$B(C_6F_5)_3$: A New Class of Strong and Bulky Lewis Acid for *Exo*-Selective Intermolecular Diels-Alder Reactions of Unreactive Acyclic Dienes with *α,β*-Enals

Jia-Hui Zhou[1], Bing Jiang[1], Fei-Fan Meng[1], Yun-He Xu[1*] and Teck-Peng Loh[1,2*]

[1]*Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China*

[2]*Division of Chemistry & Biological Chemistry, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798.*

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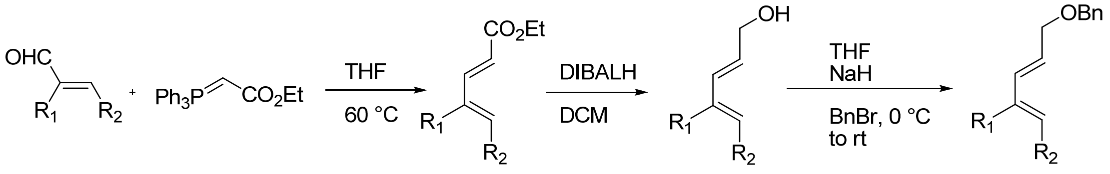
1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 25 ºC on Bruker Advance 400M NMR spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica *gel* with ethyl acetate and petroleum ether.

2. Typical procedure for the synthesis of starting materials.

2.1 The synthesis of **1a, 1g** and **1m**.



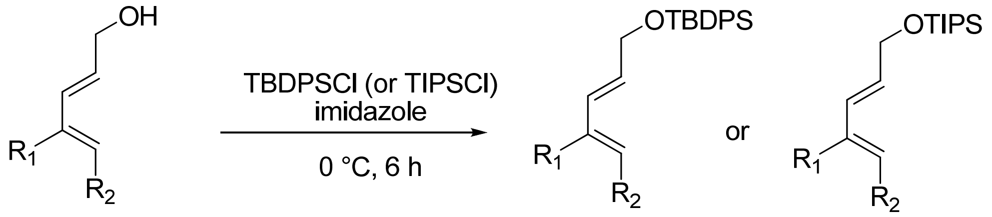
1a, 1g, 1m

Tiglic aldehyde (10 g, 0.12 mmol) was added to a solution of carb(ethoxymethylene) triphenyl phosphorane (60g, 0.18 mol) in THF (250 mL) at 60 °C. The solution was stirred overnight at 60 °C. The the reaction mixture was filtered and the filtrate was concentrated in vacuo. The unsaturated esters could be obtained after purification via column chromatography (EA/PE = 2:98). (R_1= -CH_3, R_2 = -CH_3, yellow oil, 15.9 g, yield: 86%; R_1= -Ph, R_2 = -CH_3, colorless oil, 40.1 g, yield: 60%; R_1= -CH_3, R_2 = -CH_2CH_3, colorless oil, 17.9 g, isolated yield: 89%).

The unsaturated esters (10 mmol) was dissolved in dry DCM (13 mL) and cooled to -78 °C. To this solution, DIBALH (1.0 M in hexanes, 25 mL, 25 mmol) was added dropwise and the reaction mixture was stirred at this temperature for 30 min. Then the reaction was quenched with MeOH (about 4.5 mL), saturated aqueous solution of sodium potassium tartrate (120 mL) and Et_2O (120 mL). The mixture was stirred vigorously at room temperature until there was sufficient separation of the two phases. The organic phase was separated and anqueous phase was washed twice with DCM (15 mL×2). The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 and finally concentrated in vacuo. The alcohol could be obtained after purification via column chromatography (EA/PE = 20:80). (R_1= -CH_3, R_2 = -CH_3, colorless oil, 1.01 g, yield: 90%; R_1= -Ph, R_2 = -CH_3, colorless oil, 1.69 g, yield: 97%; R_1= -CH_3, R_2 = -CH_2CH_3, colorless oil, 1.16 g, isolated yield: 92%).

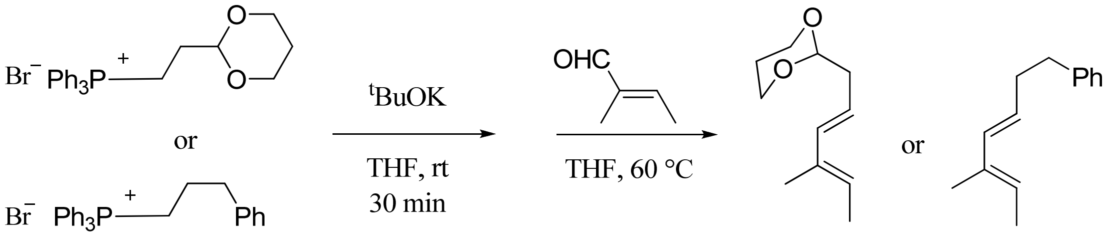
The alcohol (10 mmol) was added to a solution of sodium hydride (15 mmol) in THF (28 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes after which benzyl bromide (10.8 mmol) was added. The reaction was warmed slowly to room temperature and stirred for 3 hours. Saturated NH_4Cl solution was added dropwise at 0 °C to quench the reaction. The reaction mixture was filtered, and washed with ethyl acetate. The combined organic layer was washed with water, brine, dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. The product (**1a, 3g, 3m**) could be obtained after purification via flash column chromatography (EA/PE = 2:98). (**1a,** yellow oil, 1.82 g, yield: 90%; **1g,** colorless oil, 1.83 g, yield: 85%; **1m,** colorless oil, 1.93 g, yield: 73%).

2.2 The synthesis of **1d, 1e, 1f, 1h** and **1n**.



To a solution of alcohol (6 mmol) in DCM (14 mL) was added imidazole (12 mmol) at 0 °C. After imidazole was dissolved, TBDPSCl (or TIPSCl) (6.6 mmol) was added to the reaction mixture. The mixture was stirred at 0 °C to room temperature for 6 hours. The reaction was poured into ice water and extracted with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo. The crude product was purified by flash column chromatography (EA/PE = 2:98) to get the products (**1d, 1e, 1f, 1h, 1n**). (**1d,** colorless oil, 1.01 g, yield: 68%; **1e,** colorless oil, 1.97 g, yield: 94%; **1f,** colorless oil, 1.32 g, yield: 65%; **1h,** colorless oil, 1.50 g, yield: 69%; **1n,** colorless oil, 1.74 g, yield: 71%).

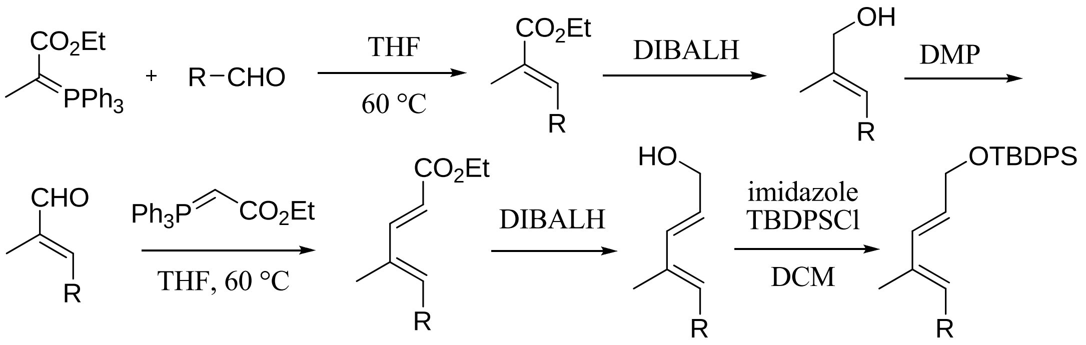
2.3 The synthesis of **1b** and **1c.**



1c 1b

To a solution of Wittig reagent (10 mmol) in THF was added ^{t}BuOK (15 mmol) at 0 °C to room temperature for 30 minutes, after which the aldehyde (10 mmol) was added and the mixture was heated to 60 °C overnight. The reaction was poured into ice water and extracted with ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Then the solvent was removed in vacuo. Purification via flash column chromatography (EA/PE = 3:97) was carried out to get the product (**1b, 1c**). (**1b,** colorless oil, 0.59 g, yield: 32%; **1c,** colorless oil, 0.42 g, yield: 23%).

2.4 The synthesis of **1i** to **1k**.



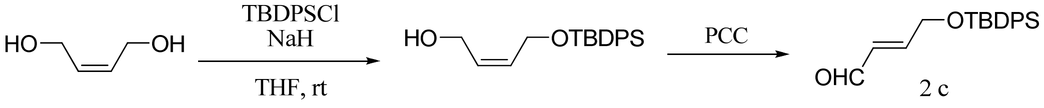
To a solution of Wittig reagent (15 mmol) in THF (25 mL) was added the corresponding aldehyde (15 mmol) at 60 °C. The reaction mixture was stirred overnight. Then the mixture was filtered, and the filtrate was concentrated in vacuo. Purification via column chromatography (EA/PE = 2:98) to afford the unsaturated esters.

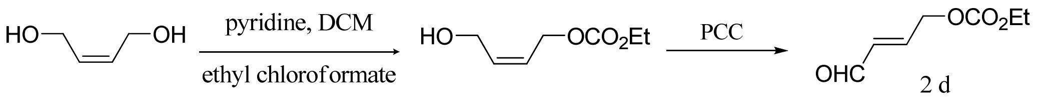
The unsaturated esters (10 mmol) was dissolved in dry DCM (13 mL) and cooled to -78 °C. To this solution, DIBALH (1.0 M in hexanes, 25 mL, 25 mmol) was added dropwise and the reaction mixture was stirred at this temperature for 30 minutes. Then the reaction was quenched with MeOH (about 4.5 mL), saturated aqueous solution of sodium potassium tartrate (120 mL) and Et_2O (120 mL). The mixture was stirred vigorously at room temperature until there was sufficient separation of the two phases. The organic phase was separated and anqueous phase was washed twice. The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 and finally concentrated in vacuo.

The crude product was dissolved in 10 mL DCM and added directly into a solution of DMP (15 mmol) in 30 mL DCM. The mixture was stirred vigorously at room temperature for 30 minutes. The reaction was quenched with 10% aqueous sodium thiosulfate and saturated aqueous sodium bicarbonate and was continued to stir for 10 min. The organic phase was separated and the aqueous phase was washed twice with DCM (5 mL×2). The combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo.

The crude aldehydes could be used to react with the Wittig reagent directly according to the procedures above. Following the reduction and protection steps also could be carried out according to the procedures above, and the products **1i** to **1k** could be obtained. (**1i, 1j, 1k,** colorless oil. The total yields of the products are between 30-50%).

2.5 The synthesis of **2c** and **2d**.





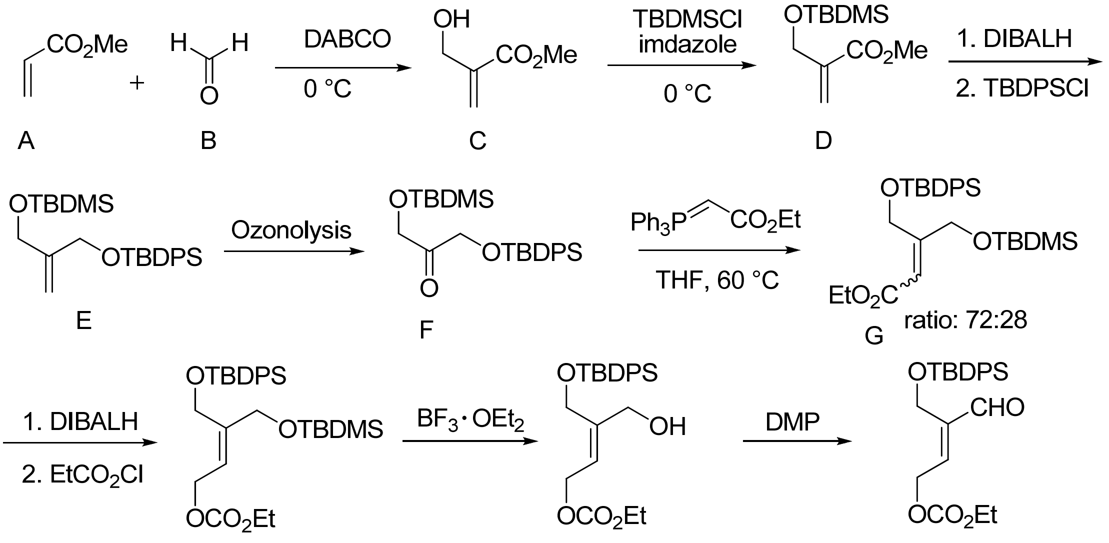
To a suspension of NaH (20 mmol) in THF 40 mL was added *cis*-2-butene-1,4-diol (20 mmol) at room temperature. After being stirred for 1 hour, TBDPSCl (20 mmol) was added to the mixture and the whole was stirred for 6 h. The reaction mixture was diluted with ether and washed with 10% aq K_2CO_3 and brine. The water layer was extracted with ether and the combined organic layer was dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue purified via column chromatography (EA/PE = 20:80) to afford the product[1]. (colorless oil, 3.78 g, yield: 58%).

To a solution of *cis*-2-butene-1,4-diol (20 mmol) in DCM (150 mL) was added dropwise ethyl chloroformate (20 mmol) and pyridine (40 mmol) under ice-cooling, and the resulting mixture was stirred at room temperature overnight and then evaporated in vacuo. To the residue obtained was added ethyl acetate. The organic layer washed with saturated aqueous sodium chloride solution and dried with anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under reduced pressure. The residue purified via column chromatography (EA/PE = 20:80) to afford the product . (colorless oil, 0.9 g, yield: 65%).

The *cis*-2-butene-1,4-diol protected by –OTBDPS or $–OCO_2Et$ (20 mmol) dissolved in DCM (35 mL) was added to pyridinium chlorochromate (40 mmol), and silica gel (9 g) in DCM (150 mL) at 0 °C. The reaction mixture was warmed slowly to room temperature and stirred for 4 hours. Then the mixture was filtered through a sintered glass funnel packed with silica gel and washed with DCM. The filtrate was dried over anhydrous $MgSO_4$. Purified via column chromatography (EA/PE = 10:90) to afford the product (**2c, 2d)**[2]. (**2c,** white solid, 4.53 g, yield: 70%; **2d,** colorless oil, 1.48 g, yield: 47%).

2.6 The synthesis of **2g**.

The compound **2g** could be prepared according to the following synthetic route. [3] Note: The product G could be obtained as a mixture of *E* and *Z* isomers. The mixture should be separated at this step for use in next step. And the Lewis acid $BF_3.OEt_2$ was used for the deprotection reaction from compound **H** to **I**.[4]



3. Reference

[1] Y. Yoshimura, Y. Yamazaki, Y. Saito, H. Takahata, *Tetrahedron* **2009,** *65,* 9091.

[2] W.-R. Roush, J.-A. Straub, M.-S. VanNieuwenhze, *J. Org. Chem.* **1991,** *56,* 1643.

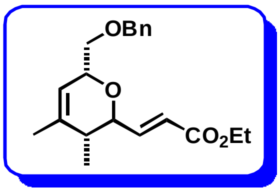
[3] C. Z. Yu, B. Liu, L. Q. Hu. *J. Org. Chem.* **2001,** *66,* 5413.

[4] K.-C. Nicolaous, K. Namoto, A. Ritzen, *J. Am. Chem. Soc.* **2001,** *123,* 9313.

4. Typical procedure for the synthesis of diels-alder products

The dienophile (0.2 mmol) in CH_2Cl_2 (0.2 mL) was added dropwise to a stirred solution of 4Å molecular sieve (20 mg, excess) and $B(C_6F_5)_3$ (0.02 mmol, 10 mg) in DCM (0.1 ml) at -78 ℃. And the mixture was stirred for another 15 minutes. Subsequently, the diene (0.4 mmol) pre-diluted in CH_2Cl_2 (0.2 mL) was added dropwise. The reaction was maintained at -78 ℃ with constant stirring for 48 hours. The reaction was quenched with saturated $NaHCO_3$, extracted with DCM twice. The combined organic extracts were washed with brine, and dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuum. Purification by flash column chromatography with ethyl acetate and petroleum was carried out to afford the pure compound.

5. Characterization data for the products



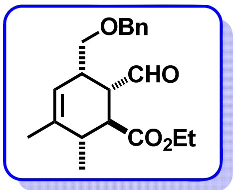
3aa”

(*E*)-ethyl 3-(6-(benzyloxymethyl)-3,4-dimethyl-3,6-dihydro-2*H*-pyran-2-yl)acrylate;

3aa” was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 49 mg (EA/PE = 10:90), yield, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.27 (5H, m), 6.90 (1H, dd, *J* = 15.6, 4.0 Hz), 6.13 (1H, dd, *J* = 15.6, 2.0 Hz), 5.34-5.31 (1H, m), 4.64 (1H, d, *J* = 12.2 Hz), 4.59 (1H, d, *J* = 12.2 Hz), 4.41-4.35 (1H, m), 4.34-4.29 (1H, m), 4.21 (2H, q, *J* = 7.2 Hz), 3.55 (1H, dd, *J* = 10.2, 6.4 Hz), 3.48 (1H, dd, *J* = 10.2, 4.8 Hz), 2.03-1.94 (1H, m), 1.75 (3H, t, *J* = 1.6 Hz), 1.30 (3H, t, *J* = 7.2 Hz), 0.94 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 166.6, 146.6, 139.3, 138.4, 128.4, 127.7, 127.6, 121.0, 120.1, 75.5, 75.1, 73.5, 73.2, 60.3, 37.6, 21.6, 14.3, 13.5 ppm;

HRMS (ESI) m/z calculated for $C_{20}H_{26}O_4H$ $[M+H]^+$: 331.1909, found 331.1906.



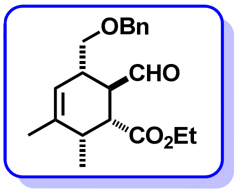
3aa’

ethyl-5-(benzyloxymethyl)-6-formyl-2,3-dimethylcyclohex-3-enecarboxylate;

3aa’ was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 16 mg (EA/PE = 10:90), yield, 24%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (1H, s), 7.35-7.25 (5H, m), 5.44-5.33 (1H, m), 4.41 (1H, d, *J* = 11.6 Hz), 4.30 (1H, d, *J* = 12.0 Hz), 4.21 (2H, q, *J* = 7.2 Hz), 3.44-3.36 (1H, m), 3.15-3.00 (3H, m), 2.55-2.45 (1H, m), 2.30-2.19 (1H, m), 1.67 (3H, d, *J* = 0.8 Hz), 1.31 (3H, t, *J* = 7.0 Hz), 1.10 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 201.0, 175.5, 139.5, 137.7, 128.4, 127.8, 127.7, 120.1, 73.0, 70.4, 60.6, 52.1, 44.2, 37.7, 36.8, 21.3, 17.6, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{20}H_{26}O_4H$ $[M+H]^+$: 331.1909, found 331.1907.



