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Supplemental Information

Direct Synthesis of Bicyclic Acetals via Visible Light Catalysis

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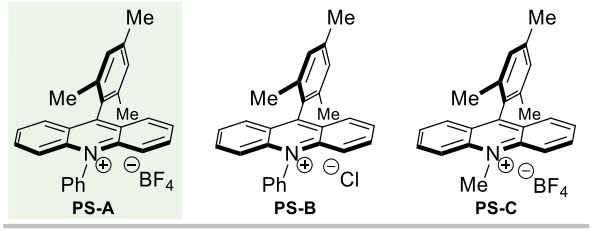
Supporting Information

I. Transparent Methods

General Information

All solvents were distilled according to general practice prior to use. Solvents for flash column chromatography were technical grade and distilled prior to use. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker 400 MHz (100 MHz for ^{13}C) nuclear resonance spectrometers unless otherwise specified. ^{1}H and ^{13}C NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. Chemical shifts (δ) are given in parts per million and referenced to the residual solvent signal; and all coupling constants are reported in Hz. The following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Thin-layer chromatography (TLC) was conducted with 0.25 mm Yantai silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with phosphomolybdic acid in EtOH. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at Peking University; Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

Preparation of acridinium photocatalysts



Photocatalysts (PS-A, PS-B, PS-C) used in this study were synthesized by the method of Fukuzumi et al. (Fukuzumi et al., 2004). Tetrafluoroboric acid (diethyl ether complex) was used for hydrolysis in PS-A and PS-C synthesis. HCl (4.0 M in 1, 4-dioxane) was used for hydrolysis in PS-B synthesis. Spectral data for these compounds matches the reported value in the literature.

9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (PS-A):

Yellow solid. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.14 (s, 2H), 7.89 (dq, J = 14.2, 7.4, 6.8 Hz, 5H), 7.79 (t, J = 7.7 Hz, 2H), 7.75 – 7.69 (m, 2H), 7.60 (d, J = 9.1 Hz, 2H), 7.18 (s, 2H), 2.49 (s, 3H), 1.83 (s, 6H).

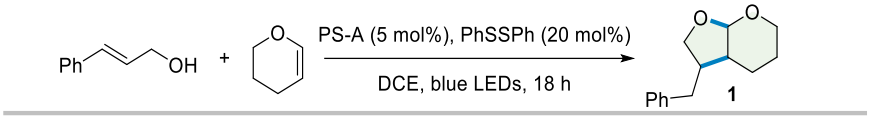
9-mesityl-10-phenylacridin-10-ium chloride (PS-B)：

Yellow solid. ^{1}H NMR (300 MHz, Chloroform-d) δ 8.23 (ddd, J = 8.9, 6.2, 1.8 Hz, 2H), 7.97 – 7.81 (m, 7H), 7.72 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 9.0 Hz, 2H), 7.14 (s, 2H), 2.44 (s, 3H), 1.78 (s, 6H).

9-mesityl-10-methylacridin-10-ium tetrafluoroborate (PS-C):

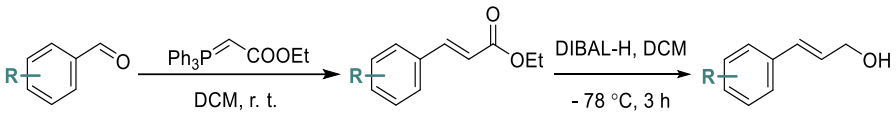
Yellow solid. ^{1}H NMR (300 MHz, Chloroform-d) δ 8.81 (d, J = 9.3 Hz, 2H), 8.41 (ddd, J = 9.3, 6.5, 1.8 Hz, 2H), 8.05 – 7.59 (m, 4H), 7.15 (s, 2H), 5.11 (s, 3H), 2.48 (s, 3H), 1.73 (s, 6H).

General procedure for acetals



PhSSPh (0.04 mmol, 8.7 mg), Mes-Acr-PhBF$_4$ (PS-A) (0.02 mmol, 4.6 mg) and (E)-3-phenylprop-2-en-1-ol (0.2 mmol, 26.8 mg) were weighed in an oven-dried 8 mL vial equipped with a magnetic starring bar. The reaction vial was capped with a rubber septum and anhydrous DCE (3 mL) was added under an argon atmosphere. Then 3, 4-dihydro-2H-pyran (0.8 mmol, 73 μL) was added and the reaction vessel was fixed on a blue LED light reaction equipment (1 W, 452 nm). After TLC indicated a full conversion (usually 18 hours), the reaction was purified by flash silica gel column chromatography directly.

General procedure for substrates

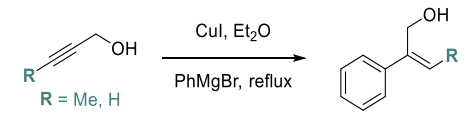


Step 1:

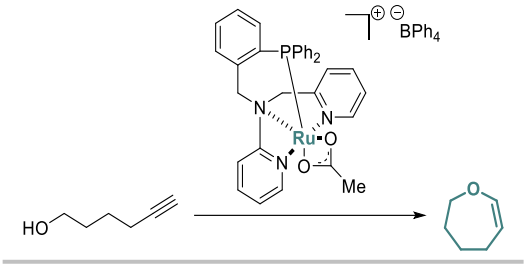
To a stirred solution of aldehyde (10.3 mmol) in DCM (20 mL) at room temperature was added ethyl (triphenylphosphoranylidene)acetate (1.1 eq, 11.3 mmol). The reaction solution was stirred for 15 hours and then concentrated under vacuum condition. The residue was purified by flash silica gel column chromatography directly.

Step 2:

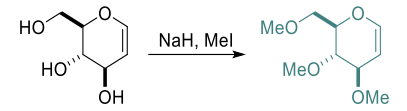
To a solution of corresponding ester (8.84 mmol) in DCM (70 mL) at -78 ^{o}C was added a 1.0 M solution of DIBAL-H (in hexane, 2.5 eq, 22 mmol) dropwise. After 3 hours, the reaction mixture was warmed to room temperature and quenched with 1N HCl (40 mL). The aqueous phase was separated and extracted with DCM. The combined organic extracts were washed with $NaHCO_3$, dried over Na_2SO_4. Then the solution was filtered and concentrated under vacuum condition. The residue was further purified by flash silica gel column chromatography.



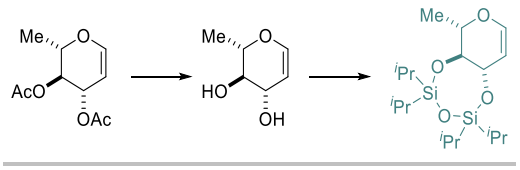
To a solution of PhMgBr (25 mmol) in 30 ml of Et_2O was added CuI (0.29 g, 1.5 mmol). The mixture was stirred at room temperature for 0.5 hours. Then a solution of corresponding propargyl alcohol (10 mmol) in 10 mL Et_2O was added slowly. After the addition was completed, the reaction mixture was refluxed for 24 hours. After cooling to room temperature, an aqueous solution of NH_4Cl was added slowly. The organic layer was separated and aqueous layer was extracted with Et_2O. The combined organic extracts were dried over Na_2SO_4. Then the solution was filtered and concentrated under vacuum condition. The residue was purified by flash silica gel column chromatography (Duan et al., 2009).



Catalyst [Ru(N_3P)(OAc)][BPh_4] (0.005 mmol) was added to a solution of alkynol (17.6 mmol) in THF (15 mL). The resulting solution was stirred at 80 °C and monitored by TLC. When the maximum conversion was reached, the desired product was isolated by flash column chromatography on silica gel (Liu et al., 2010).

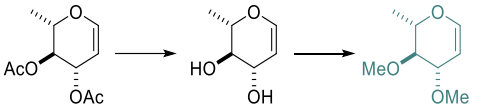


D-Galactal (730 mg, 5 mmol), which had been pre-dried under vacuum in a flame-dried flask for 1 h, was dissolved in anhydrous DMF (30 mL) under a N_2 atmosphere. The reaction mixture was cooled to 0 °C, after which NaH (60% wt in mineral oil, 900 mg, 22.5 mmol) was added portionwise. When addition was completed the reaction was allowed to warm to room temperature. After being stirred at room temperature for 30 min, the solution was cooled to 0 °C and iodomethane (140 µL, 22.5 mmol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred for another 3 hours, and quenched with MeOH (0.5 mL). The solution was diluted with EtOAc (40 mL) and washed with water (3x 20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated in vacuum. Purification by column chromatography afforded target product as a pale yellow liquid (752 mg, 80%). Proton and carbon NMR were consistent with literature data (Balmond et al., 2014).



3, 4-O-Di-acetyl-L-rhamnal (520 mg, 2.43 mmol) was dissolved in a solution of MeOH (8 mL), H_2O (1 mL) and Et_3N (1 mL), and stirred for 18 hours. Then the solvent was removed to afford L-rhamnal as a solid. L-Rhamnal and imidazole (332 mg, 4.88 mmol) were dissolved in distilled pyridine (20 mL) under N_2 atmosphere and the solution was cooled to 0 °C. 1,3-Dichloro-

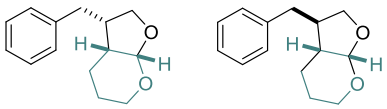
1,1,3,3-tetraisopropyldisiloxane (1.2 mL, 3.75 mmol) was added dropwise and the solution was then allowed to warm to room temperature and stirred for 18 h. The reaction was quenched with H_2O (30 mL), extracted with EtOAc (50 mL). The organic layer was washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated in vacuum. Following purification by column chromatography afforded the desired product as a white solid (846 mg, 96%).



3, 4-O-Di-acetyl-L-rhamnal (1.0 g, 4.67 mmol) was dissolved in a solution of MeOH (15 mL), H_2O (2 mL) and Et_3N (2 mL) and stirred for 18 hours. Then the solvents were removed and the residue was dissolved in EA, washed with H_2O and brine, and dried over Na_2SO_4. Following purification by column chromatography, L-rhamnal was obtained as a white solid (546 mg, 90% yield). L-rhamnal (546 mg, 4.2 mmol) was dissolved in anhydrous DMF (25 mL) under N_2 atmosphere. The reaction mixture was cooled to 0 °C, after which NaH (60%wt in mineral oil, 504 mg, 12.6 mmol) was added portionwise. When addition was completed the reaction was allowed to warm to room temperature. After being stirred at room temperature for 30 min, the solution was cooled to 0 °C and iodomethane (78 µL, 12.6 mmol) was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred for another 3 hours, and quenched with MeOH (0.5 mL). The solution was diluted with EtOAc (40 mL) and washed with water (3 x 20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated in vacuum. Purification by column chromatography afforded the target product as a pale yellow liquid (498 mg, 75%). Proton and carbon NMR were consistent with literature data.

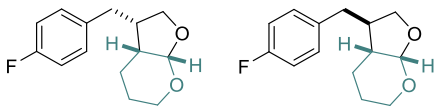
II. Date S1: ^{1}H NMR and ^{13}C NMR spectra data of products (Related to Figure 3-5)

3-benzylhexahydro-4H-furo[2,3-b]pyran (1)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (35.3 mg, 81% yield, dr = 1.8:1). Proton and carbon NMR were consistent with literature data. **Cis-syn: ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 2H), 5.29 (d, *J* = 3.7 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.82 – 3.74 (m, 2H), 3.65 (t, *J* = 8.1 Hz, 1H), 2.79 –2.55 (m, 3H), 1.96 (m, 1H), 1.79 – 1.73 (m, 1H), 1.86 – 1.53 (m, 3H). **Cis-anti: ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32–7.26 (m, 2H), 7.24–7.19 (m, 1H), 7.19–7.14 (m, 2H), 5.04 (d, *J* = 3.6 Hz, 1H), 4.18 (t, *J* = 8.2 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.65 (t, *J* = 8.1 Hz, 1H), 3.43 (td, *J* = 11.3, 2.4 Hz, 1H), 2.87 (dd, *J* = 13.3, 5.2 Hz, 1H), 2.79–2.55 (m, 2H), 1.86-1.53 (m, 4H), 1.38–1.32 (m, 1H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 140.12, 140.08, 128.51, 128.49, 128.36, 126.22, 126.18, 102.13, 101.96, 73.64, 69.87, 64.37, 60.98, 43.84, 42.52, 39.42, 38.73, 36.58, 33.38, 23.17, 22.45, 20.74, 19.57. **HRMS** calculated for $C_{14}H_{18}O_2$ (M + Na^+): 241.1149, found: 241.1202.

3-(4-fluorobenzyl)hexahydro-4H-furo[2,3-b]pyran (2)



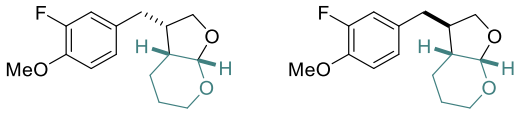
Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (30.7 mg, 65% yield, dr = 1.3:1). Proton and carbon NMR were consistent with literature data (Yan et al., 2012). **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.11 (m, 2H), 7.00 – 6.93 (m, 2H), 5.27 (d, *J* = 3.7 Hz, 1H), 3.90 – 3.83 (m, 1H), 3.81 – 3.71 (m, 2H), 3.67 – 3.58 (m, 1H), 2.77 – 2.47 (m, 3H), 2.00 – 1.90 (m, 1H), 1.78 – 1.71 (m, 1H), 1.88 – 1.44 (m, 3H). **Cis-anti: ^{1}H NMR** (400 MHz, Chloroform-d) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (m, 2H), 7.00 – 6.93 (m, 2H), 5.02 (d, *J* = 3.4 Hz, 1H), 4.15 (t, *J* = 8.2 Hz, 1H), 3.90 – 3.83 (m, 1H), 3.67 – 3.58 (m, 1H), 3.46 – 3.37 (m, 1H), 2.82 (dd, *J* = 12.8, 4.6 Hz, 1H), 2.77 – 2.47 (m, 2H), 1.88 – 1.44 (m, 4H), 1.34 (m, *J* = 10.1, 5.4, 3.0 Hz, 1H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 162.66 (d, *J* = 245.3 Hz), 162.60 (d, *J* = 245.0 Hz), 135.72 , 135.69,

129.88 (d, *J* = 8.0 Hz), 129.72 (d, *J* = 7.07 Hz), 115.41 (d, *J* = 21.2 Hz), 115.39 (d, *J* = 21.4 Hz), 102.11, 101.93, 73.52, 69.76, 64.38, 60.99, 43.79, 42.60, 39.53, 37.89, 36.52, 32.62, 23.11, 22.45, 20.69, 19.54. **HRMS** calculated for $C_{14}H_{17}FO_2$ (M + Na^+): 259.1105, found: 259.1105.

3-(4-phenoxybenzyl)hexahydro-4H-furo[2,3-b]pyran (3)

Eluent for purification: hexane: ethyl acetate = 10:1. White solid (36.0 mg, 58% yield, dr = 1.4:1). **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.37 – 7.29 (m, 2H), 7.16 – 7.05 (m, 3H), 7.07 – 6.98 (m, 2H), 6.98 – 6.88 (m, 2H), 5.30 (d, J = 3.7 Hz, 1H), 3.90 (t, J = 7.7 Hz, 1H), 3.85 – 3.74 (m, 2H), 3.72 – 3.58 (m, 1H), 2.80 – 2.51 (m, 3H), 1.98 (ddt, J = 12.1, 10.2, 5.0 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.60 – 1.46 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.15 – 7.06 (m, 3H), 7.03 – 6.97 (m, 2H), 6.97 – 6.91 (m, 2H), 5.05 (d, *J* = 3.5 Hz, 1H), 4.20 (t, *J* = 8.2 Hz, 1H), 3.89 (ddt, *J* = 11.7, 4.3, 2.4 Hz, 1H), 3.65 (dd, *J* = 8.4, 7.5 Hz, 1H), 3.49 – 3.38 (m, 1H), 2.84 (dd, *J* = 13.0, 4.7 Hz, 1H), 2.69 – 2.50 (m, 2H), 1.91 – 1.76 (m, 2H), 1.76 – 1.62 (m, 3H), 1.41 – 1.29 (m, 1H). **Cis-syn: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.35, 155.59, 134.97, 129.69, 129.54, 123.12, 119.00, 118.70, 101.97, 69.86, 60.99, 42.65, 36.58, 32.67, 23.16, 19.57. **Cis-anti: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.41, 155.52, 135.01, 129.72, 129.69, 123.07, 119.07, 118.60, 102.13, 73.61, 64.38, 43.78, 39.55, 37.95, 22.48, 20.75. **HRMS** calculated for $C_{20}H_{22}O_3$ (M + Na^+): 333.1461, found: 333.1459.

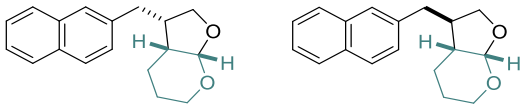
3-(3-fluoro-4-methoxybenzyl)hexahydro-4H-furo[2,3-b]pyran (4)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (36.7 mg, 69% yield, dr = 1.1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for two diastereomers is given herein. **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.90 – 6.86 (m, 1H), 6.87 – 6.84 (m, 2H), 5.27 (d, *J* = 3.7 Hz, 1H), 3.86 (s, 4H), 3.75 (ddd, *J* = 12.8, 10.2, 7.9 Hz, 2H), 3.67 – 3.55 (m, 1H), 2.70 – 2.45 (m, 3H), 1.94 (dtd, *J* = 10.3, 6.3, 3.9 Hz, 1H), 1.85 – 1.70 (m, 2H), 1.67 – 1.51 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.87 – 6.82 (m, 3H), 5.02 (d, *J* = 3.3 Hz, 1H), 4.16 (t, *J* = 8.2 Hz, 1H), 3.86 (s, 4H), 3.67 – 3.55 (m, 1H), 3.46 – 3.37 (m, 1H), 2.77 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.70

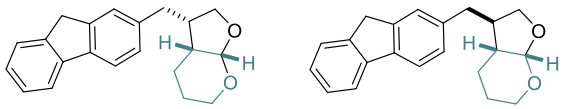
– 2.45 (m, 2H), 1.85 – 1.70 (m, 2H), 1.67 – 1.51 (m, 2H), 1.33 (dq, *J* = 13.1, 2.9, 2.5 Hz, 1H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 153.49 (d, *J* = 246.3 Hz), 153.47 (d, *J* = 246.9 Hz), 145.98 (d, *J* = 5.7 Hz), 145.93 (d, *J* = 5.7 Hz), 133.16, 133.11, 123.99 (d, *J* = 19.6 Hz), 123.96 (d, *J* = 12.6 Hz), 116.22 (d, *J* = 32.4 Hz), 116.08 (d, *J* = 3.5 Hz), 113.51 (d, *J* = 2.0 Hz), 113.49 (d, *J* = 2.0 Hz), 102.09, 101.92, 73.48, 69.73, 64.36, 60.99, 56.31, 56.30, 43.75, 42.45, 39.44, 37.77, 36.51, 32.47, 23.10, 22.46, 20.71, 19.53. **HRMS** calculated for $C_{15}H_{19}FO_3$ (M + Na^+): 289.1210, found: 289.1203.

3-(naphthalen-2-ylmethyl)hexahydro-4H-furo[2,3-b]pyran (5)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (26.8 mg, 50% yield, dr = 1.1:1). **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.80 (m, 3H), 7.62 (d, J = 1.7 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.32 (dd, J = 8.4, 1.8 Hz, 1H), 5.31 (d, J = 3.7 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.88 – 3.75 (m, 2H), 3.66 (dtd, J = 11.3, 3.3, 1.7 Hz, 1H), 2.91 (dd, J = 10.8, 5.7 Hz, 1H), 2.87 – 2.75 (m, 2H), 2.05 – 1.95 (m, 1H), 1.82 (dq, J = 9.7, 2.2 Hz, 1H), 1.68 – 1.58 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.88 – 7.73 (m, 3H), 7.61 (d, J = 1.7 Hz, 1H), 7.52 – 7.38 (m, 2H), 7.31 (dd, J = 8.5, 1.8 Hz, 1H), 5.07 (d, J = 3.7 Hz, 1H), 4.21 (t, J = 8.0 Hz, 1H), 3.89 (dq, J = 11.7, 2.6 Hz, 1H), 3.70 (dd, J = 8.4, 7.3 Hz, 1H), 3.44 (ddd, J = 11.6, 10.6, 2.3 Hz, 1H), 3.15 – 2.96 (m, 1H), 2.85 – 2.66 (m, 2H), 1.93 (dq, J = 9.0, 4.8, 4.0 Hz, 1H), 1.85 – 1.64 (m, 3H), 1.42 – 1.29 (m, 1H). **Cis-syn: ^{13}C NMR** (101 MHz, Chloroform-d) δ 137.60, 133.55, 132.10, 128.18, 127.62, 127.40, 126.94, 126.56, 126.10, 125.40, 101.99, 69.93, 61.02, 42.35, 36.65, 33.60, 23.17, 19.61. **Cis-trans: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.61, 133.53, 132.12, 128.13, 127.62, 127.44, 127.08, 126.69, 126.09, 125.40, 102.15, 73.68, 64.37, 43.93, 39.34, 38.97, 22.55, 20.78. **HRMS** calculated for $C_{18}H_{20}O_2$ (M + Na^+): 291.1356, found: 291.1356.

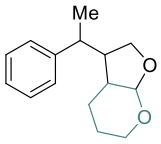
3-((9H-fluoren-2-yl)methyl)hexahydro-4H-furo[2,3-b]pyran (6)



Eluent for purification: hexane: ethyl acetate = 10:1. White solid (34.9 mg, 57% yield, dr = 1.4:1). **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-

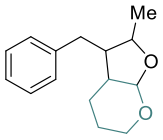
d) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.54 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 7.18 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.31 (d, *J* = 3.7 Hz, 1H), 3.90 (d, *J* = 14.7 Hz, 3H), 3.86 – 3.75 (m, 2H), 3.66 (ddq, *J* = 11.0, 3.1, 1.7 Hz, 1H), 2.92 – 2.58 (m, 3H), 2.00 (dt, *J* = 10.8, 2.9 Hz, 1H), 1.80 (dt, *J* = 9.4, 2.6 Hz, 1H), 1.66 – 1.58 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.54 (dq, *J* = 7.4, 1.0 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.34 – 7.27 (m, 2H), 7.24 – 7.06 (m, 1H), 5.06 (d, *J* = 3.6 Hz, 1H), 4.22 (t, *J* = 8.1 Hz, 1H), 3.95 – 3.81 (m, 3H), 3.74 – 3.63 (m, 1H), 3.44 (ddd, *J* = 11.6, 10.7, 2.3 Hz, 1H), 2.96 – 2.84 (m, 1H), 2.77 – 2.58 (m, 2H), 1.98 – 1.85 (m, 1H), 1.83 – 1.65 (m, 3H), 1.43 – 1.30 (m, 1H). **Cis-syn: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.69, 143.07, 141.49, 139.94, 138.79, 126.98, 126.73, 126.47, 125.02, 124.98, 119.83, 119.65, 101.99, 69.94, 61.00, 42.73, 36.82, 36.64, 33.55, 23.19, 19.61. **Cis-trans: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.66, 143.10, 141.52, 139.95, 138.79, 127.14, 126.73, 126.47, 125.18, 125.00, 119.82, 119.67, 102.19, 73.71, 64.39, 43.89, 39.68, 38.92, 36.82, 22.52, 20.77. **HRMS** calculated for $C_{21}H_{22}O_2$ (M + Na^+): 329.1512, found: 329.1512.

3-(1-phenylethyl)hexahydro-4H-furo[2,3-b]pyran (7)



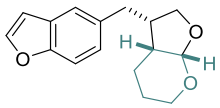
Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (35.8 mg, 77% yield, dr = 2.4:1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.12 (m, 3H), 5.00 (d, *J* = 3.4 Hz, 1H), 4.01 (t, *J* = 8.6 Hz, 1H), 3.89 (dtd, *J* = 11.7, 3.9, 1.4 Hz, 1H), 3.54 (dd, *J* = 8.8, 6.7 Hz, 1H), 3.44 (ddd, *J* = 11.5, 10.4, 2.6 Hz, 1H), 2.75 (dq, *J* = 8.7, 6.9 Hz, 1H), 2.50 (qd, *J* = 8.1, 6.2 Hz, 1H), 1.97 – 1.37 (m, 4H), 1.25 (m, 1H), 1.31 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (three isomers)** (101 MHz, Chloroform-*d*) δ 145.69, 145.25, 145.03, 128.56, 128.52, 128.44, 127.49, 127.12, 126.84, 126.50, 126.47, 126.37, 102.65, 102.38, 101.94, 72.69, 71.81, 68.92, 64.39, 64.14, 60.74, 48.01, 44.60, 44.42, 44.17, 43.30, 43.16, 42.25, 38.14, 35.77, 25.45, 24.06, 23.30, 22.57, 21.46, 21.08, 20.73, 20.56, 18.89. **HRMS** calculated for $C_{15}H_{20}O_2$ (M + Na^+): 255.1356, found: 255.1354.

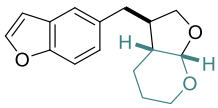
3-benzyl-2-methylhexahydro-4H-furo[2,3-b]pyran (8)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (21.3 mg, 46% yield, dr = 2.5:2.5:1.8:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (s, 2H), 7.21 (d, *J* = 3.0 Hz, 3H), 5.04 (d, *J* = 3.6 Hz, 1H), 4.57 (p, *J* = 6.7 Hz, 1H), 3.89 – 3.87 (m, 1H), 3.40 (dt, *J* = 11.3, 2.2 Hz, 1H), 2.89 – 2.82 (m, 1H), 2.70 (dd, *J* = 7.7, 3.2 Hz, 1H), 2.60 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.94 (dd, *J* = 6.5, 3.1 Hz, 1H), 1.74 (s, 1H), 1.56 (dt, *J* = 10.7, 3.7 Hz, 3H), 1.10 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR (four isomers)** (126 MHz, Chloroform-*d*) δ 140.53, 140.37, 139.79, 128.94, 128.51, 128.47, 128.40, 126.27, 126.19, 126.08, 126.05, 101.56, 100.82, 100.51, 100.18, 82.11, 73.86, 64.44, 64.19, 61.06, 60.92, 50.43, 46.33, 45.08, 43.36, 42.58, 38.03, 37.59, 37.04, 34.62, 31.31, 30.98, 25.39, 23.56, 23.31, 22.63, 22.44, 22.19, 21.40, 20.82, 20.79, 20.72, 19.84, 18.85, 17.38. **HRMS** calculated for $C_{15}H_{20}O_2$ (M + Na^+): 255.1356, found: 255.1355.

3-(benzofuran-5-ylmethyl)hexahydro-4H-furo[2,3-b]pyran (9)

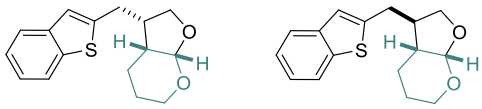




Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (35.6 mg, 69% yield, dr = 1.4:1). **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 2.2 Hz, 1H), 7.49 – 7.33 (m, 2H), 7.10 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.72 (dd, *J* = 2.2, 1.0 Hz, 1H), 5.29 (d, *J* = 3.7 Hz, 1H), 3.89 (t, *J* = 7.8 Hz, 1H), 3.79 (ddd, *J* = 10.1, 8.6, 5.3 Hz, 2H), 3.66 (ddq, *J* = 11.1, 3.1, 1.8 Hz, 1H), 2.83 (dd, *J* = 10.6, 6.0 Hz, 1H), 2.78 – 2.67 (m, 2H), 2.03 – 1.90 (m, 1H), 1.80 (ddd, *J* = 9.9, 6.6, 4.4 Hz, 1H), 1.63 – 1.53 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 2.2 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.09 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.72 (dd, *J* = 2.2, 1.0 Hz, 1H), 5.05 (d, *J* = 3.6 Hz, 1H), 4.25 – 4.11 (m, 1H), 3.92 – 3.82 (m, 1H), 3.74 – 3.62 (m, 1H), 3.43 (ddd, *J* = 11.6, 10.7, 2.3 Hz, 1H), 3.07 – 2.88 (m, 1H), 2.74 – 2.59 (m, 2H), 1.88 (ddt, *J* = 8.9, 5.9, 2.9 Hz, 1H), 1.84 – 1.64 (m, 3H), 1.34 (m, 1H). **Cis-syn: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.67, 145.28, 134.55, 127.64, 124.72, 120.45, 111.25, 106.33, 101.99, 69.91, 60.99, 43.01, 36.60, 33.27, 23.17, 19.58. **Cis-anti: ^{13}C NMR**

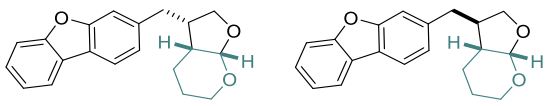
(101 MHz, Chloroform-*d*) δ 153.71, 145.26, 134.53, 127.62, 124.89, 120.63, 111.22, 106.36, 102.16, 73.65, 64.36, 43.80, 39.93, 38.64, 22.52, 20.77. **HRMS** calculated for $C_{16}H_{18}O_3$ (M + Na^+): 281.1148, found: 281.1148.

3-(benzo[b]thiophen-2-ylmethyl)hexahydro-4H-furo[2,3-b]pyran (10)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (41.6 mg, 76% yield, dr = 1.4:1). **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 – 7.71 (m, 1H), 7.68 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.08 – 6.97 (m, 1H), 5.31 (d, *J* = 3.7 Hz, 1H), 4.03 (t, *J* = 8.1 Hz, 1H), 3.80 (ddd, *J* = 13.1, 6.7, 3.0 Hz, 2H), 3.72 – 3.60 (m, 1H), 3.05 (ddd, *J* = 14.9, 7.9, 1.0 Hz, 1H), 2.94 (ddd, *J* = 14.9, 7.6, 1.1 Hz, 1H), 2.87 – 2.73 (m, 1H), 2.09 (dq, *J* = 9.3, 2.7 Hz, 1H), 1.81 (ddd, *J* = 11.2, 6.4, 3.3 Hz, 1H), 1.63 – 1.56 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.36 – 7.27 (m, 2H), 7.02 (d, *J* = 1.0 Hz, 1H), 5.07 (d, *J* = 3.6 Hz, 1H), 4.33 (t, *J* = 8.4 Hz, 1H), 3.95 – 3.85 (m, 1H), 3.72 (dd, *J* = 8.6, 7.4 Hz, 1H), 3.49 – 3.37 (m, 1H), 3.13 (ddd, *J* = 14.9, 5.5, 1.1 Hz, 1H), 2.89 (ddd, *J* = 14.9, 9.0, 1.0 Hz, 1H), 2.81 – 2.67 (m, 1H), 1.92 (dq, *J* = 9.1, 2.9 Hz, 1H), 1.89 – 1.65 (m, 3H), 1.42 – 1.31 (m, 1H). **Cis-syn: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.76, 139.93, 139.27, 124.26, 123.75, 122.84, 122.13, 121.19, 101.92, 69.77, 61.11, 42.36, 36.62, 28.80, 23.06, 19.52. **Cis-trans: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.78, 139.94, 139.42, 124.25, 123.76, 122.88, 122.14, 121.39, 102.03, 73.48, 64.32, 43.93, 39.62, 33.94, 22.62, 20.77. **HRMS** calculated for $C_{16}H_{18}O_2S$ (M + Na^+): 297.0920, found: 297.0920.

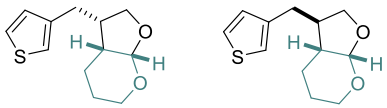
3-((hexahydro-4H-furo[2,3-b]pyran-3-yl)methyl)dibenzo[b,d]furan (11)



Eluent for purification: hexane: ethyl acetate = 10:1. White solid (46.2 mg, 75% yield, dr = 1.4:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.73 (t, *J* = 2.1 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.21 (m, 1H), 5.31 (d, *J* = 3.7 Hz,

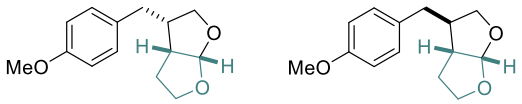
1H), 3.93 – 3.84 (m, 1H), 3.84 – 3.77 (m, 2H), 3.73 – 3.63 (m, 1H), 2.94 – 2.85 (m, 1H), 2.82 – 2.66 (m, 2H), 1.99 (q, *J* = 4.8 Hz, 1H), 1.81 – 1.58 (m, 4H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.73 (t, *J* = 2.1 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.21 (m, 1H), 5.06 (d, *J* = 3.7 Hz, 1H), 4.21 (t, *J* = 8.0 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.73 – 3.63 (m, 1H), 3.43 (td, *J* = 11.3, 2.4 Hz, 1H), 3.07 – 2.95 (m, 1H), 2.82 – 2.66 (m, 2H), 1.96 – 1.87 (m, 1H), 1.81 – 1.58 (m, 3H), 1.33 (m, 1H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 156.51, 154.91, 154.86, 134.61, 127.64, 127.46, 127.17, 124.42, 124.40, 124.06, 122.66, 120.58, 120.56, 120.17, 120.06, 111.70, 111.54, 111.52, 102.19, 102.00, 73.64, 69.90, 64.37, 61.03, 43.87, 43.00, 39.95, 38.68, 36.66, 33.36, 23.18, 22.55, 20.78, 19.64. **HRMS** calculated for $C_{20}H_{20}O_3$ (M + Na^+): 331.1305, found: 331.1302.

3-(thiophen-3-ylmethyl)hexahydro-4H-furo[2,3-b]pyran (12)



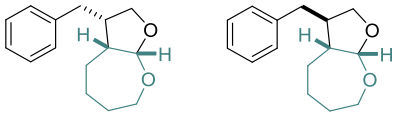
Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (30.0 mg, 67% yield, dr = 1.3:1). **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 1H), 6.97 – 6.86 (m, 2H), 5.29 (d, *J* = 3.7 Hz, 1H), 3.94 (t, *J* = 7.8 Hz, 1H), 3.77 (ddd, *J* = 12.8, 10.3, 7.7 Hz, 2H), 3.65 (dtd, *J* = 11.4, 3.3, 1.6 Hz, 1H), 2.83 – 2.57 (m, 3H), 1.99 (ddt, *J* = 12.1, 10.2, 4.9 Hz, 1H), 1.74 (m, 1H), 1.62 – 1.45 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 3.9 Hz, 1H), 6.96 – 6.88 (m, 2H), 5.03 (d, *J* = 3.3 Hz, 1H), 4.25 (t, *J* = 8.1 Hz, 1H), 3.89 (ddt, *J* = 11.7, 4.2, 2.5 Hz, 1H), 3.67 – 3.59 (m, 1H), 3.48 – 3.32 (m, 1H), 2.94 – 2.81 (m, 1H), 2.71 – 2.56 (m, 2H), 1.83 (m, 1H), 1.80 – 1.62 (m, 3H), 1.41 – 1.29 (m, 1H). **Cis-syn: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.36, 127.90, 125.71, 120.59, 101.97, 69.98, 61.05, 41.85, 36.63, 27.98, 23.13, 19.47. **Cis-anti: ^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.42, 128.03, 125.76, 120.75, 102.11, 73.75, 64.38, 43.89, 38.84, 33.14, 22.45, 20.75. **HRMS** calculated for $C_{12}H_{16}O_2S$ (M + Na^+): 247.0763, found: 247.0763.

3-(4-methoxybenzyl)hexahydrofuro[2,3-b]furan (13)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (28.1 mg, 60% yield, dr = 1.9:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomer is given herein. **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.11 – 7.05 (m, 2H), 6.83 (dd, *J* = 8.6, 2.0 Hz, 2H), 5.71 (d, *J* = 4.9 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.88 – 3.83 (m, 2H), 3.79 (s, 3H), 3.54 (dd, *J* = 10.2, 8.4 Hz, 1H), 2.77 (tt, *J* = 10.9, 5.2 Hz, 1H), 2.68 (dd, *J* = 11.0, 4.5 Hz, 1H), 2.62 (dd, *J* = 8.2, 3.3 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.08 – 1.95 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.11 – 7.05 (m, 2H), 6.83 (dd, *J* = 8.6, 2.0 Hz, 2H), 5.74 (d, *J* = 5.1 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.88 – 3.83 (m, 2H), 3.79 (s, 3H), 3.61 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.62 (dd, *J* = 8.2, 3.3 Hz, 2H), 2.55 (ddt, *J* = 8.5, 5.5, 3.0 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.08 – 1.95 (m, 1H), 1.89 – 1.83 (m, 1H), 1.66 – 1.57 (m, 1H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 158.05, 158.03, 131.99, 131.96, 129.76, 129.21, 113.96, 113.90, 109.82, 109.17, 72.21, 72.19, 69.13, 67.76, 55.25, 48.36, 47.47, 45.43, 44.00, 38.69, 32.88, 31.91, 25.12. **HRMS** calculated for $C_{14}H_{18}O_3$ ($M + Na^+$): 257.1148, found: 257.1150.

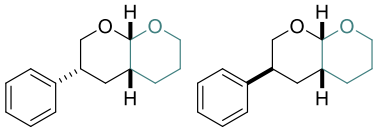
3-benzyloctahydrofuro[2,3-b]oxepine (14)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (25.1 mg, 54% yield, dr = 2.1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomer is given herein. **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 3H), 5.22 (d, *J* = 5.5 Hz, 1H), 4.05 (td, *J* = 4.0, 1.2 Hz, 1H), 4.02 (td, *J* = 4.0, 1.2 Hz, 1H), 3.77 (dd, *J* = 8.5, 6.1 Hz, 1H), 3.69 (dd, *J* = 8.5, 5.9 Hz, 1H), 2.60 (dd, *J* = 13.4, 10.5 Hz, 1H), 2.47 – 2.30 (m, 2H), 1.86 – 1.79 (m, 2H), 1.67 (ddt, *J* = 8.8, 5.8, 3.2 Hz, 2H), 1.44 – 1.33 (m, 3H). **Cis-trans: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 3H), 5.16 (d, *J* = 5.6 Hz, 1H), 4.15 – 4.07 (m, 2H), 3.48 (t, *J* = 8.5 Hz, 1H), 3.38 (ddd, *J* = 12.6, 6.0, 2.6 Hz, 1H), 2.83 (dd, *J* = 13.6, 5.3 Hz, 1H), 2.55 – 2.40 (m, 2H), 2.47 – 2.30 (m, 2H), 2.04 – 1.97 (m, 1H), 1.86 – 1.79 (m, 2H), 1.67 (ddt, *J* = 8.8, 5.8, 3.2 Hz, 2H), 1.44 – 1.33 (m, 2H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 140.92, 140.04, 128.65, 128.58, 128.43, 126.17, 125.96, 109.91, 109.53,

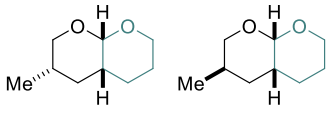
73.29, 71.96, 69.28, 68.91, 51.10, 48.49, 45.29, 42.83, 38.21, 34.07, 32.76, 32.33, 28.85, 26.70, 25.29, 24.72. **HRMS** calculated for $C_{15}H_{20}O_2$ (M + Na^+): 255.1356, found: 255.1355.

3-phenylhexahydro-2H, 5H-pyrano[2,3-b]pyran (15)



Eluent for purification: hexane: ethyl acetate = 20:1. Colorless oil (24.0mg, 55% yield, dr = 3:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **Cis-syn: ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 4.88 (d, J = 2.2 Hz, 1H), 4.19 – 4.06 (m, 1H), 3.99 – 3.85 (m, 1H), 3.79 – 3.66 (m, 1H), 3.65 – 3.52 (m, 1H), 3.15 – 3.02 (m, 1H), 1.94-1.92 (m, 1H), 1.92 – 1.75 (m, 2H), 1.75 – 1.70 (m, 2H), 1.70 – 1.59 (m, 1H), 1.59 – 1.51 (m, 1H). **Cis-anti: ^{1}H NMR** (400 MHz, Chloroform-d) δ 7.35 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 4.81 (d, J = 2.6 Hz, 1H), 4.19 – 4.06 (m, 1H), 3.99 – 3.85 (m, 1H), 3.79 – 3.66 (m, 1H), 3.65 – 3.52 (m, 1H), 2.95 (tt, J = 11.9, 4.0 Hz, 1H), 2.22 (q, J = 12.5 Hz, 1H), 2.07 – 1.94 (m, 2H), 1.92 – 1.75 (m, 1H), 1.70 – 1.59 (m, 2H), 1.35 – 1.24 (m, 1H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 142.11, 141.55, 128.52, 127.42, 127.36, 126.71, 97.96, 97.23, 71.91, 67.52, 66.02, 61.68, 42.31, 36.97, 34.99, 34.81, 34.07, 29.40, 28.10, 25.03, 23.21, 20.54. **HRMS** calculated for $C_{14}H_{18}O_2$ (M + Na^+): 241.1199, found: 241.1202.

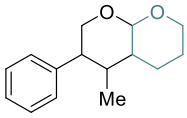
3-methylhexahydro-2H, 5H-pyrano[2,3-b]pyran (16)



Eluent for purification: hexane: ethyl acetate = 20:1. Colorless oil (16.2 mg, 52% yield, dr = 3:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomer is given herein. **Cis-syn: ^{1}H NMR** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.69 (d, *J* = 2.6 Hz, 1H), 3.92 (ddd, *J* = 11.4, 4.4, 2.5 Hz, 1H), 3.89 – 3.81 (m, 1H), 3.62 (m, 1H), 3.10 (dd, *J* = 11.4, 10.3 Hz, 1H), 1.83 – 1.70 (m, 3H), 1.62 – 1.50 (m, 3H), 1.48 – 1.43 (m, 1H), 1.34 – 1.25 (m, 1H), 0.78 (d, *J* = 6.7 Hz, 3H). **Cis-anti: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.69 (d, *J* = 2.6 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.58 – 3.46 (m, 2H), 3.41 (t, *J* = 11.1 Hz, 1H), 1.83 – 1.70 (m, 3H), 1.62 – 1.50 (m, 3H), 1.41 – 1.34 (m, 1H), 1.25 – 1.17 (m, 1H), 0.81 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 97.96, 97.30, 67.42,

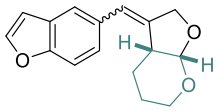
67.06, 62.89, 34.59, 30.98, 30.67, 30.41, 28.12, 25.43, 20.48, 19.73, 17.27, 16.65. **HRMS** calculated for $C_9H_{16}O_2$ (M + H^+): 157.1223, found: 157.1223.

4-methyl-3-phenylhexahydro-2H,5H-pyrano[2,3-b]pyran (17)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (37.6 mg, 81% yield, dr = 8.3:4.3:3.3:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 5.01 (d, *J* = 3.4 Hz, 1H), 4.01 (t, *J* = 8.6 Hz, 1H), 3.54 (td, *J* = 8.5, 1.9 Hz, 2H), 3.46 (ddd, *J* = 11.6, 10.5, 2.7 Hz, 1H), 2.54 – 2.47 (m, 1H), 1.94 (q, *J* = 3.3 Hz, 2H), 1.80 – 1.69 (m, 1H), 1.57 – 1.51 (m, 1H), 1.43 (m, 1H), 1.32 (m, 1H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 145.70, 145.25, 128.52, 128.44, 127.49, 127.12, 126.47, 126.37, 102.65, 102.38, 72.68, 71.81, 64.39, 64.13, 44.61, 44.16, 43.30, 43.16, 42.25, 24.06, 22.57, 21.08, 20.73, 20.55. **HRMS** calculated for $C_{15}H_{20}O_2$ (M + Na^+): 255.1356, found: 255.1355.

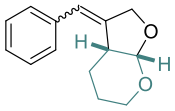
3-(benzofuran-5-ylmethylene)hexahydro-4H-furo[2,3-b]pyran (18)



Eluent for purification: hexane: ethyl acetate = 20:1. Colorless oil (30.0 mg, 67% yield, E:Z = 4:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two isomers is given herein. **E-isomer**: **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.62 (d, J = 2.2 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.22 (dd, J = 8.6, 1.8 Hz, 1H), 6.76 (dd, J = 2.3, 1.0 Hz, 1H), 6.40 (dd, J = 10.3, 2.3 Hz, 1H), 5.26 (d, J = 3.9 Hz, 1H), 4.76 (dt, J = 12.9, 1.9 Hz, 1H), 4.46 (dd, J = 12.8, 1.8 Hz, 1H), 3.95 – 3.86 (m, 1H), 3.68 (dtd, J = 11.1, 4.0, 1.4 Hz, 1H), 3.05 – 2.95 (m, 1H), 1.99 (m, 1H), 1.71 – 1.58 (m, 1H), 1.57 – 1.54 (m, 2H). **Z-isomer**: **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.62 (d, J = 2.2 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.37 (d, J = 1.7 Hz, 1H), 7.12 (dd, J = 8.6, 1.9 Hz, 1H), 6.76 (dd, J = 2.3, 1.0 Hz, 1H), 6.40 (dd, J = 10.3, 2.3 Hz, 1H), 5.21 (d, J = 3.8 Hz, 1H), 4.93 (dt, J = 13.6, 2.5 Hz, 1H), 4.83 (dt, J = 13.6, 2.2 Hz, 1H), 3.95 – 3.86 (m, 1H), 3.51 (td, J = 11.2, 2.5 Hz, 1H), 2.85 (m, 1H), 2.18 (m, 1H), 1.71 – 1.58 (m, 1H), 1.57 – 1.54 (m, 1H), 1.29 (d, J = 3.8 Hz, 1H). **^{13}C NMR (E & Z mixture)** (101 MHz, Chloroform-d) δ 153.95,

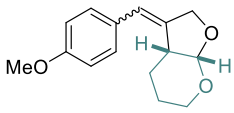
153.74, 145.53, 145.50, 140.70, 138.49, 132.14, 131.75, 127.76, 127.65, 124.80, 124.56, 121.64, 120.61, 120.24, 111.33, 111.26, 106.66, 106.62, 101.34, 100.62, 70.02, 70.00, 64.46, 61.56, 43.47, 38.33, 23.26, 23.03, 22.55, 20.62. **HRMS** calculated for $C_{16}H_{16}O_3$ (M + Na^+): 279.0992, found: 279.0988.

3-benzylidenehexahydro-4H-furo[2,3-b]pyran (19)



Eluent for purification: hexane: ethyl acetate = 20:1. Colorless oil (22.5 mg, 52% yield, E:Z = 5.6:1). **E-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 2H), 7.28 (d, *J* = 12.3 Hz, 3H), 6.31 (q, *J* = 2.0 Hz, 1H), 5.26 (d, *J* = 3.9 Hz, 1H), 4.75 (dt, *J* = 13.1, 1.9 Hz, 1H), 4.45 (ddd, *J* = 13.1, 2.0, 0.6 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.69 (dtd, *J* = 11.0, 3.8, 1.4 Hz, 1H), 3.02 – 2.95 (m, 1H), 2.05 – 1.94 (m, 1H), 1.72 – 1.63 (m, 1H), 1.61 – 1.54 (m, 2H). **Z-isomer**: **^{1}H NMR**(400 MHz, Chloroform-*d*) δ 7.35 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.19 – 7.11 (m, 2H), 6.29 (q, *J* = 2.6 Hz, 1H), 5.20 (d, *J* = 3.8 Hz, 1H), 4.90 (dt, *J* = 13.8, 2.5 Hz, 1H), 4.80 (dt, *J* = 13.9, 2.2 Hz, 1H), 3.93 – 3.81 (m, 1H), 3.50 (td, *J* = 11.3, 2.4 Hz, 1H), 2.84 (s, 1H), 2.21 – 2.07 (m, 1H), 2.08 – 1.92 (m, 1H), 1.72 – 1.63 (m, 1H), 1.36 (dq, *J* = 13.7, 3.4 Hz, 1H). **E-isomer**: **^{13}C NMR** (101 MHz, Chloroform-d) δ 141.89, 136.74, 128.47, 127.85, 126.90, 121.51, 101.29, 69.85, 61.46, 38.30, 23.23, 22.58. **Z-isomer**: **^{13}C NMR** (101 MHz, Chloroform-d) δ 139.95, 136.99, 128.54, 127.91, 126.65, 120.49, 100.56, 70.01, 64.46, 43.56, 23.01, 20.59. **HRMS** calculated for $C_{14}H_{16}O_2$ (M + H^+): 217.1123, found: 217.1124.

