Fe_3O_4-chitosan immobilized Cu(II) Schiff base catalyst for the microwave-assisted amination of aryl halides in water

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1. General Procedures

All chemical reagents including Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$; 98%), Fe(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$; 99%), ammonium hydroxide (NH_4OH; 30-33%), ethanol (EtOH; 96%), chitosan (low molecular weight), glacial acetic acid (CH_3COOH; 99%), sodium sulfate (Na_2SO_4; 99%), actyl-2-furan ($C_6H_6O_2$; 99%), copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$; 99%), acetone (reagent grade), all substituted aryl aldehydes, piperidine ($C_5H_{11}N$;99%), morpholine (C_4H_9NO 99%) and pyrrolidine (C_4H_9N 99%) were purchased from Aldrich. All these chemicals were of analytical grade and used without any further purification. Double deionized water was used in all experimental procedures. Analytical thin layer chromatography (TLC) was performed on silica plates with aluminum backings (250 μm with indicator F-254). Compounds were visualized under UV light. Products were characterized using SHIMADZU GAS CHROMATOGRAPHY MASS SPECTROMETER (GCMS-QP2020 NX) NeXIS GC-2030 ^1H NMR. The column parameters of GC-MS were set to a maximum temperature of 300 °C, a length of 30.0 m, an inner diameter of 0.25 mm, and a film thickness of 0.25 μm. The mass spectrometry parameters were set to an ion source temperature of 200 °C, an interface temperature of 270 °C, and a solvent cut time of 3 min. The ^1H spectra were recorded on a Bruker 500MHz Ascend Aeon (BBFO room temperature probe) with Avance III HD console for all of the cross-coupled products respectively.

2. Instrumentation

The thermogravimetric analysis (TGA) was performed using a thermo-balance instrument-type TGA-50, SHIMADZU, Japan. TGA analyses were performed in static air with a heating rate of 10 °C/ min. FTIR spectra were recorded using an FTIR Bruker Platinum Spectrometer (Germany) fitted with an attenuated total reflection (ATR) unit, with single reflection geometry. X-ray diffraction (XRD) patterns were obtained using Bruker D8 Advance powder X-ray diffractometer (Germany) with CuKα radiation source. Maximum voltage: 40kV and maximum Current: 40mA. Field-emission scanning electron microscopy (FE-SEM) images were recorded using TESCON VEGA3 (Brno–Kohoutovice, Czech Republic) XM variable pressure, accelerating voltage: max. 30k. For collecting SEM images, Sputter Coating System was used for preparing the sample. Quorum Technology Mini Sputter Coater, SC7620 (United Kingdom). Target: Gold / palladium (80% & 20%); 57mm Ø x 0.1mm thick, sputtering gas: argon, chamber pressure: 10^{-2} mbar, sputtering time: 120 seconds, plasma current: 18mA, applied voltage: 1 kV, carbon fibre evaporation. Energy dispersive X-ray spectroscopy (EDX) was recorded using Oxford Instruments X-Max 50 EDS detector (LN2 free system). Resolution: 125 eV (United Kingdom). TEM analysis of samples were done by dispersed in ethanol and drop coated onto the TEM grid (holey carbon on a copper grid with 300 mesh from Electron Microscopy Sciences) for further analysis. The structural characterization was performed by employing an aberration corrected TEM (Thermo Fisher Scientific, Titan G2), at 300 kV and equipped with a Cs probe corrector. X-ray photoelectron spectroscopy (XPS, Nexsa G2, Thermoscientific, U.K) was employed to investigate the chemical state of Fe_3O_4@CS@Schiffbase@Cu materials using mono-chromatized Al- Kα

radiation (1486.6 eV) under ultra-high vacuum (~10-10 mbar). Software used for data acquisition: Avantage V6.4.1 Thermo Scientific™ iCAP™ 7400 ICP-OES Analyzer has been used for the determination of Cu content in the catalyst Fe_3O_4@CS@AF@Cu composite.

3. Characterization of the catalyst

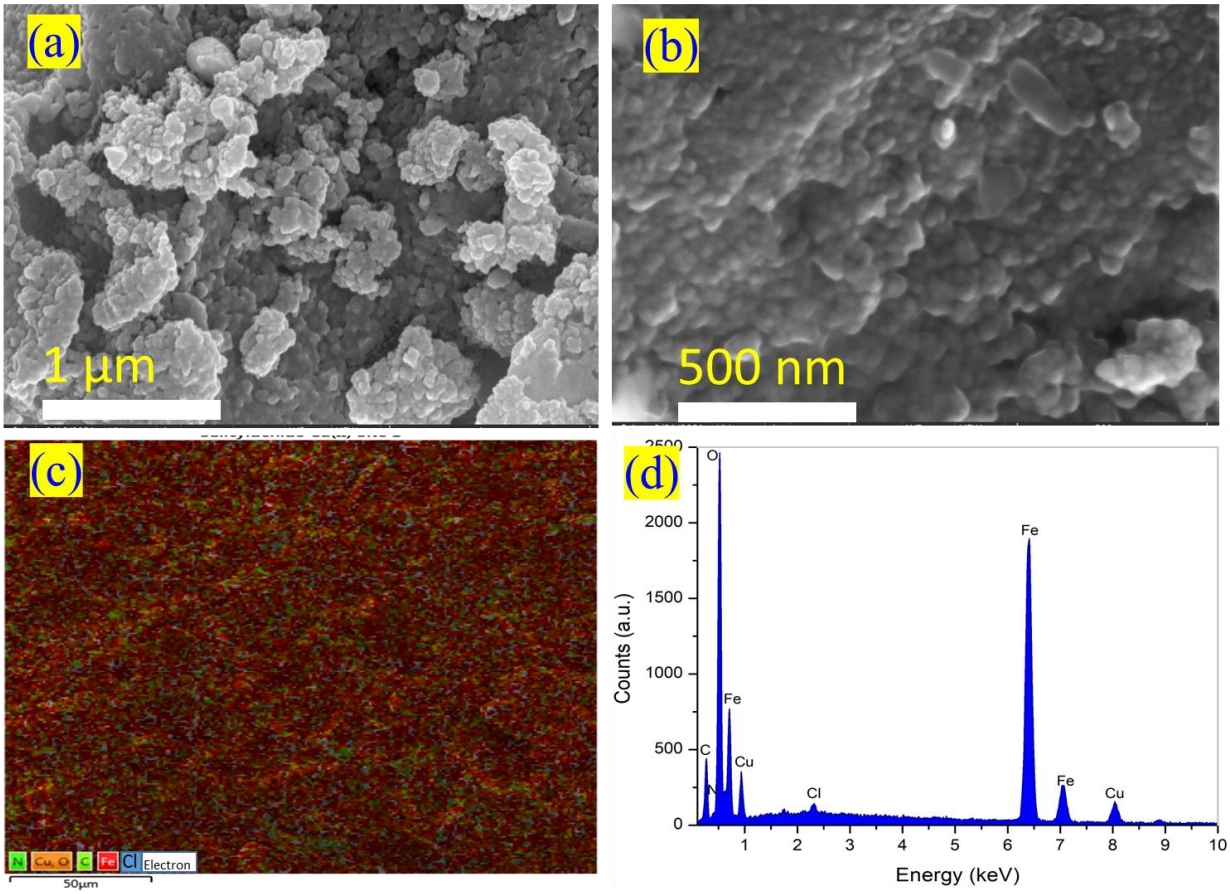


Figure. S1. FE-SEM images of Fe_3O_4@CS@AF@Cu (a) and (b) at different magnification, Energy dispersive X-ray (EDX) mapping (c) and elemental mapping (d) after use of 5^{th} catalytic reaction of the reaction

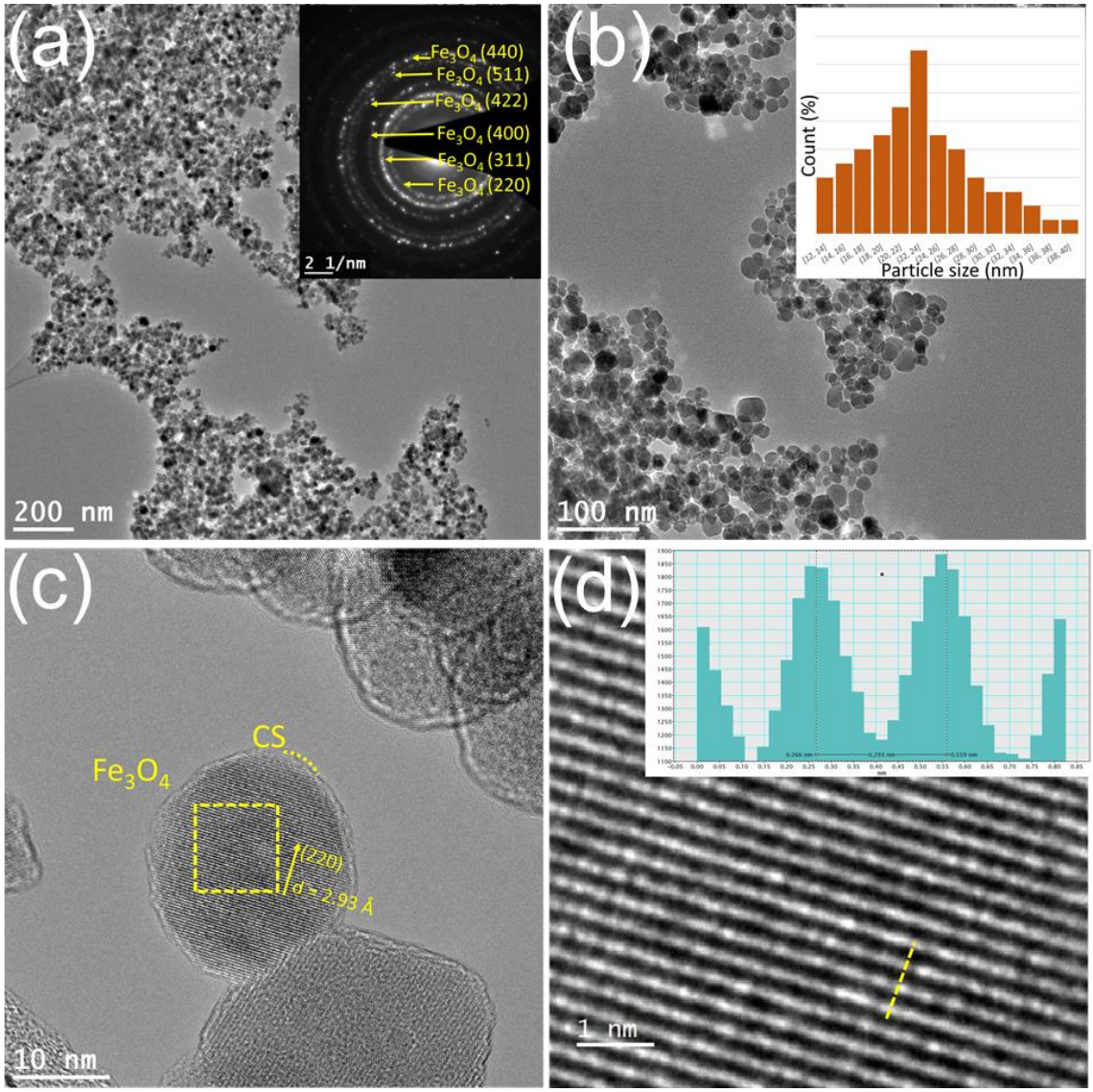


Figure S2: (a-b) The bright field TEM micrographs showing Fe_3O_4@CS nanoparticles. The inset in the figure (a) shows the selected area electron diffraction (SAED). The SAED pattern was indexed to polycrystalline face-cantered cubic (fcc) Fe_3O_4 [(440), (511), (422), (400), (311), and (220)] (JCPDS File no. 19-0629). The inset in figure (b) shows the histogram of particle size distribution. The crystal size distribution obtained by statistical image analysis shows the average size of 23±4.5 nm. (c) The bright filed HRTEM micrograph of Fe_3O_4@CS nanoparticles. The

Fe_3O_4 nanoparticles are successfully grafted by the CS matrix. The inset rectangle is enlarged in the figure (d). The inset in (d) shows the intensity profile corresponding to the dotted line marked in the figure. The intensity profile reveals the inter planner spacing of 2.93 Å corresponding to (220) plane in Fe_3O_4

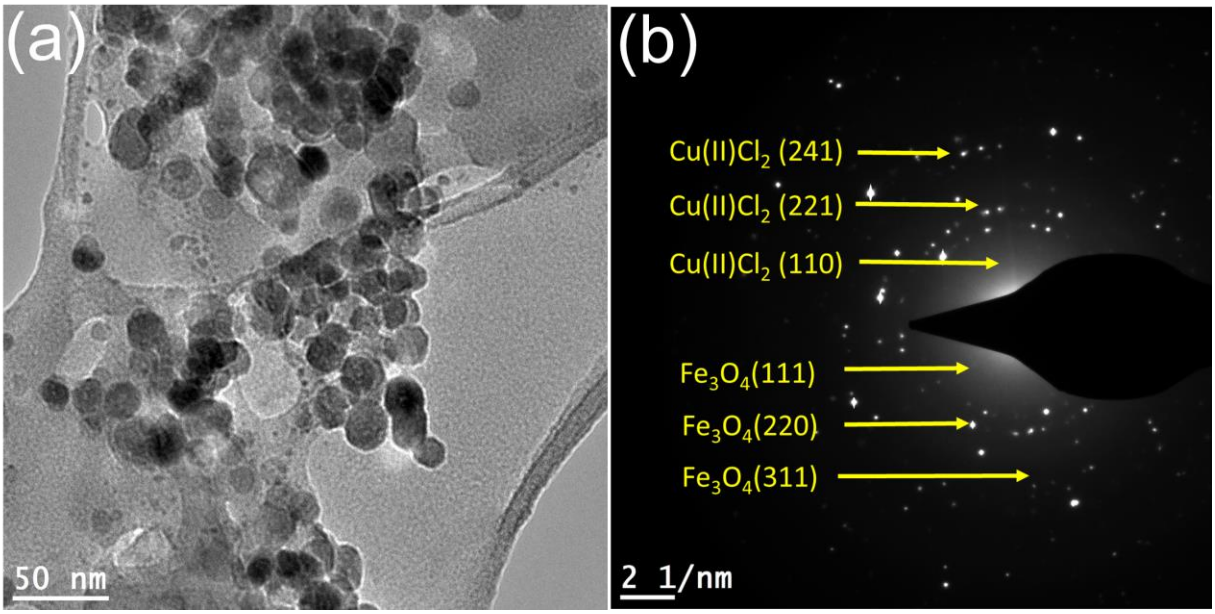


Figure. S3. The bright field TEM micrographs (a) and SAED pattern (b) of Fe_3O_4@CS@AF@Cu after the 5th catalytic cycle of the reaction

4. Determination of copper content in the catalyst by inductively coupled plasma-optical emission spectrometry (ICP-OES)

Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to analyse the content of copper in the catalyst. First, the catalyst material Fe_3O_4@CS@AF@Cu is digested following the standard procedure. 29.35 mg of the catalyst is digested in 10 mL of HNO_3, followed by addition of 5 mL of 30% H_2O_2, the solution volume is allowed to be reduced to 5.0 mL, then diluted to 500 mL with distilled deionized water. The original sample solution was then diluted 10

20 and 33 times further. Working standards of copper are prepared from a stock solution of 1938 ppb made by dissolving 5.2 mg of $CuCl_2 \cdot H_2O$ in 9.0% (w/v) hydrochloric acid, then 1000, 800, 600, 400, 200 and 100 ppb standards are prepared using serial dilutions.

The calibration curve for the analysis is given in **Figure S4** below

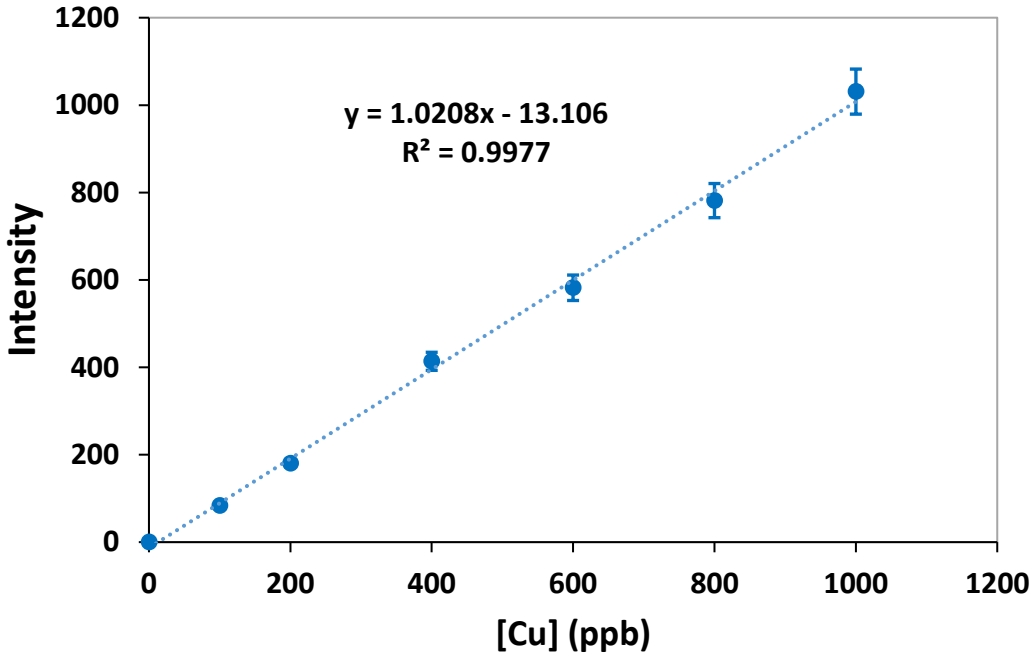


Figure S4. ICP-OES copper calibration curve used to determine the content of copper in the catalyst material

Intensities of the diluted samples and working standards are given in the **Table S1** below.

Table S1. Working standards and sample intensities obtained from the ICP-OES

Cu wavelength = 324.270		
	Cu (ppb)	**Intensity**
Blank	0.00	0
STD-1	100.00	84.00329
STD-2	200.00	180.5132
STD-3	400.00	413.7426
STD-4	600.00	582.0288
STD-5	800.00	781.4639
STD-6	1000.00	1030.863
Sample - 10 DIL		454.1823

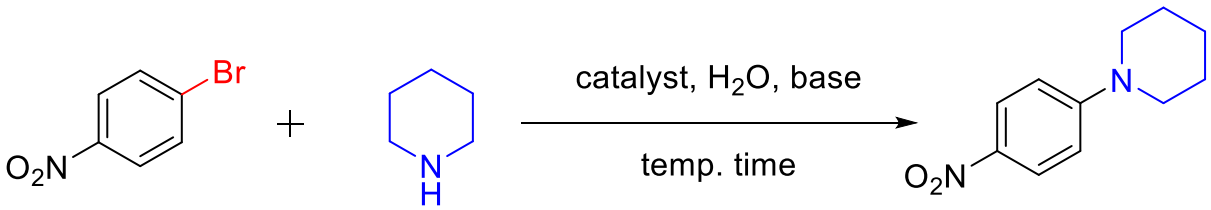
Sample - 20 DIL		222.8932
Sample – 33 DIL		137.0004
Used sample-original		426.049203
Used sample-2 DIL		198.693797
Used sample-3 DIL		124.292184

The copper content of the catalyst is found to be 8.01

Determination of Cu content of the used catalyst:

Following the above-mentioned procedure 2.64 mg of the used catalyst is digested in 5.0 mL of HNO_3, followed by addition of 2.5 mL of 30% H_2O_2, the solution volume is allowed to be reduced to 2.0 mL, and then diluted to 500 mL with distilled deionized water. The original sample solution was then diluted 2 and 3 times further. The copper content of the used catalyst is found to be 7.90 %.

Table S2: Optimization of amination of 1-bromo-4-nitrobenzene with piperidine[a]



[a] Reaction conditions: 1-bromo-4-nitrobenzene (1.0 mmol), piperidine (1.1 mmol), base (2.0 mmol), solvent H_2O (5 ml), catalyst Fe_3O_4@CS@AF@Cu.

Entry	Catalyst	Amount (mol% Cu)	Base	Temp. (°C)	Time (h)	Yield[b] (%)
1	-	-	K_2CO_3	r. t.	16 h	-
2	-	-	K_2CO_3	100	16 h	-

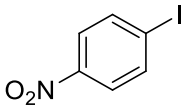
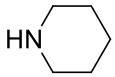
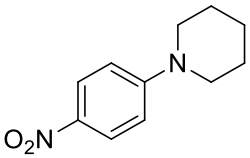
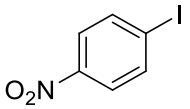
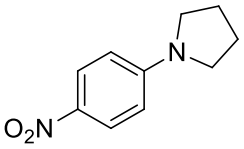
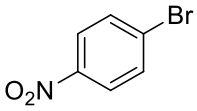
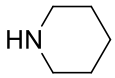
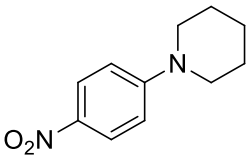
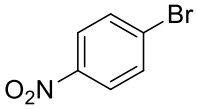
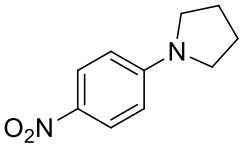
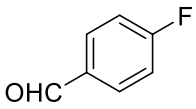
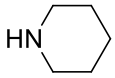
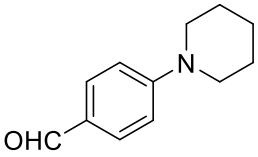
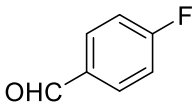
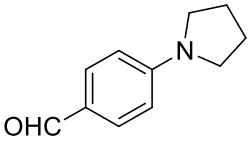
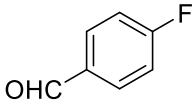
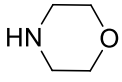
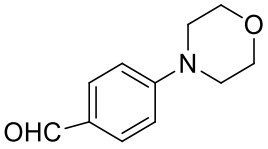
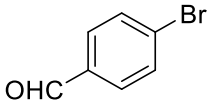
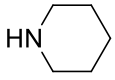
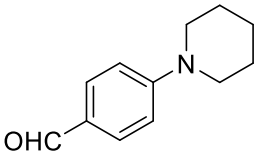
3	Fe_3O_4	20 mg (-)	K_2CO_3	100	16 h	10[c]
4	Fe_3O_4@CS@AF	2 mg (-)	K_2CO_3	100	16 h	15[c]
5	Fe_3O_4@CS@AF@Cu	20 mg (2.5)	K_2CO_3	100	16 h	85[c]
6	Fe_3O_4@CS@AF@Cu	20 mg (2.5)	$KHCO_3$	100	16 h	80[c]
7	Fe_3O_4@CS@AF@Cu	20 mg (2.5)	$NaHCO_3$	100	16 h	65[c]
8	Fe_3O_4@CS@AF@Cu	20 mg (2.5)	K_2CO_3	100	2 h	95[d]
9	Fe_3O_4@CS@AF@Cu	10 mg (1.3)	K_2CO_3	100	2 h	98[d]
10	Fe_3O_4@CS@AF@Cu	5 mg (0.63)	K_2CO_3	100	2 h	98[d]
11	Fe_3O_4@CS@AF@Cu	2.5 mg (0.32)	K_2CO_3	100	2 h	90[d]
12	Fe_3O_4@CS@AF@Cu	5.0 mg (0.63)	K_2CO_3	100	1 h	98[d]
13	Fe_3O_4@CS@AF@Cu	5.0 mg (0.63)	K_2CO_3	100	0.5 h	88[d]

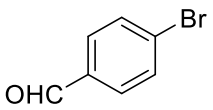
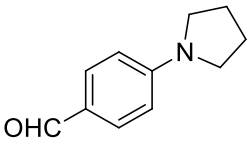
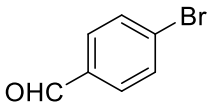
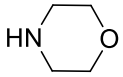
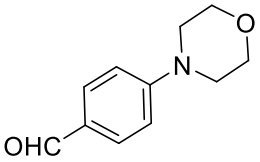
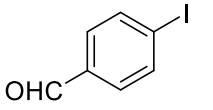
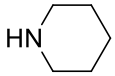
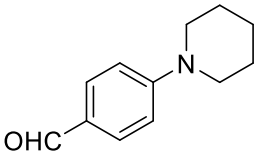
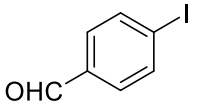
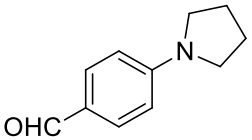
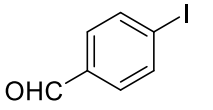
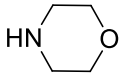
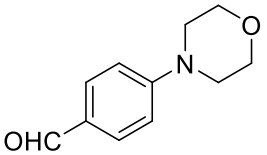
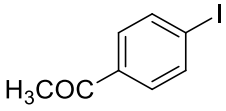
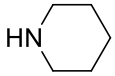
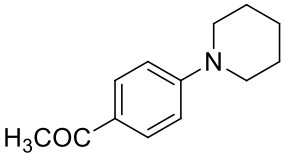
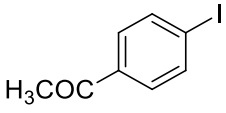
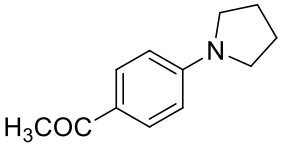
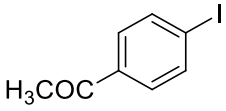
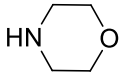
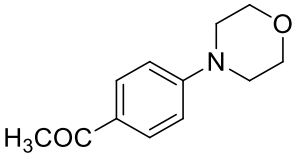
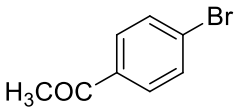
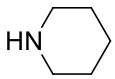
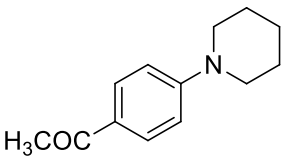
[b] Yield was determined using GC-MS

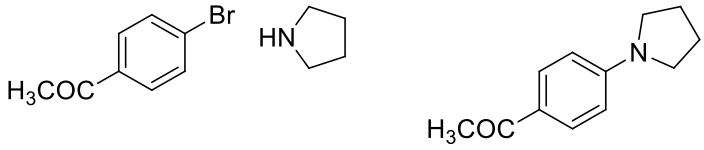
[c] Traditional heating

[d] microwave heating

Table S3: Substrate scope of amination of different aryl halides with different amines using Fe_3O_4@CS@AF@Cu[a]

Entry	Aryl halide	Amine	Product	Time (h)	Yield[b] (%)	TON[c]	TOF[d] h^{-1}
1				1	98	156	156
2				1	98	156	156
3				1	99	157	157
4				1	98	156	156
5				1	99	157	157
6				1	97	154	154
7				1	96	152	152
8				1	95	151	151

9				1	96	152	152
10				1	94	149	149
11				1	99	157	157
12				1	98	156	156
13				1	96	152	152
14				1	97	154	154
15				2	85	135	67
16				3	80	127	42
17				1	97	154	154

18		3	75	119	40

[a] Reaction conditions: aryl halide (1.0 mmol), amine (1.1 mmol), K_2CO_3 (2.0 mmol), H_2O (5 ml), catalyst Fe_3O_4@CS@Af@Cu (5 mg, 0.63 mol% Cu)

