Electronic Supporting information for

Iridium-catalyzed selective α-methylation of ketones with methanol

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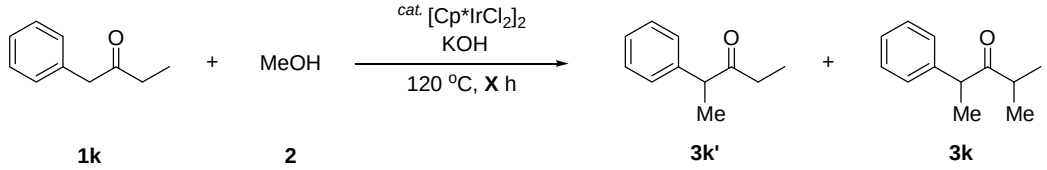
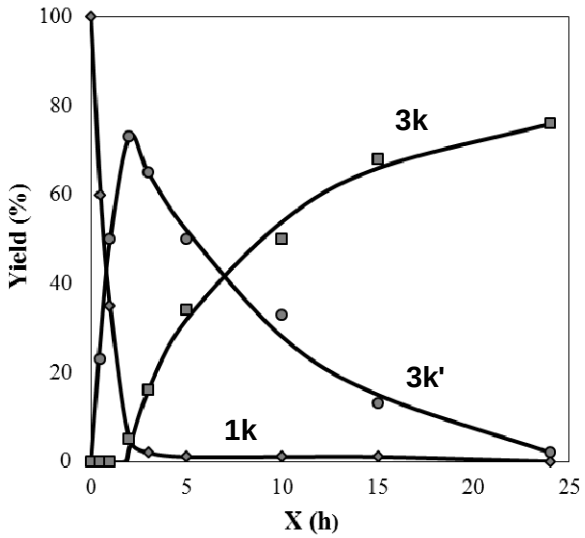
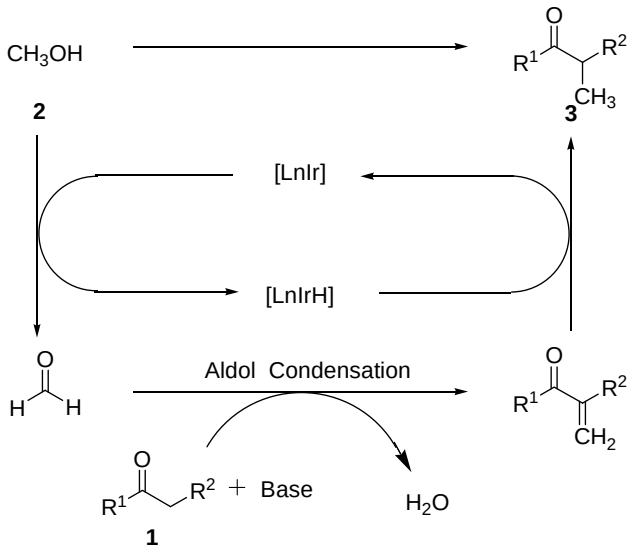
Fig. S1. Time-course monitoring of reaction of **1k** with **2**.





A mixture of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol), KOH (28 mg, 0.5 mmol), **1k** (0.15 g, 1.0 mmol) and **2** (1.5 mL) was stirred at 120 °C for **X** h under Ar in a pressure tube. The conversions and yields of products were estimated from peak areas based on an internal standard using GC.

Fig. S2. Plausible reaction pathway



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, 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**,[1] **3h**,[7] **3j**,[8] **3k**,[9] **3k'**,[9] **6a**,[10] **6b**,[11] **6c**,[12] **8aa**,[13] **8ba**,[14] **8ca**,[15] **8la**,[16] **8ab**,[17] **8ac**,[18] **8ad**,[19] and **8ae**,[20] were reported previously.

Experimental Procedure

A typical reaction was carried out as follows (Table 1, entry 1): A mixture of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol), KOH (28 mg, 0.5 mmol), **1a** (0.12 g, 1 mmol) and **2** (1.5 mL) was stirred at 120 °C for 15 h under Ar in a pressure tube. The conversions and yields of products were estimated from peak areas based on an internal standard using GC and the product **3a** was obtained in 87 % yield. The product **3a** was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane / ethyl acetate = 30 / 1) in 83 % yield (123 mg).

A typical reaction was carried out as follows (Table 2, entry 1): A mixture of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol), KOH (28 mg, 0.5 mmol), **5a** (0.12 g, 1 mmol) and **2** (1.5 mL) was stirred at 120 °C for 15 h under Ar in a pressure tube. The product **6a** was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane / ethyl acetate = 30 / 1) in 76 % yield (100 mg).

A typical reaction was carried out as follows (Table 4, entry 1): A mixture of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol), KOH (28 mg, 0.5 mmol), **1a** (0.24 g, 2 mmol), **2** (1 mL) and **7a** (0.11 g, 1 mmol) was stirred at 140 °C for 15 h under Ar. The product **8aa** was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane / ethyl acetate = 30 / 1) and Kugelrohr distillation (70 °C (pot) / 0.3 mmHg, 1 h) in 81 % yield (182 mg).

A typical reaction was carried out as follows (Table 4, entry 7): A mixture of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol), KOH (28 mg, 0.5 mmol), **1a** (0.14 g, 1.2 mmol) and **7d** (0.10 g, 1 mmol) was stirred at 80 °C for 2 h under Ar in a pressure tube. After **2** (1.5 mL) was added, the reaction mixture was stirred at 140 °C for 15 h under Ar. The product **8ad** was isolated by column chromatography (230-400 mesh silica gel, *n*-hexane) and Kugelrohr distillation (70 °C (pot) / 0.3 mmHg, 1 h) in 89 % yield (194 mg).

3i:^{1}H-NMR ($CDCl_3$) δ 2.78-2.64 (m, 2H), 1.67-1.61 (m, 1H), 1.33-1.19 (m, 13H), 1.09-1.03 (m, 9H) 0.89-0.86 (t, 3H); ^{13}C-NMR δ 218.6 (C), 44.4 (CH), 39.6 (CH), 33.2 (CH_2), 31.8 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 27.5 (CH_2), 22.6 (CH_3), 18.4 (CH_3), 18.2 (CH_3), 16.8 (CH_3), 14.0 (CH_3); IR (neat, cm^{-1}) : 2963, 2928, 2855, 1713, 1464, 1381, 1024; GC-MS (EI) *m/z* (relative intensity) 212 (5) $[M]^+$, 169 (6), 141 (7), 113 (2), 100 (74), 99 (18), 85 (73), 71 (95), 57 (80), 43 (100), 29 (12); HRMS (EI) *m/z* calcd for $C_{14}H_{28}$ $[M]^+$ 212.2146, found 212.2140.

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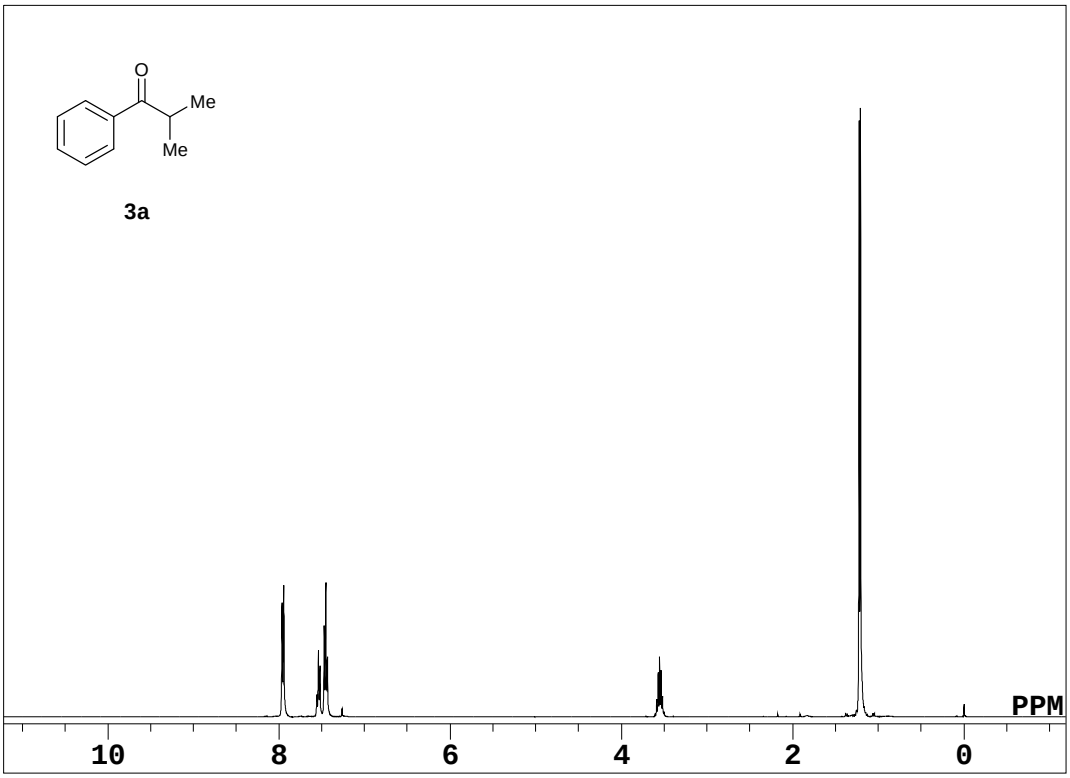
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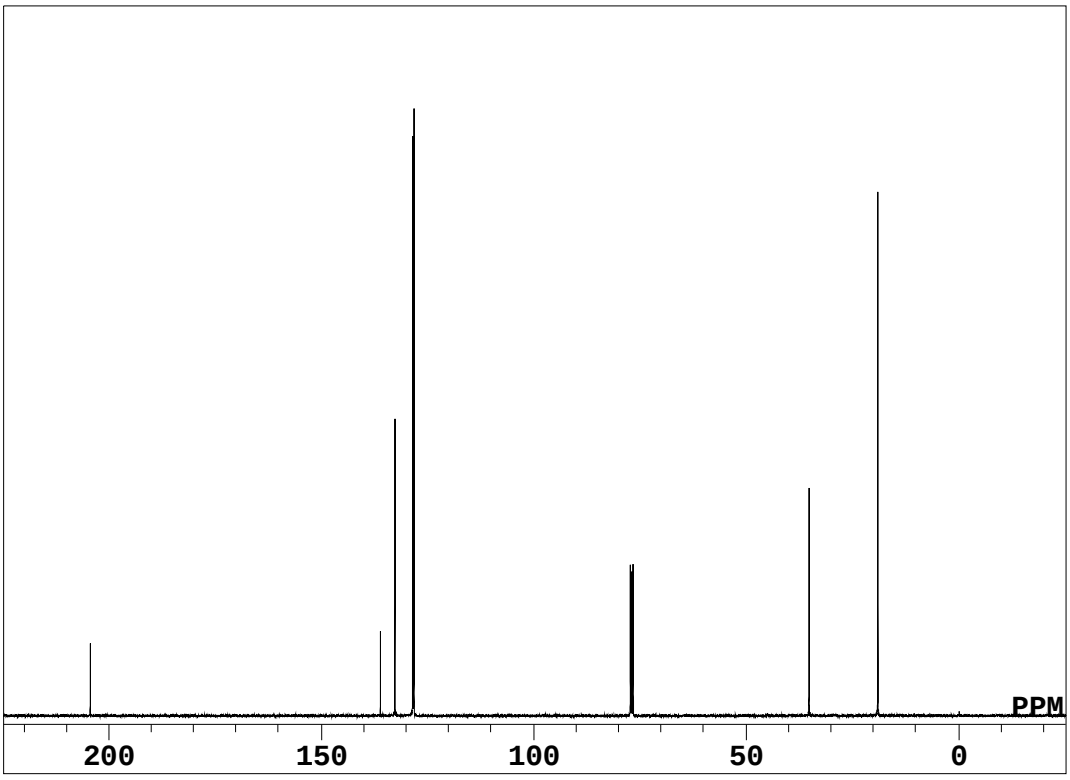
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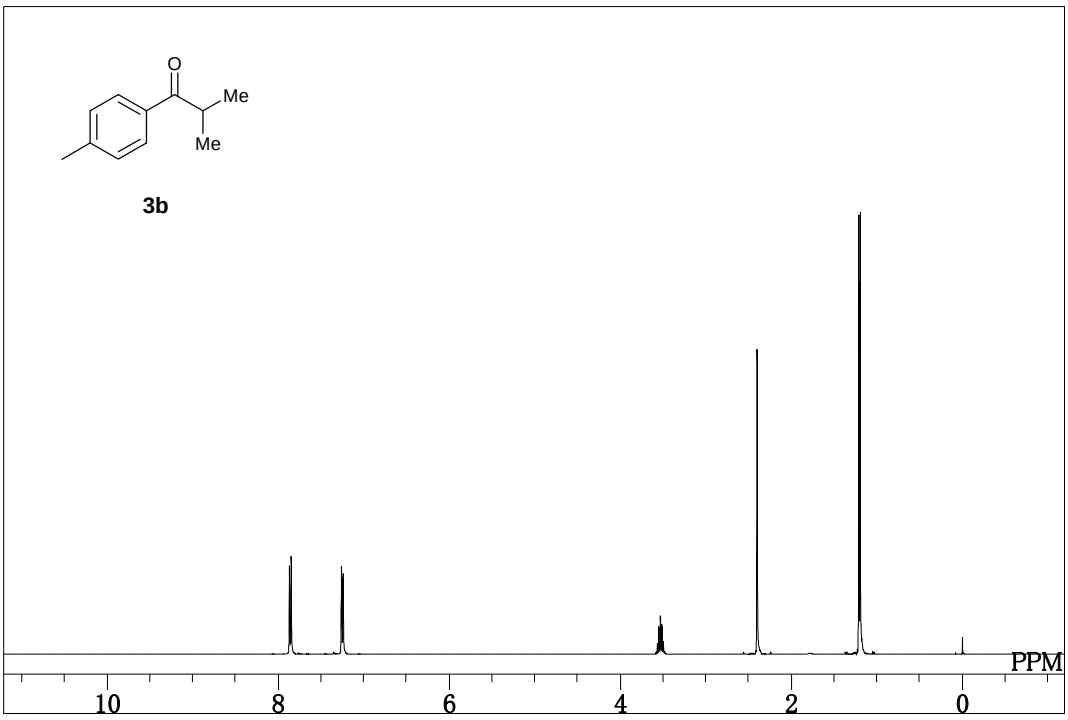
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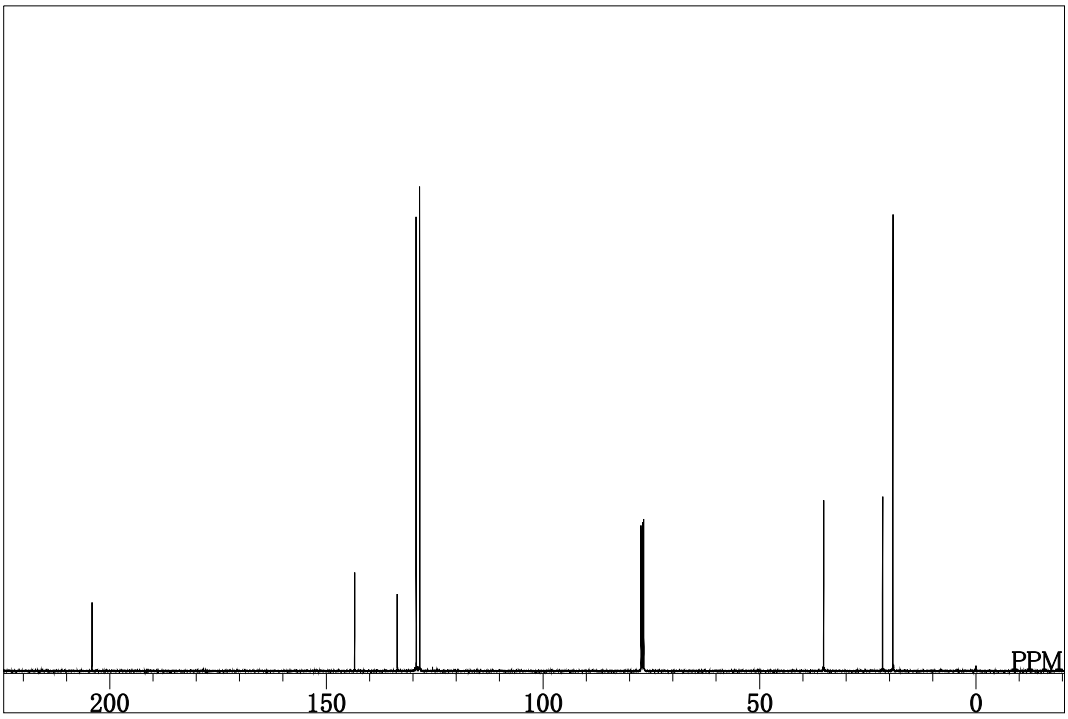
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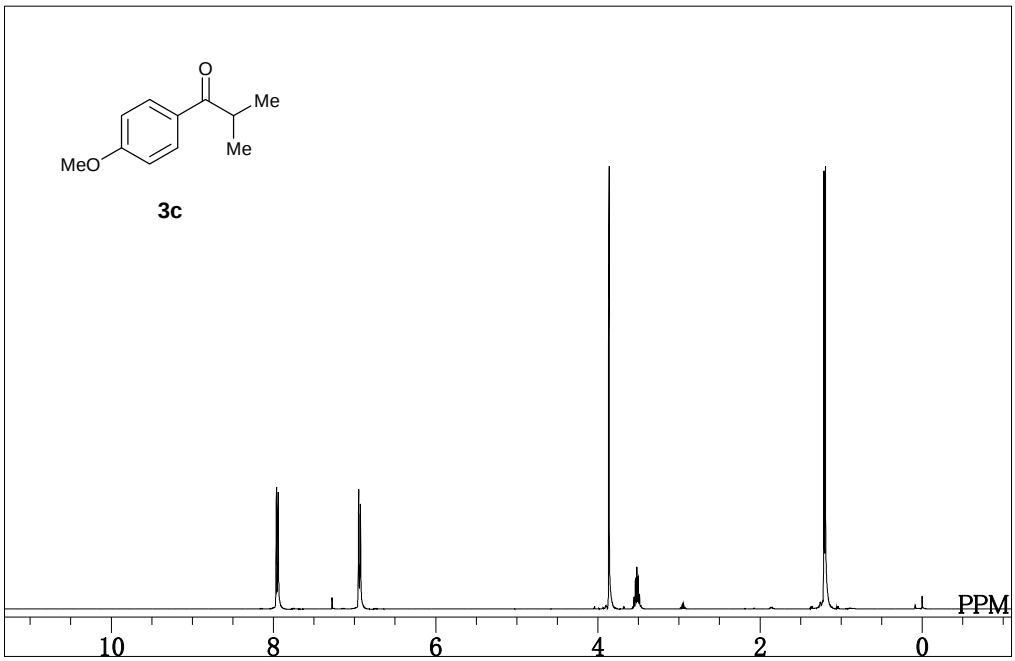

