Supporting Information

# (±)-*trans*-1,2-Cyclohexanediamine-based bis(NHC) ligand for Cu-catalyzed asymmetric conjugate addition reaction

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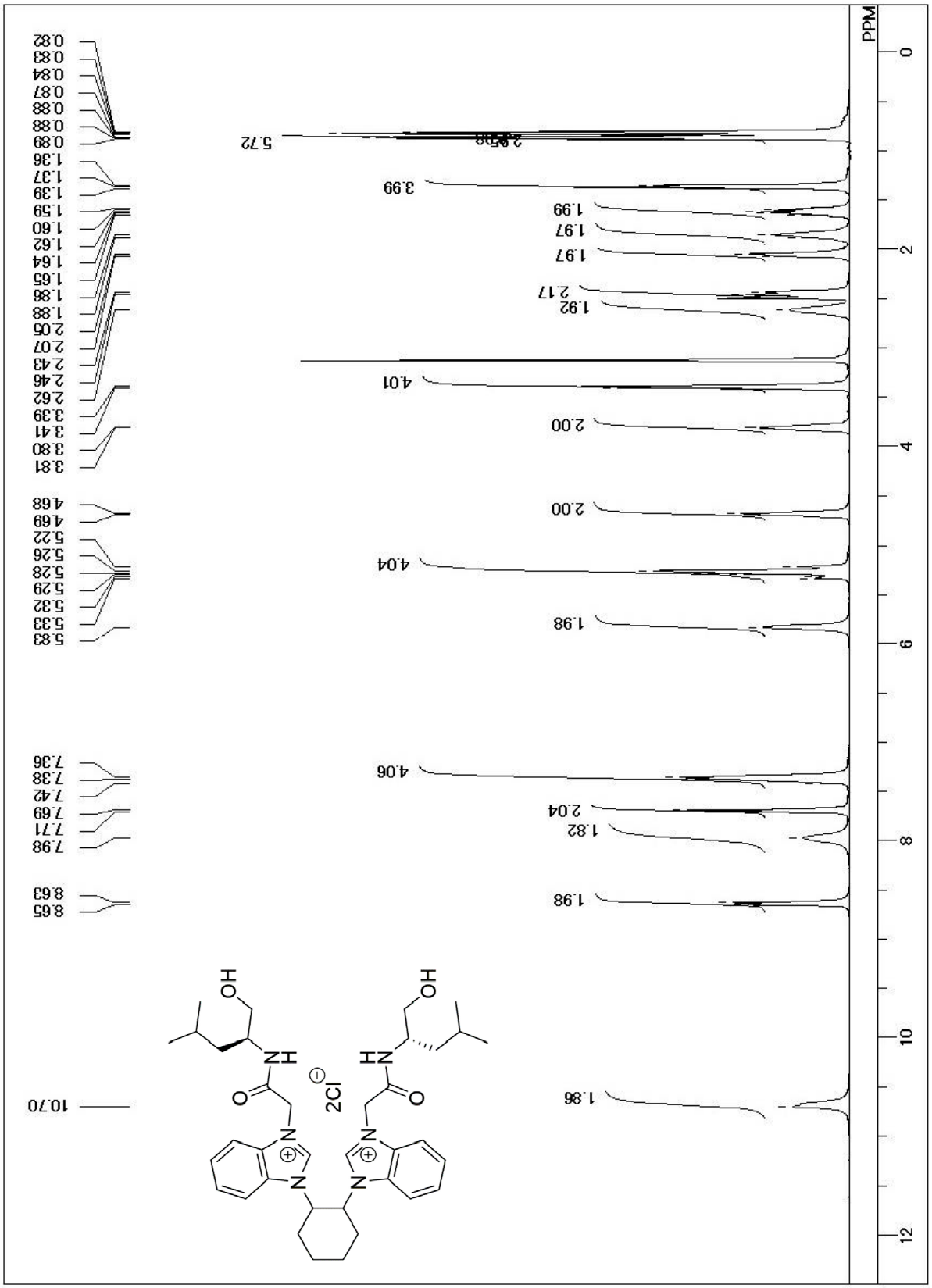
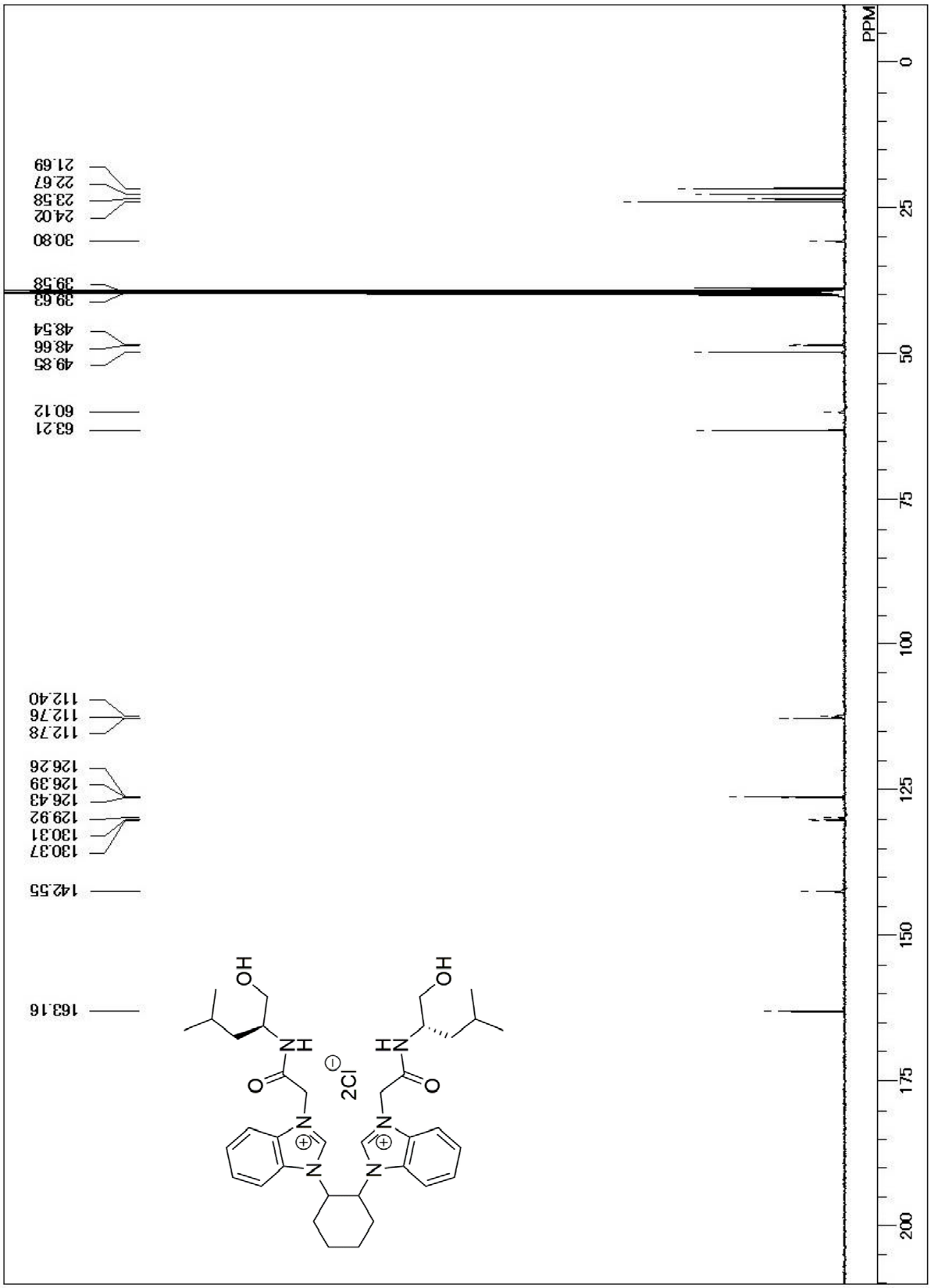


$^{13}$C-NMR Spectra for (*rac*; *S*,*S*)-**L1**



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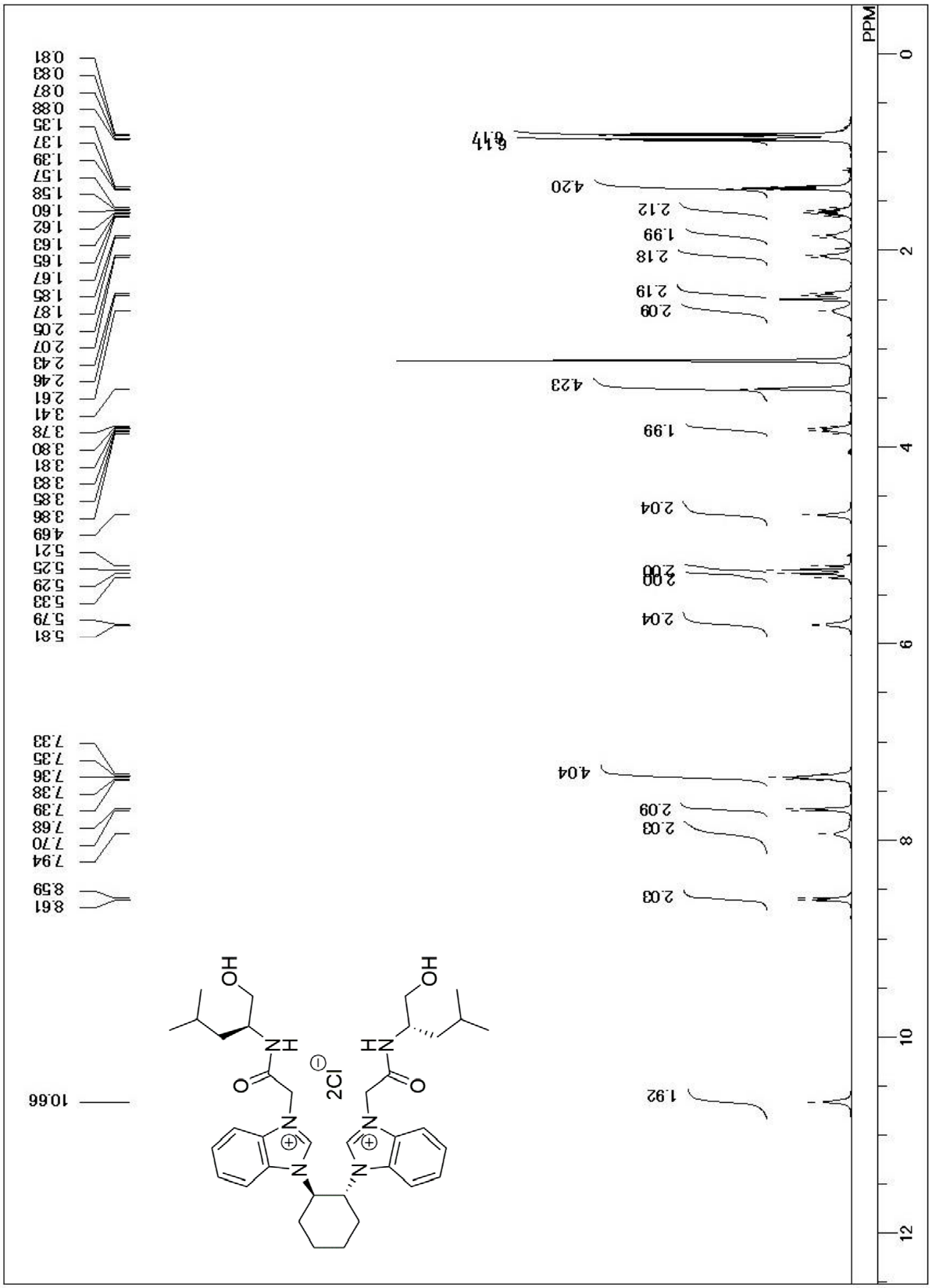

