Electronic Supplementary Information

# Iridium-catalyzed rection of enones with alcohols affording 1,3-Diketones

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## Table of Contents

## General

GC analysis was performed with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). $^1$H and $^{13}$C NMR were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with $Me_4Si$ as the internal standard. The products were characterized by $^1$H NMR, $^{13}$C NMR, DEPT, and GC-MS. The yields of products were estimated from the peak areas based on the internal standard technique using GC.
Compounds **3a**,[1] **3b**,[2] **3c**,[3] **3d**,[4] **3e**,[5] **3f**, [6] **3g**, [7] **3h**,[1] **3i**,[8] **3j**,[9] and **3k**[10] were reported previously.

## Experimental Procedure

**A typical reaction was carried out as follows (Table 1 , entry 1):** A mixture of $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), P(*n*-Oct)$_3$ (74 mg, 0.2 mmol), *i*-PrOH (180 mg, 3 mmol), $Na_2SO_3$ (50 mg, 0.4 mmol), **1a** (481 mg, 5 mmol) and **2a** (108 mg, 1 mmol) in *p*-xylene (1 mL) was stirred at 120 °C for 15h under Ar in a pressure tube. The conversions and yields of products ware estimated from peak areas based on internal standard using GC and the product **3a** was obtained in 82% yield. The product (**3a**) was isolated by column chromatography (230-400 mesh silica gel, *n*-Hexane/ethyl acetate = 40 / 1) in 71% yield (144 mg). Product was further purified by preparative-scale GPC system equipped with Jaigel-1H (i.d. 20 × 600 mm) and Jaigel-1H (i.d. 20 × 600 mm) columns using $CHCl_3$ as an eluent.

**The labeling experiment with 1a and benzaldehyde using *i*-PrOH-d$_8$ was carried out as follows (Eq.2):** A mixture of $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), P(*n*-Oct)$_3$ (74 mg, 0.2 mmol), *i*-PrOH-*d*$_8$ (204 mg, 3 mmol), **1a** (481 mg, 5 mmol) and benzaldehyde (106 mg, 1 mmol) in *p*-xylene (1 mL) was stirred at 120 °C for 15h under Ar in a pressure tube. The product (a 1: 1 mixture of **3a** and **3a'**) was isolated by column chromatography (230-400 mesh silica gel, *n*-Hexane/ethyl acetate = 40 / 1) in 62% yield (126 mg). Product was further purified by preparative-scale GPC system equipped with Jaigel-1H (i.d. 20 × 600 mm) and Jaigel-2H (i.d. 20 × 600 mm) columns using $CHCl_3$ as an eluent. The deuterium incorporation of the product was estimated by $^1$H, $^{13}$C NMR, HMQC, HMBC and GC-MS spectra.

**3a'**: $^1$H-NMR ($CDCl_3$) δ 1.73-2.61 (m, 7H), 4.34-4.36 (m, 1H), 7.43-7.91 (m, 5H); $^{13}$C-NMR ($CDCl_3$) δ 22.9 (CDH), 27.2 ($CH_2$), 30.0 ($CH_2$), 42.2 ($CH_2$), 58.7 (CH), 128.5 (CH), 128.6 (CH), 133.2 (CH), 136.5 (C), 197.5 (CO), 208.6 (CO); IR (neat) 2935, 1710, 1675, 1598, 1581 cm$^{-1}$; GCMS (EI, 70eV, relative intensity) *m/z* 203 ($M^+$, 20), 175 (5), 156 (1), 145 (4), 131 (3), 116 (2), 105 (100), 91 (2), 77 (47), 51 (12); HRMS (EI) (*m/z*) calcd for $C_{13}H_{13}DO_2$: 203.1054, found: 203.1057.

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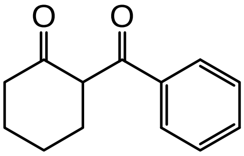

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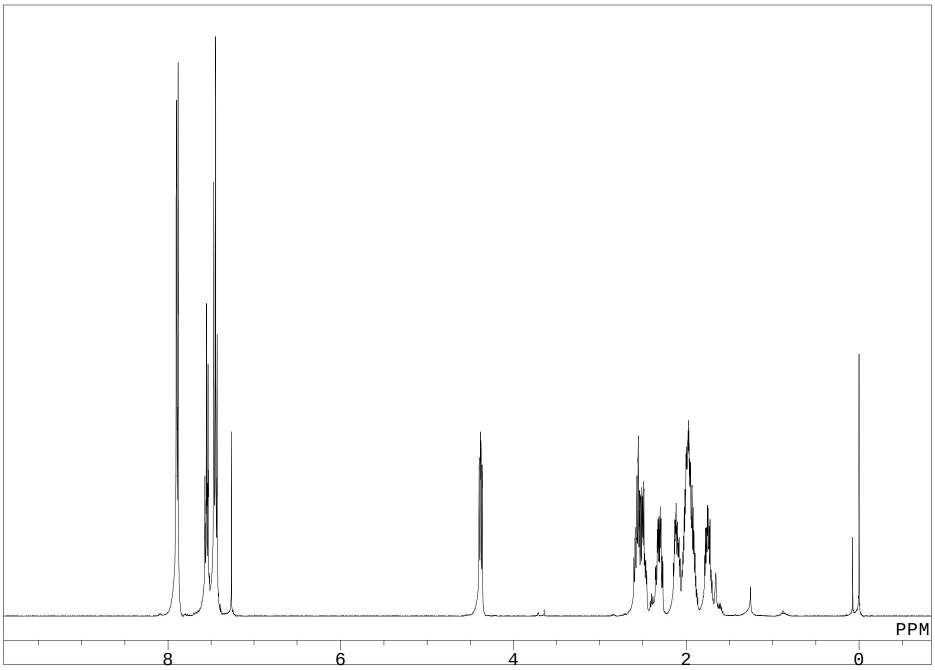

