# Lewis Acid Catalysis in Supercritical Carbon Dioxide ($scCO_2$). Use of Poly(ethyleneglycol) Derivatives and Perfluoroalkylbenzenes as Surfactant Molecules Which Enable Efficient Catalysis in $scCO_2$

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**Experimental Section**

**General.** Tetramethylsilane (TMS) served as internal standard (δ = 0) for $^1$H NMR, $CDCl_3$ was used as internal standard (δ = 77) for $^{13}$C NMR, and $CF_3COOH$ was used as internal standard (δ = –76.5) for $^{19}$F NMR. Column chromatography was performed on Silica gel 60 (Merck) and preparative thin-layer chromatography was carried out using Wakogel B-5F.

**Materials.** The perfluorobenzenes surfactants were prepared by the method described below. All reagents and solvents were used after purification according to usual methods.

**Typical Experimental Procedure for the Aldol Reaction in scCO$_2$–PEG system. Synthesis of Methyl 3-benzylamino-2,2-dimethyl-3-phenylpropionate (3a).**[1] $Yb(OTf)_3$ (16 mg, 0.026 mmol) and a small stirring bar were placed in a 10 mL stainless steel autoclave under argon atmosphere. Imine **1a** (103 mg, 0.53 mmol), silicon enolate **2a** (113 mg, 0.65 mmol), and poly(ethylene glycol) (44 mg, average *Mw* = 400) were mixed in a small ampoule and put in the autoclave separately to prevent reactions under neat conditions before the autoclave was filled with $CO_2$. $CO_2$ was cooled at –10 °C and charged with an HPLC pump. During the introduction of $CO_2$, the autoclave was heated and then pressure and temperature were adjusted to 15 MPa, and 50 °C. The mixture was stirred for 3 h, and the reactor was cooled with ice and then the pressure was released. After hydrolytic work-up with aqueous $NaHCO_3$ and ethyl ether, the organic layer was dried with anhydrous $Na_2SO_4$. After being concentrated, the residue was subjected to preparative TLC to give **3a** as a pale yellow oil (113 mg, 72% yield): $^1$H NMR ($CDCl_3$) δ 1.03 (s, 3 H), 1.12 (s, 3 H), 3.64 (s, 3 H), 3.40 (d, *J* = 13.2 Hz, 1 H), 3.66 (d, *J* = 13.2 Hz, 1 H), 3.89 (s, 1 H), 7.19-7.38 (m, 10 H); $^{13}$C NMR ($CDCl_3$) δ 19.4, 24.1, 47.4, 51.4, 51.8, 67.7, 126.8, 127.4, 127.9, 128.1, 128.2, 129.0, 139.1, 140.5, 177.7.

**Methyl 2,2-dimethyl-3-phenyl-3-phenylaminopropionate (3b):**[2] $^1$H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.27 (s, 3 H), 3.64 (s, 3 H), 4.49 (s, 1 H), 6.45-6.62 (m, 3 H), 6.99-7.07 (m, 2 H), 7.18-7.28 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 20.7, 24.5, 47.0, 52.0, 64.9, 113.4, 117.3, 127.4, 128.0, 128.3, 129.0, 139.2, 146.9, 177.0.

**Methyl 2,2-dimethyl-5-phenyl-3-phenylamino-4-pentenoate (3c):**[2] $^1$H NMR ($CDCl_3$) δ 1.29 (s, 3 H), 1.32 (s, 3 H), 3.67 (s, 3 H), 4.13 (d, *J* = 7.1 Hz, 1 H), 6.09 (dd, *J* = 7.2, 15.8 Hz, 1 H), 6.55 (d, *J* = 15.8 Hz, 1 H), 6.63-6.70 (m, 3 H), 7.10-7.17 (m, 2 H), 7.19-7.34 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 21.6, 23.5, 47.0, 52.0, 62.6, 113.7, 117.6, 126.5, 127.2, 127.6, 128.5, 129.2, 132.9, 136.7, 147.3, 177.0.

**Methyl 3-(2'-furyl)-2,2-dimethyl-3-phenylaminopropionate (3d):**[3] $^1$H NMR ($CDCl_3$) δ 1.26 (s, 3 H), 1.27 (s, 3 H), 3.68 (s, 3 H), 4.71 (s, 1 H), 6.15 (d, *J* = 3.2 Hz, 1 H), 6.25 (dd, *J* = 1.8, 3.2 Hz, 1 H), 6.61-6.72 (m, 3 H), 7.09-7.15 (m, 2 H), 7.30 (dd, *J* = 0.9, 1.8 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) δ 19.9, 23.6, 47.3, 51.6, 51.8, 61.5, 108.9, 109.9, 126.9, 128.1, 128.3, 140.2, 141.8, 153.6, 177.3.