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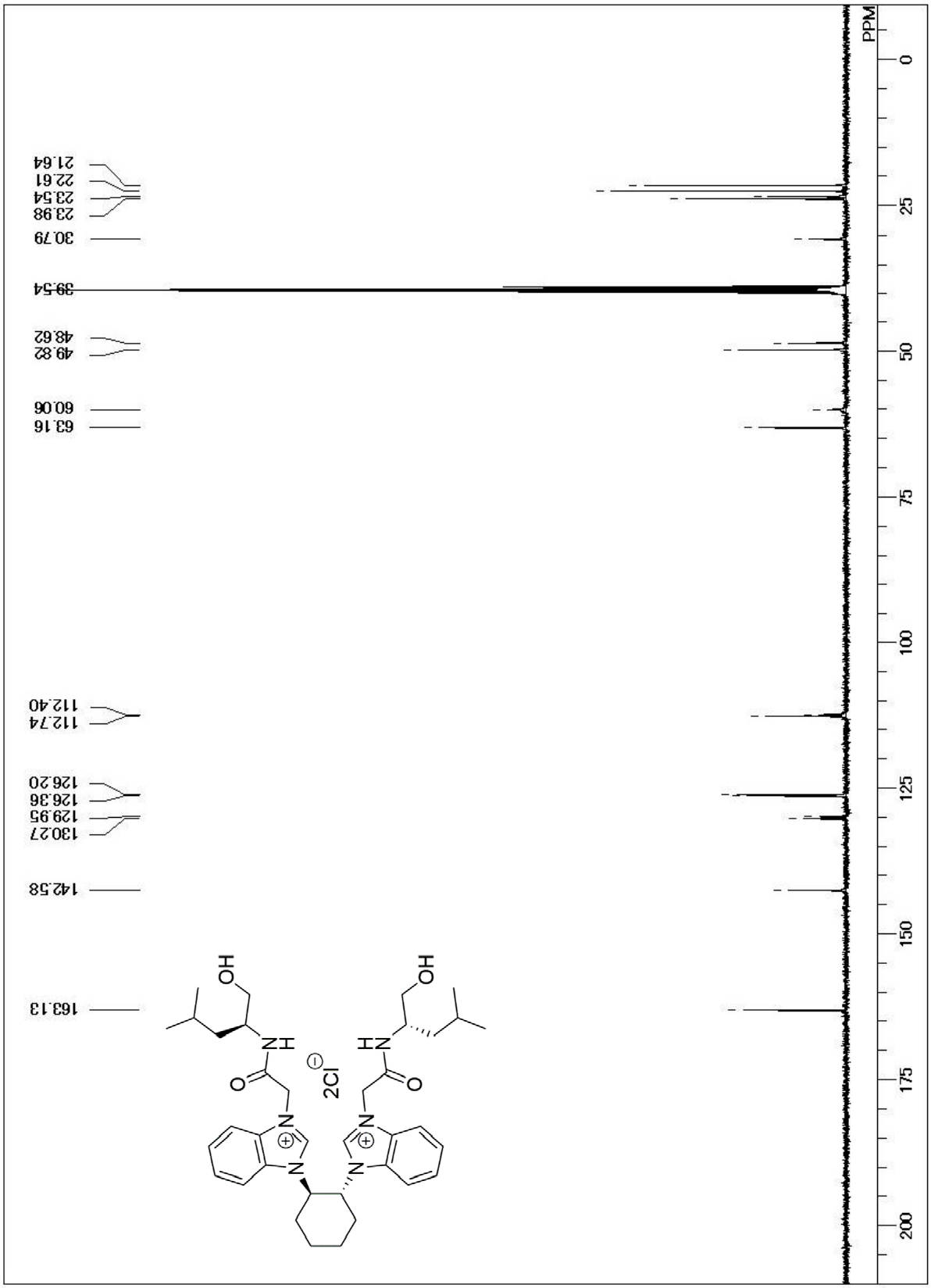

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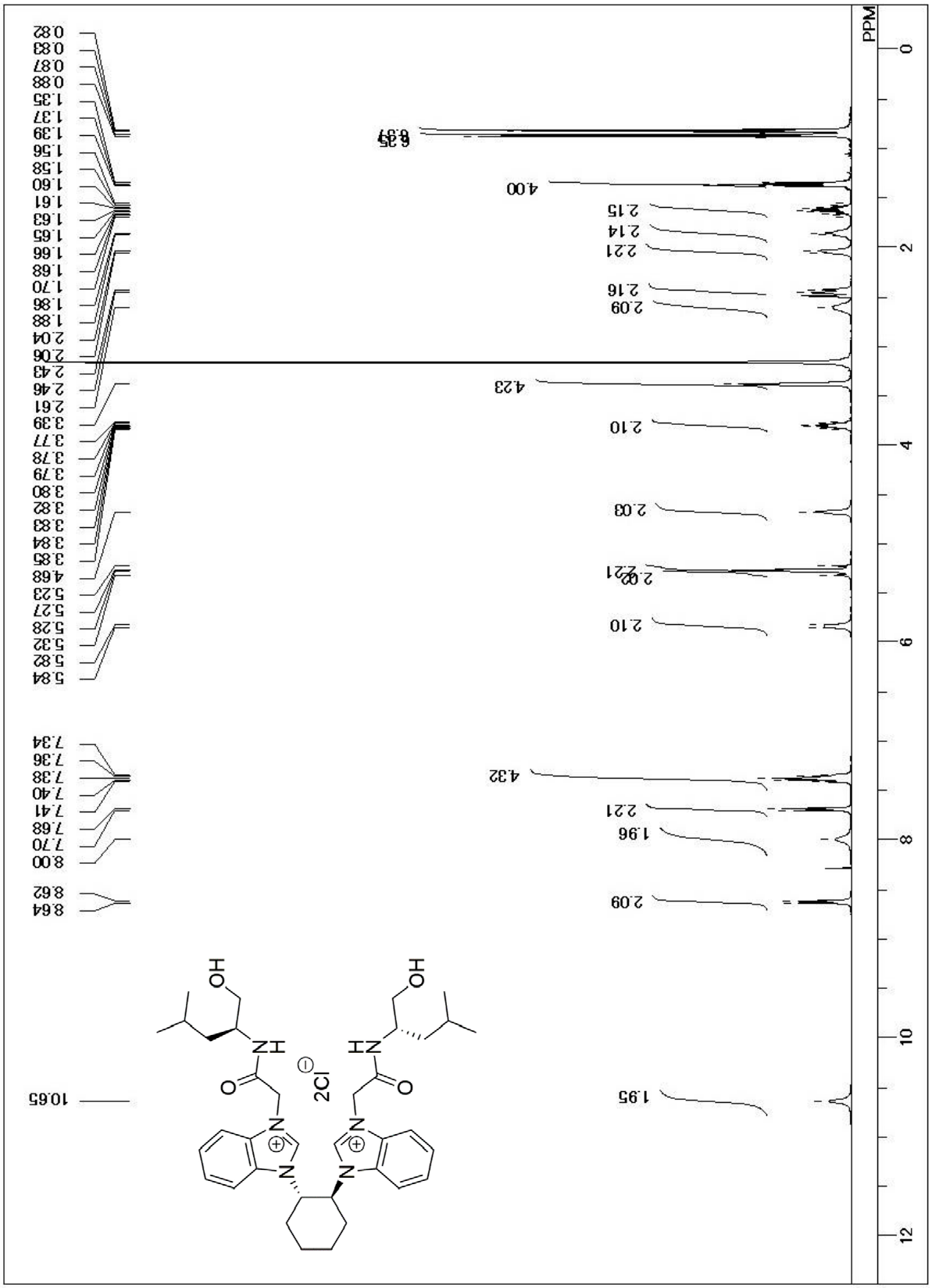

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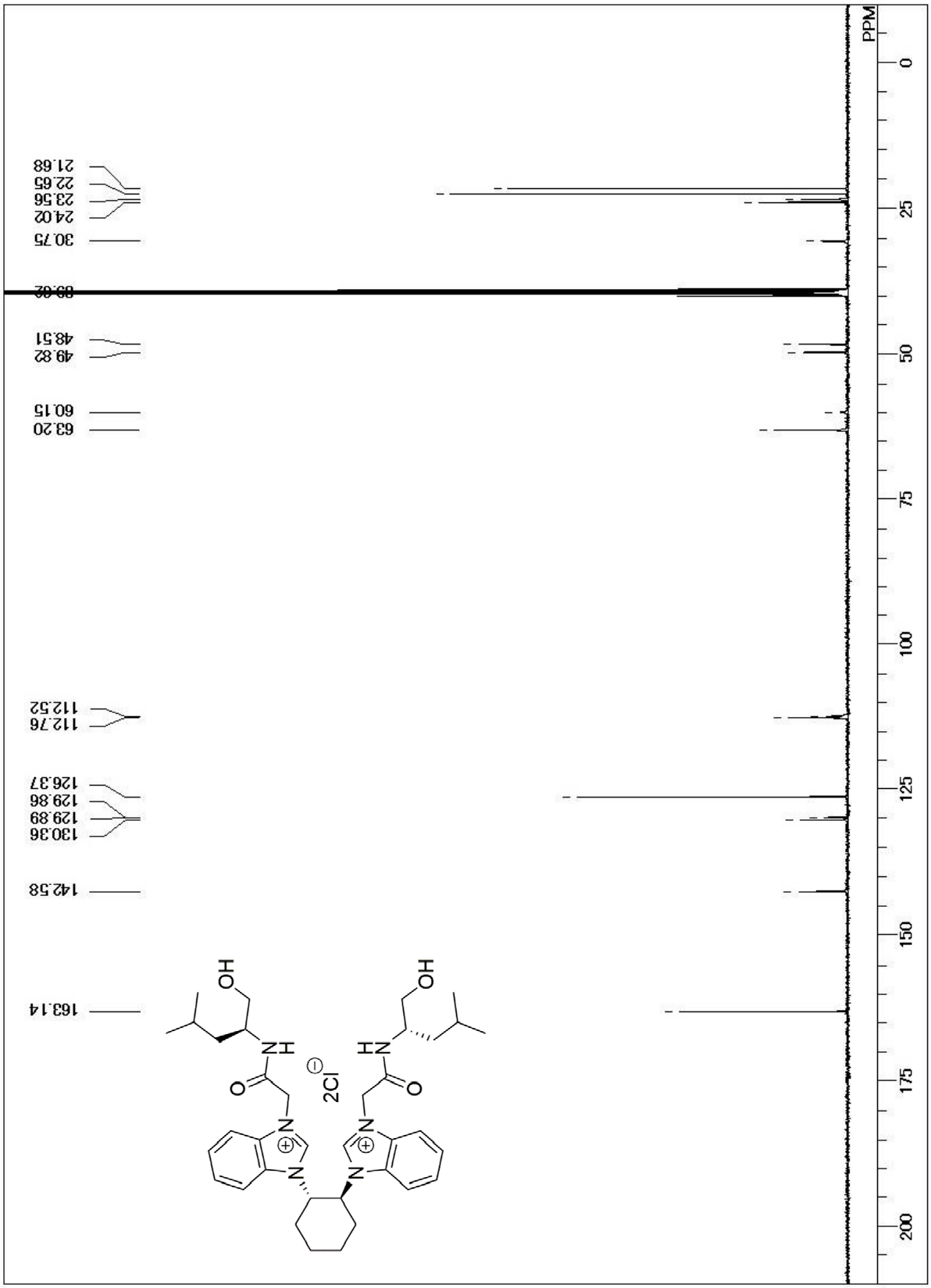

