Palladium Oxide-Decorated Mesoporous Silica on Graphene Oxide Nanosheets as Heterogeneous Catalyst for Synthesis of □-Substituted Indole Derivatives

Digvijay Sah, Javaid Shabir, Surabhi, Padmini Gupta and Subho Mozumdar*

Department of Chemistry, University of Delhi, Delhi-110007, India

Electronic Supplementary Information (ESI)

Table of Contents

Spectral Data of Representative Products

1. 2-((1H-indol-3-yl)(phenyl)methyl)malononitrile

White Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (brs, 1H), 7.34-7.45 (m, 7H), 7.28 (d, 1H, J = 7.6 Hz), 7.21 (t, 1H, J = 8.4 Hz), 7.06 (t, 1H, J = 8 Hz), 4.93 (d, 1H, J = 6.4 Hz), 4.45 (d, 1H, J = 6.4 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.16, 136.34, 129.26, 128.83, 128.25, 125.95, 123.19, 122.25, 120.39, 118.76, 112.55, 112.29, 112.24, 111.64, 44.23, 29.72 ppm. HRMS (ES): Calcd: 271.1113. Found: 272.1187 $[M+H]^+$ and 273.1218 $[MH+2]^+$. FT-IR (ν_{max}/cm^{-1}, KBr): 3342, 3064, 2884, 2258, 1623, 1582, 1547, 1224, 700 cm^{-1}.

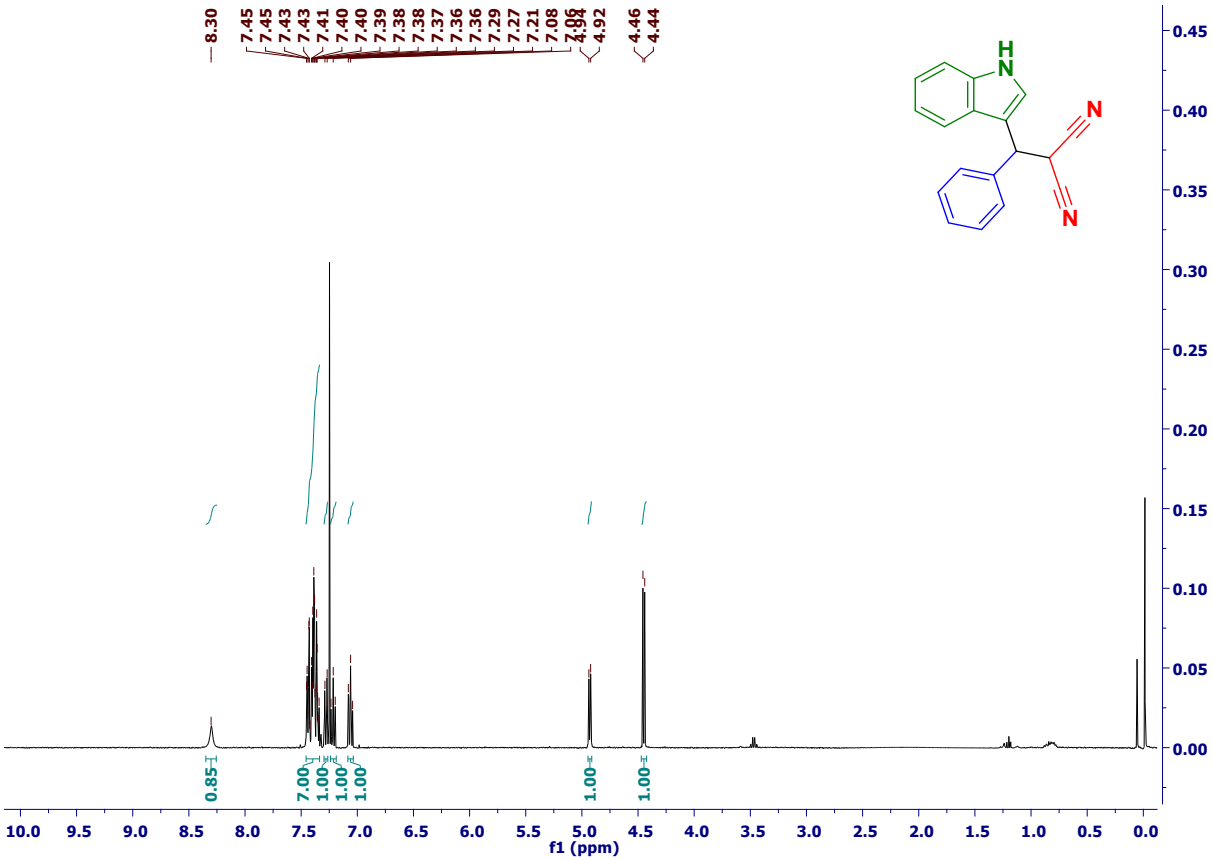


Fig. 1(a): ^{1}H-NMR of 2-((1H-indol-3-yl)(phenyl)methyl)malononitrile

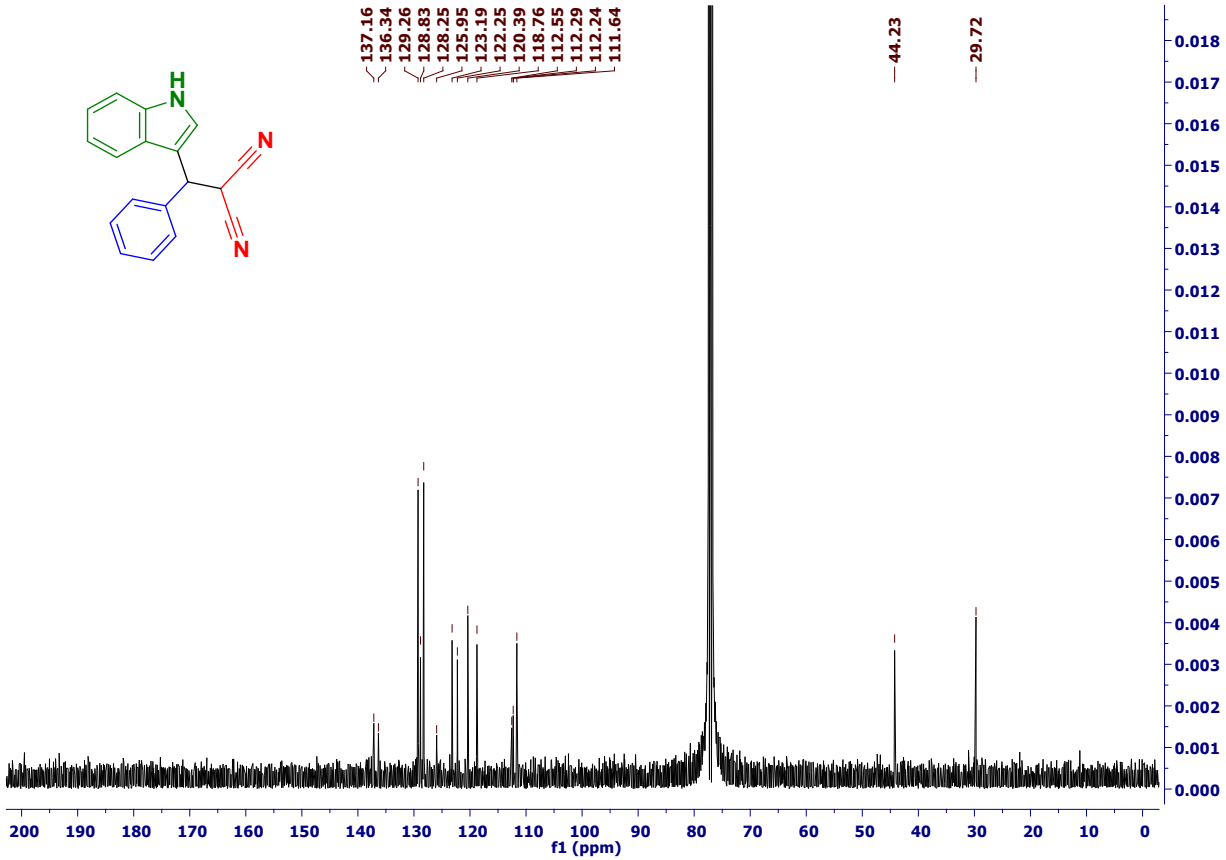


Fig. 1(b): ^{13}C-NMR of 2-((1H-indol-3-yl)(phenyl)methyl)malononitrile

2. 2-((1H-indol-3-yl)(4-nitrophenyl)methyl)malononitrile

Light Yellow Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (brs, 1H), 8.26 (d, 2H, J = 8.4 Hz), 7.65 (d, 2H, J = 8.8 Hz), 7.41 (d, 2H, J = 8.4 Hz), 7.19 (d, 1H, J = 8 Hz), 7.08 (t, 1H, J = 7.2 Hz), 5.05 (d, 1H, J = 6.0 Hz), 4.52 (d, 1H, J =6.0 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.15, 144.09, 136.38, 129.52, 125.49, 124.47, 123.61, 122.34, 120.78, 118.36, 111.95, 111.75, 111.68, 111.18, 43.83, 29.13 ppm. HRMS (ES): Calcd: 316.0966. Found: 317.1038 $[M+H]^+$ and 318.1068 $[MH+2]^+$. FT-IR (ν_{max}/cm^{-1}, KBr): 3318, 3066, 2907, 2253, 1603, 1522, 1349, 1229, 749 cm^{-1}.

