Supporting Information

For

Catalytic Intermolecular Carbon Electrophile Induced Semipinacol Rearrangement

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General information

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum was 60-90 °C. All other solvent were purified according to standard conditions. 1H and 13C NMR spectra were recorded in CDCl3 or CD3COCD3 solution on Bruker AX-400 MHz instruments and spectral data were reported in ppm with tetramethylsilane (TMS) as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI technique. Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis employing a Darcel Chiracel AD column and optical rotation was detected on RUDOLPH A21202-J APTV/GW.

General procedure of the catalytic intermolecular carbon electrophile induced semipinacol rearrangement (Table 2):

To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added substrate (0.2 mmol), ethylglyoxalate (0.4 mmol.), 5Å molecular sieve (200 mg), THF (2 mL, acetone for the preparation of 3d) and Cu(OTf)2 (10 mol%) at room temperature (-10 °C for 3d) (For synthesis of 3b, the substrate 1b was dissolved in half of the solvent and was added in 1 h with syringe pump). The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification.

The reaction system above containing 3b was filtered and washed with additional THF (3 mL), HF (40% aq., 0.5 mL) was added and the mixture was stirred for 1h and quenched with K2CO3. The mixture was filtered with a short pad of Celite, concentrated and subjected to column chromatography on silica gel to afford 3a (2 steps, 79% yield).
General procedure of the three component reaction (Table 3):

For 3g-3i (entries 1-3):
To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added ethyl glyoxalate (2.0 mmol) 5Å molecular sieve (1 g), aniline derivatives (1.0 mmol), Cu(OTf)2 (2 mol%) and acetone (5 mL). 1b (1.0 mmol in 5 mL acetone) was then added to the system using syringe pump in 1 h at room temperature. The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification. (PE:DCM:EA = 25:75:1)

For 3j (entry 4):
To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added substrate 1b (0.2 mmol), ethyl glyoxalate (0.4 mmol), 5Å molecular sieve (200 mg), aniline derivative 4b (0.2 mmol), THF (2 mL) and Cu(OTf)2 (15 mol%) at room temperature. The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification.

Catalytic asymmetric enantioselective version of the reaction (Scheme 3 in the manuscript):

To an oven dried Schlenk tube charged with a magnetic stirring bar was sequentially added 1g (0.2 mmol), ethyl glyoxalate 2 (0.4 mmol), 5Å molecular sieve (100 mg/mL solvent), THF (2 mL) and (S, S)-BuBOX (15 mol%), finally Cu(OTf)2 (15 mol%) was added. The reaction was monitored by TLC until all the substrate disappeared and the mixture was directly subjected to column chromatography on silica gel for purification (PE:DCM:EA = 5:5:1, then PE:EA = 2:1). 3ea: (60.0 mg, 76%, dr 11:1), 3eß: (15.8 mg, 20%).
Preparation of substrates and spectroscopic data of key compounds:

Preparation of substrates:

The tertiary alcohol substrates were dissolved in DCM followed by addition of imidazole. After being cooled to 0 °C TBSCI was added in one portion. After fully conversion of the substrates, the reaction was quenched with saturated NaHCO₃ (aq.) and extracted with DCM, the combined organic layer was dried with Na₂SO₄, filtered, concentrated under reduced pressure and purified by column chromatography on silica gel.

The tertiary alcohol substrate was dissolved in DCM followed by addition of Et₃N. After being cooled to 0 °C TMSCI was added in one portion. After fully conversion of the substrates, the reaction was quenched with saturated NaHCO₃ (aq.) and extracted with DCM, the combined organic layer was dried with Na₂SO₄, filtered, concentrated under reduced pressure and purified by column chromatography on silica gel.