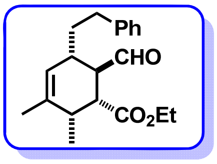
3aa

ethyl-5-((benzyloxy)methyl)-6-formyl-2,3-dimethylcyclohex-3-enecarboxylate;

3aa was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 53 mg (EA/PE = 10:90), yield, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (1H, d, *J* = 2.4 Hz), 7.37-7.28 (5H, m), 5.19-5.14 (1H, m), 4.52 (1H, d, *J* = 12.0 Hz), 4.44 (1H, d, *J* = 12.0 Hz), 4.20-4.11 (2H, m), 3.49 (1H, dd, *J* = 9.4, 5.0 Hz), 3.32 (1H, dd, *J* = 9.4, 8.4 Hz), 3.04 (1H, dd, *J* = 12.4, 5.2 Hz), 2.91-2.83 (1H, m), 2.70-2.60 (1H, m), 2.54-2.44 (1H, m), 1.73 (3H, s), 1.26 (3H, t, *J* = 7.2 Hz), 0.93 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 205.0, 173.5, 139.1, 138.0, 128.4, 127.6, 127.6, 120.0, 73.9, 73.1, 60.8, 46.8, 45.6, 39.9, 35.4, 21.9, 15.4, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{20}H_{26}O_4H$ $[M+H]^+$: 331.1909, found 331.1912.



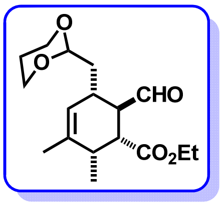
3ba

ethyl 6-formyl-2,3-dimethyl-5-phenethylcyclohex-3-enecarboxylate;

3ba was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 31 mg (EA/PE = 5:95), yield, 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (1H, d, *J* = 2.8 Hz), 7.29-7.26 (2H, m), 7.20-7.16 (3H, m), 5.39-5.32 (1H, m), 4.21-4.12 (2H, m), 2.98 (1H, dd, *J* = 12.0, 5.2 Hz), 2.81-2.72 (2H, m), 2.58-2.46 (2H, m), 2.38-2.29 (1H, m), 1.92-1.83 (1H, m), 1.77 (3H, t, *J* = 2.0 Hz), 1.70-1.63 (1H, m), 1.26 (3H, t, *J* = 7.0 Hz), 0.95 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 204.2, 173.4, 141.9, 137.8, 128.4, 128.3, 125.9, 122.8, 60.8, 46.6, 46.3, 36.6, 35.7, 35.2, 32.5, 22.0, 15.4, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{20}H_{26}O_3Na$ $[M+Na]^+$: 337.1780, found 337.1776.



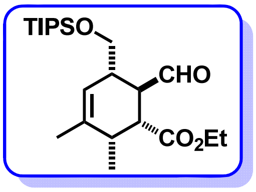
3ca

ethyl-5-((1,3-dioxan-2-yl)methyl)-6-formyl-2,3-dimethylcyclohex-3-enecarboxylate;

3ca was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky yellow oil, isolated 23 mg (EA/PE = 5:95), yield, 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (1H, d, *J* = 2.0 Hz), 5.27-5.23 (1H, m), 4.57-4.52 (1H, m), 4.20-4.04 (4H, m), 3.76-3.67 (2H, m), 2.93-2.86 (2H, m), 2.54-2.41 (2H, m), 2.12-2.00 (1H, m), 1.79-1.66 (4H, m), 1.55-1.42 (1H, m), 1.35-1.23 (4H, m), 0.92 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 204.7, 173.3, 137.3, 123.5, 100.6, 66.8, 66.7, 60.7, 46.8, 46.7, 40.0, 35.2, 33.0, 25.6, 21.9, 15.3, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{17}H_{26}O_5H$ $[M+H]^+$: 311.1858, found 311.1858.



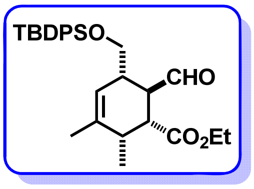
3da

ethyl-6-formyl-2,3-dimethyl-5-(((triisopropylsilyl)oxy)methyl)cyclohex-3-enecarboxylate;

3da was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky light yellow oil, isolated 66 mg (EA/PE = 5:95), yield, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (1H, d, *J* = 2.0 Hz), 5.20-5.15 (1H, m), 4.19-4.11 (2H, m), 3.74 (1H, dd, *J* = 9.6, 5.0 Hz), 3.53 (1H, dd, *J* = 9.6, 8.0 Hz), 3.04 (1H, dd, *J* = 12.2, 5.0 Hz), 2.94-2.88 (1H, m), 2.58-2.45 (2H, m), 1.73 (3H, t, *J* = 1.6 Hz), 1.26 (3H, t, *J* =7.2 Hz), 1.08-1.03 (21H, m), 0.94 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 205.0, 173.7, 139.0, 120.3, 67.4, 60.7, 46.8, 45.3, 42.7, 35.4, 21.9, 18.0, 15.4, 14.2, 11.9 ppm;

HRMS (ESI) m/z calculated for $C_{22}H_{40}O_4SiH$ $[M+H]^+$: 397.2774, found 397.2774.



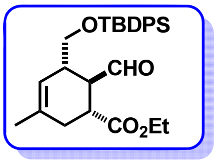
3ea

ethyl-5-(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-2,3-dimethylcyclohex-3-enecarboxylate;

3ea was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 95 mg (EA/PE = 5:95), yield, 99%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (1H, d, *J* = 1.6 Hz), 7.69-7.64 (4H, m), 7.44-7.38 (6H, m), 5.12-5.05 (1H, m), 4.23-4.11 (2H, m), 3.66 (1H, dd, *J* = 10.0, 4.8 Hz), 3.49 (1H, dd, *J* = 10.0, 7.6 Hz), 3.07-2.96 (2H, m), 2.61-2.53 (1H, m), 2.52-2.46 (1H, m), 1.71 (3H, t, *J* = 1.6 Hz), 1.27 (3H, t, *J* =7.2 Hz), 1.05 (9H, s), 0.94 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 205.08, 173.61, 139.0, 135.6, 135.6, 133.3, 133.1, 129.8, 127.8, 120.4, 67.5, 60.8, 46.8, 45.1, 42.1, 35.4, 26.8, 21.8, 19.2, 15.4, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{29}H_{38}O_4SiH$ $[M+H]^+$: 479.2618, found 479.2617.



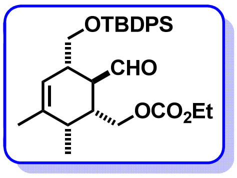
3fa

ethyl-5-(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-3-methylcyclohex-3-enecarboxylate;

3fa was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 83 mg (EA/PE = 5:95), yield, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (1H, d, *J* = 2.4 Hz), 7.66-7.62 (4H, m), 7.46-7.37 (6H, m), 5.17-5.10 (1H, m), 4.13 (2H, q, *J* = 7.1 Hz), 3.64 (1H, dd, *J* = 10.0, 5.2 Hz), 3.50 (1H, dd, *J* = 10.0, 8.0 Hz), 2.96-2.89 (1H, m), 2.80-2.75 (1H, m), 2.69-2.60 (1H, m), 2.29-2.23 (1H, m), 2.18-2.11 (1H, m), 1.67 (3H, s), 1.25 (3H, t, *J* = 7.2 Hz), 1.03 (9H, s) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 204.1, 174.4, 135.6, 135.6, 133.8, 133.2, 133.1, 129.8, 127.7, 120.4, 67.3, 60.9, 50.9, 41.5, 41.1, 32.4, 26.8, 23.1, 19.1, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{28}H_{36}O_4SiNa$ $[M+Na]^+$: 487.2281, found 487.2297.



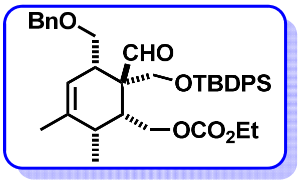
3ed

(5-(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-2,3-dimethylcyclohex-3-en-1-yl)methyl ethyl carbonate;

3ed was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 47 mg (EA/PE = 10:90), yield, 46%. ^1H NMR (400 MHz, $CDCl_3$): δ 9.68 (1H, d, *J* = 4.0 Hz), 7.64-7.62 (4H, m), 7.43-7.36 (6H, m), 5.18-5.12 (1H, m), 4.22-4.06 (4H, m), 3.55 (1H, dd, *J* = 10.0, 4.8 Hz), 3.41 (1H, dd, *J* = 10.0, 7.2 Hz), 2.76-2.67 (1H, m), 2.41-2.36 (2H, m), 2.28-2.20 (1H, m), 1.70 (3H, t, *J* = 2.0 Hz), 1.31 (3H, t, *J* = 7.2 Hz), 1.02 (9H, s), 0.94 (3H, d, *J* = 7.2 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 203.8, 154.8, 139.9, 135.7, 135.6, 134.8, 133.2, 133.2, 129.7, 127.7, 127.7, 120.2, 68.0, 66.9, 64.2, 48.3, 39.9, 37.8, 34.6, 26.7, 21.9, 19.2, 14.3, 13.6 ppm;

HRMS (ESI) m/z calculated for $C_{30}H_{40}O_5SiNa$ $[M+Na]^+$: 531.2543, found 531.2546.



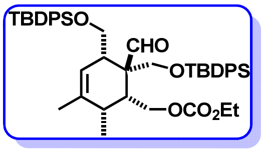
3ag

(5-((benzyloxy)methyl)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-2,3-dimethylcyclohex-3-en-1-yl)methyl ethyl carbonate.

3ag was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; white solid, isolated 56 mg (EA/PE = 10:90), yield, 45%. ^1H NMR (400 MHz, $CDCl_3$): δ 9.70 (1H, s), 7.66-7.59 (4H, m), 7.44-7.30 (8H, m), 7.26-7.23 (1H, m), 7.11-7.08 (2H, m), 5.08-5.03 (1H, m), 4.65 (1H, dd, *J* = 11.2, 10.0 Hz), 4.26-4.16 (5H, m), 4.05 (1H, d, *J* = 10.8 Hz), 3.83 (1H, d, *J* = 10.8 Hz), 3.15 (1H, dd, *J* = 9.6, 6.8 Hz), 3.03 (1H, t, *J* = 9.2 Hz), 2.87-2.81 (1H, m), 2.61-2.53 (1H, m), 2.46-2.37 (1H, m), 1.67 (3H, s), 1.30 (3H, t, *J* = 7.2 Hz), 1.08 (9H, s), 1.05 (3H, d, *J* = 7.6 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 206.01, 154.89, 137.80, 137.55, 136.05, 135.92, 132.76, 132.58, 129.91, 129.84, 128.28, 127.70, 127.68, 127.45, 127.40, 119.18, 72.91, 70.28, 67.22, 63.89, 62.11, 53.46, 42.63, 42.11, 33.66, 26.98, 21.81, 19.07, 14.32, 13.87 ppm;

HRMS (ESI) m/z calculated for $C_{38}H_{48}O_6SiH$ $[M+H]^+$: 629.3298, found 629.3296.



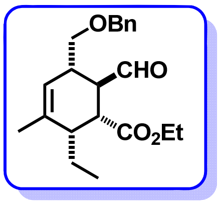
3eg

(5,6-bis(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-2,3-dimethylcyclohex-3-en-1-yl)methyl ethyl carbonate;

3eg was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; white solid, isolated 26 mg (EA/PE = 10:90), yield, 17%. ^1H NMR (400 MHz, $CDCl_3$): δ 9.83 (1H, s), 7.66-7.61 (4H, m), 7.55-7.45 (4H, m), 7.42-7.26 (12H, m), 4.94-4.89 (1H, m), 4.65 (1H, t, *J* = 10.6 Hz), 4.29-4.16 (4H, m), 3.81 (1H, d, *J* = 10.8 Hz), 3.29 (1H, dd, *J* = 10.4, 6.4 Hz), 3.23 (1H, dd, *J* = 10.4, 9.6 Hz), 2.81-2.73 (1H, m), 2.62-2.56 (1H, m), 2.45-2.36 (1H, m), 1.61 (3H, s), 1.30 (3H, t, *J* = 7.2 Hz), 1.07 (9H, s), 0.98 (3H, d, *J* = 7.6 Hz), 0.90 (9H, s) ppm;

^{13}C NMR(100 MHz, CDCl$_3$): δ 206.1, 154.9, 137.7, 136.0, 136.0, 135.5, 133.1, 132.8, 132.7, 132.6, 129.9, 129.8, 129.7, 129.6, 127.7, 127.7, 127.6, 119.0, 67.3, 64.1, 63.9, 62.3, 53.4, 45.6, 42.2, 33.7, 27.0, 26.7, 21.8, 19.1, 19.0, 14.3, 13.8 ppm;

HRMS (ESI) m/z calculated for $C_{47}H_{60}O_6Si_2Na$ [M+Na]$^+$: 799.3826, found 799.3848.



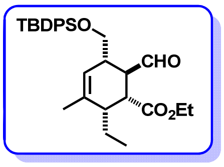
3ga

ethyl-5-((benzyloxy)methyl)-2-ethyl-6-formyl-3-methylcyclohex-3-enecarboxylate;

3ga was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 53 mg (EA/PE = 10:90), yield: 77%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.02 (1H, d, *J* = 2.0 Hz), 7.37-7.27 (5H, m), 5.24-5.19 (1H, m), 4.53 (1H, d, *J* = 12.0 Hz), 4.49 (1H, d, *J* = 12.4 Hz), 4.14 (2H, qd, *J* = 7.2, 1.2 Hz), 3.50 (1H, dd, *J* = 9.2, 5.2 Hz), 3.32 (1H, t, *J* = 8.8 Hz), 3.02 (1H, dd, *J* = 12.2, 5.0 Hz), 2.95-2.89 (1H, m), 2.67-2.58 (1H, m), 2.39-2.35 (1H, m), 1.76 (3H, t, *J* = 1.8 Hz), 1.52-1.42 (1H, m), 1.40-1.30 (1H, m), 1.26 (3H, t, *J* = 7.2 Hz), 0.89 (3H, t, *J* = 7.6 Hz) ppm;

^{13}C NMR(100 MHz, CDCl$_3$): δ 205.0, 173.8, 138.4, 138.1, 128.4, 127.6, 127.6, 120.5, 74.1, 73.1, 60.8, 46.8, 46.5, 42.0, 39.5, 24.2, 22.9, 14.1, 13.2 ppm;

HRMS (ESI) m/z calculated for $C_{21}H_{28}O_4H$ [M+H]$^+$: 345.2066, found 345.2068.



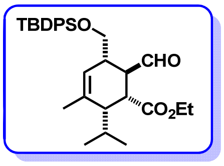
3ha

ethyl-5-(((tert-butyldiphenylsilyl)oxy)methyl)-2-ethyl-6-formyl-3-methylcyclohex-3-enecarboxylate;

3ha was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 83 mg (EA/PE = 5:95), yield: 85%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.09 (1H, s), 7.68-7.63 (4H, m), 7.46-7.37 (6H, m), 5.17-5.08 (1H, m), 4.21-5.09 (2H, m), 3.65 (1H, dd, *J* = 10.0, 5.2 Hz), 3.47 (1H, dd, *J* = 9.6, 8.0 Hz), 3.04-2.98 (2H, m), 2.58-2.50 (1H, m), 2.38-2.32 (1H, m), 1.73 (3H, t, *J* = 1.4 Hz), 1.49-1.42 (1H, m), 1.36-1.29 (1H, m), 1.27 (3H, t, *J* = 7.2 Hz), 1.05 (9H, s), 0.88 (3H, t, *J* = 7.6 Hz) ppm;

^{13}C NMR(100 MHz, CDCl$_3$): δ 205.0, 173.8, 138.4, 135.6, 133.3, 133.1, 129.8, 127.7, 120.9, 67.6, 60.7, 46.6, 46.3, 42.0, 41.8, 26.8, 24.3, 22.9, 19.2, 14.2, 13.3 ppm;

HRMS (ESI) m/z calculated for $C_{30}H_{40}O_4SiNa$ [M+Na]$^+$: 515.2593, found 515.2610.



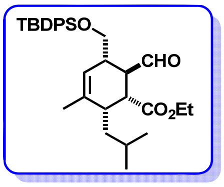
3ia

ethyl-5-(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-2-isopropyl-3-methylcyclohex-3-enecarboxylate;

3ia was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 95 mg (EA/PE = 5:95), yield: 94%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.12 (1H, d, *J* = 2.0 Hz), 7.68-7.63 (4H, m),7.46-7.36 (6H, m), 5.26-5.19 (1H, m), 4.21-4.09 (2H, m), 3.64 (1H, dd, *J* = 10.0, 5.2 Hz), 3.47 (1H, dd, *J* = 10.0, 8.8 Hz), 3.03 (1H, dd, J = 12.4, 4.8 Hz), 2.97-2.92 (1H, m), 2.64-2.54 (1H, m), 2.44-2.39 (1H, m), 1.72 (3H, s), 1.66-1.60 (1H, m), 1.27 (3H, t, *J* = 7.2 Hz), 1.05 (9H, s), 1.00 (3H, d, *J* = 6.8 Hz), 0.80 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, CDCl$_3$): δ 205.1, 174.0, 136.7, 135.7, 135.6, 133.3, 133.0, 129.8, 127.7, 121.6, 67.6, 60.8, 48.1, 46.2, 46.2, 42.3, 29.1, 26.8, 25.0, 24.9, 20.8, 19.1, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{31}H_{42}O_4SiNa$ [M+Na]$^+$: 529.2750, found 529.2758.



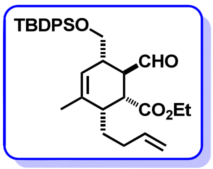
3ja

ethyl-5-(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-2-isobutyl-3-methylcyclohex-3-enecarboxylate;

3ja was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 102 mg (EA/PE = 5:95), yield, 98%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.09 (1H, d, *J* = 2.0 Hz), 7.68-7.62 (4H, m),7.46-7.36 (6H, m), 5.09-5.03 (1H, m), 4.19-4.03 (2H, m), 3.65 (1H, dd, *J* = 10.2, 5.0 Hz), 3.47 (1H, dd, *J* = 10.0, 8.0 Hz), 3.06-2.94 (2H, m), 2.58-2.50 (1H, m), 2.43-2.39 (1H, m), 1.73 (3H, s), 1.51-1.41 (1H, m), 1.31-1.23 (1H, m), 1.27 (3H, t, *J* = 7.0 Hz), 1.12-1.07 (1H, m), 1.05 (9H, s), 0.86 (6H, t, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, CDCl$_3$): δ 205.0, 173.8, 139.7, 135.6, 135.6, 133.3, 133.1, 129.8, 127.7, 120.2, 67.5, 60.7, 46.6, 45.8, 41.7, 41.5, 38.4, 27.1, 26.8, 22.9, 22.8, 22.7, 19.2, 14.1 ppm;

HRMS (ESI) m/z calculated for $C_{32}H_{44}O_4SiNa$ [M+Na]$^+$: 543.2906, found 543.2920.



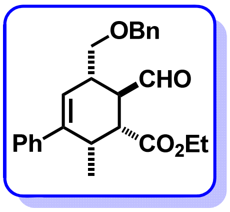
3ka

ethyl-2-(but-3-en-1-yl)-5-(((tert-butyldiphenylsilyl)oxy)methyl)-6-formyl-3-methylcyclohex-3-enecarboxylate;

3ka was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 82 mg (EA/PE = 5:95), yield: 79%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.08 (1H, d, *J* = 2.0 Hz), 7.68-7.62 (4H, m),7.46-7.36 (6H, m), 5.76-5.66 (1H, m), 5.14-5.10 (1H, m), 5.00-4.93 (2H, m), 4.21-4.09 (2H, m), 3.66 (1H, dd, *J* = 10.2, 5.0 Hz), 3.48 (1H, dd, *J* = 10.0, 7.6 Hz), 3.04-2.97 (2H, m), 2.57-2.50 (1H, m), 2.44-2.39 (1H, m), 2.08-1.93 (2H, m), 1.73 (3H, s), 1.55-1.46 (1H, m), 1.40-1.32 (1H, m), 1.27 (3H, t, *J* = 7.2 Hz), 1.05 (9H, s) ppm;

^{13}C NMR(100 MHz, CDCl$_3$): δ 204.9, 173.7, 138.5, 138.2, 135.6, 133.3, 133.1, 129.8, 127.8, 121.0, 114.9, 67.5, 60.8, 46.5, 46.2, 41.8, 39.8, 32.9, 30.9, 26.8, 22.8, 19.2, 14.2 ppm;

HRMS (ESI) m/z calculated for $C_{32}H_{42}O_4SiH$ [M+H]$^+$: 519.2931, found 519.2935.



