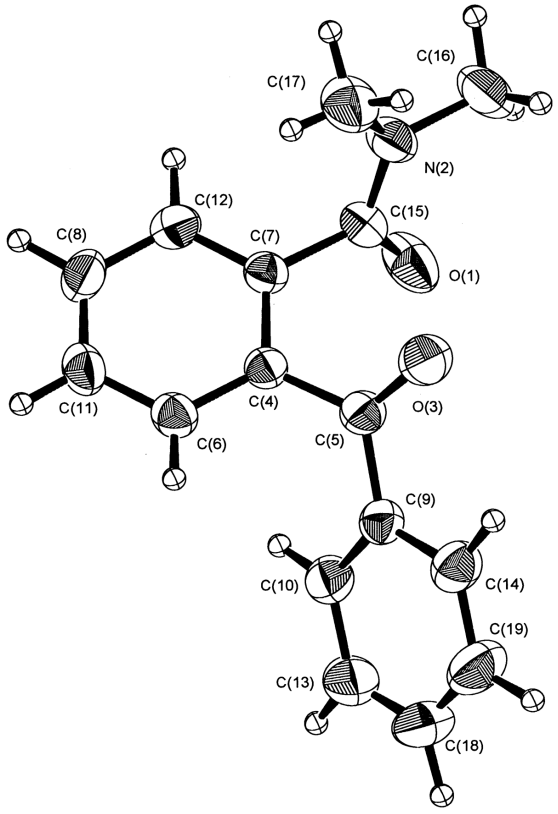
# Supporting Information

## Absolute Asymmetric Synthesis by Nucleophilic Carbonyl Addition using Chiral Crystals of Achiral Amides

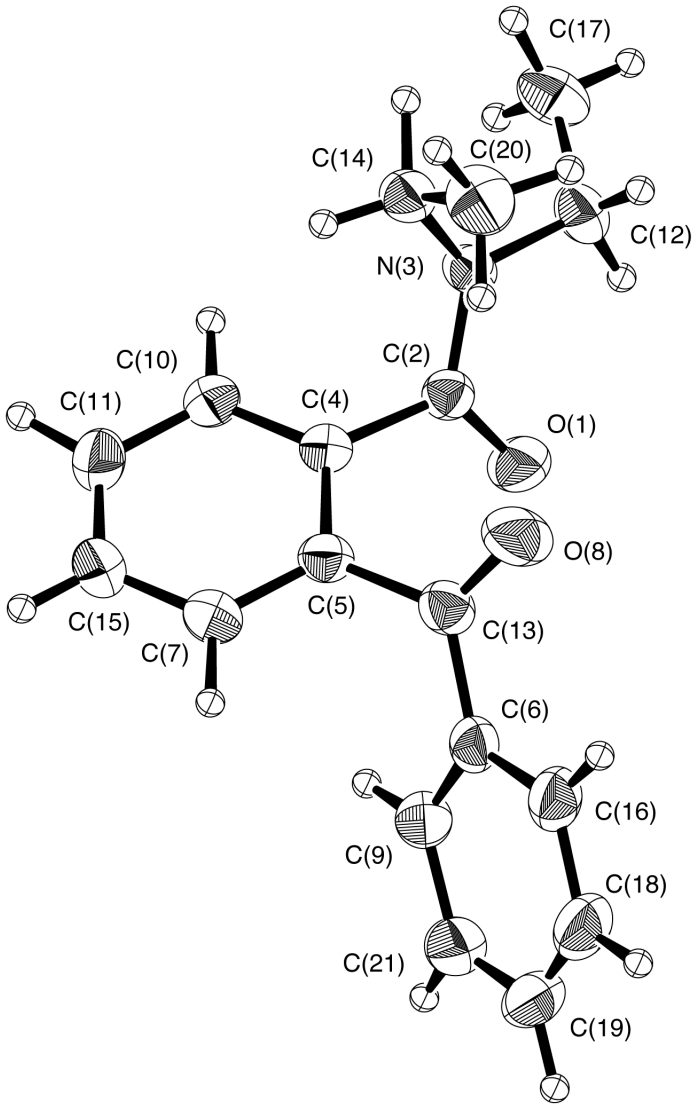
**Masami Sakamoto,* Shuichiro Kobaru, Takashi Mino, and Tsutomu Fujita**
*Department of Materials Technology, Faculty of Engineering, Chiba University,*
*Yayoi-cho, Chiba 263-8522, Japan. Fax: 81 43 290 3401; Tel:81 43 290 3387; E-mail: sakamotom@faculty.chiba-u.jp*