Spectroscopic data of key compounds:

![Colorless oil.](image)

1H NMR (400 MHz, CDCl₃, ppm): δ 4.89 (t, J = 4.0 Hz, 1H), 4.02 (t, J = 5.2 Hz, 2H), 2.33 (tt, J₁ = 2.8 Hz , J₂ = 9.2 Hz, 2H), 2.14-2.02 (m, 4H), 1.81 (quint, J = 5.6 Hz, 2H), 1.75-1.60 (m, 1H), 1.51 (sext, J = 9.6 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H); 13C NMR (100 MHz, CDCl₃, ppm): δ 155.7, 94.9, 76.4, 66.0, 35.5, 25.9, 22.2, 20.2, 18.0, 13.2, 3.3; HRMS (ESI) calcd for C₁₅H₂₉O₂Si [M+H]+: 269.1931, found 269.1934.
Colorless oil.

$^1$H NMR (400 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 4.91 (t, $J = 4.0$ Hz, 1H), 4.00 (t, $J = 5.2$ Hz, 2H), 2.38-2.27 (m, 2H), 2.11-2.00 (m, 5H), 1.82-1.74 (m, 2H), 1.73-1.61 (m, 1H), 0.07 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 156.7, 95.8, 77.4, 66.7, 36.3, 23.0, 20.9, 13.9, 1.9; HRMS (ESI) calcd for C$_9$H$_{15}$O$_2$ $[M$-TMS$+H]^+$: 155.1067, found 155.1070.

Colorless oil.

$^1$H NMR (400 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 4.97 (t, $J = 2.0$ Hz, 1H), 4.34 (t, $J = 9.2$ Hz, 2H), 2.64 (dt, $J_1 = 2.4$ Hz , $J_2 = 9.2$ Hz, 2H), 2.32 (tt, $J_1 = 2.8$ Hz , $J_2 = 8.8$ Hz, 2H), 2.13 (dq, $J_1 = 2.8$ Hz , $J_2 = 9.6$ Hz, 2H), 1.69 (tq, $J_1 = 2.8$ Hz , $J_2 = 9.6$ Hz, 1H), 1.55 (sext, $J = 9.2$ Hz, 1H), 0.88 (s, 9H), 0.06 (s, 6H); $^{13}$C NMR (100 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 161.9, 95.8, 73.7, 70.7, 37.0, 30.6, 26.3, 18.6, 13.8, -3.1; HRMS (ESI) calcd for C$_{14}$H$_{27}$O$_2$Si $[M$+H$]^+$: 255.1775, found 255.1773.

Colorless oil.

$^1$H NMR (400 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 4.84 (t, $J = 2.4$ Hz, 1H), 4.31 (t, $J = 9.2$ Hz, 2H), 2.61 (dt, $J_1 = 2.4$ Hz , $J_2 = 9.6$ Hz, 2H), 1.88-1.72 (m, 6H), 1.70-1.56 (m, 2H), 0.87 (s, 9H), 0.08 (s, 6H); $^{13}$C NMR (100 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 162.5, 95.1, 81.6, 70.3, 39.9, 30.6, 26.3, 23.9, 18.9, -3.0; HRMS (ESI) calcd for C$_{15}$H$_{29}$O$_2$Si $[M$+H$]^+$: 269.1931, found 269.1937.

Colorless crystal, MP 65-67 °C.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 4.85 (brs, 1H), 4.44 (d, $J = 8.8$ Hz, 1H), 4.33-4.20 (m, 1H), 4.20-4.05 (m, 1H), 3.32-3.81 (m, 1H), 3.48 (dt, $J_1 = 3.6$ Hz , $J_2 = 7.2$ Hz, 1H), 2.32-2.23 (m, 1H), 2.13-2.02 (m, 2H), 2.02-1.92 (m, 1H), 1.89-1.75 (m, 2H), 1.75-1.65 (m, 1H), 1.63-1.53 (m, 1H), 1.48-1.30 (m, 3H), 2.02-1.92 (t, $J = 6.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 174.2, 116.3, 84.4, 79.1, 63.1, 61.6, 43.8, 37.2, 34.9, 20.6, 20.3, 19.0, 14.0; HRMS (ESI) calcd for C$_{13}$H$_{24}$NO$_5$ $[M$+NH$_4$$]^+$: 274.1649, found 274.1653.

Colorless oil.