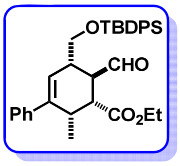
3ma

ethyl-5-((benzyloxy)methyl)-4-formyl-2-methyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-3-carboxylate;

3ma was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; white solid, isolated 18 mg (EA/PE = 5:95), yield, 23%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.11 (1H, d, *J* = 2.0 Hz), 7.38-7.20 (10H, m), 5.72 (1H, d, *J* = 2.8 Hz), 4.57 (1H, d, *J* = 12.0 Hz), 4.53 (1H, d, *J* = 12.0 Hz), 4.20 (2H, qd, *J* = 7.0, 0.8 Hz), 3.63 (1H, dd, *J* = 9.2, 5.2 Hz), 3.49-3.42 (1H, m), 3.30-3.26 (1H, m), 3.23 (1H, dd, *J* = 11.8, 5.0 Hz), 3.04-2.98 (1H, m), 2.92-2.84 (1H, m), 1.29 (3H, t, *J* = 7.0 Hz), 0.89 (3H, d, *J* = 6.8 Hz) ppm;

^{13}C NMR(100 MHz, $CDCl_3$): δ 204.7, 173.4, 143.4, 140.2, 138.0, 128.5, 127.7, 127.6, 127.5, 126.3, 123.1, 73.5, 73.2, 61.0, 47.2, 45.4, 40.3, 33.2, 16.2, 14.3 ppm;

HRMS (ESI) m/z calculated for $C_{25}H_{28}O_4H$ $[M+H]^+$: 393.2066, found 393.2083.



3na

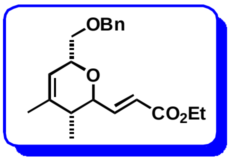
ethyl-5-(((tert-butyldiphenylsilyl)oxy)methyl)-4-formyl-2-methyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-3-carboxylate;

3na was synthesized via general procedure by using Lewis acid $BF_3{\cdot}Et_2O$; sticky colorless oil, isolated 60 mg (EA/PE = 5:95), yield, 56%. ^1H NMR (400 MHz, $CDCl_3$): δ 10.15 (1H, d, *J* = 2.0 Hz), 7.73-7.68 (4H, m), 7.47-7.39 (6H, m), 7.34-7.27 (5H, m), 5.69 (1H, d, *J* = 2.8 Hz), 4.22 (2H, q, *J* = 7.1 Hz), 3.79 (1H, dd, *J* = 10.0, 4.8 Hz), 3.67 (1H, dd, *J* = 10.0, 7.2 Hz), 3.35-3.27 (1H, m), 3.26-3.22 (1H, m), 3.18-3.11 (1H, m), 2.81-2.73 (1H, m), 1.31 (3H, t, *J* = 7.2 Hz), 1.08 (9H, s), 0.91 (3H, d, *J* = 6.8 Hz) ppm;

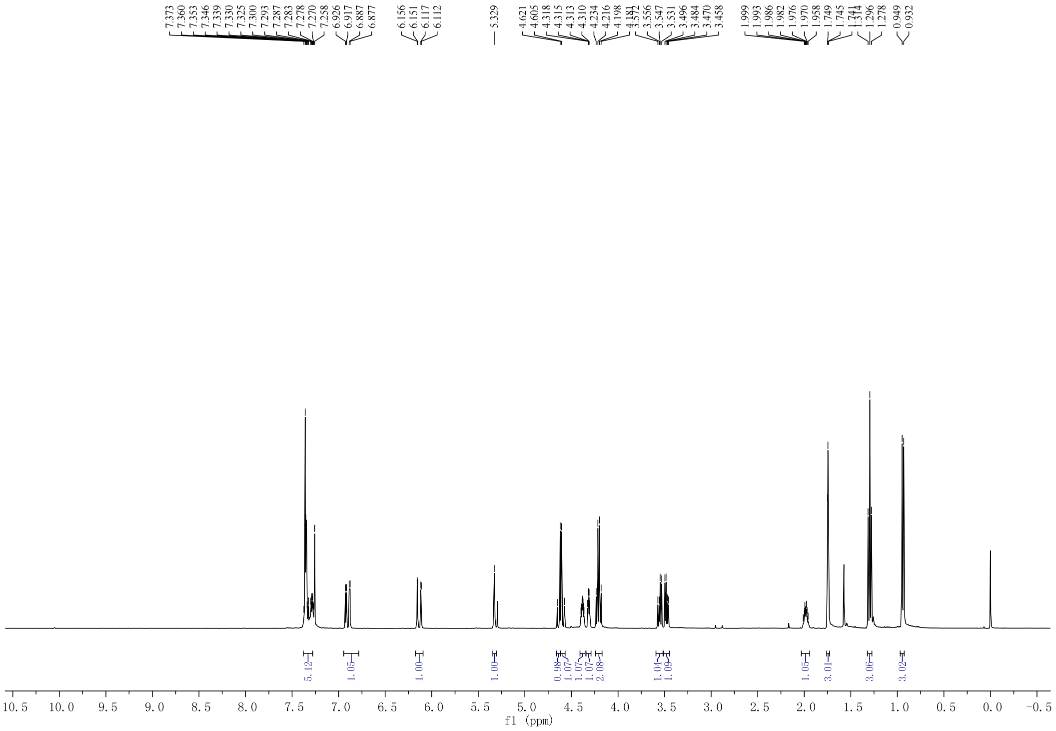
^{13}C NMR(100 MHz, $CDCl_3$): δ 204.8, 173.4, 143.3, 140.3, 135.6, 135.6, 133.2, 133.0, 129.9, 128.5, 127.8, 127.5, 126.3, 123.7, 66.9, 61.0, 47.1, 44.7, 42.4, 33.1, 26.8, 19.2, 16.1, 14.3 ppm;

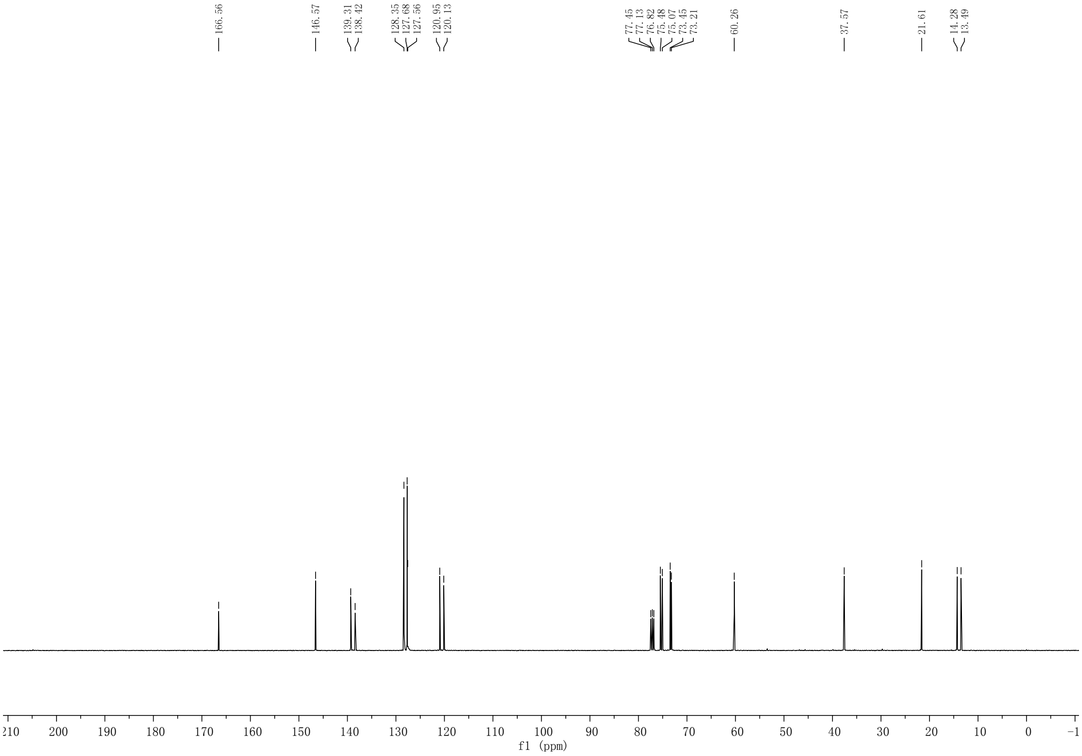
HRMS (ESI) m/z calculated for $C_{34}H_{40}O_4SiNa$ $[M+Na]^+$: 563.2593, found 563.2599.

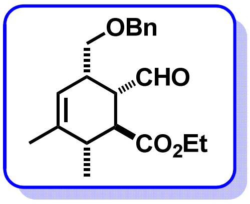
6. NMR spectra for the products



3aa”



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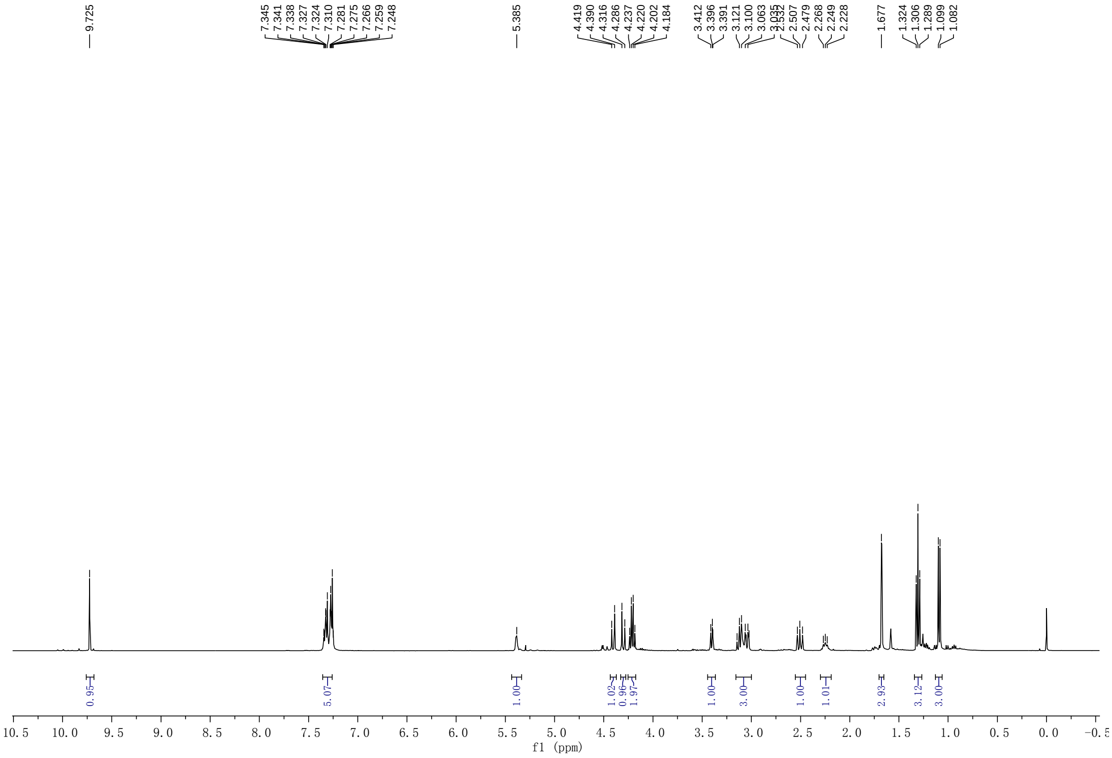
3aa’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0.96
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1.01
2.93
3.12
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6.5
6.0
5.5
5.0
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2.5
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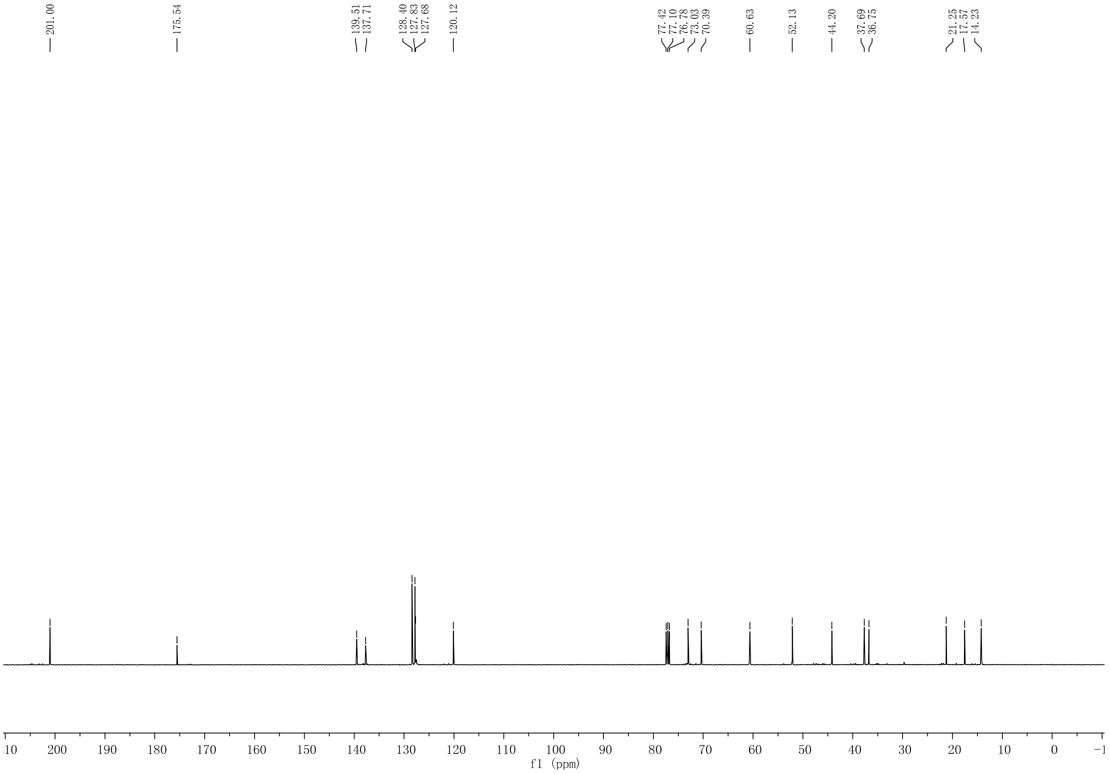
f1 (ppm)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200
190
180
170
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100
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70
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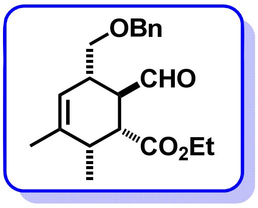
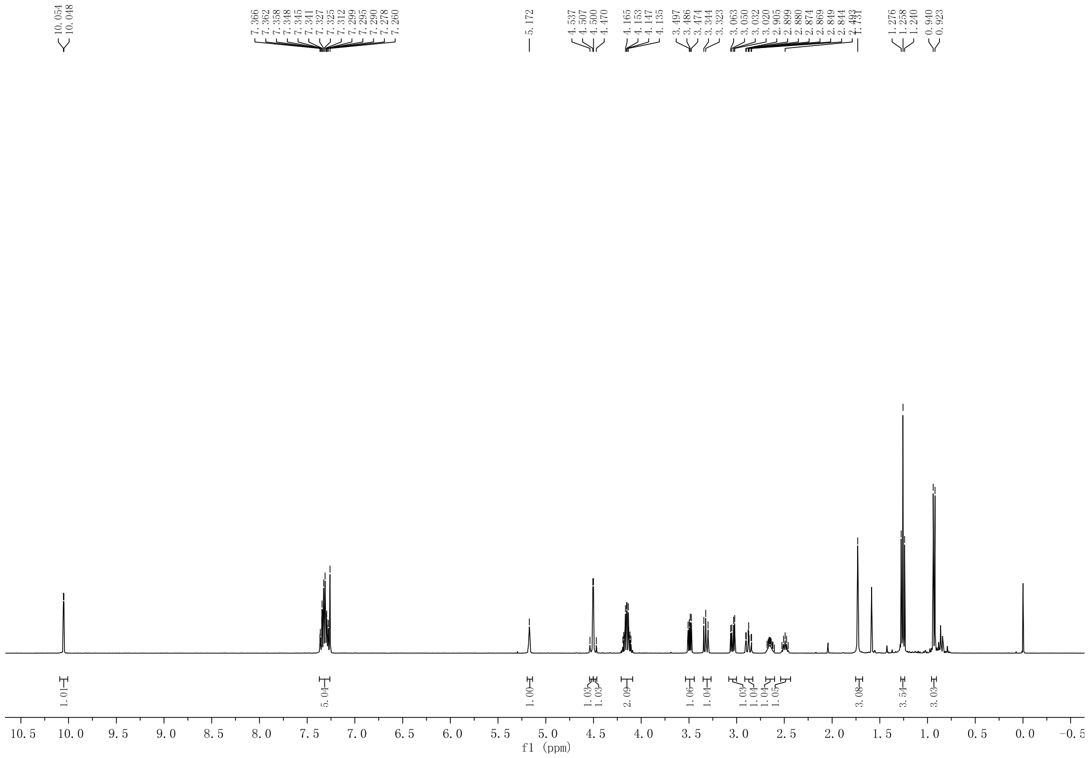
40
30
20
10
0
-1
f1 (ppm)


