Green and efficient: iron-catalyzed selective oxidation of olefins to carbonyls with O_2

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Supporting Information

Contents

1. General information

Solvents used in these experiments were reagent grade or better. DCE was refluxed over CaH_2 and distilled under N_2 atmosphere. Olefins and iron salts were purchased from commercial suppliers and used without further purification unless otherwise specified. PyBisulidine ligands were synthesised as reported in the literature.[1] Analytical thin-layer chromatography (TLC) was conducted with TLC Silica gel 60 F254 (Merck) and plates were revealed under UV irradiation, iodine, potassium permanganate or vanillin staining. Flash column chromatography was performed using Aldrich Silica Gel 60 and columns were packed according to the dry method and equilibrated with the appropriate eluent prior to use. HPLC grade solvents were used and the solvent mixtures used as eluent are understood as volume/volume. ^{1}H NMR spectra were recorded on a Bruker Advance 400 (400 MHz) NMR spectrometer and reported in units of parts per million (ppm) relative to tetramethyl silane (δ 0 ppm) or $CDCl_3$ (δ 7.26 ppm). Multiplicities are given as: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet) or m (multiplet). ^{13}C NMR spectra were recorded on a Bruker Advance 400 (100 MHz) NMR spectrometer and reported in ppm relative to $CDCl_3$ (δ 77.0 ppm). Coupling constants were reported as a J value in Hz. Mass spectra were obtained by electrospray ionization (ESI) or chemical ionization (CI) at the Analytical Services of the Chemistry Department, University of Liverpool and EPSRC National Mass Spectrometry Service Centre, College of Medicine, Swansea University. IR spectra were recorded on a Jacso FT/IR-4200 type A spectrometer. GC analyses were performed using a Varian star GC spectrometer.

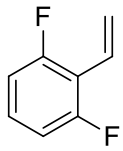
Warning: all the oxidation reactions described here should be carried out with caution due to its potential fire and explosion hazards. All the reactions were performed using O_2 (15% v/v in N_2).

2. Preparation of substrates

2.1. Synthesis and characterization of styrenes

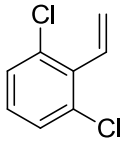
Styrenes were synthesized via methylenation of the corresponding ketones according to the literature.[2]

1,3-Difluoro-2-vinylbenzene[3](1m)



Colorless liquid, 98% isol. yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.16 (dq, *J* = 6.3, 2.0 Hz, 1H), 6.89-6.85 (m, 2H), 6.73 (dd, *J* = 18.0, 11.9 Hz, 1H), 6.04 (d, *J* = 18.0 Hz, 1H), 5.58 (dd, *J* = 11.9, 1.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 162.3 (d, $J_{C\text{-}F}$ = 250.3 Hz), 162.2 (d, $J_{C\text{-}F}$ = 250.2 Hz), 128.2 (t, $^3J_{C\text{-}F}$ = 10.8 Hz), 123.4, 121.4 (d, $^3J_{C\text{-}F}$ = 7.7 Hz), 111.5 (d, $^2J_{C\text{-}F}$ = 19.2 Hz), 111.4 (d, $^2J_{C\text{-}F}$ = 19.3 Hz). **HRMS** (CI) m/z calc'd $C_8H_7F_2$ $[M + H]^+$: 141.0511, found: 141.0516.

1,3-Dichloro-2-vinylbenzene[4] (1n)

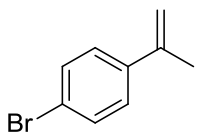


Colorless liquid, 98% isol. yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.37-7.30 (m, 2H), 7.10 (t, *J* = 8.2 Hz, 1H), 6.71 (dd, *J* = 17.9, 11.7 Hz, 1H), 5.80 (d, *J* = 17.9 Hz, 1H), 5.73 (d, *J* = 11.7 Hz,1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 135.0, 134.2, 130.9, 130.4, 128.4, 128.2, 126.9, 122.9. **HRMS** (CI) m/z calc'd $C_8H_7Cl_2$ $[M + H]^+$: 172.9919, found: 172.9925.

2.2. Syntheses and characterization of 1,1-disubstituted styrenes

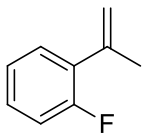
1,1-Disubstituted styrenes were synthesized via methylenation of the corresponding ketones according to the literature.[2]

4-Bromo-*α*-methylstyrene[5] (3b)



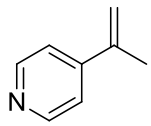
Colorless liquid, 95% isol. yield. Purification by flash chromatography (Hexane/ AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.46-7.42 (m, 2H), 7.34-7.31 (m, 2H), 5.35 (d, *J* = 0.4 Hz, 1H), 5.10 (q, *J* = 1.2 Hz, 1H), 2.12 (d, *J* = 0.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 142.6, 140.5, 131.6, 127.5, 121.7, 113.4, 22.1. **HRMS** (CI) m/z calc'd C_9H_9Br $[M + H]^+$: 196.9961, found: 196.9957.

1-Fluoro-2-(prop-1-en-2-yl)benzene[6] (3e)



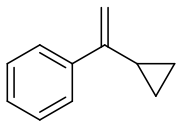
Colorless liquid, 95% isol. yield. Purification by flash chromatography (Hexane/ AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.65-7.62 (m, 1H), 7.38-7.36 (m, 1H), 7.20-7.17 (m, 2H), 5.16 (d, *J* = 2.0 Hz, 1H), 5.13 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 156.8 (d, $J_{C\text{-}F}$ = 249.7 Hz), 143.1, 129.7 (d, $^3J_{C\text{-}F}$ = 7.2 Hz), 128.7 (d, $^3J_{C\text{-}F}$ = 7.0 Hz**)**, 124.3, 113.5, 22.1. **HRMS** (CI) m/z calc'd $C_9H_{10}F$ $[M + H]^+$: 137.0761, found:137.0766.

(Pyridin-4-yl)-*α*-methylstyrene[7] **(3f)**



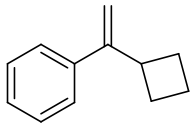
Yellowish liquid, 87% isol. yield. Purification by flash chromatography (AcOEt/Hexane, 3/2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.55 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.33 (dd, J = 4.8, 1.6 Hz, 2H), 5.57 (s, 1H), 5.26 (q, *J* = 1.6 Hz, 1H), 2.14 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 150.2, 133.4, 132.5, 132.4, 128.8, 120.5, 116.3, 21.2. **HRMS** (CI) m/z calc'd $C_8H_{10}N$ $[M + H]^+$: 120.0808, found: 120.0810.

(1-Cyclopropylvinyl)benzene[8] **(3g)**



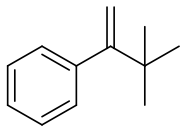
Colorless liquid, 97% isol. yield. Purification by flash chromatography (Hexane/ AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.61-7.58 (m, 2H), 7.36-7.25 (m, 3H), 5.27 (d, *J* = 0.8 Hz, 1H), 4.93 (t, *J* = 1.2 Hz, 1H), 1.68-1.65 (m, 1H), 0.87-0.81 (m, 3H), 0.60-0.57 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 149.7, 142.0, 128.5, 127.8, 126.5, 109.4, 16.0, 7.0. **HRMS** (CI) m/z calc'd $C_{14}H_{13}$ $[M + H]^+$: 145.1012, found: 145.1012.

(1-Cyclobutylvinyl)benzene[9] **(3h)**



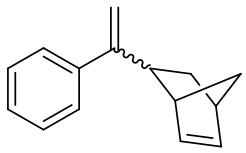
Colorless liquid, 87% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.46-7.13 (m, 5H), 5.38 (s, 1H), 5.02 (s, 1H), 3.56-3.34 (m, 1H), 2.31-2.15 (m, 2H), 2.08-1.92 (m, 3H), 1.87-1.74 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 152.0, 140.7, 128.1, 127.2, 126.1, 109.7, 39.5, 28.4, 17.7. **HRMS** (CI) m/z calc'd $C_{12}H_{15}$ $[M + H]^+$: 159.1168, found: 159.1169.

(3,3-Dimethylbut-1-en-2-yl)benzene[10] **(3j)**



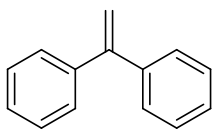
Colorless liquid, 87% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 159.8, 143.4, 129.0, 127.2, 126.2, 111.5, 29.6. **HRMS** (CI) m/z calc'd $C_{12}H_{17}$ $[M + H]^+$: 161.1325, found: 161.133.

***endo/exo*-5-(1-Phenylvinyl)bicilo[2.2.1]hept-2-ene (3k)**



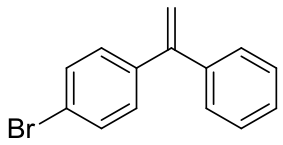
Colorless liquid, 87% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.4-7.38 (m, 2H), 7.33-7.27 (m, 3H), 6.20 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.14 (t, *J* = 2.8 Hz, 1H), 5.27 (s, 1H), 5.10 (s, 1H), 2.86 (d, *J* = 4.0 Hz, 2H), 2.56 (t, *J* = 6.6 Hz, 1H), 1.52 (t, *J* = 8.0 Hz, 1H), 1.43-1.38 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 152.8, 143.0, 137.5, 137.0, 128.1,127.1, 126.4, 110.0, 45.9, 45.5, 42.4, 42.2, 32.8. **HRMS** (CI) m/z calc'd $C_{15}H_{17}$ $[M + H]^+$: 197.1325, found: 197.1329.

Ethene, 11-diyldibenzene[11] **(3n)**



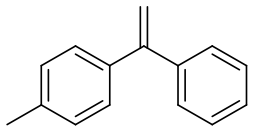
Colorless liquid, 96% isol. yield. Purification by flash chromatography (Hexane/ AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.34-7.24 (m, 10H), 5.46 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 150.0, 141.6, 128.2, 128.1, 127.7, 114.3. **HRMS** (CI) m/z calc'd $C_{14}H_{13}$ $[M + H]^+$: 181.1012, found: 181.1013.

1-(4-Bromophenyl)-1-phenylethylene[12] **(3o)**



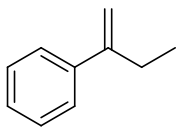
Colorless liquid, 95% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 17/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.57 (d, *J* = 8.2 Hz, 2H), 7.25 (m, 5H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.54 (s, 1H), 5.52 (s, 1H).). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 149.0, 140.9, 140.4, 131.3, 129.9, 128.3, 128.2, 127.9, 121.7, 114.7. **HRMS** (CI) m/z calc'd $C_{14}H_{11}Br$ $[M + H]^+$: 259.0117, found: 259.0128.

1-(4-Methylphenyl)-1-phenylethene[13] **(3p)**



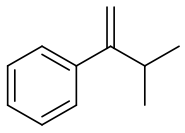
Colorless liquid, 96% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 17/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.25-7.39 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.44 (s, 1H), 5.41 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 150.0, 141.7, 138.8, 137.6, 128.9, 128.4, 128.3, 128.2, 127.8, 113.8, 21.3. **HRMS** (CI) m/z calc'd $C_{15}H_{15}$ $[M + H]^+$: 195.1168, found: 195.1172.

But-1-en-2-ylbenzene[12] **(9a)**



Colorless liquid, 97% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.42-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.28-7.23 (m, 1H), 5.27 (s, 1H), 5.06 (q, *J* = 1.6 Hz, 1H), 2.54-2.49 (m, 2H), 1.11 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 150.4, 141.9, 128.6, 127.6, 126.4, 111.3, 28.4, 13.3. **HRMS** (CI) m/z calc'd $C_{10}H_{13}$ $[M + H]^+$: 133.1012, found: 133.1011.

(3-Methylbut-1-en-2-yl)benzene[14] **(9b)**

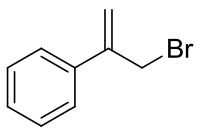


Colorless liquid, 96% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.36-7.24 (m, 5H), 5.14 (d, *J* = 0.2 Hz, 1H), 5.03 (t, *J* = 1.6 Hz, 1H), 1.71 (m, 1H), 1.10 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 156.1, 143.2, 128.5, 127.4, 127.0, 110.3, 19.8, 11.0. **HRMS** (CI) m/z calc'd $C_{11}H_{14}$ $[M +H]^+$: 147.1168, found: 147.1174.

2.3. Synthesis and characterisation of β-allyl bromides

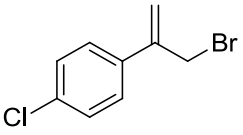
β-Allyl bromides were synthesized by halogenation of α-methylstyrene as reported in the literature.[15]

(3-Bromoprop-1-en-2-yl)benzene[15] **(3l)**



Colorless liquid, 87% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.59-7.56 (m, 2H), 7.46-7.43 (m, 3H), 5.56 (s, 1H), 5.49 (s, 1H), 4.39 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 144.2, 137.8, 128.6, 128.4, 126.3, 117.3, 34.4.

1-(3-Bromoprop-1-en-2-yl)-4-chlorobenzene[15] **(3m)**

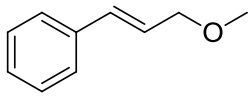


Colorless liquid, 87% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.47-7.27 (m, 4H), 5.54 (s, 1H), 5.50 (s, 1H), 4.35 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 143.2, 136.0, 134.1, 128.7, 117.7, 33.8.

2.4. Synthesis and characterization of cinnamyl alcohol derivatives

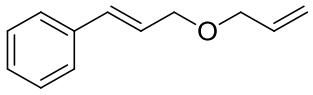
Cinnamyl ethers were synthesized as described in the literature.

Cinnamyl methyl ether[16] **(5d)**



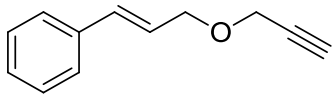
Pale yellow liquid, 95% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.39 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26-7.23 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.09 (dd, *J* = 6.4, 1.1 Hz, 2H), 3.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 136.7, 132.4, 128.5, 127.6, 126.4, 125.9, 73.1, 57.9.

Allyl-*trans*-cinnamyl ether[17] **(5e)**



Yellow liquid, 89% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.38 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26-7.23 (m, 1H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.0 Hz, 1H), 6.00-5.90 (m, 1H), 5.31 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.21 (dd, *J* = 10.4, 1.0 Hz, 1H), 4.15 (dd, *J* = 5.9, 1.0 Hz, 2H), 4.05 (d, *J* = 5.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 136.7, 134.7, 132.4, 128.5, 127.6, 126.4, 126.0, 117.1, 71.1, 70.7.

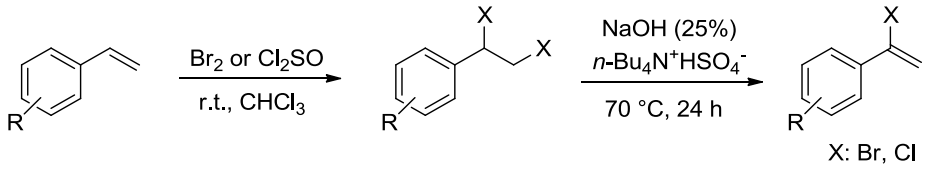
Cinnamyl propargyl ether[18] **(5f)**



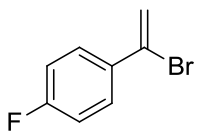
Colorless liquid, 89% isol. yield. Purification by flash chromatography (Hexane/AcOEt, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.39 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.26-7.23 (m, 1H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.25 (dd, *J* = 6.1, 1.3 Hz, 2H), 4.20 (d, *J* = 2.2 Hz, 2H), 2.4 (t, *J* = 2.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 136.5, 133.4, 128.5, 127.8, 126.5, 125.0, 79.7, 74.5, 70.2, 57.0.

2.5. Synthesis and characterization of vinyl halides

Vinyl bromides and chlorides were synthesized according to the two step procedure bellow.[19,20]

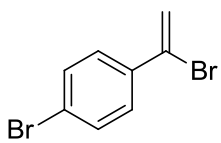


1-(1-Bromovinyl)-4-fluorobenzene (7b)



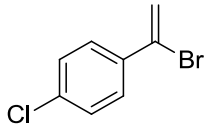
Yellow liquid (81% yield). Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.64-7.58 (m, 2H), 7.16-7.07 (m, 2H), 6.10 (d, *J* = 1.4 Hz, 1H), 5.81 (d, *J* = 1.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 162.7 ($^{1}J_{C\text{-}F}$ = 249 Hz), 136.1, 128.0 ($^{3}J_{C\text{-}F}$ = 9 Hz), 122.3, 116.7, 115.2 ($^{2}J_{C\text{-}F}$ = 21 Hz).

1-(1-Bromovinyl)-4-bromobenzene[21] **(7c)**



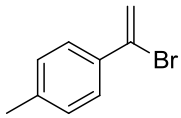
Yellow liquid, 87% yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.06 (m, 2H), 6.97 (m, 2H), 5.65 (d, *J* = 1.8 Hz, 2H), 5.50 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 138.5, 131.2, 130.0, 128.7, 123.6, 118.1.

1-(1-Bromovinyl)-4-chlorobenzene[22] **(7d)**



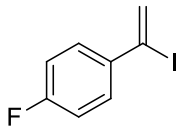
Yellow liquid, 74% yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.56-7.21 (m, 4H), 6.13 (s, 1H), 5.84 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 139.0, 133.6, 128.9, 127.5, 123.3, 118.3.

1-(1-Bromovinyl)-4-methylbenzene[23] **(7e)**



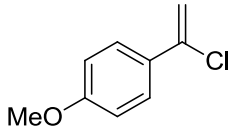
Yellow liquid, 72% yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.50 (d, *J* = 7.0 Hz, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 6.11 (d, *J* = 1.8 Hz, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 139.1, 135.7, 131.0, 128.9, 125.9, 116.8, 21.1.

1-Fluoro-4-(1-iodovinyl)benzene[24] **(7f)**



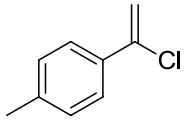
Yellow liquid, 42% yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.25-7.67 (m, 4H), 6.47 (s, 1H), 6.08 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 161.5 ($^{1}J_{C\text{-}F}$ = 250.1 Hz), 131.1, 127.8 ($^{3}J_{C\text{-}F}$ = 8.1 Hz), 119.3, 116.4 ($^{2}J_{C\text{-}F}$ = 22.2 Hz), 96.7.

1-(1-Chlorovinyl)-4-methoxybenzene[25] **(7g)**



Yellow liquid, 68% yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.70-7.62 (m, 2H), 6.93-6.85 (m,2H), 5.71 (s, 1H), 5.45 (s, 1H), 3.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 160.2, 139.4, 129.4, 127.6, 113.6, 110.7, 55.3.

1-(1-Chlorovinyl)-4-methylbenzene[26] **(7h)**

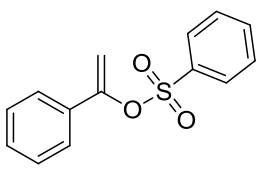


Yellow liquid, 69% yield. Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.59 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.78 (d, *J* = 1.7 Hz, 1H), 5.51 (d, *J* = 1.7 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 139.4, 134.9, 129.8, 127.3, 121.8, 21.4.

2.6. Preparation of vinyl sulfonate esters

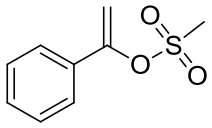
Vinyl sulfonate esters were prepared via hydrosulfonation of alkynes with sulfonic acids as reported in the literature.[27]

1-Phenylvinyl benzenesulfonate[27] **(7i)**



Yellow liquid, 69% yield. Purification by flash chromatography (Hexane/ AcOEt, 6/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.91 (t, *J* = 8.2 Hz, 2H), 7.59-7.40 (m, 5H), 7.31-7.26 (m, 3H), 5.41 (d, *J* = 2.9 Hz, 1H), 5.10 (d, *J* = 2.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 152.8, 135.0, 134.0, 133.2, 129.3, 129.0, 128.3(9), 128.3(8), 125.4, 103.3.

1-Phenylvinyl methanesulfonate[27] (7j)

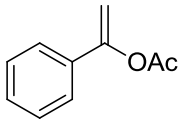


Yellow liquid, 69% yield. Purification by flash chromatography (Hexane/ AcOEt, 6/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.58-7.56 (m, 2H), 7.39-7.38 (m, 3H), 5.54 (d, *J* = 3.0 Hz, 1H), 5.38 (d, *J* = 3.0 Hz, 1H), 3.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 152.3, 133.1, 129.8, 128.8, 125.5, 103.3, 38.3.

2.7. Preparation of 1-phenylvinyl acetates

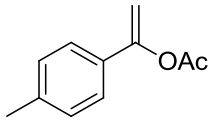
1-Phenylvinyl acetates were prepared according to the method reported by Shi.[28]

1-Phenylvinyl acetate[28] (7k)



Yellow liquid (78% yield). Purification by flash chromatography (Hexane/ AcOEt, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.48-7.45 (m, 2H), 7.35-7.33 (m, 3H), 5.49 (d, *J* = 2.1 Hz, 1H), 5.03 (d, *J* = 2.2 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 169.1, 152.9, 134.2, 128.9, 128.5, 124.8, 102.1, 21.0.

1-(*p*-Tolyl)vinyl acetate[28] (7l)

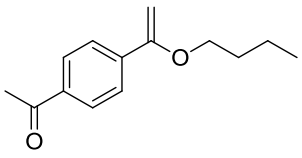


Yellow liquid (83% yield). Purification by flash chromatography (Hexane/ AcOEt, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.35 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.43 (d, *J* = 2.1 Hz, 1H), 4.96 (d, *J* = 2.1 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 169.1, 153.0, 139.0, 131.4, 129.2, 124.7, 101.2, 21.2, 21.0.

2.8. Preparation of 1-(4-(1-(butenyloxy)vinyl)aryl)ethanones

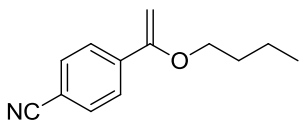
1-(4-(1-(butenyloxy)vinyl)phenyl)ethanone was prepared as reported by Xiao.[29]

1-(4-(1-Butoxyvinyl)phenyl)ethanone[29] (7m)



Yellow liquid (61% yield). Purification by flash chromatography (Hexane/ AcOEt, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.79 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 4.71 (d, *J* = 2.9 Hz, 1H), 4.20 (d, *J* = 2.9 Hz, 1H), 3.54 (t, *J* = 6.8 Hz, 2H), 2.20 (s, 3H), 1.48-1.24 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 197.8, 164.2, 135.9, 134.6, 128.9, 126.5, 79.9, 65.6, 32.8, 19.1, 14.2.

4-(1-Butoxyvinyl)benzonitrile (7n)

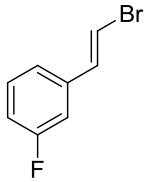


Colorless liquid (69% yield). Purification by flash chromatography (Hexane/ AcOEt, 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.73 (d, *J* = 8.2Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 4.76 (d, *J* = 3.0 Hz, 1H), 4.35 (d, *J* = 3.0 Hz, 1H), 3.87 (t, *J* = 7.3 Hz, 2H), 1.58-1.53 (m, 2H), 1.30-1.28 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 164.7, 134.6, 132.0, 127.4, 118.5, 111.7, 79.8, 65.4, 32.9, 19.1, 14.2.

