Supporting Information For:

Engineering Fused Coumarin Dyes: Molecular Level Understanding of Aggregation Quenching and Tuning Electroluminescence via Alkyl Chain Substitution

Sunil Kumar,[a] Punita Singh,[b] Ritu Srivastava,[b] Rik Rani Koner,[a] Avijit Pramanik,[c] Jomon Mathew,[d] Sougata Sinha,[a] Madhu Rawat,[e] R. S. Anand,[e] Subrata Ghosh[a,*]

[a]*School of Basic Sciences, Indian Institute of Technology Mandi, Mandi-175001, H.P, India*

[b]*Centre for Organic Electronics,National Physical Laboratory, New Delhi, India*

[c]*Department of Chemistry and Biochemistry, Jackson State University, Jackson, Mississippi 39217, United States*

[d]*Schulich Faculty of Chemistry and the Lise Meitner Minerva Center for Computational Quantum Chemistry, Technion-Israel Institute of Technology, Haifa, Israel*

[e]*ElectricalEngineering Department, Indian Institute of Technology Kanpur, Kanpur-208016, India*

1. Synthesis

1.1. General procedure for the synthesis of 1, 2, 3:

To the solution of ethylcyanoacetate (1mmol) in ethanol was added sodium acetate (0.4mmol) and reaction mixture was stirred for 5 min at room temperature followed by the drop wise addition of corresponding aldehyde (benzaldehyde, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde) (1mmol) over 5 min and then the reaction mixture was refluxed at 110 ºC for 3 hours. Reaction mixture was then allowed to cool to room temperature. Precipitates were washed with ethanol and dried over vacuum yielding 59-73% product.

Ethyl 2-cyano-3-phenylacrylate 1. m.p. 82°C. ^{1}H NMR (400 MHz, $CDCl_3$-d_1, δ): 8.25 (s, 1H), 8.0 (d, J = 7.6 Hz, 2H; Ar H), 7.58 (m, 3H, Ar H), 4.39 (q, J = 7.2 Hz, 2H, OCH2), 1.40 (t, J = 7.2 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 161.8, 155.1, 133.4, 131.3, 130.8, 129.4, 115.6, 102.6, 62.4, 14.0; IR (KBr): ν = 3068, 3035, 2984.5, 2215.8, 1722.1, 1604.3, 1570.6, 1497.7, 1441.6, 1379.3, 1363, 1301.3, 1262, 1200.3, 1082.5. 1004, 964.6, 886.1, 841.2, 768.3 cm^{-1}; HRMS (ESI, m/z): [M + Na] calcd for C12H11NO2Na, 224.0687; found, 224.0668.

Ethyl 2-cyano-3-(4-methoxyphenyl) acrylate 2. m.p. 83°C. ^{1}H NMR (400 MHz, $CDCl_3$-d_1 , δ): 8.17 (s, 1H), 8.0 (d, J = 8.8 Hz, 2H, Ar H), 7.0 (d, J = 8.8 Hz, 2H, Ar H), 4.36 (q, J = 7.2 Hz, 2H, OCH2), 3.89 (s, 3H, OCH3), 1.38 (t, J = 7.2 Hz, 3H, CH3);^{13}C NMR ($CDCl_3$-d_1, δ): IR (KBr): ν = 3074.3, 3029.4, 2995.5, 2950.8, 2221.5, 1716.5, 1581.8, 1559.4, 1509, 1430.4, 1363, 1323.8, 1211.6, 1177.9, 1121.8, 1082.5, 987.1, 841.2, 757.1 cm^{-1}: HRMS (ESI, m/z): [M + Na] calcd for C13H13NO3Na, 254.07931, 254.0795

Ethyl 3-(4-chlorophenyl)-2-cyanoacrylate 3. m.p. 90°C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.42 (s, 1H, Ar H), 8.07 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H, Ar H), 4.32(q, J = 7.6 Hz, 2H, OCH2), 1.3 (t, J = 7.2 Hz, 3H; CH3); ^{13}C NMR (DMSO-d_6, δ): 161.6, 153.7, 138.0, 132.5, 131.2, 130.2, 129.5, 129.4, 115.4, 103.2, 62.5, 14.0; IR (KBr): ν = 3051.8, 2984.5, 2906, 2221.5, 1727.7, 1615.5, 1587.5, 1559.4, 1497.7, 1413.5, 1357.4, 1256.4, 1194.7, 1082.5, 1015.2, 981.2, 835.6, 757 cm^{-1}: HRMS (ESI, m/z): [M + Na] calcd for C12H10ClNO2Na, 258.0286, 258.0297.

1.2. General procedure for the synthesis of 4, 5, 6, 7.

Literature procedure [1] was used to synthesize compound 5. To synthesize compound 4 and 6-7 above procedure was utilized using α-naphthol and 1, 6-dihydroxynaphthalene respectively as starting reactants. General procedure is as follows: A suspension of 1-3 (1eq) and α-naphthol/ 1, 6 -Dihydroxynaphthalene (1eq) in ethanol (30ml) was refluxed for 10hr using pyridine as catalyst. Reaction mixture was then allowed to cool overnight. Precipitates formed were obtained by filtration and washed with ethanol to get the product (22 40% yield).

2-oxo-4-phenyl-2H-benzo[h]chromene-3-carbonitrile 4. m.p. ^{1}H NMR (400 MHz, $CDCl_3$-d_1, δ): 8.62 (d, J = 8.9 Hz, 1H, Ar H), 7.9 (d, J = 8.72Hz, 1H, Ar H), 7.78-7.70 (m, 2H, Ar H), 7.67-7.63 (m, 4H, Ar H), 7.55-7.51 (m, 2H, Ar H), 7.30 (d, J = 8.8 Hz, 1H, Ar H); ^{13}C NMR ($CDCl_3$-d_1, δ): 164.9, 157.4, 152.6, 136, 132, 131.1, 130.9, 129.3, 128.6, 128.1, 128.08, 125.3, 123.4, 122.8, 114, 100.7; IR (KBr): ν = 2924.8, 2857.3, 2232.5, 1692, 1618.8, 1534.4 1472.5, 1382.5, 1213.6, 875.8, 757.6 cm^{-1}: LCMS, [M+2H] calcd for C20H13NO2, 299.0946; found, .299.1302

8-hydroxy-2-oxo-4-phenyl-2H-benzo[h]chromene-3-carbonitrile 5. m.p. 349°C. ^{1}H NMR (600 MHz, DMSO-d_6, δ): 8.3 (d, J = 8.4 Hz 1H, Ar H), 7.6 (m, 3H, Ar H), 7.59-7.56 (m, 3H, Ar H), 8.73 (d, J = 7.2 Hz, 1H, Ar H), 7.2 (s, 1H, Ar H), 7.0 (d, J = 9.0 Hz, 1H, Ar H); ^{13}C NMR (DMSO-d_6, δ): 164.0, 159.6, 157.1, 152, 138.1, 132.3, 130.3, 128.6, 128.1, 124.5, 123.3, 122.7, 122.0, 115.4, 114.5, 111.1, 109.6, 98.0; IR (KBr): ν = 3420.2, 2924.8, 2857.3, 2232.5, 1692, 1618.8, 1534.4 1472.5, 1382.5, 1213.6, 875.8, 757.6 cm^{-1}: HRMS (ESI, m/z): [M - H]+ calcd for C20H11NO3, 312.0660; found, 312.0661.

8-hydroxy-4-(4-methoxyphenyl)-2-oxo-2H-benzo[h]chromene-3-carbonitrile 6. m.p. 335°C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.34 (d, J = 9.2 Hz, 1H, Ar H), 7.63 (d, J = 8.8 Hz, 1H, Ar H), 7.55 (d, J = 8.4 Hz, 2H, Ar H), 7.34- 7.31 (m, 1H, Ar H), 7.25 – 7.17 (m, 4H, Ar H), 3.89 (s, 3H, OCH3); ^{13}C NMR (DMSO-d_6, δ): 161.1, 161.0, 159.8, 157.6, 138.3, 130.5, 124.9, 124.5, 123.5, 123.2, 120.2, 115.8, 114.4, 111.5, 109.8, 97.8, 55.4; IR (KBr): ν = 3439, 2232.7, 1705.3, 1610, 1587.5, 1542.6, 1509, 1396.7, 1351.8, 1273.3, 1228.4, 1186.3, 1020.8, 869.8, 757.1 cm^{-1}: LCMS = 342.14 $[M-H]^{+}$, 343.09 [M+].

4-(4-chlorophenyl)-8-hydroxy-2-oxo-2H-benzo[h]chromene-3-carbonitrile 7. m.p. 361°C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.34 (d, J = 9.2 Hz, 1H, Ar H), 7.74 (d, J = 8.4 Hz, 2H, Ar H), 7.62 (d, J = 8.4 Hz, 3H, Ar H), 7.34- 7.25 (m, 1H, Ar H), 7.25 (s, 1H, Ar H), 7.06 (d, J = 8.8 Hz, 1H, Ar H); ^{13}C NMR (DMSO-d_6, δ): 163.2, 160.0, 157.4, 152.3, 138.4, 135.5, 131.5, 130.4, 129.2, 124.9, 123.8, 123.0,120.4, 115.7, 114.7, 111.4, 109.9, 98.6; IR (KBr): ν = 3422, 2227, 1705, 1621.1, 1531.4, 1469.6, 1391, 1262, 1222.8, 1172.3, 1088.1, 1009.6, 987.1, 914, 824.2, 757.1 cm^{-1}; LCMS = 346.8 $[M+ H]^{+}$.

1.3. General procedure for the synthesis of compounds 8 – 22.

To the dichloromethane (4ml) suspension of compound 4 – 7 (1mmol) was added triethylamine (3mmol) and was stirred at 0ºC for 10 minutes followed by drop wise addition of corresponding acid chlorides (8-21)/ethylchloroformate (22) (1.1mmol) at the same temperature. Reaction mixture was then allowed to come to room temperature and stirred for further 3 hours. After the completion of reaction as indicated by TLC (thin layer chromatography), the reaction mixture was quenched with water, extracted with dichloromethane and washed with water (3X 1ml). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to get the pure product (70 76 % yield).

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl acetate 8. m.p. 227°C. ^{1}H NMR (500 MHz, $CDCl_3$-d_1 , δ): 8.63 (d, J = 8.8Hz, IH, Ar H), 7.65-7.59 (m, 5H, Ar H), 7.52- 7.5 (m, 2H, Ar H), 7.46 (dd, J1 = 7 Hz, J2 = 2.1Hz, 1H, Ar H), 7.31 (d, J = 8.8Hz, 1H, Ar H), 2.38(s, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 169.07, 164.7, 157.2, 152.4, 152.3, 137.3, 132.2, 131.2, 129.3, 128.6, 125.3, 124.9, 123.8, 123.3, 120.6, 119.1, 113.8, 113.6, 100.7 cm^{-1}; IR (KBr): ν = 2922.3, 2983.2, 2219.2, 1725.21, 1642.3, 1611.9, 1586.5, 1535.5, 1352.4, 1317, 1246.4, 1200, 1143.8, 1015, 914.2, 818.8, 757.1 cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C22H13NO4, 356.0924; found, 356.0922.

3-cyano-4-(4-methoxyphenyl)-2-oxo-2H-benzo[h]chromen-8-yl acetate 9. m.p. 231°C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.52 (d, J = 9.2 Hz, 1H, Ar H),7.89 - 7.85 (m, 2H, Ar H), 7.63-7.57 (m, 3H, Ar H), 7.36 (d, J = 8.8 Hz, 1H, Ar H), 7.25 (d, J = 8.8 Hz, 2H, Ar H), 3.9 (s, 3H, OCH3), 2.36 (s, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 169.13, 164.54, 162.06, 157.52, 152.43, 152.27, 137.26, 130.75, 125.39, 124.83, 124.16, 123.29, 119.09, 114.79, 100.99, 55.69, 21.37; IR (KBr): ν = 2928.3, 2973.2, 2217.06, 1722.11, 1632.3, 1609.9, 1587.5, 1537.5, 1357.4, 1307, 1256.4, 1194.7, 1149.8, 1015, 914.2, 818.8, 757.1 cm^{-1}; LCMS: 386.11 $[M + H]^+$, 403.10 $[M+ NH_4]^+$.

4-(4-chlorophenyl)-3-cyano-2-oxo-2H-benzo[h]chromen-8-yl acetate 10. m.p. 236°C. ^{1}H NMR (500 MHz, $CDCl_3$-d_1, δ): 8.6 (d, J = 9.1 Hz, 1H; Ar H), 7.66-7.61 (M, 4H; Ar H), 7.4 (d, J = 8.5 Hz, 3H; Ar H), 7.2 (d, J = 9.1 Hz, 1H; ArH), 2.3 (s, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 174.3, 143.7, 141, 140.5, 137.4, 136.2, 129.1, 127.8, 127.2, 127.7, 124.4, 121.9, 121.2, 119.8, 119.5, 119.3, 119.1, 114.5, 111.7, 109.4, 21.2; IR (KBr): ν = 3063, 2227.06, 1744, 1733.3, 1632.3, 1581.8, 1542.2, 1475.2, 1357.4, 1278.8, 1194.7, 1155.4, 1009, 1065, 902.8, 818.2, 762 cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C22H12ClNO4, 390.0533; found, 390.0539.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl propionate 11. m.p. 186°C. ^1H NMR (400 MHz, $CDCl_3$-d_1, δ): 8.65 (d, J = 9.1 Hz, 1H, Ar H), 7.67-7.60 (m, 5H; ArH), 7.54-7.51 (m, 2H; ArH), 7.49-7.45 (m, 1H, ArH), 7.3 (d, J = 8.8 Hz, 1H, ArH), 2.69 (q, J = 7.5 Hz, 2H, CH2), 1.32 (t, J = 7.5 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 172.7, 164.8, 157.3, 152.5, 137.3,132.2, 131.2, 129.3, 128.6, 125.3, 124.9, 123.8, 123.4, 120.6, 119.1, 113.9, 113.5, 100.6, 27.9, 9.1; IR (KBr): ν = 3063, 2227.06, 1744, 1733.3, 1632.3, 1581.8, 1542.2, 1475.2, 1357.4, 1278.8, 1194.7, 1155.4, 1009, 1065, 902.8, 818.2, 762 cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C23H15NO4, 370.1079; found, 370.1073.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl butyrate 12. m.p. 178°C. ^1H NMR (400 MHz, $CDCl_3$-d_1, δ): 8.65 (d, J = 9.1 Hz, 1H, Ar H), 7.66-7.60 (m, 5H; ArH), 7.54-7.51 (m, 2H; ArH), 7.48-7.46 (m, 1H, ArH), 7.3 (d, J = 8.8 Hz, 1H, ArH), 2.63 (t, J = 7.4 Hz, 2H, CH2), 1.86 - 1.81 (m, 2H, CH2), 1.09 (t, J = 7.4 Hz, 3H) ; ^{13}C NMR ($CDCl_3$-d_1, δ): 171.8, 165, 157, 152.4, 137.3, 132.2, 131.2, 129.3, 128.6, 125.3, 124.9, 123.8, 123.4, 120.6, 119.1, 113.9, 113.5, 99.8, 100.6, 36.3, 18.5, 13.8; IR (KBr): ν = 3063, 2227.06, 1744, 1733.3, 1632.3, 1581.8, 1542.2, 1475.2, 1357.4, 1278.8, 1194.7, 1155.4, 1009, 1065, 902.8, 818.2, 762 cm^{-1}. HRMS (ESI, m/z): $[M + H]^+$ calcd for C24H18NO4, 384.1236; found, 384.1253.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl pentanoate 13. m.p.168°C. ^{1}H NMR (400 MHz, $CDCl_3$-d_1, δ): 8.65 (d, J = 9.16 Hz, 1H, Ar H), 7.66- 7.60 (m, 5H, Ar H), 7.53-7.51(m, 2H, Ar H), 7.49- 7.45 (m, 1H, Ar H), 7.32 (d, J = 8.8 Hz, 1H, Ar H), 2.65 (t, J = 7.4 Hz, 2H, CH2), 1.81- 1.77 (m, 2H, CH2), 1.54- 1.44 (m, 2H, CH2), 1.0 (t, J = 7.2 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 172.04, 164.8, 152.5, 137.4, 132.2, 131.2, 129.3, 128.6, 125.3, 124.9 123.8, 123.4, 120.6, 119.1, 113.8, 113.5, 100, 34.2, 27.0, 22.3, 13.8; IR (KBr): ν = 2955.8, 2933.3, 2227.8, 1744.4, 1733.3, 1633.3, 1538.9, 1477.8, 1355.6, 1161.1, 1133.3, 1100, 755.5cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C25H19NO4, 398.1392; found, 398.1396.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl 3-methylbutanoate 14. m.p. 174°C. ^{1}H NMR (400 MHz, $CDCl_3$-d_1, δ) 8.65 (d, J =9.16 Hz, 1H, Ar H), 7.65 – 7.6(m, 5H, Ar H), 7.53 – 7.51 (m, 2H, ArH), 7.48 – 7.45 (m, 1H, ArH), 7.33 (d, J = 8.92 Hz, 1H, Ar H), 2.52(d, J = 7.24 Hz, 2H, CH2), 2.32 – 2.26(m, 1H, CH), 1.0 (d, J = 6.64 Hz, 6H, 2CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 171.2, 164.8, 157.2, 152.4, 137.3, 132.3, 131.2, 129.3, 128.5, 125.3, 124.9, 123.7, 120.6, 119.1, 113.5, 100.6; IR (KBr): ν = 2972.2, 2940, 2227.8, 1733.3, 1725.2, 1627.8, 1538.8, 1472.2, 1150, 1094.4, 761.1 cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C25H19NO4, 398.1392; found, 398.1391.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl heptanoate 15. m.p.147°C. ^{1}H NMR (500 MHz, $CDCl_3$-d_1, δ): 8.63 (d, J = 9 Hz, 1H, Ar H), 7.65- 7.59 (m, 5H; Ar H), 7.52-7.50 (m, 2H, Ar H), 7.45 (dd, J1 = 9Hz, J2 = 2Hz, 1H, Ar H), 7.31(d, J = 9Hz,1H, Ar H) 2.63 (t, J = 7.5 Hz, 2H, CH2), 1.81-1.75 (m, 3H, CH2), 1.36-1.33 (m, 5H, CH2), 0.9 (t, J = 7 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ):172.04, 164.8, 157.2, 152.5, 137.4, 132.2, 131.3, 129.3, 128.6, 125.3, 124.9, 123.8, 123.4, 120.6, 119.1, 113.8, 113.5, 100.6, 34.5, 31.5, 28.8, 24.9, 22.5, 14.1; IR (KBr): ν = 2933.3, 2857.3, 2222.5, 1733.3, 1725.4, 1627.8, 1544.4, 1466.7, 1361.1, 1161.1,, 1133.3, 1094.4, 761.1 cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C27H23NO4, 426.1705; found, 426.1709.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl dodecanoate 16. m.p. 154°C ^1H NMR (400 MHz, $CDCl_3$-d_1, δ): 8.64 (d, J = 9.16 Hz, 1H, Ar H), 7.66 – 7.60 (m, 5H, Ar H), 7.53 – 7.51 (m, 2H, Ar H), 7.47 – 7.45 (m, 1H, Ar H), 7.28 (d,J = 8.92 Hz, 1H, Ar H), 2.63 (t, J = 7.4 Hz, 2H, CH2), 1.81 - 1.79 (m, 2H), 1.44 (m, 16H) 0.88 (t, J = 6.64 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 172.04, 164.8, 157.3, 152.4, 137.4, 132.2, 131.1, 129.3, 128.6, 125.3, 124.9 123.8, 123.4, 120.6, 119.1, 113.8, 113.5, 100.6, 34.5, 32.0, 29.7, 29.6, 29.4, 29.3, 29.2, 24.9, 22.7, 14.2; IR (KBr): ν = 2921.2, 2850.3, 2223.7, 1738.8, 1728, 1629.8, 1586.2, 1542.6, 1471.8, 1139.4, 1155.8, 1106.7, 758 cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C32H33NO4, 496.2488; found, 496.2489.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl tetradecanoate 17. m.p. 151°C. ^1H NMR (400 MHz, $CDCl_3$-d_1, δ): 8.64 (d, J = 9.2 Hz, 1H, Ar H), 7.65 – 7.59 (m, 5H, Ar H), 7.53 – 7.52 (m, 2H, Ar H), 7.48 – 7.45 (m, 1H, ArH), 7.32 (d, J = 7.2 Hz, 1H, Ar H), 2.63 (t, J = 7.2 Hz, 2H, CH2), 1.44 - 1.26 (m, 22H, CH2), 0.87 (t, J = 7.2 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 171.9, 164.7, 157.2, 152.4, 137.3, 132.2, 131.2, 129.3, 128.6, 125.3, 124.9 123.7, 123.4, 120.6, 119, 113.8, 113.5, 100.6, 34.5, 32.0,29.6,29.5, 29.45, 29.3, 29.2, 24.9, 22.7, 14.2 ; IR (KBr): ν = 2927.8, 2850, 2222.2, 1738.9, 1725.3, 1622, 1583.3, 1533.3, 1472.2, 1161.1, 1133.3, 1109, 761.1 cm^{-1}. HRMS (ESI, m/z): $[M + H]^+$ calcd for C34H37NO4, 524.2801; found, 524.2804.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl palmitate 18. m.p. 151°C. ^{1}H NMR (500 MHz, $CDCl_3$-d_1, δ): 8.63 (d, J = 9.1 Hz, 1H, Ar H), 7.65 – 7.59 (m, 5H, Ar H), 7.52 – 7.50 (m, 2H, Ar H), 7.46 – 7.44 (m, 1H, ArH), 7.31 (d, J = 8.8 Hz, 1H, Ar H), 2.63 (t, J = 7.6 Hz, 2H, CH2), 1.46 - 1.24 (m, 26H, CH2), 0.87 (t, J = 7.0 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$-d_1, δ): 171.9, 164.7, 157.2, 152.4, 137.3, 132.2, 131.2, 129.3, 128.6, 125.3, 124.9 123.7, 123.4, 120.6, 119, 113.8, 113.5, 100.6, 34.5, 32.0, 29.78, 29.74, 29.6, 29.5, 29.4, 29.3, 29.2, 24.9, 22.7, 14.2; IR (KBr): ν = 2926.4, 2850, 2221.8, 1738.9, 1725.3, 1624, 1573.3, 1535.3, 1473.2, 1160.1, 1133.3, 1109, 761.6 cm^{-1}: HRMS (ESI, m/z): $[M + H]^+$ calcd for C36H40NO4, 552.3114; found, 552.3110.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl benzoate 19. m.p. 263°C. ^{1}H NMR (500 MHz, $CDCl_3$-d_1, δ): 8.7 (d, J = 8.5 Hz, 1H, Ar H), 8.25- 8.23 (m, 2H; ArH), 7.8 (m, 1H, Ar H), 7.7-7.52 (m, 10H, Ar H), 7.34 (d, J = 8.5 Hz, 1H, ArH) ; ^{13}C NMR ($CDCl_3$-d_1, δ): 164.87, 164.80, 157.2, 152.6, 137.4, 134.2, 132.2, 131.3, 130.4, 129.3, 128.8, 128.6, 125.4, 124.9, 123.9, 123.5, 120.7, 119.3, 113.8, 113.6, 100.7; IR (KBr): ν = 3006, 2928, 2227, 1733.3, 1632.3, 1587.5, 1542.5, 1475.2, 1351.8, 1263, 1228.4, 1149.8, 1065, 897.3, 818.8, 745.8 cm^{-1}; HRMS (ESI, m/z): $[M + H]^+$ calcd for C27H15NO4, 418.1079; found, 418.1077.

3-cyano-4-(4-methoxyphenyl)-2-oxo-2H-benzo[h]chromen-8-yl benzoate 20. m.p. 251°C. ^{1}H NMR (500 MHz, $CDCl_3$-d_1, δ): 8.70 (d, J = 9.0 Hz, 1H, Ar-H), 8.25 (m, 2H, Ar-H), 7.80 (d, J = 2.3 Hz, Ar-H), 7.72-7.5 (m, 6H, Ar-H), 7.42 (d, J = 8.8 Hz, 1H, Ar-H), 7.16-7.14 (m, 2H, Ar-H); 13C NMR (500 MHz, $CDCl_3$, δ): 164.9, 164.5, 162.0, 130.7, 130.4, 128.9, 125.4, 124.8, 123.4, 119.3, 114.8, 100.1, 55.7; IR (KBr): ν = 3120, 2950, 2234.4, 1713.3, 1620, 1581.5, 1542.6, 1511, 1391.2, 1349.2, 1273.3, 1229.4, 1166.3, 1020.8, 873.6, 746.6; LCMS = 448 $[M+H]^+$, 465.0 $[M+NH_4]^+$.

4-(4-chlorophenyl)-3-cyano-2-oxo-2H-benzo[h]chromen-8-yl benzoate 21. m.p. 280°C. 1H NMR (500 MHz, $CDCl_3$-d_1, δ): 8.70 (d, J = 9.15 Hz, 1H, Ar-H), 8.25 (d, J = 7.6 Hz, 2H, Ar-H), 7.71-7.61 (m, 5H, Ar-H), 7.56 (t, J = 7.75 Hz, 2H, Ar-H), 7.49 (d, J = 8.3 Hz, 2H, Ar-H), 7.31 (d, 8.85 Hz, 1H, Ar-H); 13C NMR (500 MHz, $CDCl_3$, δ): 164.7, 163.43, 156.8, 152.68, 152.56, 137.6, 137.3, 134.1, 130.3, 132.2, 129.9, 129.6, 128.7, 125.3, 125.0, 123.5, 123.3120.6, 119.2, 113.5, 113.1, 100.6; IR (KBr): ν = 3013, 2945, 2229.4, 1720.3, 1631, 1579.3, 1539.4, 1501, 1391.2, 1345.4, 1270.3, 1229.4, 1150.3, 1025, 873, 747; LCMS = 451.8 $[M]^+$, 469.0 $[M+NH_4]^+$.

3-cyano-2-oxo-4-phenyl-2H-benzo[h]chromen-8-yl ethyl carbonate 22. m.p. 202°C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.54 (d, J = 9.2 Hz, 1H, Ar H), 8.0 (m, 1H, Ar H), 7.86 (m, 1H, Ar H), 7.74 – 7.69 (m, 4H, Ar H), 7.62 – 7.59 (m, 2H, ArH), 7.27 (d, J = 9.2 Hz, 1H, Ar H), 4.31 (q, J = 7.2 Hz, 2H, OCH2), 1.33 (t, J = 7.2 Hz, 3H, CH3; ^{13}C NMR ($CDCl_3$-d_1, δ): 164.81, 157.23, 153.15, 152.59, 152.43, 137.33, 131.27, 129.3, 128.6, 125.5, 125.0, 123.9, 122.7, 118.4, 100.7, 65.5, 14.3; IR (KBr): ν = 2984.5, 2928.4, 2227, 1761.4, 1739, 1626.7, 1593, 1548.2, 1475.2, 1363, 1262, 1245.3, 1228.4, 1161, 1105, 987.1, 891.7, 757.1 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ calcd for C23H16NO5, 386.1028; found, 386.1140.

	compound 5	compound 8
emperical formula	$C_{20} H_{11} N O_3$	$C_{22} H_{13} N O_4$
fw	313.30	355.33
crystal system	orthorhombic	orthorhombic
space group	*P* 2(1)2(1)2	*P* ca2(1)
a, Å	13.1356(12)	7.3791 (18)
b, Å	10.4952(10)	9.568(2)
c, Å	10.6469 (10)	25.226(2)
α, β, γ, deg	90, 90, 90	90, 90, 90
V $Å^3$	1467.8(2)	1781.0(7)
Z/r/μ	4/1.418/0.096	4/1.325/0.092
collected/indep reflns	3393/2761	2705/2328
GOF	1.161	1.181
final R indices R1	0.0545	0.0423
wR2	0.1357	0.0887
R indices (all data) R1	0.0773	0.0575
wR2	0.1817	0.1121

Table S1: Crystal Data and Structure Refinement for **5** and **8.**

compound	$(\Phi_{sol})^{a,b}$	compound	$(\Phi_{sol})^{a.b}$
4	0.08	**15**	0.059
5	0.11	**16**	0.059
8	0.06	**17**	0.07
10	0.069	**18**	0.059
11	0.049	**19**	0.081
12	0.029	**21**	0.076
13	0.069	**6**	0.047
14	0.066		

[a]values reported with respect to quinine sulphate. [b]All vaues reported for THF solution.

Table S2 : Quantum yield values calculated for studied compounds.

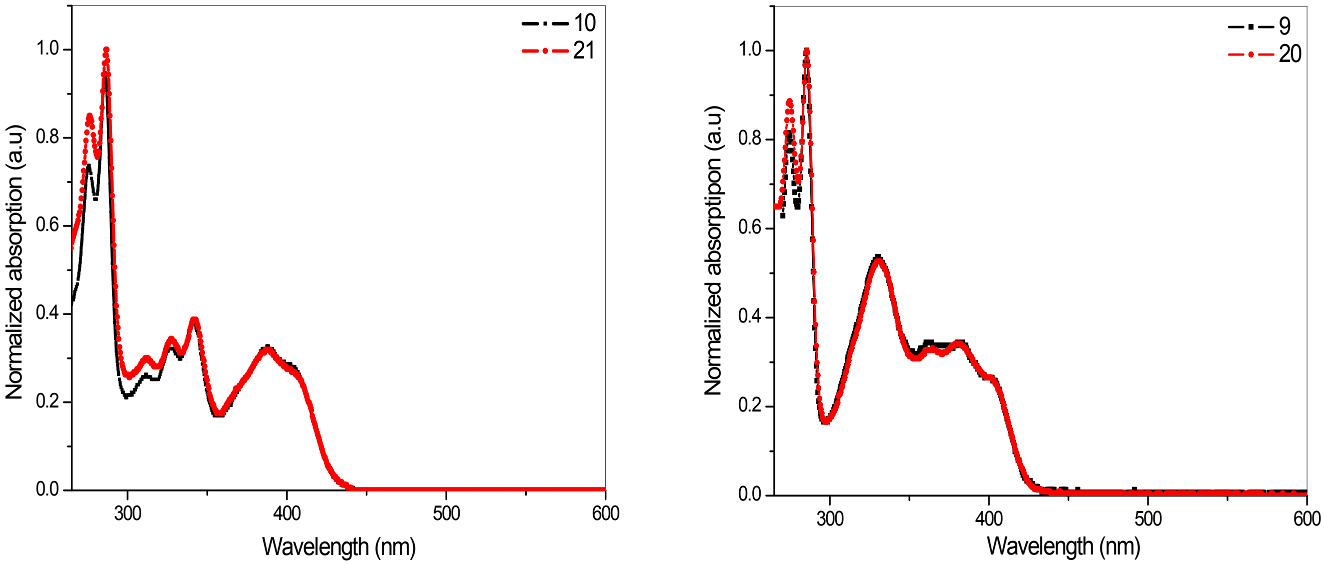


Fig. S1. Absorption spectra recorded for compounds **10** and **21** (left) and compounds **9** and **20** (right) in the 5uM THF solution.

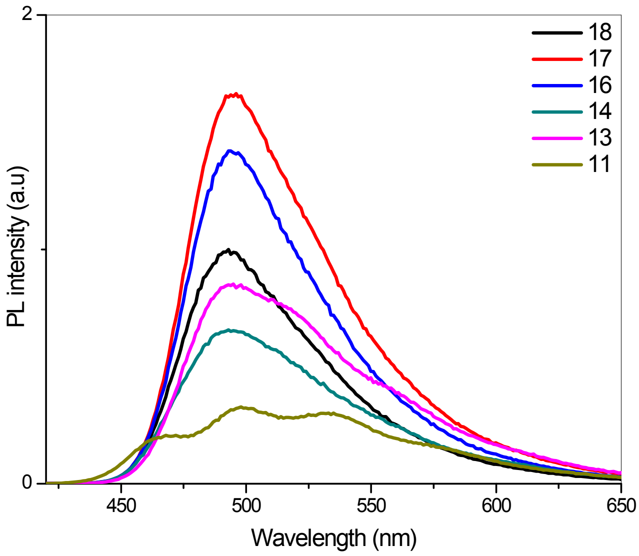


Fig. S2. PL spectra recorded for compounds **11, 13, 14, 16, 17** and **18** in powder form.

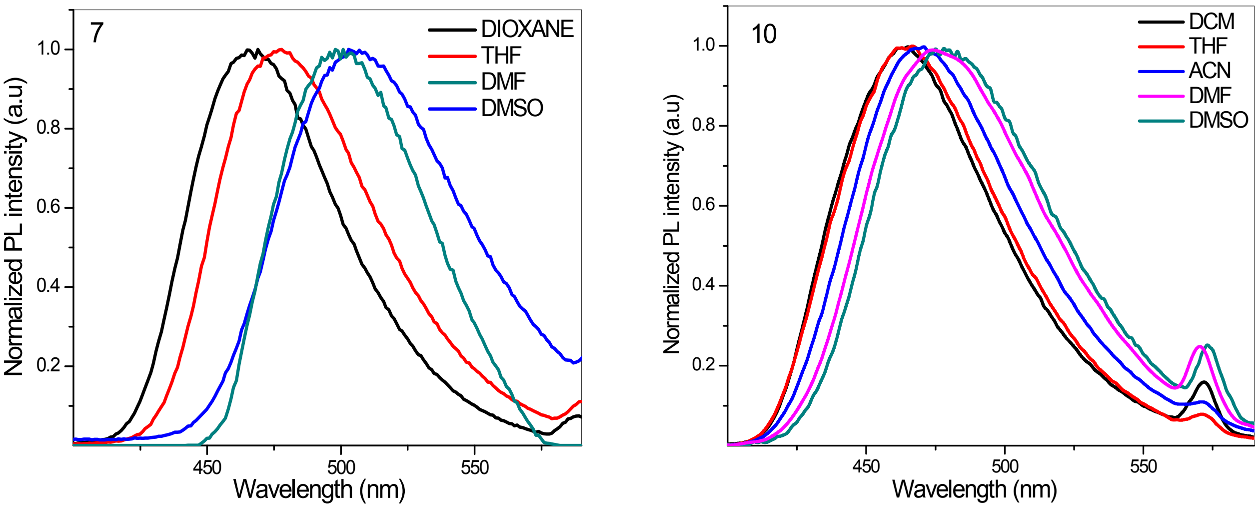


Fig. S3. Fluorescence solvatochromic behavior of compounds **7** (left) and **10** (right).

