Electronic Supplementary Material (ESI) for RSC Advances

Supporting information

A Simple Diamine as Ligand in Iron-Catalyzed Regioselective Allylic Alkylation

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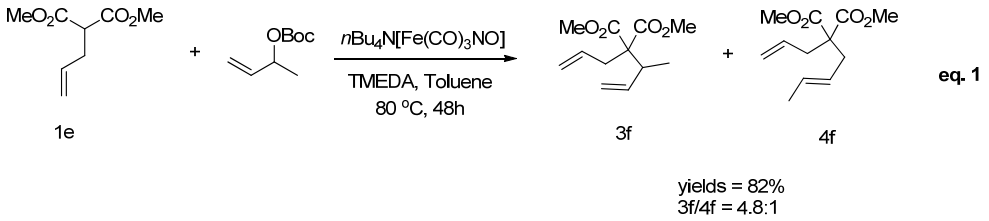
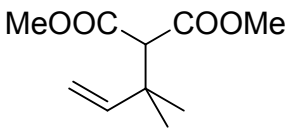
General Information: Commercial reagents were used as received, unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 400 spectrometer, respectively, in $CDCl_3$ as the solvent. Chemical shifts were reported in the δ scale relative to residual $CHCl_3$ (7.26 ppm) for ^{1}H NMR and to the central line of $CDCl_3$ (77.0 ppm) for ^{13}C NMR. Data for ^{1}H NMR are reported as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), intergration, coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

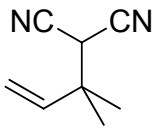
General procedure for Iron catalyzed regioselective allylic alkylation between nucleophiles 1 and allyl carbonates 2: 2.5 µl (0.0165 mmol, 5.5 mol%) TMEDA was added directly a solution of iron complex (6.3mg, 0.015 mmol, 5 mol%) in anhydrous toluene (0.3 ml) under an atmoshpere of nitrogen. The solution was heated to 80 °C and stirred for 20 min. The mixture was cooled to room temperature and then the nucleophile 1 (0.06 mmol, 2 eq.) and the allyl carbonate 2 (0.03 mmol, 1 eq.) were added. The reaction mixture was heated in the sealed Schlenk tube for 10 h at 80 °C. The reaction mixture was directly purified by silica gel chromatography (hexane/EtOAc 15:1) to afford the desired product as colourless oil.





3a

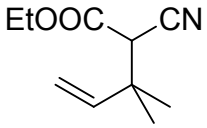
Dimethyl 2-(2-methylbut-3-en-2-yl)malonate (3a) (Table 2, entry 1): The title compound was prepared according to the general procedure, as described above in 93% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 6.03 (dd, 1H, J_1 = 10.8 Hz, J_2 = 17.6 Hz), 4.99-6.06 (m, 2H), 3.69 (s, 6H), 3.36 (s, 1H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 144.6, 112.3, 60.6, 52.0, 38.9, 25.0.



3b

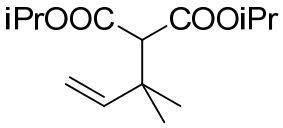
2-(2-methylbut-3-en-2-yl)malononitrile (3b) (Table 2, entry 4): The title compound

was prepared according to the general procedure, as described above in 87% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.90 (dd, 1H, J_1 = 10.8 Hz, J_2 = 17.2 Hz), 3.55 (s, 1H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8, 117.0, 111.6, 40.5, 35.1, 24.3.



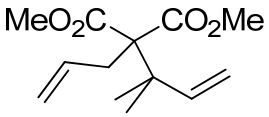
3c

Ethyl 2-cyano-3,3-dimethylpent-4-enoate (3c) (Table 2, entry 3): The title compound was prepared according to the general procedure, as described above in 90% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.92 (dd, 1H, J_1 = 10.4 Hz, J_2 = 17.2 Hz), 5.14-5.18 (m, 2H), 4.21-4.29 (m, 2H), 3.38 (s, 1H), 1.30-1.32 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 142.2, 114.3, 62.4, 48.7, 39.9, 25.2, 24.5, 14.0.



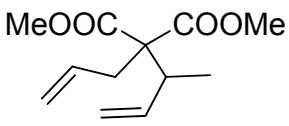
3d

Diisopropyl 2-(2-methylbut-3-en-2-yl)malonate (3d) (Table 2, entry 2): The title compound was prepared according to the general procedure, as described above in 88% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 6.08 (dd, 1H, J_1 = 10.8 Hz, J_2 = 17.6 Hz), 4.99-5.07 (m, 4H), 3.26 (s, 1H), 1.25 (s, 12H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 145.0, 111.9, 68.4, 61.1, 38.7, 25.2, 21.7, 21.6, 21.5.