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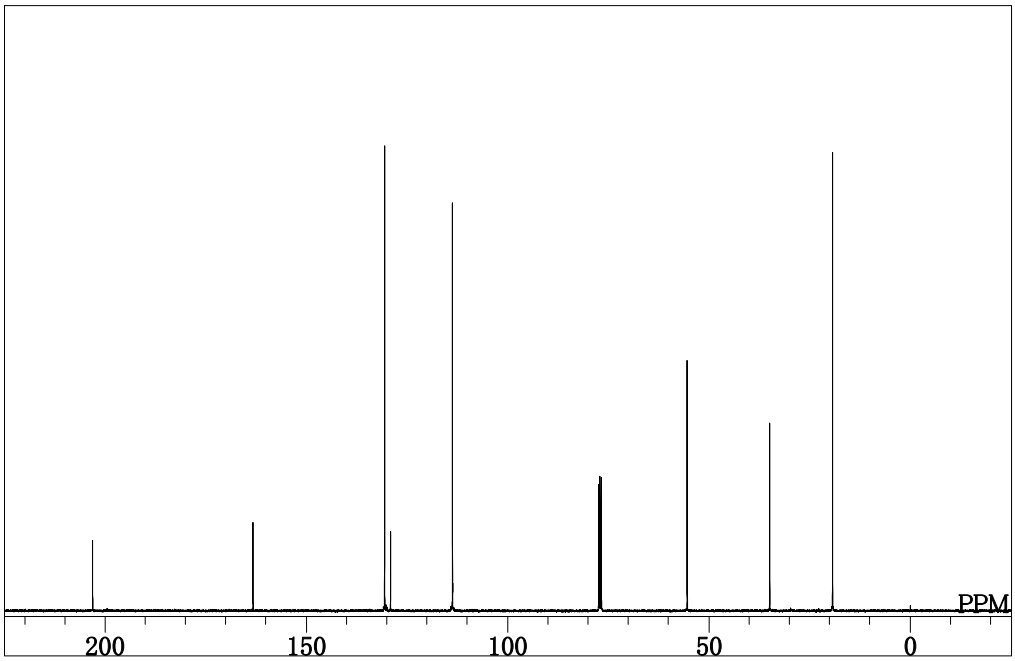

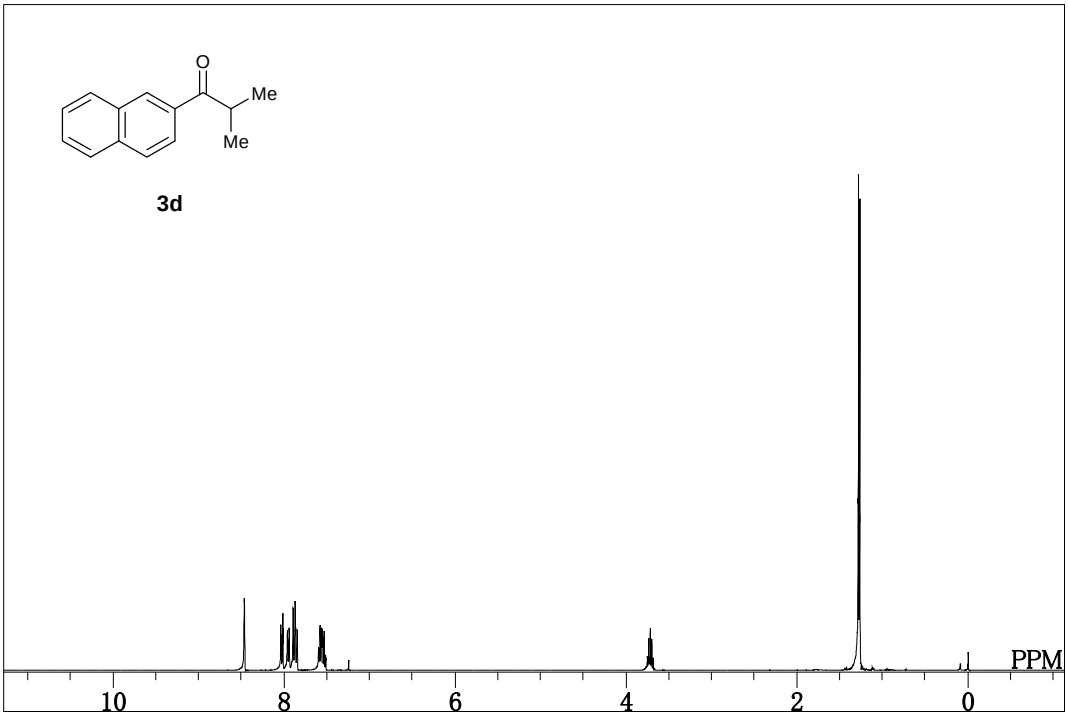

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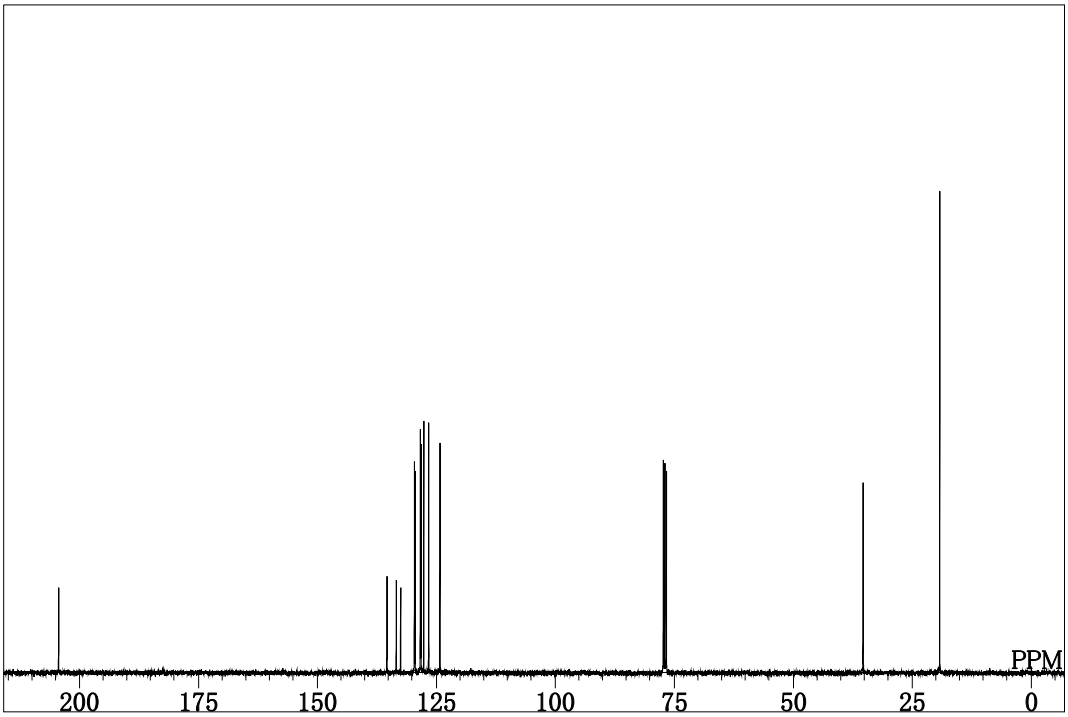

