High Efficient Construction of Novel Bridged Pentacyclic Skeleton via Six-component Domino Reaction under Microwave Irradiation

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1. General methods

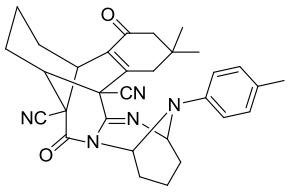
Melting points were measured using a XT-4 micro melting point apparatus and were uncorrected. IR spectra were recorded with a Varian F-1000 spectrometer using KBr disks; absorptions are reported as cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were obtained in DMSO-d_6 solution, using a Agilent Vnmrs-300 MHz, Agilent Inova-400 MHz, Bruker Avance III-400 MHz, Agilent DD2-600 MHz spectrometer. *J* values are reported in hertz and chemical shifts are expressed in parts per million downfield from TMS as the internal standard. HRMS analyses were carried out using a Bruker micrOTOF-QII mass spectrometer with ESI resource. X-Ray diffraction analysis was recorded on a Smart-1000 diffractometer. Microwave irradiation was carried out with Initiator 2.5 Microwave Synthesizers from Biotage, Uppsala, Sweden. The reaction temperatures were measured by infrared detector during microwave heating.

2. General procedure for the Synthesis of 5, 7, 9, 11.

Glutaraldehyde (**1**) (2.0 mmol), malononitrile (**2**) (2.0 mmol), 1,3-dicarbonyl compounds (**3**, **6**, **8** or **10**) (1 mmol) and amines (**4**) (1.0 mmol) was introduced in a 5 mL initiator reaction vial, and 50 mol% piperidine as well as ethanol (2 mL) were then successively added. Subsequently, the reaction vial was closed and then prestirred for 10 s. The mixture was irradiated at 100^{o}C. The reaction was monitored by TLC. After the completion, the reaction mixture was then cooled to room temperature. The precipitate was collected and purified by column chromatography (petroleum ether:acetone = 12:1) to give the crude products. The crude products were further purified by recrystallization from DMF and water to give the products **5**, **7**, **9** or **11**.

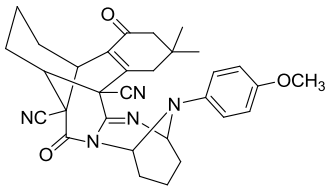
3. Characterizations for all compounds

13,13-Dimethyl-8,11-dioxo-20-(*p*-tolyl)-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5a)



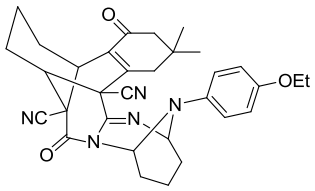
Isolated as a white solid; mp 216–218 ℃; IR (KBr, *v*, cm^{-1}): 2924, 2869, 2249, 1695, 1636, 1509, 1461, 1346, 1261, 1236, 1090, 836; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.01 (d, *J* = 8.4 Hz, 2H, ArH), 6.76 (d, *J* = 8.4 Hz, 2H, ArH), 6.12 (s, 1H, CH), 5.76 (s, 1H, CH), 3.55 (s, 1H, CH), 3.28 (s, 1H, CH), 2.17 (s, 3H, CH_3), 2.10 (t, *J* = 16.0 Hz, 3H, 3 × CH), 1.99–1.83 (m, 6H, 6 × CH), 1.69 (d, *J* = 16.4 Hz, 1H, CH), 1.65–1.53 (m, 4H, 4 × CH), 1.24 (d, *J* = 18.0 Hz, 1H, CH), 1.13–1.03 (m, 1H, CH), 0.78 (s, 3H, CH_3), 0.64 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.4, 164.7, 147.3, 147.2, 145.1, 131.7, 130.6, 118.5, 117.8, 116.5, 115.3, 68.9, 63.7, 52.8, 49.6, 48.1, 34.6, 34.4, 32.1, 29.4, 29.3, 29.0, 25.4, 25.0, 20.3, 15.8, 14.1; HRMS calcd for $C_{31}H_{32}N_5O_2$ $[M-H]^-$: 506.2556, found: 506.2556.

20-(4-Methoxyphenyl)-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5b)



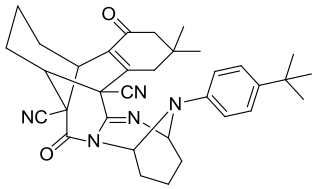
Isolated as a white solid; mp 218–220 ℃; IR (KBr, *v*, cm^{-1}): 2953, 2905, 2252, 1696, 1639, 1513, 1451, 1374, 1252, 1035, 934, 837; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.80 (s, 4H, ArH), 6.07 (s, 1H, CH), 5.70 (s, 1H, CH), 3.66 (s, 3H, CH_3O), 3.55 (s, 1H, CH), 3.28 (s, 1H, CH), 2.17–2.08 (m, 3H, 3 × CH), 1.98–1.80 (m, 7H, 7 × CH), 1.64–1.59 (m, 4H, 4 × CH), 1.29 (d, *J* = 18.0 Hz, 1H, CH), 1.14–1.05 (m, 1H, CH), 0.79 (s, 3H, CH_3), 0.65 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.5, 164.8, 154.3, 147.2, 140.9, 131.7, 117.8, 115.3, 69.2, 64.2, 55.6, 52.9, 49.9, 48.2, 34.7, 34.5, 32.3, 29.6, 29.4, 29.1, 25.5, 25.0, 15.8, 14.1; HRMS calcd for $C_{31}H_{32}N_5O_3$ $[M-H]^-$: 522.2505, found: 522.2492.

20-(4-Ethoxyphenyl)-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5c)



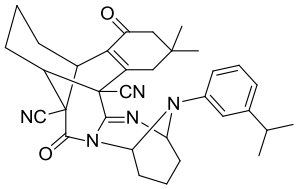
Isolated as a white solid; mp 220–222 ℃; IR (KBr, *v*, cm^{-1}): 2952, 2871, 2249, 1707, 1649, 1515, 1394, 1004, 963, 938, 803; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.78 (s, 4H, ArH), 6.06 (s, 1H, CH), 5.68 (s, 1H, CH), 3.92–3.88 (m, 2H, CH_2O), 3.53 (s, 1H, CH), 3.29 (s, 1H, CH), 2.18–2.08 (m, 3H, 3 × CH), 2.03–1.82 (m, 7H, 7 × CH), 1.64–1.59 (m, 4H, 4 × CH), 1.33 (s, 1H, CH), 1.27 (t, *J* = 6.8 Hz, 3H, CH_3), 1.18–1.08 (m, 1H, CH), 0.79 (s, 3H, CH_3), 0.66 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.5, 164.8, 153.6, 147.2, 140.8, 131.7, 117.8, 115.7, 115.4, 69.2, 64.2, 63.6, 52.9, 49.9, 48.2, 34.8, 34.5, 32.2, 29.6, 29.2, 25.5, 25.0, 15.8, 15.2, 14.1; HRMS calcd for $C_{32}H_{36}N_5O_3$ $[M+H]^+$: 538.2818, found: 538.2803.

20-(4-(Tert-butyl)phenyl)-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5d)



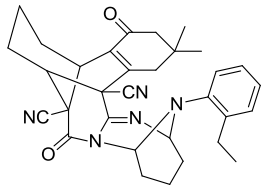
Isolated as a white solid; mp 240–242 ℃; IR (KBr, *v*, cm^{-1}): 2950, 2870, 2250, 1692, 1640, 1519, 1367, 1345, 1255, 1093, 820, 746, 691; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.31 (d, *J* = 8.4 Hz, 2H, ArH), 6.87 (d, *J* = 8.4 Hz, 2H, ArH), 5.73 (s, 1H, CH), 5.43 (s, 1H, CH), 2.78–2.72 (m, 2H, 2 × CH), 2.47–2.41 (m, 1H, CH), 2.45 (d, *J* = 15.6 Hz, 1H, CH), 2.26 (d, *J* = 15.6 Hz, 1H, CH), 2.07–1.84 (m, 8H, 8 × CH), 1.67–1.56 (m, 3H, 3 × CH), 1.34–1.29 (m, 1H, CH), 1.24 (s, 9H, $(CH_3)_3C$), 1.20–1.15 (m, 1H, CH), 1.04 (s, 3H, CH_3), 0.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 196.1, 164.3, 147.6, 146.5, 145.1, 132.4, 129.8, 126.3, 120.3, 118.4, 117.4, 114.9, 67.7, 67.3, 52.3, 50.5, 48.0, 36.8, 34.7, 32.8, 29.9, 28.2, 25.9, 24.9, 15.7, 14.8; HRMS calcd for $C_{34}H_{40}N_5O_2$ $[M+H]^+$: 550.3182, found: 550.3177.

20-(3-Isopropylphenyl)-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5e)



Isolated as a white solid; mp 232–234 ℃; IR (KBr, *v*, cm^{-1}): 2956, 2870, 2250, 1690, 1638, 1513, 1457, 1365, 1243, 1088, 935, 826, 765; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.07 (t, *J* = 8.0 Hz, 1H, ArH), 6.93 (s, 1H, ArH), 6.79 (d, *J* = 7.6 Hz, 1H, ArH), 6.45 (d, *J* = 8.0 Hz, 1H, ArH), 6.18 (s, 1H, CH), 5.85 (s, 1H, CH), 3.54 (s, 1H, CH), 3.27 (s, 1H, CH), 2.78–2.71 (m, 1H, CH), 2.15 (d, *J* = 18.0 Hz, 1H, CH), 2.07–1.94 (m, 6H, 6 × CH), 1.92–1.87 (m, 2H, 2 × CH), 1.66–1.51 (m, 5H, 5 × CH), 1.32 (d, *J* = 18.4 Hz, 1H, CH), 1.12 (d, *J* = 6.8 Hz, 3H, CH_3), 1.10 (d, *J* = 7.2 Hz, 3H, CH_3), 1.07–1.03 (m, 1H, CH), 0.76 (s, 3H, CH_3), 0.57 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.5, 164.6, 147.2, 145.3, 141.6, 131.6, 127.9, 127.7, 118.7, 117.8, 116.6, 115.4, 68.7, 64.0, 52.8, 49.9, 48.1, 34.6 34.4, 32.9, 32.2, 29.7, 29.1, 25.4, 25.0, 24.4, 24.3, 15.7, 14.1; HRMS calcd for $C_{33}H_{38}N_5O_2$ $[M+H]^+$: 536.3026, found: 536.3035.

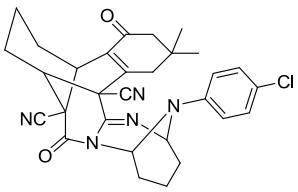
20-(2-Ethylphenyl)-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5f)



Isolated as a white solid; mp 224–226 ℃; IR (KBr, *v*, cm^{-1}): 2933, 2869, 2250, 1693, 1637, 1511, 1468, 1356, 1253, 1236, 1090, 836; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.27 (d, *J* = 7.2 Hz, 1H, ArH), 7.08-7.01 (m, 2H, ArH), 6.36 (d, *J* = 7.2 Hz, 1H, ArH), 5.67 (s, 1H, CH), 4.98 (s, 1H, CH), 3.57 (s, 1H, CH), 3.35 (s, 1H, CH), 2.69–2.57 (m, 2H, 2 × CH), 2.36 (d, *J* = 18.4 Hz, 1H, CH), 2.26 (s, 2H, CH_2), 2.16–2.07 (m, 3H, 3 × CH), 2.02–1.91 (m, 5H, 5 × CH), 1.82 (d, *J* = 12.4 Hz, 1H, CH), 1.66 (s, 4H, 4 × CH), 1.19 (t, *J* = 7.2 Hz, 3H, CH_3), 0.88 (s, 3H, CH_3), 0.81 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.6, 164.3, 147.3, 146.9, 146.3, 145.2, 138.6, 137.7, 132.2, 130.1, 127.6, 127.1, 125.6, 124.6, 121.0, 118.3, 69.7, 67.8, 53.1, 52.5, 48.3, 48.0, 36.6, 35.3, 34.8, 34.5, 32.6, 30.2, 29.2, 28.2, 25.6, 23.7, 14.7; HRMS calcd for $C_{32}H_{34}N_5O_2$ $[M-H]^-$:

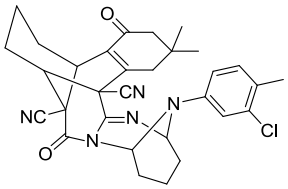
520.2713, found: 520.2694.

20-(4-Chlorophenyl)-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5g)



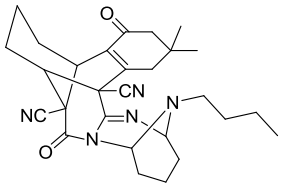
Isolated as a white solid; mp 272–274 ℃; IR (KBr, *v*, cm^{-1}): 2953, 2870, 2256, 1694, 1635, 1496, 1371, 1349, 1242, 1090, 1006, 939, 833, 818, 745; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.28 (d, J = 8.8 Hz, 2H, ArH), 6.93 (d, J = 7.2 Hz, 2H, ArH), 6.15 (s, 1H, CH), 5.80 (s, 1H, CH), 3.56 (s, 1H, CH), 3.28 (s, 1H, CH), 2.20–2.07 (m, 3H, 3 × CH), 1.99–1.88 (m, 6H, 6 × CH), 1.70 (d, J = 16.4 Hz, 1H, CH), 1.64–1.52 (m, 4H, 4 × CH), 1.27 (d, J = 17.6 Hz, 1H, CH), 1.14–1.04 (m, 1H, CH), 0.80 (s, 3H, CH_3), 0.66 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 196.1, 164.2, 147.3, 145.2, 145.0, 132.3, 126.5, 118.3, 117.3, 114.9, 68.3, 67.4, 52.3, 50.5, 48.0, 37.0, 34.7, 34.3, 32.8, 31.6, 28.2, 15.7, 14.9; HRMS calcd for $C_{30}H_{29}ClN_5O_2$ $[M-H]^-$: 526.2010, found: 526.1996.

20-(3-Chloro-4-methylphenyl)-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5h)



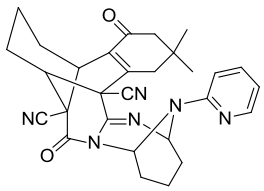
Isolated as a white solid; mp 276–278 ℃; IR (KBr, *v*, cm^{-1}): 2953, 2871, 2252, 1696, 1639, 1513, 1451, 1373, 1252, 1184, 1126, 1089, 1035, 934, 837; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.19 (s, 1H, ArH), 6.94 (s, 1H, ArH), 6.80 (s, 1H, ArH), 6.17 (s, 1H, CH), 5.85 (s, 1H, CH), 3.57 (s, 1H, CH), 3.28 (s, 1H, CH), 2.19 (s, 3H, CH_3), 2.10–1.87 (m, 9H, 9 × CH), 1.61–1.53 (m, 5H, 5 × CH), 1.25–1.05 (m, 2H, 2 × CH), 0.79 (s, 3H, CH_3), 0.60 (s, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 195.2, 164.9, 147.3, 147.1, 146.7, 134.7, 132.5, 131.8, 128.3, 117.8, 116.8, 115.3, 115.2, 68.6, 63.4, 52.7, 49.7, 48.1, 34.5, 34.4, 32.1, 29.3, 28.9, 25.5, 25.4, 24.9, 18.9, 15.7, 13.9; HRMS calcd for $C_{31}H_{31}ClN_5O_2$ $[M-H]^-$: 540.2166, found: 540.2169.

20-Butyl-13,13-dimethyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5i)



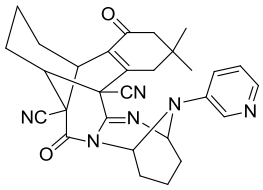
Isolated as a white solid; mp 216–218 ℃; IR (KBr, *v*, cm^{-1}): 2955, 2872, 2248, 1697, 1638, 1465, 1374, 1333, 1264, 1233, 1148, 1089, 1054, 865, 844, 772, 738; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 5.17 (s, 1H, CH), 4.60 (s, 1H, CH), 3.47 (s, 1H, CH), 3.28 (s, 1H, CH), 2.45–2.38 (m, 2H, CH_2), 2.20–2.10 (m, 4H, 4 × CH), 2.03–1.93 (m, 2H, 2 × CH), 1.79–1.67 (m, 4H, 4 × CH), 1.59–1.47 (m, 4H, 4 × CH), 1.35–1.28 (m, 3H, 3 × CH), 1.24–1.16 (m, 2H, 2 × CH), 1.03 (s, 1H, CH), 1.00 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 0.82 (t, *J* = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 200.9, 169.6, 151.5, 150.3, 137.0, 122.8, 120.4, 74.8, 73.7, 57.5, 57.2, 55.3, 53.1, 39.9, 39.2, 37.3, 34.8, 34.4, 34.0, 32.3, 30.4, 29.9, 25.0, 20.7, 19.0; HRMS calcd for $C_{28}H_{34}N_5O_2$ $[M-H]^-$: 472.2713, found: 472.2750.

13,13-Dimethyl-8,11-dioxo-20-(pyridin-2-yl)-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5j)



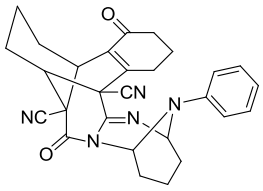
Isolated as a white solid; mp 264–265 ℃; IR (KBr, *v*, cm^{-1}): 2956, 2870, 2248, 1696, 1638, 1472, 1434, 1369, 1344, 1265, 1092, 1069; 786, 741; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.08 (s, 1H, ArH), 7.68 (t, *J* = 8.0 Hz, 1H, ArH), 7.15 (d, *J* = 8.8 Hz, 1H, ArH), 6.88 (t, *J* = 5.6 Hz, 1H, ArH), 6.80 (s, 1H, CH), 6.09 (s, 1H, CH), 3.56 (s, 1H, CH), 3.23 (s, 1H, CH), 2.24 (d, *J* = 18.0 Hz, 1H, CH), 2.15–2.06 (m, 2H, 2 × CH), 2.00–1.89 (m, 5H, 5 × CH), 1.83–1.75 (m, 1H, CH), 1.63–1.49 (m, 5H, 5 × CH), 1.33 (d, *J* = 18.0 Hz, 1H, CH), 1.21–1.11 (m, 1H, CH), 0.78 (s, 3H, CH_3), 0.49 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.5, 164.1, 157.3, 148.3, 147.7, 146.8, 139.2, 131.6, 117.9, 117.2, 115.3, 110.3, 66.5, 61.3, 52.7, 49.9, 48.2, 34.6, 34.2, 28.8, 28.6, 26.2, 25.5, 25.0, 15.7, 14.5; HRMS calcd for $C_{29}H_{31}N_6O_2$ $[M+H]^+$: 495.2508, found: 495.2511.

13,13-Dimethyl-8,11-dioxo-20-(pyridin-3-yl)-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5k)



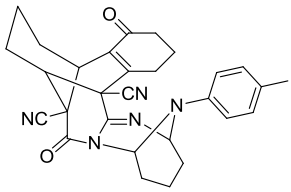
Isolated as a white solid; mp 270–271 ℃; IR (KBr, *v*, cm^{-1}): 2959, 2872, 2246, 1694, 1667, 1632, 1486, 1466, 1365, 1337, 1270, 1246, 1091, 1021, 805, 710; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.17–8.16 (m, 1H, ArH), 8.02 (s, 1H, ArH), 7.46 (d, *J* = 7.2 Hz, 1H, ArH), 7.33–7.30 (m, 1H, ArH), 6.21 (s, 1H, CH), 5.79 (s, 1H, CH), 3.59 (s, 1H, CH), 3.29 (s, 1H, CH), 2.20 (d, *J* = 18.0 Hz, 1H, CH), 2.09 (d, *J* = 16.4 Hz, 2H, 2 × CH), 2.00–1.83 (m, 7H, 7 × CH), 1.62–1.54 (m, 4H, 4 × CH), 1.26 (d, *J* = 18.0 Hz, 1H, CH), 1.18–1.10 (m, 1H, CH), 0.79 (s, 3H, CH_3), 0.61 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.6, 164.7, 162.8, 147.4, 146.8, 143.6, 143.3, 140.8, 138.4, 131.8, 125.3, 124.8, 124.5, 117.7, 115.2, 68.8, 63.6, 52.8, 52.3, 49.6, 48.1, 48.0, 34.6, 32.1, 29.5, 25.6, 15.7, 13.9; HRMS calcd for $C_{29}H_{31}N_6O_2$ $[M+H]^+$: 495.2508, found: 495.2525.

8,11-Dioxo-20-phenyl-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5l)



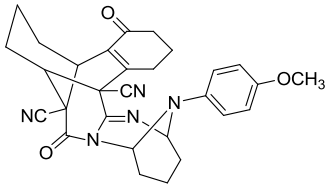
Isolated as a white solid; mp 224–226 ℃; IR (KBr, *v*, cm^{-1}): 2954, 2871, 2249, 1693, 1637, 1496, 1460, 1334, 1238, 1094, 760, 696; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.19 (t, *J* = 7.2 Hz, 2H, ArH), 6.90 (d, *J* = 7.2 Hz, 1H, ArH), 6.85 (d, *J* = 8.4 Hz, 2H, ArH), 6.14 (s, 1H, CH), 5.70 (s, 1H, CH), 3.52 (s, 1H, CH), 3.29 (s, 1H, CH), 2.50–2.44 (m, 1H, CH), 2.34–2.26 (m, 1H, CH), 2.09 (d, *J* = 14.4 Hz, 1H, CH), 2.00–1.81 (m, 8H, 8 × CH), 1.62–1.46 (m, 5H, 5 × CH), 1.34–1.24 (m, 1H, CH), 0.82 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.2, 164.7, 149.5, 147.3, 147.1, 132.2, 130.0, 121.9, 118.5, 117.9, 117.1, 115.3, 68.5, 64.6, 52.1, 48.1, 36.8, 34.3, 29.5, 29.2, 25.9, 25.4, 25.0, 21.1, 15.4, 14.1; HRMS calcd for $C_{28}H_{26}N_5O_2$ $[M-H]^-$: 464.2087, found: 464.2127.

8,11-Dioxo-20-(*p*-tolyl)-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epi butane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicar bonitrile (5m)



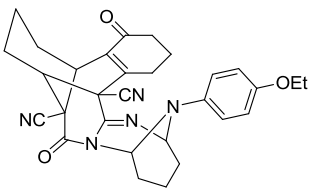
Isolated as a white solid; mp 230–232 ℃; IR (KBr, *v*, cm^{-1}): 2952, 2871, 2249, 1694, 1641, 1512, 1451, 1381, 1342, 1262, 1112, 1094, 751, 705; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.98 (d, *J* = 8.4 Hz, 2H, ArH), 6.73 (d, *J* = 8.4 Hz, 2H, ArH), 6.08 (s, 1H, CH), 5.65 (s, 1H, CH), 3.51 (s, 1H, CH), 3.28 (s, 1H, CH), 2.46–2.40 (m, 1H, CH), 2.35–2.28 (m, 1H, CH), 2.16 (s, 3H, CH_3), 2.08–2.05 (m, 1H, CH), 1.98–1.75 (m, 8H, 8 × CH), 1.59 (s, 3H, 3 × CH), 1.53–1.45 (m, 2H, 2 × CH), 1.33–1.25 (m, 1H, CH), 0.84 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.2, 164.6, 149.5, 146.9, 144.9, 132.2, 130.8, 130.3, 117.9, 117.0, 115.3, 68.5, 64.6, 52.1, 48.0, 36.7, 34.2, 29.4, 29.1, 25.8, 25.4, 25.0, 20.9, 20.3, 15.4, 14.1; HRMS calcd for $C_{29}H_{30}N_5O_2$ $[M+H]^+$: 480.2400, found: 480.2368.

20-(4-Methoxyphenyl)-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9 ,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5n)



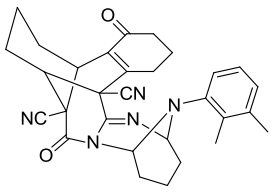
Isolated as a white solid; mp 190–192 ℃; IR (KBr, *v*, cm^{-1}): 2940, 2870, 2255, 1683, 1635, 1512, 1454, 1365, 1254, 1096, 1035, 968, 835; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.77 (s, 4H, ArH), 6.03 (s, 1H, CH), 5.57 (s, 1H, CH), 3.64 (s, 3H, CH_3O), 3.50 (s, 1H, CH), 3.29 (s, 1H, CH), 2.50–2.46 (m, 1H, CH), 2.36–2.30 (m, 1H, CH), 2.10–2.06 (m, 1H, CH), 1.97–1.87 (m, 8H, 8 × CH), 1.66–1.50 (m, 5H, 5 × CH), 1.34–1.24 (m, 1H, CH), 0.94 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.3, 164.7, 154.5, 149.5, 147.0, 140.9, 132.3, 118.4, 117.9, 115.3, 115.2, 68.8, 65.3, 55.8, 52.2, 48.1, 36.9, 34.4, 34.3, 29.6, 29.3, 26.0, 25.5, 25.0, 21.1, 15.5, 14.1; HRMS calcd for $C_{29}H_{28}N_5O_3$ $[M-H]^-$: 494.2192, found: 494.2227.

20-(4-Ethoxyphenyl)-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5o)



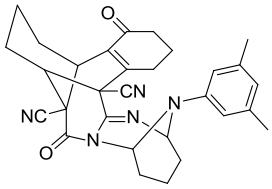
Isolated as a white solid; mp 218–220 ℃; IR (KBr, *v*, cm^{-1}): 2950, 2875, 2248, 1699, 1647, 1513, 1449, 1379, 1237, 1039, 945, 820; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.75 (s, 4H, ArH), 6.02 (s, 1H, CH), 5.56 (s, 1H, CH), 3.92–3.86 (m, 2H, CH_2O), 3.51 (s, 1H, CH), 3.28 (s, 1H, CH), 2.38–2.30 (m, 1H, CH), 2.10–2.06 (m, 1H, CH), 1.97–1.86 (m, 9H, 9 × CH), 1.67–1.59 (m, 3H, 3 × CH), 1.50 (t, *J* = 13.6 Hz, 2H, 2 × CH), 1.30 (d, *J* = 6.8 Hz, 1H, CH), 1.25 (t, *J* = 7.2 Hz, 3H, CH_3), 0.96 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.3, 164.7, 153.7, 149.5, 146.9, 140.8, 132.3, 120.3, 118.4, 115.8, 68.8, 65.3, 63.7, 52.2, 48.1, 36.9, 34.3, 29.6, 29.3, 26.0, 25.5, 25.1, 21.2, 15.5, 15.2, 14.1; HRMS calcd for $C_{30}H_{30}N_5O_3$ $[M-H]^-$: 508.2349, found: 508.2389.

20-(2,3-Dimethylphenyl)-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5p)



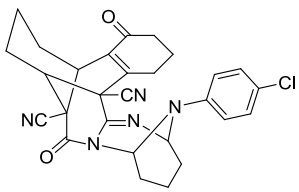
Isolated as a white solid; mp 226–228 ℃; IR (KBr, *v*, cm^{-1}): 2948, 2874, 2248, 1696, 1679, 1641, 1471, 1375, 1339, 1270, 1093, 788, 725; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.08 (t, *J* = 8.0 Hz, 1H, ArH), 6.07 (d, *J* = 7.6 Hz, 1H, ArH), 6.68 (d, *J* = 8.0 Hz, 1H, ArH), 5.13 (s, 1H, CH), 4.95 (s, 1H, CH), 3.30 (s, 1H, CH), 3.02 (s, 1H, CH), 2.90–2.82 (m, 1H, CH), 2.61–2.57 (m, 2H, 2 × CH), 2.39–2.35 (m, 1H, CH), 2.23 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.12–2.01 (m, 4H, 4 × CH), 1.96–1.82 (m, 5H, 5 × CH), 1.70 (d, *J* = 14.0 Hz, 1H, CH), 1.58–1.52 (m, 2H, 2 × CH), 1.43–1.33 (m, 1H, CH), 1.10 (s, 1H, CH); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 195.7, 164.0, 148.6, 147.4, 147.2, 138.8, 133.0, 131.2, 126.9, 126.8, 118.1, 117.7, 115.1, 69.7, 68.7, 52.0, 48.2, 37.3, 36.0, 34.9, 30.4, 29.9, 26.4, 26.2, 25.1, 22.2, 21.0, 15.7, 14.7, 14.6; HRMS calcd for $C_{30}H_{31}N_5O_2$ $[M]^+$: 493.2478, found: 493.2473.

20-(3,5-Dimethylphenyl)-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5q)



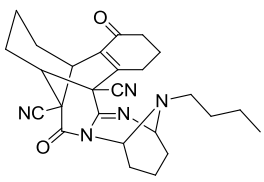
Isolated as a white solid; mp 226–228 ℃; IR (KBr, ν, cm^{-1}): 2924, 2865, 2245, 1690, 1640, 1592, 1461, 1364, 1267, 1196, 1177, 883, 832, 754; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.53 (s, 1H, ArH), 6.43 (s, 2H, ArH), 6.08 (s, 1H, CH), 5.65 (s, 1H, CH), 3.53 (s, 1H, CH), 3.30 (s, 1H, CH), 2.35 (t, J = 12.0 Hz, 1H, CH), 2.10 (s, 6H, 2 × CH_3), 2.06 (s, 1H, CH), 1.96–1.86 (m, 9H, 9 × CH), 1.61 (s, 3H, 3 × CH), 1.49 (t, J = 17.6 Hz, 2H, 2 × CH), 1.35–1.29 (m, 1H, CH), 0.76 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.4, 164.6, 149.7, 147.4, 146.8 139.0, 132.1, 123.5, 118.0, 115.3, 115.0, 68.6, 64.6, 51.9, 48.1, 37.0, 34.2, 34.1, 29.6, 29.2, 26.0, 25.4, 25.0, 21.6, 21.1, 15.4, 14.2; HRMS calcd for $C_{30}H_{30}N_5O_2$ $[M-H]^-$: 492.2400, found: 492.2395.

20-(4-Chlorophenyl)-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5r)



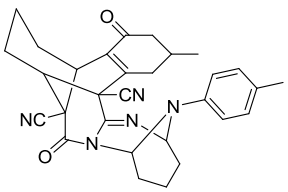
Isolated as a white solid; mp 256–258 ℃; IR (KBr, ν, cm^{-1}): 2942, 2870, 2248, 1698, 1679, 1639, 1495, 1345, 1246, 1092, 1005, 944, 820, 745, 705; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.34 (d, J = 8.8 Hz, 2H, ArH), 6.99 (d, J = 8.8 Hz, 2H, ArH), 5.79 (s, 1H, CH), 5.48 (s, 1H, CH), 3.31 (s, 1H, CH), 2.91 (s, 1H, CH), 2.87–2.79 (m, 1H, CH), 2.59–2.52 (m, 2H, 2 × CH), 2.38–2.34 (m, 1H, CH), 2.10–2.04 (m, 2H, 2 × CH), 1.99–1.97 (m, 3H, 3 × CH), 1.91–1.79 (m, 4H, 4 × CH), 1.67–1.49 (m, 3H, 3 × CH), 1.40–1.30 (m, 1H, CH), 1.07 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.5, 164.0, 148.4, 147.4, 146.6, 132.9, 129.7, 126.3, 120.3, 117.5, 114.9, 67.7, 67.0, 51.7, 47.9, 37.2, 35.8, 34.8, 29.8, 26.2, 25.9, 24.9, 22.1, 15.5, 14.4; HRMS calcd for $C_{28}H_{27}ClN_5O_2$ $[M+H]^+$: 500.1853, found: 500.1831.

