Pd(II) Catalysed Intermolecular Diamination of Conjugated Dienes

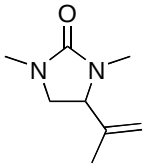
Gregory L. J. Bar, Guy C. Lloyd-Jones* and Kevin I. Booker-Milburn*

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

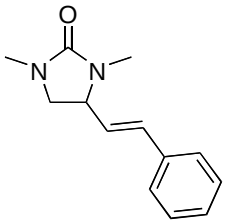
Supplementary Information

General Diamination Procedure – Method A

In a Schlenk tube fitted with a Young's tap was placed bis(acetonitrile)dichloropalladium (0.013 mg, 0.05 mmol, 5 mol%), 1,3-diethyl urea (0.116 g, 1 mmol, 1 equiv.). The vessel was then evacuated and refilled with 1 atm oxygen. Dimethoxyethane (2 mL) was then added and the Schlenk was again evacuated and refilled with oxygen three times. The resulting orange solution was stirred at RT under oxygen atmosphere for 30 mn, at which point the diene was added at once, causing a colour change from orange to red or brownish. The resulting mixture was further stirred for 30 mn under oxygen at RT, and finally, the vessel was sealed at RT under oxygen and heated to 60°C overnight. The solvent was then removed, the residue dissolved in the minimum amount of ethyl acetate and purified by flash chromatography using the appropriate eluent system indicated.



2 days, 49%; R_f 0.25 (5/5 pet ether/EtOAc); ν_{max} (thin film) 1689, 1497, 1395, 1240 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.01 (1H, m, MeC=CH*H*), 4.97 (1H, m, MeC=CH*H*), 3.87 (1H, app.dd, 9.0 Hz, 8.0 Hz, NC*H*CH_2N), 3.41 (1H, app.t, 9.0 Hz, NCHCH*H*N), 3.00 (1H, app.dd, 8.0 Hz, 9.0 Hz, N-CHCH*H*N), 2.79 (3H, s, NCH_3), 2.66 (3H, s, NCH_3), 1.67 (3H, dd, 1.0 Hz, 1.5 Hz, CH_2=C-CH_3) ppm; δ_C (67.5 MHz, $CDCl_3$) 161.7 (C=O), 142.4 (Me*C*=CH_2), 115.1 (MeC=*C*H_2), 62.0 (N*C*HCH_2N), 50.0 (NCH-*C*H_2N), 31.0 (N*C*H_3), 29.2 (N*C*H_3), 16.5 (CH_3C=*C*H_2) ppm; *m/z* (CI, NH_3): 183 (M^++NH_4^+, 7%), 155 (M+H^+, 100%); Found: M+H^+, 155.1177. $C_8H_{15}N_2O$ requires for M+H^+, 155.118

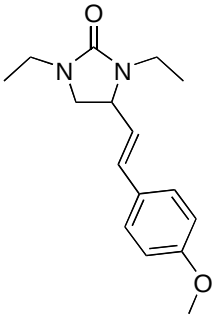


1 day, 78%; R_f 0.25 (5/5 pet ether/EtOAc); ν_{max} (thin film) 1687, 1448, 1242 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.40-7.30 (5H, m, C*H* aromatics), 6.62 (1H, d, 16.0 Hz, Ph-C*H*=CH), 6.06 (1H, dd, 8.5 Hz, 16.0 Hz, Ph-CH=C*H*-), 3.95 (1H, app.q, 8.5 Hz, 8.5Hz, NCH_2-C*H*N), 3.51 (1H, app.t, 8.5 Hz, NCH*H*-CHN), 3.03 (1H, app.t, 8.5 Hz, NCH*H*-CHN), 2.81 (3H, s, NCH_3), 2.72 (3H, s, NCH_3) ppm; δ_C (67.5 MHz, $CDCl_3$)

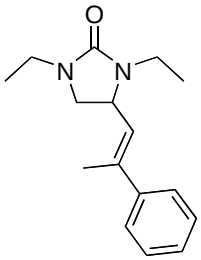
161.6 (*C*=O), 136.0 (C_{phenyl}), 134.3 (Ph-CH=*C*H-), 128.7 (2 x *C*H aromatics), 128.3 (Ph-*C*H=CH-), 127.5 (*C*H aromatics), 126.6 (2 x *C*H aromatics), 59.1 (N*C*H-CH_2N), 51.8 (NCH-*C*H_2N), 31.4 (N*C*H_3), 29.5 (N*C*H_3) ppm; *m/z* (CI, NH_3) 217 (M^++H^+, 100%); Found: M+H^+, 217.1343. $C_{13}H_{17}N_2O$ requires for M+H^+, 217.1341

