Supporting information

For

New magnetic nanoparticle-supported Lewis acidic ionic liquid as a highly effective and recyclable catalyst for the synthesis of benzoxanthenes and pyrroles under solvent-free sonication.

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Table of contents

Section S1. Chemicals, supplies and instruments	**S1-S2**
Section S2. General procedure	**S2-S3**
Section S3. Optimization of the reaction condition	**S4-S8**
Section S4. Spectral data	**S9-S26**
Section S5. ^{1}H, ^{13}C NMR and HRMS spectroscopy	**S27-S76**
Section S6. References	**S77-S79**

Section S1. Chemicals, supplies and instruments

Chemicals and supplies

4-*tert*-Butylbenzaldehyde (assay 97%), 4-fluorobenzaldehyde (assay 98%), 4-chlorobenzaldehyde (assay 97%), 4-bromobenzaldehyde (grade reagentPlus®, assay 99%), 3-chlorobenzaldehyde (assay 97%), 3-bromobenzaldehyde (assay 97%), 2-chlorobenzaldehyde (assay 99%), 2-bromobenzaldehyde (assay 98%), salicylaldehyde (reagent grade, assay 98%), 2-nitrobenzaldehyde (assay 98%), cyclohexane-carbaldehyde (assay 97%), benzo[*d*][1,3]dioxole-5-carbaldehyde (piperonal, assay 99%), 2-hydroxy-5-methylbenzaldehyde (assay 98%), 2-hydroxy-5-nitrobenzaldehyde (assay 98%), 4-(dimethylamino)benzaldehyde (ACS reagent, assay 99%), aniline (ACS reagent, ≥ 99.5%), *o*-toluidine (assay ≥ 99%), 3,5-dichoroaniline (assay ≥ 98%), 2,5-dichoroaniline (assay ≥ 99%), 3,4-dichoroaniline (assay ≥ 99%), 2,5-dibromoaniline (assay ≥ 98%), triethylenetetramine (assay ≥ 97.0% (T)), tetraethylenepent-amine (technical grade), phenylhydrazine (assay 97%), 2,4-dinitrophenylhydrazine (reagent grade, 97%), 4-nitroaniline (assay ≥ 99%), 4-nitro-*o*-phenylenediamine (assay 98%), 2-amino-4-nitrophenol (assay ≥ 99.0% (NT)), 2-amino-*p*-cresol (assay 97%), 4-aminobenzonitrile (assay 98%), 4-iodoaniline (assay 98%), 2-aminobiphenyl (assay 97%), methyl 4-aminobenzoate (assay 98%), and 4-aminophenol (assay 99%), 2,4-dinitroaniline (assay 98%), 4-amino-3-hydroxybenzoic acid (assay 97%) were abtained form Sigma-Aldrich. Butyraldehyde (for synthesis), benzaldehyde (for synthesis), 4-methylbenzaldehyde (for synthesis), 2-naphthol (for synthesis), cinnam-aldehyde (for synthesis) were obtained from Merck.

Analytical techniques

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 instruments using $CDCl_3$ as solvent and solvent peaks or TMS as internal standards. HRMS (ESI) data were collected using Bruker micrOTOF-QII MS at 80 eV. FT-IR spectra were recorded in the form of KBr pellets by a Bruker Vertex 70. GC-MS analyses were performed on an Agilent GC system 7890 equipped with a mass selective detector Agilent 5973N and a capillary DB-5MS column (30m x 250 μm x 0.25

μm). Analytical thin-layer chromatography (TLC) was acquired on F-254 silica gel coated aluminum plates from Merck. Silica gel column chromatography was carried out with silica gel (60, 230-400 mesh) from Merck. Thermal gravimetric analysis (TGA) was obtained using a TA Q500 thermal analysis system with the sample held in a platinum pan in a continuous airflow. Ultrasonic irradiation-assisted reactions were performed on an Elma sonic S30H Ultrasonic cleaning unit at the frequency of 37 kHz. Raman spectra were recorded on a Horiba Xplora One using a 532 nm argon ion laser. ICP-MS was recorded on a PerkinElmer 350X. Scanning electron microscope (SEM) was performed on an S4800 Hitachi, Japan. The electron diffraction spectroscopy (EDS) was conducted on a Horiba H7593. ICP-OES was recorded on a PerkinElmer 350X.

Section S2. General procedure

Preparation of magnetic Fe_3O_4 nanoparticle (MNPs) [1]

MNP was synthesized by simple co-precipitation of ferric and ferrous ions in an alkaline condition. Typically, $FeCl_3.6H_2O$ (20 mmol) and $FeSO_4.7H_2O$ (10 mmol) were dissolved in 100 mL deionized water. The mixture was stirred at 80 ^oC and then KOH (12 mmol) was added and stirred continuously within 2 h. The black precipitate, after being collected by a permanent magnet, was washed with water (3 x 100 mL) and ethanol (3 x 50 mL). This MNP material was dried at 60-70 ^oC under *vacuo* for 1 h.

General procedure for the synthesis of LAIL@MNP

The imidazolium chloride ionic liquid was synthesized according to a procedure reported in the literature [2]. A mixture of 3-chloroethoxy-propylsilane (5.0 mmol, 1.2 mL) and imidazole (5.0 mmol, 0.34 g) was stirred at reflux for 17 h. The ionic liquid obtained as a yellowish viscous liquid was diluted in 50 mL of ethanol-water (1:1 volume ratio) solution. To the freshly prepared suspension of MNP material in 100 mL of 1:1 ethanol-water was added the above ionic liquid solution and the mixture was sonicated at 40 ^oC for 4 h. The resultant IL@MNP was washed with dichloromethane and dried at 70 ^oC in *vacuo*. To synthesize LAIL@MNP, a mixture of IL@MNP (1.0 g) and $ZnCl_2$ (1.0 mmol) in ethanol (50 mL) was refluxed for 24 h. After cooling to room temperature, the catalyst was separated by a magnet,

washed with ethanol, and dried at 100 ^{o}C for 5 h. The LAIL@MNP was characterized by FT-IR, SEM, TEM, TGA, Raman, and SEM-EDS. The loading amount of Zn metal was determined based on ICP-OES.

General procedure for one-pot multicomponent reaction

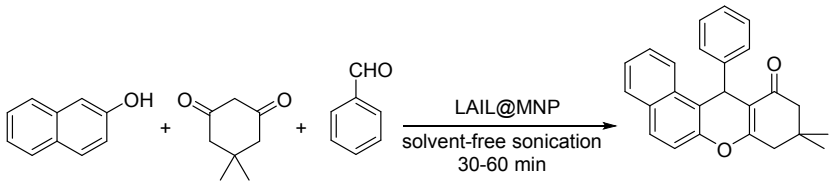
A mixture of 2-naphthol (1.0 mmol, 0.144 g), benzaldehyde (1.0 mmol, 0.106 g), dimedone (1.0 mmol, 0.140 g) was reacted under solvent-free sonication in the presence of LAIL@MNP (15 mg) at 80 ^{o}C for 30 min. Upon completion of the reaction (monitored by TLC), ethyl acetate (15 mL) was added and the solid catalyst was removed from organic solution by a magnet. The catalyst was washed with ethyl acetate (2 x 5 mL) followed by ethanol (3 x 5 mL) and then reused for next cycles after drying under vacuum. Meanwhile, the organic solution was dried over $MgSO_4$ and then concentrated under reduced pressure. The resultant crude product was recrystallized from ethanol to yield pure benzoxanthene whose structure was by ^{1}H and ^{13}C NMR.

General procedure for Paal-Knorr reaction

A mixture of aniline (1.0 mmol), acetonylacetone (1.2 mmol) and LAIL@MNP (15 mg) was reacted under solvent-free sonication for an appropriate time. Upon completion of the reaction (monitored by TLC and GC), ethyl acetate (15 mL) was added and the solid catalyst was removed from the organic solution by a magnet. The catalyst was washed with ethyl acetate (2 x 5 mL) followed by ethanol (3 x5 mL) and then reused for next cycles after drying under vacuum. Meanwhile, the organic solution was dried over $MgSO_4$ and the solvent was removed by a rotary evaporator. The crude product was purified through silica gel chromatography using ethyl acetate–hexane (1:9). The purified pyrrole was then characterized by ^{1}H and ^{13}C NMR, GC-MS or HRMS (ESI).

Section S3. Optimization of the reaction condition

Table S1. Optimization of reaction conditions[a]



Entry	Temperature (°C)	Time (min)	Catalyst loading (mg)	Yield[b] (%)
1	r.t.	1	15	14
2	r.t.	5	15	19
3	r.t.	10	15	24
4	r.t.	15	15	32
5	r.t.	20	15	43
6	r.t.	25	15	55
7	r.t.	30	15	67
8	r.t.	45	15	75
9	r.t.	60	15	88
10	r.t.	90	15	90
11	r.t.	120	15	94
12	80	1	15	23
13	80	5	15	25
14	80	10	15	31
15	80	15	15	40
16	80	20	15	66
17	80	25	15	75
18	80	30	15	96
19	80	45	15	96
20	80	60	15	95
21	80	90	15	97
22	80	120	15	99
23	80	30	0	10
24	80	30	1	65
25	80	30	5	77

Entry	Temperature (°C)	Time (min)	Catalyst loading (mg)	Yield[b] (%)
26	80	30	10	81
27	80	30	20	97
28	80	30	25	99
29	80	30	30	94
30	80	30	35	95
31	80	30	50	96
32	80	30	100	99

[a]Reaction condition: 2-naphthol, dimedone, and benzaldehyde in the presence of LAIL@MNP.

[b]Isolated yields.

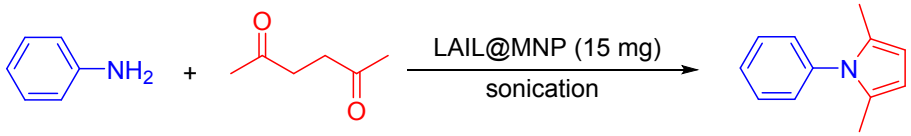
Table S2. Effect of catalysts and solvents.[a]

Entry	Catalyst	Solvent[b]	Yield[c] (%)
1	[BMIM]PF_6	Solvent-free	70
2	[EMIM]Cl	Solvent-free	77
3	[BMIM]OTf	Solvent-free	71
4	[TMSPIM][d]	Solvent-free	60
5	$AlCl_3$	Solvent-free	84
6	$FeCl_3$	Solvent-free	80
7	$CuCl_2$	Solvent-free	81
8	$HfCl_4$	Solvent-free	80
9	$ZnCl_2$	Solvent-free	85
10	Al_2O_3	Solvent-free	61
11	Fe_2O_3	Solvent-free	65
12	MgO	Solvent-free	58
13	CuO	Solvent-free	63
14	Cu_2O	Solvent-free	51
15	ZnO	Solvent-free	69
16	$CuFe_2O_4$	Solvent-free	57
17	$ZnFe_2O_4$	Solvent-free	55
18	γ-Fe_2O_3	Solvent-free	64

Entry	Catalyst	Solvent[b]	Yield[c] (%)
19	Nano Fe_3O_4	Solvent-free	68
20	None	Solvent-free	10
21	LAIL@MNP	Solvent-free	96
22	LAIL@MNP	Butan-2-ol	42
23	LAIL@MNP	Ethanol	59
24	LAIL@MNP	Propan-2-ol	61
25	LAIL@MNP	Dichloromethane	50
26	LAIL@MNP	Tetrahydrofuran	54
27	LAIL@MNP	Acetone	73
28	LAIL@MNP	DMF	68
29	LAIL@MNP	Acetonitrile	77
30	LAIL@MNP	Dimethyl sulfoxide	65
31	LAIL@MNP	Ethyl acetate	59
32	LAIL@MNP	Chloroform	65
33	LAIL@MNP	CPME	57
34	LAIL@MNP	Hexane	55
35	LAIL@MNP	Toluene	63
36	LAIL@MNP	Dioxane	61

[a]Reaction condition: 2-naphthol (1.0 mmol), dimedone (1.0 mmol), benzaldehyde (1.0 mmol) and catalyst (15 mg). [b]Solvents (1.5 mL). [c]Isolated yield. [d]3-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium chloride.

Table S3. Optimization of reaction conditions.[a]



Entry	Time (min)	Catalyst loading (mg)	Molar ratio (mmol)	Yield[b] (%)
1	1	15	1:1.2	26
2	2	15	1:1.2	29
3	3	15	1:1.2	32

4	5	15	1:1.2	46
5	7	15	1:1.2	54
6	10	15	1:1.2	58
7	15	15	1:1.2	70
8	30	15	1:1.2	95 (91)[c]
9	30	0	1:1.2	43
10	30	1	1:1.2	59
11	30	5	1:1.2	57
12	30	10	1:1.2	67
13	30	50	1:1.2	93
14	30	15	1:1	66
15	30	15	1:1.1	67
16	30	15	1:1.3	59
17	30	15	1:1.4	65
18	30	15	1:1.5	59
19	30	15	1:2	51
20	30	15	1:3	51
21	30	15	1:4	50
22	30	15	1:5	46

[a]*Reaction condition*: Aniline (1.0 mmol), acetonylacetone (1.2 mmol) and Fe_3O_4@SiO_2-IL-Zn_xCl_y (15 mg) under solvent-free sonication. [b]Yield was reported by GC. [c]Yield in parenthesis was isolated yield.

Table S4. Effect of various catalysts and solvents.

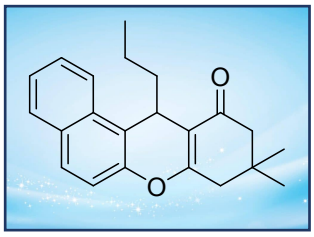
Entry	Catalyst	Solvent	Yield (%)
1	[BMIM]PF_6	Solvent-free	73
2	[EMIM]Cl	Solvent-free	74
3	[BMIM]OTf	Solvent-free	79
4	$AlCl_3$	Solvent-free	86
5	$FeCl_3$	Solvent-free	87
6	$CuCl_2$	Solvent-free	83

7	$HfCl_4$	Solvent-free	84
8	$ZnCl_2$	Solvent-free	84
9	Al_2O_3	Solvent-free	25
10	Fe_2O_3	Solvent-free	35
11	MgO	Solvent-free	19
12	CuO	Solvent-free	57
13	Cu_2O	Solvent-free	17
14	ZnO	Solvent-free	55
15	$CuFe_2O_4$	Solvent-free	28
16	$ZnFe_2O_4$	Solvent-free	15
17	Fe_3O_4	Solvent-free	30
18	γ-Fe_2O_3	Solvent-free	49
19	No catalyst	Solvent-free	43
20	LAIL@MNP	Solvent-free	95
21	LAIL@MNP	Dichloromethane	14
22	LAIL@MNP	Tetrahydrofurane	16
23	LAIL@MNP	2-Butanol	46
24	LAIL@MNP	Ethanol	53
25	LAIL@MNP	Propan-2-ol	48
26	LAIL@MNP	Acetone	57
27	LAIL@MNP	DMF	6
28	LAIL@MNP	Acetonitrile	28
29	LAIL@MNP	Dimethyl sulfoxide	14
30	LAIL@MNP	Ethyl acetate	Trace
31	LAIL@MNP	CPME	10
32	LAIL@MNP	Toluene	15
33	LAIL@MNP	Dioxane	13
34	LAIL@MNP	Chloroform	70

[a]*Reaction condition*: Aniline (1.0 mmol), acetonylacetone (1.2 mmol) Fe_3O_4@SiO_2-IL-Zn_xCl_y (15 mg), and solvent (2.0 mL) under sonication for 30 min. [b]Yield was reported by GC.

Section S4. Spectral data

9,9-Dimethyl-12-propyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[20]

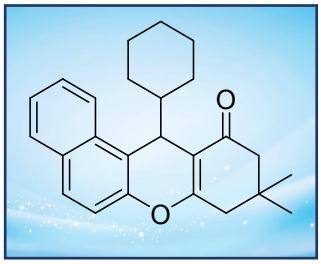


Yellow powder, M.p. = 170–171 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.89–7.87 (d, J = 8.0 Hz, 1H), 7.63–7.62 (d, J = 6.5 Hz, 1H), 7.61–7.59 (d, J = 9.5 Hz, 1H), 7.48–7.45 (t, J = 8.0 Hz, 15.5 Hz, 1H), 7.19 (s, 1H), 6.65–6.63 (d, J = 9.5 Hz, 1H), 3.36 (s, 2H), 2.93–2.89 (q, J = 7.5 Hz, 15.0 Hz, 2H), 1.60–1.53 (m, 3H), 1.51 (s, 4H), 1.32–1.29 (t, J = 7.5 Hz, 15.0 Hz, 3H), 1.13–1.10 (t, J = 7.5 Hz, 15 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 187.8, 151.5, 151.4, 143.6, 139.7, 139.6, 134.1, 134.0, 131.5, 131.1, 130.3, 128.0, 125.6, 32.6, 29.9, 26.2, 235, 15.7, 15.7, 15.2, 15.1, 1.2.

12-Cyclohexyl-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[21]

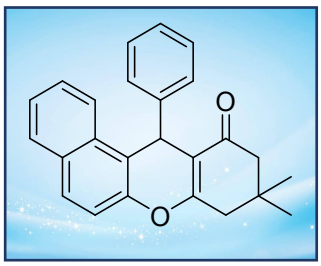


Yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.10 (d, J = 8.5 Hz, 1H), 7.83 – 7.81 (d, J = 8.0 Hz, 1H), 7.71 – 7.69 (d, J = 9.0 Hz, 1H), 7.56 – 7.53 (t, J = 7.0 Hz, 1H), 7.45 – 7.42 (t, J = 7.0 Hz, 1H), 7.23 – 7.22 (d, J = 8.5 Hz, 1H), 4.69 – 4.68 (d, J = 3.4 Hz, 1H), 2.63 – 2.50 (q, J = 17.5 Hz, 2H), 2.43 – 2.29 (q, J = 16.5 Hz, 2H), 1.84 – 1.81 (d, J = 13.0 Hz, 1H), 1.75 – 1.66 (m, 3H), 1.57 – 1.51 (m, 2H), 1.41 – 1.39 (d, J = 11.0 Hz, 1H), 1.25 (s, 3H), 1.14 (s, 3H), 0.96 – 0.87 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 167.0, 149.3, 131.6, 131.5, 128.4, 127.7, 126.5, 124.7, 123.6, 118.7, 117.0, 112.4, 51.1, 45.7, 41.5, 32.8, 31.9, 31.3, 29.9, 28.9, 27.4, 26.8, 26.4, 26.4.

9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydro-11*H*-benzo[a]xanthen-11-one[22]

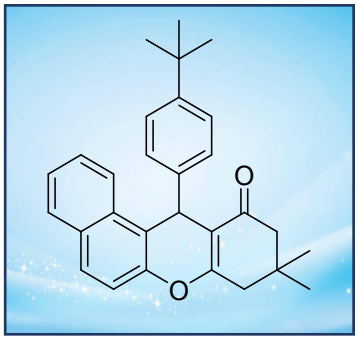


White powder, M.p. = 154–155 °C.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05–8.03 (d, J = 8.0 Hz, 1H), 7.92–7.90 (d, J = 9.0 Hz, 2H), 7.50–7.47 (dt, J = 1.0 Hz, 7.0 Hz, 1H), 7.46–7.45 (d, J = 9.0 Hz, 1H), 7.44–7.41 (dt, J = 1.0 Hz, 8.0 Hz, 1H), 7.30–7.28 (d, J = 7.5 Hz, 2H), 7.19–7.16 (t, J = 7.5 Hz, 15.5 Hz, 2H), 7.06–7.03 (t, J = 7.5 Hz, 14.5 Hz, 1H), 5.57 (s, 1H), 2.70 – 2.57 (q, J = 17.0 Hz, 2H), 2.35 – 2.32 (d, J = 16.0 Hz, 1H), 2.14 – 2.11 (d, J = 16.0 Hz, 1H), 1.06 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 196.4, 164.3, 147.7, 145.3, 131.6, 131.1, 129.6, 129.0, 128.6, 128.6, 127.6, 126.7, 125.4, 123.7, 117.8, 117.6, 113.7, 50.6, 40.7, 34.6, 32.4, 29.3, 26.7.

12-(4-(*tert*-Butyl)phenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



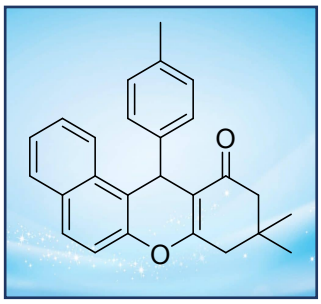
White powder, M.p. = 209 – 210 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–8.03 (d, J = 8.5 Hz, 1H), 7.78–7.77 (d, J = 7.5 Hz, 1H), 7.75–7.74 (d, J = 9 Hz, 1H), 7.46–7.43 (dt, J = 1.5 Hz, 7 Hz, 1H), 7.39–

7.36 (t, J = 8.0 Hz, 1H), 7.33–7.31 (d, J = 9.0 Hz, 1H), 7.24–7.22 (d, J = 8.5 Hz, 2H), 7.17–7.15 (d, J = 8.5 Hz, 2H), 5.68 (s, 1H), 2.58–2.56 (d, J = 7.0 Hz, 2H), 2.29–2.27 (d, J = 7.0 Hz, 2H), 1.19 (s, 9H), 1.14 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 163.9, 148.7, 147.8, 141.7, 131.5, 128.6, 128.3, 127.9, 126.9, 125.1, 124.8, 123.8, 118.0, 117.1, 114.5, 51.0, 41.5, 34.1, 32.3, 31.27, 29.1, 27.5.

9,9-Dimethyl-12-(*p*-tolyl)-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[23]

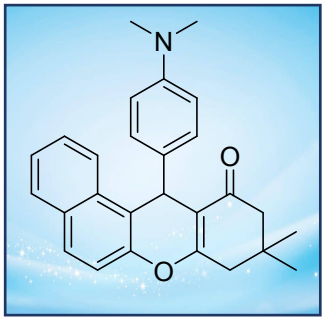


White powder, M.p. = 181–182 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02–8.01 (d, J = 8.5 Hz, 1H), 7.78–7.74 (t, J = 11.0 Hz, 20.0 Hz, 2H), 7.45–7.42 (t, J = 7.5 Hz, 15.0 Hz, 1H), 7.38–7.35 (t, J = 7.5 Hz, 14.5 Hz, 1H), 7.33–7.31 (d, J = 9.0 Hz, 1H), 7.24–7.23 (d, J = 6.5 Hz, 2H), 6.99–6.97 (d, J = 8.0 Hz, 2H), 5.68 (s, 1H), 2.57 (s, 2H), 2.32–2.23 (q, J = 16.0 Hz, 13.0 Hz, 2H), 2.20 (s, 3H), 1.12 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 163.8, 147.7, 141.9, 135.7, 131.5, 131.4, 129.0, 128.7, 128.4, 128.3, 127.0, 124.9, 123.7, 117.9, 117.1, 114.4, 51.0, 41.5, 34.3, 32.3, 29.3, 27.3, 21.0.

12-(4-Dimethylamino)phenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[20]

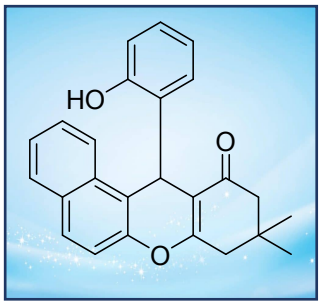


White powder, M.p. = 200 – 201 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.03 (d, J = 8.5 Hz, 1H), 7.77 – 7.72 (dd, J = 8.0 Hz, 9.0 Hz, 2H), 7.44 – 7.41 (t, J = 7.5 Hz, 15.5 Hz, 1H), 7.37 – 7.34 (t, J = 7.0 Hz, 14.5 Hz, 1H), 7.31 – 7.29 (d, J = 9.0 Hz, 1H), 7.19 – 7.17 (d, J = 8.5 Hz, 2H), 6.55 – 6.54 (d, J = 8.5 Hz, 2H), 5.61 (s, 1H), 2.82 (s, 6H), 2.56 (s, 2H), 2.32 – 2.23 (q, J = 16.5 Hz, 8.5 Hz, 2H), 1.11 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 163.5, 148.9, 147.7, 133.3, 131.5, 129.2, 129.0, 128.4, 128.3, 126.9, 124.7, 123.9, 118.4, 117.0, 114.7, 112.4, 112.3, 51.0, 41.4, 40.5, 33.6, 32.3, 29.2, 27.4.

12-(2-Hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[24]

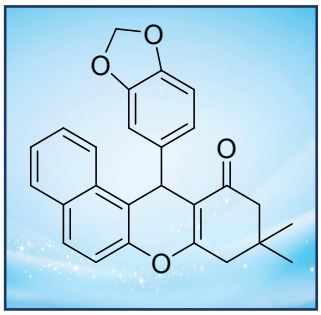


White powder, M.p. = 225 – 226 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.79 – 7.76 (t, J = 9.0 Hz, 3H), 7.68 – 7.66 (d, J = 8.5 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.34 – 7.32 (d, J = 9.0 Hz, 1H), 7.01 – 7.00 (t, J = 2.0 Hz, 1H), 6.61 – 6.60 (t, J = 3.0 Hz, 1H), 5.77 (s, 1H), 2.61 (s, 2H), 2.43 – 2.34 (q, J = 16.5 Hz, 13.0 Hz, 2H), 1.15 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 166.8, 152.9, 133.1, 132.7, 131.6, 131.1, 129.1, 128.7, 128.2, 127.9, 127.5, 127.4, 125.3, 123.5, 121.5, 118.8, 116.6, 50.3, 41.6, 30.9, 30.5, 29.7, 29.2, 29.0, 28.0, 27.5.

12-(Benzo[*d*][1,3]dioxol-5-yl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[25]

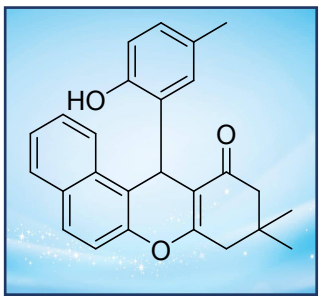


White powder, M.p. = 234 – 235 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 – 7.97 (d, J = 8.5 Hz, 1H), 7.79 – 7.77 (d, J = 8.0 Hz, 1H), 7.76 – 7.75 (d, J = 9.0 Hz, 1H), 7.46 – 7.43 (t, J = 7.0 Hz, 1H), 7.40 – 7.37 (t, J = 8.0 Hz, 1H), 7.32 – 7.30 (d, J = 9.0 Hz, 1H), 6.86 – 6.84 (dd, J = 2.0 Hz, 1H), 6.79 – 6.78 (d, J = 1.5 Hz, 1H), 6.62 – 6.61 (d, J = 8.0 Hz, 1H), 5.83 – 5.79 (d, 5.64 (s, 1H), 2.56 (s, 2H), 2.33 – 2.25 (q, J = 16.5 Hz, 2H), 1.12 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 163.8, 147.7, 147.5, 145.8, 138.9, 131.5, 131.4, 128.8, 128.4, 127.0, 124.9, 123.7, 121.8, 117.7, 117.1, 114.1, 109.0, 107.9, 100.7, 51.0, 41.4, 34.3, 32.3, 29.7, 29.2, 28.0, 27.3.

12-(2-Hydroxy-5-methylphenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



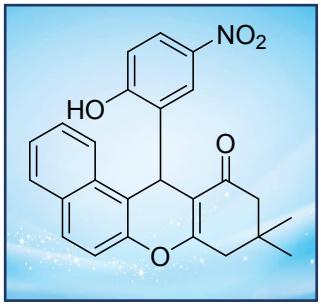
White powder, M.p. = 178 – 179 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.79 – 7.77 (m, 2H), 7.72 – 7.70 (d, J = 8.5 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.35 – 7.33 (d, J = 8.5 Hz, 1H), 6.91 – 6.89 (d, J = 8.0 Hz, 1H), 6.80 – 6.78 (d, J = 8.0 Hz, 1H), 6.37 (s, 1H), 5.75 (s, 1H), 2.66 – 2.56 (q, J = 17.5 Hz, 2H), 2.42 – 2.34 (q, J = 16.5 Hz, 2H), 1.96 (s, 3H), 1.14 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5, 166.7, 150.5, 147.9, 132.5, 131.6, 131.3, 130.6, 129.0, 128.9, 128.7, 128.2, 127.5, 125.2, 123.6, 118.6, 117.6, 116.63, 114.1, 50.3, 41.6, 32.5, 28.87, 28.0, 27.5, 20.6.

HRMS (ESI) *m/z* calcd for $[M + Na]^+$ $C_{26}H_{24}O_3Na^+$ 407.16232, found 407.16252

12-(2-Hydroxy-5-nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[26]

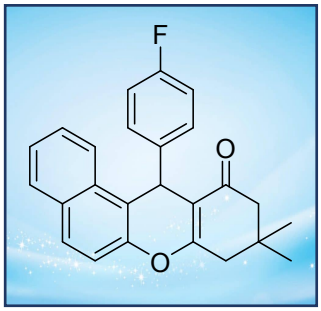


Yellow powder, M.p. = 117 – 118 °C

^{1}H-NMR (500 MHz, $CDCl_3$/DMSO) δ 7.74 (m, 1H), 7.44 – 7.38 (m, 4H), 7.06 – 7.02 (q, J = 7.0 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.55 – 6.51 (m, 1H), 5.47 (s, 1H), 2.26 (s, 2H), 1.96 – 1.74 (m, 2H), 0.75 (s, 3H), 0.60 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$/DMSO) δ 197.2, 165.4, 160.4, 147.8, 140.5, 132.7, 131.3, 129.2, 128.6, 127.3, 126.3, 125.1, 123.8, 123.4, 117.3, 116.6, 50.7, 41.3, 40.4, 40.2, 40.0, 39.9, 39.7, 32.3, 29.3, 27.0.

12-(4-Fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[27]



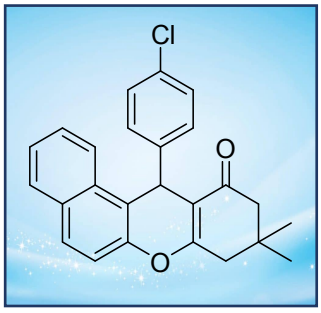
White powder, M.p. = 185–186 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.92 (d, J = 8.5 Hz, 1H), 7.80 – 7.76 (t, J = 8.5 Hz, 17.5 Hz, 2H), 7.46 – 7.42 (dt, J = 1.5 Hz, 7.0 Hz, 1H), 7.40 – 7.37 (dt, J =

1.0 Hz, 8.0 Hz, 1H), 7.33 – 7.32 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.28 (dt, *J* = 2.5 Hz, 5.5 Hz, 2H), 6.87 – 6.83 (t, *J* = 8.5 Hz, 2H), 5.70 (s, 1H), 2.57 (s, 2H), 2.33 – 2.23 (q, *J* = 16.0 Hz, 16.5 Hz, 2H), 1.12 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 163.9, 161.2 (d, *J* = 243.0 Hz, 1C), 147.8, 140.6, 131.5, 131.3, 129.9 (d, *J* = 8.0 Hz, 1C), 129.8, 129.0, 128.5, 127.1, 125.0, 123.5, 117.4, 117.0, 115.0 (d, *J* = 21.1 Hz, 1C), 114.13, 50.9, 41.4, 34.0, 32.3, 29.3, 27.1.

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[28]

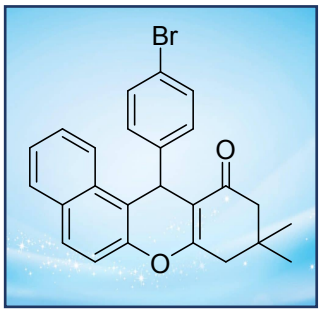


White powder, M.p. = 181–182 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.90 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.77 (t, *J* = 7.5 Hz, 16.0 Hz, 2H), 7.46 – 7.42 (dt, *J* = 1.0 Hz, 7.0 Hz, 1H), 7.40 – 7.37 (dt, *J* = 1.0 Hz, 8.0 Hz, 1H), 7.33 – 7.32 (d, *J* = 9.0 Hz, 1H), 7.28 – 7.26 (d, *J* = 8.5 Hz, 2H), 7.14 – 7.13 (d, *J* = 8.5 Hz, 2H), 5.69 (s, 1H), 2.57 (s, 2H), 2.33 – 2.23 (q, *J* = 16.0 Hz, 17.0 Hz, 2H), 1.12 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 164.0, 147.8, 143.3, 131.9, 131.5, 131.2, 129.8, 128.5, 127.1, 125.0, 123.5, 117.1, 117.0, 113.9, 50.9, 41.4, 34.2, 32.2, 29.3, 27.1.

12-(4-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[27]

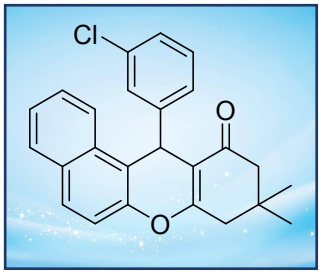


White powder, M.p. = 186–187 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.89 (d, J = 8.0 Hz, 1H), 7.80 – 7.77 (t, J = 7.5 Hz, 2H), 7.46 – 7.42 (dt, J = 1.5 Hz, 7.0 Hz, 1H), 7.40 – 7.37 (dt, J = 1.0 Hz, 8.0 Hz, 1H), 7.33 – 7.31 (d, J = 9.0 Hz, 1H), 7.30 – 7.28 (d, J = 8.5 Hz, 2H), 7.22 – 7.21 (d, J = 8.5 Hz, 2H), 5.68 (s, 1H), 2.57 (s, 2H), 2.33 – 2.23 (q, J = 16.0 Hz, 16.5 Hz, 2H), 1.12 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 164.1, 147.8, 143.8, 131.5, 131.4, 131.2, 130.2, 129.1, 128.5, 127.1, 125.0, 123.5, 120.1, 117.0, 117.0, 113.8, 50.9, 41.4, 34.3, 32.3, 29.3, 27.2.

12-(3-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[20]

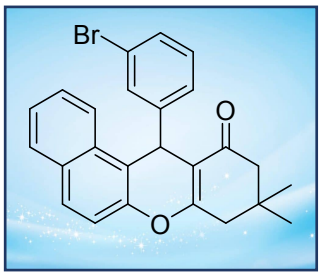


White powder, M.p. = 173–174 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.91 (d, J = 8.0 Hz, 1H), 7.81 – 7.78 (t, J = 6.5 Hz, 2H), 7.47 – 7.44 (dt, J = 1.0 Hz, 7.0 Hz, 1H), 7.41 – 7.38 (dt, J = 1.0 Hz, 8.0 Hz, 1H), 7.34 – 7.32 (d, J = 9.0 Hz, 1H), 7.29 – 7.26 (t, J = 7.5 Hz, 2H), 7.13 – 7.10 (t, J = 8.0 Hz, 1H), 7.05 – 7.03 (d, J = 8.0 Hz, 1H), 5.69 (s, 1H), 2.62 – 2.54 (q, J = 17.5 Hz, 2H), 2.33 – 2.25 (q, J = 16.0 Hz, 10.5 Hz, 2H), 1.12 (s 3H), 0.98 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 164.1, 147.8, 146.7, 134.1, 131.6, 131.3, 129.4, 129.2, 128.5, 128.4, 127.2, 126.8, 126.6, 125.0, 123.5, 117.1, 116.9, 113.7, 50.9, 41.4, 34.5, 32.3, 29.2, 27.2.

12-(3-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[29]

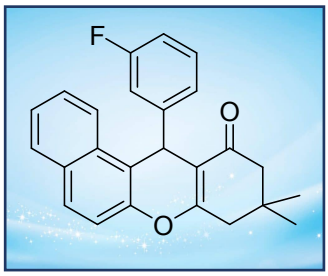


White powder, M.p. = 177–178 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.92 (d, J = 8.5 Hz, 1H), 7.81 – 7.78 (t, J = 7.0 Hz, 15.5 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.34 – 7.33 (d, J = 9.0 Hz, 2H), 7.21 – 7.18 (m, 1H), 7.07 – 7.04 (t, J = 8.0 Hz, 1H), 5.69 (s, 1H), 2.62 – 2.54 (q, J = 17.5 Hz, 4.5 Hz, 2H), 2.33 – 2.25 (q, J = 16.5 Hz, 8.5 Hz, 2H), 1.12 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 164.2, 147.8, 147.0, 131.6, 131.3, 131.2, 129.7, 129.5, 129.2, 128.5, 127.3, 127.2, 125.0, 123.3, 122.5, 50.9, 41.4, 34.5, 32.3, 29.2, 27.2.

12-(3-Fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[30]

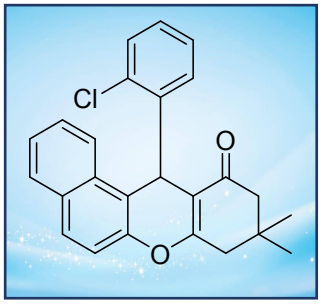


White powder, M.p. = 155-156 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.94 (d, J = 8.5 Hz, 1H), 7.81 – 7.77 (t, J = 7.0 Hz, 15.5 Hz, 2H), 7.46 – 7.43 (t, J = 7.0 Hz, 15.5 Hz, 1H), 7.41 – 7.38 (t, J = 7.0 Hz, 15.0 Hz, 1H), 7.35 – 7.33 (d, J = 9.0 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.02 – 7.00 (d, J = 10.5 Hz, 1H), 6.78 – 6.75 (t, J = 8.5 Hz, 16.5 Hz, 1H), 5.74 (s, 1H), 2.58 (s, 2H), 2.34 – 2.25 (q, J = 16.0 Hz, 12.0 Hz, 2H), 1.13 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 196.8, 164.2, 162.9 (d, J = 243.9 Hz, 1C), 147.8, 147.2 (d, J = 6.4 Hz, 1C), 131.5, 131.3, 129.6 (d, J = 8.1 Hz, 1C), 129.1, 128.5, 127.1, 125.0, 124.2 (d, J = 2.6 Hz, 1C), 123.5, 117.1, 117.0, 115.4, 115.2, 113.8, 113.4, 113.2, 50.9, 41.4, 34.5, 32.2, 29.3, 27.1.

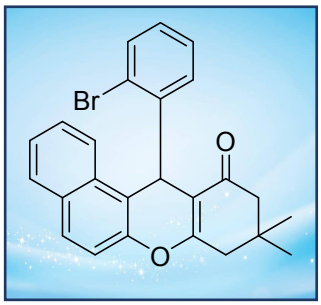
12-(2-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[27]



Yellowish powder, M.p. = 180–181 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24–8.23 (d, J = 8.5 Hz, 1H), 7.77–7.74 (t, J = 8.0 Hz, 2H), 7.50–7.47 (t, J = 8.0 Hz, 1H), 7.40–7.37 (t, J = 8.0 Hz, 1H), 7.31–7.27 (t, J = 9.0 Hz, 3H), 7.08–7.05 (t, J = 7.0 Hz, 1H), 7.01–6.98 (dt, J = 1.5 Hz, 7.5 Hz, 1H), 6.01 (s, 1H), 2.61 (s, 2H), 2.34–2.22 (q, J = 16.0 Hz, 2H), 1.14 (s, 3H), 1.01 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 164.3, 147.7, 142.2, 133.0, 131.7, 131.4, 130.0, 129.1, 128.4, 127.7, 127.1, 126.9, 126.4, 125.0, 124.0, 123.3, 118.1, 117.1, 113.5, 109.5, 50.9, 41.5, 33.0, 32.2, 29.4, 27.1.