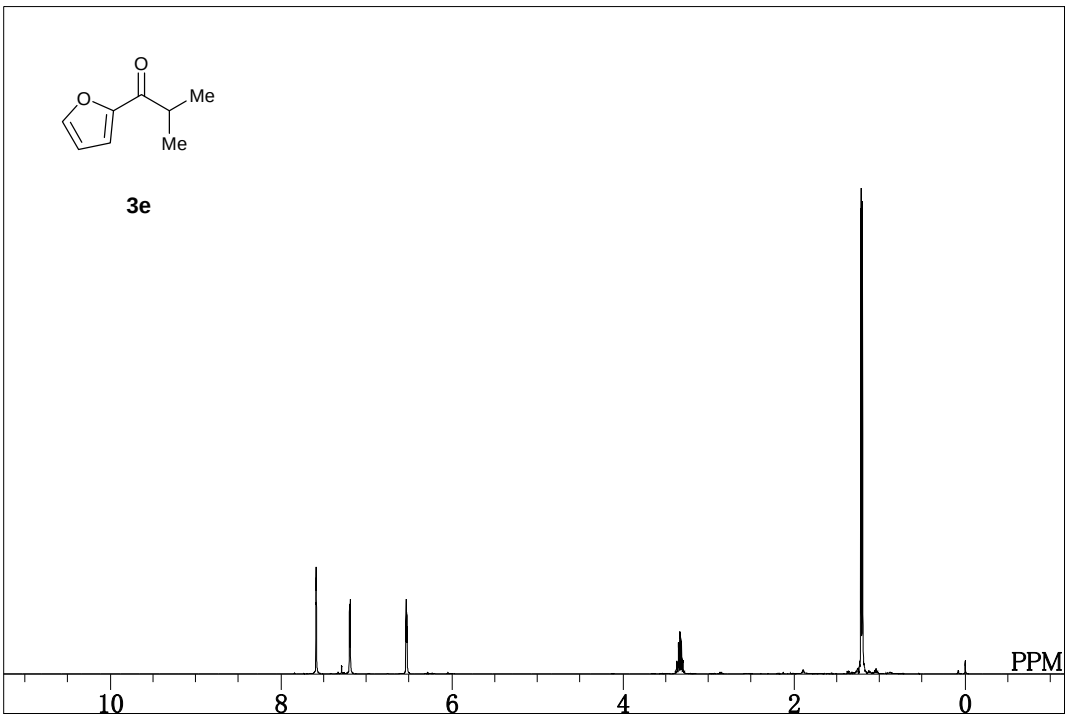
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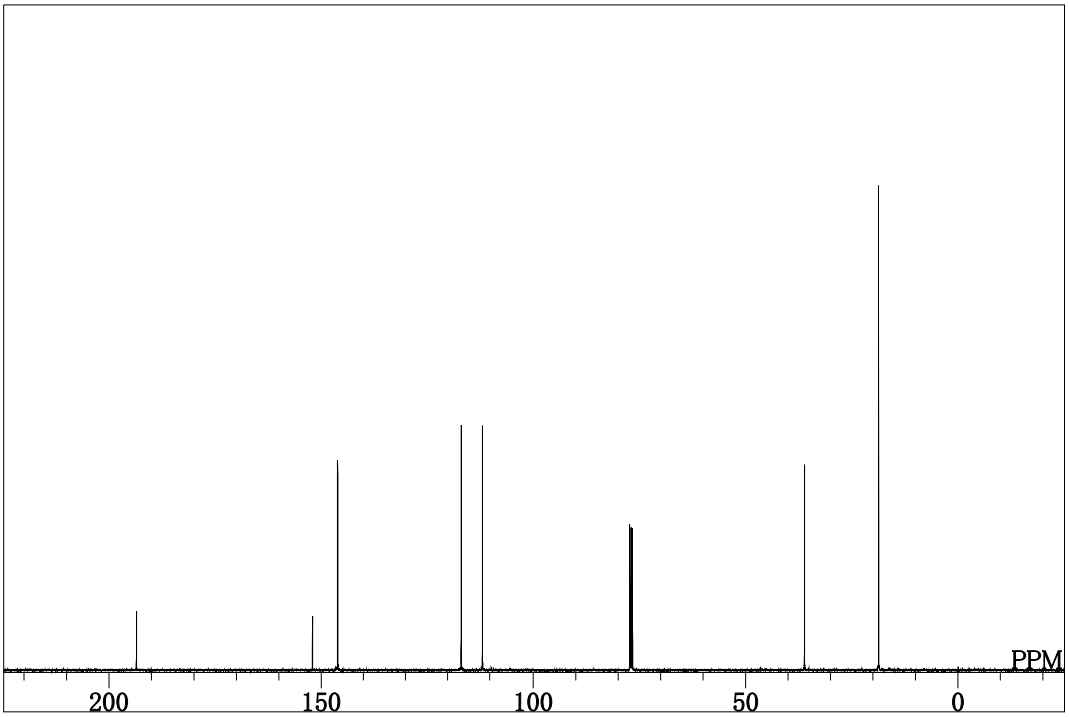
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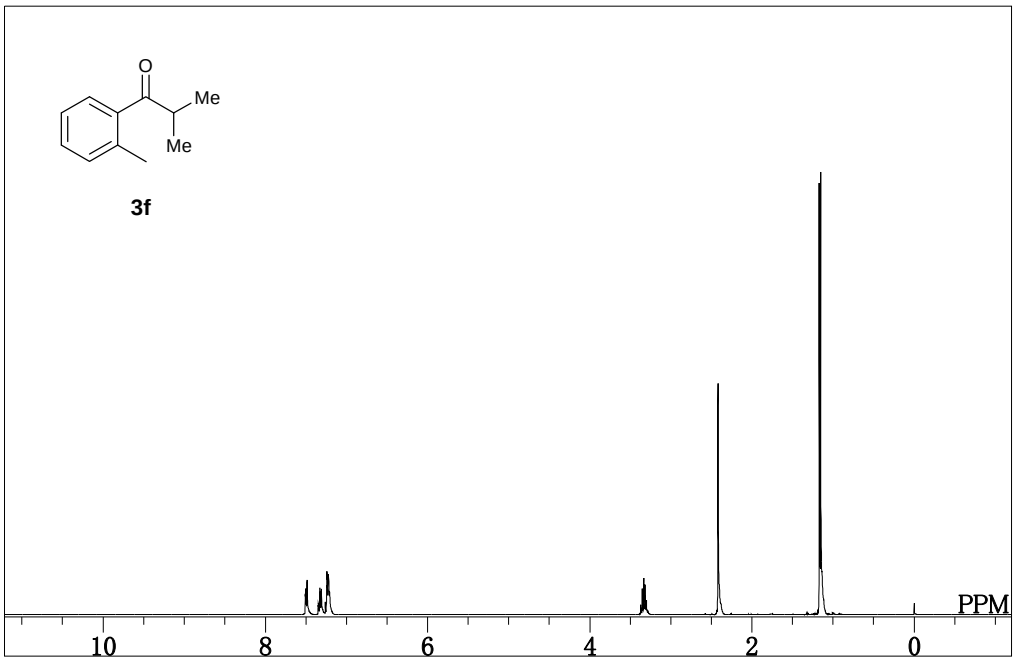

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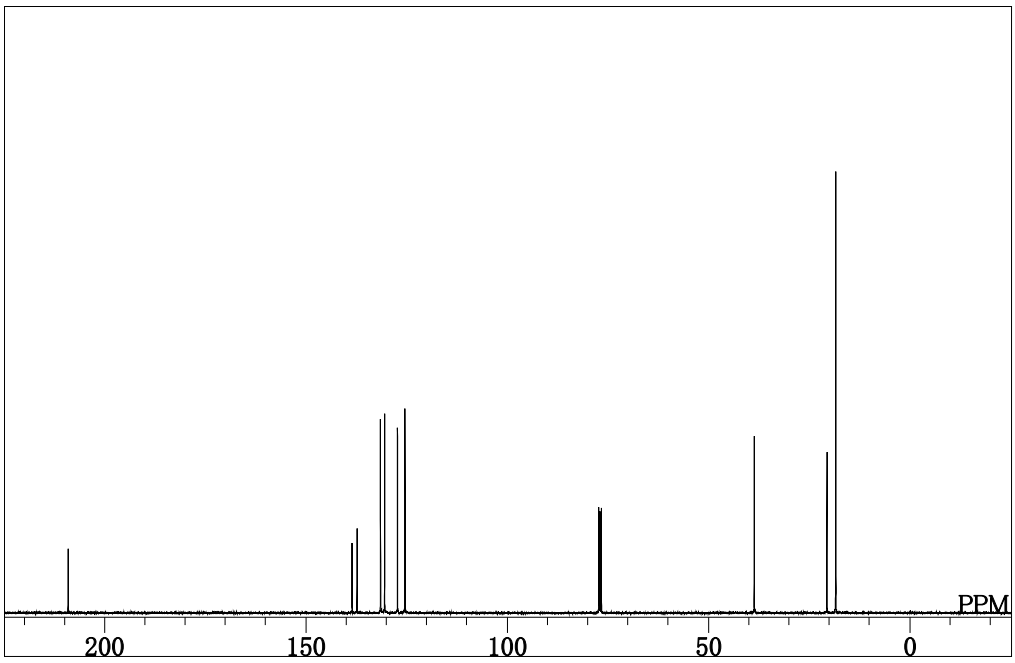

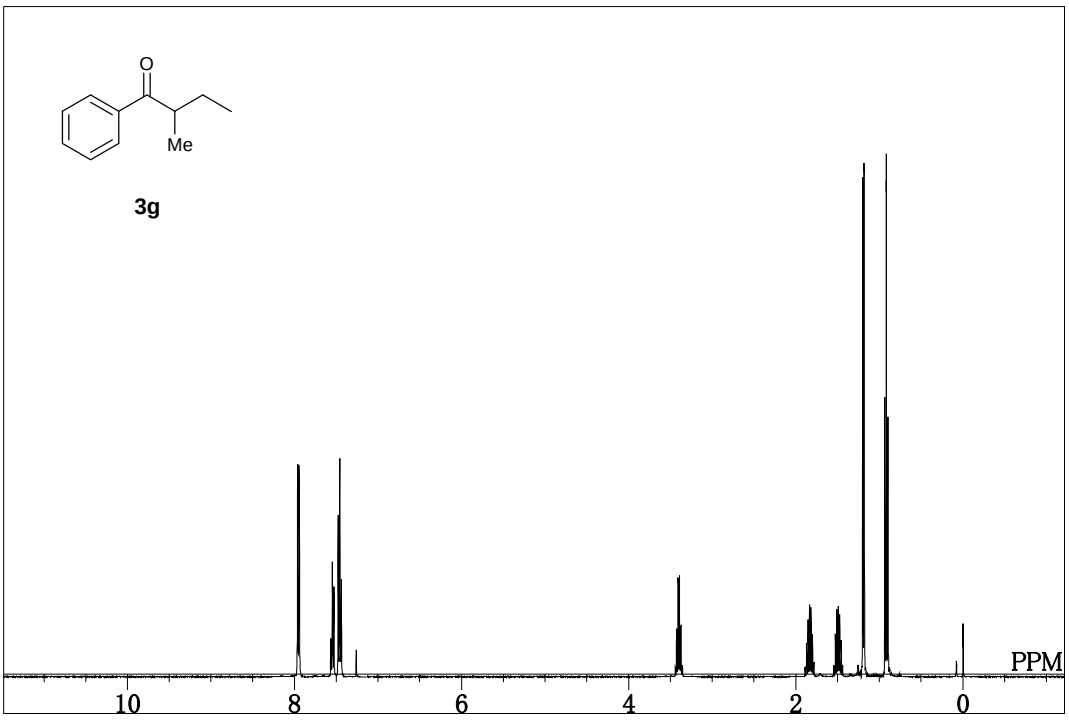

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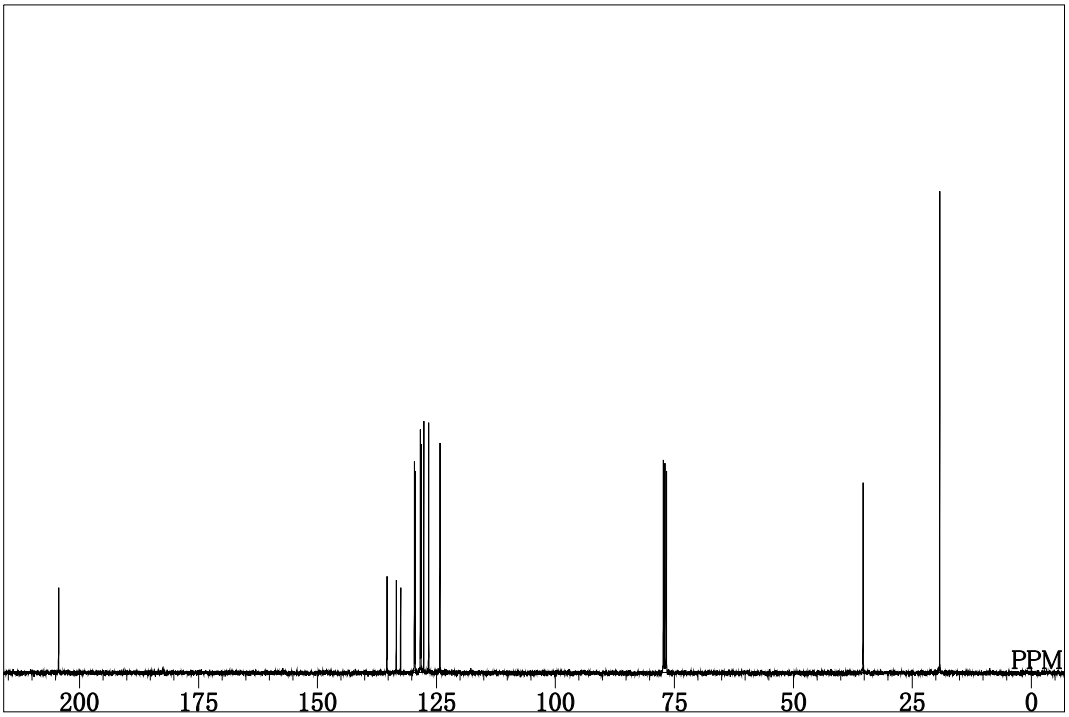

