

Supplementary Information

Ionic Liquid Catalyzed Convenient Synthesis of Imidazo[1,2-a]quinoline under Sonic Condition

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General procedure for preparation of ionic liquid [DBU][Ac]

Aliquot of acetic acid (1 equiv.) was added over a period of 15 min to DBU (1 equiv.) by maintaining the temperature below 5 °C in an ice bath under ultrasound. The reaction mixture was exposed to ultrasound for an additional period of 15 min at ambient temperature. The oily residue obtained was dried in vacuum at 60 °C for 1 h to afford [DBU][Ac] as a light yellow, viscous liquid; ¹H NMR (400 MHz, D₂O) δ 1.766 (s, 3H, CH₃), 1.517-1.671 (m, 6H, H3, H4, H5), 1.842-1.901 (m, 2H, H10), 2.394-2.650 (m, 2H, H6), 3.164-3.193 (m, 2H, H2), 3.278-3.437 (m, 4H, H11, H9); ¹³C NMR (100 MHz, D₂O) δ 19.5, 23.3, 25.9, 27.3, 28.4, 32.8, 37.9, 48.2, 54.1, 165.9, 179.4.

Analytical data for compound 4a-I

5-(4-Nitrophenyl)-1,2,3,5,6,7,8,9-Octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (4a)¹

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.048 (s, 1H), 8.164 (d, 2H, *J* 8.4 Hz), 7.569 (d, 2H, *J* 8.4 Hz), 4.707 (s, 1H), 4.421 (s, 2H), 2.585-2.428 (m, 2H), 2.206 (d, 1H, *J* 16.4 Hz), 2.023 (d, 1H, *J* 16.0 Hz), 1.055 (s, 3H), 0.893 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 194.3, 170.7, 153.3, 149.6, 149.6, 146.8, 129.2, 124.0, 118.3, 108.8, 62.9, 56.5, 49.9, 49.4, 38.7, 38.0, 32.3. ESI-MS *m/z* 379.0 [M + H]⁺. Anal. Calc. for C₂₀H₁₈N₄O₄ (378.38 g mol⁻¹): C, 63.48; H, 4.79; N, 14.81%. Found: C, 63.27; H, 4.86; N, 14.95%.

5-(4-Fluorophenyl)-1,2,3,5,6,7,8,9-Octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (4b)¹

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.959 (s, 1H), 7.292 (s, 2H), 7.103 (t, 2H, *J* 8.4 Hz), 4.534 (s, 1H), 4.401 (s, 2H), 2.566-2.398 (m, 2H), 2.192 (d, 1H, *J* 16.0 Hz), 2.017 (d, 1H, *J* 16.0 Hz), 1.047 (s, 3H), 0.886 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 194.3, 170.8, 160.3, 149.2, 148.9,

142.3, 136.1, 130.0, 129.3, 118.6, 116.2, 114.8, 109.7, 63.9, 50.1, 49.3, 38.6, 32.2. ESI-MS: *m/z* 351.8 [M + H]⁺. Anal. Calc. for C₂₀H₁₈FN₃O₂ (351.37 g mol⁻¹): C, 68.36; H, 5.16; N, 11.96%. Found: C, 68.67; H, 5.07; N, 11.74%.

5-(4-Chlorophenyl)-1,2,3,5,6,7,8,9-Octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (4c)¹

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.874 (s, 1H), 7.277-7.995 (m, 4H), 4.530 (s, 1H), 4.402 (s, 2H), 2.563-2.403 (m, 2H), 2.193 (d, 1H, *J* 16.4 Hz), 2.019 (d, 1H, *J* 16.8 Hz), 1.052 (s, 3H), 0.886 (s, 3H); APT NMR (100 MHz, DMSO-*d*₆) δ 194.2, 170.7, 149.1, 145.1, 131.7, 129.7, 128.6, 118.5, 109.4, 63.6, 50.0, 38.7, 37.4, 32.2 ppm. Anal. Calc. for C₂₀H₁₈ClN₃O₂ (367.83 g mol⁻¹): C, 65.31; H, 4.93; N, 11.42%. Found: C, 65.44; H, 5.01; N, 11.21%.

5-Phenyl-1,2,3,5,6,7,8,9-Octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (4d)¹

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.942 (s, 1H), 7.192-7.310 (m, 5H), 4.512 (s, 1H), 4.418 (s, 2H), 2.579-2.412 (m, 2H), 2.200 (d, 1H, *J* 16.4 Hz), 2.021 (d, 1H, *J* 16.0 Hz), 1.057 (s, 3H), 0.904 (s, 3H); APT NMR (100 MHz, DMSO-*d*₆) δ 194.2, 170.7, 149.1, 149.0, 146.1, 128.7, 127.7, 127.1, 118.7, 109.8, 64.0, 50.1, 38.7, 37.8, 32.2 ppm. Anal. Calc. for C₂₀H₁₉N₃O₂ (333.38 g mol⁻¹): C, 72.05; H, 5.74; N, 12.60%. Found: C, 72.34; H, 5.56; N, 12.49%.

5-(3-Nitrophenyl)-1,2,3,5,6,7,8,9-Octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (4e)¹

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.040 (s, 1H), 7.608-8.089 (m, 4H), 4.741 (s, 1H), 4.421 (2H, dd, *J* 17.2 Hz), 2.591-2.466 (m, 2H), 2.215 (d, 1H, *J* 16.4 Hz), 2.028 (d, 1H, *J* 16.0 Hz), 1.059 (s, 3H), 0.910 (s, 3H); APT NMR (100 MHz, DMSO-*d*₆) δ 194.3, 170.8, 149.7, 148.3, 134.9, 122.3, 122.2, 122.1, 118.4, 108.8, 63.0, 49.9, 49.4, 38.7, 37.8, 32.3 ppm. Anal. Calc. for C₂₀H₁₈N₄O₄ (378.38 g mol⁻¹): C, 63.48; H, 4.79; N, 14.81%. Found: C, 63.87; H, 4.61; N, 14.60%.

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5-(2-Nitrophenyl)-1,2,3,5,6,7,8,9-octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (**4f**)

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 12.053 (s, 1H), 7.407-7.800 (m, 4H), 5.232 (s, 1H), 4.407 (s, 2H), 2.538-2.369 (m, 2H), 2.129 (d, 1H, J 16.0 Hz), 1.907 (d, 1H, J 16.4 Hz), 1.017 (s, 3H), 0.802 (s, 3H); APT NMR (100 MHz, DMSO- d_6) δ 194.2, 170.7, 150.2, 149.1, 140.6, 131.5, 128.3, 123.8, 118.0, 110.0, 62.7, 49.6, 38.5, 32.4, 32.2, 26.2 ppm. Anal. Calc. for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_4$ (378.38 g mol $^{-1}$): C, 63.48; H, 4.79; N, 14.81%. Found: C, 63.22; H, 5.06; N, 14.65%.

5-(4-Methoxyphenyl)-1,2,3,5,6,7,8,9-octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (**4g**)¹

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.974 (s, 1H), 7.274-7.945 (m, 4H), 4.534 (s, 1H), 4.412 (s, 2H), 3.803 (s, 3H), 2.563-2.403 (m, 2H), 2.193 (d, 1H, J 16.4 Hz), 2.019 (d, 1H, J 16.8 Hz), 1.125 (s, 3H), 0.896 (s, 3H); APT NMR (100 MHz, DMSO- d_6) δ 194.33, 170.8, 149.7, 148.3, 148.2, 128.7, 127.7, 118.7, 109.8, 64.0, 57.1, 49.3, 49.2, 38.7, 37.2, 32.2 ppm. Anal. Calc. for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_2$ (363.41 g mol $^{-1}$): C, 69.41; H, 5.82; N, 11.56%. Found: C, 69.22; H, 5.79; N, 11.78%.

5-(2-Chlorophenyl)-1,2,3,5,6,7,8,9-octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (**4h**)

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.930 (s, 1H), 7.188-7.380 (m, 4H), 5.069 (s, 1H), 4.435 (2H, dd, J 16.8 Hz), 3.803 (s, 3H), 2.563-2.403 (m, 2H), 2.193 (d, 1H, J 16.0 Hz), 1.990 (d, 1H, J 16.0 Hz), 1.062 (s, 3H), 0.945 (s, 3H); APT NMR (100 MHz, DMSO- d_6) δ 194.1, 170.6, 149.7, 149.3, 143.5, 131.9, 130.8, 129.6, 128.7, 127.9, 118.1, 109.3, 63.2, 50.0, 49.3, 38.7, 34.96, 32.3, 29.8, 26.9 ppm. Anal. Calc. for $\text{C}_{20}\text{H}_{18}\text{ClN}_3\text{O}_2$ (367.83 g mol $^{-1}$): C, 65.31; H, 4.93; N, 11.42%. Found: C, 65.47; H, 4.63; N, 11.58%.

5-(4-Bromophenyl)-1,2,3,5,6,7,8,9-octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (**4i**)¹

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.976 (s, 1H), 7.488 (d, 2H, J 8.4 Hz), 7.229 (d, 2H, J 8.8 Hz), 4.510 (s, 1H), 4.399 (s, 2H), 2.567-2.400 (m, 2H), 2.192 (d, 1H, J 16.4 Hz), 2.017 (d, 1H, J 16.0 Hz), 1.049 (s, 3H), 0.888 (s, 3H); APT NMR (100 MHz, DMSO- d_6) δ 194.3, 170.7, 149.3, 149.1, 145.5, 133.2, 132.6, 131.6, 120.2, 118.5, 109.4, 63.5, 49.3, 32.2 ppm. Anal. Calc. for $\text{C}_{20}\text{H}_{18}\text{BrN}_3\text{O}_2$

(412.28 g mol $^{-1}$): C, 58.26; H, 4.40; N, 10.19%. Found: C, 58.32; H, 4.47; N, 10.23%.

