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SUPPLEMENTARY MATERIAL TO

Synthesis, characterization and antimicrobial activity of novel benzofuran- and thiophene-containing diketoxime derivatives

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ANALYTICAL AND SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS

*2,2'-Thiobis[1-(2-benzofuranyl)ethanone] (**1**)*. Yield: 80 %, 5.6 g; m.p.: 144–145 °C; Anal. Calcd. for $C_{20}H_{14}O_4S$: C, 68.56; H, 4.03 %. Found: C, 68.59; H, 4.01 %; FTIR (KBr, cm^{-1}): 1680 & 1663 (C=O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 8.00 (2H, *s*, H-3), 7.83 (2H, *d*, J = 7.8 Hz, H4), 7.70 (2H, *d*, J = 8.4 Hz, H7), 7.55 (2H, *dd*, J = 7.2 Hz & 8.40 Hz, H6), 7.38 (2H, *dd*, J =7.1 & 7.5 Hz, H5), 4.11 (4H, *s*, CH_2); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 185.48 (C=O), 155.58 (C8), 151.37 (C2), 129.21 (C9), 127.20 (C6), 124.65 (C5), 124.26 (C5), 115.59 (C7), 112.74 (C3), 37.66 (CH_2).

*1,1´-(2,5-Thiophenediyl)bis[1-(2-benzofuranyl)methanone] (**2**)*. Yield: 60 %, 0.89 g; m.p.: 223–224 °C; Anal. Calcd. for $C_{22}H_{12}O_4S$: C, 70.96; H, 3.25 %. Found: C, 70.92; H, 3.24 %; FTIR (KBr, cm^{-1}) : 1618 (C=O), 1185 (C–O–C); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.37 (2H, *s*, H3), 7.84 (2H, *s*, H12), 7.79 (2H, *d*, J = = 7.6 Hz, H4), 7.69 (2H, *d*, J = 8.4 Hz, H7), 7.56 (2H, *dd*, J = 7.6 & 8.0 Hz, H6), 7.39 (2H, *t*, J =7.6 Hz, H5); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 174.84 (C=O), 155.86 (C8), 151.94 (C2), 147.17 (C11), 133.94 (C12), 128.63 (C9), 126.75 (C6), 124.15 (C5), 123.34 (C4), 115.57 (C7), 112.39 (C3).

*1,1´-(2,5-Thiophenediyl)bis[1-(2-benzofuranyl)methanone], 1,1´-dioxime (**3**)*. Yield: 90 %, 0.97 g; m.p.: 272–274 °C; Anal. Calcd. for $C_{22}H_{14}N_2O_4S$: C, 65.66; H, 3.51; N, 6.96 %. Found: C, 65.63; H, 3.55; N, 6.95 %; FTIR (KBr, cm^{-1}): 3250–3000 (OH), 1583 (C=N), 1030 (N–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / / ppm): 13.1 (2H, *s*, OH *E*,*E*-isomer), 12.8 (2H, *s*, OH *Z*,*Z*-isomer, 7.9–7.29 (24H, *m*, benzofuran & thiophene rings H); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / / ppm): 154.78, 153.43, 151.54, 145.12, 142.09, 141.86, 141.15, 133.76, 131.72,

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130.29, 130.15, 128.11, 128.01, 127.88, 126.94, 125.87, 123.89, 122.84, 122.22, 114.00, 112.06, 111.89, 108.13, 108.05.

*1,1′-(2,5-Thiophenediyl)bis[1-(2-benzofuranyl)methanone], 1,1′-bis(*O-*benzoyloxime) (4a)*. Yield: 69 %, 0.10 g; m.p.: 167–168 °C; Anal. Calcd. for $C_{36}H_{22}N_2O_6S$: C, 70.81; H, 3.63; N, 4.59 %. Found: C, 70.85; H, 3.68; N, 4.61 %; FTIR (KBr, cm^{-1}): 1751 (C=O), 1557 (C=N), 1050 (N–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 8.2–7.2 (44H, *m*, benzofuran, thiophene & phenyl ring H); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 163.07 (C-13 *anti*-isomer), 162.91 (C-13 *syn*-isomer), 155.59 (C-9 *anti*-isomer), 154.77 (C-9 *syn*-isomer), 148.73 (C-2 *anti*-isomer), 148.66 (C-2 *syn*-isomer), 143.82 (C-12 *anti*-isomer), 140.67 (C-12 *syn*-isomer), 138.32 (C-10 *anti*-isomer), 135.01 (C-10 *syn*-isomer), 134.30 (C-11 *anti*-isomer), 134.02 (C-11 *syn*-isomer), 131.84 (C-17 *anti*-isomer), 131.66 (C-17 *syn*-isomer, 130.26 (C-14 *anti*-isomer), 130.02 (C-14 *syn*-isomer), 129.34 (C-15, C-19 *anti*-isomer), 129.07 (C-15, C-19 *syn*-isomer) , 128.21 (C-16, C-18 *anti*-isomer), 128.08 (C-16, C-18 *syn*-isomer), 127.90 (C-7 *anti*-isomer), 127.54 (C-7 *syn*-isomer), 127.30 (C-4 *anti*-isomer), 127.18 (C-4 *syn*-isomer), 124.37 (C-6 *anti*-isomer), 124.14 (C-6 *syn*-isomer), 123.33 (C-5 *anti*-isomer), 122.70 (C-5 *syn*-isomer), 113.42 (C-8 *anti*-isomer), 113.17 (C-8 *syn*-isomer), 112.06 (C-3 *anti*- & *syn*-isomer).

