# Electronic Supplementary Information

## ~ Experimental Procedures and Spectral/Analytical Data ~

# Tandem-Type Pd(II)-Catalyzed Oxidative Heck Reaction/ Intramolecular C–H Amidation Sequence: A Novel Route to 4-Aryl-2-Quinolinones

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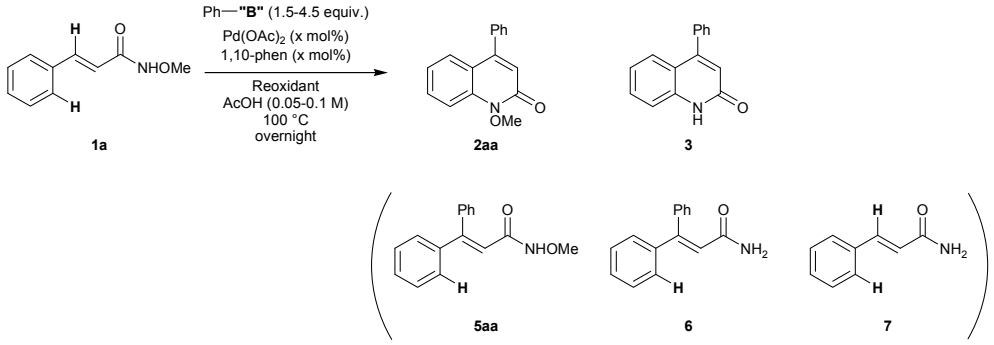
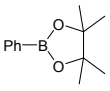
**General Comments**

All reactions were carried out under an Ar atmosphere unless otherwise noted. Acetic acid was purchased from Sigma-Aldrich (>99%) and used as received. All other commercially available materials, including boronic acids and palladium, copper, and silver salts, were used as received. Starting *N*-methoxy-3-arylacrylamides (**1a**–**h**) were prepared from 3-arylacrylic acids and *O*-methylhydroxylamine via the formation of the corresponding acid chlorides.

Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. $^{1}$H-NMR spectra were recorded on a JEOL JNM-AL400 (400 MHz) spectrometer. Chemical shifts (δ) are given from TMS (0 ppm) in $CDCl_3$ or from residual non-deuterated solvent peak in DMSO-$d_6$ (2.49 ppm), and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, td = triple doublet, m = multiplet, br.s = broad singlet, and br = broad signal. $^{13}$C-NMR spectra were recorded on a JEOL JNM-AL400 (100 MHz) spectrometer and chemical shifts (δ) are given from $^{13}CDCl_3$ (77.0 ppm) or DMSO-$d_6$ (39.7 ppm). Mass spectra and high resolution mass spectra were measured on a JEOL JMS-DX303 and JMS-700/JMS-T 100 GC spectrometer, respectively. Elemental analyses were performed by Yanaco CHN CORDER MT-6.

**Table S1** Detailed Results of Optimization of Reaction Conditions[a]




| | | | | Yield[b] (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Entry | Ph–**"B"** (equiv.) | x (mol%) | Reoxidant (equiv.) | **2aa** | **3** | **5aa** | **6** | **7** | **1a** |
| 1 | $(PhBO)_3$ (1.5) | 30 | $K_2S_2O_8$ (2) | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | $(PhBO)_3$ (1.5) | 30 | Oxone (2) | 0 | 4 | 0 | 40 | 0 | 0 |
| 3 | $(PhBO)_3$ (1.5) | 30 | $Cu(OAc)_2$ (2) | 0 | 19 | 0 | 14 | 0 | 0 |
| 4 | $(PhBO)_3$ (1.5) | 30 | $Cu(OAc)_2 \cdot nH_2O$ (2) | 0 | 22 | 0 | 13 | 0 | 0 |
| 5 | $(PhBO)_3$ (1.5) | 30 | $Cu(TFA)_2 \cdot nH_2O$ (2) | 0 | 31 | 0 | 4 | 0 | 0 |
| 6 | $(PhBO)_3$ (1.5) | 30 | $Cu(TFA)_2 \cdot nH_2O$ (2) + AgOTs (2) | 0 | 52 | 0 | 0 | 0 | 0 |
| 7 | $(PhBO)_3$ (1.5) | 30 | $Cu(TFA)_2 \cdot nH_2O$ (2) + $Ag_2CO_3$ (2) | 0 | 50 | 0 | 0 | 0 | 0 |
| 8 | $(PhBO)_3$ (1.5) | 30 | $Cu(TFA)_2 \cdot nH_2O$ (2) + AgOAc (2) | 0 | 53 | 0 | 0 | 0 | 0 |
| 9 | $(PhBO)_3$ (1.5) | 30 | $Cu(TFA)_2 \cdot nH_2O$ (2) + AgOTf (2) | 0 | 61 | 0 | 0 | 0 | 0 |
| 10 | $(PhBO)_3$ (1.5) | 30 | $Cu(TFA)_2 \cdot nH_2O$ (2) + $Ag_2O$ (2) | 0 | 68 | 0 | 3 | 0 | 0 |
| 11 | $(PhBO)_3$ (1.5) | 10 | $Cu(TFA)_2 \cdot nH_2O$ (2) + $Ag_2O$ (2) | 0 | 49 | 0 | 5 | 0 | 0 |
| 12 |  (4.5) | 10 | $Cu(TFA)_2 \cdot nH_2O$ (2) + $Ag_2O$ (2) | 0 | 48 | 0 | 3 | 0 | 0 |
| 13 | $PhBF_3K$ (4.5) | 10 | $Cu(TFA)_2 \cdot nH_2O$ (2) + $Ag_2O$ (1) | 0 | 55 | 0 | 2 | 0 | 0 |
| **14** | **$PhB(OH)_2$ (4.5)** | **10** | **$Cu(TFA)_2 \cdot nH_2O$ (2) + $Ag_2O$ (1)** | **0** | **60** | **0** | **2** | **0** | **0** |
| 15 | $PhB(OH)_2$ (4.5) | 10 | $Cu(TFA)_2 \cdot nH_2O$ (2) + $Ag_2O$ (4) | 66 | 0 | 0 | 0 | 0 | 0 |
| 16 | $PhB(OH)_2$ (4.5) | 10 | $Cu(TFA)_2 \cdot nH_2O$ (1) + $Ag_2O$ (4) | 64 | 0 | 24 | 0 | 0 | 12 |
| **17** | **$PhB(OH)_2$ (4.5)** | **10** | **$Cu(TFA)_2 \cdot nH_2O$ (1) + $Ag_2O$ (8)** | **76** | **0** | **0** | **0** | **0** | **0** |
| 18 | $PhB(OH)_2$ (4.5) | 10 | $Cu(TFA)_2 \cdot nH_2O$ (1) + $Ag_2O$ (10) | 65 | 0 | 0 | 0 | 0 | 0 |
| **19[c]** | **$PhB(OH)_2$ (4.5)** | **10** | **$Cu(TFA)_2 \cdot nH_2O$ (1) + $Ag_2O$ (8)** | **81** | **0** | **0** | **0** | **0** | **0** |
| 20[d] | $PhB(OH)_2$ (4.5) | 10 | $Cu(TFA)_2 \cdot nH_2O$ (1) + $Ag_2O$ (8) | 54 | 0 | 0 | 0 | 0 | 28 |
| 21 | $PhB(OH)_2$ (4.5) | 10 | $Ag_2O$ (8) | 44 | 0 | 44 | 0 | 0 | 0 |
| 22 | $PhB(OH)_2$ (4.5) | 10 | none | 0 | 0 | 16 | 7 | 14 | 16 |
| 23 | $PhB(OH)_2$ (4.5) | 0 | $Cu(TFA)_2 \cdot nH_2O$ (1) | 0 | 0 | 0 | 0 | 22 | 53 |
| 24 | $PhB(OH)_2$ (4.5) | 0 | $Ag_2O$ (8) | 0 | 0 | 0 | 0 | 0 | 95 |