2.9. Preparation of β-bromostyrenes

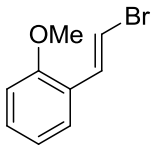
1-Bromostyrenes were prepared according to the literature.[30]

(*E*)-1-(2-Bromovinyl)-3-fluorobenzene[31]



Colorless liquid (64 % yield). Purification by flash chromatography (Hexane/ AcOEt, 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.49 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.40-7.32 (m, 2H), 7.05 (dd, *J* = 8.2, 1.3 Hz, 2H), 6.49 (dd, *J* = 8.2, 1.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 162.5 (d, $J_{C\text{-}F}$ = 243.7 Hz), 136.9 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 131.3, 129.7 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 124.9, 115.3 (q, $^2J_{C\text{-}F}$ = 22.4 Hz), 107.7.

(*E*)-1-(2-Bromovinyl)-2-methoxybenzene[32]



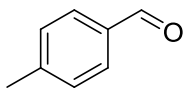
White solid (50 % yield). Purification by flash chromatography (Hexane/ AcOEt, 6/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.65 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 10.9Hz, 1H), 7.23-7.20 (m, 1H), 6.96-6.93 (m, 2H), 6.51 (d, *J* = 10.9 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 159.3, 133.0, 128.6, 120.7, 111.2, 110.7, 108.3, 55.6.

3. General procedure for the aerobic cleavage of olefins

3.1. $Fe(OTf)_3$-L1 catalyzed aerobic C=C cleavage of styrenes

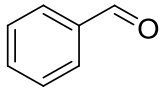
In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. A styrene (0.75 mmol) was added by syringe and the reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 6 hours. The reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc) to afford the unreacted starting material and the aldehyde product.

4-Methylbenzaldehyde[33] **(2a)**



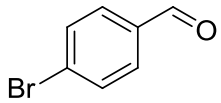
Colorless liquid (96% isol. yield, 0.72 mmol, 86.4 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.96 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 192.0, 145.5, 134.2, 129.8, 129.7, 21.9. **IR (neat)** ν = 3084, 2917, 1705, 1670, 1608, 1514, 1281, 1179, 1117, 807, 806, 751, 540, 467 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_9O $[M + H]^+$: 121.0648, found: 121.0645.

Benzaldehyde[33] **(2b)**



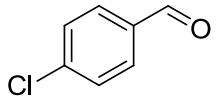
Colorless liquid (77% isol. yield, 0.58 mmol, 61.4 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.02 (s, 1H), 8.13-8.10 (m, 2H), 7.89-7.87 (m, 1H), 7.65-7.62 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 192.8, 136.8, 134.8, 129.9, 129.4. **IR (neat)** ν = 3062, 2819, 2736, 1698, 1652, 1598, 1583, 1454, 1390, 1311, 1207, 1162, 1070, 1020, 1002, 825, 744, 682, 642. **HRMS** (CI) m/z calc'd C_7H_6O $[M + H]^+$: 107.0492, found: 107.0488.

4-Bromobenzaldehyde[33] **(2c)**



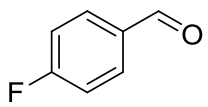
White solid (79% isol. yield, 0.59 mmol, 146.0 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.98, 7.76 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.68 (dd, *J* = 8.3, 2.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 191.4, 137.2, 132.8, 131.3, 130.2. **IR (neat)** ν = 2857, 2761, 1683, 1583, 1569, 1475, 1386, 1290, 1199, 1149, 1062, 1006, 829, 808, 678. **HRMS** (CI) m/z calc'd C_7H_6BrO $[M + H]^+$: 184.9597, found: 184.9595.

4-Chlorobenzaldehyde[34] **(2d)**



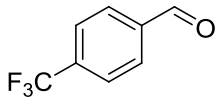
White solid (87% isol. yield, 0.65 mmol, 91.1 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.98 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.8, 140.9, 134.7, 130.9, 129.4. **IR (neat)** ν = 2840, 2654, 2588, 1702, 1590, 1573, 1486, 1400, 1286, 1257, 1207, 1166, 1087, 1012, 966, 937, 823, 761. **HRMS** (CI) m/z calc'd C_7H_6ClO $[M + H]^+$: 141.0102, found: 141.0100.

4-Fluorobenzaldehyde[35] **(2e)**



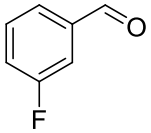
Colorless oil (78% isol. yield, 0.58 mmol, 71.8 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.97 (s, 1H), 7.99-7.90 (m, 2H), 7.32-7.21 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.4, 167.8 ($^1J_{C\text{-}F}$ = 255.1 Hz), 133.0 ($^4J_{C\text{-}F}$ = 3.0 Hz), 132.2 ($^3J_{C\text{-}F}$ = 10.5 Hz), 116.4 ($^2J_{C\text{-}F}$ = 22.1 Hz). **IR (neat)** ν = 3098, 1701, 1601, 1508, 1424, 1312, 1291, 1225, 1156, 1129, 853, 845, 767, 609, 495 cm^{-1}. **HRMS** (CI) m/z calc'd C_7H_6OF $[M + H]^+$: 121.0397, found: 125.0398.

4-(Trifluoromethyl)benzaldehyde[33] **(2f)**



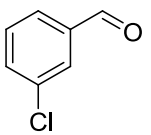
Colorless liquid (90% isol. yield, 0.67 mmol, 116.4 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, DMSO-d6): δ (ppm) = 10.12 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d6): δ (ppm) = 193.0, 166.5, 134.9, 130.5, 126.4, 122.8. **IR (neat)** ν = 2670, 2549, 1691, 1583, 1515, 1425, 1315, 1286, 1162, 1135, 1106, 1058, 1016, 937, 858, 775, 754, 700. **HRMS** (CI) m/z calc'd $C_8H_6F_3O$ $[M + H]^+$: 175.0366, found: 175.0364.

3-Fluorobenzaldehyde[36] **(2g)**



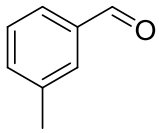
Colorless liquid (93% isol. yield, 0.70 mmol, 86.9 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.99 (s, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.68-7.54 (m, 2H), 7.34-7.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.9, 164.3 ($^1J_{C\text{-}F}$ = 248.3 Hz), 138.4 ($^3J_{C\text{-}F}$ = 6.2 Hz), 130.8 ($^3J_{C\text{-}F}$ = 8.0 Hz), 126.0 ($^3J_{C\text{-}F}$ = 3.1 Hz), 121.7 ($^2J_{C\text{-}F}$ = 22.1 Hz), 115.4 ($^2J_{C\text{-}F}$ = 22.2 Hz). **IR (neat)** ν = 3067, 3021, 1712, 1698, 1608, 1413, 1287, 1154, 769, 748, 640, 485 cm^{-1}. **HRMS** (CI) m/z calc'd C_7H_6FO $[M + H]^+$: 125.0398, found: 125.0395.

3-Chlorobenzaldehyde[36] **(2h)**



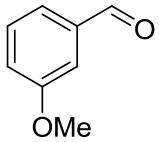
Colorless liquid (75% isol. yield, 0.56 mmol, 78.5 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.98 (s, 1H), 7.95 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.58-7.74 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.8, 137.8, 135.4, 134.4, 130.4, 127.9, 126.5. **IR (neat)** ν = 2937, 2836, 1714, 1678, 1588, 1573, 1488, 1420, 1400, 1253, 1169, 1127, 1013, 712, 681 cm^{-1}. **HRMS** (CI) m/z calc'd C_7H_6ClO $[M + H]^+$: 141.0102, found: 141.0106.

3-Methylbenzaldehyde[35] **(2i)**



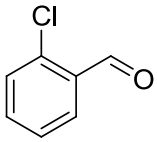
Colorless liquid (95% isol. yield, 0.71 mmol, 85.2 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.00 (s, 1H), 7.69-7.67 (m, 2H), 7.46-7.40 (m, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 192.6, 138.9, 136.4, 135.3, 130.0, 128.8, 127.2, 21.2. **IR (neat)** ν = 3078, 2921, 1701, 1606, 1588, 1488, 1433, 1278, 1246, 1158, 1142, 778, 745, 684, 653 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_8O $[M + H]^+$: 121.0648, found: 121.0646.

3-Methoxybenzaldehyde[37] **(2j)**



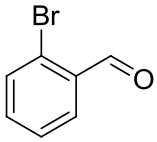
Colourless liquid (78% isol. yield, 0.58 mmol, 78.8 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.98 (s, 1H), 7.47-7.42 (m, 2H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.26-7.16 (m, 1H), 3.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 192.5, 160.5, 138.2, 130.4, 123.9, 121.9, 112.4, 55.8. **IR (neat)** ν = 2840, 2732, 1698, 1587, 1482, 1457, 1436, 1382, 1321, 1286, 1261, 1203, 1145, 1066, 1037, 1006, 927, 869, 833, 815, 786, 744, 678, 628. **HRMS** (CI) m/z calc'd $C_8H_9O_2$ $[M + H]^+$: 137.0597, found: 137.0596.

2-Chlorobenzaldehyde[36] **(2k)**



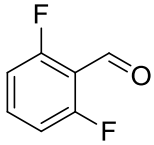
Colourless liquid (95% isol. yield, 0.71 mmol, 100.0 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.49 (s, 1H), 7.92 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.46-7.44 (m, 1H), 7.41-7.37 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 189.8, 137.9, 135.1, 132.4, 130.6, 129.3, 127.3. **IR (neat)** ν =2870, 2642, 1694, 1590, 1564, 1473, 1442, 1394, 1289, 1266, 1199, 1160, 1127, 1089, 1050, 1034, 956, 913, 824, 793, 751, 743, 710, 684, 644, 632, 556, 520 cm^{-1}. **HRMS** (CI) m/z calc'd C_7H_6ClO $[M + H]^+$: 141.0102, found: 141.0107.

2-Bromobenzaldehyde[36] **(2l)**



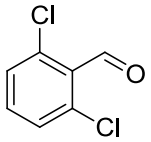
Colourless liquid (96% isol. yield, 0.72 mmol, 132.9 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.37 (s, 1H), 7.93-7.91 (m, 1H), 7.67-7.64 (m, 1H), 7.46-7.43 (m, 2H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 191.9, 135.3, 133.9, 133.5, 129.8, 127.9, 127.1. **IR (neat)** ν = 2868, 2633, 1693, 1586, 1567, 1471, 1438, 1392, 1293, 1263, 1199, 1160, 1123, 1085, 1043, 1026, 967, 945, 901, 869, 822, 791, 741, 685, 654, 630, 551, 540, 526 cm^{-1}. **HRMS** (CI) m/z calc'd C_7H_6BrO $[M + H]^+$: 184.9597, found: 184.9599.

2,6-Difluorobenzaldehyde[38] **(2m)**



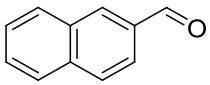
Colourless liquid (79% isol. yield, 0.59 mmol, 84.0 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.37 (s, 1H), 7.59-7.55 (m, 1H), 7.03-6.98 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 184.6 (t, $^{3}J_{C\text{-}F}$ = 4.6 Hz), 164.5 (d, $J_{C\text{-}F}$ = 261.8 Hz **)**, 164.4 (d, $J_{C\text{-}F}$ = 261.6 Hz), 136.2, 112.6 (d, $^{2}J_{C\text{-}F}$ = 19.9 Hz), 112.5 (d, $^{2}J_{C\text{-}F}$ = 19.9 Hz). **IR (neat)** ν = 2872, 2670, 2539, 1693, 1621, 1587, 1571, 1516, 1469, 1412, 1356, 1305, 1292, 1272, 1238, 1204, 1188, 1130, 1118, 1080, 1060, 1016, 919, 881, 826, 801, 792, 768, 732, 714, 692, 592, 575, 518 cm^{-1}. **HRMS** (CI) m/z calc'd $C_7H_5F_2O$ $[M + H]^+$: 143.0303, found: 143.0309.

2,6-dichlorobenzaldehyde[39] **(2n)**



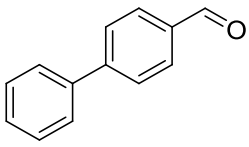
Colourless liquid (58% isol. yield, 0.43 mmol, 75.8 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.5 (s, 1H), 7.42-7.40 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 188.8, 136.8, 133.6, 130.4, 129.7. **IR (neat)** ν = 1694, 1575, 1433, 1402, 1185, 1093, 841, 774, 658, 604, 579, 570, 562, 536 cm^{-1}. **HRMS** (CI) m/z calc'd $C_7H_5Cl_2O$ $[M + H]^+$: 174.9712, found: 174.9719.

2-Naphthaldehyde[35] **(2o)**



White solid (30% isol. yield, 0.22 mmol, 34.4 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.17 (s, 1H), 8.35 (s, 1H), 8.02-7.85 (m, 4H), 7.64-7.57 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 192.6, 136.8, 134.9, 134.5, 133.0, 129.9, 129.5, 128.5, 127.5, 123.1. **IR (neat)** ν = 3062, 2846, 2829, 1689, 1661, 1598, 1402, 1365, 1165, 1142, 909, 800, 746, 699, 501 cm^{-1}. **HRMS** (CI) m/z calc'd $C_{11}H_9O$ $[M + H]^+$: 157.0648, found: 157.0646.

Biphenyl-4-carboxaldehyde[34] **(2p)**

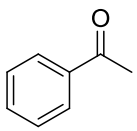


White solid (57% isol. yield, 0.43 mmol, 78.2 mg). Purification by flash chromatography (Hexane/ AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.06 (s, 1H), 7.95 (dd, *J* = 1.6, 8.4 Hz, 2H), 7.75 (dd, *J* = 1.5, 8.4 Hz, 2H), 7.64 (dd, *J* = 1.8, 8.4 Hz, 2H), 7.62-7.50 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 192.3, 140.1, 135.6, 130.6, 129.4, 128.8, 128.1, 127.7. **IR (neat)** ν = 3058, 3033, 2829, 2736, 1695, 1602, 1562, 1482, 1450, 1411, 1386, 1307, 1213, 1166, 1078, 1008, 833, 761, 725, 694. **HRMS** (CI) m/z calc'd $C_{13}H_{10}O$ $[M + H]^+$: 183.0805, found: 183.0805.

3.2. $Fe(OTf)_3$-L4 catalyzed aerobic C=C cleavage of α-substituted styrenes

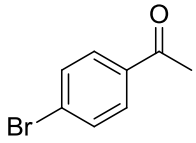
In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76×10^{-3} mmol, 2.9 mg) and **L4** (5.78×10^{-3} mmol, 5.4 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. An α-substituted styrene (0.50 mmol) was added by syringe and the reaction tube was degassed, charged with dioxygen gas (1 atm, 3 times) and keep under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react for 8 hours. The reaction was purified by silica gel column chromatography (Hexane/EtOAc) to afford the unreacted starting material and the ketone product.

Acetophenone[35] **(4a)**



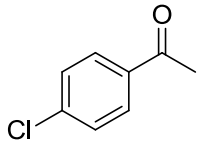
Colorless liquid (87% isol. yield, 0.43 mmol, 51.6 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.97-7.95 (m, 2H), 7.59-7.54 (m, 1H), 7.48-7.45 (m, 2H), 2.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 198.5, 137.5, 133.5, 129.1, 128.9, 128.7, 27.0. **IR (neat)** ν = 1681, 1598, 1583, 1448, 1357, 1303, 1265, 1178, 1078, 1024, 952, 761, 686. **HRMS** (CI) m/z calc'd C_8H_9O $[M + H]^+$: 121.0648, found: 121.0647.

4-Bromoacetophenone[40] **(4b)**



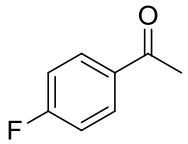
White solid (85% isol. yield, 0.42 mmol, 83.7 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.84-7.80 (m, 2H), 7.62-7.59 (m, 2H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 197.4, 136.2, 132.3, 130.2, 128.7, 26.9. **IR (neat)** ν = 1670, 1583, 1482, 1425, 1396, 1353, 1267, 1178, 1074, 1008, 954, 819, 750, 711. **HRMS** (CI) m/z calc'd C_8H_8BrO $[M + H]^+$: 198.9754, found: 198.9750.

4-Chloroacetophenone[40] **(4c)**



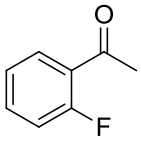
Colorless liquid (83% isol. yield, 0.41 mmol, 63.4 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.91-7.88 (m, 2H), 7.45-7.42 (m, 2H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 197.2, 139.9, 135.8, 130.1, 129.2, 26.9. **IR (neat)** ν = 1683, 1587, 1486, 1428, 1394, 1357, 1261, 1174, 1087, 1016, 954, 823, 757, 620. **HRMS** (CI) m/z calc'd C_8H_8ClO $[M + H]^+$: 155.0259, found: 155.0264.

4-Fluoroacetophenone[35] **(4d)**



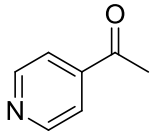
Colorless liquid (98% isol. yield, 0.49 mmol, 67.6 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.00-7.97 (m, 2H), 7.16-7.11 (m, 2H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 196.8, 167.4 (d, $^1J_{C\text{-}F}$ = 253.1 Hz) , 134.0, 133.9 (d, $^4J_{C\text{-}F}$ = 3.0 Hz) , 131.3 (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 116.1 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 26.9. **IR (neat)** ν = 1681, 1594, 1500, 1407, 1361, 1261, 1224, 1153, 1103, 1012, 958, 833. **HRMS** (CI) m/z calc'd C_8H_8FO $[M + H]^+$: 139.0554, found: 139.0551.

2-Fluoroacetophenone[29] **(4e)**



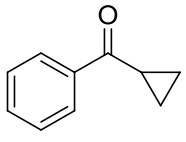
Colorless liquid (97% isol. yield, 0.48 mmol, 66.8 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.94-7.91 (m, 2H), 7.36-7.33 (m, 2H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 194.2 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 161.3 (d, $J_{C\text{-}F}$ 249.3 Hz), 134.7 (d, $^2J_{C\text{-}F}$ = 20.4 Hz), 130.5 (d, $^3J_{C\text{-}F}$ = 9.0 Hz), 127.8, 125.6 (d, $^2J_{C\text{-}F}$ = 20.6 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 27.1. **IR (neat)** ν = 1683, 1608, 1581, 1479, 1452, 1421, 1360, 1283, 1231, 1209, 1155, 1113, 1071, 1023, 965, 866, 828, 758, 699, 591, 534 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_8FO $[M + H]^+$: 139.0554, found: 139.0552.

4-Acetylpyridine[40] **(4f)**



Yellow liquid (20% isol. yield, 0.10 mmol, 12.2 mg). Purification by flash chromatography (Hexane/ AcOEt, 2/3). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.82 (dd, J = 1.6, 4.4 Hz, 2H), 7.74 (dd, *J* = 1.6, 5.6 Hz, 2H), 2.64 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 197.7, 151.3, 143.1, 121.6, 27.0. **IR (neat)** ν = 1691, 1598, 1554, 1407, 1361, 1265, 1216, 1062, 995, 962, 815. **HRMS** (CI) m/z calc'd C_7H_8NO $[M + H]^+$: 122.0601, found: 122.0606.

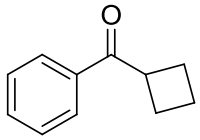
Cyclopropyl phenyl ketone[41] **(4g)**



Colorless liquid (87% isol. yield, 0.43 mmol, 62.9 mg). Purification by flash chromatography (Hexane/AcOEt, 25/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.03-8.01 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.45 (m, 2H), 2.71-2.65 (m, 1H), 1.26-1.19 (m, 2H), 1.08-1.03 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 201.0, 138.4, 133.1, 128.9, 128.4, 17.5, 12.0. **IR (neat)** ν = 3062, 3008, 1666, 1598, 1577,

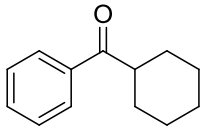
1448, 1382, 1224, 1178, 1033, 987, 869, 815, 782, 703, 646. **HRMS** (CI) m/z calc'd $C_{10}H_{11}O$ [M + H]$^+$: 147.0805, found: 147.0804.

Cyclobutyl phenyl ketone[42] **(4h)**



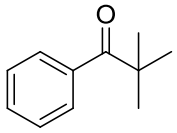
Colorless liquid (54% isol. yield, 0.27 mmol, 43.2 mg). Purification by flash chromatography (Hexane/ AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.98-7.87 (m, 2H), 7.71-7.62 (m, 1H), 7.58-7.50 (m, 2H), 4.05 (q, *J* = 6.7 Hz, 1H), 2.54-2.38 (m, 3H), 2.21-2.02 (m, 2H), 1.97-1.84 (m, 1H). **IR (neat)** ν = 2983, 2942, 1674, 1597, 1579, 1448, 1346, 1248, 1221, 1177, 966, 771, 737, 692, 659 cm^{-1}.**^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 201.0, 135.6, 132.8, 128.5, 128.3, 42.2, 25.1, 18.1. **HRMS** (CI) m/z calc'd $C_{11}H_{13}O$ [M + H]$^+$: 161.0961, found: 161.0960.

Cyclohexyl phenyl ketone[36] **(4i)**



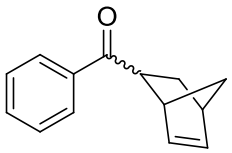
Colorless liquid (73% isol. yield, 0.36 mmol, 67.8 mg). Purification by flash chromatography (Hexane/ AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, J = 7.8 Hz, 2H), 7.74-7.68 (m, 1H), 7.64-7.58 (m, 2H), 3.37 (q, *J* = 7.0 Hz, 1H), 1.97-1.35 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 203.9, 136.3, 132.7, 128.5, 128.2, 45.6, 29.4, 26.2, 25.8. **IR (neat)** ν = 2928, 2853, 1679, 1597, 1580, 1447, 1288, 1250, 1206, 1172, 973, 763, 696, 660 cm^{-1}. **HRMS** (CI) m/z calc'd $C_{13}H_{17}O$ [M + H]$^+$: 189.1274, found: 189.1267.

2,2-Dimethyl-1-phenylpropan-1-one[43] **(4j)**



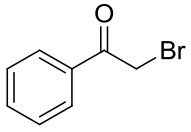
Colorless liquid (54% isol. yield, 0.27 mmol, 43.4 mg). Purification by flash chromatography (Hexane/ AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.70-7.67 (m, 2H), 746-7.37 (m, 3H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 209.3, 138.6, 130.8, 128.0, 127.8, 44.2, 28.0. **IR (neat)** ν = 2969, 2932, 2906, 2872, 1673, 1599, 1584, 1477, 1460, 1444, 1395, 1366, 1277, 1191, 1175, 1114, 1076, 1037, 1026, 1002, 959, 847, 817, 795, 718, 697, 644, 618, 591, 561, 549, 543 cm^{-1}. **HRMS** (CI) m/z calc'd $C_{11}H_{15}O$ [M + H]$^+$: 163.1117, found: 163.1121.