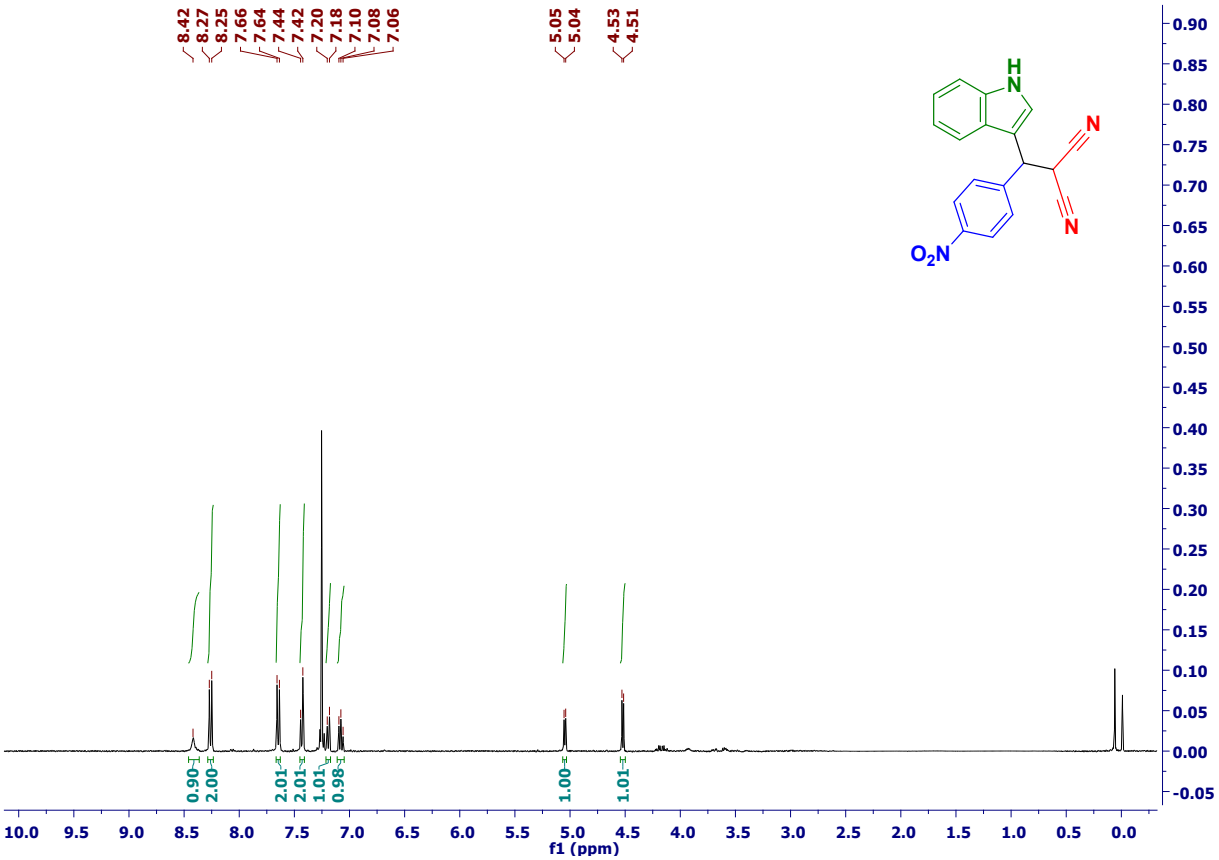


Fig. 2(a): ^{1}H-NMR of 2-((1H-indol-3-yl)(4-nitrophenyl)methyl)malononitrile

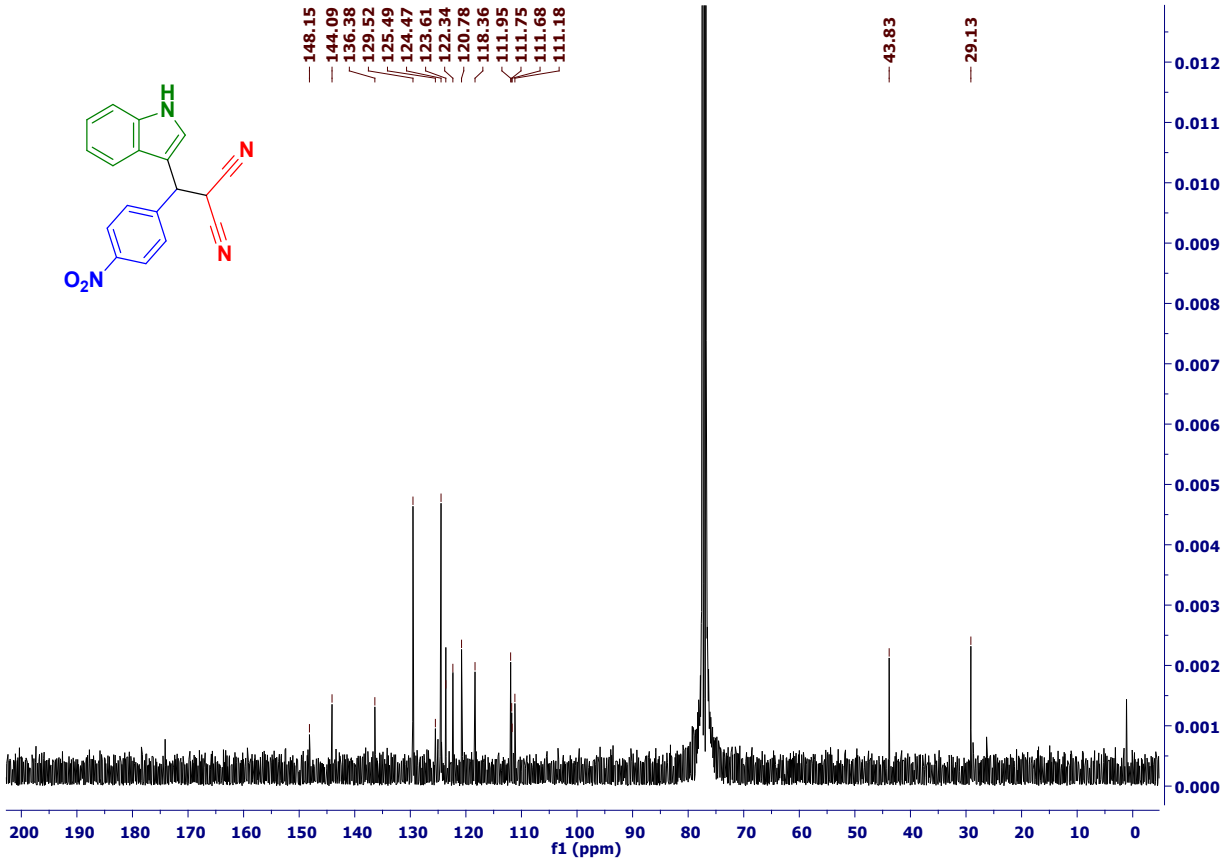


Fig. 2(b): ^{13}C-NMR of 2-((1H-indol-3-yl)(4-nitrophenyl)methyl)malononitrile

3. 2-((4-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile

Orange-White Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (brs, 1H), 7.33-7.40 (m, 6H), 7.20-7.24 (m, 2H), 7.06 (t, 1H, J = 8.4 Hz), 4.89 (d, 1H, J = 6.4 Hz), 4.44 (d, 1H, J = 6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.37, 135.62, 134.85, 129.71, 129.53, 128.48, 125.73, 123.33, 122.14, 120.45, 118.71, 112.14, 112.07, 112.02, 43.57, 29.56 ppm. HRMS (ES): Calcd: 305.0720. Found: 306.0793 $[M+H]^+$ and 307.0823 $[MH+2]^+$. FT-IR (ν_{max}/cm^{-1}, KBr): 3410, 3059, 2898, 2252, 1678, 1545, 1490, 1223, 1094, 746, 581 cm^{-1}.

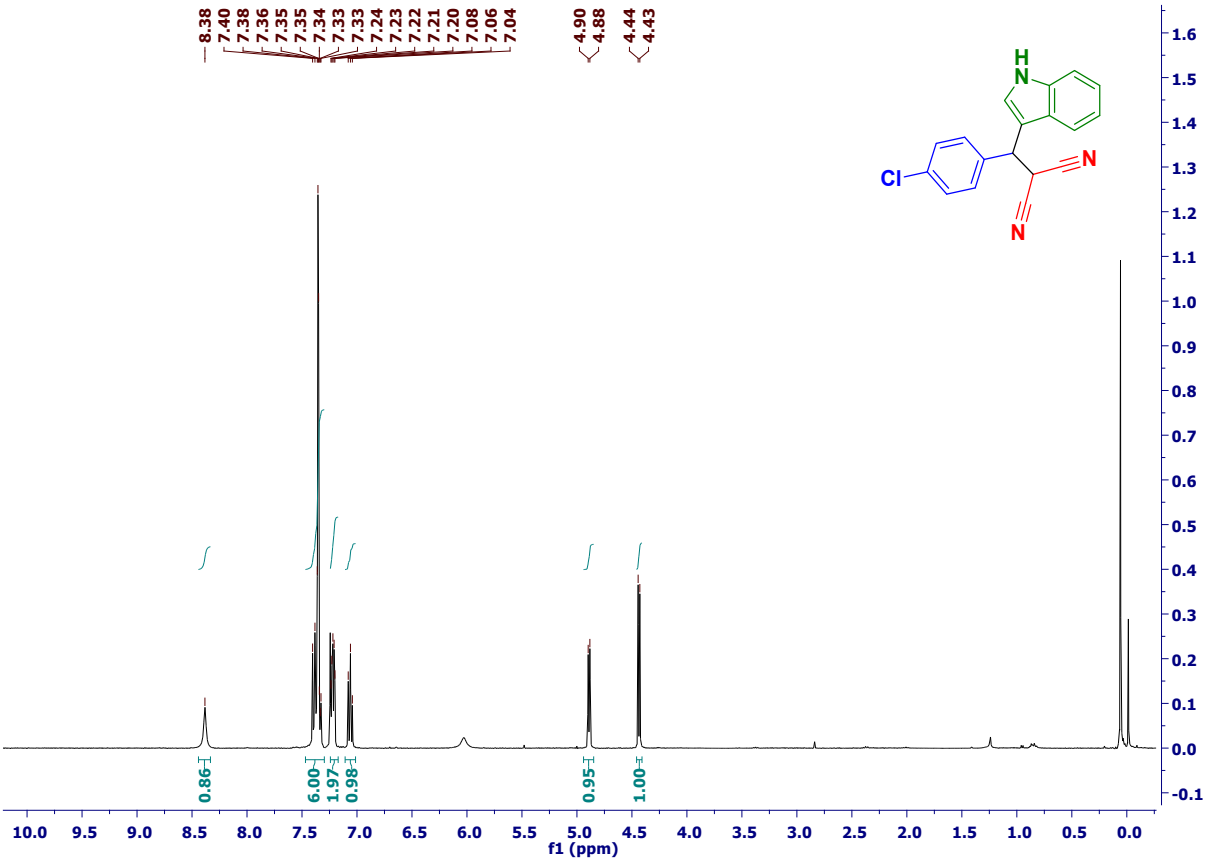


Fig. 3(a): ^{1}H-NMR of 2-((4-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile

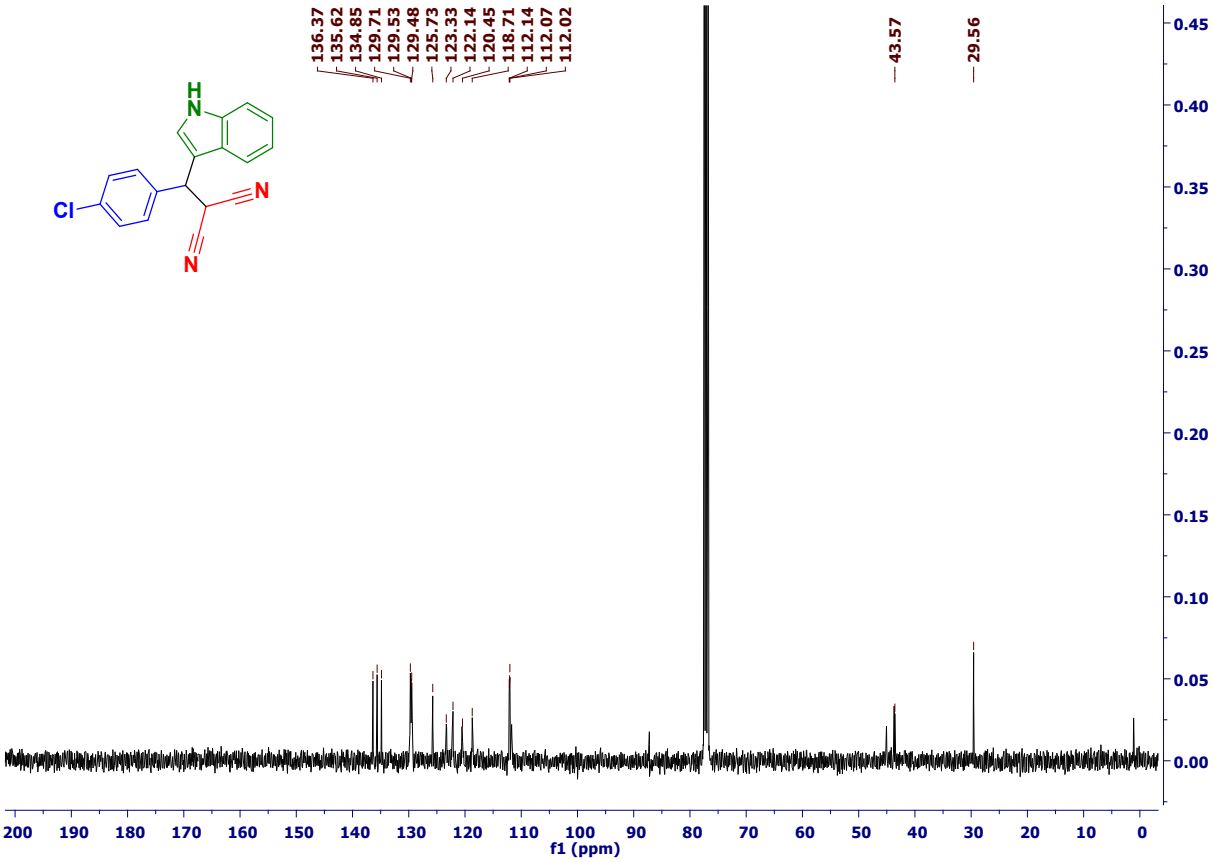


Fig. 3(b): ^{13}C-NMR of 2-((4-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile

4. 2-((2-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile

Orange-Red Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (brs, 1H), 7.57 (d, 1H, J = 2 Hz), 7.48 (dd, 1H, J = 8 Hz, J_2 = 1.2 Hz), 7.40 (d, 1H, J = 8.8 Hz), 7.26-7.32 (m, 2H), 7.18-7.24 (m, 3H), 7.06 (t, 1H, J = 8 Hz), 5.53 (d, 1H, J = 5.6 Hz), 4.54 (d, 1H, J = 6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.26, 134.63, 133.58, 130.20, 130.15, 130.05, 127.83, 126.09, 123.29, 122.52, 120.44, 118.67, 112.14, 112.02, 111.65, 111.03, 40.10, 27.71 ppm. HRMS (ES): Calcd: 305.0734. Found: 306.0807 $[M+H]^+$ and 307.0840 $[MH+2]^+$.

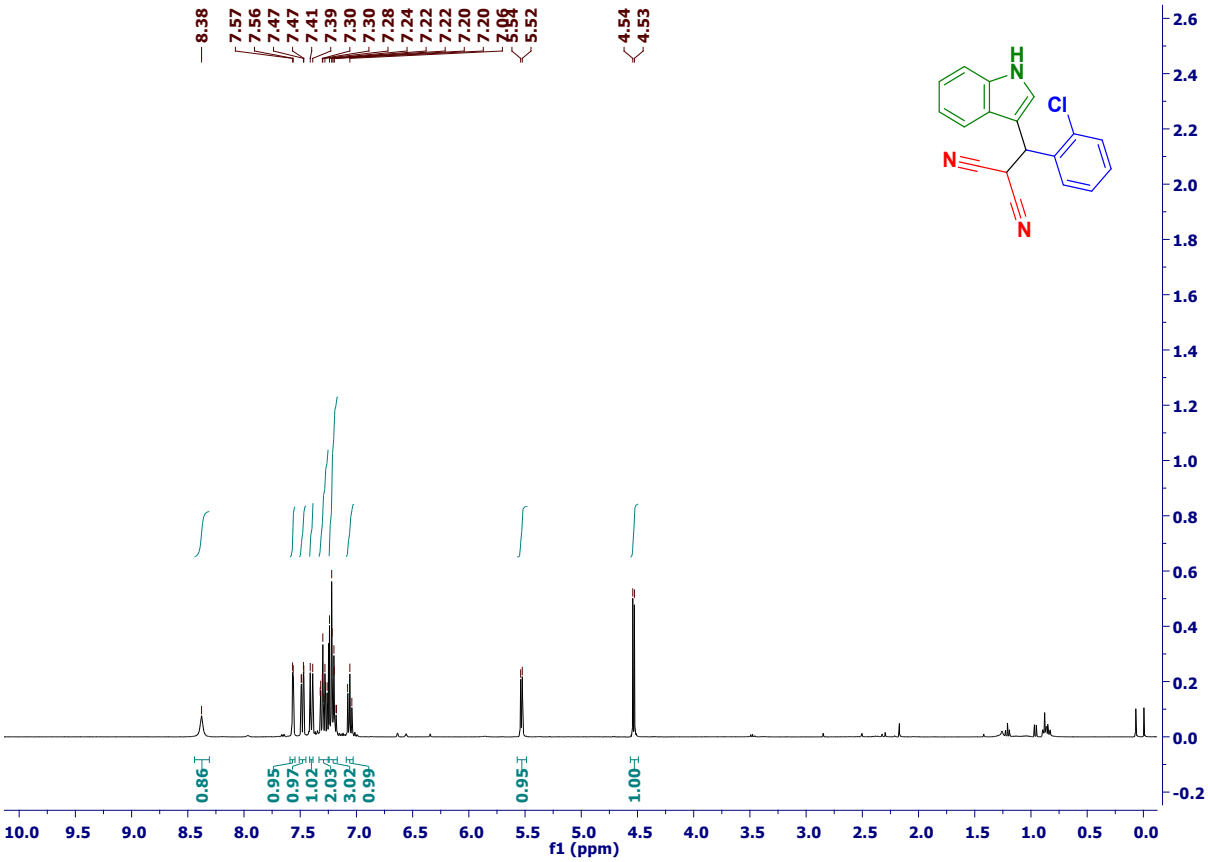


Fig. 4(a): ^{1}H-NMR of 2-((2-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile