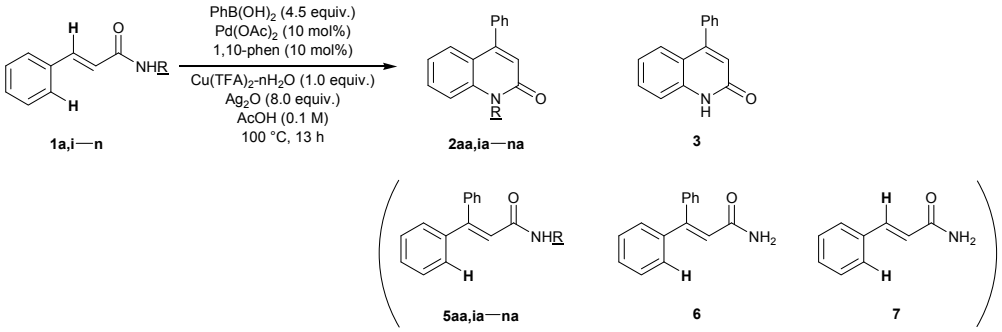
[a] Reactions were carried out on a 0.11 mmol scale.

[b] Isolated yield.

[c] The reaction mixture was first stirred at 100 ºC for 1 h and then stirred at 120 ºC for 10 h.

[d] Under an $O_2$ atmosphere.

**Table S2** Effect of Substituent R on Nitrogen Atom[a]




| | | Yield[b] (%) | | | | | |
|---|---|---|---|---|---|---|---|
| Entry | R | **2** | **3** | **5** | **6** | **7** | **1** |
| 1 | OMe (**1a**) | 76 (**2aa**) | 0 | 0 (**5aa**) | 0 | 0 | 0 |
| 2 | OBn (**1i**) | 56 (**2ia**) | 0 | 17 (**5ia**) | 0 | 0 | 0 |
| 3 | OH (**1j**) | 0 (**2ja**) | 0 | 0 (**5ja**) | 0 | 0 | 58 |
| 4 | OPh (**1k**) | <17 (**2ka**) | 0 | 9 (**5ka**) | 0 | 0 | 0 |
| 5 | OPiv (**1l**) | 0 (**2la**) | 0 | 0 (**5la**) | 20 | 23 | 0 |
| 6[c] | H (**1m**) | 0 (**2ma**) | 0 | 86 (**5ma**) | (= **5ma**) | 0 | 0 |
| 7 | Ts (**1n**) | 0 (**2na**) | 0 | 81 (**5na**) | 0 | 0 | 0 |

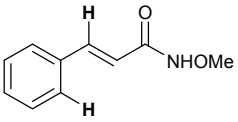
[a] Reactions were carried out on a 0.11 mmol scale.

[b] Isolated yield.

[c] Reaction was carried out in the presence of 2 equiv. of $Cu(TFA)_2 \bullet nH_2O$ and 1 equiv. of $Ag_2O$.