5-(2,4-Dichlorophenyl)-1,2,3,5,6,7,8,9-octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (**4j**)

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.968 (s, 1H), 7.714 (s, 1H), 7.518 (d, 2H, J 2.0 Hz), 7.364 (d, 2H, J 1.6 Hz), 5.035 (s, 1H), 4.430 (s, 2H), 2.568-2.421 (m, 2H), 2.184 (d, 1H, J 16.0 Hz), 1.989 (d, 1H, J 16.0 Hz), 1.054 (s, 3H), 0.937 (s, 3H); APT NMR (100 MHz, DMSO- d_6) δ 194.1, 170.6, 157.2, 132.9, 132.3, 131.5, 131.4, 130.6, 118.0, 108.9, 62.7, 50.1, 49.7, 39.6, 34.6, 32.2 ppm. Anal. Calc. for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{N}_3\text{O}_2$ (402.27 g mol $^{-1}$): C, 59.71; H, 4.26; N, 10.45%. Found: C, 59.38; H, 4.41; N, 10.62%.

5-(3,4,5-trimethoxyphenyl)-1,2,3,5,6,7,8,9-octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (**4k**)

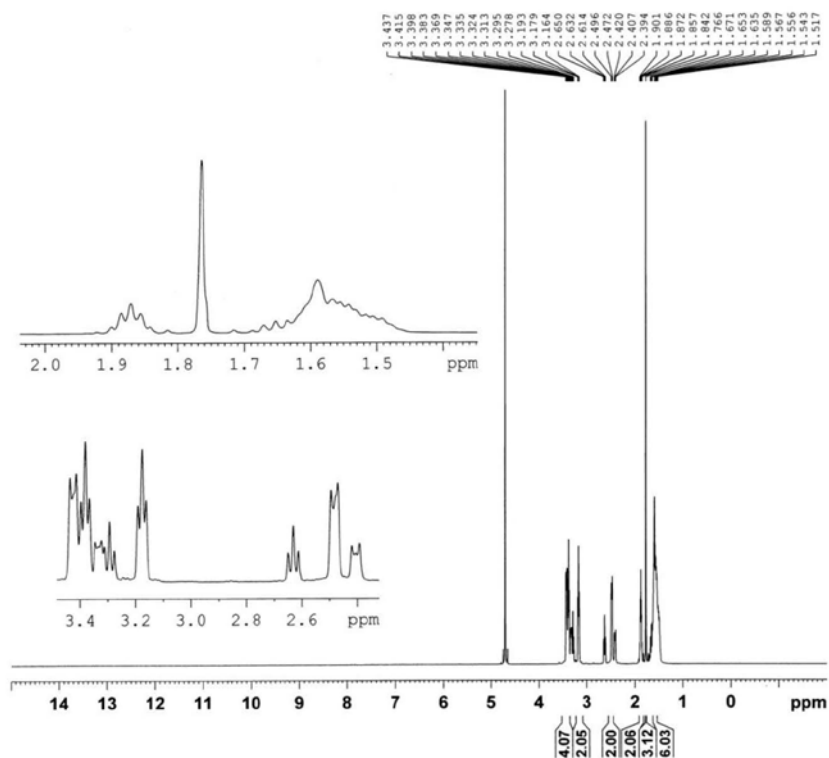
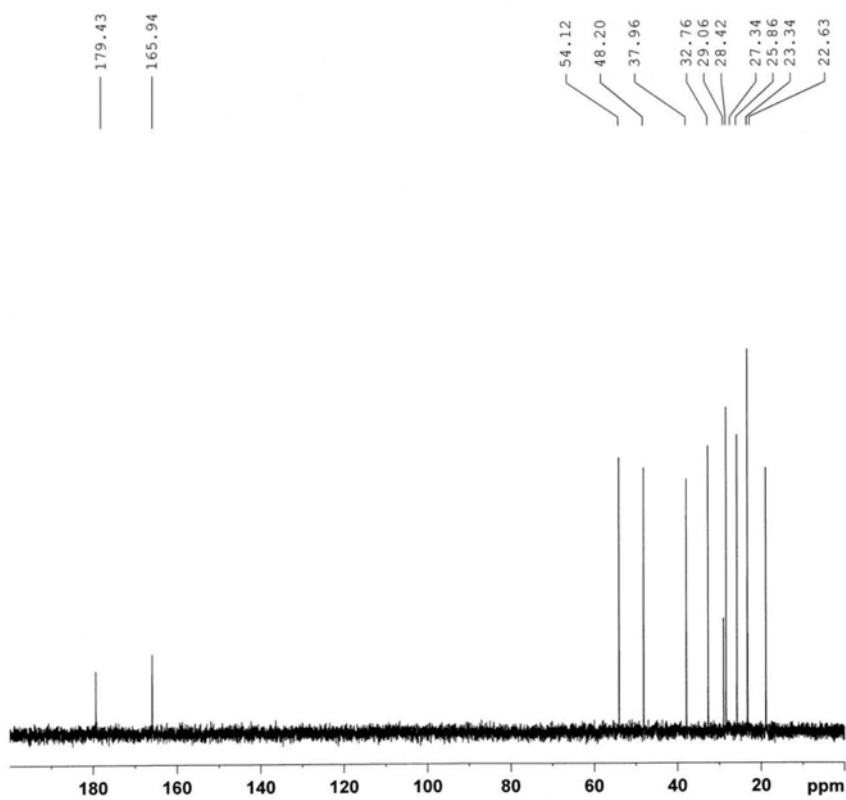
$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.967 (s, 1H), 7.240 (s, 2H), 4.519 (s, 1H), 4.399 (s, 2H), 3.826 (s, 9H), 2.577-2.408 (m, 2H), 2.193 (d, 1H, J 16.4 Hz), 2.018 (d, 1H, J 16.0 Hz), 1.046 (s, 3H), 0.898 (s, 3H); APT NMR (100 MHz, DMSO- d_6) δ 194.2, 170.7, 149.3, 149.1, 138.6, 118.5, 109.4, 104.5, 63.5, 60.3, 54.3, 49.3, 42.2, 39.4, 32.2 ppm. Anal. Calc. for $\text{C}_{23}\text{H}_{25}\text{N}_3\text{O}_5$ (423.16 g mol $^{-1}$): C, 65.24; H, 5.95; N, 9.92%. Found: C, 65.65; H, 5.69; N, 9.77%.

5-(4-(Dimethylamino)trimethoxyphenyl)-1,2,3,5,6,7,8,9-octahydro-8,8-dimethyl-2,6-dioxoimidazo[1,2-a]quinoline-4-carbonitrile (**4l**)

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 11.948 (s, 1H), 7.863 (d, 2H, J 8.4 Hz), 7.069 (d, 2H, J 8.8 Hz), 4.707 (s, 1H), 4.421 (s, 2H), 3.105 (s, 6H), 2.585-2.428 (m, 2H), 2.207 (d, 1H, J 16.4 Hz), 2.023 (d, 1H, J 16.0 Hz), 1.058 (s, 3H), 0.895 (s, 3H); APT NMR (100 MHz, DMSO- d_6) δ 194.3, 170.7, 153.3, 149.6, 129.2, 124.0, 118.3, 111.6, 108.9, 62.9, 56.5, 49.9, 49.3, 42.5, 38.7, 38.0, 32.2 ppm. Anal. Calc. for $\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_2$ (376.45 g mol $^{-1}$): C, 70.19; H, 6.43; N, 14.88%. Found: C, 70.31; H, 6.37; N, 14.91%.

Reference

- Tu, S.; Li, C.; Li, G.; Cao, L.; Shao, Q.; Zhou, D.; Jiang, B.; Zhou, J.; Xia, M.; *J. Comb. Chem.* **2007**, *9*, 1144.

Spectral data for ionic liquid and compound **4a-I****Figure S1.** ¹H NMR spectrum (400 MHz, D₂O) of ionic liquid.**Figure S2.** ¹³C NMR spectrum (100 MHz, D₂O) of ionic liquid.

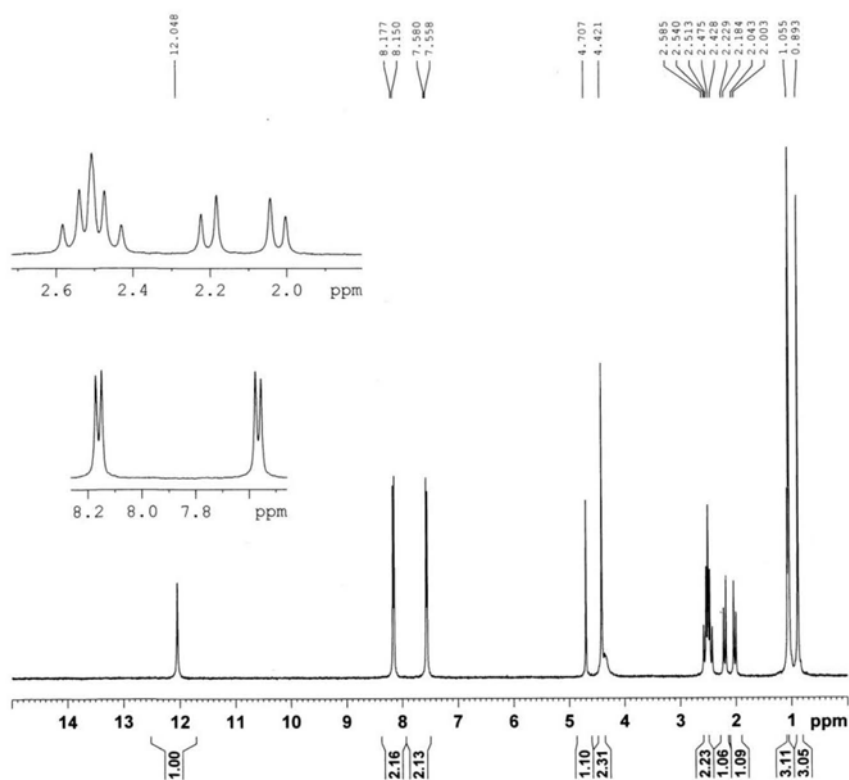


Figure S3. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of **4a**.

