

Supporting information

Ni-catalyzed the efficient conversion of phenols protected with 2, 4, 6-trichloro-1, 3, 5- triazine (TCT) to olefins

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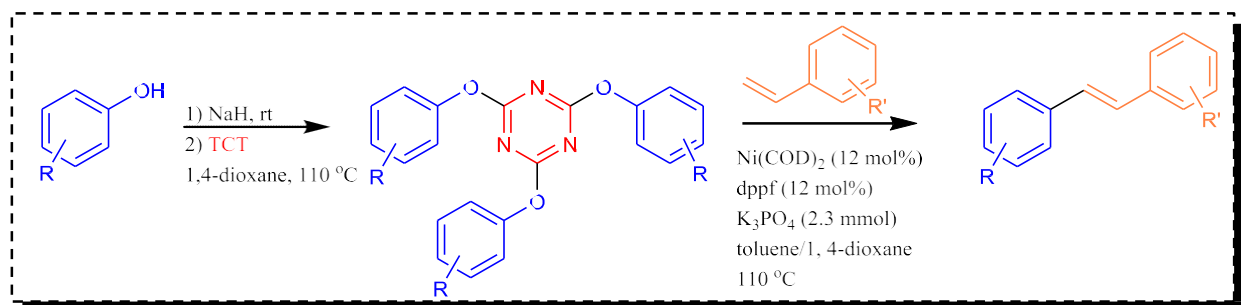
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General Information:

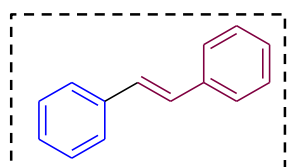
Solvents, reagents and chemicals were obtained from Merck, Acros, and Sigma-Aldrich chemical companies. Purification of the products by chromatography technique on silica gel 60 Merck (230–240 mesh) were conducted using gradient of *n*-hexane/ethyl acetate. All of the products were characterized by ^1H NMR and ^{13}C NMR spectra which were recorded on Bruker Avance DPX 250 and 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard in pure CDCl_3 . Data are reported as follows: chemical shifts (δ) in ppm, multiplicity (s = singlet, br = broad signal, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet). Elemental analysis was determined using ThermoFinnigan Flash EA 1112 Series.

Experimental Section:

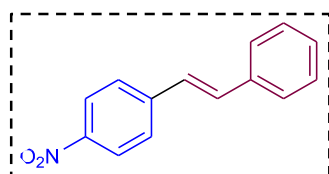
In a flask, NaH (0.6 mmol) was added to a stirring mixture of phenol (1.0 mmol) in dry 1,4-dioxane (1.5 mL) at room temperature and stirred for 1h. Then, TCT (0.37 mmol) was added and the mixture was stirred for 10h at 100 °C which delivered TAT in good yield. Then, the reaction was cooled down to room temperature and K_3PO_4 (2.3 mmol), $\text{Ni}(\text{COD})_2$ (12 mol%), and dppf (12 mol%) were weighed and added in a glove box. Then, the olefin derivative (1.2 mmol) and 1,4-dioxane/toluene (1: 2, 3.0 mL) was added under nitrogen. The reaction was heated at 110 °C overnight. Then, the mixture was cooled down to room temperature and TLC was taken. The mixture was filtered and the solvent was evaporated to give the crude mixture. The pure product was isolated using column chromatography on silica gel using *n*-hexane/ETOAc as eluent.



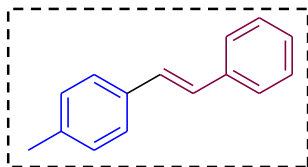
Product Characterization Data



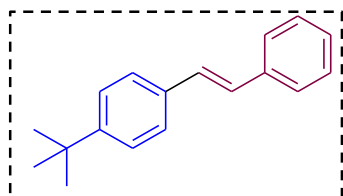
(3aa')¹: ^1H NMR (250 MHz, CDCl_3) δ (ppm): 7.67-7.63 (m, 4H), 7.52-7.46 (m, 4H), 7.42-7.39 (m, 2H), 7.24 (s, 2H); ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 137.3, 128.7, 127.6, 126.5. Anal. Calcd for $\text{C}_{14}\text{H}_{12}$ (180.24): C, 93.29; H, 6.71. Found: C, 93.36; H, 6.64.