*1,1′-(2,5-Thiophenediyl)bis[1-(2-benzofuranyl)methanone], 1,1′-bis[*O-*(2--thienylcarbonyl)oxime] (**4b**)*. Yield: 75 %, 0.11 g; m.p.: 174–175 °C; Anal. Calcd. for $C_{32}H_{18}N_2O_6S_3$: C, 61.72; H, 2.91; N, 4.50 %. Found: C, 61.75; H, 2.92; N, 4.55 %; FTIR (KBr, cm^{-1}): 1744 (C=O), 1553 (C=N), 1046 (N–O); ^{1}H-NMR (400 MHz, DMSO--d_6, δ / ppm): 7.33–8.15 (34 H, *m*, benzofuran ring H and others of the thiophene ring), 7.32 (1H, *dd*, *J* = 5.1 Hz & 3.5 Hz, H_a at thiophene ring for *amphi*-isomer), 7.14 (1H, *dd*, *J* = 5.8 Hz & 3.6 Hz, $H_a{}^1$ proton at thiophene ring for *amphi*-isomer); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 158.64, 155.57, 154.80, 148.90, 148.76, 148.72, 148.55, 148.51, 143.59, 140.34, 137.92, 136.41 136.36, 136.26, 136.22, 136.06, 135.94, 135.86, 135.73 134.69, 133.94, 133.77, 132.40, 131.52, 130.25, 130.20, 129.87, 129.42, 129.35, 129.17, 128.44, 128.34, 127.66, 127.58, 127.39, 124.67, 124.61, 124.44, 124.38, 123.63, 123.57, 123.05, 117.20, 116.94, 113.97, 113.73, 112.45, 112.33.

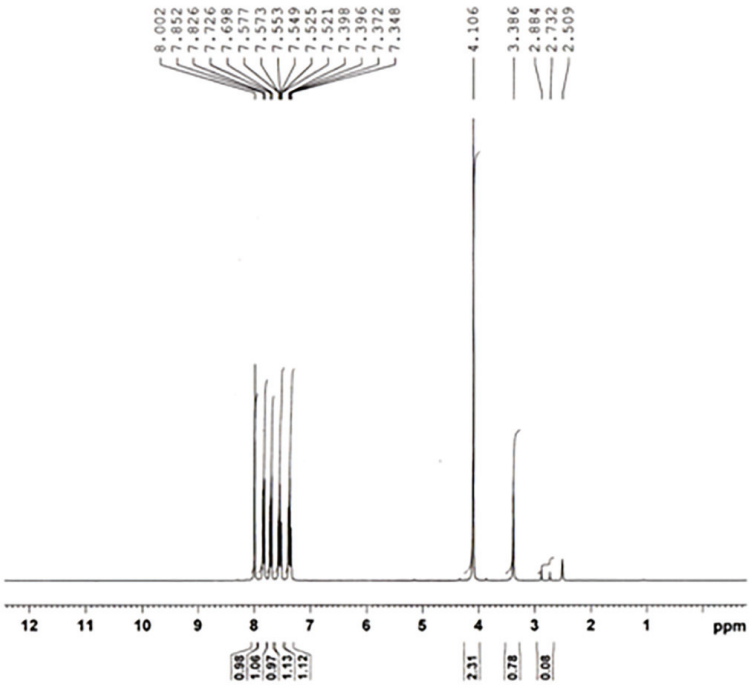
*1,1′-(2,5-Thiophenediyl)bis[1-(2-benzofuranyl)methanone], 1,1′-bis(*O-*2-furoyloxime) (**4c**)*. Yield: 67 %, 0.10 g; m.p.: 162–163 °C; Anal. Calcd. for $C_{32}H_{18}N_2O_8S$: C, 65.08; H, 3.07; N, 4.74 %. Found: C, 65.05; H, 3.11; N, 4.71 %; FTIR (KBr, cm^{-1}): 1754 (C=O), 1575 (C=N), 1059 (N–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 8.25–7.30 (32H, *m*, benzofuran ring H, thiophene ring H and others of the furan ring), 6.87 (2H, *s*, H_b at furan ring, % 41, *anti*-isomer), 6.82 & 6.63 (2H, 2×*s*, $H_a{}^1$ & H_a at furan ring, 59 %, *amphi*-isomer); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 155.54, 155.50, 154.95, 154.88, 154.86, 154.60, 154.58 149.71, 149.65, 148.93, 148.89, 148.87, 148.67, 148.47, 143.39, 143.37,

141.97, 141.93, 141.83, 141.55, 140.45, 137.62, 135.90, 134.79, 134.24, 133.77, 132.44, 131.45 128.55, 128.44, 127.64, 127.53, 124.68, 124.63, 124.43, 123.74, 123.68, 123.04, 121.19, 121.04, 117.82, 117.56, 113.77, 113.54, 113.43, 113.16, 112.45, 112.31.

