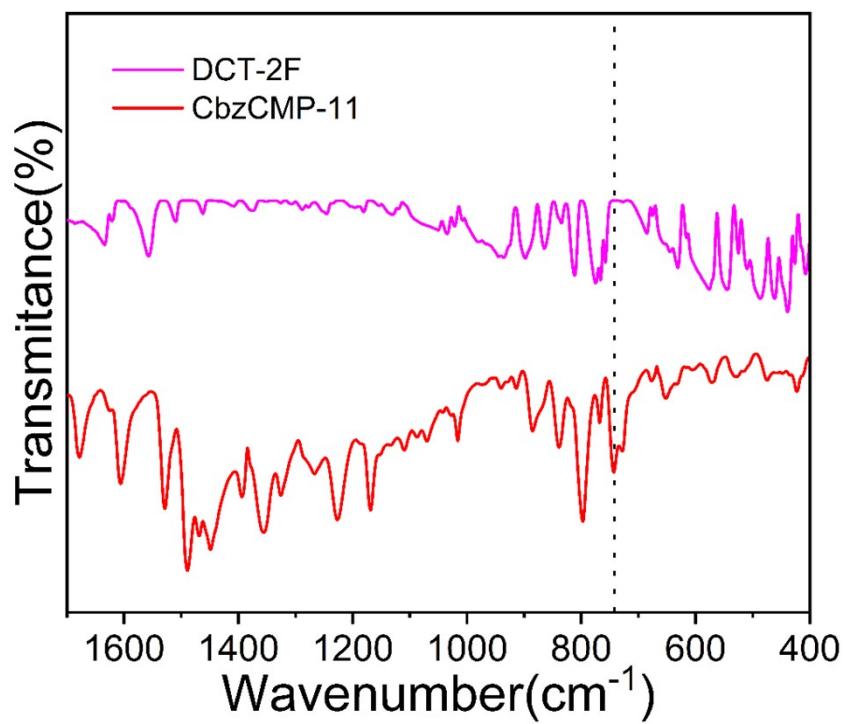


Figure S2. FT-IR of DCT-2F and CbzCMP-11

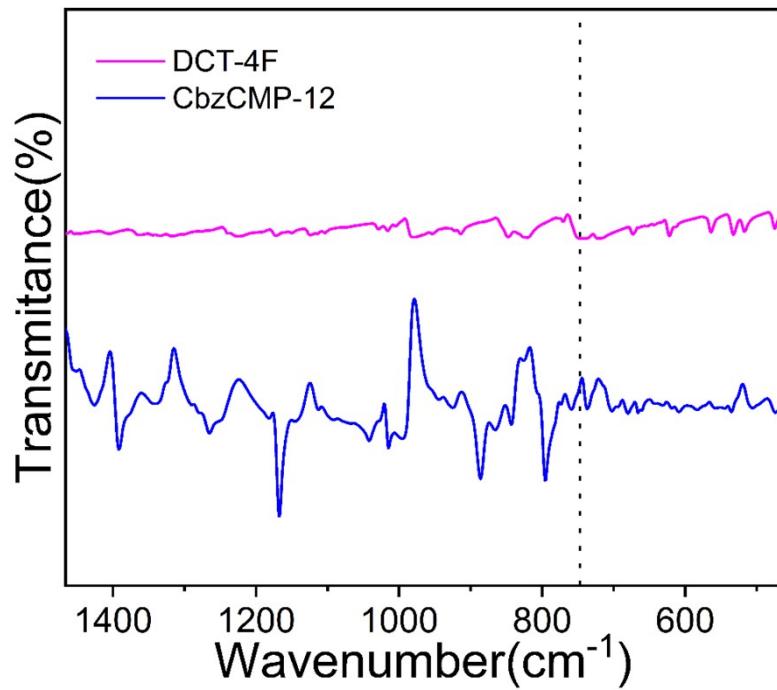


Figure S3. FT-IR of DCT-4F and CbzCMP-12

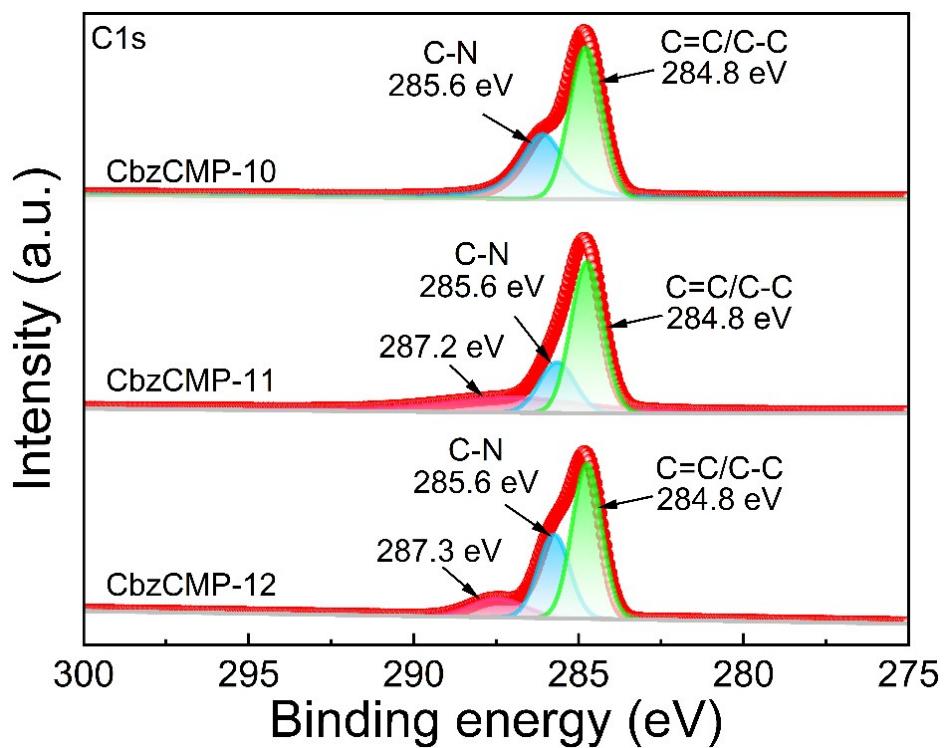


Figure S4. XPS spectra of C 1s

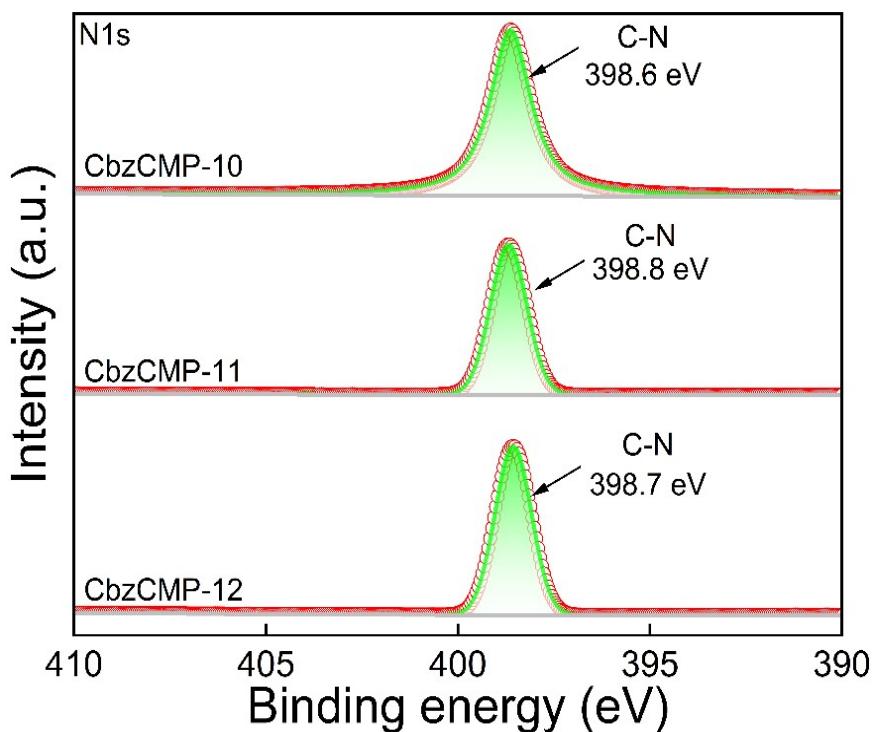


Figure S5. XPS spectra of N 1s

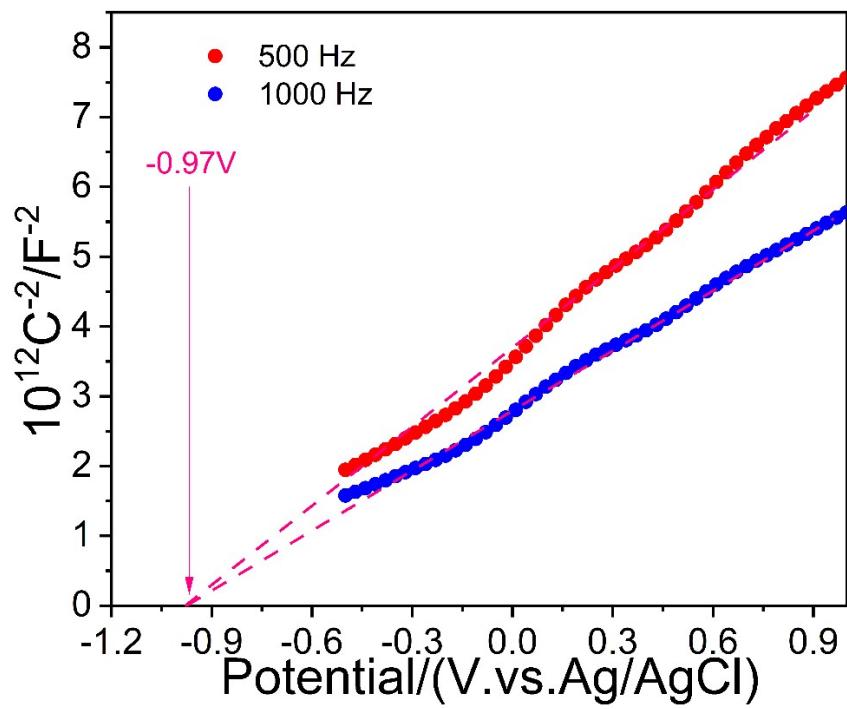


Figure S6. Mott-Schottky plots for CbzCMP-10 in 0.2 M Na_2SO_4 aqueous solution at 500 and 1000 Hz

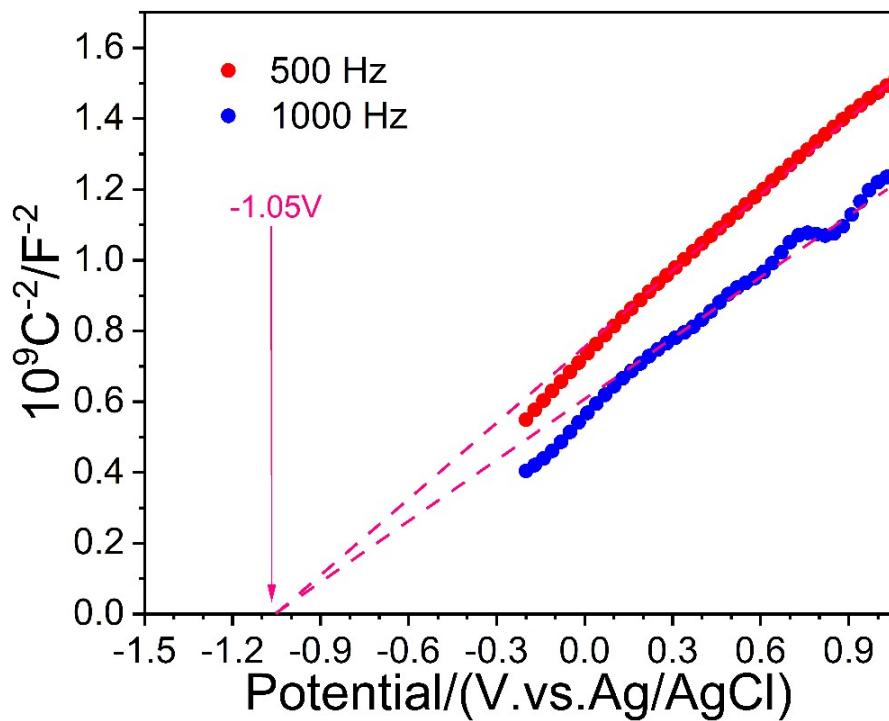


Figure S7. Mott-Schottky plots for CbzCMP-11 in 0.2 M Na_2SO_4 aqueous solution at 500 and 1000 Hz

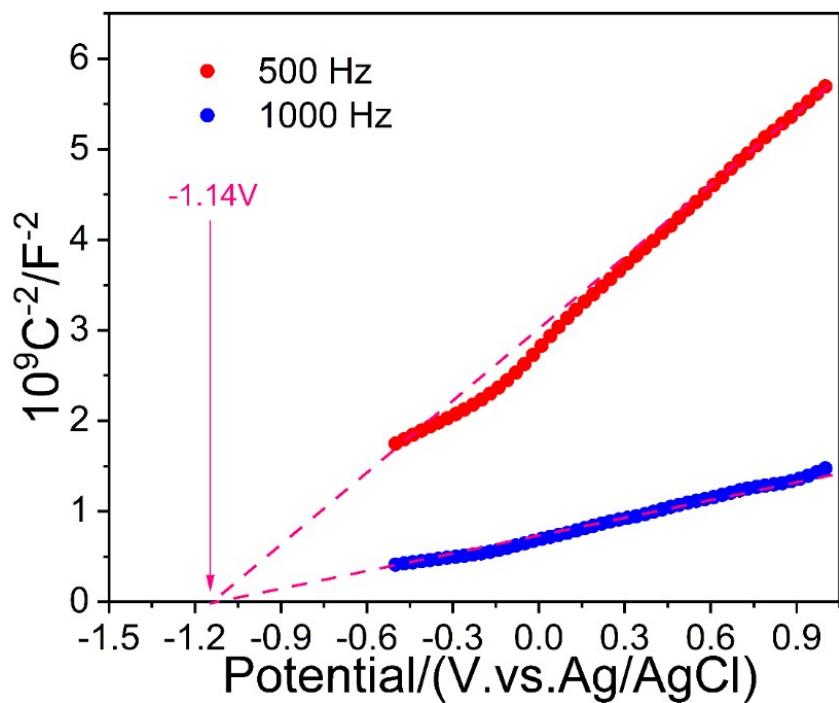


Figure S8. Mott-Schottky plots for CbzCMP-12 in 0.2 M Na₂SO₄ aqueous solution at 500 and 1000 Hz

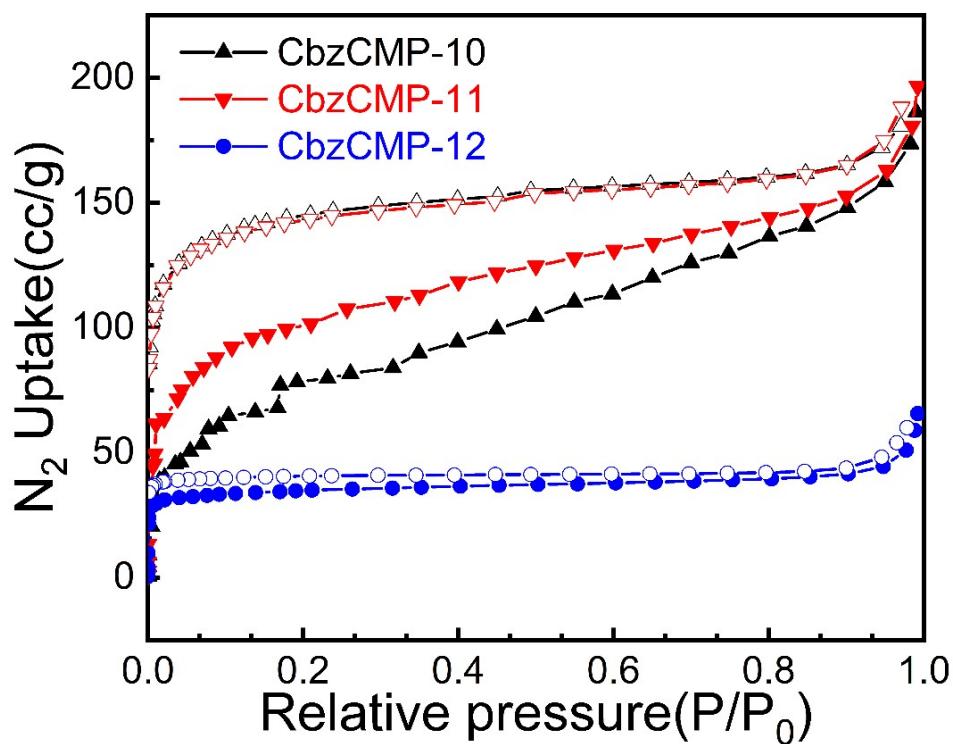


Figure S9. Nitrogen sorption isotherms of CbzCMP-10, CbzCMP-11 and CbzCMP-12 at 77 K

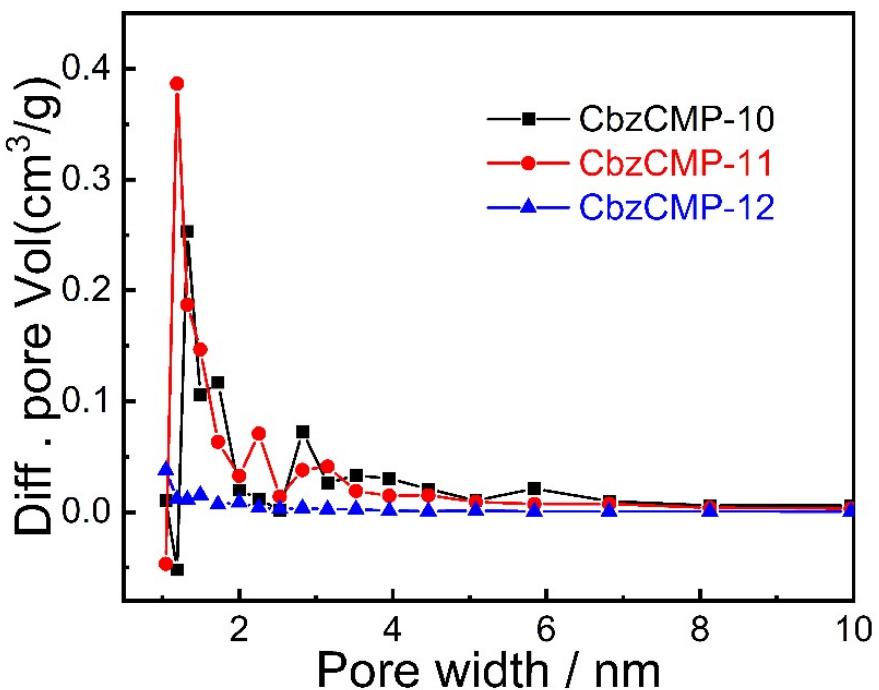


Figure S10. Pore size distributions of CbzCMP-10, CbzCMP-11 and CbzCMP-12

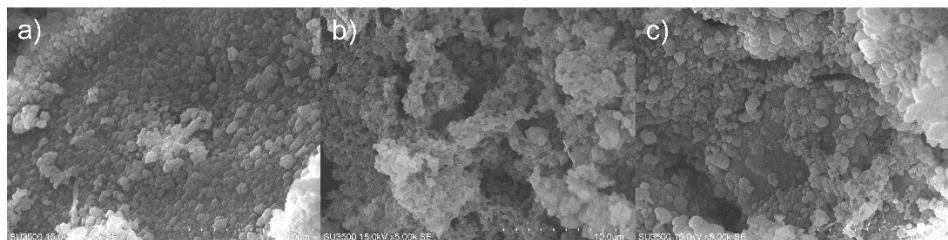


Figure S11. SEM (a, b, and c) images for CbzCMP-*n* (*n*=10, 11 and 12).

Table S1. Optimization of the photocatalytic conditions

Entry	Variation	Time(h)	Con. (%)	Sel. (%)
1	DCT	6	N. D	N. D
2	DCT-2F	6	N. D	N. D
3	DCT-4F	6	N. D	N. D
4	No light	6	N. D	N. D
5	N ₂	6	N. D	N. D
6	No photocatalyst	6	N. D	N. D
7	benzoquinone	6	7	>99
8	NaN ₃	6	12	> 99

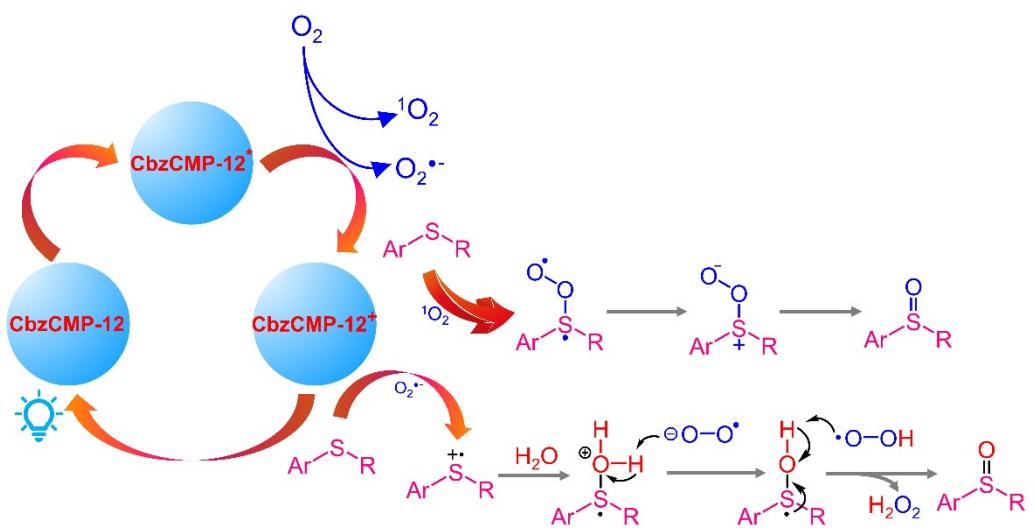


Figure S12. Proposed photocatalytic mechanism for the selective oxidation of sulfides by the CbzCMP-12 under visible light irradiation.

