

Supporting Information

Rapid construction of five contiguous stereocenters in a multi-cascade reaction

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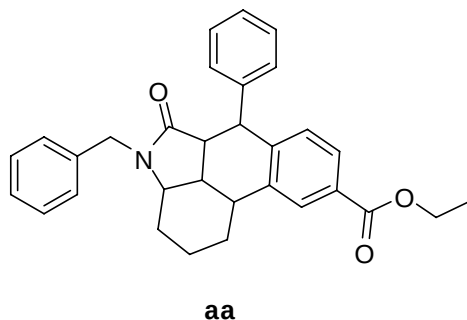
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1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar and Acros Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^1H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded on a Bruker Avance 300 spectrometer with CDCl_3 as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the ^1H NMR spectra as 0.00 ppm and CDCl_3 resonance in the ^{13}C spectra as 77.0 ppm. All coupling constants (J values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300–400 mesh. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets in the $4000\text{--}400\text{ cm}^{-1}$ ranges on a Nicolet 5DX spectrometer. Mass spectra were performed on Micromass GCT-MS. 2D NMR and HRMS were performed at the State-Authorized Analytical Center at University of Science and Technology of China. X-ray Crystallography diffraction data of ab, ae, al and bb were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) with a graphite monochromator using the ω -scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

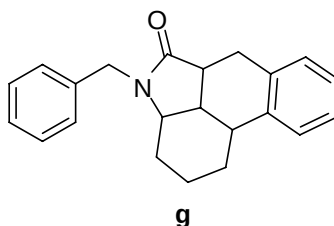
General procedures: A typical procedure for the palladium-catalyzed cascade reaction of the dienes with aryl halides: *N*-benzyl-*N*-(cyclohex-2-enyl)cinnamamide (**a**) (1.59 g, 5 mmol), ethyl 4-bromobenzoate (1.37 g, 6 mmol), Pd(OAc)₂ (18.2 mg, 0.05 mmol), and Ph₃P (25.6 mg, 0.1 mmol) were added to the degassed solution of (*n*Bu)₃N (2.78 mL, 10 mmol) in DMF (10 mL). After the mixture was stirred for half an hour at room temperature, it was then heated at 150°C for 18 h under argon atmosphere and then quenched with water, extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with hydrochloric acid (5 %), sodium carbonate (5 %), saturated sodium chloride solution and dried over MgSO₄, and then concentrated. The residue was purified by flash chromatography column (8:1 petroleum ether/EtOAc) to give the corresponding fused hydronaphthoindolone.

2. Physical Data for Fused Heterocycles



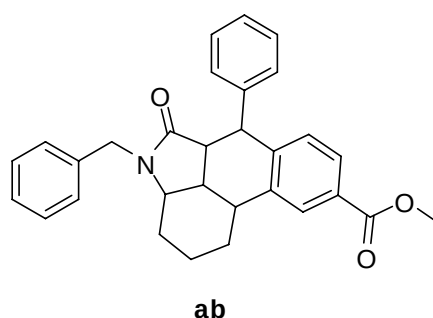
Ethyl 4-benzyl-5-oxo-6-phenyl-1,2,3,3a,3a¹,4,5,5a,6,10b-decahydronaphtho[3,2,1-cd]indole-9-carboxylate (aa):

Colorless crystals; 1.96 g (84 % yield); m.p. 124-126 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.98 (s, 1H; Ar-H), 7.81 (d, 1H, *J* = 8.0 Hz; Ar-H), 7.26-7.22 (m, 4H; Ar-H), 7.18-7.10 (m, 5H; Ar-H), 6.82 (d, 2H, *J* = 7.1 Hz; Ar-H), 4.92-4.83 (m, 2H; Ar-CHH-), 4.42-4.35 (m, 2H; -CHHCH₃), 3.89 (d, 1H, *J* = 15.2 Hz; Ar-CH-), 3.27 (m, 1H, N-CH-), 3.11-3.05 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.58 (m, 1H; O=C-CH-CH-), 2.18-2.15 (m, 1H; N-CH-CHH-CHH-CHH-), 2.12-2.05 (m, 1H; N-CH-CHH-), 1.81-1.77 (m, 1H; N-CH-CHH-CHH-CHH-), 1.42-1.37 (m, 3H; -CH₂CH₃), 1.31-1.23 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.10-1.06 (m, 1H; N-CH-CHH-CHH-); ¹³C NMR (75.5 MHz, CDCl₃): δ 172.1, 166.1, 143.1, 141.2, 140.6, 136.6, 131.1, 130.5, 130.1, 128.9, 128.1, 127.3, 127.0, 126.8, 126.2, 60.6, 54.3, 44.3, 43.8, 41.5, 38.1, 32.2, 30.4, 27.6, 22.1, 14.1; FT-IR (neat): ν_{max} 2939, 1710 (C=O), 1687 (C=O), 1610, 1599, 1419, 1290, 1269 (C-N), 709 cm⁻¹; HRMS (EI) *m/z* calcd for C₃₁H₃₁NO₃: 465.2304; found: 465.2296.



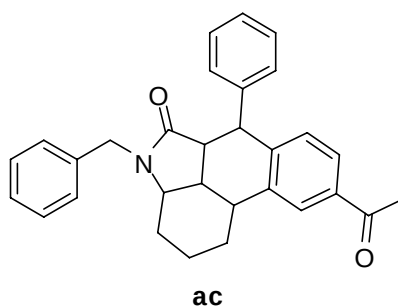
4-Benzyl-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a¹H)-one (g):

White solid; 0.21 g (13 % yield); m.p. 150-152 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.35-7.26 (m, 5H; Ar-H), 7.20-7.16 (m, 4H; Ar-H), 4.92 (d, 1H, *J* = 14.9 Hz; Ar-CHH-), 4.16 (d, 1H, *J* = 14.7 Hz; Ar-CHH-), 3.47 (m, 1H; N-CH-), 3.28-3.22 (m, 1H; O=C-CH-CHH-), 2.95-2.92 (m, 1H; O=C-CH-CHH-), 2.82-2.70 (m, 2H; O=C-CH-CHH-, O=C-CH-CH-CH-), 2.24 (m, 1H; O=C-CH-CH-CH-), 1.99 (d, 2H, *J* = 7.3 Hz; N-CH-CH-CH-CHH-, N-CH-CHH-), 1.77 (d, 1H, *J* = 7.7 Hz; N-CH-CH-CH-CHH-, N-CH-CHH-), 1.34-1.18 (m, 3H; N-CH-CHH-CHH-, N-CH-CHH-); ¹³C NMR (75.5 MHz, CDCl₃): δ 174.5, 139.9, 136.0, 135.0, 129.9, 129.0, 128.5, 128.3, 127.8, 127.8, 127.2, 125.8, 55.0, 44.3, 40.3, 38.5, 36.2, 30.4, 30.0, 27.0, 22.4; FT-IR (neat): ν_{max} 2933, 1681 (C=O), 1494, 1446, 1415, 1390 (C-N), 1319, 746 cm⁻¹; HRMS (EI) *m/z* calcd for C₂₂H₂₃NO: 317.1780; found: 317.1775.



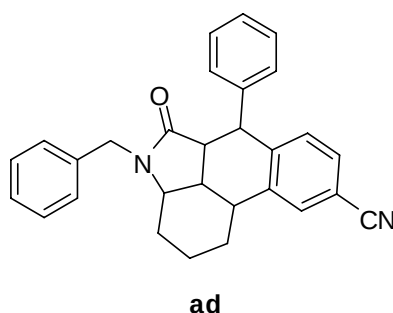
Methyl 4-benzyl-5-oxo-6-phenyl-1,2,3,3a,3a¹,4,5,5a,6,10b-decahydronaphtho[3,2,1-cd]indole-9-carboxylate (ab):

Colorless crystals; 1.58 g (70 % yield); m.p. 123-126 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.99 (s, 1H; Ar-H), 7.80 (d, 1H, J = 8.0 Hz; Ar-H), 7.26-7.22 (m, 4H; Ar-H), 7.19-7.10 (m, 5H; Ar-H), 6.82 (d, 2H, J = 6.5 Hz; Ar-H), 4.92-4.83 (m, 2H; Ar-CHH), 3.92 (s, 3H; COOCH_3), 3.86 (s, 1H; Ar-CH), 3.32-3.24 (m, 1H; N-CH-), 3.11-3.04 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.63-2.54 (m, 1H; O=C-CH-CH-), 2.15-2.11 (m, 1H; N-CH-CHH-CHH-CHH-), 2.10-2.05 (m, 1H; N-CH-CHH-), 1.79 (m, 1H, N-CH-CHH-CHH-CHH-), 1.35-1.26 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.22-1.06 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 172.1, 166.6, 143.3, 141.2, 140.5, 136.5, 131.1, 130.5, 130.2, 128.5, 128.1, 127.3, 127.2, 127.1, 126.8, 126.2, 54.3, 51.7, 44.3, 43.8, 41.5, 38.1, 32.2, 30.4, 27.6, 22.1; FT-IR (neat): ν_{max} 2933, 1693 (C=O), 1680, (C=O), 1600, 1494, 1433, 1415, 1305 (C-N), 723 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{30}\text{H}_{29}\text{NO}_3$: 451.2147; found: 451.2150.



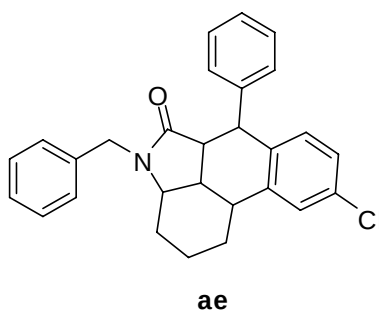
9-Acetyl-4-benzyl-6-phenyl-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a^{1H})-one (ac):

White solid; 1.69 g (78 % yield); m.p. 133-135 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.81 (s, 1H; Ar-H), 7.60-7.57 (m, 1H; Ar-H), 7.39-7.32 (m, 5H; Ar-H), 7.30-7.26 (m, 5H; Ar-H), 6.92 (d, 1H, $J = 8.2$ Hz; Ar-H), 4.82, 4.21 (dd, 2H, $J = 14.9$ Hz, 11.5Hz; Ar-CHH-), 4.03 (d, 1H, $J = 14.9$ Hz; Ar-CH-), 3.47-3.44 (m, 1H; N-CH-), 3.07-2.95 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.55 (s, 3H; COCH_3), 2.53-2.46 (m, 1H; O=C-CH-CH-), 2.16 (d, 1H, $J = 9.9$ Hz; N-CH-CHH-CHH-CHH-), 1.86 (m, 1H; N-CH-CHH-), 1.53 (m, 1H; N-CH-CHH-CHH-CHH-), 1.37-1.22 (m, 3H; N-CH-CHH-, N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 197.5, 172.9, 145.5, 143.3, 140.5, 136.8, 134.9, 130.7, 129.2, 128.5, 128.3, 128.1, 127.8, 127.1, 126.4, 126.0, 53.7, 47.4, 44.1, 42.1, 39.9, 38.9, 30.6, 30.4, 26.7, 26.2, 22.5; FT-IR (neat): ν_{max} 1687 (C=O), 1680 (C=O), 1600, 1562, 1421, 1357 (C-N), 1265, 1120, 761 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{30}\text{H}_{29}\text{NO}_2$: 435.2198; found: 435.2196.



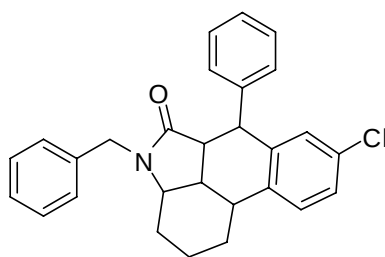
4-Benzyl-5-oxo-6-phenyl-1,2,3,3a,3a¹,4,5,5a,6,10b-decahydronaphtho[3,2,1-cd]indole-9-carbonitrile (ad):

White solid; 1.79 g (86 % yield); m.p. 166-168 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.58 (s, 1H; Ar-H), 7.43 (d, 1H, J = 8.0 Hz; Ar-H), 7.26-7.19 (m, 4H; Ar-H), 7.15-7.08 (m, 5H; Ar-H), 6.82 (d, 2H, J = 5.9 Hz; Ar-H), 4.90-4.82 (m, 2H; Ar-CHH-), 3.89 (d, 1H, J = 15.2 Hz;; Ar-CH), 3.31-3.27 (m, 1H; N-CH-), 3.07-3.01 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.62-2.55 (m, 1H; O=C-CH-CH-) 2.06 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.81 (m, 1H; N-CH-CHH-CHH-CHH-), 1.36-1.23 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.18-1.06 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 171.7, 143.7, 142.3, 139.9, 136.4, 132.8, 131.9, 130.5, 129.6, 128.1, 127.4, 127.0, 126.9, 126.5, 118.5, 110.5, 54.2, 44.4, 43.8, 41.2, 37.9, 31.9, 30.4, 27.5, 22.1; FT-IR (neat): ν_{max} 2227 (CN), 1687 (C=O), 1491, 1437, 1354 (C-N), 1244, 700 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}$: 418.2045; found: 418.2043.



4-Benzyl-9-chloro-6-phenyl-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a¹H)-one (ae):

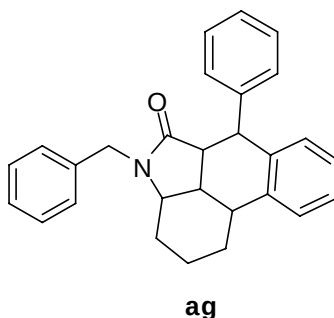
Colorless crystals; 1.64 g (77 % yield); m.p. 153-156 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.23-7.15 (m, 4H; Ar-H), 7.11-7.09 (m, 5H; Ar-H), 7.01-6.99 (m, 2H; Ar-H), 6.78 (d, 2H, $J = 5.7$ Hz; Ar-H), 4.81 (t, 2H, $J = 15.3$ Hz; Ar-CHH-), 3.85 (d, 1H, $J = 15.0$ Hz; Ar-CH), 3.27-3.19 (m, 1H; N-CH-), 3.05-2.93 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.53-2.49 (m, 1H; O=C-CH-CH-CH-), 1.93 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.75 (m, 1H; N-CH-CHH-CHH-CHH-), 1.28-1.21 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.16-1.02 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 172.1, 142.7, 140.7, 136.6, 136.4, 132.2, 132.1, 130.5, 128.5, 128.1, 127.2, 127.1, 126.8, 126.6, 126.2, 54.3, 43.8, 43.7, 41.7, 38.0, 31.9, 30.4, 27.6, 22.1$; FT-IR (neat): ν_{max} 2928, 1672 (C=O), 1593, 1494, 1433, 1356 (C-N), 1247, 719 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{26}\text{ClNO}$: 427.1703; found: 427.1705.



af

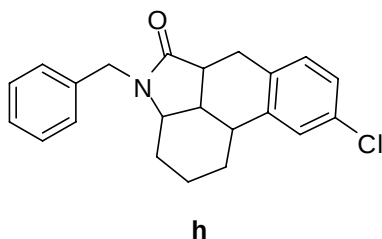
4-Benzyl-8-chloro-6-phenyl-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a1H)-one (af):

Colorless crystals; 1.41 g (66 % yield); m.p. 151-154 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.32-7.23 (m, 5H; Ar-H), 7.20-7.09 (m, 5H; Ar-H), 7.02-7.00 (m, 2H; Ar-H), 6.82 (s, 1H; Ar-H), 4.91-4.82 (m, 2H; Ar-CHH-), 3.89 (d, 1H, $J = 15.1$ Hz; Ar-CH-), 3.31-3.18 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 3.03 (m, 1H; N-CH-), 2.56 (m, 1H; O=C-CH-CH-), 2.02 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.79 (m, 1H; N-CH-CHH-CHH-CHH-), 1.36-1.32 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.28-1.19 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 172.1$, 142.7, 140.7, 136.6, 136.4, 132.2, 130.5, 128.5, 128.1, 127.2, 127.1, 126.8, 126.6, 126.2, 54.3, 43.8, 43.7, 41.7, 38.0, 31.9, 30.4, 27.6, 22.1; FT-IR (neat): ν_{max} 2928, 1691 (C=O), 1647, 1560, 1437, 1350 (C-N), 1247, 1074, 779, 696 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{26}\text{ClNO}$: 427.1703; found: 427.1695.



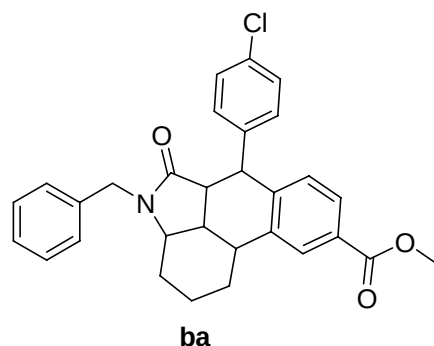
4-Benzyl-6-phenyl-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a¹H)-one (ag):

White solid; 0.86 g (44 % yield); m.p. 170-173 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.48 (s, 1H; Ar-H), 7.39-7.29 (m, 5H; Ar-H), 7.26-7.21 (m, 6H; Ar-H), 6.93 (d, 2H, J = 8.2 Hz; Ar-H), 4.82 (d, 1H, J = 14.9 Hz; Ar-CHH-), 4.18 (d, 1H, J = 11.5 Hz; Ar-CHH-), 4.03 (d, 1H, J = 14.9 Hz; Ar-CH-), 3.46-3.43 (m, 1H; N-CH-), 3.03-2.93 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.51-2.44 (m, 1H; O=C-CH-CH-CH-), 2.08 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.87 (m, 1H; N-CH-CHH-CHH-CHH-), 1.36-1.32 (m, 1H; N-CH-CHH-), 1.29-1.17 (m, 2H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 172.6, 145.6, 142.7, 141.3, 136.7, 132.6, 131.3, 129.3, 128.3, 128.2, 127.8, 127.2, 126.7, 118.5, 109.9, 53.6, 47.4, 44.2, 41.9, 39.6, 38.7, 30.38, 26.6, 22.5; HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{27}\text{NO}$: 393.2093; found: 393.2092.



