Supplementary Information (SI) for Reaction Chemistry & Engineering.
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Magnetic Mesoporous Zirconium Phosphate: Highly Efficient and Reusable Catalyst for Green Synthesis of Tetrazole and Benzazole through Alcohol Oxidation

Maryam Tukhani[a], *Alireza Najafi Chermahini**[, a], *Abdolreza Hajipour**[, a]

[a] *aDepartment of Chemistry, Isfahan University of Technology, 84154-83111 Isfahan, Iran;*

**E-mail: anajafi@iut.ac.ir; najafy@gmail.com, Tel:+983133913256*

Outline

1. Figures

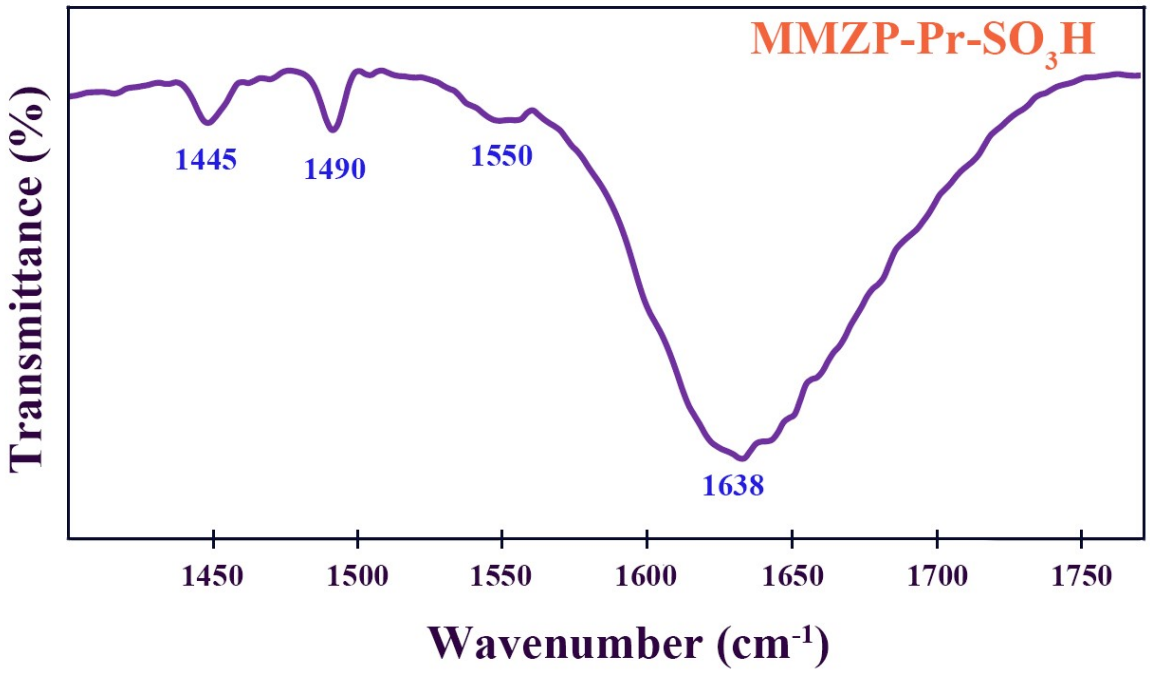
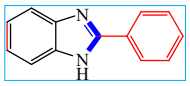


Figure S1. Pyridine FT-IR spectra of MMZP-Pr-SO_3H catalyst

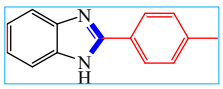
2. Spectral data for synthesized compounds

1.1. 2-Phenyl-1H-benzoimidazole



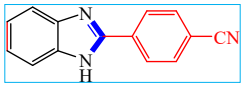
White solid; yield: 92%; m.p: 290-292 °C; IR (KBr) (υ_{max}, cm^{-1}): 1551 (C=N), 3455 (NH); ^{1}H NMR (250 MHz, DMSO-d6): δ (ppm) = 7.22-7.33 (m, 2H), 7.55-7.66 (m, 4H), 8.22-8.26 (m, 2H), 12.99 (s, 1H); Anal. Calcd. for $C_{13}H_{10}N_2$: C,80.39; H,5.19; N,14.42. Found: C, 80.29; H, 5.21; N, 14.40.

1.2. 2-p-Tolyl-1H-benzoimidazole



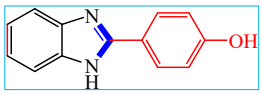
White solid, yield: 90%; m.p: 276-278 °C; IR (KBr) (υ_{max}, cm^{-1}): 1550 (C=N), 2980 (CH_3), 3436 (NH). ^{1}H NMR (250 MHz, DMSO-d6): δ (ppm) = 2.36 (s, 3H), 7.14-7.22 (m, 2H), 7.33 (d, J= 7.5 Hz, 2H), 7.48-7.63 (m, 2H), 8.05-8.08 (d, J=0 Hz, 2H), 12.92 (s, 1H); Anal. Calcd. for $C_{14}H_{12}N_2$: C,80.74; H,5.81; N,13.45. Found: C, 80.69; H, 5.90; N, 13.43.

1.3. 4-(1H-Benzoimidazol-2-yl)-benzonitrile



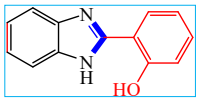
White solid, yield: 84%; m.p: 267-269 °C; IR (KBr) (υ_{max}, cm^{-1}): 1615 (C=N), 2223 (Nitril), 3436 (NH); ^{1}H NMR (250 MHz, DMSO-d6): δ (ppm) = 7.23 (s, 2H), 7.625 (d, J= 27.5 Hz, 2H), 7.995 (d, J= 7.5 Hz, 2H), 8.315 (d, J=7.5 Hz, 2H), 13.18 (s, 1H). Anal. Calcd. for $C_{14}H_9N_3$: C, 76.70; H, 4.11; N, 19.17. Found: C, 76.85; H, 4.20; N, 19.27.

1.4. 4-(1H-Benzoimidazol-2-yl)-phenol



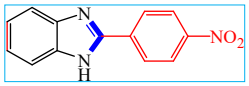
With crystals; yield: 91%; m.p: 255-257 °C; ^{1}H NMR (250 MHz, DMSO-d6): δ (ppm) = 3.36 (s, 1H), 6.86-6.92 (m, 2H), 7.09-7.15 (m, 2H), 7.49-7.52 (m,2H), 7.96-8.01 (m, 2H), 12.41 (s, 1H); ^{13}C NMR (62.9 MHz, DMSO-d6): δ (ppm) = 115.64, 120.86, 121.46, 128.05, 151.77, 159.34; Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33; O, 7.61. Found: C, 74.17; H, 4.90; N, 13.40; O, 7.42.

1.5. 2-(1H-Benzoimidazol-2-yl)-phenol



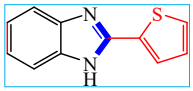
With crystals; yield: 81%; m.p: 242-244 °C; ^{1}H NMR (250 MHz, DMSO-d6): δ (ppm) = 6.97-7.04 (2H, m), 7.26-7.40 (3H, m), 7.65 (2H, d, J = 20 Hz), 8.03-8.07 (1H, m), 13.17 (2H, s); ^{13}C NMR (62.9 MHz, DMSO-d6): δ (ppm) = 111.49, 112.54, 117.14, 117.88, 119.05, 122.41, 123.14, 126.15, 131.66, 151.66, 157.99; Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33; O, 7.61. Found: C, 74.19; H, 4.70; N, 13.42; O, 7.36.

1.6. 2-(4-Niro-phenyl)-1H-benzoimidazole



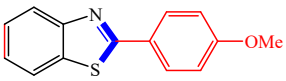
Yellow solid; yield: 85%; m.p: 272-274 °C; ^{1}H NMR (250 MHz, DMSO-d6): δ (ppm) = 7.25 (t, J= 5 Hz, 2H), 7.56 (t, J=5 Hz, 2H), 8.40 (t, J=30 Hz, 4H), 13.12 (s, 1H). ^{13}C NMR (62.9 MHz, DMSO-d6): δ (ppm) = 116.72, 124.44, 127.31, 128.52, 129.04, 132.39, 141.25, 152.82, 154.09. Anal. Calcd. for $C_{13}H_9N_3O_2$: C,65.27; H,3.79; N,17.56; O,13.38. Found: C, 65.32; H, 3.90; N, 17.40; O, 13.42.

1.7. 2-Thiophen-2-yl-1H-benzoimidazole



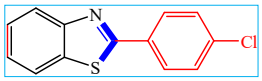
White solid; yield: 90%; m.p 331-333 °C; ^{1}H NMR (250 MHz, DMSO-d6): δ (ppm) = 7.15-7.23 (m; 4H), 7.69-7.72 (m, 1H), 7.80-7.82 (m, 2H), 12.92 (s, 1H); ^{13}C NMR (62.9 MHz, DMSO-d6): δ (ppm) = 111, 118.5, 121.7, 122.6, 126.6, 128.2, 128.7, 133.6, 134.6, 144.7. 146.9; Anal. Calcd. for $C_{14}H_{12}N_2S$: C, 65.97; H, 4.03; N, 13.99. Found: C, 66.05; H, 4.10; N, 13.42.

1.8. 2-(4-Methoxy-phenyl)-benzothiazole



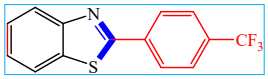
White solid; yield: 93%; m.p: 130-¬132 °C; IR (KBr) (υ_{max}, cm^{-1}): 1250 (C-O), 1612 (C=N), 2962 (CH_3); ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.89 (s, 3H), 6.85 (d, J=7.5 Hz, 2H), 7.25-7.49 (m, 2H), 7.84-8.04 (m, 3H); Anal. Calcd. for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 68.62; H, 4.78; N, 5.72.

1.9. 2-(4-Chloro-phenyl)-benzothiazole



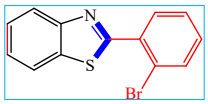
White solid; yield: 80 %; m.p: 96-98 °C, IR (KBr) (υ_{max}, cm^{-1}): 1088 (C-Cl), 1643 (C=N); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.23-7.31 (m, 2H), 7.37-7.43 (m, 2H), 7.46-7.50 (m, 1H), 7.68-7.70 (m,1H), 8.06-8.12 (m,2H); Anal. Calcd. for $C_{13}H_8ClNS$: C, 63.54; H, 3.28; N, 5.70. Found: C, 63.52; H, 3.38; N, 5.62.

1.10. 2-(4-Trifluoromethyl-phenyl)-benzothiazole



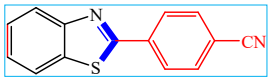
Yellow solid; yield: 81%; m.p 94-96 °C; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.16 (t, J= 2.5 Hz, 2H), 7.31-7.48 (m, 2H), 7.65-7.69 (m, 2H), 7.83-7.87 (m, 1H), 8.01-8.04 (d, J=0 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 121.7, 123.6, 125.1, 125.8, 126.0, 126.4, 126.6, 128.0, 129.8, 133.8, 145.2, 153.9, 169.8; Anal. Calcd. for $C_{14}H_8F_3NS$: C, 60.21; H, 2.89; N, 5.02. Found: C, 60.32; H, 2.78; N, 5.12.

1.11. 2-(2-Bromo-phenyl)-benzothiazole



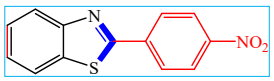
White solid; yield: 74%; m.p: 134-136 °C; IR (KBr) (υ_{max}, cm^{-1}): 1100 (C-Br), 1643 (C=N); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.28-7.36 (m, 1H), 7.40-7.47 (m, 2H), 7.49-7.57 (m, 1H), 7.71-7.75 (m, 1H), 7.93-8.03 (m, 2H), 8.13-8.17 (m, 1H); Anal. Calcd. for $C_{13}H_8BrNS$: C, 53.81; H, 2.78; N, 4.83. Found: C, 50.73; H, 2.62; N, 4.86.

1.12. 4-Benzothiazol-2-yl-benzonitrile



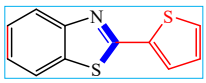
White solid; yield: 96 %; m.p: 180-182 °C; IR (KBr) (υ_{max}, cm^{-1}): 1612 (C=N), 2223 (Nitrile),^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.42-7.58 (m, 2H), 7.77-7.80 (m, 2H), 7.945 (d, J=7.5 Hz, 1H), 8.115 (d, J=7.5 Hz, 1H), 8.18-8.22 (m, 2H); Anal. Calcd. for $C_{14}H_8N_2S$: C, 71.16; H, 3.41; N, 11.86. Found: C, 71.26; H, 3.36; N, 11.96.

1.13. 2-(4-Nitro-phenyl)-benzothiazole



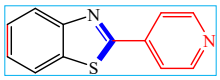
White solid; yield: 85 %; m.p: 230-231 °C; IR (KBr) (υ_{max}, cm^{-1}): 1338-1516 (NO_2), 1612 (C=N); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.44-7.59 (m, 2H), 7.67-7.71 (m, 1H), 8.255 (d, J=2.5 Hz, 1H), 8.29-8.30 (m, 2H), 8.34-8.39 (m, 2H); Anal. Calcd. for $C_{13}H_8N_2O_2S$: C, 60.93; H, 3.15; N, 10.93. Found: C, 60.73; H, 3.20; N, 11.06.