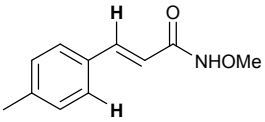
**Representative Procedure for Preparation of Cinnamamides (1a–h)**

***N*-Methoxy-3-phenylacrylamide (1a)**




To a solution of cinnamic acid (2.0 g, 13.5 mmol) in $CH_2Cl_2$ (20 mL) were added oxalyl chloride (1.7 mL, 20.3 mmol) and a few drops of DMF at room temperature. After being stirred for 1 h at room temperature, *O*-methylhydroxylamine hydrochloride (1.7 g, 20.3 mmol) was added. The reaction mixture was cooled to 0 °C and stirred for 20 minutes, and then pyridine (5.4 mL, 40.5 mmol) was added dropwise and stirred for 1 h at room temperature. The resulting mixture was treated with 1N HCl (20 mL) and the aqueous phase was extracted with AcOEt (20 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-AcOEt (2 : 1)] to give **1a** (1.9 g, 81%) as a white solid. Recrystallization from hexane/$CHCl_3$ gave **1a** as white prisms; mp 91–92 ºC (lit.[1] 93–95 °C); IR ν (film, $cm^{-1}$) 3171, 1659, 1627, 1065; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.84 (3H, s), 6.60 (1H, br.s), 7.32 (3H, br.s), 7.50 (2H, br.s), 7.75 (1H, d, *J* = 16.4 Hz), 10.44 (1H, br.s); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 64.4, 117.0, 127.9, 128.8, 129.9, 134.6, 141.8, 164.8; MS *m/z* (relative intensity) 177 ($M^+$, 62), 131 (100); HRMS calcd for $C_{10}H_{11}NO_2$ 177.0790, found 177.0781.

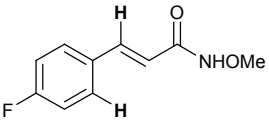
***N*-Methoxy-3-(4-methylphenyl)acrylamide (1b)**




Yield: 86%

Recrystallization from hexane/AcOEt gave **1b** as white prisms; mp 111–112 ºC; IR ν (film, $cm^{-1}$) 3172, 1660, 1626, 1065; $^1$H-NMR (400 MHz, DMSO-$d_6$) δ 2.31 (3H, s), 3.65 (3H, s), 6.35 (1H, d, *J* = 15.6 Hz), 7.21 (2H, d, *J* = 8.0 Hz), 7.46 (2H, d, *J* = 8.0 Hz), 7.46 (1H, d, *J* = 15.6 Hz), 11.23 (1H, br.s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ 21.0, 63.4, 117.4, 127.6, 129.5 (2 signals), 131.8, 139.6, 162.9; MS *m/z* (relative intensity) 191 ($M^+$, 81), 145 (100); HRMS calcd for $C_{11}H_{13}NO_2$ 191.0946, found 191.0945.

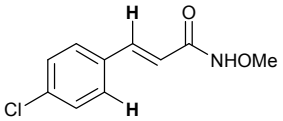
***N*-Methoxy-3-(4-fluorophenyl)acrylamide (1c)**




Yield: 35%

Recrystallization from hexane/AcOEt gave **1c** as white prisms; mp 113–114 ºC; IR ν (film, $cm^{-1}$) 3175, 1661, 1628, 1601, 1510, 1065; $^1$H-NMR (400 MHz, DMSO-$d_6$) δ 3.65 (3H, s), 6.36 (1H, d, *J* = 16.0 Hz), 7.23 (2H, t, *J* = 9.0 Hz), 7.48 (1H, d, *J* = 16.0 Hz), 7.64 (2H, br.s), 11.26 (1H, br.s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ 63.3, 115.8 (*J* = 21.4), 118.4, 129.8 (*J* = 6.6 Hz), 131.2 (*J* = 3.3 Hz), 138.3, 162.5, 162.3 (*J* = 248.5 Hz); MS *m/z* (relative intensity) 195 ($M^+$, 81), 149 (100); HRMS calcd for $C_{10}H_{10}FNO_2$ 195.0696, found 195.0698.

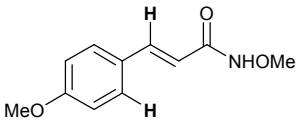
**_N_-Methoxy-3-(4-chlorophenyl)acrylamide (1d)**




Yield: 72%

Recrystallization from hexane/AcOEt gave **1d**; mp 145–146 ºC; IR ν (film, $cm^{-1}$) 3182, 1658, 1625, 1492, 1063; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ 3.67 (3H, s), 6.41 (1H, d, $J$ = 16.4 Hz), 7.45 (2H, d, $J$ = 8.4 Hz), 7.47 (1H, d, $J$ = 16.4 Hz), 7.59 (2H, d, $J$ = 8.4 Hz), 11.29 (1H, br.s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ 63.3, 119.4, 128.9, 129.3, 133.6, 134.1, 138.2, 162.4; MS *m/z* (relative intensity) 211 ($M^+$, 77), 165 (100); HRMS calcd for $C_{10}H_{10}{}^{35}ClNO_2$ 211.0400, found 211.0394.

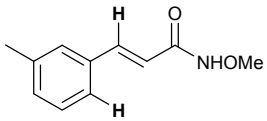
**_N_-Methoxy-3-(4-methoxylphenyl)acrylamide (1e)**




Yield: 68%

Recrystallization from hexane/AcOEt gave **1e** as pale white prisms; mp 130–132 °C (lit.[2] 132–135 °C); IR ν (film, $cm^{-1}$) 3166, 1652, 1608, 1515, 1174; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ 3.64 (3H, s), 3.77 (3H, s), 6.26 (1H, d, $J$ = 15.6 Hz), 6.96 (2H, d, $J$ = 8.0 Hz), 7.44 (1H, d, $J$ = 15.6 Hz), 7.52 (2H, d, $J$ = 8.0 Hz), 11.20 (1H, br.s); $^{13}$C-NMR (100MHz, DMSO-$d_6$) δ 55.3, 63.4, 114.4, 115.9, 127.2, 129.3, 139.3, 160.5, 163.1; MS *m/z* (relative intensity) 207 ($M^+$, 66), 161 (100); HRMS calcd for $C_{11}H_{13}NO_3$ 207.0895, found 207.0879.