12-(2-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[31]



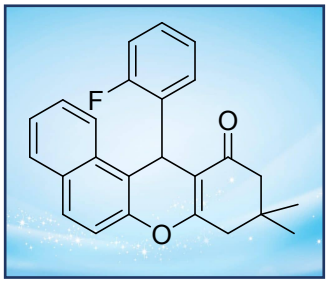
Pinkish powder, M.p. = 175–176 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32–8.31 (d, J = 8.5 Hz, 1H), 7.77–7.74 (t, J = 7.0 Hz, 2H), 7.51–7.47 (t, J = 8.0 Hz, 2H), 7.40–7.37 (t, J = 7.5 Hz, 1H), 7.30–7.29 (d,

J = 8.5 Hz, 1H), 7.26–7.23 (t, *J* = 10 Hz, 1H), 7.10–7.07 (t, *J* = 7.5 Hz, 1H), 6.92–6.89 (t, *J* = 7.5 Hz, 1H), 5.97 (s, 1H), 2.61 (s, 2H), 2.33–2.22 (q, *J* = 16 Hz, 2H), 1.14 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.7, 164.1, 147.7, 133.4, 131.8, 131.4, 129.2, 128.4, 127.8, 127.6, 127.1, 1245.0, 124.5, 123.5, 117.1, 51.0, 41.6, 35.3, 32.1, 29.3, 27.2.

12-(2-Fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[32]

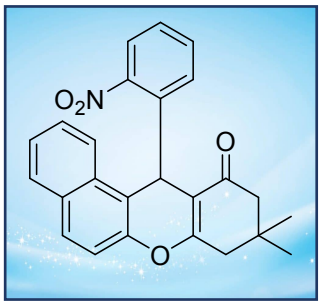


White powder, M.p. = 155-156 ^{o}C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12–8.10 (d, *J* = 8.5 Hz, 1H), 7.78–7.73 (q, *J* = 8.0 Hz, 4.0 Hz, 2H), 7.50–7.47 (t, *J* = 8.0 Hz, 15.0 Hz, 1H), 7.40–7.37 (t, *J* = 7.5 Hz, 14.5 Hz, 1H), 7.34–7.29 (m, 2H), 7.07–7.00 (m, 1H), 6.97–6.92 (m, 2H), 5.89 (s, 1H), 2.61 (s, 2H), 2.34–2.32 (q, *J* = 16.5 Hz, 2H), 1.14 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 164.4, 160.0 (d, *J* = 245.6 Hz, 1C), 152.9, 147.7, 131.5, 131.4, 130.9 (d, *J* = 4.1 Hz, 1C), 129.0 (t, *J* = 18.4 Hz, 44.6 Hz, 1C), 128.4, 128.2 (t, *J* = 5.0 Hz, 13.5 Hz, 1C), 127.9, 127.5, 127.2, 125.3, 124.9, 124.1 (d, *J* = 3.3 Hz, 1C), 123.5, 123.2 (d, *J* = 3.4 Hz, 1C), 121.5, 118.9, 117.1, 116.6, 115.6 (d, *J* = 22.6 Hz, 1C), 112.8, 50.8, 50.3, 41.4, 33.3, 29.4, 29.2 (d, *J* = 2.0 Hz, 1C), 29.0, 28.0, 27.1.

9,9-Dimethyl-12-(2-nitrophenyl)-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one[33]

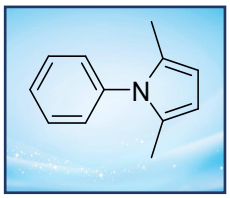


Yellow powder, M.p. = 223 – 224 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.56 – 8.54 (d, J = 8.5 Hz, 1H), 7.86 – 7.84 (dd, J = 1.5 Hz, 1.0 Hz, 1H), 7.83 – 7.81 (d, J = 9.0 Hz, 1H), 7.80 – 7.78 (d, J = 8.0 Hz, 1H), 7.48 – 7.45 (t, J = 6.5 Hz, 1H), 7.41 – 7.39 (t, J = 7.0 Hz, 1H), 7.33 – 7.32 (d, J = 9.0 Hz, 1H), 7.27 – 7.24 (t, J = 6.5 Hz, 1H), 7.19 – 7.16 (t, J = 7.0 Hz, 1H), 7.06 – 7.04 (dd, J = 1.5 Hz, 8.0 Hz, 1H), 6.58 (s, 1H), 2.59 – 2.48 (q, J = 17.5 Hz, 19.0 Hz, 2H), 2.29 – 2.18 (m, 2H), 1.09 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 196.8, 163.8, 149.3, 148.3, 139.2, 132.7, 131.8, 131.6, 131.1, 129.7, 128.2, 127.6, 127.1, 125.3, 124.7, 124.5, 116.9, 116.2, 113.4, 50.5, 41.5, 32.2, 30.9, 30.3, 29.1, 27.0.

2,5-Dimethyl-1-phenyl-1*H*-pyrrole[14, 16, 18, 34-36]



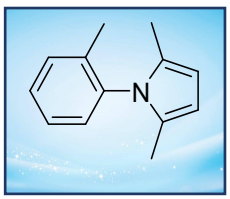
Yellow powder, M.p. 52-54 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.46 (t, J = 7.0 Hz, 2H), 7.43 – 7.40 (t, J = 7.5 Hz, 1H), 7.24 – 7.23 (d, J = 7.0 Hz, 2H), 5.93 (s, 2H), 2.06 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 129.0, 128.8, 128.3, 127.6, 105.6, 13.0.

GC-MS (EI, 70 eV) *m/z* 171 ($[M]^+$)

2,5-Dimethyl-1-(*o*-tolyl)-1*H*-pyrrole[12, 16, 34, 36]



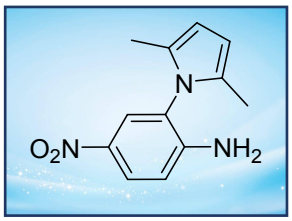
Yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.32 (m, 2H), 7.29 – 7.27 (m, 1H), 7.17 – 7.15 (d, J = 7.5 Hz, 2H), 5.91 (s, 2H), 1.94 (s, 3H), 1.92 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 130.7, 128.9, 128.3, 128.2, 126.6, 105.2, 29.7, 17.0, 12.5.

GC-MS (EI, 70 eV) *m/z* 185 ($[M]^+$)

1-(2'-Amino-4'-nitrophenyl)-2,5-dimethyl-1*H*-pyrrole



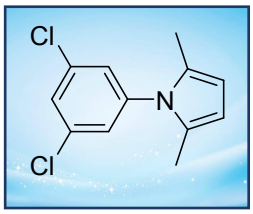
Yellow powder, M.p. = 128-130 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 2H), 7.21 – 7.19 (d, J = 9.0 Hz, 1H), 5.97 (s, 2H), 3.82 (s, 2H), 1.97 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 130.3, 130.2, 124.0, 118.0, 112.8, 109.8, 107.1, 12.2.

HRMS (ESI) *m/z* calcd for $[M + H]^+$ $C_{12}H_{14}N_3O_2^+$ 230.1049, found 230.1011.

1-(3,5-Dichlorophenyl)-2,5-dimethyl-1*H*-pyrrole[37]



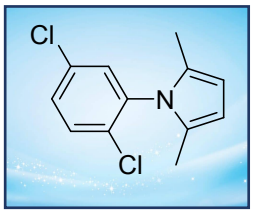
Orange powder, M.p. 79-81 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.41 (t, J = 2.0 Hz, 1H), 7.15 – 7.14 (d, J = 1.5 Hz, 2H), 5.90 (s, 2H), 2.06 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 135.2, 128.6, 128.6, 127.0, 106.7, 29.7, 13.0.

GC-MS (EI, 70 eV) *m/z* 239 ($[M]^+$)

1-(2,5-Dichlorophenyl)-2,5-dimethyl-1*H*-pyrrole[38]



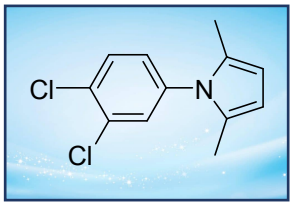
Black powder, M.p. 136-137 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.50 (d, J = 8.5 Hz, 1H), 7.42 – 7.39 (dd, J = 2.5 Hz, 2.5 Hz, 1H), 7.36 – 7.35 (d, J = 2.5 Hz, 1H), 5.97 (s, 2H), 2.01 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 133.0, 132.7, 131.0, 130.8, 129.8, 128.6, 106.2, 12.5.

GC-MS (EI, 70 eV) *m/z* 239 ($[M]^+$)

1-(3,4-Dichlorophenyl)-2,5-dimethyl-1*H*-pyrrole[14, 16, 34, 36]



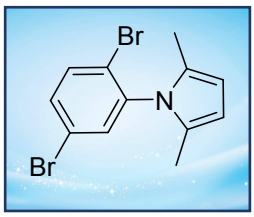
Yellow powder, M.p. 101-103 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.54 (d, J = 8.5 Hz, 1H), 7.35 (d, J = 2.5 Hz, 1H), 7.10 – 7.08 (m, 1H), 5.91 (s, 2H), 2.05 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 133.0, 132.0, 130.8, 130.2, 128.7, 127.6, 106.5, 13.0.

GC-MS (EI, 70 eV) *m/z* 239 ($[M]^+$)

1-(2,5-Dibromophenyl)-2,5-dimethyl-1*H*-pyrrole



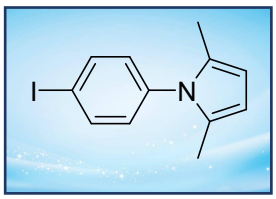
Yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (d, J = 8.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 5.92 (s, 2H), 1.97 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 140.0, 134.3, 133.6, 133.0, 128.4, 123.5, 121.3, 106.1, 12.6.

GC-MS (EI, 70 eV) *m/z* 326 ($[M]^+$)

1-(4-Iodophenyl)-2,5-dimethyl-1*H*-pyrrole[39, 40]



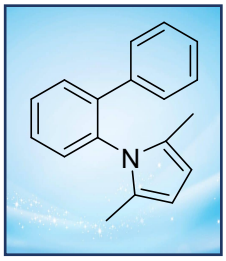
Yellow powder, M.p. 63-65 ˚C

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.79 (d, J = 8.5 Hz, 2H), 6.97 – 6.96 (d, J = 8.0 Hz, 2H), 5.90 (s, 2H), 2.03 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.8, 138.3, 130.2, 128.6, 106.2, 92.9, 13.0.

GC-MS (EI, 70 eV) *m/z* 297 ($[M]^+$).

1-([1,1'-Biphenyl]-2-yl)-2,5-dimethyl-1*H*-pyrrole[41]



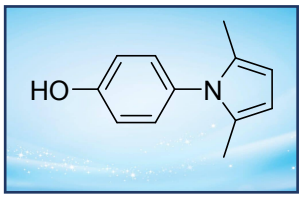
Yellow powder, M.p. 98-99 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.53 (dd, J = 1.5 Hz, 8 Hz, 1H), 7.48 – 7.45 (dt, J = 1.5 Hz, 1H), 7.43 – 7.39 (dt, J = 1.5 Hz, 1H), 7.25 – 7.22 (m, 4H), 7.01 – 6.99 (dd, J = 2.0 Hz, 2H), 5.76 (s, 2H), 1.84 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 138.7, 136.4, 130.82, 129.9, 128.5, 128.5, 128.3, 128.2, 128.0, 127.3, 105.8, 12.9.

GC-MS (EI, 70 eV) *m/z* 247 ($[M]^+$)

1-(4-Hydroxyphenyl)-2,5-dimethyl-1*H*-pyrrole[11, 12, 17, 40]



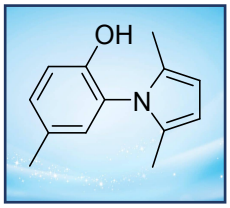
Yellow powder, M.p. 105-107 ˚C

^{1}H-NMR (500 MHz, DMSO-d_6) δ 9.66 (s, 1H), 7.01 – 6.98 (m, 2H), 6.85 – 6.82 (m, 2H), 5.71 (s, 2H), 1.90 (s, 6H).

^{13}C-NMR (125 MHz, DMSO-d_6) δ 157.2, 130.0, 129.5, 128.1, 116.1, 105.7, 13.3.

GC-MS (EI, 70 eV) *m/z* 187 ([M]$^{+}$).

1-(2'-Hydroxy-5'-methylphenyl)-2,5-dimethyl-1*H*-pyrrole



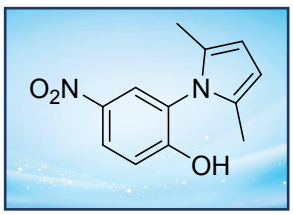
Black oil

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.14 – 7.12 (dd, *J* = 2.0 Hz, 2.0 Hz, 1H), 6.96 – 6.95 (d, *J* = 8.5 Hz, 1H), 6.92 – 6.91 (d, *J* = 1.5 Hz, 1H), 5.94 (s, 2H), 5.08 (s, 1H), 2.31 (s, 3H), 1.98 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 130.5, 130.1, 129.4, 129.0, 116.5, 115.9, 106.7, 20.4, 12.3.

HRMS (ESI) *m/z* calcd for $[M + H]^+$ $C_{13}H_{16}NO^+$ 202.1226, found 202.1201.

1-(2'-Hydroxy-5'-nitrophenyl)-2,5-dimethyl-1*H*-pyrrole



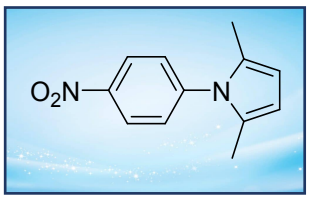
Orange powder, M.p. 167-170 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 – 8.24 (dd, *J* = 2.5 Hz, 2.5 Hz, 1H), 8.09 – 8.08 (d, *J* = 3 Hz, 1H), 7.18 – 7.16 (d, *J* = 9.5 Hz, 1H), 5.99 (s, 2H), 1.99 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 141.3, 129.1, 126.1, 125.7, 116.8, 107.9, 12.3.

HRMS (ESI) *m/z* calcd for $[M + H]^+$ $C_{12}H_{13}N_2O_3^+$ 233.0920, found 233.0939.

2,5-Dimethyl-1-(4-nitrophenyl)-1*H*-pyrrole[11, 12, 14, 16, 36]



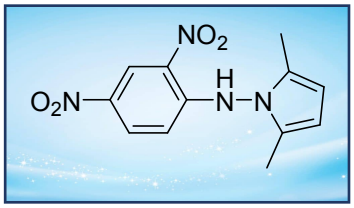
Yellow powder, M.p. 144-146 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.34 (d, J = 9.0 Hz, 2H), 7.40 – 7.38 (d, J = 9.0 Hz, 2H), 5.96 (s, 2H), 2.07 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 144.8, 128.8, 124.6, 109.0, 107.4, 29.7.

GC-MS (EI, 70 eV) *m/z* 216 ($[M]^+$)

***N*-(2,4-Dinitrophenyl)-2,5-dimethyl-1*H*-pyrrol-1-amine**[42-45]

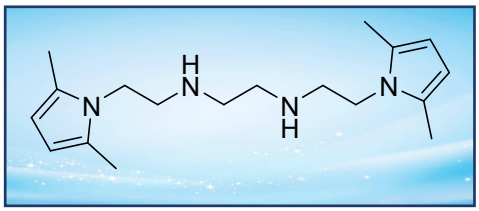


Yellow powder, M.p. 182-184 ˚C

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 9.19 – 9.18 (d, J = 2.5 Hz, 1H), 8.27 – 8.24 (m, 1H), 6.22 – 6.20 (d, J = 9.5 Hz, 1H), 5.94 (s, 2H), 2.08 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 139.2, 130.9, 127.4, 123.5, 114.6, 105.7, 11.1.

***N*^{1},*N*^{2}-bis(2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)ethyl)ethane-1,2-diamine**



Yellow oil

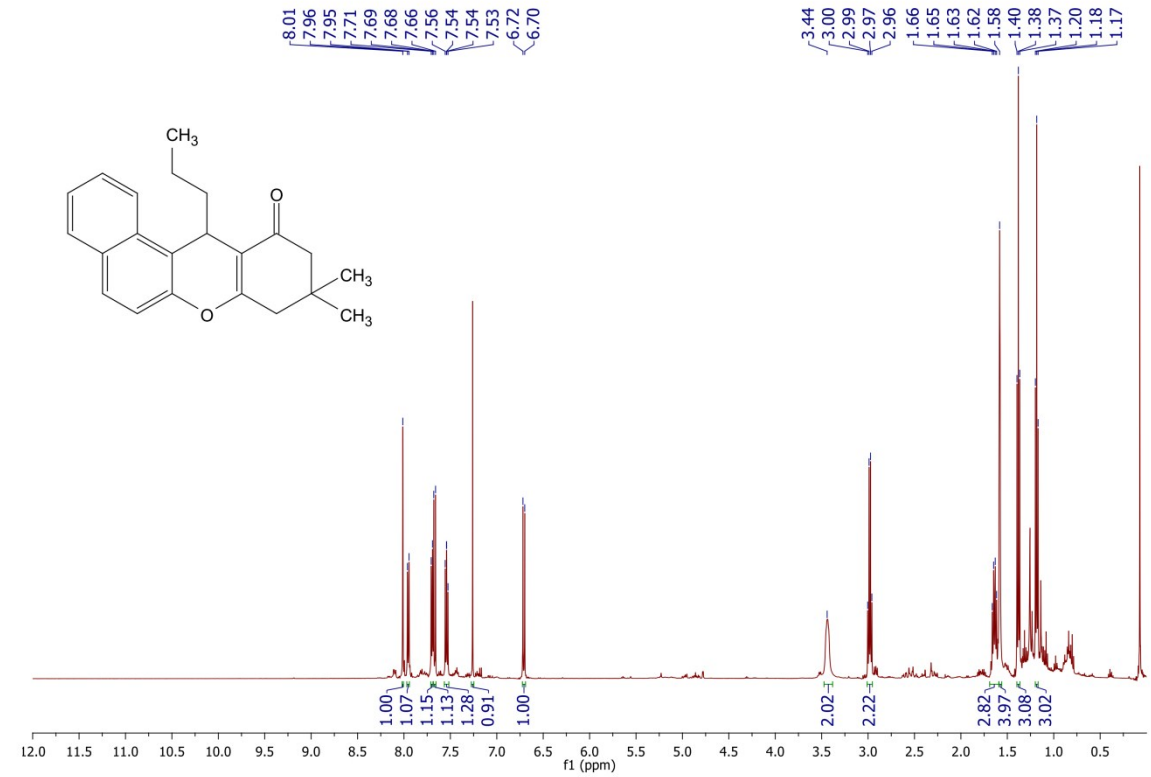
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 – 5.76 (d, J = 5.0 Hz, 4H), 3.88 – 3.85 (t, J = 7.0 Hz, 4H), 2.83 – 2.81 (t, J = 7.0 Hz, 4H), 2.71 (s, 4H), 2.23 (s, 12H).

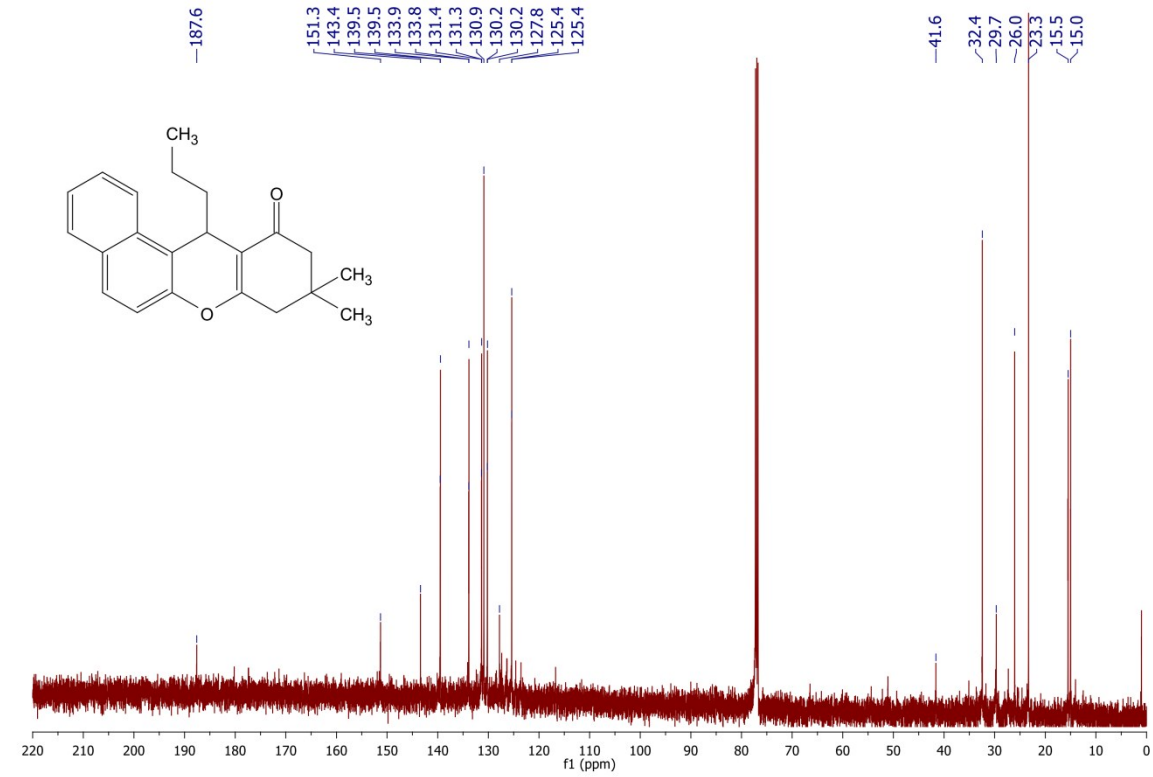
^{13}C NMR (125 MHz, $CDCl_3$) δ 127.6, 105.4, 49.7, 49.0, 43.7, 12.6.

HRMS (ESI) *m/z* calcd for $[M + H]^+$ $C_{18}H_{31}N_4^+$ 303.2543, found 303.2575.

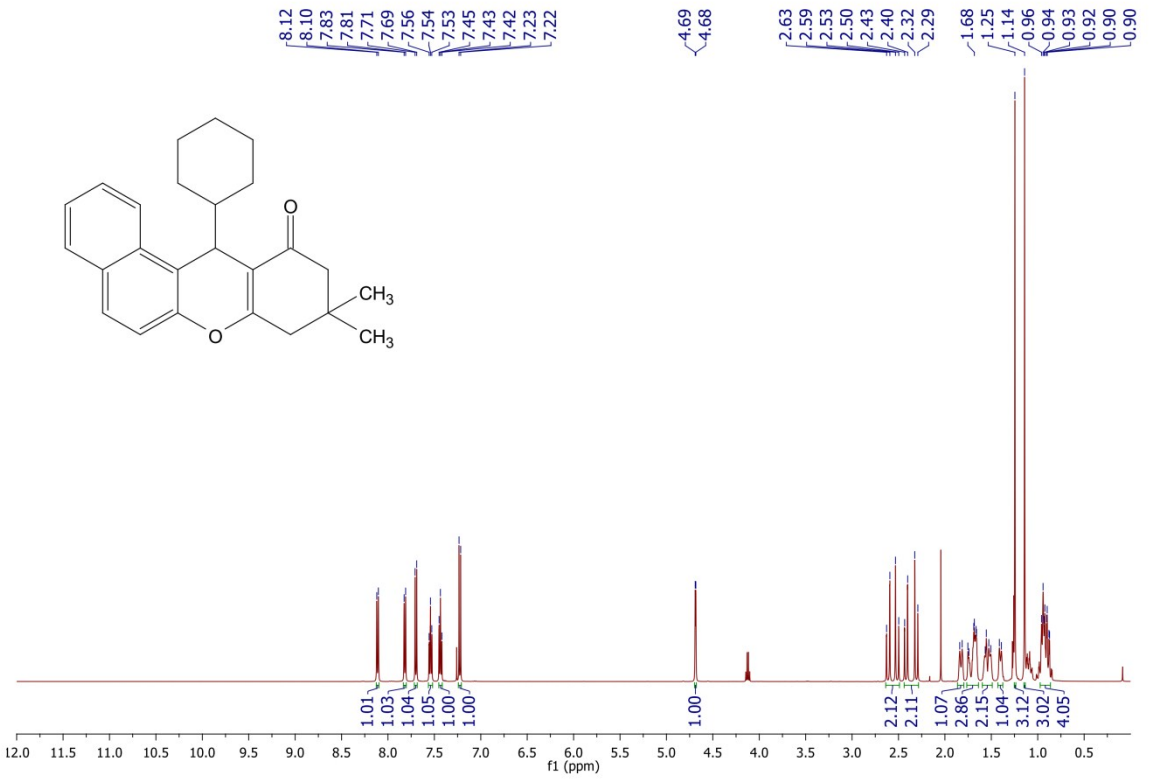
Section S5. ^{1}H, ^{13}C NMR and HRMS spectroscopy

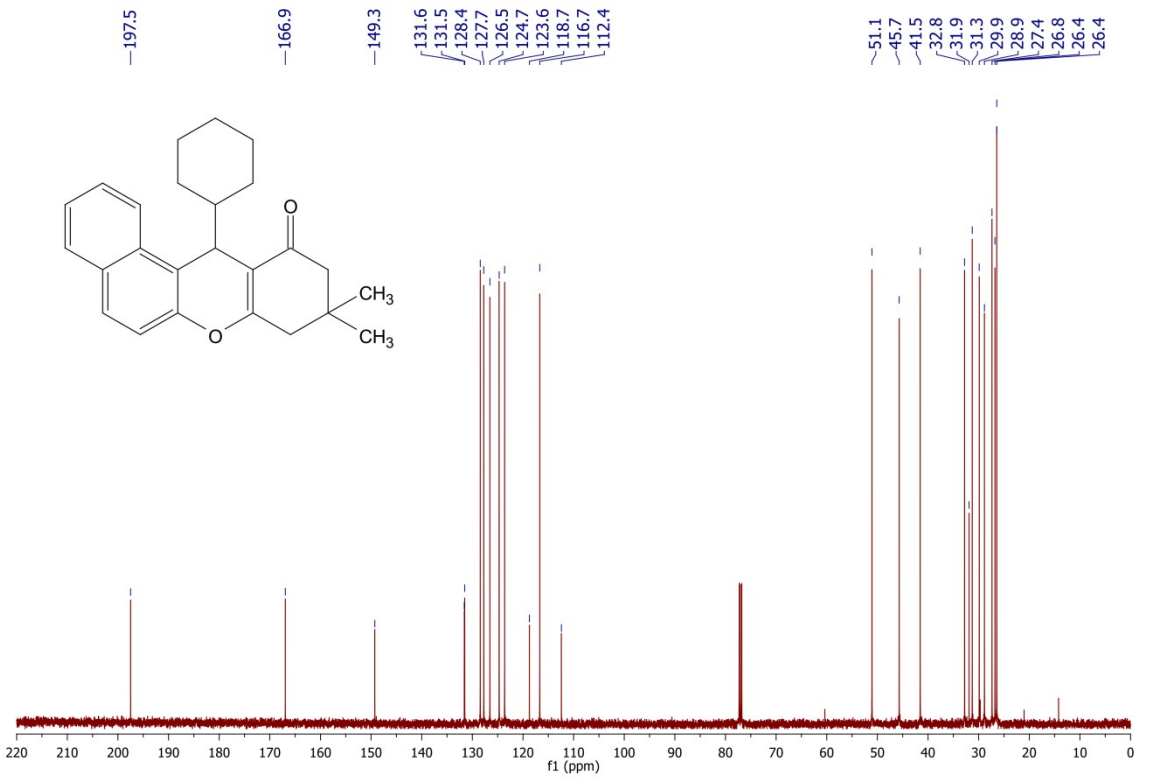
^{1}H and ^{13}C NMR of 9,9-Dimethyl-12-propyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



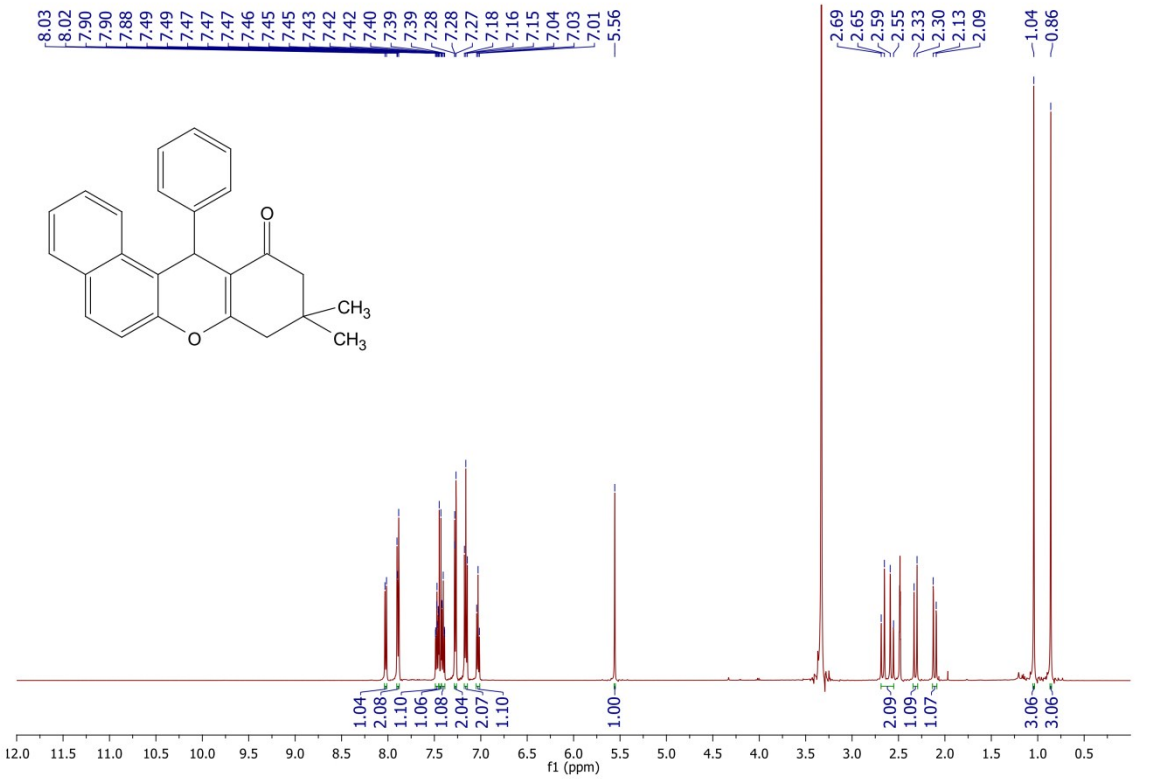


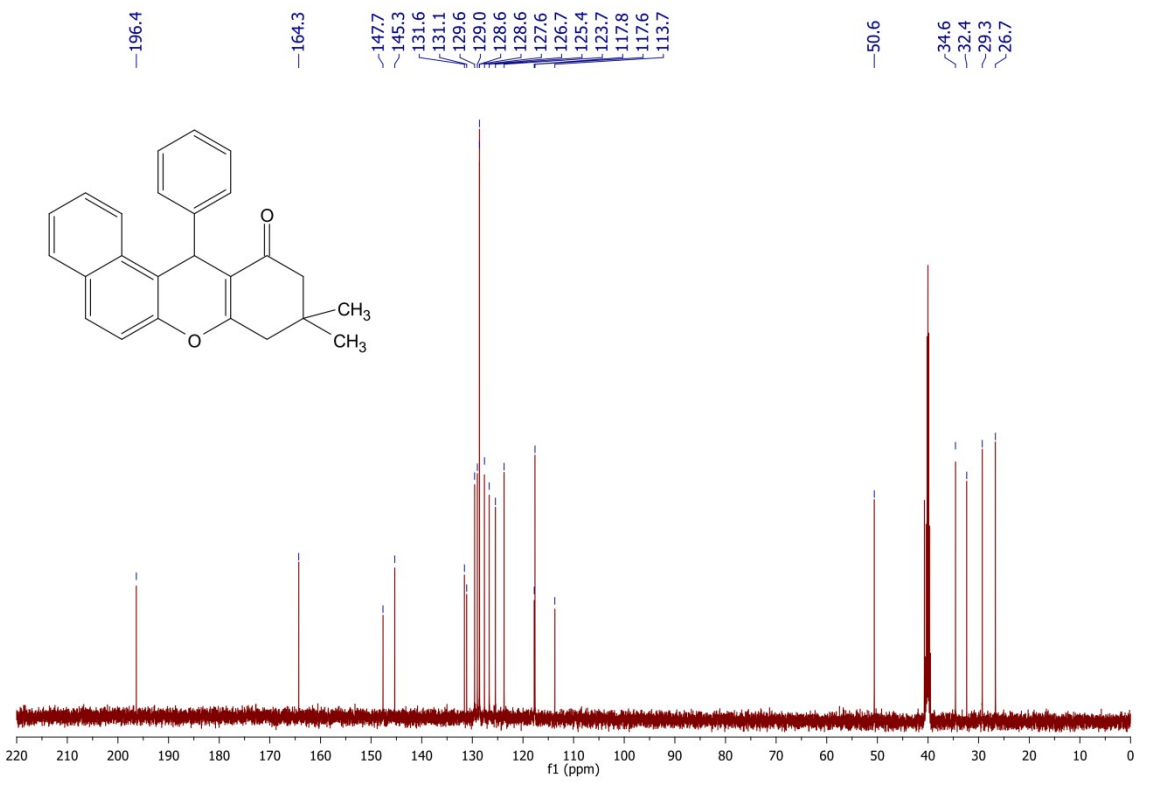
^{1}H and ^{13}C NMR of 12-cyclohexyl-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



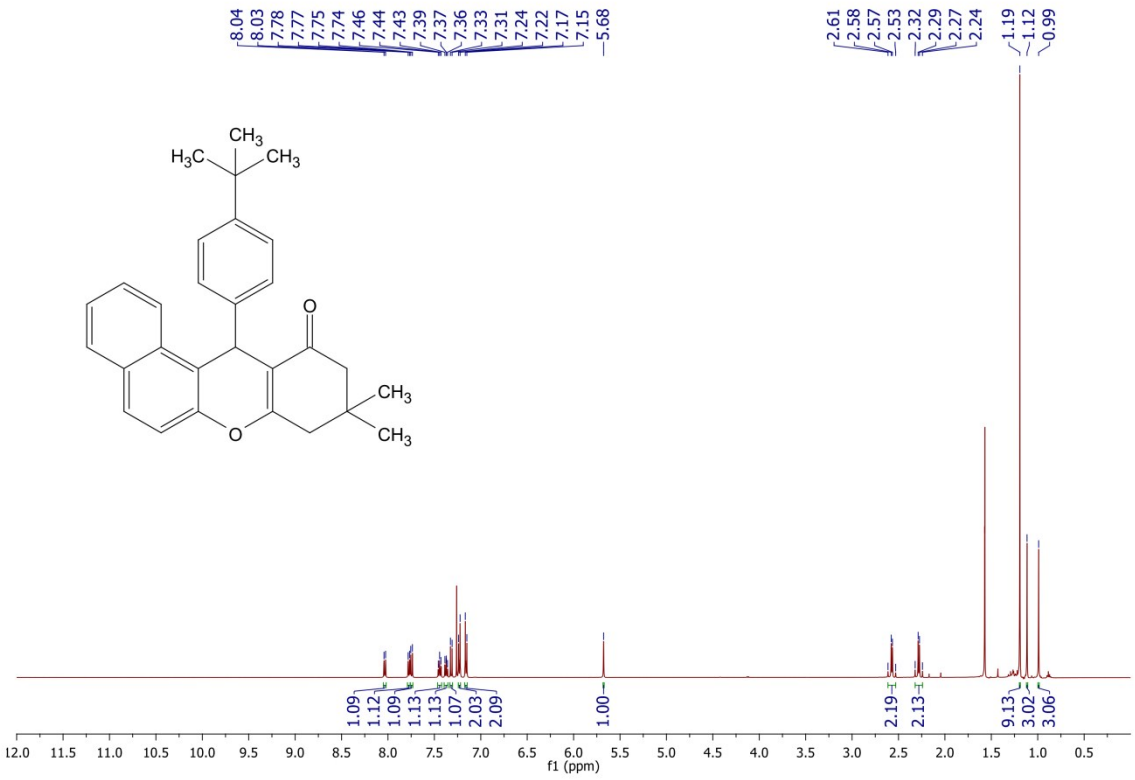


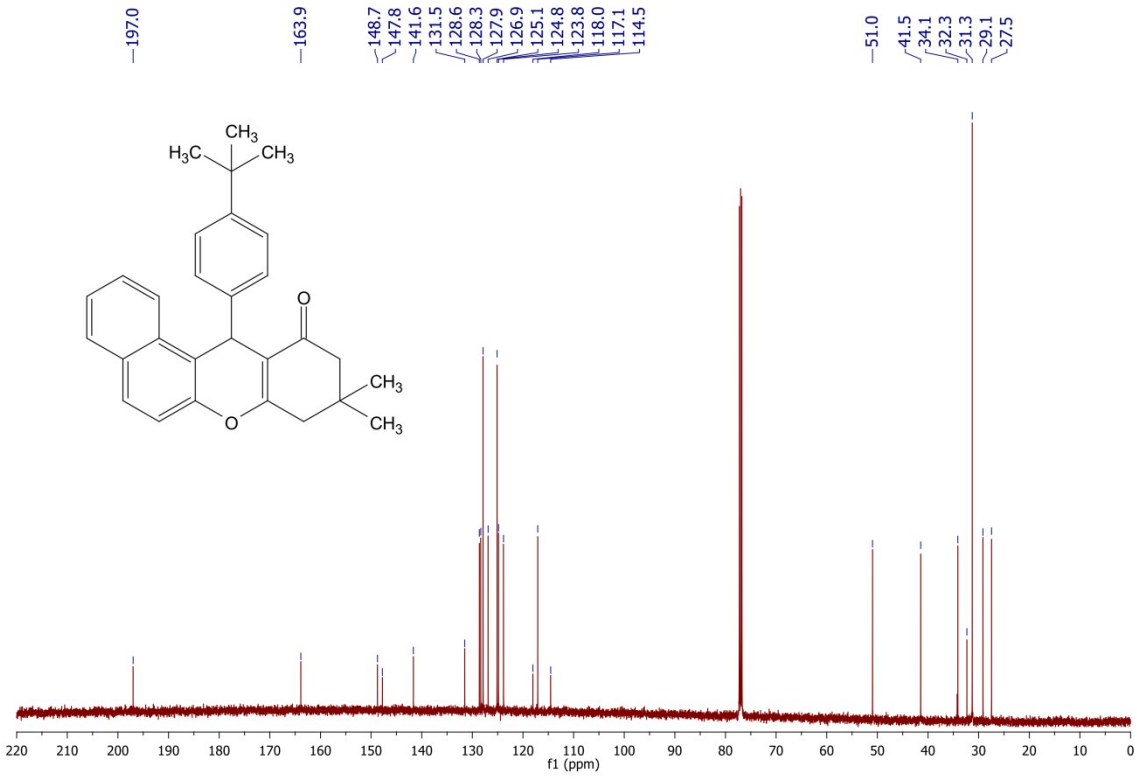
^{1}H and ^{13}C NMR of 9,9-dimethyl-12-phenyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



