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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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 obtained from 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 Fe₃O₄ nanoparticle (MNPs) 

MNP was synthesized by simple co-precipitation of ferric and ferrous ions in an alkaline condition. Typically, FeCl₃.6H₂O (20 mmol) and FeSO₄.7H₂O (10 mmol) were dissolved in 100 mL deionized water. The mixture was stirred at 80 °C 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 °C 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. 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 °C for 4 h. The resultant IL@MNP was washed with dichloromethane and dried at 70 °C in vacuo. To synthesize LAIL@MNP, a mixture of IL@MNP (1.0 g) and ZnCl₂ (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 °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), dimesdone (1.0 mmol, 0.140 g) was reacted under solvent-free sonication in the presence of LAIL@MNP (15 mg) at 80 °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 MgSO₄ and then concentrated under reduced pressure. The resultant crude product was recrystallized from ethanol to yield pure benzoxanthene whose structure was by ¹H and ¹³C 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 x 5 mL) and then reused for next cycles after drying under vacuum. Meanwhile, the organic solution was dried over MgSO₄ 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 ¹H and ¹³C NMR, GC-MS or HRMS (ESI).
Section S3. Optimization of the reaction condition

Table S1. Optimization of reaction conditions$^a$

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<tr>
<th>Entry</th>
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<th>Time (min)</th>
<th>Catalyst loading (mg)</th>
<th>Yield$^b$ (%)</th>
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*aReaction condition: 2-naphthol, dimedone, and benzaldehyde in the presence of LAIL@MNP.

*bIsolated yields.

**Table S2.** Effect of catalysts and solvents. 

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*aReaction condition: 2-naphthol (1.0 mmol), dimedone (1.0 mmol), benzaldehyde (1.0 mmol) and catalyst (15 mg). bSolvents (1.5 mL). cIsolated yield. d3-(3-(trimethoxysilyl)propyl)-1H-imidazol-3-ium chloride.

**Table S3.** Optimization of reaction conditions.*

![](image.png)

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<th>Entry</th>
<th>Time (min)</th>
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<td>Entry</td>
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*aReaction condition: Aniline (1.0 mmol), acetonylacetone (1.2 mmol) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-IL-ZnCl<sub>y</sub> (15 mg) under solvent-free sonication. bYield was reported by GC. cYield in parenthesis was isolated yield.

**Table S4.** Effect of various catalysts and solvents.
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*Reaction condition: Aniline (1.0 mmol), acetonylacetone (1.2 mmol) Fe₃O₄@SiO₂-IL-ZnₓClᵧ (15 mg), and solvent (2.0 mL) under sonication for 30 min. *Yield was reported by GC.
Section S4. Spectral data

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

Yellow powder, M.p. = 170–171 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-11H-benzo[a]xanthen-11-one

Yellow oil

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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).
**13C NMR** (125 MHz, CDCl₃) 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-11H-benzo[a]xanthen-11-one**

White powder, M.p. = 154–155 °C.

**1H NMR** (500 MHz, DMSO-d₆) 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).

**13C NMR** (125 MHz, DMSO-d₆) 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-11H-benzo[a]xanthen-11-one**

White powder, M.p. = 209 – 210 °C

**1H NMR** (500 MHz, CDCl₃) 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).

**13C NMR** (125 MHz, CDCl₃) 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-11H-benzo[a]xanthen-11-one**

White powder, M.p. = 181–182 °C

**1H NMR** (500 MHz, CDCl₃) δ 8.02–8.01 (d, J = 8.5 Hz, 1H), 7.78–7.74 (t, J = 11.0 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).

**13C NMR** (125 MHz, CDCl₃) 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-11H-benzo[a]xanthen-11-one**
White powder, M.p. = 200 – 201 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-11H-benzo[a]xanthen-11-one$^{24}$

![Diagram](image.png)

White powder, M.p. = 225 – 226 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-11H-benzo[a]xanthen-11-one$^{25}$
White powder, M.p. = 234 – 235 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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, $J$ = 8.0 Hz, 1H), 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$_3$) $\delta$ 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-11H-benzo[a]xanthen-11-one

White powder, M.p. = 178 – 179 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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).
\(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)Na\(^+\) 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

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)/DMSO) \(\delta\) 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).