1.14. 2-Thiophen-2-yl-benzothiazole



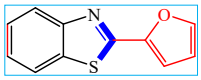
White solid; yield: 86%; mp: 99-100 °C; IR (KBr) (υ_{max}, cm^{-1}): 1643 (C=N); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm)= 7.28-7.31 (m, 2H), 7.37-7.40 (m, 1H), 7.57-7.60 (m, 1H), 7.72-7.76 (m, 1H), 7.88-7.90 (m, 1H), 7.93-7.97 (m, 1H); Anal. Calcd. for $C_{11}H_7NS_2$: C, 60.80; H, 3.25; N, 6.45. Found: C, 60.65; H, 3.35; N, 6.33.

1.15. 2-Pyridin-4-yl-benzothiazole



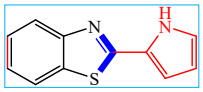
White solid; yield: 87%; mp: 134-135 °C; IR (KBr) (υ_{max}, cm^{-1}): 1643 (C=N); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.42-7.49 (m, 1H), 7.51-7.58 (m, 1H), 7.92-7.97 (m, 3H), 8.11-8.15 (m, 1H), 8.76-8.78 (m, 2H); Anal. Calcd. for $C_{12}H_8N_2S$: C, 67.90; H, 3.80; N, 13.20. Found: C, 68.0; H, 3.84; N, 13.26.

1.16. 2-Furan-2-yl-benzothiazole



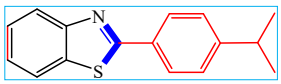
Yellow solid; yield: 88%; mp: 103-104 °C; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.53-6.54 (t, J=0 Hz, 1H), 7.11-7.13 (m, 1H), 7.28-7.34 (m, 1H), 7.39-7.45 (m, 1H), 7.53-7.54 (m, 1H), 7.80-7.84 (m, 1H), 7.96-8.0 (m, 1H); ^{13}C NMR (62.9 MHz, CDCl3): δ (ppm) = 111.4, 112.5, 121.5, 123.1, 125.2, 126.4, 134.3, 144.7, 148.7, 153.7, 157.54. Anal. Calcd. for $C_{11}H_7NOS$: C, 65.65; H, 3.51; N, 6.96. Found: C, 65.60; H, 3.54; N, 6.93.

1.17. 2-(1H-Pyrrol-2-yl)-benzothiazole



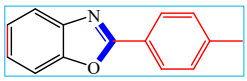
Yellow solid; yield: 87%; mp: 159-160 °C;^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.24-6.26 (m, 1H), 6.79-6.80 (m, 2H), 6.88 (t, J= 5 Hz, 1H), 7.24-7.36 (m, 1H), 7.75-7.83 (m, 2H), 10.36 (s, 1H); Anal. Calcd. for $C_{11}H_8N_2S$: C, 65.97; H, 4.03; N, 13.99. Found: C, 65.77; H, 4.05; N, 13.63.

1.18. 2-(4-Isopropyl-phenyl)-benzothiazole



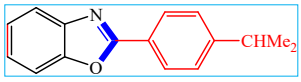
White solid; yield: 85%; m.p: 77-79 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.20-1.23 (m, 6H), 2.84-2.92 (m, 1H), 7.26-7.43 (m, 4H), 7.79-7.84 (m, 1H), 7.92-8.02 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 23.78, 34.1, 121.6, 123.0, 124.9, 126.2, 127.1, 127.6, 131.3, 134.9, 152.3, 154.1, 168.1; Anal. Calcd. for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.72; H, 5.78; N, 5.62.

1.19. 2-p-Tolyl-benzooxazole



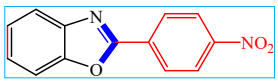
White solid; yield: 79%; m.p: 114-116 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 2.36 (s, 3H), 7.18-7.22 (m, 2H), 7.48-7.51 (m, 2H), 7.70 (t, J= 7.5 Hz, 2H), 8.07 (d, J= 7.5 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 29.5, 109,118.2, 113.0, 118.2, 120.4, 123.2, 126.3, 128.0, 129.5, 137.4, 141.5, 149.2, 164.4; Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.37; H, 5.25; N, 6.63.

1.20. 2-(4-Isopropyl-phenyl)-benzooxazole



White solid; yield: 87%; m.p: 77-79 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 1.35 (d, J= 7.5 Hz, 6H), 2.94-3.05 (m, 1H), 7.32-7.40 (m, 4H), 7.56-7.60 (m,1H), 7.75-7.79 (m, 1H), 8.17-8.20 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 23.7, 34.2, 110.5, 119.8, 124.5, 124.7, 124.8, 127.0, 127.7, 142.2, 150.7, 152.9, 154.0; Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.97; H, 6.25; N, 5.63.

1.21. 2-(4-Nitro-phenyl)-benzooxazole

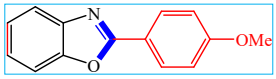


Yellow solid; yield: 73%; m.p 210-212 °C; IR (KBr) (υ_{max}, cm^{-1}): 1234 (CO), 1342,1520 (NO_2), 1582 (C=N); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.35 (t, J= 2.5 Hz, 1H), 7.375 (t, J= 2.5 Hz, 2H), 7.405 (t, J= 2.5 Hz, 1H), 7.51-7.52 (m, 2H), 7.54 (t, J= 5 Hz, 2H); Anal. Calcd. for $C_{13}H_8N_2O_3$: C, 65.0; H, 3.36; N, 11.66. Found: C, 64.97; H, 3.35; N, 11.63.

1.22. 4-Benzooxazol-2-yl-benzonitrile

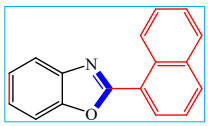
White solid; yield: 85%; m.p: 203-204 °C; IR (KBr) (υ_{max}, cm-1): 1581 (C=N), 2222 (Nitril); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 6.90-7.05 (m, 2H), 7.25 (t, J= 15 Hz, 1H), 7.355 (t, J= 17.5 Hz, 1H), 7.77 (d, J= 10 Hz, 2H), 8.015 (d, J= 7.5 Hz, 2H); Anal. Calcd. for $C_{14}H_8N_2O$: C, 76.35; H, 3.66; N, 12.22. Found: C, 76.32; H, 3.65; N, 12.33.

1.23. 2-(4-Methoxy-phenyl)-benzooxazole



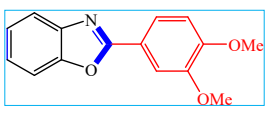
White solid; yield: 87%; m.p: 97-99 °C; 1249 (CO), 1582 (C=N), 2924 (CH_3); ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.83 (s, 3H), 6.9-7.0 (m, 2H), 7.2-7.3 (m, 4H), 7.47-7.53 (m, 1H), 7.66-7.71 (m, 1H); Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.52; H, 4.95; N, 6.32.

1.24. 2-Naphthalen-1-yl-benzooxazole



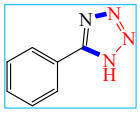
White solid; yield: 72%; m.p: 72-74 °C; ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.81 (s, 6H), 6.81-6.84 (d, J=0 Hz, 2H), 7.18-7.21 (m, 3H), 7.40-7.43 (m, 1H), 7.68-7.72 (m, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 55.9, 56.0, 110.0, 110.3, 110.9, 119.5, 119.7, 121.1, 124.4, 124.6, 142.2, 149.2, 149.1, 150.6, 151.9, 163; Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.52; H, 5.15; N, 5.37.

1.25. 2-(3,4-Dimethoxy-phenyl)-benzooxazole



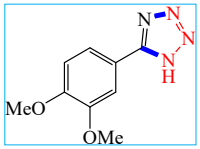
White solid; yield: 85%; m.p: 72-74 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 3.81 (s, 6H), 6.81-6.84 (d, J=0 Hz, 2H), 7.18-7.21 (m, 3H), 7.40-7.43 (m, 1H), 7.68-7.72 (m, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ (ppm) = 55.9, 56.0, 110.0, 110.3, 110.9, 119.5, 119.7, 121.1, 124.4, 124.6, 142.2, 149.2, 149.1, 150.6, 151.9, 163; Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.52; H, 5.15; N, 5.37.

1.26. 5-Phenyl-1H-tetrazole (6a)



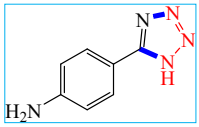
White solid; yield: 92%; m.p: 214-216 °C; FT-IR (KBr): υ_{max}.cm^{-1} 3124, 3040, 2981, 2909, 2829, 2770, 2689, 2610, 2560, 2490, 1620, 1570, 1490, 1470, 1411, 1159, 1060, 730, 710, 690; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm)= 7.58-7.65 (m, 3H), 8.04-8.06 (m, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm) = 124.19, 127.38, 129.91, 131.86, 155.80.

1.27. 5-(3,4-Dimethoxy-phenyl)-1H-tetrazole (6b)



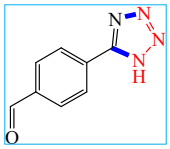
Off-White solid; yield: 90%; m.p: 198-199 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 3.84 (s, 3H), 3.86 (s, 3H), 5.97 (s, 1H), 6.79-6.81 (m, 1H), 7.28-7.25 (m, 1H), 7.39 (m, 1H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm) = 56.0, 110.2, 110.8, 120.1, 125.8, 149.0, 152.1, 169.1; Anal. Calcd. for $C_9H_{10}N_4O_2$: C, 52.42; H, 4.89; N, 27.17. Found: C, 52.12; H, 4.67; N, 26.99.

1.28. 4-(1H-Tetrazol-5-yl)-phenylamine (6c)



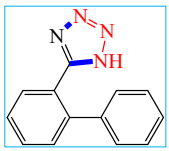
Brown solid; yield: 89%; m.p: 266-269 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 4.29 (s, 2H), 6.61 (d, J= 6.25 Hz, 2H), 7.34 (d, J= 6.25 Hz, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm) = 121.5, 133.5, 140.8, 150.1, 157.1.

1.29. 4-(1H-Tetrazol-5-yl)-benzaldehyde (6d)



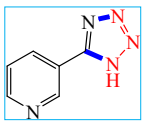
White solid; yield: 93%; m.p: 184-185 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 8.13-815 (d, J= 8.0 Hz, 2H), 8.26-8.28 (d, J= 8.0 Hz, 2H), 10.08 (s, 1H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm) = 127.17, 131.21, 136.51, 138.12, 155.62, 192.61.

1.30. 5-Biphenyl-2-yl-1H-tetrazole (6e)



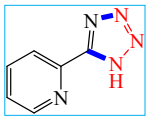
Yellow solid; yield: 84%; m.p: 226-229 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 6.92-6.96 (t, J= 6.4 Hz, 1H), 7.09-7.24 (m, 2H), 7.31-7-39 (m, 2H), 7.51-7.67 (m, 2H), 8.08-8.20 (m, 2H).

1.31. 3-(1H-Tetrazol-5-yl)-pyridine (6f)



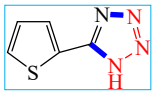
White solid; yield: 79%; m.p: 226-228 °C; FT-IR (KBr): υ_{max}.cm^{-1} 3214, 3086, 3063, 3036, 2490, 1610, 1583, 1528, 1485; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm)= 7.95-7.98 (m, 1H), 8.87-8.90 (m, 1H), 8.93-8.94 (m, H), 9.46 (S, 1H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm) = 124.39, 127.72, 141.88, 142.06, 145.67, 154.16.

1.32. 2-(1H-Tetrazol-5-yl)-pyridine (6g)



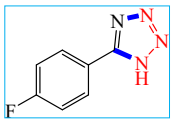
White solid; yield: 75%; m.p: 211-213 °C; FT-IR (KBr): υ_{max}.cm^{-1} 3088, 3060, 2959, 2929, 2864, 2737, 2692, 2622, 2582, 1728, 1602, 1557, 1483, 1449, 1405, 1284, 1158, 1068, 1024, 955, 795, 743, 726, 703, 637, 496; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 8.81 (m, 1H,), 8.24 (m, 1H), 8.10 (m, 1H), 7.65 (m, 1H) ; ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm) = 123.1, 126.7, 138.7, 144.0, 150.6, 155.3.

1.33. 5-Thiophen-2-yl-1H-tetrazole (6h)



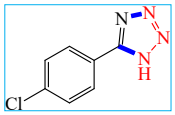
White solid; yield: 83%; m.p: 205-207 °C; FT-IR (KBr): $\upsilon_{max}.cm^{-1}$ 3109, 3074, 2975, 2799, 2782, 2733, 2629, 2571, 2510, 2466, 1832, 1601, 1513, 1412, 1235, 1139, 1050, 959, 849, 735, 721; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 7.29-7.31 (m, 1H,), 7.80-782 (m, 1H), 7.84-7.90 (m, 1H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm)= 125.46, 124.14, 129.75, 130.88, 151.73.

1.34. 5-(4-Fluoro-phenyl)-1H-tetrazole (6i)



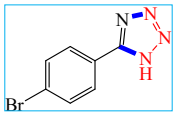
Off-white solid; yield: 96%; m.p: 191-192 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 7.19-7.23 (d, j= 7.1 Hz, 2H), 7.47-7.50 (d, j= 7.1 Hz, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm)= 127.78, 129.71, 135.44, 154.64, 166.39.

1.35. 5-(4-Chloro-phenyl)-1H-tetrazole (6j)



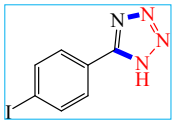
White solid; yield: 94%; m.p: 261-262 °C; FT-IR (KBr): $\upsilon_{max}.cm^{-1}$ 3089, 3059, 3010, 2981, 2910, 2849, 2731, 2619, 2540, 2469, 1610, 1559, 1491, 1440, 1159, 1096, 1049, 1015, 989, 829, 739, 510; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 7.68-7.73 (d, J= 8.4 Hz, 2H,), 7.97-781 (d, j= 6.9 Hz, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm)= 123.5, 129.2, 129.7, 130.0, 130.8, 136.4, 155.3.