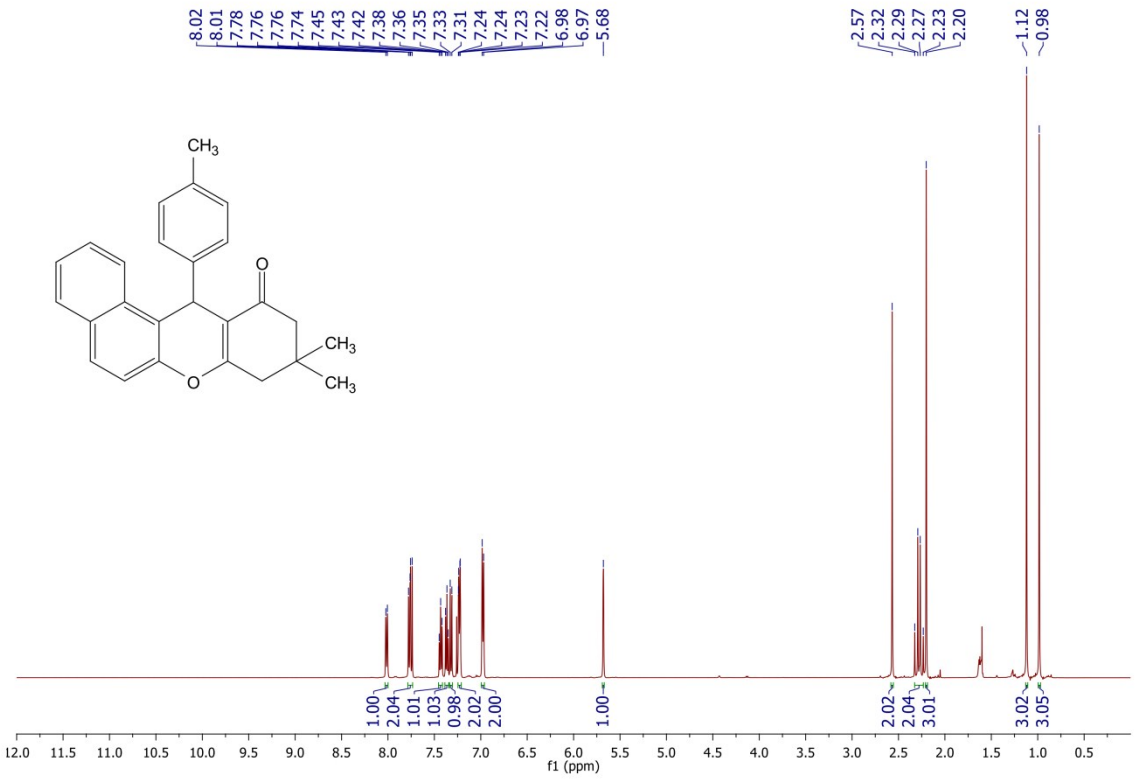


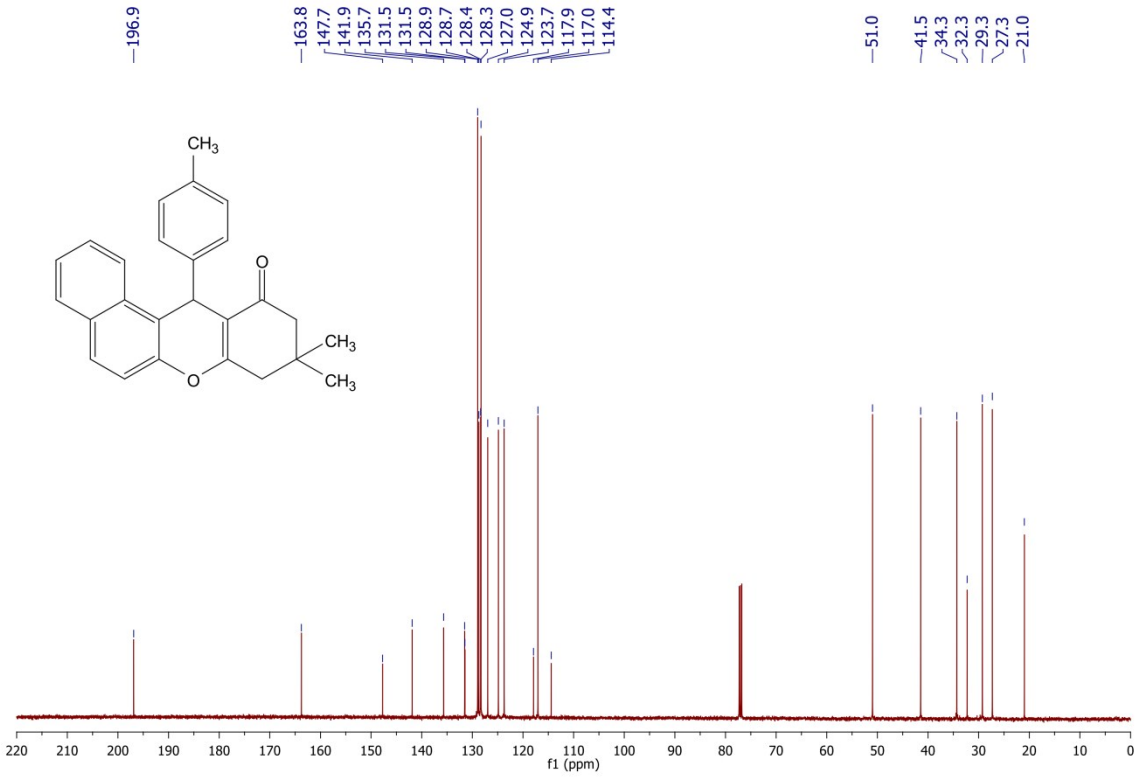
^{1}H and ^{13}C NMR of 12-(4-(*tert*-butyl)phenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



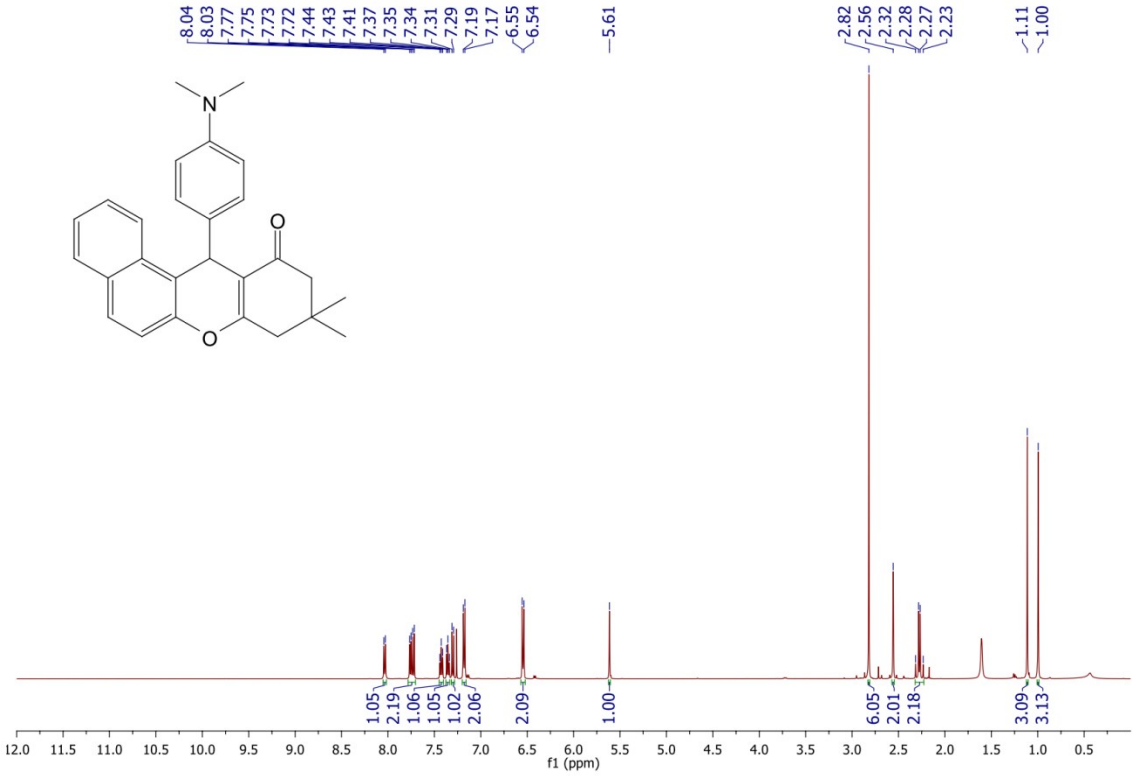


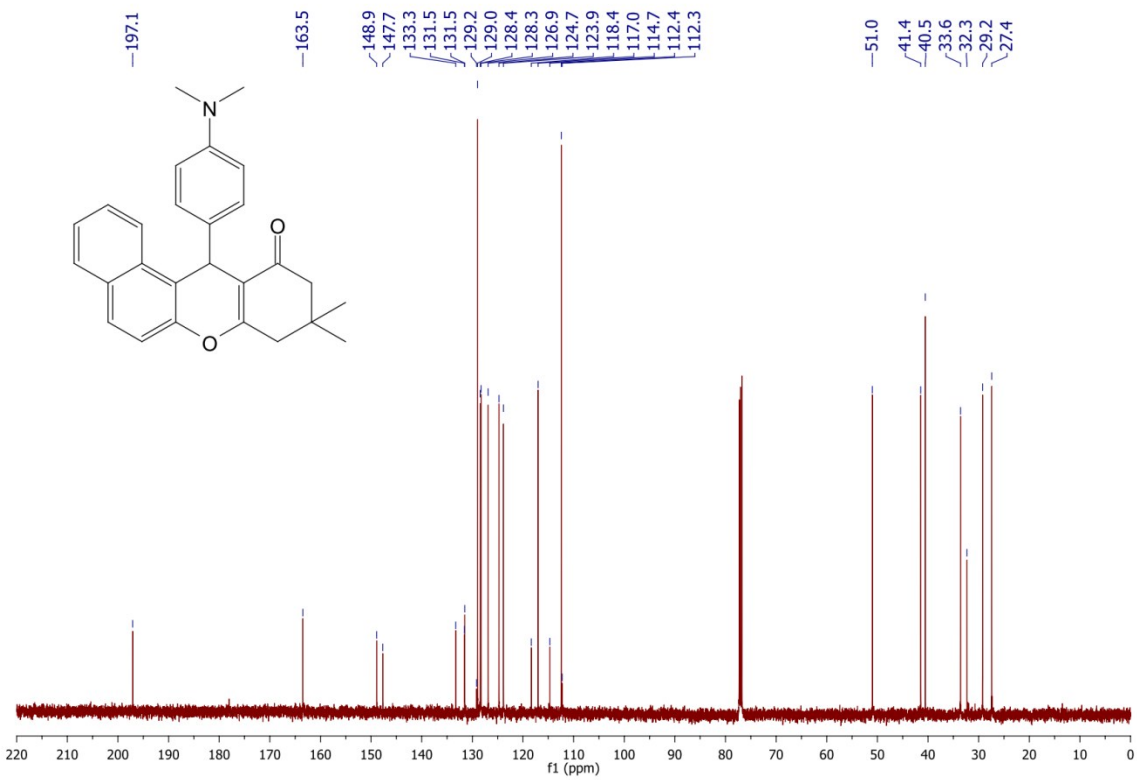
^{1}H and ^{13}C NMR of 9,9-Dimethyl-12-(*p*-tolyl)-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



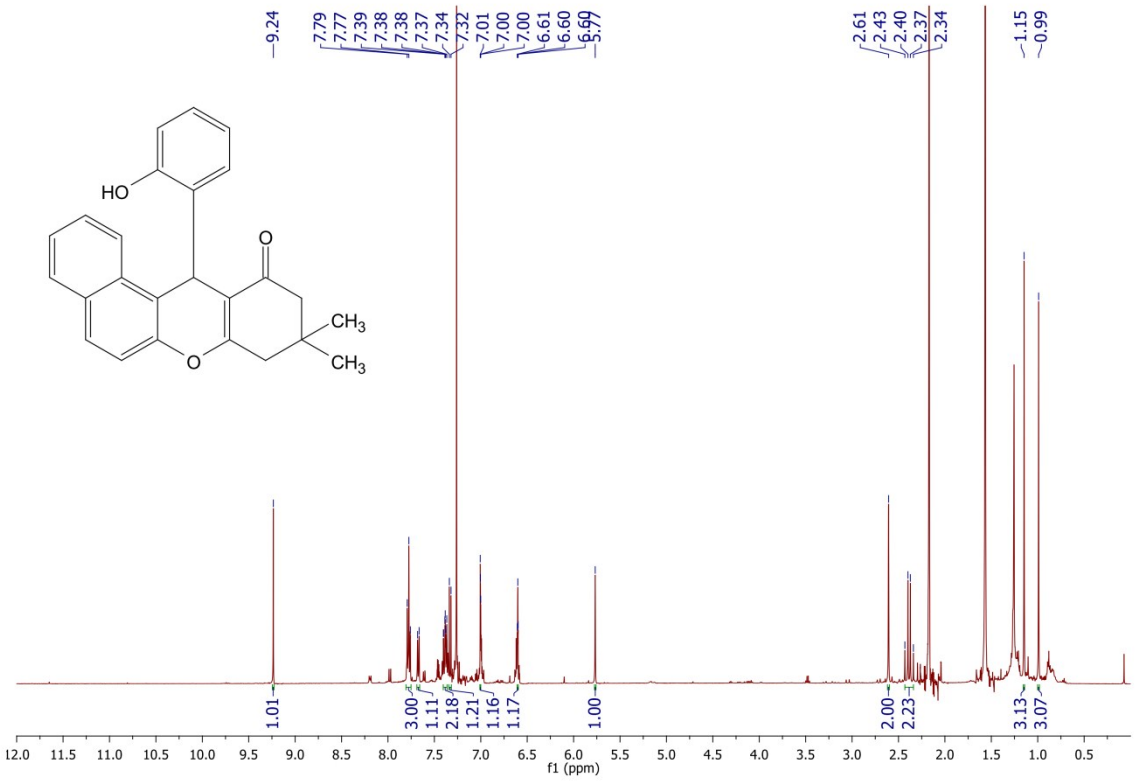


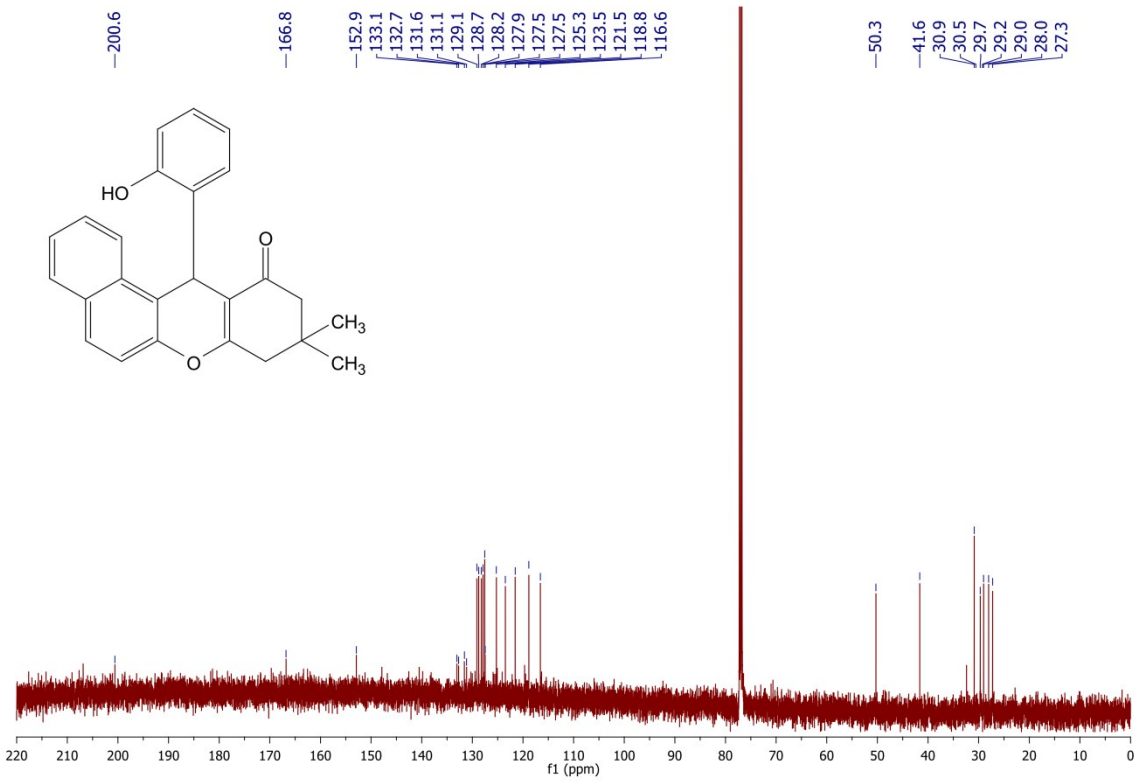
^{1}H and ^{13}C NMR of 12-(4-dimethylamino)phenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthene-11-one



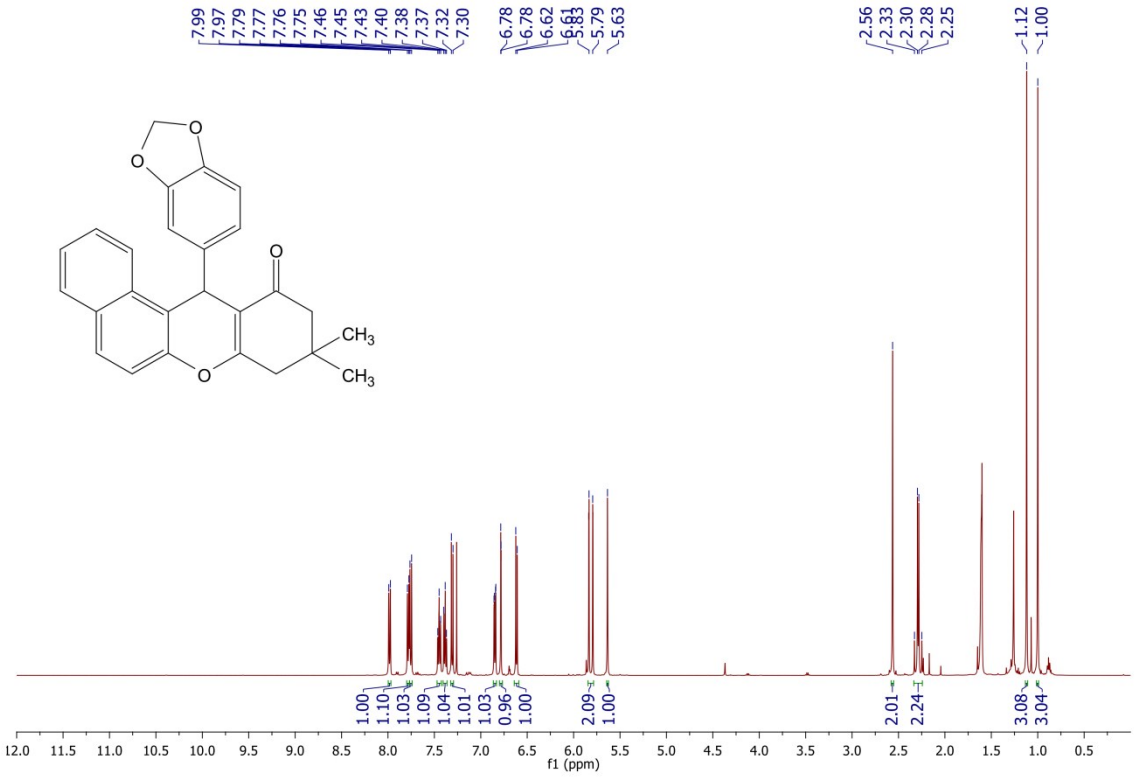


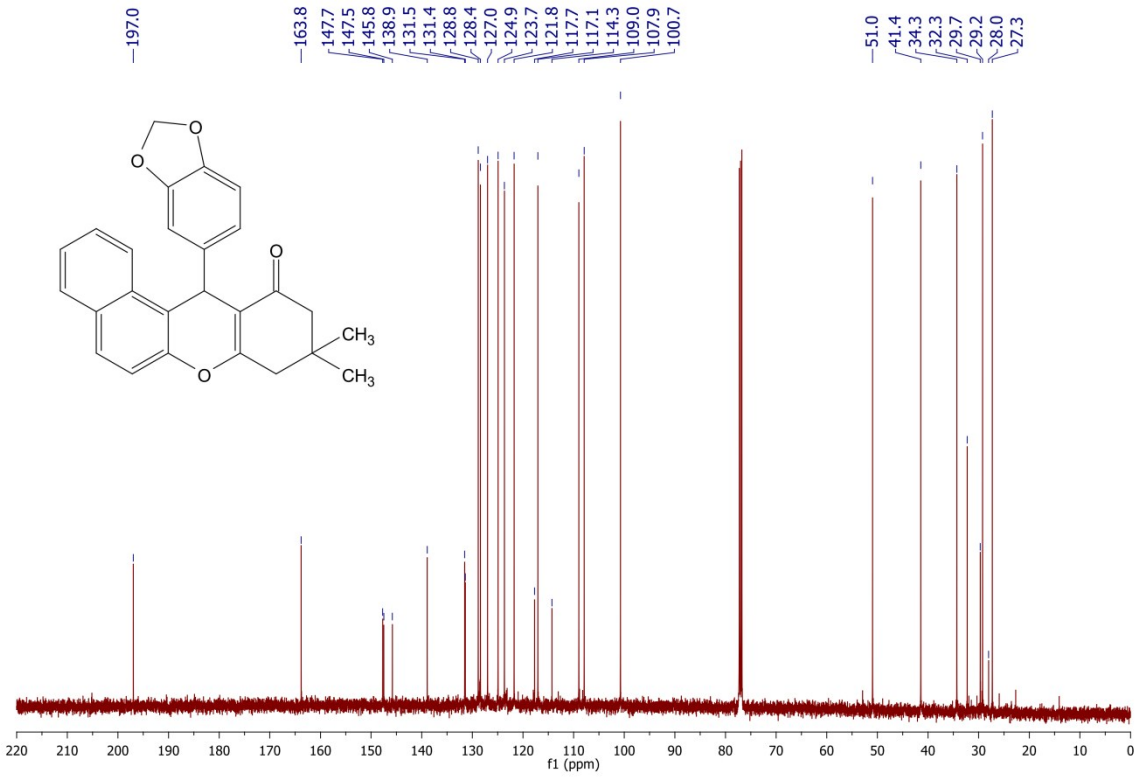
^{1}H and ^{13}C NMR of 12-(2-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



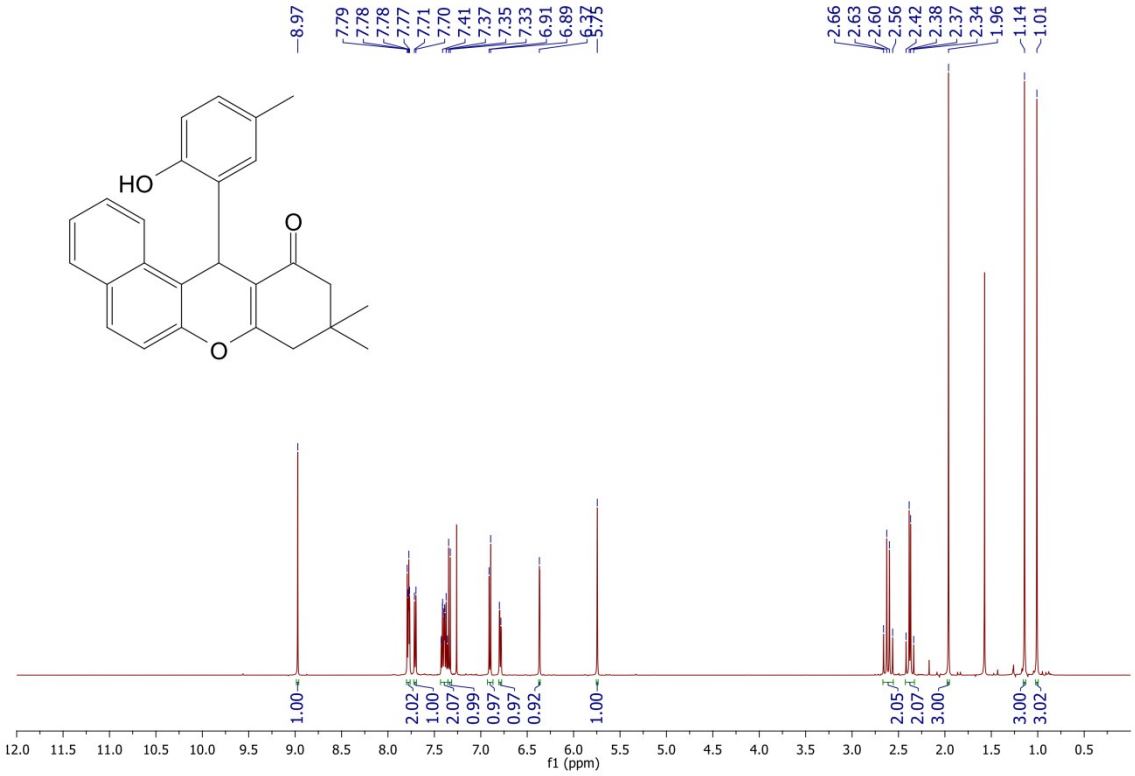


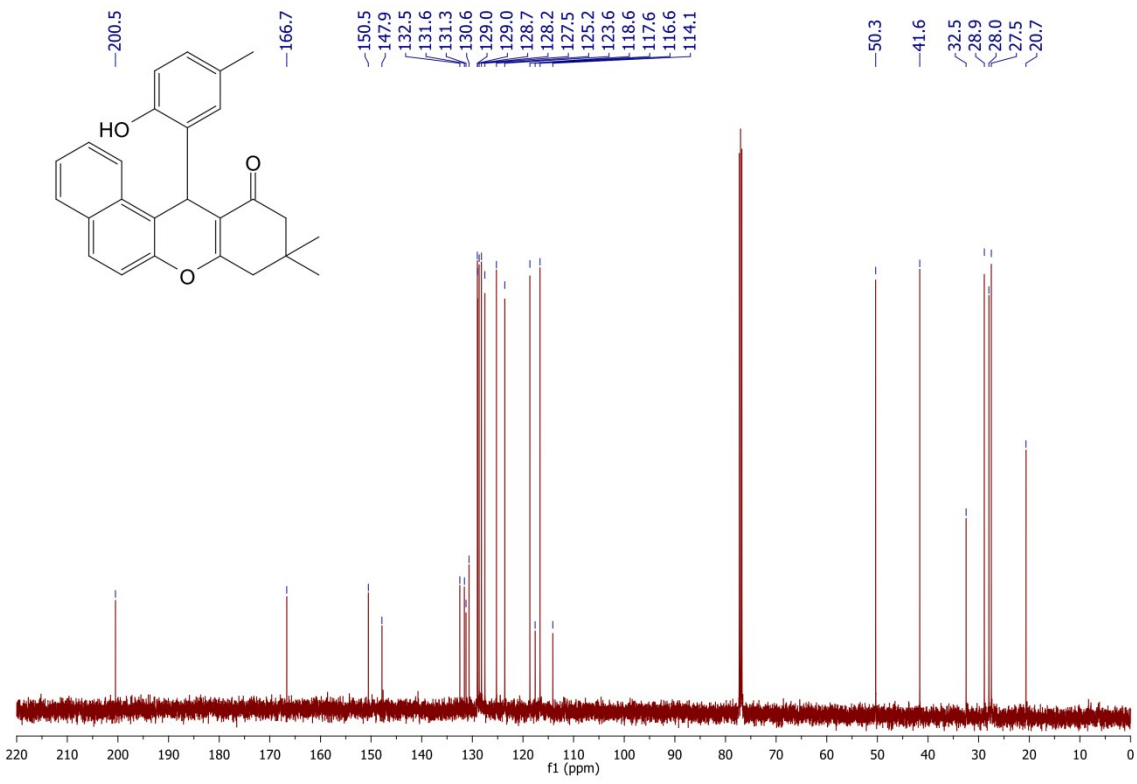
^{1}H and ^{13}C NMR of 12-(benzo[*d*][1,3]dioxol-5-yl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



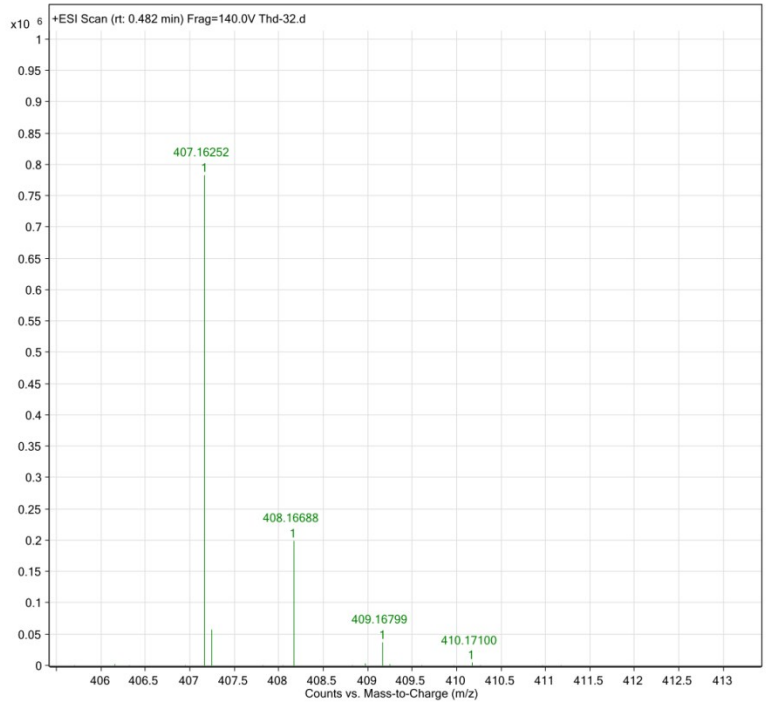


^{1}H, ^{13}C NMR and HRMS of 12-(2-hydroxy-5-methylphenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one

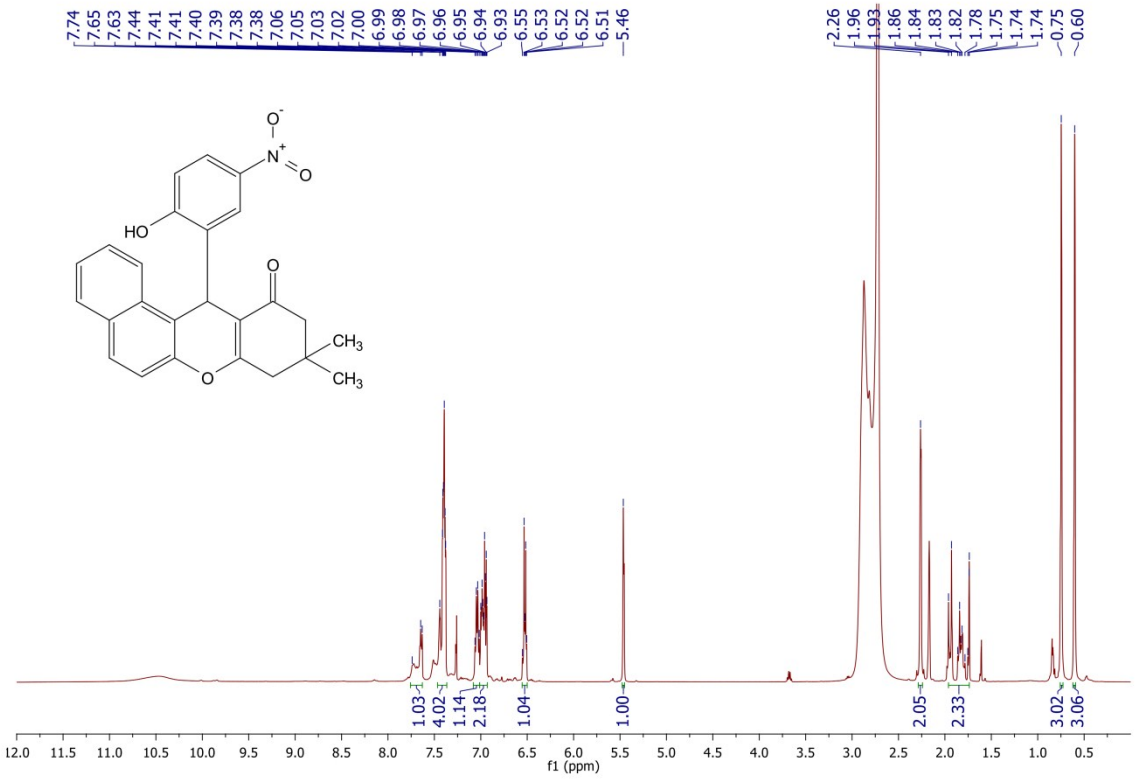


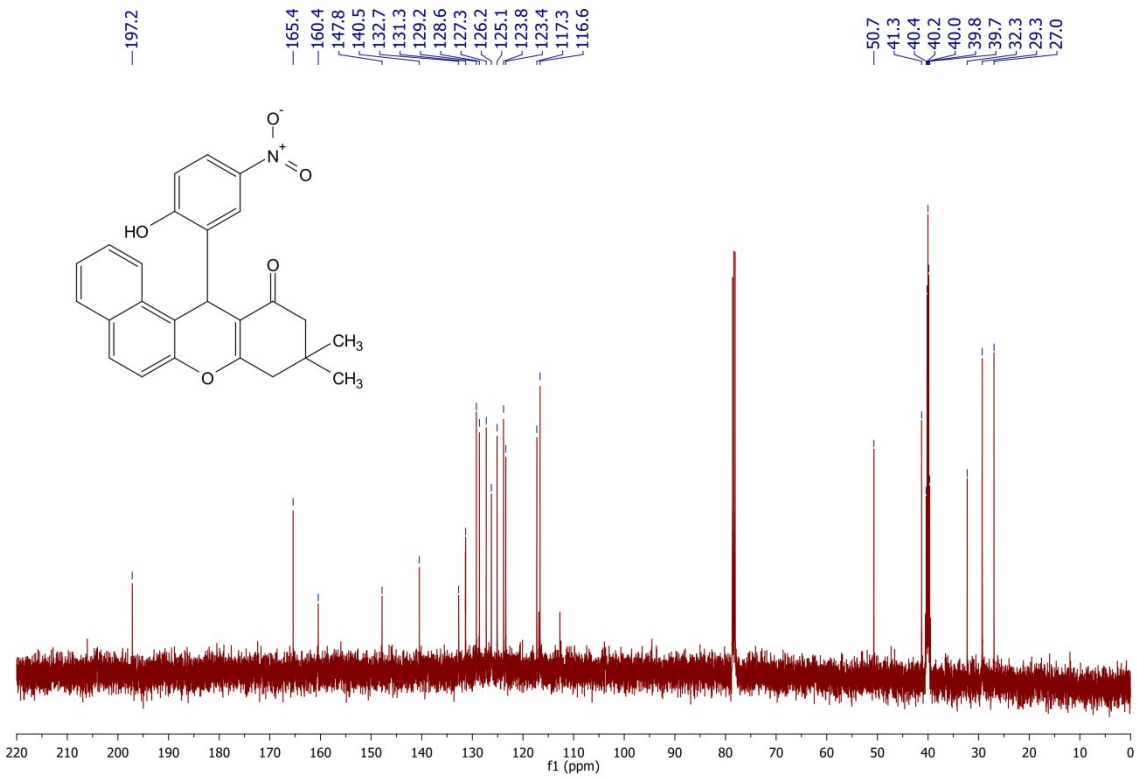


Sample Name	Thd-32	**Position**	P1-A5	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	5	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	Thd-32.d
ACQ Method	All Ion MSMS-Positive-100MeOH.m	**Comment**		**Acquired Time**	20/05/2018 5:43:24 PM