*1,1´-(2,5-Thiophenediyl)bis[1-(2-benzofuranyl)methanone], 1,1´-bis[*O*-(4--methoxybenzoyl) oxime] (**4d**)*. Yield: 76 %, 0.12 g; m.p.: 127–128 °C; Anal. Calcd. for $C_{38}H_{26}N_2O_8S$: C, 68.05 ; H, 3.91 ; N, 4.18 %. Found: C, 68.09 ; H, 3.90; N, 4.21 %; FTIR (KBr, cm^{-1}): 1743 (C=O), 1605 (C=N), 1049 (N–O); ^{1}H--NMR (400 MHz, DMSO-d_6, δ / ppm): 8.14–7.77 (20H, respectively, 15H, *m*, H-19 *anti*-isomer, H-12 *anti*-isomer, H-19 *syn*-isomer, H-5 *anti*-isomer, H-12 *syn*-isomer, H-5 *syn*-isomer, H-3 *anti*- & *syn*-isomer), 7.61–7.52 (*m*, 12H, respectively, H-8 *anti*- & *syn*-isomer, H-7 *anti*-isomer, H-7 *syn*-isomer, H-6 *anti*- & *syn*--isomer, 7.15 (4H, *d*, *J* = 8.4 Hz, H-16, H-18, 61 % *anti*-isomer, 6.83 (4H, *d*, *J* = = 8.4 Hz, H-16, H-18, 39 % *syn*-isomer), 3.87 (6H, *s*, OCH_3, 61 % *anti*-isomer), 3.75 (6H, *s*, OCH_3, 39 % *syn*-isomer); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / / ppm): 164.35 (C-13 *anti*-isomer), 164.17 (C-13 *syn*-isomer), 162.72 (C-17 *anti*- & *syn*-isomer), 155.49 (C-9 *anti*-isomer), 154.81 (C-9 *syn*-isomer), 148.81 (C-2 *anti*-isomer), 148.51 (C-2 *syn*-isomer), 144.80 (C-12 *anti*-isomer), 143.87 (C-12 *syn*-isomer), 140.60 (C-10 *anti* & *syn*-isomer), 134.57 (C-11 *anti*-isomer), 134.11 (C-11 *syn*-isomer), 132.59 (C-15, C-19 *anti*-isomer), 132.35 (C-15, C-19 *syn*-isomer), 128.35 (C-7 *anti*-isomer), 127.70 (C-7 *syn*-isomer), 127.54 (C-4 *anti*-isomer), 127.46 (C-4 *syn*-isomer), 124.64 (C-6 *anti*-isomer), 124.36 (C-6 *syn*-isomer), 123.64 (C-5 *anti*-isomer), 122.99 (C-5 *syn*-isomer), 119.98 (C-14 *anti*-isomer), 119.76 (C-14 *syn*-isomer), 115.04 (C-16, C-18 *anti*-isomer), 114.69 (C-16, C-18 *syn*-isomer), 113.48 (C-8 *anti*-isomer), 113.36 (C-8 *syn*-isomer), 112.38 (C-3, *anti*-isomer), 112.31 (C-3 *syn*-isomer), 56.17 (OCH_3, *anti*-isomer), 56.02 (OCH_3, *syn*-isomer); HMBC (400 MHz): OCH_3 (C-17), 16-H, 18-H (14-C), 6-H (7-C, 4-C), 7-H (9-C, 5-C), 8-H (9-C, 7-C, 4-C, 2-C), 3-H (7-C, 6-C, 4-C), 5-H (9-C, 4-C), 15-H, 19-H (17-C, 13-C), 12-H (11-C),

*1,1´-(2,5-thiophenediyl)bis[1-(2-benzofuranyl)methanone], 1,1´-bis[*O*-(4--ethenylphenyl)methyloxime] (**4e**)*. Yield: 62 %, 0.10 g; m.p.: 104–105 °C; Anal. Calcd. for $C_{40}H_{30}N_2O_4S$: C, 75.69; H, 4.76; N, 4.41 %. Found: C, 75.74; H, 4.71; N, 4.42 %; FTIR (KBr, cm^{-1}): 1627 (C=C stretching), 1553 (C=N), 1000 (N–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 7.85–7.25 (*m*, 40H, benzofuran ring, thiophene ring and phenyl ring protons), 6.74–6.70 (*m*, 4H, C=C–H_a protons), 5.86–5.78 (*m*, 4H, C=C–H_b protons), 5.47 (*s*, 4H, OCH_2 protons, 31 % (*anti*-isomer)), 5.40 (*s*, 4H, OCH_2 protons, 69 % (*syn*-isomer)), 5.35–5.24 (4H, *m*, C=C–H_c); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 154.91 (C-9 *anti*-isomer), 153.65 (C-9 *syn*-isomer), 150.08 (C-2 *anti*-isomer), 149.97 (C-2 *syn*-isomer), 144.33 (C-12 *anti*-isomer), 142.77 (C-12 *syn*-isomer), 142.70 (C-10 *anti*-isomer), 142.11 (C-10 *syn*-isomer), 137.49 (C-17 *anti*-isomer), 137.45 (C-17 *syn*-isomer), 137.03 (C-14

anti-isomer), 136.95 (C-14 *syn*-isomer), 136.76 (C-20 *anti*-isomer), 136.70 (C-20 *syn*-isomer), 134.01 (C-11 *anti*-isomer), 133.20 (C-11 *syn*-isomer), 131.69 (C-15, C-19 *anti*-isomer), 130.68 (C-15, C-19 *syn*-isomer), 129.26 (C-16, C-18 *anti*-isomer), 128.97 C-16, C-18 *syn*-isomer), 127.90 (C-7 *anti*-isomer), 127.87 (C-7 *syn*--isomer), 127.73 (C-4 *anti*-isomer), 127.49 (C-4 *syn*-isomer), 126.72 (C-21 *anti*--isomer), 126.68 (C-21 *syn*-isomer), 124.29 (C-6 *anti*-isomer), 124.05 (C-6 *syn*--isomer), 123.10 (C-5 *anti*-isomer), 122.44 (C-5 *syn*-isomer), 112.17 (C-8 *anti*--isomer), 112.01 (C-8 *syn*-isomer), 109.62 (C-3 *anti*-isomer), 109.56 (C-3 *syn*--isomer), 77.60 (C-13 *anti*-isomer), 77.41 (C-13 *syn*-isomer).