***S*-Ethyl 3-(2'-methoxyphenylamino)-3-phenylpropanethioate (3e):**[4] $^1$H NMR ($CDCl_3$) δ 1.26 (s, 3 H), 1.27 (s, 3 H), 3.68 (s, 3 H), 4.71 (s, 1 H), 6.15 (d, *J* = 3.2 Hz, 1 H), 6.25 (dd, *J* = 1.8, 3.2 Hz, 1 H), 6.61-6.72 (m, 3 H), 7.09-7.15 (m, 2 H), 7.30 (dd, *J* = 0.9, 1.8 Hz, 1 H); $^{13}$C NMR ($CDCl_3$) δ 14.5, 23.5, 51.8, 55.4, 55.5, 109.4, 111.2, 116.9, 121.1, 126.3, 127.4, 128.7, 136.5, 142.0, 146.9, 197.0.

***S*-Ethyl 3-(2'-methoxyphenylamino)-2-methyl-3-phenylpropanethioate (3f):** (*syn*/*anti* = 57/43)[5] $^1$H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.3 Hz, 3 H), 1.11 (d, *J* = 7.3 Hz, 1.29 H), 1.16 (t, *J* = 7.4 Hz, 1.29 H), 1.22 (d, *J* = 7.0 Hz, 1.71 H), 1.22 (t, *J* = 7.2 Hz, 1.29 H), 2.72-2.89 (m, 2 H), 2.94-3.10 (m, 1 H), 3.83 (s, 1.29 H), 3.85 (s, 1.71 H), 4.50 (d, *J* = 7.7 Hz, 0.43 H), 4.70 (d, *J* = 5.7 Hz, 0.57 H), 5.31 (brs, 1 H), 6.30 (dd, *J* = 1.5, 7.6 Hz, 0.57 H), 6.34 (dd, *J* = 1.5, 7.8 Hz, 0.43 H), 6.50-6.74 (m, 3 H), 7.14-7.32 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 12.4, 14.2, 14.5, 14.6, 15.9, 21.0, 23.3, 23.4, 54.75, 54.80, 55.57, 55.59, 60.0, 60.4, 60.9, 109.4, 109.5, 111.0, 111.3, 116.5, 116.8, 121.01, 121.04, 127.02, 127.03, 127.1, 127.2, 127.3, 127.4, 128.38, 128.44, 128.6, 136.7, 136.8, 140.9, 141.1, 146.9, 147.0, 201.5, 202.1. IR (neat) 3409, 2966, 2931, 1677, 1603, 1513, 1455, 1223, 1028, 963, 737, 702 $cm^{-1}$. HRMS (*m*/*z*) calcd. for $C_{19}H_{23}NO_2S$ ($M^+$): 329.1450; found: 329.1425.

***S*-Ethyl 3-(2'-methoxyphenylamino)-2,2-dimethyl-3-phenylthiopropane thioate (3g):** $^1$H NMR ($CDCl_3$) δ 1.17 (t, *J* = 7.4 Hz, 3 H), 1.23 (s, 3 H), 1.27 (s, 3 H), 2.83 (q, *J* = 7.4 Hz, 2 H), 3.85 (s, 3 H), 4.59 (s, 1 H), 5.29 (brs, 1 H), 6.28 (dd, *J* = 1.5, 7.6 Hz, 1 H), 6.55 (ddd, *J* = 1.5, 7.6, 7.6 Hz, 1 H), 6.62 (ddd, *J* = 1.5, 7.6, 7.6 Hz, 1 H), 6.70 (dd, *J* = 1.5, 7.6 Hz, 1 H), 7.18-7.33 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 14.4, 19.9, 23.3, 24.8, 53.5, 55.6, 64.6, 109.4, 110.9, 116.3, 121.1, 127.3, 127.9, 128.6, 137.0, 139.2, 146.9, 205.7. IR (neat) 3414, 2971, 2933, 1674, 1603, 1512, 1455, 1252, 1223, 947, 735, 706 $cm^{-1}$. HRMS (*m*/*z*) calcd. for $C_{20}H_{25}NO_2S$ ($M^+$): 343.1606; found: 343.1599.

**Methyl 3-(2'-methoxyphenylamino)-2-methyl-3-phenylpropionate (3h):**[6] (*syn*/*anti* = 38/62 at Table 3, entry 8) $^1$H NMR ($CDCl_3$) δ 1.14 (d, *J* = 7.1 Hz, 1.86 H), 1.21 (d, *J* = 7.3 Hz, 1.14 H), 2.83-2.92 (m, 0.62 H), 2.94-3.02 (m, 0.38 H), 3.59 (s, 1.14 H), 3.65 (s, 1.86 H), 3.86 (s, 1.86 H), 3.88 (s, 1.14 H), 4.51 (d, *J* = 7.8 Hz, 0.62 H), 4.73 (d, *J* = 5.4 Hz, 0.38 H), 5.04 (brs, 0.38 H), 5.28 (brs, 0.62 H), 6.33 (dd, *J*

= 1.5, 7.8 Hz, 0.38 H), 6.40 (dd, *J* = 1.5, 8.0 Hz, 0.62 H), 6.57 (ddd, *J* = 1.5, 7.8, 7.9 Hz, 0.38 H), 6.59 (ddd, *J* = 1.5, 7.9, 8.0 Hz, 0.62 H), 6.65-6.76 (m, 2 H), 7.17-7.35 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 12.1, 15.0, 46.5, 46.7, 51.75, 51.78, 55.6, 59.4, 60.5, 109.4, 109.5, 111.0, 111.1, 116.5, 116.6, 121.1, 126.8, 126.9, 127.2, 127.4, 128.4, 128.5, 136.79, 136.84, 140.9, 141.2, 146.9, 174.5, 175.3.

