Supporting Information

Expeditious Synthesis of Pyrano[2,3,4-de]quinolines via Rh(III)-Catalyzed Cascade C–H Activation/Annulation/Lactonization of Quinolin-4-ol with Alkynes

Gang Liao,a Hong Song,a Xue-Song Yin,a,b and Bing-Feng Shi*a

a Department of Chemistry, Zhejiang University, Hangzhou 310027, China.
b School of Chemical & Environmental Engineering, Wuyi University, Jiangmen, 529020, China

*To whom correspondence should be addressed. Email: bfshi@zju.edu.cn

Table of Contents:
1. General information S2
2. Experimental Section S2
2.1 General Procedure for the Preparation of tertiary propargylic alcohols(GP1) S2
2.2 General Procedure for the Rh(III)-Catalyzed reaction (GP2) S4
3. References S21
4. NMR Spectra S22
1. General Information:

1,2-dimethoxyethane was dried by Sodium and stored under nitrogen. All 4-Hydroxyauinoline substrate were purchased from commercial suppliers and used without additional purification. NMR spectra were recorded on a Brueke Avance operating for $^1$H NMR at 400 MHz, $^{13}$C NMR at 100 MHz, and $^{19}$F NMR at 376 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (77.16 ppm for $^{13}$C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization.

2. Experimental Section

2.1 General Procedure for the Preparation of tertiary propargylic alcohols (GP1)

A solution of $n$-butyllithium in hexanes (1.6 M, 33.0 mmol) was added dropwise to a solution of freshly distilled diisopropylamine (33.0 mmol) in dried THF (30 mL) at 0°C. The solution was stirred for 1 h at 0°C, then cooled to -78 °C. Propargyl ester (31.3 mmol) in dried THF (10 mL) was then added dropwise to the reaction mixture. After 1 h at the same temperature, ketone (62.6 mmol) was added, and the resulting mixture was stirred at -78 °C for 3 h. The reaction was quenched with saturated NH$_4$Cl solution, and the mixture was extracted four times with Et$_2$O. The combined organic layers were washed with brine, dried with anhydrous MgSO$_4$, and the solvents evaporated to dryness. The oily residue was purified by flash silica gel column chromatography (hexanes/EtOAc) to get propargylic alcohol.
Compounds 2a, 2ab, 2h, 2k, 2l, [1a] 2m, 2n, 2oz; [1b] 2e [1c]; 2d [1d]; 2h-2z [1e] were known compounds were known compound and were prepared according to literature. [1] 2ac, 2b, 2e, 2f, 2g were prepared according to the GP1.

**Tert-butyl 4-hydroxy-4-methylpent-2-ynoate (2ac)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.55 (s, 6H), 1.49 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.8, 88.7, 83.7, 75.6, 65.1, 30.7, 28.1; HRMS (EI) calcd for C$_{10}$H$_{16}$O$_3$ (M$^+$): 184.1099; found 184.1100.

**Methyl 4-hydroxy-4-methylhex-2-ynoate (2b)**
**Ethyl 4-hydroxy-4-methylhept-2-ynoate (2e)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.23 (q, $J$ = 7.1 Hz, 2H), 2.26 (s, 1H), 1.74 – 1.63 (m, 2H), 1.58 – 1.47 (m, 5H), 1.31 (t, $J$ = 7.1 Hz, 3H), 0.96 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.8, 90.7, 75.2, 68.1, 62.2, 45.2, 29.0, 17.9, 14.2, 14.1. HRMS (EI) calcd for C$_{10}$H$_{16}$O$_3$ (M$^+$): 184.1099; found 184.1096.

**Methyl 4-hydroxy-4,5,5-trimethylhex-2-ynoate (2f)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.77 (s, 3H), 2.13 (s, 1H), 1.48 (s, 3H), 1.05 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.1, 91.2, 75.9, 74.1, 52.8, 38.4, 25.1, 24.3. HRMS (EI) calcd for C$_{10}$H$_{16}$O$_3$ (M$^+$): 184.1099; found 184.1101.

**Methyl 4-hydroxy-4,6-dimethylhept-2-ynoate (2g)**

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.77 (s, 3H), 2.14 (s, 1H), 1.98 – 1.87 (m, 1H), 1.64 (d, $J$ = 6.3 Hz, 2H), 1.54 (s, 3H), 1.01 (dd, $J$ = 6.6, 4.0 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.1, 91.4, 75.2, 68.0, 52.9, 51.1, 30.2, 25.1, 24.2, 24.1. HRMS (EI) calcd for C$_{10}$H$_{16}$O$_3$ (M$^+$): 184.1099; found 184.1097.

