

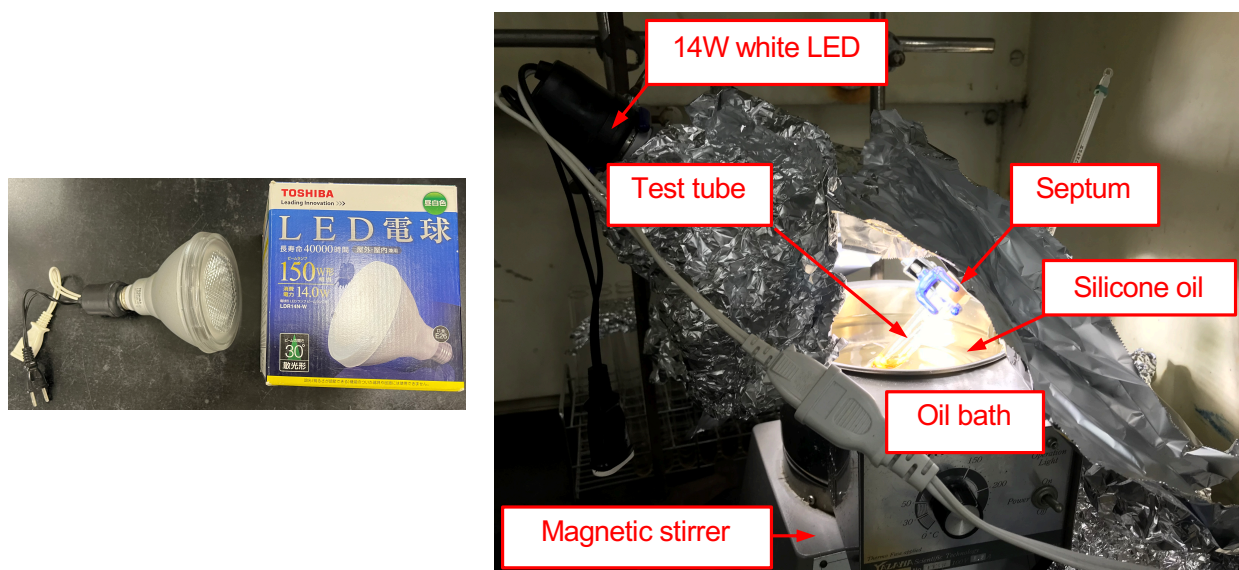
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## 1. General information

Proton NMR spectra were recorded on Agilent 400 MR (399.9 MHz) spectrometer. Chemical shifts were reported in parts per million downfield ( $\delta$ ) relative to internal tetramethylsilane (TMS,  $\delta$  0.00) or/with the solvent reference as the internal standard ( $\text{CDCl}_3$ ,  $\delta$  7.26). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet, app. t = apparent triplet), coupling constants (Hz), integration, and assignment. Carbon NMR spectra were recorded on Agilent 400 MR (100.6 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in parts per million downfield ( $\delta$ ) relative to the respective solvent reference as the internal standard ( $\text{CDCl}_3$ ,  $\delta$  77.0). Infrared (IR) spectra were recorded on a JASCO FT/IR-5300 IR spectrophotometer,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ . Mass spectra were taken with JEOL JMS-T100LP AccuTOF. Melting points were recorded on YANAKO MP-S3. Thin layer chromatography (TLC) was performed using glass TLC plates purchased from Merck (silica gel 60 F254, layer thickness: 250  $\mu\text{m}$ ), and using TLC plates purchased from Fuji Silysia Chemical, LTD (CHROMATOREX<sup>®</sup> NH-DM2035). Flash chromatography was performed using silica gel (PSQ-60B) and CHROMATOREX<sup>®</sup> NH-DM2035 purchased from Fuji Silysia Chemical, LTD. All reaction solvents were anhydrous and were purchased from FUJIFILM Wako Pure Chemical Corporation. All deuterated solvents for NMR spectroscopic measurements were purchased from KANTO CHEMICAL Co., Inc.  $\alpha,\beta$ -Unsaturated imides **1a**, **1b**, **1e–1i** were prepared using the previously reported procedure.<sup>1,2</sup>  $\alpha,\beta$ -Unsaturated amide **1c** and **1d** were prepared using the previously reported procedure.<sup>3</sup>

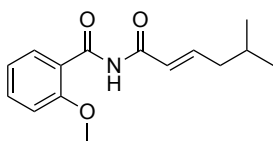
## 2. Photograph of photochemical reactor



**Figure S1.** Irradiation source: LED beam lamp (manufacture: TOSHIBA, model name: LDR14N-W, power consumption: 14 W).

### 3. Characterization of $\alpha,\beta$ -Unsaturated imides 1f, 1g, 1i, and 2-pyrrolidinones 4a–4e

Compound 1f



Pale yellow solid.

**M.p.** 68–69 °C.

**R<sub>f</sub>**: 0.12 (*n*-Hexane/AcOEt = 10/1 (v/v), TLC: silica gel 60).

**Purification**: Flash chromatography (stationary phase: spherical silica gel, PSQ-60B; eluent (isocratic elution): *n*-Hexane 100% → *n*-Hexane/AcOEt = 20/1 (v/v) → *n*-Hexane/AcOEt = 10/1 (v/v)).

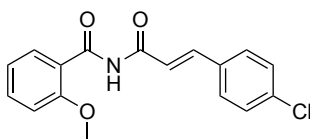
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  0.96 (d, *J* = 6.7 Hz, 6H), 1.82 (sept, *J* = 6.7, 1H), 2.20 (t, *J* = 6.6 Hz, 2H), 4.02 (s, 3H), 7.02 (d, *J* = 8.4 Hz, 1H), 7.05–7.27 (m, 3H), 7.48–7.60 (m, 1H), 8.17 (dd, *J* = 7.9, 1.9 Hz, 1H), 9.86–10.5 (br, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  2.4, 27.9, 41.8, 56.2, 111.7, 120.5, 121.6, 124.7, 132.8, 134.6, 149.6, 157.6, 163.8, 167.2.

**HRMS** (ESI-TOF): Calcd for C<sub>15</sub>H<sub>19</sub>N<sub>1</sub>Na<sub>1</sub>O [M+H]<sup>+</sup>: 284.12525. Found: 284.12626.

**IR** (KBr):  $\nu$  3329, 1679, 1600, 1480, 1018 cm<sup>-1</sup>.

Compound 1g



Colorless solid.

**M.p.** 125–127 °C.

**R<sub>f</sub>**: 0.55 (*n*-Hexane/AcOEt = 1/1 (v/v), TLC: silica gel 60).

**Purification**: Flash chromatography (stationary phase: spherical silica gel, PSQ-60B; eluent (isocratic elution): *n*-Hexane 100% → *n*-Hexane/AcOEt = 1/1 (v/v)).

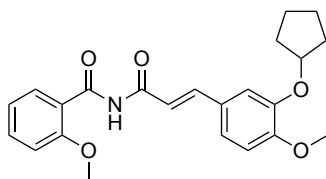
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  4.05 (s, 3H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.10–7.18 (m, 1H), 7.33–7.41 (m, 2H), 7.52–7.62 (m, 3H), 7.83 (d, *J* = 15.8 Hz, 1H), 7.84 (d, *J* = 15.8 Hz, 1H), 8.20 (dd, *J* = 7.9, 1.8 Hz, 1H), 10.1–10.5 (br, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  24.1, 32.8, 56.0, 56.2, 80.6, 111.5, 111.7, 114.2, 118.0, 120.6, 121.7, 122.7, 132.8, 134.6, 146.2, 147.8, 152.4, 157.7, 160.0, 164.0, 167.4.

**HRMS** (ESI-TOF): Calcd for C<sub>17</sub>H<sub>14</sub>Cl<sub>1</sub>N<sub>1</sub>Na<sub>1</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 338.05443. Found: 338.05599.

**IR** (KBr):  $\nu$  3321, 1674, 1619, 1480, 1013, 755 cm<sup>-1</sup>.

Compound 1i



Colorless solid.

**M.p.** 90–92 °C.

**R<sub>f</sub>**: 0.48 (*n*-Hexane/AcOEt = 1/1 (v/v), TLC: silica gel 60).

**Purification**: Flash chromatography (stationary phase: spherical silica gel, PSQ-60B; eluent (isocratic elution): *n*-Hexane 100% → *n*-Hexane/AcOEt = 5/1 (v/v) → *n*-Hexane/AcOEt = 2/1 (v/v)).