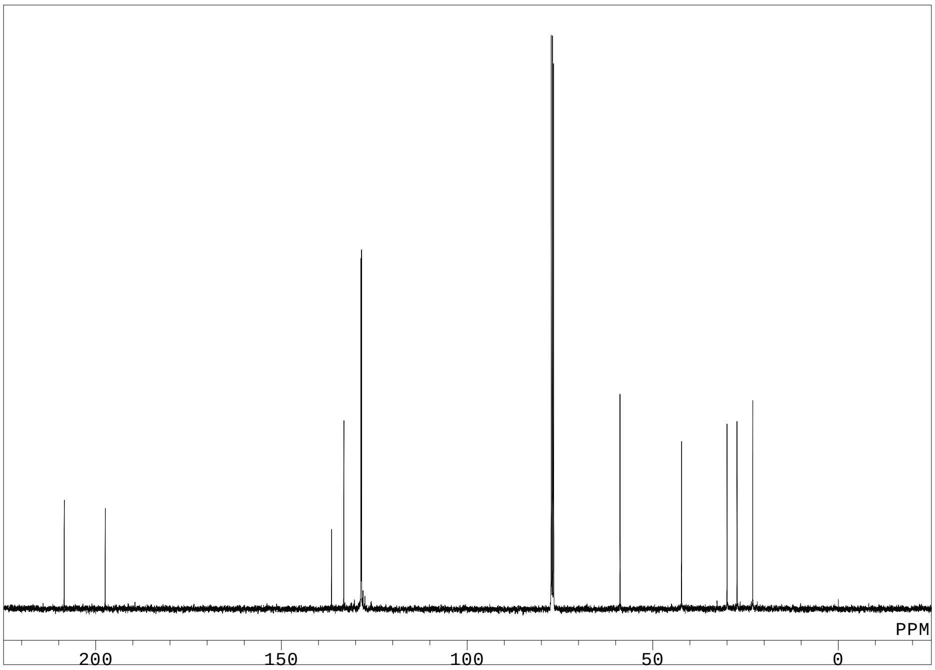

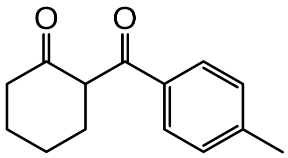

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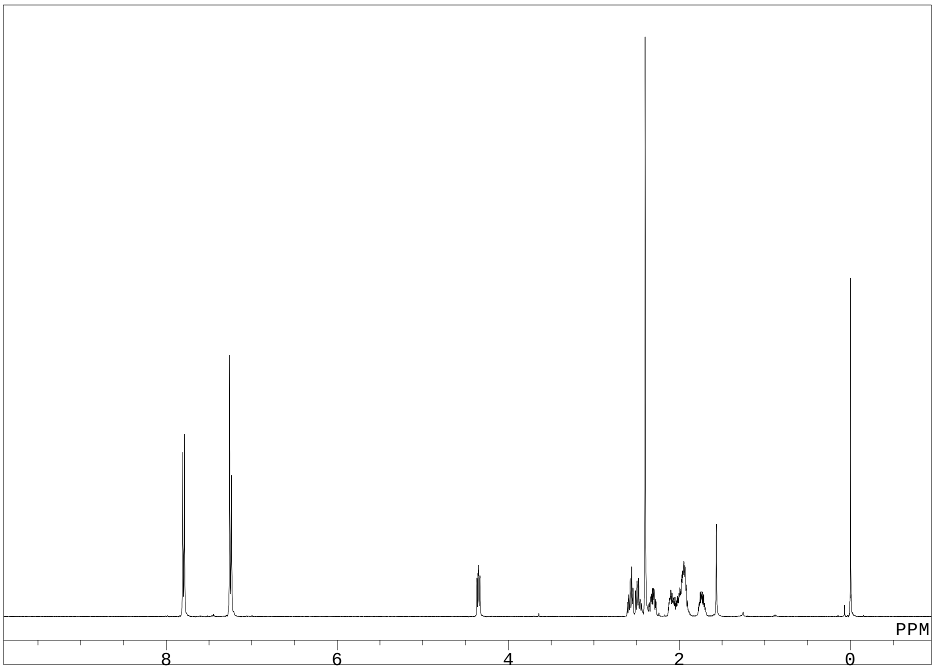