\(^{13}\text{C NMR}\) (125 MHz, CDCl\(_3\)/DMSO) \(\delta\) 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

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 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, \(J = 8.5\) Hz,
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).

\[^{13}C\text{ NMR}\ (125\text{ MHz, CDCl}_3)\ \delta 196.9, 163.9, 161.2 (d, J = 243.0 Hz, 1C), 147.8, 140.6, 131.5, 131.3, 129.9 (d, J = 8.0 Hz, 1C), 129.8, 129.0, 128.5, 127.1, 125.0, 123.5, 117.4, 117.0, 115.0 (d, J = 21.1 Hz, 1C), 114.13, 50.9, 41.4, 34.0, 32.3, 29.3, 27.1.\]

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11\(^H\)-benzo[a]xanthene-11-one\(^{28}\)

White powder, M.p. = 181–182 \(^oC\)

\[^1H\text{ NMR}\ (500\text{ MHz, CDCl}_3)\ \delta 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).

\[^{13}C\text{ NMR}\ (125\text{ MHz, CDCl}_3)\ \delta 196.8, 164.0, 147.8, 143.3, 131.9, 131.5, 131.2, 129.8, 128.5, 127.1, 125.0, 123.5, 117.1, 117.0, 113.9, 50.9, 41.4, 34.2, 32.2, 29.3, 27.1.\]

12-(4-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11\(^H\)-benzo[a]xanthene-11-one\(^{27}\)
White powder, M.p. = 186–187 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-11H-benzo[a]xanthen-11-one$^{20}$

White powder, M.p. = 173–174 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-11H-benzo[a]xanthen-11-one

White powder, M.p. = 177–178 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-11H-benzo[a]xanthen-11-one

White powder, M.p. = 155-156 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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).
\( ^{13}\text{C} \text{ NMR} \) (125 MHz, \( \text{CDCl}_3 \)) \( \delta = 196.8, 164.2, 162.9 \) (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 \(^{\circ}\)C

\( ^{1}\text{H} \text{ NMR} \) (500 MHz, \( \text{CDCl}_3 \)) \( \delta = 8.24–8.23 \) (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).

\( ^{13}\text{C} \text{ NMR} \) (125 MHz, \( \text{CDCl}_3 \)) \( \delta = 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 \(^{\circ}\)C

\( ^{1}\text{H} \text{ NMR} \) (500 MHz, \( \text{CDCl}_3 \)) \( \delta = 8.32–8.31 \) (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,
$J = 8.5 \text{ Hz, 1H}$), 7.26–7.23 (t, $J = 10 \text{ Hz, 1H}$), 7.10–7.07 (t, $J = 7.5 \text{ Hz, 1H}$), 6.92–6.89 (t, $J = 7.5 \text{ Hz, 1H}$), 5.97 (s, 1H), 2.61 (s, 2H), 2.33–2.22 (q, $J = 16 \text{ Hz, 2H}$), 1.14 (s, 3H), 1.00 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 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**

![Image](image_url)

