Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Ligand-free Ultrasmall Palladium Nanoparticles Catalysis for Mizoroki-Heck Reaction in Aqueous Micelles

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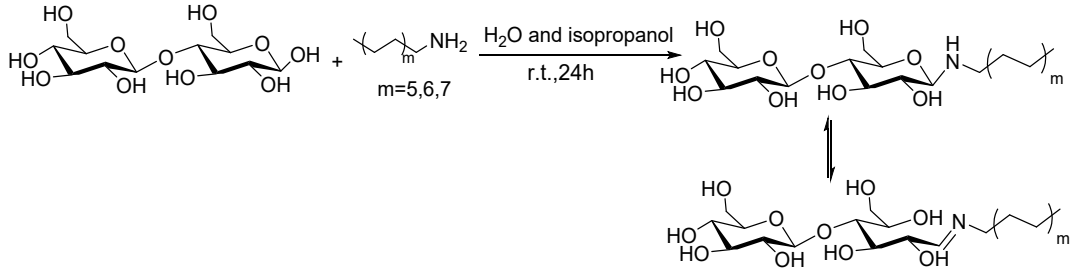
1. General Information

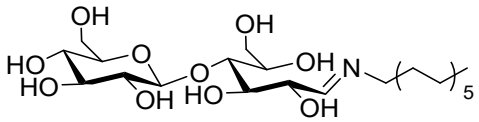
Unless otherwise noted, all reagents and solvents were general reagent grade from Greagent and Adamas and used as received. Melting points were determined on an X4-Data microscopic melting point apparatus and were uncorrected. All reactions were monitored by analytical thin-layer chromatography (TLC) (purchased from Merck) equipped with an UV detection.^{1}H NMR spectra were recorded on Bruker DRX (400/500 MHz) and ^{13}C NMR spectra on Bruker DRX (101/126 MHz) spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an AXIS Supra by Kratos Analytical Inc. Transmission electron microscopy (TEM) was performed on JEM-2100plus at an acceleration voltage of 200 kV. Dynamic light scattering (DLS) data were collected using ALV/DLS/SLS-5022F at 50 ℃. Fourier transform infrared spectroscopy (FTIR) was measured by Nicolet 6700.

2. The synthesis of sugar-based surfactants

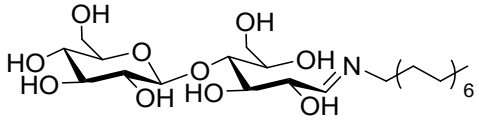
Preparation of N-alkyl lactosamine (ALA12, ALA14, ALA16)



Lactose monohydrate (6.48 g, 18 mmol) was dissolved in 60 mL of ultrapure water, and N-alkylamine (30 mmol) was dissolved in 100 mL of isopropanol. The two solutions were mixed and mechanical stirred at room temperature for 24 hours, then transfer to a 60 ^{o}C water bath for 30 minutes. The final mixture was suction filtered to remove solvent and the filter cake were rinsed three times with ethanol, recrystallized with ethanol, and dried in vacuum to give white solid powder. The yields of ALA12, ALA14, ALA16 were respectively 75%, 86%, 65%.

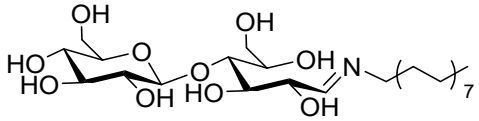


ALA12. ^{1}H NMR (400 MHz, MeOD) δ 4.38 (d, *J* = 3.2 Hz, 1H), 3.89 – 3.77 (m, 5H), 3.72 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.62 – 3.48 (m, 5H), 3.40 – 3.35 (m, 1H), 3.15 (t, *J* = 6.0 Hz, 1H), 2.91 (m, 1H), 2.65 (m, 1H), 1.58 – 1.46 (m, 2H), 1.33 (d, *J* = 12.8 Hz, 18H), 0.92 (t, *J* = 4.8 Hz, 3H). **^{13}C NMR (100 MHz, MeOD)** δ 103.72, 90.37, 79.57, 76.10, 75.87, 75.69, 73.45, 73.25, 71.19, 68.91, 61.10, 60.75, 31.67, 29.65, 29.31 (d, *J* = 7.0 Hz), 29.07, 27.00, 22.33, 13.02.



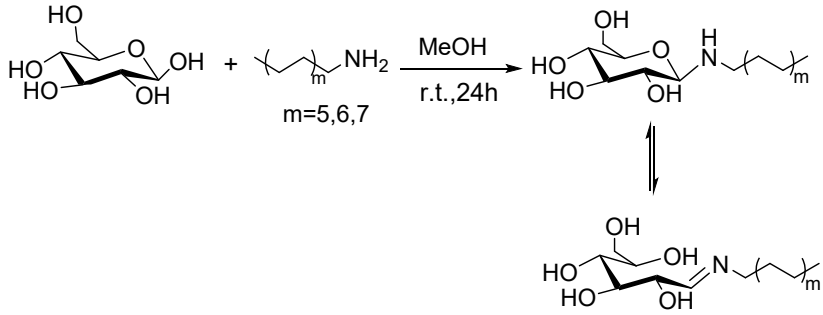
ALA14. ^{1}H NMR (400 MHz, DMSO) δ 5.12 (s, 1H), 4.80 (s, 1H), 4.64 (s, 2H), 4.49 (d, *J* = 29.6 Hz, 2H), 4.19 (dd, *J* = 12.4, 7.6 Hz, 1H), 3.76 – 3.15 (m, 14H), 2.93 (t, *J* = 8.4 Hz, 1H), 2.77 (dt, *J* = 11.2, 7.2 Hz, 1H), 1.37 (d, *J* = 6.4 Hz, 2H), 1.24 (s, 22H), 0.86 (t, *J* = 6.4 Hz, 3H).**^{13}C NMR**

(100 MHz, MeOD) δ 103.72, 90.38, 79.58, 76.10, 75.87, 75.69, 73.45, 73.25, 71.19, 68.91, 61.10, 60.75, 40.92, 31.67, 29.21 (d, *J* = 11.0 Hz), 29.07, 27.01, 26.57, 22.33, 13.02.

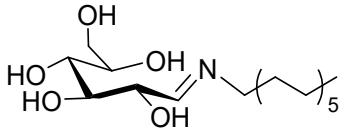


ALA16. ^{1}H NMR (400 MHz, DMSO) δ 5.12 (s, 1H), 4.80 (s, 1H), 4.64 (s, 2H), 4.49 (d, *J* = 25.6 Hz, 2H), 4.19 (dd, *J* = 12.4, 7.6 Hz, 1H), 3.76 – 3.15 (m, 14H), 2.93 (t, *J* = 8.4 Hz, 1H), 2.77 (dt, *J* = 11.2, 7.2 Hz, 1H), 1.37 (m, 2H), 1.24 (s, 22H), 0.86 (t, *J* = 6.4 Hz, 3H).**^{13}C NMR (100 MHz, MeOD)** δ 103.71, 90.37, 79.56, 76.10, 75.86, 75.68, 73.44, 73.24, 71.18, 68.91, 61.09, 60.74, 40.66, 31.67, 29.37, 29.06, 27.00, 26.48, 22.33, 13.02.

Preparation of N-alkyl glucosamine (AGA12)

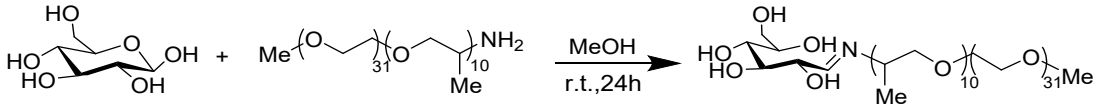


A solution of glucose (9.00 g, 50 mmol), and N-alkylamine (50 mmol) in methanol (100 mL) was mechanical stirred for 24 h at room temperature. Then the final mixture was suction filtered to remove solvent methanol, washed the filter cake three times with cyclohexane, once with water, twice with ethanol, recrystallized twice with ethanol, and dried in vacuum to give solid powder. The yields of AGA12 were respectively 87%.



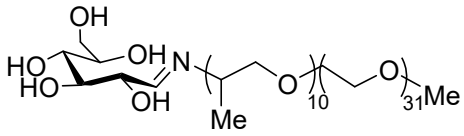
AGA12. ^{1}H NMR (400 MHz, MeOD) δ 3.91 – 3.80 (m, 2H), 3.67 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.38 (d, *J* = 8.4 Hz, 1H), 3.29 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.27 – 3.21 (m, 1H), 3.08 (t, *J* = 8.8 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.69 – 2.61 (m, 1H), 1.52 (m, 2H), 1.33 (d, *J* = 10.4 Hz, 18H), 0.92 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, DMSO)** δ 91.29, 78.03 (d, *J* = 15.3 Hz), 74.01, 71.07, 61.91, 46.03, 31.76, 30.48, 29.51 (d, *J* = 5.5 Hz), 29.18, 27.32, 22.56, 14.42.

Preparation of N-polyoxyalkyl glucosamine (GluM)



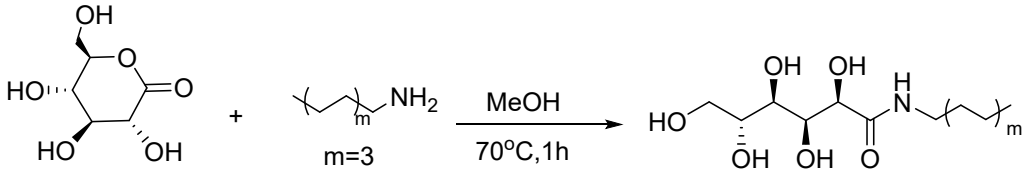
A solution of glucose (1.80 g, 10 mmol), and polyether amine M2070 (20 g, 10 mmol) in methanol (100 mL) was mechanical stirred for 24 h at room temperature. Then the final mixture

was placed at -15 °C for 5 times of recrystallization, and the supernatant liquid was removed the solvent by vacuum distillation to give yellow liquid in 85% yield.

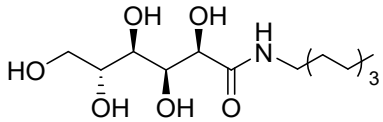


GluM. ^{1}H NMR (400 MHz, D_2O) δ 5.25 (d, *J* = 2.6 Hz, 1H), 4.67 (dd, *J* = 7.9, 0.9 Hz, 1H), 3.81 (dd, *J* = 8.5, 3.8 Hz, 13H), 3.74 (s, 124H), 3.58 (dd, *J* = 17.2, 7.0 Hz, 23H), 3.42 (s, 4H), 1.20 (d, *J* = 6.1 Hz, 30H), 1.09 (d, *J* = 6.1 Hz, 2H). **MS (MALDI-TOF):** Anal. Calced for $C_{99}H_{199}NO_{46}$: $[M+H]^+$ 2139.6. C, 55.57, H, 9.38, N, 0.65. Found: $[M+H]^+$ 2139.4. C, 54.81; H, 8.96; N, 0.94.

Preparation of N-alkyl-D-glucamide (C8NG)



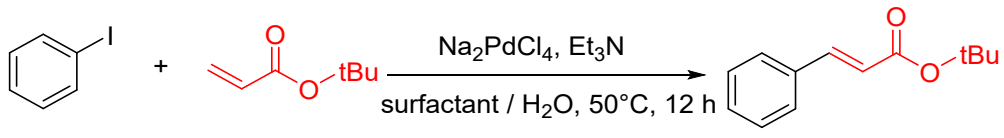
A mixture of gluconolactone (3.92 g, 22 mmol) and N-alkylamine (23 mmol) in CH_3OH (25 mL) were stirred for 1 hour at 70 °C. Then the final mixture was suction filtered to remove solvent CH_3OH, and the filter cake were rinsed three times with ethanol, recrystallized twice with methanol, and dried in vacuum to give solid powder. The yield of C8NG is 96%.



C8NG. ^{1}H NMR (400 MHz, DMSO) δ 7.59 (t, *J* = 5.9 Hz, 1H), 5.34 (d, *J* = 5.1 Hz, 1H), 4.53 (t, *J* = 5.6 Hz, 1H), 4.49~4.45 (m, 1H), 4.39 (d, *J* = 7.2 Hz, 1H), 4.33 (t, *J* = 5.7 Hz, 1H), 3.97 (dd, 1H), 3.90 (ddd, 1H), 3.58 (ddd, 1H), 3.52~3.44 (m, 2H), 3.40~3.34 (m, 1H), 3.14~3.00 (m, 2H), 1.45~1.36 (m, 2H), 1.30~1.20 (m, 10H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, DMSO)** δ 172.69, 74.10, 72.89, 71.95, 70.59, 63.85, 38.72, 31.74、29.63、29.19、26.85、22.57, 14.41.

3. Optimization of reaction conditions

Table S1 Screening of surfactants [a]



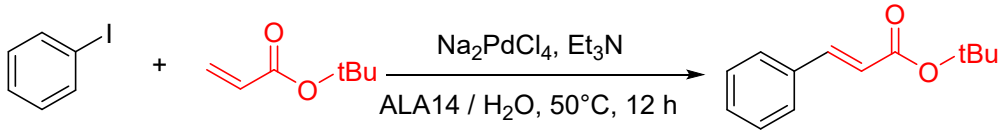
1a **2a** **3a**

Entry	Surfactant	Yield/%[b]
1	-	22
2	SDS	40
3	CTAB	62
4	Tween60	72

5	APG	58
6	AGA12	82
7	GluM	76
8	C8NG	80
9	ALA12	90
10	**ALA14**	**99**
11	ALA16	83

[a] Standard conditions: iodobenzene 1a (0.5 mmol), tert-Butyl acrylate 2a (1 mmol), Na_2PdCl_4 (0.005mmol), Et_3N (3 mmol), 10 mM surfactant/H_2O (10 mL) at 50 °C for 12 h; [b] Isolated yield.

Table S2 Screening of the amount of the surfactant in Heck reaction [a]

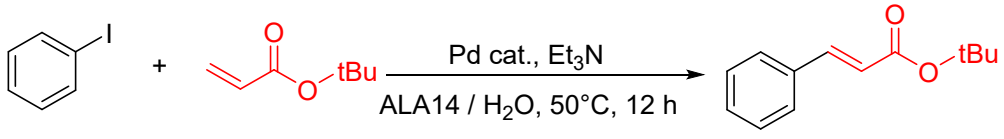


1a **2a** **3a**

Entry	Surfactant/mmol	Yield/%[b]
1	0.2	99
2	0.1	99
3	0.05	90
4	0.03	85
5	0.01	80

[a] Standard conditions: iodobenzene 1a (0.5 mmol), tert-Butyl acrylate 2a (1 mmol), Na_2PdCl_4 (0.005mmol), base (3 mmol), ALA14/H_2O (10 mL) at 50 °C for 12 h; [b] Isolated yield.

Table S3 Screening of the amount of the palladium sources in Heck reaction [a]

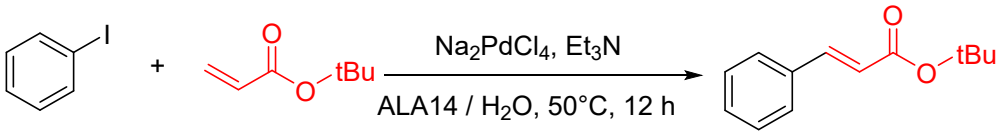


1a **2a** **3a**

Entry	Palladium sources	Palladium sources/mmol	Yield/%[b]
1	Na_2PdCl_4	0.005	99
2	$Pd(OAc)_2$	0.005	85
3	$PdCl_2$	0.005	80
4	$Pd(dba)_3$	0.005	80
5	$Pd(dba)_3$+JohnPhos	0.005	85

[a] Standard conditions: iodobenzene (0.5 mmol), tert-Butyl acrylate (1 mmol), Et_3N (3 mmol), 10 mM ALA14/H_2O (10 mL) under air at 50 °C for 12 h; [b] Isolated yield.

Table S4 Screening of the amount of the palladium sources in Heck reaction [a]

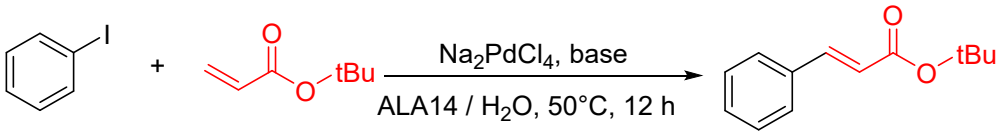


1a **2a** **3a**

Entry	Na_2PdCl_4 / mmol	Yield/%[b]
1	0.005	99
2	0.004	90
3	0.003	80

[a] Standard conditions: iodobenzene (0.5 mmol), tert-Butyl acrylate (1 mmol), Et_3N (3 mmol), 10 mM ALA14/H_2O (10 mL) under air at 50 °C for 12 h; [b] Isolated yield.

Table S5 Screening of the base sources in Heck reaction [a]

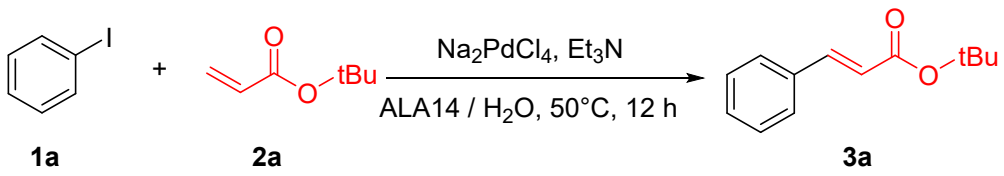


1a **2a** **3a**

Entry	Base	Yield/%[b]
1	Et_3N	99
2	K_2CO_3	72
3	Cs_2CO_3	70
4	Na_2CO_3	71
5	$KHCO_3$	65
6	$NaHCO_3$	66
7	NaOH	52
8	NaOAc	75
9	K_3PO_4	79

[a] Standard conditions: iodobenzene (0.5 mmol), tert-Butyl acrylate (1 mmol), Na_2PdCl_4 (0.005mmol), 10 mM ALA14/H_2O (10 mL) under air at 50 °C for 12 h; [b] Isolated yield.

Table S6 Screening of the amount of the base sources in Heck reaction [a]

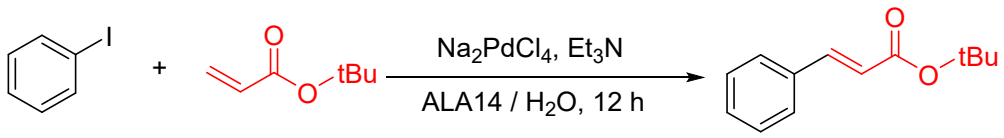


1a **2a** **3a**

Entry	Et_3N/mmol	Yield/%[b]
1	3	99
2	2	92
3	1	85
4	-	trace

[a] Standard conditions: iodobenzene (0.5 mmol), tert-Butyl acrylate (1 mmol), Na_2PdCl_4 (0.005mmol), 10 mM ALA14/H_2O (10 mL) under air at 50 °C for 12 h; [b] Isolated yield.

Table S7 Screening of the Heck reaction temperature [a]



1a **2a** **3a**

Entry	Temp. /℃	Yield/%[b]
1	60	99
2	50	99
3	40	70
4	25	20

[a] Standard conditions: iodobenzene (0.5 mmol), tert-Butyl acrylate (1 mmol), Na_2PdCl_4 (0.005mmol), Et_3N (3 mmol), 10 mM ALA14/H_2O (10 mL) under air for 12 h; [b] Isolated yield.

4. Experimental and characterization of reaction products

General procedure of Heck coupling in aqueous solution of ALA14

ALA14 aqueous solution was obtained by dissolving ALA14 in 10ml water at 50 °C. The palladium sources (0.005 mmol), base (3 mmol), iodobenzene (0.5 mmol) and tert-Butyl acrylate (1 mmol) were added to ALA14 aqueous solution (10 mL), then heated and stirred at 50 °C for 12h. When the reaction was finished, the solution mixture was cooled and extracted by adding the ethyl acetate (3 mL). The organic phases were dried over Na_2SO_4 and concentrated by vacuum concentration. Then the crude product was purified by column chromatography through silica gel, eluting with ethyl acetate/petroleum ether solvent mixture, to give the pure product. The pure product was characterized by ^1H NMR and ^{13}C NMR.

The synthesis of Pd-based catalysts

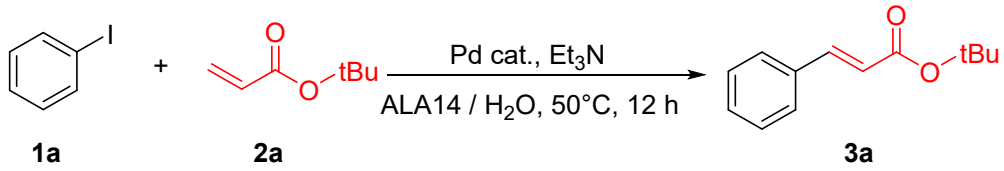
w-ALA14-Pd: ALA14 aqueous solution was obtained by dissolving ALA14 in 10ml water at 50 °C. Na_2PdCl_4 (0.005 mmol) was added to ALA14 aqueous solution (10 mL), then heated and stirred at 50 °C for 3h. Finally, w-ALA14-Pd was obtained.

w-Et_3N-Pd: Na_2PdCl_4 (0.005 mmol) and Et_3N (0.02 mmol) were added to 10 mL water, then heated and stirred at 50 °C for 3h. Finally, w-Et_3N-Pd was obtained.

w-ALA-Et_3N-Pd: ALA14 aqueous solution was obtained by dissolving ALA14 in 10ml water at 50 °C. Na_2PdCl_4 (0.005 mmol) and Et_3N (3mmol) added to ALA14 aqueous solution (10 mL), then heated and stirred at 50 °C for 3h. Finally, w-ALA14-Et_3N-Pd was obtained.

p-Et_3N-Pd: (0.005 mmol) added to Et_3N (3 mmol), then heated and stirred at 50 °C for 3h. The products were obtained through centrifugation and washing with ethanol three times, then dried for 6 h at 50 ℃ in the vacuum drying oven. Finally, p-Et_3N-Pd was obtained.

Table S8 Controlled experiment [a]



1a **2a** **3a**

Entry	Pd-based Catalyst	Yield/%[b]
1	w-ALA14-Pd	trace
2	w-Et_3N-Pd	22
3	w-ALA14-Et_3N-Pd	99
4[c]	p-Et_3N-Pd	90
5[d]	p-Et_3N-Pd	89

[a] Reaction: iodobenzene 1a (0.5 mmol), tert-Butyl acrylate 2a (1 mmol), catalyst (0.005mmol) at 50 °C for 12 h; [b] Isolated yield. iodobenzene 1a (0.5 mmol), tert-Butyl acrylate 2a (1 mmol), catalyst (0.005mmol), Et_3N ([c] 3 mmol, [d] 2mmol), 10 mM ALA14/H_2O (10 mL) at 50 °C for 12 h.

The measurement of surface tension

The surface tension (γ) was measured at 40.0 ± 0.1 °C by the pendant method using a K100 automatic surface tension meter (KRUSS, Germany). The solution is equipped with ultra-pure water.

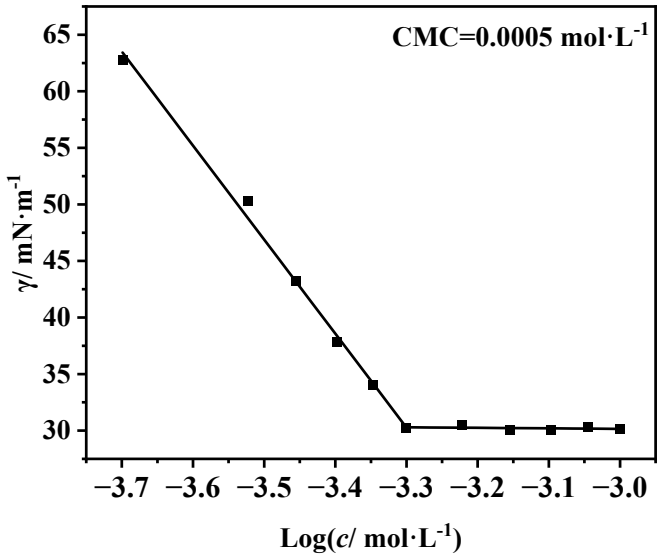


Figure S1. Surface tension (γ) of ALA14 aqueous solution as a function of surfactant molality at 40°C

The critical micelle concentration of ALA14 at 40 °C was calculated to be 0.5 mM, which was much lower than the concentration of ALA14 (10 mM) used in the reaction. Therefore, we believe that the conditions for the formation of micelles were achieved in the reaction.

The measurement of DLS

The change of micelle size before and after the dissolution of Et_3N in ALA14 aqueous solution at 50 °C was studied by dynamic light scattering (DLS). Before measurement, impurities were removed by 0.22 μm hydrophilic polyvinyl (PVDF) fluoride membrane. The size and distribution of micelles were measured by ALV / DLS / LS-5022F laser scattering system (He-Ne laser (λ = 632.8 nm)) at 90. The experimental data were analyzed by ALV-V3.0 software.

