Supporting Information

Iron-Catalyzed Alkylazidation of 1,1-Disubstituted Alkenes with Diacylperoxides and TMSN₃

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Materials and methods

All reactions were carried out under an atmosphere of nitrogen in glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Inert PureSolv MD5. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. ¹H and ¹³C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD. Data for ¹H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for ¹³C NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm). HRMS data were recorded on Bruker Impact II Q-TOF from our institute. GC data were recorded on Thermo Trace 1300. GC-MS data were recorded on Thermo ISQ QD.

Synthesis of diacyl peroxides and peresters

Caution: Diacyl peroxides and peresters have potentials to explode. Any diacyl peroxide and peresters involved reaction (as products or substrates) should be carried out with precautions!

Lauroyl peroxide (LPO) **2a** and perester **2b** and **2k** were purchased from Admas. Other peroxides were prepared by our previous work.¹

General procedure for carboazidation of alkenes

General procedure: To a dried Schlenk tube equipped with a magnetic bar, Fe(OTf)₂ (4.5 mg, 0.0125 mmol) was added. Then, this tube was flushed with nitrogen gas (3 times) and maintained a nitrogen atmosphere using a nitrogen balloon. A thoroughly mixed solution of alkene (0.25 mmol), TMSN₃ (0.5 mmol) and diacyl peroxides or peresters (0.5 mmol) in DME (1 mL) was added to the catalyst via syringe and the mixture was stirred vigorously for 2 hours at 35 °C (oil bath temp). After completion (TLC), the solvent was evaporated and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to give the corresponding product.

Characterization data for products



Following the general procedure, product **4aa** was obtained as a yellow oil (84.7 mg, 94% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.32 (m, 5H), 3.81 (s, 3H), 2.23 – 2.05 (m, 2H), 1.37 – 1.18 (m, 20H), 0.88 (t, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.9, 138.2, 129.0, 128.6, 126.0, 73.4, 53.2, 38.2, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 24.3, 14.3. HRMS (ESI) calculated for $[C_{21}H_{33}N_3NaO_2]^+$ $[M+Na^+]$: 382.2465, found: 382.2465.



Following the general procedure, product **4ba** was obtained as a yellow oil (100.2 mg, 92% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.27 (m, 10H), 5.26 (q, J = 12.2 Hz, 2H), 2.28 – 2.16 (m, 1H), 2.15 – 2.04 (m, 1H), 1.38 – 1.21 (m, 20H), 0.91 (t, J = 6.6 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 171.2, 138.2, 135.2, 128.9, 128.7, 128.6, 128.6, 128.5, 126.1, 73.3, 67.9, 38.1, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 24.3, 22.9, 14.3. HRMS (ESI) calculated for [C₂₇H₃₇N₃NaO₂]⁺ [M+Na⁺]: 458.2778, found: 458.2777.



Following the general procedure, product **4ca** was obtained as a yellow oil (79.3 mg, 85% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 100:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.23 (m, 3H), 7.22 – 7.17 (m, 2H), 3.76 (s, 3H), 3.16 (d, J = 13.8 Hz, 1H), 2.99 (d, J = 13.8 Hz, 1H), 1.92 – 1.81 (m, 1H), 1.68 (t, J = 12.6 Hz, 1H), 1.45 (dd, J = 9.8, 4.4 Hz, 1H), 1.37 – 1.16 (m, 19H), 0.88 (t, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.3, 135.2, 130.4, 128.6, 127.5, 71.2, 52.8, 43.3, 37.2,

32.1, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 24.4, 22.9, 14.4. HRMS (ESI) calculated for [C₂₂H₃₅N₃NaO₂]⁺ [M+Na⁺]: 396.2621, found: 396.2621.



Following the general procedure, product **4da** was obtained as a yellow oil (43 mg, 55% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 7:1)).¹H NMR (400 MHz, Chloroform-*d*) δ 4.35 – 4.23 (m, 2H), 3.88 (dd, J = 11.2, 5.0 Hz, 1H), 3.68 (d, J = 9.3 Hz, 1H), 2.24 (s, 1H), 1.81 – 1.65 (m, 2H), 1.42 – 1.19 (m, 24H), 0.87 (t, J = 6.8 Hz, 3H).¹³C NMR (100 MHz, Chloroform-*d*) δ 171.5, 71.2, 67.1, 62.3, 33.9, 32.1, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 23.9, 22.9, 14.4, 14.3. HRMS (ESI) calculated for [C₁₆H₃₁N₃NaO₃]⁺ [M+Na⁺]: 350.2414, found: 350.2415.