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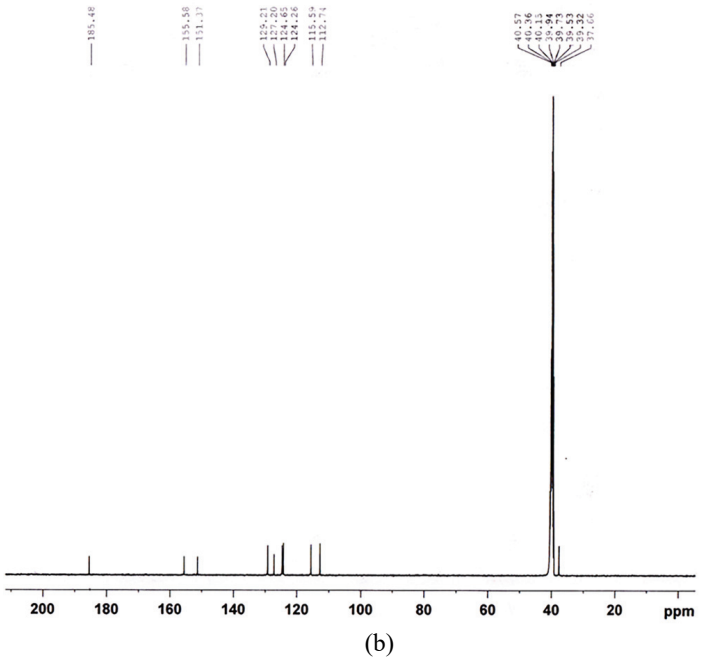
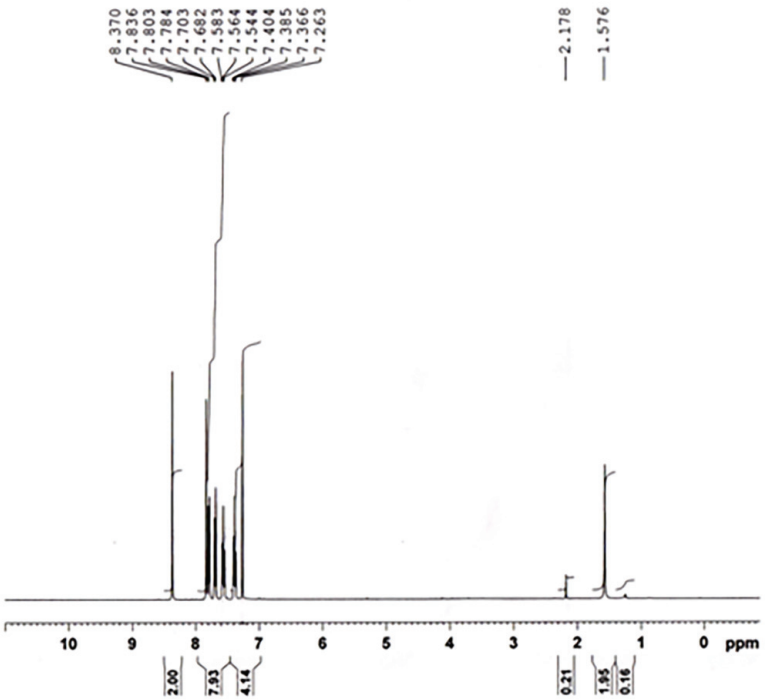


(b)

Fig. S-1. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of compound **1**.



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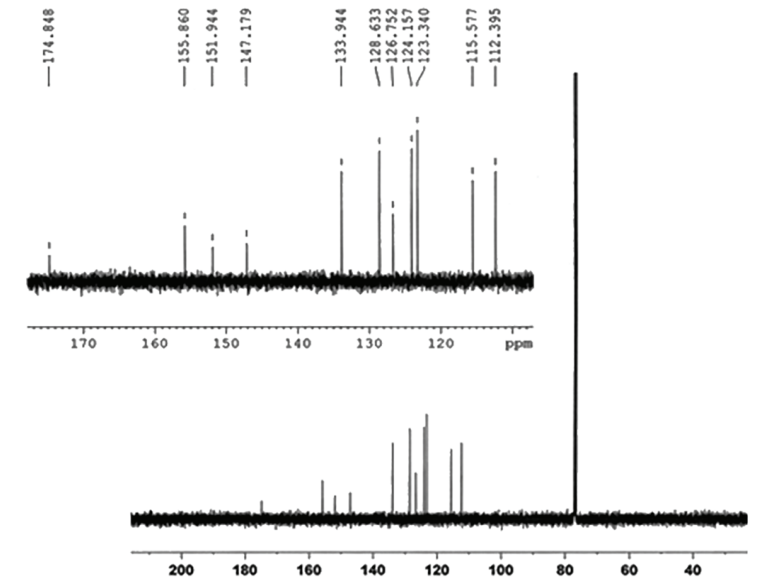
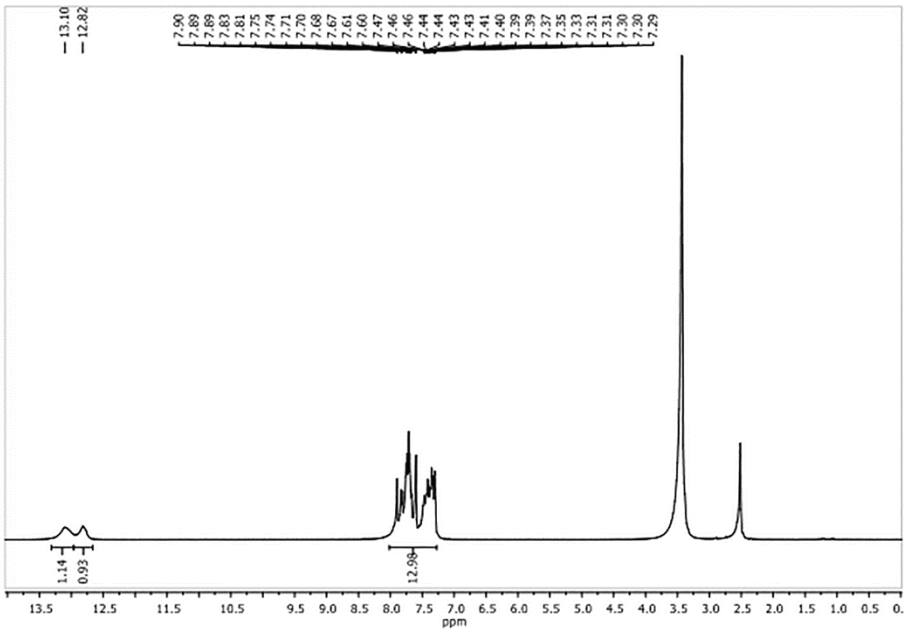


(b)

Fig. S-2. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of compound **2**.