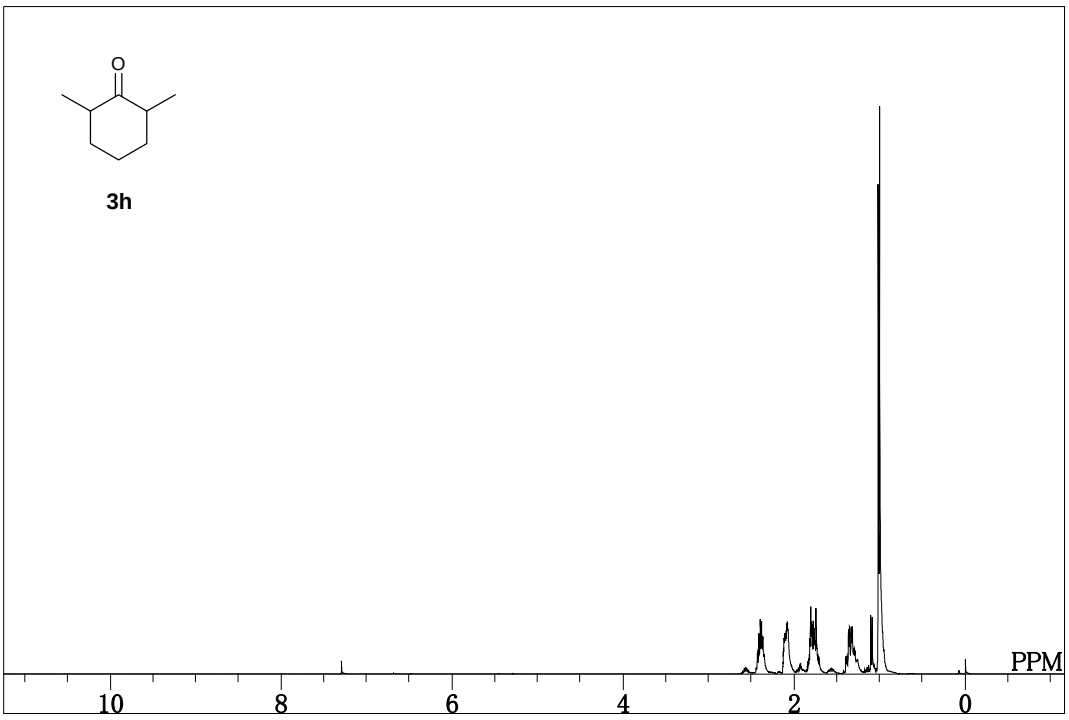

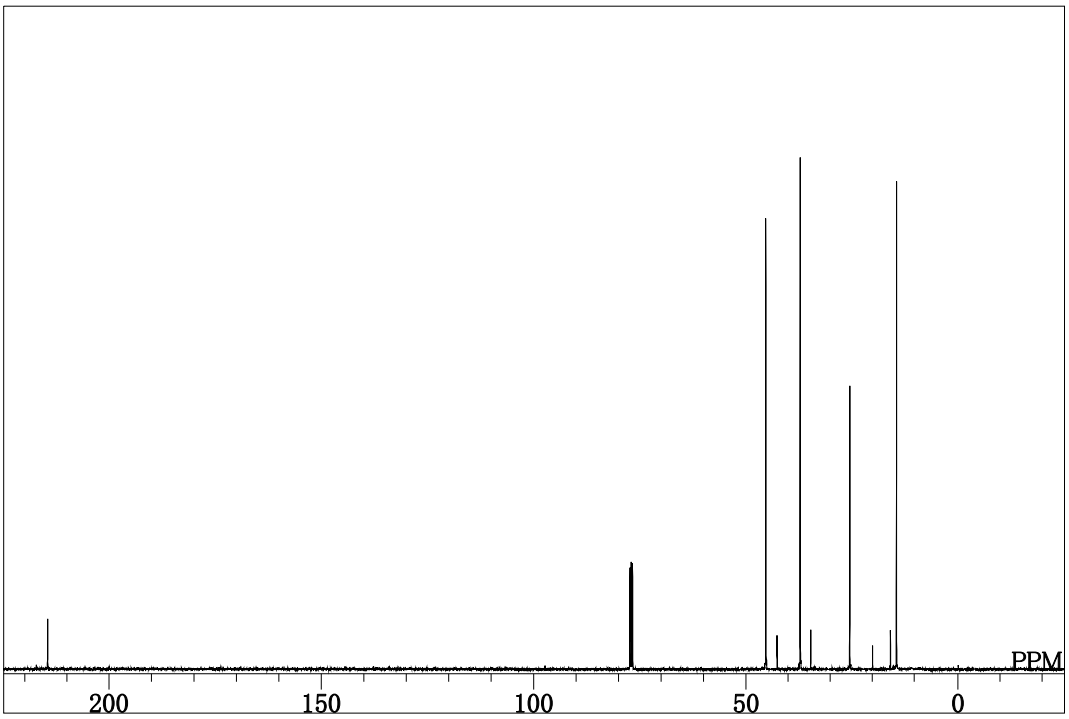

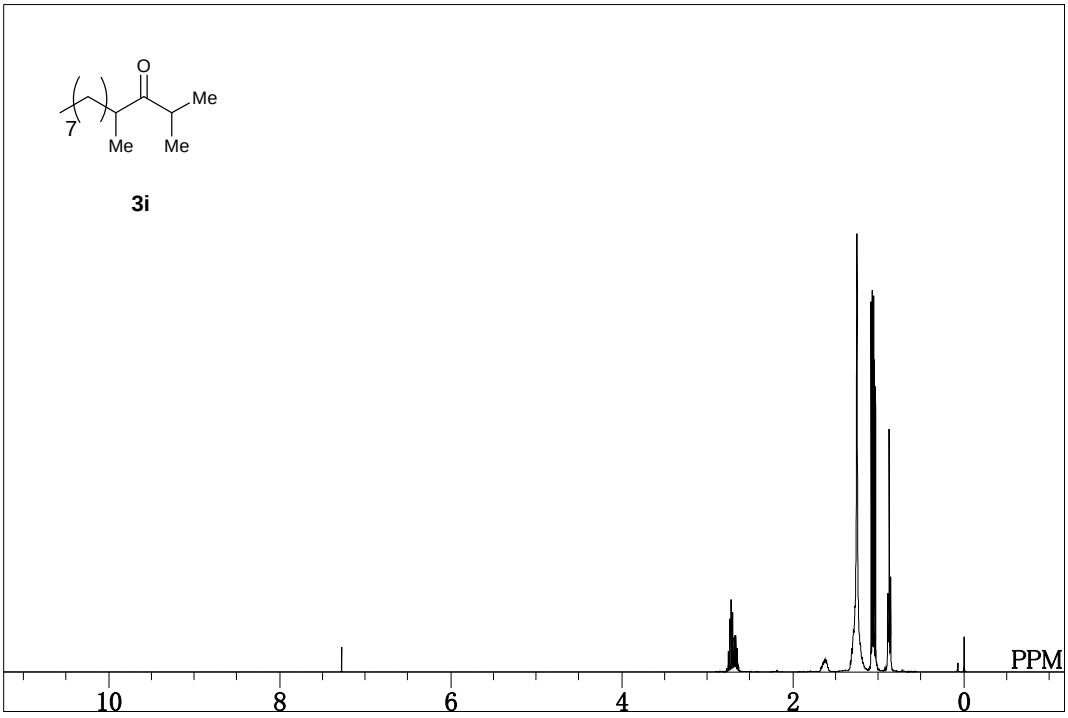

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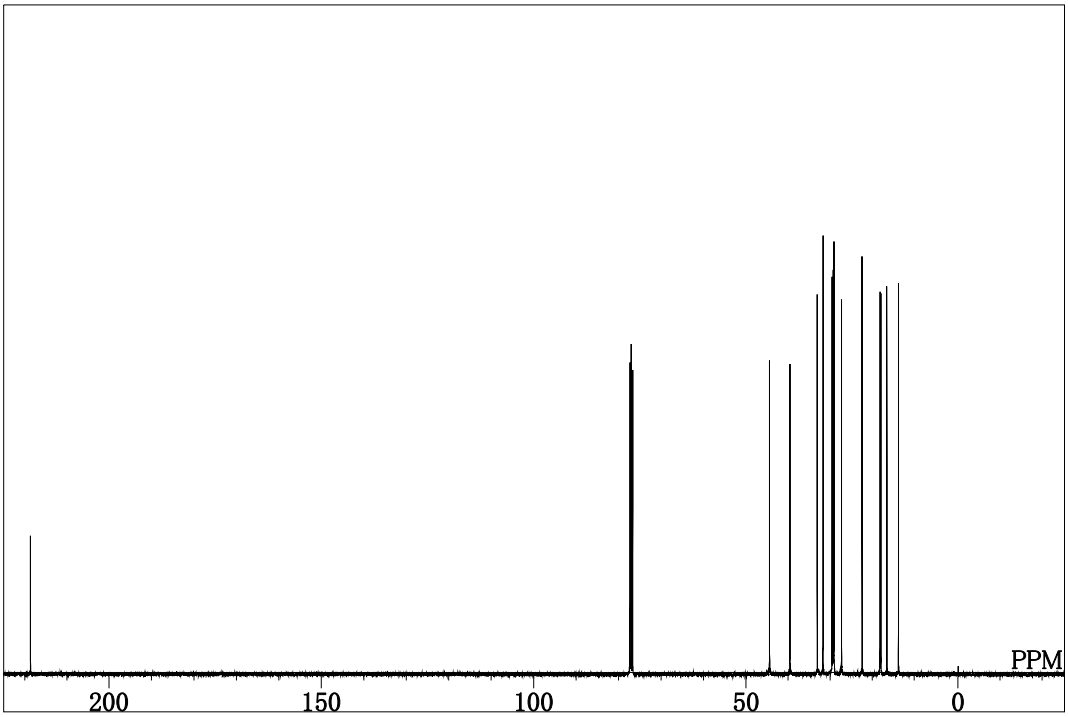

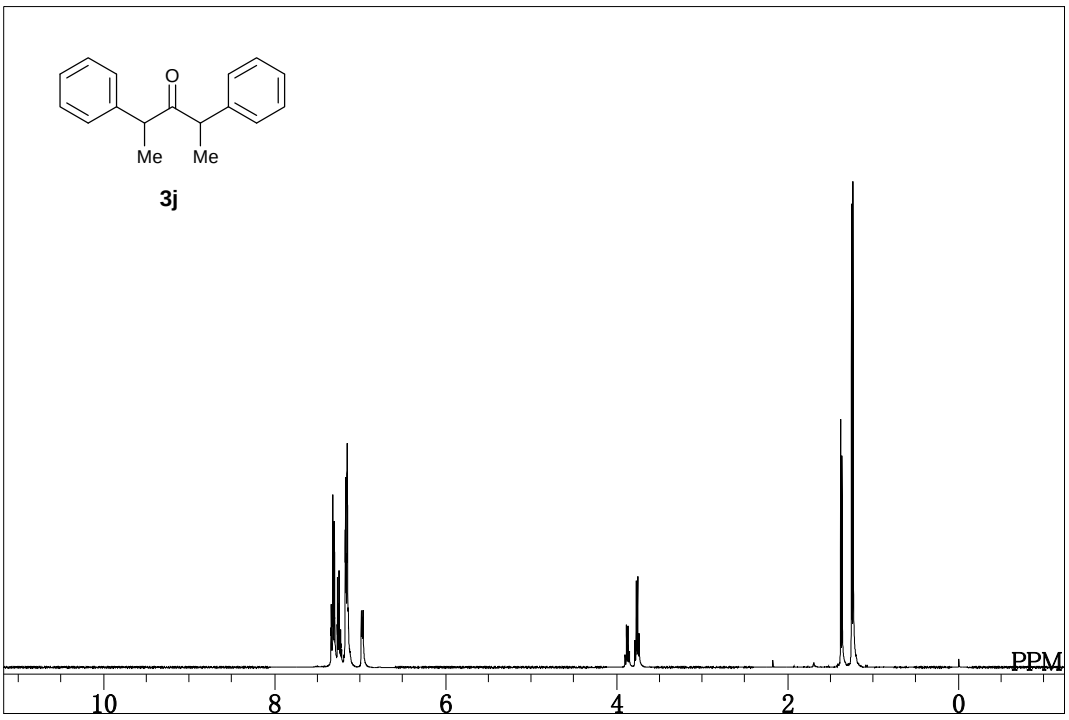

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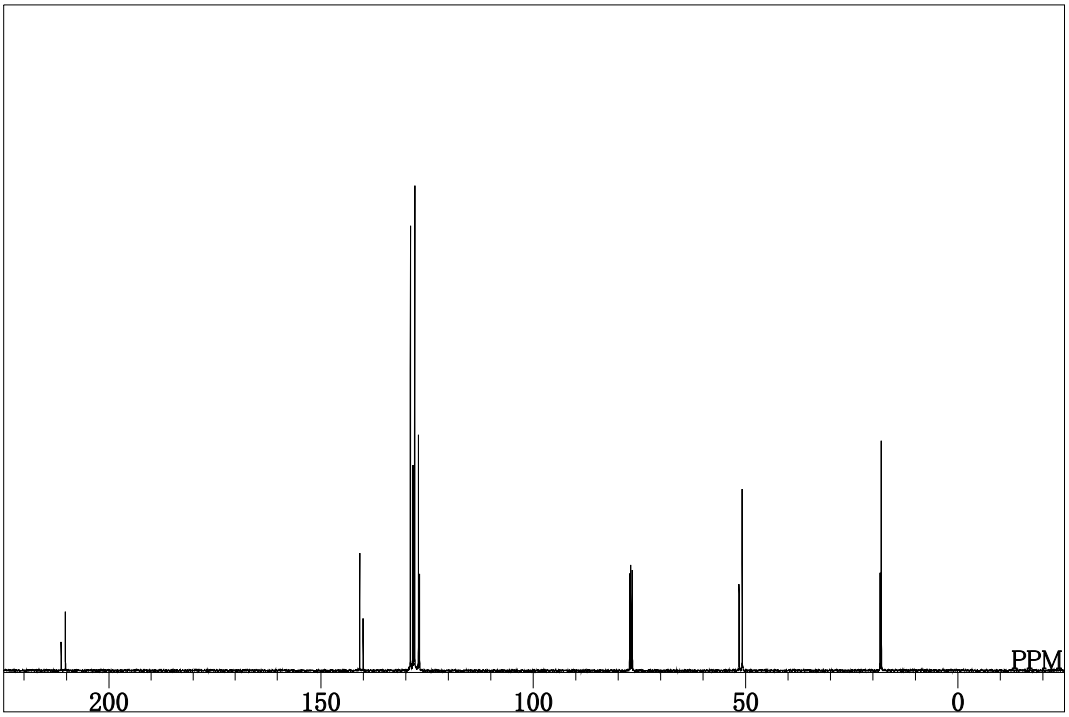