20-Butyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5s)



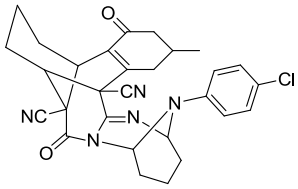
Isolated as a white solid; mp 246–248 ℃; IR (KBr, *v*, cm^{-1}): 2945, 2867, 2250, 1682, 1637, 1495, 1342, 1255, 1092, 1003, 822, 745, 704; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 4.91 (s, 1H, CH), 4.58 (s, 1H, CH), 3.46 (s, 1H, CH), 3.29 (s, 1H, CH), 2.83–2.77 (m, 1H, CH), 2.59–2.55 (m, 1H, CH), 2.39–2.31 (m, 1H, CH), 2.10–2.04 (m, 3H, 3 × CH), 1.92–1.70 (m, 8H, 8 × CH), 1.57–1.54 (m, 3H, 3 × CH), 1.37–1.26 (m, 6H, 6 × CH), 0.97–0.91 (m, 1H, CH), 0.87 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 195.6, 164.2, 148.9, 146.6, 132.7, 118.0, 115.3, 69.2, 68.2, 51.9, 51.8, 48.2, 37.2, 35.4, 34.8, 30.2, 29.8, 26.2, 25.9, 25.1, 22.1, 20.2, 15.6, 14.6, 14.3; HRMS calcd for $C_{26}H_{32}N_5O_2$ $[M+H]^+$: 446.2556, found: 446.2521.

13-Methyl-8,11-dioxo-20-(p-tolyl)-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5t)



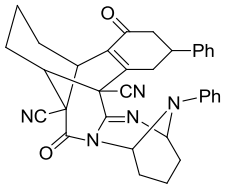
Isolated as a white solid; mp 246–247 ℃; IR (KBr, *v*, cm^{-1}): 2937, 2870, 2246, 1702, 1680, 1640, 1513, 1336, 1249, 1235, 1124, 1089, 906, 871, 821, 735; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.99 (d, *J* = 8.0 Hz, 2H, ArH), 6.75 (d, *J* = 8.4 Hz, 2H, ArH), 6.12 (s, 1H, CH), 5.76 (s, 1H, CH), 3.51 (s, 1H, CH), 3.30 (s, 1H, CH), 2.34–2.22 (m, 2H, 2 × CH), 2.18 (s, 3H, CH_3), 2.07 (d, *J* = 14.4 Hz, 1H, CH), 1.98–1.88 (m, 7H, 7 × CH), 1.59–1.46 (m, 4H, 4 × CH), 1.42–1.34 (m, 1H, CH), 1.28–1.18 (m, 1H, CH), 0.93–0.85 (m, 1H, CH), 0.67 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 195.3, 164.8, 149.2, 147.1 145.0, 132.3, 130.6, 130.3, 117.9, 116.5, 116.5, 115.6, 68.8, 63.7, 52.9, 48.1, 44.3, 34.5, 34.2, 33.8, 29.2, 29.0, 28.3, 25.4, 25.0, 20.8, 20.3, 15.2, 14.1; HRMS calcd for $C_{30}H_{32}N_5O_2$ $[M+H]^+$: 494.2556, found: 494.2537.

20-(4-Chlorophenyl)-13-methyl-8,11-dioxo-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5u)



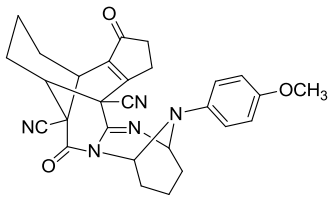
Isolated as a white solid; mp 217–219 ℃; IR (KBr, *v*, cm^{-1}): 2950, 2868, 2248, 1690, 1635, 1497, 1451, 1336, 1239, 1090, 937, 829, 745; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.26 (d, *J* = 8.8 Hz, 2H, ArH), 6.92 (d, *J* = 8.8 Hz, 2H, ArH), 6.15 (s, 1H, CH), 5.81 (s, 1H, CH), 3.54 (s, 1H, CH), 3.29 (s, 1H, CH), 2.37–2.26 (m, 2H, 2 × CH), 2.08–1.89 (m, 8H, 8 × CH), 1.59–1.51 (m, 4H, 4 × CH), 1.37 (t, *J* = 14.4 Hz, 1H, CH), 1.29–1.20 (m, 1H, CH), 0.92–0.85 (m, 1H, CH), 0.71 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 195.2, 164.7, 148.8, 147.3, 146.3, 132.4, 129.8, 125.6, 118.4, 117.8, 115.5, 68.6, 63.6, 52.8, 48.1, 44.4, 34.4, 34.3, 33.8, 29.1, 28.9, 28.3, 25.4, 25.0, 20.8, 15.2, 13.9; HRMS calcd for $C_{29}H_{29}ClN_5O_2$ $[M+H]^+$: 514.2010, found: 514.1988.

8,11-Dioxo-13,20-diphenyl-3,4,5,6,8,9,10,11,12,13,14,15-dodecahydro-2*H*-9,15,10-(epibutane[1,1,4]triyl)-2,6-epiminobenzo[4,5]azocino[1,2-*a*][1,3]diazocine-9,15-dicarbonitrile (5v)



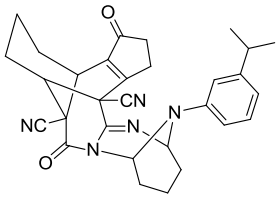
Isolated as a white solid; mp 220–224 ℃; IR (KBr, ν, cm^{-1}): 2943, 2873, 2383, 1697, 1637, 1598, 1497, 1454, 1342, 1246, 1091, 1006, 758, 700; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.40–7.36 (m, 2H, ArH), 7.31–7.28 (m, 5H, ArH), 6.99–6.94 (m, 3H, ArH), 5.81 (s, 1H, CH), 5.44 (s, 1H, CH), 3.39 (s, 1H, CH), 3.12–3.02 (m, 1H, CH), 2.88–2.55 (m, 4H, 4 × CH), 2.09–1.91 (m, 6H, 6 × CH), 1.87–1.79 (m, 1H, CH), 1.70–1.45 (m, 4H, 4 × CH), 1.23–1.06 (m, 2H, 2 × CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 195.2, 163.9, 147.6, 147.3, 146.5, 143.2, 143.1, 132.8, 129.9, 129.3, 129.3, 127.6, 127.1, 122.6, 118.5, 118.4, 117.4, 115.3, 67.9, 67.1, 52.7, 48.0, 43.4, 38.3, 36.6, 34.9, 34.8, 30.0, 29.9, 15.3, 14.7; HRMS calcd for $C_{34}H_{32}N_5O_2$ $[M+H]^+$: 542.2556, found: 542.2522.

19-(4-Methoxyphenyl)-8,11-dioxo-2,3,4,5,6,8,9,10,11,12,13,14-dodecahydro-9,14,10-(epibutane[1,1,4]triyl)-2,6-epiminocyclopenta[4,5]azocino[1,2-*a*][1,3]diazocine-9,14-dicarbonitrile (7a)



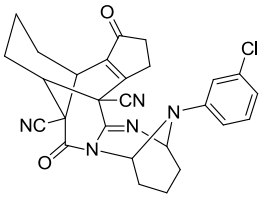
Isolated as a white solid; mp 218–220 ℃; IR (KBr, *v*, cm^{-1}): 2958, 2870, 2361, 1715, 1691, 1646, 1597, 1492, 1445, 1384, 1342, 1247, 1092, 1014, 960, 875, 867, 792, 706; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.73–6.66 (m, 4H, ArH), 5.99–5.98 (m, 1H, CH), 5.59–5.58 (m, 1H, CH), 3.69–3.66 (m, 4H, CH_3 and CH), 3.11 (s, 1H, CH), 2.55–2.50 (m, 1H, CH), 2.39–2.32 (m, 1H, CH), 2.04–1.87 (m, 7H, 7 × CH), 1.66–1.49 (m, 6H, 6 × CH), 1.22–1.84 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 203.8, 164.5, 164.3, 154.3, 146.2, 140.8, 138.6, 118.3, 114.8, 69.6, 64.9, 55.6, 50.0, 48.0, 34.9, 34.3, 34.1, 29.3, 29.0, 25.4, 24.7, 24.2, 15.2, 14.0; HRMS calcd for $C_{28}H_{27}N_5NaO_3$ $[M+Na]^+$: 504.2012, found: 504.2000.

19-(3-Isopropylphenyl)-8,11-dioxo-2,3,4,5,6,8,9,10,11,12,13,14-dodecahydro-9,14,10-(epibutane[1,1,4]triyl)-2,6-epiminocyclopenta[4,5]azocino[1,2-*a*][1,3]diazocine-9,14-dicarbonitrile (7b)



Isolated as a white solid; mp 218–219 ℃; IR (KBr, *v*, cm^{-1}): 2963, 2344, 1716, 1692, 1641, 1492, 1443, 1384, 1342, 1243, 1093, 959, 875, 790, 705; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.00 (t, *J* = 8.0 Hz, 1H, ArH), 6.88 (s, 1H, ArH), 6.78 (d, *J* = 7.6 Hz, 1H, ArH), 6.41–6.39 (m, 1H, CH), 6.16–6.15 (m, 1H, CH), 5.82–5.81 (m, 1H, CH), 3.68 (s, 1H, CH), 3.10 (s, 1H, CH), 2.77–2.73 (m, 1H, CH), 2.51–2.45 (m, 1H, CH), 2.29–2.23 (m, 1H, CH), 2.01–1.96 (m, 4H, 4 × CH), 1.95–1.83 (m, 3H, 3 × CH), 1.62–1.57 (m, 2H, 2 × CH), 1.56–1.45 (m, 4H, 4 × CH), 1.19–1.17 (m, 1H, CH), 1.14 (d, *J* = 6.8 Hz, 3H, CH_3), 1.11 (d, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 203.8, 164.4, 150.5, 147.2, 146.3, 138.5, 129.4, 119.8, 117.8, 115.6, 114.6, 113.0, 68.7, 63.9, 49.9 48.0, 34.8, 34.2, 34.0, 29.3, 28.9, 25.3, 24.7, 24.1, 15.2, 14.0; HRMS calcd for $C_{30}H_{32}N_5O_2$ $[M+H]^+$: 494.2556, found: 494.2559.

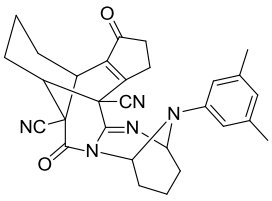
19-(3-Chlorophenyl)-8,11-dioxo-2,3,4,5,6,8,9,10,11,12,13,14-dodecahydro-9,14,10-(epibutane[1,1,4]triyl)-2,6-epiminocyclopenta[4,5]azocino[1,2-*a*][1,3]diazocine-9,



14-dicarbonitrile (7c)

Isolated as a white solid; mp 236–237 ℃; IR (KBr, *v*, cm^{-1}): 2936, 2864, 2251, 1716, 1641, 1473, 1439, 1340, 1258, 1235, 1094, 1012, 874, 751; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.66–7.63 (m, 1H, ArH), 7.18–7.14 (m, 1H, ArH), 7.03–6.99 (m, 1H, ArH), 6.37–6.35 (m, 1H, CH), 5.81–5.80 (m, 1H, CH), 5.24–5.23 (m, 1H, CH), 3.72 (s, 1H, CH), 3.16 (s, 1H, CH), 2.82–2.76 (m, 1H, CH), 2.23–1.92 (m, 9H, 9 × CH), 1.86–1.83 (m, 1H, CH), 1.72–1.53 (m, 4H, 4 × CH), 1.33–1.25 (m, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 204.2, 163.7, 162.9, 147.0, 145.9, 139.1, 134.2, 129.8, 126.7, 123.0, 119.4, 117.4, 114.5, 69.1, 68.1, 49.9, 48.0, 35.5, 35.1, 34.5, 30.5, 29.2, 26.3, 25.1, 24.2, 15.2, 14.3; HRMS calcd for $C_{27}H_{25}ClN_5O_2$ $[M+H]^+$: 486.1697, found: 486.1692.

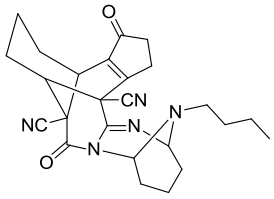
19-(3,5-Dimethylphenyl)-8,11-dioxo-2,3,4,5,6,8,9,10,11,12,13,14-dodecahydro-9,14,10-(epibutane[1,1,4]triyl)-2,6-epiminocyclopenta[4,5]azocino[1,2-*a*][1,3]diazocin



e-9,14-dicarbonitrile (7d)

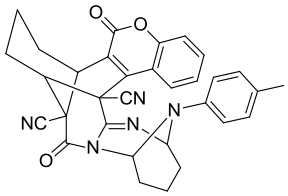
Isolated as a white solid; mp 220–222 ℃; IR (KBr, *v*, cm^{-1}): 2952, 2861, 2246, 1715, 1693, 1641, 1593, 1445, 1389, 1343, 1251, 1199, 1094, 1006, 859, 833, 700; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.54 (s, 1H, ArH), 6.38 (s, 2H, ArH), 6.07–6.06 (m, 1H, CH), 5.73–5.72 (m, 1H, CH), 3.67 (s, 1H, CH), 3.13 (s, 1H, CH), 2.55–2.51 (m, 1H, CH), 2.36–2.30 (m, 1H, CH), 2.10 (s, 6H, 2 × CH_3), 2.05–1.80 (m, 8H, 8 × CH), 1.62–1.60 (m, 2H, 2 × CH), 1.56–1.51 (m, 3H, 3 × CH), 1.22–1.19 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 209.0, 169.5, 169.3, 152.2, 151.1, 143.8, 143.4, 128.3, 122.6, 119.4, 74.1, 69.0, 54.8, 52.9, 39.7, 39.1, 39.0, 34.1, 33.8, 30.4, 29.6, 29.0, 26.4, 20.0, 18.9; HRMS calcd for $C_{29}H_{30}N_5O_2$ $[M+H]^+$: 480.2400, found: 480.2392.

19-Butyl-8,11-dioxo-2,3,4,5,6,8,9,10,11,12,13,14-dodecahydro-9,14,10-(epibutane[1,1,4]triyl)-2,6-epiminocyclopenta[4,5]azocino[1,2-*a*][1,3]diazocine-9,14-dicarbonitrile (7e)



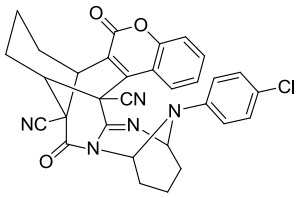
Isolated as a white solid; mp 206–207 ℃; IR (KBr, *v*, cm^{-1}): 2933, 2857, 2249, 1720, 1638, 1465, 1384, 1341, 1250, 1109, 1089, 1012, 851; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 5.16–5.15 (m, 1H, CH), 4.61–4.60 (m, 1H, CH), 3.63 (s, 1H, CH), 3.11 (s, 1H, CH), 2.96–2.90 (m, 1H, CH), 2.65–2.57 (m, 2H, 2 × CH), 2.31–2.24 (m, 1H, CH), 2.09–2.00 (m, 3H, 3 × CH), 1.98–1.89 (m, 2H, 2 × CH), 1.83–1.75 (m, 2H, 2 × CH), 1.73–1.69 (m, 2H, 2 × CH), 1.61–1.48 (m, 4H, 4 × CH), 1.35–1.24 (m, 3H, 3 × CH), 1.22–1.14 (m, 2H, 2 × CH), 0.79 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 204.1, 164.5, 163.4, 145.7, 139.2, 117.9, 114.8, 70.2, 68.5, 51.7, 50.2, 48.2, 35.1, 34.6, 34.1, 29.4, 29.3, 26.1, 24.8, 24.2, 20.1, 15.3, 14.1; HRMS calcd for $[M+H]^+$: $C_{25}H_{30}N_5O_2$ 432.2400, found: 432.2396.

8,11-Dioxo-22-(p-tolyl)-2,3,4,5,6,8,9,10,11,17-decahydro-9,17,10-(epibutane[1,1,4]triyl)-2,6-epiminochromeno[4',3':4,5]azocino[1,2-*a*][1,3]diazocine-9,17-dicarbonitrile (9a)



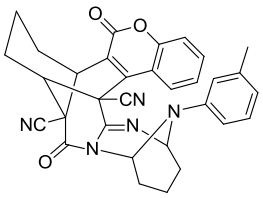
Isolated as a white solid; mp 224–226 ℃; IR (KBr, *v*, cm^{-1}): 2952, 2865, 2246, 1729, 1648, 1569, 1491, 1457, 1382, 1326, 1248, 1176, 1092, 953, 785; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.56 (d, *J* = 8.4 Hz, 1H, ArH), 7.65 (t, *J* = 7.6 Hz, 1H, ArH), 7.46–7.40 (m, 2H, ArH), 7.08 (d, *J* = 8.0 Hz, 2H, ArH), 6.81 (d, *J* = 8.0 Hz, 2H, ArH), 5.66 (s, 1H, CH), 5.44 (s, 1H, CH), 3.54 (s, 1H, CH), 2.92 (s, 1H, CH), 2.19 (s, 3H, CH_3), 2.17–2.12 (m, 1H, CH), 1.99–1.94 (m, 2H, 2 × CH), 1.88–1.75 (m, 3H, 3 × CH), 1.72–1.65 (m, 2H, 2 × CH), 1.52–1.49 (m, 1H, CH), 1.34–1.27 (m, 1H, CH), 1.02–0.98 (m, 1H, CH), 0.28–0.25 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 163.5, 158.2, 152.8, 147.2, 145.4, 139.1, 133.0, 131.6, 130.5, 126.6, 125.4, 124.4, 118.4, 117.9, 117.1, 115.7, 115.5, 68.3, 67.2, 48.3, 48.0, 38.0, 36.7, 29.6, 26.3, 24.4, 20.6, 15.6, 13.6; HRMS calcd for $C_{32}H_{28}N_5O_3$ $[M+H]^+$: 530.2192, found: 530.2163.

22-(4-Chlorophenyl)-8,11-dioxo-2,3,4,5,6,8,9,10,11,17-decahydro-9,17,10-(epibutane[1,1,4]triyl)-2,6-epiminochromeno[4',3':4,5]azocino[1,2-*a*][1,3]diazocine-9,17-dicarbonitrile (9b)



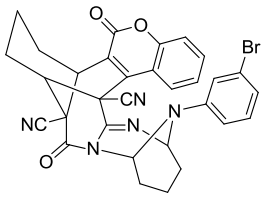
Isolated as a white solid; mp 242–243 ℃; IR (KBr, *v*, cm^{-1}): 2949, 2861, 2350, 1727, 1693, 1642, 1494, 1453, 1318, 1272, 1241, 1101, 877, 829, 755; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.20 (d, *J* = 8.4 Hz, 1H, ArH), 7.51 (t, *J* = 8.0 Hz, 1H, ArH), 7.29 (d, *J* = 8.4 Hz, 1H, ArH), 7.06 (t, *J* = 7.6 Hz, 1H, ArH), 6.56 (d, *J* = 8.8 Hz, 2H, ArH), 6.42 (d, *J* = 8.8 Hz, 2H, ArH), 5.90 (s, 1H, CH), 5.57 (s, 1H, CH), 3.80 (s, 1H, CH), 3.61 (s, 1H, CH), 2.26–2.22 (m, 1H, CH), 2.12–1.98 (m, 4H, 4 × CH), 1.94–1.90 (m, 2H, 2 × CH), 1.87–1.82 (m, 1H, CH), 1.62–1.54 (m, 3H, 3 × CH), 1.32–1.29 (m, 1H, CH); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 164.1, 157.9, 152.2, 146.9, 145.5, 140.6, 132.4, 129.7, 128.5, 126.3, 126.0, 124.1, 124.0, 120.1, 118.6, 117.4, 117.2, 115.7, 115.1, 70.4, 65.3, 48.4, 47.9, 36.7, 36.1, 29.0, 25.7, 24.6, 15.4, 14.1; HRMS calcd for $C_{31}H_{25}ClN_5O_3$ $[M+H]^+$: 550.1646, found: 550.1675.

8,11-Dioxo-22-(m-tolyl)-2,3,4,5,6,8,9,10,11,17-decahydro-9,17,10-(epibutane[1,1,4]triyl)-2,6-epiminochromeno[4',3':4,5]azocino[1,2-*a*][1,3]diazocine-9,17-dicarbonitrile (9c)



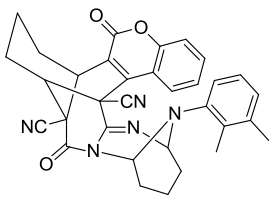
Isolated as a white solid; mp 228–229 ℃; IR (KBr, *v*, cm^{-1}): 2952, 2867, 2245, 1723, 1691, 1650, 1606, 1569, 1492, 1451, 1384, 1327, 1245, 1174, 1126, 1097, 1064, 953, 856, 760, 697; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.28–8.25 (m, 1H, ArH), 7.50–7.45 (m, 1H, ArH), 7.27–7.24 (m, 1H, ArH), 7.12–7.08 (m, 1H, ArH), 6.45 (t, *J* = 8.0 Hz, 1H, ArH), 6.22 (s, 1H, ArH), 6.19–6.12 (m, 2H, ArH), 5.95–5.94 (m, 1H, CH), 5.59–5.58 (m, 1H, CH), 3.82 (s, 1H, CH), 3.63–3.62 (m, 1H, CH), 2.29–2.22 (s, 1H, CH), 2.13–1.97 (m, 4H, 4 × CH), 1.92–1.91 (m, 1H, CH), 1.89 (s, 3H, CH_3), 1.85–1.55 (m, 5H, 5 × CH), 1.35–1.25 (m, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 164.2, 158.0, 152.2, 146.6, 146.5, 140.8, 138.1, 132.5, 128.3, 126.1, 124.0, 123.6, 123.0, 117.5, 117.4, 117.1, 115.9, 115.0, 113.6, 70.3, 65.0, 48.3, 47.8, 36.5, 35.8, 29.1, 28.9, 25.6, 24.6, 21.5, 15.4, 14.3; HRMS calcd for $C_{32}H_{28}N_5O_3$ $[M+H]^+$: 530.2192, found: 530.2163.

22-(3-Bromophenyl)-8,11-dioxo-2,3,4,5,6,8,9,10,11,17-decahydro-9,17,10-(epibutane[1,1,4]triyl)-2,6-epiminochromeno[4',3':4,5]azocino[1,2-*a*][1,3]diazocine-9,17-dicarbonitrile (9d)



Isolated as a white solid; mp 246–247 ℃; IR (KBr, *v*, cm^{-1}): 2949, 2861, 2359, 1727, 1693, 1641, 1589, 1564, 1477, 1449, 1322, 1269, 1239, 1127, 1100, 1063, 949, 879, 860, 766, 686; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.62–8.60 (m, 1H, ArH), 7.72–7.68 (m, 1H, ArH), 7.51–7.46 (m, 2H, ArH), 7.27 (t, *J* = 8.0 Hz, 1H, ArH), 7.24–7.23 (m, 1H, ArH), 7.17–7.15 (m, 1H, ArH), 6.96–6.94 (m, 1H, ArH), 5.84 (s, 1H, CH), 5.64 (s, 1H, CH), 3.59 (s, 1H, CH), 3.11 (s, 1H, CH), 2.22–2.18 (m, 1H, CH), 2.09–1.82 (m, 5H, 5 × CH), 1.76 (s, 2H, 2 × CH), 1.59–1.55 (m, 1H, CH), 1.43–1.36 (m, 1H, CH), 1.07–1.03 (m, 1H, CH), 0.34–0.27 (m, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 163.5, 158.2, 152.8, 149.1, 147.3, 139.0, 133.0, 131.8, 126.6, 125.4, 125.0, 124.3, 123.1, 121.0, 117.9, 117.1, 116.7, 115.7, 115.5, 67.8, 66.1, 48.2, 47.9, 37.7, 36.7, 29.4, 26.2, 24.4, 15.6, 13.4; HRMS calcd for $C_{31}H_{24}BrN_5NaO_3$ $[M+Na]^+$: 616.0960, found: 616.0967.

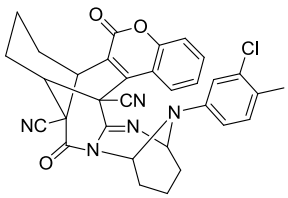
22-(2,3-Dimethylphenyl)-8,11-dioxo-2,3,4,5,6,8,9,10,11,17-decahydro-9,17,10-(epibutane[1,1,4]triyl)-2,6-epiminochromeno[4',3':4,5]azocino[1,2-*a*][1,3]diazocine-9,17-dicarbonitrile (9e)



Isolated as a white solid; mp 238–239 ℃; IR (KBr, *v*, cm^{-1}): 2945, 2871, 2345, 1697, 1640, 1502, 1385, 1327, 1253, 1228, 1118, 1094, 761; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.56–8.53 (m, 1H, ArH), 7.65–7.61 (m, 1H, ArH), 7.48–7.46 (m, 1H, ArH), 7.31–7.27 (m, 1H, ArH), 6.48 (d, *J* = 8.4 Hz, 1H, ArH), 5.76 (t, *J* = 8.0 Hz, 1H, CH), 5.57 (d, *J* = 7.6 Hz, 1H, CH), 5.43–5.42 (m, 1H, CH), 4.88–4.87 (m, 1H, CH), 3.83 (s, 1H, CH), 3.56 (s, 1H, CH), 2.32–2.28 (m, 1H, CH), 2.14–2.09 (m, 2H, 2 × CH), 2.05–2.04 (m, 6H, 2 × CH_3), 2.02–1.92 (m, 4H, 4 × CH), 1.85–1.82 (m, 1H, CH), 1.75–1.71 (m, 2H, 2 × CH), 1.61–1.58 (m, 1H, CH), 1.44–1.38 (m, 1H, CH); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 163.9, 158.1, 152.8, 146.9, 146.2, 139.9, 138.1, 133.0, 130.0, 126.7, 125.6, 124.5, 124.1, 117.8, 117.5, 116.8, 116.1, 115.8, 70.4, 69.1, 48.4, 48.0, 36.3, 36.2, 29.5, 29.3, 25.8, 24.7, 20.6, 15.4, 14.6, 14.4; HRMS calcd for $C_{33}H_{30}N_5O_3$ $[M+H]^+$: 544.2349,

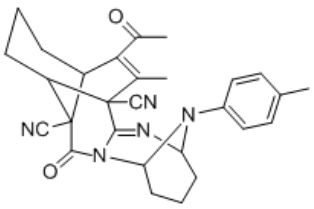
found: 544.2363.

22-(3-Chloro-4-methylphenyl)-8,11-dioxo-2,3,4,5,,8,9,10,11,17-decahydro-9,17,10-(epibutane[1,1,4]triyl)-2,6-epiminochromeno[4',3':4,5]azocino[1,2-*a*][1,3]diazocine-9,17-dicarbonitrile (9f)



Isolated as a white solid; mp 260–261 ℃; IR (KBr, *v*, cm^{-1}): 2955, 2864, 2365, 1724, 1641, 1608, 1501, 1340, 1243, 1125, 1093, 1065, 856, 802, 759; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.16–8.13 (m, 1H, ArH), 7.49–7.45 (m, 1H, ArH), 7.30–7.28 (m, 1H, ArH), 7.03–7.00 (m, 1H, ArH), 6.52 (d, *J* = 8.8 Hz, 1H, ArH), 6.37–6.36 (m, 1H, ArH), 6.31–6.29 (m, 1H, ArH), 5.93–5.92 (m, 1H, CH), 5.64–5.63 (m, 1H, CH), 3.82 (s, 1H, CH), 3.64–3.63 (m, 1H, CH), 2.26–1.95 (m, 7H, 7 × CH), 1.91 (s, 3H, CH_3), 1.86–1.81 (m, 1H, CH), 1.63–1.55 (m, 3H, 3 × CH), 1.32–1.29 (m, 1H, CH); ^{13}C NMR (150 MHz, DMSO-d_6) δ_C: 164.4, 157.9, 152.1, 146.7, 146.0, 140.8, 133.4, 132.2, 131.1, 128.4, 126.0, 124.0, 123.9, 117.4, 117.1, 116.8, 115.7, 115.5, 114.9, 70.8, 64.6, 48.3, 47.8, 36.7, 35.8, 28.8, 25.6, 24.5, 19.0, 15.4, 14.1; HRMS calcd for $C_{32}H_{26}ClN_5NaO_3$ $[M+Na]^+$: 586.1622, found: 586.1617.

15-Acetyl-14-methyl-8-oxo-16-(p-tolyl)-3,4,5,6,8,8a,9,10,11,12,12a,13-dodecahydro-2*H*-2,6-epimino-9,13-etheno[1,3]diazocino[1,2-*b*]isoquinoline-8a,13-dicarbonitrile (11a)



Isolated as a white solid; mp 209-210 ℃; IR (KBr, *v*, cm^{-1}): 2926, 2866, 2246, 1695, 1637, 1557, 1539, 1460, 1396, 1376, 1295, 1253, 1112, 1086, 1019, 925, 896; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 6.94 (d, *J* = 8.4 Hz, 2H, ArH), 6.70 (d, *J* = 8.4 Hz, 2H, ArH), 6.03 (s, 1H, CH), 5.55 (s, 1H, CH), 3.46 (s, 1H, CH), 3.25 (s, 1H, CH), 2.16 (s, 3H, CH_3), 2.12-2.09 (m, 1H, CH), 2.06 (s, 3H, CH_3), 1.99-1.88 (m, 6H, 6 ´CH), 1.61-1.56 (m, 4H, 4 ´CH), 1.32 (s, 3H, CH_3), 1.23 (s, 1H, CH); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 201.6, 164.7, 147.1, 145.2, 137.3, 131.1, 129.9, 117.9, 117.7, 115.8, 69.5, 65.1, 52.3, 47.8, 39.1, 37.7, 34.0, 30.2, 29.4, 29.1, 25.5, 25.0, 20.5, 16.0, 15.1, 14.1; HRMS calcd for $C_{28}H_{30}N_5O_2$ $[M+H]^+$: 468.2400, found: 468.2396.