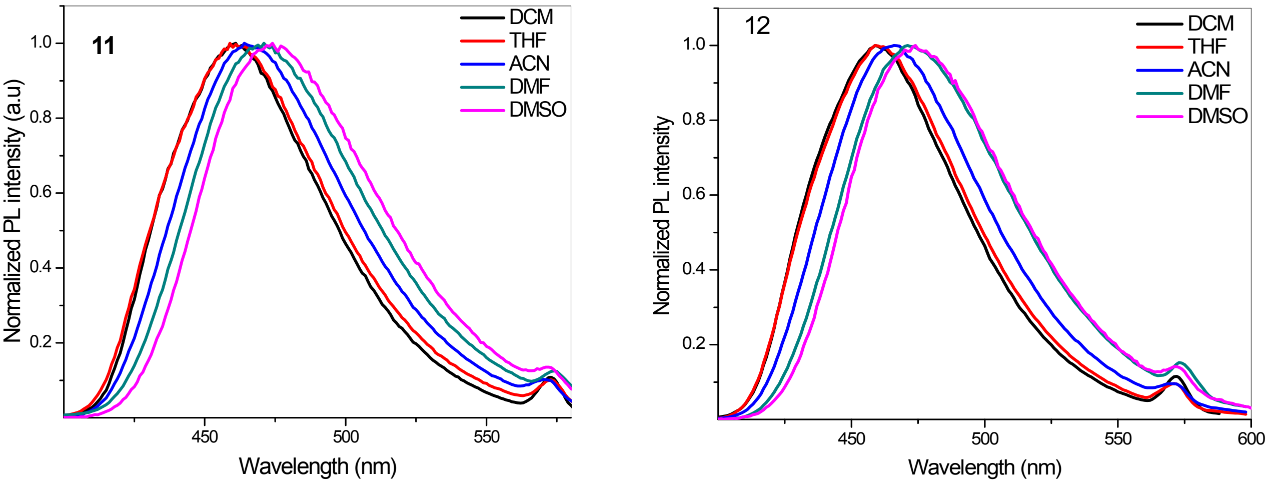


Fig. S4. Fluorescence solvatochromic behavior of compounds **11** (left) and **12** (right).

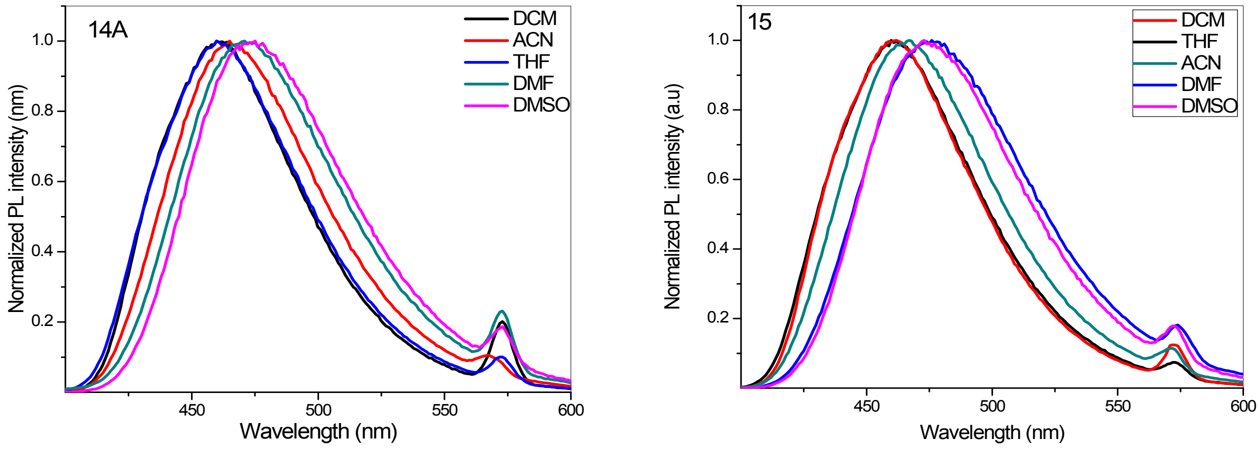


Fig. S5. Fluorescence solvatochromic behavior of compounds **14** (left) and **15** (right).

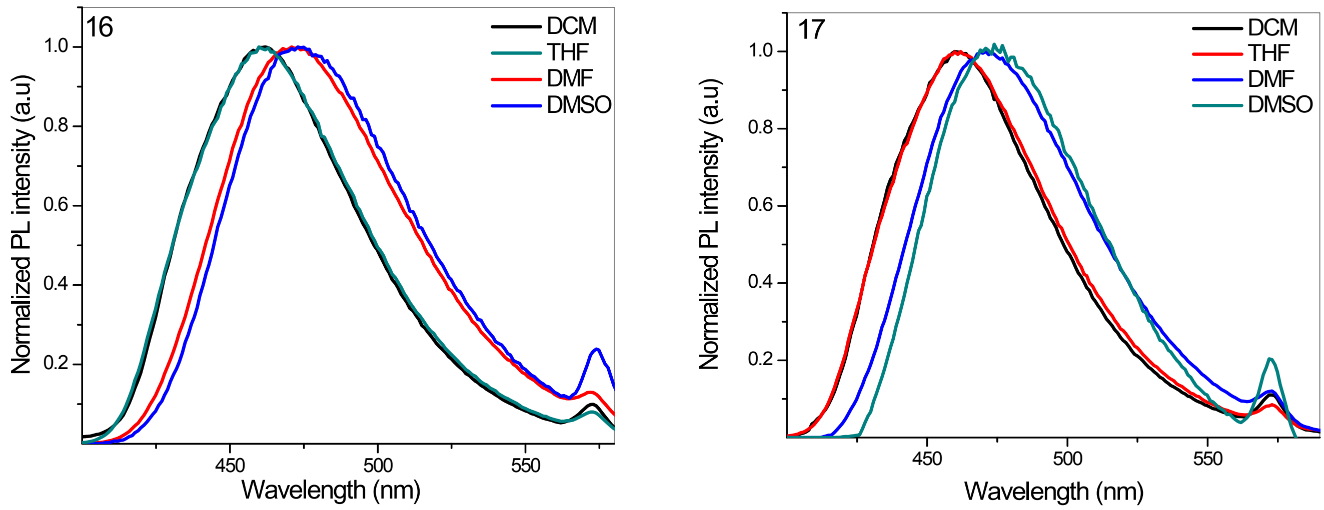
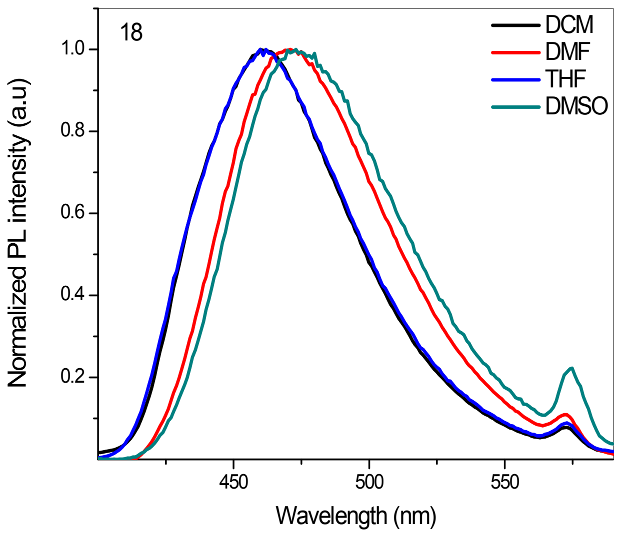


Fig. S6. Fluorescence solvatochromic behavior of compounds **16** (left) and **17** (right).



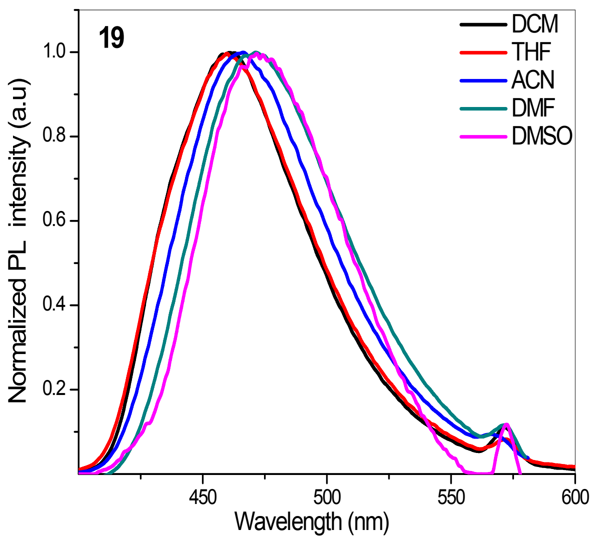
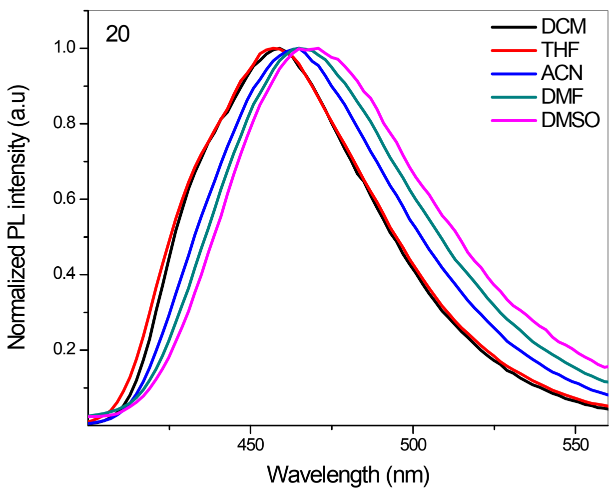


Fig. S7. Fluorescence solvatochromic behavior of compounds **18** (left) and **19** (right).



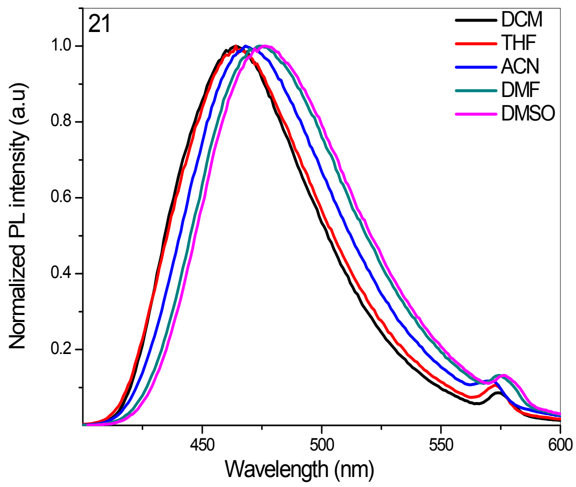


Fig. S8. Fluorescence solvatochromic behavior of compounds **20** (left) and **21** (right).

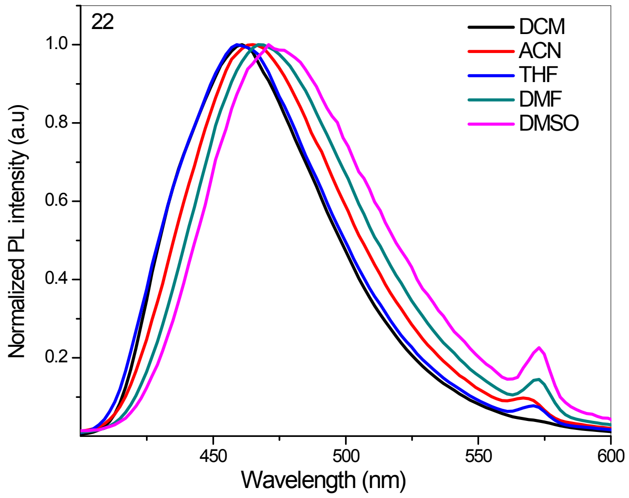


Fig. S9. Fluorescence solvatochromic behavior of compound **22**.

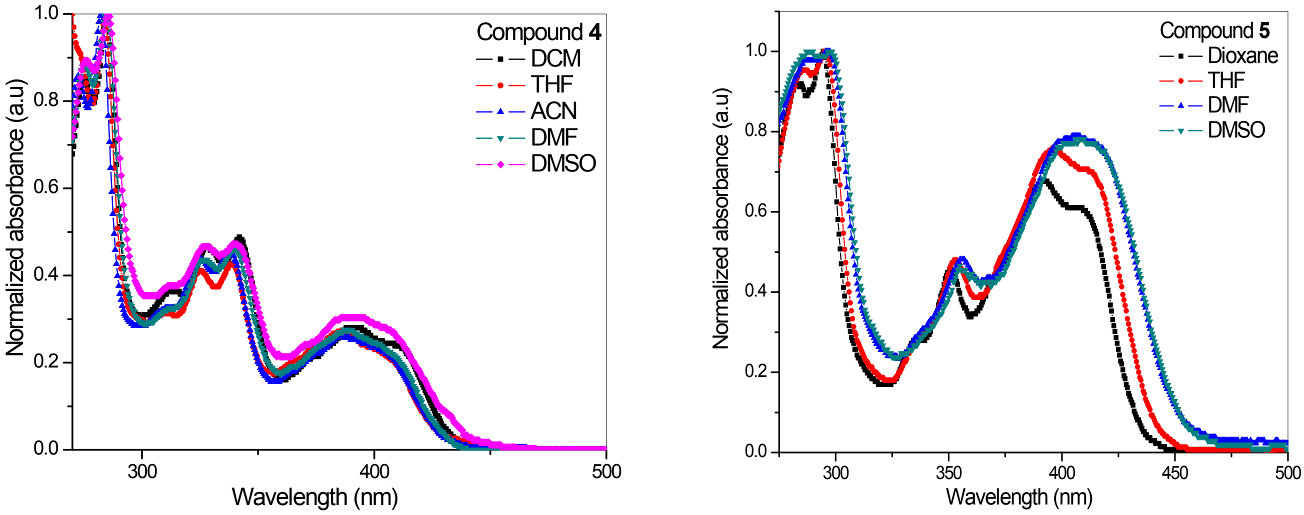
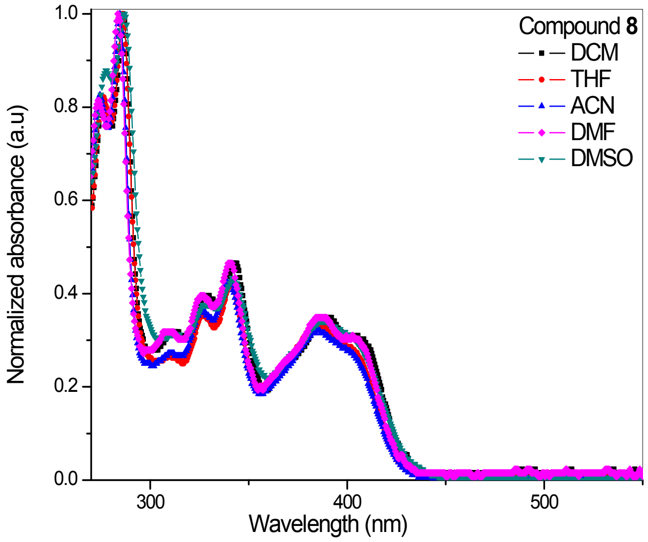


Fig. 10. UV-Visible absorption solvatochromic behavior of compound **4** (left) and **5** (right).



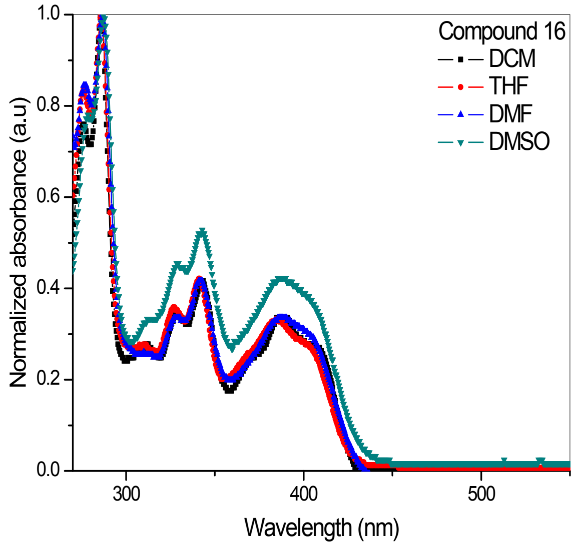
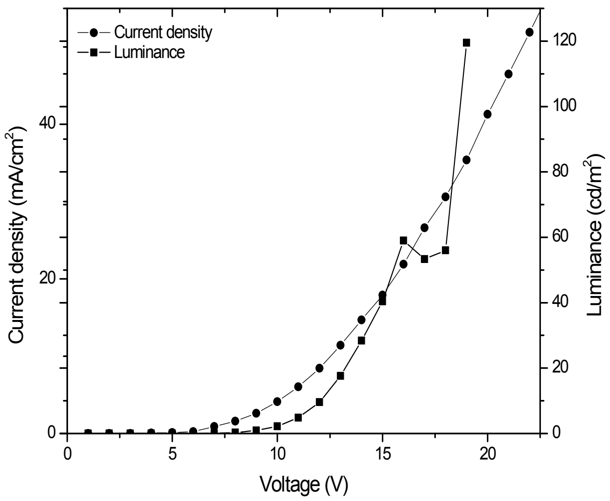


Fig. 11. UV-Visible absorption solvatochromic behavior of compound **8** (left) and **16** (right).



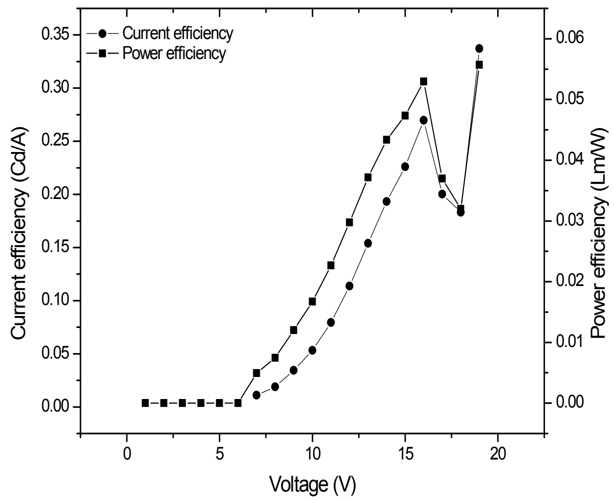


Fig. S12.J–V–L characteristics (left)and Current efficiency–voltage and power efficiency–voltage (right) of device having 0.5% of dye doped in host matrix.

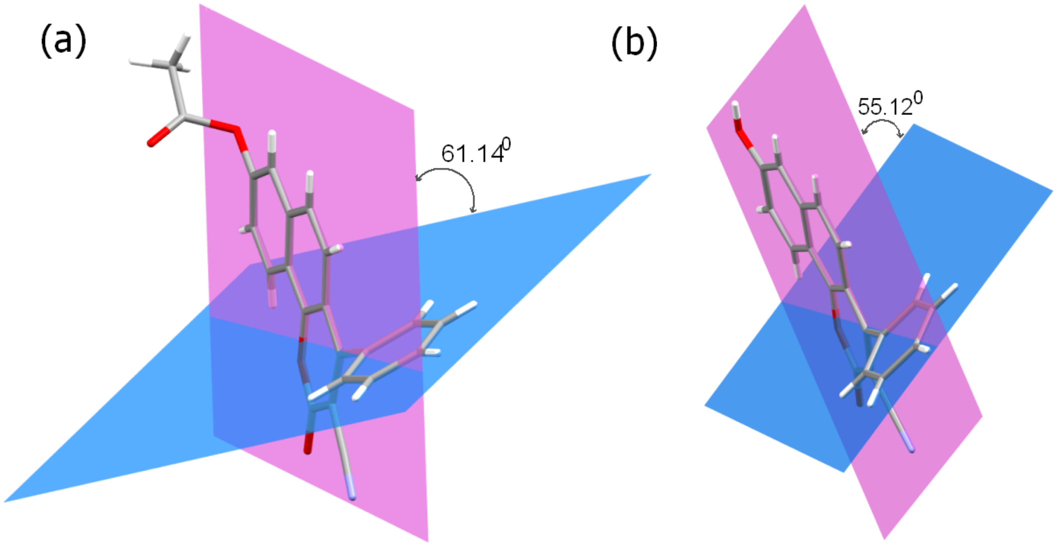


Fig. S13. Interplanar angle between 2H-benzo[h]chromen-2-one core and phenyl moiety. a) **8** and b) **5.**

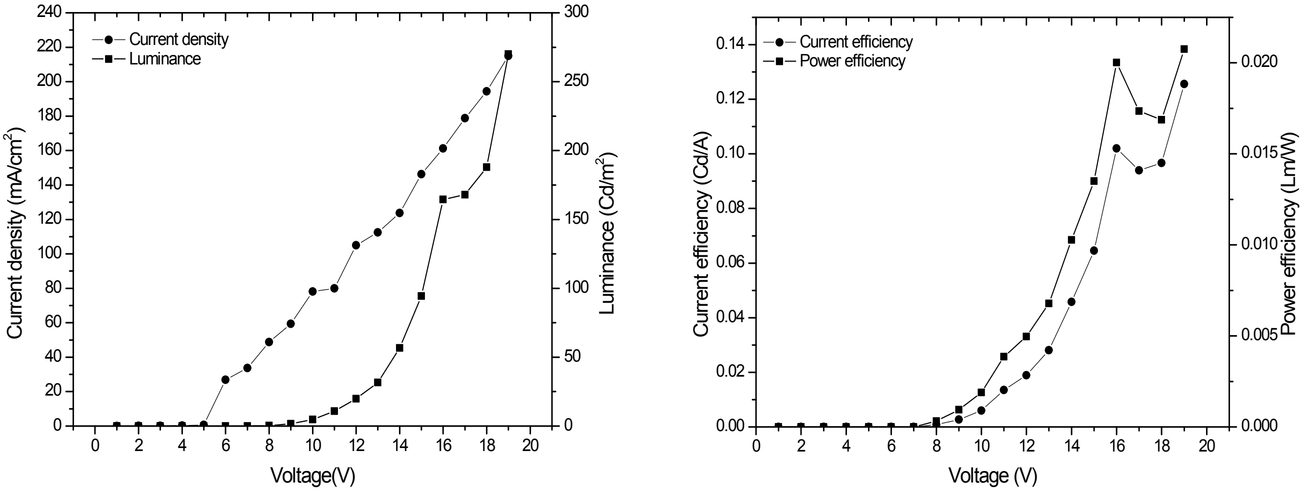


Fig. S14. J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of device having 1.5% of dye doped in host matrix.

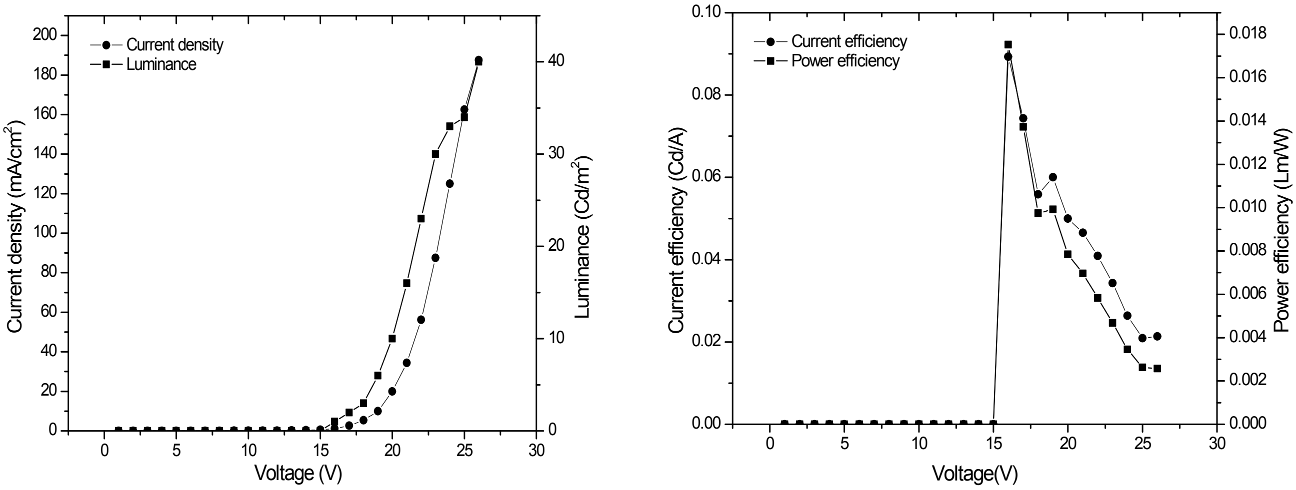


Fig. S15. J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of device having 2% of dye doped in host matrix.

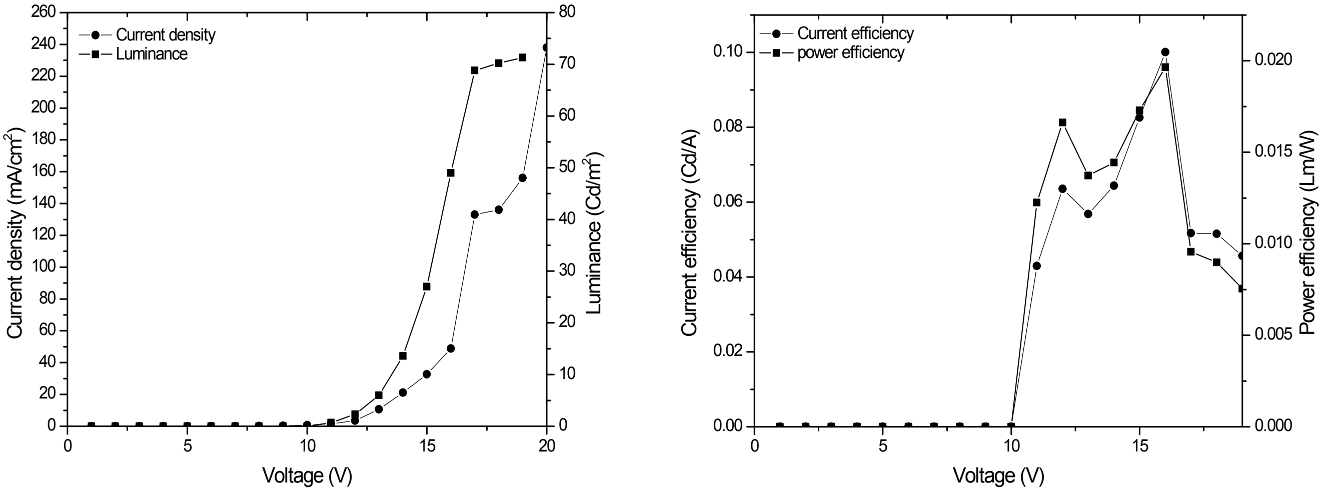


Fig. S16. J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of device having 3% of dye doped in host matrix.

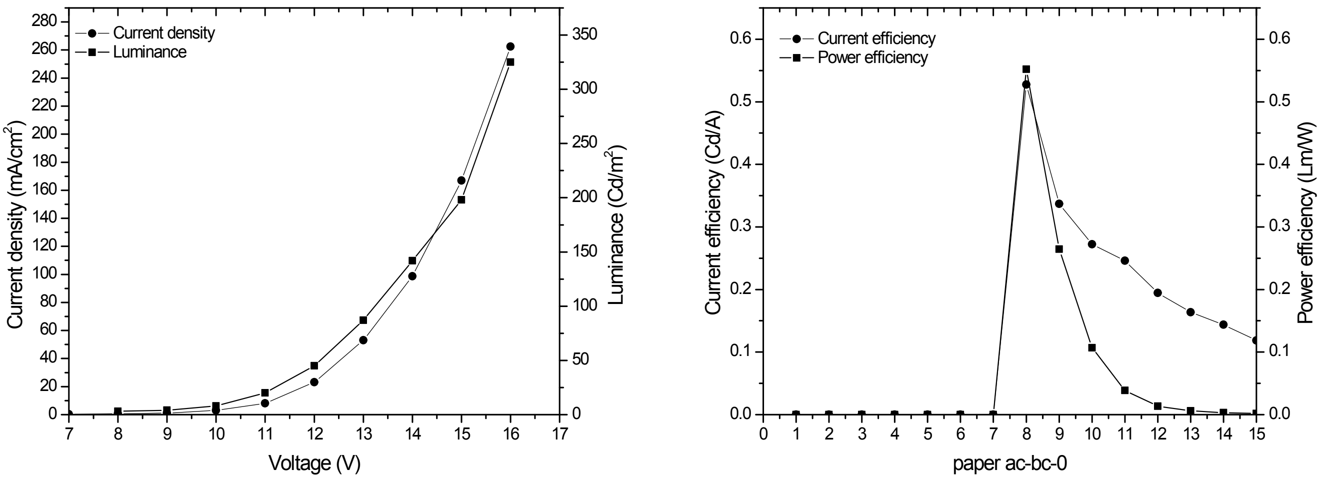


Fig. S17. J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 2.

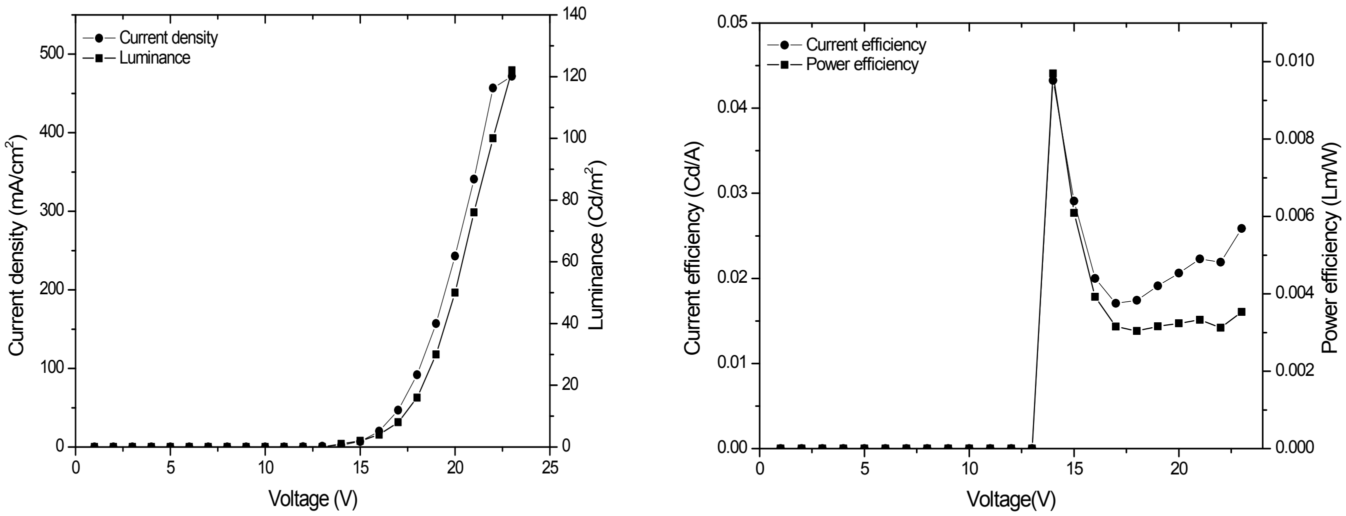


Fig. S18.J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 4.

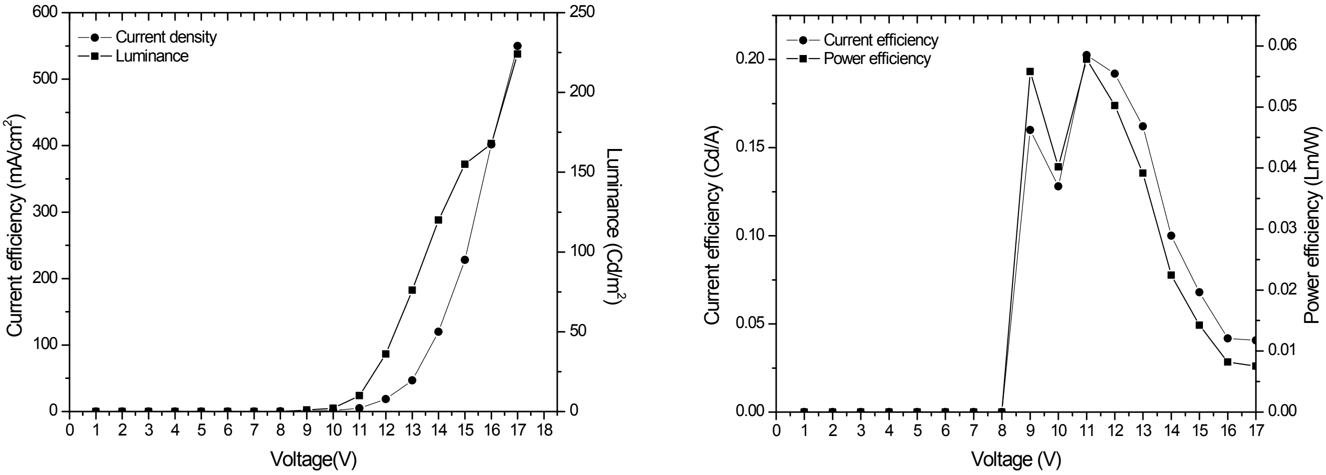


Fig. S19. J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 5.