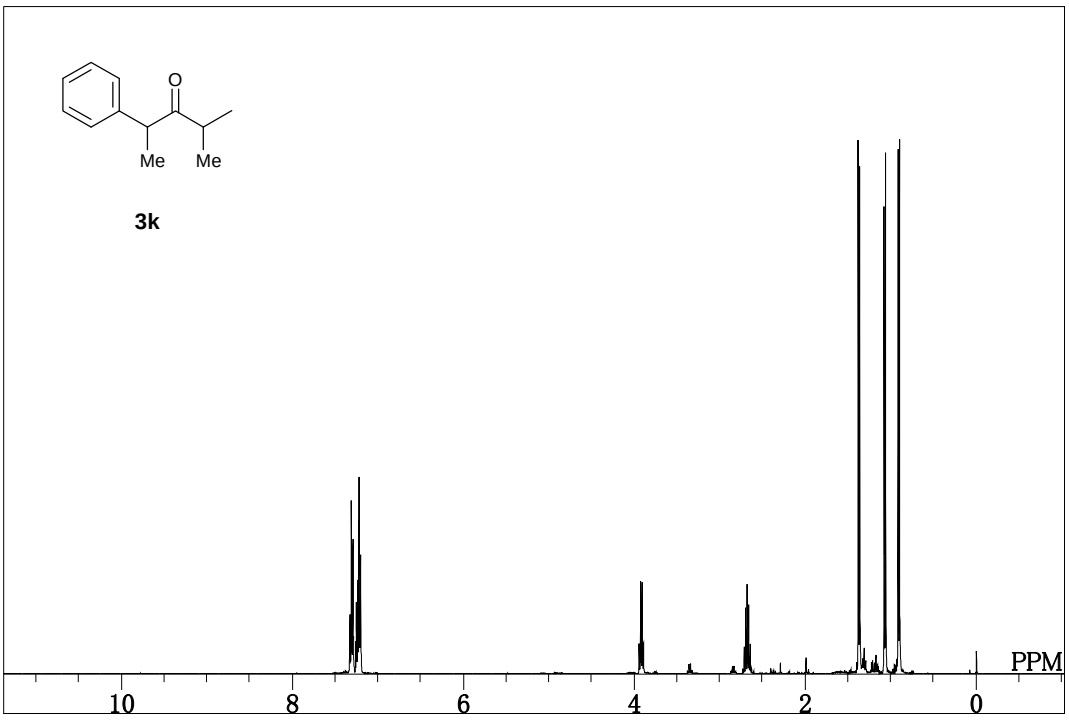

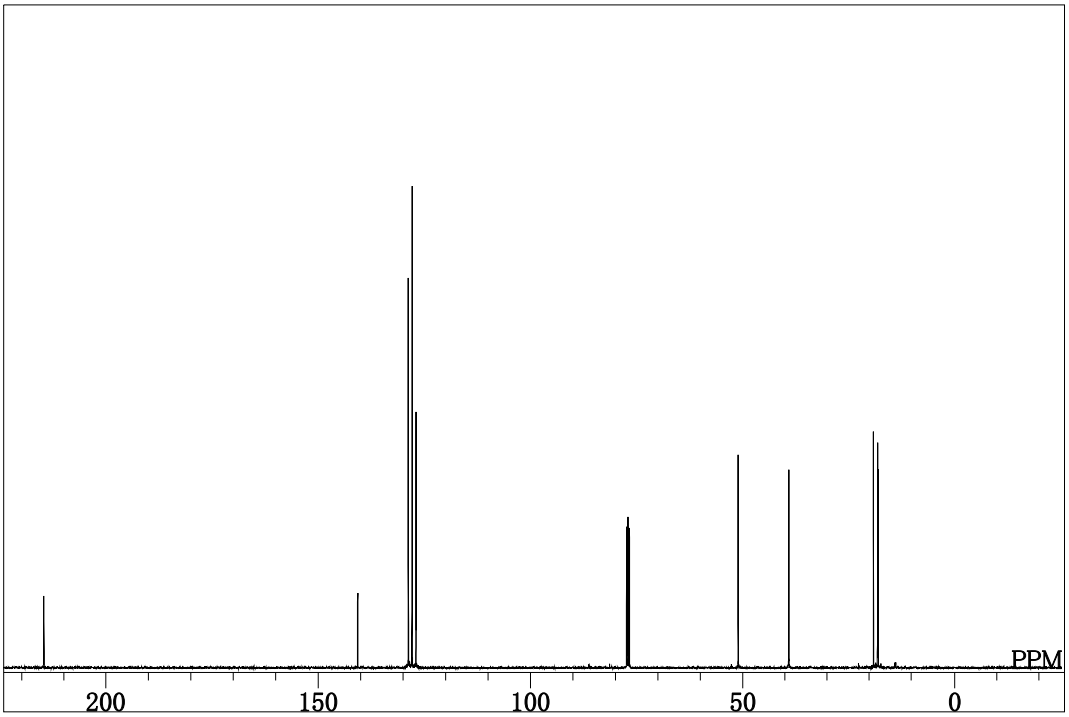

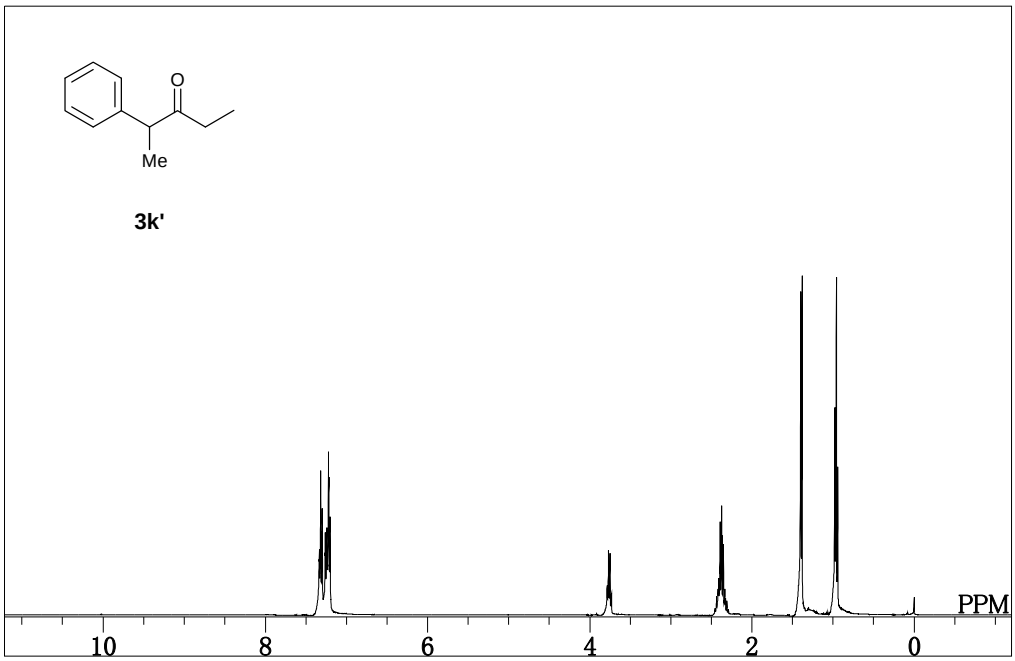

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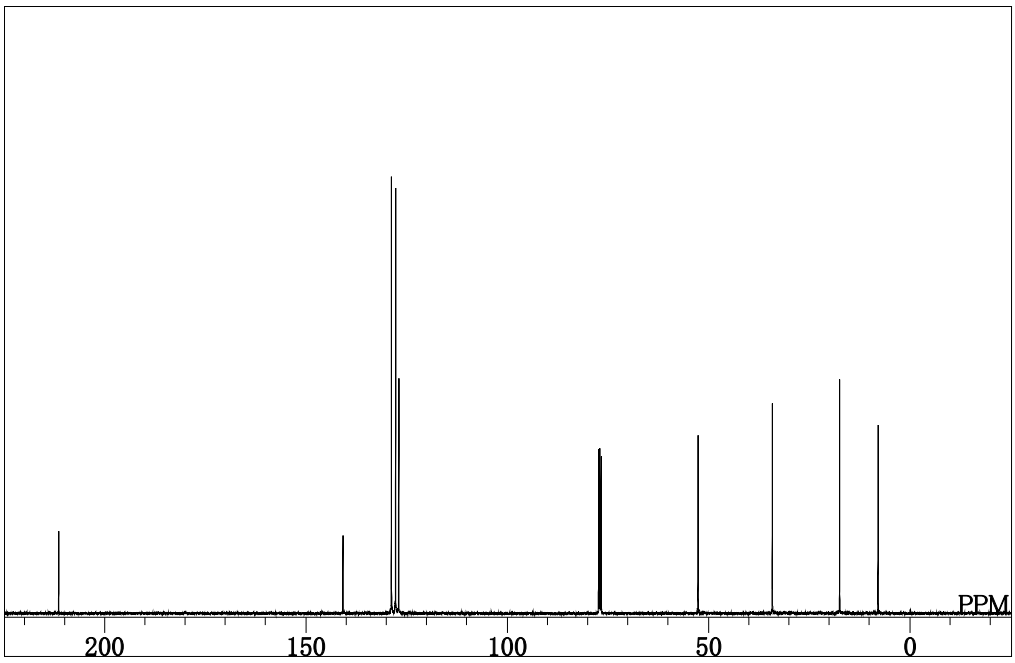

