Quadrol-Pd(II) complexes: phosphine-free precatalysts for the room-temperature Suzuki-Miyaura synthesis of nucleoside analogues in aqueous media

José Luis Serrano,[a,] Sujeet Gaware[b], Jose Antonio Pérez,[a] José Pérez,[a] Pedro Lozano[c], Santosh Kori,[b,d] Rambabu Dandela[b], Yogesh S. Sanghvi[e], Anant R. Kapdi[d,] **

[a] Departamento de Ingeniería Química y Ambiental. Área de Química Inorgánica, Universidad Politécnica de Cartagena member of European University of Technology, 30203 Cartagena, Spain

[b] Department of Chemistry, Institute of Chemical Technology-Indian Oil Odisha Campus, IIT Kharagpur Extension Centre, Mouza Samantpuri, Bhubaneswar 751013, Odisha, India.

[c] Departamento de Bioquímica y Biología Molecular B e Inmunología, Facultad de Química, Regional Campus of International Excellence "Campus Mare Nostrum", Universidad de Murcia, 30071 Murcia, Spain.

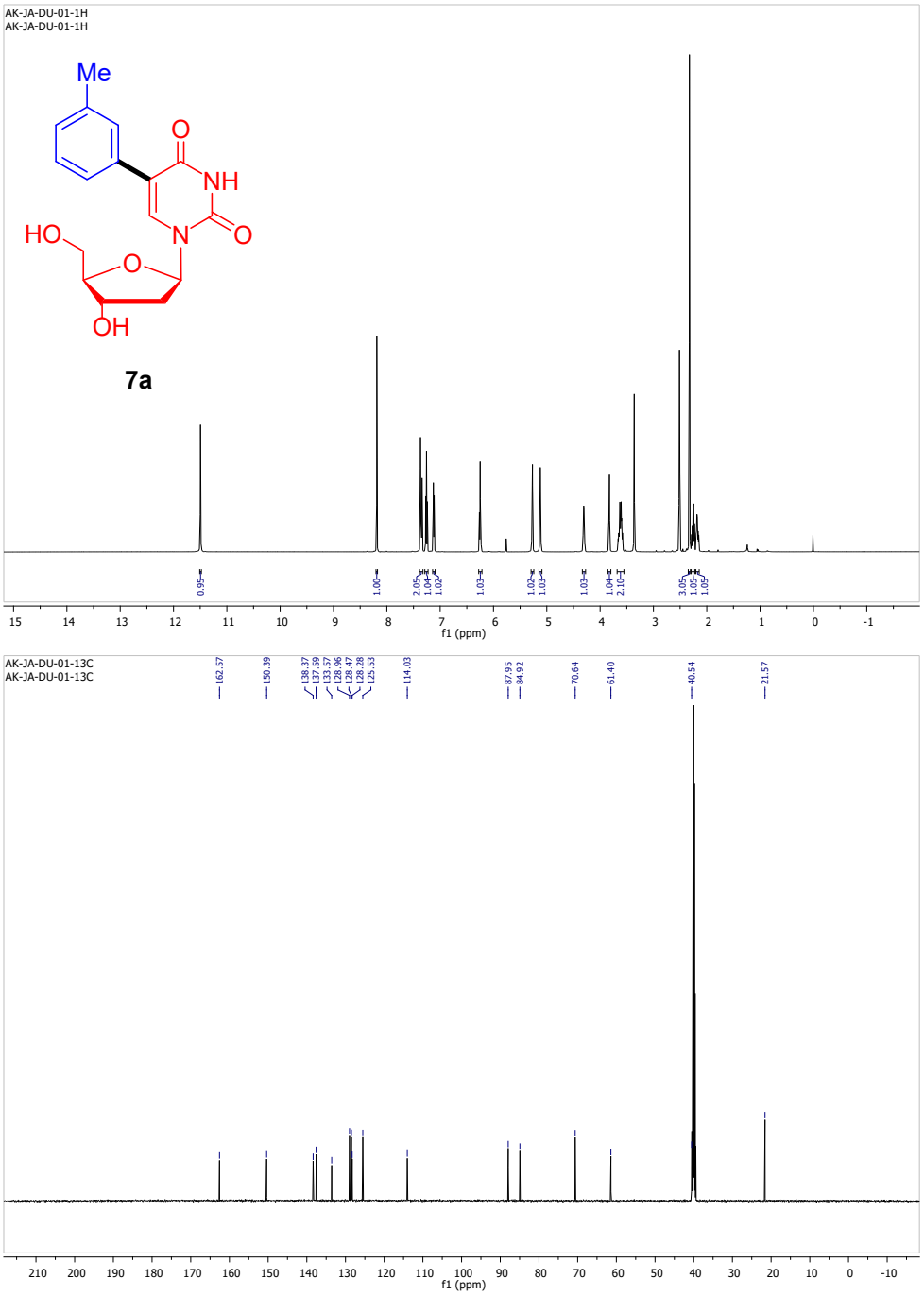
[d] Department of Chemistry, Institute of Chemical Technology, Mumbai, Nathalal Road, Matunga, Mumbai-400019, India

[e]Rasayan Inc. 2802, Crystal Ridge Road, Encinitas, California, 92024-6615, United States of America)

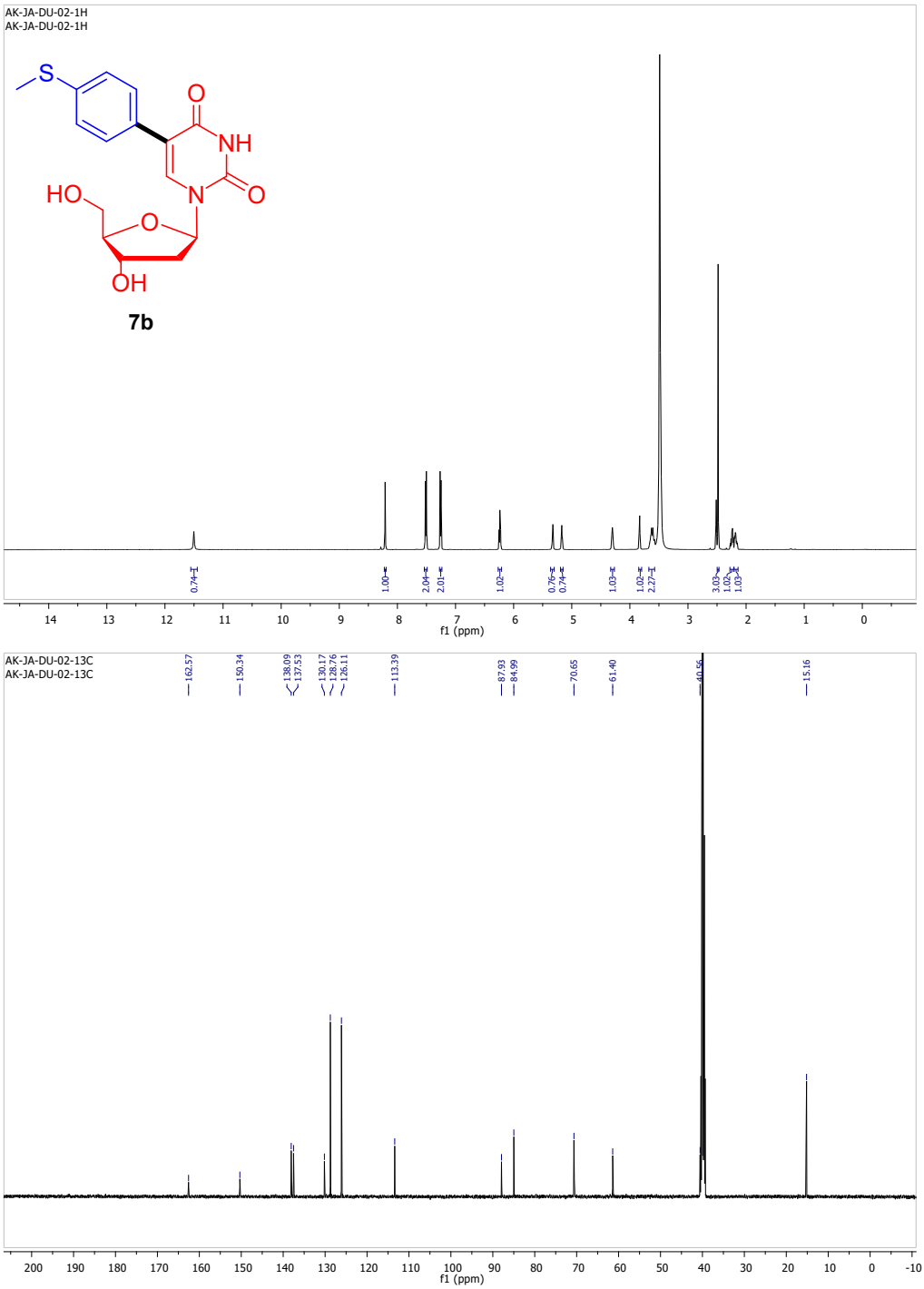
Supporting Information.

Data related to nucleoside: NMR and Spectra

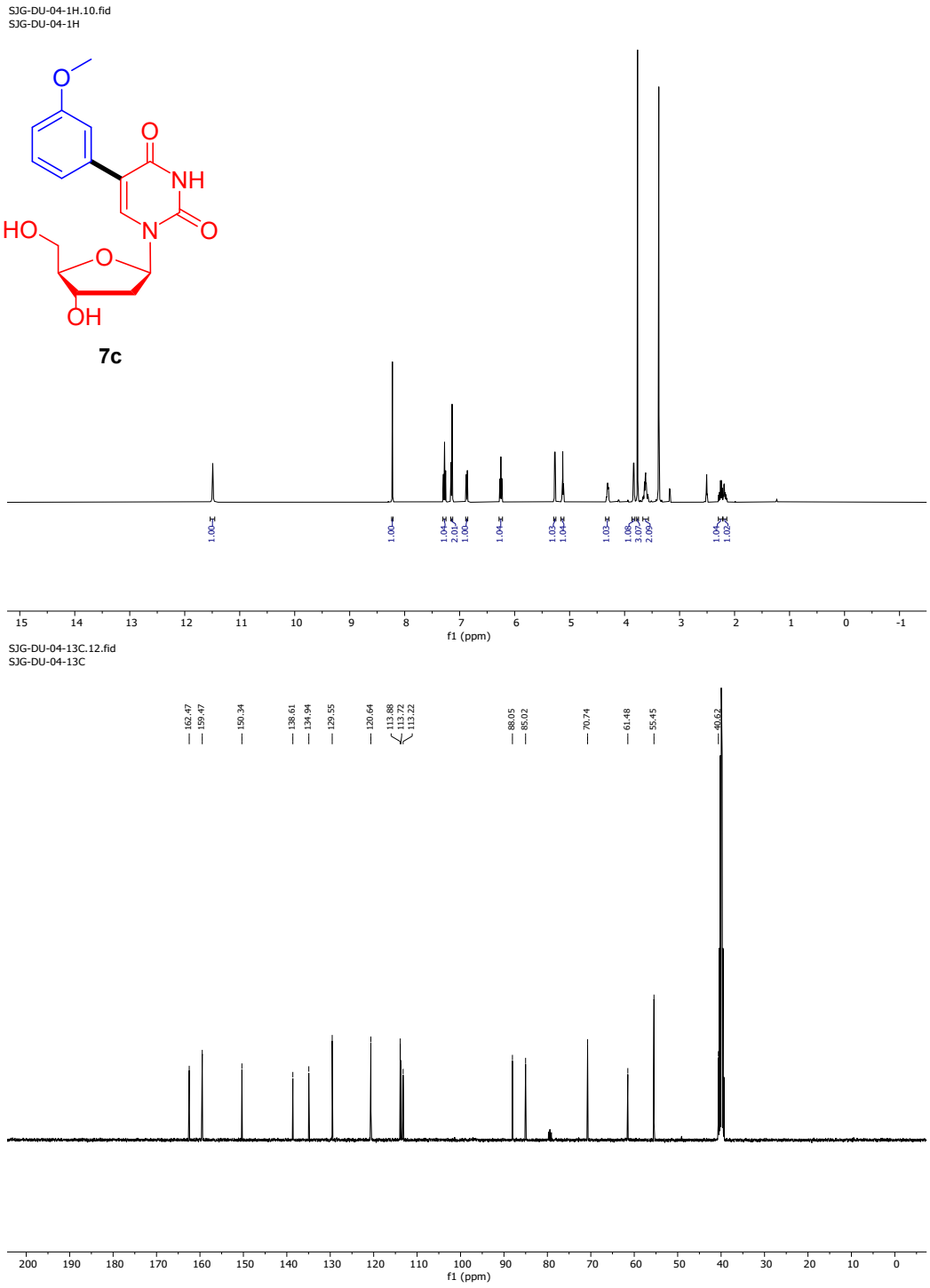
1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(m-tolyl)pyrimidine-2,4(1H,3H)-dione (7a) (133mg 84%). **^{1}H NMR** (500 MHz, DMSO) δ 11.49 (s, 1H), 8.19 (s, 1H), 7.39 – 7.32 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.25 (t, *J* = 6.6 Hz, 1H), 5.27 (d, *J* = 4.2 Hz, 1H), 5.12 (t, *J* = 4.8 Hz, 1H), 4.31 (dd, *J* = 5.3, 3.6 Hz, 1H), 3.83 (q, *J* = 2.9 Hz, 1H), 3.68 – 3.55 (m, 2H), 2.33 (s, 3H), 2.26 (dt, *J* = 13.1, 6.5 Hz, 1H), 2.17 (ddd, *J* = 13.3, 6.2, 3.7 Hz, 1H). **^{13}C NMR{^{1}H}** (126 MHz, DMSO) δ 162.5, 150.3, 138.3, 137.5, 133.5, 128.9, 128.4, 128.2, 125.5, 114.0, 87.9, 84.9, 70.6, 61.4, 40.5, 21.5. **Anal calcd**. for $C_{16}H_{18}N_2O_5$: C, 60.37; H, 5.70; N, 8.80. Found C,60.36: H, 5.80; N,8.70.