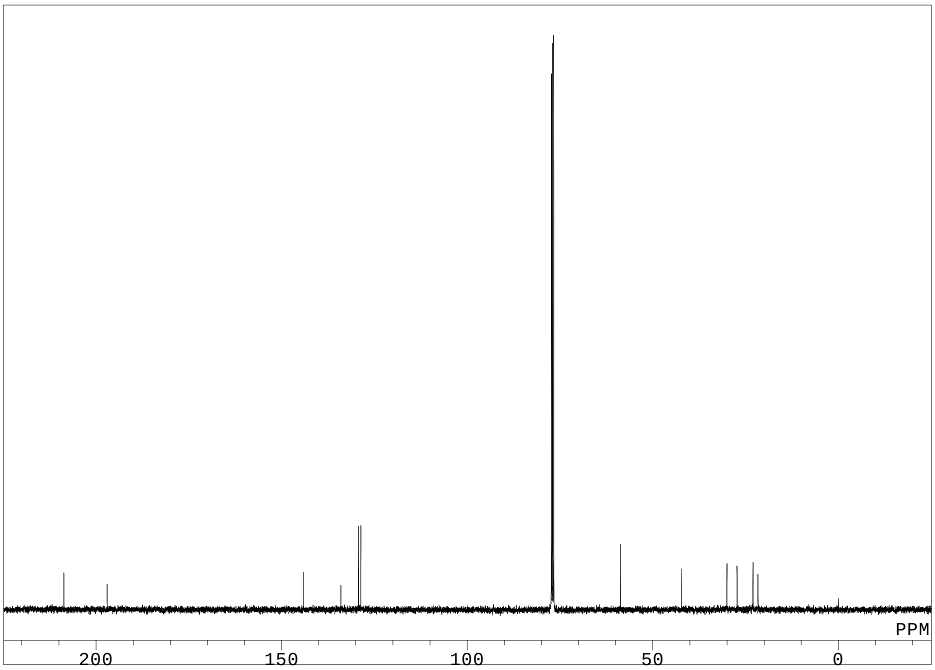

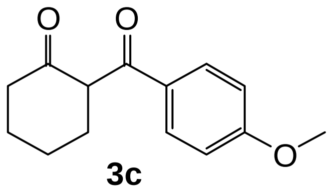

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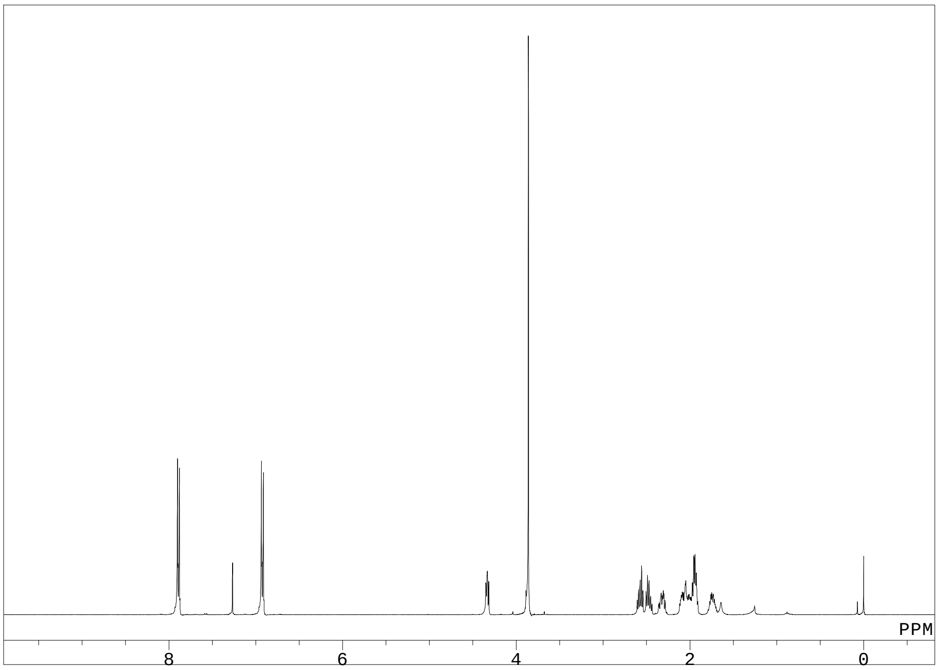

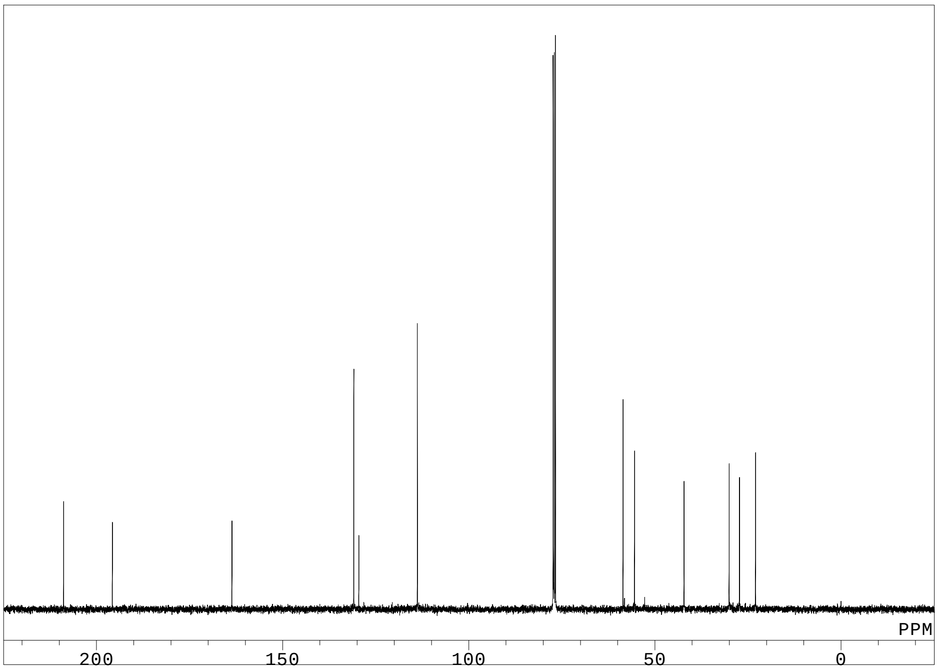

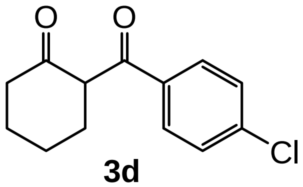

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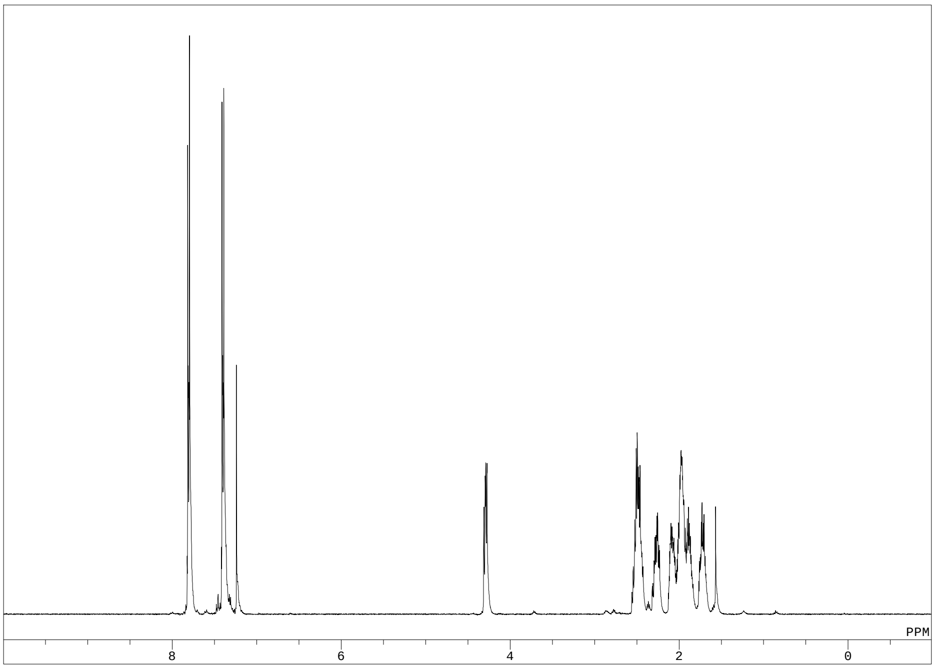