$^1$H NMR (400 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 4.50 (d, $J = 5.6$ Hz, 1H), 4.40-4.28 (m, 1H),
4.20 (q, J = 7.2 Hz, 2H), 3.68-3.55 (m, 1H), 2.25-2.12 (m, 1H), 2.01-1.82 (m, 4H), 1.81-1.70 (m, 1H), 1.68-1.57 (m, 1H), 1.57-1.33 (m, 4H), 1.26 (t, J = 7.2 Hz, 1H), 0.93 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H); 13C NMR (100 MHz, CD3COCD3, ppm): δ 170.6, 115.4, 85.6, 79.1, 64.3, 61.1, 44.4, 41.3, 39.8, 26.5, 24.5, 22.0, 21.6, 18.6, 14.8, -2.6, -2.8; HRMS (ESI) calcd for C19H34NaO5Si [M+Na]+: 393.2068, found 393.2072.

Colorless oil, inseparable mixture (dr = 5:1), for major isomer:

1H NMR (400 MHz, CDCl3, ppm): δ 4.55 (d, J = 6.0 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 4.06 (q, J = 8.0 Hz, 1H), 3.93 (q, J = 8.0 Hz, 1H), 2.78 (dt, J1 = 6.4 Hz, J2 = 9.2 Hz, 1H), 2.10-1.94 (m, 5H), 1.80-1.58 (m, 2H), 1.49-1.32 (m, 1H), 1.28 (t, J = 7.2 Hz, 1H), 0.91 (s, 9H), 0.23 (s, 3H), 0.17 (s, 3H); 13C NMR (100 MHz, CDCl3, ppm): δ 170.4, 113.4, 76.9, 69.2, 60.8, 50.6, 39.3, 35.3, 28.9, 25.7, 21.1, 17.8, 14.2, -3.3; HRMS (ESI) calcd for C18H32NaO5Si [M+Na]+: 379.1911, found 379.1915.

Colorless oil.

1H NMR (400 MHz, CDCl3, ppm): δ 4.29 (d, J = 7.2 Hz, 1H), 4.28-4.22 (m, 2H), 3.97 (dt, J1 = 4.0 Hz, J2 = 8.0 Hz, 1H), 2.97 (burs, 1H), 2.80-2.70 (m, 1H), 2.53-2.42 (m, 1H), 2.33-2.25 (m, 1H), 2.21-2.12 (m, 1H), 2.12-1.88 (m, 5H), 1.32 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3, ppm): δ 215.8, 174.2, 87.2, 69.9, 66.6, 62.3, 42.6, 34.9, 32.2, 26.5, 18.8, 14.1; HRMS (ESI) calcd for C12H18NaO5 [M+Na]+: 265.1046, found 265.1041.

Colorless crystal, MP 76-78.

1H NMR (400 MHz, CDCl3) δ 4.65 (s, 1H), 4.35-4.22 (m, 3H), 3.98 (dd, J1 = 7.2 Hz, J2 = 15.2 Hz, 1H), 3.83 (dt, J1 = 5.6 Hz, J2 = 8.0 Hz, 1H), 3.61 (d, J = 3.2 Hz, 1H), 3.01-2.87 (m, 1H), 2.22-2.18 (m, 1H), 2.06-1.94 (m, 2H), 1.85-1.58 (m, 8H), 1.30 (t, J = 7.1 Hz, 3H), 0.88 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); 13C NMR (100 MHz, CDCl3, ppm): δ 173.2, 108.7, 89.5, 70.2, 66.2, 61.8, 44.3, 36.1, 36.0, 26.0, 24.9, 24.7, 24.7, 18.4, 14.1, -2.7, -2.7; HRMS (ESI) calcd for C19H36NaO6Si [M+Na]+: 411.2173, found 411.2179.