***endo/exo*-Bicyclo[2.2.1]hept-5-en-2-yl(phenyl)methanone**[44] **(4k)**



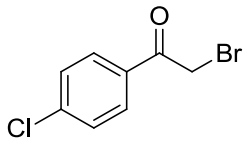
Colorless liquid (78% isol. yield, 0.39 mmol, 77.0 mg). Purification by flash chromatography (Hexane/ AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.96 (dd, *J* = 7.2, 2.7 Hz, 4H), 7.55-7.44 (m, 6H), 6.24 (s, 2H), 6.18 (dd, *J* = 5.6, 3.0 Hz, 1H), 5.82 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.85 (q, *J* = 4.0 Hz, 1H), 3.26 (s, 1H), 3.14 (dd, *J* = 8.8, 4.7 Hz, 1H), 3.09 (d, *J* = 1.1 Hz, 1H), 2.97 (s, 2H), 2.01-1.93 (m, 2H), 1.65-1.50 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 202.3, 200.8, 138.5, 137.3, 137.2, 137.0, 135.9, 132.7, 132.6, 131.8, 128.5, 128.4, 128.3, 128.2, 49.9, 47.4, 47.1, 46.5, 46.3, 42.9, 42.0, 30.9, 29.0. **IR (neat)** ν = 2972, 2942, 2869, 1676, 1596, 1580, 1447, 1332, 1272, 1252, 1225, 1208, 1177, 1158, 1094, 1076, 1064, 1045, 1024, 1002, 981, 929, 905, 859, 848, 838, 808, 797, 782, 755, 742, 717, 653, 616, 535, 522 cm^{-1}. **HRMS** (CI) m/z calc'd $C_{14}H_{15}O$ [M + H]$^+$: 199.1118, found: 199.1123.

2-Bromo-1-phenylethanone[45] **(4l)**



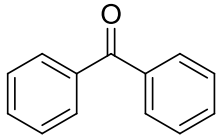
White solid (92% isol. yield, 0.46 mmol, 91.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.00 (d, *J* = 7.8 Hz, 2H), 7.64-7.60 (m, 1H), 7.58-7.50 (m, 2H), 4.52 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 193.2, 133.9, 133.7, 128.9, 128.8, 30.9. **IR (neat)** ν = 1702, 1677, 1595, 1580, 1448, 1427, 1320, 1307, 1277, 1193, 1012, 989, 749, 709, 685, 622, 608, 590, 527 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_7BrO [M + H]$^+$: 198.9753, found: 198.9753.

2-Bromo-1-(4-chlorophenyl)ethanone[45] **(4m)**



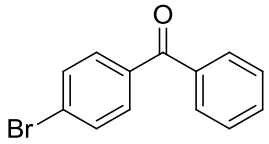
White solid (91% isol. yield, 0.45 mmol, 103.7 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 4.45 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.2, 140.5, 132.2, 130.3, 130.2, 129.2, 129.0, 30.3. **IR (neat)** ν = 2953, 1691, 1585, 1568, 1485, 1400, 1390, 1359, 1281, 1196, 1178, 1153, 1090, 1010, 991, 809, 785, 722, 664, 626, 547, 523 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_7BrClO $[M + H]^+$: 249.9629, found: 249.9625.

Benzophenone[34] **(4n)**



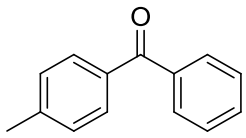
White solid (95% isol. yield, 0.47 mmol, 86.3 mg). Purification by flash chromatography (Hexane/ AcOEt 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.81-7.79 (m, 4H), 7.60-7.56 (m, 2H), 7.49-7.45 (m, 4H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 197.1, 138.0, 132.5, 130.4, 128.6. **IR (neat)** ν = 1650, 1593, 1575, 1447, 1320, 1275, 1175, 1160, 1150, 1075, 998, 944, 935, 918, 813, 764, 702, 692, 636 cm^{-1}.**HRMS** (CI) m/z calc'd $C_{13}H_{11}O$ $[M + H]^+$: 183.0804, found: 183.0808.

4-Bromobenzophenone[46] **(4o)**



White solid (63% isol. yield, 0.31 mmol, 82.2 mg). Purification by flash chromatography (Hexane/ AcOEt 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.81 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.70-7.59 (m, 5H), 7.51-7.48 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 195.6, 137.1, 136.3, 132.6, 131.6, 131.5, 129.9, 128.4, 127.5. **HRMS** (CI) m/z calc'd $C_{13}H_{10}BrO$ $[M + H]^+$: 260.991, found: 260.9917.

4-Methylbenzophenone[46] **(4p)**

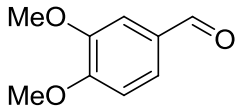


White solid (56% isol. yield, 0.28 mmol, 54.9 mg). Purification by flash chromatography (Hexane/ AcOEt 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.78 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.46 (dd, *J* = 7.7, 7.6 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 196.5, 143.2, 137.9, 134.9, 132.1, 130.3, 129.9, 128.9, 128.2, 21.6. **HRMS** (CI) m/z calc'd $C_{14}H_{13}O$ $[M + H]^+$: 197.0961, found: 197.0967.

3.3. $Fe(OTf)_3$-L1 catalyzed aerobic C=C cleavage of β-substituted styrenes

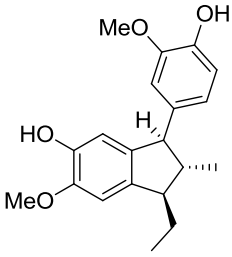
In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76×10^{-3} mmol, 2.9 mg) and **L1** (5.78×10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 40°C. A β-substituted styrene (0.5 mmol) was added by syringe and the reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 78 °C and allowed to react overnight (*circa* 16 h). The reaction was purified by silica gel column chromatography (Hexane/EtOAc) to afford the unreacted starting material and the aldehyde product.

3,4-Dimethoxybenzaldehyde[47] **(6b)**



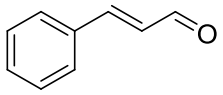
White solid (68% isol. yield, 0.34 mmol, 56.4 mg). Purification by flash chromatography (Hexane/ AcOEt 6/1 to 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.89 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.41 (s, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.9, 154.5, 149.6, 130.1, 126.8, 110.3, 108.9, 56.1, 56.0. **HRMS** (CI) m/z calc'd $C_9H_{11}O_3$ $[M + H]^+$: 167.0703, found: 167.0704.

γ-Diisoeugenol[48] **(6c)**



White solid (99% isol. yield, 0.25 mmol, 82.0 mg). Purification by flash chromatography (Hexane/ AcOEt, 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.83 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 6.48 (s, 1H), 5.56 (s, 1H), 5.51 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.73 (d, *J* = 9.4 Hz, 1H), 2.95-2.86 (m, 1H), 2.51-2.42 (m, 1H), 1.75-1.65 (m, 1H), 1.44-1.31 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 146.4, 145.1, 144.5, 144.1, 139.1, 138.7, 135.8, 121.5, 114.0, 111.0, 110.6, 107.5, 56.7, 56.1, 55.9, 49.2, 48.5, 22.4, 13.8, 12.2. **HRMS** (CI) m/z calc'd $C_{20}H_{24}O_4Na$ $[M + Na]^+$: 351.1572, found: 351.1566.

Cinnamaldehyde[34] **(6d)**

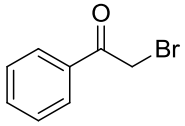


Colorless liquid (20% isol yield, 0.10 mmol, 13.2 mg). Purification by flash chromatography (Hexane/AcOEt, 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.91 (d, *J* = 7.2H, 1H), 7.81-7.42 (m, 6H), 6.72 (dd, *J* = 15.8, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 193.8, 152.9, 134.0, 131.3, 129.1, 128.5. **IR (neat)** ν = 3066, 3027, 2827, 1672, 1626, 1495, 1449, 1418, 1282, 1225, 1176, 1159, 1134, 976, 943, 911, 766, 697, 682, 589, 541, 480 cm^{-1}. **HRMS** (CI) m/z calc'd C_9H_9O $[M + H]^+$: 133.0648, found: 133.0649.

3.4. $Fe(OTf)_3$-L1 catalyzed aerobic oxygenation of vinyl halides and vinyl ethers

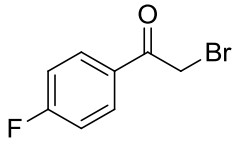
In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. DBE or DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 40°C. Next, a vinyl halide (0.50 mmol) was added by syringe. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react overnight (*circa* 16 h). The reaction mixture was purified by silica gel flash column chromatography (Hexane/EtOAc) to afford the unreacted starting material and the ketone product.

Phenacyl bromide[45] **(8a, i.e. 4l)**



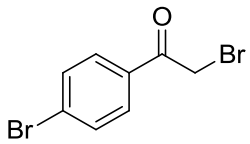
White solid (61% isol. yield, 0.30 mmol, 60.8 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.00 (d, *J* = 7.8 Hz, 2H), 7.64-7.60 (m, 1H), 7.58-7.50 (m, 2H), 4.52 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 193.2, 133.9, 133.7, 128.9, 128.8, 30.9. **IR (neat)** ν = 1702, 1677, 1595, 1580, 1448, 1427, 1320, 1307, 1277, 1193, 1012, 989, 749, 709, 685, 622, 608, 590, 527 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_7BrO $[M + H]^+$: 198.9753, found: 198.9753.

4-Fluorophenacyl bromide[45] **(8b)**



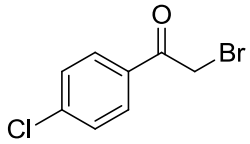
Colorless solid (65% isol. yield, 0.32 mmol, 70.4 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.00-8.10 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.51 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 189.8, 167.4 (d, $^{1}J_{C\text{-}F}$ = 256.0 Hz), 131.8 (d, $^{3}J_{C\text{-}F}$ = 10.0 Hz), 130.3 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 116.2 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 30.4. **IR (neat)** ν = 1666, 1592, 1504, 1422, 1275, 1227, 1156, 1110, 1096, 1004, 968, 860, 841, 815, 752, 680, 571, 507 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_7BrFO $[M + H]^+$: 216.9659, found: 216.9666.

4-Bromophenacyl bromide[45] **(8c)**



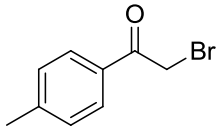
Colorless solid (97% isol. yield, 0.48 mmol, 134.6 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.90 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 4.42 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.4, 132.6, 132.2, 130.4, 129.3, 30.3. **HRMS** (CI) m/z calc'd $C_8H_7Br_2O$ $[M + H]^+$: 276.8858, found: 276.8861.

4-Chlorophenacyl bromide[45] **(8d)**



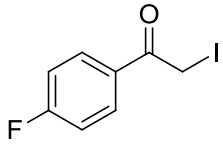
Colorless solid (75% isol. yield, 0.37 mmol, 87.5 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 4.45 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.2, 140.5, 132.2, 130.3, 130.2, 129.2, 129.0, 30.3. **IR (neat)** ν = 2953, 1691, 1585, 1568, 1485, 1400, 1390, 1359, 1281, 1196, 1178, 1153, 1090, 1010, 991, 809, 785, 722, 664, 626, 547, 523 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_7BrClO $[M + H]^+$: 249.9629, found: 249.9625.

4-Methylphenacyl bromide[45] **(8e)**



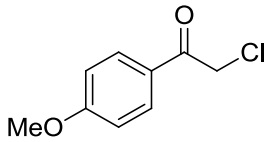
Colorless solid (99% isol. yield, 0.49 mmol, 105.3 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, *J* = 8.00 Hz, 2H), 7.37 (d, *J* = 8.00 Hz, 2H), 4.51 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.97, 145.0, 131.5, 129.5, 129.0, 30.8. **IR (neat)** ν = 3001, 2952, 2915, 1691, 1605, 1572, 1408, 1391, 1315, 1282, 1216, 1193, 1180, 1119, 758, 683, 581, 550, 454 cm^{-1}. **HRMS** (CI) m/z calc'd $C_9H_{10}BrO$ $[M + H]^+$: 212.991, found: 212.9917.

4-Fluorophenacyl iodide[49] **(8f)**



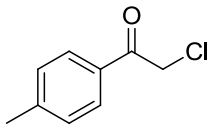
Colorless solid (50% isol. yield, 0.25 mmol, 66.0 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.09 (d, *J* = 8.0 Hz, 2H), 7.16 (m, 2H), 4.42 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 196.5, 167.3 (d, $^{1}J_{C\text{-}F}$ = 254.9 Hz), 132.3, 130.4 (d, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 115.9 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 13.9. **IR (neat)** ν = 1666, 1592, 1504, 1422, 1275, 1227, 1156, 1110, 1096, 1004, 968, 860, 841, 752, 680, 571, 507, 464 cm^{-1}. **HRMS** (CI) m/z calc'd C_8H_7FIO $[M + H]^+$: 264.952, found: 264.9525.

4-Methoxyphenacyl chloride[50] **(8g)**



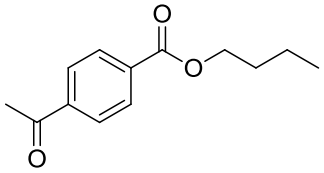
Colorless solid (50% isol. yield, 0.25 mmol, 46.0 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.00 (d, *J* = 8.0 Hz, 2H), 6.99 (m, 2H), 4.70 (s, 2H), 3.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 196.8, 163.4, 130.6, 130.3, 113.6, 55.5, 45.7. **IR (neat)** ν = 1705, 1695, 1623, 1420, 1389, 1257, 1219, 1204, 1175, 1153, 1120, 1098, 1040, 989, 742, 689, 624 cm^{-1}. **HRMS** (CI) m/z calc'd $C_9H_{10}ClO_2$ $[M + H]^+$: 185.0364, found: 185.0359.

4-Methylphenacyl chloride[51] **(8h)**



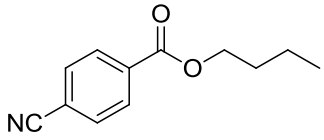
Colorless solid (50% isol. yield, 0.25 mmol, 42.1 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.10 (d, *J* = 8.0 Hz, 2H), 7.37 (m, 2H), 4.71 (s, 2H), 2.52 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 196.5, 145.5, 130.6, 129.5, 128.6, 45.9, 21.8. **IR (neat)** ν = 2921, 1773, 1709, 1684, 1606, 1447, 1410, 1375, 1221, 1206, 1169, 1121, 1035, 999, 837, 822, 747, 730, 681, 636, 590, 571, 522, 444 cm^{-1}. **HRMS** (CI) m/z calc'd $C_9H_{10}ClO$ $[M + H]^+$: 169.0415, found: 169.0413.

Butyl 4-acetylbenzoate (8m)



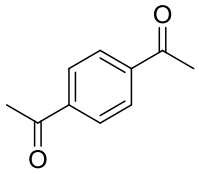
Colorless liquid (76 % isol. yield, 0.38 mmol, 83.4 mg). Purification by flash chromatography (Hexane/AcOEt, 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.20 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.2 Hz, 2H), 4.18 (t, *J* = 6.7 Hz, 2H), 2.68 (s, 3H), 1.67-1.63 (m, 2H), 1.43-1.37 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 197.7, 166.7, 141.0, 134.9, 130.4, 128.3, 64.5, 31.1, 18.9, 13.8.

Butyl 4-cyanobenzoate (8n)



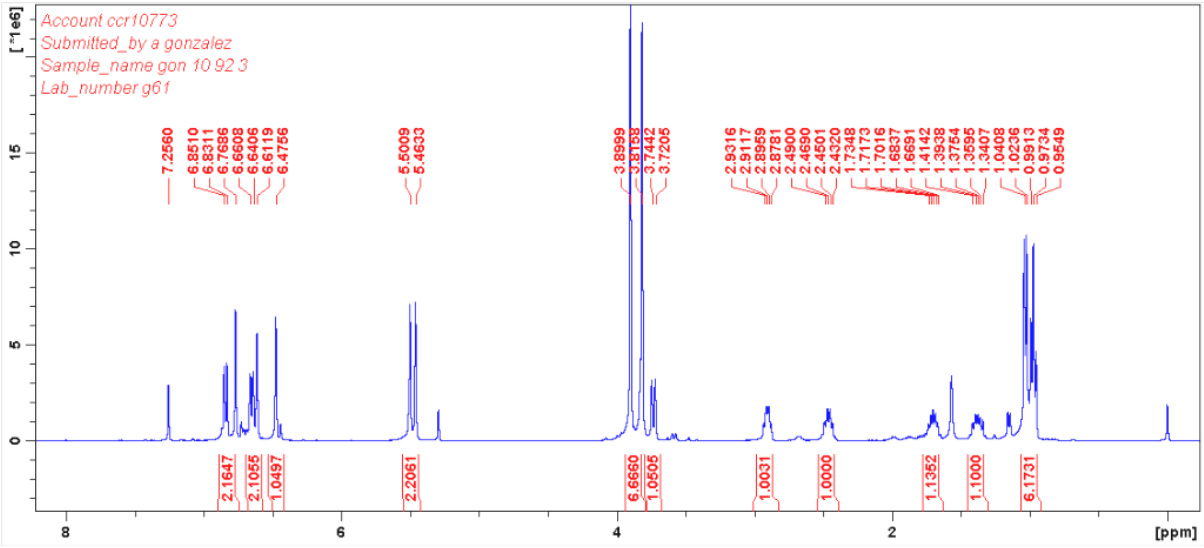
Colorless liquid (78 % isol. yield, 0.39 mmol, 79.1 mg). Purification by flash chromatography (Hexane/AcOEt, 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.05 (dd, *J* = 8.2, 2.0 Hz, 2H), 7.77 (dd, *J* = 8.2, 2.0 Hz, 2H), 4.13 (q, *J* = 6.0 Hz, 2H), 1.64-1.62 (m, 2H), 1.44-1.39 (m, 2H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.8, 140.4, 132.4, 128.8, 118.0, 116.2, 68.7, 31.9, 19.2, 13.8.

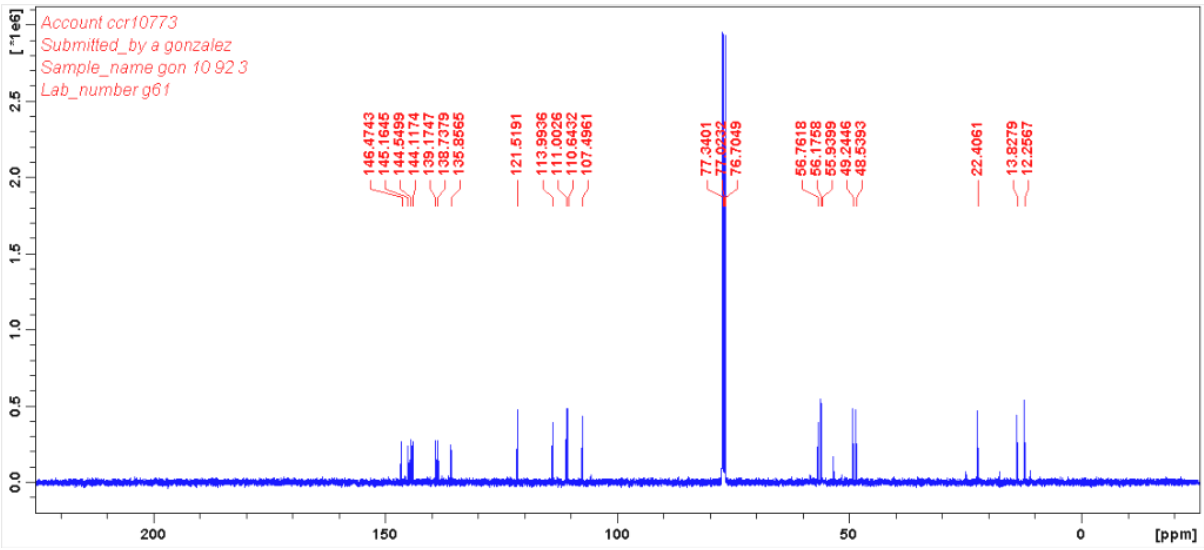
1,1'-(1,4-Phenylene)diethanone[52] **(8m')**



Colorless liquid (10 % isol. yield, 0.05 mmol, 8.0 mg). Purification by flash chromatography (Hexane/AcOEt, 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.04 (s, 4H), 2.65 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 197.3, 140.6, 128.5, 26.9. **HRMS** (CI) m/z calc'd $C_{10}H_{11}O_2$ $[M + H]^+$: 163.0754, found: 163.0760.

4. NMR characterization of γ-diisoeugenol



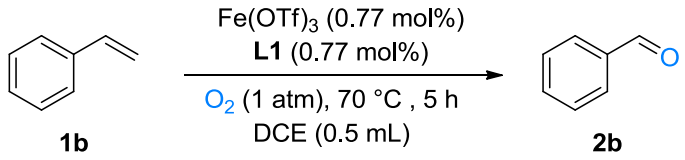


5. Mechanistic investigations

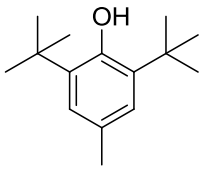
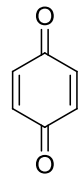
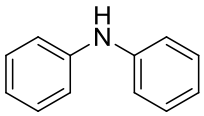
5.1. Radical trapping experiments

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. The tube was sealed, degassed and left under an inert atmosphere (3 times). Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, styrene (0.75 mmol, 90 µL) and a certain amount of radical trapping reagent were added. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 5 hours. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 20/1) to afford the unreacted starting material and the aldehyde product.

Table S1. Effect of the radical trap in the Fe(OTf)$_3$-L1 catalyzed aerobic cleavage of styrene



1b **2b**

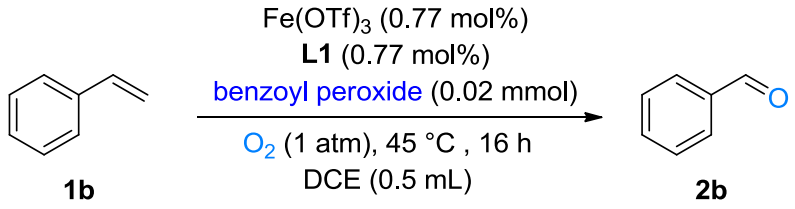
Radical probe	Entry	rad probe/catalyst	Benzaldehyde (isol. yield %)[a]
	1	1	N.R.
	2	5	N.R.
	3	10	N.R.
$BrCCl_3$	4	5	72
	5	10	65
	6	5	54
	7	10	8
	8	5	N.R.
	9	10	N.R.

