Electronic Supplementary Material (ESI) for RSC Advances
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Supporting information

Amine-Functional Polysiloxanes (AFPs) as Efficient Polymeric Organocatalyst for Amino Catalysis: Efficient multicomponent Gewald Reaction, α-Allylic Alkylation of Aldehydes, and Knoevenagel Condensation

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1. General Remarks

All reaction flask and solvent were dried according to standard method prior to use. Amino-functional Polysiloxane (AFP) **1d** and **1e** were purchased from Hangzhou Bald Silicone Co., Ltd. (0.21-0.55 mmol /g polysiloxane, Mw ~1900). **1d,** IR (cm^{-1}): 2962, 2905, 1412, 1261, 1093, 864, 800; GPC: M_w: 2200, M_w/M_n=2.18; **1e,** IR (cm^{-1}): 2962, 2905, 1412, 1260, 1092, 1020, 884, 800; GPC: M_w: 1900 M_w/M_n=1.94. Gel permeation chromatographic analysis (GPC) measurements were conducted on waters GPC, Flash column chromatography was performed over silica (100-200 mesh). NMR spectra were recorded on a 400-MHz spectrometer (Avance 400). ^{13}C NMR spectra were obtained with broadband proton decoupling. For spectra recorded in $CDCl_3$, unless noted, chemical shifts were recorded relative to the internal TMS (tetramethylsilane) reference signal. GC-MS was performed on TRACE DSQ. IR spectra were recorded using a FTIR apparatus (Nicolot 5700). Thin layer chromatography was performed using Silica.

1. The NMR spectral data of **1d**, and **1e**

1d: ^1H-NMR ($CDCl_3$, 400MHz), δ =2.803-2.833 (t, NHCH_2, 2H), 2.667-2.707 (t, C$H_2$$NH_2$, 2H), 2.601-2.637 (t, C$H_2$NH, 2H), 1.515-1.612 (m, CH_2, 2H), 0.506-0.540 (t, Si CH_2, 2H), 0.088-0.109 (m, $SiCH_3$, 489)； ^{13}C-NMR ($CDCl_3$, 100MHz), δ = 52.9, 52.3, 41.8, 23.5, 14.9, 0.579-1.384.

1e: ^1H-NMR ($CDCl_3$, 400MHz), δ =2.613-2.718 (m, $SiCCCH_2NHCH$, 3H), 2.336-2.371 (m, CH_2, 2H), 2.243-2.253(m, CH_2, 6H), 1.659-1.745 (m, CH_2, 2H),

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1.530-1.608 (m, CH_2, 2H), 0.496-0.537 (m, $SiCH_2$, 2H), 0.089-0.110 (m, $SiCH_3$, 396); ^{13}C-NMR ($CDCl_3$, 100MHz), δ = 58.2, 53.0, 48.4, 45.5, 27.9, 23.3, 14.9, 0.607-1.348.

Table S1. Recovery and Recycling of Amino-functional polysiloxane **1e** in the α-allylic alkylation of isobutyraldehyde[a]

Run	AFP	RecoveryYield of **1e** (%)	ReactionYield (%)[b]
1	**1e**	100	> 99
2	**1e**	99	> 99
3	**1e**	99	> 99
4	**1e**	98	90
5	**1e**	96	> 99
6	**1e**	98	> 99
7	**1e**	98	> 99
8	**1e**	96	> 99
9	**1e**	96	> 99
10	**1e**	95	> 99

[a] Reaction conditions: All reactions were performed in CH_3CN at room temperature with 1 mmol of 1,3-diphenylprop-2-en-1-ol, 2 mmol of isobutyraldehyde. [b] GC yield of the α-allylic alkylation of isobutyraldehyde.

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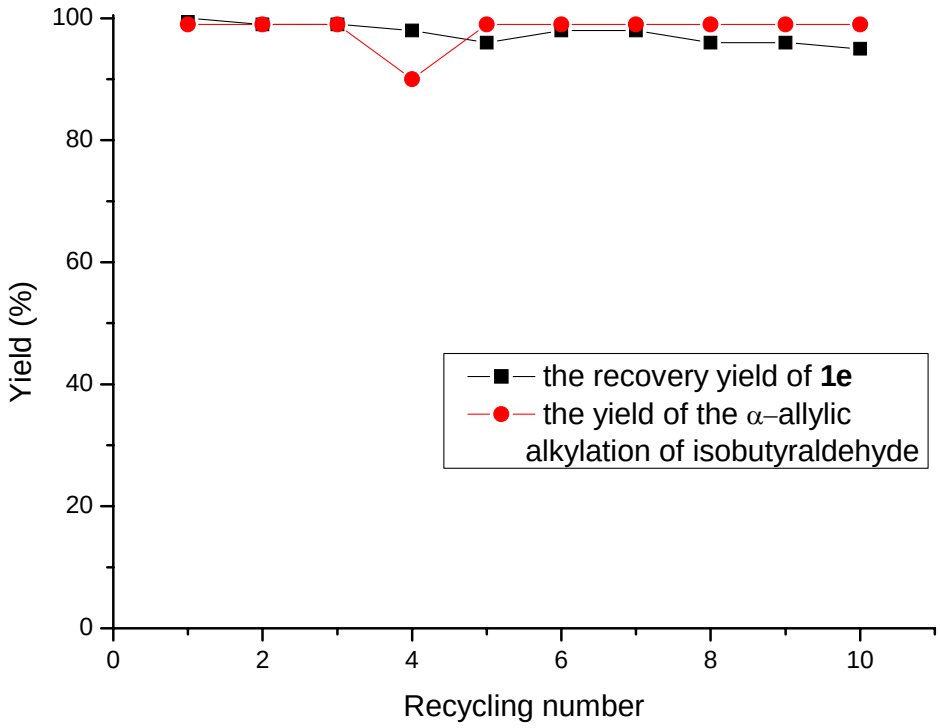

Fig S1. The recycling tests of the AFP 1e during a-allylic alkylation of isobutyraldehyde, GC yields.

2. General Procedure for Amino-functional Polysiloxane-Catalyzed Knoevenagel condensation

Acetic acid (20 mol%) and Amino-functional polysiloxane **1d** (10 mol%) was added into a solution of aldehyde (2 mmol) and a methylene-activated substrate (2.6 mmol) in CH_3CN (3 mL). After stirring at room temperature for 12h, Methanol (10 mL) was added and the supernatant liquid were dried, concentrated in vacuo, and purified by column chromatography on silica gel (hexane-EtOAc, 20:1) to gain the desired product.

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10b(**Table 3**, entry 2): ^{1}H-NMR ($CDCl_3$, 400MHz), δ =8.201 (s, -CH=C, 1H), 7.942 (t, J=6Hz, Ph-H, 2H), 7.496-7.533 (m, Ph-H, 1H), 7.453 (t, J=8.4Hz, Ph-H, 2H), 4.315-4.369 (m, J1=7.2Hz, J2=14Hz, -CH_2, 2H), 1.340-1.376 (m, J=7Hz, -CH_3, 3H).

10p(**Table 3**, entry 20): ^{1}H-NMR ($CDCl_3$, 400MHz), δ =8.173 (s, -CH=C, 1H), 7.913 (t, J = 6 Hz, Ph-H, 2H), 7.444 (t, J= 8.4 Hz, Ph-H, 2H), 4.343-4.396 (m, J_1= 7.2 Hz, J_2= 14 Hz, -CH_2, 2H),1.385 (m, J= 7 Hz, -CH_3,3H)

10q(**Table 3**, entry 21): ^{1}H-NMR ($CDCl_3$, 400MHz), δ =8.21(s, 1H), 7.734 (t, J= 11.2 Hz, 2H), 7.52-7.46 (m, J_1= 7.4 Hz, J_2= 14,2 Hz, 1H), 7.264 (t, J=7.2Hz, 1H), 4.40 (q, J_1= 7.0 Hz, J_2= 14.2 Hz, 2H), 1.40 (t, J= 7.0 Hz, -CH_3, 3H)

10r(**Table 3**, entry 22): ^{1}H-NMR ($CDCl_3$, 400MHz), δ =8.17 (s, -CH=C, 1H), 8.001 (t, J = 6 Hz, Ph-H, 2H), 7.163 (t, J= 8.4 Hz, Ph-H, 2H), 4.381-4.328 (m, J1 = 7.2 Hz, J2 = 14 Hz, -CH_2, 2H), 1.386-1.351 (m, J = 7 Hz, -CH_3, 3H).