**1H NMR** (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 5.24 (s, 1H), 4.64 (d, J = 8.4 Hz, 1H), 4.20 (dq, J₁ = 3.8, J₂ = 10.8 Hz, 2H), 3.38-3.30 (m, 2H), 2.91 (dt, J₁ = 8.0 Hz, J₂ = 12.4 Hz, 1H), 2.41 (s, 3H), 2.15 – 2.06 (m, 1H), 1.97 – 1.79 (m, 4H), 1.79 – 1.66 (m, 1H), 1.55 – 1.40 (m, 1H), 1.25 (t, J = 7.2 Hz, 3H); **13C NMR** (101 MHz, CDCl₃) δ 174.1, 143.6, 140.2, 130.3, 128.2, 116.2, 83.6, 78.5, 62.3, 57.9, 50.6, 38.1, 36.9, 25.0, 21.4, 21.4, 14.5; **HRMS** (ESI) calcd for C₁₉H₂₅NNaO₆S [M+Na⁺]: 418.1295, found 418.1263.

**HPLC** Enantiomeric excess is 91.5% determined by HPLC (Chiralcel AD, Hexane/Isopropanol 60/40, flow rate=1.0 mL/min, 240 nm): major isomer: tᵥ = 16.9 min; minor isomer: [α]₂⁵² -26º (c 1.0, CHCl₃).

Colorless crystal MP 148-149 ºC.

**1H NMR** (400 MHz, CDCl₃) δ 7.74 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.38 (d, J = 10.0 Hz, 1H), 4.22 (q, J = 7.2, 2H), 3.71 (brs, 1H), 3.68-3.52 (m, 2H), 2.67 (dd, J₁ = 7.6 Hz, J₂ = 9.6 Hz, 1H), 2.91 (dt, J₁ = 7.2 Hz, J₂ = 12.8 Hz, 1H), 2.43 (s, 3H), 2.21 (dd, J₁ = 6.0 Hz, J₂ = 12.8 Hz, 1H), 1.99 – 1.82 (m, 3H), 1.79 – 1.63 (m, 2H), 1.63 – 1.48 (m, 1H), 1.34 (t, J = 7.2 Hz, 3H); **13C NMR** (100 MHz, CDCl₃) δ 170.1, 143.3, 138.7, 129.7, 126.7, 113.7, 83.3, 77.3, 61.3, 58.9, 49.1, 37.6, 35.5, 35.0, 21.4, 20.6, 14.1; **HRMS** (ESI) calcd for C₁₉H₂₅NO₆S [M+NH₄⁺]: 395.1403, found 395.1697.

**HPLC** Enantiomeric excess is 82% determined by HPLC (Chiralcel AD, Hexane/Isopropanol 60/40, flow rate=1.0 mL/min, 246 nm): major isomer: tᵥ = 15.2 min; minor isomer: [α]₂⁵² +53º (c 1.0, CHCl₃).

Colorless amorphous solid.

**1H NMR** (400 MHz, CDCl₃, ppm) δ 7.75 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 5.06 (s, 1H), 4.50 (d, J = 9.2 Hz, 1H), 3.40-3.35 (m, 2H), 3.05-2.87 (m, 2H), 2.40 (s, 3H), 2.16 (dt, J₁ = 6.8 Hz, J₂ = 12.8 Hz, 1H), 2.09 – 2.03 (m, 1H), 1.95-1.83 (m, 2H), 1.77 (dt, J₁ = 6.8 Hz, J₂ = 13.2 Hz, 2H), 1.44 (s, 9H); **13C NMR** (100 MHz, CDCl₃, ppm) δ 173.0, 142.8, 138.1, 129.3, 127.3, 116.0, 83.6, 83.3, 78.9, 57.7, 49.3, 37.2, 36.9, 27.9, 23.9, 21.4, 20.4; **HRMS** (ESI) calcd for C₂₁H₃₃N₂O₆S [M+NH₄⁺]: 441.2054, found 441.2050.

Colorless amorphous solid.

**1H NMR** (400 MHz, CDCl₃, ppm) δ 7.75 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.27 (d, J = 10.4 Hz, 1H), 3.70 -3.52 (m, 2H), 2.67-2.58 (m, 1H), 2.58-2.50 (m, 1H), 2.44
(s, 3H), 2.22 (dd, \(J_1 = 5.6\) Hz, \(J_2 = 12.4\) Hz, 1H), 1.97-1.86 (m, 2H), 1.78-1.63 (m, 2H), 1.63-1.52 (m, 2H), 1.48 (s, 9H). \(\text{HRMS (ESI) caled for C}_{21}\text{H}_{35}\text{N}_{2}\text{O}_{6}\text{S} [\text{M+NH}_4]^+: \) 441.2054, found 441.2050. (together with 3f)

\[
\begin{align*}
\text{3g} & \alpha
\end{align*}
\]

Yellowish oil.