**Figure S1. X-Ray Crystallographic Data of *N, N*-Dimethyl-2-benzoylbenzamide 1a**



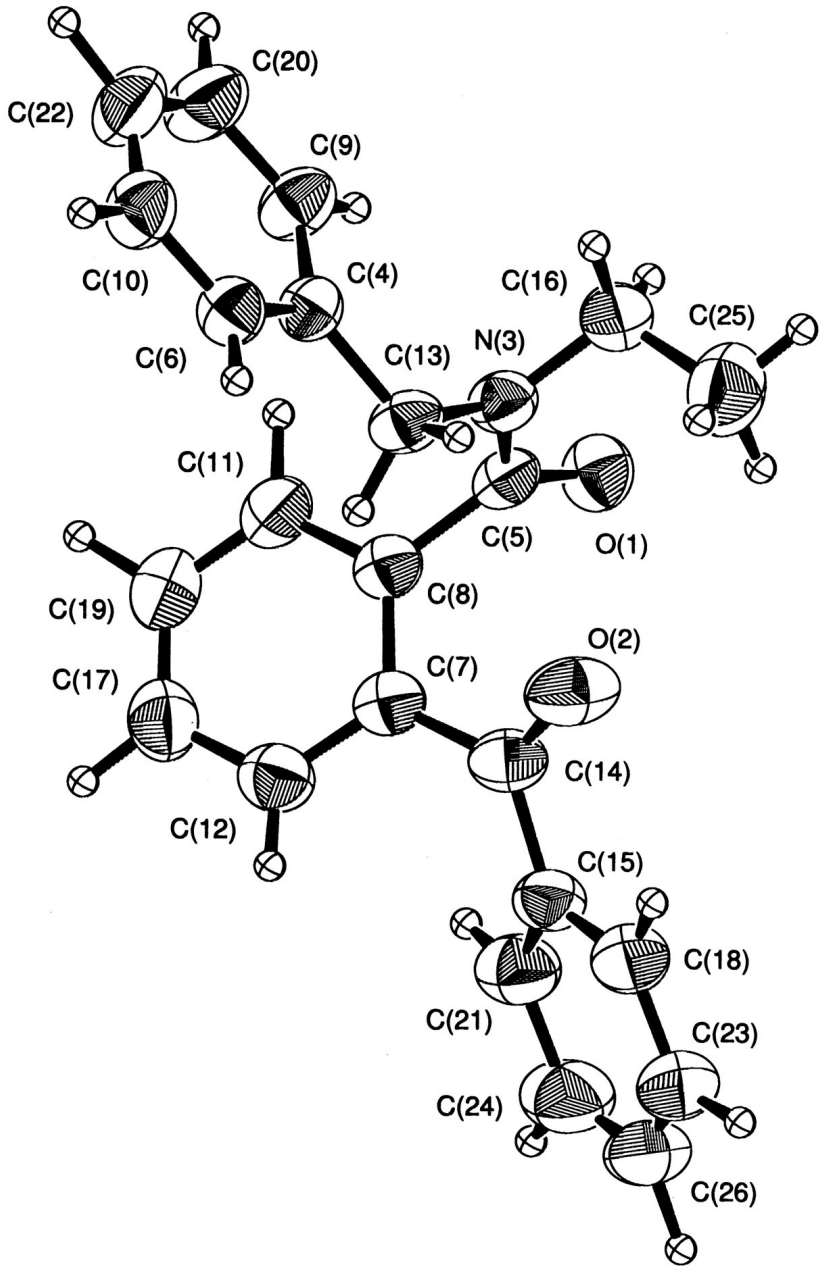

Crystal data of **1a**: $C_{16}H_{15}NO_2$, $M$ = 253.301, orthorhombic, $a$ = 10.420(2) Å, $b$ = 17.208(4) Å, $c$ = 7.519(2) Å, $U$ = 1348.3(6) Å$^3$ , $T$ = 293 K, space group $P2_12_12_1$ (no. 19), $Z$= 4, $\mu$ (Cu-K$\alpha$) = 0.66 mm$^{-1}$, 1511 reflections measured, 1326 unique ($Rint$ = 0.046) which were used in all calculations. The final $wR$ ($F^2$) was 0.151 (all data). The crystallographic data will be sent on quoting the CCDC number CCDC 215659 (e-mail: deposit@ccdc.cam.ac.uk).