OBn
CHO
CO2Et

3aa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7.295
7.290
7.278
7.260
5.172
4.537
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4.500
4.470
4.165
4.153
4.147
4.135
3.497
3.486
3.474
3.344
3.323
3.063
3.050
3.032
3.020
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2.899
2.880
2.874
2.869
2.849
2.844
2.493
1.731
1.276
1.258
1.240
0.940
0.923
1.01
5.04
1.00
1.03
1.03
2.09
1.06
1.04
1.03
1.04
1.04
1.05
3.08
3.54
3.03
10.5
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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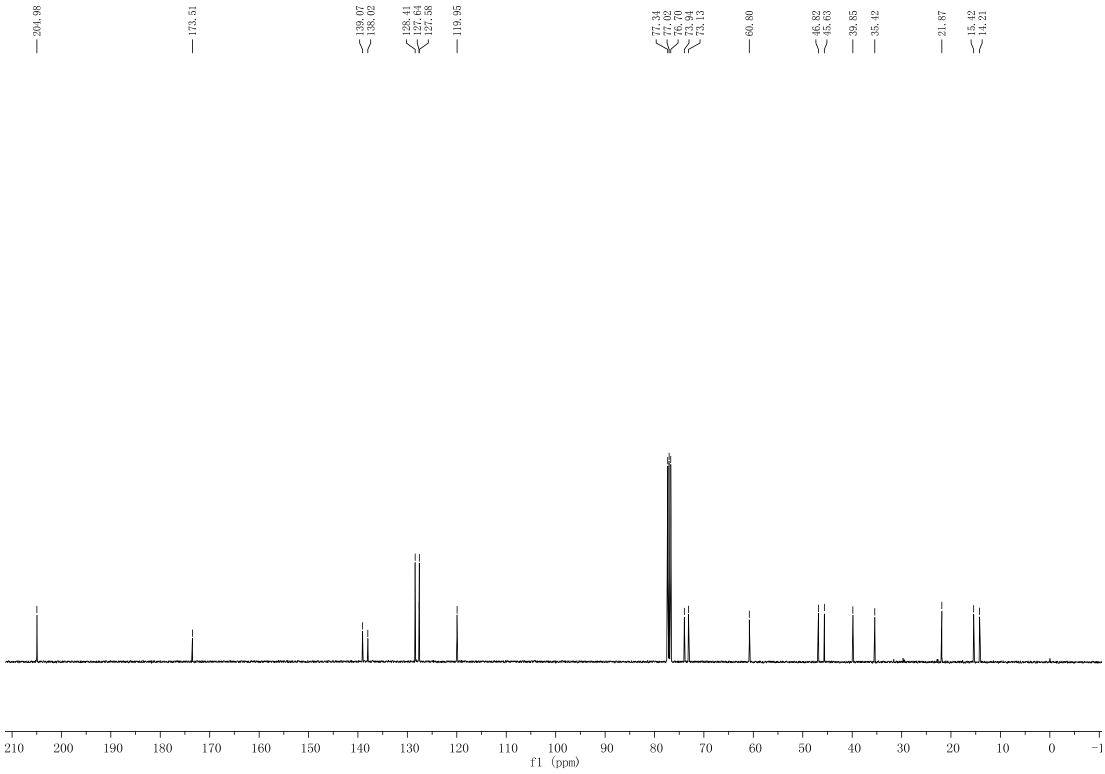
f1 (ppm)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127.58
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77.02
76.70
73.94
73.13
60.80
46.82
45.63
39.85
35.42
21.87
15.42
14.21
210
200
190
180
170
160
150
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100
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80
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30
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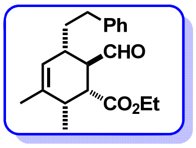
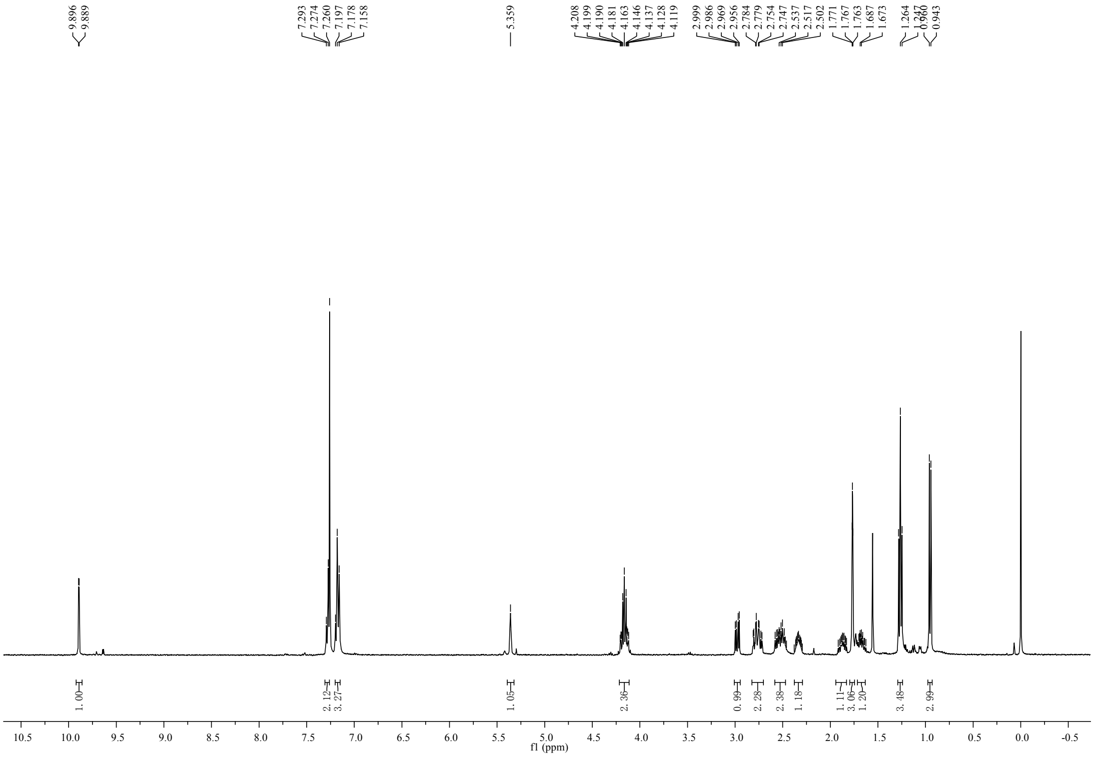
-1
f1 (ppm)


Ph
CHO
CO2Et

3ba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4.190
4.181
4.163
4.146
4.137
4.128
4.119
2.999
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2.969
2.956
2.784
2.779
2.754
2.747
2.537
2.517
2.502
1.771
1.767
1.763
1.687
1.673
1.264
1.247
0.960
0.943
1.00
2.12
3.27
1.05
2.36
0.99
2.28
2.38
1.18
1.11
3.06
1.20
3.48
2.99
10.5
10.0
9.5
9.0
8.5
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6.5
6.0
5.5
5.0
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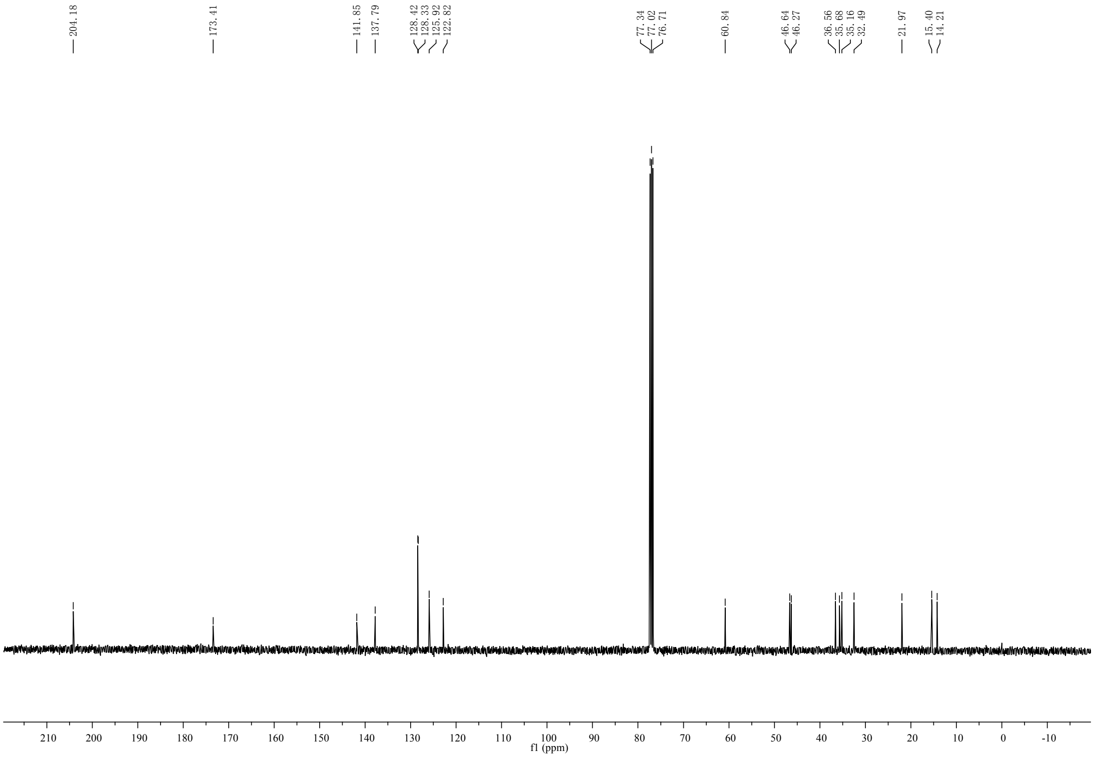
f1 (ppm)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77.02
76.71
60.84
46.64
46.27
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35.68
35.16
32.49
21.97
15.40
14.21
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200
190
180
170
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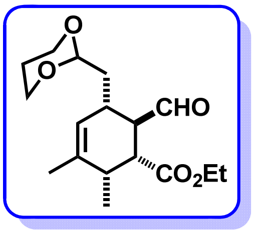
f1 (ppm)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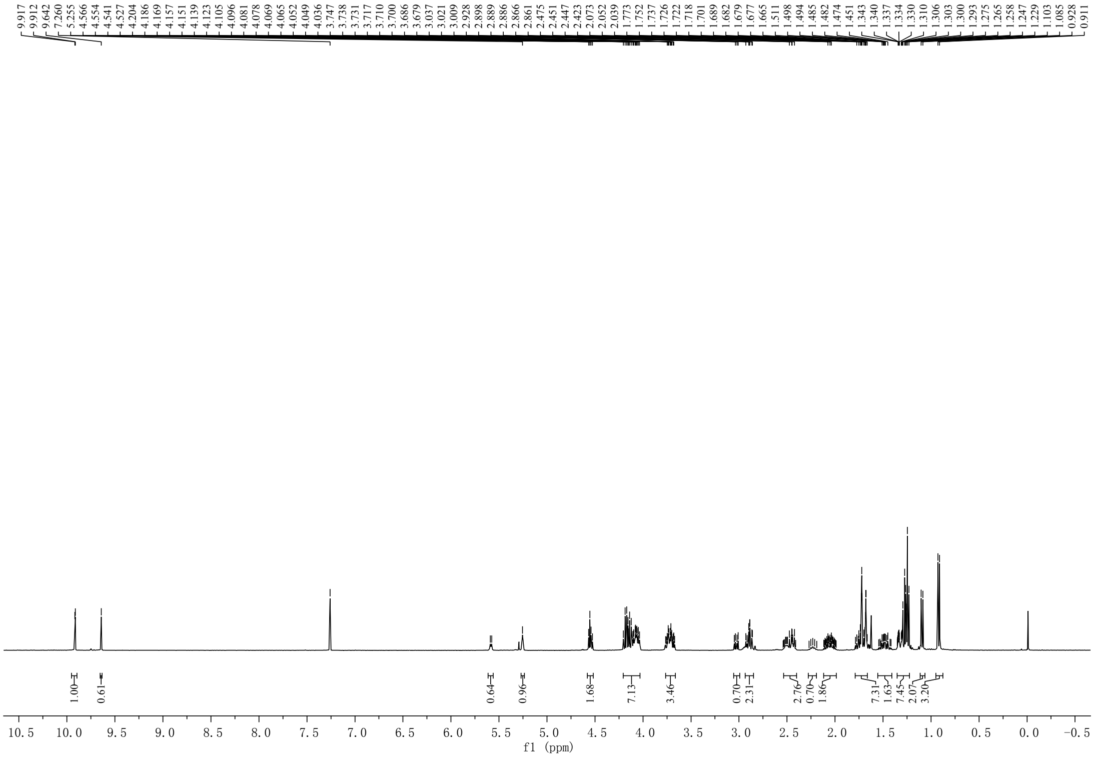
CHO
CO2Et

3ca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4.527
4.204
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4.169
4.157
4.151
4.139
4.123
4.105
4.096
4.081
4.078
4.069
4.065
4.052
4.049
4.036
3.747
3.738
3.731
3.717
3.710
3.700
3.686
3.679
3.037
3.021
3.009
2.928
2.898
2.889
2.886
2.866
2.861
2.475
2.451
2.447
2.423
2.073
2.052
2.039
1.773
1.752
1.737
1.726
1.722
1.718
1.701
1.689
1.682
1.679
1.677
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1.485
1.482
1.474
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1.340
1.337
1.334
1.330
1.310
1.306
1.303
1.300
1.293
1.275
1.265
1.258
1.247
1.229
1.103
1.085
0.928
0.911
1.00
0.61
0.64
0.96
1.68
7.13
3.46
0.70
2.31
2.76
0.70
1.86
7.31
1.63
7.45
2.07
3.20
10.5
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9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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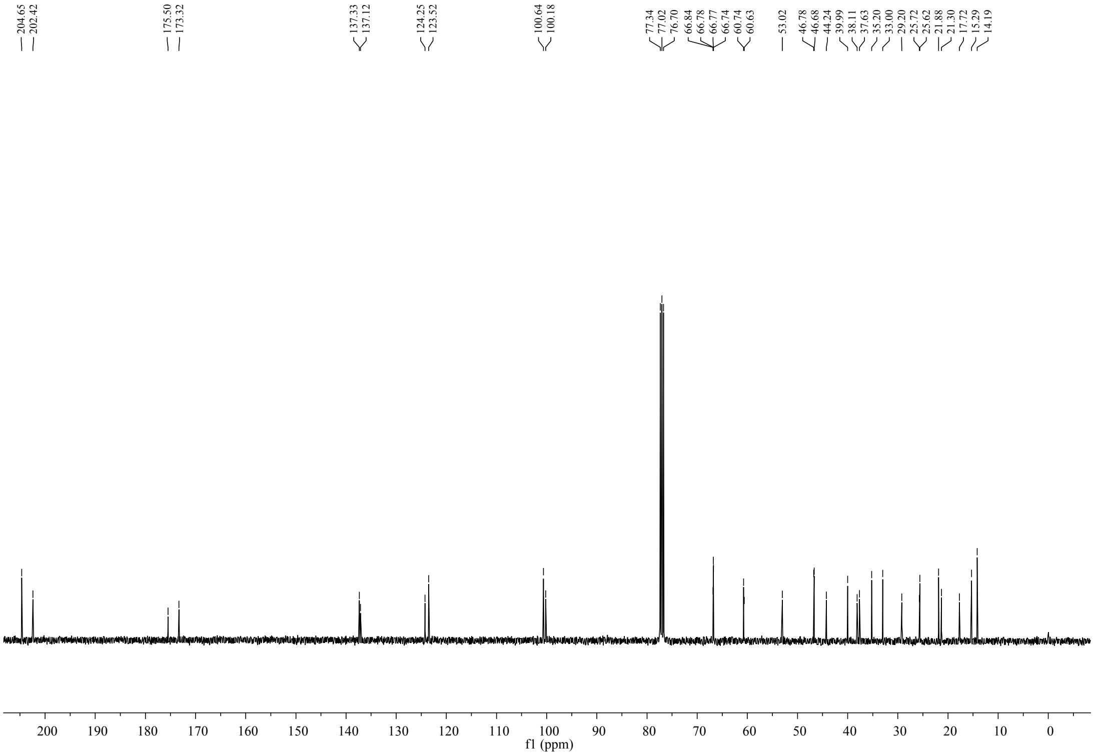
0.5
0.0
-0.5
f1 (ppm)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137.12
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123.52
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100.18
77.34
77.02
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66.78
66.77
66.74
60.74
60.63
53.02
46.78
46.68
44.24
39.99
38.11
37.63
35.20
33.00
29.20
25.72
25.62
21.88
21.30
17.72
15.29
14.19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10
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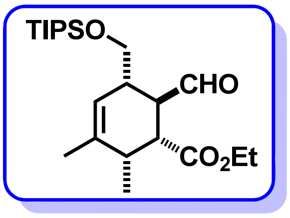
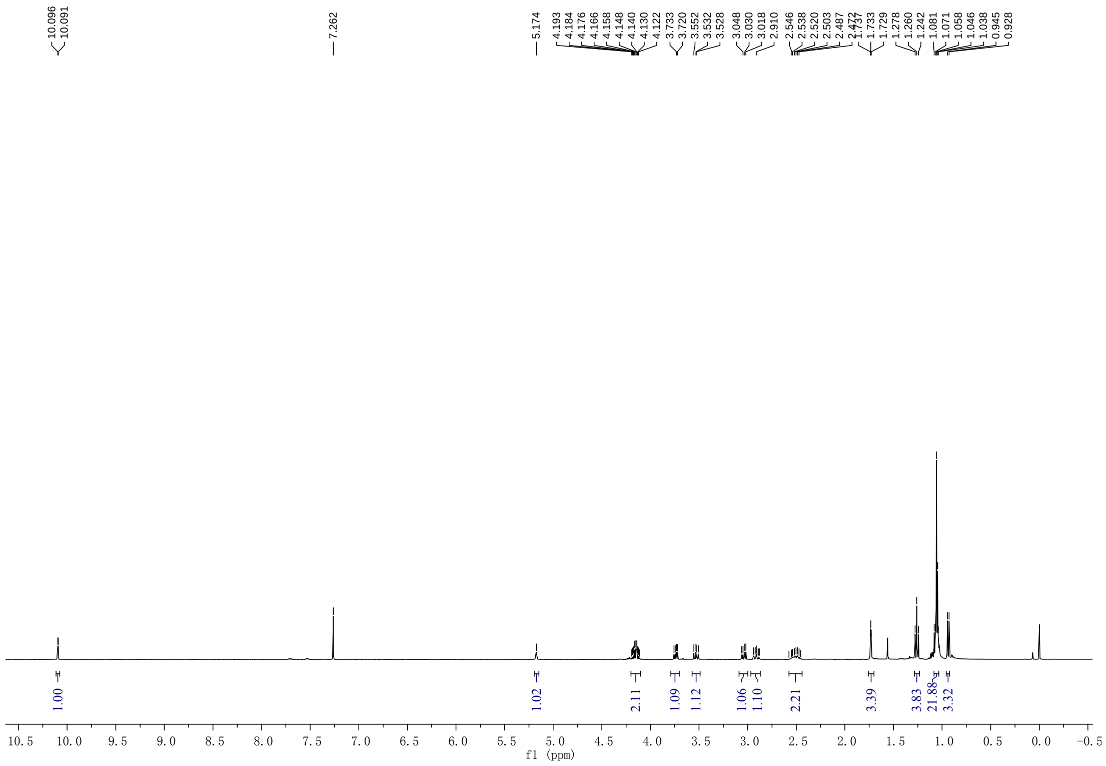
f1 (ppm)