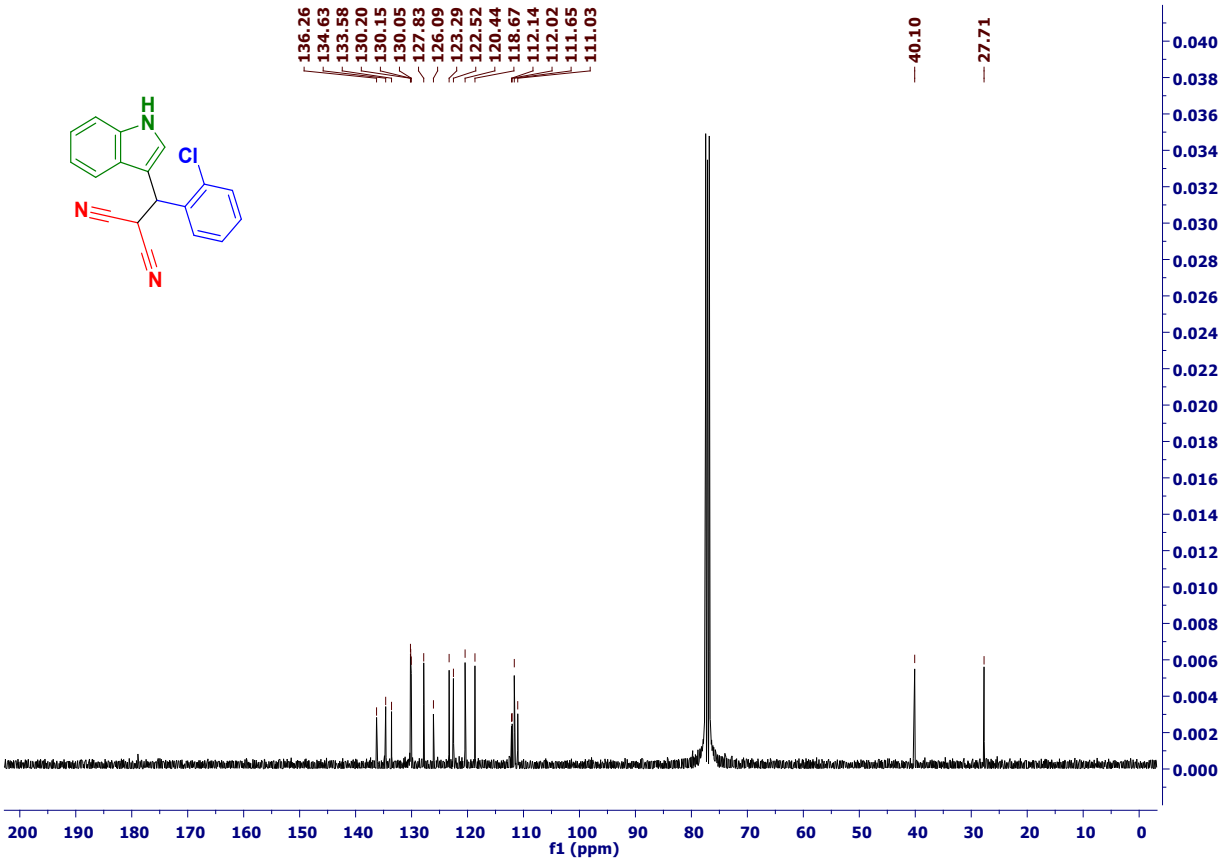


Fig. 4(b): ^{13}C-NMR of 2-((2-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile

5. 2-((5-chloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

Yellow Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (brs, 1H), 7.66 (s, 1H), 7.46 (d, 1H, J = 8 Hz), 7.34-7.36 (m, 1H), 7.31 (d, 1H, J = 8 Hz), 7.12-7.18 (m, 2H), 6.96-7.05 (m, 2H), 5.00 (s, 1H), 4.63 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.89, 147.16, 136.98, 129.93, 129.81, 129.24, 128.22, 125.43, 124.56, 122.61, 122.37, 119.84, 118.96, 118.35, 117.57, 111.54, 60.56, 32.76 ppm. HRMS (ES): Calcd: 321.0669 Found: 322.0752 $[M+H]^+$ and 323.0782 $[MH+2]^+$. FT-IR (ν_{max}/cm^{-1}, KBr): 3409, 3307, 3050, 2925, 2197, 1649, 1608, 1480, 1246, 1182, 1094, 746, 585 cm^{-1}.

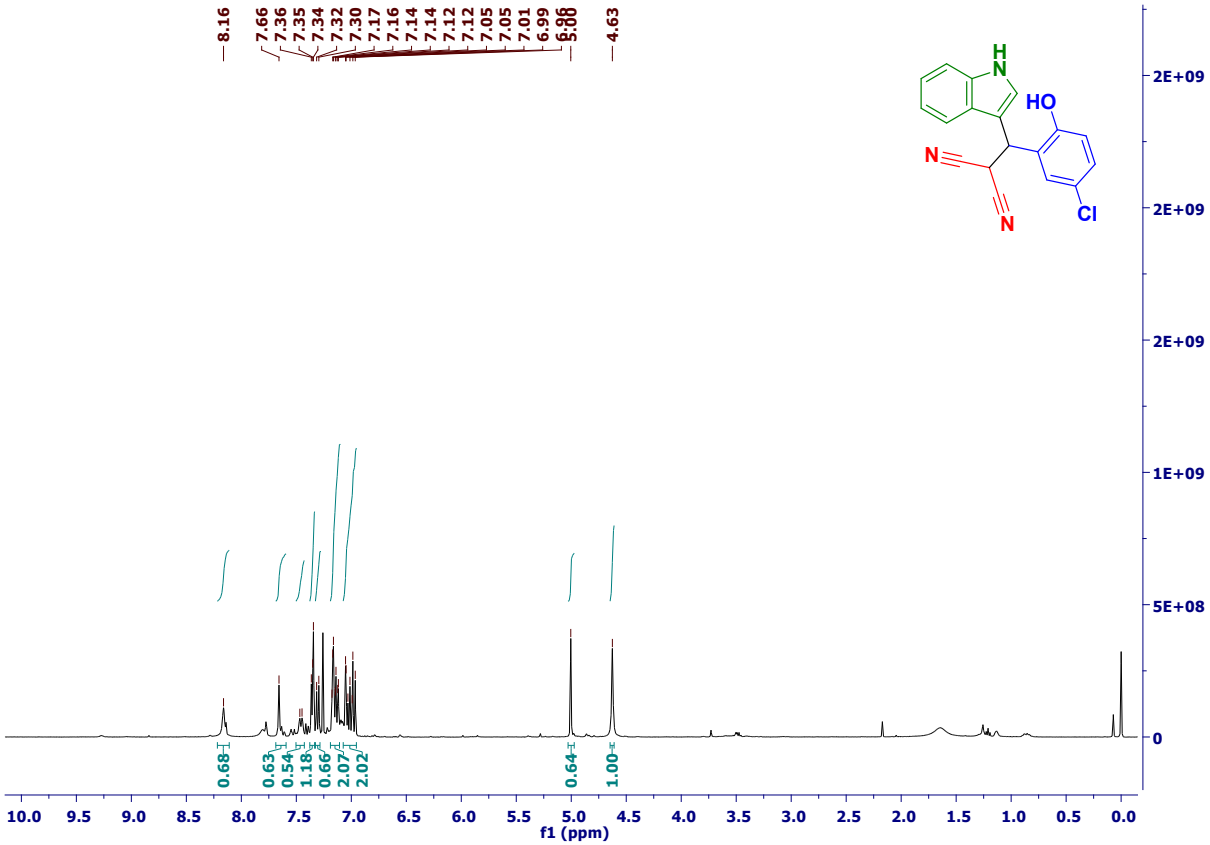


Fig. 5(a): ^{1}H-NMR of 2-((5-chloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

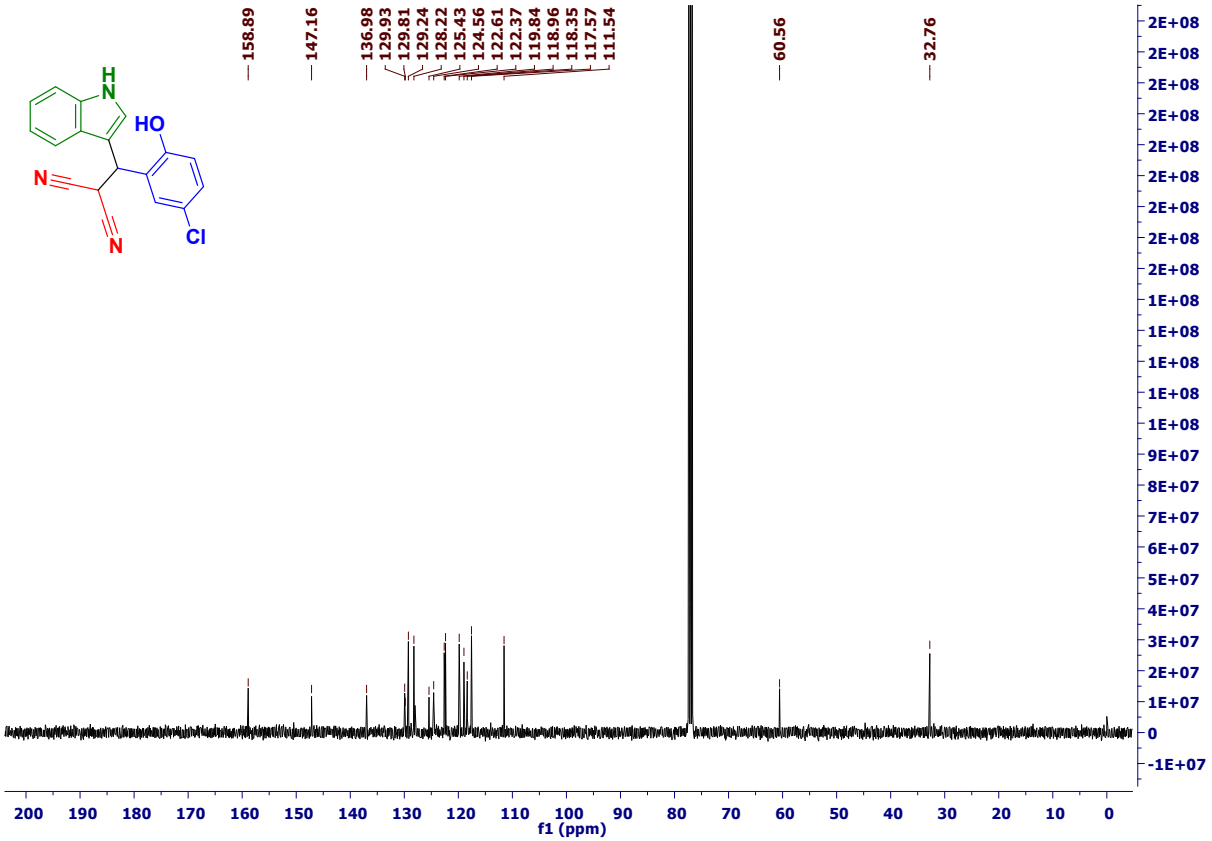


Fig. 5(b): ^{13}C-NMR of 2-((5-chloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

6. 2-((5-bromo-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

Orange Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (brs, 1H), 7.73-7.82 (m, 1H), 7.29-7.57 (m, 3H), 7.15-7.21 (m, 2H), 7.02 (t, 1H, J = 7.6 Hz), 6.93 (d, 1H, J = 8.8 Hz), 5.01 (s, 1H), 4.59 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.82, 147.72, 138.18, 137.51, 132.22, 131.15, 125.41, 124.95, 124.14, 122.58, 122.40, 119.86, 118.97, 117.94, 117.46, 111.53, 32.67. 29.69 ppm. HRMS (ES): Calcd: 365.0164 Found: 366.0219 $[M+H]^+$ and 367.0245 $[MH+2]^+$. FT-IR (ν_{max}/cm^{-1}, KBr): 3420, 3201, 3062, 2925, 2187, 1650, 1602, 1476, 1262, 1180, 1072, 743, 473 cm^{-1}.

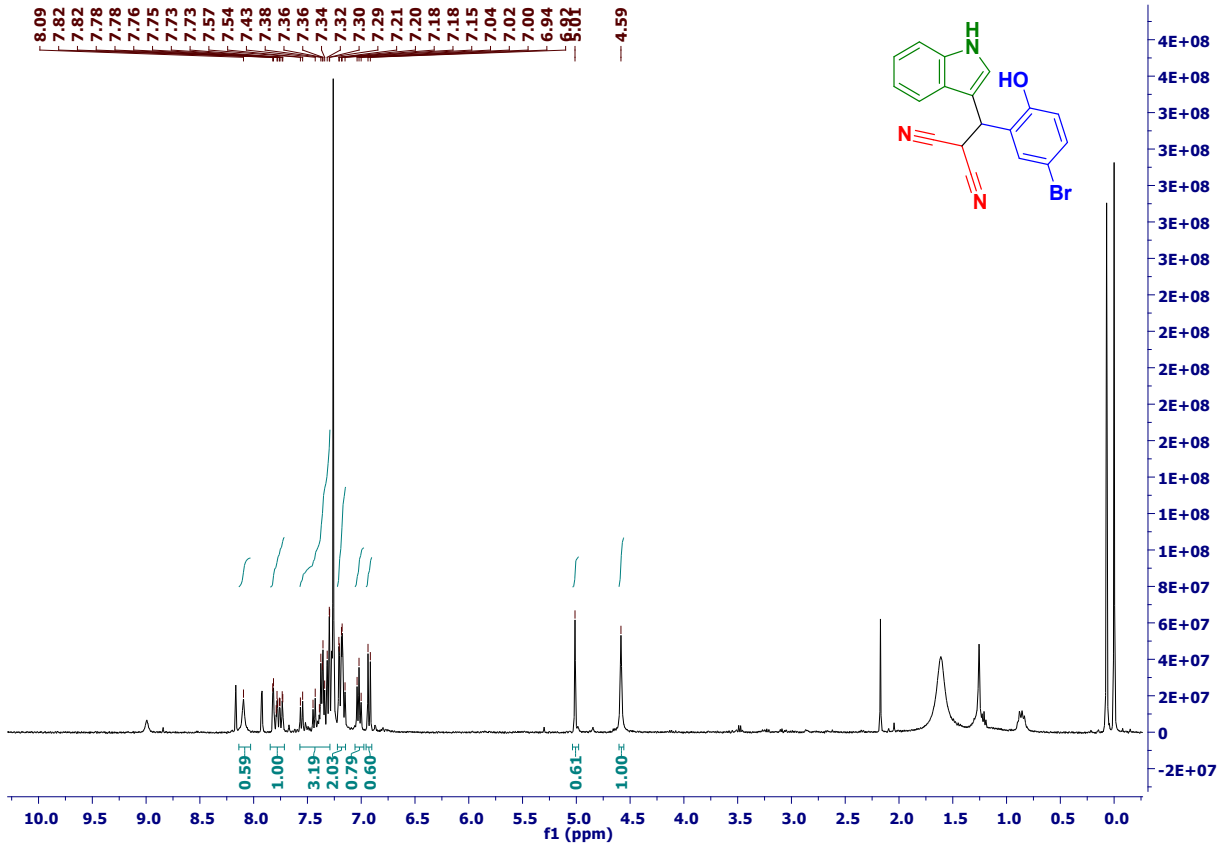


Fig. 6(a): ^{1}H-NMR of 2-((5-bromo-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