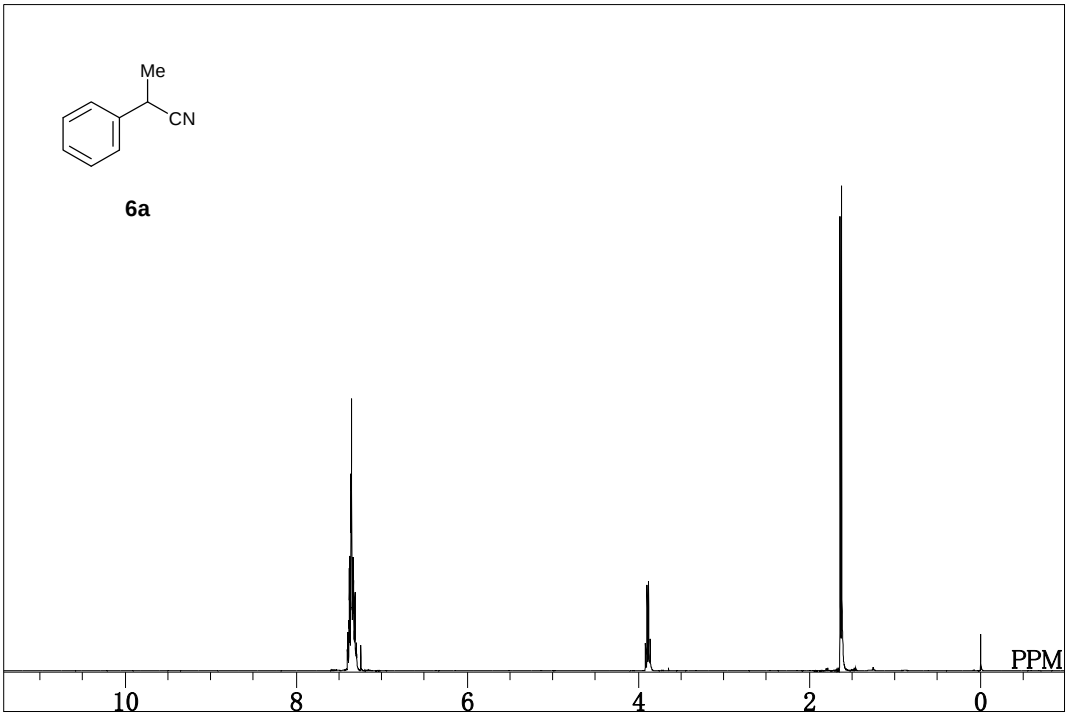

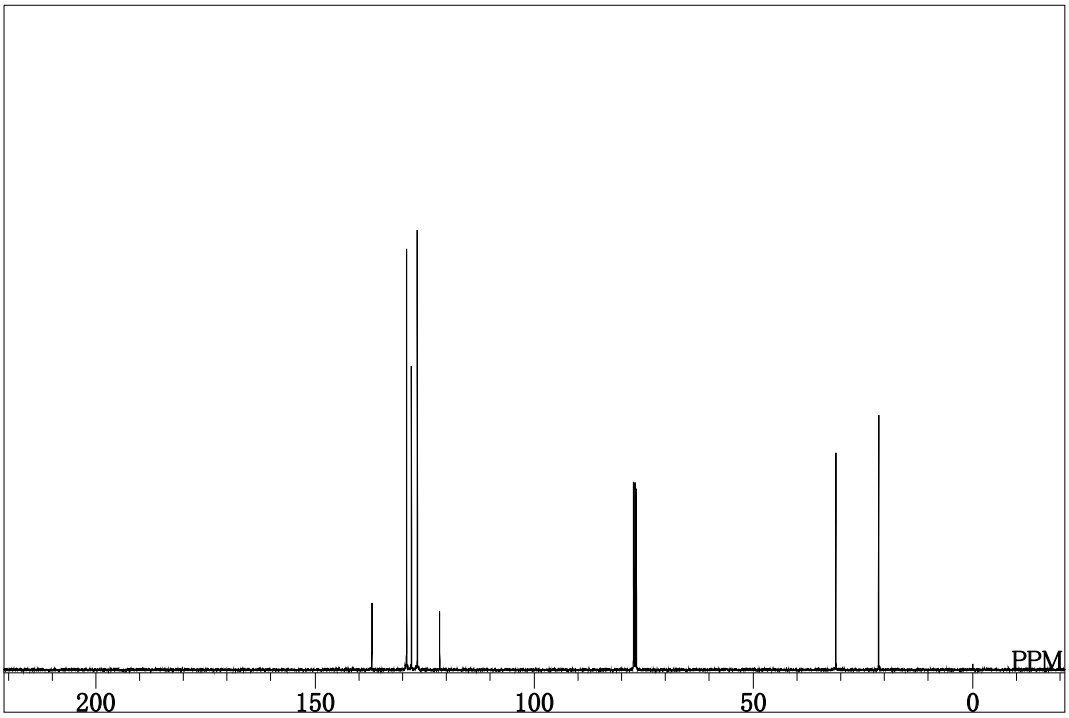

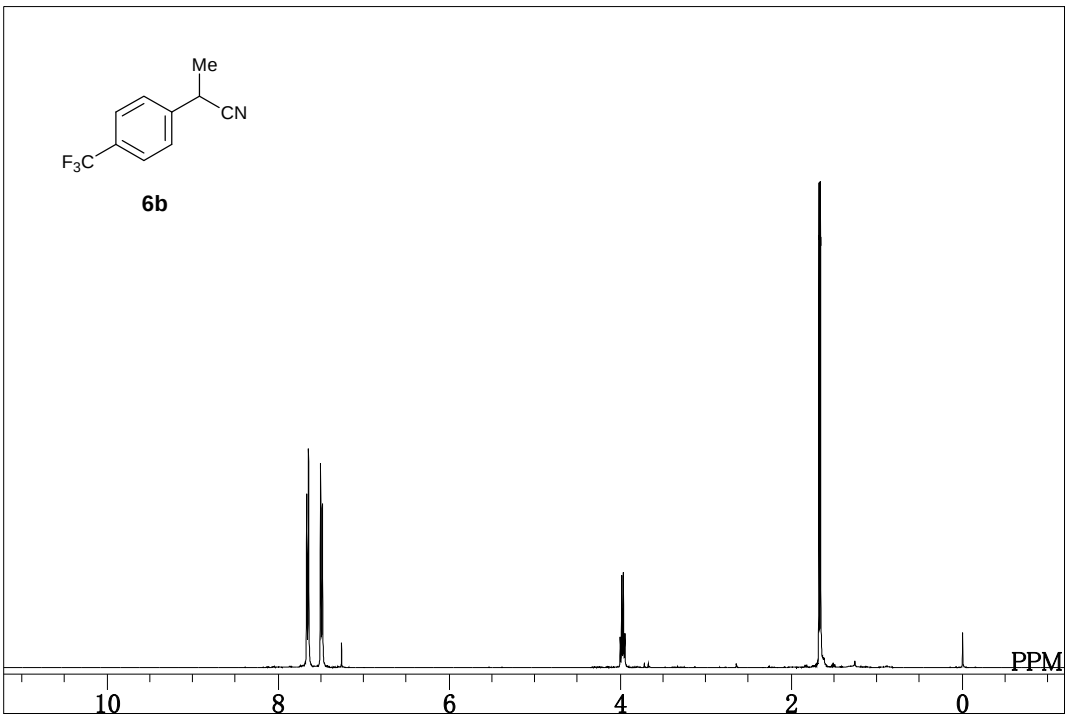

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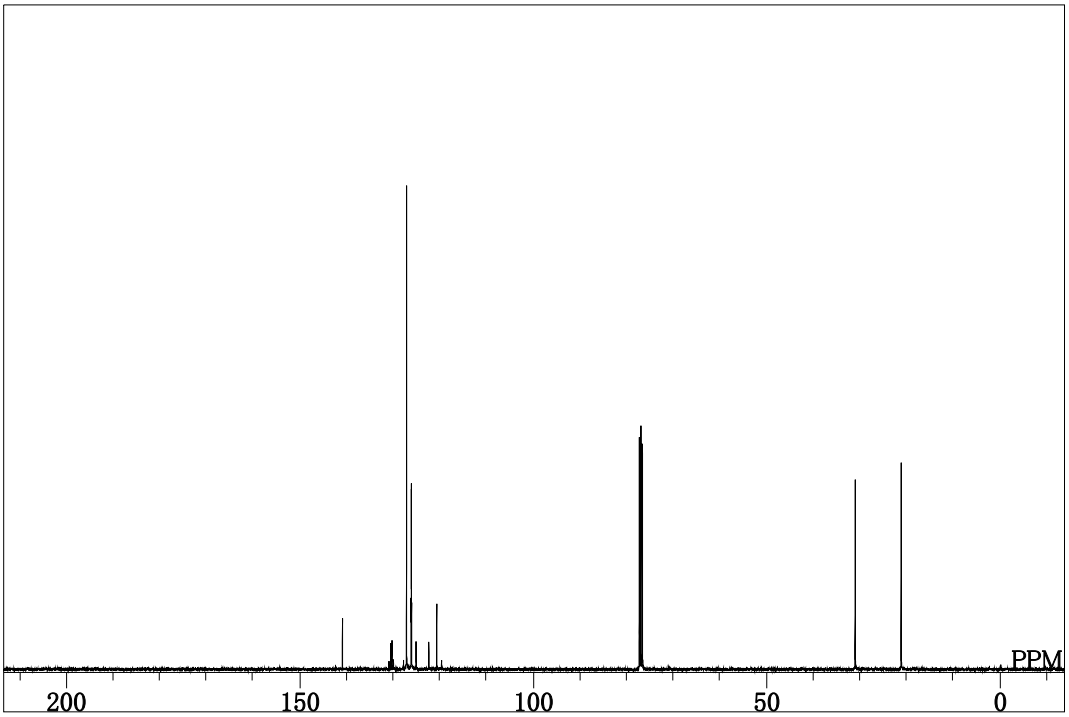

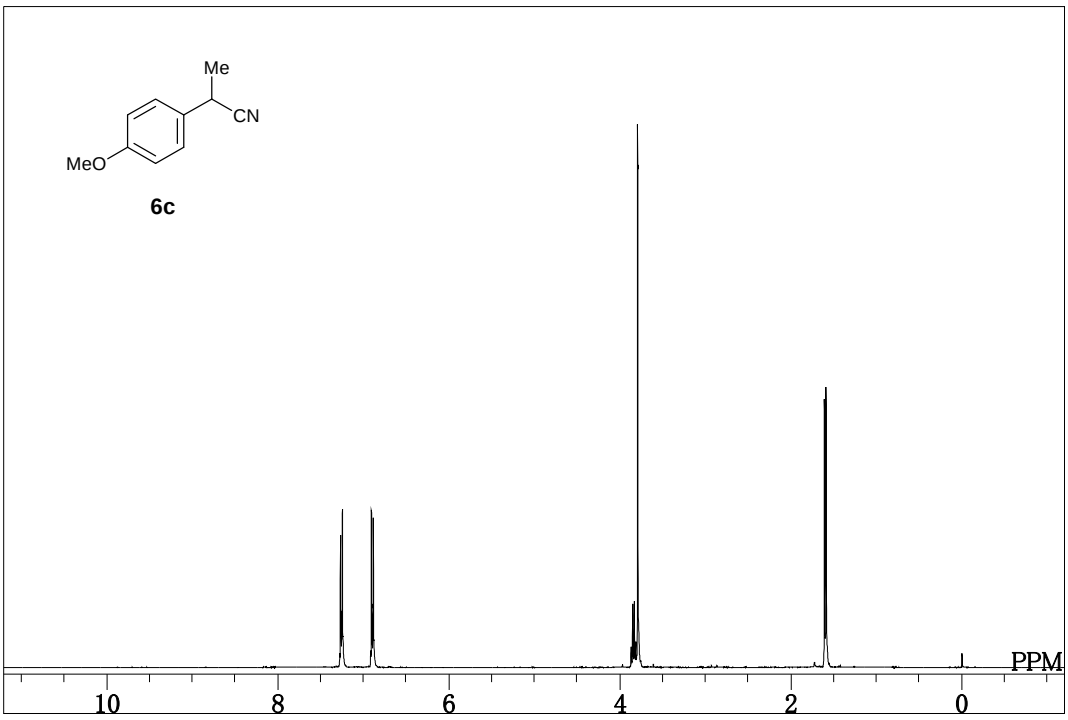

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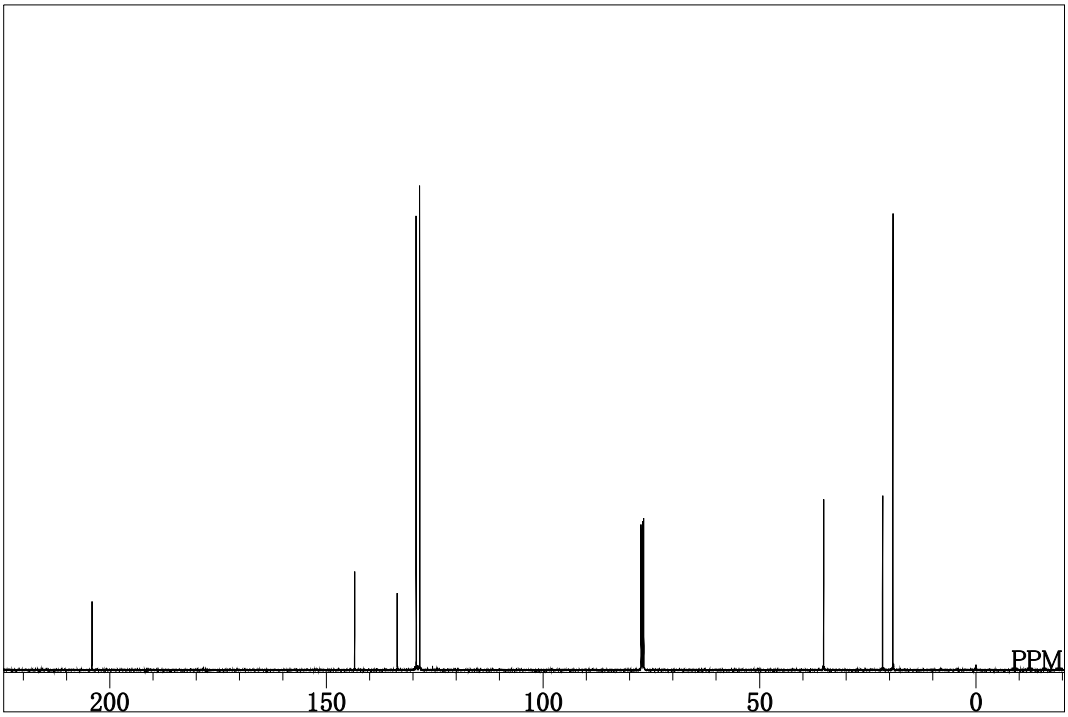

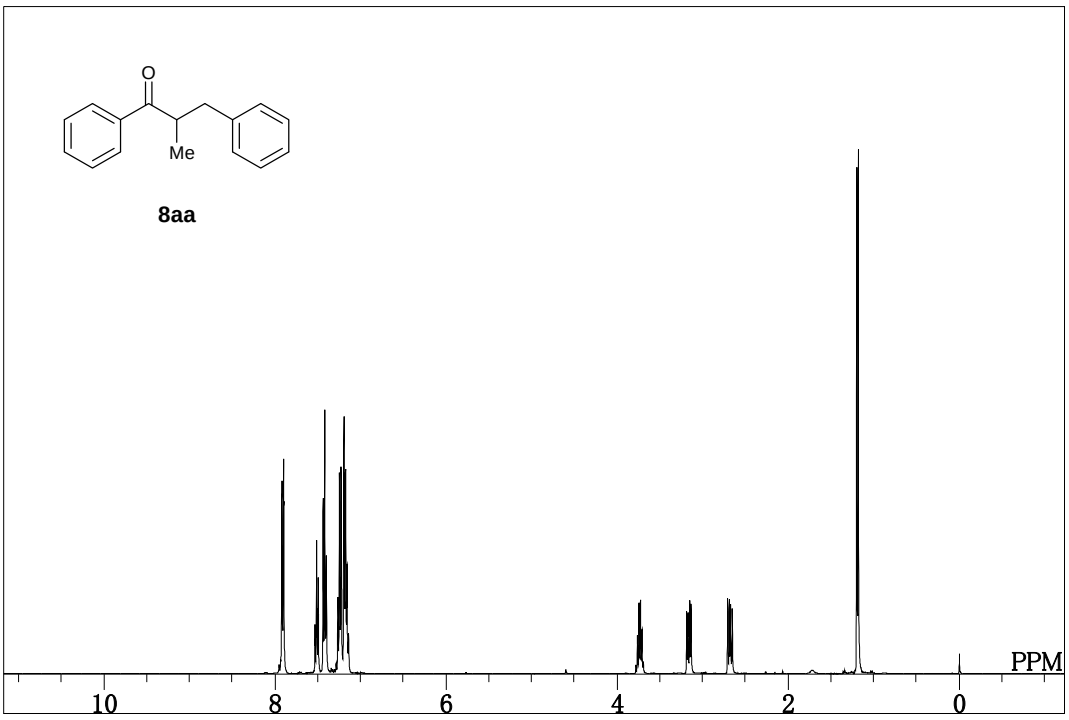

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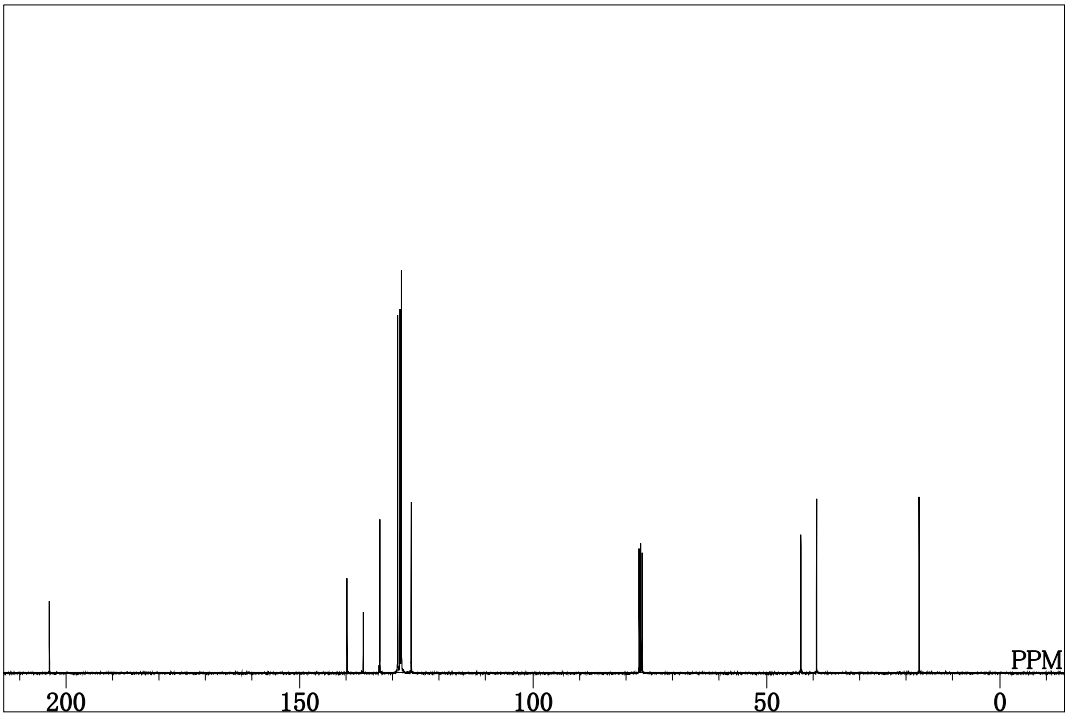