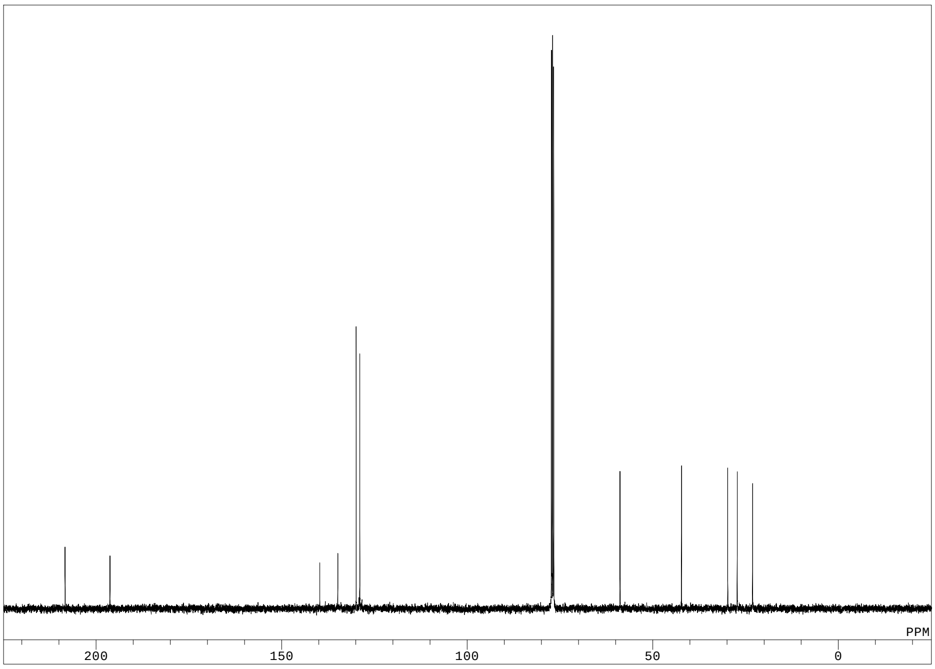

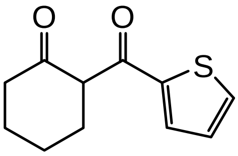

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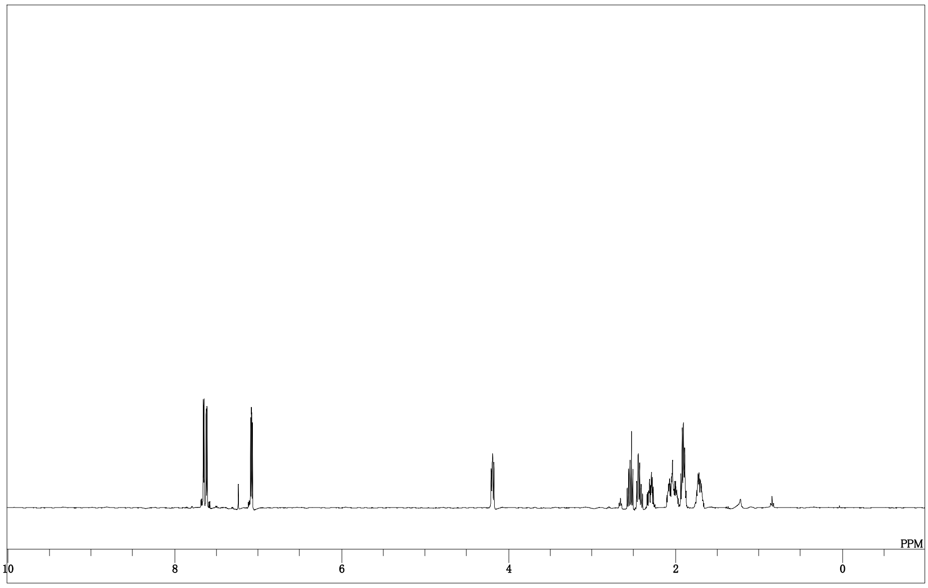