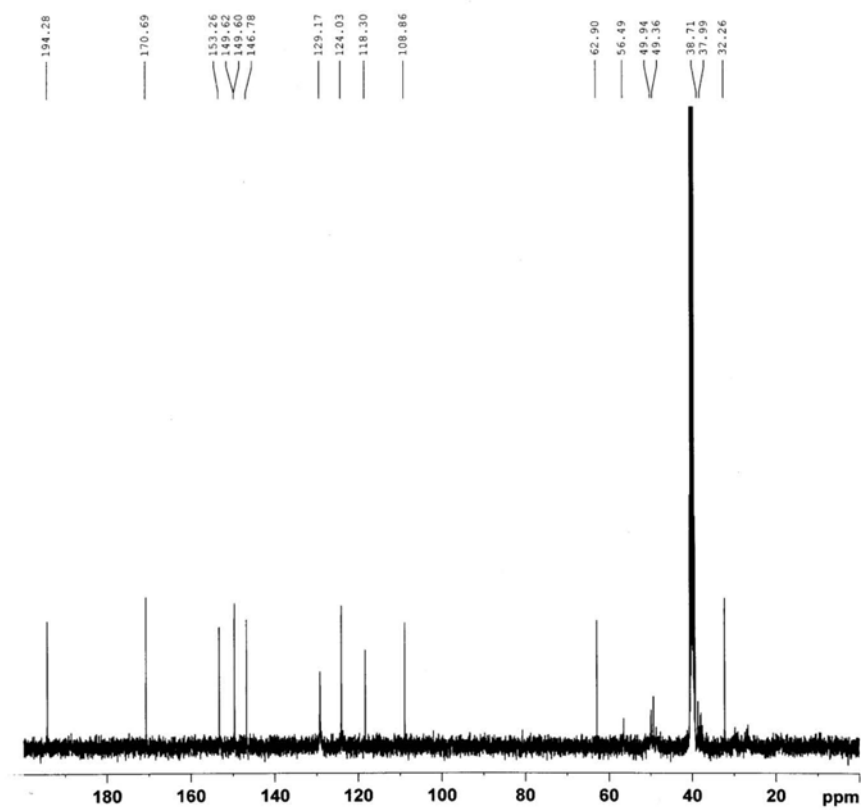
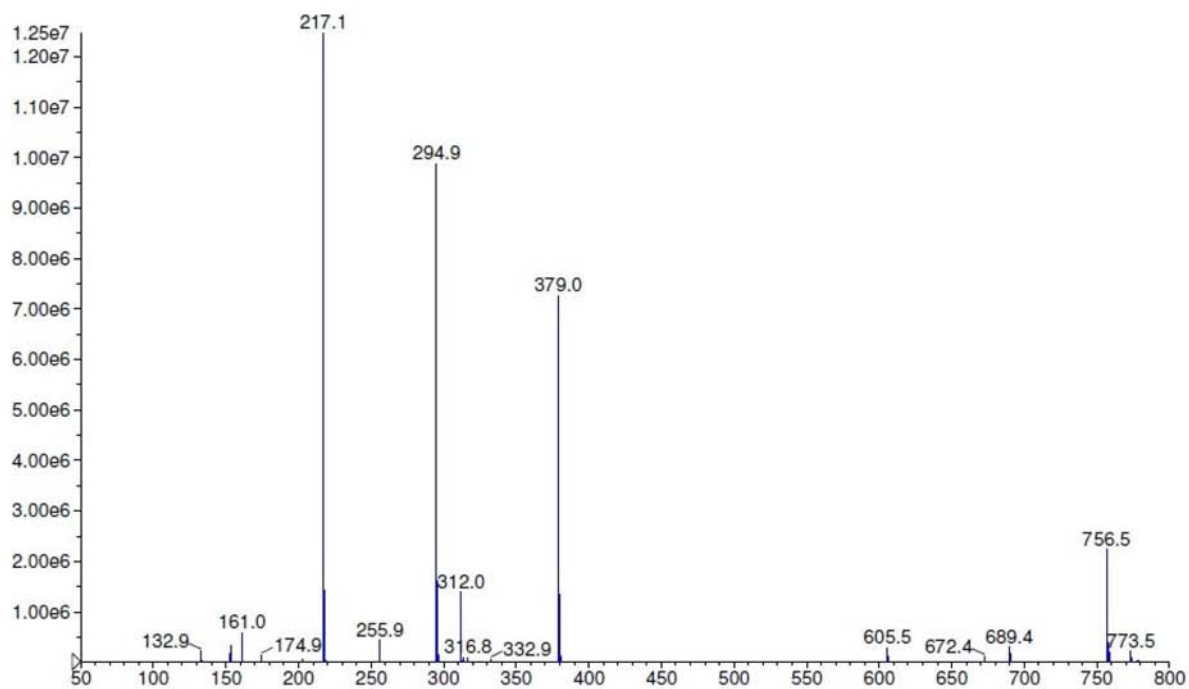
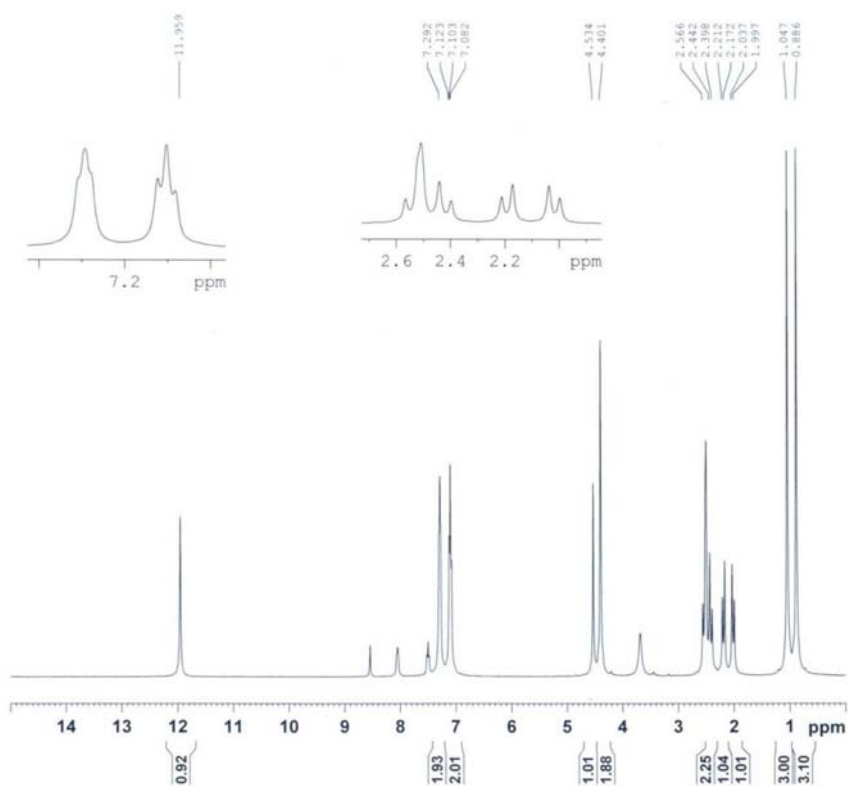


Figure S4. ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$) of **4a**.

**Figure S5.** Mass spectrum of 4a.**Figure S6.** ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of 4b.

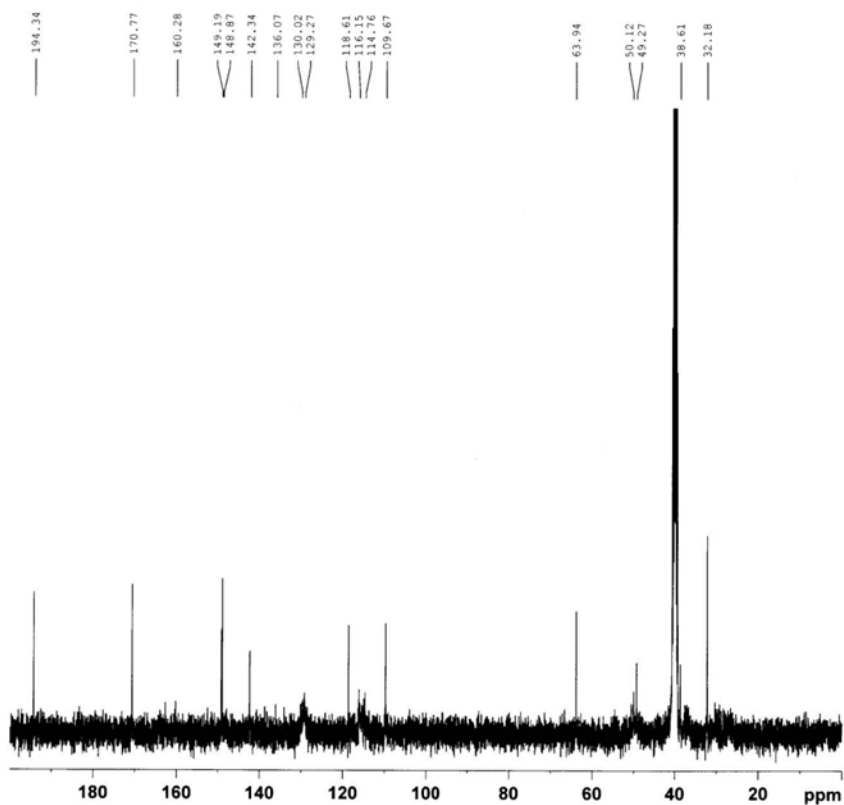


Figure S7. ^{13}C NMR spectrum (100 MHz, $\text{DMSO}-d_6$) of **4b**.