4. Crystal date of compound 5a

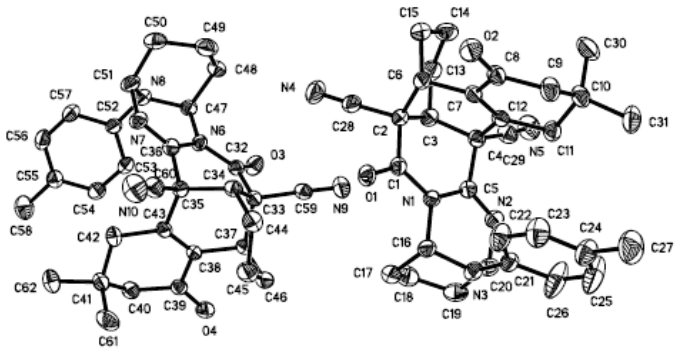


Figure 1. X-ray structure of **5a**

Table 1 Solidlographic Data of Compound **5a**

Empirical formula	$C_{31}H_{33}N_5O_2$	
Formula weight	507.62	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Solid system	Monoclinic,	
space group	$P2_1/c$	
Unit cell dimensions	a = 18.6242(19) Å	α =90 °
	b = 10.3311(7) Å	β = 106.496(2) °
	c = 29.295(3) Å	γ =90 °
Volume	5404.6(8) Å ^{3}	
Z	8	
Calculated density	1.248 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	2160	
Solid size	0.45 ×0.40 ×0.36 mm	
Theta range for data collection	2.80 to 25.02 °	
Limiting indices	-21 ≤ h ≤ 22, -12 ≤ k ≤ 7, -34 ≤ l ≤ 31	
Reflections collected	24701	
Independent reflections	9517 [R(int) = 0.0821]	
Data / restraints / parameters	9517 / 0 / 692	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2σ(I)]	R_1 = 0.0641, wR_2 = 0.1687	
R indices (all data)	R_1 = 0.1669, wR_2 = 0.2661	
Largest diff. peak and hole	0.337 and -0.225 e. Å^{-3}	

Table 2 Selected bond lengths (Å) of compound **5a**

Bond	Bond Lengths	Bond	Bond Lengths	Bond	Bond Lengths
N(1)-C(1)	1.373(5)	C(4)-C(29)	1.482(6)	C(34)-C(44)	1.519(6)
N(1)-C(5)	1.399(5)	C(4)-C(5)	1.518(6)	C(34)-C(35)	1.555(6)
N(1)-C(16)	1.506(5)	C(4)-C(12)	1.543(6)	C(35)-C(60)	1.473(6)

N(2)-C(5)	1.272(5)	C(6)-C(7)	1.499(6)	C(35)-C(36)	1.519(6)
N(2)-C(20)	1.471(6)	C(6)-C(15)	1.537(6)	C(35)-(43)	1.550(6)
N(3)-C(21)	1.421(6)	C(7)-C(12)	1.342(5)	C(37)-C(38)	1.505(5)
N(3)-C(16)	1.448(5)	C(7)-C(8)	1.483(6)	C(37)-C(46)	1.534(6)
N(3)-C(20)	1.466(6)	C(8)-C(9)	1.493(6)	C(38)-C(43)	1.328(5)
N(4)-C(28)	1.134(5)	C(9)-C(10)	1.534(6)	C(38)-C(39)	1.494(6)
N(5)-C(29)	1.130(5)	C(10)-C(30)	1.516(8)	C(39)-C(40)	1.496(6)
N(6)-C(32)	1.374(5)	C(10)-C(11)	1.526(6)	C(40)-C(41)	1.533(6)
N(6)-C(36)	1.388(5)	C(10)-C(31)	1.534(7)	C(41)-C(42)	1.521(7)
N(6)-C(47)	1.509(5)	C(11)-C(12)	1.487(6)	C(41)-C(61)	1.522(7)
N(7)-C(36)	1.273(5)	C(13)-C(14)	1.514(7)	C(41)-C(62)	1.537(6)
N(7)-C(51)	1.477(6)	C(14)-C(15)	1.507(7)	C(42)-C(43)	1.495(5)
N(8)-C(52)	1.427(6)	C(16)-C(17)	1.526(7)	C(44)-C(45)	1.514(7)
N(8)-C(47)	1.436(5)	C(17)-C(18)	1.506(7)	C(45)-C(46)	1.524(7)
N(8)-C(51)	1.462(6)	C(18)-C(19)	1.502(7)	C(47)-C(48)	1.512(6)
N(9)-C(59)	1.140(5)	C(19)-C(20)	1.526(7)	C(48)-C(49)	1.516(7)
N(10)-C(60)	1.134(6)	C(21)-C(26)	1.358(7)	C(49)-C(50)	1.532(7)
O(1)-C(1)	1.212(5)	C(21)-C(22)	1.360(7)	C(50)-C(51)	1.518(7)
O(2)-C(8)	1.229(5)	C(22)-C(23)	1.379(8)	C(52)-C(53)	1.382(6)
O(3)-C(32)	1.220(5)	C(23)-C(24)	1.353(7)	C(52)-C(57)	1.394(6)
O(4)-C(39)	1.214(5)	C(24)-C(25)	1.346(8)	C(53)-C(54)	1.388(6)
C(1)-C(2)	1.542(6)	C(24)-C(27)	1.514(8)	C(54)-C(55)	1.378(6)
C(2)-C(28)	1.479(6)	C(25)-C(26)	1.372(9)	C(55)-C(56)	1.387(7)
C(2)-C(3)	1.538(6)	C(32)-C(33)	1.530(6)	C(55)-C(58)	1.517(7)
C(2)-C(6)	1.559(6)	C(33)-C(59)	1.478(6)	C(56)-C(57)	1.367(7)
C(3)-C(13)	1.523(7)	C(33)-C(34)	1.534(6)		
C(3)-C(4)	1.555(6)	C(33)-C(37)	1.547(6)		

Table 3 Selected bond angles (°) of compound **5a**

Angles	(°)	Angles	(°)
C(1)-N(1)-C(5)	124.7(4)	C(25)-C(24)-C(23)	115.7(6)
C(1)-N(1)-C(16)	117.8(3)	C(25)-C(24)-C(27)	121.9(5)
C(5)-N(1)-C(16)	117.5(3)	C(23)-C(24)-C(27)	122.3(6)
C(5)-N(2)-C(20)	117.2(4)	C(24)-C(25)-C(26)	122.1(6)
C(21)-N(3)-C(16)	117.9(4)	C(21)-C(26)-C(25)	122.5(6)

C(21)-N(3)-C(20)	116.7(4)	N(4)-C(28)-C(2)	177.8(5)
C(16)-N(3)-C(20)	108.9(4)	N(5)-C(29)-C(4)	174.8(6)
C(32)-N(6)-C(36)	125.3(4)	O(3)-C(32)-N(6)	121.3(4)
C(32)-N(6)-C(47)	117.6(3)	O(3)-C(32)-C(33)	120.8(4)
C(36)-N(6)-C(47)	117.1(3)	N(6)-C(32)-C(33)	117.9(4)
C(36)-N(7)-C(51)	116.8(4)	C(59)-C(33)-C(32)	105.9(3)
C(52)-N(8)-C(47)	117.6(4)	C(59)-C(33)-C(34)	110.1(3)
C(52)-N(8)-C(51)	115.3(4)	C(32)-C(33)-C(34)	112.3(3)
C(47)-N(8)-C(51)	109.3(4)	C(59)-C(33)-C(37)	109.3(3)
O(1)-C(1)-N(1)	121.8(4)	C(32)-C(33)-C(37)	110.3(4)
O(1)-C(1)-C(2)	119.7(4)	C(34)-C(33)-C(37)	108.8(4)
N(1)-C(1)-C(2)	118.5(4)	C(44)-C(34)-C(33)	111.3(4)
C(28)-C(2)-C(3)	110.5(4)	C(44)-C(34)-C(35)	117.4(4)
C(28)-C(2)-C(1)	107.7(3)	C(33)-C(34)-C(35)	104.3(3)
C(3)-C(2)-C(1)	112.8(3)	C(60)-C(35)-C(36)	110.6(4)
C(28)-C(2)-C(6)	108.6(3)	C(60)-C(35)-C(43)	110.0(3)
C(3)-C(2)-C(6)	107.7(4)	C(36)-C(35)-C(43)	107.1(3)
C(1)-C(2)-C(6)	109.5(4)	C(60)-C(35)-C(34)	108.6(4)
C(13)-C(3)-C(2)	111.0(4)	C(36)-C(35)-C(34)	105.9(3)
C(13)-C(3)-C(4)	116.7(4)	C(43)-C(35)-C(34)	114.6(3)
C(2)-C(3)-C(4)	104.4(4)	N(7)-C(36)-N(6)	125.7(4)
C(29)-C(4)-C(5)	109.6(4)	N(7)-C(36)-C(35)	120.4(4)
C(29)-C(4)-C(12)	110.3(4)	N(6)-C(36)-C(35)	113.9(3)
C(5)-C(4)-C(12)	105.8(4)	C(38)-C(37)-C(46)	110.2(4)
C(29)-C(4)-C(3)	108.5(4)	C(38)-C(37)-C(33)	107.7(3)
C(5)-C(4)-C(3)	107.4(3)	C(46)-C(37)-C(33)	110.2(4)
C(12)-C(4)-C(3)	115.1(4)	C(43)-C(38)-C(39)	120.7(4)
N(2)-C(5)-N(1)	125.1(4)	C(43)-C(38)-C(37)	124.5(4)
N(2)-C(5)-C(4)	120.7(4)	C(39)-C(38)-C(37)	114.7(4)
N(1)-C(5)-C(4)	114.0(3)	O(4)-C(39)-C(38)	121.2(4)
C(7)-C(6)-C(15)	110.0(4)	O(4)-C(39)-C(40)	122.5(4)
C(7)-C(6)-C(2)	108.8(3)	C(38)-C(39)-C(40)	116.3(4)
C(15)-C(6)-C(2)	110.1(4)	C(39)-C(40)-C(41)	113.3(4)
C(12)-C(7)-C(8)	119.5(4)	C(42)-C(41)-C(61)	111.3(4)
C(12)-C(7)-C(6)	124.4(4)	C(42)-C(41)-C(40)	108.5(4)

C(8)-C(7)-C(6)	116.0(4)	C(61)-C(41)-C(40)	108.7(4)
O(2)-C(8)-C(7)	120.3(4)	C(42)-C(41)-C(62)	109.2(4)
O(2)-C(8)-C(9)	121.6(4)	C(61)-C(41)-C(62)	109.4(4)
C(7)-C(8)-C(9)	118.0(4)	C(40)-C(41)-C(62)	109.7(4)
C(8)-C(9)-C(10)	114.1(4)	C(43)-C(42)-C(41)	114.1(4)
C(30)-C(10)-C(11)	110.9(5)	C(38)-C(43)-C(42)	123.3(4)
C(30)-C(10)-C(9)	110.3(4)	C(38)-C(43)-C(35)	119.7(4)
C(11)-C(10)-C(9)	107.7(4)	C(42)-C(43)-C(35)	116.7(3)
C(30)-C(10)-C(31)	110.6(4)	C(45)-C(44)-C(34)	113.8(4)
C(11)-C(10)-C(31)	108.7(4)	C(44)-C(45)-C(46)	112.3(4)
C(9)-C(10)-C(31)	108.5(4)	C(45)-C(46)-C(37)	112.0(4)
C(12)-C(11)-C(10)	113.7(4)	N(8)-C(47)-N(6)	109.3(3)
C(7)-C(12)-C(11)	123.5(4)	N(8)-C(47)-C(48)	111.0(4)
C(7)-C(12)-C(4)	118.9(4)	N(6)-C(47)-C(48)	108.5(4)
C(11)-C(12)-C(4)	117.3(4)	C(47)-C(48)-C(49)	111.8(4)
C(14)-C(13)-C(3)	115.1(4)	C(48)-C(49)-C(50)	110.8(4)
C(15)-C(14)-C(13)	111.8(4)	C(51)-C(50)-C(49)	111.1(4)
C(14)-C(15)-C(6)	112.0(4)	N(8)-C(51)-N(7)	111.4(4)
N(3)-C(16)-N(1)	108.4(3)	N(8)-C(51)-C(50)	110.2(4)
N(3)-C(16)-C(17)	109.9(4)	N(7)-C(51)-C(50)	112.0(4)
N(1)-C(16)-C(17)	110.8(4)	C(53)-C(52)-C(57)	117.7(4)
C(18)-C(17)-C(16)	111.9(4)	C(53)-C(52)-N(8)	123.7(4)
C(19)-C(18)-C(17)	111.1(5)	C(57)-C(52)-N(8)	118.6(4)
C(18)-C(19)-C(20)	111.9(4)	C(52)-C(53)-C(54)	121.2(4)
N(3)-C(20)-N(2)	111.1(4)	C(55)-C(54)-C(53)	120.9(5)
N(3)-C(20)-C(19)	110.3(4)	C(54)-C(55)-C(56)	117.5(5)
N(2)-C(20)-C(19)	112.6(4)	C(54)-C(55)-C(58)	120.2(5)
C(26)-C(21)-C(22)	115.5(5)	C(56)-C(55)-C(58)	122.3(4)
C(26)-C(21)-N(3)	120.7(5)	C(57)-C(56)-C(55)	122.1(4)
C(22)-C(21)-N(3)	123.7(4)	C(56)-C(57)-C(52)	120.6(5)
C(21)-C(22)-C(23)	121.4(5)	N(9)-C(59)-C(33)	177.6(5)
C(24)-C(23)-C(22)	122.7(5)	N(10)-C(60)-C(35)	175.7(6)

Crystal date of compound 7b

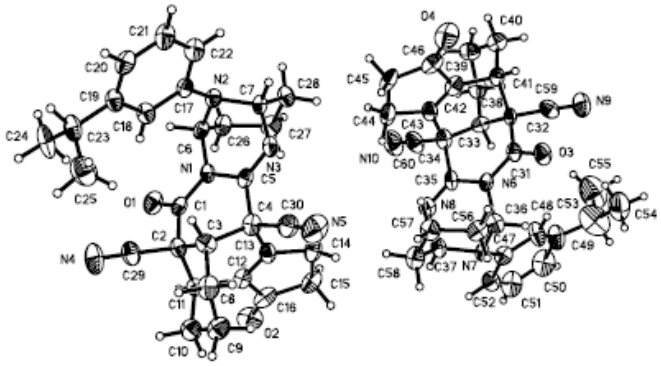


Figure 2. The Crystal Structure of **7b**.

Table 4 Crystallographic Data of Compound **7b**

Empirical formula	$C_{30}H_{31}N_5O_2$
Formula weight	493.60
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic,
space group	*P*-1
Unit cell dimensions	a = 11.2710(9) Å α =104.601(2) °
	b = 12.7401(11) Å β = 104.109(2) °
	c = 18.7802(16) Å γ =96.4400(10) °
Volume	2487.2 (4) Å ^{3}
Z	4
Calculated density	1.318 Mg/m^3
Absorption coefficient	0.085 mm^{-1}
F(000)	1048
Crystal size	0.23 × 0.10 × 0.07 mm
Theta range for data collection	2.31 to 25.02 °
Limiting indices	$-13 \le h \le 12$, $-15 \le k \le 14$, $0 \le l \le 22$
Reflections collected	8528
Independent reflections	8528 [R(int) = 0.0000]
Data / restraints / parameters	8528 / 0 / 672
Goodness-of-fit on F^2	1.112
Final R indices [$I>2\sigma(I)$]	R_1 = 0.1445, wR_2 = 0.2761
R indices (all data)	R_1 = 0.3220, wR_2 = 0.3257
Largest diff. peak and hole	0.552 and -0.454 e. Å^{-3}

Table 5 Selected bond lengths (Å) of compound **7b**

Bond	Bond Lengths	Bond	Bond Lengths	Bond	Bond Lengths
N(1)-C(1)	1.372(10)	C(4)-C(5)	1.500(12)	C(33)-C(38)	1.544(12)
N(1)-C(5)	1.422(10)	C(4)-C(30)	1.503 (13)	C(34)-C(60)	1.471(13)

N(1)-C(6)	1.480(10)	C(4)-C(13)	1.526(11)	C(34)-C(35)	1.511(12)
N(2)-C(6)	1.414(9)	C(6)-C(26)	1.473(11)	C(34)-C(43)	1.543(12)
N(2)-C(17)	1.420(10)	C(7)-C(28)	1.536(11)	C(36)-C(56)	1.464(12)
N(2)-C(7)	1.446(9)	C(8)-C(9)	1.472(12)	C(37)-C(58)	1.517(12)
N(3)-C(5)	1.252(10)	C(9)-C(10)	1.542(12)	C(38)-C(39)	1.470(11)
N(3)-C(7)	1.395(10)	C(10)-C(11)	1.496(11)	C(39)-C(40)	1.546(12)
N(4)-C(29)	1.123(11)	C(11)-C(12)	1.522(11)	C(40)-C(41)	1.492(11)
N(5)-C(30)	1.093(11)	C(12)-C(13)	1.324(11)	C(41)-C(42)	1.511(11)
N(6)-C(31)	1.356(10)	C(12)-C(16)	1.423(11)	C(42)-C(43)	1.302(11)
N(6)-C(35)	1.408(10)	C(13)-C(14)	1.531(11)	C(42)-C(46)	1.482(12)
N(6)-C(36)	1.500(11)	C(14)-C(15)	1.497(11)	C(43)-C(44)	1.494(11)
N(7)-C(47)	1.423(10)	C(15)-C(16)	1.552(13)	C(44)-C(45)	1.570(13)
N(7)-C(36)	1.438(9)	C(17)-C(22)	1.371(11)	C(45)-C(46)	1.498(13)
N(7)-C(37)	1.461(10)	C(17)-C(18)	1.401(10)	C(47)-C(52)	1.374(11)
N(8)-C(35)	1.231(10)	C(18)-C(19)	1.445(11)	C(47)-C(48)	1.376(11)
N(8)-C(37)	1.479(11)	C(19)-C(20)	1.345(11)	C(48)-C(49)	1.384(13)
N(9)-C(59)	1.188(11)	C(19)-C(23)	1.453(12)	C(49)-C(50)	1.327(14)
N(10)-C(60	1.110(11)	C(20)-C(21)	1.373(12)	C(49)-C(53)	1.471(18)
O(1)-C(1)	1.193(9)	C(21)-C(22)	1.388(11)	C(50)-C(51)	1.367(14)
O(2)-C(16)	1.196(10)	C(23)-C(25)	1.494(13)	C(51)-C(52)	1.378(13)
O(3)-C(31)	1.218(10)	C(23)-C(24)	1.537(12)	C(53)-C(55)	1.492(19)
O(4)-C(46)	1.211(11)	C(26)-C(27)	1.535(11)	C(53)-C(54)	1.503(18)
C(1)-C(2)	1.551(12)	C(27)-C(28)	1.517(11)	C(56)-C(57)	1.520(11)
C(2)-C(29)	1.460(12)	C(31)-C(32)	1.545(12)	C(57)-C(58)	1.528(12)
C(2)-C(3)	1.515(11)	C(32)-C(59)	1.441(13)		
C(2)-C(11)	1.547(11)	C(32)-C(33)	1.533(11)		
C(3)-C(8)	1.500(12)	C(32)-C(41)	1.579(11)		
C(3)-C(4)	1.551(11)	C(33)-C(34)	1.479(11)		

Table 6 Selected bond angles (°) of compound **7b**

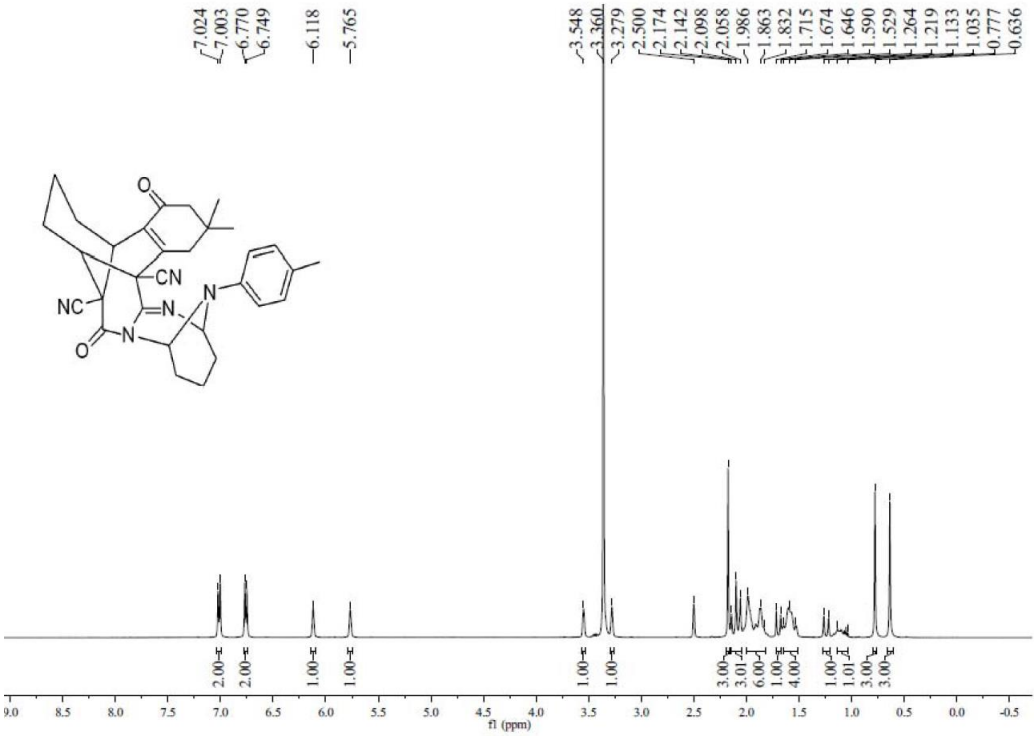
Angles	(°)	Angles	(°)
C(1)-N(1)-C(5)	124.5(8)	C(19)-C(23)-C(24)	115.0(9)
C(1)-N(1)-C(6)	119.9(7)	C(25)-C(23)-C(24)	110.8(9)
C(5)-N(1)-C(6)	115.6(7)	C(6)-C(26)-C(27)	110.5(7)
C(6)-N(2)-C(17)	120.4(7)	C(28)-C(27)-C(26)	111.3(7)

C(6)-N(2)-C(7)	108.0(6)	C(27)-C(28)-C(7)	109.9(7)
C(17)-N(2)-C(7)	116.2(6)	N(4)-C(29)-C(2)	178.3(13)
C(5)-N(3)-C(7)	118.3(8)	N(5)-C(30)-C(4)	176.8(13)
C(31)-N(6)-C(35)	126.8(9)	O(3)-C(31)-N(6)	123.0(9)
C(31)-N(6)-C(36)	117.8(7)	O(3)-C(31)-C(32)	121.0(8)
C(35)-N(6)-C(36)	115.2(7)	N(6)-C(31)-C(32)	115.8(8)
C(47)-N(7)-C(36)	119.5(7)	C(59)-C(32)-C(33)	110.6(8)
C(47)-N(7)-C(37)	115.5(7)	C(59)-C(32)-C(31)	107.1(7)
C(36)-N(7)-C(37)	107.8(7)	C(33)-C(32)-C(31)	113.5(7)
C(35)-N(8)-C(37)	116.7(8)	C(59)-C(32)-C(41)	106.9(7)
O(1)-C(1)-N(1)	123.0(9)	C(33)-C(32)-C(41)	108.5(6)
O(1)-C(1)-C(2)	119.1(9)	C(31)-C(32)-C(41)	110.0(7)
N(1)-C(1)-C(2)	117.4(8)	C(34)-C(33)-C(32)	105.8(7)
C(29)-C(2)-C(3)	109.4(8)	C(34)-C(33)-C(38)	118.0(8)
C(29)-C(2)-C(11)	110.8(7)	C(32)-C(33)-C(38)	110.3(7)
C(3)-C(2)-C(11)	108.1(7)	C(60)-C(34)-C(33)	107.5(8)
C(29)-C(2)-C(1)	104.6(7)	C(60)-C(34)-C(35)	108.4(8)
C(3)-C(2)-C(1)	113.6(7)	C(33)-C(34)-C(35)	108.6(8)
C(11)-C(2)-C(1)	110.2(6)	C(60)-C(34)-C(43)	112.0(8)
C(8)-C(3)-C(2)	112.8(7)	C(33)-C(34)-C(43)	111.3(7)
C(8)-C(3)-C(4)	115.7(8)	C(35)-C(34)-C(43)	109.0(7)
C(2)-C(3)-C(4)	104.7(7)	N(8)-C(35)-N(6)	126.8(10)
C(5)-C(4)-C(30)	109.4(8)	N(8)-C(35)-C(34)	121.0(9)
C(5)-C(4)-C(13)	110.1(7)	N(6)-C(35)-C(34)	112.0(8)
C(30)-C(4)-C(13)	107.2(7)	N(7)-C(36)-C(56)	113.2(8)
C(5)-C(4)-C(3)	109.2(7)	N(7)-C(36)-N(6)	106.5(7)
C(30)-C(4)-C(3)	111.2(8)	C(56)-C(36)-N(6)	114.4(8)
C(13)-C(4)-C(3)	109.7(7)	N(7)-C(37)-N(8)	112.2(7)
N(3)-C(5)-N(1)	123.9(8)	N(7)-C(37)-C(58)	111.8(7)
N(3)-C(5)-C(4)	122.9(9)	N(8)-C(37)-C(58)	108.2(8)
N(1)-C(5)-C(4)	113.1(8)	C(39)-C(38)-C(33)	115.0(8)
N(2)-C(6)-C(26)	113.9(7)	C(38)-C(39)-C(40)	113.7(8)
N(2)-C(6)-N(1)	107.2(7)	C(41)-C(40)-C(39)	110.1(8)
C(26)-C(6)-N(1)	113.3(7)	C(40)-C(41)-C(42)	110.9(7)
N(3)-C(7)-N(2)	114.0(7)	C(40)-C(41)-C(32)	111.5(7)

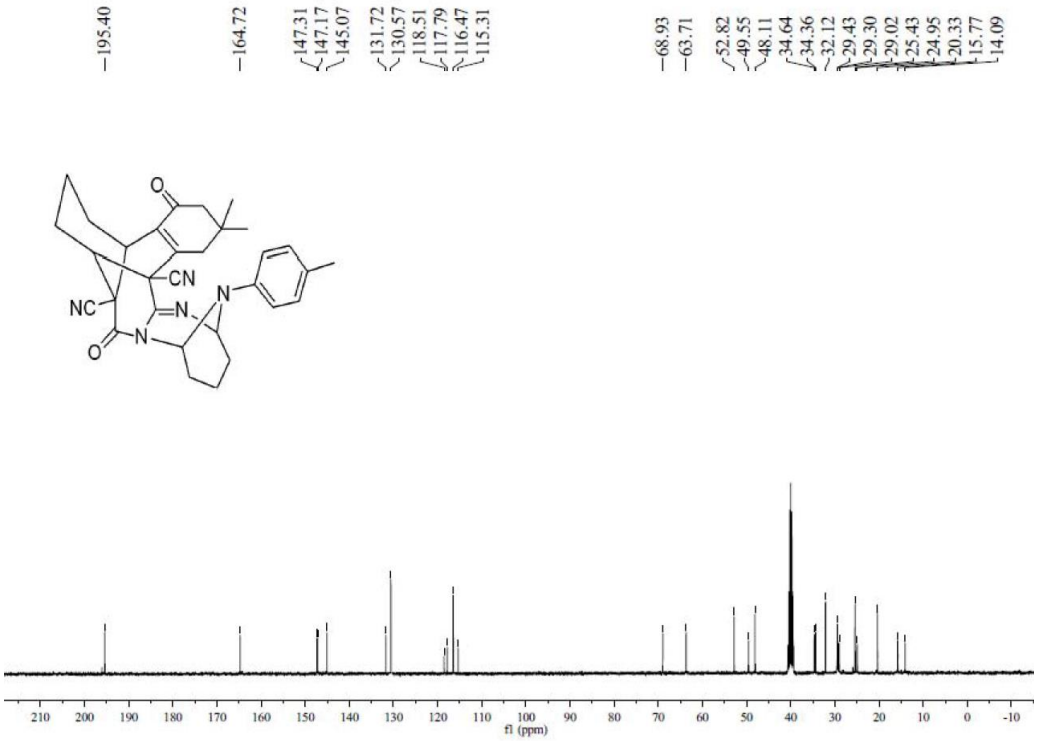
N(3)-C(7)-C(28)	110.1(7)	C(42)-C(41)-C(32)	104.4(7)
N(2)-C(7)-C(28)	110.0(7)	C(43)-C(42)-C(46)	110.3(10)
C(9)-C(8)-C(3)	116.9(8)	C(43)-C(42)-C(41)	124.6(9)
C(8)-C(9)-C(10)	112.4(8)	C(46)-C(42)-C(41)	124.9(9)
C(11)-C(10)-C(9)	110.1(8)	C(42)-C(43)-C(44)	115.1(9)
C(10)-C(11)-C(12)	109.2(7)	C(42)-C(43)-C(34)	122.6(9)
C(10)-C(11)-C(2)	111.8(7)	C(44)-C(43)-C(34)	121.9(9)
C(12)-C(11)-C(2)	107.4(7)	C(43)-C(44)-C(45)	101.6(8)
C(13)-C(12)-C(16)	112.5(9)	C(46)-C(45)-C(44)	106.1(8)
C(13)-C(12)-C(11)	121.6(8)	O(4)-C(46)-C(42)	126.4(11)
C(16)-C(12)-C(11)	125.8(9)	O(4)-C(46)-C(45)	126.9(9)
C(12)-C(13)-C(4)	124.5(8)	C(42)-C(46)-C(45)	106.7(9)
C(12)-C(13)-C(14)	111.0(8)	C(52)-C(47)-C(48)	118.3(9)
C(4)-C(13)-C(14)	124.1(8)	C(52)-C(47)-N(7)	119.8(9)
C(15)-C(14)-C(13)	104.1(8)	C(48)-C(47)-N(7)	121.8(8)
C(14)-C(15)-C(16)	105.3(7)	C(47)-C(48)-C(49)	122.0(10)
O(2)-C(16)-C(12)	125.8(10)	C(50)-C(49)-C(48)	118.1(12)
O(2)-C(16)-C(15)	127.5(9)	C(50)-C(49)-C(53)	117.4(13)
C(12)-C(16)-C(15)	106.6(8)	C(48)-C(49)-C(53)	122.9(12)
C(22)-C(17)-C(18)	119.6(8)	C(49)-C(50)-C(51)	121.9(11)
C(22)-C(17)-N(2)	118.6(8)	C(50)-C(51)-C(52)	120.3(10)
C(18)-C(17)-N(2)	121.8(7)	C(47)-C(52)-C(51)	119.3(10)
C(17)-C(18)-C(19)	119.7(8)	C(49)-C(53)-C(55)	112.9(16)
C(20)-C(19)-C(18)	118.0(9)	C(49)-C(53)-C(54)	118.2(15)
C(20)-C(19)-C(23)	121.5(9)	C(55)-C(53)-C(54)	111.7(15)
C(18)-C(19)-C(23)	120.5(8)	C(36)-C(56)-C(57)	110.4(7)
C(19)-C(20)-C(21)	122.2(9)	C(56)-C(57)-C(58)	111.1(8)
C(20)-C(21)-C(22)	120.5(9)	C(37)-C(58)-C(57)	108.9(8)
C(17)-C(22)-C(21)	120.0(9)	N(9)-C(59)-C(32)	177.2(11)
C(19)-C(23)-C(25)	111.2(9)	N(10)-C(60)-C(34)	177.8(14)