TIPSO
CHO
CO2Et

3da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4.148
4.140
4.130
4.122
3.733
3.720
3.552
3.532
3.528
3.048
3.030
3.018
2.910
2.546
2.538
2.520
2.503
2.487
2.472
1.737
1.733
1.729
1.278
1.260
1.242
1.081
1.071
1.058
1.046
1.038
0.945
0.928
1.00
1.02
2.11
1.09
1.12
1.06
1.10
2.21
3.39
3.83
21.88
3.32
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
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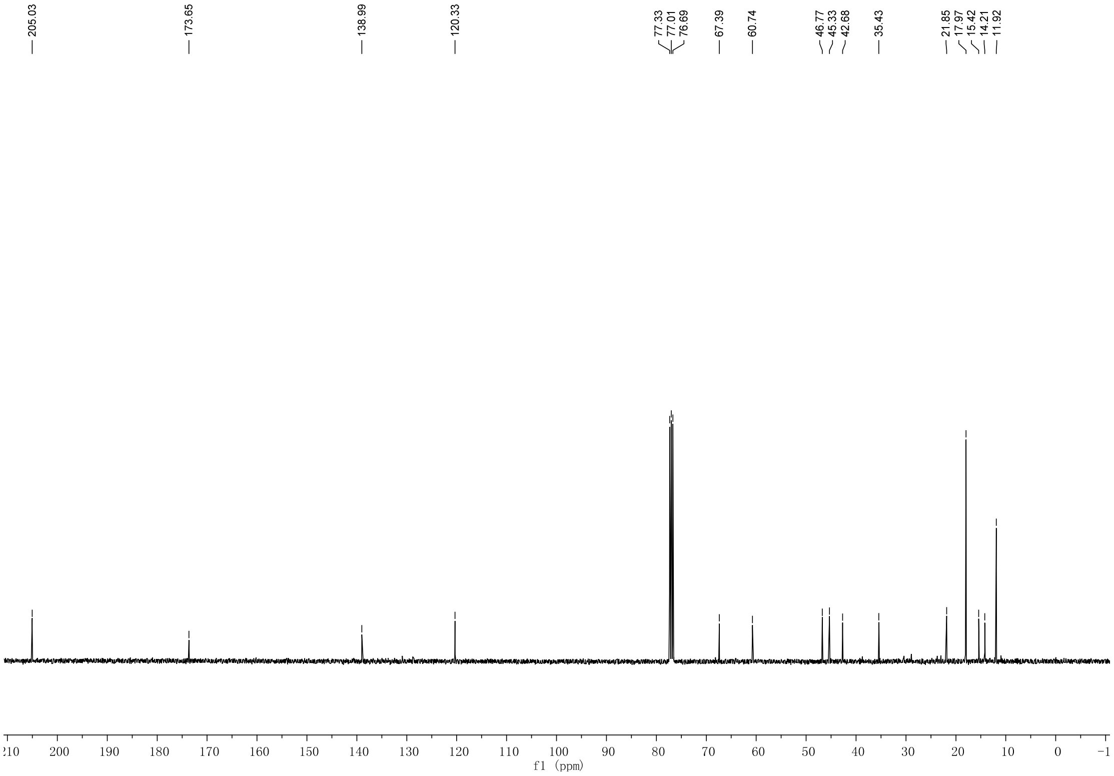
f1 (ppm)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77.33
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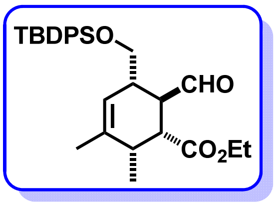
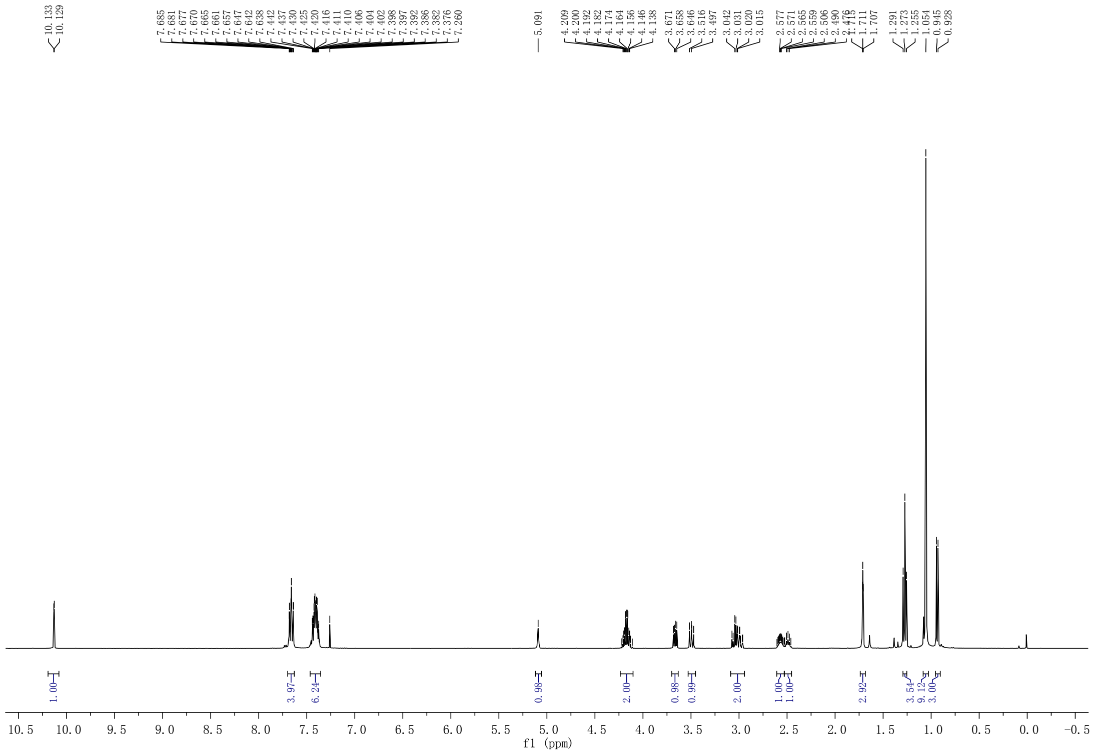
60.74
46.77
45.33
42.68
35.43
21.85
17.97
15.42
14.21
11.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


TBDPSO
CHO
CO2Et

3ea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7.661
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7.437
7.430
7.425
7.420
7.416
7.411
7.410
7.406
7.404
7.402
7.398
7.397
7.392
7.386
7.382
7.376
7.260
5.091
4.209
4.200
4.192
4.182
4.174
4.164
4.156
4.146
4.138
3.671
3.658
3.646
3.516
3.497
3.042
3.031
3.020
3.015
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2.571
2.565
2.559
2.506
2.490
2.476
1.715
1.711
1.707
1.291
1.273
1.255
1.054
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0.928
1.00
3.97
6.24
0.98
2.00
0.98
0.99
2.00
1.00
1.00
2.92
3.51
9.12
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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0.5
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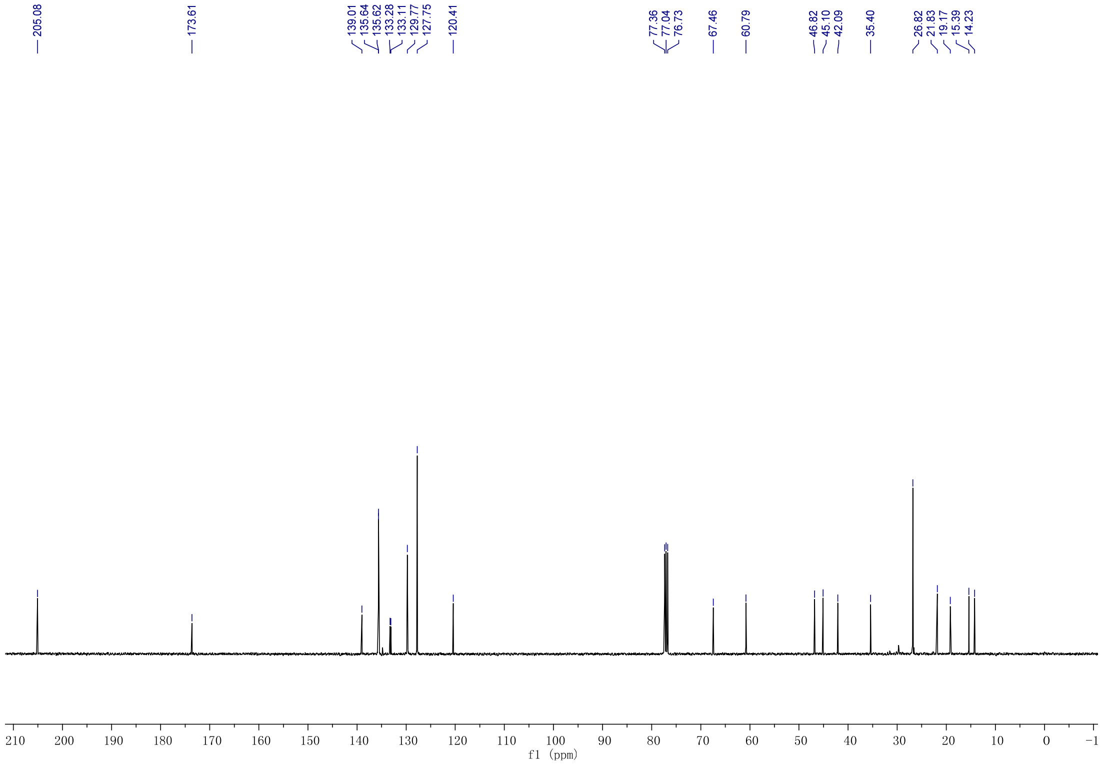
-0.5
f1 (ppm)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120.41
77.36
77.04
76.73
67.46
60.79
46.82
45.10
42.09
35.40
26.82
21.83
19.17
15.39
14.23
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
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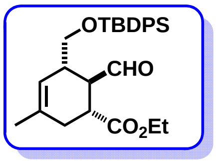
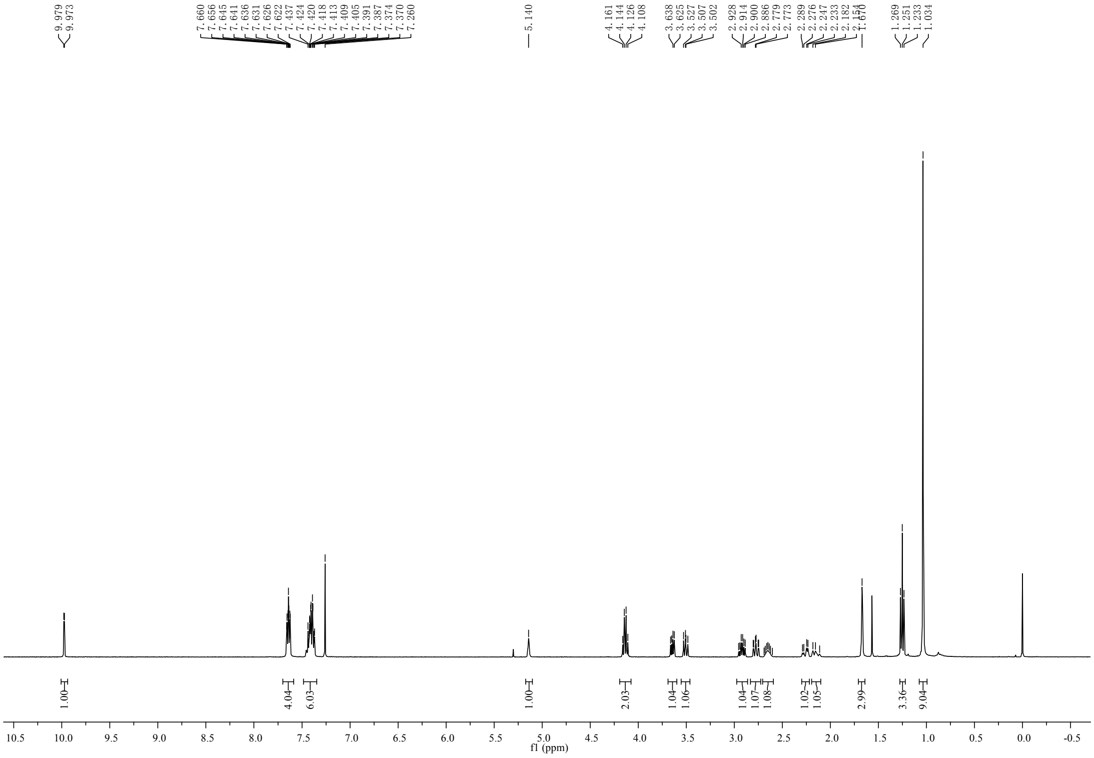
50
40
30
20
10
0
-1
f1 (ppm)


OTBDPS
CHO
CO2Et

3fa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7.418
7.413
7.409
7.405
7.391
7.387
7.374
7.370
7.260
5.140
4.161
4.144
4.126
4.108
3.638
3.625
3.527
3.507
3.502
2.928
2.914
2.900
2.886
2.779
2.773
2.289
2.276
2.247
2.233
2.182
2.151
1.670
1.269
1.251
1.233
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1.00
4.04
6.03
1.00
2.03
1.04
1.06
1.04
1.07
1.08
1.02
1.05
2.99
3.36
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8.5
8.0
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6.0
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5.0
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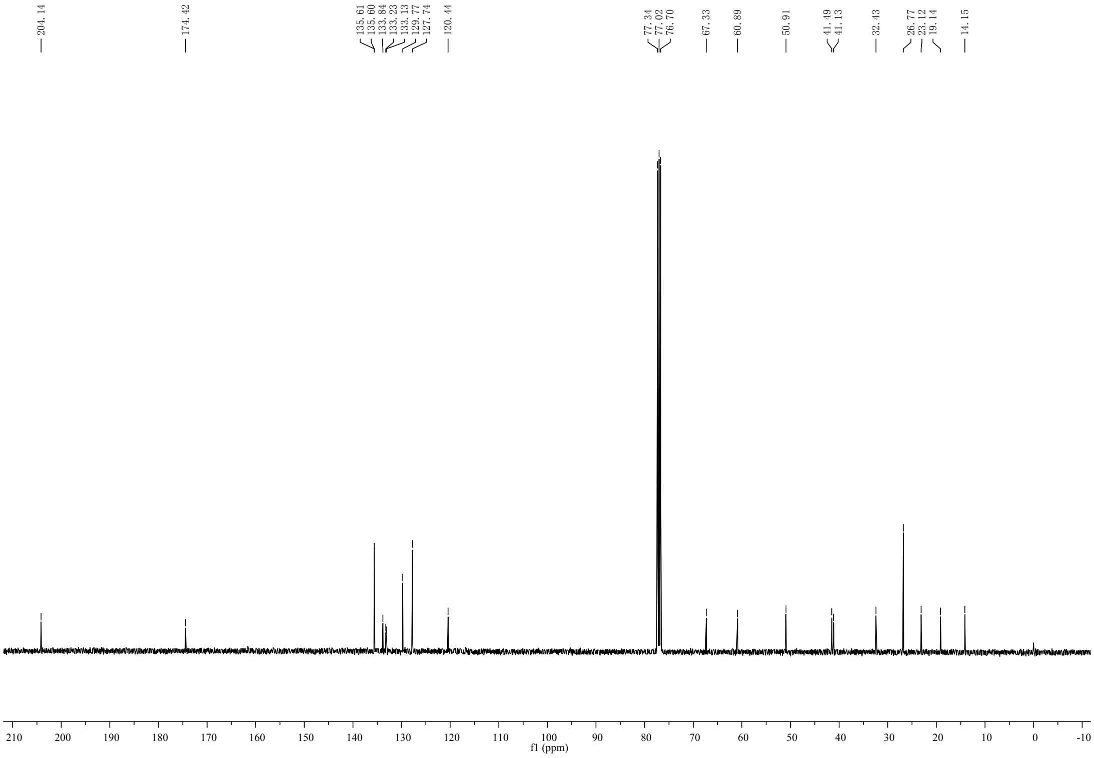
f1 (ppm)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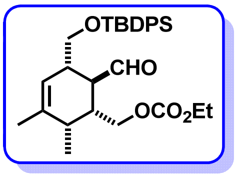
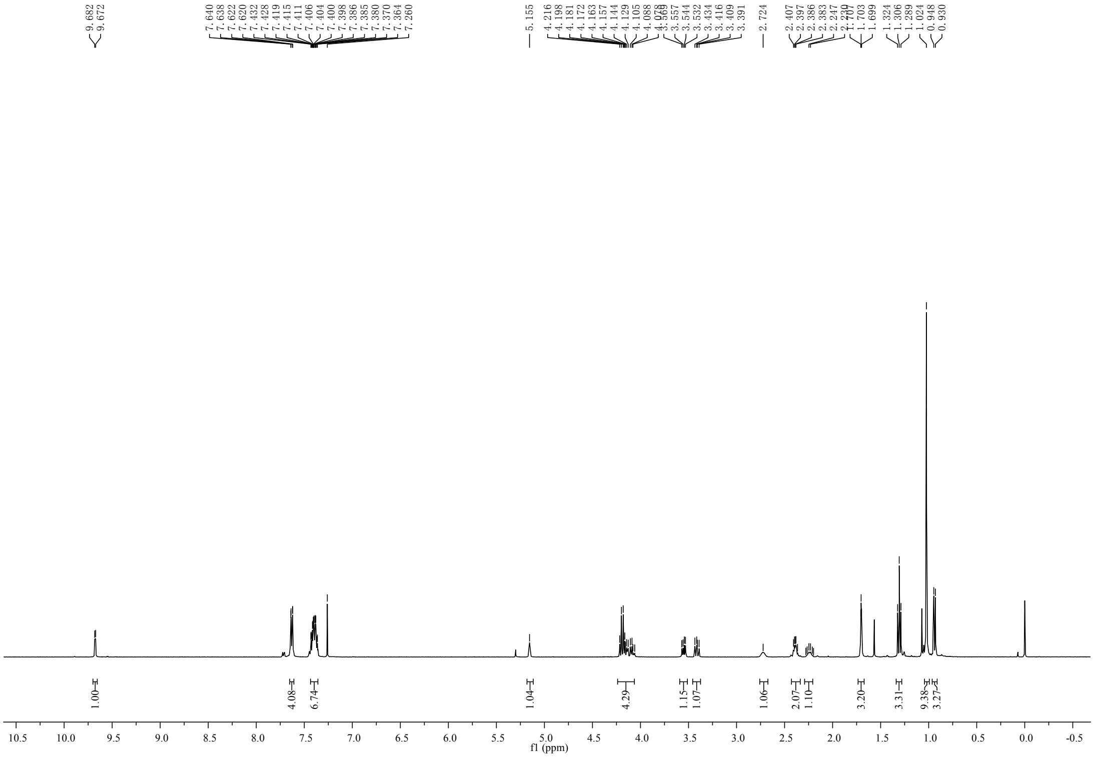
77.02
76.70
67.33
60.89
50.91
41.49
41.13
32.43
26.77
23.12
19.14
14.15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBDPS
CHO
OCO2Et