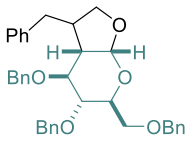
3-(4-methoxybenzylidene)hexahydro-4H-furo[2,3-b]pyran (20)



Eluent for purification: hexane: ethyl acetate = 20:1. Colorless oil (30.0 mg, 67% yield, E:Z = 4.6:1). **E-isomer**: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.26 – 7.18 (m, 2H), 6.91 – 6.84 (m, 2H), 6.24 (q, *J* = 1.9 Hz, 1H), 5.25 (d, *J* = 3.9 Hz, 1H), 4.72 (dt, *J* = 12.8, 1.9 Hz, 1H), 4.42 (dd, *J* = 12.9, 1.8 Hz, 1H), 3.99 – 3.85 (m, 1H), 3.82 (s, 3H), 3.69 (dtd, *J* = 11.0, 3.9, 1.6 Hz, 1H), 3.03 – 2.87 (m, 1H), 2.04 – 1.95 (m, 1H), 1.67 – 1.55 (m, 3H). **Z-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 – 7.02 (m, 2H), 6.94 – 6.85 (m, 2H), 6.23 (q, *J* = 2.6 Hz, 1H), 5.19 (d, *J* = 3.8 Hz, 1H), 4.88 (dt, *J* = 13.7, 2.5 Hz, 1H), 4.77 (dt, *J* = 13.7, 2.2 Hz, 1H),

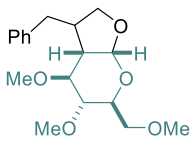
3.88 (ddt, *J* = 9.7, 4.0, 1.6 Hz, 1H), 3.82 (s, 3H), 3.50 (ddd, *J* = 11.6, 10.9, 2.4 Hz, 1H), 2.87 – 2.72 (m, 1H), 2.20 – 2.07 (m, 1H), 1.99 (m, 1H), 1.68 – 1.61 (m, 1H), 1.36 (dt, *J* = 13.7, 3.5 Hz, 1H). **E-isomer**: **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.57, 139.84, 129.48, 129.09, 120.96, 113.96, 101.34, 69.91, 61.47, 55.30, 38.21, 23.22, 22.65. **Z-isomer**: **^{13}C NMR** (101 MHz, Chloroform-d) δ 158.29, 137.45, 129.89, 129.14, 119.82, 113.99, 100.59, 70.01, 64.45, 55.28, 43.41, 23.00, 20.60. **HRMS** calculated for $C_{15}H_{18}O_3$ (M + Na^+): 269.1148, found: 269.1147.

3-benzyl-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)hexahydro-4H-furo[2,3-b]pyran (21)



Eluent for purification: hexane: ethyl acetate = 6:1. Colorless oil (47.3 mg, 43% yield, dr = 1.8:1.6:1.2:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.15 (m, 18H), 7.11 – 7.01 (m, 2H), 5.57 (d, *J* = 5.3 Hz, 1H), 4.69 – 4.50 (m, 5H), 4.44 (d, *J* = 11.0 Hz, 1H), 4.08 (dd, *J* = 8.9, 6.7 Hz, 1H), 3.83 (dt, *J* = 9.2, 3.1 Hz, 1H), 3.74 (dd, *J* = 10.6, 3.8 Hz, 1H), 3.70 – 3.62 (m, 2H), 3.58 (dd, *J* = 8.9, 4.3 Hz, 1H), 3.43 (t, *J* = 6.8 Hz, 1H), 2.65 (d, *J* = 7.8 Hz, 2H), 2.51 (dq, *J* = 11.2, 3.6 Hz, 1H), 2.27 – 2.14 (m, 1H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 140.10, 139.46, 138.46 , 138.43, 138.41, 138.12, 138.08, 138.01, 129.06, 128.89, 128.63, 128.55, 128.52, 128.49, 128.46, 128.42, 128.40, 128.36, 128.34, 128.32, 128.30, 127.98, 127.92, 127.89, 127.84, 127.78, 127.75, 127.72 , 127.70, 127.58, 127.55, 127.43, 127.38, 126.36, 126.29, 126.17, 102.55, 102.33, 102.24, 101.15, 81.20, 80.88, 79.23, 79.07, 77.54, 77.25, 77.19, 75.69, 75.25, 74.91, 74.85, 74.50, 74.40, 74.12, 73.99, 73.93, 73.70, 73.62, 73.50, 73.46, 73.40, 73.31, 72.90, 72.00, 71.67, 71.55, 71.53, 70.83, 69.32, 69.22, 69.08, 68.47, 49.71, 47.73, 46.68, 46.36, 42.71, 42.54, 40.43, 40.39, 39.60, 38.88, 38.23, 34.87. **HRMS** calculated for $C_{36}H_{38}O_5$ (M + H^+): 551.2792, found: 551.2789.

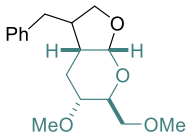
3-benzyl-4,5-dimethoxy-6-(methoxymethyl)hexahydro-4H-furo[2,3-b]pyran (22)



Eluent for purification: hexane: ethyl acetate = 6:1. Colorless oil (31.2 mg, 47%

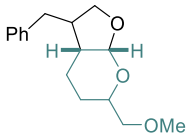
yield, dr = 1.5:1.5:1.4:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 5.40 (d, *J* = 4.3 Hz, 1H), 3.81 (t, *J* = 8.0 Hz, 1H), 3.76 – 3.70 (m, 1H), 3.70 – 3.64 (m, 3H), 3.63 (s, 3H), 3.57 (s, 3H), 3.42 (s, 3H), 3.41 – 3.31 (m, 2H), 3.12 (dd, *J* = 13.8, 4.9 Hz, 1H), 2.72 (dddd, *J* = 15.8, 10.6, 7.6, 5.1 Hz, 1H), 2.48 (dd, *J* = 13.8, 10.1 Hz, 1H), 2.21 (ddd, *J* = 9.4, 5.5, 4.2 Hz, 1H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 141.44, 140.55, 140.23, 139.44, 129.03, 128.86, 128.61, 128.53, 128.52, 128.41, 128.39, 128.28, 126.40, 126.24, 126.13, 125.97, 102.56, 102.42, 102.25, 101.11, 83.16, 82.66, 80.54, 80.33, 79.07, 78.32, 77.40, 76.83, 74.11, 74.06, 73.88, 73.85, 71.93, 71.72, 71.61, 71.58, 71.13, 71.02, 70.73, 70.60, 60.42, 60.23, 59.91, 59.30, 59.18, 59.06, 58.95, 58.63, 58.59, 58.54, 57.54, 48.94, 47.17, 45.81, 45.65, 42.62, 42.33, 40.31, 40.25, 39.51, 38.81, 37.89, 34.35. **HRMS** calculated for $C_{18}H_{26}O_5$ (M + Na^+): 345.1672, found: 345.1672.

3-benzyl-5-methoxy-6-(methoxymethyl)hexahydro-4H-furo[2,3-b]pyran (23)



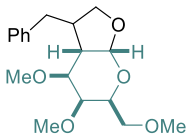
Eluent for purification: hexane: ethyl acetate = 6:1. Colorless oil (32.1 mg, 55% yield, dr = 1.3:1.2:1.2:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.13 (m, 3H), 5.47 (d, *J* = 5.4 Hz, 1H), 4.23 – 4.16 (m, 1H), 3.91 – 3.73 (m, 1H), 3.71 – 3.62 (m, 1H), 3.62 – 3.52 (m, 2H), 3.39 (s, 3H), 3.35 – 3.29 (m, 1H), 3.25 (s, 3H), 2.81 – 2.47 (m, 3H), 2.19 – 2.09 (m, 1H), 2.08 – 1.98 (m, 1H), 1.93 – 1.77 (m, 1H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 140.27, 139.84, 139.80, 139.67, 128.89, 128.79, 128.59, 128.57, 128.53, 128.50, 128.38, 128.26, 126.33, 126.30, 126.26, 126.18, 103.10, 102.56, 101.96, 101.25, 75.06, 74.60, 73.77, 73.57, 73.31, 73.25, 72.36, 72.31, 72.23, 72.09, 71.61, 71.56, 71.52, 71.19, 69.88, 59.31, 59.26, 57.07, 56.59, 56.57, 56.40, 44.75, 44.64, 42.33, 42.09, 41.25, 40.25, 39.38, 38.55, 37.73, 36.85, 34.17, 33.11, 27.62, 27.56, 25.68, 22.13. **HRMS** calculated for $C_{17}H_{24}O_4$ (M + Na^+): 315.1567, found: 315.1566.

3-benzyl-6-(methoxymethyl)hexahydro-4H-furo[2,3-b]pyran (24)



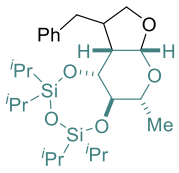
Eluent for purification: hexane: ethyl acetate = 6:1. Colorless oil (34.1 mg, 65% yield, dr = 2.4:1.1:1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.16 – 7.12 (m, 2H), 5.09 (d, *J* = 3.2 Hz, 1H), 4.19 (t, *J* = 8.2 Hz, 1H), 3.64 (t, *J* = 8.3 Hz, 1H), 3.58 – 3.49 (m, 1H), 3.47 – 3.41 (m, 1H), 3.39 (d, *J* = 8.8 Hz, 1H), 3.36 (s, 3H), 2.85 (dd, *J* = 12.9, 4.5 Hz, 1H), 2.67 – 2.52 (m, 2H), 1.84 (ddq, *J* = 10.1, 5.0, 2.3, 1.8 Hz, 2H), 1.76 (tt, *J* = 12.1, 3.2 Hz, 2H), 1.40 (m, 1H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 140.85, 140.04, 139.97, 139.93, 128.75, 128.62, 128.52, 128.49, 128.30, 126.23, 126.20, 126.07, 102.99, 102.65, 102.62, 101.18, 75.60, 75.47, 75.39, 75.27, 74.09, 73.55, 72.39, 71.61, 70.53, 69.56, 69.02, 68.56, 59.24, 44.90, 44.02, 42.44, 39.44, 39.09, 38.78, 38.59, 36.15, 36.01, 33.12, 25.25, 24.34, 23.67, 22.68, 21.81, 19.45. **HRMS** calculated for $C_{16}H_{22}O_3$ (M + Na^+): 285.1461, found: 285.1465.

3-benzyl-4,5-dimethoxy-6-(methoxymethyl)hexahydro-4H-furo[2,3-b]pyran (25)



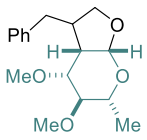
Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (35.4 mg, 55% yield, dr = 6.7:6:5.7:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 – 7.27 (m, 2H), 7.24 7.18 (m, 3H), 5.42 (d, *J* = 4.2 Hz, 1H), 3.79 – 3.76 (m, 2H), 3.71 – 3.69 (m, 1H), 3.67 – 3.65 (m, 1H), 3.64 (s, 3H), 3.57 (s, 3H), 3.44 (dd, *J* = 4.6, 1.6 Hz, 2H), 3.41 (s, 3H), 3.35 – 3.32 (m, 1H), 3.11 (dd, *J* = 9.8, 2.5 Hz, 1H), 2.75 (ddd, *J* = 7.5, 5.9, 4.2 Hz, 1H), 2.64 – 2.59 (m, 1H), 2.21 – 2.17 (m, 1H). **^{13}C NMR (four isomers)** (126 MHz, Chloroform-*d*) δ 141.10, 140.50, 139.69, 128.91, 128.67, 128.51, 128.50, 128.37, 128.27, 126.29, 126.21, 125.90, 102.74, 102.31, 101.04, 80.87, 80.83, 80.67, 74.77, 74.20, 72.64, 71.93, 71.51, 71.30, 71.14, 70.97, 70.91, 70.91, 70.39, 69.94, 69.63, 61.05, 60.83, 60.67, 59.19, 59.19, 59.16, 57.09, 57.03, 55.49, 48.16, 44.33, 42.48, 42.41, 40.95, 40.02, 39.80, 39.00, 35.26. **HRMS** calculated for $C_{18}H_{26}O_5$ (M + Na^+): 345.1672, found: 345.1672.

10-benzyl-2,2,4,4-tetraisopropyl-6-methylhexahydro-6H-furo[3',2':5,6]pyrano[3,4-f][1,3,5,2,4]trioxadisilepine (26)



Eluent for purification: hexane: ethyl acetate = 6:1. Colorless oil (44.6 mg, 44% yield, dr = 2.3:2.2:2.2:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.12 (m, 3H), 5.44 (d, *J* = 4.5 Hz, 1H), 4.19 – 3.99 (m, 1H), 3.82 – 3.67 (m, 2H), 3.40 (t, *J* = 8.9 Hz, 1H), 3.29 – 3.22 (m, 1H), 2.79 – 2.59 (m, 1H), 2.25 (dt, *J* = 9.5, 5.0 Hz, 1H), 1.98 (dd, *J* = 9.0, 4.5 Hz, 1H), 1.37 (d, *J* = 6.2 Hz, 1H), 1.15 – 1.00 (m, 31H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 140.77, 140.22, 139.51, 129.18, 128.78, 128.69, 128.56, 128.50, 128.47, 128.43, 128.21, 126.26, 126.09, 102.31, 101.86, 101.00, 77.91, 77.57, 77.21, 76.74, 76.33, 75.89, 74.01, 73.61, 73.52, 71.10, 71.06, 70.59, 70.54, 69.36, 68.63, 52.26, 49.36, 48.29, 43.41, 42.58, 41.05, 39.82, 39.00 , 35.08, 18.14, 17.92, 17.90, 17.81, 17.75, 17.71, 17.67, 17.60, 17.53, 17.49, 17.44, 17.42, 17.38, 17.32, 17.30, 17.30, 17.25, 17.23, 17.21, 16.99, 13.48, 12.98, 12.97, 12.92, 12.87, 12.78, 12.76, 12.73, 12.71, 12.34, 12.24, 12.20, 12.19. **HRMS** calculated for $C_{27}H_{46}O_5Si_2$ ($M + Na^+$): 529.2776, found: 529.2768.

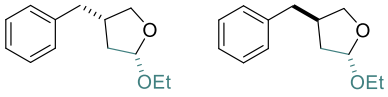
3-benzyl-4,5-dimethoxy-6-methylhexahydro-4H-furo[2,3-b]pyran (27)



Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (36.7mg, 77% yield, dr = 2.3:2:1.2:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomer is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 2H), 7.20 (t, *J* = 6.9 Hz, 3H), 5.44 (d, *J* = 5.7 Hz, 1H), 4.18 (dd, *J* = 8.8, 6.6 Hz, 1H), 3.70 – 3.63 (m, 1H), 3.63 (s, 3H), 3.37 (d, *J* = 4.2 Hz, 3H), 3.32 (t, *J* = 9.2 Hz, 1H), 3.05 – 2.95 (m, 2H), 2.83 (dd, *J* = 8.9, 5.4 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.53 – 2.36 (m, 1H), 2.17 (dq, *J* = 20.3, 5.3 Hz, 1H), 1.29 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 141.41, 140.62, 140.28, 139.48, 129.03, 128.85, 128.56, 128.54, 128.51, 128.44, 128.41, 128.29,

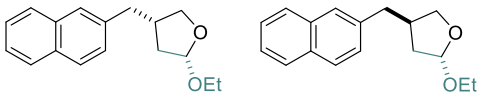
126.40, 126.23, 126.13, 126.01, 102.25, 102.13, 101.92, 100.85, 86.91, 84.50, 83.46, 83.03, 82.72, 82.57, 80.11, 78.74, 77.23, 74.06, 73.80, 71.75, 70.69, 70.53, 70.23, 68.00, 67.55, 60.78, 60.60, 60.43 , 59.04, 58.76, 58.51, 58.44, 57.54, 48.97, 47.30, 45.97, 42.70, 42.35, 40.39, 40.21 , 39.54, 38.95, 38.20, 34.32, 18.65, 18.42, 17.94, 17.40. **HRMS** calculated for $C_{17}H_{24}O_4$ ($M + Na^+$): 315.1567, found: 315.1565.

4-benzyl-2-ethoxytetrahydrofuran (28)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (33.4 mg, 81% yield, dr = 1.4:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **cis-isomer**: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.1, 6.8 Hz, 3H), 7.23 – 7.15 (m, 2H), 5.19 – 5.09 (m, 1H), 3.91 (dd, *J* = 8.4, 7.1 Hz, 1H), 3.74 (ddq, *J* = 27.0, 9.6, 7.1 Hz, 1H), 3.65 – 3.55 (m, 1H), 3.44 (ddq, *J* = 18.4, 9.6, 7.1 Hz, 1H), 2.84 – 2.71 (m, 2H), 2.49 (ddd, *J* = 15.9, 8.7, 7.4 Hz, 1H), 2.21 (ddd, *J* = 13.3, 9.1, 5.6 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). **trans-isomer**: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.1, 6.8 Hz, 3H), 7.23 – 7.15 (m, 2H), 5.19 – 5.09 (m, 1H), 3.99 (dd, *J* = 8.4, 7.0 Hz, 1H), 3.74 (ddq, *J* = 27.0, 9.6, 7.1 Hz, 1H), 3.65 – 3.55 (m, 1H), 3.44 (ddq, *J* = 18.4, 9.6, 7.1 Hz, 1H), 2.74 – 2.64 (m, 3H), 2.00 (ddd, *J* = 13.1, 7.1, 1.3 Hz, 1H), 1.71 (ddd, *J* = 13.2, 7.9, 5.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (trans & cis mixture)** (126 MHz, Chloroform-*d*) δ 140.86, 140.56, 128.69, 128.62, 128.44, 126.13, 126.05, 104.42, 103.95, 71.79, 71.72, 63.09, 62.69, 40.15, 39.93, 39.28, 39.16, 38.83, 15.37, 15.26. **HRMS** calculated for $C_{13}H_{18}O_2$ ($M + Na^+$): 229.1199, found: 229.1197.

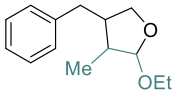
2-ethoxy-4-(naphthalen-2-ylmethyl)tetrahydrofuran (29)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (32.3 mg, 63% yield, dr = 1.1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **cis-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 3H), 7.64 – 7.59 (m, 1H), 7.45 (pd, *J* = 6.9, 1.6 Hz, 2H), 7.32 (dt, *J* = 8.4, 2.0 Hz, 1H), 5.20 – 5.13 (m, 1H), 3.94 (dd, *J* = 8.3, 7.2 Hz, 1H), 3.82 –

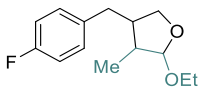
3.61 (m, 2H), 3.46 (ddq, *J* = 16.8, 9.7, 7.0 Hz, 1H), 2.95 (dd, *J* = 7.8, 2.1 Hz, 2H), 2.60 (ddd, *J* = 15.8, 8.6, 7.3 Hz, 1H), 2.23 (ddd, *J* = 13.4, 9.1, 5.6 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H). **trans-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 3H), 7.64 – 7.59 (m, 1H), 7.45 (pd, *J* = 6.9, 1.6 Hz, 2H), 7.32 (dt, *J* = 8.4, 2.0 Hz, 1H), 5.20 – 5.13 (m, 1H), 4.04 – 3.98 (m, 1H), 3.82 – 3.61 (m, 2H), 3.46 (ddq, *J* = 16.8, 9.7, 7.0 Hz, 1H), 2.89 – 2.80 (m, 3H), 2.04 (ddd, *J* = 12.8, 6.2, 1.9 Hz, 1H), 1.77 (ddd, *J* = 12.7, 7.5, 5.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 138.35, 138.06, 133.59, 133.55, 128.04, 128.02, 127.61, 127.46, 127.31, 127.29, 126.85, 126.77, 126.01, 125.98, 125.32, 125.28, 104.41, 103.95, 71.74, 63.10, 62.70, 40.10, 40.04, 39.45, 39.17, 38.82, 38.70, 15.38, 15.25. **HRMS** calculated for $C_{17}H_{20}O_2$ (M + Na^+): 279.1356, found: 279.1355.

4-benzyl-2-ethoxy-3-methyltetrahydrofuran (30)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (39.6 mg, 90% yield, dr = 2.4:2:1.7:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomers is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (m, 2H), 7.23 – 7.15 (m, 3H), 4.91 (d, *J* = 4.8 Hz, 1H), 4.00 – 3.89 (m, 1H), 3.84 – 3.62 (m, 1H), 3.55 (t, *J* = 8.3 Hz, 1H), 3.44 (m, 1H), 2.96 – 2.75 (m, 2H), 2.59 – 2.45 (m, 1H), 2.39 – 2.28 (m, 1H), 1.24 (td, *J* = 7.1, 0.9 Hz, 3H), 1.03 – 0.99 (m, 3H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 141.51, 140.77, 140.56, 140.47, 128.80, 128.59, 128.52, 128.44, 128.42, 128.39, 128.35, 126.06, 126.02, 125.80, 110.88 , 110.04, 105.52, 105.37, 72.47, 72.09, 71.36, 71.22, 63.42, 63.07, 62.79, 62.74, 48.15, 46.06, 44.73, 44.23, 42.03, 41.48, 41.47, 40.49, 38.87, 38.32, 35.53, 33.79, 16.94, 15.45, 15.36, 15.27, 15.24, 11.76, 11.68, 9.14. **HRMS** calculated for $C_{14}H_{20}O_2$ (M + Na^+): 243.1356, found: 243.1354.

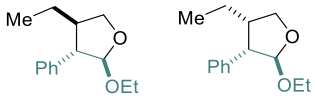
2-ethoxy-4-(4-fluorobenzyl)-3-methyltetrahydrofuran (31)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (33.3mg, 70% yield, dr = 1.8:1.6:1.1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomers is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 –

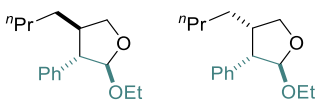
7.06 (m, 2H), 6.95 (td, *J* = 8.7, 1.8 Hz, 2H), 4.70 (d, *J* = 3.1 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.80 – 3.69 (m, 1H), 3.64 – 3.59 (m, 1H), 3.47 – 3.38 (m, 1H), 2.90 – 2.69 (m, 2H), 2.67 – 2.58 (m, 1H), 2.00 (tq, *J* = 8.7, 7.0 Hz, 1H), 1.23 – 1.20 (m, 3H), 0.98 (dd, *J* = 7.2 Hz, 3H). **^{13}C NMR (four isomers)** (101 MHz, Chloroform-*d*) δ 162.59, 162.58, 160.17, 160.15, 137.09 (d, *J* = 3.2 Hz), 136.19 (d, *J* = 3.2 Hz), 136.09 (d, *J* = 3.2 Hz), 130.08 (d, *J* = 7.7 Hz), 129.95 (d, *J* = 7.7 Hz), 129.93 (d, *J* = 7.9 Hz), 129.76, 115.29 (d, *J* = 21.1 Hz),, 115.27 (d, *J* = 21.2 Hz), 115.24 (d, *J* = 21.3 Hz), 115.18 (d, *J* = 21.1 Hz), 110.81, 110.00, 105.51, 105.32, 72.31, 71.94, 71.24, 71.06, 63.37, 63.07, 62.81, 62.75, 48.20, 45.89, 44.84, 44.17, 41.93, 41.57, 40.48, 38.04, 37.55, 34.74, 32.95, 17.01, 15.42, 15.33, 15.23, 15.20, 11.75, 11.61, 9.11. **HRMS** calculated for $C_{14}H_{19}FO_2$ (M + Na^+): 261.1261, found: 261.1260.

2-ethoxy-4-ethyl-3-phenyltetrahydrofuran (32)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (35.7 mg, 81% yield, dr = 5:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **trans-trans-isomer**: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 5.05 (d, *J* = 3.2 Hz, 1H), 4.23 (dt, *J* = 12.0, 8.1 Hz, 1H), 3.81 – 3.68 (m, 2H), 3.51 – 3.37 (m, 1H), 2.89 (dd, *J* = 8.2, 3.3 Hz, 1H), 2.28 – 2.18 (m, 1H), 1.65 – 1.57 (m, 1H), 1.50 – 1.41 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H). **cis-trans-isomer: ^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 5.13 (s, 1H), 4.23 (dt, *J* = 12.0, 8.1 Hz, 1H), 3.81 – 3.68 (m, 1H), 3.65 (dd, *J* = 9.5, 8.3 Hz, 1H), 3.51 – 3.37 (m, 1H), 3.31 (d, *J* = 7.5 Hz, 1H), 2.75 (m, 1H), 1.73 – 1.68 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.08 (dt, *J* = 13.8, 7.0 Hz, 1H), 0.82 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 142.21, 138.60, 128.72, 128.61, 128.33, 127.72, 126.57, 110.89, 108.97, 72.55, 72.18, 63.43, 62.64, 58.96, 54.58, 50.26, 43.25, 24.93, 21.74, 15.32, 15.30, 13.07, 12.81. **HRMS** calculated for $C_{14}H_{20}O_2$ (M +Na^+): 243.1356, found: 243.1356.

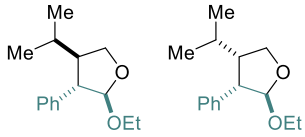
4-butyl-2-ethoxy-3-phenyltetrahydrofuran (33)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil

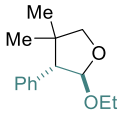
(44.7 mg, 90% yield, dr = 7.7:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **trans-trans-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.27 – 7.16 (m, 3H), 5.03 (d, *J* = 3.3 Hz, 1H), 4.25 – 4.16 (m, 1H), 3.78 – 3.67 (m, 2H), 3.41 (dq, *J* = 9.6, 7.0 Hz, 1H), 2.87 (dd, *J* = 8.4, 3.3 Hz, 1H), 2.27 (dtdd, *J* = 9.9, 8.6, 7.2, 5.5 Hz, 1H), 1.60 – 1.48 (m, 1H), 1.44 – 1.35 (m, 1H), 1.25 – 1.14 (m, 7H), 0.82 (t, *J* = 7.0 Hz, 3H). **cis-trans-isomer: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.27 – 7.16 (m, 3H), 5.12 (s, 1H), 4.25 – 4.16 (m, 1H), 3.78 – 3.67 (m, 1H), 3.66 – 3.59 (m, 1H), 3.41 (dq, *J* = 9.6, 7.0 Hz, 1H), 3.28 (d, *J* = 7.5 Hz, 1H), 2.84 – 2.75 (m, 1H), 1.60 – 1.48 (m, 1H), 1.25 – 1.14 (m, 7H), 1.06 – 1.02 (m, 1H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.06, 138.57, 128.66, 128.56, 128.28, 127.70, 126.54, 126.51, 110.81, 108.86, 72.74, 72.31, 63.43, 61.85, 59.20, 54.65, 48.60, 41.25, 31.64, 30.59, 28.23, 22.80, 22.69, 15.29, 15.25, 13.91. **HRMS** calculated for $C_{16}H_{24}O_2$ (M + Na^+): 271.1669, found: 271.1671.

2-ethoxy-4-isopropyl-3-phenyltetrahydrofuran (34)



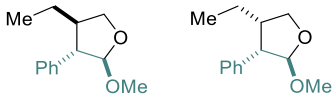
Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (43.7 mg, 88% yield, dr = 2.8:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **trans-trans-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.18 (m, 5H), 4.95 (d, *J* = 2.5 Hz, 1H), 4.17 (t, *J* = 8.0 Hz, 1H), 3.82 – 3.64 (m, 2H), 3.49 – 3.34 (m, 1H), 3.01 (dd, *J* = 7.4, 2.5 Hz, 1H), 2.15 – 2.03 (m, 1H), 1.75 (dp, *J* = 8.8, 6.6 Hz, 1H), 1.20 (dt, *J* = 16.8, 7.1 Hz, 3H), 0.87 – 0.82 (m, 6H). **cis-trans-isomer: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.18 (m, 5H), 5.01 (s, 1H), 4.22 (t, *J* = 8.5 Hz, 1H), 3.82 – 3.64 (m, 2H), 3.49 – 3.34 (m, 1H), 3.30 (d, *J* = 7.2 Hz, 1H), 2.53 (tdd, *J* = 10.7, 8.6, 7.1 Hz, 1H), 1.20 (dt, *J* = 16.8, 7.1 Hz, 3H), 1.08 (dq, *J* = 10.9, 6.5 Hz, 1H), 0.87 – 0.82 (m, 3H), 0.77 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.65, 138.72, 129.03, 128.53, 128.30, 127.74, 126.58, 126.32, 111.23, 109.49, 71.55, 71.03, 62.99, 62.50, 57.41, 55.58, 54.08, 49.24, 31.48, 27.41, 21.93, 21.85, 21.70, 21.04, 15.27. **HRMS** calculated for $C_{15}H_{22}O_2$ (M + Na^+): 257.1512, found: 257.1511.

2-ethoxy-4,4-dimethyl-3-phenyltetrahydrofuran (35)



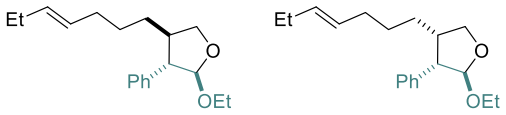
Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (22.0 mg, 50% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 2H), 7.22 – 7.17 (m, 1H), 7.14 – 7.08 (m, 2H), 5.34 (d, *J* = 4.8 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.73 (dq, *J* = 9.5, 7.1 Hz, 1H), 3.66 (d, *J* = 8.1 Hz, 1H), 3.39 (dq, *J* = 9.5, 7.1 Hz, 1H), 2.93 (d, *J* = 4.8 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.03 (s, 3H), 0.69 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.38, 128.91, 128.17, 126.74, 109.17, 80.00, 64.00, 62.54, 43.39, 24.75, 22.86, 15.30. **HRMS** calculated for $C_{14}H_{20}O_2$ ($M + Na^+$): 243.1356, found: 243.1355.

4-ethyl-2-methoxy-3-phenyltetrahydrofuran (36)



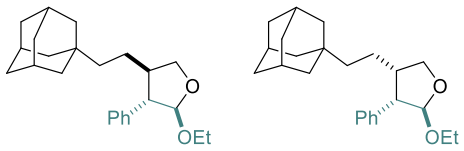
Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (28.4 mg, 69% yield, dr = 5:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **trans-trans-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 2H), 7.18 – 7.09 (m, 3H), 4.86 (d, *J* = 3.1 Hz, 1H), 4.20 – 4.11 (m, 1H), 3.59 (ddd, *J* = 12.6, 9.7, 8.4 Hz, 1H), 3.27 (s, 3H), 2.79 (dd, *J* = 8.2, 3.1 Hz, 1H), 2.15 (dtdd, *J* = 9.9, 8.3, 7.3, 5.7 Hz, 1H), 1.51 (dtd, *J* = 15.0, 7.5, 5.7 Hz, 1H), 1.45 – 1.29 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H). **cis-trans-isomer: ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 2H), 7.18 – 7.09 (m, 3H), 4.93 (s, 1H), 4.20 – 4.11 (m, 1H), 3.59 (ddd, *J* = 12.6, 9.7, 8.4 Hz, 1H), 3.31 (s, 3H), 3.22 (d, *J* = 7.5 Hz, 1H), 2.69 – 2.56 (m, 1H), 1.51 (dtd, *J* = 15.0, 7.5, 5.7 Hz, 1H), 1.45 – 1.29 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (trans & cis mixture)** (126 MHz, Chloroform-*d*) δ 205.16, 204.81, 157.10, 154.80, 128.78, 123.41, 123.38, 122.56, 120.34, 110.83, 110.80, 103.78, 103.73, 57.67, 57.54, 33.58, 33.35, 32.95, 31.89, 19.76, 17.95, 16.83, 16.45, 12.21, 12.09. **HRMS** calculated for $C_{13}H_{18}O_2$ ($M + H^+$): 207.1380, found: 207.1370.

2-ethoxy-4-((E)-hept-4-en-1-yl)-3-phenyltetrahydrofuran (37)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (30.6 mg, 53% yield, dr = 5:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **trans-trans-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.26 – 7.20 (m, 3H), 5.38 – 5.23 (m, 2H), 5.02 (d, *J* = 3.3 Hz, 1H), 4.24 – 4.16 (m, 1H), 3.80 – 3.65 (m, 2H), 3.49 – 3.35 (m, 1H), 2.87 (dd, *J* = 8.4, 3.3 Hz, 1H), 2.27 (dtdd, *J* = 10.0, 8.6, 7.3, 5.6 Hz, 1H), 1.99 – 1.87 (m, 4H), 1.54 (ddd, *J* = 13.2, 10.7, 6.3 Hz, 1H), 1.40 (dtd, *J* = 13.2, 8.7, 6.5 Hz, 1H), 1.28 – 1.23 (m, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). **cis-trans-isomer:** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.15 (m, 1H), 5.38 – 5.23 (m, 2H), 5.11 (s, 1H), 4.24 – 4.16 (m, 1H), 3.80 – 3.65 (m, 1H), 3.62 (dd, *J* = 9.6, 8.2 Hz, 1H), 3.49 – 3.35 (m, 1H), 3.28 (d, *J* = 7.5 Hz, 1H), 2.79 (dt, *J* = 16.6, 8.3 Hz, 1H), 1.99 – 1.87 (m, 4H), 1.54 (ddd, *J* = 13.2, 10.7, 6.3 Hz, 1H), 1.40 (dtd, *J* = 13.2, 8.7, 6.5 Hz, 1H), 1.28 – 1.23 (m, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 142.05, 141.99, 132.37, 131.93, 128.66, 128.56, 127.69, 126.55, 110.81, 108.86, 72.69, 72.69, 63.44, 63.42, 59.14, 54.59, 48.45, 41.19, 32.56, 32.38, 31.59, 31.35, 28.56, 28.33, 25.52, 20.45, 15.27, 14.30, 13.90. **HRMS** calculated for $C_{19}H_{28}O_2$ (M + Na^+): 311.1982, found: 311.1981.

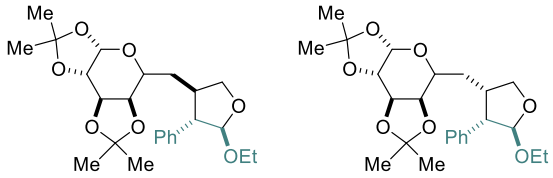
4-(2-((3r,5r,7r)-adamantan-1-yl)ethyl)-2-ethoxy-3-phenyltetrahydrofuran (38)



Eluent for purification: hexane: ethyl acetate = 100:1. Colorless oil (51.0 mg, 72% yield, dr = 7.1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the two diastereomers is given herein. **trans-trans-isomer**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.27 – 7.16 (m, 3H), 5.02 (d, *J* = 3.3 Hz, 1H), 4.19 (dd, *J* = 8.2, 7.2 Hz, 1H), 3.81 – 3.57 (m, 2H), 3.43 (ddq, *J* = 16.7, 9.7, 7.0 Hz, 1H), 2.87 (dd, *J* = 8.2, 3.2 Hz, 1H), 2.18 (dddd, *J* = 13.1, 9.8, 8.7, 7.4 Hz, 1H), 1.95 – 1.87 (m, 3H), 1.71 – 1.47 (m, 8H), 1.39 (d, *J* = 2.8 Hz, 6H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.02 – 0.85 (m, 2H). **cis-trans-isomer:** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.27 – 7.16 (m,

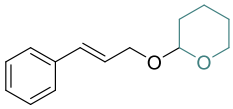
3H), 5.10 (s, 1H), 4.19 (dd, *J* = 8.2, 7.2 Hz, 1H), 3.81 – 3.57 (m, 2H), 3.43 (ddq, *J* = 16.7, 9.7, 7.0 Hz, 1H), 3.28 (d, *J* = 7.5 Hz, 1H), 2.70 (qd, *J* = 9.0, 4.4 Hz, 1H), 1.95 – 1.87 (m, 2H), 1.87 – 1.80 (m, 1H), 1.71 – 1.47 (m, 8H), 1.37 – 1.30 (m, 6H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.02 – 0.85 (m, 3H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 142.20, 138.39, 128.75, 128.56, 128.24, 127.70, 126.53, 126.51, 110.83, 108.97, 72.78, 72.38, 63.38, 62.56, 59.24, 54.37, 49.09, 43.41, 43.06, 42.31, 42.19, 41.99, 37.20, 37.14, 37.10, 32.13, 32.05, 29.69, 28.83, 28.68, 28.63, 24.92, 20.97, 15.29, 15.27. **HRMS** calculated for $C_{24}H_{34}O_2$ (M + Na^+): 377.2451, found: 377.2453.

(3aS,5aR,8aR,8bS)-5-((5-ethoxy-4-phenyltetrahydrofuran-3-yl)methyl)-2,2,7,7 tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (39)



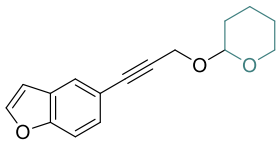
Eluent for purification: hexane: ethyl acetate = 10:1. Colorless oil (Z: 42 mg, 78% yield, dr = 2.6:2:1; E: 42 mg, 69% yield, dr = 1.1:1). Isolated as an inseparable mixture of diastereomers. Spectral data for the major diastereomers is given herein. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.14 (m, 5H), 5.47 (dd, *J* = 5.2, 1.9 Hz, 1H), 5.01 (t, *J* = 3.2 Hz, 1H), 4.51 (m, 1H), 4.34 – 4.21 (m, 2H), 3.95 – 3.93 (m, 1H), 3.80 – 3.69 (m, 2H), 3.64 – 3.56 (m, 1H), 3.39 (m, 1H), 2.90 (dt, *J* = 8.7, 3.1 Hz, 1H), 2.62 – 2.52 (m, 1H), 1.79 – 1.76 (m, 1H), 1.63 – 1.49 (m, 1H), 1.50 (s, 3H), 1.44 – 1.37 (m, 9H), 1.17 (td, *J* = 7.1, 2.5 Hz, 3H). **^{13}C NMR (trans & cis mixture)** (101 MHz, Chloroform-*d*) δ 141.39, 141.35, 138.51, 128.68, 128.57, 128.44, 127.85, 127.77, 126.65, 126.62, 126.59, 110.81, 110.00, 109.07, 109.01, 108.98, 108.75, 108.24, 108.16, 96.52, 96.46, 96.41, 77.24, 73.12, 72.99, 72.85, 72.16, 71.77, 70.91, 70.89, 70.43, 70.38, 70.28, 67.47, 66.21, 65.69, 63.43, 63.34, 62.54, 59.30, 59.00, 47.27, 43.87, 36.95, 32.50, 32.21, 29.68, 29.20, 26.02, 25.98, 25.91, 24.86, 24.82, 24.44, 24.25, 15.29, 15.18. **HRMS** calculated for $C_{24}H_{34}O_7$ (M + Na^+): 457.2197, found: 457.2196

2-(cinnamyloxy)tetrahydro-2H-pyran (40)



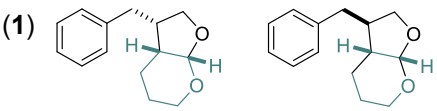
Eluent for purification: hexane: ethyl acetate = 20:1. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 6.64 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.33 (ddd, *J* = 15.9, 6.6, 5.6 Hz, 1H), 4.72 (dd, *J* = 4.2, 3.0 Hz, 1H), 4.42 (ddd, *J* = 12.9, 5.6, 1.6 Hz, 1H), 4.17 (ddd, *J* = 12.9, 6.6, 1.4 Hz, 1H), 3.93 (ddd, *J* = 11.3, 8.0, 3.4 Hz, 1H), 3.61 – 3.49 (m, 1H), 1.94 – 1.82 (m, 1H), 1.81 – 1.71 (m, 1H), 1.67 – 1.51 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 136.81, 132.30, 128.50, 127.59, 126.48, 126.01, 97.86, 67.63, 62.24, 30.64, 25.48, 19.48. **HRMS** calculated for $C_{14}H_{18}O_2$ (M + Na^+): 241.1199, found: 241.1197.

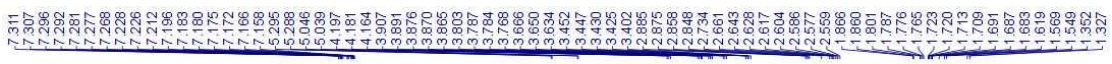
5-(3-((tetrahydro-2H-pyran-2-yl)oxy)prop-1-yn-1-yl)benzofuran



Eluent for purification: hexane: ethyl acetate = 20:1. Colorless oil (6 mg, 23% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 1.5 Hz, 1H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.37 (m, 2H), 6.75 (d, *J* = 2.1 Hz, 1H), 4.94 (t, *J* = 3.5 Hz, 1H), 4.61 – 4.43 (m, 2H), 3.92 (ddd, *J* = 11.6, 9.0, 3.0 Hz, 1H), 3.59 (dtd, *J* = 11.0, 4.3, 1.6 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.79 (tt, *J* = 10.2, 3.4 Hz, 1H), 1.72 – 1.57 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.65, 145.83, 128.28, 127.50, 125.09, 117.30, 111.47, 106.50, 96.89, 86.13, 83.70, 62.08, 54.90, 30.37, 25.45, 19.14. **HRMS** calculated for $C_{16}H_{16}O_3$ (M + Na^+): 279.0992, found: 279.0993.

(1)

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7.281
7.277
7.268
7.228
7.226
7.212
7.196
7.183
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7.175
7.172
7.166
7.158
5.295
5.288
5.046
5.039
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4.181
4.164
3.907
3.891
3.876
3.870
3.865
3.803
3.787
3.784
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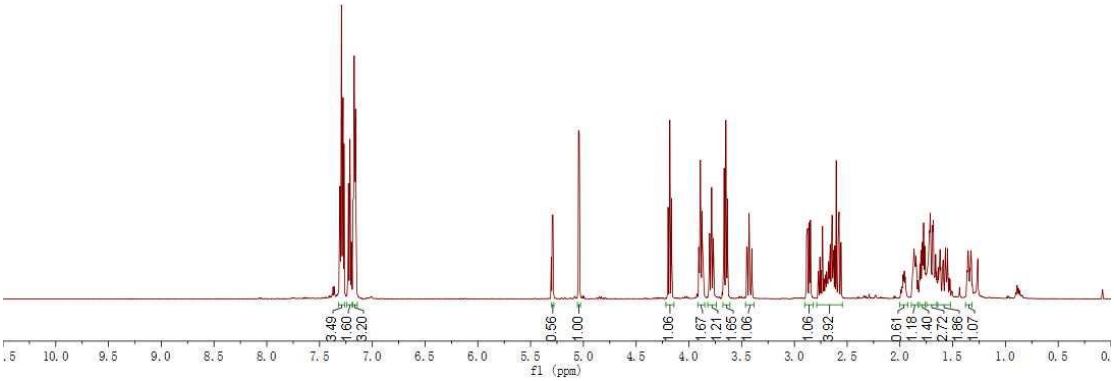
1.352
1.327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1.06
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1.65
1.06
1.06
3.92
0.61
1.18
1.40
2.72
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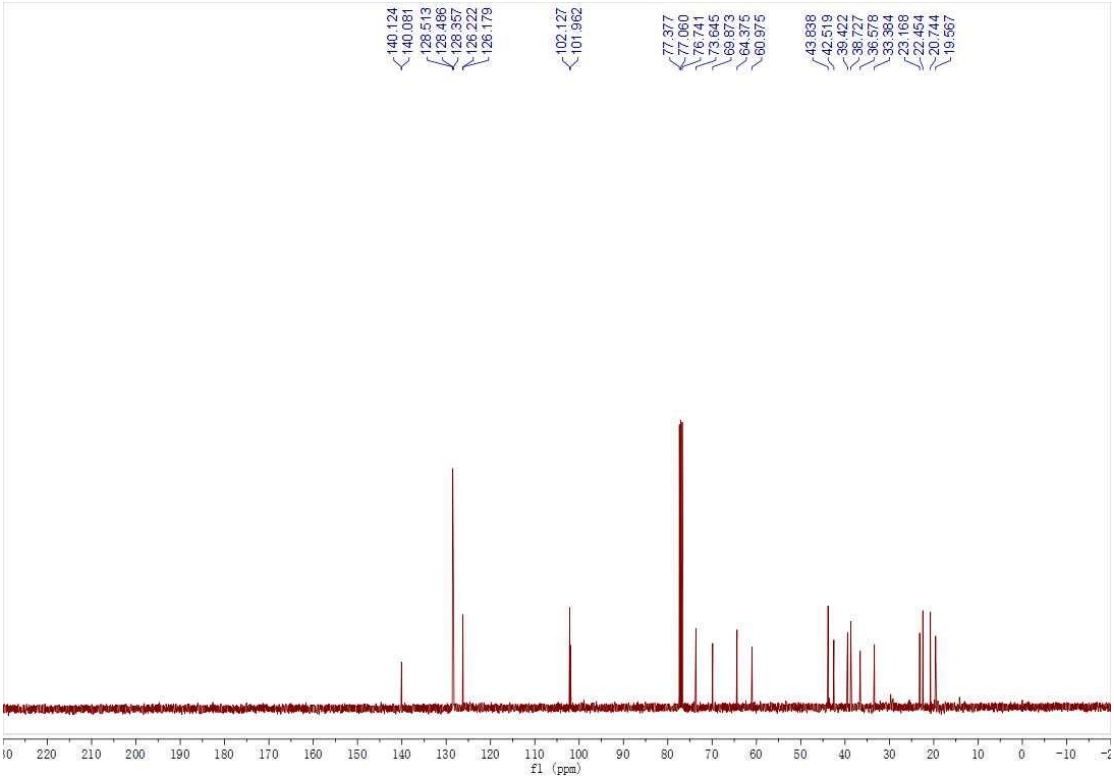
1.07
f1 (ppm)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126.222
126.179
102.127
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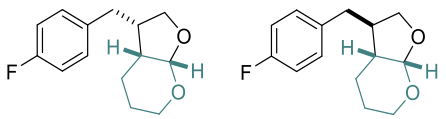
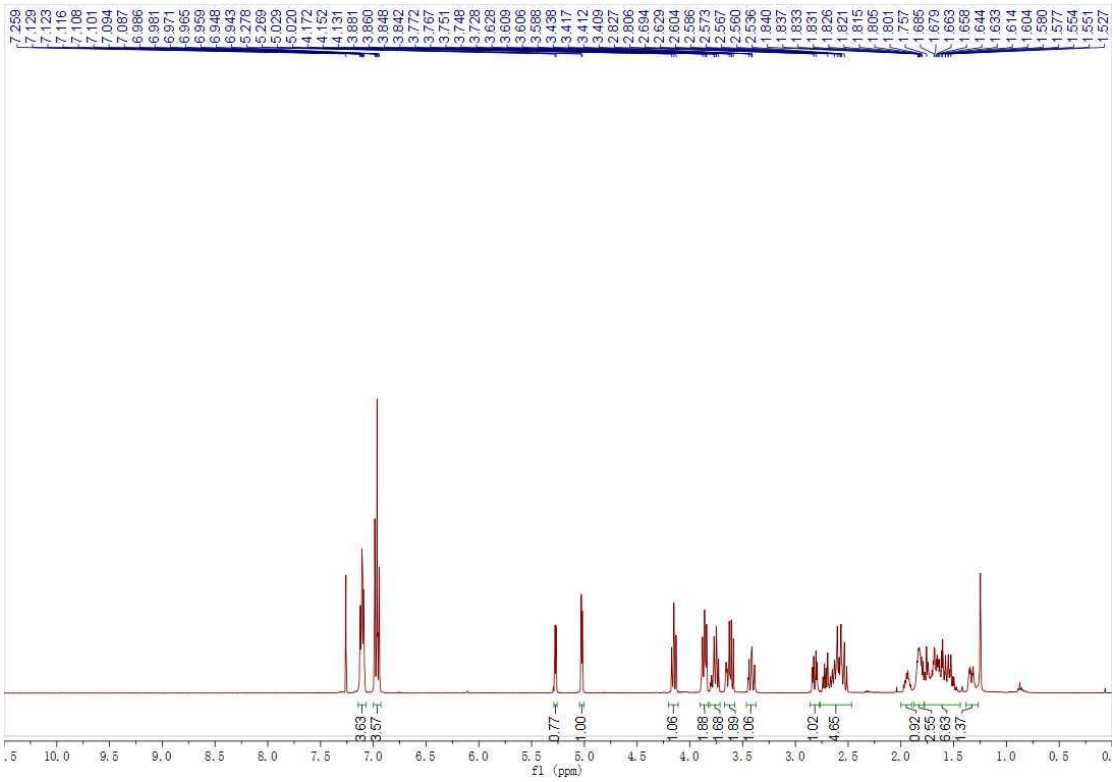
22.454
20.744
19.567
f1 (ppm)

(**2**)