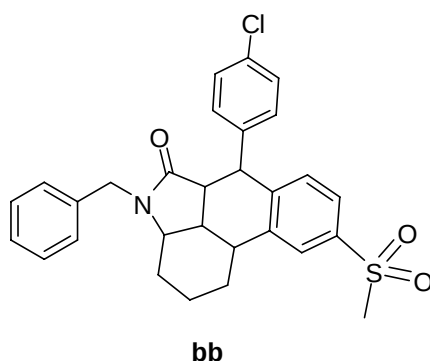
4-Benzyl-9-chloro-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a^{1H})-one (h):

Colorless crystals; m.p. 163-165 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.34-7.12 (m, 8H; Ar-H), 4.92 (d, 1H, $J = 14.9$ Hz; Ar-CHH-), 4.12 (d, 1H, $J = 15.0$ Hz; Ar-CHH-), 3.46 (t, 1H, $J = 9.9$ Hz; N-CH-); 3.21 (d, 1H, $J = 11.6$ Hz; O=C-CH-CHH-), 2.91 (t, 1H, $J = 11.6$ Hz; O=C-CH-CHH-), 2.76-2.68 (m, 2H; O=C-CH-CHH-, O=C-CH-CH-CH-), 2.23 (m, 1H; O=C-CH-CH-CH-), 1.97 (m, 2H; N-CH-CH-CH-CHH-, N-CH-CHH-), 1.78 (m, 1H; N-CH-CH-CH-CHH-), 1.34-1.17 (m, 3H; N-CH-CHH-, N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 148.8, 142.1, 137.2, 133.7, 131.8, 131.4, 129.1, 128.6, 128.1, 127.5, 126.4, 55.1, 44.6, 40.3, 38.7, 36.5, 30.5, 29.8, 27.3, 22.7; FT-IR (neat): ν_{max} 2939, 1681 (C=O), 1481, 1417, 1361 (C-N), 1240, 700 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{22}\text{H}_{22}\text{ClNO}$: 351.1390; found: 351.1387.



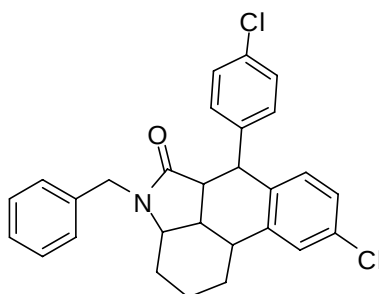
Methyl 4-benzyl-6-(4-chlorophenyl)-5-oxo-1,2,3,3a,3a¹,4,5,5a,6,10b-decahydro naphtho[3,2,1-cd]indole-9-carboxylate (ba):

Colorless crystals; 1.38 g (57 % yield); m.p. 143-145 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.98 (s, 1H; Ar-H), 7.81 (d, 1H, $J = 7.7$ Hz; Ar-H), 7.26 -7.26 (m, 2H; Ar-H), 7.21 -7.12 (m, 4H; Ar-H), 7.06 -7.04 (d, 2H, $J = 8.4$ Hz; Ar-H), 6.86 (m, 2H; Ar-H), 4.84 (d, 2H, $J = 15.2$ Hz; Ar-CHH-), 3.92 (s, 3H; COOCH_3), 3.88 (m, 1H; Ar-CH), 3.32 (m, 1H; N-CH-), 3.07 (m, 2H; $\text{O}=\text{C}-\text{CH}-$, $\text{O}=\text{C}-\text{CH}-\text{CH}-\text{CH}-$), 2.52-2.47 (m, 1H; $\text{O}=\text{C}-\text{CH}-\text{CH}-$), 2.11-2.05 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.82 (m, 1H; N-CH-CHH-CHH-CHH-), 1.34-1.26 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.22-1.06 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 172.2, 166.9, 143.1, 141.5, 139.4, 136.8, 132.6, 132.2, 131.4, 130.7, 129.1, 128.5, 127.7, 127.7, 127.4, 54.7, 52.1, 44.3, 44.1, 41.7, 38.4, 32.6, 30.7, 27.9, 22.4; FT-IR (neat): ν_{max} 1718($\text{C}=\text{O}$), 1683 ($\text{C}=\text{O}$), 1489, 1417, 1332 ($\text{C}-\text{N}$), 1267, 754 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{30}\text{H}_{28}\text{ClNO}_3$: 485.1758; found: 485.1760.



4-Benzyl-6-(4-chlorophenyl)-9-(methylsulfonyl)-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a¹H)-one (bb):

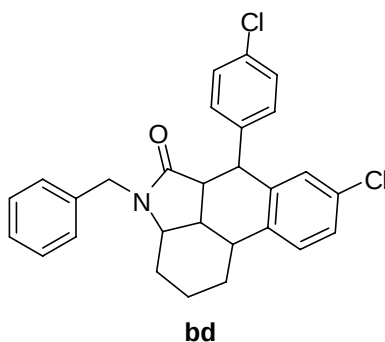
White solid; 1.14 g (45 % yield); m.p. 164-166 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.77 (s, 1H; Ar-H), 7.57-7.55 (d, 2H, J = 8.2 Hz; Ar-H), 7.35-7.24 (m, 5H; Ar-H), 7.19-7.16 (d, 2H, J = 7.9 Hz; Ar-H), 7.02-6.99 (d, 2H, J = 8.2 Hz; Ar-H), 4.82-4.77 (d, 1H, J = 11.9 Hz; Ar-CHH-), 4.22-4.18 (d, 1H, J = 11.5 Hz; Ar-CHH-), 4.06 (d, 1H, J = 14.9 Hz; Ar-CH-), 3.47 (m, 1H; N-CH-), 3.10-3.05 (m, 1H; O=C-CH-), 3.4 (s, 3H; SO_2CH_3), 2.97-2.89 (m, 1H; O=C-CH-CH-CH-), 2.47 (m, 1H; O=C-CH-CH-), 2.15 (m, 1H; N-CH-CHH-CHH-CHH-), 1.87 (m, 1H; N-CH-CHH-), 1.64 (m, 1H; N-CH-CHH-CHH-CHH-), 1.57-1.49 (m, 1H; N-CH-CHH-), 1.36-1.17 (m, 2H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 172.8, 146.1, 142.1, 141.6, 138.7, 136.9, 132.9, 131.8, 130.9, 128.7, 128.7, 128.2, 128.1, 127.6, 125.0, 54.1, 47.1, 44.5, 44.4, 42.3, 39.9, 39.3, 30.7, 27.0, 22.8; FT-IR (neat): ν_{max} 2929, 1685 (C=O), 1491, 1419, 1311 (C-N), 1149, 765 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{29}\text{H}_{28}\text{ClINO}_3\text{S}$: 505.1478; found: 505.1475.



bc

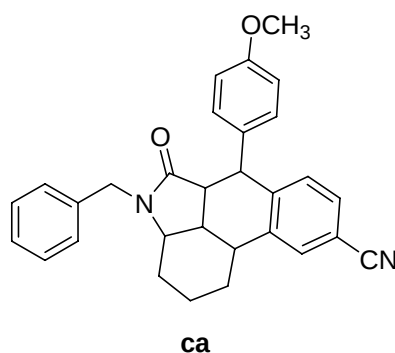
4-Benzyl-9-chloro-6-(4-chlorophenyl)-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a ^1H)-one (bc):

Colorless crystals; 1.73 g (75 % yield); m.p. 161-163 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.26-7.19 (m, 2H; Ar-H), 7.13-7.10 (m, 4H; Ar-H), 7.07-6.99 (m, 4H; Ar-H), 6.86 (m, 2H; Ar-H), 4.82 (m, 2H; Ar-CHH-), 3.90 (d, 1H, $J = 15.1$ Hz; Ar-CH), 3.28 (m, 1H; N-CH-), 3.11-3.01 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.48-2.43 (m, 1H; O=C-CH-CH-), 2.03 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.80-1.65 (m, 1H; N-CH-CHH-CHH-CHH-), 1.35-1.21 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.17-1.06 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 172.6, 143.1, 140.2, 139.6, 137.7, 136.9, 132.7, 132.5, 132.2, 131.2, 129.1, 128.5, 127.6, 127.5, 127.4, 127.2, 126.9, 54.9, 44.3, 43.4, 41.9, 38.4, 32.4, 30.7, 27.9, 22.5; FT-IR (neat): ν_{max} 1697 (C=O), 1587, 1481, 1425, 1303 (C-N), 1244, 1085, 893 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{Cl}_2\text{NO}$: 461.1313; found: 461.1308.



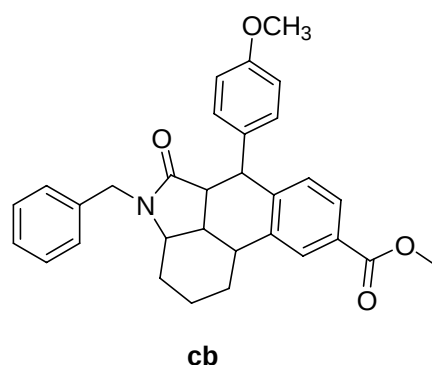
4-Benzyl-8-chloro-6-(4-chlorophenyl)-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a¹H)-one (bd):

Colorless crystals; 1.75 g (76 % yield); m.p. 164-166 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.26-7.21 (m, 6H; Ar-H), 7.08-7.06 (m, 4H; Ar-H), 6.84 (m, 2H; Ar-H), 4.82 (m, 2H; Ar-CHH-), 3.90 (d, 1H, $J = 15.1$ Hz; Ar-CH), 3.28 (m, 1H; N-CH-), 3.00 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.48 (m, 1H; O=C-CH-CH-), 2.01 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.79 (m, 1H; N-CH-CHH-CHH-CHH-), 1.28-1.25 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.24-1.09 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 172.2, 139.6, 139.4, 136.8, 132.6, 132.2, 131.3, 130.8, 130.4, 128.5, 127.7, 127.5, 127.3, 54.7, 44.3, 43.8, 41.7, 38.0, 32.6, 30.8, 27.9, 22.4; FT-IR (neat): ν_{max} 1689 (C=O), 1614, 1597, 1440, 1344 (C-N), 1611, 1089 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{25}\text{Cl}_2\text{NO}$: 461.1313; found: 461.1309.



4-Benzyl-6-(4-methoxyphenyl)-5-oxo-1,2,3,3a,3a¹,4,5,5a,6,10b-decahydronaphtho[3,2,1-cd]indole-9-carbonitrile (ca):

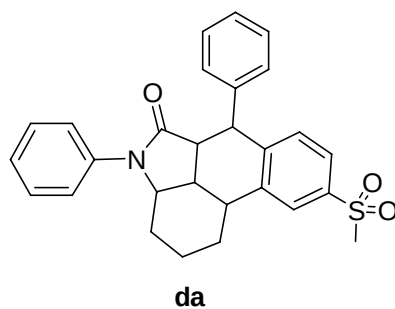
White solid; 1.43 g (64 % yield); m.p. 197-199 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.57 (s, 1H, Ar-H) 7.42 (d, 1H, $J = 7.5$ Hz; Ar-H), 7.30-7.17 (m, 4H; Ar-H), 7.00 (d, 2H, $J = 7.5$ Hz; Ar-H), 6.86-6.78 (m, 4H; Ar-H), 4.82 (m, 2H; Ar-CHH-), 3.92 (d, 1H, $J = 15.0$ Hz; Ar-CH), 3.80 (s, 3H; $-\text{OCH}_3$), 3.33-3.31 (m, 1H; N-CH-), 3.04-2.98 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.60-2.56 (m, 1H; O=C-CH-CH-), 2.06-2.04 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.82-1.71 (m, 1H; N-CH-CHH-CHH-CHH-), 1.35-1.26 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.22-1.09 (m, 1H; N-CH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 172.2, 158.4, 144.3, 142.5, 136.8, 133.1, 132.5, 132.3, 131.8, 129.9, 128.4, 127.4, 127.3, 118.8, 113.1, 110.8, 55.2, 54.6, 44.3, 43.9, 41.6, 38.3, 32.3, 30.7, 27.9, 22.3; FT-IR (neat): ν_{max} 2222 (CN), 1691 (C=O), 1606, 1510, 1435, 1352 (C-N), 1244, 1031, 833 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2$: 448.2151; found: 448.2154.



Methyl 4-benzyl-6-(4-methoxyphenyl)-5-oxo-1,2,3,3a,3a¹,4,5,5a,6,10b-decahydro naphtho[3,2,1-cd]indole-9-carboxylate (cb):

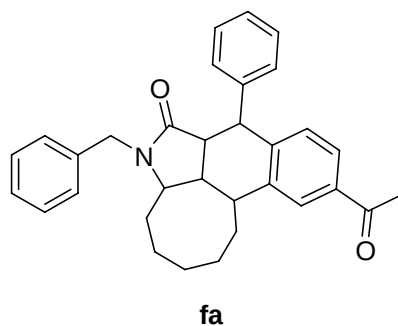
Colorless crystals; 1.76 g (73 % yield); m.p. 201-204 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.97 (s, 1H; Ar-H), 7.80-7.78 (d, 1H, $J = 6.6$ Hz; Ar-H), 7.18-7.15 (m, 4H; Ar-H), 7.04-7.01 (d, 2H, $J = 8.6$ Hz; Ar-H), 6.86-6.84 (d, 2H, $J = 5.4$ Hz; Ar-H), 6.79-6.76 (d, 2H, $J = 8.7$ Hz; Ar-H), 4.85 (t, 2H, $J = 13.9$ Hz; Ar-CHH-), 3.91 (s, 3H; $-\text{COO}-\text{CH}_3$),

3.78 (s, 3H; COCH₃), 3.94-3.81 (m, 1H; Ar-CH-), 3.31-3.28 (m, 1H; N-CH-), 3.09-3.01 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 2.60-2.55 (m, 1H; O=C-CH-CH-), 2.10 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.81-1.76 (m, 1H; N-CH-CHH-CHH-CHH-), 1.34-1.23 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.21-1.10 (m, 1H; N-CH-CHH-CHH-); ¹³C NMR (75.5 MHz, CDCl₃): δ 158.2, 144.0, 141.4, 136.9, 133.1, 131.8, 131.5, 130.5, 128.4, 127.6, 127.4, 127.2, 112.9, 55.2, 54.8, 52.1, 44.2, 43.9, 41.9, 38.4, 32.6, 30.7, 28.1, 22.4; FT-IR (neat): ν_{max} 1716 (C=O), 1685 (C=O), 1610, 1512, 1413, 1356 (C-N), 1244, 1037, 748 cm⁻¹; HRMS (EI) *m/z* calcd for C₃₁H₃₁NO₄: 481.2253; found: 481.2247.



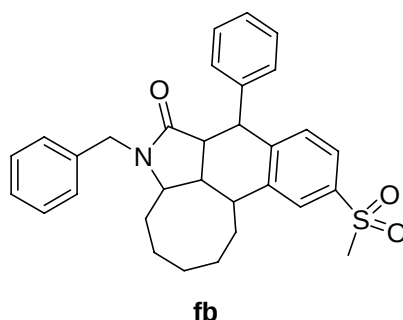
9-(Methylsulfonyl)-4,6-diphenyl-1,2,3,3a,4,5a,6,10b-octahydronaphtho[3,2,1-cd]indol-5(3a¹H)-one (da):

White solid; 1.17 g (51 % yield); m.p. 175-178 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.83 (s, 1H; Ar-H), 7.61-7.56 (m, 3H; Ar-H), 7.40-7.33 (m, 3H; Ar-H), 7.31-7.24 (m, 4H; Ar-H), 7.14-7.03 (m, 2H; Ar-H), 4.28 (t, 2H, *J* = 17.6 Hz; Ar-CH, N-CH-), 3.24-3.16 (m, 2H; O=C-CH-, O=C-CH-CH-CH-), 3.05 (s, 3H; SO₂CH₃), 2.72 (m, 1H; O=C-CH-CH-), 1.99 (m, 2H; N-CH-CHH-CHH-CHH-, N-CH-CHH-), 1.61-1.58 (m, 1H; N-CH-CHH-CHH-CHH-), 1.54-1.40 (m, 2H; N-CH-CHH-, N-CH-CHH-CHH-), 1.26-1.22 (m, 1H; N-CH-CHH-CHH-); ¹³C NMR (75.5 MHz, CDCl₃): δ 172.6, 146.6, 143.1, 141.8, 138.5, 132.2, 129.6, 128.9, 128.6, 128.1, 127.1, 125.1, 124.7, 120.9, 56.8, 47.8, 44.4, 43.6, 39.5, 39.4, 30.6, 27.1, 23.1; FT-IR (neat): ν_{max} 1701 (C=O), 1595, 1494, 1384 (C-N), 1286, 1157, 1120, 769 cm⁻¹; HRMS (EI) *m/z* calcd for C₂₈H₂₇NO₃S: 457.1712; found: 457.1707.



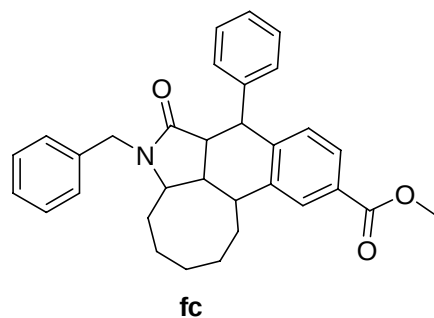
11-Acetyl-6-benzyl-8-phenyl-1,2,3,4,5,5a,6,7a,8,12b-decahydrobenzo[f]cycloocta[cd]isoindol-7(5a¹H)-one (fa):

White solid; 1.90 g (82 % yield); m.p. 224-227 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.84-7.79 (m, 2H; Ar-H), 7.68 (s, 1H; Ar-H), 7.45-7.39 (m, 2H; Ar-H), 7.36-7.30 (m, 3H; Ar-H), 7.08 (m, 1H; Ar-H), 6.95 (m, 2H; Ar-H), 6.33 (d, 2H, *J* = 7.4 Hz; Ar-H), 4.84 (d, 1H, *J* = 15.1 Hz; Ar-CHH-), 4.34 (d, 1H, *J* = 3.8 Hz; Ar-CHH-), 3.71-3.59 (m, 2H; O=C-CH-CH-, N-CH-), 3.16 (m, 1H; N-CH-CH-CH-), 2.90 (m, 2H; O=C-CH-CHH-, O=C-CH-CH-), 2.60 (s, 3H; -CO-CH₃), 2.28-2.24 (m, 1H; N-CH-CH-CHH-), 2.04-1.97 (m, 2H; N-CH-CH-CHH-, N-CH-CHH-CHH-CHH-), 1.83-1.76 (m, 3H; N-CH-CHH-CHH-CHH-, N-CH-CH-CHH-CHH-, N-CH-CHH-CHH-CHH-), 1.76-1.61 (m, 3H; N-CH-CH-CHH-CHH-, N-CH-CHH-CHH-CHH-, N-CH-CHH-CHH-CHH-), 1.24-1.19 (m, 1H; N-CH-CHH-CHH-CHH-); ¹³C NMR (75.5 MHz, CDCl₃): δ 198.1, 173.0, 145.7, 140.4, 137.4, 135.3, 131.2, 128.2, 127.9, 127.1, 126.9, 126.7, 126.1, 124.4, 55.2, 45.9, 45.4, 43.4, 38.4, 36.9, 32.6, 27.1, 26.6, 26.5, 25.7, 23.4; FT-IR (neat): ν_{max} 1672 (C=O), 1600 (C=O), 1492, 1371 (C-N), 1253, 704 cm⁻¹; HRMS (EI) *m/z* calcd for C₃₂H₃₃NO₂: 463.2511; found: 463.2509.