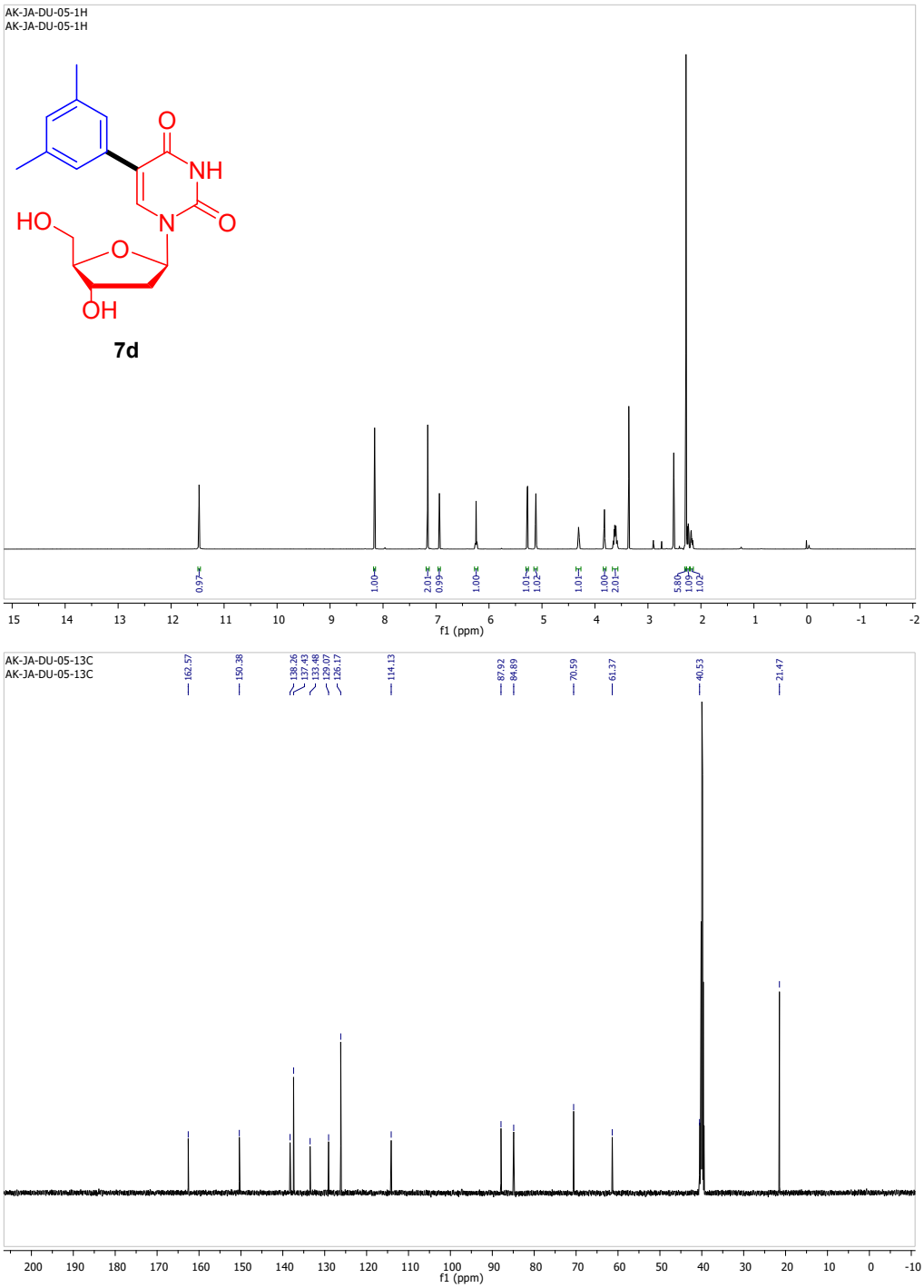
1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(4 (methylthio)phenyl)pyrimidine-2,4(1H,3H)-dione (7b) (0.126 g, 72%) :- **^{1}H NMR** (500 MHz, DMSO) δ 11.50 (s, 1H), 8.21 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.24 (t, *J* = 6.6 Hz, 1H), 5.33 (d, *J* = 4.0 Hz, 1H), 5.17 (t, *J* = 4.5 Hz, 1H), 4.30 (s, 1H), 3.83 (d, *J* = 2.9 Hz, 1H), 3.65 – 3.57 (m, 2H), 2.48 (s, 3H), 2.25 (dt, *J* = 13.0, 6.4 Hz, 1H), 2.17 (ddd, *J* = 13.3, 6.0, 3.8 Hz, 1H). **^{13}C NMR{^{1}H}** (126 MHz, DMSO) δ 162.5, 150.3, 138.0, 137.5, 130.1, 128.7, 126.1, 113.3, 87.9, 84.9, 70.6, 61.4, 40.5, 15.1. The spectral data were in accordance with those reported in the literature[1].



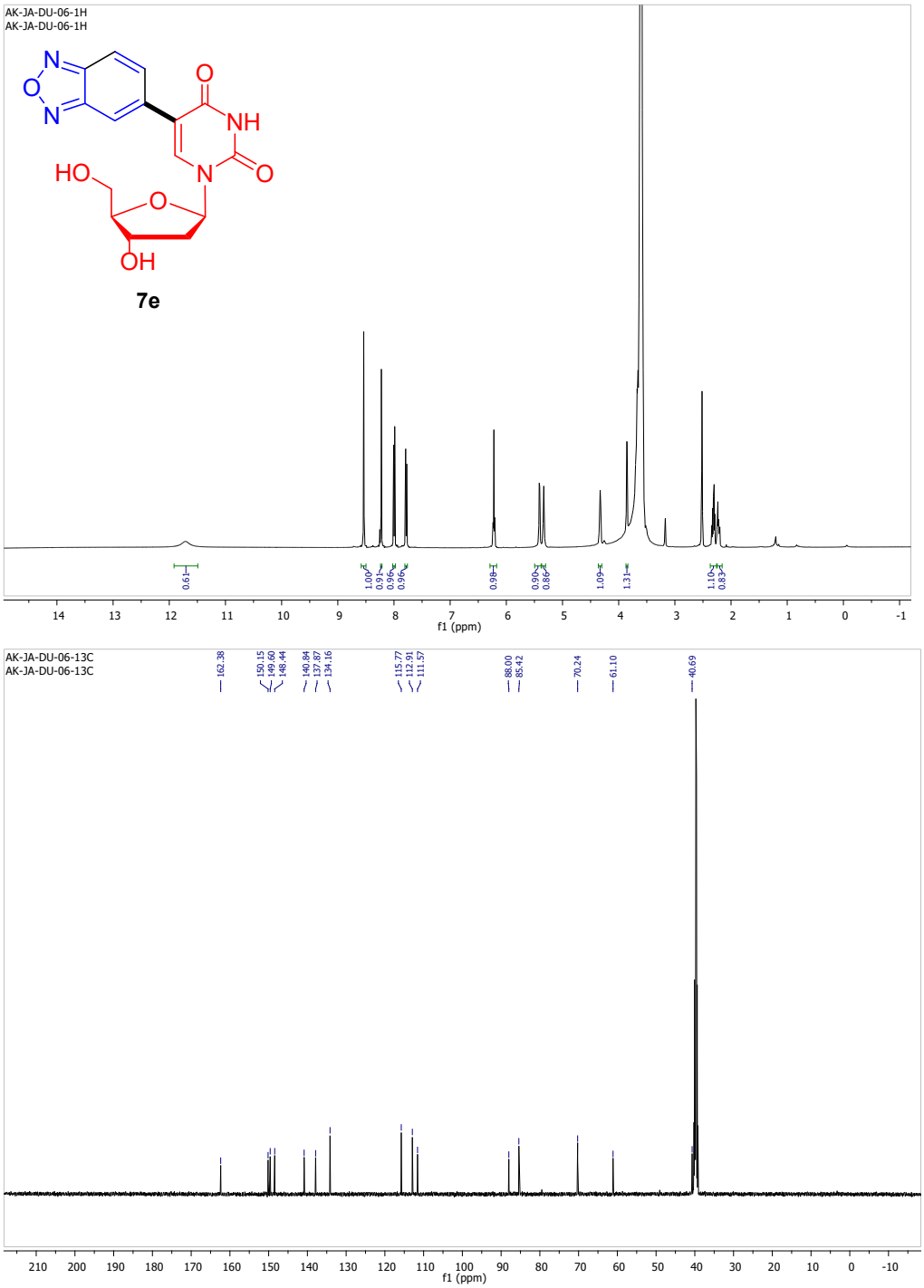
1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(3-methoxyphenyl)pyrimidine-2,4(1H,3H)-dione (7c) :- (0.125 g , 75%) **^{1}H NMR** (400 MHz, DMSO) δ 11.49 (s, 1H), 8.22 (s, 1H), 7.30 – 7.25 (m, 1H), 7.16 – 7.13 (m, 2H), 6.89 – 6.85 (m, 1H), 6.25 (t, *J* = 6.6 Hz, 1H), 5.27 (d, *J* = 4.3 Hz, 1H), 5.12 (t, *J* = 5.0 Hz, 1H), 4.31 (td, *J* = 7.3, 3.7 Hz, 1H), 3.87 – 3.81 (m, 1H), 3.76 (s, 3H), 3.67 – 3.57 (m, 2H), 2.29 – 2.22 (m, 1H), 2.18 (ddd, *J* = 13.3, 6.3, 3.7 Hz, 1H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 162.4, 159.4, 150.3, 138.6, 134.9, 129.5, 120.6, 113.8, 113.2, 88.0, 85.0, 70.7, 61.4, 55.4, 40.6. The spectral data were in accordance with those reported in the literature[2].



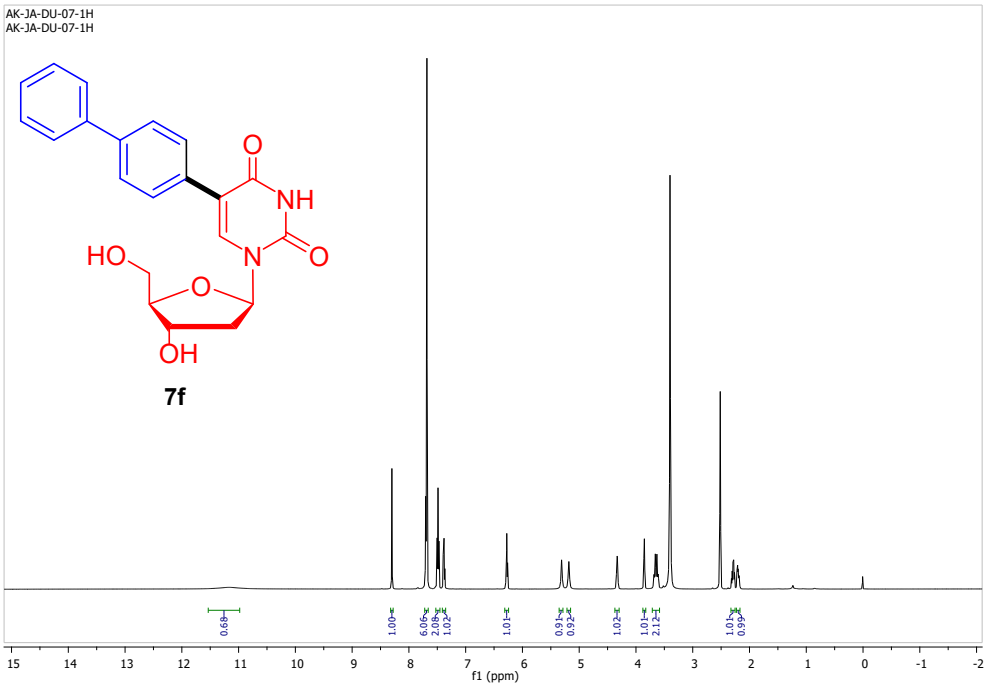
5-(3,5-dimethylphenyl)-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (7d) :- (0.116 g, 70%) **^{1}H NMR** (500 MHz, DMSO) δ 11.47 (s, 1H), 8.16 (s, 1H), 7.16 (s, 2H), 6.94 (s, 1H), 6.24 (t, *J* = 6.6 Hz, 1H), 5.27 (d, *J* = 4.3 Hz, 1H), 5.11 (t, *J* = 4.9 Hz, 1H), 4.31 (dq, *J* = 7.7, 3.8 Hz, 1H), 3.82 (q, *J* = 3.1 Hz, 1H), 3.62 (qdd, *J* = 11.8, 4.7, 3.4 Hz, 2H), 2.28 (s, 6H), 2.25 (dd, *J* = 13.4, 6.7 Hz, 1H), 2.17 (ddd, *J* = 13.3, 6.2, 3.7 Hz, 1H). **^{13}C NMR{^{1}H}** (126 MHz, DMSO) δ 162.5, 150.3, 138.2, 137.4, 133.4, 129.0, 126.1, 114.1, 87.9, 84.8, 70.59, 61.3, 40.5, 21.4. The spectral data were in accordance with those reported in the literature[1].