3e

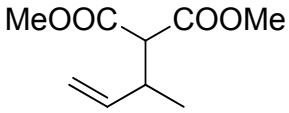
Dimethyl 2-allyl-2-(2-methylbut-3-en-2-yl)malonate (3e) (Table 2, entry 4): The title compound was prepared according to the general procedure, as described above in 87% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 6.19 (dd, 1H, J_1 = 10.8 Hz, J_2 = 17.6 Hz), 5.77-5.87 (m, 1H), 4.93-5.04 (m, 4H), 3.69 (s, 6H), 2.61 (d, 2H, J = 6.8 Hz), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 144.3, 135.0, 117.7, 112.8, 65.1, 51.5, 42.0, 37.3, 24.0.



3f

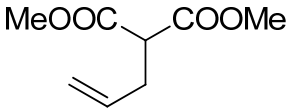
2-(2-methylbut-3-en-2-yl)malononitrile (3f) (Supporting information, eq. 1): The title compound was prepared according to the general procedure, as described above in 87% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.70-5.81 (m, 2H), 5.03-5.11(m, 4H), 3.71(s, 3H),

3.70(s, 3H), 2.82-2.89 (m, 1H), 2.60-2.63 (m, 2H), 1.09 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 170.6, 138.9, 133.2, 118.3, 116.2, 51.9, 51.8, 42.0, 38.5, 16.4.



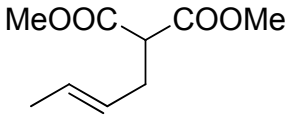
3g

Dimethyl 2-(but-3-en-2-yl)malonate (3g) (Table 3, entry 3): The title compound was prepared according to the general procedure, as described above in 94% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.71-5.80 (m, 1H), 4.99-5.10(m, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 3.31 (d, 1H, *J* = 8.8 Hz), 2.90-2.99 (m, 1H) , 1.09 (s, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 168.5, 139.6, 115.4, 57.4, 52.3, 52.2, 38.0, 17.8.



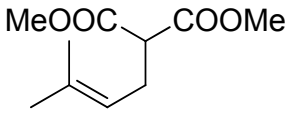
3h

Dimethyl 2-allylmalonate (3h) (Table 3, entry 7): The title compound was prepared according to the general procedure, as described above in 88% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.72-5.82 (m, 1H), 5.05-5.15 (m, 2H), 3.74 (s, 6H), 3.47 (t, 1H, *J* = 7.6 Hz), 2.65 (t, 2H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 133.9, 117.6, 52.4, 51.3, 32.8.



3i

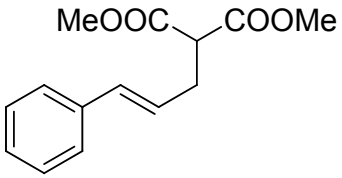
Dimethyl 2-(but-2-en-1-yl)malonate (3i) (Table 3, entry 5): The title compound was prepared according to the general procedure, as described above in 91% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.49-5.58 (m, 1H), 5.32-5.40 (m, 1H), 3.72 (s, 6H), 3.94 (t, 1H, *J* = 7.2 Hz), 2.56 (t, 2H, *J* = 7.2 Hz), 1.63 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 128.4, 126.2, 52.3, 51.9, 31.8, 17.8.



3j

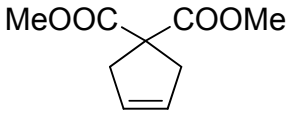
Dimethyl 2-(3-methylbut-2-en-1-yl)malonate (3j) (Table 3, entry 2): The title compound was prepared according to the general procedure, as described above in 87% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.03-5.07 (m, 1H), 3.73(s, 6H), 3.37 (t, 1H, *J* = 8.0 Hz), 2.59 (t, 2H, *J* = 7.6 Hz), 1.68 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 169.5, 135.0, 119.4, 52.4, 51.8, 27.6, 25.7, 17.6.



3k

Dimethyl 2-cinnamylmalonate (3k) (Table 3, entry 6): The title compound was prepared according to the general procedure, as described above in 84% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.22-7.37 (m, 5H), 6.51 (d, 1H, *J* = 16 Hz), 6.13-6.21 (m, 1H), 3.76 (s, 6H), 3.56 (t, 1H, *J* = 7.6 Hz), 2.82-2.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 136.9, 132.8, 128.4, 127.3, 126.1, 100.3, 52.4, 51.6, 32.1.



3l

Dimethyl cyclopent-3-ene-1,1-dicarboxylate (3l) (Table 3, entry 8): The title compound was prepared according to the general procedure, as described above in 41% yield. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 5.64 (s, 2H), 3.76 (s, 6H), 3.05 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 127.8, 52.8, 40.9.