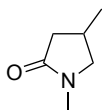
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  1.52–1.74 (m, 2H), 1.75–2.15 (m, 6H), 3.89 (s, 3H), 4.05 (s, 3H), 4.75–4.95 (m, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.09–7.20 (m, 2H), 7.23 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.47–7.63 (m, 1H), 7.72 (d, *J* = 15.7 Hz, 1H), 7.85 (d, *J* = 15.7 Hz, 1H), 8.21 (dd, *J* = 7.9, 1.7 Hz, 1H), 10.1–10.4 (br, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  24.1, 32.8, 56.0, 56.2, 80.6, 111.5, 111.7, 114.2, 118.0, 120.6, 121.7, 122.7, 132.8, 134.6, 146.2, 147.8, 152.4, 157.7, 160.0, 164.0, 167.8.

**HRMS** (ESI-TOF): Calcd for C<sub>23</sub>H<sub>26</sub>N<sub>1</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 396.18167. Found: 396.18110.

**IR** (KBr):  $\nu$  3329, 1672, 1598, 1509, 1161 cm<sup>-1</sup>.

Compound 4a



Colorless oil.

**R<sub>f</sub>**: 0.22 (AcOEt 100%, TLC: silica gel 60), 0.55 (*n*-Hexane/AcOEt = 4/1 (v/v), TLC: CHROMATOREX<sup>®</sup> NH-DM2035).

**Purification**: Flash chromatography (stationary phase: spherical silica gel; eluent (isocratic elution): *n*-Hexane/AcOEt = 1/1 (v/v) → AcOEt 100%).

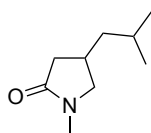
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  1.12 (d, *J* = 6.7 Hz, 3H), 2.01 (dd, *J* = 16.3, 6.7 Hz, 1H), 2.36–2.50 (m, 1H), 2.54 (dd, *J* = 16.3, 8.7 Hz, 1H), 2.83 (s, 3H), 2.95 (dd, *J* = 9.5, 5.9 Hz, 1H), 3.48 (dd, *J* = 9.5, 7.7 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  20.0, 26.1, 29.5, 39.1, 56.8, 174.6.

**HRMS** (ESI-TOF): Calcd for C<sub>6</sub>H<sub>12</sub>N<sub>1</sub>O<sub>1</sub> [M+H]<sup>+</sup>: 114.09160. Found: 114.09189.

**IR** (film):  $\nu$  3443, 2963, 2930, 2873, 1671, 1504, 1453, 1405, 1270 cm<sup>-1</sup>.

Compound 4b



Colorless oil.

**R<sub>f</sub>**: 0.17 (*n*-Hexane/AcOEt = 10/1 (v/v), TLC: CHROMATOREX<sup>®</sup> NH-DM2035).

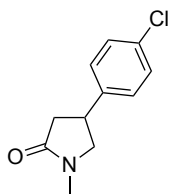
**Purification** (performed twice): (First) Flash chromatography (stationary phase: spherical silica gel; eluent (isocratic elution): *n*-Hexane 100% → *n*-Hexane/AcOEt = 4/1 (v/v) → *n*-Hexane/AcOEt = 2/1 (v/v) → *n*-Hexane/AcOEt = 1/1 (v/v), (Second) Flash chromatography (stationary phase: spherical silica gel, CHROMATOREX<sup>®</sup> NH-DM2035; eluent: *n*-Hexane/AcOEt = 10/1 (v/v)).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  0.90 (d, *J* = 4.0 Hz, 3H), 0.92 (d, *J* = 4.0 Hz, 3H), 1.33 (ddd, *J* = 7.2, 7.2, 2.3 Hz, 2H), 1.58 (sept, *J* = 6.7 Hz, 1H), 2.03 (dd, *J* = 15.9, 7.4 Hz, 1H), 2.33–2.57 (m, 2H), 2.82 (s, 3H), 2.99 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.45 (dd, *J* = 9.6, 7.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta_C$  29.6, 36.6, 38.7, 56.6, 128.1, 129.0, 132.9, 141.1, 173.5.

**HRMS** (ESI-TOF): C<sub>9</sub>H<sub>18</sub>N<sub>1</sub>O<sub>1</sub> [M+H]<sup>+</sup>: 156.13839. Found: 156.13884.

**IR** (film):  $\nu$  2955, 1693, 1501, 1467, 1402, 1295 cm<sup>-1</sup>.

**Compound 4c**

Colorless oil.

**R<sub>f</sub>**: 0.21 (AcOEt 100%, TLC: silica gel 60).

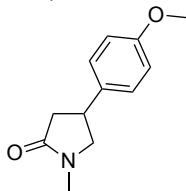
**Purification** (performed twice): (First) Flash chromatography (stationary phase: spherical silica gel; eluent (isocratic elution): *n*-Hexane 100% → *n*-Hexane/AcOEt = 1/1 (v/v) → AcOEt 100%), (Second) Flash chromatography (stationary phase: spherical silica gel, CHROMATOREX<sup>®</sup> NH-DM2035; eluent: *n*-Hexane/AcOEt = 1/1 (v/v)).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 2.49 (dd, *J* = 16.9, 8.0 Hz, 1H), 2.81 (dd, *J* = 16.9, 9.2 Hz, 1H), 2.91 (s, 3H), 3.36 (dd, *J* = 9.8, 6.8 Hz, 1H), 3.49-3.61 (m, 1H), 3.75 (dd, *J* = 9.8, 8.3 Hz, 1H), 7.13-7.19 (m, 2H), 7.28-7.35 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 14.5, 40.5, 60.2, 62.4, 64.3, 73.3, 111.5, 118.4, 126.1, 127.5, 128.8, 131.3, 141.8, 149.0, 167.0.

**HRMS** (FAB): C<sub>11</sub>H<sub>13</sub>ClN<sub>1</sub>O<sub>1</sub> [M+H]<sup>+</sup>: 210.068794. Found: 210.06857.

**IR** (film): ν 2923, 1692, 1495, 1401, 1258, 1091, 1013, 826, 772 cm<sup>-1</sup>.

**Compound 4d**

Colorless oil.

**R<sub>f</sub>**: 0.31 (AcOEt 100%, TLC: silica gel 60).

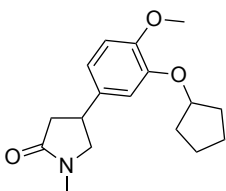
**Purification** (performed twice): (First) Flash chromatography (stationary phase: spherical silica gel, PSQ-60B; eluent: AcOEt 100%), (Second) Flash chromatography (stationary phase: spherical silica gel, PSQ-60B; eluent: AcOEt 100%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 2.51 (dd, *J* = 16.6, 8.7 Hz, 1H), 2.78 (dd, *J* = 17.1, 8.7 Hz, 1H), 2.92 (s, 3H), 3.36 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.46-3.59 (m, 1H), 3.72 (dd, *J* = 9.6, 8.3 Hz, 1H), 3.80 (s, 3H), 6.83-6.91 (m, 2H), 7.10-7.18 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 29.5, 36.5, 38.9, 55.3, 56.9, 114.2, 127.7, 134.5, 158.6, 173.9.

**HRMS** (ESI-TOF): C<sub>12</sub>H<sub>16</sub>N<sub>1</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 206.11836. Found: 206.11810.

**IR** (film): ν 2932, 1686, 1515, 1247, 1181, 1032, 832 cm<sup>-1</sup>.

**Compound 4e**

Pale yellow oil.

**R<sub>f</sub>**: 0.09 (*n*-Hexane/AcOEt = 1/1 (v/v) , TLC: silica gel 60), 0.31 (AcOEt 100%, TLC: silica gel 60).

**Purification**: Flash chromatography (stationary phase: spherical silica gel, PSQ-60B; eluent: *n*-Hexane/AcOEt = 1/1 (v/v)).