F
H
O
H
O
F
H
O
H
O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1.831
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1.658
1.644
1.633
1.614
1.604
1.580
1.577
1.554
1.551
1.527
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3.57
0.77
1.00
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1.89
1.06
1.02
4.65
0.92
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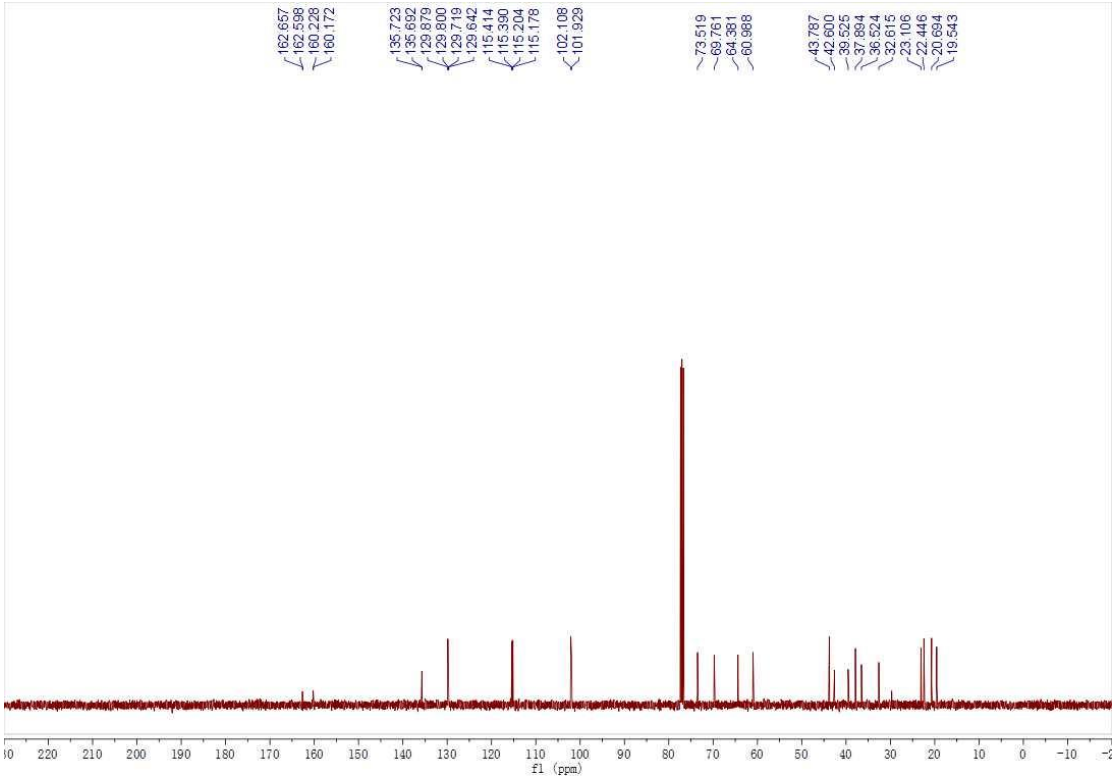
6.63
1.37
f1 (ppm)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129.800
129.719
129.642
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115.390
115.204
115.178
102.108
101.929
73.519
69.761
64.381
60.988
43.787
42.600
39.525
37.894
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32.615
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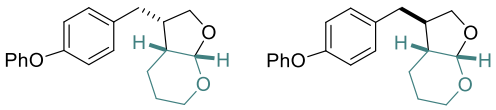
22.446
20.694
19.543
f1 (ppm)

(**3**)


PhO
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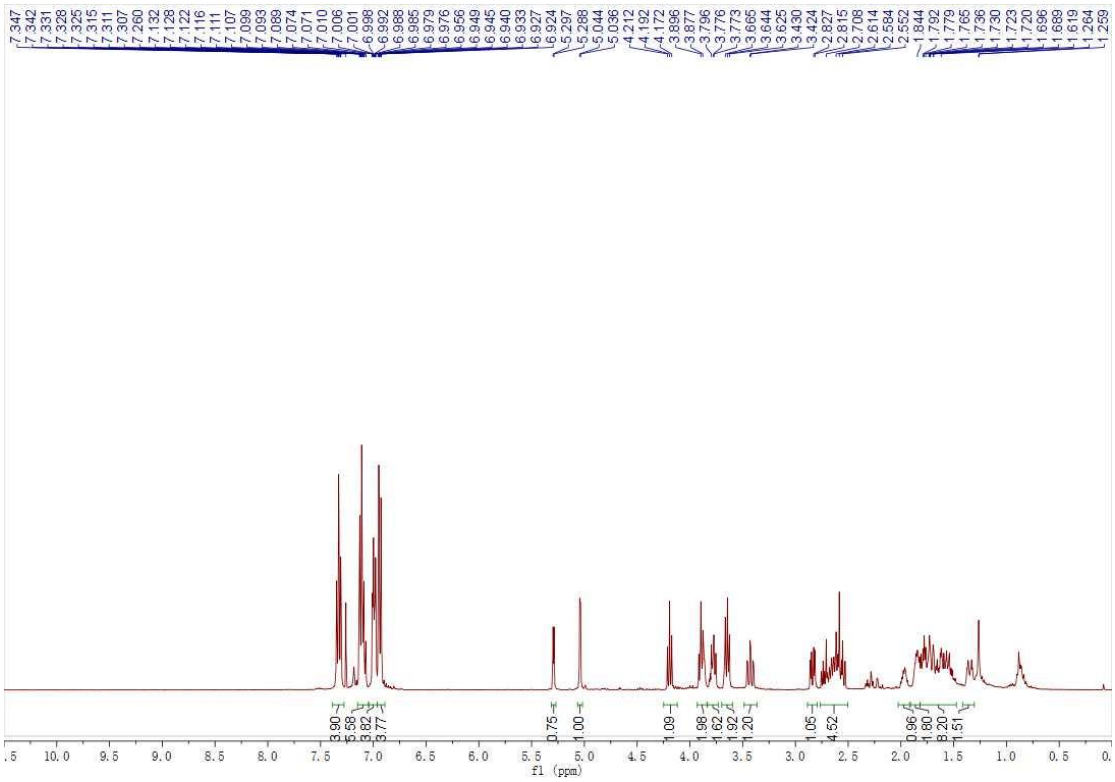
O
H
O
PhO
H
O
H
O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7.099
7.093
7.089
7.074
7.071
7.010
7.006
7.001
6.998
6.992
6.988
6.985
6.979
6.976
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6.949
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2.815
2.708
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1.730
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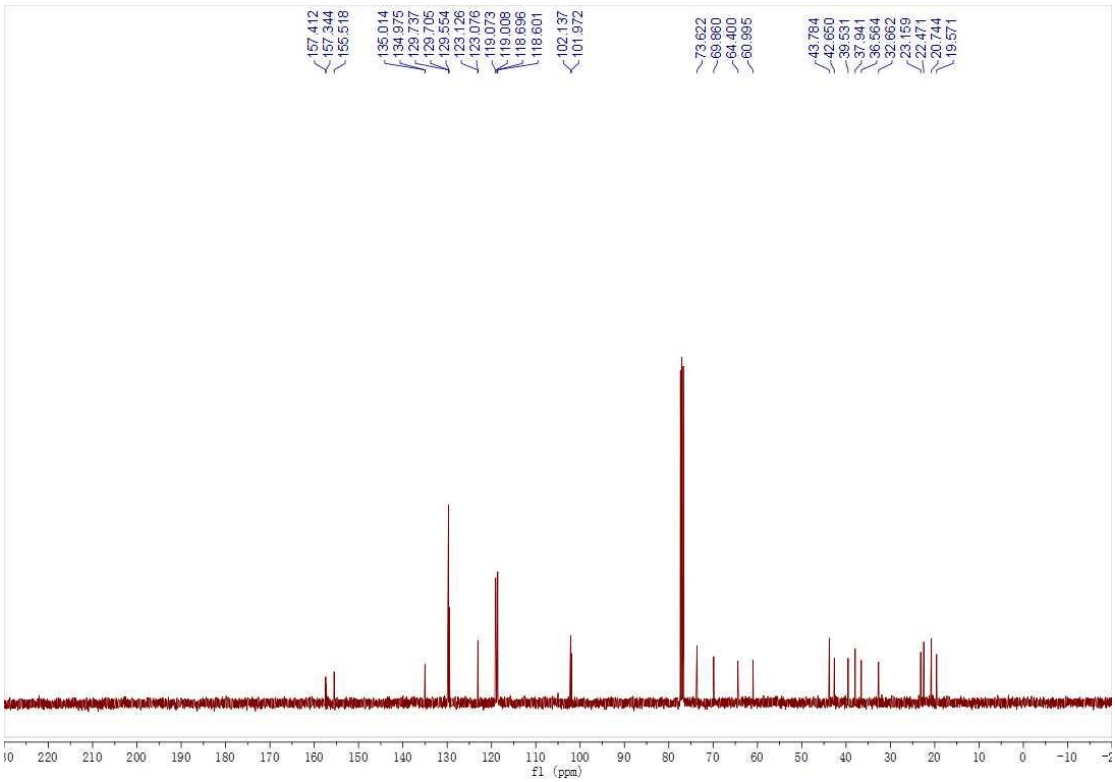
1.720
1.696
1.689
1.619
1.264
1.259
3.90
5.68
3.92
3.77
0.75
1.00
1.09
1.98
1.62
1.92
1.20
1.05
4.52
0.96
1.80
8.20
1.51
f1 (ppm)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129.705
129.554
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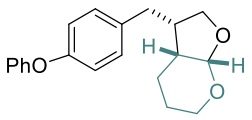
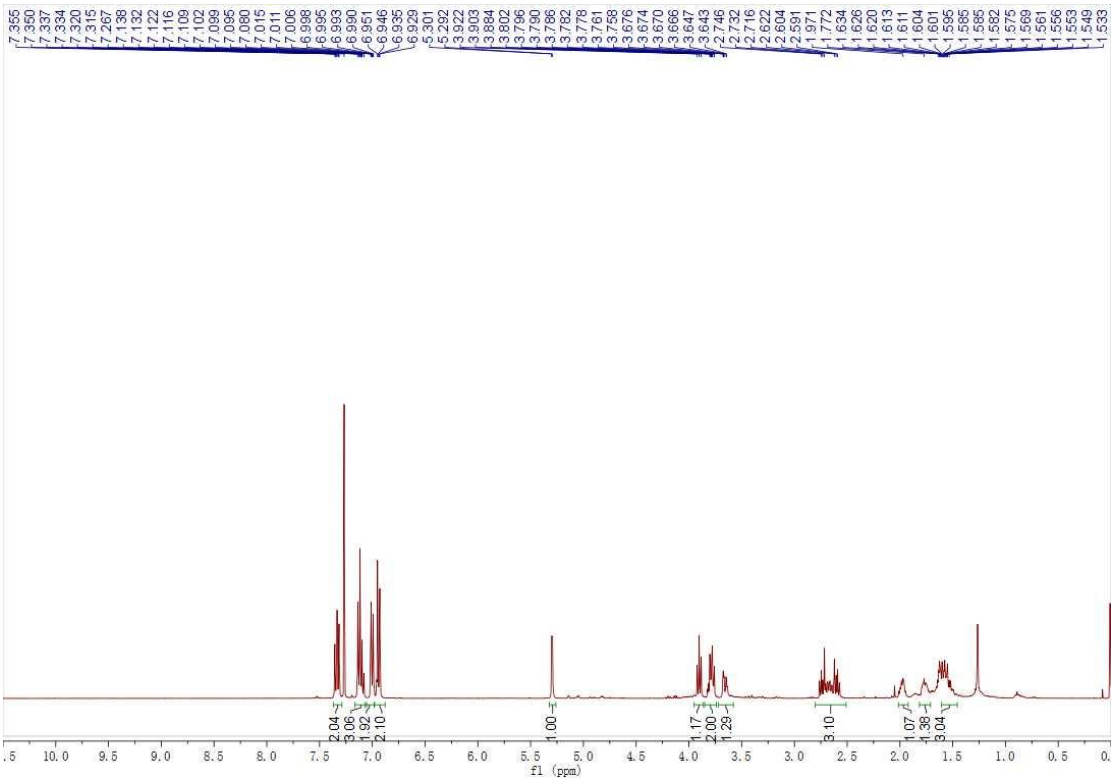
123.076
119.073
119.008
118.696
118.601
102.137
101.972
73.622
69.860
64.400
60.995
43.784
42.650
39.531
37.941
36.564
32.662
23.159
22.471
20.744
19.571
f1 (ppm)


PhO
H
O
H
O

cis-syn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7.267
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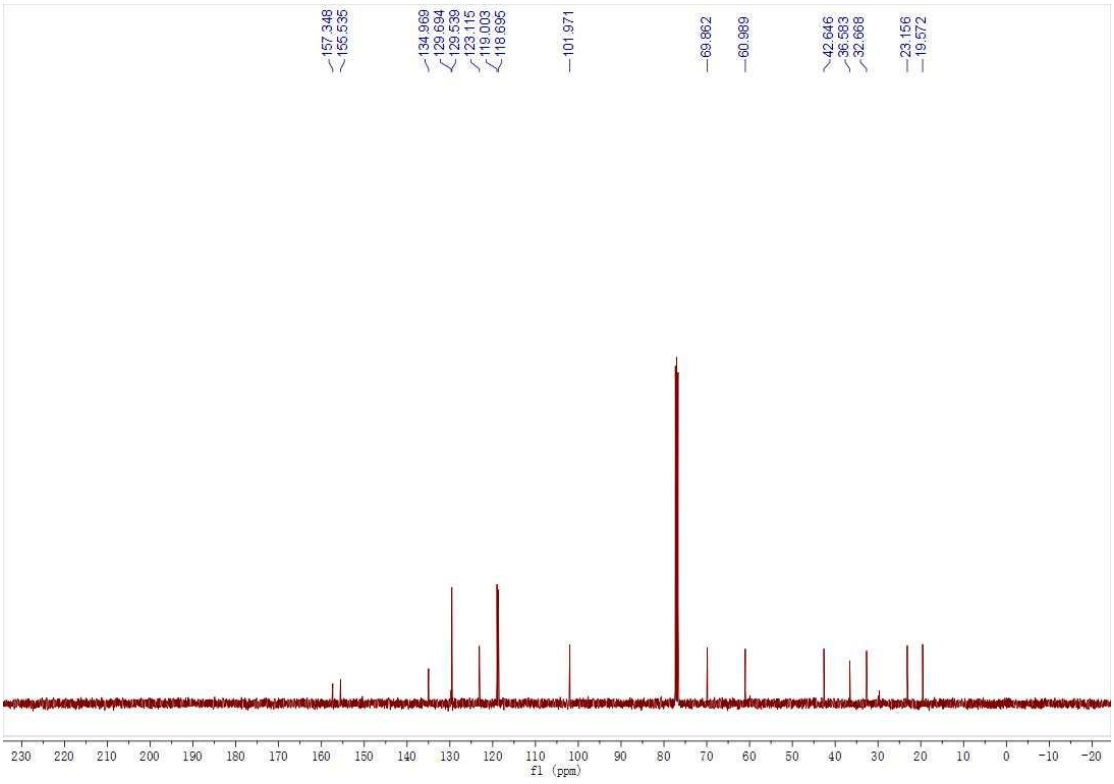
7.132
7.122
7.116
7.109
7.102
7.099
7.095
7.080
7.015
7.011
7.006
6.998
6.995
6.993
6.990
6.951
6.946
6.935
6.929
5.301
5.292
3.922
3.903
3.884
3.802
3.796
3.790
3.786
3.782
3.778
3.761
3.758
3.676
3.674
3.670
3.666
3.647
3.643
2.746
2.732
2.716
2.622
2.604
2.591
1.971
1.772
1.634
1.626
1.620
1.613
1.611
1.604
1.601
1.595
1.585
1.585
1.582
1.575
1.569
1.561
1.556
1.553
1.549
1.533
2.04
3.06
1.92
2.10
1.00
1.17
2.00
1.29
3.10
1.07
1.38
3.04
f1 (ppm)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155.535
134.969
129.694
129.539
123.115
119.003
118.695
101.971
69.862
60.989
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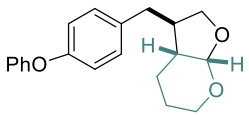
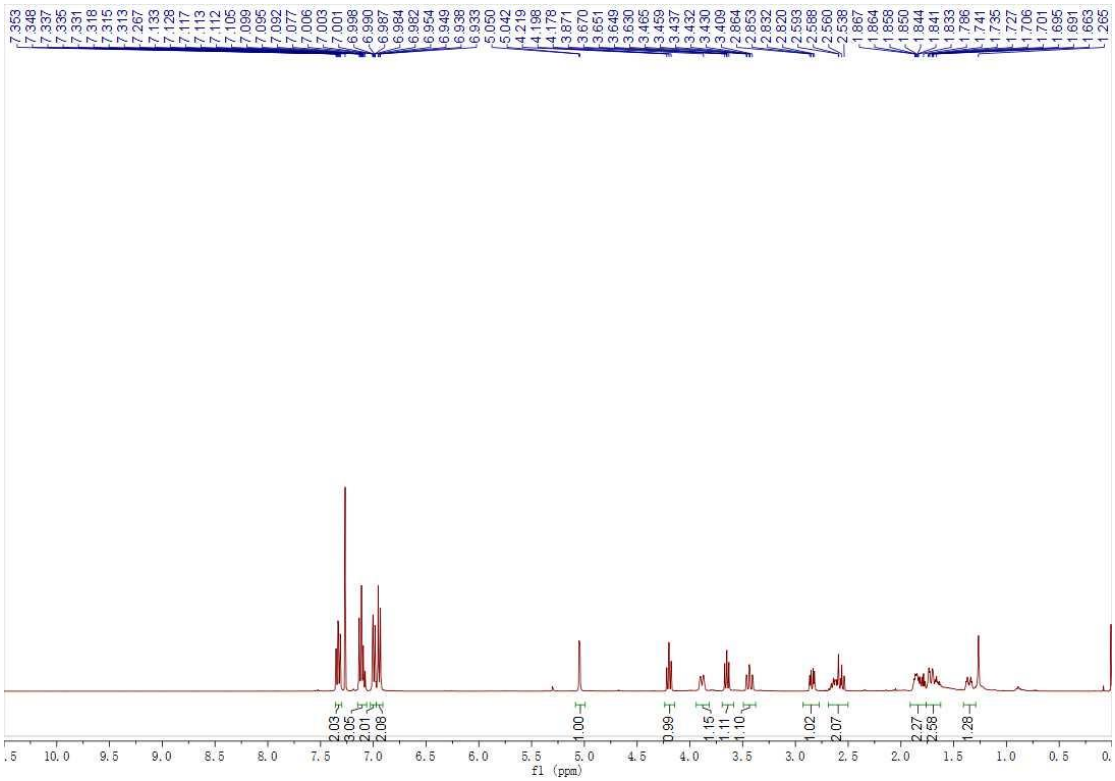
36.383
32.668
23.156
19.572
f1 (ppm)


PhO
H
O
H
O

cis-anti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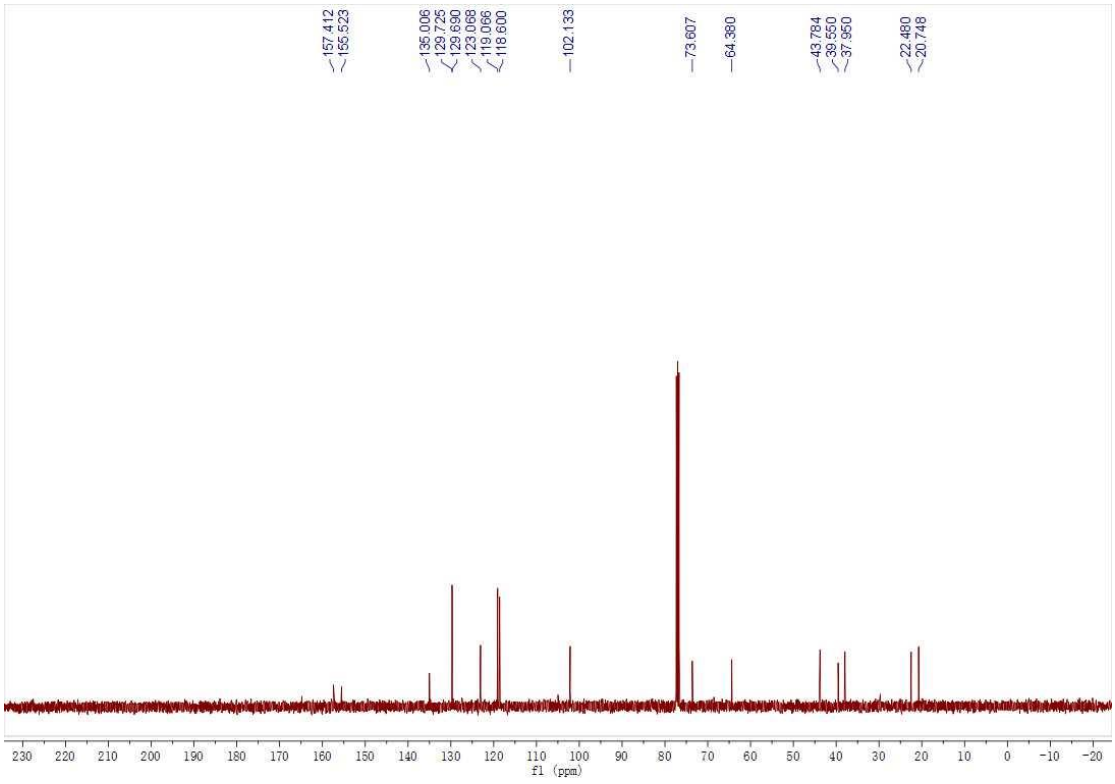
7.315
7.313
7.267
7.133
7.128
7.117
7.113
7.112
7.105
7.099
7.095
7.092
7.077
7.006
7.003
7.001
6.998
6.990
6.987
6.984
6.982
6.954
6.949
6.938
6.933
5.050
5.042
4.219
4.198
4.178
3.871
3.670
3.651
3.649
3.630
3.465
3.459
3.437
3.432
3.430
3.409
2.864
2.853
2.832
2.820
2.593
2.588
2.560
2.538
1.867
1.864
1.858
1.850
1.844
1.841
1.833
1.786
1.741
1.735
1.727
1.706
1.701
1.695
1.691
1.663
1.265
2.03
3.05
2.01
2.08
1.00
0.99
1.15
1.11
1.10
1.02
2.07
2.27
2.58
1.28
f1 (ppm)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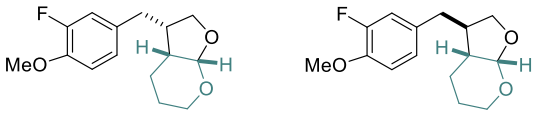
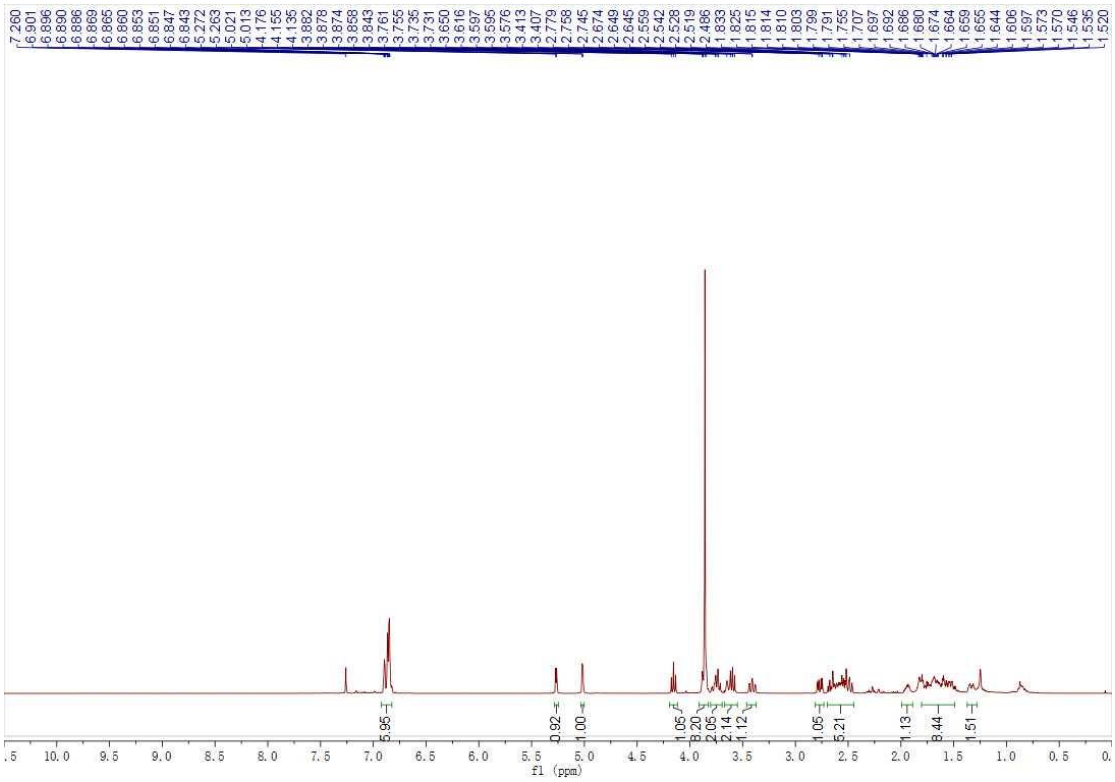
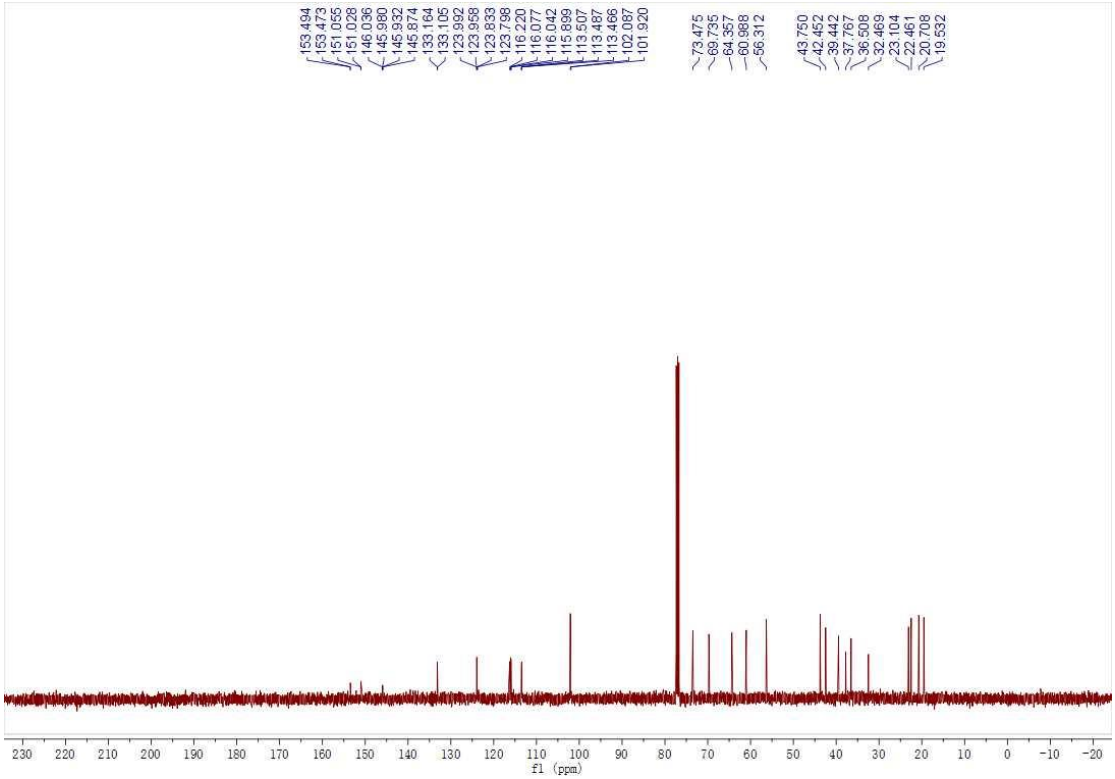
135.006
129.725
129.690
123.068
119.066
118.600
102.133
73.607
64.380
43.784
39.550
37.950
22.480
20.748
f1 (ppm)

(**4**)


F
MeO
H
O
H
O
F
MeO
H
O
H
O


7.260
6.901
6.896
6.890
6.886
6.869
6.865
6.860
6.853
6.851
6.847
6.843
5.272
5.263
5.021
5.013
4.176
4.155
4.135
3.882
3.878
3.874
3.858
3.843
3.761
3.755
3.735
3.731
3.650
3.616
3.597
3.595
3.576
3.413
3.407
2.779
2.758
2.745
2.674
2.649
2.645
2.559
2.542
2.528
2.519
2.486
1.833
1.825
1.815
1.814
1.810
1.803
1.799
1.791
1.755
1.707
1.697
1.692
1.686
1.680
1.674
1.664
1.659
1.655
1.644
1.606
1.597
1.573
1.570
1.546
1.535
1.520
5.95
0.92
1.00
1.05
3.20
2.05
2.14
1.12
1.05
5.21
1.13
8.44
1.51
f1 (ppm)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145.980
145.932
145.874
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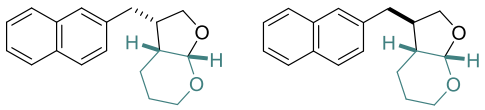
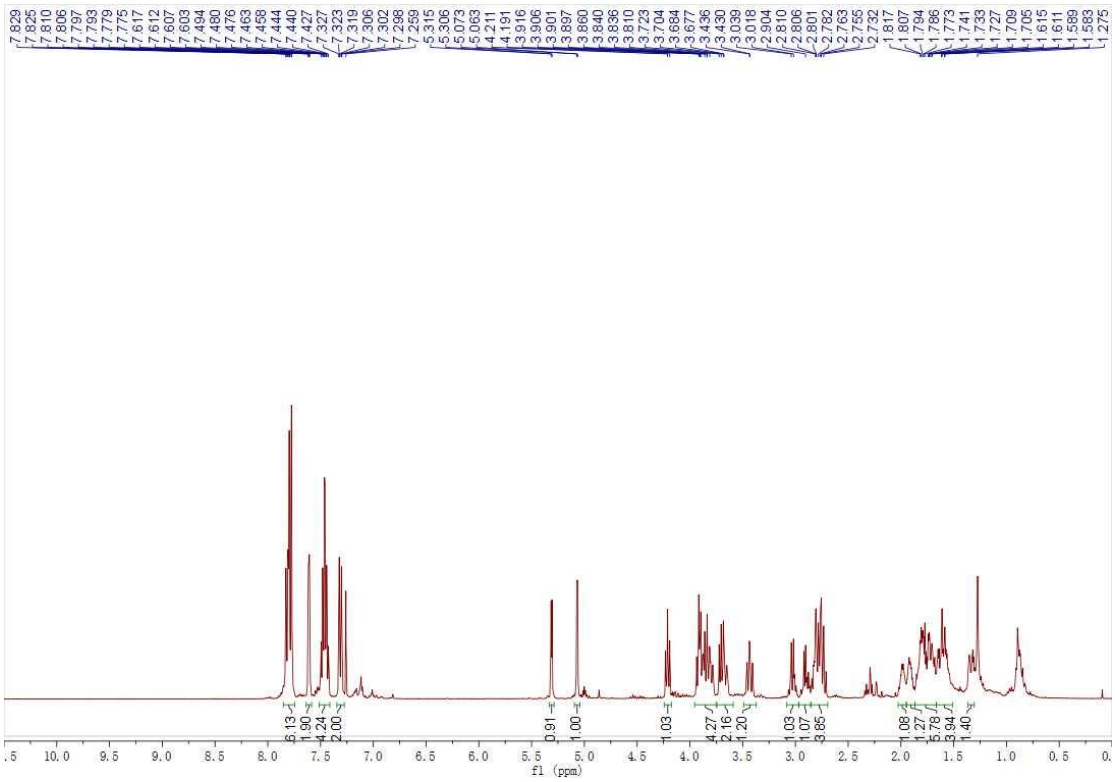
123.992
123.958
123.833
123.798
116.220
116.077
116.042
115.899
113.507
113.487
113.466
102.087
101.920
73.475
69.735
64.357
60.988
56.312
43.750
42.452
39.442
37.767
36.508
32.469
23.104
22.461
20.708
19.532
f1 (ppm)

(5)


H
O
H
O
H
O
H
O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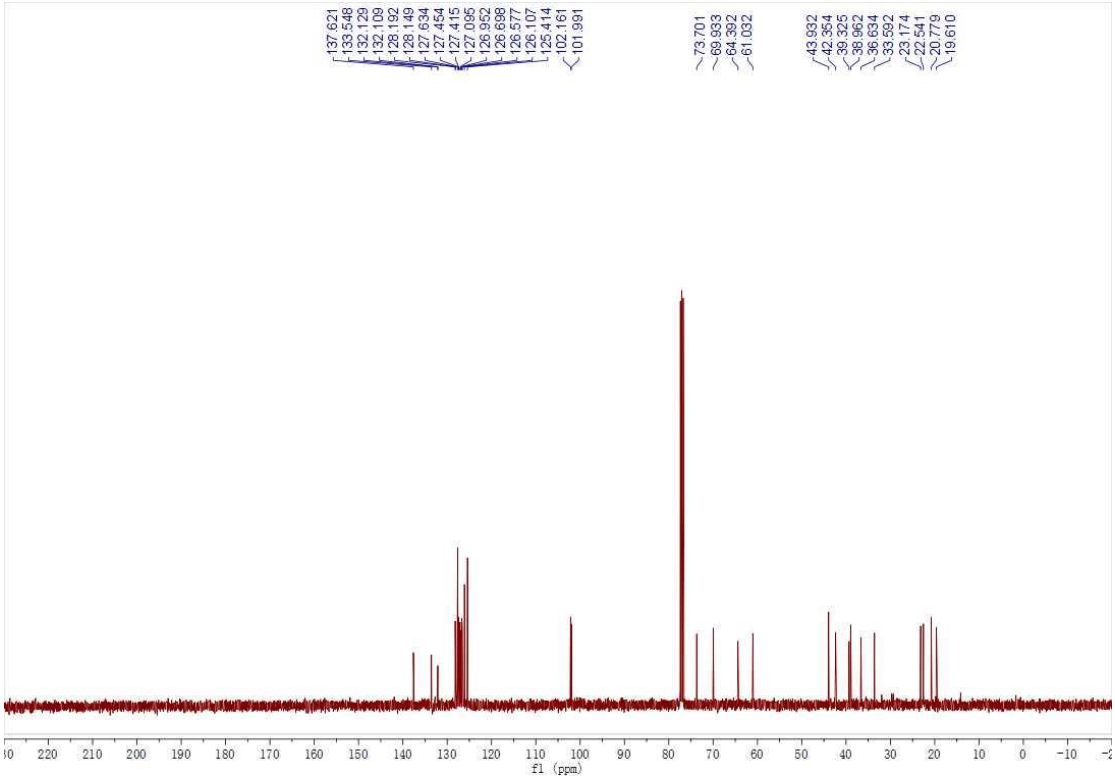
7.797
7.793
7.779
7.775
7.617
7.612
7.607
7.603
7.494
7.480
7.476
7.463
7.458
7.444
7.440
7.427
7.327
7.323
7.319
7.306
7.302
7.298
7.259
5.315
5.306
5.073
5.063
4.211
4.191
3.916
3.906
3.901
3.897
3.860
3.840
3.836
3.810
3.723
3.704
3.684
3.677
3.436
3.430
3.039
3.018
2.904
2.810
2.806
2.801
2.782
2.763
2.755
2.732
1.817
1.807
1.794
1.786
1.773
1.741
1.733
1.727
1.709
1.705
1.615
1.611
1.589
1.583
1.275
6.13
1.90
4.24
2.00
0.91
1.00
1.03
4.27
2.16
1.20
1.03
1.07
3.85
1.08
1.27
5.78
3.94
1.40
f1 (ppm)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132.129
132.109
128.192
128.149
127.634
127.454
127.415
127.095
126.952
126.698
126.577
126.107
125.414
102.161
101.991
73.701
69.933
64.392
61.032
43.932
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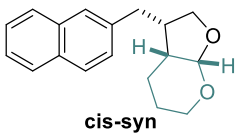
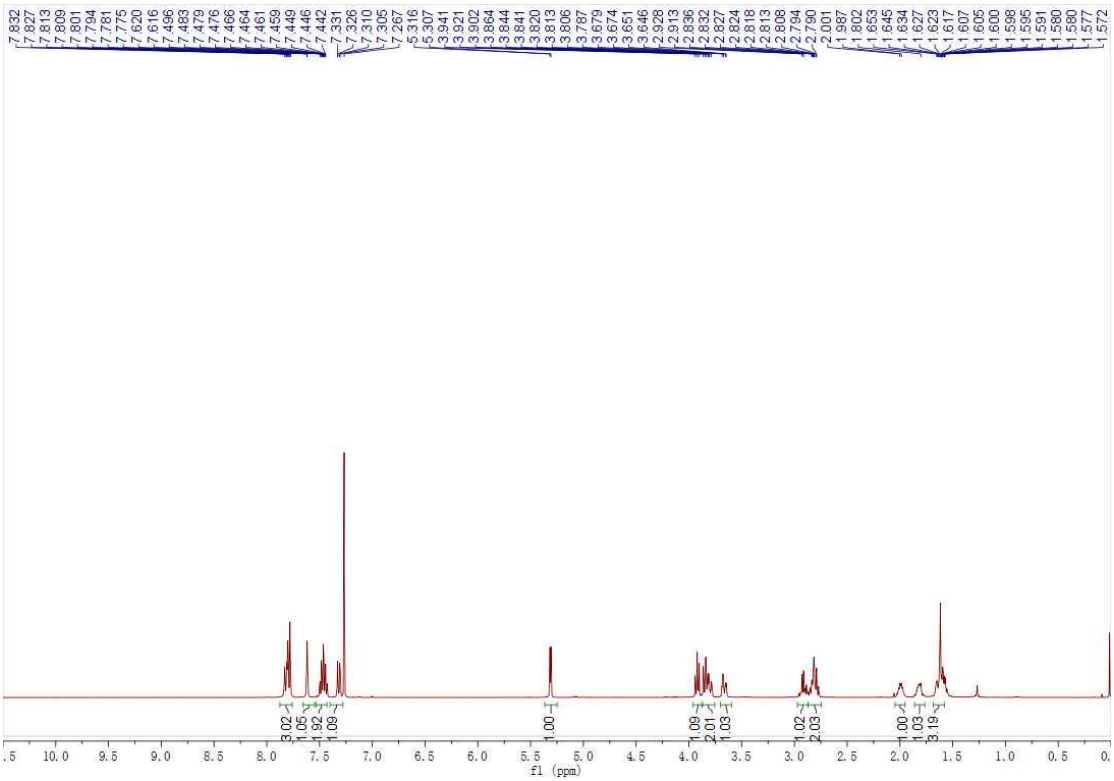
39.325
38.962
36.634
33.592
23.174
22.541
20.779
19.610
f1 (ppm)


H
O
H
O

cis-syn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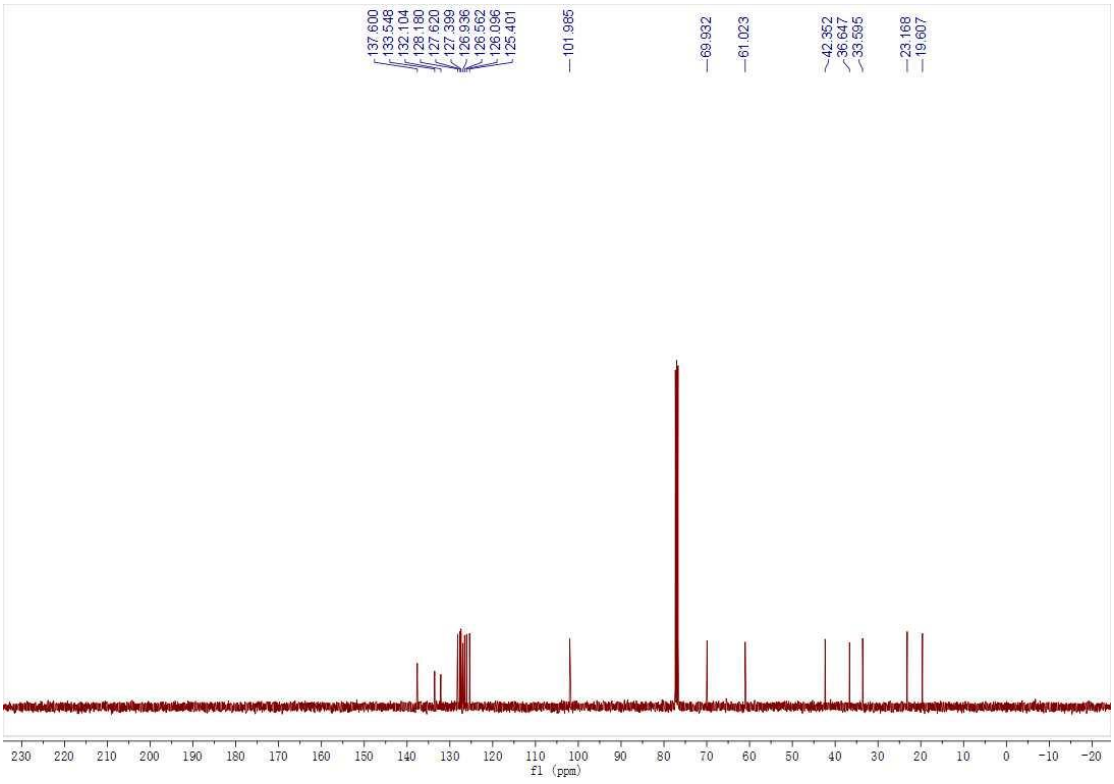
7.794
7.781
7.775
7.620
7.616
7.496
7.483
7.479
7.476
7.466
7.464
7.461
7.459
7.449
7.446
7.442
7.331
7.326
7.310
7.305
7.267
5.316
5.307
3.941
3.921
3.902
3.864
3.844
3.841
3.820
3.813
3.806
3.787
3.679
3.674
3.651
3.646
2.928
2.913
2.896
2.832
2.827
2.824
2.818
2.813
2.808
2.794
2.790
2.001
1.987
1.802
1.653
1.645
1.634
1.627
1.623
1.617
1.607
1.605
1.600
1.598
1.595
1.591
1.580
1.580
1.577
1.572
3.02
1.05
1.92
1.09
1.00
1.09
2.01
1.03
1.02
2.03
1.00
1.03
3.19
f1 (ppm)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127.399
126.936
126.562
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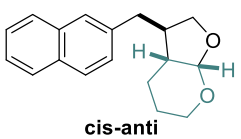
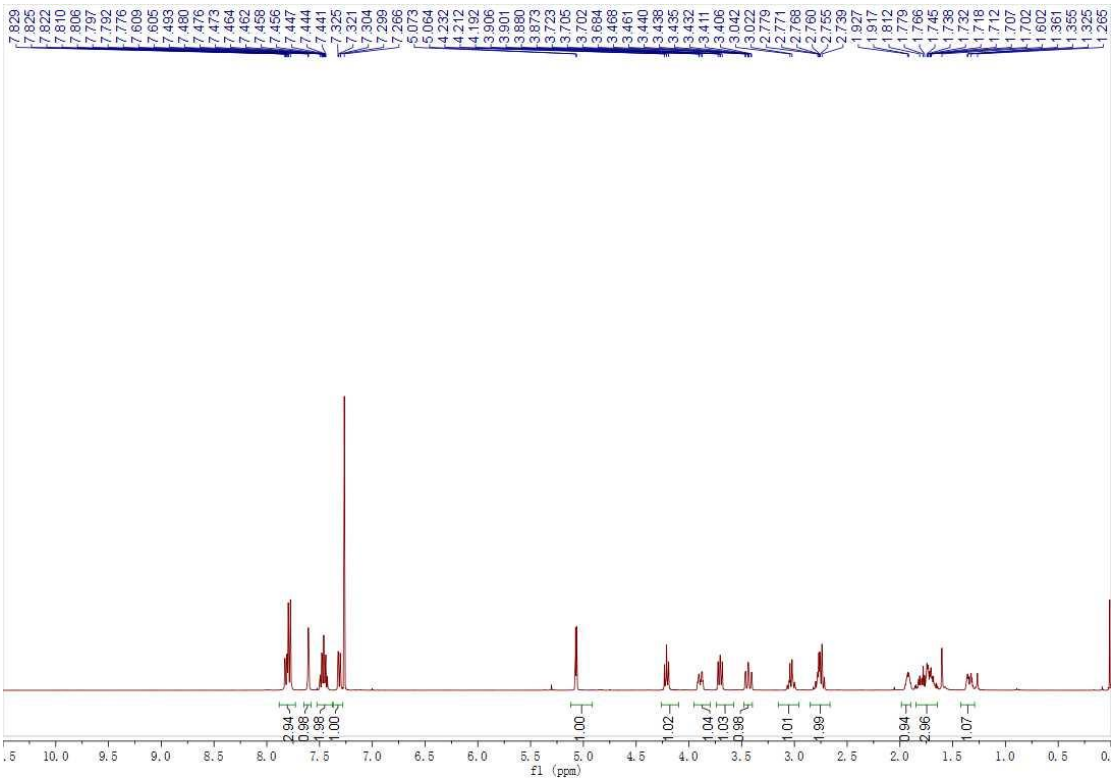
125.401
101.986
69.932
61.023
42.352
36.647
33.595
23.168
19.607
f1 (ppm)


H
O
H
O

cis-anti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7.822
7.810
7.806
7.797
7.792
7.776
7.609
7.605
7.493
7.480
7.476
7.473
7.464
7.462
7.458
7.456
7.447
7.444
7.441
7.325
7.321
7.304
7.299
7.266
5.073
5.064
4.232
4.212
4.192
3.906
3.901
3.880
3.873
3.723
3.705
3.702
3.684
3.468
3.461
3.440
3.438
3.435
3.432
3.411
3.406
3.042
3.022
2.779
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2.760
2.755
2.739
1.927
1.917
1.812
1.779
1.766
1.745
1.738
1.732
1.718
1.712
1.707
1.702
1.602
1.361
1.355
1.325
1.265
2.94
0.98
1.98
1.00
1.00
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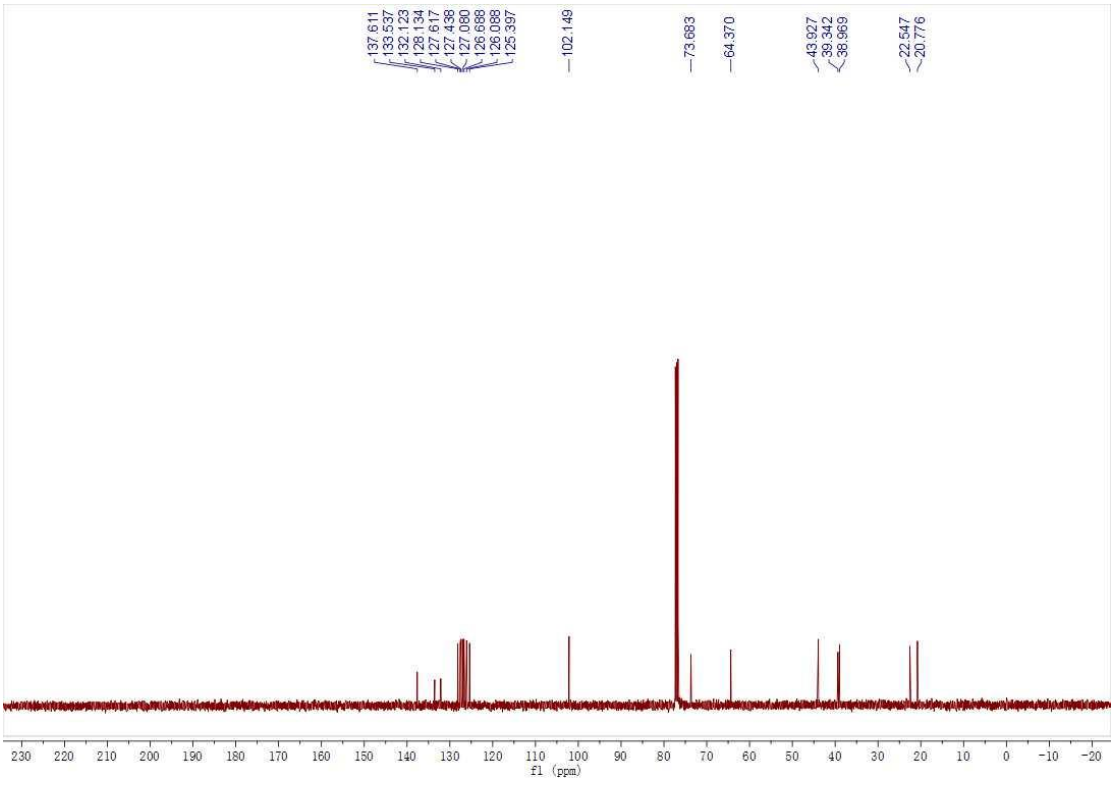
1.04
1.03
0.98
1.01
1.99
0.94
2.96
1.07
f1 (ppm)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127.617
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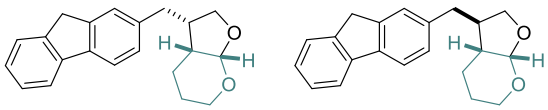
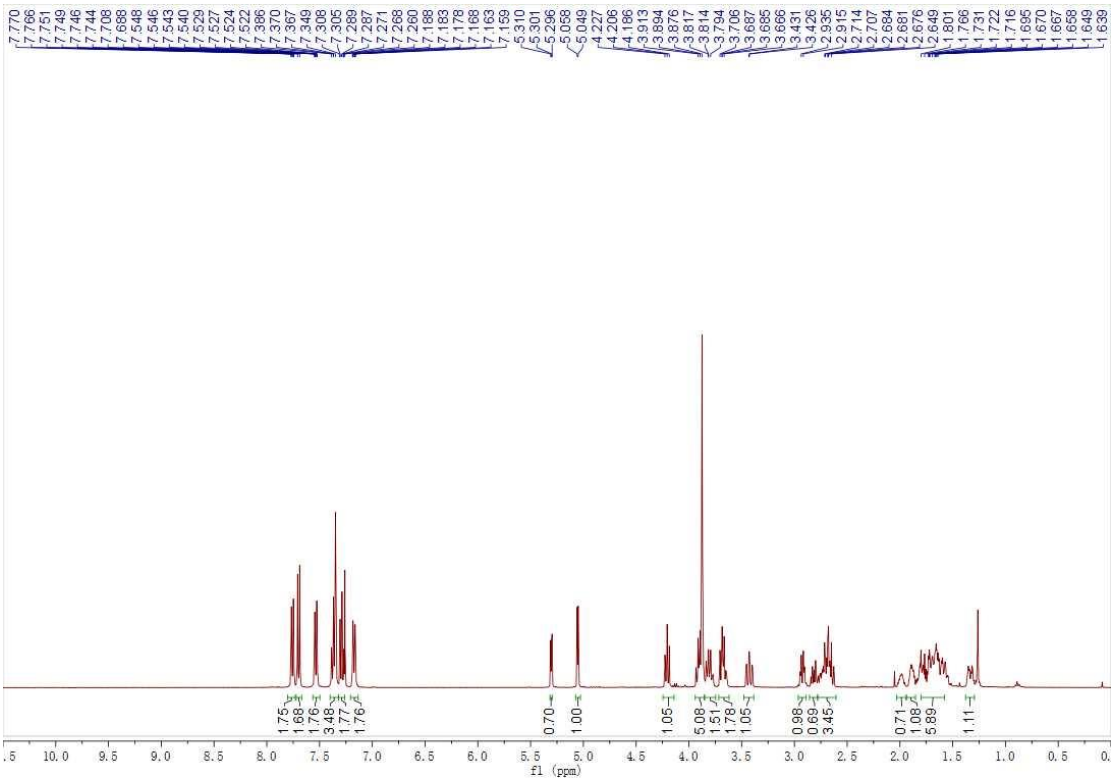
127.060
126.688
126.088
125.397
102.149
73.683
64.370
43.927
39.342
38.969
22.547
20.776
f1 (ppm)