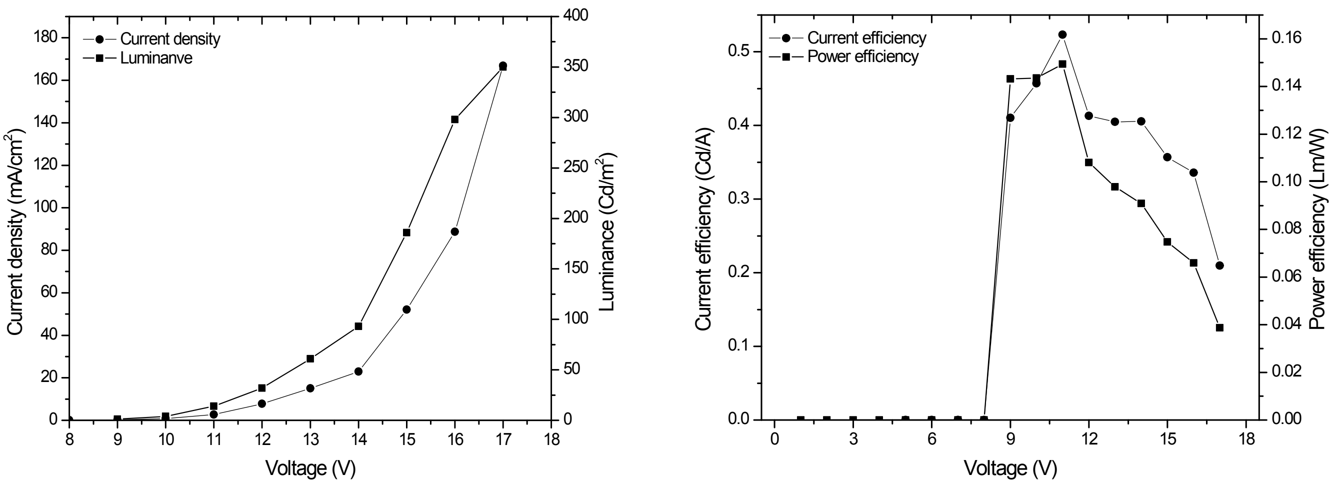


Fig. S20. J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 6.

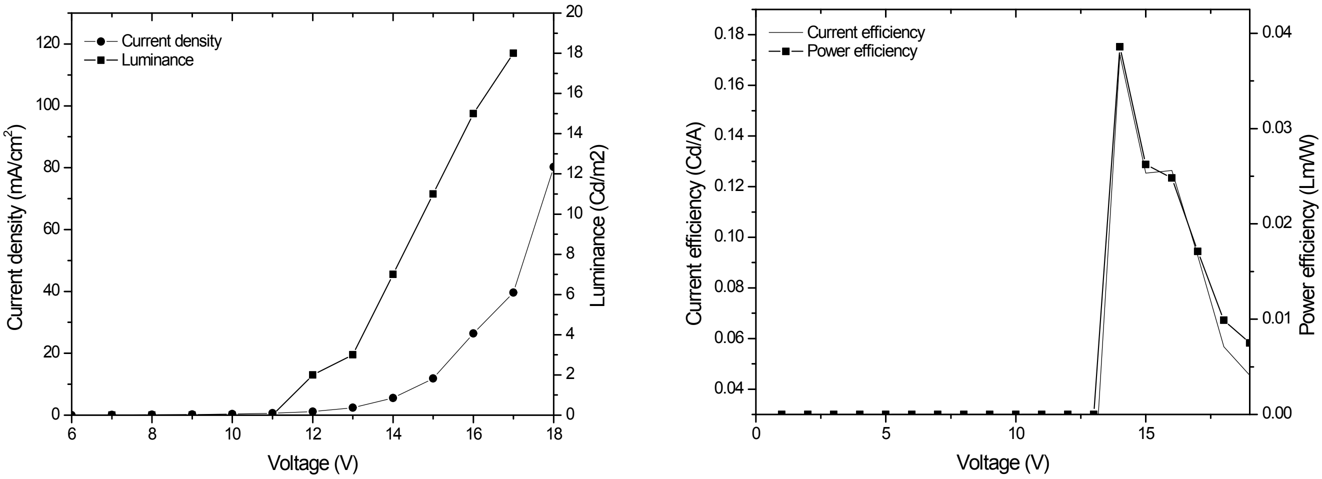


Fig. S21. J–V–L characteristics (left) and Current efficiency–voltage and power efficiency–voltage (right) of Device 7.

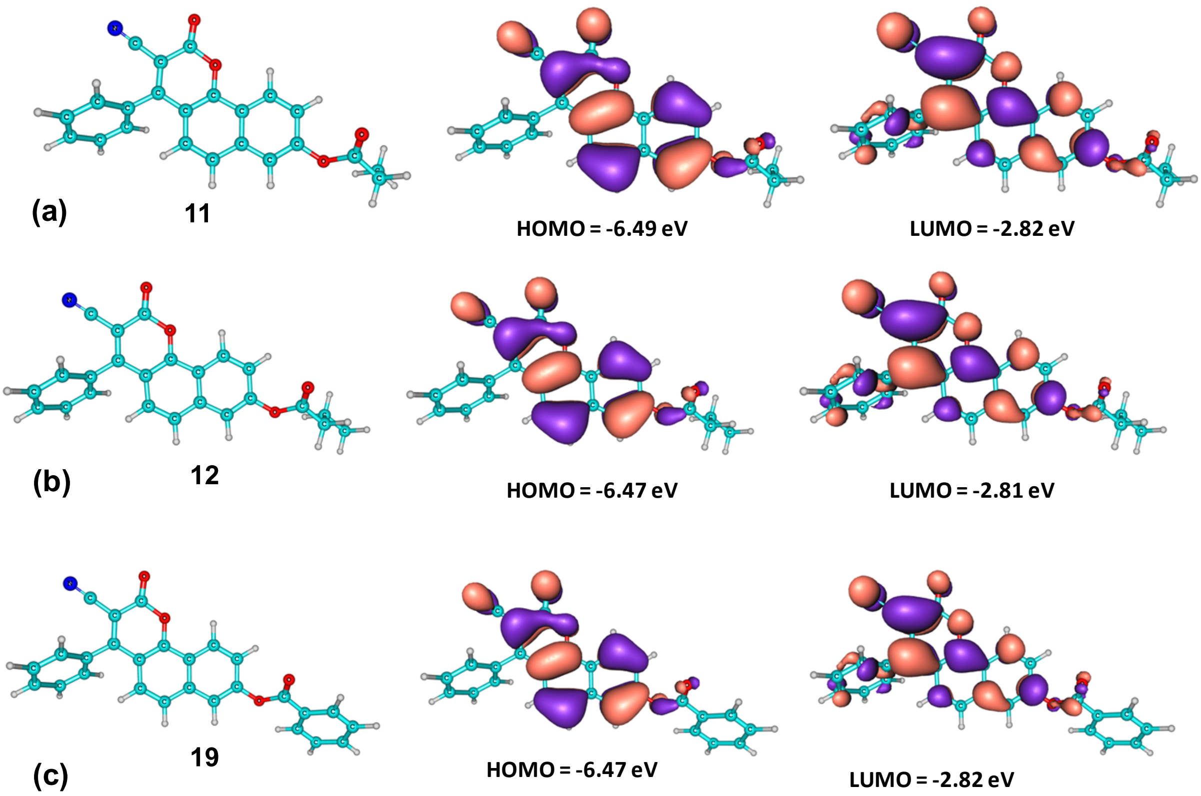
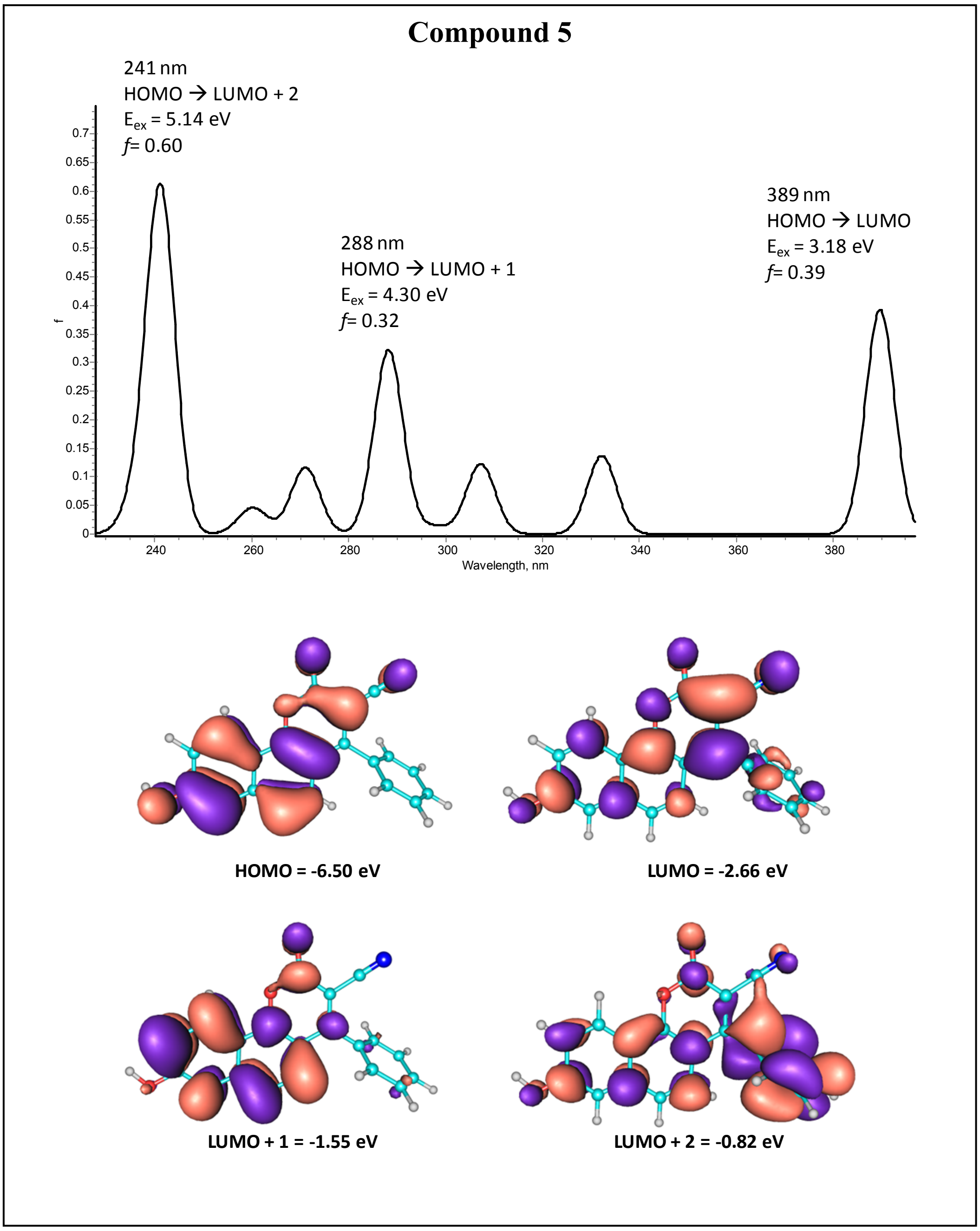
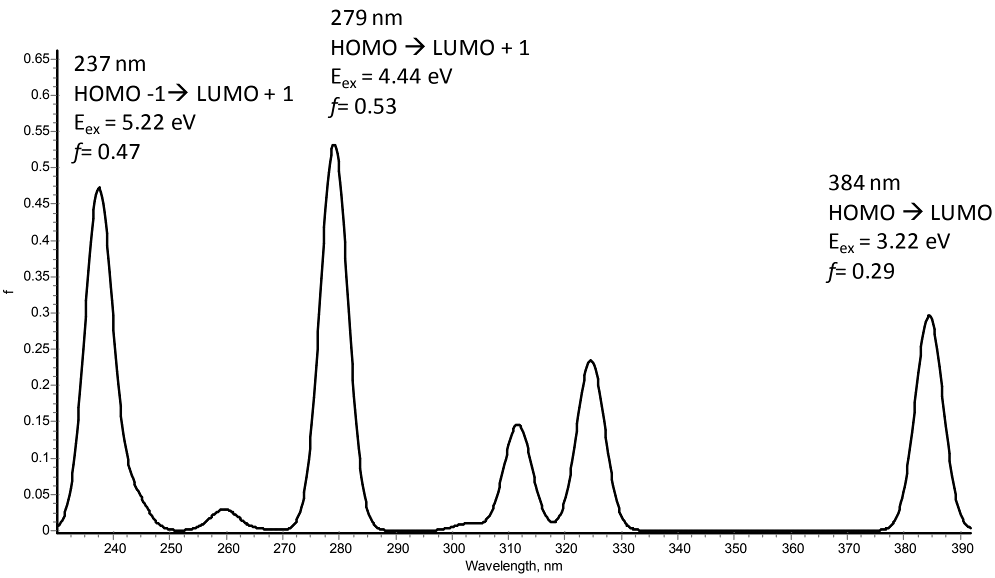


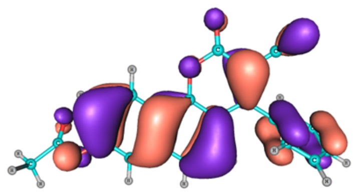
Fig. S22. a) Optimized structure and frontier molecular orbitals of **11**. b) Optimized structure and frontier molecular orbitals of **12.** c) Optimized structure and frontier molecular orbitals of **19**.

Fig. S23. TD-DFT absorption spectra of compounds 5, 8, 11, 12 and 19 calculated at PBE0/6-311G(d,p) in THF using the conductor-like polarizable continuum model (CPCM). Peaks are characterized with their absorption wavelength, major electronic transition, excitation energy (E_{ex}) and oscillator strength (*f*) are given. KS orbitals involved in electronic transitions are also depicted.

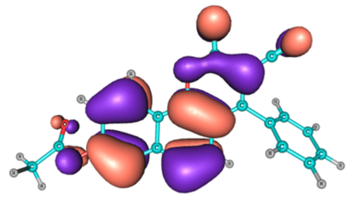


Compound 8

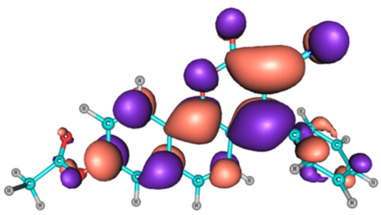




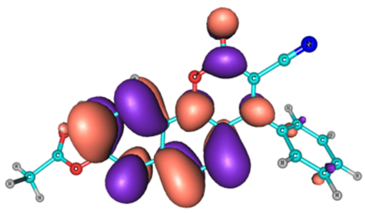
HOMO - 1 = -7.40 eV



HOMO = -6.71 eV

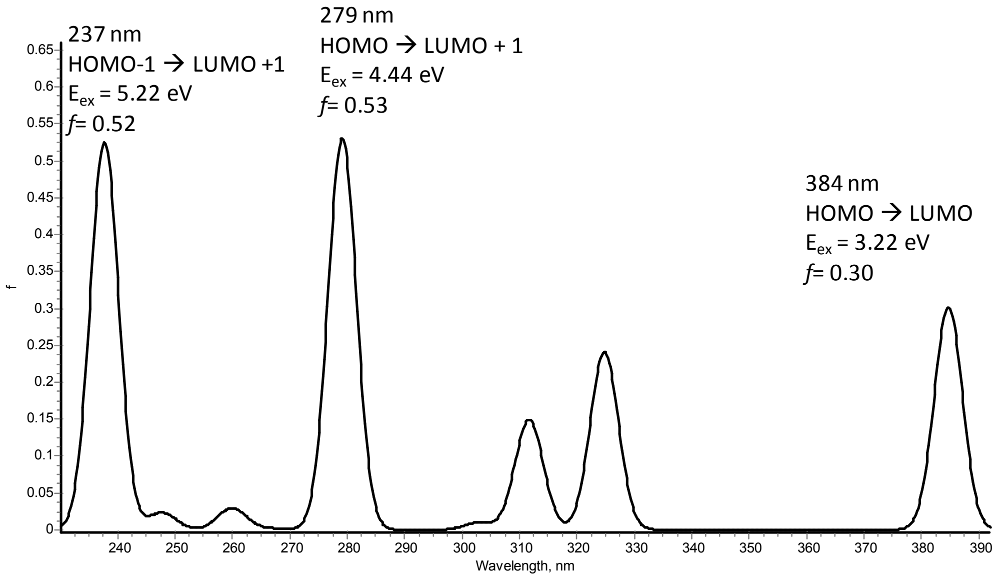


LUMO = -2.78 eV

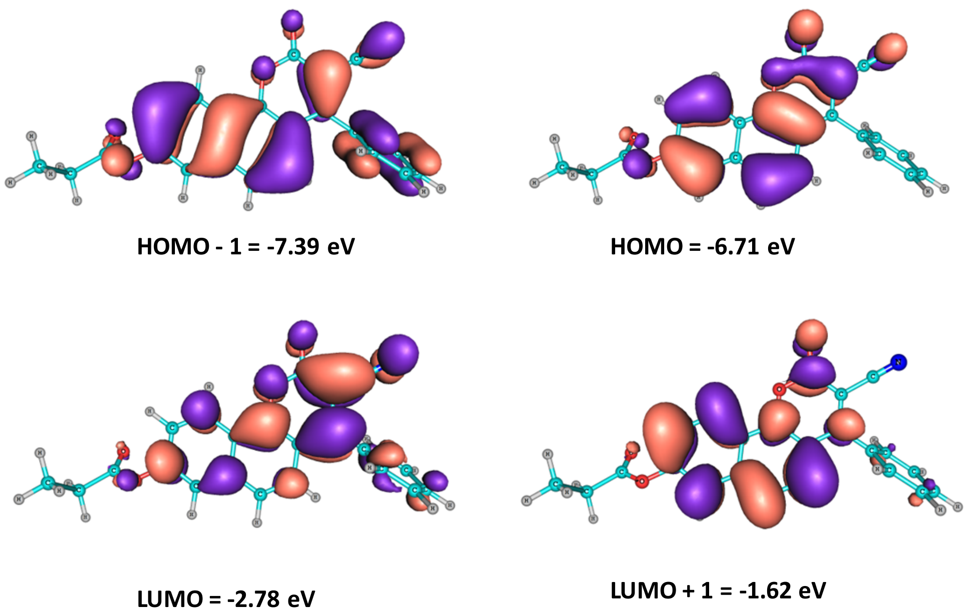


LUMO + 1 = -1.62 eV

Compound 11

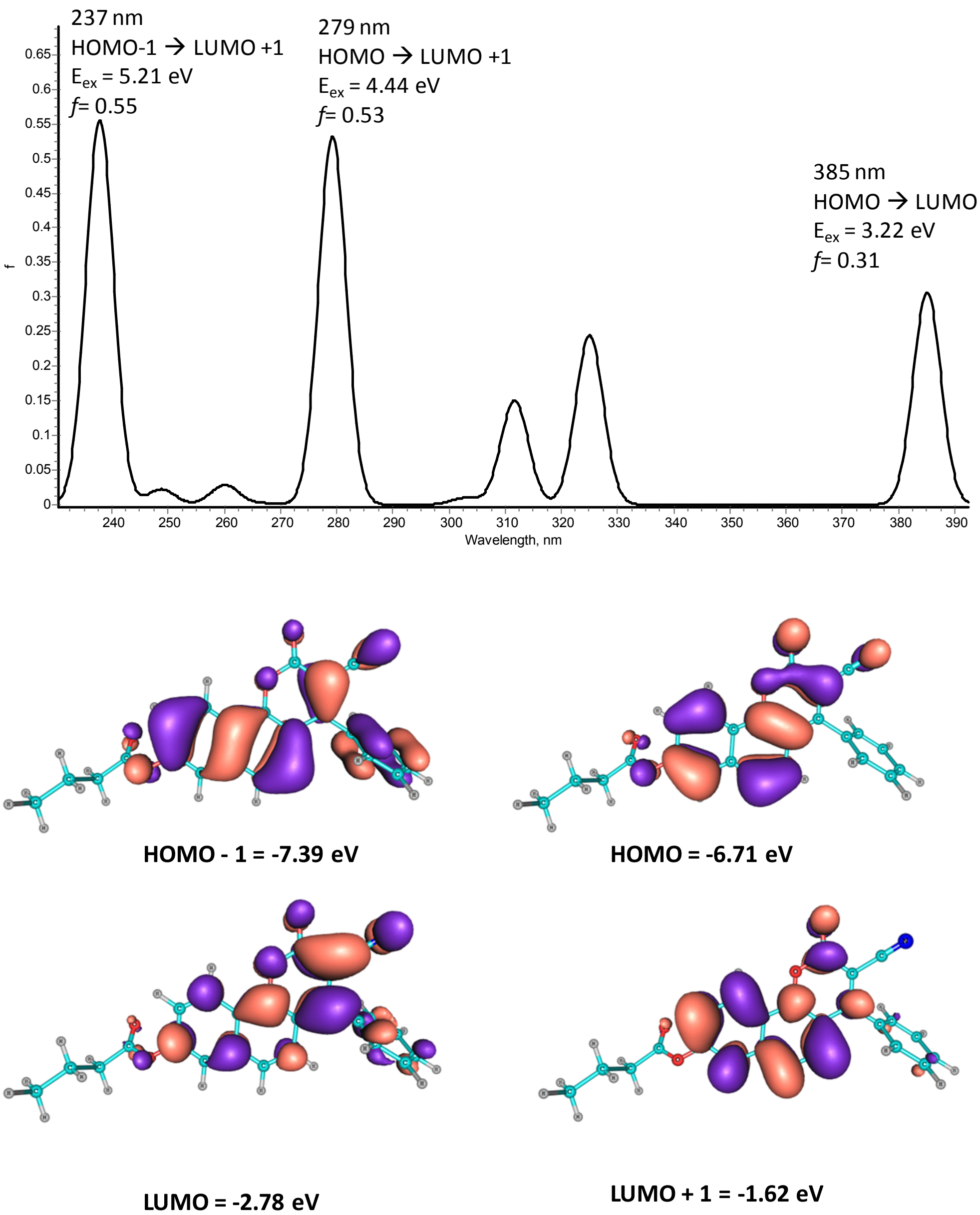


237 nm
HOMO-1 → LUMO +1
E_{ex} = 5.22 eV
f= 0.52
279 nm
HOMO → LUMO + 1
E_{ex} = 4.44 eV
f= 0.53
384 nm
HOMO → LUMO
E_{ex} = 3.22 eV
f= 0.30
f
Wavelength, nm

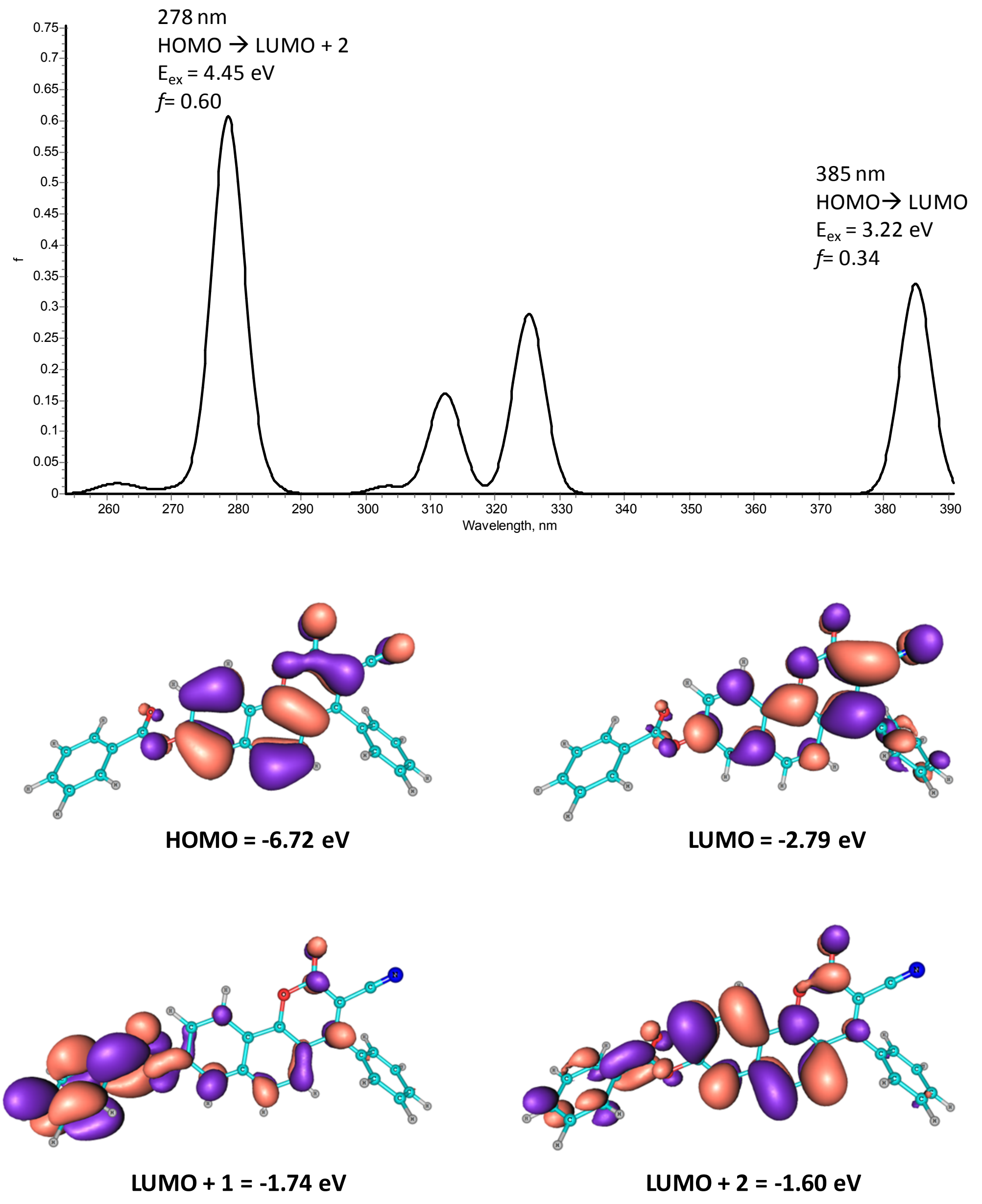


HOMO - 1 = -7.39 eV
HOMO = -6.71 eV
LUMO = -2.78 eV
LUMO + 1 = -1.62 eV

Compound 12


237 nm
HOMO-1 → LUMO +1
E_{ex} = 5.21 eV
f= 0.55
279 nm
HOMO → LUMO +1
E_{ex} = 4.44 eV
f= 0.53
385 nm
HOMO → LUMO
E_{ex} = 3.22 eV
f= 0.31
f
Wavelength, nm
HOMO - 1 = -7.39 eV
HOMO = -6.71 eV
LUMO = -2.78 eV
LUMO + 1 = -1.62 eV

Compound 19


278 nm
HOMO → LUMO + 2
E_{ex} = 4.45 eV
f= 0.60
385 nm
HOMO→ LUMO
E_{ex} = 3.22 eV
f= 0.34
f
Wavelength, nm
HOMO = -6.72 eV
LUMO = -2.79 eV
LUMO + 1 = -1.74 eV
LUMO + 2 = -1.60 eV

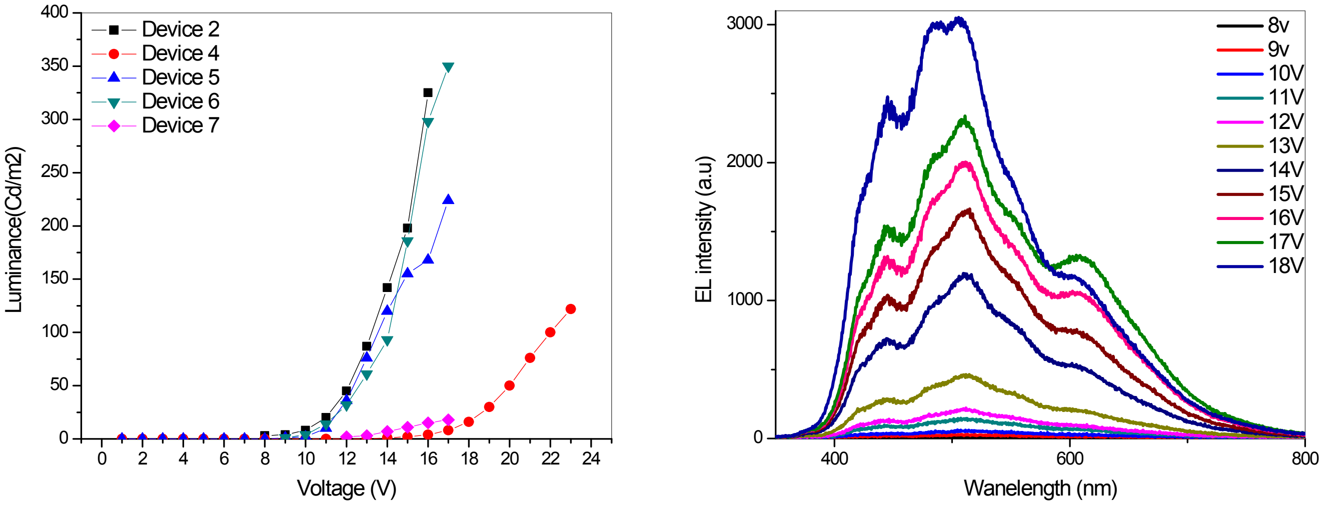


Fig. S24. Voltage – Luminance characteristic for Devices 2, 4, 5, 6 and 7 (left) and EL spectra of Device 2 at different voltages (right).

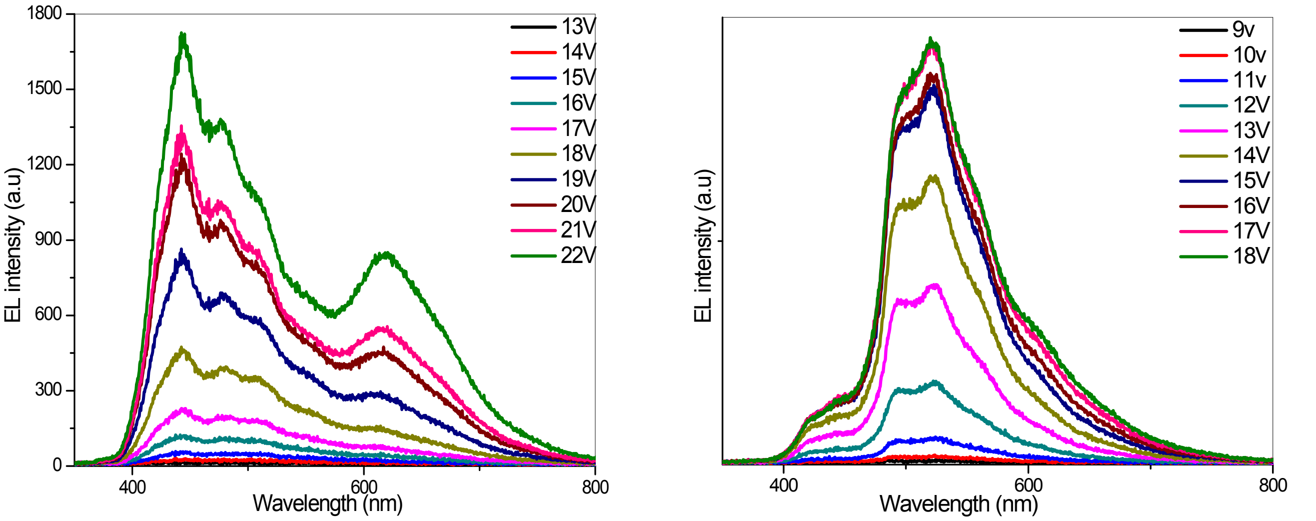


Fig. S25. EL spectra of Device 4 (left) and Device 5 (right) at different voltages.