Following the general procedure, product **4ea** was obtained as a yellow oil (30 mg, 42% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 80:1)). ¹H NMR (400 MHz, Chloroformd) δ 3.84 – 3.80 (m, 1H), 3.79 (s, 3H), 1.88 – 1.70 (m, 2H), 1.45 – 1.37 (m, 2H), 1.35 – 1.19 (m, 18H), 0.87 (t, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 171.5, 62.2, 52.8, 32.1, 31.6, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.2, 25.9, 22.9, 14.3. HRMS (ESI) calculated for [C₁₅H₂₉N₃NaO₂]⁺ [M+Na⁺]: 306.2152, found: 306.2153.



Following the general procedure, product **4fa** was obtained as a yellow oil (78.3 mg, 84% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 50:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.28 (m, 5H), 5.21 (d, J = 2.3 Hz, 2H), 1.83 – 1.74 (m, 1H), 1.72 – 1.62 (m, 1H), 1.47 (s, 3H), 1.33 – 1.20 (m, 20H), 0.88 (t, J = 6.7 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.4, 135.3, 128.6, 128.4, 128.2, 67.4, 66.6, 38.2, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 24.0, 22.7, 22.4, 14.1. HRMS (ESI) calcd for [C₂₂H₃₅N₃NaO₂]⁺ [M+Na⁺]: 396.2621, found: 396.2618.



Following the general procedure, product **4ga** was obtained as a yellow oil (49.7 mg, 56% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 20:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 3.82 (s, 3H), 3.69 (s, 3H), 2.95 (d, *J* = 16.3 Hz, 1H), 2.67 (d, *J* = 16.3 Hz, 1H), 1.89 – 1.67 (m, 2H), 1.44 – 1.37 (m, 1H), 1.34 – 1.19 (m, 19H), 0.87 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.0, 170.2, 67.1, 53.1, 52.3, 41.5, 37.6, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 23.9, 22.9, 14.3. HRMS (ESI) calculated for [C₁₈H₃₃N₃NaO₄]⁺ [M+Na⁺]: 378.2363, found: 378.2363.



Following the general procedure, product **4ha** was obtained as a yellow oil (59 mg, 84% yield, $R_f = 0.3$ (petroleum ether)). ¹H NMR (400 MHz, Chloroform-*d*) δ 3.79 (dd, J = 8.6, 4.9 Hz, 1H), 2.63 – 2.46 (m, 2H), 1.83 – 1.65 (m, 2H), 1.49 – 1.37 (m, 2H), 1.32 – 1.22 (m, 18H), 1.08 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 208.5, 68.2, 33.1, 32.1, 31.1, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 26.0, 22.9, 7.6. HRMS (ESI) calcd for [C₁₆H₃₁N₃NaO]⁺ [M+Na⁺]: 304.2359, found: 304.2360.

Following the general procedure, product **4ia** was obtained as a yellow oil (56.8 mg, 75% yield, $R_f = 0.2$ (petroleum ether/dichloromethane = 4:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 2.73 – 2.50 (m, 2H), 2.26 – 1.95 (m, 2H), 1.95 – 1.79 (m, 2H), 1.56 – 1.51 (m, 2H), 1.42 – 1.37 (m, 18H), 0.87 (t, J = 6.7 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 117.9, 116.6, 62.1, 38.4, 33.8, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 24.5, 22.9, 14.3, 13.2. HRMS (ESI) calcd for [C₁₇H₂₉N₅Na]⁺ [M+Na⁺]: 326.2315, found: 326.2315.



Following the general procedure, product **4ja** was obtained as a yellow oil (106.4 mg, 99% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 40:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.79 (s, 1H), 4.76 (s, 1H), 4.43 (s, 1H), 2.33 (d, J = 13.2 Hz, 1H), 2.19 (dd, J = 15.6, 1.5 Hz, 1H), 2.14 – 1.94 (m, 3H), 1.79 (d, J = 12.1 Hz, 1H), 1.73 – 1.69 (m, 1H), 1.59 – 1.51 (m, 4H), 1.41 – 1.24 (m, 23H), 0.87 (t, J = 6.7 Hz, 3H), 0.78 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 173.9, 149.3, 106.7, 77.5, 71.2, 46.7, 43.5, 42.2, 41.3, 36.9, 34.7, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 28.0, 23.5, 22.9, 22.8, 21.0, 18.0, 14.3. HRMS (ESI) calculated for [C₂₆H₄₃N₃NaO₂]⁺ [M+Na⁺]: 452.3247, found: 452.3247.