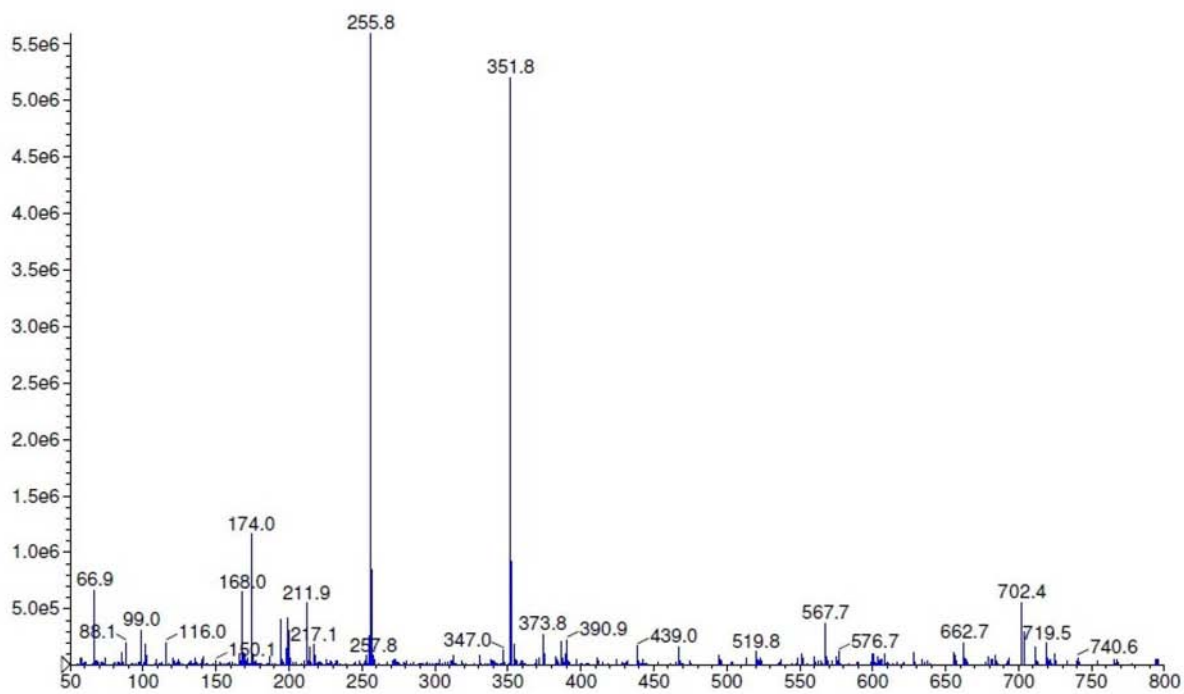


Figure S8. Mass spectrum of **4b**.

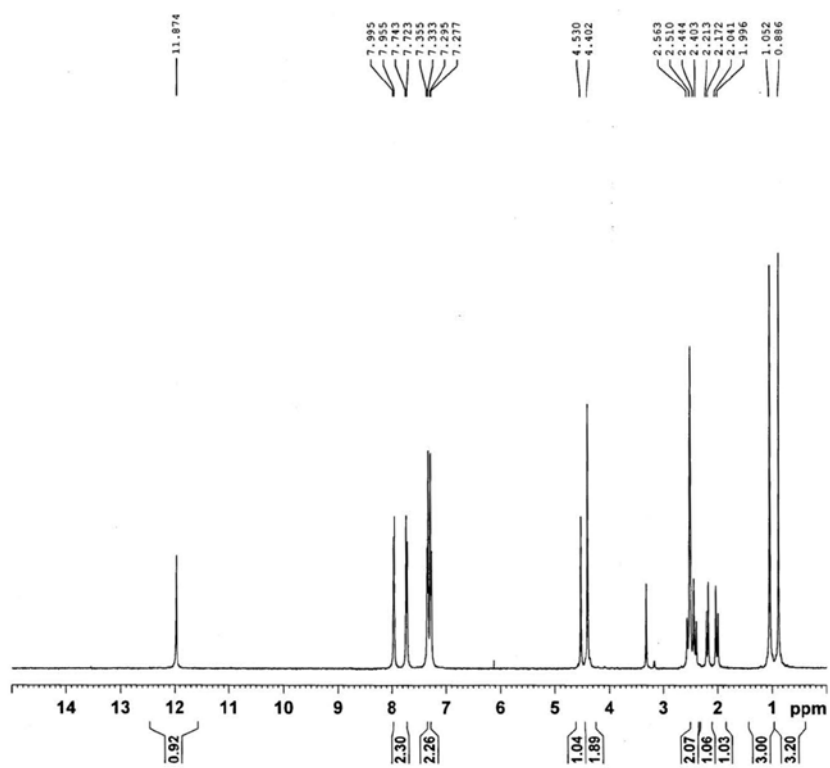


Figure S9. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of 4c.

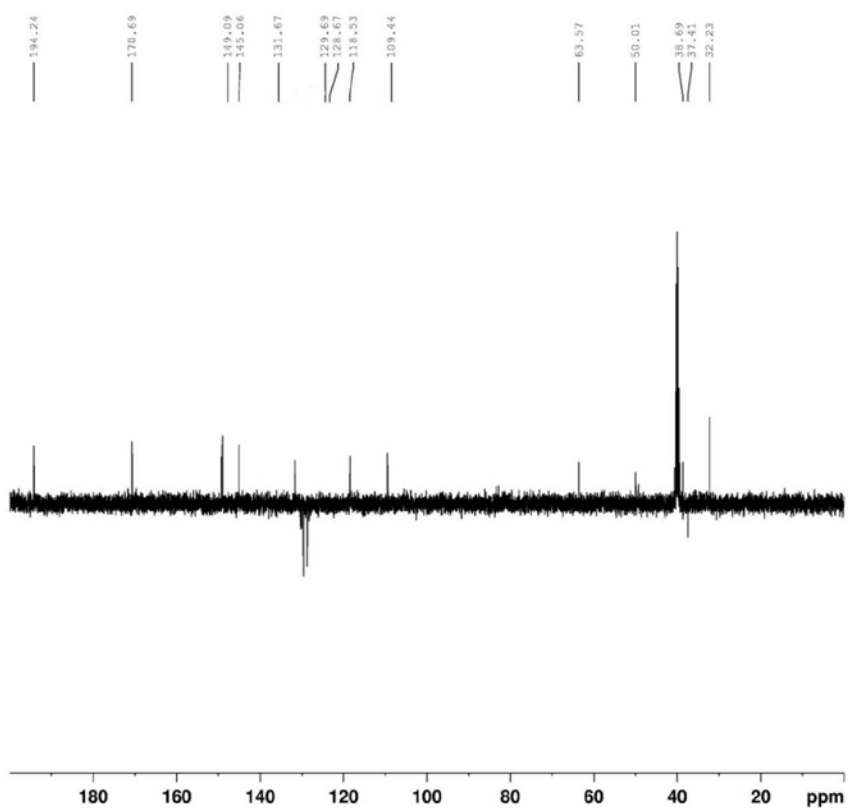


Figure S10. APT spectrum (100 MHz, DMSO-*d*₆) of 4c.

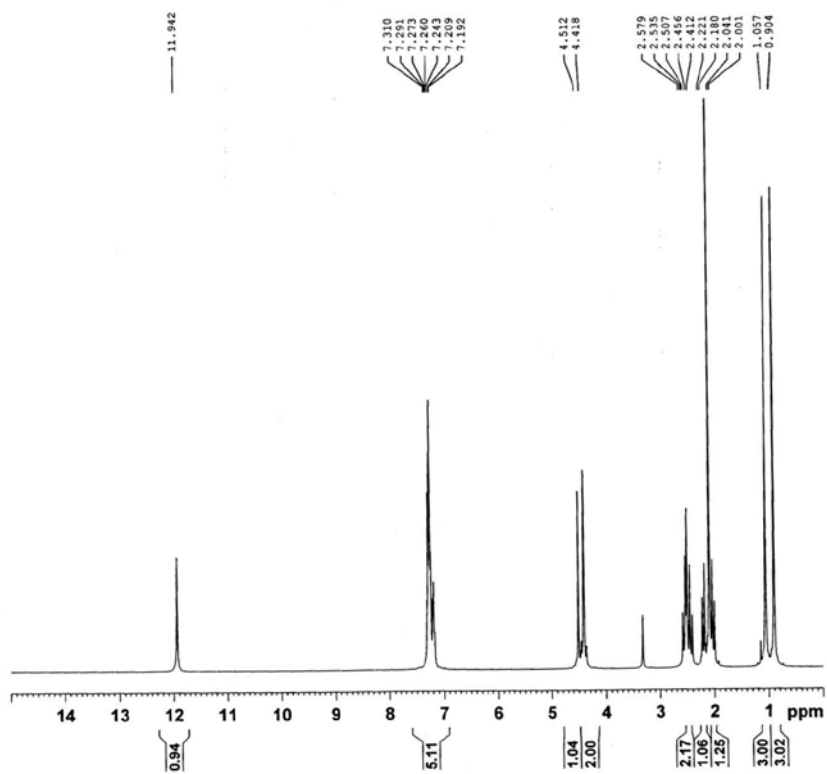


Figure S11. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **4d**.