[a]N.R. = No reaction

5.2. Effect of a radical initiator

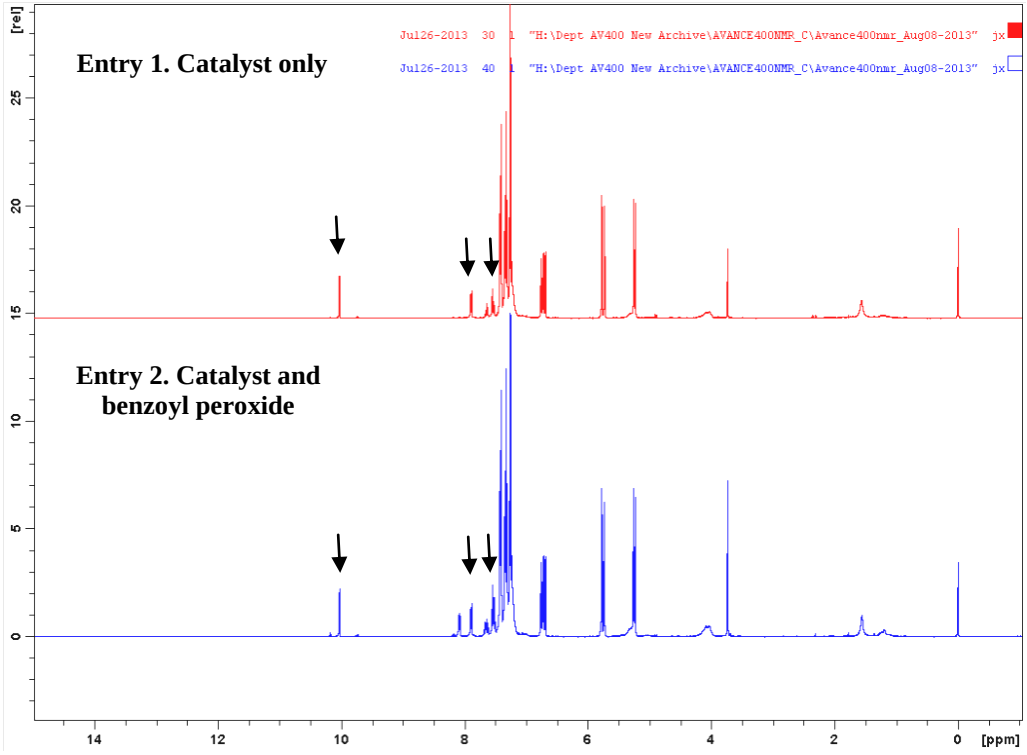
In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76×10^{-3} mmol, 2.9 mg) and **L1** (5.78×10^{-3} mmol, 5.3 mg) were added. The tube was sealed, degassed and left under an inert atmosphere (3 times). Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35 °C. Next, styrene (0.75 mmol, 90 µL) and the radical initiator benzoyl peroxide (0.02 mmol) were added. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 45 °C and allowed to react overnight. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 20/1) to afford the unreacted starting material and the aldehyde product. The same procedure was repeated in the absence of the radical initiator.

Table S2. Aerobic cleavage of styrene in the presence of a radical initiator. The ^{1}H NMR resonances corresponding to the benzaldehyde product are highlighted under the black arrow.

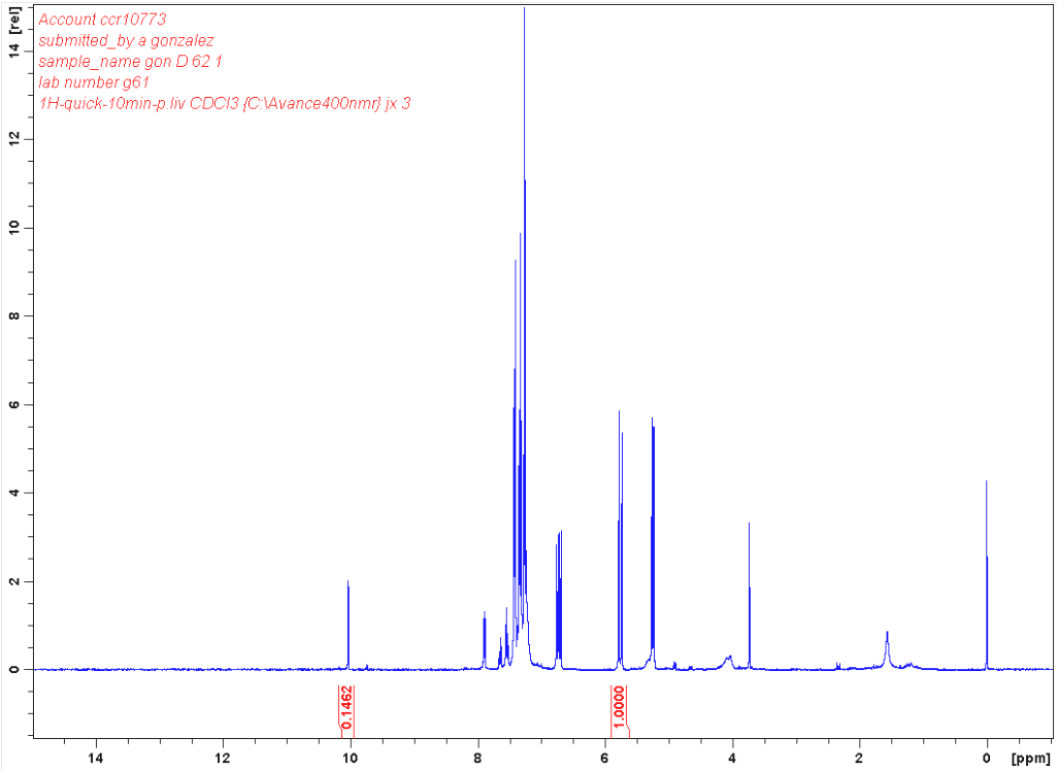


1b **2b**

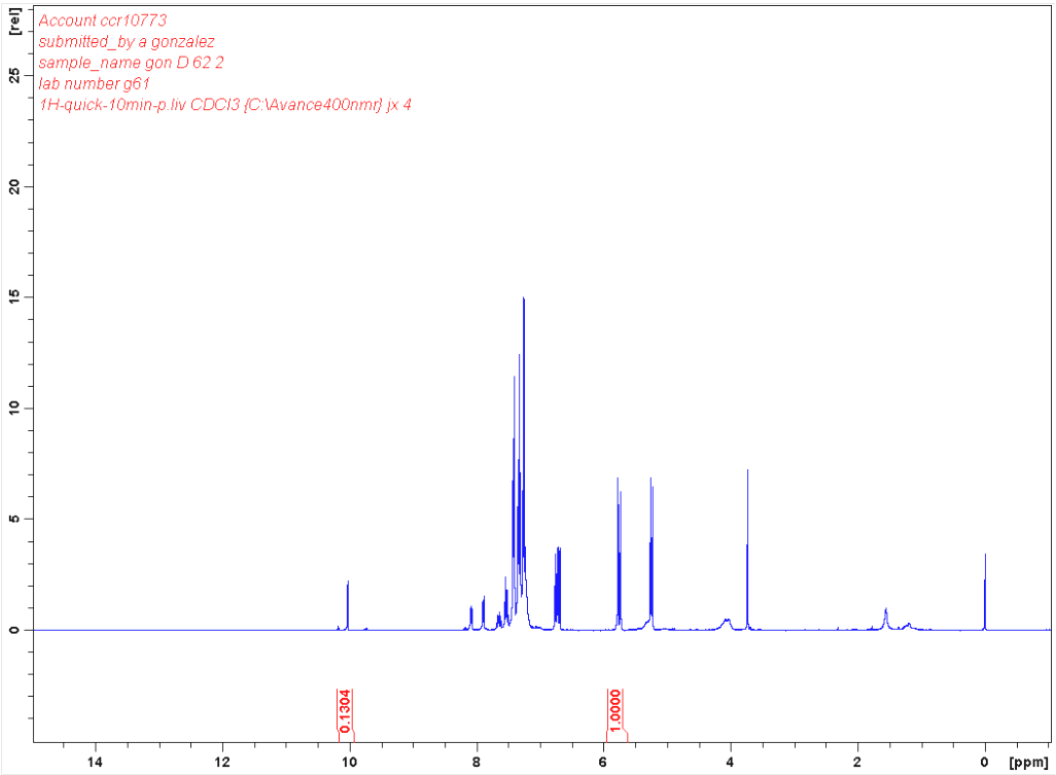
Entry	Catalyst	Benzaldehyde (isol. yield %)[a]
1	$Fe(OTf)_3$**L1** only	13
2	$Fe(OTf)_3$**L1** + peroxide	12



Enlarged spectrum: Table S2, entry 1. Catalyst only



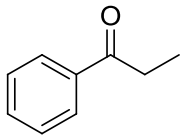
Enlarged spectrum: Table S2, entry 2. Catalyst and benzoyl peroxide



5.3. $Fe(OTf)_3$-L4 catalyzed aerobic C=C cleavage of α-alkylstyrenes posessing allylic hydrogens

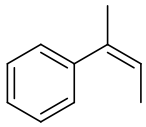
The reactions were performed according to the procedure specified in section 3.2. Reactions carried out under N_2 atmosphere were performed under the same procedure with the reaction tubes being degassed with N_2 gas instead of O_2.

Propiophenone[34] **(10a)**



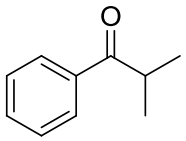
Colorless liquid (7% isol. yield, 0.04 mmol, 5.4 mg). Purification by flash chromatography (Hexane/AcOEt, 40/1 to 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.98-7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.49-7.44 (m, 2H), 3.02 (q, *J* = 6.8 Hz, 2H), 1.24 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 201.2, 137.3, 133.2, 128.9, 128.3, 32.1, 8.6. **IR (ATR)** ν = 2977, 2940, 2904, 1683, 1598, 1450, 1411, 1349, 1213, 1178, 1081, 1012, 954, 744, 690, 642. **HRMS** (CI) m/z calc'd $C_9H_{11}O$ $[M + H]^+$: 135.0805, found: 135.0811.

(Z)- 2-Buten-2-ylbenzene[53] **(11a)**



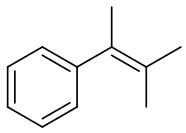
Colorless liquid (53% isol. yield, 0.26 mmol, 34.3 mg). Purification by flash chromatography (Hexane/AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.40-7.15 (m, 5H), 5.89-5.83 (m, 1H), 2.03 (s, 3H), 1.80 (dd, *J* = 1.2, 5.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 144.4, 135.9, 128.5, 126.7, 125.9, 122.8, 15.8, 14.7. **HRMS** (CI) m/z calc'd C_8H_9O $[M + H]^+$: 133.1012, found: 133.1007.

Isobutyrophenone[54] **(10b)**



Colorless liquid (36% isol. yield, 0.18 mmol, 26.7 mg). Purification by flash chromatography (Hexane/AcOEt, 40/1 to 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.97-7.94 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.44 (m, 2H), 3.56 (quintet, *J* = 7.2 Hz, 1H), 1.22 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 204.9, 136.6, 133.1, 129.0, 128.7, 35.7, 19.5. **IR (ATR)** ν = 2973, 2933, 2875, 1681, 1598, 1577, 1469, 1448, 1382, 1353, 1216, 1162, 1087, 979, 794, 696, 646. **HRMS** (CI) m/z calc'd $C_{10}H_{13}O$ $[M + H]^+$: 149.0961, found: 149.0960.

(3-Methylbut-2-en-2-yl)benzene[55] **(11b)**

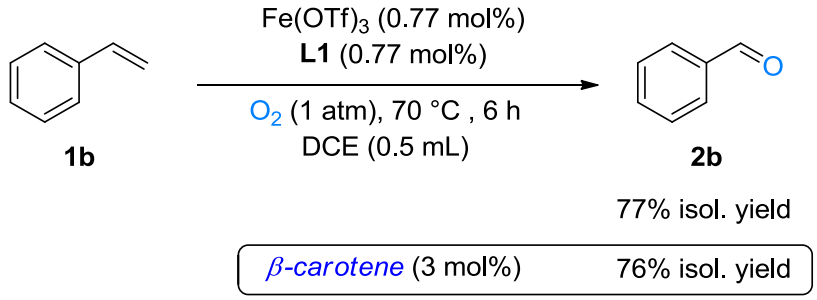


Colorless liquid (34% isol. yield, 0.17 mmol, 24.8 mg). Purification by flash chromatography (Hexane/AcOEt, 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.36-7.12 (m, 5H), 2.01 (s, 3H), 1.87 (s, 3H), 1.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 144.3, 139.6, 130.2, 128.7, 127.8, 126.9, 21.4, 21.1, 13.1. **HRMS** (CI) m/z calc'd $C_{11}H_{15}$ $[M + H]^+$: 147.1169, found: 147.1162.

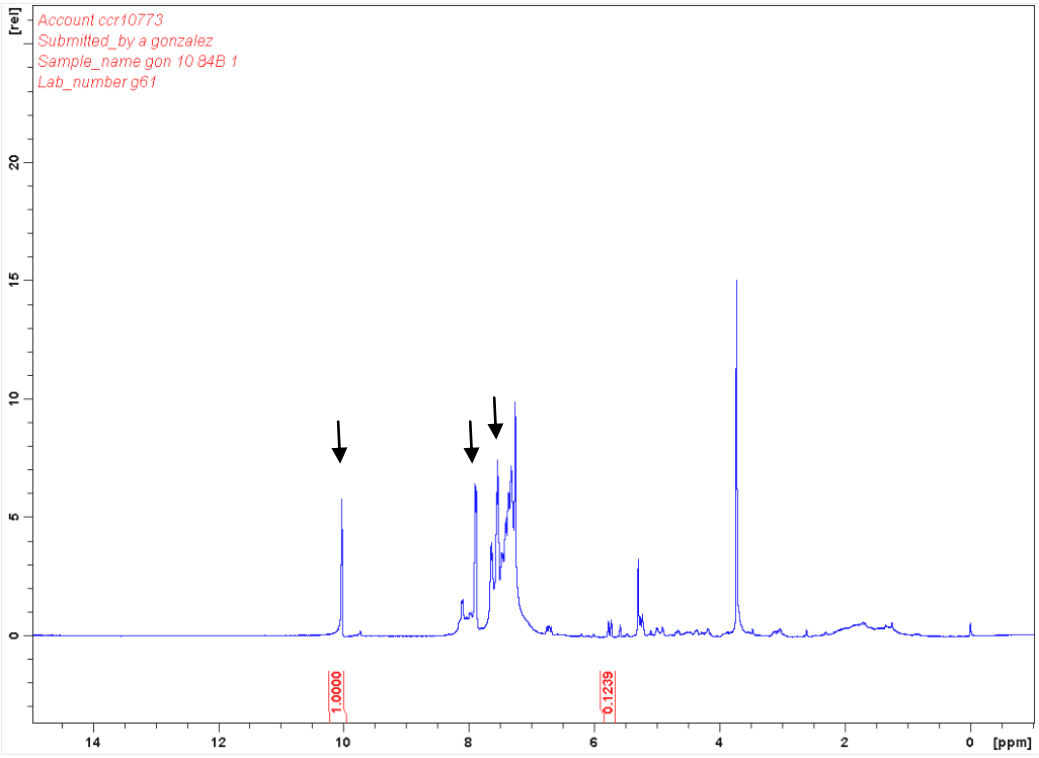
5.4. Absence of singlet oxygen formation

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76×10^{-3} mmol, 2.9 mg) and **L1** (5.78×10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, β-carotene (3 mol%, 12 mg) and styrene (0.75 mmol, 90μL) were added by syringe. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 6 hours. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the unreacted starting material and the ketone product.

Figure S1. Aerobic cleavage of styrene in the presence of β-carotene



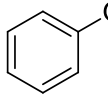
Crude ^{1}H NMR of the aerobic cleavage of styrene in the presence of β-carotene. The ^{1}H NMR resonances corresponding to the benzaldehyde product are highlighted under the black arrow.



5.5. Dehydrogenation of dienes

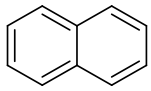
The reactions were performed according to the procedure described in section 3.2. but with O_2 replaced with N_2. The formation of H_2 gas was confirmed by GC analysis as reported.[1]

Anisole[56] (13c)



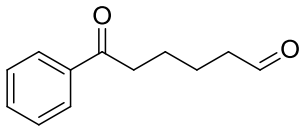
Colorless liquid (60% isol. yield, 0.30 mmol, 32.4 mg). Purification by flash chromatography (Hexane/AcOEt, 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.42-7.36 (m, 2H), 6.99-6.87 (m, 3H), 3.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 159.5, 129.7, 120.6, 113.8, 55.1. **IR (neat)** ν = 2957, 2836, 1599, 1587, 1495, 1467, 1454, 1302, 1243, 1172, 1153, 1077, 1153, 1077, 1038, 1020, 883, 783, 700, 689, 552, 509 cm^{-1}.

Naphthalene[57] **(13d)**



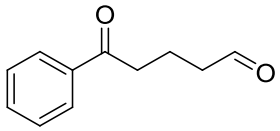
White solid. Purification by flash chromatography (Hexane/AcOEt, 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.84-7.78 (m, 4H), 7.47-7.44 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 133.8, 128.3, 126.2. **IR (ATR)** ν = 2923, 2854, 1702, 1590, 1504, 1457, 1386, 1267, 1207, 1120, 1006, 958, 775. **HRMS** (ESI) m/z calc'd $C_{10}H_9$ $[M + H]^+$: 129.0699, found: 129.0696.

6-Oxo-6-phenylhexanal[58] **(13f)**



Yellowish liquid (27% isol. yield, 0.13 mmol, 25.7 mg). Purification by flash chromatography (Hexane/AcOEt, 50/1 to 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.45 (s, 1H), 8.09-7.98 (m, 2H), 7.74-7.34 (m, 3H), 3.02 (t, *J* = 7.0Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.98-1.76 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 202.3, 199.8, 136.7, 132.7, 128.0, 128.4, 43.2, 37.8, 23.5, 21.4.

5-Oxo-5-phenylpentanal[58] **(13g)**



Yellowish liquid (20% isol. yield, 0.10 mmol, 17.6 mg). Purification by flash chromatography (Hexane/AcOEt 50/1 to 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.80 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.52-7.45 (m, 3H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.57 (t, *J* = 6.9 Hz, 2H), 2.09-2.03 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 202.0, 199.9, 137.1, 134.0, 128.7, 127.9, 43.3, 37.5, 16.8.

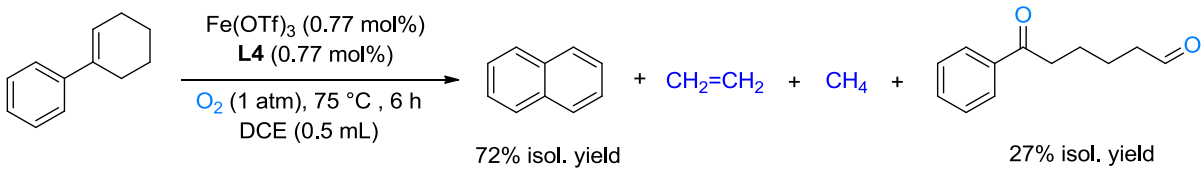
5.6. Fe(OTf)$_3$-L1 catalyzed aerobic rearrangement of 1-phenyl-1-cycloalkenes

The reactions were performed according to the procedure described in section 3.2.

5.6.1. Detection of hydrocarbons during the Fe(OTf)$_3$-L4 catalyzed conversion of 1-phenyl-1-cyclohexene to naphthalene

In a Radley's tube equipped with a magnetic stirring bar and a new rubber septum, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg), **L4** (5.78 x 10^{-3} mmol, 5.4 mg) and freshly distilled DCE (0.50 mL) were added. The reaction mixture was stirred at 35 °C for 1 hour and then 1-phenyl-1-cyclohexene (0.5 mmol) was added by syringe. The tube was sealed, degassed and charged with dioxygen gas (1 atm, 3 times) and kept under excess of oxygen (1 atm) by using a balloon. The reaction mixture was heated to 75 °C and stirred for 8 hours. For the GC analysis, a gas syringe was degassed with pure N_2 gas (5 times) and then a sample (100 μL volume) of the gas phase contained inside the sealed Radley's tube was taken and injected into a Varian star 3400 CX spectrometer (equipped with a 60 m x 0.32 mm GSGasPro capillary column). The GC chromatogram revealed formation of methane (r.t. = 4.367 min) and mainly ethene (r.t. = 4.756). The reaction was purified by silica gel flash column chromatography affording naphthalene and 6-oxo-6-phenylhexanal in 72% and 27% yield respectively.

Figure S2. Volatile hydrocarbons detected during the Fe(OTf)$_3$-L4 catalyzed aerobic rearrangement of 1-phenyl-1-cyclohexene



Sample 1: Chromatogram data

```
Print Date: Tue Jun 17 19:31:38 2014                Page 1 of 1

Title       :
Run File    : C:\STAR\MODULE16\HOSSEIN\MODULE16\MODULE16\STAR185.RUN
Method File : C:\STAR\MODULE16\ABDULLAH\ABD1.MTH
Sample ID   : Manual Sample

Injection Date: 17-JUN-14 7:21 PM     Calculation Date: 17-JUN-14 7:28 PM

Operator    : Ekaterina               Detector Type: ADCB (1 Volt)
Workstation: HARD DISK                Bus Address  : 16
Instrument : Varian Star #1           Sample Rate  : 10.00 Hz
Channel     : A = A                   Run Time     : 7.675 min

********** Star Chromatography Workstation ******* Version 4.51 **************

Run Mode         : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

                                  Ret.    Time                        Width
Peak      Peak        Result      Time    Offset     Area    Sep.     1/2    Status
 No.      Name          ()        (min)   (min)   (counts)  Code    (sec)   Codes
 ---  ------------  ----------   -------  -------  --------  ----   -----   ------
   1                   11.1941     4.367    0.000        73    BB     0.0
   2                   88.8059     4.756    0.000       578    BB     1.1
 ---  ------------  ==========   =======  =======  ========  ====   =====   ======
      Totals:        100.0000              0.000       651

Total Unidentified Counts :        651 counts

Detected Peaks: 4          Rejected Peaks: 2      Identified Peaks: 0

Multiplier: 1          Divisor: 1

Baseline Offset: 1792 microVolts

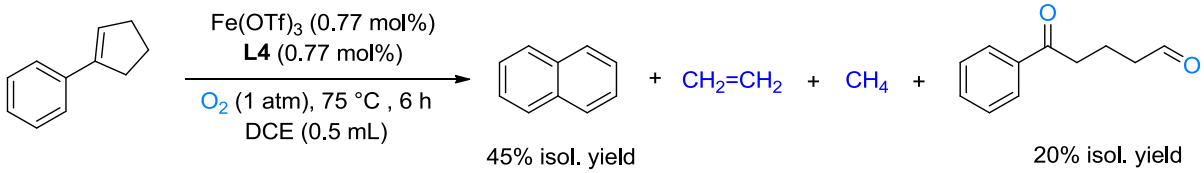
Noise (used): 17 microVolts - monitored before this run

Manual injection
```

5.6.2. Detection of hydrocarbons during the Fe(OTf)$_3$-L4 catalyzed conversion of 1-phenyl-1-cyclopentene to naphthalene

In a Radley's tube equipped with a magnetic stirring bar and a new rubber septum, Fe(OTf)$_3$ (5.76 x 10^{-3} mmol, 2.9 mg), **L4** (5.78 x 10^{-3} mmol, 5.4 mg) and freshly distilled DCE (0.50 mL) were added. The reaction mixture was stirred at 35 °C for 1 hour and 1-phenyl-1-cyclopentene (0.5 mmol) was added by syringe. The tube was sealed, degassed and charged with dioxygen gas (1 atm, 3 times) and kept under excess of oxygen (1 atm) by using a balloon. The reaction mixture was heated to 75 °C and stirred for 8 hours. For the GC analysis, a gas syringe was degassed with pure N_2 gas (5 times) and then a sample (100 µL volume) of the gas phase contained inside the sealed Radley's tube was taken and injected into a Varian star 3400 CX spectrometer (equipped with a 60 m x 0.32 mm GSGasPro capillary column). The GC chromatogram revealed mainly formation of ethene (r.t. = 4.815) and small traces of methane (r.t. = 4.509 min) among other minor products. The reaction was purified by silica gel flash column chromatography affording naphthalene and 5-oxo-5-phenylpentanal in 45% and 20% yield respectively.