### 2.2 General Procedure for the Rh(III)-Catalyzed reaction (GP2)

A mixture of quinolin-4-ol 1 (0.2 mmol), [Cp*RhCl$_2$]$_2$ (0.005 mmol, 0.0025 equiv), AgSbF$_6$ (0.02 mmol, 0.1 equiv), alkyne 2 (0.4 mmol, 2.0 equiv), Cu(OAc)$_2$ (0.4 mmol, 2.0 equiv), LiOTf (0.4 mmol, 2.0 equiv) in 2 mL DME in a 50-mL Schlenck tube (Purged with N$_2$) was heated at 100 °C for 12 h. Then a 1mL ammonium hydroxide was added and then the whole solution was stirred for 5 min. The resulting mixture was filtered with celite. The organic layer was concentrated under reduced pressure and separated on a silica gel column to provide the desired product.
8,8-dimethylfuro[3′,4′:5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3a)

The title compound 3a was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (32.9 mg 65% yield) ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, J = 5.1 Hz, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 6.9 Hz, 1H), 7.67 – 7.60 (m, 1H), 6.91 (d, J = 5.1 Hz, 1H), 1.67 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 175.5, 166.5, 158.8, 152.4, 150.3, 131.8, 127.0, 120.0, 118.0, 116.1, 105.3, 104.2, 81.1, 24.4; HRMS (EI) calcd for C₁₅H₁₁O₃N (M⁺): 253.0739; found 253.0737.

<table>
<thead>
<tr>
<th>Bond precision:</th>
<th>C-C = 0.0027 Å</th>
<th>Wavelength=0.71073</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell:</td>
<td>a=7.2462(9)</td>
<td>b=8.215(1)</td>
</tr>
<tr>
<td></td>
<td>α=90</td>
<td>β=93.583(10)</td>
</tr>
<tr>
<td>Temperature:</td>
<td>293 K</td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>1201.8(3)</td>
<td>1201.7(3)</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21/c</td>
<td>P 21/c</td>
</tr>
<tr>
<td>Hall group</td>
<td>-P 2ybc</td>
<td>-P 2ybc</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C₁₅H₁₁N O₃</td>
<td>C₁₅H₁₁N O₃</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C₁₅H₁₁N O₃</td>
<td>C₁₅H₁₁N O₃</td>
</tr>
<tr>
<td>Mr</td>
<td>253.25</td>
<td>253.25</td>
</tr>
<tr>
<td>Dx,g cm⁻³</td>
<td>1.400</td>
<td>1.400</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
Mu (mm⁻¹) 0.099
F000 528.0
F000’ 528.27
h,k,l max 8,9,24
N ref 2194
T min,T max 0.978, 0.984
T min’ 0.968

Correction method= MULTI-SCAN
Data completeness= 0.998
R(reflections)= 0.0423(1421)
wR2(reflections)= 0.1198(2190)
S = 1.031
Npar = 175

8,8-dimethylfuro[3’,4’:5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3aa)

The title compound 3aa was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (27.0mg 51% yield) 1H NMR (400 MHz, CDCl3) δ 7.76 – 7.67 (m, 2H), 7.63 (dd, J = 8.3, 7.4 Hz, 1H), 6.83 (s, 1H), 2.66 (s, 3H), 1.68 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 175.5, 166.7, 161.7, 159.0, 149.8, 131.9, 126.4, 121.9, 116.3, 115.5, 105.5, 104.1, 81.1, 25.7, 24.4. HRMS (El) calcd for C16H13O3N (M+): 267.0895; found 267.0895.

1,2-dimethoxy-8,8-dimethylfuro[3’,4’:5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3ab)
The title compound 3ab was prepared according to GP2 and was purified by chromatography (EtOAc) to give the product as a faint yellow solid (38.8mg, 76% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.54 \ (d, J = 5.2 \text{ Hz}, 1\text{H}), 7.20 \ (s, 1\text{H}), 6.76 \ (d, J = 5.2 \text{ Hz}, 1\text{H}), 3.98 \ (s, 3\text{H}), 3.94 \ (s, 3\text{H}), 1.65 \ (s, 6\text{H}). \) \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 176.6, 164.5, 158.2, 157.8, 151.5, 149.3, 142.5, 113.9, 113.2, 107.0, 103.6, 103.3, 79.6, 62.6, 56.1, 24.6. HRMS (EI) calcd for C\(_{17}\)H\(_{15}\)O\(_3\)N(M \(^+\)): 313.0950; found 313.0942.

![3-fluoro-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3ac)]

The title compound 3ac was prepared according to GP2 and was purified by chromatography (petroleum ether/dichloromethane/acetone 5:4:1) to give the product as a faint yellow solid (29.8mg, 62% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.78 \ (d, J = 4.8 \text{ Hz}, 1\text{H}), 7.72 \ (dd, J = 8.0, 4.3 \text{ Hz}, 1\text{H}), 7.40 \ (dd, J = 10.9, 8.0 \text{ Hz}, 1\text{H}), 7.04 \ (t, J = 10.1 \text{ Hz}, 1\text{H}), 1.69 \ (s, 6\text{H}). \) \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 174.6 \ (d, J_{C-F} = 2.0 \text{ Hz}), 166.3, 159.0 \ (d, J_{C-F} = 3.1 \text{ Hz}), 156.3 \ (d, J_{C-F} = 256.8 \text{ Hz}), 152.9, 140.8 \ (d, J_{C-F} = 14.6 \text{ Hz}), 119.8 \ (d, J_{C-F} = 3.8 \text{ Hz}), 118.2 \ (d, J_{C-F} = 5.0 \text{ Hz}), 116.0, 115.9 \ (d, J_{C-F} = 12.1 \text{ Hz}), 106.4, 104.2, 81.3, 24.4. HRMS (EI) calcd for C\(_{15}\)H\(_{10}\)O\(_3\)NF(M \(^+\)): 271.0654; found 271.0648.