General Diamination Procedure – Method B

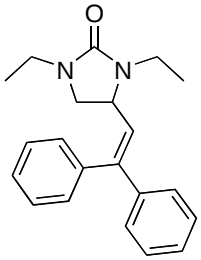
The appropriate diene (1.2 mmol, 1.2 equiv.) was added to a solution of $Pd(MeCN)_2Cl_2$ (0.013 g, 0.05 mmol, 0.05 equiv.), *p*-benzoquinone (0.108 g, 1 mmol, 1 equiv.), *N*, *N*'-diethylurea (0.116 g, 1 mmol, 1 equiv.) in 2 mL dimethoxyethane in a Schlenk tube fitted with a Young's tap. The reaction vessel was then sealed and heated at 60˚C for typically 18 to 48 h depending on the diene. The reaction was then allowed to cool to room temperature, diluted with diethyl ether (20 mL) and washed with 1M aqueous NaOH (3 x 15mL), brine (15 mL), dried with $MgSO_4$, and purified using flash chromatography on silica using a gradient elution system from 4/1 to 1/1 Pet/EtOAc.



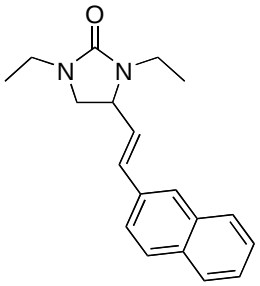
1 day, 80%; R_f 0.32 (5/5 pet ether/EtOAc); ν_{max} (thin film): 1681, 1511, 1243 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.28-7.22 (2H, m, C*H* aromatics), 6.82-6.76 (2H, m, C*H* aromatics), 6.46 (1H, d, 16.0 Hz, CH=C*H*-Phenyl), 5.83 (1H, dd, 16.0 Hz, 9.0 Hz, C*H*=CH-Phenyl), 4.04 (1H, app.q, 9.0 Hz, NCH_2-C*H*N), 3.71 (3H, s, O*C*H_3), 3.39 (1H, app.t, 9.0 Hz, NCH*H*-CHN), 3.37-3.19 (2H, m, NCH*H*CH_3, NCH*H*CH_3), 3.14-3.04 (1H, m, NCH*H*CH_3), 3.00-2.92 (1H, m, NCH*H*CH_3), 2.92 (1H, app.t, 9.0 Hz, NCH*H*-CHN), 1.02 (3H, t, 7.3 Hz, NCH_2C*H*$_3$), 0.98 (3H, t, 7.3 Hz, NCH_2C*H*$_3$); δ_C (100 MHz, $CDCl_3$): 160.6 (*C*=O), 159.7 (*C*OCH_3), 133.3 (*C*H=CH-Ph), 128.8 (CH=CH-C_{phenyl}), 127.8 (2 x CH aromatics), 125.7 (CH=*C*H-C_{phenyl}), 114.2 (2 x CH aromatics), 56.6 (NCH_2-*C*HN), 55.3 (O*C*H_3), 48.9 (N*C*H_2-CHN), 38.7 (N*C*H_2CH_3), 36.5 (N*C*H_2CH_3), 12.8 (NCH_2*C*H_3), 12.7 (NCH_2*C*H_3)
m/z (EI): 274 (M^+, 74%), 188 (79%), 153 (94%), 140 (100%); Found: M^+, 274.1675. $C_{16}H_{22}N_2O_2$ requires for M^+, 274.1681