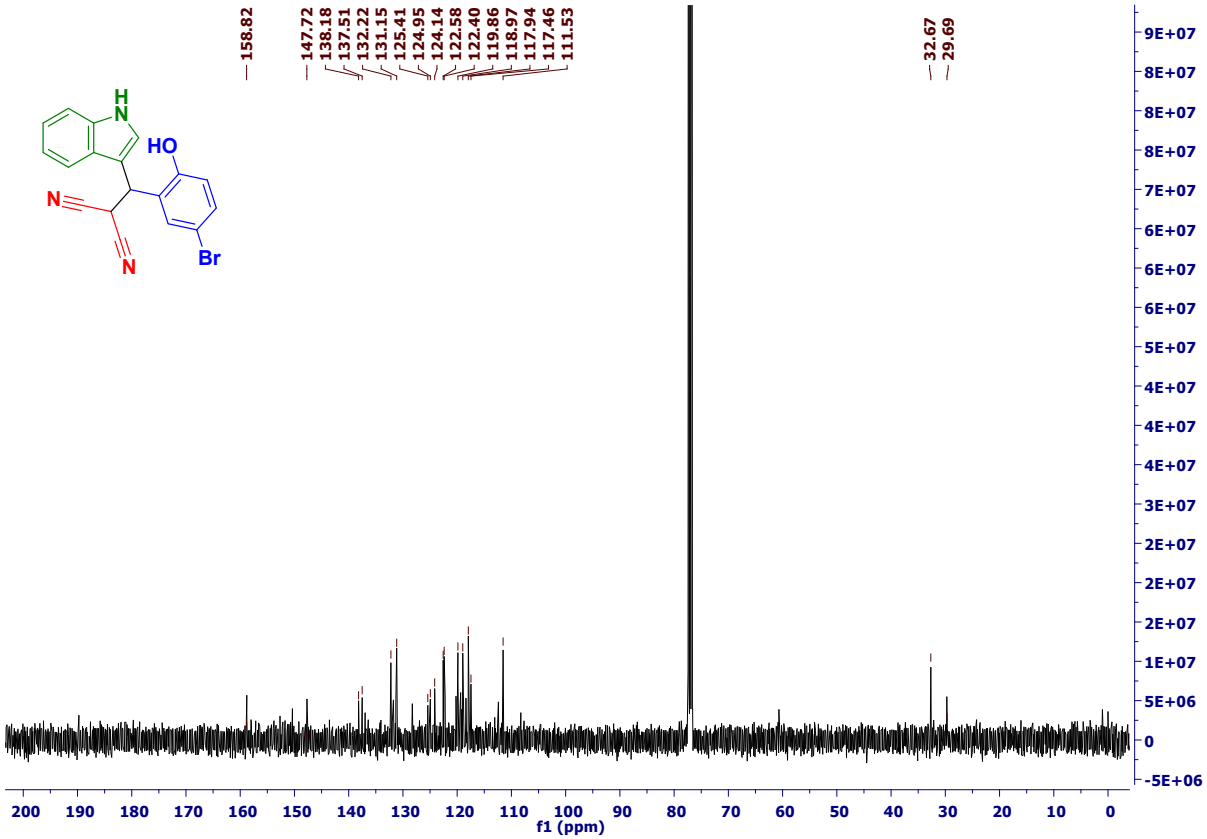


Fig. 6(b): ^{13}C-NMR of 2-((5-bromo-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

7. 2-((3,5-dichloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

Yellow Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (brs, 1H), 7.37-7.42 (m, 2H), 7.31 (d, 1H, J = 8 Hz), 7.17-7.23 (m, 2H), 6.97-7.07 (m, 2H), 5.03 (s, 1H), 4.75 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.05, 160.17, 153.42, 145.43, 140.43, 139.92, 139.04, 131.15, 128.70, 128.68, 127.76, 122.74, 122.56, 120.06, 118.84, 111.60, 45.02, 33.12 ppm. HRMS (ES): Calcd: 355.0279 Found: 356.0349 $[M+H]^+$ and 357.0337 $[MH+2]^+$. FT-IR (ν_{max}/cm^{-1}, KBr): 3405, 3200, 3070, 2919, 2193, 1652, 1576, 1519, 1186, 1156, 1096, 745, 564 cm^{-1}.

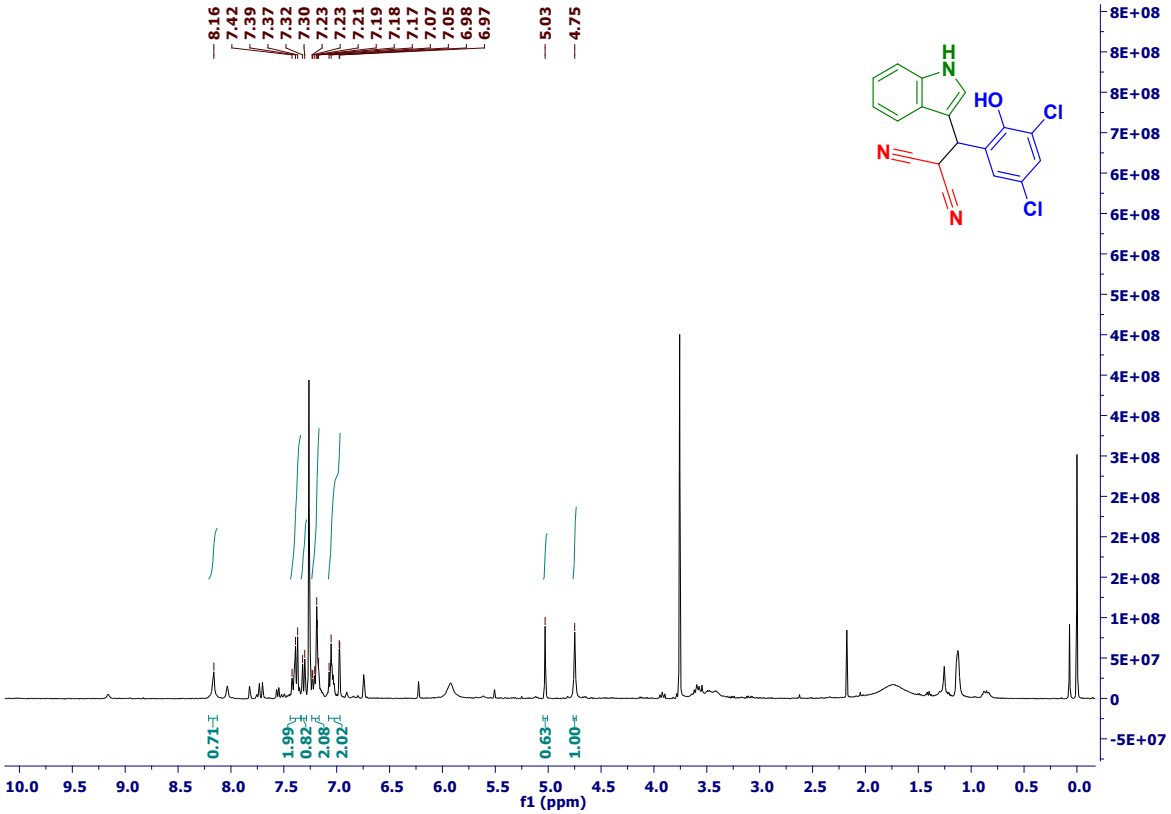


Fig. 7(a): ^{1}H-NMR of 2-((3,5-dichloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

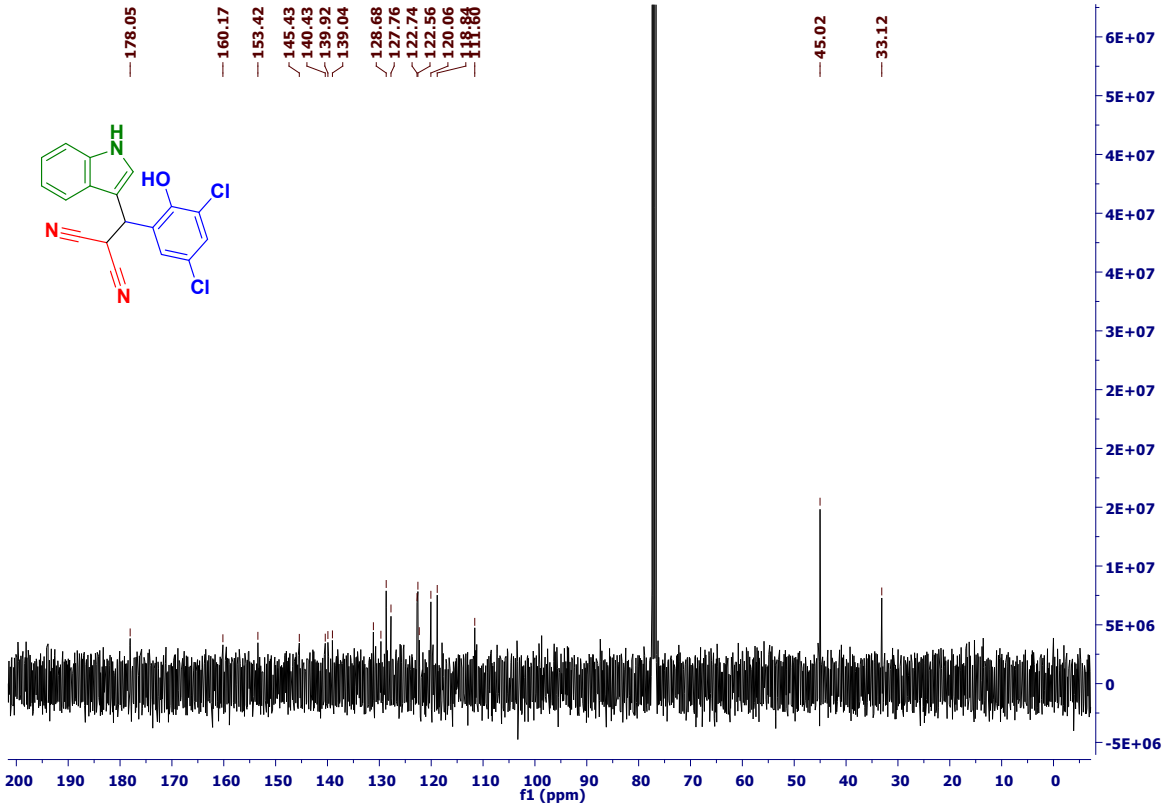


Fig. 7(b): ^{13}C-NMR of 2-((3,5-dichloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile

8. 2-((2-fluorophenyl)(1H-indol-3-yl)methyl)malononitrile

Red-Brown Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (brs, 1H), 7.48 (d, 1H, J = 2.4 Hz), 7.30-7.41 (m, 3H), 7.22 (d, 1H, J = 8Hz), 7.17 (d, 1H, J = 9.2Hz), 7.07-7.13 (m, 3H), 5.32 (d, 1H, J = 6.8Hz), 4.55 (d, 1H, J = 7.2Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.68, 136.20, 130.60, 129.85, 125.99, 125.07, 124.41, 123.23, 122.57, 120.45, 118.47, 116.20, 115.98, 112.17, 111.73, 110.99, 37.24, 28.40 ppm. HRMS (ES): Calcd: 289.1015 Found: 290.1087 $[M+H]^+$ and 291.1182 $[MH+2]^+$.

