Ionic Liquid Promoted Palladium-Catalyzed-Multicomponent Cyclocarbonylation of *o*-Iodoanilines and Allenes to form Methylene-2,3-dihydro-1*H*-quinolin-4-ones

Fangguo Ye and Howard Alper*

Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5, Canada.

E-mail: howard.alper@uottawa.ca

Supporting Information

Table of Contents

I	General	S2
II	General procedure for the cyclocarbonylation reactions	S2
III	Characterization data of 2,3-dihydro-1 <i>H</i> -quinolin-4-ones	S3
IV	References	S10
V	¹ H and ¹³ C NMR spectra of 2,3-dihydro-1 <i>H</i> -quinolin-4-ones 3-19	S11

I General

All ^1H and ^{13}C NMR spectra were recorded at room temperature on a 300 or 400 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane as the internal standard and referenced to the proton signal of the solvent (CDCl_3 7.26 ppm for proton, and 77.0 ppm for carbon magnetic resonance spectroscopy). Mass spectra were obtained on a VG7070E mass spectrometer. *o*-Iodoanilines **1a**, **1c** and allene **2a** employed in the reactions were purchased and used as received. BMIM·PF₆ was prepared by the method described in the literature.¹ *o*-Iodoanilines **1b**, **1d**² and **1e**³ and allenes **2b-2g**⁴ and **2h**⁵ were synthesized according to literature procedures.

II General Procedure for the Cyclocarbonylation reactions

A mixture of the 2-iodoaniline **1** (0.5 mmol), allene **2b** (1.0 mmol), Pd₂(dba)₃·CHCl₃ (10 mg, 0.01 mmol), 1,4-bis(diphenylphosphino)butane (4.3 mg, 0.01 mmol), diisopropylethylamine (0.17 mL, 1.0 mmol) and BMIM·PF₆ (2.5 g) was charged in a 45 mL autoclave. The autoclave was purged, pressurized with CO (5 atm) and stirred at 90 °C for 20 hours. The reaction was cooled to room temperature and extracted with diethyl ether. The solvent was removed by rotary evaporation, and the residue was subjected to short flash column chromatography using a mixture of ethyl acetate and hexane as the eluant affording the desired product.

Characterization data for new compounds are as follows.

III Spectral Data:

2,2-Dimethyl-3-methylene-2,3-dihydro-1H-quinolin-4-one (3)

IR(neat): 3327(NH), 1709(C=O), 1651(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.50(s, 6H), 4.30(s, 1H), 5.47(s, 1H), 6.23(s, 1H), 6.60(d, J = 8.4 Hz, 1H), 6.74(t, J = 4.0 Hz, 1H), 7.27-7.32(m, 1H), 7.90(dd, J = 8.0 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 28.7, 56.3, 115.9, 119.1, 128.3, 135.4, 148.8, 149.6, 183.8; HRMS(EI): calcd for $\text{C}_{12}\text{H}_{13}\text{NO}$ 187.0997, found 187.0980.

2,2,6-Trimethyl-3-methylene-2,3-dihydro-1H-quinolin-4-one (4)

IR(neat): 3327(NH), 1709(C=O), 1651(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.48(s, 6H), 2.24(s, 3H), 4.03(s, 1H), 5.44(d, J = 1.2 Hz, 1H), 6.21(d, J = 1.2 Hz, 1H), 6.52(d, J = 8.0 Hz, 1H), 7.12(dd, J = 8.2 Hz, 1.8 Hz, 1H), 7.70(dd, J = 0.8 Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.3, 28.6, 56.3, 115.9, 117.7, 118.8, 127.3, 127.7, 136.8, 147.9, 149.1, 183.9; HRMS(EI): calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$ 201.1154, found 201.1174.

2,2,6,7-Tetramethyl-3-methylene-2,3-dihydro-1H-quinolin-4-one (5)

IR(neat): 3325(NH), 1711(C=O), 1651(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.47(s, 6H), 2.16(s, 3H), 2.19(s, 3H), 3.96(s, 1H), 5.42(d, J = 0.8 Hz, 1H), 6.20(d, J = 0.8 Hz, 1H), 6.39(s, 1H), 7.65(s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 18.6, 20.4, 28.7, 56.3, 116.1, 116.6, 118.5, 126.8, 128.2, 145.9, 148.4, 149.2, 183.5; HRMS(EI): calcd for $\text{C}_{14}\text{H}_{17}\text{NO}$ 215.1310, found 215.1308.