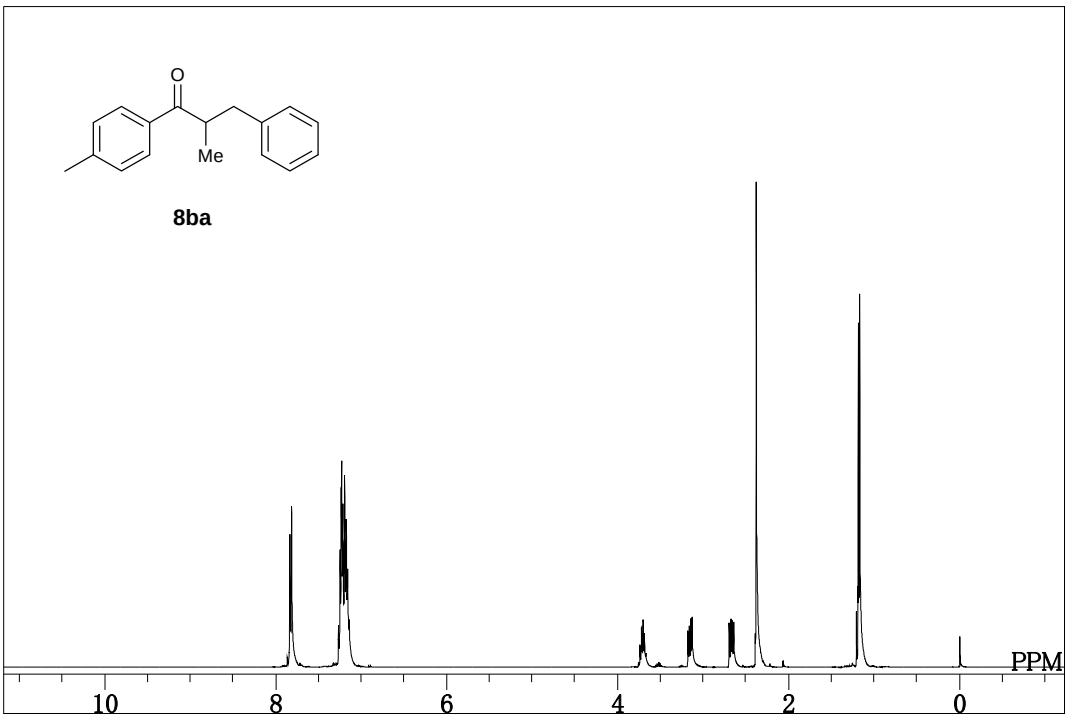

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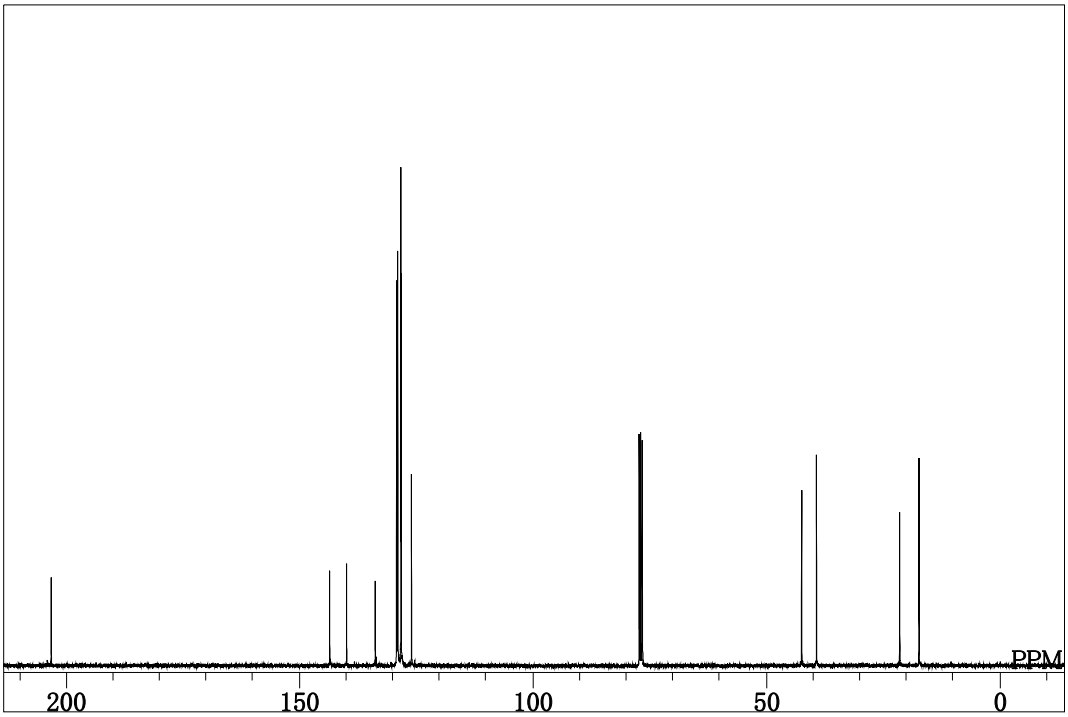

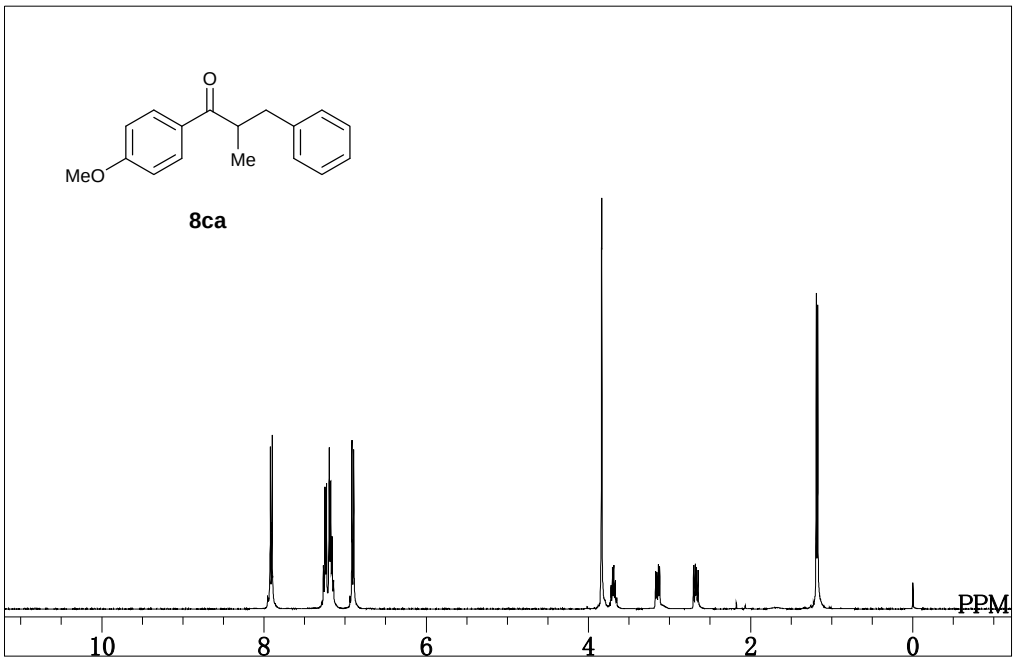

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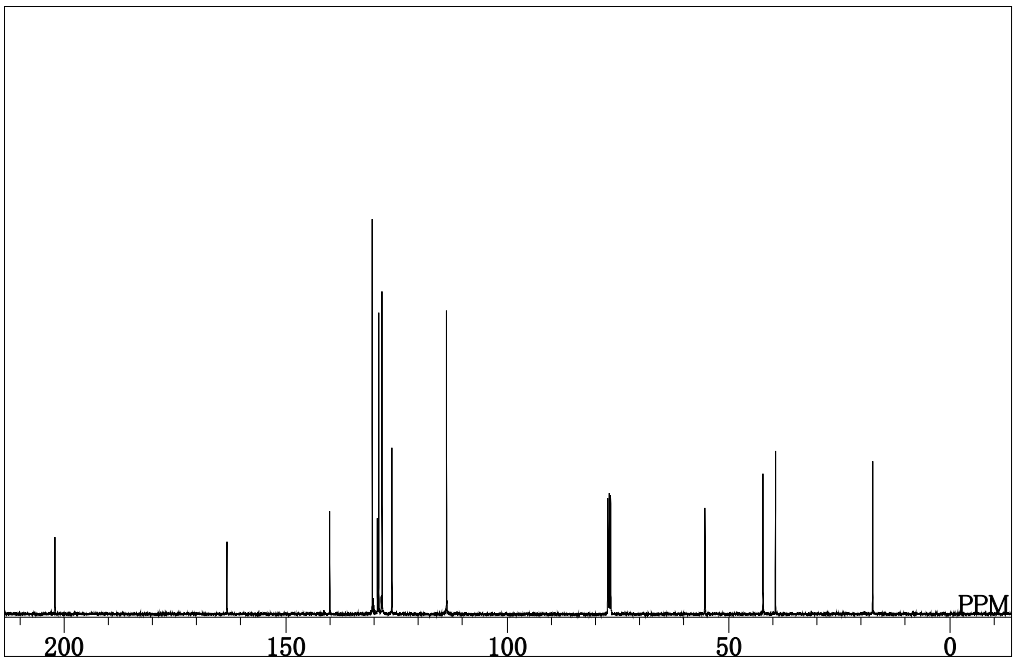

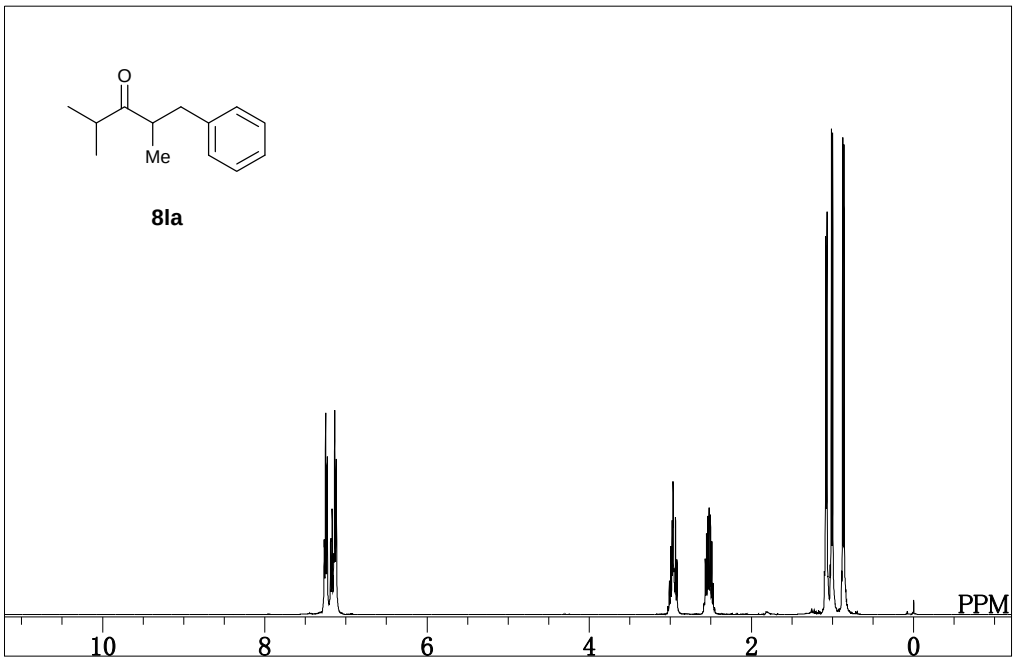

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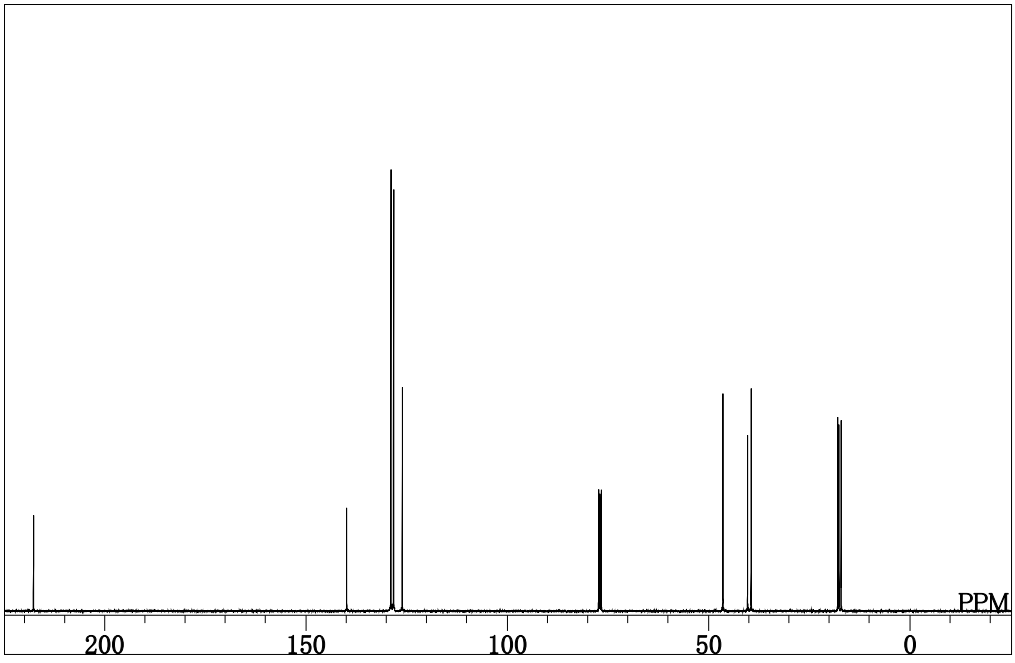

