Dendritic effects in catalysis by Pd complexes of bidentate phosphines on a dendronized support: Heck vs. carbonylation reactions

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Supporting Information
General

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Solvents were dried prior to use. Dry NMP was purchased from Sigma-Aldrich. Reagents were obtained from Sigma-Aldrich, Fluka, Strem Chemicals or Merck at the highest available purity and used as received. Pd(dba)₂ was prepared according to known procedure. All resins used are 1% crosslinked divinylbenzene-styrene copolymer, 100-200 mesh, with loading 0.77-1.30 mmol/g and were purchased from Novabiochem. HPLC grade acetonitrile and water were purchased from Bio-Lab and Merck respectively and used after filtration. HPLC experiments were carried out using an Inertsil ODS-3v column on a Jasco chromatograph equipped with a UV/Vis detector with acetonitrile and water as the eluting solvents.

Characteristic of Gn(CO₂Me) resins

G₁(CO₂Me)
Prepared from Wang Bromo PS (0.76 mmol/g).
Yield >99%, purity >99%, loading 0.69 mmol/g.

Following TFA-induced cleavage: ¹H NMR (200 MHz, CDCl₃/TFA 1:1): δ 8.35 (t, J = 1.3 Hz, 1H), 7.86 (d, J = 1.3 Hz, 2H), 4.06 (s, 6H). ¹³C NMR (100.8 MHz, CDCl₃/TFA 1:1): δ 168.4, 154.8, 130.9, 123.8, 121.5, 53.1.

G₂(CO₂Me)
Prepared from G₁(Cl) (0.50 mmol/g).
Yield >99%, purity >99%, loading 0.42 mmol/g.

Following TFA-induced cleavage: ¹H NMR (200 MHz, CDCl₃/TFA 1:1): δ 8.35 (s, 2H), 7.93 (s, 4H), 7.20 (s, 1H), 7.05 (s, 2H), 4.06 (s, 12H). ¹³C NMR (100.8 MHz, CDCl₃/TFA 1:1): δ 168.6, 154.8, 157.0, 138.1, 130.7, 123.6, 121.0, 119.5, 114.0, 69.6, 53.1.

G₃(CO₂Me)
Prepared from G₂(Cl) (0.30 mmol/g).
Yield >99%, purity >95%, loading 0.26 mmol/g.

Following TFA-induced cleavage: ¹H NMR (200 MHz, CDCl₃/TFA 1:1): δ 8.33 (s, 4H), 7.91 (s, 12H). ¹³C NMR (100.8 MHz, CDCl₃/TFA 1:1): δ 168.5, 158.5, 158.4, 138.5, 137.8, 130.7, 123.6, 120.9, 119.7, 119.4, 114.0, 113.8, 69.9, 69.7, 53.1.

Characterization of Gn(serinol-OH) resins

G₁(serinol-OH)
Prepared from G₁(Cl) (0.50 mmol/g).
Yield >99%, purity >99%, loading 0.47 mmol/g.

Following TFA-induced cleavage: ¹H NMR (200 MHz, CDCl₃/TFA 1:1): δ 7.19 (m, 3H), 4.73 (s, 4H), 4.43 (s, 4H), 4.29-4.04 (m, 2H). ¹³C NMR (100.8 MHz, CDCl₃/TFA 1:1): δ 156.7, 132.2, 131.8, 110.9, 62.9, 58.1, 55.8.

G₂(serinol-OH)
Prepared from G₂(Cl) (0.30 mmol/g).
Yield 90%, purity >95%, loading 0.25 mmol/g.

Following TFA-induced cleavage: ¹H NMR (200 MHz, CDCl₃/TFA 1:1): δ 7.56 (br, NH), 7.21-6.62 (m, 9H), 5.16 (s, 12H). ¹³C NMR (100.8 MHz, CDCl₃/TFA 1:1): δ 168.5, 158.5, 158.4, 138.5, 137.8, 130.7, 123.6, 120.9, 119.7, 119.4, 114.0, 113.8, 69.9, 69.7, 53.1.
4.92 (m, 4H), 4.74 (m, 4H), 4.45 (m, 8H), 4.11 (m, 16H-xH), 3.70 (m, xH). Partial $^{13}$C NMR (100.8 MHz, CDCl$_3$/TFA 1:1): $\delta$ 132.0, 117.9, 114.2, 112.3, 69.5, 62.9, 58.0, 55.6.

$G3$(serinol-OH)
Prepared from $G3$(Cl) (0.26 mmol/g).
Yield >99%, purity >95%, loading 0.23 mmol/g.
Following TFA-induced cleavage: $^1$H NMR (200 MHz, CDCl$_3$/TFA 1:1): $\delta$ 7.6 (br, NH), 7.24-7.07 (m, 21H), 5.08 (m, 8H), 4.78 (m, 8H), 4.50 (m, 16H), 4.20-3.96 (m, 32H). Partial $^{13}$C NMR (100.8 MHz, CDCl$_3$/TFA 1:1): $\delta$ 132.0, 117.9, 69.6, 63.3, 58.0, 55.7.

Characterization of G$n$(serinol-Cl) resins

$G1$(serinol-Cl)
Prepared from $G1$(serinol-OH) (0.47 mmol/g).
Yield >99 %, purity >99%, loading 0.44 mmol/g.
Following TFA-induced cleavage: $^1$H NMR (200 MHz, CDCl$_3$/TFA 1:1): $\delta$ 8.04 ( br, NH), 7.25 (m, 3H), 4.50 (s, 4H), 4.03 (s, 10H). $^{13}$C NMR (100.8 MHz, CDCl$_3$/TFA 1:1): $\delta$ 156.5, 131.5, 124.3, 119.2, 59.9, 50.1, 39.3. MS: found (m/z), 373.1; calcd for C$_{14}$H$_{22}$N$_2$O (MH$^+$) 373.1.

$G2$(serinol-Cl)
Prepared from $G2$(serinol-OH) (0.25 mmol/g).
Yield >99 %, purity >95%, loading 0.23 mmol/g.
Following TFA-induced cleavage: $^1$H NMR (200 MHz, CDCl$_3$/TFA 1:1): $\delta$ 8.09 ( br, NH), 7.20-6.70 (m, 9H), 5.20 (m, 4H), 4.46 (m, 8H), 4.01 (m, 20H). $^{13}$C NMR (100.8 MHz, CDCl$_3$/TFA 1:1): $\delta$ 159.8, 138.1, 134.0, 124.4, 119.3, 118.7, 114.3, 69.8, 60.0, 52.9, 39.6.

$G3$(serinol-Cl)
Prepared from $G3$(serinol-OH) (0.23 mmol/g).
Yield 53 %, purity >95%, loading 0.11 mmol/g.
Following TFA-induced cleavage: $^1$H NMR (200 MHz, CDCl$_3$/TFA 1:1): $\delta$ 8.12 (br, NH), 7.13-6.99 (m, 21H), 5.09 (m, 12H), 4.50 (m, 16H), 4.01 (m, 40H). Partial $^{13}$C NMR (100.8 MHz, CDCl$_3$/TFA 1:1): $\delta$ 159.9, 132.3, 132.1, 131.5, 129.3, 129.1, 69.9, 59.8, 50.3, 39.5.

References