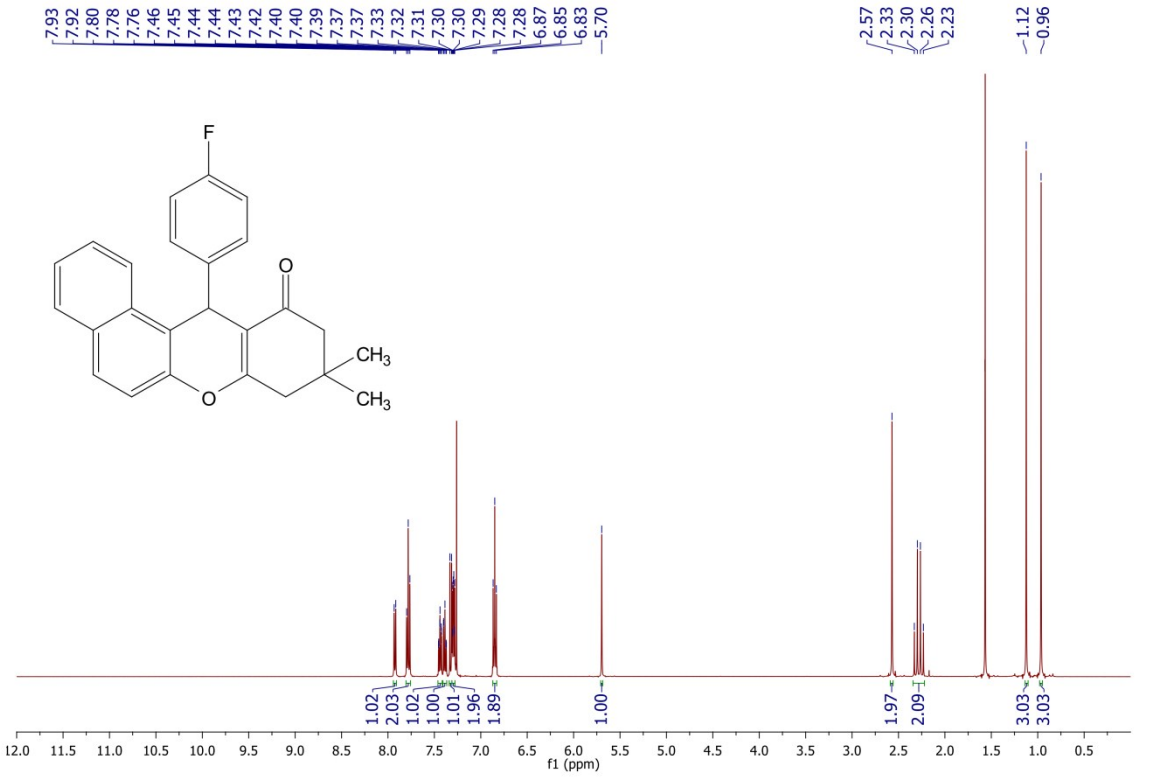


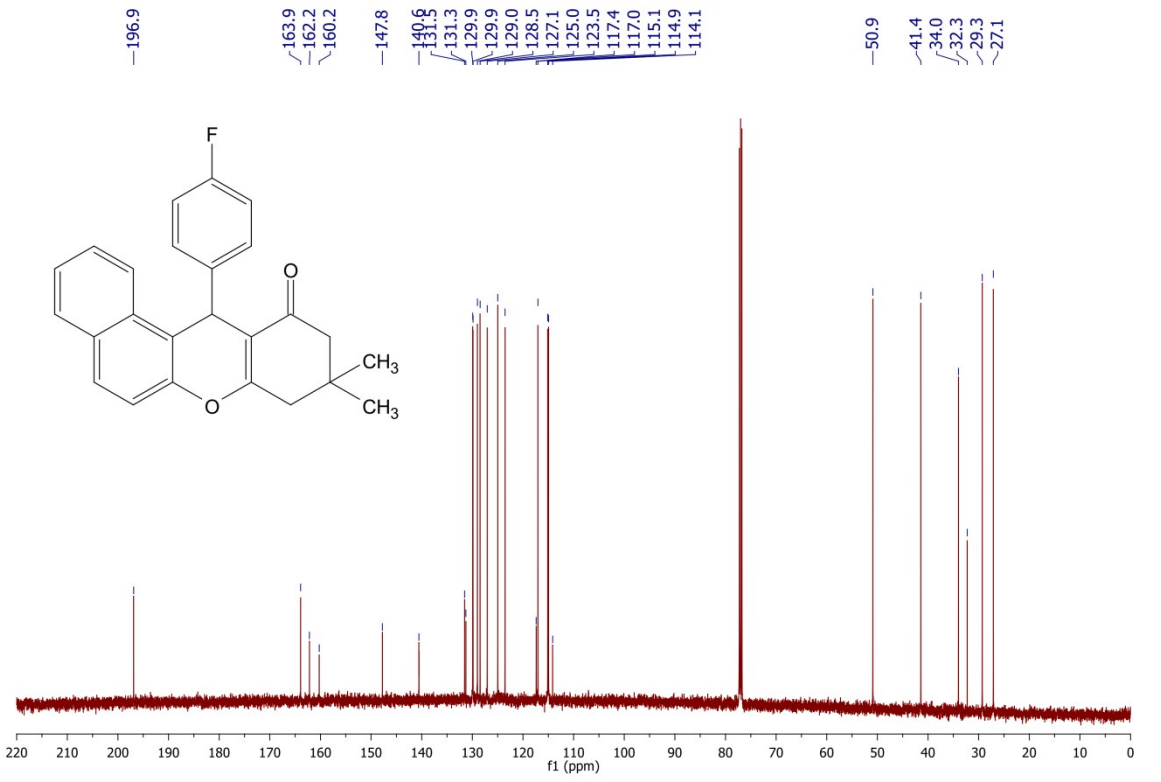
^{1}H and ^{13}C NMR of 12-(2-hydroxy-5-nitrophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



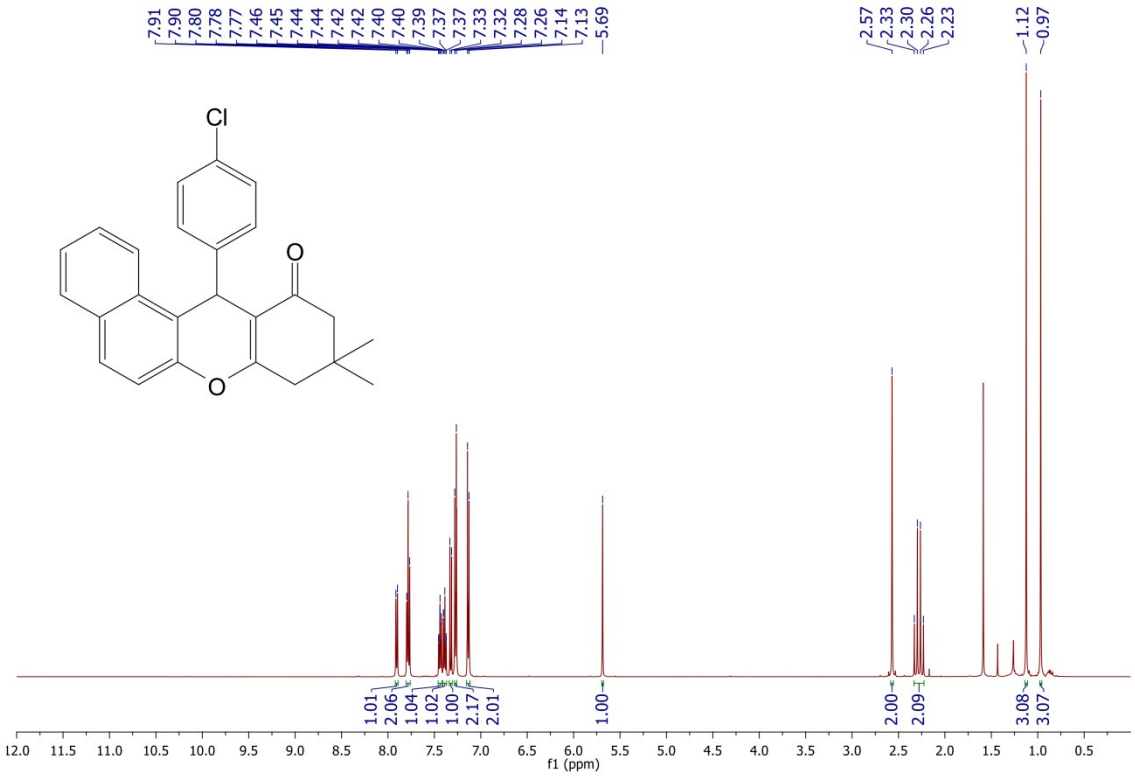


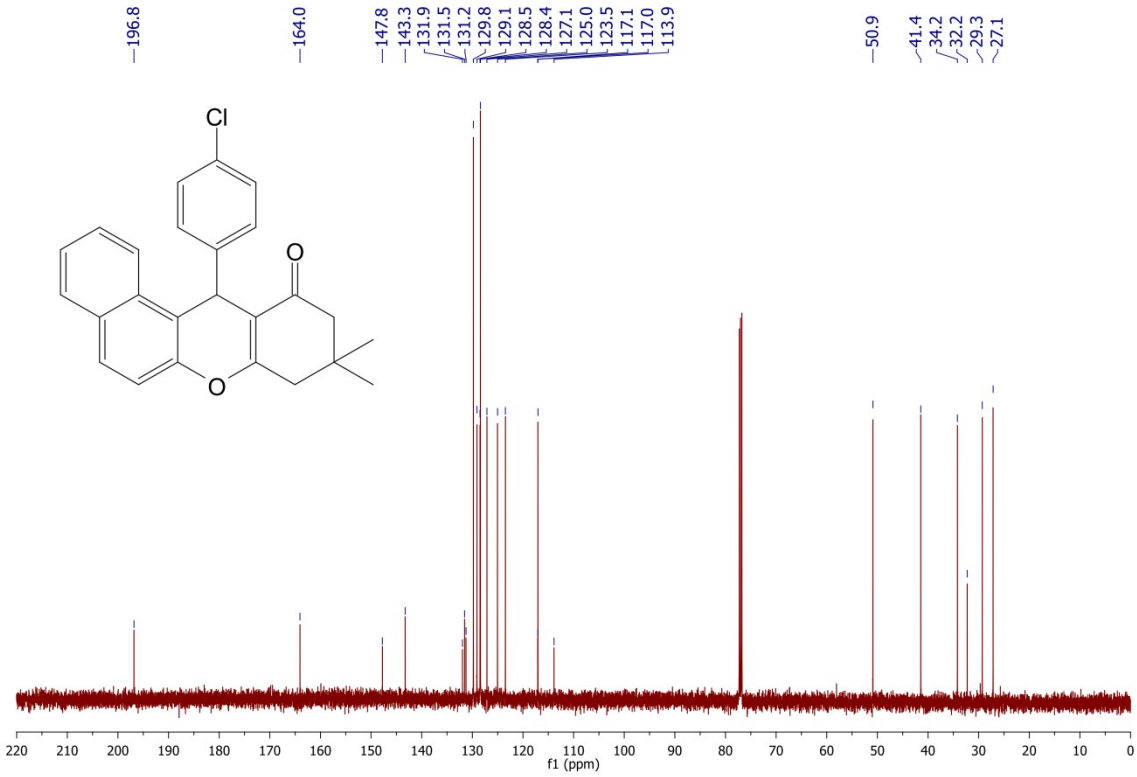
^{1}H and ^{13}C NMR of 12-(4-fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



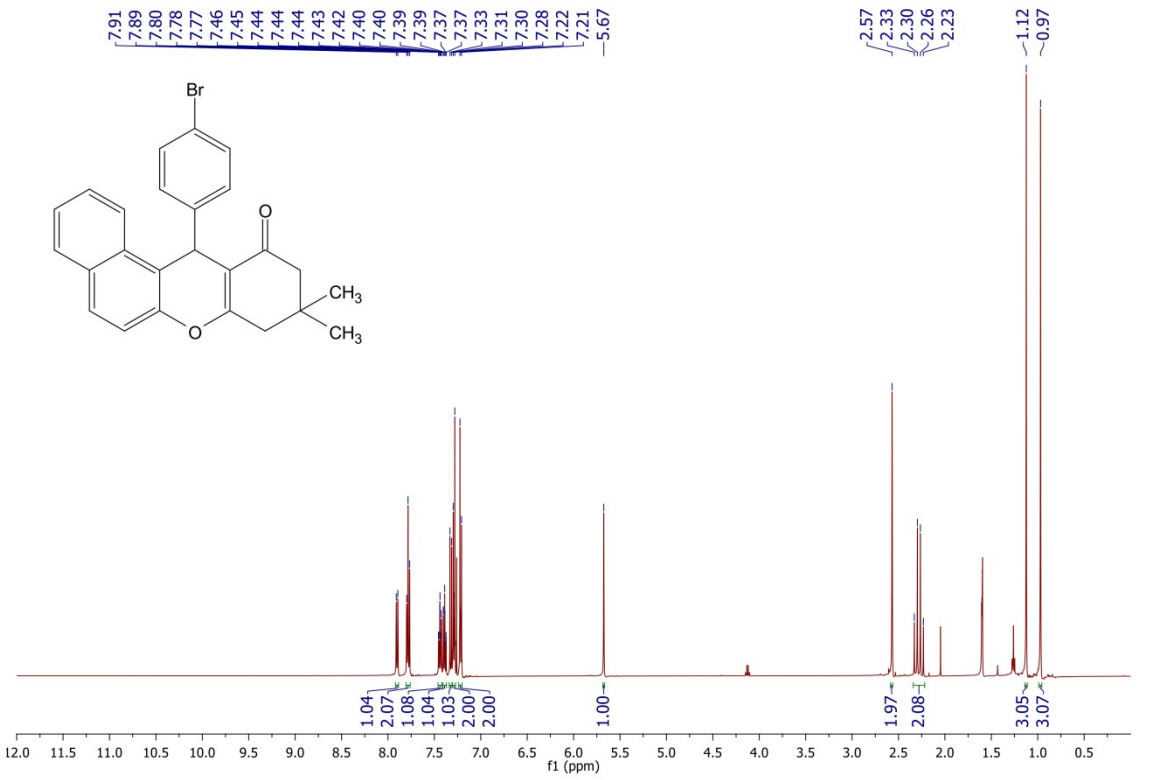


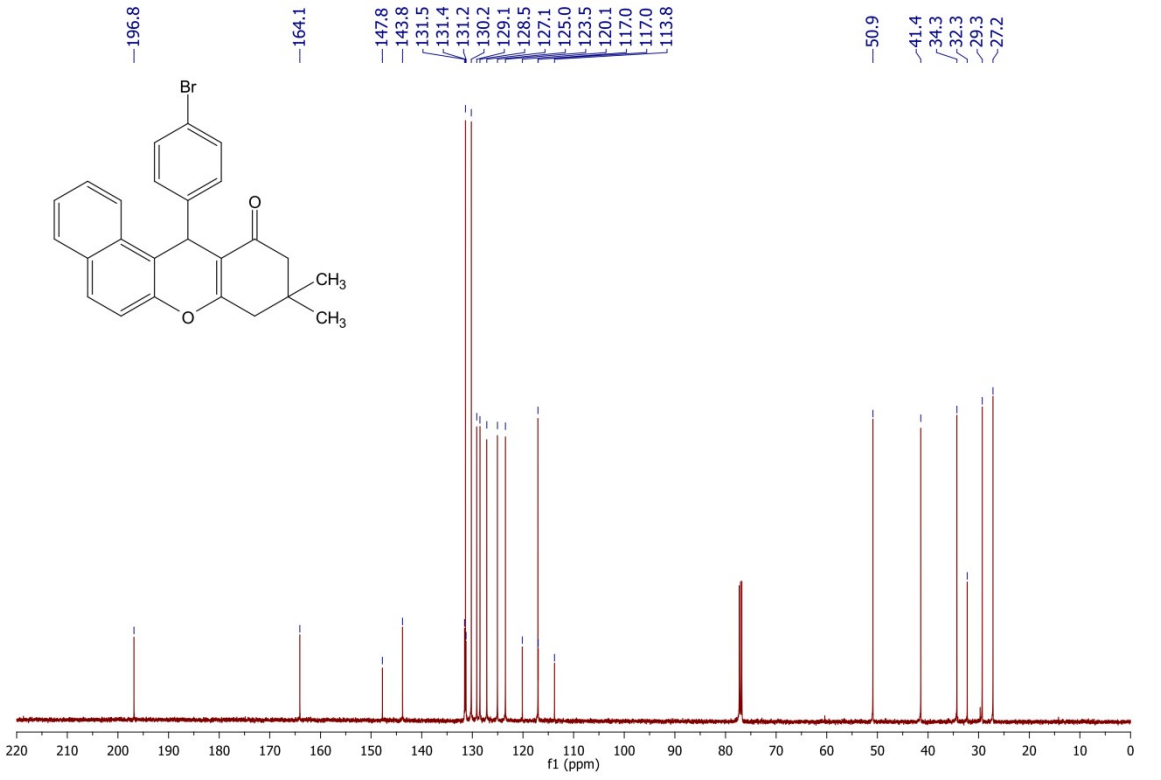
^{1}H and ^{13}C NMR of 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



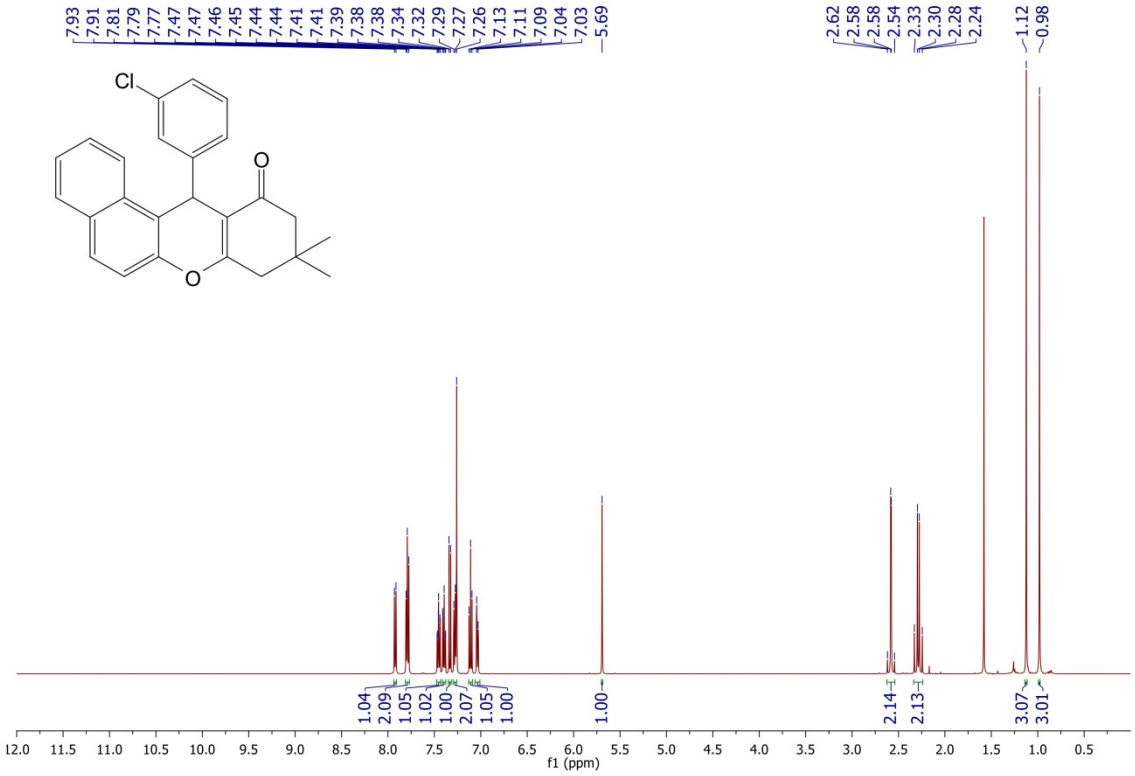


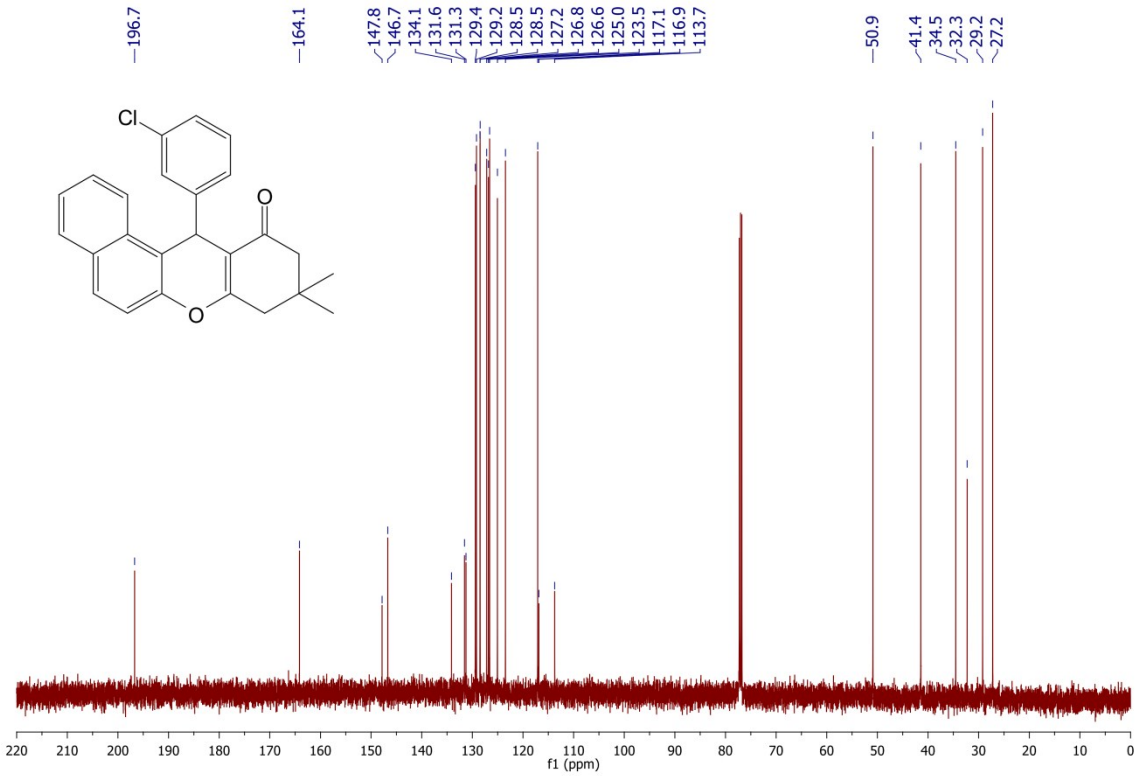
^{1}H and ^{13}C NMR of 12-(4-bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



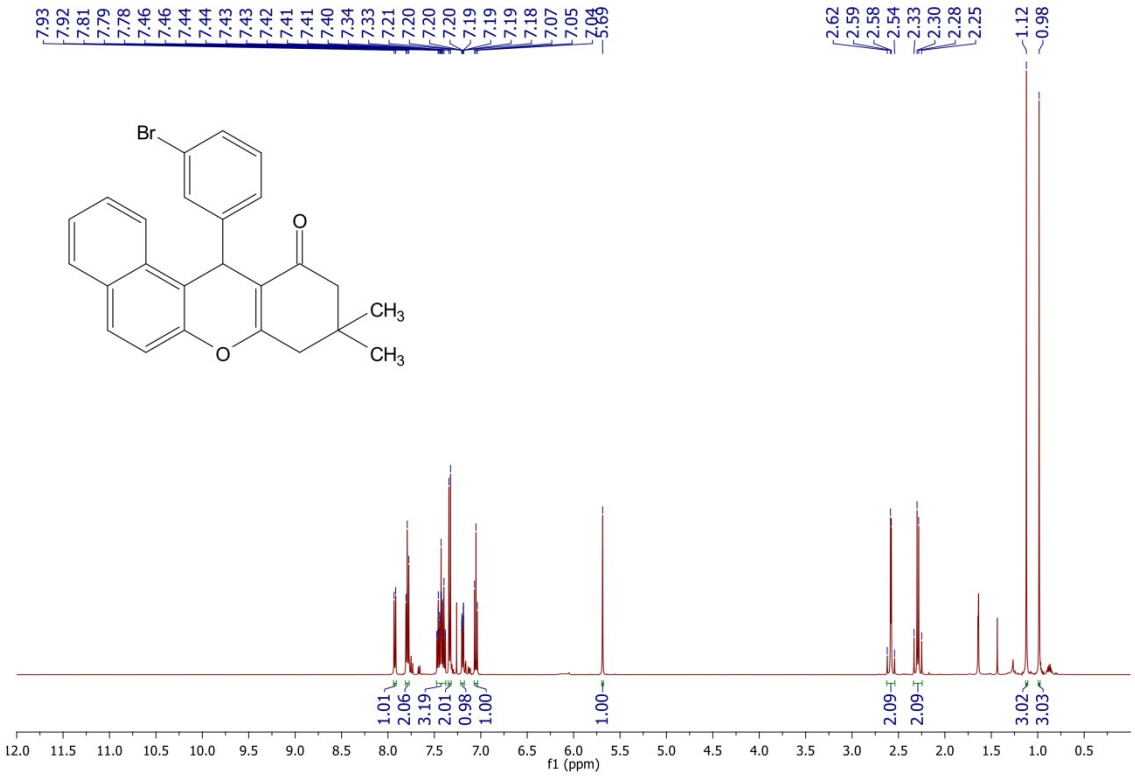


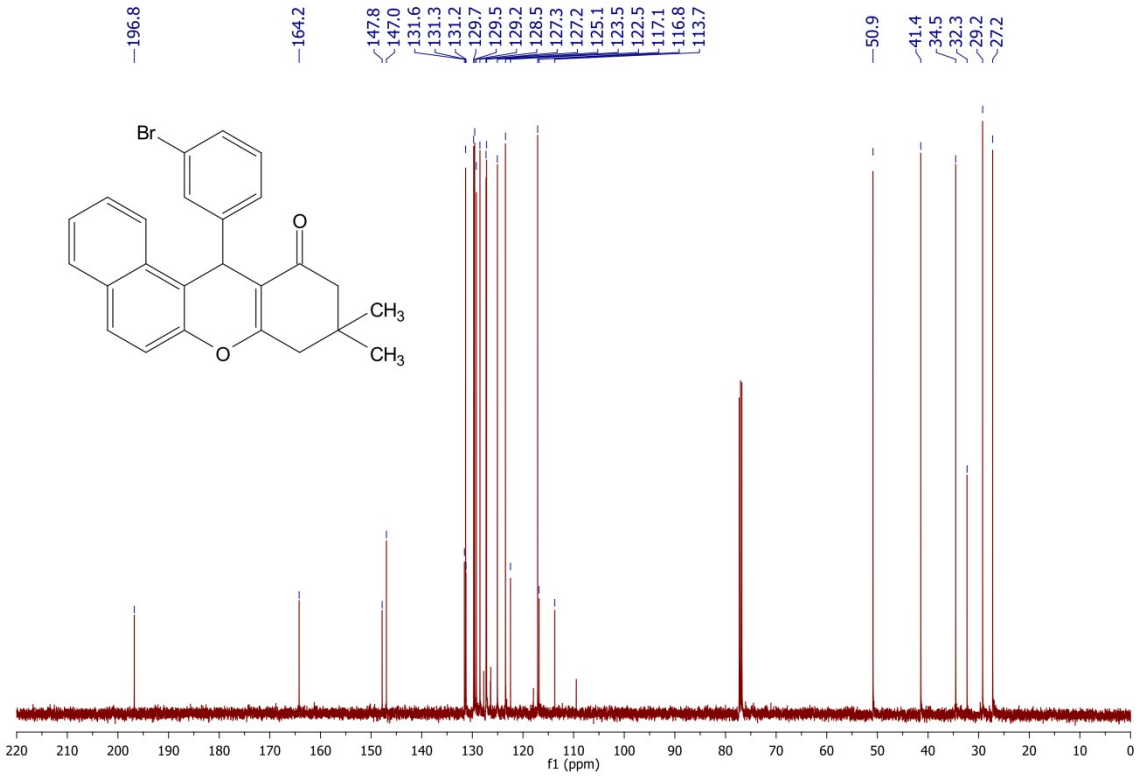
^{1}H and ^{13}C NMR of 12-(3-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



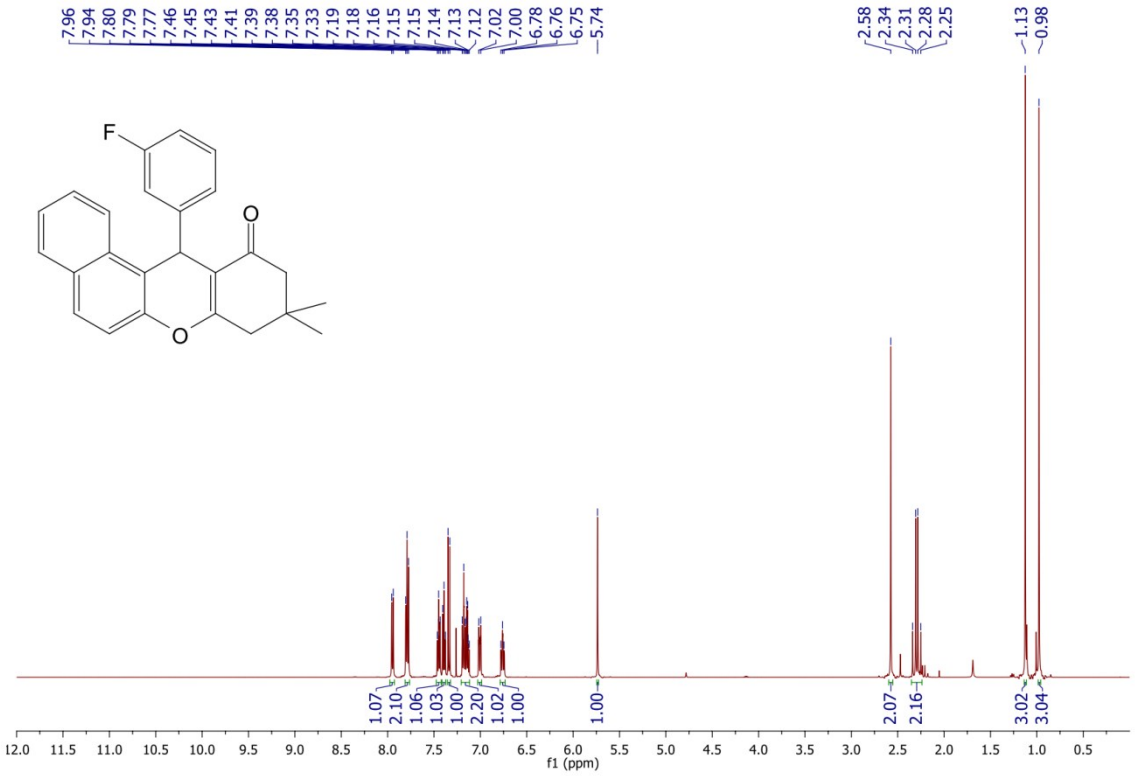


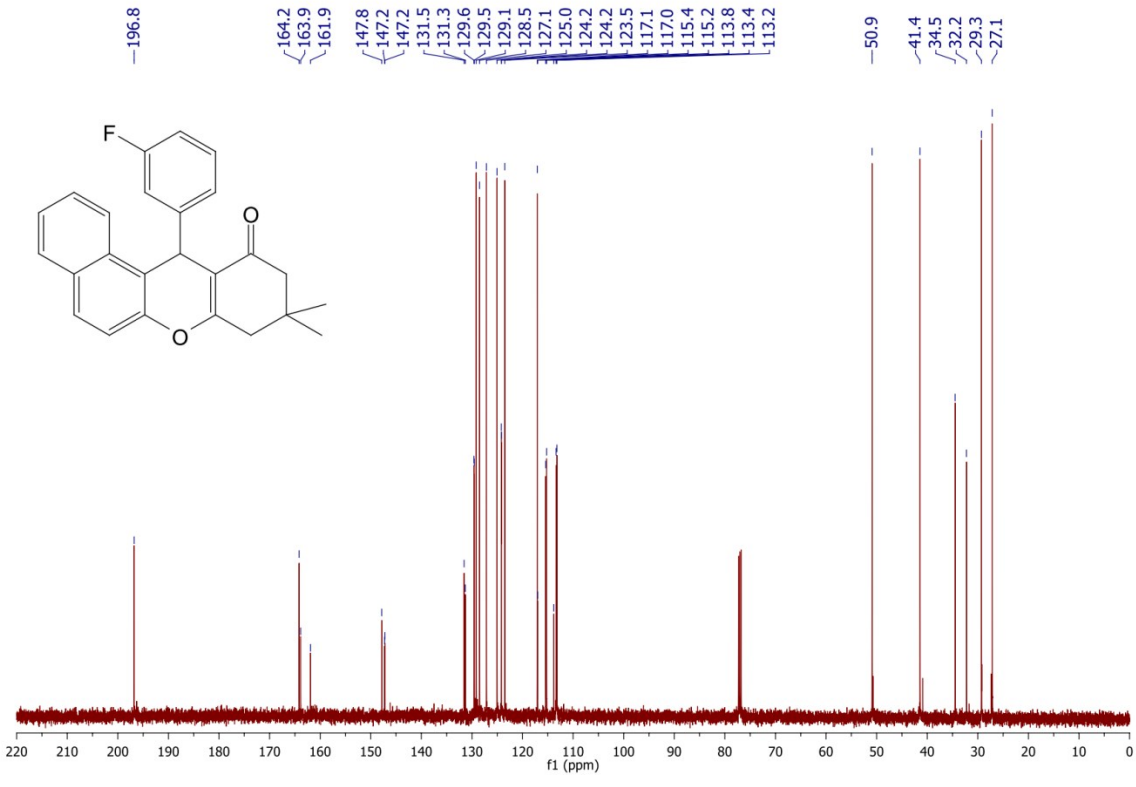
^{1}H and ^{13}C NMR of 12-(3-bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



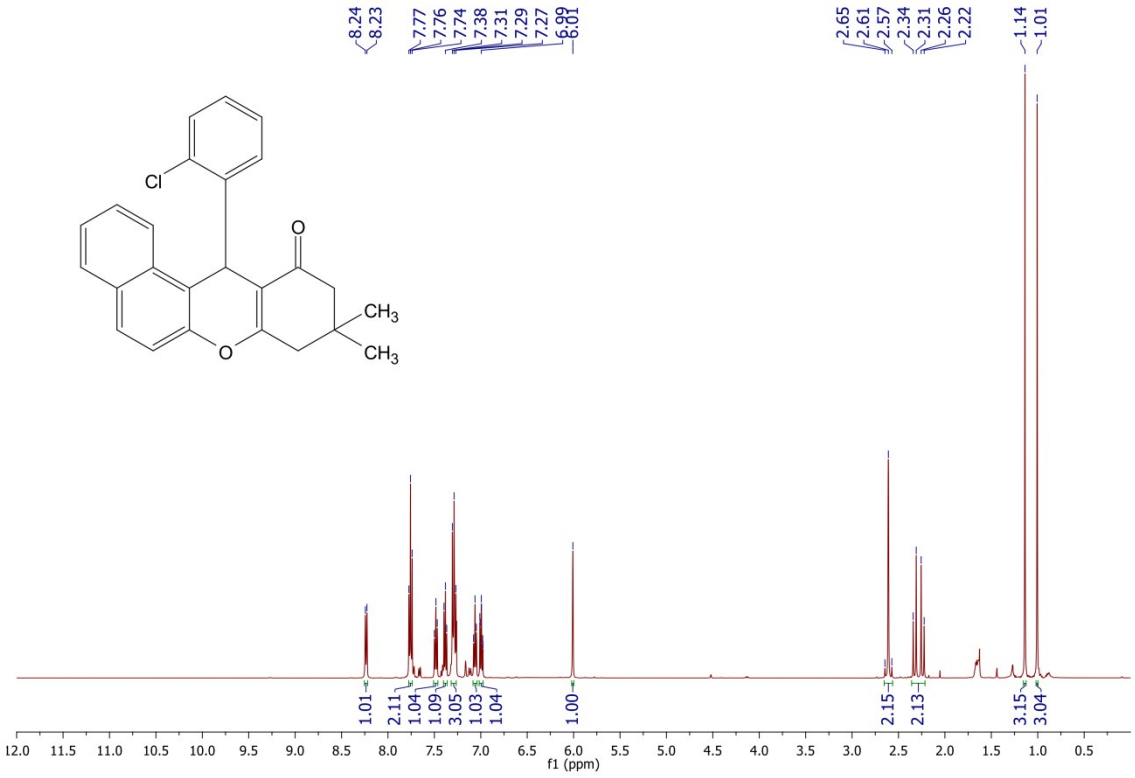


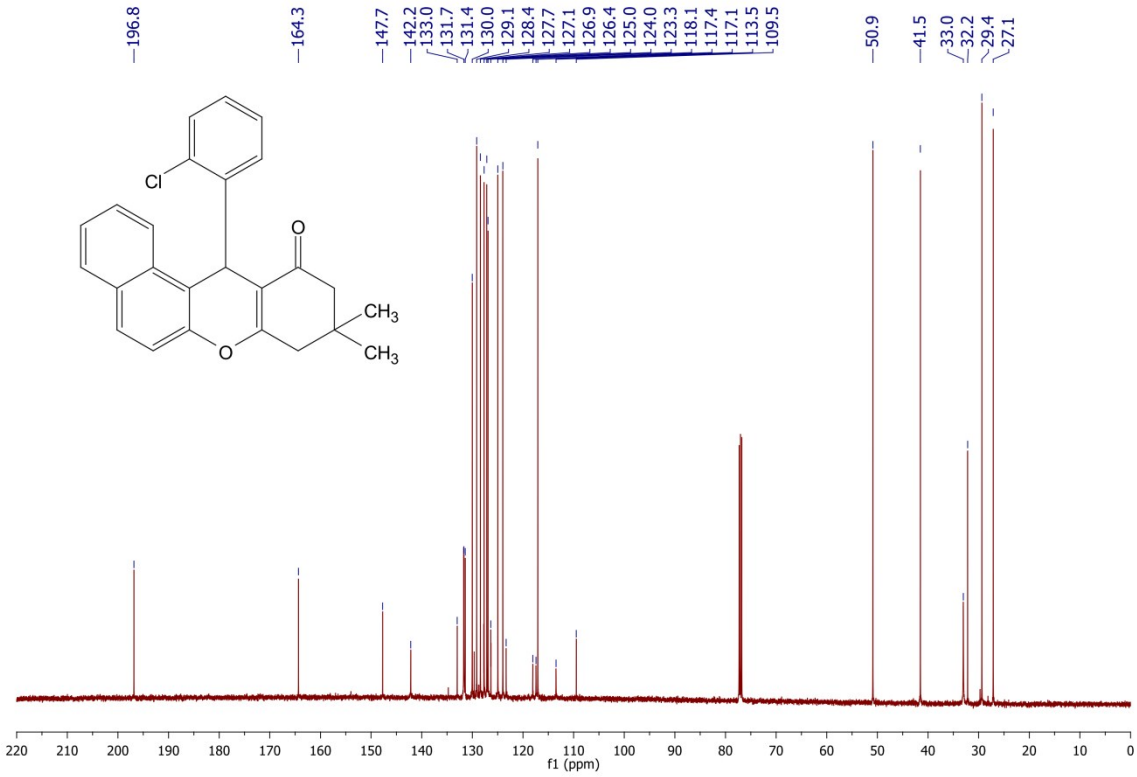
^{1}H NMR of 12-(3-fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