Figure S3. Volatile hydrocarbons detected during the Fe(OTf)$_3$-L4 catalyzed aerobic rearrangement of 1-phenyl-1-cyclopentene



Chromatogram data

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Print Date: Thu Oct 09 10:57:12 2014                    Page 1 of 1

Title       :
Run File    : C:\STAR\MODULE16\HOSSEIN\MODULE16\MODULE16\STAR247.RUN
Method File : C:\STAR\MODULE16\ABDULLAH\ABD1.MTH
Sample ID   : Manual Sample

Injection Date: 9-OCT-14 10:50 AM     Calculation Date: 9-OCT-14 10:56 AM

Operator    : Ekaterina                Detector Type: ADCB (1 Volt)
Workstation: HARD DISK                 Bus Address  : 16
Instrument : Varian Star #1            Sample Rate  : 10.00 Hz
Channel    : A = A                     Run Time     : 6.337 min

********** Star Chromatography Workstation ******* Version 4.51 **************

Run Mode         : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

                                  Ret.    Time                        Width
Peak      Peak        Result      Time    Offset     Area     Sep.    1/2     Status
 No.      Name          ()        (min)   (min)   (counts)   Code   (sec)   Codes
 --- ------------ ----------  ------- ------- --------  ---- -----  ------
   1                  1.1573    4.404   0.000        56    BV   1.5
   2                  8.3739    4.509   0.000       402    VV   7.4
   3                 82.2210    4.815   0.000      3947    VB   8.6
   4                  5.8326    5.391   0.000       280    BV   0.4
   5                  2.4152    5.582   0.000       116    VB   0.2
 --- ------------ ==========  ======= ======= ========  ---- -----  ------
     Totals:        100.0000            0.000      4801

Total Unidentified Counts :       4800 counts

Detected Peaks: 5          Rejected Peaks: 0      Identified Peaks: 0

Multiplier: 1          Divisor: 1

Baseline Offset: 1968 microVolts

Noise (used): 20 microVolts - monitored before this run

Manual injection

Revision Log:

9-OCT-14 10:56 AM: Calculated results from channel A using method:
    'C:\STAR\MODULE16\ABDULLAH\ABD1.MTH'

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```

5.6.3. Control experiments

Samples of pure gases were injected into the Varian star GC spectrometer showing the following retention times:

Methane (r.t. = 4.4)
Ethane (r.t. = 4.70)
Ethene (r.t. = 4.77)

5.7. $Fe(OTf)_3$-L1 catalyzed oxygenation of vinyl halides

5.7.1. Solvent effect

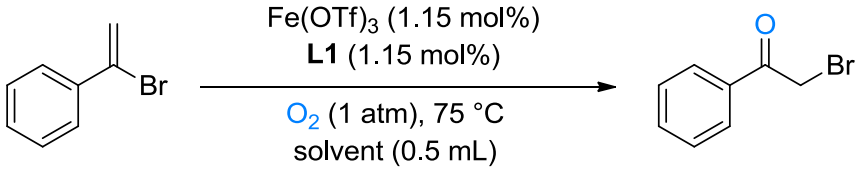
5.7.1.1. DBE and DCE as solvents

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. DBE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, α-bromostyrene (0.50 mmol, 60 µL) was added by syringe. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react for 3 hours or overnight. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the unreacted starting material and the ketone product. The same procedure was repeated using DCE as solvent.

5.7.1.2. DIE as solvent

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. Benzene (0.2 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, DIE (200 mg, 0.7 mmol) and α-bromostyrene (0.50 mmol, 60 µL) were added. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react overnight. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the ketone product.

Table S3. Effect of the solvent in the $Fe(OTf)_3$-L1 catalyzed conversion of vinyl bromide into phenacyl halide



Entry	Solvent	Reaction time / h	Conversion (%)
1	DBE	3 h	36
2	DBE	overnight	92
3	DCE	3 h	13
4	DCE	overnight	61
5	DIE	overnight	94

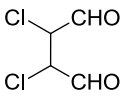
5.7.2. Solvent oxidation products

5.7.2.1. Oxidation of DCE to 2,3-dichlorosuccinaldehyde

During the oxidation of vinyl bromide to α-bromoacetophenone a new set of signals was observed in the ^{1}H NMR of the crude reaction when using DCE as solvent. Such signals were attributed to 2,3-dichlorosuccinaldehyde on the basis of predicted ^{1}H and ^{13}C NMR resonances. Attempts to isolate the

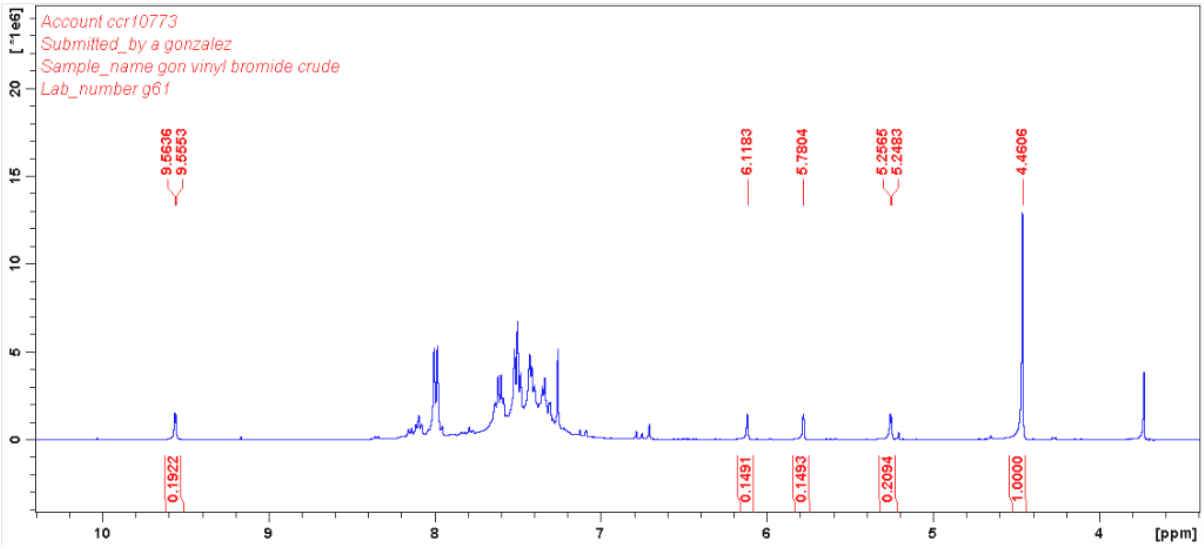
pure material were unsuccesful due to its high reactivity; however, a small fraction partially co-eluted with the phenacyl bromide product.

2,3-Dichlorosuccinaldehyde

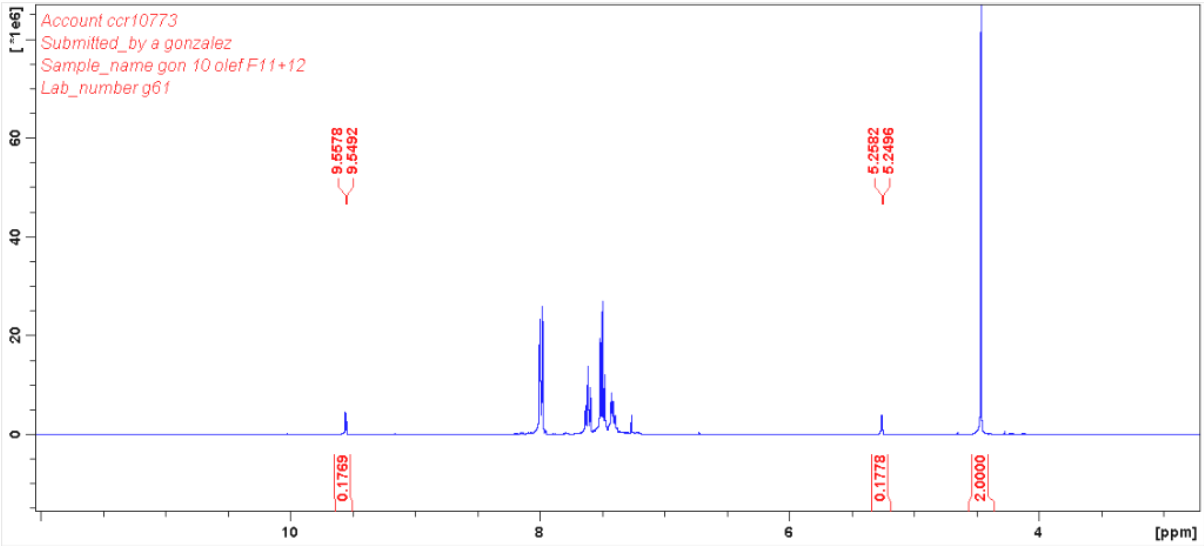


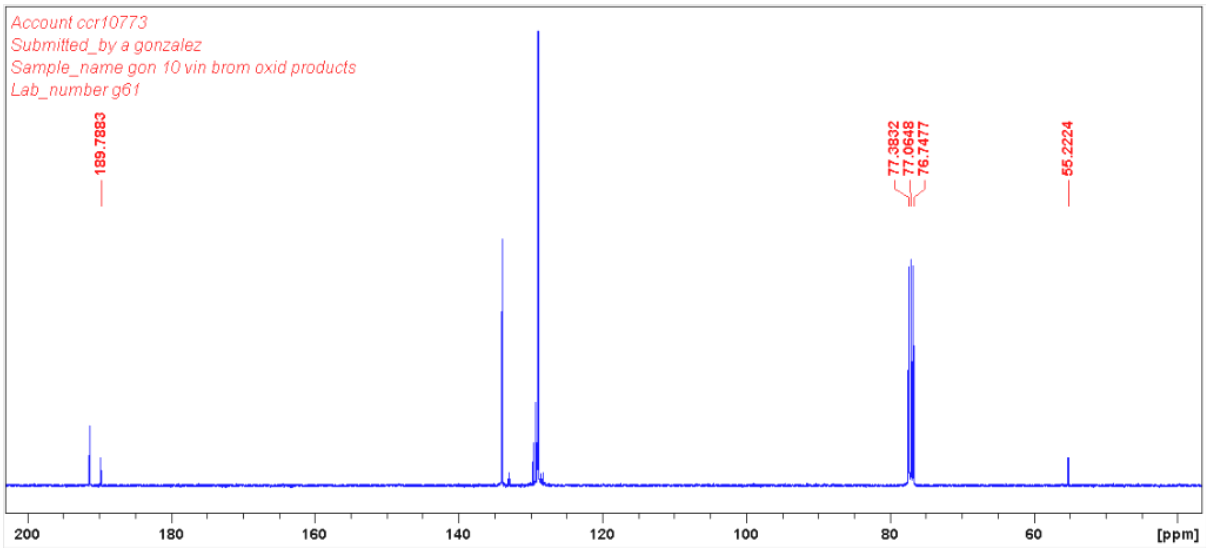
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.55 (d, *J* = 3.4 Hz, 2H), 5.25 (d, *J* = 3.4 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 189.7, 55.2.

^{1}H NMR of the crude reaction (16 hours)



^{1}H and ^{13}C NMR spectrum of the co-eluted carbonyl products

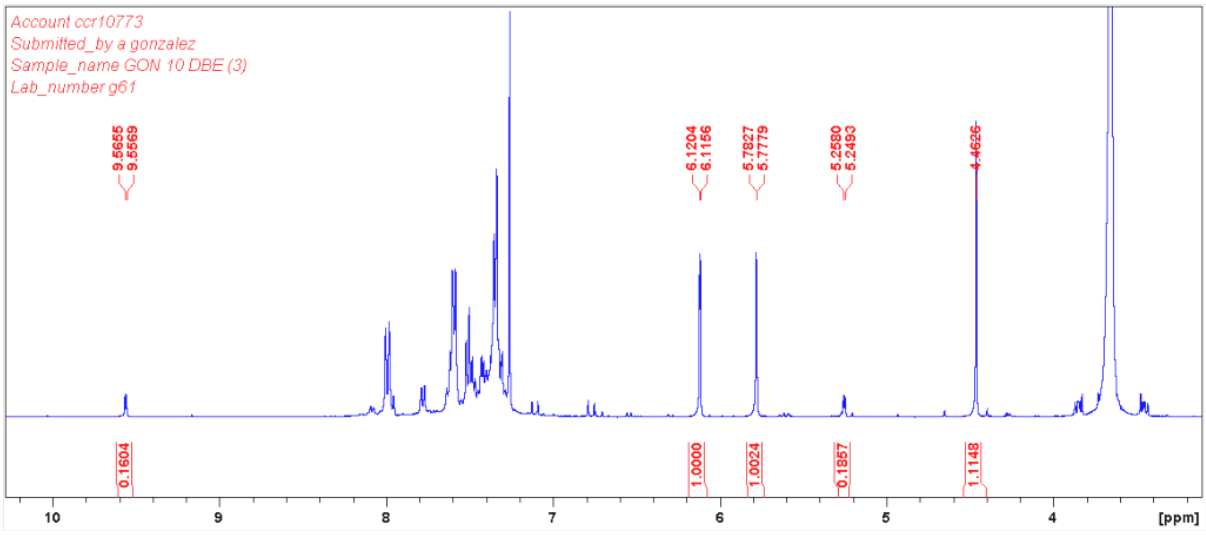




5.7.2.2. Oxidation of DBE to 2,3-dibromosuccinaldehyde

During the oxidation of vinyl bromide to α-bromoacetophenone a new set of signals was observed in the ^{1}H NMR of the crude reaction when using DBE as solvent. Such signals were attributed to 2,3-dibromosuccinaldehyde on the basis of predicted ^{1}H resonances. Attempts to isolate the pure material were unsuccesful due to its high reactivity.

^{1}H NMR of the crude reaction (3 hours)



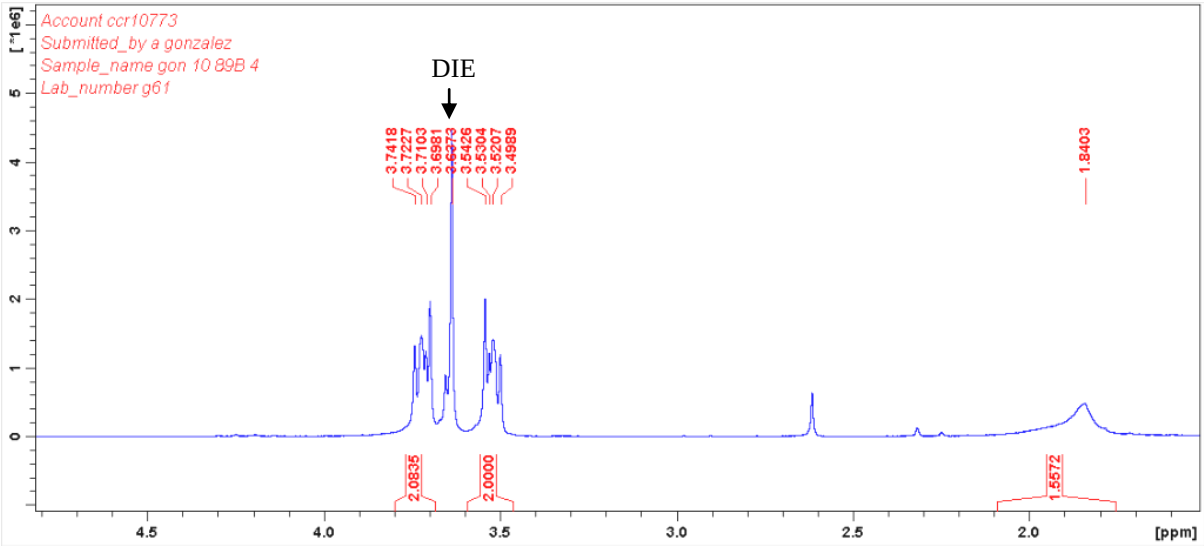
5.7.2.3. Oxidation of DIE to 2-iodoethanol

During the oxidation of vinyl bromide to α-bromoacetophenone a new set of signals was observed in the ^{1}H NMR of the crude reaction when using DIE as solvent. Those signals were attributed to the formation of 2-iodoethanol. Due to the higher stability of the alcohol product, it was partially co-eluted with the unreacted DIE.

2-Iodoethanol[59]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.74-3.69 (m, 2H), 3.54-3.49 (m, 2H), 1.84 (bs).

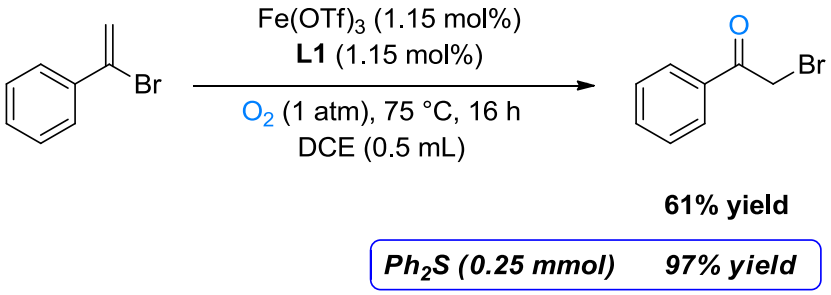
^{1}H NMR of the crude reaction (expanded)



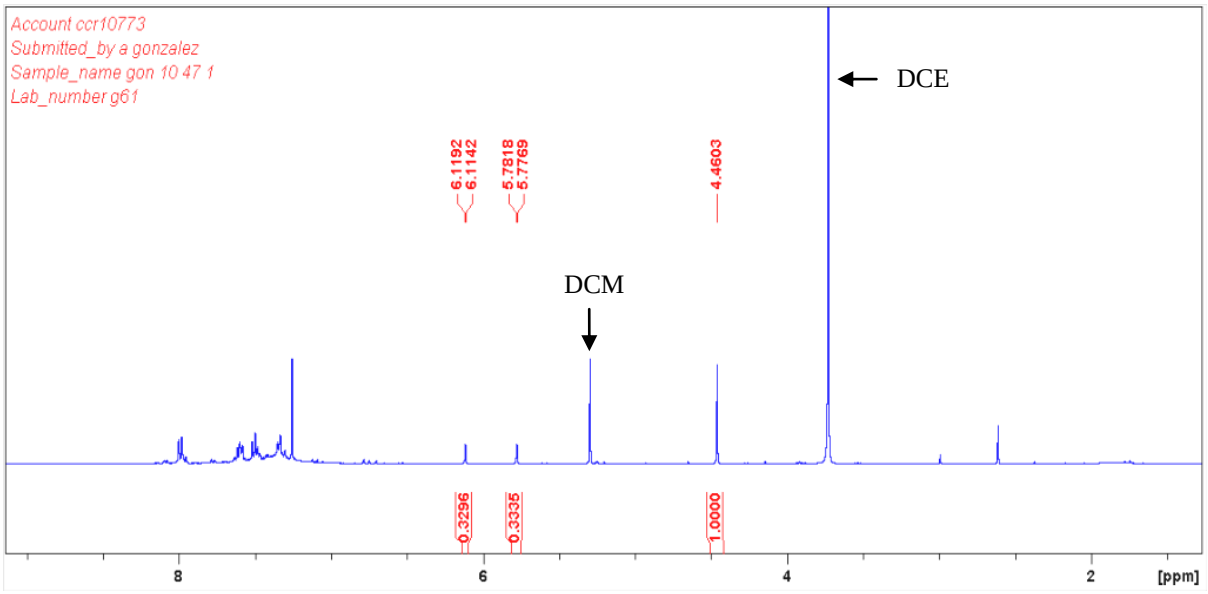
5.7.3. Oxidation in the presence of diphenyl sulfide

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, α-bromostyrene (0.50 mmol, 60 µL) and diphenyl sulphide (0.25 mmol, 40 µL) were added by syringe. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react overnight (*circa* 16 h). The reaction mixture was transfered to a flask using DCM as solvent and the solvents removed in vacuo. The reaction crude was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the unreacted starting material, the ketone product and diphenyl sulfoxide. The same procedure was repeated in the absence of diphenyl sulfide.