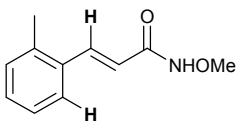
**_N_-Methoxy-3-(3-methylphenyl)acrylamide (1f)**




Yield: 86%

Recrystallization from hexane/AcOEt gave **1f** as white needles; mp 85–86 °C; IR ν (film, $cm^{-1}$) 3171, 1659, 1627, 1066; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ 2.31 (3H, s), 3.66 (3H, s), 6.39 (1H, d, $J$ = 16.0 Hz), 7.19 (1H, d, $J$ = 7.6 Hz), 7.28 (1H, t, $J$ = 7.6 Hz), 7.36 (2H, m), 7.45 (1H, d, $J$ = 16.0 Hz), 11.27 (1H, br.s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ 20.9, 63.4, 118.3, 124.8, 128.1, 128.8, 130.4, 134.5, 138.1, 139.7, 162.7; MS *m/z* (relative intensity) 191 ($M^+$, 61), 145 (100); HRMS calcd for $C_{11}H_{13}NO_2$ 191.0946, found 191.0930; *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.09; H, 7.01; N, 7.34.

**_N_-Methoxy-3-(2-methylphenyl)acrylamide (1g)**

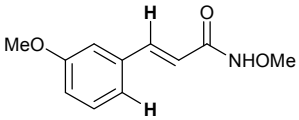



Yield: 93%

Recrystallization from hexane/AcOEt gave **1g** as white prisms; mp 96–97 ºC; IR ν (film, $cm^{-1}$) 3165, 1658, 1624, 1601,

1066; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ 2.34 (3H, s), 3.67 (3H, s), 6.32 (1H, d, $J$ = 16.0 Hz), 7.20–7.28 (3H, m), 7.52 (1H, d, $J$ = 6.4 Hz), 7.72 (1H, d, $J$ = 16.0 Hz), 11.31 (1H, br.s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ 19.3, 63.4, 119.7, 125.9, 126.4, 129.4, 130.7, 133.4, 136.8, 137.0, 162.7; MS *m/z* (relative intensity) 191 ($M^+$, 44), 145 (100); HRMS calcd for $C_{11}H_{13}NO_2$ 191.0946, found 191.0946.

**_N_-Methoxy-3-(3-methoxyphenyl)acrylamide (1h)**

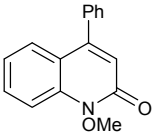



Yield: 75%.

Recrystallization from hexane/$CHCl_3$ gave **1h** as white prisms; mp 109–110 ºC; IR ν (film, $cm^{-1}$) 3165, 1660, 1627, 1581, 1261, 1157; $^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ 3.65 (3H, s), 3.77 (3H, s), 6.42 (1H, d, $J$ = 16.0 Hz), 6.95 (1H, d, $J$ = 8.0 Hz) , 7.13 (1H, s), 7.14 (1H, d, $J$ = 8.0 Hz), 7.31 (1H, t, $J$ = 8.0 Hz), 7.47 (1H, d, $J$ = 16.0 Hz), 11.29 (1H, br.s); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ 55.1, 63.4, 112.7, 115.5, 118.9, 120.0, 130.0, 136.0, 139.5, 159.6, 162.7; MS *m/z* (relative intensity) 207 ($M^+$, 56), 161 (100); HRMS calcd for $C_{11}H_{13}NO_3$ 207.0895, found 207.0890.

**Representative Procedure for 2-Quinolinone Synthesis**

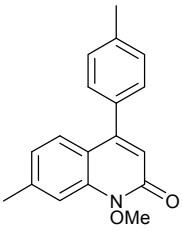
**1-Methoxy-4-phenyl-1*H*-quinolin-2-one (2aa) (Table 1, Entry15)**




A mixture of **1a** (19.8 mg, 0.11 mmol), $PhB(OH)_2$ (**4a**, 61.5 mg, 0.50 mmol), $Pd(OAc)_2$ (2.5 mg, 0.011 mmol), 1,10-phenanthroline (2.0 mg, 0.011 mmol), $Cu(TFA)_2•nH_2O$ (32.4 mg, 0.11 mmol), and $Ag_2O$ (208 mg, 0.090 mmol) in AcOH (2.2 mL, 0.05 M) was stirred at 100 °C overnight. The reaction mixture was extracted with AcOEt (5 mL× 3) and the combined organic layer was washed with brine (10 mL), and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash silica gel column chromatography [hexane-AcOEt (4 : 1)] to give **2aa** (21.3 mg, 76%) as a colorless solid.

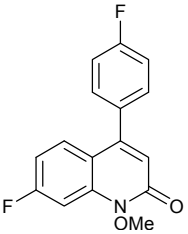
Mp 97–98 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2924, 1666; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.16 (3H, s), 6.70 (1H, s), 7.20 (1H, t, *J* = 7.9 Hz), 7.40−7.42 (2H, m), 7.46−7.53 (3H, m), 7.56 (1H, dd, *J* = 7.9, 1.2 Hz), 7.63 (1H, td, *J* = 7.5, 1.2 Hz), 7.71 (1H, dd, *J* = 7.9, 1.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 62.9, 112.0, 119.6, 121.9, 122.6, 127.5, 128.5, 128.7, 128.8, 131.1, 136.5, 137.9, 150.6, 157.2; MS *m/z* (relative intensity) 251 ($M^+$, 32), 221 (100); HRMS calcd for $C_{16}H_{13}NO_2$ 251.0946, found 251.0917.

**1-Methoxy-7-methyl-4-(4-methylphenyl)-1*H*-quinolin-2-one (2bb)**




Mp 101–102 ºC (colorless scales from AcOEt/hexane); IR ν (film, $cm^{-1}$) 2985, 1668, 1615; $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.45 (3H, s), 2.52 (3H, s), 4.15 (3H, s), 6.62 (1H, s), 7.02 (1H, d, *J* = 8.6 Hz), 7.30 (4H, br), 7.47 (1H, d, *J* = 8.6 Hz), 7.50 (1H, s); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 21.3, 22.0, 62.8, 112.0, 117.7, 120.6, 124.0, 127.5, 128.7, 129.3, 133.9, 138.1, 138.8, 142.0, 150.7, 157.6; MS *m/z* (relative intensity) 279 ($M^+$, 87), 249 (100); HRMS calcd for $C_{18}H_{17}NO_2$ 279.1259, found 279.1252.