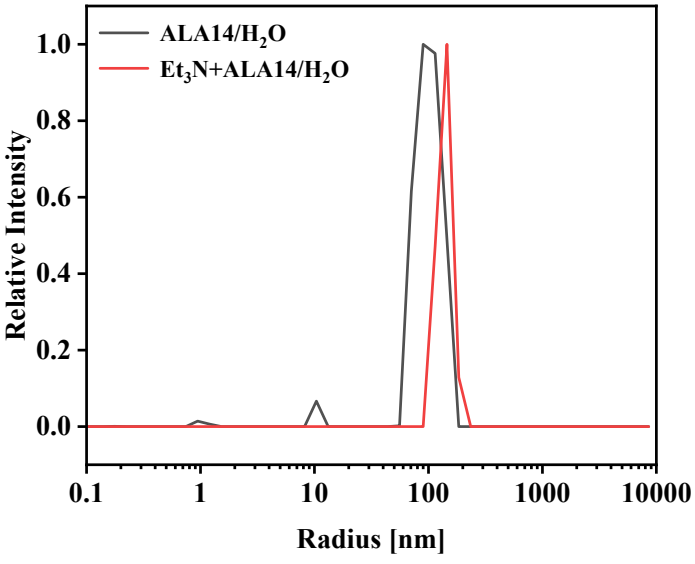


Figure S2. DLS results for micelle size distribution of 10mM ALA14 aqueous solution

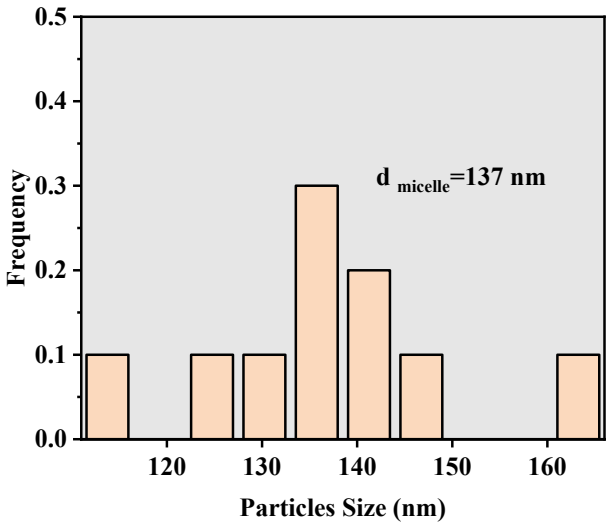


Figure S3. Particle size distribution of micelles in w-ALA14-Et_3N-Pd

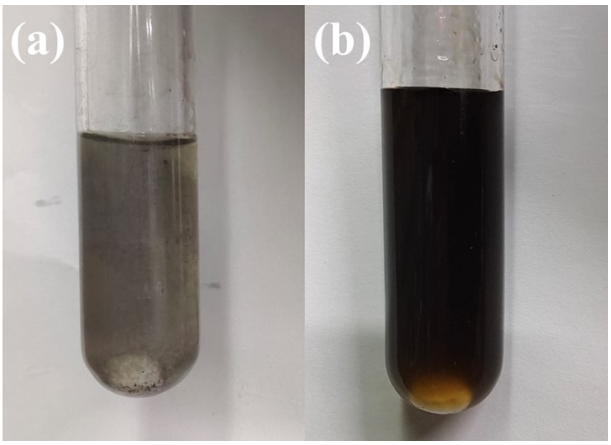


Figure S4. Appearance of (a) p-Et3N deposited in ALA14 aqueous solution, (b) w-ALA14-Et_3N-Pd aqueous solution

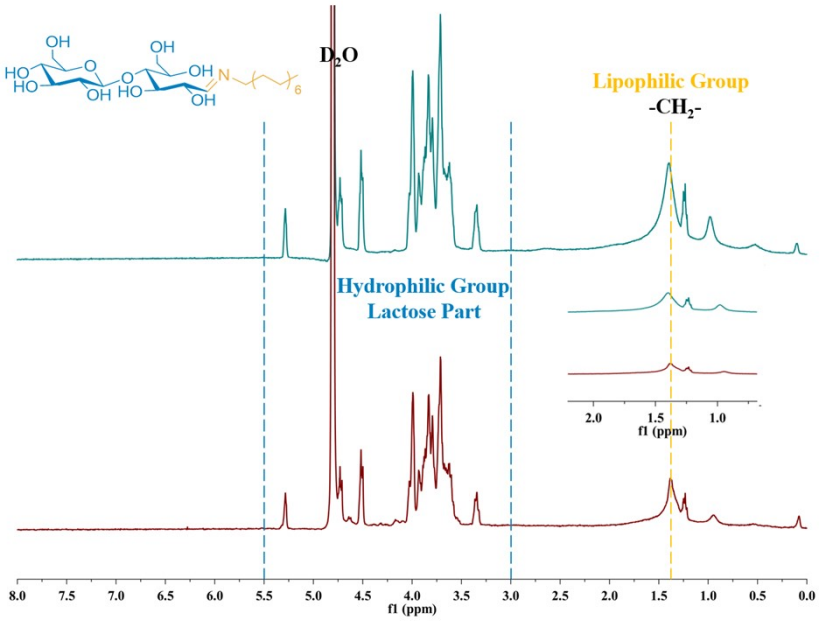


Figure S5. ^{1}H NMR spectra and peak assignments for the ALA14/D_2O (red line) and ALA14+ Na_2PdCl_4/D_2O (green line).

Kinetics study

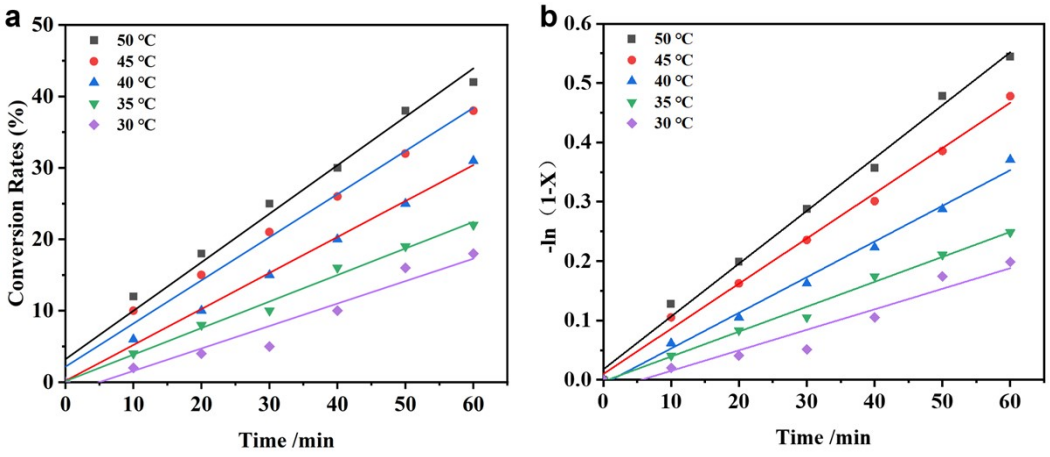


Figure S6. (a)The relationship between the reaction rate and temperature. (b) The relationship between the conversion rates and temperature.

Table S9 The activation energy of Heck reaction catalyzed by palladium-based catalyst. [a]

Entry	Catalyst	E*a* /kJ/mol[b]
1	**w-ALA14-Et_3N-Pd**	**40.49**
2	Pd@N-C	76
3	Pd/N-C	106
4	$PdCl_2$(bipy)	72.91

5	$PdCl_2$(bipy)	98.70

Recycling of ALA14/H_2O system

Once the reaction was finished at 50 °C, the reaction mixture was extracted with ethyl acetate, and ALA14 was deposited in the aqueous phase after cooling. After the organic phase containing the product was separated, the aqueous phase was heated to dissolve at 50 ° C, and the substrate (iodobenzene (0.5 mmol) and tert-butyl acrylate (1.0 mmol)) and base (Et_3N (3 mmol)) were re-added to the aqueous solution containing ALA14 and Pd NPs for the next catalytic cycle.

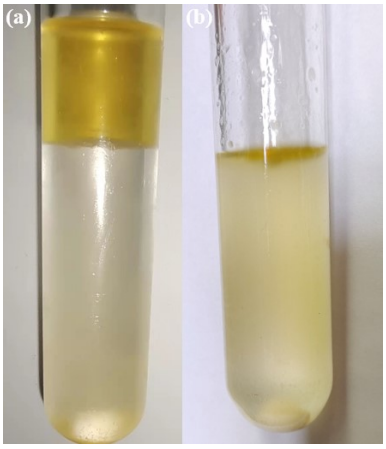
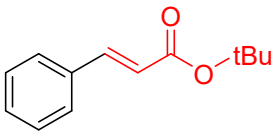
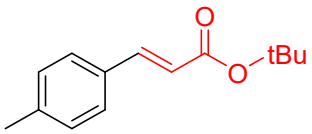


Figure S7. Appearance of (a) ALA14 aqueous solution extracted by ethyl acetate and cooled after Heck reaction, (b) ALA14 aqueous solution heated after removing the extract

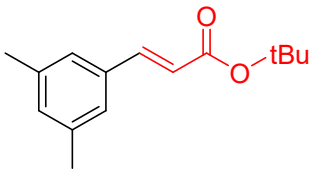
5 The Data of Charaterization



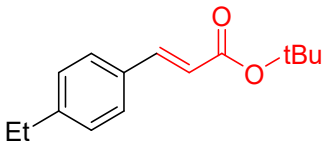
***(E)*-tert-butyl cinnamate 3a (99% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 16.0 Hz, 0H), 7.52 – 7.45 (m, 0H), 7.34 (d, *J* = 2.1 Hz, 0H), 6.35 (d, *J* = 16.0 Hz, 0H), 1.52 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.30, 142.51, 133.63, 128.91, 127.79, 126.93, 119.25, 79.46, 76.32, 76.00, 75.68, 27.19.



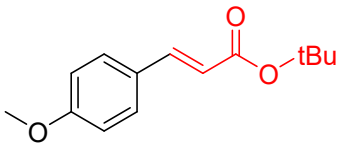
***(E)*-tert-butyl 3-(p-tolyl)acrylate 3b (95% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 16.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H), 1.52 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.66, 143.70, 140.42, 132.10, 129.70, 128.10, 119.26, 80.45, 28.37, 21.57.



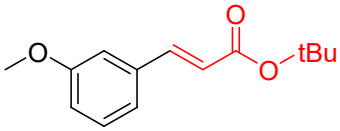
***(E)*-tert-butyl 3-(3,5-dimethylphenyl)acrylate 3c (93% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 16.0 Hz, 1H), 7.11 (s, 2H), 6.98 (s, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 2.30 (s, 6H), 1.51 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.06, 138.52, 134.81, 131.96, 126.06, 119.99, 80.55, 28.43, 21.40.



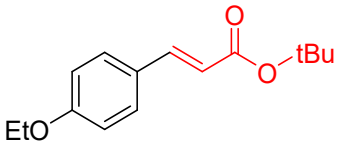
***(E)*-tert-butyl-3- (p-ethylphenyl)acrylate 3d (92% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 16.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.52 (s, 9H), 1.22 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.75, 146.79, 143.77, 132.38, 128.55, 128.24, 119.34, 80.54, 28.97, 28.42, 15.52.



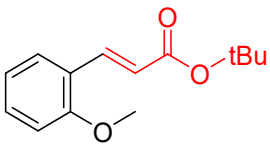
***(E)*-tert-butyl 3-(4-methoxyphenyl)acrylate 3e (87% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 15.9 Hz, 0H), 7.44 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.22 (d, *J* = 15.9 Hz, 0H), 3.81 (s, 3H), 1.51 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.67, 160.10, 142.17, 128.52, 126.39, 116.70, 113.23, 79.21, 76.31, 75.99, 75.67, 54.33, 27.21.



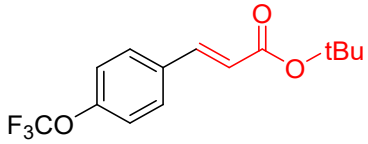
***(E)*-tert-butyl 3-(3-methoxyphenyl)acrylate 3f (87% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 4.03 (d, *J* = 7.1 Hz, 3H), 1.75 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.44, 160.06, 143.65, 136.24, 129.99, 120.89, 120.67, 116.07, 112.94, 80.71, 55.45, 28.39.



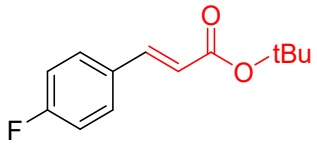
***(E)*-tert-butyl-3-(4-ethoxyphenyl)acrylate 3g (70% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 15.9 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.22 (d, *J* = 15.9 Hz, 1H), 4.04 (q, *J* = 7.0 Hz, 2H), 1.51 (s, 9H), 1.40 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.19, 161.00, 143.74, 130.02, 127.70, 118.04, 115.20, 80.65, 64.03, 28.71, 15.22.



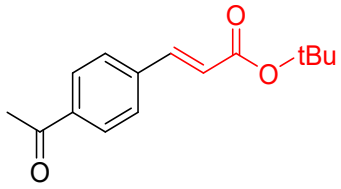
***(E)*-tert-butyl 3-(2-methoxyphenyl)acrylate 3h (58% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 16.1 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.33 – 7.27 (m, 1H), 6.95 – 6.86 (m, 2H), 6.40 (s, 1H), 3.86 (s, 3H), 1.51 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.07, 158.44, 139.13, 131.31, 128.96, 123.93, 120.92, 120.86, 111.31, 80.40, 55.67, 28.45.



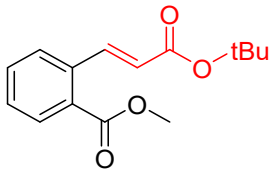
***(E)*-tert-butyl-3-(4-(trifluoromethoxy)phenyl)acrylate 3i (82% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (t, *J* = 11.9 Hz, 3H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 1.51 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.14, 150.42, 141.95, 133.55, 129.53, 121.44, 121.30, 80.97, 28.38.



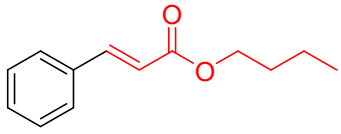
***(E)*-tert-butyl-3-(4'-fluorophenyl)acrylate 3j (87% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 16.0 Hz, 1H), 7.47 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 1.51 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.40, 164.93, 142.44, 130.01, 129.94, 116.25, 116.07, 80.80, 28.41.



***(E)*-tert-butyl-3-(4-acetylphenyl)acrylate 3k (85% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.53 (s, 0H), 6.42 (d, *J* = 16.1 Hz, 1H), 2.57 (s, 2H), 1.50 (s, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.30, 164.73, 140.94, 138.03, 136.76, 127.79, 126.98, 121.75, 79.89, 76.35, 76.03, 75.71, 27.13, 25.63.

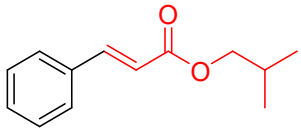


Methyl 2-[*(1E)*-3-(1,1-dimethylethoxy)-3-oxo-1-propen-1-yl]benzoate 3l (50% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 15.9 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 8.2 Hz, 1H), 6.23 (d, *J* = 15.9 Hz, 1H), 3.91 (s, 3H), 1.52 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.56, 166.09, 142.68, 136.65, 132.43, 130.93, 130.15, 129.34, 128.04, 123.22, 80.79, 52.58, 42.43, 28.30.

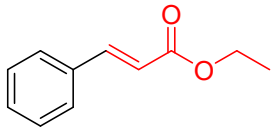


trans-Butyl cinnamate 3m (95% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.51 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.36 (dd, *J* = 5.0, 1.6 Hz, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 1.70 (dd, *J* = 14.4, 7.3 Hz, 2H), 1.49 – 1.41 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

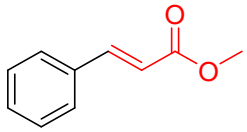
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.98, 144.51, 134.50, 130.19, 128.86, 128.05, 118.32, 64.36, 30.82, 19.23, 13.76.



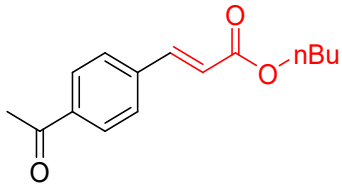
trans-Isobutyl cinnamate 3n (95% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.35 – 7.29 (m, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.96 (d, *J* = 6.7 Hz, 2H), 1.98 (dp, *J* = 13.4, 6.7 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.96, 144.54, 134.49, 130.21, 128.87, 128.06, 118.30, 70.60, 27.87, 19.17.



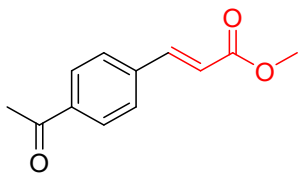
trans-Ethyl cinnamate 3o (52% isolated yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.53 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.42 – 7.37 (m, 3H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.37 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.80, 144.47, 134.42, 130.15, 128.81, 127.99, 118.25, 60.36, 14.27.



trans-Methyl cinnamate 3p (24% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.50 (s, 2H), 7.37 (s, 3H), 6.43 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.86, 133.37, 129.28, 127.88, 127.05, 116.78, 76.30, 75.99, 75.67, 50.70.

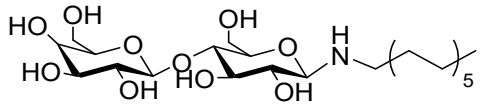


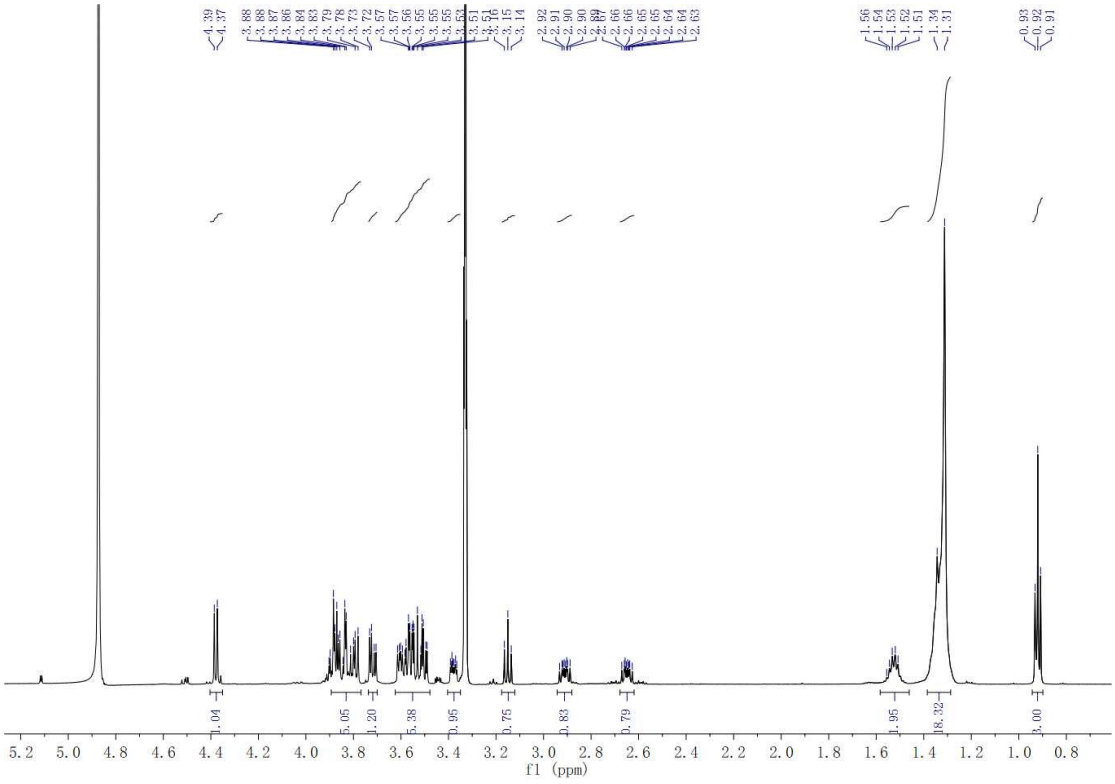
(E)-n-butyl -3-(4-acetylphenyl)acrylate 3q (97% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 16.1 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 2.58 (s, 3H), 1.69 – 1.64 (m, 2H), 1.41 (dd, *J* = 15.0, 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.52, 166.78, 143.16, 139.00, 138.15, 129.03, 128.31, 121.03, 64.87, 30.91, 26.87, 19.37, 13.92.

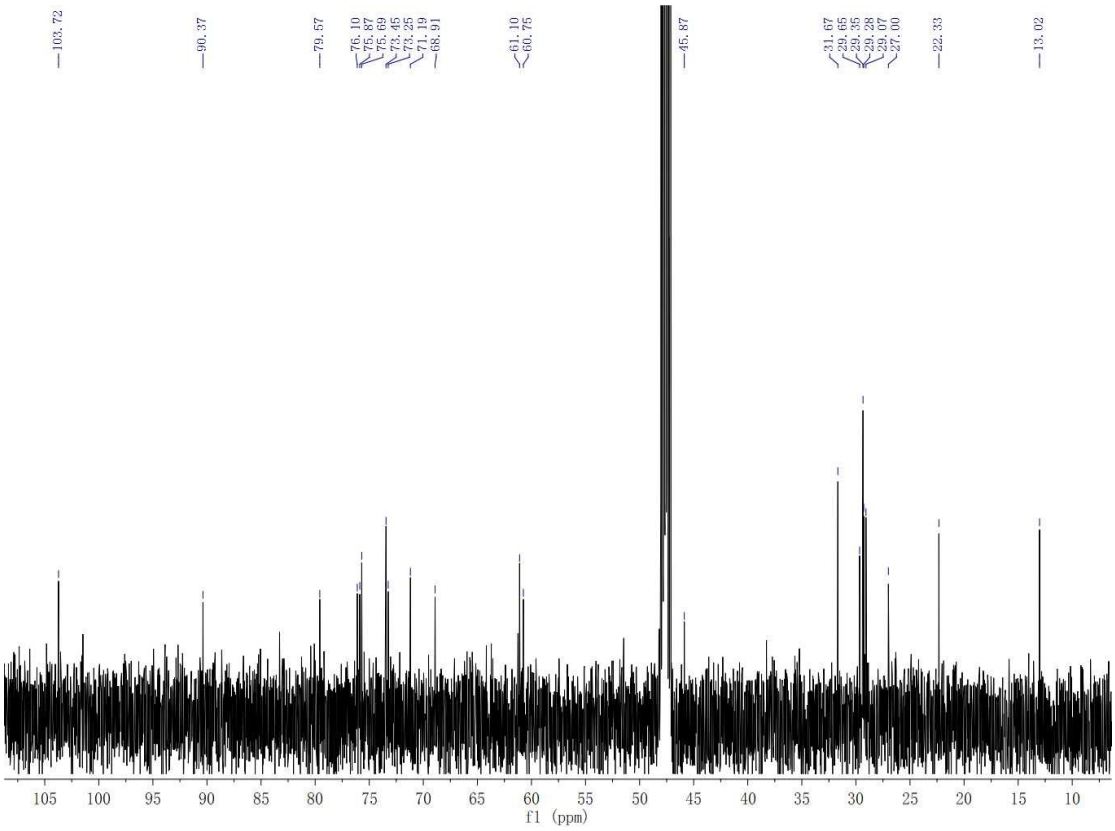


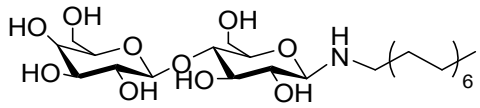
(E)-methyl-3-(4-acetylphenyl)acrylate 3r (18% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 16.1 Hz, 0H), 7.57 (d, *J* = 8.3 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 0H), 3.79 (s, 1H), 2.58 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.26, 165.89, 142.27, 137.66, 137.01, 127.83, 127.12, 119.30, 76.35, 76.03, 75.72, 50.88, 25.66.