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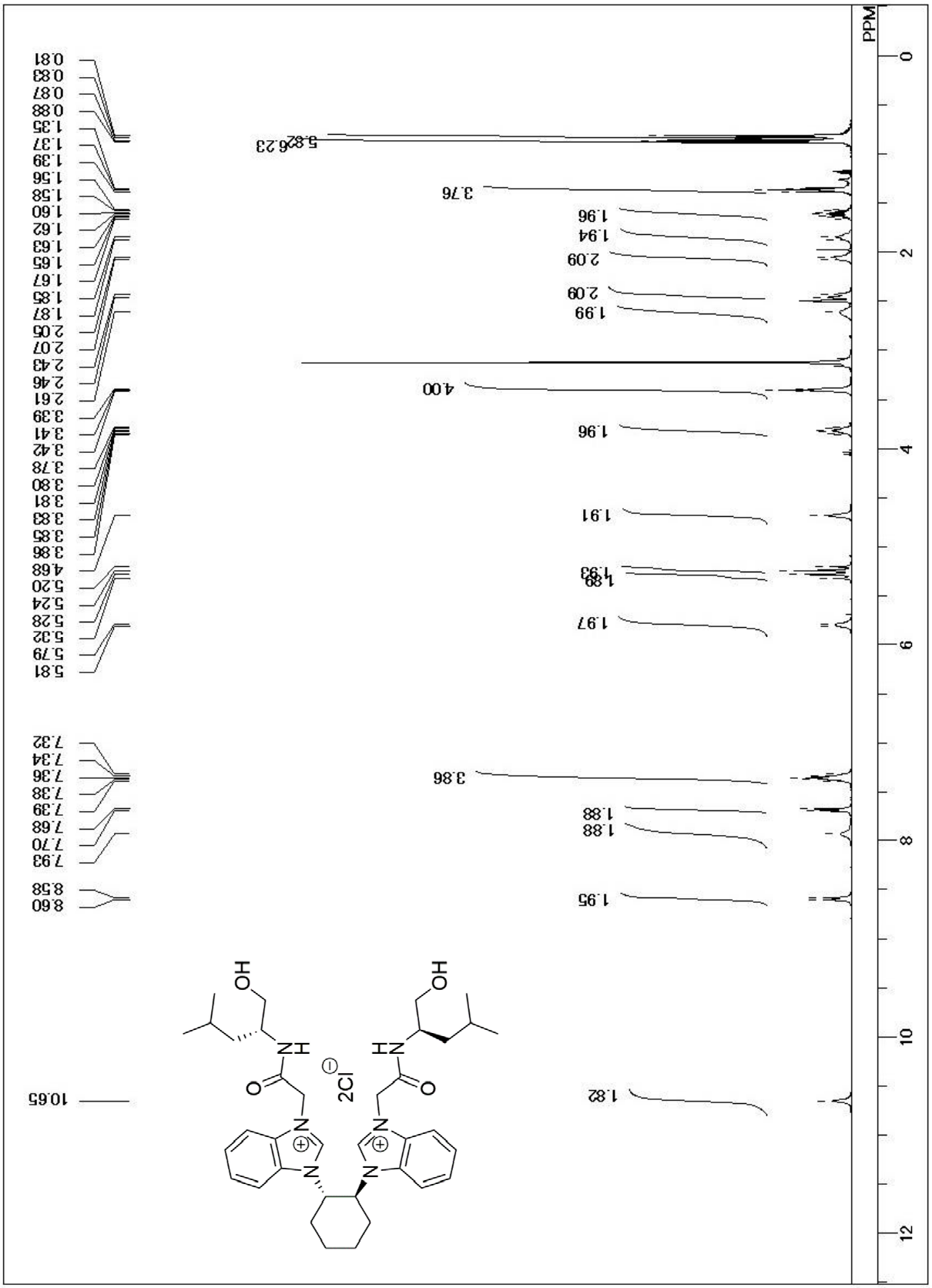
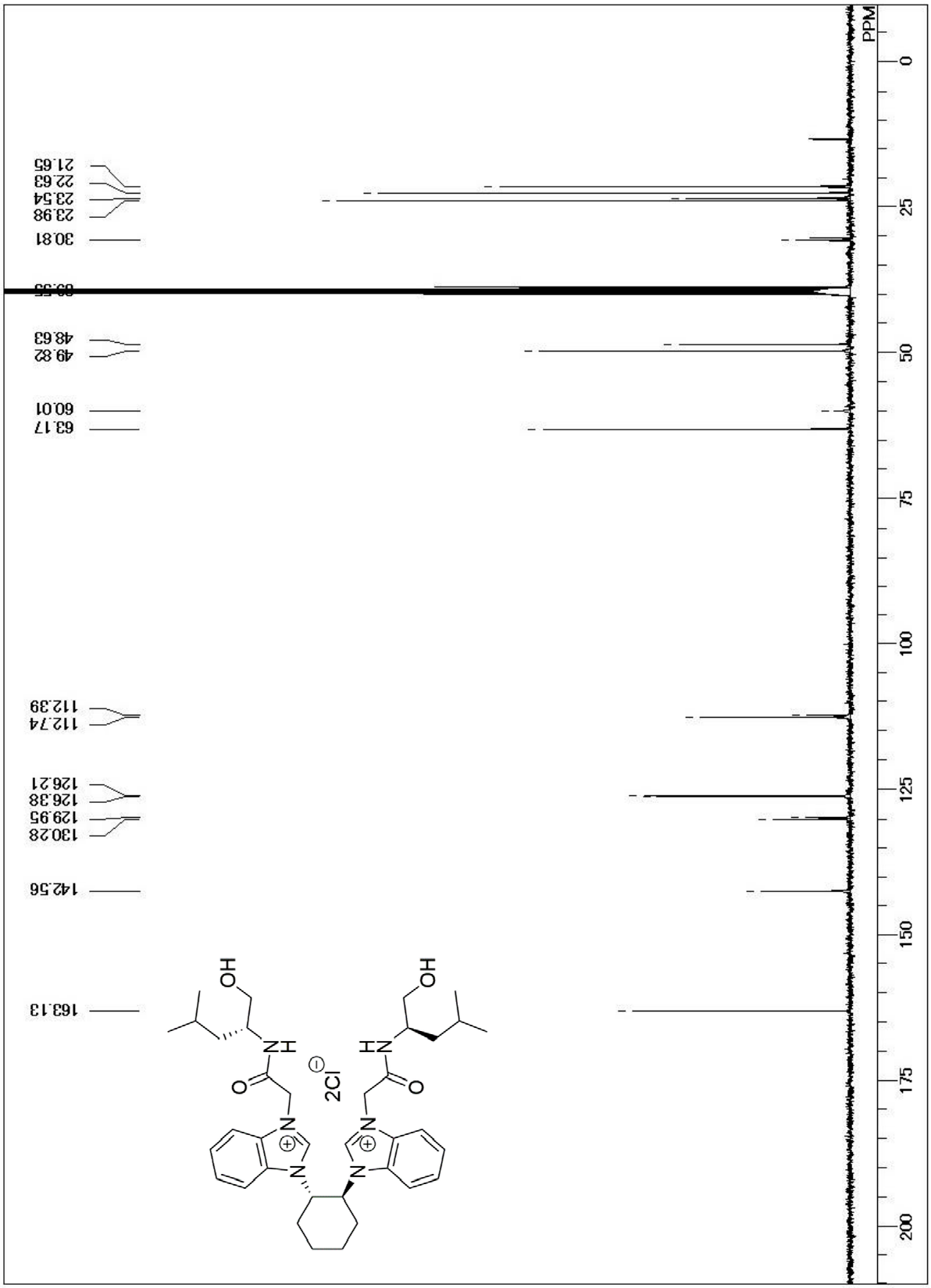