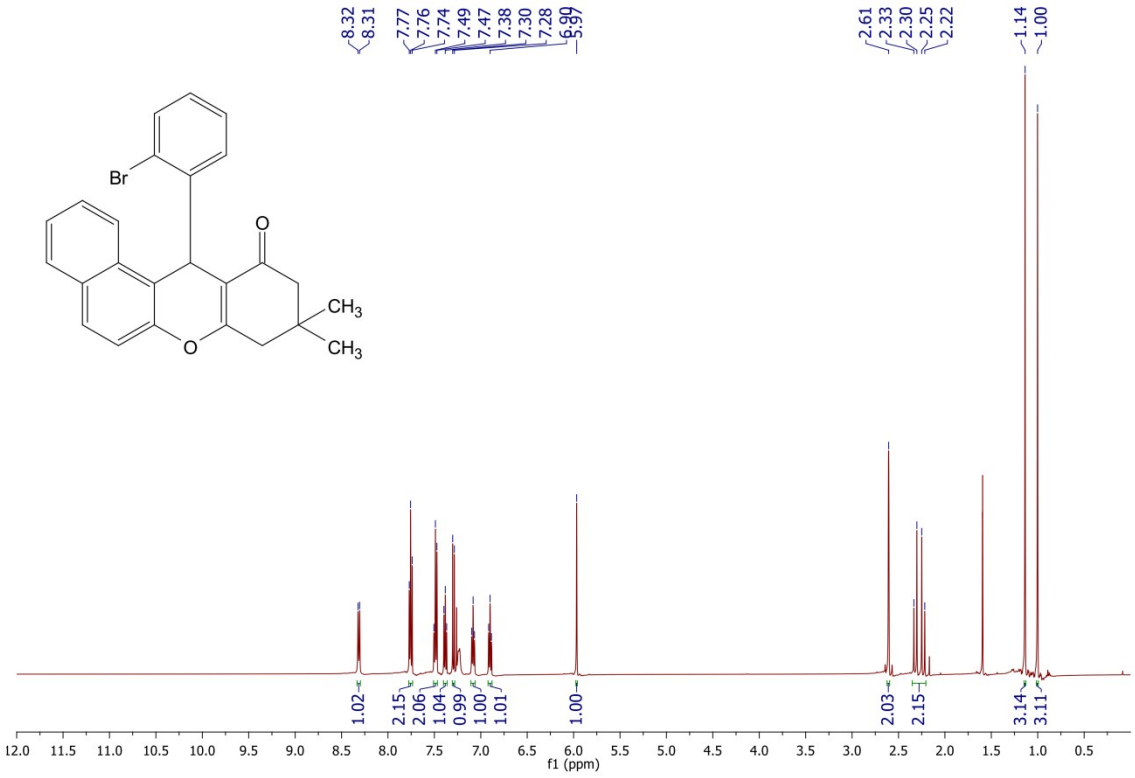


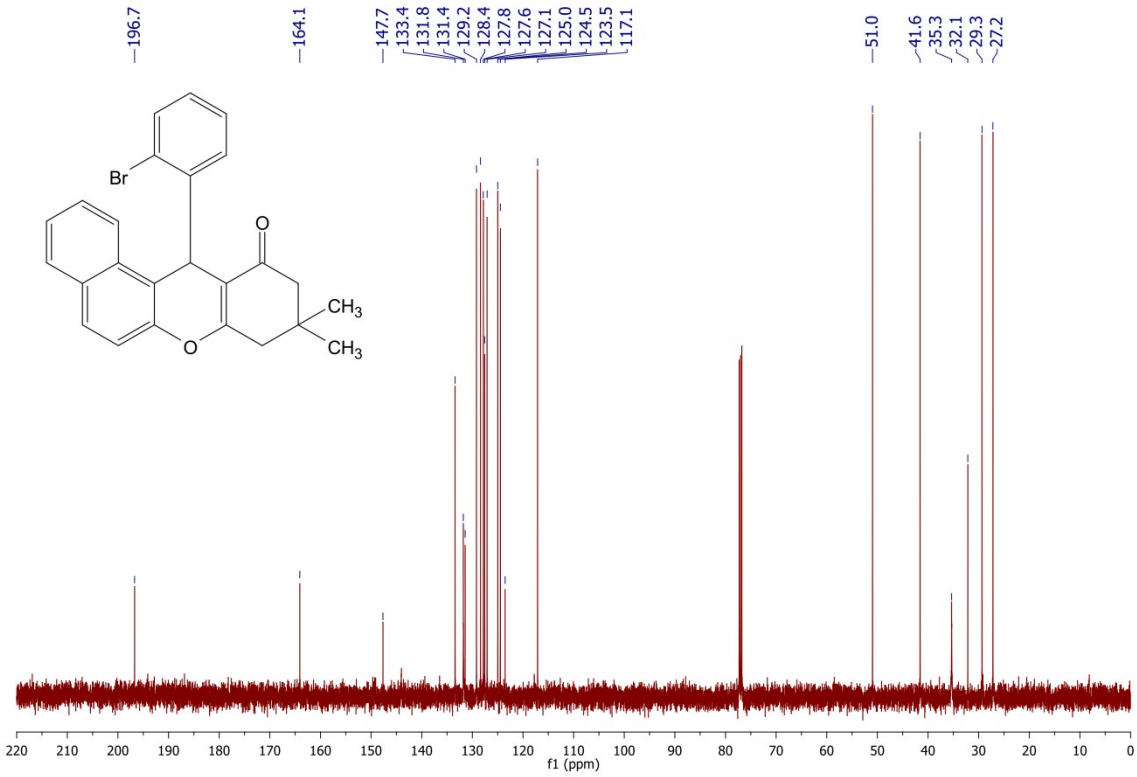
^{1}H and ^{13}C NMR of 12-(2-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



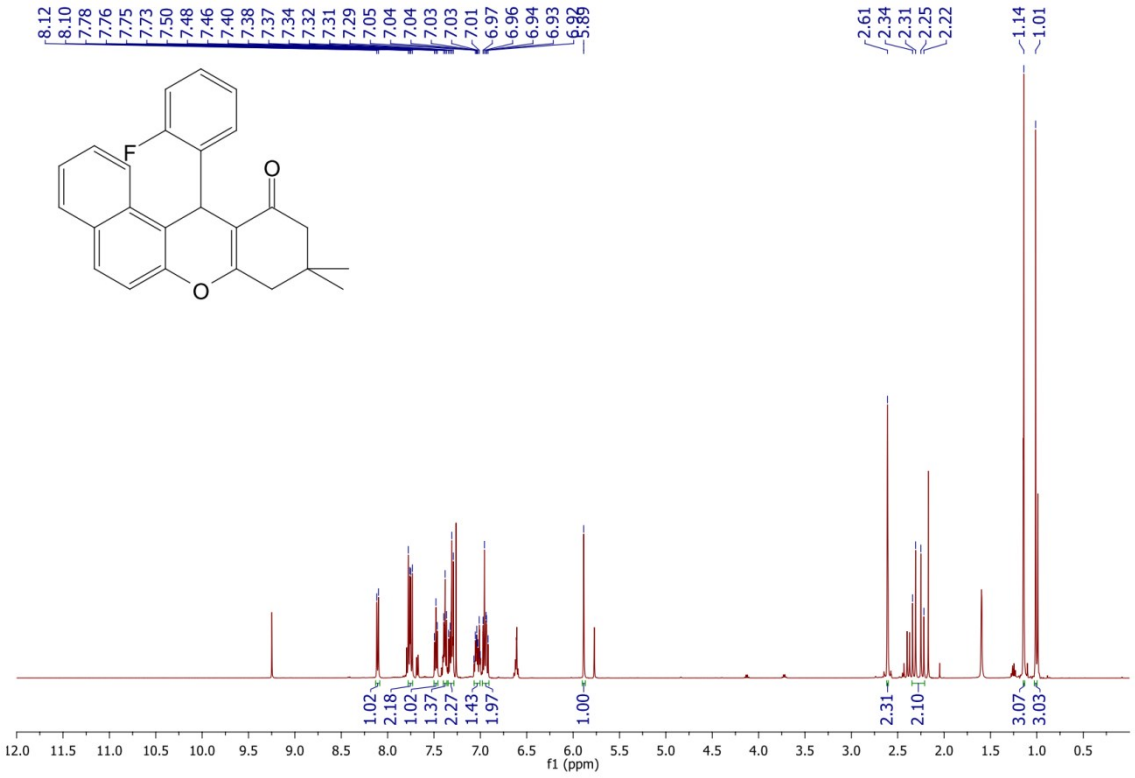


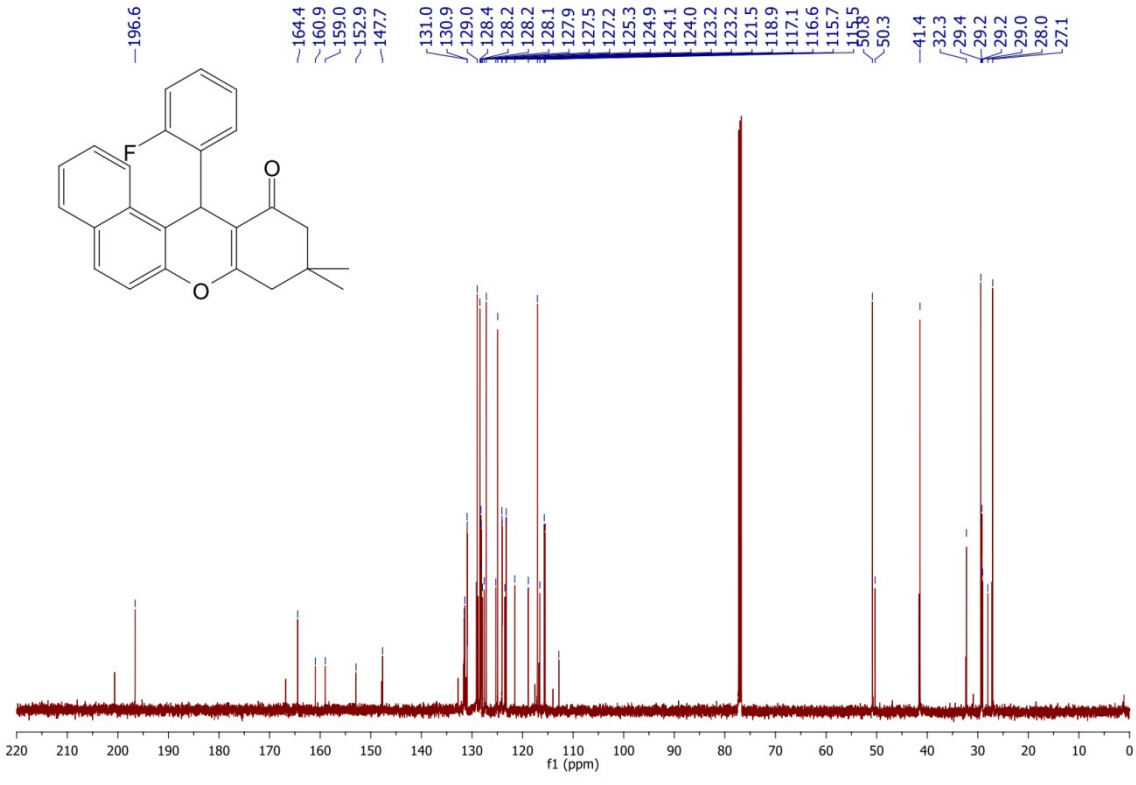
^{1}H and ^{13}C NMR of 12-(2-bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



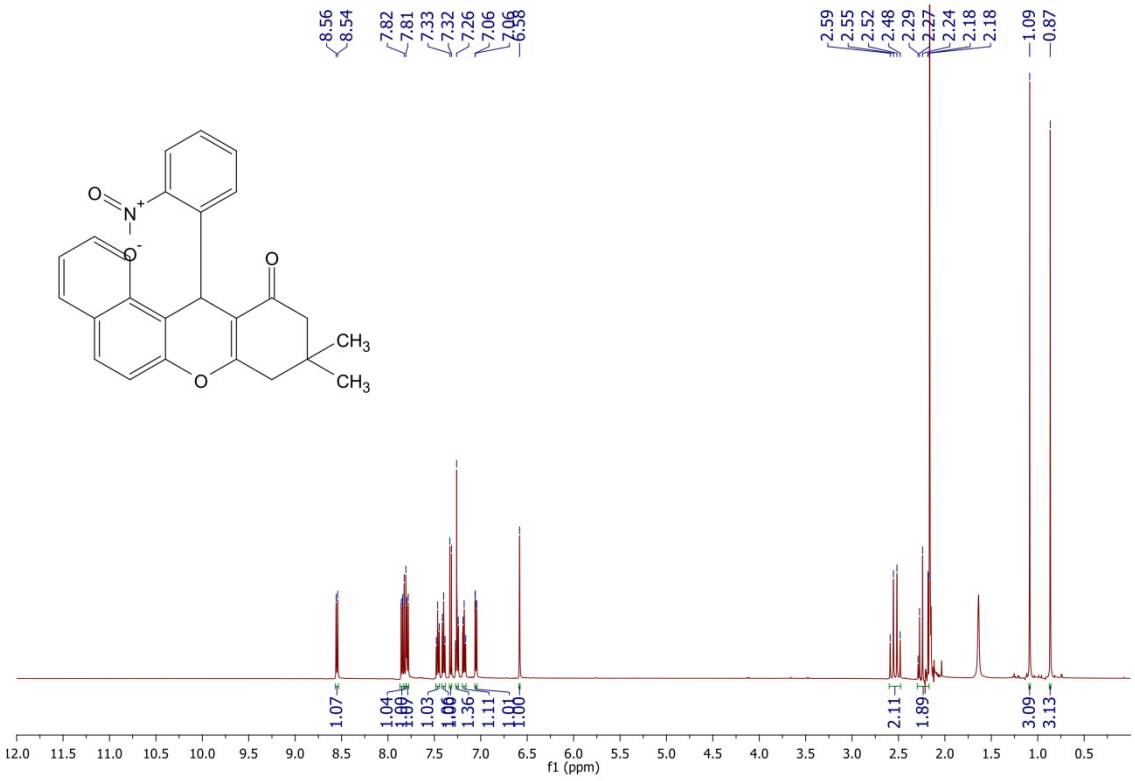


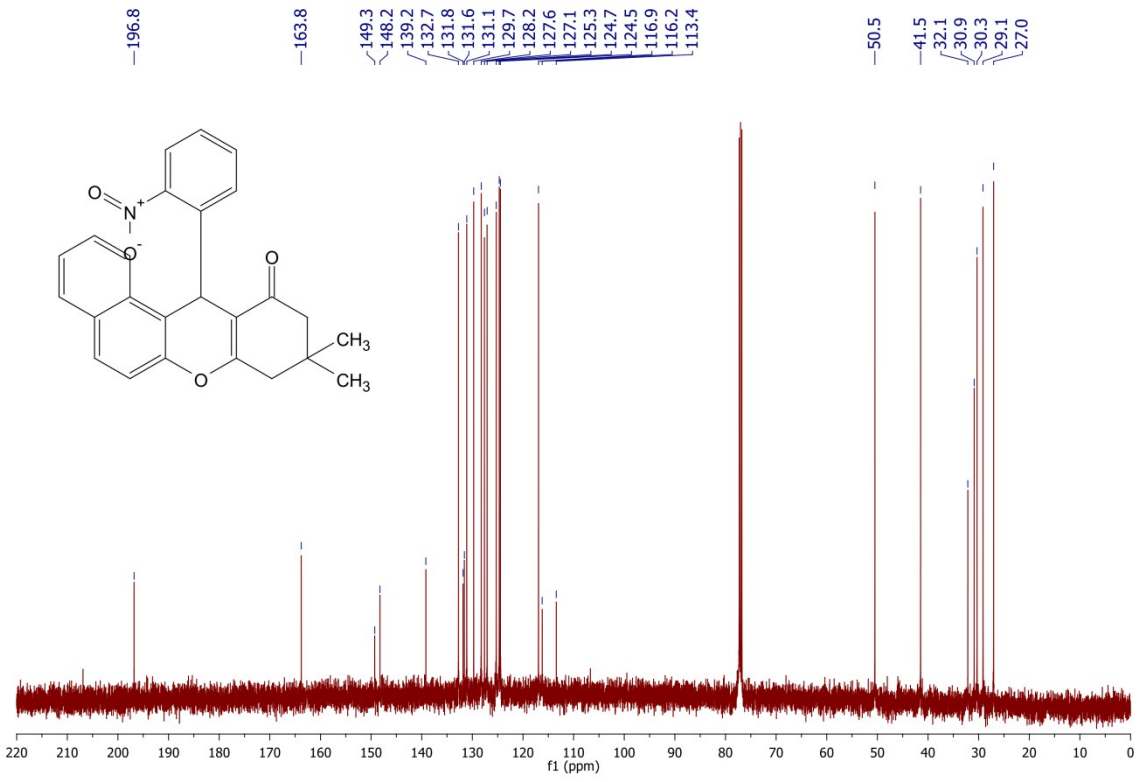
^{1}H and ^{13}C NMR of 12-(2-fluorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



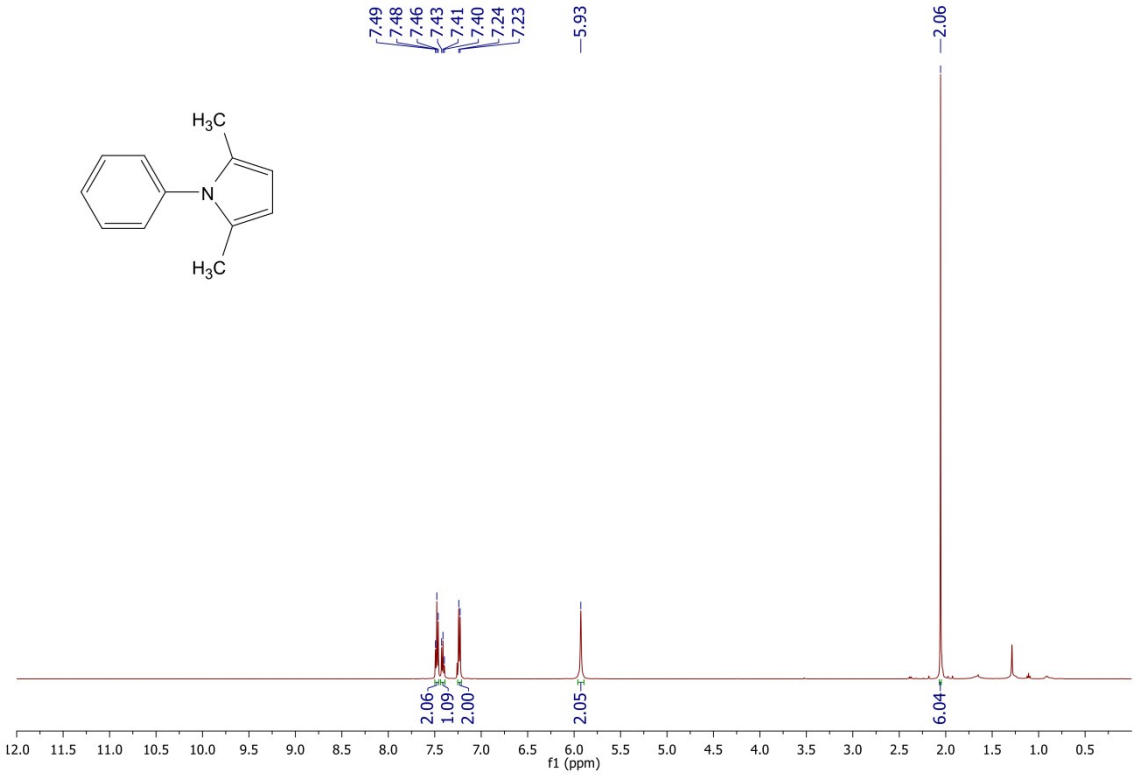


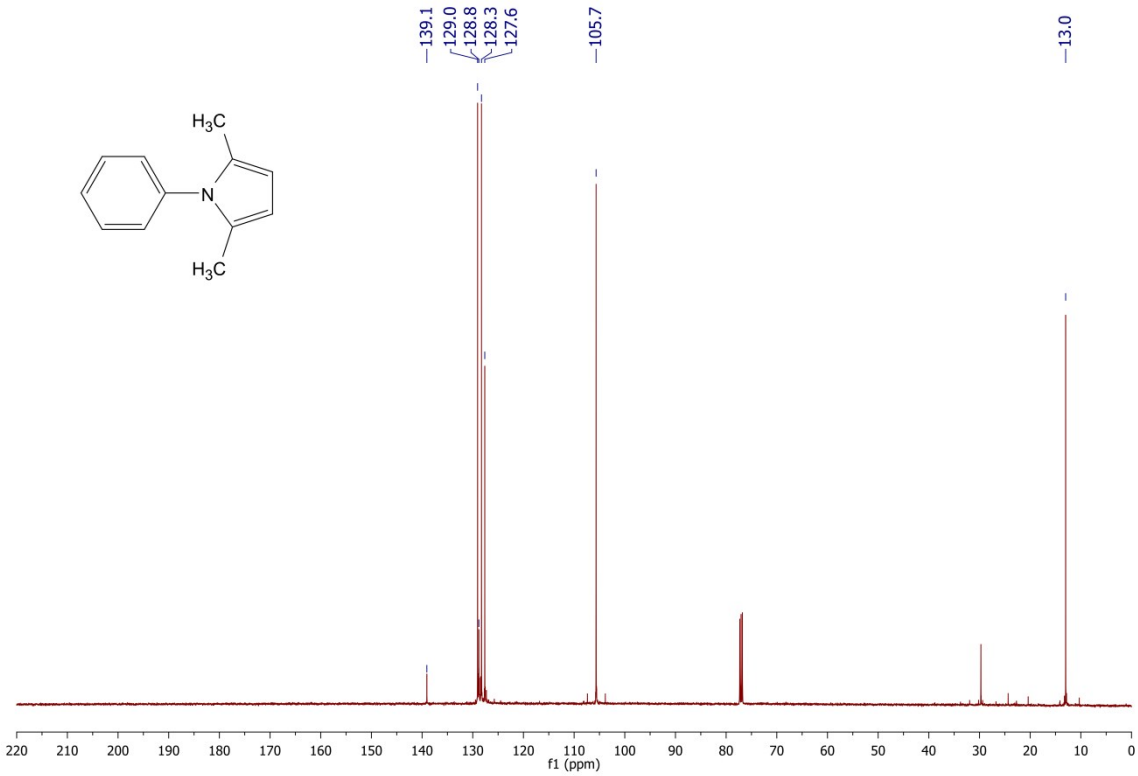
^{1}H and ^{13}C NMR of 9,9-dimethyl-12-(2-nitrophenyl)-8,9,10,12-tetrahydro-11*H*-benzo[*a*]xanthen-11-one



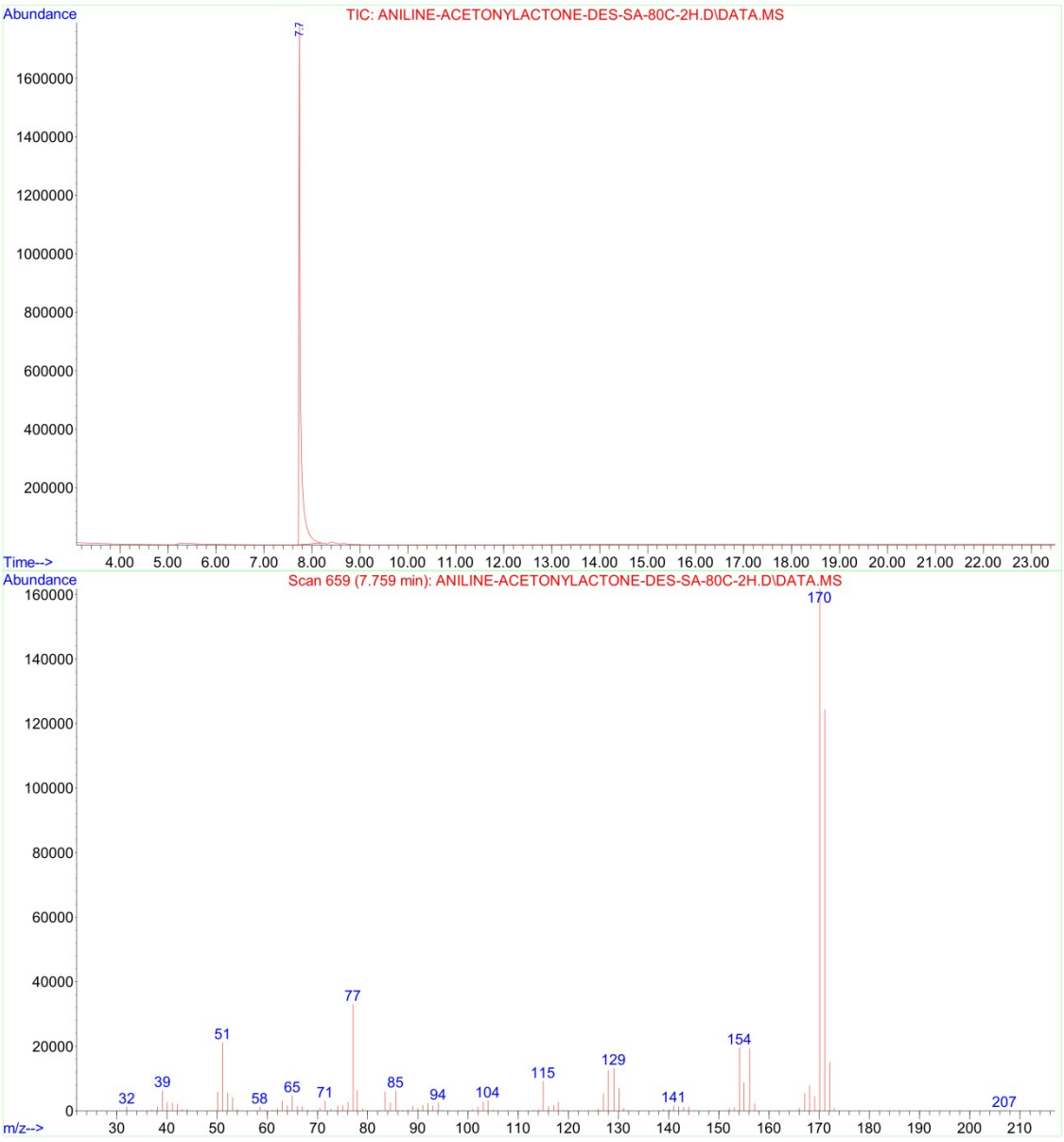


^{1}H NMR, ^{13}C NMR, and GC-MS of 2,5-Dimethyl-1-phenyl-1*H*-pyrrole

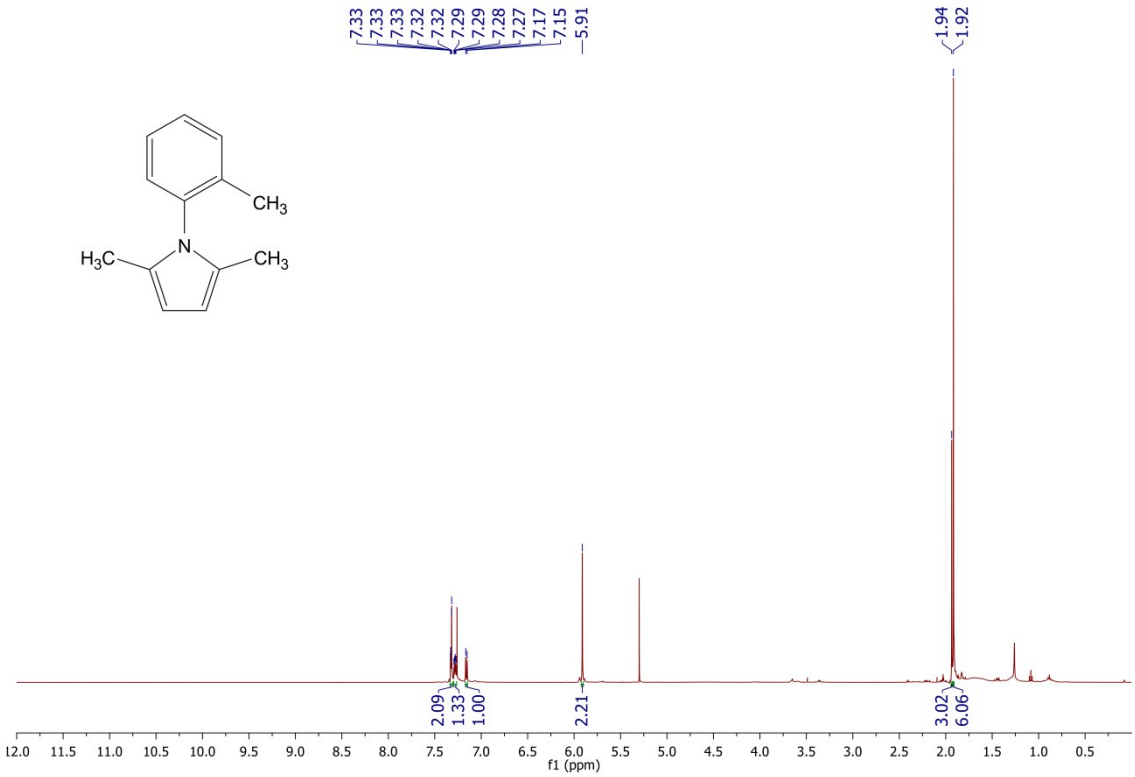


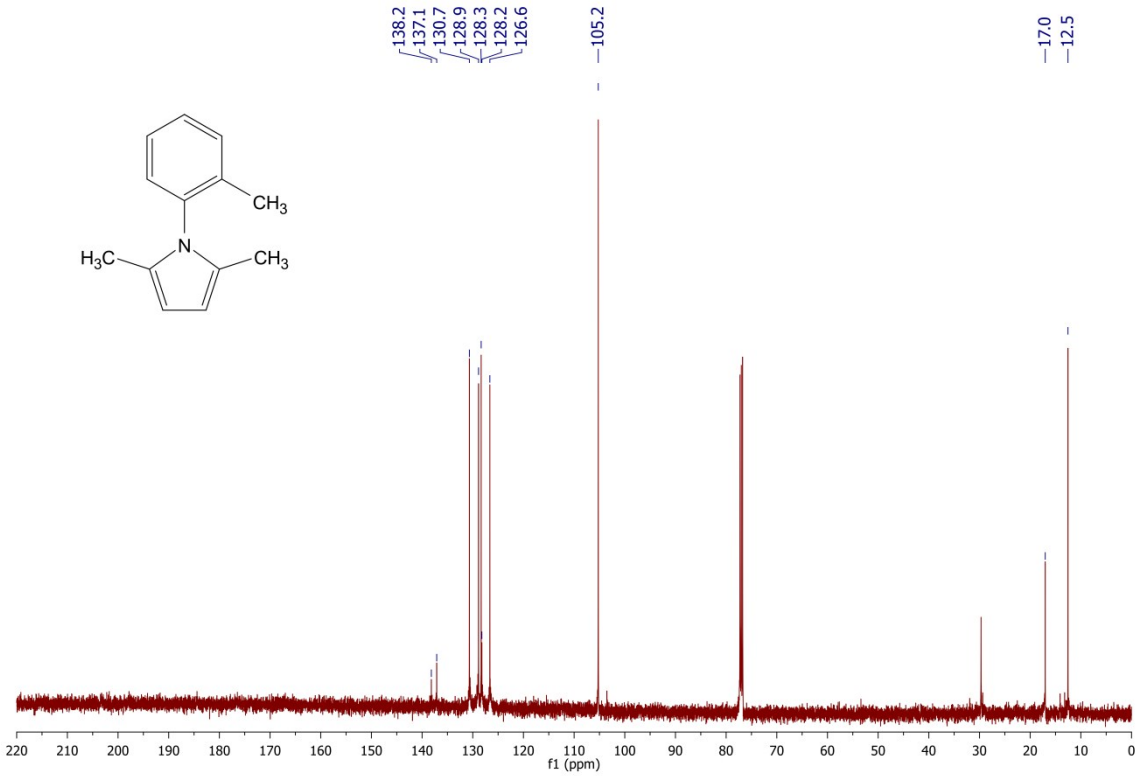


File :C:\GC-MS\2016\08.01.2016\ANILINE-ACETONYLACTONE-DES-SA-80C-2
... H.D
Operator : TRUONG HAI
Instrument : GCMSD
Acquired : 1 Aug 2016 16:44 using AcqMethod ACYLATION-SHORT-DELAY-3MIN.M
Sample Name: ANILINE-ACETONYLACTONE-DES-SA-80C-2H
Misc Info :

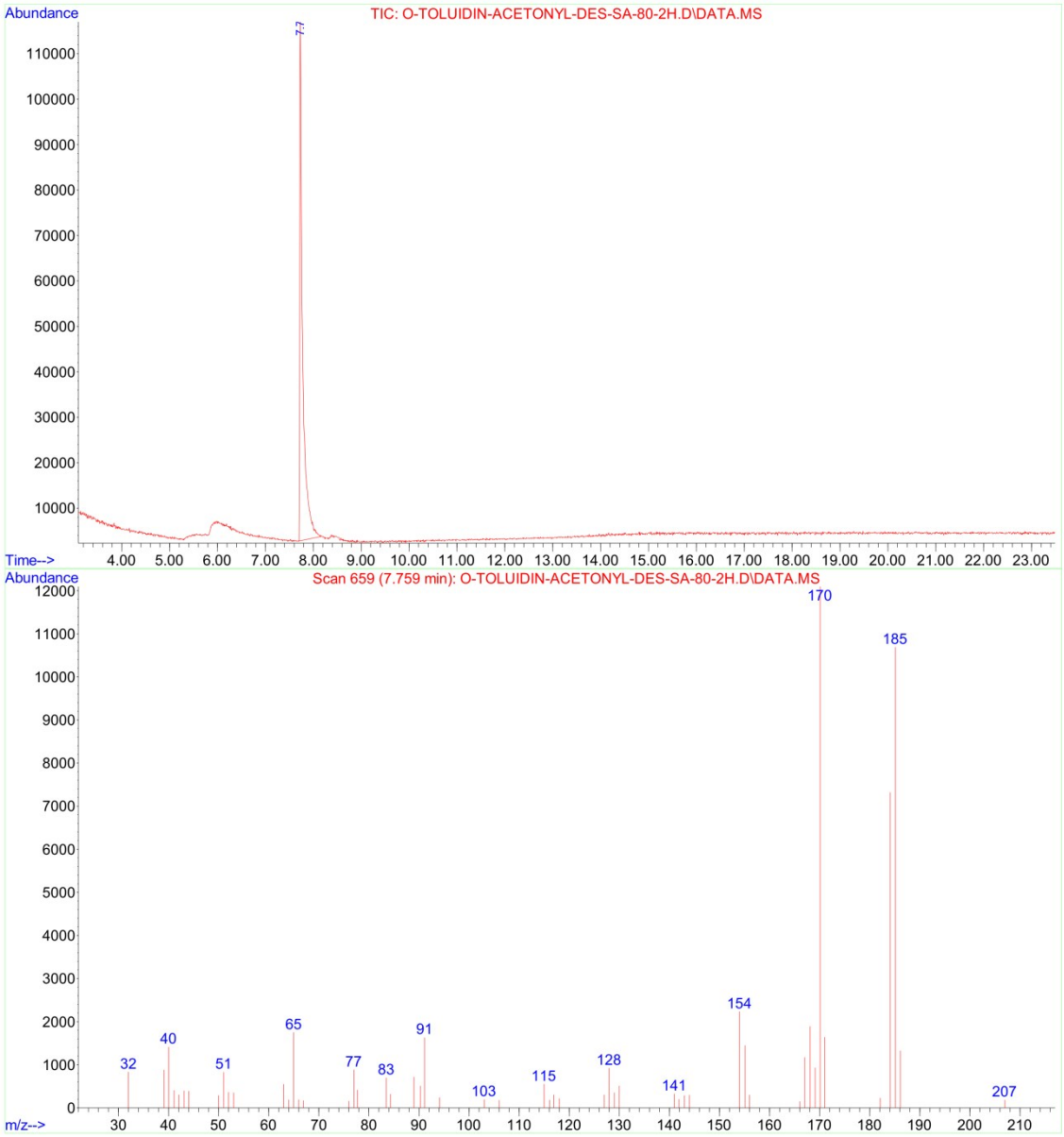


^{1}H NMR, ^{13}C NMR, and GC-MS of 2,5-Dimethyl-1-(*o*-tolyl)-1*H*-pyrrole

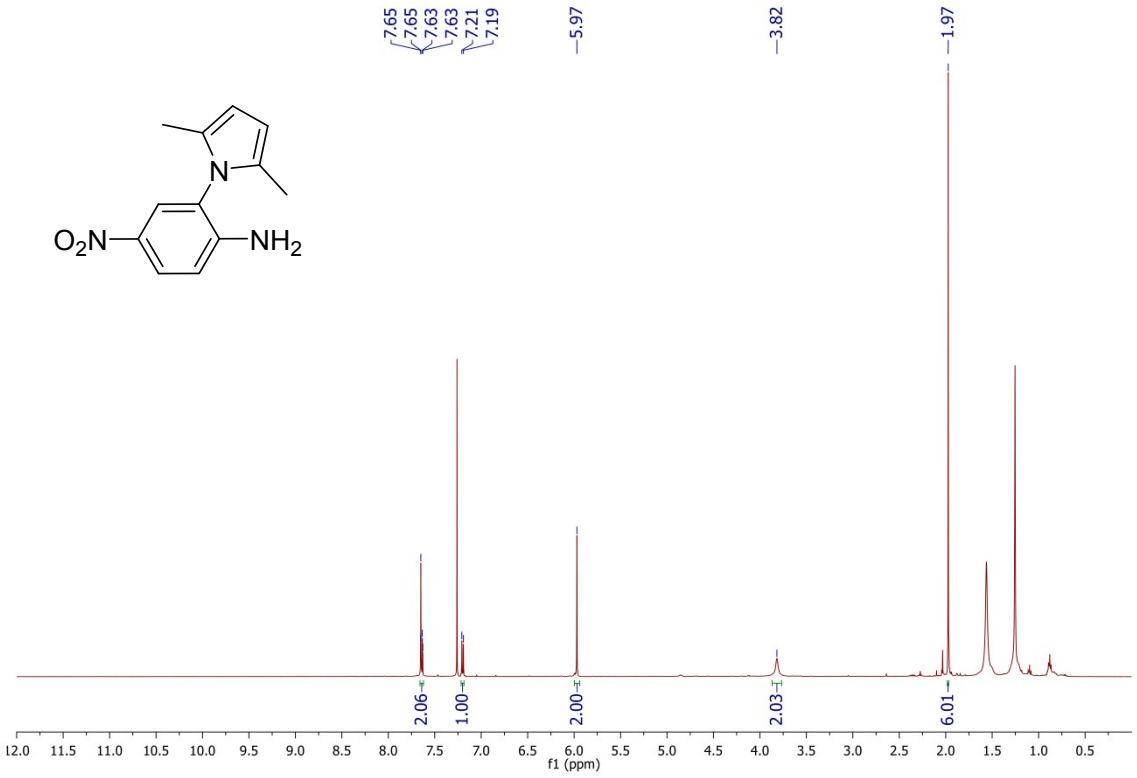


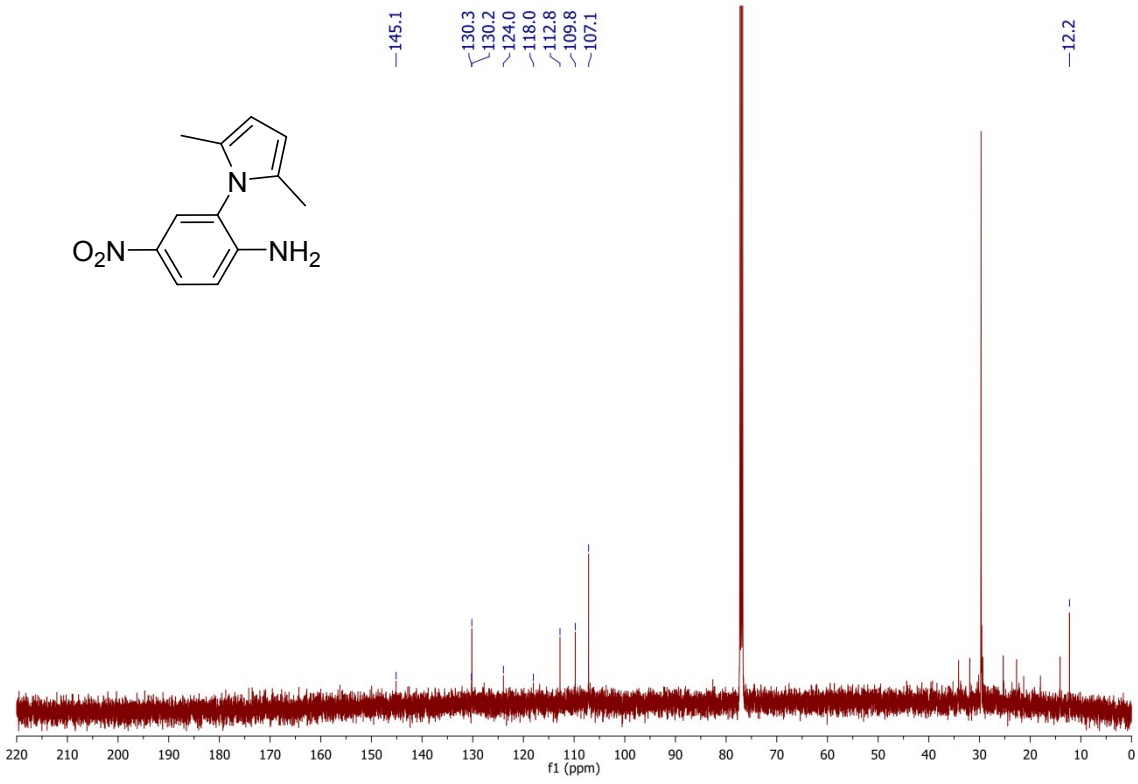


File :C:\GC-MS\2016\08.03.2016\O-TOLUIDIN-ACETONYL-DES-SA-80-2H.D
Operator : TRUONG HAI
Acquired : 4 Aug 2016 11:12 using AcqMethod ACYLATION-SHORT-DELAY-3MIN.M
Instrument : GCMSD
Sample Name: O-TOLUIDIN-ACETONYL-DES-SA-80-2H
Misc Info :
Vial Number: 3