6. The Spectra of products





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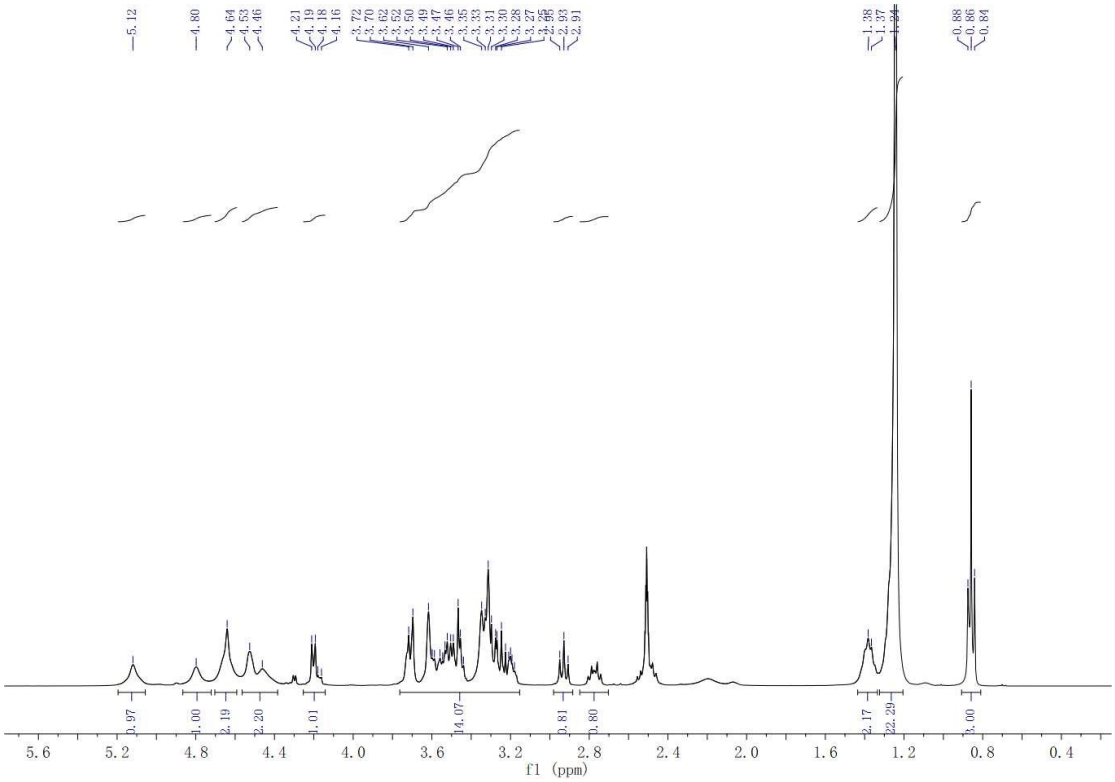
OH
O
HO
OH
O
HO
OH
H
N
6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4.16
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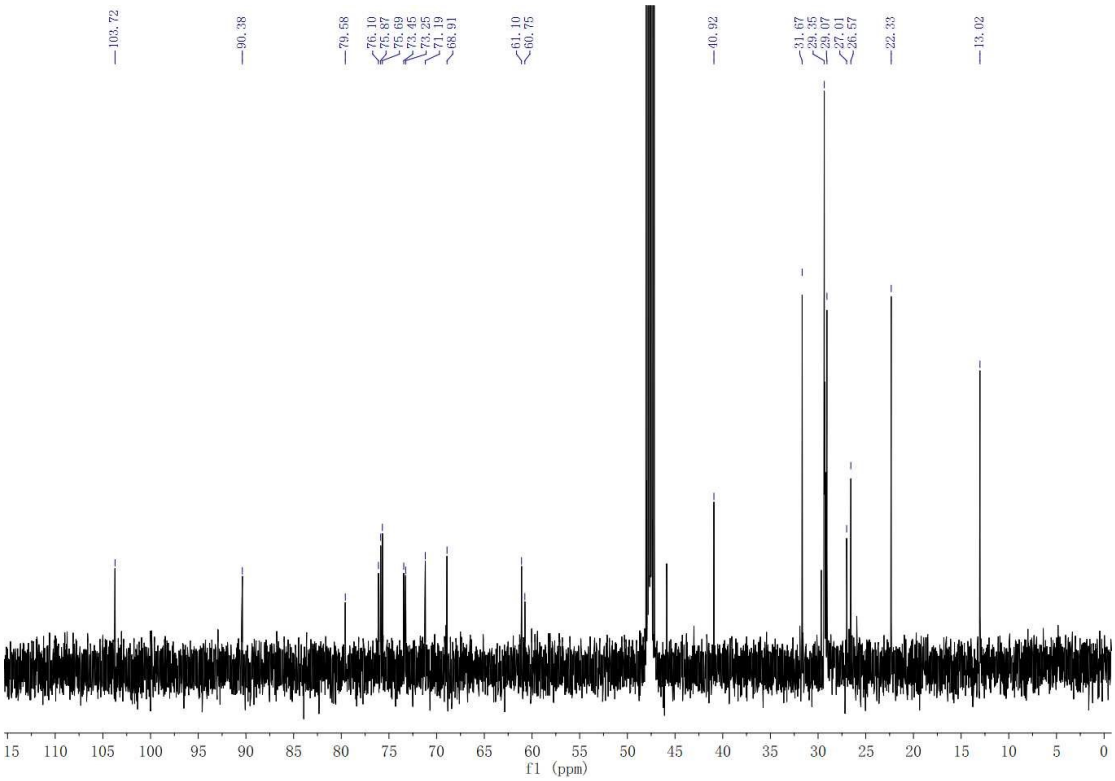
3.50
3.49
3.47
3.46
3.35
3.33
3.31
3.30
3.28
3.27
2.93
2.91
1.38
1.37
0.88
0.86
0.84
0.97
1.00
2.19
2.20
1.01
14.07
0.81
0.80
2.17
22.29
3.00
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
f1 (ppm)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100
95
90
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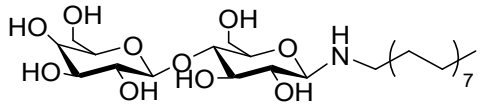
5
0
f1 (ppm)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HO
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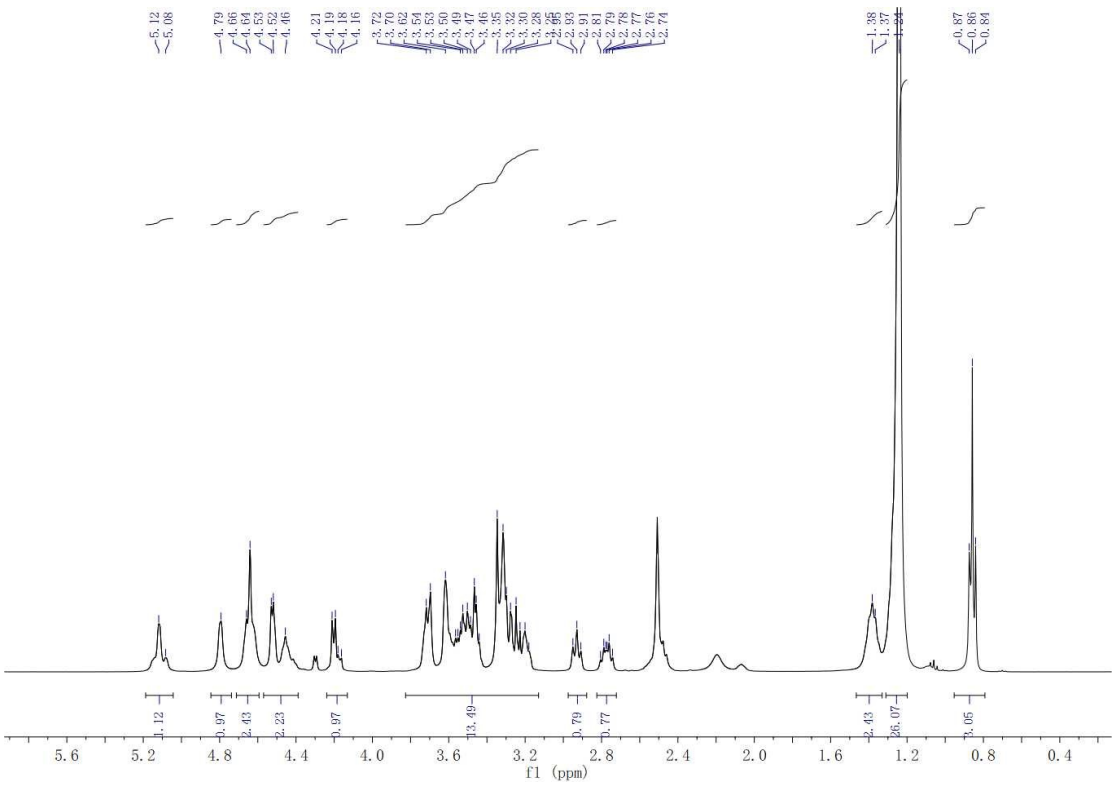
HO
OH
H
N
7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5.08
4.79
4.66
4.64
4.53
4.52
4.46
4.21
4.19
4.18
4.16
3.72
3.70
3.62
3.54
3.53
3.50
3.49
3.47
3.46
3.35
3.32
3.30
3.28
2.93
2.91
2.81
2.79
2.78
2.77
2.76
2.74
1.38
1.37
0.87
0.86
0.84
1.12
0.97
2.43
2.23
0.97
13.49
0.79
0.77
2.43
26.07
3.05
5.6
5.2
4.8
4.4
4.0
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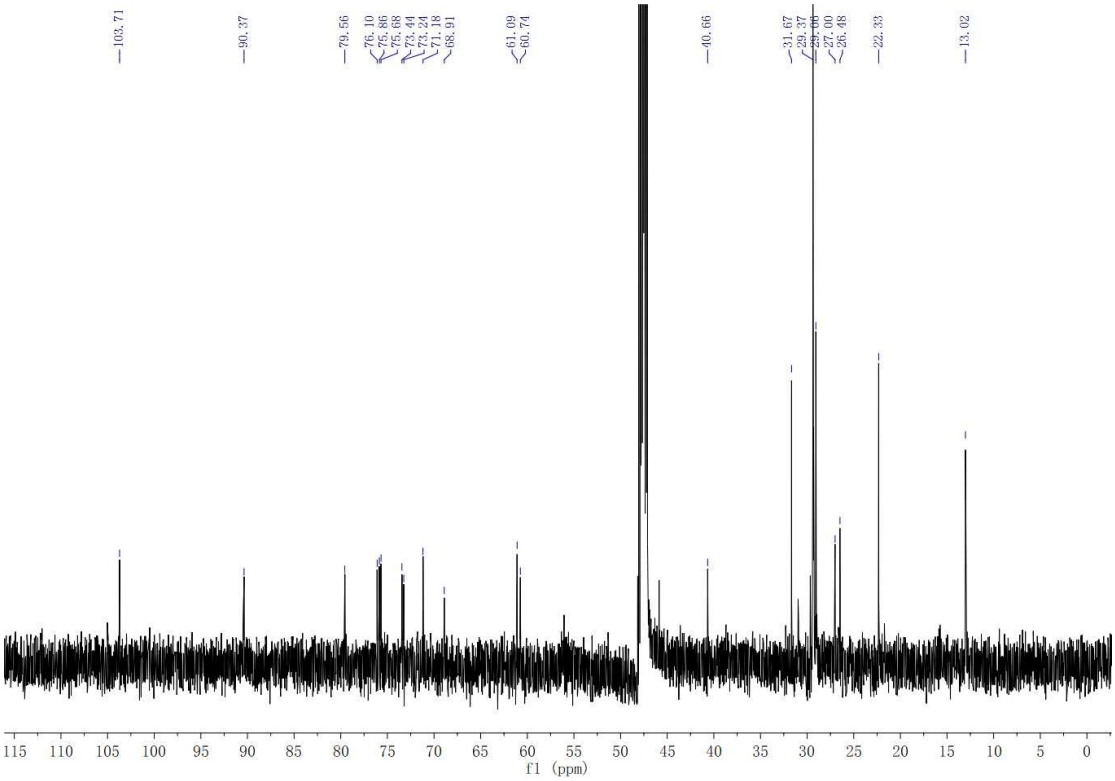
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
f1 (ppm)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76.10
75.86
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73.44
73.24
71.18
68.91
61.09
60.74
40.66
31.67
29.37
29.06
27.00
26.48
22.33
13.02
115
110
105
100
95
90
85
80
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65
60
55
50
45
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35
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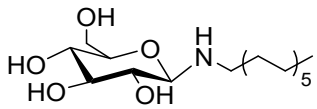
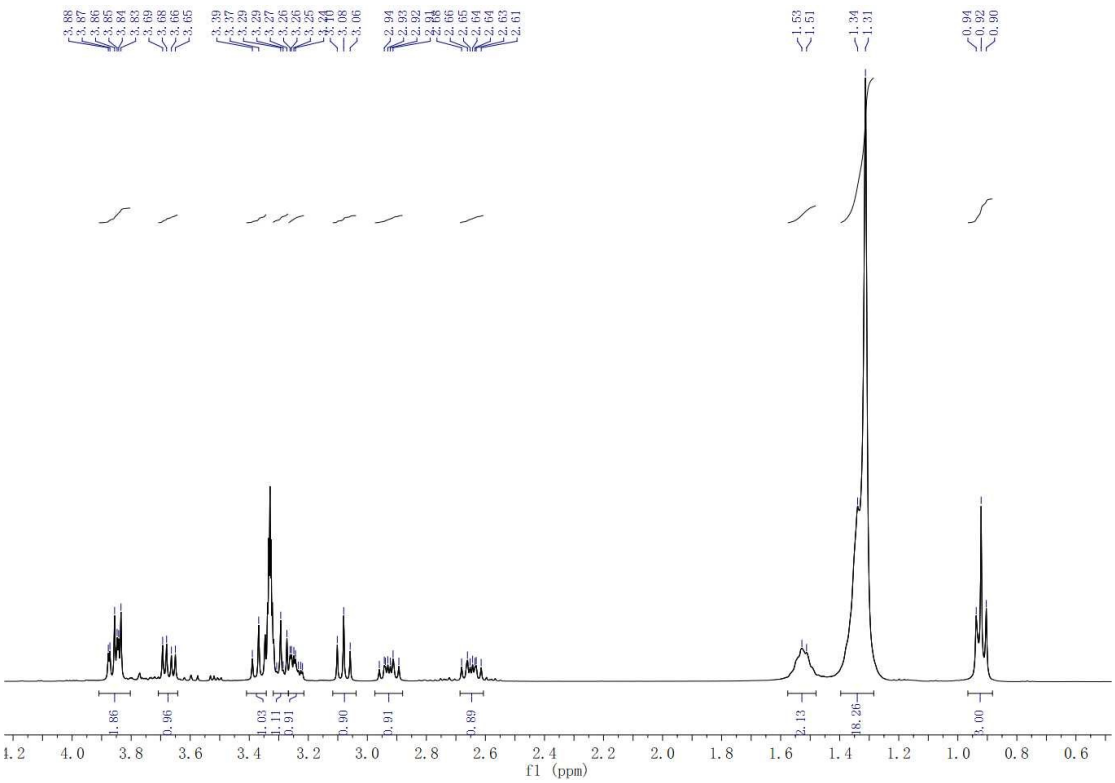
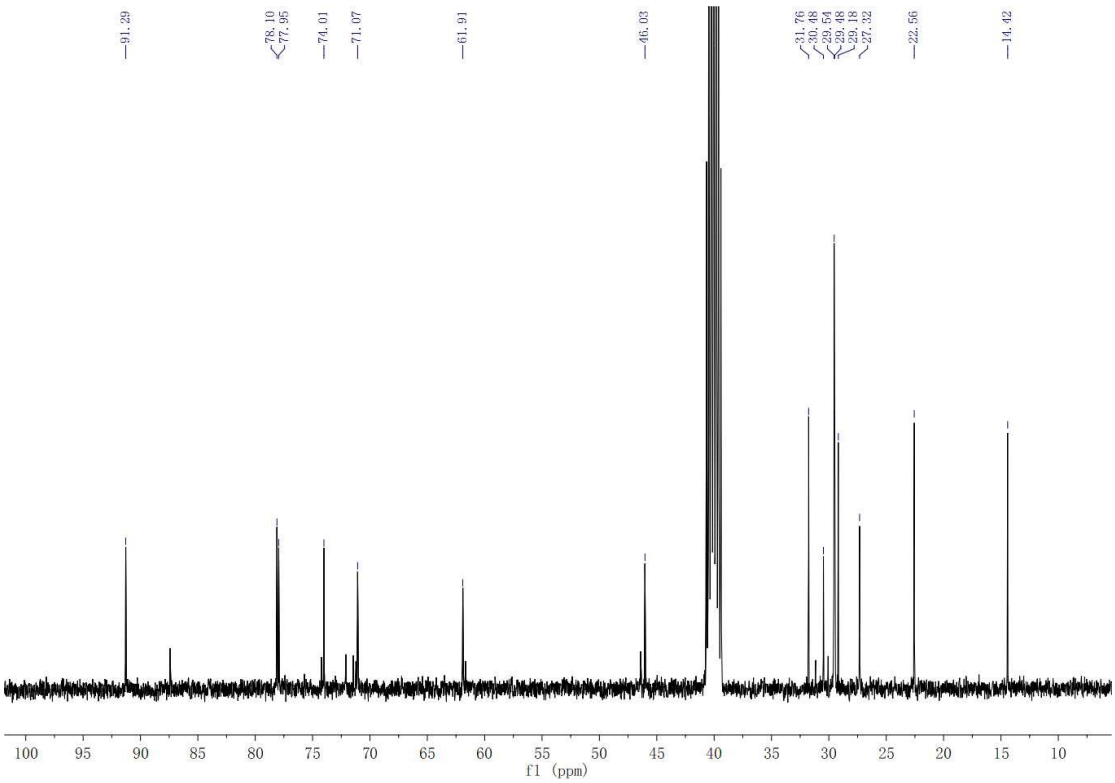
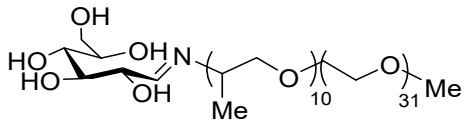
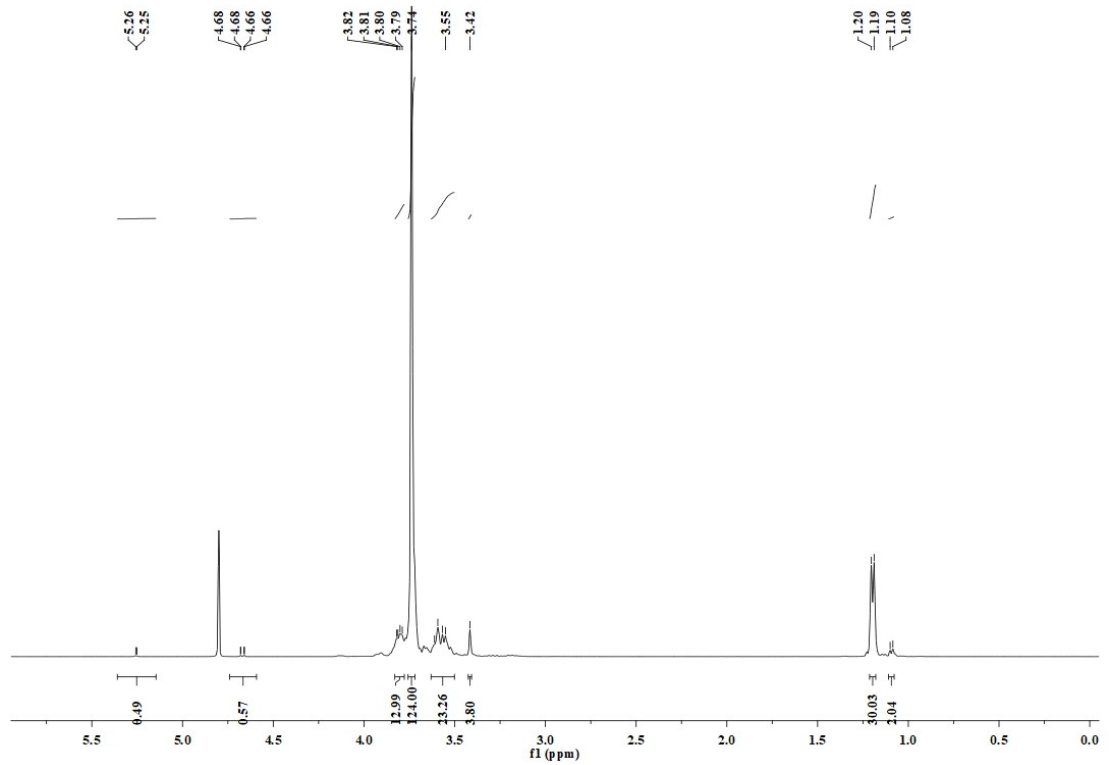
25
20
15
10
5
0
f1 (ppm)


OH
HO
HO
OH
O
H
N
5


f1 (ppm)


f1 (ppm)


OH
HO
HO
OH
OH
N
Me
O
10
O
31
Me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5.25
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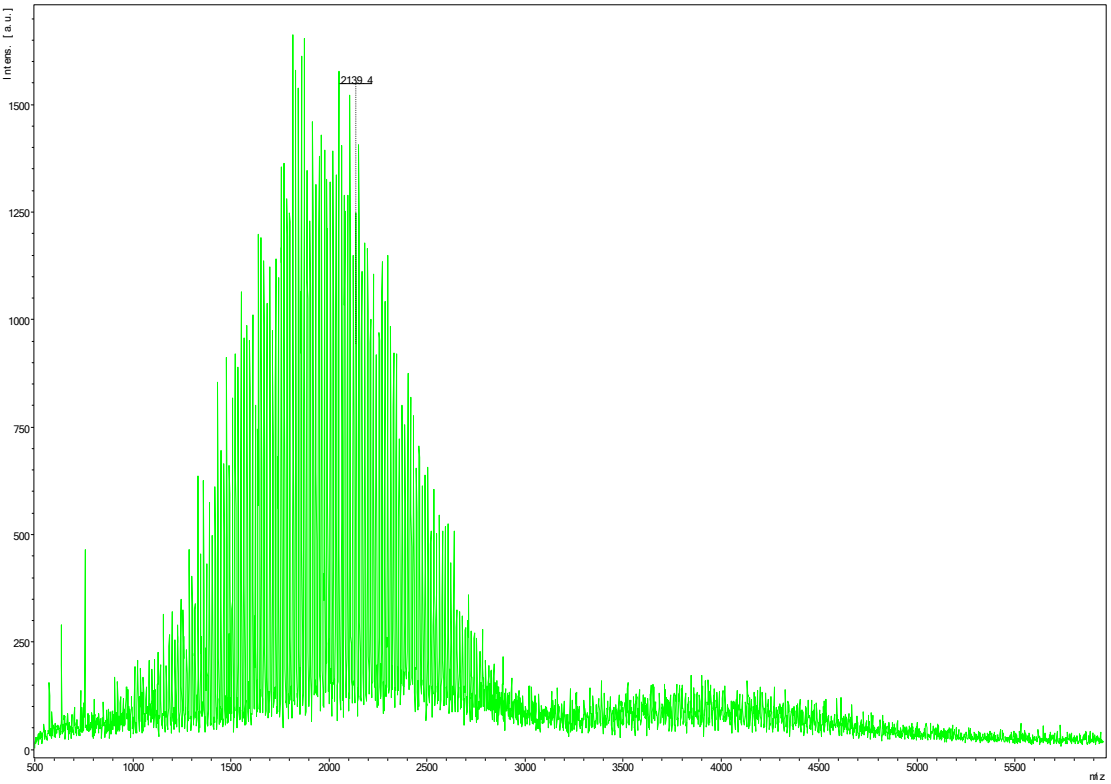
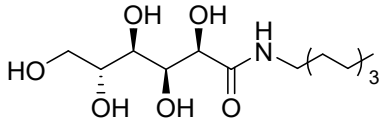
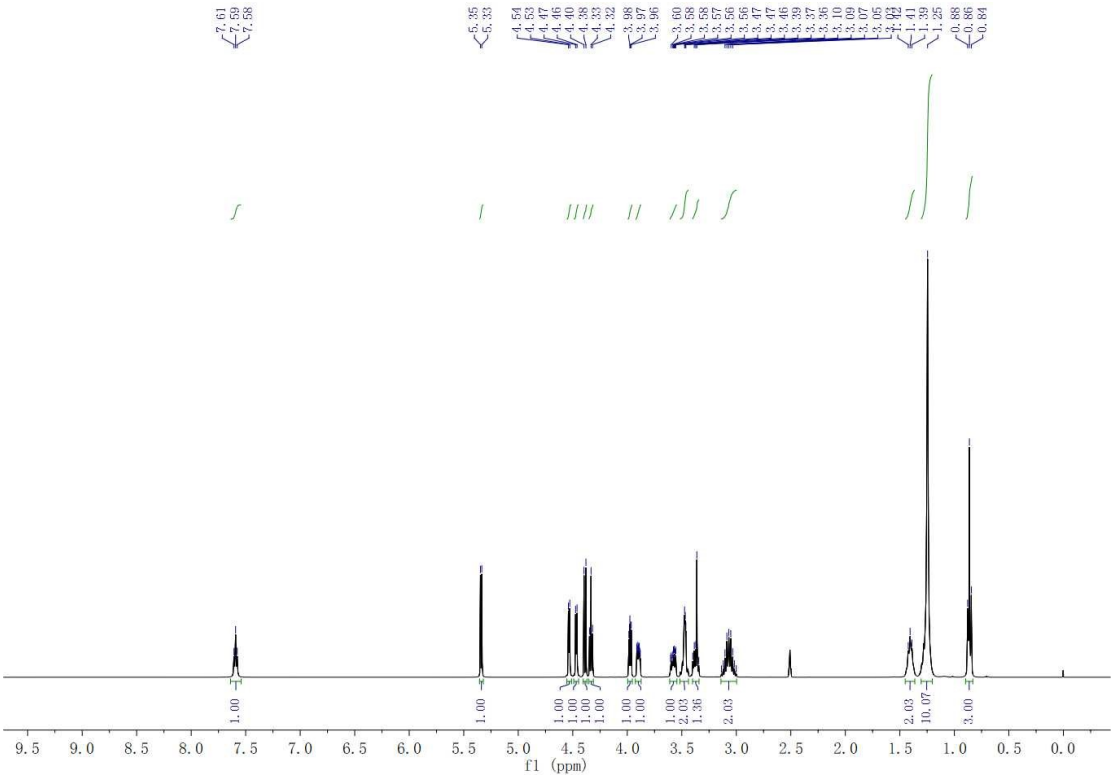
4.66
4.66
3.82
3.81
3.80
3.79
3.74
3.55
3.42
1.20
1.19
1.10
1.08
0.49
0.57
12.99
124.00
23.26
3.80
30.03
2.04
f1 (ppm)