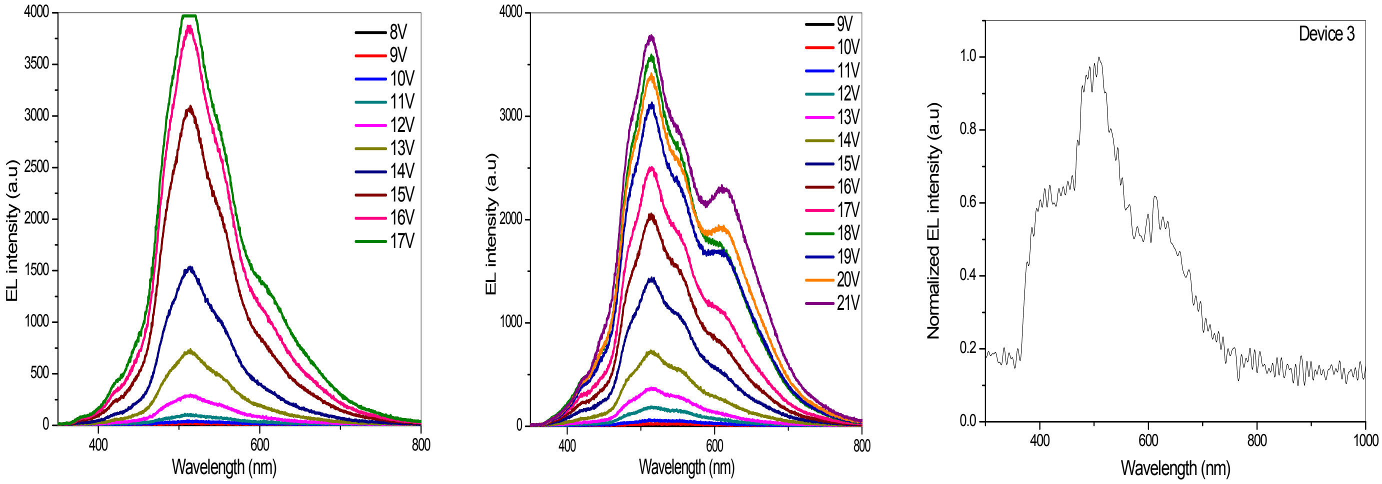


Fig. S26. EL spectra of Device 6 (left), Device 7 (middle) and Device 3 (right).

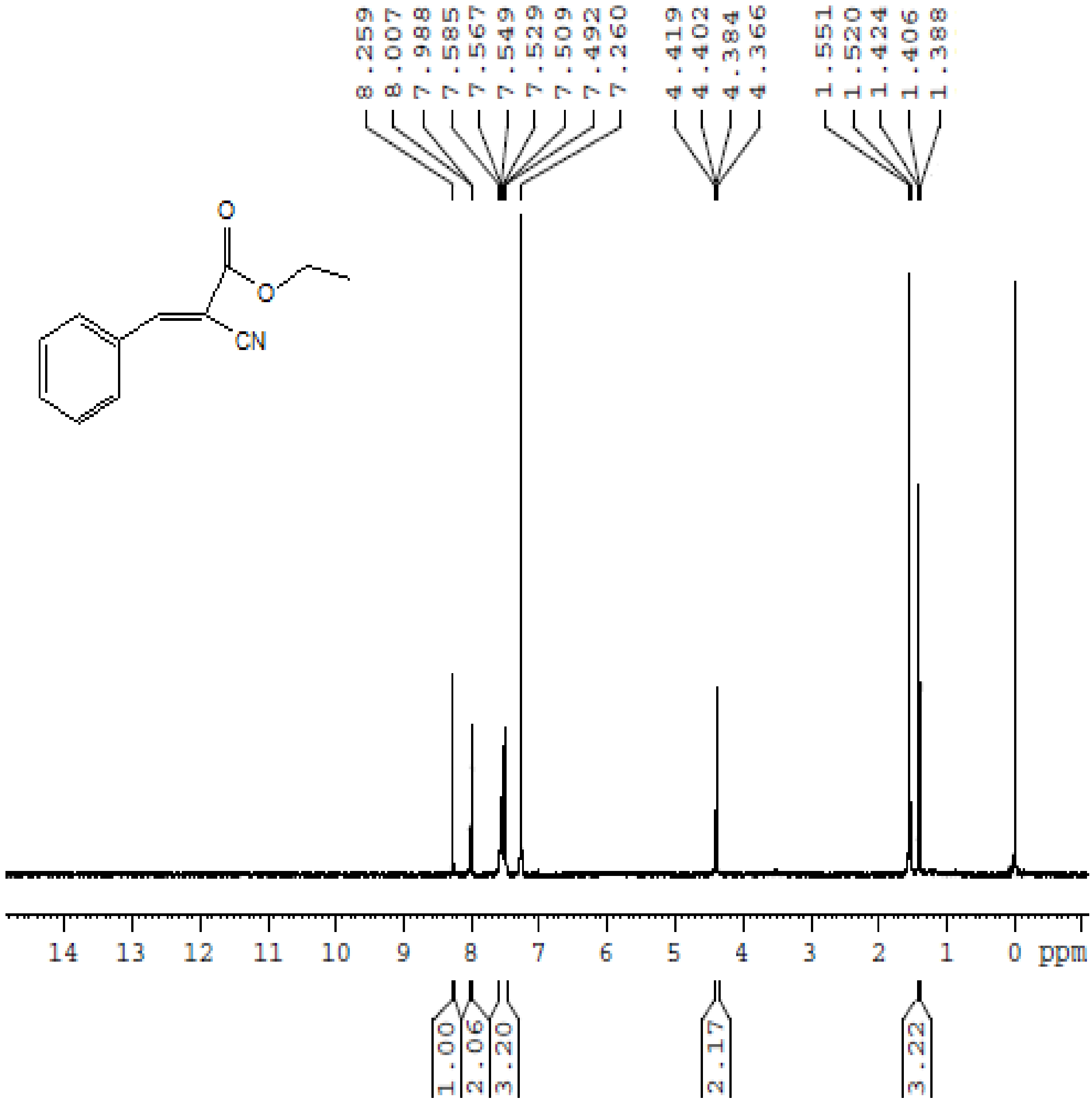


Fig. S27. ^{1}H-NMR spectra of **1**.

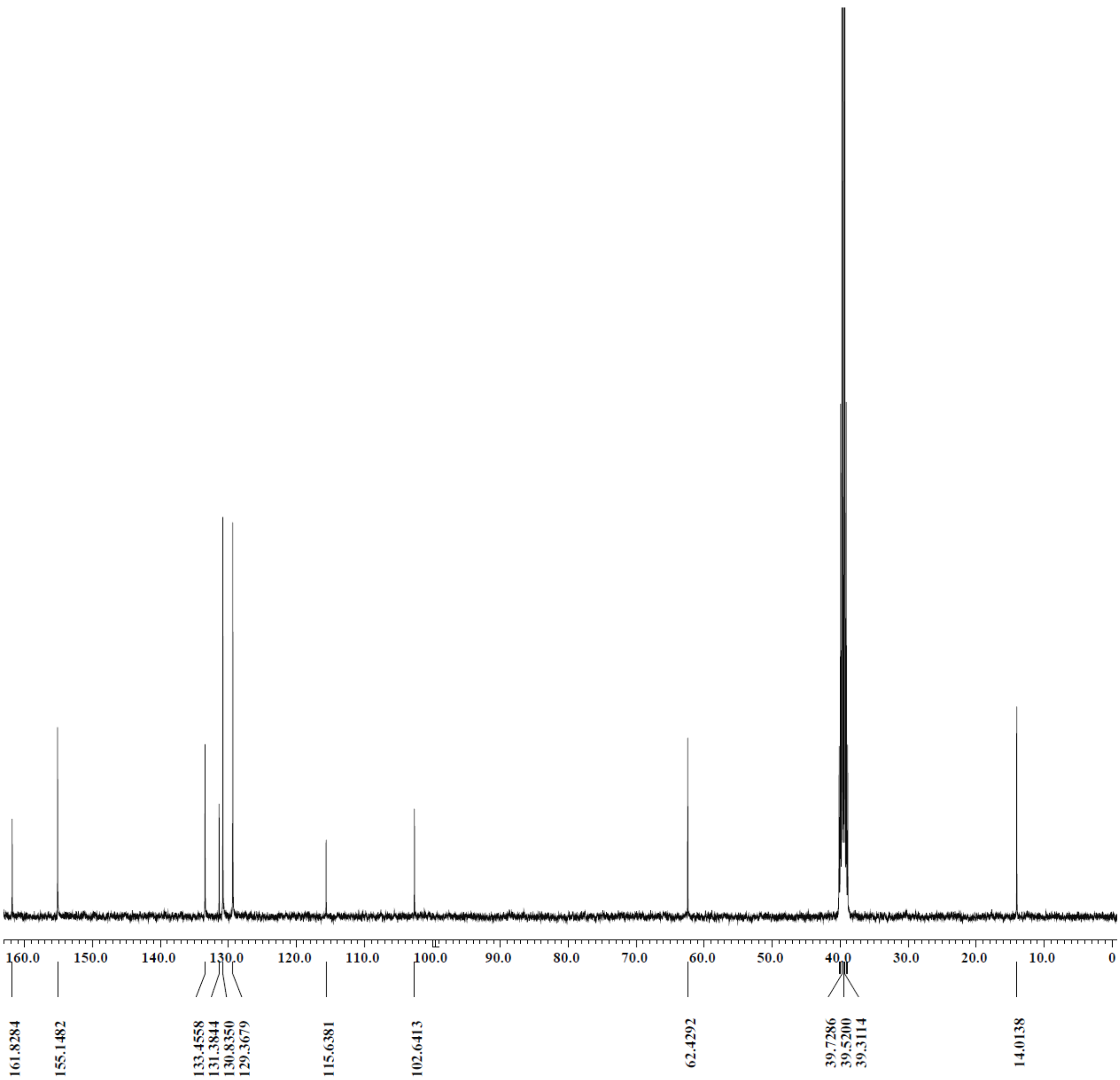


Fig. S28. ^{13}C-NMR spectra of **1**.

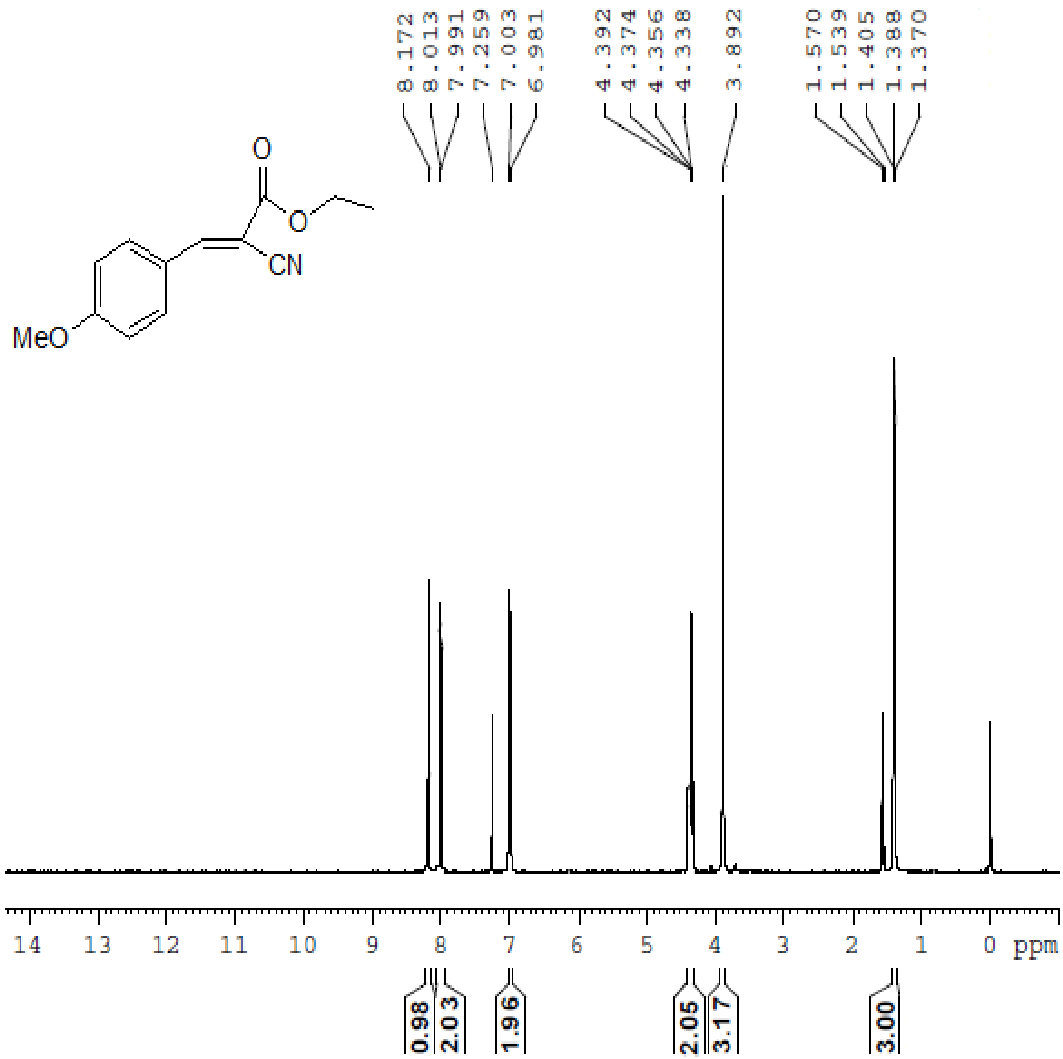


Fig. S29. ^{1}H-NMR spectra of **2**.

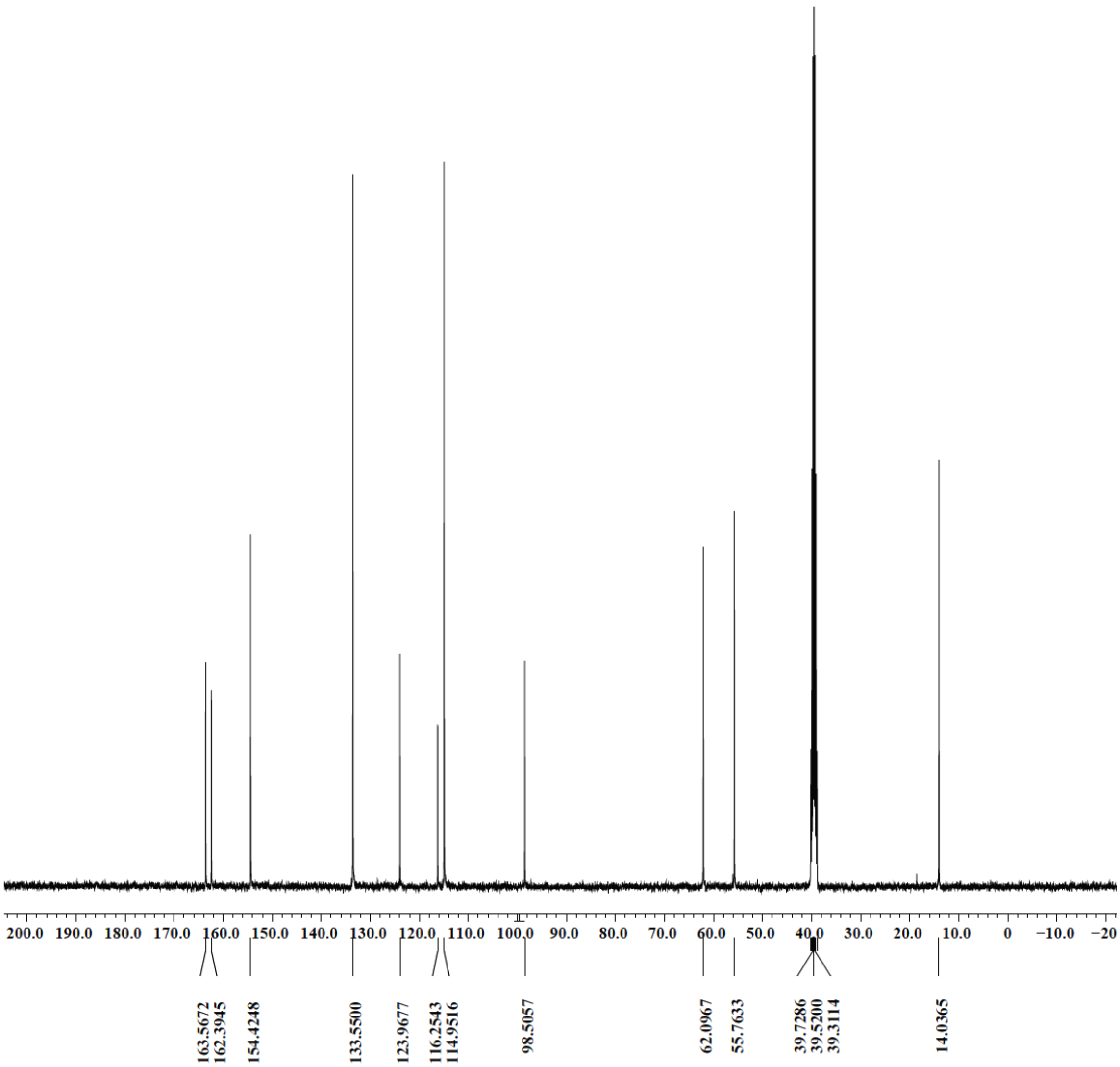


Fig. S30. ^{13}C-NMR spectra of **2.**

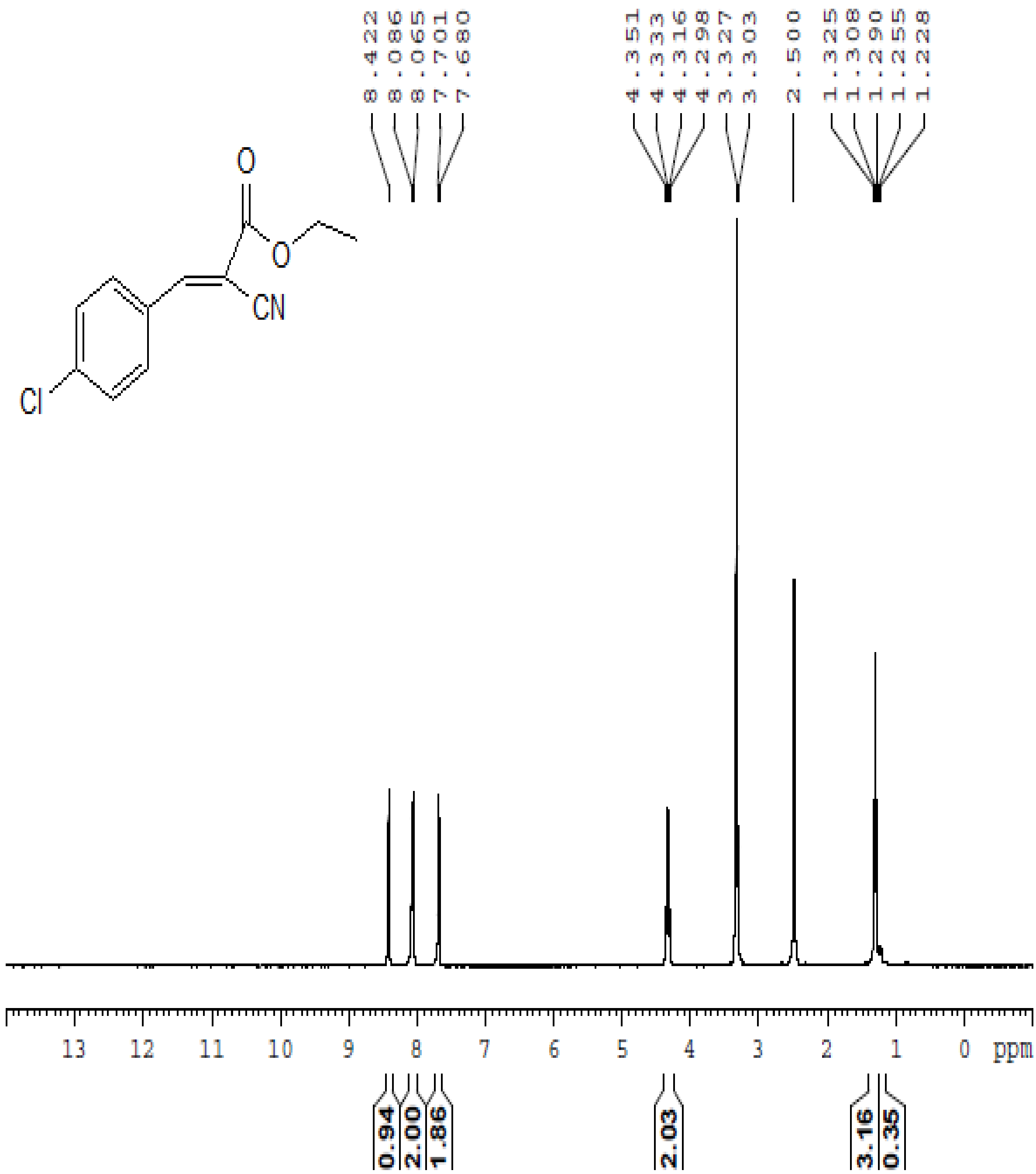


Fig. S31. ^{1}H-NMR spectra of **3**.