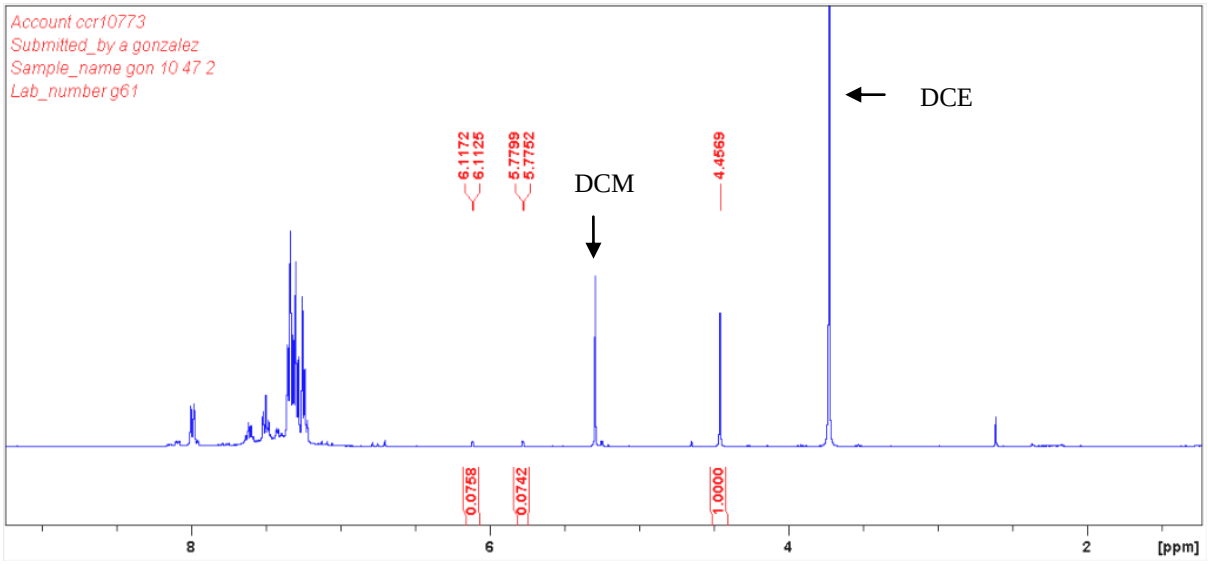
Figure S4. $Fe(OTf)_3$-L1 catalyzed oxygenation of vinyl bromide to phenacyl bromide



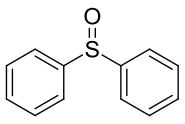
Crude ^{1}H NMR of the Fe(OTf)$_3$-L1 catalyzed oxygenation of vinyl bromide (no Ph$_2$S)



Crude ^{1}H NMR of the Fe(OTf)$_3$-L1 catalyzed oxygenation of vinyl bromide (with 0.5 equiv. Ph$_2$S)



Diphenyl sulfoxide[60]

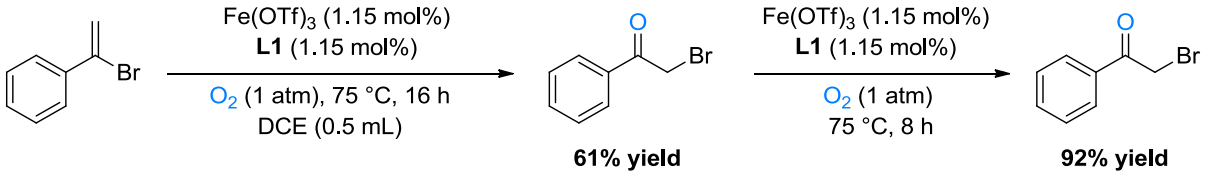


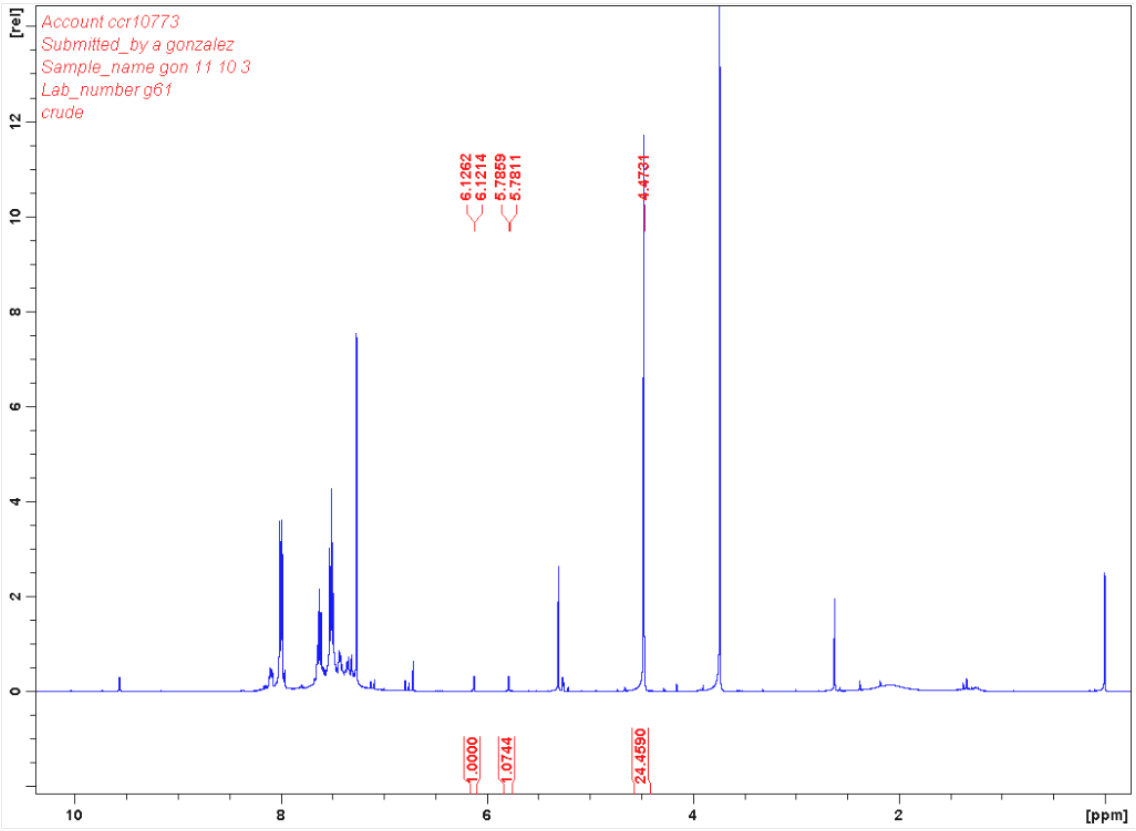
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.65 (d, J = 5.6 Hz, 4H), 7.45 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 145.6, 131.0, 129.3, 124.7. **IR (neat)**: ν = 3049, 1578, 1475, 1440, 1086, 1035, 1021, 995, 914, 755, 736, 685 cm^{-1}. **HRMS** (CI) m/z calc'd $C_{12}H_{11}OS$ $[M + H]^+$: 203.0525, found: 203.0533.

5.7.4. Effect of the 2,3-dichlorosuccinaldehyde byproduct on the $Fe(OTf)_3$-L1 catalyst

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, α-bromostyrene (0.50 mmol, 60 µL) was added by syringe. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react overnight (*circa* 16 h). Next day, a mixture of $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) was added and the reaction was heated at 75 °C for another 8 hours. The reaction mixture was transfered to a flask using DCM as solvent and the solvents removed in vacuo. The reaction crude was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the phenacyl bromide product in a 92% isolated yield.

Figure S5. The oxygenation of vinyl bromide to phenacyl bromide proceeds almost quantitatively after two sequential additions of the $Fe(OTf)_3$-L1 catalyst.

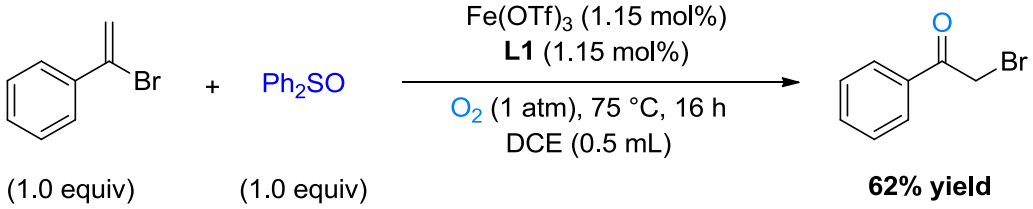


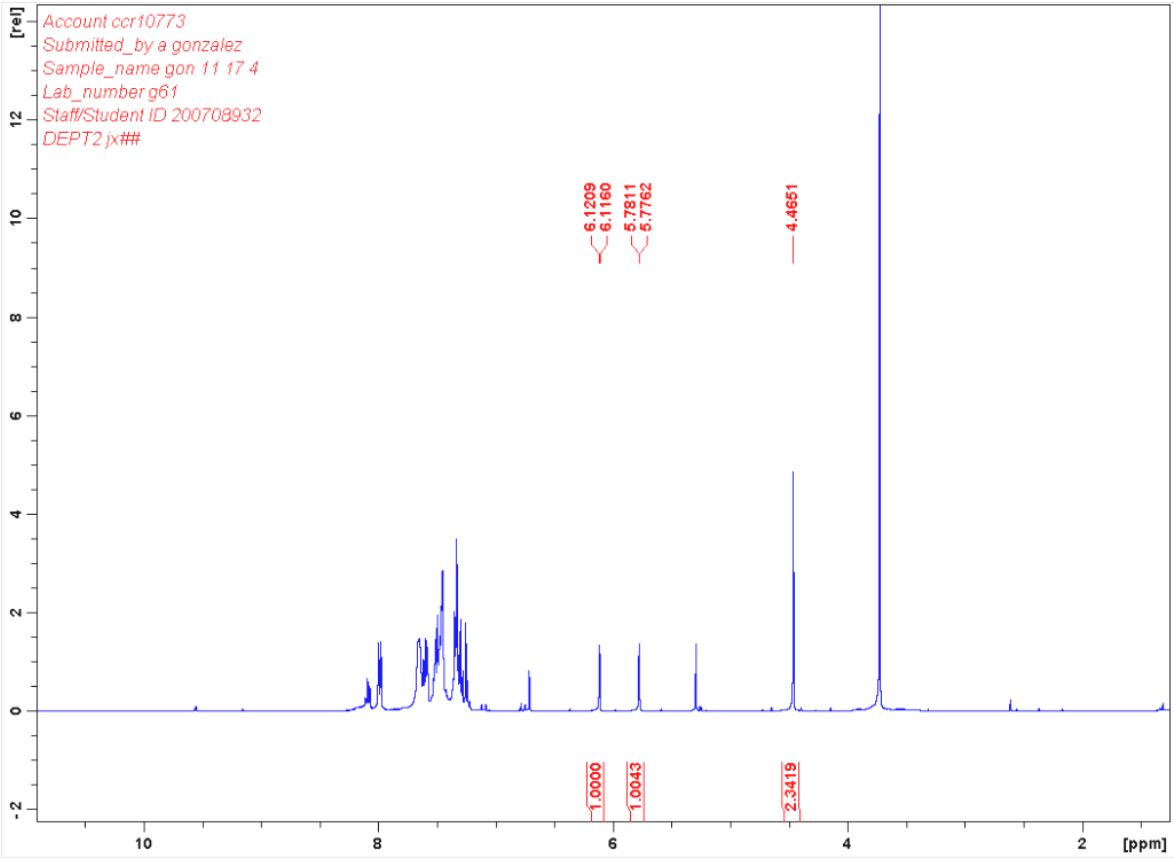


5.7.5. $Fe(OTf)_3$-L1 catalyzed oxygenation of vinyl bromide to phenacyl bromide in the presence of diphenyl sulfoxide

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, α-bromostyrene (0.50 mmol, 60 µL) and Ph_2SO (1.0 equivalent, 60 mg) were added to the reaction. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react overnight (*circa* 16 h). The reaction mixture was transfered to a flask using DCM as solvent and the solvents removed in vacuo. The reaction crude was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the phenacyl bromide product in a 62% isolated yield (69 % ^{1}H NMR conversion).

Figure S6. $Fe(OTf)_3$-L1 catalyzed oxygenation of vinyl bromide to phenacyl bromide in the presence of Ph_2SO. An excess of diphenyl sulfoxide does not exert a detrimental effect on the iron catalyst during the oxygenation of vinyl bromide.

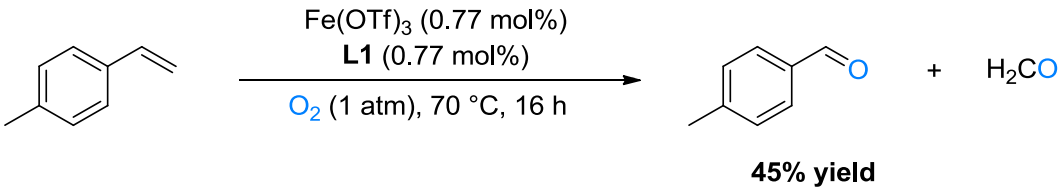




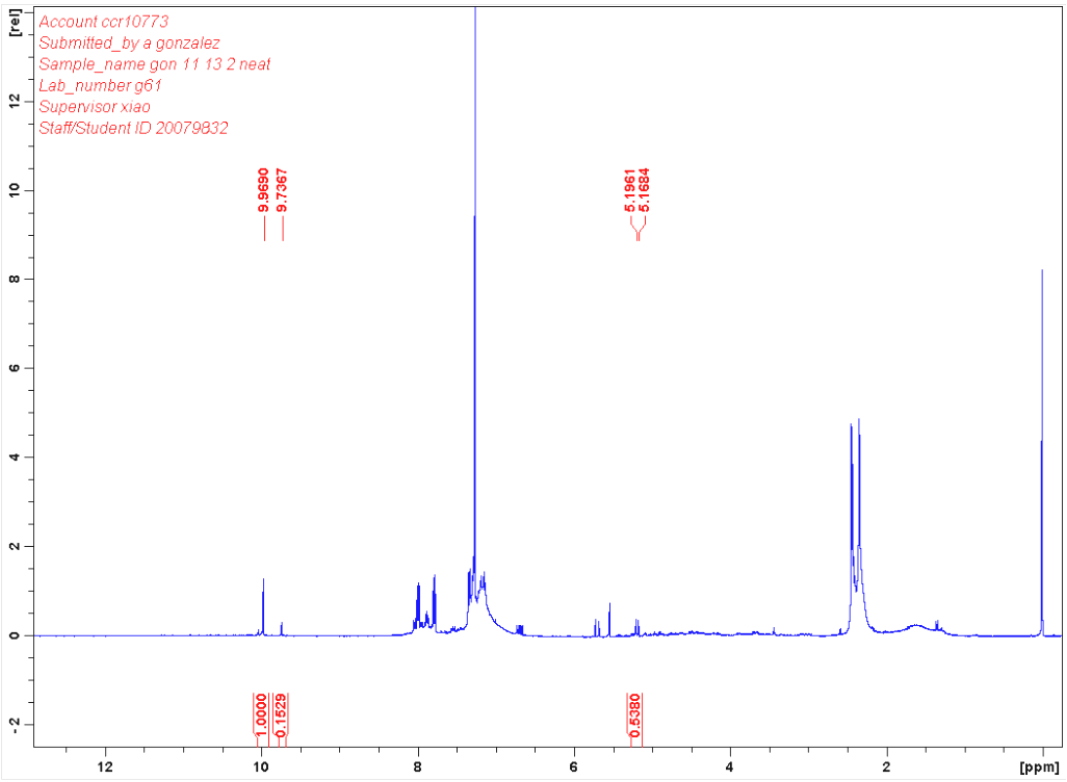
5.7.6. Neat oxidation of *p*-methylstyrene: absence of solvent participation

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.76 x 10^{-3} mmol, 5.3 mg) were added. *p*-Methylstyrene (0.75 mmol) was subsequently injected in the tube by syringe and the reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 16 hours. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the unreacted starting material and *p*-methylbenzaldehyde in 45% isol. yield.

Figure S7. $Fe(OTf)_3$-L1 catalyzed aerobic cleavage of neat p-methylstyrene. The $Fe(OTf)_3$-L1 catalyst promotes the oxidation of *p*-methylstyrene to *p*-methylbenzaldehyde and formic acid in the absence of solvent. These data indicates that the solvent is not participating in the oxidation reaction in contrast with the iron catalyzed oxidation of vinyl bromide. Note that substrate degradation is also observed due to the catalyst being made *in situ* solely in the presence of the olefin.



45% yield

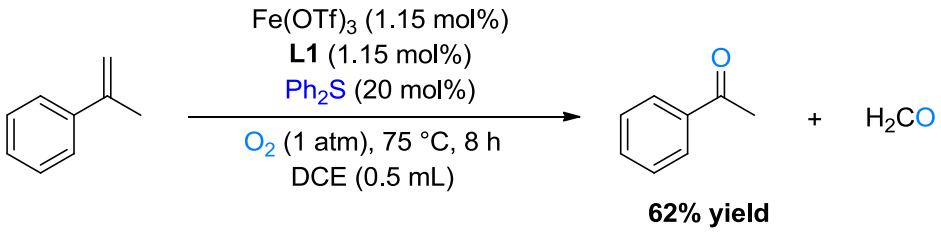


5.7.7. Oxidation of styrenes in the presence of Ph_2S

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, α-methylstyrene (0.50 mmol) and

Ph_2S (20 mol%, 60 mg) were added to the reaction. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 75 °C and allowed to react for 8 hours. The reaction mixture was transfered to a flask using DCM as solvent and the solvents removed in vacuo. The reaction crude was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the acetophenone product product in a 62% isolated yield. The same reaction was repeated using 4-chloro-α-methylstyrene as substrate.

Figure S8. $Fe(OTf)_3$-L1 catalyzed aerobic cleavage of α-methylstyrene in the presence of Ph_2S. In the presence of diphenyl sulfide the iron promoted aerobic oxidation of α-methylstyrene afforded acetophenone with 62% isolated yield. In the absence of Ph_2S, acetophenone was isolated in a 87% yield suggesting that the diphenyl sulfide is not enhancing the oxygen activation. Moreover, formic acid was also detected as byproduct suggesting a 2 + 2 addition of O_2 to the olefin substrate without solvent or Ph_2S participation. The lower yield obtained in the presence of Ph_2S is also in line with the the olefin coordination to the iron catalyst being hampered by Ph_2S.



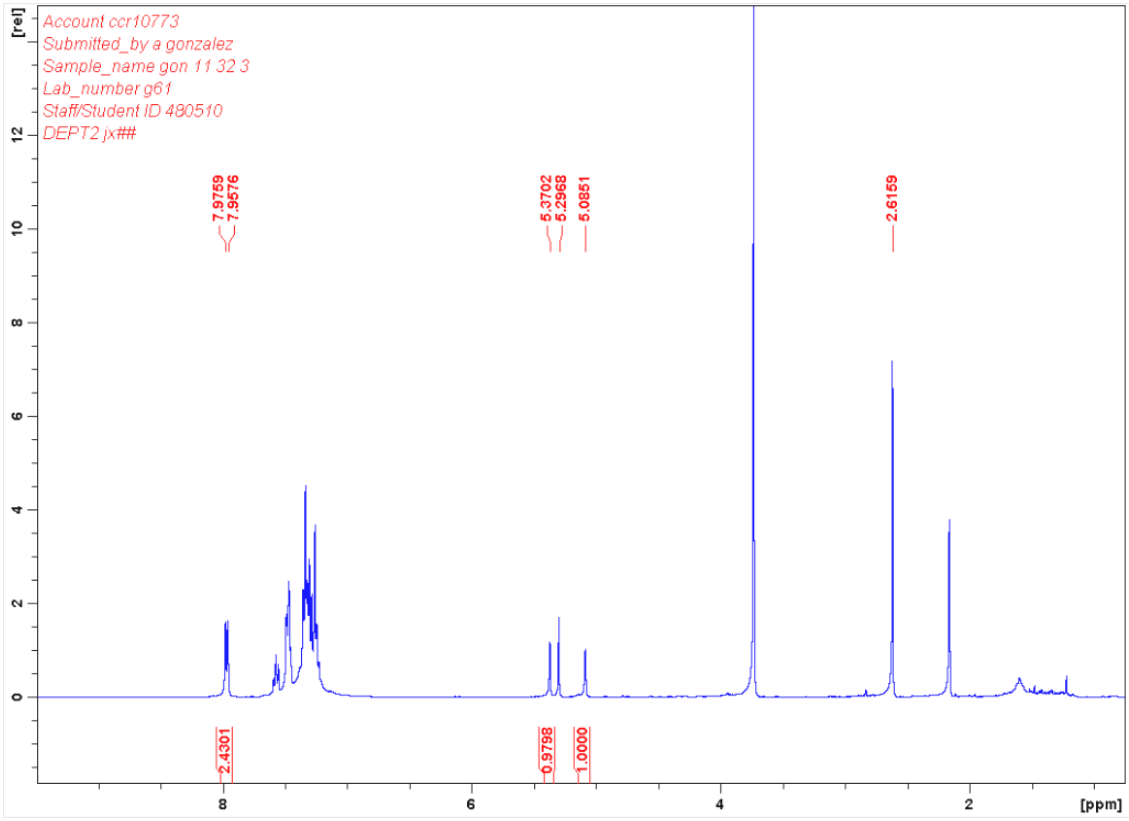
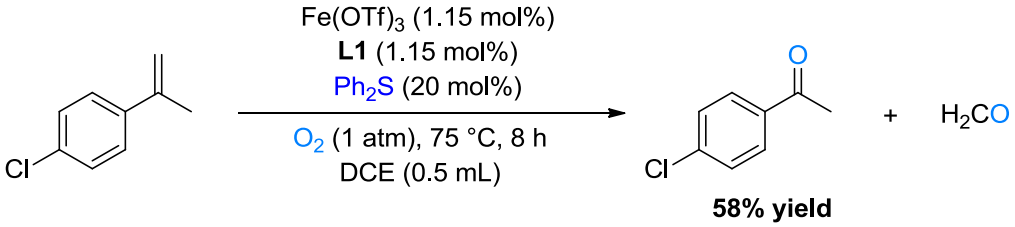
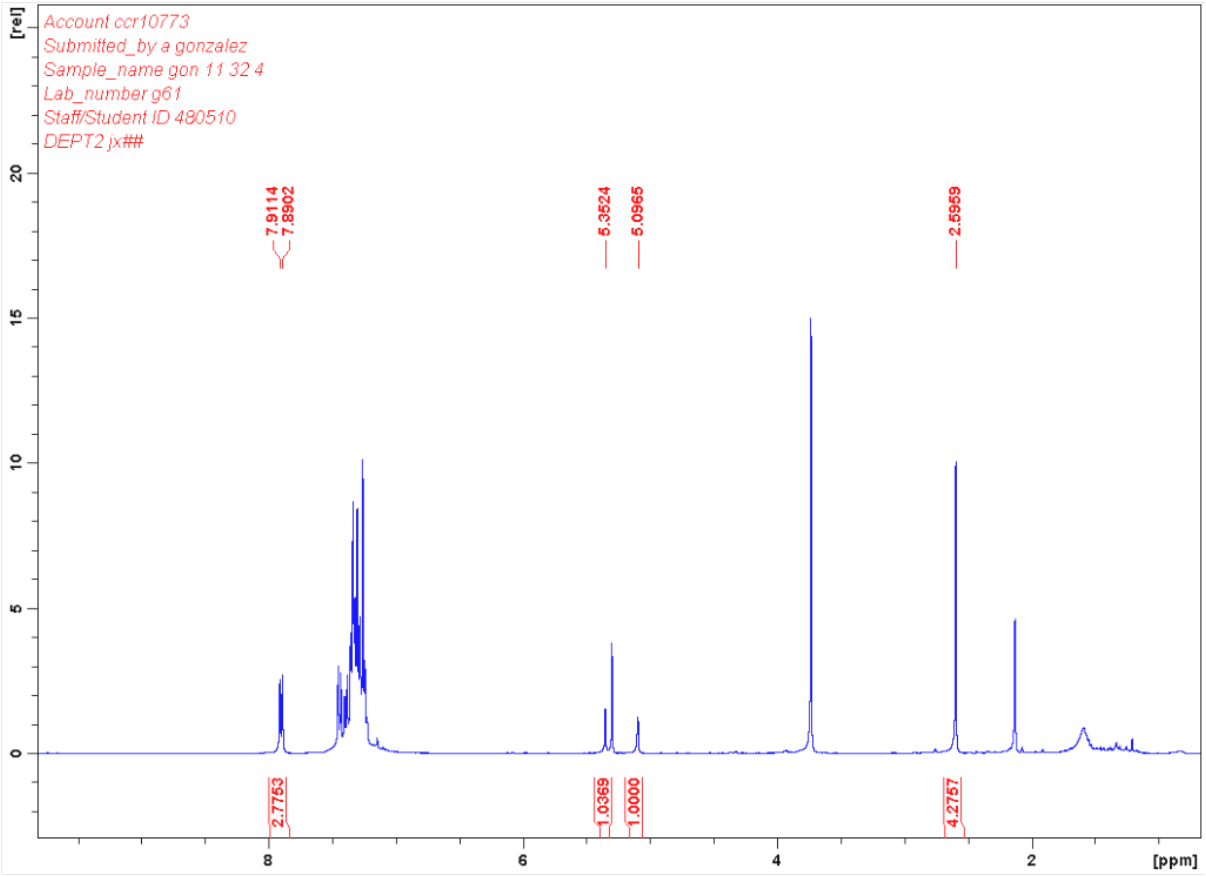


Figure S9. Fe(OTf)$_3$-L1 catalyzed aerobic cleavage of 4-chloro-α-methylstyrene in the presence of Ph$_2$S. In the presence of diphenyl sulfide the iron promoted aerobic oxidation of α-methylstyrene afforded acetophenone with 58% isolated yield. In the absence of Ph_2S, acetophenone was isolated in a 83% yield.