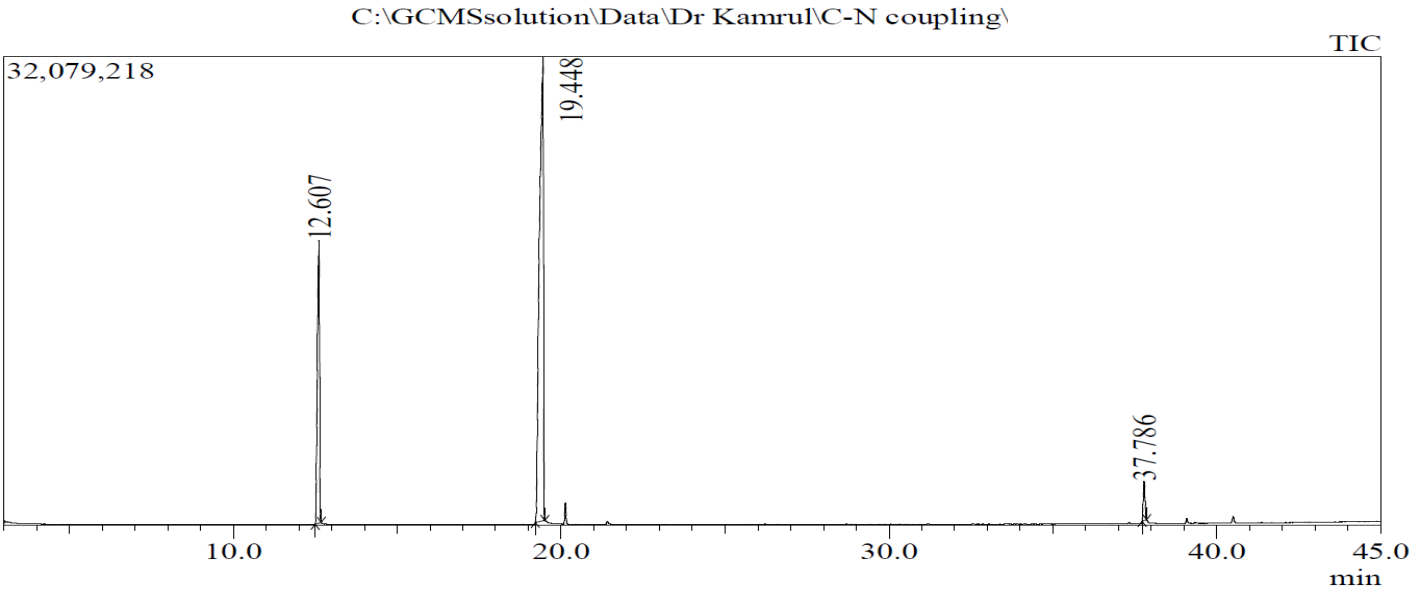
[b] Yield (%) was measured by GCMS and ^1H NMR

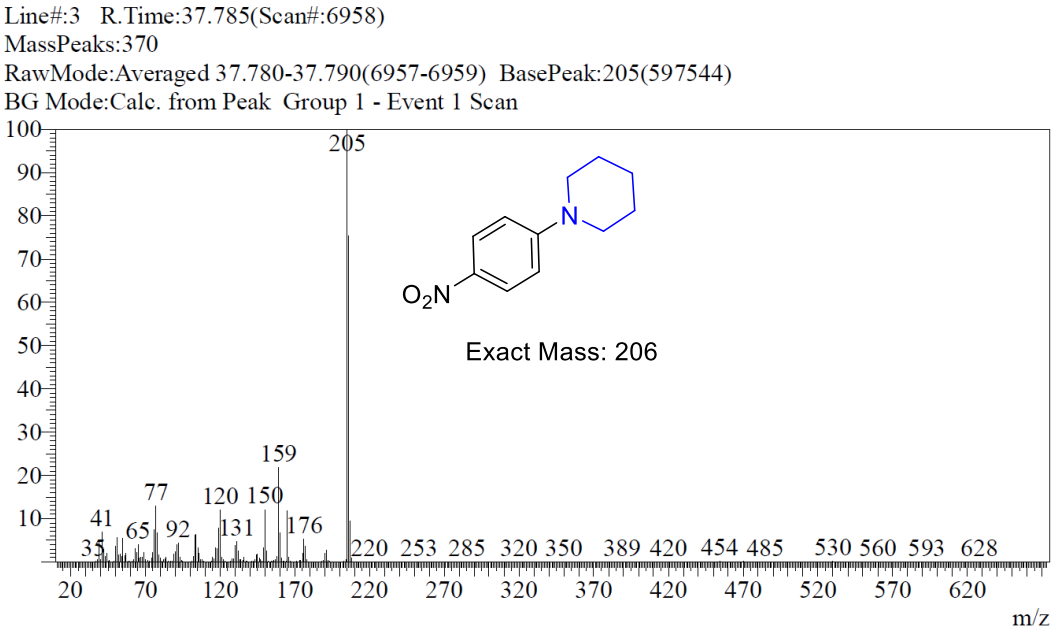
[c] Turn Over Number (TON) = number of moles of product/ number of moles of catalyst

[d] Turn Over Frequency (TOF) = number of moles of product formed per mole of catalyst/ hour

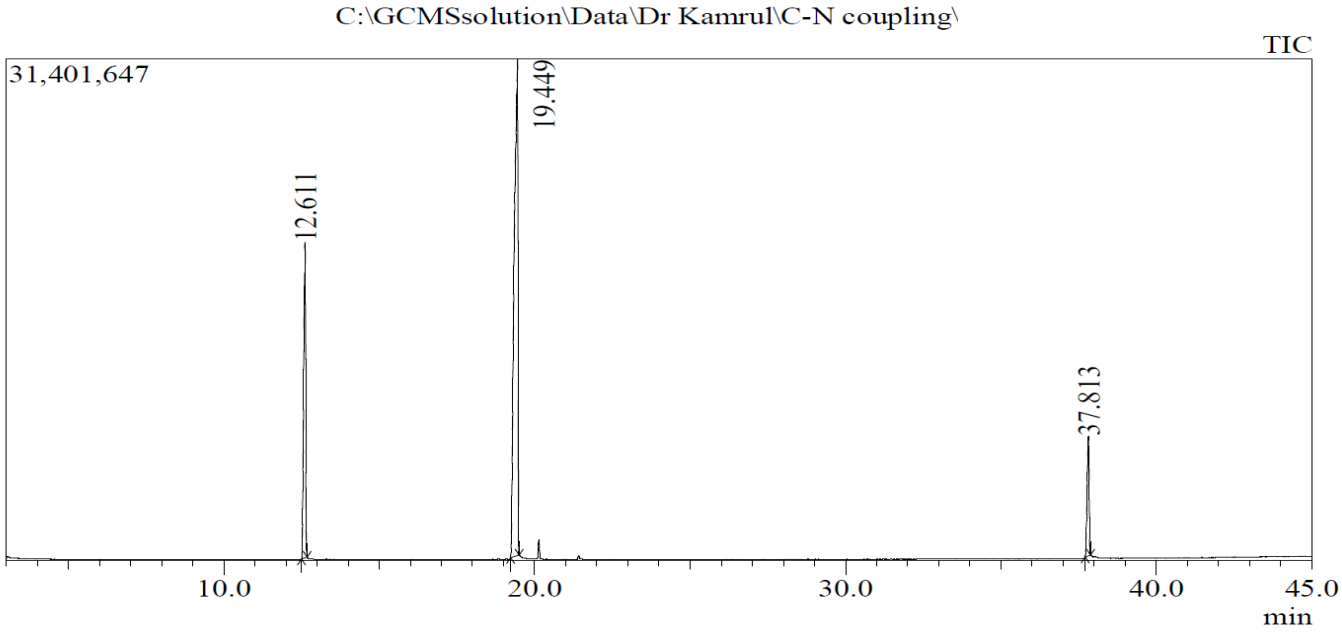
5. GC traces and mass spectra of selected products given in the Table 1

Entry 3: 4-Nitrobenzene internal standard, R_t =12.60 min. 1-Bromo-4-nitrobenzene, R_t =19.44 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.78 min.

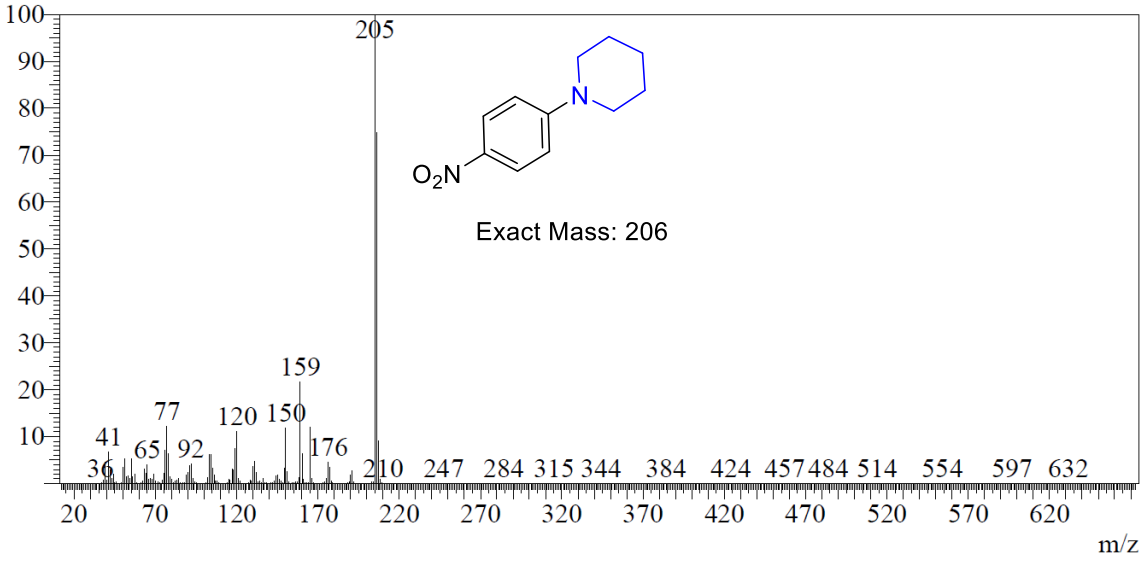




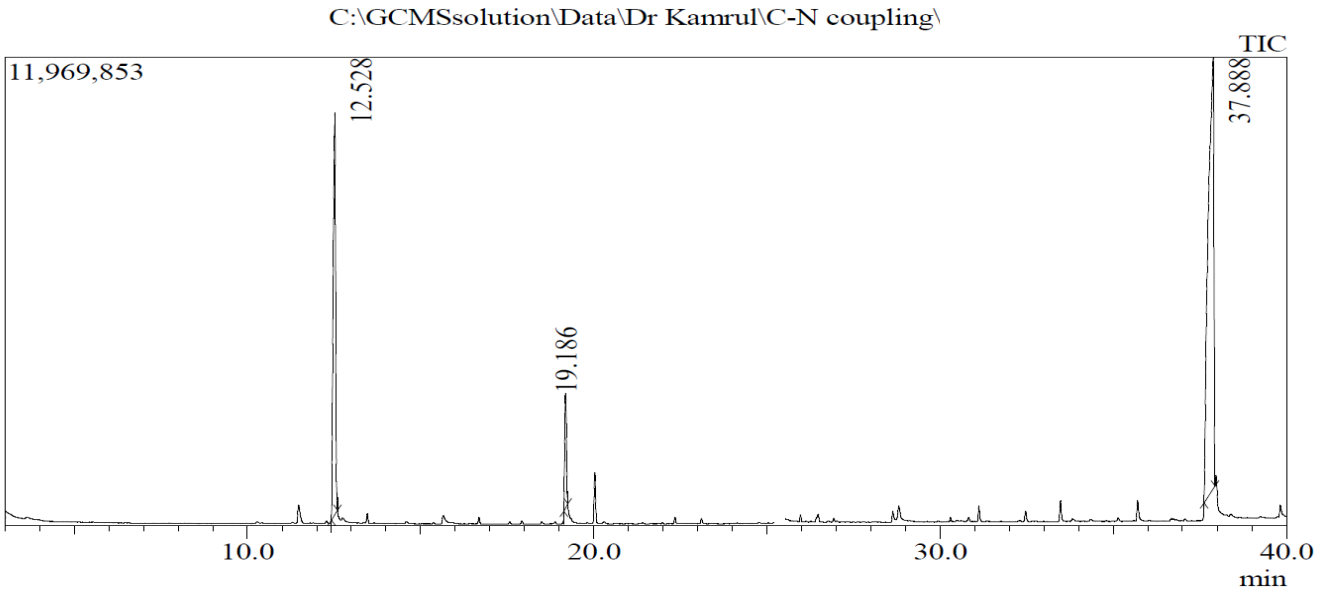
Entry 4: 4-Nitrobenzene internal standard, R_t =12.61 min. 1-Bromo-4-nitrobenzene, R_t =19.44 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.81 min.



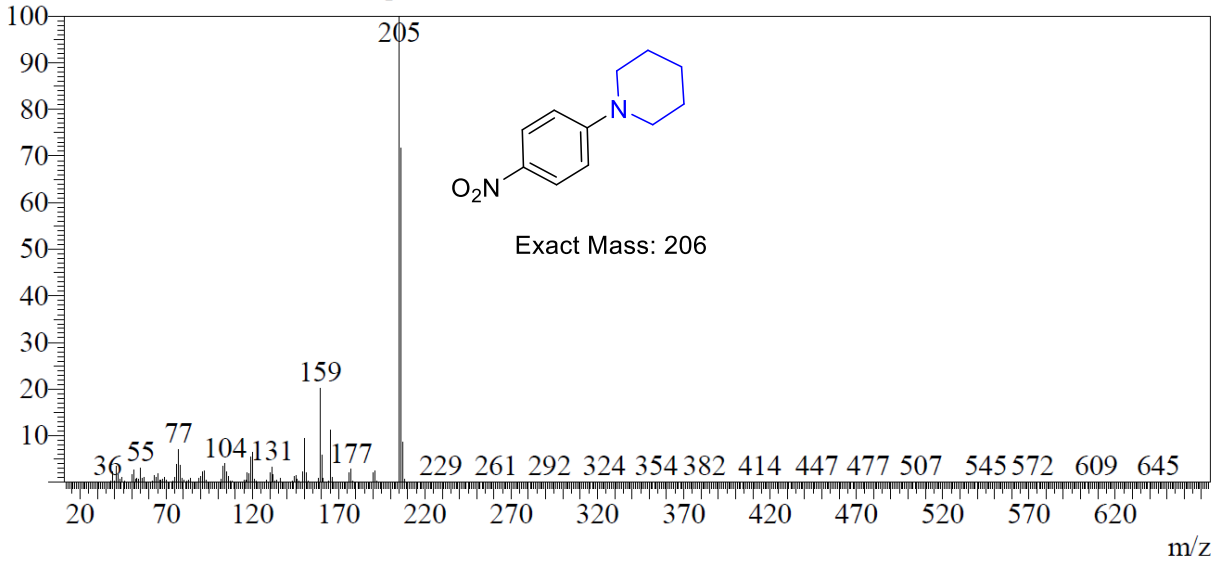
Line#:3 R.Time:37.815(Scan#:6964)
MassPeaks:367
RawMode:Averaged 37.810-37.820(6963-6965) BasePeak:205(1701773)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



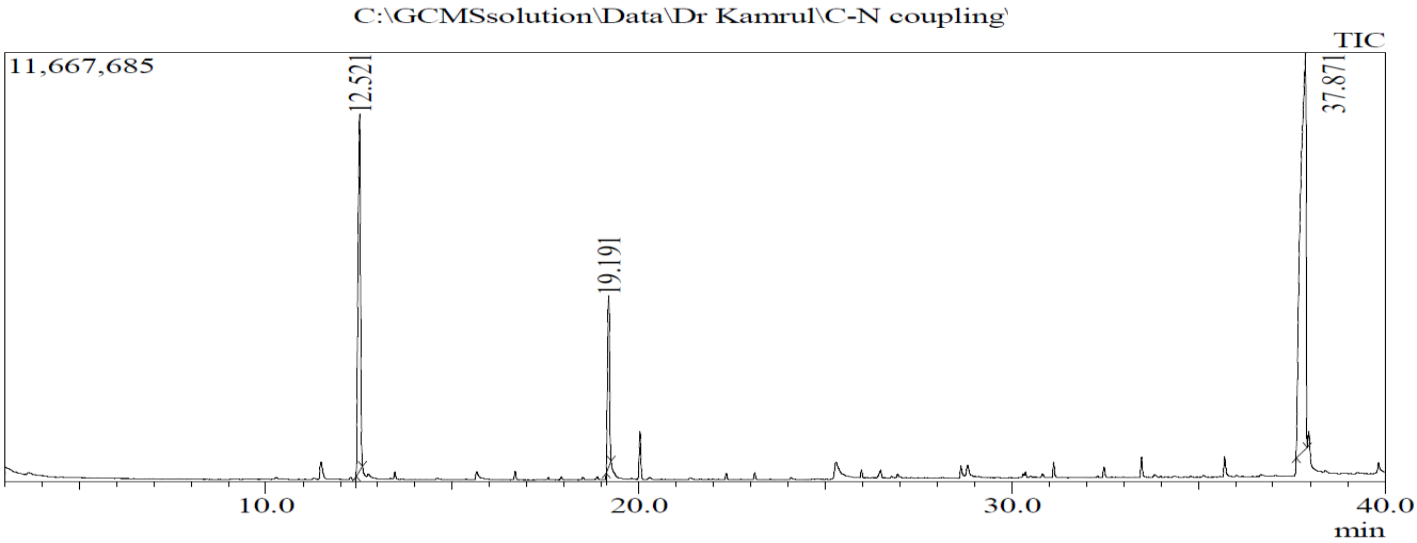
Entry 5: 4-Nitrobenzene internal standard, R_t =12.52 min. 1-Bromo-4-nitrobenzene, R_t =19.18 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.88 min.



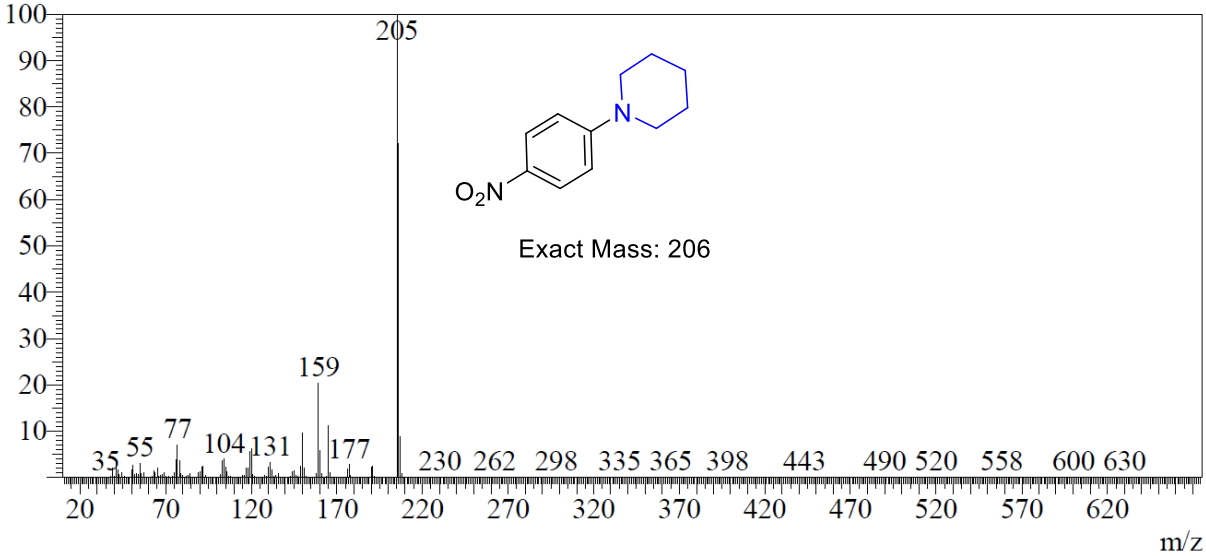
Line#:3 R.Time:37.890(Scan#:6979)
MassPeaks:269
RawMode:Averaged 37.885-37.895(6978-6980) BasePeak:205(3208884)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



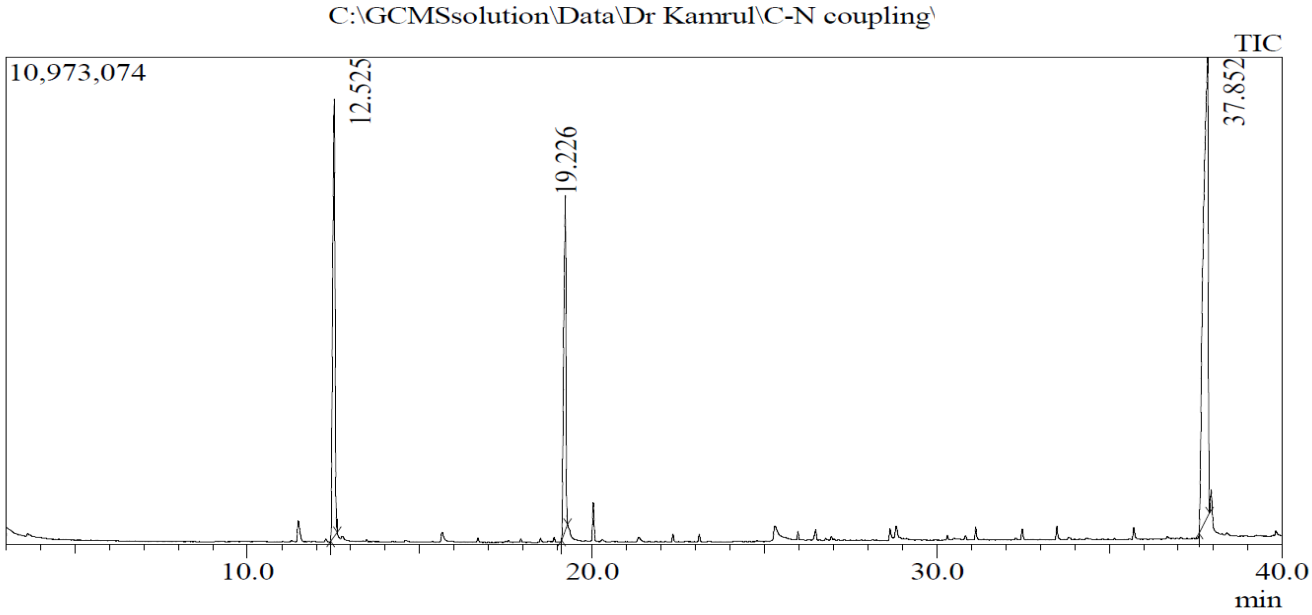
Entry 6: 4-Nitrobenzene internal standard, R_t =12.52 min. 1-Bromo-4-nitrobenzene, R_t =19.19 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.87 min.

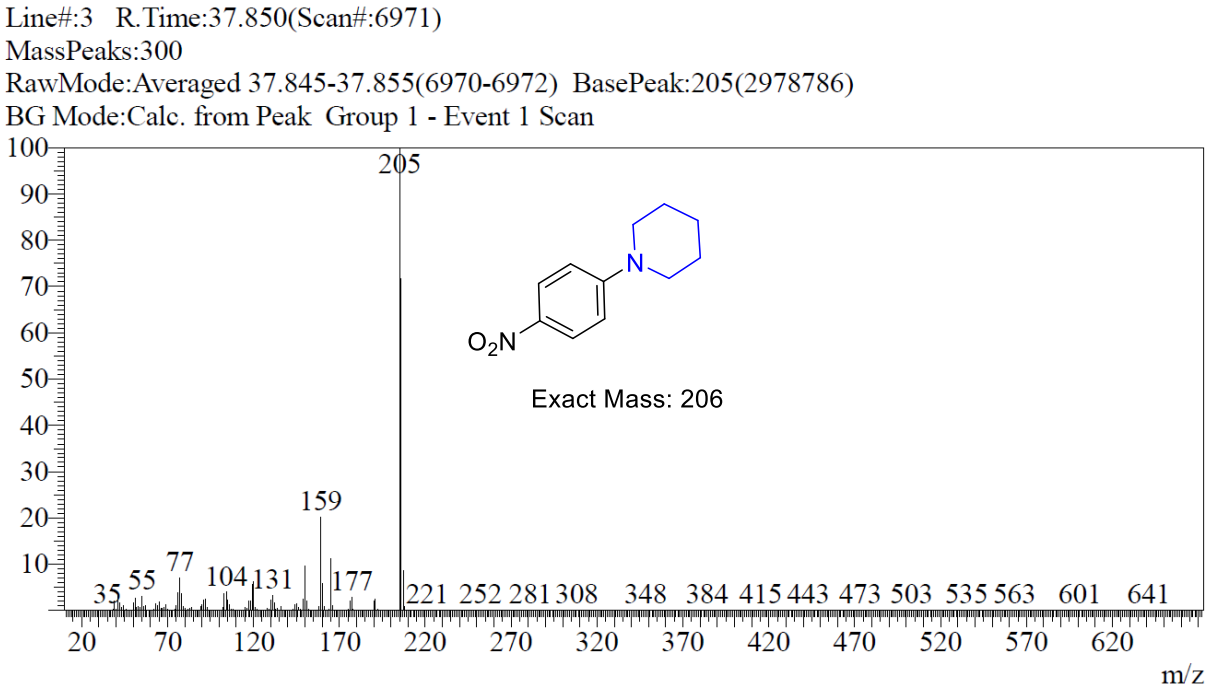


Line#:3 R.Time:37.870(Scan#:6975)
MassPeaks:262
RawMode:Averaged 37.865-37.875(6974-6976) BasePeak:205(3108078)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

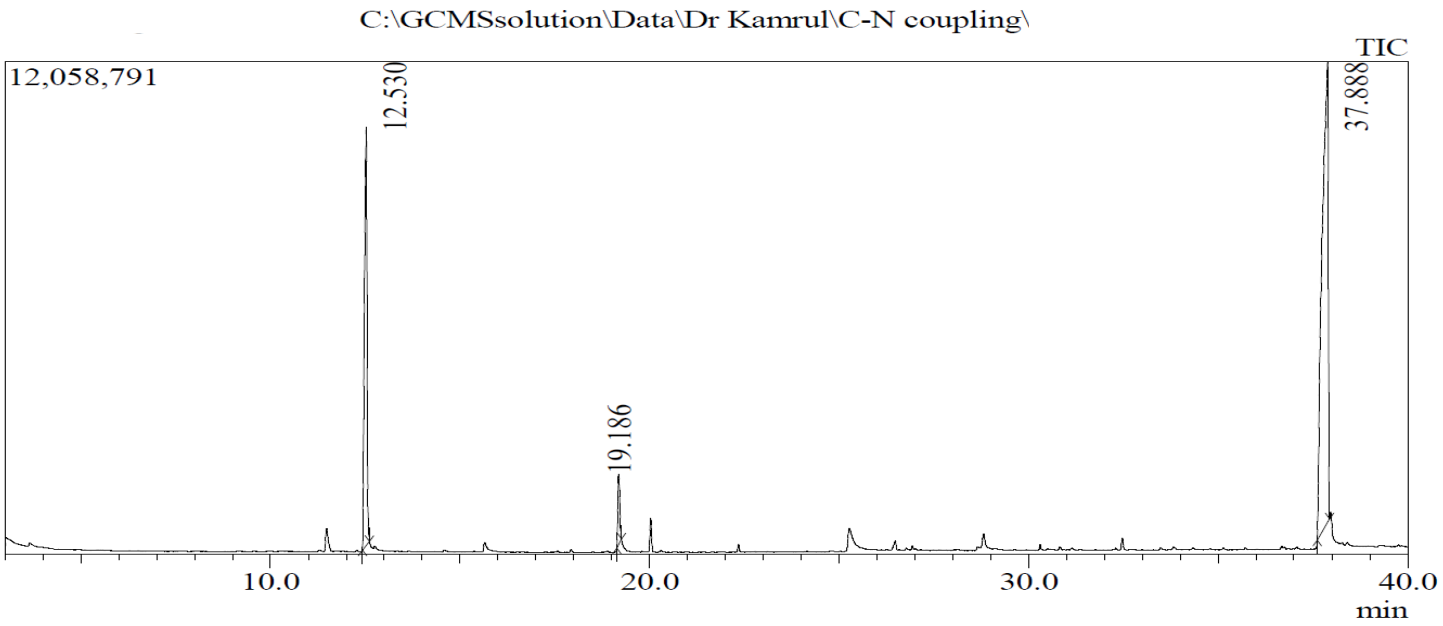


Entry 7: 4-Nitrobenzene internal standard, R_t =12.52 min. 1-Bromo-4-nitrobenzene, R_t =19.22 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.85 min.

