RhIII-catalyzed dual directing group assisted sterically hindered C-H bond activation: a unique route to meta and ortho substituted benzofurans

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Supporting Information

Table of Contents

Experimental Section S-2
Deuterium Labeling Studies of Compounds 1a, 1b and 1o S-3
Optimization Studies S-6
Synthesis and Characterization Data of Oximes S-7
Characterization Data of Benzofuran Derivatives S-13
NOE and NOESY Experiments of 3ag S-22
References S-24
1H and 13C NMR Spectra S-25
X-Ray Data of 3aa, 3ga, and 3ma S-65
General Methods.

General Procedure for the Rh(III)—Catalyzed Synthesis of Benzofurans

A seal tube initially fitted with a rubber septum containing a magnetic stir bar, oxime 1 (0.20 mmol), alkyne 2 (0.30 mmol), [RhCp*Cl₂]₂ (0.0040 mmol, 2.0 mol %) and Cu(OAc)₂·H₂O (0.70 mmol) was evacuated and purged with nitrogen gas three times. Then, MeOH (1.0 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at the indicated temperature for 12 to 48 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography (silica gel, hexane/EtOAc) to give the corresponding product 3.
Deuterium Labeling Study of 1a

A seal tube initially fitted with a rubber septum containing a magnetic stir bar, oxime 1a (0.1 mmol), [RhCp*Cl₂]₂ (0.0020 mmol, 2.0 mol %), and Cu(OAc)₂·H₂O (0.35 mmol) was evacuated and purged with nitrogen gas three times. Then, CD₃OD (0.5 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at 60 °C for 1, 5, and 24 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was evaporated in vacuum and the H/D exchange ratio was determined by ¹H NMR integration.

¹H NMR Spectra for Deuterium Labeling Study of Compound 1a
Deuterium Labeling Study of 1b

A seal tube initially fitted with a rubber septum containing a magnetic stir bar, oxime 1b (0.10 mmol), [RhCp*Cl₂]₂ (0.002 mmol, 2.0 mol %), and Cu(OAc)₂·H₂O (0.350 mmol) was evacuated and purged with nitrogen gas three times. Then, CD₃OD (0.50 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at 60 °C for 1, 5, and 24 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was evaporated in vacuum and the H/D exchange ratio was confirmed by ¹H NMR.

¹H NMR Spectra for Deuterium Labeling Study of Compound 1b
Deuterium Labeling Study of 1o

A seal tube initially fitted with a rubber septum containing magnetic stir bar, oxime 1o (0.1 mmol), [RhCp*Cl]_2 (0.002 mmol, 2.0 mol %) and Cu(OAc)_2·H_2O (0.35 mmol) was evacuated and purged with nitrogen gas three times. Then, CD_3OD (0.5 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at 60 and 100 °C for 24 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was evaporated in vacuum and confirmed by ^1H NMR.

^1H NMR Spectra for Deuterium Labeling Study of Compound 1o
Table S1. Optimization Studies for the Synthesis of Benzofuran 3aa

![Chemical structure](image)

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* Conditions: 1a (0.1 mmol), Cu(OAc)₂·H₂O (0.35 mmol) and [RhCp^+Cl]₂ (2 mol %) in solvent (0.5 mL) under N₂ for 20 h, unless otherwise noted. b Yields were determined by NMR integration method using mesitylene as internal standard. c Conversions of 1a were determined by crude ¹H NMR. d Cu(OAc)₂·H₂O (0.20 mmol) was used. e Cu(OAc)₂·H₂O (0.05 mmol) was used. f Reaction time: 30 h.
Synthesis and Characterization of Starting Materials

3-Hydroxy-4-methoxybenzaldehyde C-methyl oxime (1a)

Compound 1a was prepared using modified procedure from reported method: 3-hydroxy-4-methoxybenzaldehyde (1.5 g, 10 mmol, 1.0 equiv) was added to the solution of MeONH$_2$·HCl (1.0 g, 12 mmol, 1.2 equiv), and pyridine (3.2 g, 40 mmol, 4.0 equiv) in CH$_2$Cl$_2$ (1 M, 10 mL). The solution was stirred for 24 h at room temperature. After completion of the reaction, the solvent was removed under vacuo. The remaining residue was dissolved in CH$_2$Cl$_2$ and filtered through a short pad of silica gel. The filtrate was concentrated and purified by silica flash chromatography (hexane–EtOAc) to give the corresponding product as white solid (1.6 g, 88%).

R$_f$ = 0.61 (50% ethyl acetate in n-hexane); mp: 50-52 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.96 (s, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 7.02 (dd, $J = 8.4$, 2.0 Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 5.71 (s, OH), 3.94 (s, 3H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 148.2, 148.1, 145.8, 125.6, 120.1, 112.3, 110.4, 61.8, 55.9; HRMS (EI$^+$): calcd for C$_9$H$_{11}$NO$_3$ 181.0739, found 181.0735; IR (KBr, cm$^{-1}$): 3450, 2938 and 1612.

3-Hydroxybenzaldehyde C-methyl oxime (1b)

Compound 1b was prepared from 3-hydroxybenzaldehyde using the synthetic procedure for 1a; R$_f$ = 0.29 (20% ethyl acetate in n-hexane); white solid; mp: 62-64 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.01 (s, 1H), 7.26-7.08 (m, 3H), 6.87-6.85 (m, 1H), 5.69 (s, OH), 3.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.8, 148.6, 135.5, 130.0, 120.2, 117.2, 113.0, 62.0; HRMS (EI$^+$): calcd for C$_8$H$_9$NO$_2$ 151.0633, found 151.0630; IR (KBr, cm$^{-1}$): 3363, 2938 and 1581.

3-Hydroxy-4,5-dimethoxybenzaldehyde C-methyl oxime (1c)

This product was prepared from 3-hydroxy-4,5-dimethoxybenzaldehyde by following the synthetic procedure for 1a; R$_f$ = 0.38 (30% ethyl acetate in n-hexane); brown oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.91 (s, 1H), 6.78 (s, 1H), 6.74 (s, 1H), 5.79 (s, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 152.6, 149.4, 148.2, 136.9, 128.1, 108.0, 101.9, 62.0,
2-Bromo-5-hydroxybenzaldehyde O-methyl oxime (1d)

Compound 1d was prepared from 2-bromo-5-hydroxybenzaldehyde using the synthetic procedure of 1a.\(^2\) \(R_f = 0.45\) (30% ethyl acetate in \(n\)-hexane); white solid; mp: 81-83 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.37\) (s, 1H), 7.37 (d, \(J = 8.8\) Hz, 1H), 7.30 (d, \(J = 2.8\) Hz, 1H), 6.73 (dd, \(J = 8.8, 3.2\) Hz, 1H), 5.92 (s, OH), 3.96 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.9, 148.1, 134.0, 132.0, 119.1, 114.5, 113.6, 62.2\); HRMS (EI\(^+\)): calcd for C\(_{8}\)H\(_{8}\)BrNO\(_2\) 228.9738, found 228.9732; IR (KBr, cm\(^{-1}\)): 3402, 2939, 1566 and 1435.