3. General Procedure for recovery and recycling of Amino-functional polysiloxane 1d in the Knoevenagel condensation reaction.

Acetic acid (20 mol%) and amino-functional polysiloxane **1d** (10 mol%) was added into a solution of aldehyde (2 mmol) and malononitrile (2.6 mmol) in CH_3CN (3 mL). After stirring at room temperature for 12h, the reaction was completely that detected by TLC, methanol (10 mL) was then added to the reaction solution. The product was easily extracted by methanol because the AFP **1d** was not soluble in methanol and left in the bottom of glassware. After the extraction via liquid/gel

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separartions, the resulted was AFP **1d** was used directly for the next run.

Table S2. Recovery and Recycling of Amino-functional polysiloxane **1d** in the Knoevenagel condensation[a]

Run	RecoveryYield of **1d** (%)	ReactionYield (%)[b]
1	97	96
2	94	> 99
3	90	> 99
4	88	98
5	85	98
6	80	> 99

[a] Reaction conditions: All reactions were performed in CH_3CN at room temperature with 2 mmol of benzaldehyde, 2.6 mmol of malonitrile. [b]GC yield.

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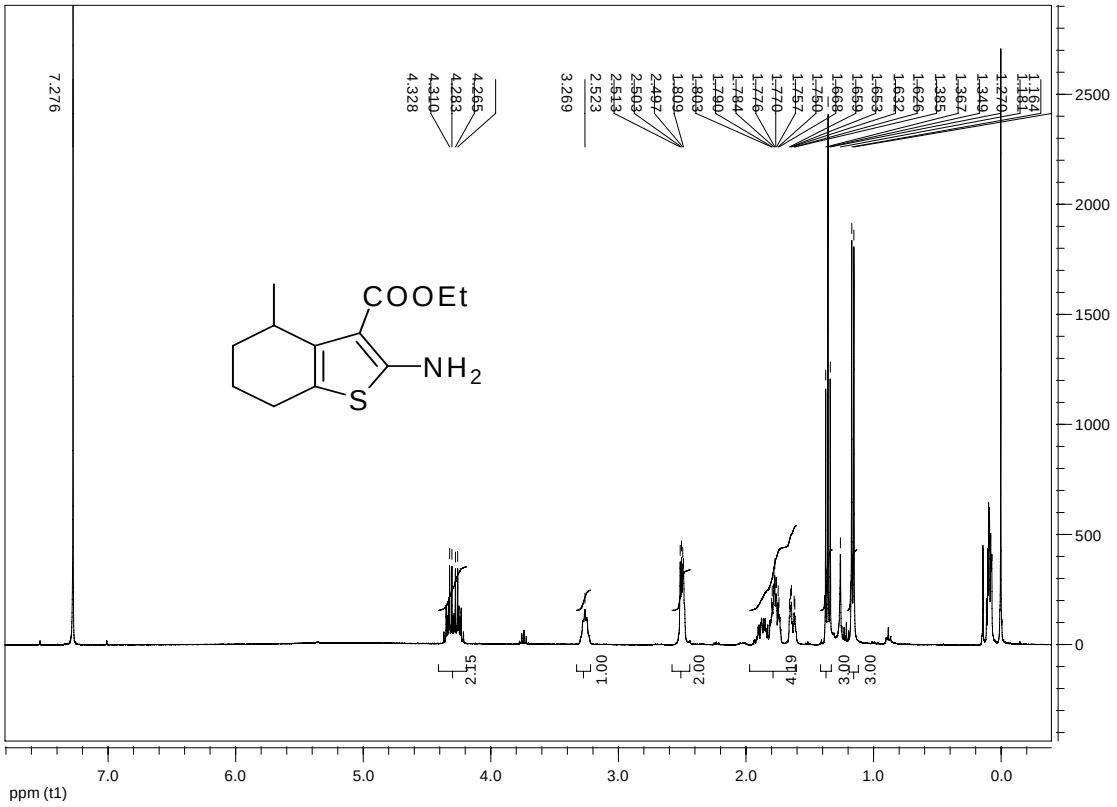
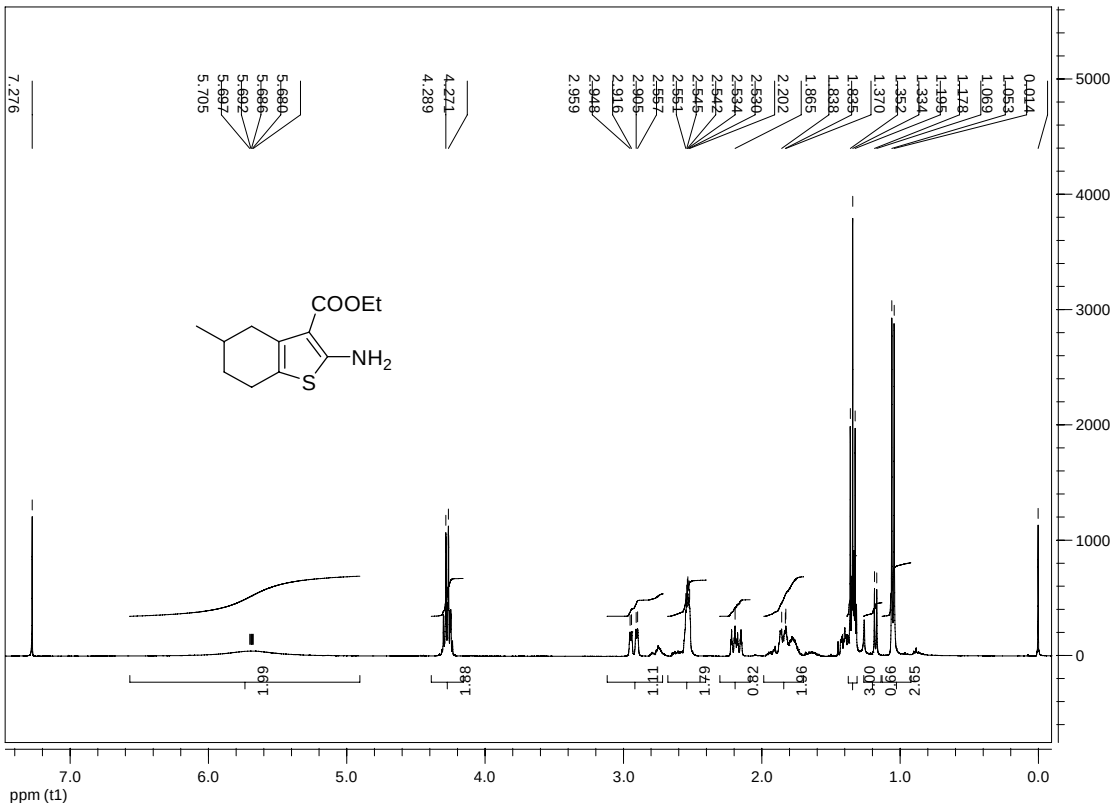
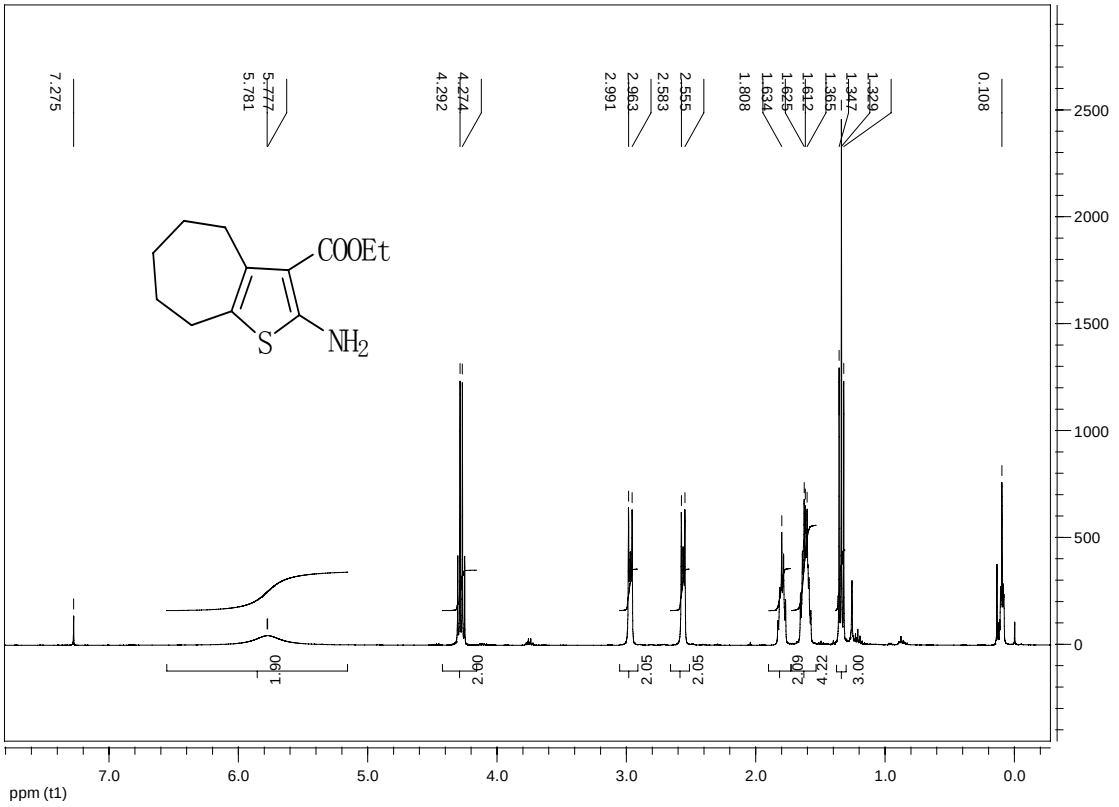
$^{1}H/^{13}C$-NMR spectrum of products