3ed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7.415
7.411
7.406
7.404
7.400
7.398
7.386
7.385
7.380
7.370
7.364
7.260
5.155
4.216
4.198
4.181
4.172
4.163
4.157
4.144
4.129
4.105
4.088
4.078
3.569
3.557
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3.532
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3.416
3.409
3.391
2.724
2.407
2.397
2.386
2.383
2.247
2.230
1.707
1.703
1.699
1.324
1.306
1.289
1.024
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0.930
1.00
4.08
6.74
1.04
4.29
1.15
1.07
1.06
2.07
1.10
3.20
3.31
9.38
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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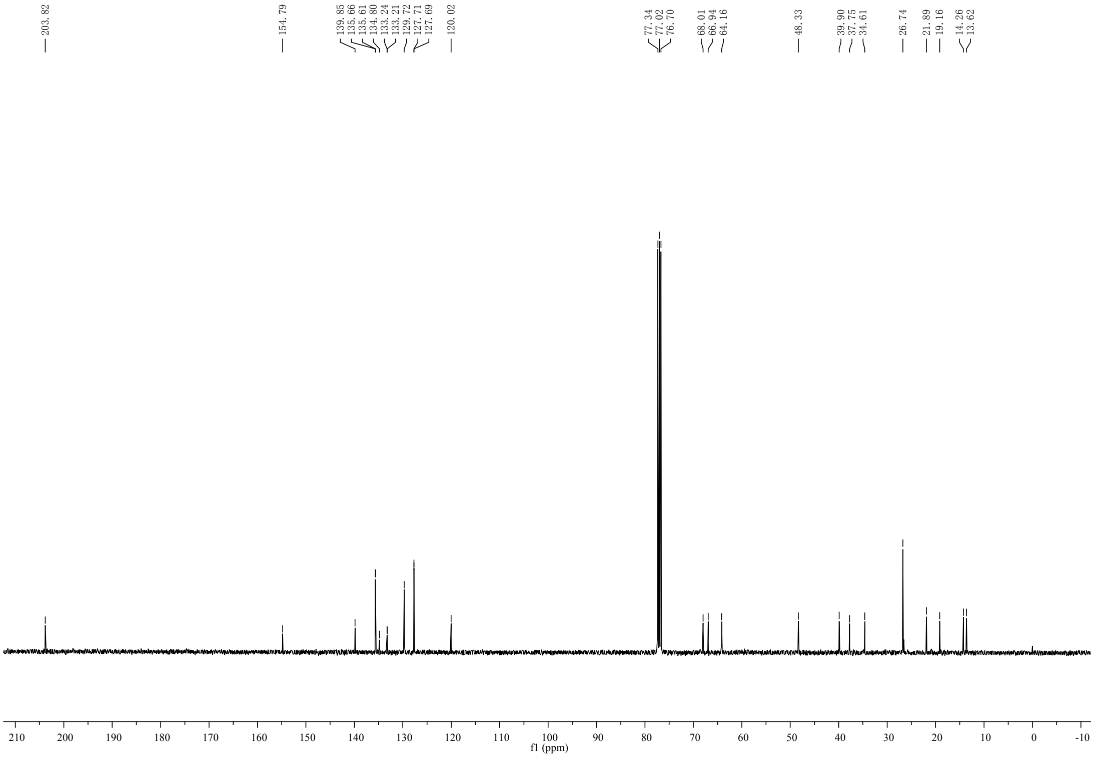
f1 (ppm)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133.21
129.72
127.71
127.69
120.02
77.34
77.02
76.70
68.01
66.94
64.16
48.33
39.90
37.75
34.61
26.74
21.89
19.16
14.26
13.62
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200
190
180
170
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100
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80
70
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50
40
30
20
10
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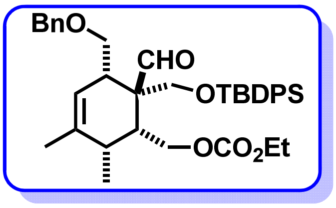
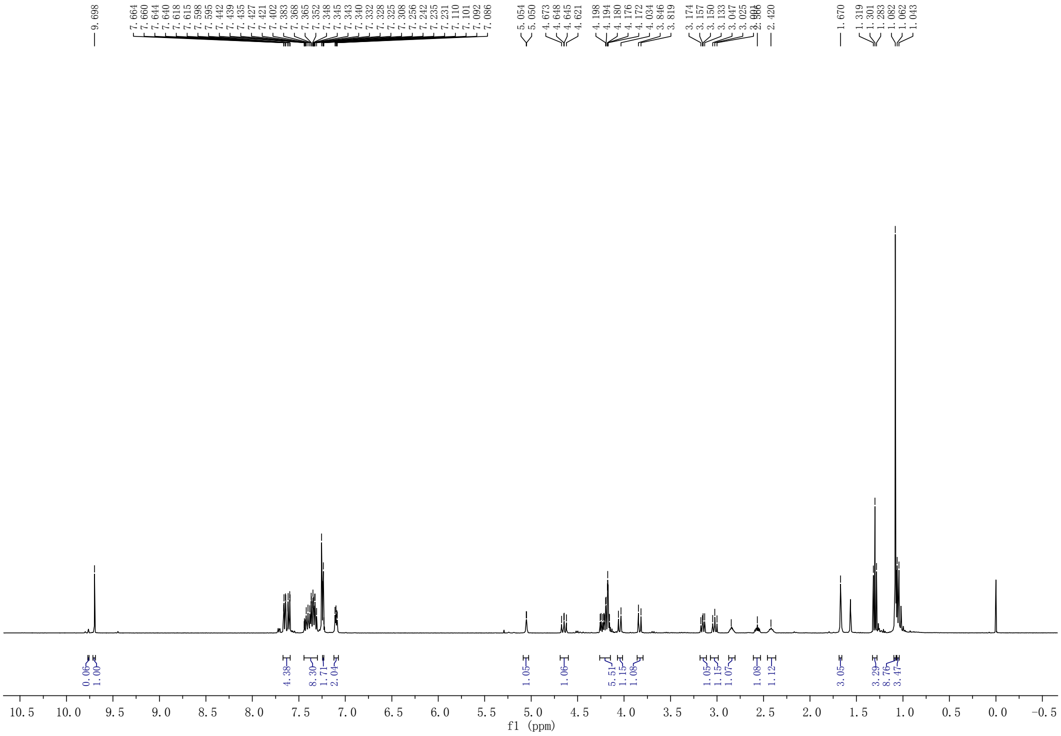
-10
f1 (ppm)


BnO
CHO
OTBDPS
OCO2Et

3ag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7.421
7.402
7.383
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7.352
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7.345
7.343
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7.332
7.328
7.325
7.308
7.256
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7.235
7.231
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7.101
7.092
7.086
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5.050
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4.194
4.180
4.176
4.172
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3.819
3.174
3.157
3.150
3.133
3.047
3.025
2.991
2.420
1.670
1.319
1.301
1.283
1.082
1.062
1.043
0.06
1.00
4.38
8.30
1.71
2.04
1.05
1.06
5.51
1.15
1.08
1.05
1.15
1.07
1.08
1.12
3.05
3.29
8.76
3.47
10.5
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
1.5
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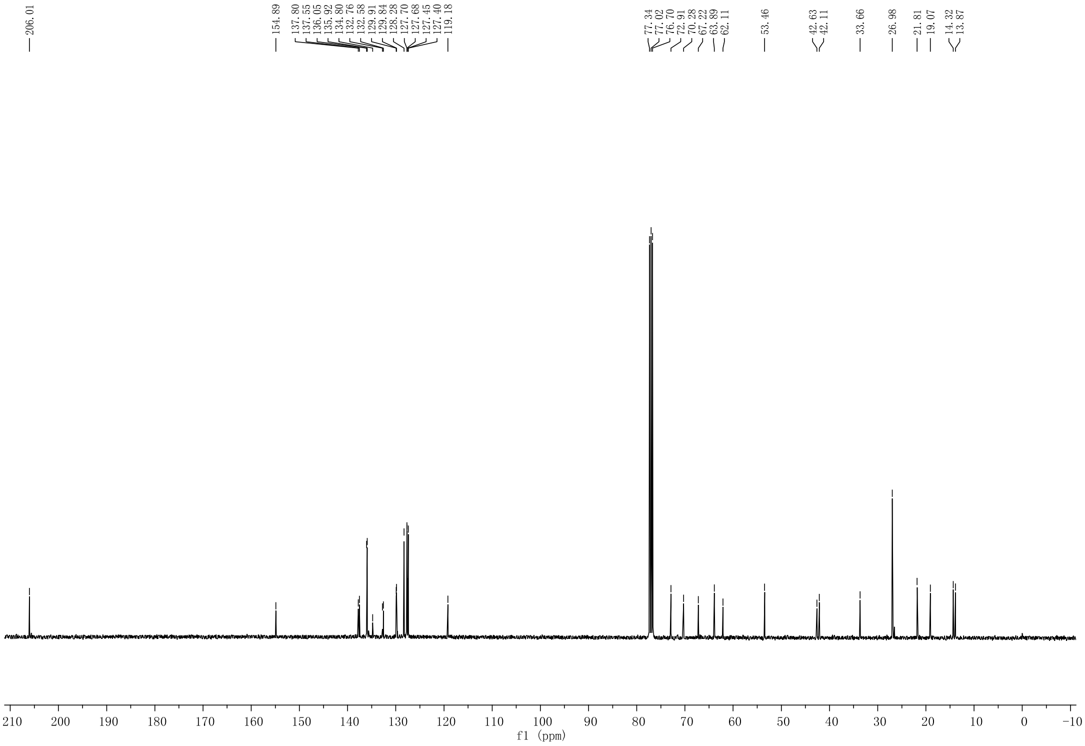
0.5
0.0
-0.5
f1 (ppm)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132.76
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129.91
129.84
128.28
127.70
127.68
127.45
127.40
119.18
77.34
77.02
76.70
72.91
70.28
67.22
63.89
62.11
53.46
42.63
42.11
33.66
26.98
21.81
19.07
14.32
13.87
210
200
190
180
170
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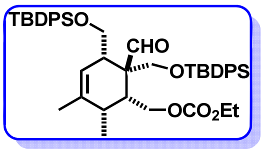
30
20
10
0
-10
f1 (ppm)


TBDPSO
CHO
OTBDPS
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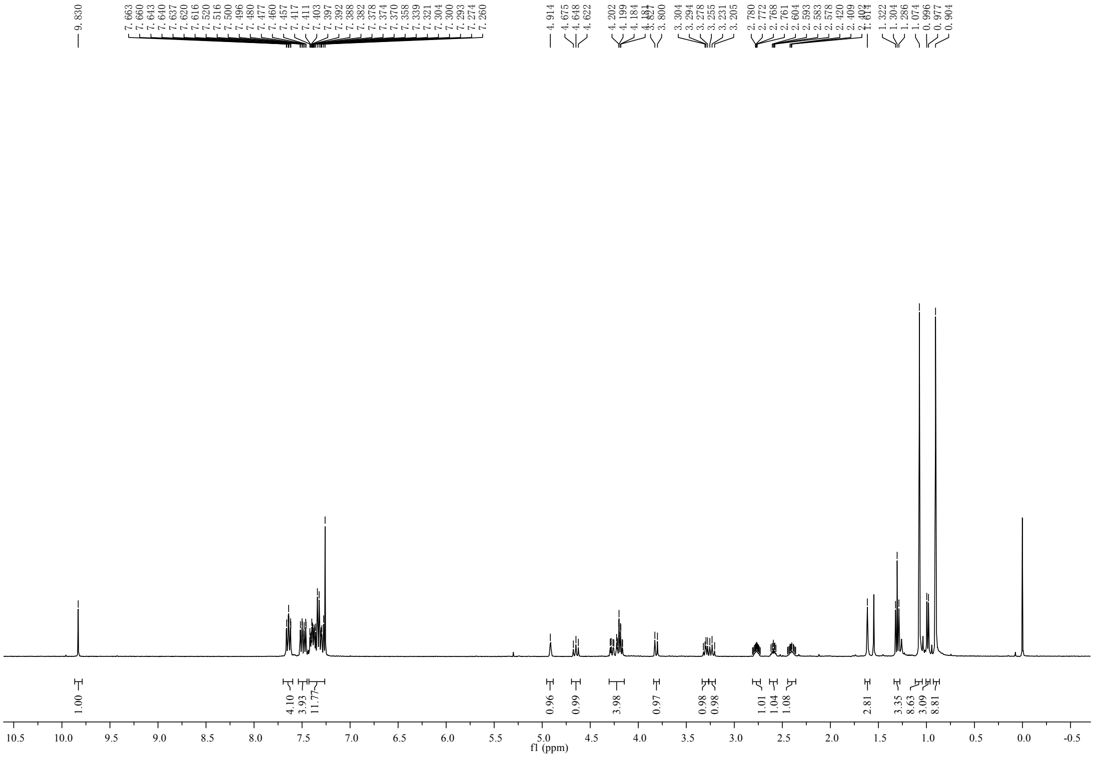
3eg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4.202
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1.04
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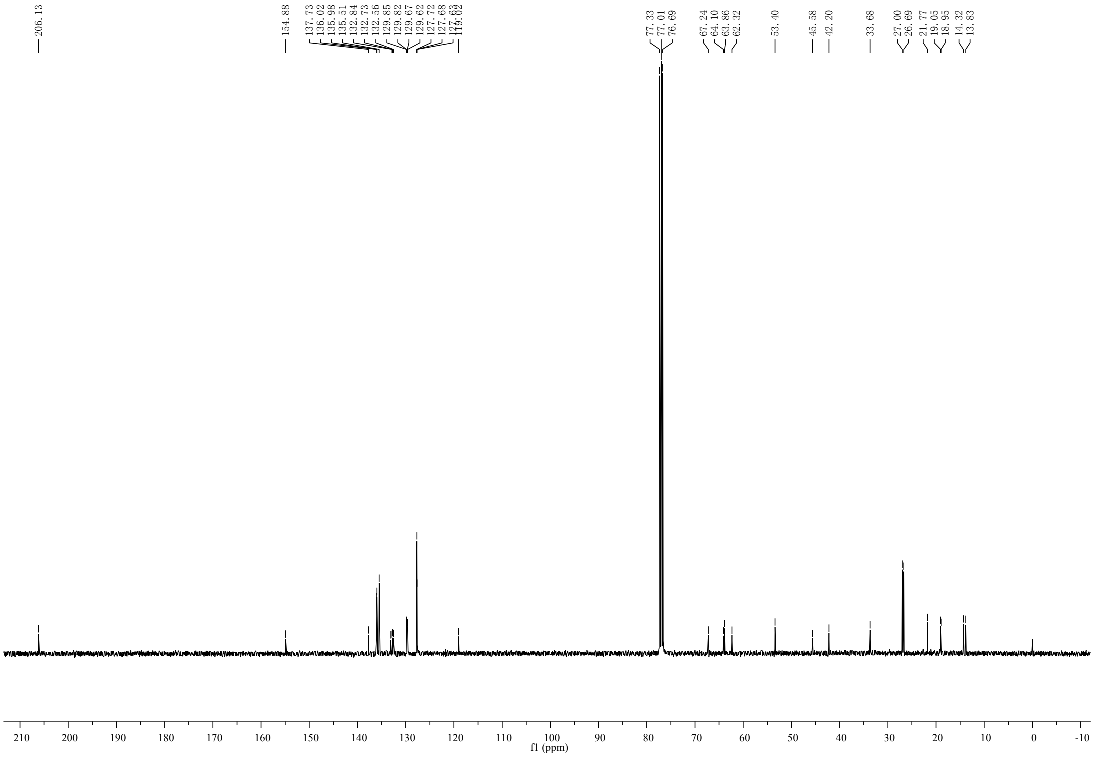
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77.01
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62.32
53.40
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42.20
33.68
27.00
26.69
21.77
19.05
18.95
14.32
13.83
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200
190
180
170
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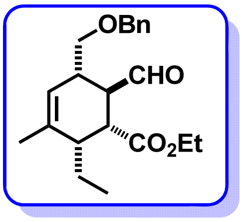
f1 (ppm)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CHO
CO2Et

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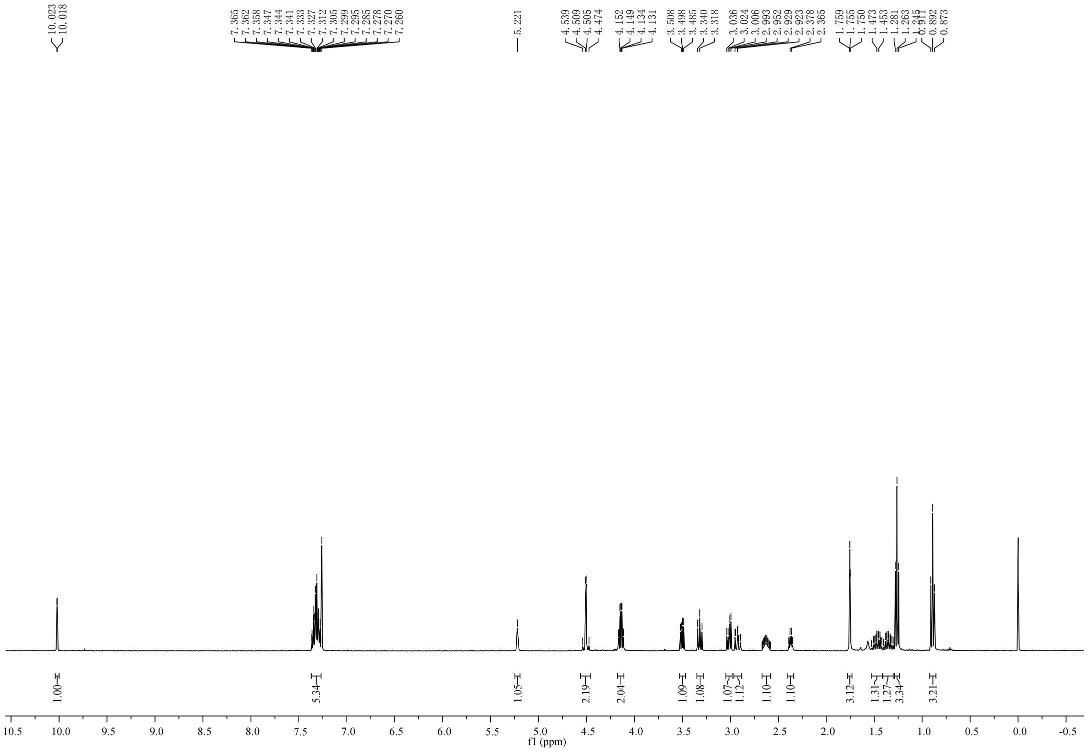
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7.260
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2.04
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3.12
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3.34
3.21
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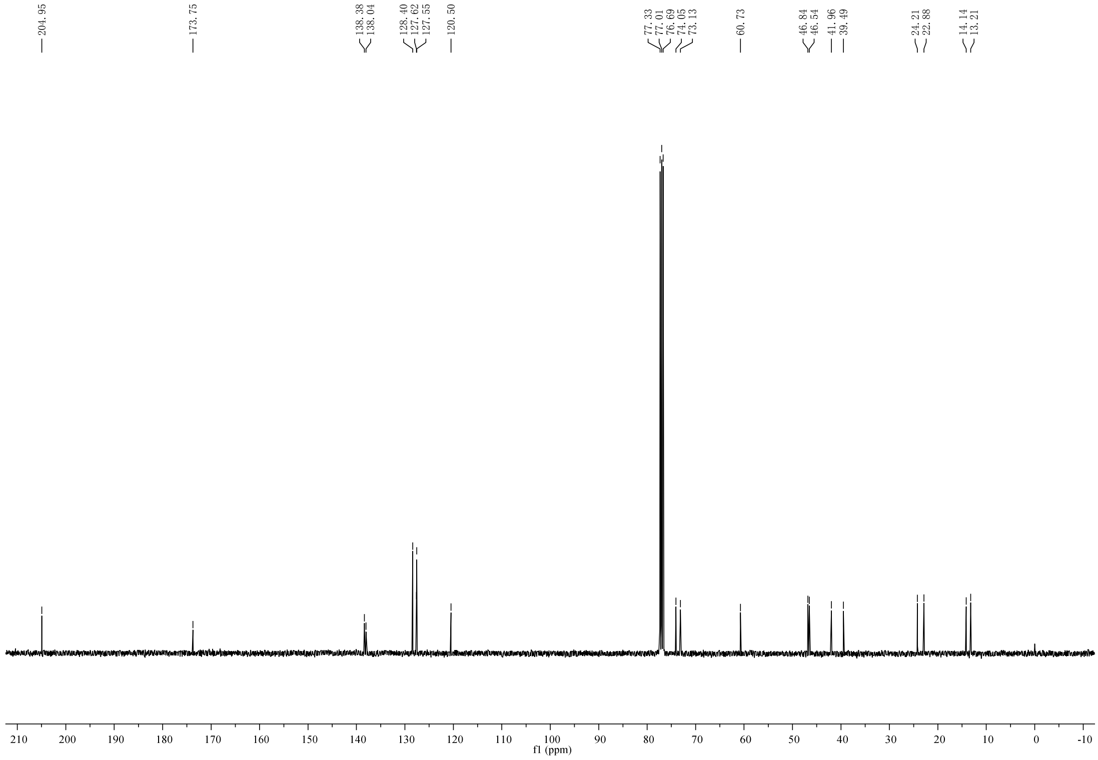
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46.84
46.51
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13.21
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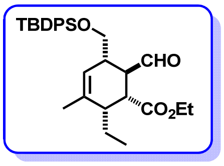
f1 (ppm)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CHO
CO2Et