3. NMR Spectra

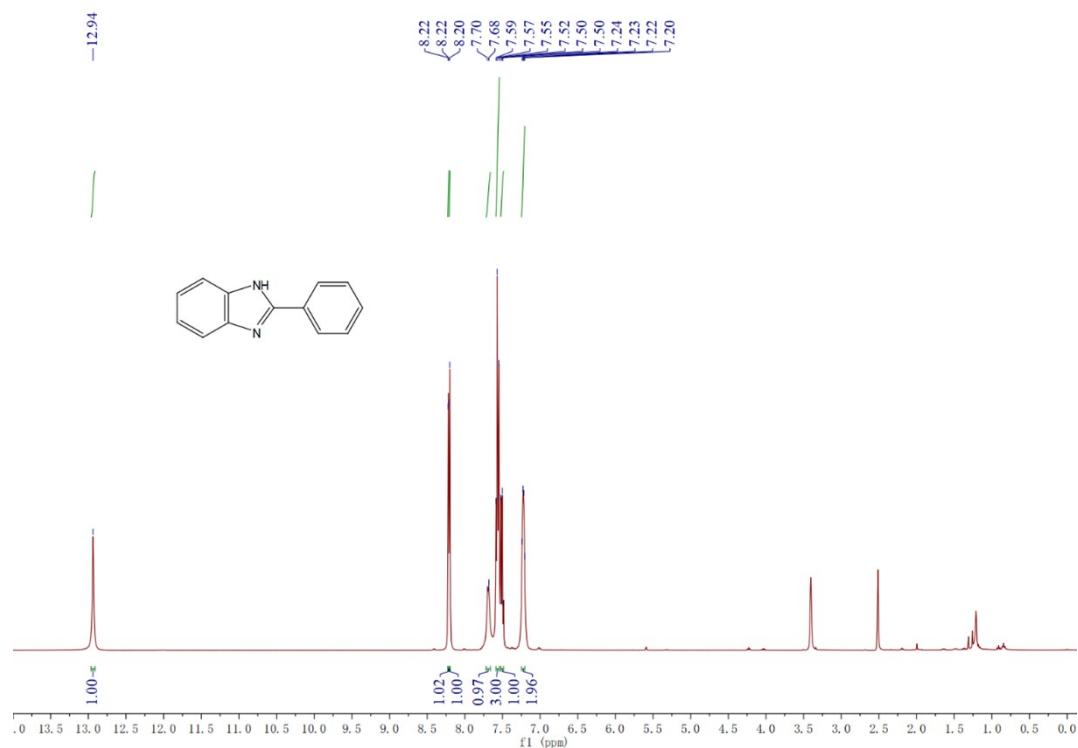


Figure S13. ^1H NMR for 2-phenyl-1H-benzo[d]imidazole

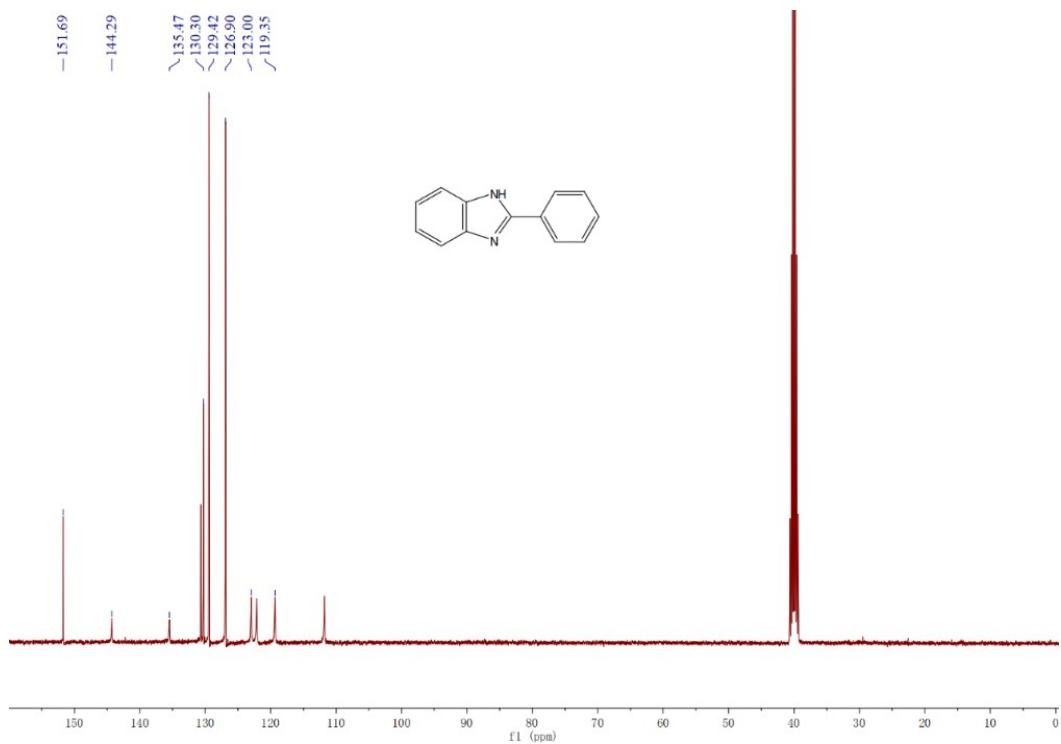


Figure S14. ^{13}C NMR for 2-phenyl-1H-benzo[d]imidazole

2-phenyl-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 12.94 (s, 1H), 8.22 (d, 1H), 8.20 (s, 1H), 7.70 (d, 1H), 7.56 (s, 3H), 7.57-7.50 (m, 1H), 7.24-7.20 (q, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 151.6, 144.2, 135.4, 130.3, 129.4, 126.9, 123.0, 119.3.

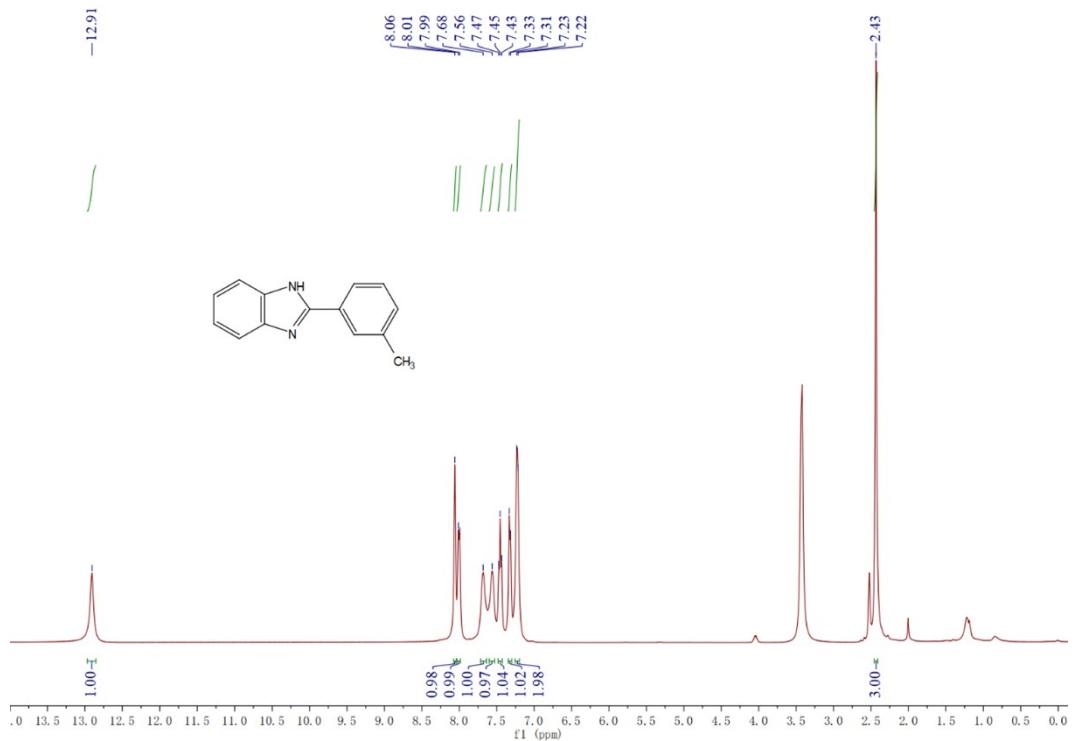


Figure S15. ^1H NMR for 2-(o-tolyl)-1H-benzo[d]imidazole

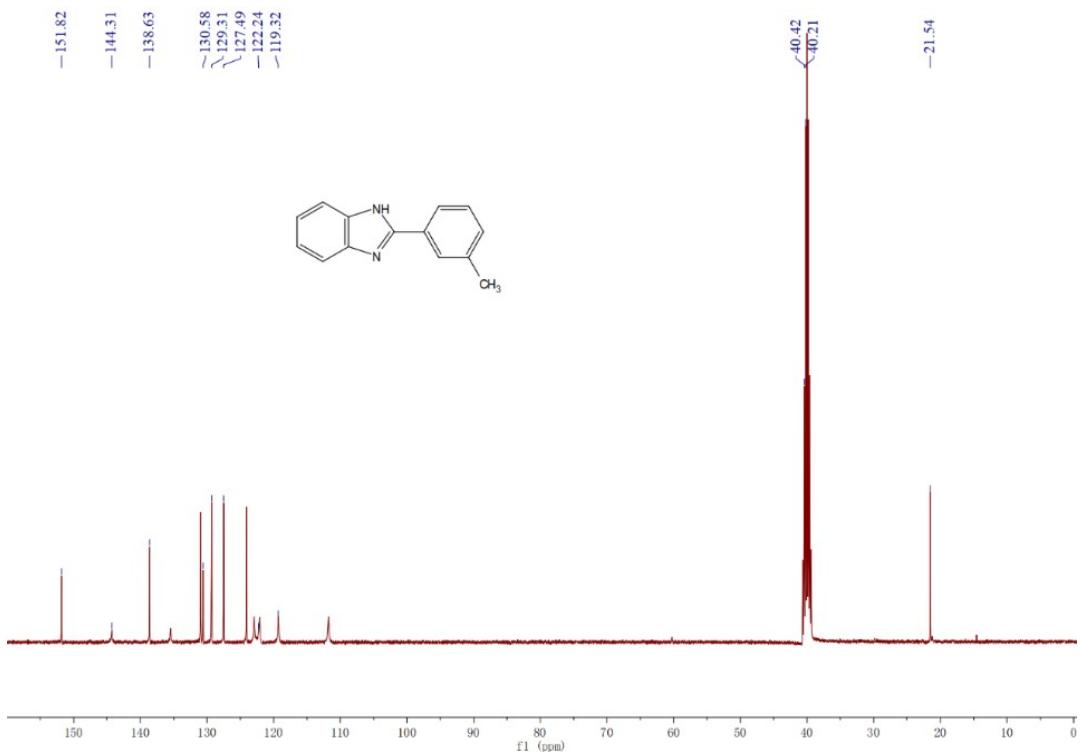


Figure S16. ^{13}C NMR for 2-(o-tolyl)-1H-benzo[d]imidazole

2-(o-tolyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.91 (s, 1H), 8.06 (s, 1H), 8.01-7.99 (d, 1H), 7.68 (s, 1H), 7.56 (s, 1H), 7.47-7.43 (t, 1H), 7.33 (s, 1H), 7.31-7.22 (t, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 151.8, 144.3, 138.6, 130.5, 129.3, 127.4, 122.2, 119.3, 40.4, 40.2, 21.5.

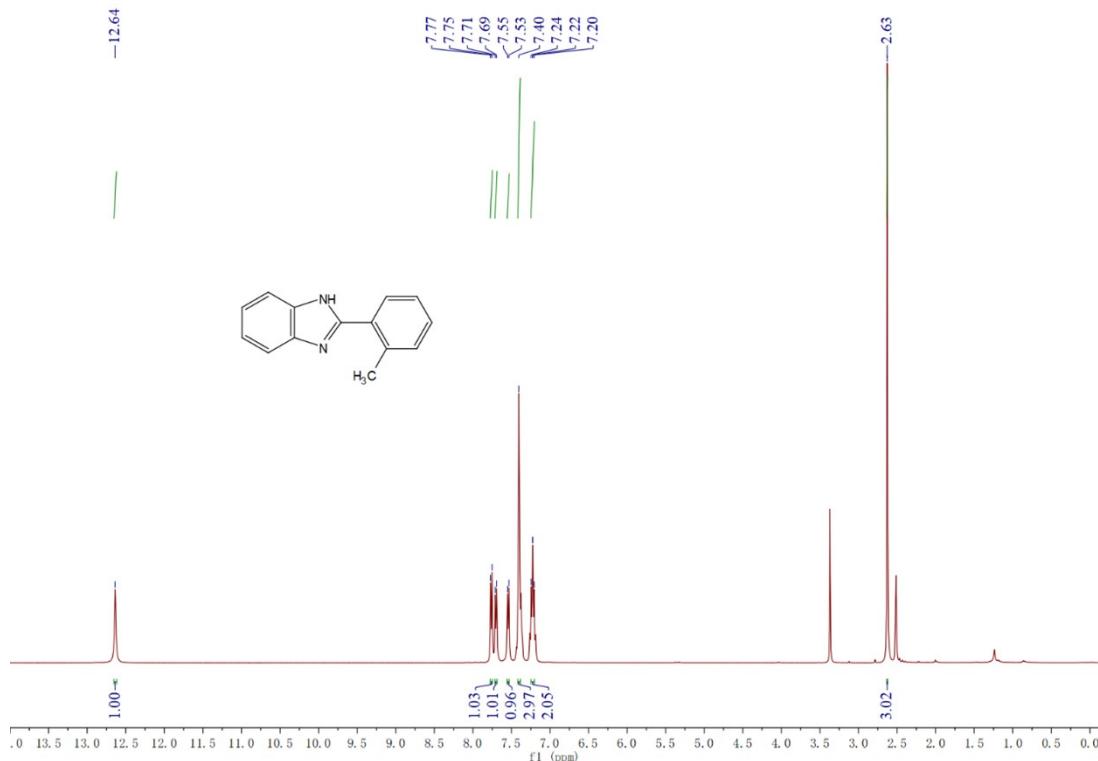


Figure S17. ^1H NMR for 2-(o-tolyl)-1H-benzo[d]imidazole

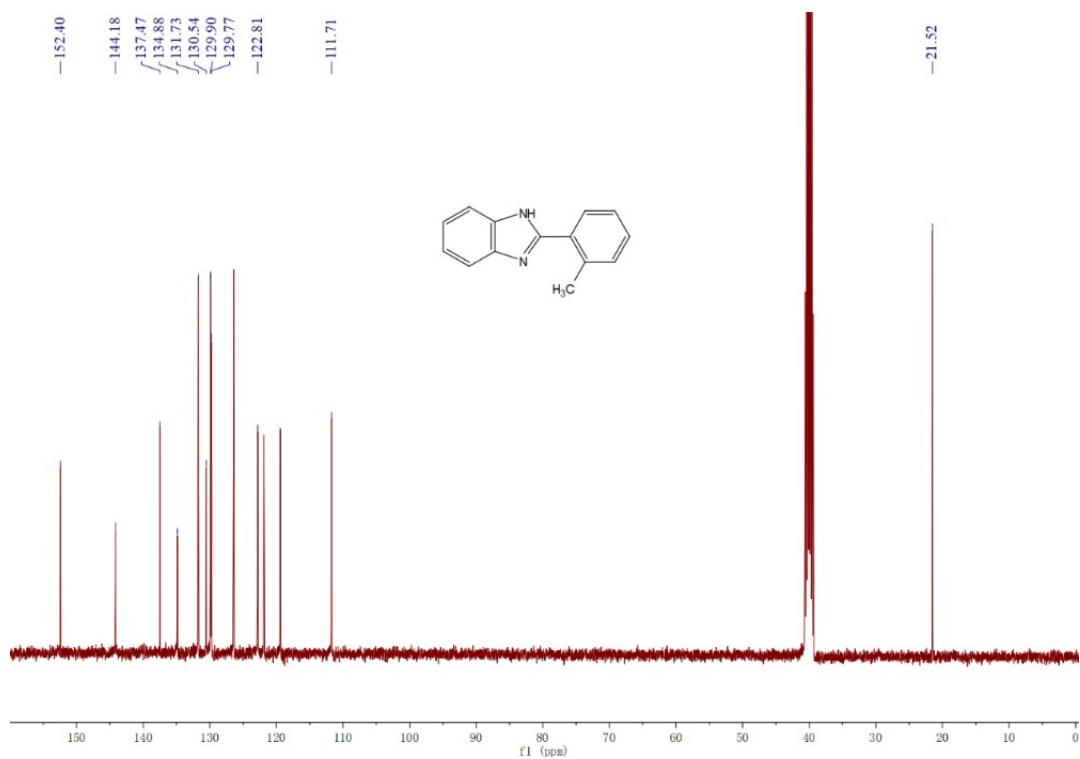


Figure S18. ^{13}C NMR for 2-(o-tolyl)-1H-benzo[d]imidazole

2-(o-tolyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 12.64 (s, 1H), 7.77 (d, 1H), 7.71 (d, 1H), 7.55 (d, 1H), 7.40(s, 3H), 7.24-7.20 (t, 2H), 2.63 (s, 3H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 152.4, 144.1, 137.4, 134.8, 131.7, 130.5, 129.9, 129.7, 122.8, 111.7, 21.5.

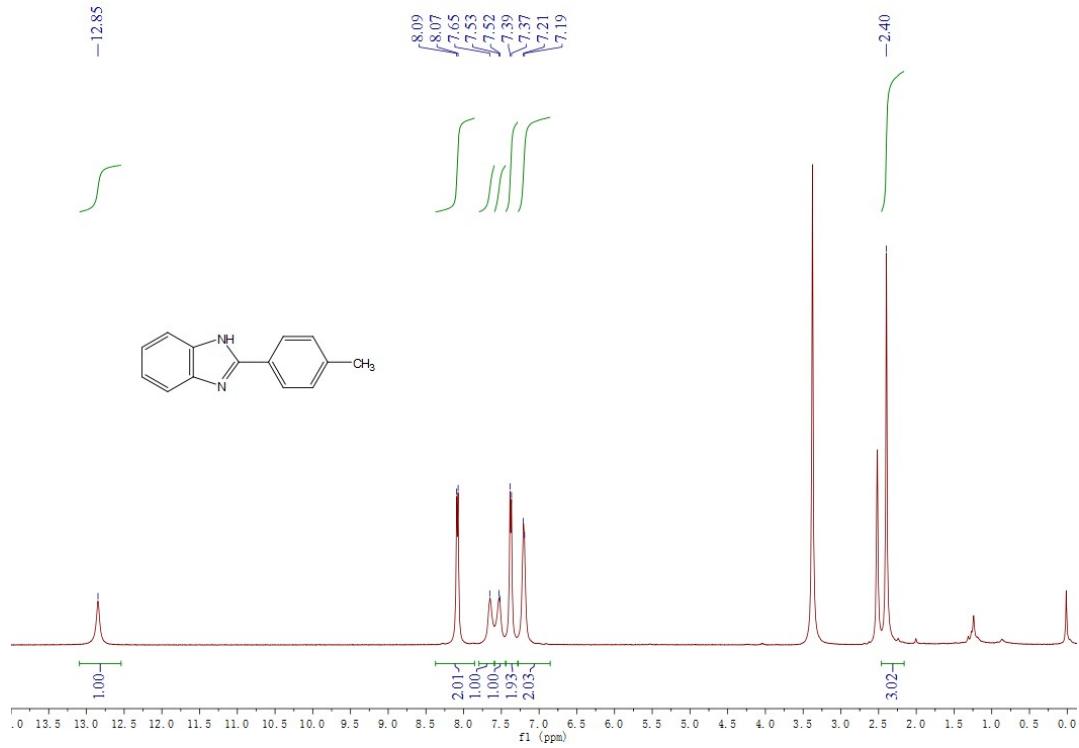


Figure S19. ¹H NMR for 2-(p-tolyl)-1H-benzo[d]imidazole

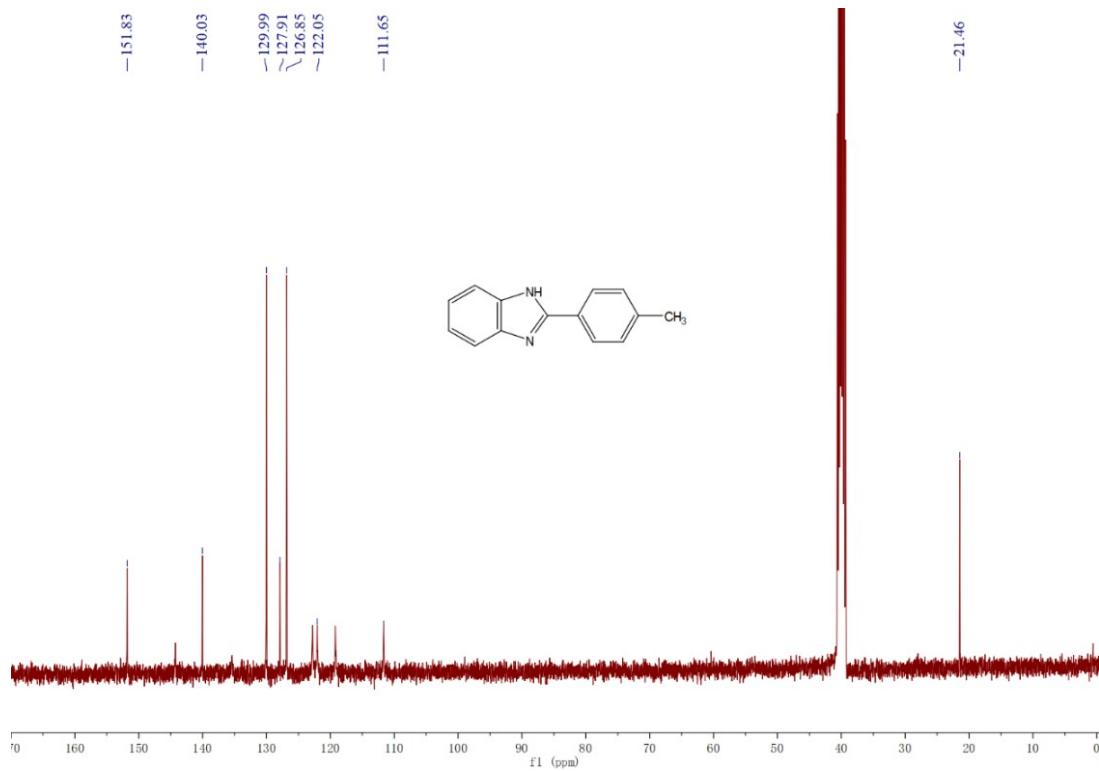


Figure S20. ¹³C NMR for 2-(p-tolyl)-1H-benzo[d]imidazole

2-(p-tolyl)-1H-benzo[d]imidazole: ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.85 (s, 1H), 8.09 (d, 2H), 7.65 (s, 1H), 7.53 (d, 1H), 7.39-7.37 (d, 2H), 7.19-7.21 (d, 2H), 7.21-7.19 (d, 2H). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ 151.8, 140.0, 129.9, 127.9, 126.8, 122.0, 111.6, 21.4.