(6)

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7.688
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7.546
7.543
7.540
7.529
7.527
7.524
7.522
7.386
7.370
7.367
7.349
7.308
7.305
7.289
7.287
7.271
7.268
7.260
7.188
7.183
7.178
7.168
7.163
7.159
5.310
5.301
5.296
5.058
5.049
4.227
4.206
4.186
3.913
3.894
3.876
3.817
3.814
3.794
3.706
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3.426
3.935
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2.707
2.684
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1.801
1.766
1.731
1.722
1.716
1.695
1.670
1.667
1.658
1.649
1.639
1.75
1.68
1.76
3.48
1.77
1.76
0.70
1.00
1.05
5.08
1.51
1.78
1.05
0.98
0.69
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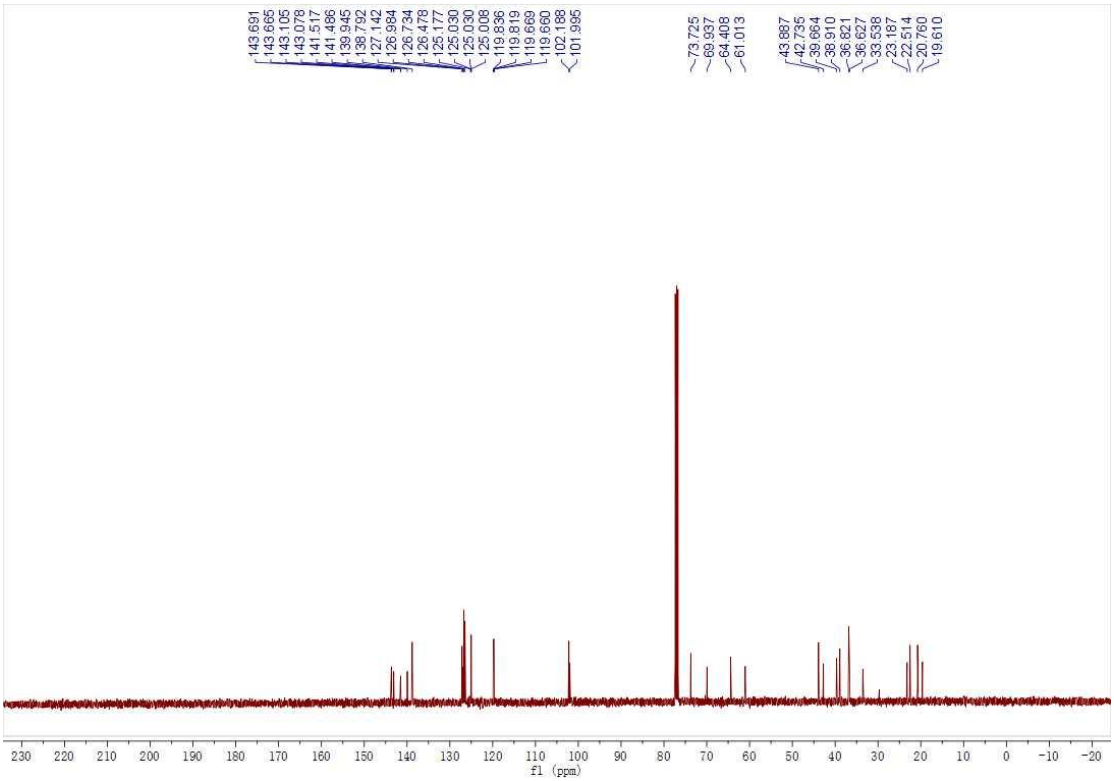
0.71
1.08
5.89
1.11
f1 (ppm)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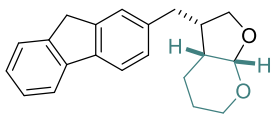
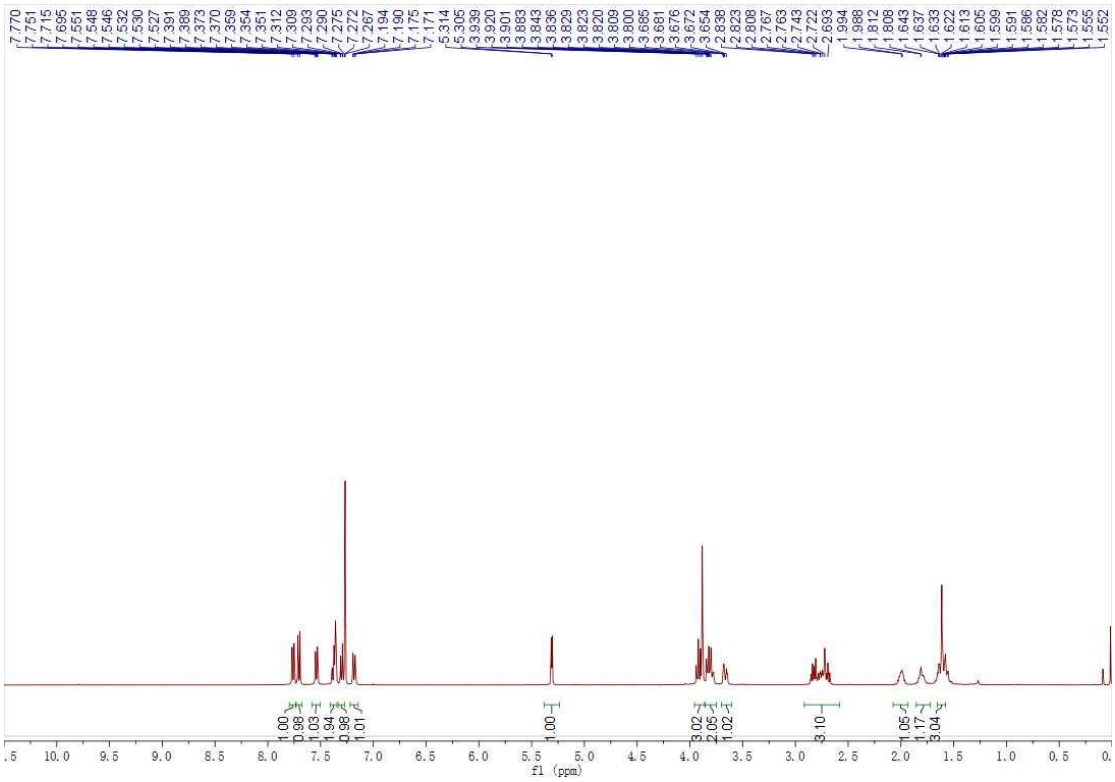
126.478
125.177
125.030
125.030
125.008
119.836
119.819
119.669
119.660
102.188
101.995
73.725
69.937
64.408
61.013
43.887
42.735
39.864
38.910
36.821
36.627
33.538
23.187
22.514
20.760
19.610
f1 (ppm)


H
O
H
O

cis-syn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7.715
7.695
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7.527
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7.389
7.373
7.370
7.359
7.354
7.351
7.312
7.309
7.293
7.290
7.275
7.272
7.267
7.194
7.190
7.175
7.171
5.314
5.305
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3.901
3.883
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3.829
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3.676
3.672
3.654
2.838
2.823
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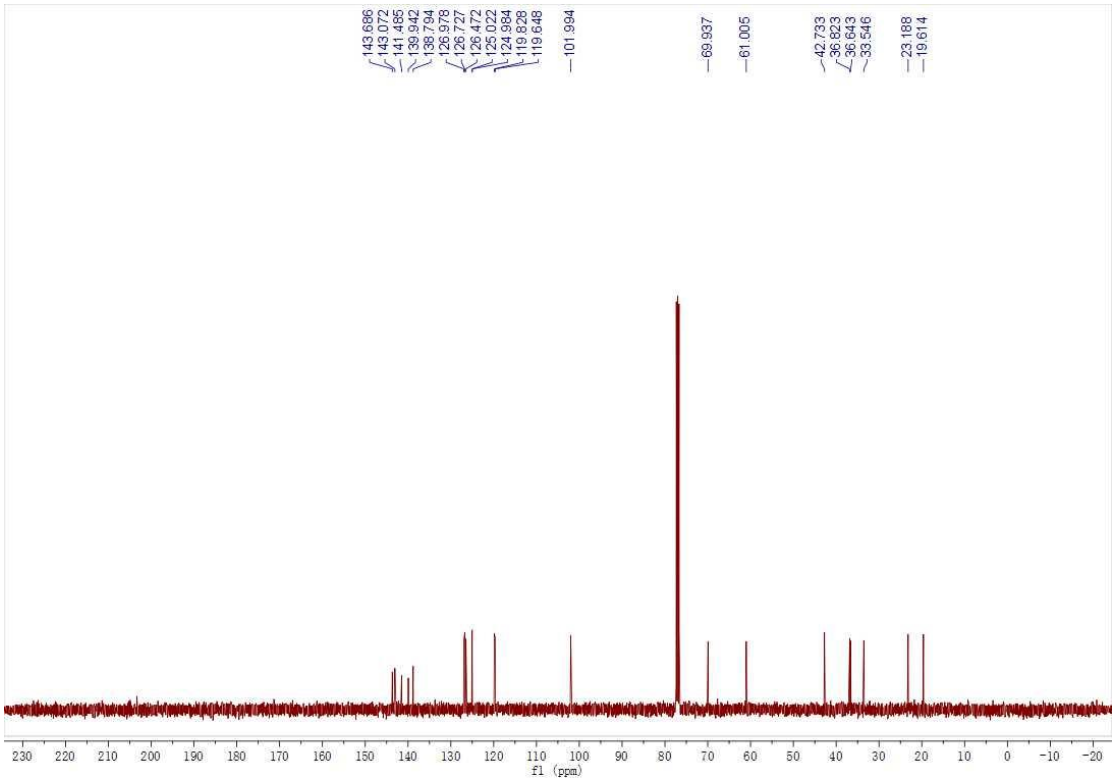
2.763
2.743
2.722
2.693
1.994
1.988
1.812
1.808
1.643
1.637
1.633
1.622
1.613
1.605
1.599
1.591
1.586
1.582
1.578
1.573
1.555
1.552
1.00
0.98
1.03
1.94
0.98
1.01
1.00
3.02
2.05
1.02
3.10
1.05
1.17
3.04
f1 (ppm)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139.942
138.794
126.978
126.727
126.472
125.022
124.984
119.828
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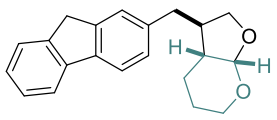
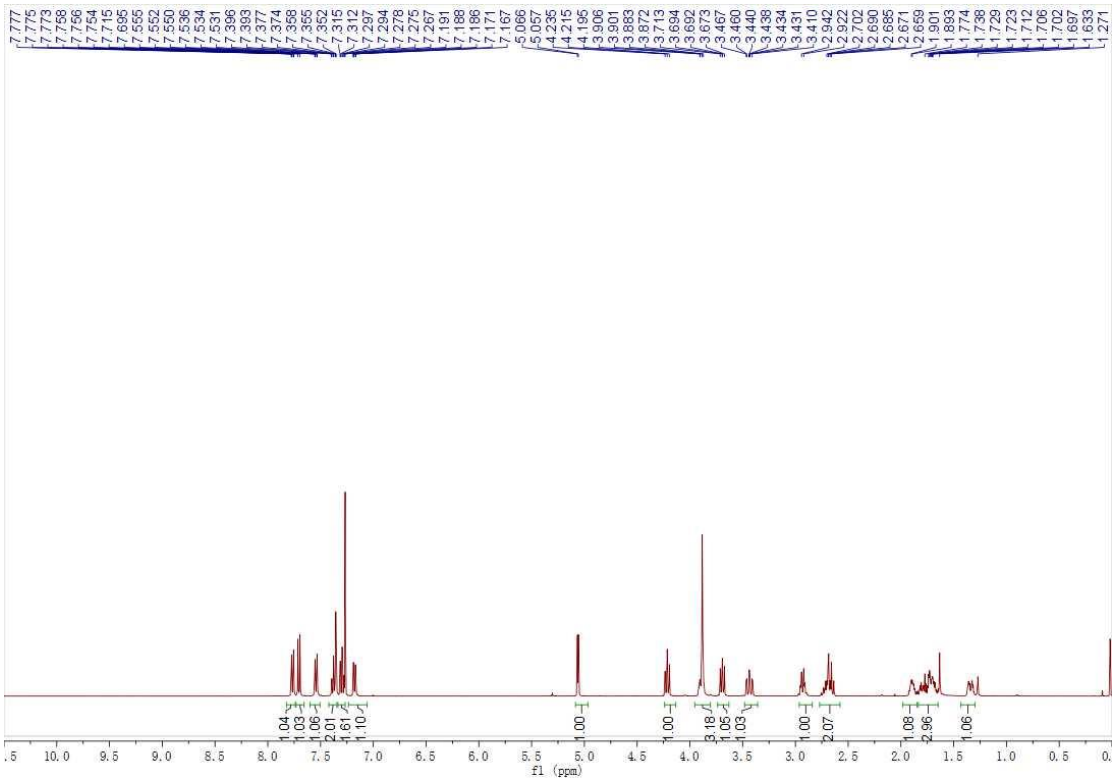
101.994
69.937
61.005
42.733
36.823
36.643
33.546
23.188
19.614
f1 (ppm)


H
O
H
O

cis-anti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7.534
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7.393
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7.374
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7.355
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7.312
7.297
7.294
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7.275
7.267
7.191
7.188
7.186
7.171
7.167
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5.057
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4.215
4.195
3.906
3.901
3.883
3.872
3.713
3.694
3.692
3.673
3.467
3.460
3.440
3.438
3.434
3.431
3.410
2.942
2.922
2.702
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2.671
2.659
1.901
1.893
1.774
1.738
1.729
1.723
1.712
1.706
1.702
1.697
1.633
1.271
1.04
1.03
1.06
2.01
1.61
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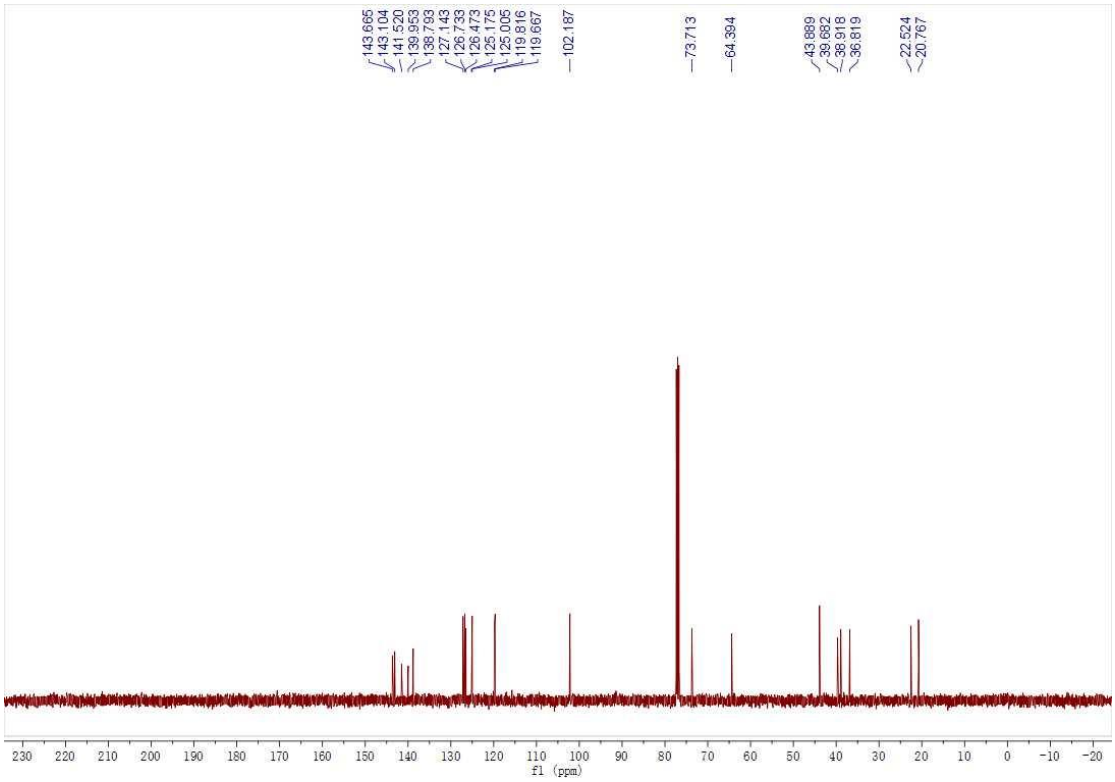
2.07
1.08
2.96
1.06
f1 (ppm)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126.473
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125.005
119.816
119.667
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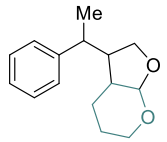
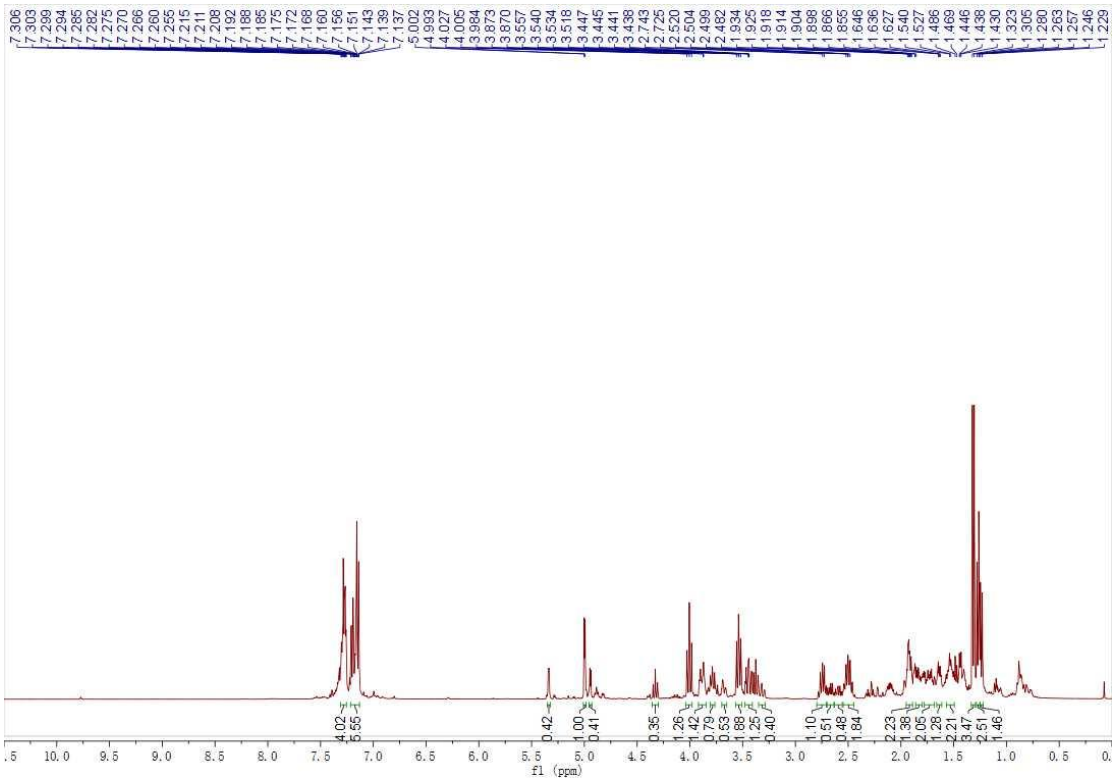
64.394
43.889
39.682
38.918
36.819
22.524
20.767
f1 (ppm)

(7)


Me
O
O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7.270
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7.255
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7.211
7.208
7.192
7.188
7.185
7.175
7.172
7.168
7.160
7.156
7.151
7.143
7.139
7.137
5.002
4.993
4.027
4.005
3.984
3.873
3.870
3.557
3.540
3.534
3.518
3.447
3.445
3.441
3.438
2.743
2.725
2.520
2.504
2.499
2.482
1.934
1.925
1.918
1.914
1.904
1.898
1.866
1.855
1.646
1.636
1.627
1.540
1.527
1.486
1.469
1.446
1.438
1.430
1.323
1.305
1.280
1.263
1.257
1.246
1.229
4.02
5.55
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1.00
0.41
0.35
1.26
1.42
0.79
0.53
1.88
1.25
0.40
1.10
0.51
0.48
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1.38
2.05
1.28
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3.47
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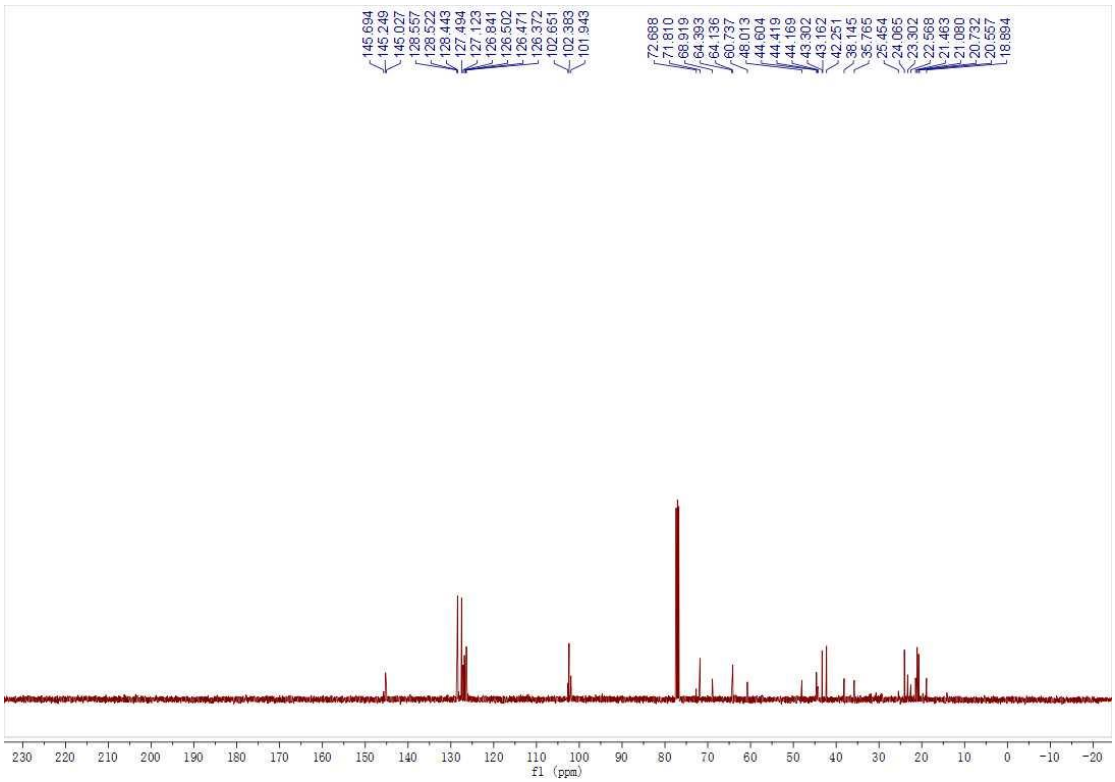
1.46
f1 (ppm)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126.471
126.372
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102.383
101.943
72.688
71.810
68.919
64.393
64.136
60.737
48.013
44.604
44.419
44.169
43.302
43.162
42.251
38.145
35.765
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23.302
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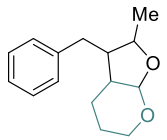
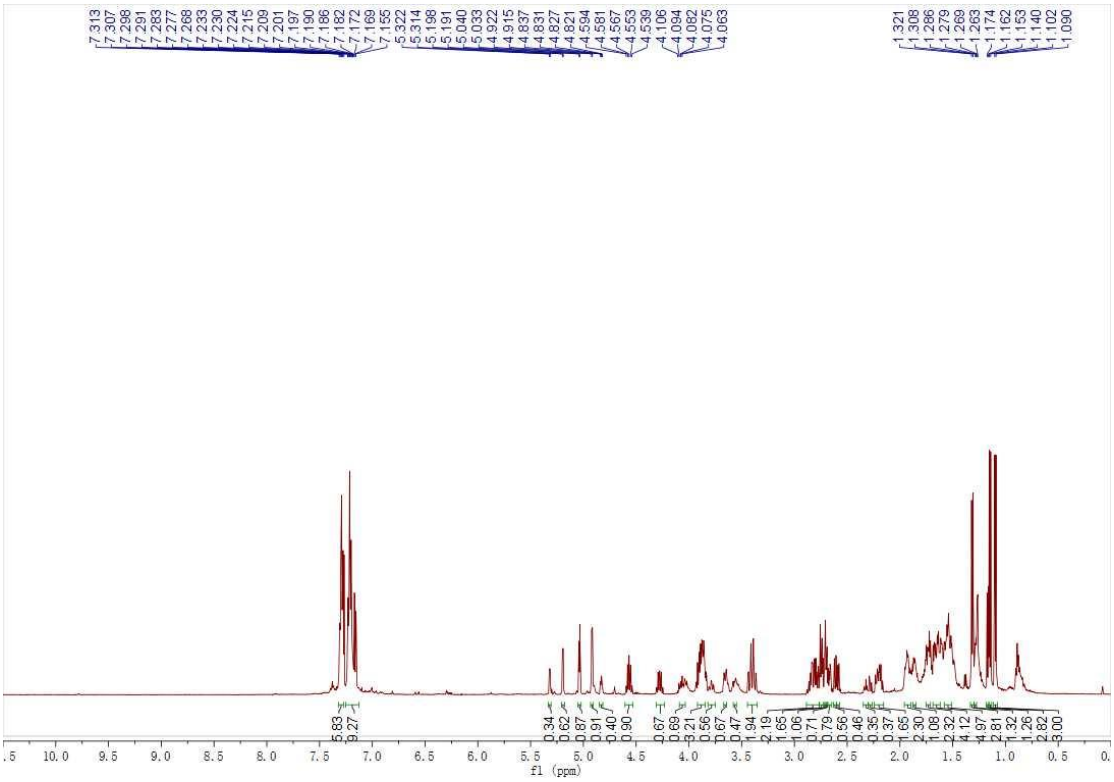
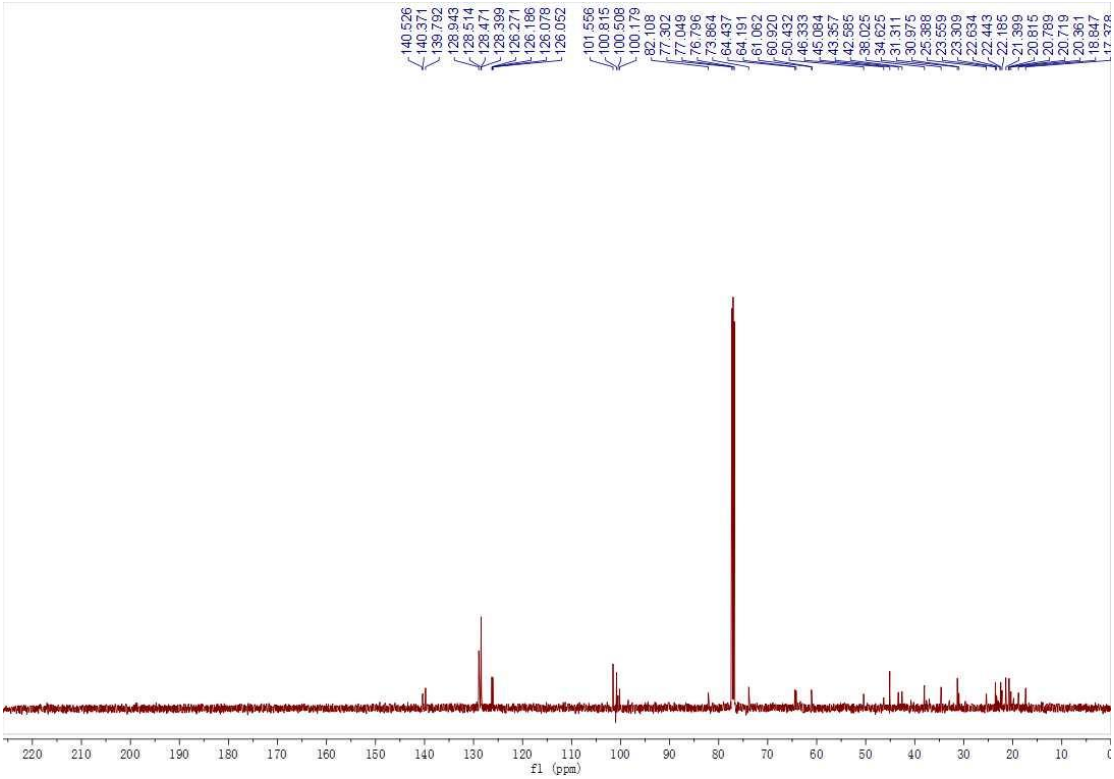
20.732
20.557
18.894
f1 (ppm)

(**8**)







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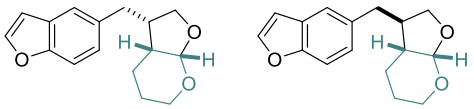
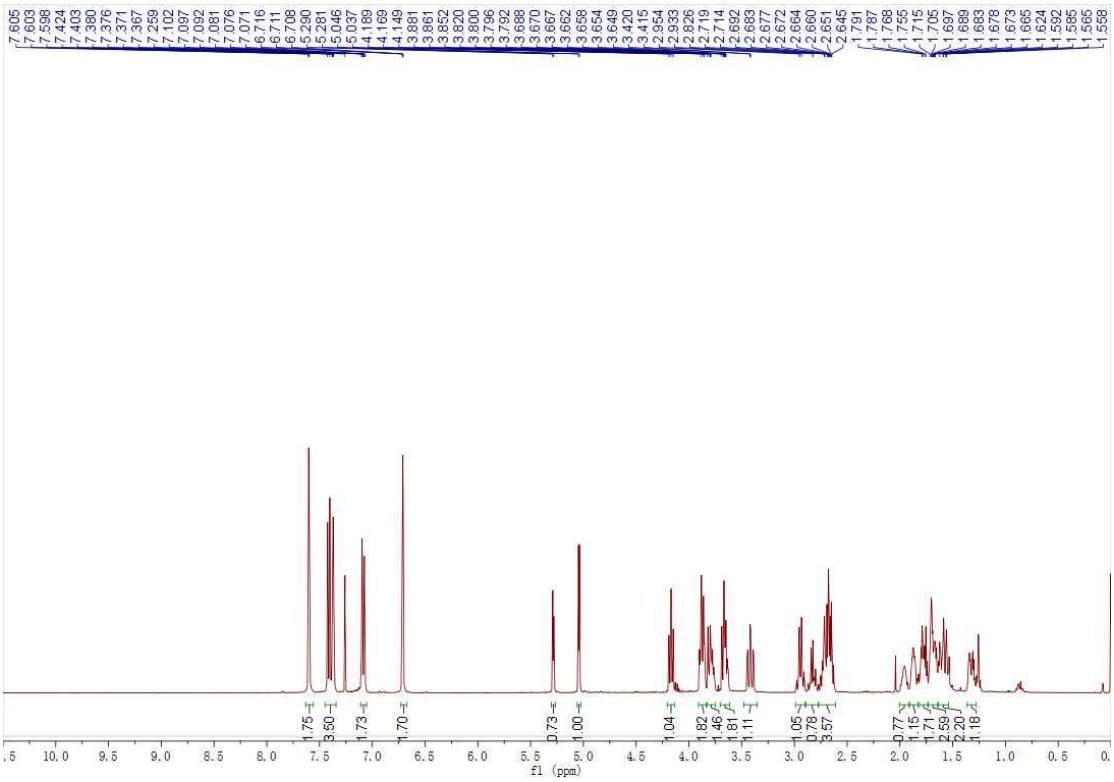
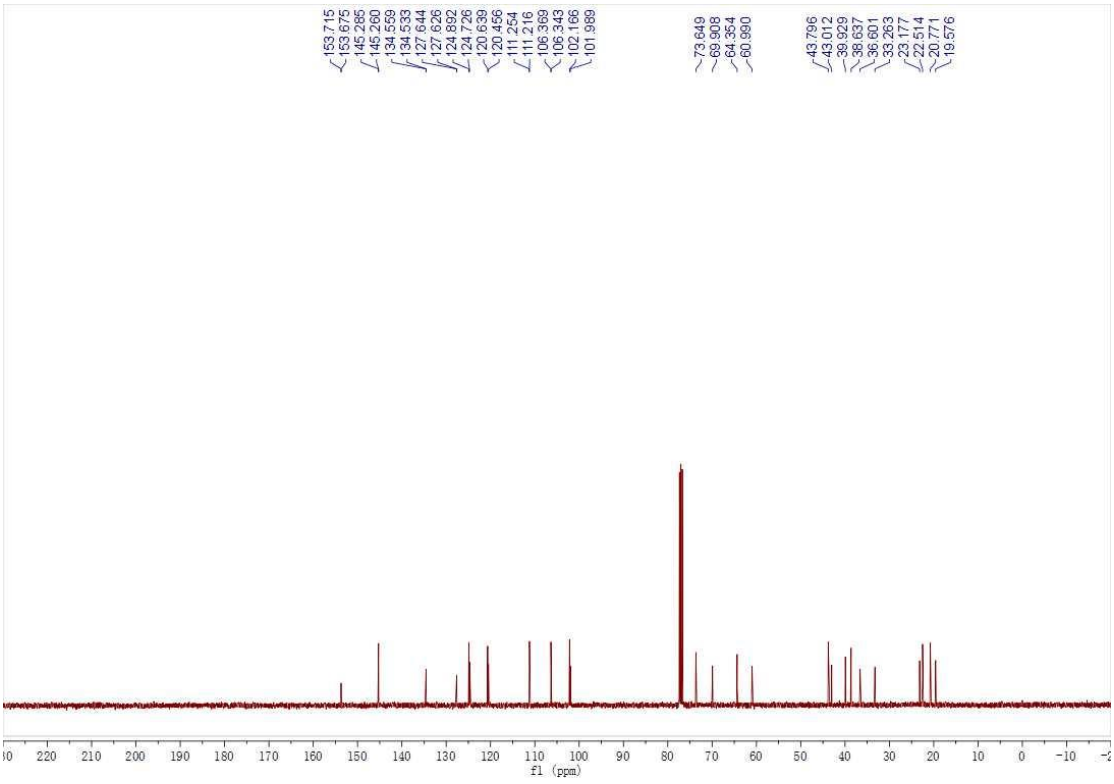
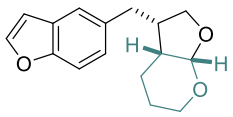
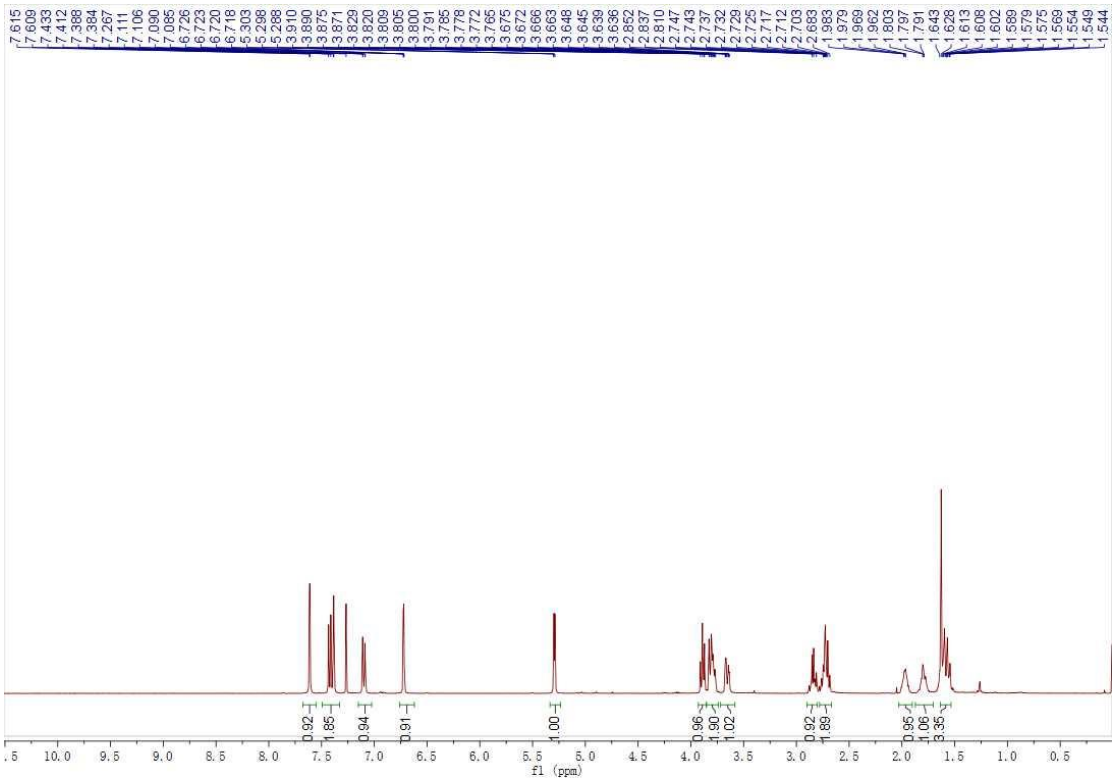







H
O
O
H
O

cis-syn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7.388
7.384
7.267
7.111
7.106
7.090
7.085
6.726
6.723
6.720
6.718
5.303
5.298
5.288
3.910
3.890
3.875
3.871
3.829
3.820
3.809
3.805
3.800
3.791
3.785
3.778
3.772
3.765
3.675
3.672
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3.663
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3.639
3.636
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2.837
2.810
2.747
2.743
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2.729
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2.712
2.703
2.683
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1.979
1.969
1.962
1.803
1.797
1.791
1.643
1.628
1.613
1.608
1.602
1.589
1.579
1.575
1.569
1.554
1.549
1.544
0.92
1.85
0.94
0.91
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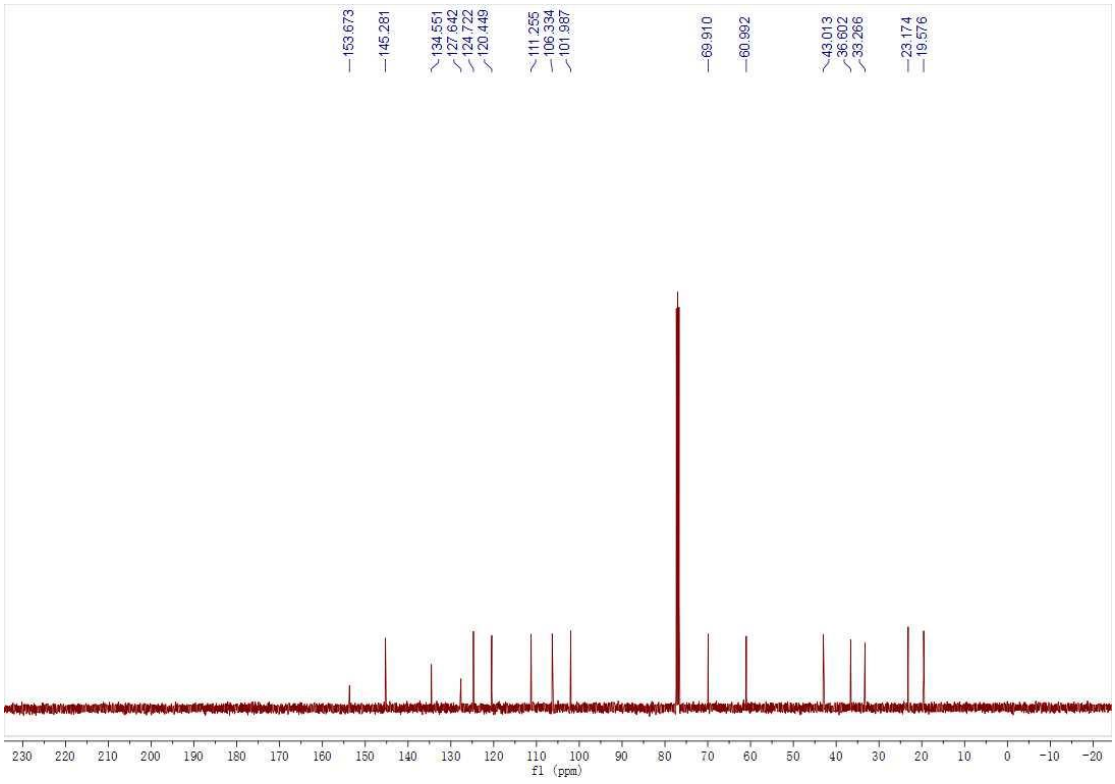
0.96
1.90
1.02
0.92
1.89
0.95
1.06
3.35
f1 (ppm)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124.722
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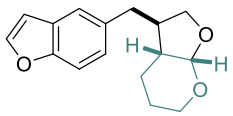
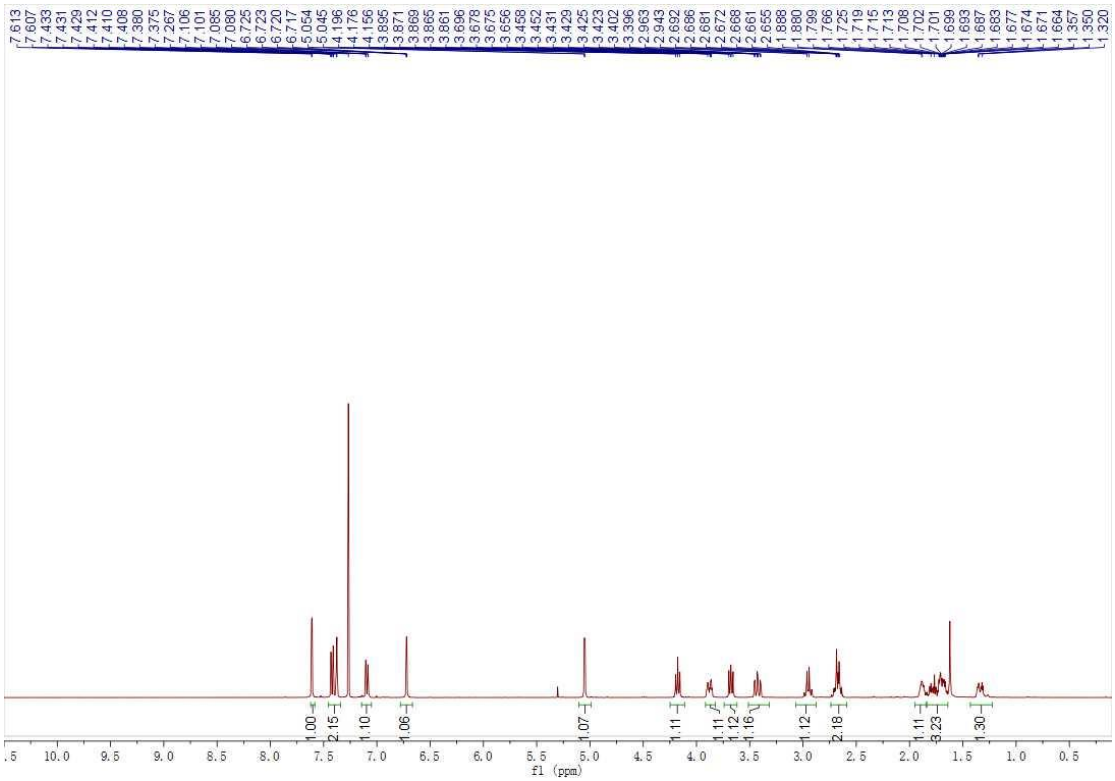
69.910
60.992
43.013
36.602
33.266
23.174
19.576
f1 (ppm)