3-Hydroxy-5-methylbenzaldehyde O-methyl oxime (1e)

Scheme S1. Synthesis of 3-Hydroxy-5-methylbenzaldehyde O-methyl oxime (1e).

Compound 1e was prepared starting from 3,5-dibromotoluene (S1-1), followed by formylation,\(^3\) acetalization,\(^4\) hydroxylation of the aryl bromide and hydrolysis to get 3-hydroxy-5-methylbenzaldehyde (S1-4).\(^5\) Then, condensation with MeONH\(_2\)·HCl to give oxime 1e. (Note: hydroxylation reaction does not work in the absence of acetal protection) \(R_f = 0.67\) (50% ethyl acetate in \(n\)-hexane); white solid; mp: 91-92 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.95\) (s, 1H), 6.92 (s, 1H), 6.87 (s, 1H), 6.66 (s, 1H), 3.94 (s, 3H), 2.29 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.8, 148.5, 140.3, 133.4, 120.9, 117.8, 110.4, 62.0, 21.2\); HRMS (EI\(^+\)): calcd for C\(_{9}\)H\(_{11}\)NO\(_2\) 165.0790,
found 165.0789; IR (KBr, cm⁻¹): 3232 and 1589.

3-Hydroxy-5-methoxybenzaldehyde O-methyl oxime (1f)

\[
\text{S2-1} \xrightarrow{\text{CH₃J, K₂CO₃, acetone, 0 °C to r.t. 16 h, 40\%}} \text{S2-2}
\]

\[
\text{S2-3} \xrightarrow{\text{CH₂ONH₂·HCl, pyridine, DCM, rt, 12 h, 84\%}} \text{1f}
\]

**Scheme S2.** Synthesis of 3-Hydroxy-5-methoxybenzaldehyde O-methyl oxime (1f)

Compound 1f was prepared starting from methyl 3,5-dihydroxybenzoate (S2-1), followed by methylation,⁶ reduction,⁷ oxidation,⁸ and condensation with MeONH₂·HCl to give oxime 1f (Scheme S2). Rᵣ = 0.31 (30% ethyl acetate in n-hexane); white solid; mp: 92-94 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.93 (s, 1H), 6.68-6.64 (m, 2H), 6.41 (m, 1H), 5.61 (s, OH), 3.94 (s, 3H), 3.77 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 161.1, 156.9, 148.5, 134.1, 106.5, 105.1, 103.4, 62.1, 55.5; HRMS (EI⁺): calcd for C₉H₁₁NO₃ 181.0739, found 181.0737; IR (KBr, cm⁻¹): 2947 and 1589.

3-Bromo-5-hydroxybenzaldehyde O-methyl oxime (1g)

\[
\text{Br-Br} \xrightarrow{\text{n-BuLi, DMF, ether, -78°C, 4 h}} \text{Br} \xrightarrow{\text{p-TSA, ethylene glycol, toluene, dean stark, 12 h}} \text{Br}
\]

\[
\text{S3-1} \xrightarrow{\text{Br}} \text{S3-2} \xrightarrow{\text{Br}} \text{S3-3} \xrightarrow{\text{MeOH₂·HCl, pyridine, DCM, rt, 12 h, 80\%}} \text{1g}
\]

**Scheme S3.** Synthesis of 3-Bromo-5-hydroxybenzaldehyde O-methyl oxime (1g)
Compound 1g was prepared starting from 1,3,5-dibromotoluene (S3-1), followed by formylation, acetalization, hydroxylation of aryl bromide and hydrolysis to get 3-hydroxy-5-methylbenzaldehyde (S1-4). Then, condensation with MeONH$_2$·HCl to give oxime 1g. (Note: hydroxylation reaction does not work in the absence of acetal protection) R$_f$ = 0.26 (30% ethyl acetate in n-hexane); white solid; mp: 71-73 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.90 (s, 1H), 7.25 (m, 1H), 7.00-6.98 (m, 2H), 5.47 (s, OH), 3.95 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 156.4, 146.8, 135.1, 123.1, 122.8, 120.0, 112.2, 62.3; HRMS (EI$^+$): calcd for C$_8$H$_8$BrNO$_2$ 405.0364, found 405.0364; IR (KBr, cm$^{-1}$): 2353, 1566 and 1435.

4-Fluoro-3-hydroxybenzaldehyde O-methyl oxime (1h)

Compound 1h was prepared from 4-fluoro-3-hydroxybenzaldehyde by following the synthetic procedure for 1a; R$_f$ = 0.70 (50% ethyl acetate in n-hexane); white solid; mp: 77-79 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.95 (s, 1H), 7.26-7.24 (m, 1H), 7.04 (m, 1H), 7.03 (m, 1H), 5.49 (brs, OH), 3.94 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 153.2, 150.8, 147.5, 143.9, 143.8, 129.3, 120.1, 120.1, 116.0, 115.8, 115.4, 62.1; HRMS (EI$^+$): calcd for C$_8$H$_8$FNO$_2$ 169.0539, found 169.0538; IR (KBr, cm$^{-1}$): 3116, 1597, 1519 and 1435.

(3-Hydroxyphenyl)(phenyl)methanone O-methyl oxime (1i); mixture of E and Z isomers

3-Hydroxybenzophenone (0.4 g, 2.0 mmol, 1.0 equiv) was added to a solution of MeONH$_2$·HCl (0.17 g, 2.4 mmol, 1.2 equiv), and pyridine (0.63 g, 8.0 mmol, 4.0 equiv) in MeOH (4 mL). The solution was heated to reflux for 24 h, the reaction was then cooled to room temperature and concentrated in vacuo. The remaining residue was dissolved in CH$_2$Cl$_2$ and filtered through a short pad of silica gel. The filtrate was purified by silica flash chromatography (n-hexane–EtOAc) to give the corresponding product as colorless oil (0.45 g, 99%); R$_f$ = 0.67 (50% ethyl acetate in n-hexane); $^1$H NMR for mixture of E and Z isomers (400 MHz, CDCl$_3$): $\delta$ = 7.55-7.27 (m, 5H), 7.18 (t, $J$ = 7.6 Hz, 1H), 7.07-6.84 (m, 3H), 4.00 (s, 3H); $^{13}$C NMR for mixture of E and Z isomers (100 MHz, CDCl$_3$): $\delta$ = 157.1, 157.0, 155.7, 155.6, 137.4, 135.8, 134.4, 132.9, 129.3, 129.0, 128.9, 128.1, 128.0, 127.7, 121.0, 120.3, 116.7, 116.1, 114.6; HRMS (EI$^+$): calcd for C$_{14}$H$_{13}$NO$_2$ 227.0946, found 227.0948; IR (KBr, cm$^{-1}$): 3400, 2938 and 1589.
1-(3-Hydroxy-4-methoxyphenyl)ethanone O-methyl oxime (1j)