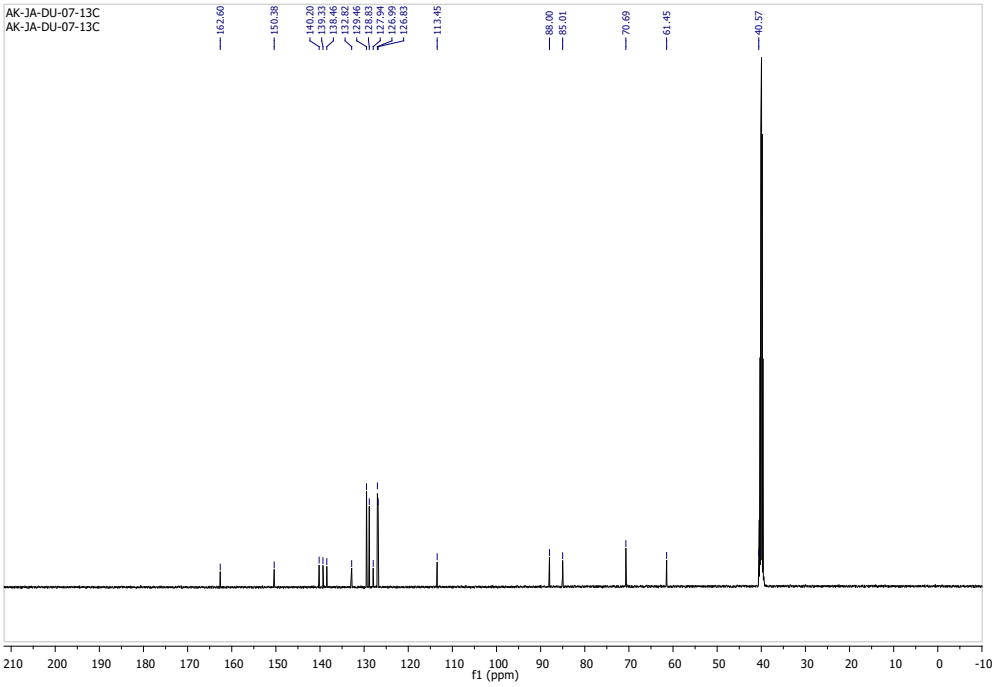


5-(benzo[c][1,2,5]oxadiazol-5-yl)-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (7e) :- (0.125 g, 72%) **^{1}H NMR** (500 MHz, DMSO) δ 11.71 (s, 1H), 8.54 (s, 1H), 8.22 (s, 1H), 8.00 (d, *J* = 9.5 Hz, 1H), 7.78 (dd, *J* = 9.5, 1.0 Hz, 1H), 6.22 (t, *J* = 6.4 Hz, 1H), 5.41 (d, *J* = 4.0 Hz, 1H), 5.33 (t, *J* = 4.4 Hz, 1H), 4.33 (s, 1H), 3.85 (dd, *J* = 6.3, 3.0 Hz, 1H), 2.37 – 2.26 (m, 1H), 2.24 – 2.16 (m, 1H). **^{13}C NMR{^{1}H}** (126 MHz, DMSO) δ 162.3, 150.1, 149.6, 148.4, 140.8, 137.8, 134.1, 115.7, 112.9, 111.5, 88.0, 85.4, 70.2, 61.1, 40.6. **Anal calcd**. For $C_{15}H_{14}N_4O_6$: C, 52.03; H, 4.08; N, 16.18; Found: C,52.05; H,4.05; N,16.33.

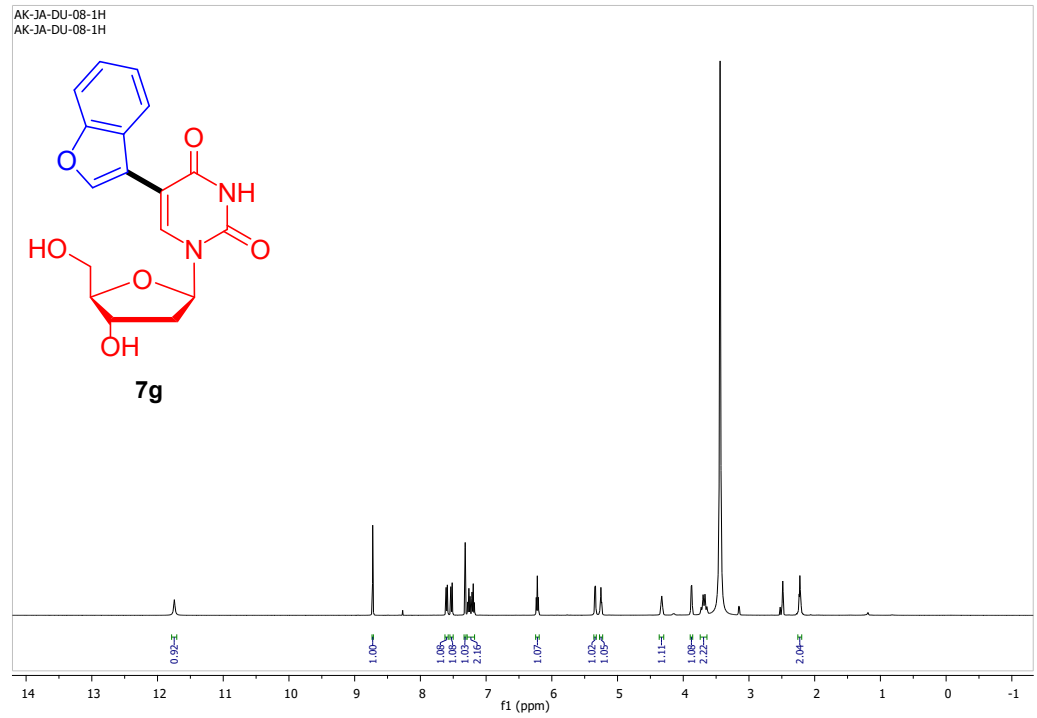


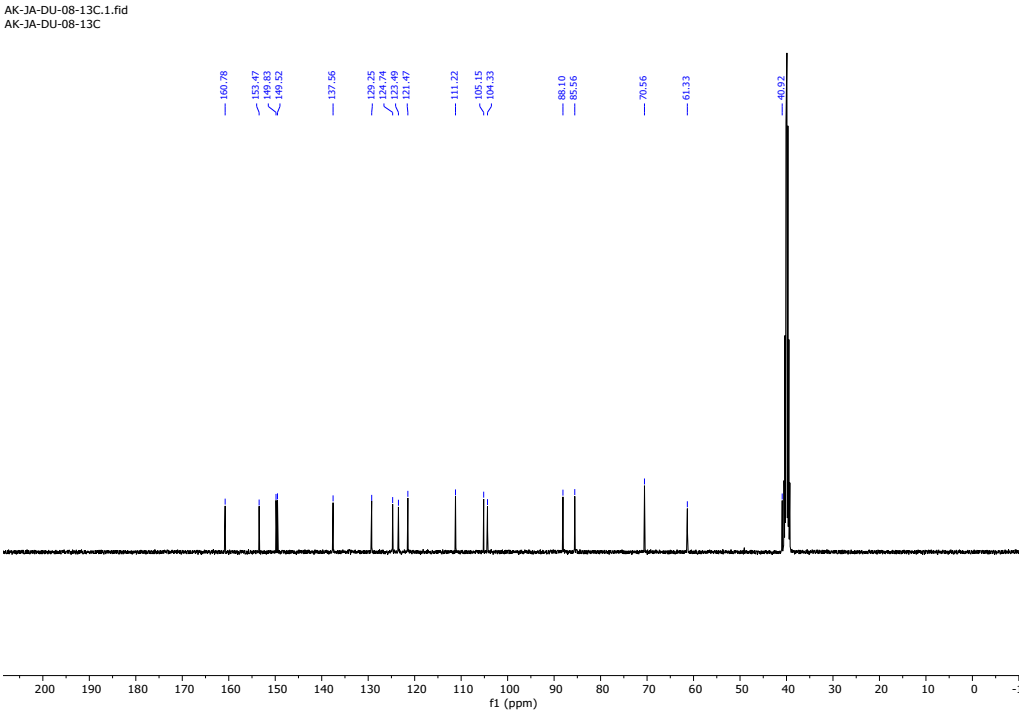
5-([1,1'-biphenyl]-4-yl)-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (7f) :- (0.118 g, 62%) **^{1}H NMR** (500 MHz, DMSO) δ 11.17 (s, 1H), 8.30 (s, 1H), 7.69 (d, *J* = 11.0 Hz, 6H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.28 (t, *J* = 6.6 Hz, 1H), 5.31 (s, 1H), 5.18 (s, 1H), 4.33 (s, 1H), 3.85 (d, *J* = 2.9 Hz, 1H), 3.65 (dd, *J* = 25.4, 11.6 Hz, 2H), 2.29 (dt, *J* = 13.0, 6.4 Hz, 1H), 2.20 (ddd, *J* = 13.2, 6.0, 3.7 Hz, 1H). **^{13}C NMR{^{1}H}** (126 MHz, DMSO) δ 162.6, 150.3, 140.2, 139.3, 138.4, 132.8, 129.4, 128.8, 127.9, 126.9, 126.8, 113.4, 88.0, 85.0, 70.6, 61.4, 40.5. The spectral data were in accordance with those reported in the literature[1].



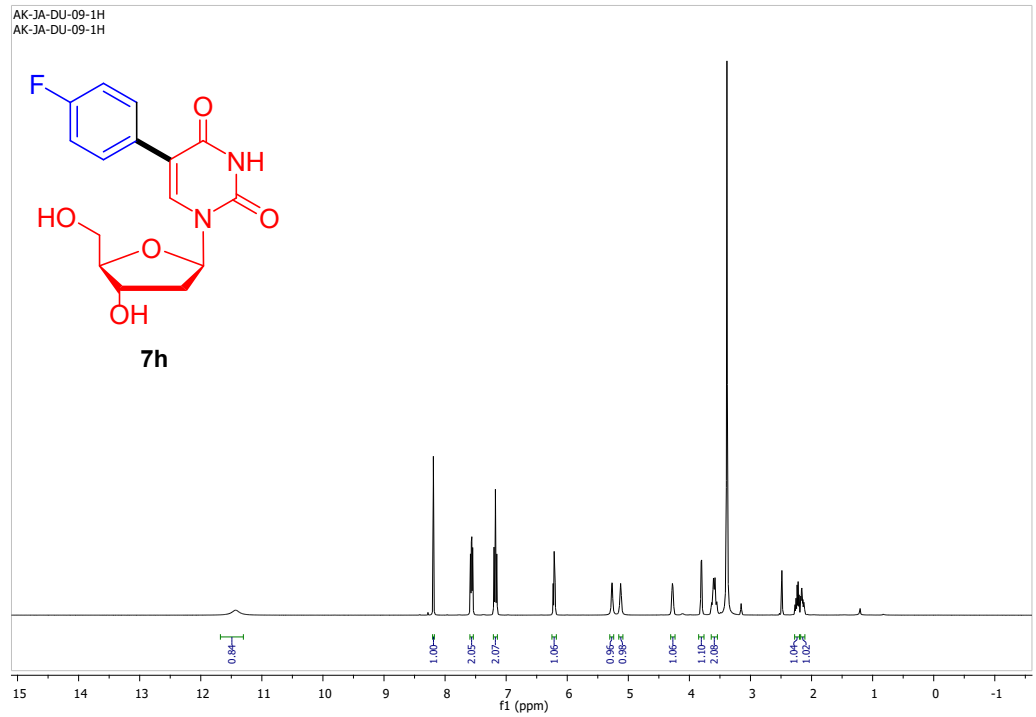


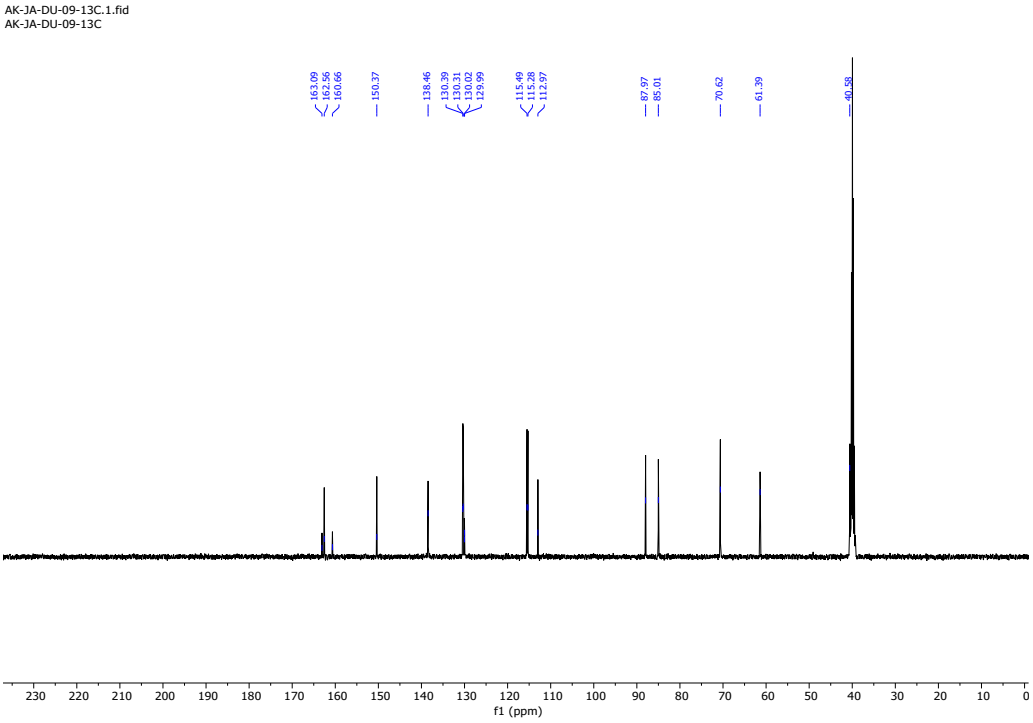
5-(benzofuran-3-yl)-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (7g) :- (0.117 g, 68%) **^{1}H NMR** (400 MHz, DMSO) δ 11.74 (s, 1H), 8.73 (s, 1H), 7.60 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.32 (s, 1H), 7.24 (ddd, *J* = 25.1, 11.2, 4.0 Hz, 2H), 6.22 (t, *J* = 6.4 Hz, 1H), 5.34 (d, *J* = 4.2 Hz, 1H), 5.25 (t, *J* = 4.2 Hz, 1H), 4.37 – 4.30 (m, 1H), 3.87 (q, *J* = 3.0 Hz, 1H), 3.74 – 3.64 (m, 2H), 2.23 (dd, *J* = 8.4, 4.2 Hz, 2H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 160.7, 153.4, 149.8, 149.5, 137.5, 129.2, 124.7, 123.4, 121.4, 111.2, 105.1, 104.3, 88.1, 85.5, 70.5, 61.3, 40.9. **Anal Calcd**. For $C_{16}H_{16}N_2O_6$ C, 59.30; H, 4.68; N, 8.14. Found C, 59.31; H, 4.54; N,8.20