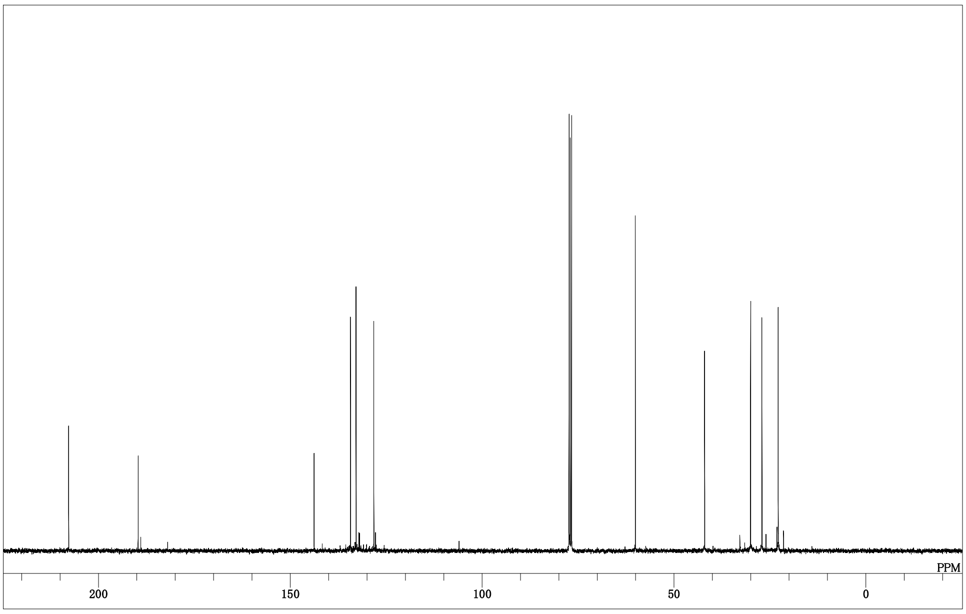

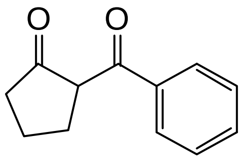

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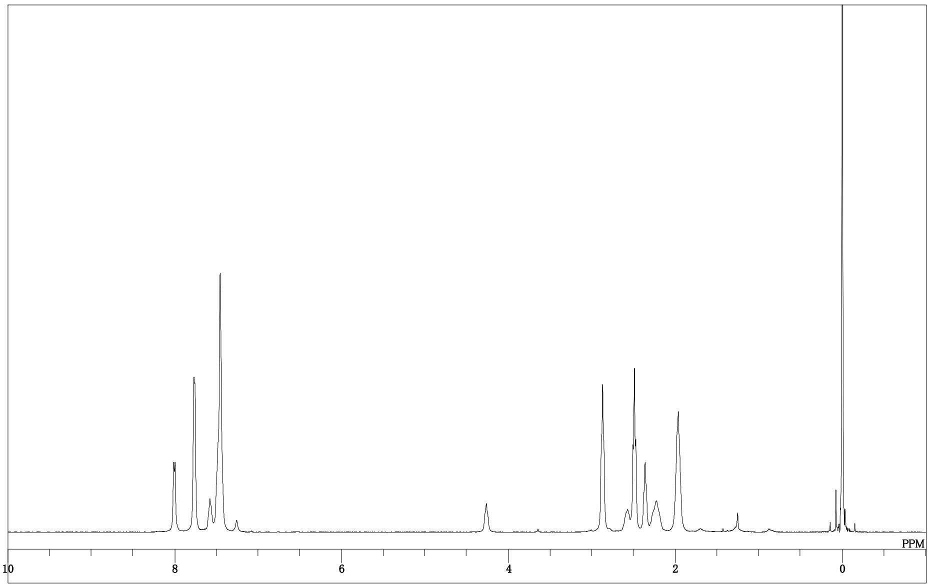

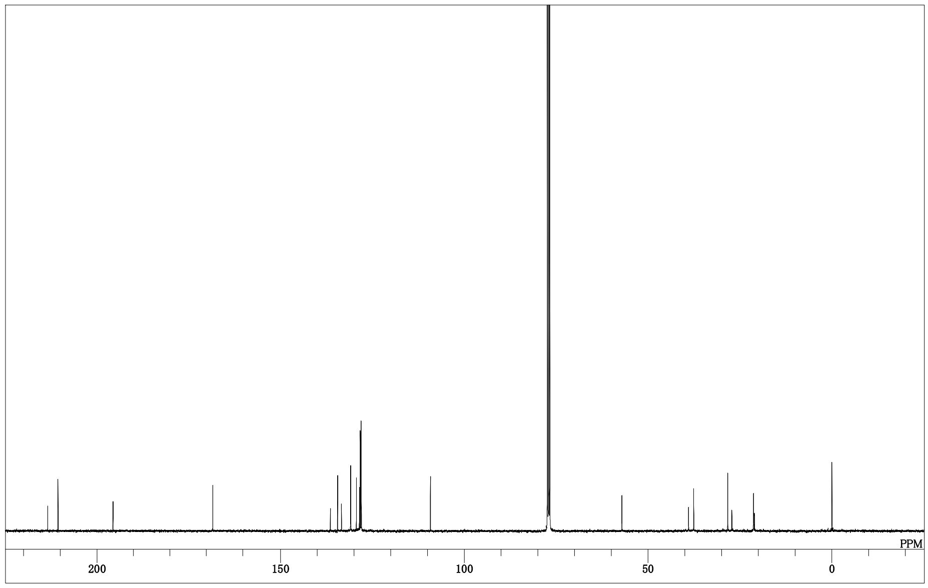

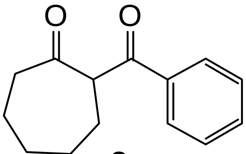

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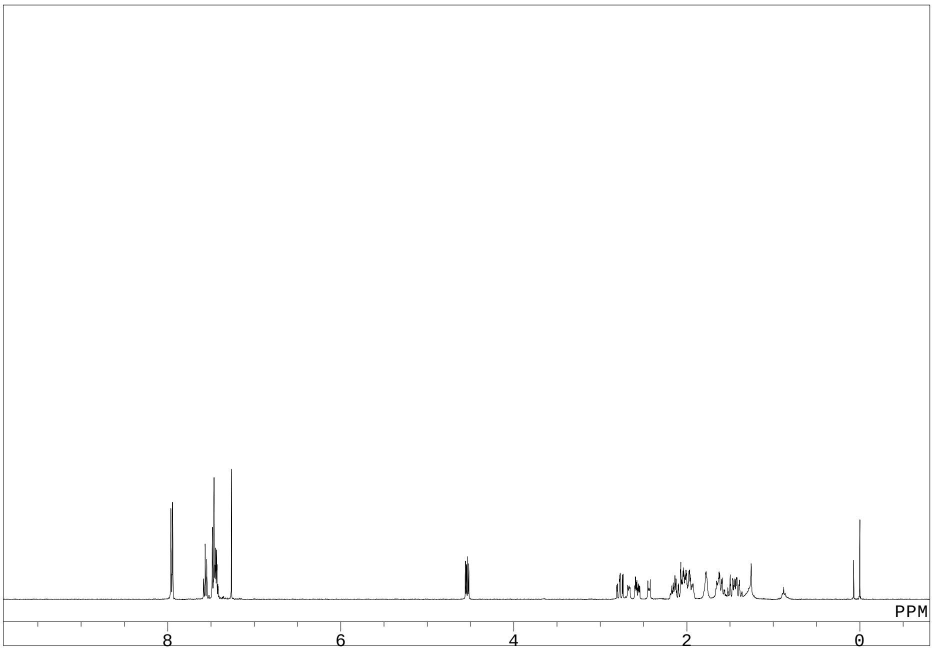