Compound 1j was prepared from 3'-hydroxy-4'-methoxyacetophenone by following the synthetic procedure for 1i; \( R_f = 0.58 \) (50% ethyl acetate in \( n \)-hexane); colorless oil; \(^1\text{H NMR (400 MHz, CDCl}_3\)): \( \delta = 7.26 \text{ (d, } J = 2.0 \text{ Hz, 1H), 7.13 \text{ (dd, } J = 8.4, 2.0 \text{ Hz, 1H), 6.80 \text{ (d, } J = 8.4 \text{ Hz, 1H), 3.97 \text{ (s, 3H), 3.86 \text{ (s, 3H), 2.17 \text{ (s, 3H); \( ^{13}\text{C NMR (100 MHz, CDCl}_3\)): \( \delta = 154.1, 147.5, 145.4, 129.9, 118.1, 112.3, 110.2, 61.7, 55.8, 12.4; \) HRMS (EI\(^+\)): calcd for C\(_{10}\)H\(_{13}\)NO\(_3\) 195.0895, found 195.0895; IR (KBr, cm\(^{-1}\)): 3450, 2939 and 1619.}

1-(3-Hydroxyphenyl)ethanone O-methyl oxime (1k)

Compound 1k was prepared from 3'-hydroxyacetophenone using the synthetic procedure of 1i; \( R_f = 0.64 \) (50% ethyl acetate in \( n \)-hexane); colorless oil; \(^1\text{H NMR (400 MHz, CDCl}_3\)): \( \delta = 7.20 \text{ (t, } J = 8.0 \text{ Hz, 1H), 7.14-7.11 \text{ (m, 2H), 6.88-6.77(m, 1H), 3.98 \text{ (s, 3H), 2.19 \text{ (s, 3H); \( ^{13}\text{C NMR (100 MHz, CDCl}_3\)): \( \delta = 155.8, 155.4, 137.8, 129.7, 118.5, 116.5, 113.0, 61.8, 13.0; \) HRMS (EI\(^+\)): calcd for C\(_9\)H\(_{11}\)NO\(_2\) 165.0790, found 165.0790; IR (KBr, cm\(^{-1}\)): 3394, 2938 and 1581.}

2-Hydroxyanthracene-9,10-dione O,O-dimethyl dioxime (1l; mixture of isomers)

The solution containing 2-hydroxyanthraquinone (0.90 g, 4.0 mmol, 1.0 equiv), and MeONH\(_2\)-HCl (0.70 g, 10.0 mmol, 2.5 equiv) in pyridine (4 mL) as solvent, was heated to reflux for 24 h. The reaction was then cooled to room temperature and the mixture was dissolved in CH\(_2\)Cl\(_2\) (20 mL). The mixture was washed with NH\(_4\)Cl\(_{aq}\) (10 mL) and organic layer was evaporated in vacuo. The residue was washed with NH\(_2\)Cl\(_{aq}\) (10 mL) and organic layer was purified by silica flash chromatography (hexane–EtOAc) to give the corresponding product as brown foam (0.53 g, 47%); \( R_f = 0.61 \) (50% ethyl acetate in \( n \)-hexane); \(^1\text{H NMR (400 MHz, CDCl}_3\)): \( \delta = 9.00 \text{ (s, OH), 8.55-8.49 \text{ (m, 1H), 8.10-7.89 \text{ (m, 2H), 7.54-7.40 \text{ (m, 3H), 7.04-6.98 \text{ (m, 1H), 4.09-4.05 \text{ (m, 6H); \( ^{13}\text{C NMR (100 MHz, CDCl}_3\)): \( \delta = 159.2, 158.9, 158.6, 158.2, 149.4, 146.7, 146.6, 146.5, 146.3, 146.2, 136.2, 134.4, 134.2, 134.1, 132.9, 132.8, 132.4, 130.8, 130.7, 130.6, 130.4, 130.3, 129.8, 129.7, 129.4, 129.2, 126.1, 125.6, 124.8, 124.6, 120.7, 119.3, 118.4, 117.8, 117.4, 117.2, 116.9, 116.7, 111.6, 110.6, 63.2, 63.1; \) HRMS (EI\(^+\)): calcd for C\(_{10}\)H\(_{13}\)NO\(_3\) 195.0895, found 195.0895; IR (KBr, cm\(^{-1}\)): 3450, 2939 and 1619.}
HRMS (EI⁺): calcd for C_{16}H_{14}N_{2}O_{3} 282.1004, found 282.1003; IR (KBr, cm⁻¹): 3300, 2938 and 1604.

2,6-Dihydroxyanthracene-9,10-dione O,O-dimethyl dioxime (1m)

Followed the synthesis of 1l and started from anthraflavic acid; R_f = 0.48 (50% ethyl acetate in n-hexane); pale yellow solid; mp: 198-200 °C; \(^1\)H NMR (400 MHz, (CD₃)₂CO) for the major isomer: \(\delta = 8.92\) (s, OH), 8.45 (d, \(J = 8.8\) Hz, 2H), 7.53 (d, \(J = 2.4\) Hz, 2H), 6.98-6.95 (m, 2H), 4.05 (s, 6H); \(^{13}\)C NMR (100 MHz, (CD₃)₂CO): \(\delta = 158.7, 158.4, 158.1, 146.1, 145.9, 145.8, 136.1, 134.0, 132.4, 132.2, 130.2, 126.9, 126.3, 124.1, 120.4, 118.9, 117.7, 117.1, 117.0, 116.5, 116.0, 111.1, 110.0, 62.6; HRMS (EI⁺): calcd for C₉H₁₁NO₃ 298.0954, found 298.0952; IR (KBr, cm⁻¹): 3355 and 1566.

6-Hydroxy-2,3-dihydro-1H-inden-1-one O-methyl oxime (1n)

Compound 1n was prepared from 6-hydroxy-1-indanone by following the synthetic procedure for 1i; R_f = 0.26 (50% ethyl acetate in n-hexane); yellow solid; mp: 172-175 °C; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.16\) (d, \(J = 8.0\) Hz, 1H), 7.11 (d, \(J = 2.4\) Hz, 1H), 6.86 (dd, \(J = 8.0, 2.4\) Hz, 1H), 5.25 (s, OH), 3.97 (s, 3H), 2.96-2.86 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 162.8, 155.0, 140.6, 137.3, 126.4, 118.5, 107.2, 62.0, 27.8, 27.0;\) HRMS (EI⁺): calcd for C_{10}H_{11}NO_{2} 177.0790, found 177.0785; IR (KBr, cm⁻¹): 3394, 2915 and 1604.