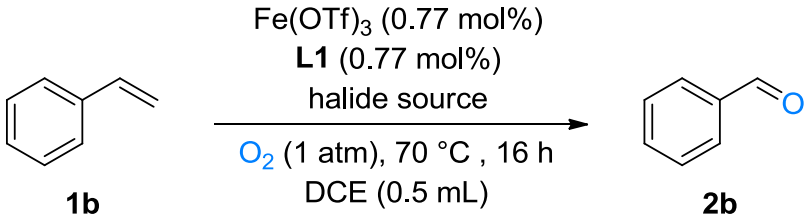
5.7.8. Neat oxidation of vinyl bromide

In a Radley's tube equipped with a magnetic stirring bar, Fe(OTf)$_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (0.011 mmol, 10.6 mg) were added. Vinyl bromide (120 mg, 1.0 mmol) was subsequently injected in the tube by syringe and the reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 16 hours. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the decomposed starting material and phenacyl bromide in 9 % isol. yield.

5.8. $Fe(OTf)_3$-L1 catalyzed aerobic cleavage of styrene in the presence of halide donors

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76×10^{-3} mmol, 2.9 mg) and **L1** (5.78×10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, styrene (0.75 mmol, 90 μL) and tetra-n-butylammonium bromide (0.07 mmol) were added to the reaction. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 16 hours. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the unreacted starting material and benzaldehyde. The same procedure was repeated using tetra-n-butylammonium bromide and tetrabutyl ammonium chloride in different amounts (0.25 and 0.4 mmol). Formation of phenacyl chloride or phenacyl bromide was not detected in any case.

Table S4. Oxidative cleavage of styrene in the presence of Br^- and Cl^- donors.



Halide source (mmol)	isol. yield **2b** (%)
n-$Bu_4N^+Br^-$ (0.07)	51
n-$Bu_4N^+Br^-$ (0.07)	8
n-$Bu_4N^+Br^-$ (0.07)	7
$Bu_4N^+Cl^-$ (0.25)	10

Table S4, entry 1. Aerobic cleavage of styrene in the presence of n-$Bu_4N^+Br^-$ (0.07 mmol)

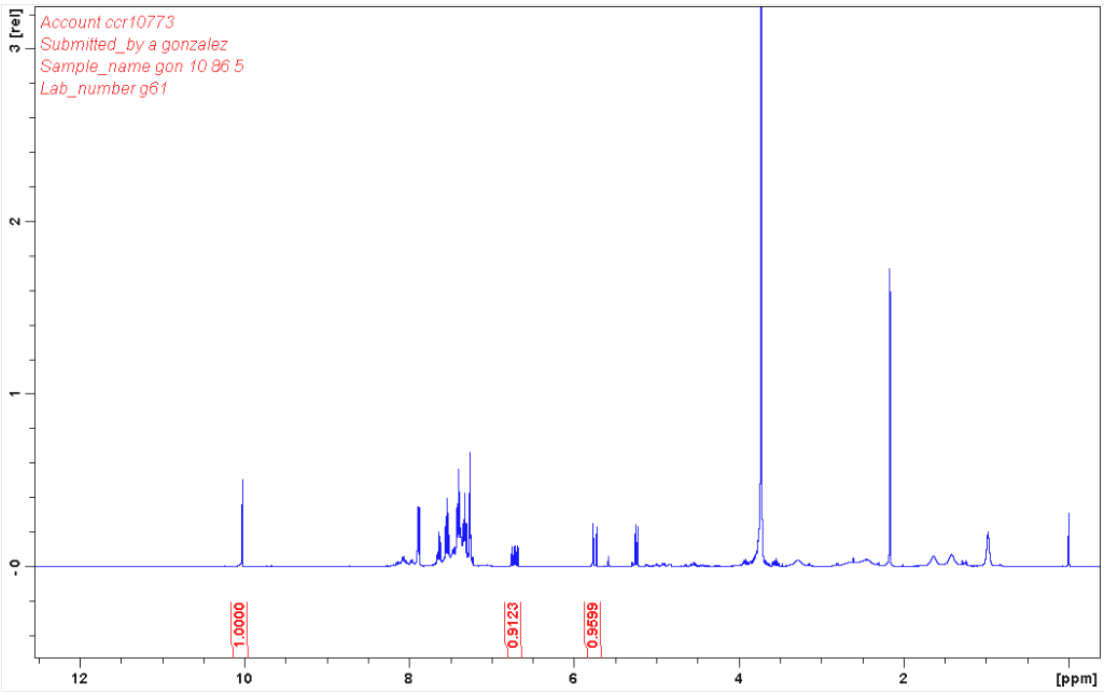


Table S4, entry 2. Aerobic cleavage of styrene in the presence of n-$Bu_4N^+Br^-$ (0.25 mmol)

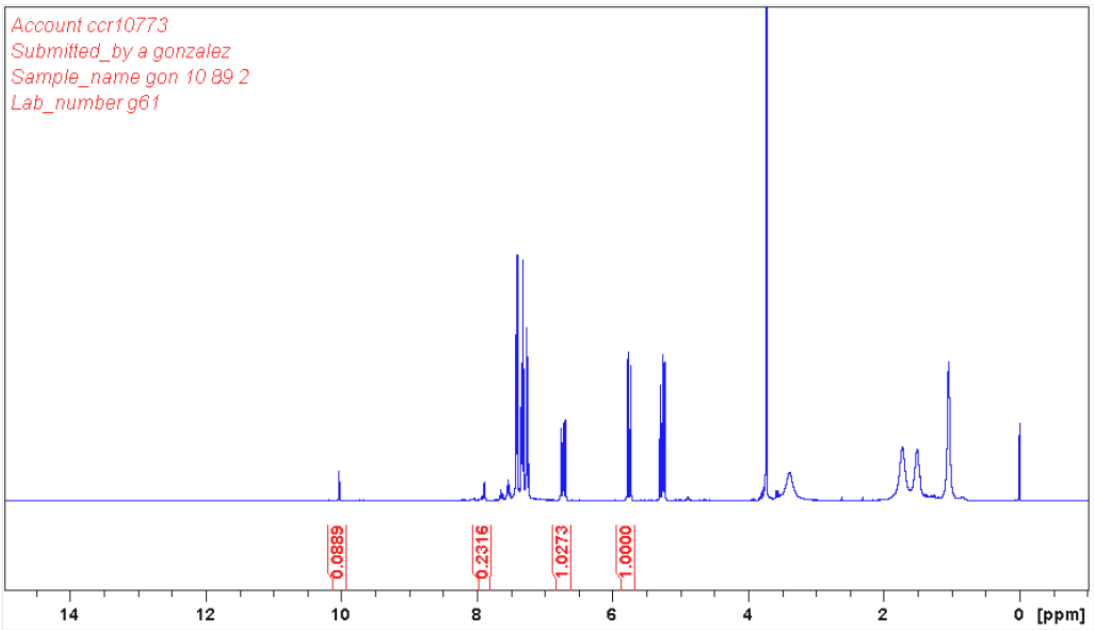


Table S4, entry 3. Aerobic cleavage of styrene in the presence of n-$Bu_4N^+Br^-$ (0.4 mmol)

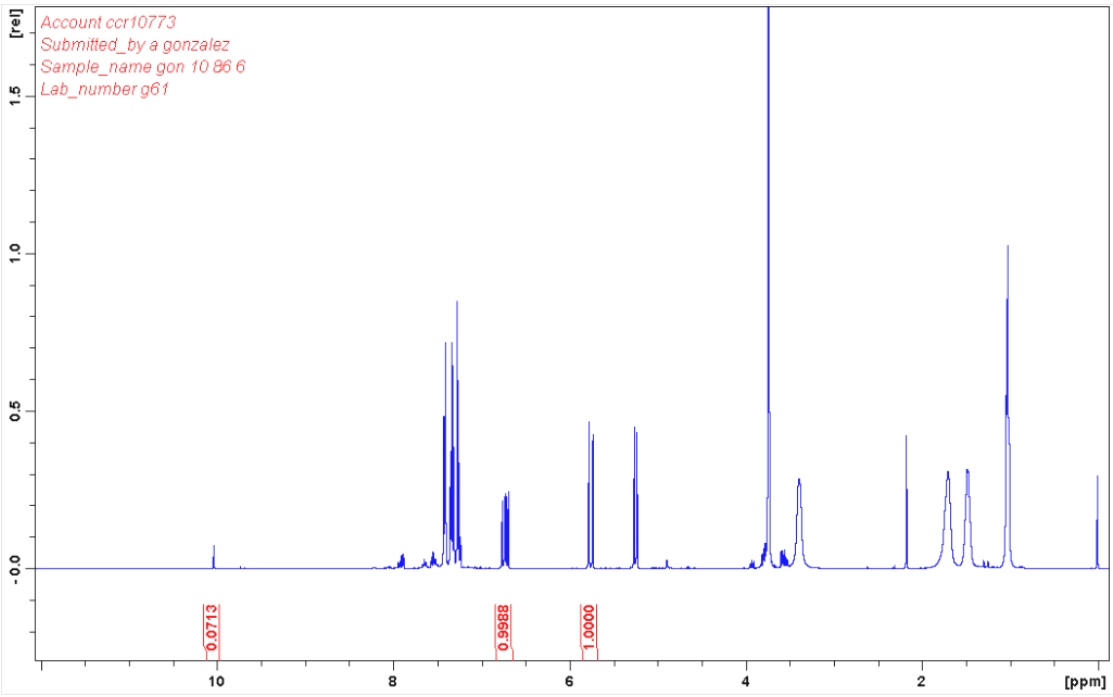
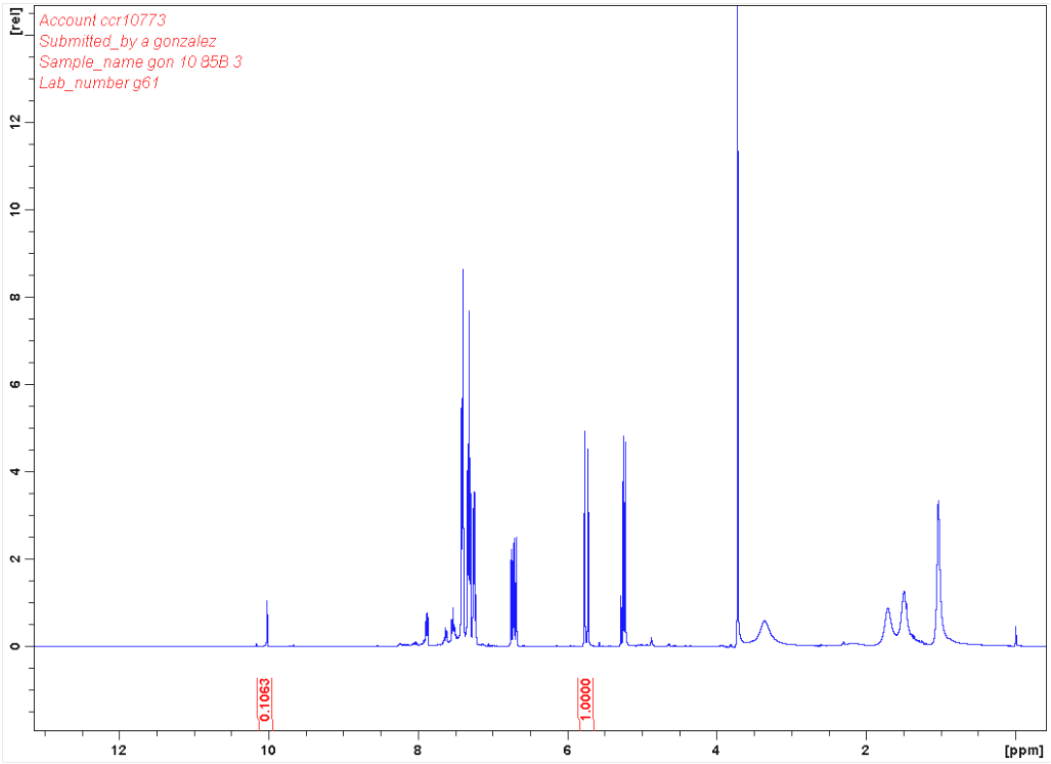


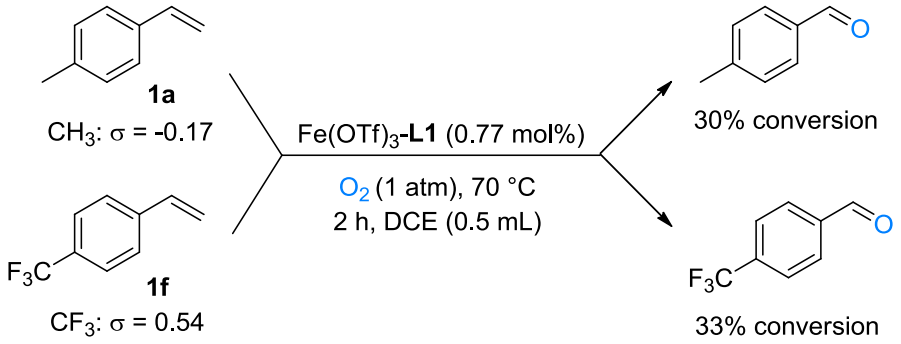
Table S4, entry 4. Aerobic cleavage of styrene in the presence of $Bu_4N^+Cl^-$ (0.25 mmol)



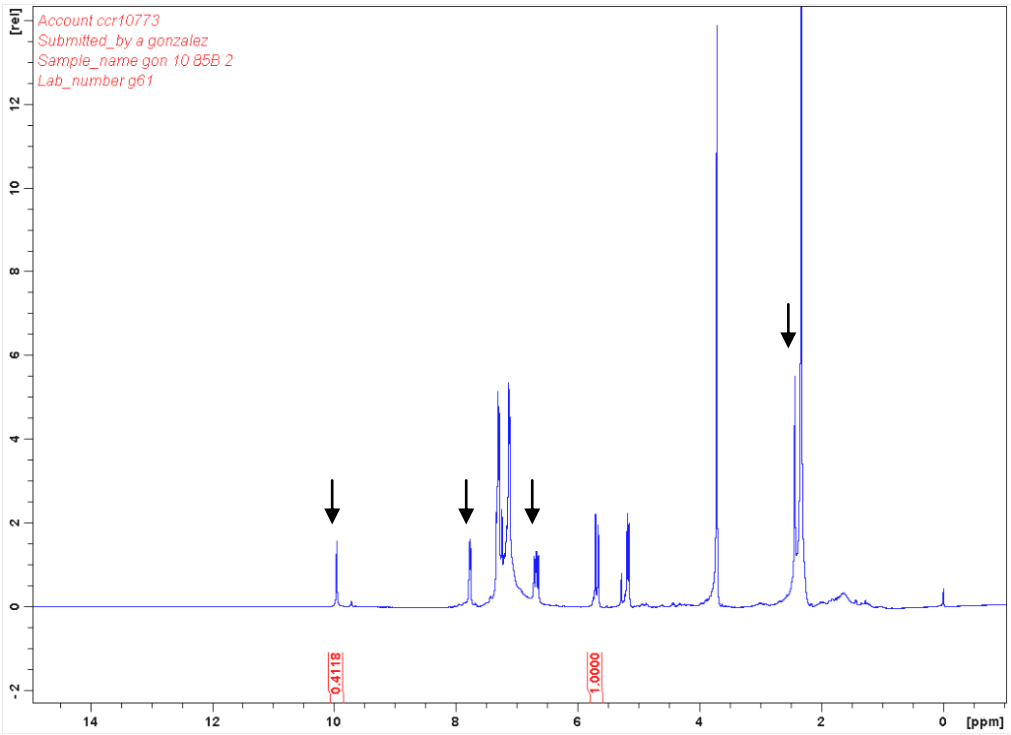
5.9. Electronic effects on styrene oxidation

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (5.78 x 10^{-3} mmol, 5.3 mg) were added. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 hour at 35°C. Next, 4-methylstyrene (0.75 mmol, 90 µLwas added to the reaction. The reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 2 hours since the substrate addition at 35 °C. The reaction was purified by silica gel flash column chromatography (Hexane/EtOAc, 30/1) to afford the unreacted starting material and benzaldehyde in 30% isolated yield. The same procedure was repeated using 4-trifluoromethylstyrene as substrate furnishing 4-trifluorobenzaldehyde in 33% isolated yield.

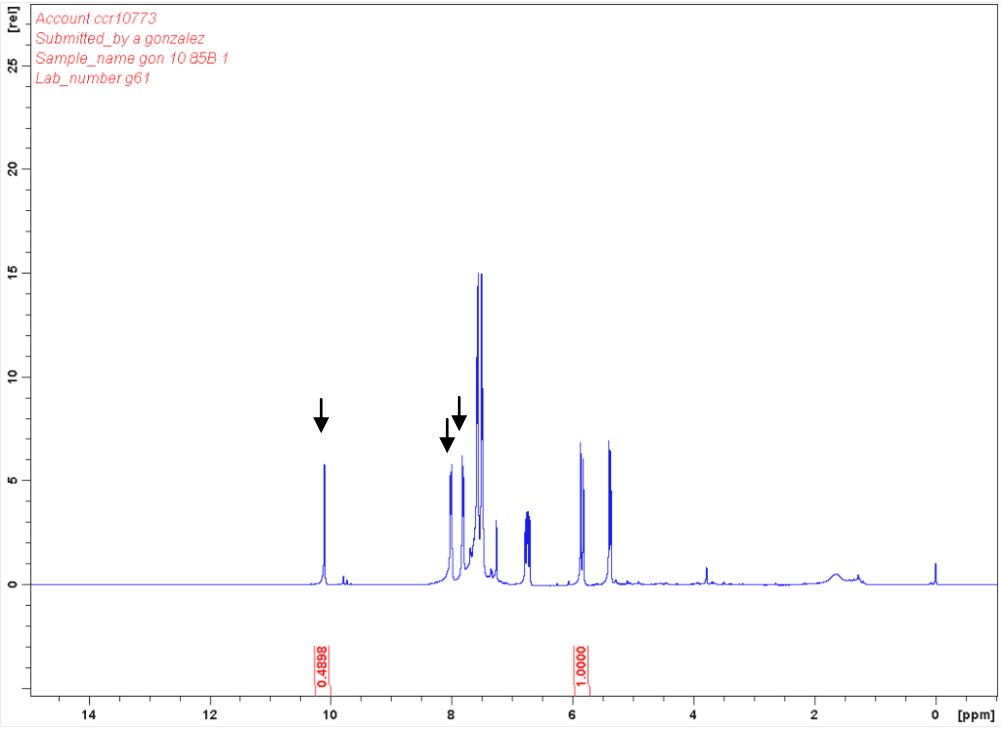
Figure S10. $Fe(OTf)_3$-L1 catalyzed aerobic cleavage of electron rich and electron deficient styrenes



Crude ^1H NMR of the $Fe(OTf)_3$-L1 catalyzed aerobic C=C cleavage of 4-methylstyrene. The ^1H NMR resonances correponding to 4-methylstyrene are highlighted under the black arrows.



Crude ^{1}H NMR of the $Fe(OTf)_3$-L1 catalyzed aerobic C=C cleavage of 4-trifluoromethylstyrene. The ^{1}H NMR resonances correponding to 4-trifluoromethylstyrene are highlighted under the black arrows.



6. Determination of the catalyst structure

6.1. Effect of ligand to iron ratio

In a Radley's tube equipped with a magnetic stirring bar, $Fe(OTf)_3$ (5.76 x 10^{-3} mmol, 2.9 mg) and **L1** (0.012 mmol, 10.6 mg) were added. The tube was degassed (3 times) and placed under an inert atmosphere. Freshly distilled DCE (0.5 mL) was injected by syringe and the reaction mixture was allowed stirring for 1 h at 35°C under N_2 atmosphere. 4-Mehtylstyrene (0.75 mmol) was added by syringe and the reaction tube was degassed with dioxygen gas (1 atm, 3 times) and kept under oxygen (1 atm) by using a balloon. The tube was gradually heated to 70 °C and allowed to react for 6 h. After cooling to room temperature, the reaction mixture was purified by silica gel column chromatography (hexane/EtOAc) to afford the unreacted starting material and the aldehyde product. The same reaction was repeated by adding **L1** (0.017 mmol, 15.9 mg) and adding **L1** (2.88 x 10^{-3} mmol, 2.7 mg), respectively. The results are given in Table 1 of the text.

6.2. Synthesis and characterisation of the iron complex

In a small Schlenk tube eqquiped with a magnetic stirring bar, $Fe(OTf)_3$ (0.1 mmol, 50.3 mg) and **L1** (0.1 mmol, 91.6 mg) were added. The tube was degassed (3 times) and placed under an inert atmosphere. Freshly distilled DCE (1.0 mL) was added by syringe and the reaction mixture was stirred for 3 h at 45 °C, resulting in the formation of a dark red solution. The Schlenck tube was cooled down to r.t. and upon addition of freshly distilled Et_2O, the iron complex was precipitated, furnishing a bright orange powder, which was filtered under N_2 and washed with distilled Et_2O. A mononuclear

Fe(III) complex [Fe**L1**$(OTf)_3$] is proposed on the basis of the following data and the effect of ligand/Fe ratio on the catalysis.

HRMS (Nano-ESI) *m/z* calc'd for $C_{57}H_{57}F_6FeN_5O_{10}S_4$ $[M - CF_3SO_3]^+$: 1269.2238; found: 1269.2217.

HRMS (Nano-ESI) *m/z* calc'd for $C_{56}H_{56}F_3FeN_5O_7S_3$ $[M - 2(CF_3SO_3) - H]^+$: 1119.2637; found: 1119.2623.

HRMS (Nano-ESI) *m/z* calc'd for $C_{55}H_{56}FeN_5O_4S_2$ $[M - 3(CF_3SO_3) - H]^{+2}$: 485.1556; found: 485.1546.

IR (neat) ν = 2964, 1595, 1459, 1224, 1160, 1112, 1085, 1025, 834, 755, 697, 636, 602, 569, 550 cm^{-1}.

Anal Calc'd for $C_{58}H_{57}F_9FeN_5O_{13}S_5$: C, 49.08, H, 4.05, N, 4.93; found: C, 49.48, H, 4.45, N, 4.87.