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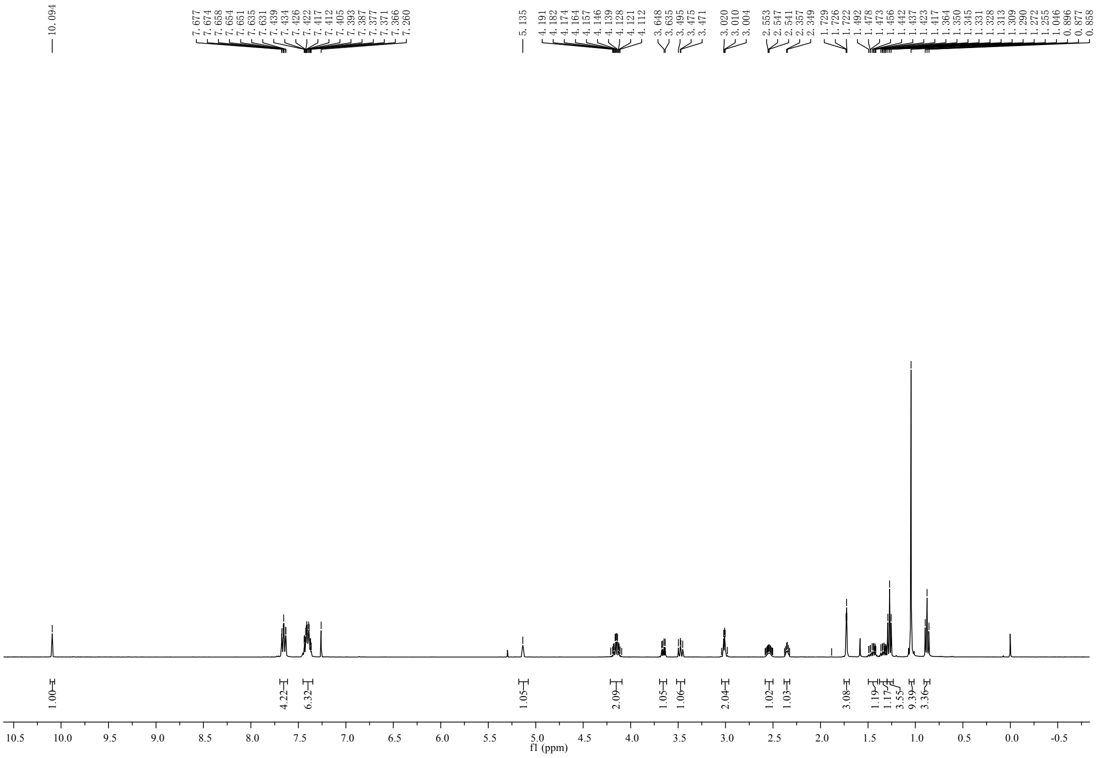
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7.412
7.405
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7.377
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7.366
7.260
5.135
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4.182
4.174
4.164
4.157
4.146
4.139
4.128
4.121
4.112
3.648
3.635
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3.475
3.471
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3.010
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2.541
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2.349
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1.726
1.722
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1.437
1.423
1.417
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1.309
1.290
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0.858
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2.09
1.05
1.06
2.04
1.02
1.03
3.08
1.19
1.17
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3.36
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10.0
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6.0
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5.0
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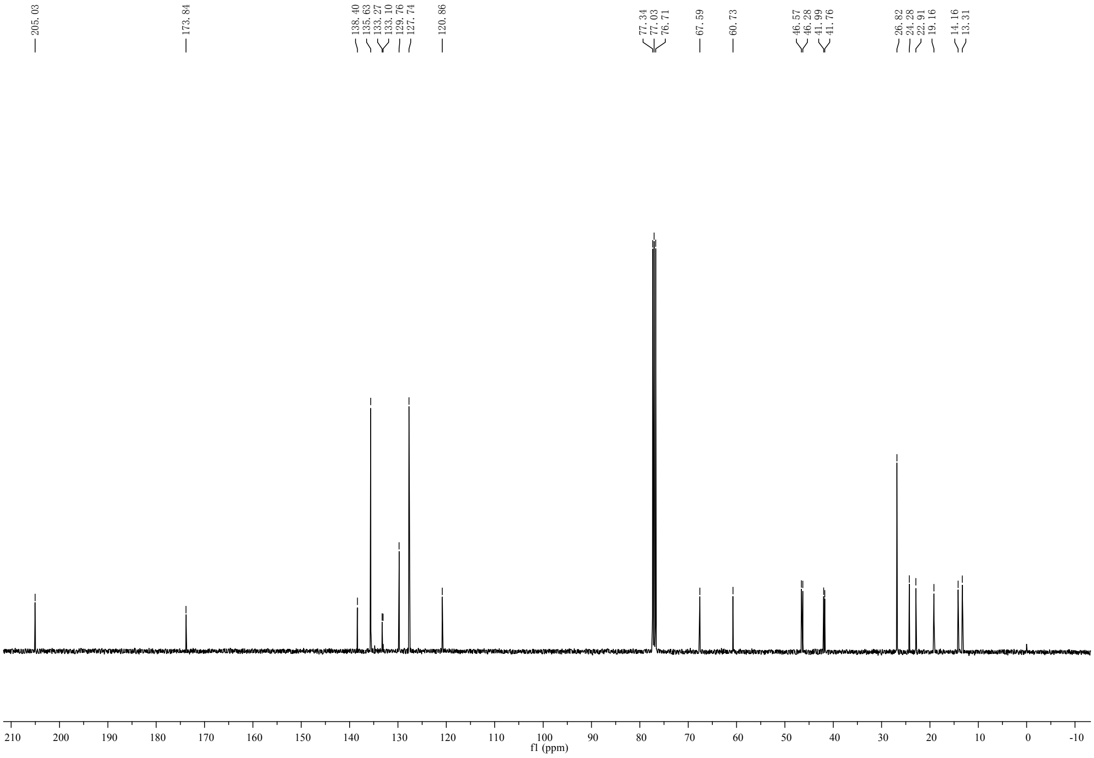
f1 (ppm)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60.73
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46.28
41.99
41.76
26.82
24.28
22.91
19.16
14.16
13.31
210
200
190
180
170
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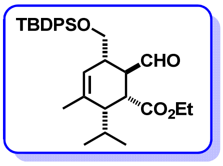
f1 (ppm)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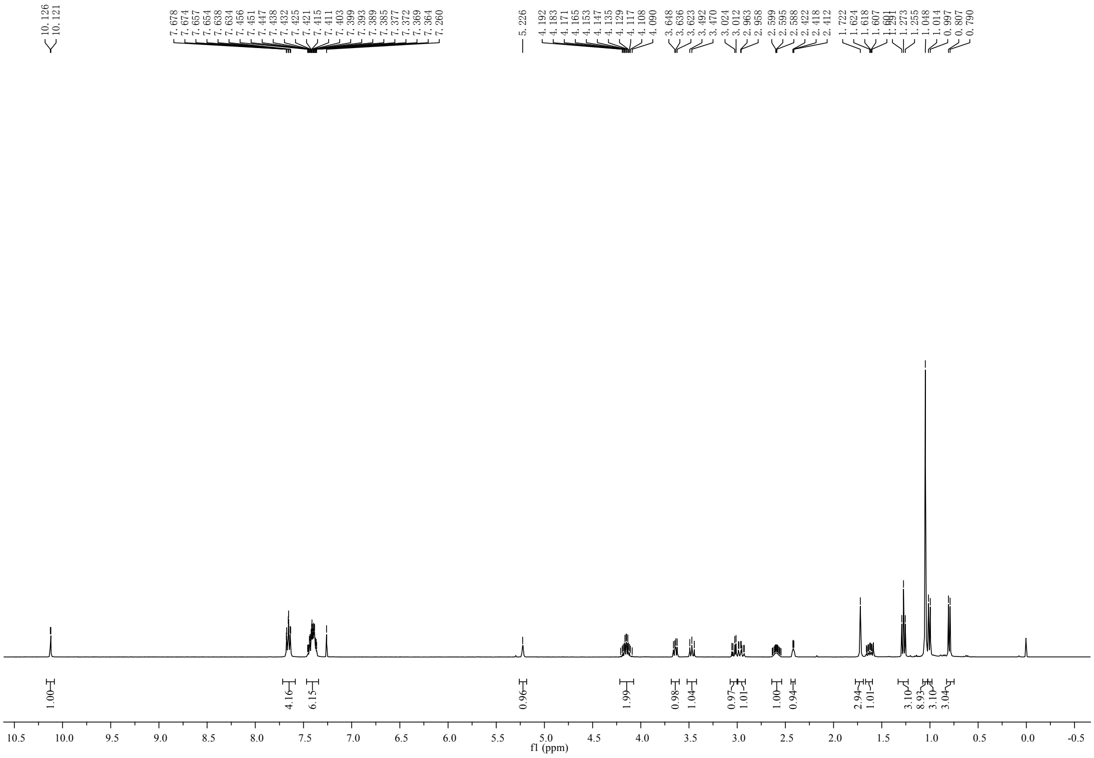
CO2Et

3ia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7.403
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7.364
7.260
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4.165
4.153
4.147
4.135
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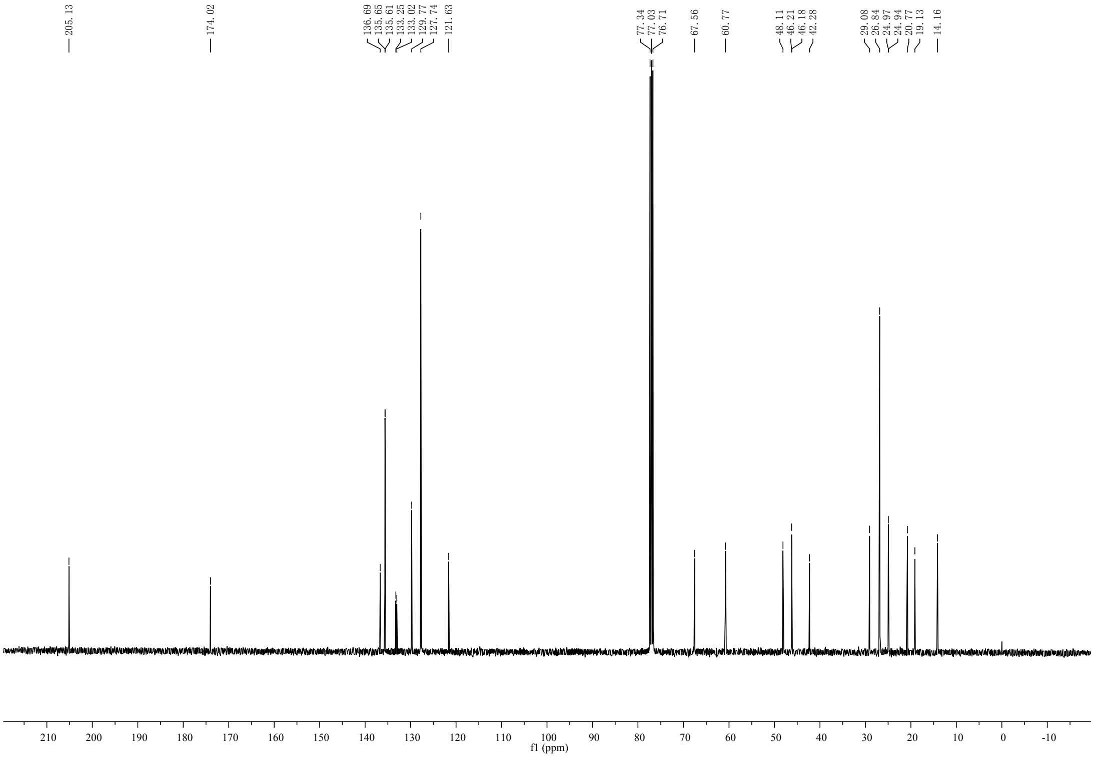
f1 (ppm)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46.18
42.28
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26.84
24.97
24.94
20.77
19.13
14.16
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200
190
180
170
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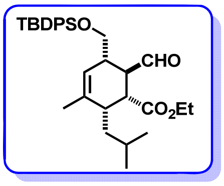
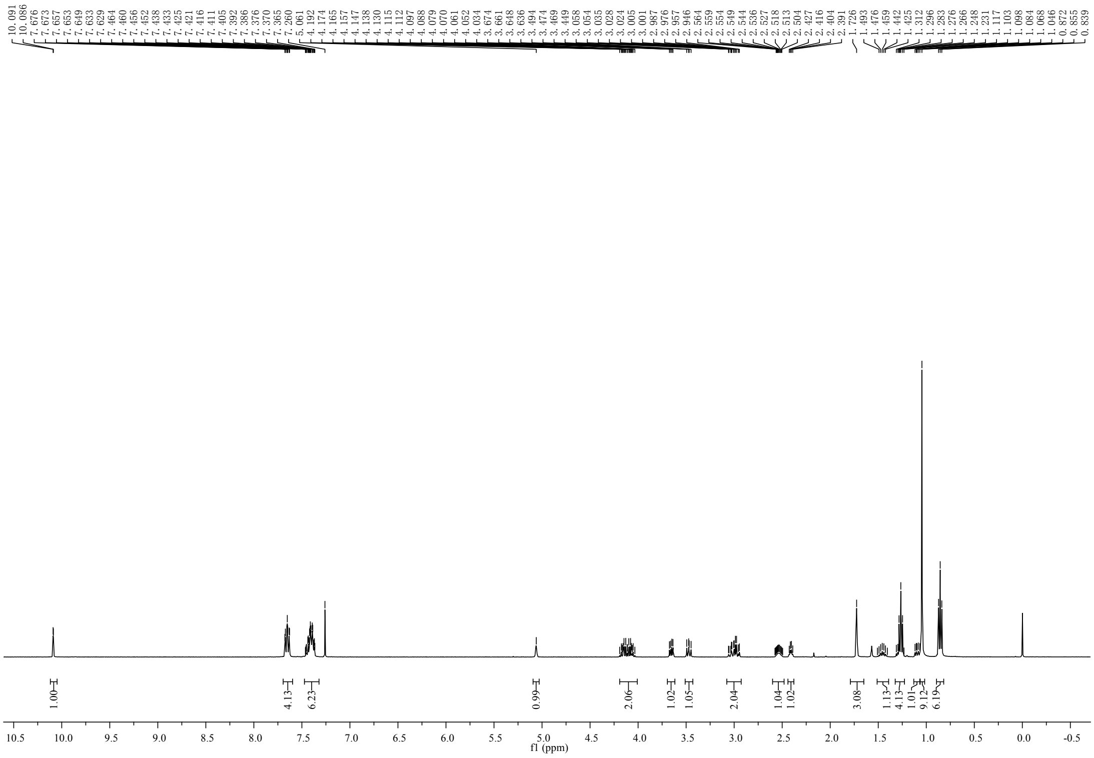
f1 (ppm)


TBDPSO
CHO
CO2Et

3ja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7.370
7.365
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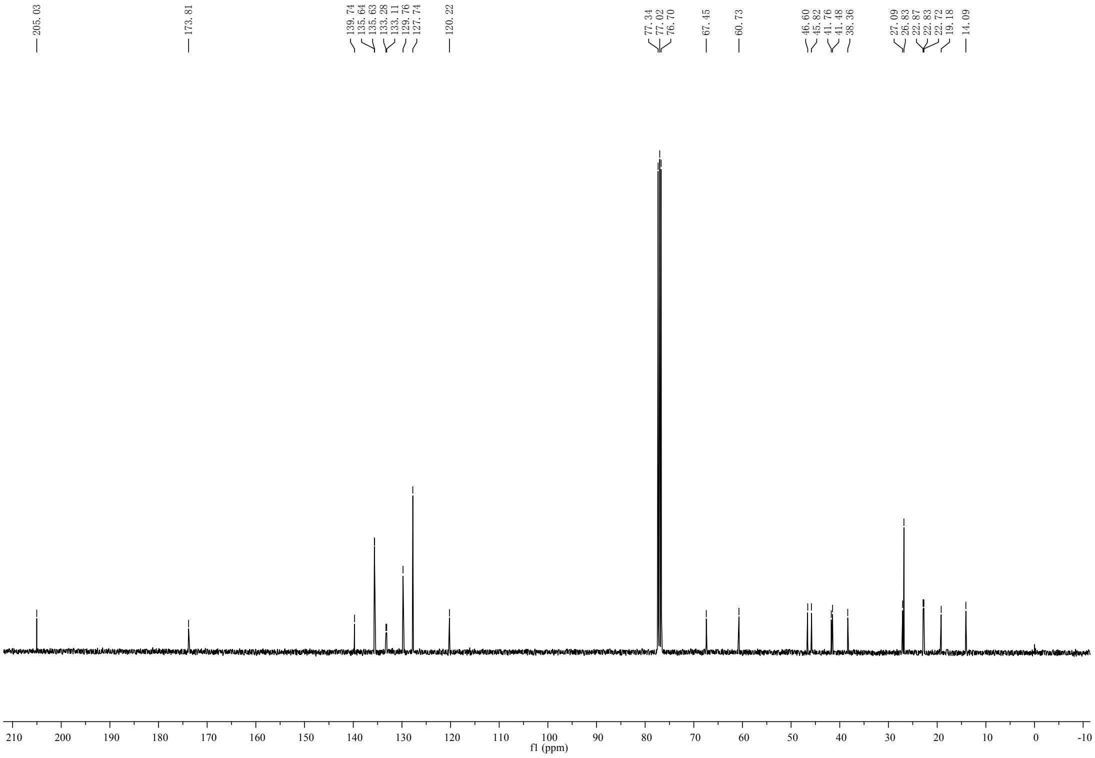
f1 (ppm)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27.09
26.83
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22.83
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180
170
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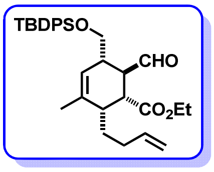
f1 (ppm)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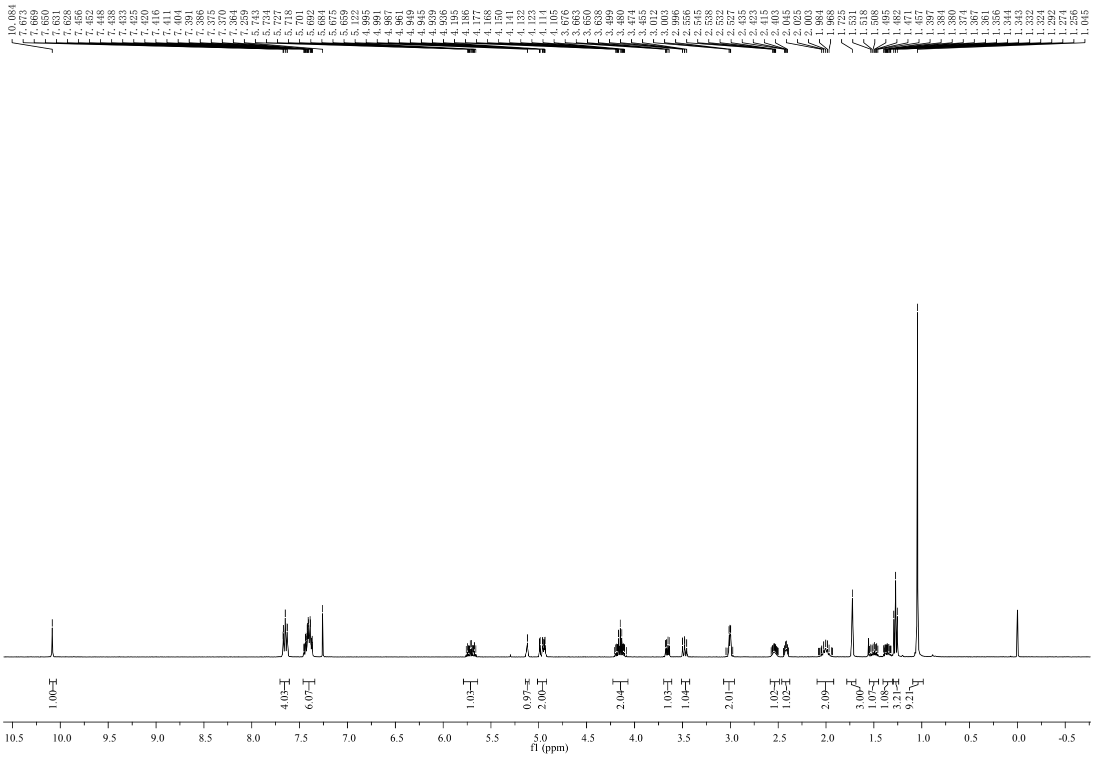
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2.01
1.02
1.02
2.09
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1.07
1.08
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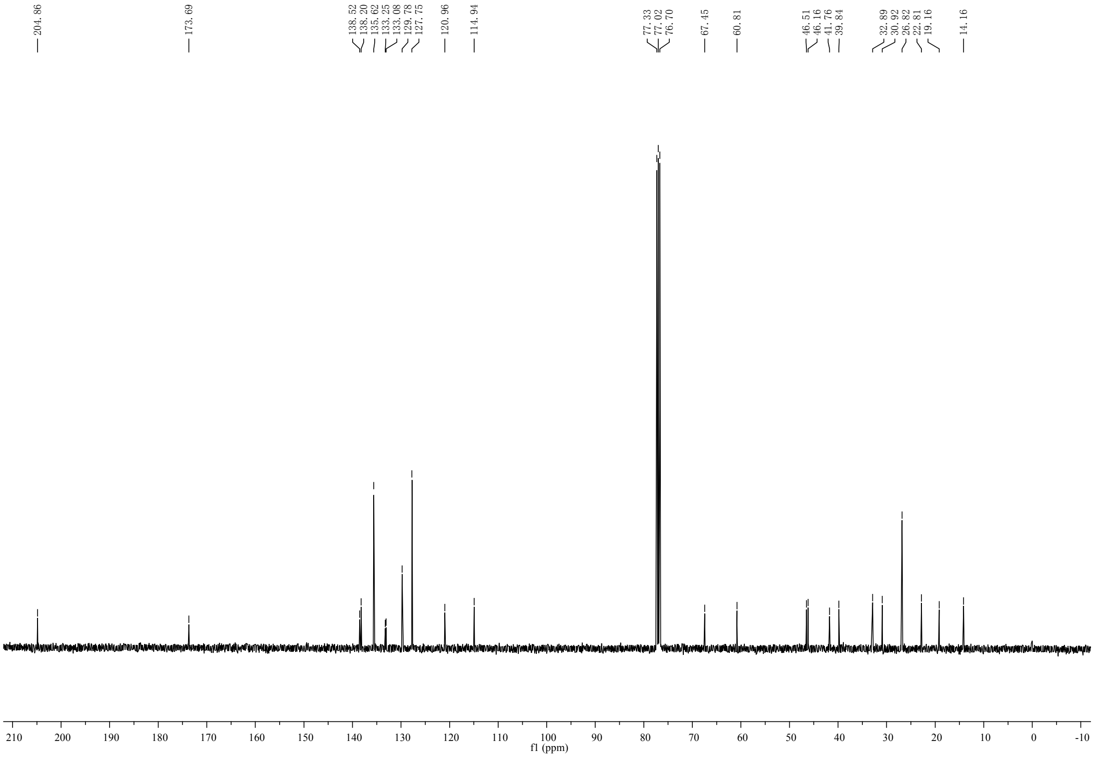
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22.81
19.16
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180
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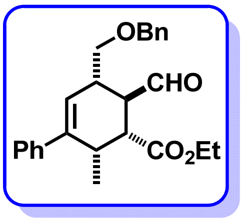
f1 (ppm)