**Figure S2. X-Ray Crystallographic Data of *N, N*-Diethyl-2-benzoylbenzamide 1b**



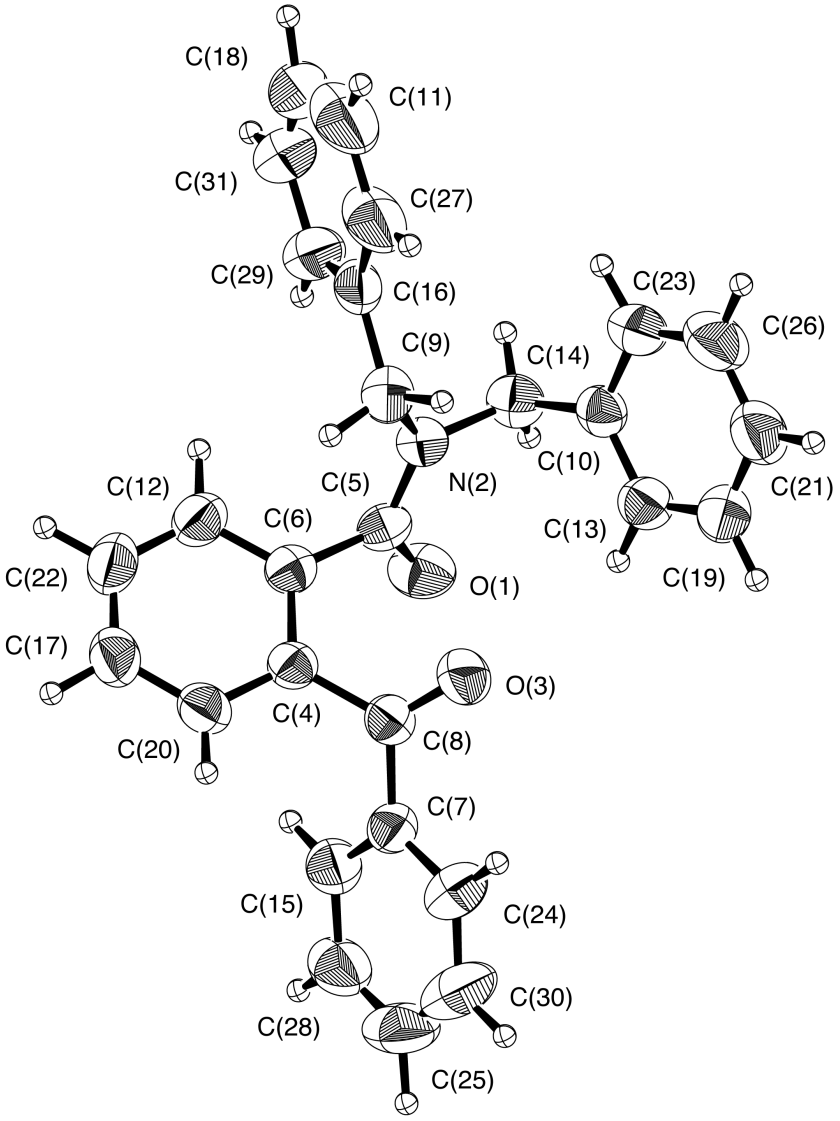

Crystal data of **1b**: $C_{18}H_{19}NO_2$, $M$ = 281.355, orthorhombic, $a$ = 10.937(5) Å, $b$ = 13.987(5) Å, $c$ = 9.896(4) Å, $U$ = 1513.8(10) Å$^3$ , $T$ = 293 K, space group $P2_12_12_1$ (no. 19), $Z$= 4, $\mu$ (Cu-K$\alpha$) = 0.64 mm$^{-1}$, 1655 reflections measured, 1616 unique (*Rint* = 0.059) which were used in all calculations. The final *wR* ($F^2$) was 0.346 (all data). The crystallographic data will be sent on quoting the CCDC numbers CCDC 215660.