***S*-Ethyl 3-cyclohexyl-3-phenylaminopropanethioate (3i):** $^1$H NMR ($CDCl_3$) δ 0.95-1.29 (m, 2 H), 1.19 (t, *J* = 7.4 Hz, 3 H), 1.50-1.92 (m, 9 H), 2.72 (dd, *J* = 6.7, 15.0 Hz, 1 H), 2.77 (dd, *J* = 5.6, 14.9 Hz, 1 H), 2.84 (q, *J* = 7.4 Hz, 2 H), 3.70-3.76 (m, 1 H), 6.61 (d, *J* = 8.1 Hz, 2 H), 6.66 (d, *J* = 7.3 Hz, 1 H), 7.14 (dd, *J* = 7.3, 8.1 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 14.6, 23.5, 26.2, 26.4, 29.1, 29.6, 41.9, 46.1, 55.8, 113.3, 117.3, 129.3, 147.4, 198.3. IR (neat) 3402, 3054, 3024, 2926, 2853, 1680, 1601, 1505, 1449, 1319, 1259, 745, 690 cm$^{-1}$. HRMS (*m*/*z*) calcd. for $C_{17}H_{25}NOS$ ($M^+$): 291.1657; found: 291.1645.

**Ethyl 3-cyclohexyl-3-phenylaminopropionate (3j):** $^1$H NMR ($CDCl_3$) δ 0.96-1.30 (m, 5 H), 1.18 (t, *J* = 7.1 Hz, 3 H), 1.47-1.93 (m, 6 H), 2.45 (dd, *J* = 7.0, 14.9 Hz, 1 H), 2.55 (dd, *J* = 5.2, 14.9 Hz, 1 H), 3.65-3.72 (m, 1 H), 4.06 (q, *J* = 7.1 Hz, 2 H), 6.59-6.69 (m, 3 H), 7.11-7.17 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 26.2, 26.4, 29.3, 29.4, 37.1, 42.1, 55.3, 60.4, 113.3, 117.1, 129.2, 129.2, 147.7, 172.3. IR (neat) 3393, 2926, 2851, 1732, 1602, 1509, 1280, 1187, 748, 692 cm$^{-1}$. MS (*m*/*z*) 275 ($M^+$). Anal. Calcd. for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09; found: C, 74.05; H, 9.08; N, 5.07.

**Methyl 3-cyclohexyl-2,2-dimethyl-3-phenylaminopropanoate (3k):**[2] $^1$H NMR ($CDCl_3$) δ 1.00-1.26 (m, 4 H), 1.19 (s, 3 H), 1.23 (s, 3 H), 1.48-1.73 (m, 7 H), 3.50 (d, *J* = 3.9 Hz, 1 H), 3.65 (s, 3 H), 4.06 (brs, 1 H), 6.59-6.65 (m, 3 H), 7.10-7.16 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 22.6, 24.3, 26.1, 26.4, 26.8, 28.5, 32.9, 41.3, 47.3, 51.8, 64.0, 112.5, 116.4, 129.3, 149.7, 178.1.

**1,3-Diphenyl-3-phenylaminopropan-1-one (3l):**[2] $^1$H NMR ($CDCl_3$) δ 3.41 (dd, *J* = 7.5, 16.1 Hz, 1 H), 3.50 (dd, *J* = 5.4, 16.1 Hz, 1 H), 5.00 (dd, *J* = 5.4, 7.5 Hz, 1 H), 6.54-6.58 (m, 2 H), 6.63-6.70 (m, 1 H), 7.06-7.11 (m, 2 H), 7.20-7.35 (m, 3 H), 7.40-7.58 (m, 5 H), 7.88-7.92 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 46.2, 54.9, 113.9, 117.9, 126.4, 127.4, 128.2, 128.7, 128.8, 129.1, 133.4, 136.6, 142.8, 146.7, 198.2.

**3-Hydroxy-1,3-diphenyl-1-propanone (5a):**[7] $^1$H NMR ($CDCl_3$) δ 3.34 (d, *J* = 4.3 Hz, 1 H), 3.35 (d, *J* = 7.6 Hz, 1 H), 5.33 (dd, *J* = 4.3, 7.6 Hz, 1 H), 7.23-7.59 (m, 8 H), 7.91-7.94 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 47.4, 70.0, 125.7, 127.7, 128.1, 128.6, 128.7, 128.8, 133.7, 142.9, 200.2.