Following the general procedure, product **4ab** was obtained as a yellow oil (50.6 mg, 92% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 5H), 3.81 (s, 3H), 2.30 – 2.21 (m, 1H), 2.18 – 2.09 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.8, 138.0, 129.0, 128.6, 126.1, 73.8, 53.2, 31.3, 8.8. HRMS (ESI) calcd for [C₁₁H₁₃N₃NaO₂]⁺ [M+Na⁺]: 242.0900, found: 242.0899.



Following the general procedure, product **4ac** was obtained as a yellow oil (61.9 mg, 90% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 5H), 3.81 (s, 3H), 2.24 – 2.16 (m, 1H), 2.11 – 2.04 (m, 1H), 1.44 – 1.14 (m, 9H), 0.87 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.9, 138.2, 129.0, 128.6, 126.0, 73.4, 53.2, 38.2, 31.7, 29.4, 24.3, 22.7, 14.2. HRMS (ESI) calcd for [C₁₅H₂₁N₃NaO₂]⁺ [M+Na⁺]: 298.1526, found: 298.1526.



Following the general procedure, product **4ad** was obtained as a yellow oil (60.5 mg, 88% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 5H), 3.81 (s, 3H), 2.23 – 2.15 (m, 1H), 2.11 – 2.04 (m, 1H), 1.30 – 1.23 (m, 1H), 1.16 – 1.09 (m, 1H), 0.88 (s, 9H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.9, 138.2, 129.0, 128.6, 126.1, 73.4, 53.2, 37.9, 33.4, 30.3, 29.4. HRMS (ESI) calcd for [C₁₅H₂₁N₃NaO₂]⁺ [M+Na⁺]: 298.1526, found: 298.1527.



Following the general procedure, product **4ae** was obtained as a yellow solid (56.6 mg, 70% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.32 (m, 5H), 7.29 – 7.24 (m, 2H), 7.20 – 7.11 (m, 3H), 3.79 (s, 3H), 2.64 – 2.55 (m, 2H), 2.27 – 2.19 (m, 1H), 2.15 – 2.05 (m, 1H), 1.68 – 1.61 (m, 2H), 1.49 – 1.39 (m, 1H), 1.38 – 1.31 (m, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.8, 142.4, 138.2, 129.0, 128.7, 128.5, 128.5, 126.0, 125.9, 73.4, 53.3, 38.1, 35.8, 31.6, 24.1. HRMS (ESI) calcd for [C₁₉H₂₁N₃NaO₂]⁺ [M+Na⁺]: 346.1526, found: 346.1526.



Following the general procedure, product **4af** was obtained as a yellow oil (54.6 mg, 74% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 30:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.31 (m, 5H), 3.82 (s, 3H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.24 – 2.15 (m, 1H), 2.13 – 2.02 (m, 1H), 1.79 – 1.72 (m, 2H), 1.53 – 1.35 (m, 3H), 1.32 – 1.26 (m, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.8, 138.0, 129.0, 128.7, 125.9, 73.3, 53.3, 45.0, 38.2, 32.4, 26.9, 23.6. HRMS (ESI) calcd for [C₁₄H₁₈ClN₃NaO₂]⁺ [M+Na⁺]: 318.0980, found: 318.0980.



Following the general procedure, product **4ag** was obtained as a yellow oil (39 mg, 54% yield, $R_f = 0.2$ (petroleum ether/ethyl acetate = 10:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.30 (m, 5H), 3.81 (s, 3H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.30 – 2.13 (m, 1H), 2.11 (s, 3H), 2.09 – 2.00 (m, 1H), 1.61 – 1.54 (m, 2H), 1.38 – 1.20 (m, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 208.8, 171.7, 138.0, 129.0, 128.7, 125.9, 73.2, 53.3, 43.5, 38.1, 30.1, 23.9, 23.7. HRMS (ESI) calcd for [C₁₅H₁₉N₃NaO₃]⁺ [M+Na⁺]: 312.1319, found: 312.1319.