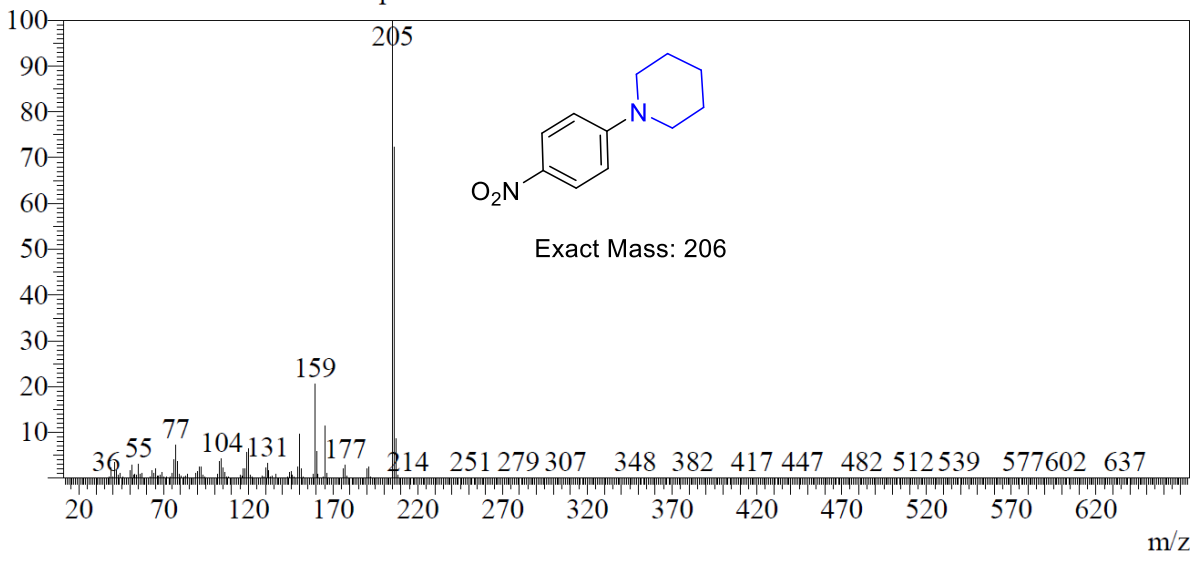




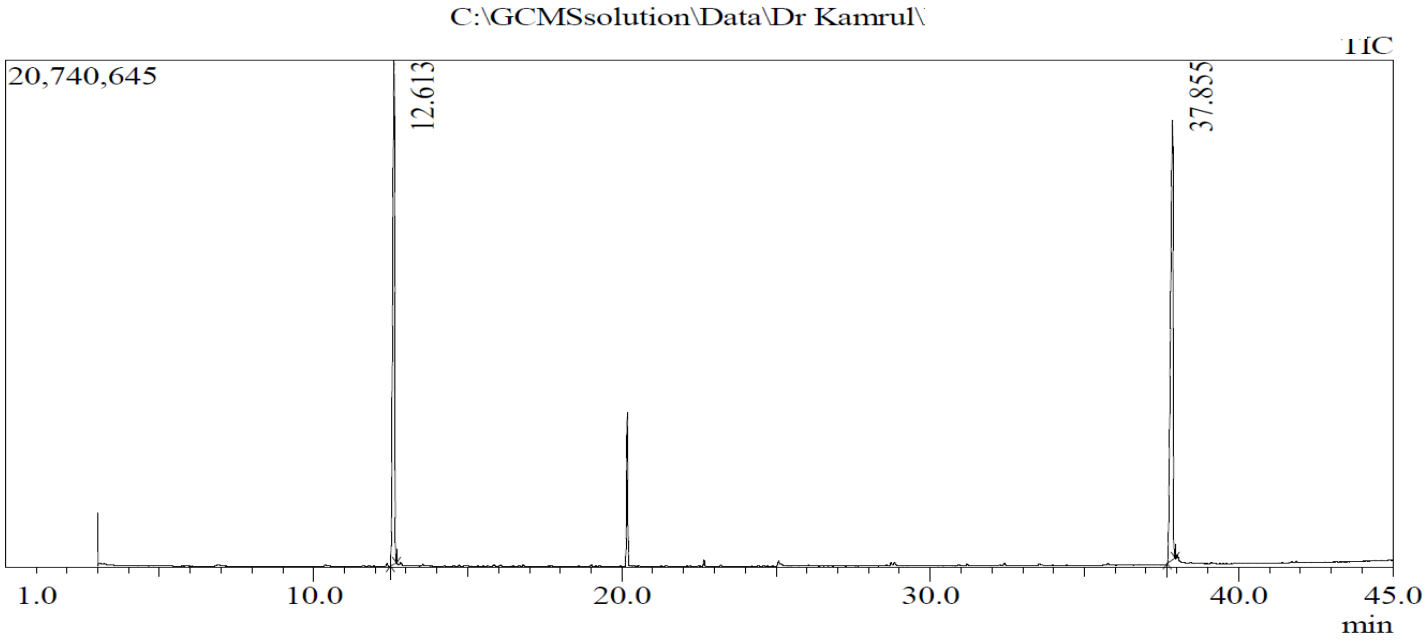
Entry 8: 4-Nitrobenzene internal standard, R_t =12.53 min. 1-Bromo-4-nitrobenzene, R_t =19.18 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.88 min.



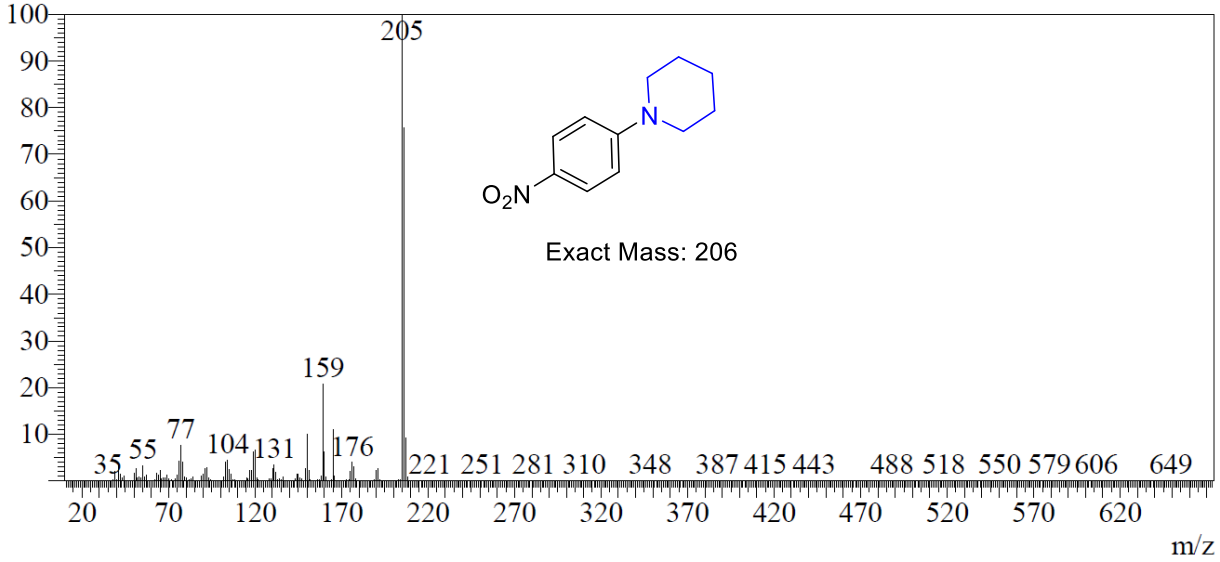
Line#:3 R.Time:37.890(Scan#:6979)
MassPeaks:303
RawMode:Averaged 37.885-37.895(6978-6980) BasePeak:205(3219250)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



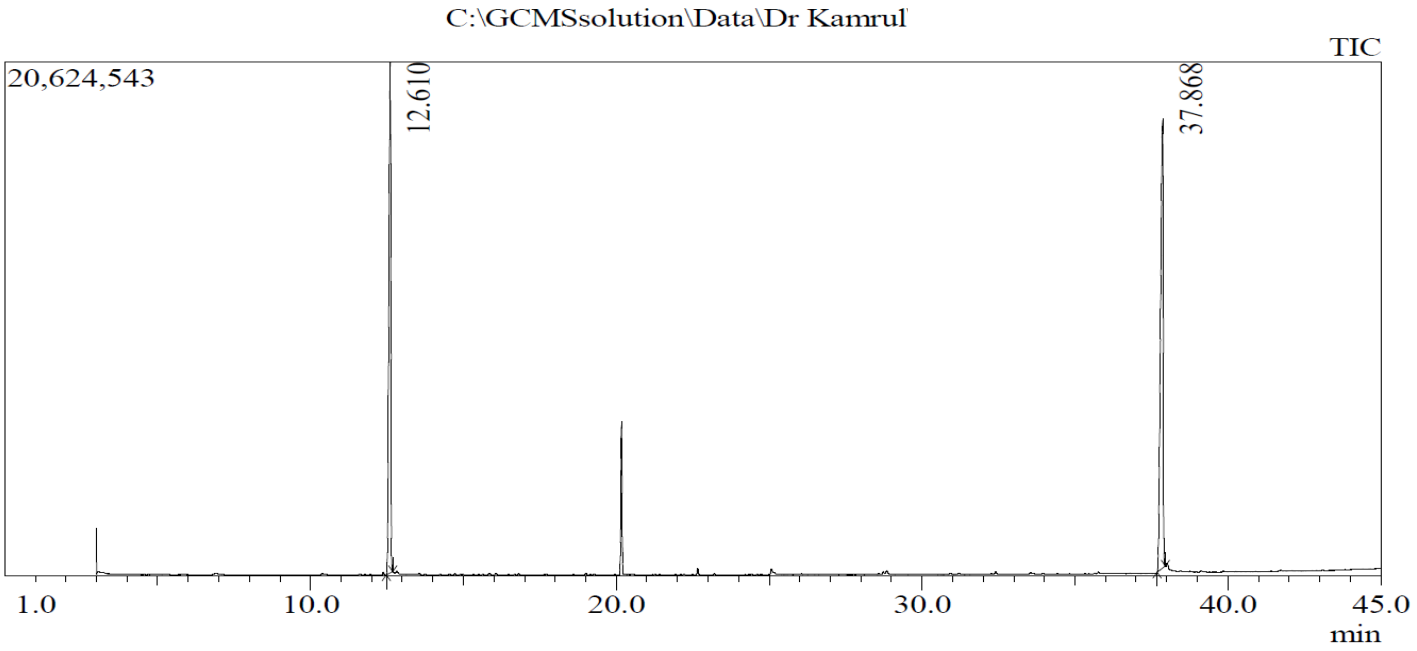
Entry 9: 4-Nitrobenzene internal standard, R_t =12.61 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.85 min.



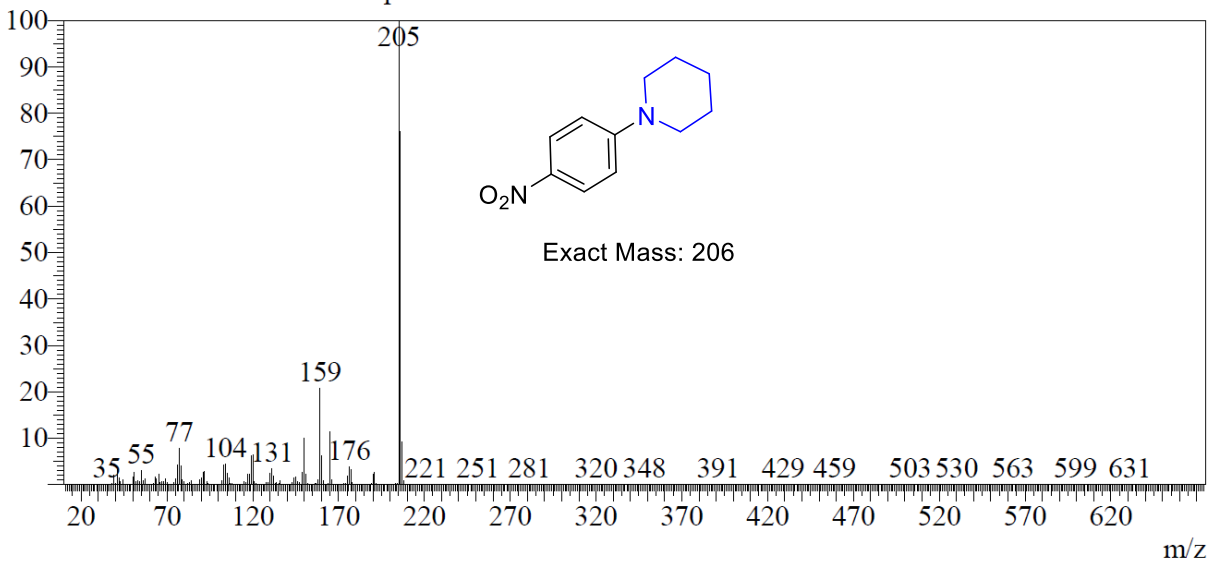
Line#:2 R.Time:37.855(Scan#:6972)
MassPeaks:410
RawMode:Averaged 37.850-37.860(6971-6973) BasePeak:205(4820990)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



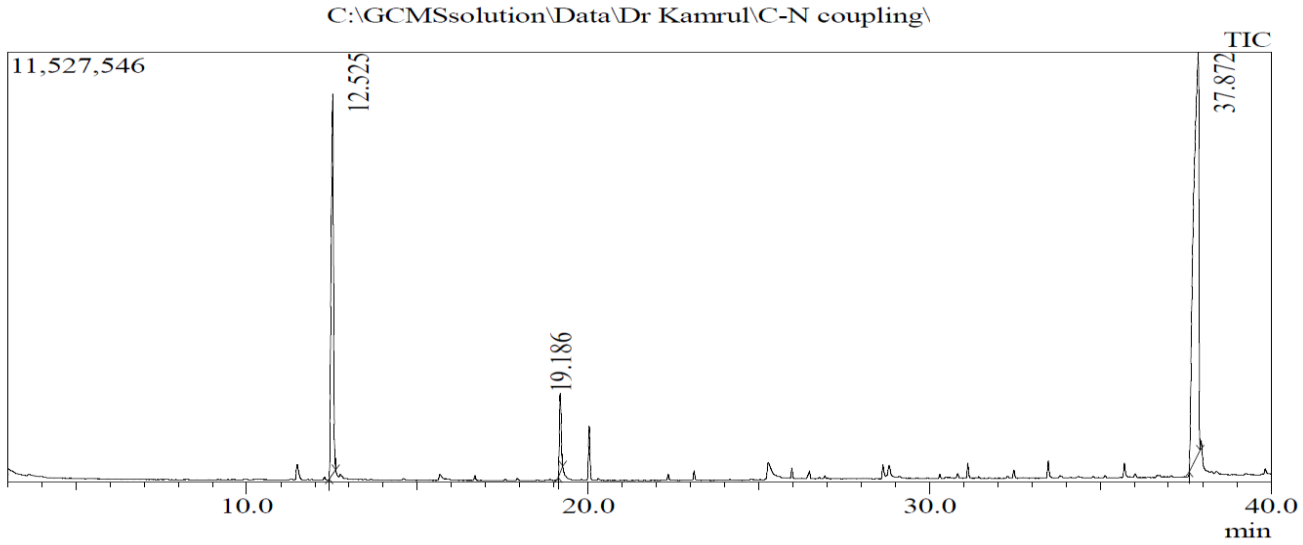
Entry 10: 4-Nitrobenzene internal standard, R_t =12.61 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.86 min.



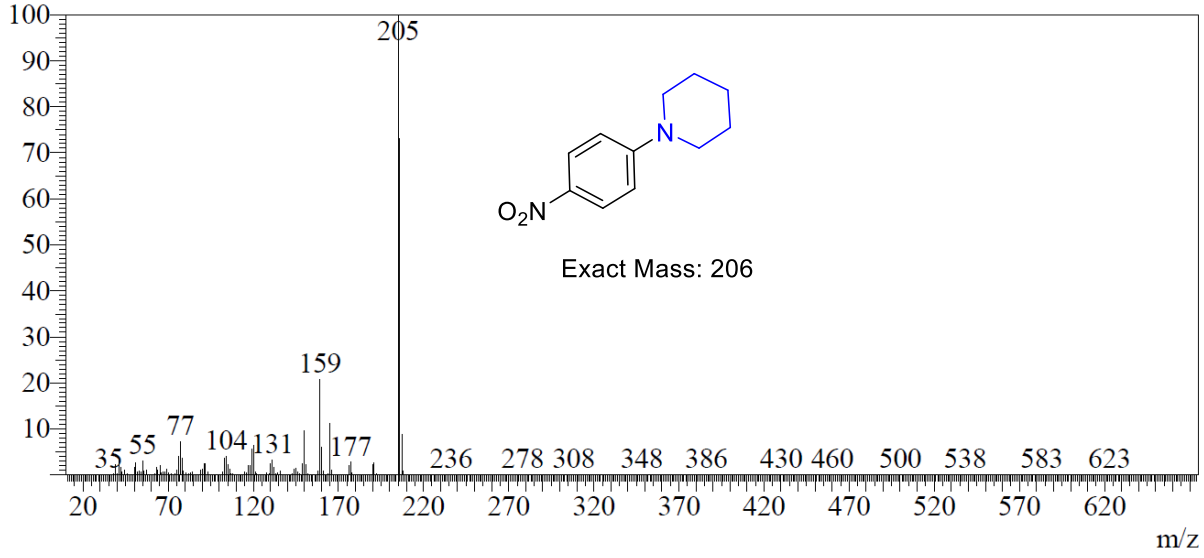
Line#:2 R.Time:37.870(Scan#:6975)
MassPeaks:399
RawMode:Averaged 37.865-37.875(6974-6976) BasePeak:205(4811899)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



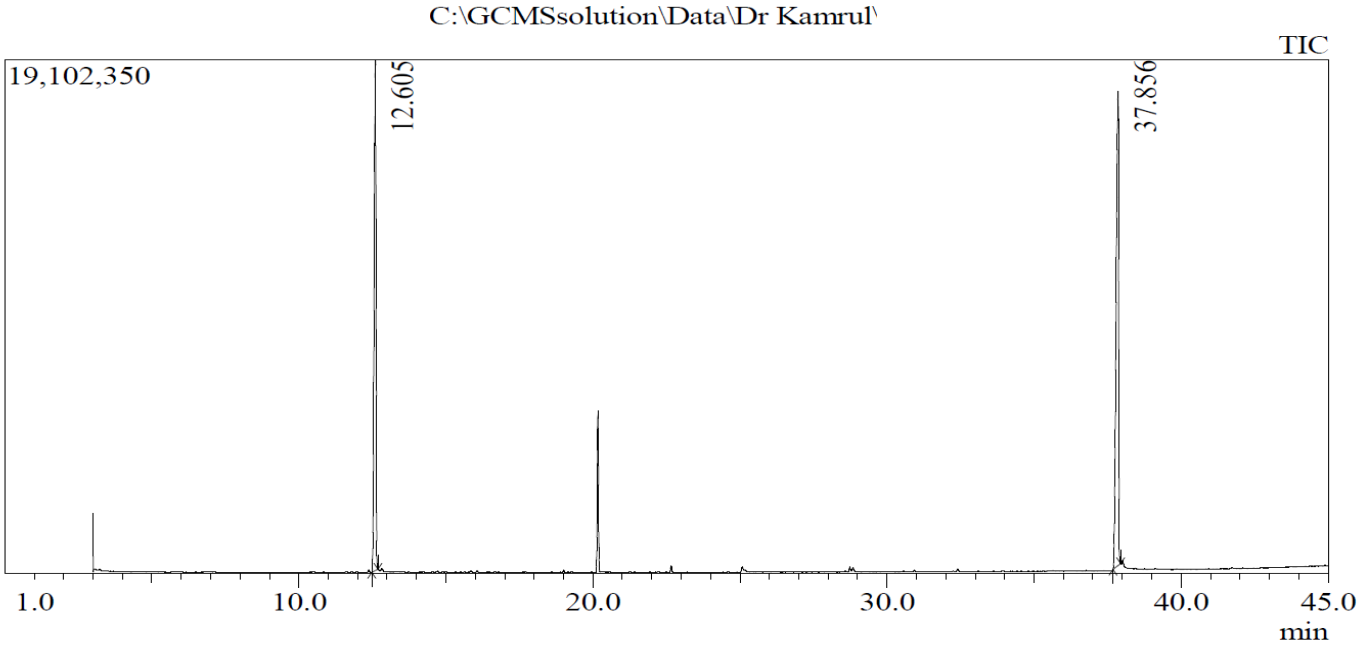
Entry 11: 4-Nitrobenzene internal standard, R_t =12.61 min. 1-Bromo-4-nitrobenzene, R_t =19.18 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.87 min.



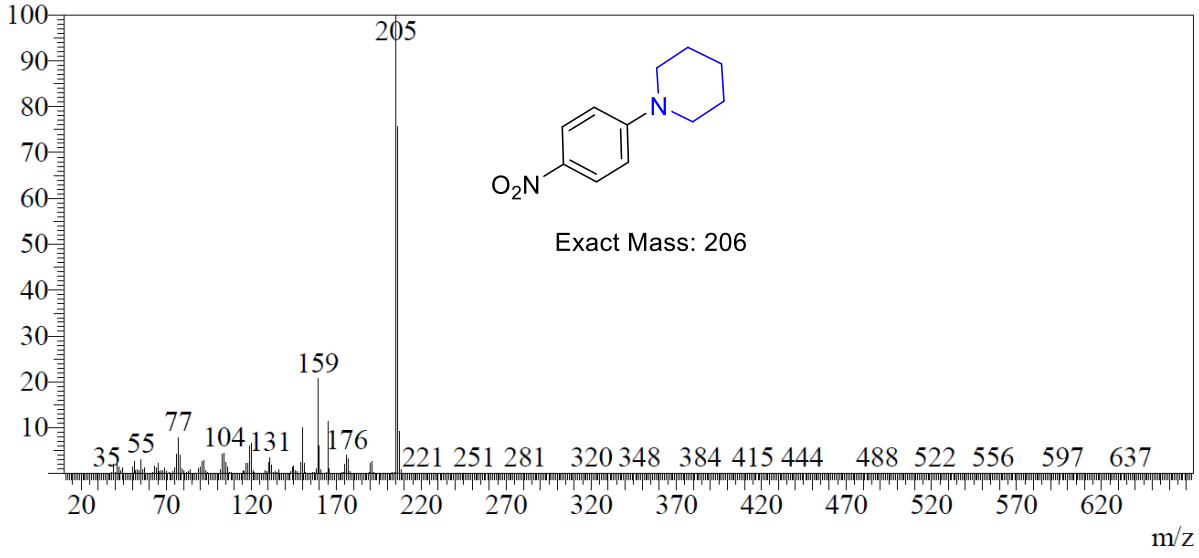
Line#:3 R.Time:37.870(Scan#:6975)
MassPeaks:271
RawMode:Averaged 37.865-37.875(6974-6976) BasePeak:205(3071390)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



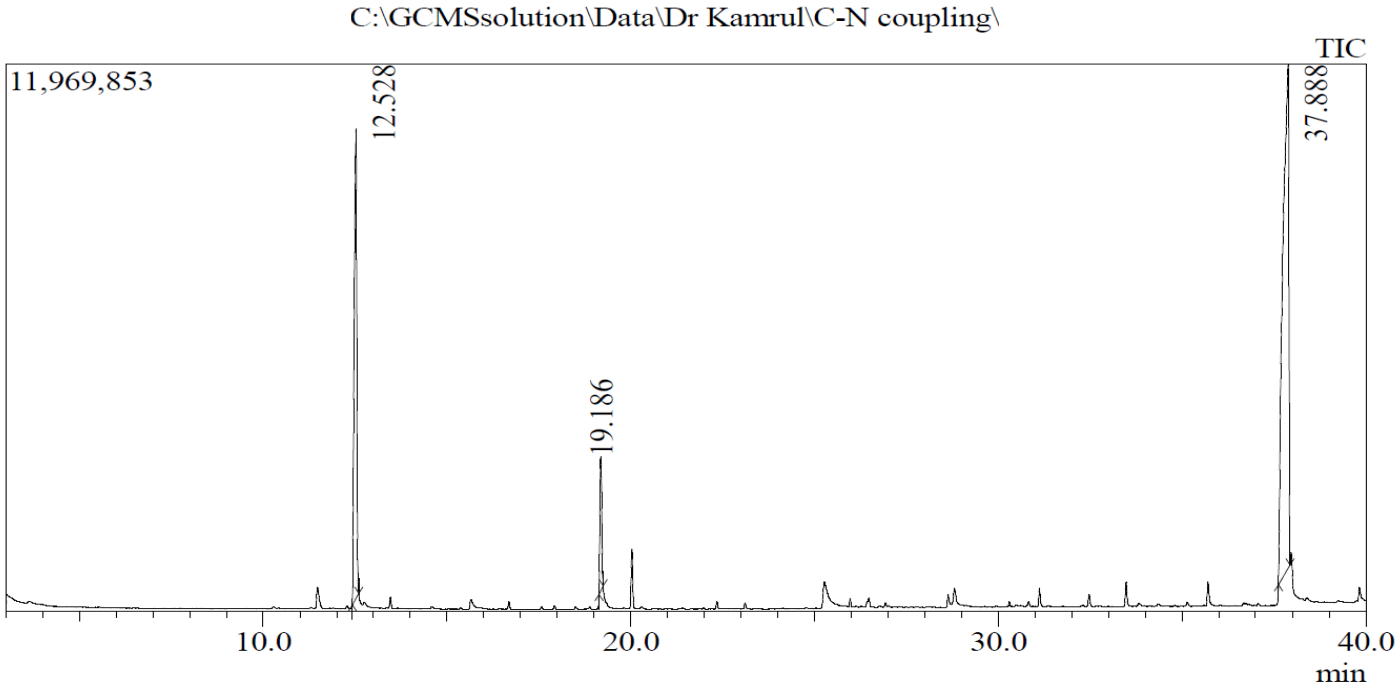
Entry 12: 4-Nitrobenzene internal standard, R_t =12.60 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.85 min.



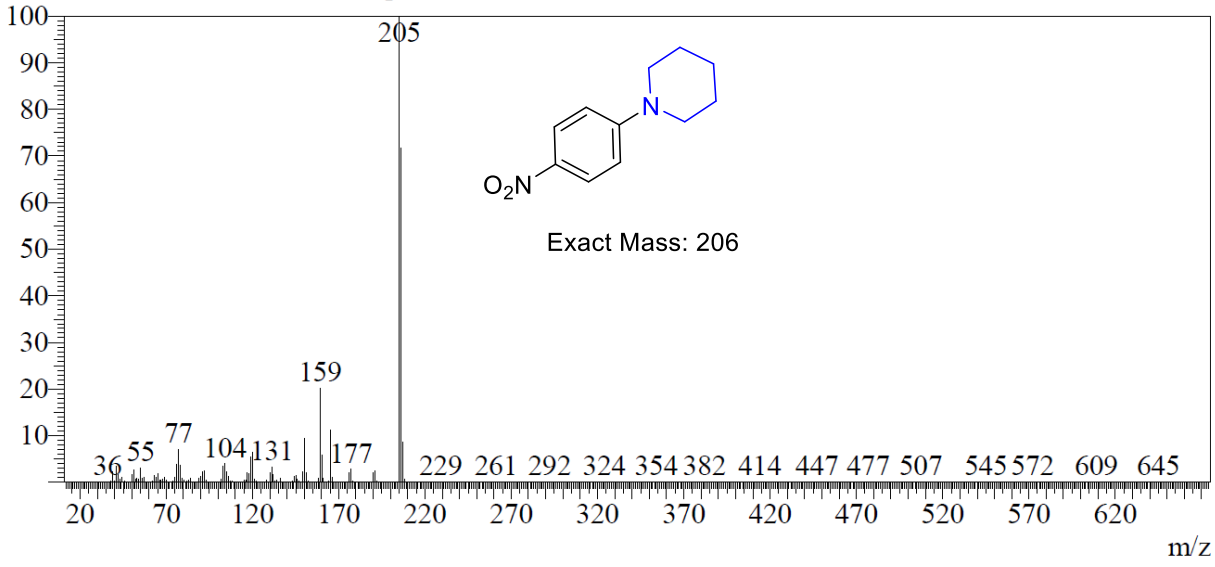
Line#:2 R.Time:37.855(Scan#:6972)
MassPeaks:358
RawMode:Averaged 37.850-37.860(6971-6973) BasePeak:205(4740901)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



Entry 13: 4-Nitrobenzene internal standard, R_t =12.52 min. 1-Bromo-4-nitrobenzene, R_t =19.18 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.88 min.