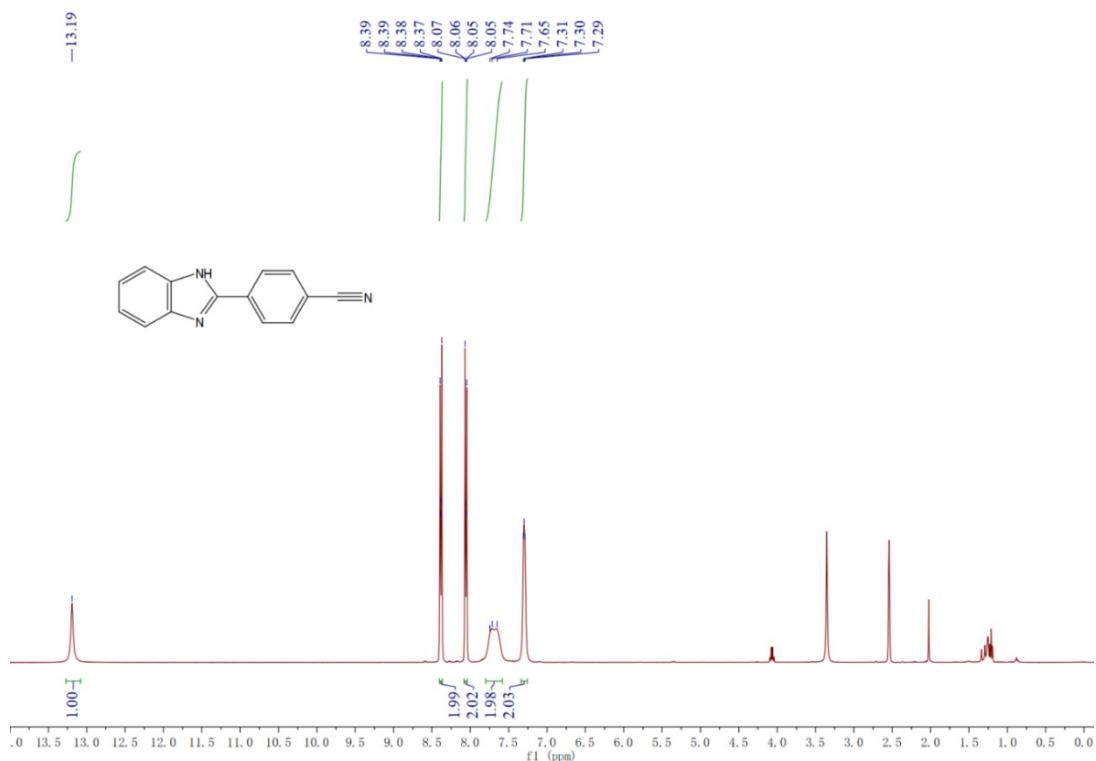


Figure S21. ^1H NMR for 4-(1H-benzo[d]imidazol-2-yl)benzonitrile

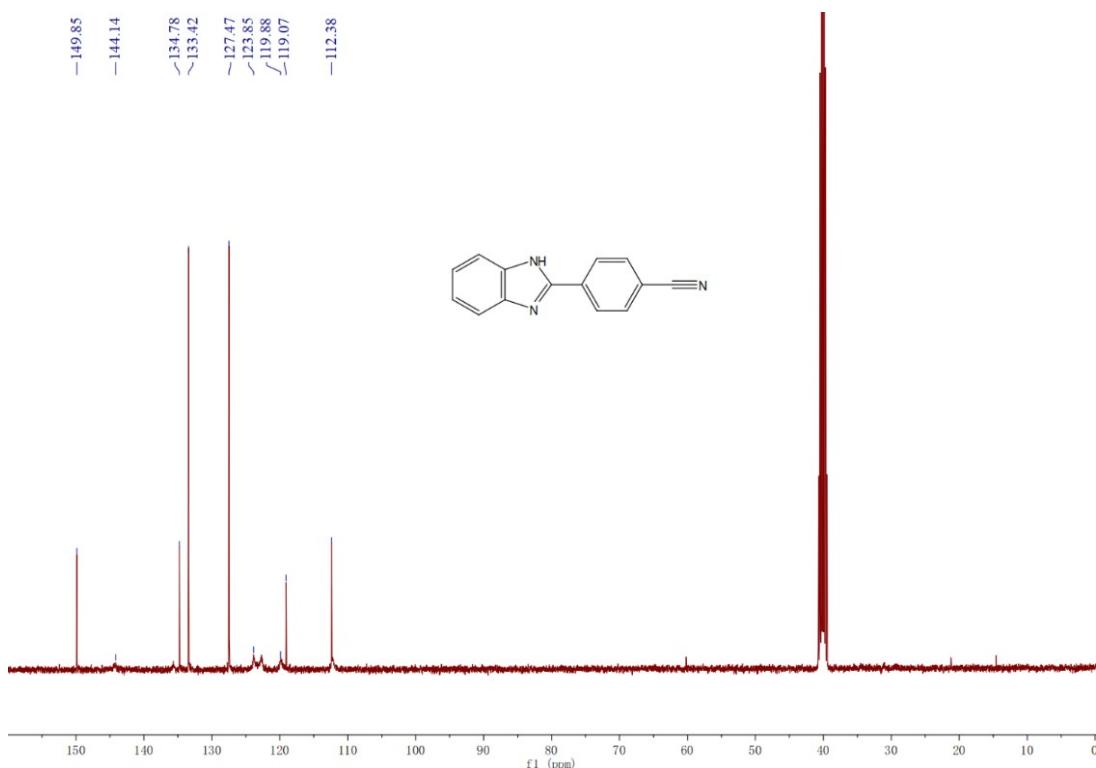


Figure S22. ^{13}C NMR for 4-(1H-benzo[d]imidazol-2-yl)benzonitrile

4-(1H-benzo[d]imidazol-2-yl)benzonitrile: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 13.19 (s, 1H), 8.39-8.37 (q, 2H), 8.07-8.05 (q, 2H), 7.74-7.65 (t, 2H), 7.31-7.29 (t, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 149.8, 144.1, 134.7, 133.4, 127.4, 123.8, 119.8, 119.0, 112.3.

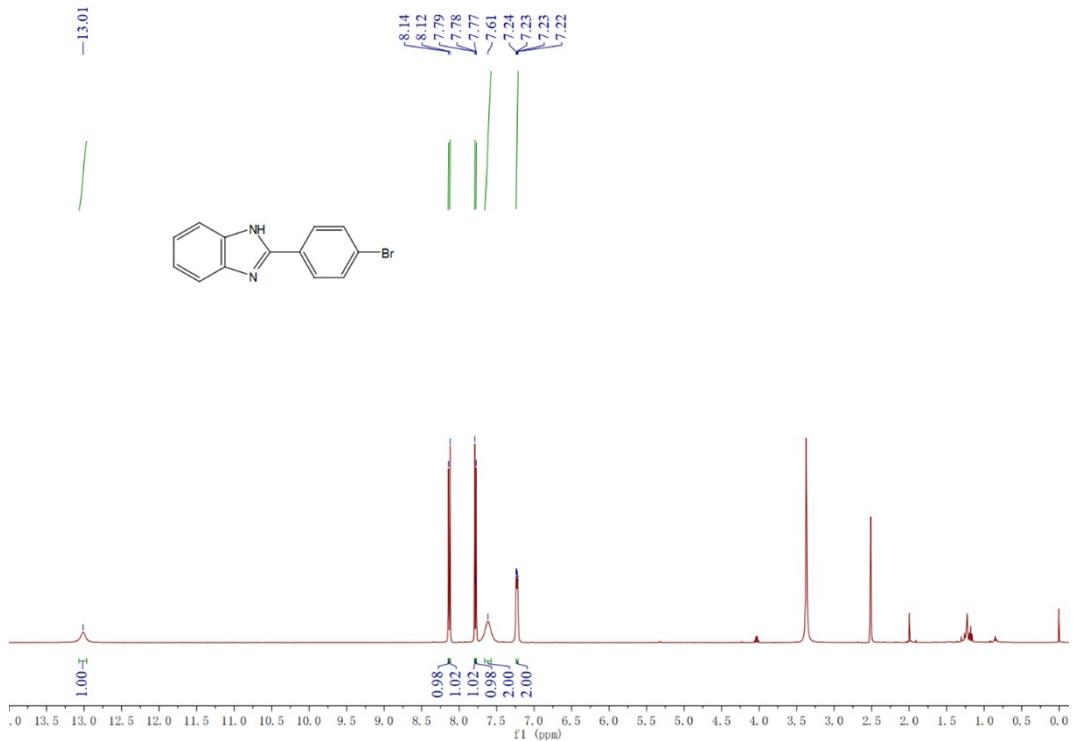


Figure S23. ^1H NMR for 2-(4-bromophenyl)-1H-benzo[d]imidazole

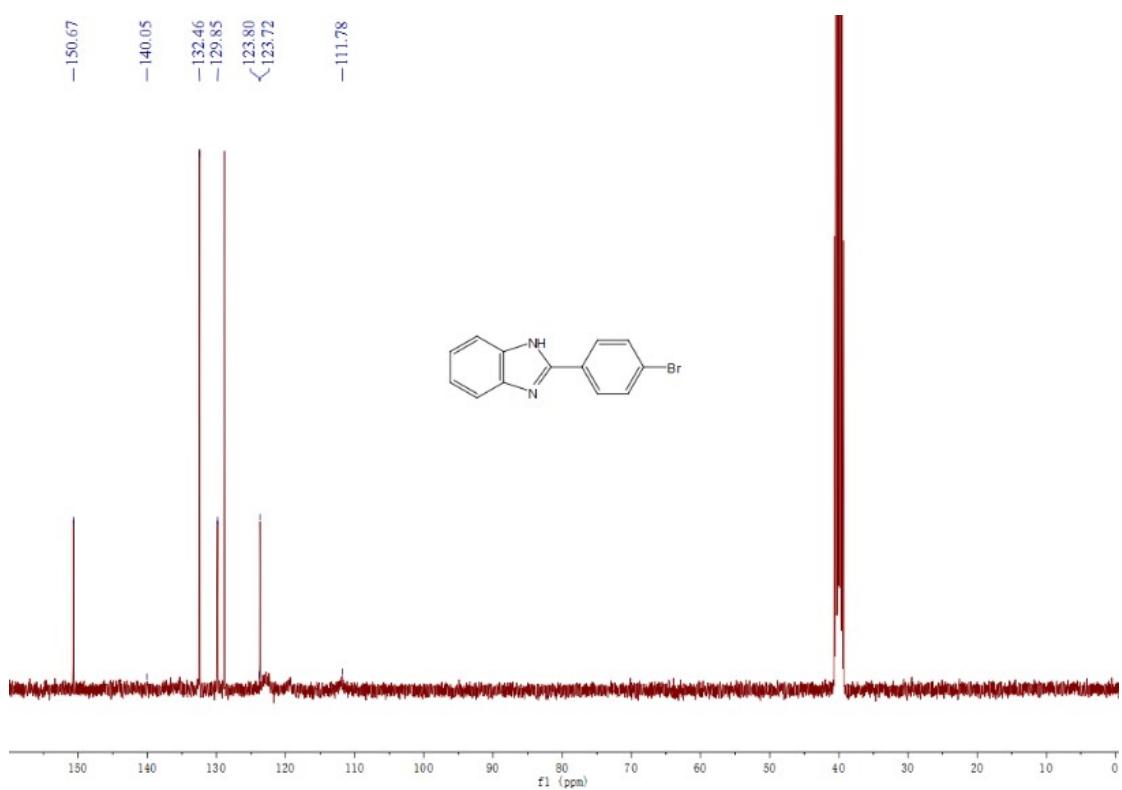


Figure S24. ^{13}C NMR for 2-(4-bromophenyl)-1H-benzo[d]imidazole

2-(4-bromophenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 13.01 (s, 1H), 8.14 (s, 1H), 8.12 (s, 1H), 7.79-7.78 (d, 1H), 7.77 (s, 1H), 7.61 (s, 2H), 7.24-7.22 (q, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 150.6, 140.0, 132.4, 129.8, 123.8, 123.7, 111.7.

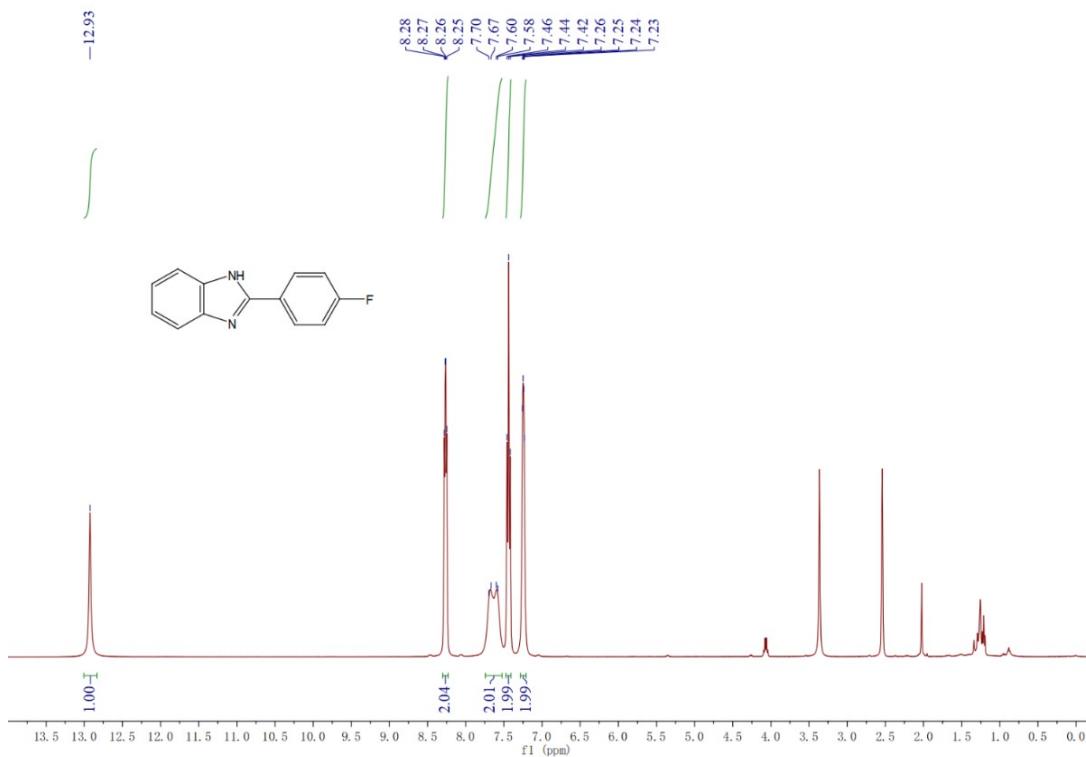


Figure S25. ^1H NMR for 2-(4-fluorophenyl)-1H-benzo[d]imidazole

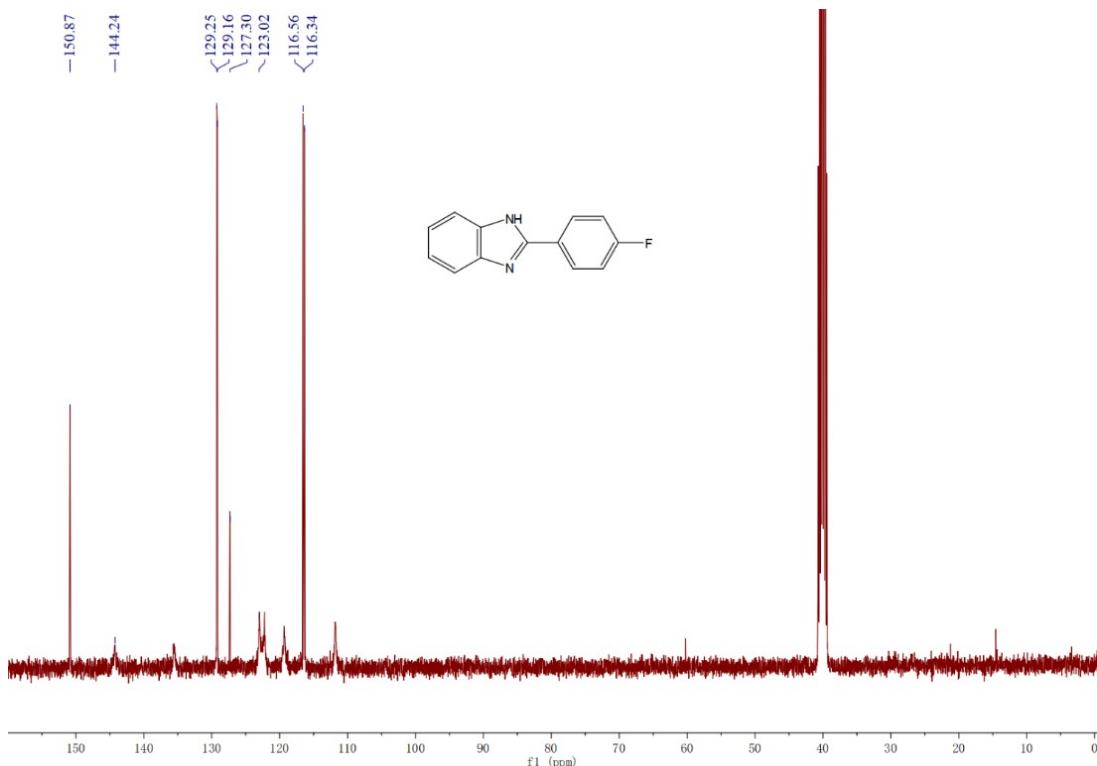


Figure S26. ^{13}C NMR for 2-(4-fluorophenyl)-1H-benzo[d]imidazole

2-(4-fluorophenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO- d_6 , 400 MHz, ppm): 12.93 (s, 1H), 8.28-8.25 (q, 2H), 7.70 (d, 2H), 7.60 (d, 2H), 7.46-7.23 (m, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): 150.8, 144.2, 129.2, 129.1, 127.3, 123.0, 116.5, 116.3.

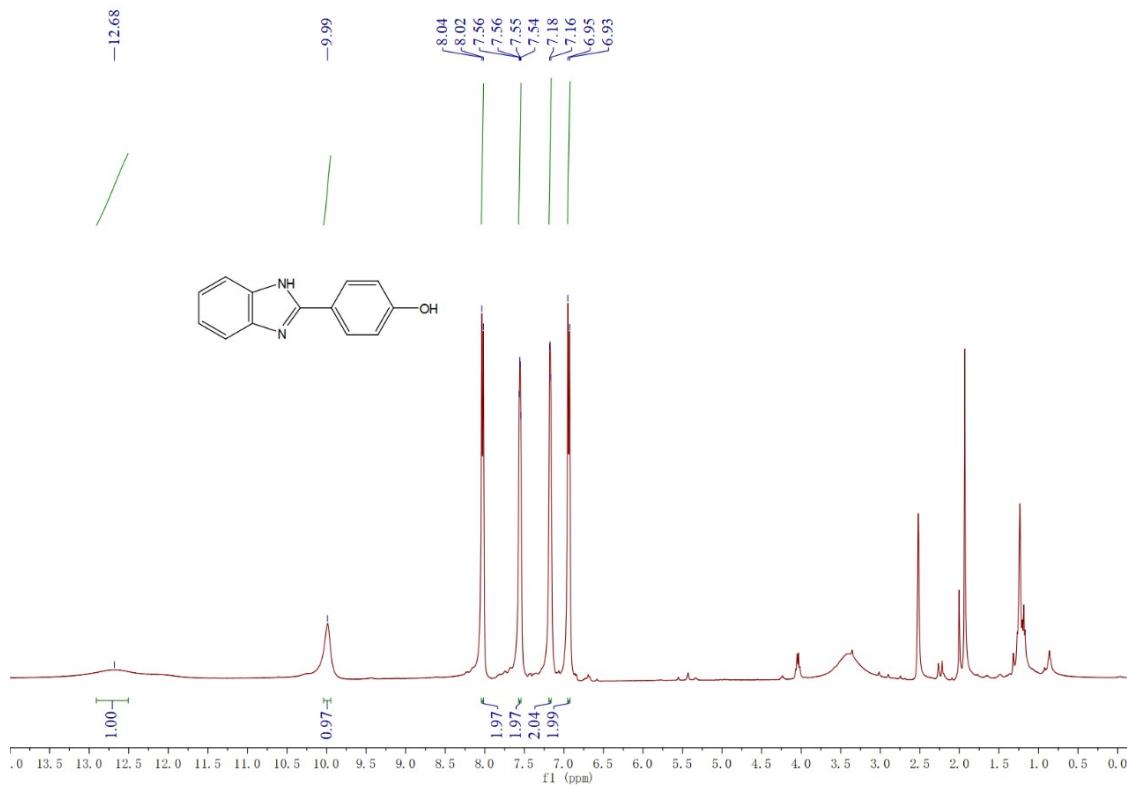


Figure S27. ^1H NMR for 4-(1H-benzo[d]imidazol-2-yl)phenol

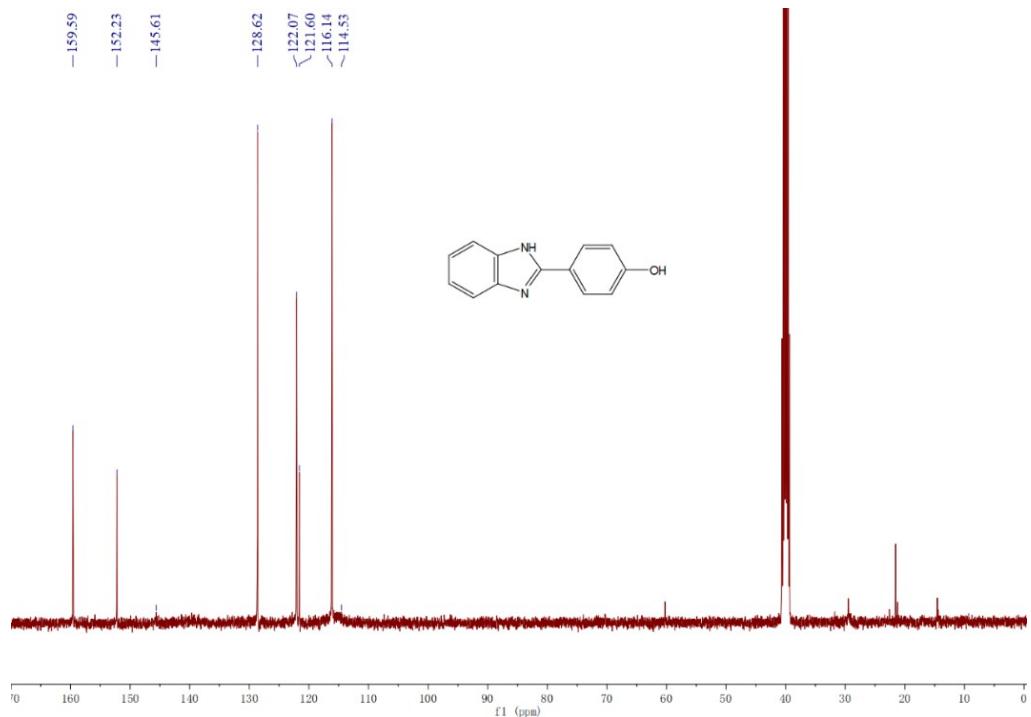


Figure S28. ^{13}C NMR for 4-(1H-benzo[d]imidazol-2-yl)phenol

4-(1H-benzo[d]imidazol-2-yl)phenol: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 13.01 (s, 1H), 8.08 (d, 2H), 7.71-7.65 (t, 1H), 7.55 (d, 1H), 7.39 (d, 2H), 7.24-7.21 (t, 1H), 2.40 (s, 3H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 153.4, 134.2, 131.3, 127.4, 127.0, 126.4, 122.8, 118.5, 112.9, 21.4.

