Novel 2-Pyridone Synthesis via Nucleophilic Addition of Malonic Esters to Alkynyl Imines

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Experimental section

IR spectra were recorded on a JASCO IR-810 spectrometer. ^{1}H NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz) or a JEOL JNM-A500 spectrometer (500 MHz) with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL EX-270 spectrometer (67.8 MHz) or a JEOL JNM-A500 spectrometer (125 MHz). Chemical shifts are reported in δ units, parts per million from the central peak of $CDCl_3$ (δ 77.0) as an internal reference. Low-resolution mass spectra were recorded on a Waters Micromass ZQ or a Mariner TK3500. Purification of products was performed by preparative TLC on silica gel Merck Kisel Gel PF254. All reagents and solvents were used after purification according to usual methods. All reactions were carried out under an argon atmosphere.

Synthesis of alkynyl aldimines 1a-1e:

To a solution of *p*-anisidine (1.85 g, 15.0 mmol) in CH_2Cl_2 (10 mL) in the presence of molecular sieves 4 A (MS 4 A) (6 g) was added a solution of 3-phenyl-2-propynal (1.95g, 15.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was warmed to rt and stirred for 1 h. The reaction mixture was filtered through a Celite pad to remove MS 4 A. The solvents were evaporated in vacuo. The crude product was recrystallized from EtOH to give **1a** (3.16_g, 90% yield). **1b**, **1c**, **1d**, and **1e** were purified by chromatography on silica gel (hexane/ethyl acetate) to give **1b** (75% yield), **1c** (53% yield), **1d** (56% yield), and **1e** (75% yield).

1a (R^3 = Ph):[1]

IR ($CHCl_3$): 3050, 2990, 2950, 2830, 2200, 1630, 1600, 1520, 1480, 1460, 1370, 1320, 1270, 1180, 1130, 1050, 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.56-7.60 (m, 2H), 7.32-7.40 (m, 3H), 7.20-7.25 (m, 2H), 6.88-6.94 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 159.3, 143.8, 140.9, 132.3, 129.6, 128.4, 122.3, 121.5, 114.4, 94.2, 87.8, 55.4.

1b (R^3 = $CH_3(CH_2)_3$):

IR ($CHCl_3$): 2970, 2930, 2880, 2800, 2200, 1680, 1620, 1590, 1510, 1470, 1450, 1360, 1300, 1260, 1190, 1180, 1120, 1040, 840, 800, 760 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.70 (t, *J* = 1.65 Hz, 1H), 7.13-7.20 (m, 2H), 6.85-6.91 (m, 2H), 3.81 (s, 3H), 2.44 (dt, *J* = 7.10, 1.65 Hz, 2H), 1.40-1.66 (m, 4H), 0.94 (t, *J* = 7.26 Hz, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 158.9, 144.0, 141.8, 122.1, 114.3, 96.9, 79.7, 55.4, 30.1, 22.0, 19.2, 13.5. MS (ESI) *m/z*: 216 $(M+H)^+$.

1c (R^3 = $TBSO(CH_2)_3$):

IR ($CHCl_3$): 2920, 2880, 2840, 2200, 1680, 1620, 1595, 1520, 1480, 1450, 1400, 1375, 1360, 1300, 1260, 1190, 1180, 1120, 1050, 980, 850, 780, 720, 670 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.69 (t, *J* = 1.65 Hz, 1H), 7.14-7.18 (m, 2H), 6.86-6.90 (m, 2H), 3.81 (s, 3H), 3.72 (t, *J* = 5.94 Hz, 2H), 2.53 (dt, *J* = 7.07, 1.65 Hz, 2H), 1.77-1.86 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 159.0, 143.9, 141.7, 122.1, 114.3, 96.5, 79.8, 61.5, 55.4, 31.2, 25.9, 18.3, 16.0, -5.4. MS (ESI) *m/z*: 332 $(M+H)^+$.

1d (R^3 = TMS):[2]
IR (neat): 2975, 2940, 2875, 2820, 1620, 1590, 1520, 1480, 1450, 1360, 1310, 1260, 1200, 1180, 1120, 1090, 1050, 850, 770, 710, 670, 550 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.16-7.22 (m, 2H), 6.87-6.92 (m, 2H), 3.81 (s, 3H), 0.26 (s, 9H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 159.4, 143.6, 140.7, 122.3, 114.4, 102.4, 100.9, 55.4, -0.6.