6-Chloro-2,2-dimethyl-3-methylene-2,3-dihydro-1H-quinolin-4-one (6)

IR(neat): 3325(NH), 1711(C=O), 1655(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.48(s, 6H), 4.18(s, 1H), 5.48(s, 1H), 6.24(s, 1H), 6.55(d, J = 8.8 Hz, 1H), 7.22(dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.86(d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 28.6, 56.3, 117.4, 118.5, 119.7, 123.2, 127.5, 135.4, 148.1, 148.2, 182.8; HRMS(EI): calcd for $\text{C}_{12}\text{H}_{12}\text{ClNO}$ 221.0607, found 221.0605.

7-Methoxy-2,2-dimethyl-3-methylene-2,3-dihydro-1H-quinolin-4-one (7)

IR(neat): 3315(NH), 1707(C=O), 1657(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.48(s, 6H), 3.80(s, 3H), 4.18(s, 1H), 5.42(d, J = 0.8 Hz, 1H), 6.00(d, J = 2.4 Hz, 1H), 6.21(d, J = 0.8 Hz, 1H), 6.33(dd, J = 8.8 Hz, 2.4 Hz, 1H),

7.86(d, J = 8.8 Hz 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 28.9, 55.3, 56.4, 97.9, 107.0, 112.2, 118.4, 130.6, 148.9, 151.7, 165.7, 182.3; HRMS(EI): calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ 217.1103, found 217.1126.

(8) IR(neat): 3336(NH), 1707($\text{C}=\text{O}$), 1649($\text{C}=\text{C}$); ^1H NMR (400 MHz, CDCl_3): δ 1.23-1.34(m, 1H), 1.42-1.63(m, 4H), 1.68-1.73(m, 3H), 2.01(d, J = 11.6 Hz, 2H), 4.66(s, 1H), 5.46(d, J = 0.8 Hz, 1H), 6.22(d, J = 0.8 Hz, 1H), 6.65(dd, J = 8.2 Hz, 0.8 Hz, 1H), 6.72(td, J = 7.5 Hz, 0.8 Hz, 1H), 7.29(td, J = 7.6 Hz, 1.6 Hz, 1H), 7.89(dd, J = 7.8 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.5, 25.0, 34.5, 56.8, 115.9, 117.9, 118.2, 118.9, 128.2, 135.4, 149.2, 149.6, 184.5; HRMS(EI): calcd for $\text{C}_{15}\text{H}_{17}\text{NO}$ 227.1310, found 227.1300.

(9) IR(neat): 3358(NH), 1683($\text{C}=\text{O}$), 1651($\text{C}=\text{C}$); ^1H NMR (400 MHz, CDCl_3): δ 1.23-1.33(m, 1H), 1.40-1.61(m, 4H), 1.66-1.71(m, 3H), 2.00(d, J = 12.0 Hz, 2H), 2.24(s, 3H), 4.57(s, 1H), 5.44(s, 1H), 6.21(s, 1H), 6.59(d, J = 8.0 Hz, 1H), 7.12(dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.68(m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.2, 21.5, 25.0, 34.4, 56.8, 116.0, 118.1, 118.7, 127.2, 127.6, 136.7, 147.4, 149.9, 184.6; HRMS(EI): calcd for $\text{C}_{16}\text{H}_{19}\text{NO}$ 241.1467, found 241.1475.

(10) IR(neat): 3340(NH), 1703($\text{C}=\text{O}$), 1649($\text{C}=\text{C}$); ^1H NMR (400 MHz, CDCl_3): δ 1.23-1.33(m, 1H), 1.41-1.60(m, 4H), 1.65-1.71(m, 3H), 2.00(d, J = 12.0 Hz, 2H), 2.16(s, 3H), 2.20(s, 3H), 4.52(s, 1H), 5.42(d, J = 0.8 Hz, 1H), 6.20(d, J = 0.8 Hz, 1H), 6.47(s, 1H), 7.64(s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 18.6, 20.4, 21.5, 25.0, 34.5, 56.8, 116.4, 116.7, 118.3, 126.7, 128.1, 145.8, 147.8, 150.0, 184.2; HRMS(EI): calcd for $\text{C}_{17}\text{H}_{21}\text{NO}$ 255.1623, found 255.1625.

(11) IR(neat): 3315(NH), 1707($\text{C}=\text{O}$), 1645($\text{C}=\text{C}$); ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.33(m, 1H), 1.43-1.62(m, 4H), 1.68-1.73(m, 3H), 2.00(d, J = 11.6 Hz, 2H), 3.80(s, 1H), 4.71(s, 1H), 5.42(d, J = 0.8 Hz, 1H), 6.07(d, J = 2.4 Hz, 1H), 6.21(d, J = 0.8 Hz, 1H), 6.32(dd, J = 9.0 Hz, 2.4 Hz, 1H), 7.85(d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 25.0, 34.8, 55.3, 56.9, 98.1, 106.9, 112.5, 118.2, 130.5, 149.6, 151.1, 165.7, 183.0; HRMS(EI): calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ 257.1416, found 257.1415.