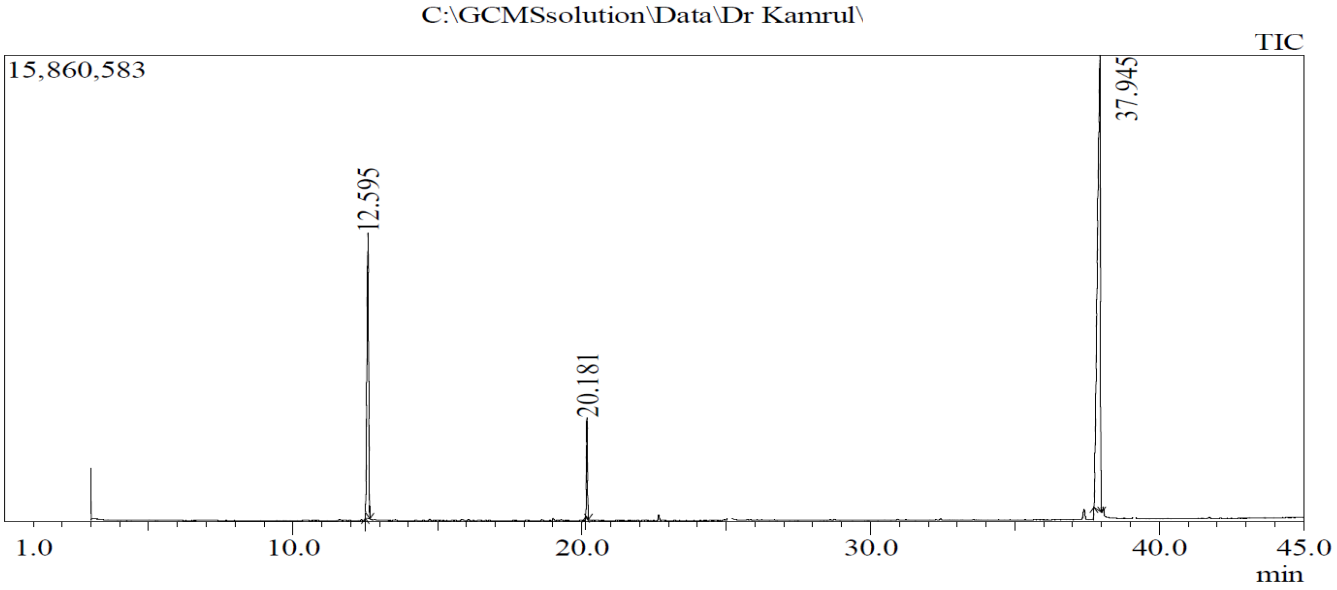


Line#:3 R.Time:37.890(Scan#:6979)
MassPeaks:269
RawMode:Averaged 37.885-37.895(6978-6980) BasePeak:205(3208884)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

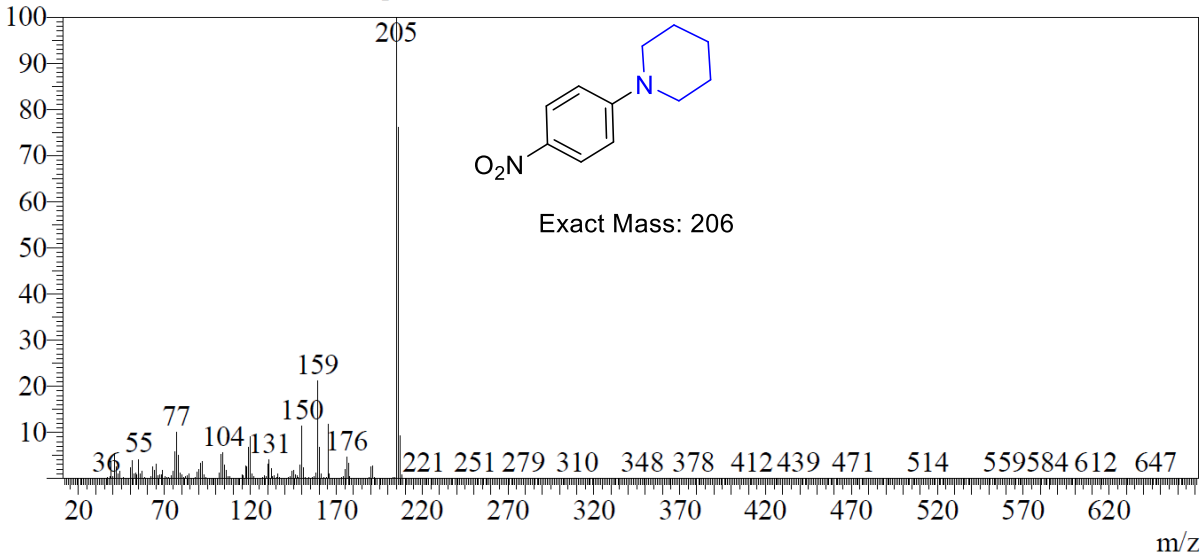


6. GC traces and mass spectra of selected products given in the Table 2

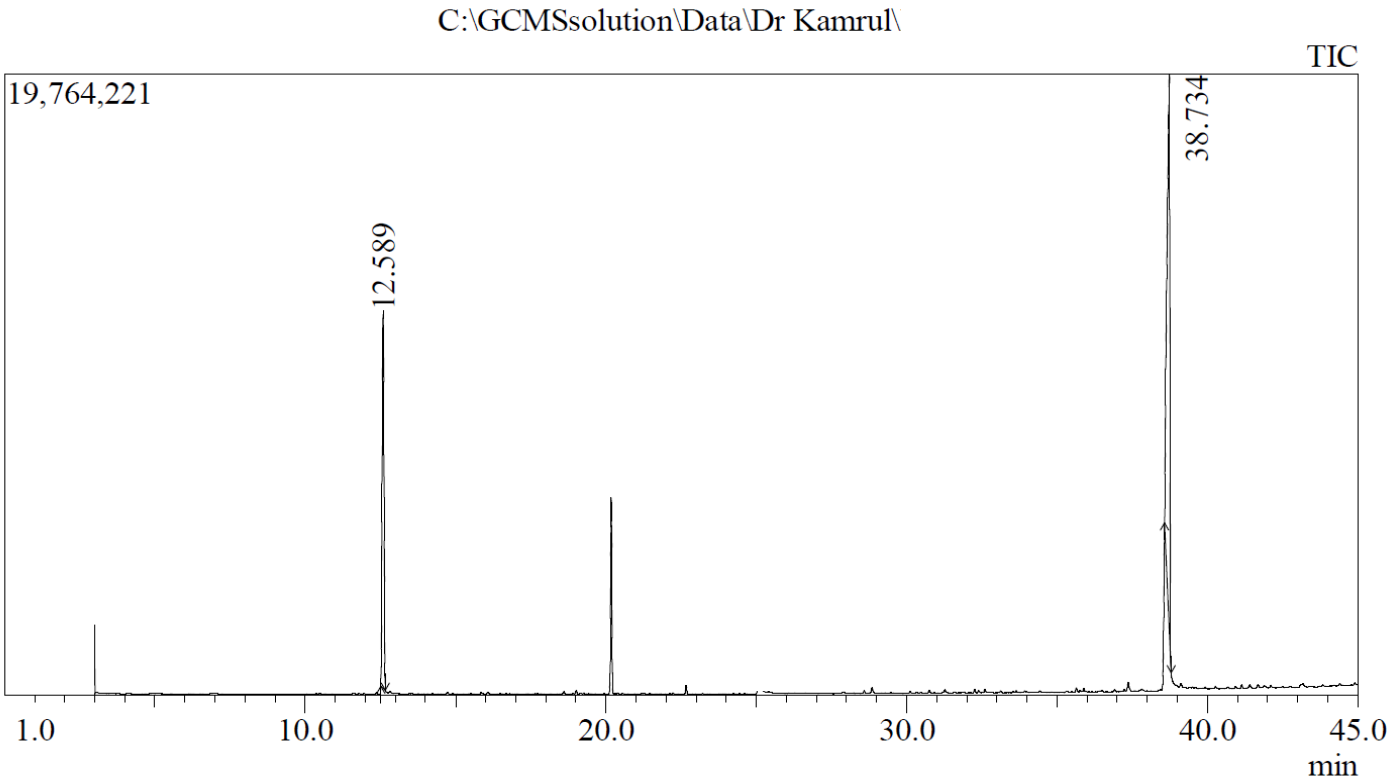
Entry 1: 4-Nitrobenzene internal standard, R_t =12.59min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.18 min. and 1-(4-nitrophenyl)piperidine, R_t =37.94 min.



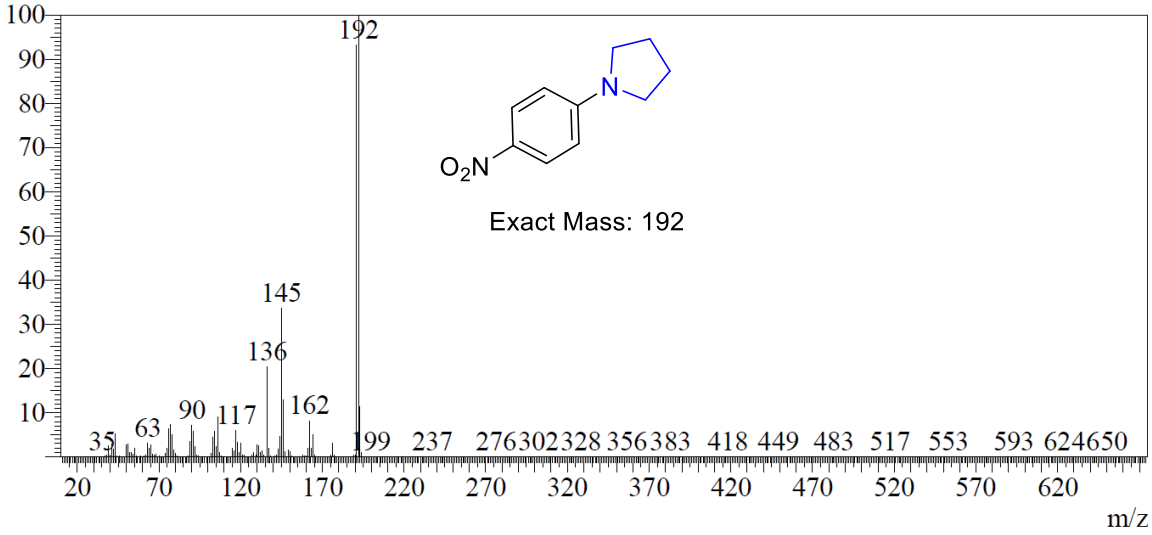
Line#:3 R.Time:37.945(Scan#:6990)
MassPeaks:400
RawMode:Averaged 37.940-37.950(6989-6991) BasePeak:205(3767681)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



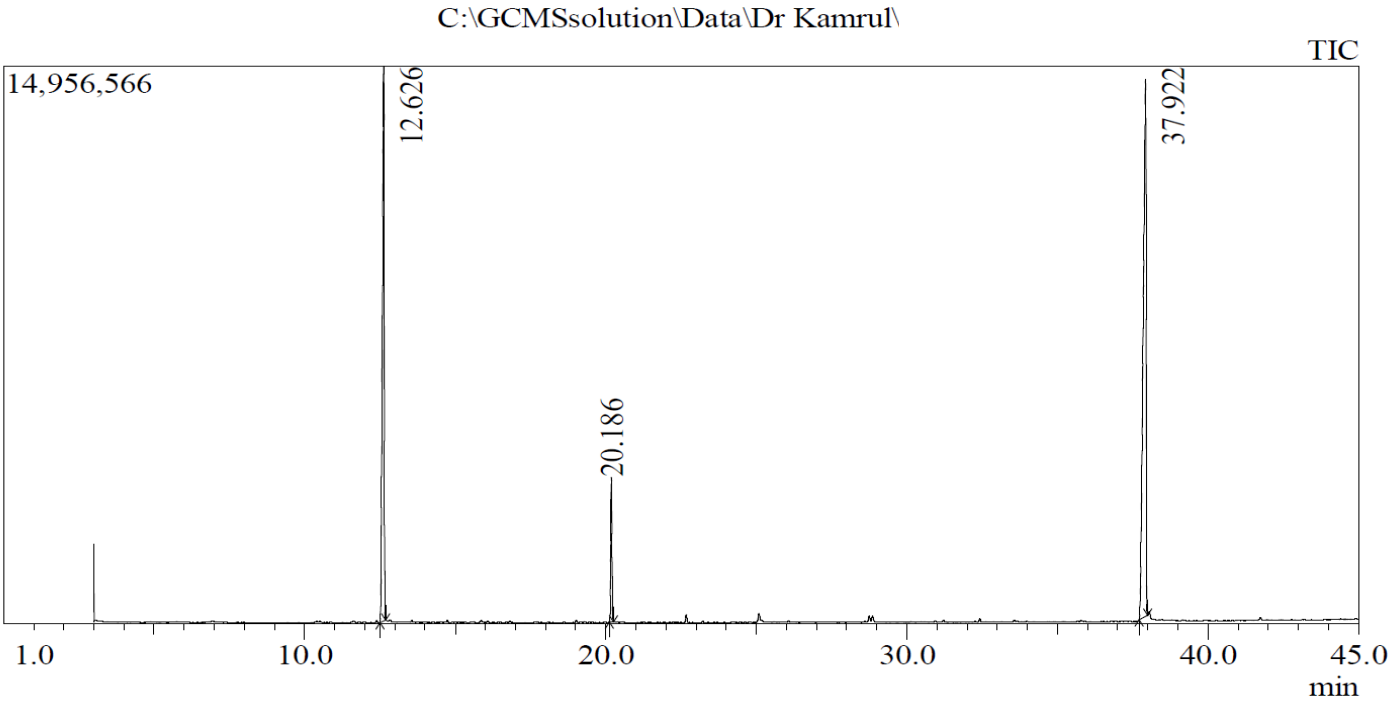
Entry 2: 4-Nitrobenzene internal standard, R_t =12.59 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.18 min. and 1-(4-nitrophenyl)pyrrolidine R_t =38.73 min.



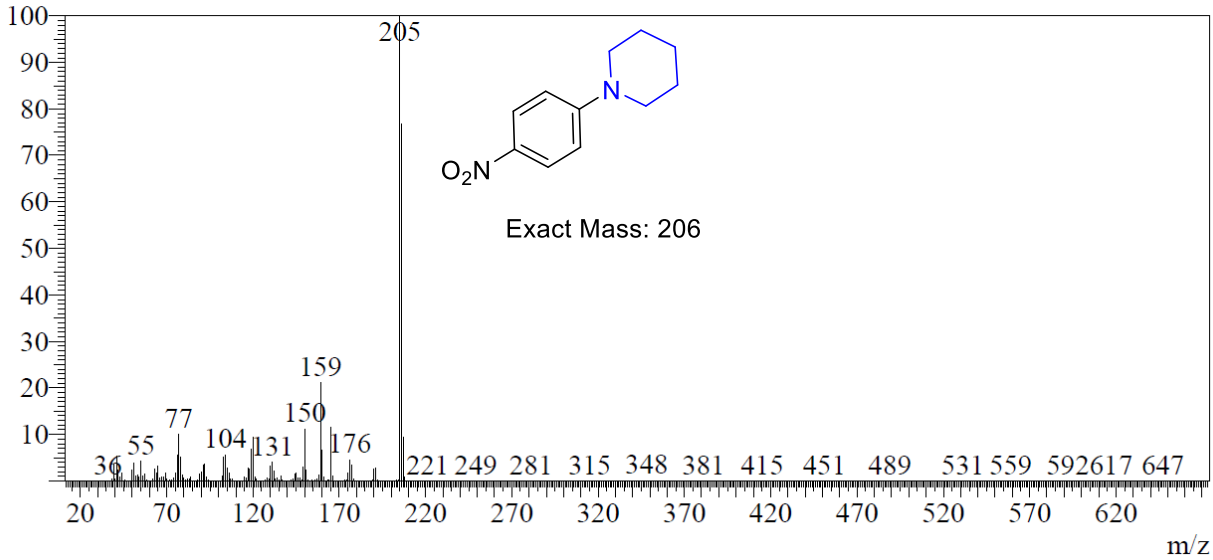
Line#:2 R.Time:38.735(Scan#:7148)
MassPeaks:274
RawMode:Averaged 38.730-38.740(7147-7149) BasePeak:192(4048493)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



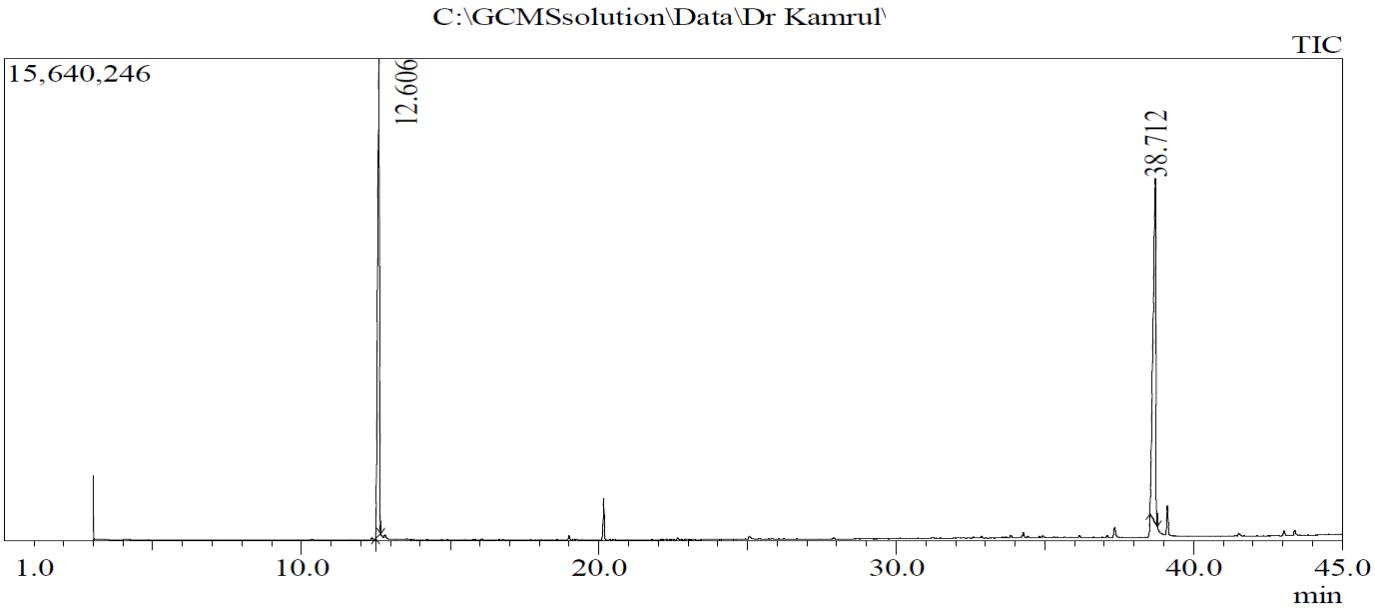
Entry 3: 4-Nitrobenzene internal standard, R_t =12.62 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.18 min. and and 1-(4-nitrophenyl)piperidine, R_t =37.92 min.



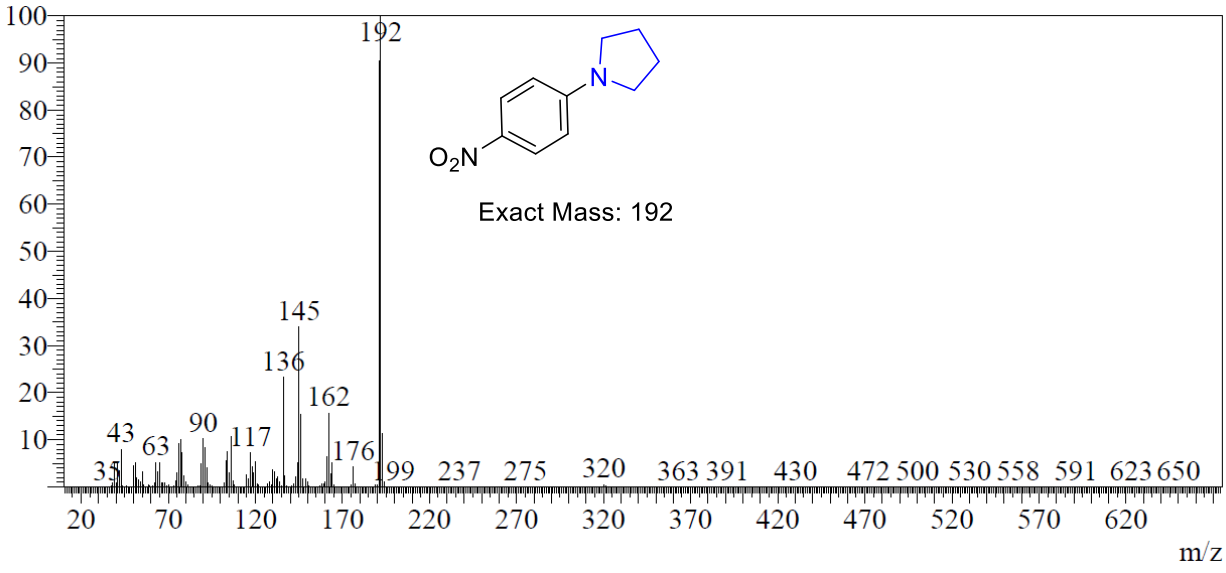
Line#:3 R.Time:37.920(Scan#:6985)
MassPeaks:419
RawMode:Averaged 37.915-37.925(6984-6986) BasePeak:205(3511030)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



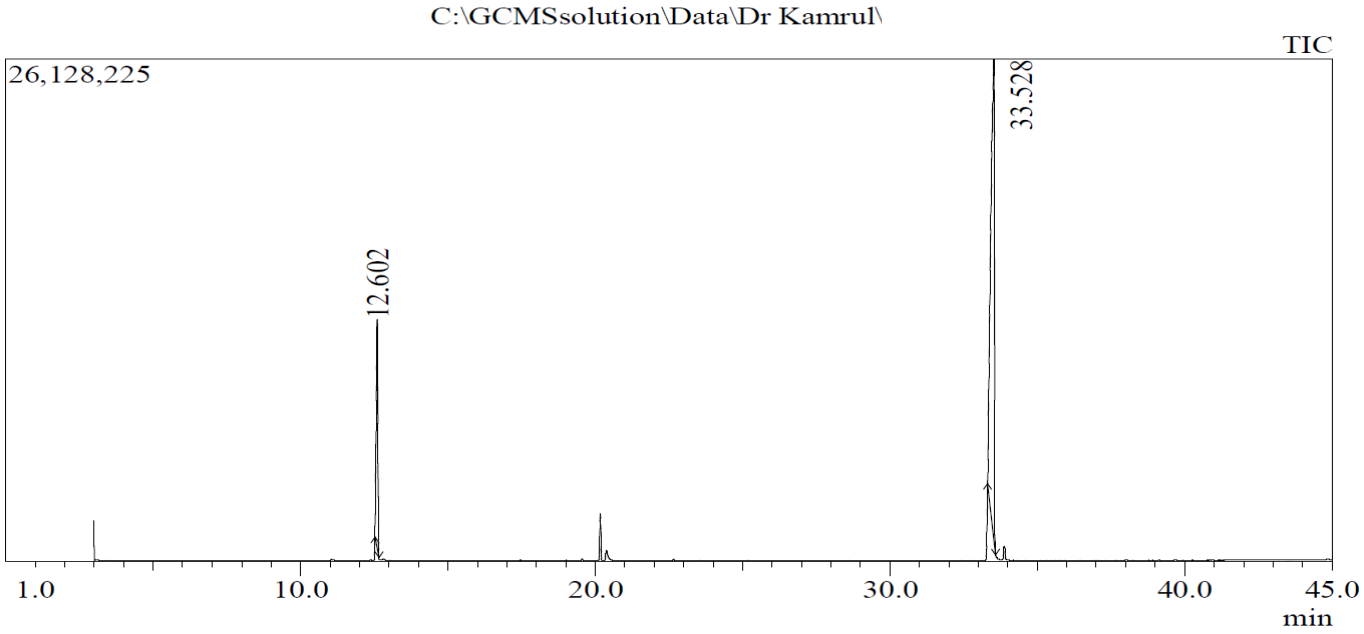
Entry 4: 4-Nitrobenzene internal standard, R_t =12.61 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.17 min. and 1-(4-nitrophenyl)pyrrolidine R_t =38.71 min.

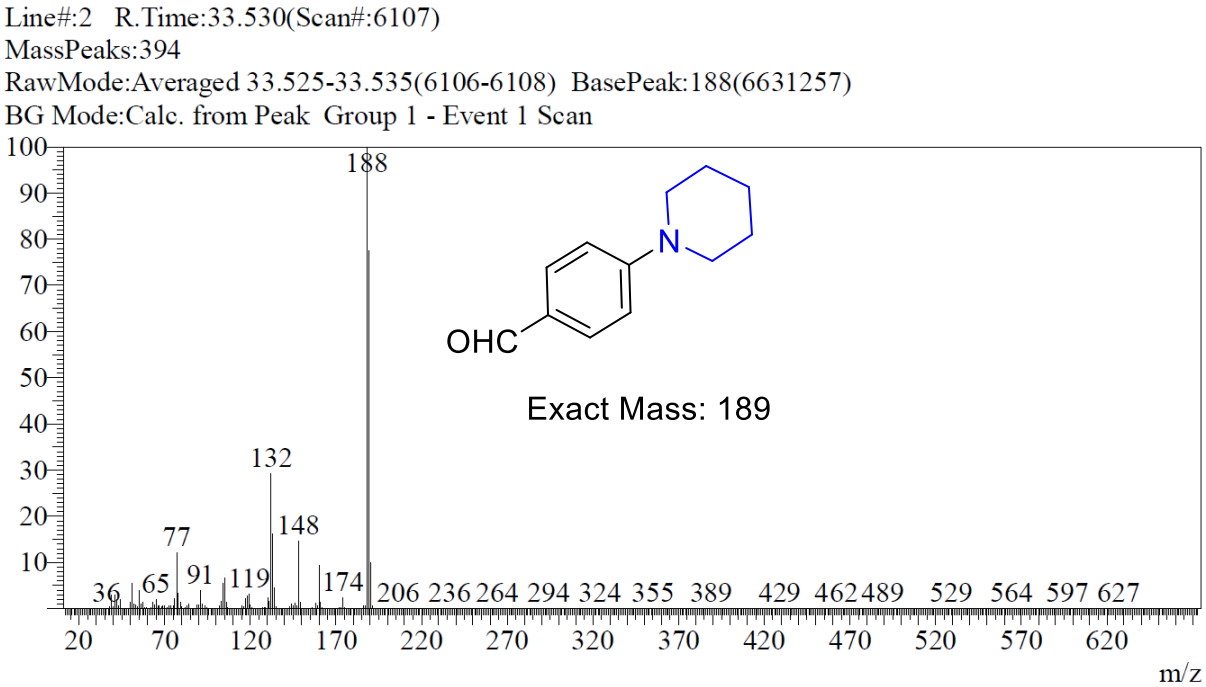


Line#:2 R.Time:38.710(Scan#:7143)
MassPeaks:419
RawMode:Averaged 38.705-38.715(7142-7144) BasePeak:192(2120331)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

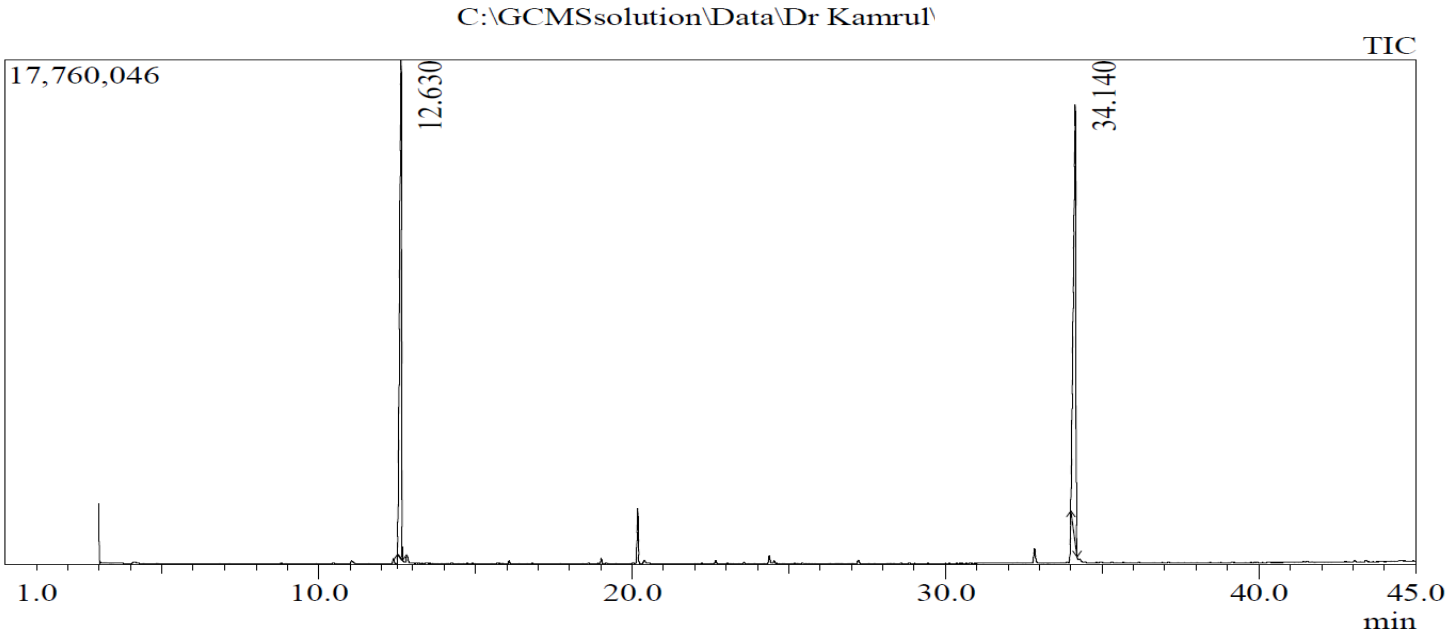


Entry 5: 4-Nitrobenzene internal standard, R_t =12.60 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.17 min. and 4-(piperidin-1-yl)benzaldehyde R_t =35.52 min.