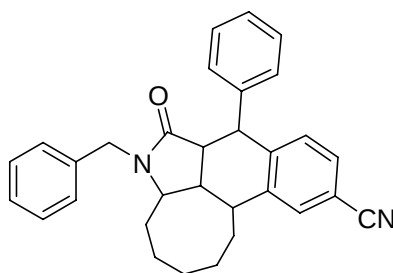
6-Benzyl-11-(methylsulfonyl)-8-phenyl-1,2,3,4,5,5a,6,7a,8,12b-decahydrobenzo[f]cycloocta[cd]isoindol-7(5a¹H)-one (fb):

White solid; 2.20 g (88 % yield); m.p. 235-238 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.79 (s, 1H; Ar-H), 7.52 (d, 1H, J = 7.0 Hz; Ar-H), 7.39-7.36 (m, 2H; Ar-H), 7.34-7.29 (m, 4H; Ar-H), 7.22-7.18 (m, 4H; Ar-H), 6.97 (d, 1H, J = 8.3 Hz; Ar-H), 4.78 (d, 1H, J = 15.2 Hz; Ar-CHH-), 4.14 (d, 2H, J = 13.8 Hz; Ar-CHH-, O=C-CH-CH-), 3.63 (m, 1H; N-CH-), 3.45 (m, 1H; N-CH-CH-CH-), 3.04 (s, 3H; SO_2CH_3), 2.70 (t, 1H, J = 12.6 Hz; O=C-CH-CHH-), 2.27-2.17 (m, 1H; O=C-CH-CH-), 2.01-1.95 (m, 5H; N-CH-CH-CHH-, N-CH-CHH-CHH-CHH-, N-CH-CH-CHH-CHH-), 1.71-1.60 (m, 3H; N-CH-CH-CHH-CHH-, N-CH-CHH-CHH-CHH-), 1.49-1.45 (m, 1H; N-CH-CHH-CHH-CHH-), 1.18-1.15 (m, 1H; N-CH-CHH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 174.1, 146.1, 143.7, 143.2, 138.7, 137.3, 131.4, 129.6, 128.9, 128.6, 127.7, 127.2, 127.0, 124.5, 56.6, 47.0, 46.6, 46.1, 44.5, 43.6, 41.5, 34.1, 32.1, 30.4, 25.1, 23.0; FT-IR (neat): ν_{max} 2914, 1705 (C=O), 1600, 1411, 1454, 1300 (C-N), 1145, 962, 700 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{31}\text{H}_{33}\text{NO}_3\text{S}$: 499.2181; found: 499.2180.



Methyl 6-benzyl-7-oxo-8-phenyl-1,2,3,4,5,5a,5a¹,6,7,7a,8,12b-dodecahydrobenzo [f]cycloocta[cd]isoindole-11-carboxylate (fc):

Colorless crystals; 1.77 g (74 % yield); m.p. 233-236 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.92 (d, 1H, $J = 7.1$ Hz; Ar-H), 7.79 (t, 3H, $J = 21.8$ Hz; Ar-H), 7.44-7.26 (m, 4H; Ar-H), 7.10-6.95 (m, 3H; Ar-H), 6.31 (d, 2H, $J = 7.5$ Hz; Ar-H), 4.84 (d, 1H, $J = 15.2$ Hz; Ar-CHH-), 4.34 (d, 1H, $J = 3.4$ Hz; Ar-CHH-), 3.95 (s, 3H; CO_2CH_3), 3.70-3.59 (m, 2H; $\text{O}=\text{C}-\text{CH}-\text{CH}-$, N-CH-), 3.15-3.14 (m, 1H; N-CH-CH-CH-), 2.90-2.86 (m, 2H; $\text{O}=\text{C}-\text{CH}-\text{CHH}-$, $\text{O}=\text{C}-\text{CH}-\text{CH}-$), 2.24-2.22 (m, 1H; N-CH-CH-CHH-), 1.99-1.94 (m, 2H; N-CH-CH-CHH-, N-CH-CHH-CHH-), 1.85-1.76 (m, 3H; N-CH-CHH-CHH-CHH-, N-CH-CH-CHH-CHH-), 1.66-1.61 (m, 3H; N-CH-CHH-CHH-CHH-, N-CH-CHH-CHH-CHH-), 1.21-1.19 (m, 1H; N-CH-CHH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 173.1, 167.4, 145.4, 140.2, 137.5, 135.3, 131.3, 128.3, 127.9, 127.7, 127.0, 126.9, 126.8, 126.1, 125.9, 55.4, 52.1, 45.9, 45.5, 43.5, 38.3, 37.0, 32.7, 27.1, 26.4, 25.8, 23.3; FT-IR (neat): ν_{max} 1716 (C=O), 1681 (C=O), 1608, 1438, 1348 (C-N), 741 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{32}\text{H}_{33}\text{NO}_3$: 479.2460; found: 479.2453.



fd

6-Benzyl-7-oxo-8-phenyl-1,2,3,4,5,5a,5a¹,6,7,7a,8,12b-dodecahydrobenzo[f]cycloocta[cd]isoindole-11-carbonitrile (fd):

Colorless crystals; 1.74 g (78 % yield); m.p. 252-254 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.56 (d, 2H, $J = 8.1$ Hz; Ar-H), 7.39-7.36 (m, 3H; Ar-H), 7.29-7.26 (m, 2H; Ar-H), 7.17-7.16 (m, 1H; Ar-H), 7.12-7.07 (m, 1H; Ar-H), 7.02-6.97 (m, 2H; Ar-H), 6.21 (d, 2H, $J = 7.3$ Hz; Ar-H), 5.03-4.98 (m, 1H; Ar-CHH-), 4.85-4.82 (m, 1H; Ar-CHH-), 3.72-3.65 (m, 2H; O=C-CH-CH-, N-CH-), 3.09-3.06 (m, 1H; N-CH-CH-CH-), 2.84-2.81 (m, 1H; O=C-CH-CHH-), 2.52-2.49 (m, 1H; O=C-CH-CH-), 2.04-1.98 (m, 2H; N-CH-CH-CHH-, N-CH-CHH-CHH-CHH-), 1.77-1.66 (m, 5H; N-CH-CH-CHH-, N-CH-CHH-CHH-CHH-, N-CH-CHH-CHH-CHH-, N-CH-CH-CHH-CHH-, N-CH-CHH-CHH-CHH-), 1.61-1.44 (m, 2H; N-CH-CH-CHH-CHH-, N-CH-CHH-CHH-CHH-), 1.26-1.14 (m, 1H; N-CH-CHH-CHH-CHH-); ^{13}C NMR (75.5 MHz, CDCl_3): δ 174.6, 148.1, 139.7, 137.0, 134.7, 132.2, 130.0, 128.4, 128.1, 128.1, 127.0, 126.8, 126.7, 125.8, 118.8, 110.0, 56.4, 47.1, 46.5, 43.6, 39.8, 37.3, 36.9, 33.1, 26.7, 24.8, 24.4, 22.3; FT-IR (neat): ν_{max} 2225 (CN), 1685 (C=O), 1604, 1494, 1448, 1350 (C-N), 1273, 756 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{31}\text{H}_{30}\text{N}_2\text{O}$: 446.2358; found: 446.2352.

3. X-Ray Structure for **aa**, **ae**, **bc**, **fa** and **h**

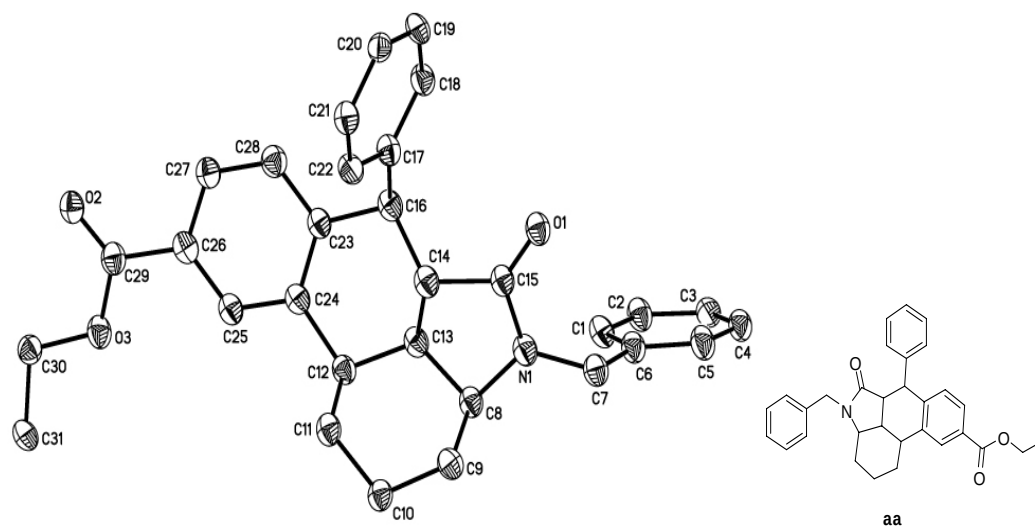


Figure 1. X-ray structure of **aa** (CCDC 715801).

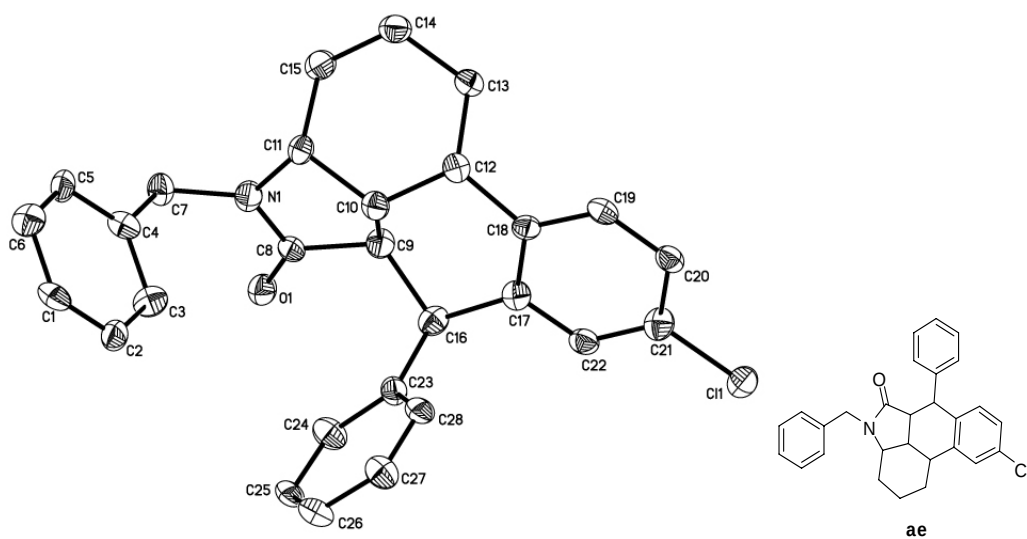


Figure 2. X-ray structure of **ae** (CCDC 715803).

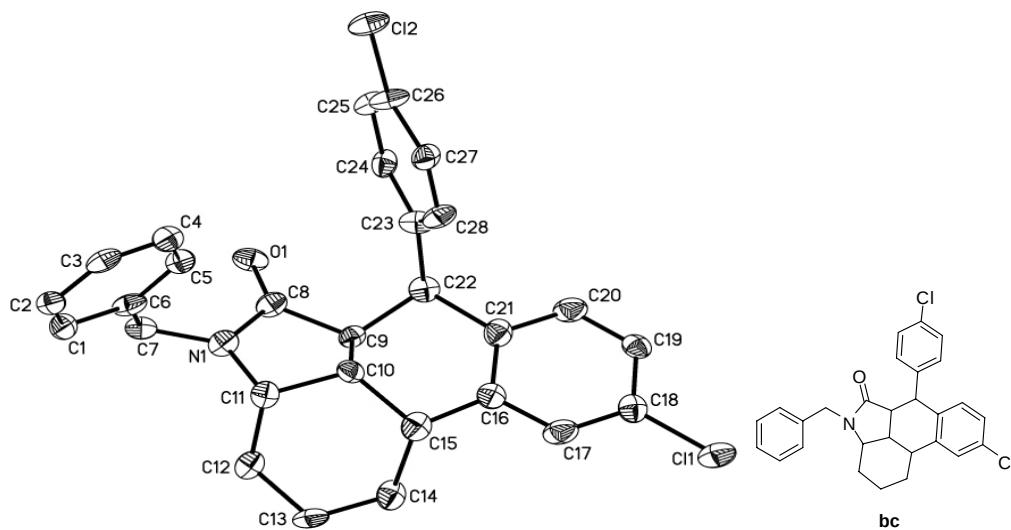


Figure 3. X-ray structure of **bc** (CCDC 715802).

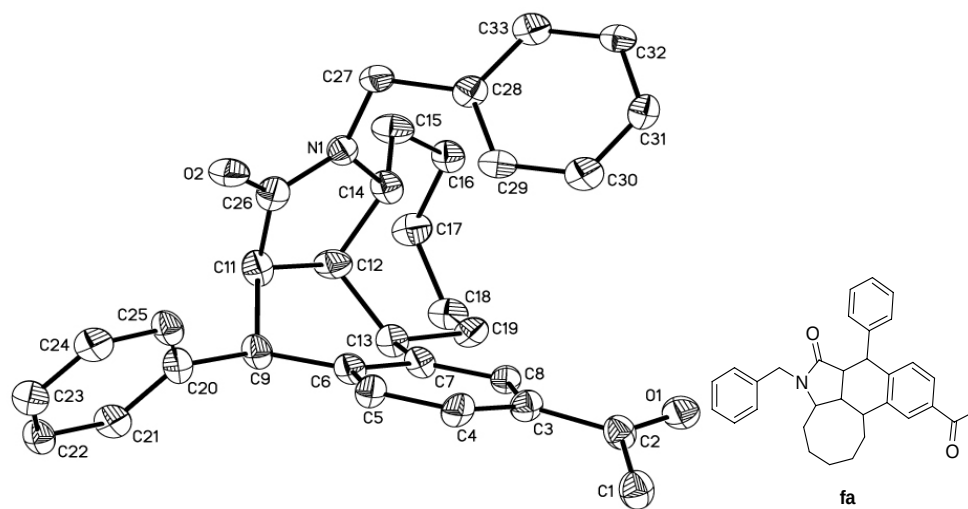


Figure 4. X-ray structure of **fa** (CCDC 715804)

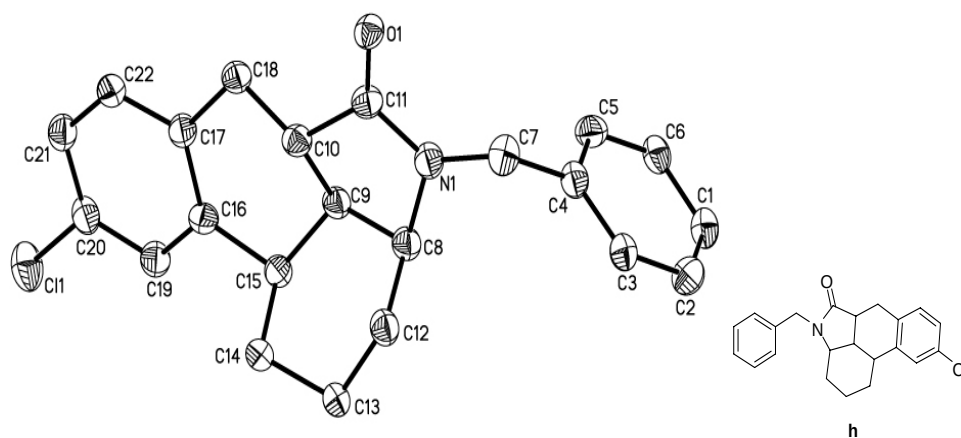
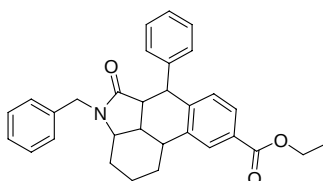
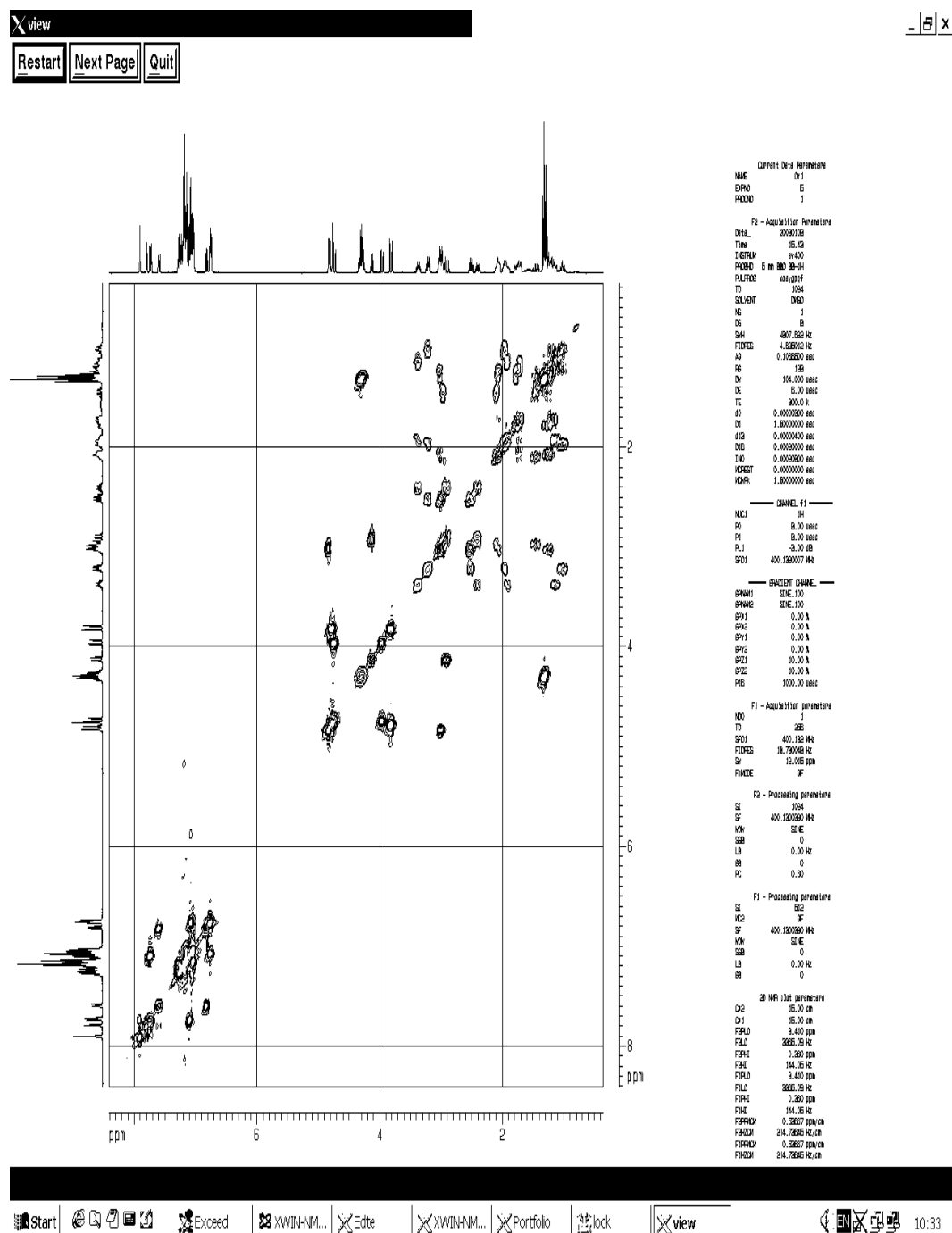