Intens. [a.u.]
2139.4
m/z


HO
OH
OH
OH
OH
H
N
O
3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4.47
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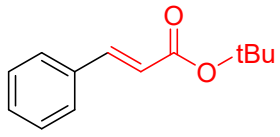
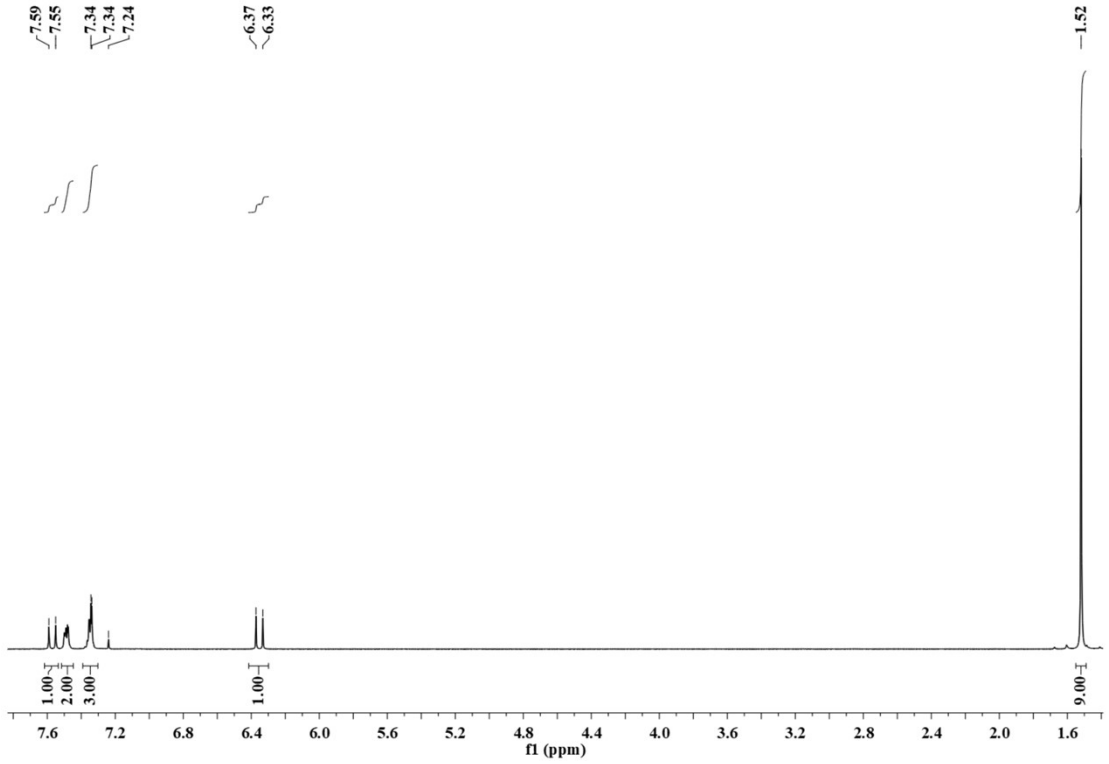
4.40
4.38
4.33
4.32
3.98
3.97
3.96
3.60
3.58
3.58
3.57
3.56
3.56
3.47
3.47
3.46
3.39
3.37
3.36
3.10
3.09
3.07
3.05
1.41
1.39
1.25
0.88
0.86
0.84
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.03
1.36
2.03
2.03
10.07
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
tBu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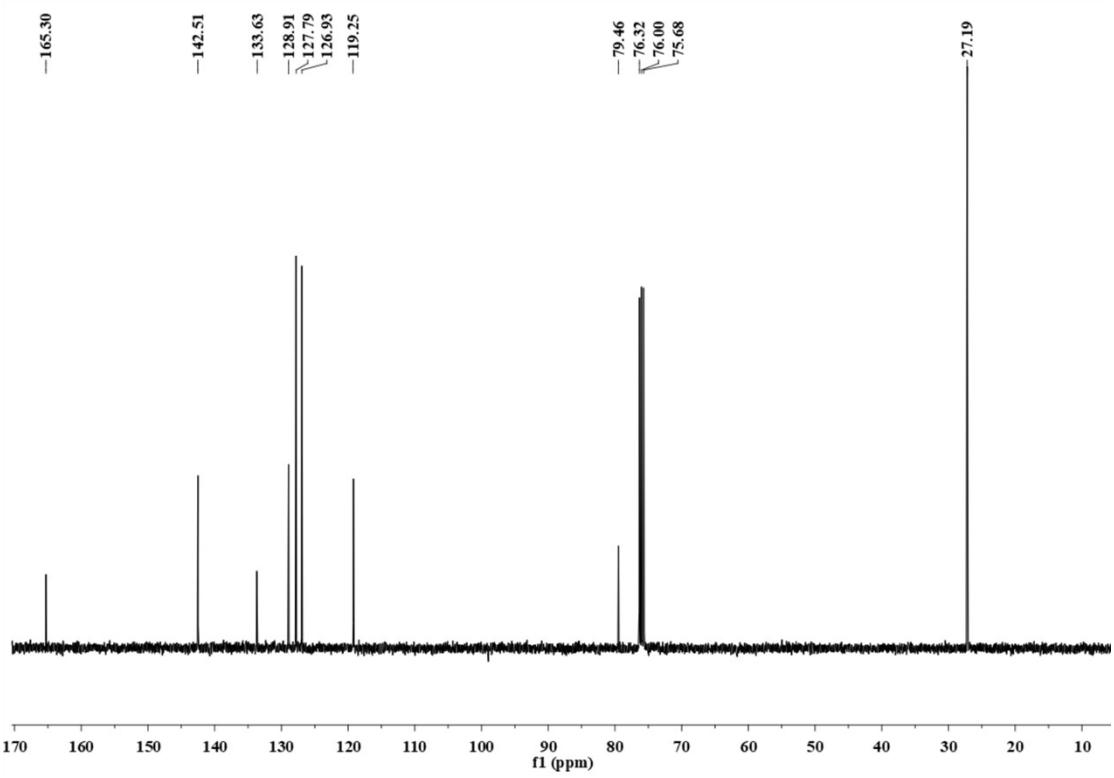
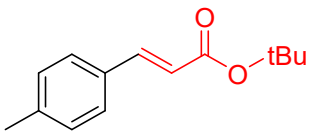
7.55
7.34
7.34
7.24
6.37
6.33
1.52
1.00
2.00
3.00
1.00
9.00
f1 (ppm)