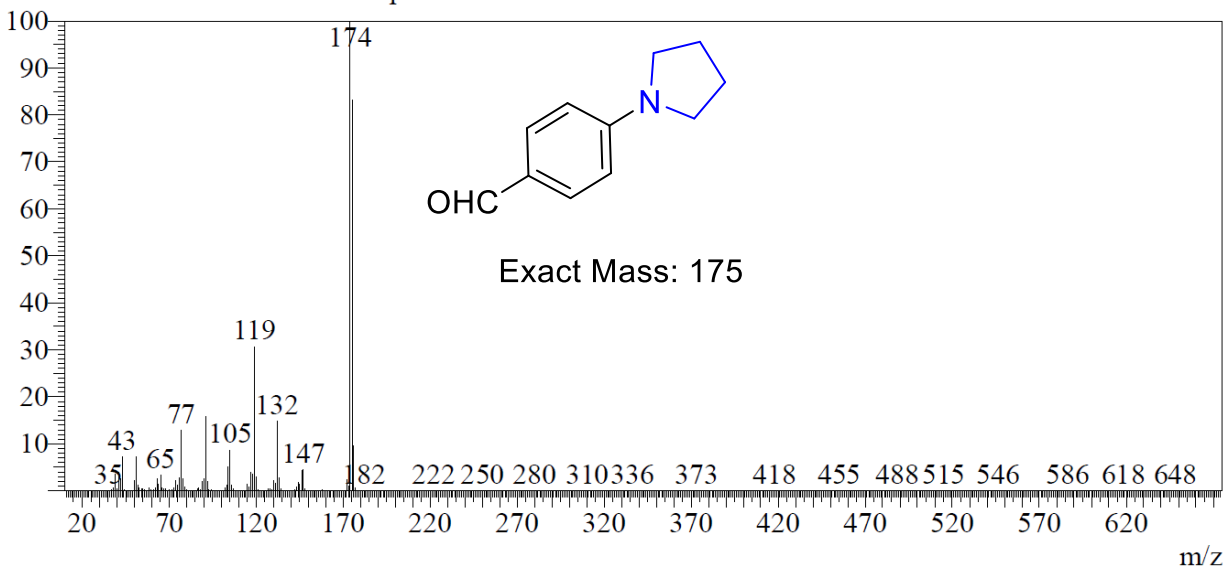




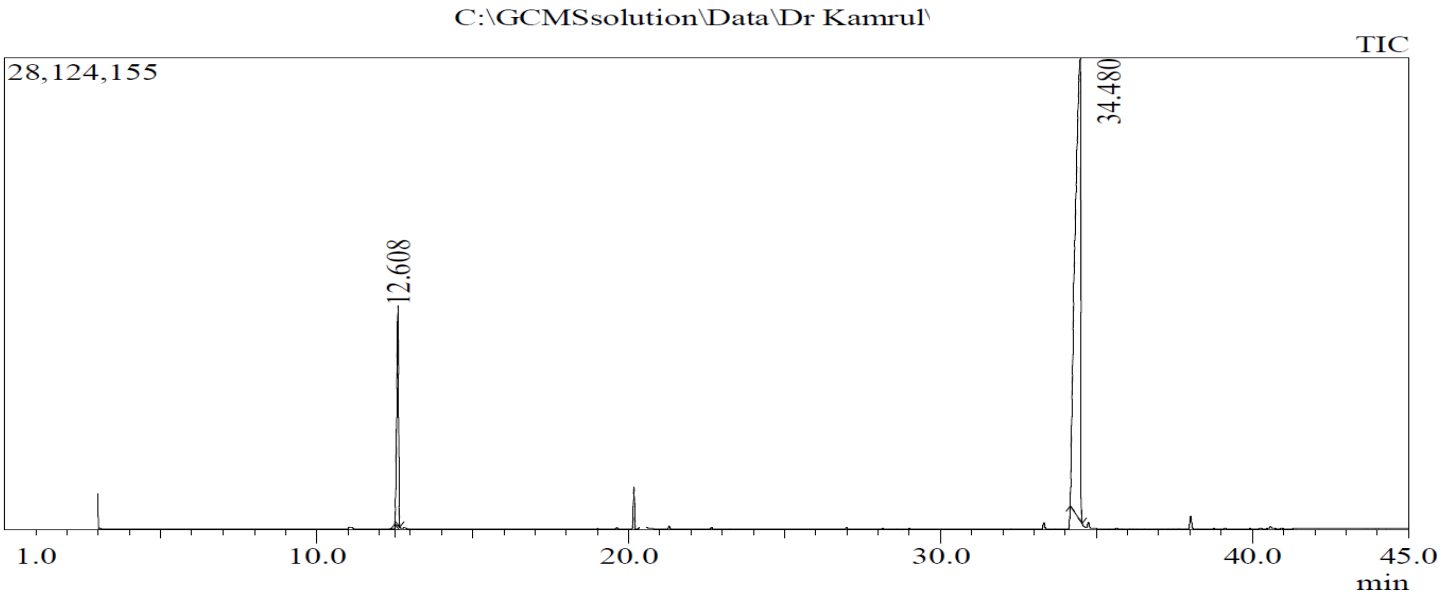
Entry 6: 4-Nitrobenzene internal standard, R_t =12.63 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.17 min. and 4-(pyrrolidin-1-yl)benzaldehyde R_t =34.14 min.



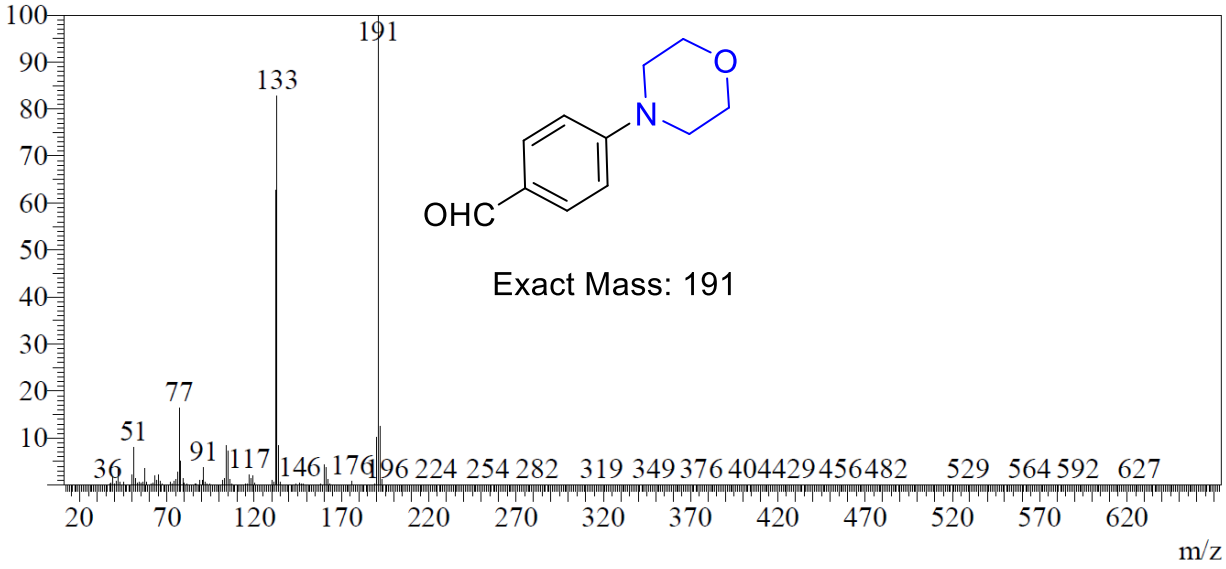
Line#:4 R.Time:34.140(Scan#:6229)
MassPeaks:374
RawMode:Averaged 34.135-34.145(6228-6230) BasePeak:174(3983851)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



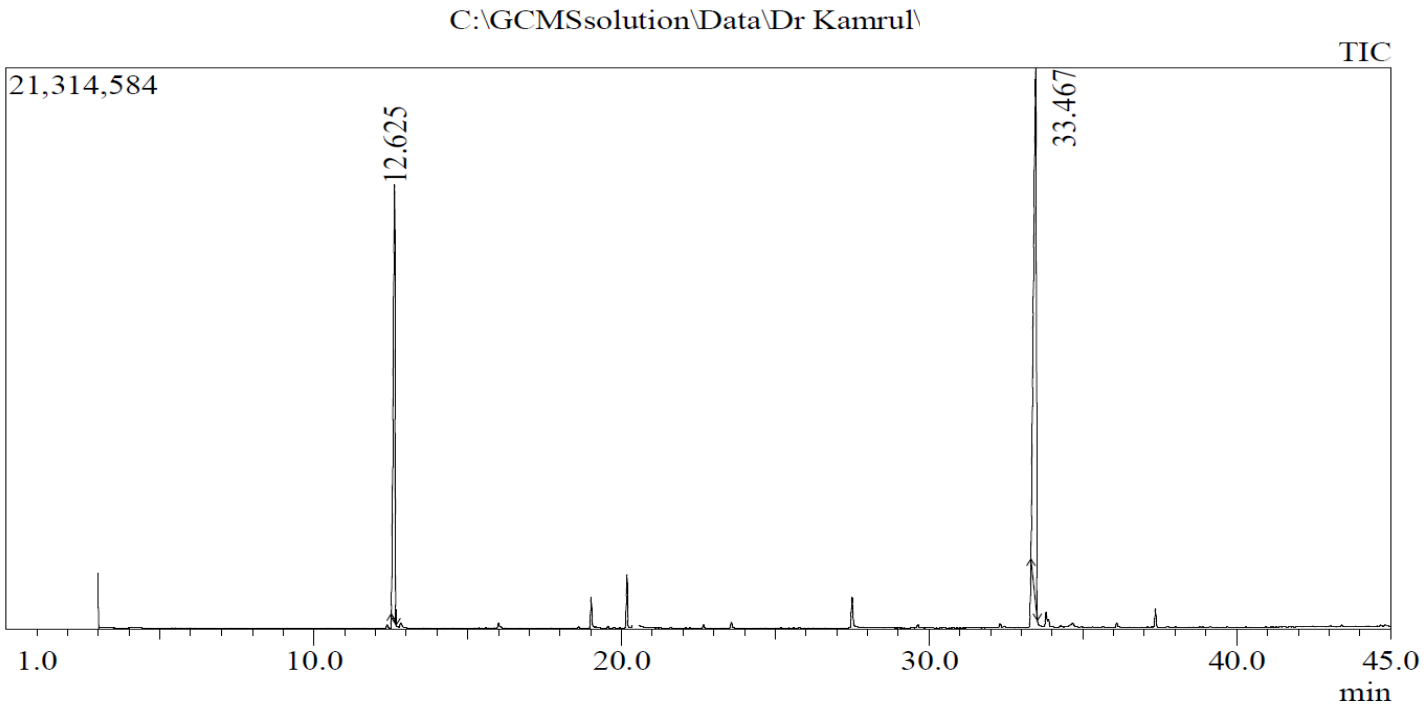
Entry 7: 4-Nitrobenzene internal standard, R_t =12.60 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.17 min. and 4-morpholinobenzaldehyde R_t =34.48 min.



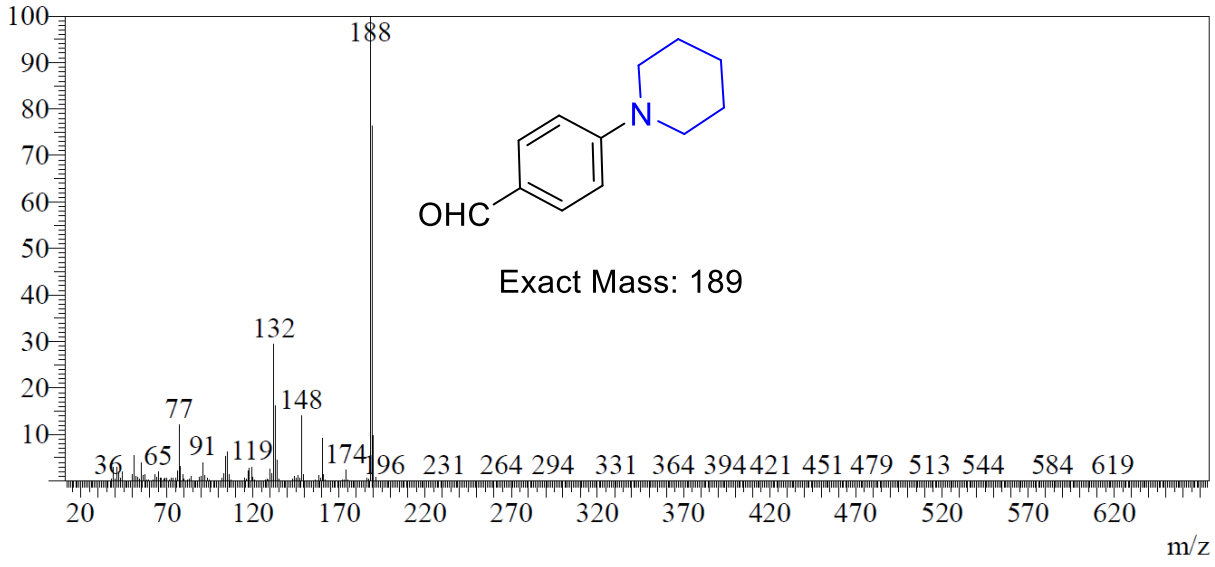
Line#:2 R.Time:34.480(Scan#:6297)
MassPeaks:387
RawMode:Averaged 34.475-34.485(6296-6298) BasePeak:191(7122498)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



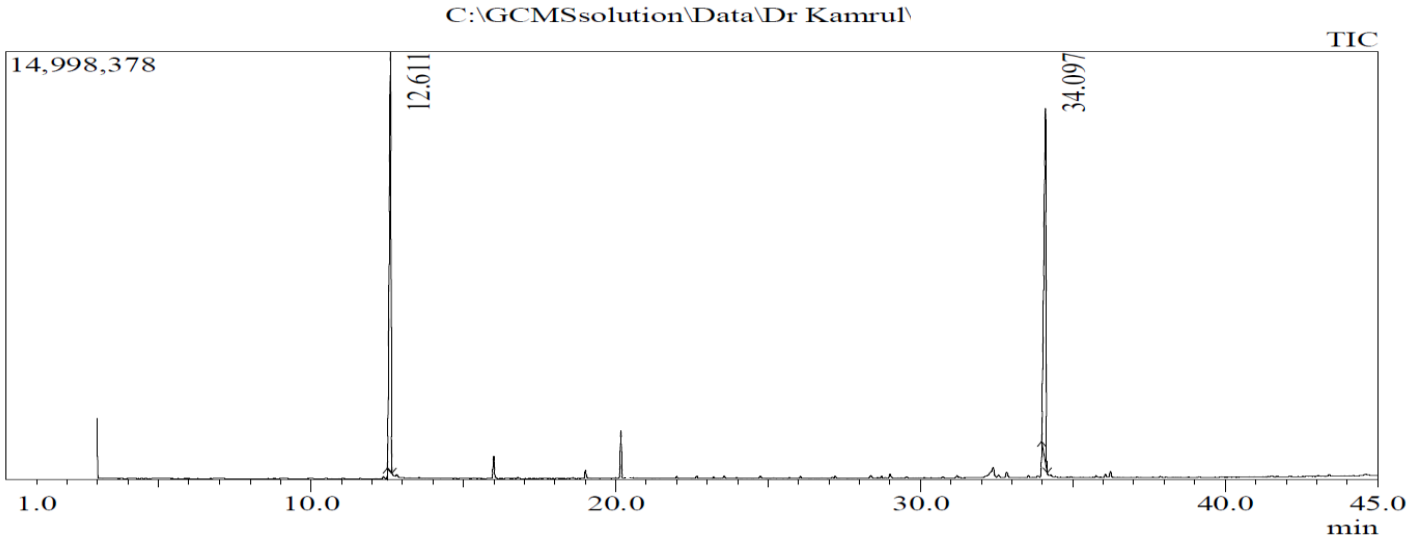
Entry 8: 4-Nitrobenzene internal standard, R_t =12.62 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.17 min. and 4-(piperidin-1-yl)benzaldehyde R_t =33.46 min.



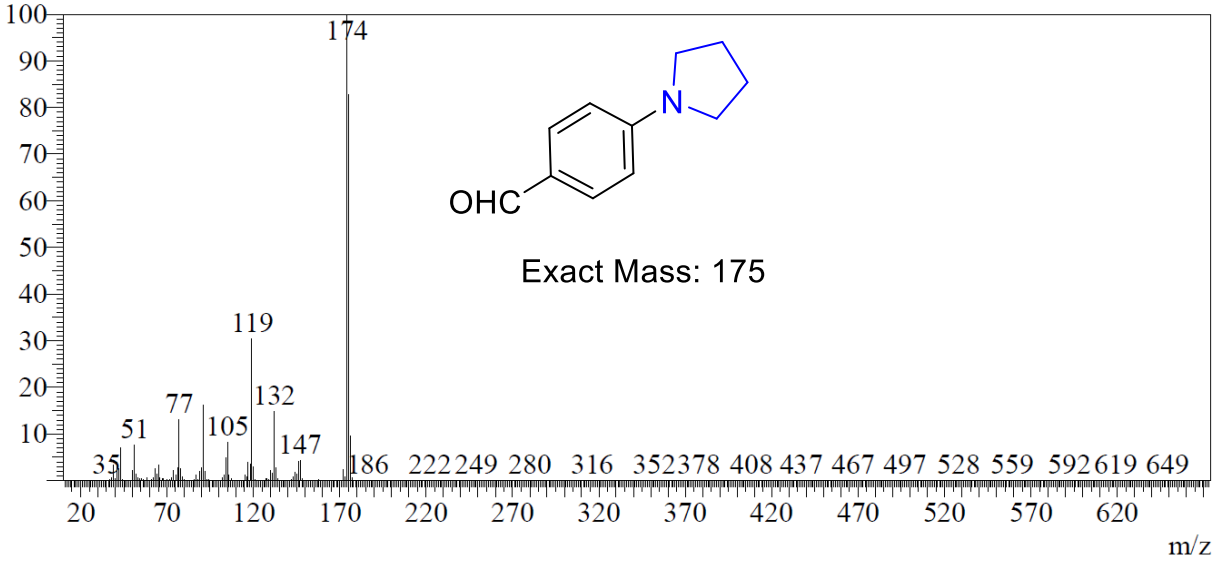
Line#:2 R.Time:33.465(Scan#:6094)
MassPeaks:396
RawMode:Averaged 33.460-33.470(6093-6095) BasePeak:188(5449686)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



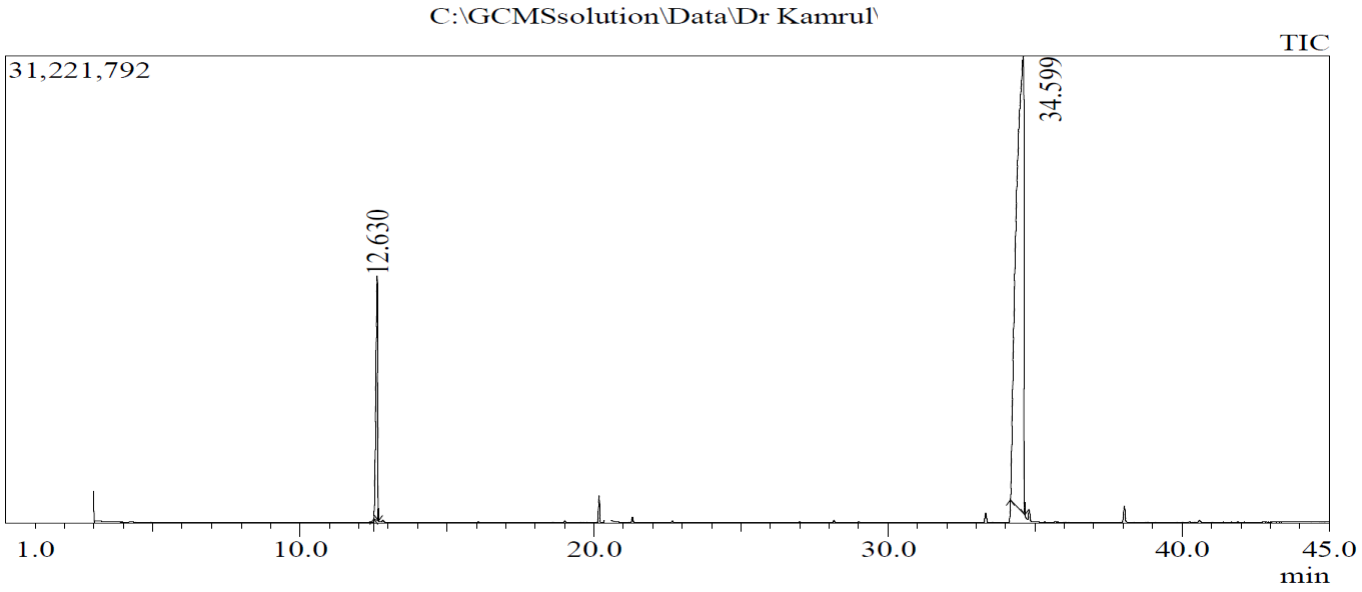
Entry 9: 4-Nitrobenzene internal standard, R_t =12.61 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.16 min. and 4-(pyrrolidin-1-yl)benzaldehyde R_t =34.09 min



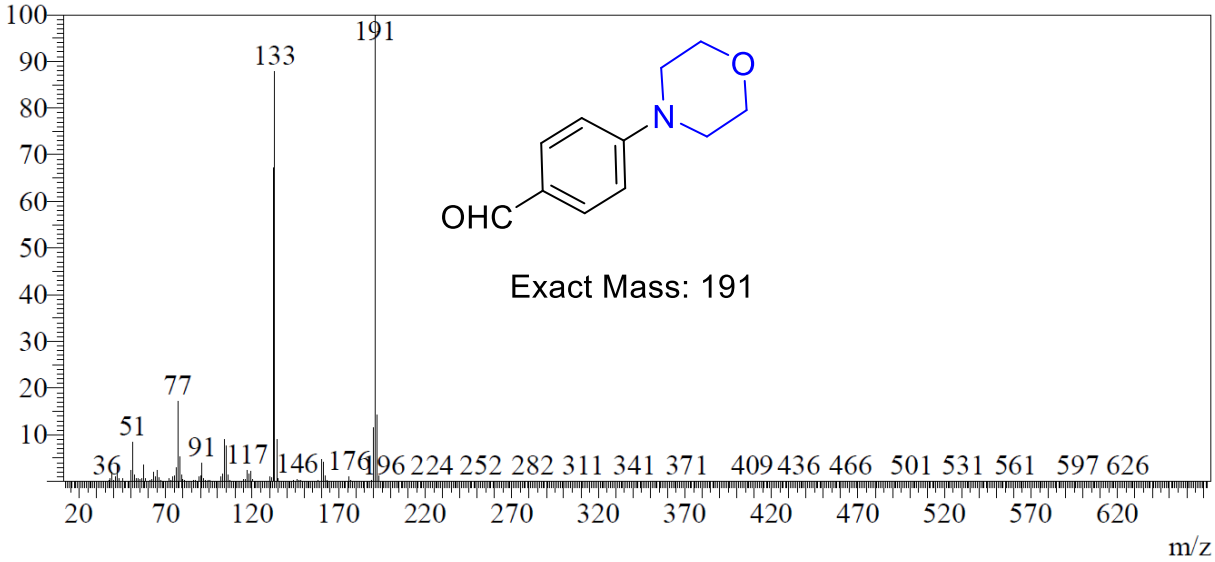
Line#:2 R.Time:34.095(Scan#:6220)
MassPeaks:392
RawMode:Averaged 34.090-34.100(6219-6221) BasePeak:174(3207807)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



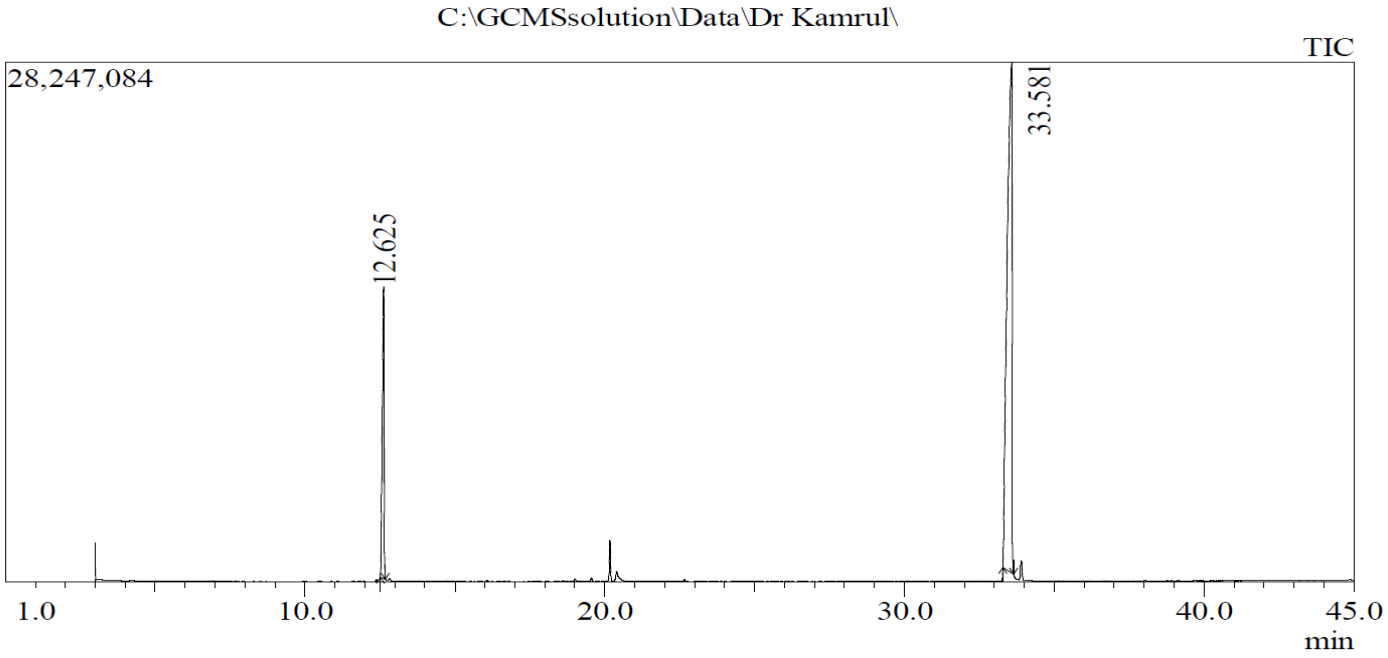
Entry 10: 4-Nitrobenzene internal standard, R_t =12.63 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.16 min. and 4-morpholinobenzaldehyde R_t =34.59 min