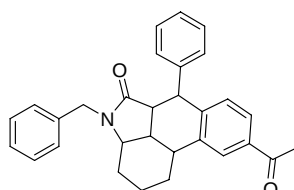
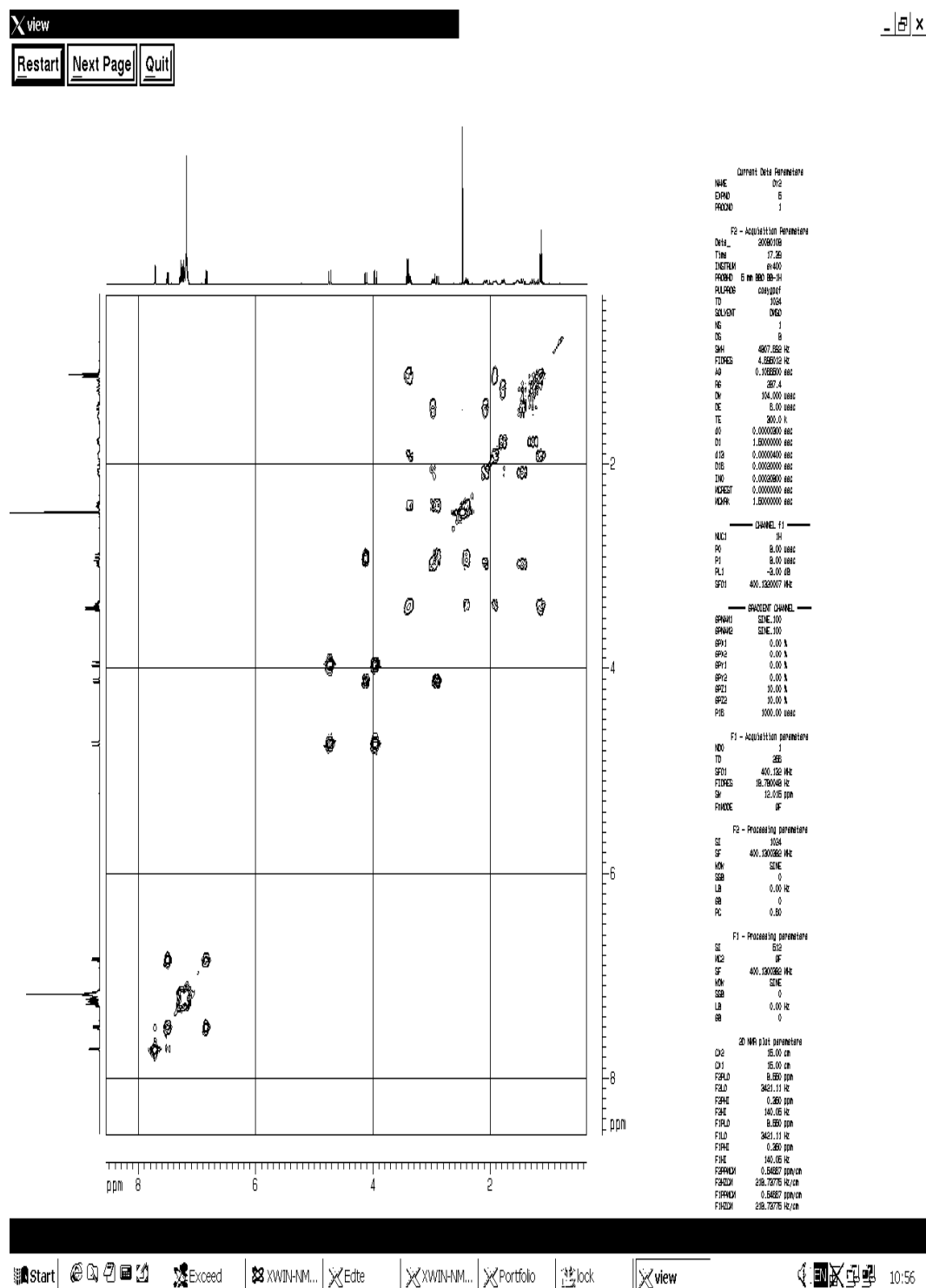
Figure 5. X-ray structure of **h** (CCDC 715805)

4. 2D ^1H - ^1H COSY and ^{13}C - ^1H COSY NMR Spectra for **aa** and **ac**

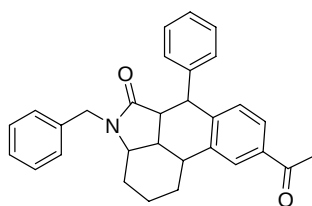
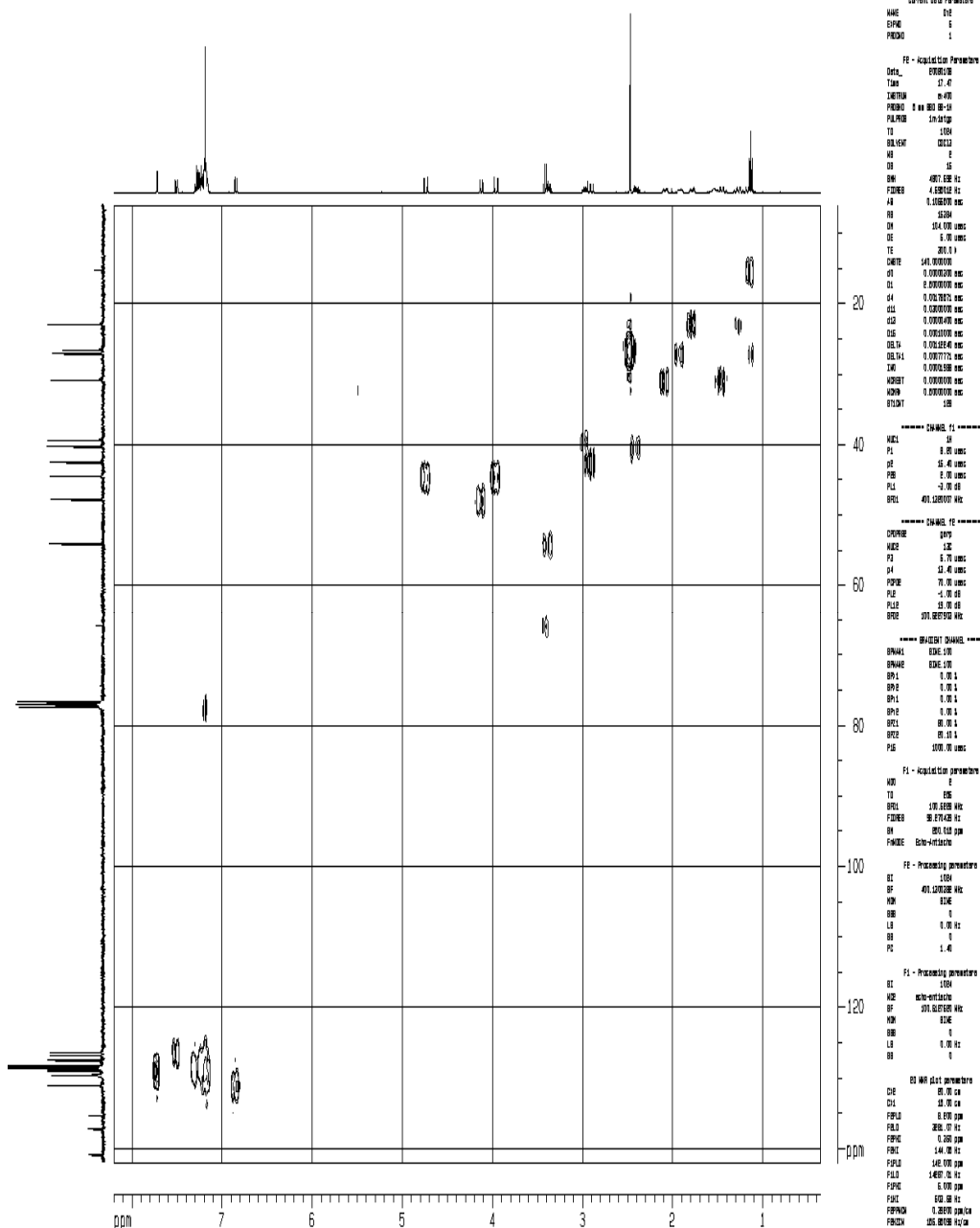


^1H - ^1H COSY of **aa**

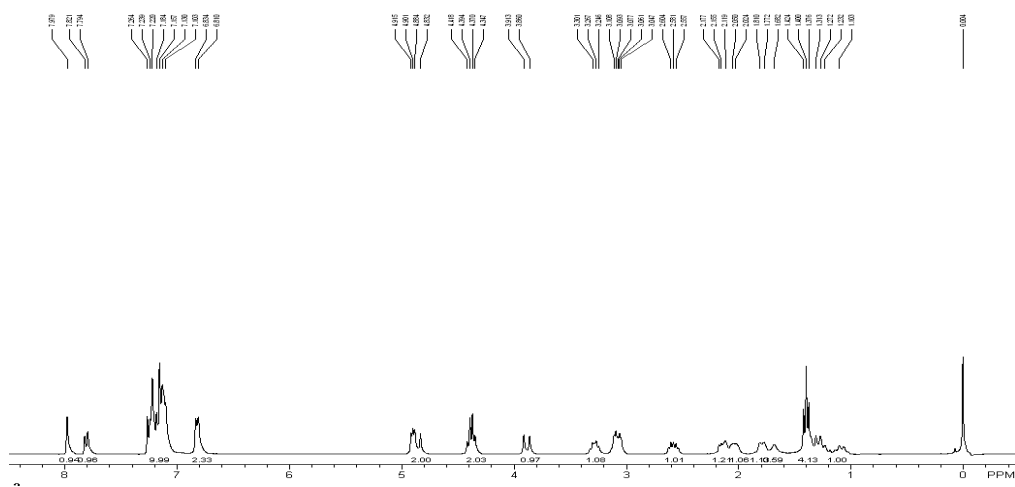
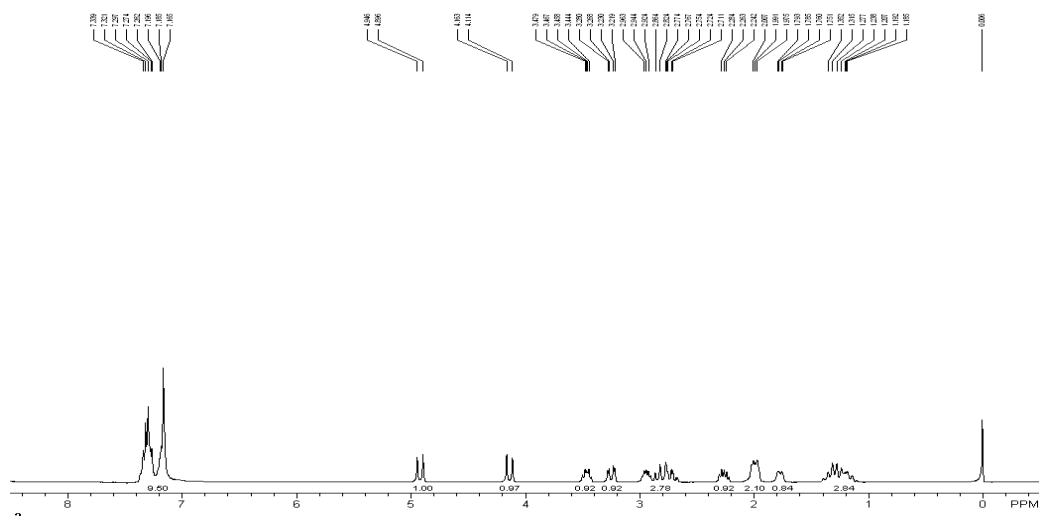


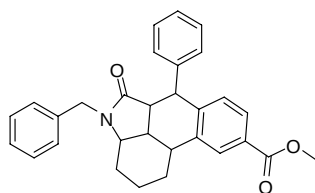
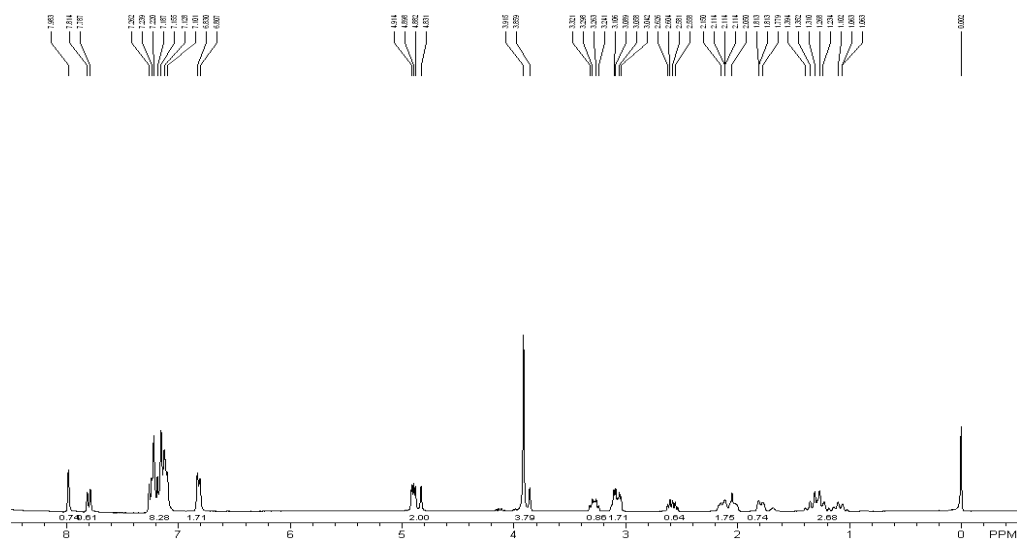


^1H - ^1H COSY of ac

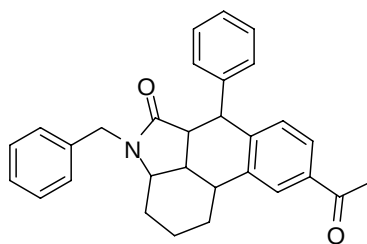
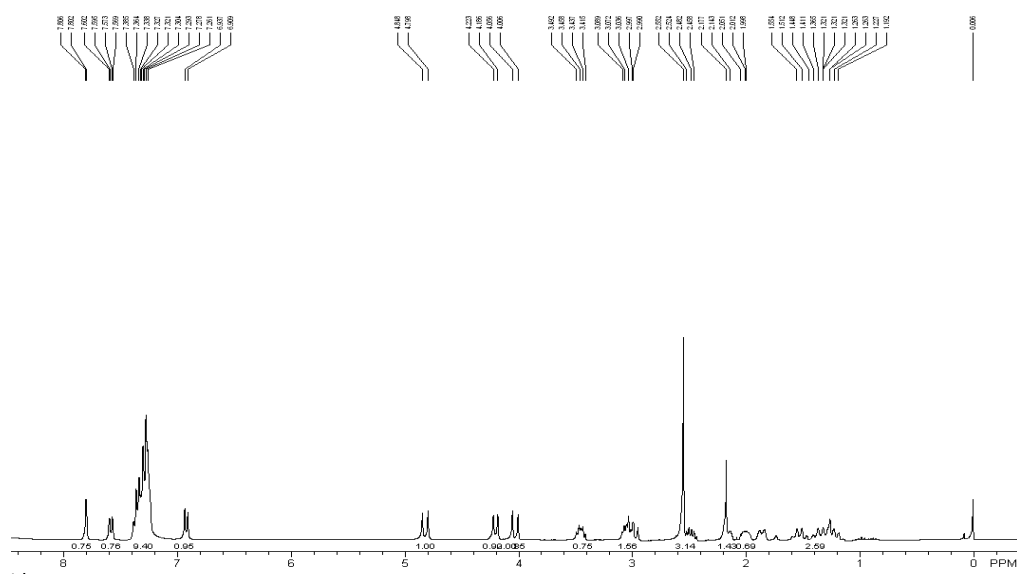
 ^{13}C - ^1H COSY of **ac**