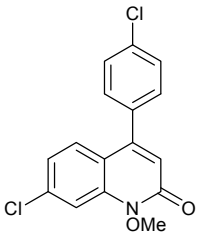
**7-Fluoro-4-(4-fluorophenyl)-1-methoxy-1*H*-quinolin-2-one (2cc)**




Mp 173–174 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2925, 1673, 1622; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.15 (3H, s), 6.61 (1H, s), 6.94 (1H, td, *J* = 8.6, 2.7 Hz), 7.20 (2H, t, *J* = 8.6 Hz), 7.36−7.40 (3H, m), 7.50 (1H, dd, *J* = 8.6, 5.4 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 63.0, 99.1 (*J* = 14.0 Hz), 111.0 (*J* = 11.6 Hz), 115.9 (*J* = 10.7 Hz), 116.2 121.0 (*J* = 1.3 Hz), 129.8 (*J* = 5.0 Hz), 130.5 (*J* = 4.2 Hz), 132.4 (*J* = 2.1 Hz), 139.7 (*J* = 5.8 Hz), 149.3, 157.3, 163.1 (*J*

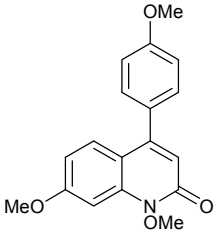
= 123.9 Hz), 164.7 (*J* = 125.2); MS *m/z* (relative intensity) 287 ($M^+$, 55), 257 (100); HRMS calcd for $C_{16}H_{11}F_2NO_2$ 287.0758, found 287.0744.

**7-Chloro-4-(4-chlorophenyl)-1-methoxy-1*H*-quinolin-2-one (2dd)**



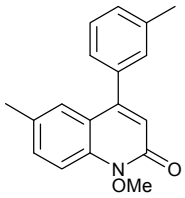

Mp 209–210 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2917, 1674; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.16 (3H, s), 6.66 (1H, s), 7.17 (1H, dd, *J* = 8.8, 2.0 Hz), 7.34 (2H, d, *J* = 8.0 Hz), 7.42 (1H, d, *J* = 8.8 Hz), 7.50 (2H, d, *J* = 8.0 Hz), 7.70 (1H, d, *J* = 2.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 63.1, 112.1, 117.9, 122.1, 123.3, 128.6, 129.1, 130.0, 134.6, 135.4, 137.9, 138.9, 149.0, 157.0; MS *m/z* (relative intensity) 319 ($M^+$, 62), 289 (100); HRMS calcd for $C_{16}H_{11}{}^{35}Cl_2NO_2$ 319.0167, found 319.0173.

**1,7-Dimethoxy-4-(4-methoxyphenyl)-1*H*-quinolin-2-one (2ee)**



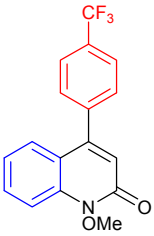

IR ν (film, $cm^{-1}$) 2923, 1664, 1610, 1248; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 3.95 (3H, s), 4.15 (3H, s), 6.52 (1H, s), 6.79 (1H, dd, *J* = 8.8, 2.4 Hz), 7.02 (2H, d, *J* = 8.8 Hz), 7.14 (1H, d, *J* = 2.4 Hz), 7.35 (2H, d, *J* = 8.8 Hz), 7.52 (1H, d, *J* = 8.8 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.4, 55.7, 62.7, 95.3, 111.1, 113.8, 114.0, 118.5, 129.20, 129.25, 130.1, 139.8, 150.3, 157.9, 160.1, 162.3; MS *m/z* (relative intensity) 311 ($M^+$, 100), 281 ($M^+$, 83); HRMS calcd for $C_{18}H_{17}NO_4$ 311.1158, found 311.1158.

**1-Methoxy-6-methyl-4-(3-methylphenyl)-1*H*-quinolin-2-one (2ff)**



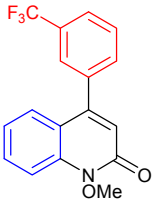

Colorless oil; IR ν (film, $cm^{-1}$) 2925, 1665; $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 2.44 (3H, s), 4.14 (3H, s), 6.66 (1H, s), 7.21 (1H, d, *J* = 7.6 Hz), 7.22 (1H, d, *J* = 1.2 Hz), 7.30 (1H, d, *J* = 7.6 Hz), 7.33 (1H, s), 7.40 (1H, t, *J* = 7.6 Hz), 7.45 (1H, dd, *J* = 8.8, 1.2 Hz), 7.60 (1H, d, *J* = 8.8 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 20.9, 21.5, 62.8, 112.0, 119.8, 121.9, 125.9, 127.3, 128.4, 129.4, 129.5, 132.3, 132.4, 136.1, 136.8, 138.4, 150.6, 157.2; MS *m/z* (relative intensity) 279 ($M^+$, 100); HRMS calcd for $C_{18}H_{17}NO_2$ 279.1259, found 279.1254.

**1-Methoxy-4-(4-trifluorophenyl)-1*H*-quinolin-2-one (2ah)**



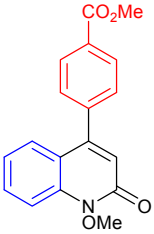

Mp 164–165 ºC (colorless needles from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2917, 1668, 1593, 1325, 1107; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.17 (3H, s), 6.71 (1H, s), 7.23 (1H, t, *J* = 8.0 Hz), 7.45 (1H, d, *J* = 8.0 Hz), 7.55 (2H, d, *J* = 8.4 Hz), 7.66 (1H, t, *J* = 8.0 Hz), 7.74 (1H, d, *J* = 8.0 Hz), 7.79 (2H, d, *J* = 8.4 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 62.9, 112.3, 119.2, 122.5, 122.9, 124.0 (*J* = 275.2 Hz), 125.7 (*J* = 3.6 Hz), 127.2, 129.3, 131.1 (*J* = 33.5 Hz), 131.6, 138.2, 140.2, 149.2, 157.0; MS *m/z* (relative intensity) 319 ($M^+$, 59), 289 (100); HRMS calcd for $C_{17}H_{12}F_3NO_2$ 319.0820, found 319.0808.