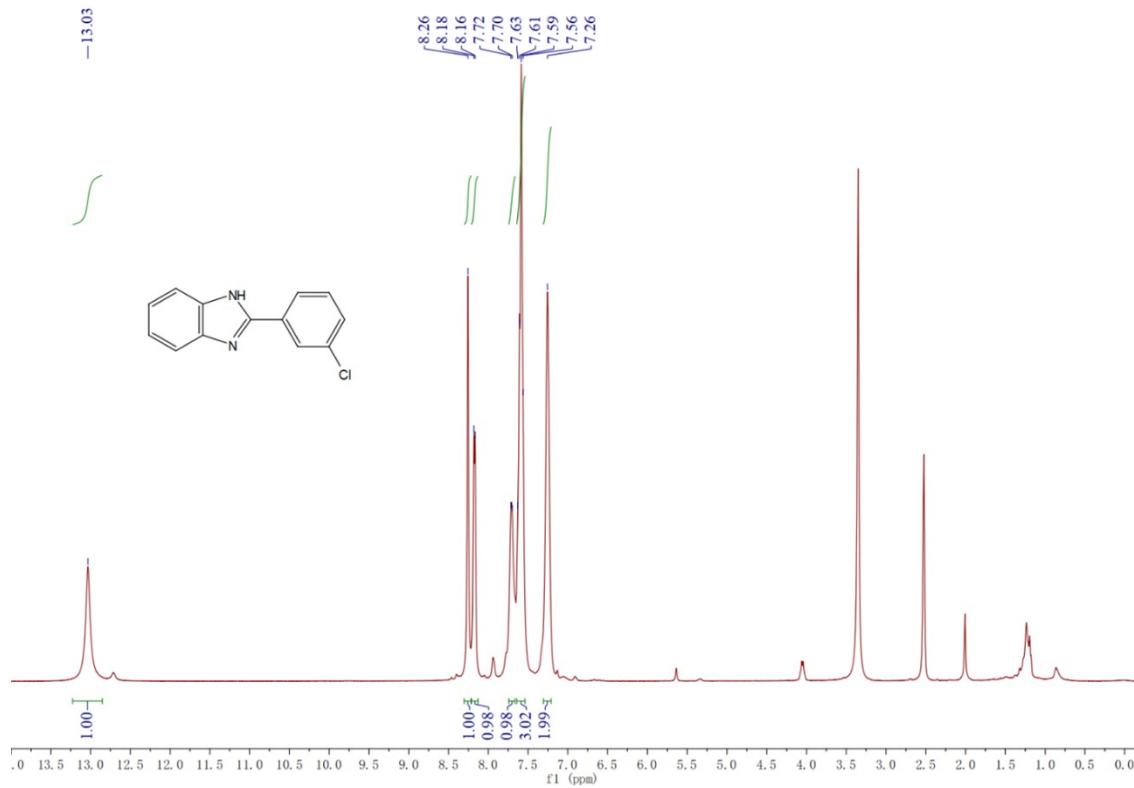


Figure S29. ^1H NMR for 2-(2-chlorophenyl)-1H-benzo[d]imidazole

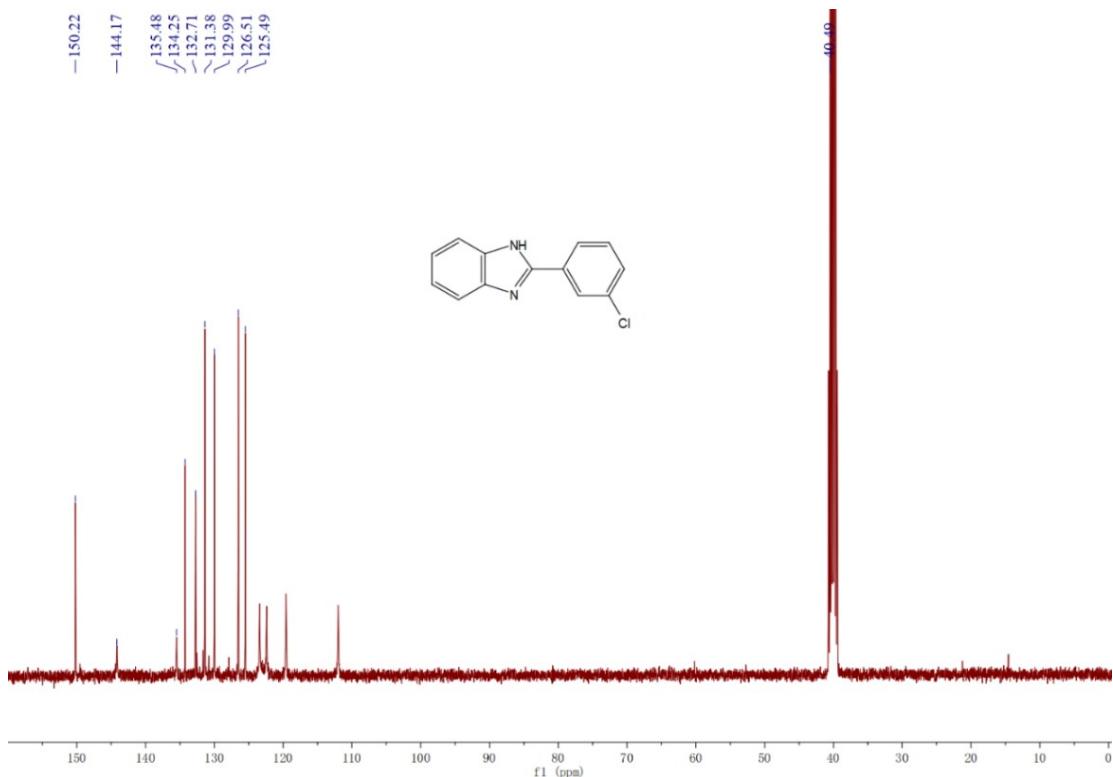


Figure S30. ^{13}C NMR for 2-(2-chlorophenyl)-1H-benzo[d]imidazole

2-(2-chlorophenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 13.03 (s, 1H), 8.26 (s, 1H), 8.18 (d, 1H), 7.72 (d, 1H), 7.63-7.56 (q, 3H), 7.26 (s, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 150.2, 144.1, 135.4, 134.2, 132.7, 131.3, 129.9, 126.5, 125.4.

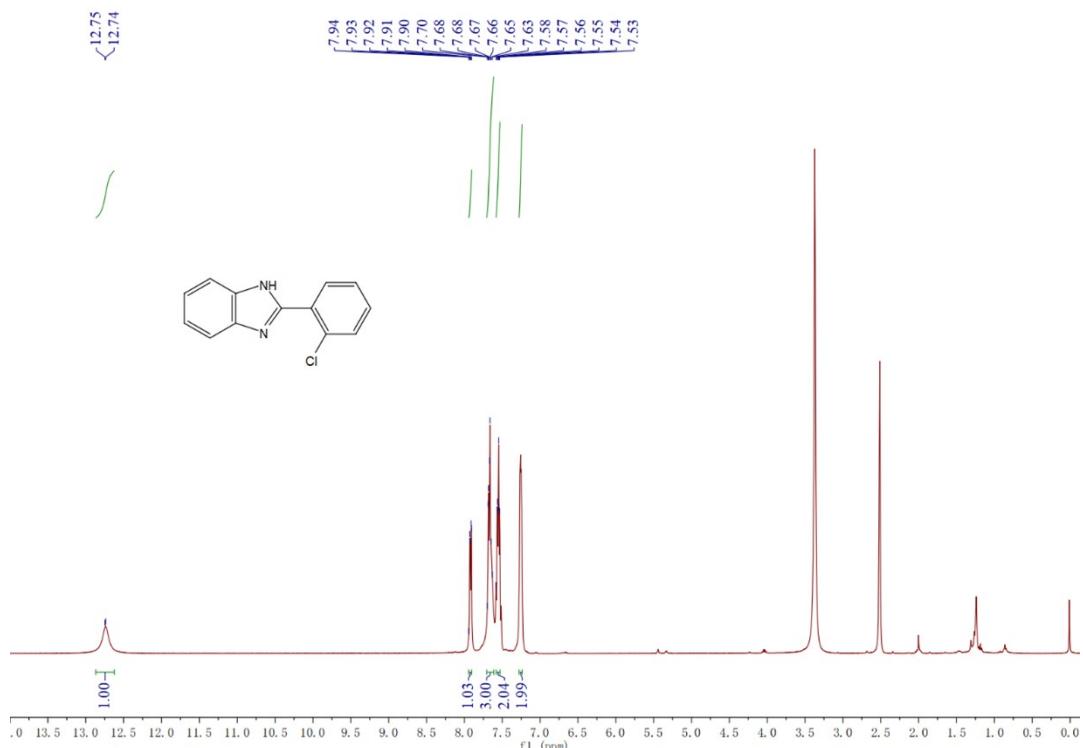


Figure S31. ^1H NMR for 2-(2-chlorophenyl)-1H-benzo[d]imidazole

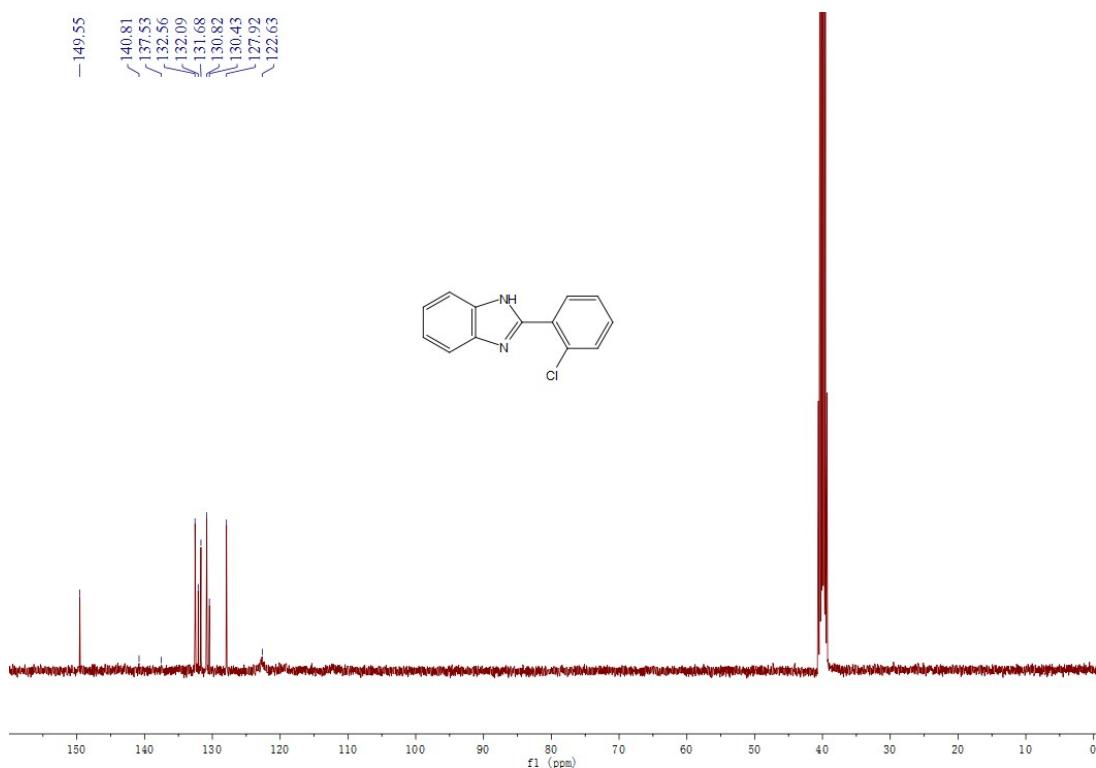


Figure S32. ^{13}C NMR for 2-(2-chlorophenyl)-1H-benzo[d]imidazole

2-(2-chlorophenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.75 (d, 1H), 7.94-7.90 (m, 1H), 7.70-7.67 (q, 3H), 7.66 (d, 2H), 7.63-7.53 (m, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 149.5, 140.8, 137.5, 132.5, 132.0, 131.6, 130.8, 130.4, 127.9, 122.6.

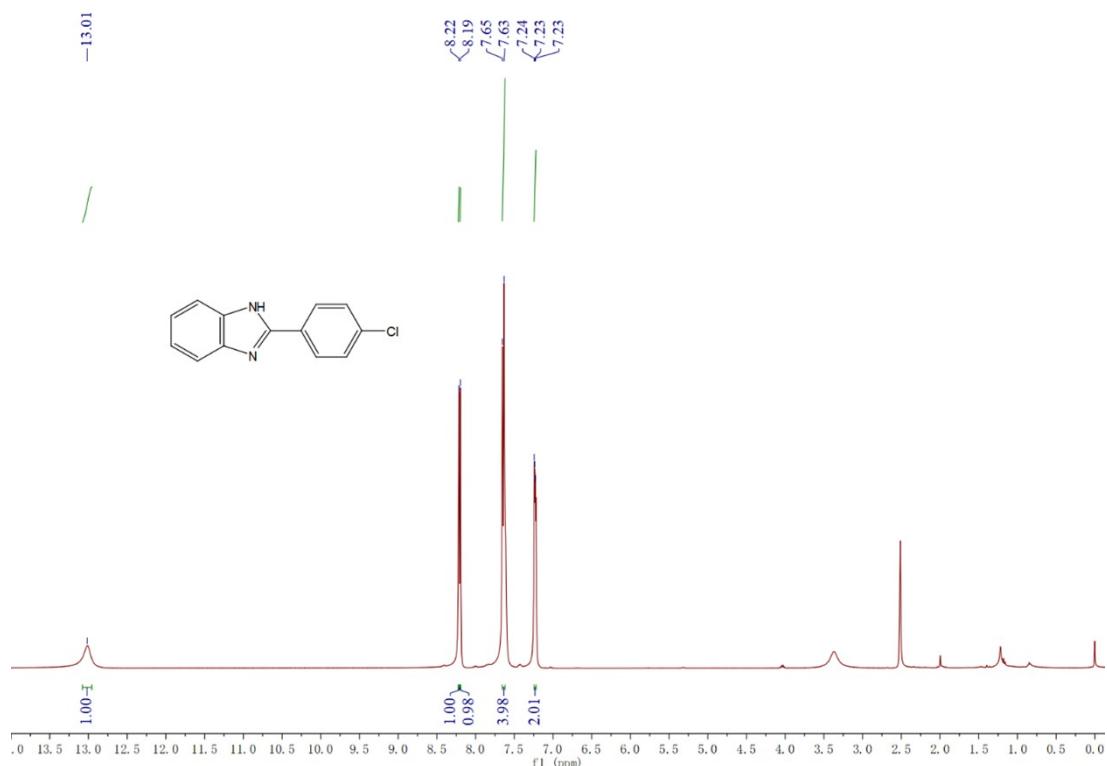


Figure S33. ^1H NMR for 2-(4-chlorophenyl)-1H-benzo[d]imidazole

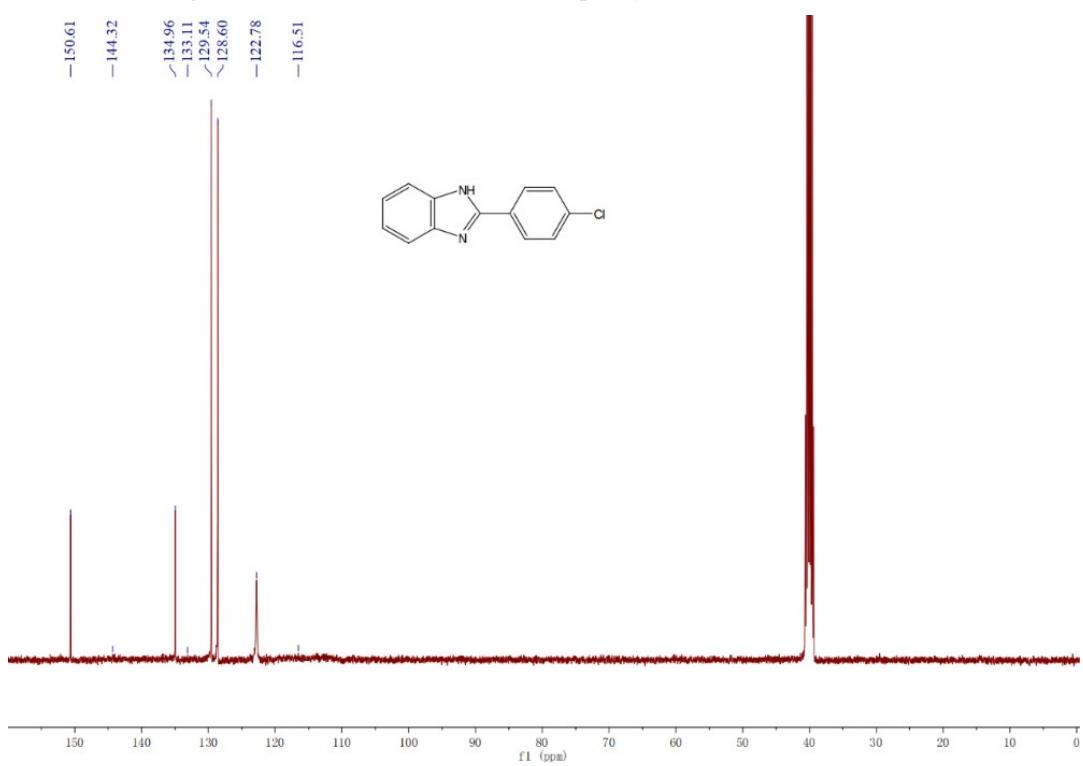


Figure S34. ^{13}C NMR for 2-(4-chlorophenyl)-1H-benzo[d]imidazole

2-(4-chlorophenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 13.01 (s, 1H), 8.22 (s, 1H), 8.19 (s, 1H), 7.65-7.63 (d, 4H), 7.24-7.23 (t, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 150.6, 144.3, 134.9, 133.1, 129.5, 128.6, 122.7, 116.5.

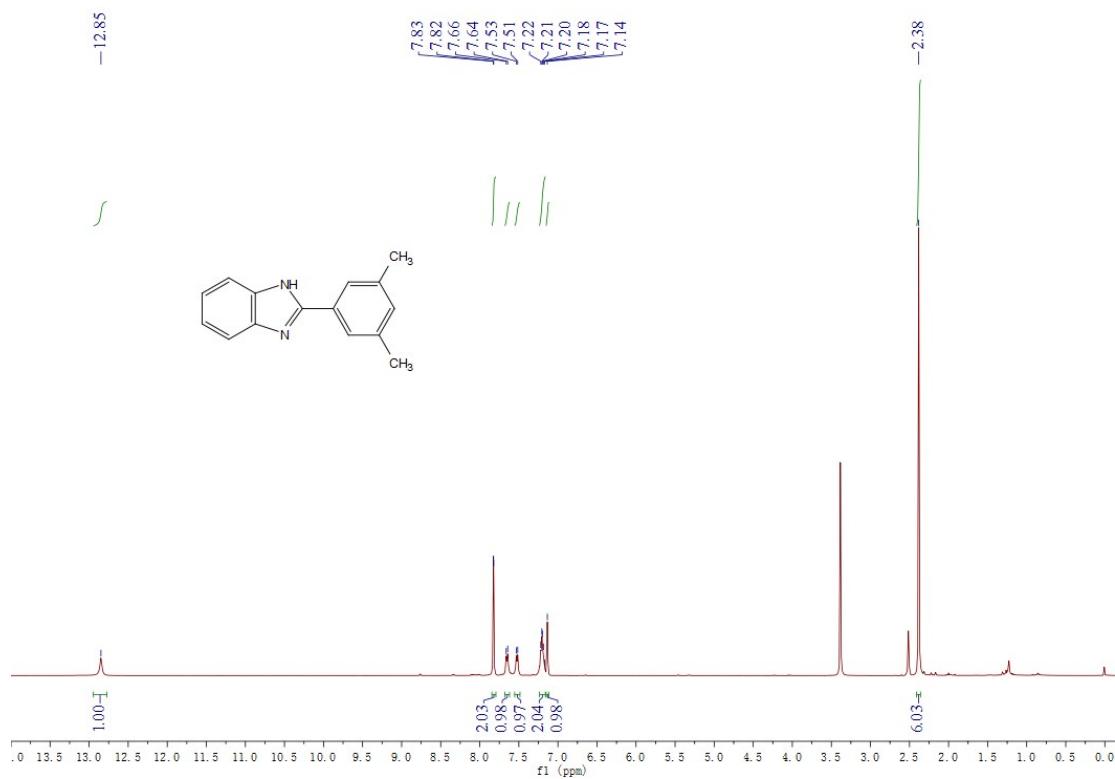


Figure S35. ^1H NMR for 2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole

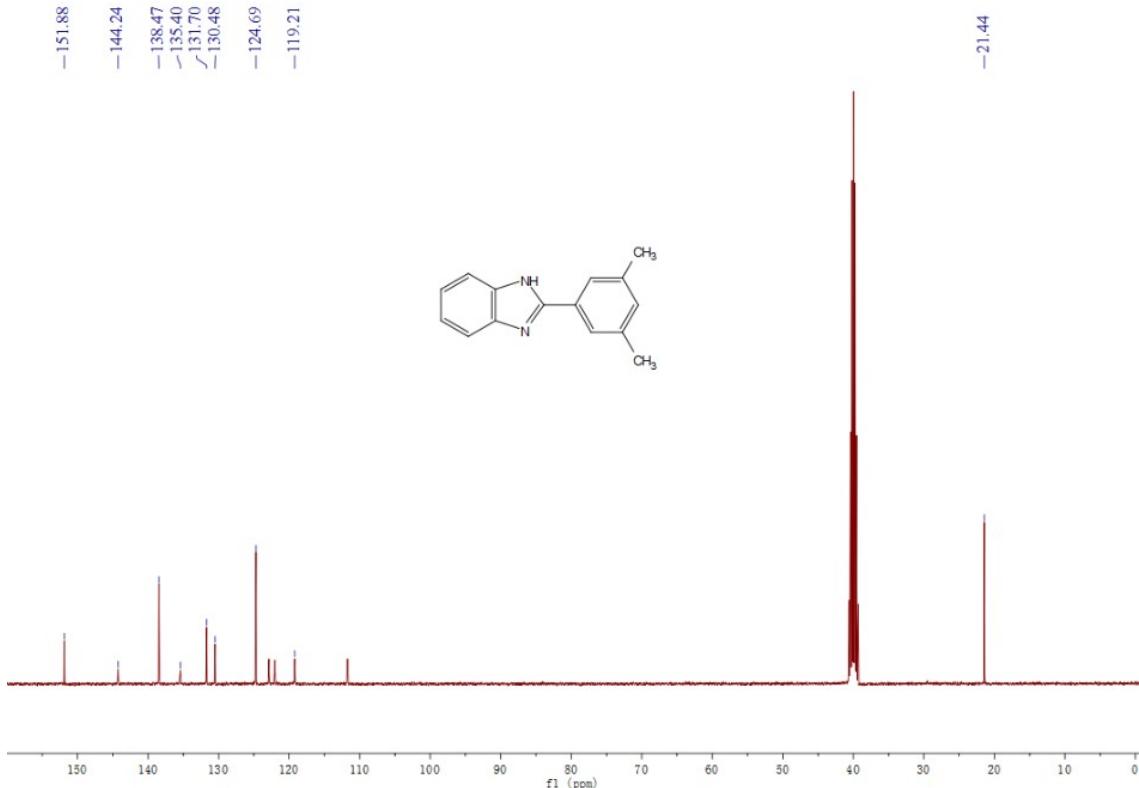


Figure S36. ^{13}C NMR for 2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole

2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 12.85 (s, 1H), 7.83-7.66 (t, 2H), 7.64 (s, 1H), 7.53 (d, 1H), 7.22 (d, 2H), 7.20-7.14 (q, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): δ 151.8, 144.2, 138.4, 135.4, 131.7, 130.4, 124.6, 119.2, 22.4.