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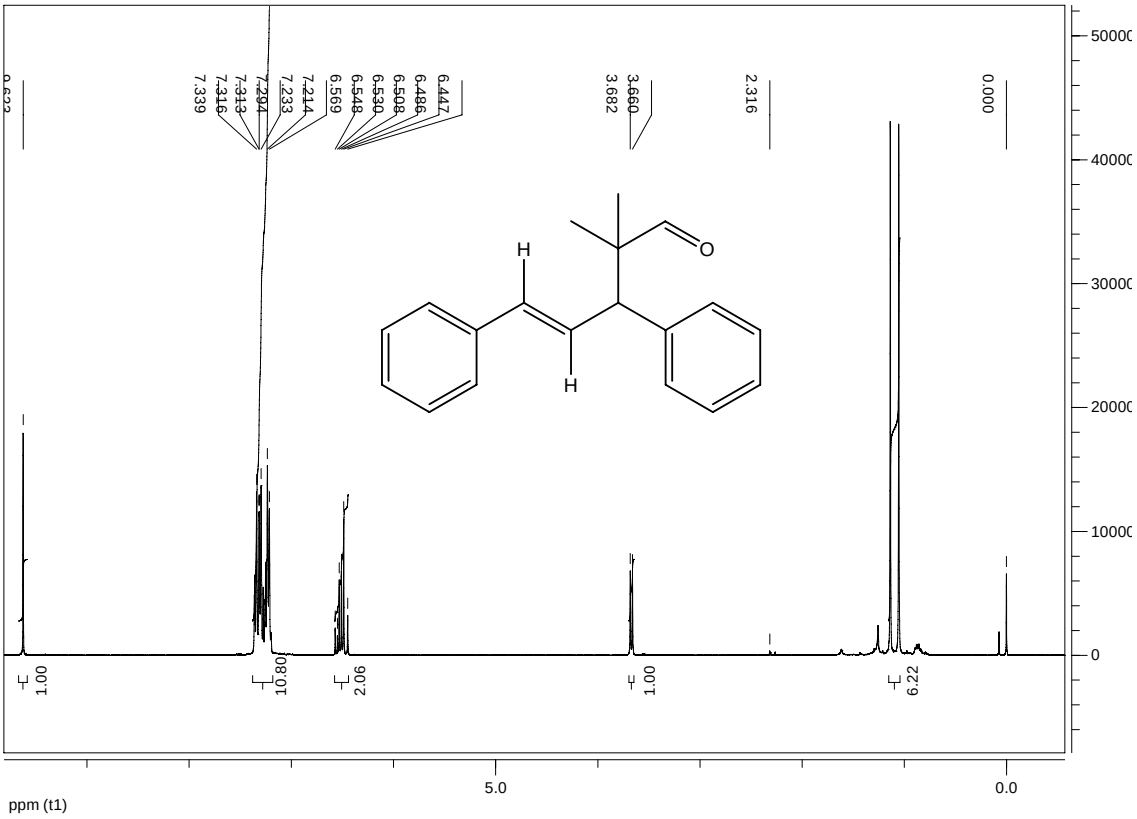
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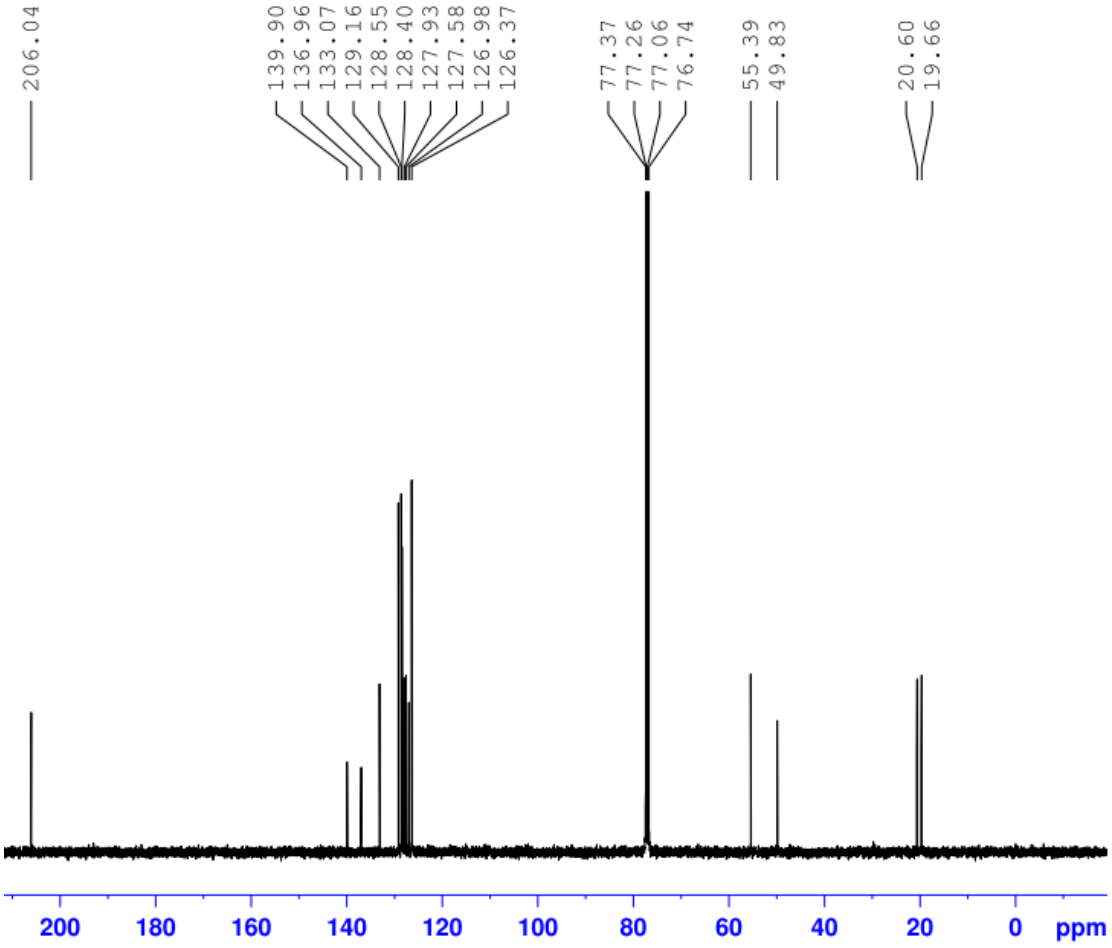