5. ^1H NMR Spectra for New Compounds

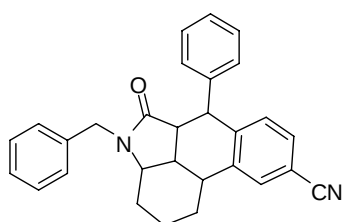
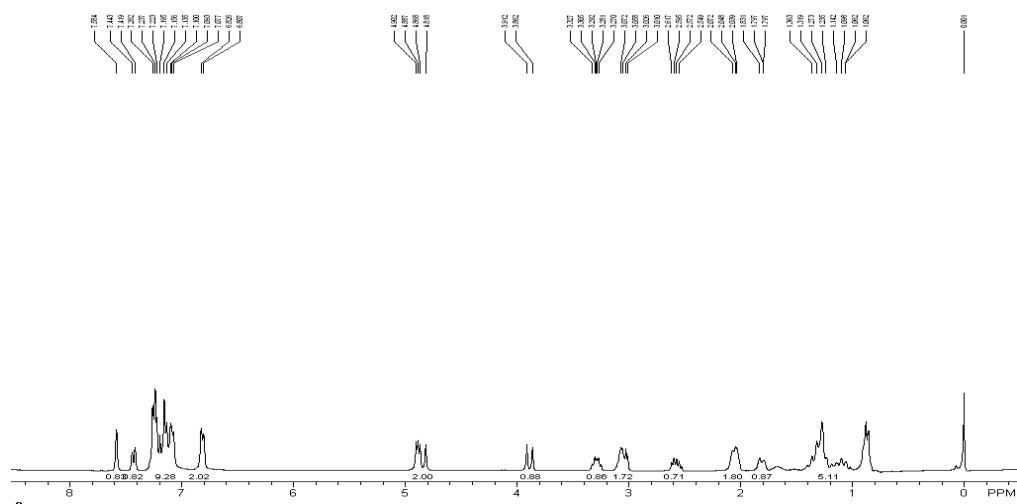




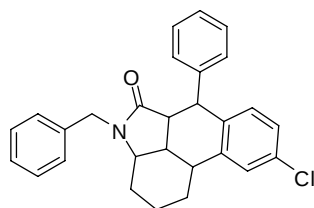
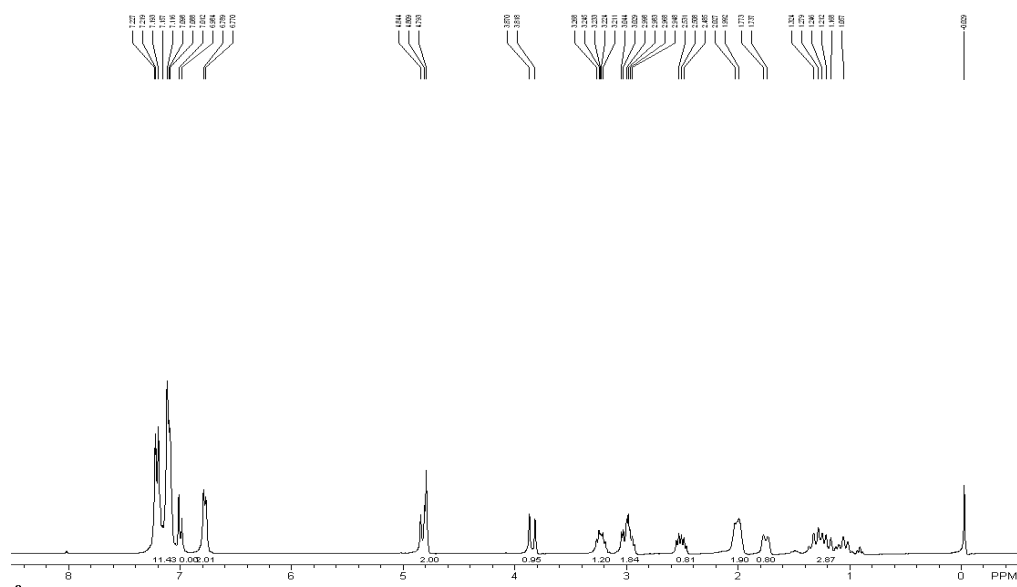
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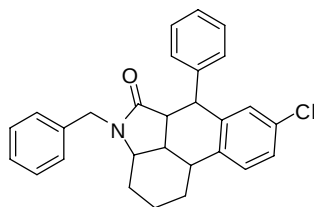
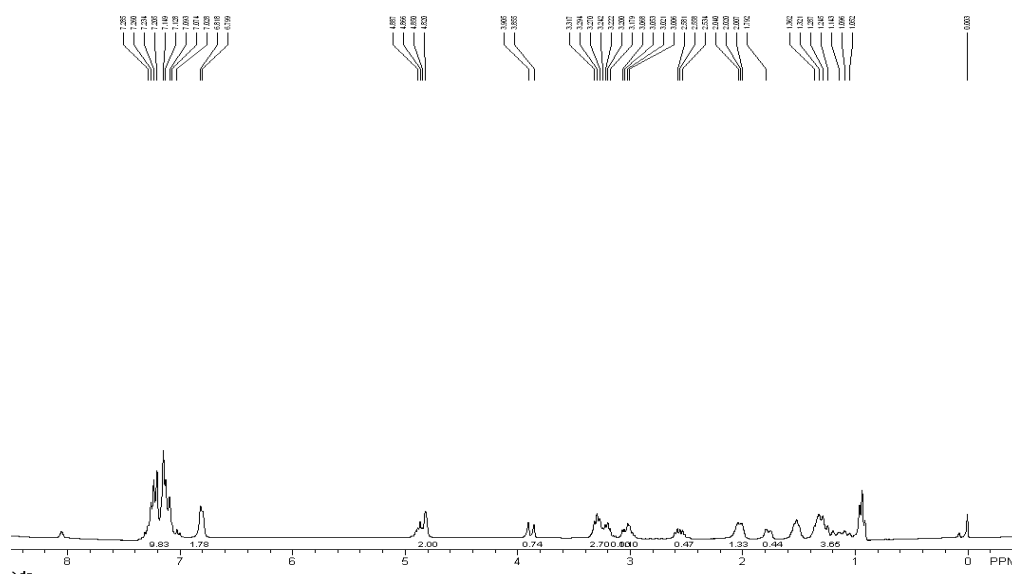
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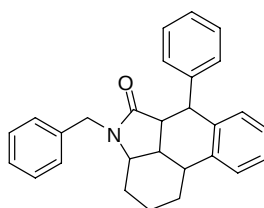
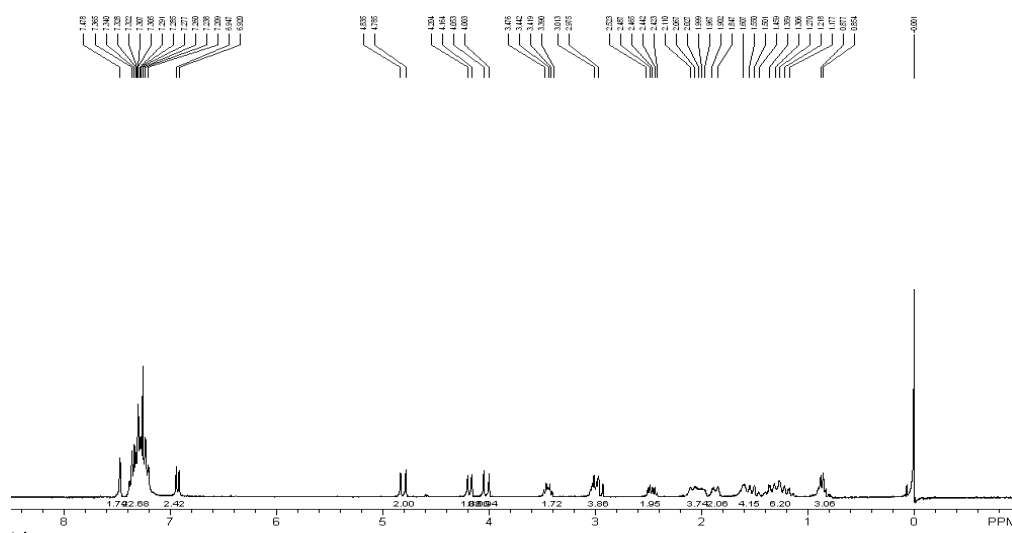
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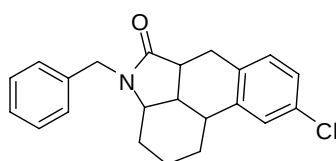
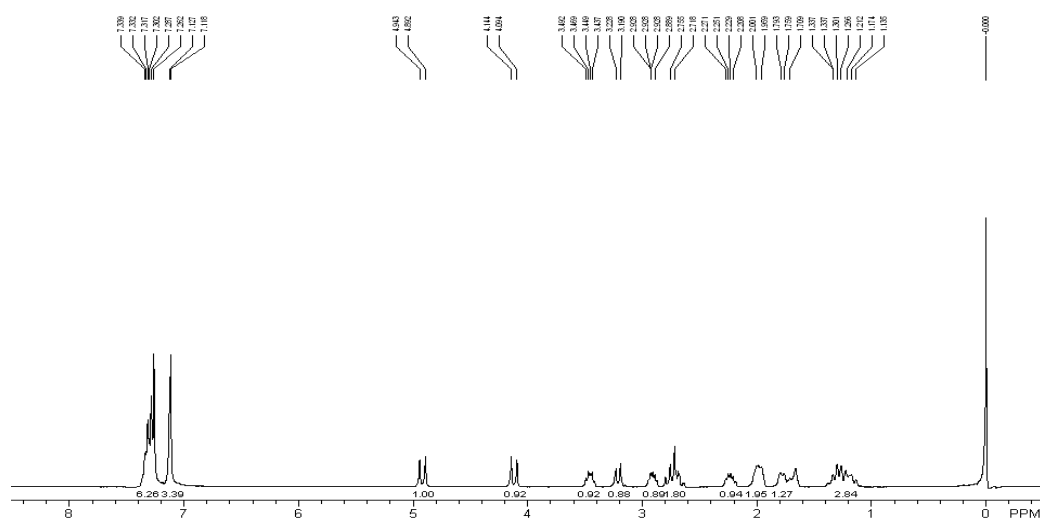
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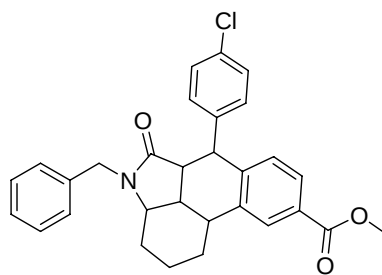
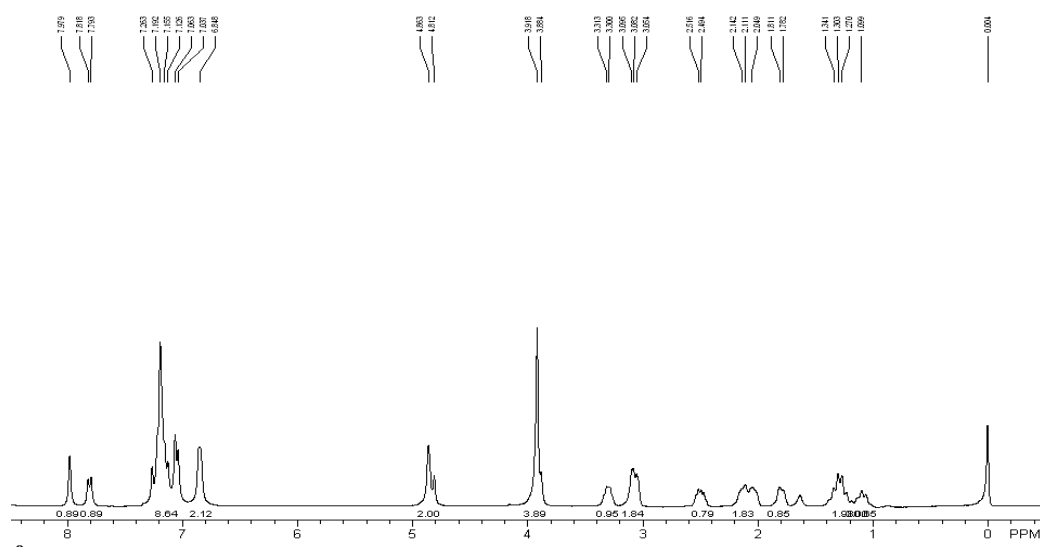
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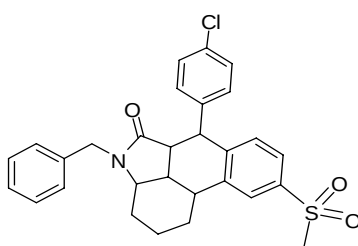
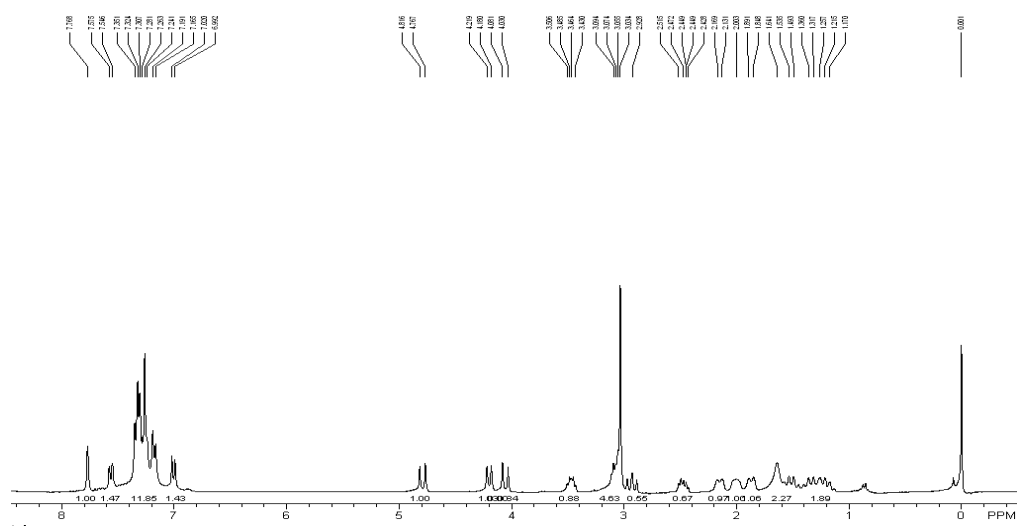
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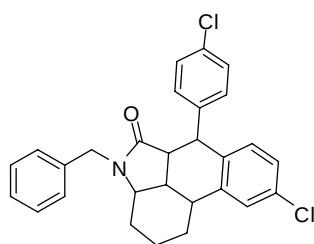
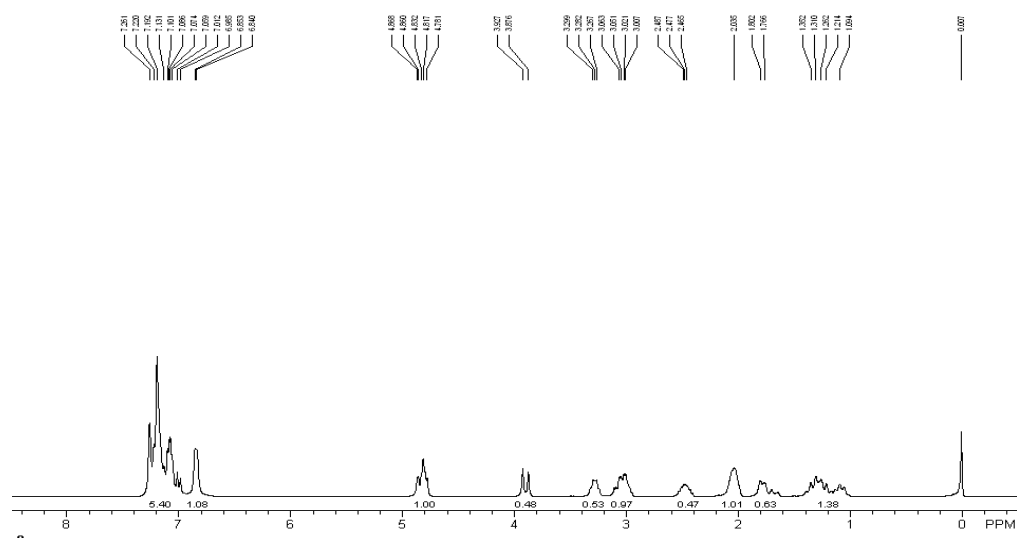
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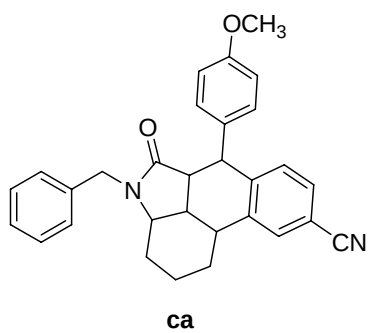
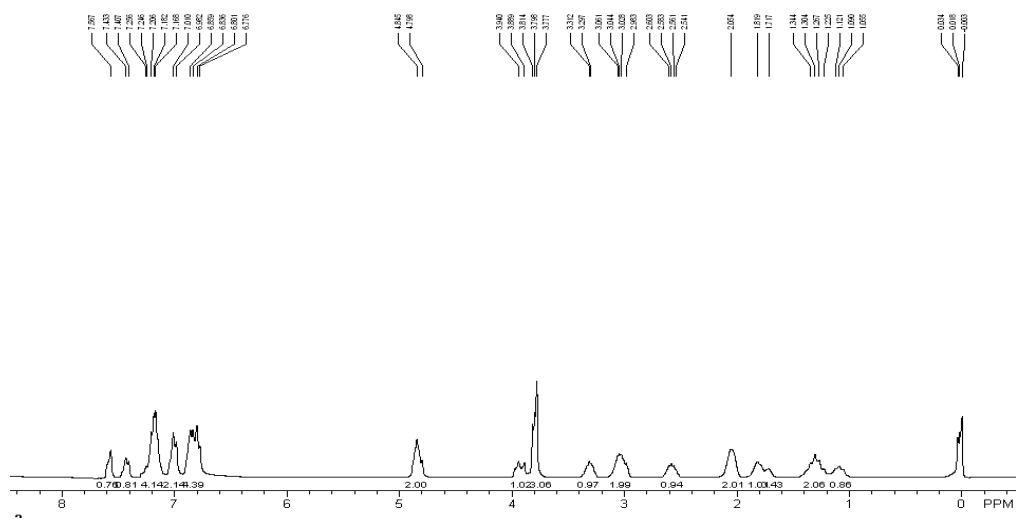
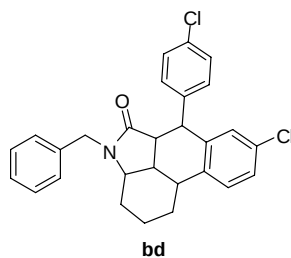
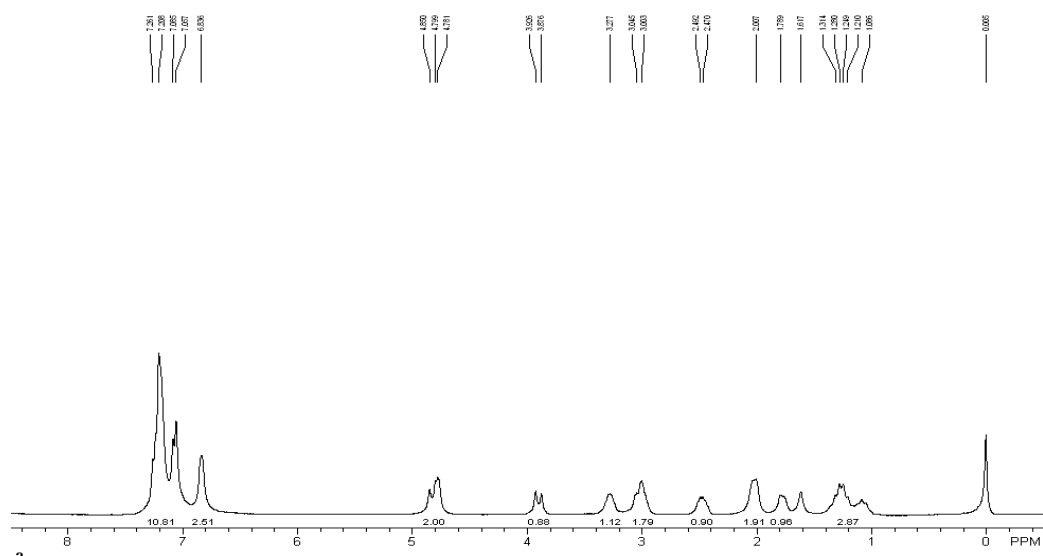
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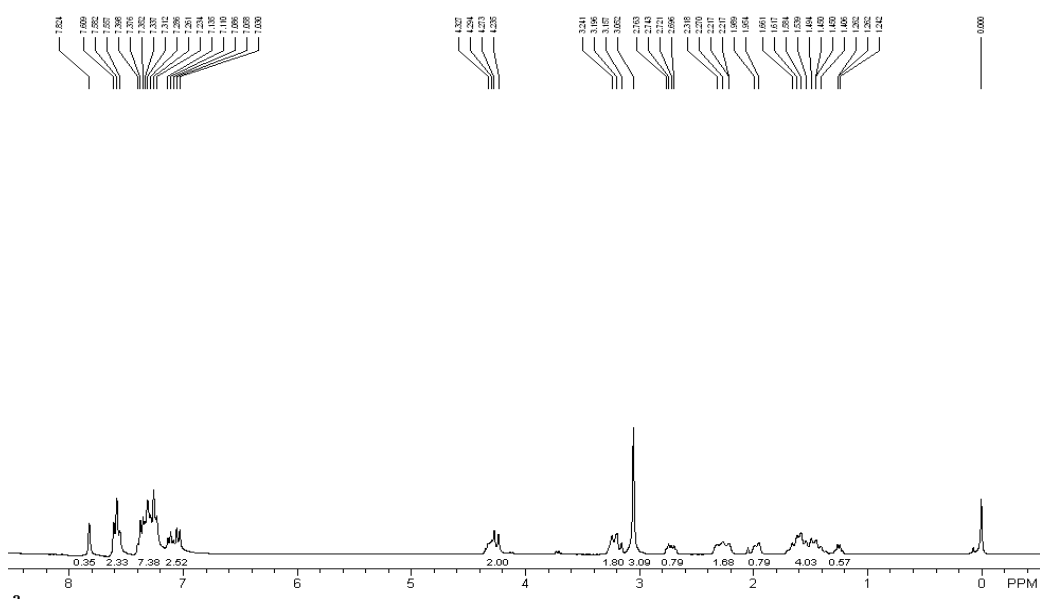
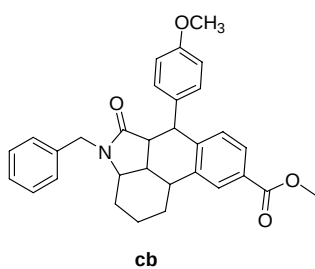
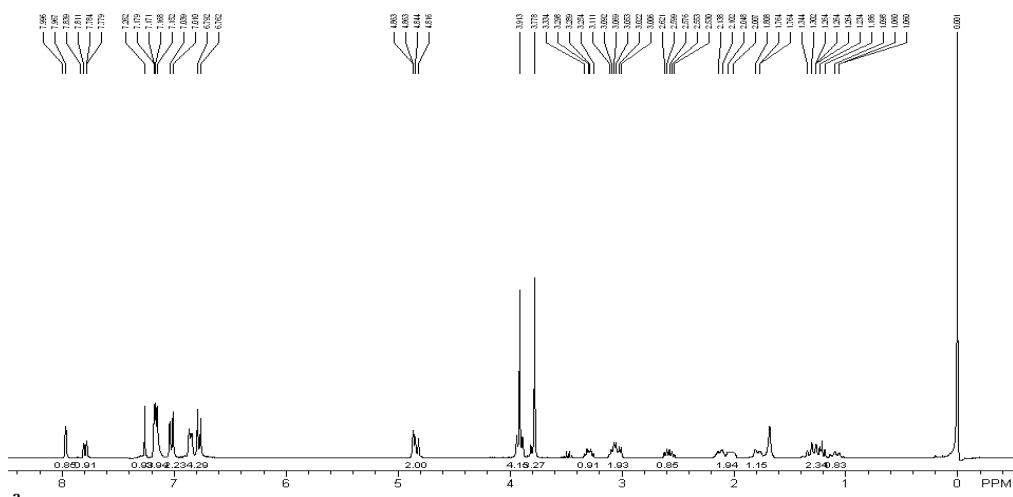