$^{13}$C-NMR Spectra for (*S,S*; *R,R*)-**L1**



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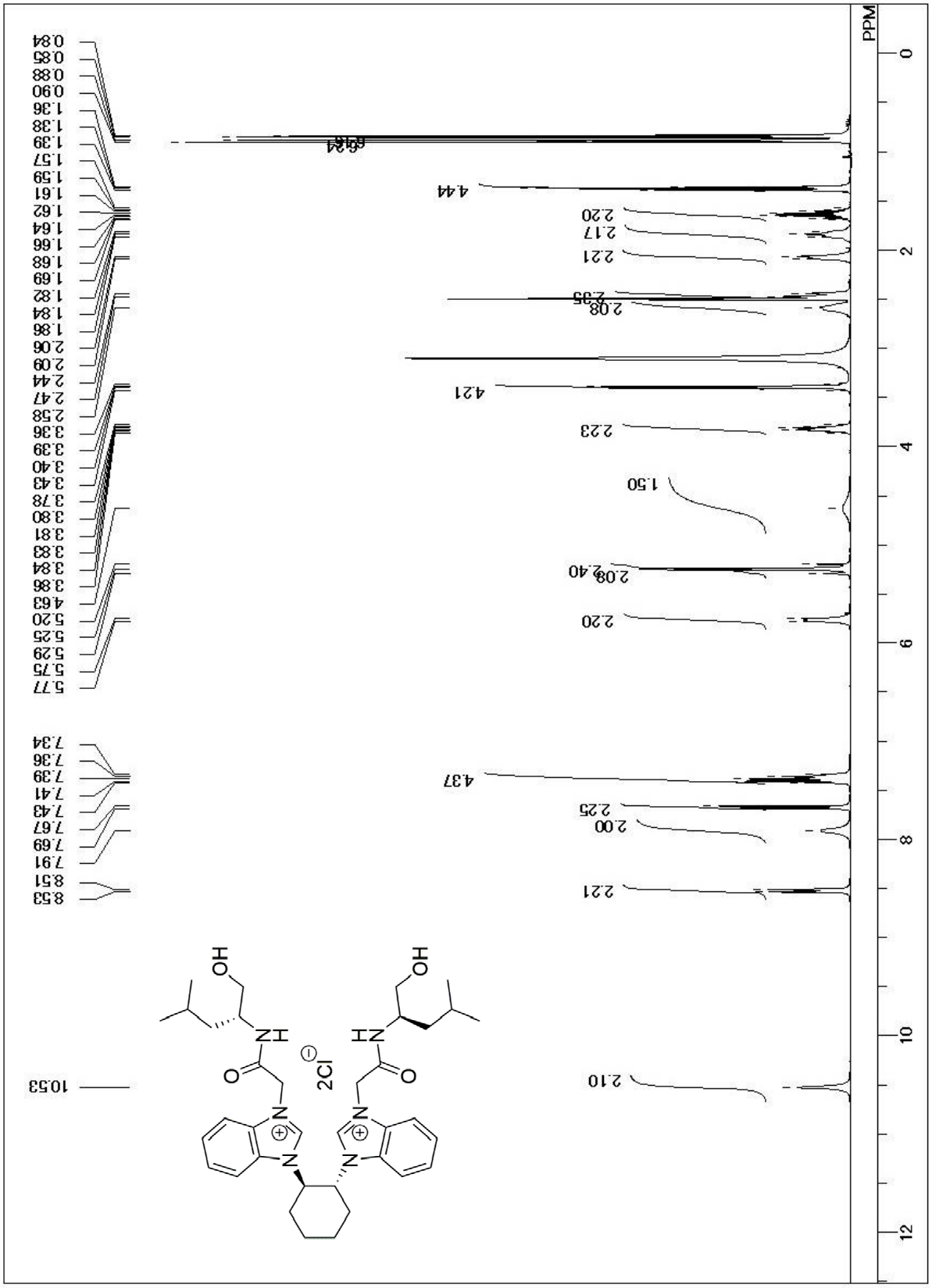

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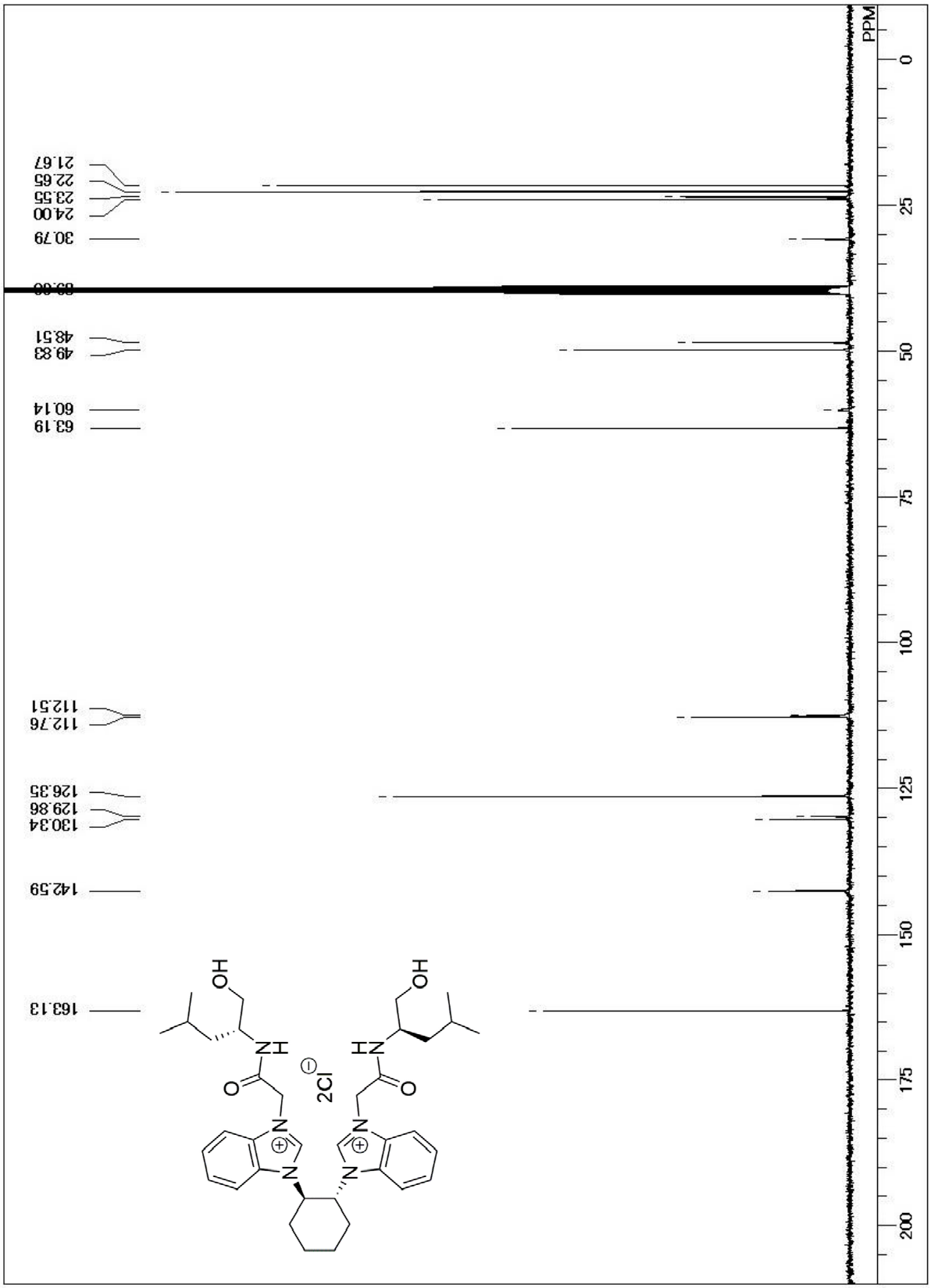
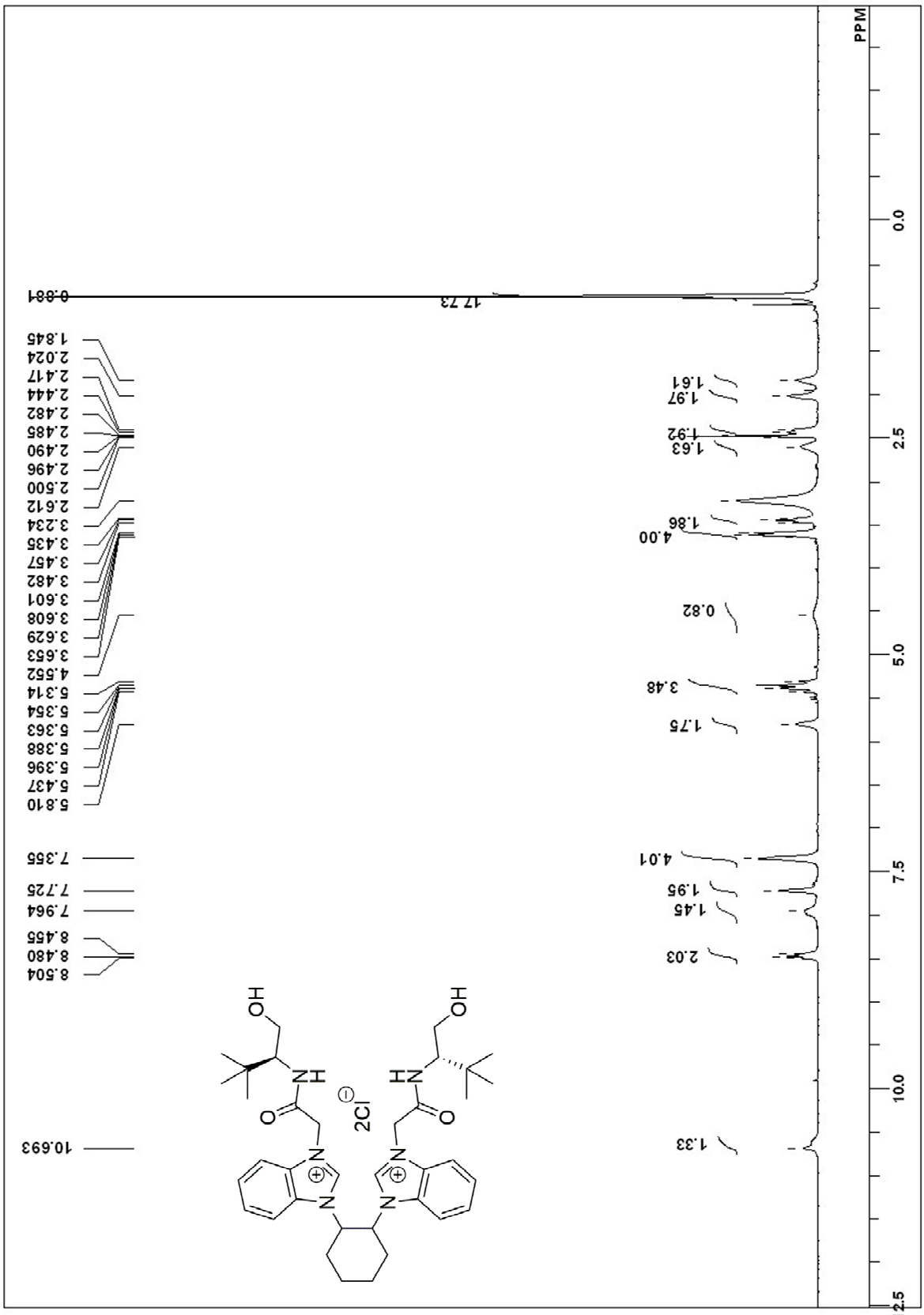