H
O
O
H
O

cis-anti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7.408
7.380
7.375
7.267
7.106
7.101
7.085
7.080
6.725
6.723
6.720
6.717
5.054
5.045
4.196
4.176
4.156
3.895
3.871
3.869
3.865
3.861
3.696
3.678
3.675
3.656
3.458
3.452
3.431
3.429
3.425
3.423
3.402
3.396
2.963
2.943
2.692
2.686
2.681
2.672
2.668
2.661
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1.799
1.766
1.725
1.719
1.715
1.713
1.708
1.702
1.701
1.699
1.693
1.687
1.683
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1.674
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2.15
1.10
1.06
1.07
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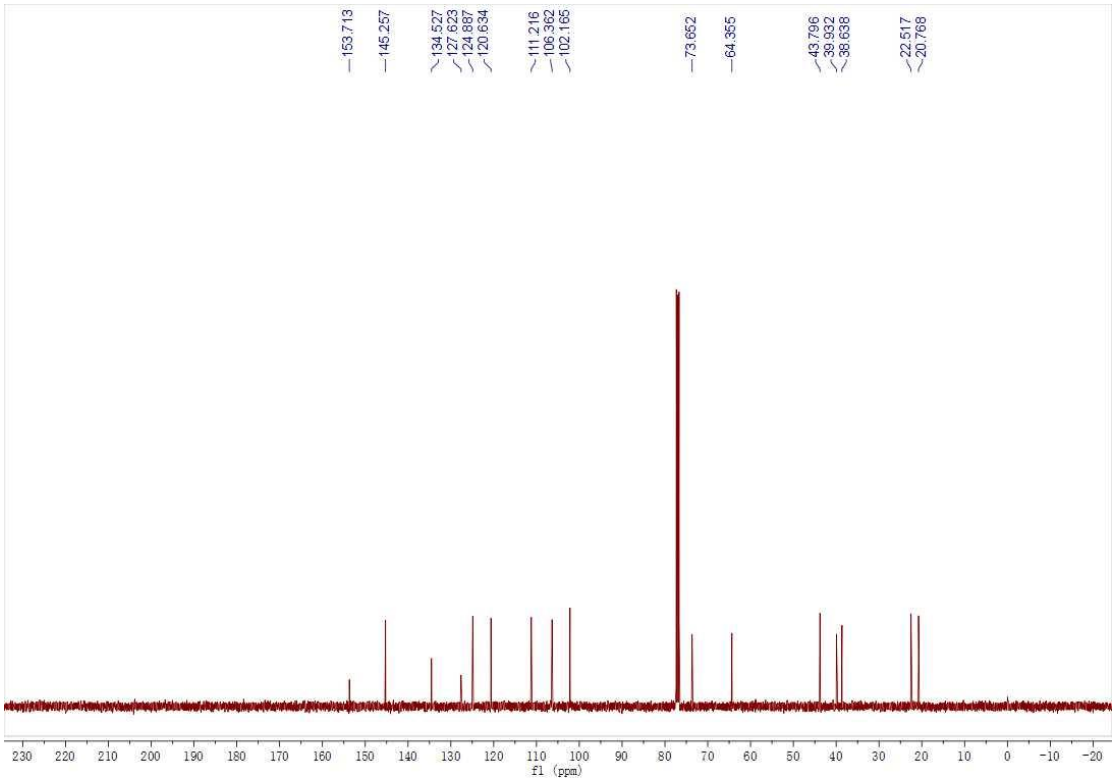
1.11
1.12
1.16
1.12
2.18
1.11
3.23
1.30
f1 (ppm)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124.887
120.634
111.216
106.362
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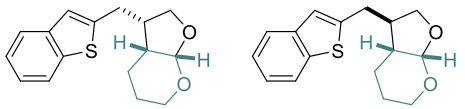
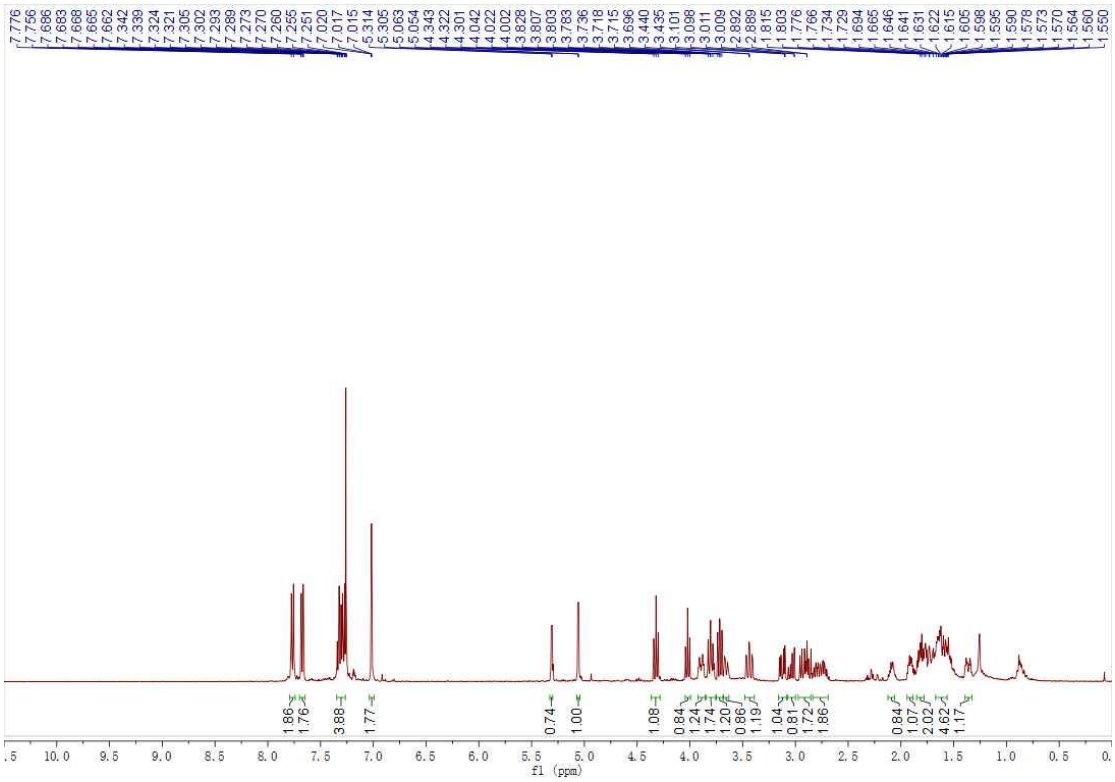
73.652
64.355
43.796
39.932
38.638
22.517
20.768
f1 (ppm)

(10)

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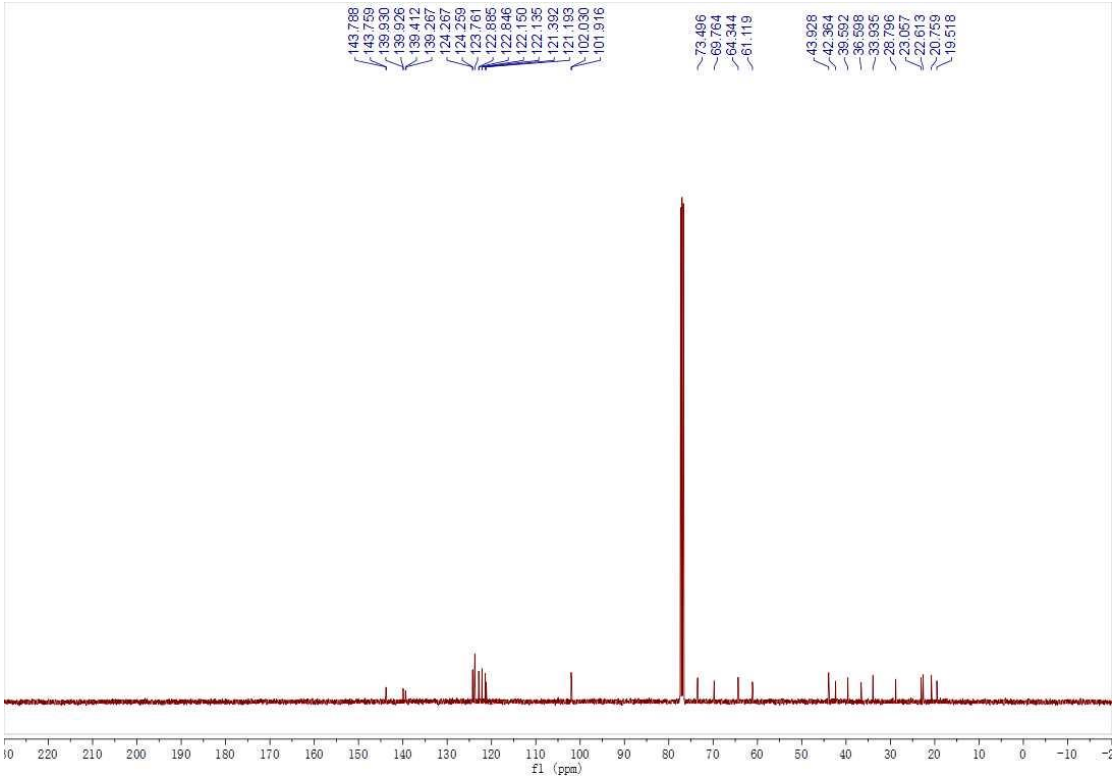
1.86 1.76 3.88 1.77 0.74 1.00 1.08 0.84 1.24 1.74 1.20 0.86 1.19 1.04 0.81 1.72 1.86 0.84 1.07 2.02 4.62 1.17
f1 (ppm)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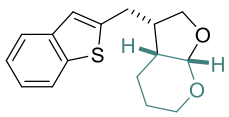
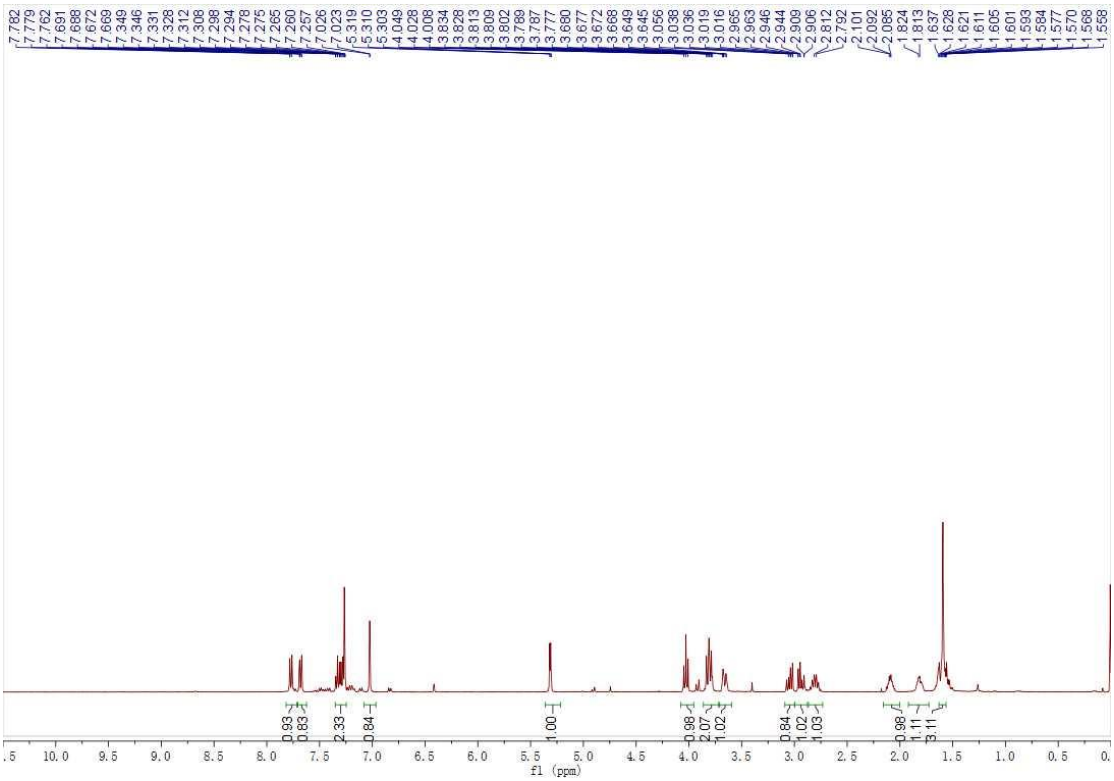
73.496 69.764 64.344 61.119
43.928 42.364 39.592 36.598 33.935 28.796 23.057 22.613 20.759 19.518
f1 (ppm)


S
H
O
H
O

cis-syn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7.275
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7.260
7.257
7.026
7.023
5.319
5.310
5.303
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4.028
4.008
3.834
3.828
3.813
3.809
3.802
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1.611
1.605
1.601
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1.584
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1.570
1.568
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2.33
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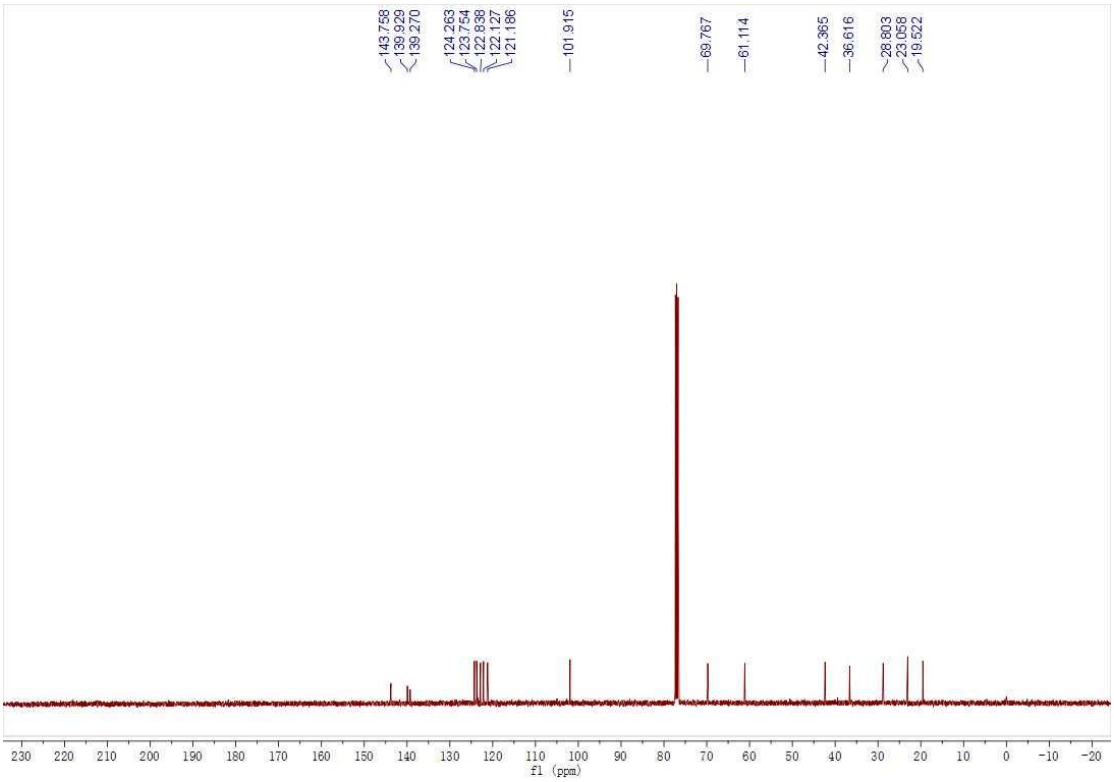
0.84
1.02
1.03
0.98
1.11
3.11
f1 (ppm)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101.915
69.767
61.114
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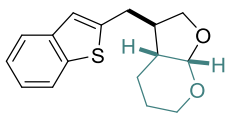
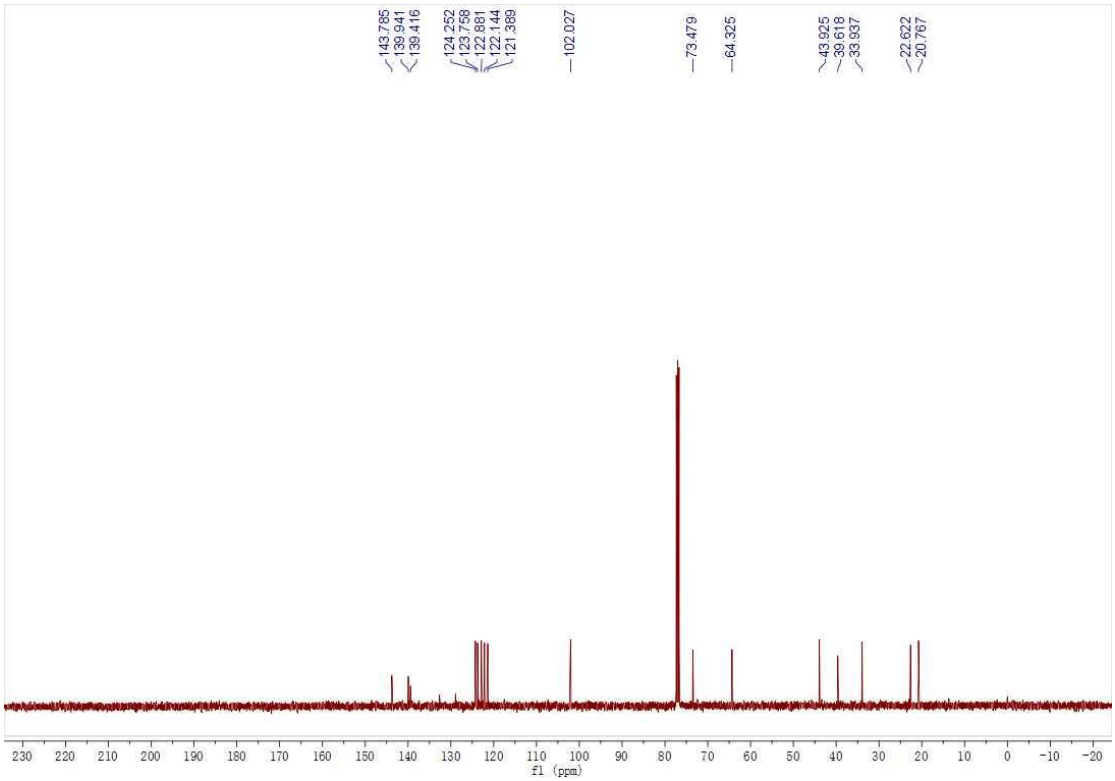
36.616
28.803
23.058
19.522
f1 (ppm)


S
H
O
H
O

cis-anti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64.325
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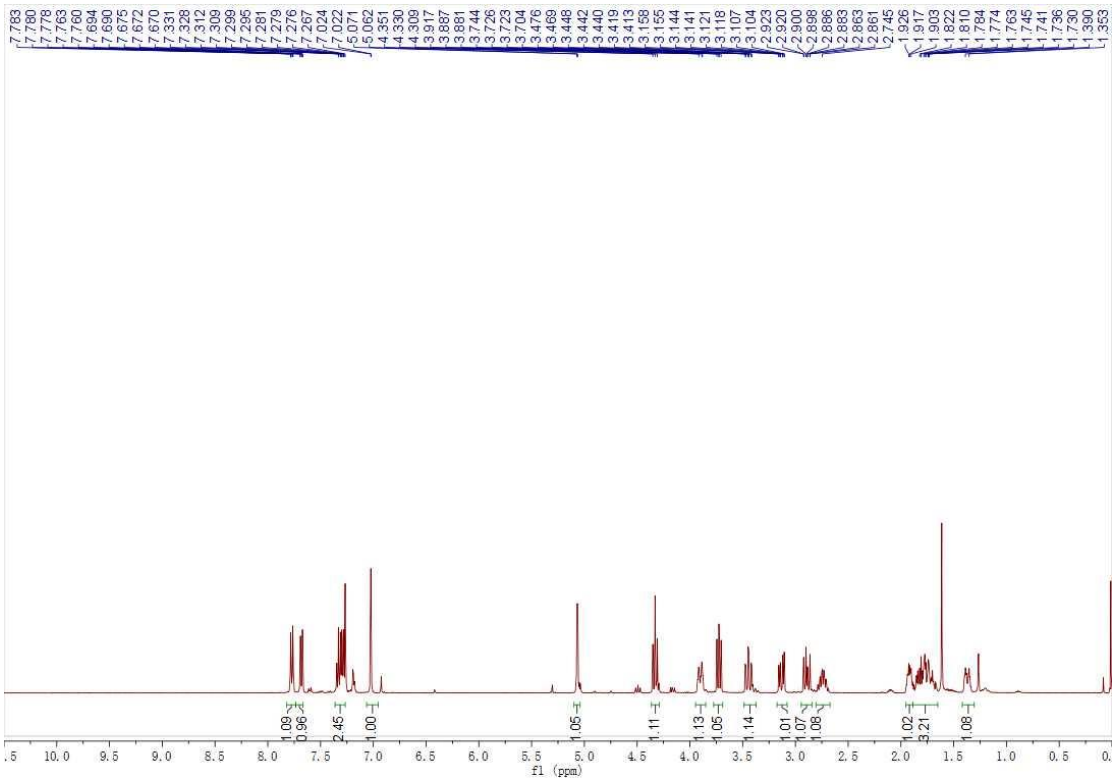
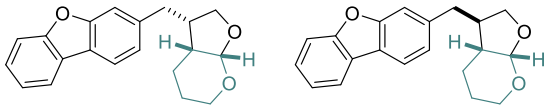
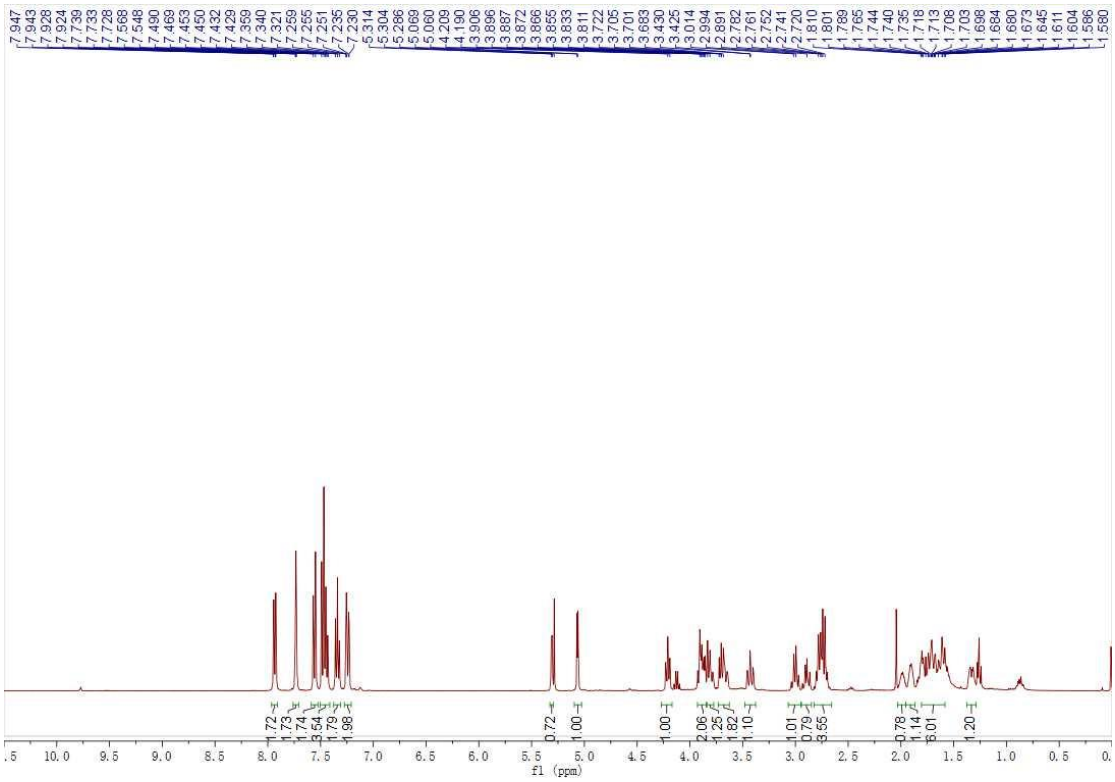
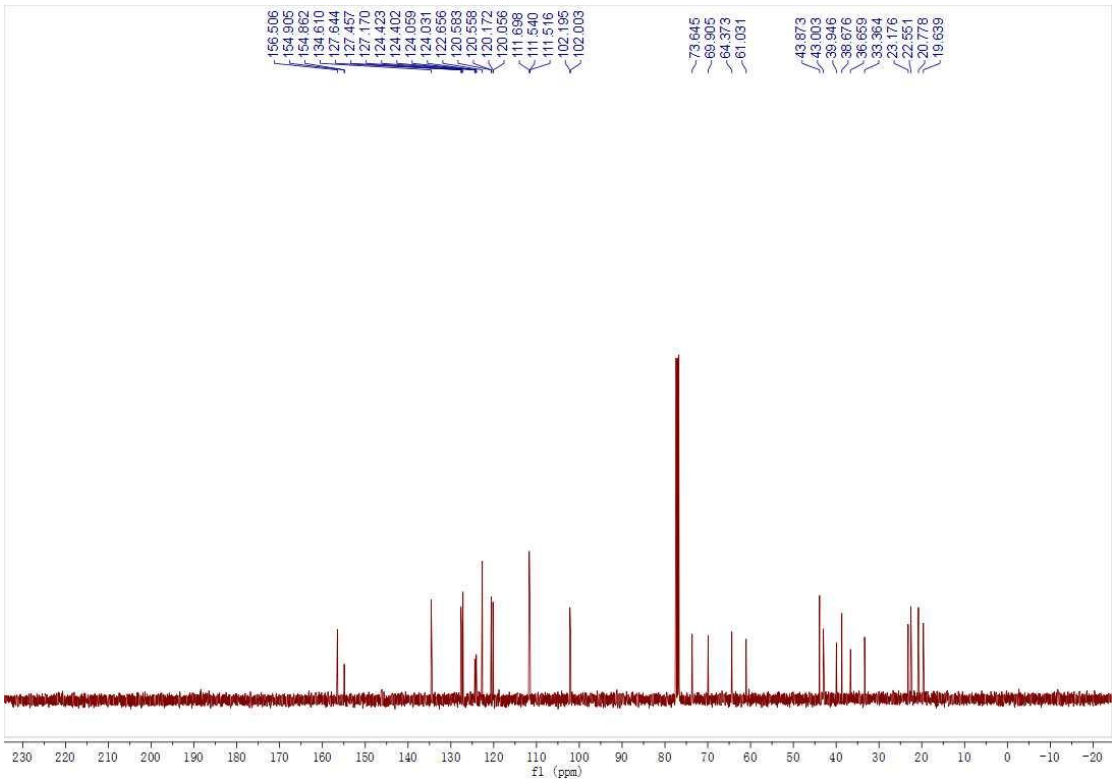
39.618
33.937
22.622
20.767
f1 (ppm)


f1 (ppm)

(11)







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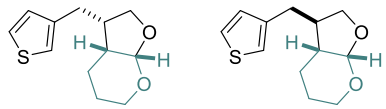

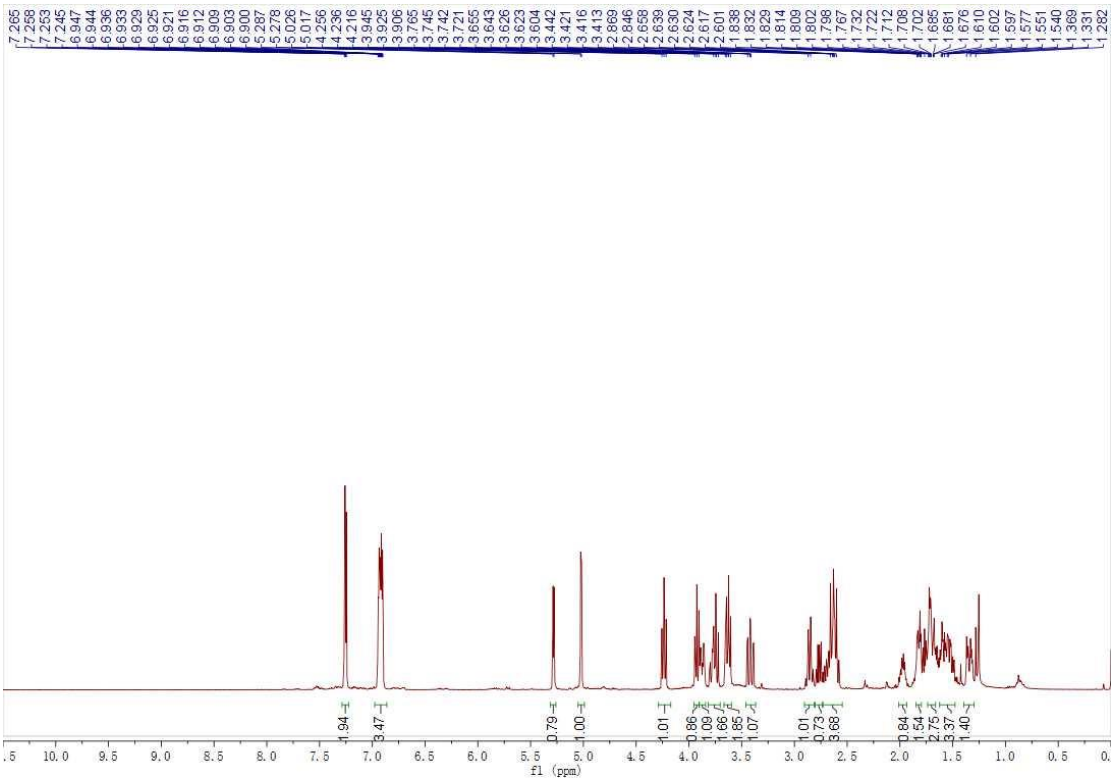
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5.017
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4.216
3.945
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3.745
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3.416
3.413
2.869
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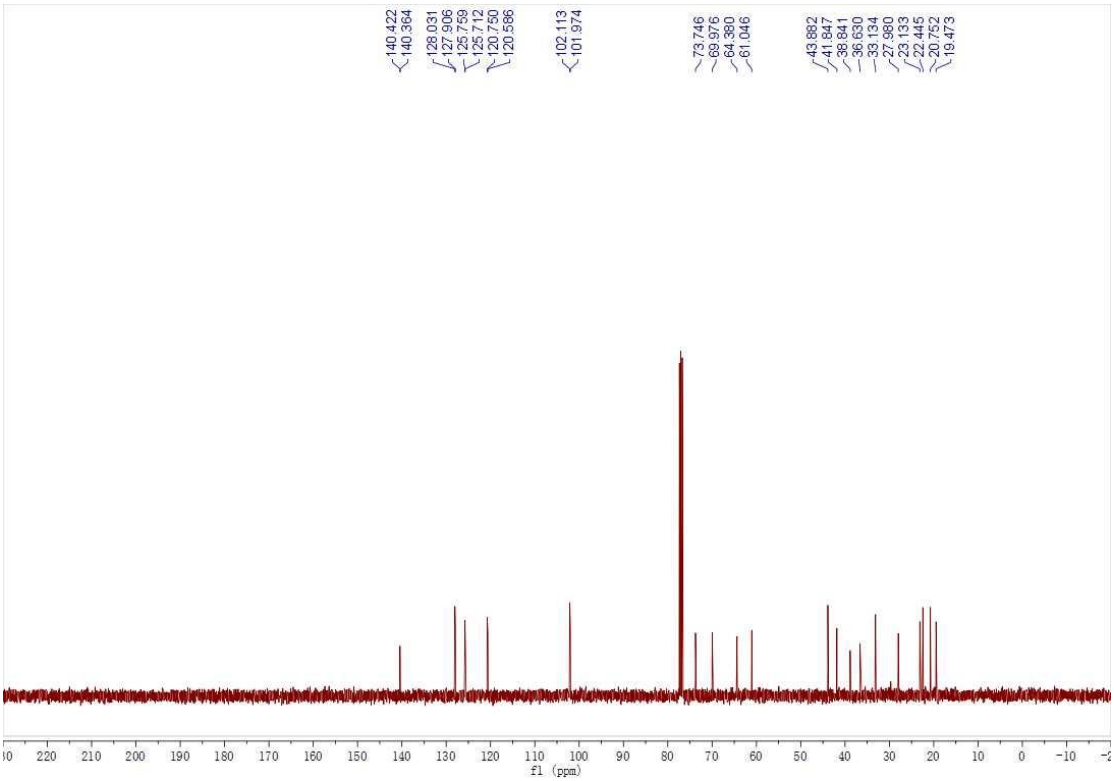
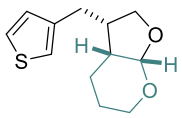
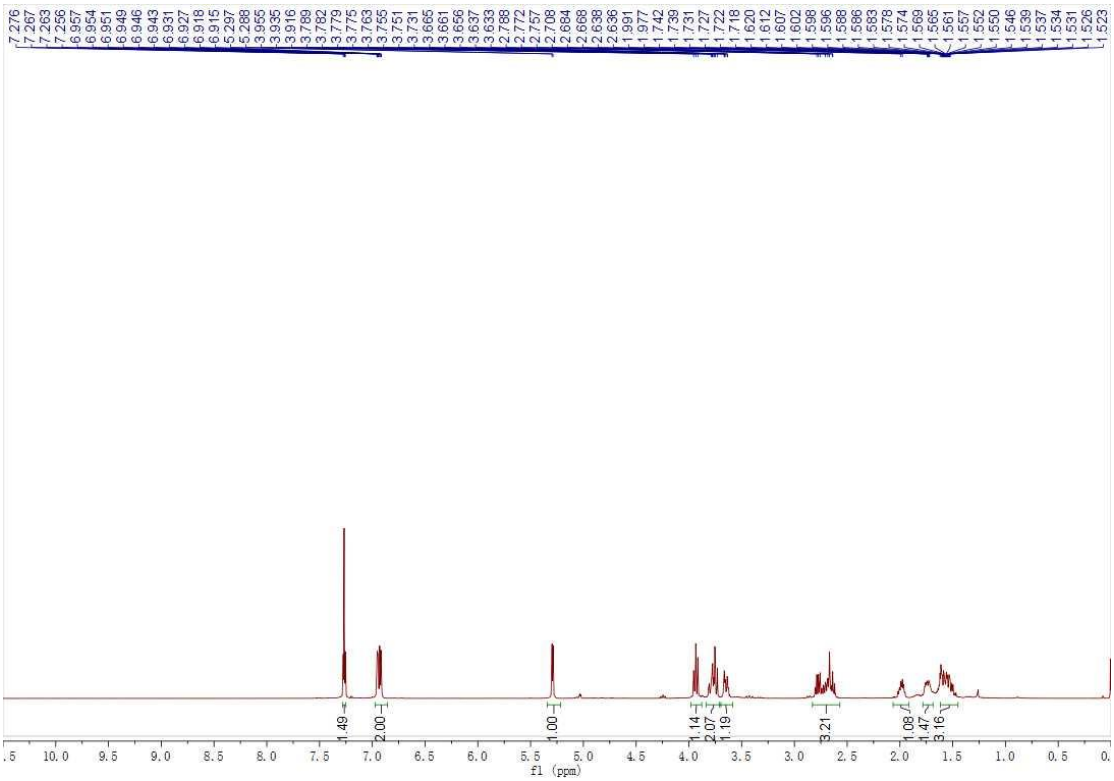
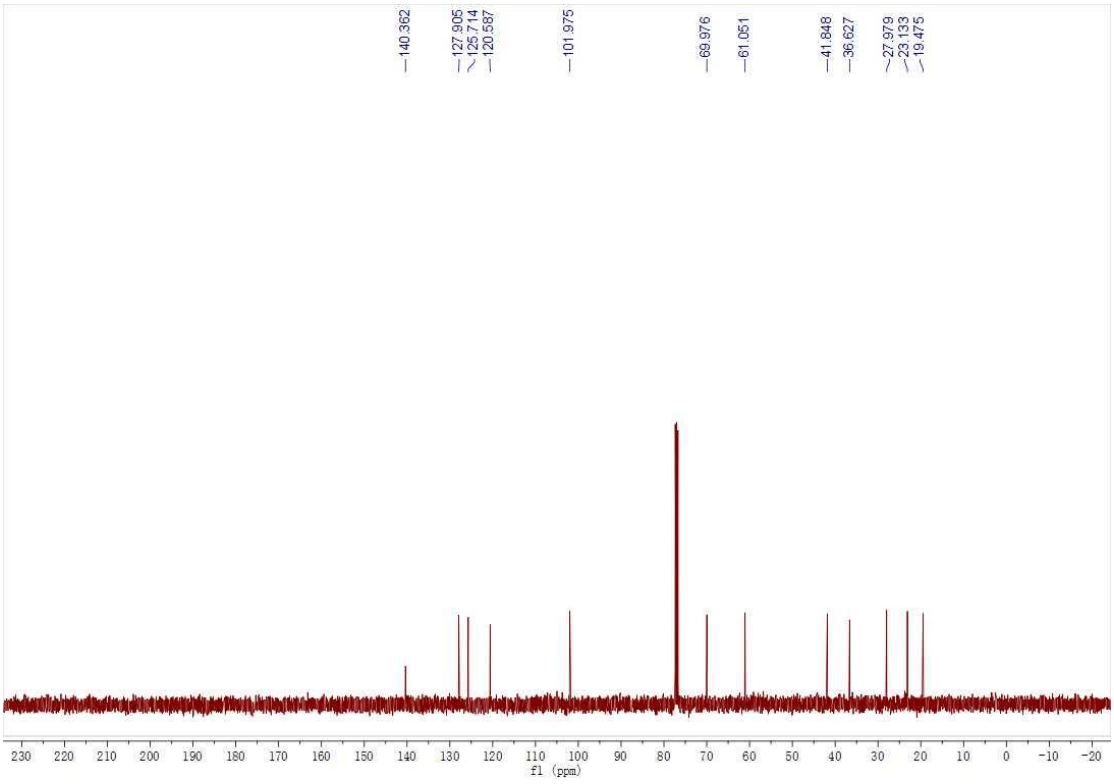
1.551
1.540
1.369
1.331
1.282
1.94
3.47
0.79
1.00
1.01
0.86
1.09
1.66
1.85
1.07
1.01
0.73
3.68
0.84
1.54
2.75
3.37
1.40
f1 (ppm)

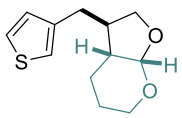

140.422
140.364
128.031
127.906
125.759
125.712
120.750
120.586
102.113
101.974
73.746
69.976
64.380
61.046
43.882
41.847
38.841
36.630
33.134
27.980
23.133
22.445
20.752
19.473
f1 (ppm)


H
O
S
H
O

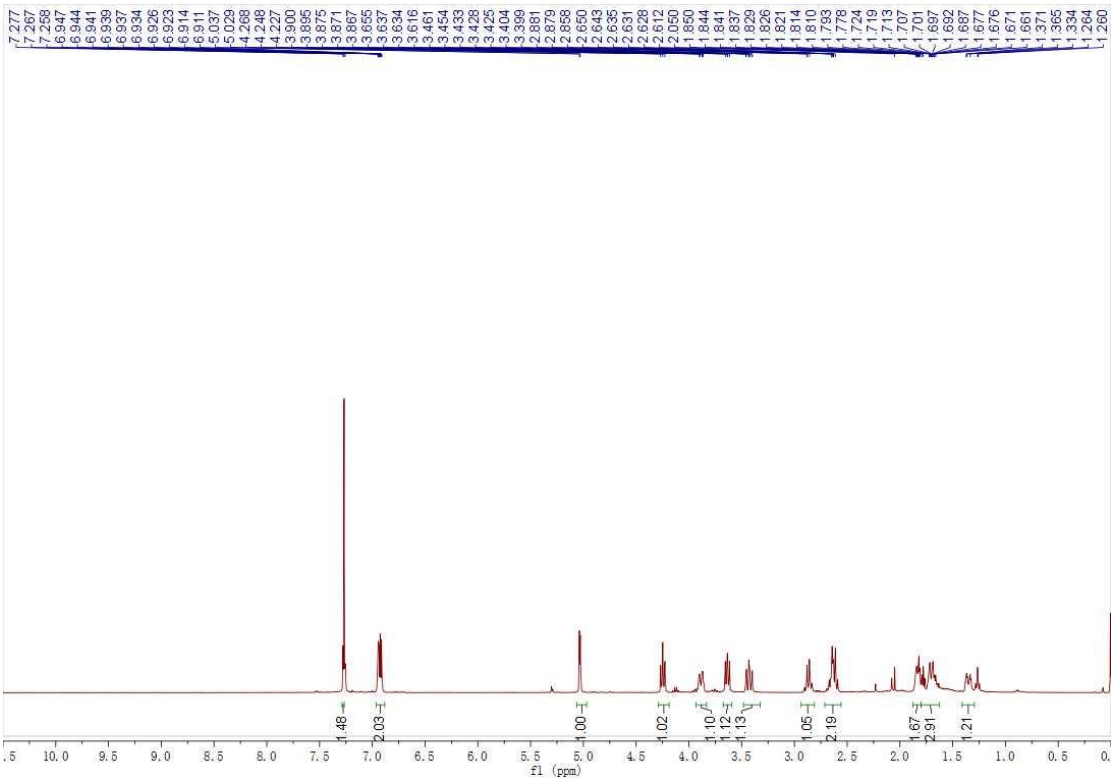
cis-syn


7.276
7.267
7.263
7.256
6.957
6.954
6.951
6.949
6.946
6.943
6.931
6.927
6.918
6.915
5.297
5.288
3.955
3.935
3.916
3.789
3.782
3.779
3.775
3.763
3.755
3.751
3.731
3.665
3.661
3.656
3.637
3.633
2.788
2.772
2.757
2.708
2.684
2.668
2.638
2.636
1.991
1.977
1.742
1.739
1.731
1.727
1.722
1.718
1.620
1.612
1.607
1.602
1.598
1.596
1.588
1.586
1.583
1.578
1.574
1.569
1.565
1.561
1.557
1.552
1.550
1.546
1.539
1.537
1.534
1.531
1.526
1.523
1.49
2.00
1.00
1.14
2.07
1.19
3.21
1.08
1.47
3.16
f1 (ppm)


140.362
127.905
125.714
120.587
101.975
69.976
61.051
41.848
36.627
27.979
23.133
19.475
f1 (ppm)


S
H
O
H
O

cis-anti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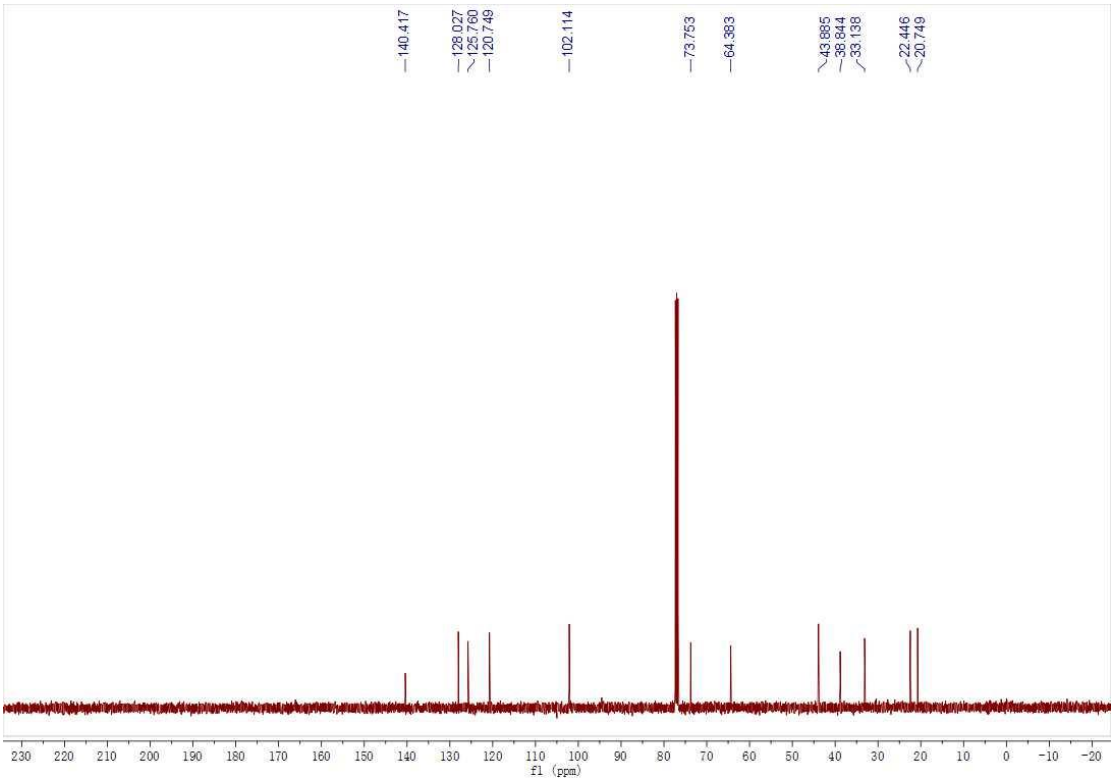
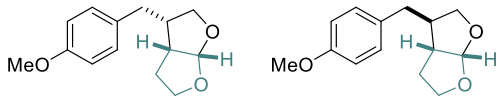
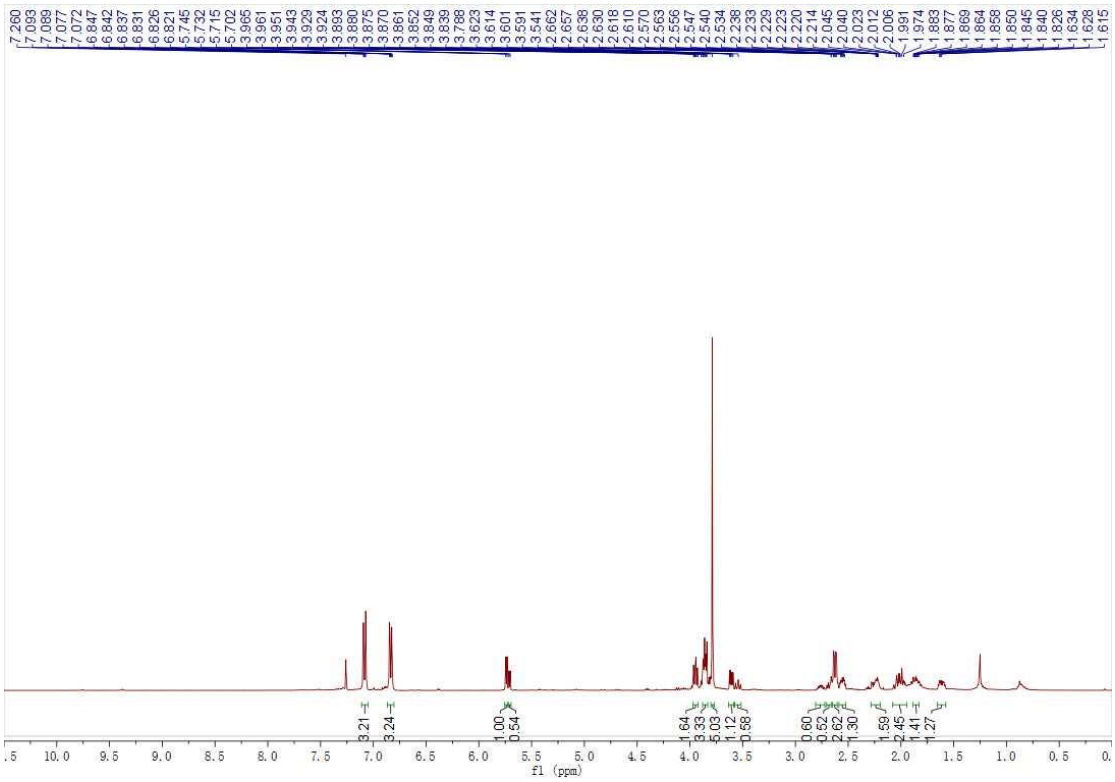
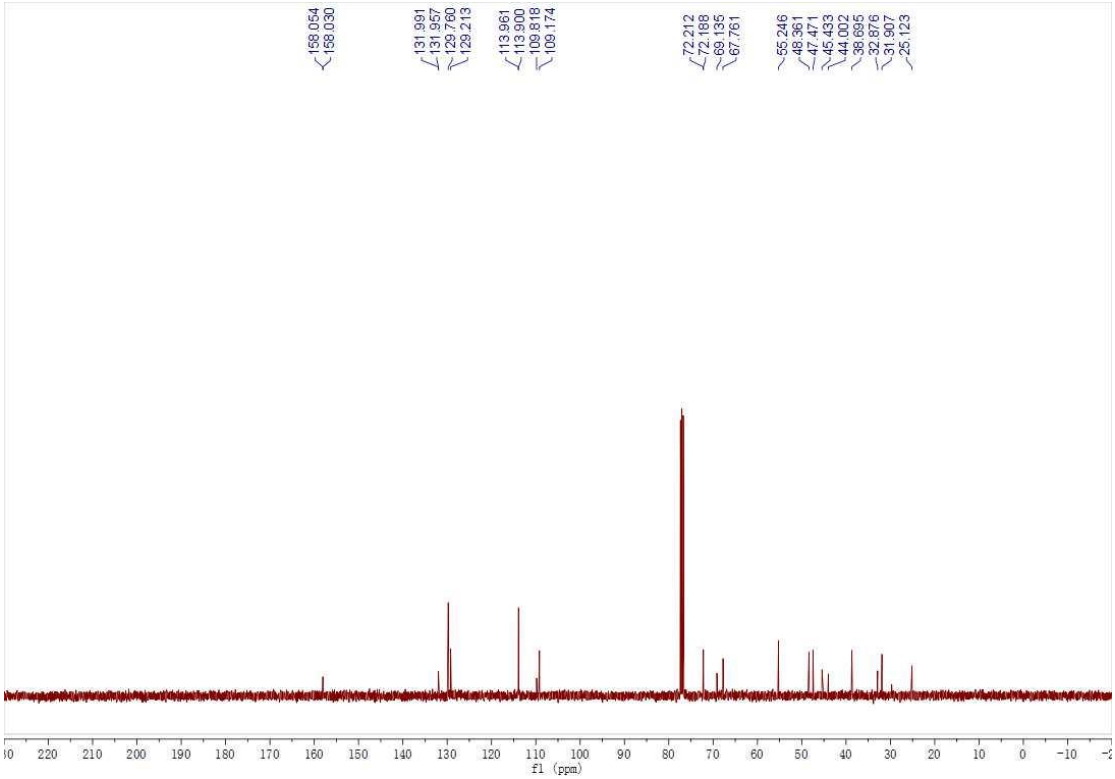
7.267
7.258
6.947
6.944
6.941
6.939
6.937
6.934
6.926
6.923
6.914
6.911
5.037
5.029
4.268
4.248
4.227
3.900
3.895
3.875
3.871
3.867
3.655
3.637
3.634
3.616
3.461
3.454
3.433
3.428
3.425
3.404
3.399
2.881
2.879
2.858
2.650
2.643
2.635
2.631
2.628
2.612
2.050
1.850
1.844
1.841
1.837
1.829
1.826
1.821
1.814
1.810
1.793
1.778
1.724
1.719
1.713
1.707
1.701
1.697
1.692
1.687
1.677
1.676
1.671
1.661
1.371
1.365
1.334
1.264
1.260
1.48
2.03
1.00
1.02
1.10
1.12
1.13
1.05
2.19
1.67
2.91
1.21
f1 (ppm)