**1-Methoxy-4-(3-trifluorophenyl)-1*H*-quinolin-2-one (2ai)**



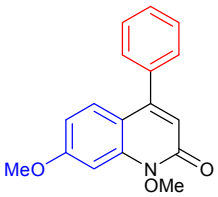

Mp 148–149 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2938, 1668, 1595, 1328, 1125; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.17 (3H, s), 6.71 (1H, s), 7.24 (1H, t, *J* = 8.0 Hz), 7.44 (1H, dd, *J* = 8.0, 1.0 Hz), 7.61–7.78 (6H, m); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 62.9, 112.3, 119.2, 123.0, 123.7 (*J* = 259.0 Hz), 125.6 (*J* = 3.8 Hz), 125.7 (*J* = 3.6 Hz), 127.1, 129.3, 131.2 (*J* = 32.7 Hz), 131.5, 132.1, 137.4, 138.1, 149.1, 157.0; MS *m/z* (relative intensity) 319 ($M^+$, 57), 289 (100); HRMS calcd for $C_{17}H_{12}F_3NO_2$ 319.0820, found 319.0802.

**1-Methoxy-4-(4-methoxycarbonylphenyl)-1*H*-quinolin-2-one (2aj)**



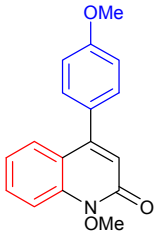

Mp 177–178 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2949, 1723, 1666, 1606, 1278; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.98 (3H, s), 4.16 (3H, s), 6.71 (1H, s), 7.22 (1H, t, *J* = 8.3 Hz), 7.48 (1H, d, *J* = 8.3 Hz), 7.51 (2H, d, *J* = 8.4 Hz), 7.65 (1H, t, *J* = 8.3 Hz), 7.72 (1H, d, *J* = 8.3 Hz), 8.18 (2H, d, *J* = 8.8 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 52.3, 62.9, 112.2, 119.2, 122.2, 122.9, 127.3, 128.9, 129.9, 130.1, 131.4, 138.1, 141.1, 149.6, 157.0, 166.5; MS *m/z* (relative intensity) 309 ($M^+$, 57), 279 (100); HRMS calcd for $C_{18}H_{15}NO_4$ 309.1001, found 309.1007.

**1,7-Dimethoxy-4-phenyl-1*H*-quinolin-2-one (2ea)**



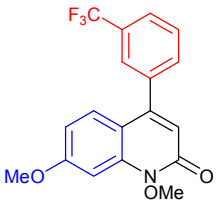

Colorless oil; IR ν (film, $cm^{-1}$) 2935, 1664, 1613, 1382, 1222; $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s), 4.16 (3H, s), 6.54 (1H, s), 6.78 (1H, dd, *J* = 8.8, 2.4 Hz), 7.15 (1H, d, *J* = 2.4 Hz), 7.39–7.52 (6H, m); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.7, 62.7, 95.3, 111.2, 113.6, 118.7, 128.6, 128.8 (2 signals), 129.2, 137.0, 139.8, 150.6, 157.8, 162.4; MS *m/z* (relative intensity) 281 ($M^+$, 100); HRMS calcd for $C_{17}H_{15}NO_3$ 281.1052, found 281.1046.

**1-Methoxy-4-(4-methoxyphenyl)-1*H*-quinolin-2-one (2ea')**



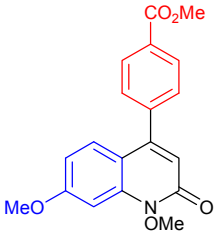

Mp 139–140 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 3383, 1667, 1609, 1250; $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 4.15 (3H, s), 6.68 (1H, s), 4.03 (2H, d, *J* = 8.8 Hz), 7.21 (1H, t, *J* = 7.9 Hz), 7.36 (2H, d, *J* = 8.8 Hz), 7.63 (2H, m), 7.70 (1H, d, *J* = 7.9 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.4, 62.9, 112.1, 114.1, 119.9, 121.7, 122.6, 127.7, 128.9, 130.2, 131.1, 138.1, 150.4, 157.4, 160.2; MS *m/z* (relative intensity) 281 ($M^+$, 61), 251 (100); HRMS calcd for $C_{17}H_{15}NO_3$ 281.1052, found 281.1053.

**1,7-Dimethoxy-4-(4-trifluorophenyl)-1*H*-quinolin-2-one (2ei)**



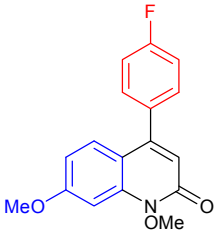

Mp 174–175 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2945, 1666, 1613, 1326, 1105; $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 3.96 (3H, s), 4.17 (3H, s), 6.54 (1H, s), 6.80 (1H, dd, *J* = 9.2, 2.4 Hz), 7.16 (1H, d, *J* = 2.4 Hz), 7.34 (1H, d, *J* = 9.2 Hz), 7.53 (2H, d, *J* = 8.8 Hz), 7.77 (2H, d, *J* = 8.8 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.8, 62.8, 95.5, 111.5, 113.2, 119.2, 123.8 (*J* = 270.5 Hz), 125.55 (*J* = 3.8 Hz), 125.63 (*J* = 3.8 Hz), 128.6, 129.3, 131.2 (*J* = 32.4 Hz), 132.1, 137.7, 139.9, 149.0, 157.5, 162.7; MS *m/z* (relative intensity) 349 ($M^+$, 82), 319 (100); HRMS calcd for $C_{18}H_{14}F_3NO_3$ 349.0926, found 349.0917.