**Figure S3. X-Ray Crystallographic Data of *N*-benzyl-*N*-ethyl-2-benzoylbenzamide 1c**




Crystal data of **1c**: $C_{23}H_{21}NO_2$, $M$ = 343.426, orthorhombic, $a$ = 14.384(4) Å, $b$ = 16.234(5) Å, $c$ = 8.049(4) Å, $U$ = 1879.6(12) Å$^3$ , $T$ = 293 K, space group $P2_12_12_1$ (no. 19), $Z$= 4, $\mu$ (Cu-K$\alpha$) = 0.61 mm$^{-1}$, 2086 reflections measured, 1810 unique (*Rint* = 0.037) which were used in all calculations. The final *wR* ($F^2$) was 0.094 (all data). The crystallographic data will be sent on quoting the CCDC numbers CCDC. 215661.

**Figure S4. X-Ray Crystallographic Data of *N,N*--dibenzyl-2-benzoylbenzamide 1d**



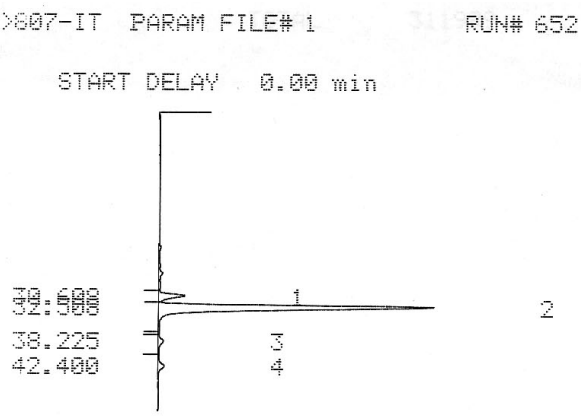

Crystal data of **1d**: $C_{28}H_{23}NO_2$, $M = 405.497$, orthorhombic, $a = 19.753(5)$ Å, $b = 22.214(7)$ Å, $c = 9.936(3)$ Å, $U = 1513.8(10)$ Å$^3$ , $T = 293$ K, space group $P2_12_12_1$ (no. 61), $Z = 8$, $\mu$ (Cu-K$\alpha$) = 0.61 mm$^{-1}$, 4437 reflections measured, 2926 unique (*Rint* = 0.050) which were used in all calculations. The final *wR* ($F^2$) was 0.217 (all data). The crystallographic data will be sent on quoting the CCDC numbers CCDC 215662.

**Determination of enantiomeric excesses.**

Chemical yields were isolated yields. Enantiomeric excesses were determined on the basis of HPLC analysis using chiralcel-OD column. The traces were shown below.

**Figure S5**. Traces of optically active **2b** (84% ee) obtained by the reaction of **1b** with *n*-butyllithium at –80°C. (a) Detector: UV-2075 (JASCO), wave-length: 254 nm; column: CHIRALCEL-OD (DAICEL); eluent: hexane: EtOH = 98 : 2; flow rate: 0.3 ml $min^{-1}$; column temp.: 32.5°C. (b) Detector: CD-2095 (JASCO)

(a)




**Compd. 2a**

-- % CALCULATION RESULT --

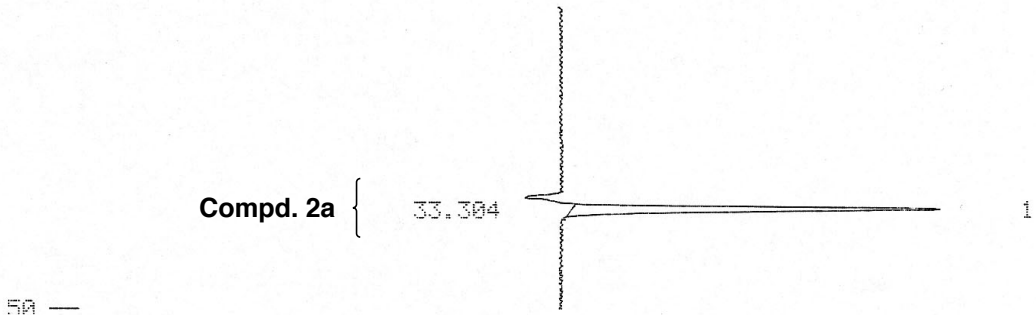
TEST-DATA

WINDOW = 0 % SCALE FACTOR = 1.0000 PEAK AREA

| PEAK# | RT(min) | AREA | HEIGHT | MK | AREA% |
|---|---|---|---|---|---|
| 1 | 30.608 | 306010 | 6376 | V | 7.5328 |
| 2 | 32.508 | 3588091 | 68728 | V | 88.3248 |
| 3 | 38.225 | 72626 | 1141 | V | 1.7878 |
| 4 | 42.400 | 95658 | 1408 | V | 2.3547 |
| | TOTAL | 4062384 | 77653 | | 100.0000 |