\(^1\text{H NMR}\) (400 MHz, CD\(_3\)COCD\(_3\), ppm): \(\delta\) 7.63 (d, \(J = 2.4\) Hz, 1H), 7.54 (dd, \(J_1 = 1.2\) Hz, \(J_2 = 8.8\) Hz, 1H), 7.41 (t, \(J = 8.0\) Hz, 1H), 7.11 (dd, \(J_1 = 2.4\) Hz, \(J_2 = 8.4\) Hz, 1H), 4.66 (d, \(J = 10.0\) Hz, 1H), 4.13 (q, \(J = 7.2\) Hz, 2H), 3.94 (dd, \(J_1 = 3.2\) Hz, \(J_2 = 10.0\) Hz, 1H), 3.53 (t, \(J = 4.0\) Hz, 1H), 2.52-2.38 (m, 2H), 2.27 (d, \(J = 9.6\) Hz, 1H), 2.23-2.12 (m, 1H), 2.10-1.98 (m, 1H), 1.96-1.92 (m, 3H), 1.92-1.70 (m, 2H), 1.61-1.49 (m, 1H), 1.14 (t, \(J = 7.2\) Hz, 3H), 0.70 (s, 9H), 0.09 (s, 3H), -0.18 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CD\(_3\)COCD\(_3\), ppm): \(\delta\) 171.3, 149.6, 146.7, 130.1, 122.4, 113.5, 111.4, 104.4, 88.0, 64.6, 63.1, 61.5, 41.5, 38.5, 36.2, 26.8, 22.8, 21.5, 20.9, 19.8, 14.7, -1.0, -1.8; \(\text{HRMS (ESI) caled for C}_{25}\text{H}_{39}\text{N}_{2}\text{O}_{6}\text{Si} [\text{M+H}]^+: \) 491.2572, found 491.2568.

\[
\begin{align*}
\text{3g} & \beta
\end{align*}
\]

Yellowish crystal, \(\text{MP}\) 110-111 °C.

\(^1\text{H NMR}\) (400 MHz, CD\(_3\)COCD\(_3\), ppm): \(\delta\) 7.85 (t, \(J = 2.4\) Hz, 1H), 7.60 (dd, \(J_1 = 1.6\) Hz, \(J_2 = 8.0\) Hz, 1H), 7.43 (t, \(J = 8.4\) Hz, 1H), 7.18 (dd, \(J_1 = 2.0\) Hz, \(J_2 = 8.0\) Hz, 1H), 4.53 (d, \(J = 8.4\) Hz, 1H), 4.16 (q, \(J = 7.2\) Hz, 2H), 4.04-3.96 (m, 1H), 3.68-3.59 (m, 1H), 2.60-2.48 (m, 1H), 2.43-2.33 (m, 1H), 2.25-2.02 (m, 3H), 1.95-1.83 (m, 1H), 1.80-1.67 (m, 2H), 1.67-1.55 (m, 1H), 1.55-1.41 (m, 1H), 1.32-1.23 (m, 1H), 1.20 (t, \(J = 7.2\) Hz, 3H), 0.95 (s, 9H), 0.34 (s, 3H), 0.22 (s, 3H); \(^{13}\text{C NMR}\) (100 MHz, CD\(_3\)COCD\(_3\), ppm): \(\delta\) 173.5, 149.7, 146.2, 130.3, 122.8, 112.8, 111.3, 105.1, 88.9, 65.0, 63.6, 61.8, 43.6, 40.5, 29.8, 27.0, 22.2, 21.3, 20.1, 19.8, 14.6, -1.3, -2.4; \(\text{HRMS (ESI) caled for C}_{19}\text{H}_{23}\text{N}_{2}\text{O}_{5} [\text{M-OTBS}]^+: \) 359.1601, found 359.1597.