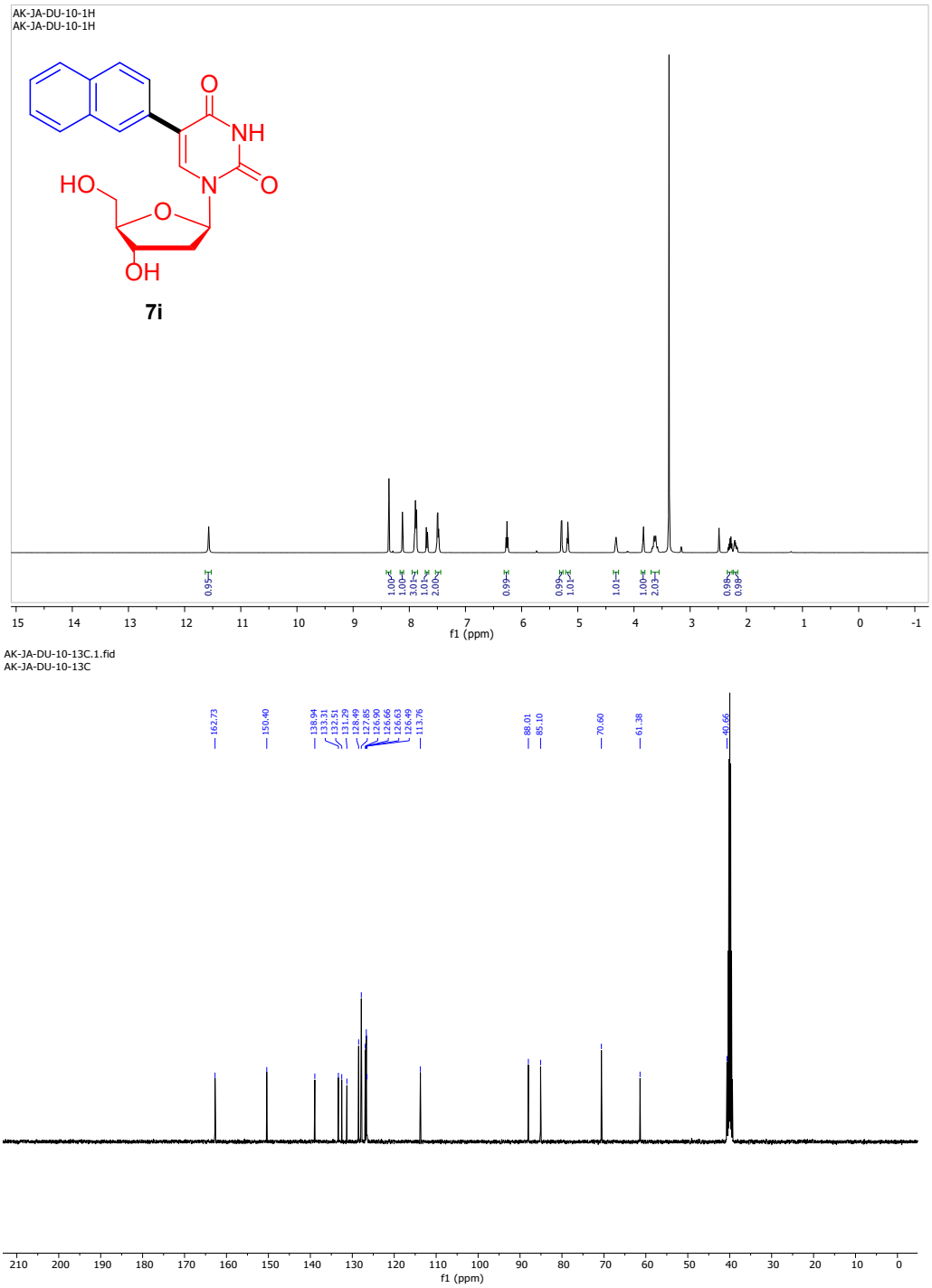


5-(4-fluorophenyl)-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidine-2,4(1H,3H)-dione (7h) :- (0.077 g, 48%) **^{1}H NMR** (400 MHz, DMSO) δ 11.43 (s, 1H), 8.19 (s, 1H), 7.59 – 7.54 (m, 2H), 7.21 – 7.14 (m, 2H), 6.21 (t, *J* = 6.6 Hz, 1H), 5.27 (d, *J* = 2.7 Hz, 1H), 5.13 (s, 1H), 4.28 (s, 1H), 3.80 (q, *J* = 2.9 Hz, 1H), 3.64 – 3.54 (m, 2H), 2.24 (dt, *J* = 13.0, 6.4 Hz, 1H), 2.15 (ddd, *J* = 13.3, 6.2, 3.8 Hz, 1H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO), 162.5, 161.8(d, J_{CF} = 245.4 Hz), 150.3, 138.4, 130.3(d, J_{CF} =8.0 Hz), 130.0 (d, J_{CF} =3.0 Hz), 115.4 (d, J_{CF} =21 Hz), 112.9, 87.9, 85.0, 70.6, 61.3, 40.5. The spectral data were in accordance with those reported in the literature[2].

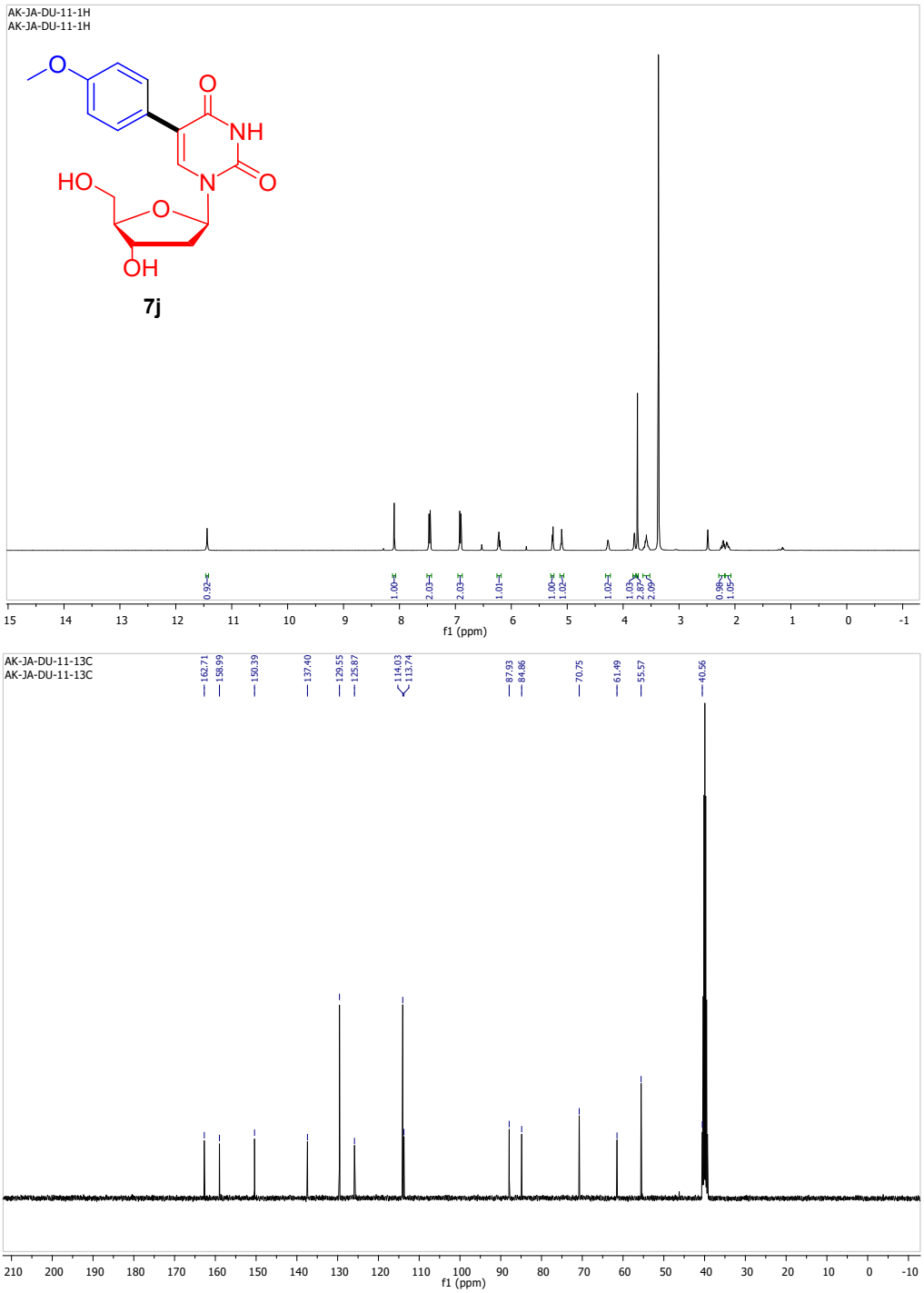




1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(naphthalen-2-yl)pyrimidine-2,4(1H,3H)-dione 7i :- (0.109 g, 62%) **^{1}H NMR** (400 MHz, DMSO) δ 11.57 (s, 1H), 8.36 (s, 1H), 8.12 (s, 1H), 7.95 – 7.85 (m, 3H), 7.68 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.53 – 7.44 (m, 2H), 6.26 (t, *J* = 6.5 Hz, 1H), 5.29 (d, *J* = 4.3 Hz, 1H), 5.18 (t, *J* = 4.7 Hz, 1H), 4.37 – 4.27 (m, 1H), 3.87 – 3.81 (m, 1H), 3.70 – 3.55 (m, 2H), 2.29 (dt, *J* = 13.0, 6.4 Hz, 1H), 2.19 (ddd, *J* = 13.3, 6.2, 3.9 Hz, 1H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 162.7, 150.4, 138.9, 133.3, 132.5, 131.2, 128.4, 127.8, 126.9, 126.6, 126.6, 126.4, 113.7, 88.0, 85.1, 70.6, 61.3, 40.6. The spectral data were in accordance with those reported in the literature[2].

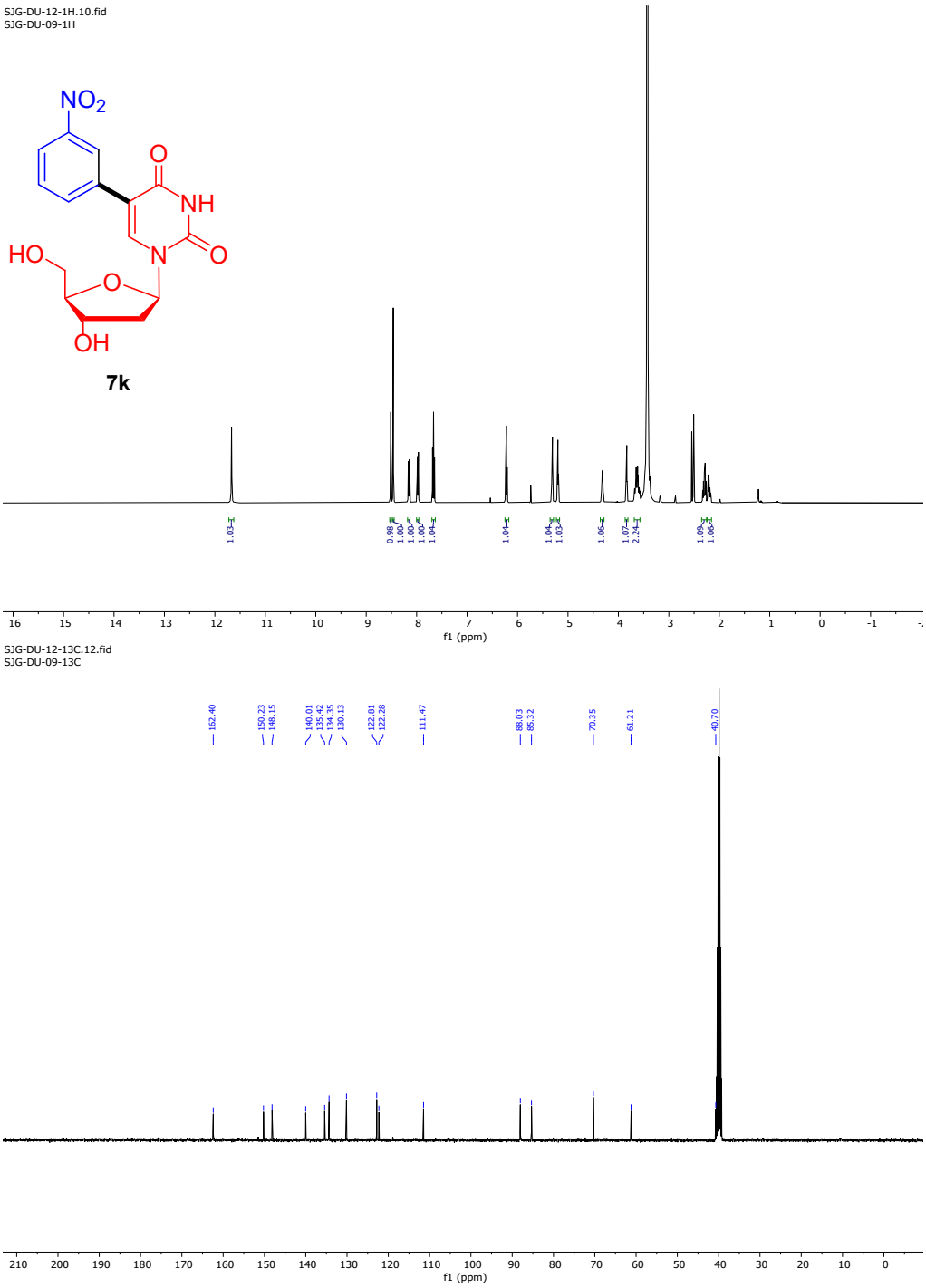


1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(4-methoxyphenyl)pyrimidine-2,4(1H,3H)-dione (7j) :- (0.127 g, 76%) **^{1}H NMR** (400 MHz, DMSO) δ 11.44 (s, 1H), 8.09 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.22 (t, *J* = 6.6 Hz, 1H), 5.26 (d, *J* = 4.2 Hz, 1H), 5.10 (t, *J* = 4.8 Hz, 1H), 4.27 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.80 (d, *J* = 3.1 Hz, 1H), 3.74 (s, 3H), 3.65 – 3.52 (m, 2H), 2.22 (dt, *J* = 13.1, 6.4 Hz, 1H), 2.13 (ddd, *J* = 13.3, 6.2, 3.6 Hz, 1H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 162.7, 158.9, 150.3, 137.4, 129.5, 125.8, 114.0, 113.7, 87.9, 84.8, 70.7, 61.4, 55.5, 40.5. The spectral data were in accordance with those reported in the literature[2].