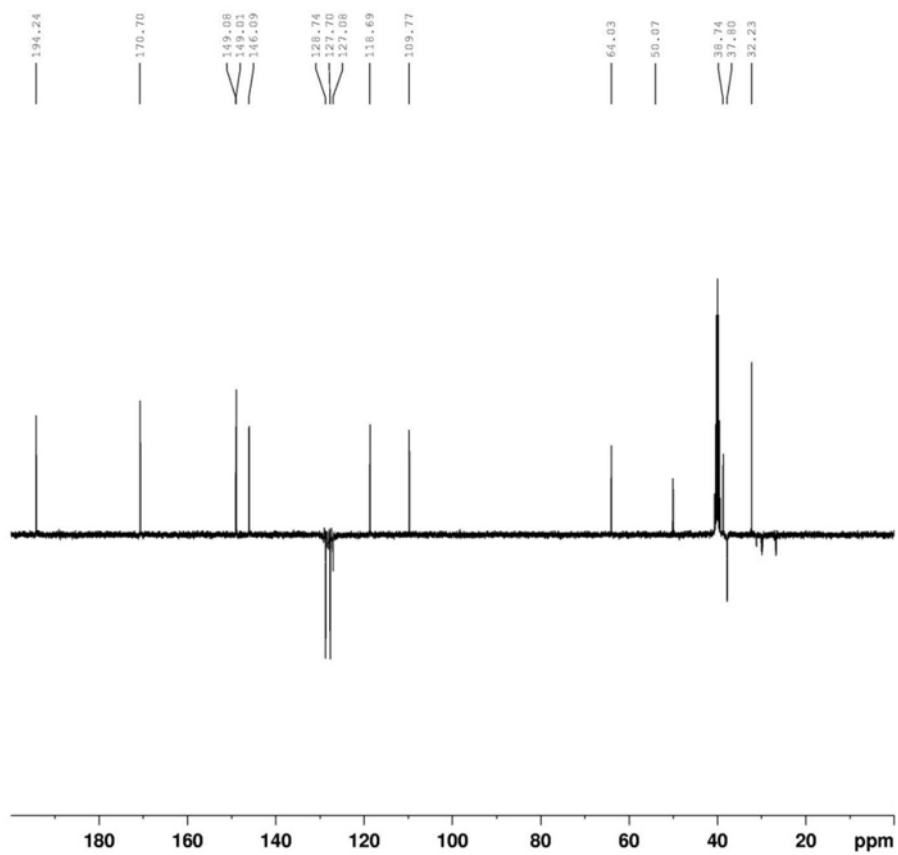


Figure S12. APT spectrum (100 MHz, DMSO-*d*₆) of **4d**.

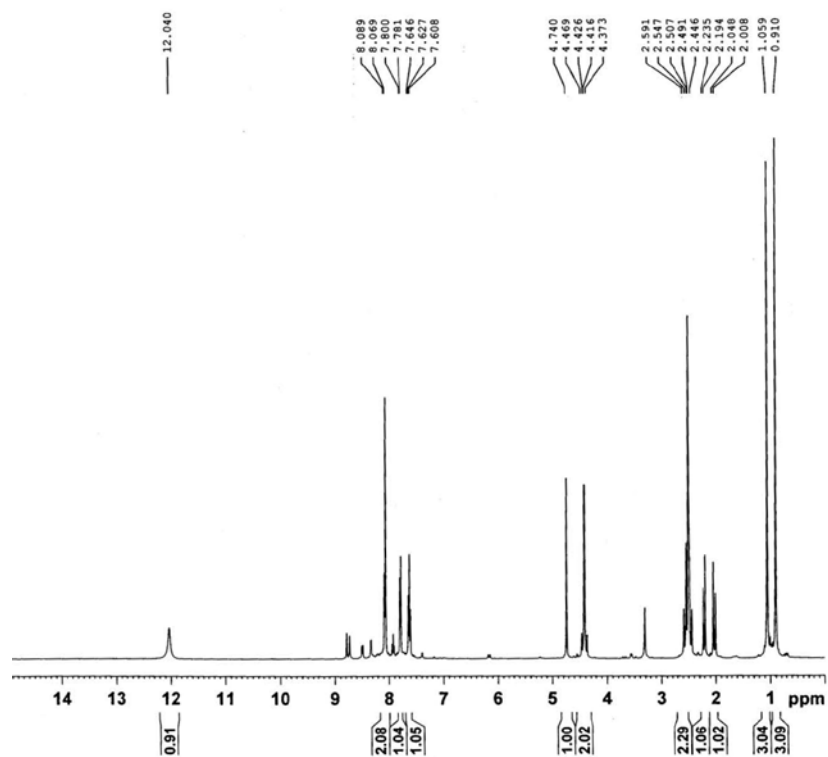


Figure S13. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of **4e**.

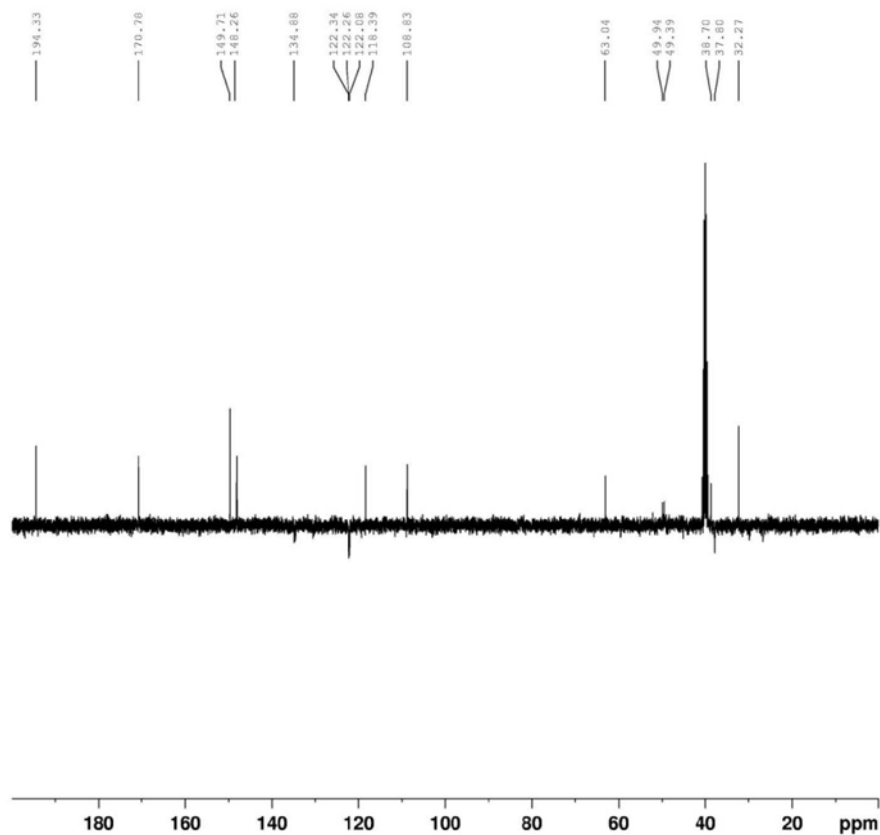


Figure S14. APT spectrum (100 MHz, $\text{DMSO-}d_6$) of **4e**.

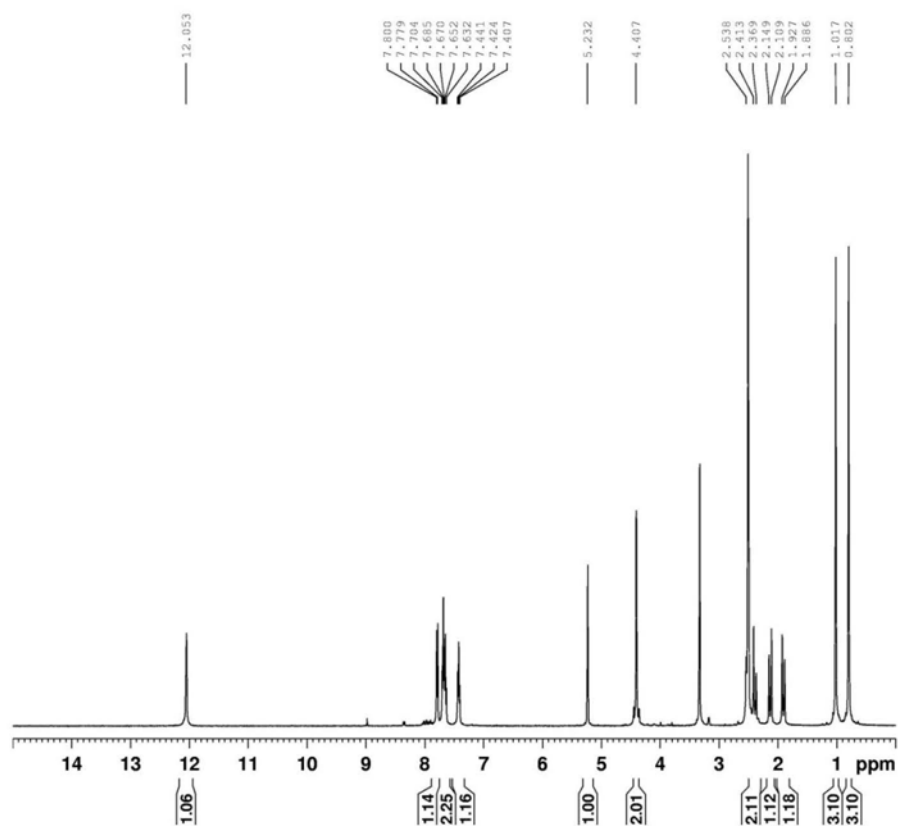


Figure S15. ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$) of **4f**.