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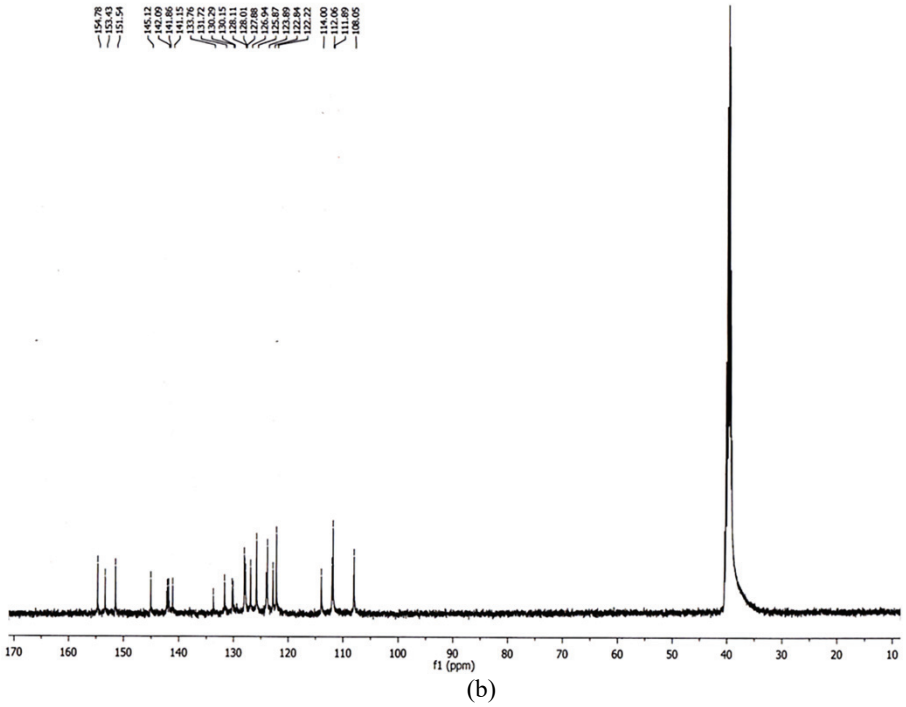
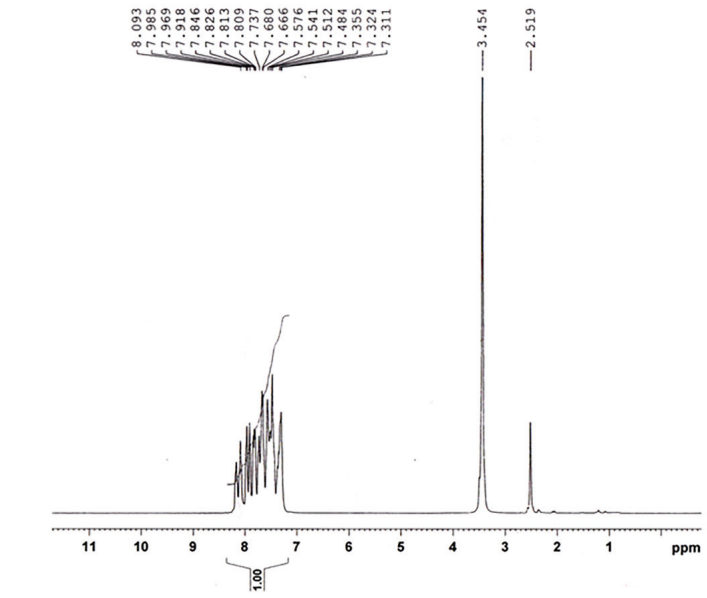


(b)

Fig. S-3. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of compound **3**.