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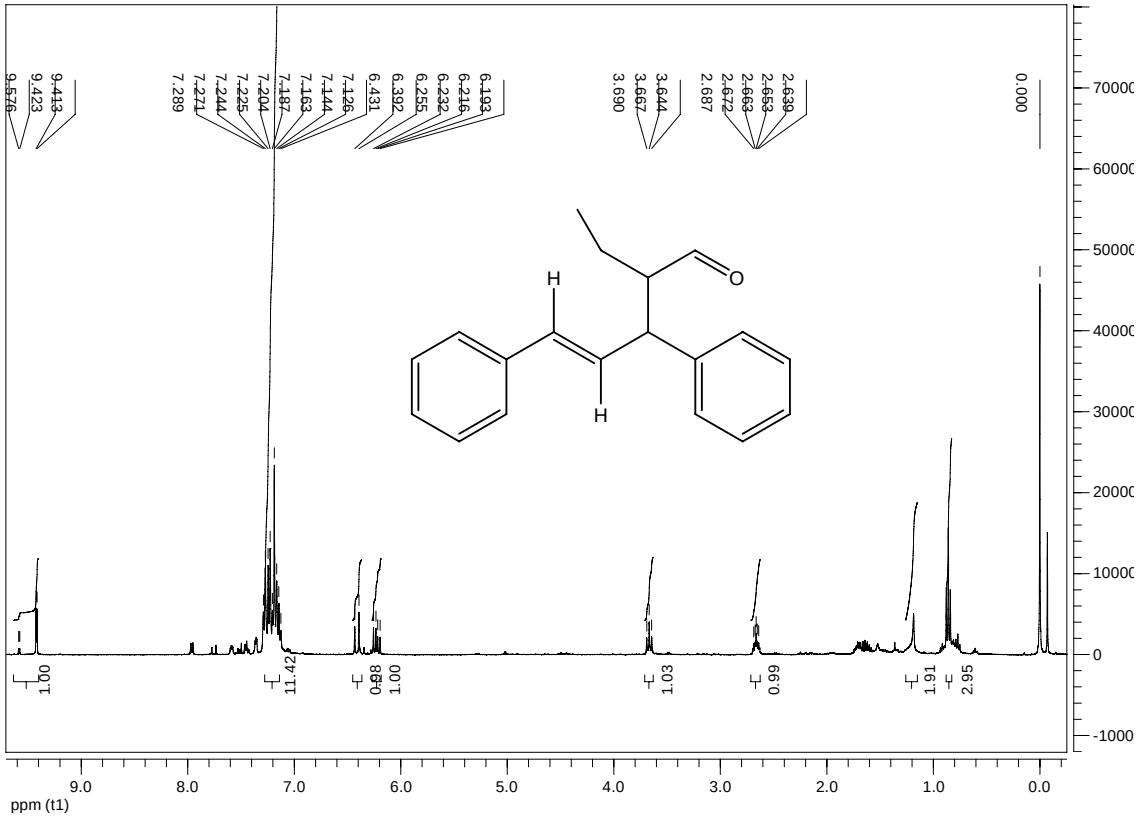
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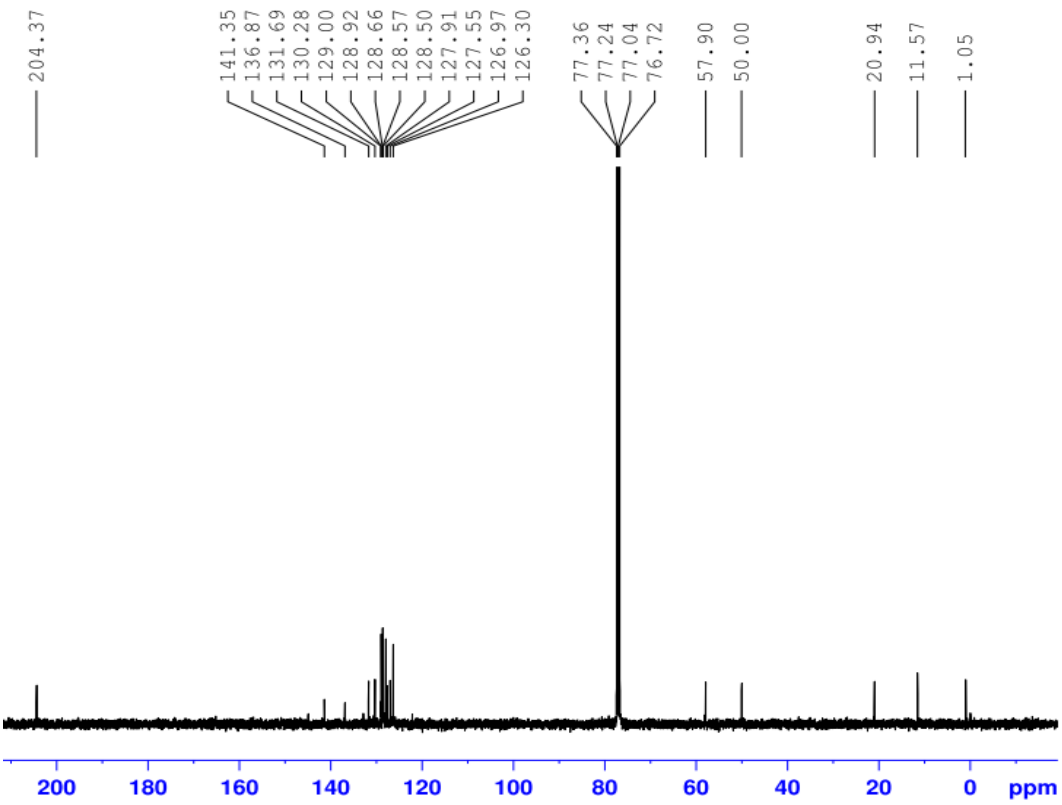