**Compd. 2a**

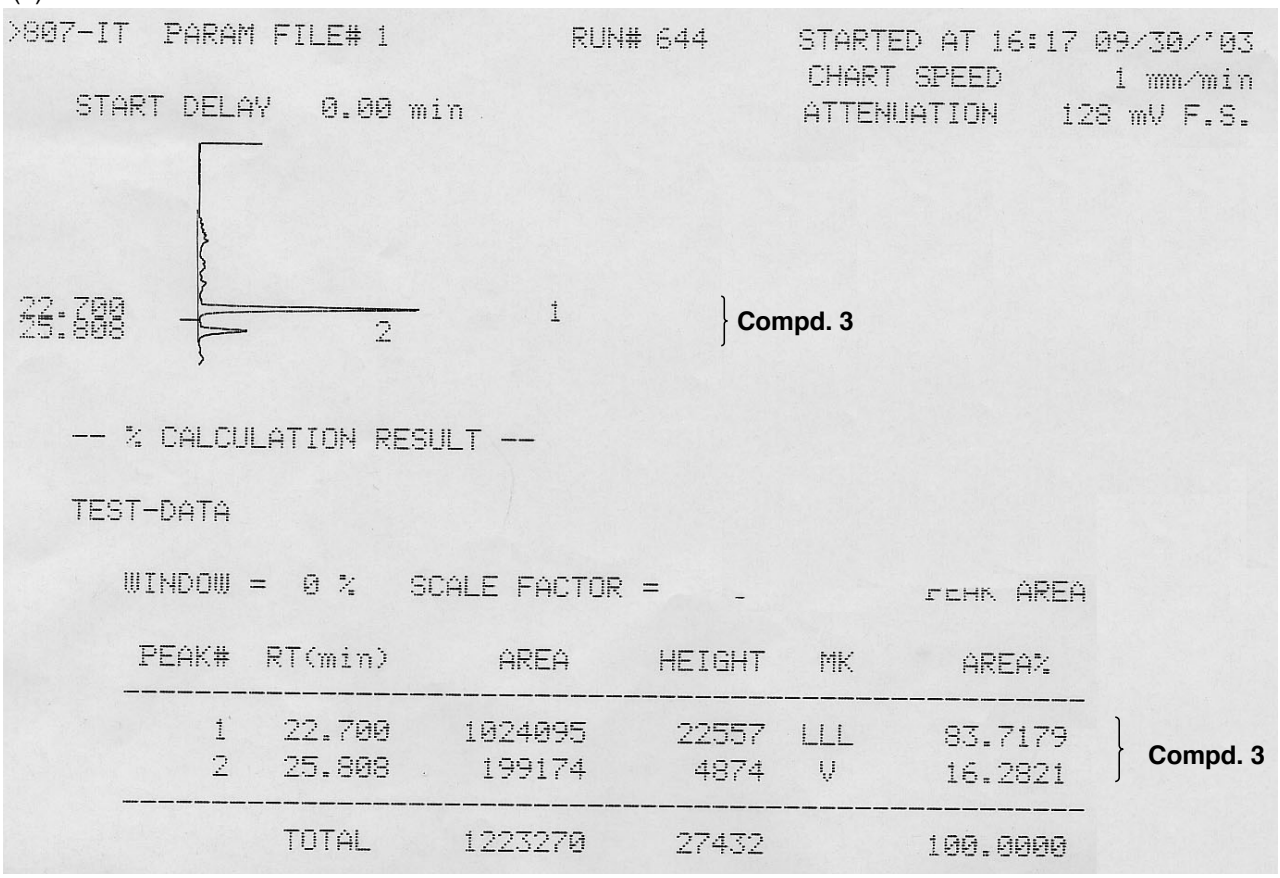
(b)




**Compd. 2a**

**Figure S6**. Traces of optically active **3** (67% ee) obtained by the reaction of **1c** with *n*-butyllithium at –60°C. (a) Detector: UV-2075 (JASCO), wave-length: 254 nm; column: CHIRALCEL-OD (DAICEL); eluent: hexane: EtOH = 98 : 2; flow rate: 0.3 ml min-1; column temp.: 30.0°C. (b) Detector: CD-2095 (JASCO)

(a)




(b)