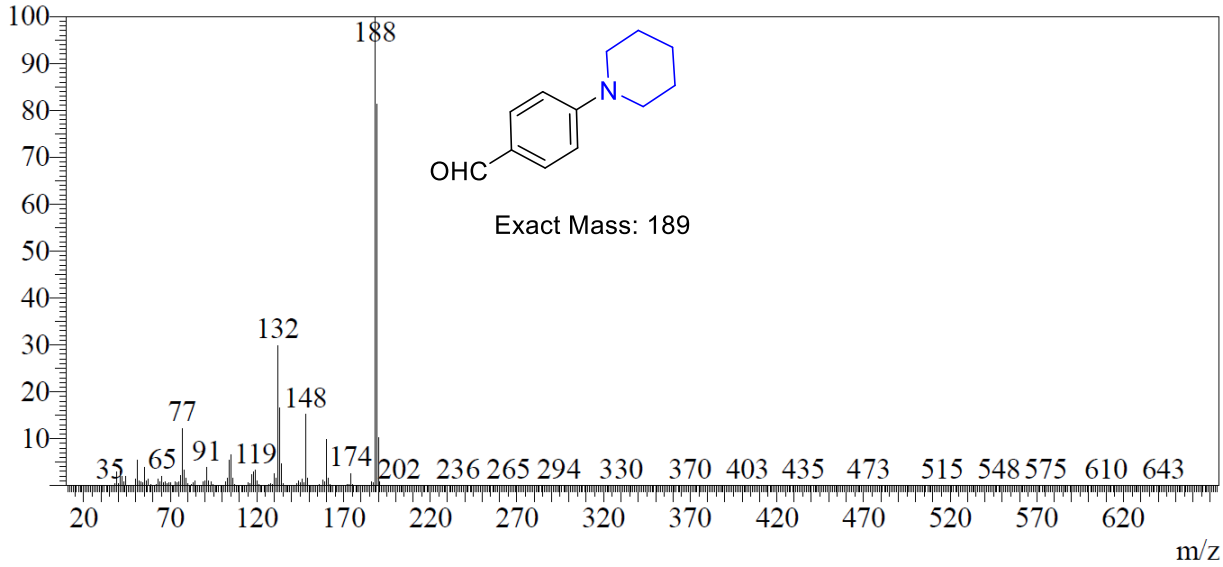
Line#:2 R.Time:34.600(Scan#:6321)
MassPeaks:423
RawMode:Averaged 34.595-34.605(6320-6322) BasePeak:191(7483661)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



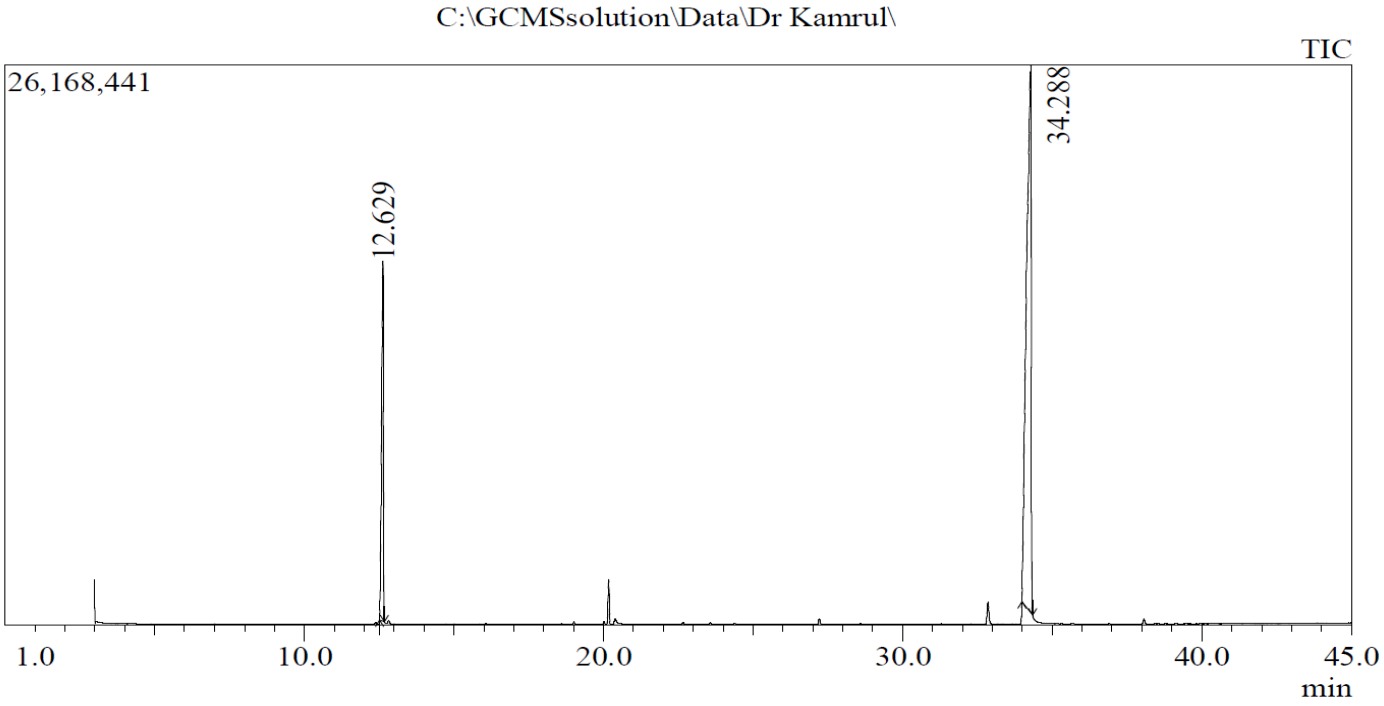
Entry 11: 4-Nitrobenzene internal standard, R_t =12.62 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.16 min. and 4-morpholinobenzaldehyde R_t =33.58 min



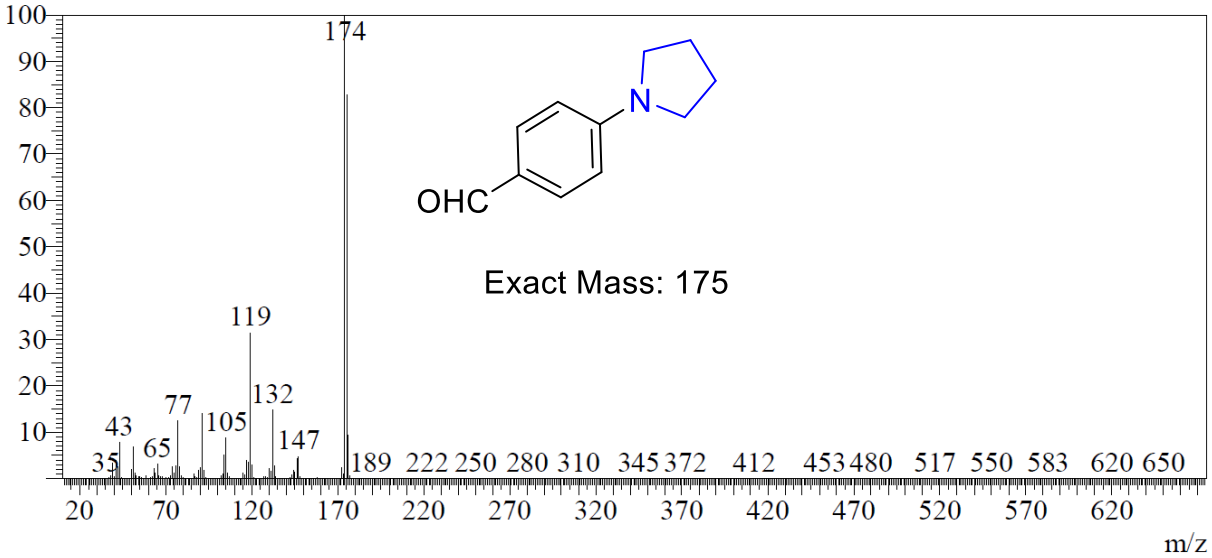
Line#:2 R.Time:33.580(Scan#:6117)
MassPeaks:390
RawMode:Averaged 33.575-33.585(6116-6118) BasePeak:188(7251643)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



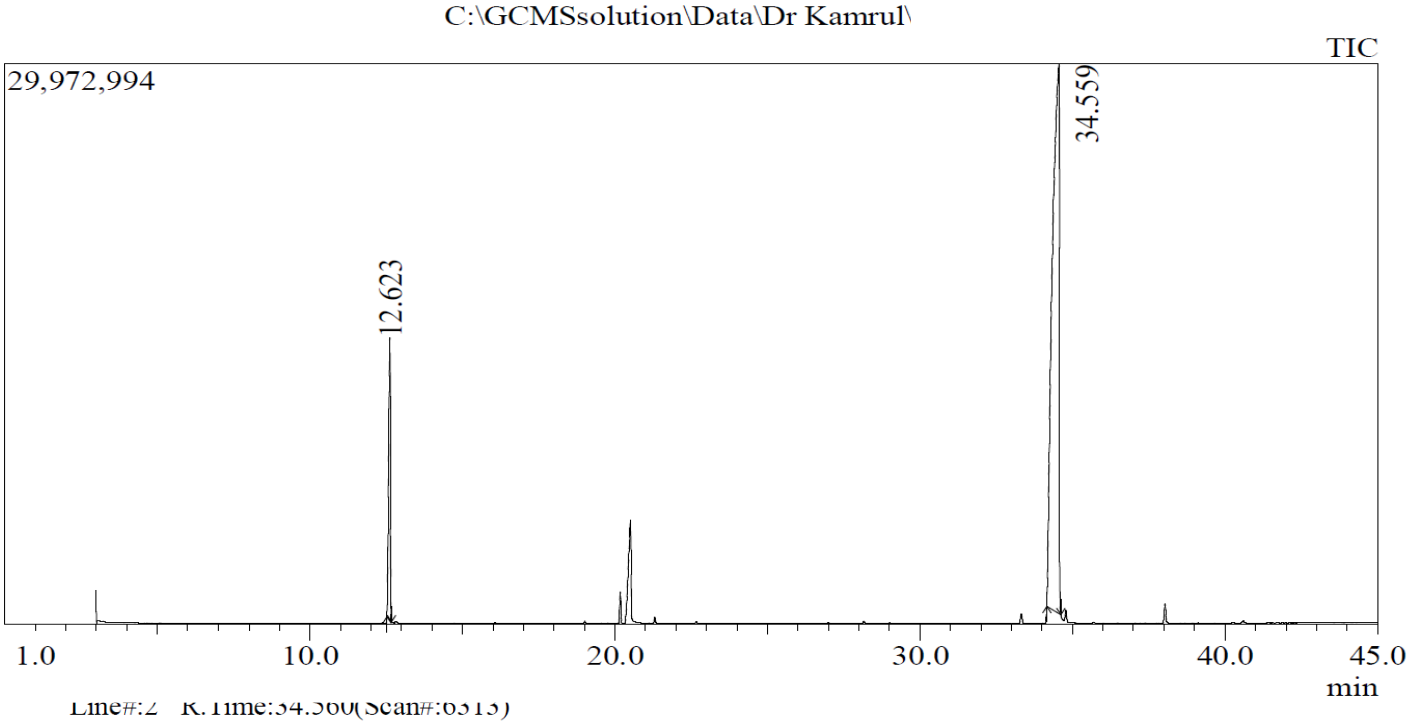
Entry 12: 4-Nitrobenzene internal standard, R_t =12.62 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.16 min. and 4-(pyrrolidin-1-yl)benzaldehyde R_t =34.28 min



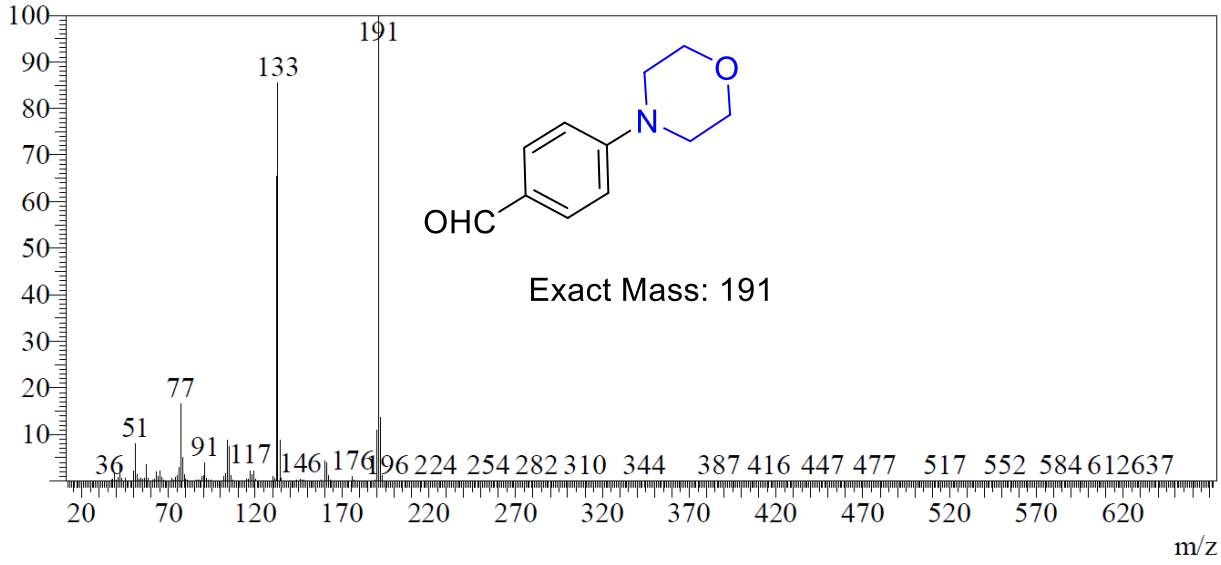
Line#:2 R.Time:34.290(Scan#:6259)
MassPeaks:371
RawMode:Averaged 34.285-34.295(6258-6260) BasePeak:174(6597490)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



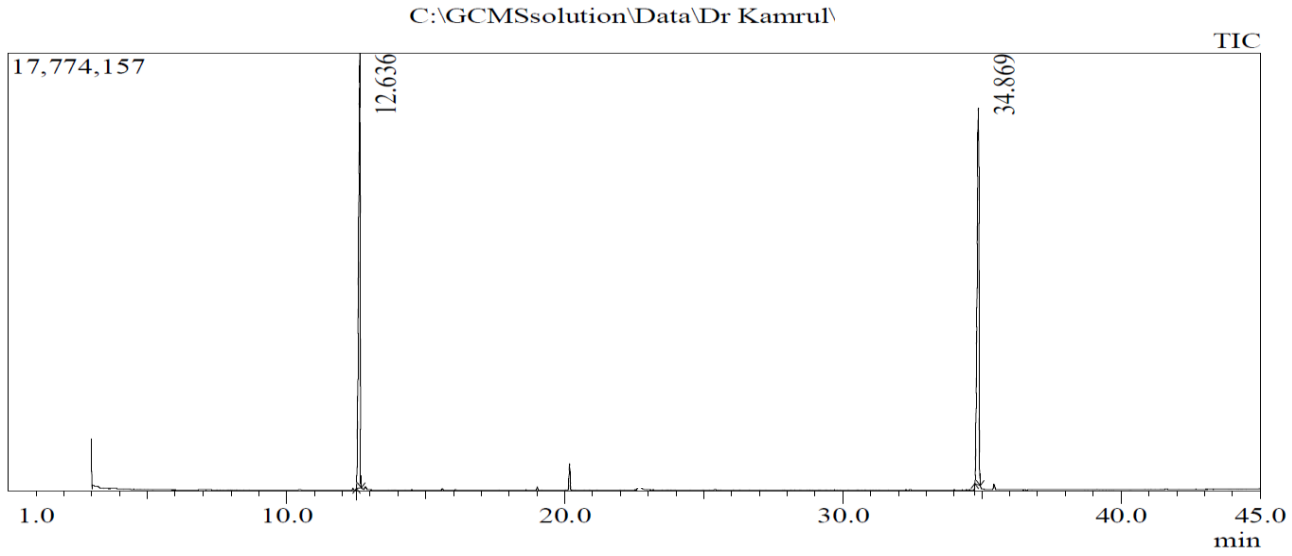
Entry 13: 4-Nitrobenzene internal standard, R_t =12.62 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.16 min. and 4-morpholinobenzaldehyde R_t =34.55 min



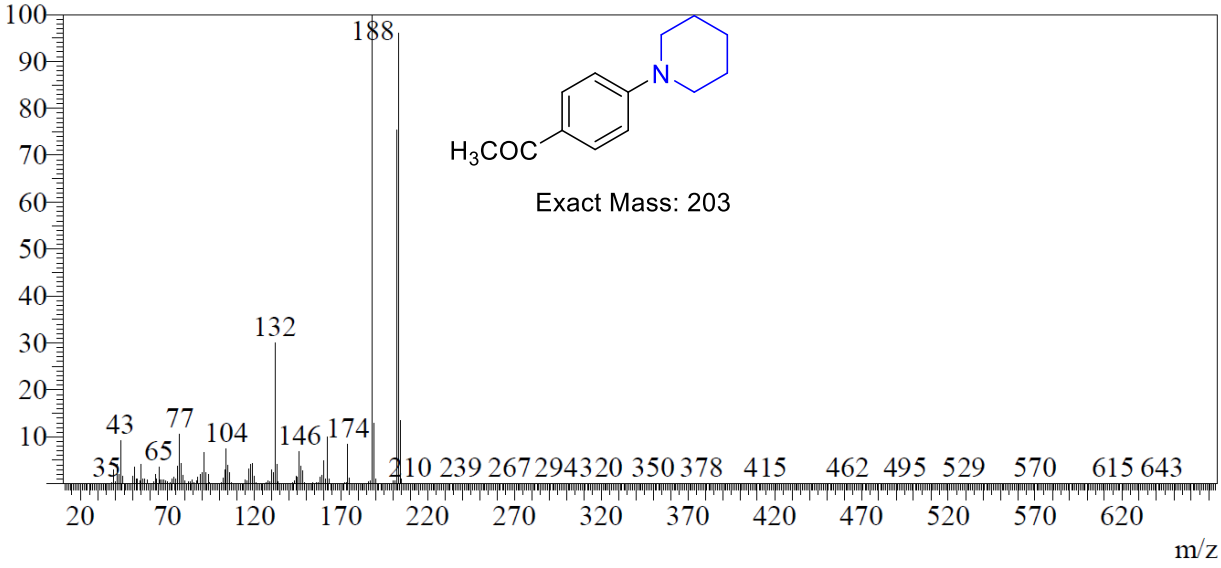
Line#:2 R.Time:34.560(Scan#:6313)
MassPeaks:401
RawMode:Averaged 34.555-34.565(6312-6314) BasePeak:191(7380720)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



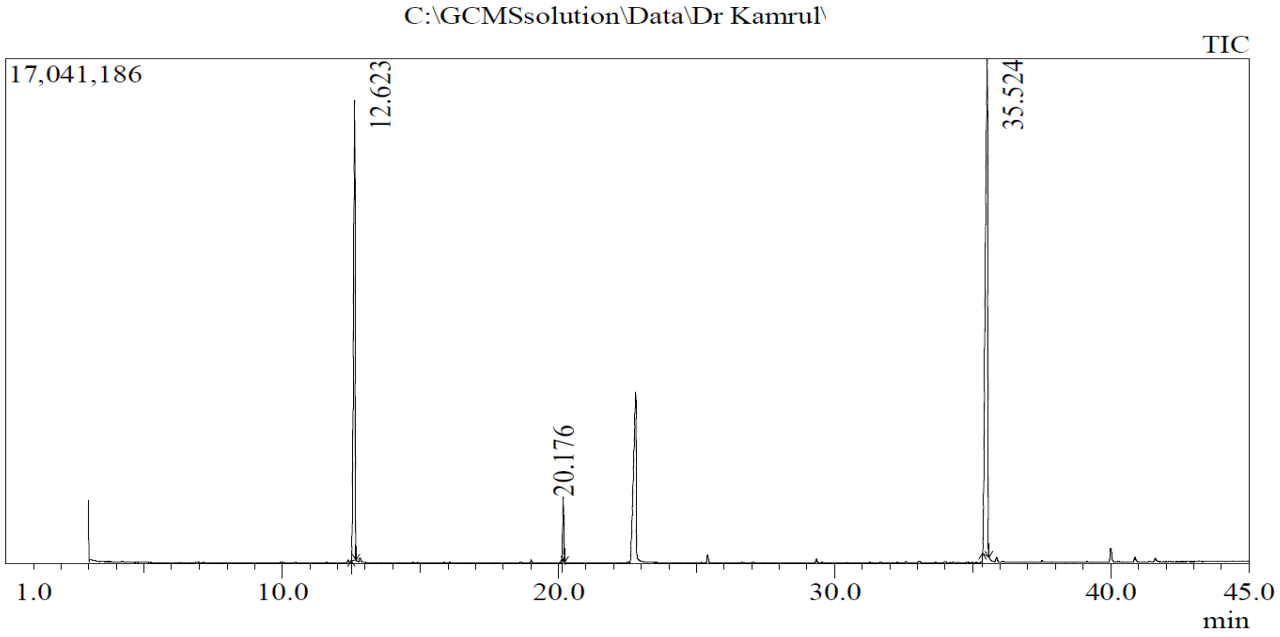
Entry 14: 4-Nitrobenzene internal standard, R_t =12.63 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-(piperidin-1-yl)phenyl)ethan-1-one R_t =34.86 min



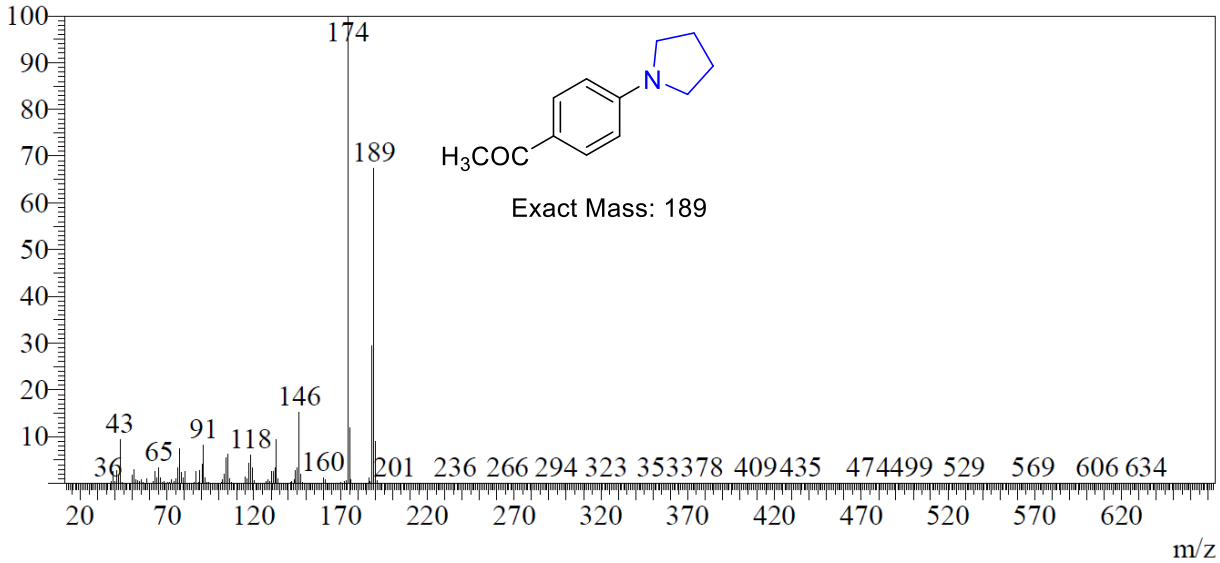
Line#:2 R.Time:34.870(Scan#:6375)
MassPeaks:380
RawMode:Averaged 34.865-34.875(6374-6376) BasePeak:188(2956002)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



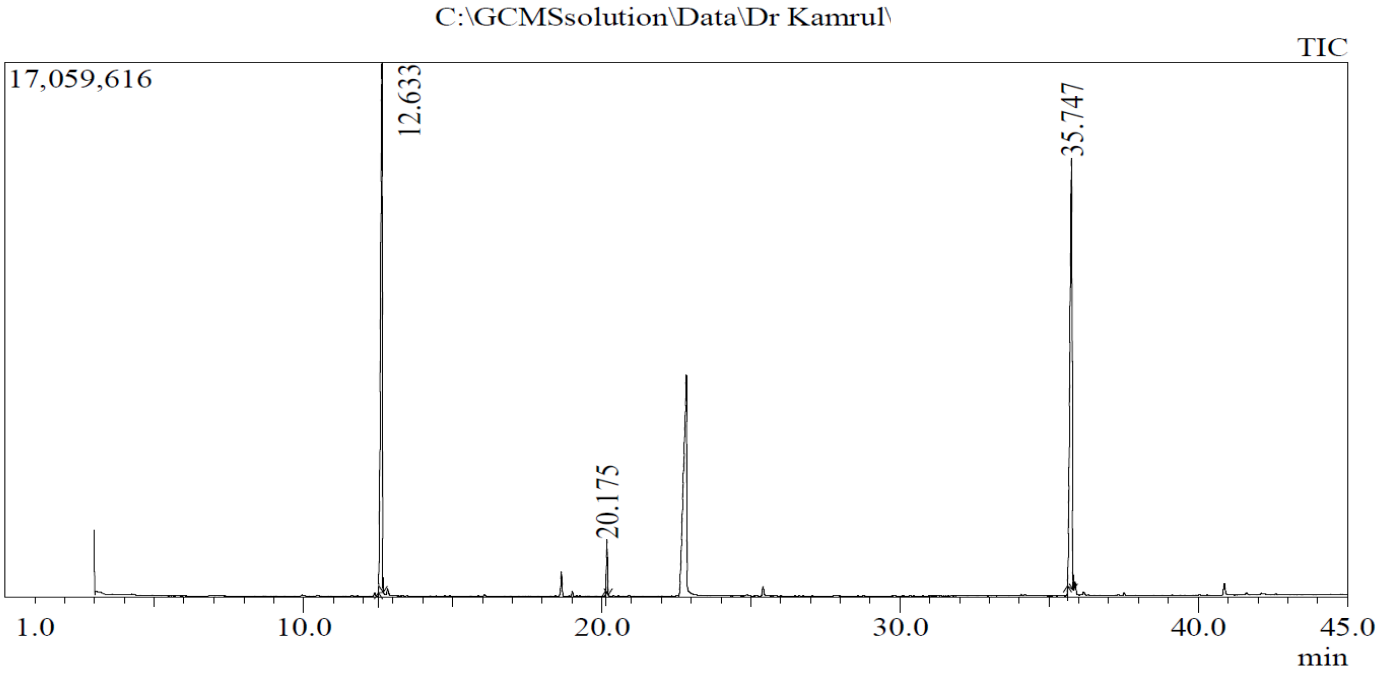
Entry 15: 4-Nitrobenzene internal standard, R_t =12.62 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min, by product 1-(4-hydroxyphenyl)ethan-1-one R*t* = 22.25 min and 1-(4-(pyrrolidin-1-yl)phenyl)ethan-1-one R_t =35.52 min