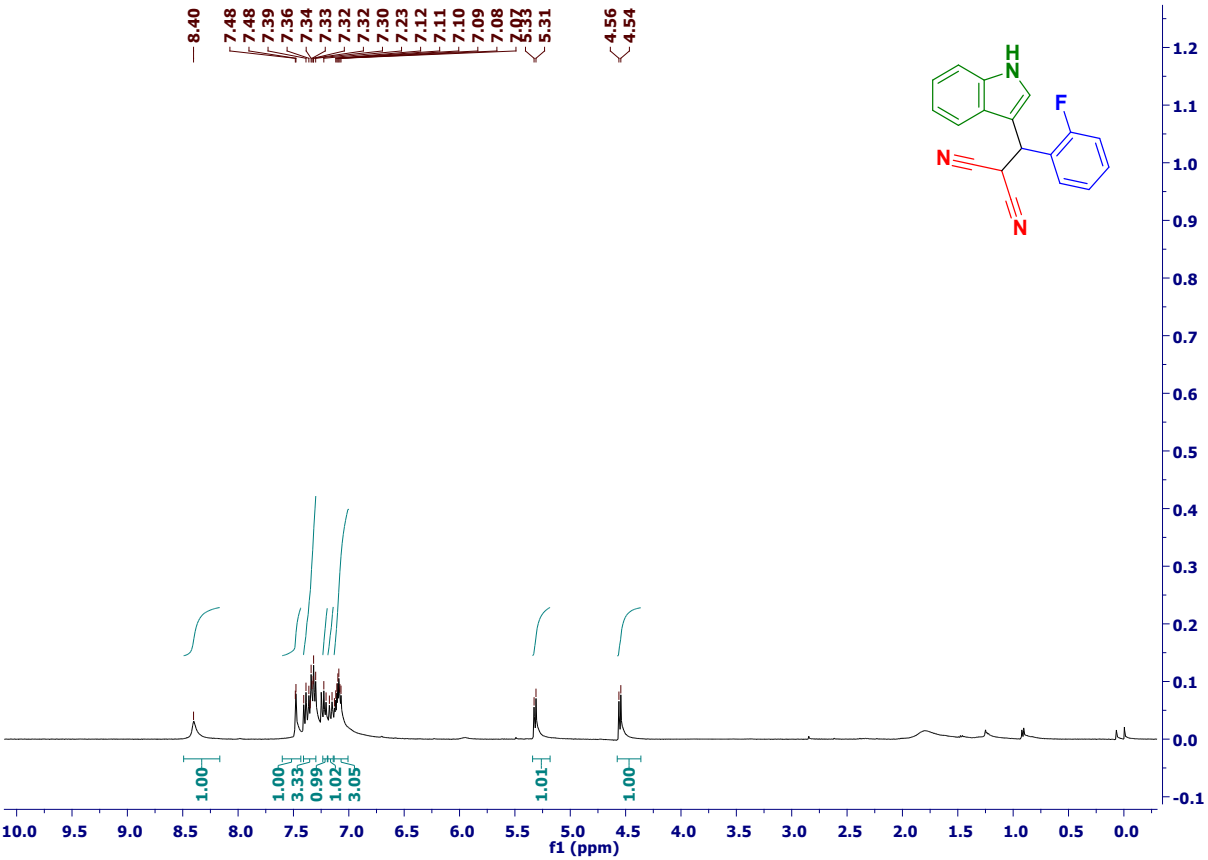


Fig. 8(a): ^{1}H-NMR of 2-((2-fluorophenyl)(1H-indol-3-yl)methyl)malononitrile

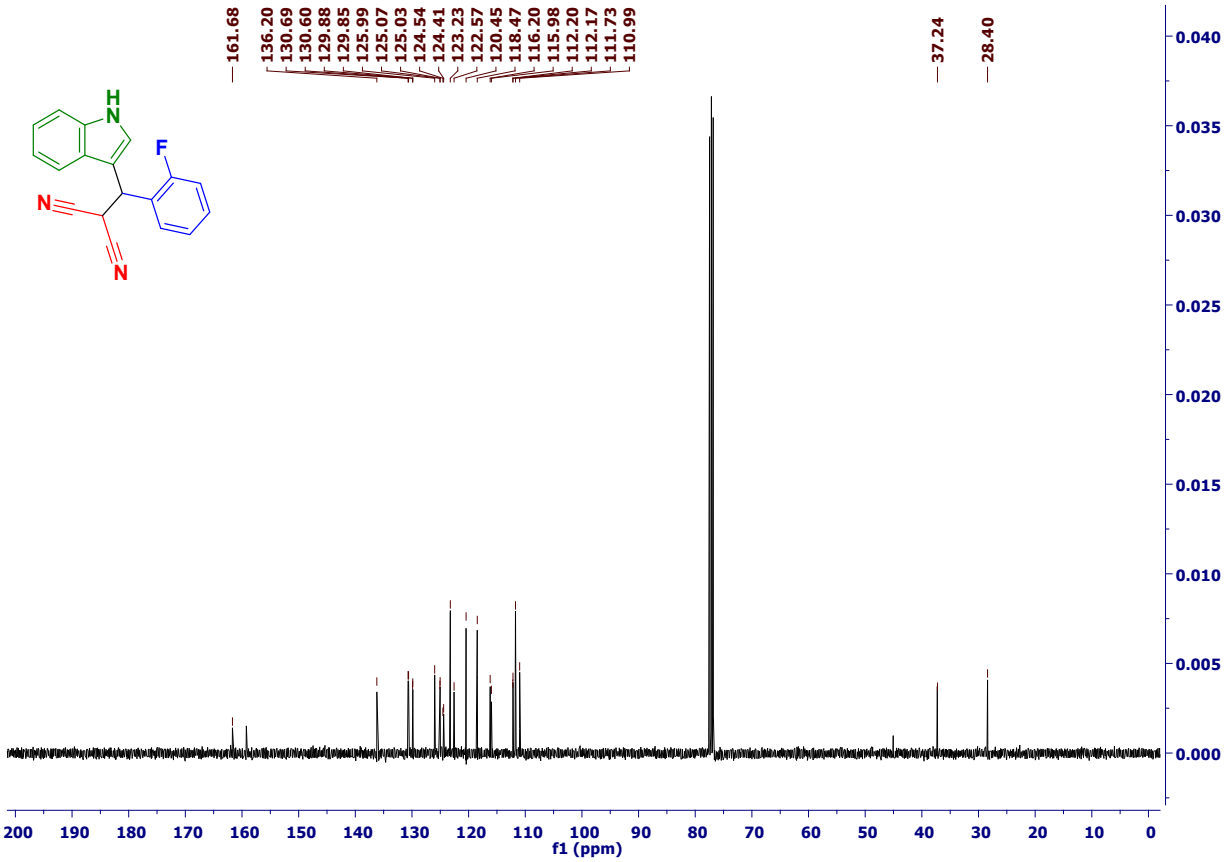


Fig. 8(b): ^{13}C-NMR of 2-((2-fluorophenyl)(1H-indol-3-yl)methyl)malononitrile

9. 2-((5-bromo-1H-indol-3-yl)(4-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

Yellow Solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.07 (s, 1H), 10.74 (s, 1H), 8.04 (d, 2H, J = 8.8 Hz), 7.30 (t, 4H, J = 8 Hz), 7.11-7.15 (m, 2H), 7.02 (d, 1H, J = 2 Hz), 5.81 (s, 1H), 2.13-2.37 (m, 4H), 0.96 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.61, 145.73, 135.21, 129.53, 126.68, 123.79, 123.31, 121.53, 121.08, 116.90, 116.23, 114.66, 114.25, 114.08, 111.51, 35.50, 32.19, 28.42 ppm. HRMS (ES): Calcd: 469.3278. Found: 470.3338 $[M+H]^+$ and 471.3333 $[MH+2]^+$.

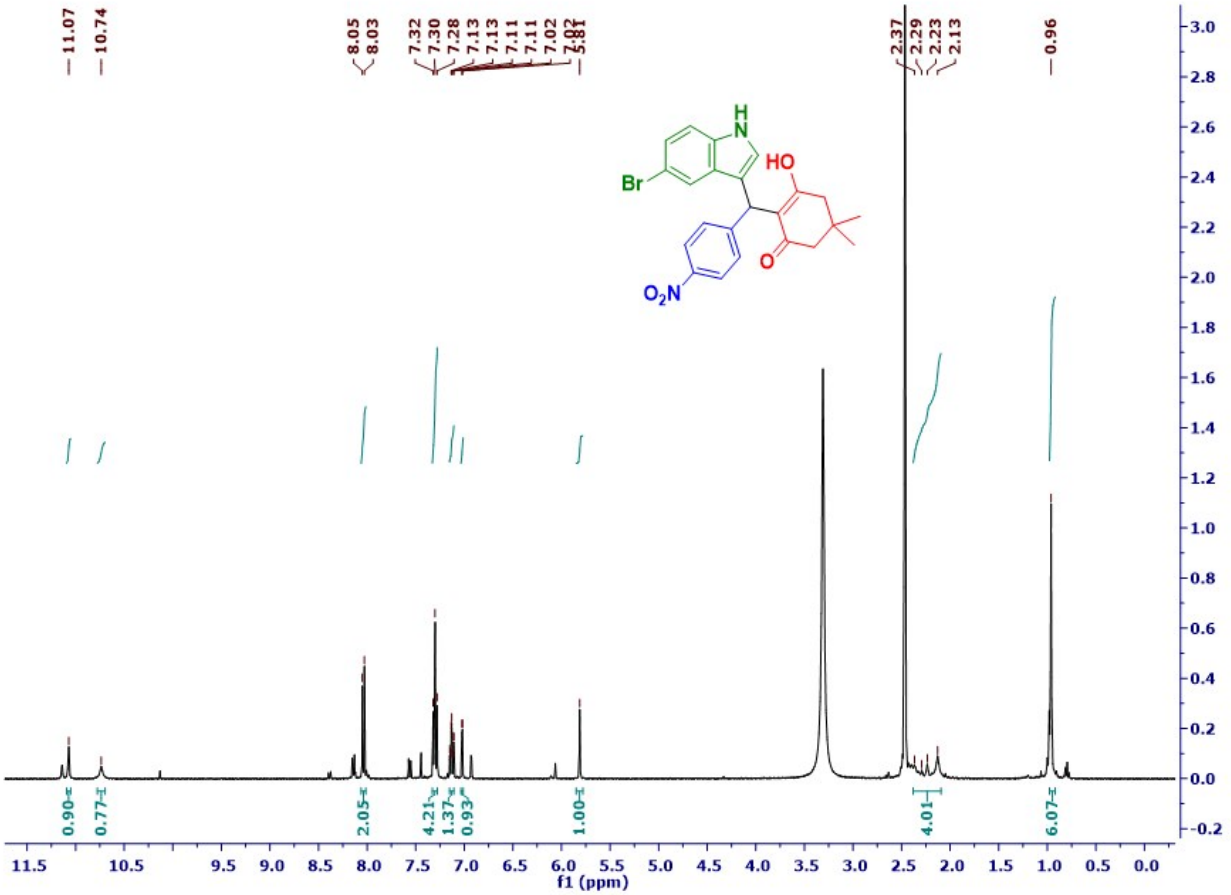


Fig. 9(a): ^{1}H-NMR of 2-((5-bromo-1H-indol-3-yl)(4-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

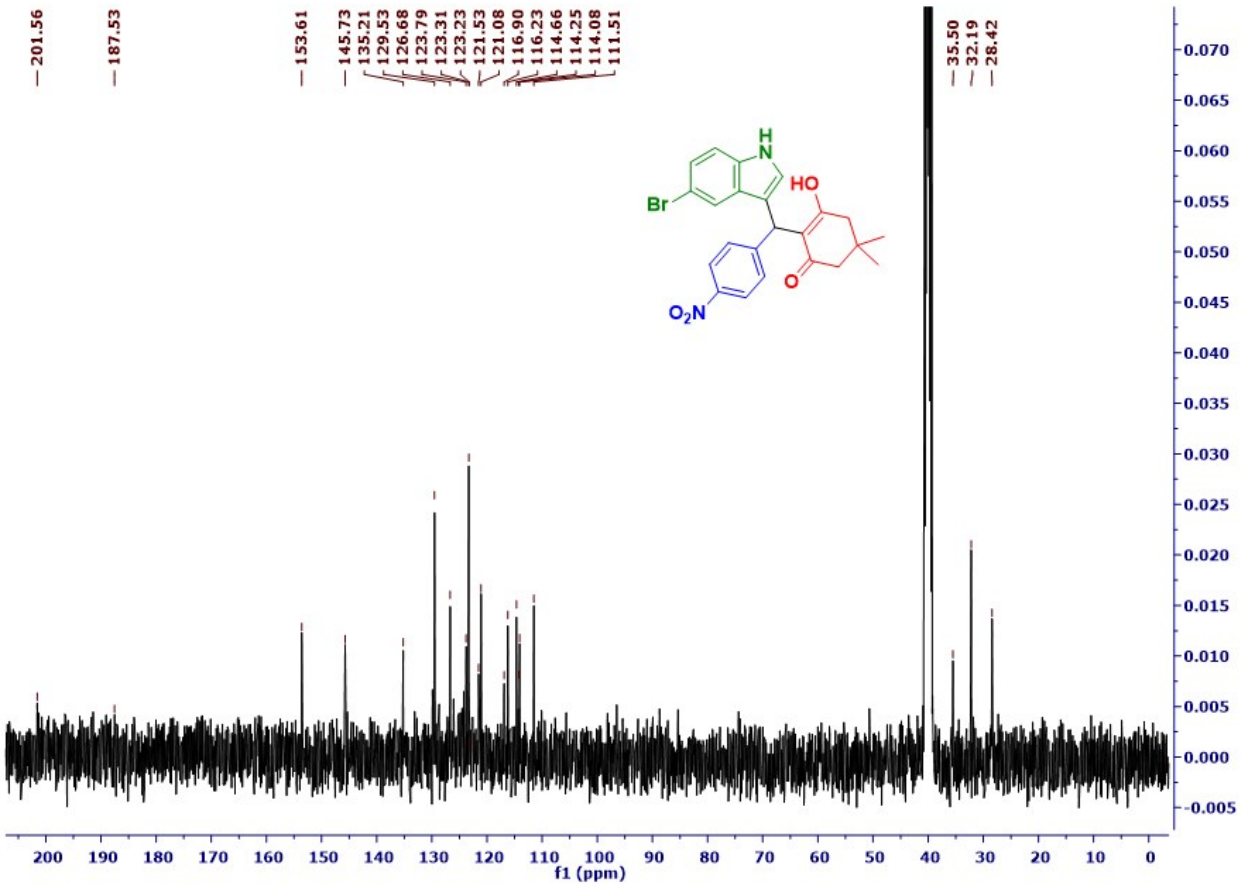


Fig. 9(b): ^{13}C-NMR of 2-((5-bromo-1H-indol-3-yl)(4-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

10. 2-((5-bromo-1H-indol-3-yl)(2-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

Orange Solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.01 (s, 1H), 10.55 (s, 1H), 7.66 (d, 1H, J = 8Hz), 7.40 (t, 1H, J = 7.6 Hz), 7.28-7.34 (m, 3H), 7.20 (d, 1H, J = 8 Hz), 7.12 (dd, 1H, J = 8.6 Hz, J_2 = 1.6 Hz), 6.90 (s, 1H), 6.14 (s, 1H), 2.04-2.31 (m, 4H), 0.92 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.23, 190.50, 155.85, 150.16, 131.93, 131.77, 129.26, 127.22, 126.60, 123.79, 121.05, 114.84, 114.69, 114.12, 111.48, 111.19, 43.57, 31.77, 28.48, 28.28 ppm. HRMS (ES): Calcd: 468.0685. Found: 469.0656 $[M+H]^+$ and 470.0740 $[MH+2]^+$.