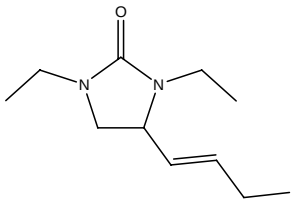
30%, 2 days; R_f 0.25 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1690, 1445, 1243 cm^{-1} δ_H (270 MHz, $CDCl_3$): 7.43-7.25 (5H, m, C*H* aromatics), 5.70 (1H, dq, 9.0 Hz, 1.5 Hz, C*H*=CMePh), 4.50 (1H, app.q, 9.0 Hz, NCH_2-C*H*N), 3.52 (1H, app.t, 9.0 Hz, NC*H*$_2$-CHN), 3.46-3.30 (2H, m, NCH*H*CH_3, NCH*H*CH_3), 3.22-3.13 (1H, m, NCH*H*CH_3), 3.09-3.00 (1H, m, NCH*H*CH_3), 2.96 (1H, app.t, 9.0 Hz, NC*H*$_2$-CHN), 2.15 (3H, br d, 1.5 Hz, HC=CC*H*$_3$), 1.11 (3H, t, 7.3 Hz, NCH_2C*H*$_3$), 1.09 (3H, t, 7.3 Hz, NCH_2C*H*$_3$); δ_C (67.5 MHz, $CDCl_3$): 160.8 (*C*=O), 142.5 (HC=C-*C*$_{Phenyl}$), 139.5 (HC=*C*-C$_{Phenyl}$), 128.5 (2 x CH aromatics), 127.7 (CH aromatics), 126.7 (H*C*=C-C$_{Phenyl}$), 125.8 (2 x CH aromatics), 51.8 (NCH_2-*C*HN), 48.7 (N*C*H_2-CHN), 38.8 (N*C*H_2CH_3), 36.8 (N*C*H_2CH_3), 16.2 (HC=C*C*H_3), 13.1 (NCH_2*C*H_3), 12.8 (NCH_2*C*H_3); m/z (ESI): 281 ($M+Na^+$, 100%), 259 ($M+H^+$, 16%); Found: $M+Na^+$, 281.1630. $C_{16}H_{22}N_2ONa$ requires for $M+Na^+$, 281.1624



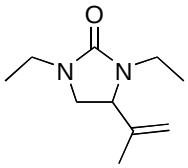
6%, 2 days; R_f 0.41 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1693, 1445, 1245 cm^{-1} δ_H (400 MHz, $CDCl_3$): 7.45-7.34 (4H, m, CH aromatics), 7.35-7.22 (4H, m, CH aromatics), 7.18-7.12 (2H, m, CH aromatics), 6.02 (1H, d, 9.0 Hz, C*H*=CPh_2), 4.10 (1H, app.q, 9.0 Hz, NCH_2-C*H*N), 3.43-3.24 (3H, m, NCH*H*CH_3, NCH*H*CH_3, NCH*H*-CHN), 3.11-3.00 (2H, m, NCH*H*CH_3, NCH*H*-CHN), 1.09 (3H, t, 7.3 Hz, NCH_2C*H*$_3$), 0.89 (3H, t, 7.3 Hz, NCH_2C*H*$_3$); δ_C (100 MHz, $CDCl_3$): 160.5 (*C*=O), 146.1 CH=*C*Ph_2), 141.0 (CH=C*C*$_{Ph}$), 138.9 (CH=C*C*$_{Ph}$), 129.5 (2 x CH aromatics), 128.6 (2 x CH aromatics), 128.4 (2 x CH aromatics), 128.1 (CH aromatics), 127.8 (CH aromatics), 127.4 (*C*H=CPh_2), 127.3 (2 x CH aromatics), 52.3 (NCH_2-*C*HN), 48.8 (N*C*H_2-CHN), 38.8 (N*C*H_2CH_3), 36.8 (N*C*H_2CH_3), 12.9 (NCH_2*C*H_3), 12.8 (NCH_2*C*H_3) m/z (EI): 320 (M^+, 74%), 291 (76%), 234 (74%), 140 (100%); Found: M^+, 320.1885. $C_{21}H_{24}N_2O$ requires for M^+, 320.1888