Following the general procedure, product **4ah** was obtained as a yellow oil (66.2 mg, 91% yield, $R_f = 0.2$ (petroleum ether/ethyl acetate = 20:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.31 (m, 5H), 3.82 (s, 3H), 3.66 (s, 3H), 2.33 (t, *J* = 7.3 Hz, 2H), 2.25 – 2.09 (m, 2H), 1.72 – 1.57 (m, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 173.5, 171.6, 137.7, 129.0, 128.7, 125.9, 73.0, 53.3, 51.8, 37.6, 33.8, 19.8. HRMS (ESI) calcd for [C₁₄H₁₇N₃NaO₄]⁺ [M+Na⁺]: 314.1111, found: 314.1111.



Following the general procedure, product **4ai** was obtained as a yellow oil (70.1 mg, 85% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 5H), 5.86 – 5.76 (m, 1H), 5.03 – 4.90 (m, 2H), 3.81 (s, 3H), 2.28 – 2.18 (m, 1H), 2.12 – 2.00 (m, 3H), 1.36 – 1.27 (m, 12H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.9, 139.4, 138.2, 129.0, 128.6, 126.0, 114.3, 73.4, 53.2, 38.2, 34.0, 29.7, 29.5, 29.5, 29.2, 29.1, 24.3. HRMS (ESI) calcd for [C₁₉H₂₇N₃NaO₂]⁺ [M+Na⁺]: 352.1995, found: 352.1995.



Following the general procedure, product **4aj** was obtained as a yellow oil (34.3 mg, 56% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.31 (m, 5H), 3.81 (s, 3H), 2.19 (dd, *J* = 14.2, 5.9 Hz, 1H), 2.07 (dd, *J* = 14.2, 7.4 Hz, 1H), 0.84 – 0.74 (m, 1H), 0.47 (d, *J* = 8.1 Hz, 2H), 0.14 – 0.07 (m, 2H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.5, 138.1, 128.7, 128.5, 125.9, 73.5, 53.0, 42.8, 6.3, 4.5. HRMS (ESI) calcd for [C₁₃H₁₅N₃NaO₂]⁺ [M+Na⁺]: 268.1056, found: 268.1056.



Following the general procedure, product **4ak** was obtained as a yellow oil (42 mg, 55% yield, dr = 1:1, $R_f = 0.3$ (petroleum ether/ethyl acetate = 50:1)).¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.31 (m, 5H), 3.80 (s, 3H), 2.21 – 2.13 (m, 1H), 2.08 – 2.01 (m, 1H), 1.43 – 1.37 (m, 1H), 1.34 – 1.15 (m, 8H), 0.90 – 0.74 (m, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.1, 172.1, 138.7, 138.7, 128.9, 128.6, 128.6, 126.1, 73.5, 73.4, 53.1, 53.1, 41.7, 41.7, 35.3, 35.2, 33.5, 33.2, 28.6, 28.5, 26.7, 26.2, 23.2, 23.1, 14.3, 14.3, 10.6, 10.5. HRMS (ESI) calcd for [C₁₇H₂₅N₃NaO₂]⁺ [M+Na⁺]: 326.1839, found: 326.1835.



Following the general procedure, product **4al** was obtained as a yellow oil (48.5 mg, 55% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 5H), 3.80 (s, 3H), 2.23 – 2.15 (m, 1H), 2.11 – 2.03 (m,

1H), 1.96 - 1.91 (m, 2H), 1.71 - 1.64 (m, 3H), 1.63 - 1.60 (m, 2H), 1.60 - 1.58 (m, 2H), 1.46 - 1.42 (m, 6H), 1.17 - 1.10 (m, 1H), 1.03 - 0.96 (m, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.8, 138.0, 128.8, 128.4, 125.9, 73.3 53.1, 42.2, 38.1, 37.1, 32.0, 31.2, 28.6. HRMS (ESI) calcd for [C₂₁H₂₇N₃NaO₂]⁺ [M+Na⁺]: 376.1995, found: 376.1995.



Following the general procedure, product **4am** was obtained as a yellow oil (64.5 mg, 76% yield, $R_f = 0.5$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-d) δ 7.46 (d, J = 7.7 Hz, 2H), 7.40 – 7.30 (m, 3H), 3.78 (s, 3H), 2.22 (d, J = 14.9 Hz, 1H), 1.94 (s, 1H), 1.91 (s, 3H), 1.73 – 1.57 (m, 11H), 1.53 (s, 1H). ¹³C NMR (100 MHz, Chloroform-d) δ 172.3, 139.6, 128.9, 128.6, 126.1, 71.9, 53.1, 50.7, 43.0, 37.0, 33.8, 29.0. [C₂₀H₂₅N₃NaO₂]+ [M+Na+]: 362.1839, found: 362.1840.