$^{1}$H-NMR Spectra for **L2**



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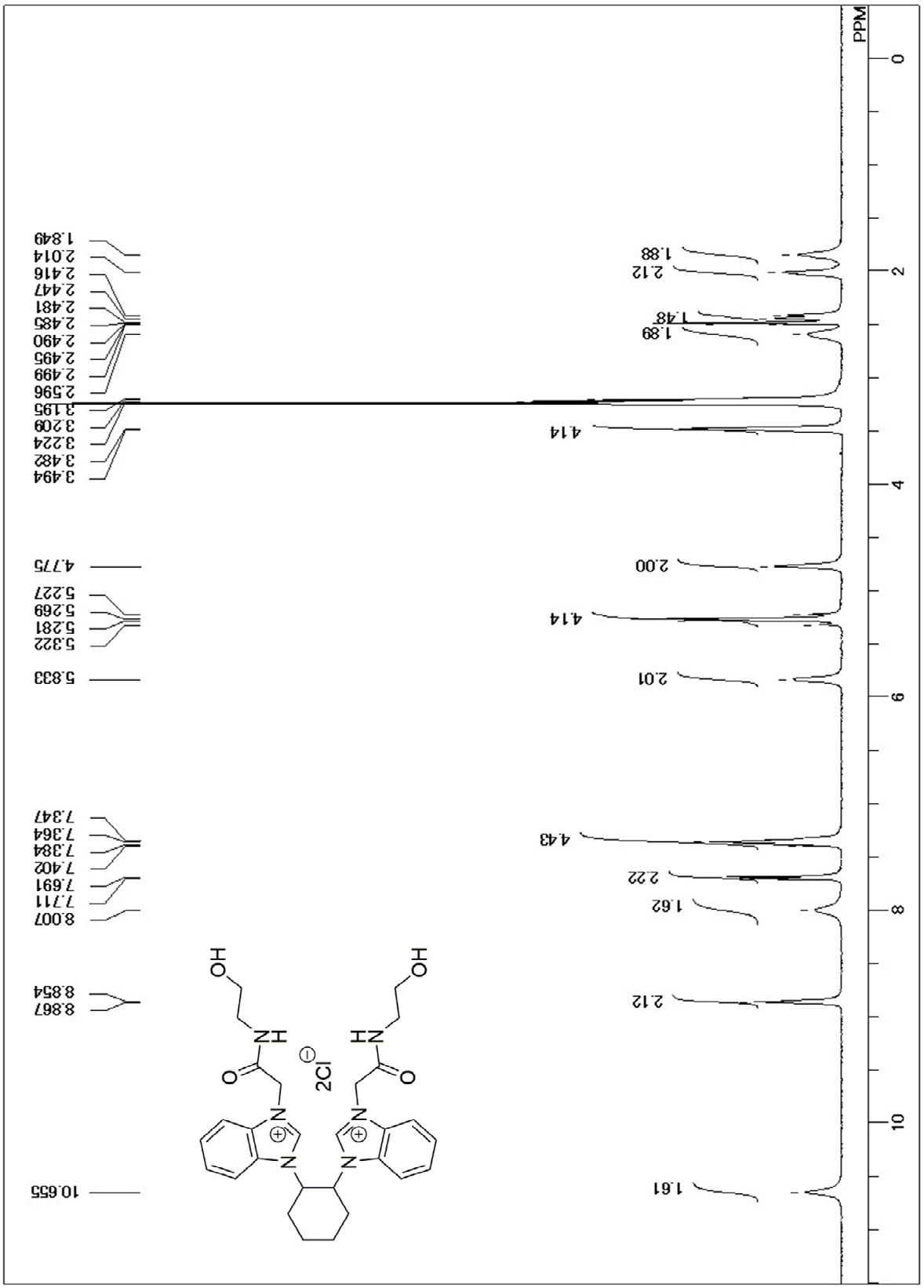

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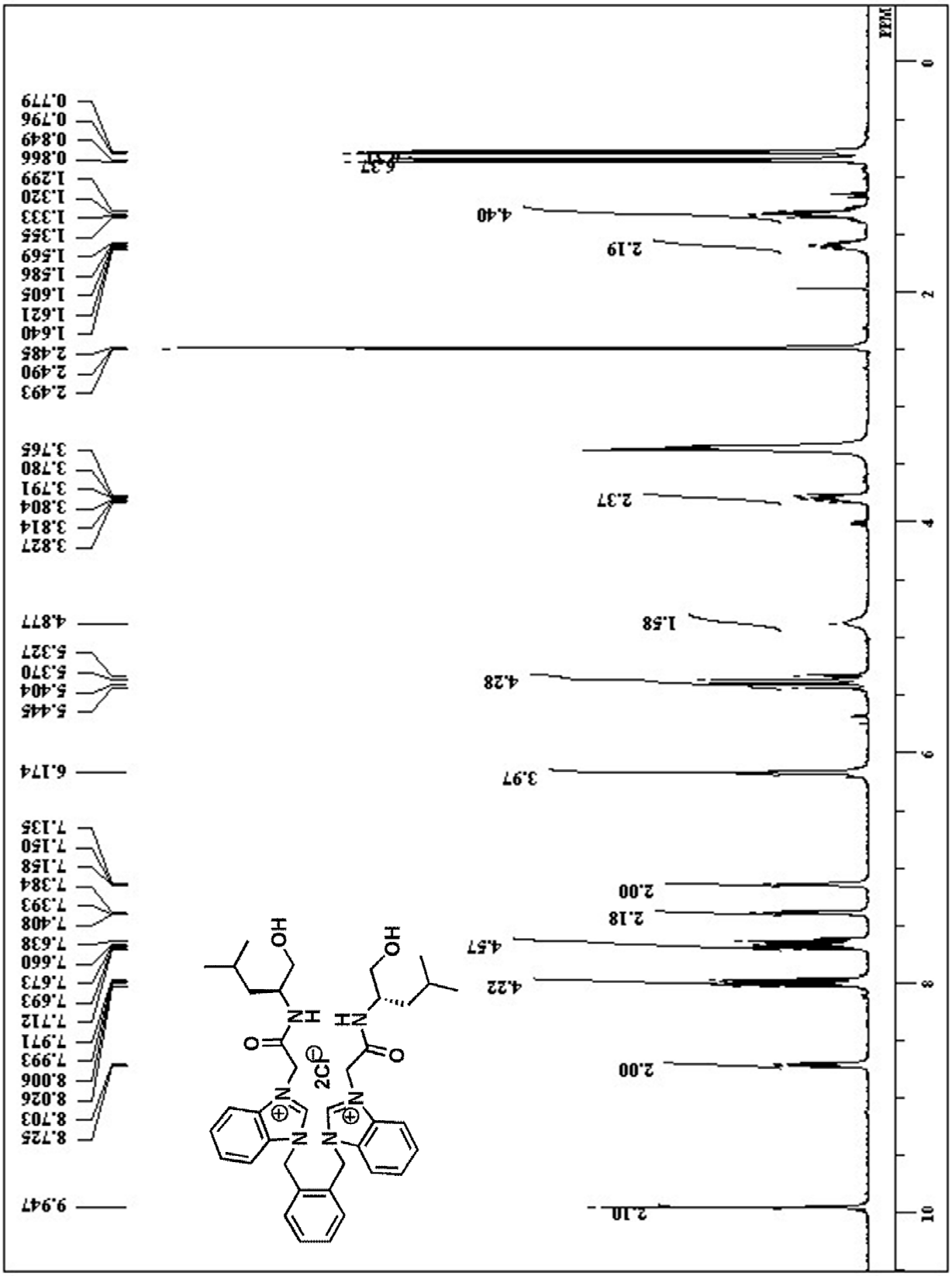

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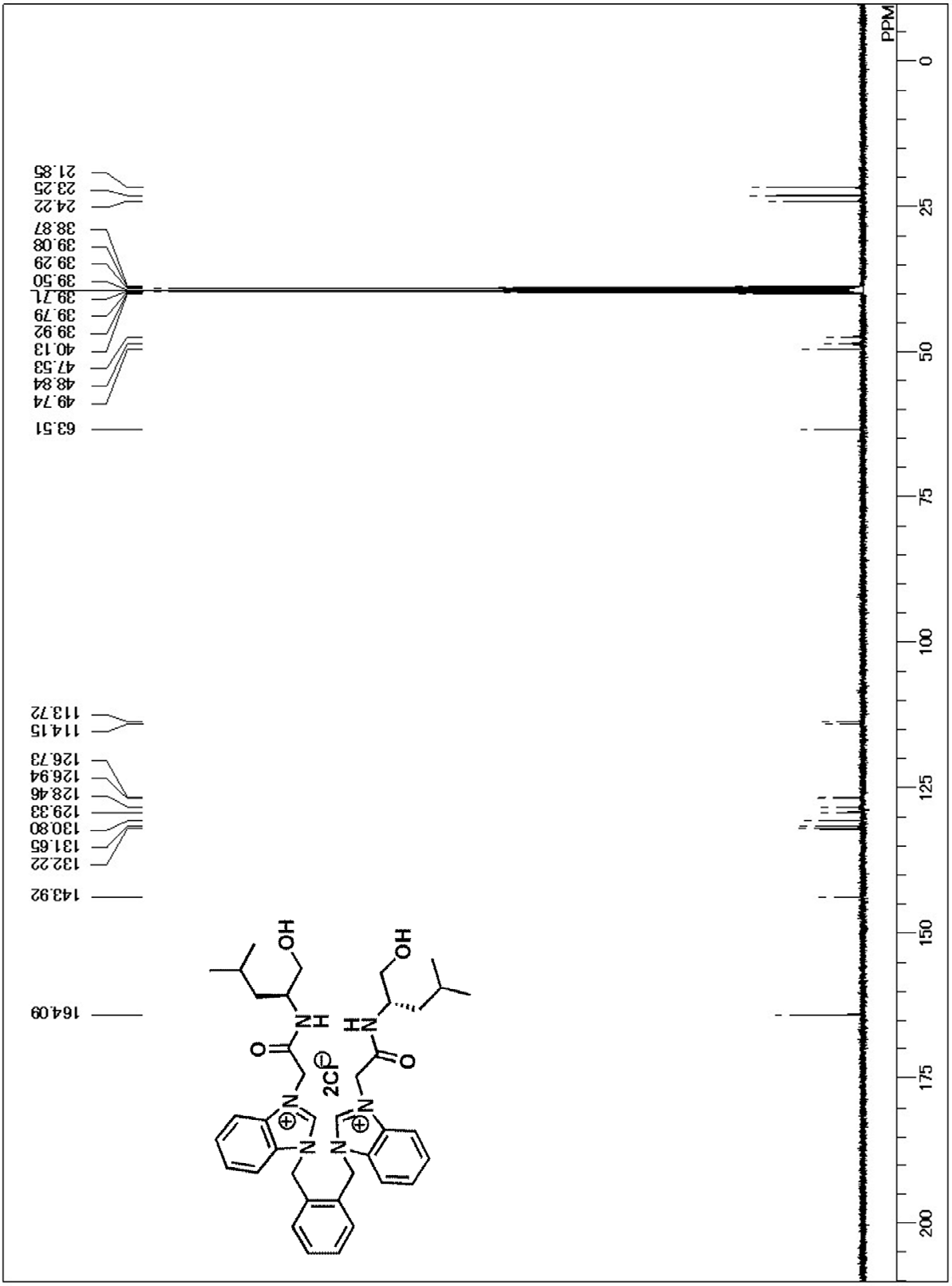