5. ^{1}H NMR and ^{13}C NMR Spectra of all compounds

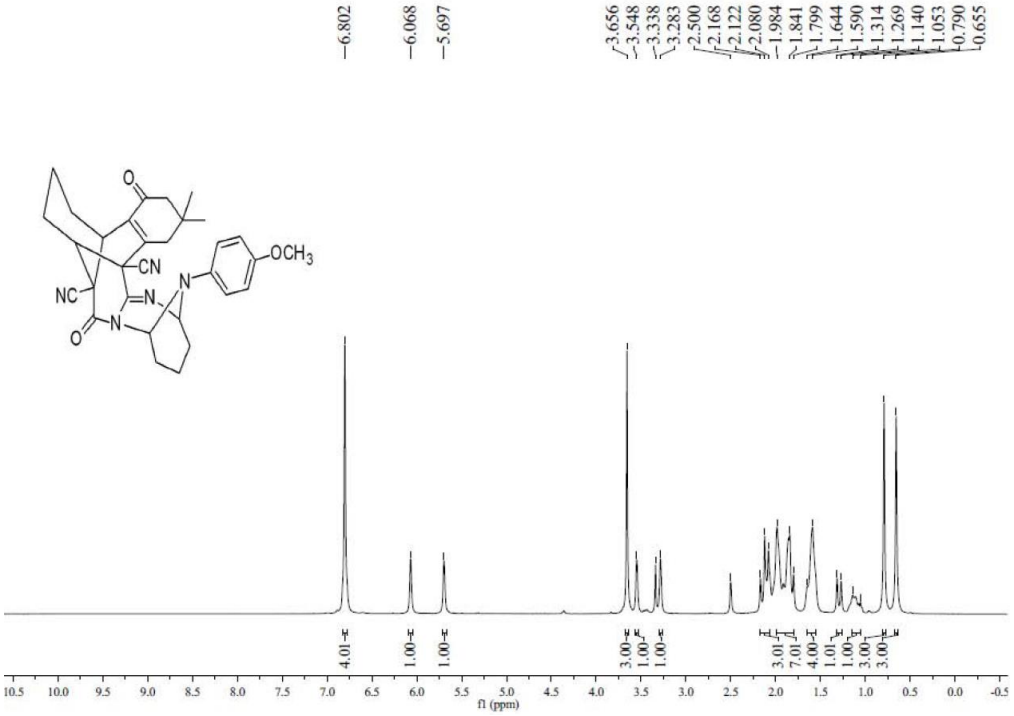
^{1}H NMR of compound **5a**



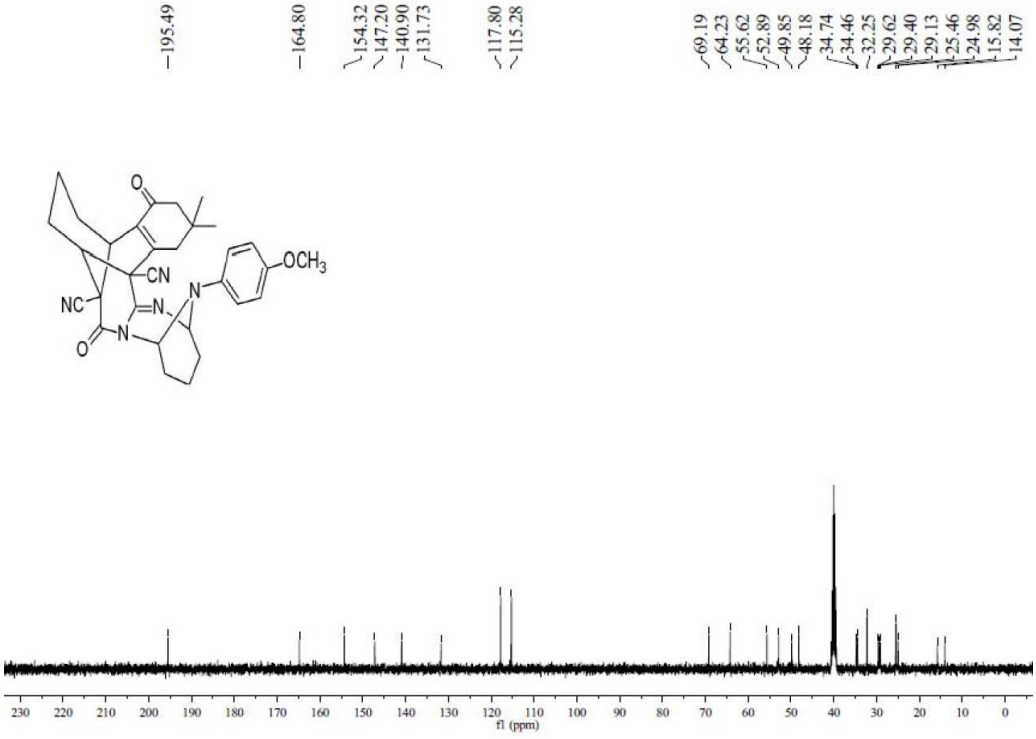
^{13}C NMR of compound **5a**



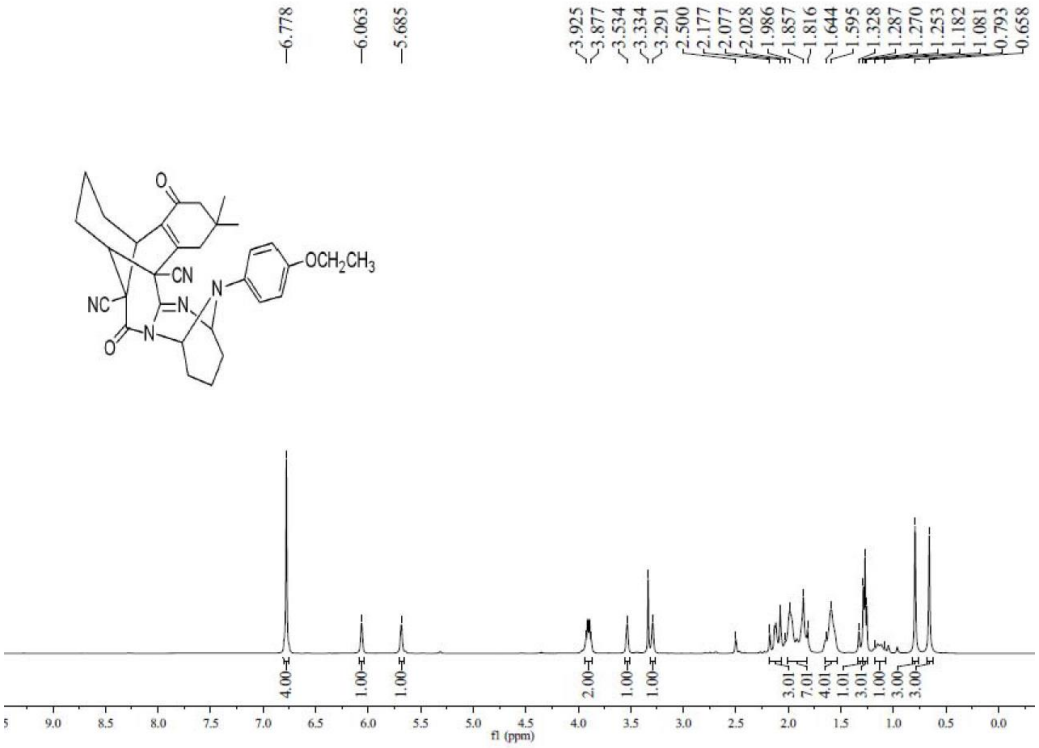
^{1}H NMR of compound **5b**



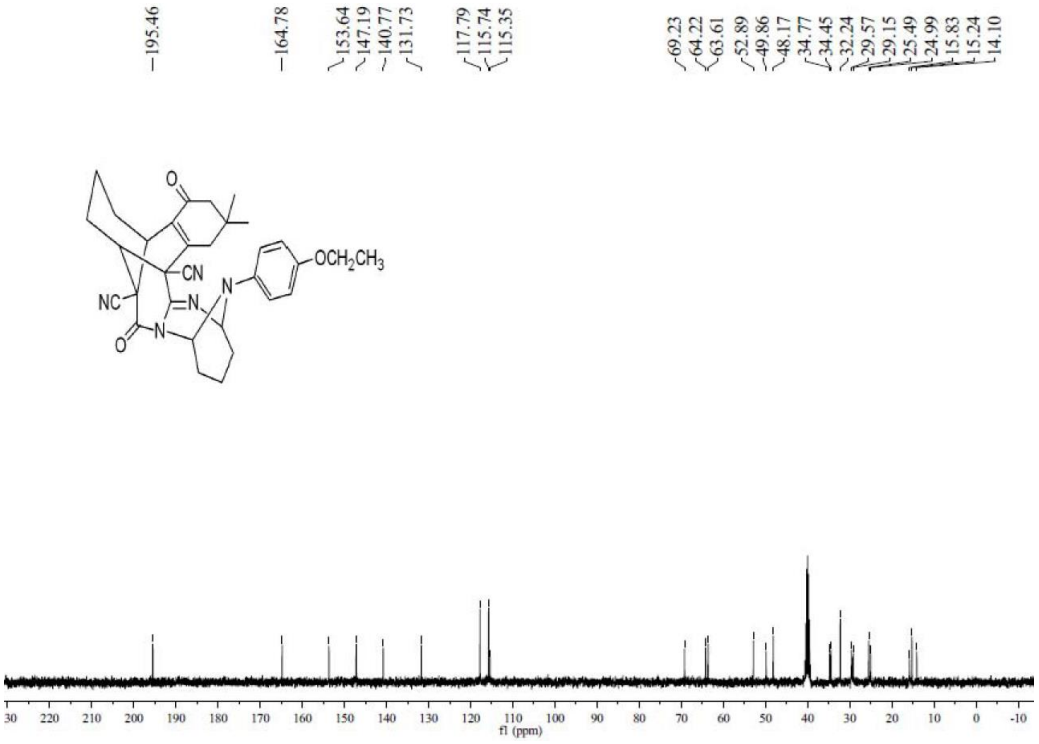
^{13}C NMR of compound **5b**



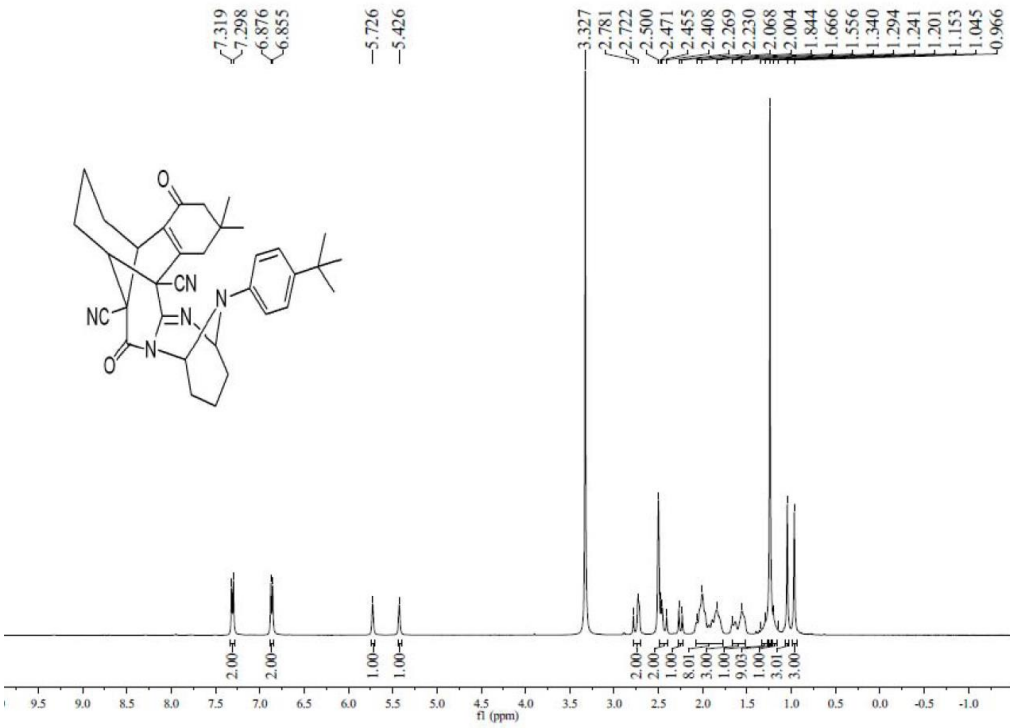
^{1}H NMR of compound **5c**



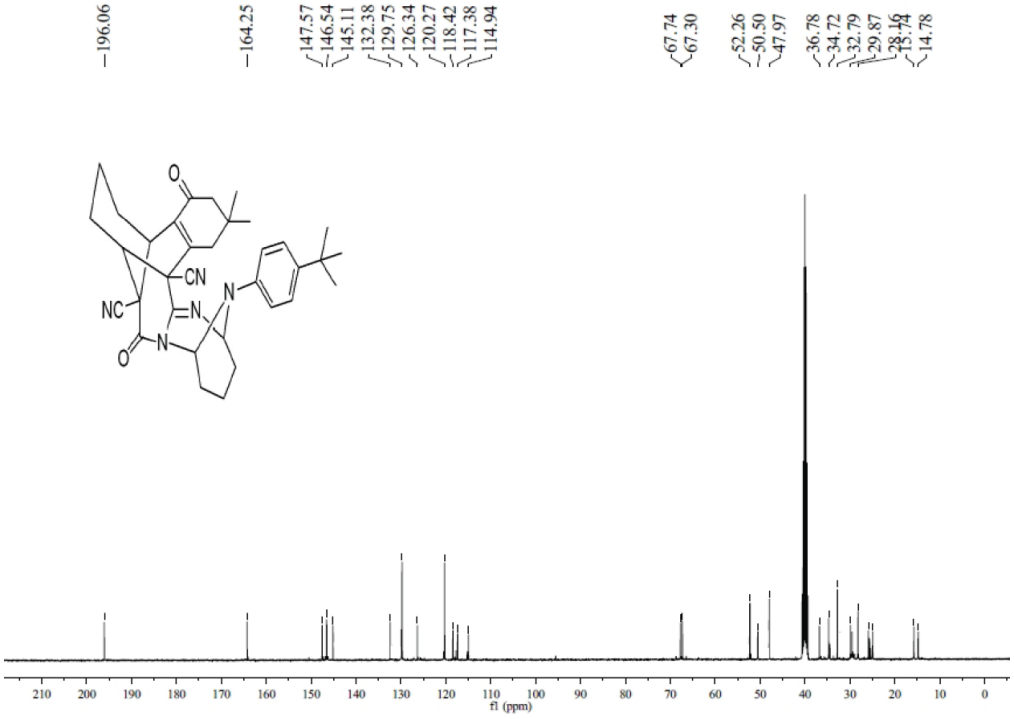
^{13}C NMR of compound **5c**



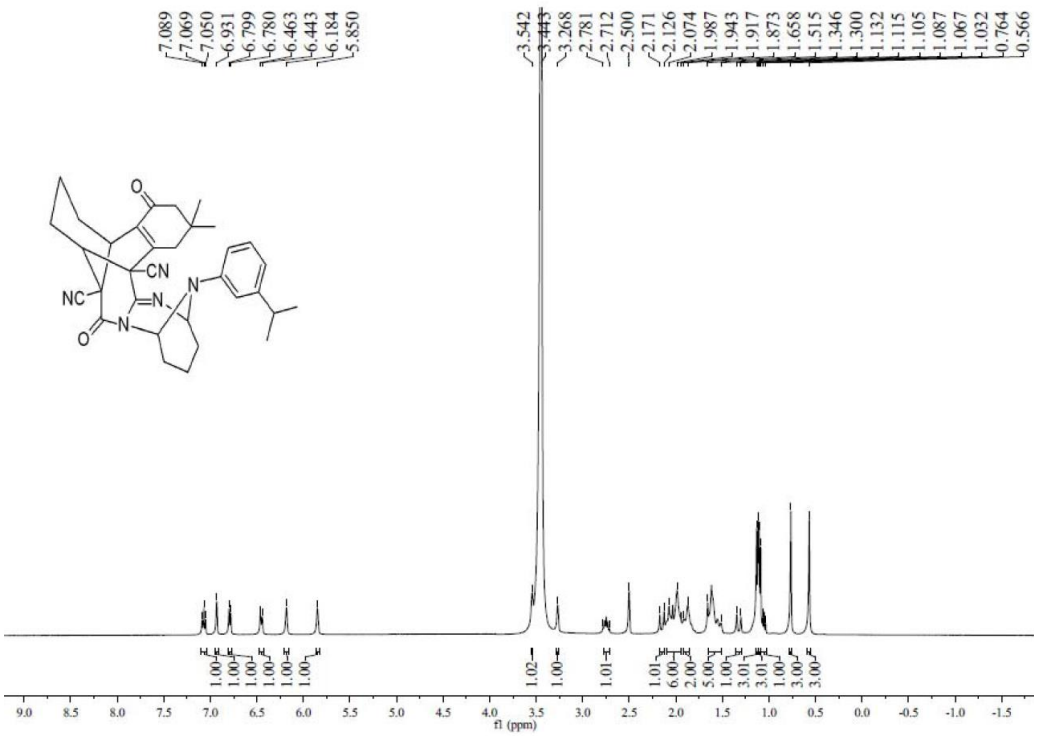
^{1}H NMR of compound **5d**



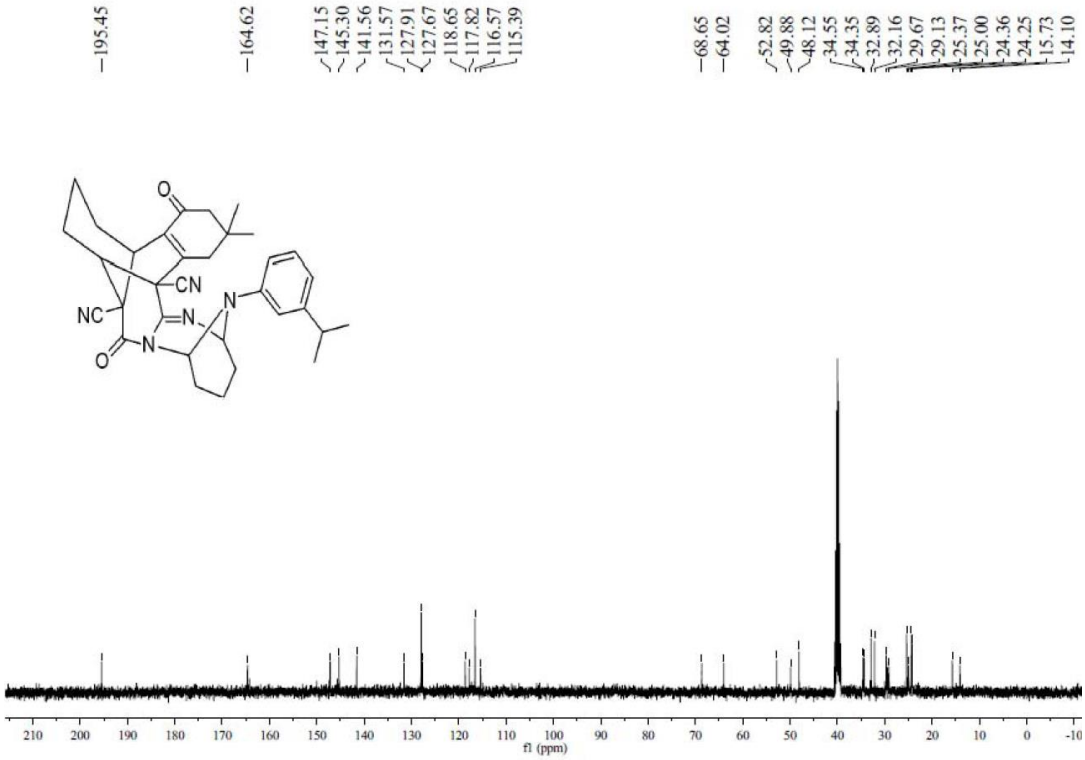
^{13}C NMR of compound **5d**



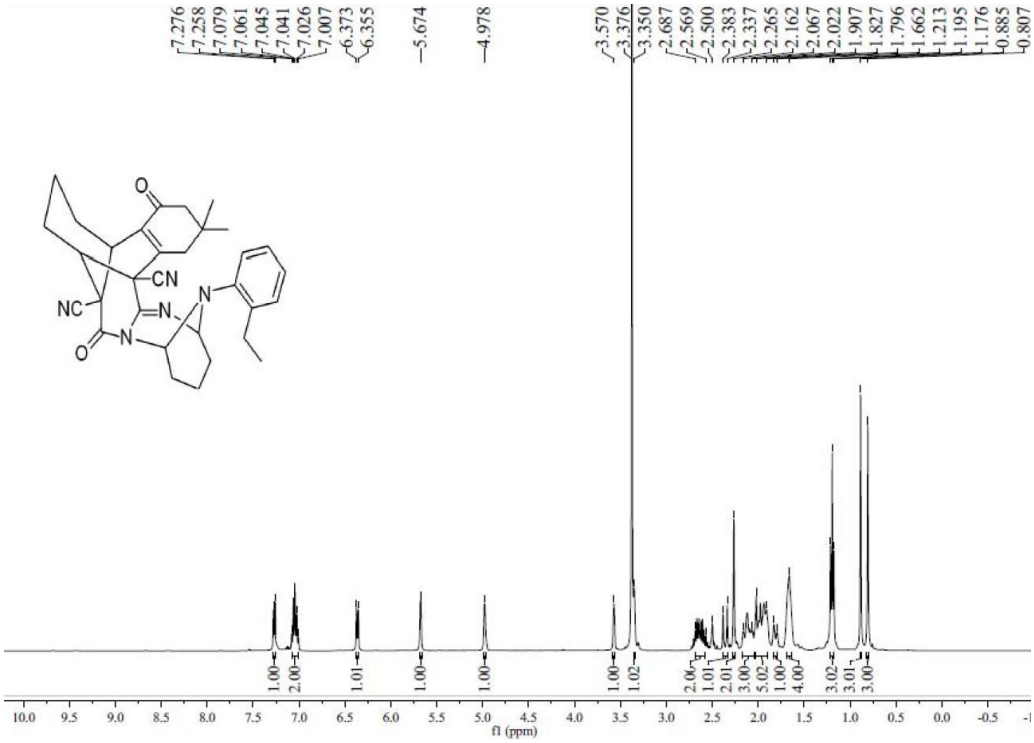
^{1}H NMR of compound **5e**



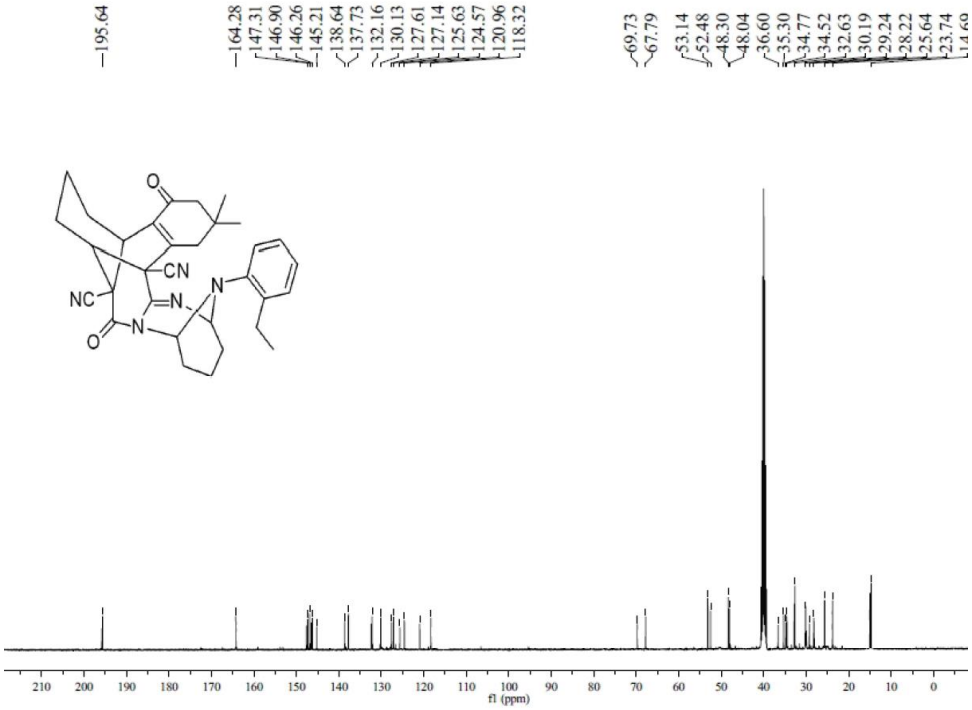
^{13}C NMR of compound **5e**



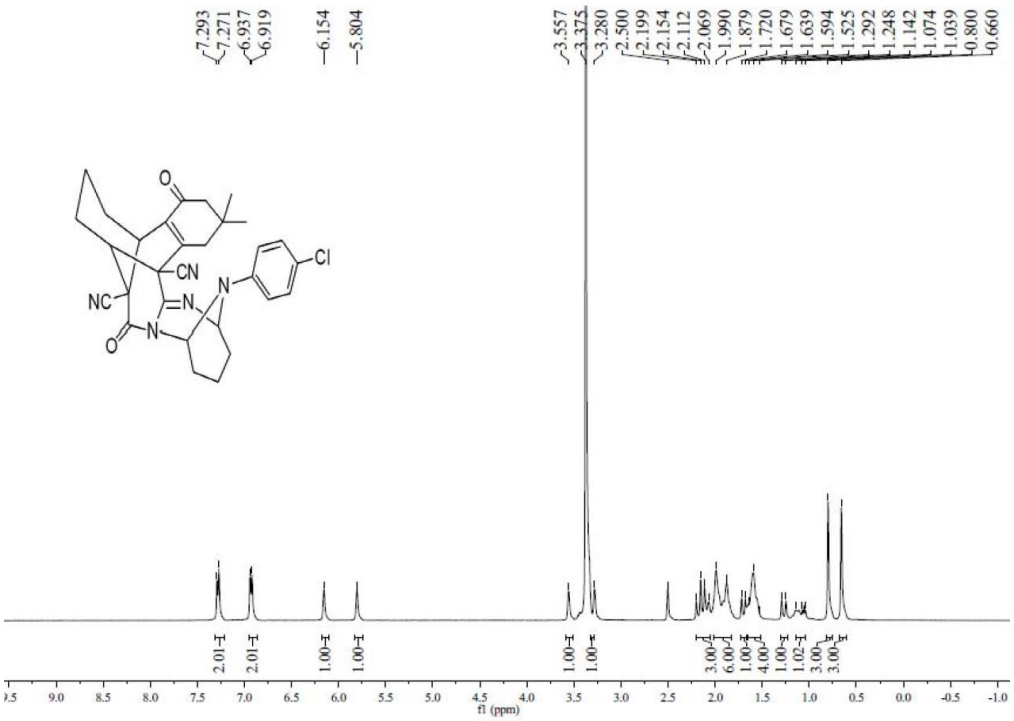
^{1}H NMR of compound **5f**



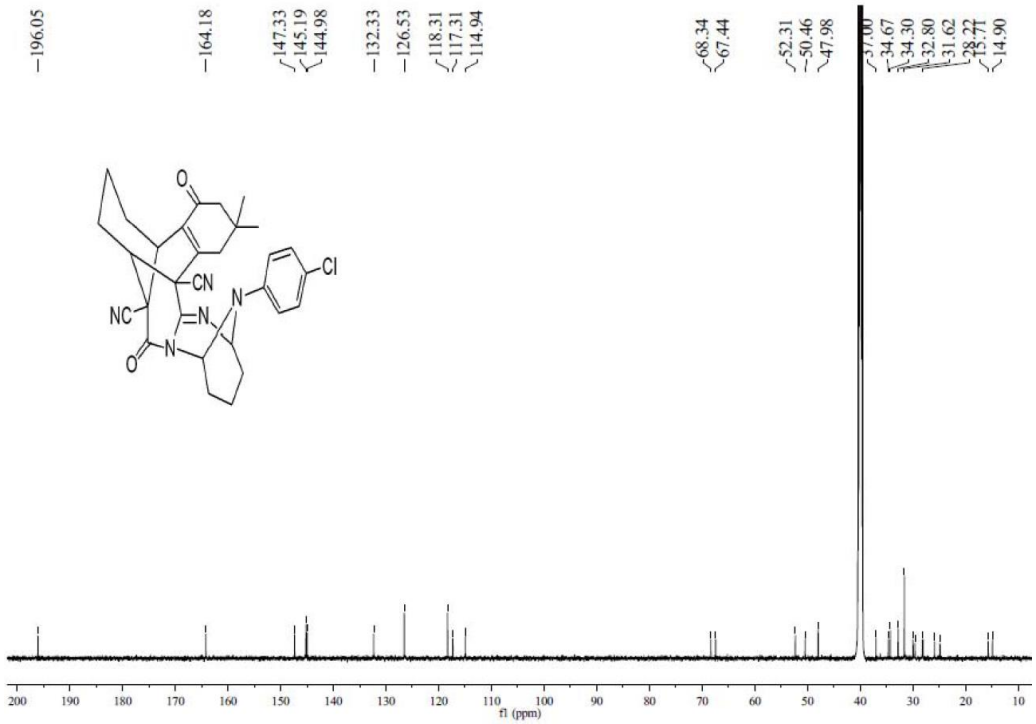
^{13}C NMR of compound **5f**



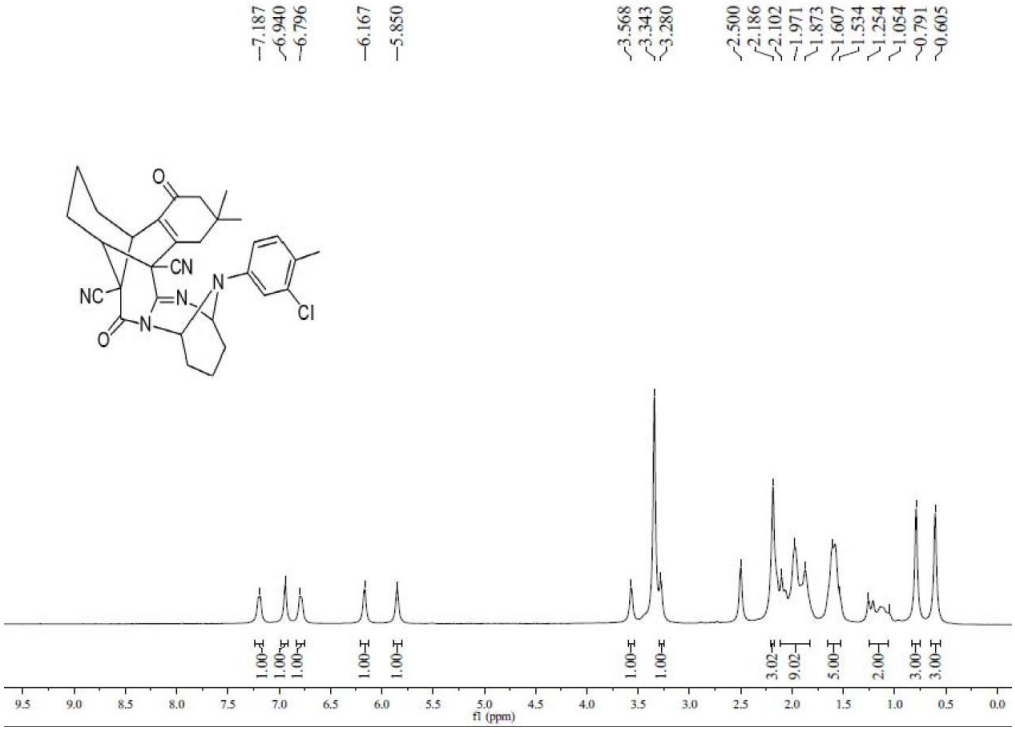
^{1}H NMR of compound **5g**