1.36. 5-(4-Bromo-phenyl)-1H-tetrazole (6k)



White solid; yield: 90%; m.p: 264-265 °C; FT-IR (KBr): $\upsilon_{max}.cm^{-1}$ 3091, 3059, 2980, 2899, 2839, 2759, 2732, 2629, 1649, 1599, 1555, 1479, 1425, 1410, 1161, 1080, 1049, 1021, 831,739, 499; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 7.80-7.82 (d, J= 6.2 Hz, 2H), 8.01-8.03 (d, J= 6.2 Hz, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm)= 123.88, 125.12, 129.31, 132.76, 135.31, 155.31

1.37. 5-(4-Iodo-phenyl)-1H-tetrazole (6l)



White solid; yield: 87%; m.p: 269-271 °C; ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) = 7.81-7.83 (d, J=.8.2 Hz, 2H,), 7.99-8.01 (d, J=.8.1 Hz, 2H,); ^{13}C NMR (62.9 MHz, DMSO-d_6): δ (ppm)= 98.9, 124.2, 124.9 129.1, 138.7, 139.2, 157.2.

3. Copies of 1HNMR and 13CNMR of synthesized compounds

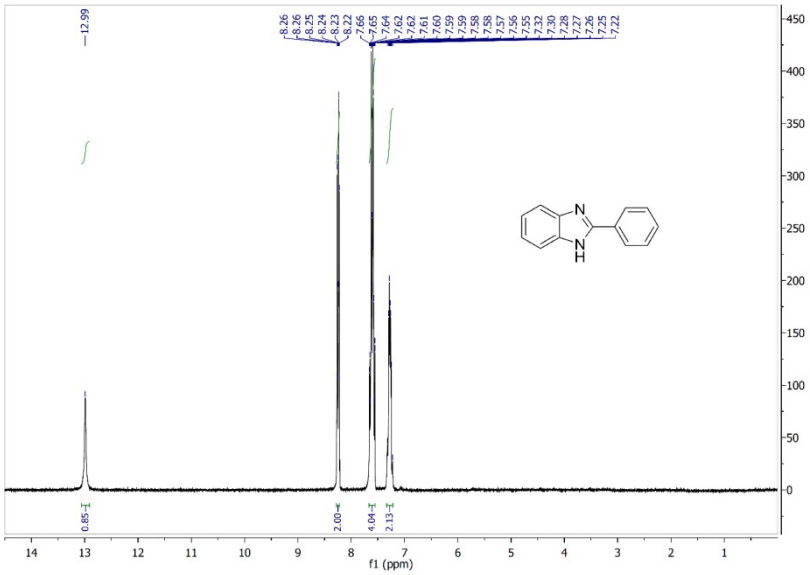


Figure S2. The ^{1}H NMR spectra of compound 3a

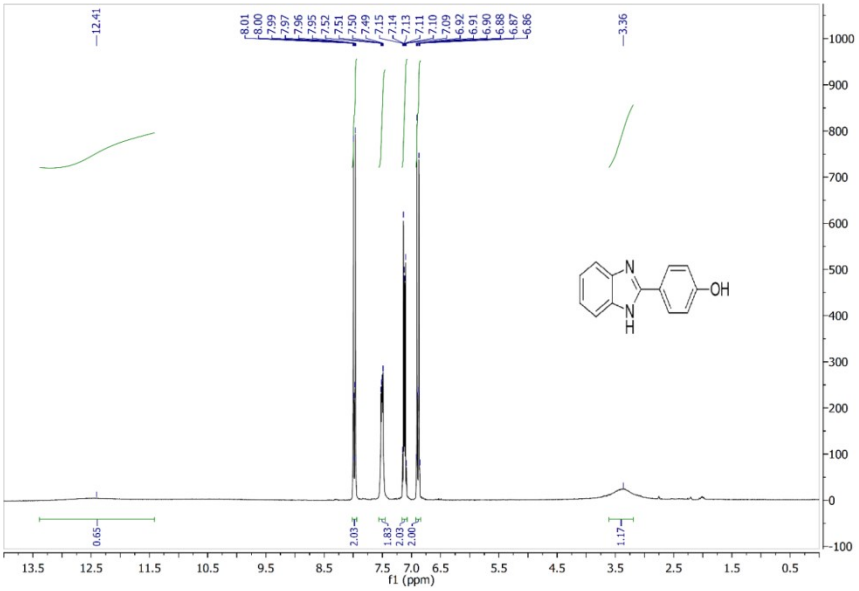


Figure S3. The ^{1}H NMR spectra of compound 3e.