Synthetic applications

A Scaled up reaction



Following the general procedure, gram scale synthesis of methyl 2-azido-2-phenyltetradecanoate were carried out, product **4aa** was obtained as a yellow oil (1.58 g, 88% yield).

Reduction of azido group to synthesize amine



The amine was prepared according literature method². To a solution of the azide **4aa** (0.50 mmol) in MeOH (10 mL) were added 10% Pd/C (10 mol %). After stirring overnight at room temperature under H₂ atmosphere, the mixture was filtered with a pad of Celite[®]. Concentration of the solvent in vacuo and the residue was purified by flash chromatography on silica gel using dichloromethane to give the product **5**.

Product **5** was obtained as a white solid (116 mg, 70% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 3:1)). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.49 (m, 2H), 7.36 – 7.33 (m, 2H), 7.28 – 7.23 (m, 1H), 3.70 (s, 1H), 2.15 – 2.10 (m, 1H), 2.01 – 1.95 (m, 1H), 1.93 (br, 2H), 1.29 – 1.21 (m, 20H), 0.89 – 0.86 (t, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 176.5, 143.5, 128.6, 127.5, 125.6, 64.0, 52.7, 40.2, 32.1, 30.1, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 24.2, 22.9, 14.3. HRMS (ESI) calcd for [C₂₁H₃₆NO₂]⁺ [M+H⁺]: 334.2741, found: 334.2742.

Preliminary mechanistic studies

With the addition of TEMPO



To a dried Schlenk tube equipped with a magnetic bar, $Fe(OTf)_2$ (4.5 mg, 0.0125 mmol) was added. Then, this tube was flushed with nitrogen gas (3 times) and maintained a nitrogen atmosphere using a nitrogen balloon. A thoroughly mixed solution of alkene (0.25 mmol), TMSN₃ (0.5 mmol) and LPO (0.5 mmol) and TEMPO (1.0 mmol) in DME (1 mL) was added to the catalyst via syringe and the mixture was stirred vigorously for 2 hours at 35 °C (oil bath temp). After completion (TLC), the solvent was evaporated and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to give the product **6** and only trace amount of product **4aa** was observed.

Compound **6** was obtained as a yellow oil (112 mg, 72% yield, $R_f = 0.3$ (petroleum ether/ethyl acetate = 60:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 3.71 (t, *J* = 6.7 Hz, 2H), 1.57 – 1.47 (m, 3H), 1.47 – 1.39 (m, 4H), 1.36 – 1.22 (m, 17H), 1.12 (d, *J* = 23.0 Hz, 12H), 0.88 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-d) δ 77.1, 59.8, 39.8, 33.3, 32.1, 30.0, 29.9, 29.9, 29.8, 29.6, 28.9, 26.7, 22.9, 20.3, 17.4, 14.4.³

A radical clock reaction



To a dried Schlenk tube equipped with a magnetic bar, $Fe(OTf)_2$ (4.5 mg, 0.0125 mmol) was added. Then, this tube was flushed with nitrogen gas (3 times) and maintained a nitrogen atmosphere using a nitrogen balloon. A thoroughly mixed solution of alkene (0.25 mmol), TMSN₃ (0.5 mmol) and diacyl peroxides (0.5 mmol) in DME (1 mL) was added to the catalyst via syringe and the mixture was stirred vigorously for 2 hours at appropriate temperature (oil bath temp). After completion (TLC), the solvent was evaporated and the residue was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to give the product **7** and no product **4an** was observed.

Compound **7** was obtained as a yellow oil (36 mg, 55% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 40:1)). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.29 (m, 5H), 5.81 – 5.70 (m, 1H), 5.11 – 4.90 (m, 2H), 3.81 (s, 3H), 2.26 – 2.14 (m, 1H), 2.12 – 2.06 (m, 3H), 1.55 – 1.42 (m, 1H), 1.43 – 1.30 (m, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 171.8, 138.1, 129.0, 128.7, 126.0, 115.4, 73.3, 53.3, 37.7, 33.7, 23.6. HRMS (ESI) calcd for [C₁₄H₁₇N₃NaO₂]⁺ [M+Na⁺]: 282.1213, found: 282.1214.

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NMR spectra





















S26













S32

