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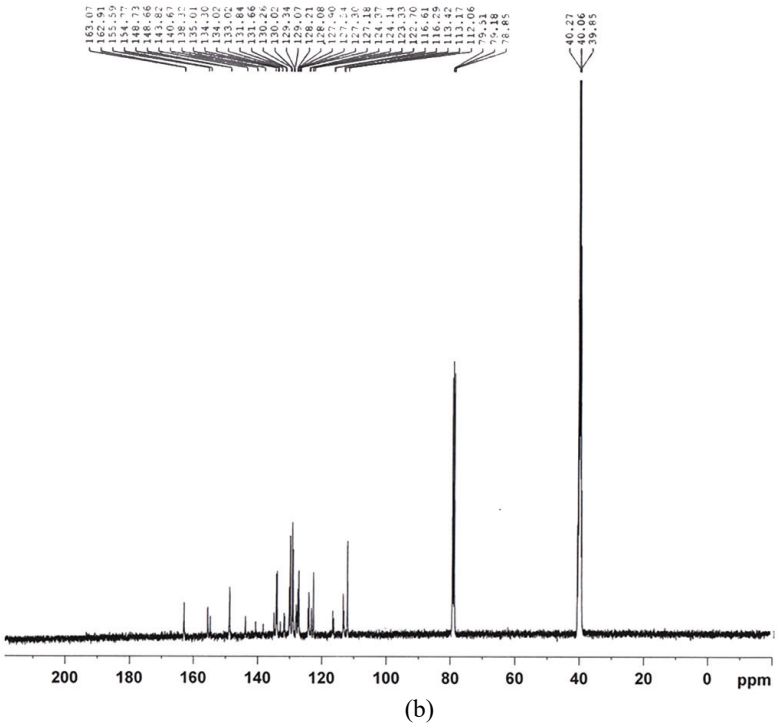
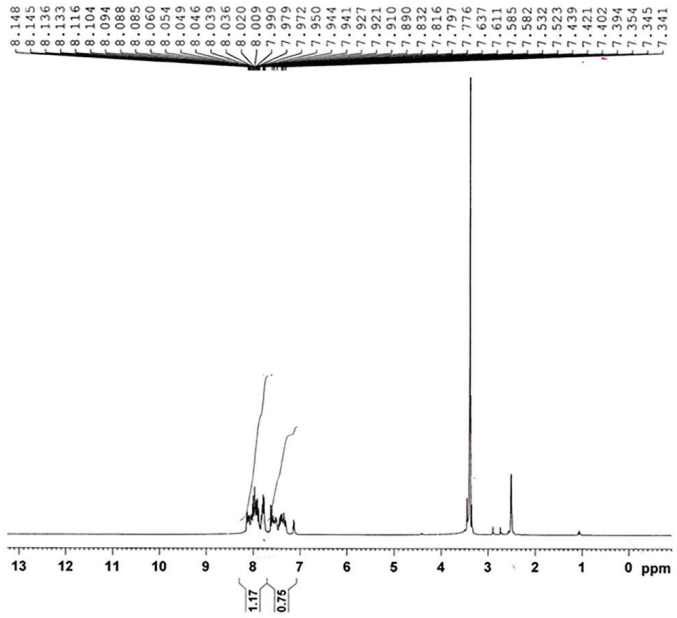
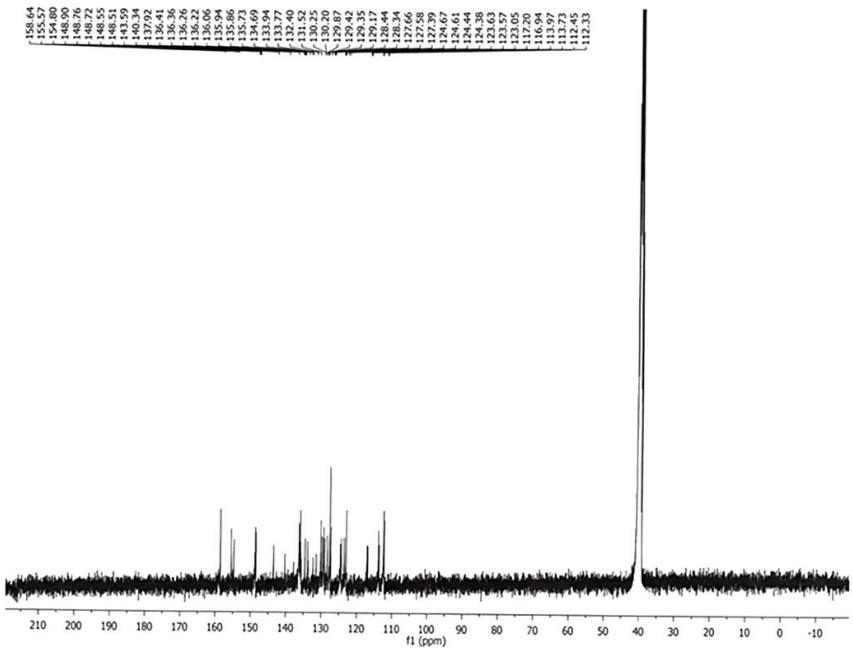


(b)

Fig. S-4. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of compound **4a**.

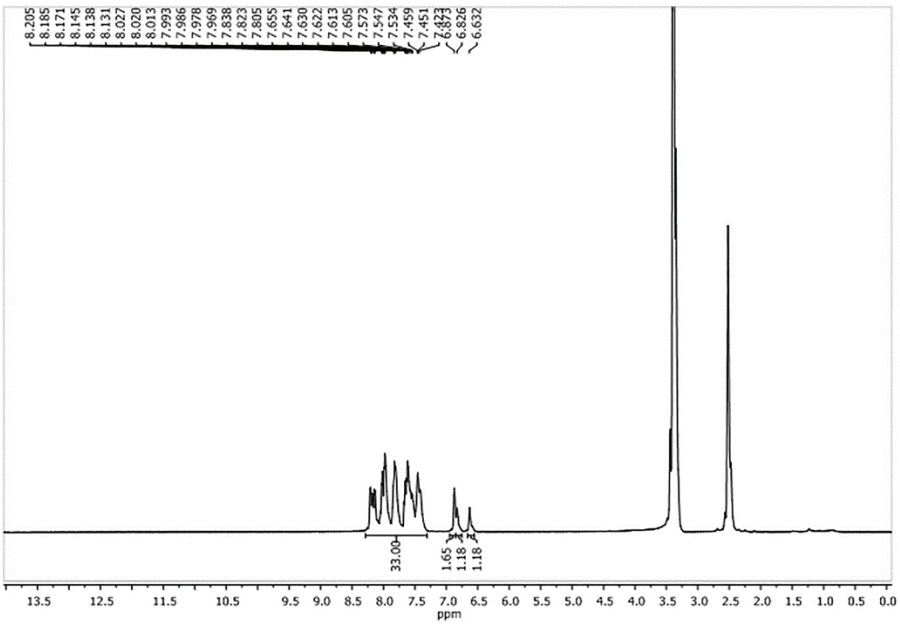


(a)



(b)

Fig. S-5. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of compound **4b**.