**3-(4'-Chlorophenyl)-3-hydroxy-1-phenyl-1-propanone (5b):**[7] $^1$H NMR ($CDCl_3$) δ 3.34 (d, *J* = 5.8 Hz, 2 H), 3.63 (brs, 1 H), 5.32 (t, *J* = 5.8 Hz, 1 H), 7.26-7.43 (m, 4 H), 7.44-7.52 (m, 2 H), 7.56-7.63 (m, 1

H), 7.94 (d, *J* = 8.3 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 47.2, 69.4, 127.1, 128.1, 128.66, 128.72, 133.3, 133.7, 136.4, 141.4, 199.9.

**3-Hydroxy-1-phenyl-3-(4'-methylphenyl)-1-propanone (5c):**[7] $^1$H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 3.34-3.38 (m, 2 H), 3.51 (brs, 1 H), 5.32 (t, *J* = 5.9 Hz, 1 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 7.43-7.50 (m, 2 H), 7.55-7.62 (m, 1 H), 7.93-7.98 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 21.1, 47.4, 69.9, 125.7, 128.1, 128.7, 129.2, 133.6, 136.6, 137.4, 140.0, 200.2.

**Ethyl 3-hydroxy-3-phenylpropionate (5d):**[8] $^1$H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 2.70-2.80 (m, 2 H), 3.26 (brs, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 5.13 (dd, *J* = 4.4, 8.2 Hz, 1 H), 7.24-7.52 (m, 5 H), 7.25-7.33 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 43.3, 60.8, 70.3, 125.7, 127.8, 128.5, 142.5, 172.4.

**Ethyl 3-hydroxy-5-phenyl-1-pent-4-enoate (5e):**[9] $^1$H NMR ($CDCl_3$) δ 1.28 (t, *J* = 7.1 Hz, 3 H), 2.57-2.71 (m, 2 H), 3.06 (brs, 1 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 4.72 (m, 1 H), 6.22 (dd, *J* = 6.2, 15.9 Hz, 1 H), 6.66 (d, *J* = 15.9 Hz, 1 H), 7.21-7.43 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 14.2, 41.5, 60.8, 68.9, 126.5, 127.8, 128.6, 129.9, 130.8, 136.4, 172.2.

**Ethyl 3-hydroxy-5-phenyl-1-pentanoate (5f):**[10] $^1$H NMR ($CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3 H), 1.64-1.92 (m, 2 H), 2.38-2.56 (m, 2 H), 2.64-2.88 (m, 2 H), 3.05 (d, *J* = 3.9 Hz, 1 H), 3.96-4.04 (m, 1 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 7.15-7.32 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 31.7, 38.1, 41.3, 60.7, 67.2, 125.9, 128.40, 128.43, 141.7, 173.0.

**Methyl 3-hydroxy-2-methyl-3-phenylpropionate (5g):**[9] $^1$H NMR ($CDCl_3$) *Syn* isomer: δ 1.12 (d, *J* = 7.1 Hz, 3 H), 2.79 (dq, *J* = 7.1, 4.1 Hz, 1 H), 3.67 (s, 3 H), 5.10 (d, *J* = 4.1 Hz, 1 H), 7.22-7.48 (m, 5 H). *Anti* isomer: δ 1.01 (d, *J* = 7.1 Hz, 3 H), 2.79 (dq, *J* = 8.4, 7.1 Hz, 1 H), 3.73 (s, 3 H), 4.75 (d, *J* = 8.4 Hz, 1 H), 7.20-7.48 (m, 5 H); $^{13}$C NMR ($CDCl_3$) *Syn* isomer: δ 10.7, 46.3, 51.9, 73.6, 125.9, 127.5, 128.2, 141.4, 176.2. *Anti* isomer: δ 14.5, 47.1, 51.9, 76.4, 126.7, 128.1, 128.5, 141.5, 176.2.

***S*-Ethyl 3-hydroxy-3-phenylpropanethioate (5h):**[10] $^1$H NMR ($CDCl_3$) δ 1.27 (t, *J* = 7.4 Hz, 3 H), 2.89-3.05 (m, 5 H), 5.19 (d, *J* = 8.4 Hz, 1 H), 7.27-7.42 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 14.6, 23.5, 52.5, 70.9, 125.6, 127.9, 128.6, 142.3, 199.1.

***S*-Ethyl 3-hydroxy-2-methyl-3-phenylpropanethioate (5i):**[11] (*syn*/*anti* = 26/74) $^1$H NMR ($CDCl_3$) [33] δ 1.02 (d, *J* = 7.2 Hz, 2.22 H), 1.16 (d, *J* = 7.2 Hz, 0.78 H), 1.22 (t, *J* = 7.4 Hz, 0.78 H), 1.26 (t, *J* = 7.4 Hz, 2.22 H), 2.82-3.04 (m, 3 H), 4.81 (d, *J* = 8.3 Hz, 0.74 H), 5.11 (d, *J* = 4.0 Hz, 0.26 H), 7.26-7.40 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 11.3, 14.6, 15.5, 23.2, 23.3, 54.9, 55.4, 73.7, 76.6, 126.0, 126.6, 127.5, 128.1,

128.2, 128.5, 141.2, 141.6, 203.7, 204.1.