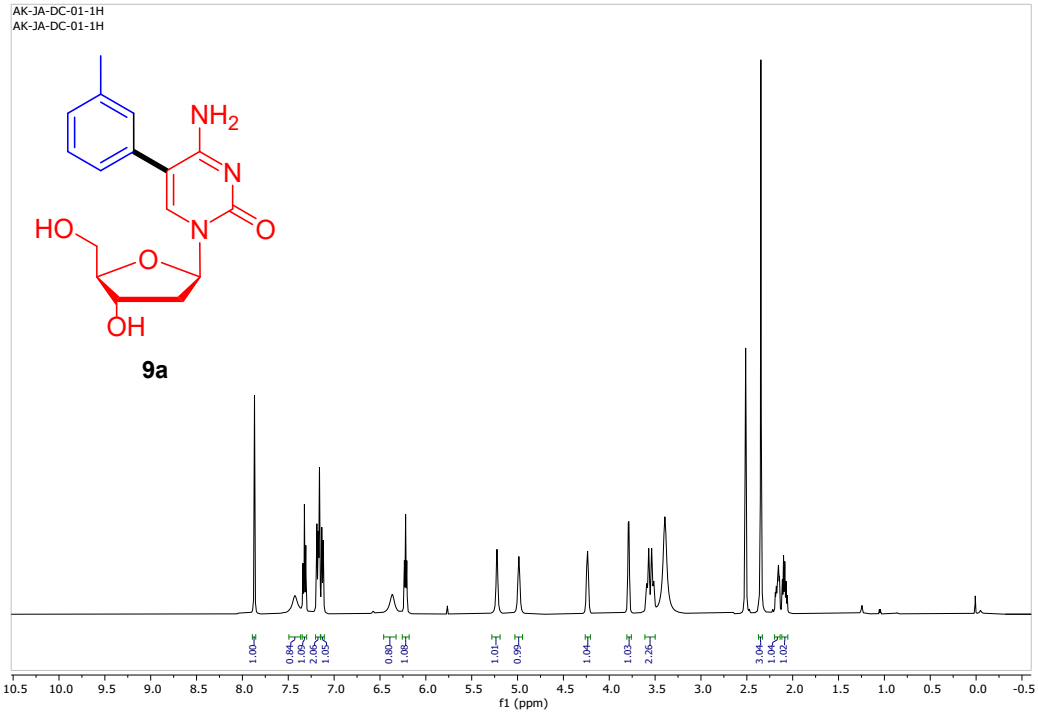
1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(3-nitrophenyl)pyrimidine-2,4(1H,3H)-dione (7k) :- (0.143 g, 82%) **^{1}H NMR** (400 MHz, DMSO) δ 11.67 (s, 1H), 8.51 (t, *J* = 2.0 Hz, 1H), 8.46 (s, 1H), 8.15 (ddd, *J* = 8.2, 2.3, 0.9 Hz, 1H), 8.00 – 7.96 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 6.22 (t, *J* = 6.4 Hz, 1H), 5.31 (d, *J* = 4.3 Hz, 1H), 5.20 (t, *J* = 4.8 Hz, 1H), 4.32 (dq, *J* = 8.0, 4.0 Hz, 1H), 3.84 (q, *J* = 3.1 Hz, 1H), 3.69 – 3.57 (m, 2H), 2.30 (dt, *J* = 12.8, 6.3 Hz, 1H), 2.20 (ddd, *J* = 13.4, 6.3, 4.1 Hz, 1H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 162.4, 150.2, 148.1, 140.0, 135.4, 134.3, 130.1, 122.8,

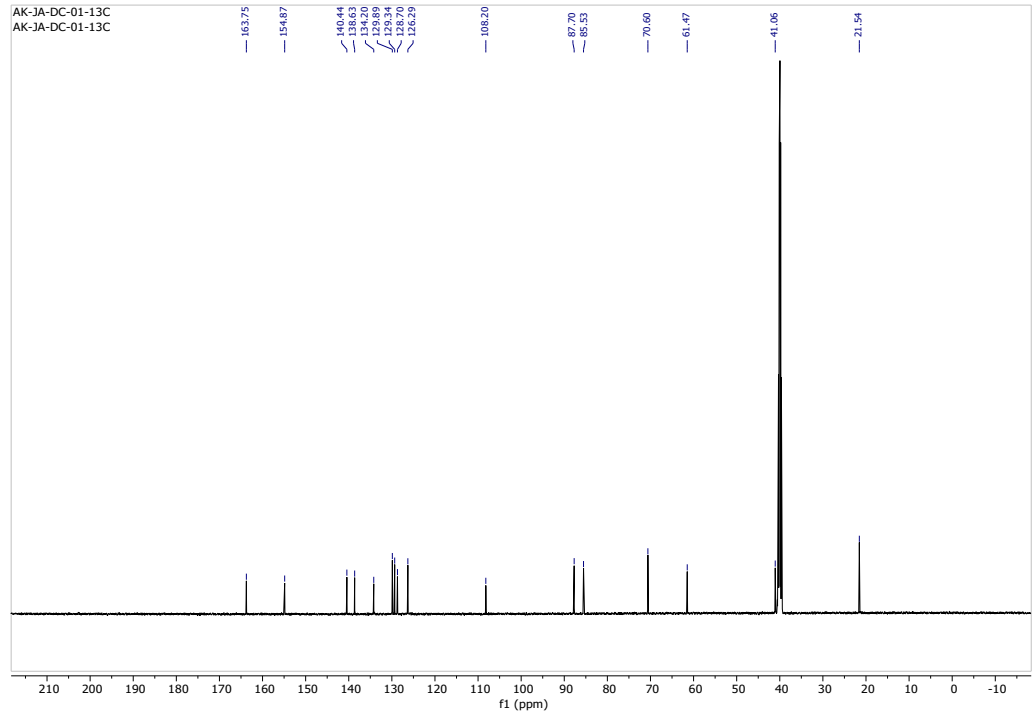
122.2, 111.4, 88.0, 85.3, 70.3, 61.2, 40.7. The spectral data were in accordance with those reported in the literature[2].



4-amino-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(m-tolyl)pyrimidin-2(1H)-one (9a) :- (0.114 g, 72%) **^{1}H NMR** (500 MHz, DMSO) δ 7.87 (s, 1H), 7.43 (s, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.37 (s, 1H), 6.22 (t, *J* = 6.5 Hz, 1H), 5.23 (s, 1H), 4.99 (s, 1H), 4.24 (s, 1H), 3.79 (d, *J* = 3.2 Hz, 1H), 3.55 (dd, *J* = 27.5, 11.6 Hz, 2H), 2.35 (s, 3H), 2.17 (ddd, *J* = 12.9, 5.8, 3.8 Hz, 1H), 2.09 (dt, *J* = 13.1, 6.5 Hz, 1H). **^{13}C NMR{^{1}H}** (126 MHz, DMSO) δ

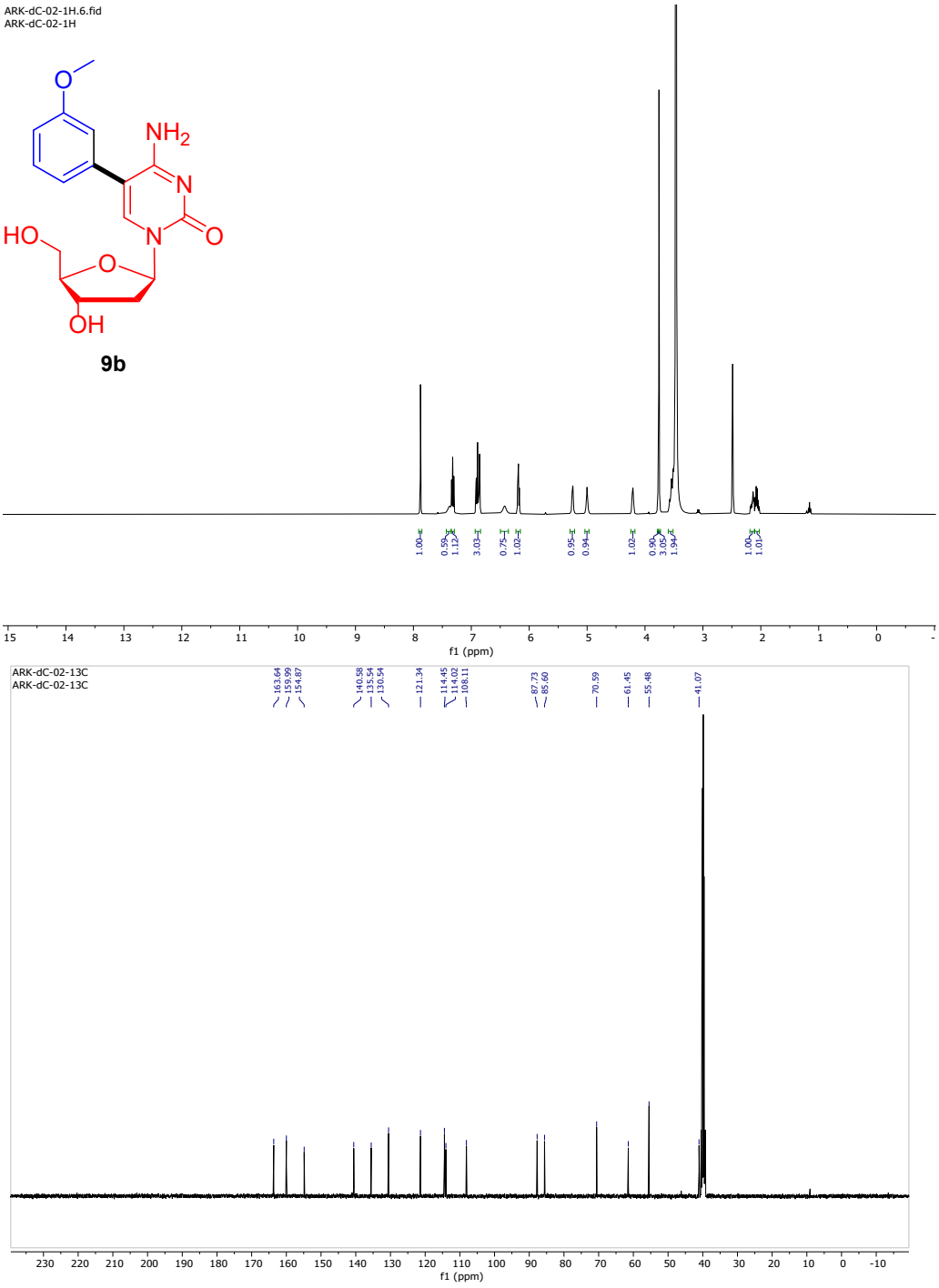
163.7, 154.8, 140.4, 138.6, 134.2, 129.8, 129.3, 128.7, 126.2, 108.2, 87.7, 85.5, 70.6, 61.4, 41.0, 21.5. **Anal Calcd**. For $C_{16}H_{19}N_3O_4$: C, 60.56; H, 6.04; N, 13.24. Found C, 60.40; H, 6.22; N, 13.37.