140.417
128.027
125.760
120.749
102.114
73.753
64.383
43.885
38.844
33.138
22.446
20.749
f1 (ppm)

(**13**)


MeO
H
O
H
O
MeO
H
O
H
O


7.260
7.093
7.089
7.077
7.072
6.847
6.842
6.837
6.831
6.826
6.821
5.745
5.732
5.715
5.702
3.965
3.961
3.951
3.943
3.929
3.924
3.893
3.880
3.875
3.870
3.861
3.852
3.849
3.839
3.788
3.623
3.614
3.601
3.591
3.541
2.662
2.657
2.638
2.630
2.618
2.610
2.570
2.563
2.556
2.547
2.540
2.534
2.238
2.233
2.229
2.223
2.220
2.214
2.045
2.040
2.023
2.012
2.006
1.991
1.974
1.883
1.877
1.869
1.864
1.858
1.850
1.845
1.840
1.826
1.634
1.628
1.615
3.21
3.24
1.00
0.54
1.64
3.33
5.03
1.12
0.58
0.60
0.52
2.62
1.30
1.59
2.45
1.41
1.27
f1 (ppm)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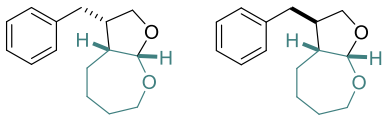
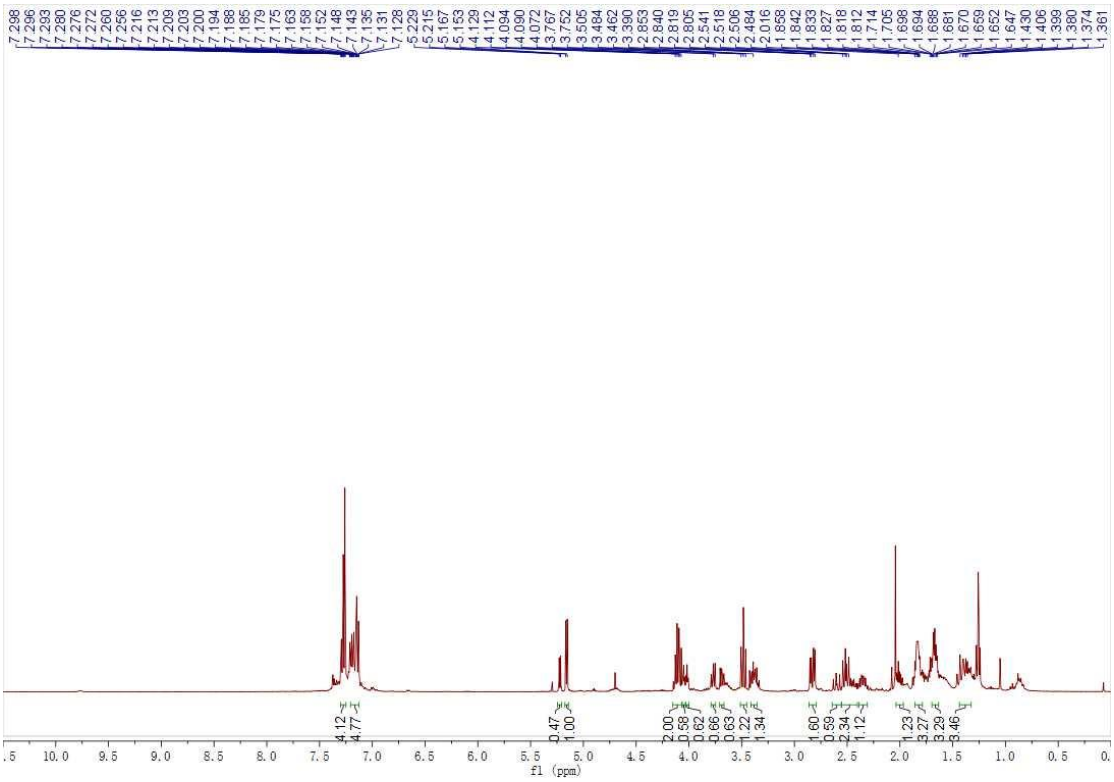
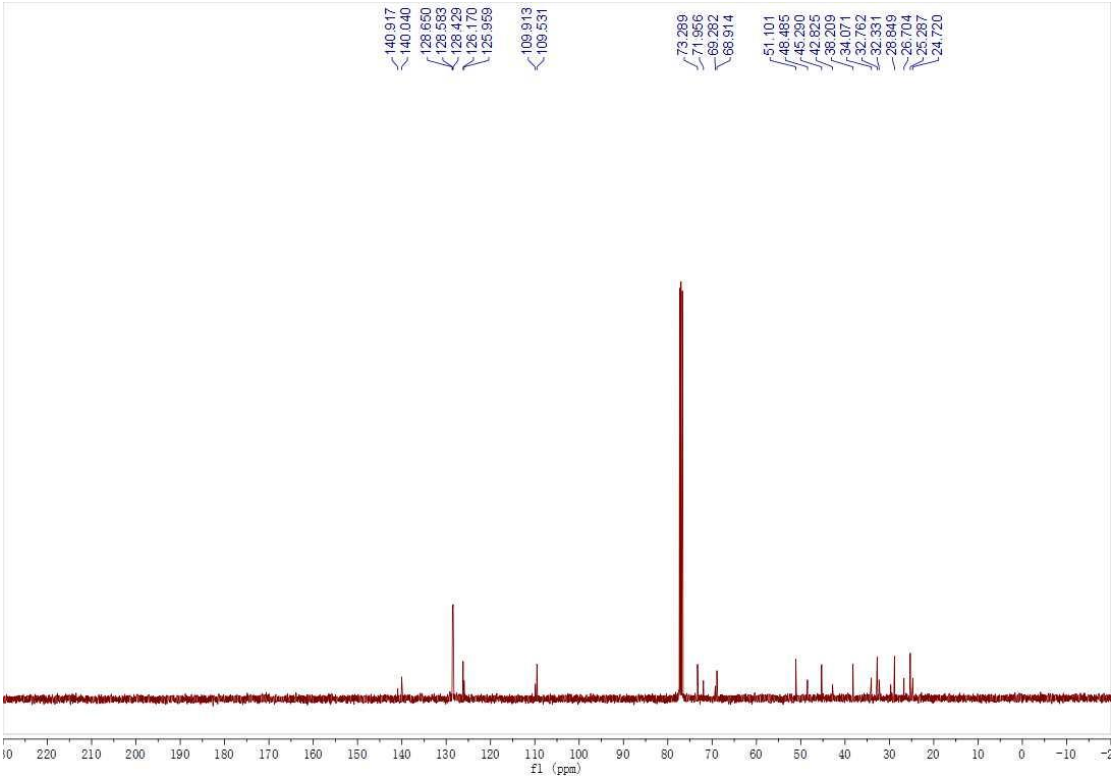
158.030
131.991
131.957
129.760
129.213
113.961
113.900
109.818
109.174
72.212
72.188
69.135
67.761
55.246
48.361
47.471
45.433
44.002
38.695
32.876
31.907
25.123
f1 (ppm)

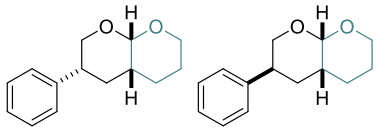
(14)

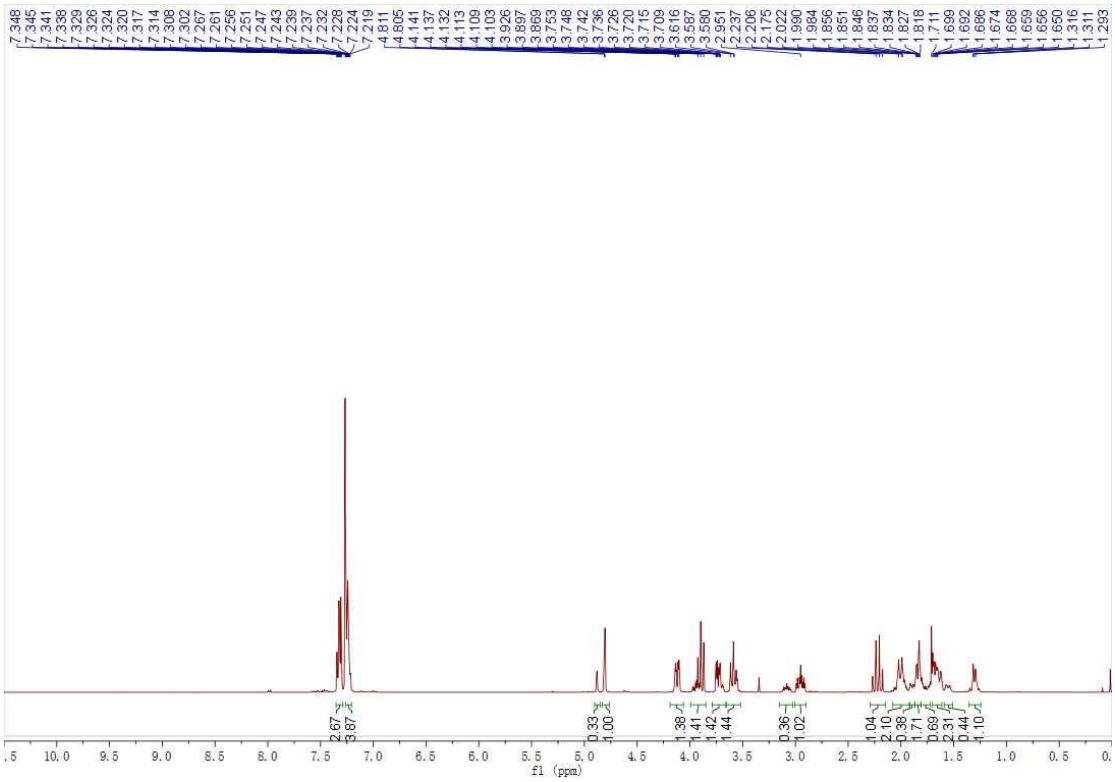



7.298
7.296
7.293
7.280
7.276
7.272
7.260
7.256
7.216
7.213
7.209
7.203
7.200
7.194
7.188
7.185
7.179
7.175
7.163
7.158
7.152
7.148
7.143
7.135
7.131
7.128
5.229
5.215
5.167
5.153
4.129
4.112
4.094
4.090
4.072
3.767
3.752
3.505
3.484
3.462
3.390
2.853
2.840
2.819
2.805
2.541
2.518
2.506
2.484
2.016
1.858
1.842
1.833
1.827
1.818
1.812
1.714
1.705
1.698
1.694
1.688
1.681
1.670
1.659
1.652
1.647
1.430
1.406
1.399
1.380
1.374
1.361
4.12
4.77
0.47
1.00
2.00
0.58
0.62
0.66
0.63
1.22
1.34
1.60
0.59
2.34
1.12
1.23
3.27
3.29
3.46
f1 (ppm)


140.917
140.040
128.650
128.583
128.429
126.170
125.959
109.913
109.531
73.289
71.956
69.282
68.914
51.101
48.485
45.290
42.825
38.209
34.071
32.762
32.331
28.849
26.704
25.287
24.720
f1 (ppm)

(15)




7.348
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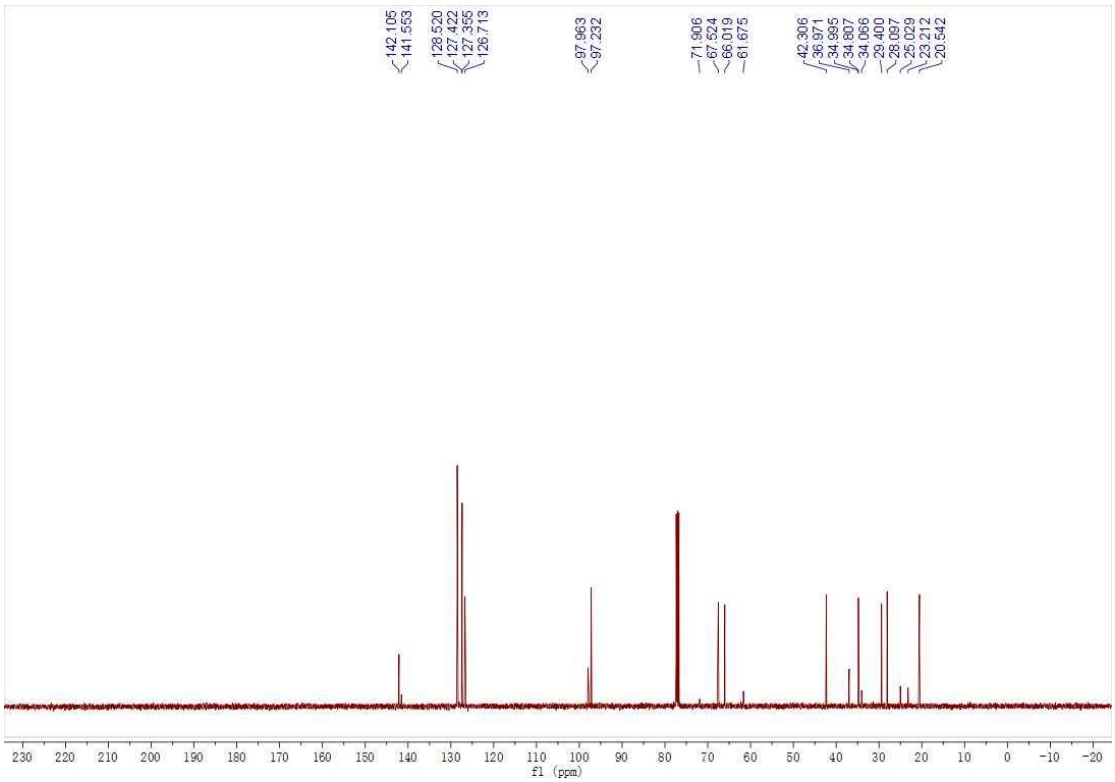
7.341
7.338
7.329
7.326
7.324
7.320
7.317
7.314
7.308
7.302
7.267
7.261
7.256
7.251
7.247
7.243
7.239
7.237
7.232
7.228
7.224
7.219
4.811
4.805
4.141
4.137
4.132
4.113
4.109
4.103
3.926
3.897
3.869
3.753
3.748
3.742
3.736
3.726
3.720
3.715
3.709
3.616
3.587
3.560
2.951
2.237
2.206
2.175
2.022
1.990
1.984
1.856
1.851
1.846
1.837
1.834
1.827
1.818
1.711
1.699
1.692
1.686
1.674
1.668
1.659
1.656
1.650
1.316
1.311
1.293
2.67
3.87
0.33
1.00
1.38
1.41
1.42
1.44
0.36
1.02
1.04
2.10
0.38
1.71
0.69
2.31
0.44
1.10
f1 (ppm)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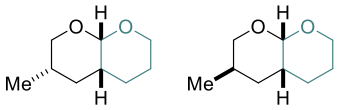
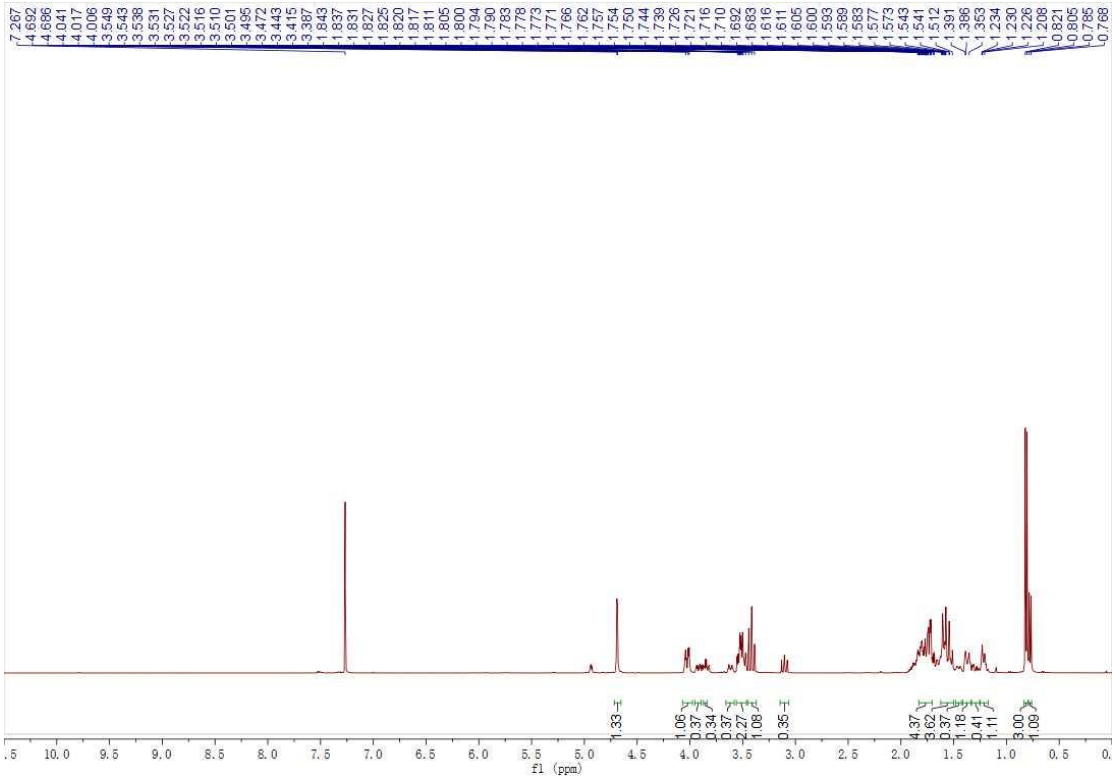
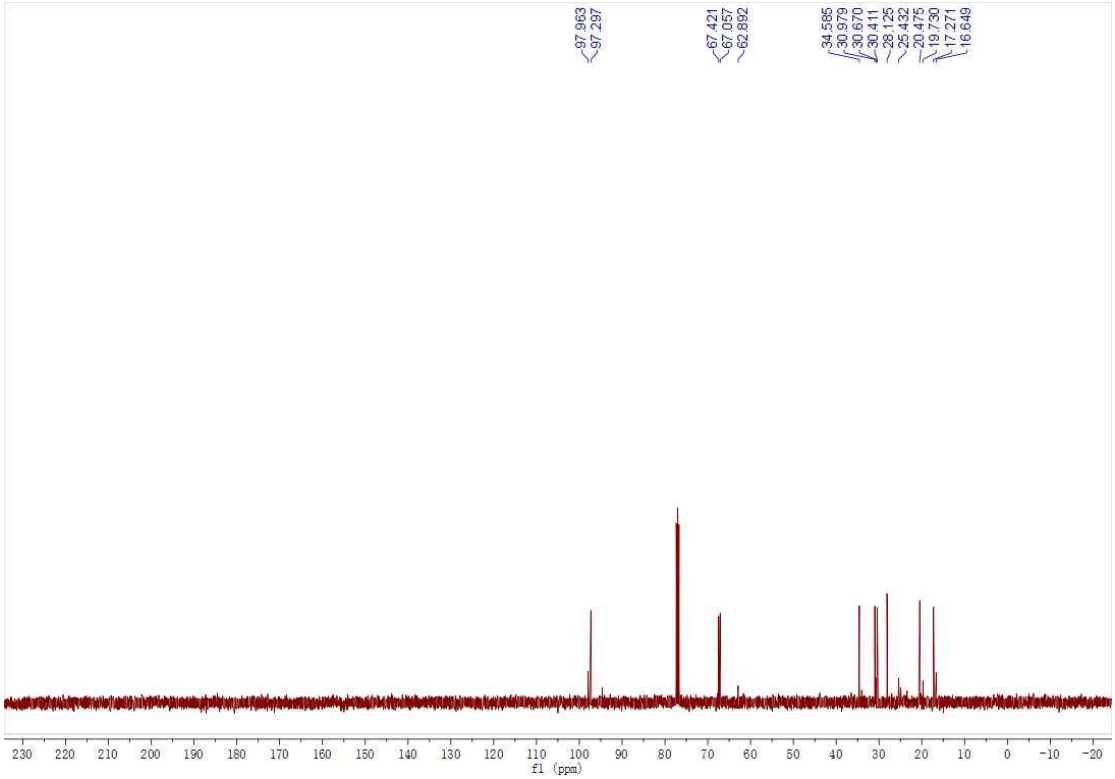
141.553
128.520
127.422
127.355
126.713
97.963
97.232
71.906
67.524
66.019
61.675
42.306
36.971
34.995
34.807
34.066
29.400
28.097
25.029
23.212
20.542
f1 (ppm)

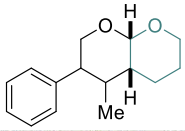
(**16**)

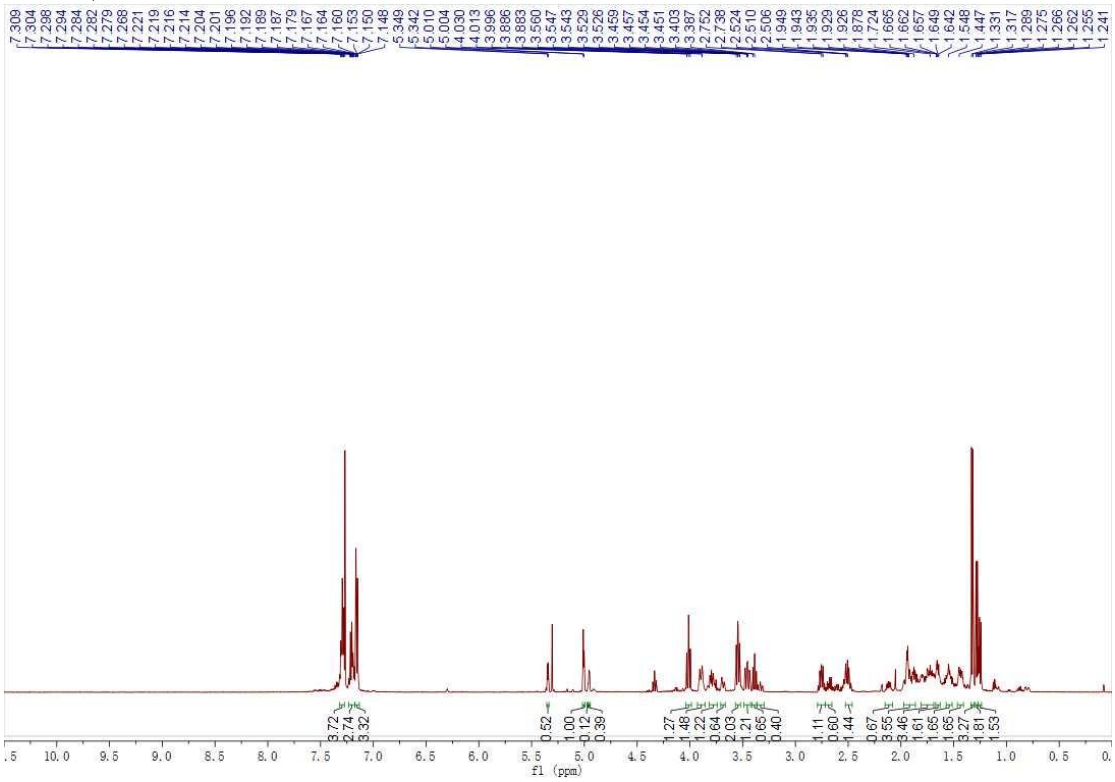

H
O
O
Me
H
H
O
O
Me
H


7.267
4.692
4.686
4.041
4.017
4.006
3.549
3.543
3.538
3.531
3.527
3.522
3.516
3.510
3.501
3.495
3.472
3.443
3.415
3.387
1.843
1.837
1.831
1.827
1.825
1.820
1.817
1.811
1.805
1.800
1.794
1.790
1.783
1.778
1.773
1.771
1.766
1.762
1.757
1.754
1.750
1.744
1.739
1.726
1.721
1.716
1.710
1.692
1.683
1.616
1.611
1.605
1.600
1.593
1.589
1.583
1.577
1.573
1.543
1.541
1.512
1.391
1.386
1.353
1.234
1.230
1.226
1.208
0.821
0.805
0.785
0.768
1.33
1.06
0.37
0.34
0.37
2.27
1.08
0.35
4.37
3.62
0.37
1.18
0.41
1.11
3.00
1.09
f1 (ppm)


97.963
97.297
67.421
67.057
62.892
34.585
30.979
30.670
30.411
28.125
25.432
20.475
19.730
17.271
16.649
f1 (ppm)

(**17**)


H
O
O
H
Me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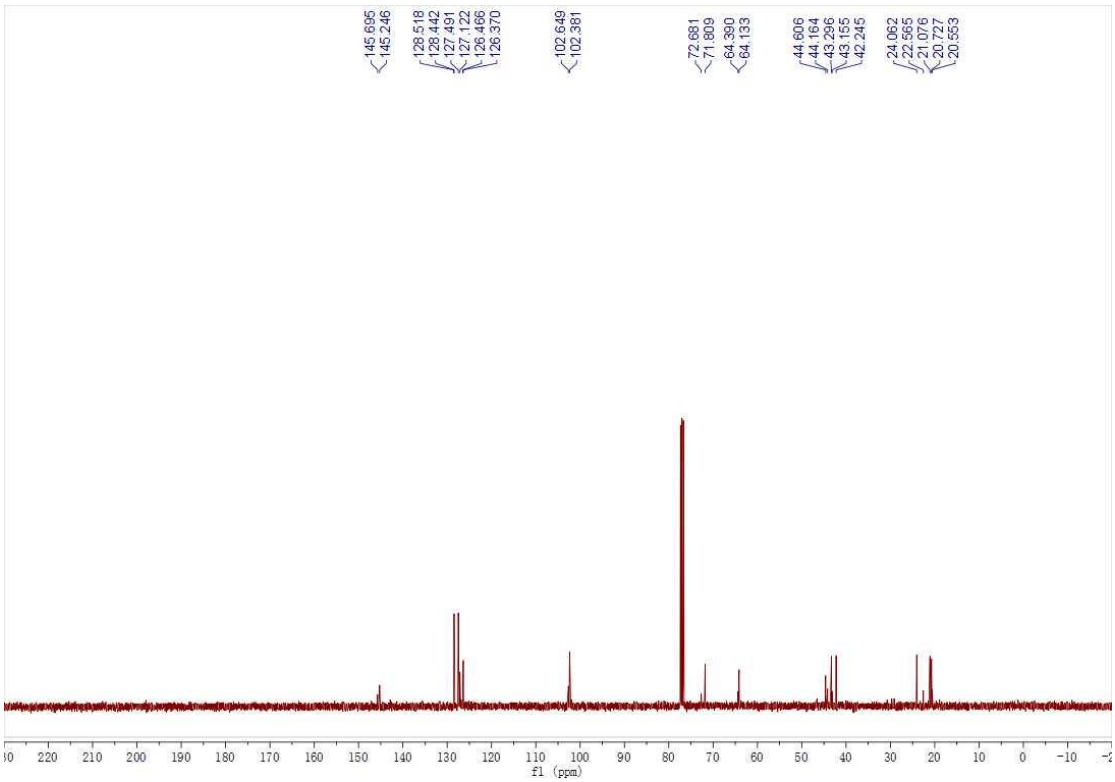
7.282
7.279
7.268
7.221
7.219
7.216
7.214
7.204
7.201
7.196
7.192
7.189
7.187
7.179
7.167
7.164
7.160
7.153
7.150
7.148
5.349
5.342
5.010
5.004
4.030
4.013
3.996
3.886
3.883
3.560
3.547
3.543
3.529
3.526
3.459
3.457
3.454
3.451
3.403
3.387
2.752
2.738
2.524
2.510
2.506
1.949
1.943
1.935
1.929
1.926
1.878
1.724
1.665
1.662
1.657
1.649
1.642
1.548
1.447
1.331
1.317
1.289
1.275
1.266
1.262
1.255
1.241
3.72
2.74
3.32
0.52
1.00
0.12
0.39
1.27
1.48
1.22
0.64
2.03
1.21
0.65
0.40
1.11
0.60
1.44
0.67
3.55
3.46
1.61
1.65
1.65
3.27
1.81
1.53
f1 (ppm)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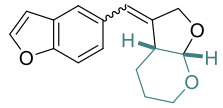
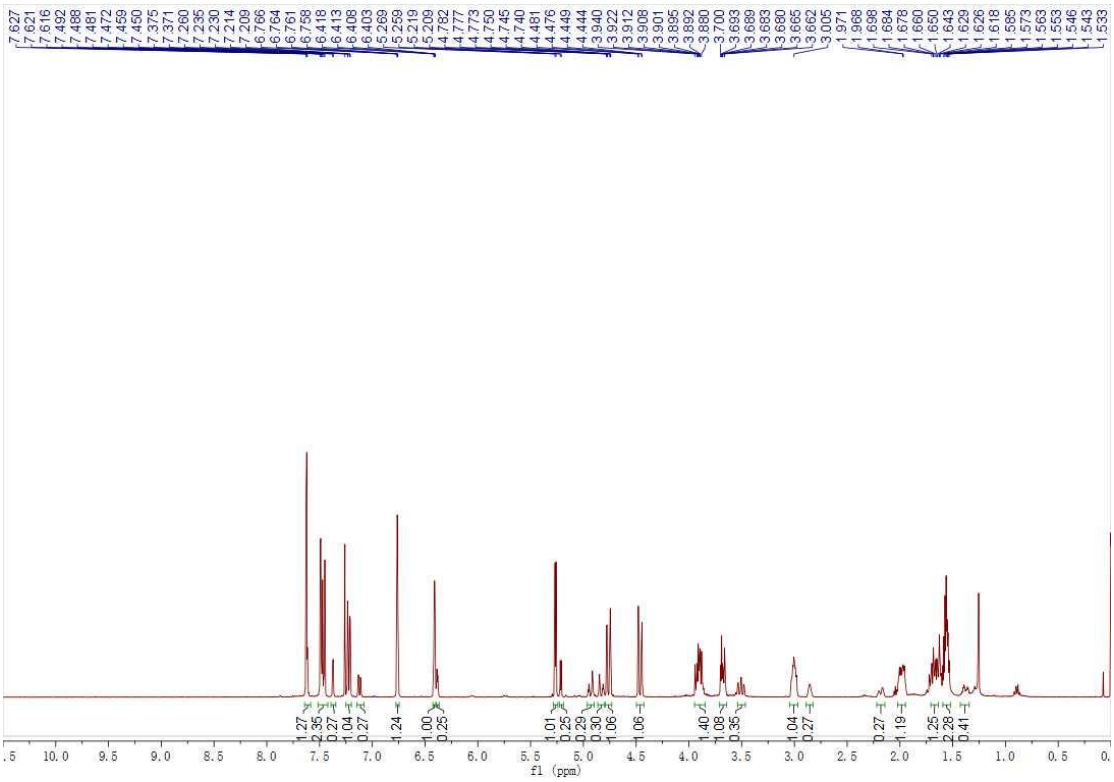
128.518
128.442
127.491
127.122
126.466
126.370
102.649
102.381
72.681
71.809
64.390
64.133
44.606
44.164
43.296
43.155
42.245
24.062
22.565
21.076
20.727
20.553
f1 (ppm)

(18)


H
O
H
O
O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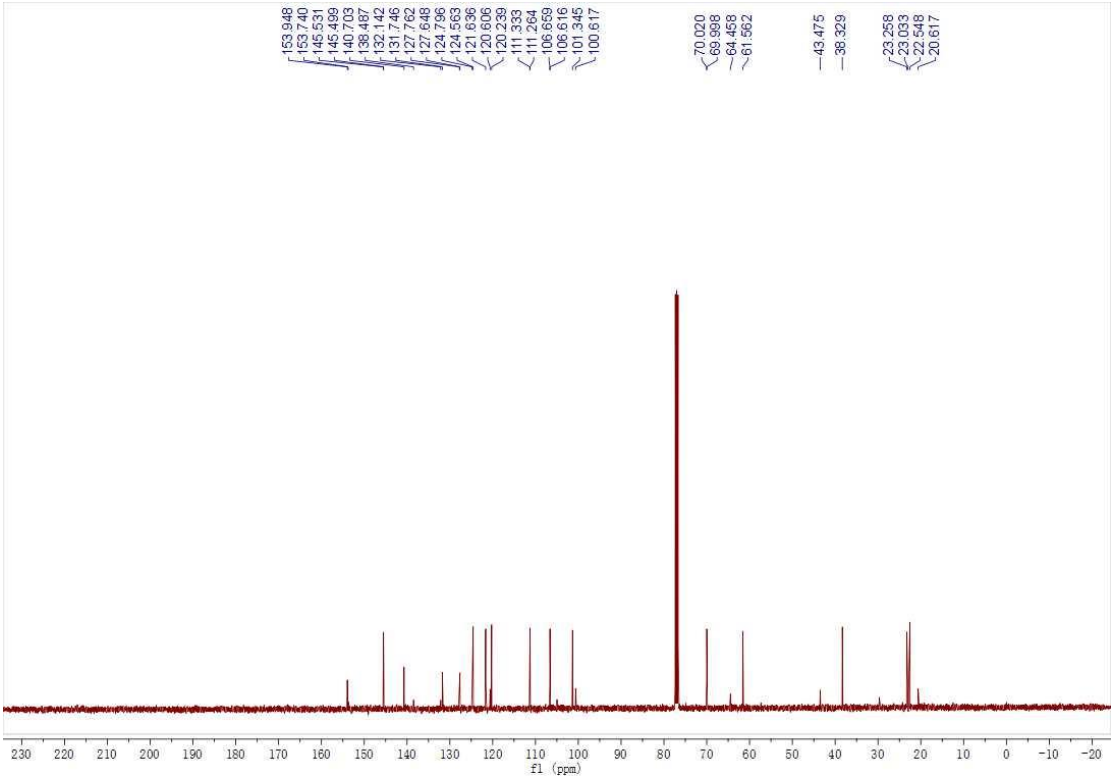
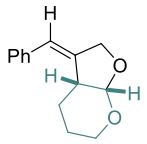
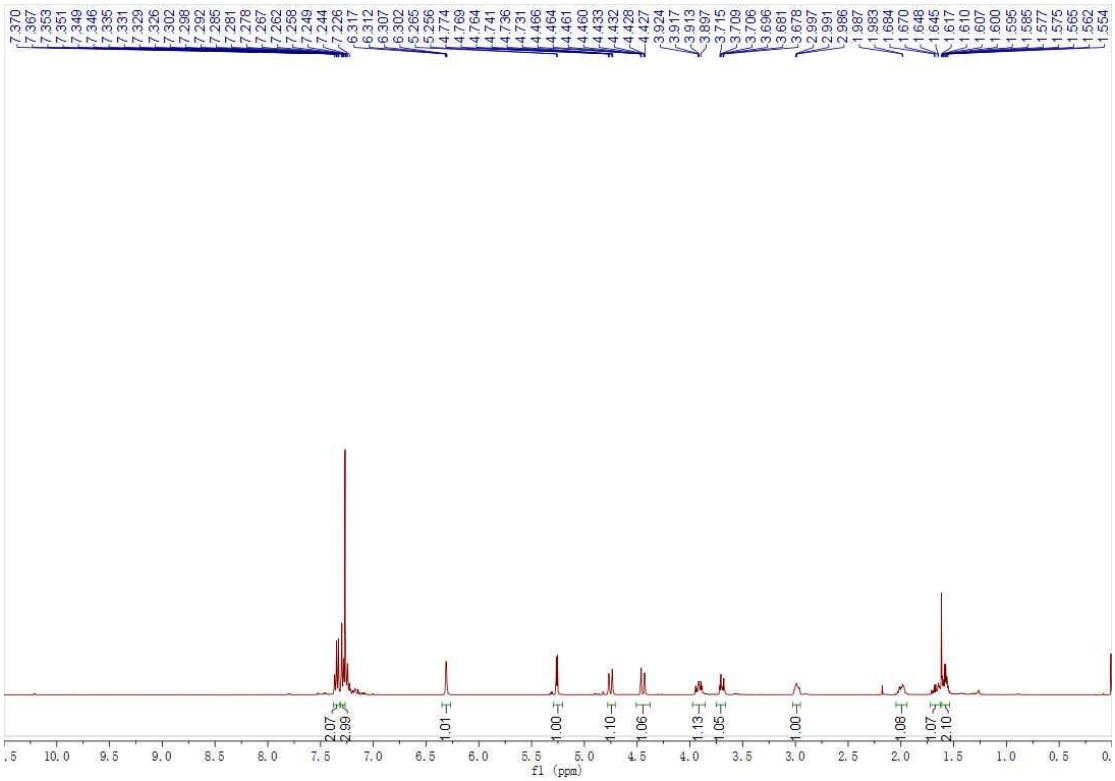
7.616
7.492
7.488
7.481
7.472
7.459
7.450
7.375
7.371
7.260
7.235
7.230
7.214
7.209
6.766
6.764
6.761
6.758
6.418
6.413
6.408
6.403
5.269
5.259
5.219
5.209
4.782
4.777
4.773
4.750
4.745
4.740
4.481
4.476
4.449
4.444
3.940
3.922
3.912
3.908
3.901
3.895
3.892
3.880
3.700
3.693
3.689
3.683
3.680
3.665
3.662
3.005
1.971
1.968
1.698
1.684
1.678
1.660
1.650
1.643
1.629
1.626
1.618
1.585
1.573
1.563
1.553
1.546
1.543
1.533
1.27
2.35
0.27
1.04
0.27
1.24
1.00
0.25
1.01
0.25
0.29
0.30
1.06
1.06
1.40
1.08
0.35
1.04
0.27
0.27
1.19
1.25
2.28
0.41
f1 (ppm)


153.948
153.740
145.531
145.499
140.703
138.487
132.142
131.746
127.762
127.648
124.796
124.563
121.636
120.606
120.239
111.333
111.264
106.659
106.616
101.345
100.617
70.020
69.998
64.458
61.562
43.475
38.329
23.258
23.033
22.548
20.617
f1 (ppm)

(**19**)


H
Ph
O
H
H
O

E-isomer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7.346
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7.331
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7.302
7.298
7.292
7.285
7.281
7.278
7.267
7.262
7.258
7.249
7.244
7.226
6.317
6.312
6.307
6.302
5.265
5.256
4.774
4.769
4.764
4.741
4.736
4.731
4.466
4.464
4.461
4.460
4.433
4.432
4.428
4.427
3.924
3.917
3.913
3.897
3.715
3.709
3.706
3.696
3.681
3.678
2.997
2.991
2.986
1.987
1.983
1.684
1.670
1.648
1.645
1.617
1.610
1.607
1.600
1.595
1.585
1.577
1.575
1.565
1.562
1.554
2.07
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1.06
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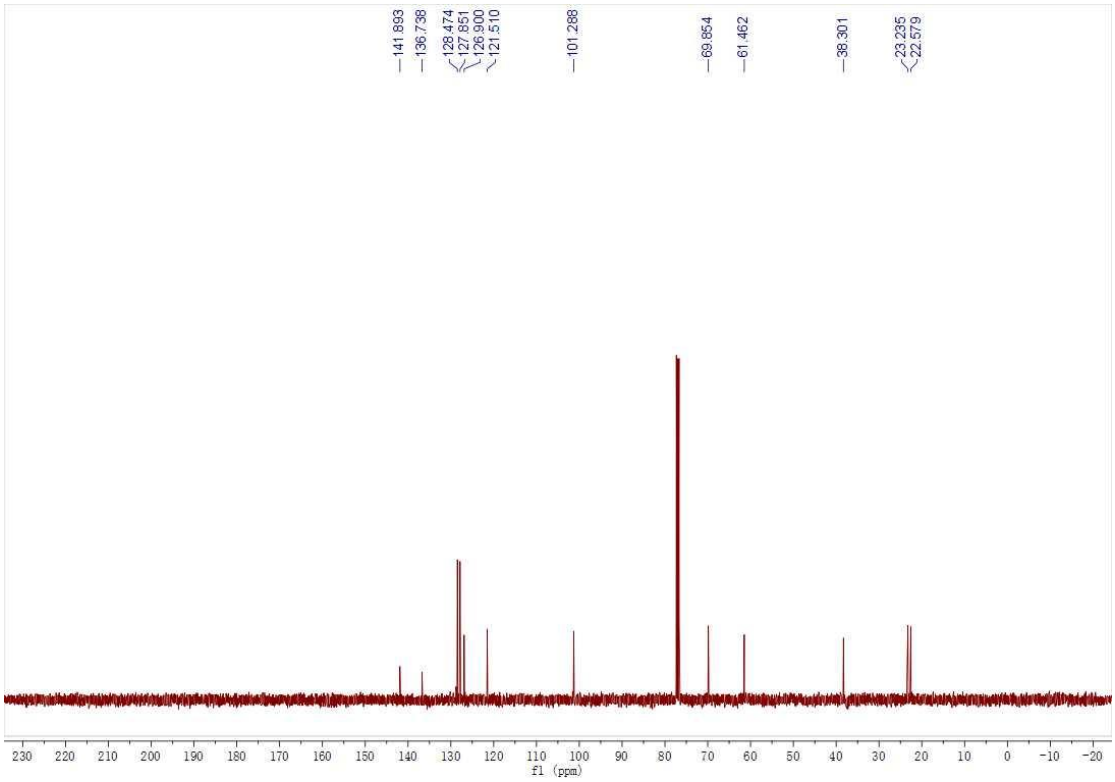
1.05
1.00
1.08
1.07
2.10
f1 (ppm)


141.893
136.738
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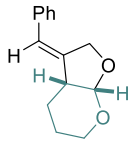
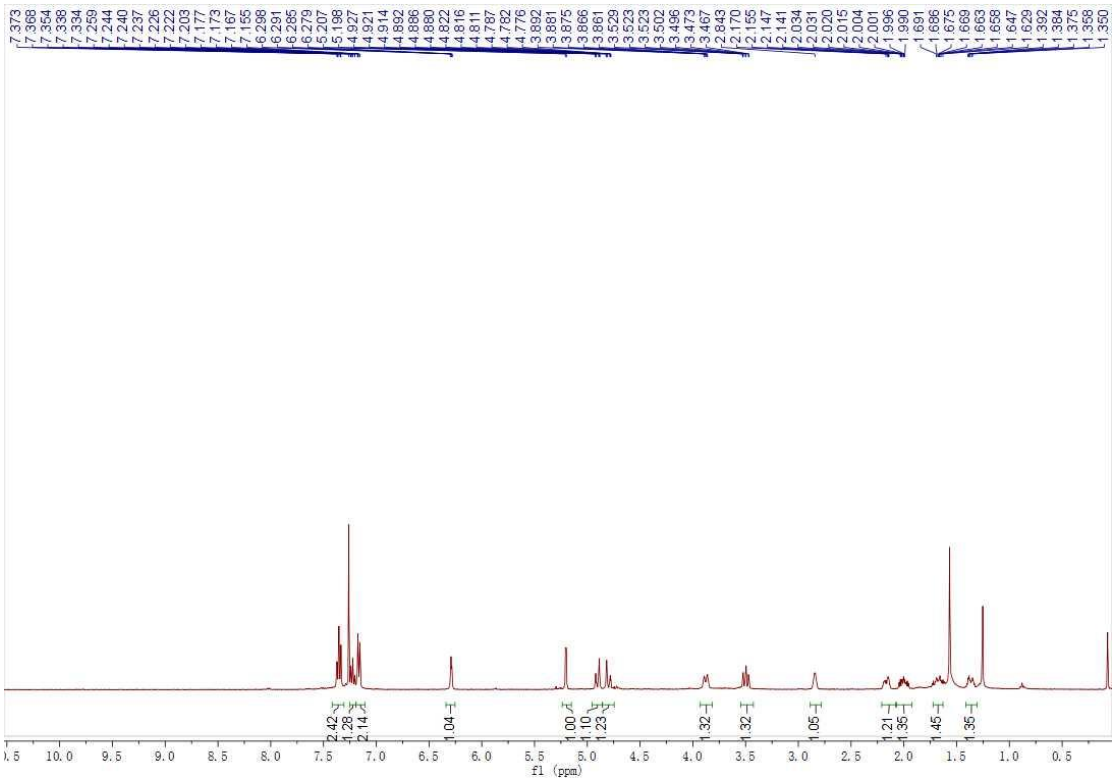
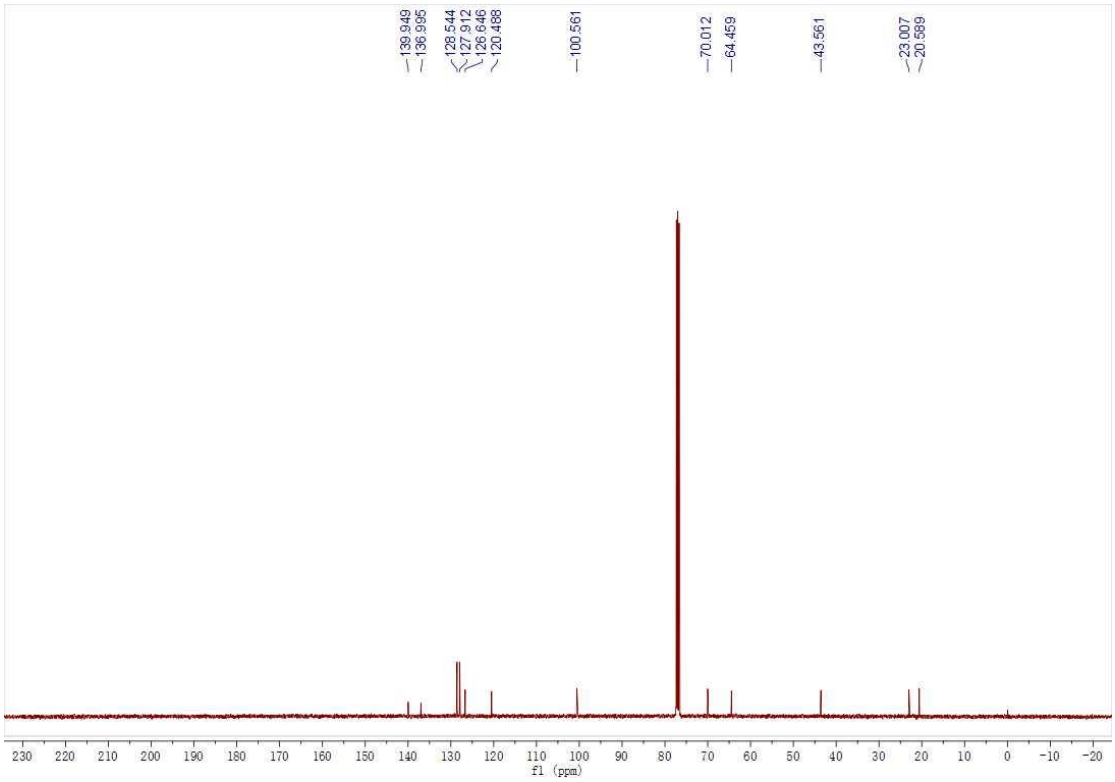
127.851
126.900
121.510
101.288
69.854
61.462
38.301
23.235
22.579
f1 (ppm)

(**19**)