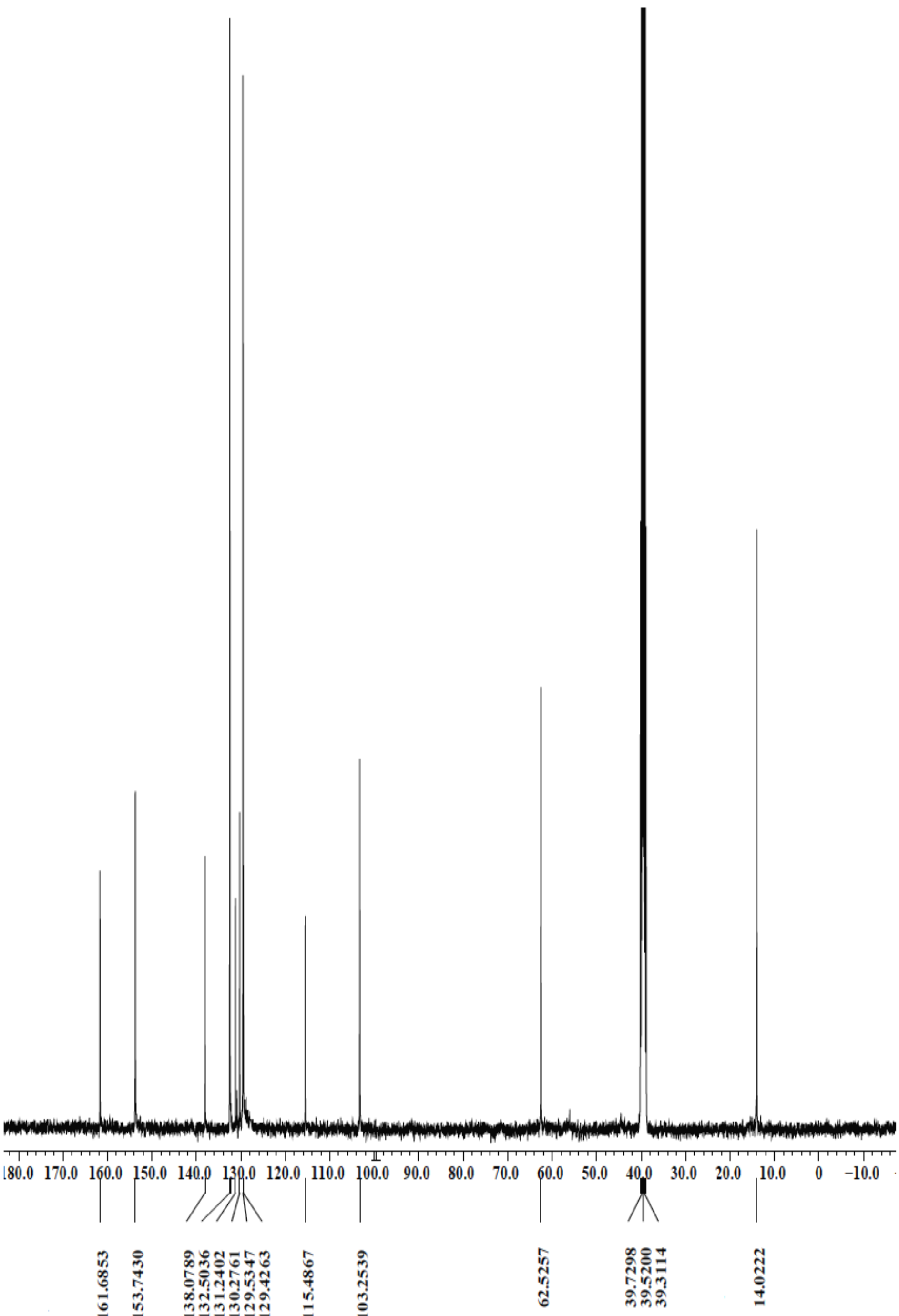


Fig. S32. ^{13}C-NMR spectra of **3.**

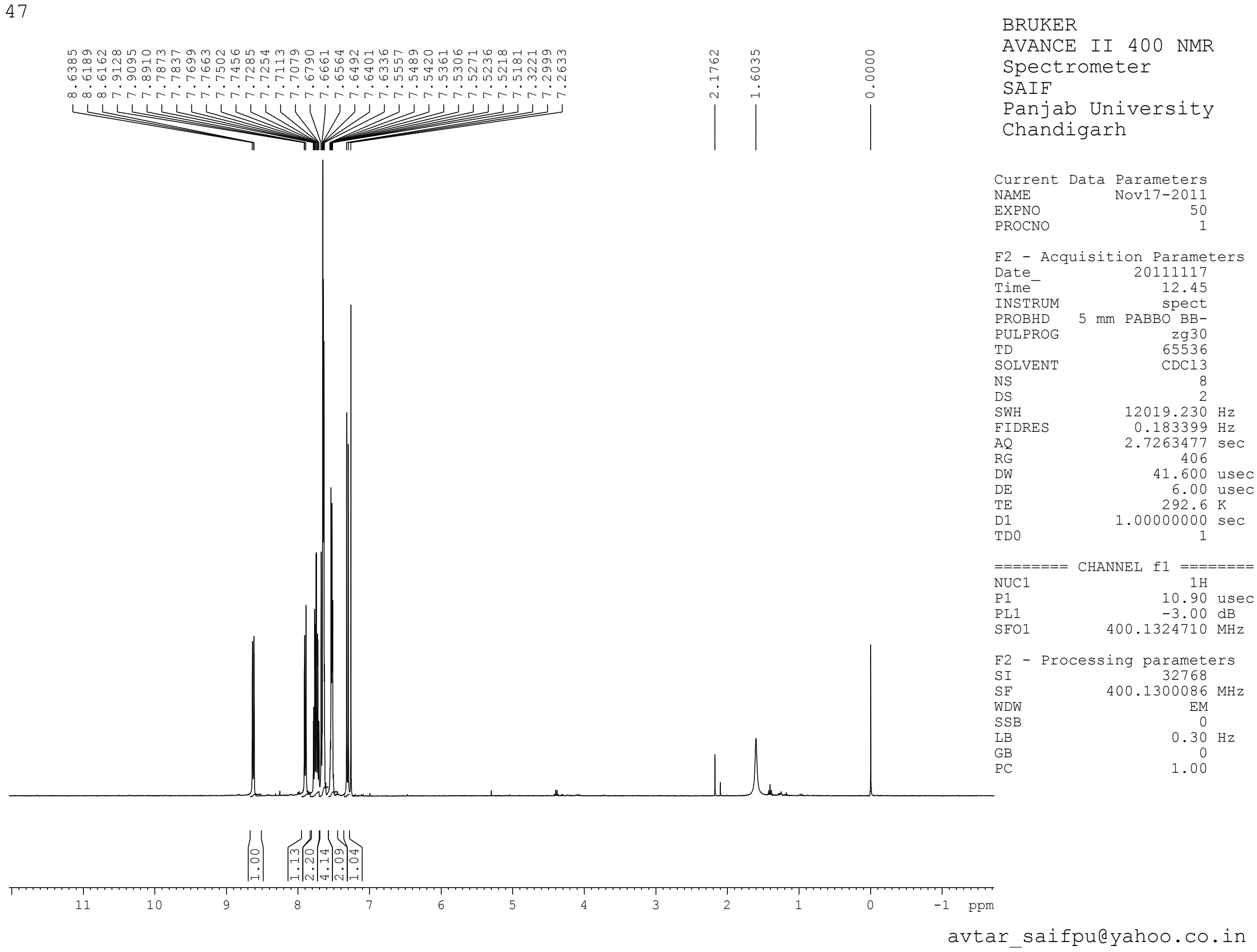


Fig. S33. ^{1}H-NMR spectra of **4.**

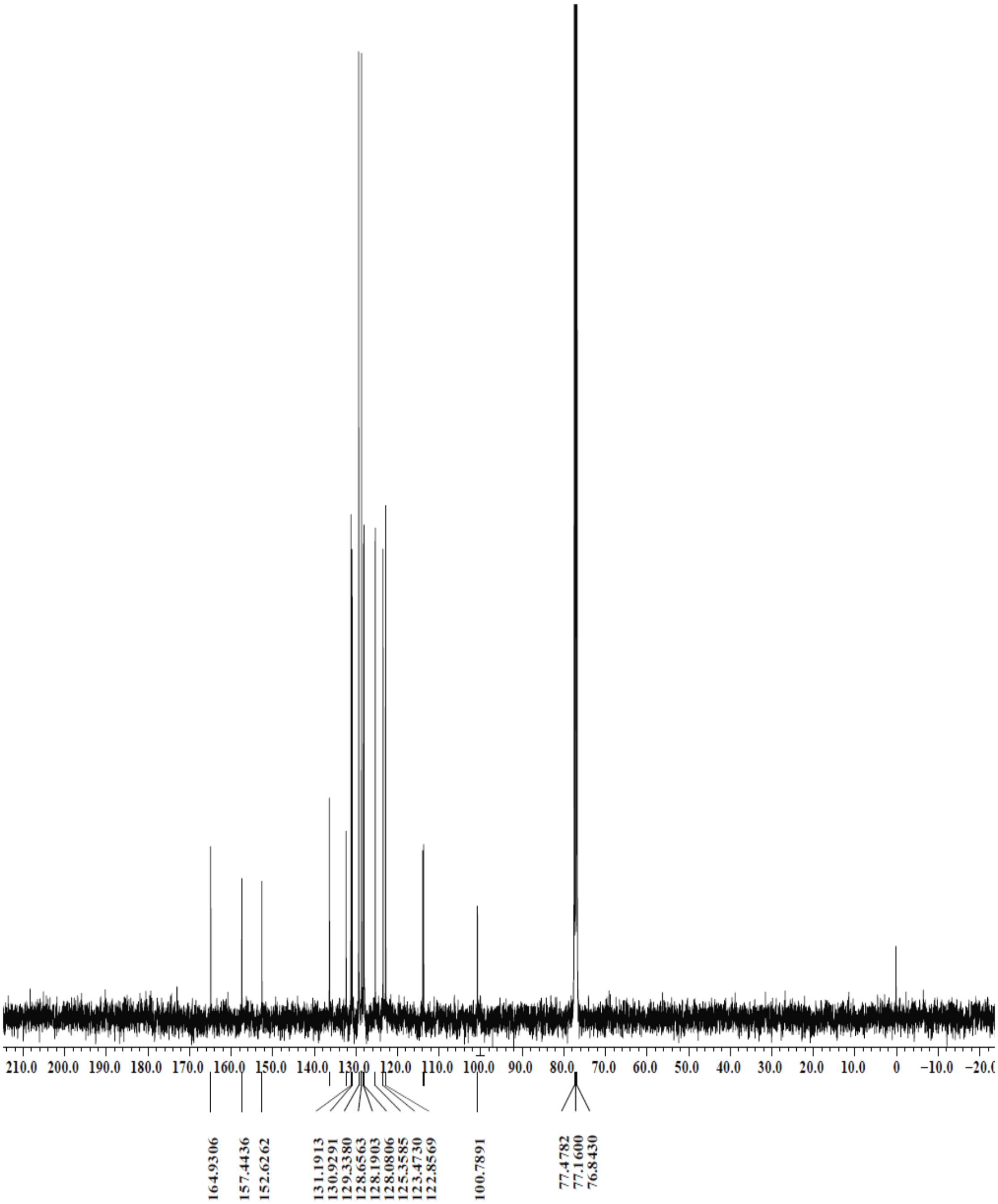


Fig. S34. ^{13}C-NMR spectra of **4.**

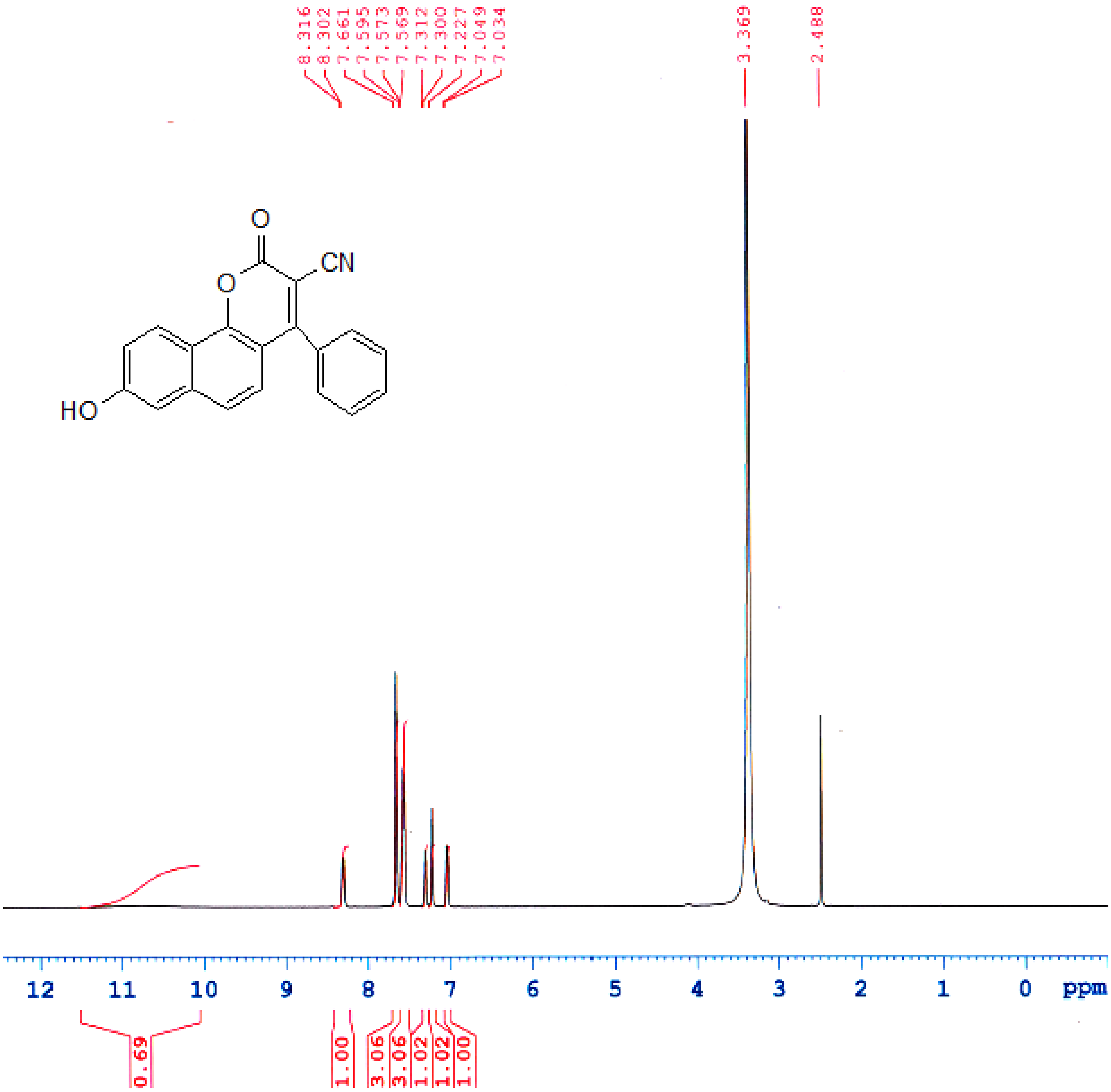


Fig. S35. ^{1}H-NMR spectra of **5.**

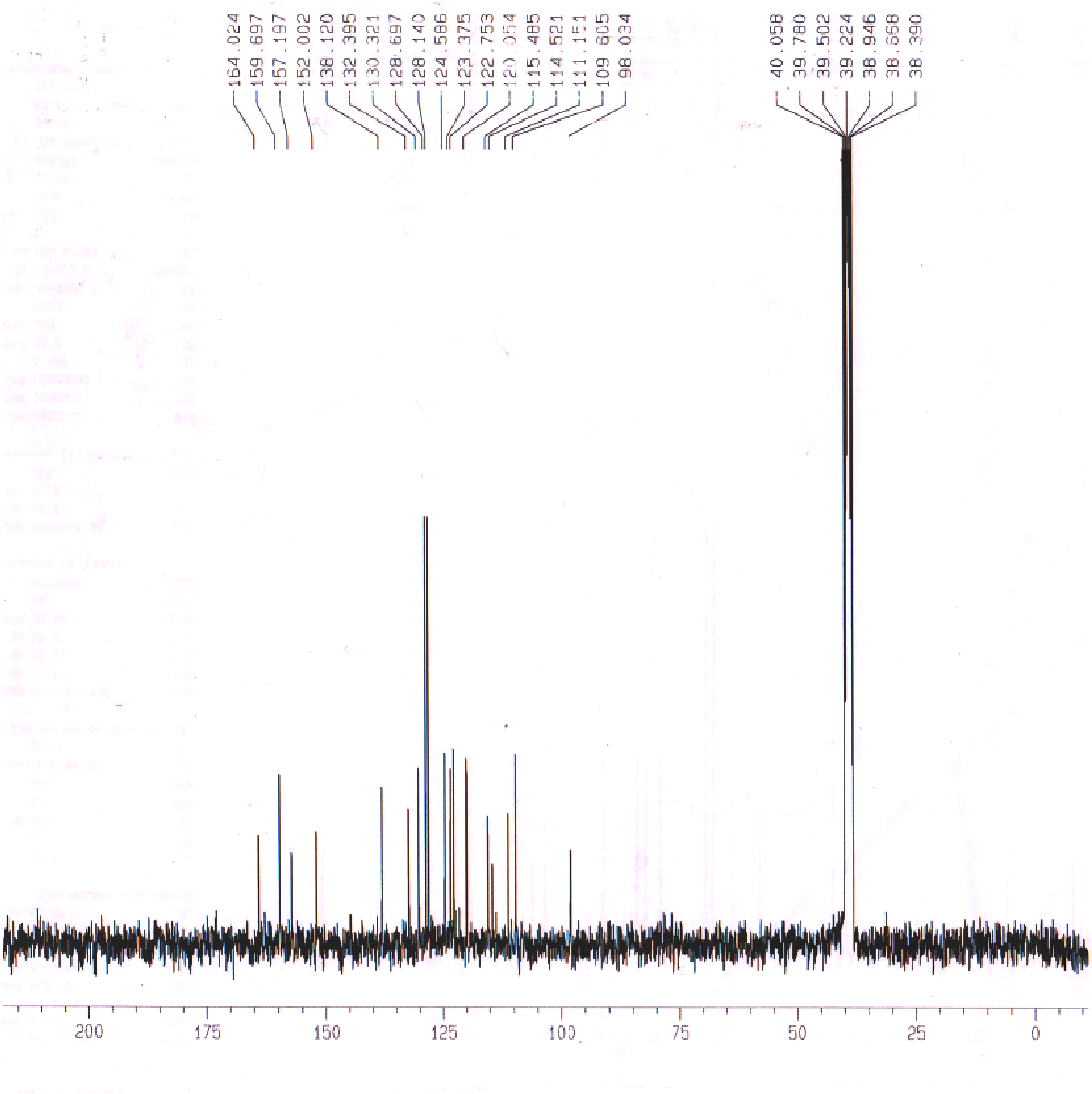


Fig. S36. ^{13}C-NMR spectra of **5.**

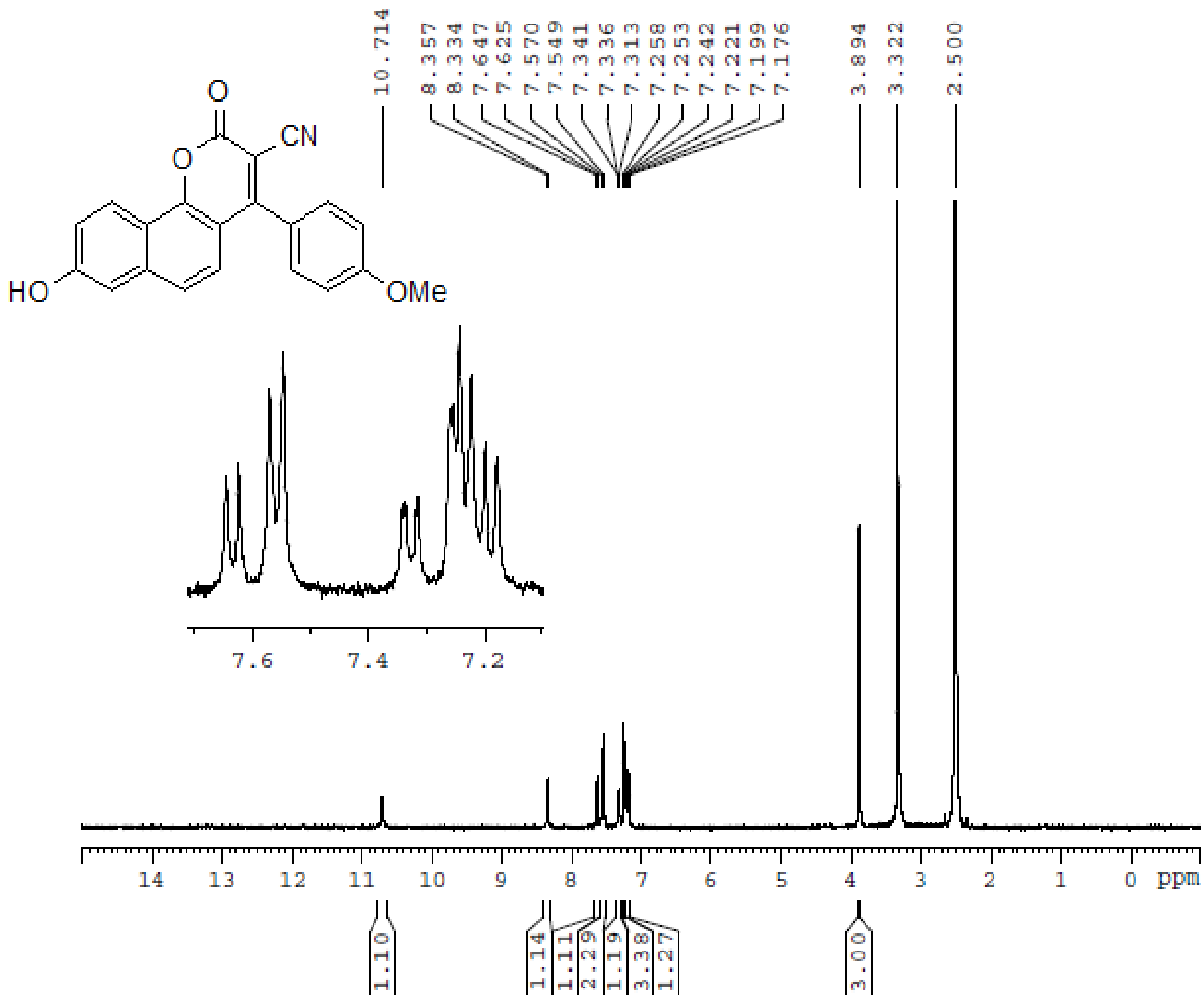


Fig. S37. ¹H-NMR spectra of **6.**

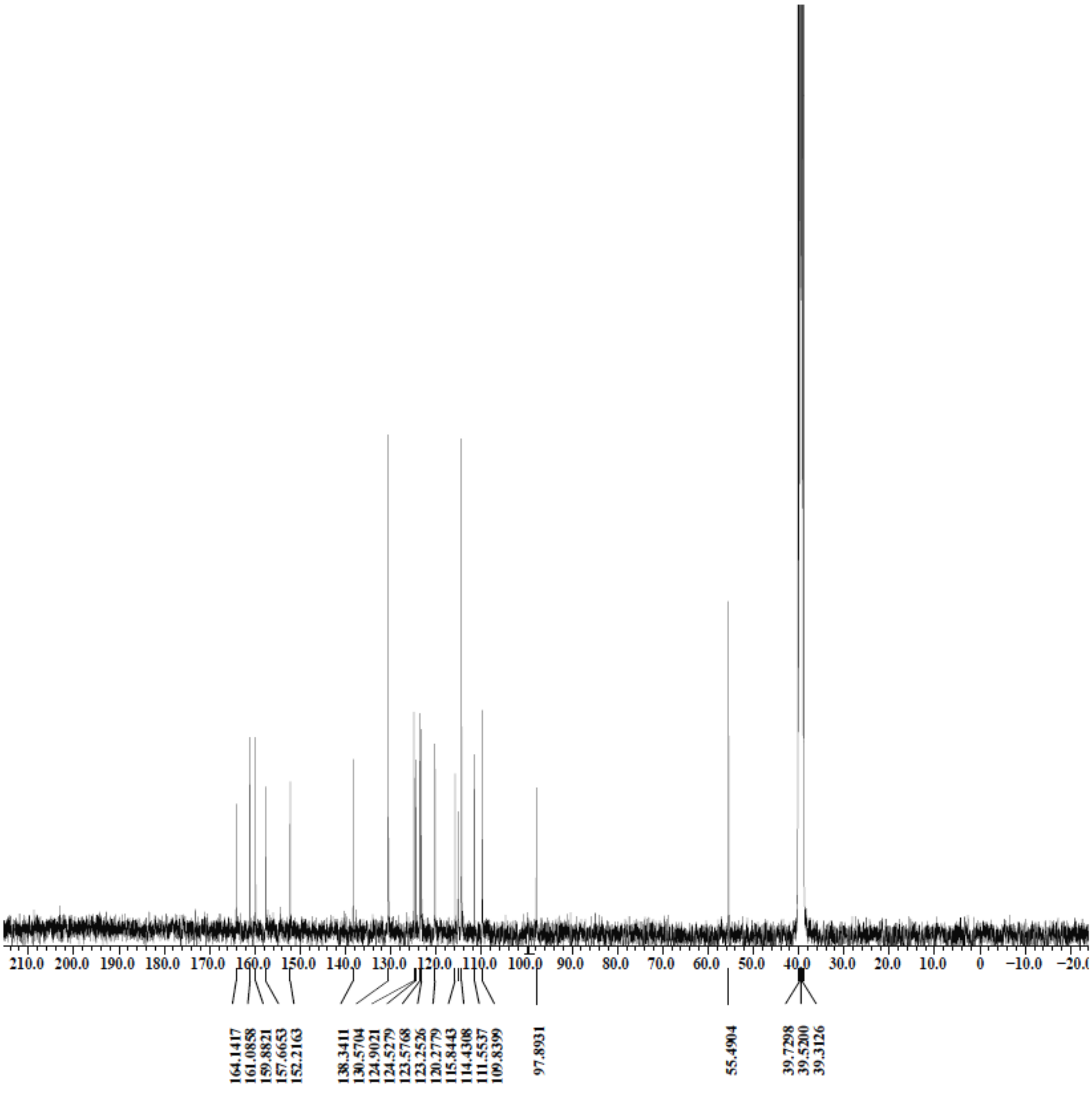


Fig. S38. ^{13}C-NMR spectra of **6.**

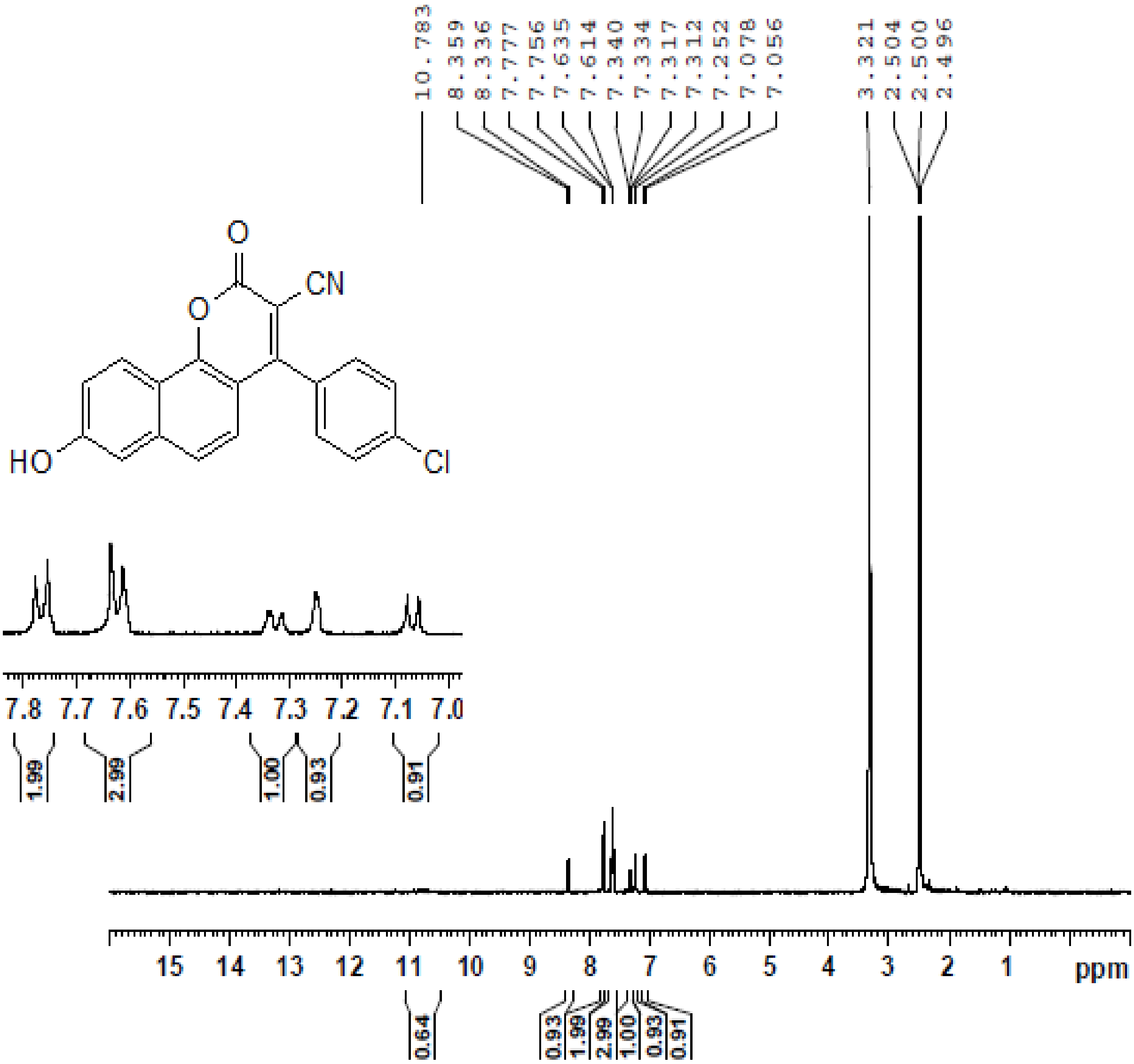


Fig. S39. ^{1}H-NMR spectra of **7.**

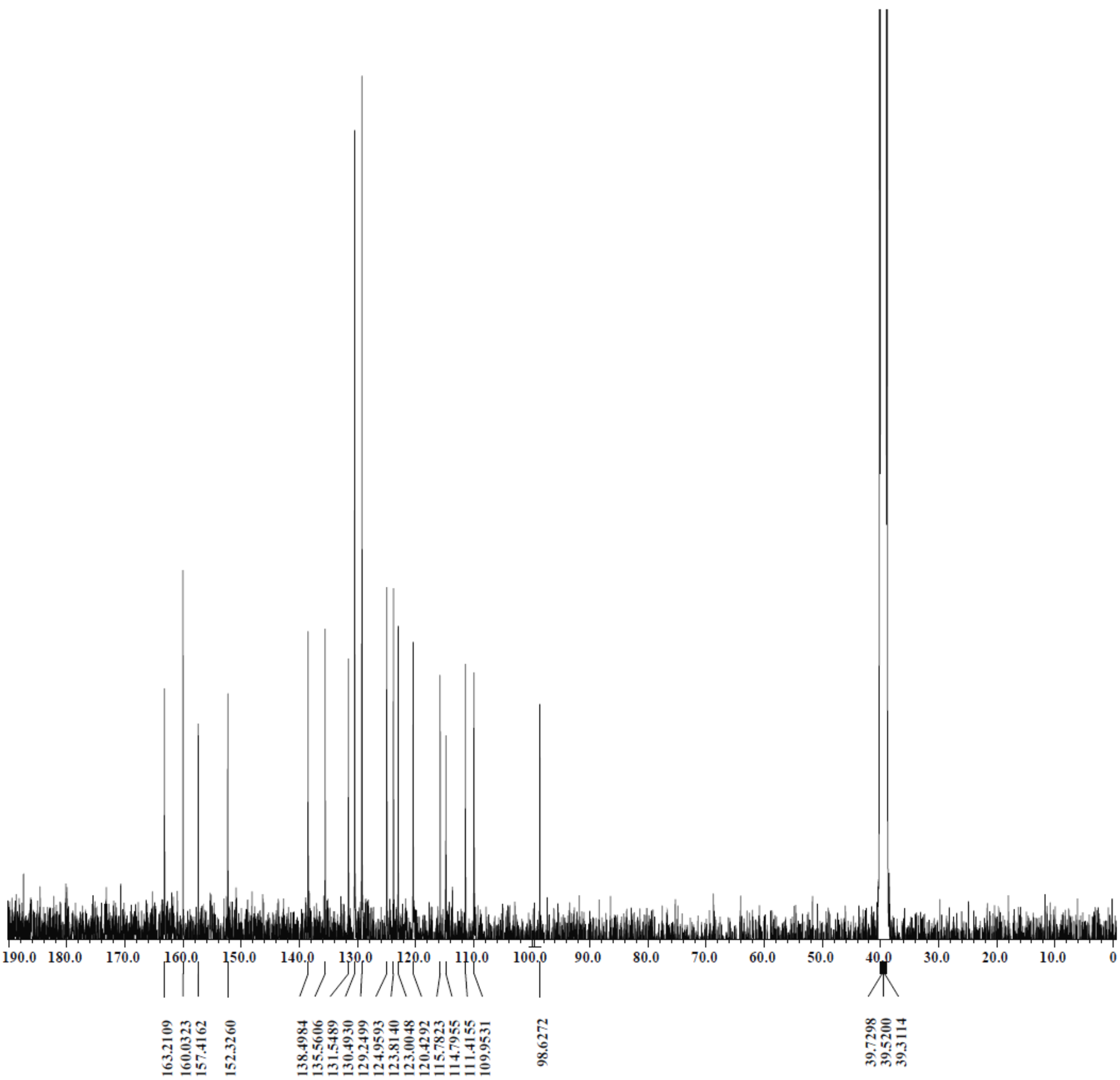
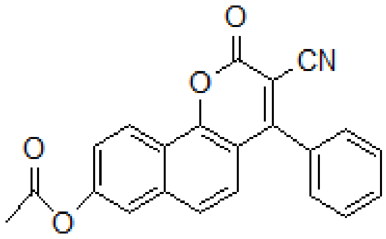