**1,7-Dimethoxy-4-(4-methoxycarbonylphenyl)-1*H*-quinolin-2-one (2ej)**



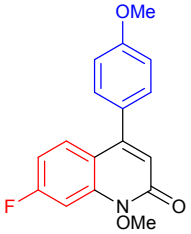

Mp 196–197 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2921, 1722, 1664, 1611, 1279; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s), 3.97 (3H, s), 4.16 (3H, s), 6.54 (1H, s), 6.79 (1H, dd, *J* = 8.8, 2.4 Hz), 7.15 (1H, d, *J* = 2.4 Hz), 7.37 (1H, d, *J* = 8.8 Hz), 7.48 (2H, d, *J* = 8.4 Hz), 8.16 (2H, d, *J* = 8.4 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 52.3, 55.7, 62.7, 95.4, 111.4, 113.1, 118.9, 128.8, 128.9, 129.9, 130.6, 139.9, 141.5, 149.5, 157.6, 162.6, 166.5; MS *m/z* (relative intensity) 339 ($M^+$, 83), 309 (100); HRMS calcd for $C_{19}H_{17}NO_5$ 339.1107, found 339.1109.

**4-(4-Fluorophenyl)-1,7-dimethoxy-1*H*-quinolin-2-one (2ec)**



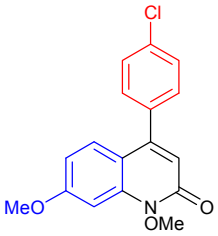

Mp 175–176 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2917, 1667, 1613, 1326; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s), 5.16 (3H, s), 6.52 (1H, s), 6.80 (1H, dd, *J* = 9.2, 2.4 Hz), 7.15 (1H, d, *J* = 2.4 Hz), 7.19 (2H, t, *J* = 8.8 Hz), 7.38 (2H, dd, *J* = 8.8, 5.2 Hz), 7.41 (1H, d, *J* = 9.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.8, 52.7, 95.3, 111.3, 113.5, 115.7 (*J* = 10.7 Hz), 118.9, 128.9, 130.6 (*J* = 4.1 Hz), 132.9 (*J* = 1.7 Hz), 139.8, 157.7, 162.5, 163.0 (*J* = 123.5 Hz); MS *m/z* (relative intensity) 299 ($M^+$, 78), 269 (100); HRMS calcd for $C_{17}H_{14}FNO_3$ 299.0958, found 299.0962.

**7-Fluoro-1-methoxy-4-(4-methoxyphenyl)-1*H*-quinolin-2-one (2ec')**



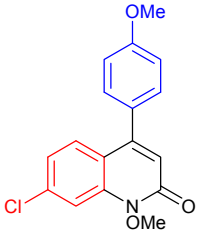

mp 148–149 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2918, 1670, 1620, 1249; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 4.15 (3H, s), 6.62 (1H, s), 6.93 (1H, td, *J* = 8.4, 2.5 Hz), 7.03 (2H, d, *J* = 8.8 Hz), 7.34 (2H, d, *J* = 8.8 Hz), 7.38 (1H, dd, *J* = 9.7, 2.5 Hz), 7.60 (1H, dd, *J* = 9.7, 6.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.4, 63.0, 99.0 (*J* = 14.0 Hz) 110.8 (*J* = 11.5 Hz), 114.2, 116.5, 120.5 (*J* = 1.7 Hz), 128.7, 130.0 (*J* = 4.1 Hz), 130.1, 139.7 (*J* = 5.8 Hz), 150.1, 157.6, 160.3, 164.6 (*J* = 125.1 Hz); MS *m/z* (relative intensity) 299 ($M^+$, 65), 269 (100); HRMS calcd for $C_{17}H_{14}FNO_3$ 299.0958, found 299.0951.

**4-(4-Chlorophenyl)-1,7-dimethoxy-1*H*-quinolin-2-one (2ed)**



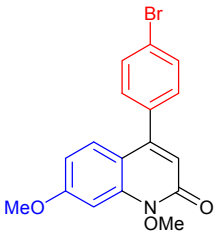

mp 187–188 ºC (yellow scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2935, 1665, 1612; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s), 4.15 (3H, s), 6.50 (1H, s), 6.79 (1H, dd, *J* = 8.8, 2.0 Hz) , 7.14 (1H, d, *J* = 2.0 Hz), 7.34 (2H, d, *J* = 8.4 Hz), 7.39 (1H, d, *J* = 8.8 Hz), 7.47 (2H, d, *J* = 8.4 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.7, 62.3, 95.4, 111.3, 113.3, 118.8, 128.8, 128.9, 130.0, 134.9, 135.3, 139.8, 149.3, 157.6, 162.5; MS *m/z* (relative intensity) 315 ($M^+$, 93), 285 (100); HRMS calcd for $C_{17}H_{14}{}^{35}ClNO_3$ 315.0662, found 315.0645.

**7-Chloro-1-methoxy-4-(4-methoxyphenyl)-1*H*-quinolin-2-one (2ed')**



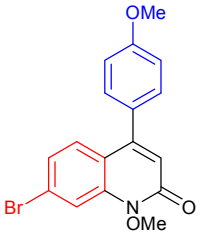

mp 162–163 ºC (yellow scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2936, 1668, 1605, 1249; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 4.15 (3H, s), 6.65 (1H, s), 7.03 (2H, d, *J* = 8.4 Hz), 7.17 (1H, dd, *J* = 8.8, 2.0 Hz), 7.34 (2H, d, *J* = 8.4 Hz), 7.54 (1H, d, *J* = 8.8 Hz), 7.69 (1H, d, *J* = 2.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.4, 63.1, 112.0, 114.2, 118.3, 121.6, 123.1, 128.4, 129.0, 130.1, 137.6, 138.8, 150.0, 157.3, 160.3; MS *m/z* (relative intensity) 315 ($M^+$, 66), 285 (100); HRMS calcd for $C_{17}H_{14}{}^{35}ClNO_3$ 315.0662, found 315.0679.