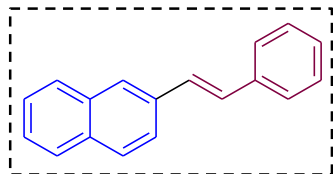
(3ba')²: ^1H NMR (250 MHz, CDCl_3) δ (ppm): 8.13 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 7.35-7.25 (m, 3H), 7.19 (d, J = 16.3 Hz, 1H), 7.05 (d, J = 16.3 Hz, 1H); ^{13}C NMR (62.9 MHz, CDCl_3) δ (ppm): 147.4, 143.8, 136.4, 133.1, 128.8, 128.0, 127.1, 126.8, 125.9, 124.5. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_2$ (225.25): C, 74.65; H, 4.92; N, 6.22. Found: C, 74.60; H, 4.87; N, 6.22.



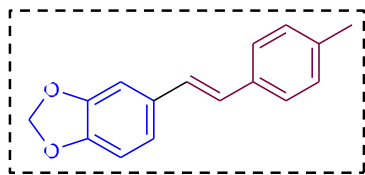
(3ca')³: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.56 (d, *J* = 8.0 Hz, 2H), 7.49-7.38 (m, 5H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.02-6.90 (m, 2H), 2.42 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 137.6, 134.7, 129.4, 128.7, 128.6, 127.7, 127.4, 126.4, 126.4, 21.3. Anal. Calcd for C₁₅H₁₄ (194.11): C, 92.74; H, 7.26. Found: C, 92.65; H, 7.35.



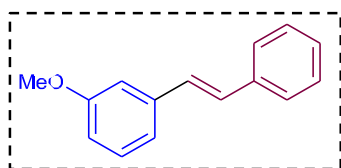
(3da')⁴: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.42 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.19-7.14 (m, 1H), 7.08 (m, 2H), 1.42 (s, 9H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 151.3, 138.2, 134.8, 128.7, 128.4, 128.1, 127.5, 126.7, 125.5, 34.5, 31.1. Anal. Calcd for C₁₈H₂₀ (236.35): C, 91.47; H, 8.53. Found C, 91.55; H, 8.45.



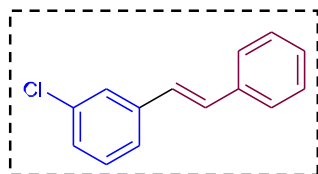
(3ea')⁵: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 8.39-8.13 (m, 4H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.67-7.64 (m, 2H), 7.55-7.35 (m, 7H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 137.3, 135.2, 133.7, 133.1, 129.3, 128.7, 128.5, 128.2, 127.5, 126.8, 126.5, 126.3, 125.3, 123.2. Anal. Calcd for C₁₈H₁₄ (230.31): C, 93.87; H, 6.13. Found C, 93.79; H, 6.21.



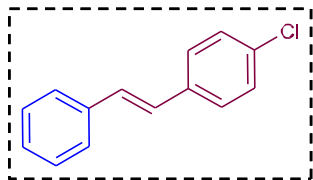
(3fb')⁶: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.50 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 16.2 Hz, 1H), 6.96 (d, *J* = 16.2 Hz, 1H), 6.84-6.71 (m, 3H), 5.97 (s, 2H), 2.41 (s, 3H).; ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 148.0, 147.1, 137.4, 134.5, 132.8, 129.9, 127.7, 127.4, 126.2, 121.9, 108.7, 104.9, 101.5, 21.8. Anal. Calcd for C₁₆H₁₄O₂ (238.29): C, 80.65; H, 5.92. Found C, 80.70; H, 5.90.