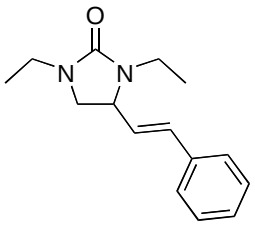
73%, 1 day; R_f 0.38 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1686, 1448, 1244 $cm^{-1;}$ δ_H (270 MHz, $CDCl_3$): 7.86-7.80 (3H, m, CH aromatics), 7.77-7.75 (1H, m, CH aromatics), 7.62-7.58 (1H, m, CH aromatics), 7.51-7.44 (2H, m, CH aromatics), 7.76 (1H, d, 16.0 Hz, CH-CH=C*H*), 6.18 (1H, dd, 16.0 Hz, 9.0 Hz, CH-C*H*=CH), 4.20 (1H, app.q, 9.0 Hz, NCH_2-C*H*N), 3.51 (1H, app.t, 9.0 Hz, NCH*H*-CHN), 3.50-3.41 (1H, m, NCH*H*CH_3), 3.40-3.31 (1H, m, NCH*H*CH_3), 3.27-3.18 (1H, m, NCH*H*CH_3), 3.14-3.05 (1H, m, NCH*H*CH_3), 3.06 (1H, app.t, 9.0 Hz, NCH*H*-CHN), 1.13 (3H, t, 7.3 Hz, NCH_2C*H*$_3$), 1.10 (3H, t, 7.3 Hz, NCH_2C*H*$_3$); δ_C (67.5 MHz, $CDCl_3$): 160.7 (*C*=O), 134.1 (CH=*C*H-napht), 133.6 (*C* aromatic), 133.5 (*C* aromatic), 133.3 (*C* aromatic), 128.6 (*C*H=CH-napht), 128.3 (*C*H aromatic), 128.2 (*C*H aromatic), 127.8 (*C*H aromatic), 126.9 (*C*H aromatic), 126.6 (*C*H aromatic), 126.4 (*C*H aromatic), 123.5 (*C*H aromatic), 56.6 (NCH_2-*C*HN), 48.8 (N*C*H_2-CHN), 38.8 (N*C*H_2CH_3), 36.7 (N*C*H_2CH_3), 12.9 (NCH_2*C*H_3), 12.8 (NCH_2*C*H_3); m/z (EI): 294 (M^+, 82%); Found: M^+, 294.1731. $C_{19}H_{22}N_2O$ requires for $M+H^+$, 294.1732



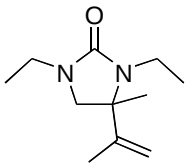
1 day, 60 %; R_f 0.25 (4/6 pet ether/EtOAc); ν_{max} (thin film): 2970, 1737, 1435, 1372, 1216, 1092 cm^{-1}; δ_H (270 MHz, $CDCl_3$): 5.78 (1H, dt, 15.0 Hz, 6.5 Hz, CH-CH=C*H*-), 5.29 (1H, ddt, 15.0 Hz, 9.0Hz, 1.5 Hz, CH-C*H*=CH-), 3.95 (1H, app.q, 9.0 Hz, NCH_2-C*H*N), 3.50-2.80 (6H, m, NCH_2-CHN, N-CH_2-CH_3, N-CH_2-CH_3), 2.15-2.02 (2H, m, CH_3-CH_2-CH=CH-), 1.09 (3H, t, 7.3 Hz, CH_3-CH_2-CH=CH-), 1.03 & 1.01 (2 x 3H, t, 7.3 Hz, N-CH_2-CH_3); δ_C (67.5 MHz, $CDCl_3$): 160.4 (N-*C*=O-N), 138.6 (-H*C*=$CHCH_2CH_3$), 113.0 (-HC=*C*HCH_2CH_3), 52.2 (N-CH_2-*C*H-N), 48.9 (N-*C*H_2-CH-N), 38.7 & 36.3 (N-*C*H_2-CH_3), 20.6 (-HC=CH*C*H_2CH_3), 13.4 (-HC=$CHCH_2$*C*H_3), 12.8 & 12.7 (N-CH_2-*C*H_3)
m/z (CI, NH_3): 197 (100%, $M+H^+$), 99 (57%); Found: $M+H^+$, 197.1646. $C_{11}H_{21}N_2O$ requires for $M+H^+$, 197.1654



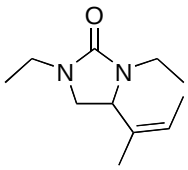
1 day, 81%; R_f 0.28 (4/6 pet ether/EtOAc); ν_{max} (thin film): 1688, 1427, 1247 cm^{-1}; δ_H (270 MHz, $CDCl_3$): 4.96-4.92 (1H, m, C=CH_2), 4.90-4.85 (1H, m, C=CH_2), 4.04-3.97 (1H, dd, 7.0 Hz, 9.0 Hz, NCH_2-C*H*N), 3.38 (1H, m, NCH_2CH$_3$), 3.34 (1H, app.t, 9.0 Hz, NCH*H*CH-N), 3.17 (1H, m, NCH*H*CH$_3$), 3.16 (1H, m, NCH*H*CH$_3$), 2.94 (1H, dd, 9.0 Hz, 7.0 Hz, NCH*H*-CHN), 2.76 (1H, m, NCH*H*CH$_3$), 1.59 (3H, br s, CH_3-C=CH$_2$), 1.02 (3H, t, 7.2 Hz, N-CH$_2$CH_3), 0.97 (3H, t, 7.2 Hz, N-CH$_2$CH_3) ppm; δ_C (67.5 MHz, $CDCl_3$) 160.5 (C=O), 142.9 (Me*C*=CH$_2$), 115.1 (MeC=*C*H$_2$), 58.9 (N*C*H-CH$_2$N), 46.8 (NCH-*C*H$_2$N), 38.4 (N*C*H$_2$CH$_3$), 36.4 (N*C*H$_2$CH$_3$), 16.5 (*C*H$_3$C=CH$_2$), 12.7 (NCH$_2$*C*H$_3$), 12.3 (NCH$_2$*C*H$_3$) ppm; *m/z* (CI, NH_3): 183 (M^++H^+, 100%); Found: M+H^+, 183.1490. $C_{10}H_{19}N_2O$ requires for M+H^+, 183.1497