1e (R^3 = 1-cyclohexenyl):
IR ($CHCl_3$): 2975, 2925, 2850, 2825, 2180, 1620, 1590, 1520, 1480, 1360, 1310, 1270, 1200, 1180, 1120, 1050, 935, 850 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.15-7.19 (m, 2H), 6.86-6.91 (m, 2H), 6.36-6.39 (m, 1H), 3.80 (s, 3H), 2.10-2.22 (m, 4H), 1.59-1.71 (m, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 159.0, 144.0, 141.5, 139.4, 122.2, 119.9, 114.3, 96.7, 85.7, 55.4, 28.6, 26.0, 22.1, 21.2. MS (ESI) *m/z*: 240 $(M+H)^+$.

Typical experimental procedure of the reaction of alkynyl imines with malonic esters: To 60% NaH or sodium alkoxide (0.400 mmol) was added a solution of malonic ester (0.500 mmol) in THF or 1,4-dioxane (2.0 mL) and a solution of alkynyl imine (0.200 mmol) in THF or 1,4-dioxane (2.0 mL) at rt. The reaction mixture was stirred under reflux for several hours (see Table 1) and then cooled to room temperature. Brine (10 mL) was added to quench the reaction. The mixture was extracted with dichloromethane (15 mL x 3). The combined organic layers were dried over sodium sulfate. The solvents were evaporated in vacuo and then the residue was purified by preparative TLC on silica gel to give 2-pyridone **8** and decarboxylated 2-pyridone **9**, respectively.

8 (R^1 = Et, R^2 = Me, R^3 = Ph):
IR ($CHCl_3$): 2980, 2925, 2830, 1735, 1670, 2630, 1530, 1480, 1460, 1390, 1360, 1310, 1270, 1190, 1160, 1130, 1110, 1040, 1020, 990, 930, 870, 850 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.33-7.46 (m, 5H), 7.13-7.18 (m, 2H), 7.00-7.05 (m, 2H), 3.96 (q, *J* = 7.26 Hz, 2H), 3.87 (s, 3H), 1.93 (s, 3H), 0.93 (t, *J* = 7.26 Hz, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 165.0, 162.6, 159.7, 148.8, 140.4, 138.7, 133.4, 28.3, 128.0, 127.6, 127.4, 127.3, 114.5, 111.0, 60.6, 55.5, 14.5, 13.6. MS (ESI) *m/z*: 364 $(M+H)^+$.

9(R^2 = Me, R^3 = Ph):
IR ($CHCl_3$): 2990, 2930, 2830, 1660, 1600, 1550, 1520, 1480, 1260, 1100, 1040, 1020, 850 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.32-7.50 (m, 7H), 7.25 (d, *J* = 7.26 Hz, 1H), 6.97-7.03 (m, 2H), 6.20 (d, *J* = 7.26 Hz, 1H), 3.86 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 163.1, 159.1, 149.3, 139.4, 134.2, 134.0, 128.3, 128.2, 128.0, 127.6, 126.9, 114.3, 108.2, 55.5, 14.4. MS (ESI) *m/z*: 292 $(M+H)^+$.

8 (R^1 = Me, R^2 = Me, R^3 = Ph):
IR ($CHCl_3$): 3020, 2980, 2930, 2830, 1740, 1660, 1620, 1520, 1440, 1390, 1360, 1300, 1260, 1230, 1200, 1140, 1040, 1020, 930, 850, 780, 760, 710 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.33-7.48 (m, 5H), 7.14-7.18 (m, 2H), 6.99-7.05 (m, 2H), 3.86 (s, 3H), 3.54 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 164.9, 162.5, 159.6, 148.8, 140.6, 138.4, 133.3, 128.3, 128.0, 127.5, 127.4, 127.3, 114.5, 110.3, 55.5., 51.6, 14.5. MS (ESI) *m/z*: 350 $(M+H)^+$.