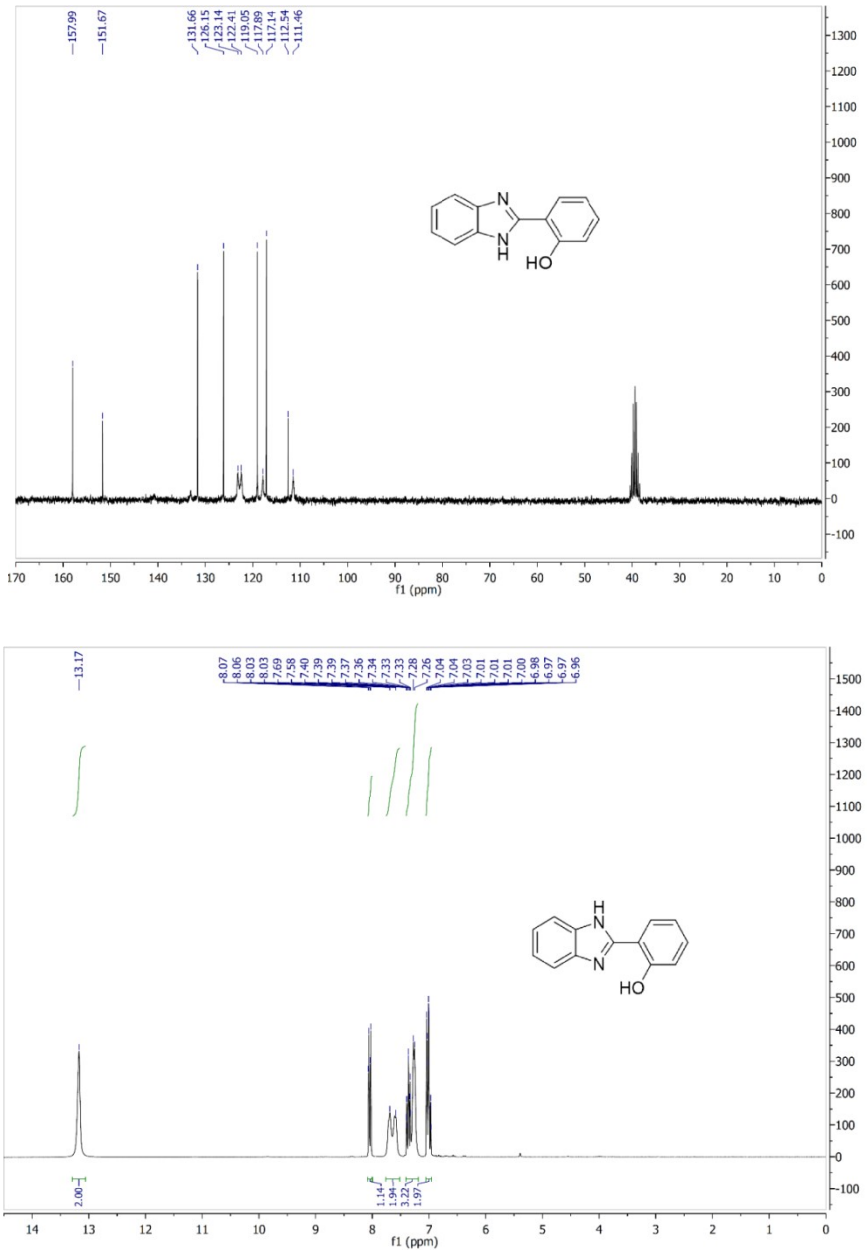


Figure S4. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3l

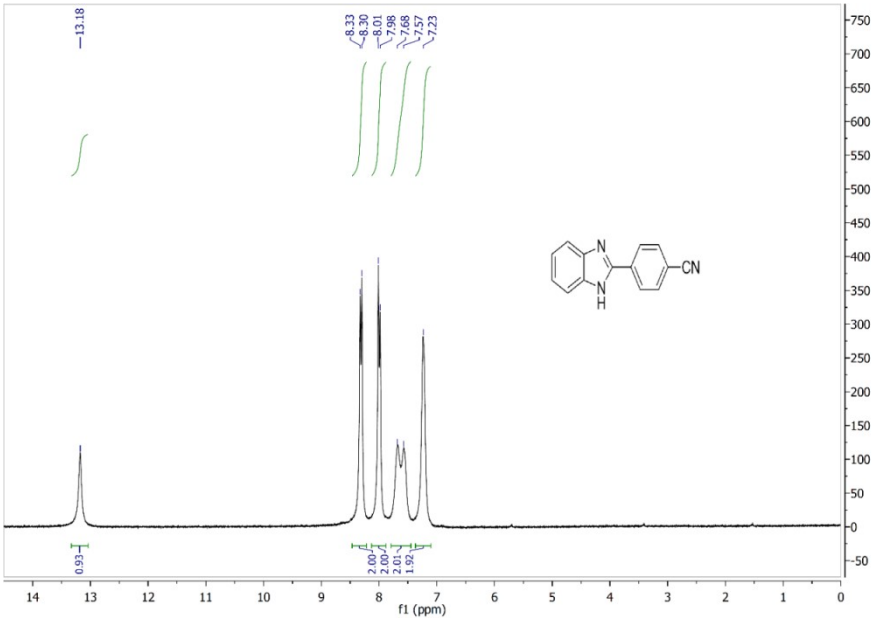


Figure S5. The ^{1}H NMR spectrum of compound 3g

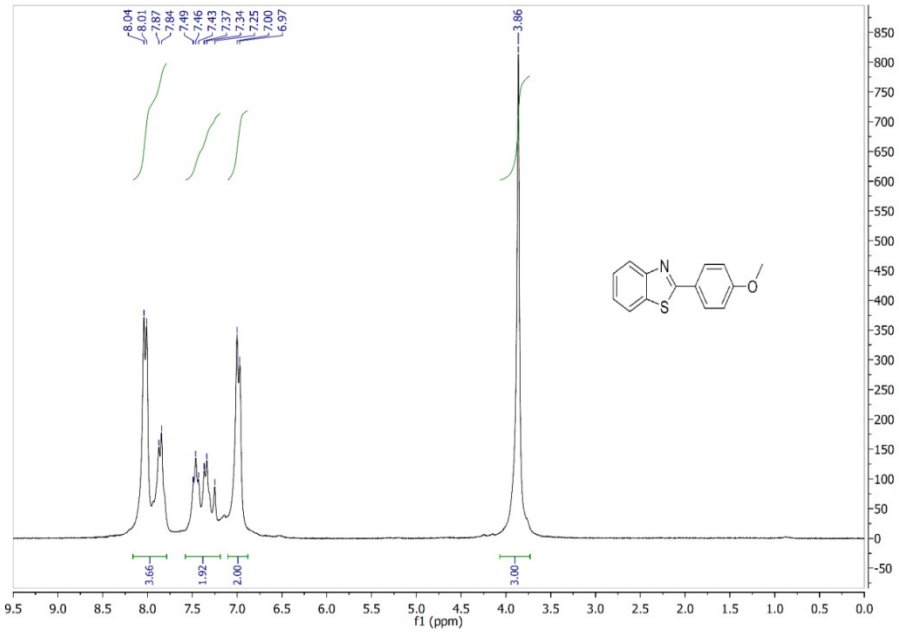


Figure S6. The ^{1}H NMR spectrum of compound 9b

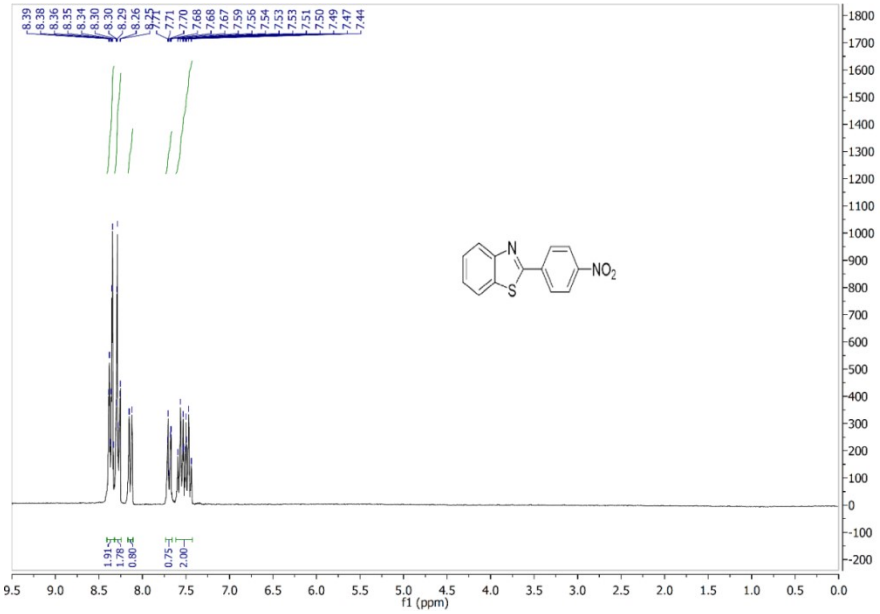


Figure S7. The ^{1}H NMR spectrum of compound 3f

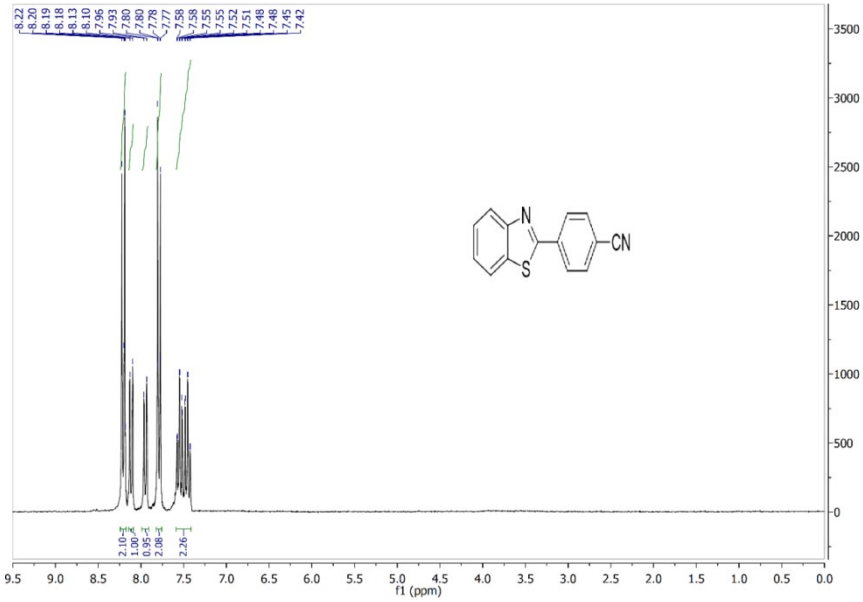


Figure S8. The ^{1}H NMR spectrum of compound 3g

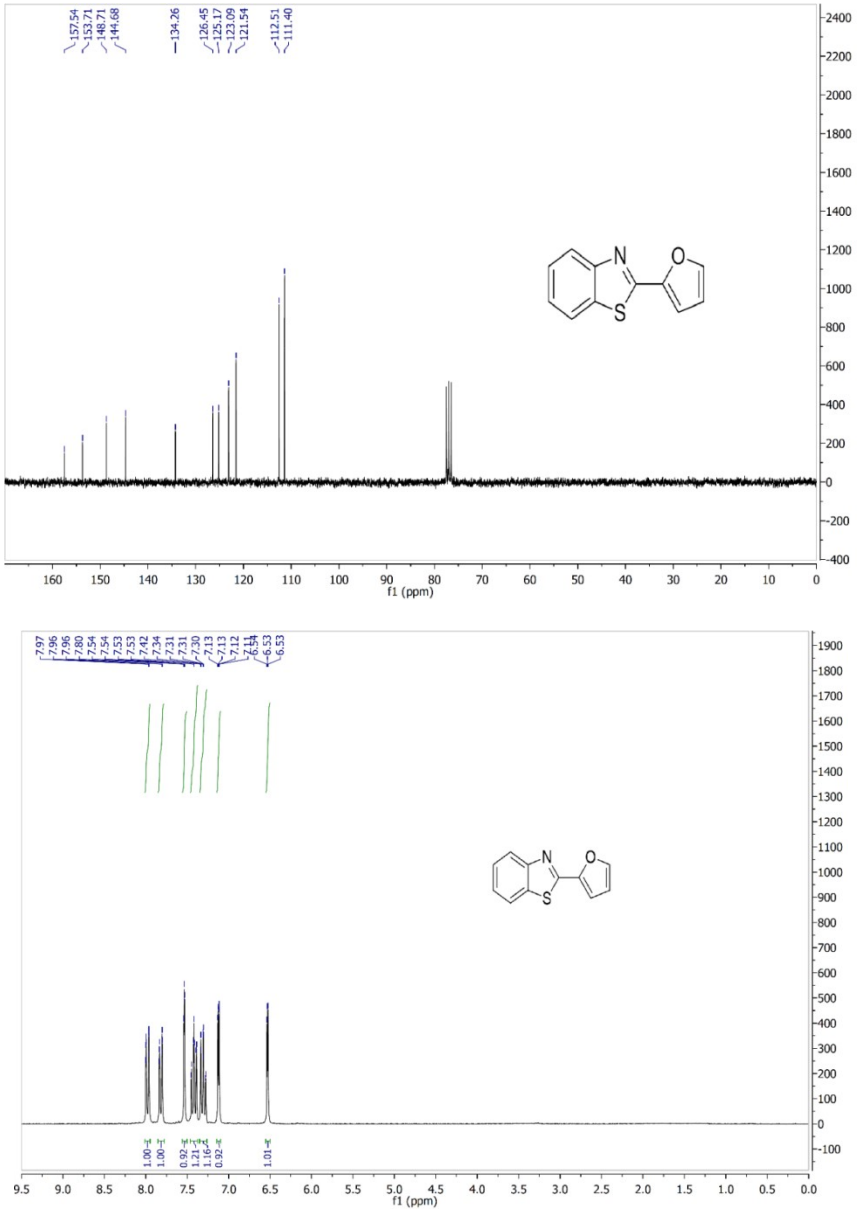