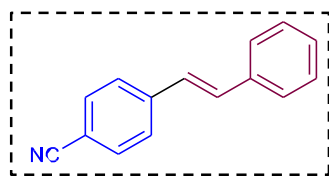
(3ga')²: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.51 (d, *J* = 7.1 Hz, 2H), 7.39-7.25 (m, 4H), 7.13-7.05 (m, 4H), 6.84-6.80 (m, 1H), 3.81 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 159.8, 138.9, 137.3, 129.5, 129.0, 128.7, 128.5, 127.6, 126.7, 119.2, 113.4, 111.6, 55.3; Anal. Calcd for C₁₅H₁₄O (210.10): C, 85.68; H, 7.19. Found: C, 85.73; H, 7.08.



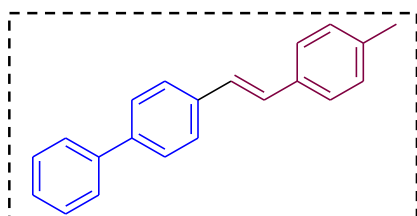
(3ha')⁷: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.55-7.52 (m, 3H), 7.41-7.37 (m, 3H), 7.29 (t, *J* = Hz, 2H), 7.22 (d, *J* = Hz, 1H), 7.12 (d, *J* = 15.9 Hz, 1H), 7.03 (d, *J* = 15.9 Hz, 1H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 139.7, 136.5, 134.3, 130.2, 129.6, 128.5, 128.0, 127.3, 127.0, 126.7, 126.0, 124.3. Anal. Calcd for C₁₄H₁₁Cl (194.28): C, 78.32; H, 5.16. Found: C, 78.35; H, 5.10.



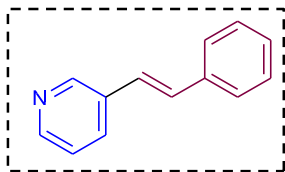
(3ac')⁸: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.49 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 3H), 7.23-7.19 (m, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 137.3, 135.4, 133.8, 130.1, 128.8, 128.2, 127.8, 127.4, 127.2, 126.7. Calcd for C₁₄H₁₁Cl (214.69): C, 78.32; H, 5.16. Found: C, 78.39; H, 5.20.



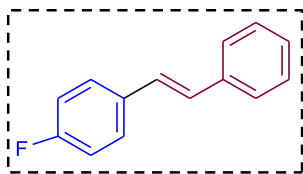
(3ia')⁷: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.76 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.53-7.46 (m, 3H), 7.30 (d, *J* = 15.5 Hz, 1H), 7.22 (d, *J* = 15.5 Hz, 1H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 140.8, 136.5, 132.7, 132.6, 128.7, 128.1, 126.7, 126.6, 126.4, 118.3, 110.5. Anal. Calcd for C₁₅H₁₁N (205.31): C, 87.77; H, 5.40; N, 6.83. Found C, 87.87; H, 5.27; N, 6.86.



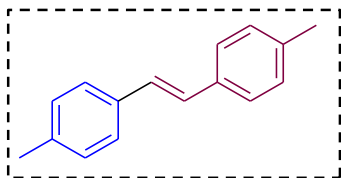
(3jb')⁹: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.73-7.68 (m, 6H), 7.58-7.55 (m, 4H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 16.1 Hz, 1H), 7.07 (d, *J* = 16.1 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 141.3, 140.4, 137.6, 136.5, 134.2, 128.9, 128.7, 128.1, 127.7, 127.6, 127.2, 126.6, 126.4, 126.1, 21.4. Anal. Calcd for C₂₁H₁₈ (270.38): C, 93.29; H, 6.71. Found C, 93.19; H, 6.81.



(3ka')¹⁰: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 8.80 (s, 1H), 8.47-8.45 (m, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.38-7.33 (m, 2H), 7.29-7.26 (m, 2H), 7.23-7.08 (m, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 148.4, 136.6, 133.0, 132.2, 130.1, 129.0, 128.0, 126.5, 125.0, 123.5. Anal. Calcd for C₁₃H₁₁N (181.24): C, 86.15; H, 6.12; N, 7.73. Found: C, 86.05; H, 6.19; N, 7.76.