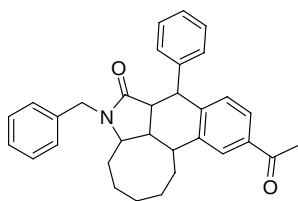
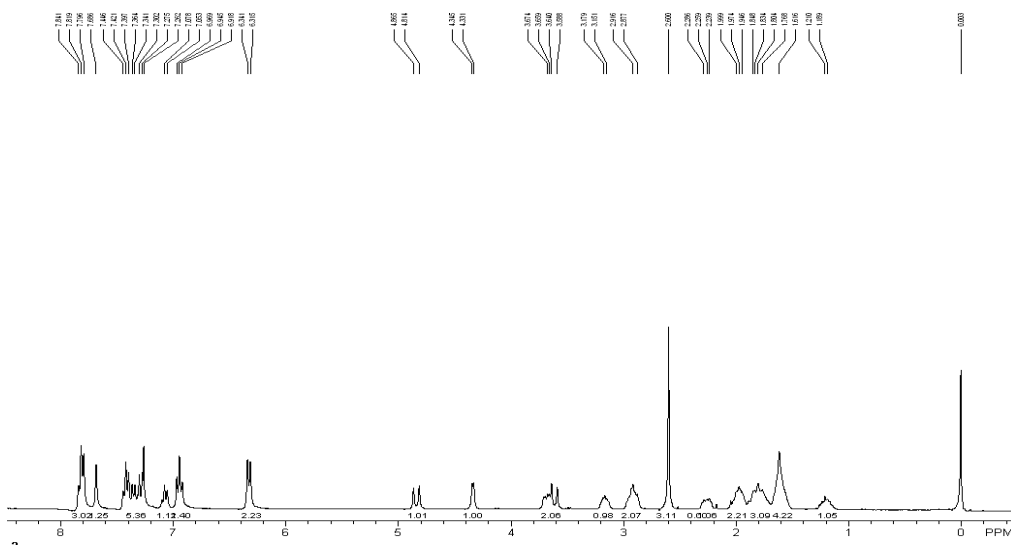
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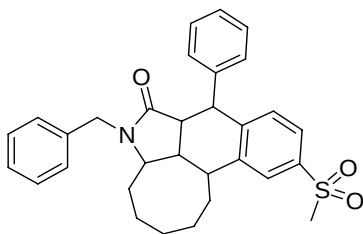
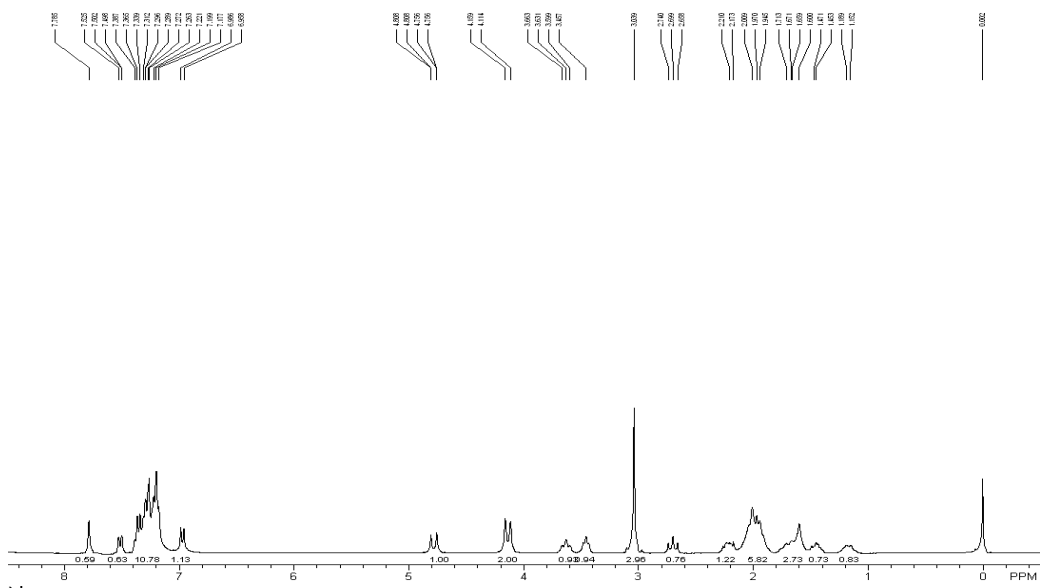
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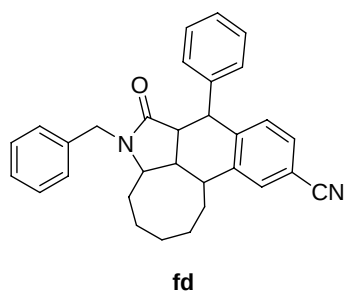
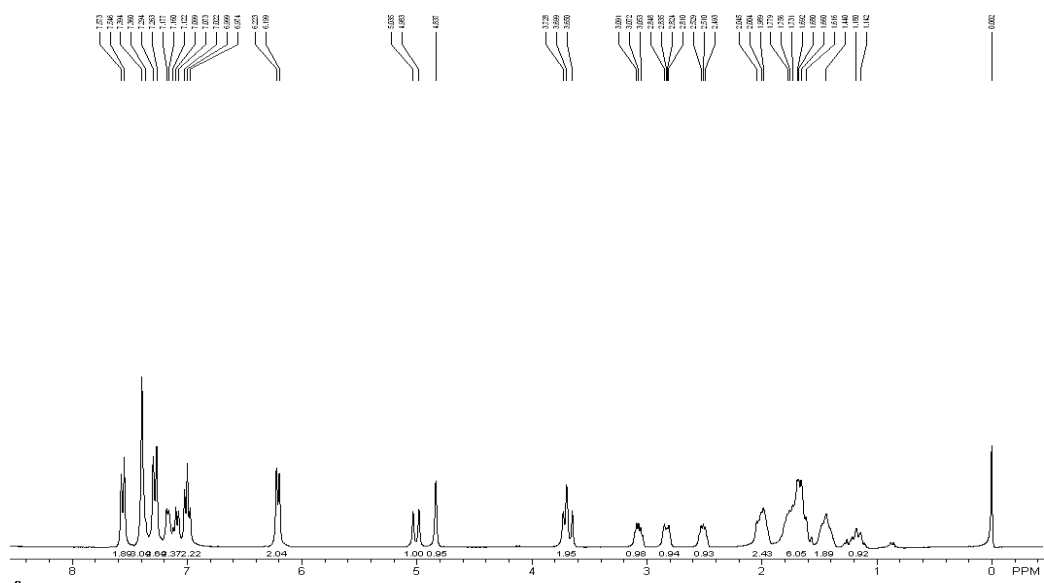
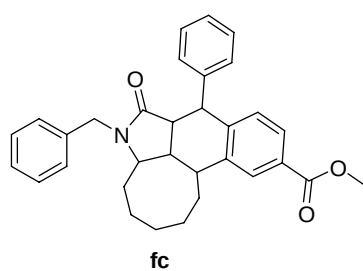
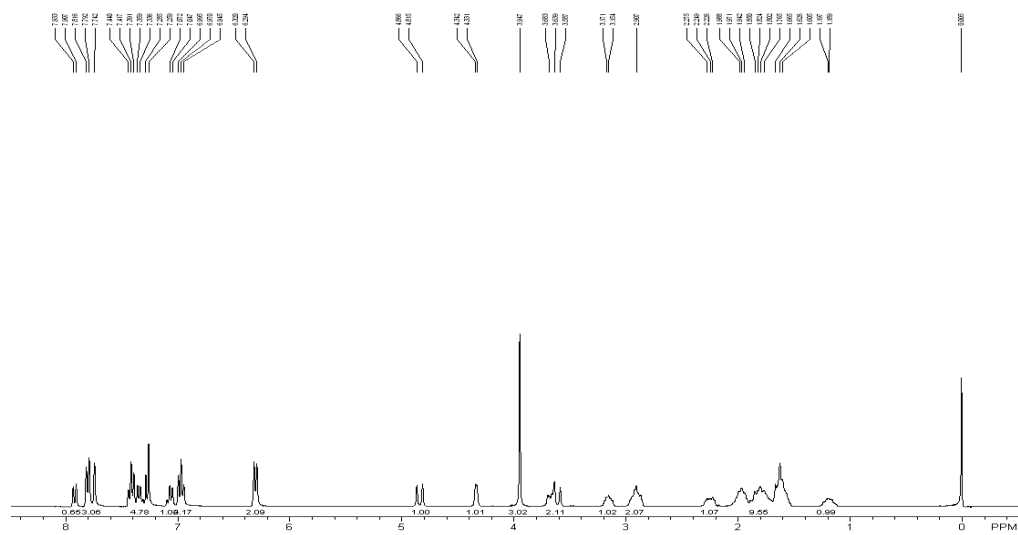