8 (R^1 = Me, R^2 = allyl, R^3 = Ph):
IR ($CHCl_3$): 3020, 2975, 2930, 2820, 1740, 1660, 1630, 1615, 1520, 1475, 1450, 1360,

1300, 1260, 1145 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.34-7.47 (m, 5H), 7.16-7.20 (m, 2H), 6.99-7.05 (m, 2H), 5.76-5.91 (m, 1H), 4.83-4.94 (m, 2H), 3.86 (s, 3H), 3.54 (s, 3H), 3.09 (d, *J* = 6.27 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 164.8, 161.8, 159.6, 149.6, 141.3, 137.7, 135.1, 133.2, 130.0, 127.8, 127.6, 127.4, 115.8, 114.5, 110.3, 55.6, 51.7, 32.7. MS (ESI) *m/z*: 376 $(M+H)^+$.

9 (R^2 = allyl, R^3 = Ph):

IR ($CHCl_3$): 2980, 2930, 2820, 1660, 1630, 1600, 1520, 1480, 1460, 1350, 1320, 1290, 1260, 1190, 1120, 1020, 930, 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.33-7.49 (m, 6H), 7.26-7.29 (m, 2H), 6.96-7.02 (m, 2H), 6.18 (d, *J* = 7.26 Hz, 1H), 5.95-6.10 (m, 1H), 4.92-5.01 (m, 2H), 3.85 (s, 3H), 3.26-3.29 (m, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 162.5, 159.2, 150.5, 139.2, 136.2, 134.7, 134.1, 128.7, 128.3, 128.1, 128.0, 127.7, 115.2, 114.4, 108.4, 55.6, 32.8. MS (ESI) *m/z*: 318 $(M+H)^+$.

8 (R^1 = Me, R^2 = (*E*)-CH=CHCH_3, R^3 = Ph):

IR ($CHCl_3$): 3030, 3000, 2950, 2830, 1750, 1670, 1530, 1460, 1330, 1270, 1160, 1050, 990, 930, 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.24-7.69 (m, 5H), 6.92-7.11 (m, 5H), 5.85 (dd, *J* = 15.5, 1.65 Hz, 1H), 3.78 (s, 3H), 3.44 (s, 3H), 1.59 (dd, *J* = 6.92, 1.65 Hz, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 165.0, 161.2, 159.7, 147.9, 140.1, 137.9, 133.4, 128.0, 127.9, 127.7, 127.5, 126.1, 124.7, 114.6, 110.8, 55.5, 51.7, 19.9. MS (ESI) *m/z*: 376 $(M+H)^+$.

8 (R^1 = Me, R^2 = Me, R^3 = $CH_3(CH_2)_3$):

IR ($CHCl_3$): 2970, 2930, 2910, 2840, 2810, 1730, 1660, 1620, 1610, 1520, 1475, 1450, 1380, 1360, 1300, 1260, 1180, 1110, 1080, 1010, 910, 840 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.27-7.30 (m, 2H), 6.97-7.00 (m, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 2.93-2.96 (m, 2H), 2.19 (s, 3H), 1.45-1.55 (m, 4H), 0.98 (t, *J* = 6.87 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 162.4, 159.5, 150.5, 141.2, 133.5, 127.6, 127.0, 114.4, 109.8, 55.5, 51.7, 31.4, 30.2, 23.2, 13.9, 12.6. MS (ESI) *m/z*: 330 $(M+H)^+$.

9 (R^2 = Me, R^3 = $CH_3(CH_2)_3$):

IR ($CHCl_3$): 2970, 2940, 2900, 2840, 2820, 1660, 1600, 1555, 1520, 1480, 1390, 1310, 1280, 1260, 1180, 1120, 1100, 900, 840 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.29 (m, 2H), 7.12 (d, *J* = 7.02 Hz, 3H), 6.96-6.97 (m, 2H), 6.06 (d, *J* = 7.02 Hz, 1H), 3.84 (s, 3H), 2.50-2.53 (m, 2H), 2.14 (s, 3H), 1.53-1.59 (m, 2H), 1.38-1.45 (m, 2H), 0.97 (t, *J* = 7.33 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 159.0, 150.5, 134.5, 133.8, 127.7, 126.4, 114.3, 108.0, 55.5, 33.2, 31.3, 22.7, 13.9, 12.4. MS (ESI) *m/z*: 272 $(M+H)^+$.