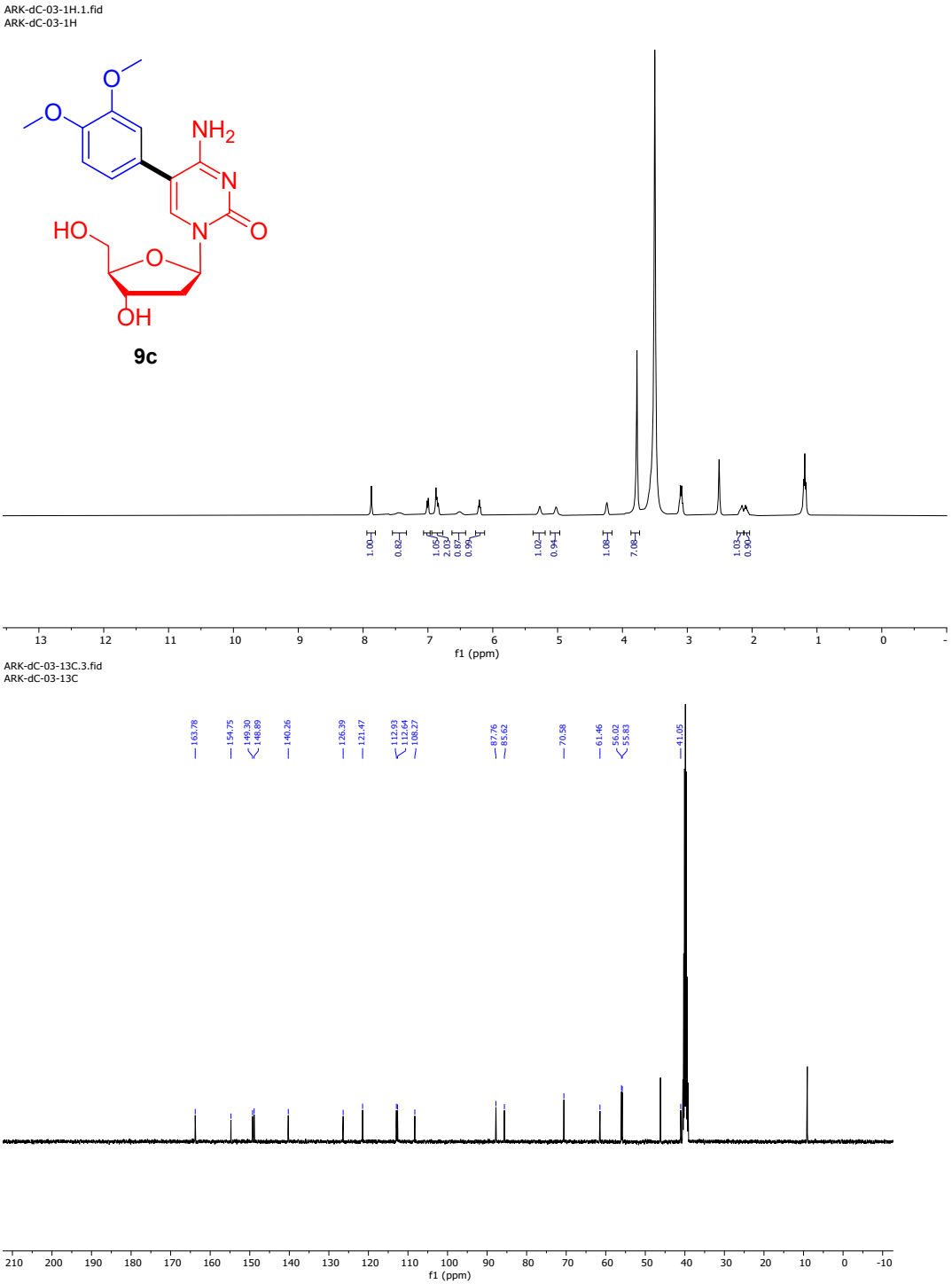
4-amino-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(3-methoxyphenyl)pyrimidin-2(1H)-one (9b) :- (0.106 g, 64%) **^{1}H NMR** (400 MHz, DMSO) δ 7.88 (d, *J* = 2.8 Hz, 392H), 7.35 (s, 1H), 7.32 (dd, *J* = 9.2, 6.5 Hz, 626H), 6.89 (tt, *J* = 3.6, 2.0 Hz, 1449H), 6.41 (s, 198H), 6.23 – 6.15 (m, 457H), 5.26 (d, *J* = 11.4 Hz, 209H), 5.04 – 4.97 (m, 294H), 4.24 – 4.17 (m, 1H),

3.79 – 3.76 (m, 1H), 3.76 (s, 2199H), 3.60 – 3.51 (m, 1H), 2.15 (ddd, *J* = 13.3, 6.0, 3.7 Hz, 761H), 2.10 – 2.02 (m, 1277H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 163.6, 159.9, 154.8, 140.5, 135.5, 130.5, 121.3, 114.4, 114.0, 108.1, 87.7, 85.6, 70.5, 61.4, 55.4, 41.0. The spectral data were in accordance with those reported in the literature[1].



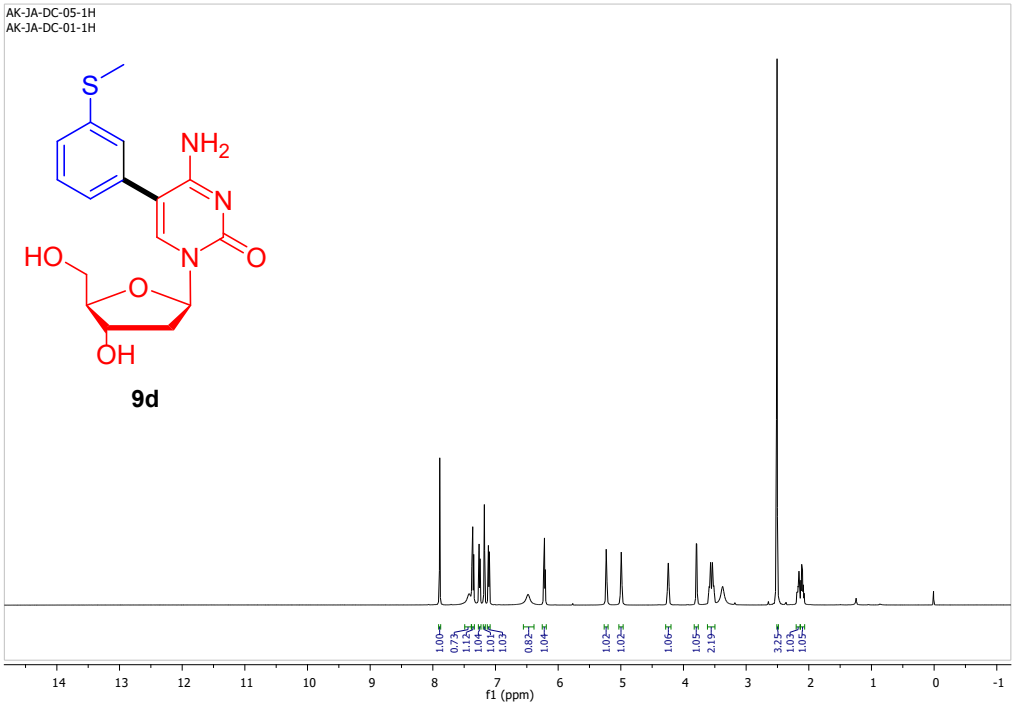
4-amino-5-(3,4-dimethoxyphenyl)-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)pyrimidin-2(1H)-one (9c) :- (0.119 g, 66%) **^{1}H NMR** (400 MHz, DMSO) δ 7.87 (s, 1H), 7.45 (s, 1H), 7.00 (d, J = 8.1 Hz, 1H), 6.94 – 6.77 (m, 2H), 6.51 (s, 1H), 6.21 (t, J = 6.2 Hz, 1H), 5.27 (s, 1H), 5.02 (s,

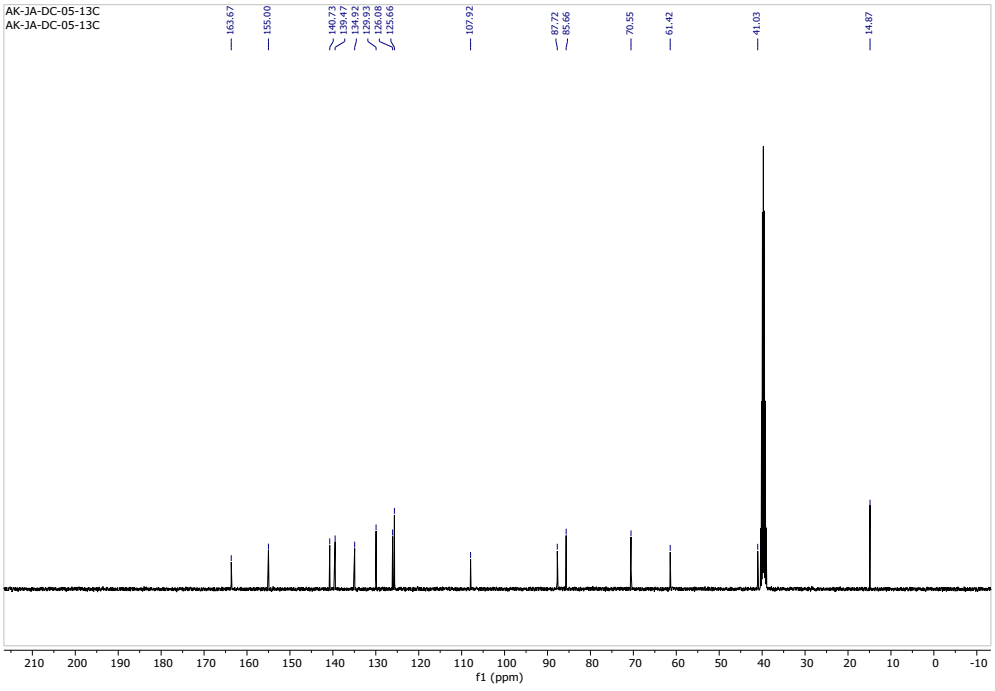
1H), 4.24 (s, 1H), 3.78 (s, 7H), 2.23 – 2.13 (m, 1H), 2.09 (dt, J = 12.8, 6.3 Hz, 1H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 41.0, 55.8, 56.0, 61.4, 70.5, 85.6, 87.7, 108.2, 112.6, 112.9, 121.4, 126.3, 140.2, 148.8, 149.3, 154.7, 163.7. **Anal calcd**. For $C_{17}H_{21}N_3O_6$: C, 56.19; H, 5.83; N, 11.56; found C, 56.33; H, 5.83; N, 11.45.



4-amino-1-((2R,4S,5R)-4-hydroxy-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-(3-(methylthio)phenyl)pyrimidin-2(1H)-one (9d) :- (0.155 g, 66%) **^{1}H NMR** (500 MHz, DMSO) δ 7.89

(s, 1H), 7.40 (d, *J* = 17.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.48 (s, 1H), 6.22 (t, *J* = 6.5 Hz, 1H), 5.23 (d, *J* = 3.8 Hz, 1H), 4.99 (t, *J* = 4.7 Hz, 1H), 4.24 (s, 1H), 3.79 (d, *J* = 3.2 Hz, 1H), 3.55 (dt, *J* = 11.7, 7.9 Hz, 2H), 2.51 (s, 3H), 2.17 (ddd, *J* = 12.8, 5.8, 3.8 Hz, 1H), 2.10 (dt, *J* = 13.1, 6.5 Hz, 1H). **^{13}C NMR{^{1}H}** (101 MHz, DMSO) δ 163.6, 155.0, 140.7, 139.4, 134.9, 129.9, 126.0, 125.6, 107.9, 87.7, 85.6, 70.5, 61.4, 41.0, 14.8. **Anal Calcd**. For $C_{15}H_{17}N_3O_4S$: C, 55.00; H, 5.48; N, 12.03; S, 9.18 Found C, 55.15; H, 5.19; N, 12.13; S, 9.21.

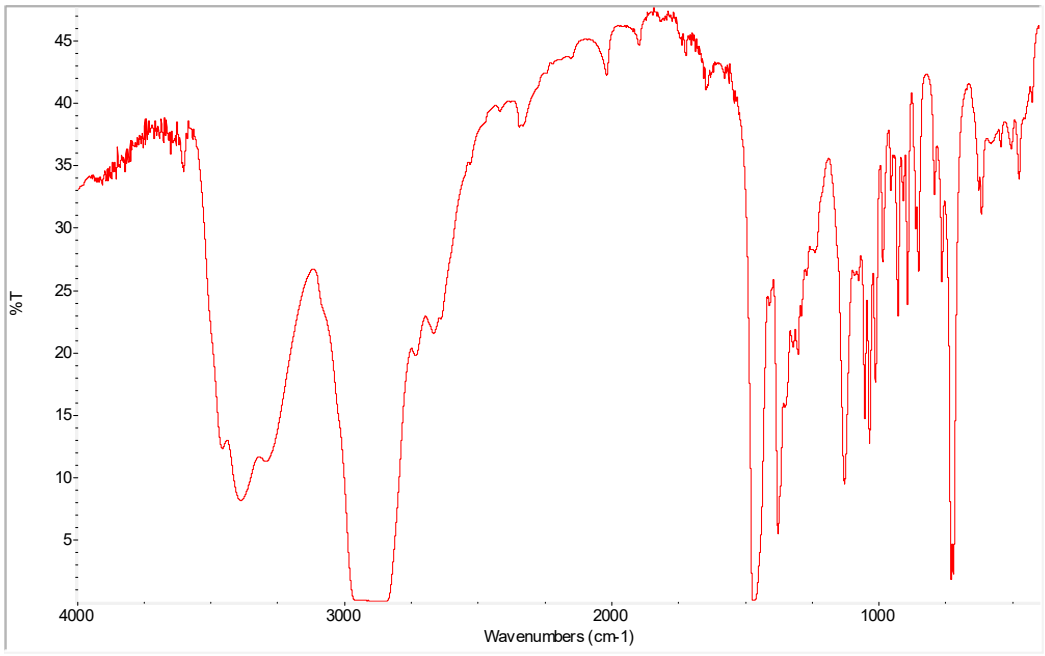




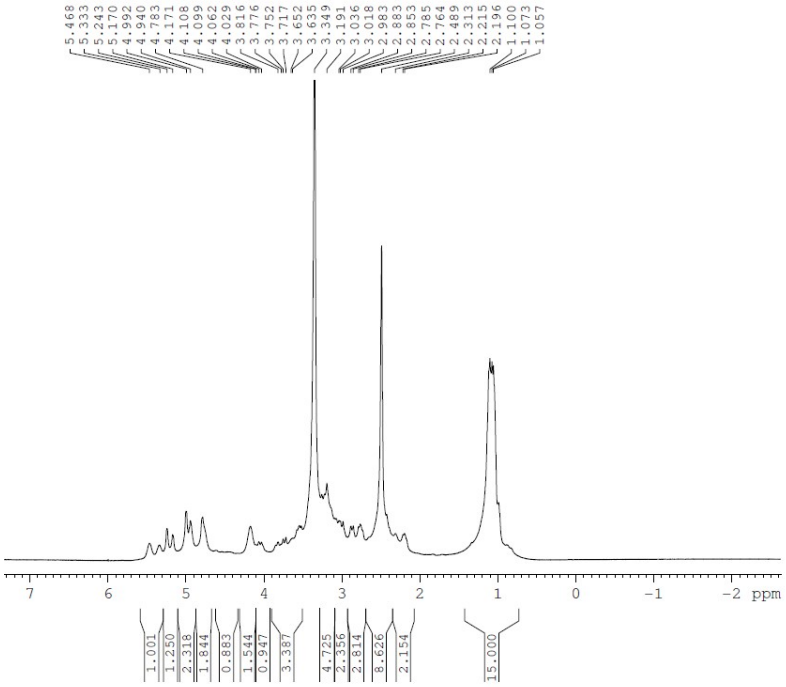
references

1) V. Gayakhe, A. V. Ardhapure, A. R. Kapdi, Y. S. Sanghvi, J. L. Serrano, *J. Org. Chem.,* 2016, **81**, 2713–2729.
2) A. R. Kapdi, V. Gayakhe, Y. S. Sanghvi, J. García, P. Lozano, I. da Silva, J. Pérez, J. L. Serrano, *RSC Adv.,* 2014, **4**, 17567–17572