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\begin{align*}
\text{3h} & \alpha
\end{align*}
\]
Yellowish oil.

$^1$H NMR (400 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 7.57 (d, $J = 8.8$ Hz, 1H), 7.27 (d, $J = 2.8$ Hz, 1H), 6.90 (dd, $J_1 = 2.8$ Hz, $J_2 = 9.2$ Hz, 1H), 4.63 (d, $J = 10.0$ Hz, 1H), 4.15 (q, $J = 7.2$ Hz, 2H), 3.97-3.90 (m, 1H), 2.46-2.32 (m, 2H), 2.26 (dt, $J_1 = 4.0$ Hz, $J_2 = 10.0$ Hz, 1H), 2.18-2.10 (m, 1H), 2.04-1.97 (m, 1H), 1.97-1.87 (m, 3H), 1.87-1.78 (m, 1H), 1.78-1.69 (m, 1H), 1.58-1.49 (m, 1H), 0.74 (s, 9H), 0.10 (s, 3H), -0.14 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 173.2, 151.0, 145.4, 135.2, 121.6, 113.4, 105.1, 100.1, 88.8, 64.8, 63.6, 62.0, 43.5, 40.1, 29.7, 27.1, 22.1, 21.2, 20.1, 19.9, 14.6, -1.3, -2.4; HRMS (ESI) calcd for C$_{25}$H$_{38}$BrN$_2$O$_6$Si [M+H]$^+$: 569.1677, found 569.1670.

![3hβ](image)

Yellowish crystal, MP 145-147 °C.

$^1$H NMR (400 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 7.59 (d, $J = 8.8$ Hz, 1H), 7.49 (d, $J = 3.2$ Hz, 1H), 6.95 (dd, $J_1 = 3.2$ Hz, $J_2 = 8.8$ Hz, 1H), 4.50 (d, $J = 8.8$ Hz, 1H), 4.24-4.10 (m, 2H), 4.00-3.90 (m, 1H), 3.65-3.55 (m, 1H), 2.60-2.50 (m, 1H), 2.42-2.32 (m, 1H), 2.21-2.00 (m, 3H), 1.92-1.70 (m, 3H), 1.63-1.44 (m, 2H), 1.40-1.25 (m, 1H), 1.21 (t, $J = 7.2$ Hz, 3H), 0.92 (s, 9H), 0.27 (s, 3H), 0.20 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 171.1, 151.0, 145.9, 135.1, 121.0, 113.1, 104.5, 100.6, 88.2, 64.5, 62.9, 61.6, 41.3, 38.2, 35.5, 26.8, 22.6, 21.6, 20.6, 19.7, 14.6, -1.1, -1.9; HRMS (ESI) calcd for C$_{25}$H$_{38}$BrN$_2$O$_6$Si [M+H]$^+$: 569.1677, found 569.1664.

![3iα](image)

Yellowish oil.

$^1$H NMR (400 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 7.48 (t, $J = 8.0$ Hz, 1H), 7.19 (s, 1H), 7.13 (dd, $J_1 = 3.2$ Hz, $J_2 = 8.0$ Hz, 2H), 4.77 (d, $J = 10.0$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 4.08 (dd, $J_1 = 3.6$ Hz, $J_2 = 6.4$ Hz, 1H), 3.69 (dd, $J_1 = 9.6$ Hz, $J_2 = 11.6$ Hz, 1H), 2.68-2.56 (m, 1H), 2.56-2.47 (m, 1H), 2.43-2.35 (m, 1H), 2.33-2.22 (m, 1H), 2.22-2.10 (m, 1H), 2.10-1.93 (m, 4H), 1.93-1.82 (m, 1H), 1.73-1.60 (m, 1H), 1.26 (t, $J = 7.2$ Hz, 3H), 0.84 (s, 9H), 0.21 (s, 3H), 0.03 (s, 3H); $^{13}$C NMR (100 MHz, CD$_3$COCD$_3$, ppm): $\delta$ 173.6, 145.6, 131.5 (q, $J_F = 31.0$ Hz), 130.1, 125.7 (d, $J_F = 270$ Hz), 120.6, 114.9 ($J_F = 3.8$ Hz), 113.5 ($J_F = 4.0$ Hz), 105.0, 88.8, 65.1, 63.5, 61.6, 43.6, 40.8, 30.0, 27.1, 22.3, 21.4, 20.2, 19.8, 14.5, -1.4, -2.3; HRMS (ESI) calcd for C$_{20}$H$_{25}$F$_3$NO$_4$ [M-TBS+H]$^+$: 400.1730, found 400.1758.
Yellowish crystal, **MP** 48-52 °C.