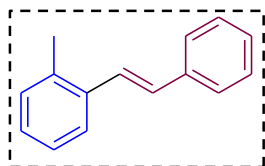


(3la')¹¹: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.75-7.70 (m, 4H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.56-7.52 (m, 1H), 7.48-7.43 (m, 4H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 162.7 (d, *J* = 247.6 Hz), 137.2, 133.6, 128.7, 128.4, 127.9 (d, *J* = 8.1 Hz), 127.7, 127.5, 126.4, 115.6 (d, *J* = 21.8 Hz). Anal. Calcd for C₁₄H₁₁F (198.24): C, 84.82; H, 5.59. Found: C, 84.82; H, 5.70.

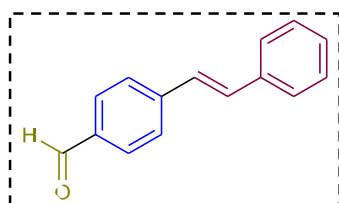


(3cb')¹²: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.38 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.00 (s, 2H), 2.38 (s, 6H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 137.9, 135.3,

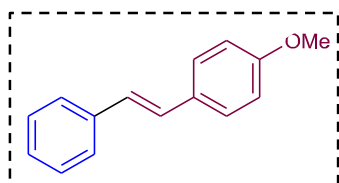
130.5, 128.2, 126.8, 21.7. Anal. Calcd for C₁₆H₁₆ (205.31): C, 92.26; H, 7.74. Found C, 92.19; H, 7.81.



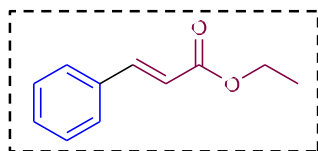
(3ja')²: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.61 (d, *J* = 8.2 Hz, 1H), 7.55-7.49 (m, 2H), 7.37-7.32 (m, 3H), 7.25-7.16 (m, 4H), 7.12 (d, *J* = 16.4 Hz, 1H), 2.26 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 138.0, 136.5, 136.0, 130.2, 129.8, 129.1, 128.4, 127.2, 127.1, 126.7, 126.6, 125.7, 20.5. Anal. Calcd for C₁₅H₁₄ (194.28): C, 92.74; H, 7.26. Found: C, 92.84; H, 7.16.



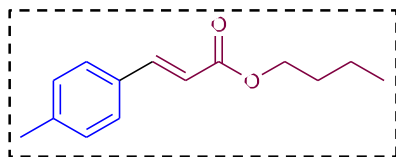
(3ka')¹³: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 10.05 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 5.54 (d, *J* = 7.5 Hz, 2H), 7.35-7.28 (m, 3H), 7.25-7.19 (m, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 191.4, 143.7, 136.8, 135.4, 132.3, 130.0, 129.1, 128.9, 127.7, 126.9. Anal. Calcd for C₁₅H₁₂O (208.26): C, 86.51; H, 5.81. Found: C, 86.59; H, 5.85.



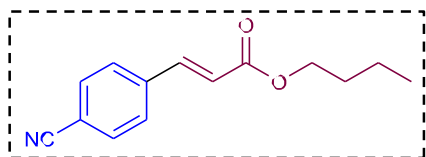
(3ag')¹⁴: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.53-7.68 (m, 4H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.28-7.24 (m, 1H), 7.10 (d, *J* = 16.1 Hz, 1H), 7.03 (d, *J* = 16.1 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 159.3, 137.5, 130.5, 128.7, 128.1, 128.0, 127.6, 127.0, 126.7, 126.6, 126.1, 114.4, 55.3. Anal. Calcd for C₁₅H₁₄O (210.27): C, 85.68; H, 6.71. Found: C, 85.76; H, 5.68.