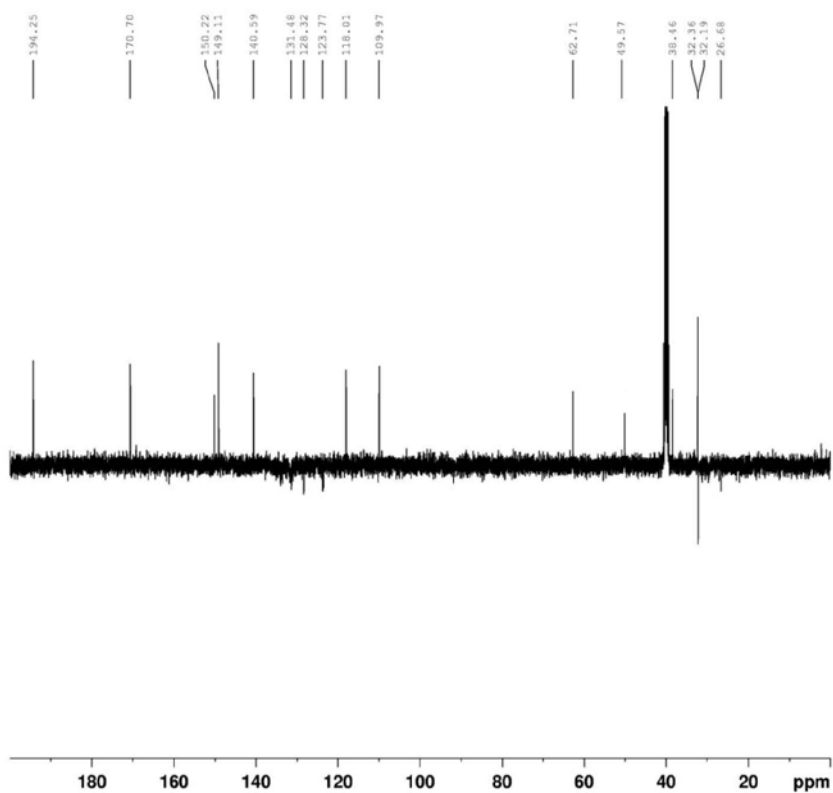


Figure S16. APT spectrum (100 MHz, $\text{DMSO}-d_6$) of **4f**.

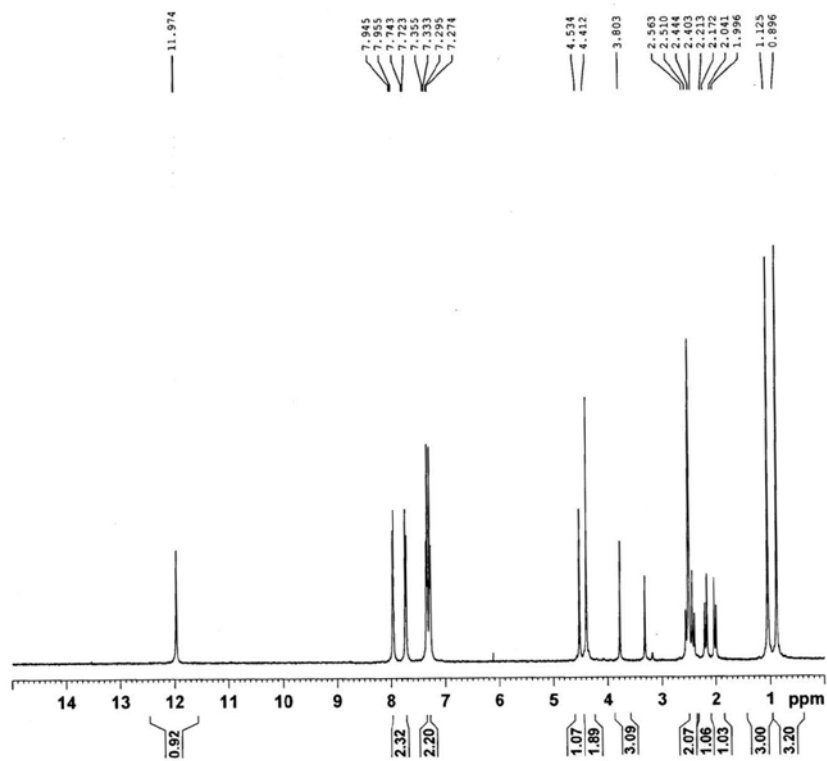


Figure S17. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **4g**.

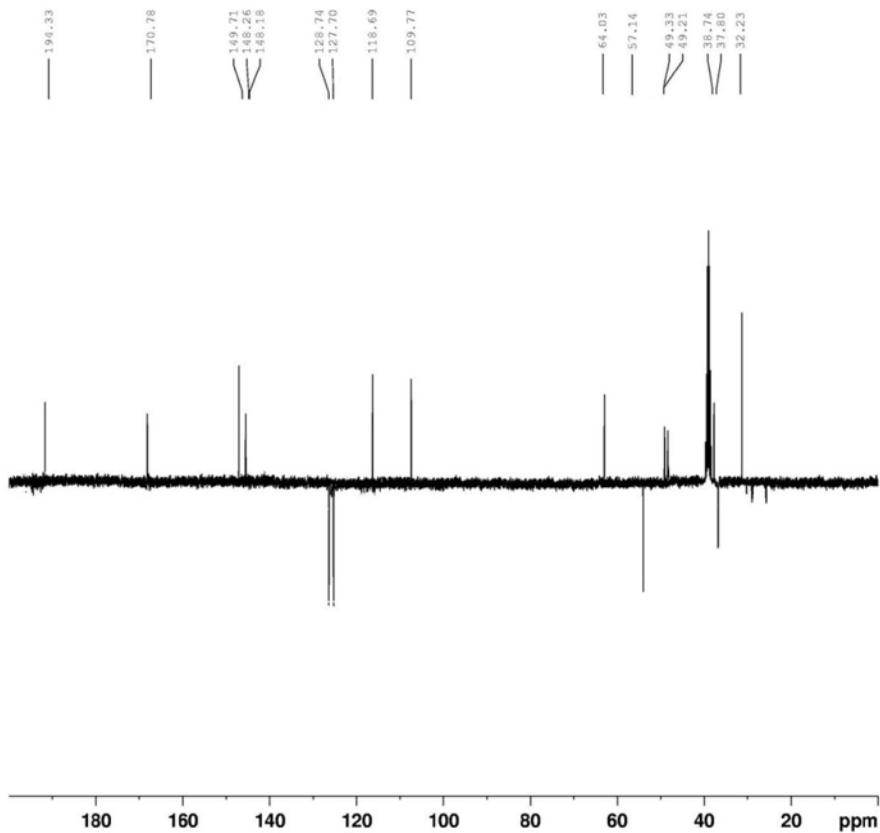


Figure S18. APT spectrum (100 MHz, DMSO-*d*₆) of **4g**.

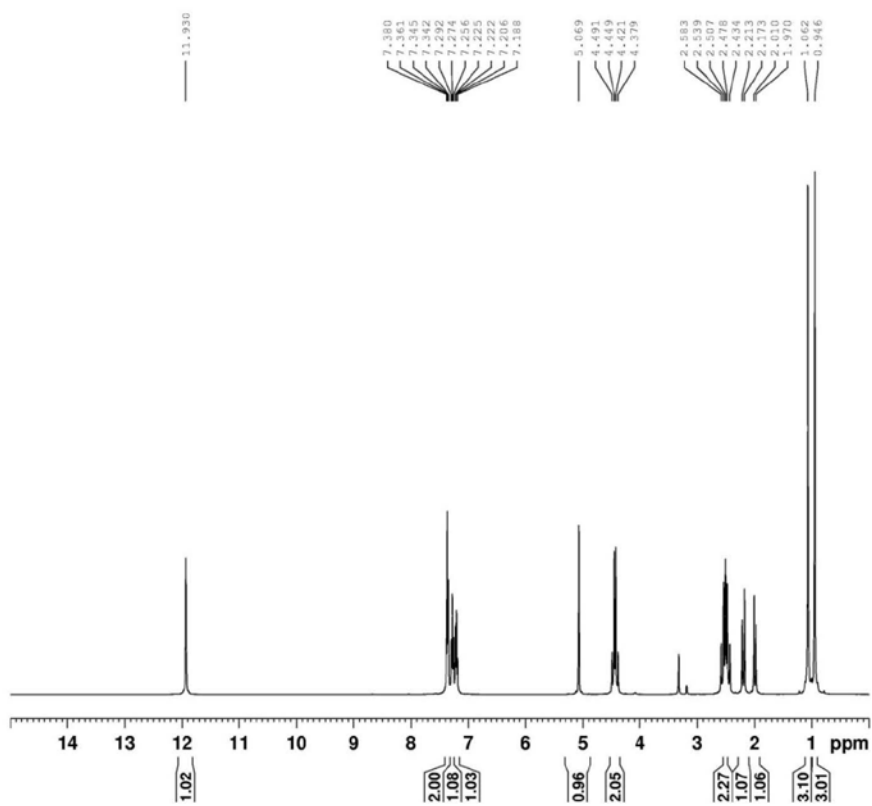


Figure S19. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **4h**.