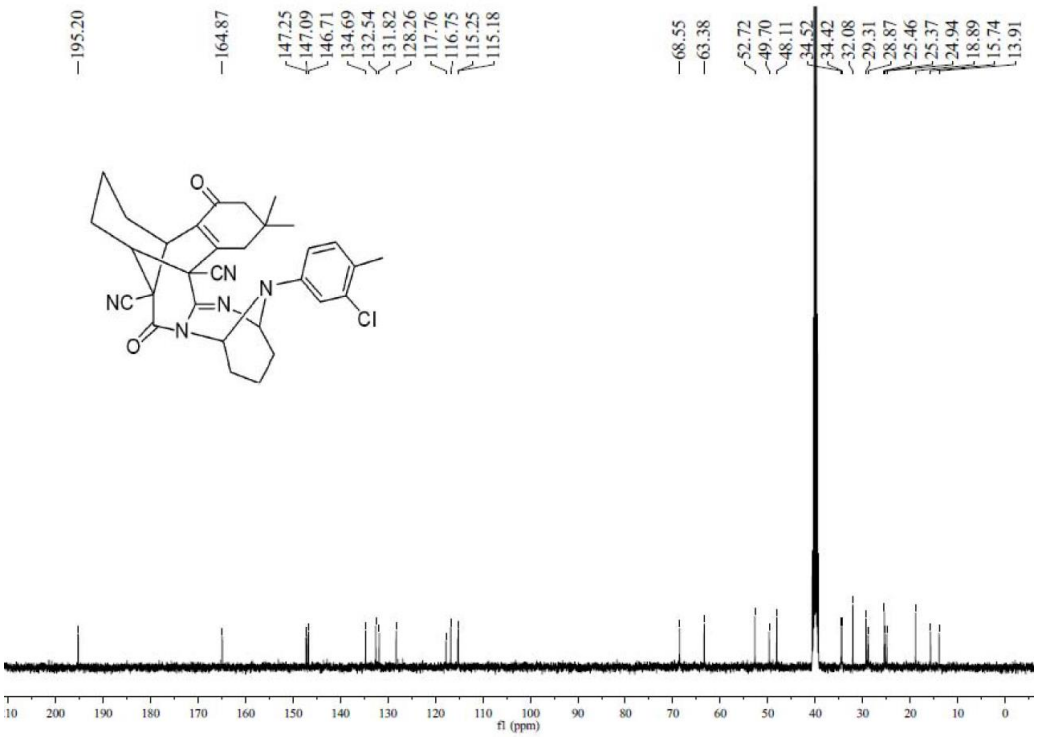
^{13}C NMR of compound **5g**



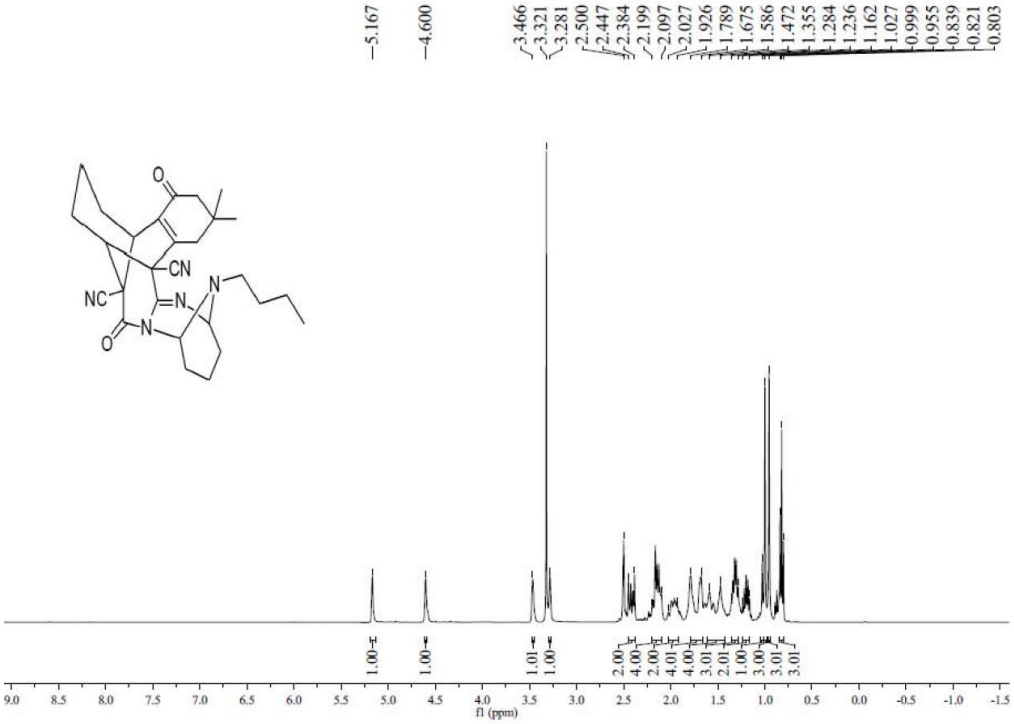
^{1}H NMR of compound **5h**



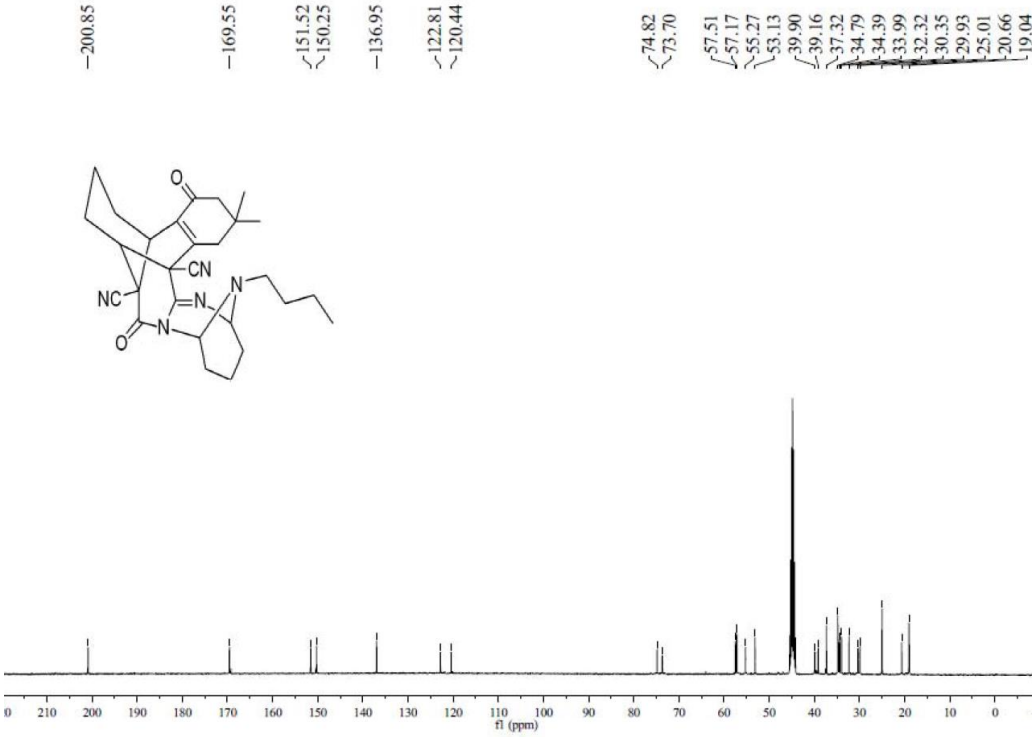
^{13}C NMR of compound **5h**



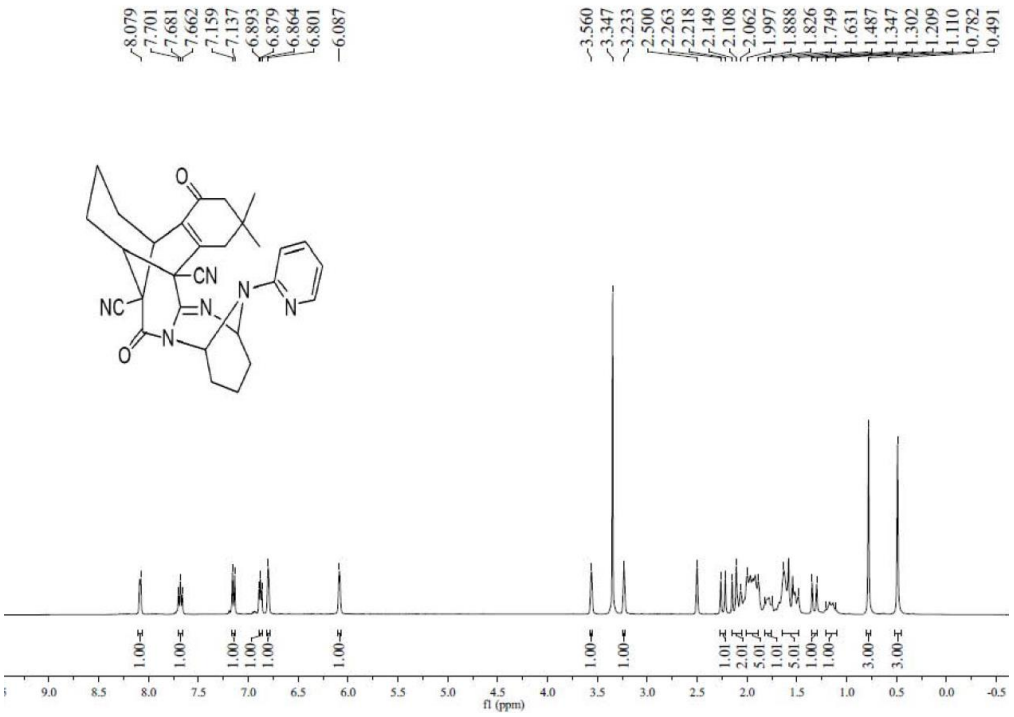
^{1}H NMR of compound **5i**



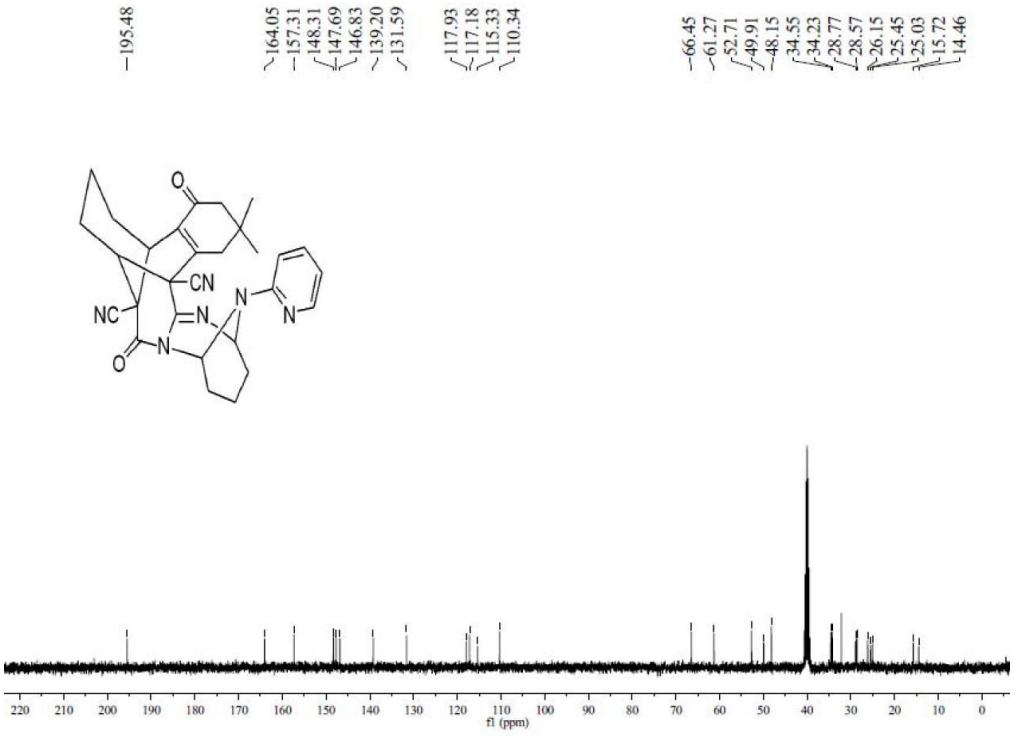
^{13}C NMR of compound **5i**



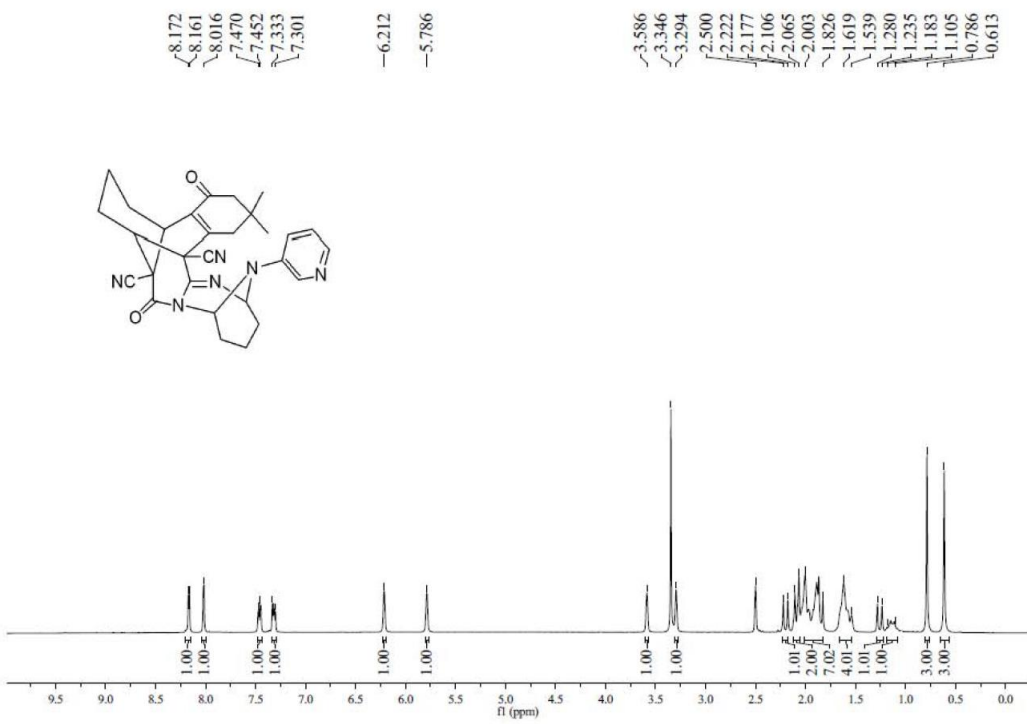
^{1}H NMR of compound **5j**



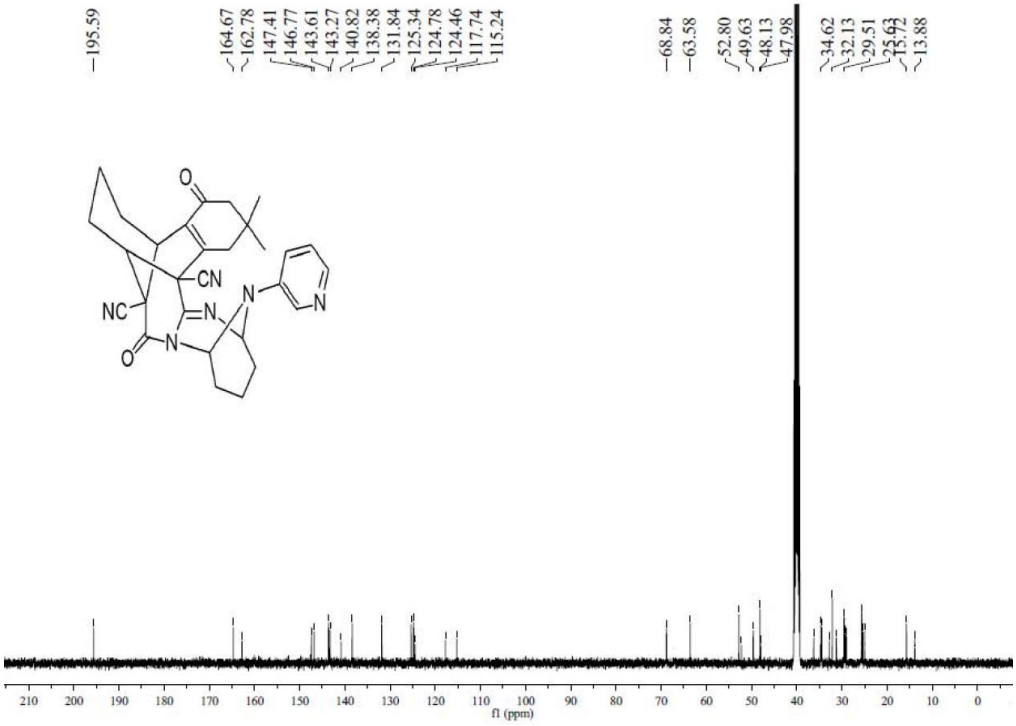
^{13}C NMR of compound **5j**



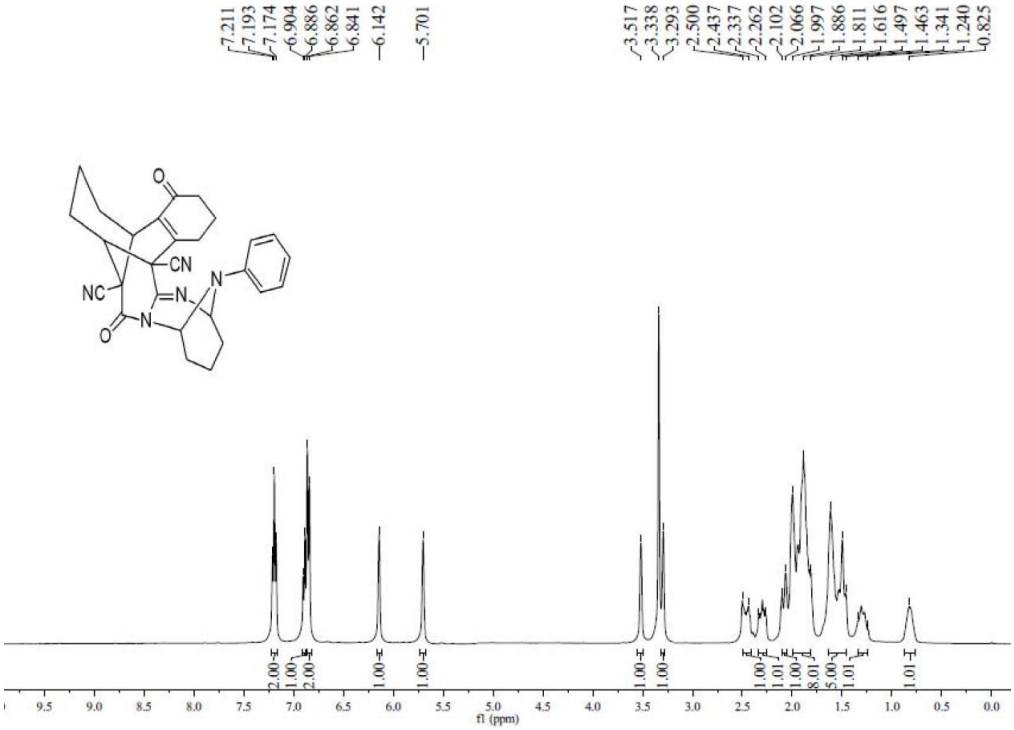
^{1}H NMR of compound **5k**



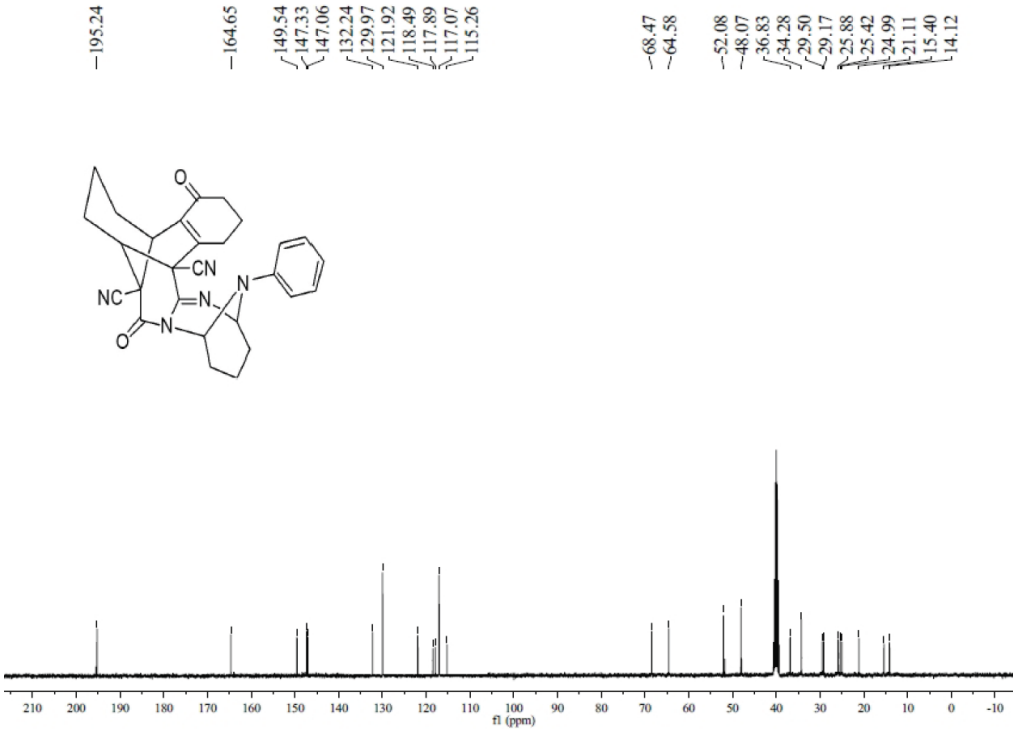
^{13}C NMR of compound **5k**



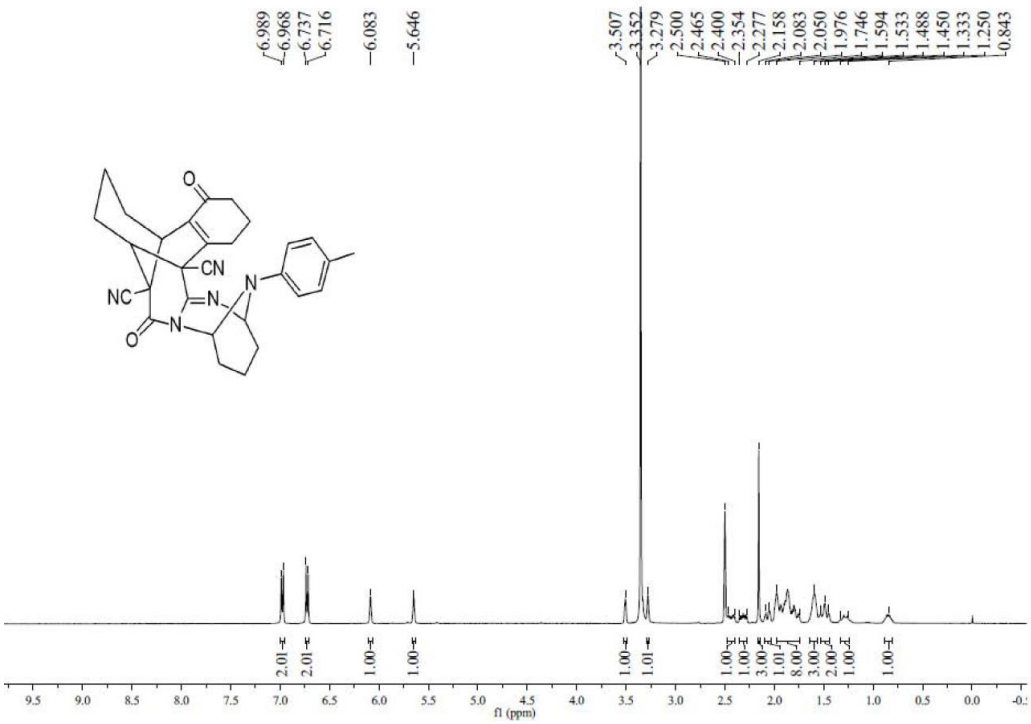
^{1}H NMR of compound **5l**



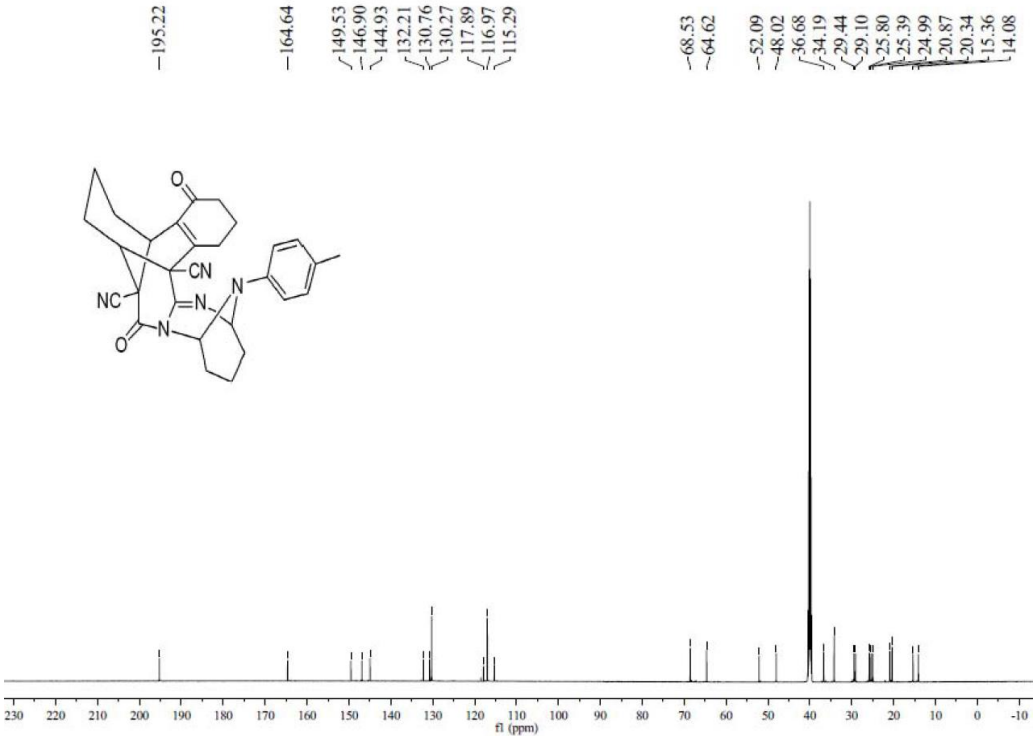
^{13}C NMR of compound **5l**



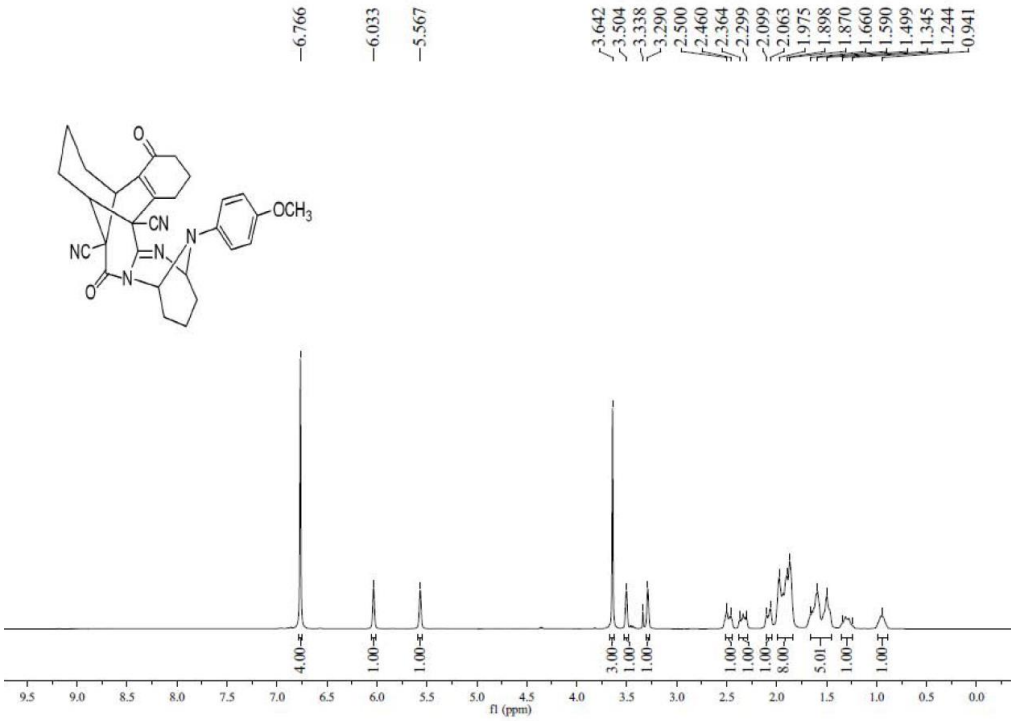
^{1}H NMR of compound **5m**



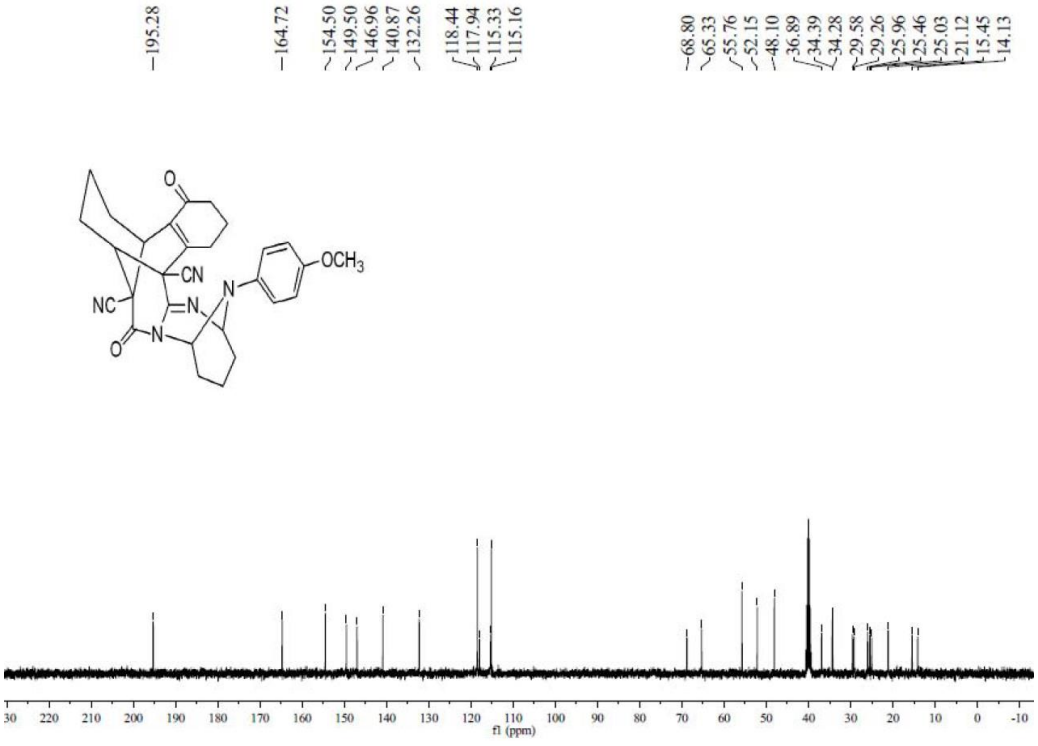
^{13}C NMR of compound **5m**



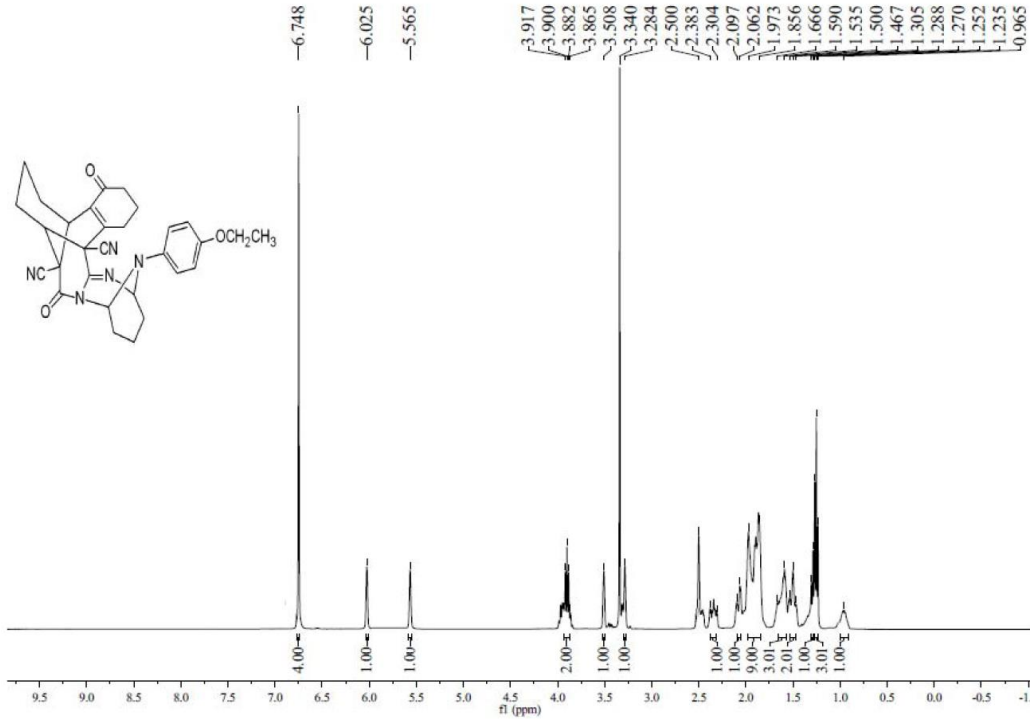