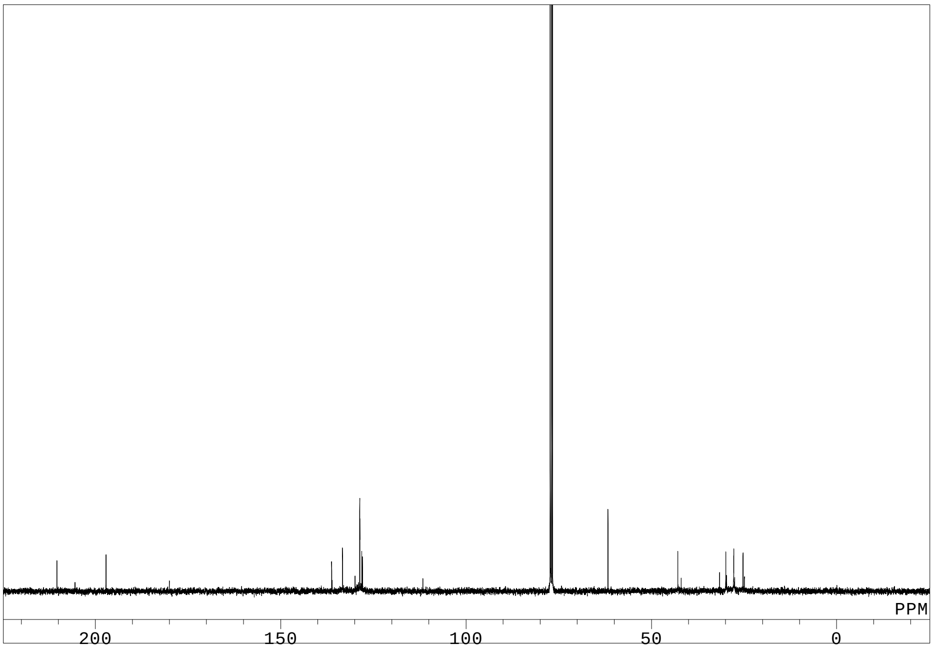

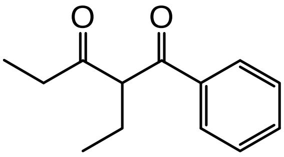

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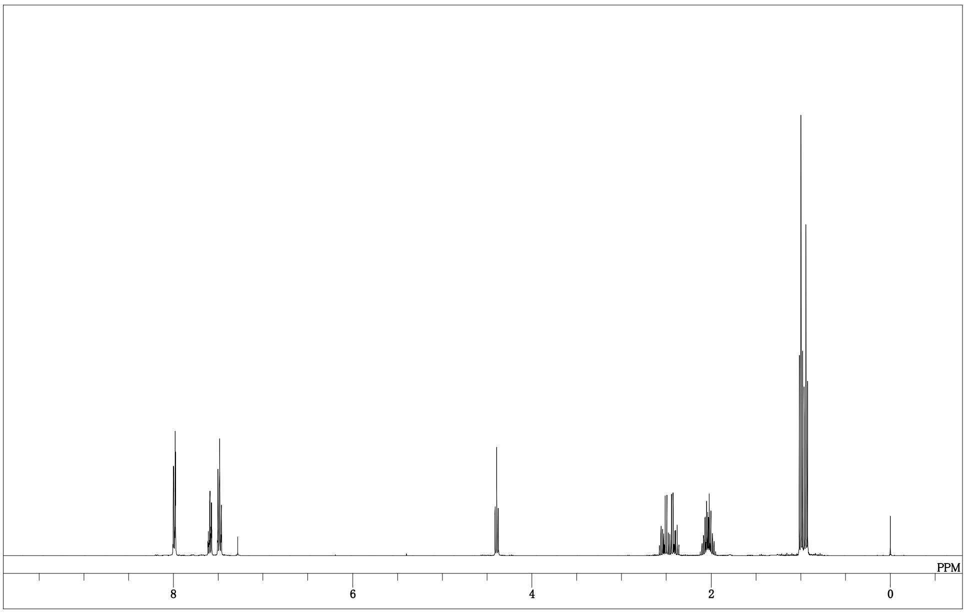