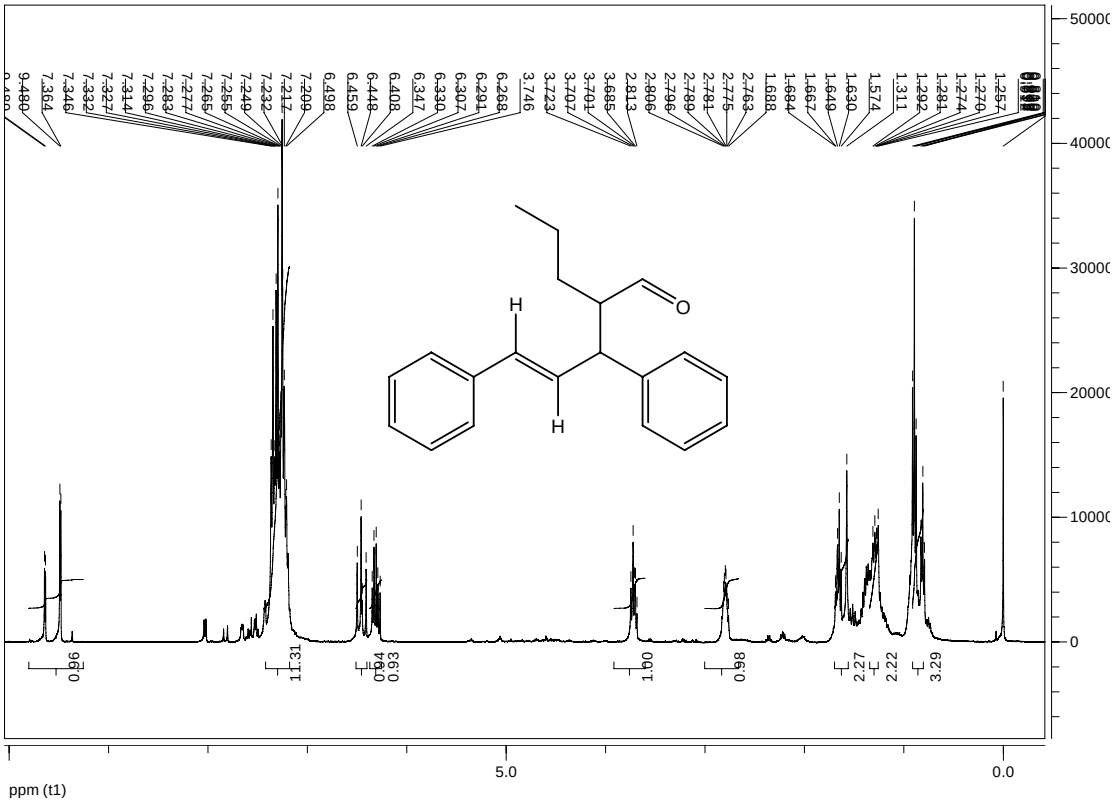

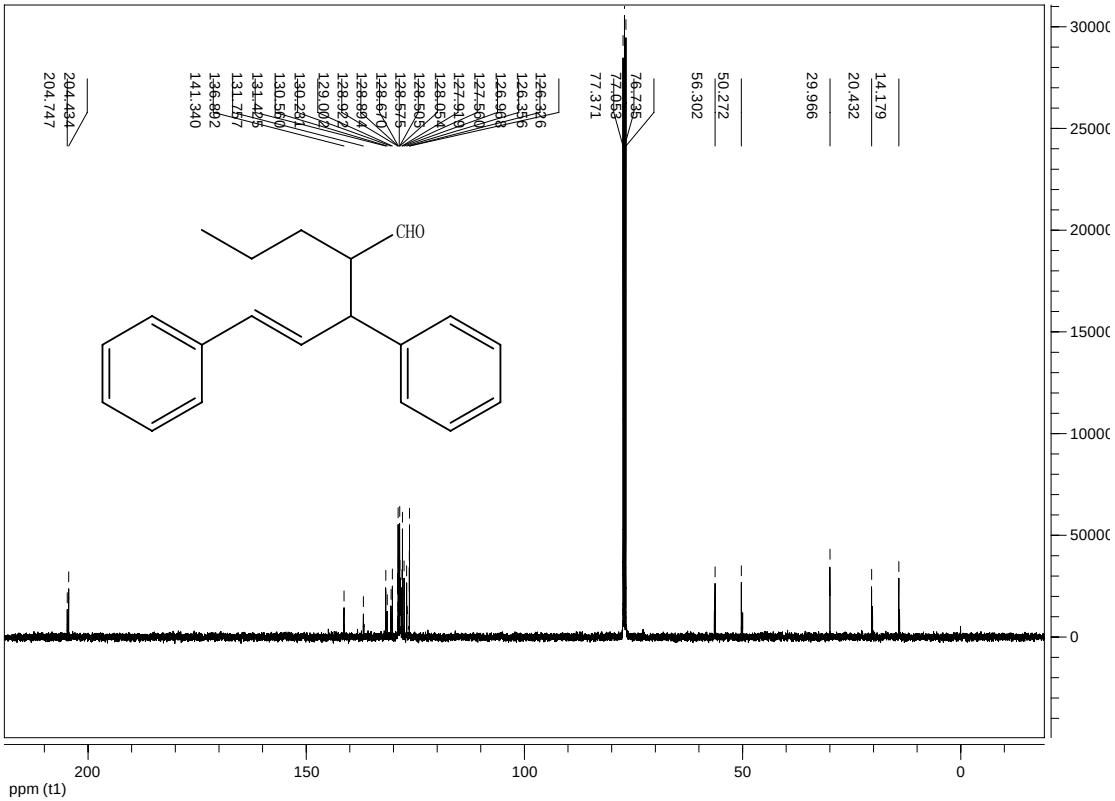
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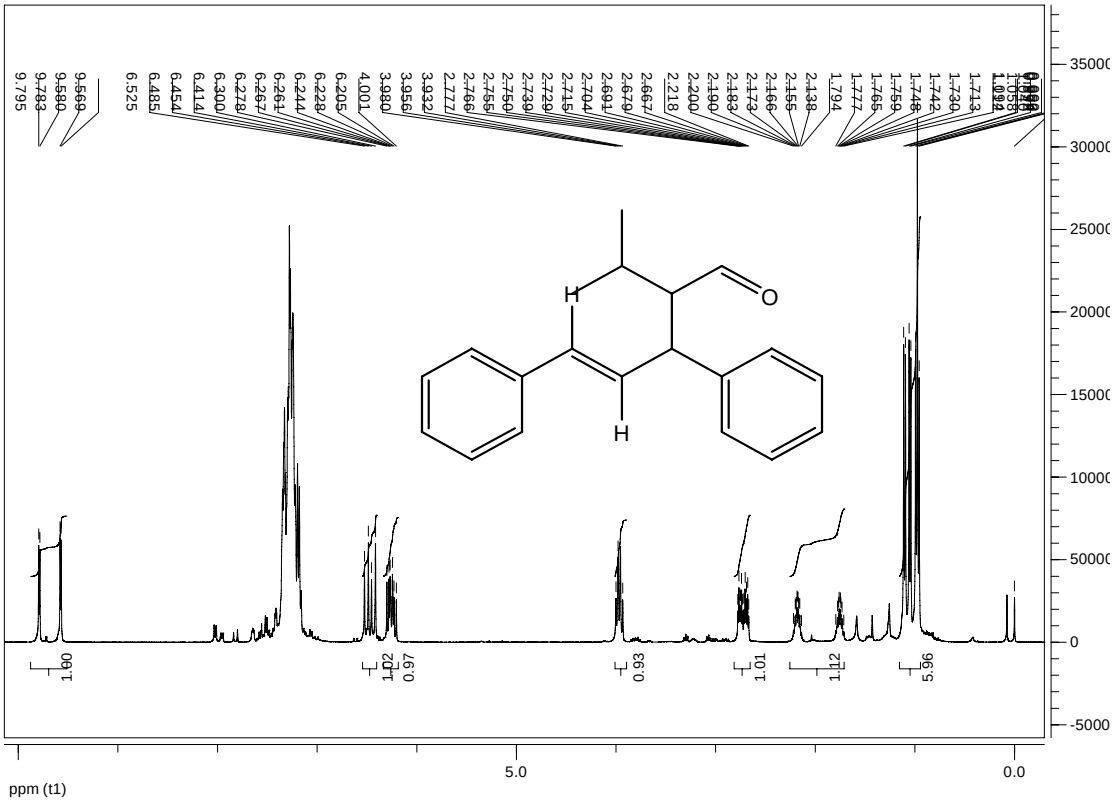
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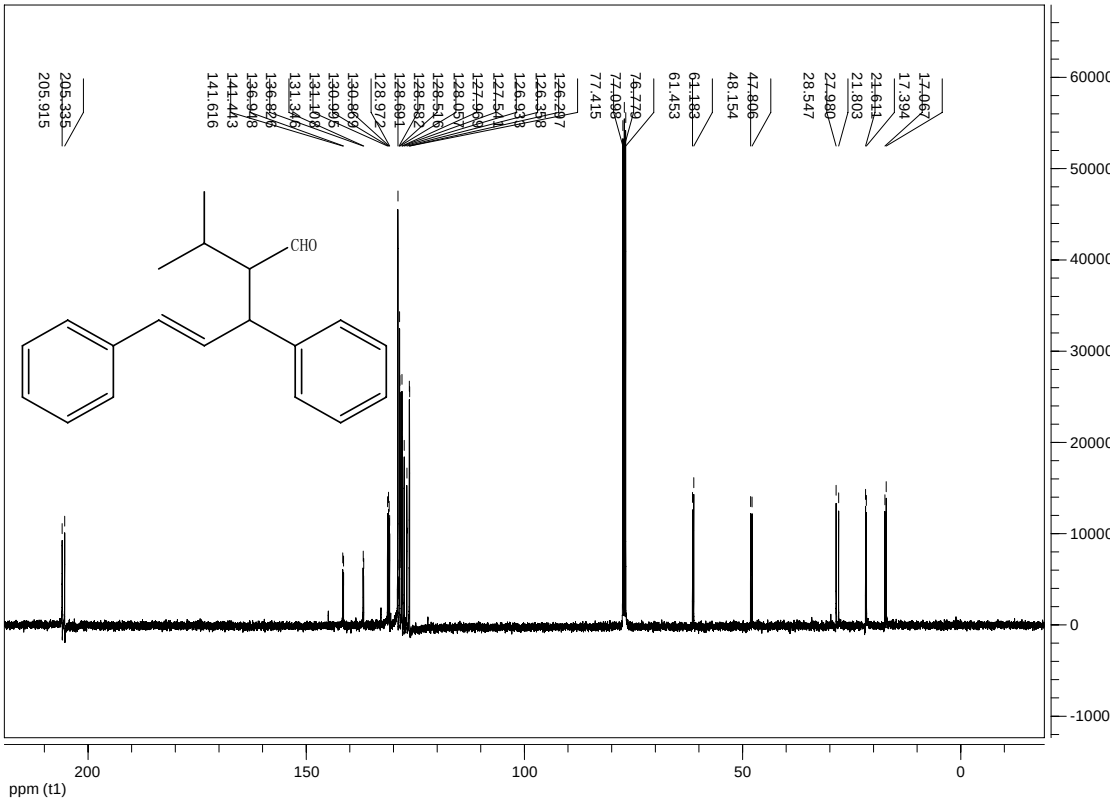