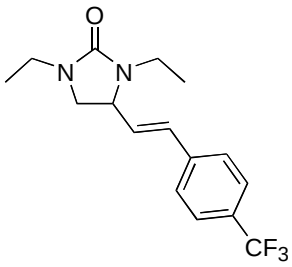
1 day, 99%; R_f 0.25 (5/5 pet ether/EtOAc); ν_{max} (thin film) 1687, 1448, 1242 cm^{-1}; δ_H (270 MHz, $CDCl_3$): 7.42-7.23 (5H, m, C*H* aromatics), 6.61 (1H, d, 16.0 Hz, PhC*H*=CH-), 6.06 (1H, dd, 9.0 Hz, 16.0 Hz, PhCH=C*H*-), 4.16 (1H, app.q, 9.0 Hz, NCH$_2$-C*H*N), 3.56-2.98 (6H, m, NCH_2-CHN, NCH_2CH$_3$, NCH_2CH$_3$), 1.11 (3H, t, 7.3 Hz, NCH$_2$CH_3), 1.07 (3H, t, 7.3Hz, NCH$_2$CH_3) ppm; δ_C (67.5 MHz, $CDCl_3$) 160.6 (*C*=O), 136.0 (CHCH=CH*C*$_{phenyl}$), 133.9 (*C*H=CH-phenyl), 128.8 (2 x *C*H aromatics), 128.3 (*C*H aromatics), 128.0 (CH=*C*H-phenyl), 126.6 (2 x *C*H aromatics), 56.5 (NCH$_2$-*C*HN), 48.8 (N*C*H$_2$-CHN), 38.7 (N*C*H$_2$CH$_3$), 36.6 (N*C*H$_2$CH$_3$), 12.9 (NCH$_2$*C*H$_3$), 12.8 (NCH$_2$*C*H$_3$) ppm; *m/z* (CI, NH_3) 245 (M^++H^+, 100%); Found: M+H^+, 245.1648. $C_{15}H_{21}N_2O$ requires for M+H^+, 245.1654



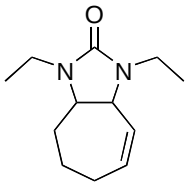
1 day, 82%; R_f 0.25 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1688, 1425 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 4.89-4.87 (1H, m, C=CH_2), 4.86 (1H, br s, C=CH_2), 3.27-3.09 (4H, NCH_2CH$_3$, NCH*H*CH$_3$, NCH*H*-CN), 2.95 (1H, d, 9.0 Hz, NCH*H*-CN), 2.86-2.71 (1H, m, NCH*H*CH$_3$), 1.62 (3H, d, 1.0 Hz, CH_3-C=CH$_2$), 1.36 (3H, s, NCH$_2$CH_3), 1.07 (3H, t, 7.3 Hz, NCH$_2$CH_3), 1.01 (3H, t, 7.3 Hz, NCH$_2$CH_3); δ_C (100 MHz, $CDCl_3$): 159.9 (*C*=O), 146.7 (CH$_3$-*C*=CH$_2$), 113.2 (CH$_3$-C=*C*H$_2$), 61.2 (NCH$_2$-*C*N), 54.5 (N*C*H$_2$-CN), 38.2 (N*C*H$_2$CH$_3$), 35.2 (N*C*H$_2$CH$_3$), 23.9 (NC-*C*H$_3$), 18.6 (*C*H$_3$-C=CH$_2$), 15.5 (NCH$_2$*C*H$_3$), 12.7 (NCH$_2$*C*H$_3$); m/z (ESI): 219 (M+Na^+, 100%), 197 (M+H^+, 18%); Found: M+Na^+, 219.1472. $C_{11}H_{20}N_2ONa$ requires for M+Na^+, 219.1468