^{1}H NMR, ^{13}C NMR, and GC-MS of 1-(2'-Amino-4'-nitrophenyl)-2,5-dimethyl-1*H*-pyrrole





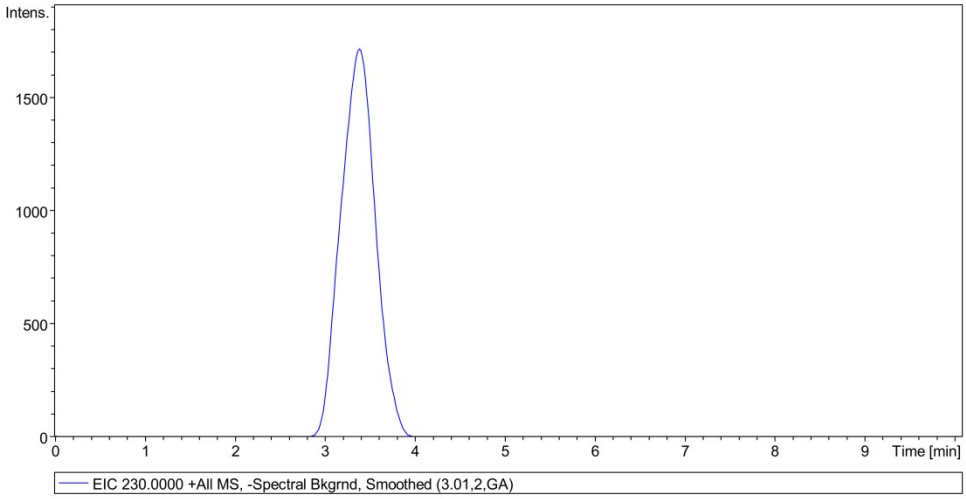
Display Report

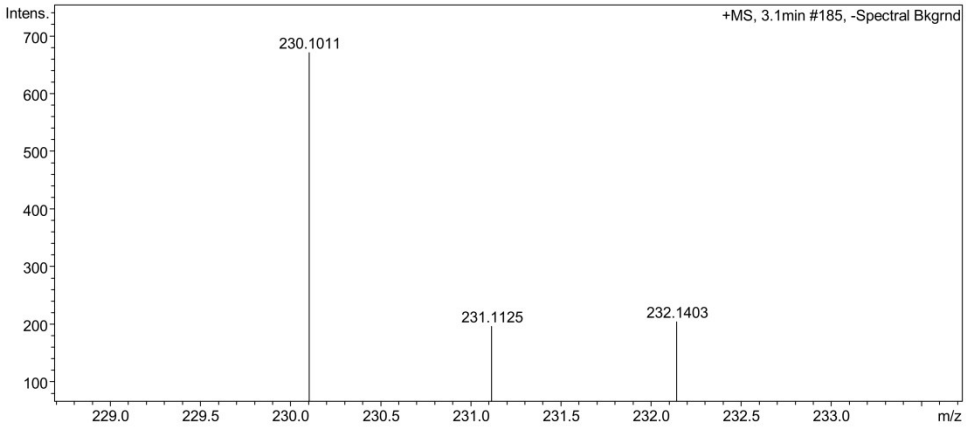
Analysis Info

Analysis Name	D:\Data\2016\4-ni_1-b,2_01_2263.d	Acquisition Date	12/29/2016 6:12:14 PM
Method	dmm 2017.m	Operator	Anh Mai
Sample Name	4-ni	Instrument	micrOTOF-Q 10187
Comment			

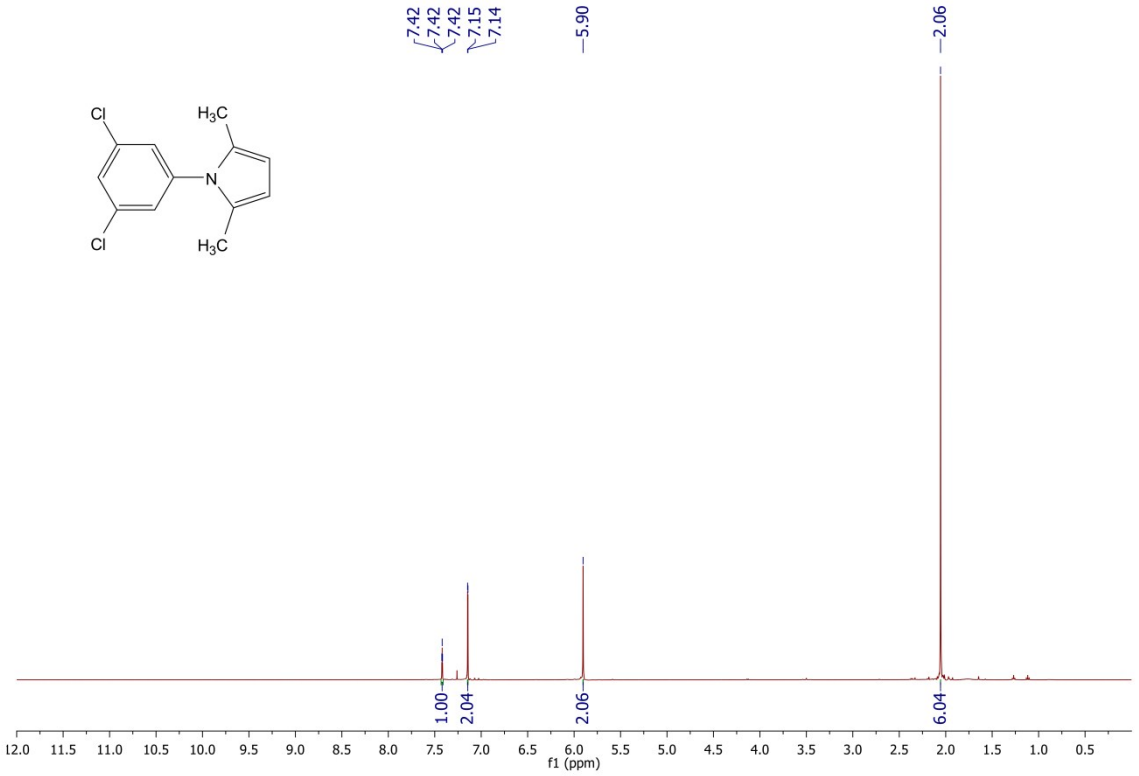
Acquisition Parameter

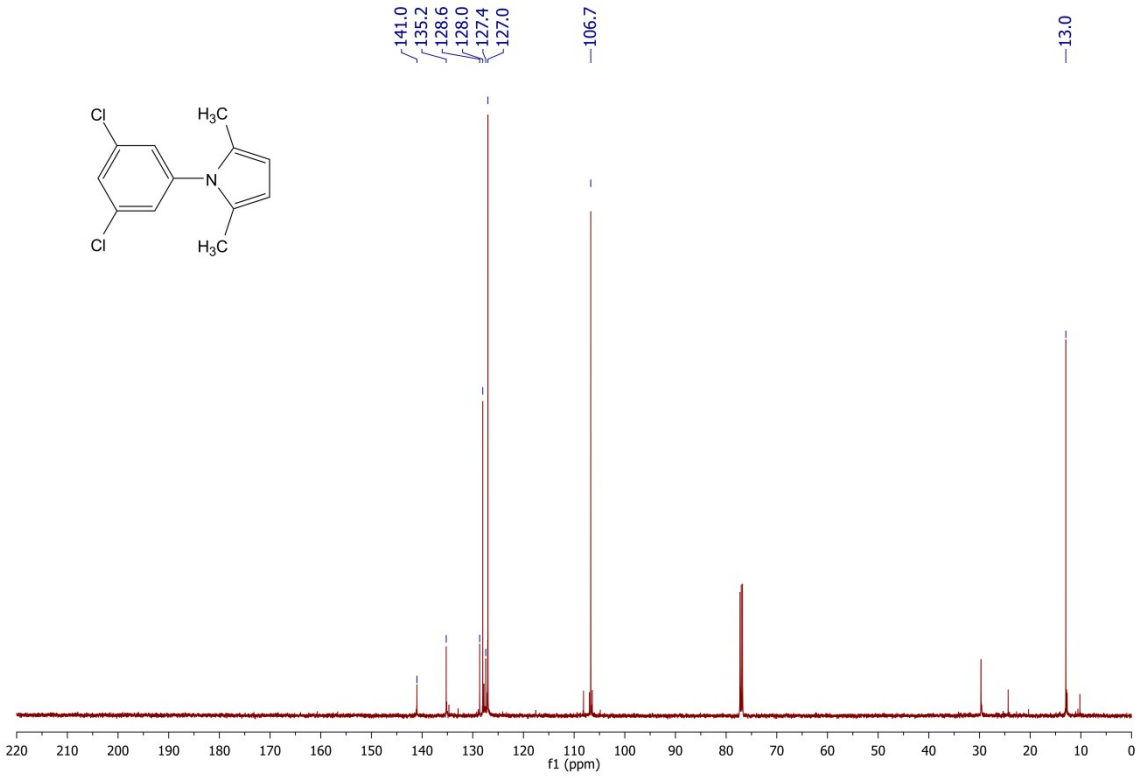
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	9.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	450.0 Vpp	Set Divert Valve	Source



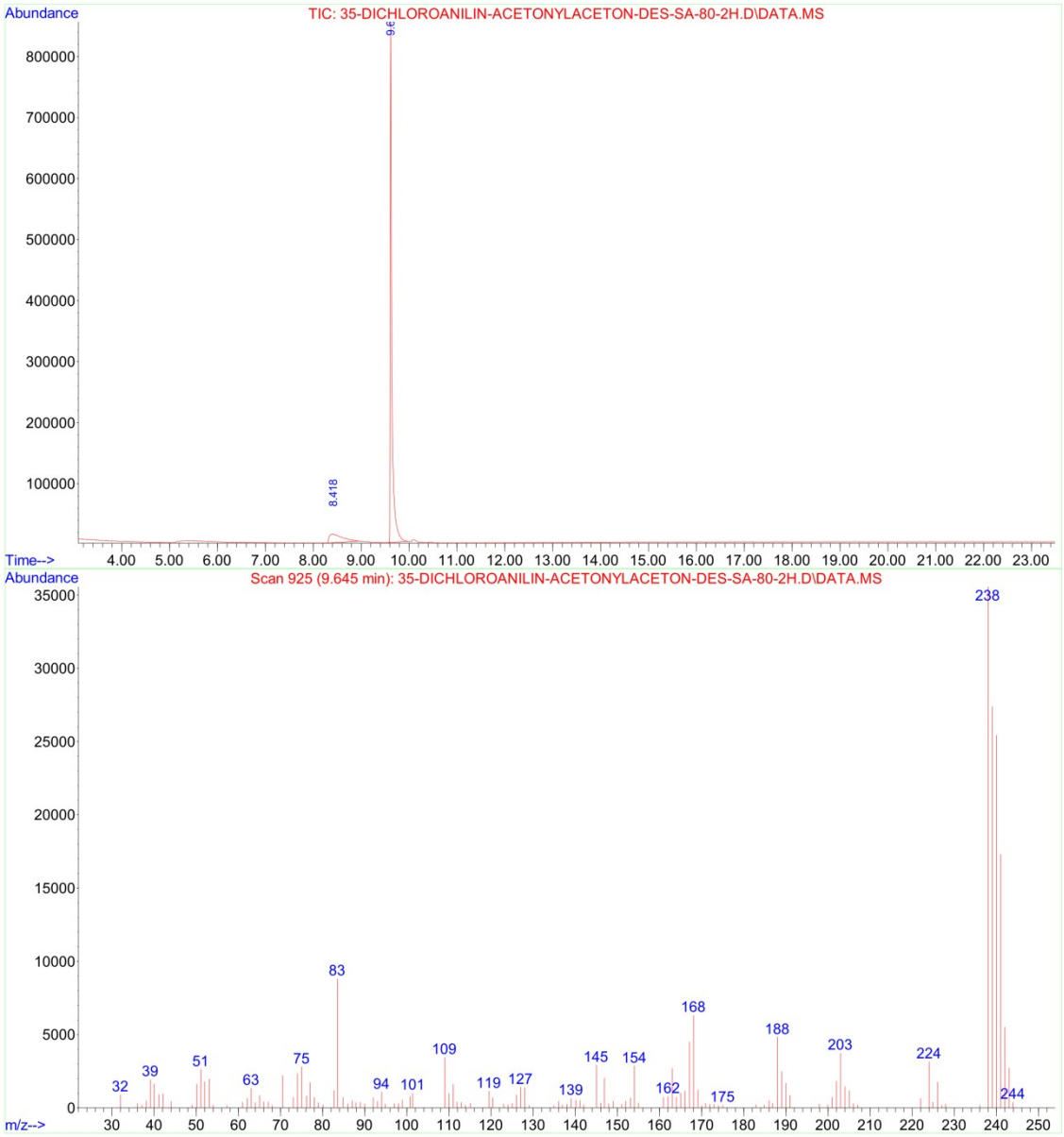


^{1}H NMR, ^{13}C NMR, and GC-MS of 1-(3,5-Dichlorophenyl)-2,5-dimethyl-1*H*-pyrrole

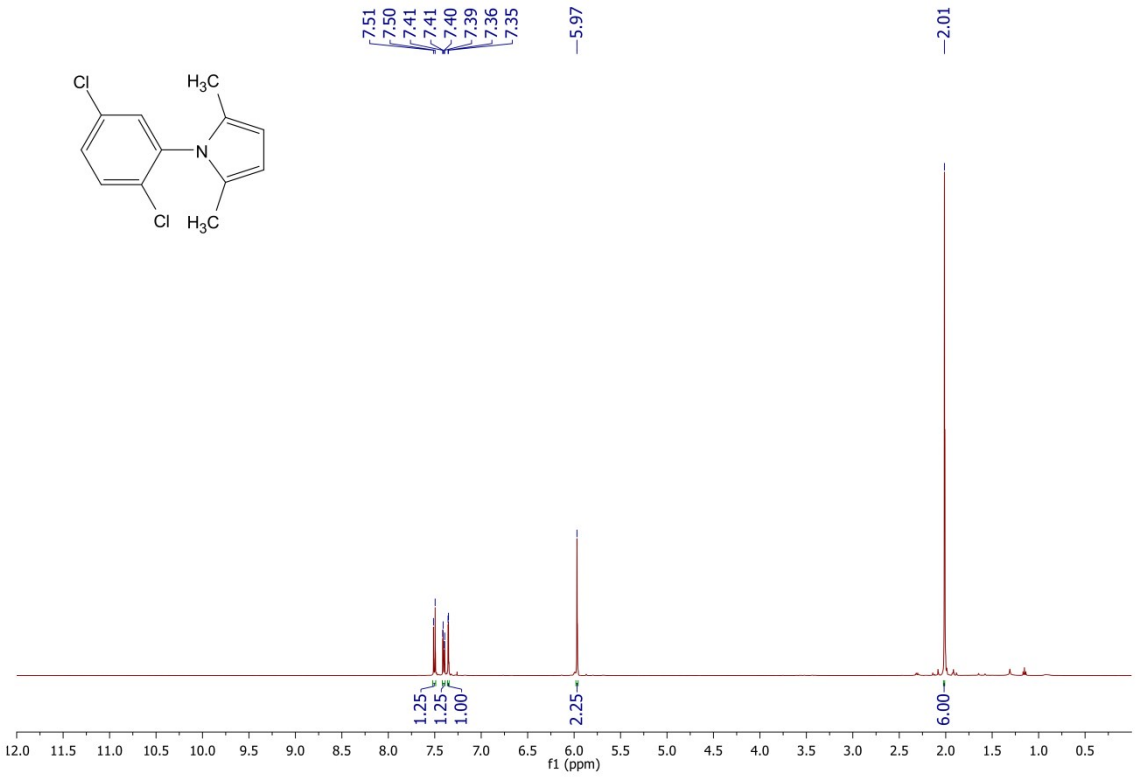


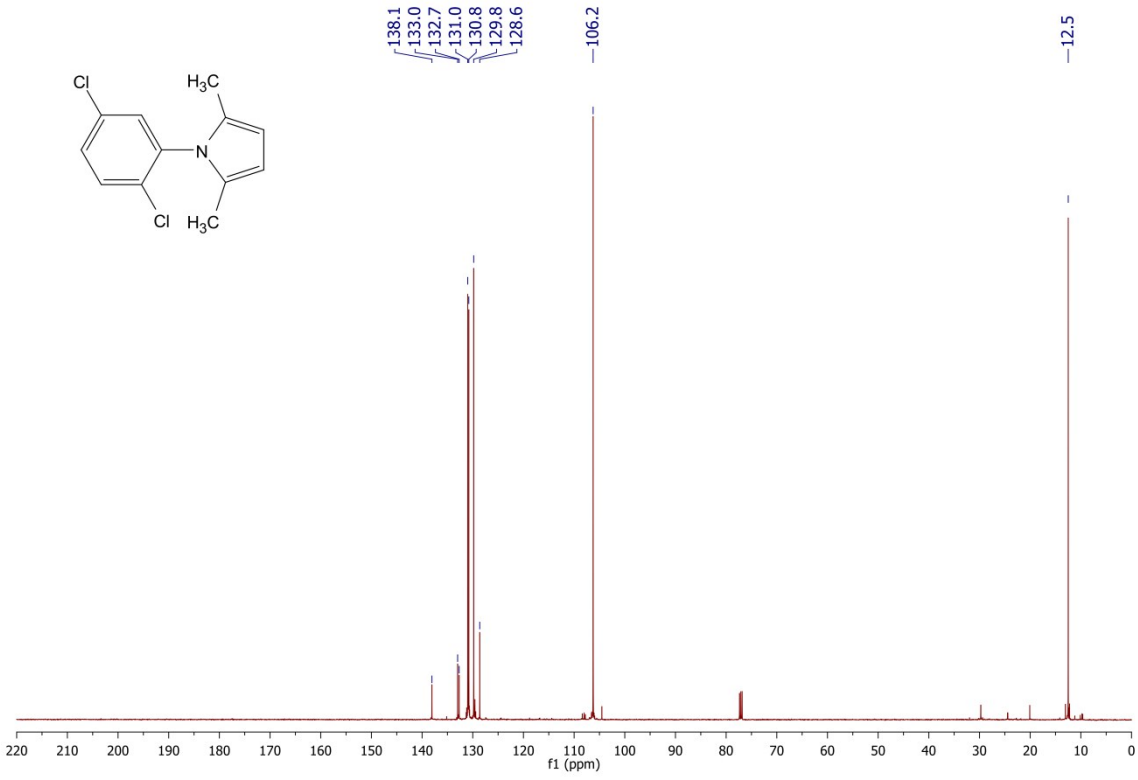


File :C:\GC-MS\2016\08.03.2016\35-DICHLOROANILIN-ACETONYLACETON-DE
... S-SA-80-2H.D
Operator : TRUONG HAI
Instrument : GCMSD
Acquired : 3 Aug 2016 18:03 using AcqMethod ACYLATION-SHORT-DELAY-3MIN.M
Sample Name: 35-DICHLOROANILIN-ACETONYLACETON-DES-SA-80-2H
Misc Info :

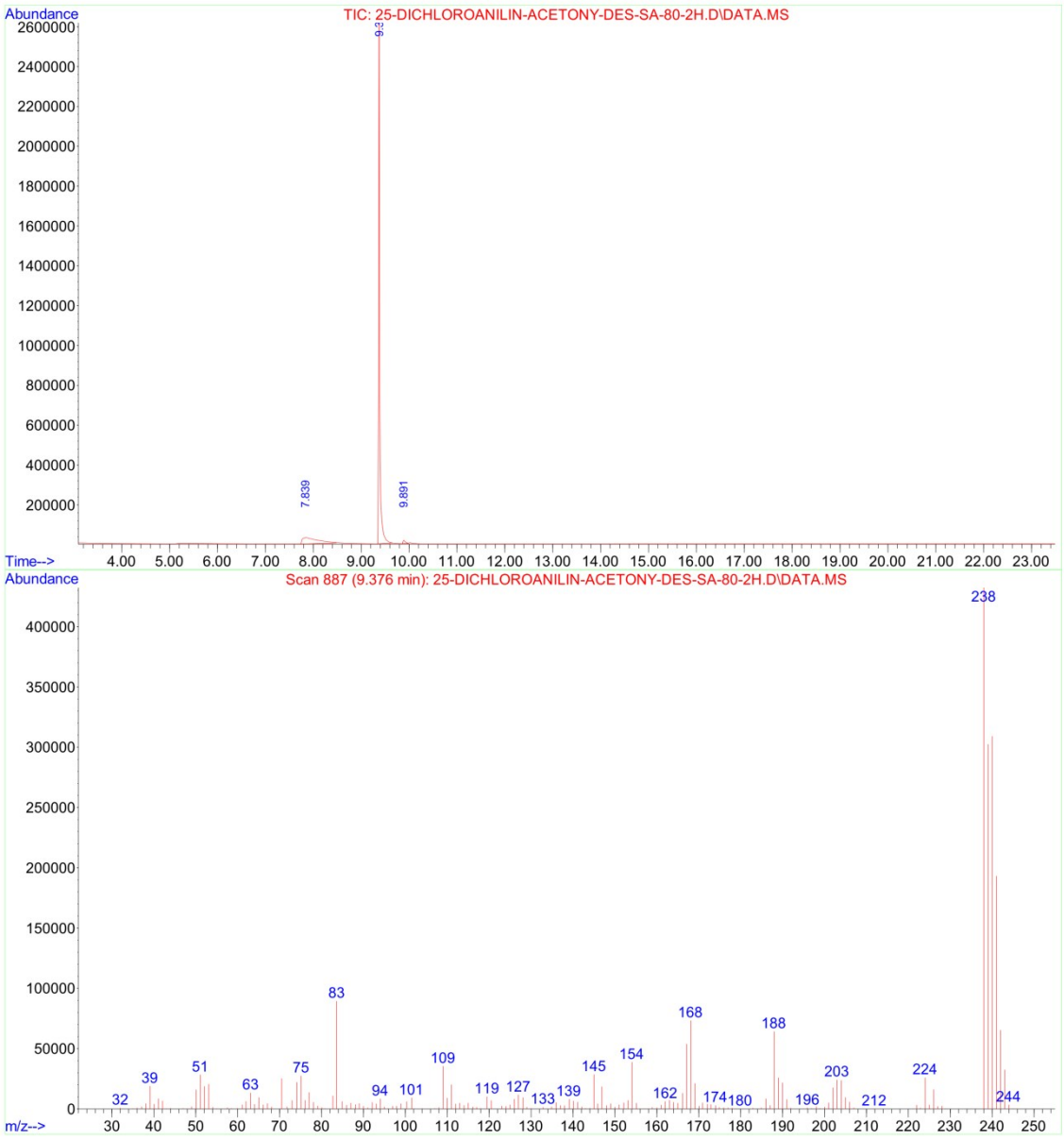


^{1}H NMR, ^{13}C NMR, and GC-MS of 1-(2,5-Dichlorophenyl)-2,5-dimethyl-1*H*-pyrrole

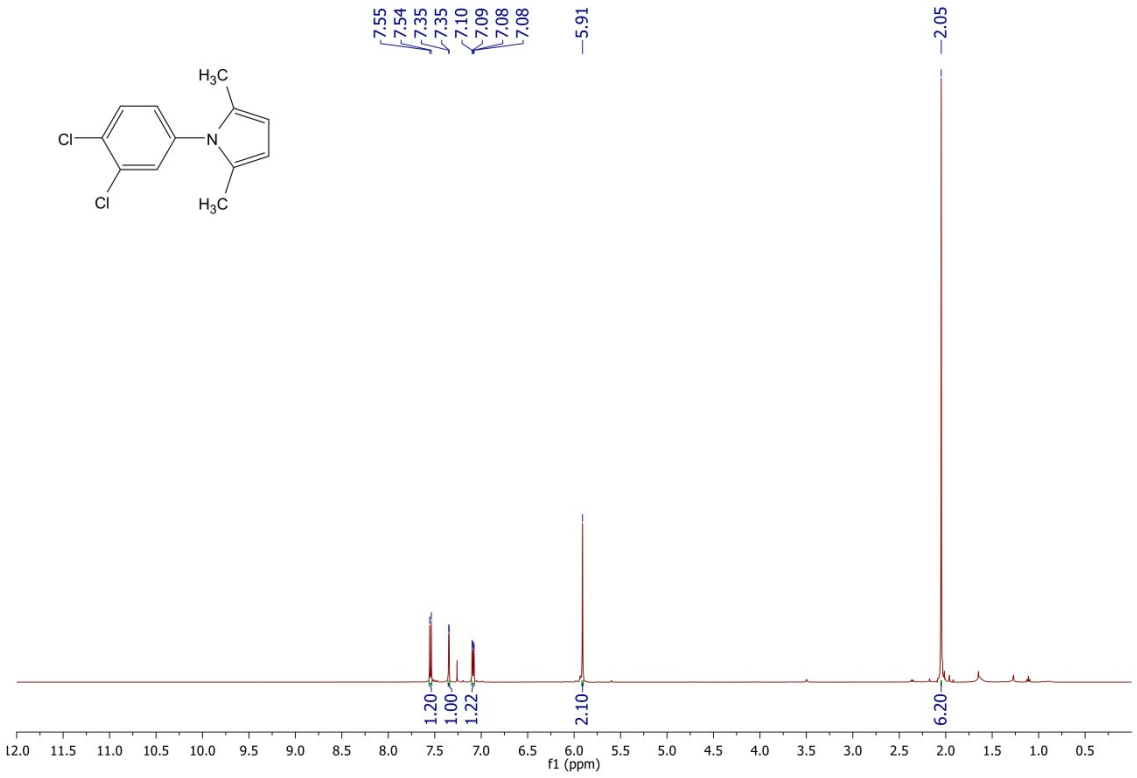


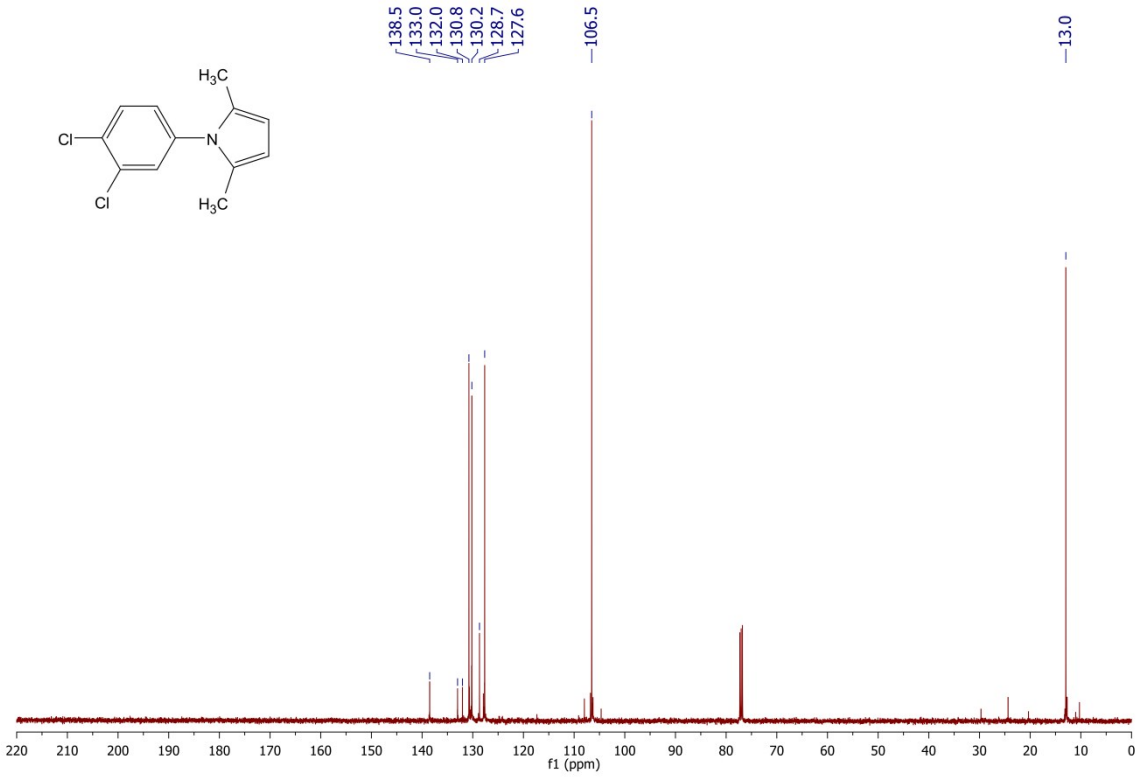


File :C:\GC-MS\2016\08.03.2016\25-DICHLOROANILIN-ACETONY-DES-SA-80
... -2H.D
Operator : TRUONG HAI
Instrument : GCMSD
Acquired : 8 Aug 2016 16:19 using AcqMethod ACYLATION-SHORT-DELAY-3MIN.M
Sample Name: 25-DICHLOROANILIN-ACETONY-DES-SA-80-2H
Misc Info :

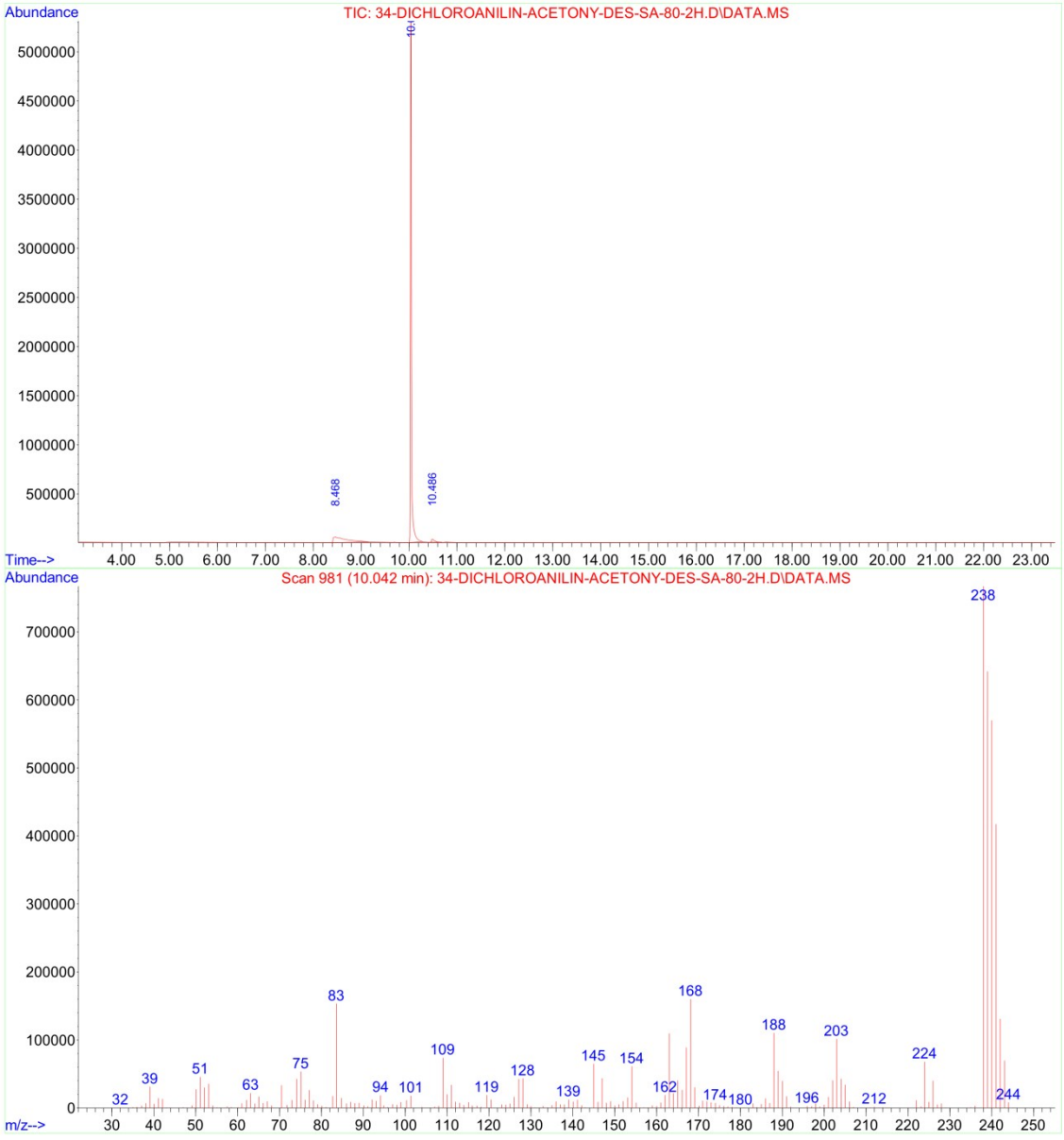


^{1}H NMR, ^{13}C NMR, and GC-MS of 1-(3,4-Dichlorophenyl)-2,5-dimethyl-1*H*-pyrrole

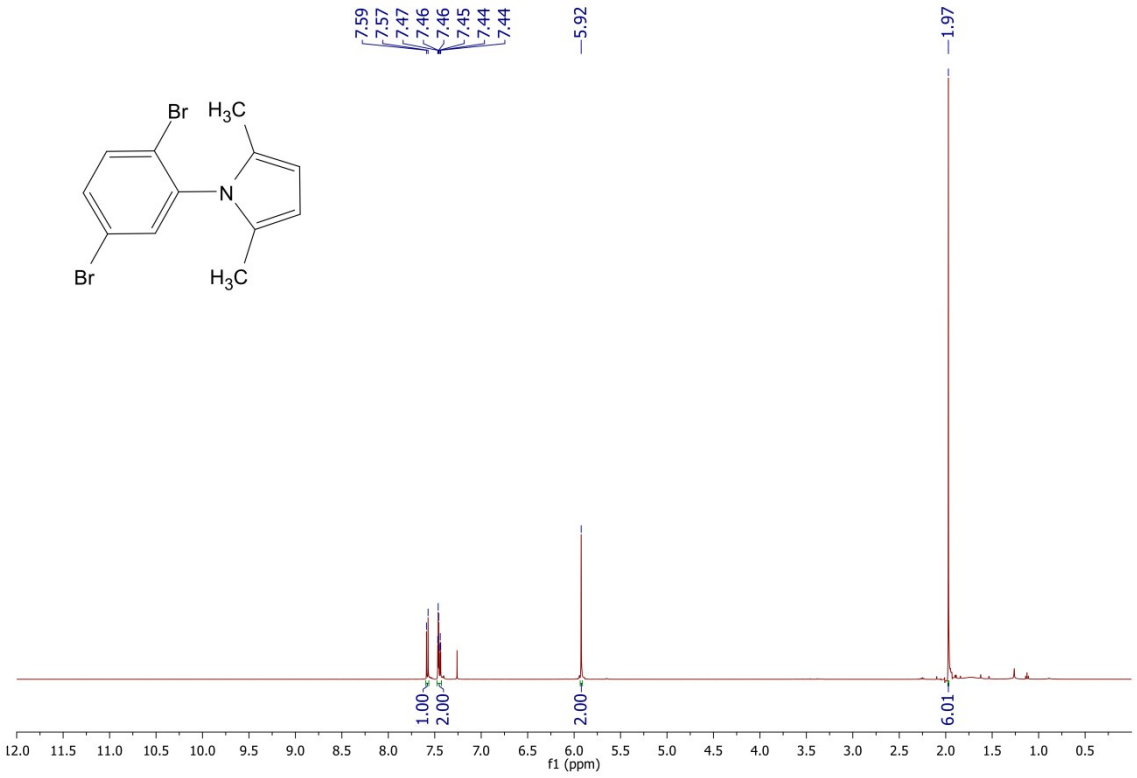


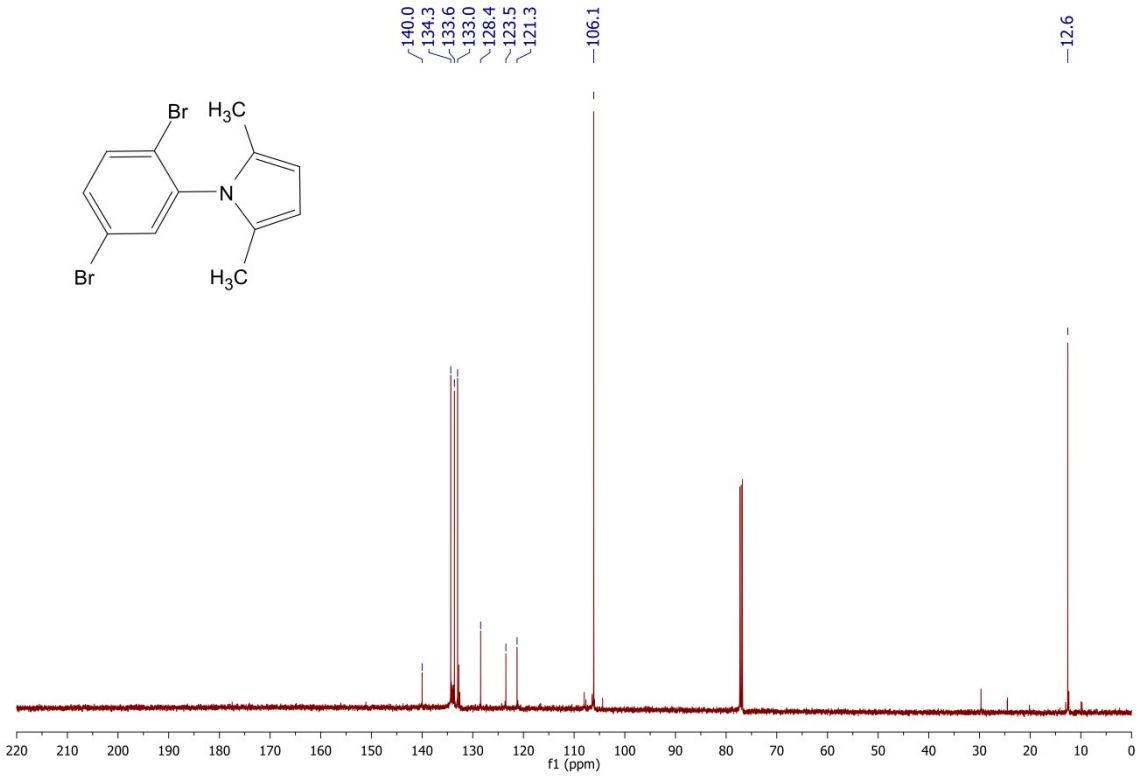


File :C:\GC-MS\2016\08.03.2016\34-DICHLOROANILIN-ACETONY-DES-SA-80
... -2H.D
Operator : TRUONG HAI
Instrument : GCMSD
Acquired : 8 Aug 2016 16:54 using AcqMethod ACYLATION-SHORT-DELAY-3MIN.M
Sample Name: 34-DICHLOROANILIN-ACETONY-DES-SA-80-2H
Misc Info :