6-Hydroxy-2-phenyl-4H-chromen-4-one O-methyl oxime (1o)

Followed the synthesis of 1l and started from 6-hydroxyflavone; R_f = 0.47 (50% ethyl acetate in n-hexane); yellow solid; mp: 153-156 °C; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.84-7.83\) (m, 2H), 7.44-7.40 (m, 4H), 7.18 (d, \(J = 8.8\) Hz, 1H), 7.00 (s, 1H), 6.95 (dd, \(J = 8.8, 3.2\) Hz, 1H), 5.93 (s, OH), 3.98(s, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 155.4, 152.8, 146.3, 144.6, 132.8, 130.2, 128.6, 125.7, 119.2, 119.0, 118.5, 107.3, 92.9, 61.7; HRMS (EI⁺): calcd for C_{16}H_{13}NO_{3} 267.0895, found 267.0900; IR (KBr, cm⁻¹): 3170 and 1627.
Characterization data of Benzofuran Derivatives

7-Methoxy-2,3-diphenylbenzofuran-4-carbaldehyde O-methyl oxime (3aa)

\[
\begin{align*}
R_f &= 0.54 \text{ (20\% ethyl acetate in } n\text{-hexane); yellow solid; mp: 140-143 \degree C; } ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 7.73 \\
&\quad \text{ (d, } J = 8.4 \text{ Hz, 1H), 7.70 (s, 1H), 7.59-7.26 \text{ (m, 10H), 6.85} \\
&\quad \text{ (d, } J = 8.4 \text{ Hz, 1H), 4.08 (s, 3H), 3.85 (s, 3H); } ^13C \text{ NMR (100 MHz, CDCl}_3\text{): } \delta = 151.4, 146.1, 145.2, 142.8, 133.4, \\
&\quad 130.4, 130.0, 129.3, 128.4, 128.3, 128.2, 126.6, 121.4, 118.0, 117.5, 107.1, 61.5, 56.1; \text{ HRMS (EI): calcd for } C_{23}H_{19}NO_3 357.1365, \\
&\quad \text{ found 357.1365; IR (KBr, cm}^{-1}\text{): 2938 and 1596.}
\end{align*}
\]

7-Methoxy-2,3-di-p-tolylbenzofuran-4-carbaldehyde O-methyl oxime (3ab)

\[
\begin{align*}
R_f &= 0.69 \text{ (30\% ethyl acetate in } n\text{-hexane); white solid; mp: 143-145 \degree C; } ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 7.71 \\
&\quad \text{ (s, 1H), 7.66 (d, } J = 8.0 \text{ Hz, 1H), 7.40 (d, } J = 8.4 \text{ Hz, 2H), 7.26 (s, 4H), 7.04 (d, } J \\
&\quad = 8.0 \text{ Hz, 2H), 6.81 (d, } J = 8.4 \text{ Hz, 1H), 4.07 (s, 3H), 3.81 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H); } ^13C \text{ NMR (100 MHz, CDCl}_3\text{): } \delta = 151.8, 146.2, 145.6, \\
&\quad 142.8, 138.4, 138.0, 130.4, 130.3, 130.0, 129.0, 127.4, 126.6, 121.3, 118.0, 116.9, 107.0, 61.6, 56.3, 21.5, 21.3; \text{ HRMS (EI): calcd for } C_{25}H_{23}NO_3 385.1678, \\
&\quad \text{ found 385.1673; IR (KBr, cm}^{-1}\text{): 2931, 2360, 1597 and 1512.}
\end{align*}
\]

7-Methoxy-2,3-bis(4-methoxyphenyl)benzofuran-4-carbaldehyde O-methyl oxime (3ac)

\[
\begin{align*}
R_f &= 0.47 \text{ (30\% ethyl acetate in } n\text{-hexane); white solid; mp: 141-143 \degree C; } ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 7.75 \\
&\quad \text{ (s, 1H), 7.66 (d, } J = 8.0 \text{ Hz, 1H), 7.46-7.44 \text{ (m, 2H), 7.30-7.28 \text{ (m, 2H), 7.00 (m, } 2H), 6.80-6.76 \\
&\quad \text{ (m, 3H), 4.06 (s, 3H), 3.88 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H); } ^13C \text{ NMR (100 MHz, CDCl}_3\text{): } \delta = 159.7, 159.6, 152.0, 146.2, 145.6, \\
&\quad 131.7, 130.6, 128.2, 125.6, 123.0, 121.3, 118.0, 115.7, 114.8, 113.8, 106.9, 61.6, 56.3, 55.3, 55.2; \text{ HRMS (EI): calcd for } C_{25}H_{23}NO_5 417.1576, \\
&\quad \text{ found 417.1578; IR (KBr, cm}^{-1}\text{): 2931, 2360, 1597 and 1512.}
\end{align*}
\]
cm⁻¹): 2939, 2839, 1612 and 1512.

2,3-Bis(4-fluorophenyl)-7-methoxybenzofuran-4-carbaldehyde O-methyl oxime (3ad)

\[ R_f = 0.66 \text{ (30% ethyl acetate in } n\text{-hexane); pale yellow solid; mp: 142-144\degree C; } \]
\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 7.67 \text{ (s, 1H), 7.66 (d, } J = 8.6 \text{ Hz, 1H), 7.48-7.44 (m, 2H), 7.37-7.34 (m, 2H), 7.21-7.17 (m, 2H), 6.97-6.92 (m, 2H), 6.83 (d, } J = 8.6 \text{ Hz, 1H), 4.06 (s, 3H), 3.80 (s, 3H); } ^{13}C \text{ NMR (100 MHz, CDCl}_3\text{): } \delta = 164.1, 163.9, 161.6, 161.5, 151.1, 146.3, 145.1, 142.9, 132.3, 132.2, 129.8, 129.3, 128.8, 128.7, 126.2, 121.9, 118.1, 116.7, 116.5, 116.3, 115.7, 115.4, 107.3, 61.7, 56.3; \]
\[ \text{HRMS (EI\textsuperscript{+}): calcld for C}_{23}\text{H}_{17}F_{2}\text{NO}_3 393.1176, \text{ found 393.1179; IR (KBr, cm}^{-1}\text{): } 2939, 2399, 1597 \text{ and 1512.} \]