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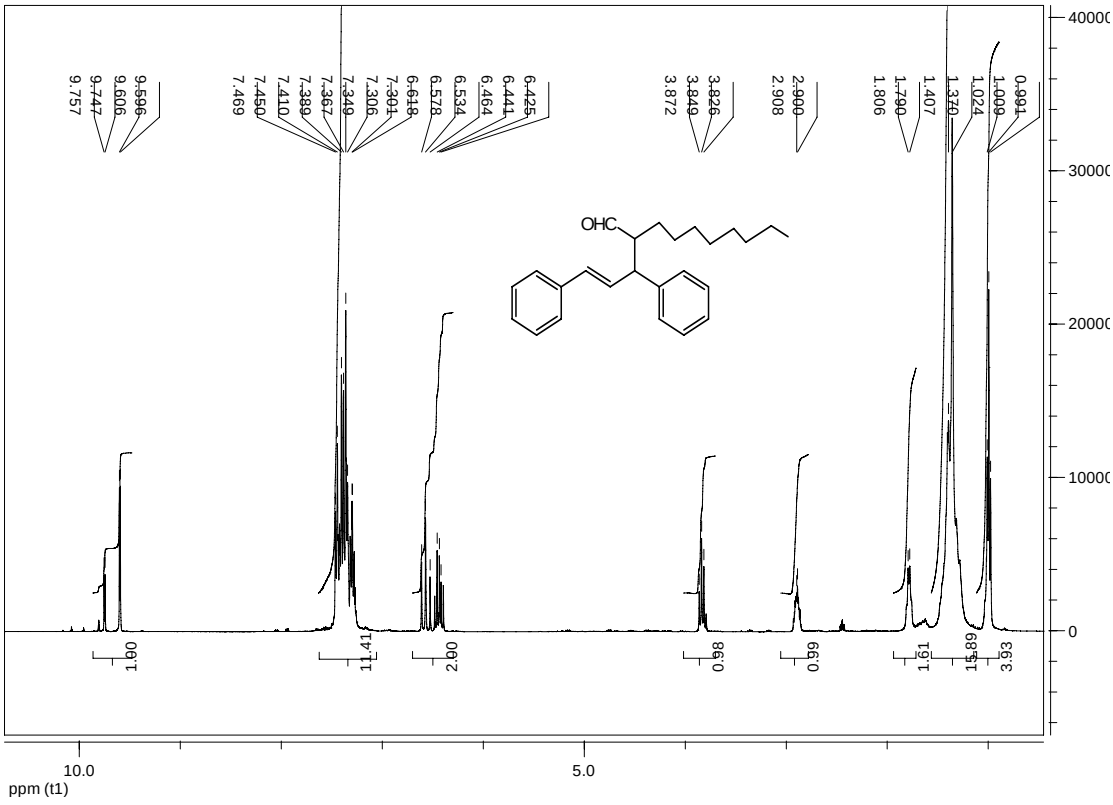
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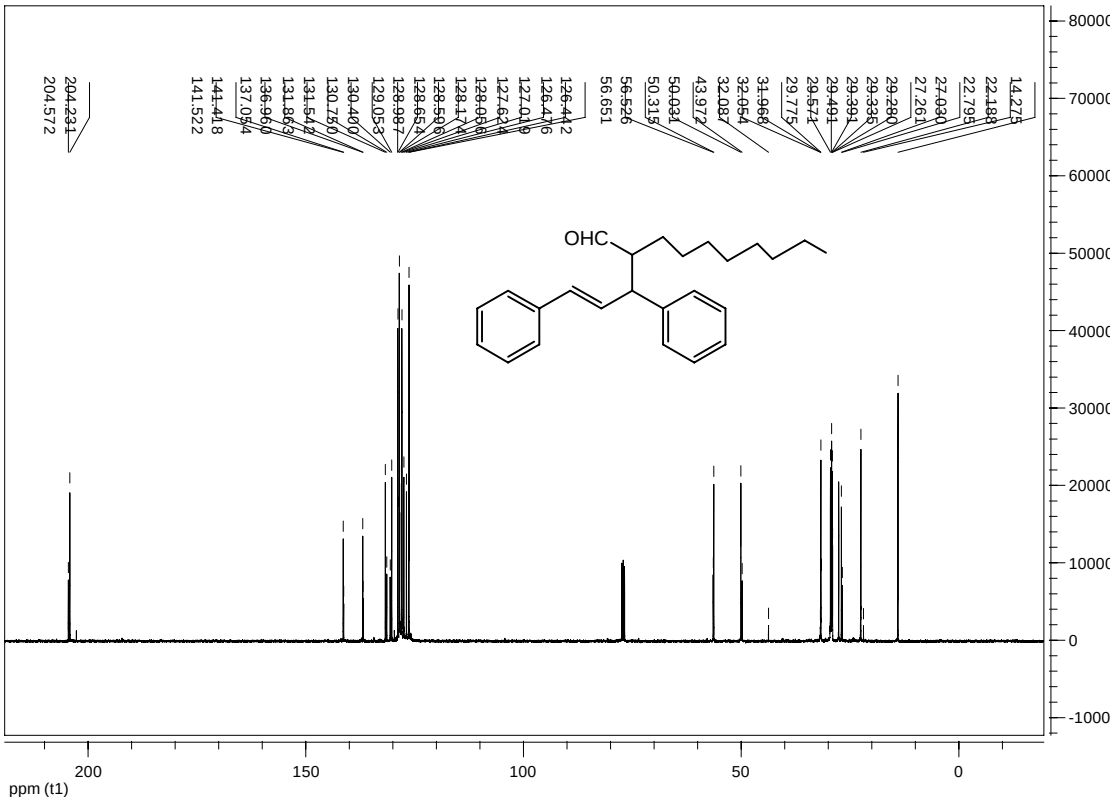