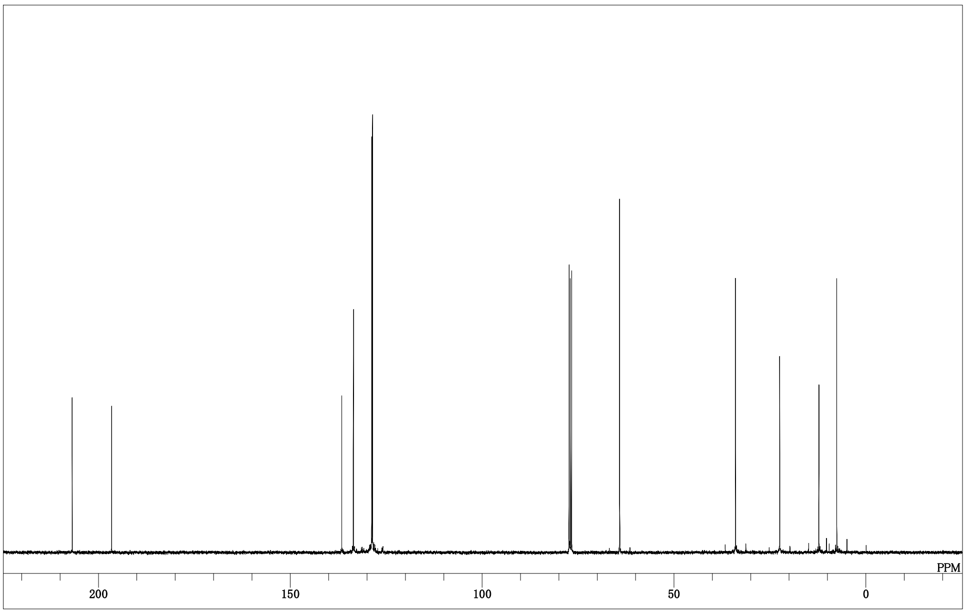

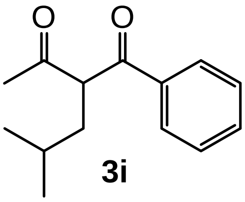

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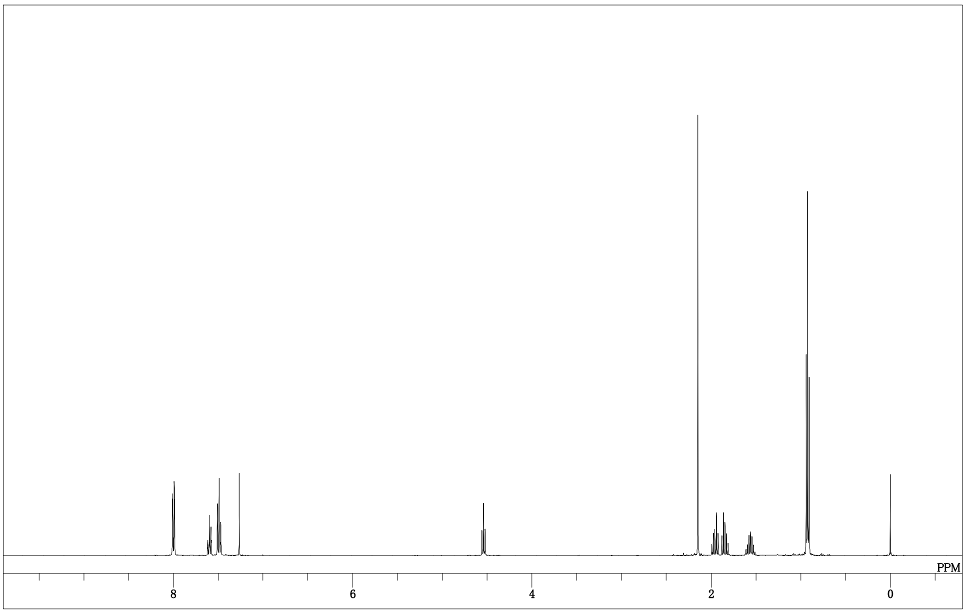

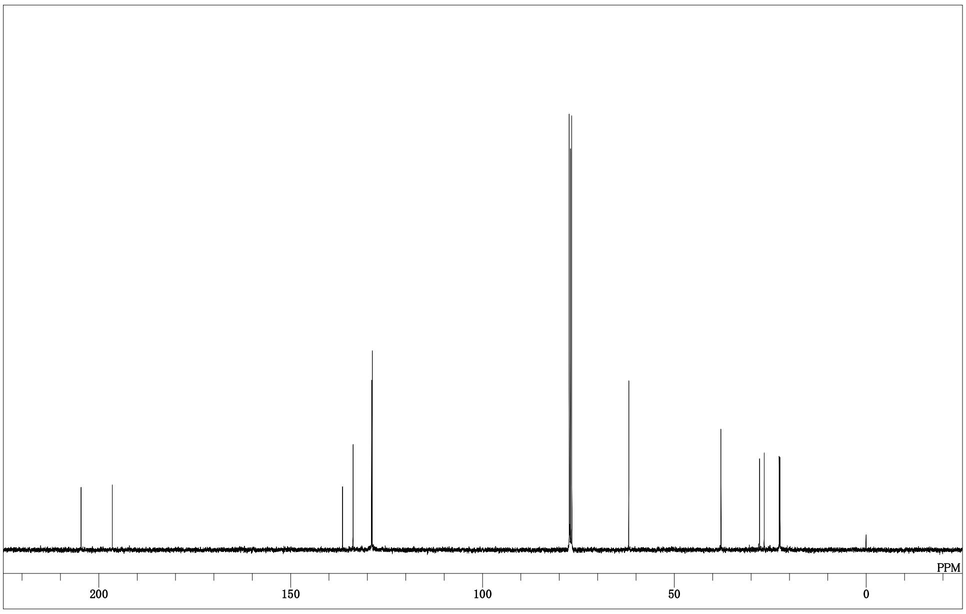

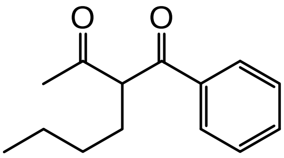

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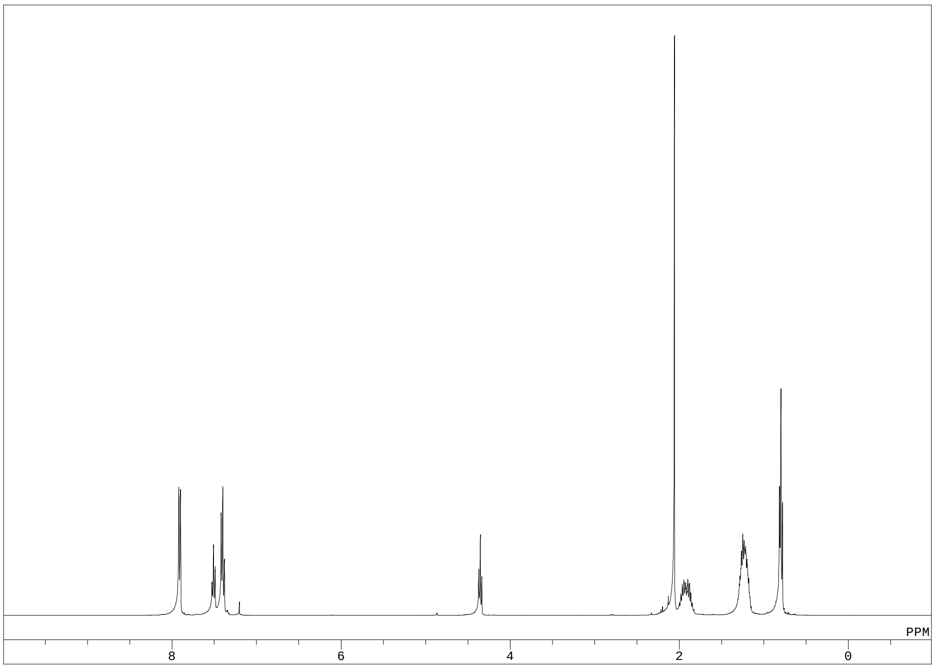