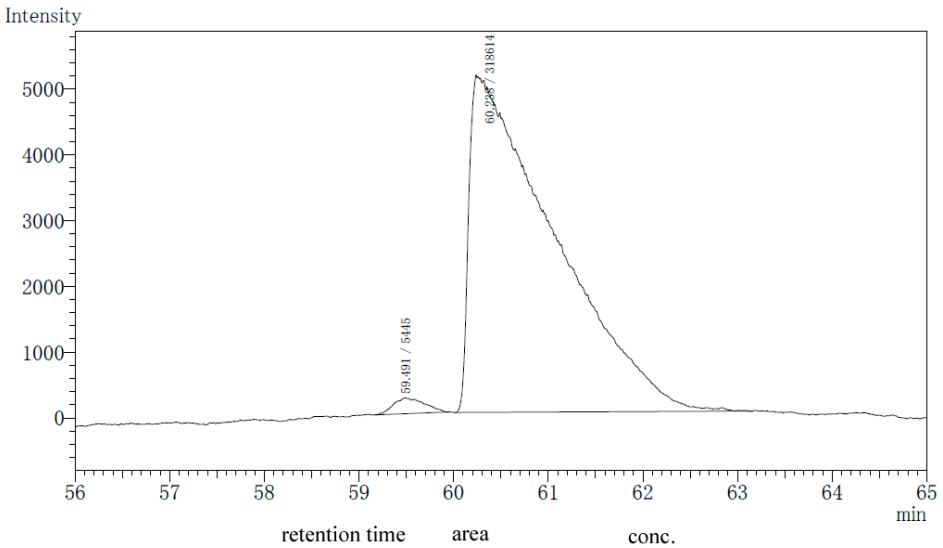
## 2. Selected Chiral GC Traces in the ACA Reaction

The enantiomeric excess of 1,4-adducts in the ACA reaction was determined by chiral GLC according to the previously reported procedures..

| | | |
|---|---|---|
| **3-Ethylcyclohexanone (4):** page 17 | GC: Supelco γ-Dex225<br>70 °C, $N_2$ gas<br>Linear velocity of 27.5 cm/s | Rt = 59 min (*S*)<br>Rt = 61 min (*R*) |
| **4-Ethylnonan-2-one (6):** pages 18-20 | GC: Supelco γ-Dex225<br>80 °C, $N_2$ gas<br>Linear velocity of 27.5 cm/s | Rt = 57 min (*R*)<br>Rt = 59 min (*S*) |
| **4-Ethyl-5-methylhexan-2-one (8):** page 21 | GC: Supelco γ-Dex225<br>65 °C, $N_2$ gas<br>Linear velocity of 27.5 cm/s | Rt = 40 min (*S*)<br>Rt = 42 min (*R*) |
| **4-Phenyl-2-hexanone** (**10**): page 22 | GC: Supelco γ-Dex225<br>105 °C, $N_2$ gas<br>Linear velocity of 27.5 cm/s | Rt = 53 min (*S*)<br>Rt = 56 min (*R*) |
| **1,3-Diphenylpentan-1-one** (**12**): page 23 | LC: AD-H<br>IPA/Hexane=2/98<br>Flow rate: 1.0 mL/min, | Rt = 8 min (*S*)<br>Rt = 11 min (*R*) |

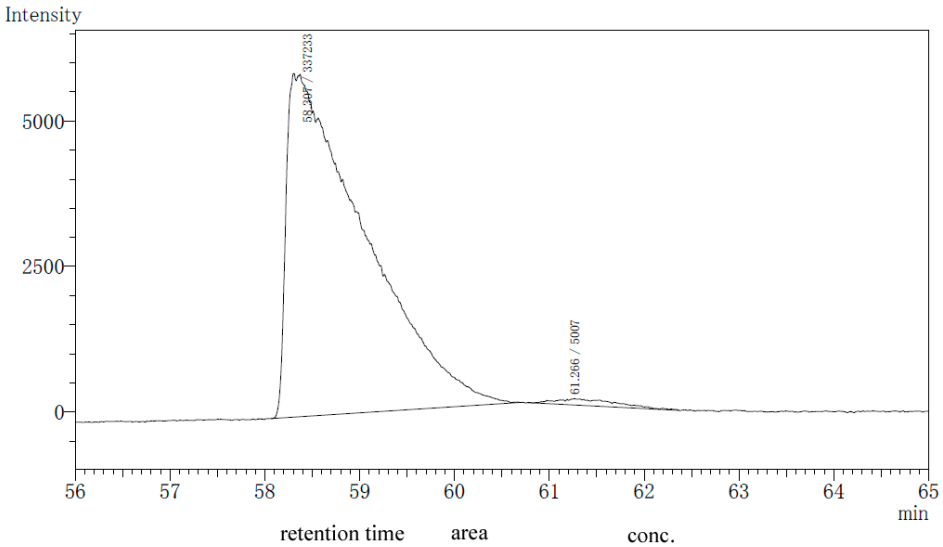
**3-Ethylcyclohexanone (4)**

Table 1, entry 2: (*R*)-**4**; 97% *ee*




| retention time | area | conc. |
|---|---|---|
| 59.491 | 5445 | 1.680 |
| 60.238 | 318614 | 98.320 |

Table 1, entry 5: (*S*)-**4**; 97% *ee*




| retention time | area | conc. |
|---|---|---|
| 58.307 | 337233 | 98.537 |
| 61.266 | 5007 | 1.463 |

**4-Ethylnonan-2-one (6)**

Table 6, entry 3: (*R*)-**6**; 86% *ee*

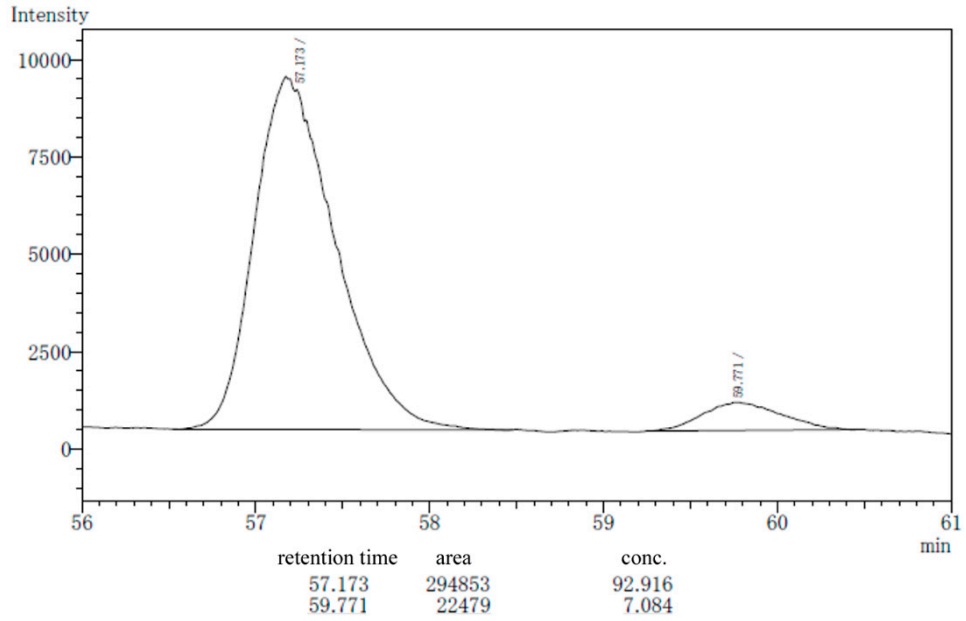



Table 6, entry 6 [Table 5, entry 14]: (*S*)-**6**; 70% *ee*

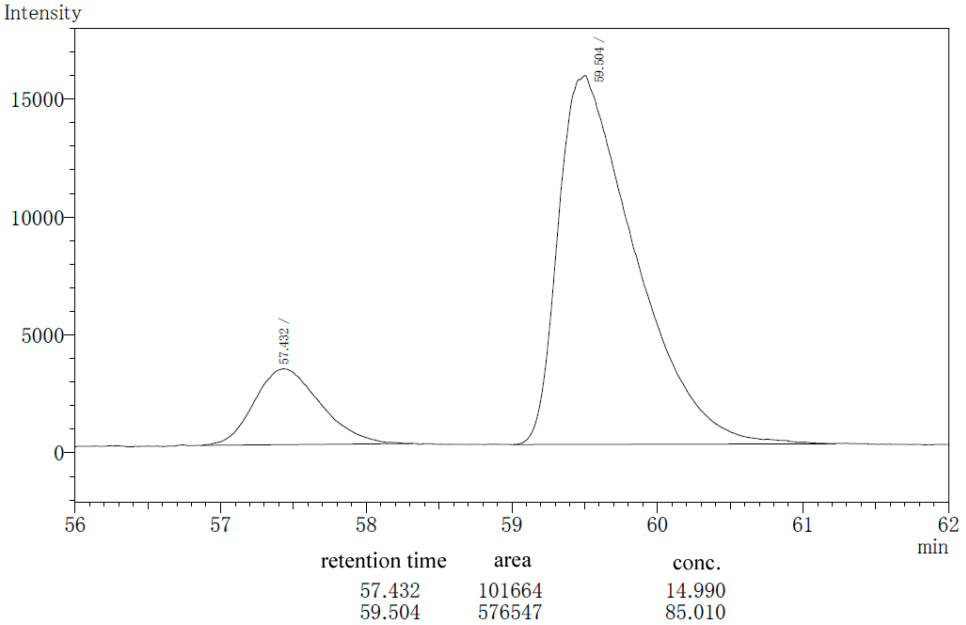
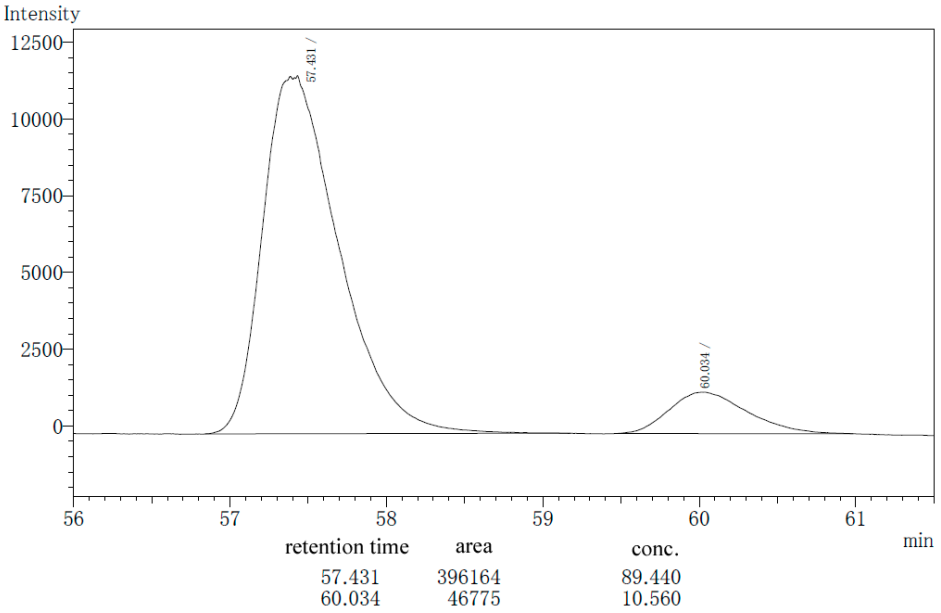
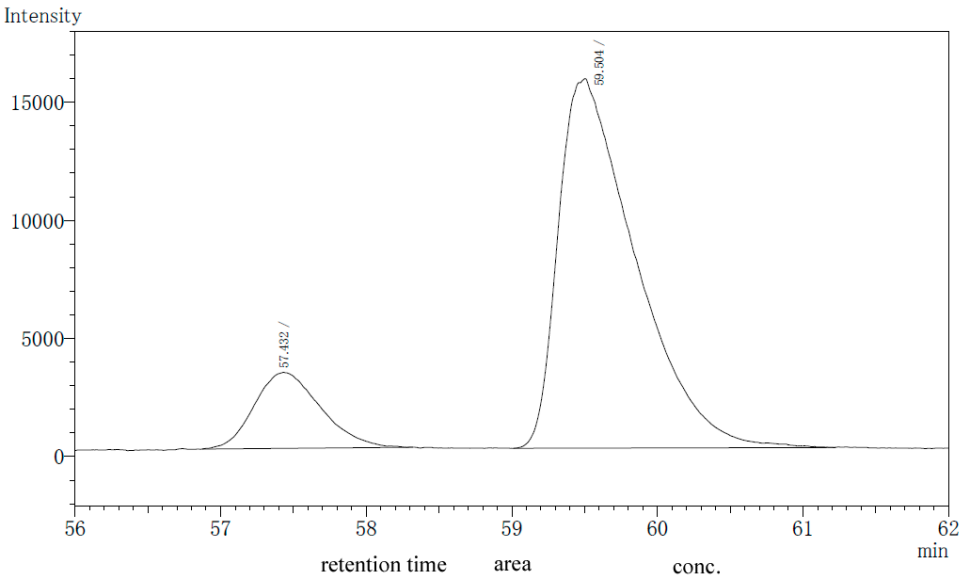