Figure S9. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3u

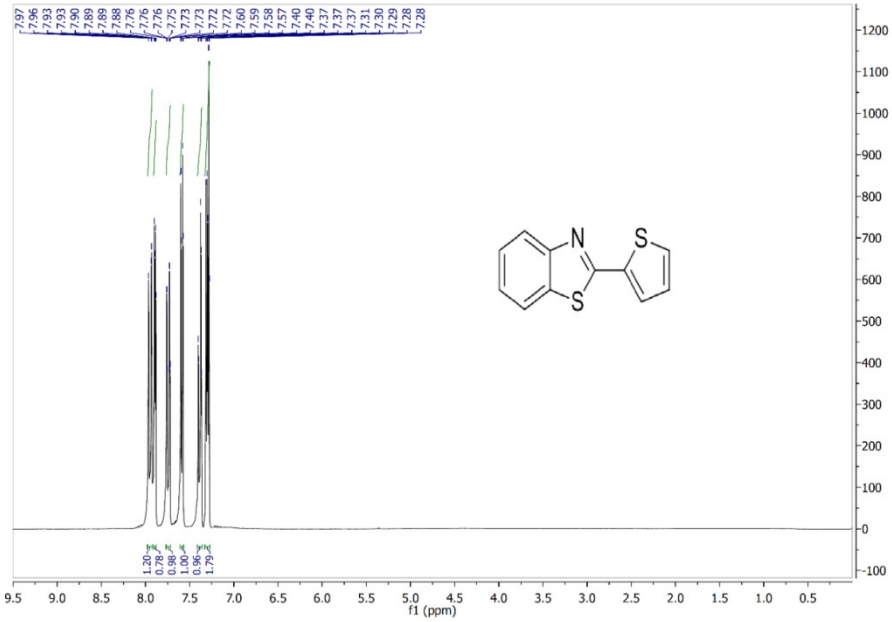


Figure S10. The ^{1}H NMR spectrum of compound 3s

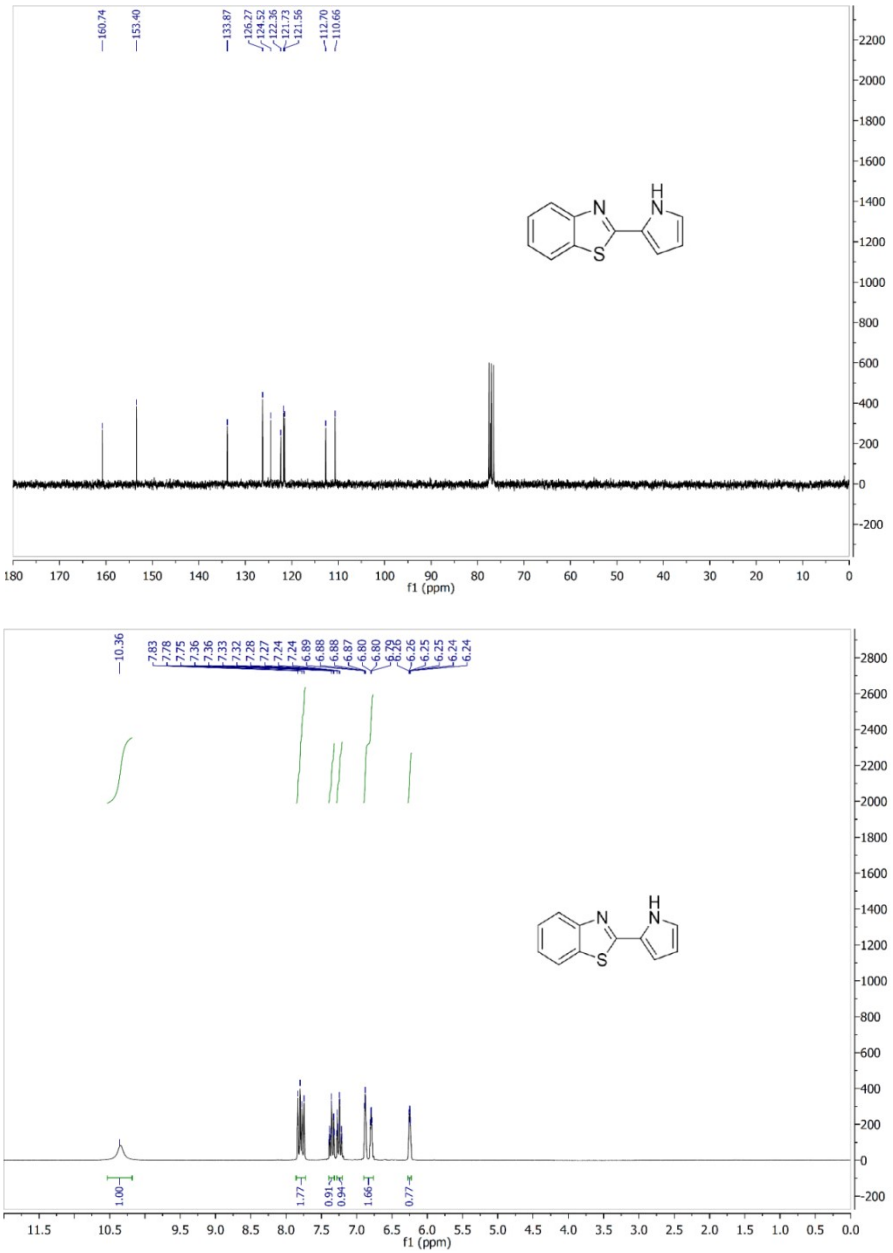


Figure S11. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3v

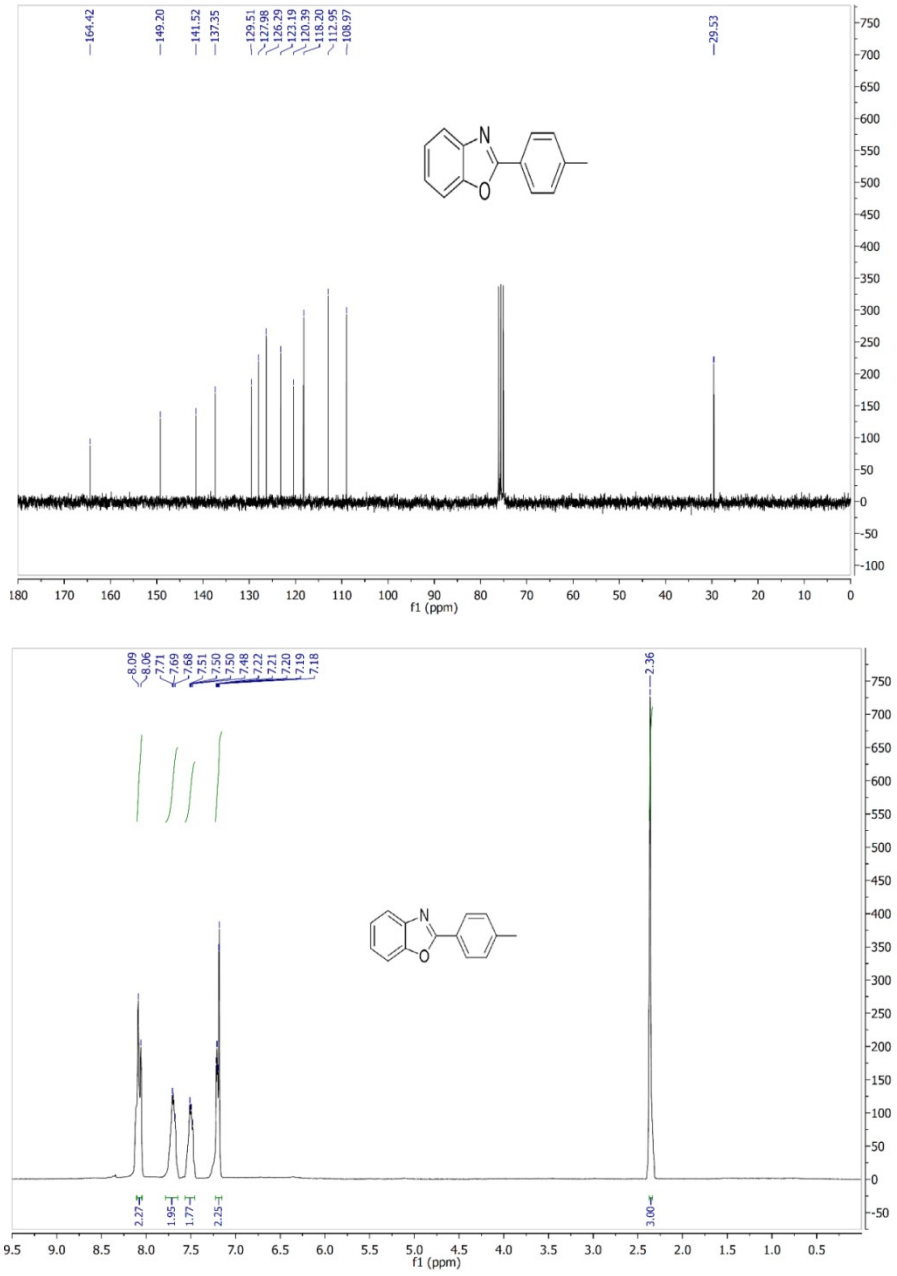


Figure S12. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3c

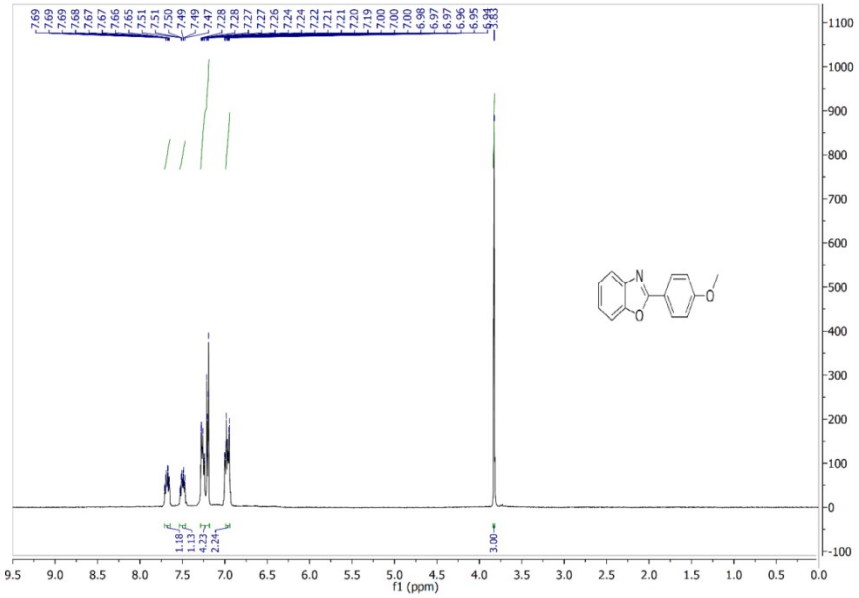


Figure S13. The ^{1}H NMR spectrum of compound 3b

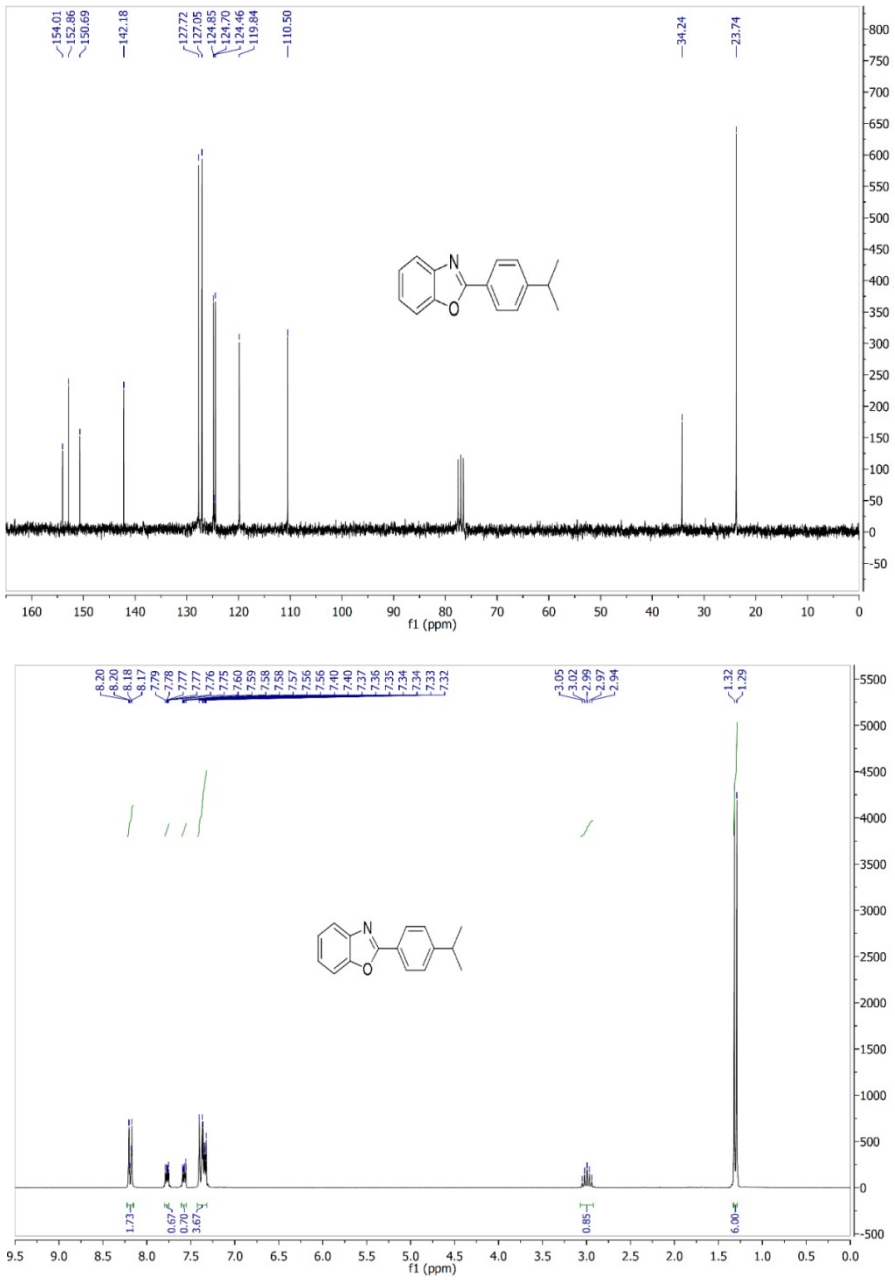


Figure S14. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3d