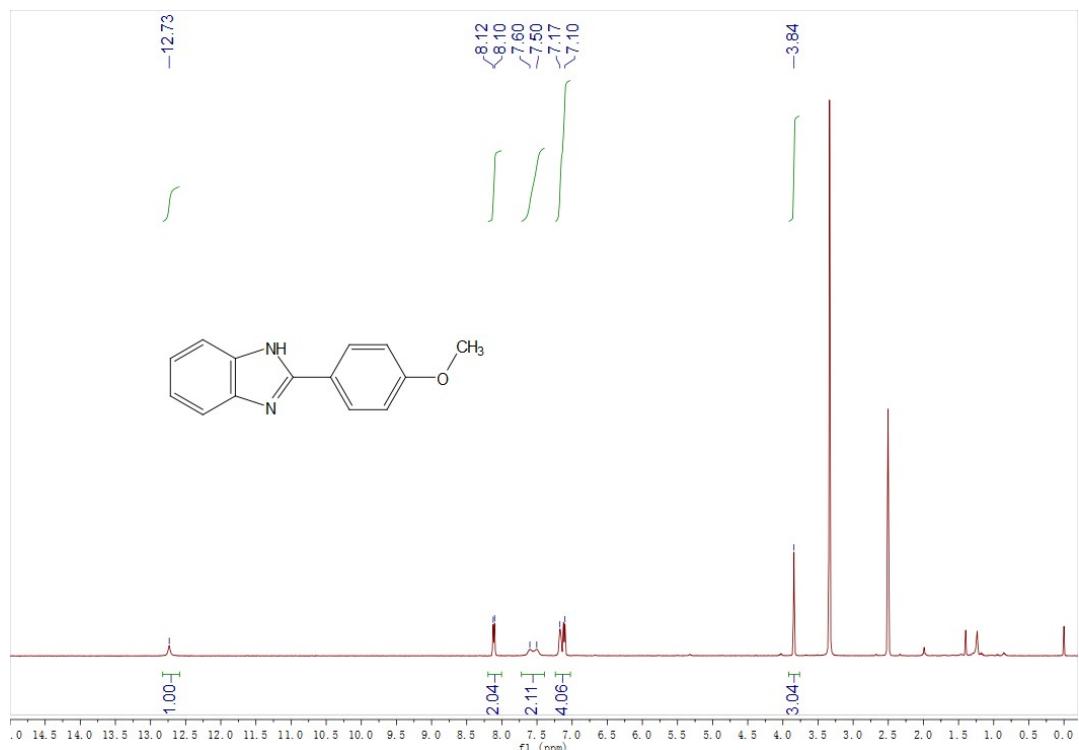


Figure S37. ^1H NMR for 2-(4-methoxyphenyl)-1H-benzo[d]imidazole

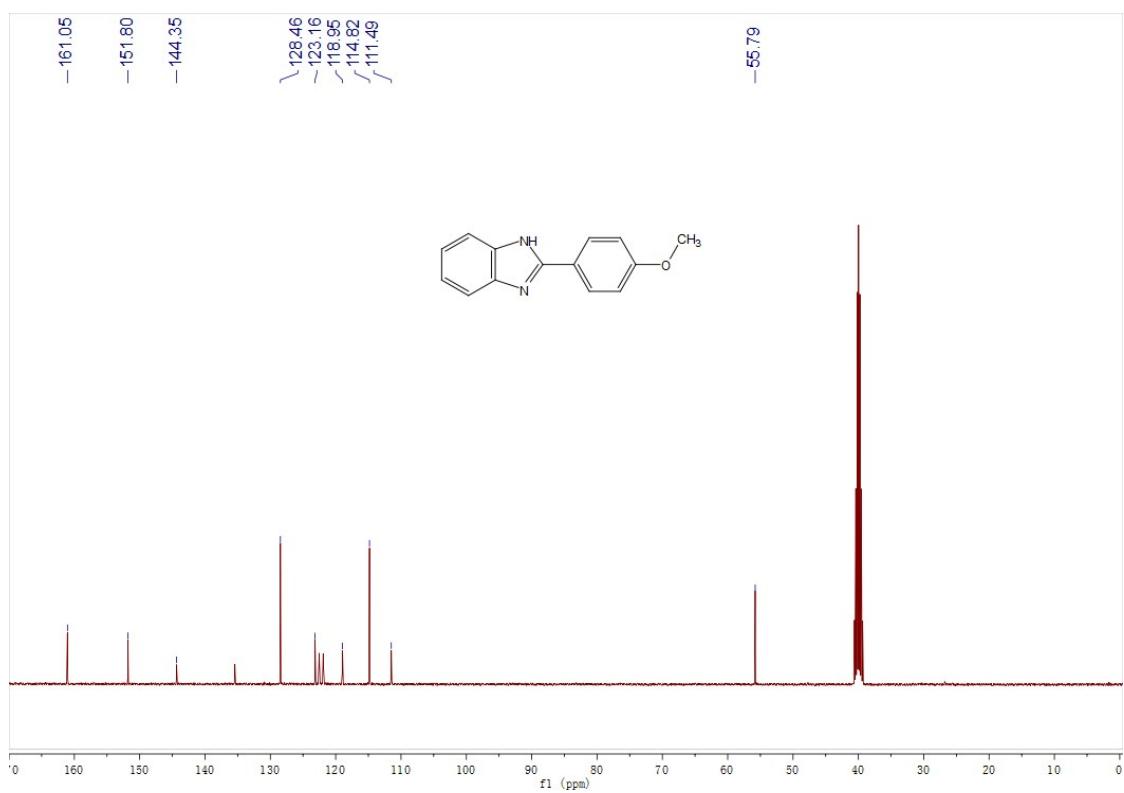


Figure S38. ^{13}C NMR for 2-(4-methoxyphenyl)-1H-benzo[d]imidazole

2-(4-methoxyphenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.73 (s, 1H), 8.12-8.10 (d, 2H), 7.60-7.50 (d, 2H), 7.17-7.10 (m, 4H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 161.05, 151.80, 144.35, 128.46, 123.16, 118.95, 114.82, 111.49, 55.79.

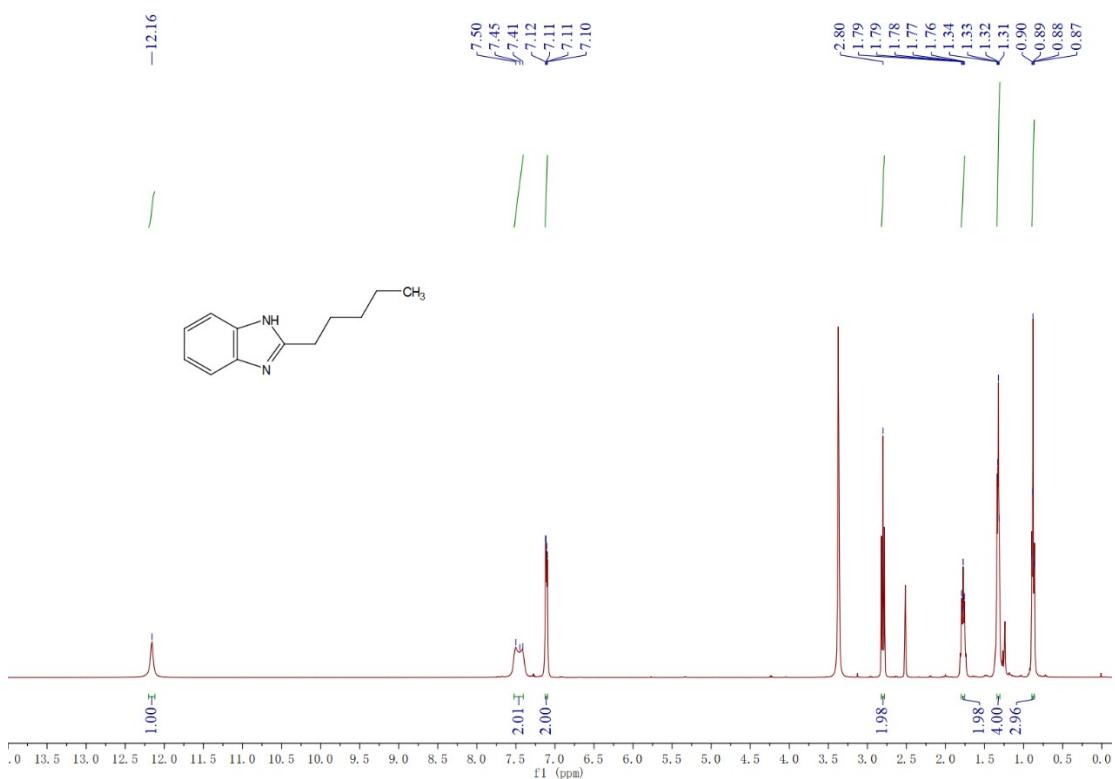


Figure S39. ^1H NMR for 2-pentyl-1H-benzo[d]imidazole

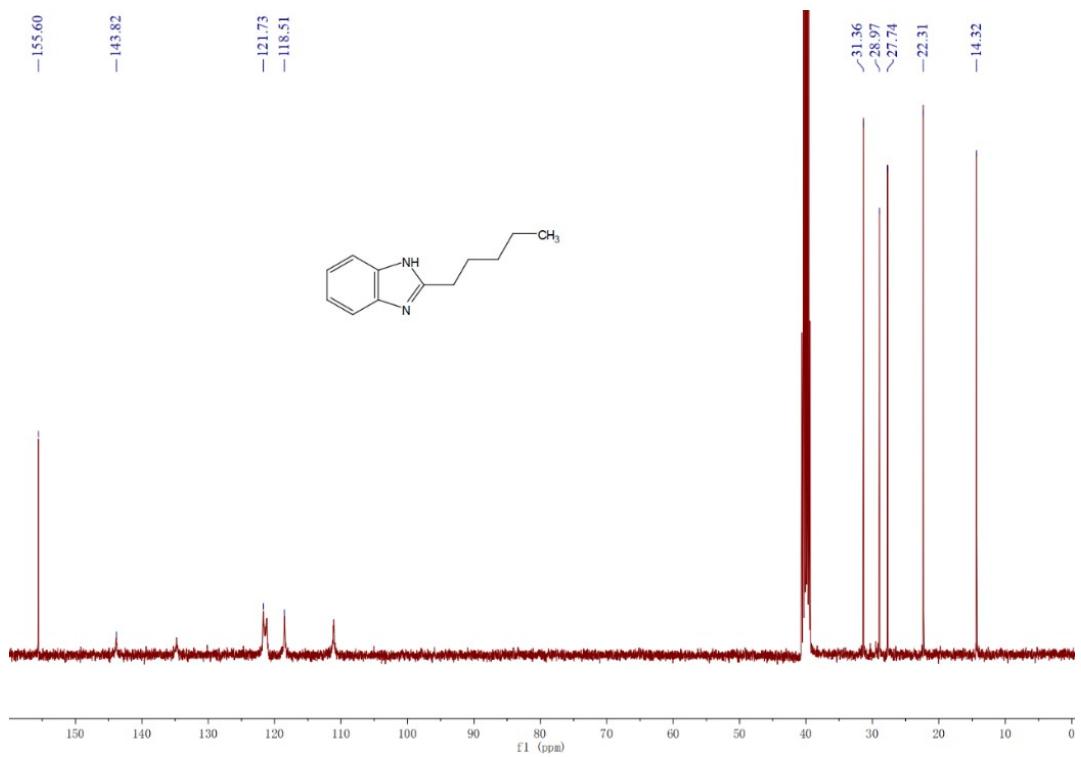


Figure S40. ^{13}C NMR for 2-pentyl-1H-benzo[d]imidazole

2-pentyl-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.16 (s, 1H), 7.50-7.41 (t, 2H), 7.12-7.10 (q, 2H), 2.80 (s, 2H), 1.79-1.76 (m, 2H), 1.34-1.31 (q, 4H), 0.90-0.87 (q, 3H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 155.6, 143.8, 121.7, 118.5, 31.3, 28.9, 27.7, 22.3, 14.3.

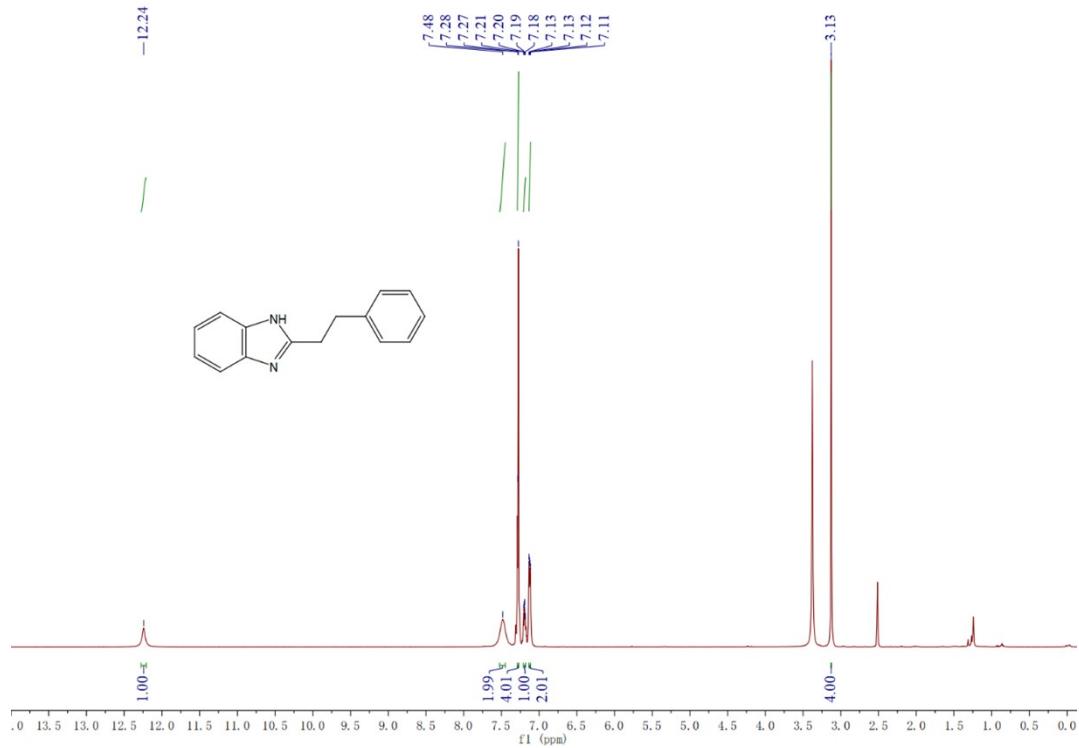


Figure S41. ^1H NMR for 2-phenethyl-1H-benzo[d]imidazole

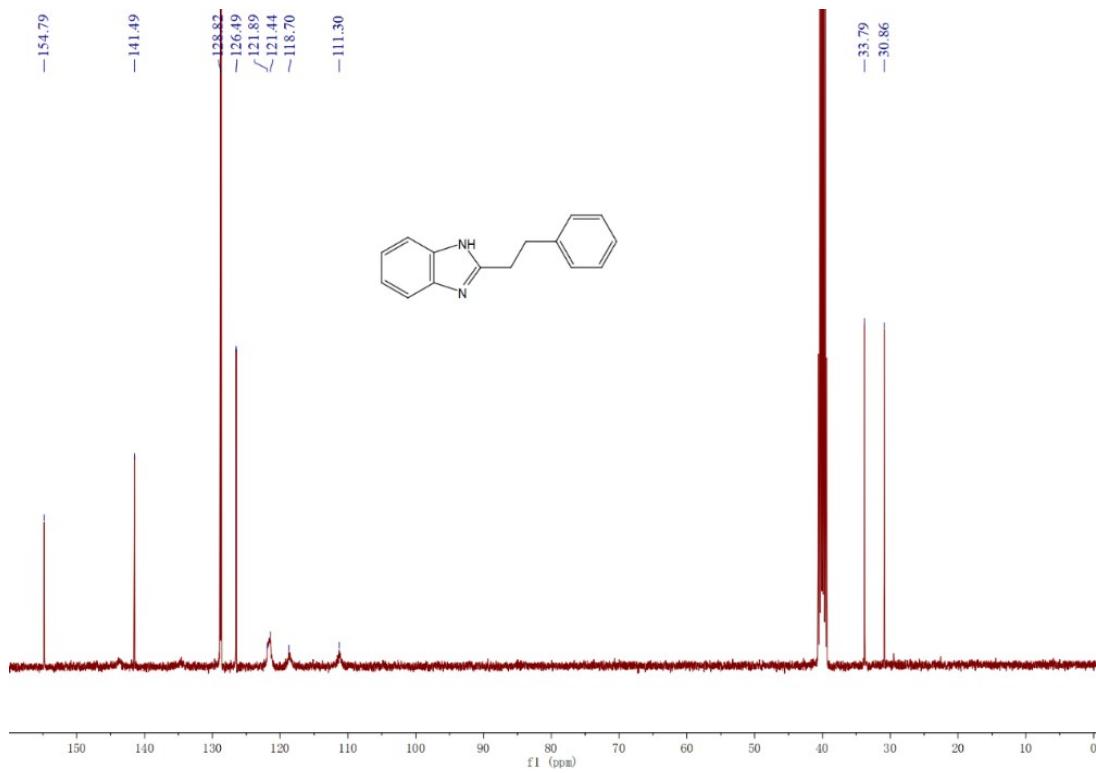


Figure S42. ^{13}C NMR for 2-phenethyl-1H-benzo[d]imidazole

2-phenethyl-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.24 (s, 1H), 7.48-7.27 (t, 2H), 7.21 (s, 4H), 7.20-7.18 (t, 1H), 7.13-7.11 (q, 2H), 3.13 (s, 4H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 154.7, 141.4, 128.8, 126.4, 121.8, 121.4, 118.7, 111.3, 33.7, 30.8.

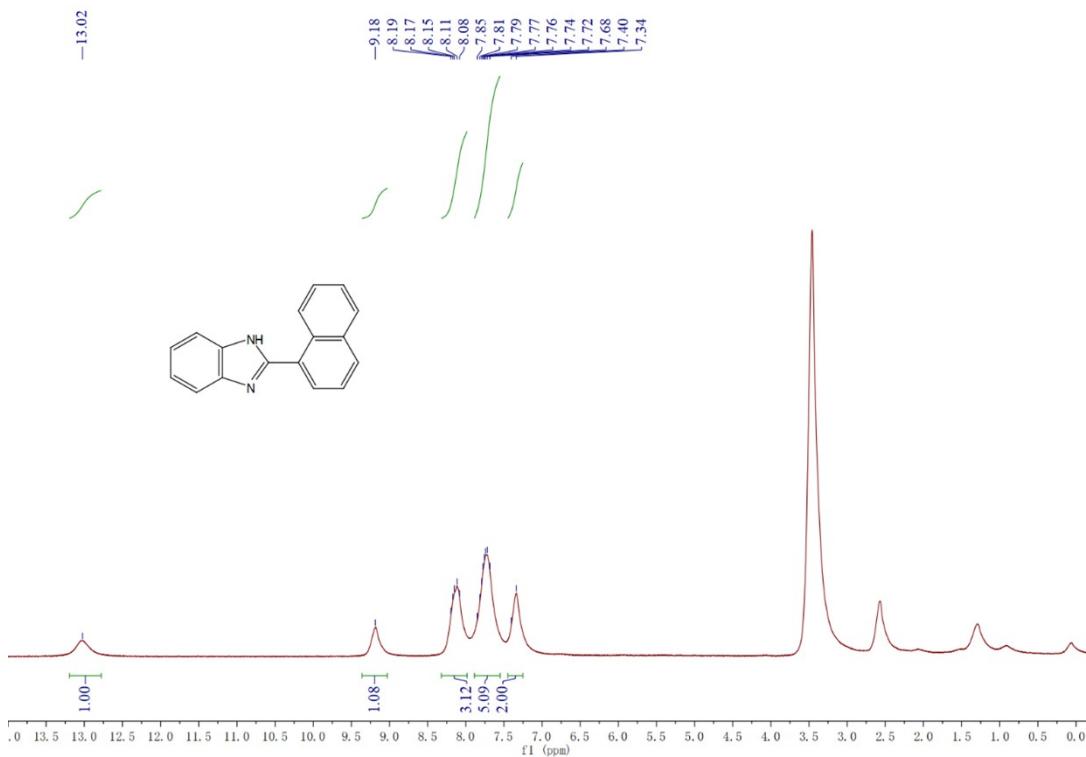


Figure S43. ^1H NMR for 2-(naphthalen-1-yl)-1H-benzo[d]imidazole

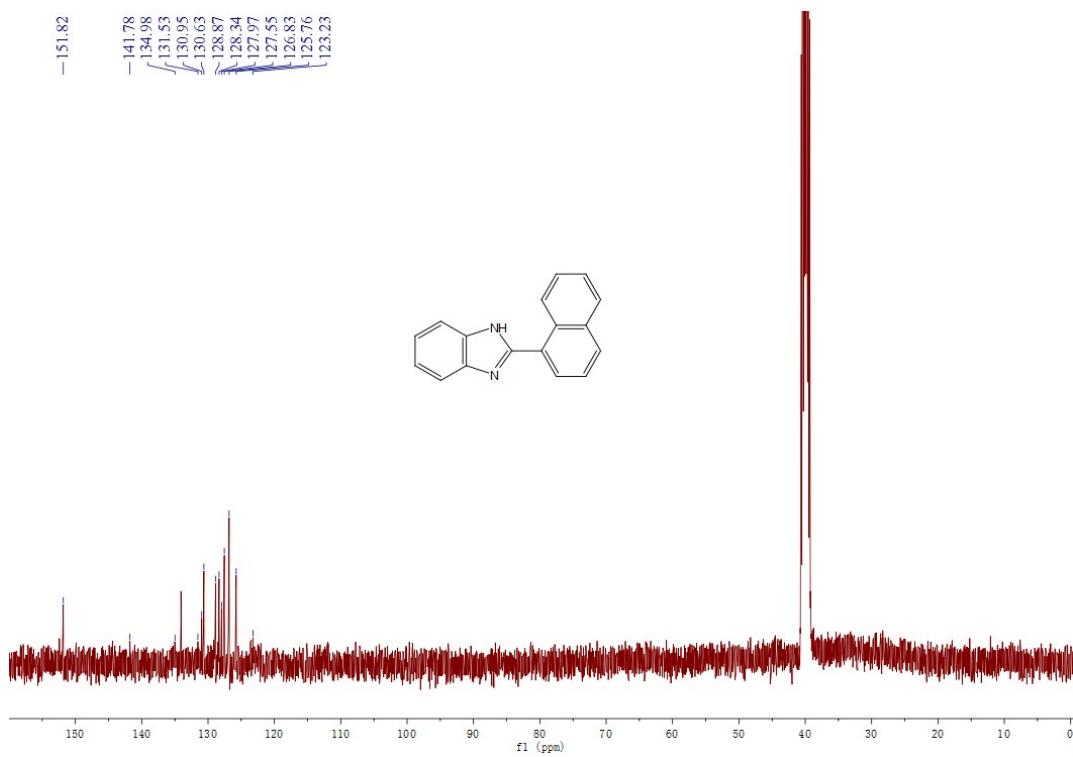


Figure S44. ^{13}C NMR for 2-(naphthalen-1-yl)-1H-benzo[d]imidazole

2-(naphthalen-1-yl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 13.02 (s, 1H), 9.18 (s, 1H), 8.19-8.08 (m, 3H), 7.85-7.68 (m, 5H), 7.40-7.34 (d, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 151.8, 141.7, 134.9, 131.5, 130.9, 130.6, 128.8, 128.3, 127.9, 127.5, 126.8, 125.7, 123.2.

