Supplementary material

PHOSPHINE FREE TETRADENTATE SALICYLALDIMINE LIGAND COMPLEXED WITH PALLADIUM: FIRST APPLICATION IN HECK REACTIONS

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Characterization of the [DAB-dendr-[1,2-N=CH-C₆H₄-OH]₄ [PdCl₂]₂

1. DAB-dendr-(CN)₄¹

IR (neat): $\nu = 2248\text{ cm}^{-1}$. ¹H NMR (60 MHz, CDCl₃): $\delta = 1.58$ (m, 4H, NCH₂CH₂CH₂CH₂N), 2.42-2.62 (m, NCH₂CH₂CH₂CH₂N & CH₂CN), 2.81-3.0 (t, 8H, NCH₂CH₂CN).

2. DAB-dendr-(NH₂)₄¹

IR (neat): $\nu = 3441, 3201\text{ cm}^{-1}$.

3. DAB-dendr-[1,2-N=CH-C₆H₄-OH]₄²

IR (KBr): $\nu = 3082, 1627, 1394, 1275\text{ cm}^{-1}$. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.41$ (br m, 4 H, -NCH₂CH₂core), 1.99 (m, 8 H, -NCH₂CH₂branches), 2.40 (t, 4H, -NCH₂ core), 2.62 (br, t, 8 H, -NCH₂branches), 3.69 (t, 8 H, C=NCH₂), 6.83-6.99 (m, 4 H, ArH), 7.16-7.26 (m, 12 H, ArH), 8.32 (s, 4 H, N=CH). MS (ESI): $m/z = 733.45$.

4. [DAB-dendr-[1,2-N=CH-C₆H₄-OH]₄ [PdCl₂]₂

mp 183 °C (dec). IR (KBr): $\nu = 2926, 1621, 1313\text{ cm}^{-1}$. MS (ESI): $m/z = 1083.8\text{ [M}^+]$. Anal Calcd for C₄₄H₅₄Cl₄N₆O₅Pd₂: C, 47.97; H, 4.94; N, 7.63. Found: C, 48.04; H, 5.06; N, 7.26.

Characterization of products of Heck reaction

1. (*E*) Cinnamic acid (**4a**):³

IR (CHCl₃): $\nu = 3424, 3030, 2917, 1695, 1633, 1221, 1171, 979 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 6.42$ (d, $J = 15.9 \text{ Hz}$, 1 H, CH), 7.55 (m, 6 H), 7.72 (d, $J = 16 \text{ Hz}$, 1 H, CH).

2. (*E*) Cinnamionitrile (**4b**):⁴

IR (CHCl₃): $\nu = 2924, 2216, 1619, 1182, 748 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 5.93$ (d, $J = 16.8 \text{ Hz}$, 1H, CH), 7.35-7.74 (m, 6 H, CH & ArH).

3. (*E*) Methyl cinnamate (**4c**):⁴

IR (CHCl₃): $\nu = 2949, 1715, 1636, 1170, 863 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 3.75$ (3 H, s, OCH₃), 6.49 (d, $J = 16.14 \text{ Hz}$, 1 H, CH), 7.50 (m, 5 H, ArH), 7.76 (d, $J = 16.14 \text{ Hz}$, 1 H, CH).

4. (*E*) Ethyl cinnamate (**4d**):⁵

IR (CHCl₃): $\nu = 2928, 1712, 1638, 1175, 864 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 1.46$ (t, $J = 23.7 \text{ Hz}$, 3 H, CH₃), 4.41 (q, $J = 21.3 \text{ Hz}$, 2 H, CH₂), 6.49 (d, $J = 16.08 \text{ Hz}$, 1 H, CH), 7.43 (m, 5 H, ArH), 7.77 (d, $J = 16.38, 1 \text{ H, CH}$).

5. (*E*) *n*-butyl cinnamate (**4e**):⁵

IR (CHCl₃): $\nu = 2930, 1713, 1638, 1170, 864 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 1.07$ (t, $J = 6.3 \text{ Hz}$, 3 H, CH₃), 1.25 (m, 2 H, CH₂), 1.65 (m, 2 H, CH₂), 4.24 (t, $J = 12.24 \text{ Hz}$, 2 H, CH₂), 6.46 (d, $J = 15.9 \text{ Hz}$, 1 H, CH), 7.41 (m, 5 H, ArH), 7.72 (d, $J = 16.08 \text{ Hz}$, 1 H, CH).

6. (*E*) *t* – Butyl cinnamate (4f):⁶

IR (CHCl₃): $\nu = 2930, 1711, 1637, 1150, 871 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 1.51$ (s, 9 H, *t*-Bu), 6.40 (d, $J = 16.14$ Hz, 1 H, CH), 7.65 (m, 5 H, ArH), 7.76 (d, $J = 15.6$ Hz, 1 H, CH).

7. (*E*) Stilbene (4g):⁵

IR (KBr): $\nu = 2925, 1951, 1876, 1814, 1495, 1452, 1156, 1071, 1171, 1638, 1170, 963 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 7.00$ (s, 2 H, CH), 7.19-7.34 (m, 10 H, ArH).

8. (*E*) *p*- chloro cinnamotrile (4h):⁷

mp 82-83 °C (Lit⁷ 84-85 °C). IR (KBr): $\nu = 2927, 2217, 1623, 1480, 1181 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 5.90$ (d, $J = 16.86$ Hz, 1 H, CH), 7.30 (m, 4 H, ArH), 7.61 (d, $J = 13.44$ Hz, 1 H, CH).

9. (*E*) *p*- methyl cinnamotrile (4i):⁷

mp 68-69 °C (Lit⁷ 70-71 °C). IR (KBr): $\nu = 2924, 2216, 1607, 1182, 968 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 2.37$ (s, 3 H, CH₃), 5.86 (d, $J = 16.62$ Hz, 1 H, CH), 7.39 (m, 4 H, ArH), 7.73 (d, $J = 8.04$ Hz, 1 H, CH).

10. (*E*) *p*-chloro methyl cinnamate (4j):⁸

mp 75-76 °C (Lit⁸ 76 °C). IR (KBr): $\nu = 2950, 1707, 1630, 1170, 820 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): $\delta = 3.74$ (s, 3 H, CH₃), 6.44 (d, $J = 15.9$ Hz, 1 H, CH), 7.39-7.70 (m, 5 H, CH & ArH).

11. (*E*) *p*- methyl methyl cinnamate (4k):⁸

mp 55 °C (Lit⁸ 56 °C). IR (KBr): $\nu = 2922, 1710, 1632, 1169, 817 \text{ cm}^{-1}$.

¹H NMR (60 MHz, CDCl₃): δ = 3.10 (s, 3 H, CH₃), 3.72 (s, 3 H, OCH₃), 6.40 (d, *J* = 15.9 Hz, 1 H, CH), 7.43-7.70 (m, 5 H, CH & ArH).

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