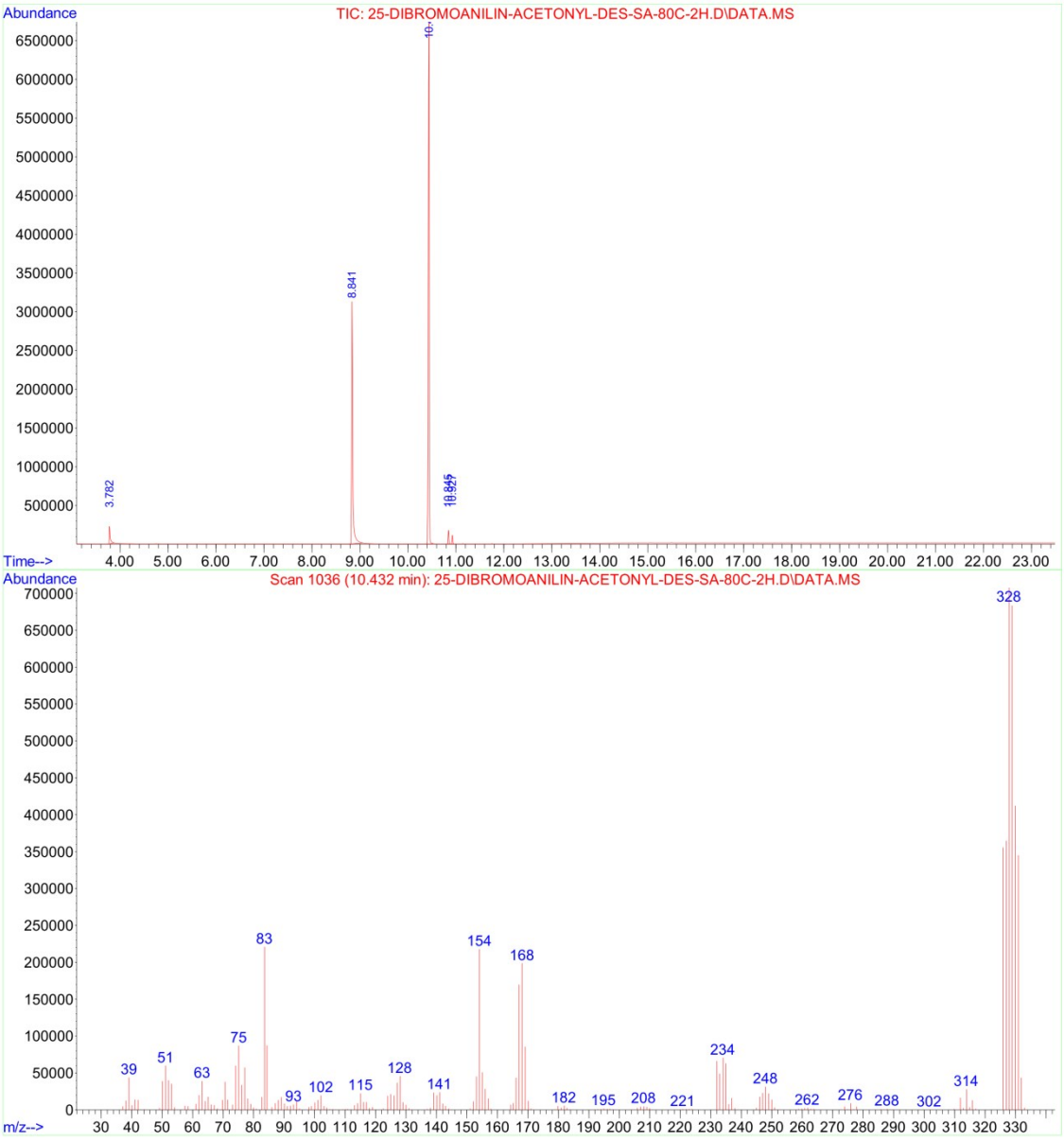


^{1}H NMR, ^{13}C NMR, and GC-MS of 1-(2,5-Dibromophenyl)-2,5-dimethyl-1*H*-pyrrole

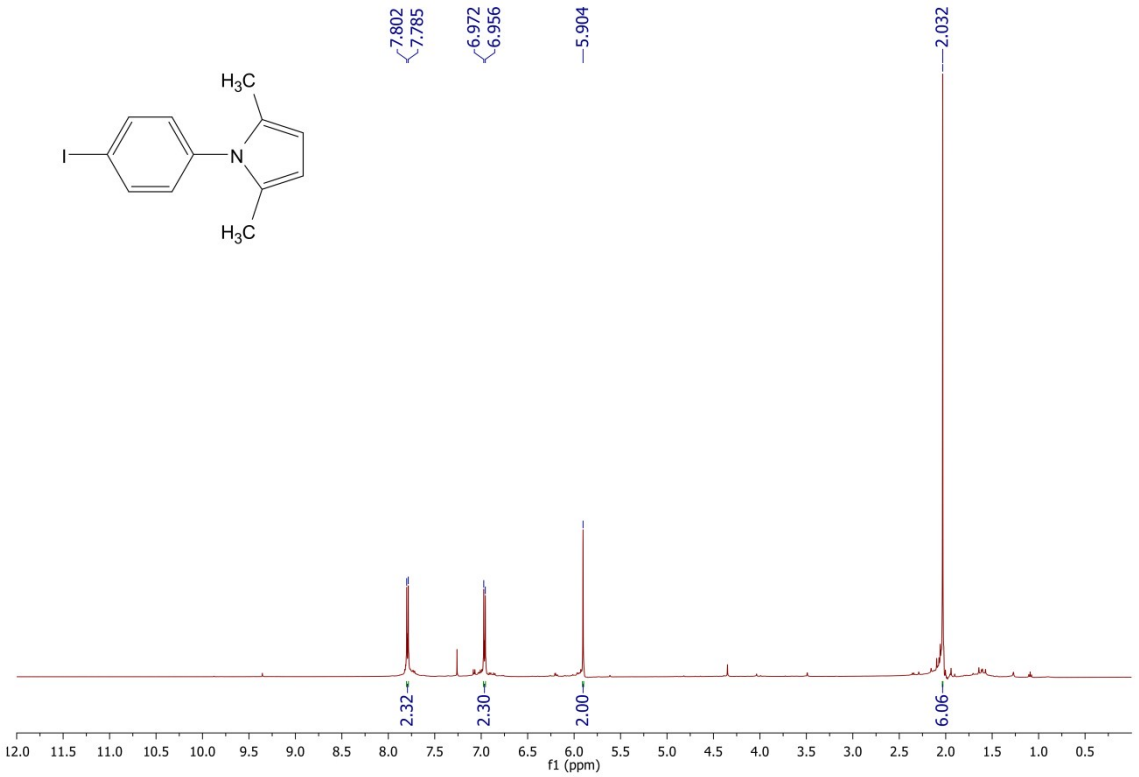


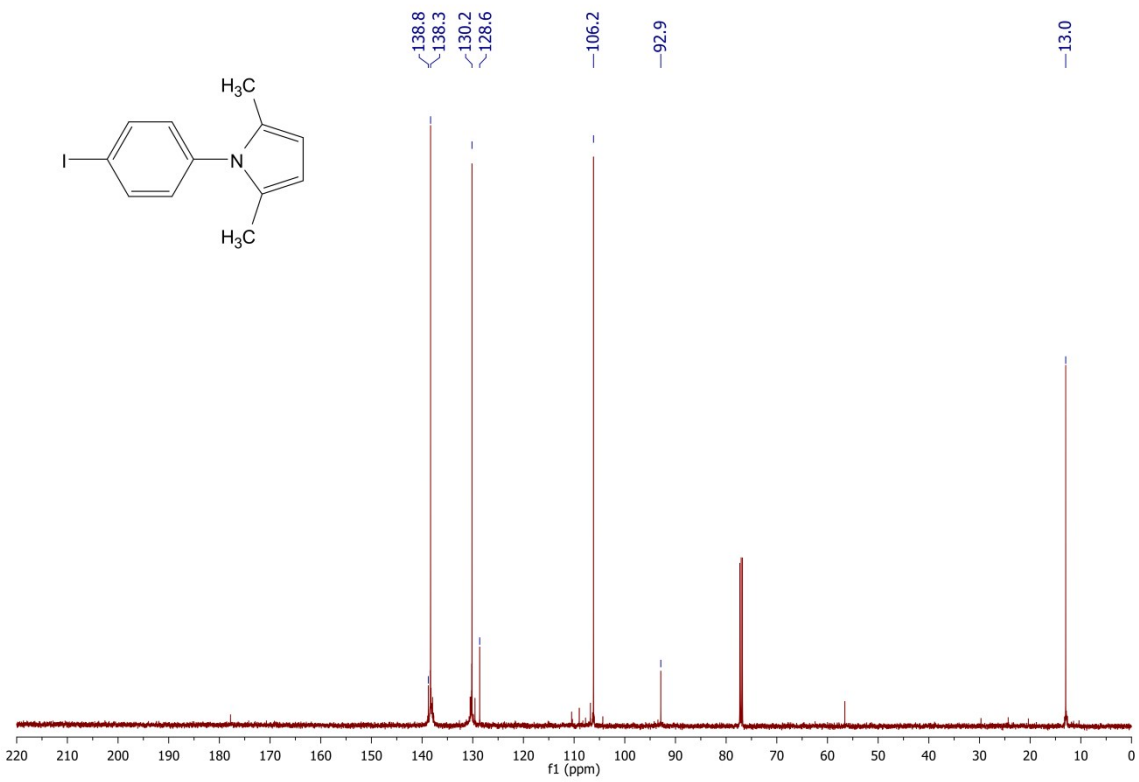


File :C:\GC-MS\2016\08.17.2016\25-DIBROMOANILIN-ACETONYL-DES-SA-80
... C-2H.D
Operator : TRUONG HAI
Instrument : GCMSD
Acquired : 17 Aug 2016 13:03 using AcqMethod ACYLATION-SHORT-DELAY-3MIN.M
Sample Name: 25-DIBROMOANILIN-ACETONYL-DES-SA-80C-2H
Misc Info :



^{1}H NMR, ^{13}C NMR, and GC-MS of 1-(4-Iodophenyl)-2,5-dimethyl-1*H*-pyrrole





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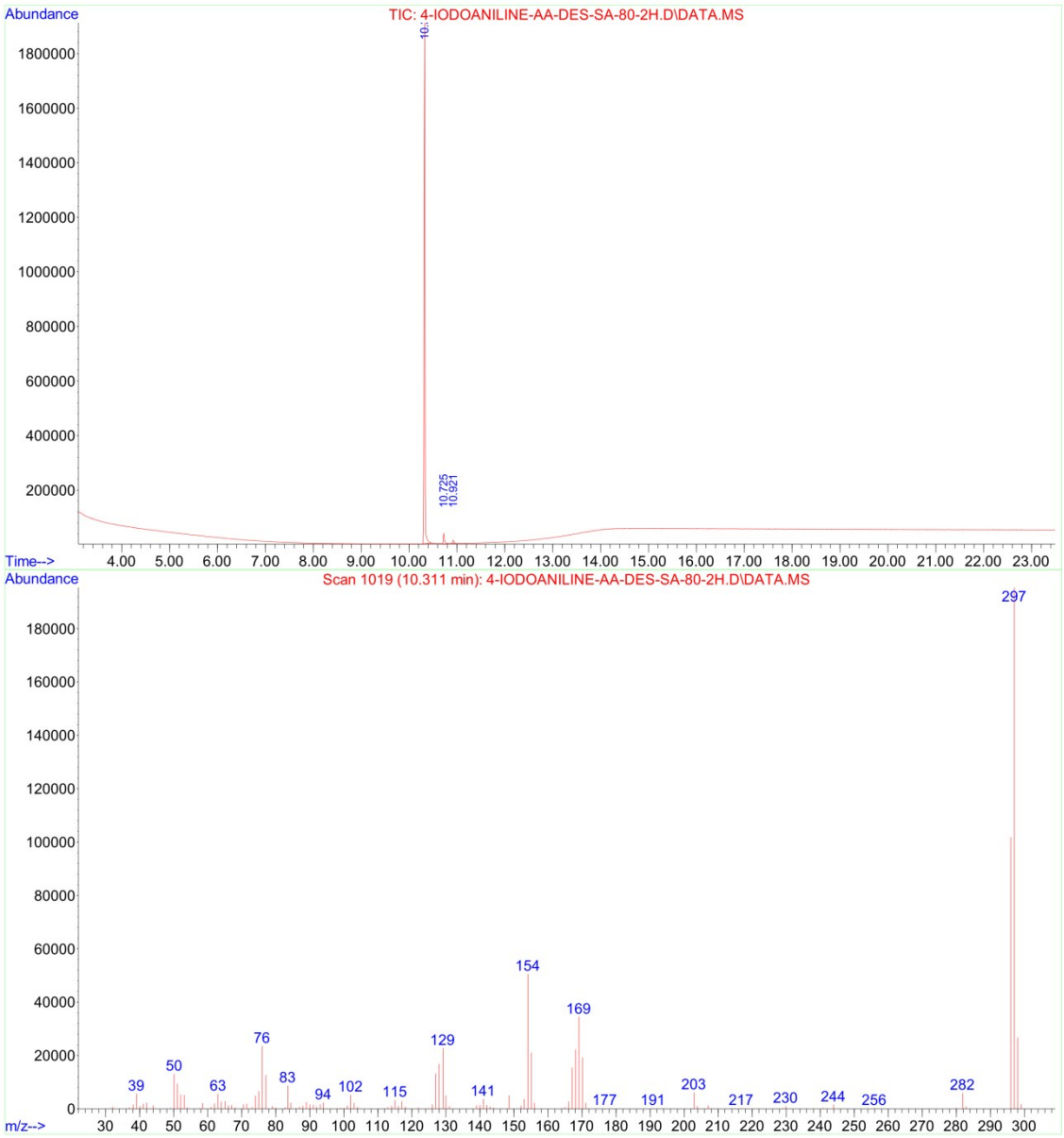
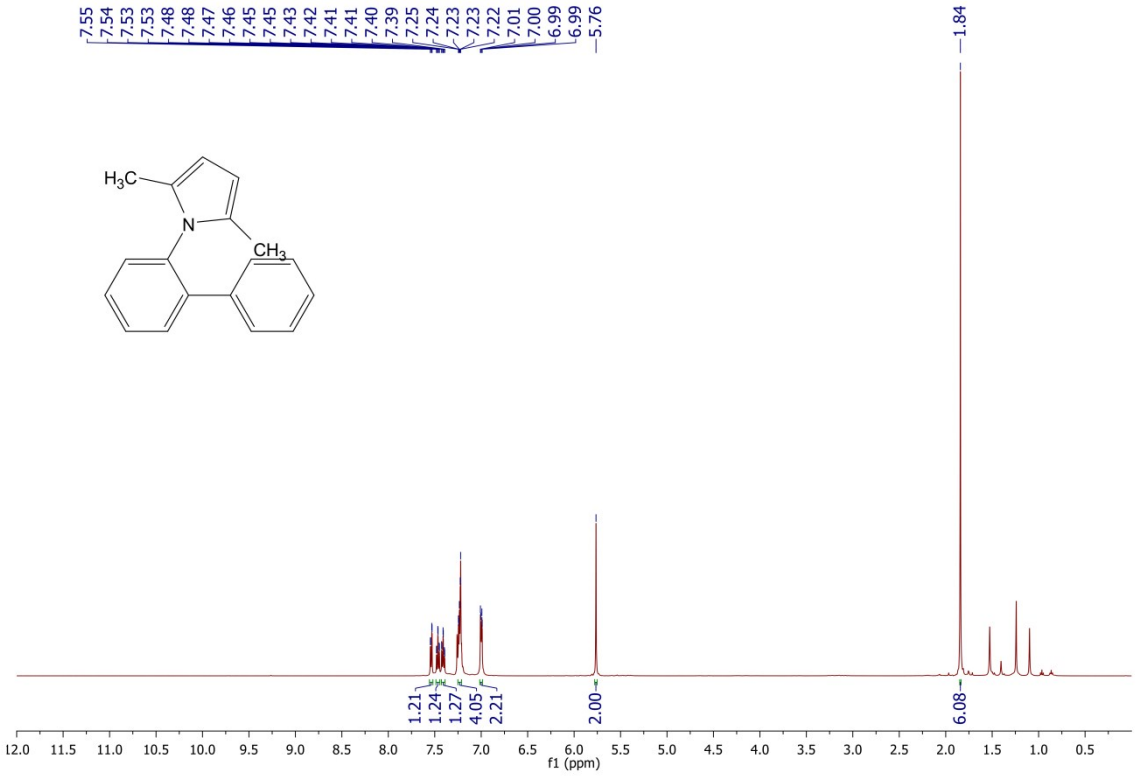
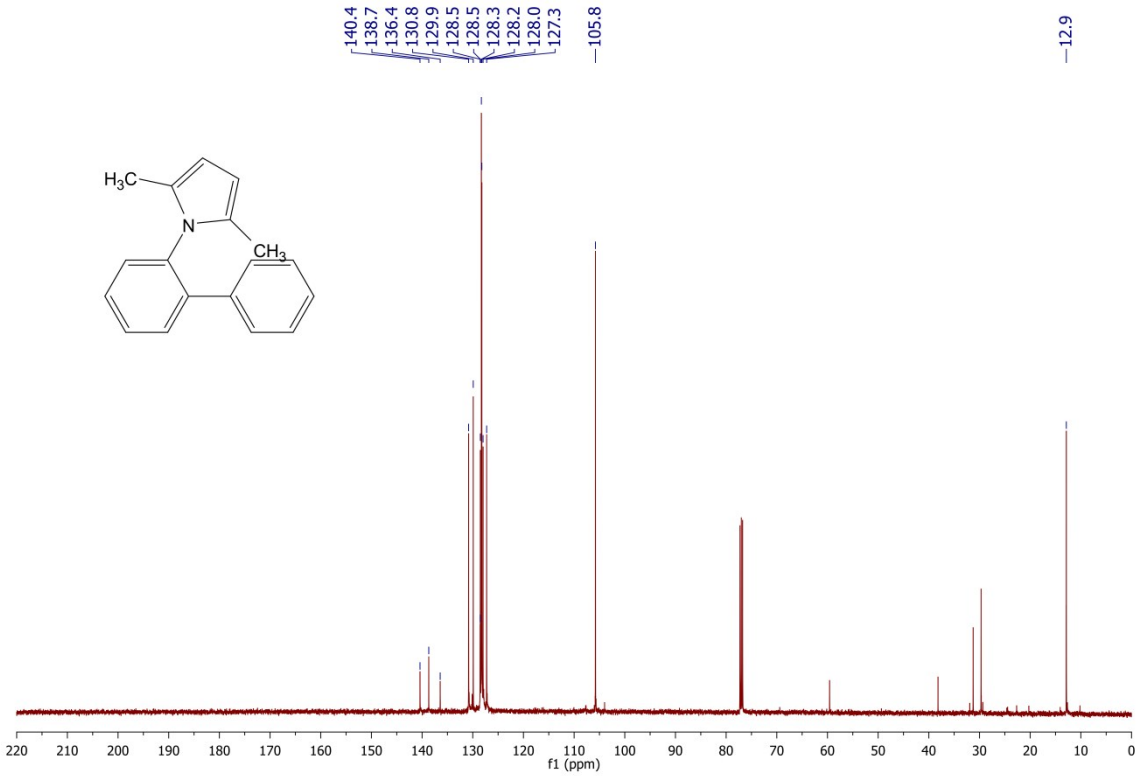
Instrument : GCMSD
Sample Name: 4-IODOANILINE-AA-DES-SA-80-2H
Misc Info :
Vial Number: 2



^{1}H NMR, ^{13}C NMR, and GC-MS of 1-([1,1'-Biphenyl]-2-yl)-2,5-dimethyl-1*H*-pyrrole





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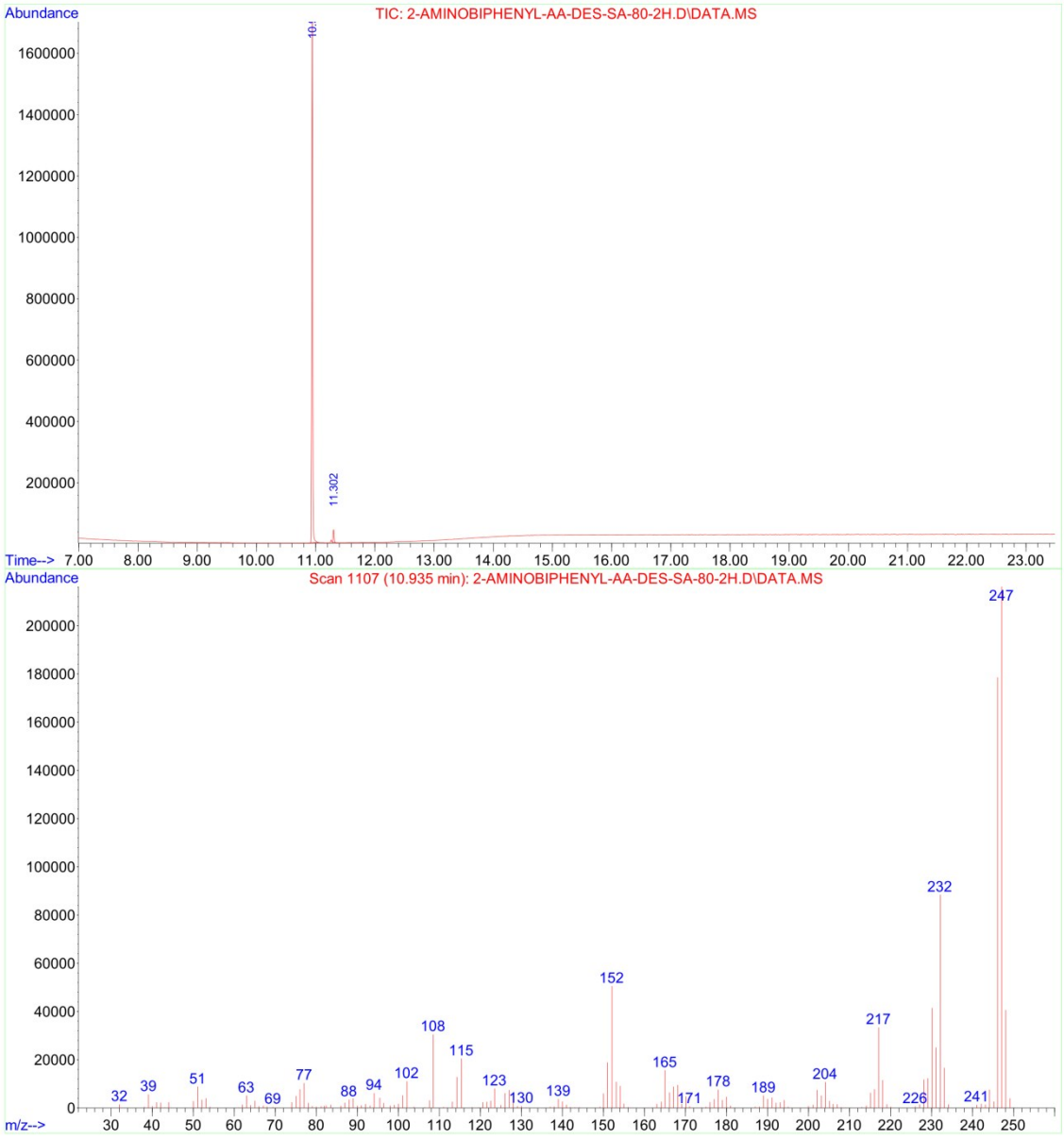
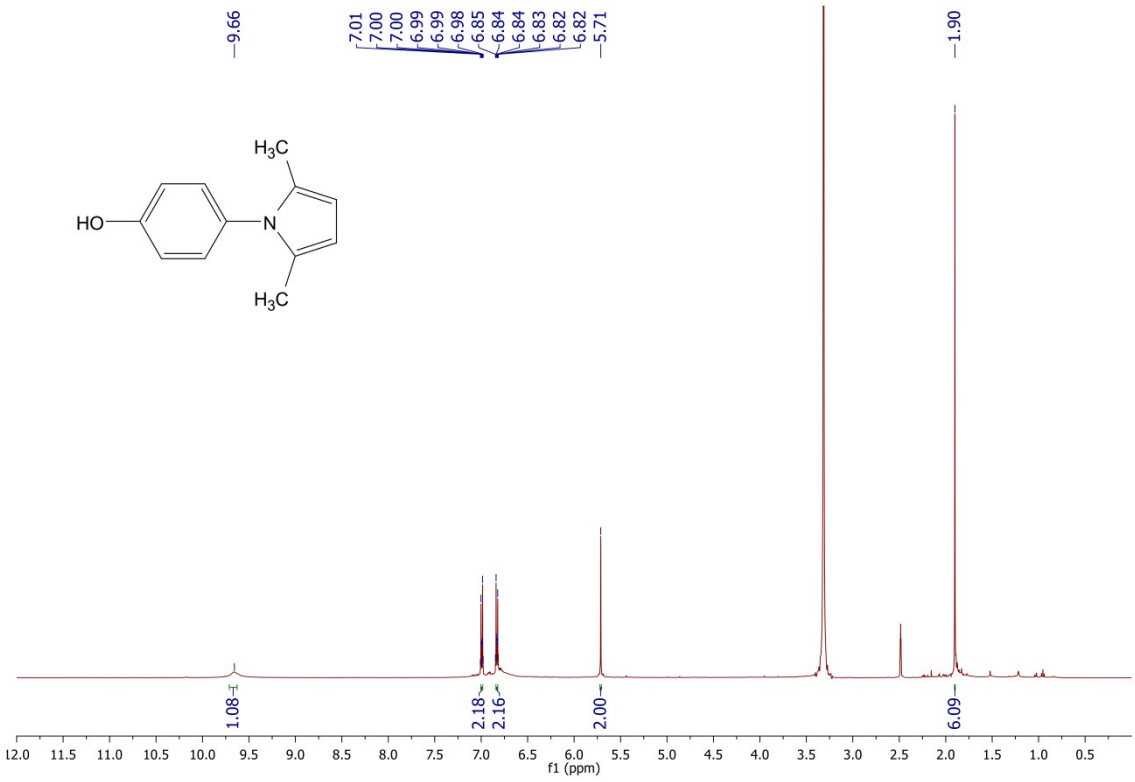
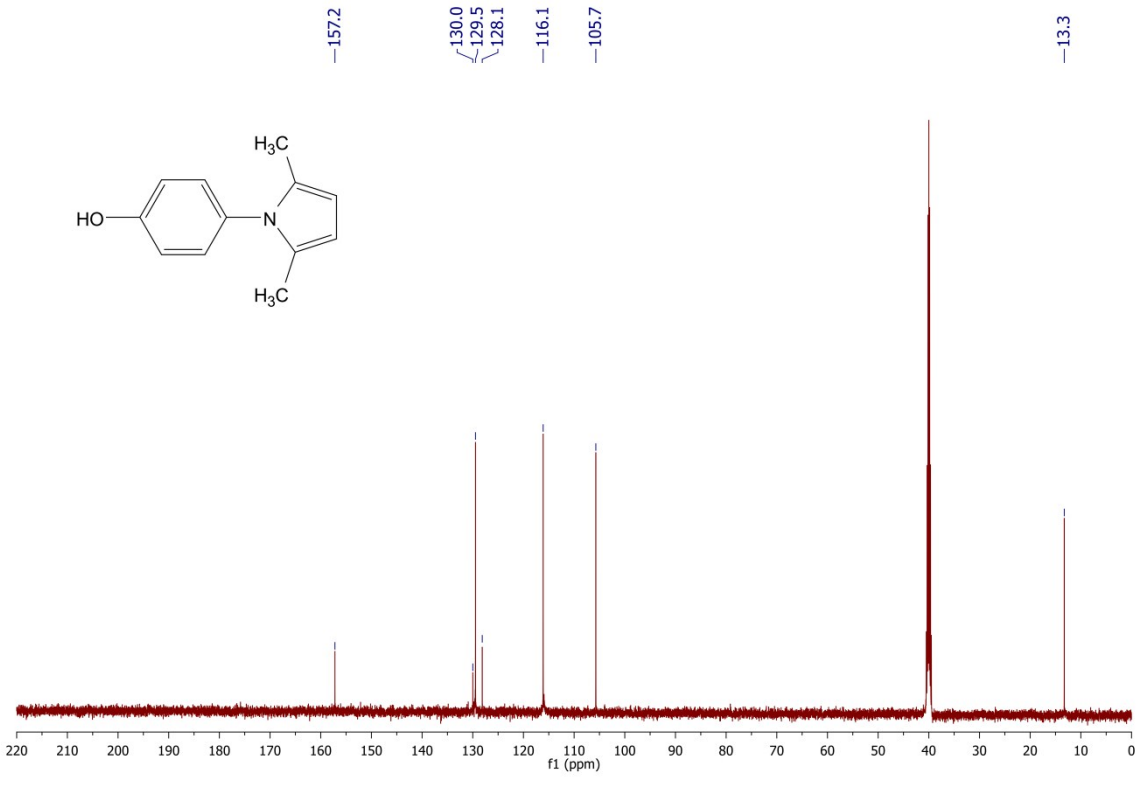
Acquired : 3 Nov 2016 14:21 using AcqMethod ACYLATION-SHORT-DELAY-3MIN.M
Instrument : GCMSD
Sample Name: 2-AMINOBIPHENYL-AA-DES-SA-80-2H
Misc Info :
Vial Number: 8



^{1}H NMR, ^{13}C NMR, and GC-MS of 1-(4-Hydroxyphenyl)-2,5-dimethyl-1*H*-pyrrole





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Instrument : GCMSD
Sample Name: 4-AMINOPHENOL-0-4
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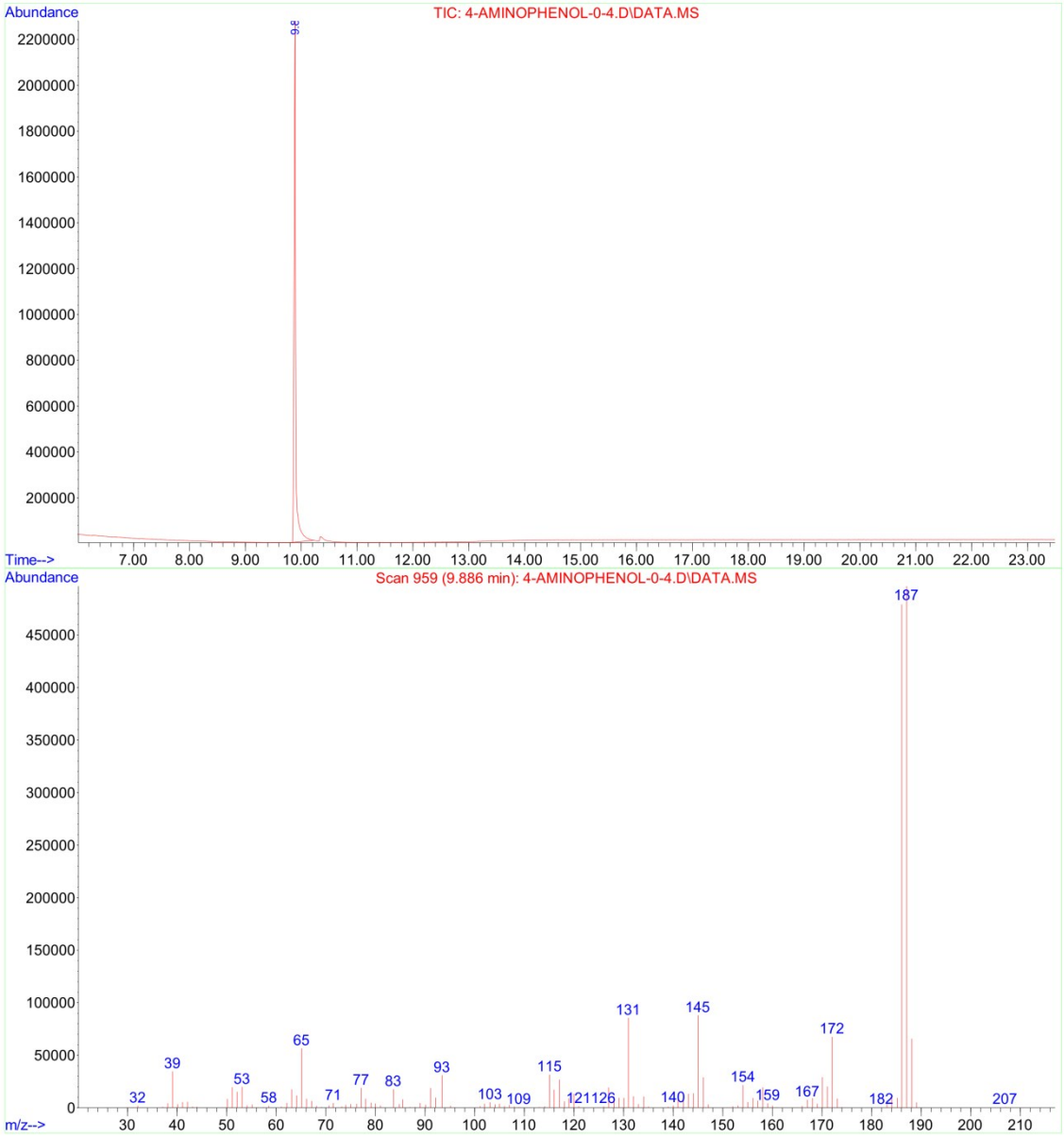
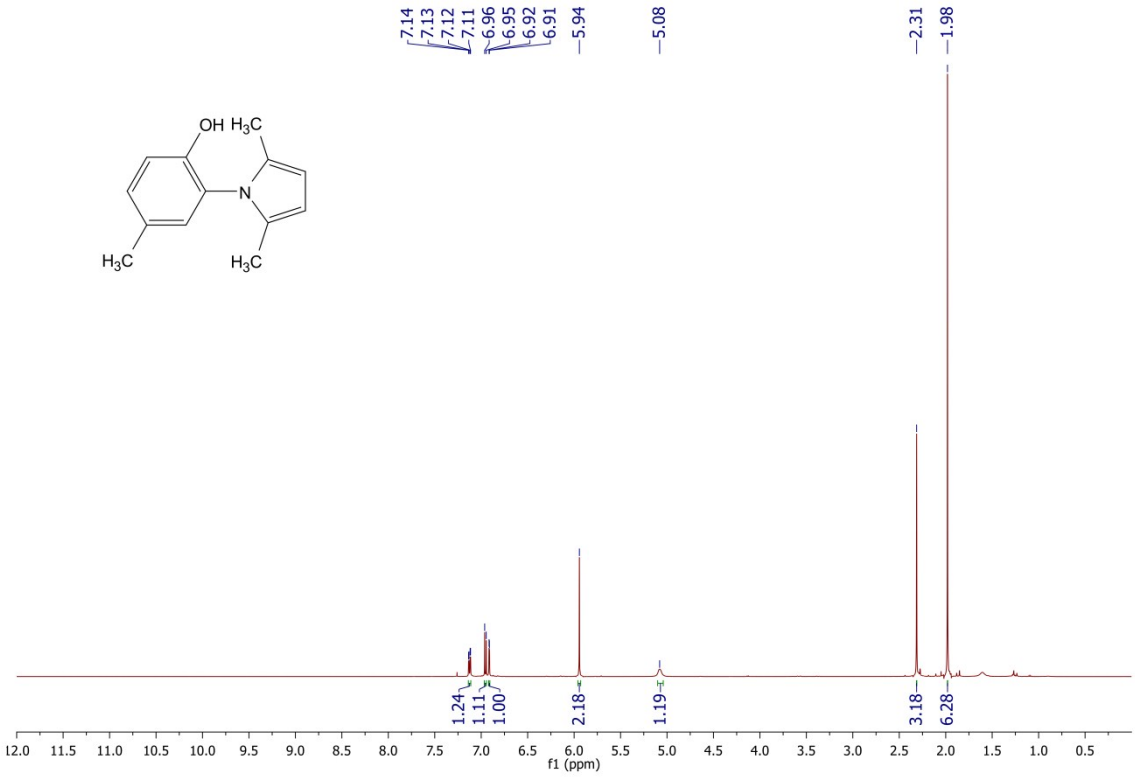
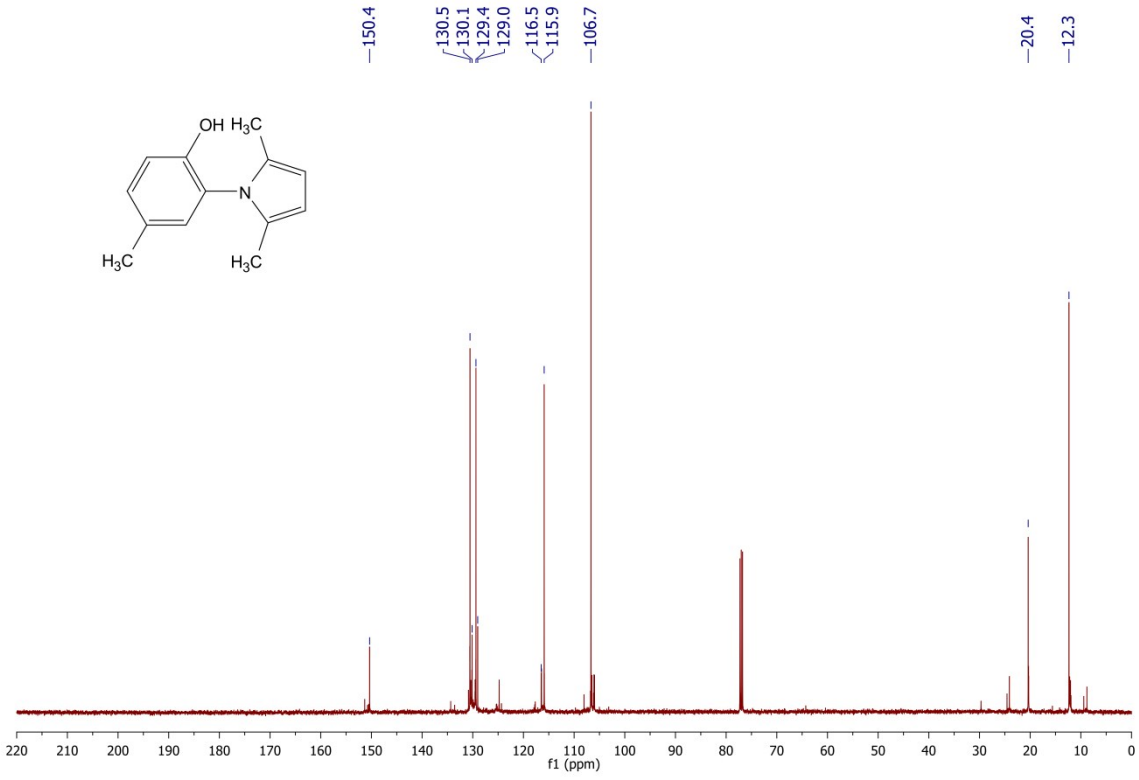