![2-chloro-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3ad)]

The title compound 3ad was prepared according to GP2 and was purified by chromatography (petroleum ether/dichloromethane/acetone 5:4:1) to give the product as a faint yellow solid (37mg, 64% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.73 \ (d, J = 5.1 \text{ Hz}, 1\text{H}), 7.81 \ (d, J = 1.6 \text{ Hz}, 1\text{H}), 7.76 \ (d, J = 1.7 \text{ Hz}, 1\text{H}), 6.94 \ (d, J = 5.2 \text{ Hz}, 1\text{H}), 1.68 \ (s, 6\text{H}). \) \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 176.3, 166.0, 158.9, 153.4, 150.9, 138.5, 126.0, 123.6, 117.2, 116.5, 105.6, 103.6, 81.4, 24.4. HRMS (EI) calcd for C\(_{15}\)H\(_{10}\)O\(_3\)NCl(M \(^+\)): 287.0349; found 287.0356.
6-bromo-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3ae)

![Chemical Structure](image)

The title compound 3ae was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (47.1mg, 71% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.78 (s, 1H), 7.87 – 7.78 (m, 2H), 7.70 (dd, $J = 8.6, 7.2$ Hz, 1H), 1.73 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.0, 166.2, 155.1, 154.0, 148.7, 131.9, 127.3, 121.5, 118.9, 117.0, 104.8, 100.7, 81.4, 24.4. HRMS (EI) calcd for C$_{15}$H$_{10}$O$_3$NBr (M$^+$): 330.9844; found 330.9841.

6-iodo-8,8-dimethylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3af)

![Chemical Structure](image)

The title compound 3af was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (56.1mg, 74% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.91 (s, 1H), 7.88 – 7.78 (m, 2H), 7.75 – 7.67 (m, 1H), 1.73 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 175.1, 166.1, 155.1, 154.0, 149.1, 132.0, 127.0, 121.3, 118.9, 116.7, 104.8, 81.3, 73.5, 24.3. HRMS (EI) calcd for C$_{15}$H$_{10}$O$_3$NI (M$^+$): 378.9705; found 378.9705.

8-ethyl-8-methylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3b)

![Chemical Structure](image)
The title compound 3b was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (35.8mg, 67% yield). $^1$H NMR (400 MHz, CDCl3) δ 8.73 (d, $J = 5.0$ Hz, 1H), 7.92 – 7.75 (m, 2H), 7.69 (dd, $J = 8.6$, 7.2 Hz, 1H), 6.94 (d, $J = 5.1$ Hz, 1H), 2.11 – 2.01 (m, 1H), 2.01 – 1.92 (m, 1H), 1.67 (s, 3H), 0.98 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ 174.5, 166.9, 158.8, 152.4, 150.4, 131.8, 127.0, 122.0, 118.0, 116.1, 105.4, 105.3, 83.9, 30.2, 22.9, 7.8. HRMS (EI) calcd for C$_{16}$H$_{13}$O$_3$N(M$^+$): 267.0895; found 267.0898.

8,8-diethylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3c)

The title compound 3c was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (33.7mg, 60% yield). $^1$H NMR (400 MHz, CDCl3) δ 8.73 (d, $J = 4.9$ Hz, 1H), 7.94 – 7.76 (m, 2H), 7.69 (dd, $J = 8.6$, 7.2 Hz, 1H), 6.93 (d, $J = 5.1$ Hz, 1H), 2.07 (dq, $J = 14.9$, 7.4 Hz, 2H), 1.97 (dq, $J = 14.7$, 7.4 Hz, 2H), 0.96 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl3) δ 173.3, 167.3, 158.8, 152.4, 150.4, 131.9, 127.0, 121.9, 116.0, 106.7, 105.3, 87.0, 77.2, 28.9, 7.6. HRMS (EI) calcd for C$_{17}$H$_{15}$O$_3$N (M$^+$) 281.1052; found 281.1051.