2-Methyl-3-methylene-2-phenyl-2,3-dihydro-1H-quinolin-4-one (12)

IR(neat): 3323(NH), 1705(C=O), 1651(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.79(d, J = 2.0 Hz, 3H), 4.90(s, 1H), 5.41(d, J = 2.8 Hz, 1H), 6.36(s, 1H), 6.71-6.73(m, 2H), 7.20-7.24(m, 1H), 7.27-7.33(m, 3H), 7.41(d, J = 7.2 Hz, 2H), 7.82(dd, J = 8.6 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 28.7, 62.3, 115.7, 118.2, 118.5, 121.2, 126.2, 127.4, 128.4, 128.5, 135.6, 144.2, 148.3, 149.9, 183.7; HRMS(EI): calcd for $\text{C}_{17}\text{H}_{15}\text{NO}$ 249.1154, found 249.1170.

5,5a,6,7,8,9,10,11-Octahydro-5-aza-cyclonona[b]naphthalen-13-one (13) IR(neat): 3323(NH), 1753(C=O), 1659(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.24-1.45(m, 6H), 1.53-1.62(m, 1H), 1.69-1.78(m, 1H), 1.83-1.92(m, 2H), 2.03-2.13(m, 1H), 2.41-2.49(m, 1H), 4.51(s, 1H), 4.67(dd, J = 11.2 Hz, 4.8 Hz, 1H), 6.59(dd, J = 8.4 Hz, 0.8 Hz, 1H), 6.69(td, J = 12.5 Hz, 0.8 Hz, 1H), 7.10-7.15(m, 1H), 7.23-7.28(m, 1H), 7.90(dd, J = 8.0 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 24.4, 26.3, 27.1, 27.2, 34.7, 53.0, 115.9, 117.6, 118.3, 128.2, 134.6, 135.1, 140.1, 149.8, 183.1; HRMS(EI): calcd for $\text{C}_{16}\text{H}_{19}\text{NO}$ 241.1467, found 241.1457.

2-Methyl-5,5a,6,7,8,9,10,11-octahydro-5-aza-cyclonona[b]naphthalen-13-one (14) IR(neat): 3323(NH), 1733(C=O), 1683(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.25-1.45(m, 6H), 1.51-1.59(m, 1H), 1.70-1.76(m, 1H), 1.84-1.91(m, 2H), 2.06-2.16(m, 1H), 2.22(s, 3H), 2.41-2.48(m, 1H), 4.37(s, 1H), 4.65(dd, J = 11.4 Hz, 0.8 Hz, 1H), 6.53(d, J = 8.4 Hz, 1H), 7.08-7.15(m, 2H), 7.70(d, J = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.2, 21.7, 24.4, 26.3, 27.1, 27.2, 34.6, 53.1, 116.0, 118.2, 126.9, 127.6, 134.9, 136.4, 139.9, 147.8, 183.1; HRMS(EI): calcd for $\text{C}_{17}\text{H}_{21}\text{NO}$ 255.1623, found 255.1610.

2-Chloro-5,5a,6,7,8,9,10,11-octahydro-5-aza-cyclonona[b]naphthalen-13-one (15) IR(neat): 3323(NH), 1718(C=O), 1659(C=C); ^1H NMR (400 MHz, CDCl_3): δ 1.24-1.45(m, 6H), 1.54-1.62(m, 1H), 1.70-1.93(m, 3H), 2.03-2.13(m, 1H), 2.42-2.50(m, 1H), 4.52(s, 1H), 4.68(dd, J = 11.4 Hz, 4.8 Hz, 1H), 6.56(d, J = 8.8 Hz, 1H), 7.11-7.14(m, 1H), 7.19(dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.85(d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.5, 24.3, 26.2, 27.1, 27.2, 34.6, 53.0, 117.5, 118.9, 122.8, 127.4, 133.9, 135.0, 141.0, 148.1, 182.1; HRMS(EI): calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}$ 275.1077, found 275.1078.

3-Butylidene-2-propyl-2,3-dihydro-1H-quinolin-4-one (16a) IR(neat): 3333(NH), 1683(C=O), 1651(C=C); ^1H NMR (400 MHz, CDCl_3): δ 0.90(t, J = 7.2 Hz, 3H), 0.97(t, J = 7.4 Hz, 1H), 1.29-1.60(m, 6H),

1.68-1.78(m, 1H), 2.06-2.24(m, 1H), 4.42(dd, $J = 7.6$ Hz, 6.0 Hz, 3H), 4.50(s, 1H), 6.58(dd, $J = 8.4$ Hz, 0.4 Hz, 1H), 6.68-6.72(m, 1H), 6.82-6.86(m, 1H), 7.24-7.29(m, 1H), 7.90(dd, $J = 7.6$ Hz, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 13.8, 14.0, 19.0, 22.1, 30.1, 38.0, 52.9, 115.7, 117.7, 118.6, 128.3, 135.2, 135.8, 139.6, 149.7, 183.6; HRMS(EI): calcd for $\text{C}_{16}\text{H}_{21}\text{NO}$ 243.1623, found 243.1642.