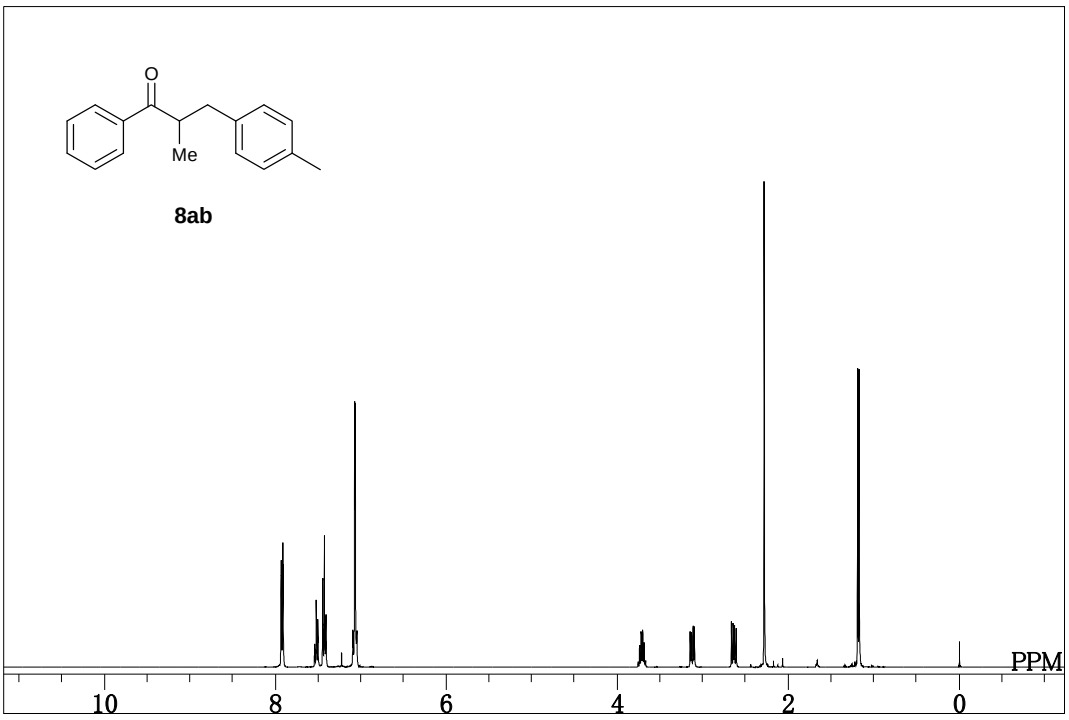
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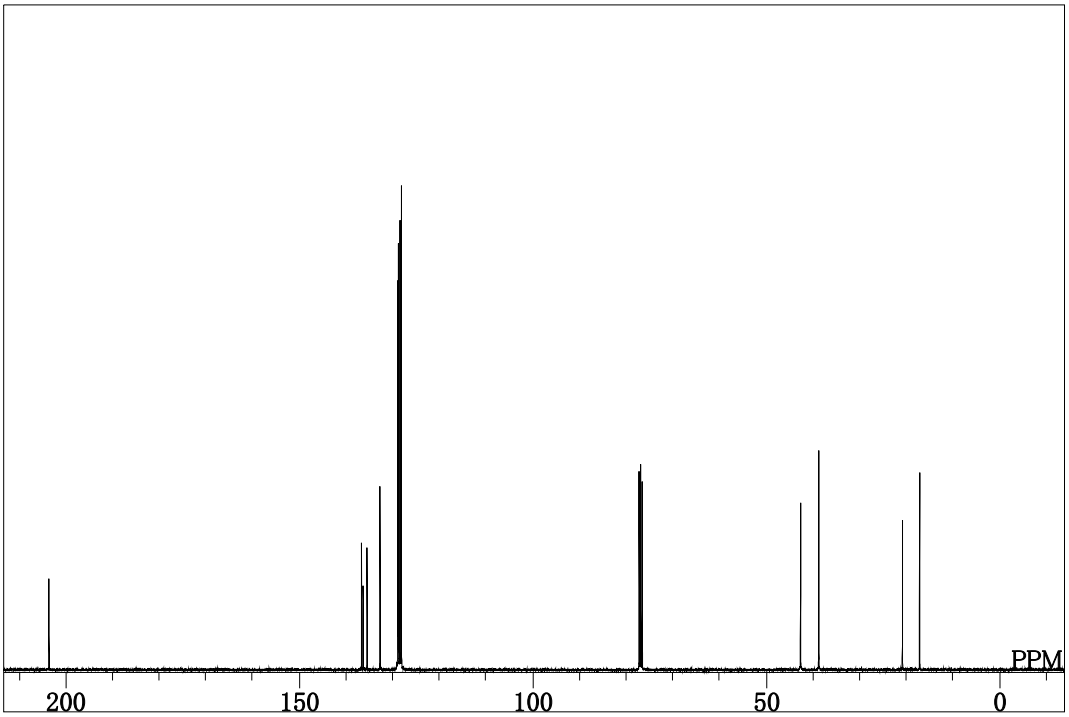
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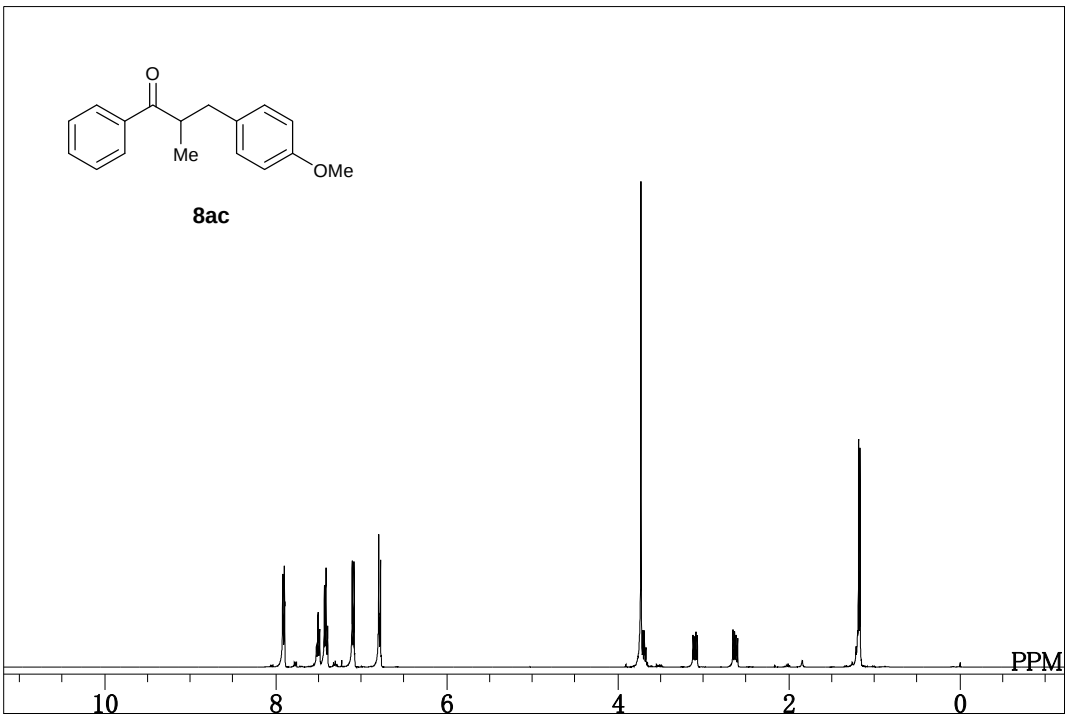

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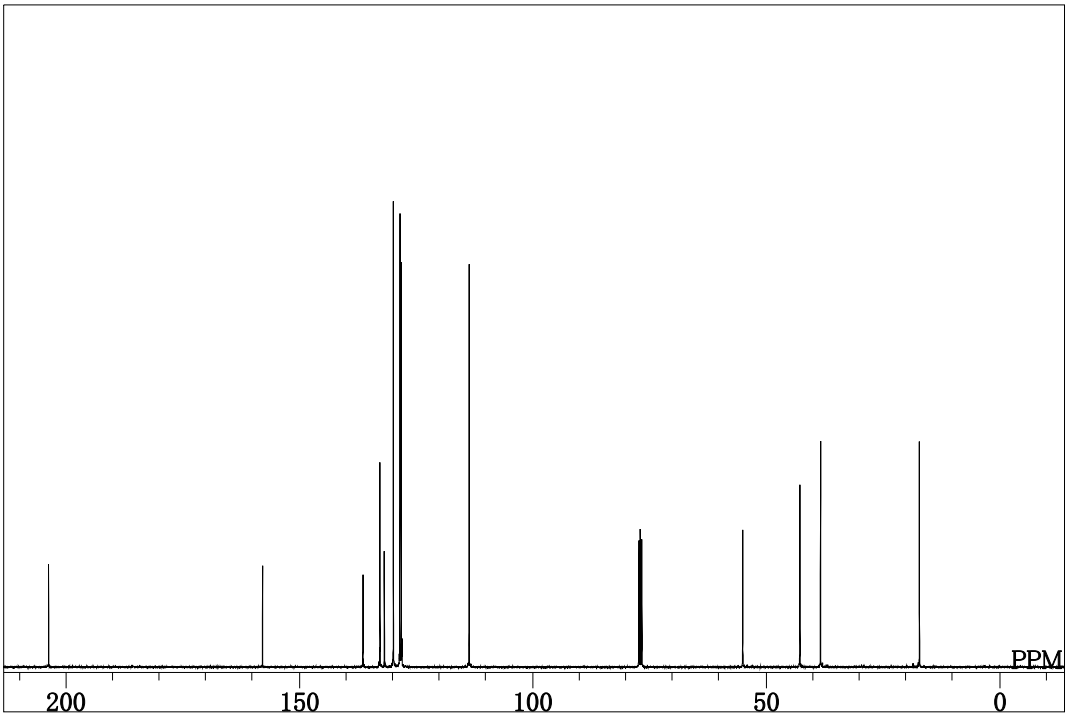

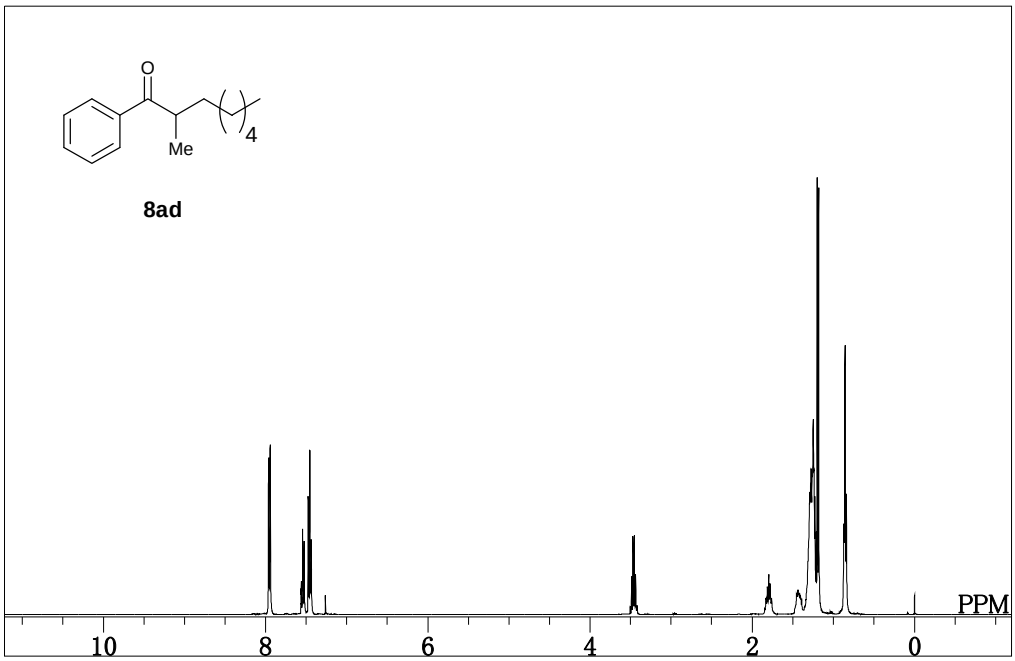

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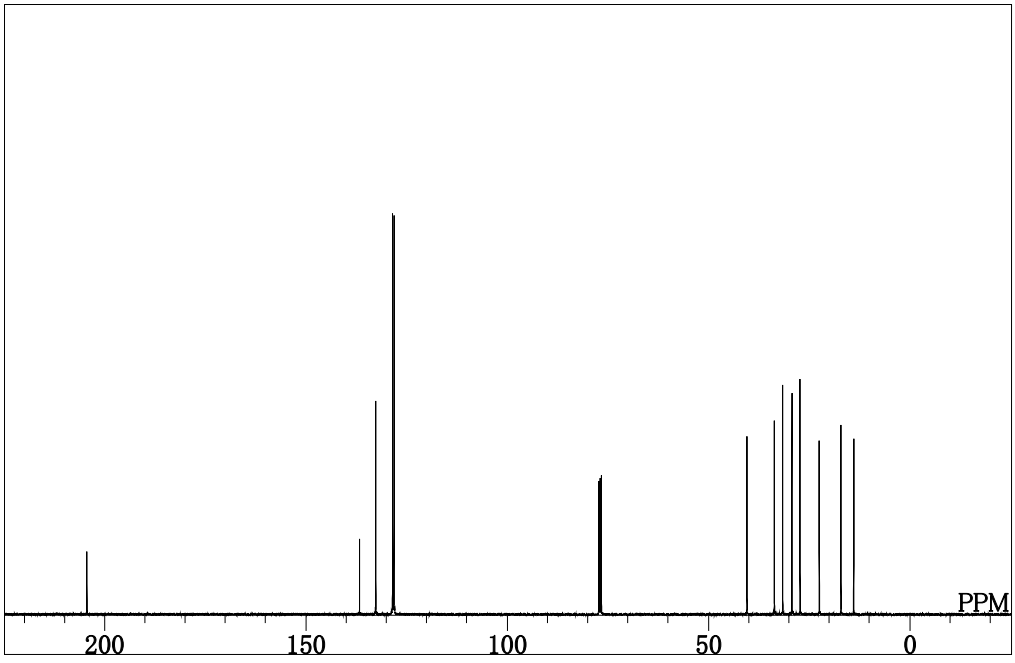

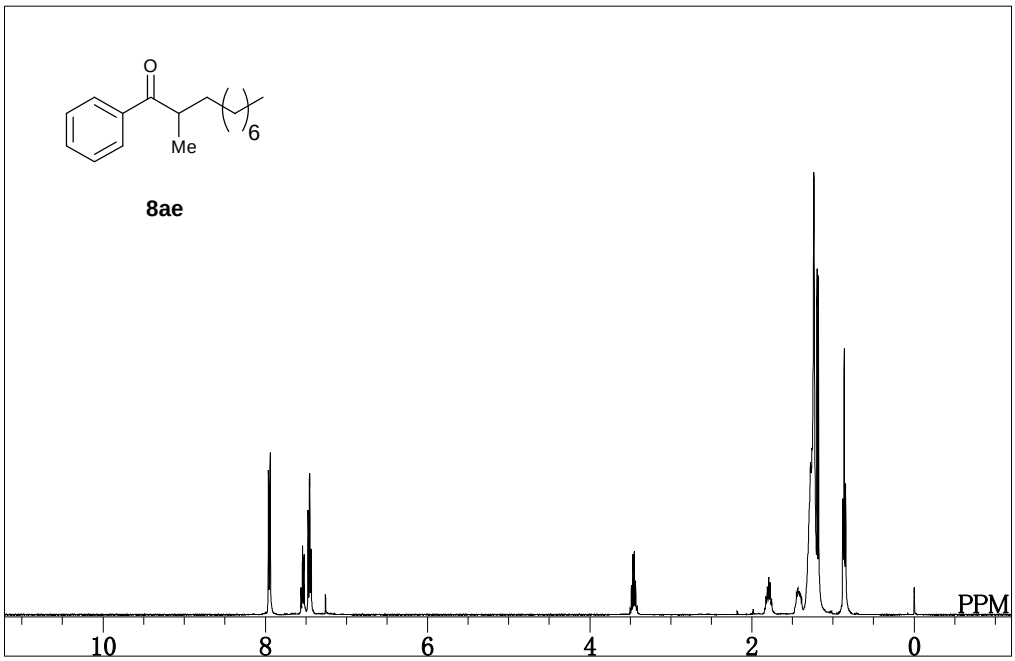

8ae