2 days, 43%; R_f 0.25 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1685, 1425, 1252 cm^{-1} δ_H (400 MHz, $CDCl_3$): 5.61-5.48 (1H, m, C=C*H*), 4.01 (1H, dd, 7.5 Hz, 9.0 Hz, NCH_2-C*H*N), 3.51-3.16 (4H, m, N*C*H_2CH_3, NCH*H*CH_3, NCH*H*-CHN), 3.00 (1H, dd, 9.0 Hz, 7.5 Hz, NCH*H*-CHN), 2.86-2.77 (1H, m, N*C*H_2CH_3), 1.64 (3H, d, 6.0 Hz, CH_3-C=CHC*H*$_3$), 1.54 (3H, br s, C*H*$_3$-C=CH), 1.09 (3H, t, 7.3 Hz, NCH_2C*H*$_3$), 1.01 (3H, t, 7.3 Hz, NCH_2C*H*$_3$); δ_C (100 MHz, $CDCl_3$): 160.6 (*C*=O), 133.4 (CH_3-*C*=CHCH$_3$), 124.4 (CH_3-C=*C*HCH$_3$), 60.7 (NCH_2-*C*HN), 46.7 (N*C*H_2-CHN), 38.5 (N*C*H_2CH_3), 36.2 (N*C*H_2CH_3), 13.3 (*C*H_3-C=CHCH$_3$), 12.7 (NCH_2*C*H_3), 12.4 (NCH_2*C*H_3), 10.4 (CH_3-C=CH*C*H$_3$); m/z (ESI): 219 ($M+Na^+$, 100%), 197 ($M+H^+$, 20%); Found: $M+Na^+$, 219.1472. $C_{11}H_{20}N_2ONa$ requires for $M+Na^+$, 219.1468

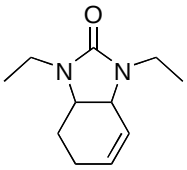


2 days, >99%; R_f 0.38 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1683, 1428, 1254 cm^{-1} δ_H (400 MHz, $CDCl_3$): 7.59 (2H, d, 8.5 Hz, CH aromatics), 7.49 (2H, d, 8.5 Hz, CH aromatics), 6.65 (1H, d, 16.0 Hz, NCH-CH=C*H*), 6.19 (1H, dd, 16.0Hz, 9.0 Hz, NCH-C*H*=CH), 4.19 (1H, app.q, 9.0 Hz, NC*H*-CH=CH), 3.52 (1H, app.t, 9.0 Hz, NCH-CH*H*N), 3.48-3.39 (1H, m, NCH*H*CH_3), 3.38-3.28 (1H, m, NCH*H*CH_3), 3.27-3.17 (1H, m, NCH*H*CH_3), 3.12-3.00 (2H, m, NCH*H*CH_3, NCH-CH*H*N), 1.12 (3H, t, 7.3 Hz, NCH_2C*H*$_3$), 1.08 (3H, t, 7.3 Hz, NCH_2C*H*$_3$); δ_C (100 MHz, $CDCl_3$): 160.4 (*C*=O), 139.5 (CH=CH-*C*phenyl), 132.3 (NCH-*C*H=CH), 130.8 (NCH-CH=*C*H), 129.9 (q, 32.3 Hz, *C*-CF_3), 126.8 (4 x CH aromatics), 125.5 (q, 3.8 Hz, C-*C*F_3), 56.1 (N*C*H-CH_2N), 48.5 (NCH-*C*H_2N), 38.6 (N*C*H_2CH_3), 36.6 (N*C*H_2CH_3), 12.7 (NCH_2*C*H_3), 12.6 (NCH_2*C*H_3); m/z (EI): 312 (M^+, 100%); Found: M^+, 312.1441. $C_{16}H_{19}N_2OF_3$ requires for M^+, 312.1449

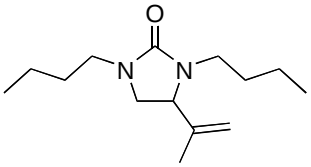


2 days, 68%; R_f 0.20 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1668, 1451, 1260 cm^{-1} δ_H (400 MHz, $CDCl_3$): 5.68 (1H, dtd, 11.5 Hz, 6.5 Hz, 2.0 Hz, NCH-CH=C*H*), 5.50-5.44 (1H, m, NCH-C*H*=CH), 4.33-4.27 (1H, m, NC*H*-CH=CH), 3.58 (1H, dt, 9.0 Hz,