2-Methyl-3-styryl-2,3-dihydro-1H-quinolin-4-one (17a)

IR(neat): 3356(NH), 1703($\text{C}=\text{O}$), 1655($\text{C}=\text{C}$); ^1H NMR (400 MHz, CDCl_3): δ 1.33(d, $J = 6.4$ Hz, 3H), 3.14(td, $J = 9.4$ Hz, 0.8 Hz, 1H), 3.68-3.76(m, 1H), 4.40(s, 1H), 6.14-6.20(m, 1H), 6.57(d, $J = 16.0$ Hz, 1H), 6.67(d, $J = 8.4$ Hz, 1H), 6.74(td, $J = 7.4$ Hz, 0.8 Hz, 1H), 7.20-7.25(m, 1H), 7.28-7.33(m, 3H), 7.38-7.41(m, 2H), 7.85(dd, $J = 8.0$ Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.4, 53.2, 57.6, 115.5, 118.0, 118.4, 124.3, 126.5, 127.6, 128.0, 128.5, 135.0, 135.3, 136.8, 150.4, 194.0; HRMS(EI): calcd for $\text{C}_{18}\text{H}_{17}\text{NO}$ 263.1310, found 263.1305.

3-Benzylidene-2-methyl-2,3-dihydro-1H-quinolin-4-one (18a)

IR(neat): 3279(NH), 1731($\text{C}=\text{O}$), 1651($\text{C}=\text{C}$); ^1H NMR (400 MHz, CDCl_3): δ 1.51(d, $J = 8.8$ Hz, 3H), 4.36(s, 1H), 4.88-4.95(m, 1H), 6.60(d, $J = 11.2$ Hz, 1H), 6.75(t, $J = 10.0$ Hz, 1H), 7.26-7.46(m, 6H), 7.70(s, 1H), 7.97(dd, $J = 10.6$ Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 22.1, 48.9, 116.0, 118.0, 118.4, 128.3, 128.6, 128.7, 129.6, 135.1, 135.3, 135.5, 137.3, 149.2, 184.1; HRMS(EI): calcd for $\text{C}_{17}\text{H}_{15}\text{NO}$ 249.1154, found 249.1146.

(2-Methyl-4-oxo-1,4-dihydro-2H-quinolin-3-ylidene)-acetic acid ethyl ester (19)

IR(neat): 3350(NH), 1713($\text{C}=\text{O}$), 1663($\text{C}=\text{C}$); ^1H NMR (400 MHz, CDCl_3): δ 1.32(t, $J = 7.0$ Hz, 3H), 1.43(d, $J = 6.8$ Hz, 3H), 4.24(qd, $J = 7.0$ Hz, 1.6 Hz, 2H), 4.45(s, 1H), 5.60-5.66(m, 1H), 6.60(d, $J = 8.4$ Hz, 1H), 6.69-6.73(m, 1H), 6.80(d, $J = 0.8$ Hz, 1H), 7.29-7.33(m, 1H), 7.88(dd, $J = 8.0$ Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.2, 22.3, 49.0, 60.9, 116.1, 117.2, 118.0, 121.9, 128.4, 136.3, 149.9, 150.2, 165.6, 181.6; HRMS(EI): calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_3$ 245.1052, found 245.1063.

IV Reference:

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^1H NMR and ^{13}C NMR of **3**

400 MHz, CDCl₃, YF06061

¹H NMR and ¹³C NMR of **5**
400 MHz, CDCl₃, 06201

400 MHz, CDCl₃, YF06141

¹H NMR and ¹³C NMR of **7**

400 MHz, CDCl₃, YF08221

400 MHz, CDCl₃, 07131

400 MHz, CDCl₃, 07201

¹H NMR and ¹³C NMR of **10**
400 MHz, CDCl₃, YF07161

¹H NMR and ¹³C NMR of **11**

400 MHz, CDCl₃, YF07171

400 MHz, CDCl₃, 06262

¹H NMR and ¹³C NMR of **13**

400 MHz, CDCl₃, YF07191

400 MHz, CDCl₃, 07182

¹H NMR and ¹³C NMR of **15**

400 MHz, CDCl₃, YF07061

400 MHz, CDCl₃, 072412

¹H NMR and ¹³C NMR of **17a**

400 MHz, CDCl₃, YF07041-3

300 MHz, CDCl₃, 07261-2

¹H NMR and ¹³C NMR of **19**

400 Mhz, CDCl₃, 07102