8-isopropyl-8-methylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3d)

The title compound 3d was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (37.7mg, 67% yield). $^1$H NMR (400 MHz, CDCl3) δ 8.71 (d, $J = 5.0$ Hz, 1H), 7.86 – 7.75 (m, 2H), 7.68 (dd, $J = 8.4$, 7.4 Hz, 1H), 6.93 (d, $J = 5.1$ Hz, 1H), 2.24 – 2.14 (m, 1H), 1.67 (s, 3H), 1.12 (d, $J = 6.8$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ 175.0, 167.1, 158.8, 152.4, 150.3,
131.9, 126.9, 122.0, 118.0, 116.0, 105.4, 105.3, 86.1, 34.6, 21.3, 17.2, 16.8. HRMS (EI) calcd for \( \text{C}_{17}\text{H}_{15}\text{O}_3\text{N}(\text{M}^+) \): 281.1052; found 281.1052.

**8-methyl-8-propylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3e)**

The title compound 3e was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (35.4mg, 63% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.72 (s, 1H), 7.81 (d, \( J = 8.5 \) Hz, 1H), 7.77 (d, \( J = 7.1 \) Hz, 1H), 7.66 (t, \( J = 7.8 \) Hz, 1H), 6.93 (d, \( J = 4.7 \) Hz, 1H), 2.04 – 1.93 (m, 1H), 1.92 – 1.81 (m, 1H), 1.66 (s, 3H), 1.53 – 1.39 (m, 1H), 1.36 – 1.26 (m, 1H), 0.93 (t, \( J = 7.3 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 174.8, 166.9, 158.8, 152.4, 146.9, 131.8, 127.1, 122.1, 116.1, 105.4, 105.2, 83.7, 39.1, 23.3, 16.8, 14.0. HRMS (EI) calcd for \( \text{C}_{17}\text{H}_{15}\text{O}_3\text{N}(\text{M}^+) \): 281.1052 ; found 281.1055.

**8-(tert-butyl)-8-methylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3f)**

The title compound 3f was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (31.7mg, 54% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.71 (d, \( J = 5.1 \) Hz, 1H), 7.86 – 7.76 (m, 2H), 7.68 (t, \( J = 7.8 \) Hz, 1H), 6.93 (d, \( J = 5.1 \) Hz, 1H), 1.67 (s, 3H), 1.13 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 175.3, 167.2, 158.7, 152.4, 150.4, 131.9, 127.0, 122.1, 118.0, 116.1, 105.6, 105.3, 88.4, 37.5, 25.4, 19.3. HRMS (EI) calcd for \( \text{C}_{18}\text{H}_{17}\text{O}_3\text{N}(\text{M}^+) \): 295.1208; found 295.1211.

**8-isobutyl-8-methylfuro[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3g)**

\[ \text{C}_{18}\text{H}_{17}\text{O}_3\text{N} \]
The title compound 3g was prepared according to GP2 and was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (41.3 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 4.8$ Hz, 1H), 7.82 (d, $J = 8.7$ Hz, 1H), 7.78 (d, $J = 7.0$ Hz, 1H), 7.67 (dd, $J = 8.4$, 7.4 Hz, 1H), 6.94 (d, $J = 5.1$ Hz, 1H), 1.99 (dd, $J = 7.8$ Hz, 1H), 1.82 – 1.73 (m, 2H), 1.66 (s, 3H), 0.97 (d, $J = 6.3$ Hz, 3H), 0.92 (d, $J = 6.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.0, 166.9, 158.8, 152.5, 150.4, 131.9, 127.0, 122.1, 118.0, 116.2, 105.3, 105.2, 83.7, 45.4, 24.4, 24.1, 24.0, 23.6. HRMS (EI) calcd for C$_{18}$H$_{17}$O$_3$N(M$^+$): 295.1208 ; found 295.1205.

8,8-diphenylfuro[3′,4′:5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3h)

The title compound 3h was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (38.5mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (s, 1H), 7.89 – 7.81 (m, 2H), 7.74 – 7.66 (m, 1H), 7.53 – 7.46 (m, 4H), 7.43 – 7.39 (m, 6H), 6.98 (d, $J = 4.9$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.4, 166.5, 158.8, 152.5, 150.3, 137.3, 131.9, 129.5, 129.0, 127.5, 127.1, 121.9, 116.6, 105.8, 87.5. HRMS (EI) calcd for C$_{25}$H$_{15}$O$_3$N(M$^+$): 377.1052 ; found 377.1056.

8-methyl-8-phenylfuro[3′,4′:5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3i)
The title compound 3i was prepared according to GP2 and was purified by chromatography (petroleum ether/dichloromethane/acetone 5:4:1) to give the product as a faint yellow solid (33.4mg, 53% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.75 (d, $J = 5.2$ Hz, 1H), 7.88 (d, $J = 8.5$ Hz, 1H), 7.55 – 7.47 (m, 3H), 7.44 – 7.39 (m, 3H), 7.04 (d, $J = 5.2$ Hz, 1H), 6.78 (d, $J = 6.7$ Hz, 1H), 2.18 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.4, 159.3, 153.0, 150.6, 139.9, 138.8, 136.5, 131.0, 129.8, 129.6, 129.3, 126.3, 122.9, 119.7, 117.5, 105.8, 85.4, 23.9. HRMS (EI) calcd for C$_{20}$H$_{13}$O$_3$N(M$^+$): 315.0895; found 315.0895.