3.5 Hz, NC*H*-CH_2), 3.52-3.35 (2H, m, NCH_2CH_3), 3.01-2.88 (2H, m, NCH_2CH_3), 2.17-2.03 (2H, m, NCH-CH_2-CH_2-CH_2), 1.79-1.71 (1H, m, NCH-CH_2-CH_2-CH_2), 1.63-1.40 (3H, m, NCH-CH_2-CH_2-CH_2), 1.01 (3H, t, 7.3 Hz, NCH_2CH_3), 1.00 (3H, t, 7.3 Hz, NCH_2CH_3); δ_C (100 MHz, $CDCl_3$): 159.7 (*C*=O), 130.0 (NCH-CH=*C*H), 126.4 (NCH-*C*H=CH), 55.0 (N*C*H-CH=CH), 54.5 (N*C*H-CH_2), 35.9 (NCH_2CH_3), 35.7 (NCH_2CH_3), 26.5 NCH-CH_2-CH_2-*C*H_2), 25.6 (NCH-*C*H_2-CH_2-CH_2), 25.6 (NCH-CH_2-*C*H_2-CH_2), 12.9 (NCH_2CH_3), 12.8 (NCH_2CH_3); m/z (ESI): 231 ($M+Na^+$, 100%), 209 ($M+H^+$, 15%); Found: $M+Na^+$, 231.1473. $C_{12}H_{20}N_2O_1Na$ requires for $M+Na^+$, 231.1468



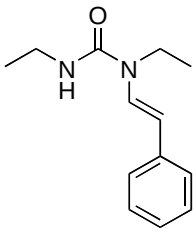
1 day, 15% or 1day 36% with 5h addition of benzoquinone via syringe pump; R_f 0.30 (4/6 pet ether/EtOAc); ν_{max} (thin film) 1685, 1427, 1252 $cm^{-1;}$ δ_H (400 MHz, $CDCl_3$): 6.00 (1H, ddd, 10.3 Hz, 4.0 Hz, 1.0Hz, NCH-CH=C*H*), 5.75 (1H, m, NCH-C*H*=CH), 3.91 (1H, m, NC*H*-CH=CH), 3.69 (1H, dt, 7.5 Hz, 3.5 Hz, NC*H*-CH_2), 3.56-3.45 (2H, m, NCH_2CH_3), 3.09-2.97 (2H, m, NCH_2CH_3), 2.16-2.05 (1H, m, NCH-CH_2-CH_2), 1.99-1.88 (1H, m, NCH-CH_2-CH_2), 1.85-1.68 (2H, m, (2H, m, NCH-CH_2-CH_2), 1.13 (3H, t, 7.0 Hz, NCH_2CH_3), 1.11 (3H, t, 7.0 Hz, NCH_2CH_3); δ_C (100 MHz, $CDCl_3$): 160.3 (*C*=O), 131.5 (NCH-CH=*C*H), 122.8 (NCH-*C*H=CH), 51.9 (N*C*H-CH=CH), 50.5 (N*C*H-CH_2), 35.9 (NCH_2CH_3), 35.7 (NCH_2CH_3), 22.7 (NCH-CH_2-*C*H_2), 21.2 (NCH-*C*H_2-CH_2), 13.2 (NCH_2CH_3), 12.8 (NCH_2CH_3); m/z (ESI): 217 ($M+Na^+$, 100%), 195($M+H^+$, 20%); Found: $M+Na^+$, 217.1314. $C_{11}H_{18}N_2ONa$ requires for $M+Na^+$, 217.1311