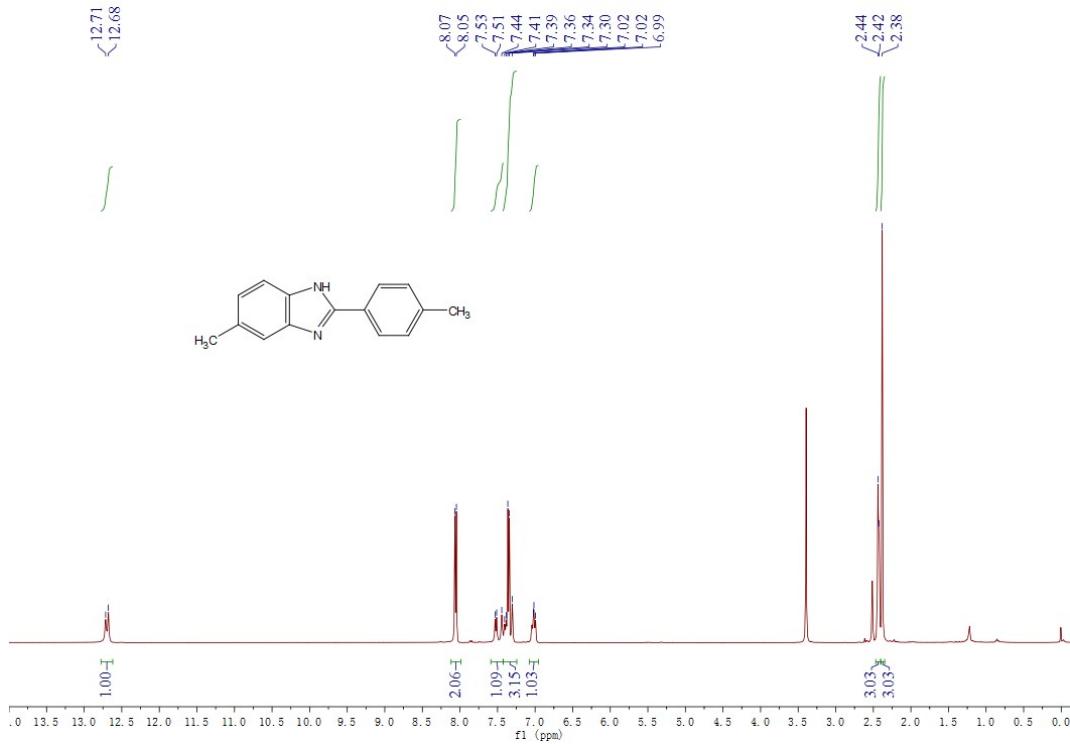


Figure S45. ^1H NMR for 5-methyl-2-(p-tolyl)-1H-benzo[d]imidazole

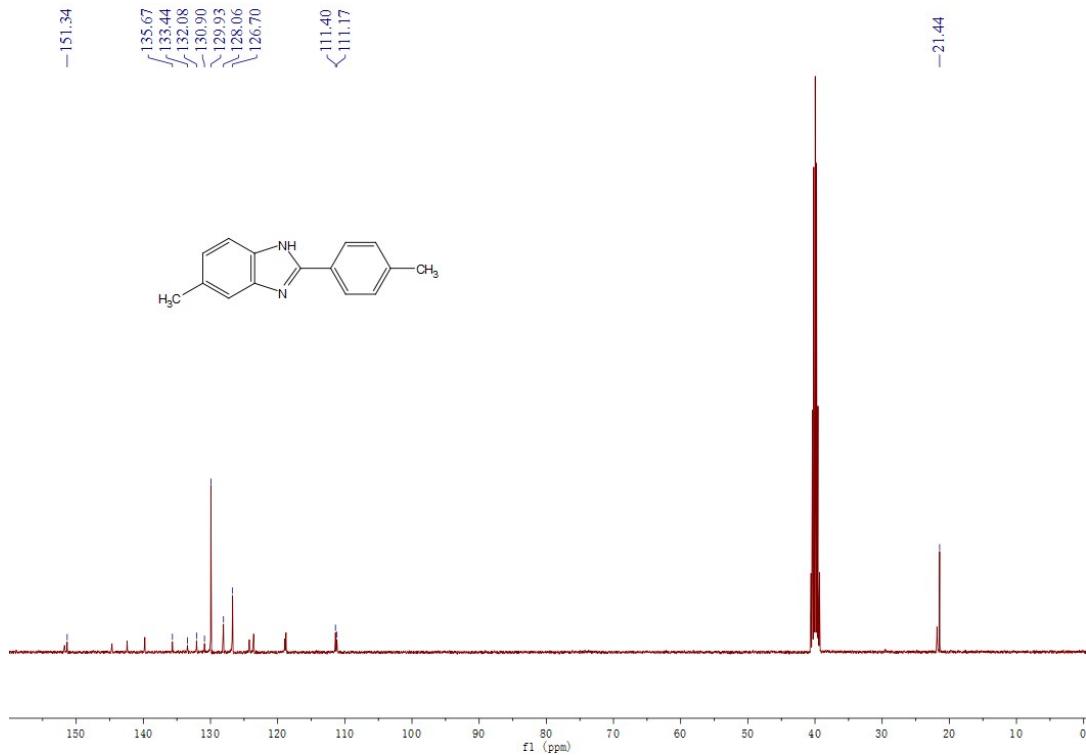


Figure S46. ^{13}C NMR for 5-methyl-2-(p-tolyl)-1H-benzo[d]imidazole

5-methyl-2-(p-tolyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.71-12.68 (d, 1H), 8.07 (d, 2H), 7.53 (d, 1H), 7.44-7.41 (d, 3H), 7.39-6.99 (m, 1H), 2.44 (d, 3H), 2.38 (s, 3H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 151.3, 135.6, 133.4, 132.0, 130.9, 129.9, 128.0, 126.7, 111.4, 111.1, 21.4.

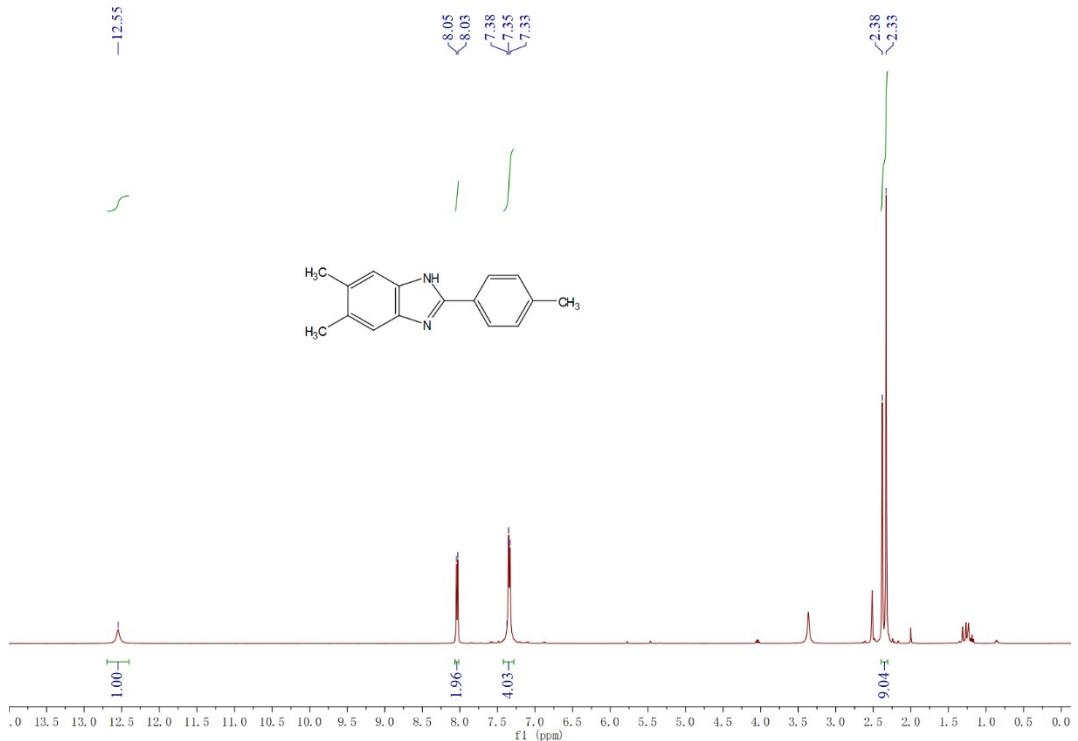


Figure S47. ^1H NMR for 5,6-dimethyl-2-(p-tolyl)-1H-benzo[d]imidazole

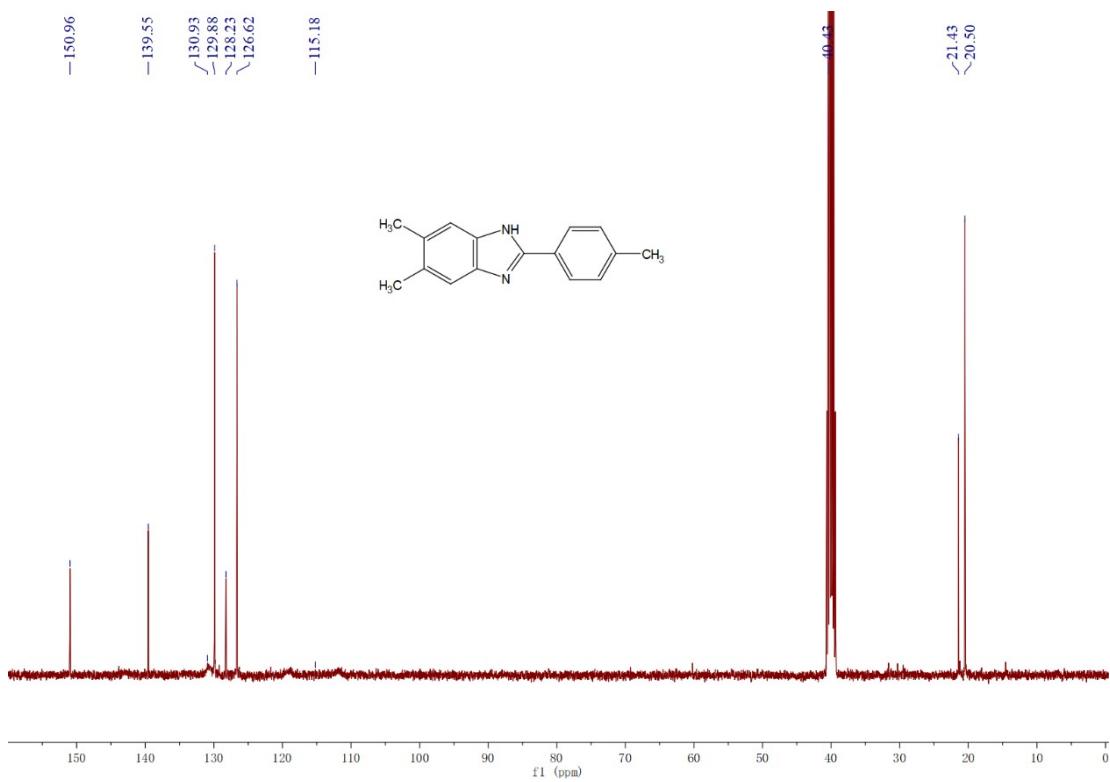


Figure S48. ^{13}C NMR for 5,6-dimethyl-2-(p-tolyl)-1H-benzo[d]imidazole

5,6-dimethyl-2-(p-tolyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 12.55 (s, 1H), 8.05 (d, 2H), 7.38-7.33 (t, 4H); ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): δ 150.9, 139.5, 130.9, 129.8, 128.2, 126.6, 115.1, 40.42.

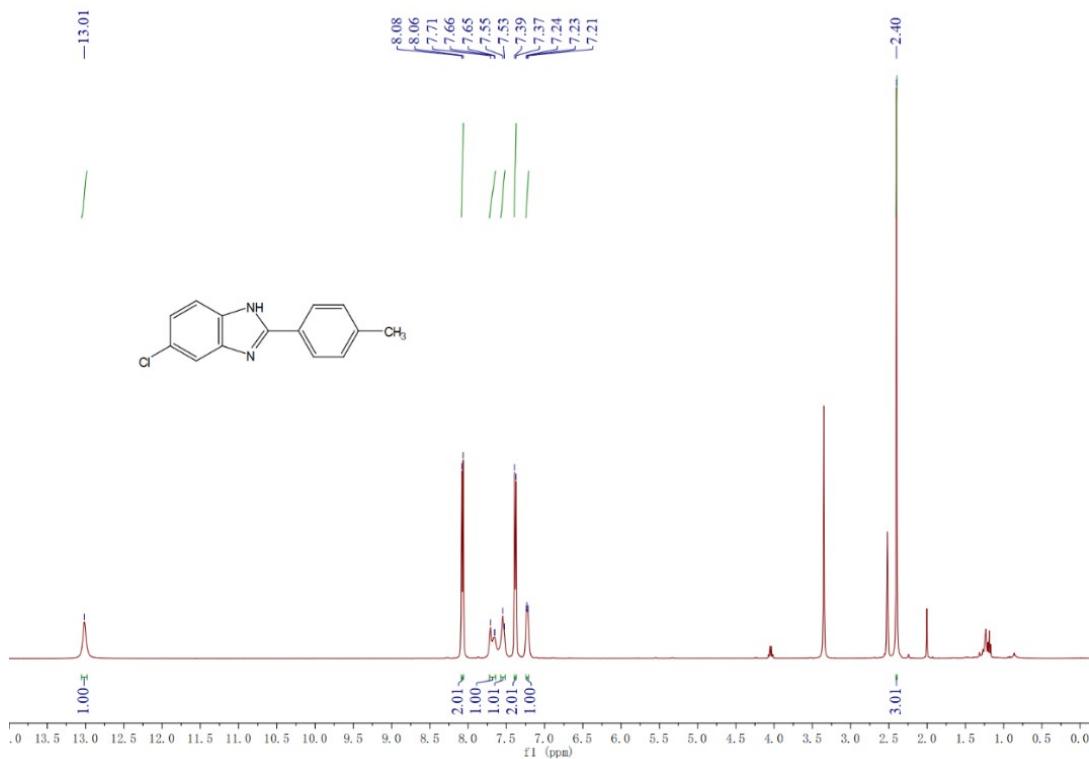


Figure S49. ^1H NMR for 5-chloro-2-(p-tolyl)-1H-benzo[d]imidazole

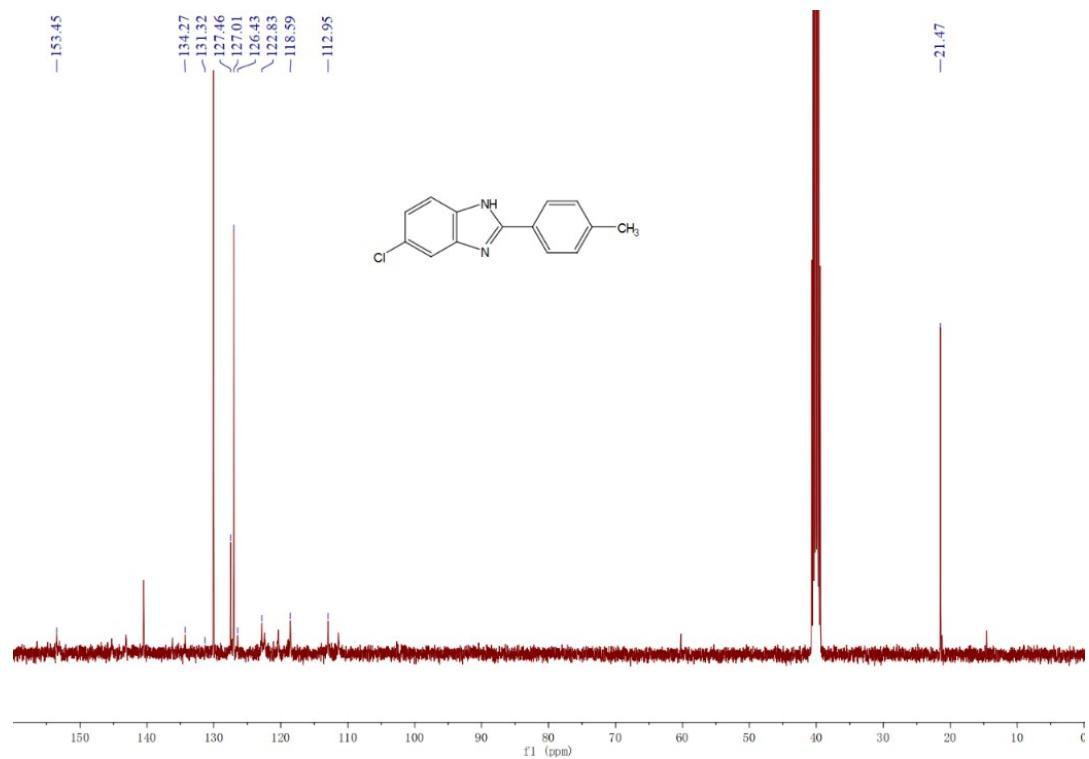


Figure S50. ^{13}C NMR for 5-chloro-2-(p-tolyl)-1H-benzo[d]imidazole

5-chloro-2-(p-tolyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 13.01 (s, 1H), 8.08 (d, 2H), 7.71-7.65 (t, 1H), 7.55 (d, 1H), 7.39 (d, 2H), 7.24-7.21 (t, 1H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 153.4, 134.2, 131.3, 127.4, 127.0, 126.4, 122.8, 118.5, 112.9.

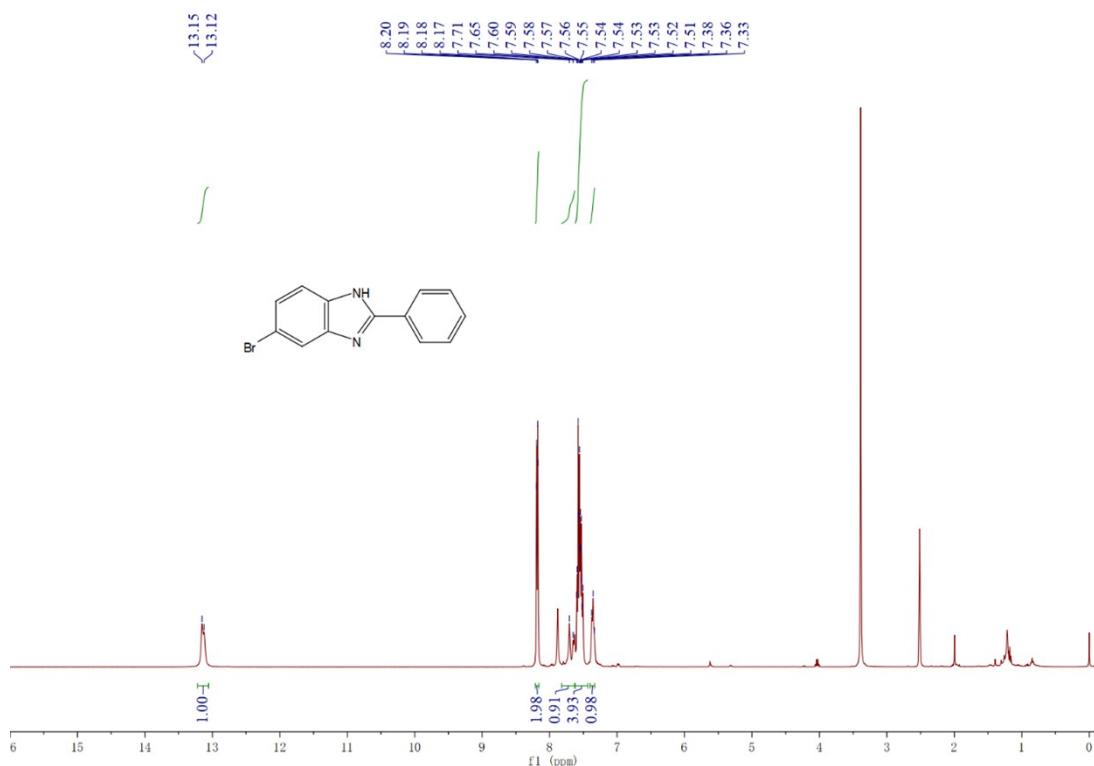


Figure S51. ^1H NMR for 5-bromo-2-phenyl-1H-benzo[d]imidazole

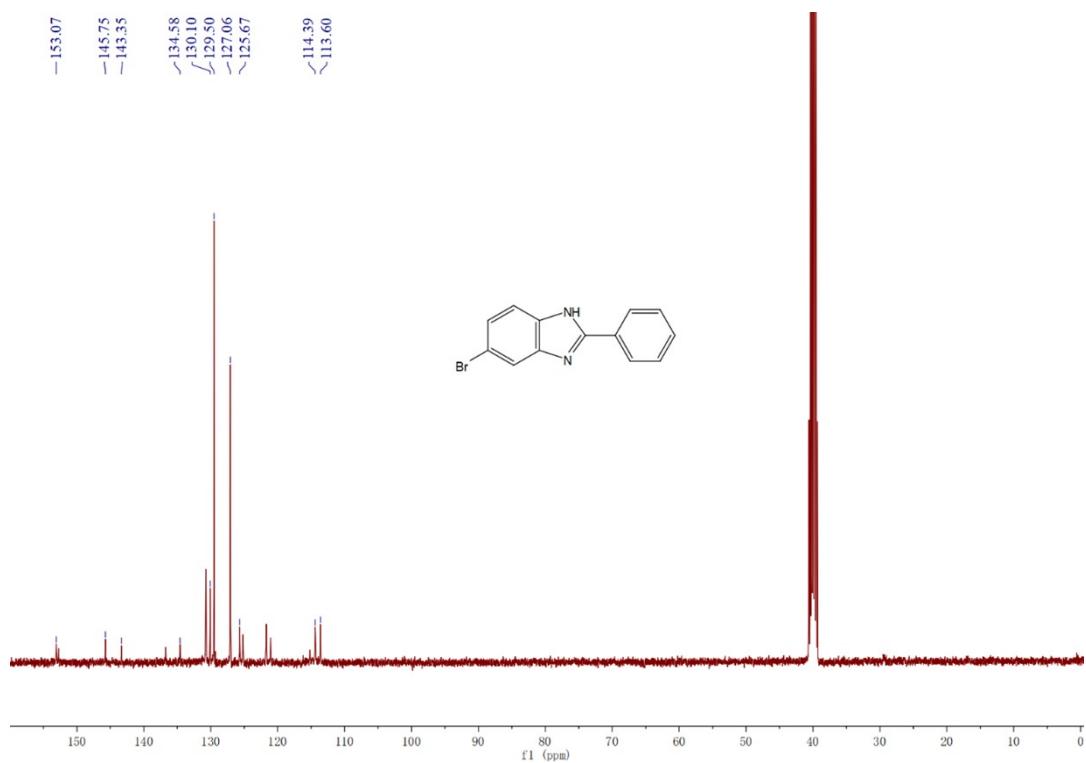


Figure S52. ^{13}C NMR for 5-bromo-2-phenyl-1H-benzo[d]imidazole

5-bromo-2-phenyl-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 13.15-13.12 (d, 1H), 8.20-8.17 (q, 2H), 7.71-7.57 (m, 1H), 7.56 (d, 4H), 7.54-7.33 (m, 1H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 153.0, 145.7, 143.3, 134.5, 130.1, 129.5, 127.0, 125.6, 114.3, 113.6.



Figure S53. ^1H NMR for 5-bromo-2-(4-bromophenyl)-1H-benzo[d]imidazole

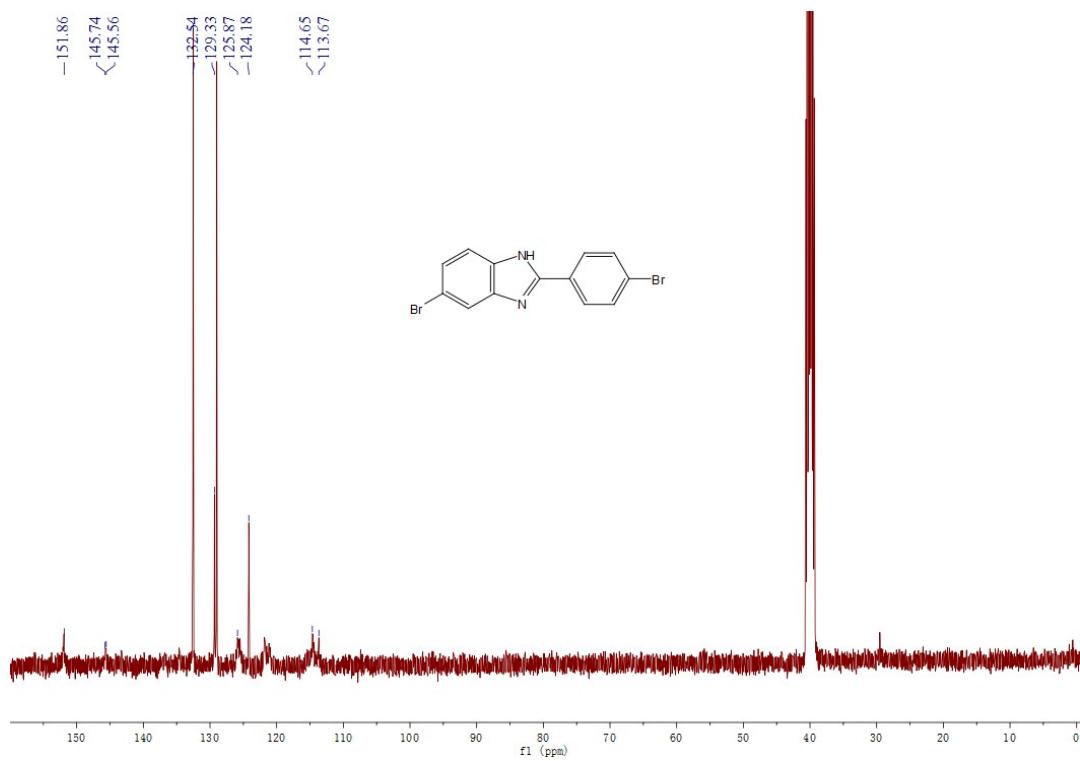


Figure S54. ^{13}C NMR for 5-bromo-2-(4-bromophenyl)-1H-benzo[d]imidazole

5-bromo-2-(4-bromophenyl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 13.23 (s, 1H), 8.13 (d, 2H), 7.87-7.78 (t, 3H), 7.74-7.57 (d, 1H), 7.38 (d, 1H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 151.8, 145.7, 145.5, 132.5, 129.3, 125.8, 124.1, 114.6, 113.6.