8-methyl-8-(p-tolyl)furo[3',4':5,6]pyrano[2,3,4-de]quinolin-10(8H)-one (3j)

The title compound 3j was prepared according to GP2 and was purified by chromatography (petroleum ether/dichloromethane/acetone 5:4:1) to give the product as a faint yellow solid (30.3mg, 46% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (d, $J = 5.2$ Hz, 1H), 7.87 (d, $J = 8.7$ Hz, 1H), 7.52 (dd, $J = 8.6$, 7.3 Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.03 (d, $J = 5.2$ Hz, 1H), 6.77 (d, $J = 7.1$ Hz, 1H), 2.35 (s, 4H), 2.18 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.5, 159.3, 153.0, 150.6, 139.9, 138.7, 133.4, 131.0, 129.9, 129.6, 126.3, 122.9, 119.7, 117.5, 105.8, 85.4, 23.9, 21.3. HRMS (EI) calcd for C$_{21}$H$_{15}$O$_3$N(M$^+$): 329.1052; found 329.1051.

10'H-spirocyclopentane-1,8'-furo[3',4':5,6]pyrano[2,3,4-de]quinolin-10'-one (3k)
The title compound **3k** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (34.6 mg, 62% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (s, 1H), 7.81 (d, $J$ = 8.5 Hz, 1H), 7.76 (d, $J$ = 7.1 Hz, 1H), 7.66 (d, $J$ = 7.8 Hz, 1H), 2.49 – 1.76 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.1, 166.8, 159.0, 152.4, 150.5, 131.9, 127.0, 122.2, 116.0, 105.4, 105.3, 90.9, 36.5, 25.2. HRMS (EI) calcd for C$_{17}$H$_{13}$O$_3$N(M$^+$) 279.0895; found 279.0899.

10’H-spiro[cyclohexane-1,8’-furo[3’,4’:5,6]pyrano[2,3,4-de]quinolin]-10’-one (**3l**)

The title compound **3l** was prepared according to **GP2** and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (42.2 mg, 71% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J$ = 5.1 Hz, 1H), 7.81 (t, $J$ = 8.2 Hz, 2H), 7.68 (dd, $J$ = 8.4, 7.4 Hz, 1H), 6.93 (d, $J$ = 5.1 Hz, 1H), 2.02 – 1.91 (m, 2H), 1.87 – 1.80 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.9, 166.9, 158.9, 152.4, 150.3, 131.8, 126.9, 122.2, 118.1, 116.0, 105.3, 104.4, 82.9, 33.3, 24.4, 21.7. HRMS (ESI) calcd for C$_{18}$H$_{15}$O$_3$N(M$^+$): 293.1052; found 293.1057.

5,6-diphenylpyrano[2,3,4-de]quinoline (**4a**)
The title compound 4a was prepared according to GP2 and was purified by chromatography (petroleum ether/dichloromethane/acetone 5:4:1) to give the product as a faint yellow solid (60.4 mg, 94% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.65 (s, 1H), 7.70 (d, $J$ = 8.5 Hz, 1H), 7.48 (t, $J$ = 7.9 Hz, 1H), 7.44 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 7.28 – 7.17 (m, 4H), 6.82 (d, $J$ = 4.9 Hz, 1H), 6.65 (d, $J$ = 7.3 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.6, 152.3, 150.1, 149.2, 134.8, 133.4, 131.4, 130.7, 129.3, 129.1, 128.9, 128.1, 127.9, 125.2, 119.5, 118.5, 116.2, 103.2. HRMS (EI) calcd for C$_{23}$H$_{15}$ON(M$^+$) 321.1154; found 321.1153.

5,6-di-p-tolylpyrano[2,3,4-de]quinoline (4b)

The title compound 4b was prepared according to GP2 and was purified by chromatography (petroleum ether/dichloromethane/acetone 5:4:1) to give the product as a faint yellow solid (66.4 mg, 95% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 (d, $J$ = 5.1 Hz, 1H), 7.68 (d, $J$ = 8.5 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.24 – 7.17 (m, 4H), 7.13 (d, $J$ = 7.9 Hz, 2H), 7.01 (d, $J$ = 8.0 Hz, 2H), 6.79 (d, $J$ = 5.2 Hz, 1H), 6.64 (d, $J$ = 7.3 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.6, 152.1, 150.0, 149.1, 138.8, 137.6, 131.8, 131.6, 131.3, 130.6, 130.5, 129.9, 128.8, 128.6, 124.7, 118.8, 118.3, 116.0, 103.0, 21.4, 21.3. HRMS (EI) calcd for C$_{25}$H$_{19}$ON(M$^+$): 349.1467; found 349.1470.