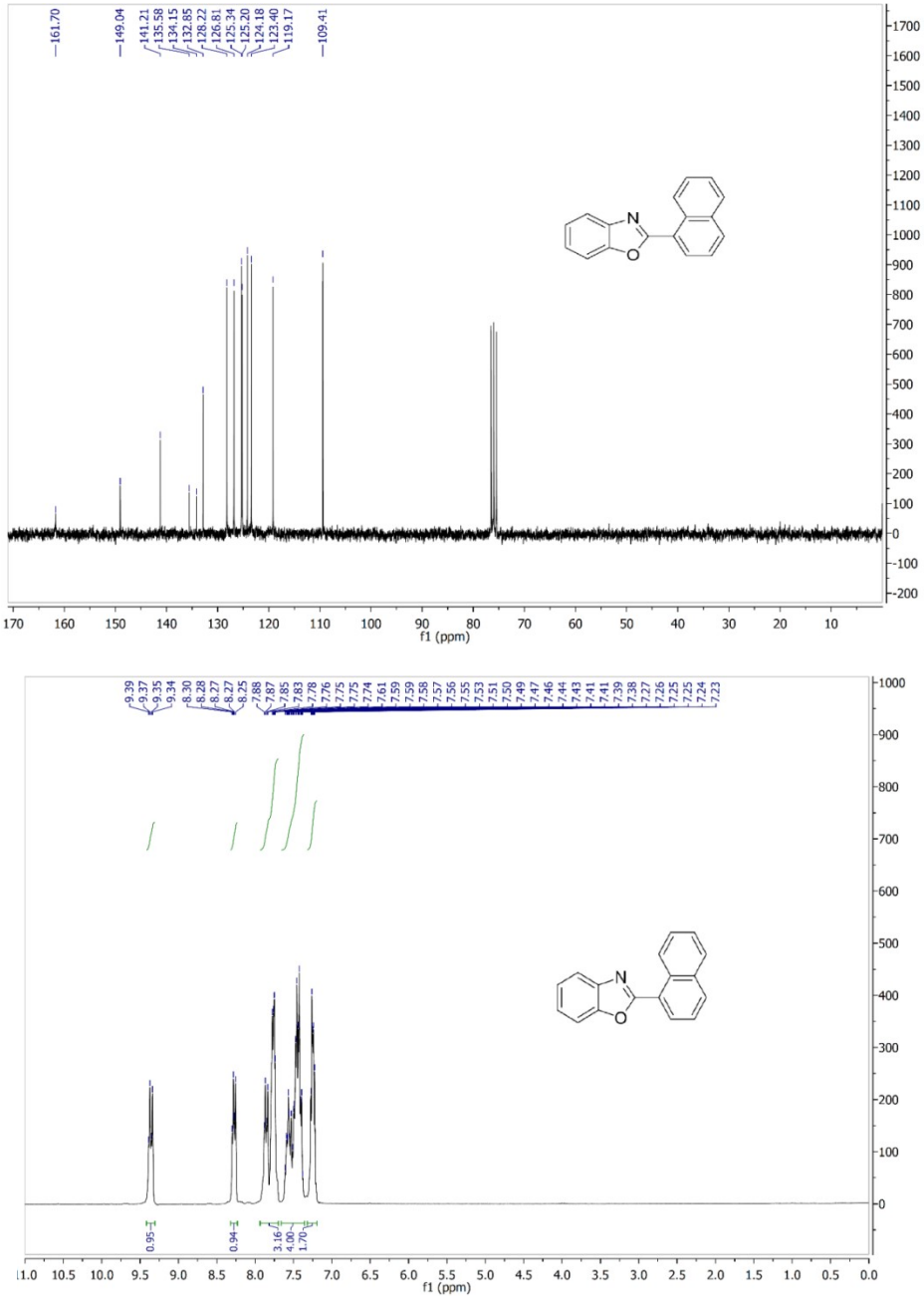


Figure S15. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3q

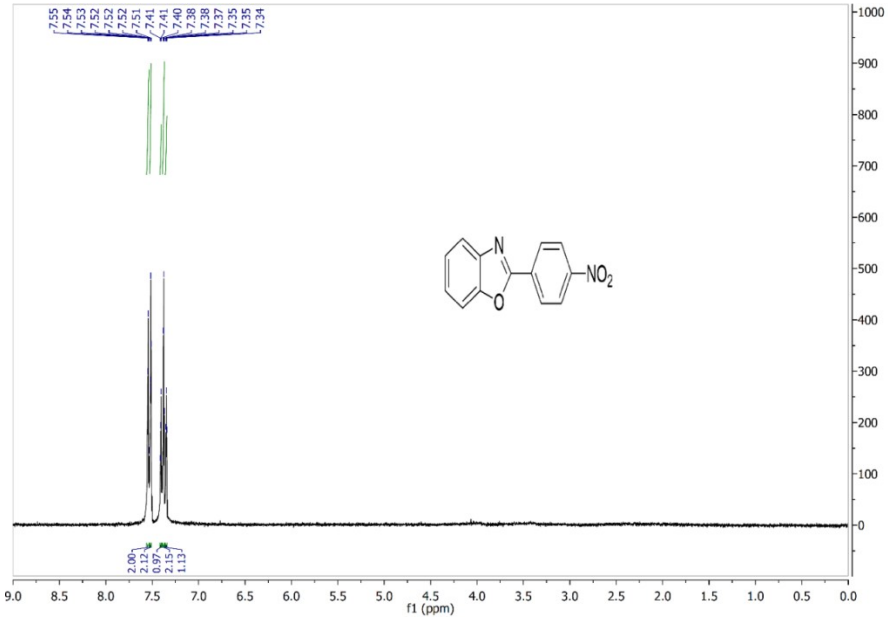


Figure S16. The ^{1}H NMR spectrum of compound 3f

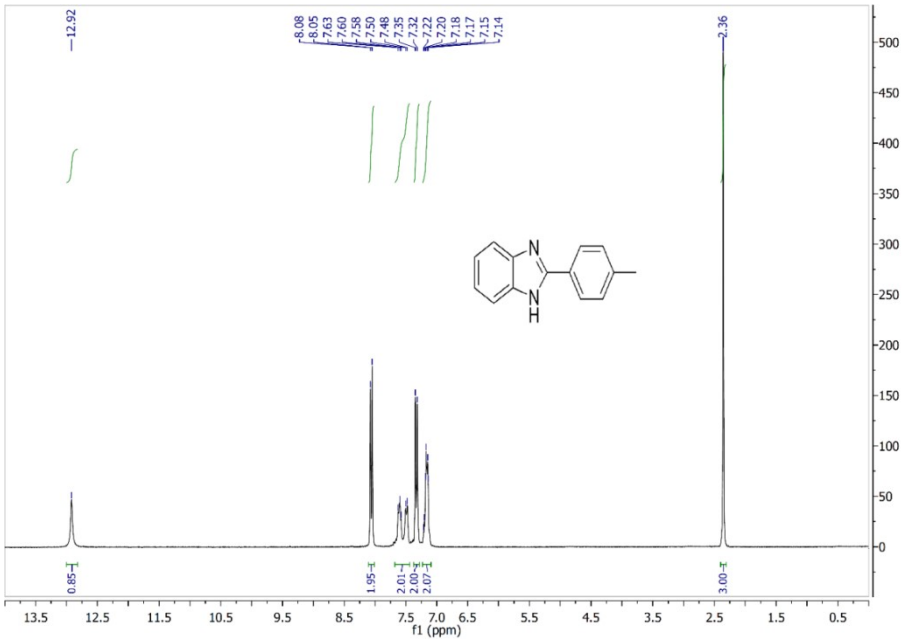


Figure S17. The ^{1}H NMR spectrum of compound 3c

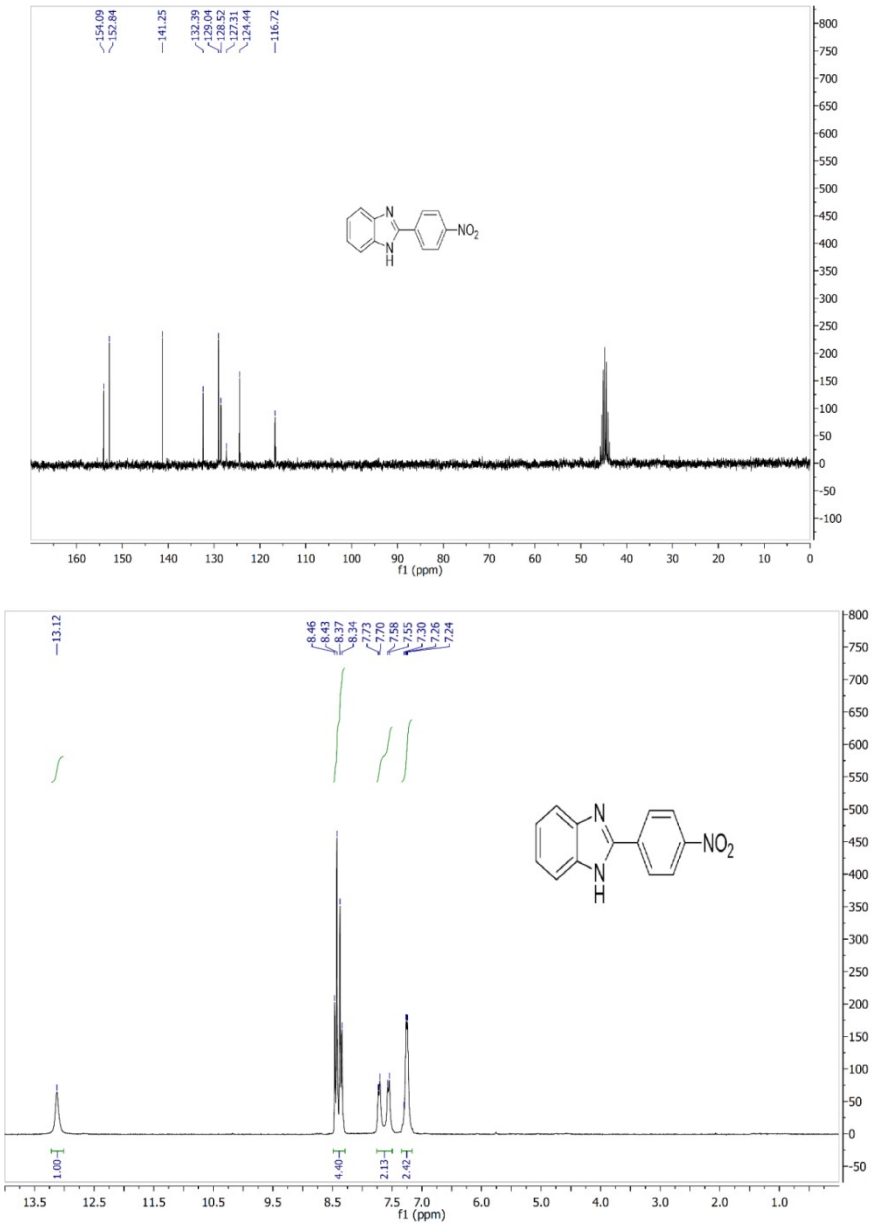


Figure S18. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3f

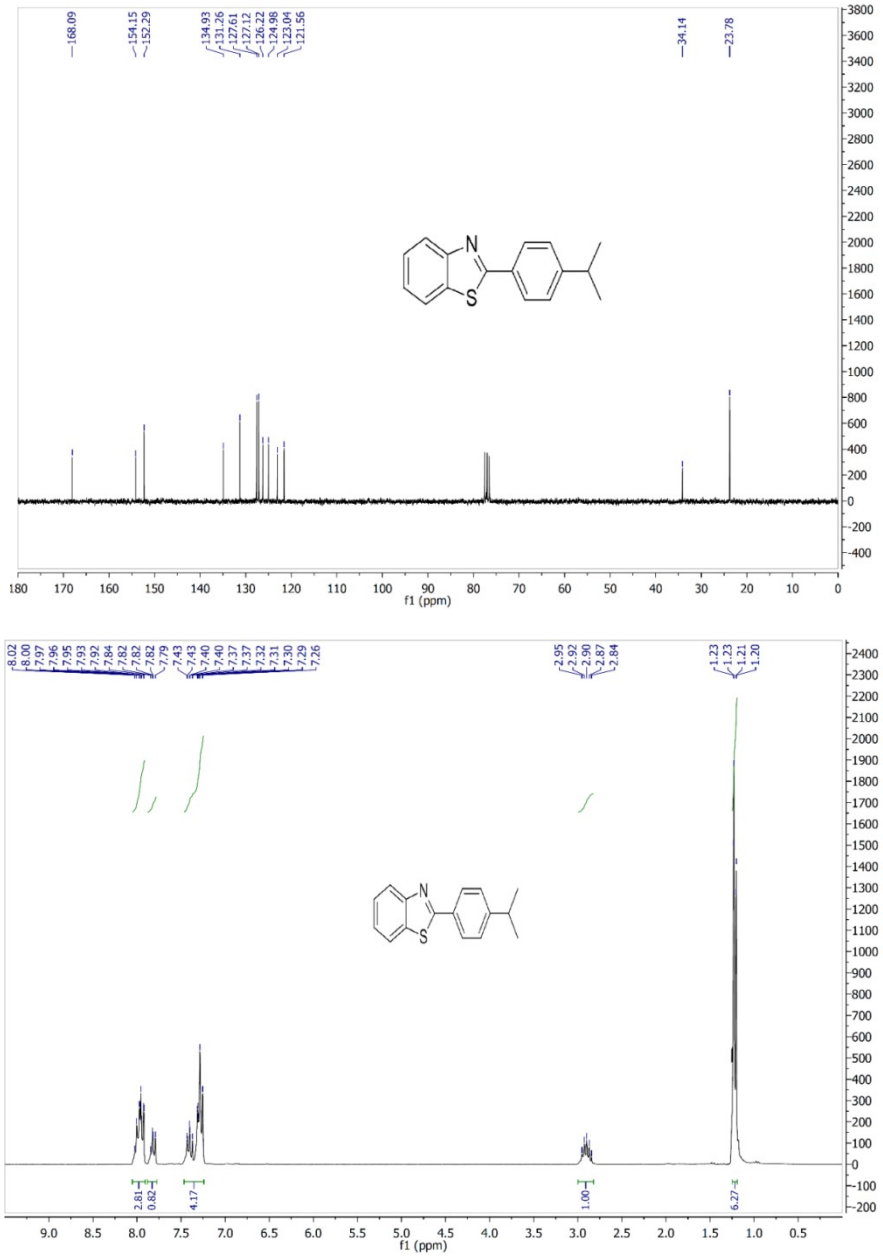


Figure S19. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3d