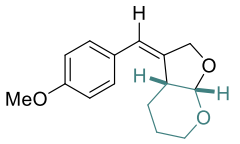


Z-isomer

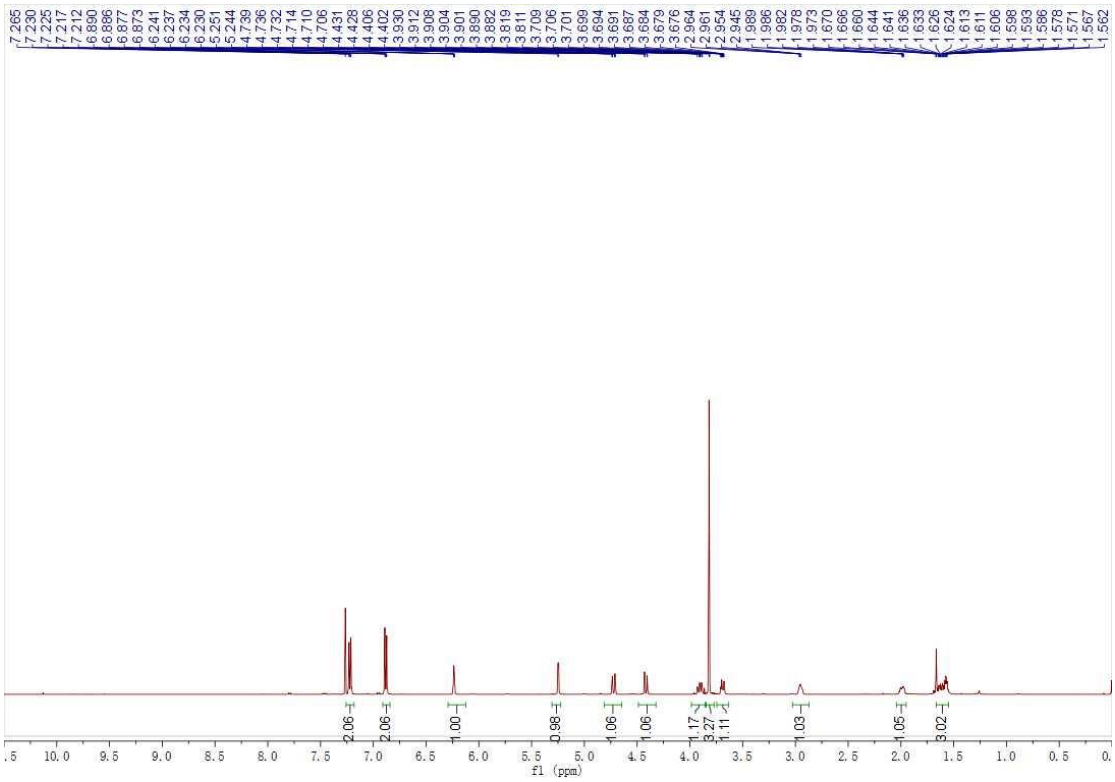




(**20**)


H
MeO
H
O
H
O

E-isomer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6.877
6.873
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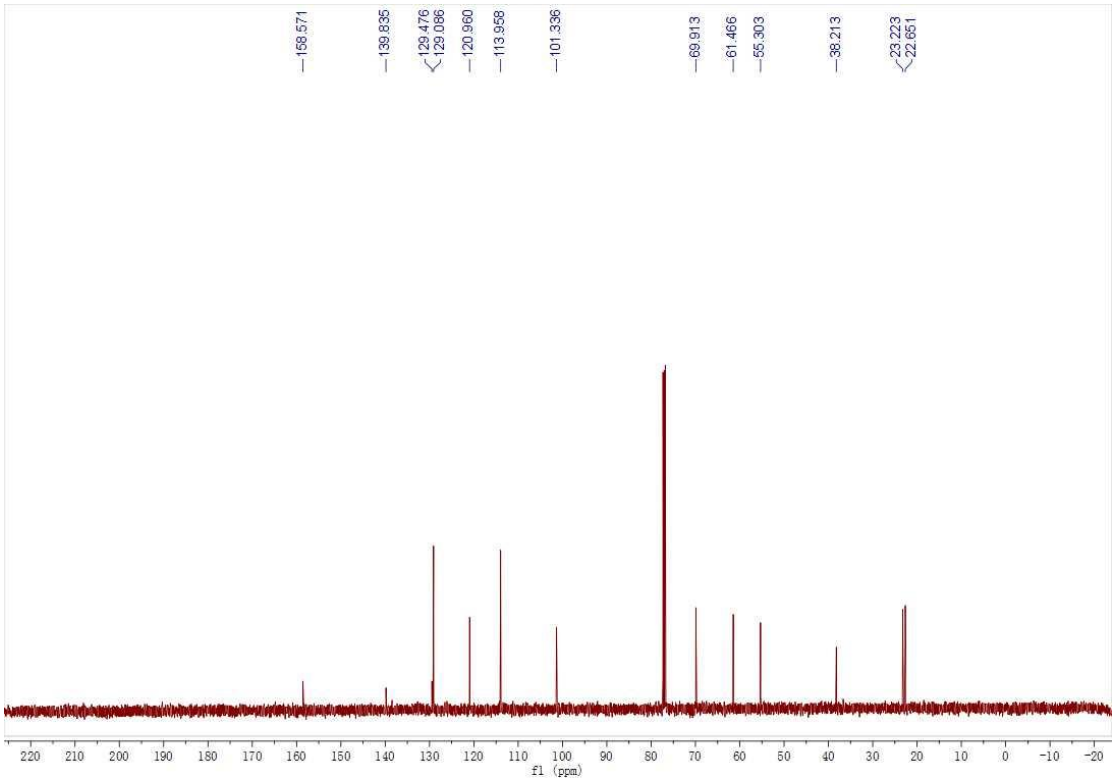
6.237
6.234
6.230
5.251
5.244
4.739
4.736
4.732
4.714
4.710
4.706
4.431
4.428
4.406
4.402
3.930
3.912
3.908
3.904
3.901
3.890
3.882
3.819
3.811
3.709
3.706
3.701
3.699
3.694
3.691
3.687
3.684
3.679
3.676
2.964
2.961
2.954
2.945
1.989
1.986
1.982
1.978
1.973
1.670
1.666
1.660
1.644
1.641
1.636
1.633
1.626
1.624
1.613
1.611
1.606
1.598
1.593
1.586
1.578
1.571
1.567
1.562
2.06
2.06
1.00
0.98
1.06
1.06
1.17
3.27
1.11
1.03
1.05
3.02
f1 (ppm)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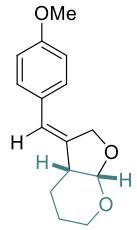
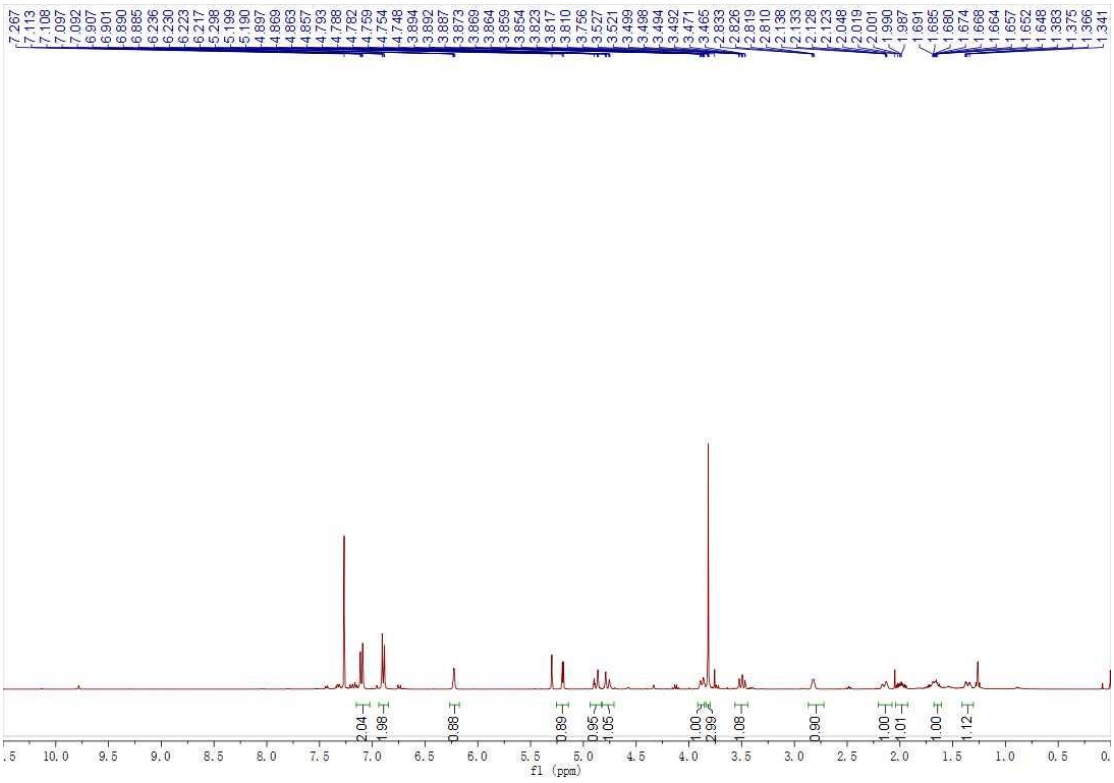
139.835
129.476
129.086
120.960
113.958
101.336
69.913
61.466
55.303
38.213
23.223
22.651
f1 (ppm)

(**20**)


OMe
H
H
O
H
O

Z-isomer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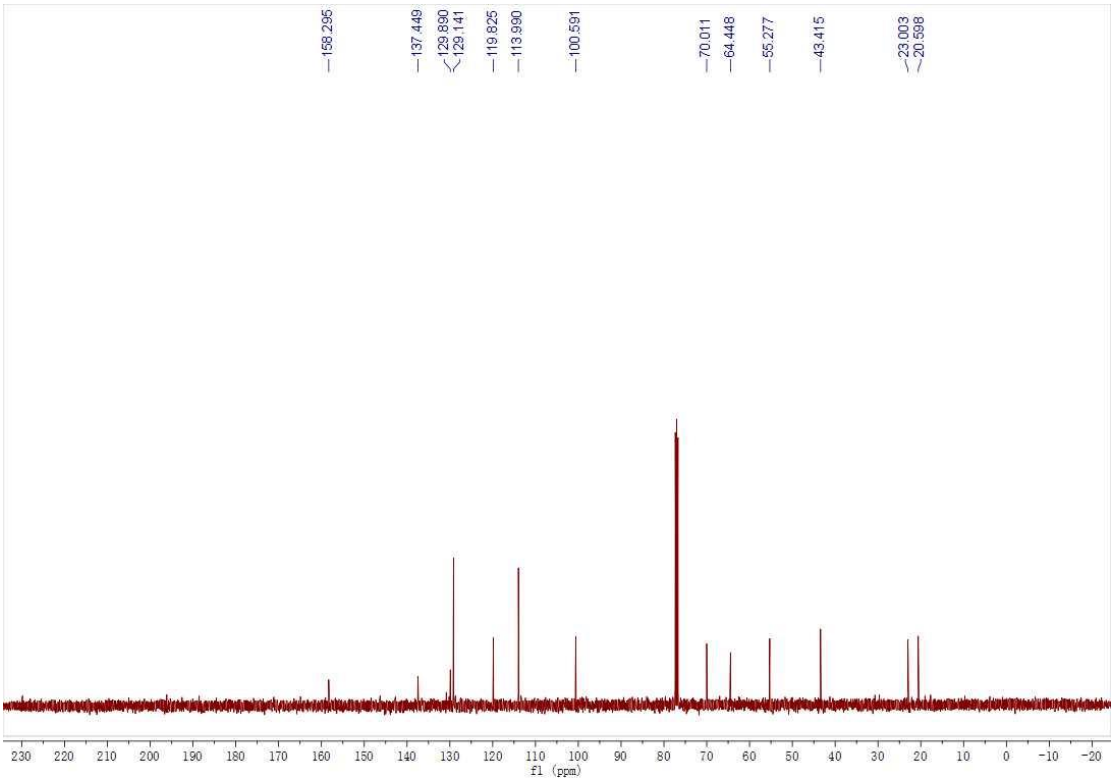
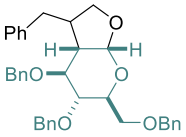
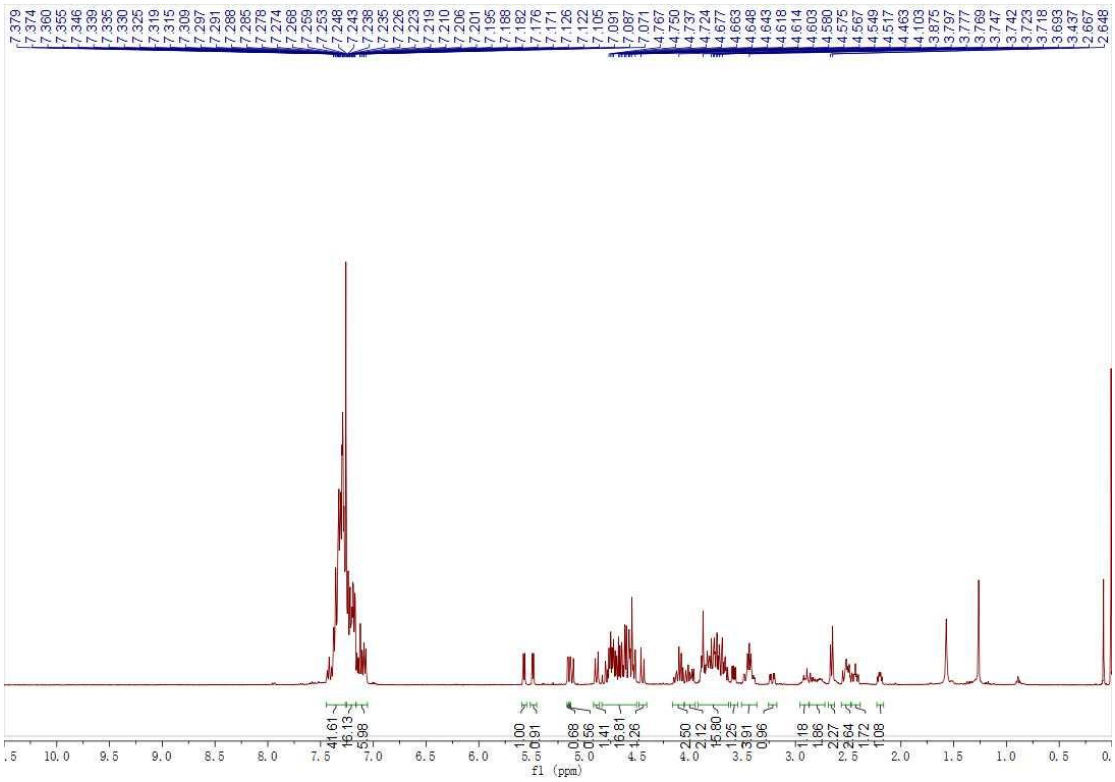
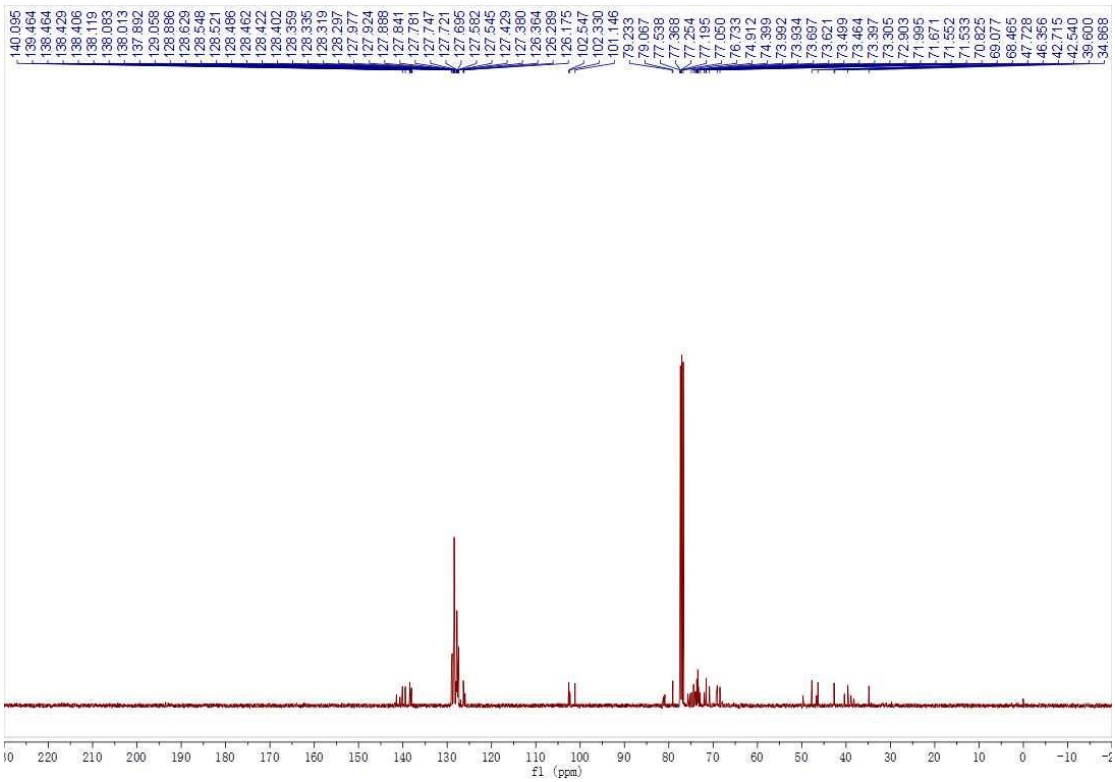
7.108
7.097
7.092
6.907
6.901
6.890
6.885
6.236
6.230
6.223
6.217
5.298
5.199
5.190
4.897
4.869
4.863
4.857
4.793
4.788
4.782
4.759
4.754
4.748
3.894
3.892
3.887
3.873
3.869
3.864
3.859
3.854
3.823
3.817
3.810
3.756
3.527
3.521
3.499
3.498
3.494
3.492
3.471
3.465
2.833
2.826
2.819
2.810
2.138
2.133
2.128
2.123
2.048
2.019
2.001
1.990
1.987
1.691
1.685
1.680
1.674
1.668
1.664
1.657
1.652
1.648
1.383
1.375
1.366
1.341
2.04
1.98
0.88
0.89
0.95
1.05
1.00
2.99
1.08
0.90
1.00
1.01
1.00
1.12
f1 (ppm)


158.295
137.449
129.890
129.141
119.825
113.990
100.591
70.011
64.448
55.277
43.415
23.003
20.598
f1 (ppm)

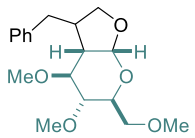
(21)

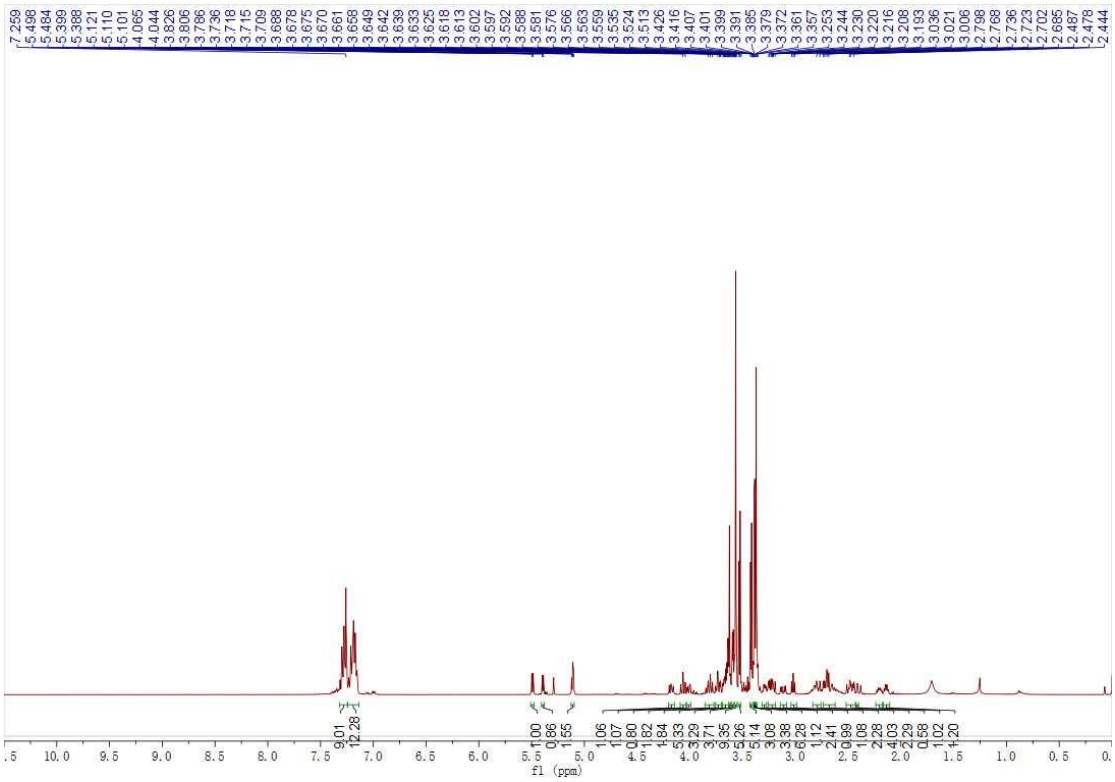


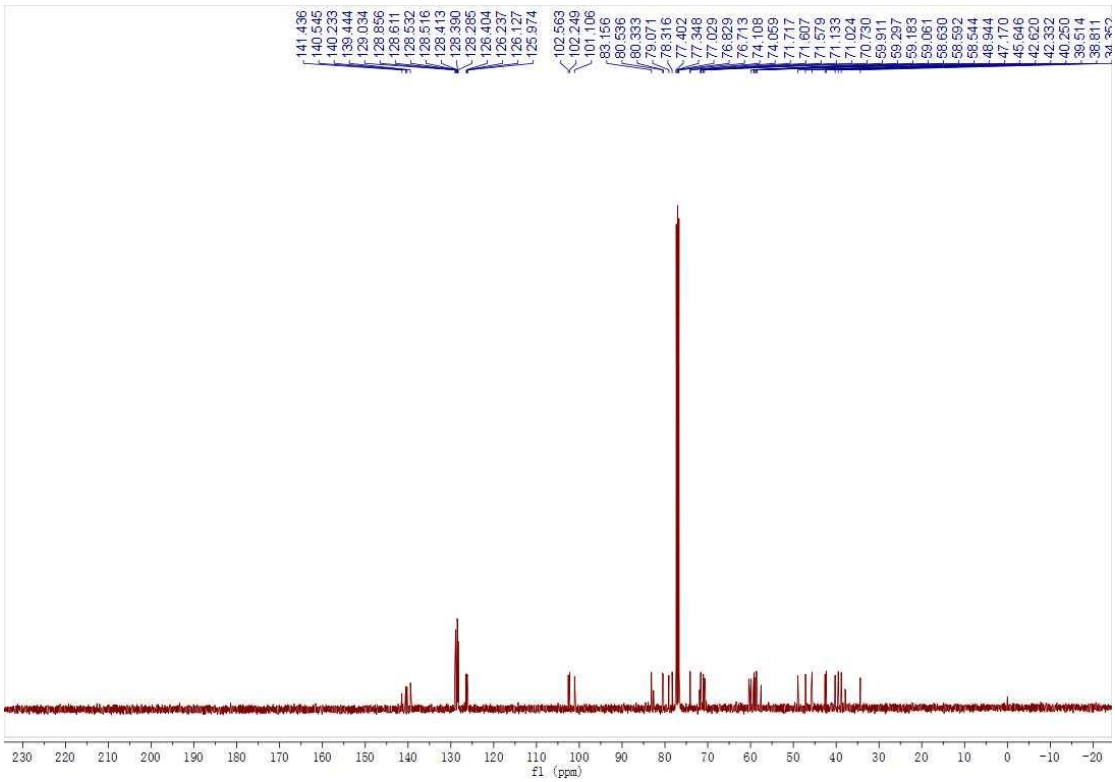




(22)







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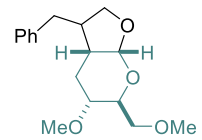
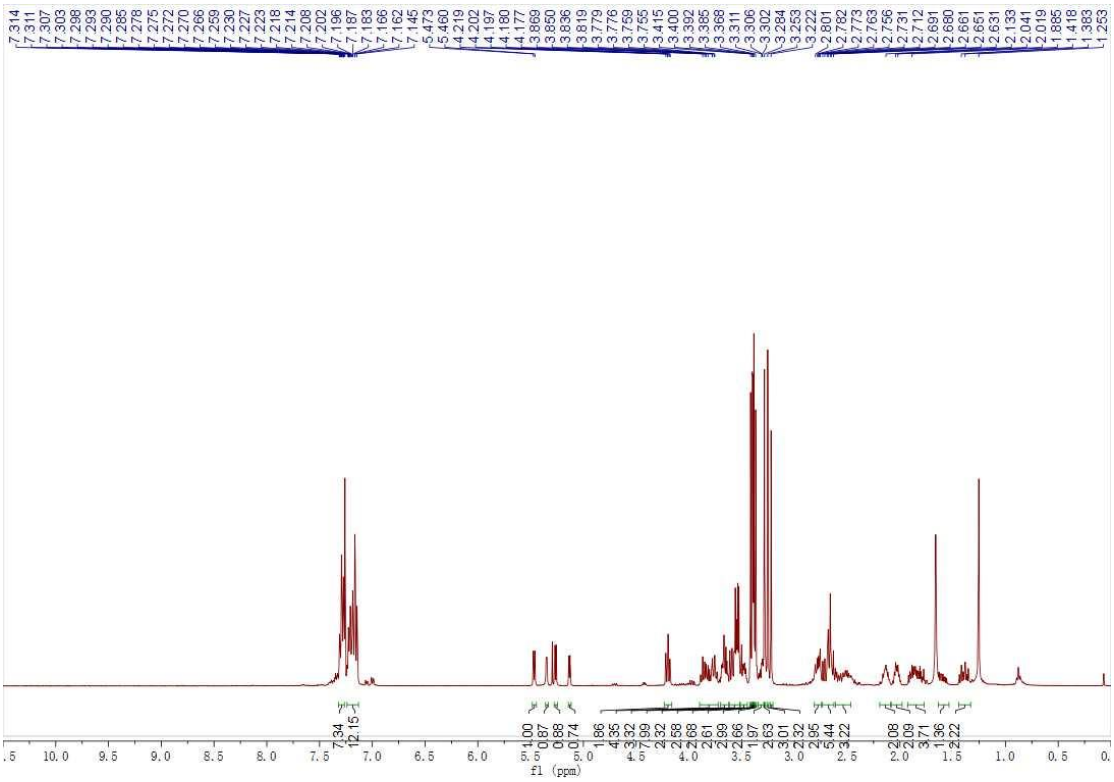
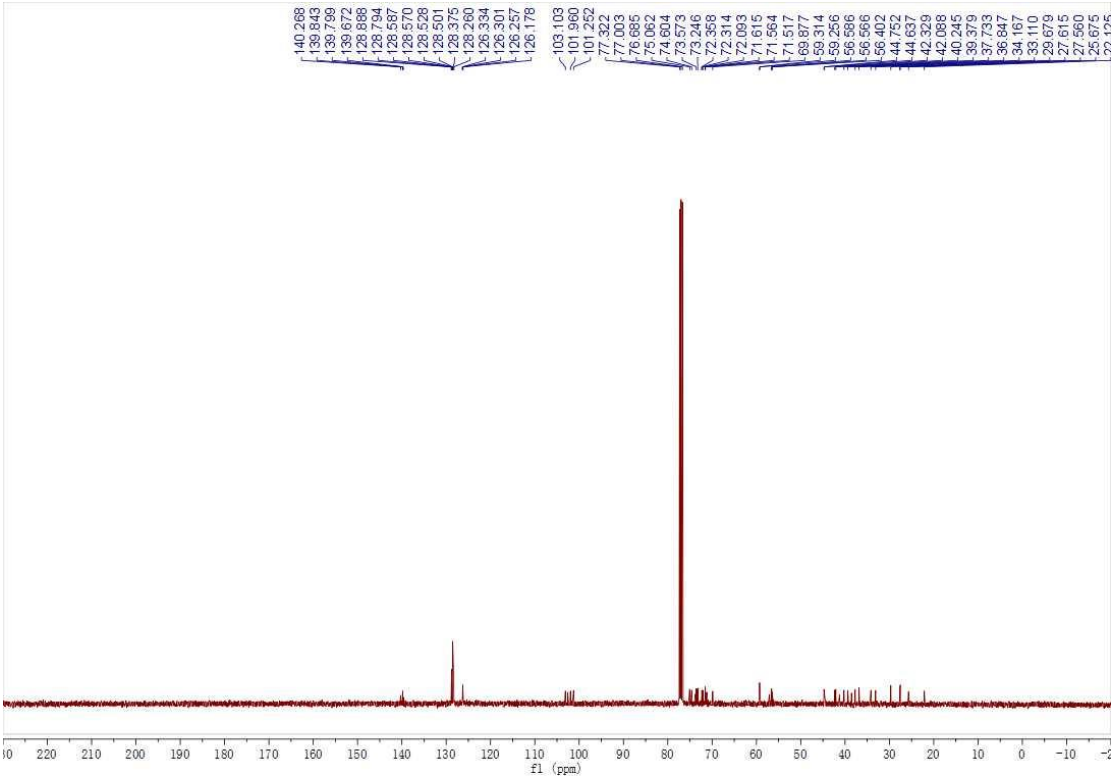
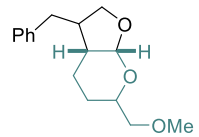
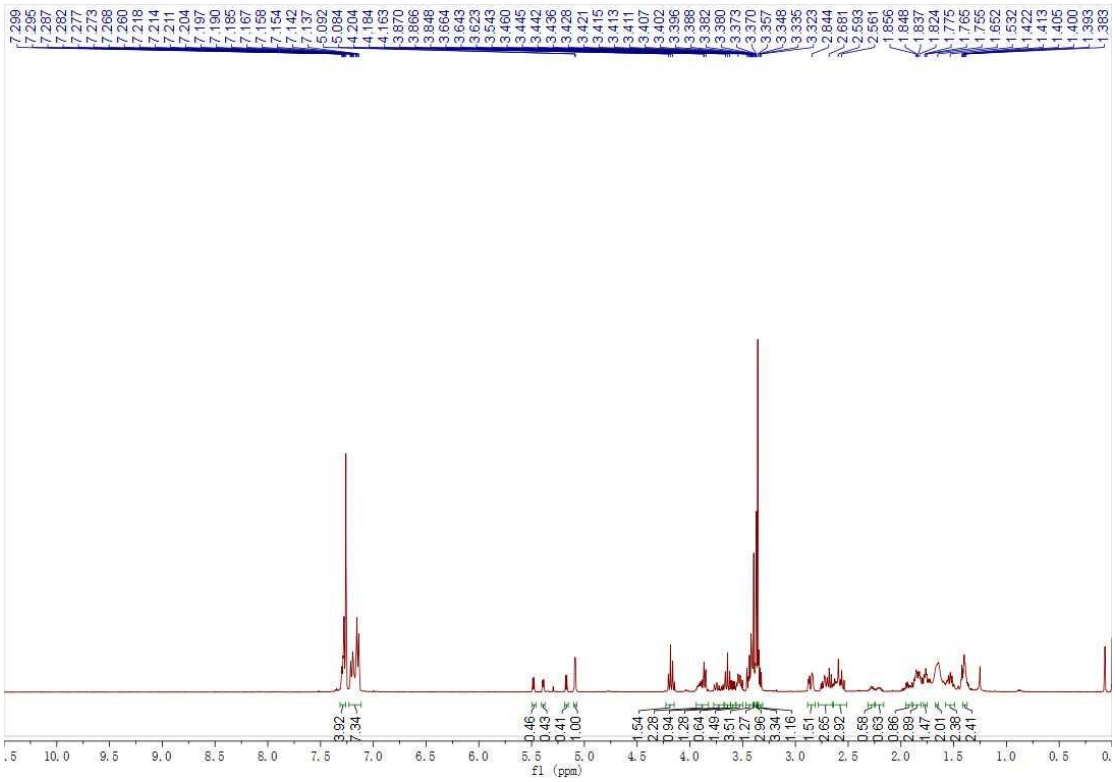


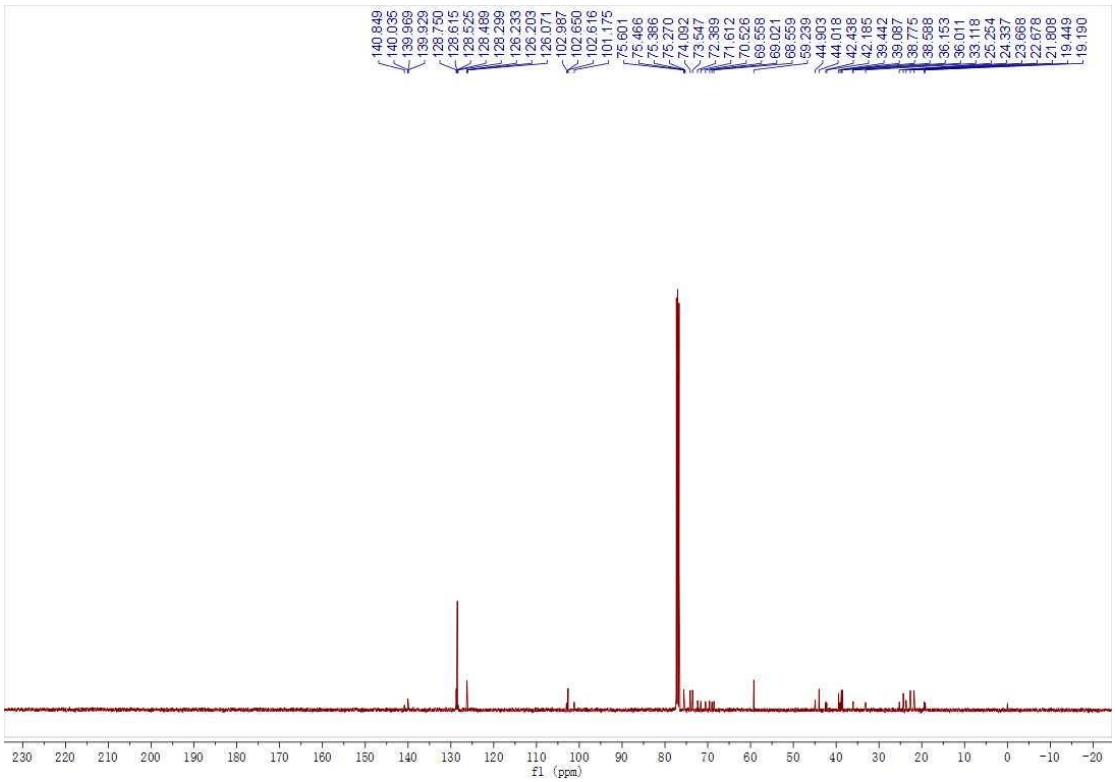




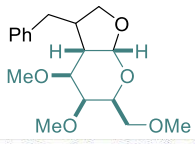
(24)

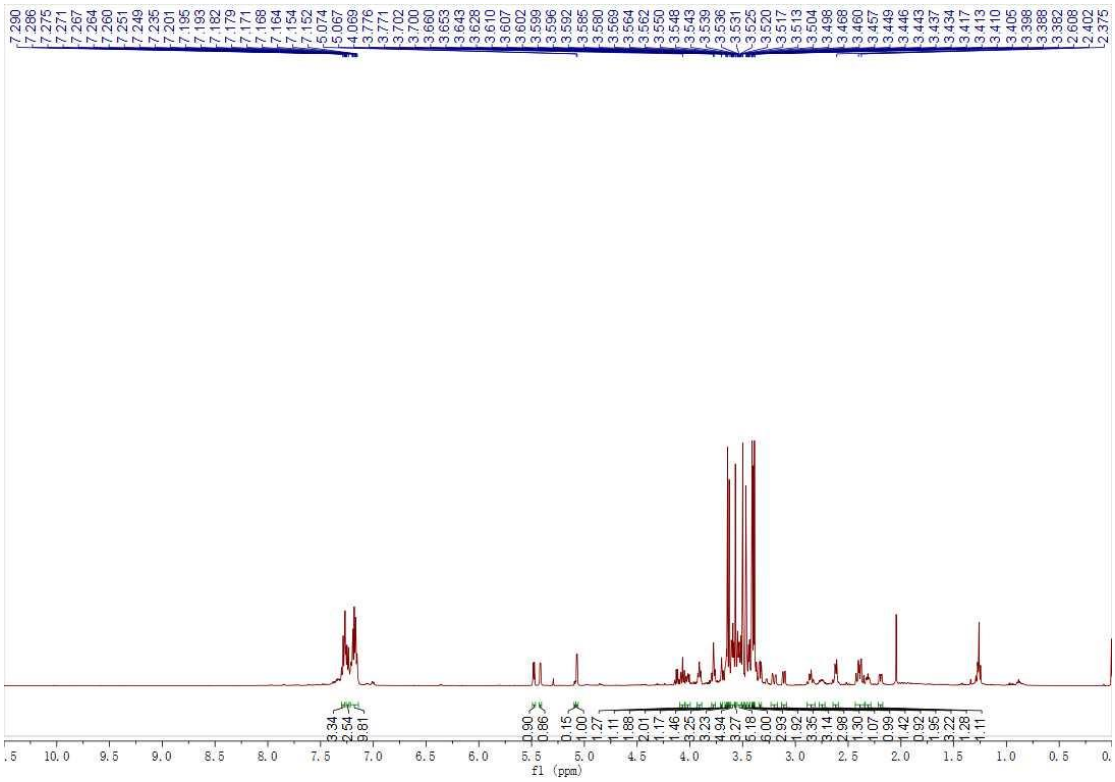


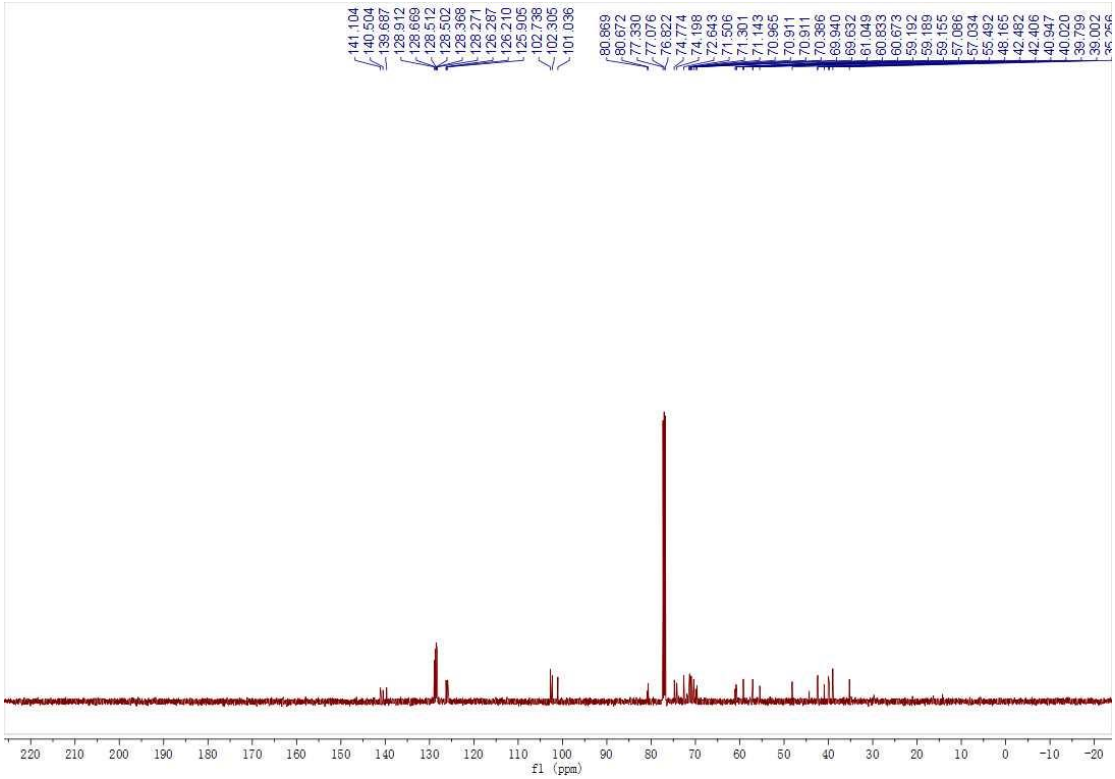




(**25**)







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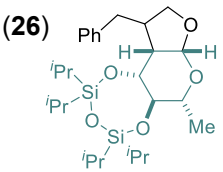

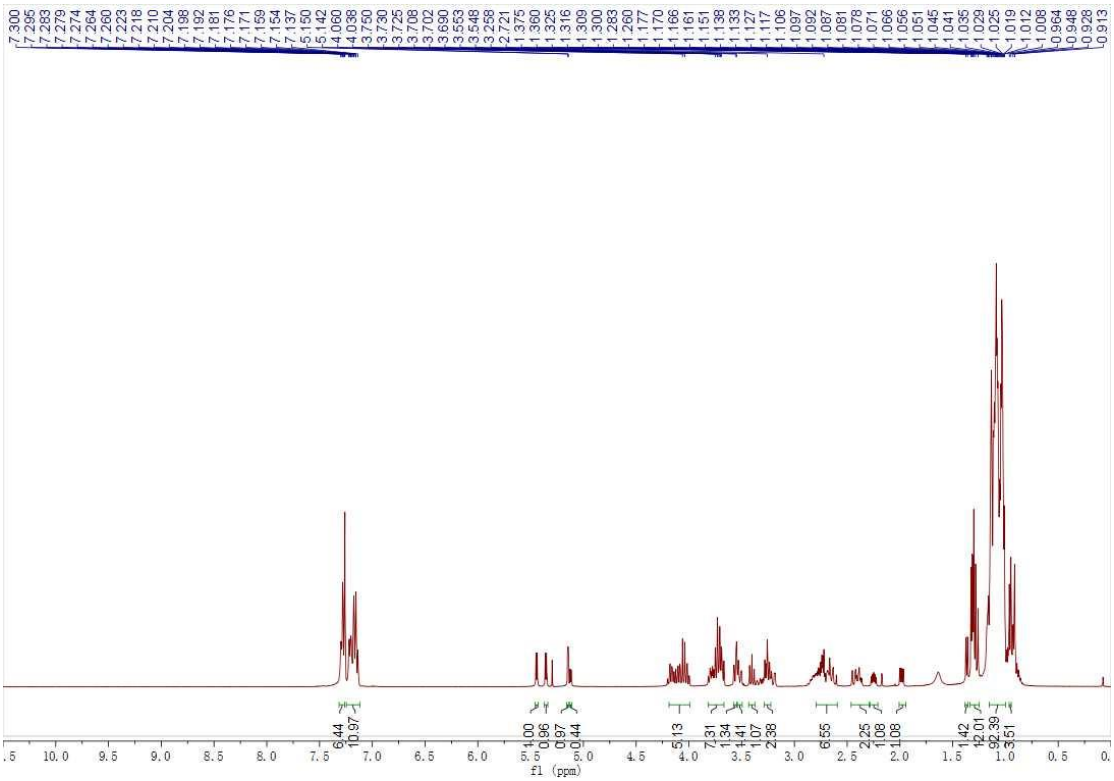

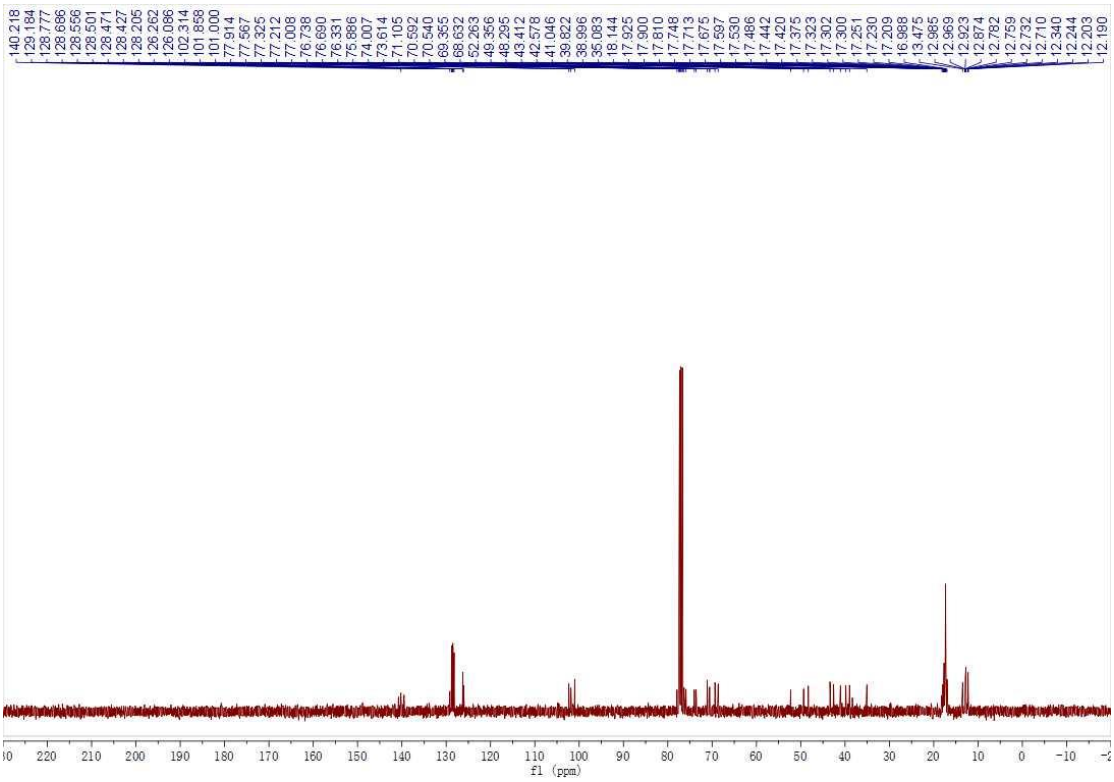

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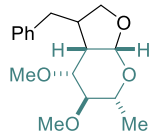
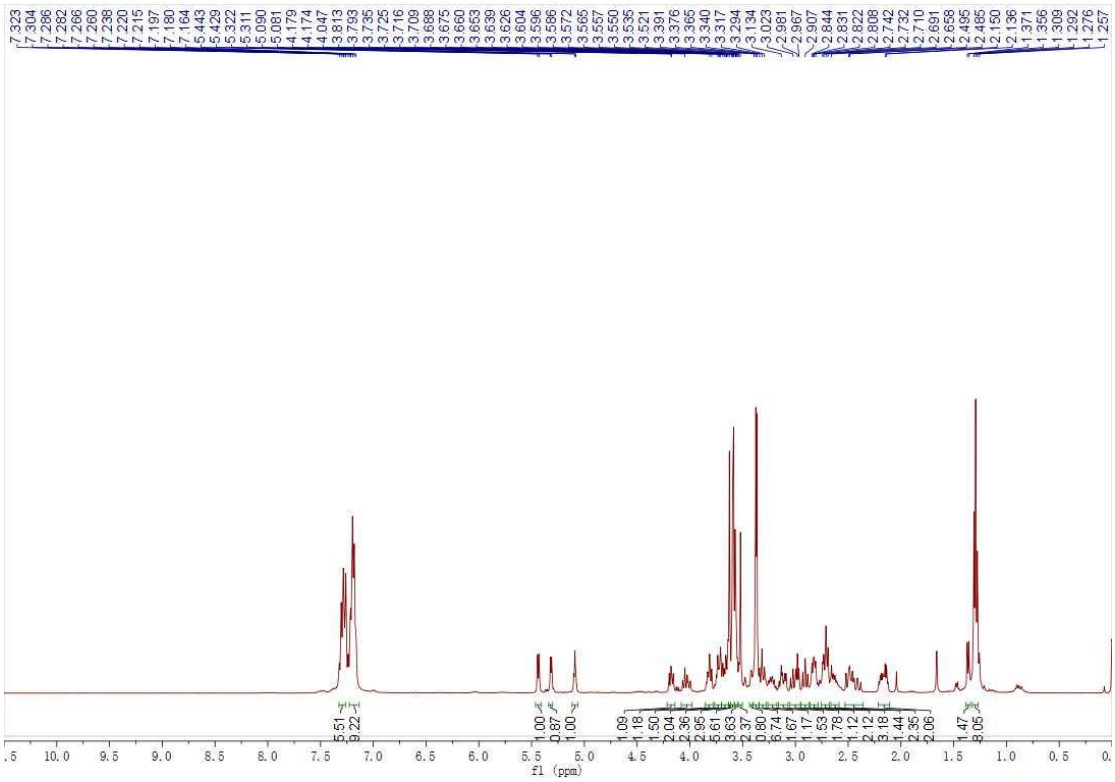
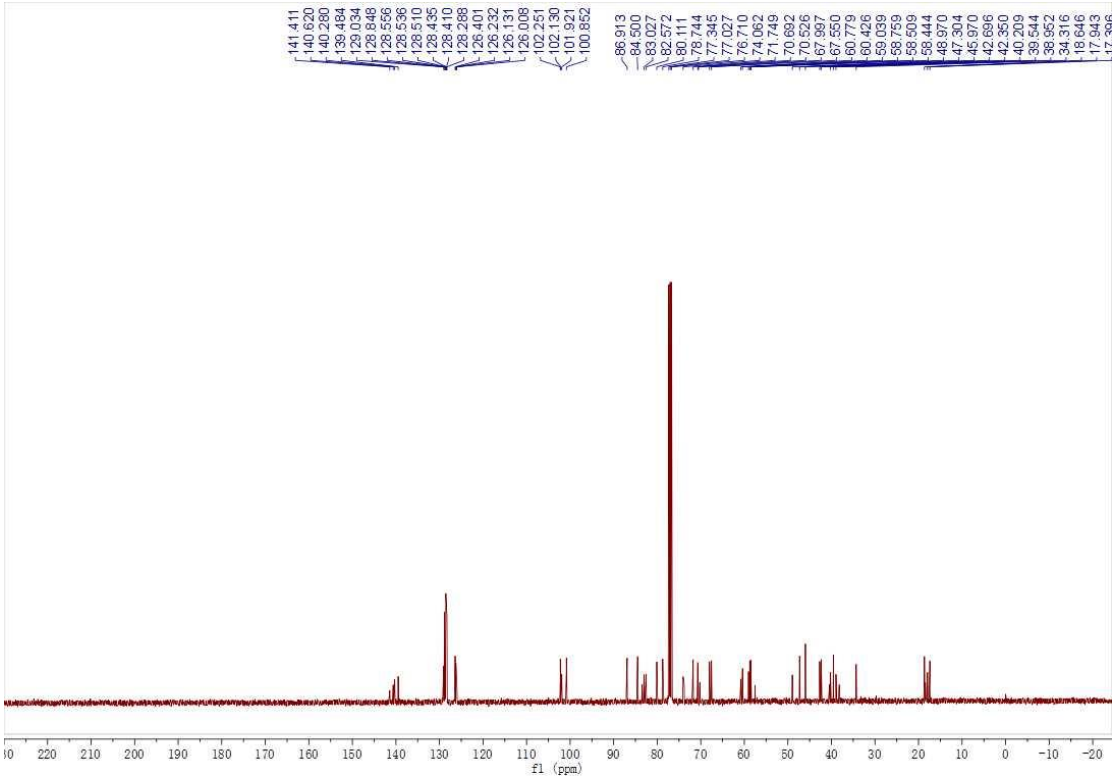
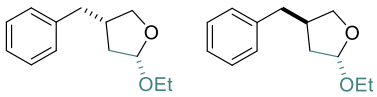
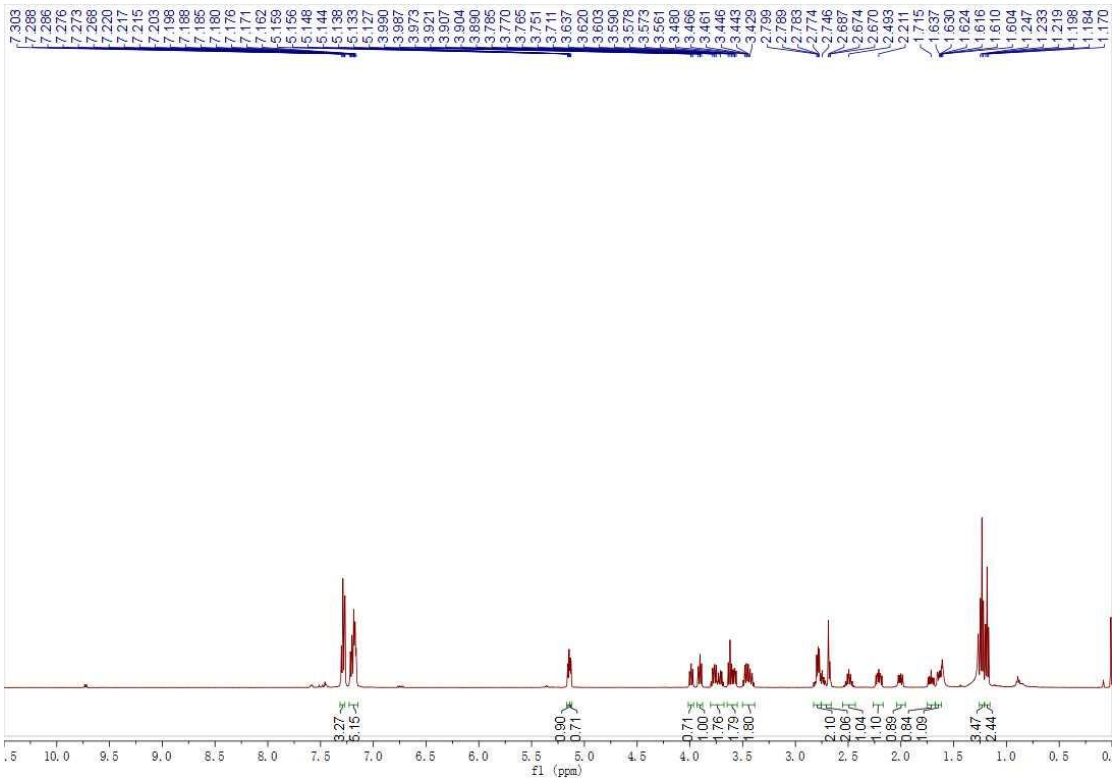