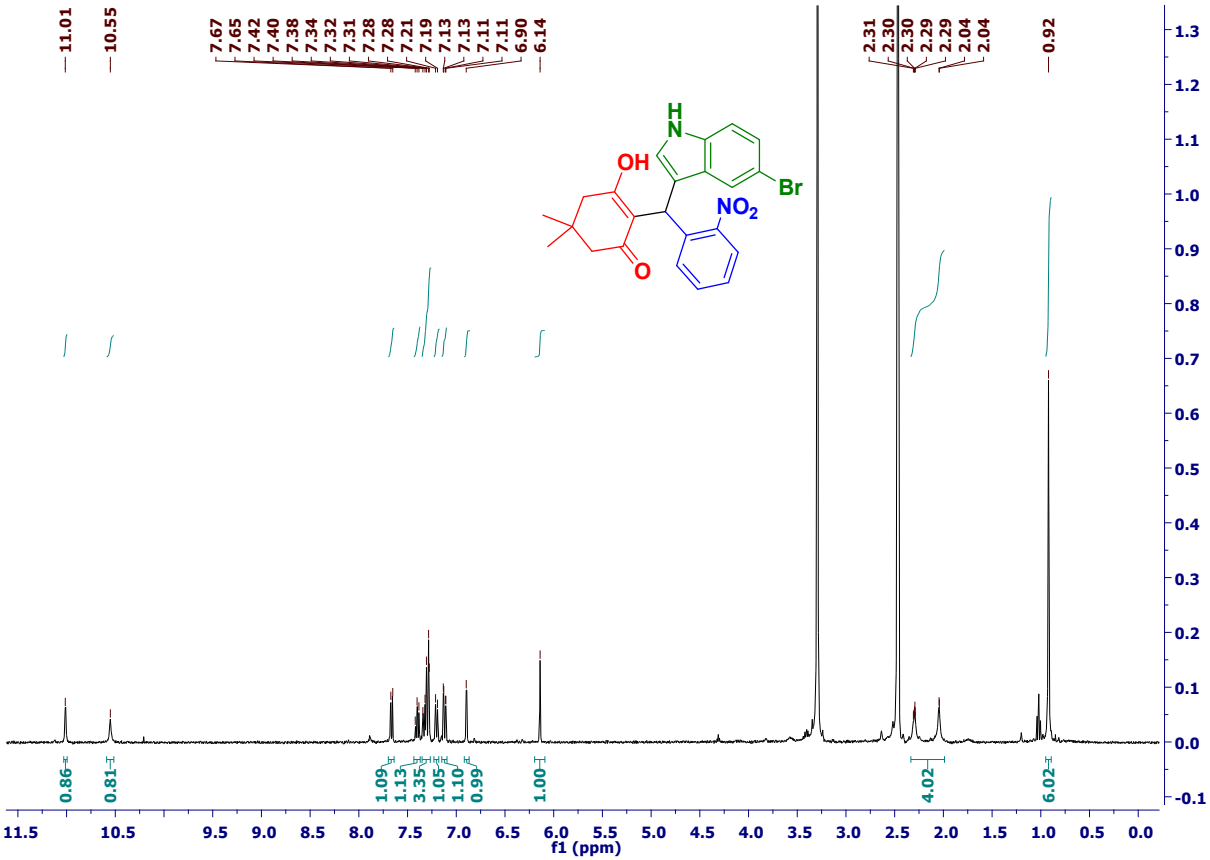


Fig. 10(a): ^{1}H-NMR of 2-((5-bromo-1H-indol-3-yl)(2-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

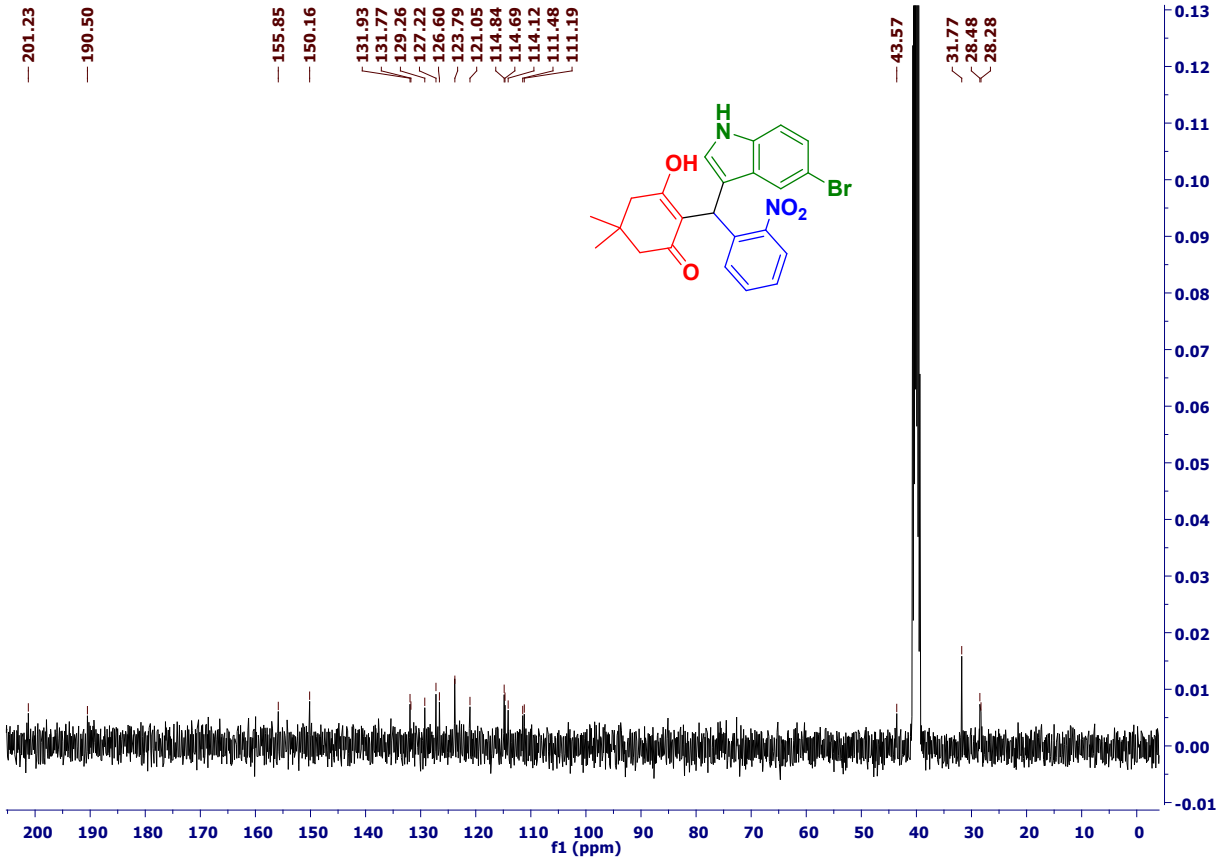


Fig. 10(b): ^{13}C-NMR of 2-((5-bromo-1H-indol-3-yl)(2-nitrophenyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

11. 2-((1H-indol-3-yl)(pyridin-2-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

White Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, 1H, J = 1H, J = 4 Hz), 7.96 (brs, 1H), 7.81 (t, 1H, J = 7.6 Hz), 7.59 (d, 1H, J = 8 Hz), 7.53 (d, 1H, J = 1.6 Hz), 7.25-7.30 (m, 2H), 7.13-7.20 (m, 2H), 6.89 (d, 1H, J = 2 Hz), 6.17 (s, 1H), 2.24-2.38 (m, 4H), 1.01 (s, 6H) ppm, ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.63, 185.97, 146.69, 139.35, 139.21, 135.09, 125.04, 124.34, 123.33, 122.55, 122.23, 116.59, 112.46, 67.70, 66.55, 38.15, 31.43 ppm. HRMS (ES): Calcd: 346.1679. Found: 347.1742 $[M+H]^+$ and 348.1734 $[MH+2]^+$.

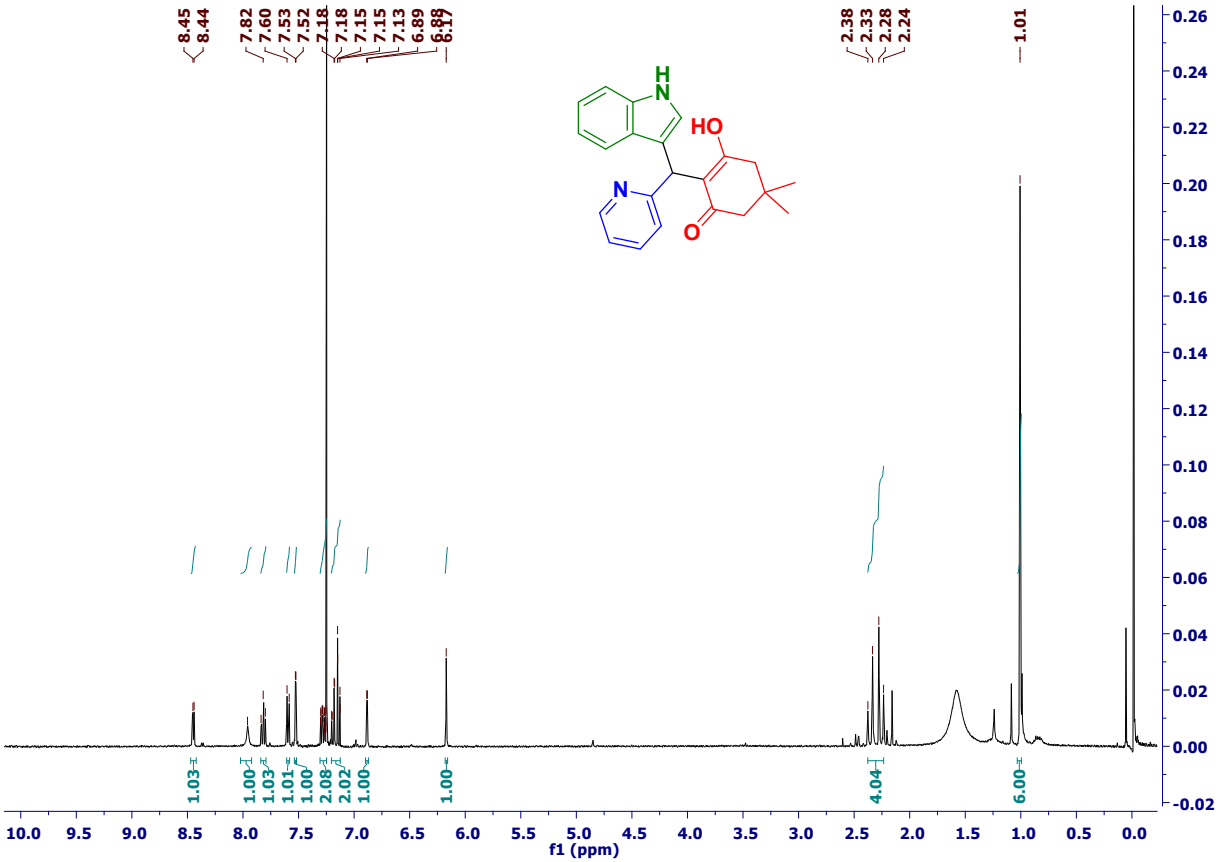


Fig. 11(a): ^{1}H-NMR of 2-((1H-indol-3-yl)(pyridin-2-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

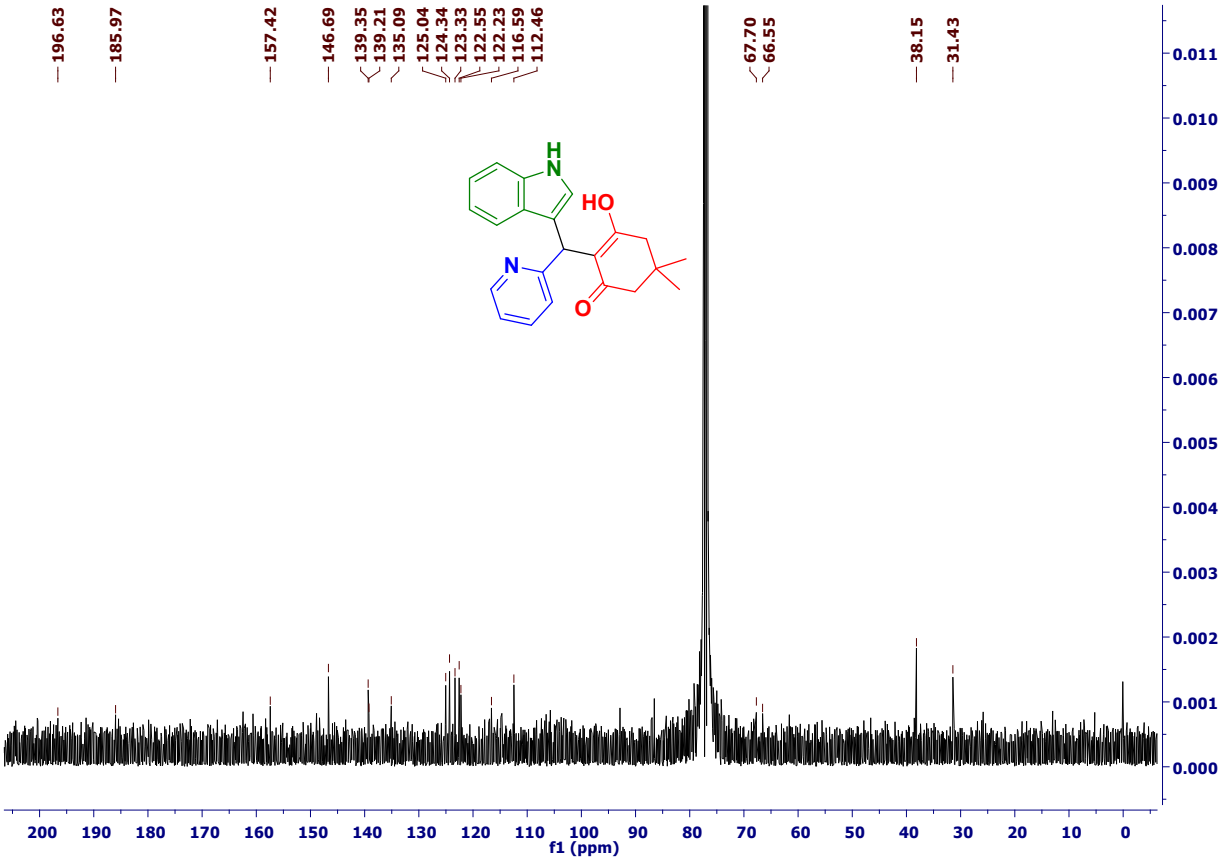


Fig. 11(b): ^{13}C-NMR of 2-((1H-indol-3-yl)(pyridin-2-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

12. 2-((3-bromophenyl)(1H-indol-3-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

Red Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.46-7.48 (m, 1H), 7.43 (d, 1H, J = 4Hz), 7.32-7.38 (m, 3H), 7.14-7.24 (m, 3H), 7.09 (t, 1H, J = 7.6Hz), 5.85 (s, 1H), 1.22-1.25 (m, 2H), 1.08 (s, 6H), 0.85-1.02 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.43, 184.52, 144.23, 137.21, 131.52, 131.42, 130.30, 129.94, 127.09, 126.45, 123.55, 122.78, 120.34, 119.38, 117.49, 114.71, 111.72, 54.17, 36.78, 32.02, 31.68, 29.80, 28.44 ppm. HRMS (ES): Calcd:423.0834 Found: 424.0834 $[M+H]^+$ and 425.0838 $[MH+2]^+$.