2,3-Bis(4-chlorophenyl)-7-methoxybenzofuran-4-carbaldehyde O-methyl oxime (3ae)

\[ R_f = 0.66 \text{ (30% ethyl acetate in } n\text{-hexane); yellow solid; mp: 125-128\degree C; } \]
\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta = 7.69 \text{ (s, 1H), 7.65 (d, } J = 8.4 \text{ Hz, 1H), 7.49-7.45 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.31 (m, 2H), 7.24-7.21 (m, 2H), 6.84 (d, } J = 8.4 \text{ Hz, 1H), 4.06 (s, 3H), 3.80 (s, 3H); } ^{13}C \text{ NMR (100 MHz, CDCl}_3\text{): } \delta = 150.8, 146.3, 145.1, 143.1, 134.7, 134.6, 132.8, 131.8, 129.8, 129.5, 128.8, 128.5, 128.3, 128.1, 122.1, 118.2, 116.9, 107.5, 61.7, 56.3; \]
\[ \text{HRMS (EI\textsuperscript{+}): calcld for C}_{23}\text{H}_{17}Cl_2\text{NO}_3 425.0585, \text{ found 425.0586; IR (KBr, cm}^{-1}\text{): } 2931, 2399, 1728 \text{ and 1597.} \]
2,3-Bis(4-bromophenyl)-7-methoxybenzofuran-4-carbaldehyde \( O \)-methyl oxime (3af)

\[
\begin{align*}
R_f &= 0.50 \text{ (20\% ethyl acetate in } n\text{-hexane)}; \text{ yellow solid; mp: 161-164 °C}; \quad \text{\textsuperscript{1}H NMR (400 MHz, CDCl}{}_{3}\text{): } \delta = 7.72 \text{ (s, 1H)}, 7.66 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.63 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 7.40 \text{ (d, } J = 8.4 \text{ Hz, 2H)}, 7.33 \text{ (d, } J = 8.4 \text{ Hz, 2H)}, 7.07 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 6.85 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 4.07 \text{ (s, 3H)}, 3.82 \text{ (s, 3H)}; \quad \text{\textsuperscript{13}C NMR (100 MHz, CDCl}{}_{3}\text{): } \delta = 150.8, 146.3, 145.0, 143.1, 132.7, 132.3, 132.1, 131.7, 129.3, 128.7, 128.2, 122.9, 122.1, 118.1, 117.0, 107.5, 61.7, 56.2; \quad \text{HRMS (EI\textsuperscript{+})}: \text{ calcd for C}_{23}H_{17}Br_2NO_3 512.9575, \text{ found 512.9561}; \quad \text{IR (KBr, cm}\textsuperscript{-1}): 2931 \text{ and 1596.}
\end{align*}
\]

3ag (mixture of isomers)

\[
\begin{align*}
R_f &= 0.51 \text{ (20\% ethyl acetate in } n\text{-hexane)}; \text{ yellow solid; mp: 129-132 °C}; \quad \text{\textsuperscript{1}H NMR for major isomer (400 MHz, CDCl}{}_{3}\text{): } \delta = 8.62 \text{ (s, 1H)}, 7.74 \text{ (d, } J = 7.2 \text{ Hz, 2H)}, 7.65 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.50-7.38 \text{ (m, 3H)}, 6.82 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 4.04 \text{ (s, 3H)}, 4.01 \text{ (s, 3H)}, 2.98 \text{ (q, } J = 7.2 \text{ Hz, 2H)}, 1.35 \text{ (t, } J = 7.2 \text{ Hz, 3H)}; \quad \text{\textsuperscript{13}C NMR for major isomer (100 MHz, CDCl}{}_{3}\text{): } \delta = 146.8, 146.7, 146.0, 130.6, 129.5, 128.9, 128.8, 128.1, 127.9, 122.3, 121.5, 118.4, 107.0, 62.1, 56.4, 29.9, 20.2, 18.7, 15.4; \quad \text{HRMS (EI\textsuperscript{+})}: \text{ calcd for C}_{19}H_{19}NO_3 309.1365, \text{ found 309.1358}; \quad \text{IR (KBr, cm}\textsuperscript{-1}): 2931 \text{ and 1604.}
\end{align*}
\]

7-Methoxy-2,3-dipropylbenzofuran-4-carbaldehyde \( O \)-methyl oxime (3ah)

\[
\begin{align*}
R_f &= 0.57 \text{ (20\% ethyl acetate in } n\text{-hexane)}; \text{ yellow solid; mp: 57-59 °C}; \quad \text{\textsuperscript{1}H NMR (400 MHz, CDCl}{}_{3}\text{): } \delta = 8.49 \text{ (s, 1H)}, 7.58 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 6.73 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 4.00 \text{ (s, 3H)}, 3.99 \text{ (s, 3H)}, 2.73-2.65 \text{ (m, 4H)}, 1.78-1.56 \text{ (m, 4H)}, 0.97 \text{ (t, } J = 7.6 \text{ Hz, 6H)}; \quad \text{\textsuperscript{13}C NMR (100 MHz, CDCl}{}_{3}\text{): } \delta = 156.2, 146.6, 146.1, 143.2, 128.9, 121.6, 117.4, 114.9, 105.6, 61.8, 56.0, 28.2, 26.8, 23.7, 21.8, 13.9, 13.8; \quad \text{HRMS (EI\textsuperscript{+})}: \text{ calcd for C}_{19}H_{23}NO_3 289.1678, \text{ found 289.1683}; \quad \text{IR (KBr, cm}\textsuperscript{-1}): 2962 \text{ and 1596.}
\end{align*}
\]
6-Methoxy-3,4,8,9-tetrapropylfuro[2,3-\(h\)]isoquinoline (3ah')

\[
\text{R}_f = 0.41 \text{ (20\% ethyl acetate in n-hexane); brown solid; mp: 78-81 °C; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \\
\delta = 9.35 \text{ (s, 1H), 7.02 (s, 1H), 4.13 (s, 3H), 3.01-2.85 (m, 6H), 2.78 (t, } J = 7.6 \text{ Hz, 2H), 1.83-1.67 (m, 8H), 1.11-0.95 (m, 12H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \\
\delta = 155.8, 151.9, 148.4, 144.2, 142.5, 134.7, 128.2, 124.9, 118.3, 116.7, 96.8, 55.7, 37.6, 30.7, 28.2, 27.4, 23.7, 23.5, 23.1, 22.1, 14.7, 14.4, 14.0, 13.8; \text{ HRMS (EI): calcd for C}_{24}\text{H}_{33}\text{NO}_2 367.2511, found 367.2510; IR (KBr, cm}^{-1}\text{): 3178 and 1612.}
\]

7-Methoxy-2,3-bis(methoxymethyl)benzofuran-4-carbaldehyde O-methyl oxime (3ai)

\[
\text{R}_f = 0.30 \text{ (30\% ethyl acetate in n-hexane); yellow solid; mp: 110-112 °C; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \\
\delta = 9.18 \text{ (s, 1H), 7.64 (d, } J = 8.0 \text{ Hz, 1H), 6.65 (d, } J = 8.0 \text{ Hz, 1H), 4.67 (s, 2H), 4.35 (s, 2H), 4.12 (s, 3H), 3.89 (s, 3H), 3.47 (s, 3H), 3.34 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \\
\delta = 154.3, 151.6, 151.0, 141.0, 140.5, 132.3, 126.9, 121.6, 121.0, 66.9, 63.8, 63.5, 58.2, 57.9, 56.1; \text{ HRMS (EI): calcd for C}_{15}\text{H}_{19}\text{NO}_5 293.1263, found 293.1260; IR (KBr, cm}^{-1}\text{): 2924, 2854, 1589 and 1458.}
\]