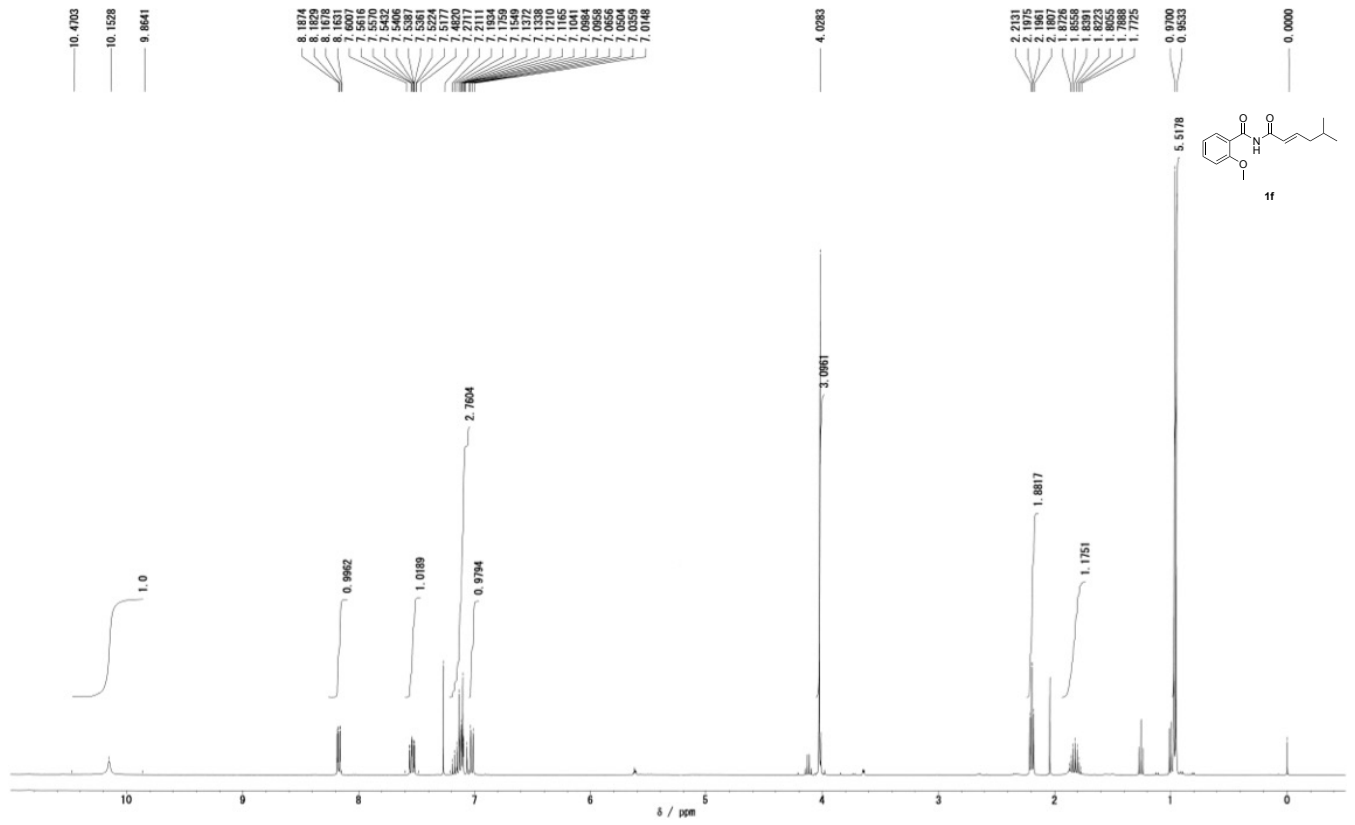
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 1.57-1.71 (m, 2H), 1.75-1.99 (m, 6H), 2.51 (dd, *J* = 16.9, 8.3 Hz, 1H), 2.79 (dd, *J* = 16.9, 9.2 Hz, 1H), 2.90 (s, 3H), 3.36 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.44-3.56 (m, 1H), 3.72 (dd, *J* = 9.5, 8.3 Hz, 1H), 3.82 (s, 3H), 4.70-4.83 (m, 1H), 6.71-6.77 (m, 2H), 6.79-6.85 (m, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 24.0, 29.5, 32.8, 36.8, 38.9, 56.1, 56.9, 80.6, 112.2, 113.7, 118.7, 134.7, 147.9, 149.1, 173.9.

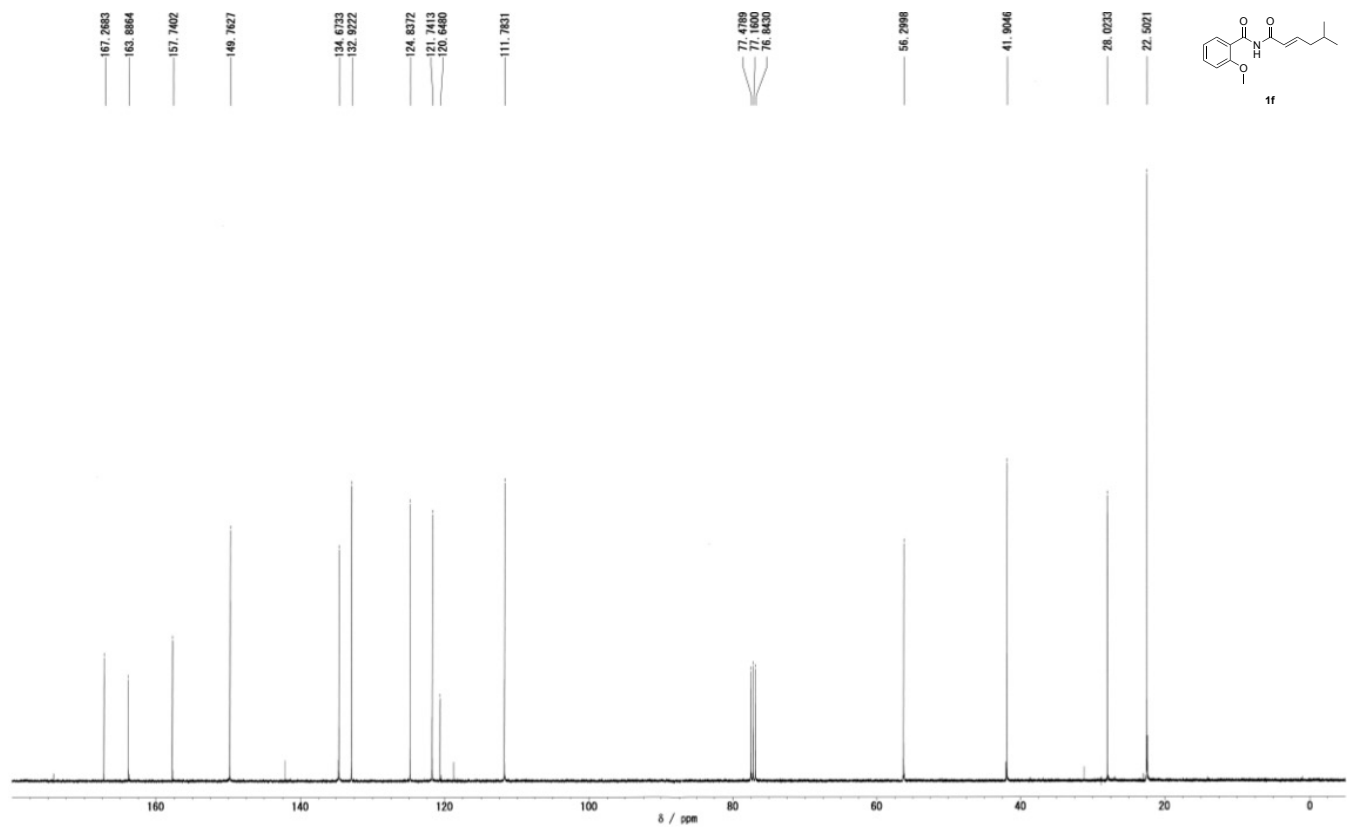
**HRMS** (ESI-TOF): Calcd for C<sub>12</sub>H<sub>24</sub>N<sub>1</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 290.17664. Found: 290.17562.