Table 7, entry 1 [Table 5, entry 6]: (*R*)-**6**; 78% *ee*



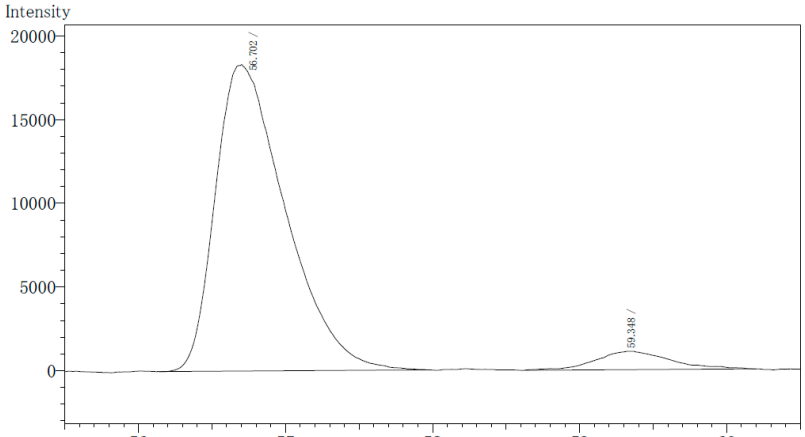

| retention time | area | conc. |
|---|---|---|
| 57.431 | 396164 | 89.440 |
| 60.034 | 46775 | 10.560 |

Table 7, entry 2 [Table 5, entry 14]: (*S*)-**6**; 70% *ee*



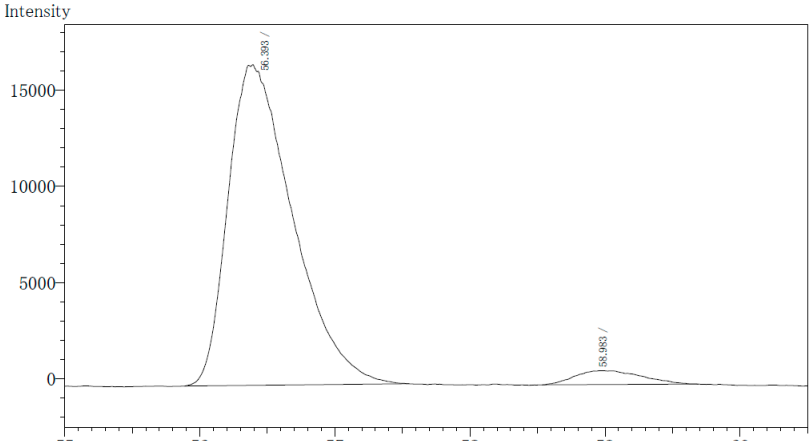

| retention time | area | conc. |
|---|---|---|
| 57.432 | 101664 | 14.990 |
| 59.504 | 576547 | 85.010 |

Table 8, entry 1: (*R*)-**6**; 88% *ee*



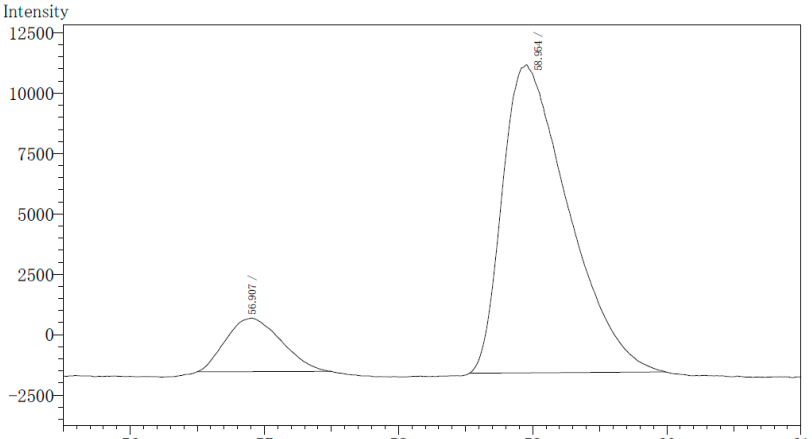

| retention time | area | conc. |
|---|---|---|
| 56.702 | 607221 | 94.009 |
| 59.348 | 38696 | 5.991 |

Table 8, entry 4: (*R*)-**6**; 91% *ee*




| retention time | area | conc. |
|---|---|---|
| 56.393 | 555126 | 95.730 |
| 58.983 | 24762 | 4.270 |

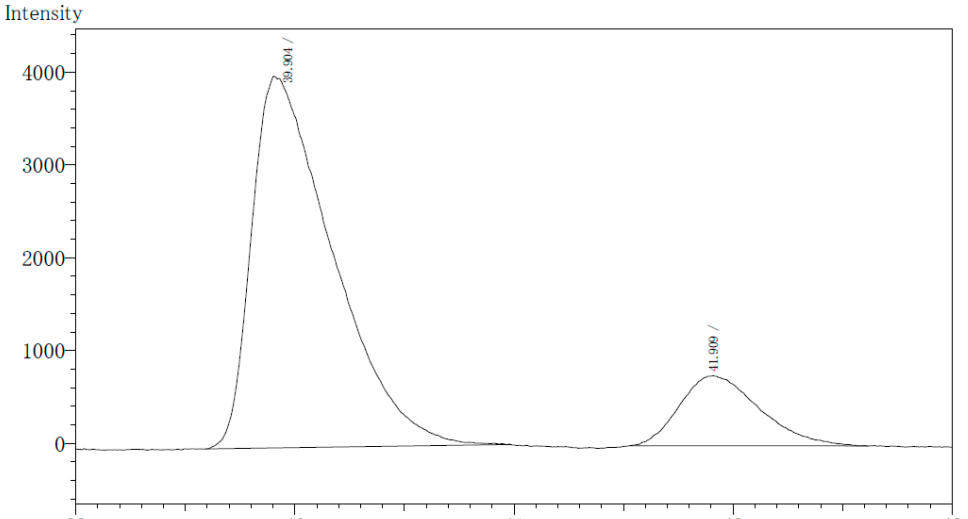
Table 8, entry 5: (*S*)-**6**; 75% *ee*




| retention time | area | conc. |
|---|---|---|
| 56.907 | 63549 | 12.683 |
| 58.954 | 437495 | 87.317 |

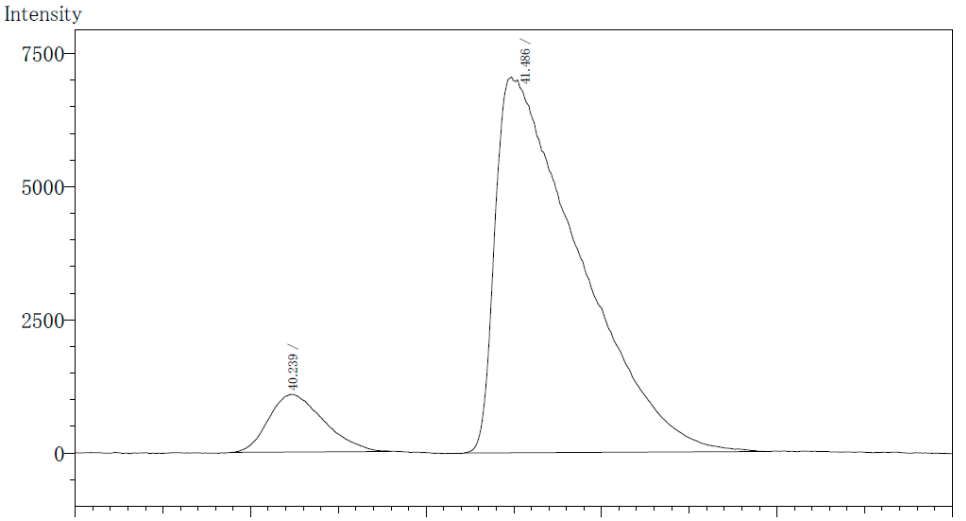
**4-Ethyl-5-methylhexan-2-one (8)**

Table 7, entry 3: (*S*)-**8**; 69% *ee*




| retention time | area | conc. |
|---|---|---|
| 39.904 | 102943 | 84.311 |
| 41.909 | 19157 | 15.689 |

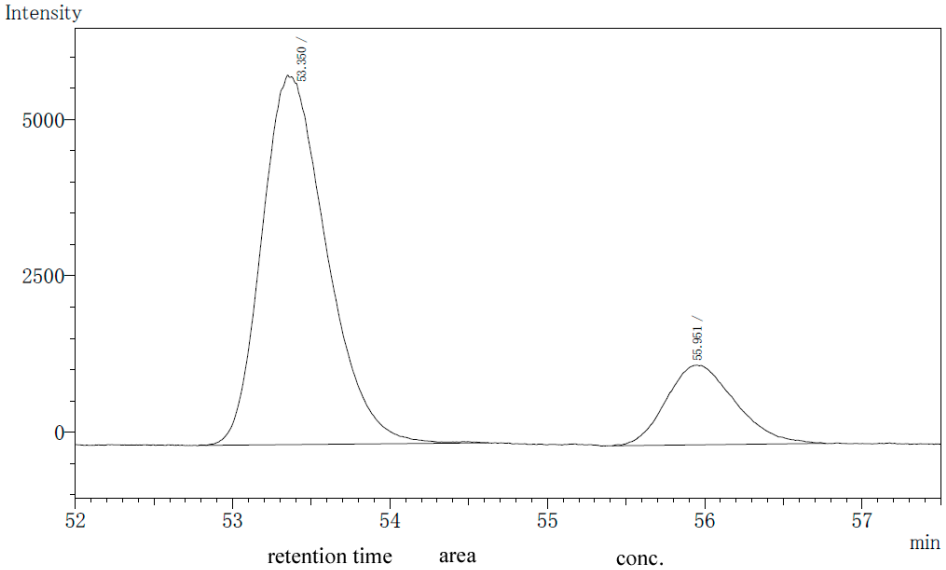
Table 7, entry 4: (*R*)-**8**; 82% *ee*




| retention time | area | conc. |
|---|---|---|
| 40.239 | 23553 | 9.111 |
| 41.486 | 234960 | 90.889 |