2,3-Diphenylbenzofuran-4-carbaldehyde O-methyl oxime (3ba)

\[
\text{R}_f = 0.54 \text{ (20\% ethyl acetate in n-hexane); yellow solid; mp: 115-118 °C; } ^1\text{H NMR (400 MHz, CDCl}_3\text{): } \\
\delta = 7.75 \text{ (d, } J = 7.6 \text{ Hz, 1H), 7.74 (s, 1H), 7.59-7.27 \text{ (m, 12H), 3.86 (s, 3H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \\
\delta = 154.0, 151.4, 145.5, 133.7, 130.4, 130.2, 129.4, 128.5, 128.4 (2C), 126.6, 125.7, 124.6, 120.4, 117.3, 112.1, 61.8; \text{ HRMS (EI): calcd for C}_{22}\text{H}_{17}\text{NO}_2 327.1259, found 327.1266; IR (KBr, cm}^{-1}\text{): 2938 and 1596.}
\]
6,7-Dimethoxy-2,3-diphenylbenzofuran-4-carbaldehyde O-methyl oxime (3ca)

![Chemical Structure](image)

R_f = 0.59 (30% ethyl acetate in n-hexane); orange solid; mp: 112-114 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 6 = 7.60 (s, 1H), 7.50-7.44 (m, 5H), 7.41-7.38 (m, 3H), 7.24-7.21 (m, 3H), 4.30 (s, 3H), 3.95 (s, 3H), 3.80 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 6 = 151.1, 148.9, 145.5, 145.1, 135.6, 133.6, 130.4, 130.2, 129.5, 128.6, 128.4, 128.3, 126.3, 125.5, 118.5, 117.3, 113.0, 105.8, 61.8, 61.0, 57.0; HRMS (EI\(^+\)): calcd for C\(_{24}\)H\(_{21}\)NO\(_4\) 387.1471, found 387.1470; IR (KBr, cm\(^{-1}\)): 2939, 1604, 1512 and 1250.

3da (with 60% debromination product)

![Chemical Structure](image)

R_f = 0.54 (20% ethyl acetate in n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): 6 = 7.98 (s, 1H), 7.52-7.23 (m, 12H), 3.40 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 6 = 153.2, 153.0, 145.5, 133.5, 130.7, 130.1, 129.9, 128.7, 128.4, 127.7, 127.2, 125.2, 117.9, 117.8, 113.1, 61.6; HRMS (EI\(^+\)): calcd for C\(_{22}\)H\(_{16}\)BrNO\(_2\) 405.0364, found 405.0358; IR (KBr, cm\(^{-1}\)): 3055, 2938 and 1604.

6-Methyl-2,3-diphenylbenzofuran-4-carbaldehyde O-methyl oxime (3ea)

![Chemical Structure](image)

R_f = 0.85 (50% ethyl acetate in n-hexane); pale yellow solid; mp: 111-113 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 6 = 7.69 (s, 1H), 7.56 (s, 1H), 7.50-7.47 (m, 5H), 7.41-7.39 (m, 2H), 7.37 (s, 1H), 7.25-7.22 (m, 3H), 3.83 (s, 3H), 2.48 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 6 = 154.5, 150.8, 145.7, 135.1, 133.9, 130.4, 129.4, 128.4, 128.2, 126.5, 125.0, 121.4, 117.3, 112.6, 61.8, 21.6; HRMS (EI\(^+\)): calcd for C\(_{23}\)H\(_{19}\)NO\(_2\) 341.1416, found 341.1416; IR (KBr, cm\(^{-1}\)): 2939 and 1604.
6-Methoxy-2,3-diphenylbenzofuran-4-carbaldehyde O-methyl oxime (3fa)

\[
\text{R}_f = 0.68 \text{ (30\% Ethyl acetate in } n\text{-hexane); white solid; mp: 100-102 ^\circ C; } \text{^1H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.68 \text{ (s, 1H), 7.51-7.46 (m, 5H), 7.43-7.40 (m, 2H), 7.38 (d, J = 2.4 Hz, 1H), 7.26-7.23 (m, 3H), 7.13 (d, J = 2.4 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H); } \text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta = 157.9, 155.1, 150.5, 145.1, 133.8, 130.4, 130.3, 129.3, 128.4, 128.3, 127.9, 126.2, 125.6, 122.9, 117.1, 107.3, 98.0, 61.9, 55.9; } \text{HRMS (EI^+): calcd for C}_{23}\text{H}_{19}\text{NO}_3 \text{357.1365, found 357.1363; IR (KBr, cm}^{-1}\text{): 3062, 2939 and 1620.}
\]

6-Bromo-2,3-diphenylbenzofuran-4-carbaldehyde O-methyl oxime (3ga)

\[
\text{R}_f = 0.81 \text{ (30\% ethyl acetate in } n\text{-hexane); white solid; mp: 112-115 ^\circ C; } \text{^1H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.87 \text{ (d, J = 1.6 Hz, 1H), 7.69 (d, J = 1.6 Hz, 1H), 7.60 (s, 1H), 7.51-7.46 (m, 5H), 7.39-7.37 (m, 2H), 7.26-7.24 (m, 3H), 3.83 (s, 3H); } \text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta = 154.3, 152.0, 144.1, 133.1, 130.4, 129.8, 129.5, 128.7, 128.5, 127.8, 126.7, 123.3, 118.0, 117.2, 115.2, 62.1; } \text{HRMS (EI^+): calcd for C}_{22}\text{H}_{16}\text{BrNO}_2 \text{405.0364, found 405.0364; IR (KBr, cm}^{-1}\text{): 2276, 1736 and 1604.}
\]

7-Fluoro-2,3-diphenylbenzofuran-4-carbaldehyde O-methyl oxime (3ha)

\[
\text{R}_f = 0.82 \text{ (30\% ethyl acetate in } n\text{-hexane); yellow solid; mp: 160-162 ^\circ C; } \text{^1H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.66 \text{ (quart, J = 4.4 Hz, 1H), 7.60 (s, 1H), 7.53-7.47 (m, 5H), 7.41-7.38 (m, 2H), 7.28-7.25 (m, 3H), 7.04 (m, 1H), 3.80 (s, 3H); } \text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta = 152.4, 149.8, 147.3, 144.7, 141.4, 132.9, 131.9, 130.4, 129.7, 129.5, 128.9, 128.8, 128.5, 126.8, 121.7, 121.4, 121.3, 117.7, 111.4, 111.3, 61.9; } \text{HRMS (EI^+): calcd for C}_{22}\text{H}_{16}\text{FNO}_2 \text{345.1165, found 345.1162; IR (KBr, cm}^{-1}\text{): 2337, 1581 and 1396.}
\]
(2,3-Diphenylbenzofuran-4-yl)(phenyl)methanone O-methyl oxime (3ia)

\[ R_f = 0.63 \ (20\% \ \text{ethyl acetate in} \ \text{n-hexane}); \ \text{white solid; mp:} \ \text{128-131}^\circ\text{C}; \ \text{^1H NMR} \ (400 \ \text{MHz, CDCl}_3): \ \delta = 7.63 \ (d, J = 8.0 \ \text{Hz, 1H}), 7.48-7.11 \ (m, 17H), 3.76 \ (s, 3H); \ \text{^13C NMR} \ (100 \ \text{MHz, CDCl}_3): \ \delta = 154.3, 154.0, 151.5, 133.3, 133.1, 130.9, 130.4, 130.3, 129.9, 128.8, 128.4, 128.3, 128.2, 127.5, 127.1, 127.0, 125.6, 124.2, 117.9, 111.7, 62.1; \ \text{HRMS (EI^+): calecd for} \ C_{28}H_{21}NO_2 403.1572, \ \text{found} 403.1563; \ \text{IR (KBr, cm}^{-1}): 2931 \ \text{and 1604}. \]