6.3. Olefin coordination

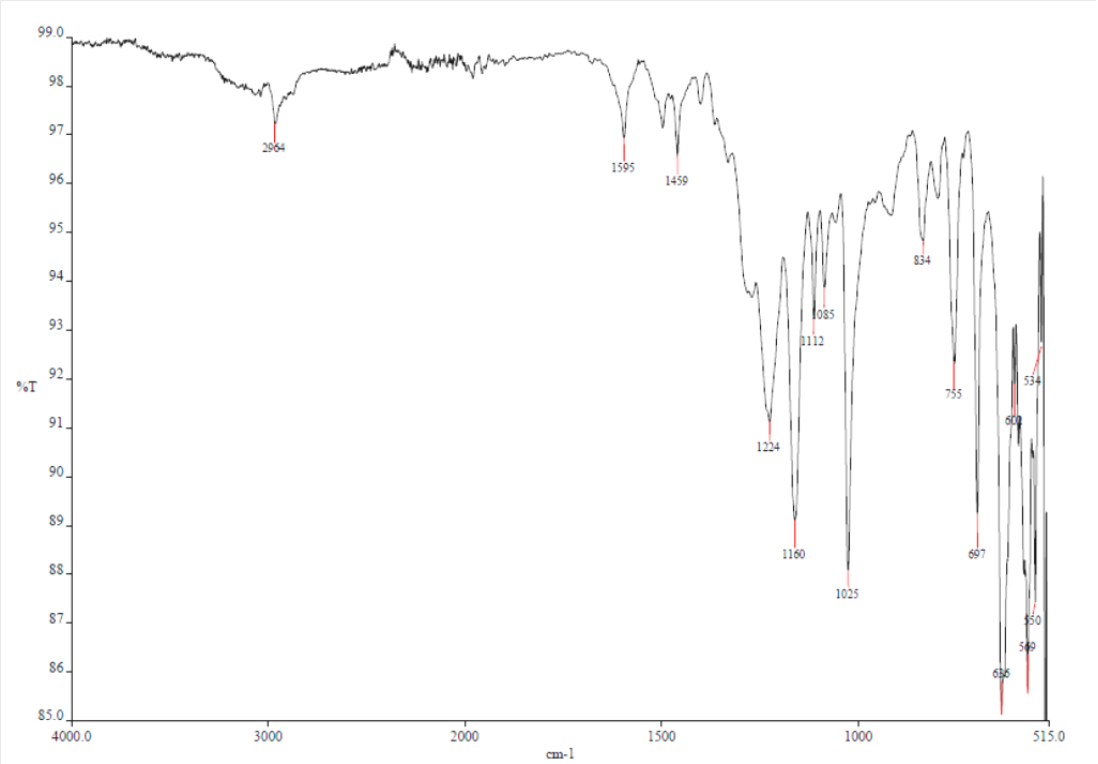
In a small Schlenk tube eqquiped with a magnetic stirring bar, $Fe(OTf)_3$ (0.1 mmol, 50.3 mg) and **L1** (0.1 mmol, 91.6 mg) were added. The tube was degassed (3 times) and placed under an inert atmosphere. C_6D_6 (1.0 mL) was added by syringe and and the reaction mixture was stirred for 3 h at 45 °C, resulting in the formation of a dark red solution. Styrene (0.1 mmol, 11.5 μL) was added to the reaction mixture, which was stirred at 50 °C for another hour resulting in a dark brown solution. Then the solution was cooled down to r.t. and the solvent evaporated in vacuo. Upon evaporation, the solution changed colour to dark red, suggesting decoordination of the olefin. The resulting solid was anslysed by IR spectroscopy and compared with the pure catalyst and pure styrene. Attempts to determine olefin coordination by NMR were unsuccessful due to the catalyst being paramagnetic.

Styrene: IR (neat) ν = 3081, 3059, 3027, 1629, 1600, 1575, 1494, 1412, 1334, 1317, 1289, 1202, 1156, 1082, 1020, 990, 905, 774, 694 cm^{-1}.

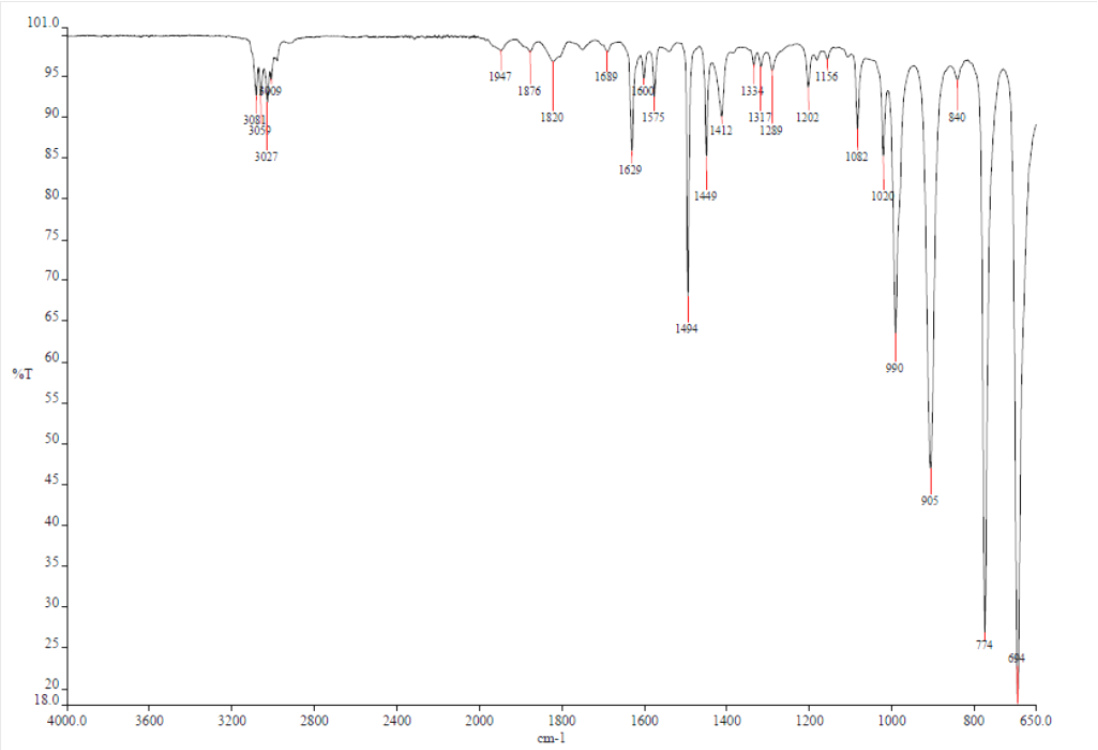
$Fe(OTf)_3$-L1 and styrene premixed: IR (neat) ν = 3064, 2965, 1596, 1495, 1458, 1400, 1330, 1279, 1234, 1161, 1112, 1085, 1026, 993, 911, 838, 812, 796, 777, 756, 697 cm^{-1}.

IR spectra

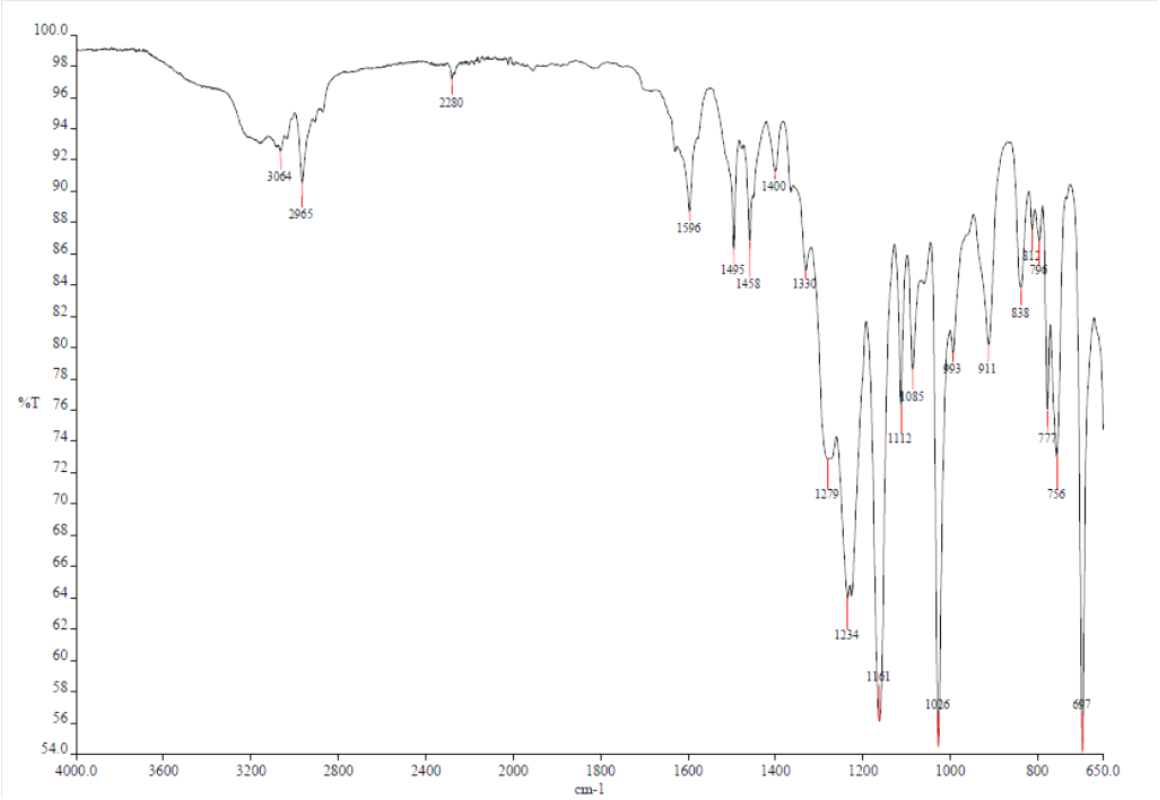
Catalyst only



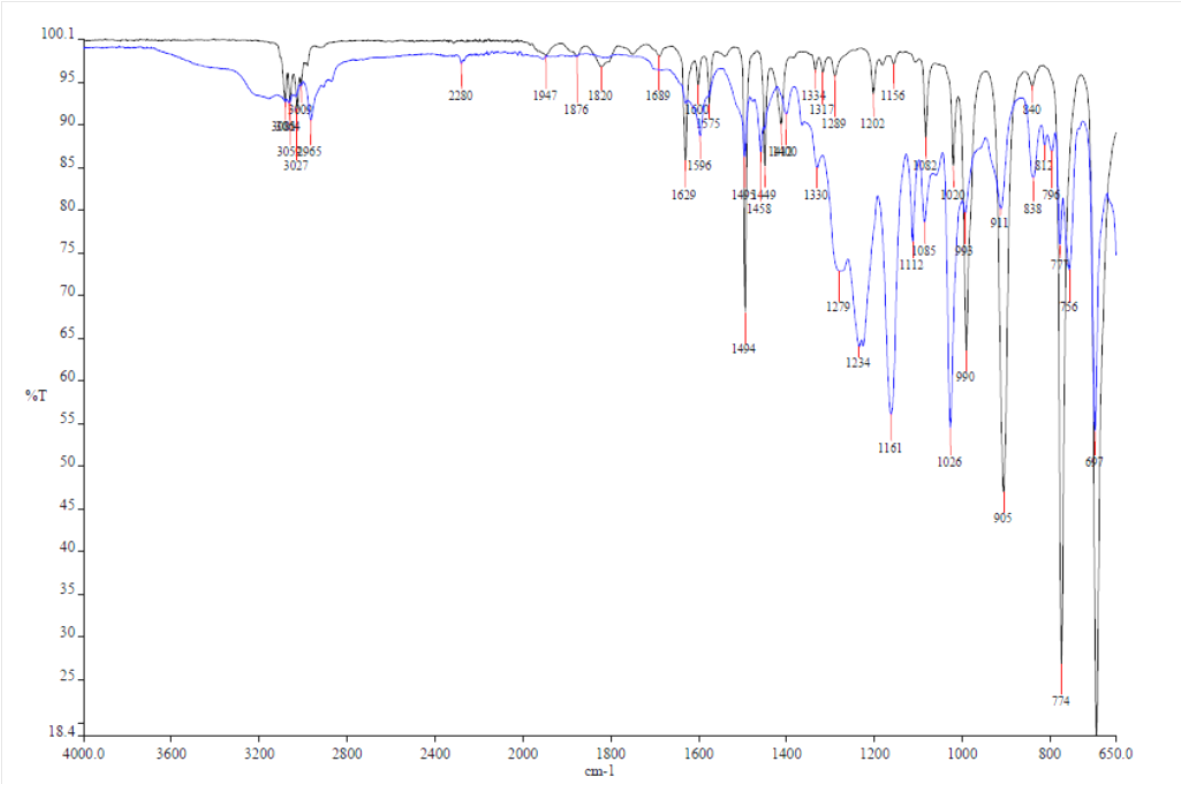
Styrene

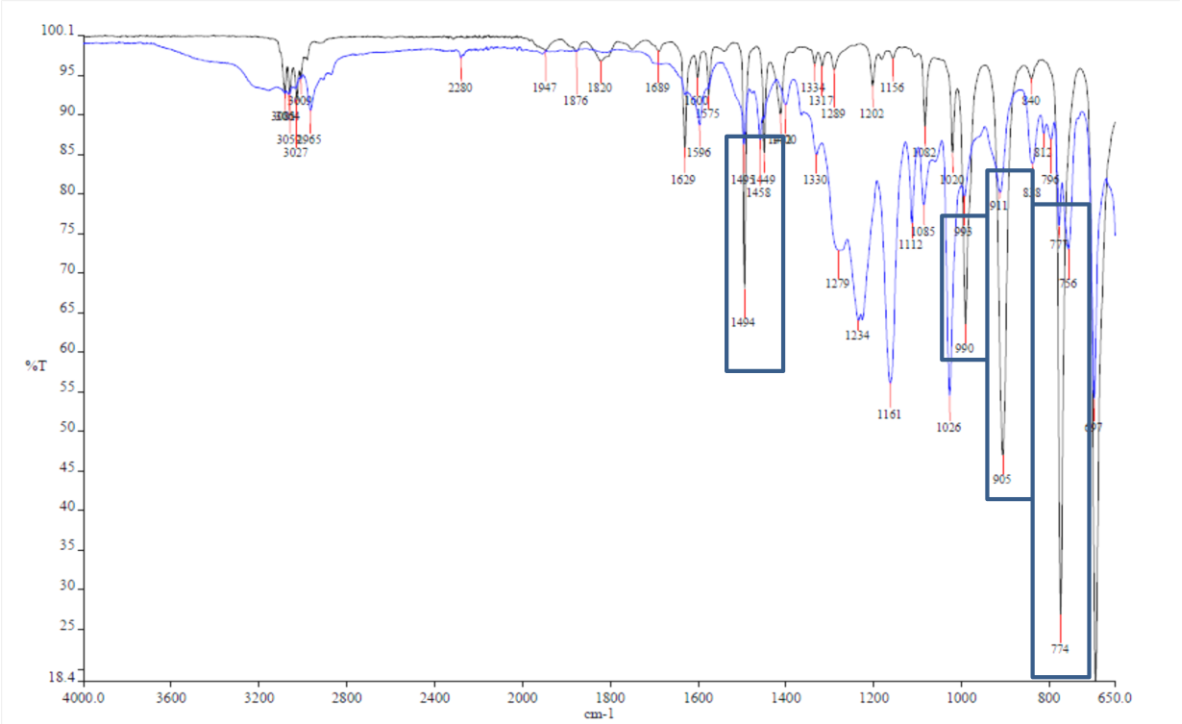


Iron catalyst and styrene premixed



Catalyst and styrene premixed (blue) overlapped with styrene alone (black)





7. References

[1] Gonzalez-de-Castro, A.; Robertson, C. M.; Xiao, J. *J. Am. Chem. Soc*. **2014**, *136*, 8350.

[2] Hikeda, H.; Hoshi, Y.; Namai, H.; Tanaka, F.; Goodman, J. L.; Mizuno, K. *Chem. Eur. J.* **2007**, *13*, 9207.

[3] Sung, J. C.; Jensen, N. H.; Kurome, T.; Kadari, S.; manzano, M. L.; Malberg, J. E.; Caldarone, B.; Roth, R. L.; Kozikowski, A. P. *J. Med. Chem*. **2009**, *66*, 1102

[4] Smith, C. R.; Rajanbabu, T. V. *Tetrahedron* **2010**, *66*, 1102.

[5] Ohsugi, S.-I.; Nishide, K.; Node, M. *Tetrahedron* **2003**, *59*, 1859.

[6] Bremond, J.-P.; Donnier, M.; Limouzin, Y. *J. Organomet. Chem*. **1975**, *90*, 279.

[7] Feuer, H.; Doty, J.; Lawrence, J. P. *J. Org. Chem*. **1973**, *38*, 417.

[8] Liwosz, T. W.; Chemler, S. R. *Chem. Eur. J.* **2013**, *19*, 12771.

[9] Hansen, A. I.; Ebran, J.-P.; Gogsig, T. M.; Skrydstrup, T. *J. Org. Chem*. **2007**, *17*, 6464.

[10] Stec, J.; Thomas, E.; Dixon, S.; Whitby, R. J. *Chem. Eur. J*. **2011**, *17*, 4896.

[11] Modak, A.; Deb, A.; Patra, T.; Rana, S.; Maity, S.; Maity, D. *Chem. Commun*. **2012**, *48*, 4253.

[12] Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett*. **2006**, *8*, 693.

[13] Ganapathy, D.; Sekar, G. *Org. Lett*. **2014**, *16*, 3856.

[14] Bert, K.; Noel, T.; Kimpe, W.; Goeman, J. L.; Van Der Eycken, J. *Org. Biomol. Chem*. **2012**, *10*, 8539.

[15] Yamakana, M.; Arisawa,M.; Nishida, A.; Nakagawa, M. *Tetrahedron Lett*. **2002**, *43*, 2403.

[16] Matsubara, R.; Jamison. T. F. *J. Am. Chem. Soc*. **2010**, *132*, 6880.

[17] Okamoto, R.; Tanaka, K. *Org. Lett*. **2013**, *15*, 2112.

[18] Barluenga, J.; Aznar, F.; Liz, R.; Bayod, M. *J. Org. Chem*. **1987**, *52*, 5190.

[19] Koch, H. F.; Ladder, G.; Koch, J. G.; Bodgman, D. J.; Brown, G. H.; Carlson, C. A.; Dean, A. B.; Hage, R.; Han, P.; Hopman, J. C. P.; James, L. A.; Knape, P. M.; Roos, E. C.; Sardina, M. L.; Sawyer, R. A.; Scott, B. O.; Testa, C. A. III; Wickman, S. D. *J. Am. Chem. Soc*. **1997**, *119*, 9965.
[20] Tanaka, K.; Hosokama, A.; Yoshida, K. *Synthesis* **1999**, *2*, 249.
[21] Furrows, M. E.; Myers, A. G. *J. Am. Chem. Soc.* **2004**, *126*, 5436.
[22] Gassman, P. G.; Harrington, C. K. *J. Org. Chem*. **1984**, *49*, 2258.
[23] Von Roman, R.; Ruhdorfer, J.; Knorr, R. *Synthesis* **1993**, *10*, 985.
[24] Brondani, P. B.; Dudek, H.; Reis, J. S.; Fraaije, M. W.; Andrade, L. H. *Tetrahedron Asym*. **2012**, *23*, 703.
[25] Barluenga, J.; Moriel, P.; Aznar, F.; Valdes, C. *Adv. Synth. Catal*. **2006**, *348*, 347.
[26] Jung, M. E.; Light, L. A. *J. Org. Chem*. **1982**, *47*, 1084.
[27] Yang, Y.; Moschetta, E. G.; Rioux, R. M. *ChemCatChem* **2013**, *5*, 3005.
[28] Song, C.-X.; Cai, G.-X.; Farrell, T. R.; Jiang, Z.-P.; Li, H.; Gan, L.-B.; Shi, Z.-J. *Chem. Commun*. **2009**, *40*, 6002.
[29] Mo, J.; Xu, L.; Xiao, J. *J. Am. Chem. Soc*. **2005**, *127*, 751.
[30] Mao, J.; Bao, W. *Org. Lett*. **2014**, *16*, 2646.
[31] Pappula, V.; Donthir, R. R.; Darapaneni, C. M.; Subbarayappa, A. *Tetrahedron Lett*. **2014**, *55*, 1793.
[32] Huang, Y.-L.; Chen, Y.-H.; Hsien, K.-C.; Chen, Y.-L.; Kao, C.-L. *Tetrahedron Lett*. **2009**, *50*, 1834.
[33] Li, H.; Misal Castro, L. C.; Zheng, J.; Roisnel, T.; Dorcet, V.; Sortais, J.-B.; Darcel, C. *Angew. Chem. Int. Ed.* **2013**, *125*, 8203.
[34] Iinuma, M.; Moriyama, K.; Togo, H. *Tetrahedron* **2013**, *69*, 2961.
[35] Wang, A.; Jiang, H. *J. Org. Chem*. **2010**, *75*, 2321.
[36] Feng, Q.; Song, Q. *J. Org. Chem*. **2014**, *79*, 1867.
[37] Xie, A.; Zhou, X.; Feng, L.; Hu, X.; Dong, W. *Tetrahedron* **2014**, *70*, 3514.
[38] Sun, H.; DiMagni, S. G. *Angew. Chem. Int. Ed*. **2006**, *45*, 2720.
[39] Perez, J. M.; Cano, R.; Yus, M.; Ramon, D. J. *Eur. J. Org. Chem*. **2012**, *24*, 4548.
[40] Chen, Z.-W.; Ye, D.-N.; Quian, Y.-P.; Ye, M.; Liu, L.-X. *Tetrahedron* **2013**, *69*, 6116.
[41] Hanson, S. K.; Wu, R.; Silks, L. A. *Org. Lett*. **2011**, *13*, 1908.
[42] Somers, J. B. M.; Couture, A.; Lablanche-Combier, A.; Laarhoven, W. H. *J. Am. Chem. Soc*. **1985**, *107*, 1387.
[43] Steves, J. E.; Stahl, S. S. *J.Am. Chem. Soc*. **2013**, *135*, 15742.
[44] CAS No: 6056-35-5
[45] Jiang, Q.; Sheng, W.; Guo, C. *Green Chem*. **2013**, *15*, 2175
[46] Li, M.; Wang, C., Ge, H. *Org. Lett*. **2011**, *13*, 2062.
[47] Korsanger, S.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. *J. Org. Chem*. **2013**, *78*, 6112.
[48] Kouznetsov, V. V.; Merchan Arenas, D. R. *Tetrahedron Lett*. **2009**, *50*, 1546.
[49] Yadav, J. S.; Kondaji, G.; Shiva Ram Reddy, M.; Srihari, P. *Tetrahedron Lett*. **2008**, *49*, 3810.
[50] Maji, T.; Karmakar, A.; Reiser, O. *J. Org. Chem*. **2011**, *76*, 736.
[51] Chen, Z.-W.; Ye, D.-N.; Ye, M.; Zhou, Z.-G.; Li, S.-H.; Liu, L.-X. *Tetrahedron Lett*. **2014**, *55*, 1373.
[52] Ruan, J.; Iggo, J. A.; Berry, N. G.; Xiao, J. *J. Am. Chem. Soc*. **2010**, *132*, 16689.
[53] Romney, D. K.; Miller, S. J. *Org. Lett*. **2012**, *14*, 1138.
[54] Yin, L.; Wu, J.; Xiao, J.; Cao, S. *Tetrahedron Lett*. **2012**, *53*, 4418.
[55] Waser, J.; Carreira, E. M. *Angew. Chem. Int. Ed*. **2004**, *43*, 4099.
[56] Sawamara, Y.; Yabe, Y.; Shigetsura, M.; Yamada, T.; Nagata, S.; Fujiwara, Y.; Maegawa, T.; Manguchi, Y.; Sajiki, H. *Adv. Synth. Catal*. **2012**, *354*, 777.

[57] Barbero, N.; Martin, R. *Org. Lett*. **2012**, *14*, 796.
[58] Atmaca, U.; Usanmaz, H. K.; Celik, M. *Tetrahedron Lett*. **2014**, *56*, 2230.
[59] Coskun, T.; Conifer, C. M.; Stevenson, L. C.; Britovsek, G. J. P. *Chem. Eur. J*. **2013**, *19*, 6840.
[60] Boruah, J. J.; Das, S. P.; Ankireddy, S. R.; Gogoi, S. R.; Islam, N. S. *Green Chem*. **2013**, *15*, 2944.