***S*-Ethyl 3-hydroxy-2,2-dimethyl-3-phenylpropanethioate (5j):**[12] $^1$H NMR ($CDCl_3$) δ 1.11 (s, 3 H), 1.21 (s, 3 H), 1.25 (t, *J* = 7.4 Hz, 3 H), 2.87 (q, *J* = 7.4 Hz, 2 H), 4.93 (s, 1 H), 7.25-7.34 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 14.4, 19.0, 23.3, 23.6, 54.3, 78.9, 127.7, 127.8, 139.9, 207.9.

***tert*-Butyl 3-hydroxy-2-methyl-3-phenylpropionate (5k):**[13] (*syn*/*anti* = 29/71) $^1$H NMR ($CDCl_3$) δ 1.02 (d, *J* = 7.1 Hz, 2.13 H), 1.13 (d, *J* = 7.1 Hz, 0.87 H), 1.43 (s, 2.61 H), 1.47 (s, 6.39 H), 2.76 (m, 0.71 H), 2.78-2.92 (m, 1 H), 2.97 (m, 0.29 H), 4.78 (dd, *J* = 3.8, 7.9 Hz, 0.71 H), 5.07-5.09 (m, 0.29 H), 7.23-7.37 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 11.4, 15.5, 29.66, 29.70, 48.25, 48.35, 55.0, 55.6, 73.8, 76.7, 126.1, 126.6, 127.4, 128.0, 128.2, 128.4, 141.8, 175.3.

***iso*-Propyl 3-hydroxy-2-methyl-3-phenylpropionate (5l):**[14] (*syn*/*anti* = 37/63 at Table 4, entry 15) $^1$H NMR ($CDCl_3$) δ 1.03 (d, *J* = 7.1 Hz, 1.89 H), 1.12 (d, *J* = 7.1 Hz, 1.11 H), 1.16 (d, *J* = 6.2 Hz, 1.11 H), 1.21 (d, *J* = 6.2 Hz, 1.11 H), 1.21 (d, *J* = 6.2 Hz, 1.89 H), 1.24 (d, *J* = 6.2 Hz, 1.89 H), 2.70-2.82 (m, 1 H), 3.04 (brs, 1 H), 4.74 (d, *J* = 8.2 Hz, 0.63 H), 5.00 (dq, *J* = 6.2, 6.2 Hz, 0.37 H), 5.06 (dq, *J* = 6.2, 6.2 Hz, 0.63 H), 5.07 (d, *J* = 4.2 Hz, 0.37 H), 7.24-7.38 (m, 5 H); $^{13}$C NMR ($CDCl_3$) δ 11.0, 14.5, 21.61, 21.63, 21.66, 21.7, 46.5, 47.2, 68.07, 68.13, 73.7, 76.3, 126.1, 126.6, 127.4, 127.9, 128.2, 128.4, 141.4, 141.7, 175.4.

**Phenyl 3-hydroxy-2-methyl-3-phenylpropionate (5m):**[15] (*syn*/*anti* = 34/66) $^1$H NMR ($CDCl_3$) δ 1.14 (d, *J* = 7.1 Hz, 1.98 H), 1.29 (d, *J* = 7.1 Hz, 1.02 H), 2.96-3.08 (m, 1 H), 4.83 (d, *J* = 8.6 Hz, 0.66 H), 5.13 (d, *J* = 5.0 Hz, 0.34 H), 6.84-6.89 (m, 1 H), 6.99-7.04 (m, 1 H), 7.13-7.22 (m, 1 H), 7.26-7.40 (m, 7 H); $^{13}$C NMR ($CDCl_3$) δ 11.5, 14.4, 46.9, 47.4, 74.1, 76.4, 121.4, 121.5, 125.9, 126.2, 126.7, 127.8, 128.2, 128.4, 128.6, 129.37, 129.41, 141.4, 150.4, 150.5, 174.0, 174.3.

**Preparation of 1-dodecyloxy-4-heptadecafluorooctylbenzene (6a).**[16,17] Into a 50 mL glass autoclave, 4-dodecyloxy-iodobenzene (0.30 g, 0.8 mmol), 1-iodononafluorobutane (5.54 g, 16 mmol), activated cupper (1.02 g, 16 mmol), and pyridine (8 mL) were added, and the mixture was heated at 150 °C for 48 h. After cooling to room temperature, water (10 mL) and 1*N* aq. HCl (2 mL) were added, and the mixture was then filtered with celite and eluted with hexane. The filtrate was washed with 1*N* aq. HCl (30 mL x 5) and water (30 mL x 3). After drying with sodium sulfate, the crude product was purified by column chromatography (silica gel, eluted by hexane) to give **6a** (139 mg, 0.29 mmol, 36 % yield) as a white solid: M.p. 54-55 °C. $^1$H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3 H), 1.24-1.50 (m, 18 H), 1.80 (dq,