^{1}H NMR of compound **5n**



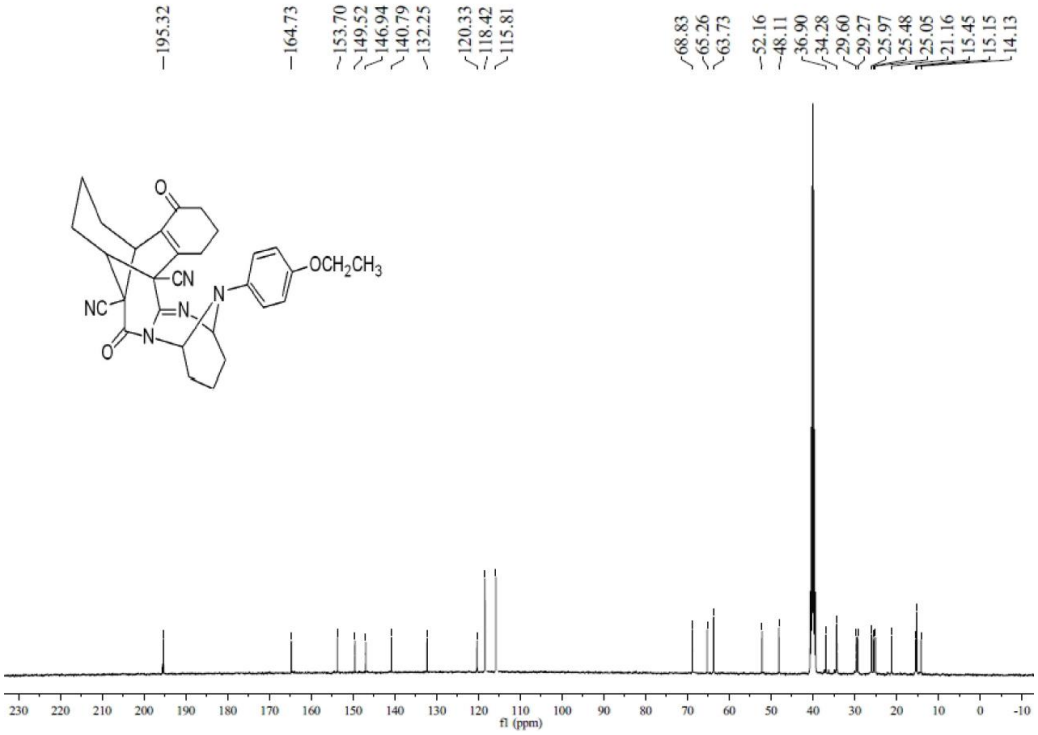
^{13}C NMR of compound **5n**



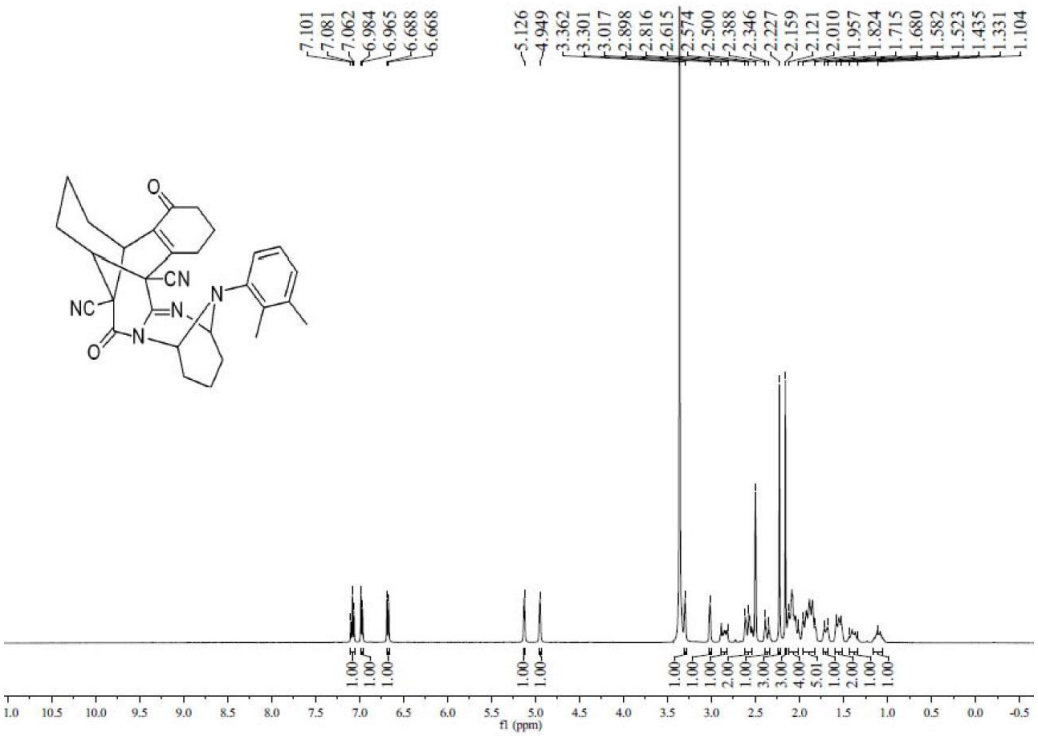
^{1}H NMR of compound **5o**



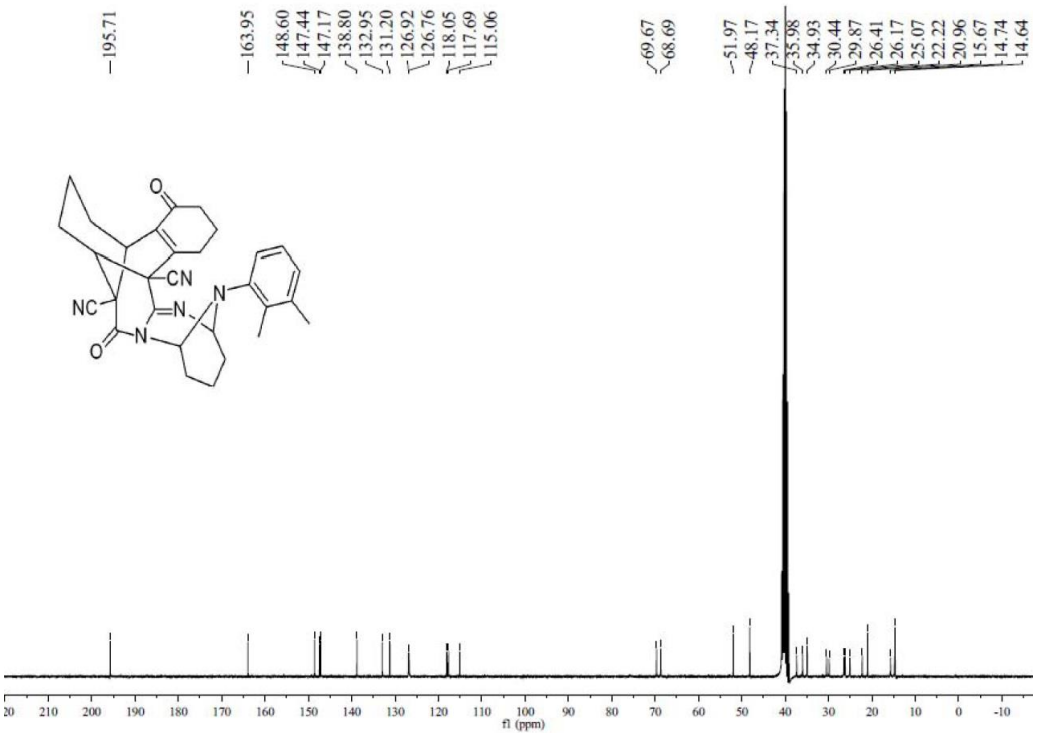
^{13}C NMR of compound **5o**



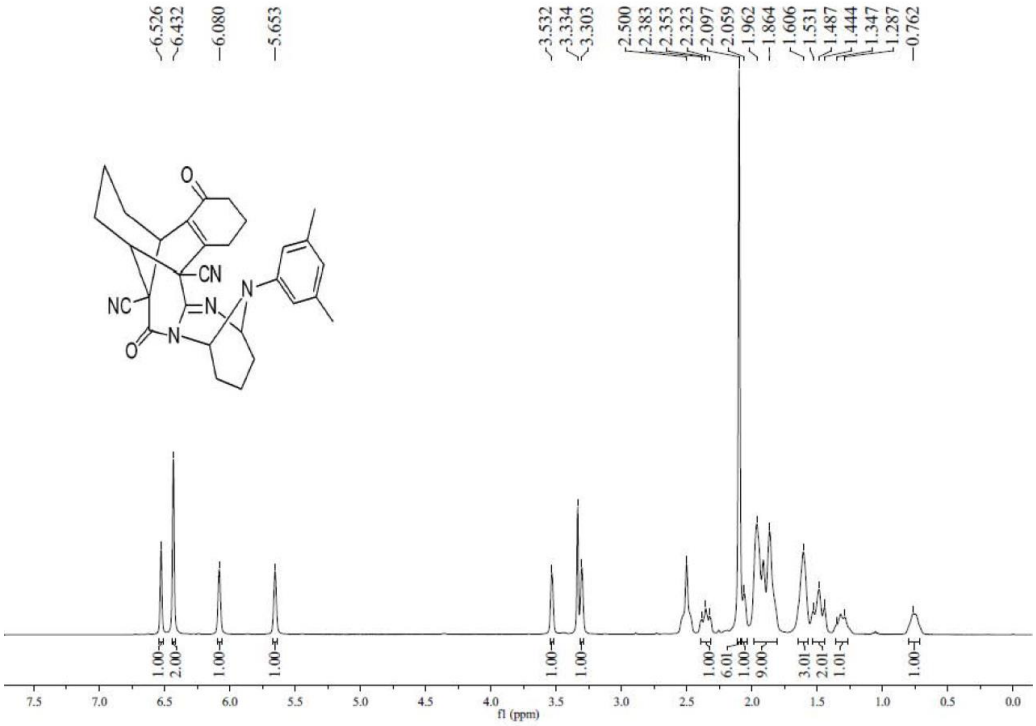
^{1}H NMR of compound **5p**



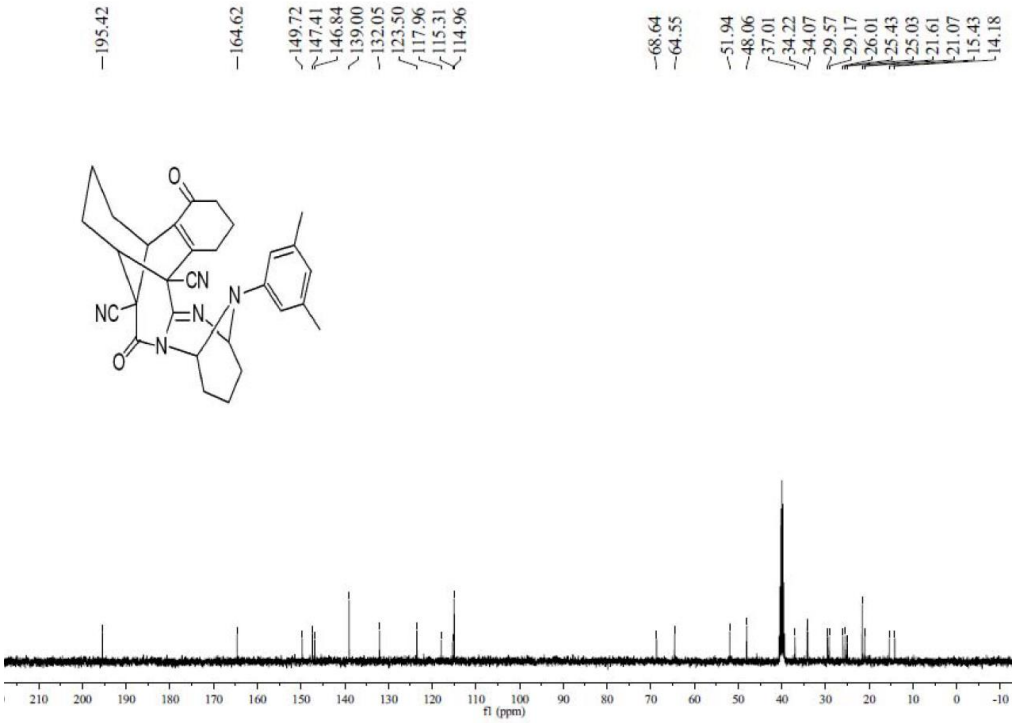
^{13}C NMR of compound **5p**



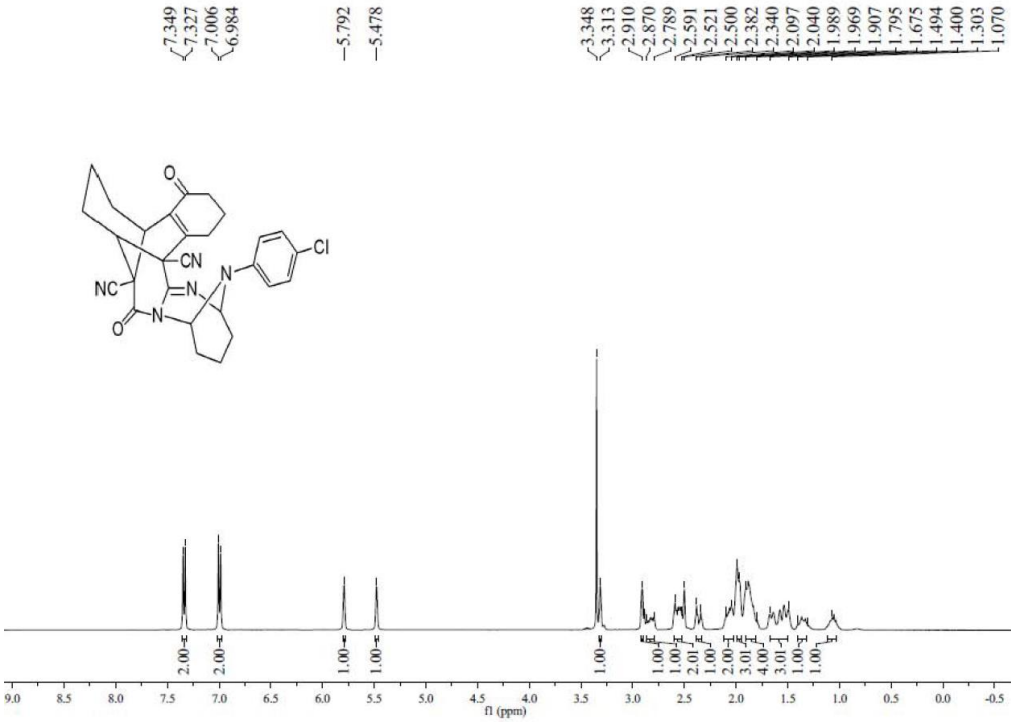
^{1}H NMR of compound **5q**



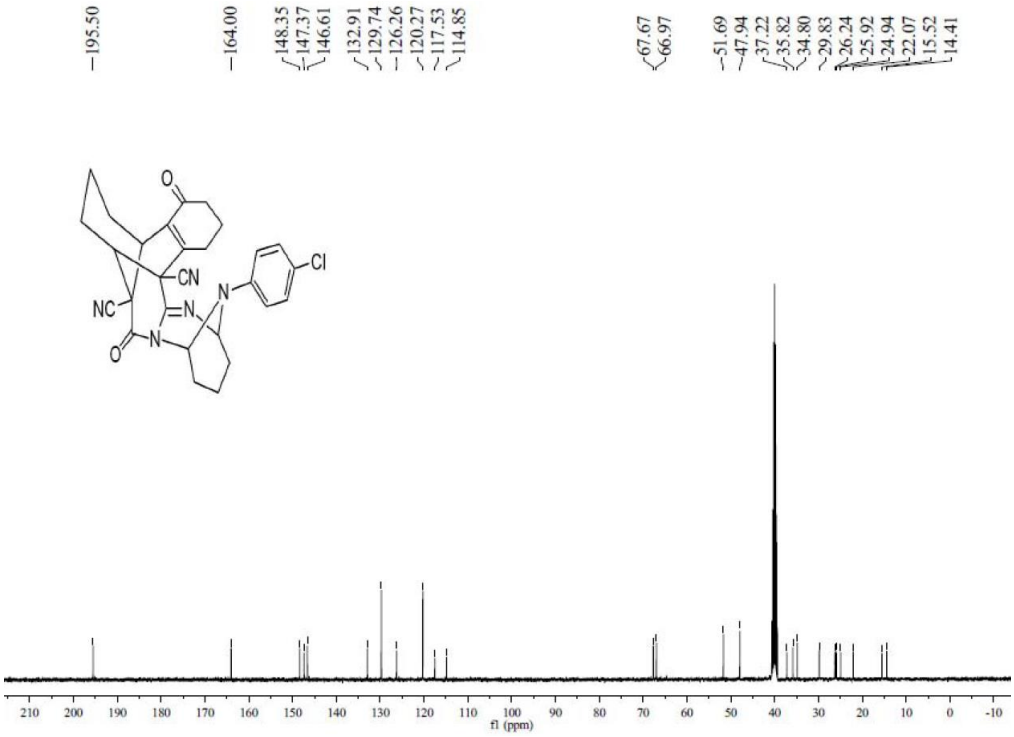
^{13}C NMR of compound **5q**



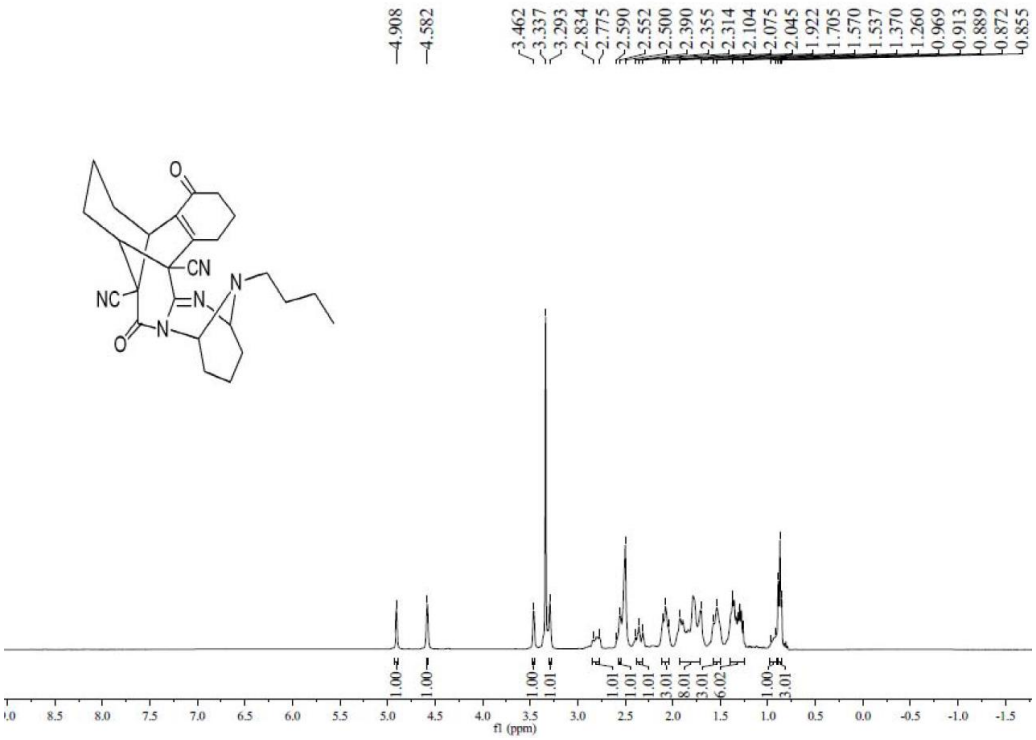
^{1}H NMR of compound **5r**



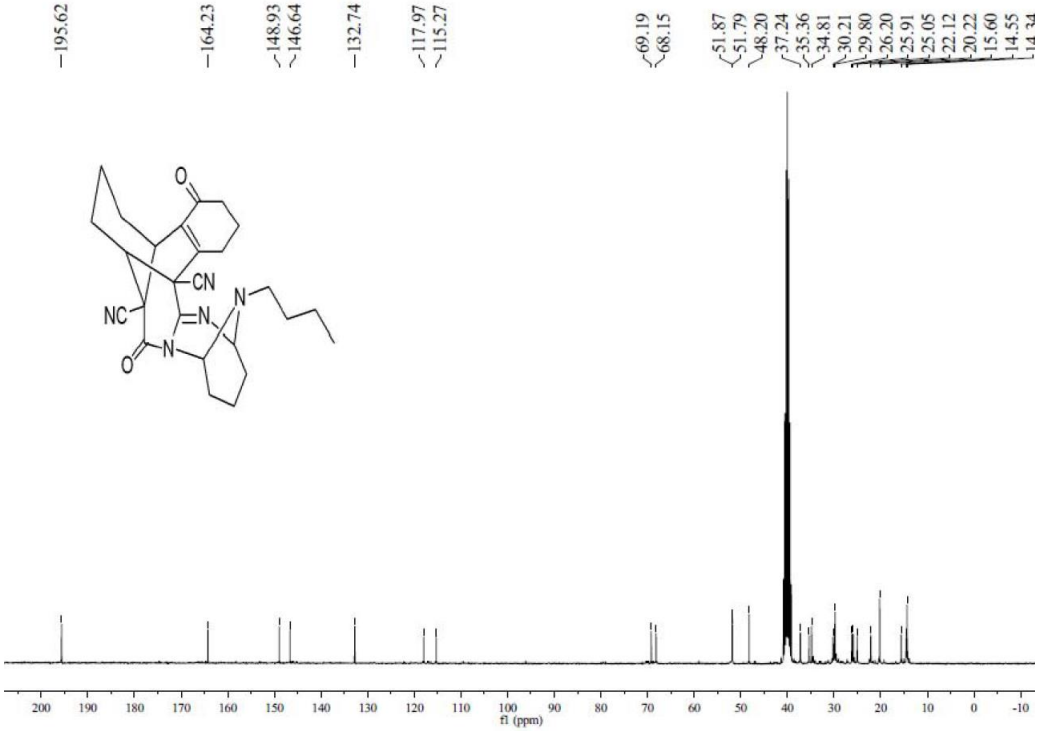
^{13}C NMR of compound **5r**



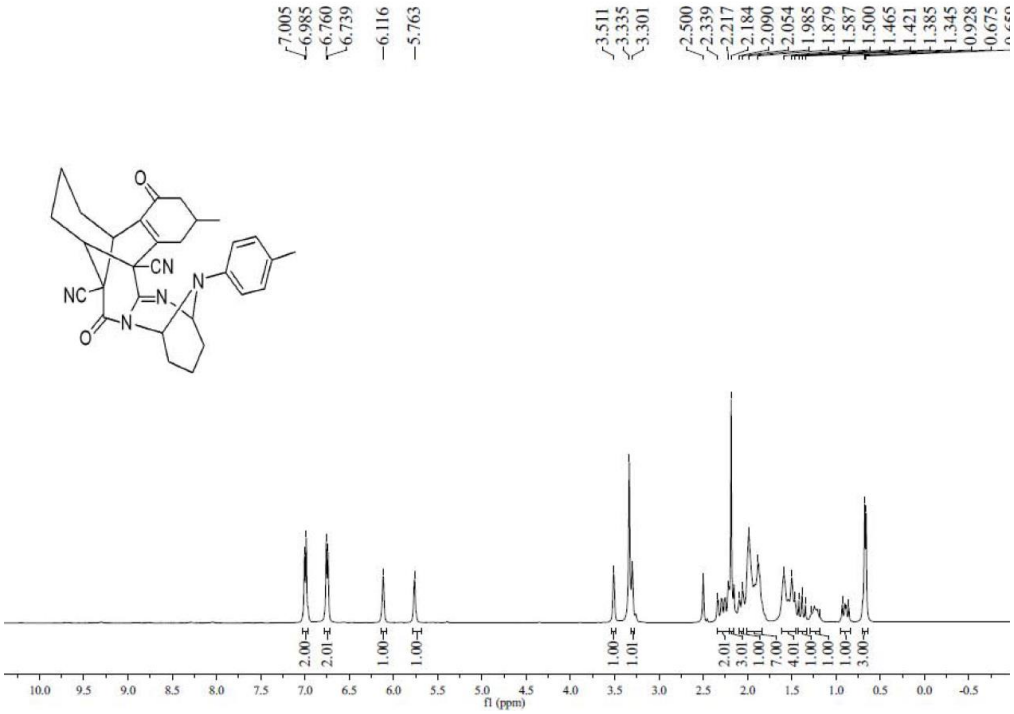
^{1}H NMR of compound **5s**



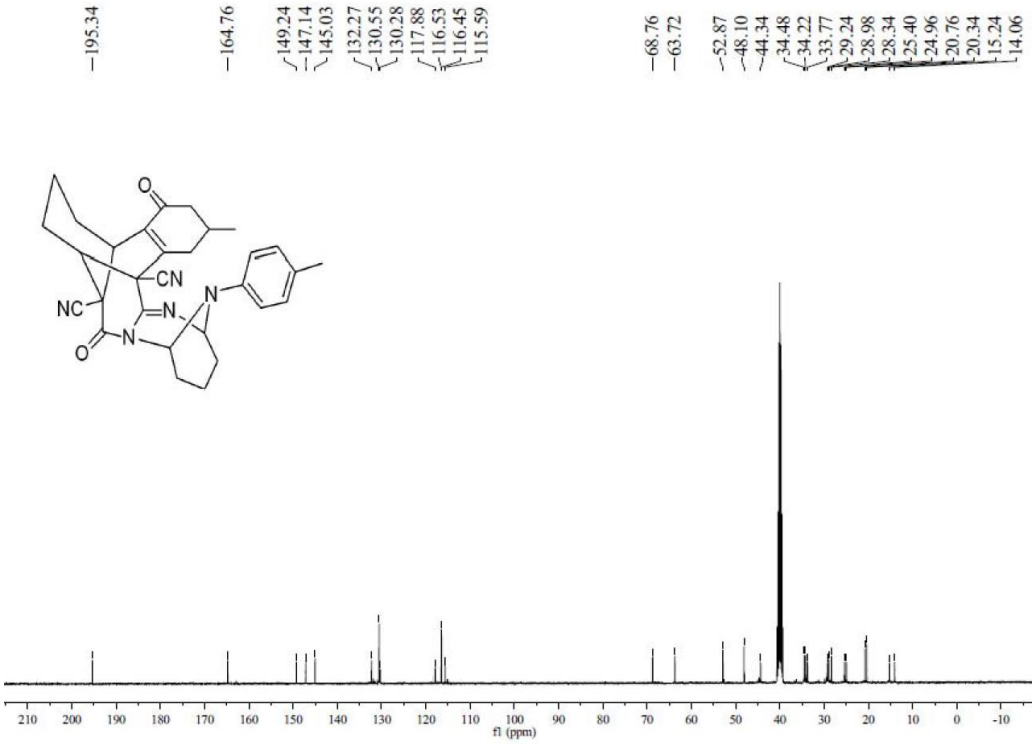
^{13}C NMR of compound **5s**



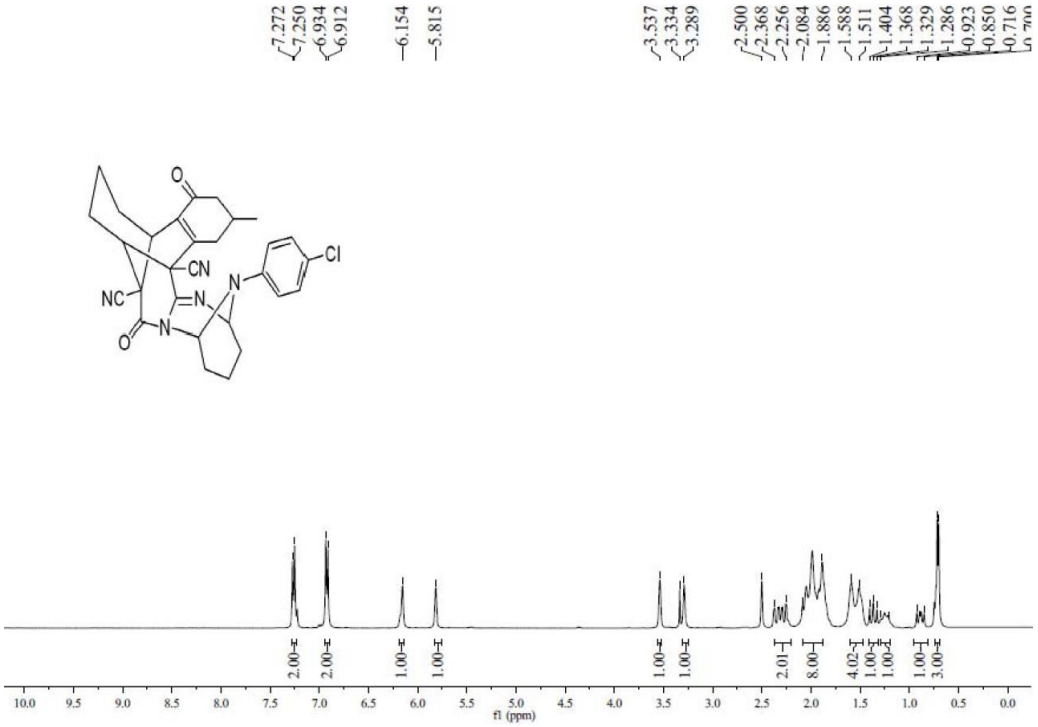
^{1}H NMR of compound **5t**



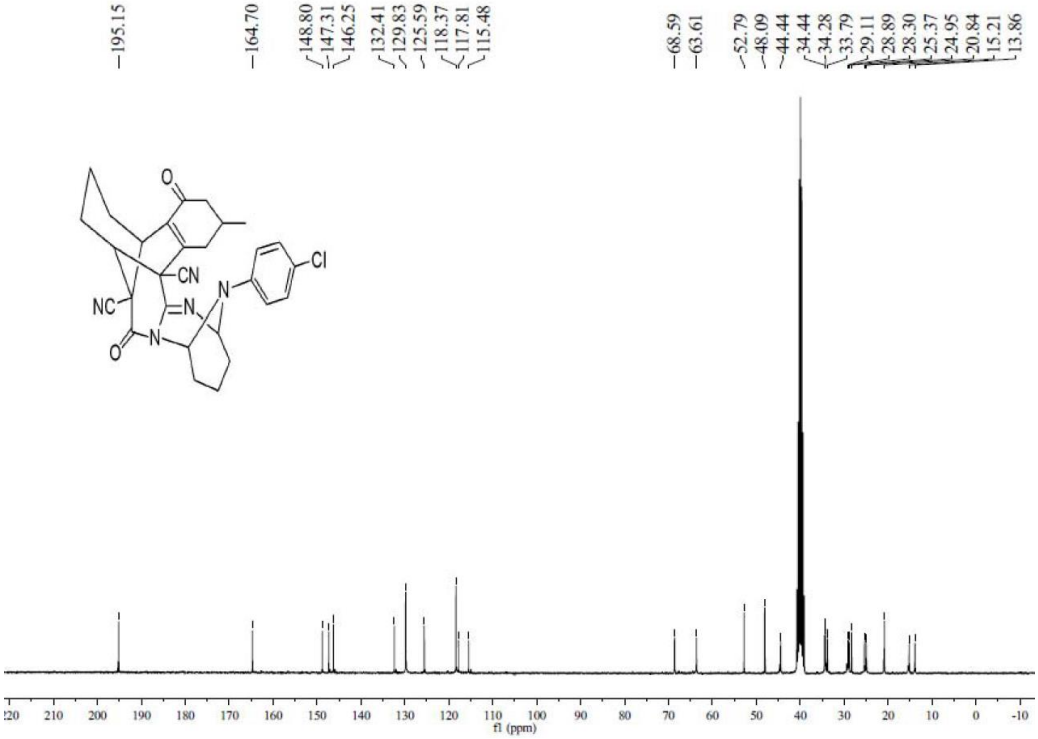
^{13}C NMR of compound **5t**