White powder, M.p. = 155-156 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12–8.10 (d, $J = 8.5 \text{ Hz, 1H}$), 7.78–7.73 (q, $J = 8.0 \text{ Hz, 2H}$), 7.50–7.47 (t, $J = 8.0 \text{ Hz, 15.0 Hz, 1H}$), 7.40–7.37 (t, $J = 7.5 \text{ Hz, 14.5 Hz, 1H}$), 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, $J = 16.5 \text{ Hz, 2H}$), 1.14 (s, 3H), 1.01 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 196.6, 164.4, 160.0 (d, $J = 245.6 \text{ Hz, 1C}$), 152.9, 147.7, 131.5, 131.4, 130.9 (d, $J = 4.1 \text{ Hz, 1C}$), 129.0 (t, $J = 18.4 \text{ Hz, 44.6 Hz, 1C}$), 128.4, 128.2 (t, $J = 5.0 \text{ Hz, 13.5 Hz, 1C}$), 127.9, 127.5, 127.2, 125.3, 124.9, 124.1 (d, $J = 3.3 \text{ Hz, 1C}$), 123.5, 123.2 (d, $J = 3.4 \text{ Hz, 1C}$), 121.5, 118.9, 117.1, 116.6, 115.6 (d, $J = 22.6 \text{ Hz, 1C}$), 112.8, 50.8, 50.3, 41.4, 33.3, 29.4, 29.2 (d, $J = 2.0 \text{ Hz, 1C}$), 29.0, 28.0, 27.1.

**9,9-Dimethyl-12-(2-nitrophenyl)-8,9,10,12-tetrahydro-11$H$-benzo[a]xanthen-11-one**
2,5-Dimethyl-1-phenyl-1H-pyrrole$^{14, 16, 18, 34-36}$

Yellow powder, M.p. 52-54 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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)-1H-pyrrole$^{12, 16, 34, 36}$

Yellow powder, M.p. 52-54 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 139.1, 129.0, 128.8, 128.3, 127.6, 105.6, 13.0.
Yellow oil

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrole

Yellow powder, M.p. = 128-130 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$O$_2$ $^+$ 230.1049, found 230.1011.

1-(3,5-Dichlorophenyl)-2,5-dimethyl-1H-pyrrole

Orange powder, M.p. 79-81 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrole

S21
Black powder, M.p. 136-137 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrole$^{14,16,34,36}$

Yellow powder, M.p. 101-103 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrole

Yellow oil

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrole$^{39,40}$

![1-(4-Iodophenyl)-2,5-dimethyl-1H-pyrrole](image)

Yellow powder, M.p. 63-65 °C

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrole$^{41}$

![1-([1,1'-Biphenyl]-2-yl)-2,5-dimethyl-1H-pyrrole](image)

Yellow powder, M.p. 98-99 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrole$^{11,12,17,40}$
Yellow powder, M.p. 105-107 °C

$^1$H-NMR (500 MHz, DMSO-$d_6$) $\delta$ 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-$d_6$) $\delta$ 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-1H-pyrrole**

Black oil

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 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$_3$) $\delta$ 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-1H-pyrrole**

Orange powder, M.p. 167-170 °C

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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).
$^{13}\text{C NMR}$ (125 MHz, CDCl$_3$) $\delta$ 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$_2$O$_3^+$ 233.0920, found 233.0939.

2,5-Dimethyl-1-(4-nitrophenyl)-1H-pyrrole$^{11, 12, 14, 16, 36}$

![2,5-Dimethyl-1-(4-nitrophenyl)-1H-pyrrole](image)

Yellow powder, M.p. 144-146 °C

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrol-1-amine$^{42-45}$

![N-(2,4-Dinitrophenyl)-2,5-dimethyl-1H-pyrrol-1-amine](image)

Yellow powder, M.p. 182-184 °C

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-1H-pyrrol-1-yl)ethyl)ethane-1,2-diamine

![N^1,N^2-bis(2-(2,5-Dimethyl-1H-pyrrol-1-yl)ethyl)ethane-1,2-diamine](image)

Yellow oil
$^{1} \text{H NMR}$ (500 MHz, CDCl$_{3}$) $\delta$ 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).