$J$ = 6.9, 6.9 Hz, 2 H), 3.99 (t, $J$ = 6.5 Hz, 2 H), 6.96 (d, $J$ = 8.8 Hz, 2 H), 7.48 (d, $J$ = 8.8 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 26.0, 29.1, 29.4, 29.59, 29.63, 29.68, 29.71, 32.0, 68.3, 105-119 (m), 114.5, 120.6 (t, $J$ = 24.8 Hz), 128.4 (t, $J$ = 6.2 Hz), 162.0; $^{19}$F NMR ($CDCl_3$) δ –126.4 (bs, 2 F), –123.0 (bs, 2 F), –122.2 (bs, 6 F), –121.6 (bs, 2 F), –110.0 (t, $J$ = 14.6 Hz, 2 F), –81.1 (t, $J$ = 10.0 Hz, 3 F). IR (KBr) 2921, 2853, 1615, 1518, 1475, 1370, 1257, 1211, 1144, 1112, 1090, 1051, 1017, 952, 845, 661, 559 cm$^{-1}$. MS ($m/z$) 680 ($M^+$). Anal. Calcd. for $C_{26}H_{29}F_{17}O$: C, 45.89; H, 4.30; found: C, 46.04; H, 4.60. After column chromatography, *p*-dodecyloxyiodobenzene was recovered (150 mg, 48 % recovery).

**1-Dodecyloxy-4-nonafluorobutylbenzene (6b):** $^1$H NMR ($CDCl_3$) δ 0.88 (t, $J$ = 7.0 Hz, 3 H), 1.24-1.50 (m, 18 H), 1.80 (dq, $J$ = 7.0, 7.0 Hz, 2 H), 3.99 (t, $J$ = 6.6 Hz, 2 H), 6.97 (d, $J$ = 8.8 Hz, 2 H), 7.48 (d, $J$ = 8.8 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 26.0, 28.9, 29.4, 29.57, 29.60, 29.6, 29.7, 31.9, 68.3, 106-120 (m), 114.4, 120.5 (t, $J$ = 24.8 Hz), 128.4, 161.9; $^{19}$F NMR ($CDCl_3$) δ –125.8-–126.1 (m, 2 F), –123.1-–123.3 (m, 2 F), –110.2 (dt, $J$ = 2.8, 13.3 Hz, 2 F), –81.4 (ddt, $J$ = 2.7, 2.7, 9.8 Hz, 3 F). IR (neat) 2927, 2853, 1614, 1519, 1466, 1349, 1232, 1135, 869, 826, 742, 686, 594, 526 cm$^{-1}$. HRMS ($m/z$) calcd. for $C_{22}H_{29}F_9O$ ($M^+$): 480.2075; found: 480.2058.

**1-Dodecyloxybenzene (6c):** $^1$H NMR ($CDCl_3$) δ 0.88 (t, $J$ = 6.7 Hz, 3 H), 1.24-1.50 (m, 18 H), 1.80 (dq, $J$ = 6.7, 6.7 Hz, 2 H), 3.95 (t, $J$ = 6.6 Hz, 2 H), 6.86-6.96 (m, 3 H), 7.25-7.33 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 14.1, 22.7, 26.0, 29.27, 29.34, 29.4, 29.57, 29.59, 29.62, 29.65, 31.9, 67.8, 114.4, 120.4, 129.4, 159.1. IR (KBr) 2925, 2845, 1600, 1497, 1466, 1248, 1085, 1040, 750, 697 cm$^{-1}$.

**1-Hexyloxy-4-heptadecafluorooctylbenzene (6d):** M.p. 28-29 °C. $^1$H NMR ($CDCl_3$) δ 0.91 (t, $J$ = 9.0 Hz, 3 H), 1.30-1.53 (m, 6 H), 1.80 (dq, $J$ = 7.0, 7.0 Hz, 2 H), 4.00 (t, $J$ = 6.5 Hz, 2 H), 6.97 (d, $J$ = 9.0 Hz, 2 H), 7.49 (d, $J$ = 9.0 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 14.0, 22.6, 25.7, 29.1, 31.5, 68.2, 107.0-116.8 (m), 114.4, 118.6 (t, $J$ = 33.0 Hz), 120.5 (t, $J$ = 24.8 Hz), 128.4 (t, $J$ = 6.2 Hz), 161.9; $^{19}$F NMR ($CDCl_3$) δ –126.4 (bs, 2 F), –123.0 (bs, 2 F), –122.2 (bs, 6 F), –121.6 (bs, 2 F), –110.0 (t, $J$ = 14.8 Hz, 2 F), –81.1 (t, $J$ = 10.0 Hz, 3 F). IR (KBr) 2941, 2869, 1615, 1521, 1473, 1202, 1155, 1105, 845, 652, 559 cm$^{-1}$. MS ($m/z$) 596 ($M^+$). Anal. Calcd. for $C_{20}H_{17}F_{17}O$: C, 40.28; H, 2.87; found: C, 40.00; H, 2.96.