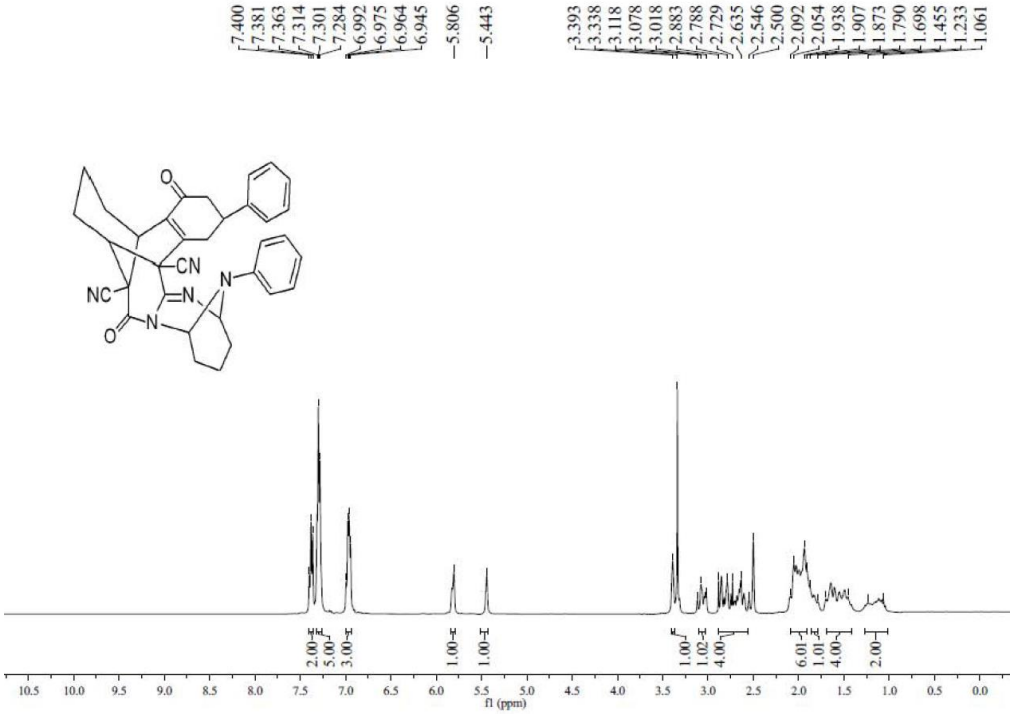
^{1}H NMR of compound **5u**



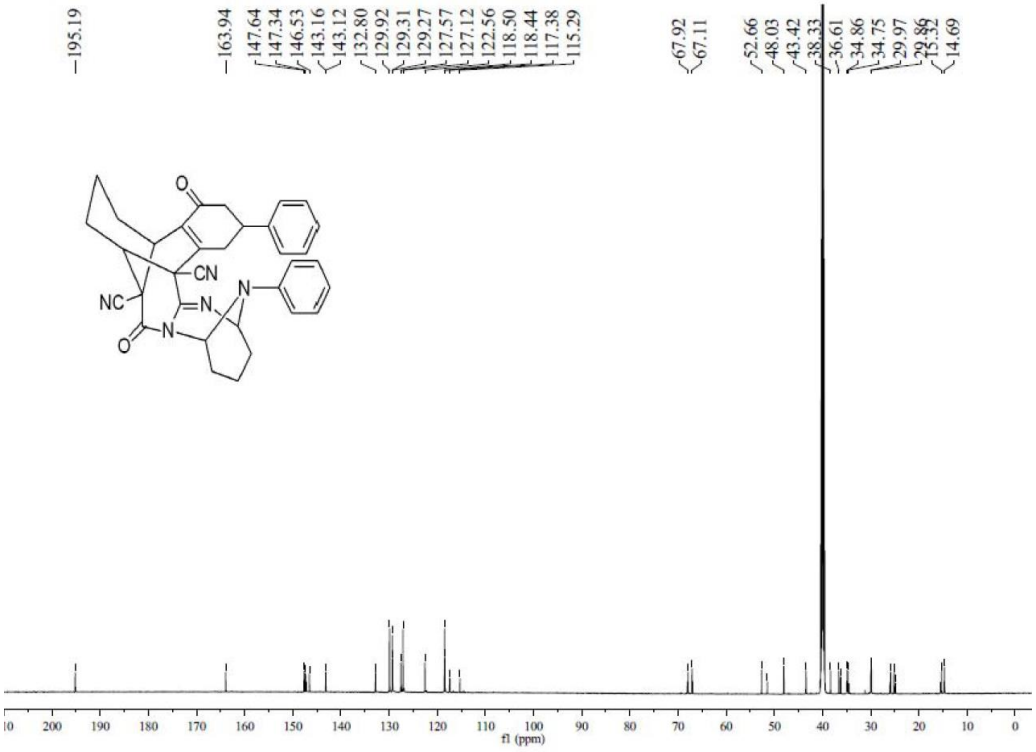
^{13}C NMR of compound **5u**



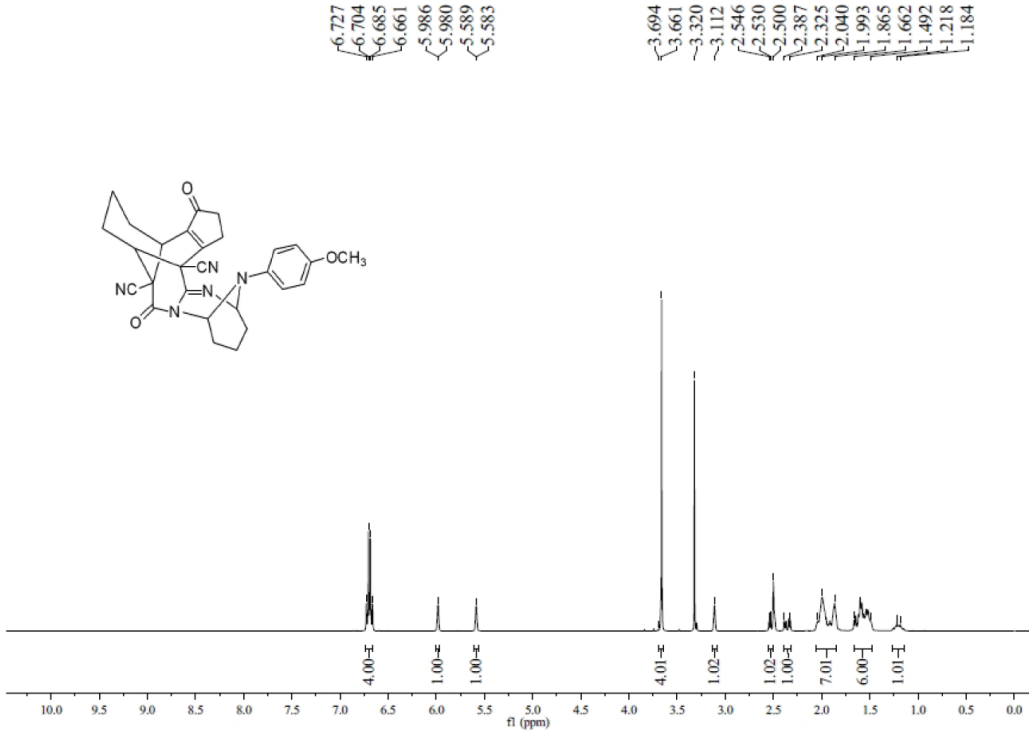
^{1}H NMR of compound **5v**



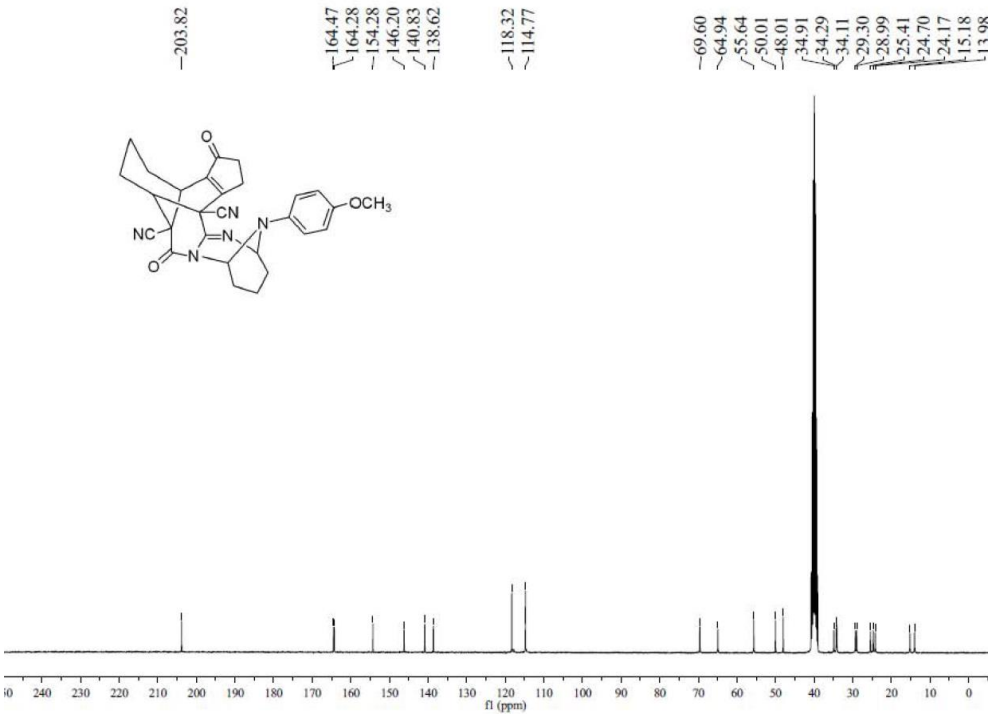
^{13}C NMR of compound **5v**



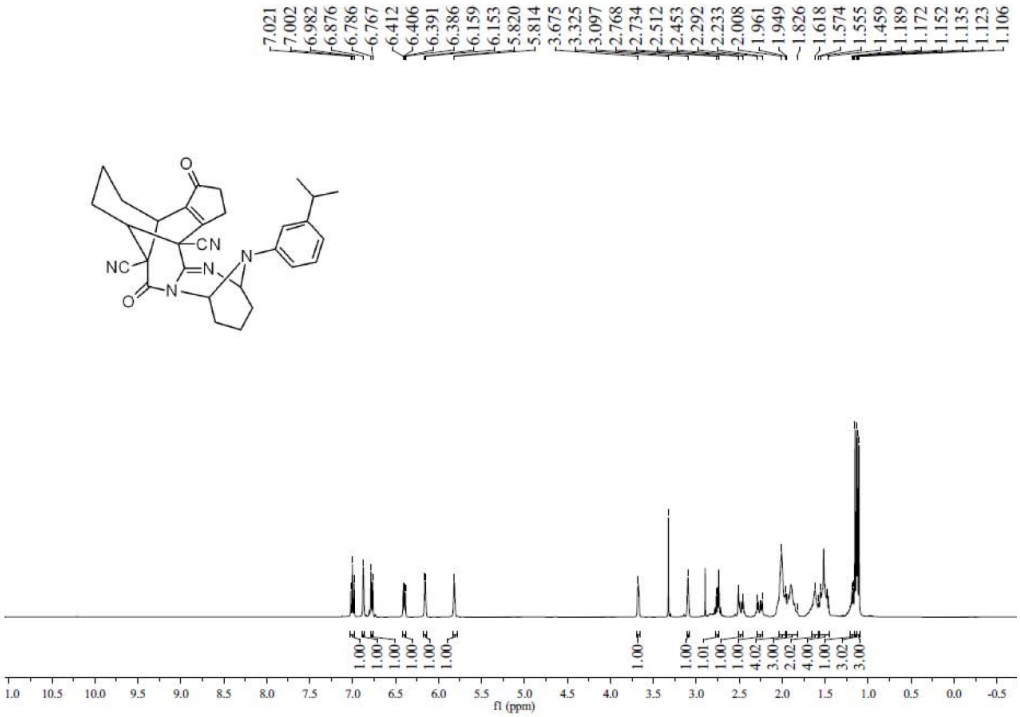
^{1}H NMR of compound **7a**



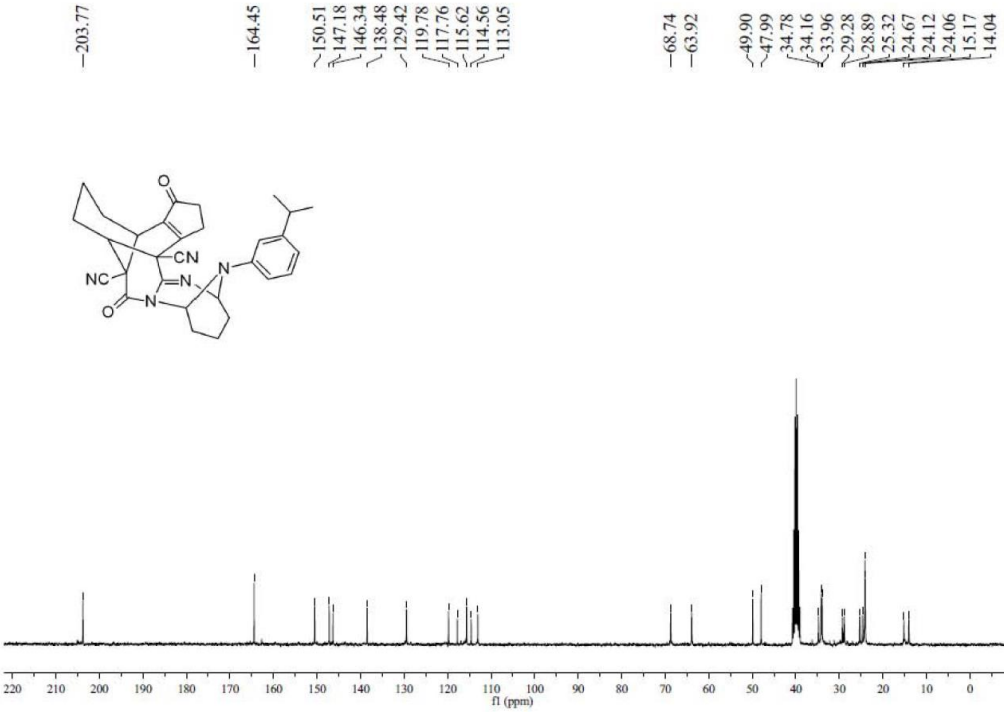
^{13}C NMR of compound **7a**



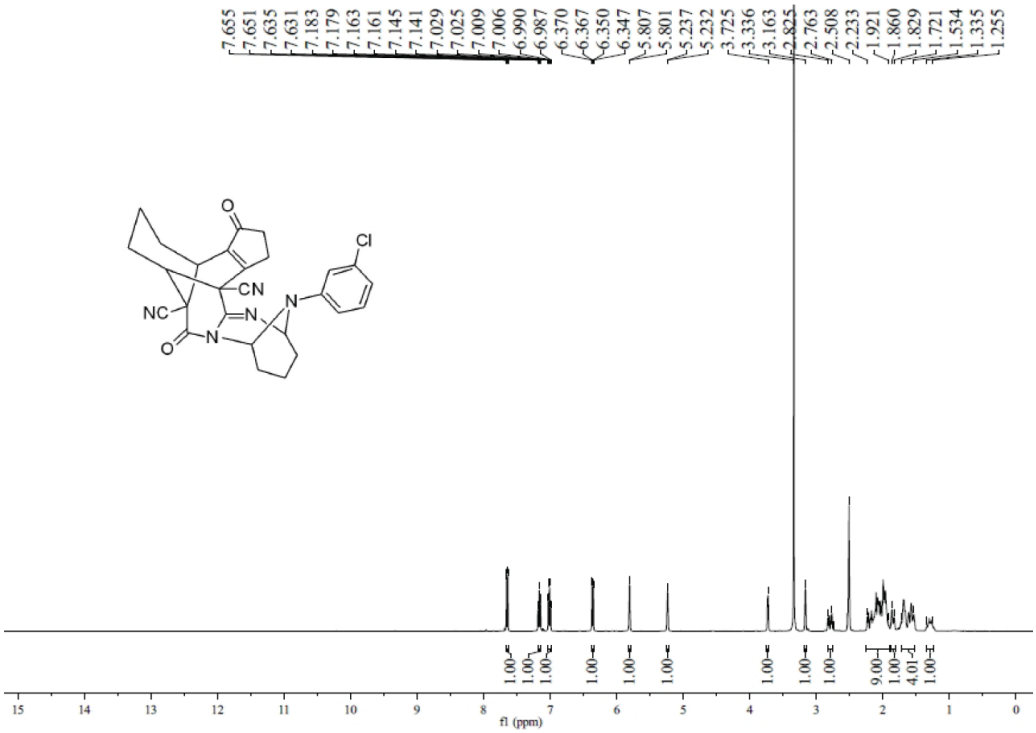
^{1}H NMR of compound **7b**



^{13}C NMR of compound **7b**



^{1}H NMR of compound **7c**



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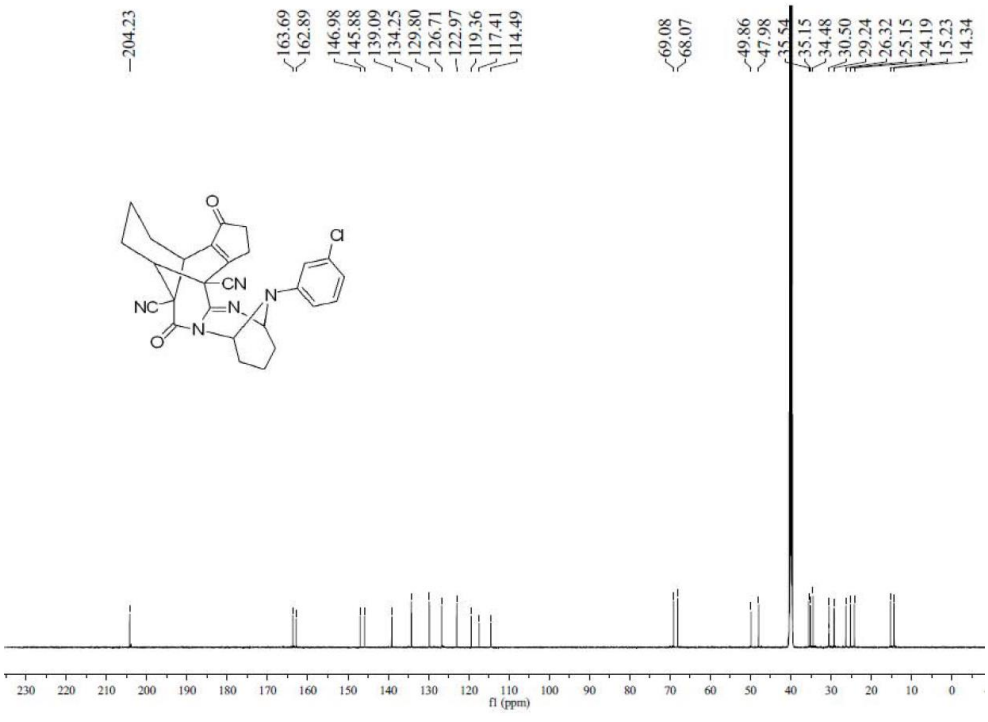
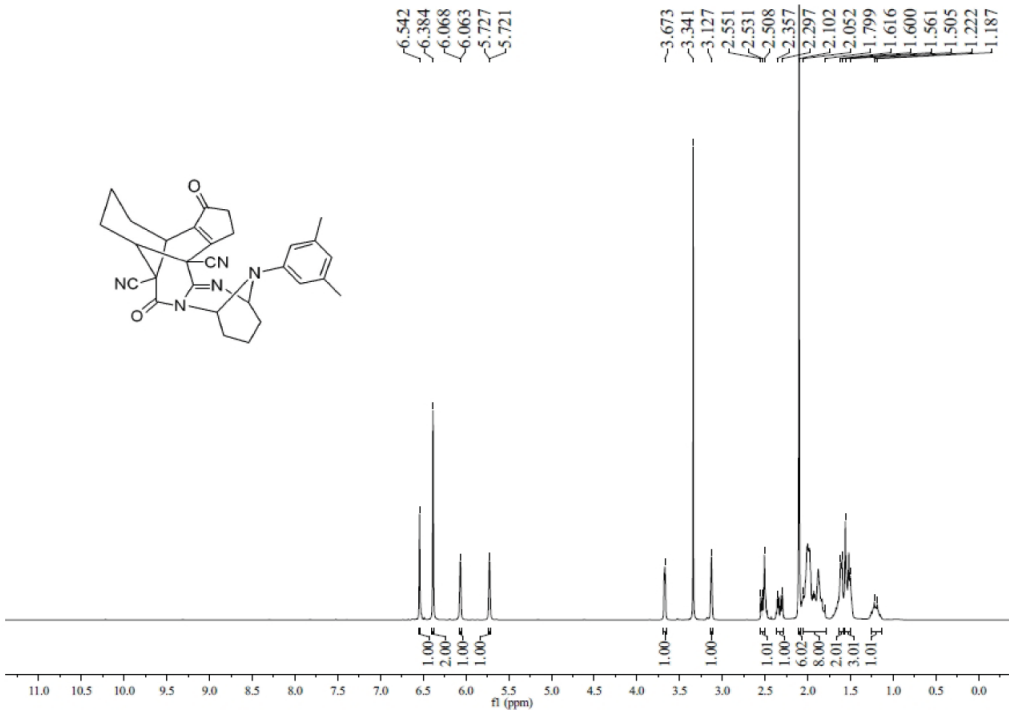
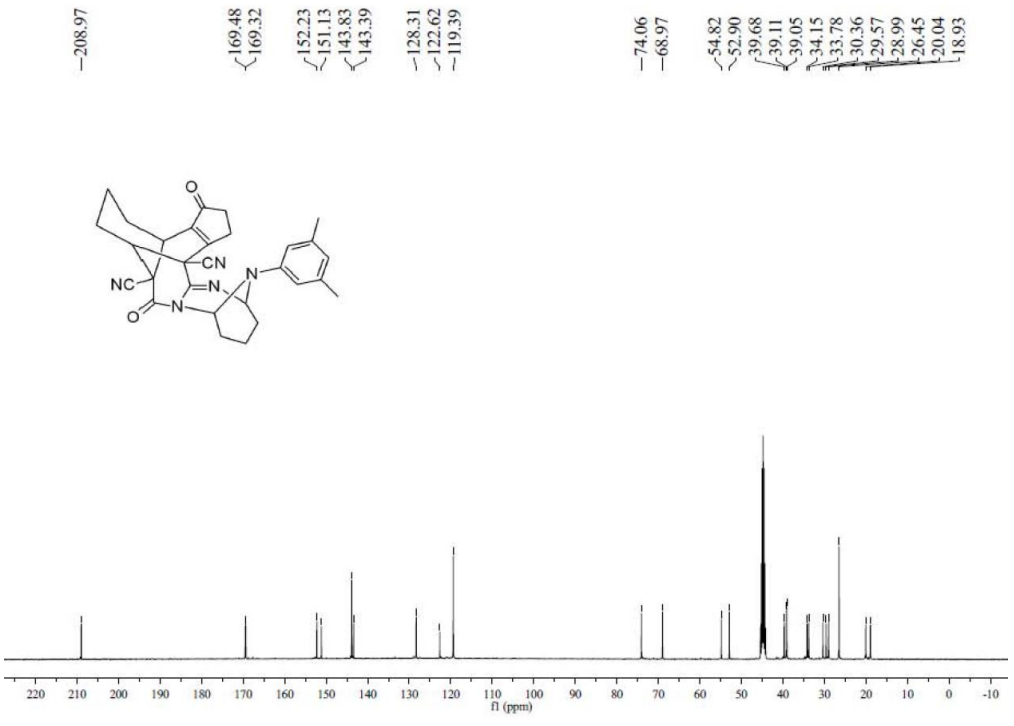


^{1}H NMR of compound **7d**



^{13}C NMR of compound **7d**



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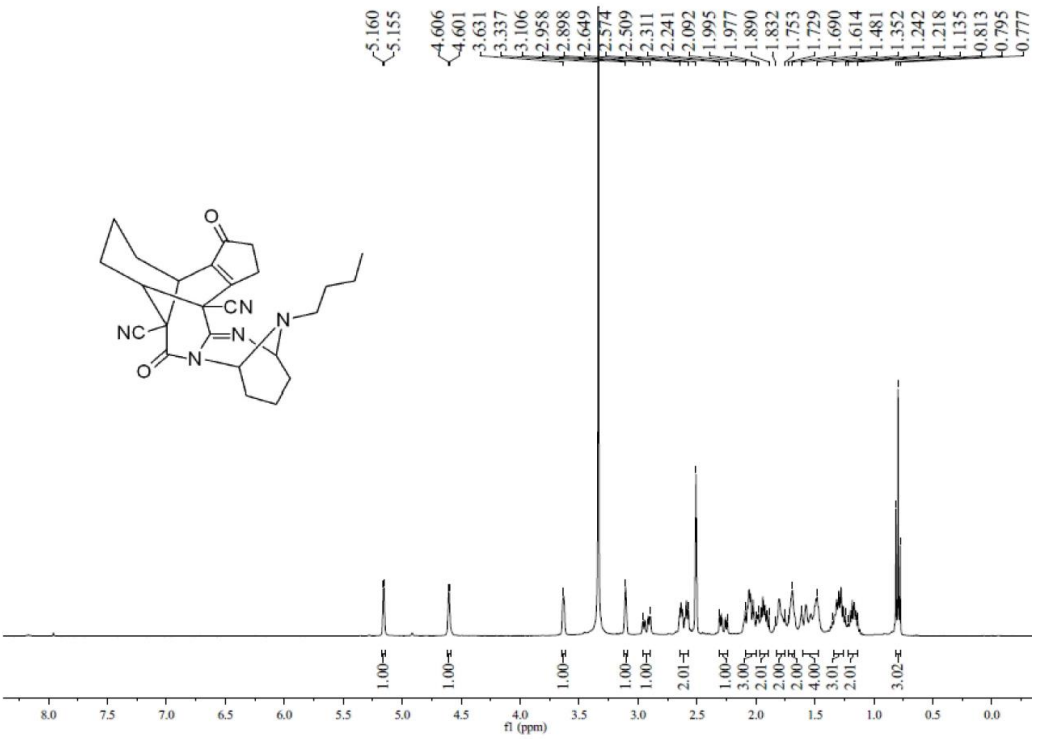
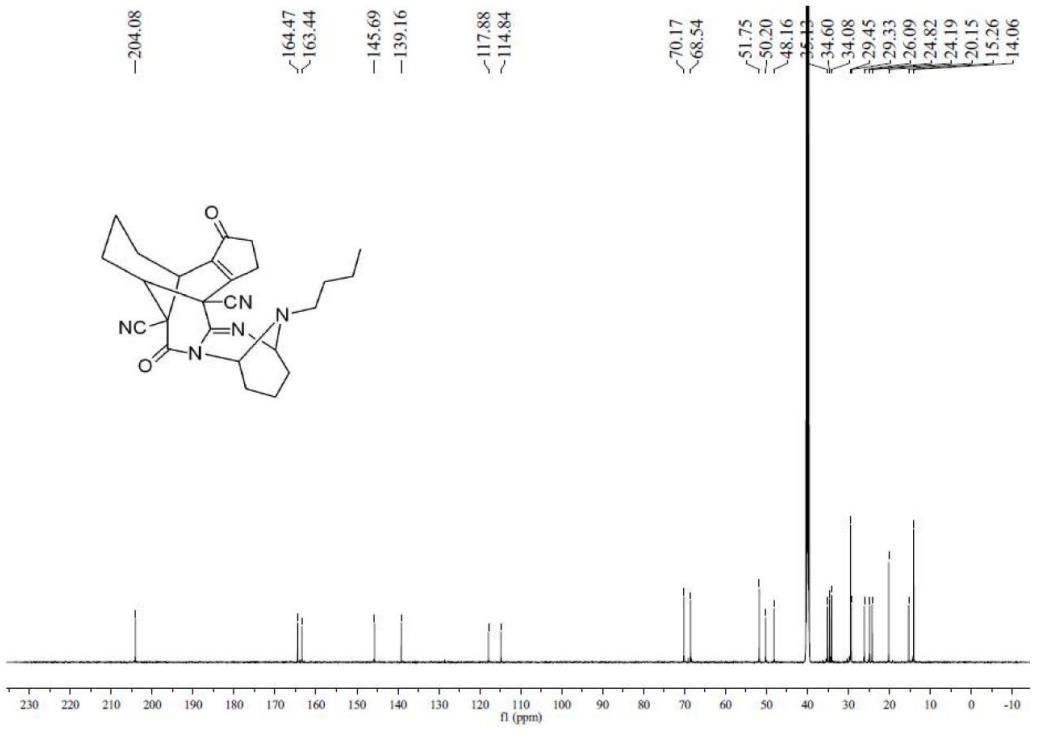
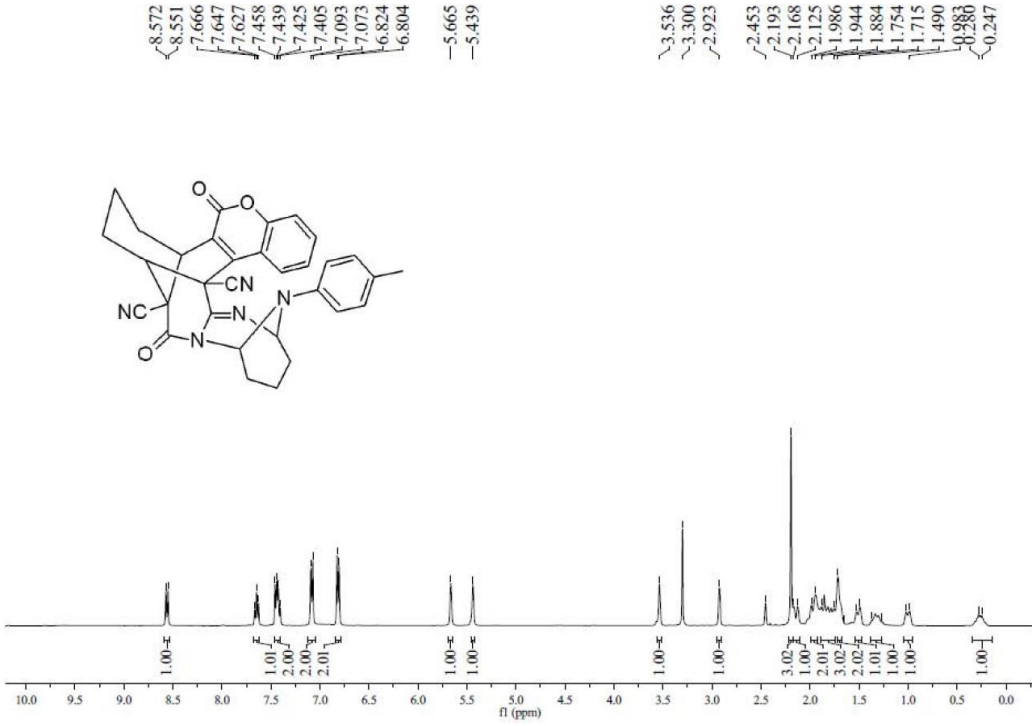