165.30
142.51
133.63
128.91
127.79
126.93
119.25
79.46
76.32
76.00
75.68
27.19
f1 (ppm)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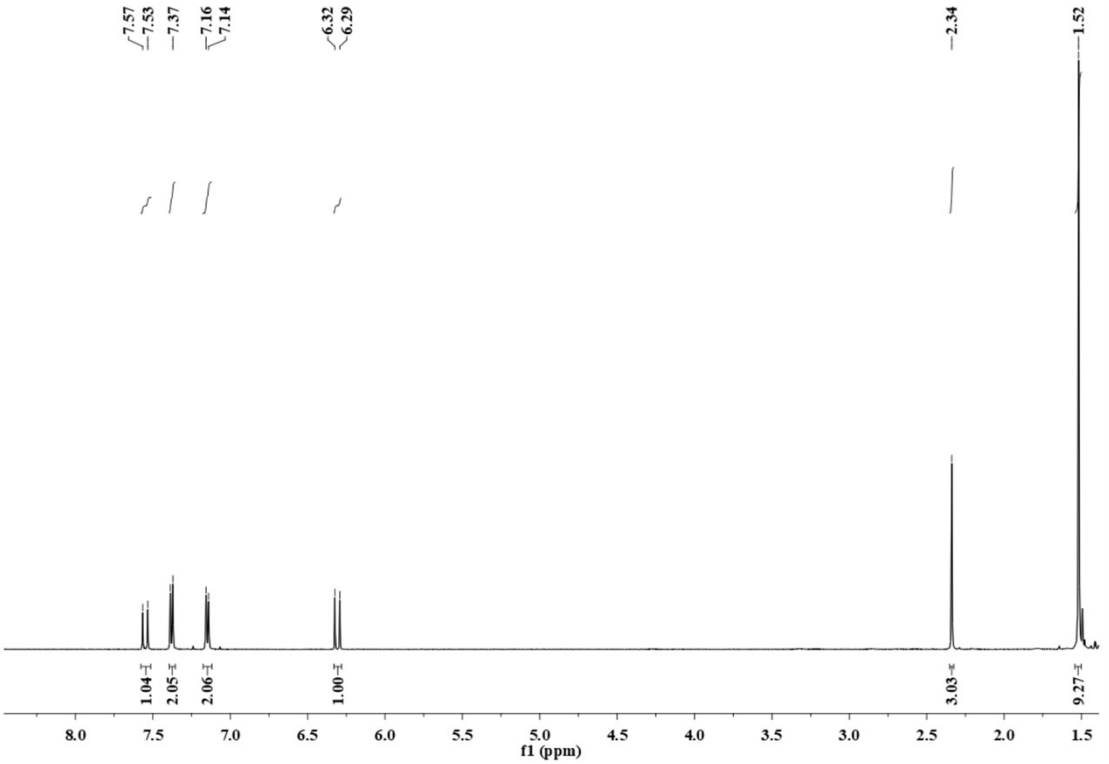
tBu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7.16
7.14
6.32
6.29
2.34
1.52
1.04
2.05
2.06
1.00
3.03
9.27
8.0
7.5
7.0
6.5
6.0
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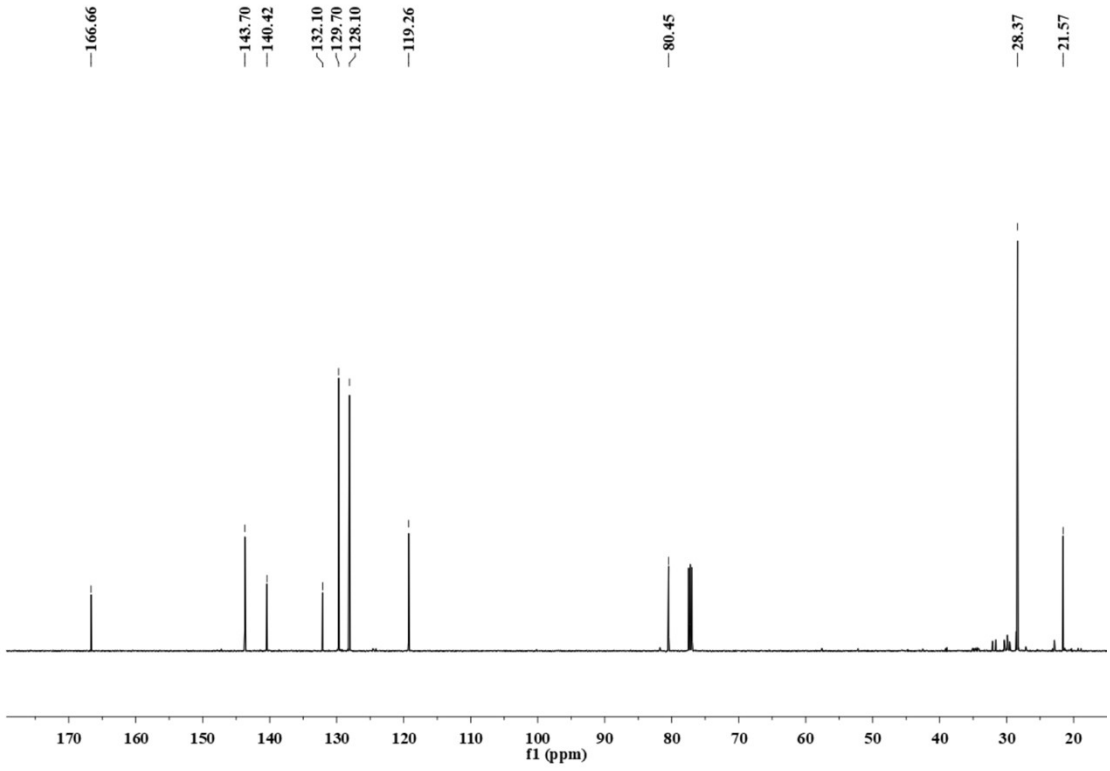
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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128.10
119.26
80.45
28.37
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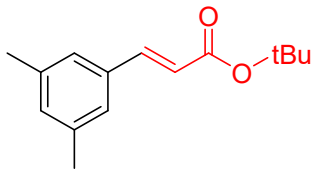
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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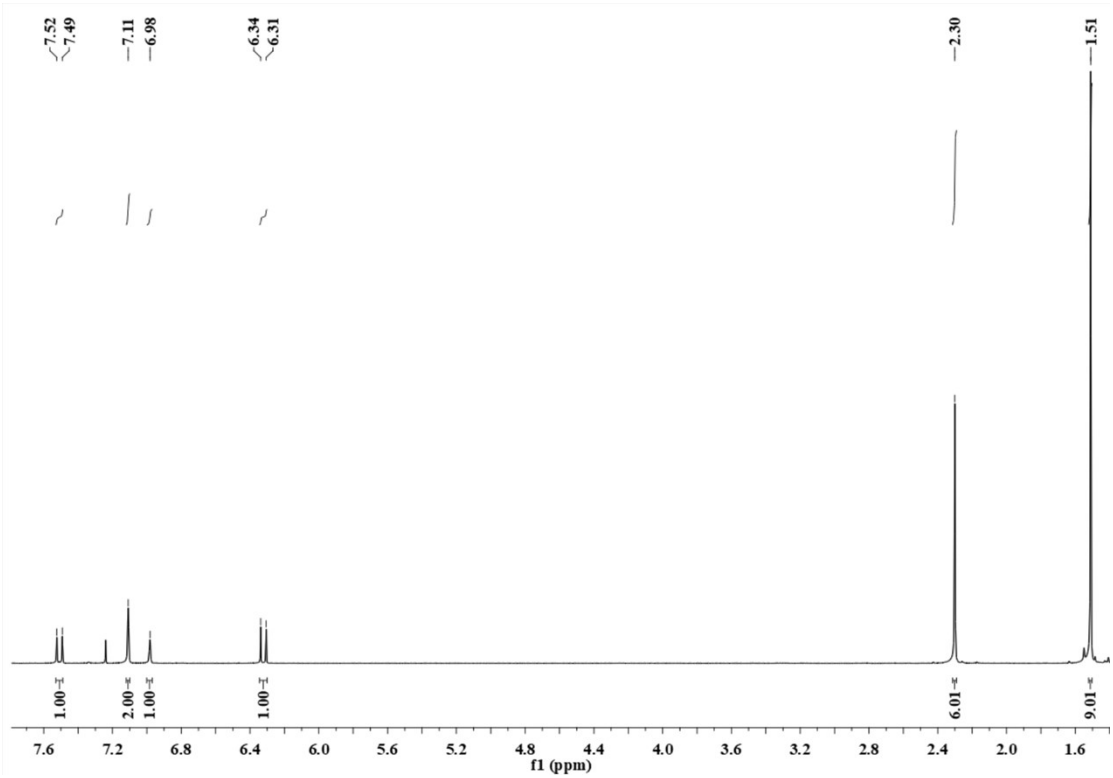
O
tBu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7.49
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6.31
2.30
1.51
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2.00
1.00
1.00
6.01
9.01
7.6
7.2
6.8
6.4
6.0
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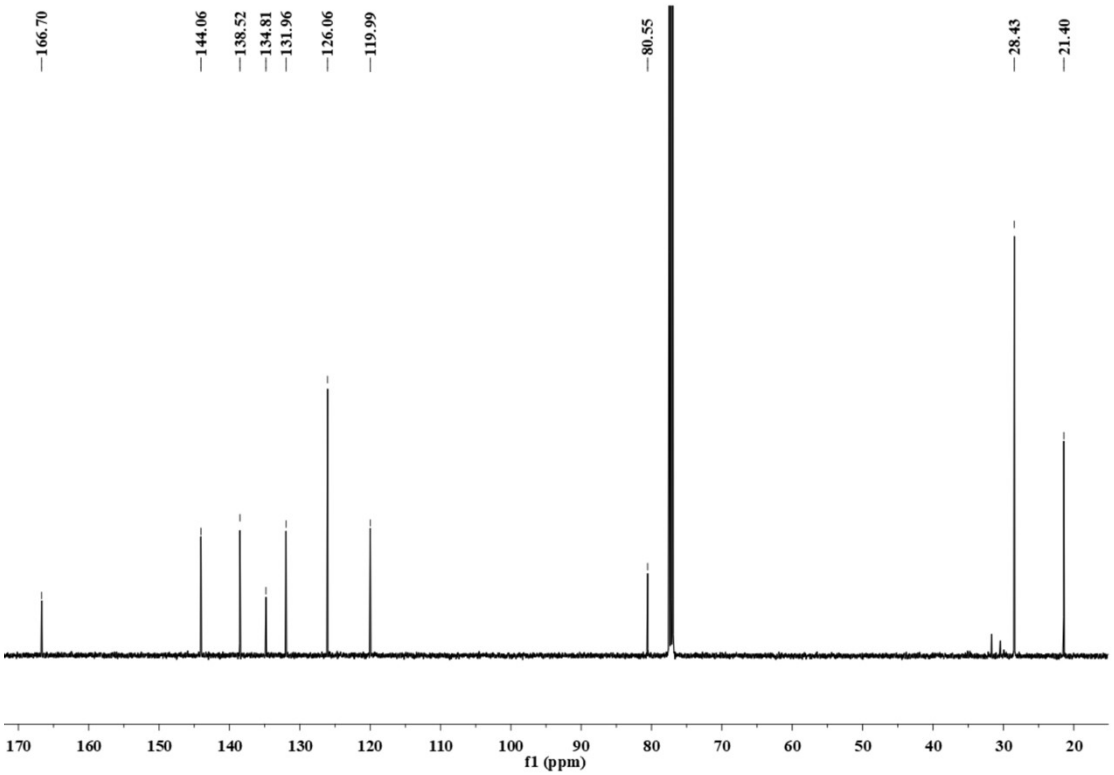
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
f1 (ppm)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144.06
138.52
134.81
131.96
126.06
119.99
80.55
28.43
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140
130
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110
100
90
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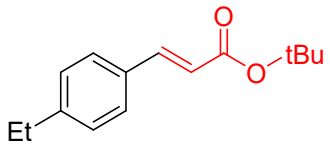
70
60
50
40
30
20
f1 (ppm)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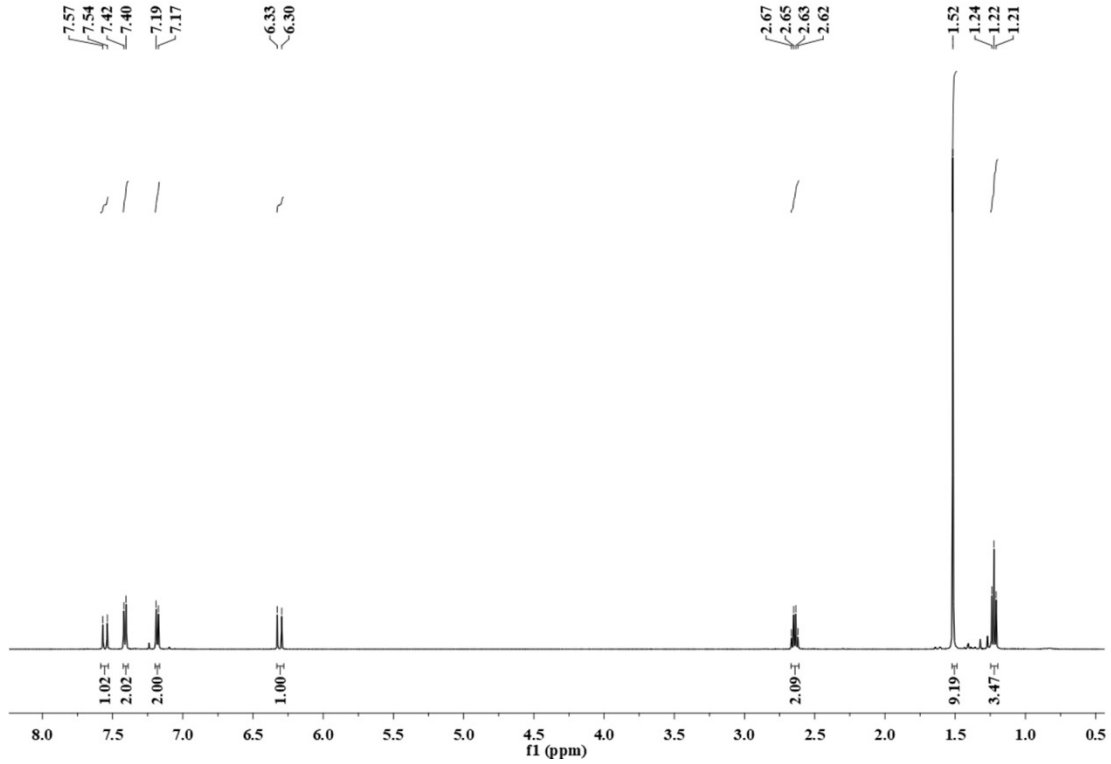
tBu
Et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7.40
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7.17
6.33
6.30
2.67
2.65
2.63
2.62
1.52
1.24
1.22
1.21
1.02
2.02
2.00
1.00
2.09
9.19
3.47
8.0
7.5
7.0
6.5
6.0
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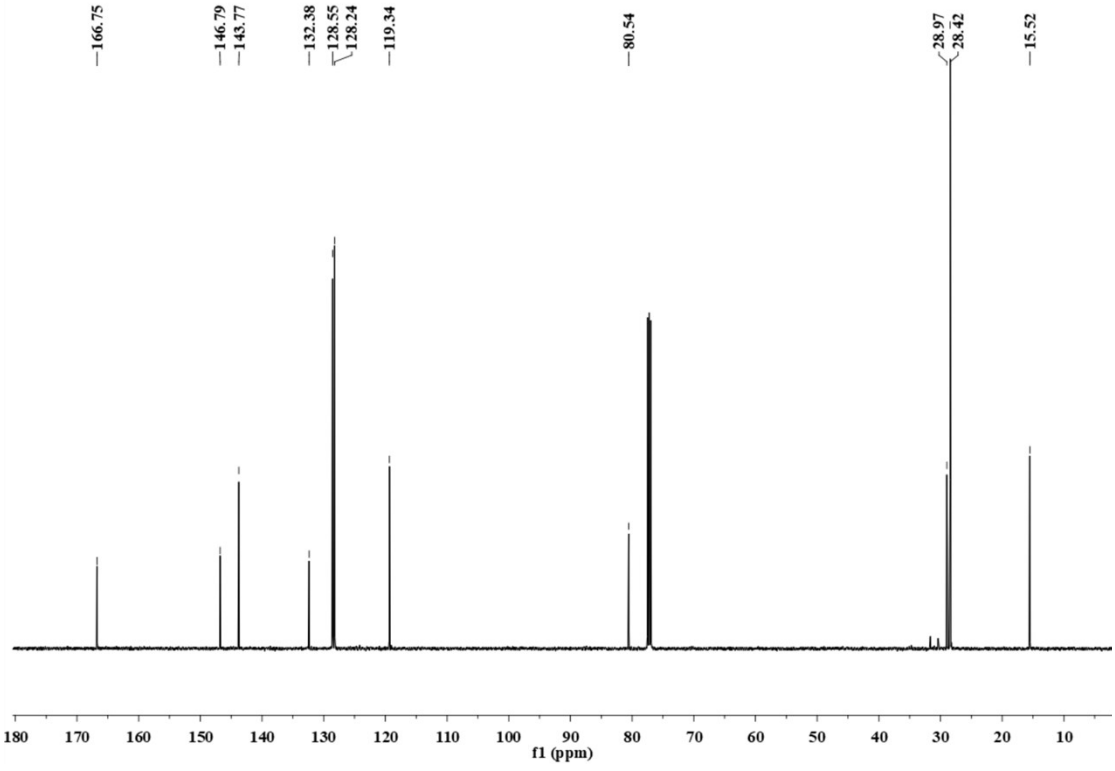
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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128.55
128.24
119.34
80.54
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28.42
15.52
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140
130
120
110
100
90
80
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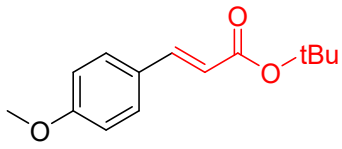
60
50
40
30
20
10
f1 (ppm)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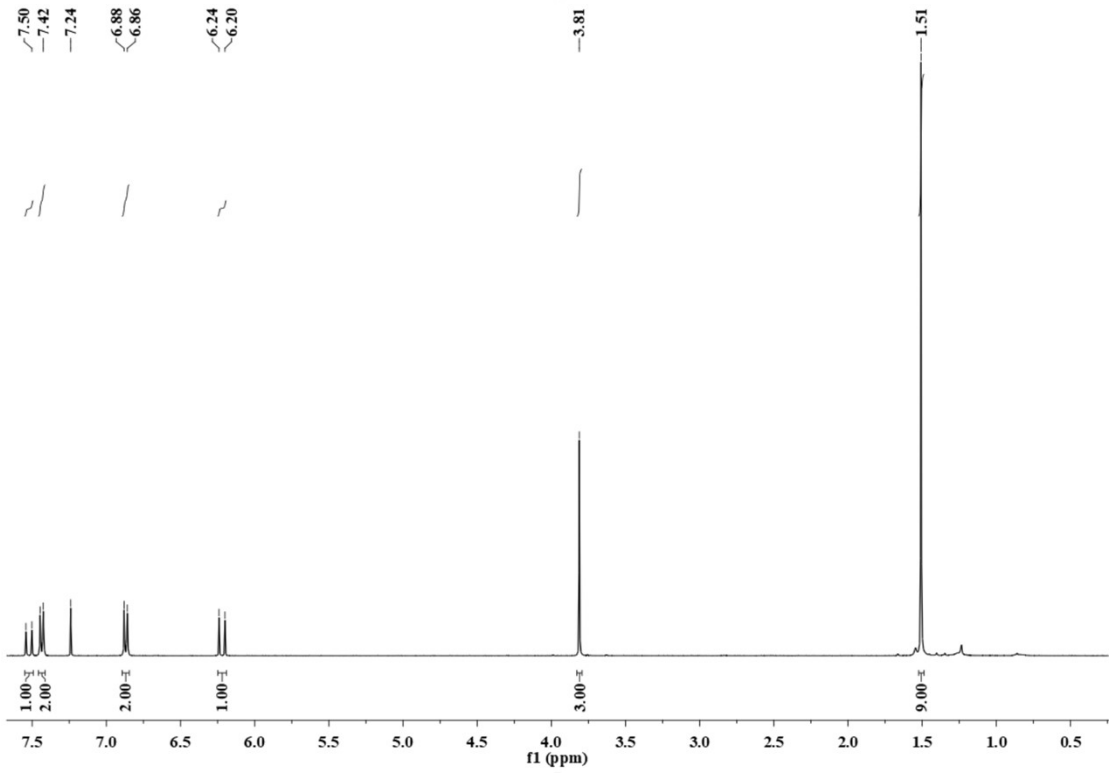
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6.24
6.20
3.81
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1.00
2.00
2.00
1.00
3.00
9.00
7.5
7.0
6.5
6.0
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5.0
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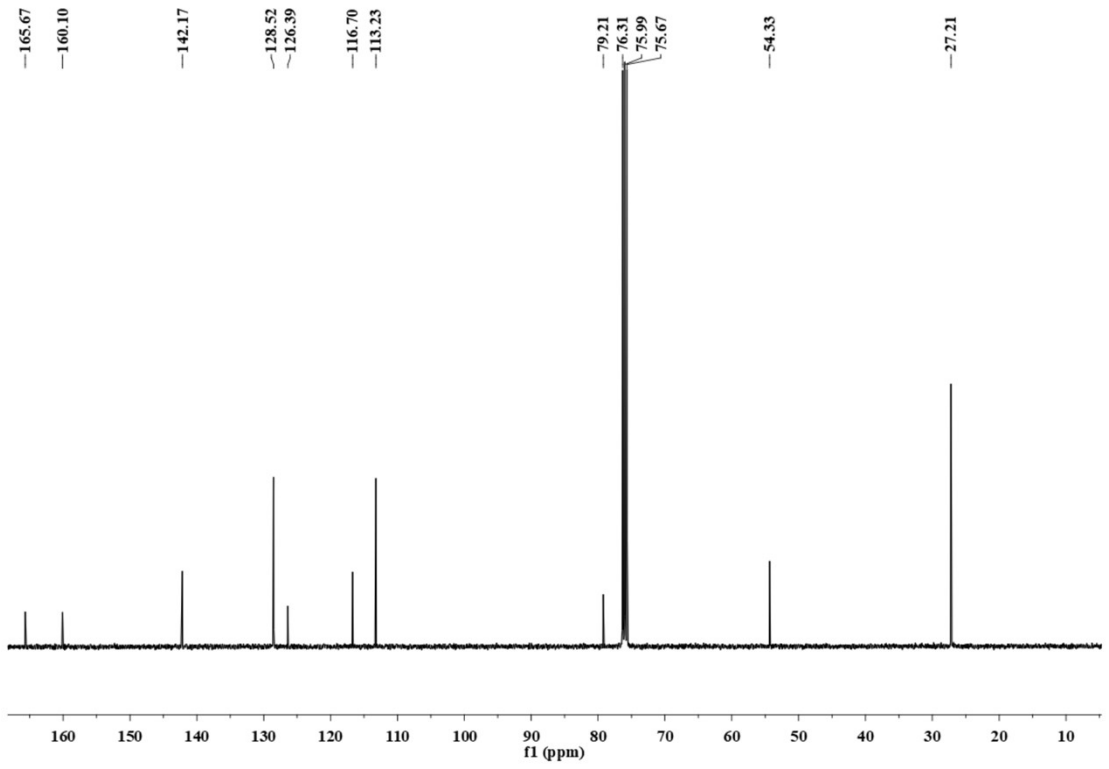
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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116.70
113.23
79.21
76.31
75.99
75.67
54.33
27.21
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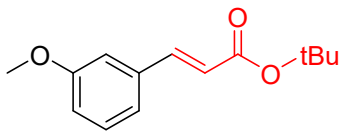
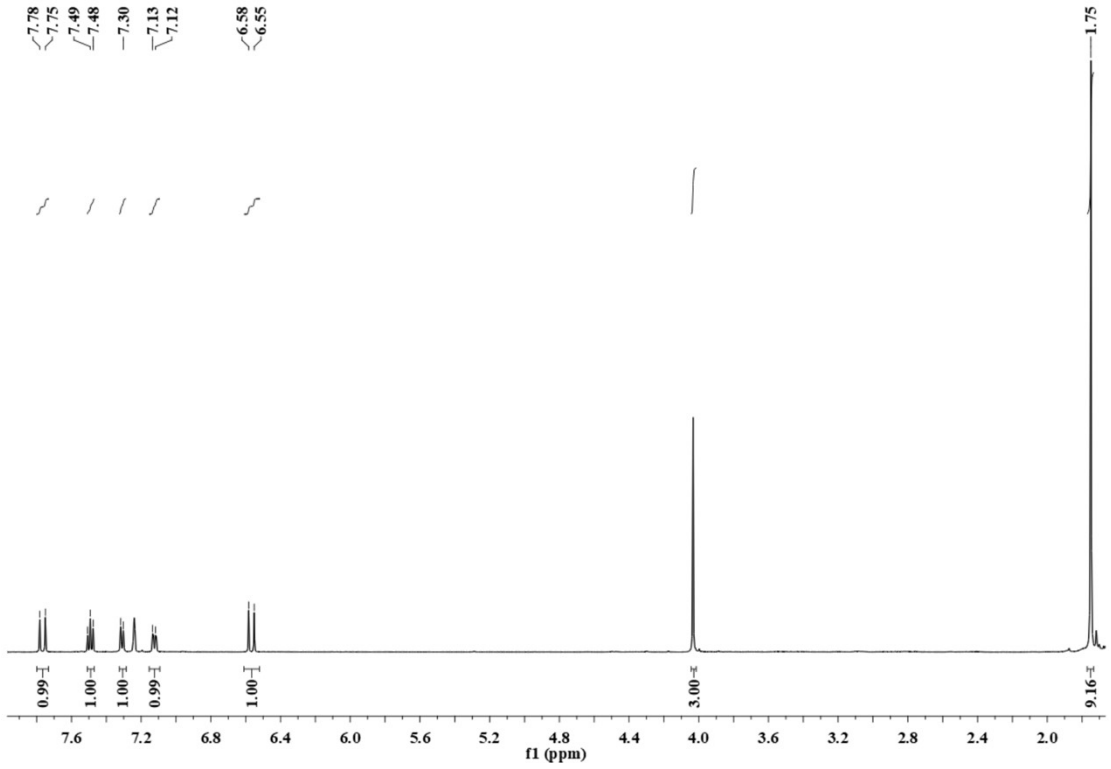
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
O
tBu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7.12
6.58
6.55
1.75
0.99
1.00
1.00
0.99
1.00
3.00
9.16
7.6
7.2
6.8
6.4
6.0
5.6
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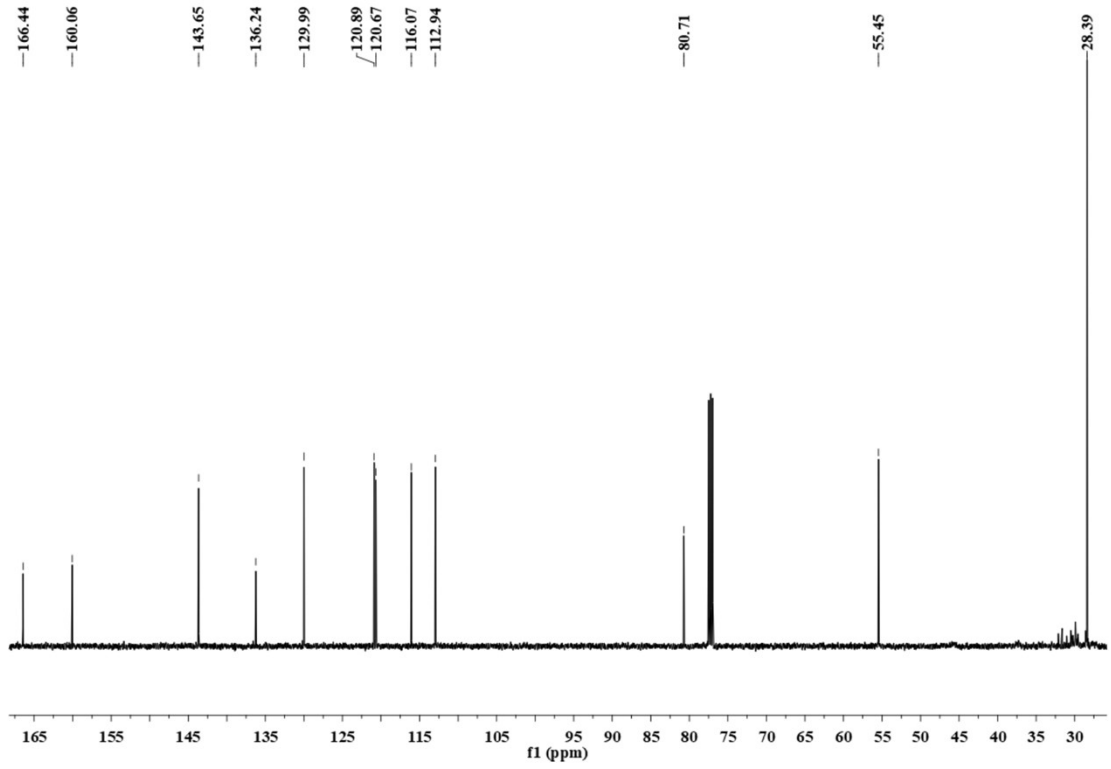
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
f1 (ppm)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120.67
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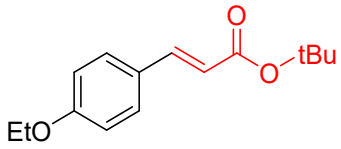
112.94
80.71
55.45
28.39
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)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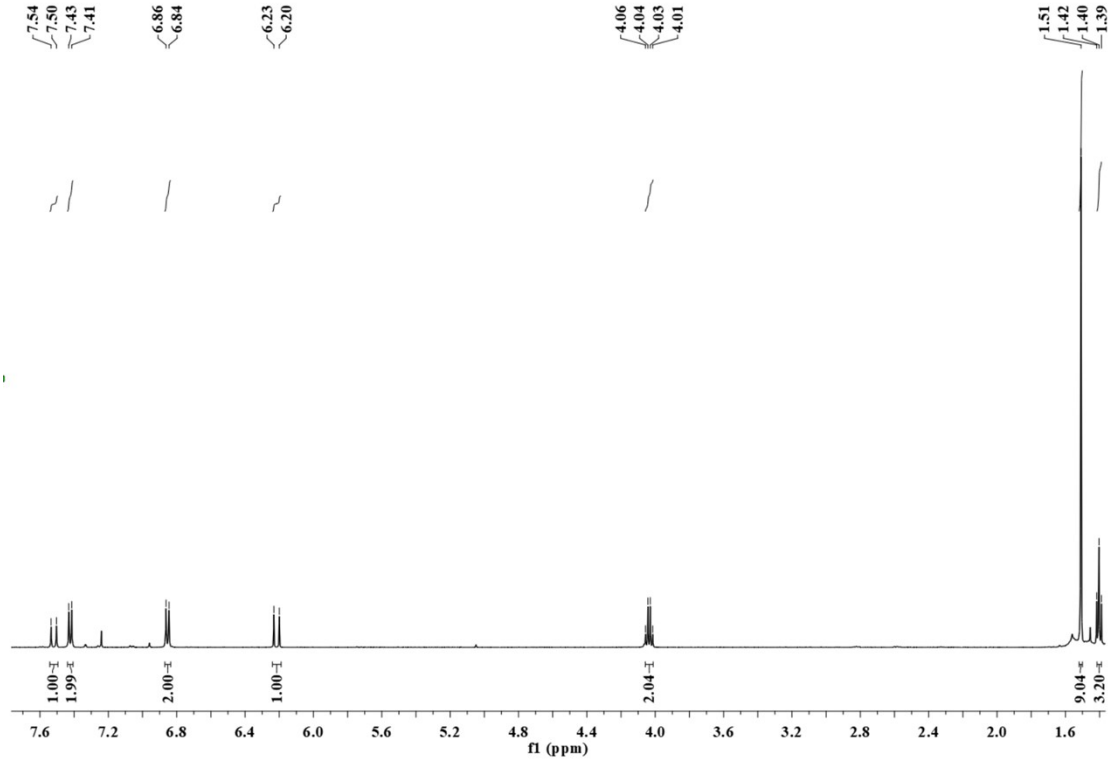
EtO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6.84
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6.20
4.06
4.04
4.03
4.01
1.51
1.42
1.40
1.39
1.00
1.99
2.00
1.00
2.04
9.04
3.20
7.6
7.2
6.8
6.4
6.0
5.6
5.2
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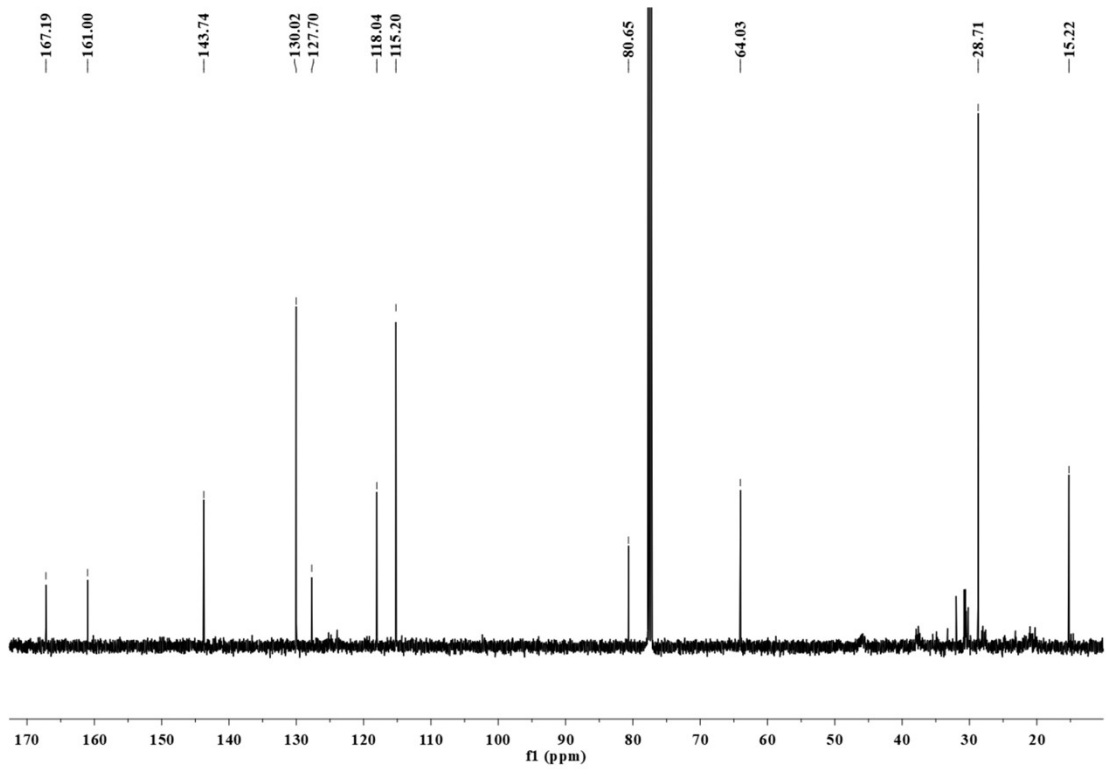
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
f1 (ppm)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118.04
115.20
80.65
64.03
28.71
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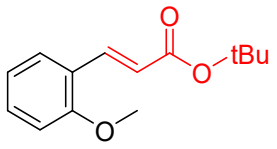
70
60
50
40
30
20
f1 (ppm)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tBu
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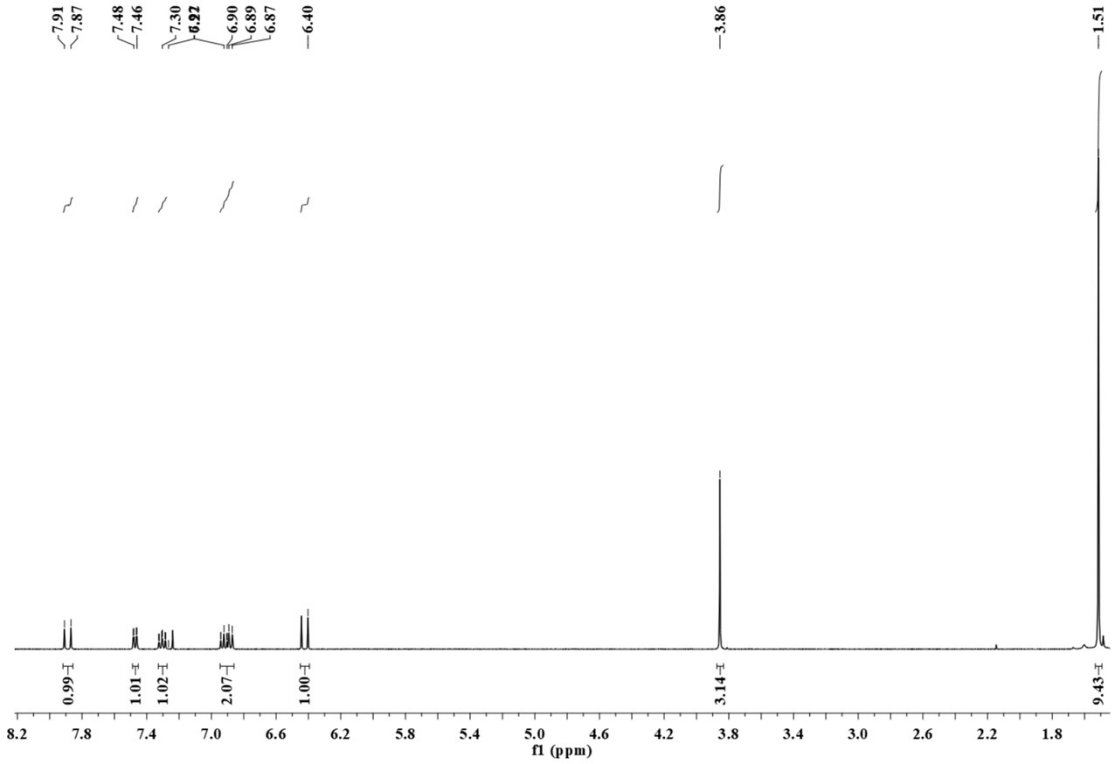
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6.89
6.87
6.40
3.86
1.51
0.99
1.01
1.02
2.07
1.00
3.14
9.43
8.2
7.8
7.4
7.0
6.6
6.2
5.8
5.4
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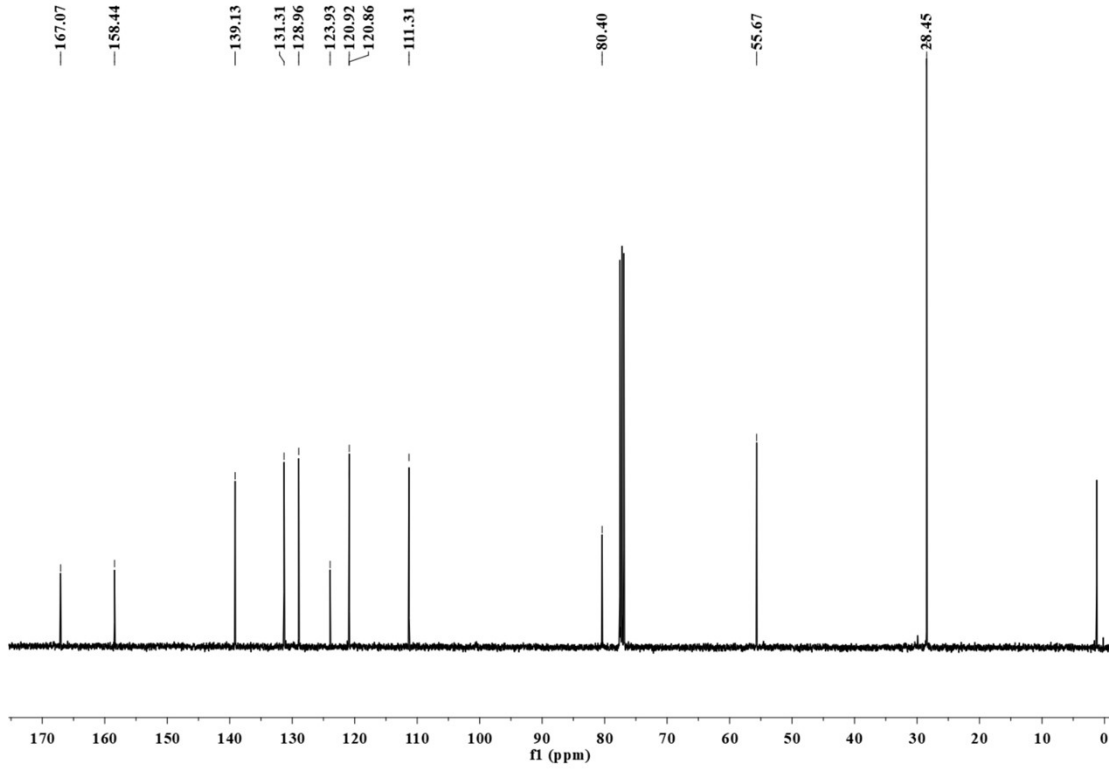
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
f1 (ppm)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131.31
128.96
123.93
120.92
120.86
111.31
80.40
55.67
28.45
170
160
150
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130
120
110
100
90
80
70
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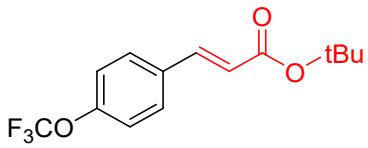
50
40
30
20
10
0
f1 (ppm)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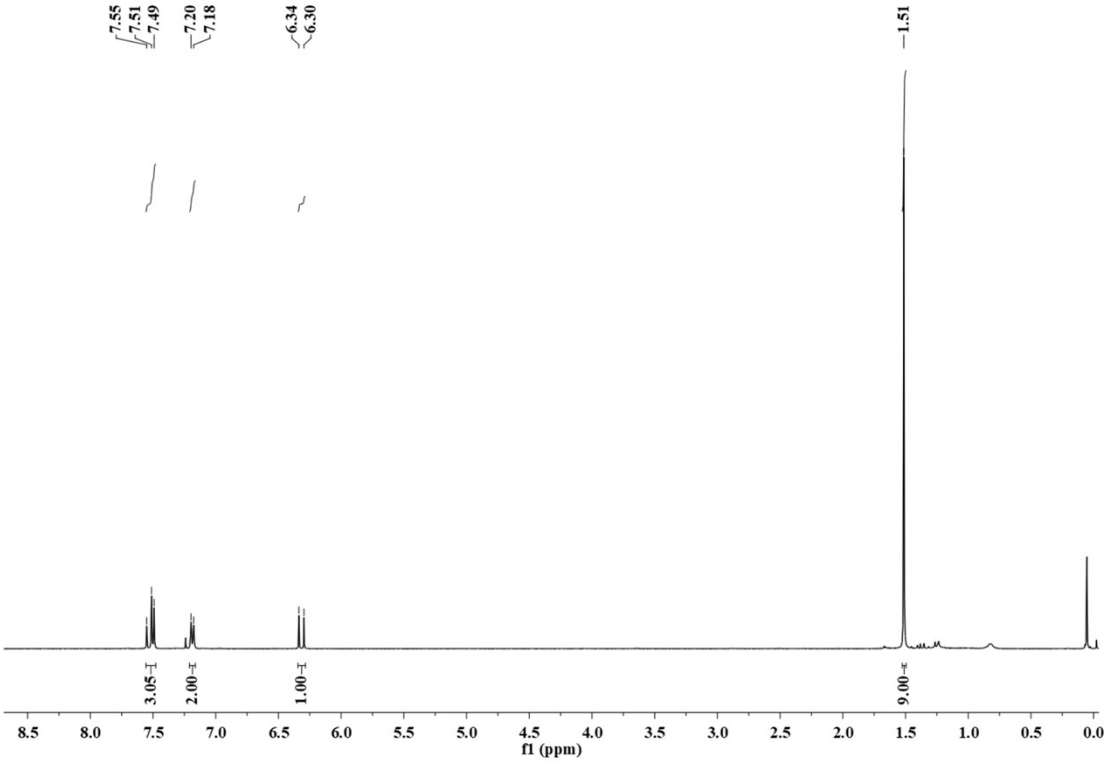
tBu
F3CO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7.49
7.20
7.18
6.34
6.30
1.51
3.05
2.00
1.00
9.00
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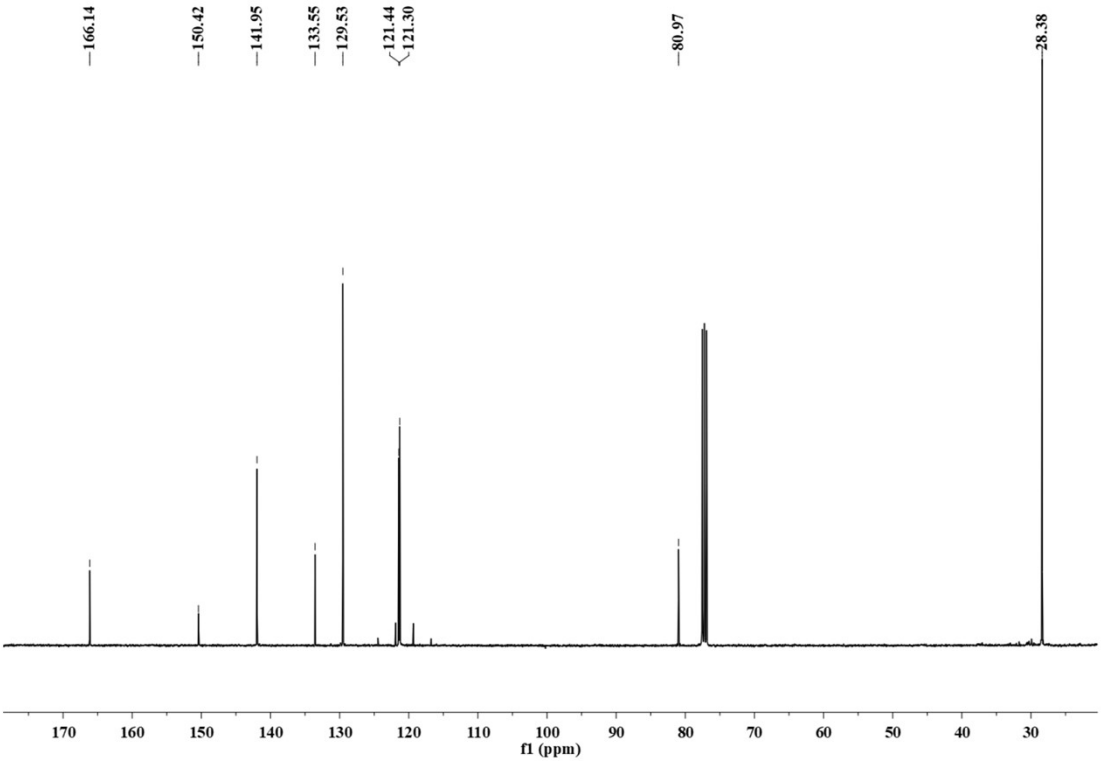
f1 (ppm)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121.30
80.97
28.38
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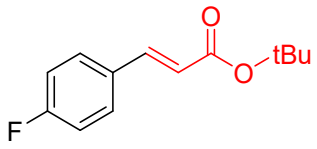
f1 (ppm)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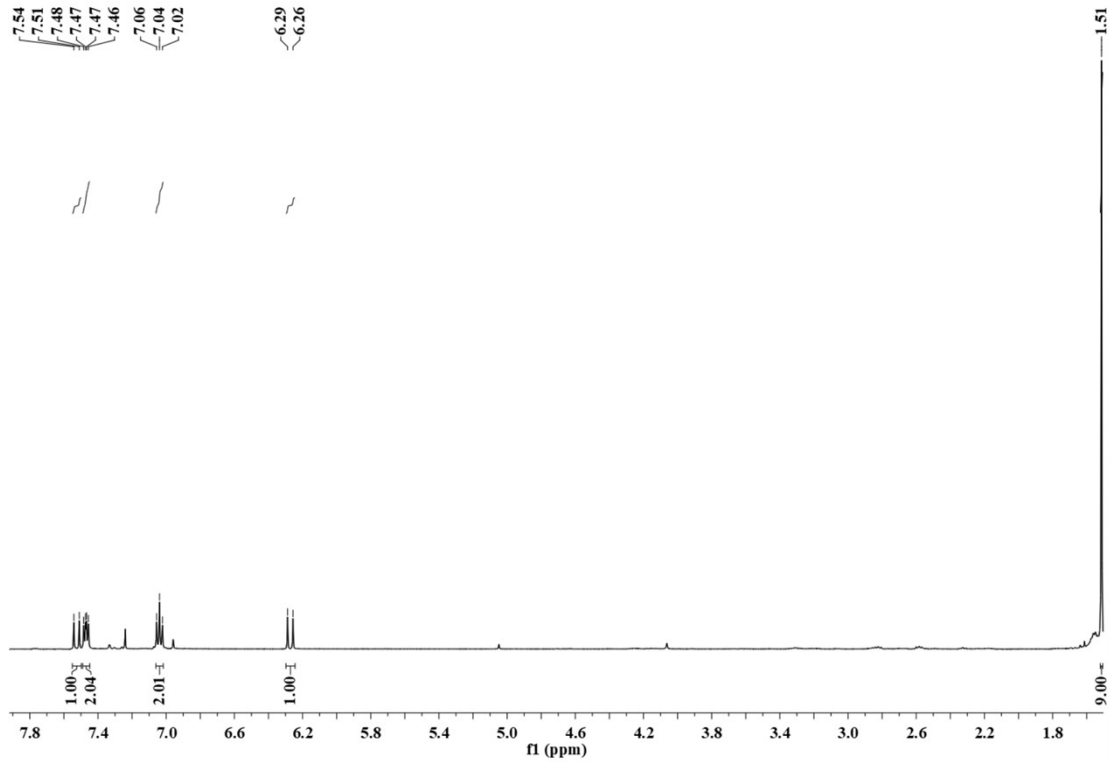
F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1.00
2.04
2.01
1.00
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7.4
7.0
6.6
6.2