Fig. S40. ^{13}C-NMR spectra of **7.**



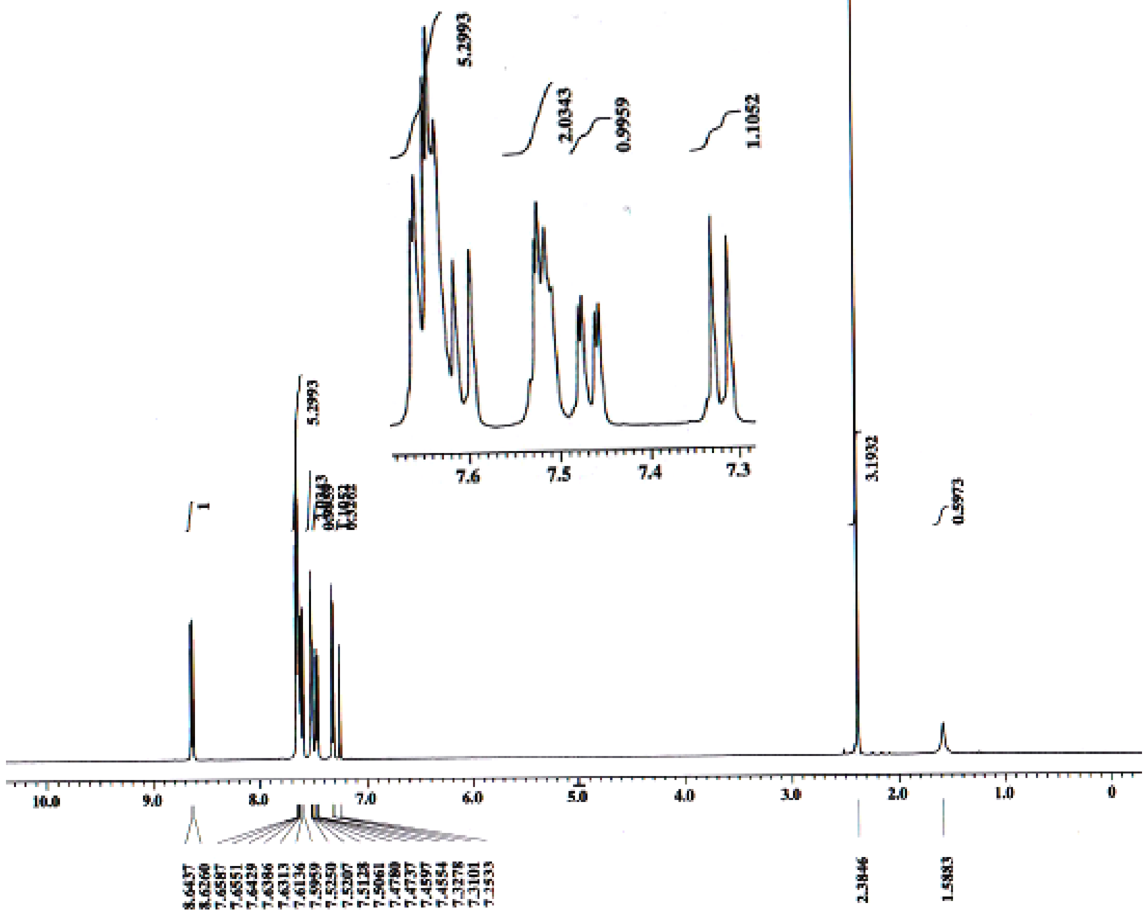


Fig. S41. ^{1}H-NMR spectra of **8.**

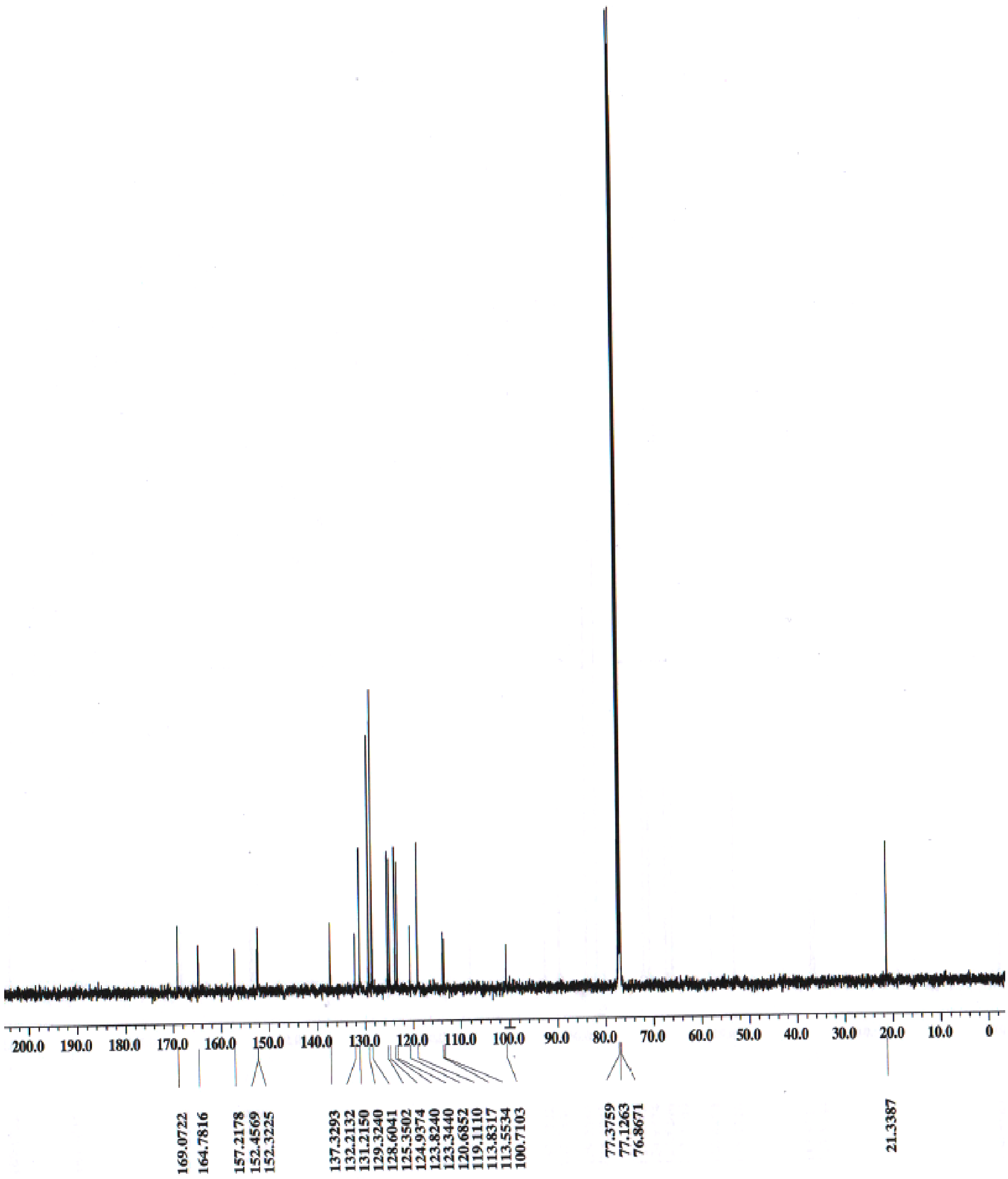


Fig. S42. ^{13}C-NMR spectra of **8.**

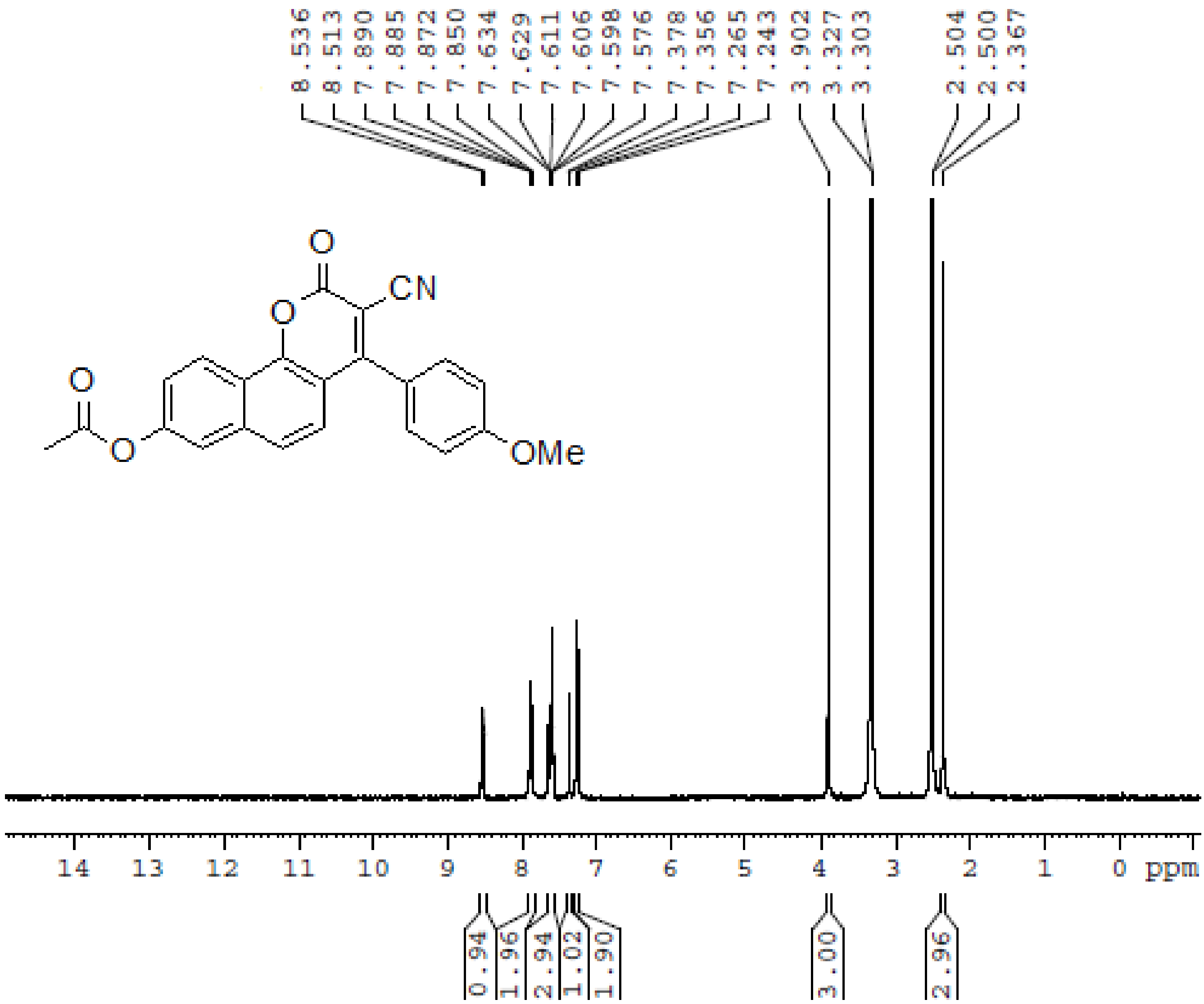


Fig. S43. ^{1}H-NMR spectra of **9.**

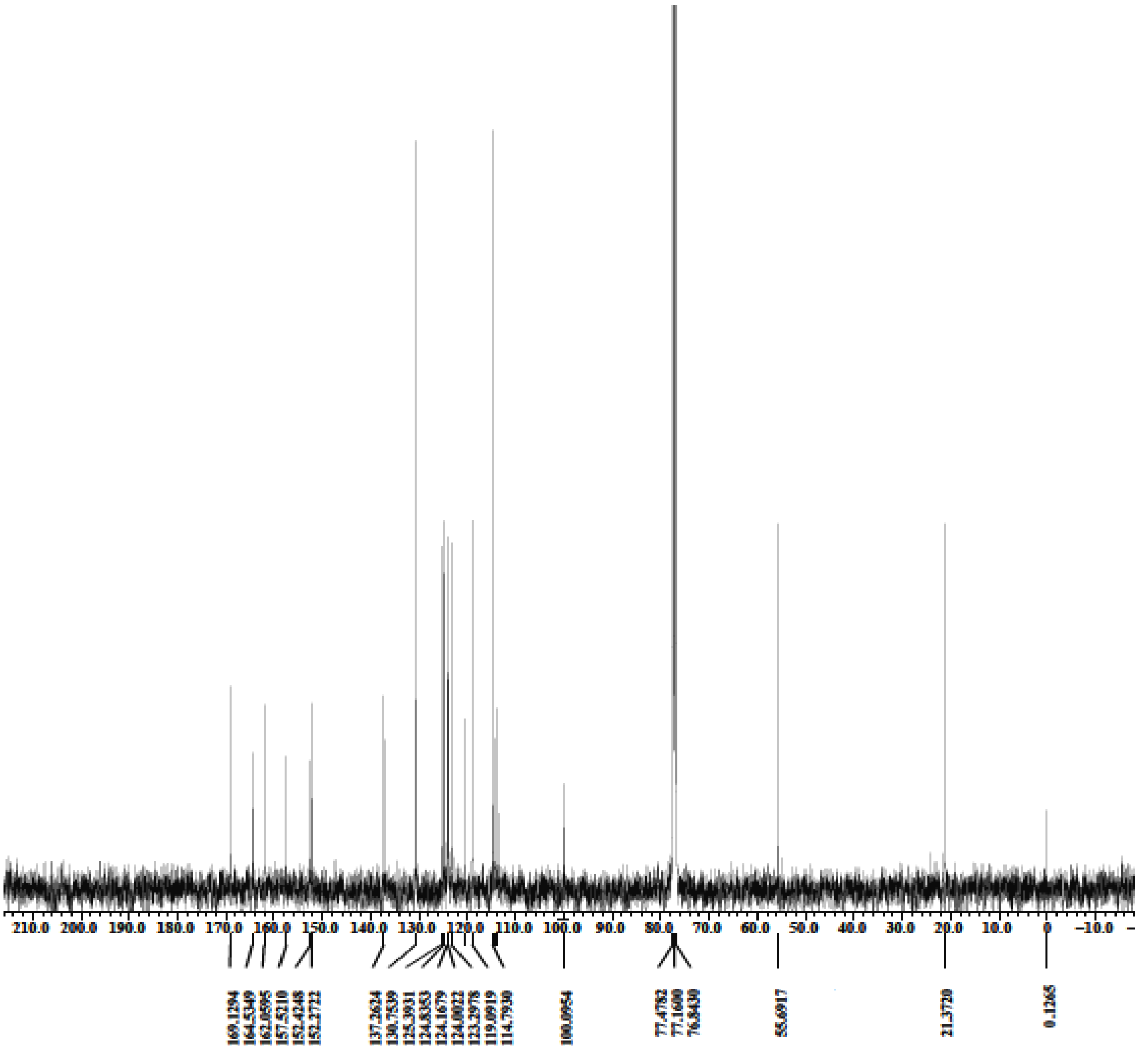


Fig. S44. ^{13}C-NMR spectra of **9**

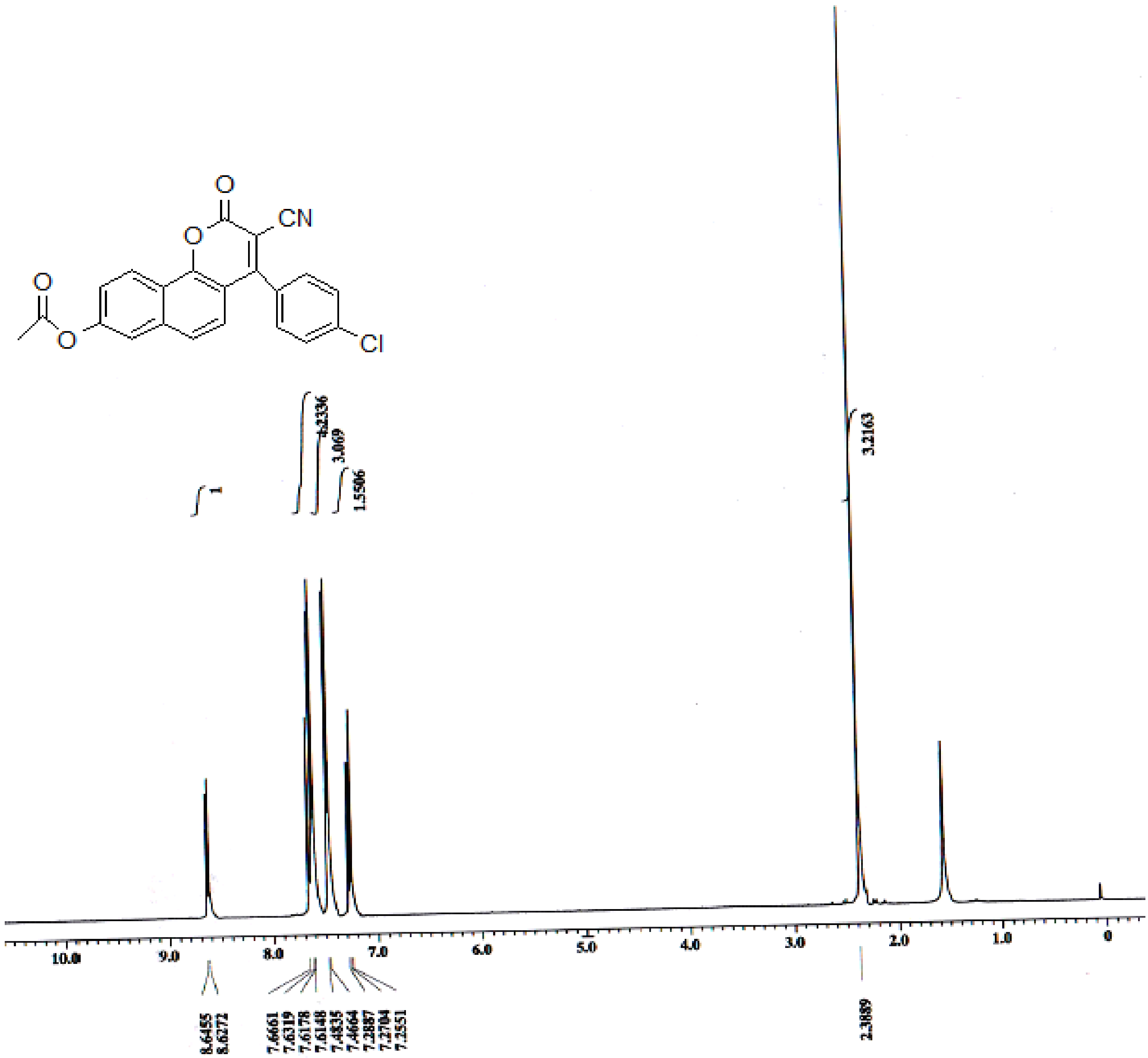


Fig. S45. ^{1}H-NMR spectra of **10**

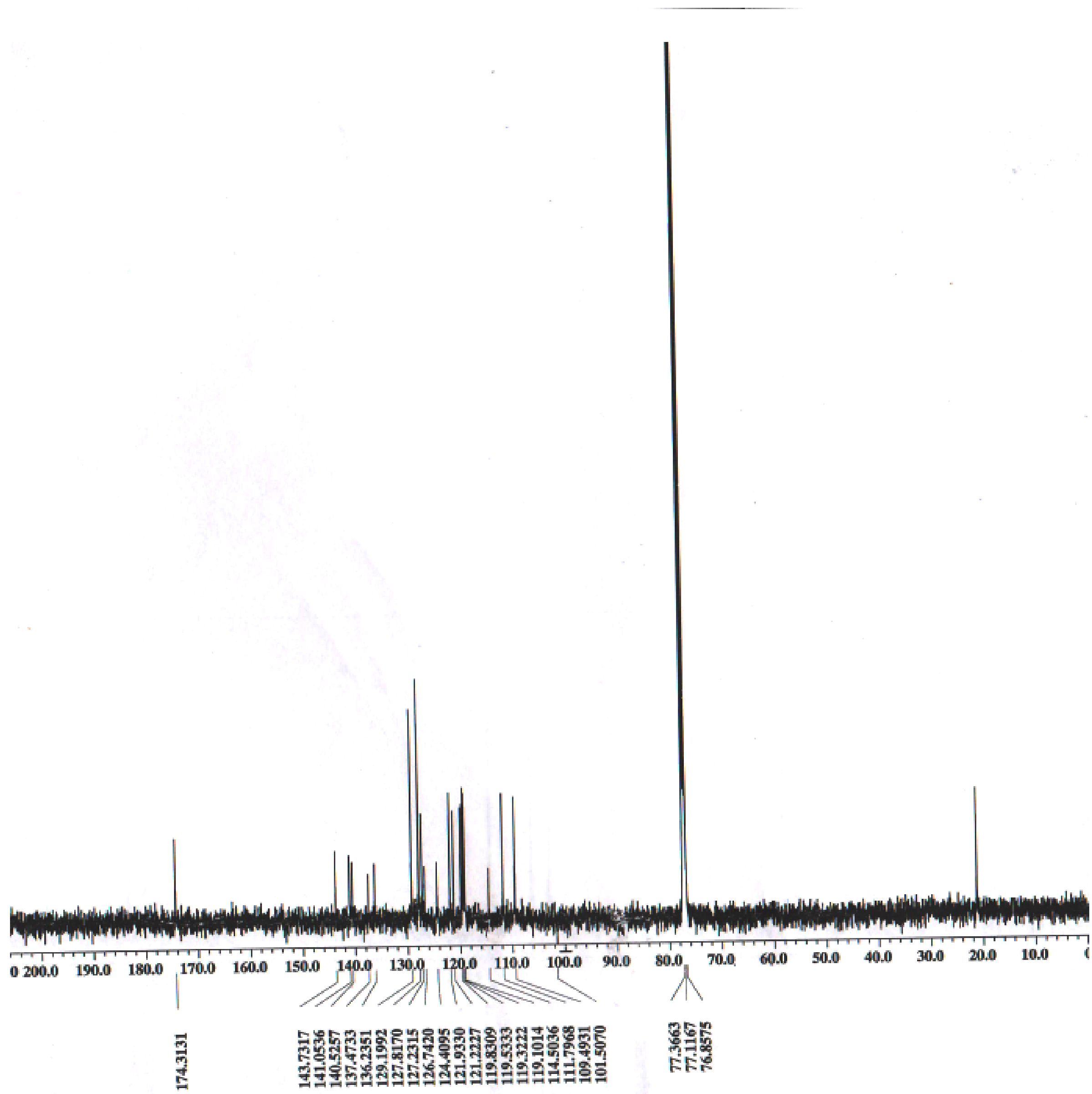


Fig. S46. ^{13}C-NMR spectra of **10.**

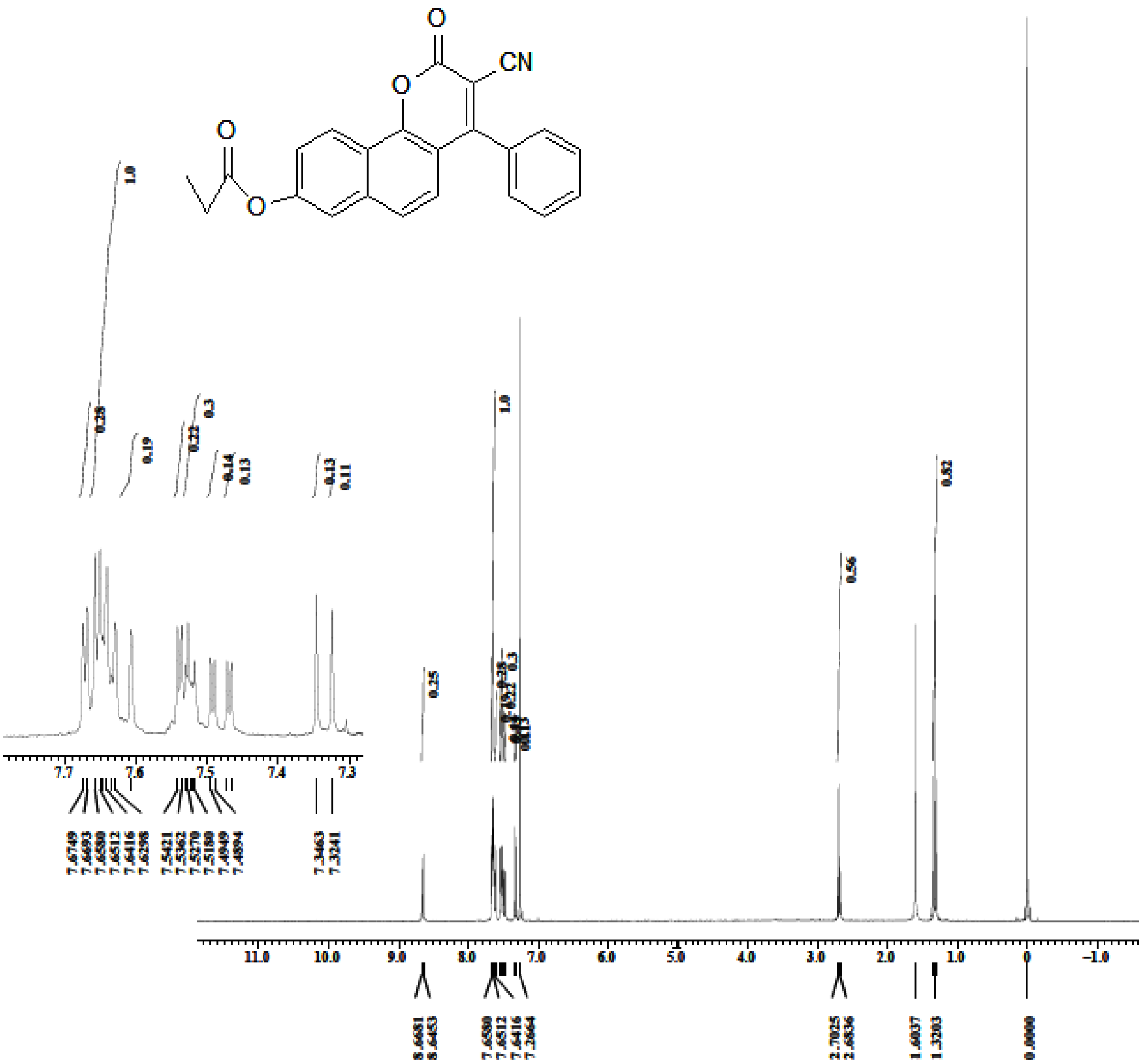


Fig. S47. ^{1}H-NMR spectra of **11**

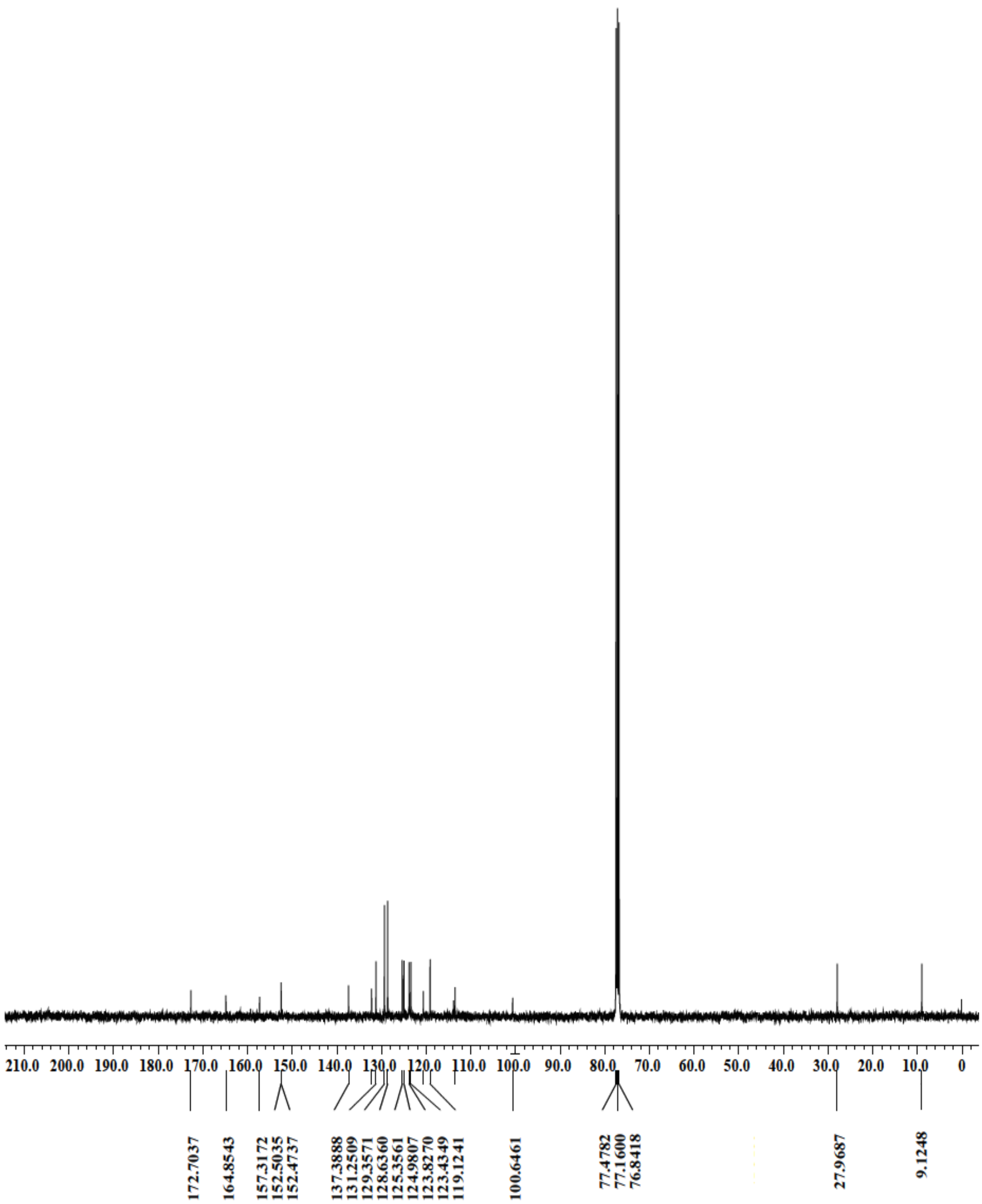


Fig. S48. ^{13}C-NMR spectra of **11**

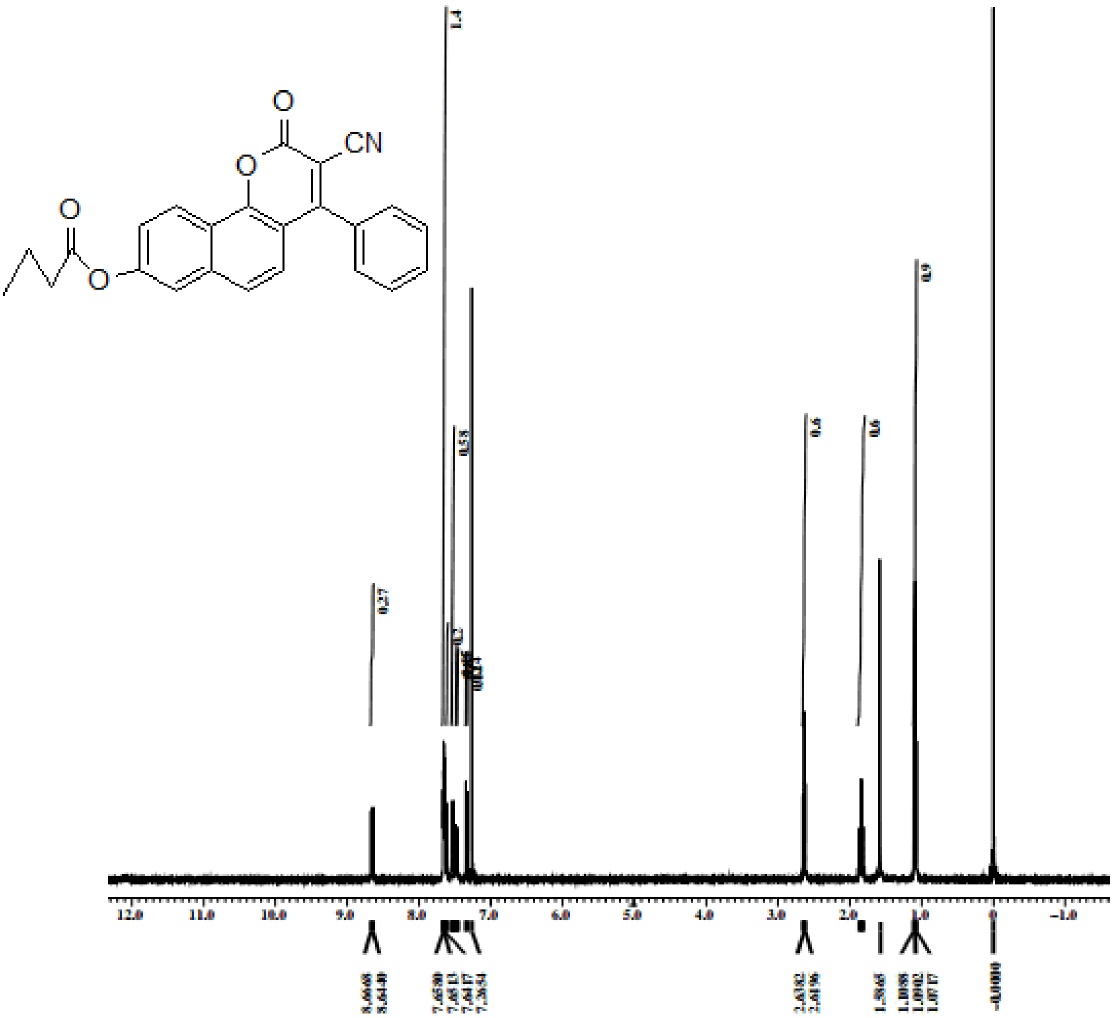


Fig. S49. ^{1}H-NMR spectra of **12.**

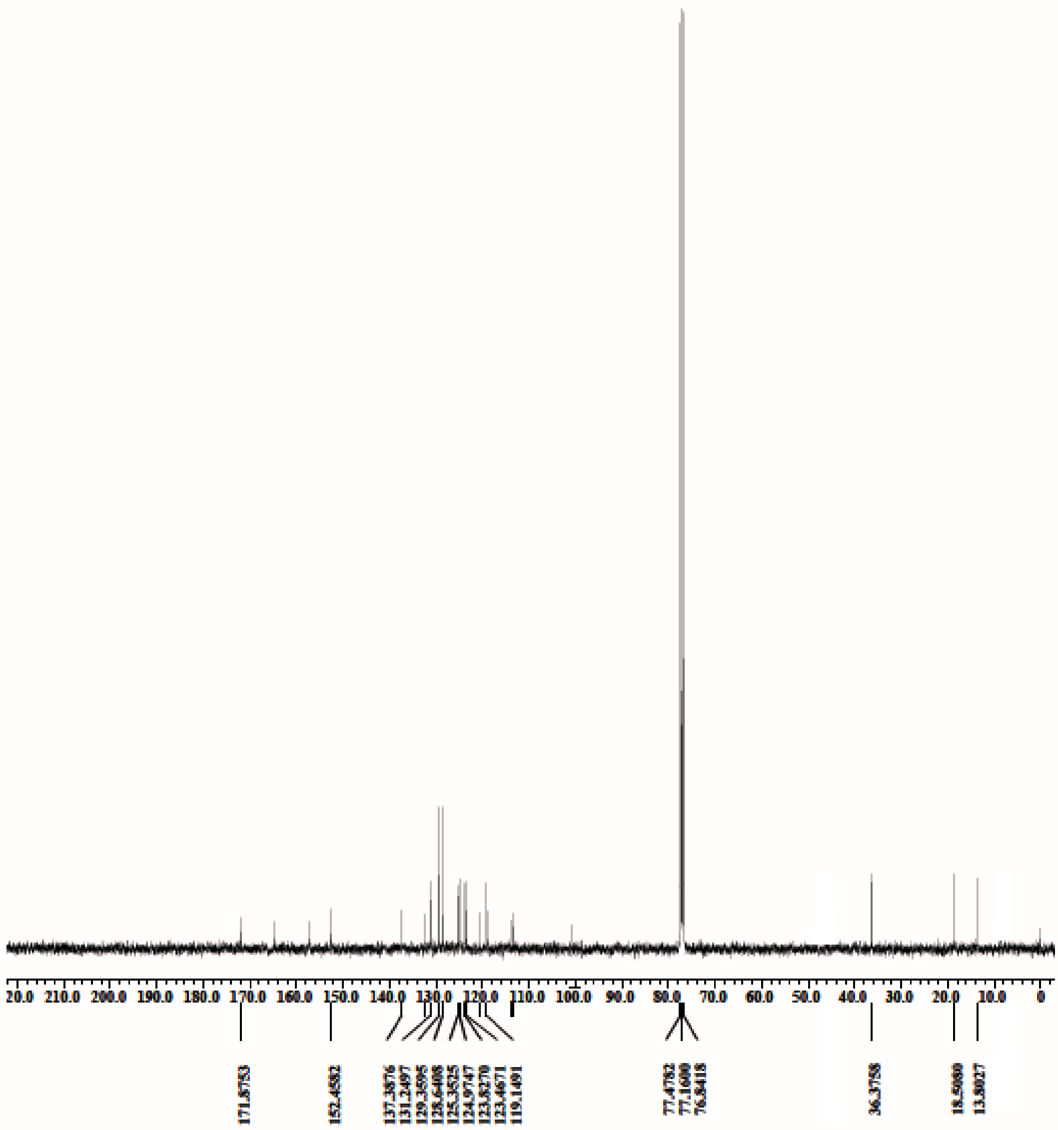


Fig. S50. ^{13}C-NMR spectra of **12.**

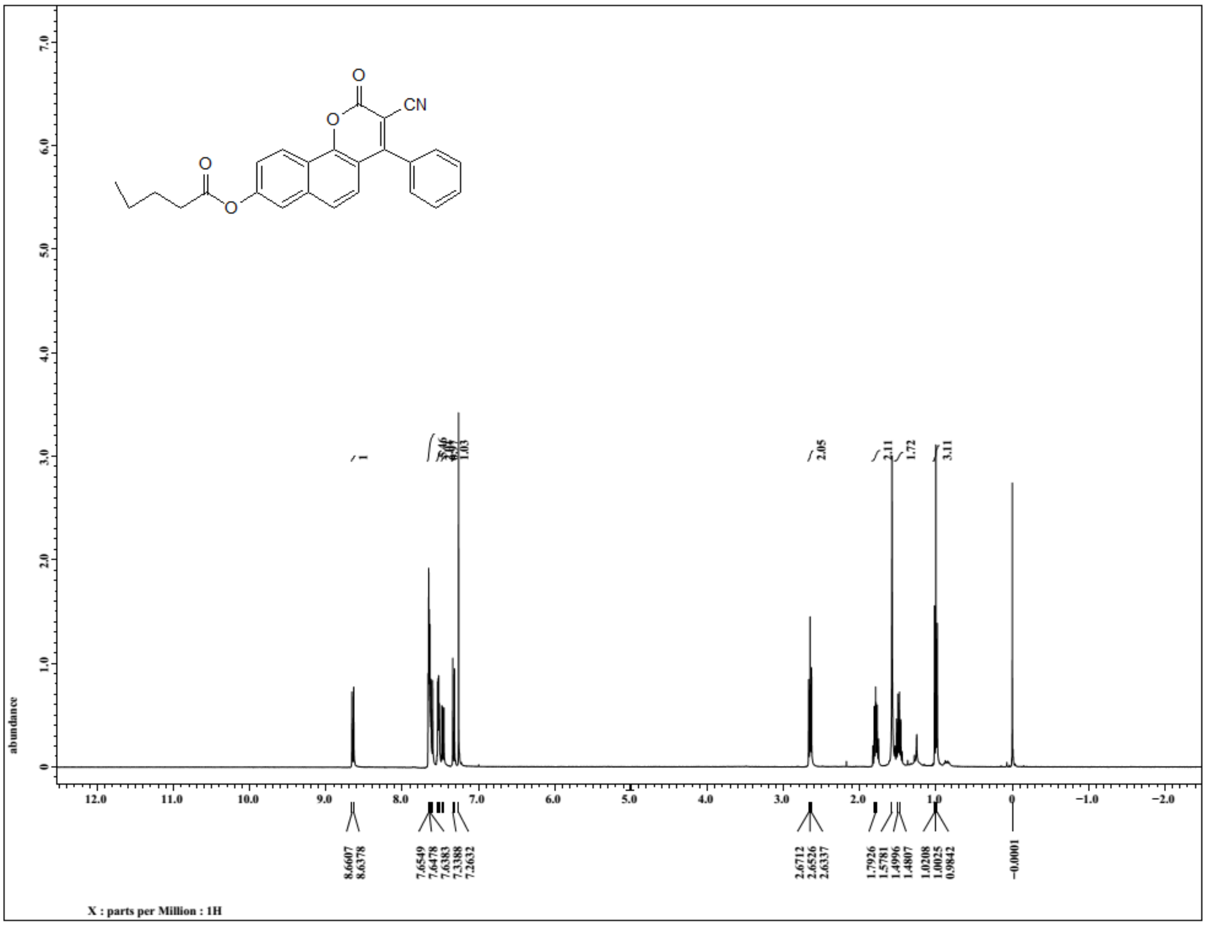