5,6-bis(4-(tert-butyl)phenyl)pyrano[2,3,4-de]quinoline (4c)
The title compound 4c was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (81.5 mg, 94% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.61 (d, $J$ = 5.3 Hz, 1H), 7.69 (d, $J$ = 8.5 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.41 (d, $J$ = 8.3 Hz, 2H), 7.27 – 7.13 (m, 6H), 6.79 (d, $J$ = 5.3 Hz, 1H), 6.66 (d, $J$ = 7.3 Hz, 1H), 1.35 (s, 9H), 1.26 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.8, 152.0, 151.1, 149.8, 149.0, 131.8, 131.7, 131.5, 130.5, 130.3, 128.6, 126.2, 124.8, 124.6, 119.0, 118.4, 116.3, 103.1, 34.8, 34.7, 31.5, 31.2. HRMS (EI) calcd for C$_{31}$H$_{31}$ON(M$^+$): 433.2400; found 433.2403.

5,6-bis(4-methoxyphenyl)pyrano[2,3,4-de]quinoline (4d)

The title compound 4d was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (70.2 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.65 (d, $J$ = 5.2 Hz, 1H), 7.71 (d, $J$ = 8.5 Hz, 1H), 7.56 – 7.45 (m, 1H), 7.30 – 7.23 (m, 2H), 7.18 (d, $J$ = 2.7 Hz, 2H), 6.97 (d, $J$ = 8.6 Hz, 2H), 6.82 (d, $J$ = 5.2 Hz, 1H), 6.79 – 6.73 (m, 2H), 6.68 (d, $J$ = 7.3 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.9, 159.7, 159.3, 152.1, 150.0, 151.1, 149.1, 149.0, 150.1, 149.1, 132.0, 131.9, 131.5, 130.5, 127.1, 125.9, 124.6, 118.3, 118.0, 115.9, 114.8, 113.4, 103.1, 55.4, 55.3. HRMS (EI) calcd for C$_{25}$H$_{19}$ON$_3$(M$^+$): 381.1359; found 381.1356.

5,6-bis(2-fluorophenyl)pyrano[2,3,4-de]quinoline (4e)

The title compound 4e was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (57.9
mg, 81% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (d, $J = 4.7$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.42 (t, $J = 7.9$ Hz, 1H), 7.27 – 7.14 (m, 3H), 7.09 (t, $J = 6.9$ Hz, 1H), 7.02 – 6.85 (m, 4H), 6.70 (d, $J = 5.1$ Hz, 1H), 6.51 (d, $J = 7.2$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.8 (d, $J = 2.3$ Hz, 1F), -112.9(d, $J = 2.3$ Hz, 1F). $^{13}$C NMR (101 MHz, CDCl$_3$) 160.6 (d, $J_{C-F}$=248.7 Hz), 160.0 (d, $J_{C-F}$=252.6 Hz), 159.7, 152.1, 149.8, 146.7, 132.2 (d, $J_{C-F}$=3.0 Hz), 131.6 (d, $J_{C-F}$=8.3 Hz), 131.5, 131.2 (d, $J_{C-F}$=2.2 Hz), 130.4 (d, $J_{C-F}$=8.1 Hz), 129.7, 125.5, 124.5 (d, $J_{C-F}$=3.6 Hz), 123.9 (d, $J_{C-F}$=3.6 Hz), 121.6 (d, $J_{C-F}$=16.3 Hz), 121.4 (d, $J_{C-F}$=14.9 Hz), 118.4, 116.6, 116.0, 115.9 (d, $J_{C-F}$=24.4 Hz), 115.9 (d, $J_{C-F}$=19.1 Hz), 103.4. HRMS (EI) calcd for C$_{23}$H$_{13}$OF$_2$N (M$^+$): 357.0960; found 357.0959.

5,6-bis(3-fluorophenyl)pyrano[2,3,4-de]quinoline (4f)

The title compound 4f was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (57.2 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.65 (d, $J = 5.1$ Hz, 1H), 7.73 (d, $J = 8.6$ Hz, 1H), 7.49 (t, $J = 7.9$ Hz, 1H), 7.40 (dd, $J = 14.2$, 7.6 Hz, 1H), 7.17 (dd, $J = 14.2$, 7.6 Hz, 1H), 7.09 (t, $J = 9.0$ Hz, 1H), 7.06 – 6.93 (m, 5H), 6.82 (d, $J = 5.1$ Hz, 1H), 6.63 (d, $J = 7.3$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.4, -112.5. $^{13}$C NMR (101 MHz, CDCl$_3$) 163.5 (d, $J_{C-F}$=248.7 Hz), 162.3 (d, $J_{C-F}$=247.1 Hz), 159.2, 152.5, 150.0, 148.0 (d, $J_{C-F}$=2.7 Hz),136.6 (d, $J_{C-F}$=8.0 Hz), 135.1(d, $J_{C-F}$=8.2 Hz), 131.4, 131.2 (d, $J_{C-F}$=8.5 Hz), 130.5, 129.6 (d, $J_{C-F}$=8.2 Hz), 126.5 (d, $J_{C-F}$=3.1 Hz), 125.8, 124.8 (d, $J_{C-F}$=3.1 Hz), 119.1 (d, $J_{C-F}$=2.0 Hz), 118.3, 117.6 (d, $J_{C-F}$=21.6 Hz), 116.5, 116.4, 116.1 (d, $J_{C-F}$=21.2 Hz), 115.9 (d, $J_{C-F}$=23.7 Hz), 115.5 (d, $J_{C-F}$=21.0 Hz), 103.3. HRMS (EI) calcd for C$_{23}$H$_{13}$OF$_2$N (M$^+$): 357.0960; found 357.0956.