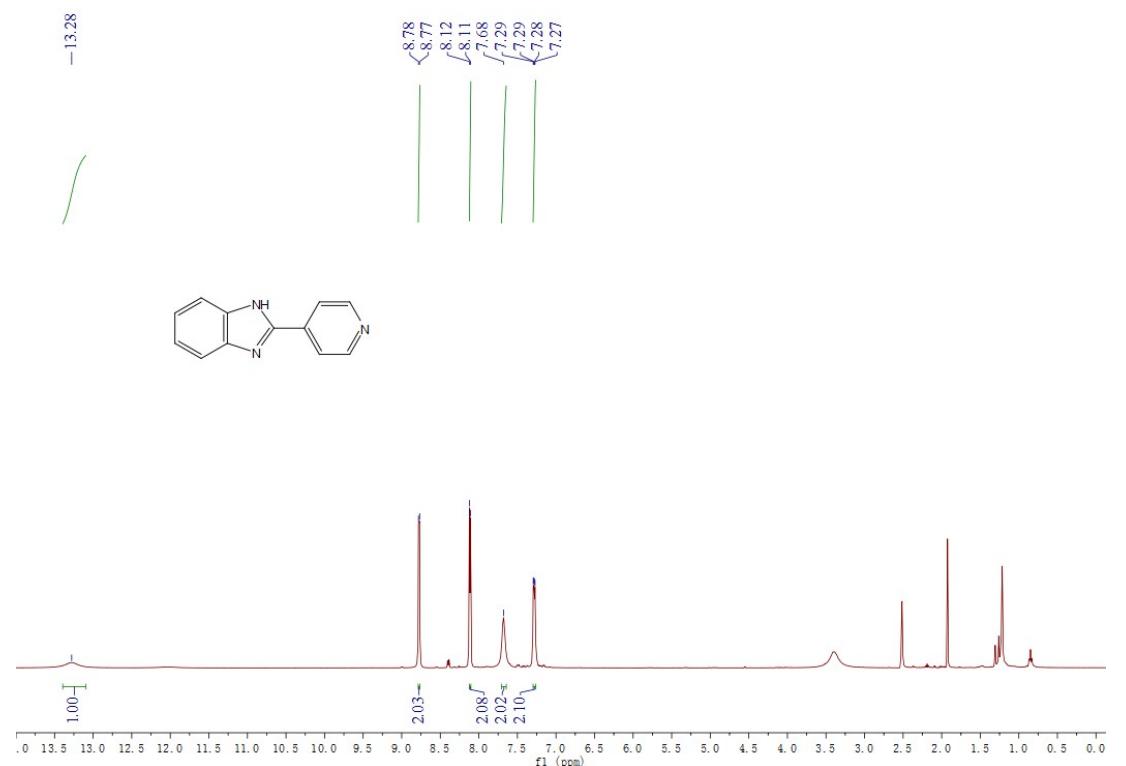


Figure S55. ^1H NMR for 2-(pyridin-4-yl)-1H-benzo[d]imidazole

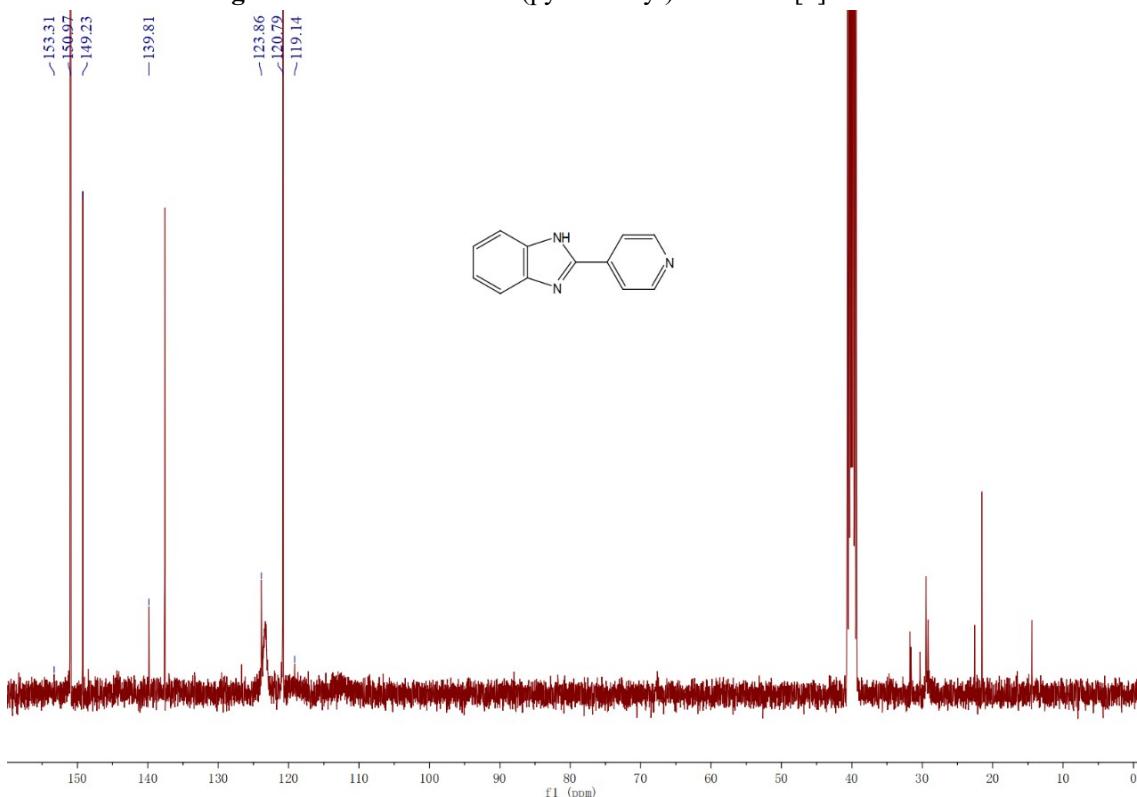


Figure S56. ^{13}C NMR for 2-(pyridin-4-yl)-1H-benzo[d]imidazole

2-(pyridin-4-yl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): 13.28 (s, 1H), 8.78 (d, 2H), 8.12 (d, 2H), 7.68 (s, 2H), 7.29-7.27 (q, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): 153.3, 150.9, 149.2, 139.8, 123.8, 120.7, 119.1.

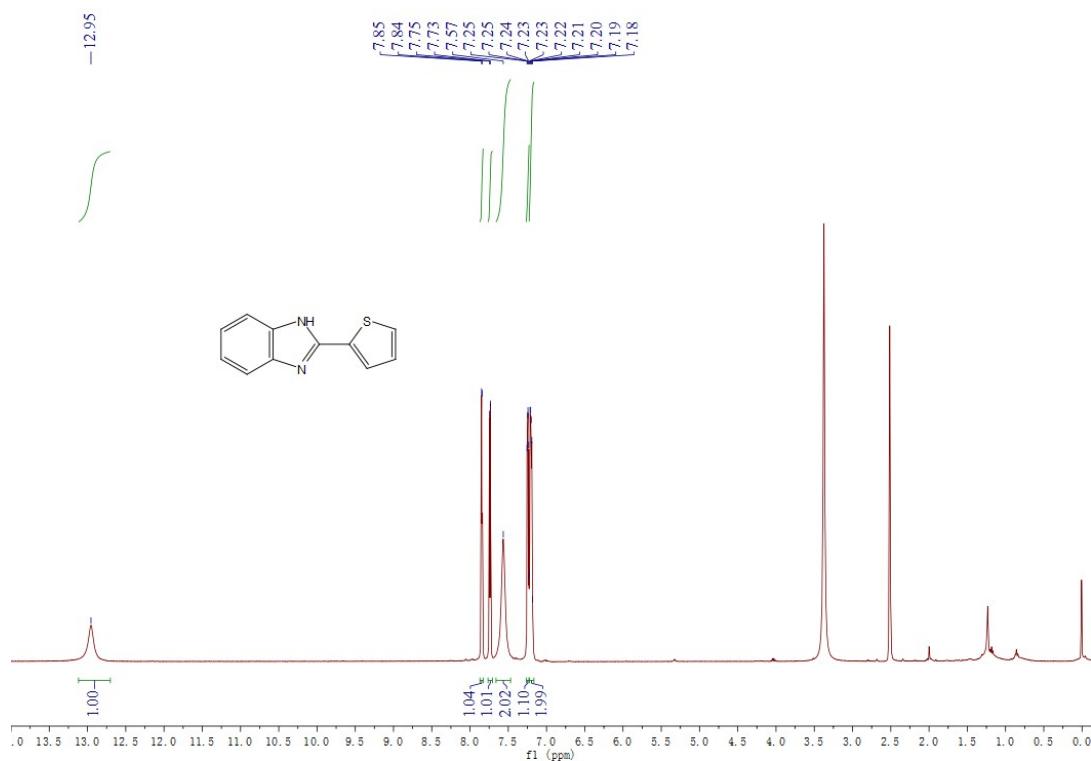


Figure S57. ^1H NMR for 2-(thiophen-2-yl)-1H-benzo[d]imidazole

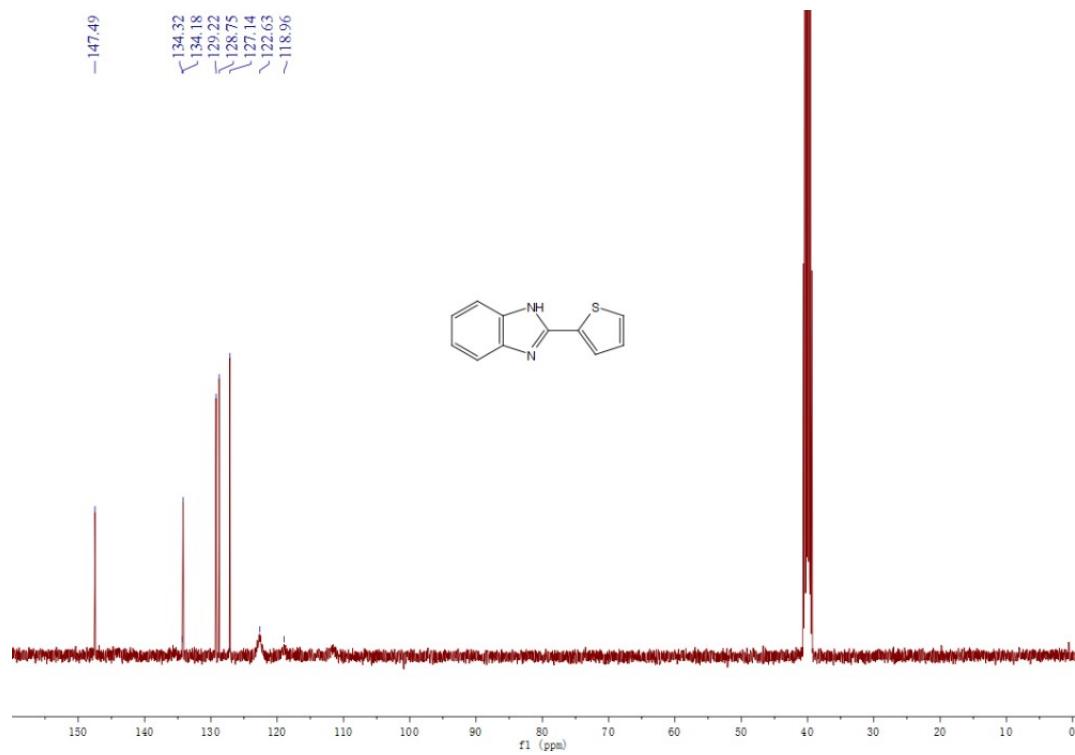


Figure S58. ^{13}C NMR for 2-(thiophen-2-yl)-1H-benzo[d]imidazole

2-(thiophen-2-yl)-1H-benzo[d]imidazole: ^1H NMR (DMSO-d₆, 400 MHz, ppm): δ 12.95 (s, 1H), 7.85 (d, 1H), 7.75-7.57 (t, 1H), 7.25 (s, 2H), 7.23-7.23 (q, 1H), 7.22-7.18 (m, 2H); ^{13}C NMR (DMSO-d₆, 100 MHz, ppm): δ 147.4, 134.3, 134.1, 129.2, 128.7, 127.1, 122.6, 118.9.

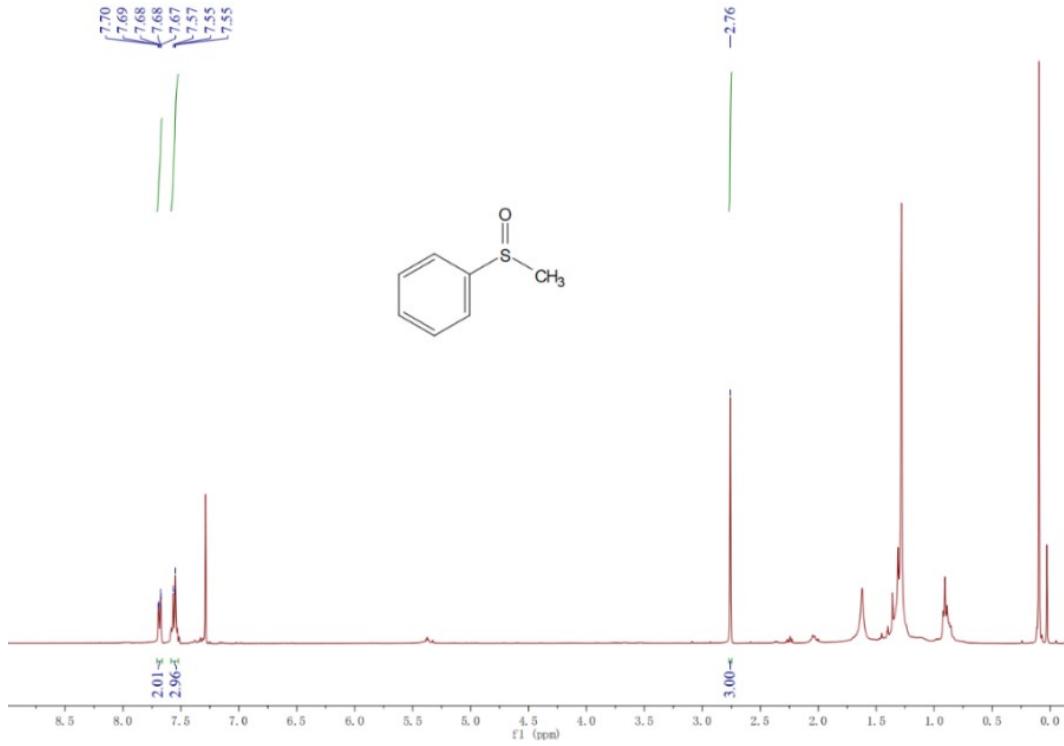


Figure S59. ^1H NMR for (methylsulfinyl)benzene

(methylsulfinyl)benzene: ^1H NMR (CDCl_3 , 400 MHz, ppm): 7.70-7.67 (m, 2H), 7.57-7.55 (t, 3H), 2.76 (s, 3H).

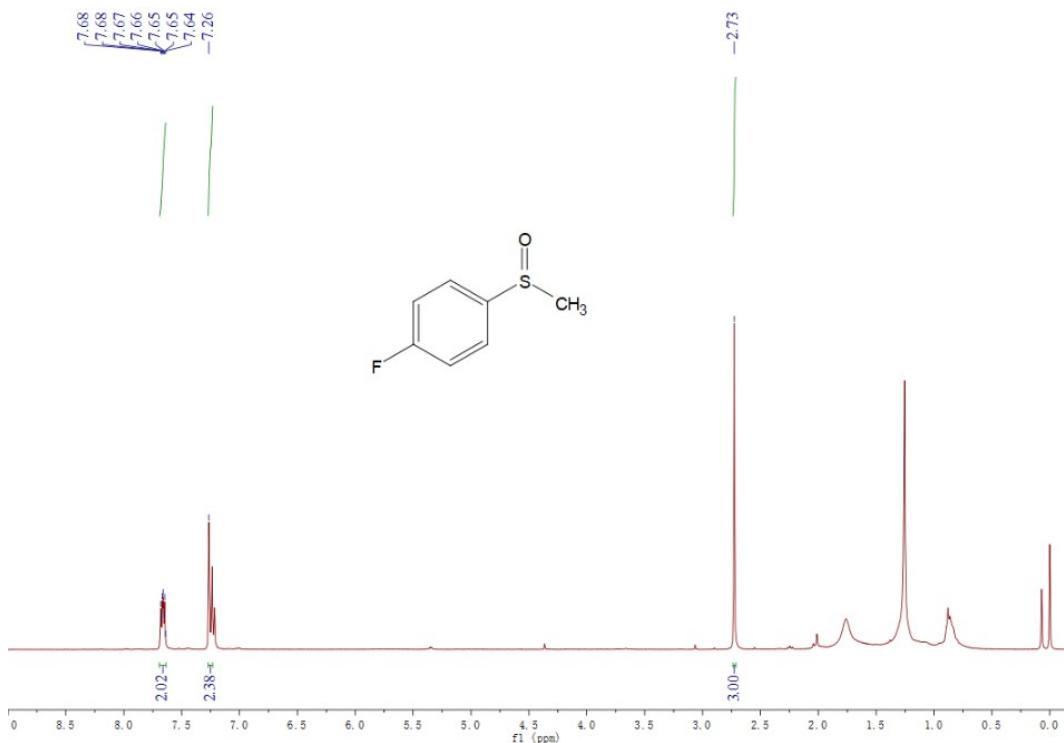


Figure S60. ^1H NMR for 1-fluoro-4-(methylsulfinyl)benzene

1-fluoro-4-(methylsulfinyl)benzene: ^1H NMR (CDCl_3 , 400 MHz, ppm): 7.68-7.64 (m, 2H), 7.26 (s, 2H), 2.73 (s, 3H).

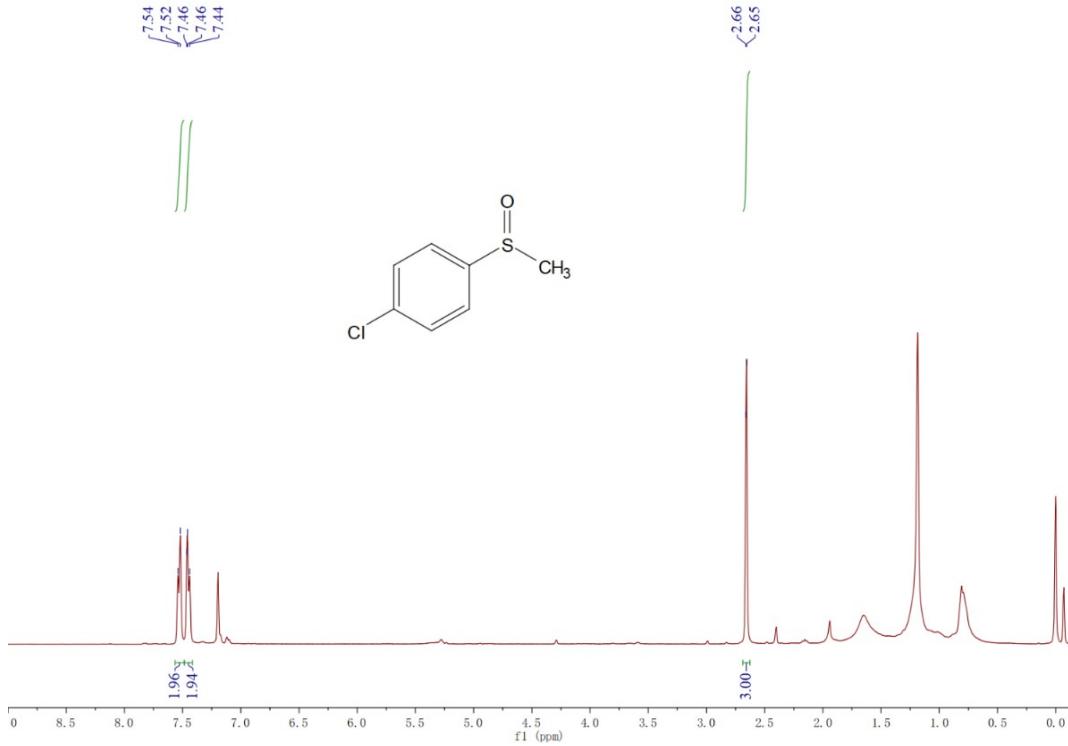


Figure S61. ^1H NMR for 1-chloro-4-(methylsulfinyl)benzene

1-chloro-4-(methylsulfinyl)benzene: ^1H NMR (CDCl_3 , 400 MHz, ppm): 7.54 (d, 2H), 7.46-7.44 (t, 2H), 2.66 (d, 3H).

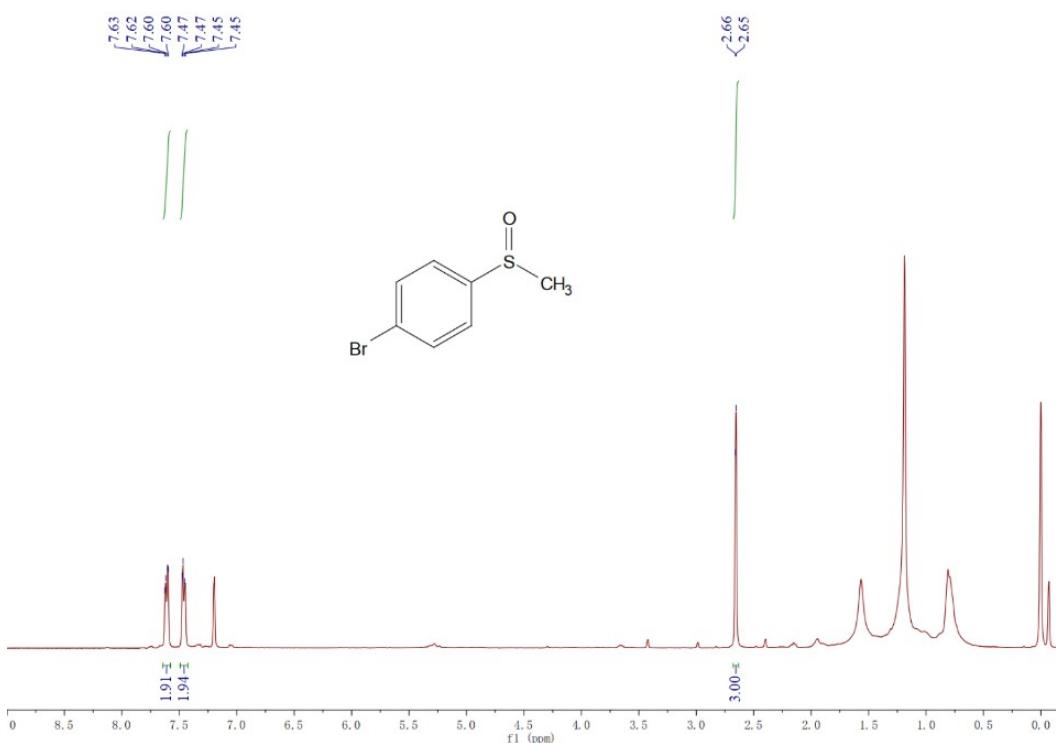


Figure S62. ^1H NMR for 1-bromo-4-(methylsulfinyl)benzene

1-bromo-4-(methylsulfinyl)benzene: ^1H NMR (CDCl_3 , 400 MHz, ppm): 7.63-7.60 (q, 2H), 7.47-7.45 (q, 2H), 2.66 (d, 3H).