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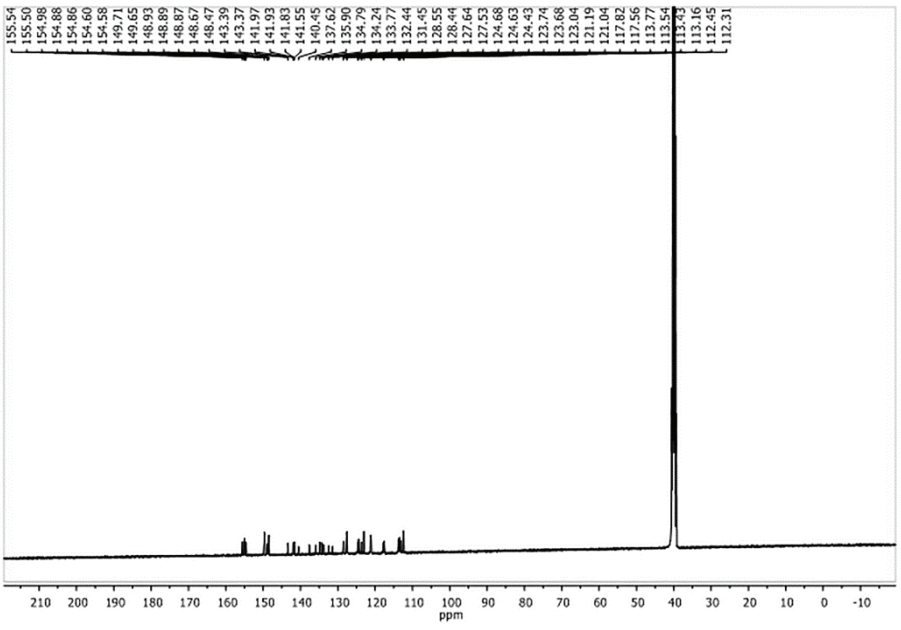
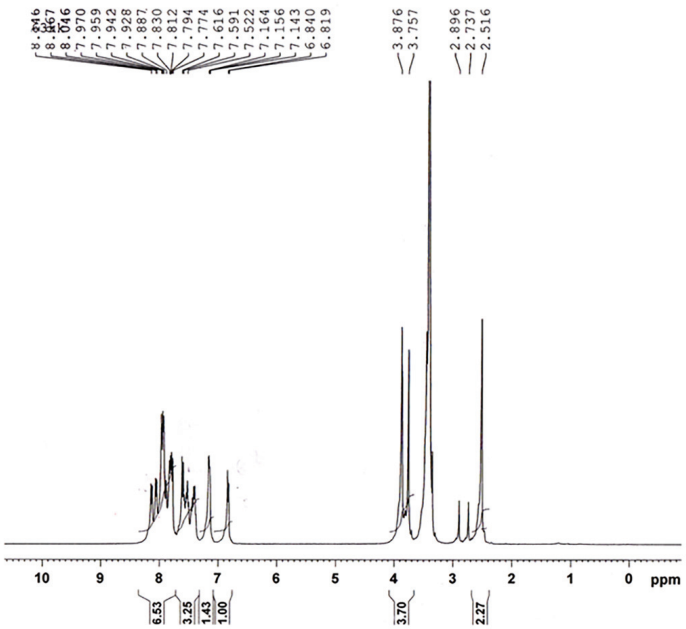


(b)

Fig. S-6. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of compound **4c**.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7.156
7.143
6.840
6.819
3.876
3.757
2.896
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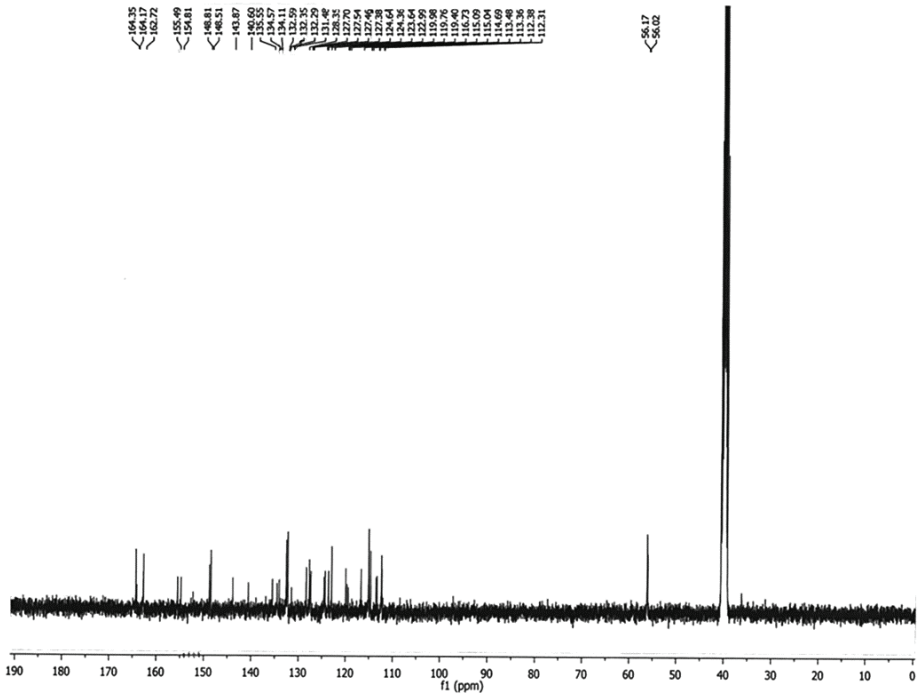
1.43
1.00
3.70
2.27