5,6-bis(4-fluorophenyl)pyrano[2,3,4-de]quinolone (4g)
The title compound 4g was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (57.9 mg, 81% yield). $^1$H NMR (400 MHz, CDCl₃) δ 8.63 (d, $J = 5.1$ Hz, 1H), 7.72 (d, $J = 8.6$ Hz, 1H), 7.53 – 7.42 (m, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 2H), 7.10 (t, $J = 8.6$ Hz, 2H), 6.95 – 6.85 (m, 2H), 6.79 (d, $J = 5.2$ Hz, 1H), 6.61 (d, $J = 7.3$ Hz, 1H). $^{19}$F NMR (376 MHz, CDCl₃) δ -110.8, -113.0. $^{13}$C NMR (101 MHz, CDCl₃) 162.8 (d, $J_{C,F}=251.5$ Hz), 161.5 (d, $J_{C,F}=249.0$ Hz), 159.4, 152.2, 149.9, 148.6, 132.5 (d, $J_{C,F}=8.1$ Hz), 131.4, 131.1, 131.0, 130.4 (d, $J_{C,F}=3.6$ Hz), 129.3 (d, $J_{C,F}=3.5$ Hz), 125.3, 118.5, 118.2, 116.6 (d, $J_{C,F}=21.6$ Hz), 116.2, 115.2 (d, $J_{C,F}=21.8$ Hz), 103.2. HRMS (EI) calcd for C$_{23}$H$_{13}$OF$_2$N (M⁺): 357.0960; found 357.0961

5,6-bis(4-chlorophenyl)pyrano[2,3,4-de]quinoline (4h)

The title compound 4h was prepared according to GP2 and was purified by chromatography (petroleum ether / dichloromethane / acetone 5:4:1) to give the product as a faint yellow solid (73.4 mg, 94% yield). $^1$H NMR (400 MHz, CDCl₃) δ 8.66 (s, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.48 (t, $J = 7.9$ Hz, 1H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.23 – 7.15 (m, 6H), 6.81 (d, $J = 4.6$ Hz, 1H), 6.61 (d, $J = 7.3$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl₃) δ 159.3, 152.5, 150.1, 148.4, 135.2, 134.3, 133.0, 132.1, 131.6, 131.4, 130.7, 130.4, 129.9, 128.5, 125.7, 118.8, 116.3, 103.4. HRMS (EI) calcd for C$_{23}$H$_{13}$O$_3$NCl$_2$(M⁺): 389.0374; found 389.0378.
5,6-bis(4-bromophenyl)pyrano[2,3,4-de]quinoline (4i)

The title compound 4i was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (43.1 mg, 41% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.65 (s, 1H), 7.72 (d, $J$ = 8.5 Hz, 1H), 7.55 (d, $J$ = 8.3 Hz, 2H), 7.48 (t, $J$ = 8.0 Hz, 1H), 7.37 (d, $J$ = 8.6 Hz, 2H), 7.19 – 7.07 (m, 4H), 6.80 (d, $J$ = 5.1 Hz, 1H), 6.61 (d, $J$ = 7.3 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.3, 152.4, 150.0, 148.4, 133.4, 133.2, 132.8, 132.4, 132.0, 131.4, 130.6, 129.0, 125.6, 123.6, 122.5, 118.9, 118.3, 116.3, 103.3. HRMS (EI) calcd for C$_{23}$H$_{13}$OBr$_2$N (M$^+$): 476.9358; found 476.9361.

5,6-bis(4-(trifluoromethyl)phenyl)pyrano[2,3,4-de]quinoline (4j)

The title compound 4j was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (75.0 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (d, $J$ = 5.2 Hz, 1H), 7.78 (d, $J$ = 8.5 Hz, 1H), 7.70 (d, $J$ = 8.1 Hz, 2H), 7.57 – 7.45 (m, 3H), 7.42 – 7.36 (m, 4H), 6.83 (d, $J$ = 5.3 Hz, 1H), 6.59 (d, $J$ = 7.3 Hz, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.7, -62.97. $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.3, 152.3, 149.7, 148.2, 138.1, 138.2, 131.6, 131.2, 131.1 (q, $J_{C-F}$=33.6 Hz), 130.5 (q, $J_{C-F}$=33.0 Hz), 129.4, 126.6 (q, $J_{C-F}$=3.7 Hz), 125.9, 125.2 (q, $J_{C-F}$=3.8 Hz), 123.8 (q, $J_{C-F}$=273.4 Hz), 124.0 (q, $J_{C-F}$=273.5 Hz), 119.7, 118.3, 116.7, 103.3. HRMS (EI) calcd for C$_{25}$H$_{13}$OBr$_2$N (M$^+$): 457.0896; found 457.0899.
5,6-diethylpyrano[2,3,4-de]quinoline (4k)