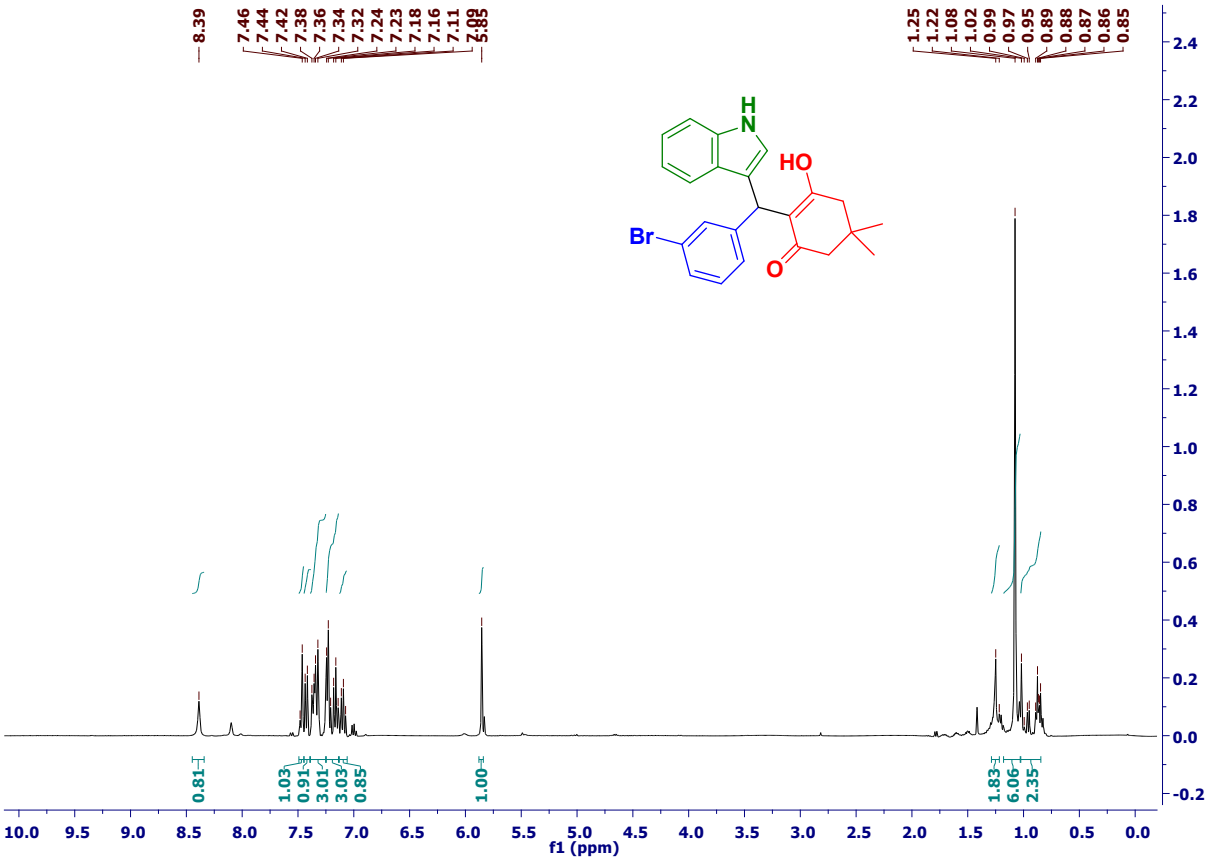


Fig. 12(a): ^{1}H-NMR of 2-((3-bromophenyl)(1H-indol-3-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

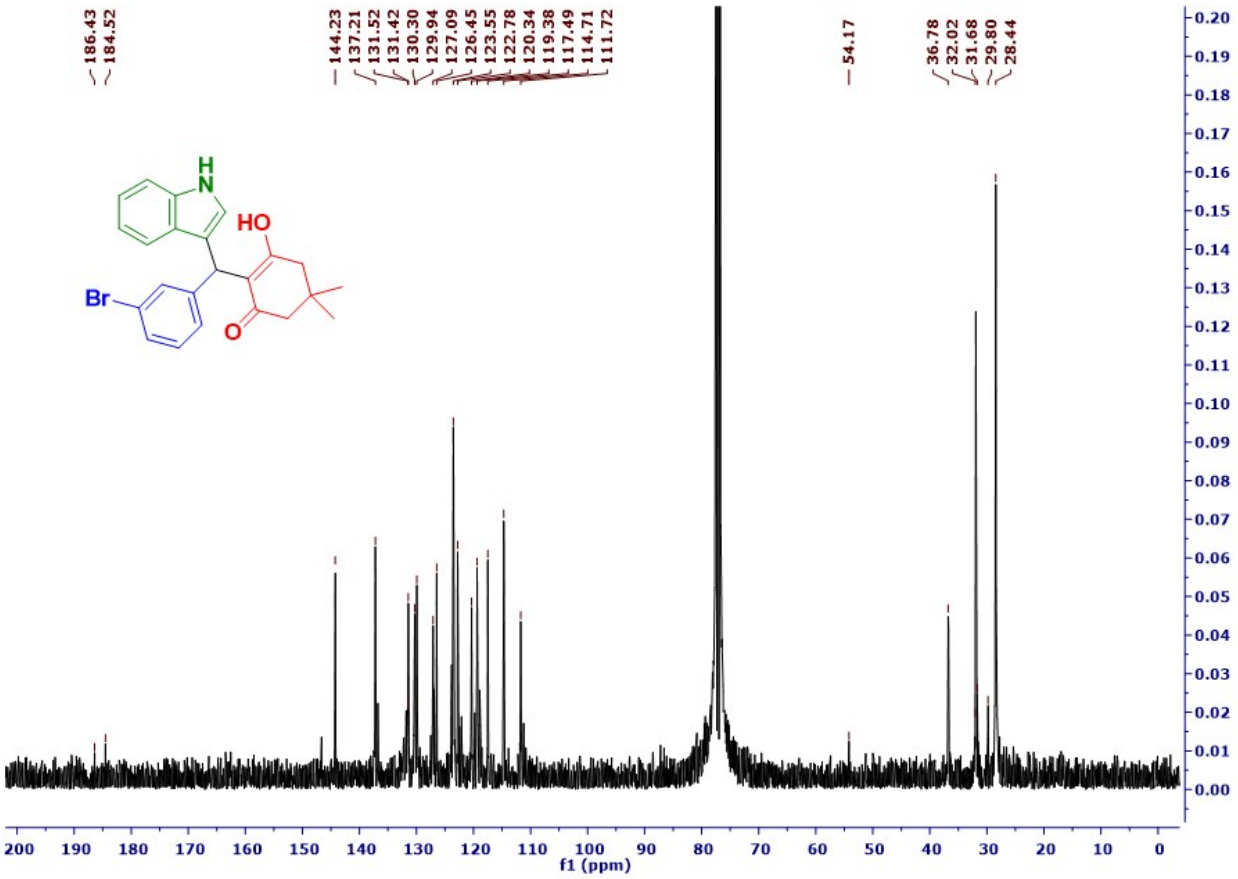


Fig. 12(b): ^{13}C-NMR of 2-((3-bromophenyl)(1H-indol-3-yl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

13. 2-((5-bromo-1H-indol-3-yl)(p-tolyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

Reddish Yellow Solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (brs, 1H), 7.54 (s, 1H), 7.28 (d, 1H, J = 8.8 Hz), 7.12-7.21 (m, 5H), 6.62 (s, 1H), 5.82 (s, 1H), 2.32 (s, 3H), 1.07-1.24 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.30, 171.65, 138.25, 136.58, 135.86, 135.42, 129.68, 128.40, 128.10, 126.14, 124.54, 122.28, 117.73, 115.66, 113.39, 113.00, 112.41, 109.45, 43.09, 39.53, 36.04, 31.93, 28.36, 21.15 ppm. HRMS (ES): Calcd: 437.0983. Found: 438.1062 $[M+H]^+$ and 439.1082 $[MH+2]^+$.

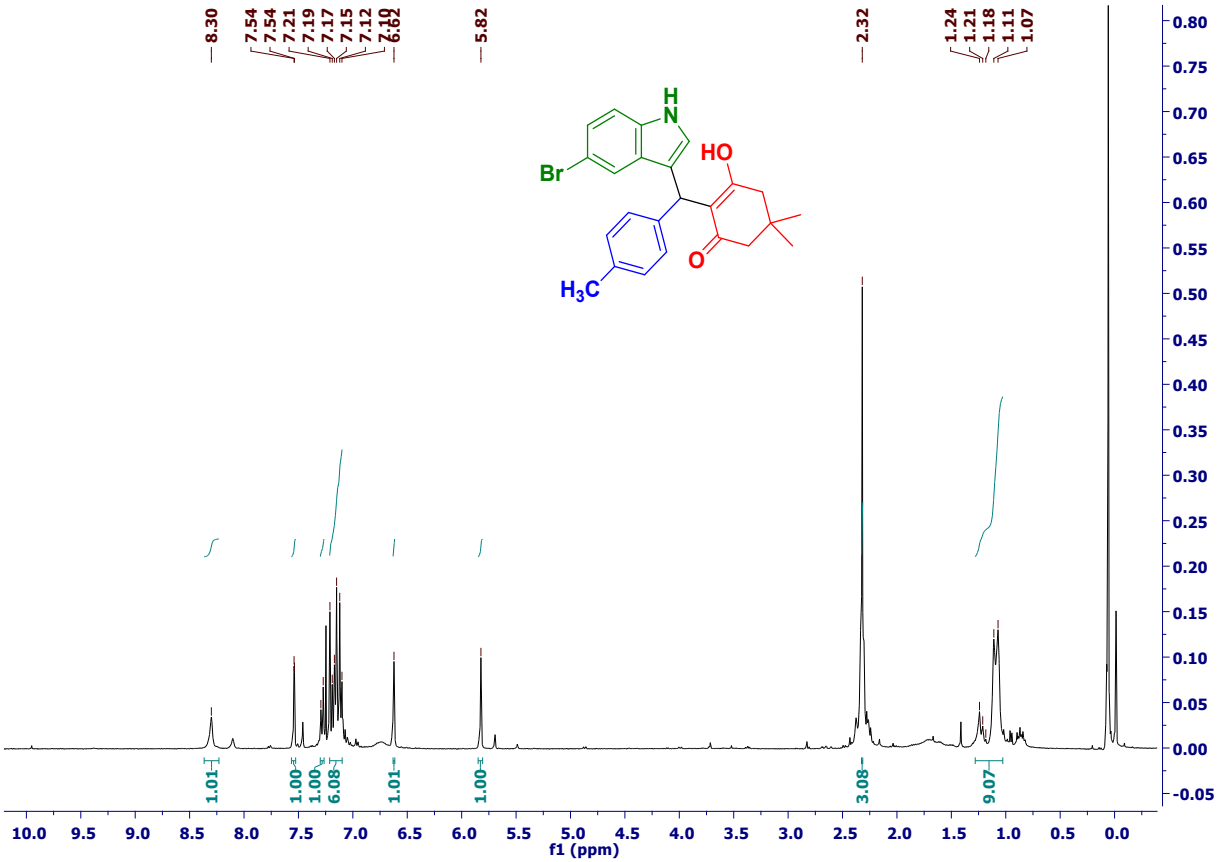


Fig. 13(a): ^{1}H-NMR of 2-((5-bromo-1H-indol-3-yl)(p-tolyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

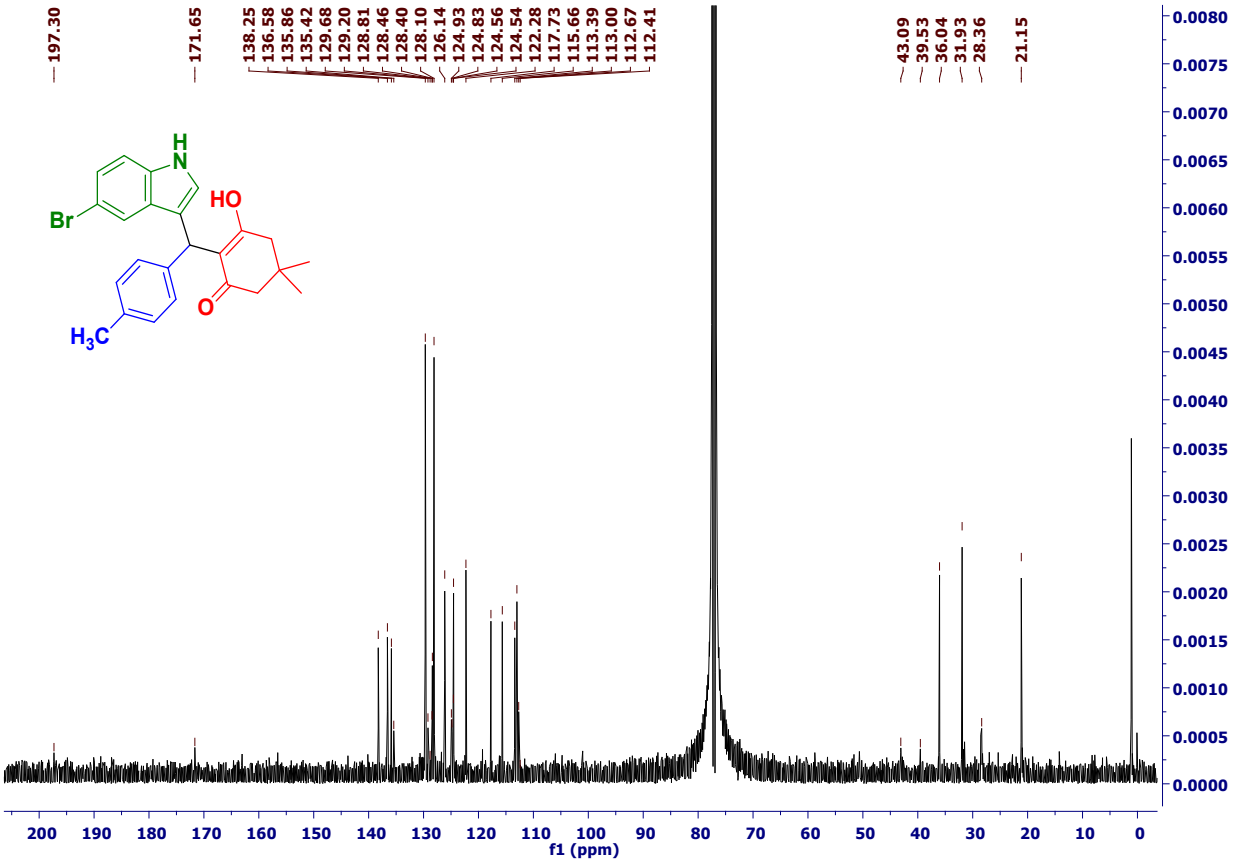
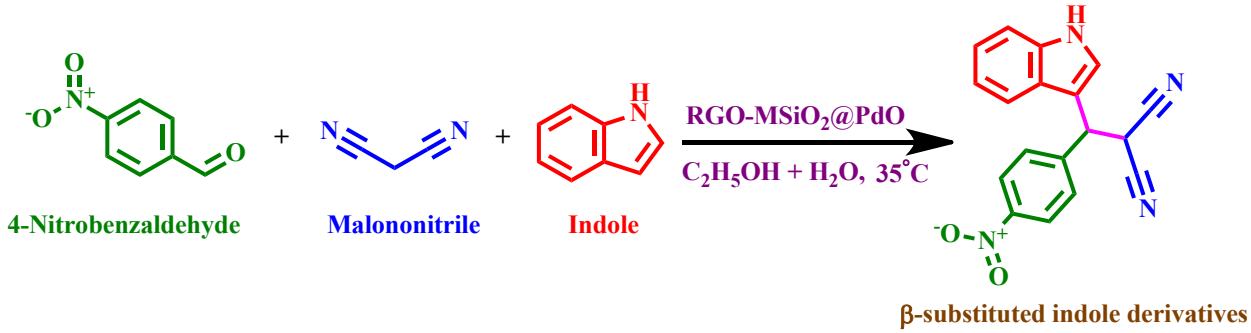