1-(7-Methoxy-2,3-diphenylbenzofuran-4-yl)ethanone O-methyl oxime (3ja)

\[ R_f = 0.49 \ (20\% \ \text{ethyl acetate in} \ \text{n-hexane}); \ \text{white solid; mp:} \ \text{129-131}^\circ\text{C}; \ \text{^1H NMR} \ (400 \ \text{MHz, CDCl}_3): \ \delta = 7.58-7.25 \ (m, 10H), 7.07 \ (d, J = 8.0 \ \text{Hz, 1H}), 6.83 \ (d, J = 8.0 \ \text{Hz, 1H}), 4.07 \ (s, 3H), 3.72 \ (s, 3H), 1.53 \ (s, 3H); \ \text{^13C NMR} \ (100 \ \text{MHz, CDCl}_3): \ \delta = 155.6, 151.4, 145.7, 143.5, 133.4, 130.6, 130.4, 129.0, 128.5, 128.3, 128.2, 127.6, 127.2, 124.3, 124.0, 117.9, 106.5, 61.4, 56.3, 16.8; \ \text{HRMS (EI^+): calecd for} \ C_{24}H_{21}NO_3 371.1521, \ \text{found} 371.1511; \ \text{IR (KBr, cm}^{-1}): 2931 \ \text{and 1619}. \]

1-(2,3-Diphenylbenzofuran-4-yl)ethanone O-methyl oxime (3ka)

\[ R_f = 0.64 \ (20\% \ \text{ethyl acetate in} \ \text{n-hexane}); \ \text{colorless oil; ^1H NMR} \ (400 \ \text{MHz, CDCl}_3): \ \delta = 7.59-7.54 \ (m, 3H), 7.43-7.27 \ (m, 9H), 7.13 \ (d, J = 7.2 \ \text{Hz, 1H}), 3.72 \ (s, 3H), 1.59 \ (s, 3H); \ \text{^13C NMR} \ (100 \ \text{MHz, CDCl}_3): \ \delta = 155.6, 154.3, 133.6, 131.6, 130.6, 128.5, 128.3, 127.6, 127.5, 127.0, 124.4, 123.2, 117.6, 111.5, 61.5, 16.7; \ \text{HRMS (EI^+): calecd for} \ C_{23}H_{19}NO_2 341.1416, \ \text{found} 341.1407; \ \text{IR (KBr, cm}^{-1}): 2931 \ \text{and 1604}. \]
1,2-Diphenylanthra[2,1-b]furan-6,11-dione O,O-dimethyl dioxime (3la; mixture of isomers)

R_f = 0.51 (20% ethyl acetate in n-hexane); pale yellow oil; 1H NMR for major isomer (400 MHz, CDCl_3): δ = 8.60 (t, J = 8.8 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.67-7.26 (m, 14H), 4.17 (s, 3H), 3.28 (s, 3H); 13C NMR (100 MHz, CDCl_3): δ = 155.3, 155.1, 152.8, 147.2, 147.0, 145.0, 144.9, 134.9, 134.8, 134.2, 131.5, 130.5, 130.4, 130.3 (2C), 130.0, 129.8, 129.5, 129.2, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.6, 127.0, 126.9, 126.7, 126.3, 124.9, 124.8, 124.2, 121.4, 118.5, 118.4, 112.0, 110.9, 63.0, 62.9, 62.9, 62.04; HRMS (EI): calcd for C_{30}H_{22}N_2O_3 458.1630, found 458.1629; IR (KBr, cm\(^{-1}\)): 2931 and 1565.

1,2,7,8-Tetraphenylanthra[2,1-b:6,5-b’]difuran-6,12-dione O,O-dimethyl dioxime (3ma)

R_f = 0.43 (20% ethyl acetate in n-hexane); yellow solid; mp: 311-314 °C; 1H NMR (400 MHz, CDCl_3): δ = 8.03 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.54-7.29 (m, 20H), 3.28 (s, 6H); 13C NMR (100 MHz, CDCl_3): δ = 154.9, 152.7, 145.2, 134.8, 130.5, 130.4, 128.9, 128.4, 128.3, 128.2, 127.7, 127.1, 125.3, 125.0, 118.4, 110.5, 62.1; HRMS (EI): calcd for C_{44}H_{30}N_2O_4 650.2206, found 650.2215; IR (KBr, cm\(^{-1}\)): 2933 and 1573.

1,2-Diphenyl-6H-indeno[5,4-b]furan-8(7H)-one O-methyl oxime (3na)

R_f = 0.66 (20% ethyl acetate in n-hexane); yellow solid; mp: 150-153 °C; 1H NMR (400 MHz, CDCl_3): δ = 7.56-7.51 (m, 4H), 7.43-7.42 (m, 4H), 7.27-7.22 (m, 4H), 3.31 (s, 3H), 3.08 (t, J=6.4 Hz, 2H), 2.85-2.82 (m, 2H); 13C NMR (100 MHz, CDCl_3): δ = 162.2, 153.7, 144.2, 135.3, 131.4, 130.7, 129.2, 128.2, 128.1, 127.9, 127.3, 126.8, 125.3, 125.1, 121.2, 118.9, 112.8, 61.4, 28.8, 26.3; HRMS (EI): calcd for C_{24}H_{19}NO_2 353.1416, found 353.1417; IR (KBr, cm\(^{-1}\)): 2931 and 1604.
1,2,7-Triphenyl-9H-furo[3,2-f]chromen-9-one O-methyl oxime (3oa)

\[ \text{R}_f = 0.68\ (20\% \text{ ethyl acetate in } n\text{-hexane}); \text{white solid;} \]
\[ \text{mp: } 199-202\ ^\circ\text{C};\text{ }^1\text{H NMR (400 MHz, CDCl}_3\text{): }\delta = 7.89-7.87\ (m, 2H), 7.64 (d, } J = 8.8\ \text{Hz, 1H}, 7.47-7.34\ (m, 10H), 7.31 (d, } J = 8.4\ \text{Hz, 1H}, 7.26-7.25\ (m, 3H), 7.02\ (s, 1H), 3.16\ (s, 3H);\text{ }^1\text{C NMR (100 MHz, CDCl}_3\text{): }\delta = 153.8, 153.7, 151.5, 149.8, 143.1, 136.7, 132.7, 130.8, 129.9, 128.5, 128.2, 128.1, 127.8, 127.8, 127.7, 127.5, 126.8, 125.4, 124.9, 123.6, 114.7, 113.3, 112.4, 93.8, 60.7;\text{ HRMS (EI\textsuperscript{+}): calcd for C}_{30}H_{22}NO_3 443.1521, found 443.1520; IR (KBr, cm\textsuperscript{-1}): 2931 and 1643.\]