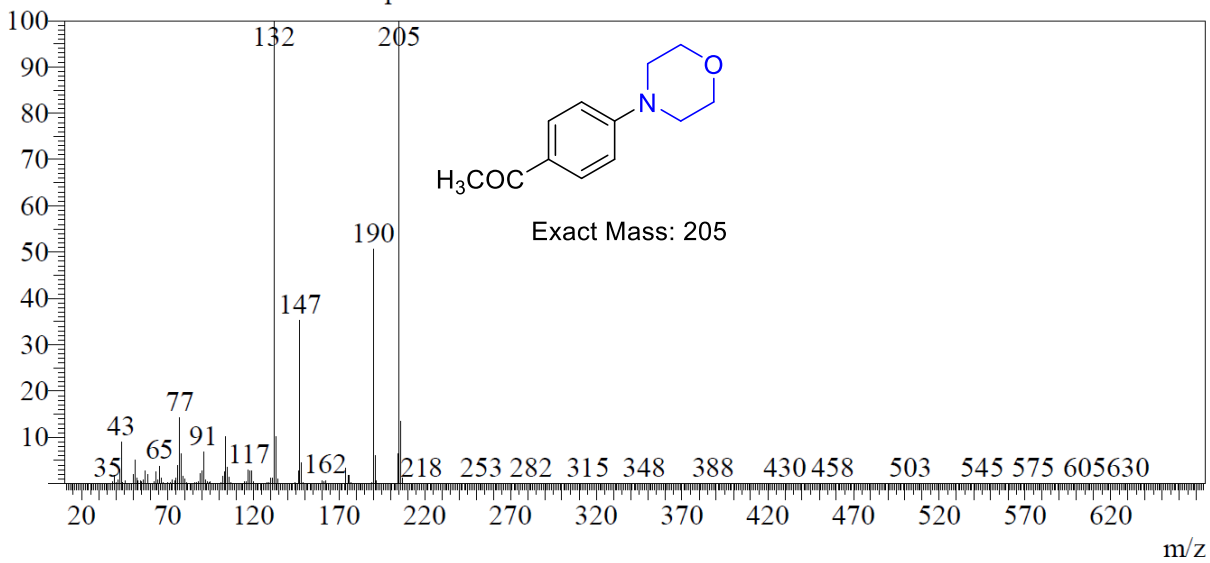
Line#:3 R.Time:35.525(Scan#:6506)
MassPeaks:391
RawMode:Averaged 35.520-35.530(6505-6507) BasePeak:174(4394940)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



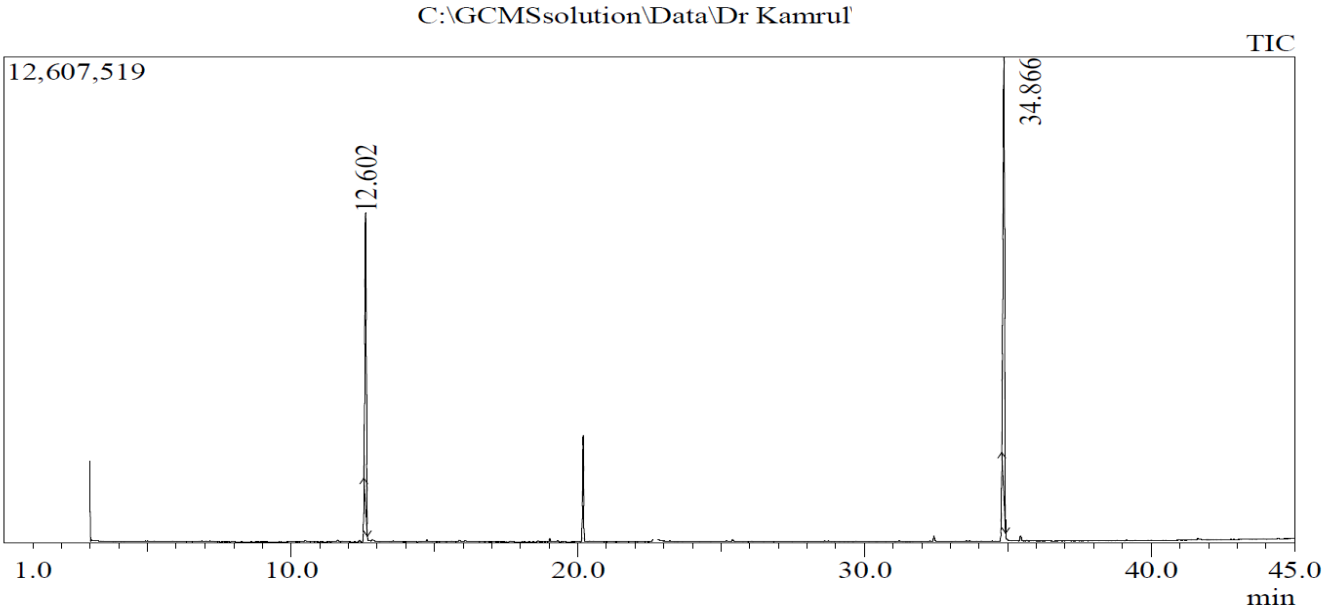
Entry 16: 4-Nitrobenzene internal standard, R_t =12.63 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min, by product 1-(4-hydroxyphenyl)ethan-1-one R*t* = 22.25 min and 1-(4-morpholinophenyl)ethan-1-one R_t =35.74 min



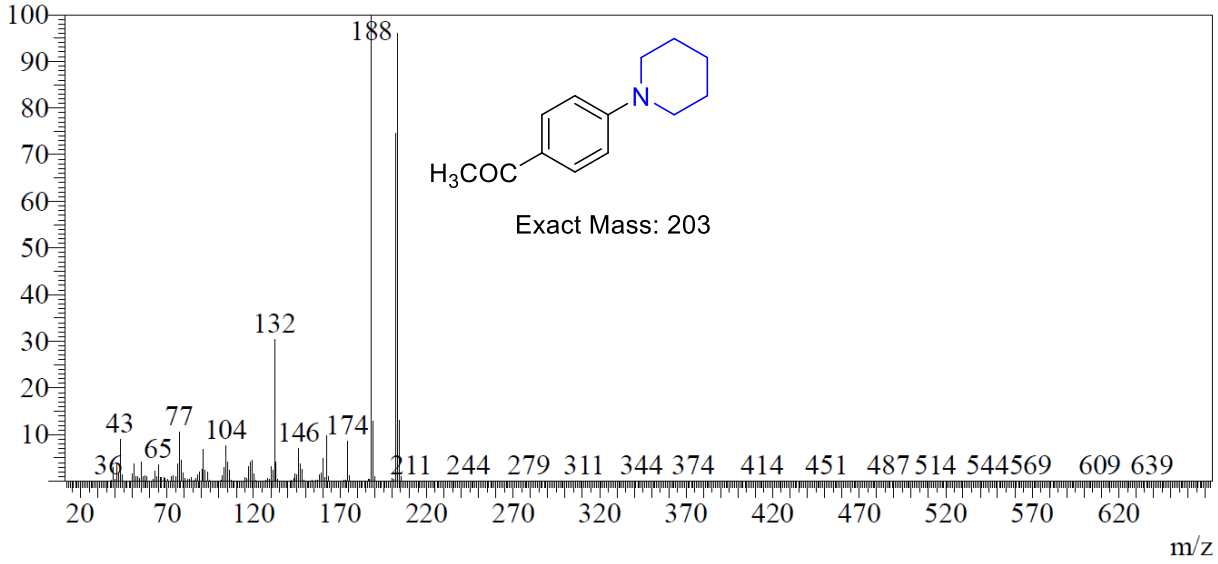
Line#:3 R.Time:35.745(Scan#:6550)
MassPeaks:357
RawMode:Averaged 35.740-35.750(6549-6551) BasePeak:205(2963044)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



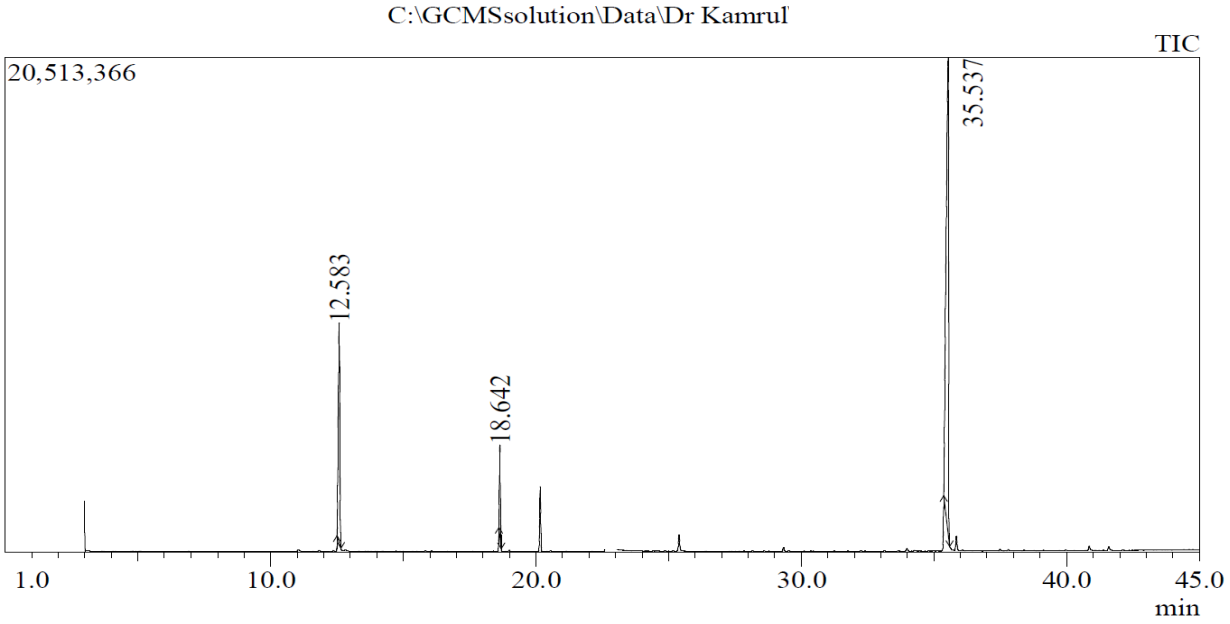
Entry 17: 4-Nitrobenzene internal standard, R_t =12.60 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min, and 1-(4-(piperidin-1-yl)phenyl)ethan-1-one R_t =34.86 min



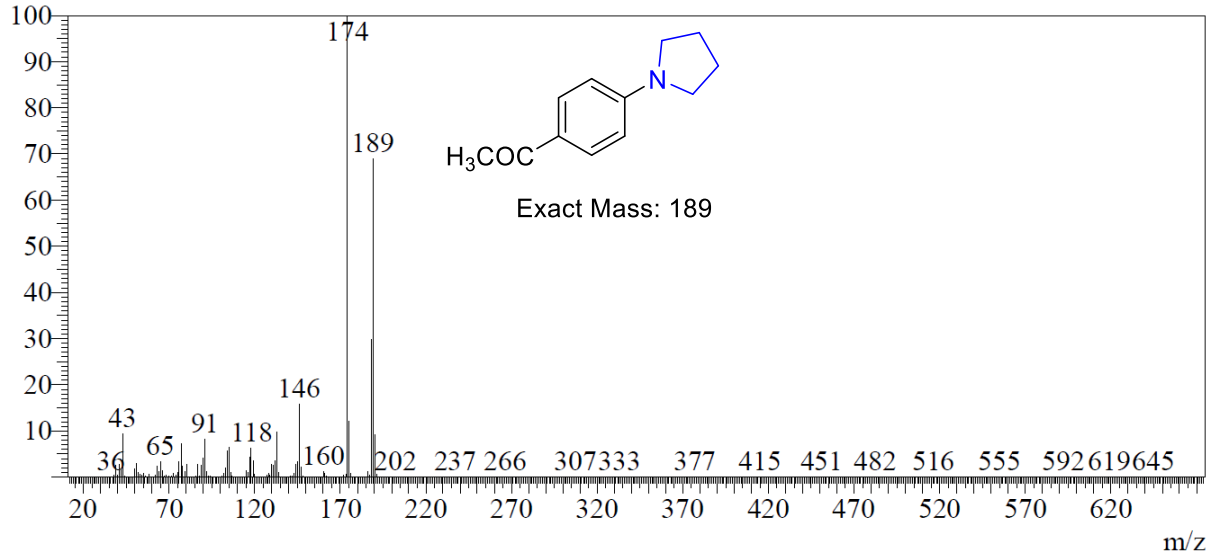
Line#:2 R.Time:34.865(Scan#:6374)
MassPeaks:390
RawMode:Averaged 34.860-34.870(6373-6375) BasePeak:188(2201581)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



Entry 18: 4-Nitrobenzene internal standard, R_t =12.58 min, 1-(4-bromophenyl)ethan-1-one Rt = 18.64 min, Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min, and 1-(4-(pyrrolidin-1-yl)phenyl)ethan-1-one R_t =35.53 min



Line#:3 R.Time:35.535(Scan#:6508)
MassPeaks:390
RawMode:Averaged 35.530-35.540(6507-6509) BasePeak:174(5151108)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



7. ^{1}H NMR spectra of selected crude products given in the Table 1

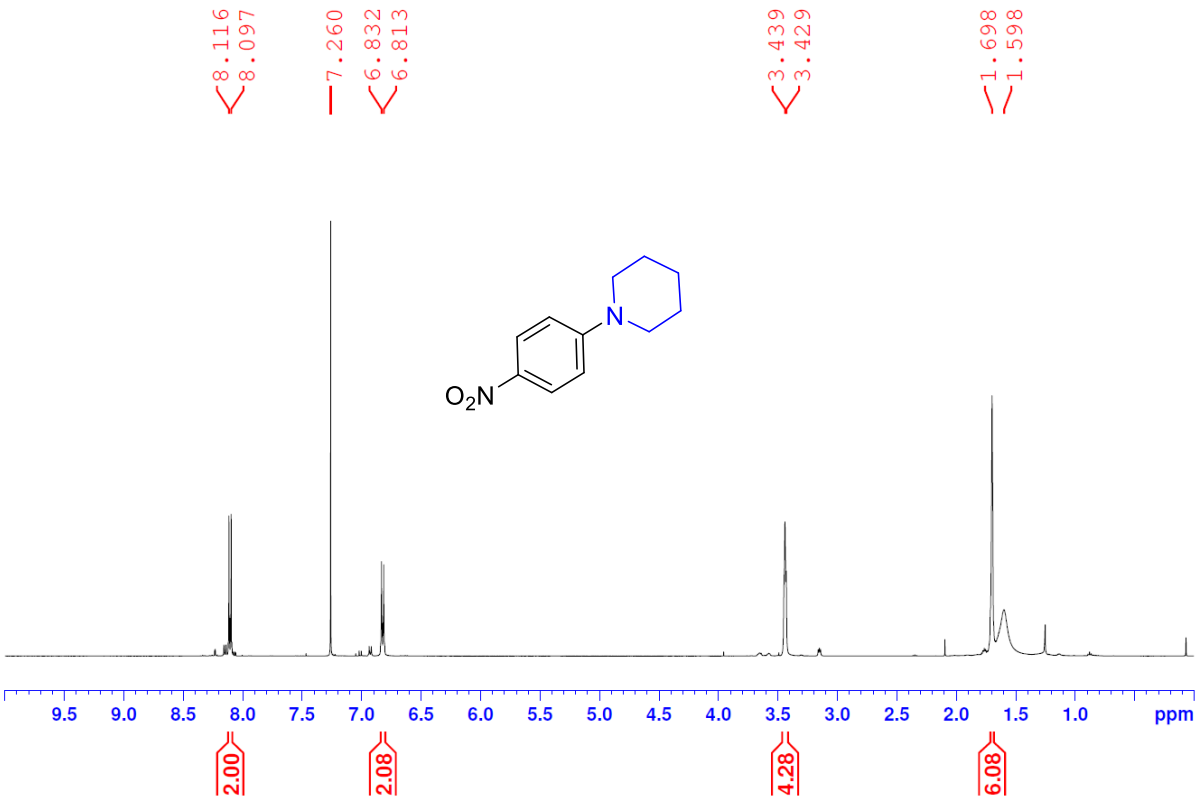


Fig. S5. ^{1}H NMR spectrum of 1-(4-nitrophenyl)piperidine (Table 2, entry 1) in $CDCl_3$

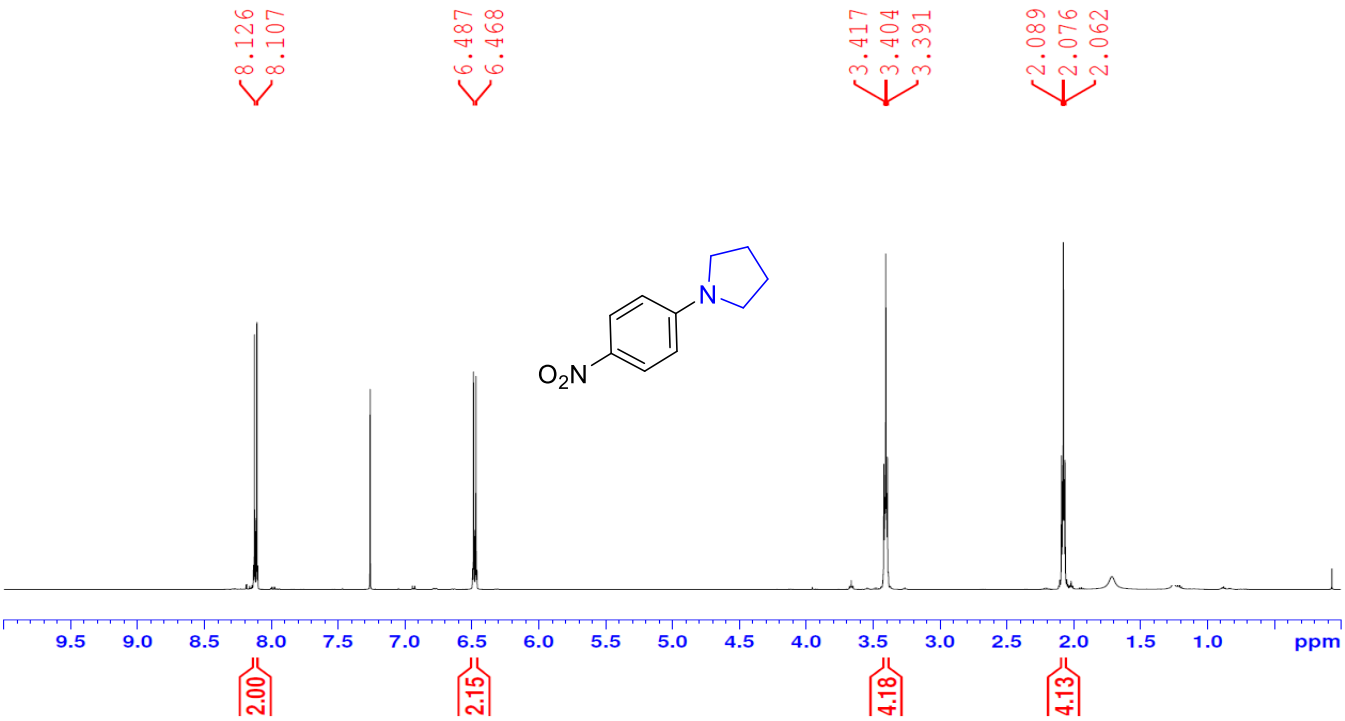


Fig. S6. ^{1}H NMR spectrum of 1-(4-nitrophenyl)pyrrolidine (Table 2, entry 2) in $CDCl_3$

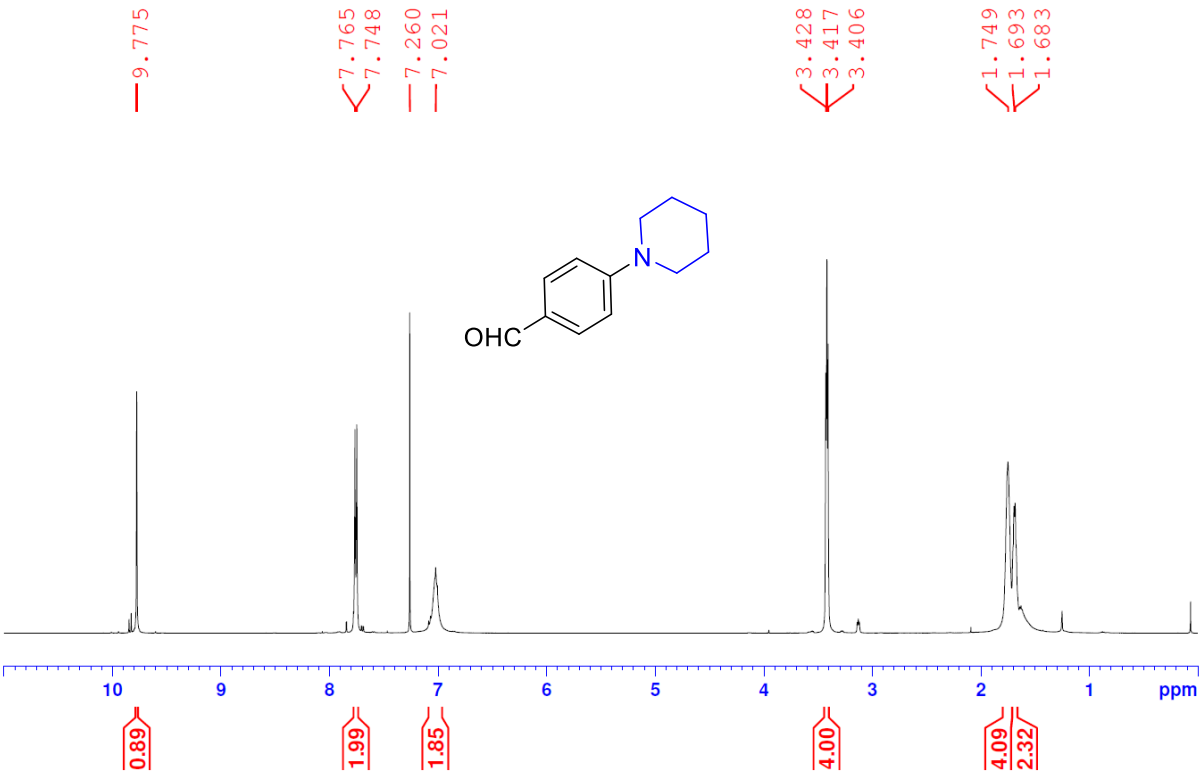


Fig. S7. ^{1}H NMR spectrum of 4-(piperidin-1-yl)benzaldehyde (Table 2, entry 7) in $CDCl_3$

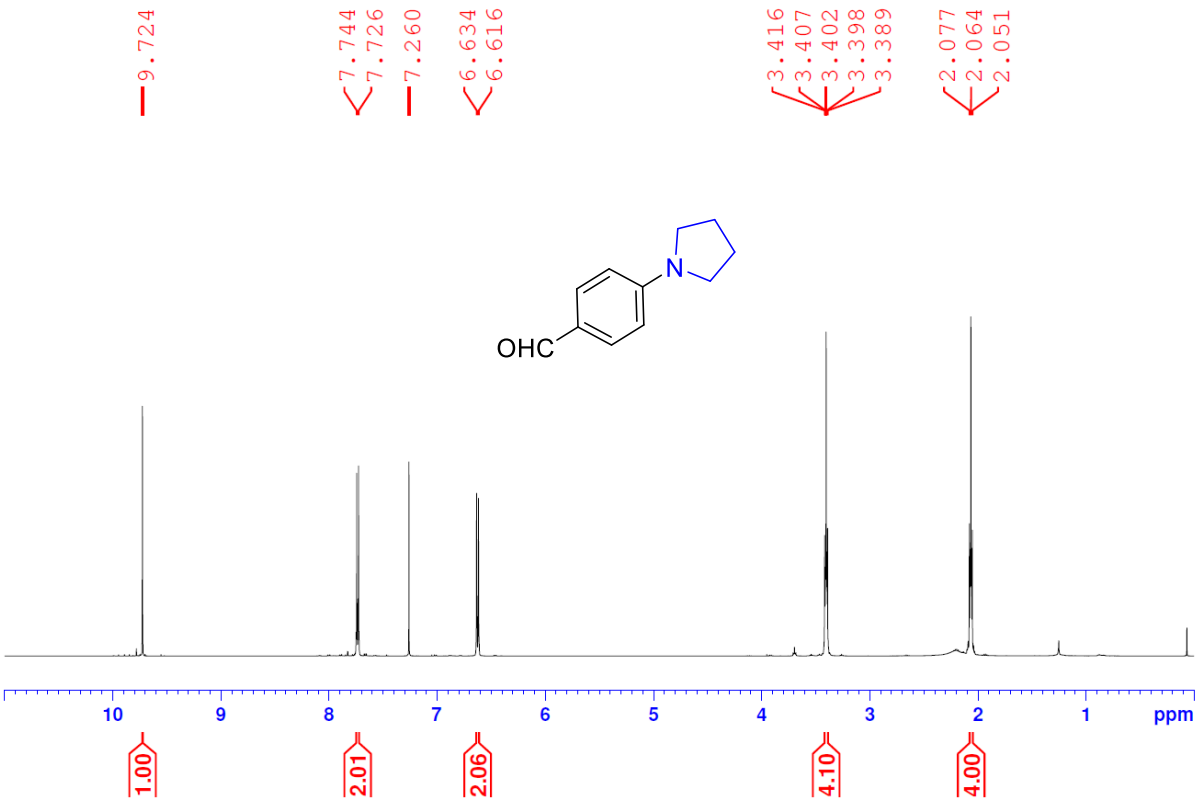


Fig. S8. ^{1}H NMR spectrum of 4-(pyrrolidin-1-yl)benzaldehyde (Table 2, entry 8) in $CDCl_3$

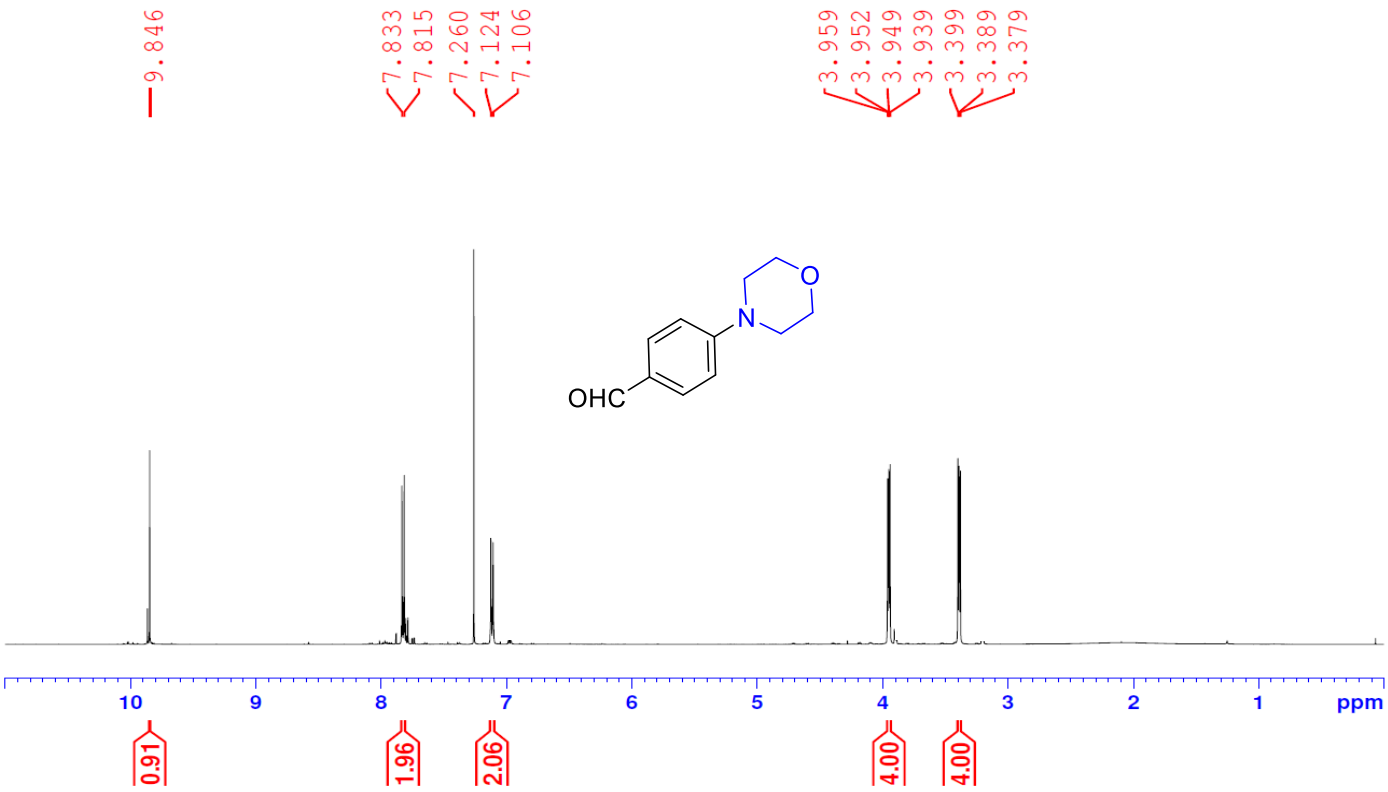


Fig. S9. ^{1}H NMR spectrum of 4-morpholinobenzaldehyde (Table 2, entry 9) in $CDCl_3$