Fig. S51. ^{1}H-NMR spectra of **13.**

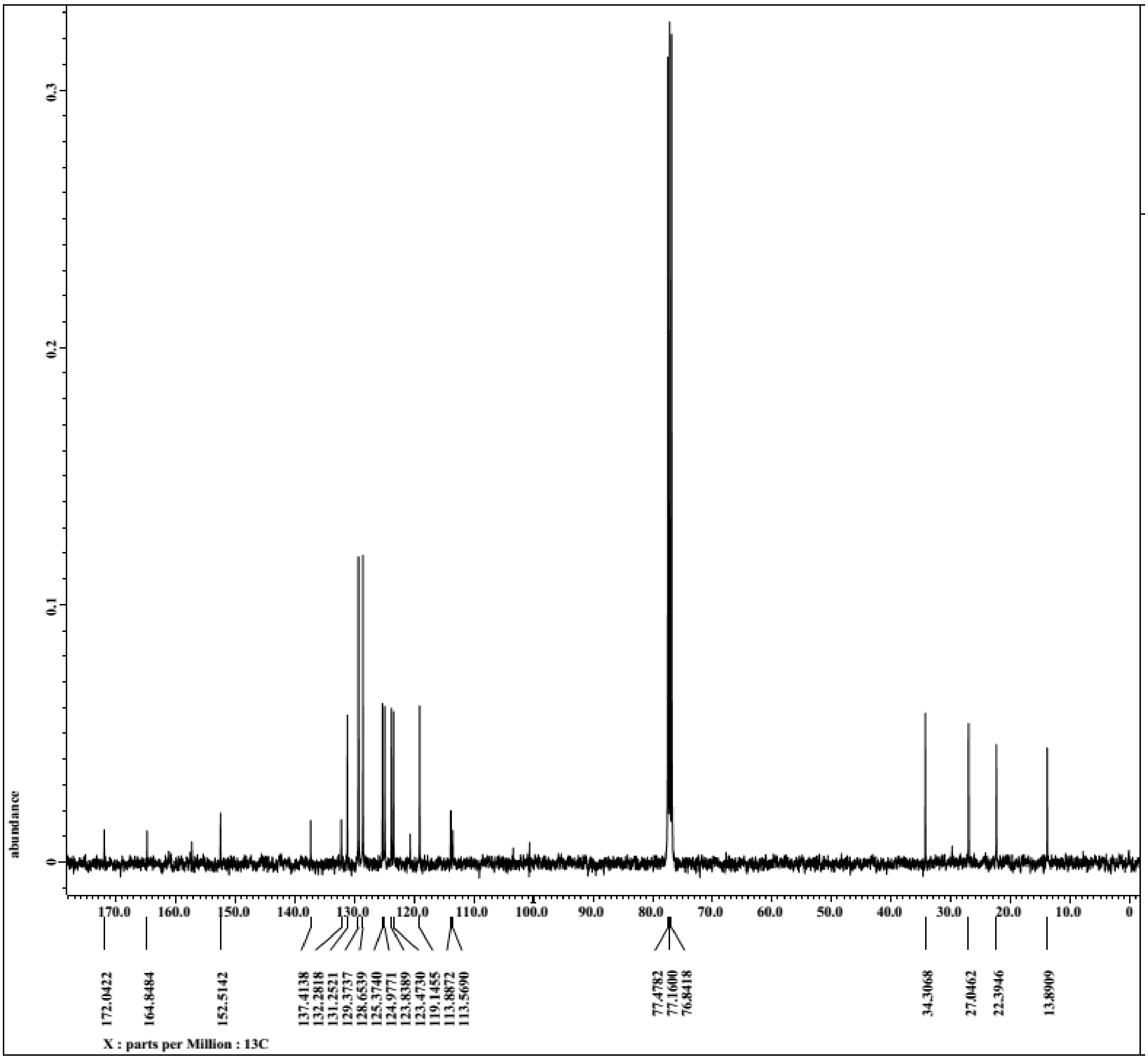


Fig. S52. ^{13}C-NMR spectra of **13.**

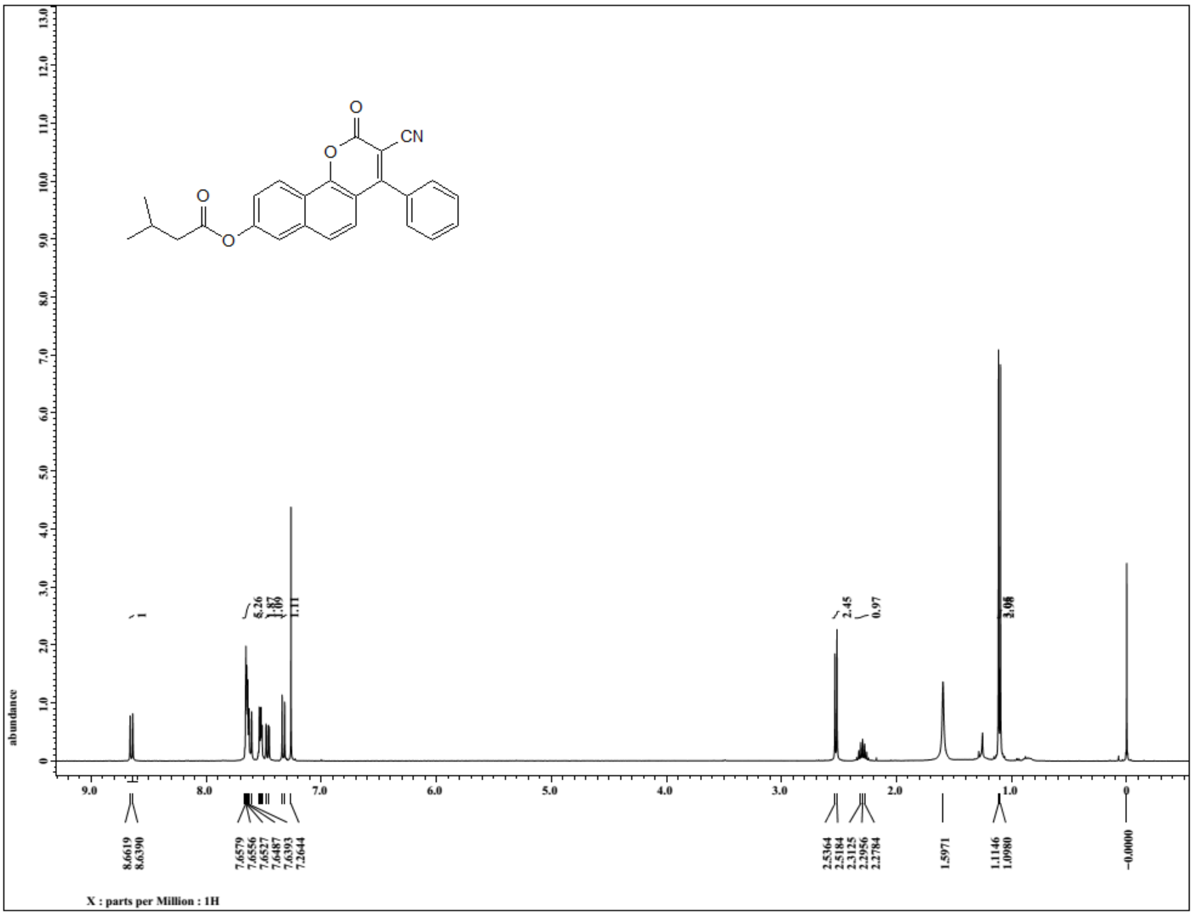


Fig. S53. ^{1}H-NMR spectra of **14.**

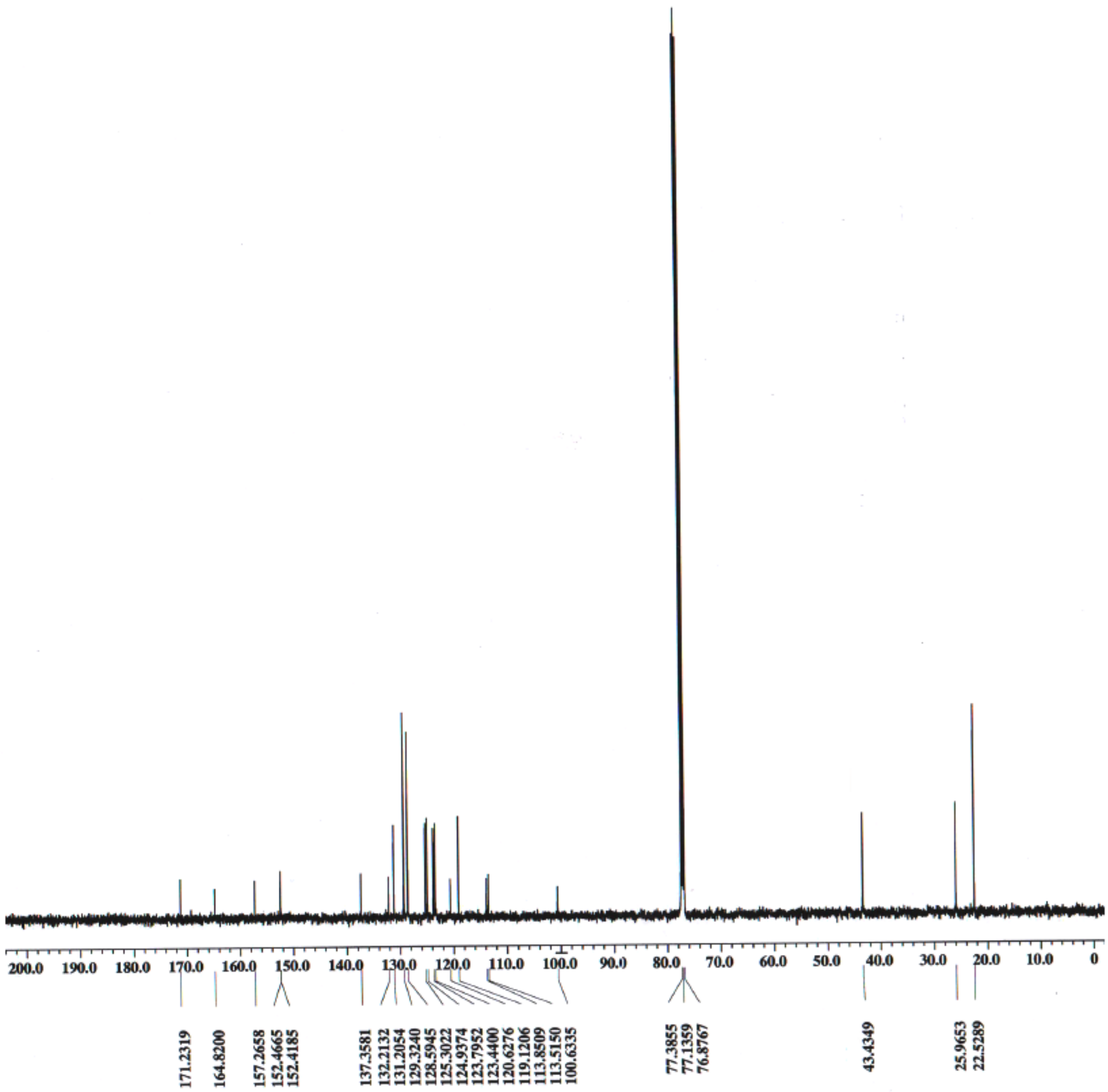


Fig. S54. ^{13}C-NMR spectra of **14.**

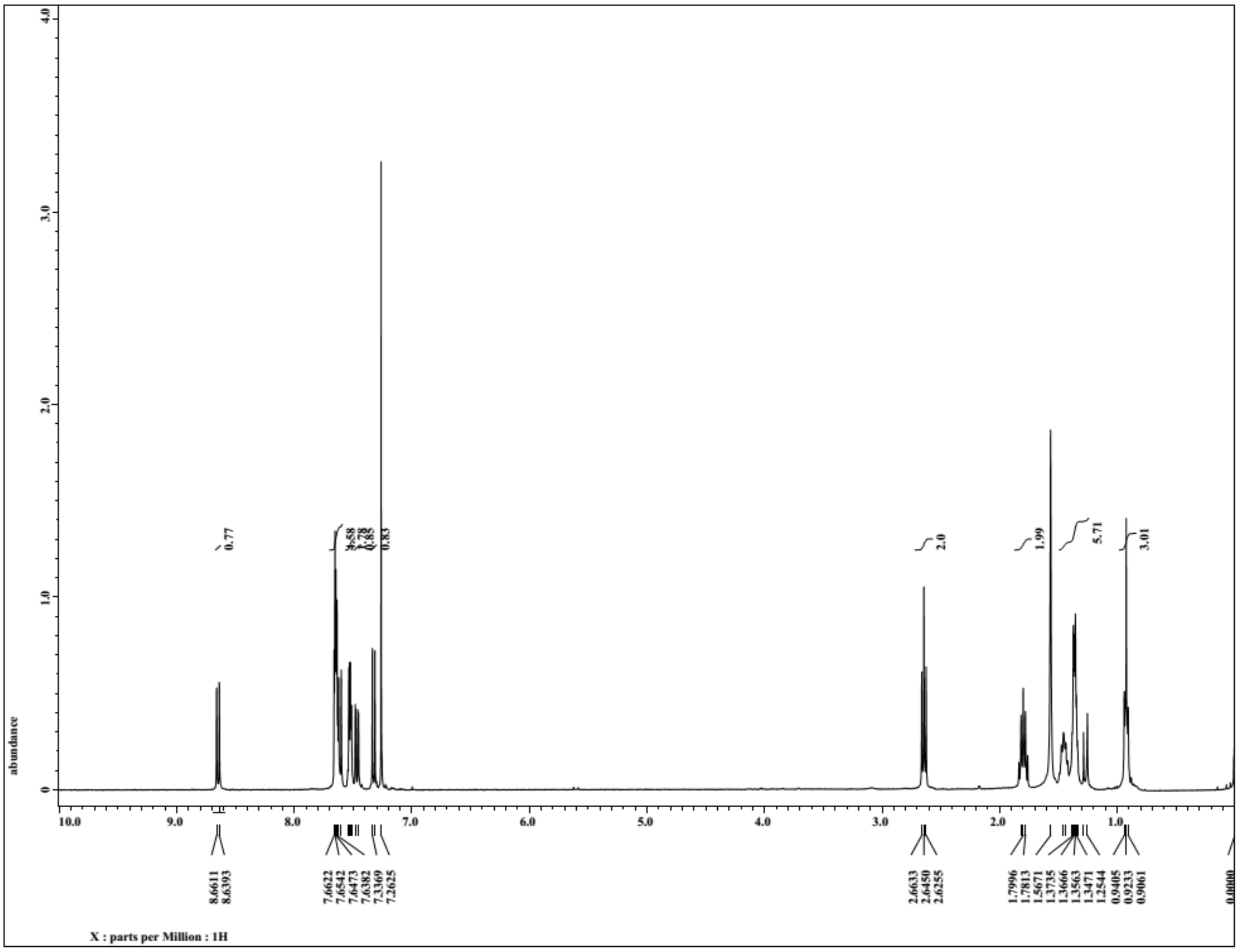


Fig. S55. ^{1}H-NMR spectra of **15.**

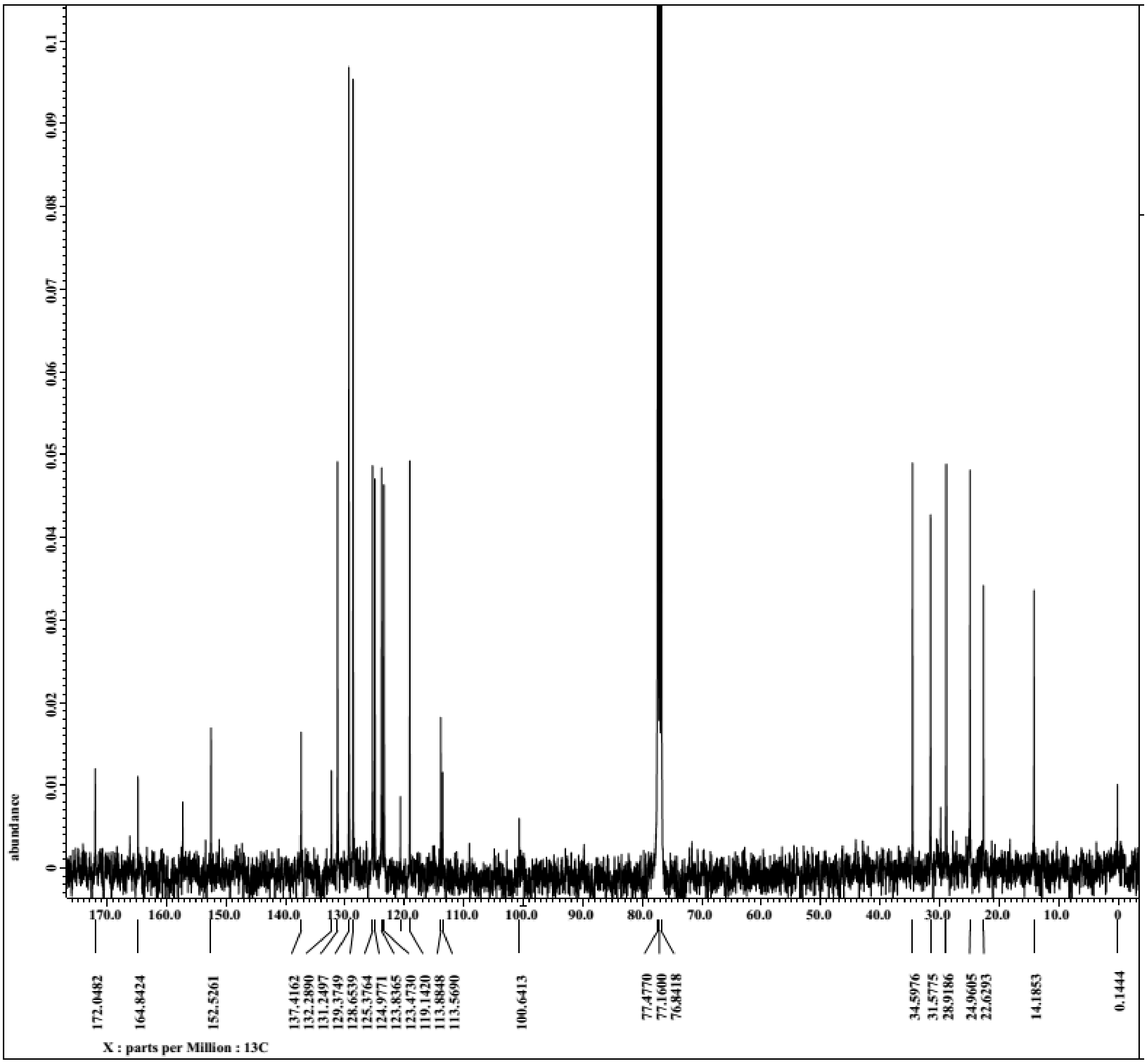


Fig. S56. ^{13}C-NMR spectra of **15.**

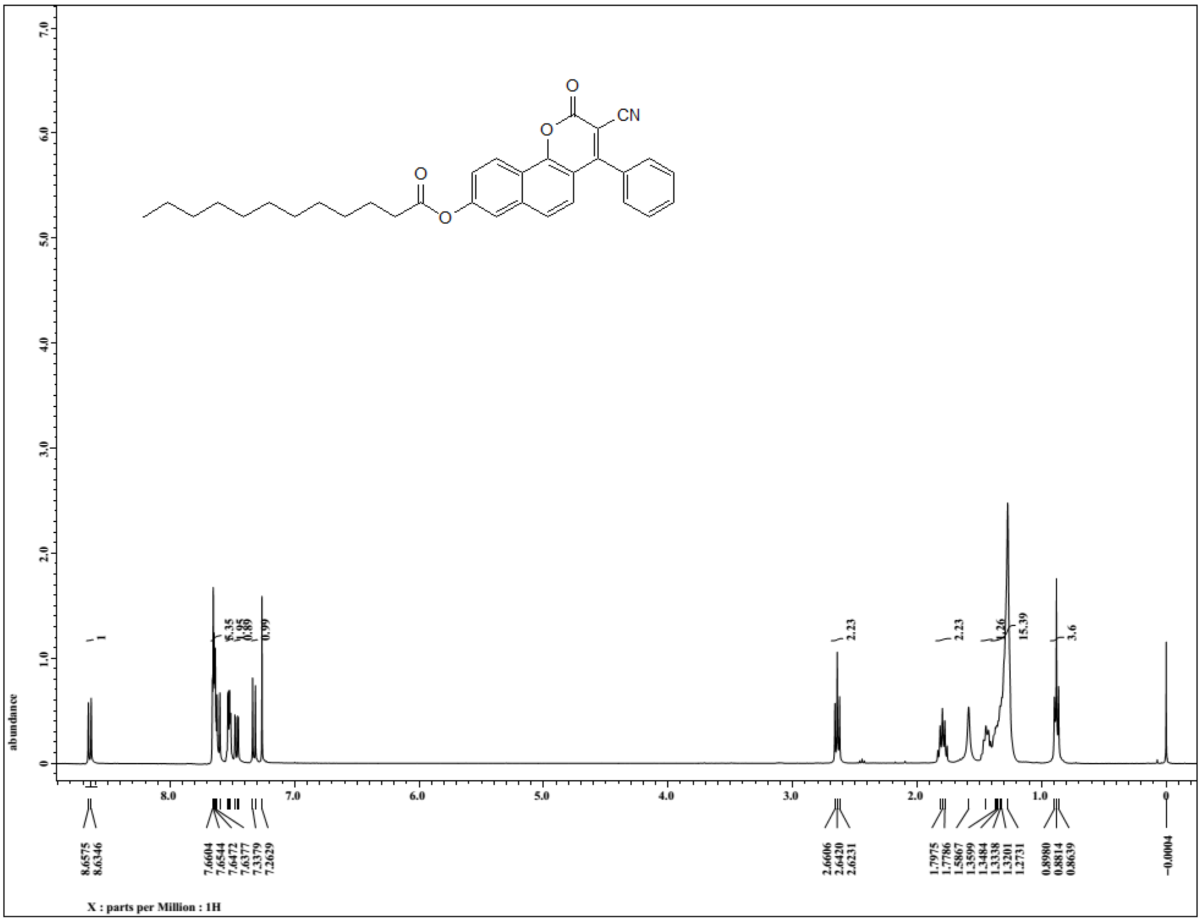


Fig. S57. ^{1}H-NMR spectra of **16.**

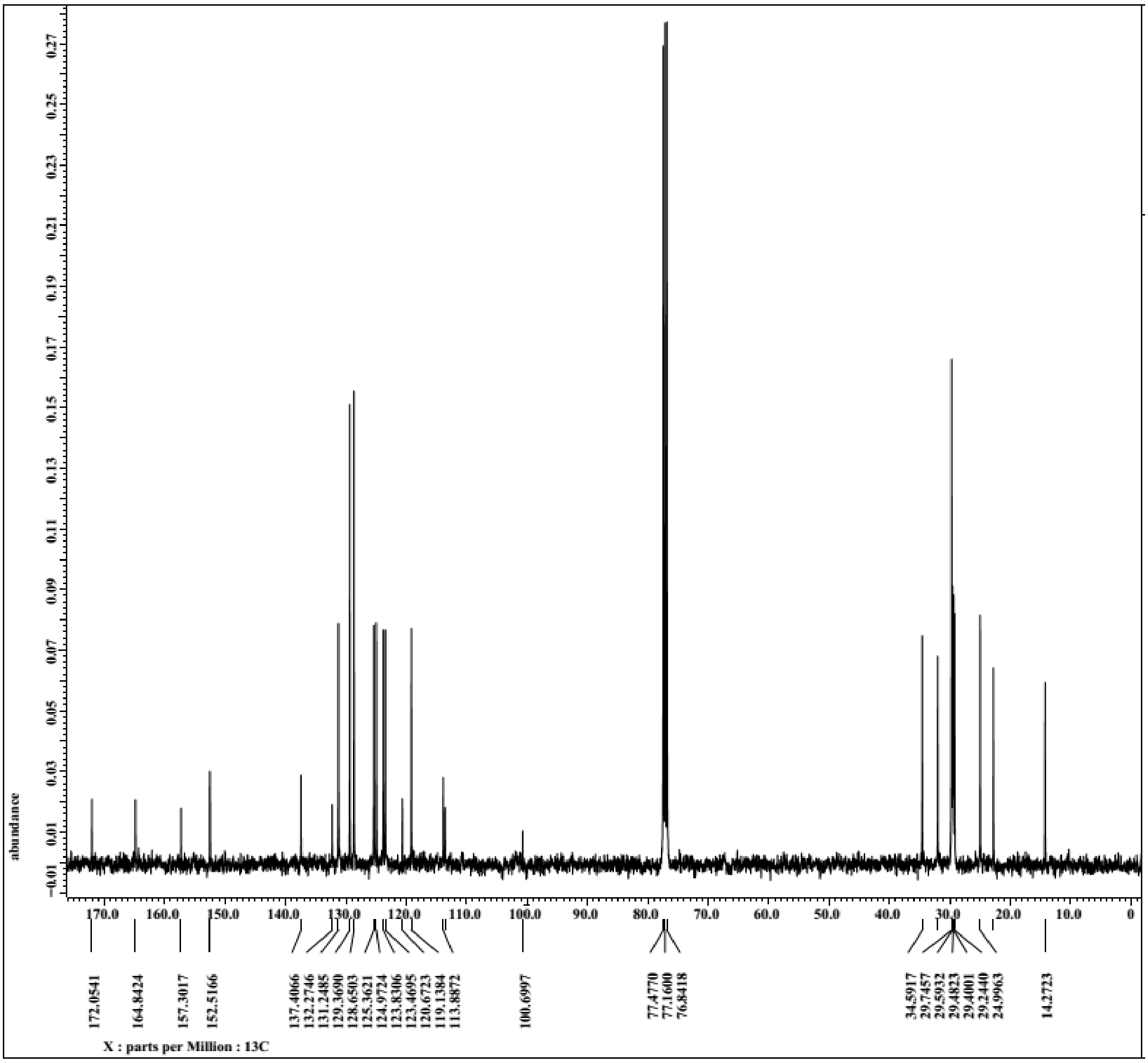


Fig. S58. ^{13}C-NMR spectra of **16.**

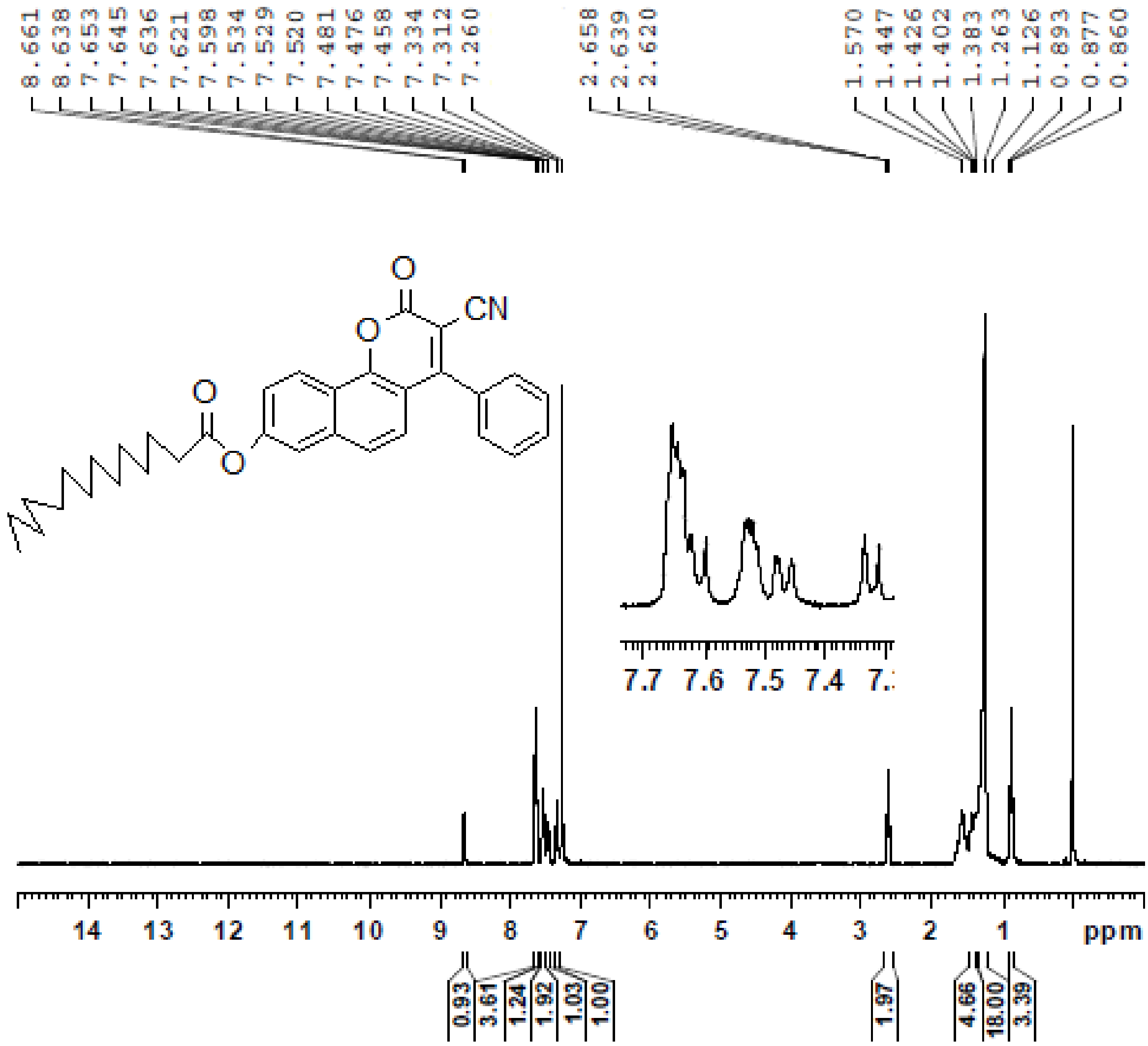


Fig. S59. [1]H-NMR spectra of **17.**

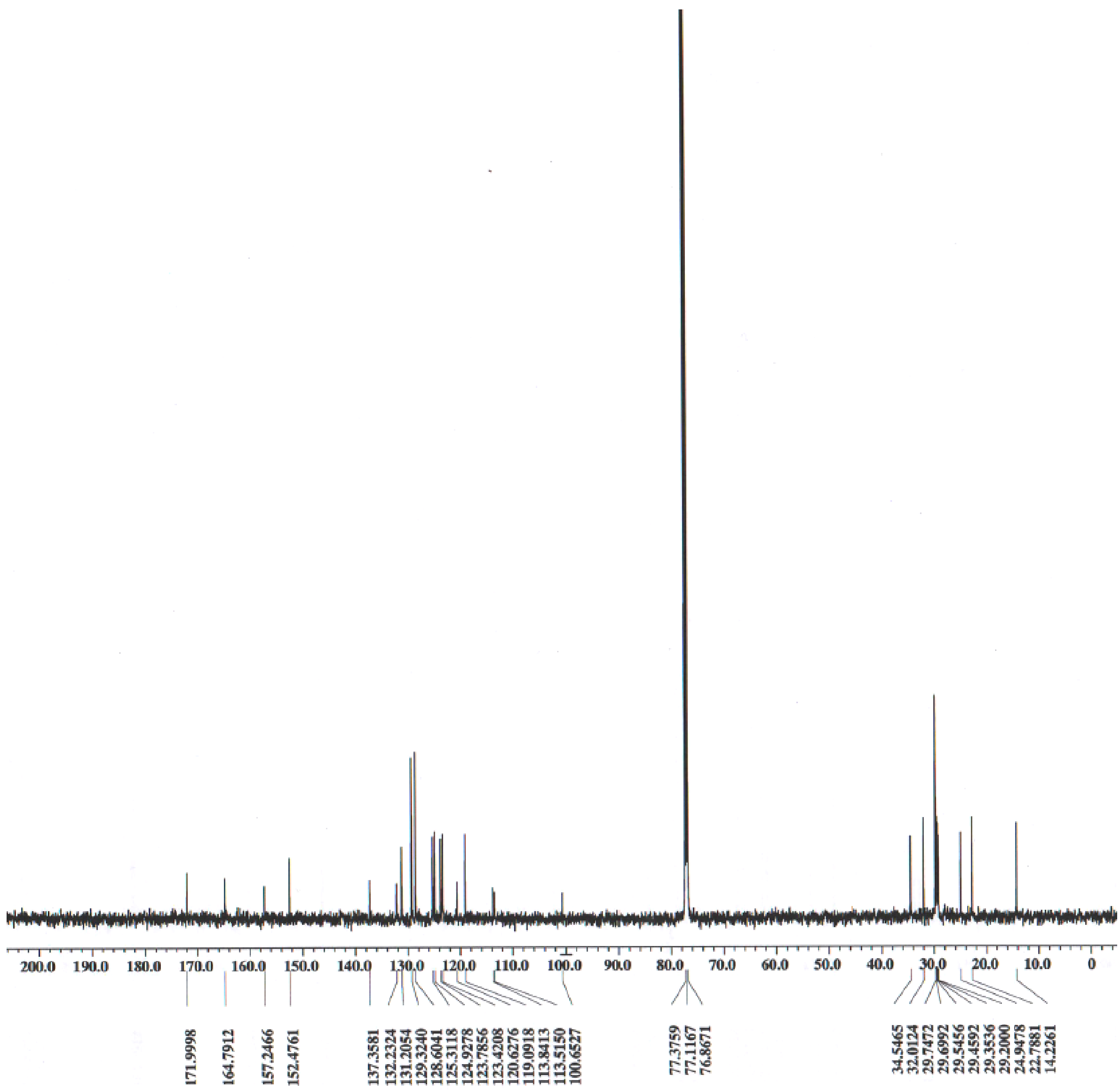


Fig. S60. ^{13}C-NMR spectra of **17.**

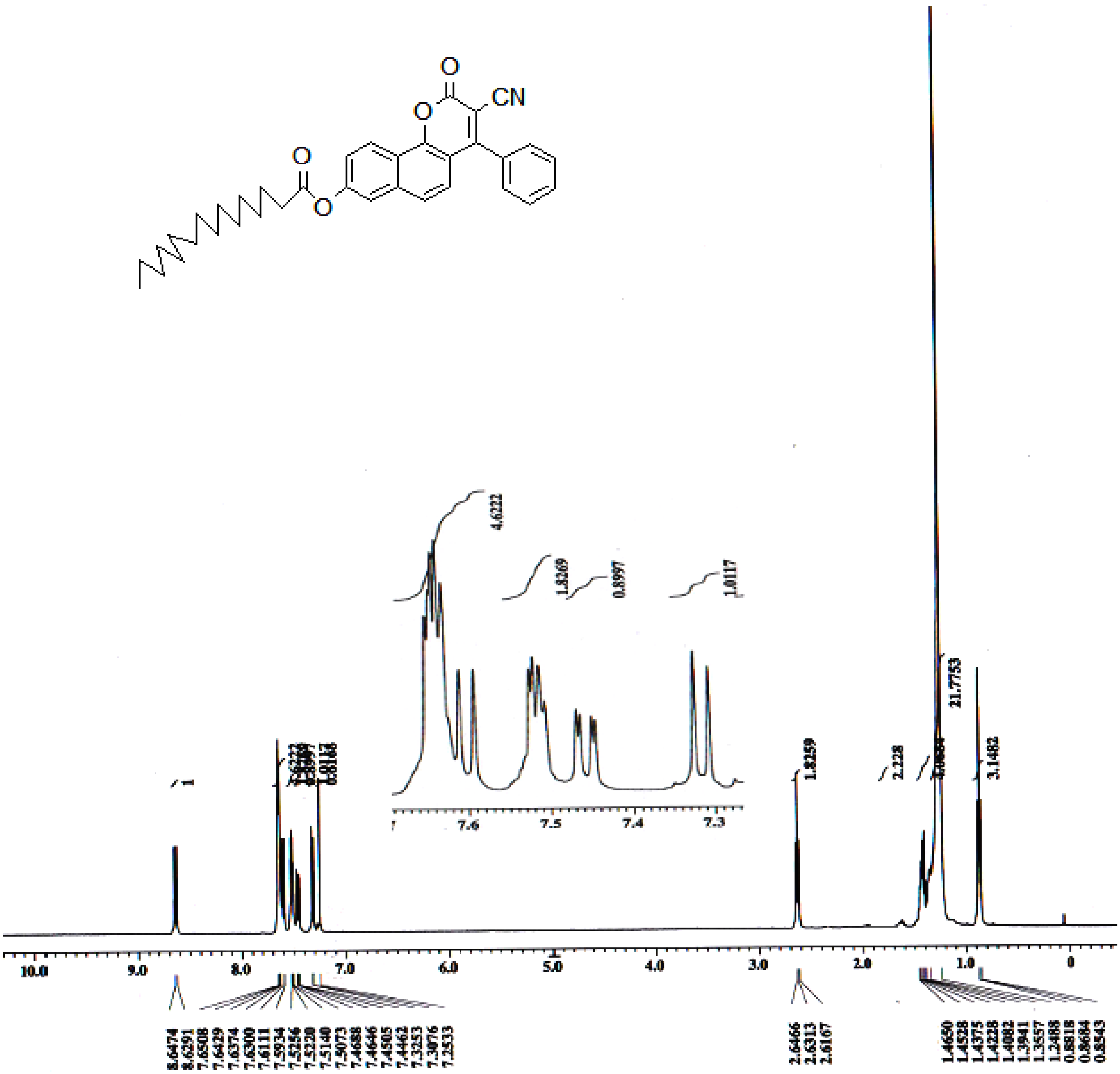


Fig. S61. ^{1}H-NMR spectra of **18.**