**1H NMR** (400 MHz, CD$_3$COCD$_3$, ppm): δ 7.37 (t, $J = 8.0$ Hz, 1H), 7.32 (s, 1H), 7.10-7.02 (m, 2H), 4.50 (d, $J = 8.4$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 4.07-3.97 (m, 1H), 3.68-3.58 (m, 1H), 2.55-2.45 (m, 1H), 2.41-2.30 (m, 1H), 2.18-2.00 (m, 3H), 1.95-1.84 (m, 1H), 1.75-1.57 (m, 3H), 1.57-1.43 (m, 1H), 1.28-1.15 (m, 1H), 1.18 (t, $J = 7.2$ Hz, 3H), 0.96 (s, 9H), 0.30 (s, 3H), 0.22 (s, 3H); **13C NMR** (100 MHz, CD$_3$COCD$_3$, ppm): δ 171.4, 146.2, 131.0 (q, $J_F = 31.0$ Hz), 130.0, 125.8 (d, $J_F = 270$ Hz), 120.1, 115.5 ($J_F = 2.9$ Hz), 113.8 ($J_F = 3.6$ Hz), 104.2, 87.9, 64.5, 63.1, 61.3, 41.6, 38.0, 36.6, 26.8, 23.0, 21.5, 21.0, 19.7, 14.6, -1.0, -1.8; **HRMS** (ESI) calcd for C$_{20}$H$_{23}$F$_3$NO$_3$ [M-OTBS]$^+$: 382.1625, found 382.1626.

Yellowish viscous oil.

**1H NMR** (400 MHz, CD$_3$COCD$_3$, ppm) δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 6.4$ Hz, 1H), 7.62 (s, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.27 (dd, $J_1 = 2.8$ Hz, $J_2 = 8.8$ Hz, 1H), 4.69 (d, $J = 8.4$ Hz, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.63 (dt, $J_1 = 4.0$ Hz, $J_2 = 8.8$ Hz, 1H), 3.39 (td, $J_1 = 6.8$ Hz, $J_2 = 8.8$ Hz, 1H), 3.11 (dd, $J_1 = 3.6$ Hz, $J_2 = 12.8$ Hz, 1H), 2.97 (dt, $J_1 = 8.0$ Hz, $J_2 = 12.8$ Hz, 1H), 2.82 (s, 1H), 2.43 (s, 3H), 2.36 (dd, $J_1 = 6.0$ Hz, $J_2 = 12.8$ Hz, 1H), 2.29-2.10 (m, 2H), 1.93-1.79 (m, 2H), 1.69-1.57 (m, 1H), 1.20 (t, $J = 7.2$ Hz, 3H); **13C NMR** (101 MHz, CD$_3$COCD$_3$, ppm) δ 171.3, 151.2, 146.2, 144.0, 140.0, 135.2, 130.5, 128.1, 123.0, 114.6, 102.3, 101.9, 83.6, 62.6, 62.2, 53.2, 50.6, 35.8, 35.2, 26.0, 21.5, 21.4, 21.4, 14.6; **HRMS** (ESI) calcd for C$_{23}$H$_{27}$BrN$_3$O$_6$S [M-OH]$^+$: 576.0798, found 576.0780.
ORTEM drawing of 3a