**IR** (film): ν 2955, 1689, 1515, 1262, 1138, 1029 cm<sup>-1</sup>.

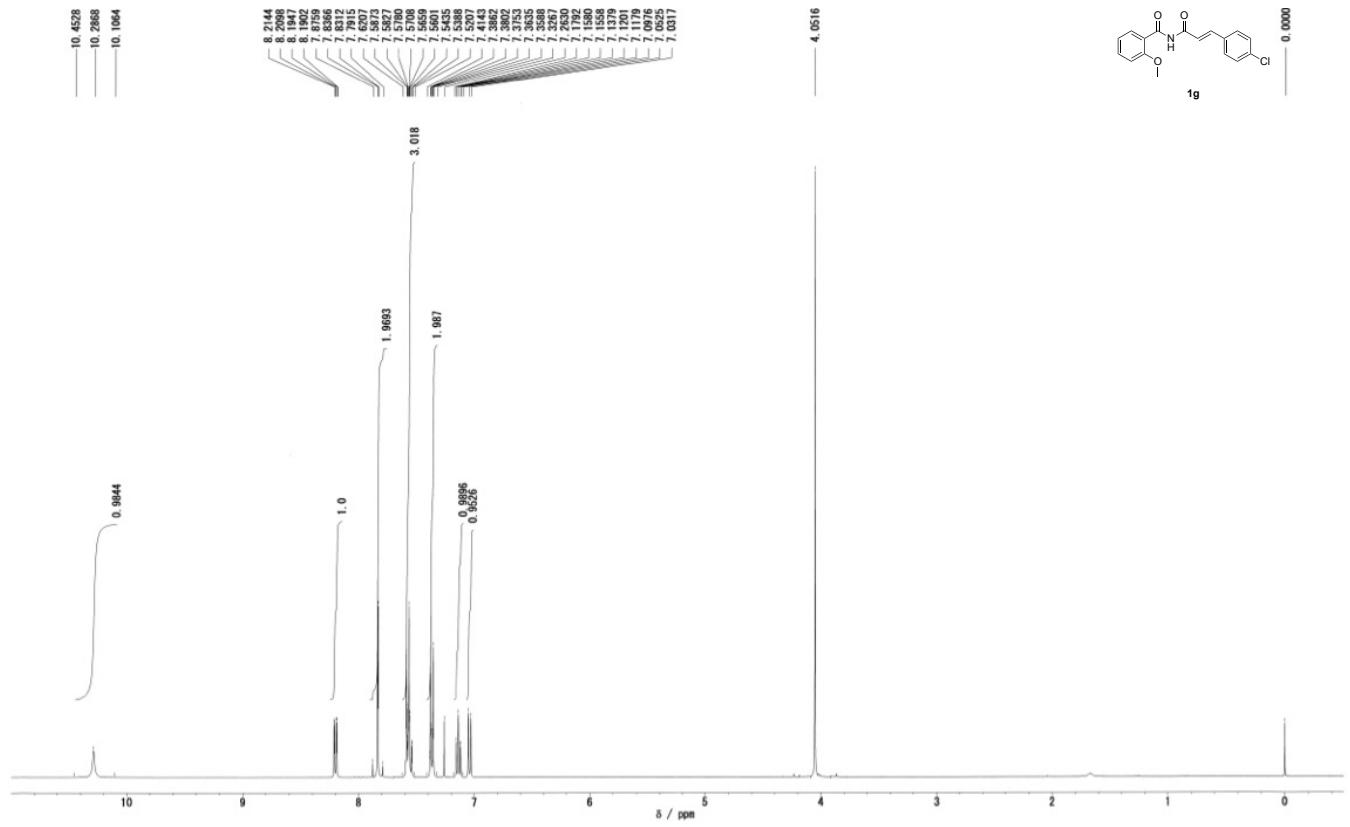
<sup>1</sup>H NMR spectrum of **1f**



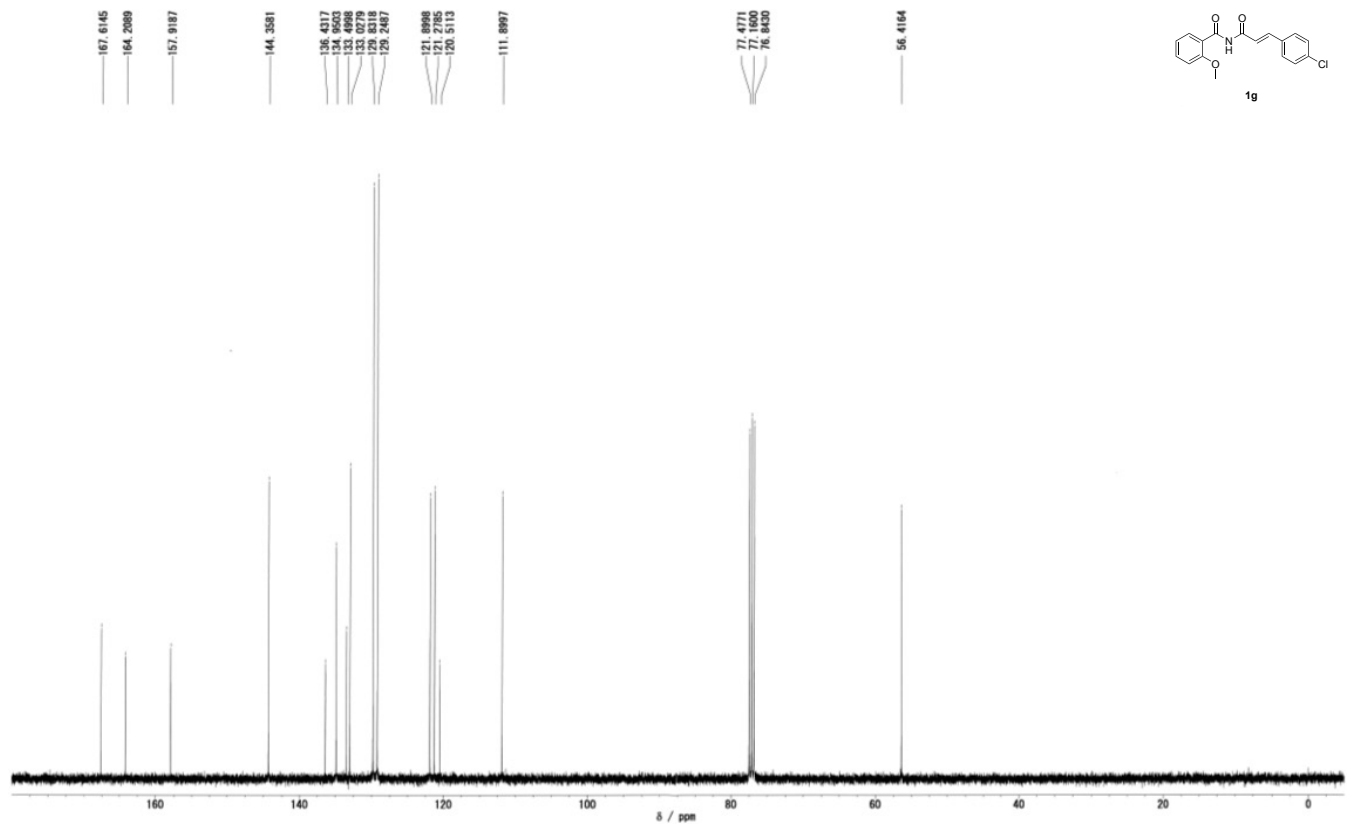
<sup>13</sup>C NMR spectrum of **1f**



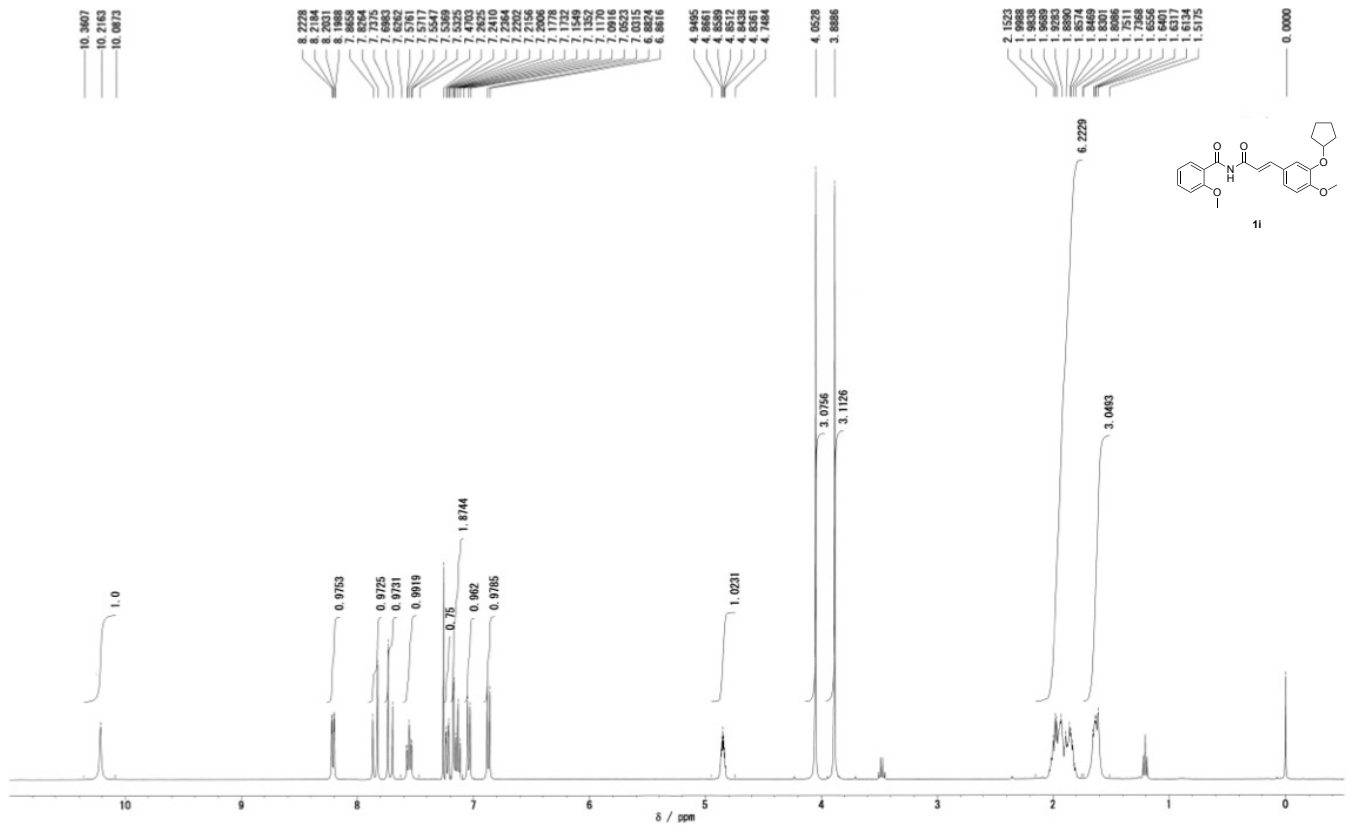
<sup>1</sup>H NMR spectrum of **1g**



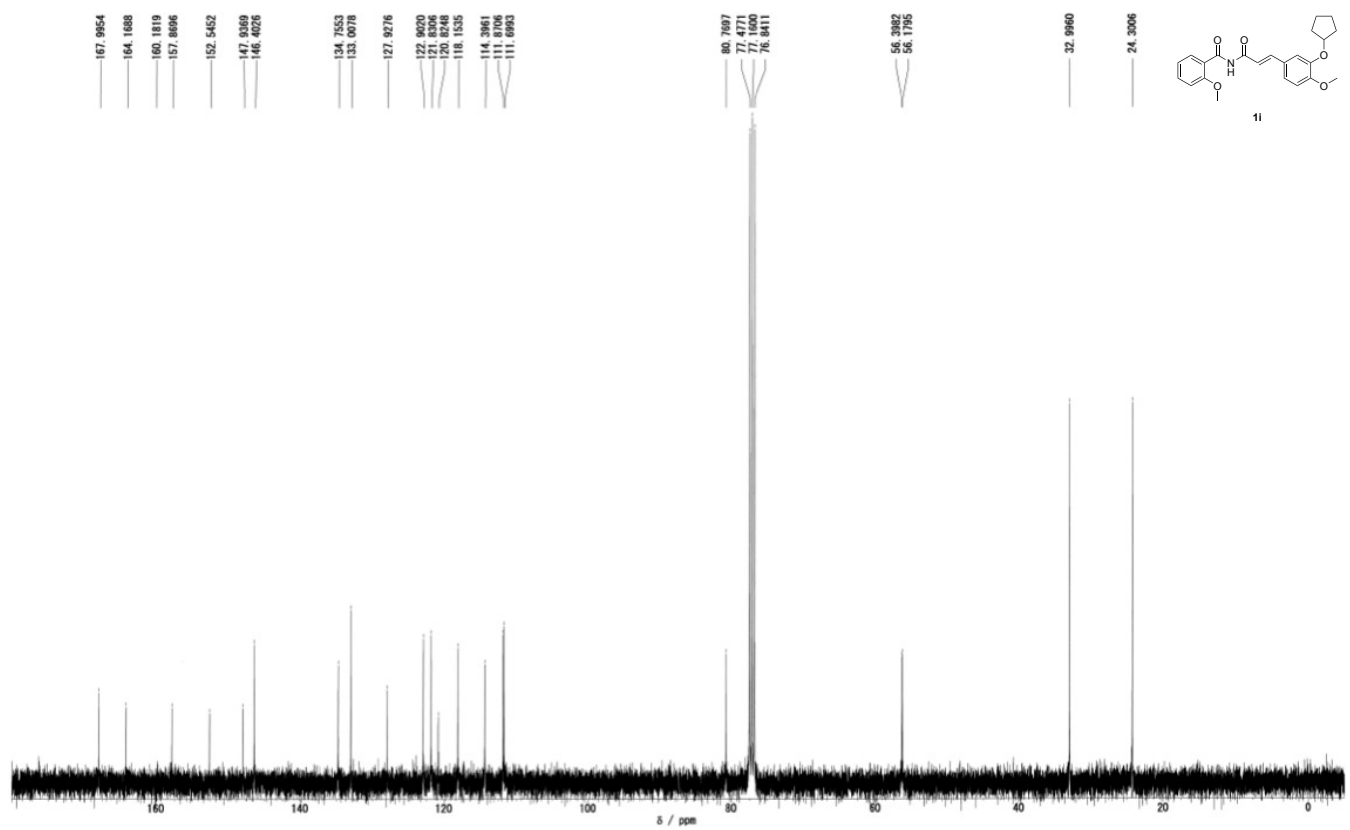