^{1}H NMR, ^{13}C NMR, and HRMS of 1-(2'-Hydroxy-5'-methylphenyl)-2,5-dimethyl-1*H*-pyrrole





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Analysis Info

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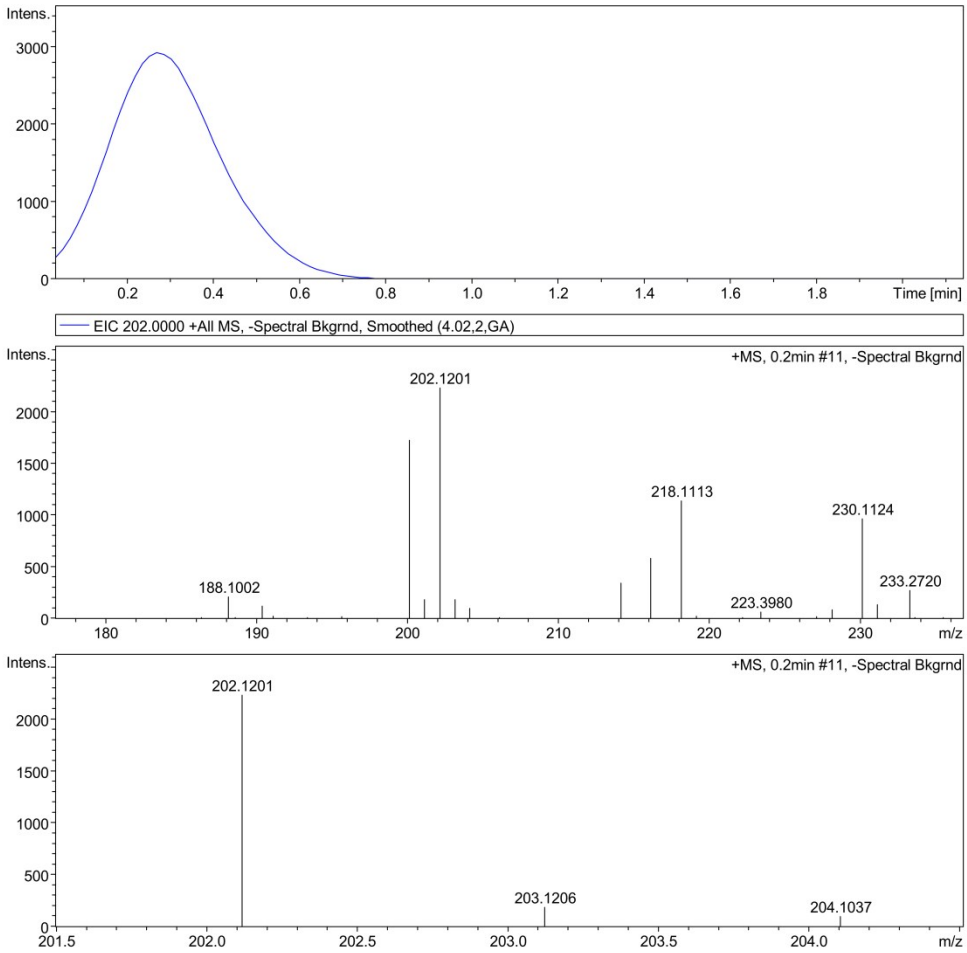
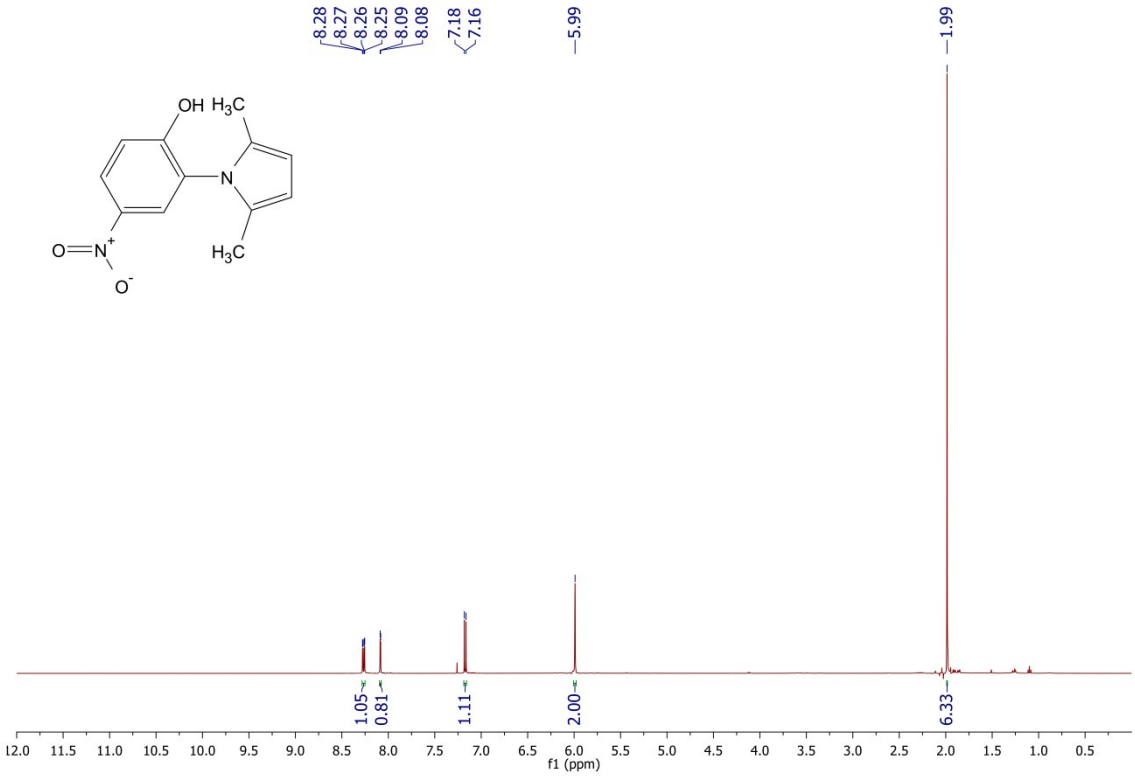
Method	dmm 2017.m	Operator	Anh Mai
Sample Name	2 ami	Instrument	micrOTOF-Q 10187
Comment			

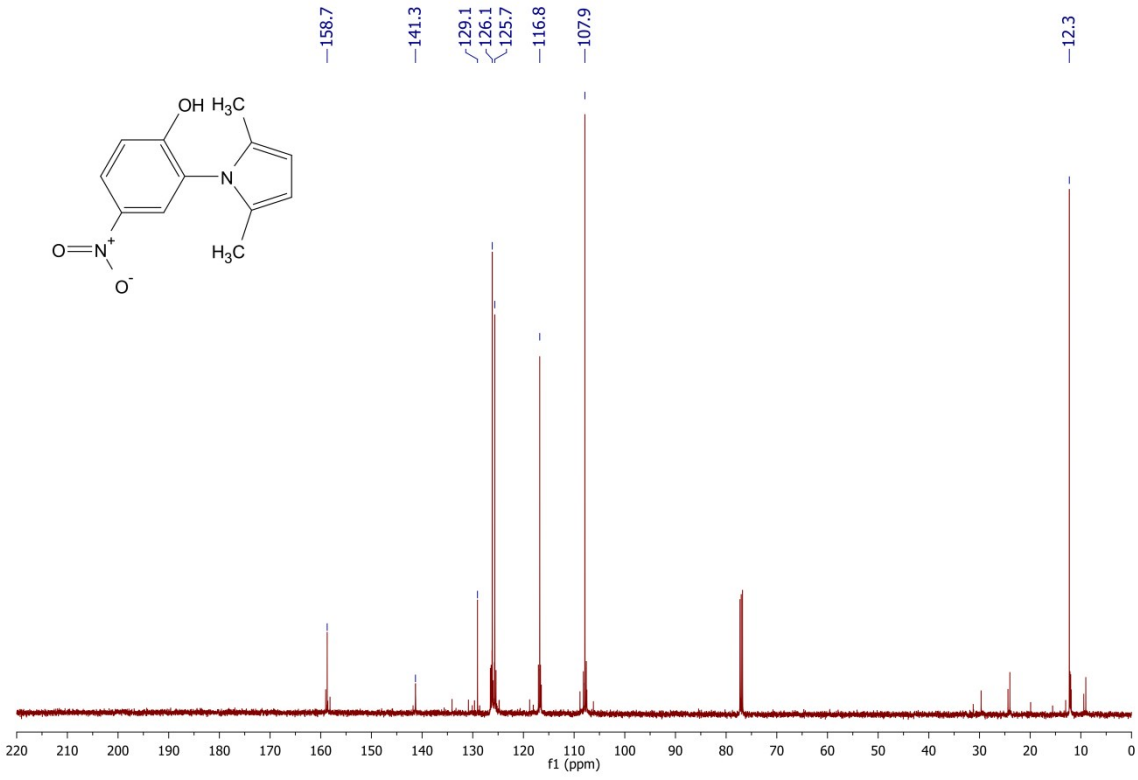
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	9.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



^{1}H NMR, ^{13}C NMR, and HR-MS of 1-(2'-Hydroxy-5'-nitrophenyl)-2,5-dimethyl-1*H*-pyrrole





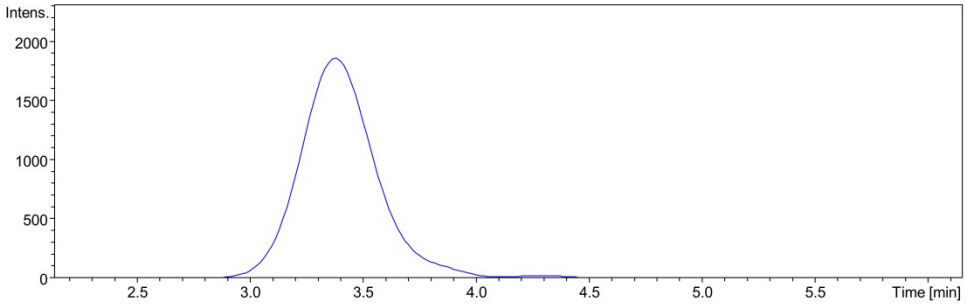
Display Report

Analysis Info

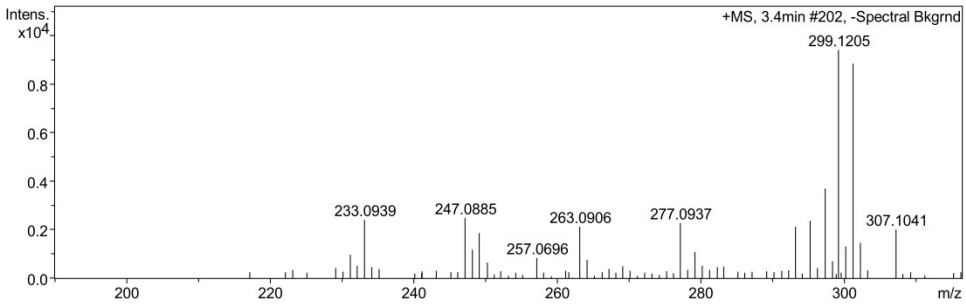
Analysis Name	D:\Data\2016\2 amino 4 ntro_1-b,3_01_2264.d	Acquisition Date	12/29/2016 6:23:13 PM
Method	dmm 2017.m	Operator	Anh Mai
Sample Name	2 amino 4 ntro	Instrument	micrOTOF-Q 10187
Comment			

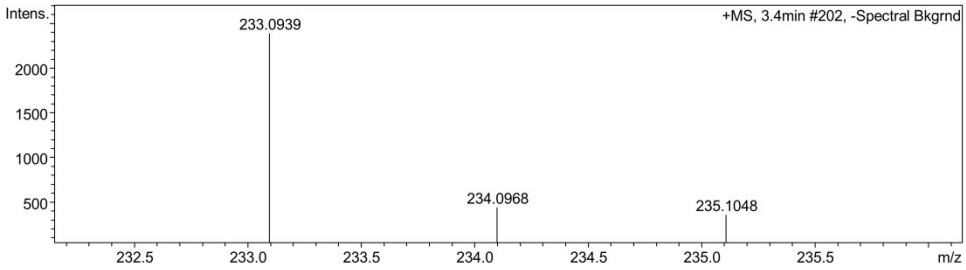
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	9.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	450.0 Vpp	Set Divert Valve	Source

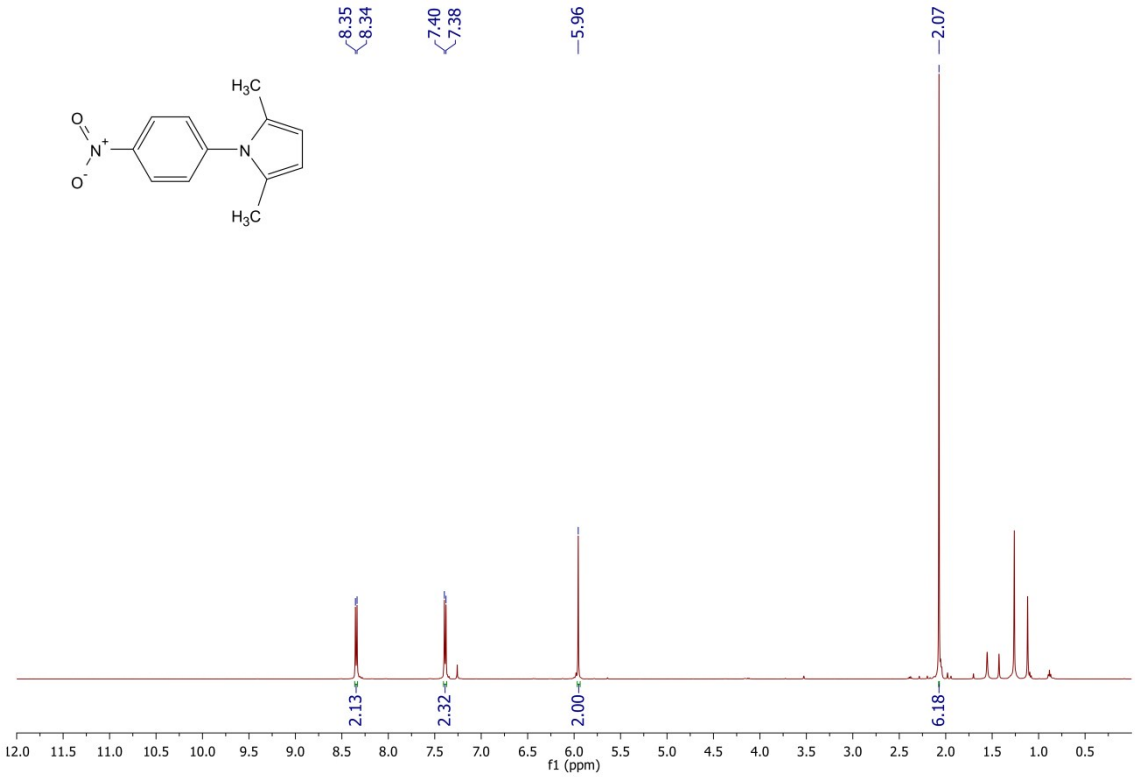


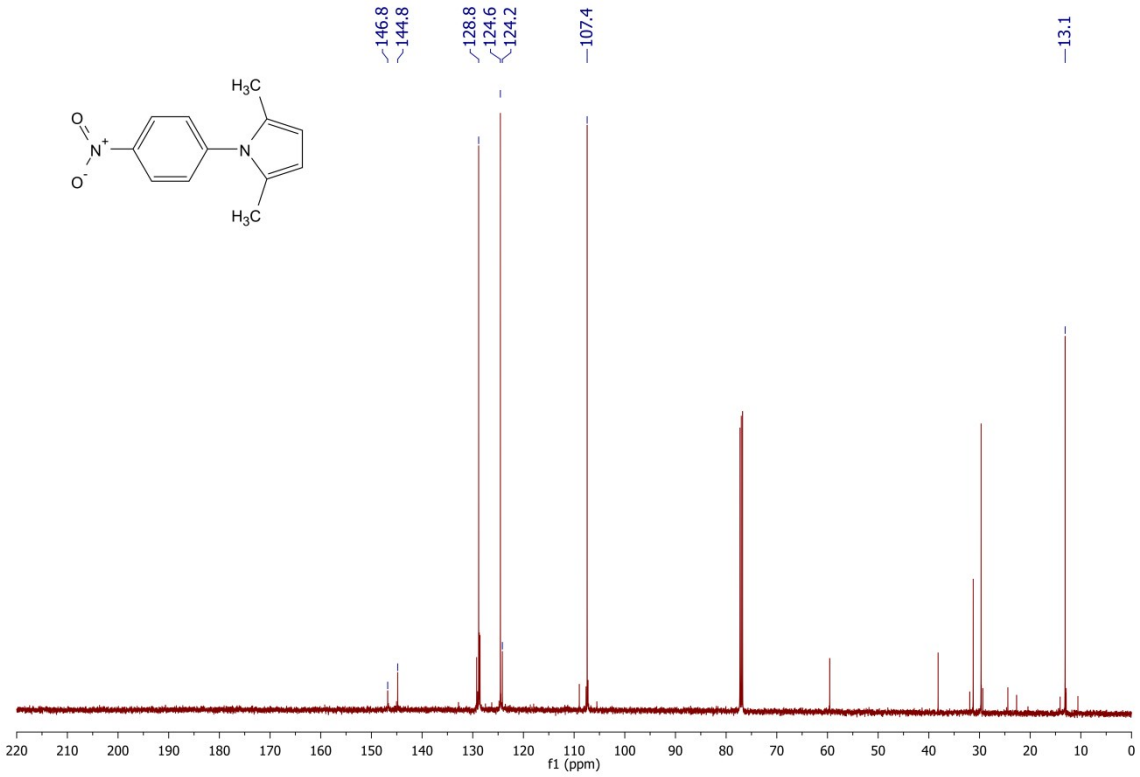
EIC 233.0000 +All MS, -Spectral Bkgrnd, Smoothed (4.01,2,GA)





^{1}H NMR, ^{13}C NMR, and GC-MS of 2,5-dimethyl-1-(4-nitrophenyl)-1*H*-pyrrole





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Operator : Thao Tran
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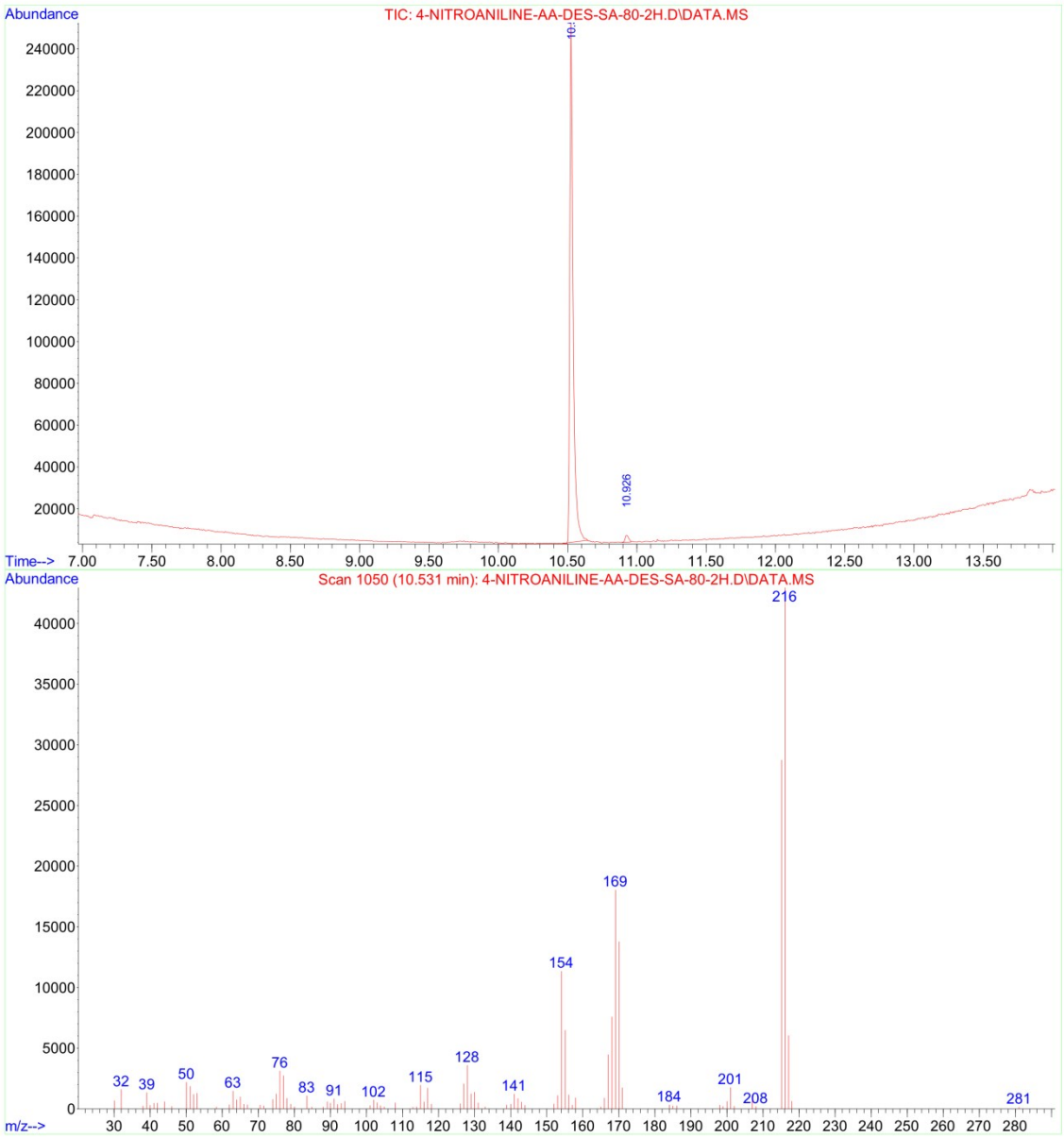
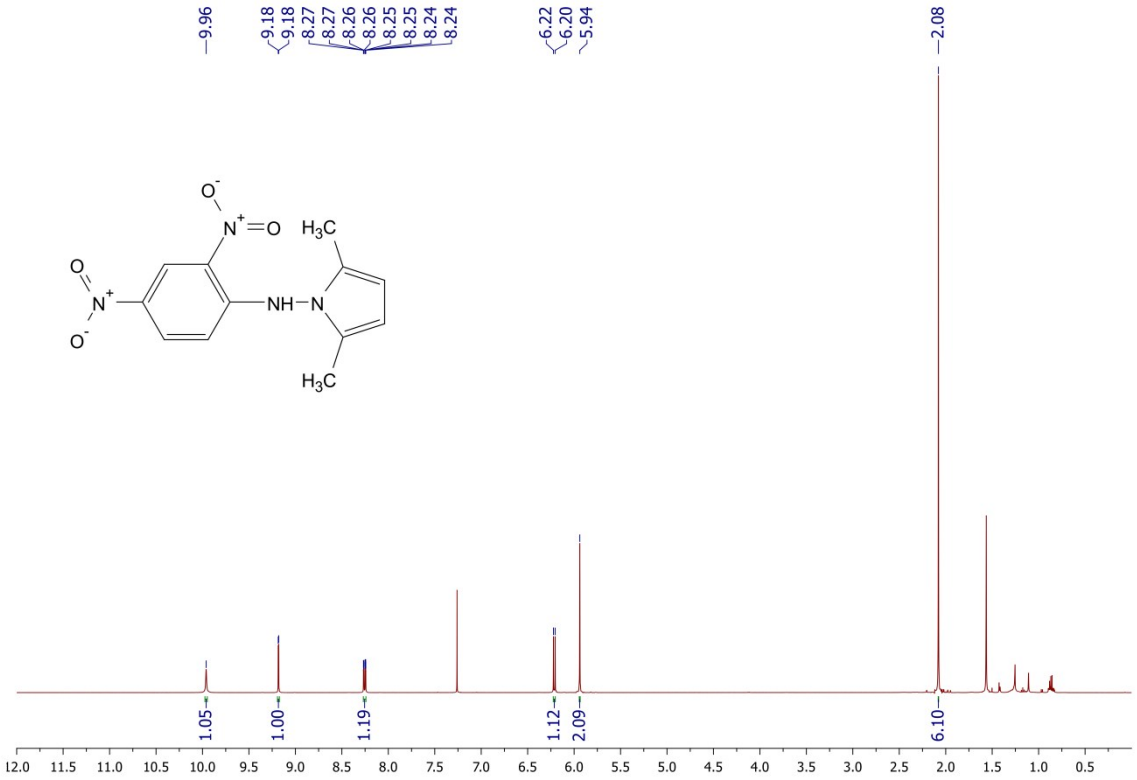
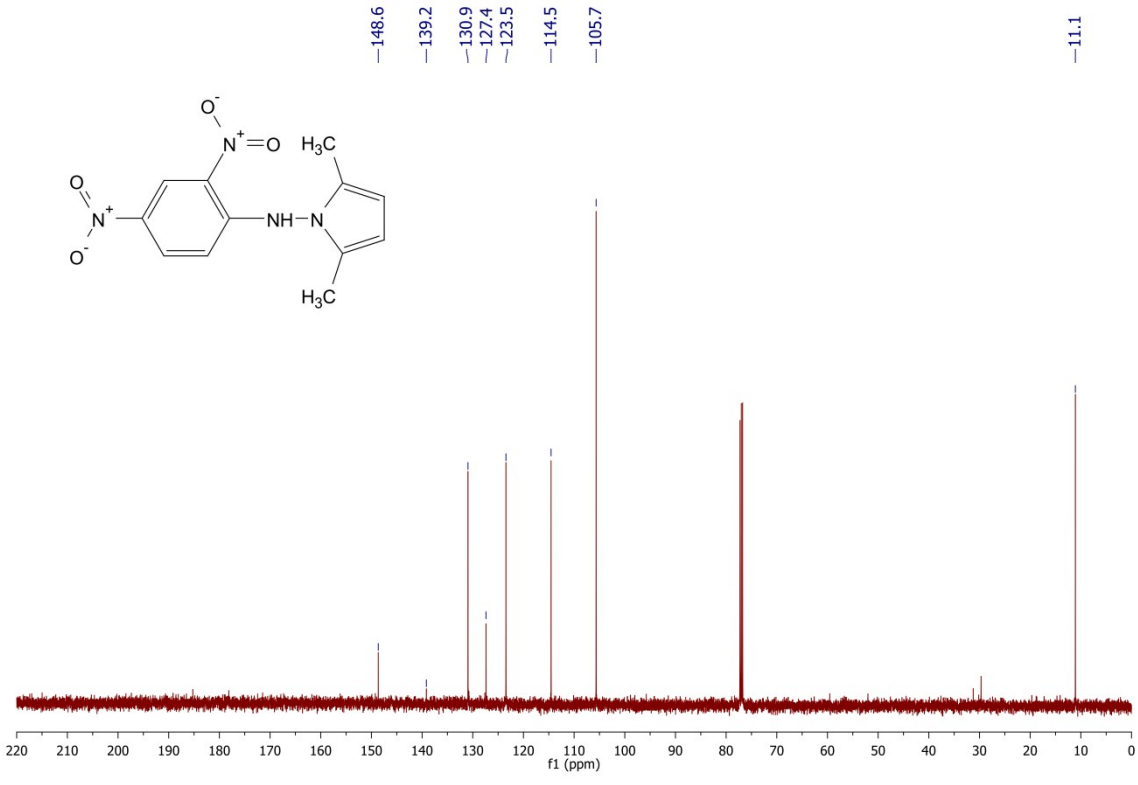
Instrument : GCMSD
Sample Name: 4-NITROANILINE-AA-DES-SA-80-2H
Misc Info :
Vial Number: 1

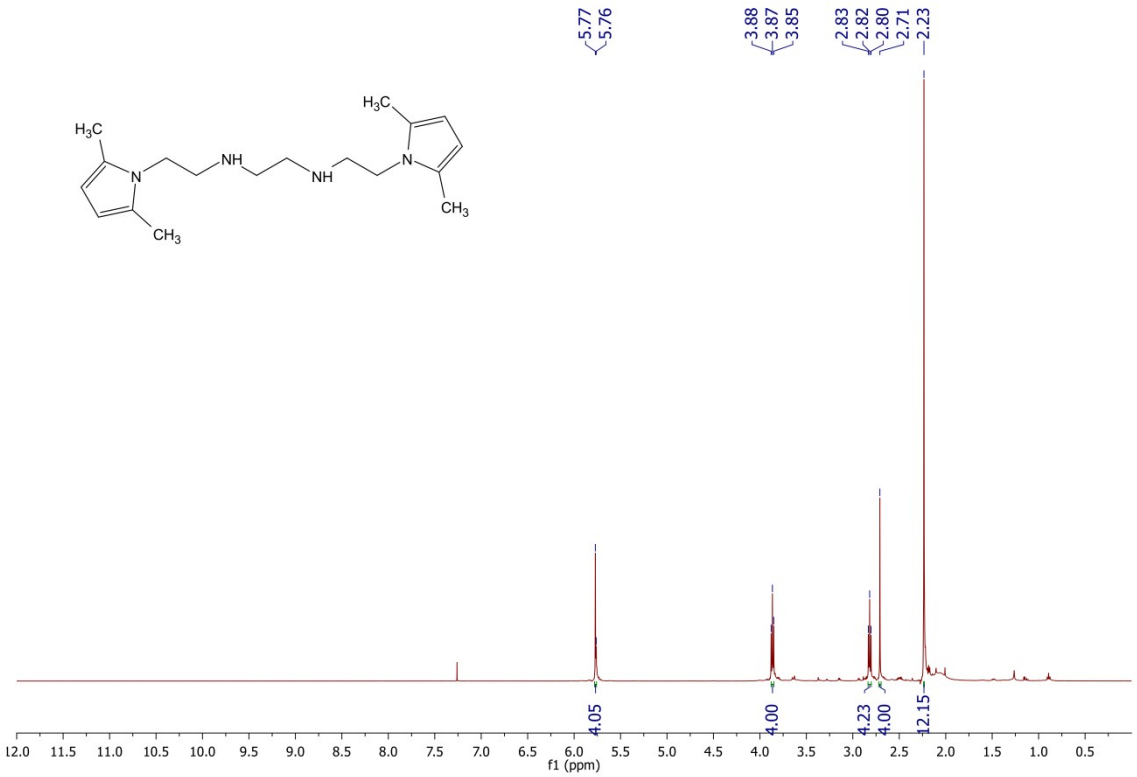


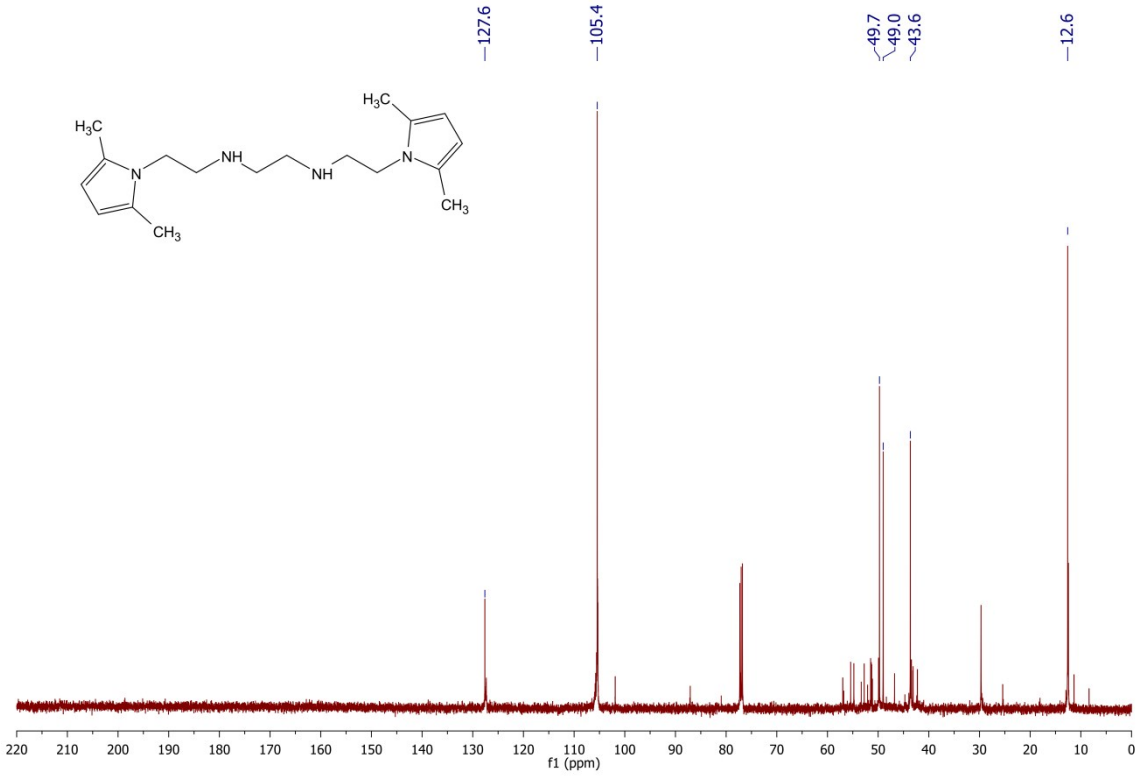
^{1}H NMR, ^{13}C NMR, and GC-MS of *N*-(2,4-dinitrophenyl)-2,5-dimethyl-1*H*-pyrrol-1-amine





^{1}H NMR, ^{13}C NMR, and HRMS of N_1,N_2-bis(2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)ethyl)ethane-1,2-diamine





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Analysis Info

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Sample Name	triet	Instrument	micrOTOF-Q 10187
Comment			

Acquisition Parameter

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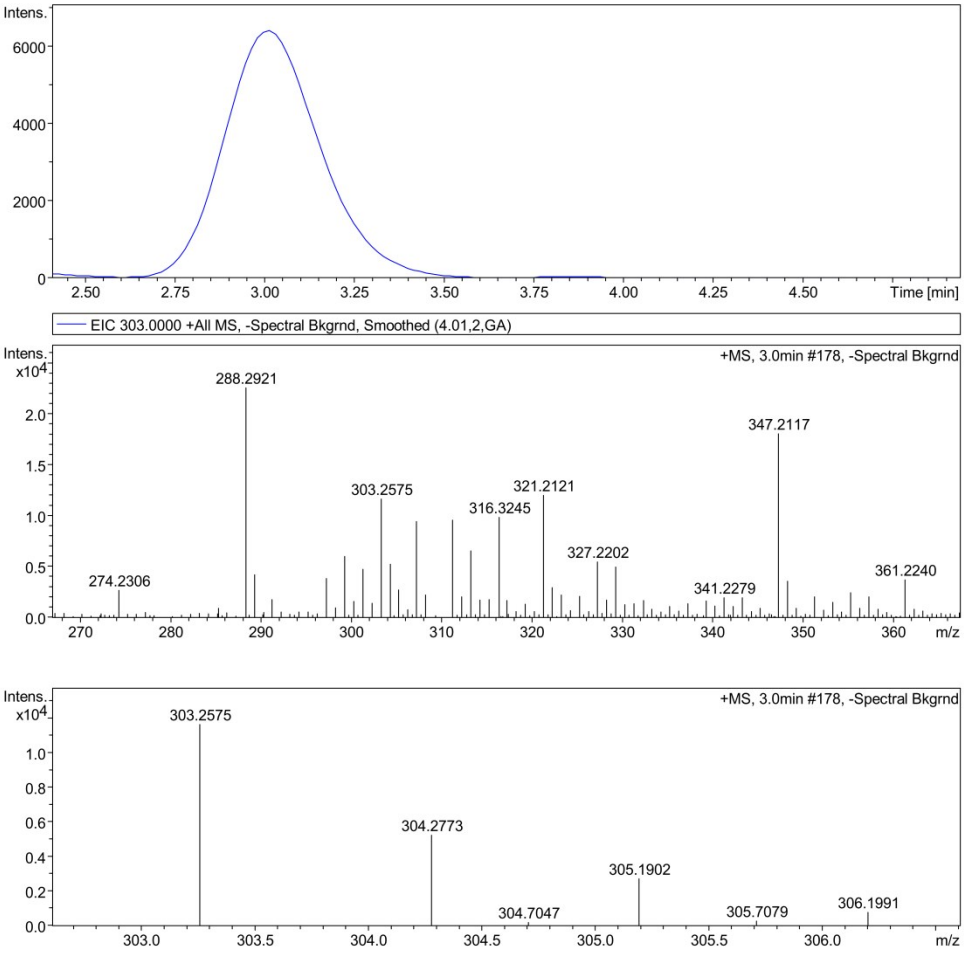
Scan End	1000 m/z	Set Collision Cell RF	450.0 Vpp	Set Divert Valve	Source



Section S6. References

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