ORTEM drawing of 3hβ
zqw-55TBS

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$\text{EtO}_2\text{C}$

$\text{O}$

$\text{OH}$

$3e_\beta, X = \text{NTs}$
zqw−952−d

$^{1} \text{BuO}_2 \text{C}_- \text{O}_- \text{OH}

3f_{\beta}, X = \text{NTs}

ppm

Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Material (ESI) for Chemical Communications
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Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Signal 1: DAD1 C, Sig=246,16 Ref=360,100

Peak RetTime Type Width     Area      Height     Area
#   [min]        [min]   [mAU*s]     [mAU]        %
---|-------|----|-------|----------|----------|--------|
1  16.920 VV    0.5288 1.93985e4   542.99091  48.0985
2  17.888 VB    0.6812 2.09323e4   429.04163  51.9015

Totals :                  4.03309e4   972.03253

Results obtained with enhanced integrator!

Final Summed Peaks Report

Data File C:\HPCHEM\1\DATA\ZHANGQW\ZQW07212.D
Sample Name: zqw-N
AD hex:ip=60:40 1ml/min

Injection Date : 7/25/2002 1:00:54 AM
Sample Name : zqw-N   Location : Vial 1
Acq. Operator : zhangqw
Acq. Method : C:\HPCHEM\1\METHODS\ZHANGQW.M
Last changed : 7/25/2002 12:59:11 AM by zhangqw
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ZHANGQW.M
Last changed : 7/25/2002 2:05:55 AM by ZDY

Instrument 1 7/25/2002 2:02:55 AM zhangqw
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000

Signal 1: DAD1 D, Sig=240,16 Ref=360,100

<table>
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<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.208</td>
<td>VV</td>
<td>0.3608</td>
<td>1452.43188</td>
<td>62.11741</td>
<td>4.2630</td>
</tr>
<tr>
<td>2</td>
<td>15.886</td>
<td>VP</td>
<td>0.5634</td>
<td>3.26179e4</td>
<td>866.06079</td>
<td>95.7370</td>
</tr>
</tbody>
</table>

Totals: 3.40703e4 928.17820

Results obtained with enhanced integrator!

Final Summed Peaks Report

Signal 1: DAD1 D, Sig=240,16 Ref=360,100
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 D, Sig=246,16 Ref=360,100

Peak RetTime Type Width   Area     Height     Area   %
#   [min]     [min]    [mAU*s]   [mAU]    %
---|-------|----|-------|----------|----------|--------|
1  15.260 BV 0.6259 5231.52295 124.59288  48.5024
2  16.818 VB 0.5982 5554.58740 139.00560  51.4976

Totals : 1.07861e4 263.59848

Results obtained with enhanced integrator!

Summed Peaks Report

Signal 1: DAD1 D, Sig=246,16 Ref=360,100

Final Summed Peaks Report

Signal 1: DAD1 D, Sig=246,16 Ref=360,100
Data File C:\HPCHEM\DATA\ZHANGQW\ZQW07215.D 
AD hex:ipr=60:40 1ml/min

Injection Date : 7/25/2002 1:45:47 AM
Sample Name : zqw-N-chiral-d Location : Vial 1
Acq. Operator : zhangqw
Acq. Method : C:\HPCHEM\METHODS\ZHANGQW.M
Last changed : 7/25/2002 12:41:15 AM by ZDY
(modified after loading)
Analysis Method : C:\HPCHEM\METHODS\ZHANGQW.M
Last changed : 7/25/2002 1:48:54 AM by ZDY
(modified after loading)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 D, Sig=246,16 Ref=360,100

Peak RetTime Type  Width     Area      Height    Area %
#   [min]        [min]   [mAU*s]     [mAU]    %
----|-------|----|-------|----------|----------|--------|
1  14.842 VV    0.6101 2905.15674   74.64555  8.8810
2  15.933 VBA   0.6005 2.98069e4   742.27356  91.1190

Totals :                  3.27121e4   816.91911

Results obtained with enhanced integrator!

Summed Peaks Report

Signal 1: DAD1 D, Sig=246,16 Ref=360,100

Final Summed Peaks Report

Signal 1: DAD1 D, Sig=246,16 Ref=360,100