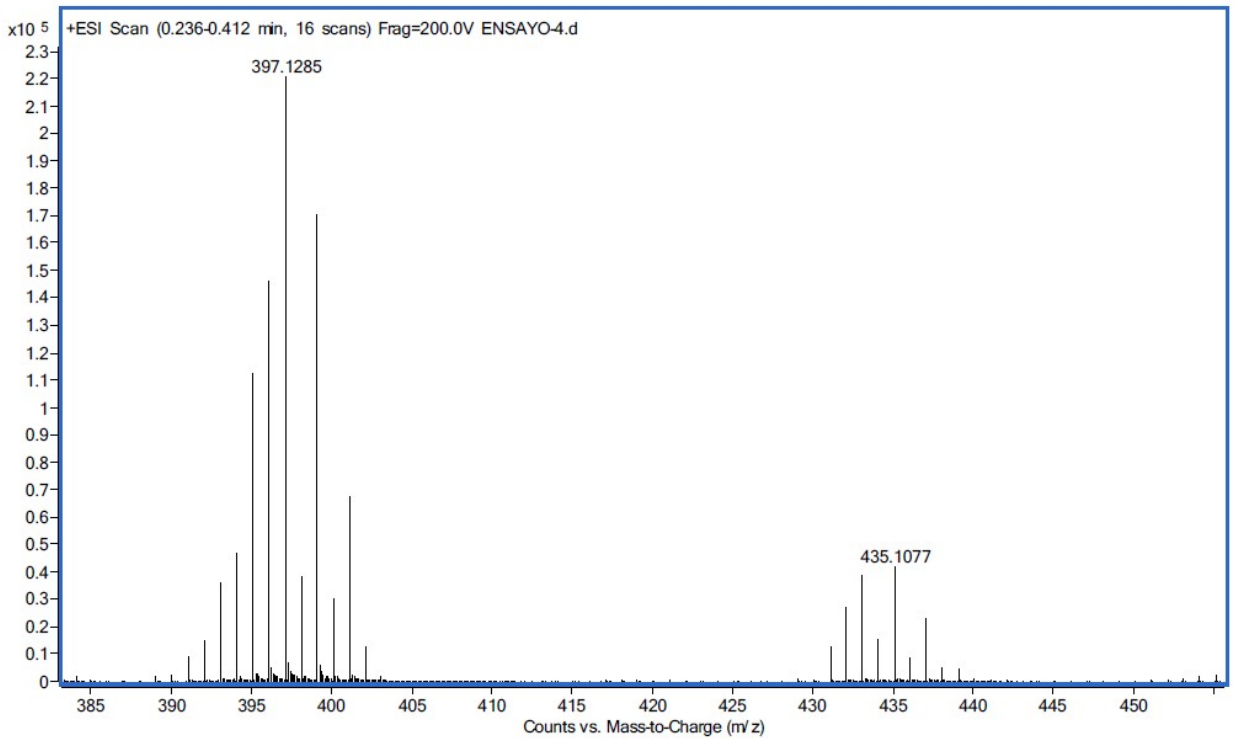
Experimental characterization of [$PdCl_2$(THPEN)] (1).



IR of [$PdCl_2$(THPEN)] (**1**).

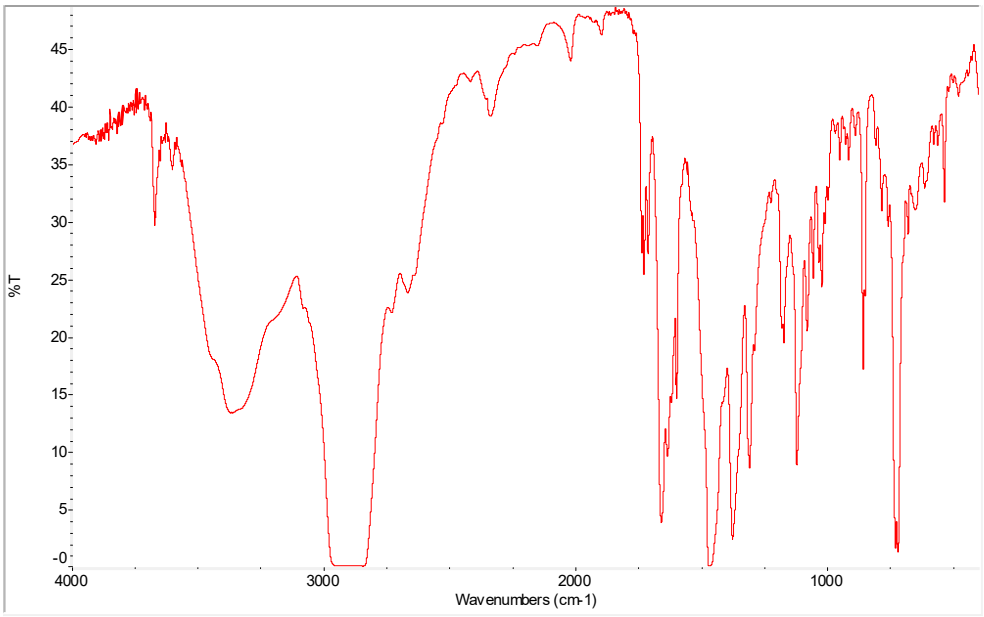


RMN-^{1}H in dmso-d_6 of [$PdCl_2$(THPEN)] (**1**).

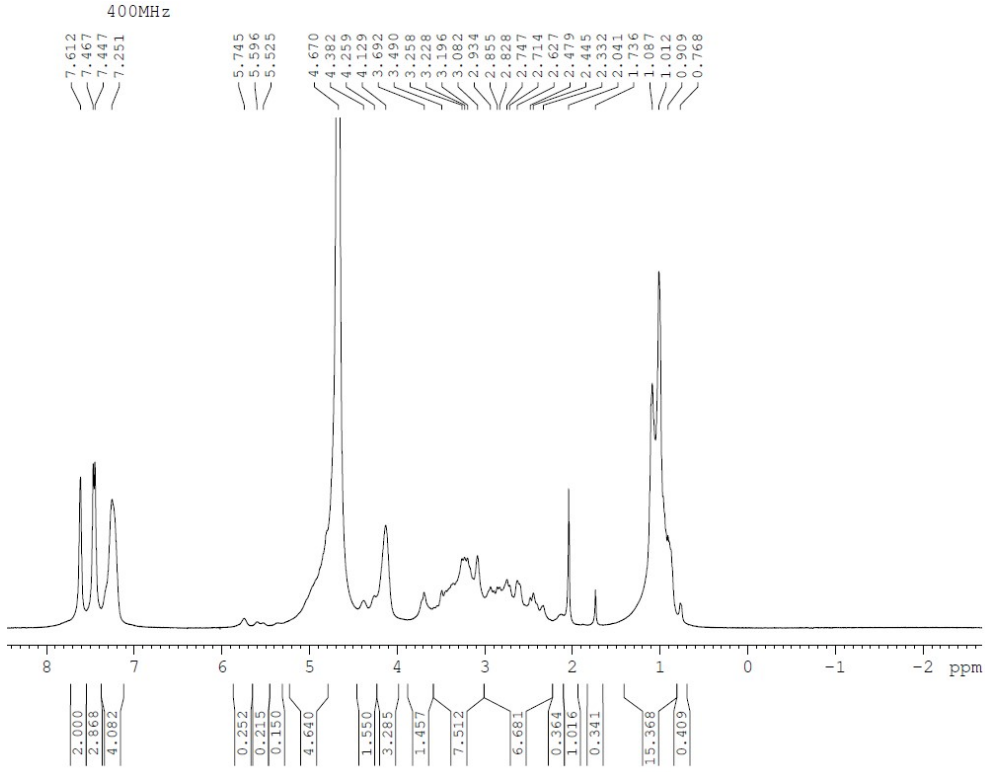


ESI-MS of $[PdCl_2(THPEN)]$ (**1**).

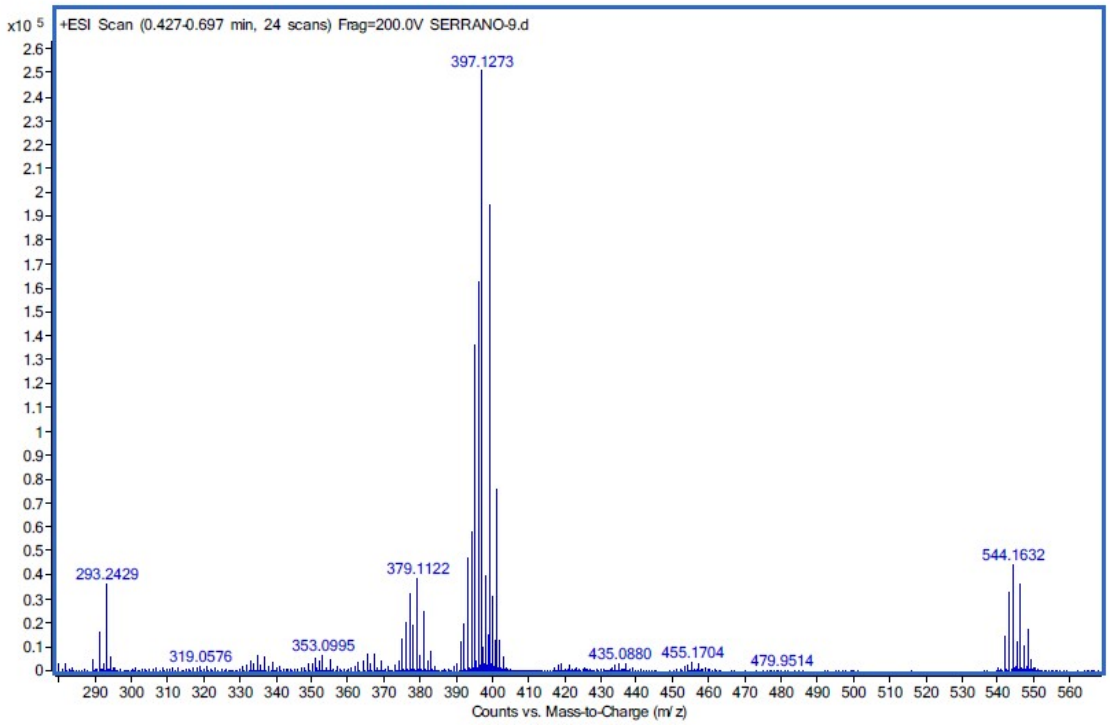
Experimental characterization of [Pd(phthal)$_2$(THPEN)] (2).



IR of [Pd(phthal)$_2$(THPEN)] (**2**).

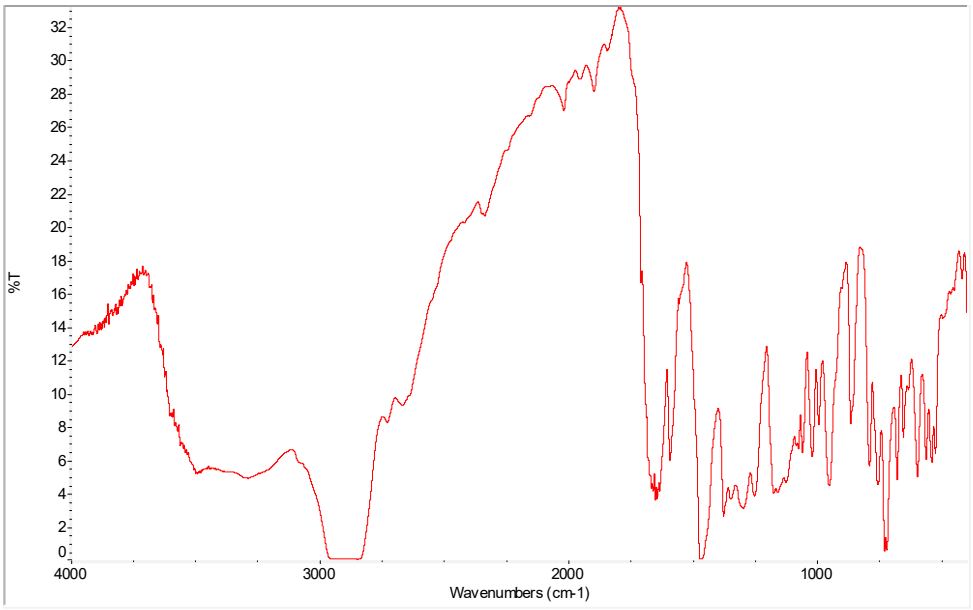


RMN-^{1}H in D_2O of [Pd(phthal)$_2$(THPEN)] (**2**).