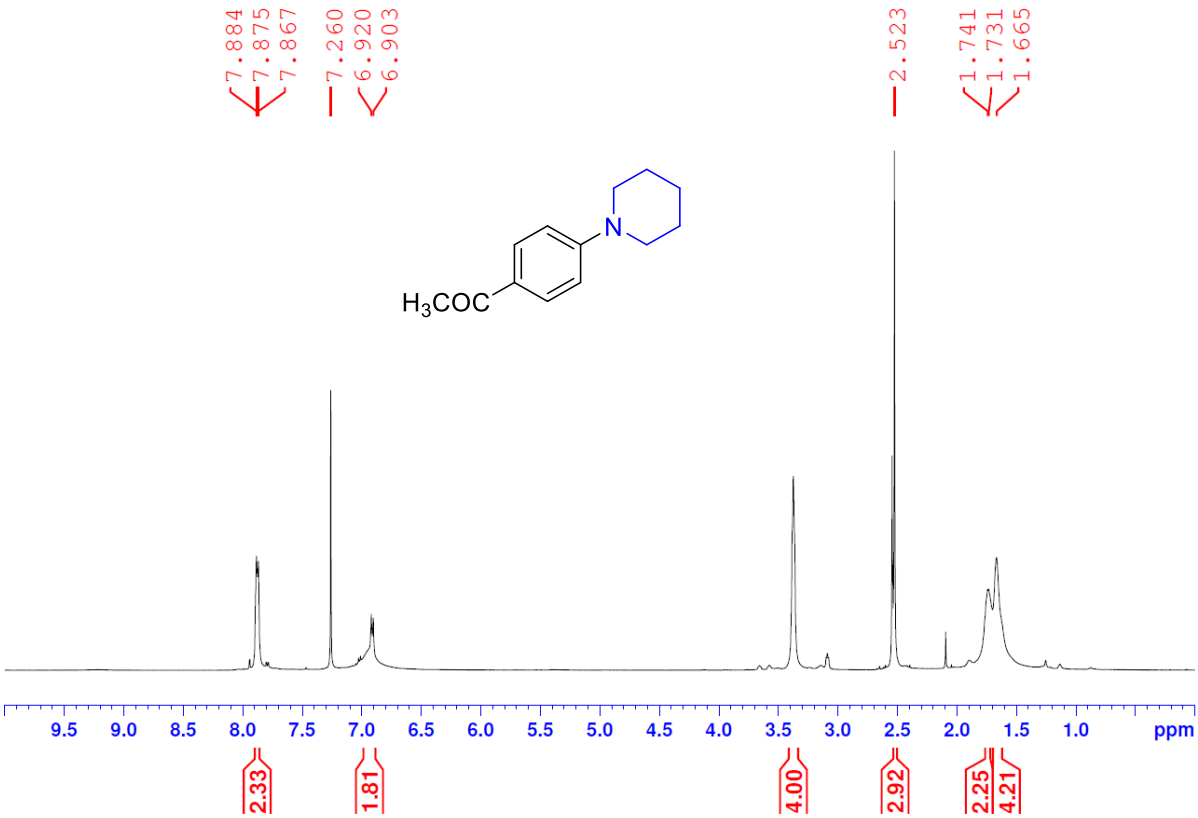


Fig. S10. ^{1}H NMR spectrum of 1-(4-(piperidin-1-yl)phenyl)ethan-1-one (Table 2, entry 16) in $CDCl_3$

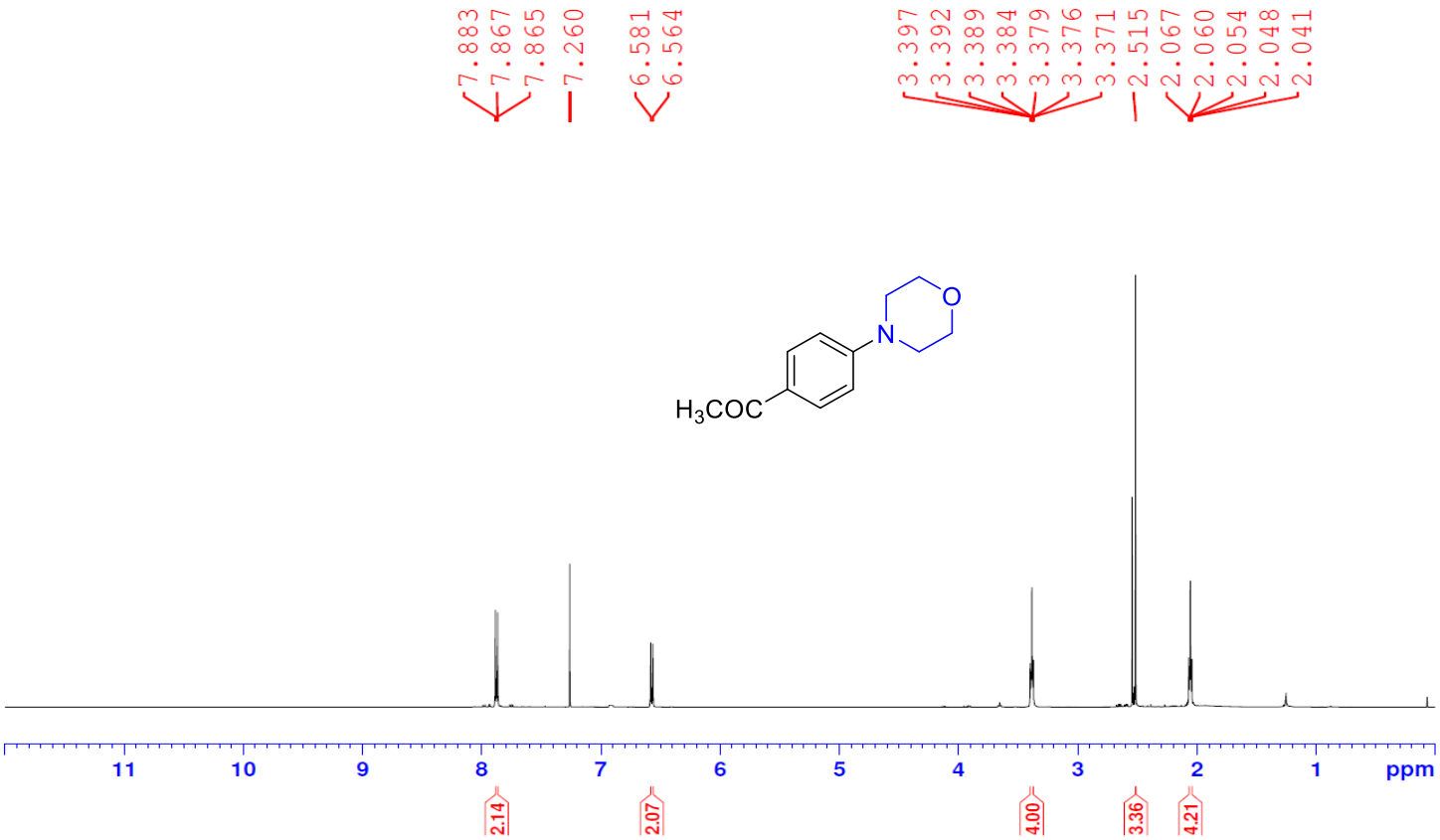
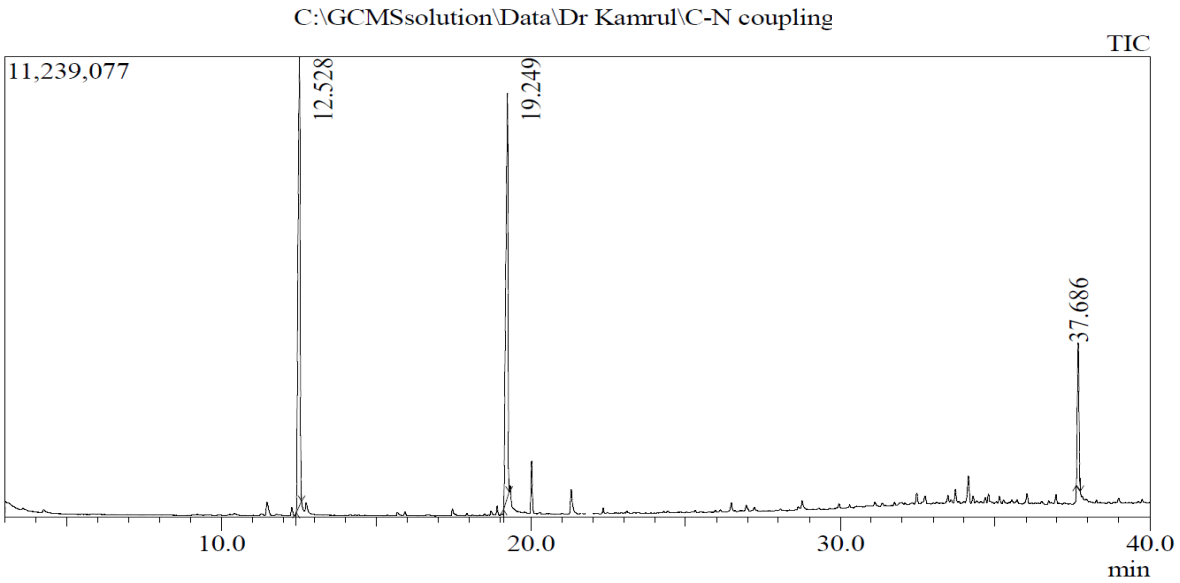
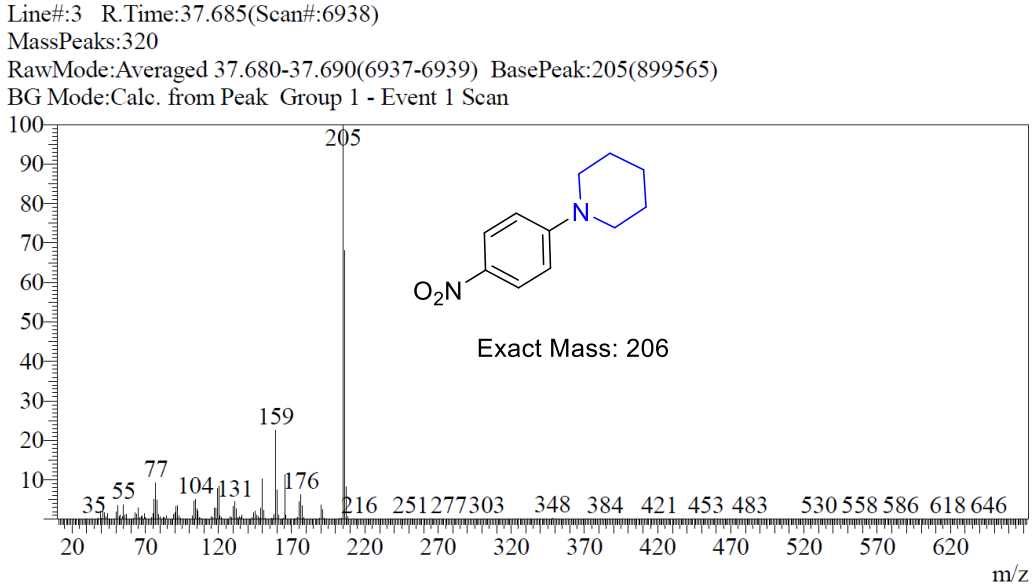


Fig. S11. ^{1}H NMR spectrum of 1-(4-morpholinophenyl)ethan-1-one (Table 2, entry 16) in $CDCl_3$

8. GC traces and mass spectra of the crude products of typical C-N coupling reaction during hot filtration test

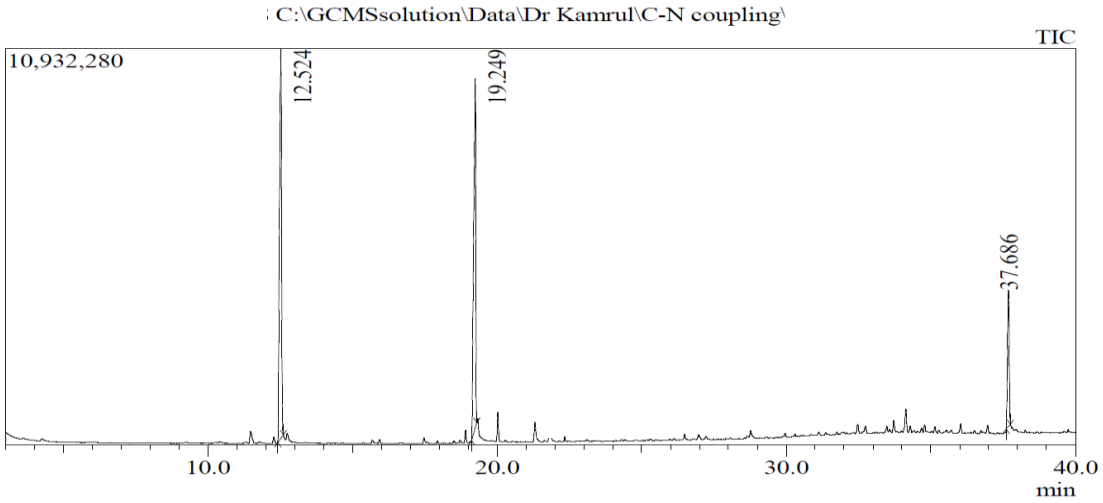
a) **After 30% completion of the reaction within 20 min under optimized condition:** 4-Nitrobenzene internal standard, R_t =12.52 min. 1-Bromo-4-nitrobenzene, R_t =19.24 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.68 min.



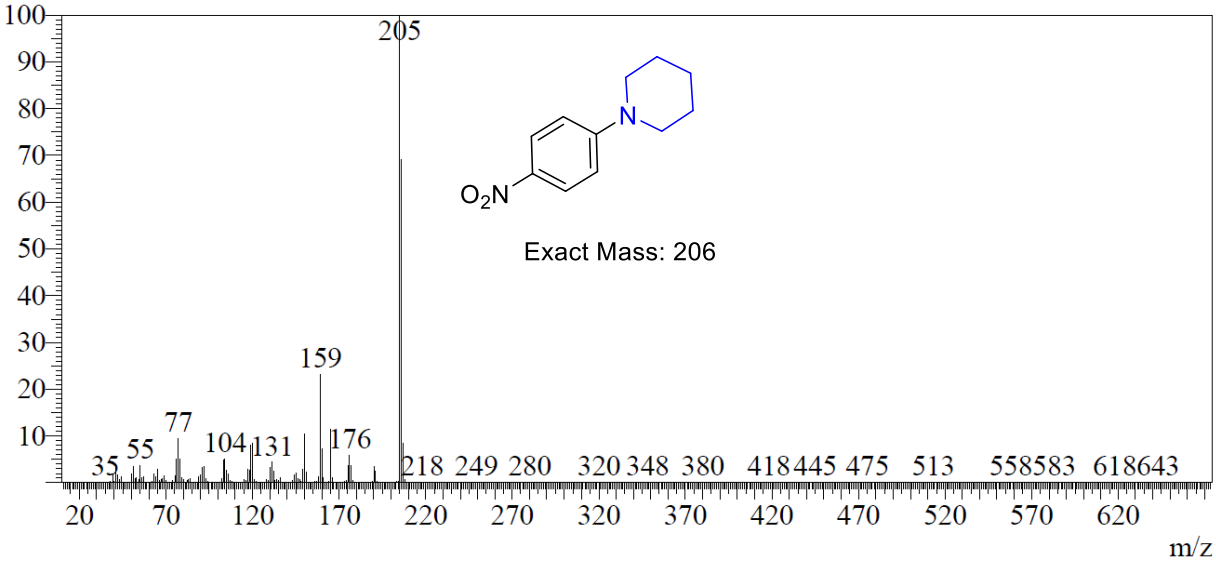


b) **Liquid part of the reaction mixture after 1h heating under optimized reaction conditions:** Nitrobenzene internal standard, R_t =12.52 min. 1-Bromo-4-nitrobenzene, R_t

=19.24 min. Butylated Hydroxy Toluene (BHT) from solvent R*t* = 20.15 min. and 1-(4-nitrophenyl)piperidine, R_t =37.68 min.

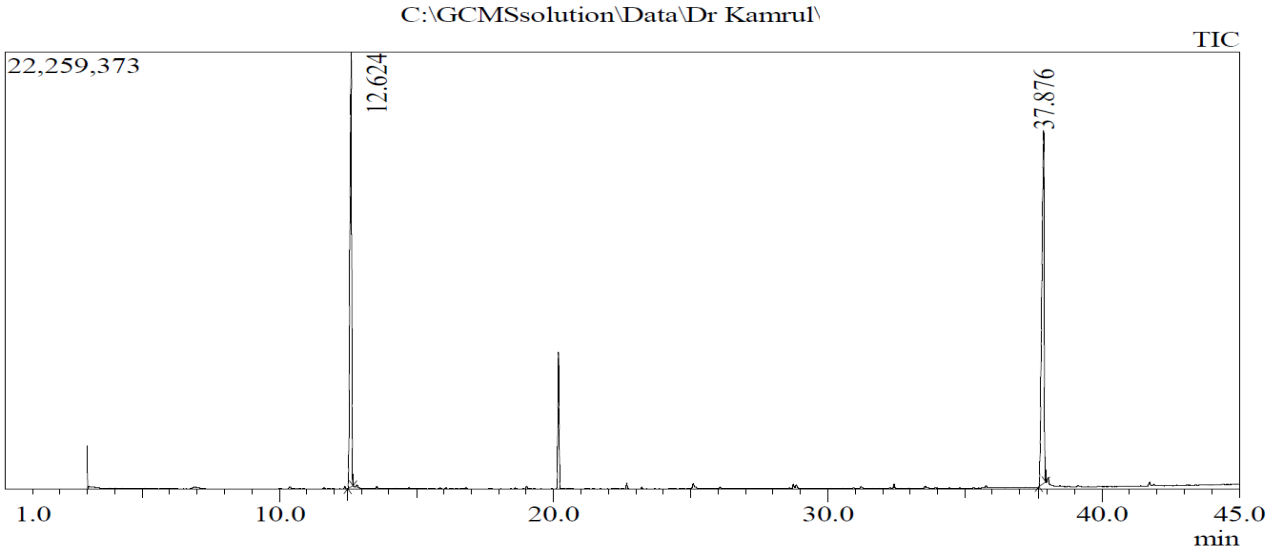


Line#:3 R.Time:37.685(Scan#:6938)
MassPeaks:321
RawMode:Averaged 37.680-37.690(6937-6939) BasePeak:205(951180)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

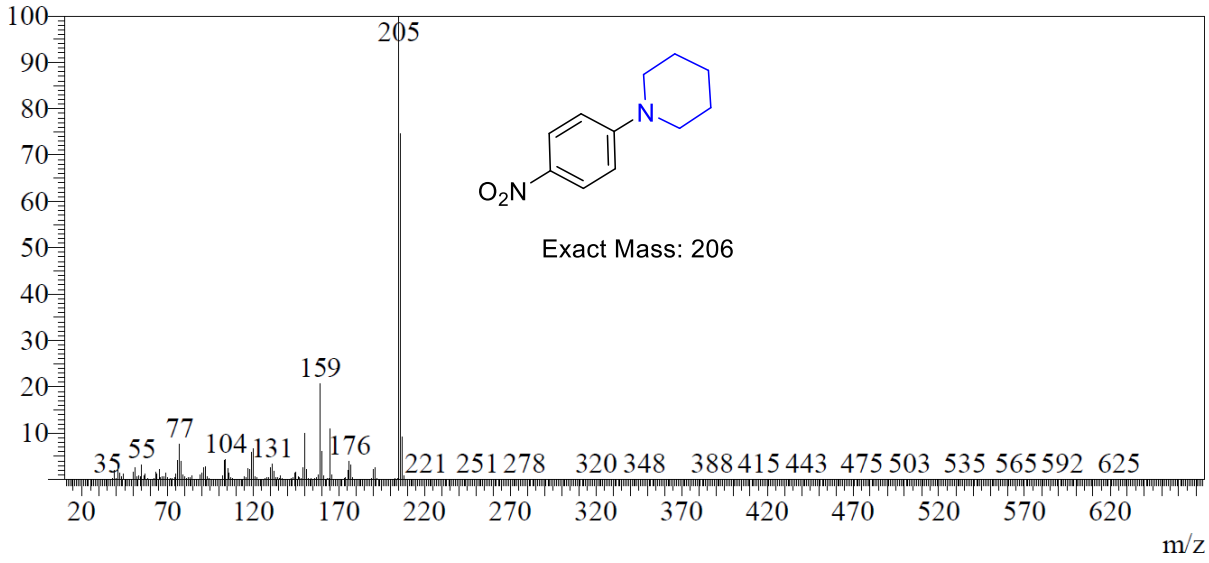


9. GC traces and mass spectra of the crude products of recycling experiments

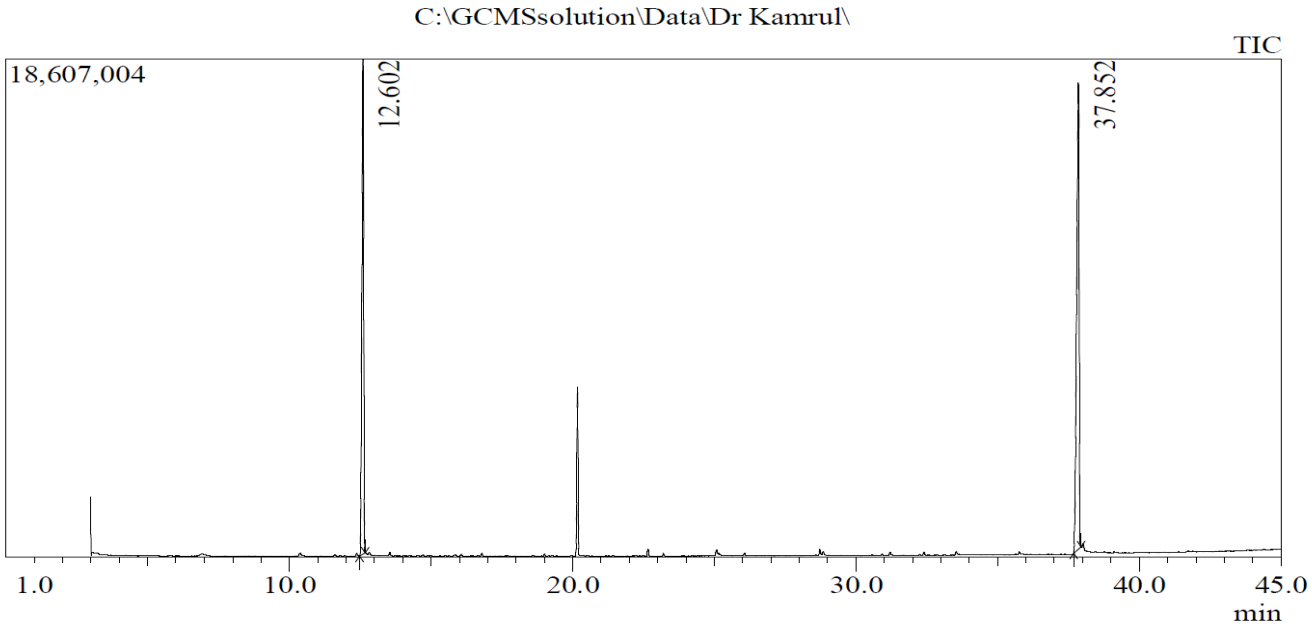
a) 1st cycle of recycle experiment: 4-Nitrobenzene as internal standard, R_t =12.62 min, butylated hydroxytoluene (BHT) from solvent R_t = 20.15 min and product and 1-(4-nitrophenyl)piperidine, R_t =37.87 min.



Line#:2 R.Time:37.875(Scan#:6976)
MassPeaks:396
RawMode:Averaged 37.870-37.880(6975-6977) BasePeak:205(4898341)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan



a) 5th cycle of recycle experiment: 4-Nitrobenzene as internal standard, R_t =12.60 min, butylated hydroxytoluene (BHT) from solvent R_t = 20.15 min and product and 1-(4-nitrophenyl)piperidine, R_t =37.85 min.



Line#:2 R.Time:37.850(Scan#:6971)
MassPeaks:415
RawMode:Averaged 37.845-37.855(6970-6972) BasePeak:205(4654685)
BG Mode:Calc. from Peak Group 1 - Event 1 Scan

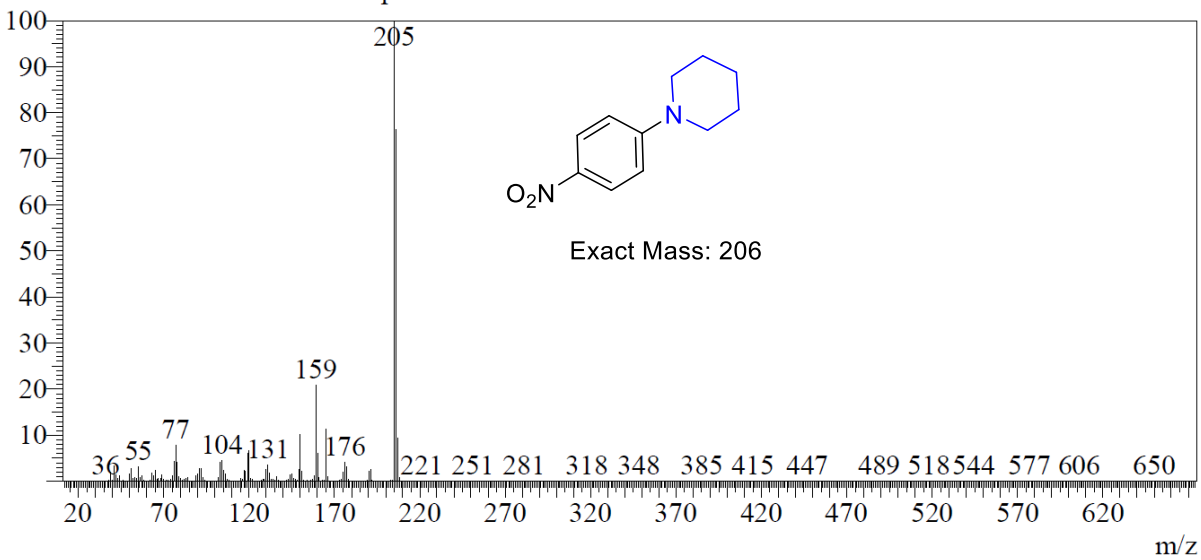


Table S4. A comparison of the Fe_3O_4@CS@AF@Cu catalyst with previously reported Fe_3O_4 based heterogeneous catalysts for the C-N coupling of aryl halides

Entry	Aryl halide	amine	Catalyst	Conditions	Yield %	Ref
1	1-Bromo-4-nitrobenzene	Imidazole	CTSN/Fe_3O_4 –Cu (10.0 mg)	DMF, CTAB (0.5 mmol) K_2CO_3, USW bath (50 kHz, 200 W)	96	(Taheri-Ledari et al., 2019)
2	1-Bromo-4-nitrobenzene	Morpholine	Fe_3O_4@Fe-Cu/MCM-41 (15.0 mg)	H_2O, TBAB, Na_2CO_3, 100 °C,	95	(Abdollahi-Alibeik and Ramazani 2022)
3	1-Iodo-4-nitrobenzene	Imidazole	Fe_3O_4@SiO_2 /Ligand/Cu(P) (0.6 mol%)	DMF, Cs_2CO_3, 100 °C, 2.5 h	96	(Zahmatkesh et al., 2019)
4	Bromobenzene	Morpholine	Fe_3O_4@pectin/ Pd (0.013 g, 0.1 mol%)	DMF, Et_3N, 100 °C, 12 h, N_2	95	(Zhang et al., 2020)
5	1-Iodo-4-methoxybenzene	Piperidine	Fe_3O_4@SiO_2 @GA/ Cu (100 mg)	H_2O, Cs_2CO_3, 100 °C, 12 h	55	(Ge et al., 2021)
6	Bromobenzene	Morpholine	Fe_3O_4@PVA /CuCl (0.5 mol%)	DMF, Et_3N, 120 °C, 8 h, N_2	95	(Hemmati et al., 2020)
7	Bromobenzene	Morpholine	Fe_3O_4@PDA /Pd(II) (0.5 mol%)	DMF, Cs_2CO_3, 100 °C, 10h	96	(Veisi et al., 2018)
8	1-Bromo-4-nitrobenzene	Piperidine	Fe_3O_4@CS@AF@Cu (0.63 mol%)	H_2O, K_2CO_3, 100 °C, 1h	99	This work

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