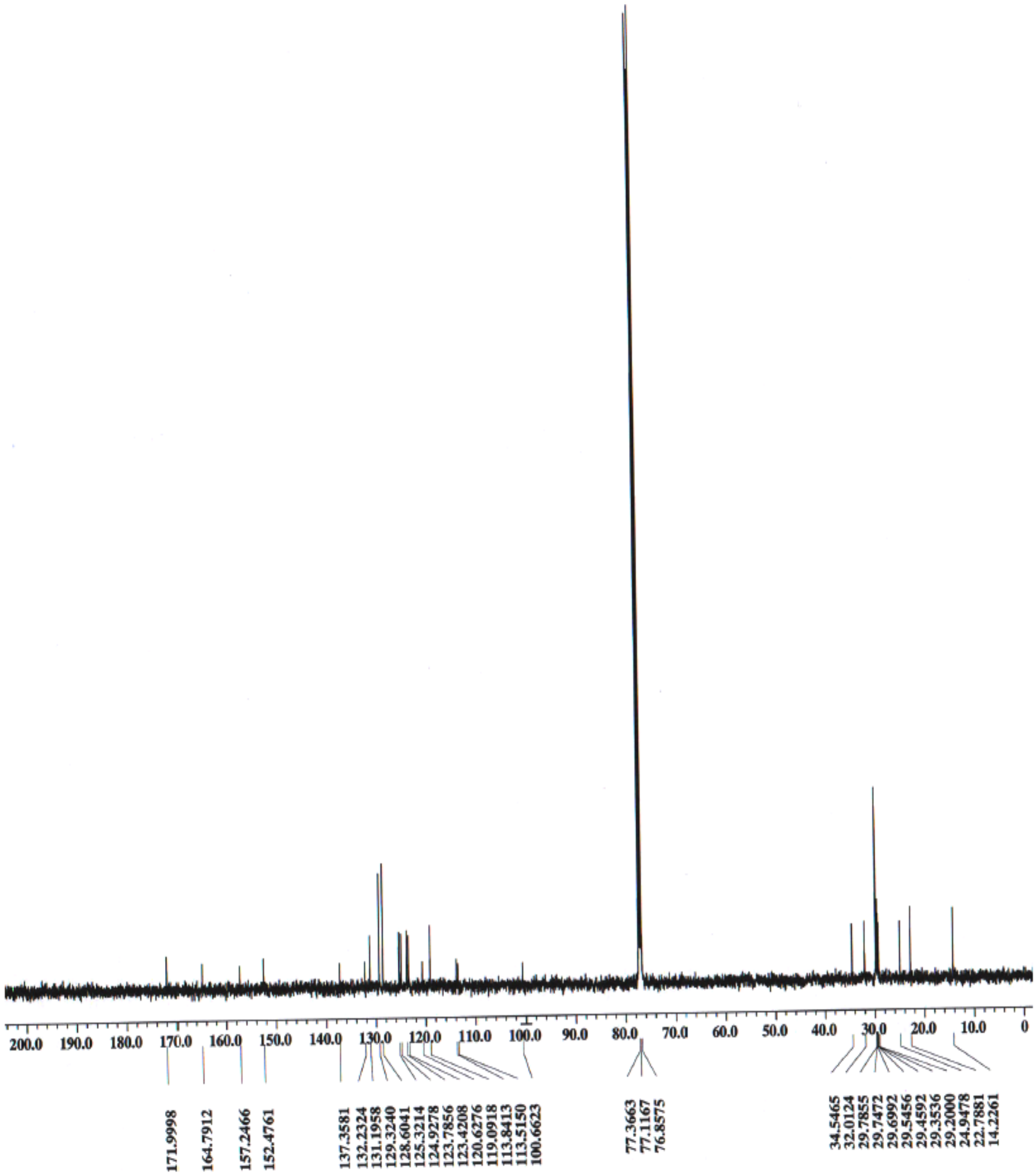


Fig. S62. ^{13}C-NMR spectra of **18.**

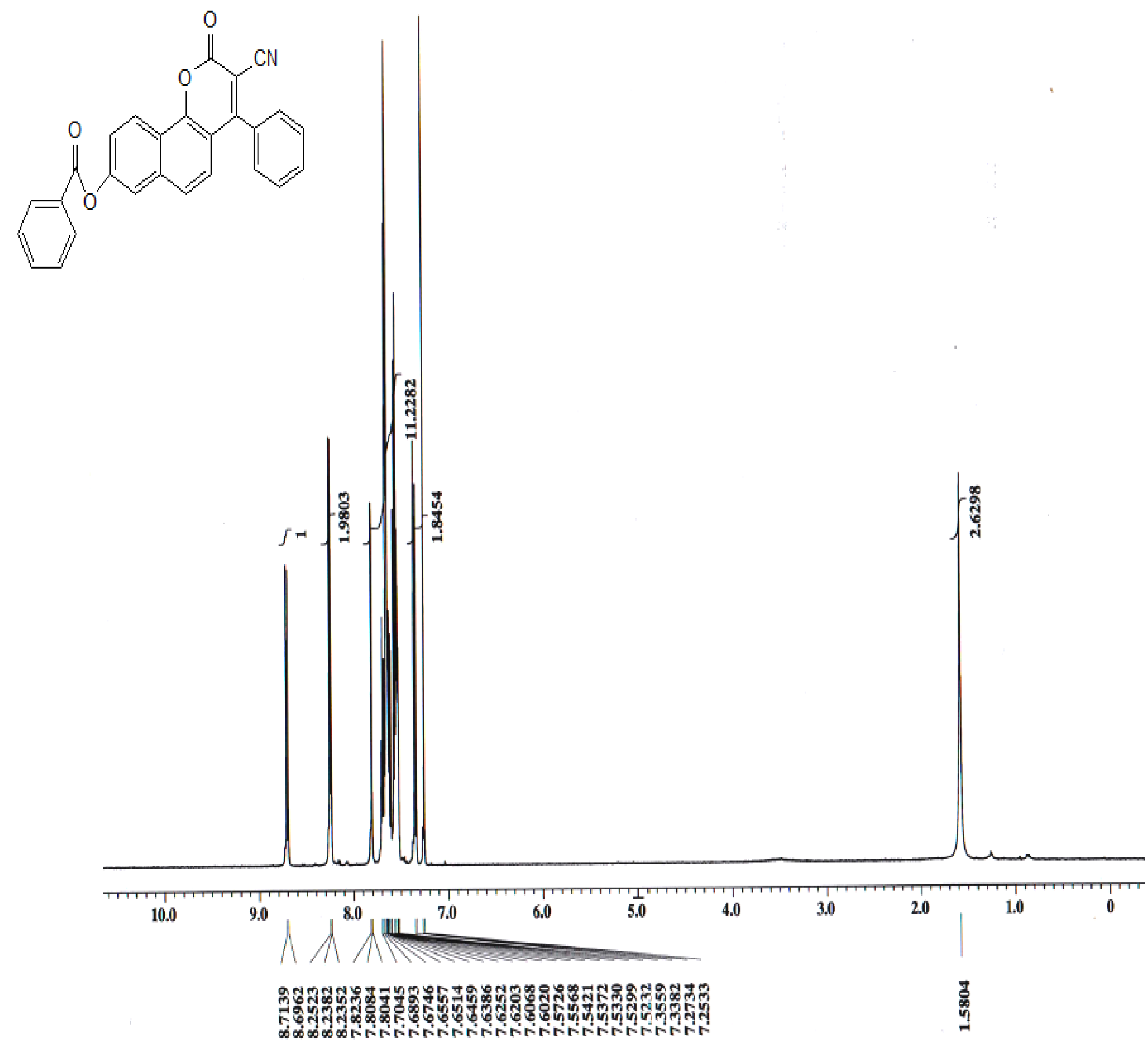


Fig. S63. ¹H-NMR spectra of **19.**

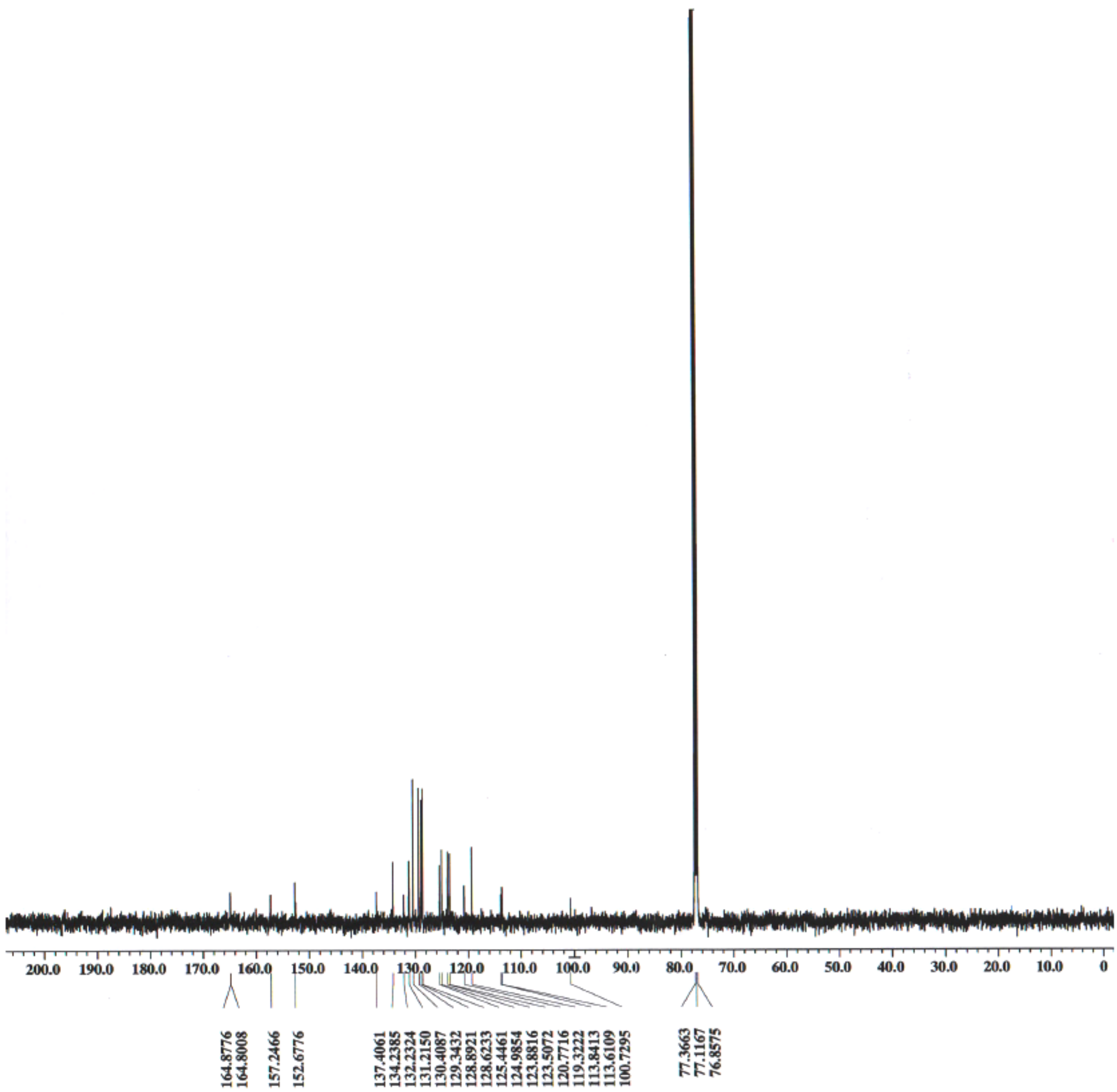


Fig. S64. ^{13}C-NMR spectra of **19.**

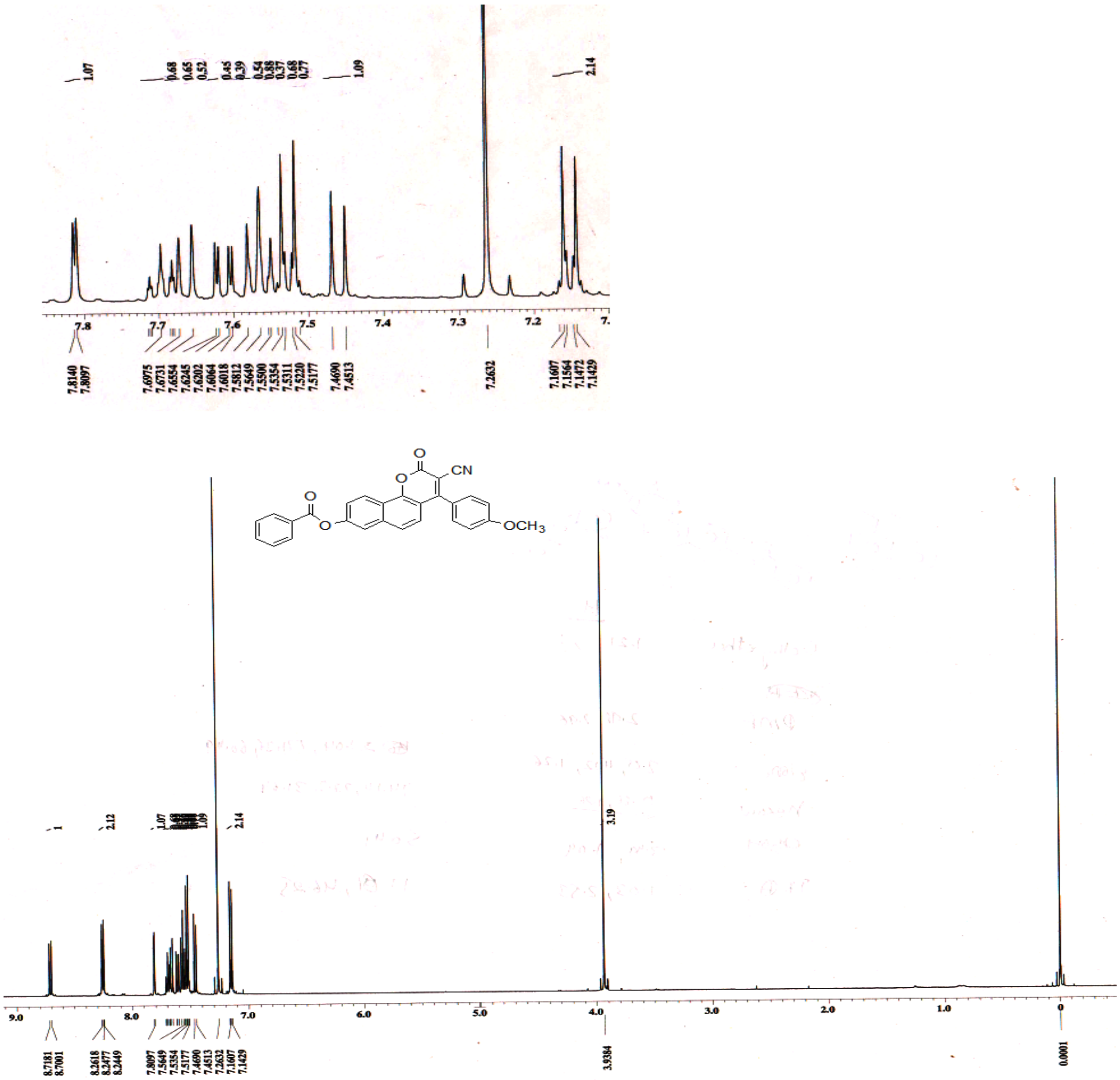


Fig. S65. ^{13}H-NMR spectra of **20**

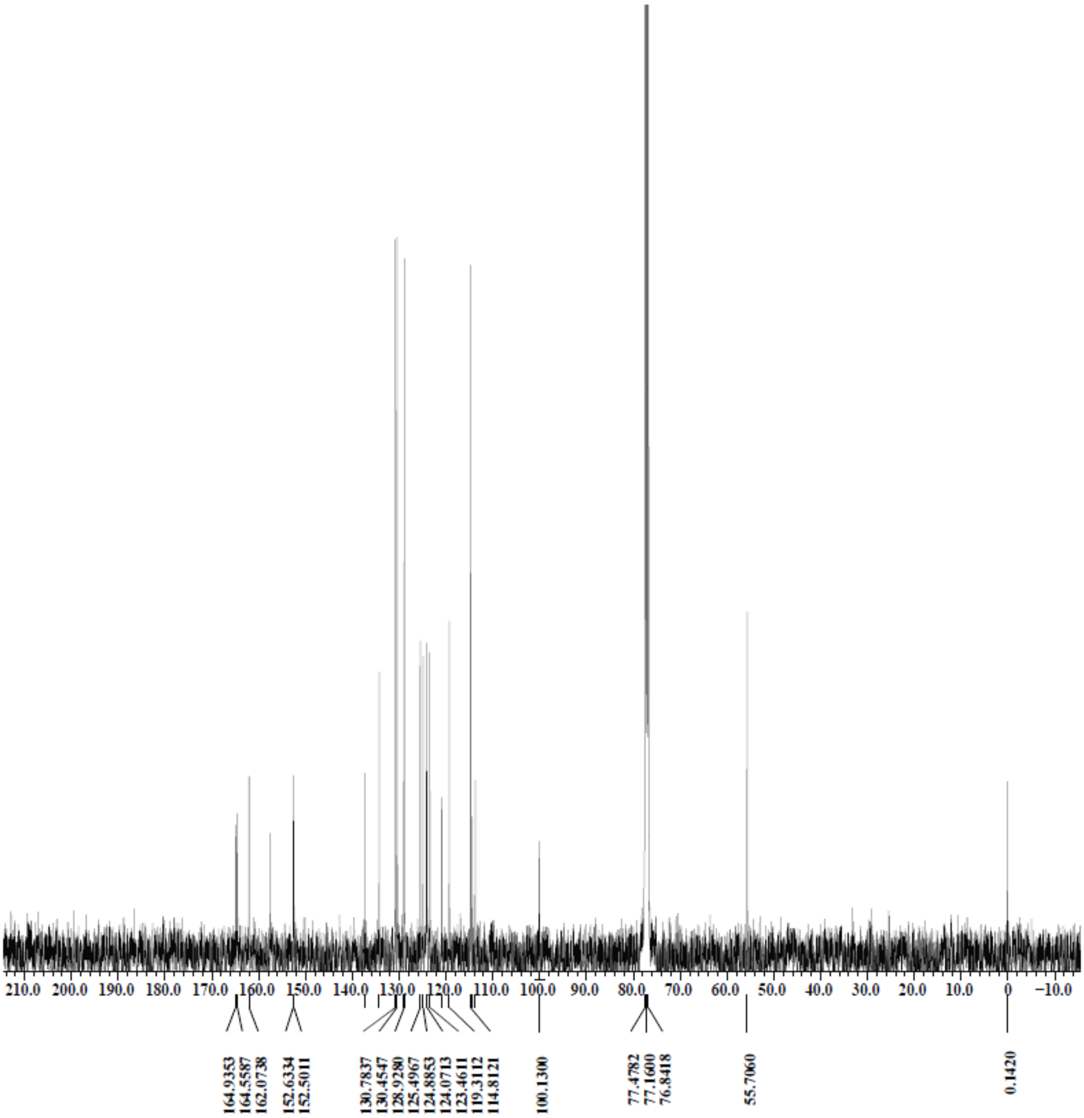


Fig. S66. ^{13}C-NMR spectra of **20.**

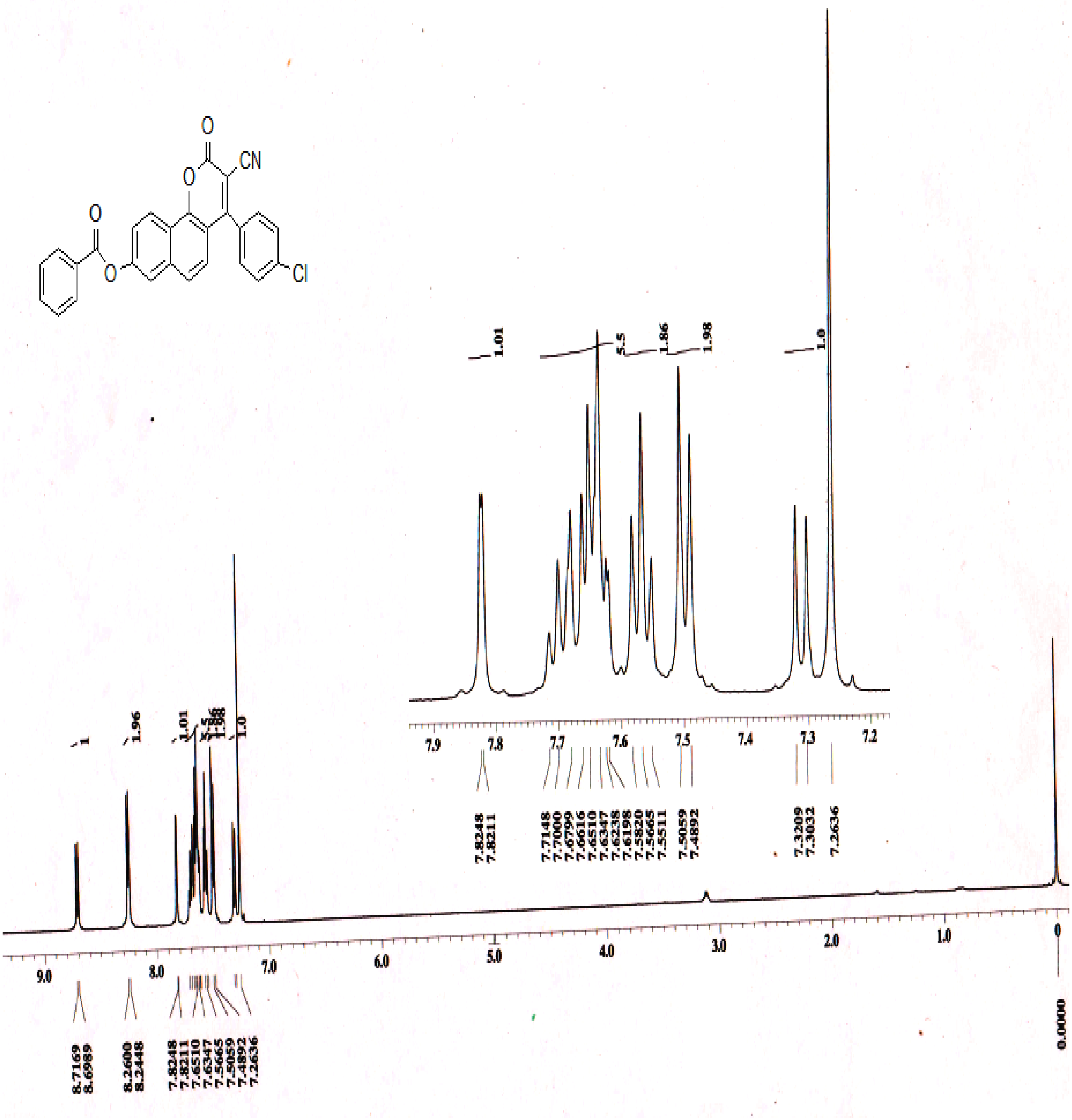


Fig. S67. ^{1}H-NMR spectra of **21.**

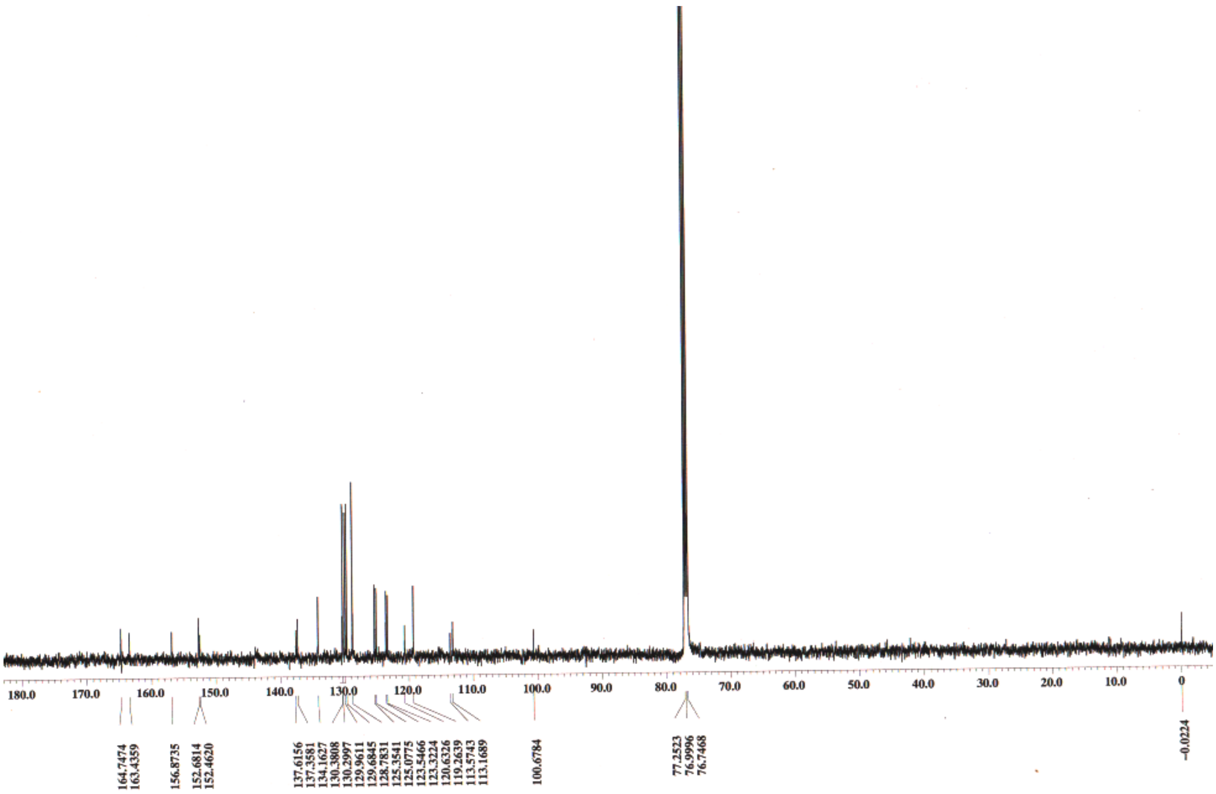


Fig. S68. ^{13}C-NMR spectra of **21.**

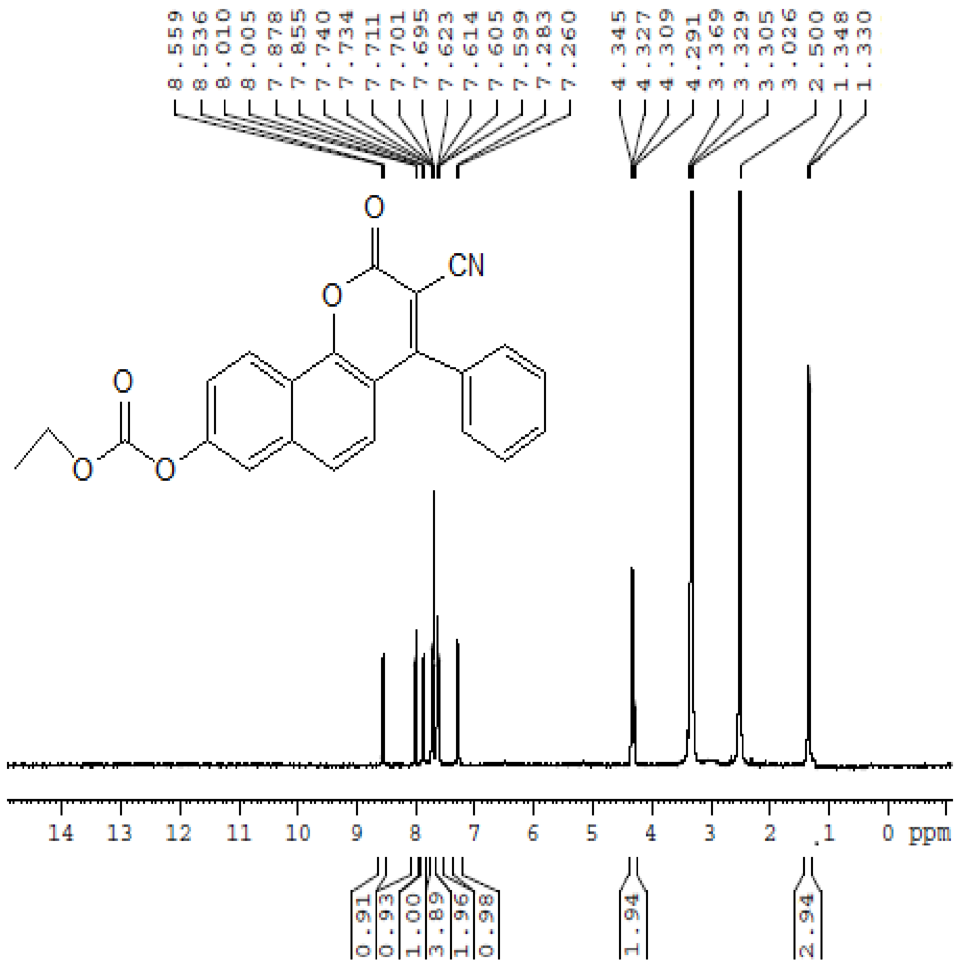


Fig. S69. ^{1}H-NMR spectra of **22.**

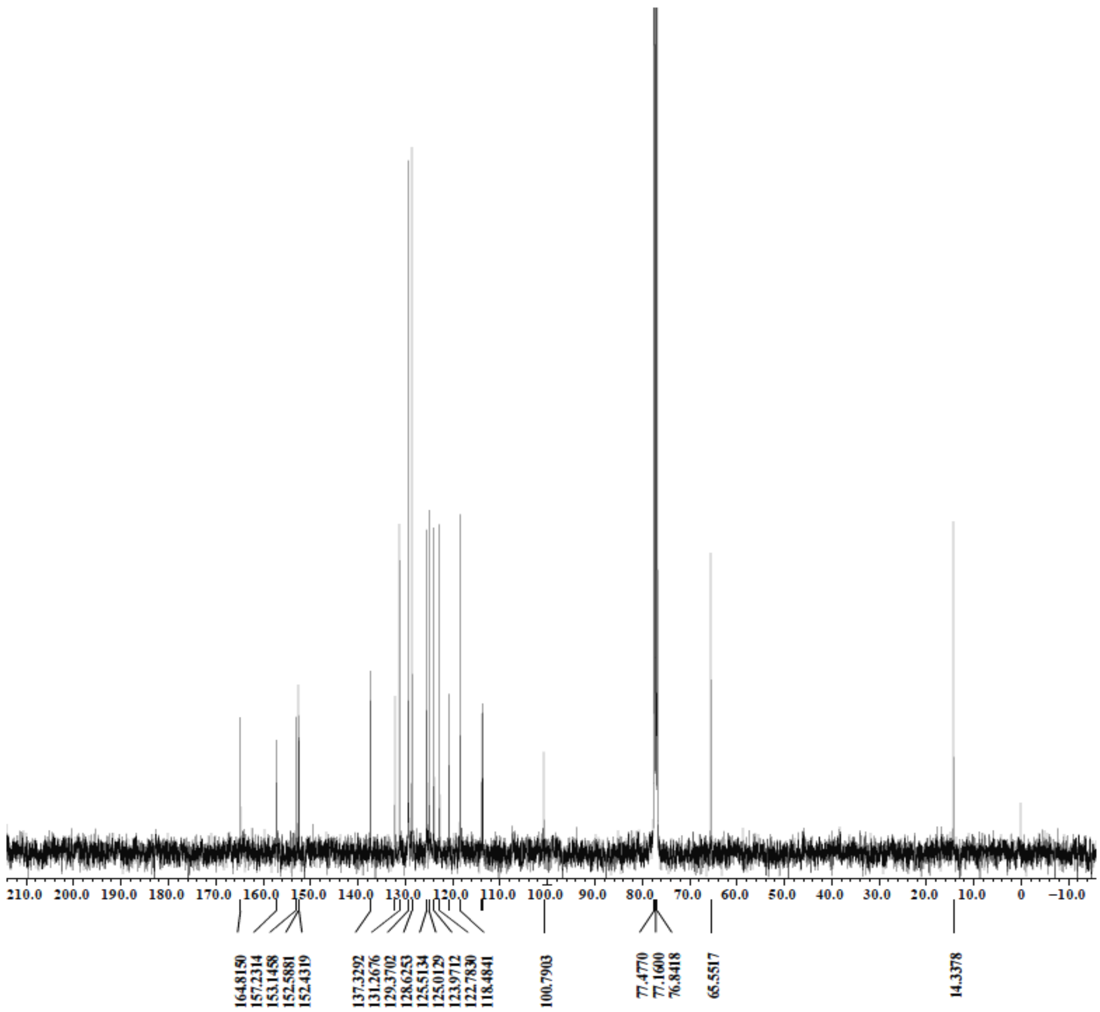


Fig. S70. ^{13}C-NMR spectra of **22.**

References**:**

[1] S. E.-D. N. A. F. Mohamed Abd El Aziz Ez-Taweel, A. Ghani Ali Elagamey, S.Zaki Ahmed Sowellim, in *Anales de qui'mica*, Vol. 91, 1995, 589.