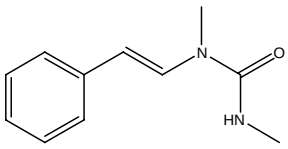
1 day, 81 %. As 9/1 mixture of regioisomers; R_f 0.60 (4/6 pet ether/EtOAc); ν_{max} (thin film) 2970, 1757, 1435, 1364, 1228, 1104 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 5.01-4.98 (1H, m, C=CH*H*), 4.96-4.93 (1H, m, C=CH*H*), 4.06 (1H, dd, 6.5 Hz, 9.0 Hz, NCH_2-C*H*N), 3.50-3.38 (2H, m, NCH-CH*H*N, NCH*H*-CH_2), 3.23-3.13 (2H, m, NCH*H*-CH_2, NCH*H*-CH_2), 3.08-3.01 (1H, m, NCH*H*-CH_2), 2.81-2.70 (1H, m, NCH-CH*H*N), 1.57 (3H, m, CH_3-C=CH_2), 1.55-1.22 (8H, m,), 0.92 (3H, t, 7.3 Hz, CH_2CH_3), 0.90 (3H, t, 7.3 Hz, CH_2CH_3); δ_C (100 MHz, $CDCl_3$): 161.1 (*C*=O), 143.2 (*C*=CH_2), 115.1 (C=*C*H_2), 59.1 (N*C*H-CH_2N), 47.5 (NCH-*C*H_2N), 43.8 (NCH_2), 41.2 (NCH_2), 29.6 (*C*H_2), 29.4 (*C*H_2), 20.0 (*C*H_2), 19.9 (*C*H_2), 16.3 (*C*H_3-C=CH_2), 13.7(CH_2CH_3), 13.6 (CH_2CH_3); m/z (ESI): 261 (100%, $M+Na^+$), 239 (20%, $M+H^+$); Found: $M+Na^+$, 261.1944. $C_{14}H_{26}N_2ONa$ requires for $M+Na^+$, 261.1937.

Amination of Styrene

Styrene and 1,3-diethylurea were reacted according to the General Diamination Procedure (Method B) above:



1 days, 44%; R_f 0.22 (6/4 pet ether/EtOAc); ν_{max} (thin film) 3330, 1626, 1533, 1245 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 7.54 (1H, d, 14.5 Hz, NC*H*=CH), 7.38-7.15 (4H, m, CH aromatics), 7.13-7.07 (1H, m, CH aromatics), 5.79 (1H, d, 14.5 Hz, NCH=C*H*), 5.23 (1H, br s, NH), 3.63 (2H, q, 6.8 Hz, NC*H*$_2$CH$_3$), 3.36-3.28 (2H, m, NC*H*$_2$CH$_3$), 1.21 (3H, t, 7.3 Hz, NCH$_2$C*H*$_3$), 1.16 (3H, t, 7.3 Hz, NCH$_2$C*H*$_3$); δ_C (100 MHz, $CDCl_3$): 155.4 (*C*=O), 137.6 (NCH=CH-*C*phenyl), 128.7 (2 x CH aromatics), 127.6 (NCH=*C*H), 125.7 (CH aromatics), 125.2 (2 x CH aromatics), 108.2 (N*C*H=CH), 38.9 (N*C*H$_2$CH$_3$), 15.4 (NCH$_2$*C*H$_3$), 12.6 (NCH$_2$*C*H$_3$); m/z (ESI): 241 ($M+Na^+$, 100%) Found: $M+Na^+$, 241.1317. $C_{13}H_{18}N_2ONa$ requires for $M+Na^+$, 241.1311



Bis(acetonitrile)dichloropalladium (0.013 mg, 0.05 mmol, 5 mol%), cuprous chloride (0.005 g, 0.005 mmol, 5 mol%) and 1,3-dimethylurea (0.088 g, 1 mmol, 1 equiv.) were placed in a Schlenk tube with a Young's valve tap. The Schlenk tube was evacuated and refilled with oxygen, and dimethoxyethane (2 mL) was added. The resulting yellow solution was stirred under oxygen (1 atm) for approximately 30 min to get a pale green/blue solution. Finally, styrene (0.520 g, 5 mmol, 5 equiv.) was added to the reaction mixture. Under oxygen, the Schlenk was sealed and the reaction allowed to proceed at 50 ^oC for 3 days. The resuling solution was adsorbed on silica and flash column chromatography afforded the title compound as a yellow oil in 52 % yield (0.1 g). Yellow oil, R_f 0.22 (5/5 pet ether/EtOAc), ν_{max} (thin film) 3335, 1629, 1528, 1317, 1260 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.66 (1H, d, 13.5 Hz, NC*H*=CHPh), 7.30-7.24 (5H, m, C*H* aromatics), 5.74 (1H, d, 13.5 Hz, NCH=C*H*Ph), 5.45 (1H, m, N*H*CH$_3$), 3.11 (3H, =CHN(C=O)C*H*$_3$), 2.84 (3H, d, NHC*H*$_3$) ppm; δ_C (67.5 MHz, $CDCl_3$) 156.6 (*C*=O), 137.5 (*C*–CH=CH), 128.8 (2x*C*H aromatic), 128.5 (*C*H aromatic), 125.6 (C–CH=*C*H-N), 125.1 (2x*C*H aromatic), 108.0 (C–*C*H=CH-N), 31.0 (N*C*H$_3$) , 27.7 (HN*C*H$_3$) ppm