$^{13} \text{C NMR}$ (125 MHz, CDCl$_{3}$) $\delta$ 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

![NMR Spectra]
$^1$H and $^{13}$C NMR of 9,9-Dimethyl-12-($p$-tolyl)-8,9,10,12-tetrahydro-11H-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-11H-benzo[a]xanthen-11-one
\(^1H\) 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[\textit{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[α]xanthen-11-one
$^1$H NMR, $^{13}$C NMR, and GC-MS of 2,5-Dimethyl-1-phenyl-$1H$-pyrrole
$^1$H NMR, $^{13}$C NMR, and GC-MS of 2,5-Dimethyl-1-(o-tolyl)-1$H$-pyrrole
$^{1}H$ NMR, $^{13}C$ NMR, and GC-MS of 1-(2'-Amino-4'-nitrophenyl)-2,5-dimethyl-$1H$-pyrrole

![Chemical Structure](image)

[Graph of NMR Spectra]

S52
**Display Report**

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- **Method**: dmm 2017.m
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- **Comment**: 
- **Acquisition Date**: 12/29/2016 6:12:14 PM
- **Operator**: Anh Mai
- **Instrument**: micrOTOF-Q 10187

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**Graph 2**

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**Bruker Compass DataAnalysis 4.0** printed: 12/30/2016 3:20:00 PM Page 1 of 2
$^1$H NMR, $^{13}$C NMR, and GC-MS of 1-(3,5-Dichlorophenyl)-2,5-dimethyl-$^1$H-pyrrole
$^1$H NMR, $^{13}$C NMR, and GC-MS of 1-(2,5-Dichlorophenyl)-2,5-dimethyl-$^1$H-pyrrole
$^{1}H$ NMR, $^{13}C$ NMR, and GC-MS of 1-(3,4-Dichlorophenyl)-2,5-dimethyl-$^{1}H$-pyrrole
$^1$H NMR, $^{13}$C NMR, and GC-MS of 1-(2,5-Dibromophenyl)-2,5-dimethyl-$1H$-pyrrole
$^1$H NMR, $^{13}$C NMR, and GC-MS of 1-(4-Iodophenyl)-2,5-dimethyl-$1H$-pyrrole
$^1\text{H} \text{ NMR}, \ 1^3\text{C} \text{ NMR, and GC-MS of } 1-([1,1'-\text{Biphenyl}]-2-yl)-2,5\text{-dimethyl}-1H\text{-pyrrole}$
$^1$H NMR, $^{13}$C NMR, and GC-MS of 1-(4-Hydroxyphenyl)-2,5-dimethyl-1$H$-pyrrole
Sample Name: 4-AMINOPHENOL-0-4
Vial Number: 2
$^1$H NMR, $^{13}$C NMR, and HRMS of 1-(2'-Hydroxy-5'-methylphenyl)-2,5-dimethyl-1$H$-pyrrole
Display Report

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Comment:

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Graphs:
- Intens. vs. Time (min)
- Intens. vs. m/z

Bruker Compass DataAnalysis 4.0
printed: 12/30/2016 4:04:31 PM
Page 1 of 2
$^1$H NMR, $^{13}$C NMR, and HR-MS of 1-(2'-Hydroxy-5'-nitrophenyl)-2,5-dimethyl-1H-pyrrole
### Display Report

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<td>Positive</td>
</tr>
<tr>
<td>Positive</td>
<td>4000 V</td>
</tr>
<tr>
<td>Set Capillary</td>
<td>0 m/z</td>
</tr>
<tr>
<td>Set End Plate Offset</td>
<td>-500 V</td>
</tr>
<tr>
<td>Set Divert Valve</td>
<td>Source</td>
</tr>
<tr>
<td>Set Dry Heater</td>
<td>200 °C</td>
</tr>
<tr>
<td>Set Dry Gas</td>
<td>9.0 l/min</td>
</tr>
</tbody>
</table>

**Graphs**

1. **EIC 233.0000** +MS, -Spectral Bkgd, Smoothed (4,01,2,GA)
2. **+MS, 3.4min #002, -Spectral Bkgd**
3. **+MS, 3.4min #002, -Spectral Bkgd**

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$^1$H NMR, $^{13}$C NMR, and GC-MS of 2,5-dimethyl-1-(4-nitrophenyl)-1$H$-pyrrole
$^1$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-1H-pyrrol-1-yl)ethyl)ethane-1,2-diamine
Section S6. References