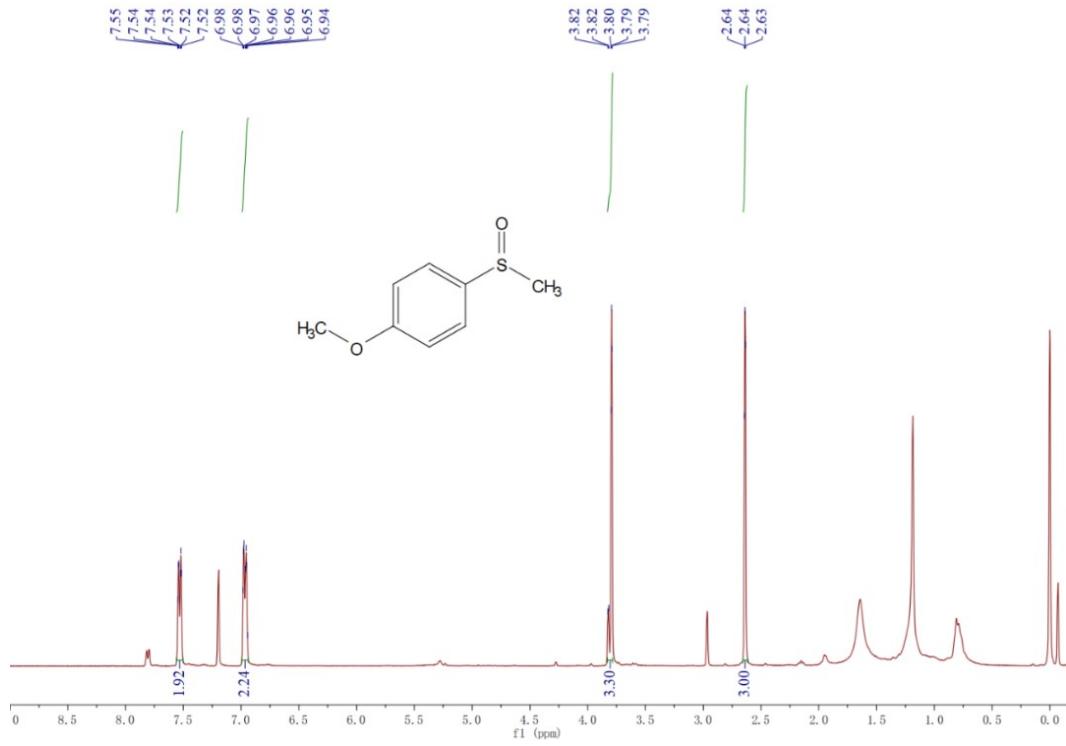


Figure S63. ^1H NMR for 1-methoxy-4-(methylsulfinyl)benzene

1-methoxy-4-(methylsulfinyl)benzene: ^1H NMR (CDCl_3 , 400 MHz, ppm): 7.55-7.52 (m, 2H), 6.98-6.94 (m, 2H), 3.82-3.79 (m, 3H), 2.64-2.63 (t, 3H).

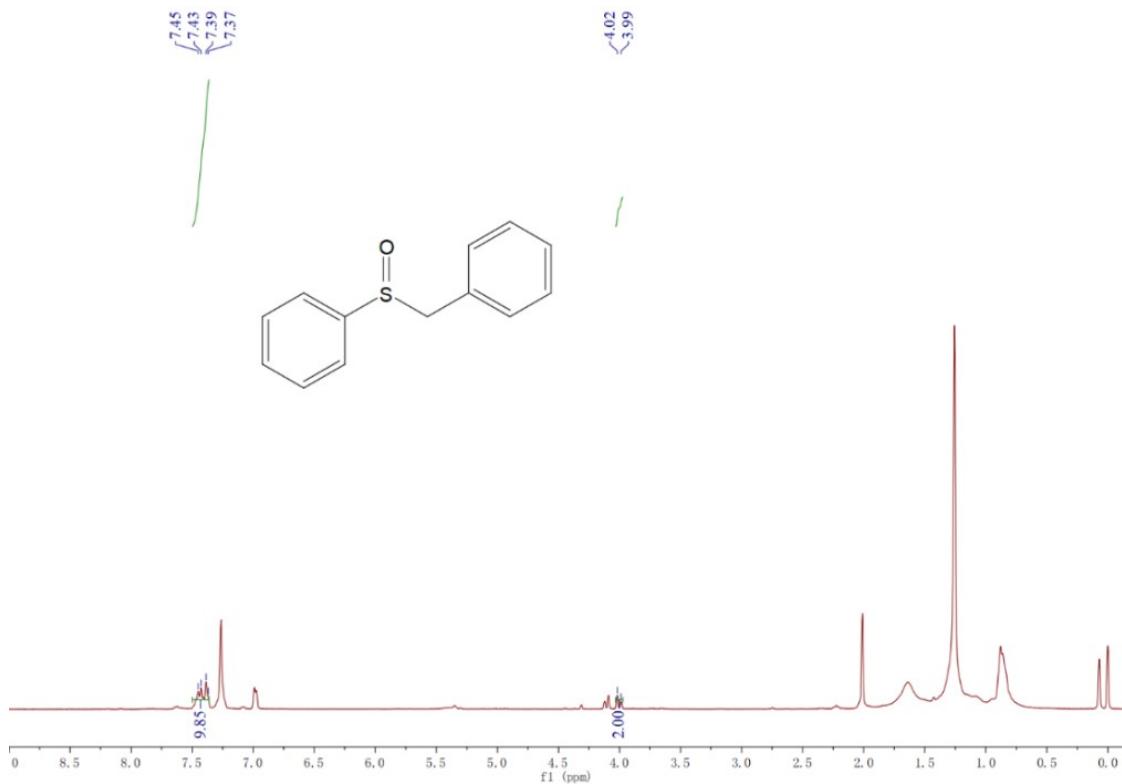


Figure S64. ^1H NMR for (benzylsulfinyl)benzene

(benzylsulfinyl)benzene: ^1H NMR (CDCl_3 , 400 MHz, ppm): 7.45-7.37 (q, 10H), 4.02-3.99 (d, 2H).

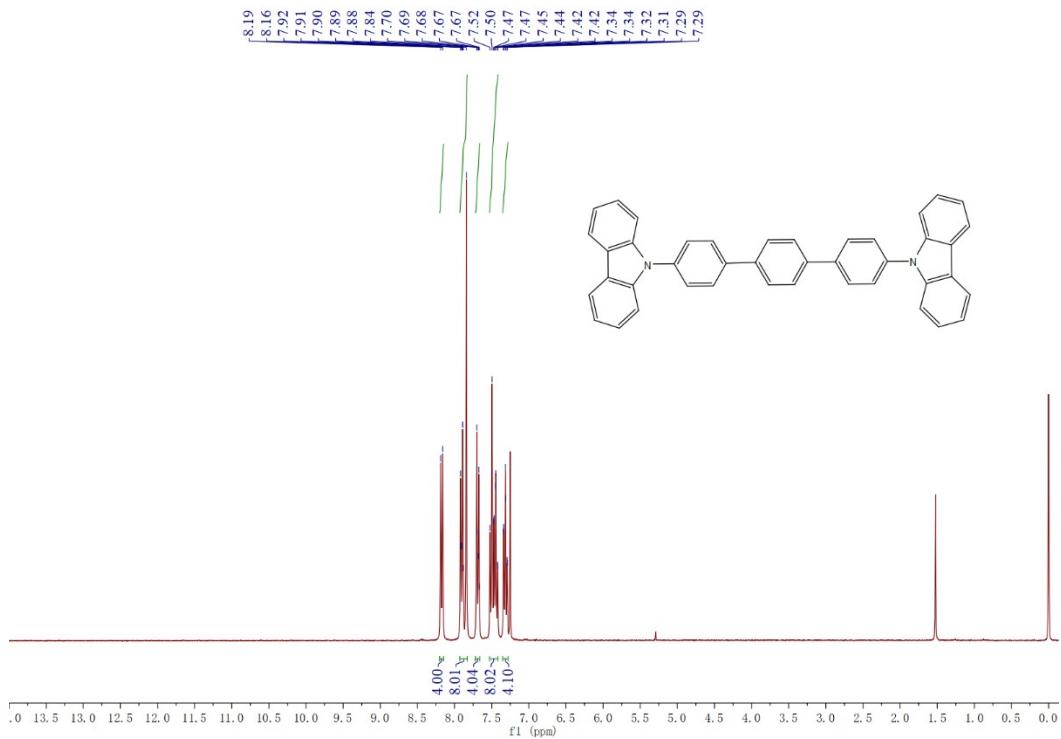


Figure S65. ¹H NMR for 4,4''-di(9H-carbazol-9-yl)-1,1':4',1''-terphenyl

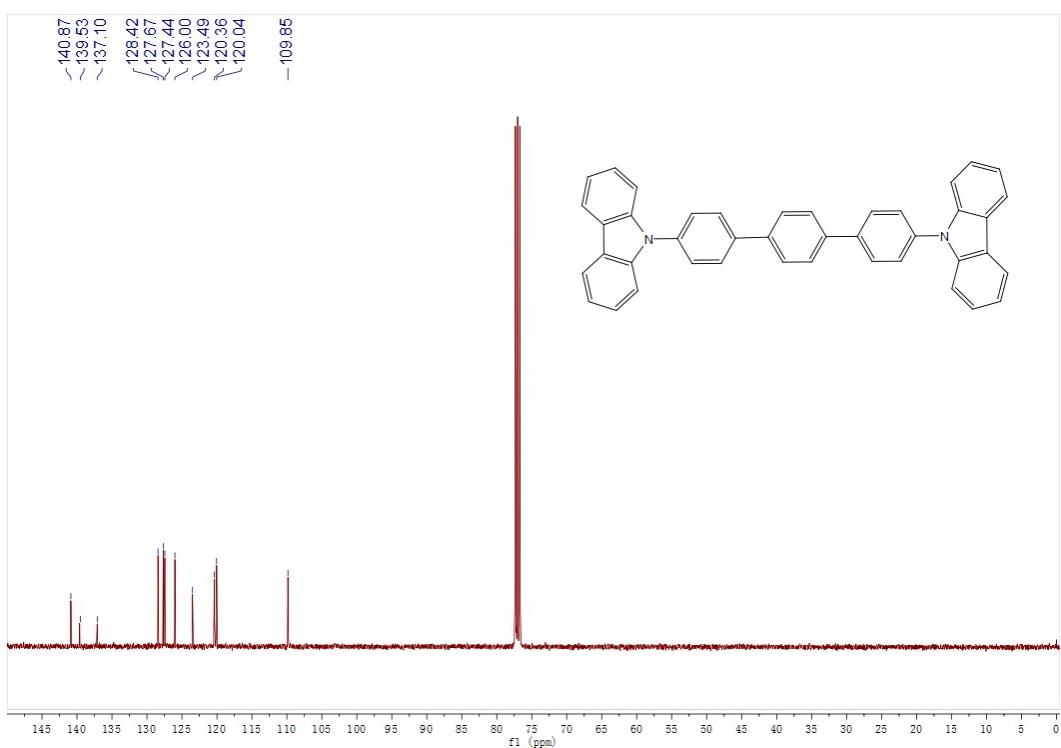


Figure S66. ¹³C NMR for 4,4''-di(9H-carbazol-9-yl)-1,1':4',1''-terphenyl

4,4''-di(9H-carbazol-9-yl)-1,1':4',1''-terphenyl: ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.19-8.16 (m, 4H), 7.92-7.88 (m, 8H), 7.84-7.67 (m, 4H), 7.52-7.42 (m, 8H), 7.34-7.29 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 140.87, 139.53, 137.10, 128.42, 127.67, 127.44, 126.00, 123.49, 120.36, 120.04.

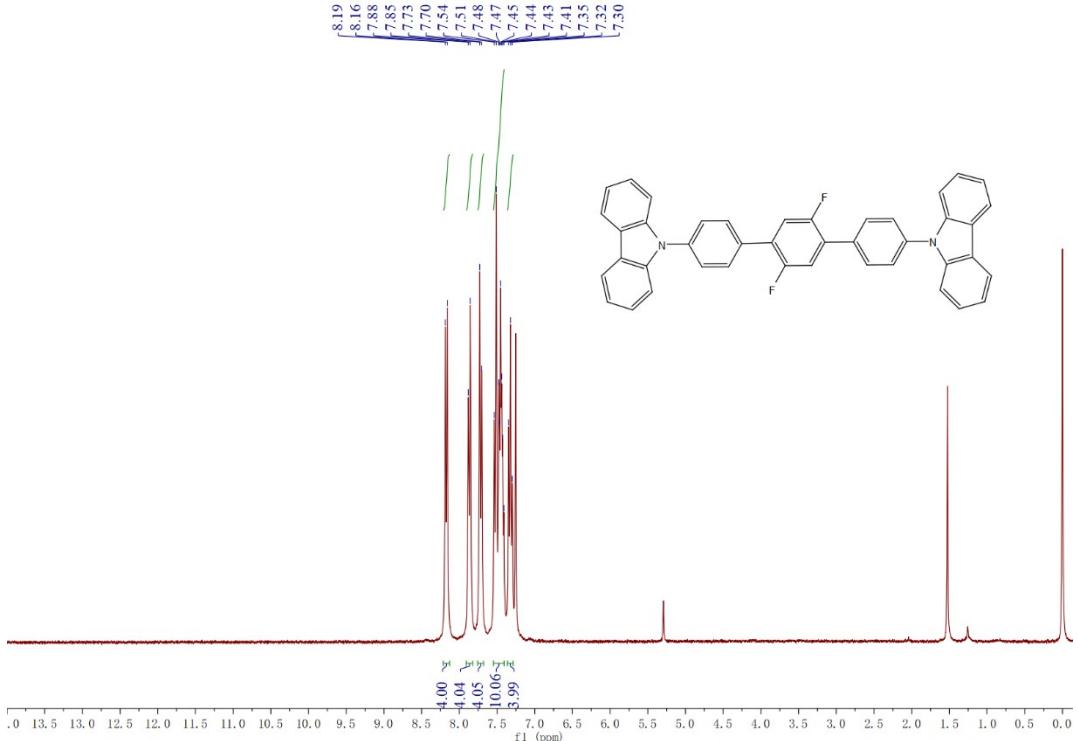


Figure S67. ¹H NMR for 9,9'-(2',5'-difluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole)

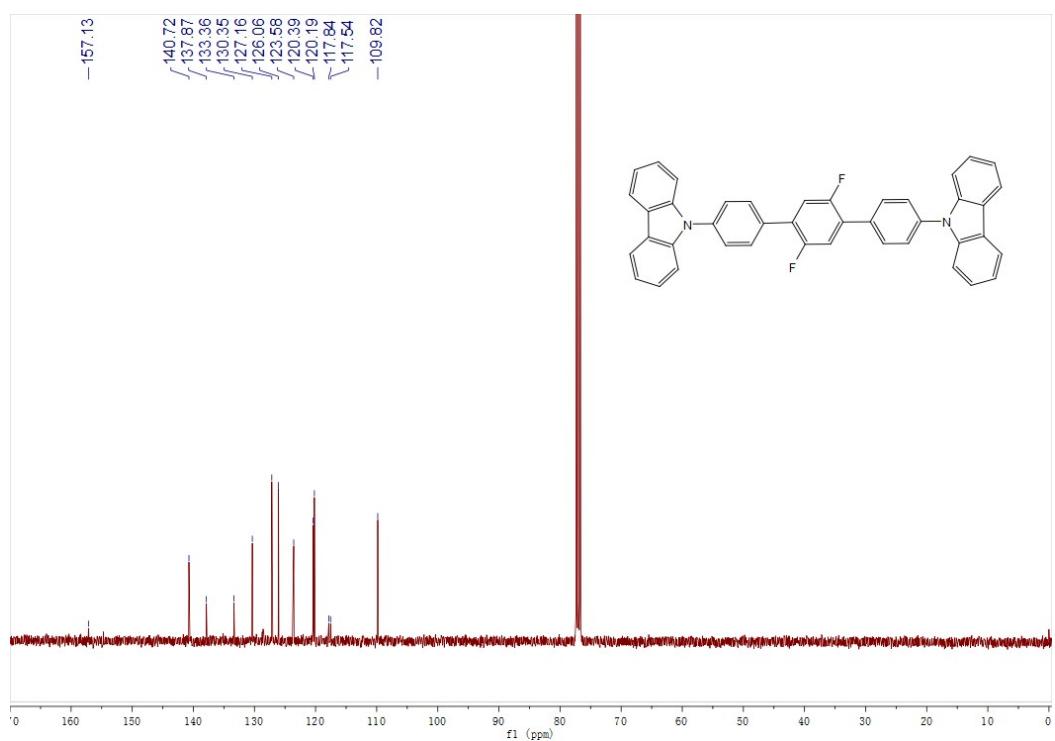


Figure S68. ¹³C NMR for 9,9'-(2',5'-difluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole)

9,9'-(2',5'-difluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole): ¹H NMR (CDCl_3 , 400 MHz, ppm): δ 8.19-8.16 (d, 4H), 7.88-7.85 (d, 4H), 7.73-7.70 (d, 4H), 7.54-7.41 (m, 10H), 7.35-7.30 (t, 4H); ¹³C NMR (CDCl_3 , 100 MHz, ppm): δ 157.13, 140.72, 137.87, 133.36, 130.35, 127.16, 126.06, 123.58, 120.39, 120.19, 117.84, 117.54, 109.82.

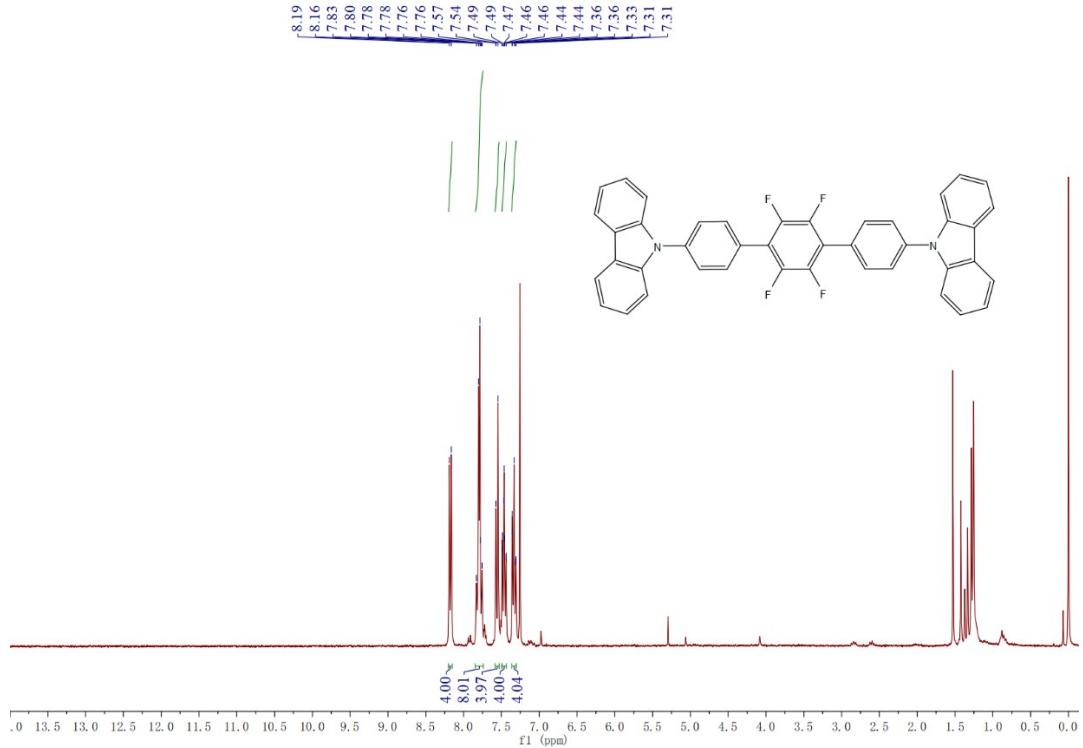


Figure S69. ¹H NMR for 9,9'-(2',3',5',6'-tetrafluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole)

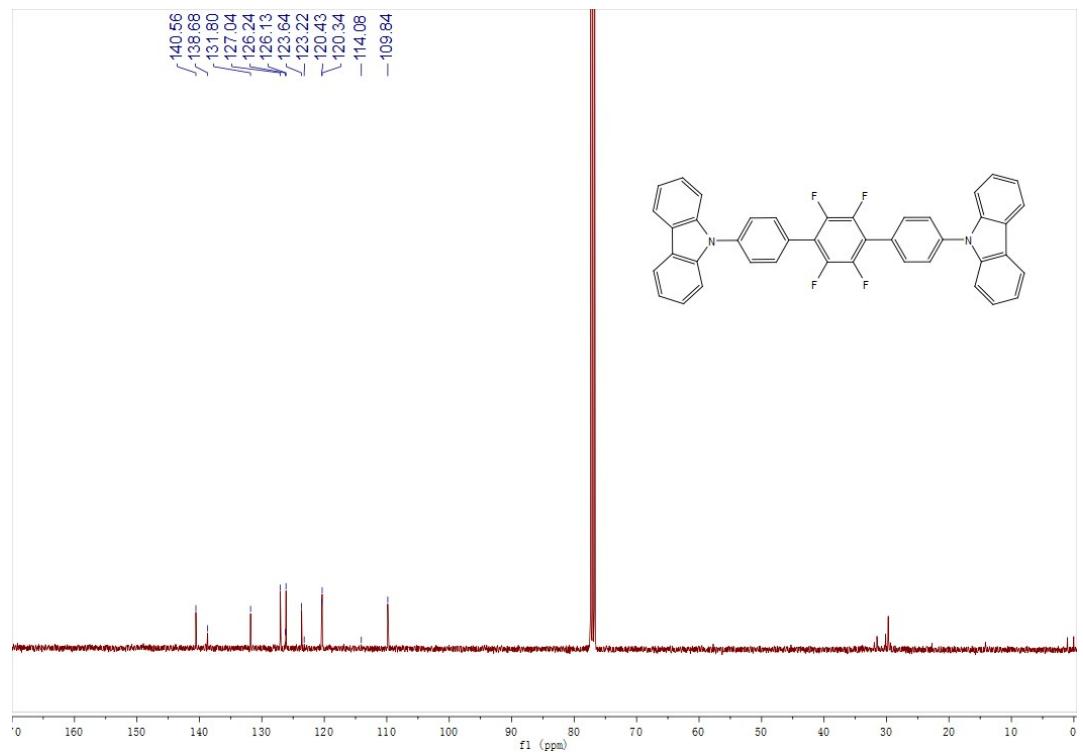


Figure S70. ¹³C NMR for 9,9'-(2',3',5',6'-tetrafluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole)

9,9'-(2',3',5',6'-tetrafluoro-[1,1':4',1"-terphenyl]-4,4"-diyl)bis(9H-carbazole): ¹H NMR (CDCl_3 , 400 MHz, ppm): δ 8.19-8.16 (d, 4H), 7.83-7.57 (m, 8H), 7.54-7.49 (d, 4H), 7.47-7.44 (m, 4H), 7.36-7.31 (q, 4H); ¹³C NMR (CDCl_3 , 100 MHz, ppm): δ 140.56, 138.68, 131.80, 127.04, 126.24, 126.13, 123.64, 123.22, 120.43, 120.34, 114.08, 109.84.