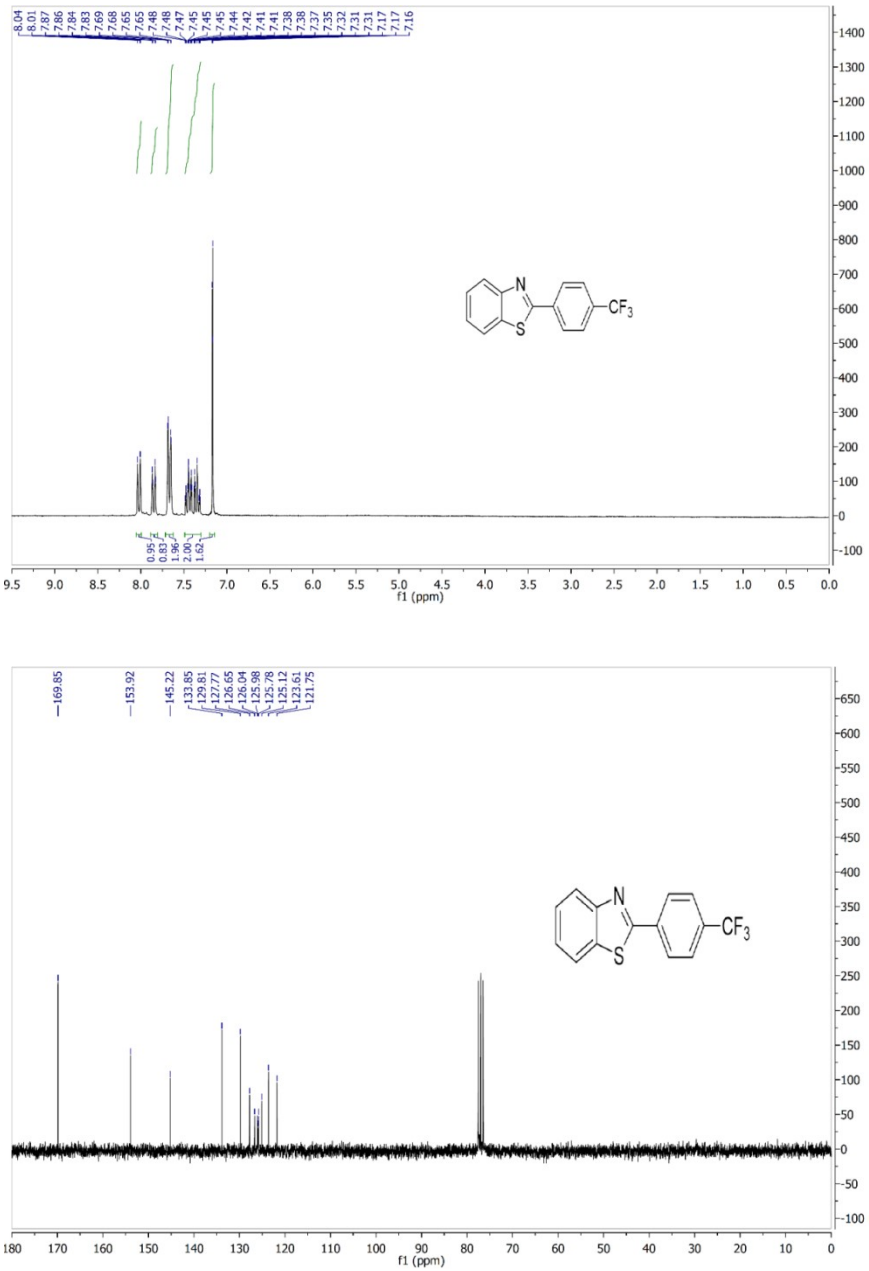


Figure S20. The ^{1}H NMR and ^{13}C NMR spectrum of compound 3i

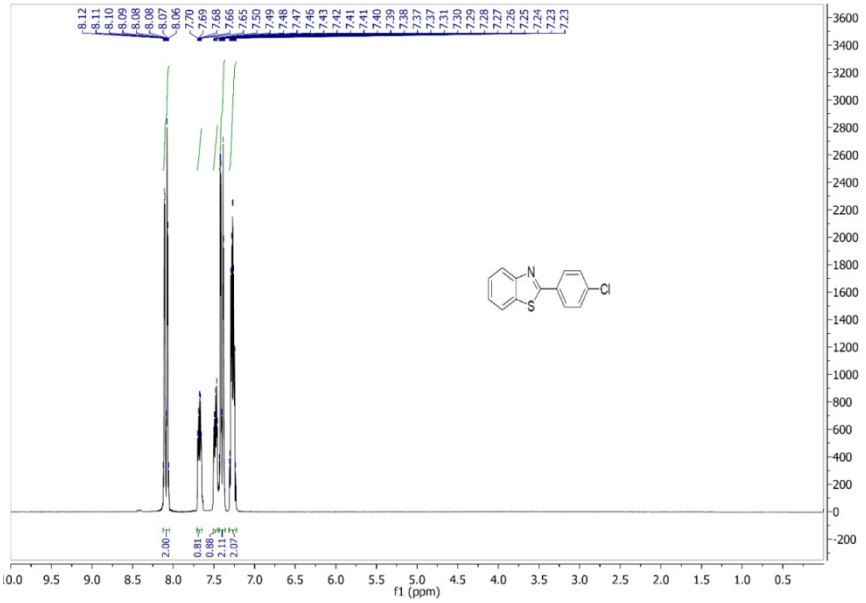


Figure S21. The ^{1}H NMR spectrum of compound 3h

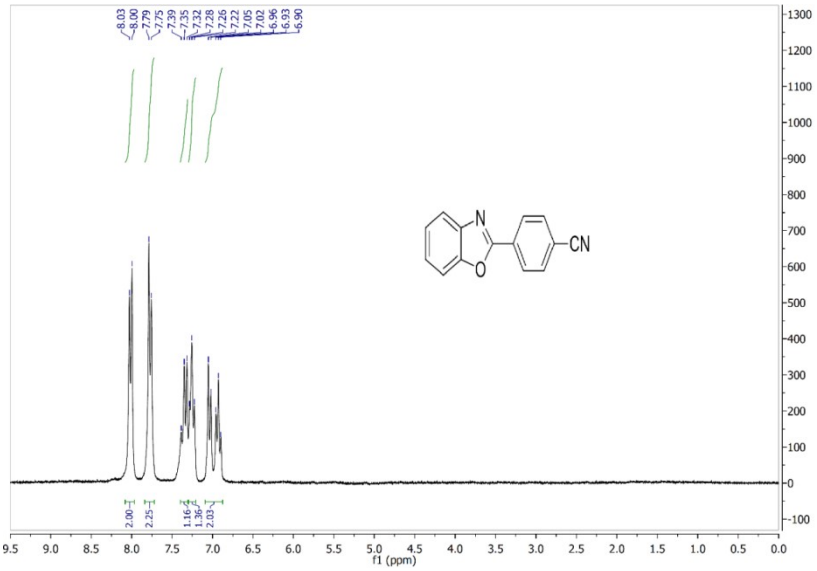


Figure S22. The ^{1}H NMR spectrum of compound 3g

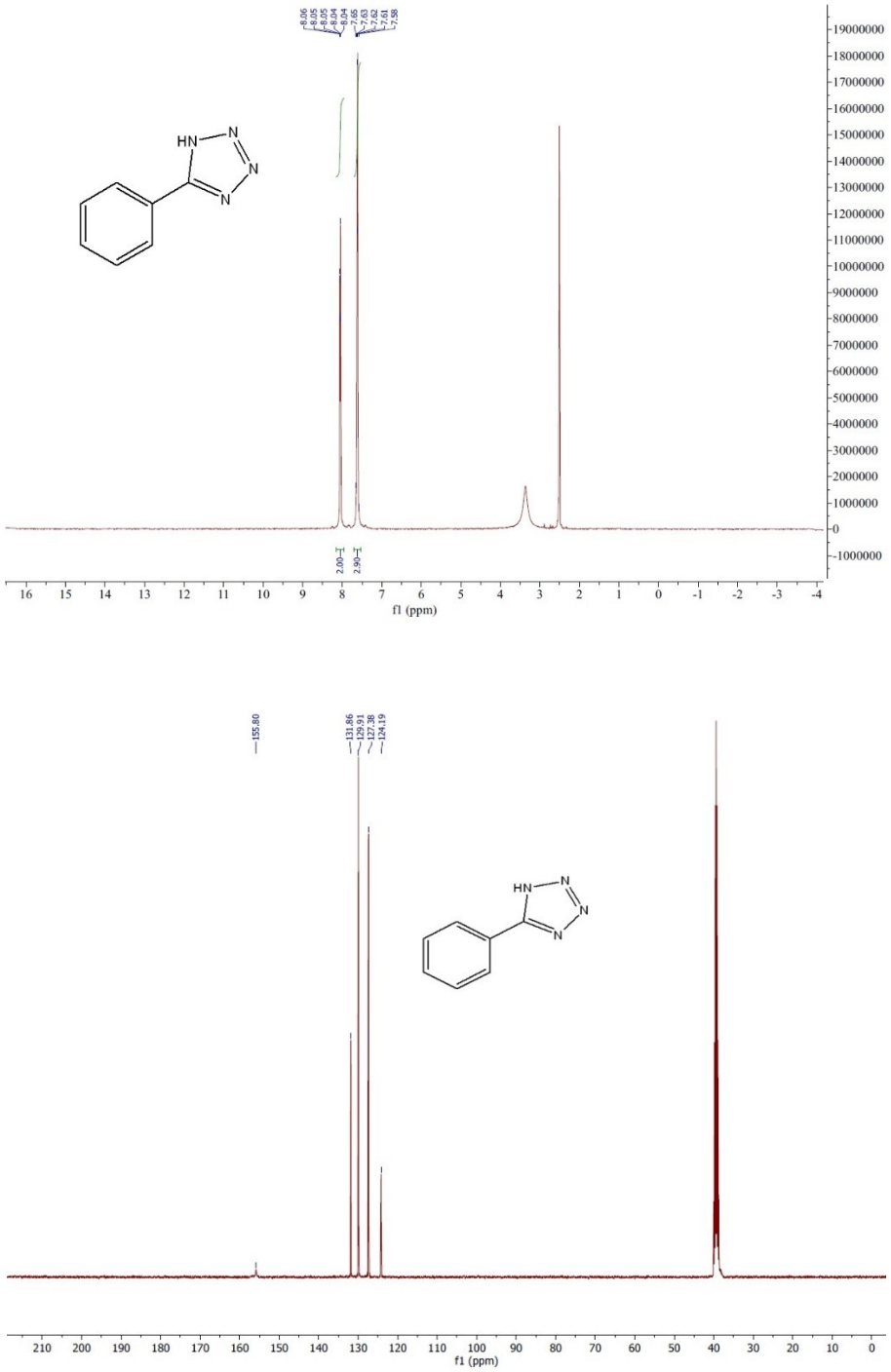


Figure S23 The ^{1}H NMR and ^{13}C NMR spectrum of compound 6a

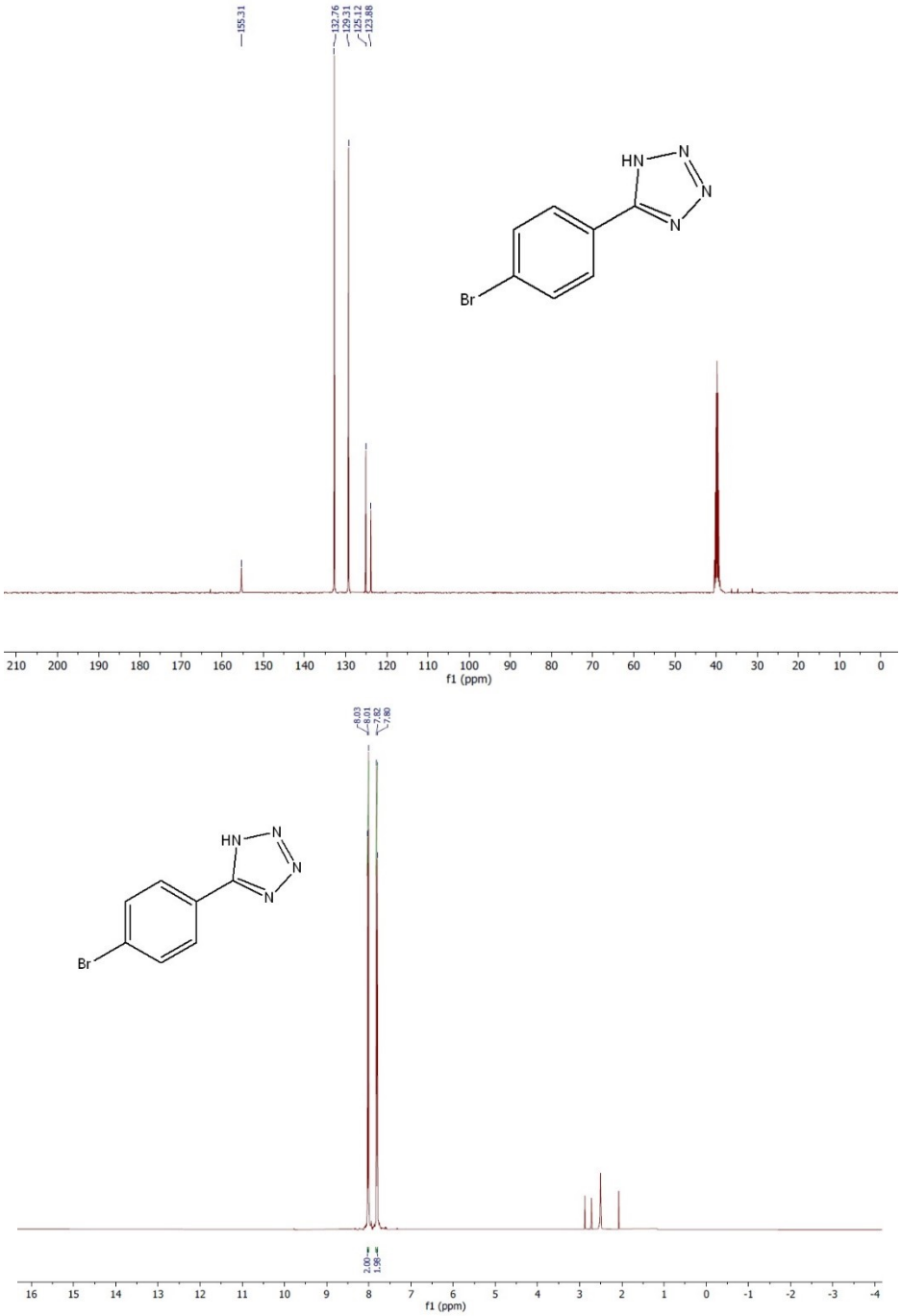


Figure S24. The ^{1}H NMR and ^{13}C NMR spectrum of compound 6k

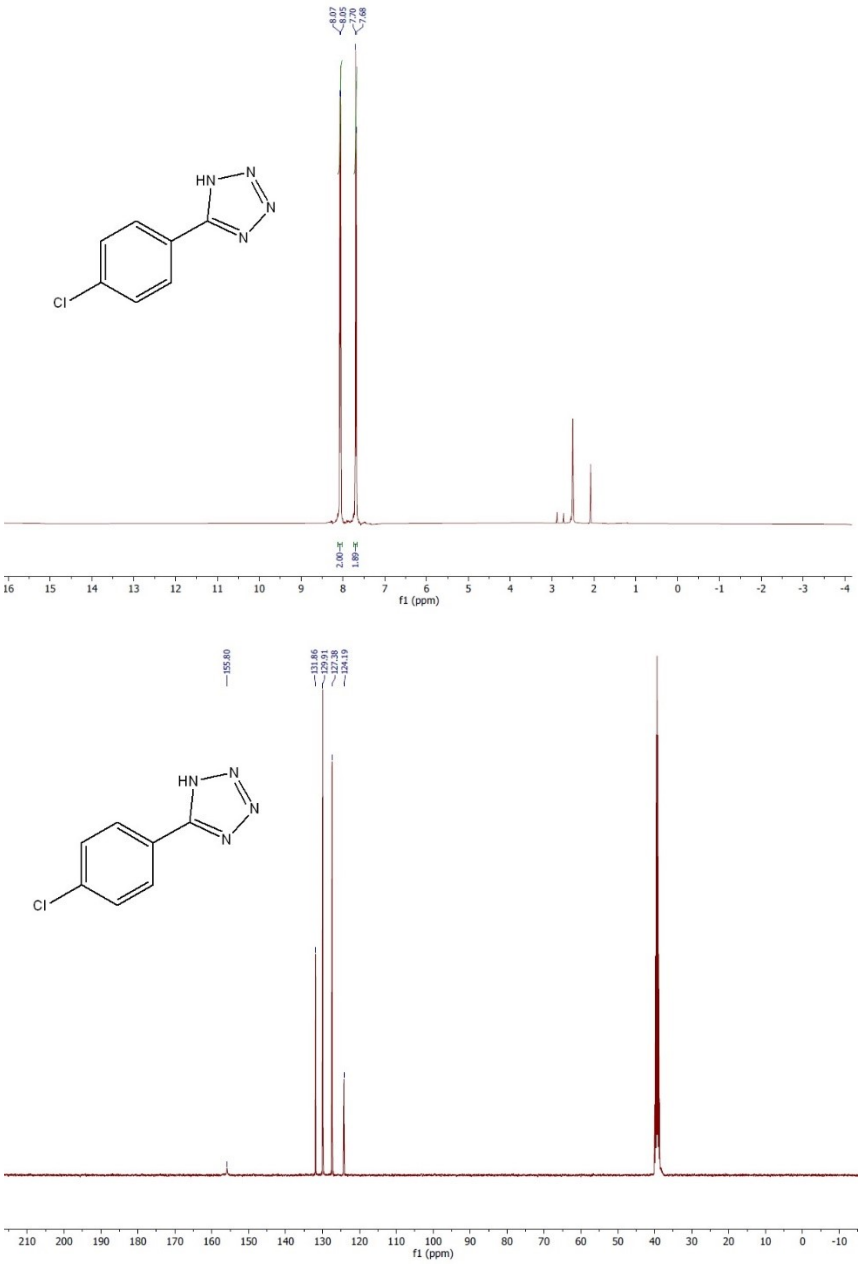