8 (R^1 = Me, R^2 = Me, R^3 = TBSO$(CH_2)_3$):

IR ($CHCl_3$): 2940, 2910, 2870, 2850, 1735, 1670, 1630, 1520, 1450, 1300, 1270, 1100, 1020, 850, 780 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.22-7.31 (m, 2H), 6.96-7.05 (m, 2H), 3.84 (s, 3H), 3.79 (s, 3H), 3.74 (t, *J* = 6.10 Hz, 2H), 2.98-3.04 (m, 2H), 2.21 (s, 3H), 1.72-1.82 (m, 2H), 0.92 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 165.4, 162.4, 159.5, 150.1, 141.2, 133.5, 127.6, 127.3, 114.4, 109.8, 62.9, 55.5, 51.7, 32.4, 27.0, 25.9, 18.3, 12.5, -5.3. MS (ESI) *m/z*: 446 $(M+H)^+$.

9 (R^2 = Me, R^3 = TBSO$(CH_2)_3$):

IR ($CHCl_3$): 2980, 2940, 2840, 1660, 1600, 1520, 1480, 1390, 1265, 1180, 1110, 1040, 970, 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.24-7.28 (m, 2H), 7.12 (d, *J* = 7.09, 1H), 6.94-6.98 (m, 2H), 6.07 (d, *J* = 7.09 Hz, 1H), 3.84 (s, 3H), 3.67 (t, *J* = 6.11 Hz, 2H), 2.59, (t, *J* = 7.80 Hz, 2H), 2.14 (s, 3H), 1.72-1.83 (m, 2H), 0.91 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (67.8 MHz, $CDCl_3$): δ 162.9, 159.0, 150.0, 134.4, 133.8, 127.6, 126.6, 114.3, 108.0, 62.2, 55.5, 32.2, 29.8, 25.9, 18.2, 12.3, -5.3. MS (ESI) *m/z*: 388 $(M+H)^+$.

8 (R^1 = Et, R^2 = Me, R^3 = TBSO$(CH_2)_3$):

IR ($CHCl_3$): 2980, 2930, 2840, 1725, 1660, 1610, 1520, 1470, 1380, 1300, 1270, 1180, 1140, 1115, 1030, 990, 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.26-7.32 (m, 2H), 6.97-7.02 (m, 2H), 4.27 (q, *J* = 7.26 Hz, 2H), 3.85 (s, 3H), 3.73 (t, *J* = 6.27 Hz, 2H), 2.98-3.04 (m, 2H), 2.21 (s, 3H), 1.73-1.83 (m, 2H), 1.32 (t, *J* = 7.26 Hz, 3H), 0.92 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 165.0, 162.4, 159.5, 150.1, 141.0, 133.6, 127.6, 127.3, 114.4, 110.2, 62.9, 60.7, 55.5, 32.5, 27.0, 25.9, 18.3, 14.3, 12.5, -5.3. MS (ESI) *m/z*: 460 $(M+H)^+$.

8 (R^1 = Me, R^2 = allyl, R^3 = TBSO$(CH_2)_3$):

IR ($CHCl_3$): 2960, 2900, 2820, 1730, 1650, 1600, 1515, 1460, 1440, 1350, 1300, 1260, 1160, 1110, 1040, 990, 960, 920, 840 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.22-7.27 (m, 2H), 6.95-7.01 (m, 2H), 5.86-6.00 (m, 1H), 4.99-5.14 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 3.73 (t, *J* = 5.93 Hz, 2H), 3.44 (d, *J* = 6.27 Hz, 2H), 2.98-3.04 (m, 2H), 1.72-1.83 (m, 2H), 0.92 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 165.3, 161.8, 159.6, 151.1, 142.0, 135.2, 133.4, 128.9, 127.6, 115.4, 114.4, 109.7, 63.0, 55.6, 51.8, 33.2, 31.0, 26.7, 26.0, 18.3, -5.3. MS (ESI) *m/z*: 472 $(M+H)^+$.

9 (R^2 = allyl, R^3 = TBSO$(CH_2)_3$):

IR ($CHCl_3$): 2980, 2930, 2840, 1665, 1600, 1520, 1480, 1320, 1265, 1180, 1115, 1020, 1000, 970, 920 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.26-7.30 (m, 2H), 7.17 (d, *J* = 6.93, 1H), 6.94-6.99 (m, 2H), 6.09 (d, *J* = 6.93 Hz, 1H), 5.90-6.00 (m, 1H), 4.97-5.12 (m, 2H), 3.83 (s, 3H), 3.68 (t, *J* = 5.94 Hz, 2H), 3.41 (d, *J* = 6.27 Hz, 2H), 2.58-2.63 (m, 2H) 1.75-1.85 (m, 2H), 0.92 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 162.4, 159.1, 151.0, 135.8, 134.6, 134.3, 128.3, 127.7, 115.0, 114.3, 108.0, 62.3, 55.6, 32.7, 31.1, 29.3, 25.9, 18.3, -5.3. MS (ESI) *m/z*: 414 $(M+H)^+$.