![Chemical structure of 5,6-diethylpyrano[2,3,4-de]quinoline (4k)](image)

The title compound 4k was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (41.0 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (s, 1H), 7.68 (d, $J$ = 8.5 Hz, 1H), 7.59 (t, $J$ = 7.9 Hz, 1H), 6.97 (d, $J$ = 7.3 Hz, 1H), 6.69 (d, $J$ = 5.2 Hz, 1H), 2.62 – 2.40 (m, 4H), 1.26 (t, $J$ = 7.5 Hz, 3H), 1.18 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.0, 153.2, 151.3, 149.7, 131.8, 130.1, 123.5, 115.5, 113.1, 102.9, 23.9, 19.8, 12.9, 12.6. HRMS (EI) calcd for C$_{15}$H$_{15}$ON (M$^+$): 225.1148; found 225.1147.

5,6-dipropylpyrano[2,3,4-de]quinoline (4l)

![Chemical structure of 5,6-dipropylpyrano[2,3,4-de]quinoline (4l)](image)

The title compound 4l was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (39.5 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (d, $J$ = 5.0 Hz, 1H), 7.64 (d, $J$ = 8.5 Hz, 1H), 7.56 (t, $J$ = 7.9 Hz, 1H), 6.92 (d, $J$ = 7.2 Hz, 1H), 6.66 (d, $J$ = 5.2 Hz, 1H), 2.54 – 2.34 (m, 4H), 1.79 – 1.64 (m, 2H), 1.63 – 1.41 (m, 2H), 1.10 – 0.96 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.6, 152.2, 151.8, 150.3, 131.4, 130.3, 124.0, 118.7, 114.5, 113.1, 102.8, 32.5, 28.7, 21.4, 21.2, 14.4, 14.0. HRMS (EI) calcd for C$_{17}$H$_{19}$ON (M$^+$): 253.1461; found 253.1465.

5,6-dibutylpyrano[2,3,4-de]quinoline (4m)

![Chemical structure of 5,6-dibutylpyrano[2,3,4-de]quinoline (4m)](image)
The title compound 4m was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (34.3 mg, 61% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 (s, 1H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 7.3$ Hz, 1H), 6.66 (d, $J = 3.1$ Hz, 1H), 2.54 – 2.36 (m, 6H), 1.71 – 1.62 (m, 3H), 1.59 – 1.50 (m, 3H), 1.45 – 1.28 (m, 11H), 1.00 – 0.86 (m, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.5, 152.3, 151.7, 150.4, 131.4, 130.4, 129.3, 124.1, 114.5, 113.0, 102.9, 32.2, 31.6, 30.6, 27.9, 27.6, 26.7, 22.7, 22.6, 14.2, 14.1. HRMS (EI) calc'd for C$_{21}$H$_{27}$ON (M$^+$):309.2087; found 309.2086.

5,6-di(thiophen-2-yl)pyrano[2,3,4-de]quinoline (4n)

The title compound 4n was prepared according to GP2 and was purified by chromatography (petroleum ether /dichloromethane /acetone 5:4:1) to give the product as a faint yellow solid (30.0 mg, 45% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (s, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.60 (d, $J = 5.0$ Hz, 1H), 7.50 (t, $J = 7.9$ Hz, 1H), 7.30 (d, $J = 4.9$ Hz, 1H), 7.27 – 7.23 (m, 1H), 7.19 (d, $J = 3.5$ Hz, 1H), 7.09 (d, $J = 3.0$ Hz, 1H), 6.96 (t, $J = 4.4$ Hz, 1H), 6.86 (d, $J = 4.9$ Hz, 1H), 6.63 (d, $J = 7.3$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.8, 152.4, 149.7, 146.2, 135.0, 134.4, 131.9, 131.6, 129.9, 129.2, 128.7, 128.6, 128.5, 127.0, 125.2, 116.6, 110.4, 103.3. HRMS (EI) calc'd for C$_{19}$H$_{11}$ONS$_2$ (M$^+$):333.0277; found 333.0280.
3. References

(c) R. M. Carlson, J. R. Peterson, B. J. Hoop, K. J. Jensen, Synthetic Communications, 1982, 12, 977;
(d) S. Yu, N. Keiichi, K. Tanaka, J. Am. Chem. Soc. 2010, 132, 7896;
4. NMR Spectra

2ac
$3ab$

![Diagram of 3ab molecule with spectral data.]
4a
4n