<sup>13</sup>C NMR spectrum of **1g**



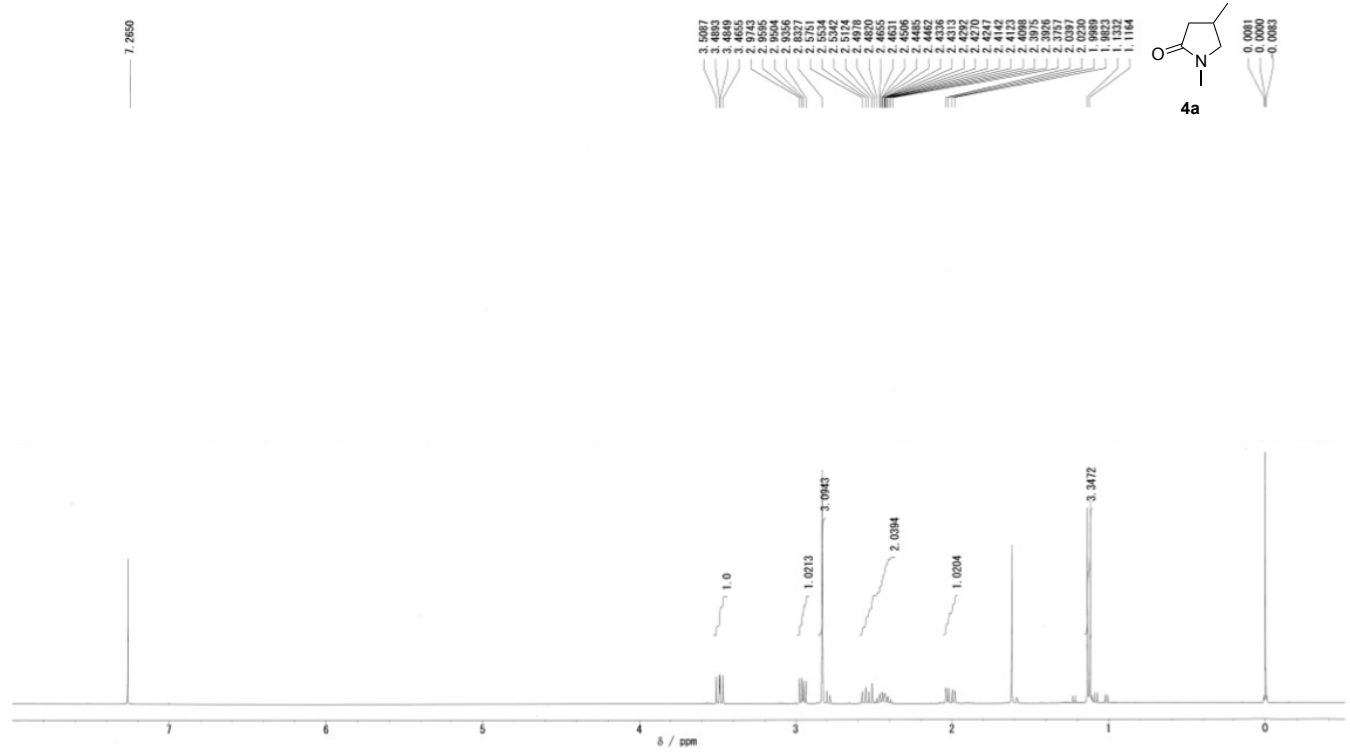
<sup>1</sup>H NMR spectrum of **1i**



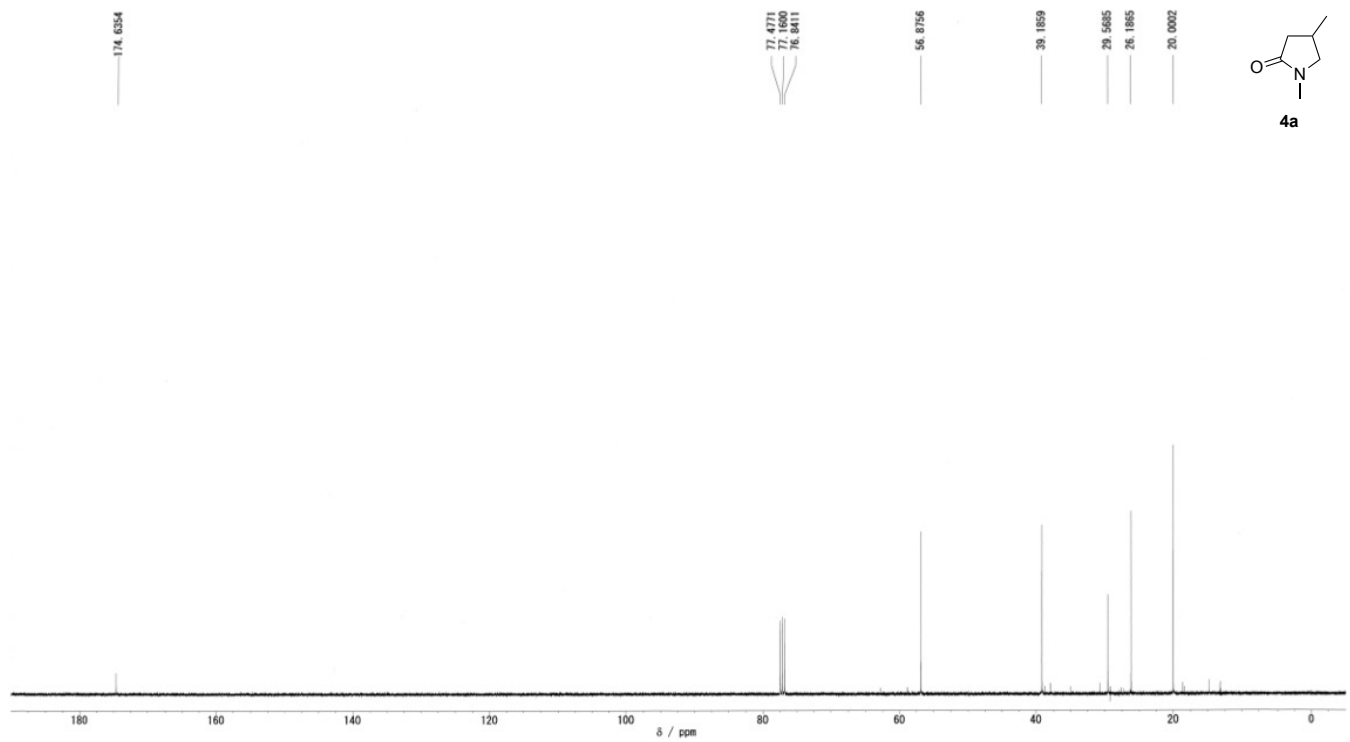
<sup>13</sup>C NMR spectrum of **1i**



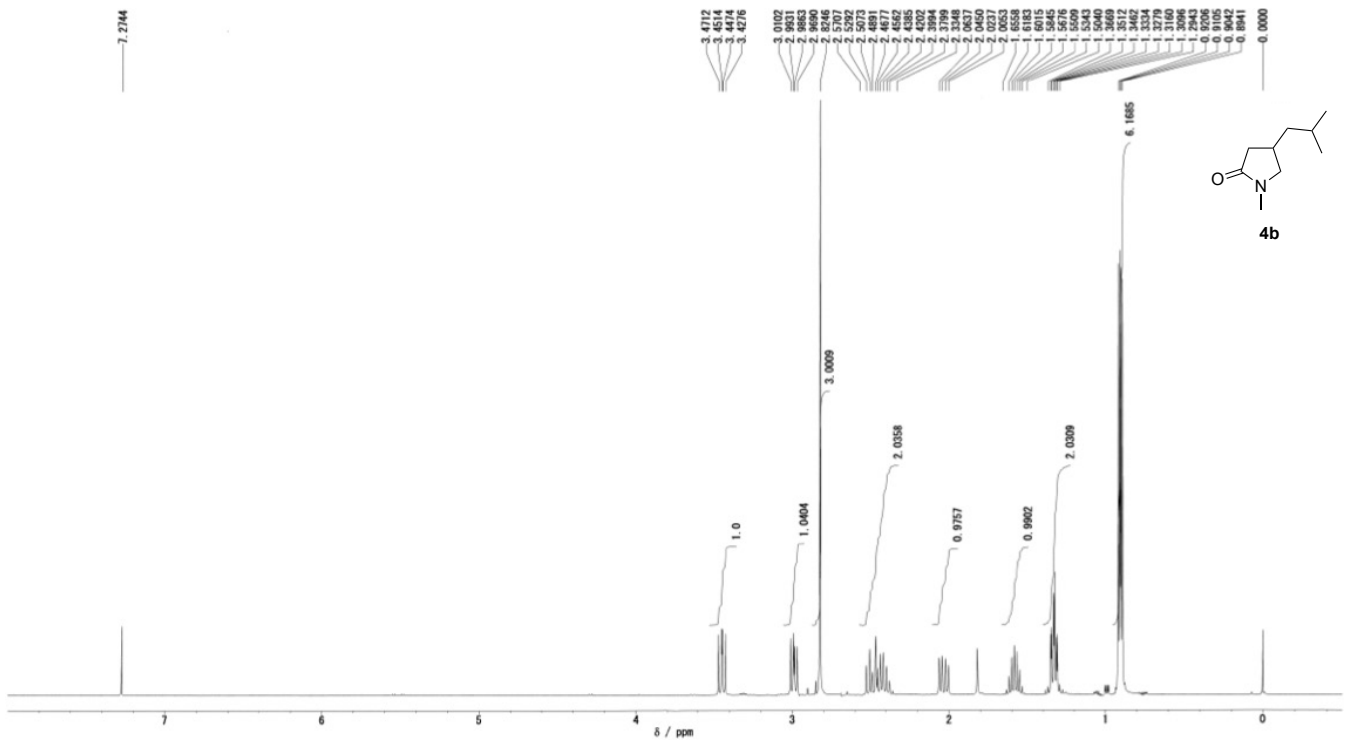
<sup>1</sup>H NMR spectrum of **4a**



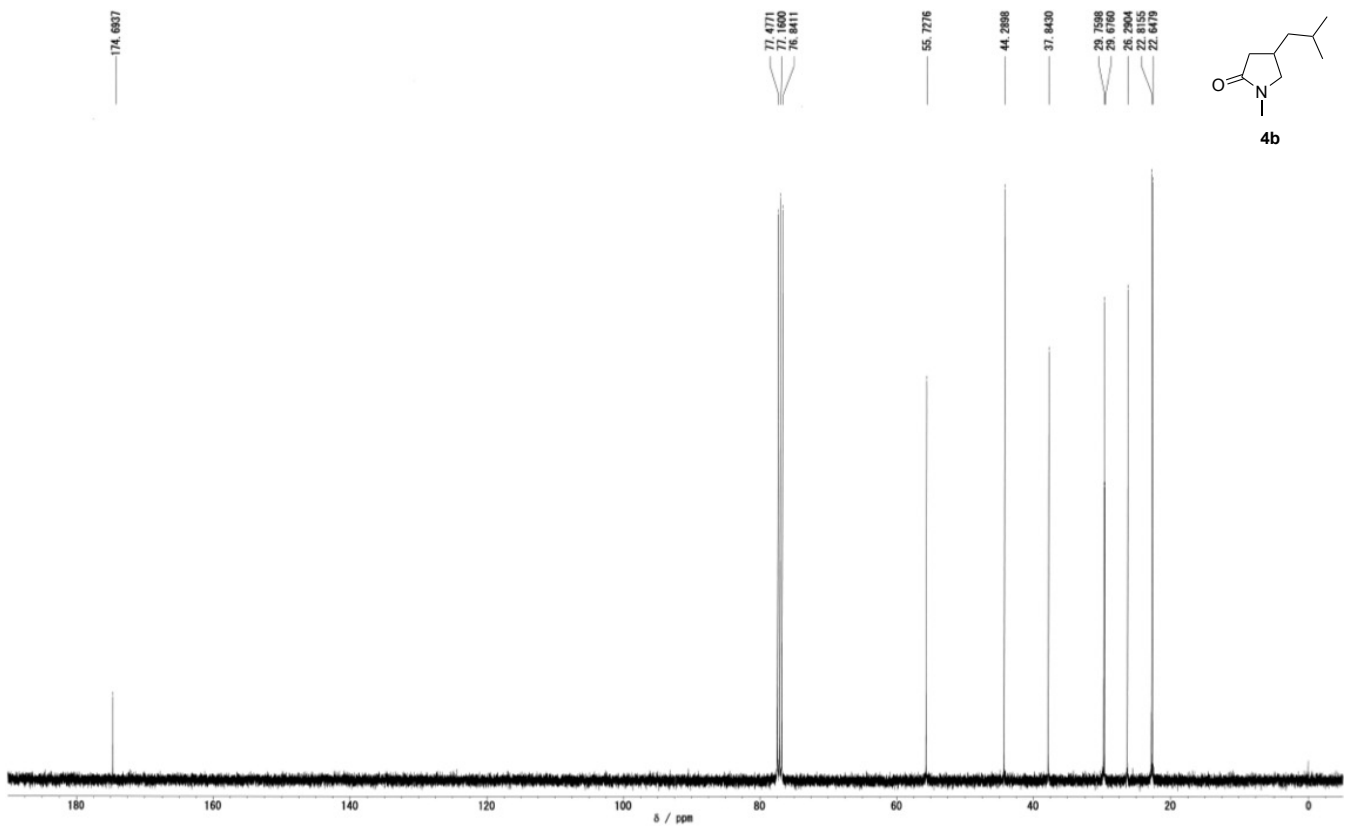
<sup>13</sup>C NMR spectrum of **4a**