9 (R^2 = Me, R^3 = H):

IR ($CHCl_3$): 2990, 2950, 2840, 1680, 1610, 1580, 1530, 1485, 1460, 1400, 1320, 1300, 1190, n1170, 1130, 1115, 1100, 1055, 1020, 910, 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.19-7.31 (m, 4H), 6.94-7.00 (m, 2H), 6.13 (dd, *J* = 13.5, 6.77 Hz, 1H), 3.83 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 162.9, 159.1, 136.7, 135.6, 134.1, 130.5, 127.5, 114.2, 105.3, 55.4, 17.3. MS (ESI) *m/z*: 216 $(M+H)^+$.

8 (R^1 = Me, R^2 = Me, R^3 = 1-cyclohexenyl):

IR ($CHCl_3$): 2990, 2930, 2830, 1740, 1680, 1660, 1640, 1620, 1530, 1460, 1400, 1365, 1320, 1190, 1150, 1120, 1060, 1030, 1020, 940, 860, 840 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): 8.08 (s, 1H), 7.27-7.32 (m, 2H), 6.96-7.02 (m, 2H), 5.41-5.44 (m, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 1.99-2.34 (m, 7H), 1.70-1.83 (m, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 165.0, 162.7, 159.5, 151.2, 140.8, 136.1, 133.4, 127.5, 126.8, 123.9, 114.4, 110.0, 55.5, 51.7, 28.8, 25.0, 22.7, 21.9, 13.7. MS (ESI) *m/z*: 354 $(M+H)^+$.

8 (R^1 = Me, R^2 = allyl, R^3 = 1-cyclohexenyl):

IR ($CHCl_3$): 2980, 2930, 2820, 1740, 1680, 1660, 1635, 1605, 1520, 1480, 1460, 1360, 1320, 1180, 1150, 1120, 1080, 1040, 1020, 980, 920, 850 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): 8.13 (s, 1H), 7.27-7.34 (m, 2H), 6.96-7.01 (m, 2H), 5.87-6.02 (m, 1H), 5.45-5.48 (m, 1H), 4.95-5.11 (m, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.39-3.50 (m, 1H), 3.19-3.27 (m, 1H), 2.00-2.33 (m, 4H), 1.64-1.85 (m, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 164.9, 162.1, 159.6, 152.0, 141.7, 136.2, 135.5, 133.3, 128.5, 127.6, 124.4, 115.5, 114.4,

109.9, 55.6, 51.8, 32.7, 29.4, 25.0, 22.7, 21.9. MS (ESI) *m/z*: 380 $(M+H)^+$.

8 (R^1 = Bn, R^2 = Me, R^3 = TBSO$(CH_2)_3$):

IR ($CHCl_3$): 3050, 2940, 2840, 1730, 1675, 1635, 1520, 1480, 1390, 1300, 1260, 1170, 1120, 1010, 850, 780, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.33-7.36 (m, 5H), 7.23-7.27 (m, 2H), 6.95-6.98 (m, 2H), 5.25 (s, 2H), 3.83 (s, 3H), 3.66 (t, *J* = 5.94 Hz, 2H), 2.97-3.03 (m, 2H), 2.19 (s, 3H), 1.71-1.79 (m, 2H), 0.92 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 164.8, 162.4, 159.5, 150.1, 141.2, 135.8, 133.5, 128.6, 128.4, 128.4, 127.6, 127.4, 114.5, 109.8, 66.5, 62.8, 55.5, 32.4, 27.1, 25.9, 18.3, 12.5, -5.3. MS (ESI) *m/z*: 522 $(M+H)^+$.

14 (R^4 = Bn):[3]

IR ($CHCl_3$): 3050, 3020, 2940, 2870, 1760, 1510, 1470, 1410, 1380, 1280, 1250, 960, 920, 760, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.34-7.38 (m, 10H), 5.17 (s, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 155.1, 135.1, 128.6, 128.5, 128.3, 69.7.

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