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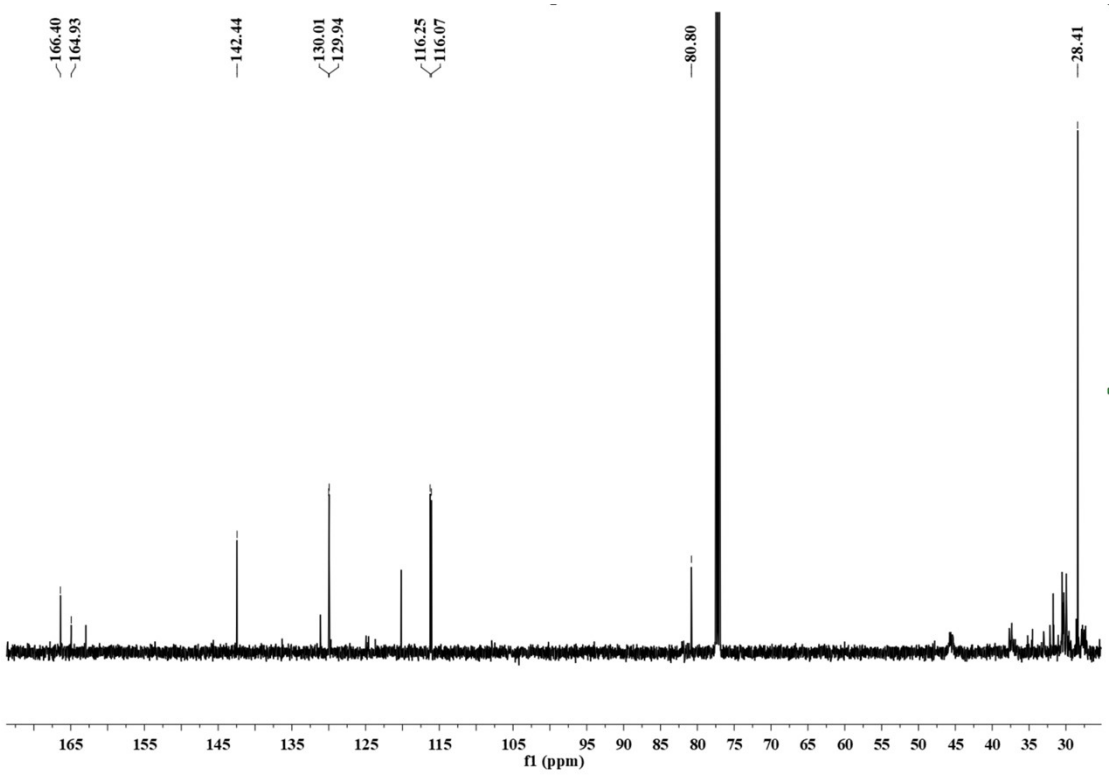
2.6
2.2
1.8
f1 (ppm)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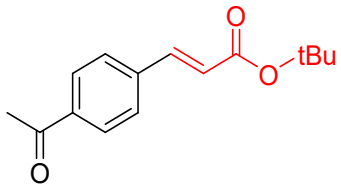
f1 (ppm)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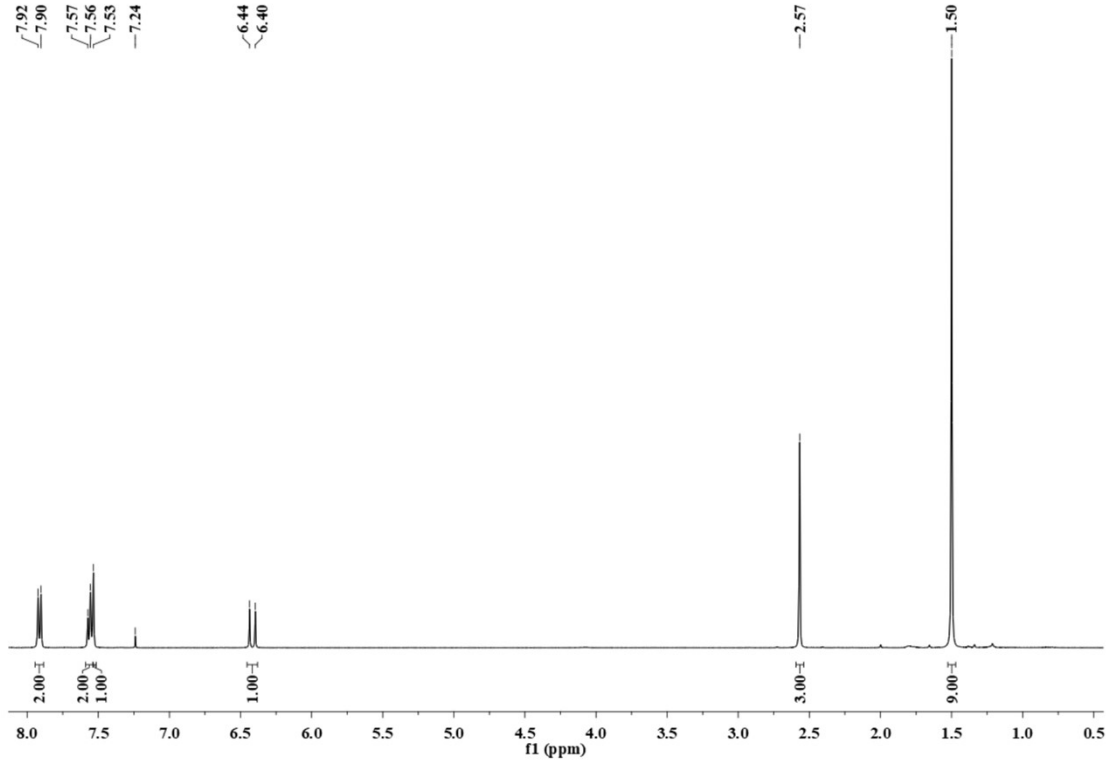
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6.40
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2.00
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1.00
3.00
9.00
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7.0
6.5
6.0
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3.0
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1.5
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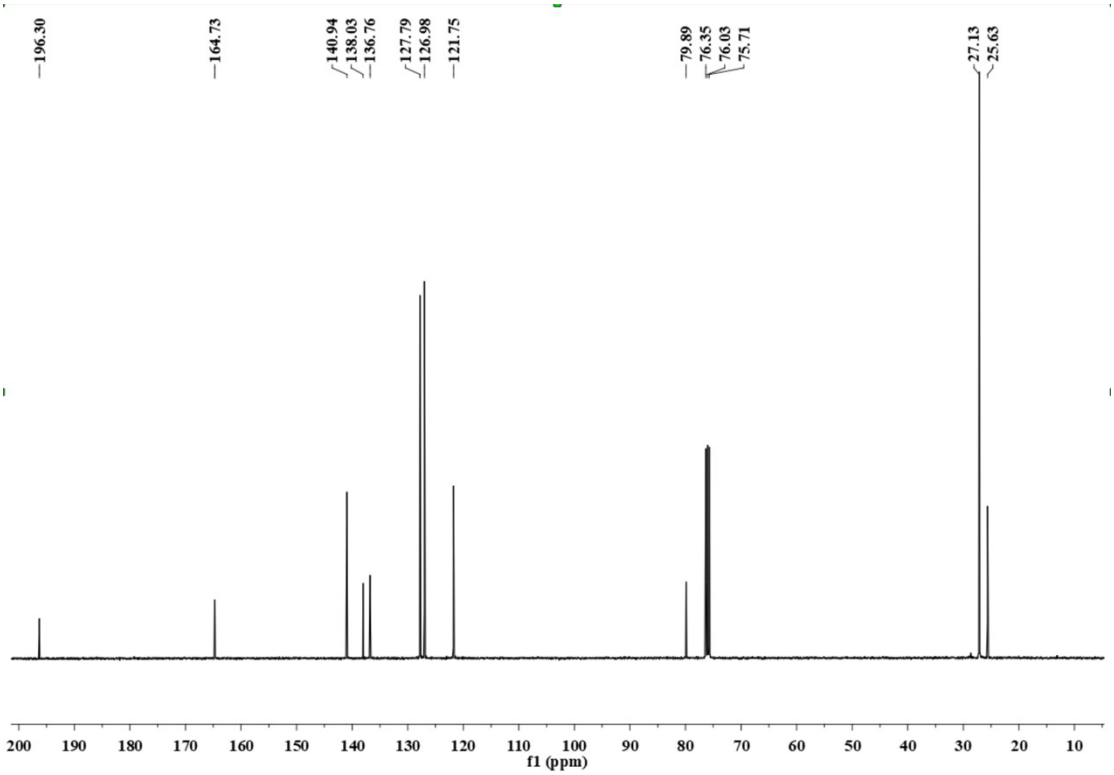
0.5
f1 (ppm)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121.75
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76.03
75.71
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25.63
200
190
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100
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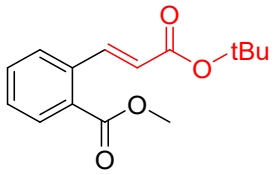
10
f1 (ppm)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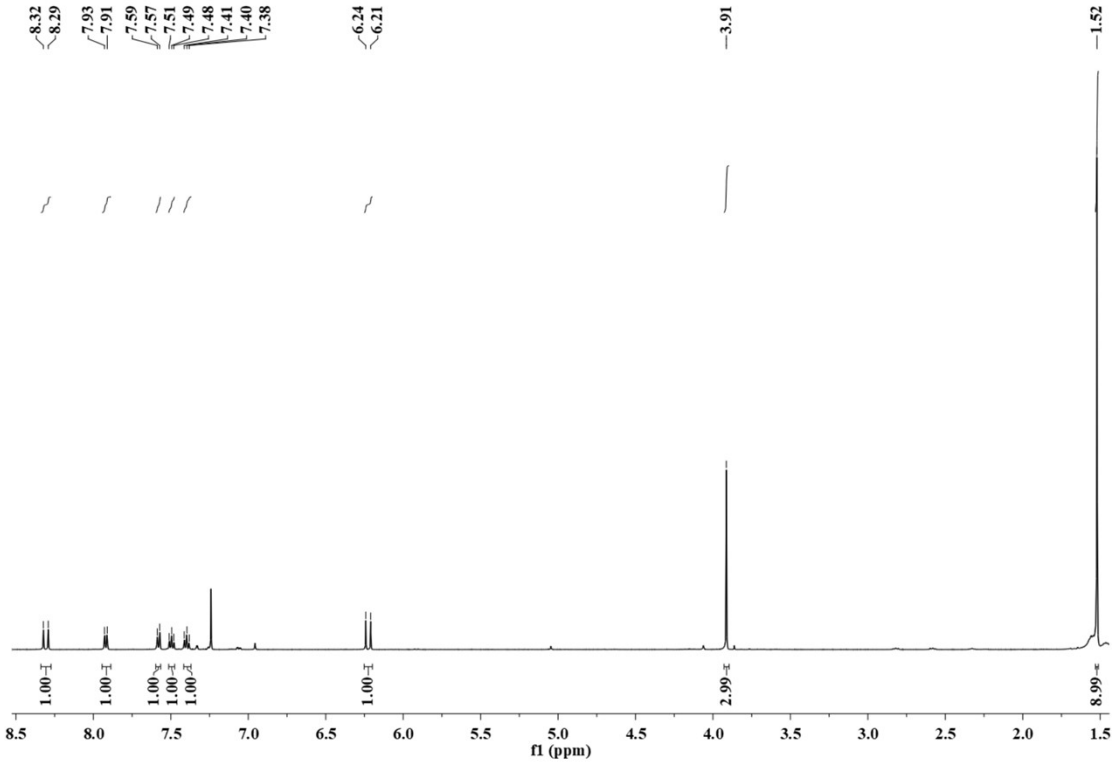
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6.21
3.91
1.52
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1.00
1.00
1.00
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1.00
2.99
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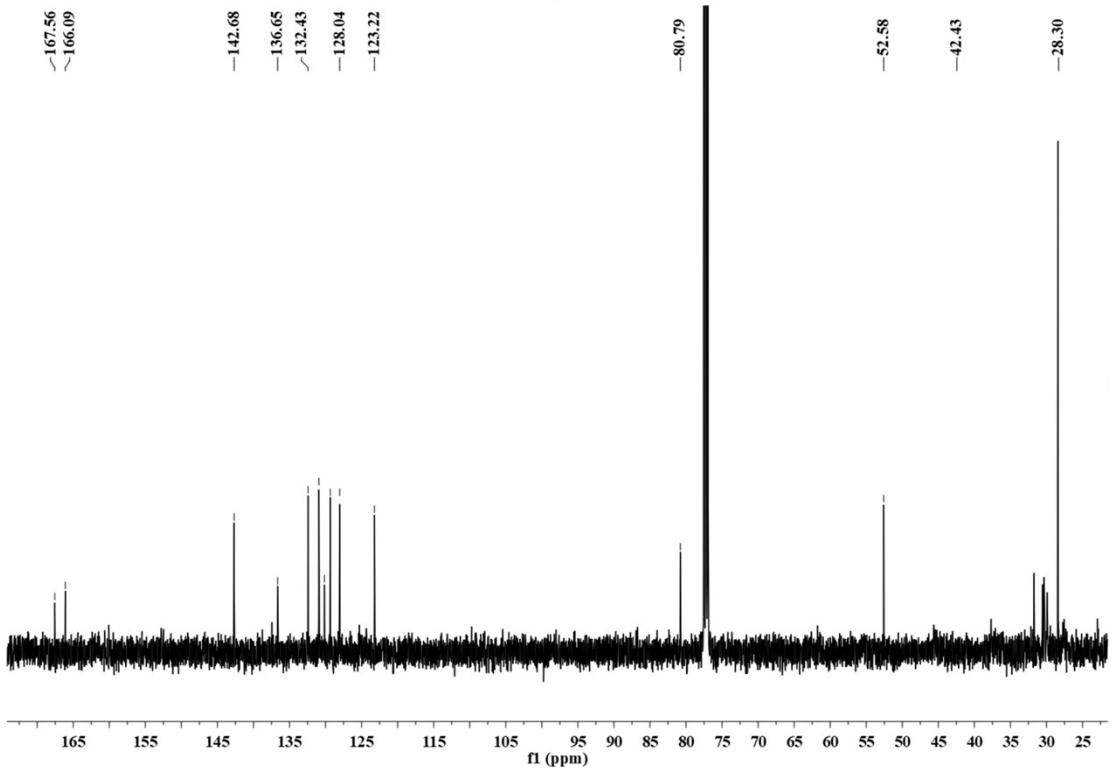
1.5
f1 (ppm)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128.04
123.22
80.79
52.58
42.43
28.30
165
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145
135
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50
45
40
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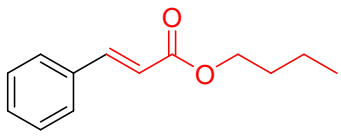
30
25
f1 (ppm)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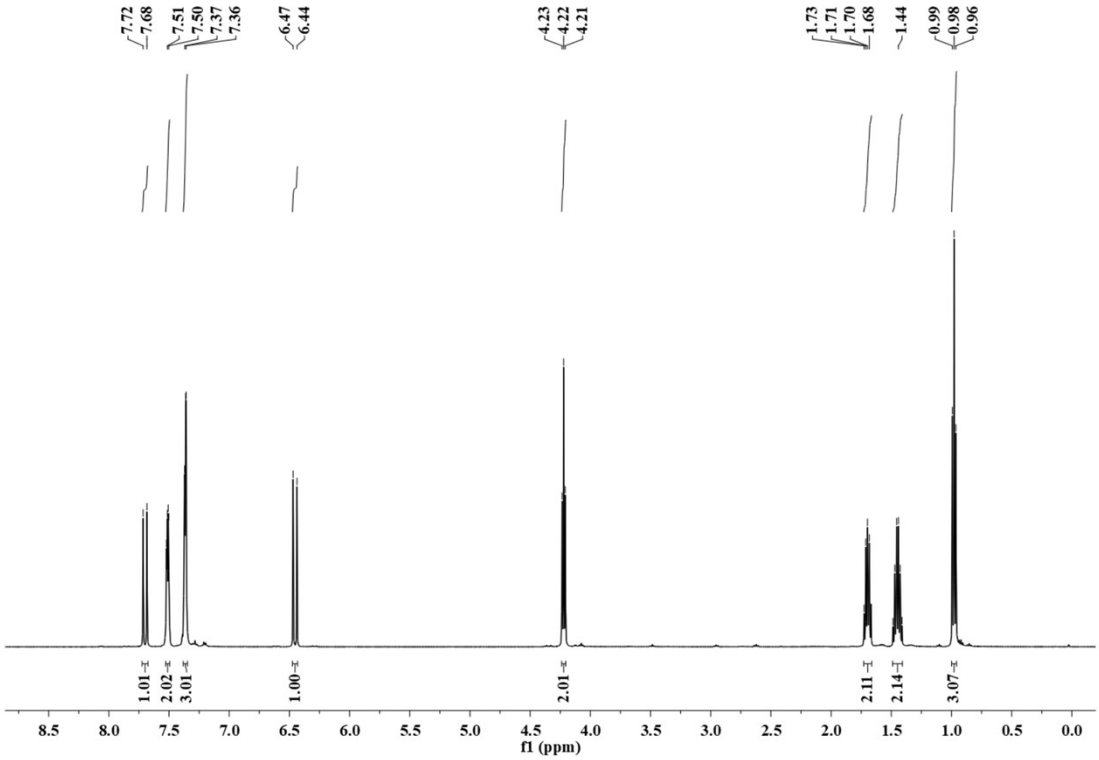
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6.47
6.44
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4.22
4.21
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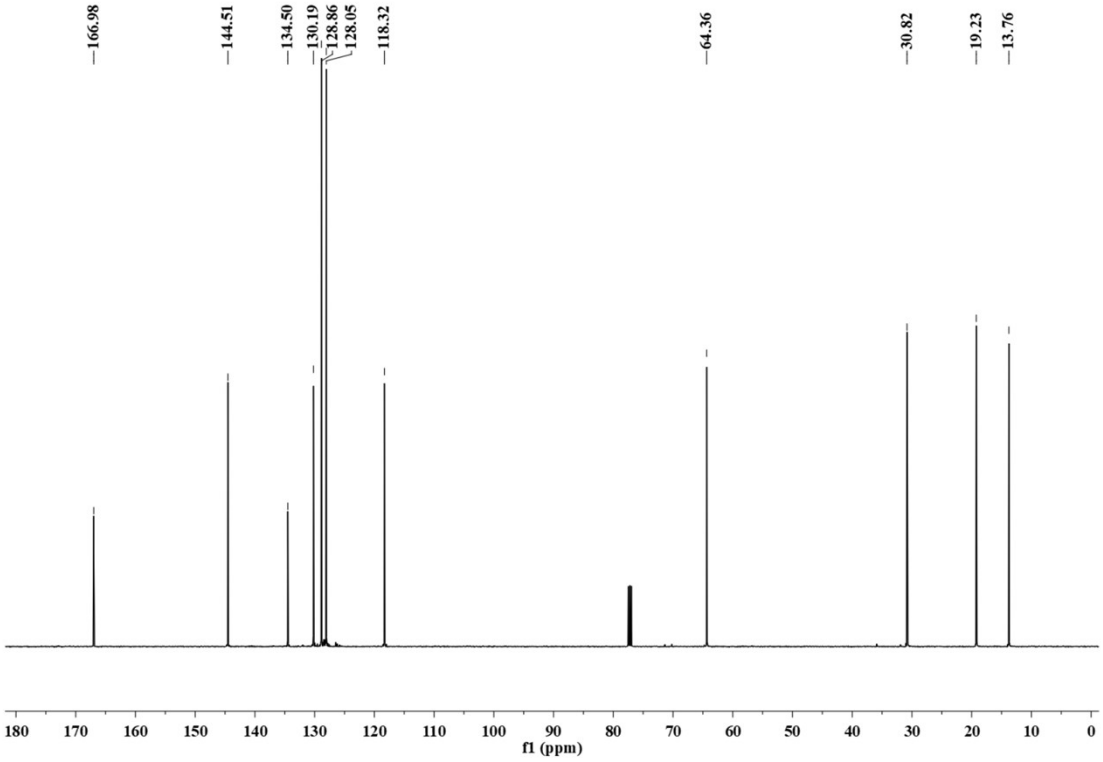
1.71
1.70
1.68
1.44
0.99
0.98
0.96
1.01
2.02
3.01
1.00
2.01
2.11
2.14
3.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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64.36
30.82
19.23
13.76
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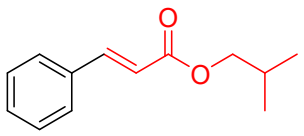
f1 (ppm)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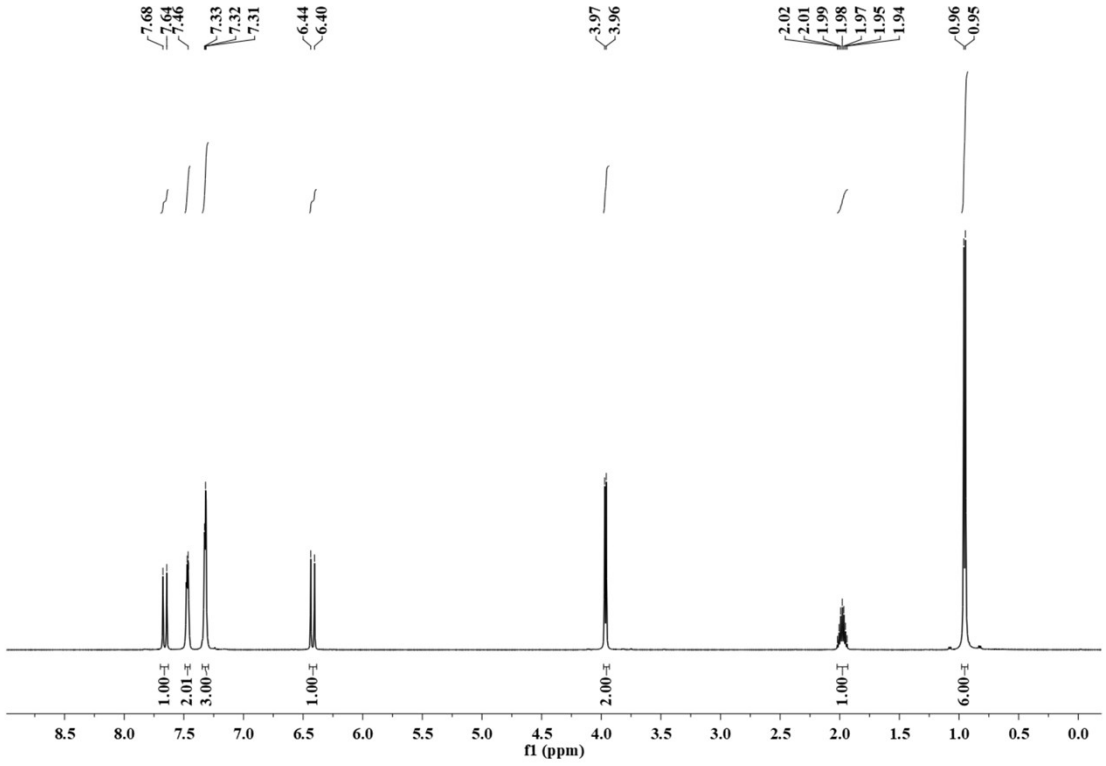
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6.40
3.97
3.96
2.02
2.01
1.99
1.98
1.97
1.95
1.94
0.96
0.95
1.00
2.01
3.00
1.00
2.00
1.00
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
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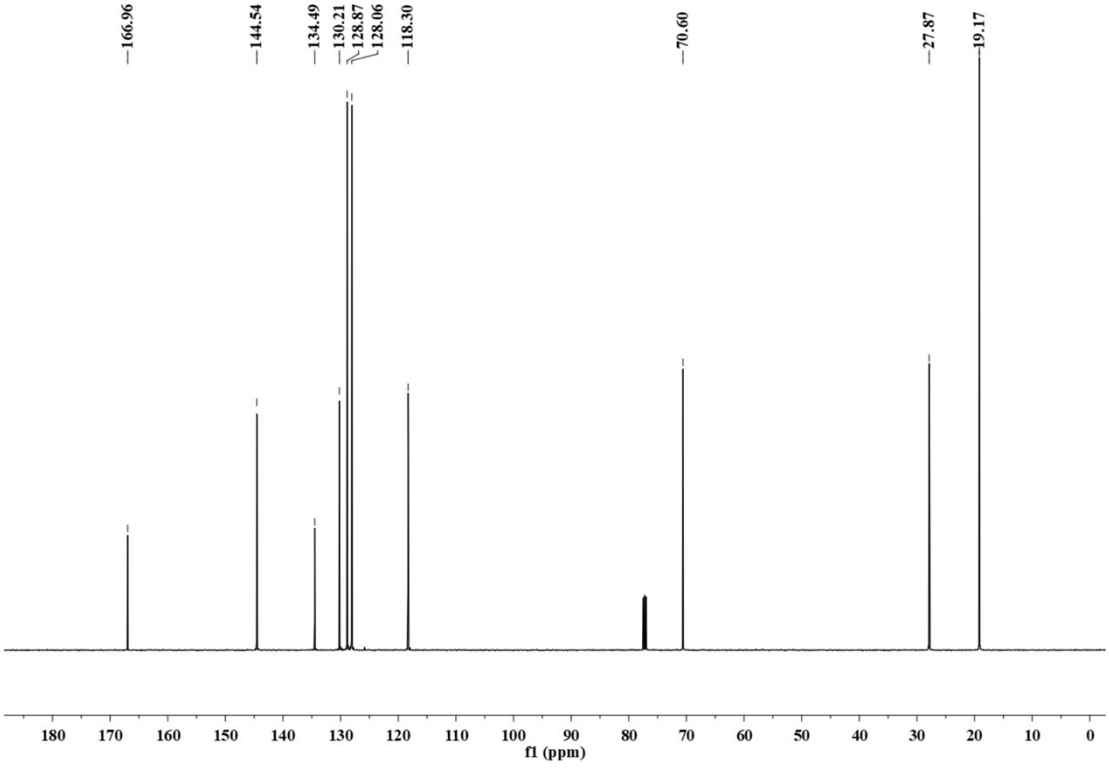
0.0
f1 (ppm)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19.17
180
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40
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10
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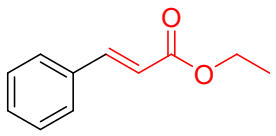
f1 (ppm)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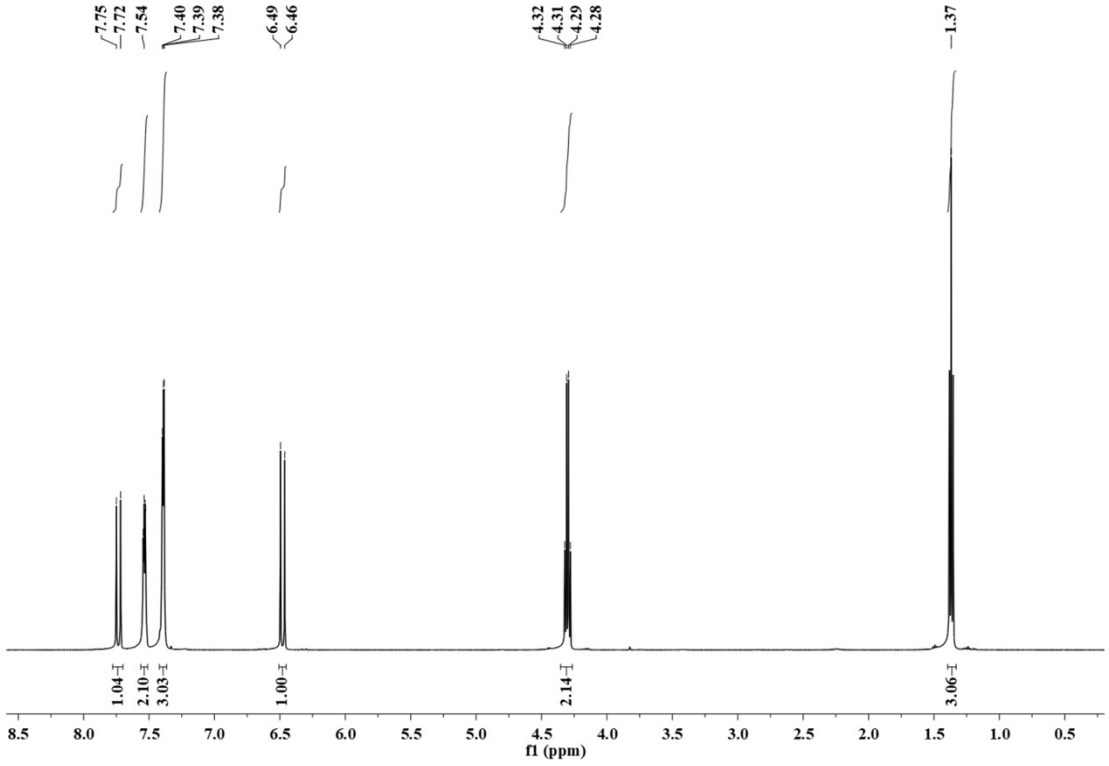
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4.28
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1.04
2.10
3.03
1.00
2.14
3.06
8.5
8.0
7.5
7.0
6.5
6.0
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1.5
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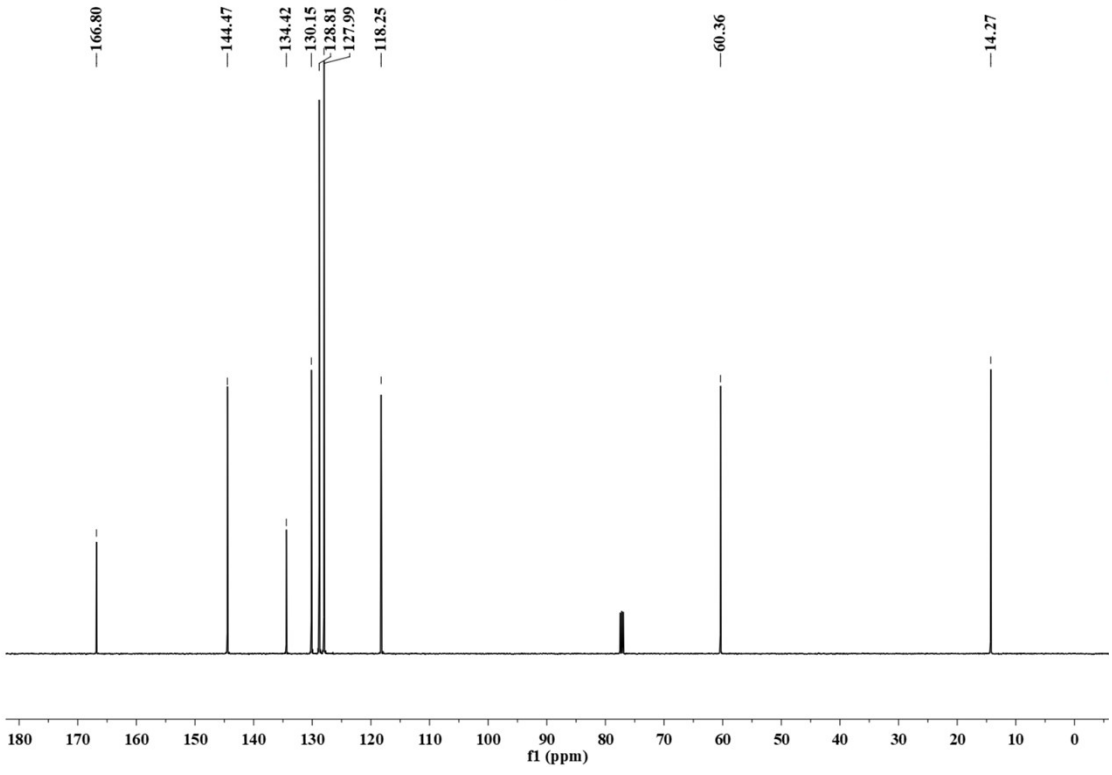
f1 (ppm)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90
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50
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30
20
10
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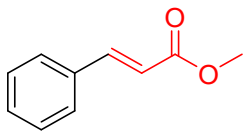
f1 (ppm)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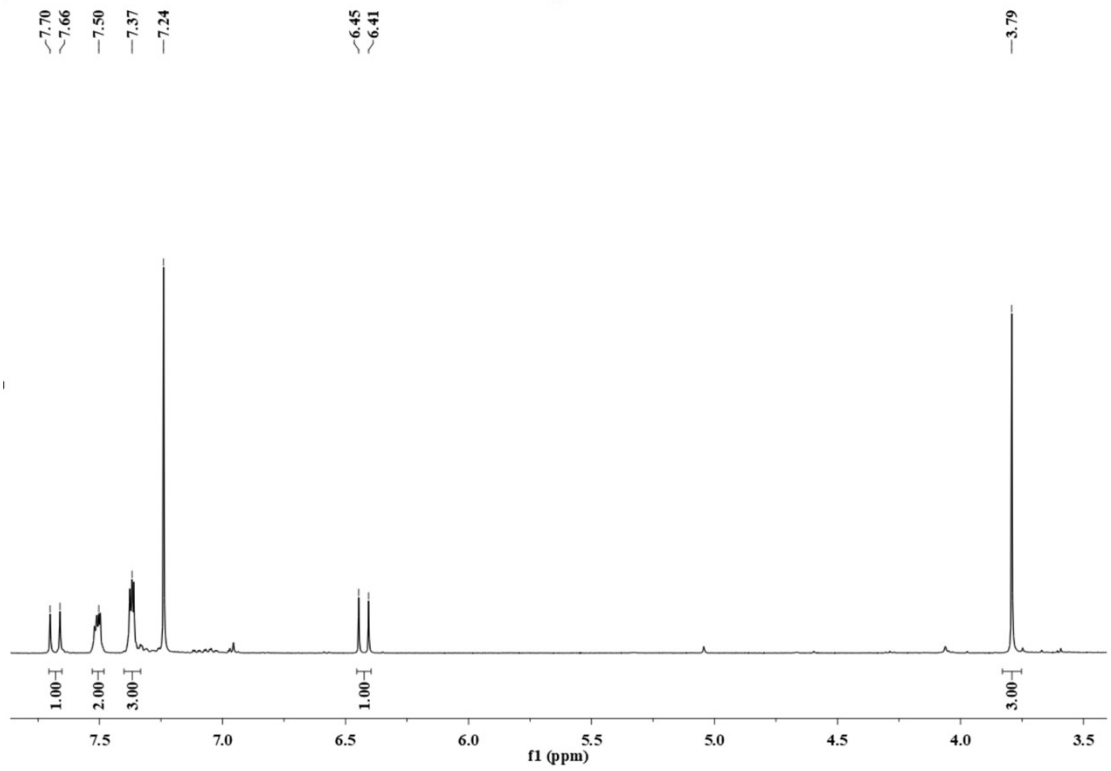
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2.00
3.00
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6.5
6.0
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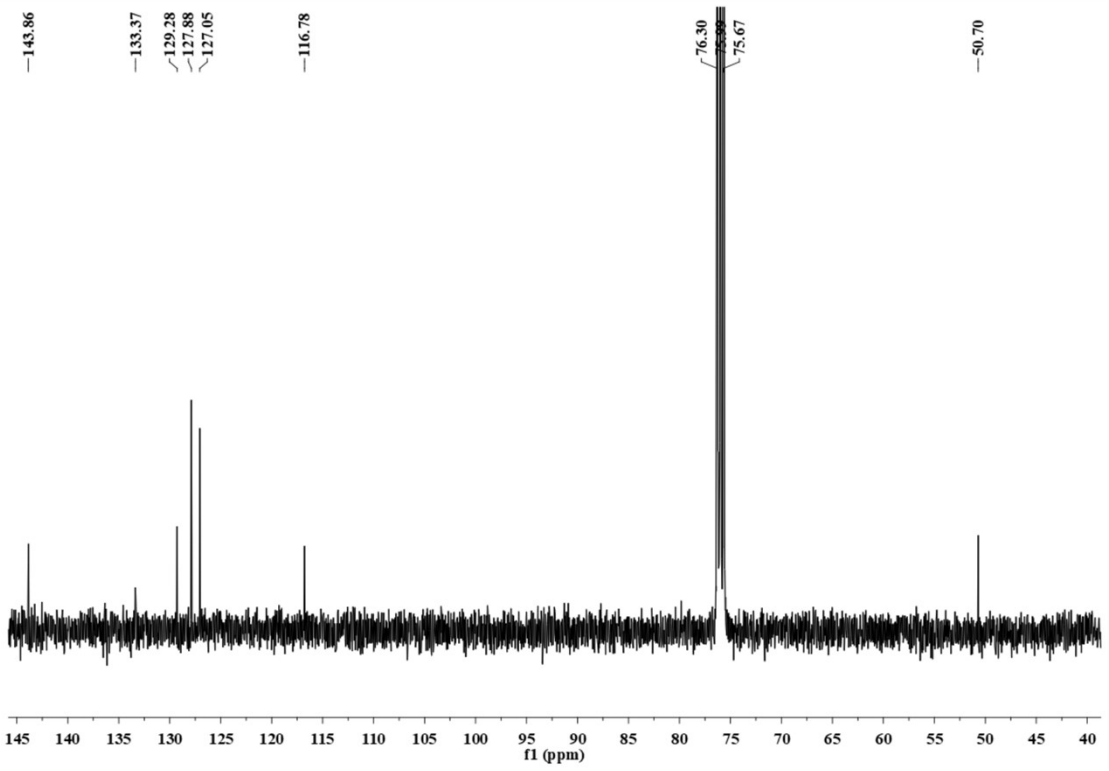
4.5
4.0
3.5
f1 (ppm)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65
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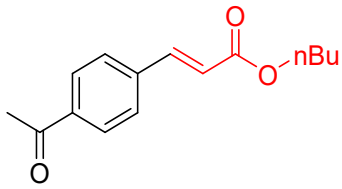
45
40
f1 (ppm)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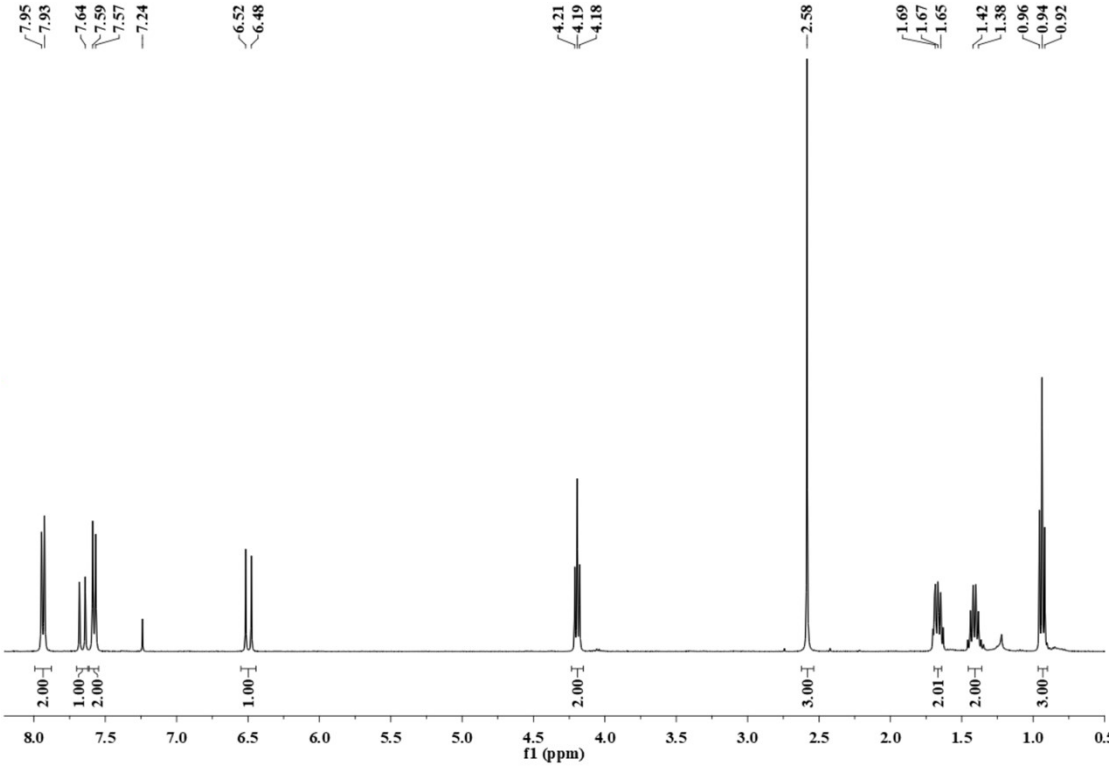
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1.42
1.38
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0.94
0.92
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1.00
2.00
1.00
2.00
3.00
2.01
2.00
3.00
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7.0
6.5
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2.0
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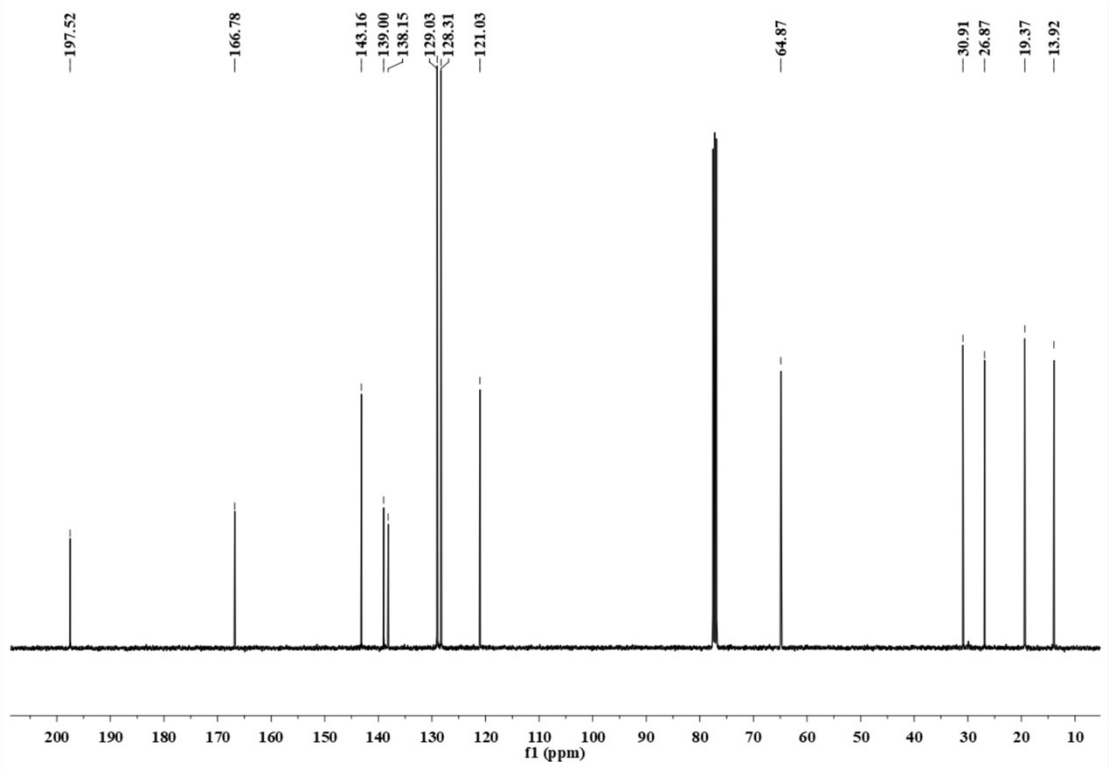
1.0
f1 (ppm)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26.87
19.37
13.92
200
190
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120
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100
90
80
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60
50
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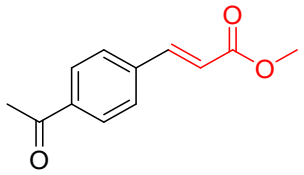
30
20
10
f1 (ppm)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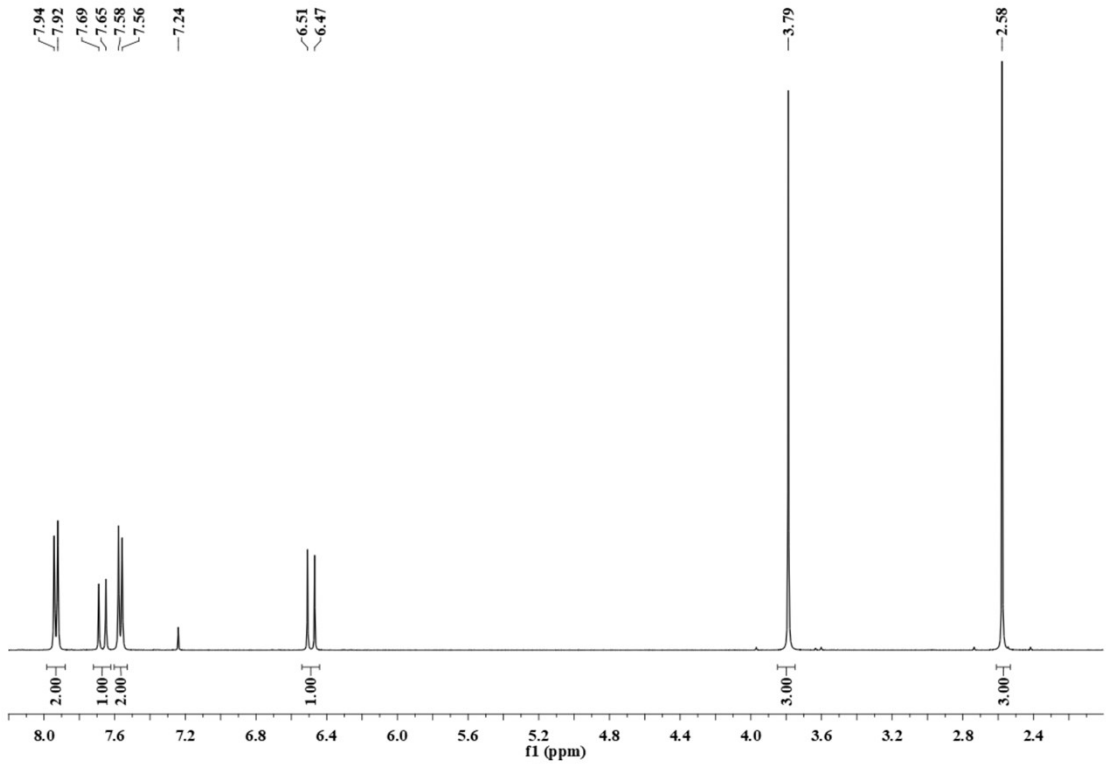
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3.00
3.00
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7.2
6.8
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4.4
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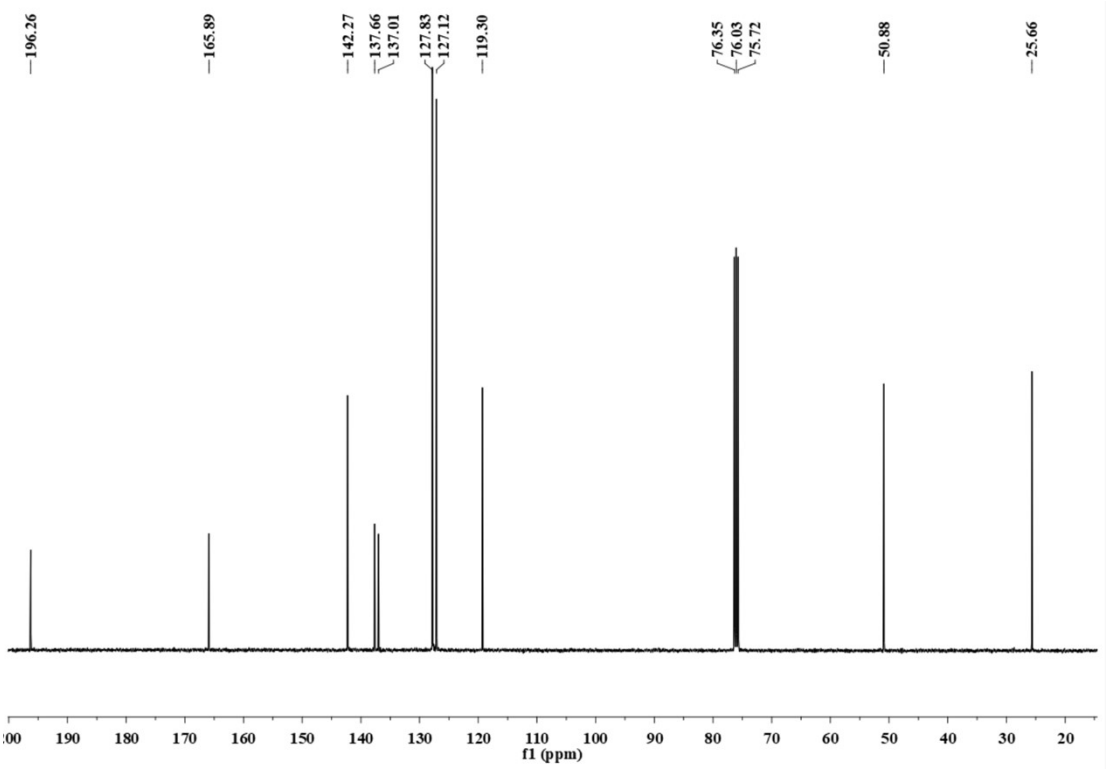
3.2
2.8
2.4
f1 (ppm)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00
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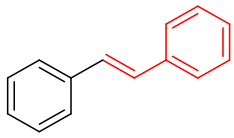
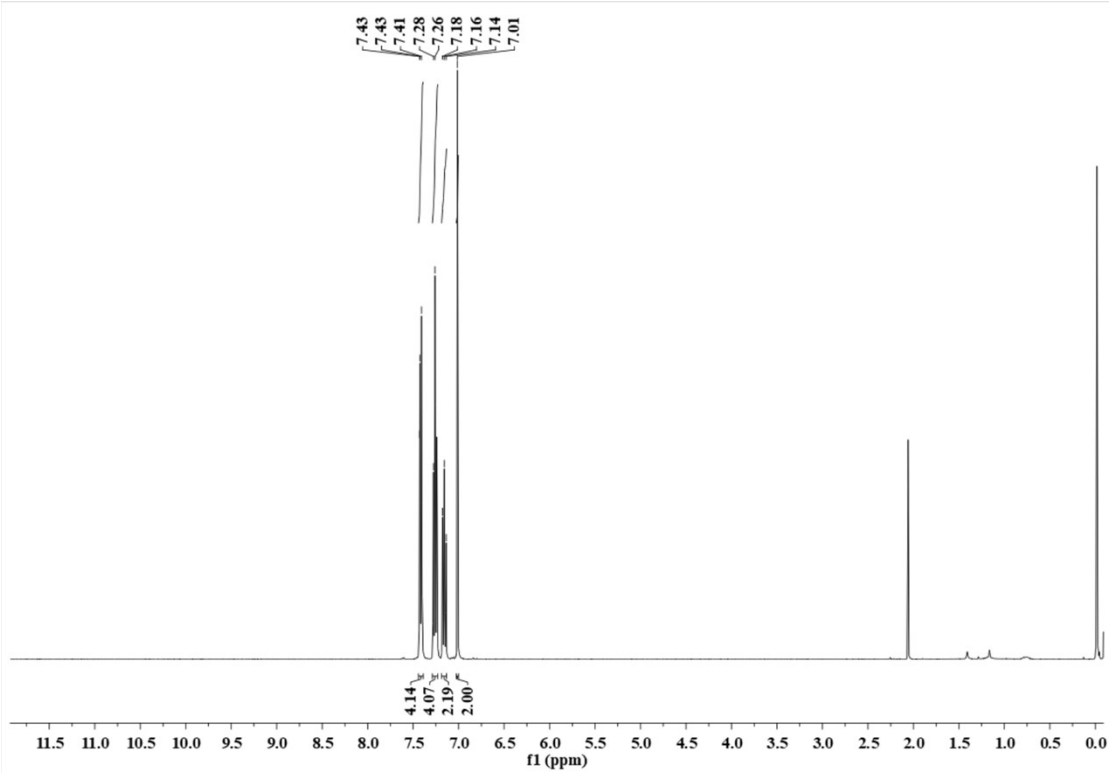
30
20
f1 (ppm)