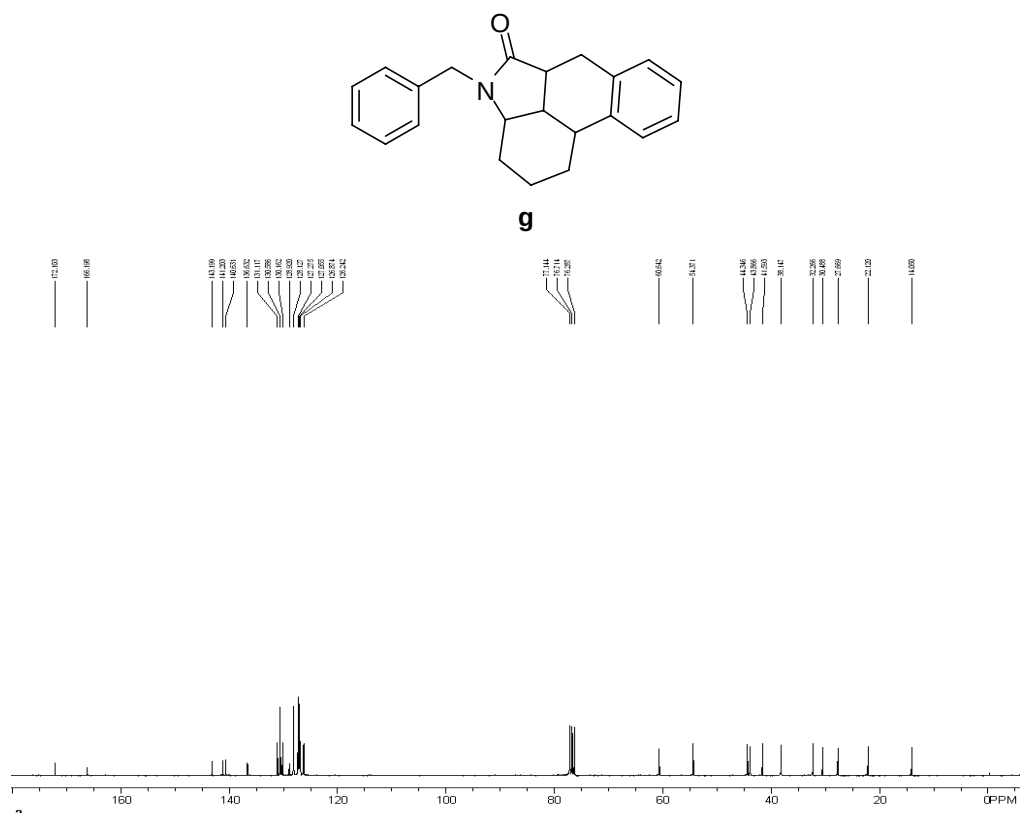
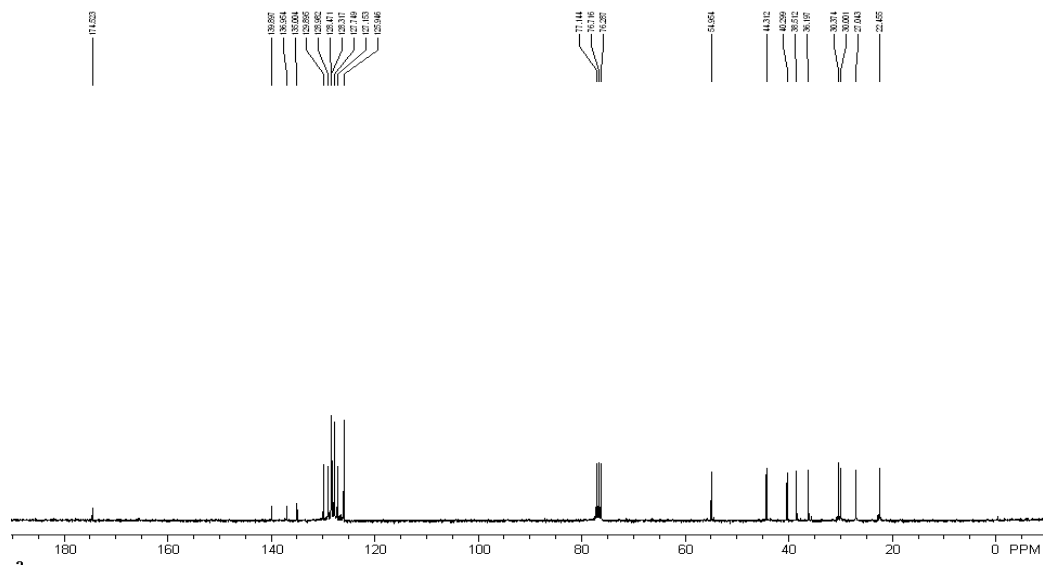
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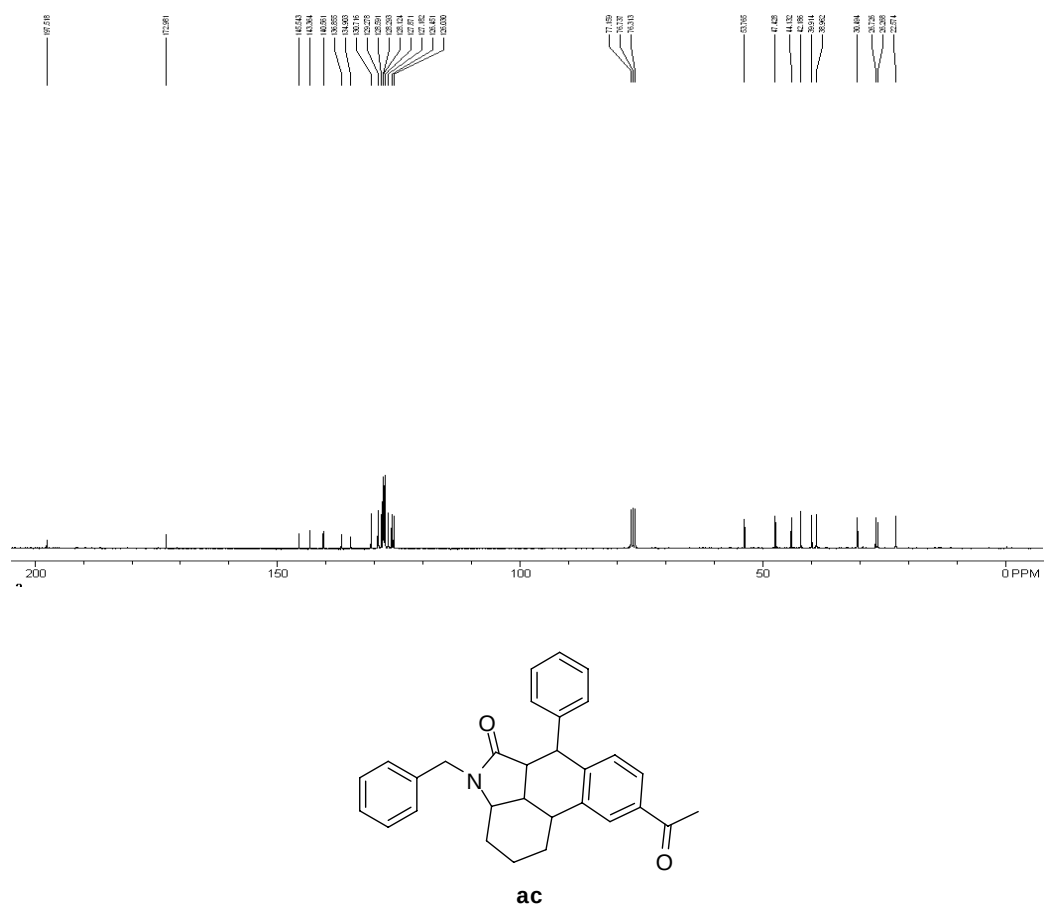
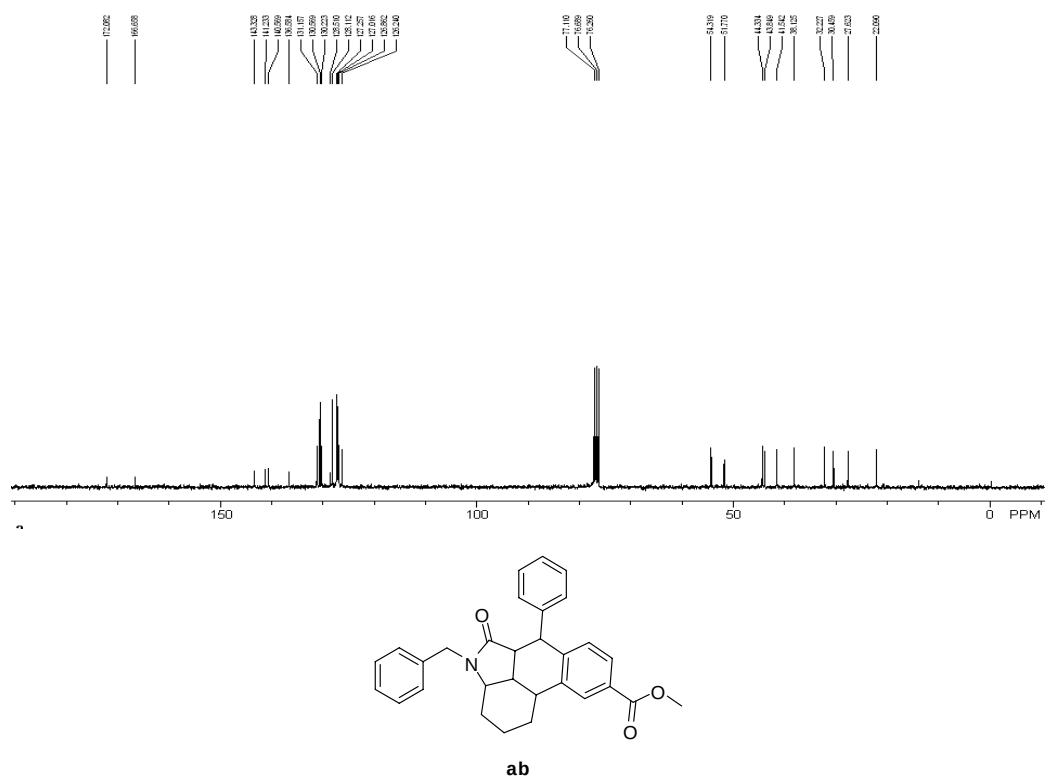


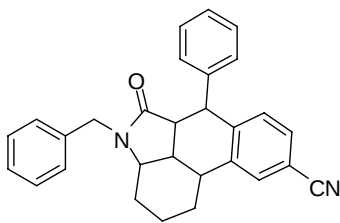
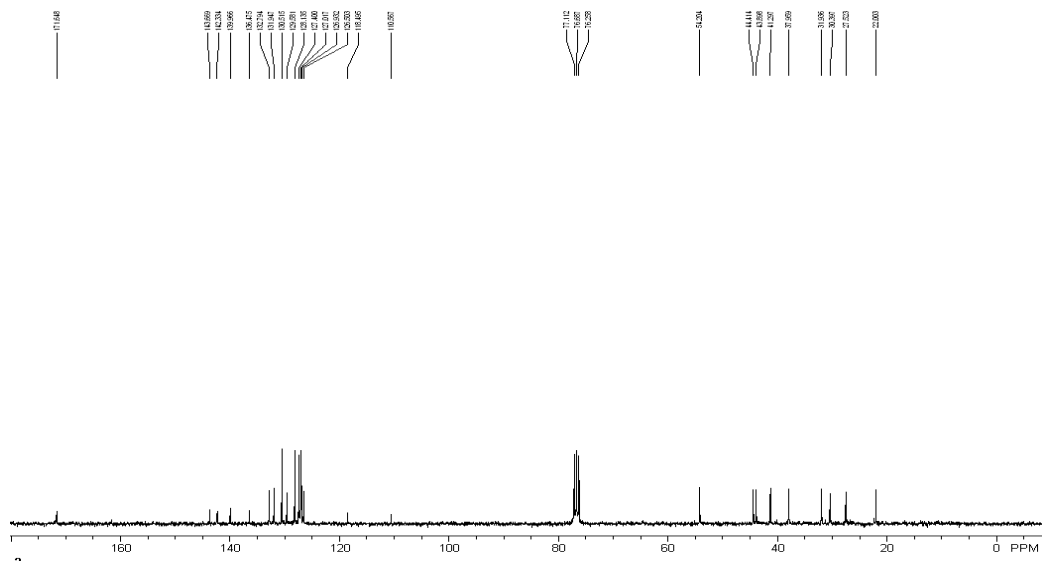
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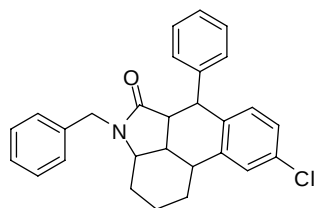
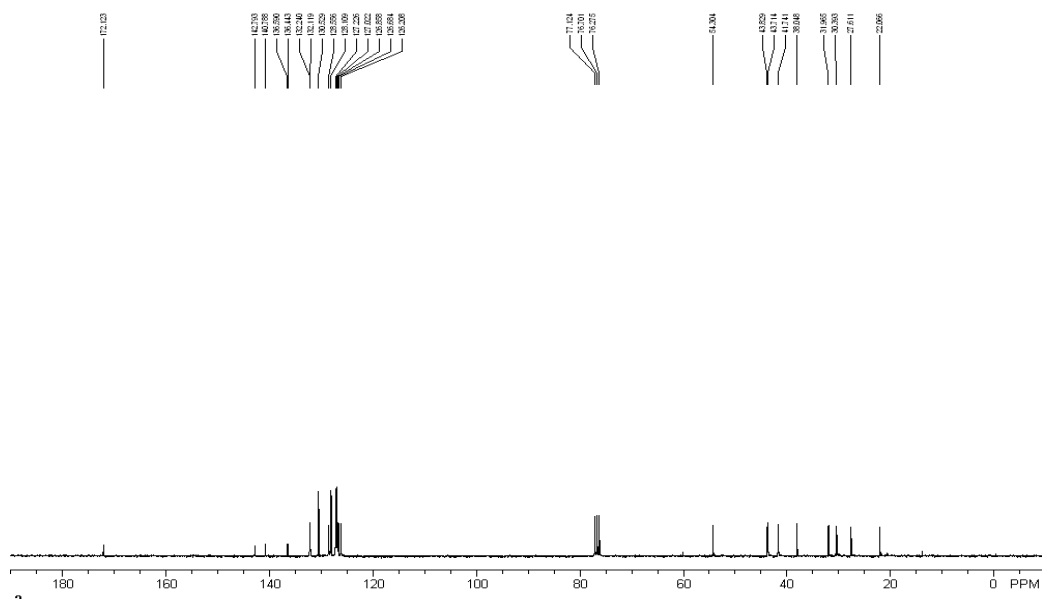
6. ^{13}C NMR Spectra for New Compounds



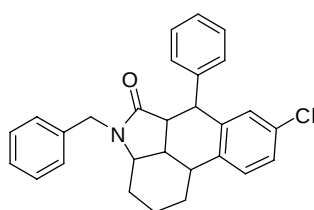
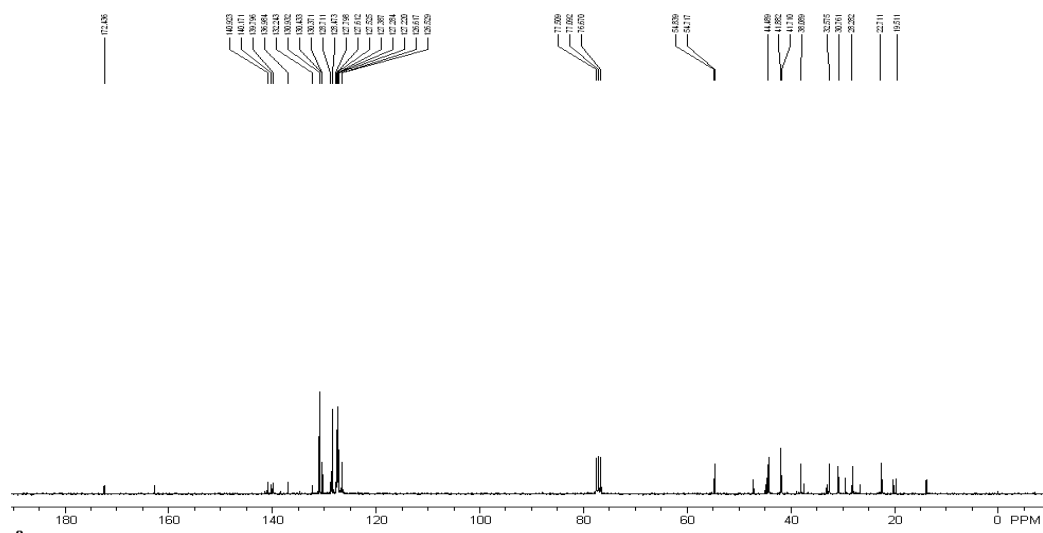