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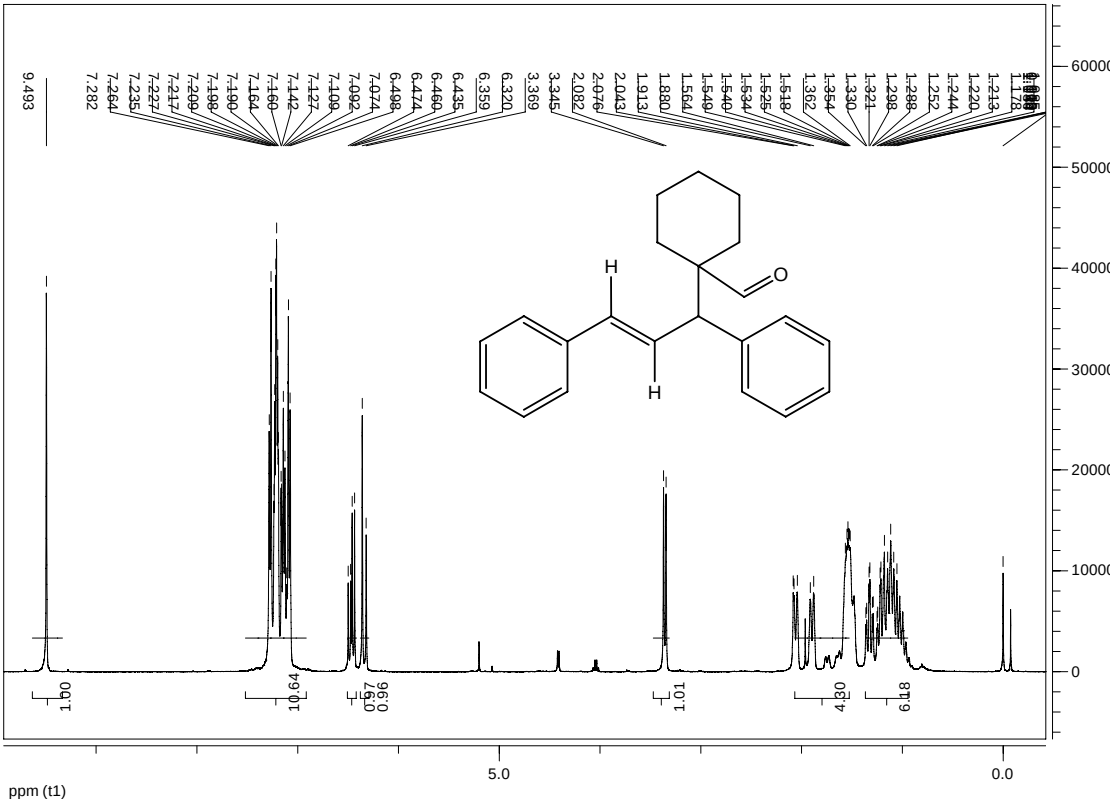
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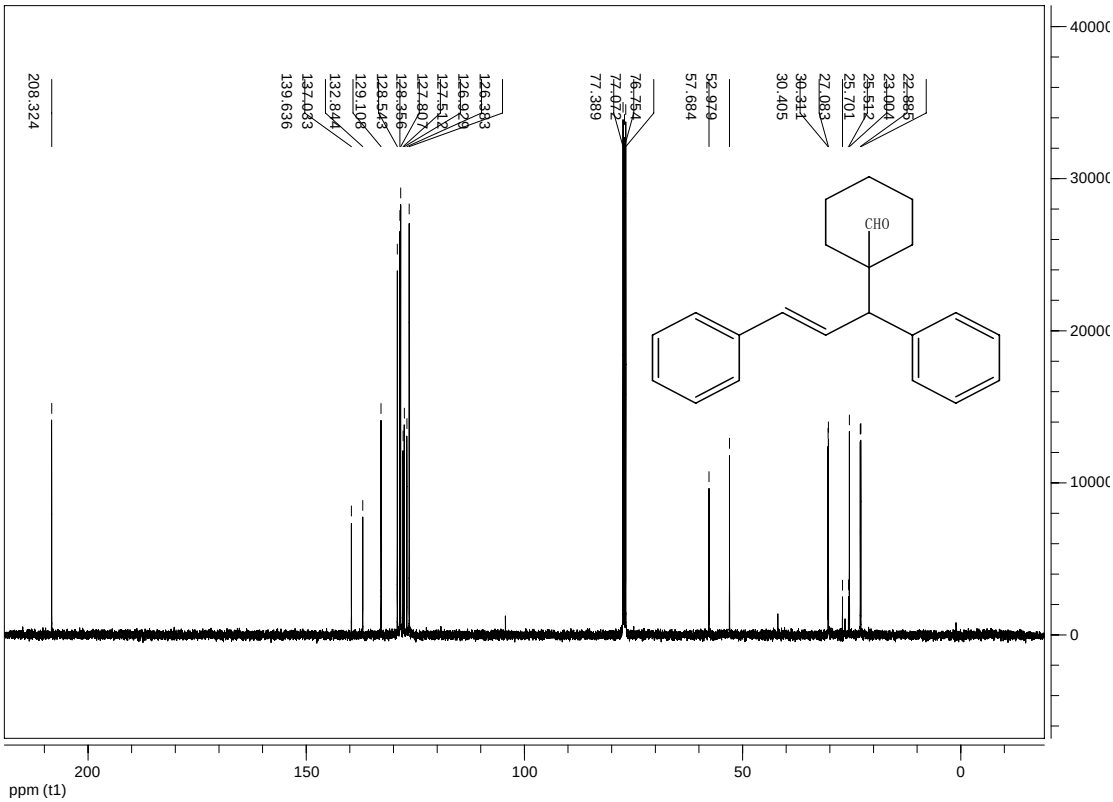
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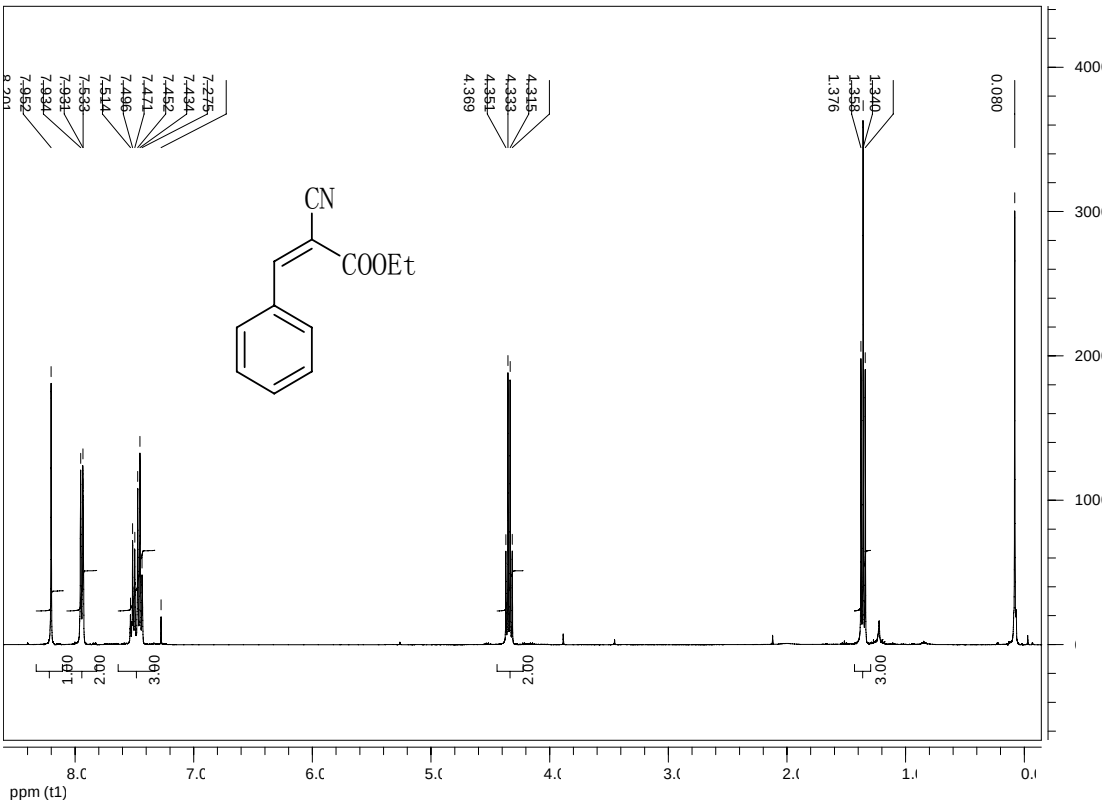