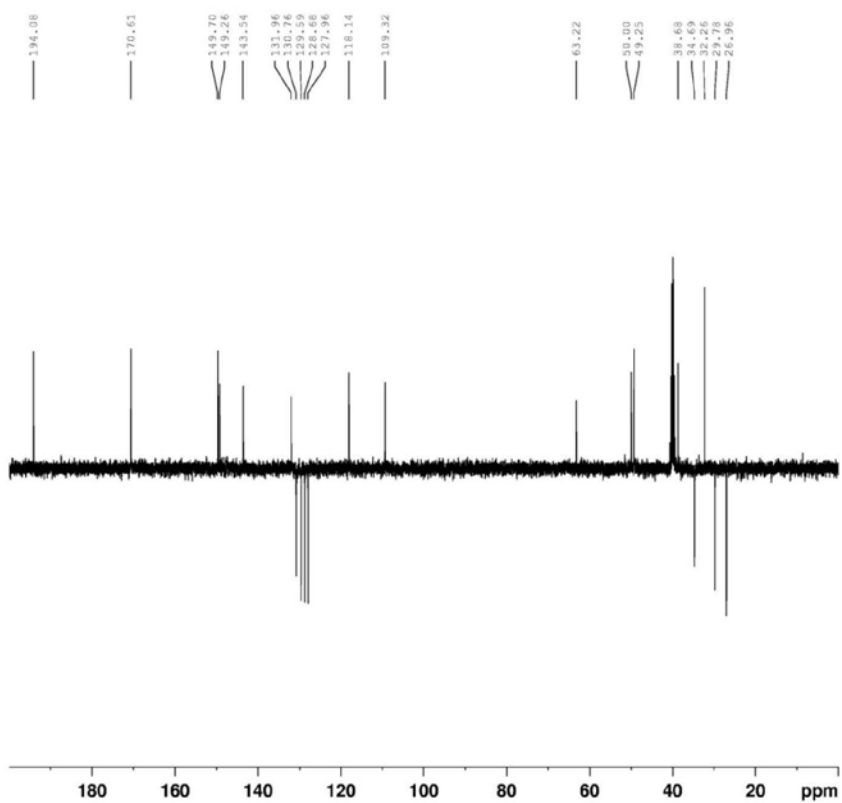


Figure S20. APT spectrum (100 MHz, DMSO-*d*₆) of **4h**.

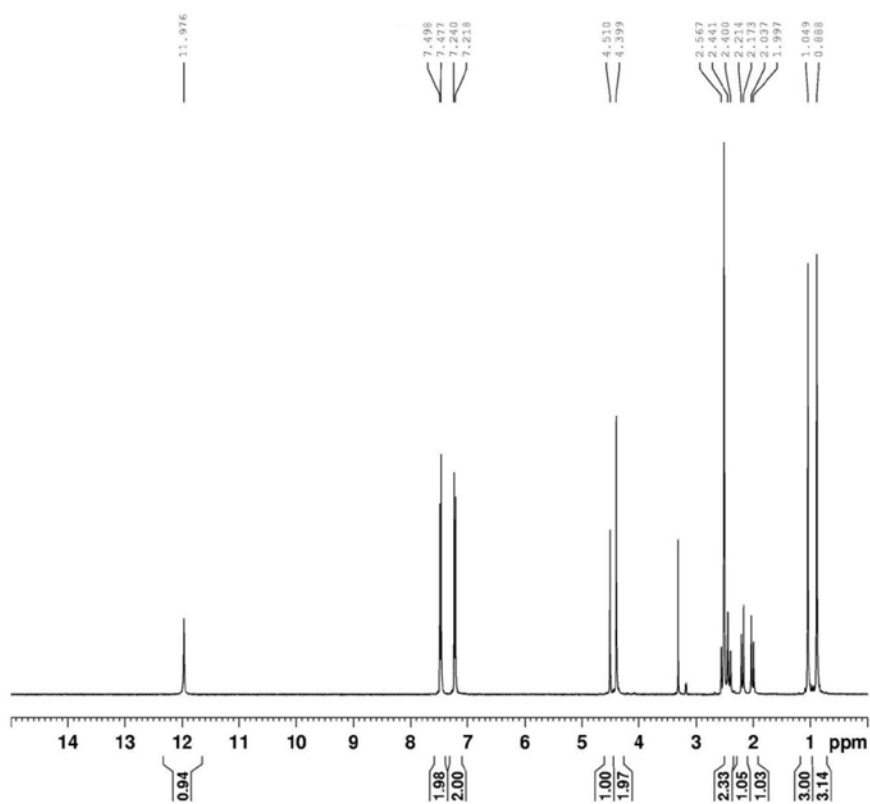


Figure S21. ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$) of **4i**.

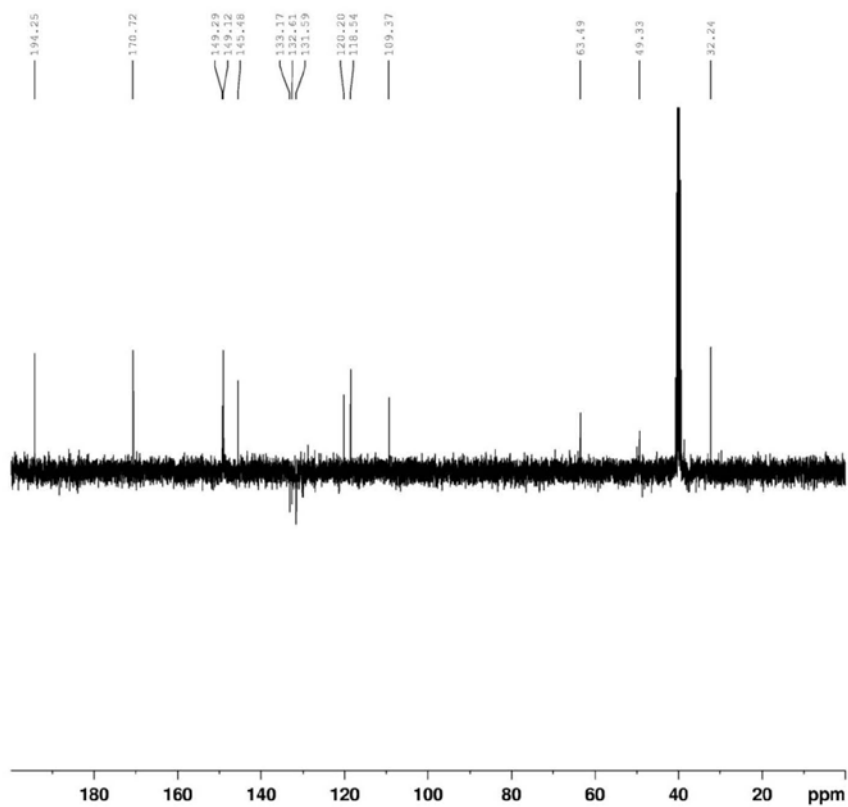


Figure S22. APT spectrum (100 MHz, $\text{DMSO-}d_6$) of **4i**.

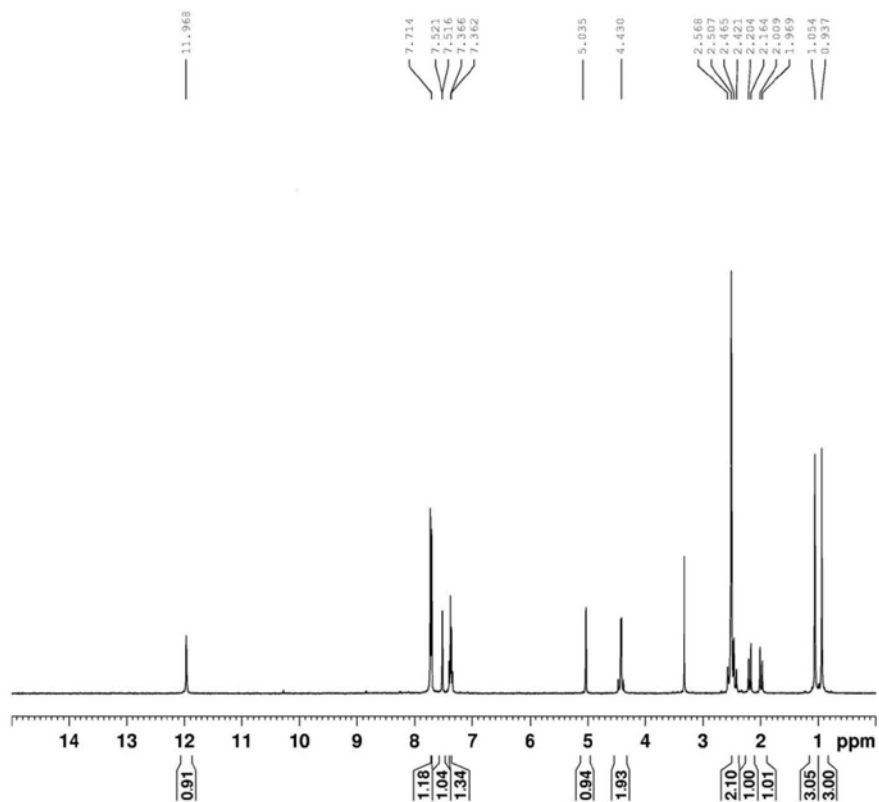


Figure S23. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **4j**.

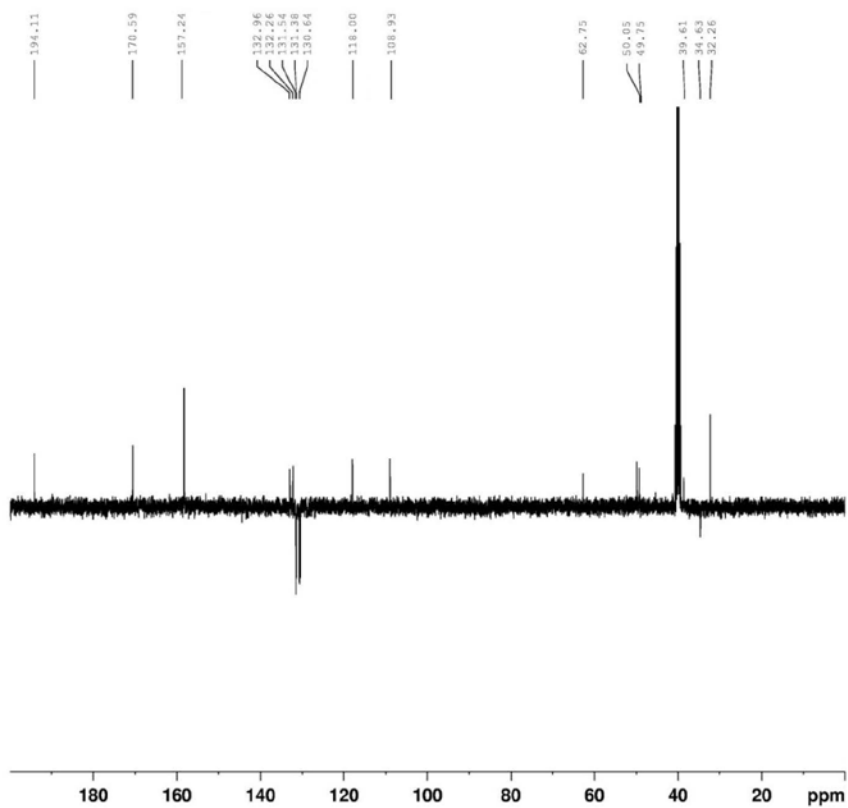


Figure S24. APT spectrum (100 MHz, DMSO-*d*₆) of **4j**.