Fig. 13(b): ^{13}C-NMR of 2-((5-bromo-1H-indol-3-yl)(p-tolyl)methyl)-3-hydroxy-5,5-dimethylcyclohex-2-enone

Calculation of green chemistry matrices



M.W.	**151.12 g/mol**	**66.06 g/mol**	**117.15 g/mol**	**316.31 g/mol**
mmol	**1**	**1**	**1**	**0.98**
amount	**0.151 g**	**0.066 g**	**0.117 g**	**0.310 g**

a) E-factor: The calculated E-factor for chemical transformation signifies the total amount of waste generated. It can be calculated as mass of waste divided by total mass of product formed. The ideal E-factor value is zero.

$$\text{E-factor} = [(Mass\ of\ waste)/(Mass\ of\ product)]$$

Where,

$$\text{Mass of waste} = Total\ mass\ of\ stoichiometric\ reactant - Total\ mass\ of\ product\ formed$$

$$\text{E-factor} = (0.151 + 0.066 + 0.117 - 0.310)/0.310$$

$$= 0.077$$

b) Atom Economy (AE): The calculated atom economy values signify the percentage of atoms wasted in a chemical transformation. The ideal atom economy value is 100% which indication the complete conversion of reactants into product. Higher the value of atom economy, the greener is the chemical transformation.

$$\text{AE} = \frac{[M.W.\ of\ product]}{\sum(M.W.\ of\ stoichiometric\ reactants)} \text{ X } 100$$

$$= [316.31 / (151.12 + 66.06 + 117.15)] \text{ X } 100$$

$$= 94.61\%$$

c) Carbon Efficiency (CE): It signifies the percentage of carbon atoms left in the product in respect to the carbon atoms of the reactants.

$$\text{CE} = \frac{[(No.\ of\ moles\ of\ product)(No.\ of\ carbon\ in\ product)]}{\sum[(No.\ of\ moles\ of\ reactant)(No.\ of\ carbon\ in\ reactant)]} \text{ X } 100$$

$$= \frac{(0.98\ X\ 18)}{[(1\ X\ 7) + (1\ X\ 3) + (1\ X\ 8)]} \text{ X } 100 = 98\ \%$$

d) Process Mass Intensity (PMI): It is defined as the ratio of total mass used in a process to the mass of product.

$$\text{PMI} = \frac{\sum(Mass\ of\ stoichiometric\ reactants)}{Mass\ of\ product}$$

$$= \frac{(0.151\ +\ 0.066\ +\ 0.117)}{0.310}$$

$$= 1.077$$

Alternatively,

$$\text{PMI} = \text{E-factor} + 1 = 0.077 + 1 = 1.077$$

e) Reaction Mass Efficiency (RME): It is defined as the percentage ratio of mass of product to the sum of total mass of stoichiometric reactants.

$$\text{RME} = \frac{Mass\ of\ product}{\sum(Mass\ of\ stoichiometric\ reactants)} \text{ X } 100$$

$$= \frac{0.310}{(0.151\ +\ 0.066\ +\ 0.117)} \text{ X } 100$$

$$= 92.81\ \%$$

Table D1: Optimization of effective catalyst, catalyst amount and an appropriate solvent for access

Entry	Solvent	Catalyst (mg, mol%)	Temp. (°C)	Time (min.)	Yield[a] (%)
1.	Solvent less	RGO-$MSiO_2$/PdO (10, 0.17)	R.T.	90	Traces
2.	Solvent less	RGO-$MSiO_2$/PdO (15, 0.25)	60	90	42
3.	C_2H_5OH	RGO-$MSiO_2$/PdO (10, 0.17)	R.T.	60	74
4.	C_2H_5OH	RGO-$MSiO_2$/PdO (7, 0.12)	50	30	82
5.	C_2H_5OH	RGO-$MSiO_2$/PdO (10, 0.17)	50	30	92
6.	C_2H_5OH	RGO-$MSiO_2$/PdO (10, 0.17)	80	60	76
7.	CH_2Cl_2	RGO-$MSiO_2$/PdO (10, 0.17)	40	90	63
8.	DMSO	RGO-$MSiO_2$/PdO (10, 0.17)	80	90	59
9.	Toluene	RGO-$MSiO_2$/PdO (10, 0.17)	50	90	46
10.	THF	RGO-$MSiO_2$/PdO (10, 0.17)	40	90	52
11.	$CHCl_3$	RGO-$MSiO_2$/PdO (10, 0.17)	40	90	64
12.	H_2O	RGO-$MSiO_2$/PdO (10, 0.17)	R.T.	60	53
13.	H_2O	RGO-$MSiO_2$/PdO (10, 0.17)	50	60	71
14.	H_2O + C_2H_5OH (1:1)	RGO-$MSiO_2$/PdO (10, 0.17)	50	15	98
15.	**H_2O + C_2H_5OH (1:1)**	**RGO-$MSiO_2$/PdO (10, 0.17)**	**35**	**15**	**98**
16.	H_2O + C_2H_5OH (1:1)	GO (25)	50	90	15
17.	H_2O + C_2H_5OH (1:1)	RGO-$MSiO_2$ (20)	50	90	23
18.	H_2O + C_2H_5OH (1:1)	-	50	120	-

Reaction conditions: Active methylene compound (1 mmol), 4-Nitrobenzaldehyde (1mmol), Indole (1mmol), [a]Isolated yield.

-substituted indole derivatives by using RGO-$MSiO_2$/PdO HY-NM as catalyst.

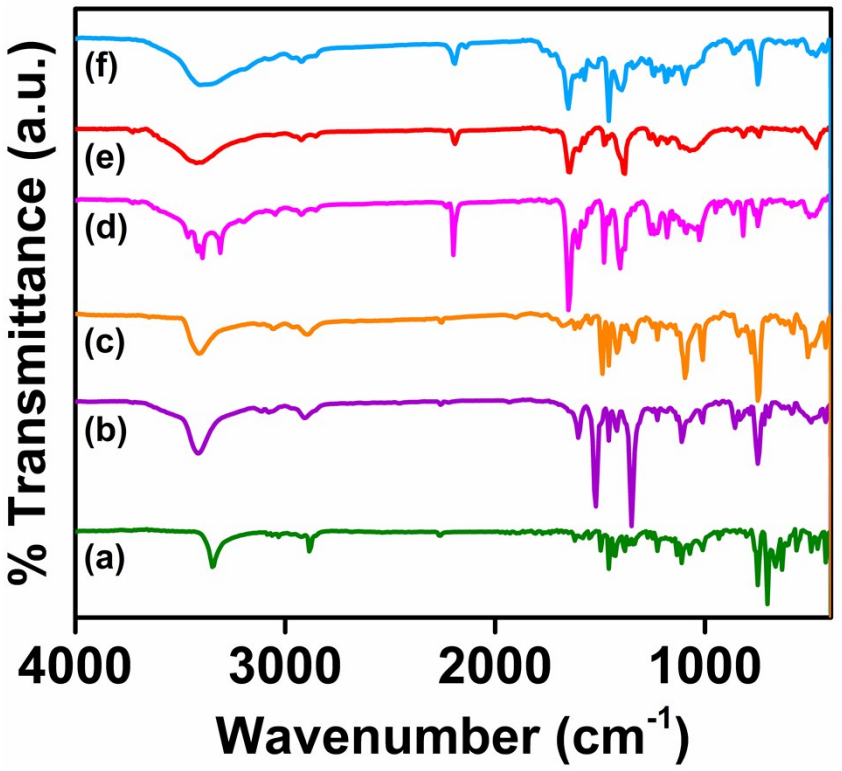
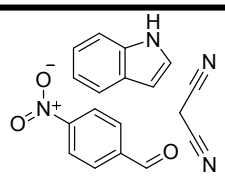
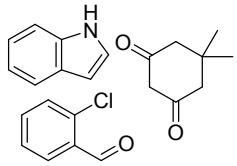


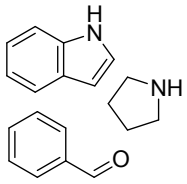
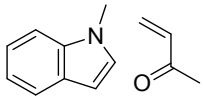
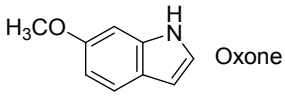
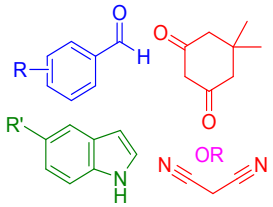
Fig. 14: FTIR spectrum of **(a)** 2-((1H-indol-3-yl)(phenyl)methyl)malononitrile, **(b)** 2-((1H-indol-3-yl)(4-nitrophenyl)methyl)malononitrile, **(c)** 2-((4-chlorophenyl)(1H-indol-3-yl)methyl)malononitrile, **(d)** 2-((5-chloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile, **(e)** 2-((5-bromo-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile, **(f)** 2-((3,5-dichloro-2-hydroxyphenyl)(1H-indol-3-yl)methyl)malononitrile.

Table D2: Comparative study of RGO-$MSiO_2$/PdO with previously published diverse reports based on GO/SiO_2 catalysts.

S.N.	Final Catalyst (Support)	Morphology	Surface Area (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)	Application	Ref.
1.	GO/SiO_2	Mesoporous Sphere	-	10.24	-	-	[1]
2.	Cu(II)-IIP-2 (MS/MGO)	Mesoporous Sheet	194.1 (279.6)	-	-	Synthesis of 1-methyl-4-(p-tolyloxy)benzene	[2]
3.	Cu@CD-PEG-mesoGO (CD-PEG-mesoGO)	Mesoporous Sheet	592.34 (798.23)	5.97 (6.8)	-	Synthesis of 1,2,3-triazole and 2-arylbenzimide	[3]
4.	GOSCh	Sheet	10.16	70.8	1.078	Water Treatment	[4]
5.	GCS	Sheet	328	-	-	Water Treatment	[5]
6.	GSF@AuNPs (RGO-PMS)	Mesoporous Sheet	470.87 (879.67)	-	-	Cancer Cell Detection	[6]
7.	RGO-PMS@AuNPs	Mesoporous Sheet	542.34 (862.37)	3.1	-	Cancer Cell Detection	[7]
8.	rGO@mSiO_2-1	Mesoporous Sheet	755	8.9	1.92	-	[8]
9.	RGO-$MSiO_2$/PdO (RGO-$MSiO_2$)	Mesoporous Sheet	574.2 (583.3)	12.49 (17.26)	1.685 (1.978)	Synthesis of -substituted indole derivatives	This Work

Table D3: Comparative study of RGO-$MSiO_2$/PdO with previously published diverse reports based on other GO nanocomposites for the synthesis of -substituted indole derivatives.

S.N.	Reactants	Catalyst (Amount)	Reaction Conditions	Yield (%)	Ref.
1.		RGO/ZnO, (5 Wt %)	50 °C, 30 min	95	[9]
2.		GO-IL-NH_2, (10 mg)	50 °C, 30 min	98	[10]

3.		MGO-IL-NH_2, (20 mg)	50 ˚C, 60 min	92	[11]
4.		GO (20 wt %)	R.T., 5.5 h	80	[12]
5.	 Oxone	Nano Au-Pd-rGO, (0.5 mol %)	R.T., 5 h	91	[13]
6.		RGO-$MSiO_2$/PdO, (10 mg)	35 ˚C, 15 min	98	This Work

References

1 C. M. Yoon, S. Lee, S. H. Hong and J. Jang, *J. Colloid Interface Sci.*, 2015, **438**, 14–21.

2 P. Fang, W. Xia, Y. Zhou, Z. Ai, W. Yin, M. Xia, J. Yu, R. A. Chi and Q. Yue, *Chem. Eng. J.*, 2020, **385**, 123847.

3 S. Bahadorikhalili, L. Ma'mani, H. Mahdavi and A. Shafiee, *Microporous Mesoporous Mater.*, 2018, **262**, 207–216.

4 S. Azizkhani, E. Mahmoudi, N. Abdullah, M. H. S. Ismail, A. W. Mohammad and S. A. Hussain, *Polymers (Basel).*, 2020, **12**, 1922.

5 X. Liu, H. Zhang, Y. Ma, X. Wu, L. Meng, Y. Guo, G. Yu and Y. Liu, *J. Mater. Chem. A*, 2013, **1**, 1875–1884.

6 S. K. Maji, A. K. Mandal, K. T. Nguyen, P. Borah and Y. Zhao, *ACS Appl. Mater. Interfaces,* 2015, **7**, 9807-9817.

7 S. K. Maji, S. Sreejith, A. K. Mandal, X. Ma and Y. Zhao, *ACS Appl. Mater. Interfaces,* 2014, **6**, 13648-13656.

8 Y. Liu, W. Li, D. Shen, C. Wang, X. Li, M. Pal, R. Zhang, L. Chen, C. Yao, Y. Wei, Y. Li, Y. Zhao, H. Zhu, W. Wang, A. M. El-Toni, F. Zhang and D. Zhao, Chem. Mater., 2015, **27**, 5577-5586.

9 U. C. Rajesh, J. Wang, S. Prescott, T. Tsuzuki and D. S. Rawat, *ACS Sustain. Chem. Eng.*, 2015, **3**, 9–18.

10 C. Garkoti, J. Shabir, P. Gupta, M. Sharma and S. Mozumdar, *New J. Chem.*, 2017, **41**, 15545–15554.

11 C. Garkoti, J. Shabir and S. Mozumdar, *ChemistrySelect*, 2020, **5**, 4337–4346.

12 A. Vijay Kumar and K. Rama Rao, *Tetrahedron Lett.*, 2011, **52**, 5188–5191.

13 S. B. Gohain, M. Basumatary, P. K. Boruah, M. R. Das and A. J. Thakur, *Green Chem.*, 2020, **22**, 170–179.