(a)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164.17
162.72
155.49
154.81
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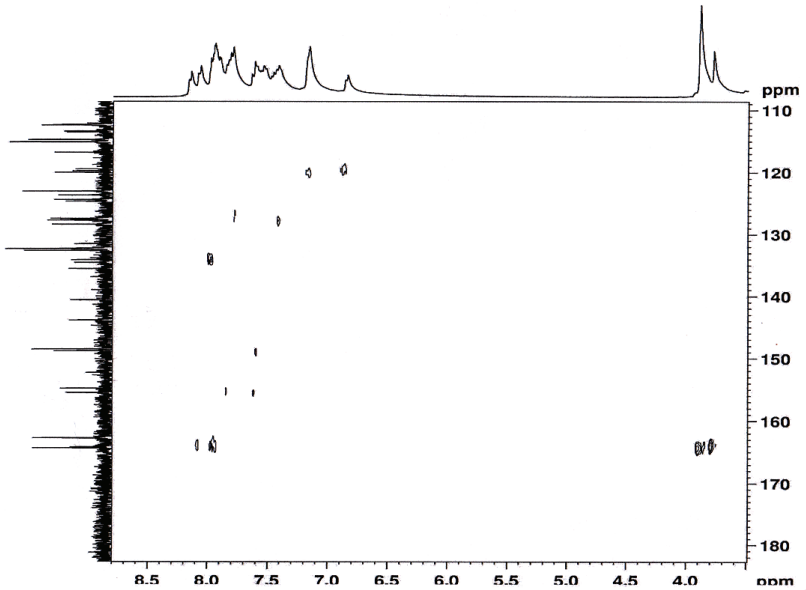
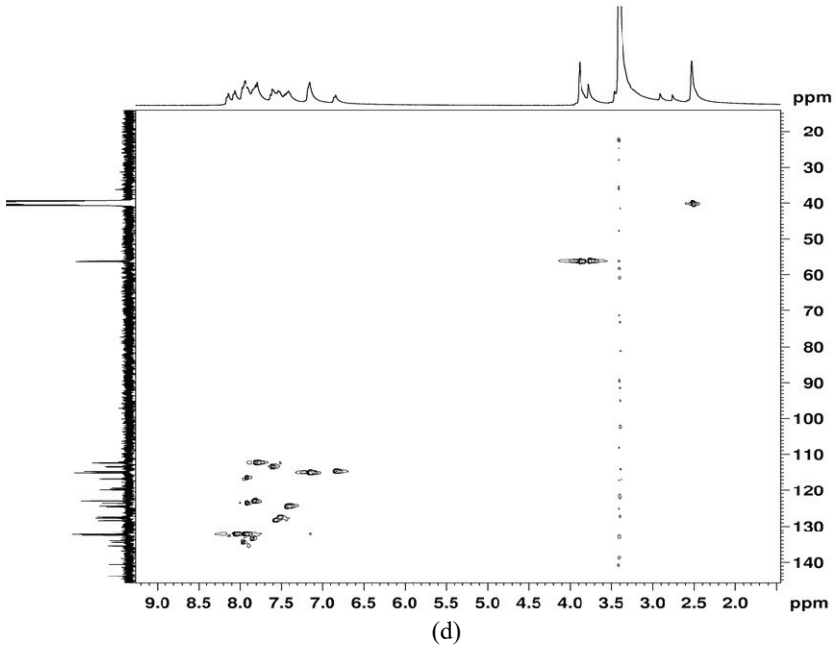
f1 (ppm)

(b)

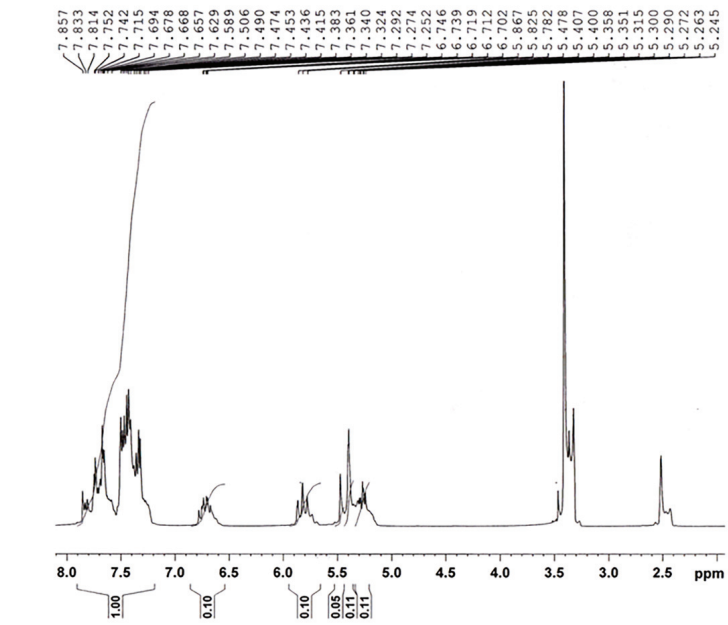


(c)

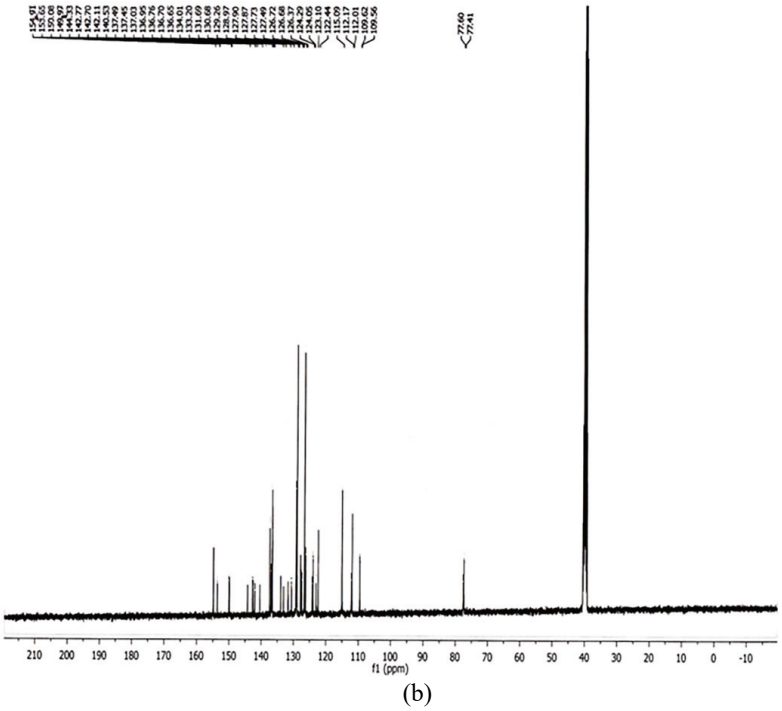


(d)

Fig. S-7. a) ^{1}H-NMR, b) ^{13}C-NMR, c) HMBC and d) HSQC spectra of compound **4d**.



(a)



(b)

Fig. S-8. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of compound **4e**.