**1-Methoxy-4-heptadecafluorooctylbenzene (6e):**[18] M.p. 28-30 °C. $^1$H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 6.99 (d, $J$ = 8.9 Hz, 2 H), 7.51 (d, $J$ = 8.9 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 55.3, 107.5-119.0 (m), 114.0, 120.9 (t, $J$ = 24.8 Hz), 128.5 (t, $J$ = 6.2 Hz), 137.7, 142.3, 162.4; $^{19}$F NMR ($CDCl_3$) δ –126.4 (s, 2

F), –123.0 (s, 2 F), –122.2 (s, 6 F), –110.0 (t, $J$ = 14.1 Hz, 2 H), –81.1 (t, $J$ = 10.0 Hz, 3 F). IR (KBr) 2970, 2844, 1615, 1519, 1205, 1146, 1027, 842, 651, 560 $cm^{-1}$.

**Typical Experimental Procedure for the Aldol Reaction in $scCO_2$–perfluoroalkylbenzene system. Synthesis of 3-Hydroxy-1,3-diphenyl-1-propanone (5a).**[7] **:** $Sc(OTf)_3$ (13 mg, 0.026 mmol), 1-dodecyloxy-4-heptadecafluorooctylbenzene **6a** (20 mg), and a small stirring bar were placed in a 10 mL stainless steel autoclave under argon atmosphere. Aldehyde **4a** (54 mg, 0.51 mmol) and silicon enolate **2i** (116 mg, 0.60 mmol) were mixed in a small ampoule and put in the autoclave separately to prevent reactions under neat conditions before the autoclave was filled with $CO_2$. $CO_2$ was cooled at –10 °C and charged with a HPLC pump. During the introduction of $CO_2$, the autoclave was heated and then pressure and temperature were adjusted to 15 MPa and 50 °C. The mixture was stirred for 3 h, and the reactor was cooled with ice and then the pressure was released. After hydrolytic work-up with water and dichloromethane, the organic layer was dried with anhydrous $Na_2SO_4$. The aqueous layer was concentrated in vacuo to give a crystalline residue, which was dried under reduced pressure at 200 °C for 4 h to afford 13 mg (quantitive recovery) of $Sc(OTf)_3$ as colorless crystals. The organic layer was concentrated, and the residue was treated with an aq. HCl/THF solution (10 mL, 1 N aq. HCl:THF=1:9) at 0 °C for 1 h. After adding water, the mixture was extracted with dichloromethane and the organic layer was dried with anhydrous $Na_2SO_4$. After filtration and concentration, dichloromethane (5 mL) was added to the residue and extracted with perfluorohexanes (FC-72, 15 mL) for several times. The fluorous layer was concentrated to give **6a** (20 mg, quantitative recovery). The dichloromethane layer was concentrated and the residue was subjected to preparative TLC to give the aldol adduct **5a** as a pale yellow oil (92 mg, 80% yield).

**4-(3'-Indolyl)-2-butanone (7a):**[19] $^1$H NMR ($CDCl_3$) δ 2.05 (s, 3 H), 2.76 (t, $J$ = 7.4 Hz, 2 H), 2.94-3.00 (m, 2 H), 6.86-6.89 (m, 1 H), 7.00-7.07 (m, 1 H), 7.08-7.14 (m, 1 H), 7.23-7.27 (m, 1 H), 7.48-7.53 (m, 1 H), 7.94 (brs, 1 H); $^{13}$C NMR ($CDCl_3$) δ 19.3, 30.0, 44.1, 111.1, 115.1, 118.6, 119.2, 121.4, 122.0, 127.1, 136.3, 208.8.

**3-(3'-Indolyl)-1,3-diphenyl-1-propanone (7b):**[19] $^1$H NMR ($CDCl_3$) δ 3.71 (dd, $J$ = 7.5, 16.7 Hz, 1 H), 3.81 (dd, $J$ = 7.5, 16.7 Hz, 1 H), 5.06 (t, $J$ = 7.1 Hz, 1 H), 6.94-7.02 (m, 2 H), 7.10-7.17 (m, 2 H), 7.21-7.44 (m, 8 H), 7.49-7.55 (m, 1 H), 7.90-7.94 (m, 2 H), 7.98 (brs, 1 H); $^{13}$C NMR ($CDCl_3$) δ 38.2, 45.2,

111.1, 119.2, 119.4, 119.5, 121.4, 122.1, 126.3, 126.6, 127.8, 128.1, 128.4, 128.6, 133.0, 136.6, 137.1, 144.2, 198.6.

**4-{3'-(1'-Methylindolyl)}-2-butanone (7c):**[19] $^1$H NMR ($CDCl_3$) δ 2.13-2.17 (m, 3 H), 2.80-2.87 (m, 2 H), 3.01-3.08 (m, 2 H), 3.71-3.75 (m, 3 H), 6.82-6.86 (m, 1 H), 7.08-7.15 (m, 1 H), 7.20-7.32 (m, 2 H), 7.55-7.61 (m, 1 H); $^{13}$C NMR ($CDCl_3$) δ 19.2, 30.0, 32.5, 44.3, 109.2, 113.6, 118.65, 118.68, 121.5, 126.3, 127.5, 136.9, 208.7.