Figure S25. The ^{1}H NMR and ^{13}C NMR spectrum of compound 6j

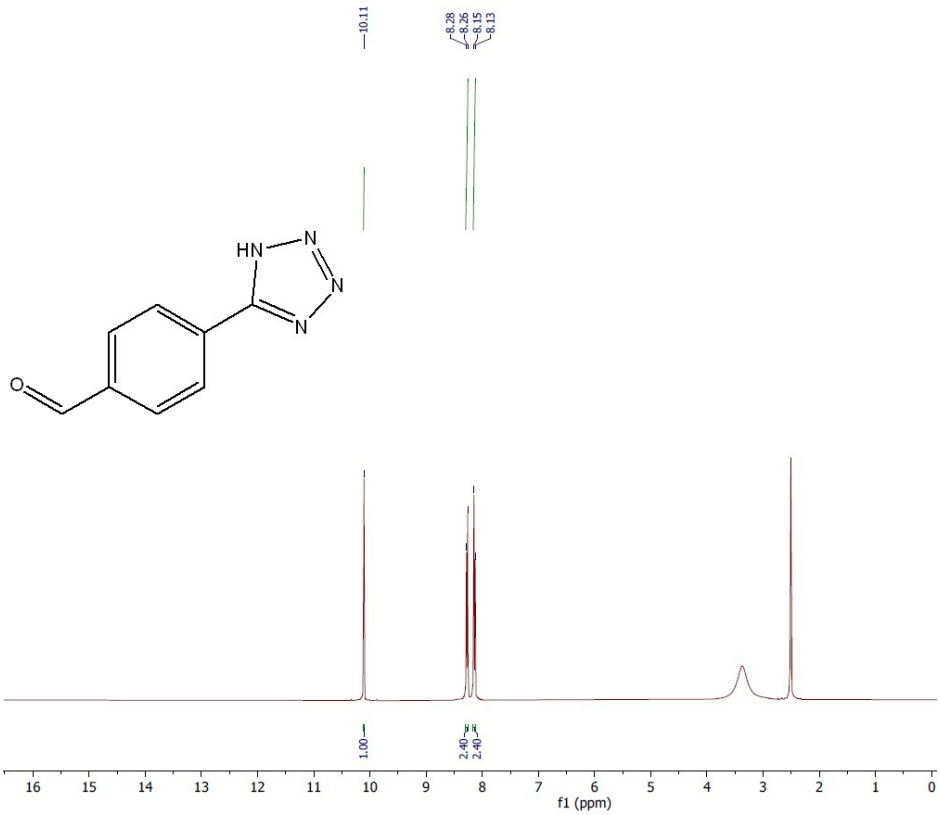


Figure S26. The ^{1}H NMR spectrum of compound 6d

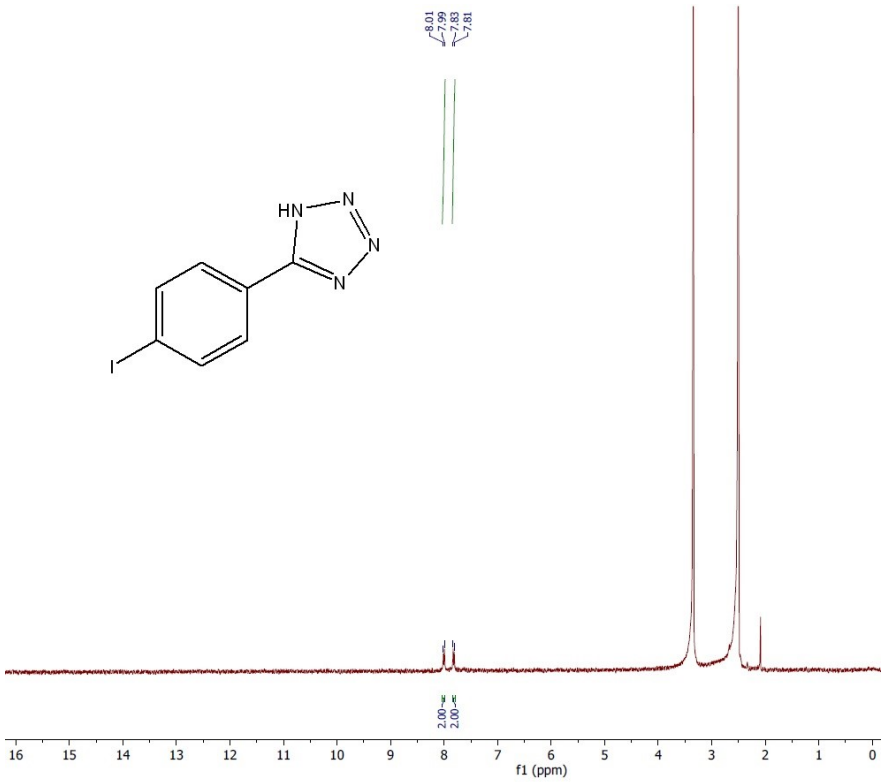


Figure S27. The ^{1}H NMR spectrum of compound 6l

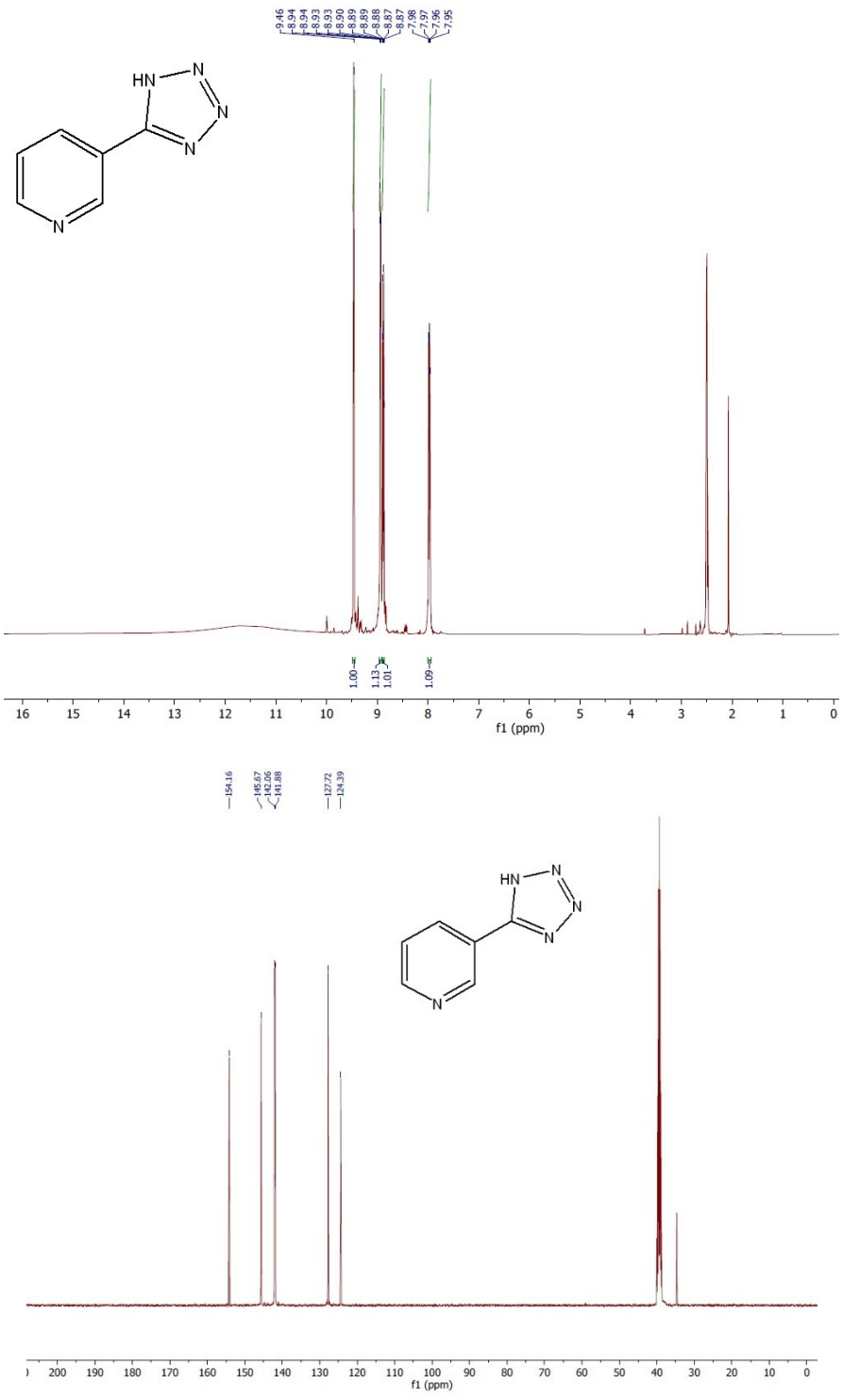


Figure S28. The ^{1}H NMR and ^{13}C NMR spectrum of compound 6f

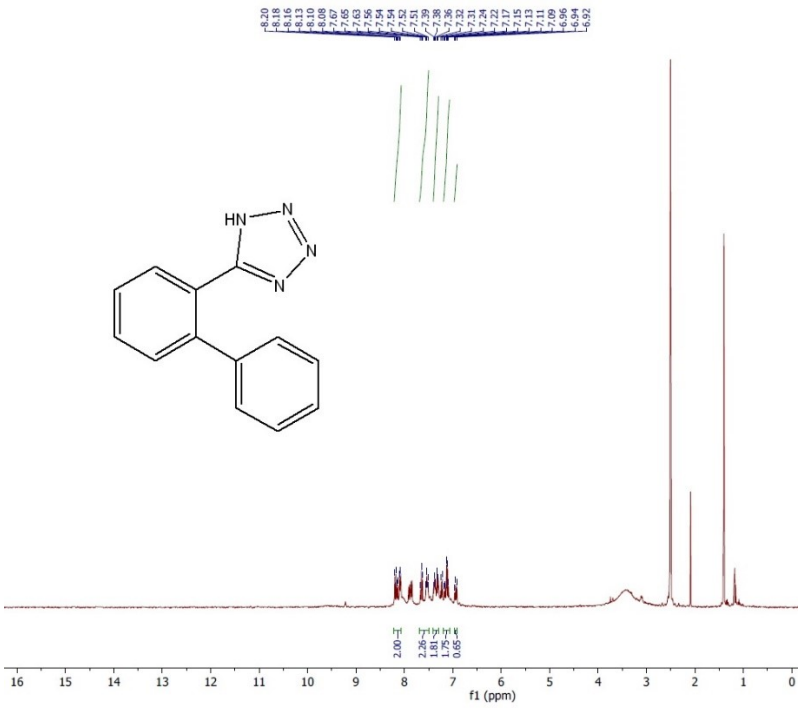


Figure S29. The ^{1}H NMR spectrum of compound 6e

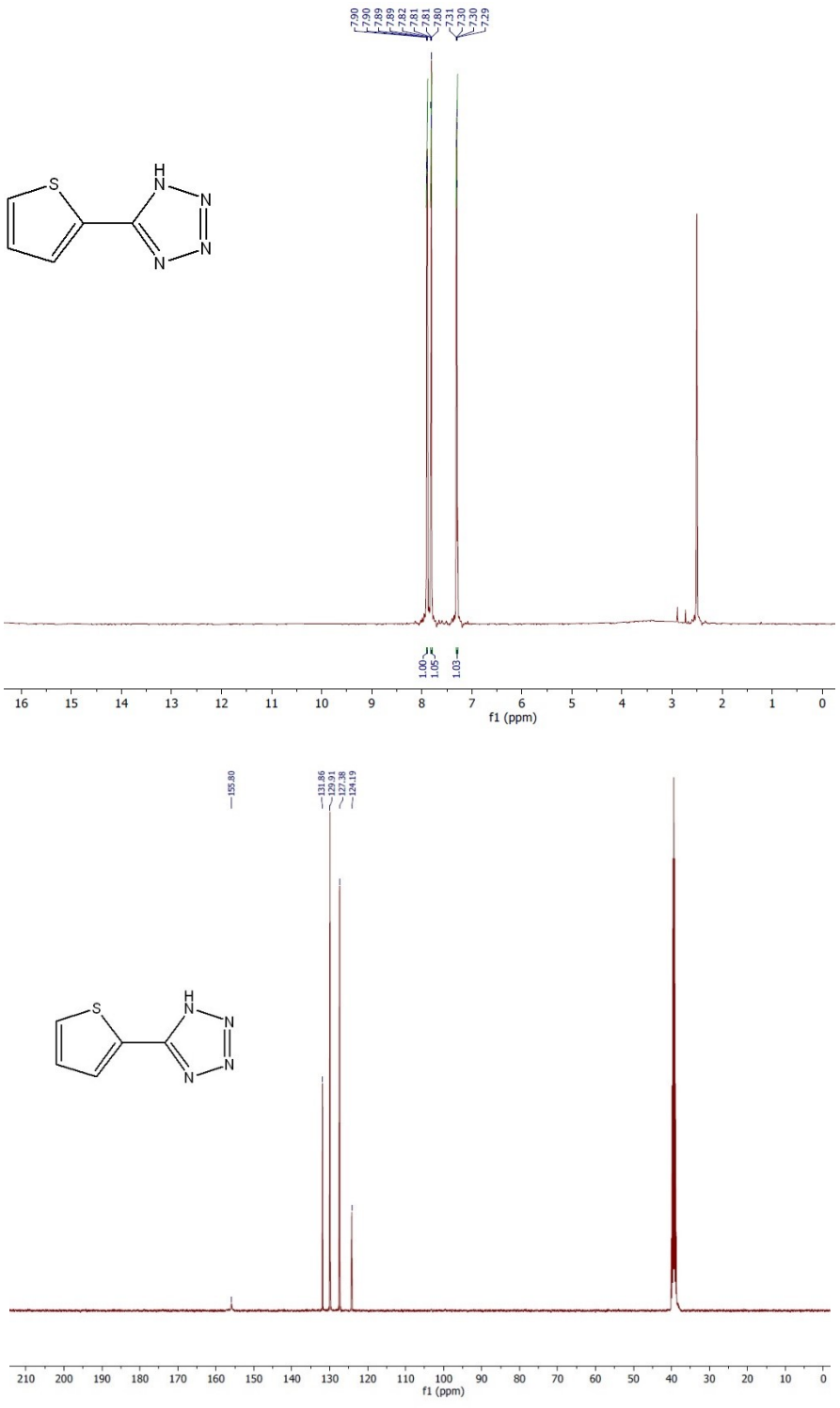


Figure S30. The ^{1}H NMR and ^{13}C NMR spectrum of compound 6h