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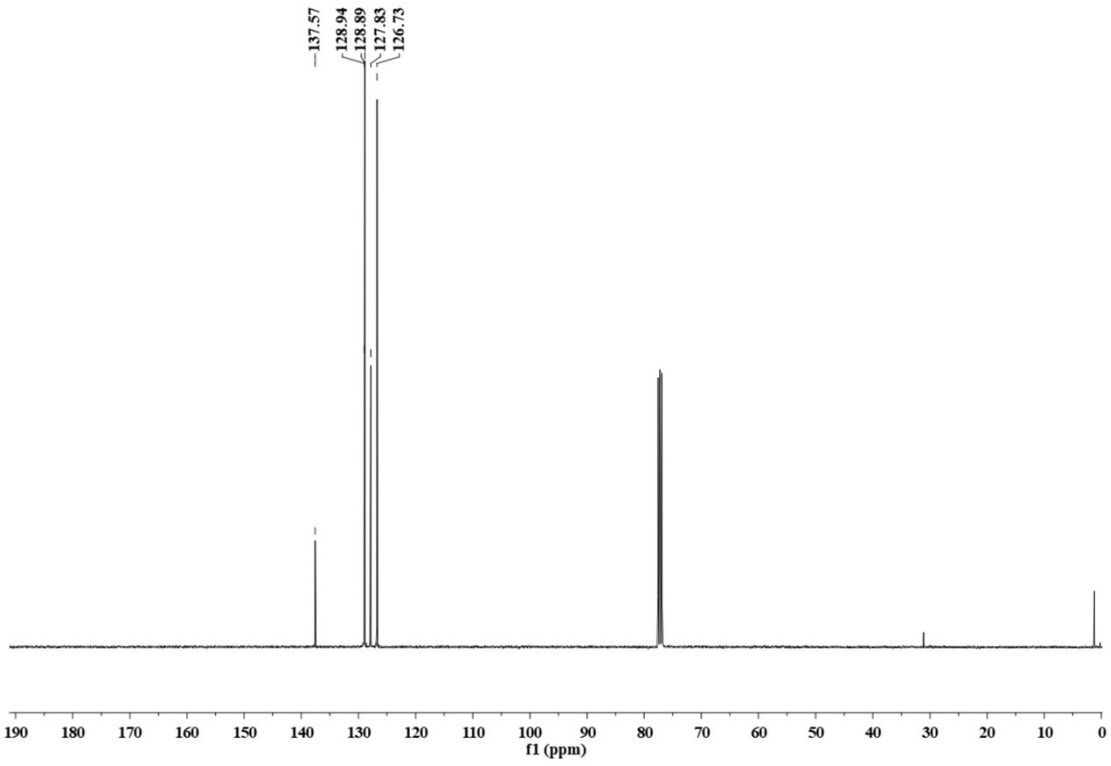
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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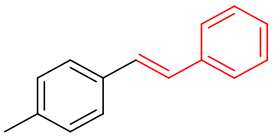
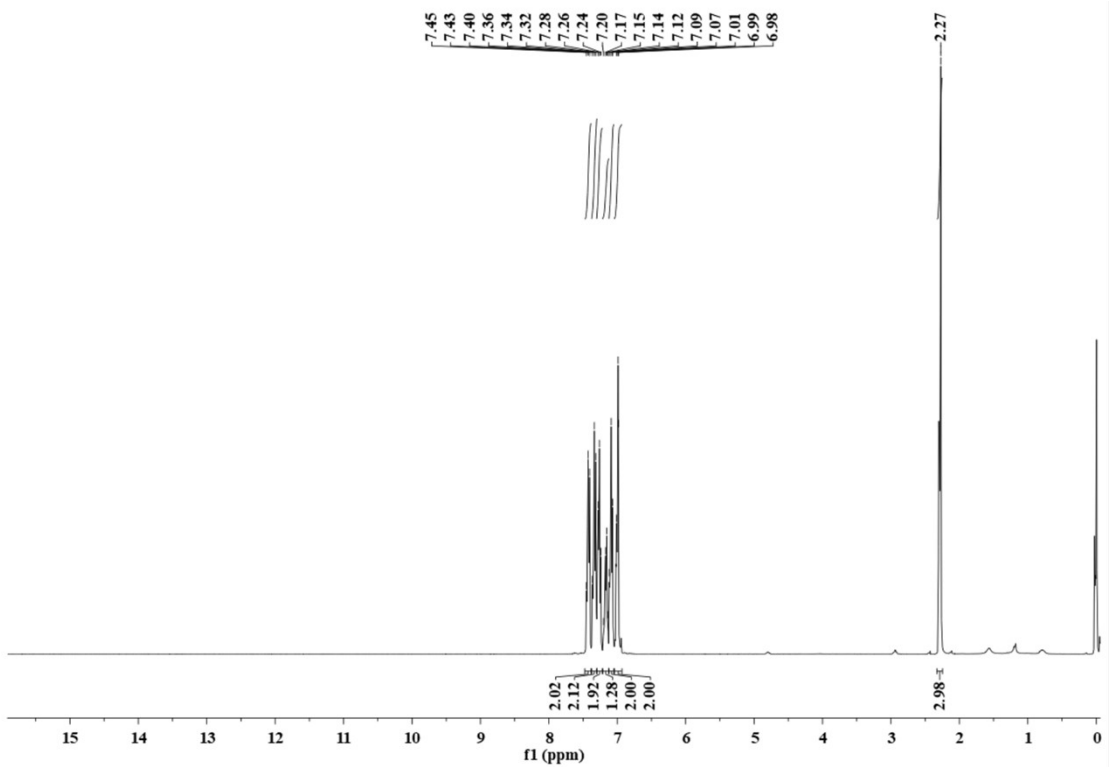
f1 (ppm)