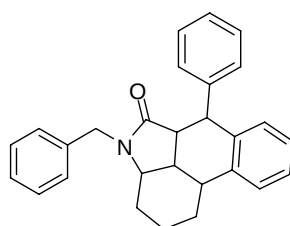
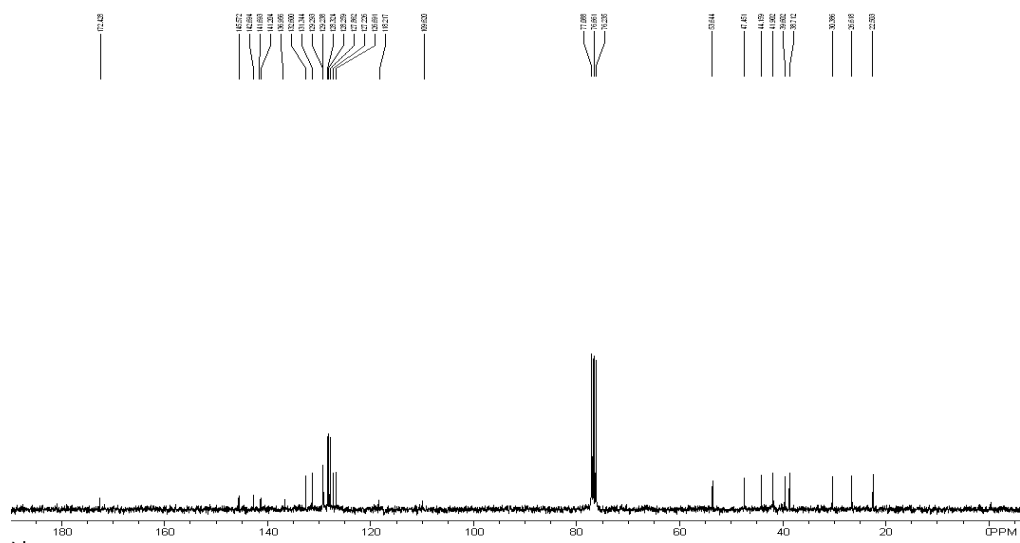
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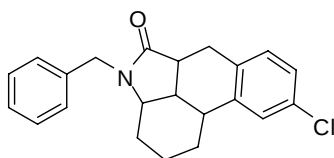
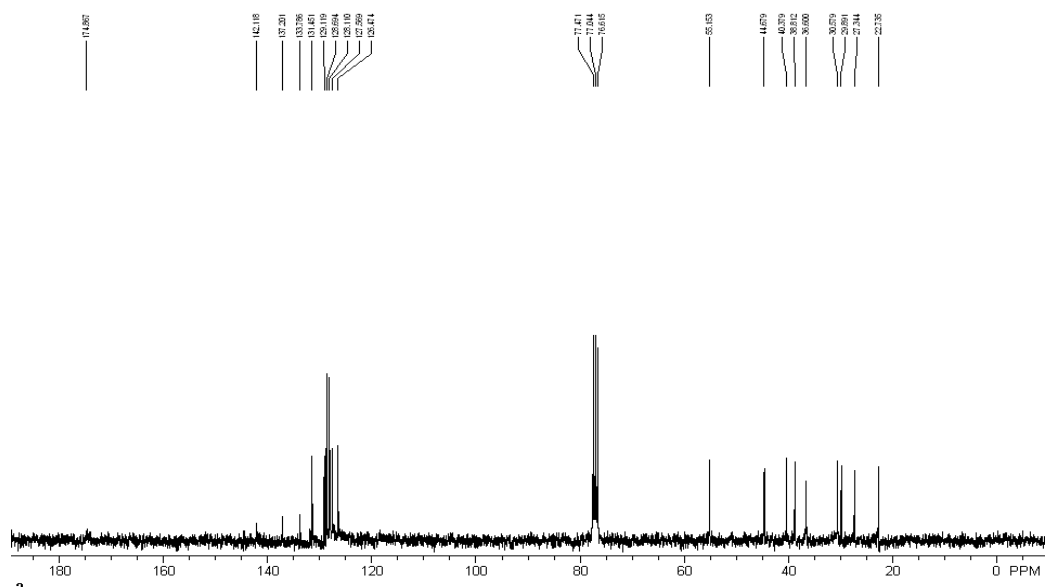
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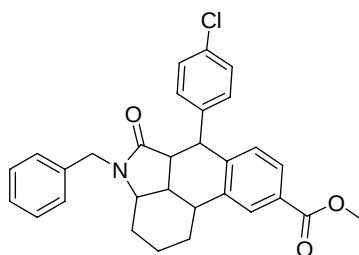
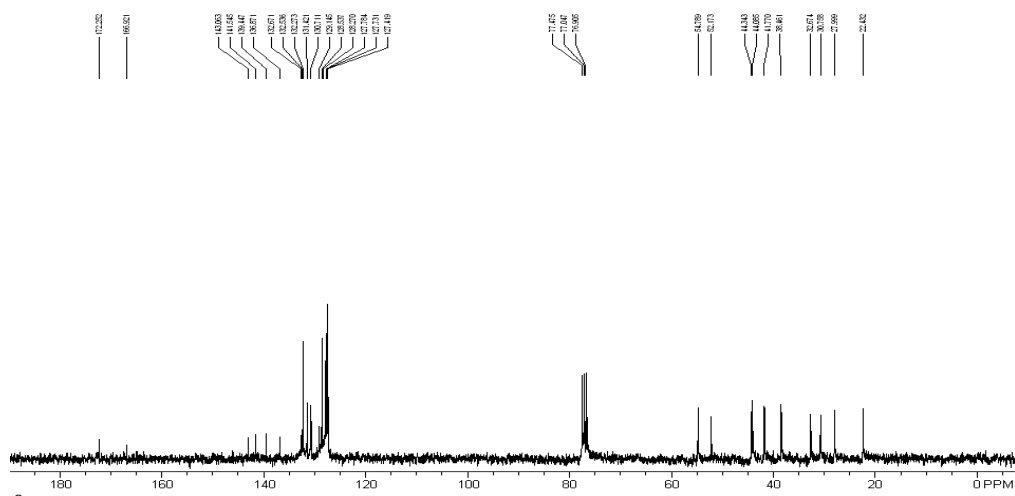
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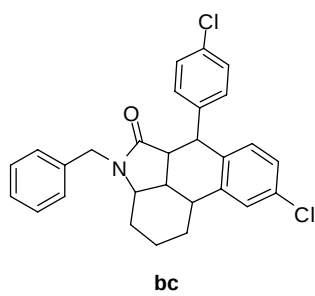
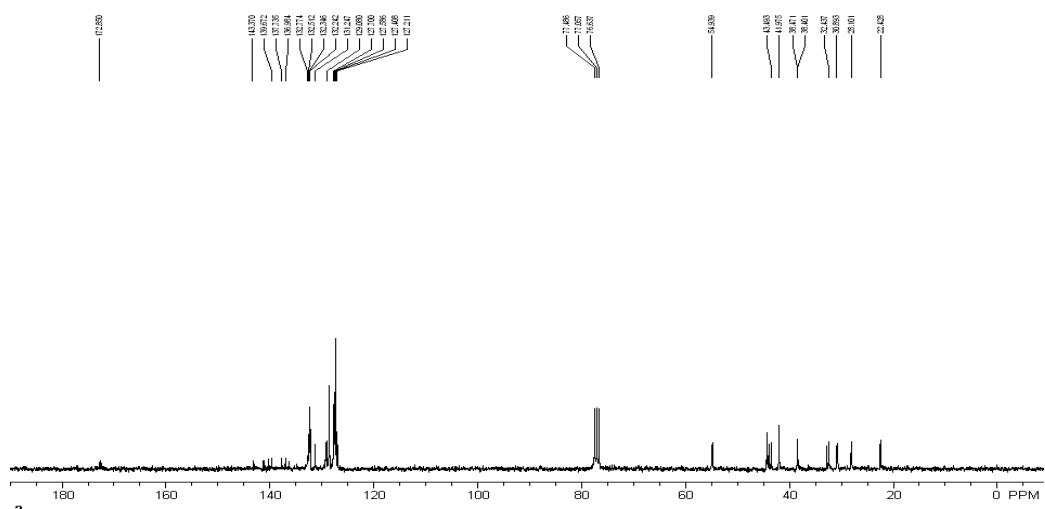
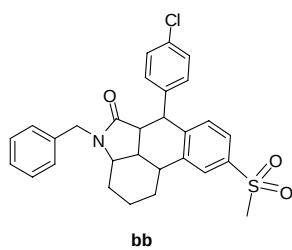
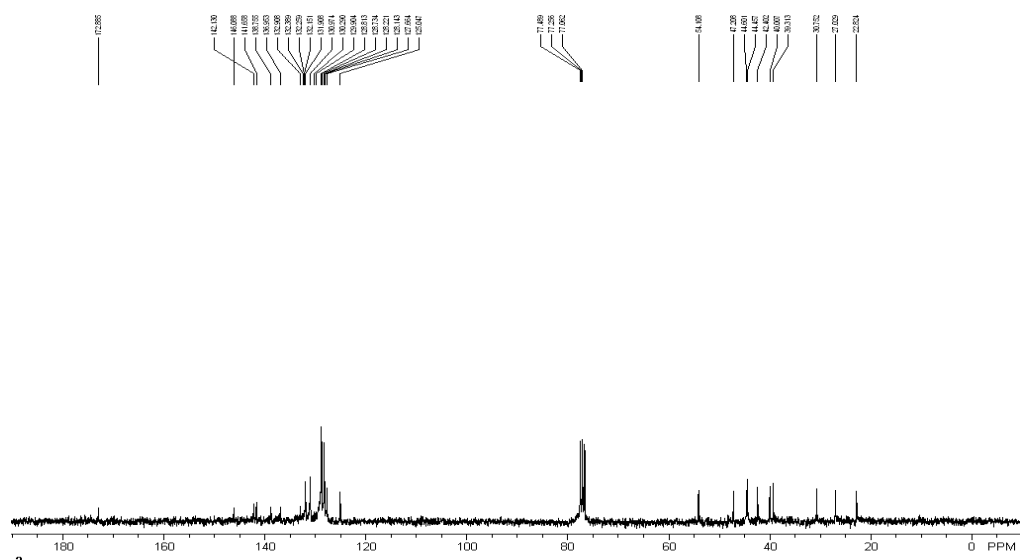
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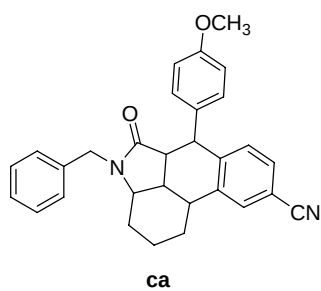
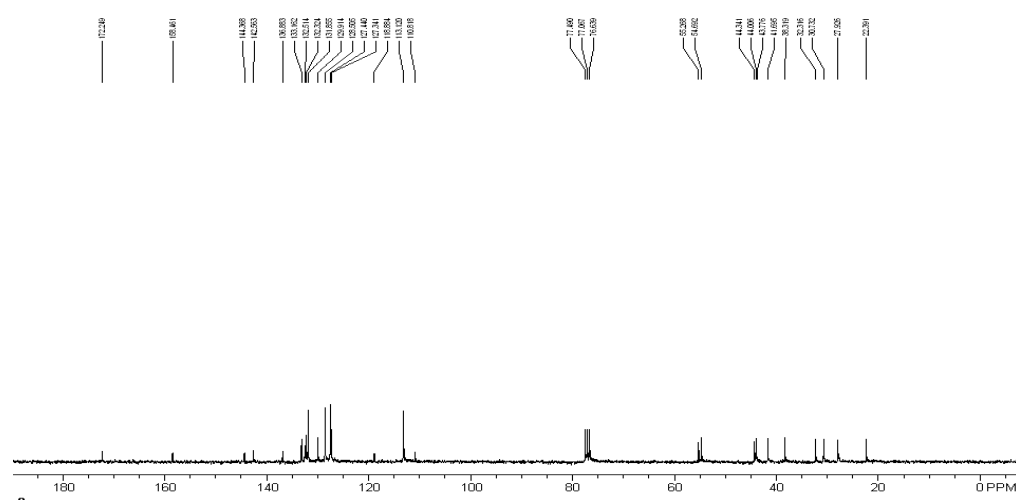
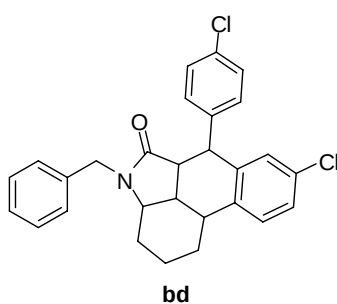
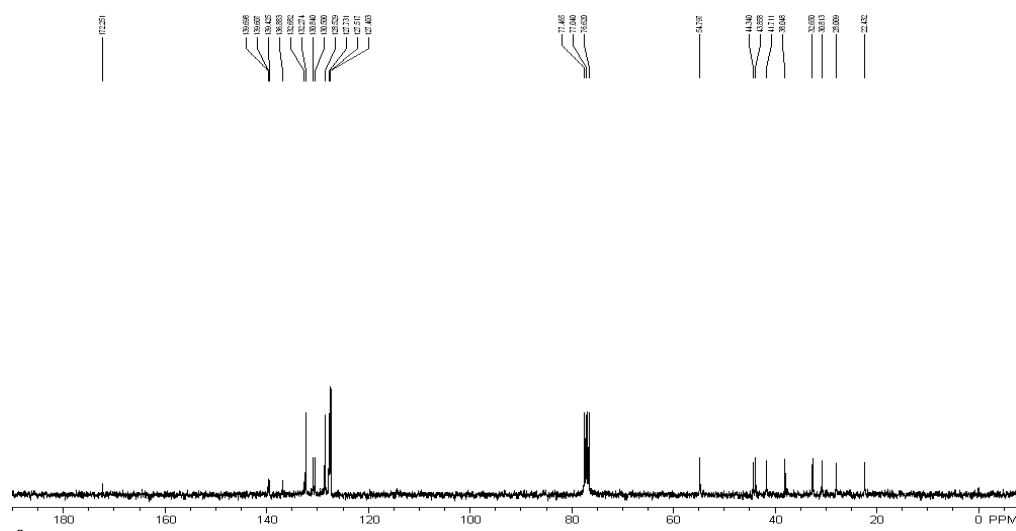


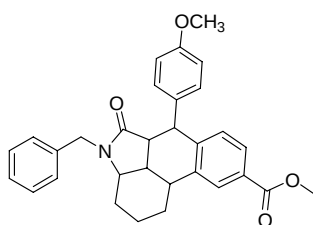
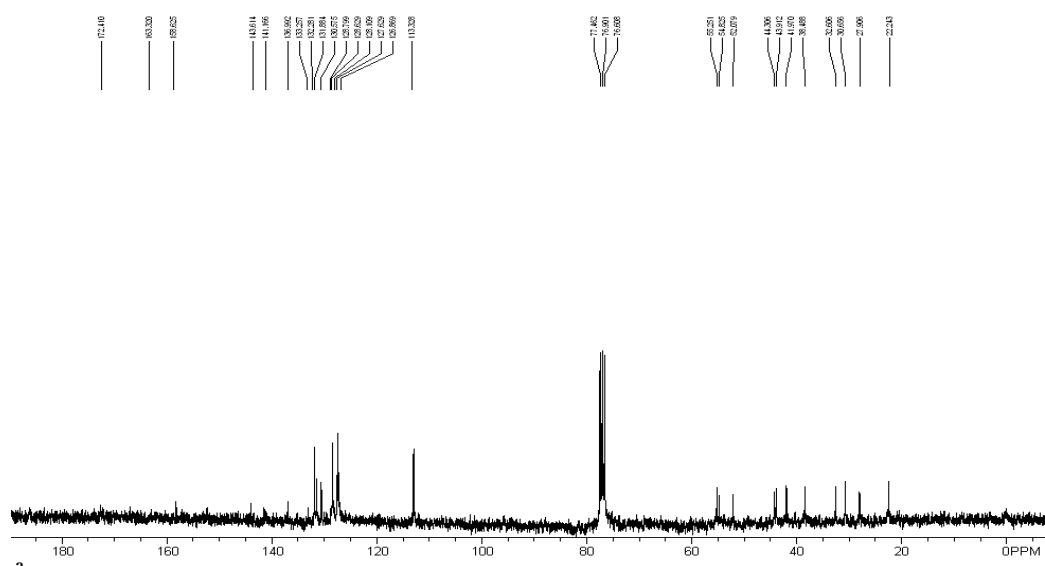
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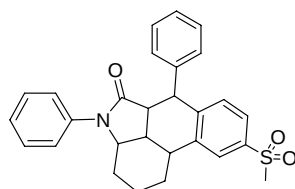
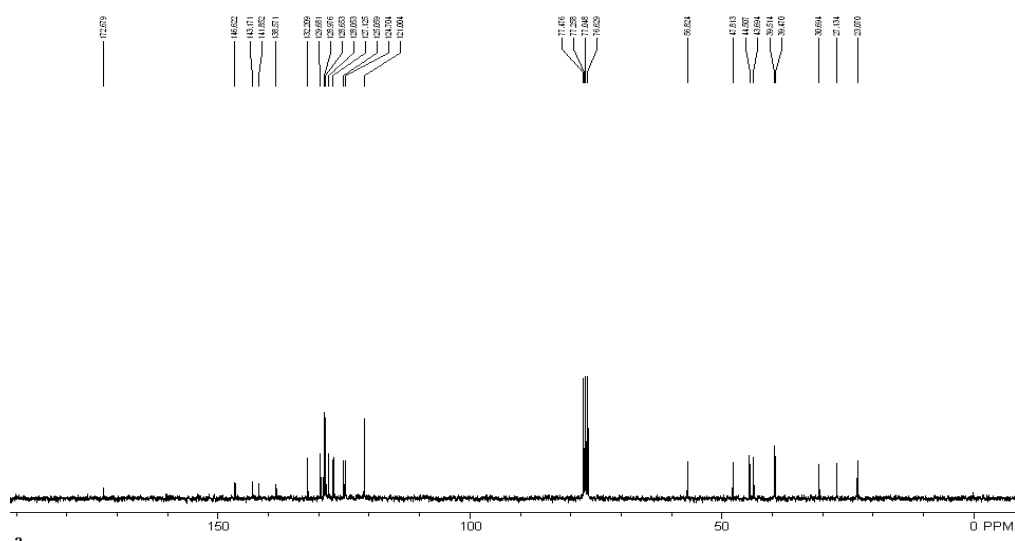
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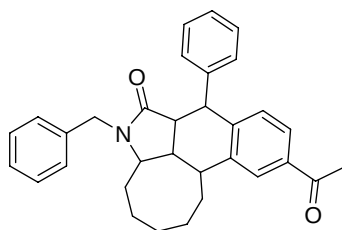
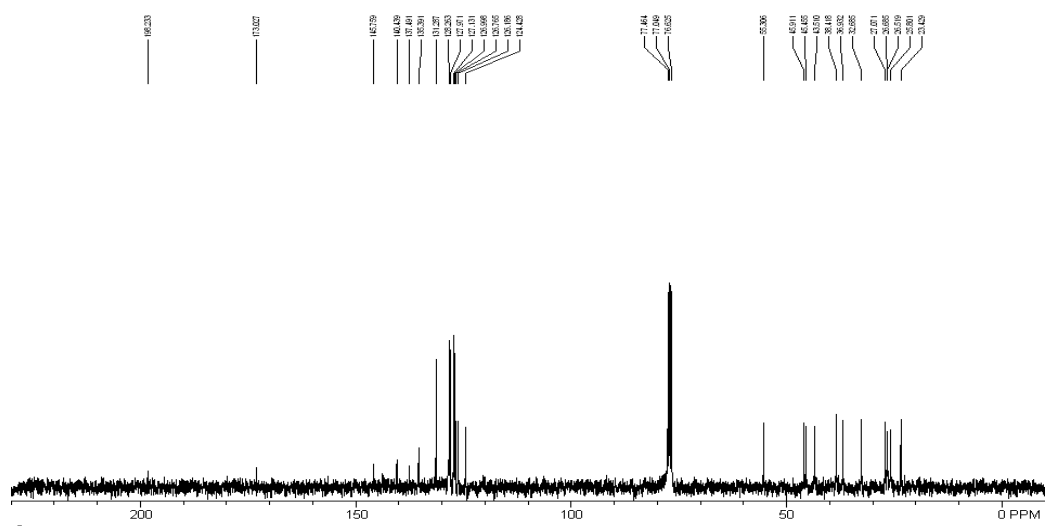




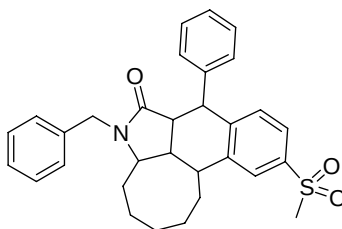
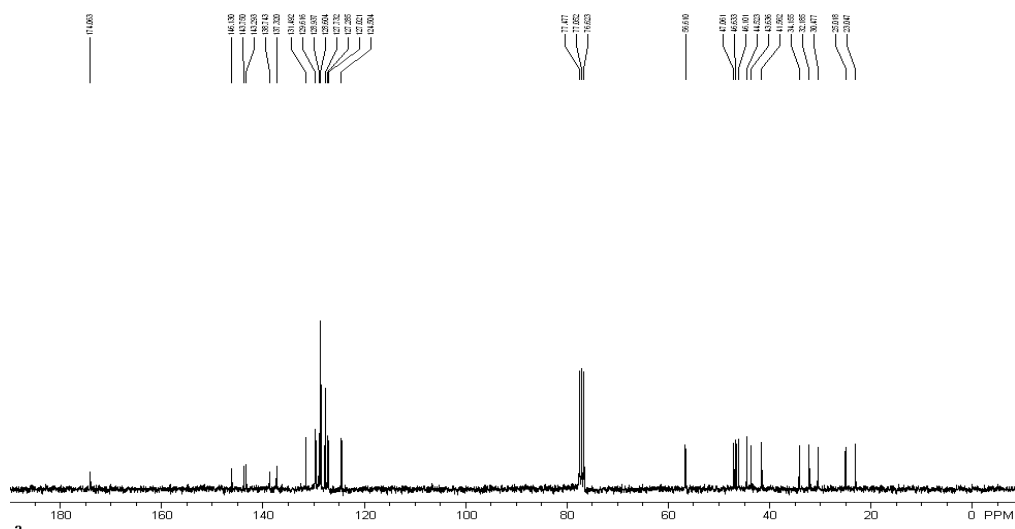
cb



da



fa



fb