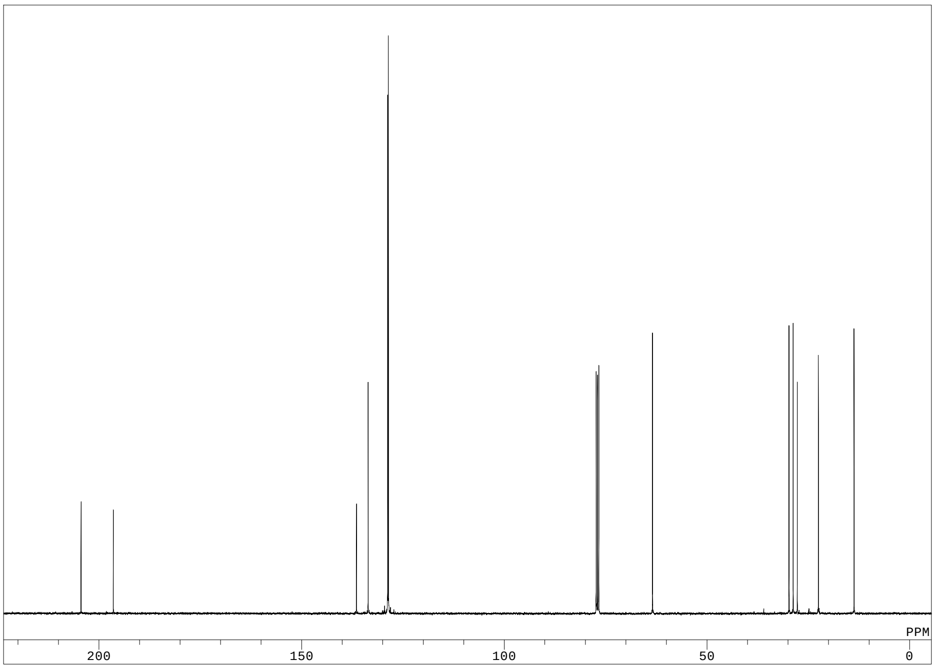

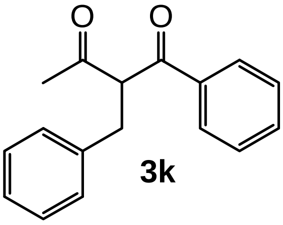

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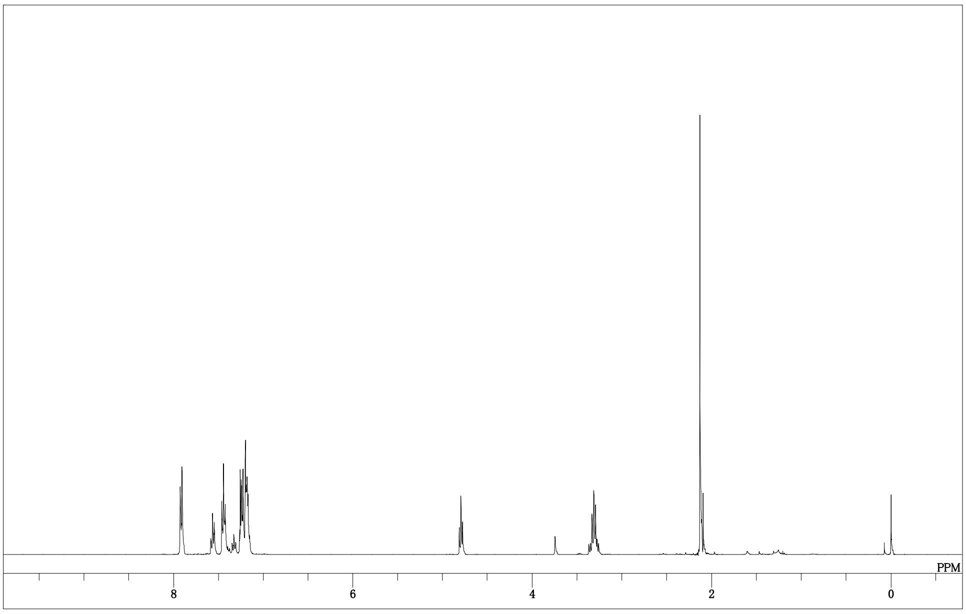

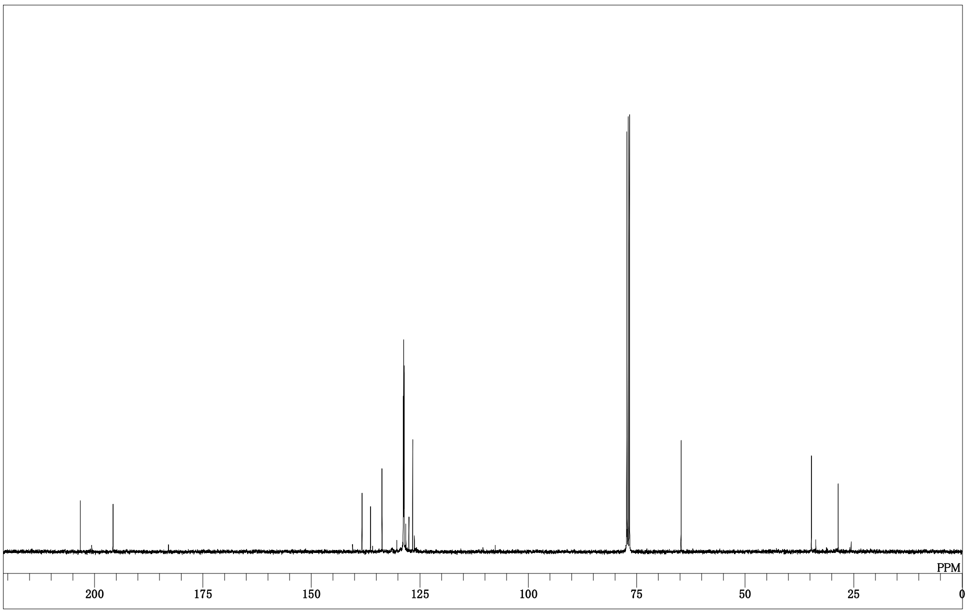

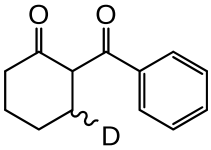

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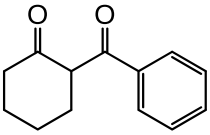

**3a'** **3a**

1 : 1