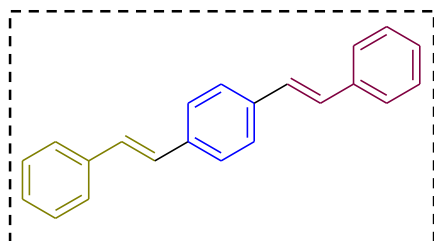
(3ah')¹⁵: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.60 (d, *J* = 16.0 Hz, 1H), 7.45-7.41 (m, 2H), 7.30-7.27 (m, 3H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 166.9, 144.9, 134.4, 130.2, 128.8, 128.0, 118.2, 60.7, 14.4. Anal. Calcd for C₁₁H₁₂O₂ (176.21): C, 74.98; H, 6.86. Found: C, 74.89; H, 6.84.



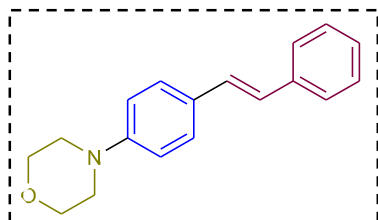
(3cj')¹⁶: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.65 (d, *J* = 16.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 16.0 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 2.36 (s, 3H), 1.74-1.62 (m, 2H), 1.50-1.36 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 167.1, 144.5, 140.4, 131.7, 129.5, 128.0, 117.3, 64.3, 30.9, 21.5, 19.3, 13.7. Anal. Calcd for C₁₄H₁₈O₂ (218.29): C, 77.03; H, 8.31. Found: C, 77.11; H, 8.35.



(3ij')¹³: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.69-7.60 (m, 5H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.23 (t, *J* = 6.5 Hz), 1.75-1.64 (m, 2H), 1.53-1.36 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 166.2, 142.3, 138.8, 132.5, 128.3, 121.8, 118.6, 113.2, 64.9, 30.6, 19.4, 13.6. Anal. Calcd for C₁₄H₁₅NO₂ (229.27): C, 73.34; H, 6.59; N, 6.11. Found: C, 73.30; H, 6.65; N, 6.03.

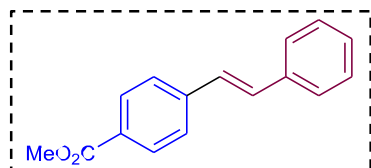


(5a')¹⁷: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.51-7.47 (m, 8H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.25-7.22 (m, 2H), 7.11-7.07 (m, 4H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 137.7, 136.7, 128.7, 128.2, 127.4, 126.9, 126.4. Anal. Calcd for C₂₂H₁₈ (282.39): C, 93.57; H, 6.43. Found: C, 93.46; H, 6.54.



(7a')¹⁸: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 7.64 (d, *J* = 7.8 Hz, 2H), 7.56-7.45 (m, 4H), 7.37-7.21 (m, 3H), 7.16-7.02 (m, 2H), 3.81 (t, *J* = 4.9 Hz, 4H), 3.13 (t, *J* = 4.9 Hz, 4H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 151.0, 138.0, 129.8, 128.7, 128.5, 127.9, 127.4,

126.8, 126.5, 115.6, 67.1, 48.7. Anal. Calcd for C₁₈H₁₉NO (265.36): C, 81.47; H, 7.22; N, 5.28. Found: C, 81.53; H, 7.18; N, 5.26.



(8a')¹⁹: ¹H NMR (250 MHz, CDCl₃) δ (ppm): 8.02 (d, *J* = 8.3 Hz, 2H), 7.63-7.54 (m, 4H), 7.46-7.31 (m, 3H), 7.12 (d, *J* = 16.4 Hz, 1H), 7.03 (d, *J* = 16.4 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ (ppm): 166.3, 141.8, 137.3, 131.5, 130.6, 129.7, 128.8, 128.1, 127.8, 127.0, 126.5, 52.5. Anal. Calcd for C₁₆H₁₄O₂ (238.29): C, 80.65; H, 5.92. Found: C, 80.65; H, 6.01.

References:

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