6-Methoxy-8,9-diphenyl-3,4-dipropylfuro[2,3-h]isoquinoline (4)

\[ \text{R}_f = 0.23\ (20\% \text{ ethyl acetate in } n\text{-hexane}); \text{yellow solid;} \]
\[ \text{mp: } 155-158\ ^\circ\text{C};\text{ }^1\text{H NMR (400 MHz, CDCl}_3\text{): }\delta = 8.65\ (s, 1H), 7.59-7.50\ (m, 7H), 7.28-7.24\ (m, 3H), 7.14\ (s, 1H), 4.19\ (s, 3H), 3.03-2.86\ (m, 4H), 1.77-1.70\ (m, 4H), 1.12\ (t, } J = 7.2\ \text{Hz, 3H}, 1.01\ (t, } J = 7.2\ \text{Hz, 3H};\text{ }^1\text{C NMR (100 MHz, CDCl}_3\text{): }\delta = 152.5, 151.4, 148.4, 144.2, 142.5, 135.0, 133.8, 130.3, 129.7, 128.5, 128.4, 128.2, 128.1, 126.4, 126.2, 119.3, 118.1, 55.9, 37.6, 30.7, 23.7, 23.6, 14.7, 14.4;\text{ HRMS (EI\textsuperscript{+}): calcd for C}_{30}H_{29}NO_2\text{ 435.2198, found 435.2196; IR (KBr, cm\textsuperscript{-1}): 2962 and 1612.}\]
NOE and NOESY spectra of 3ag

NOE spectra of compound 3ag
NOESY spectra of compound 3ag
References
**1H and 13C NMR Spectra**

$^1$H and $^{13}$C spectra of compound 1a
$^1$H and $^{13}$C spectra of compound 1b
$^1$H and $^{13}$C spectra of compound 1c
$^1$H and $^{13}$C spectra of compound 1d
$^{1}$H and $^{13}$C spectra of compound 1e
$^1$H and $^{13}$C spectra of compound 1f
$^1$H and $^{13}$C spectra of compound 1g
$^1$H and $^{13}$C spectra of compound 1h
$^1$H and $^{13}$C spectra of compound 1i
$^{1}$H and $^{13}$C spectra of compound 1j
$^1$H and $^{13}$C spectra of compound 1k
$^1$H and $^{13}$C spectra of compound II
$^1$H and $^{13}$C spectra of compound 1m
$^1$H and $^{13}$C spectra of compound 1n
$^1$H and $^{13}$C spectra of compound 1o
H and $^{13}\text{C}$ spectra of compound 3aa
$^1$H and $^{13}$C spectra of compound 3ab
$^1$H and $^{13}$C spectra of compound 3ac
$^1$H and $^{13}$C spectra of compound 3ad
$^1$H and $^{13}$C spectra of compound 3ae
$^1$H and $^{13}$C spectra of compound 3af
$^1$H and $^{13}$C spectra of compound 3ag
$^1$H and $^{13}$C spectra of compound 3ah
$^1$H and $^{13}$C spectra of compound 3ah’
$^1$H and $^{13}$C spectra of compound 3ai
$^{1}H$ and $^{13}C$ spectra of compound 3ba
$^1$H and $^{13}$C spectra of compound 3ca
$^1$H and $^{13}$C spectra of compound 3da
$^1$H and $^{13}$C spectra of compound 3ea
$^1$H and $^{13}$C spectra of compound 3fa
$^1$H and $^{13}$C spectra of compound 3ga
$^1$H and $^{13}$C spectra of compound 3ha
$^1$H and $^{13}$C spectra of compound 3ia
$^1$H and $^{13}$C spectra of compound 3ja
$^1$H and $^{13}$C spectra of compound 3ka
$^1$H and $^{13}$C spectra of compound 3la
$^1$H and $^{13}$C spectra of compound 3ma
$^{1}$H and $^{13}$C spectra of compound 3na
$^1$H and $^{13}$C spectra of compound 3oa
$^1$H and $^{13}$C spectra of compound 4
The X-ray structure

X-ray structure of 3aa

Table 1. Crystal data and structure refinement for mo_130319lt_0m (3aa).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Identification code</td>
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<tr>
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<td>Wavelength</td>
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<tr>
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<td>c = 15.1186(7) Å</td>
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F(000) 752

Crystal size 0.30 x 0.28 x 0.26 mm³

Theta range for data collection 1.86 to 26.42°.

Index ranges -14 ≤ h ≤ 8, -13 ≤ k ≤ 13, -16 ≤ l ≤ 18

Reflections collected 14922

Independent reflections 3747 [R(int) = 0.0289]

Completeness to theta = 26.42° 99.6 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9486 and 0.8897

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 3747 / 0 / 246

Goodness-of-fit on F² 1.019

Final R indices [I > 2σ(I)] R1 = 0.0400, wR2 = 0.0983

R indices (all data) R1 = 0.0506, wR2 = 0.1053

Largest diff. peak and hole 0.576 and -0.210 e.Å⁻³
X-ray structure of 3ga

Table 1. Crystal data and structure refinement for 130931LT (3ga).

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<td>Space group</td>
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Theta range for data collection: 1.17 to 26.42°.
Index ranges: -21 <= h <= 21, -12 <= k <= 12, -12 <= l <= 12
Reflections collected: 14119
Independent reflections: 3664 [R(int) = 0.0353]
Completeness to theta = 26.42°: 99.6 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.9486 and 0.7854
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 3664 / 0 / 236
Goodness-of-fit on F²: 1.130
Final R indices [I>2sigma(I)]: R1 = 0.0256, wR2 = 0.0615
R indices (all data): R1 = 0.0388, wR2 = 0.0786
Largest diff. peak and hole: 0.344 and -0.289 e.Å⁻³
X-ray structure of 3ma

![Chemical Structure of 3ma](image)

Table 1. Crystal data and structure refinement for mo_130940lt_0m(3ma).

<table>
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<tr>
<td>Space group</td>
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<td>Density (calculated)</td>
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<td>Crystal size</td>
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<td>Theta range for data collection</td>
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<td>Index ranges</td>
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<td>Independent reflections</td>
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<td>Completeness to theta = 26.48°</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>Final R indices [$I &gt; 2\sigma(I)$]</td>
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<td>Largest diff. peak and hole</td>
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