**2-(3'-Indolyl)-2-phenyl-1-nitroethane (7d):**[19] $^1$H NMR ($CDCl_3$) δ 4.92 (dd, *J* = 8.3, 12.3 Hz, 1 H), 5.04 (dd, *J* = 7.5, 12.3 Hz, 1 H), 5.17 (dd, *J* = 7.5, 8.4 Hz, 1 H), 6.96-7.00 (m, 1 H), 7.06 (ddd, *J* = 1.0, 7.1, 8.0 Hz, 1 H), 7.18 (ddd, *J* = 1.0, 7.1, 8.2 Hz, 1 H), 7.21-7.35 (m, 7 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 8.04 (brs, 1 H); $^{13}$C NMR ($CDCl_3$) δ 41.5, 79.5, 111.3, 114.3, 118.9, 119.9, 121.6, 122.6, 126.0, 127.5, 127.7, 128.9, 136.4, 139.1.

**1'-Hydroxy-2'-acetonaphthone (8a):**[20] $^1$H NMR ($CDCl_3$) δ 2.69 (s, 3 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 7.53 (ddd, *J* = 1.3, 7.0, 8.3 Hz, 1 H), 7.58-7.66 (m, 1 H), 7.63 (d, *J* = 8.3 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 8.46 (d, *J* = 8.3 Hz, 1 H), 14.02 (s, 1 H); $^{13}$C NMR ($CDCl_3$) δ 26.9, 113.2, 118.3, 124.4, 124.9, 125.2, 125.9, 127.4, 130.0, 137.3, 162.5, 204.3.

**2'-Methoxy-1'-acetonaphthone (8b):**[21] $^1$H NMR ($CDCl_3$) δ 7.89 (d, *J* = 9.2 Hz, 1 H), 7.80 (d, *J* = 8.1 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.48 (ddd, *J* = 1.5, 6.9, 8.1 Hz, 1 H), 7.37 (ddd, *J* = 1.2, 6.9, 8.1 Hz, 1 H), 7.29 (d, *J* = 9.2 Hz, 1 H), 3.98 (s, 3 H), 2.65 (s, 3 H); $^{13}$C NMR ($CDCl_3$) δ 32.7, 56.4, 112.8, 123.6, 124.1, 125.1, 127.7, 128.1, 128.8, 130.3, 131.4, 153.9, 205.2.

**2,4-Dimethylbenzophenone (8c):**[22] $^1$H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 2.39 (s, 3 H), 7.05 (d, *J* = 7.8 Hz, 1 H), 7.11 (s, 1 H), 7.24 (d, *J* = 7.8 Hz, 1 H), 7.41-7.47 (m, 2 H), 7.54-7.60 (m, 1 H), 7.77-7.81 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 20.1, 21.4, 125.7, 128.3, 129.2, 130.1, 131.9, 132.8, 135.6, 137.3, 138.2, 140.6, 198.5.

**1-Phenylsulfonylacetylpyrrole (8d):**[23] $^1$H NMR ($CDCl_3$) 2- isomer: δ 2.35 (s, 3 H), 6.36 (dd, *J* = 3.2, 3.4 Hz, 1 H), 7.06 (dd, *J* = 1.7, 3.4 Hz, 1 H), 7.48-7.56 (m, 2 H), 7.57-7.64 (m, 1 H), 7.83 (dd, *J* = 1.7, 3.2 Hz, 1 H), 7.96-8.00 (m, 1 H), 8.00-8.03 (m, 1 H). 3- isomer: δ 2.41 (s, 3 H), 6.69 (dd, *J* = 1.7, 3.3 Hz, 1 H), 7.16 (dd, *J* = 2.2, 3.3 Hz, 1 H), 7.64-7.70 (m, 1 H), 7.52-7.60 (m, 2 H), 7.75 (dd, *J* = 1.7, 2.2 Hz, 1 H), 7.90-7.93 (m, 1 H), 7.93-7.96 (m, 1 H); $^{13}$C NMR ($CDCl_3$) 2- isomer: δ 26.9, 110.4, 124.4, 128.1,

128.6, 130.4, 133.3, 133.6, 138.9, 185.7. 3- isomer: δ 27.2, 112.4, 121.6, 124.5, 127.1, 129.4, 129.7, 134.6, 138.0, 192.8.

**2',4',6'-Trimethylacetophenone (8e):**[24] $^{1}$H NMR ($CDCl_3$) δ 2.21 (s, 6 H), 2.27 (s, 3 H), 2.45 (s, 3 H), 6.83 (s, 2 H); $^{13}$C NMR ($CDCl_3$) δ 19.1, 21.0, 128.4, 132.3, 138.3, 139.8, 208.6.

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