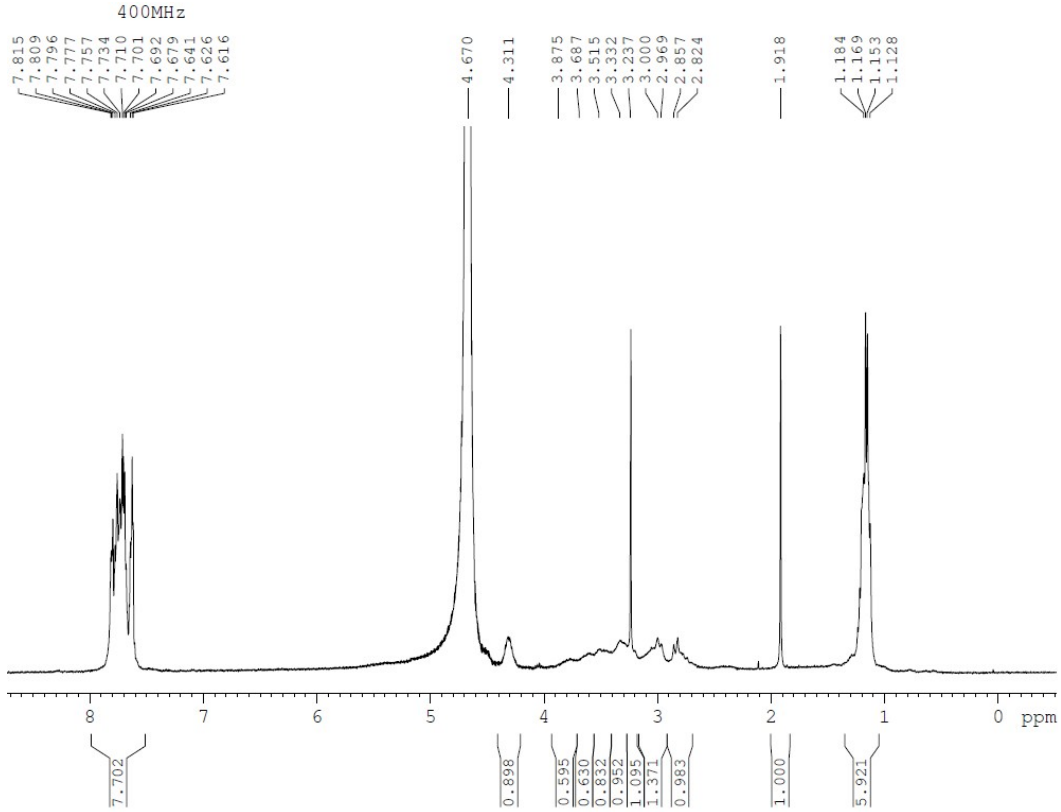


ESI-MS of $[Pd(phthal)_2(THPEN)]$ (**2**)

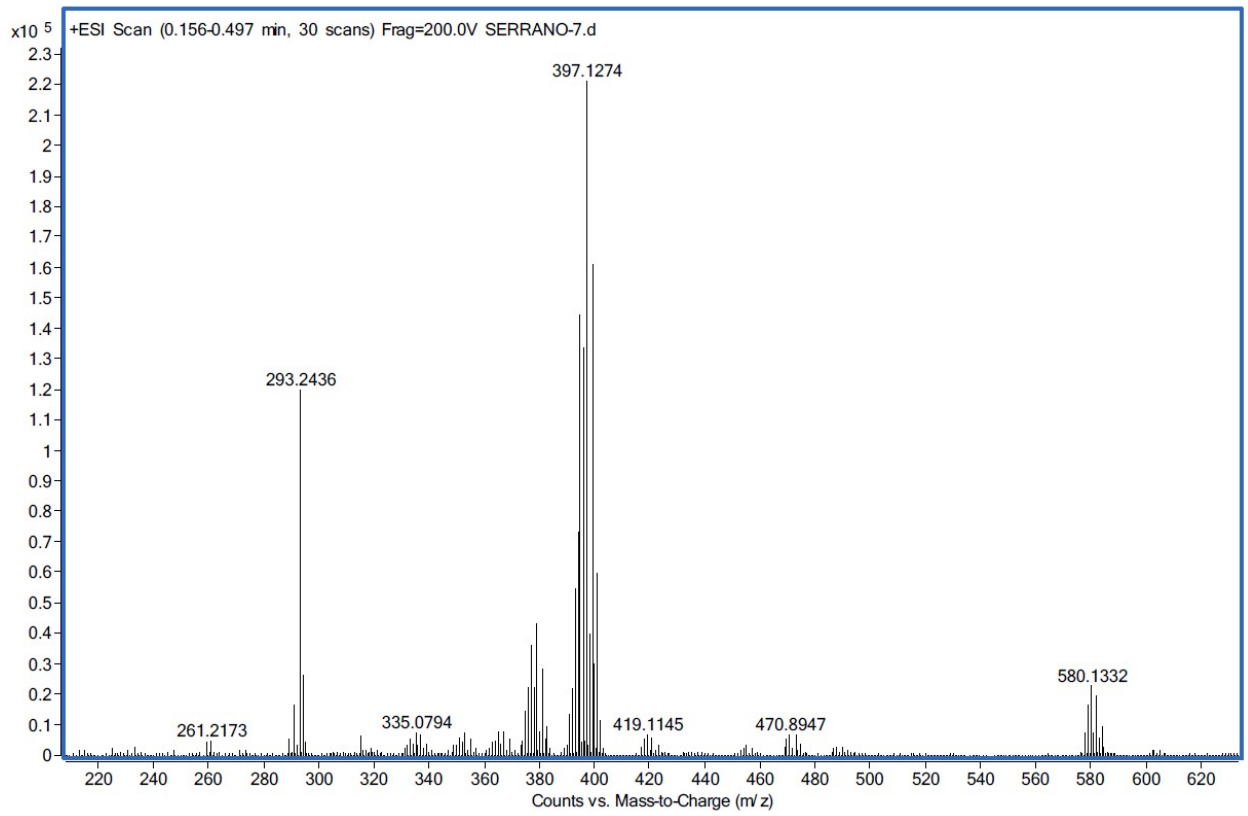
Experimental characterization of [Pd(sacc)$_2$(THPEN)] (3).



IR of [Pd(sacc)$_2$(THPEN)] (**3**).

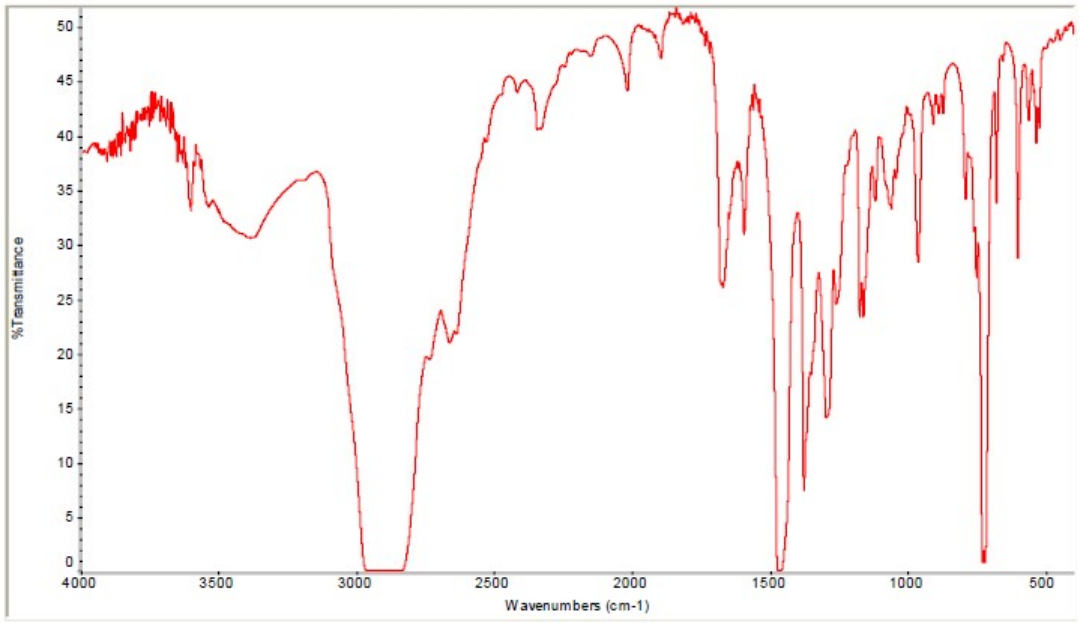


RMN-^{1}H in D_2O of [Pd(sacc)$_2$(THPEN)] (**3**).

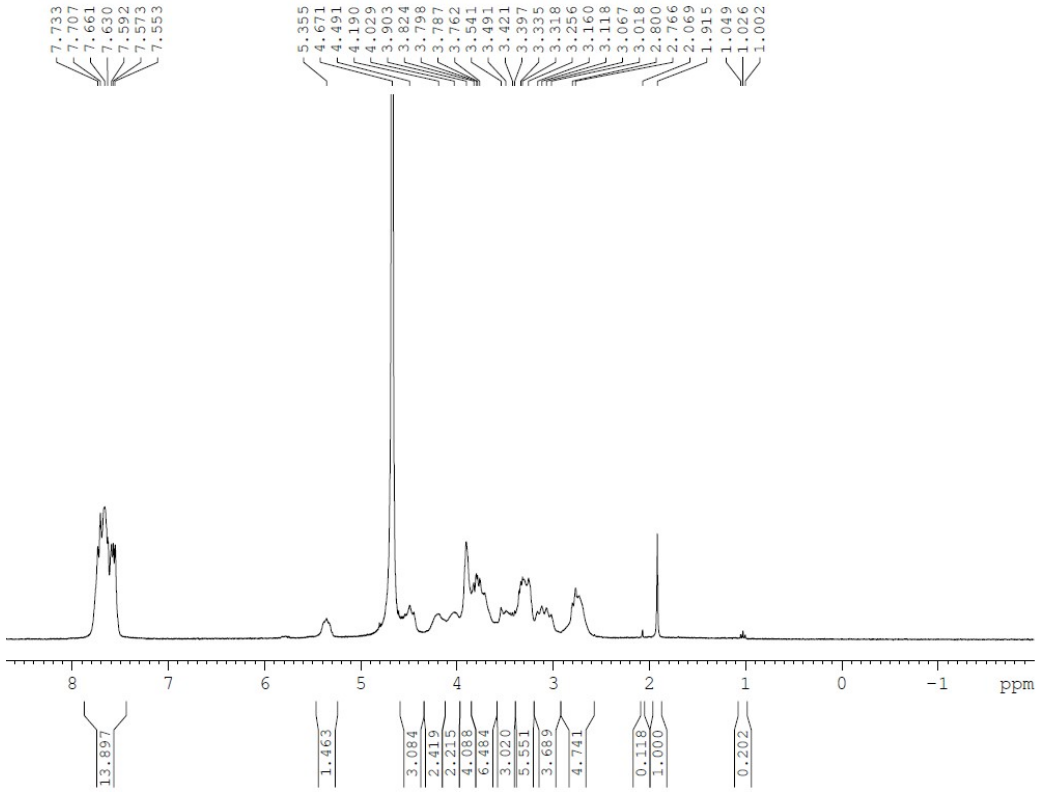


ESI-MS of $[Pd(sacc)_2(THPEN)]$ (**3**).

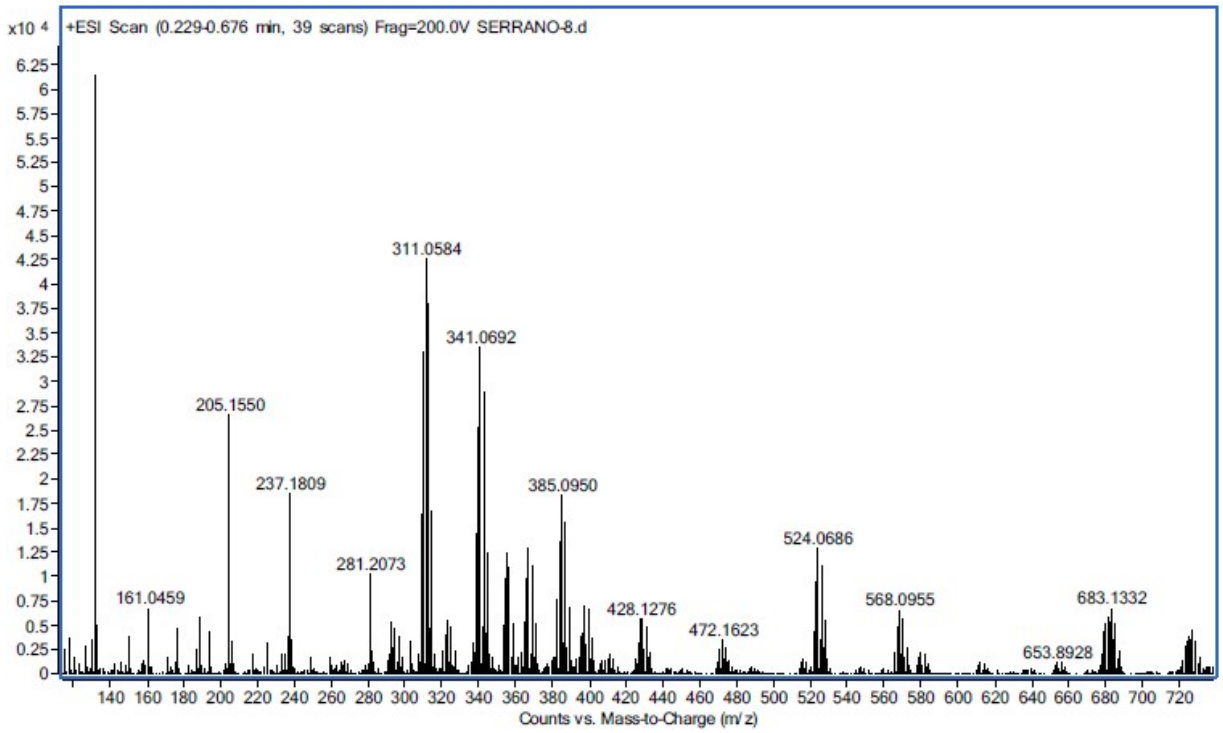
Experimental characterization of [Pd(sacc)$_2$(THEEN)] (4).



IR of [Pd(sacc)$_2$(THEEN)] (**4**).



RMN-^{1}H in D_2O of [Pd(sacc)$_2$(THEEN)] (**4**).



ESI-MS of $[Pd(sacc)_2(THEEN)]$ (**4**).