<sup>1</sup>H NMR spectrum of **4b**

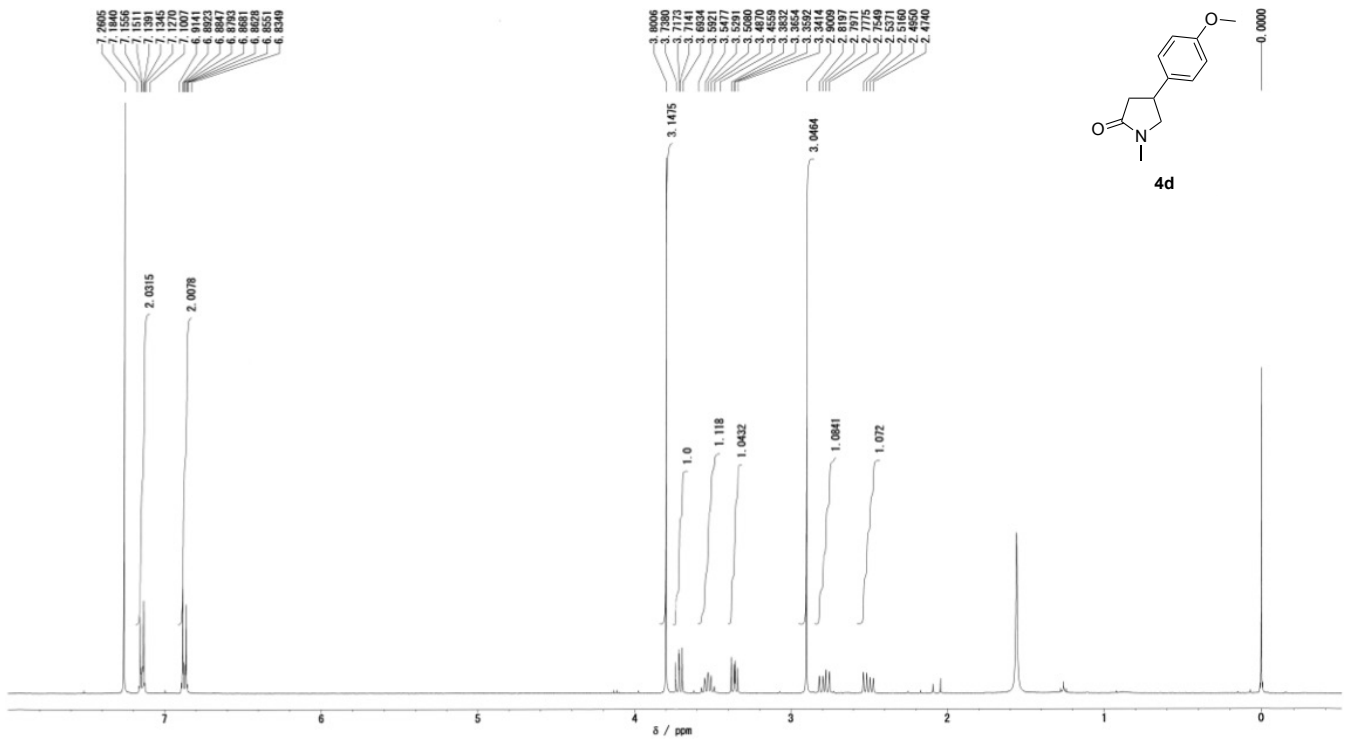


<sup>13</sup>C NMR spectrum of **4b**

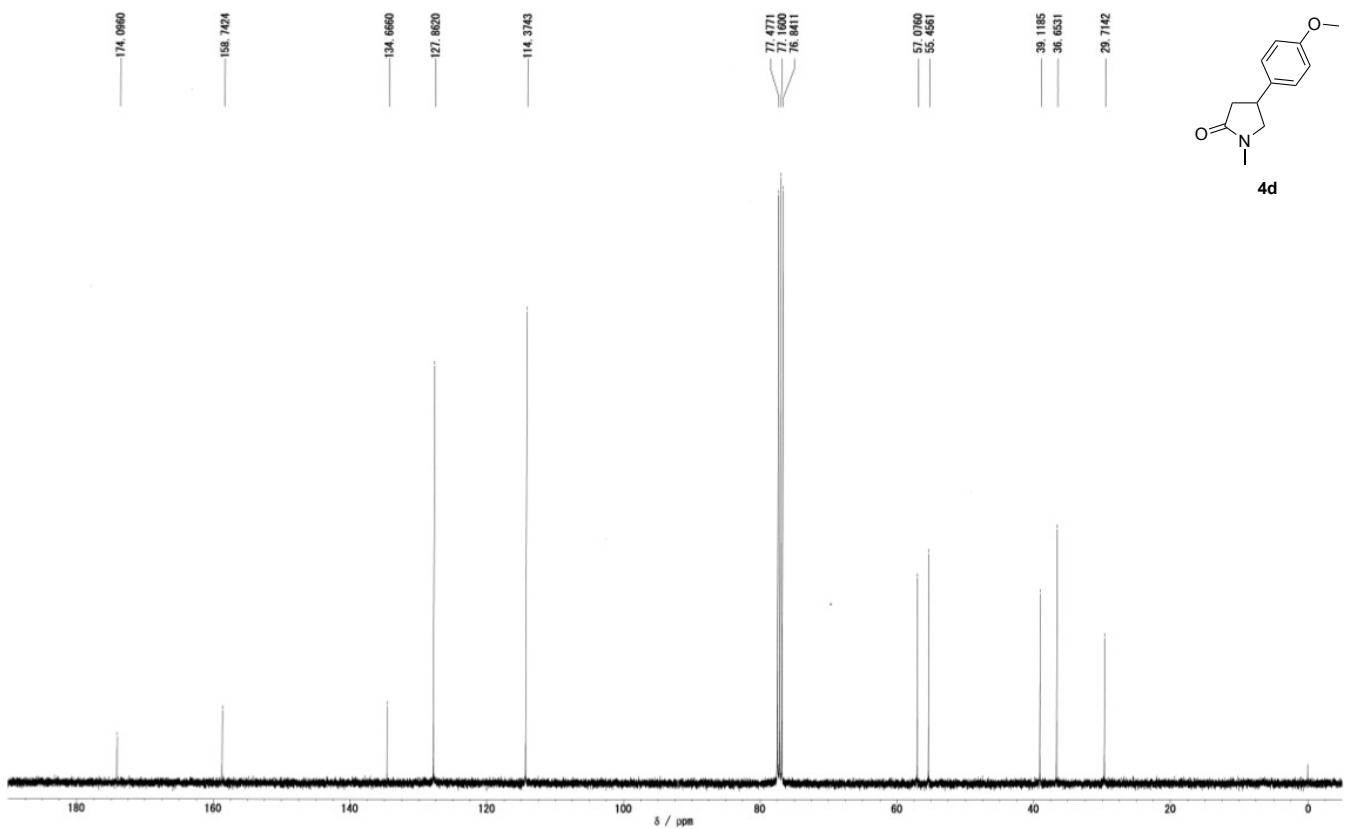




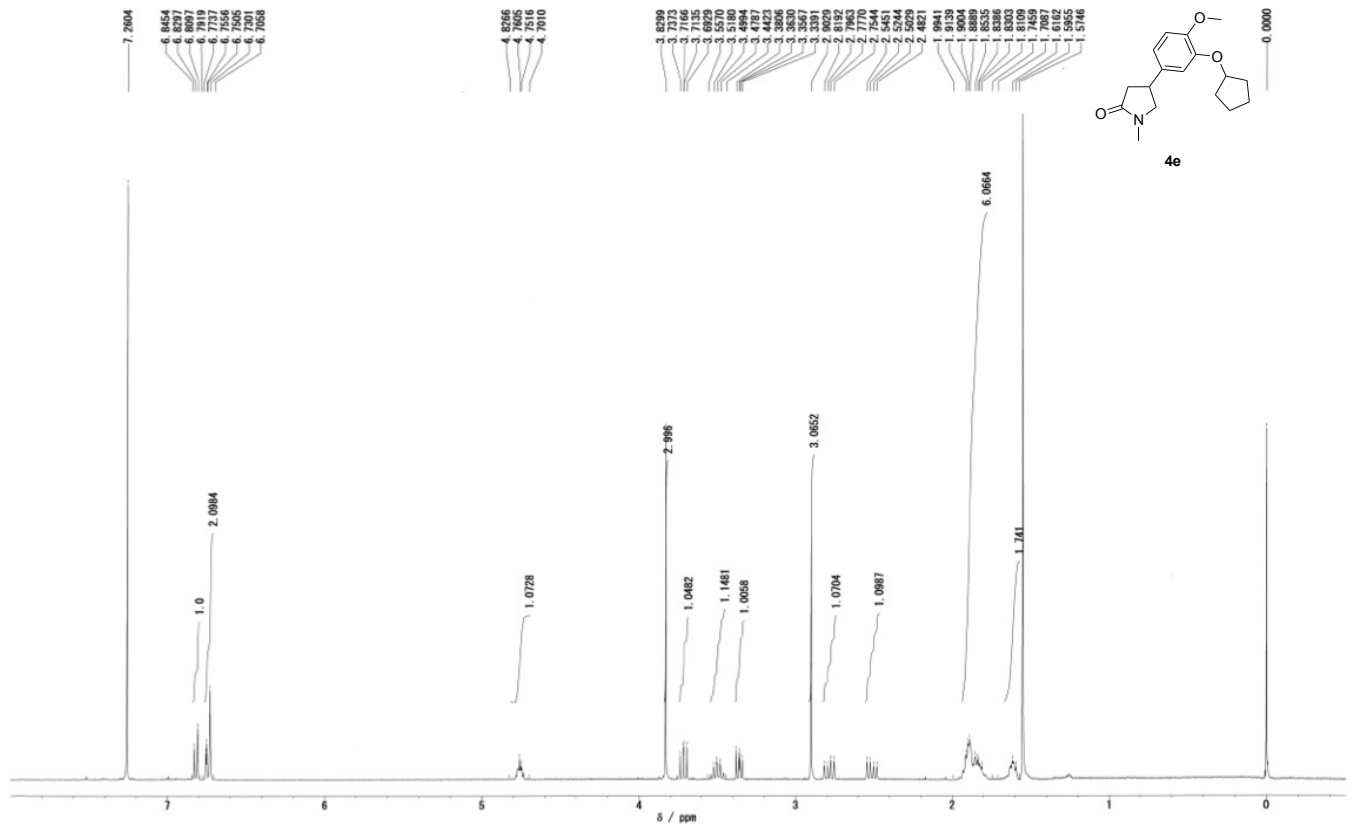
<sup>1</sup>H NMR spectrum of **4d**



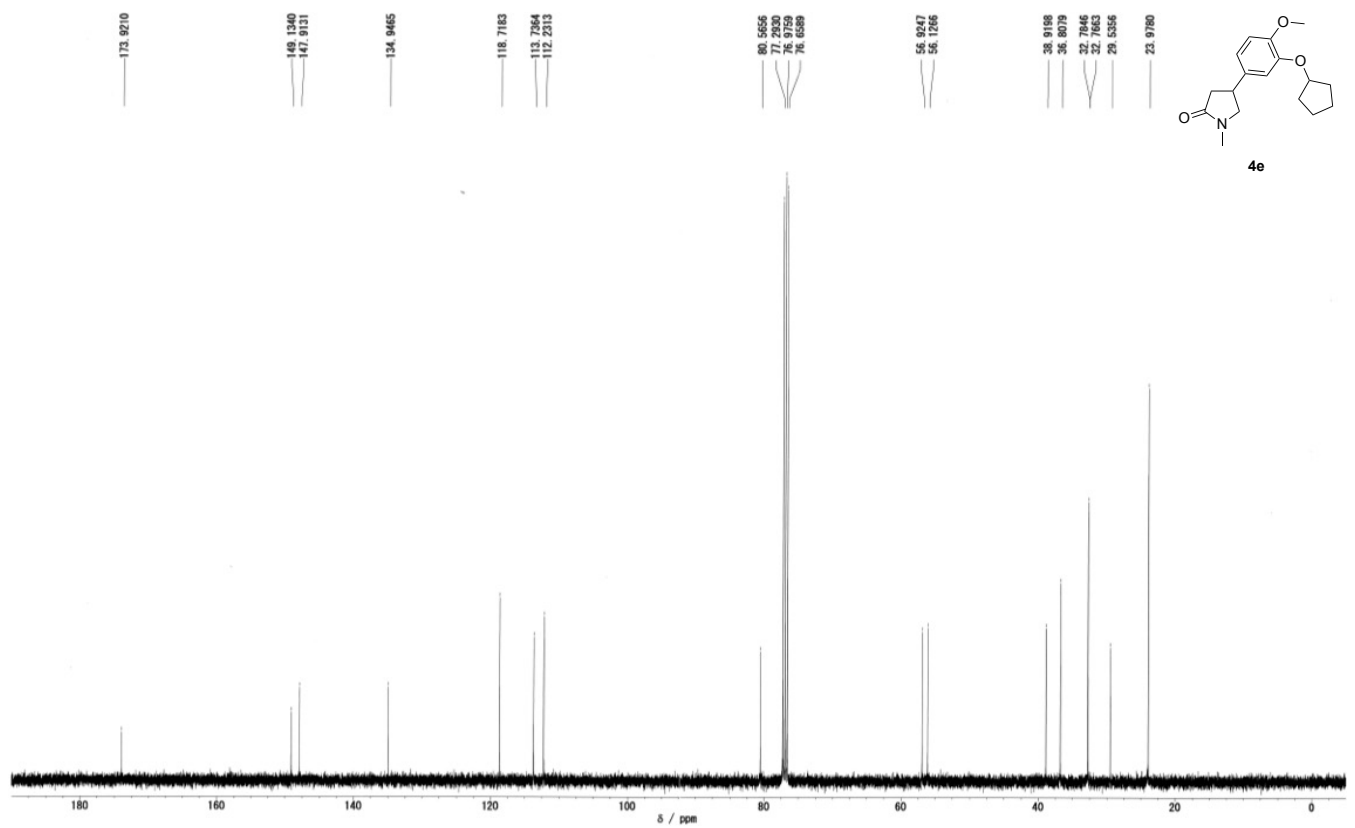
<sup>13</sup>C NMR spectrum of **4d**



<sup>1</sup>H NMR spectrum of 4e



<sup>13</sup>C NMR spectrum of 4e



## 4. References

- [1] (a) J. K. Myers, E. N. Jacobsen, *J. Am. Chem. Soc.*, 1999, **121**, 8959; (b) M. P. Sibi, N. Prabakaran, S. G. Ghorpade, C. P. Jasperse, *J. Am. Chem. Soc.*, 2003, **125**, 11796; (c) T. Inokuma, Y. Hoashi, Y. Takemoto, *J. Am. Chem. Soc.*, 2006, **128**, 9413. (d) K. Itoh, S. Nagao, K. Tokunaga, S. Hirayama, F. Karaki, T. Mizuguchi, K. Nagai, N. Sato, M. Suzuki, M. Hashimoto, H. Fujii, *Chem. Eur. J.*, 2021, **27**, 5171.
- [2] D. A. Evans, S. G. Nelson, *J. Am. Chem. Soc.*, 1997, **119**, 6452.
- [3] (a) C. Kashima, H. Harada, I. Kita, I. Fukuchi, A. Hosomi, *Synthesis*, 1994, 61. (b) M. P. Sibi, K. Itoh, *J. Am. Chem. Soc.*, 2007, **129**, 8064.