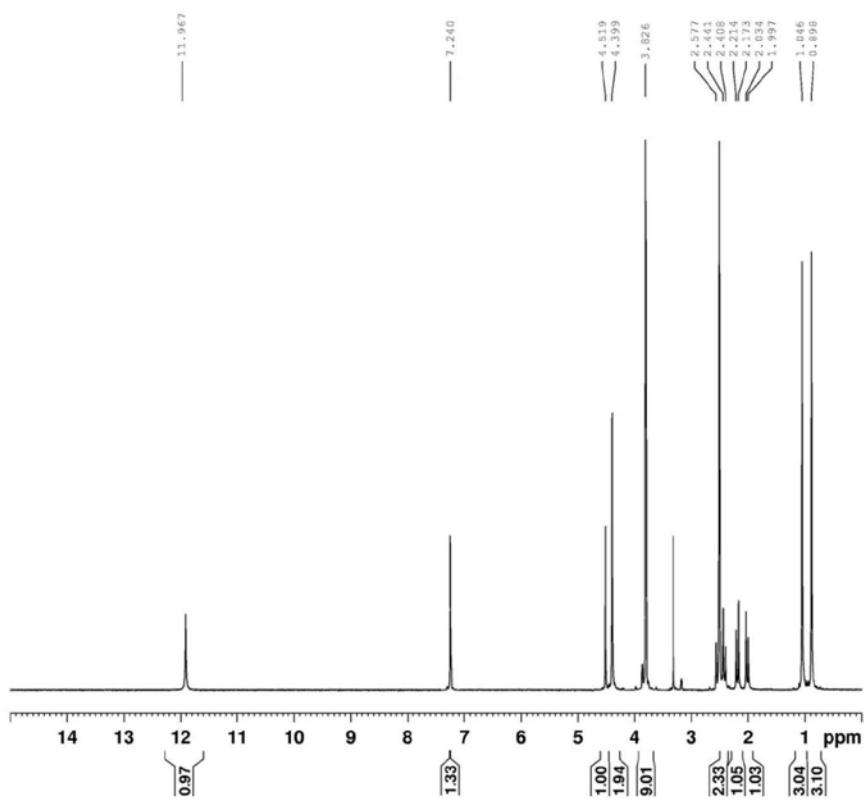


Figure S25. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of **4k**.

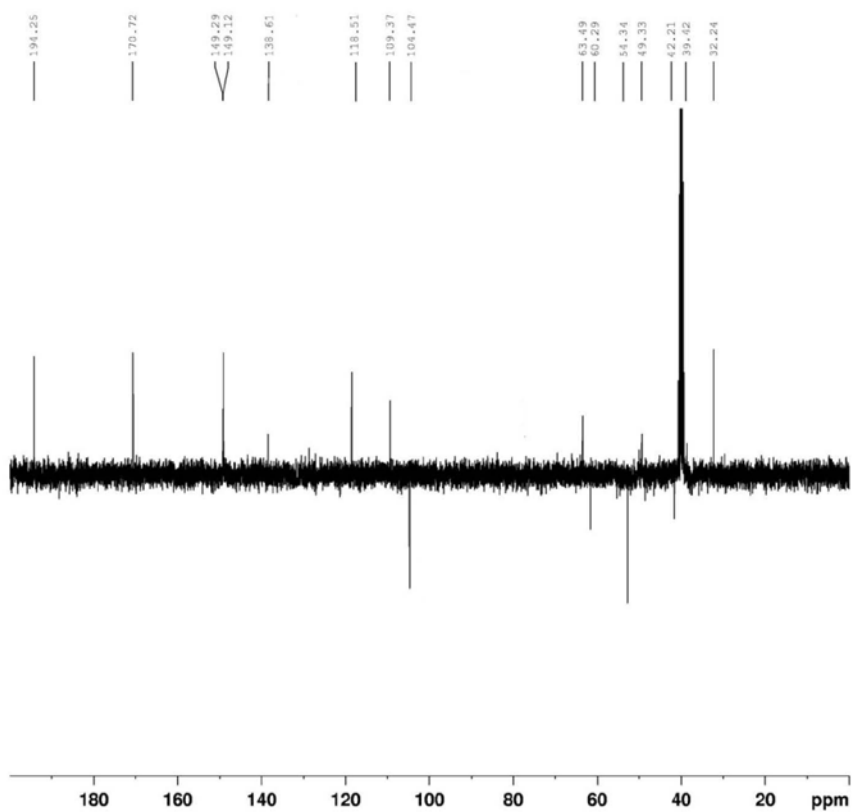


Figure S26. APT spectrum (100 MHz, DMSO-*d*₆) of **4k**.

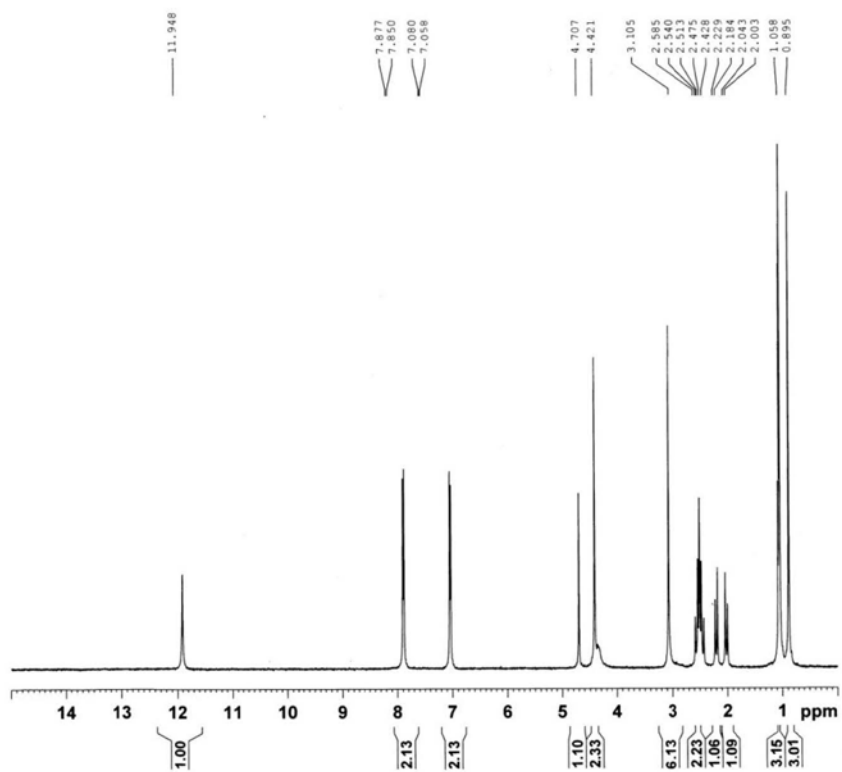


Figure S27. ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of 41.

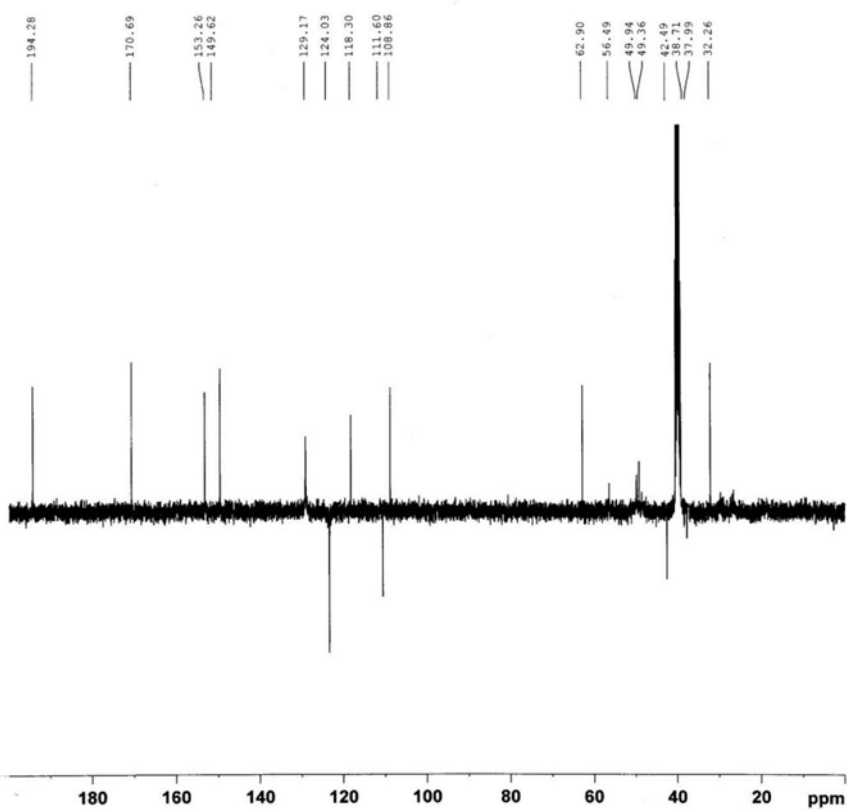


Figure S28. APT spectrum (100 MHz, DMSO-*d*₆) of 41.