**4-(4-Bromophenyl)-1,7-dimethoxy-1*H*-quinolin-2-one (2ek)**



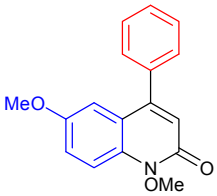

Mp 175–176 ºC (colorless scales from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2934, 1664, 1611, 1222; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s), 4.15 (3H, s), 6.51(1H, s), 6.79 (1H, dd, *J* = 9.2, 2.4 Hz), 7.14 (1H, d, *J* = 2.4 Hz), 7.28 (2H, d, *J* = 8.4 Hz), 7.39 (1H, d, *J* = 9.2 Hz), 7.63 (2H, d, *J* = 8.4 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.8, 62.7, 95.4, 111.4, 113.3, 118.8, 123.2, 128.8, 130.4, 131.9, 135.9, 139.9, 149.4, 157.7, 162.5; MS *m/z* (relative intensity) 361 ($M^+$+2, 78), 359 ($M^+$, 77), 331, (100), 329 (99); HRMS calcd for $C_{17}H_{14}{}^{79}BrNO_3$ 359.0157, found 359.0143.

**7-Bromo-4-(4-methoxyphenyl)-1*H*-quinolin-2-one (2ek')**



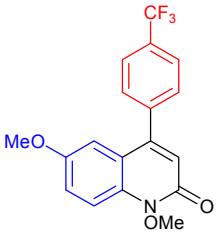

IR ν (film, $cm^{-1}$) 2923, 1670, 1609, 1255; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 4.15 (3H, s), 6.67 (1H, s), 7.03 (2H, d, *J* = 8.8 Hz), 7.31 (1H, dd, *J* = 8.6, 2.0 Hz), 7.33 (2H, d, *J* = 8.8 Hz), 7.46 (1H, d, *J* = 8.6 Hz), 7.86 (1H, d, *J* = 2.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.4, 63.1, 114.2, 114.9, 118.7, 121.8, 125.8, 125.9, 128.4, 129.0, 130.1, 138.9, 150.1, 157.3, 160.3; MS *m/z* (relative intensity) 361 ($M^+$+2, 89), 359 ($M^+$, 89), 331, (100), 329 (100); HRMS calcd for $C_{17}H_{14}{}^{79}BrNO_3$ 359.0157, found 359.0125.

**1,6-Dimethoxy-4-phenyl-1*H*-quinolin-2-one (2ha)**



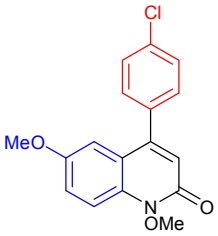

Mp 150–151 ºC (colorless prisms from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2937, 1660, 1034; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.73 (3H, s), 4.15 (3H, s), 6.71 (1H, s), 7.01 (1H, d, *J* = 2.8 Hz), 7.26 (1H, dd, *J* = 9.2, 2.4 Hz), 7.41–7.54 (5H, m), 7.64 (1H, d, *J* = 9.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.7, 62.9, 110.0, 113.5, 119.5, 120.6, 122.7, 128.7, 128.9, 132.7, 136.7, 150.0, 155.2, 156.8; MS *m/z* (relative intensity) 281 ($M^+$, 100); HRMS calcd for $C_{17}H_{15}NO_3$ 281.1052, found 281.1053.

**1,6-Dimethoxy-4-(4-trifluorophenyl)-1*H*-quinolin-2-one (2hh)**




Mp 165–166 ºC (colorless prisms from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2918, 1659, 1325; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.75 (3H, s), 4.15 (3H, s), 6.70 (1H, s), 6.88 (1H, d, *J* = 2.4 Hz), 7.28 (1H, dd, *J* = 9.2, 2.4 Hz), 7.56 (2H, d, *J* = 8.0 Hz), 7.66 (1H, d, *J* = 9.2 Hz), 7.79 (2H, d, *J* = 8.0 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.7, 62.9, 109.6, 113.7, 119.8, 120.0, 123.1, 123.9 (*J* = 264.2 Hz), 125.8 (*J* = 3.8 Hz), 129.1, 131.1 (*J* = 32.1 Hz), 132.8, 140.3, 148.5, 155.4, 156.5; MS *m/z* (relative intensity) MS *m/z* (relative intensity) 349 ($M^+$, 81); HRMS calcd for $C_{18}H_{14}F_3NO_3$ 349.0926, found 349.0940.

**4-(4-Chlorophenyl)-1,6-dimethoxy-1*H*-quinolin-2-one (2hd)**




Mp 187–188 ºC (colorless needles from $CHCl_3$/hexane); IR ν (film, $cm^{-1}$) 2936, 1660; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.75 (3H, s), 4.14 (3H, s), 6.68 (1H, s), 6.93 (1H, d, $J$ = 2.8 Hz), 7.26 (1H, dd, $J$ = 9.2, 2.8 Hz), 7.37 (2H, d, $J$ = 8.8 Hz), 7.49 (2H, d, $J$ = 8.8 Hz), 7.64 (1H, d, $J$ = 9.2 Hz); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 55.7, 62.9, 109.6, 113.7, 119.8, 120.3, 122.9, 129.1, 130.0, 132.7, 135.1, 148.8, 155.3, 156.6; MS *m/z* (relative intensity) 315 ($M^+$, 100); HRMS calcd for $C_{17}H_{14}{}^{35}ClNO_3$ 315.0662, found 315.0651.

**References**

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2) S. A. Glover, A. Goosen, G¥C. W. McCleland and J. L. Schoonraad, *Tetrahedron*, 1987, **43**, 2577.