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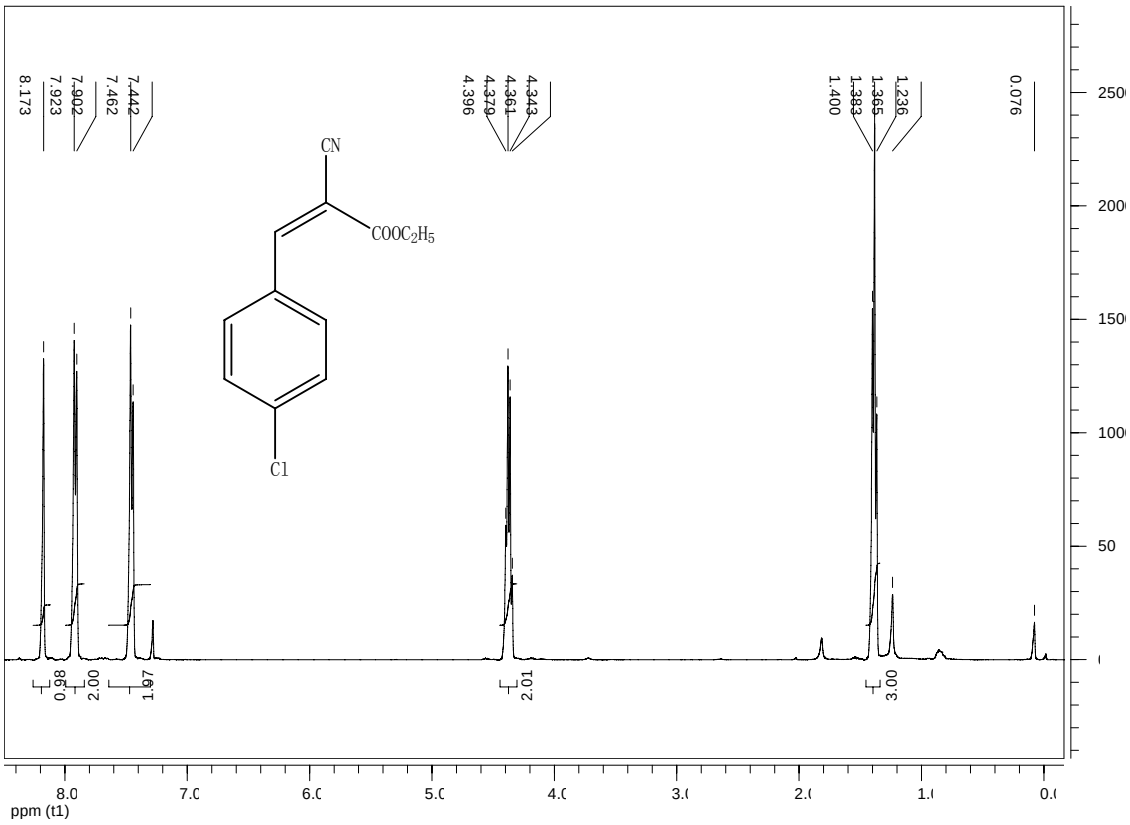
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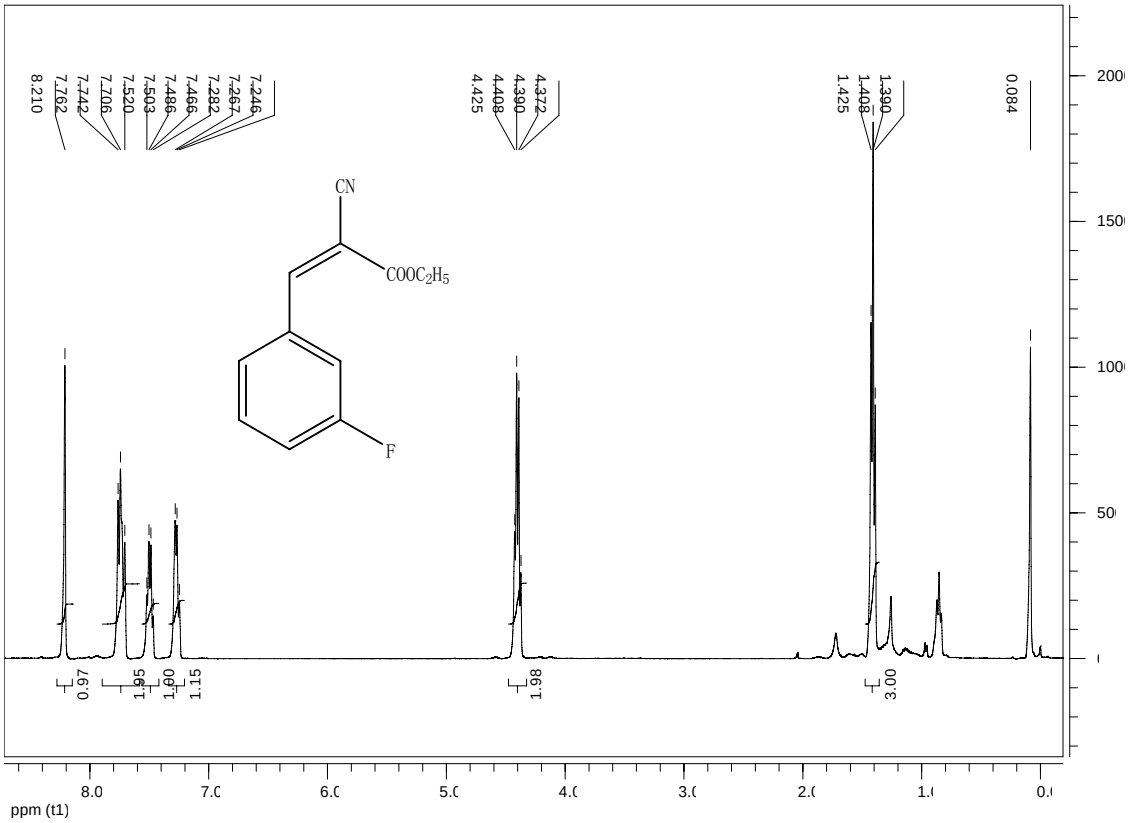
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