OBn
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Ph
CO2Et

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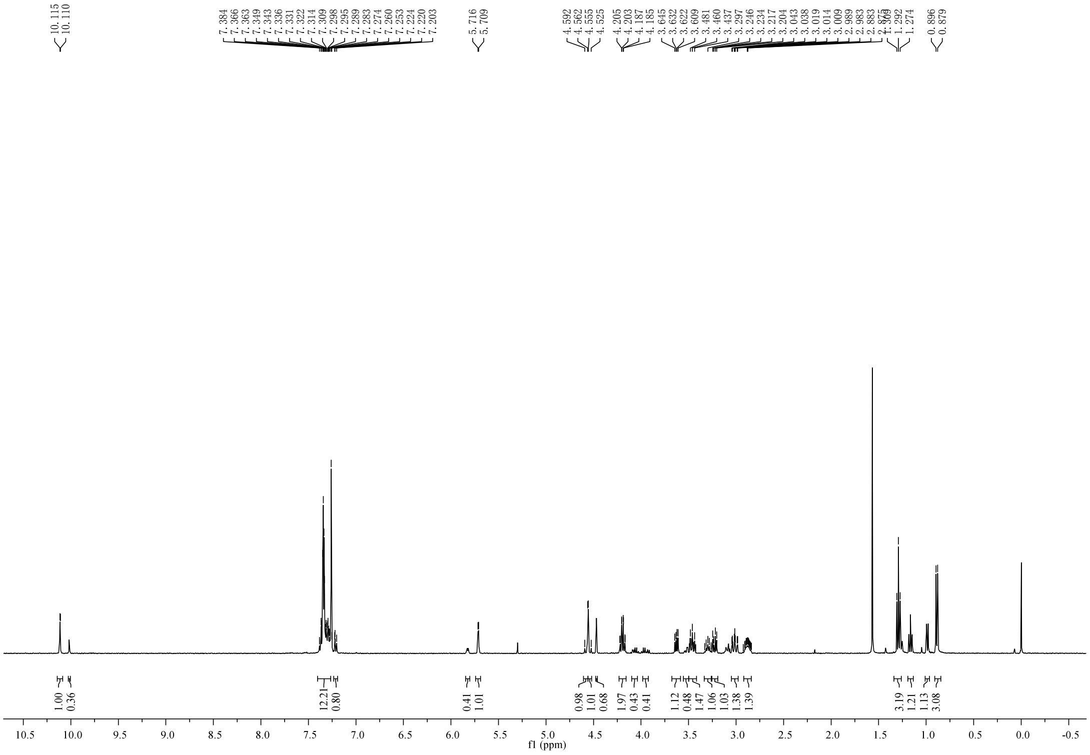
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1.13
3.08
10.5
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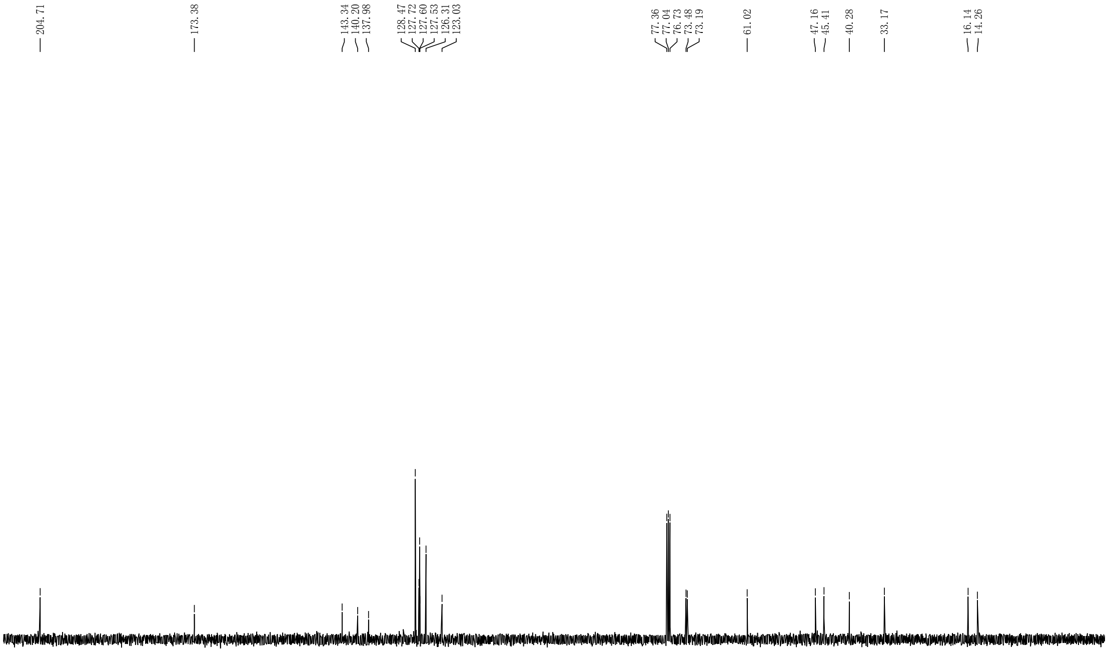
f1 (ppm)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73.19
61.02
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33.17
16.14
14.26
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180
170
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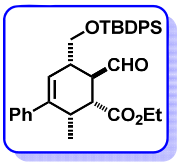
-10
f1 (ppm)


OTBDPS
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Ph
CO2Et

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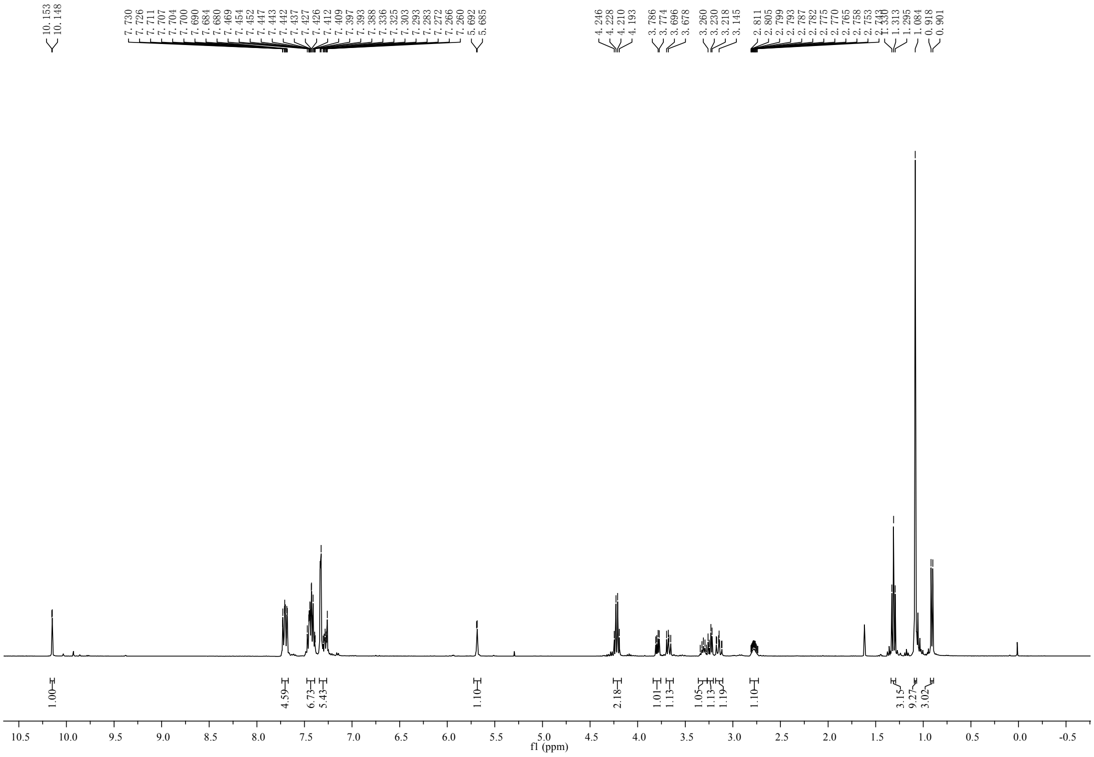
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4.210
4.193
3.786
3.774
3.696
3.678
3.260
3.230
3.218
3.145
2.811
2.805
2.799
2.793
2.787
2.782
2.775
2.770
2.765
2.758
2.753
2.743
1.330
1.313
1.295
1.084
0.918
0.901
1.00
4.59
6.73
5.43
1.10
2.18
1.01
1.13
1.05
1.13
1.19
1.10
3.15
9.27
3.02
10.5
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
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3.0
2.5
2.0
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1.0
0.5
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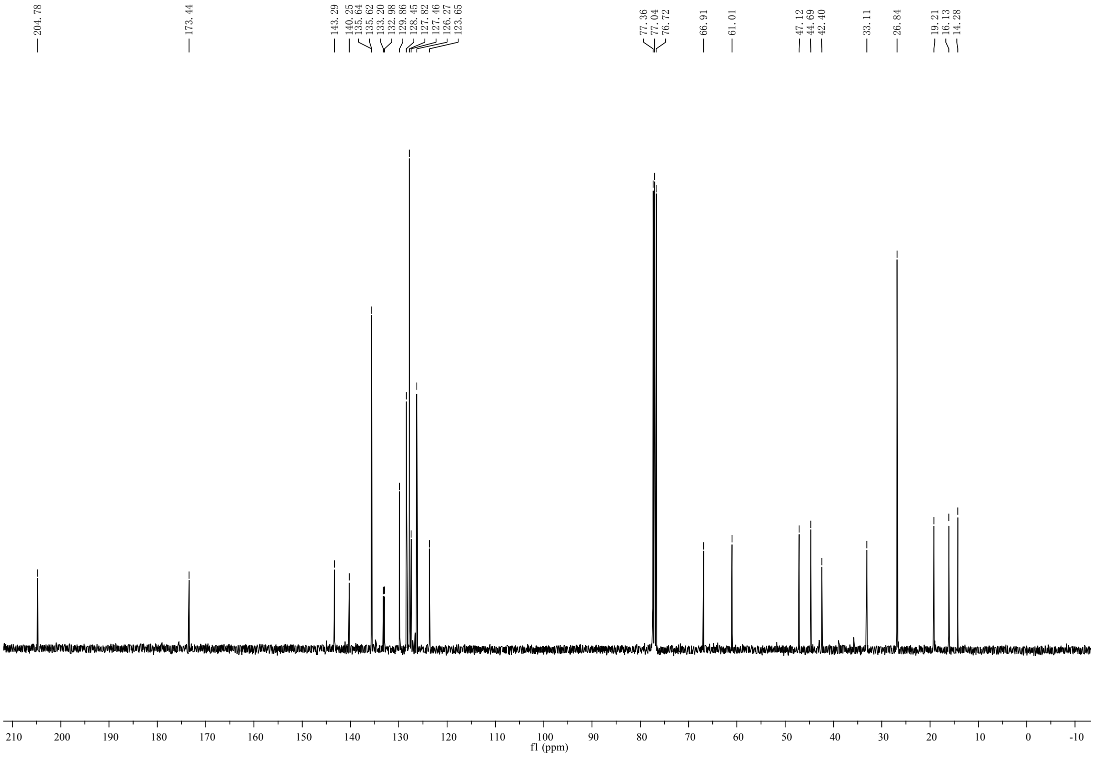
-0.5
f1 (ppm)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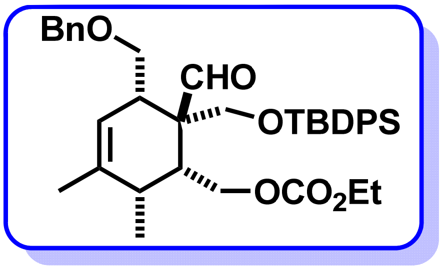
77.36
77.04
76.72
66.91
61.01
47.12
44.69
42.40
33.11
26.84
19.21
16.13
14.28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

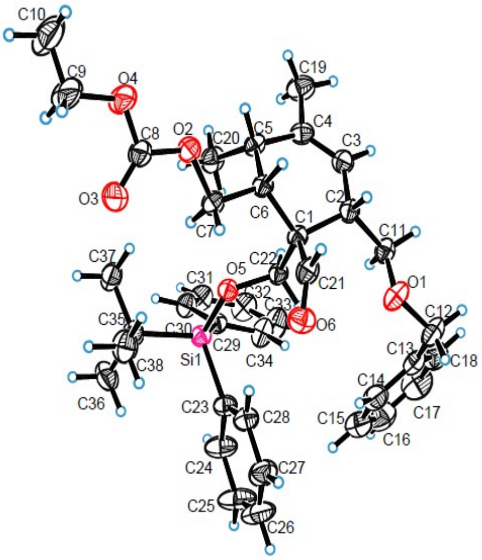
7. Crystal data for the products

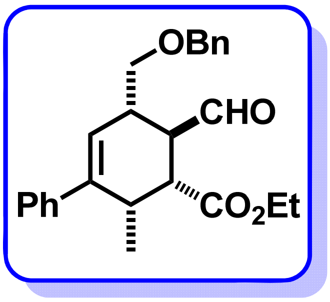


3ag

Table 1 Crystal data and structure refinement for zjh130502

Identification code	zjh130502
Empirical formula	$C_{38}H_{48}O_6Si$
Formula weight	628.85
Temperature/K	291(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.2348(5)
b/Å	11.3819(6)
c/Å	14.1336(6)
α/°	87.511(4)
β/°	81.820(4)
γ/°	82.982(4)
Volume/Å^3	1774.90(14)
Z	2
ρ_{calc}mg/mm^3	1.177
m/mm^{-1}	0.110
F(000)	676.0
Crystal size/mm^3	0.36 × 0.3 × 0.28
2Θ range for data collection	6.38 to 52.74°
Index ranges	$-13 \le h \le 14$, $-12 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	15023
Independent reflections	7167[R(int) = 0.0246]
Data/restraints/parameters	7167/3/423
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	$R_1 = 0.0562$, $wR_2 = 0.1307$
Final R indexes [all data]	$R_1 = 0.0804$, $wR_2 = 0.1460$
Largest diff. peak/hole / e Å^{-3}	0.33/-0.32





3ma

Table 1 Crystal data and structure refinement for ZJH128-2.

Identification code	ZJH128-2
Empirical formula	$C_{25}H_{28}O_4$
Formula weight	392.47
Temperature/K	291(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.87280(10)
b/Å	17.7824(5)
c/Å	21.2004(6)
α/°	90
β/°	92.679(2)
γ/°	90
Volume/Å^3	2211.59(10)
Z	4
ρ_{calc}mg/mm^3	1.179
m/mm^{-1}	0.630
F(000)	840.0
Crystal size/mm^3	0.36 × 0.32 × 0.27
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection	6.49 to 139.604°
Index ranges	$-7 \leq h \leq 7$, $-18 \leq k \leq 21$, $-23 \leq l \leq 25$
Reflections collected	11206
Independent reflections	4062 [R_{int} = 0.0186, R_{sigma} = 0.0199]
Data/restraints/parameters	4062/28/272
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0589, wR_2 = 0.1685
Final R indexes [all data]	R_1 = 0.0678, wR_2 = 0.1791
Largest diff. peak/hole / e Å^{-3}	0.42/-0.37