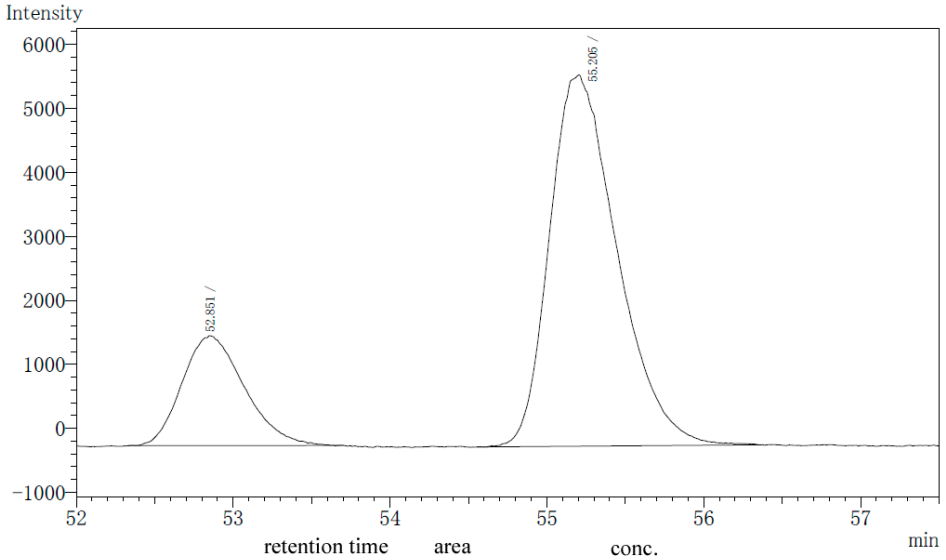
**4-Phenyl-2-hexanone (10)**

Table 7, entry 7: (*S*)-**10**; 63% *ee*




| retention time | area | conc. |
|---|---|---|
| 53.350 | 169182 | 81.325 |
| 55.951 | 38851 | 18.675 |

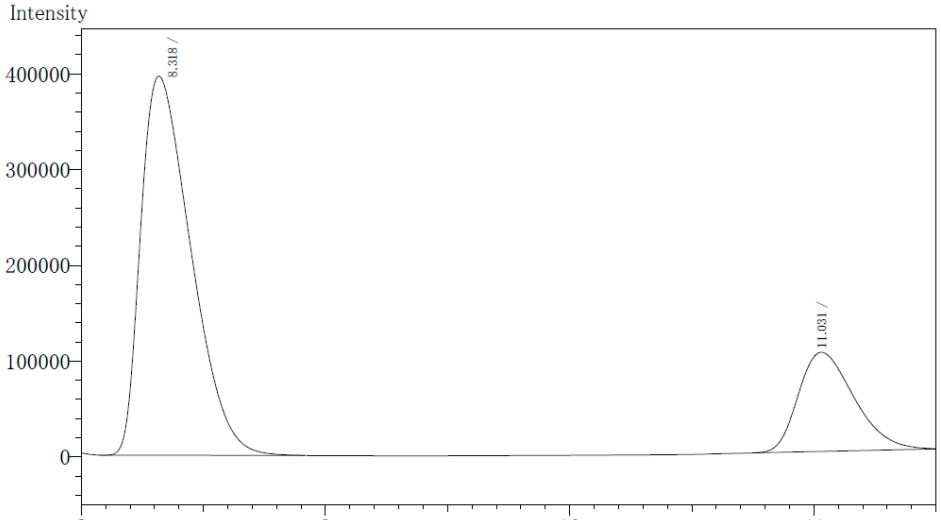
Table 7, entry 8: (*R*)-**10**; 57% *ee*




| retention time | area | conc. |
|---|---|---|
| 52.851 | 47325 | 21.413 |
| 55.205 | 173680 | 78.587 |

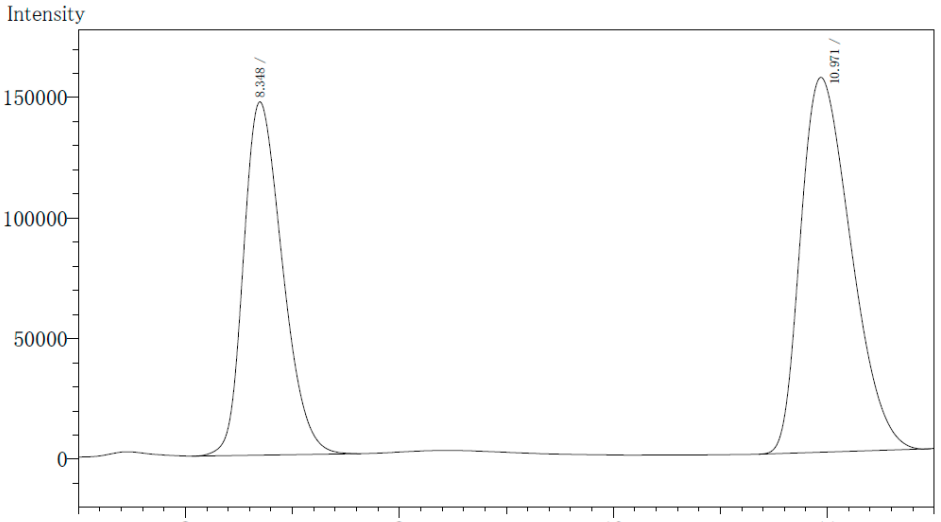
**1,3-Diphenylpentan-1-one (12)**

Table 7, entry 9: (*S*)-**12**; 55% *ee*




| retention time | area | conc. |
|---|---|---|
| 8.318 | 5647780 | 77.503 |
| 11.031 | 1639364 | 22.497 |

Table 7, entry 10: (*R*)-**12**; 15% *ee*




| retention time | area | conc. |
|---|---|---|
| 8.348 | 1853778 | 42.204 |
| 10.971 | 2538613 | 57.796 |

**Table S1.** Systematic studies on several reaction parameters in the CuOAc-catalyzed conjugate addition reaction of acyclic enone **5** yielding (*R*)-**6**[a]

| Entry | CuOAc/**L1** [mol%] | Solv. | Temp./Time | Yield [%] | *ee* [%] |
|---|---|---|---|---|---|
| 1[b] | 6/4.5 | THF | r.t./3 h | 78 | 60 |
| 2 | 4.5/6 | THF | r.t./3 h | 72 | 56 |
| 3 | 6/6 | THF | r.t./3 h | 87 | 56 |
| 4 | 4/4 | THF | r.t./3 h | 79 | 60 |
| 5 | 3/3 | THF | r.t./3 h | 78 | 59 |
| 6 | 4/4 | 2-MeTHF | r.t./3 h | 56 | 40 |
| 7 | 4/4 | 1,4-dioxane | r.t./3 h | 13 | 13 |
| 8 | 4/4 | $Et_2O$ | r.t./3 h | 46 | 39 |
| 9 | 4/4 | $^t$BuOMe | r.t./3 h | 33 | 42 |
| 10 | 4/4 | DME | r.t./3 h | 43 | 70 |
| 11 | 4/4 | diglyme | r.t./3 h | 43 | 75 |
| 12 | 4/4 | toluene | r.t./3 h | 43 | 41 |
| 13 | 4/4 | DME | r.t./24 h | 84 | 66 |
| 14 | 4/4 | DME | 0°C/24 h | 49 | 78 |
| 15 | 4/4 | DME | 0°C/48 h | 78 | 73 |
| 16 | 4/4 | DME | -10°C/48 h | 69 | 75 |
| 17[c] | 4/4 | DME | 0°C/48 h | 60 | 62 |
| 18[d] | 4/4 | DME | 0°C/48 h | 74 | 77 |

[a] To a solution of CuOAc and (*rac*; *S*,*S*)-**L1** in solvent (9 mL), $Et_2Zn$ (3 mmol) was added first, then **5** (1 mmol). The reaction mixture was stirred at room temperature for 3 h. [b] The same data is shown in Table 2, entry 5. [c] DME (6 mL) was used. [d] DME (12 mL) was used.

**Table S2.** Systematic studies on several reaction parameters in the $Cu(ClO_4)_2$-catalyzed conjugate addition reaction of acyclic enone **5** yielding (*S*)-**6**[a]

| Entry | $Cu(ClO_4)_2$/**L1** [mol%] | Solv. | Temp./Time | Yield [%] | *ee* [%] |
|---|---|---|---|---|---|
| 1[b] | 6/4.5 | THF | r.t./3 h | 31 | 50 |
| 2 | 4.5/6 | THF | r.t./3 h | 44 | 34 |
| 3 | 6/6 | THF | r.t./3 h | 29 | 34 |
| 4 | 6/3 | THF | r.t./3 h | 39 | 46 |
| 5 | 6/3 | 2-MeTHF | r.t./3 h | 26 | 43 |
| 6 | 6/3 | 1,4-dioxane | r.t./3 h | <5 | <1 |
| 7 | 6/3 | $Et_2O$ | r.t./3 h | <5 | *ent*-6 |
| 8 | 6/3 | $^t$BuOMe | r.t./3 h | 55 | 9 |
| 9 | 6/3 | DME | r.t./3 h | 28 | 34 |
| 10 | 6/3 | diglyme | r.t./3 h | 22 | <1 |
| 11 | 6/3 | toluene | r.t./3 h | 15 | 18 |
| 12 | 6/3 | THF | r.t./24 h | 49 | 54 |
| 13 | 6/3 | THF | 0°C/24 h | 89 | 70 |
| 14 | 6/3 | THF | -5°C/24 h | 82 | 67 |
| 15 | 6/3 | THF | -10°C/24 h | 90 | 69 |
| 16 | 6/3 | THF | -20°C/24 h | 87 | 66 |
| 17[c] | 6/3 | DME | 0°C/24 h | 93 | 69 |
| 18[d] | 6/3 | DME | 0°C/24 h | 94 | 71 |

[a] To a solution of $Cu(ClO_4)_2$ and (*rac*; *S*,*S*)-**L1** in solvent (9 mL), $Et_2Zn$ (3 mmol) was added first, then **5** (1 mmol). The reaction mixture was stirred at room temperature for 3 h. [b] The same data is shown in Table 1, entry 11. [c] DME (6 mL) was used. [d] DME (12 mL) was used.