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7.09
7.07
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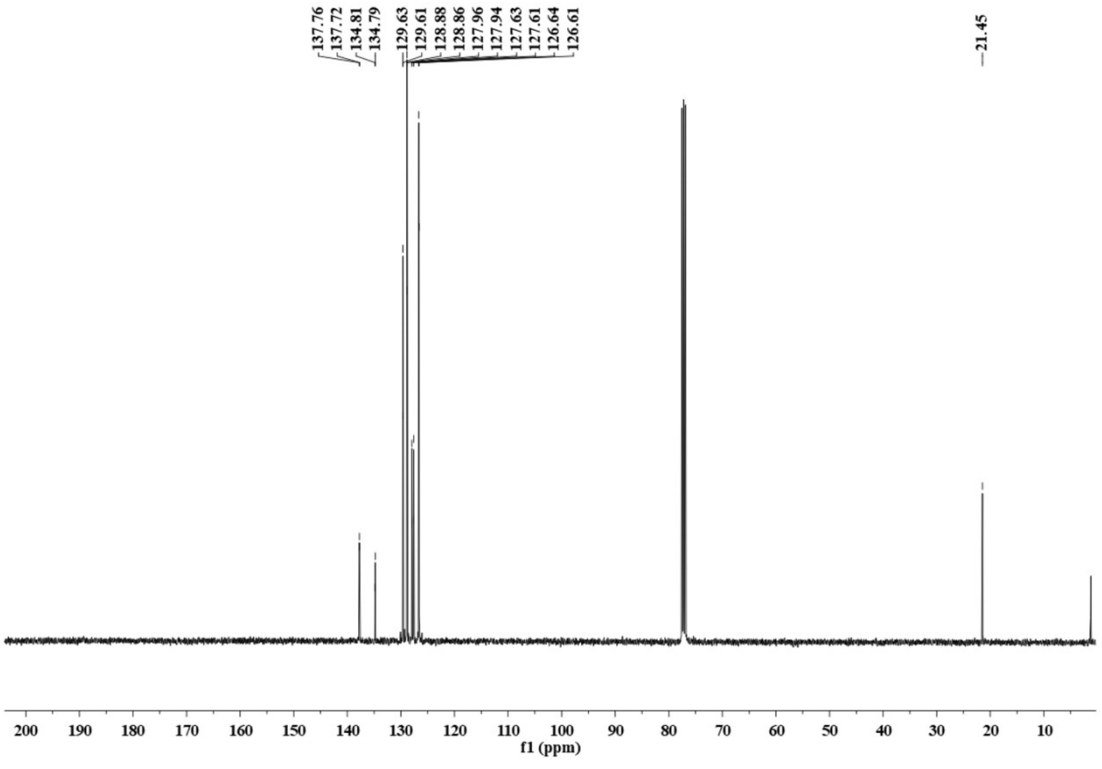
2.98
f1 (ppm)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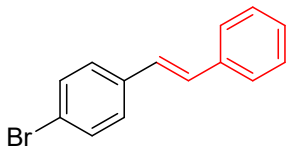
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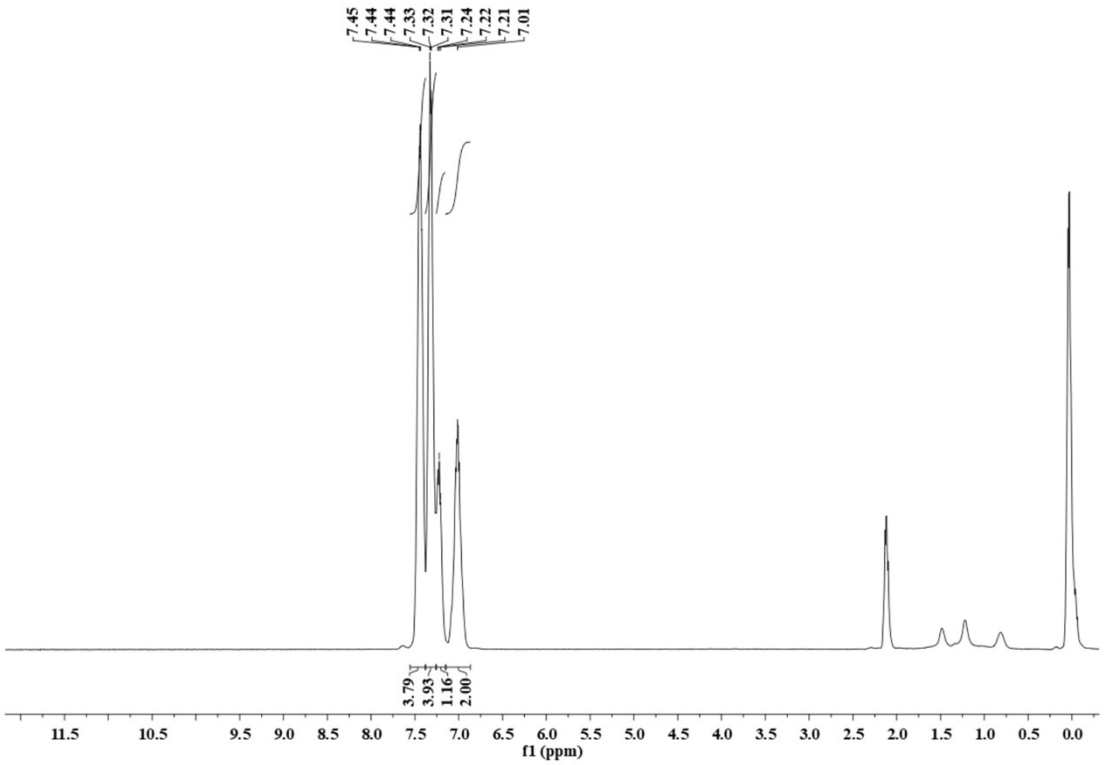
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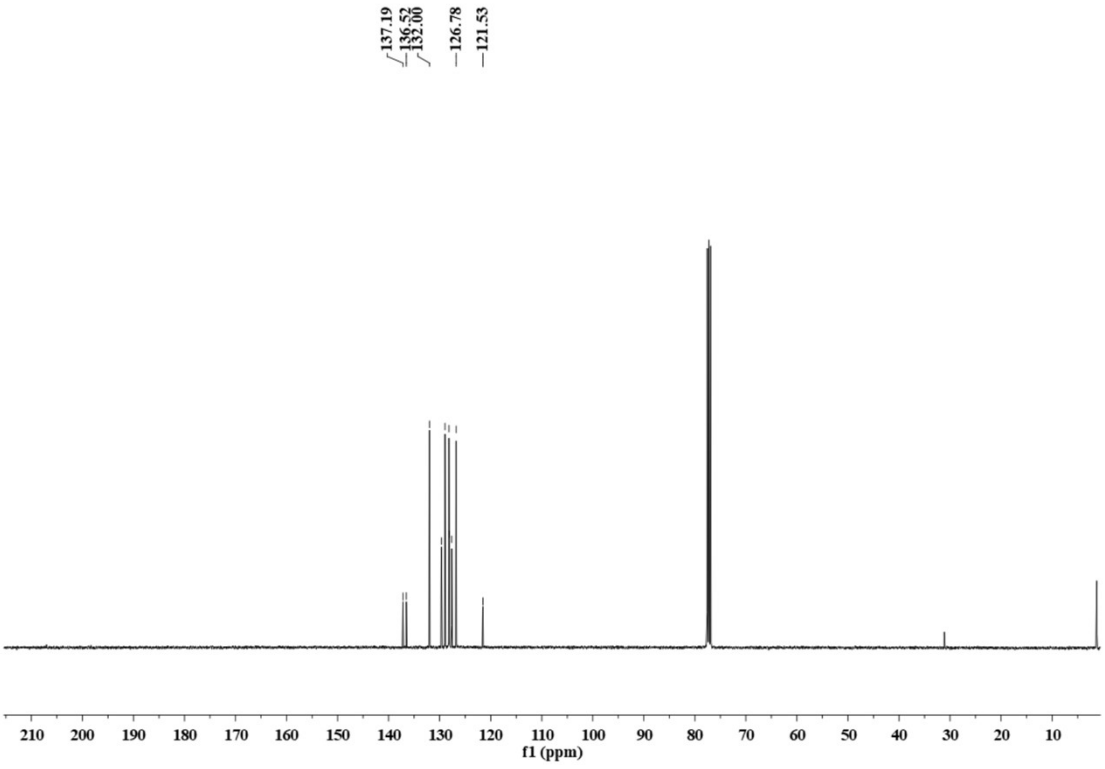
7.44
7.33
7.32
7.31
7.24
7.22
7.21
7.01
3.79
3.93
1.16
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


137.19
136.52
132.00
126.78
121.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)