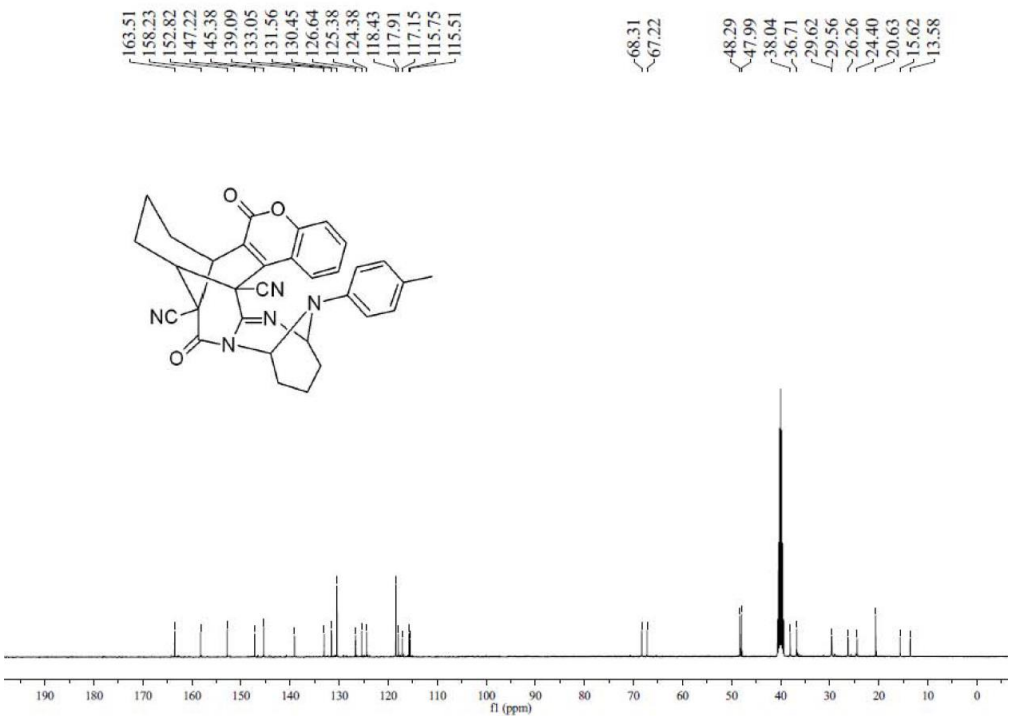
^{13}C NMR of compound **7e**



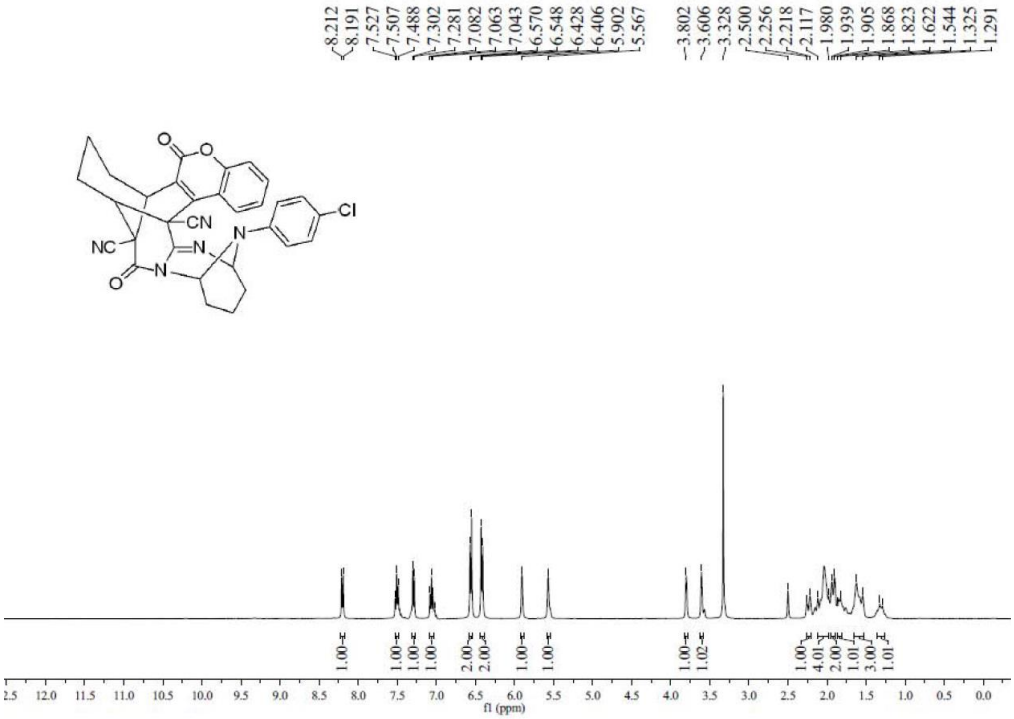
^{1}H NMR of compound **9a**



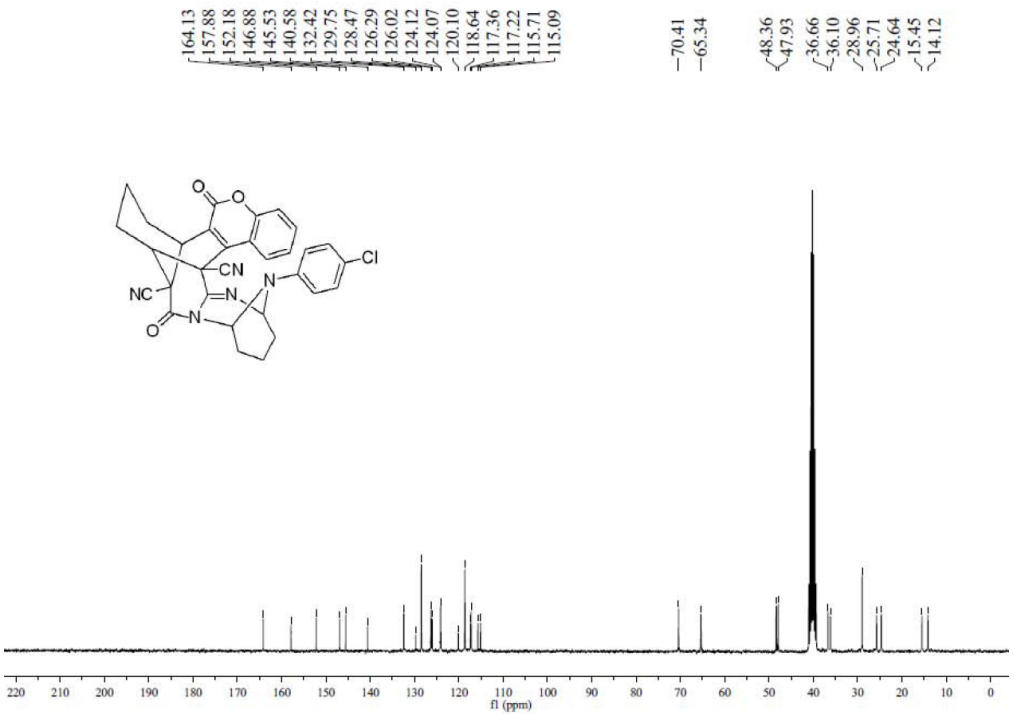
^{13}C NMR of compound **9a**



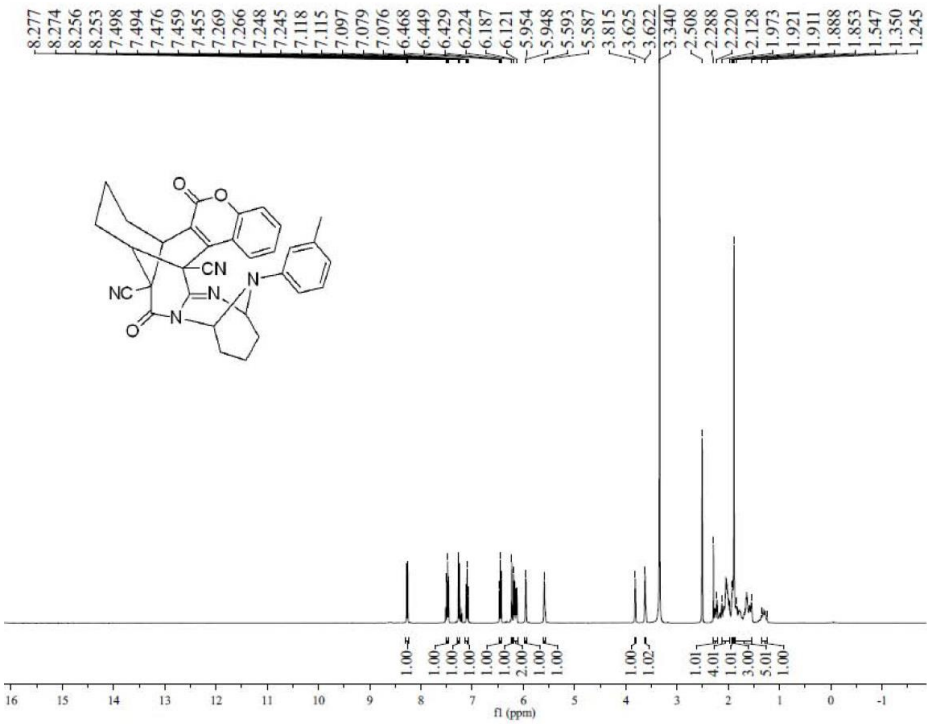
^{1}H NMR of compound **9b**



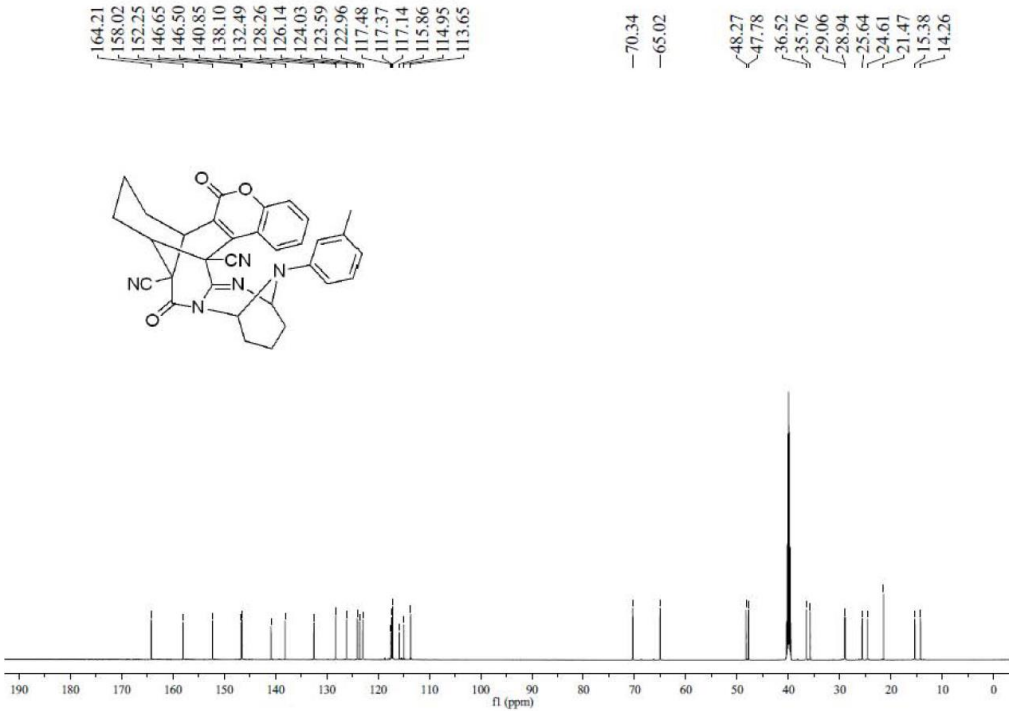
^{13}C NMR of compound **9b**



^{1}H NMR of compound **9c**



^{13}C NMR of compound **9c**



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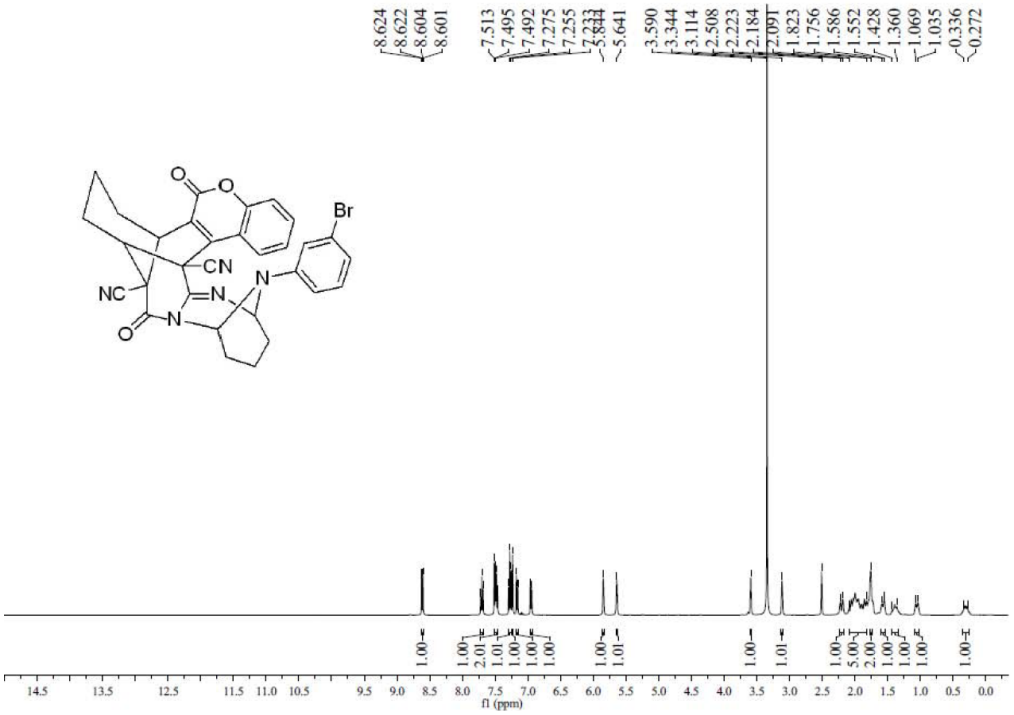
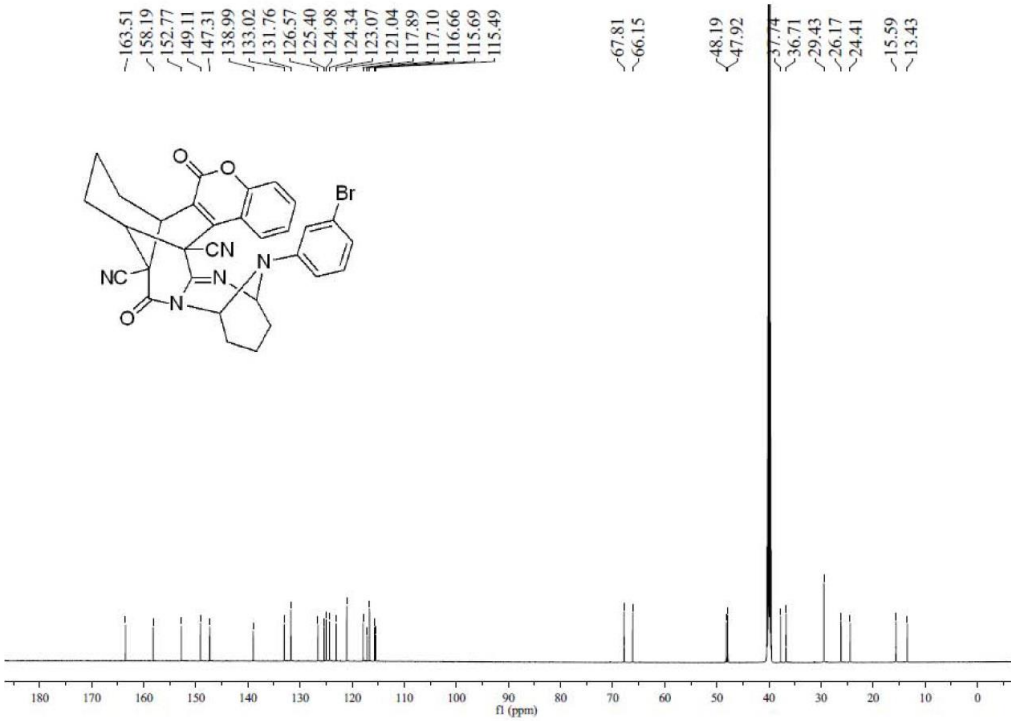


^{13}C NMR of compound **9d**



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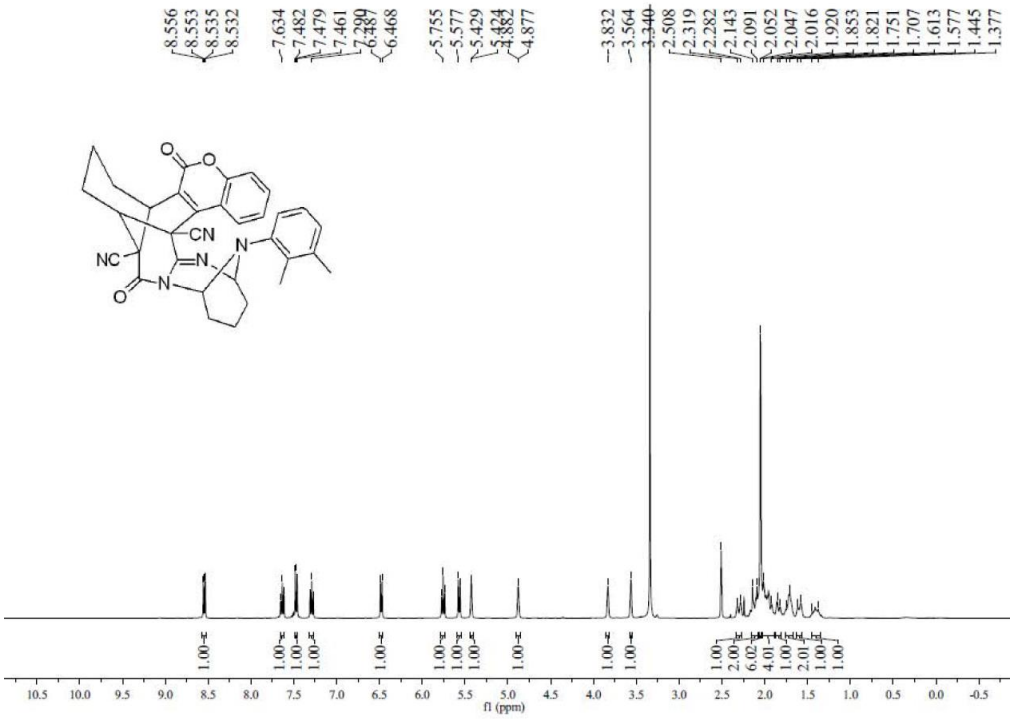
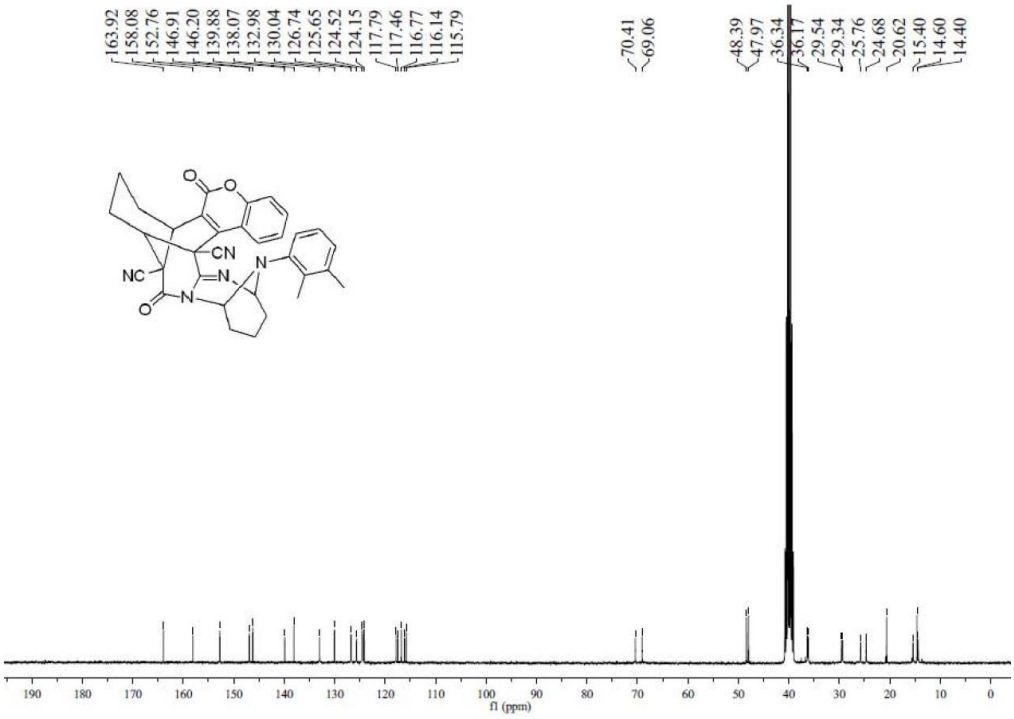
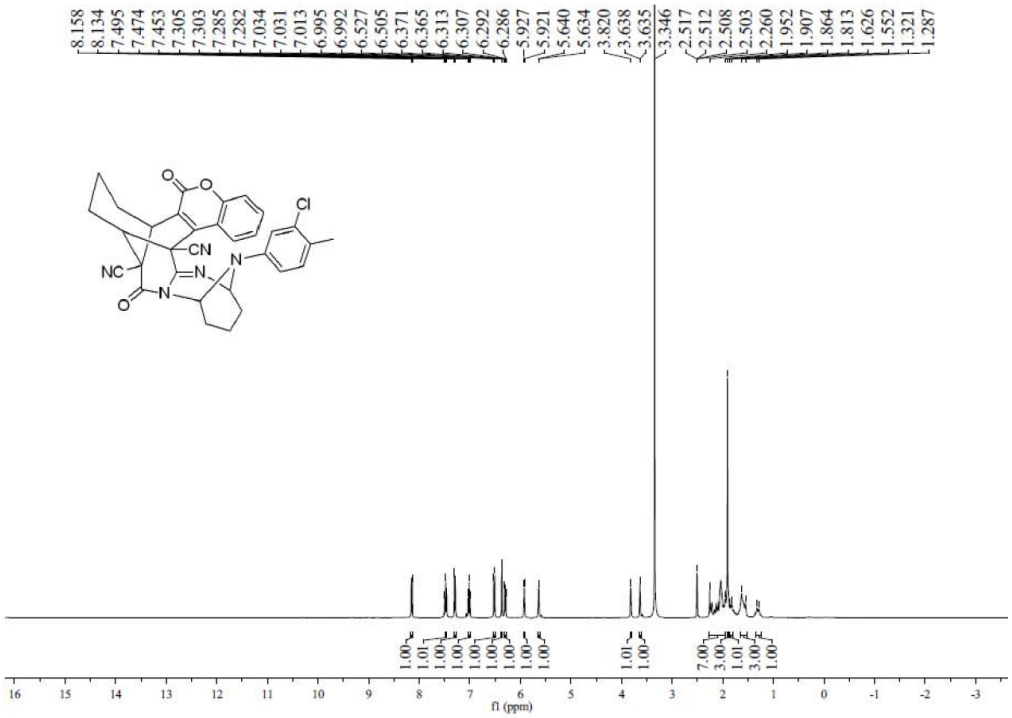


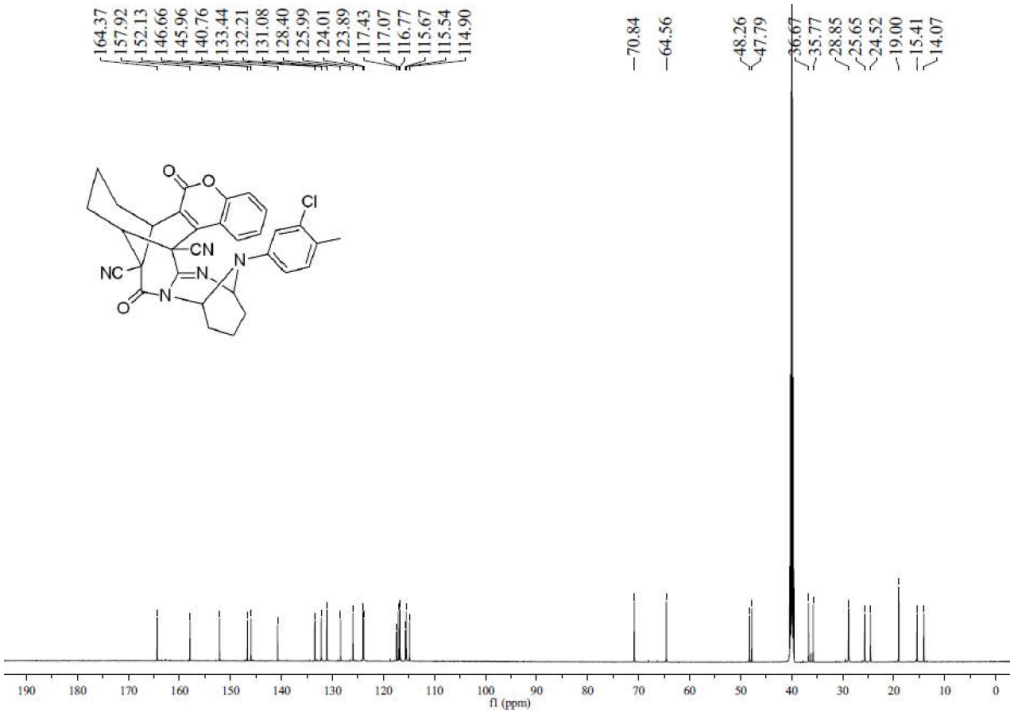
^{13}C NMR of compound **9e**



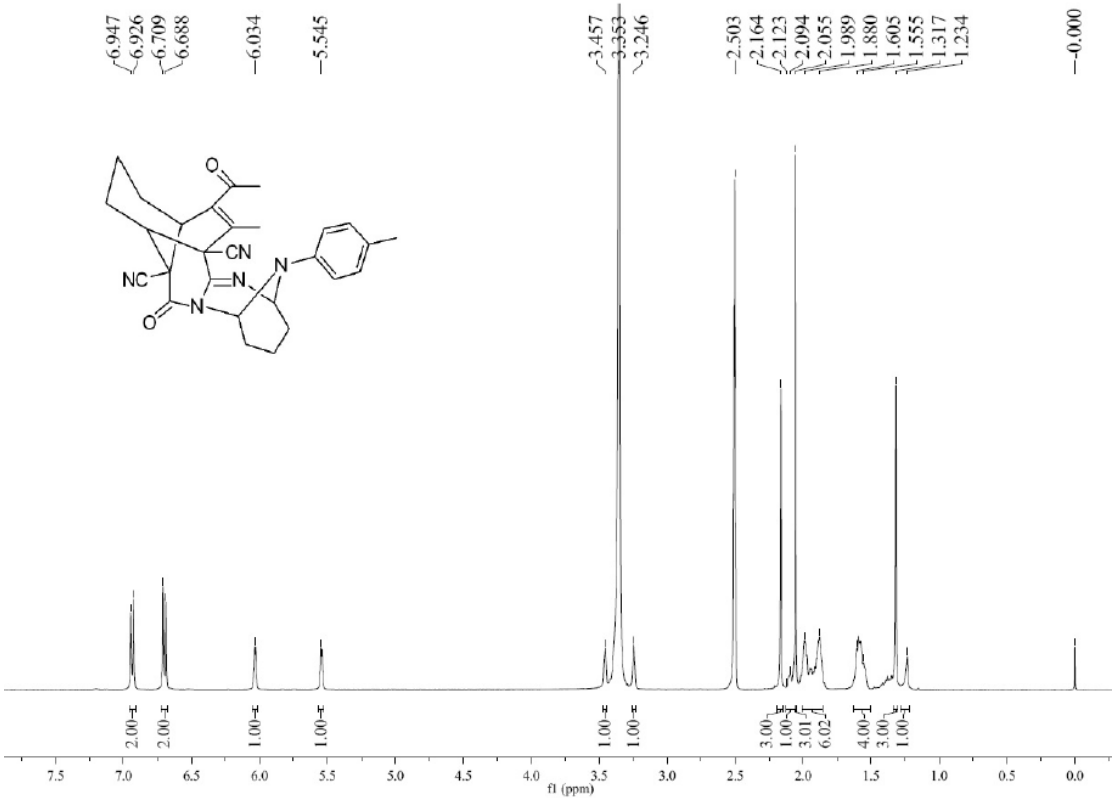
^{1}H NMR of compound **9f**



^{13}C NMR of compound **9f**



^{1}H NMR of compound **11a**



^{13}C NMR of compound **11a**