(28) 
OEt
OEt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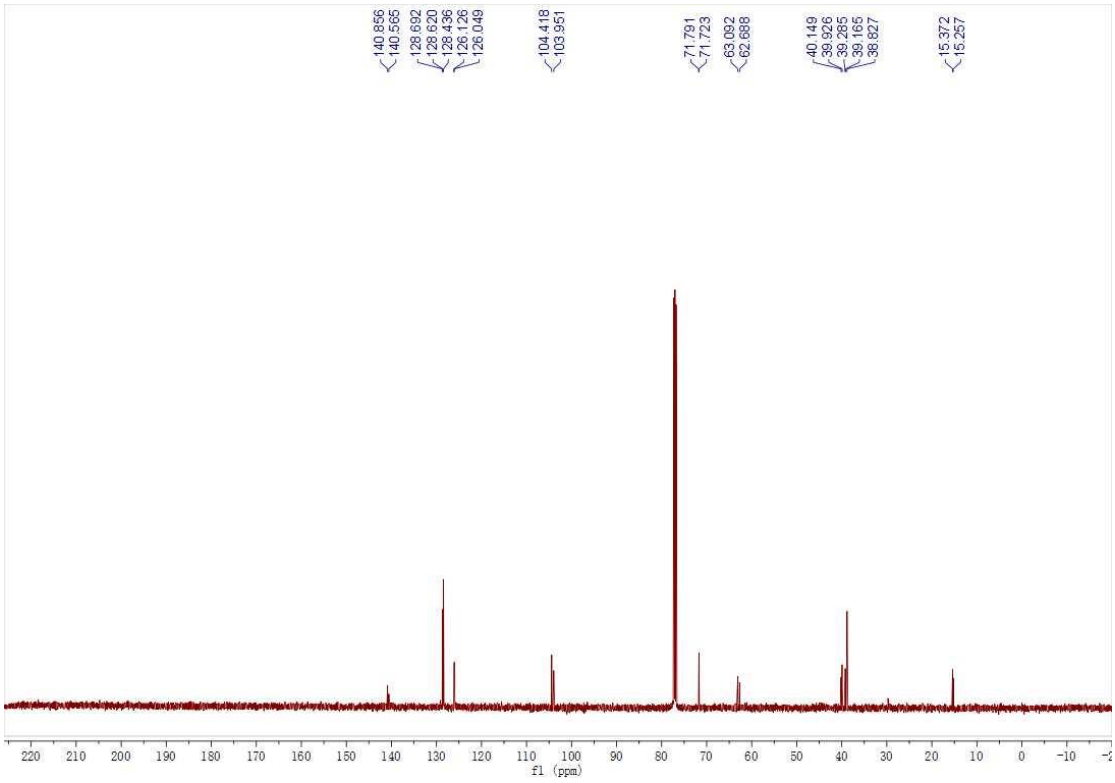
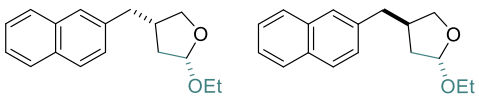
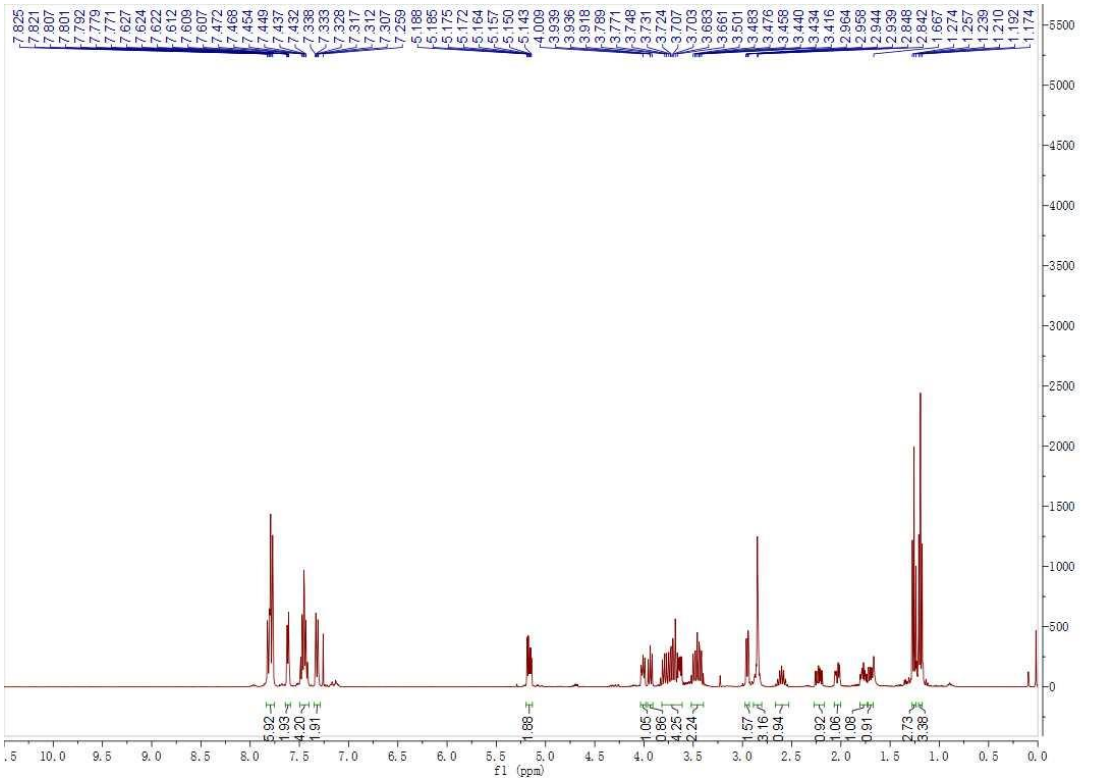
3.27 5.15 0.90 0.71 0.71 1.00 1.76 1.79 1.80 2.10 2.06 1.04 1.10 0.89 0.84 1.09 3.47 2.44
f1 (ppm)


140.856 140.565 128.692 128.620 128.436 126.126 126.049 104.418 103.951 71.791 71.723 63.092 62.688 40.149 39.926 39.285 39.165 38.827 15.372 15.257
f1 (ppm)

(**29**)


OEt
OEt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7.779
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7.609
7.607
7.472
7.468
7.454
7.449
7.437
7.432
7.338
7.333
7.328
7.317
7.312
7.307
7.259
5.188
5.185
5.175
5.172
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3.416
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2.848
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4.20
1.91
1.88
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0.92
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0.91
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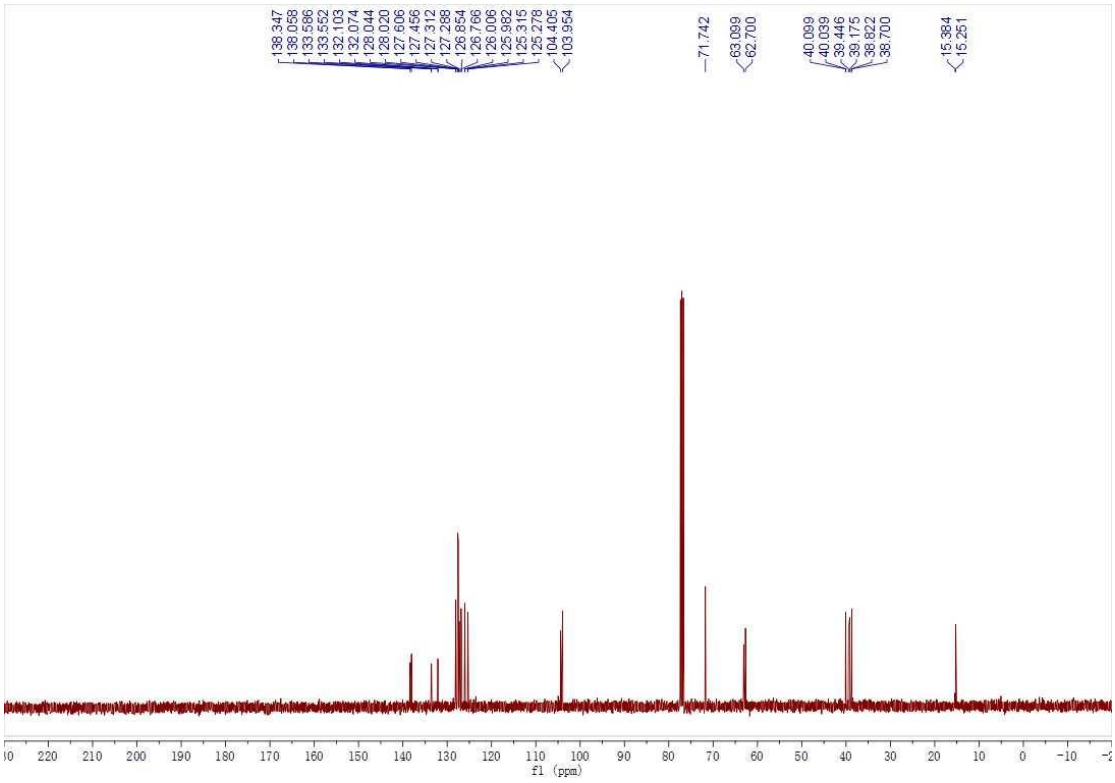
3.38
f1 (ppm)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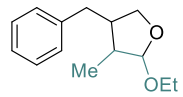
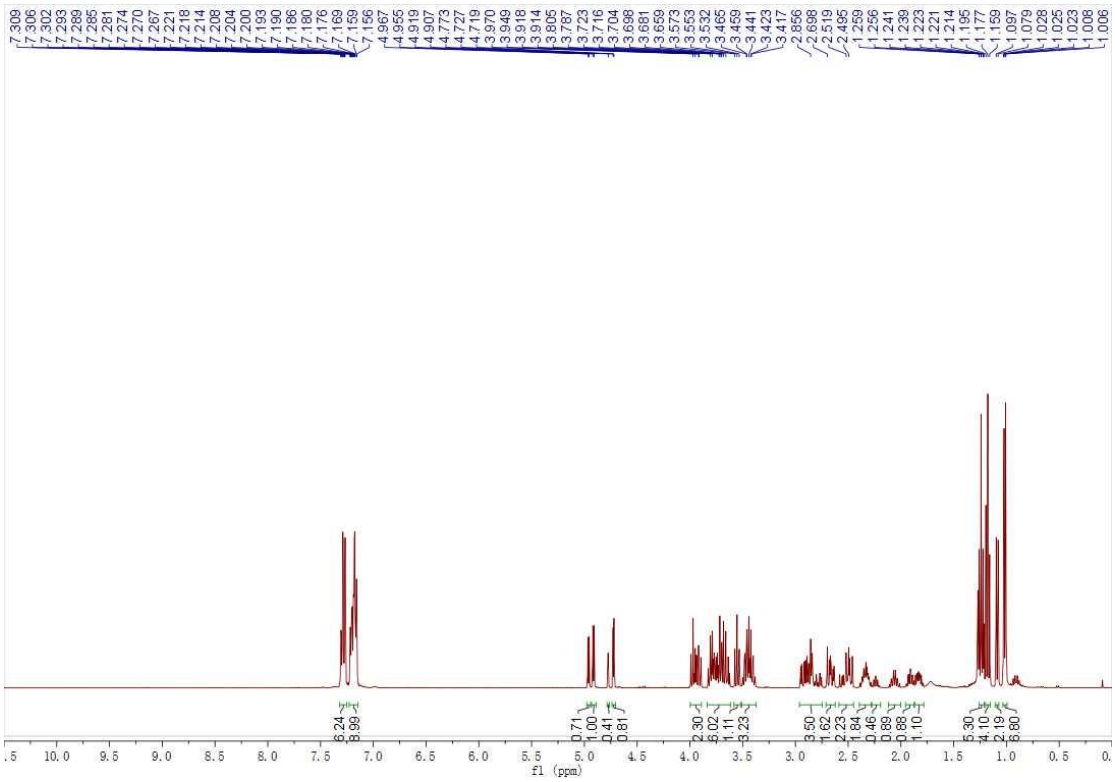
132.074
128.044
128.020
127.606
127.456
127.312
127.288
126.854
126.766
126.006
125.982
125.315
125.278
104.405
103.954
71.742
63.099
62.700
40.099
40.039
39.446
39.175
38.822
38.700
15.384
15.251
f1 (ppm)

(30)


Me
OEt
O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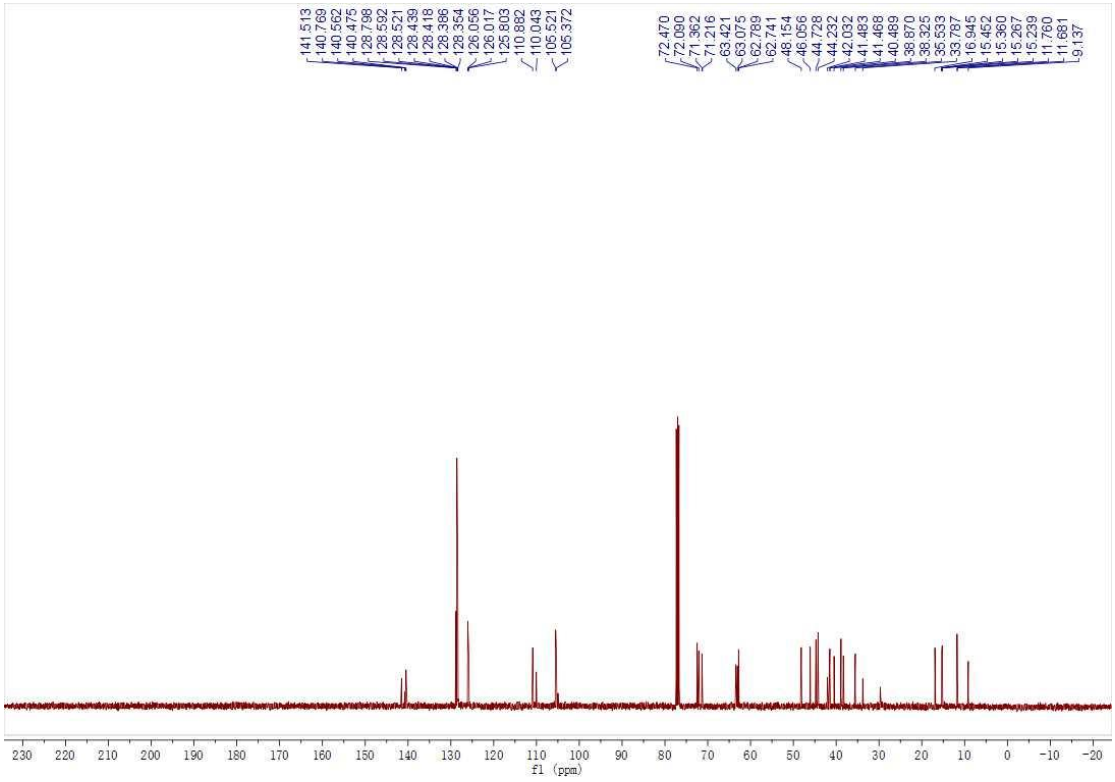
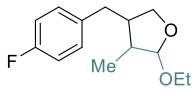
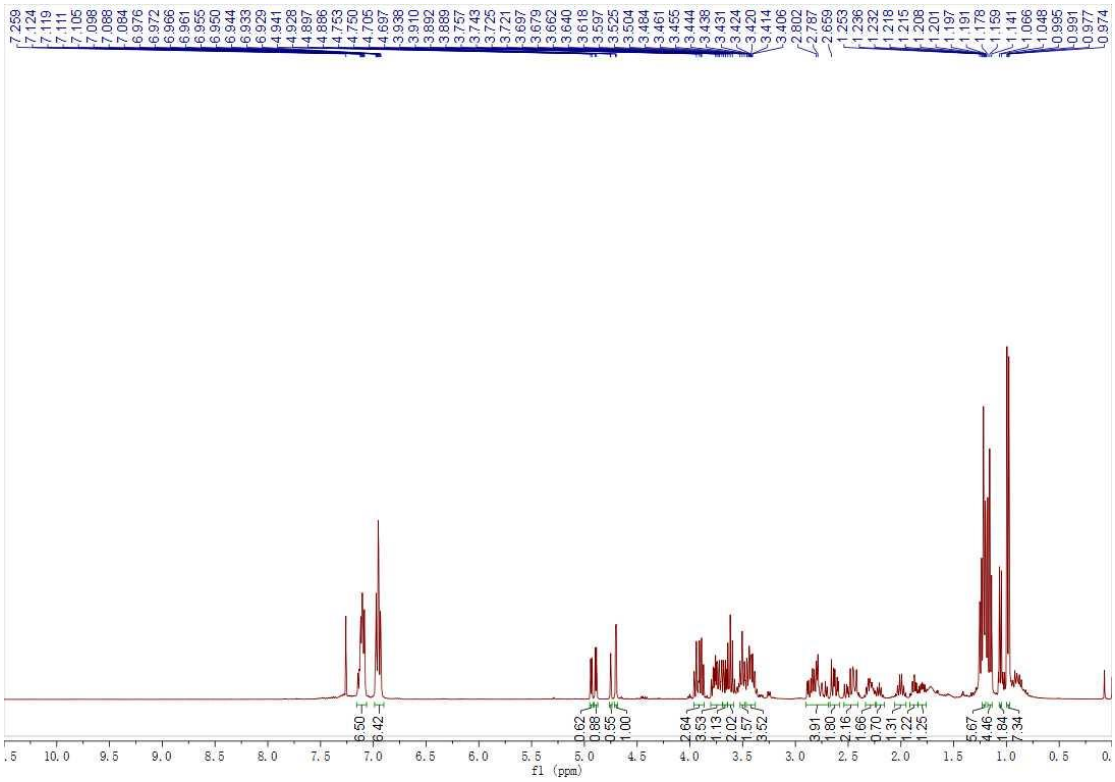
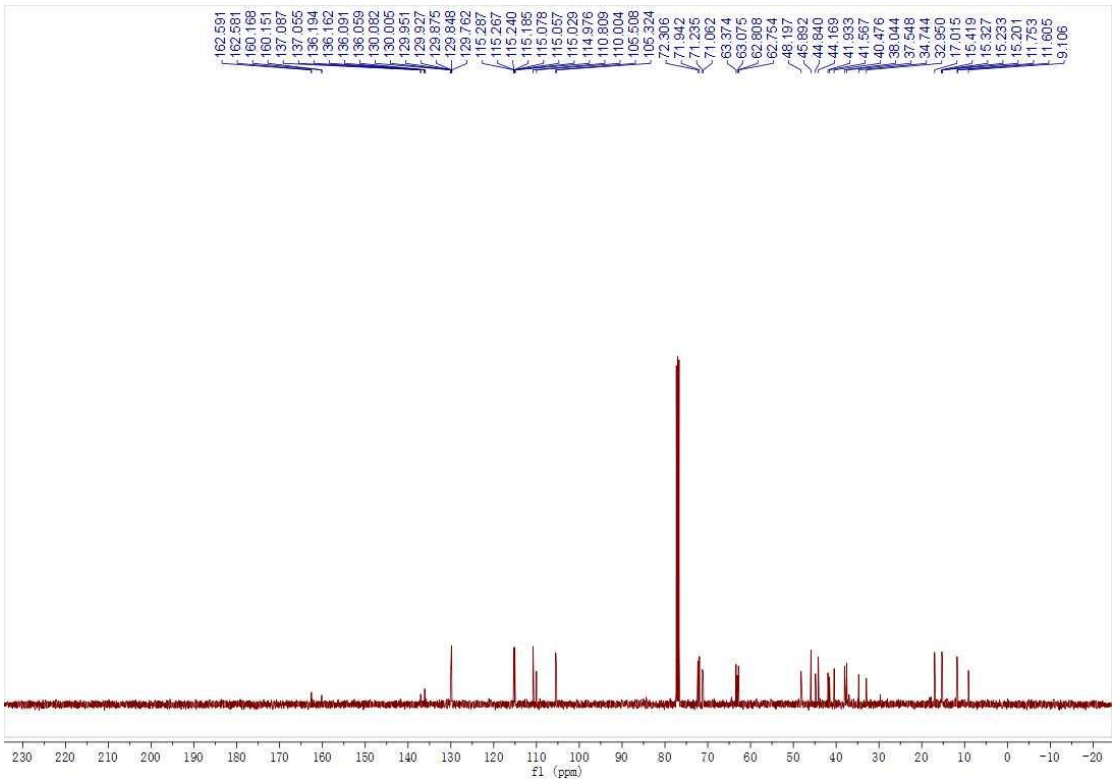
7.306
7.302
7.293
7.289
7.285
7.281
7.274
7.270
7.267
7.221
7.218
7.214
7.208
7.204
7.200
7.193
7.190
7.186
7.180
7.176
7.169
7.159
7.156
4.967
4.955
4.919
4.907
4.773
4.727
4.719
3.970
3.949
3.918
3.914
3.805
3.787
3.723
3.716
3.704
3.698
3.681
3.659
3.573
3.553
3.532
3.465
3.459
3.441
3.423
3.417
2.856
2.698
2.519
2.495
2.259
1.256
1.241
1.239
1.223
1.221
1.214
1.195
1.177
1.159
1.097
1.079
1.028
1.025
1.023
1.008
1.006
6.24
8.99
0.71
1.00
0.41
0.81
2.30
6.02
1.11
3.23
3.50
1.62
2.23
1.64
0.46
0.89
0.88
1.10
5.30
4.10
2.19
8.80
f1 (ppm)


141.513
140.769
140.562
140.475
128.798
128.592
128.521
128.439
128.418
128.386
128.354
126.056
126.017
125.803
110.882
110.043
105.521
105.372
72.470
72.090
71.362
71.216
63.421
63.075
62.789
62.741
48.154
46.056
44.728
44.232
42.032
41.483
41.468
40.489
38.870
38.325
35.533
33.787
16.945
15.452
15.360
15.267
15.239
11.760
11.681
9.137
f1 (ppm)

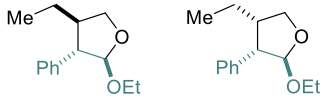
(31)

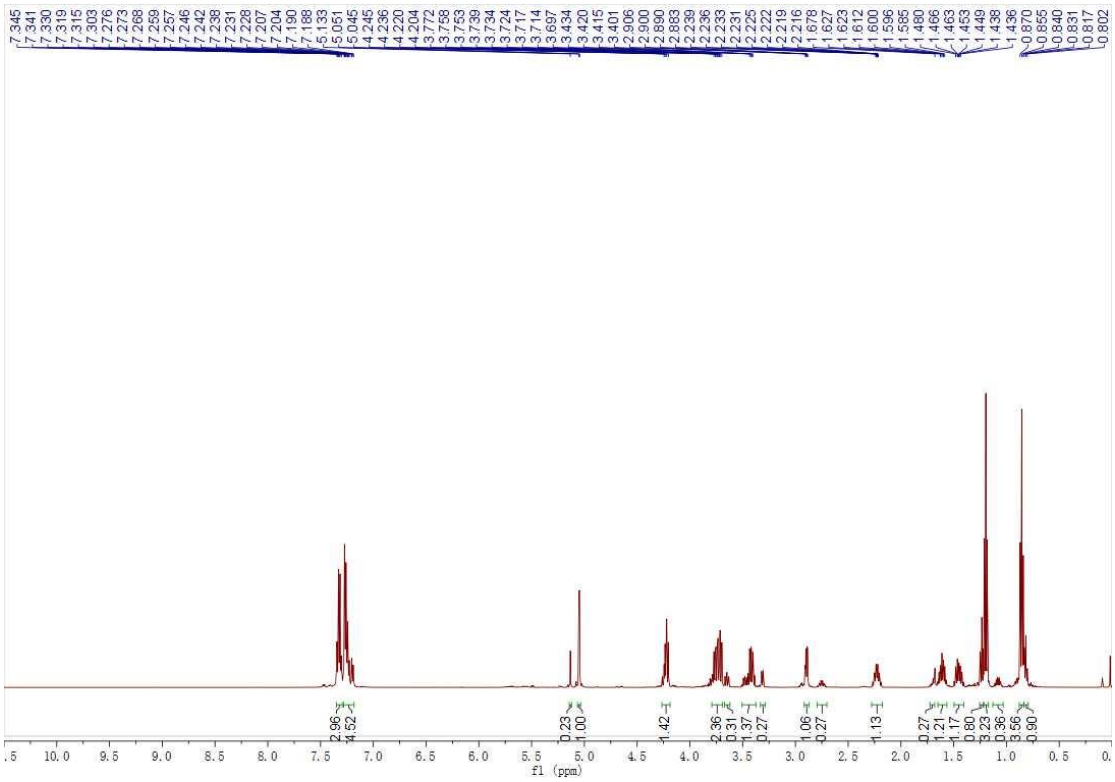






(32)


Me
Ph
O
OEt
Me
Ph
O
OEt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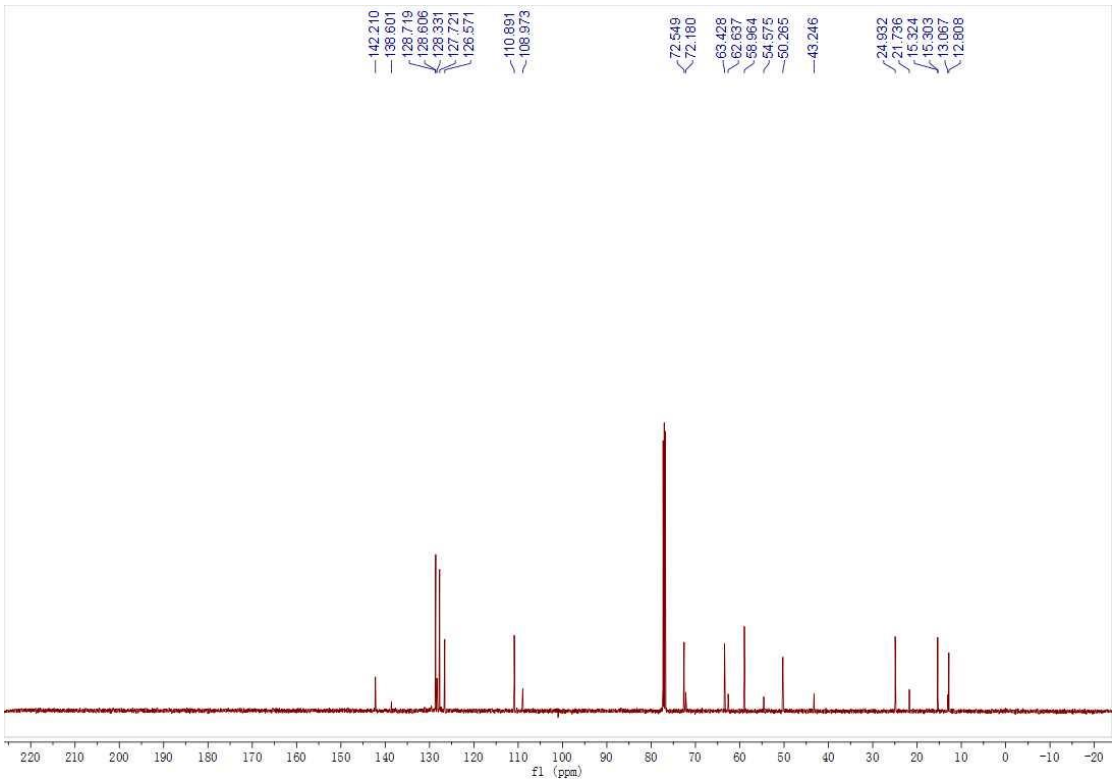
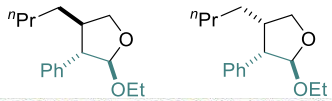
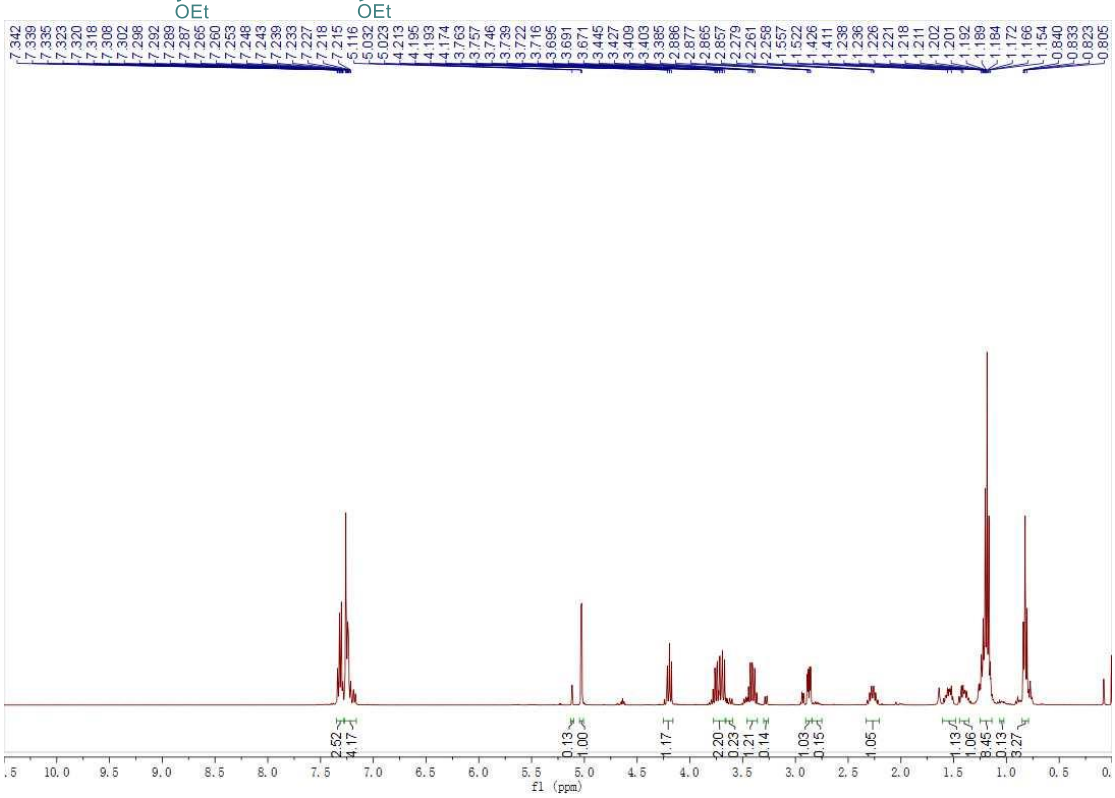
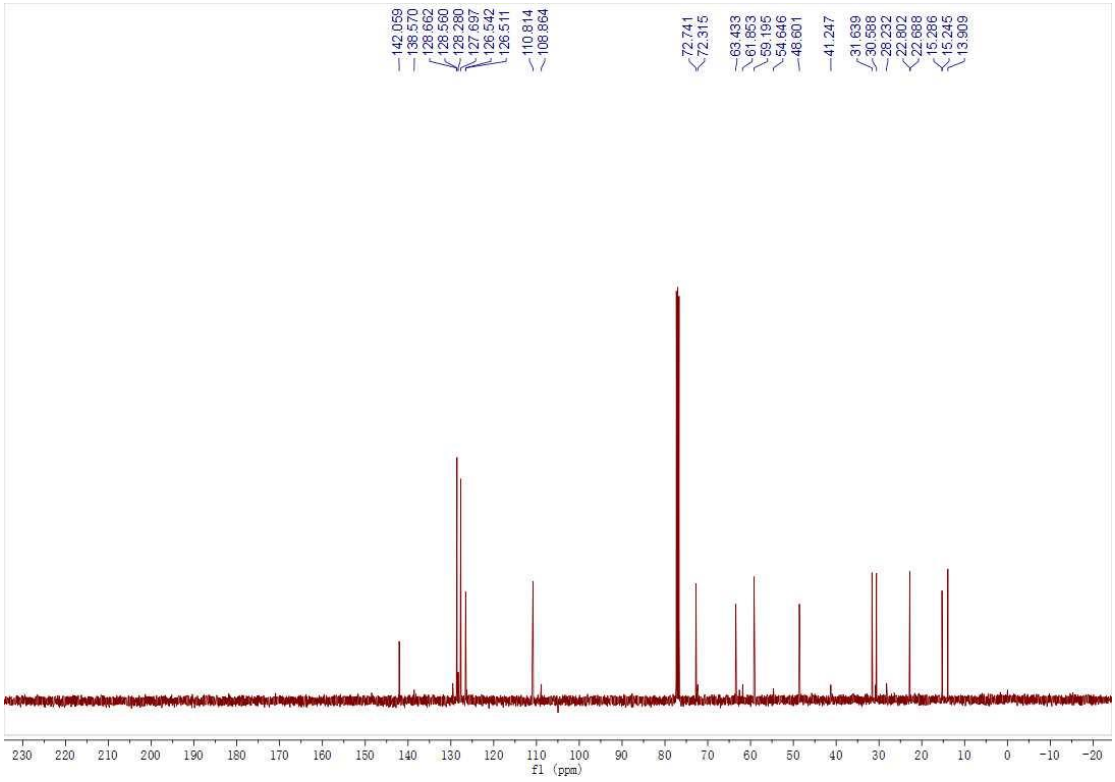
7.341
7.330
7.319
7.315
7.303
7.276
7.273
7.268
7.259
7.257
7.246
7.242
7.238
7.231
7.228
7.207
7.204
7.190
7.188
5.133
5.051
5.045
4.245
4.236
4.220
4.204
3.772
3.758
3.753
3.739
3.734
3.724
3.717
3.714
3.697
3.434
3.420
3.415
3.401
2.906
2.900
2.890
2.883
2.239
2.236
2.233
2.231
2.225
2.222
2.219
2.216
1.678
1.627
1.623
1.612
1.600
1.596
1.585
1.480
1.466
1.463
1.453
1.449
1.438
1.436
0.870
0.855
0.840
0.831
0.817
0.802
2.96
4.52
0.23
1.00
1.42
2.36
0.31
1.37
0.27
1.06
0.27
1.13
0.27
1.21
1.17
0.80
3.23
0.36
3.56
0.90
f1 (ppm)


142.210
138.601
128.719
128.606
128.331
127.721
126.571
110.891
108.973
72.549
72.180
63.428
62.637
58.964
54.575
50.265
43.246
24.932
21.736
15.324
15.303
13.067
12.808
f1 (ppm)

(33)


nPr
Ph
O
OEt
nPr
Ph
O
OEt


7.342
7.339
7.335
7.323
7.320
7.318
7.308
7.302
7.298
7.292
7.289
7.287
7.265
7.260
7.253
7.248
7.243
7.239
7.233
7.227
7.218
7.215
5.116
5.032
5.023
4.213
4.195
4.193
4.174
3.763
3.757
3.746
3.739
3.722
3.716
3.695
3.691
3.671
3.445
3.427
3.409
3.403
3.385
2.886
2.877
2.865
2.857
2.279
2.261
2.258
1.557
1.522
1.426
1.411
1.238
1.236
1.226
1.221
1.218
1.211
1.202
1.201
1.192
1.189
1.184
1.172
1.166
1.154
0.840
0.833
0.823
0.805
2.52
4.17
0.13
1.00
1.17
2.20
0.23
1.21
0.14
1.03
0.15
1.05
1.13
1.06
8.45
0.13
3.27
f1 (ppm)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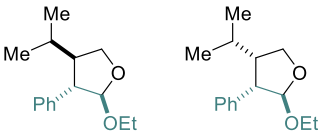
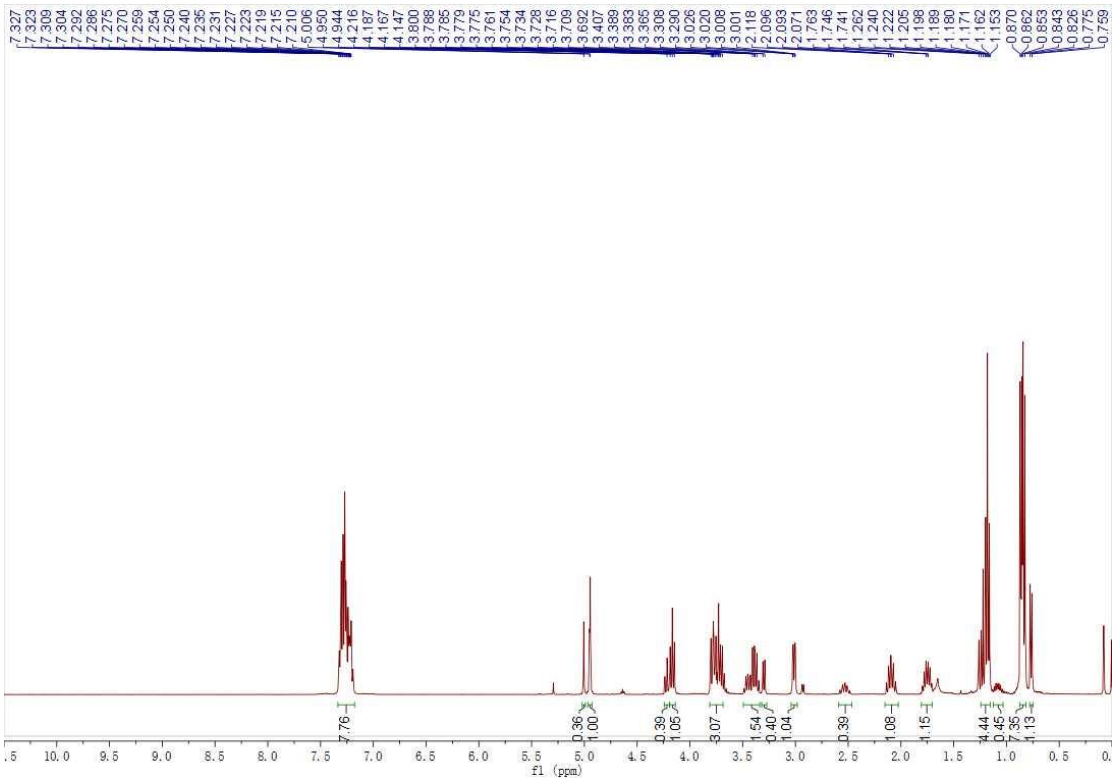
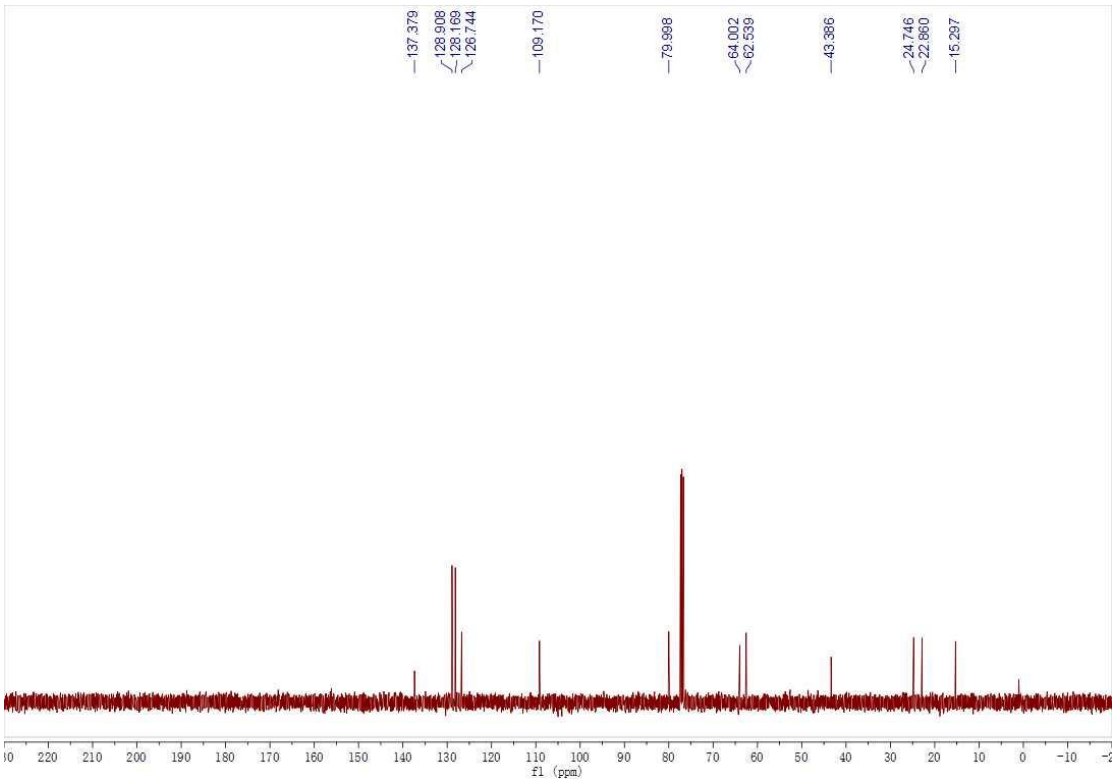
128.662
128.560
128.280
127.697
126.542
126.511
110.814
108.864
72.741
72.315
63.433
61.853
59.195
54.646
48.601
41.247
31.639
30.388
28.232
22.802
22.688
15.286
15.245
13.909
f1 (ppm)

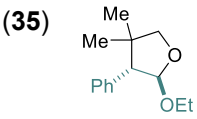
(**34**)

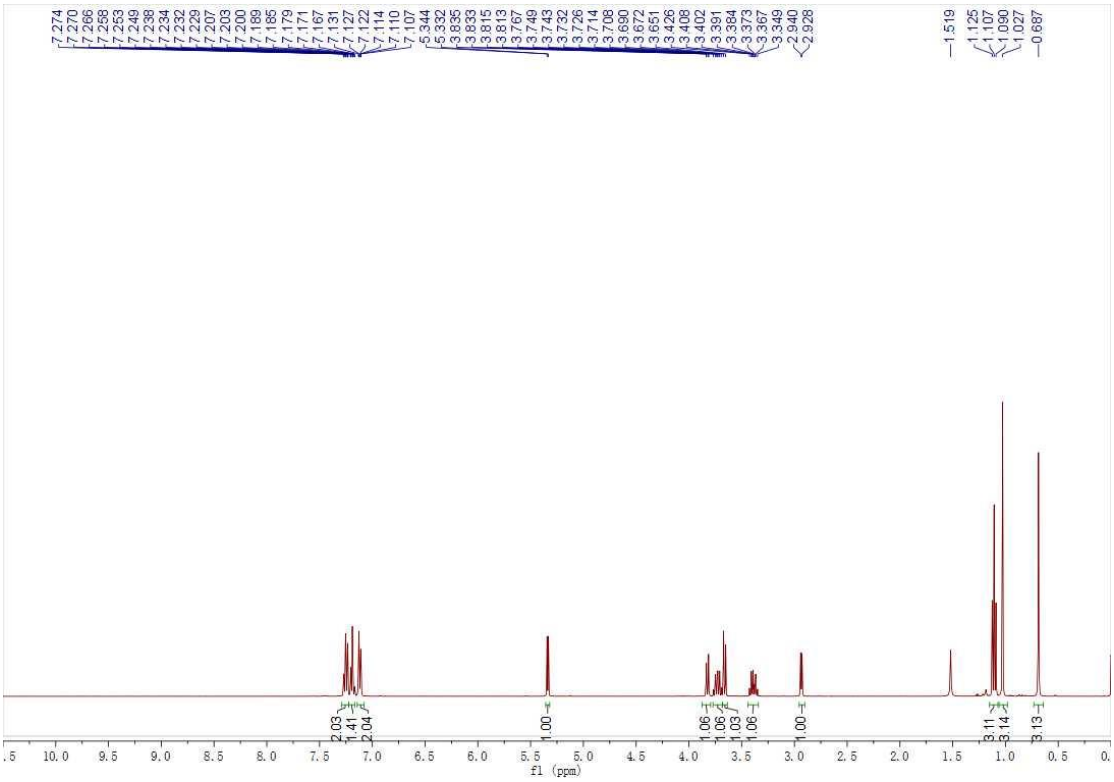

Me
Me
Ph
O
OEt
Me
Me
Ph
O
OEt

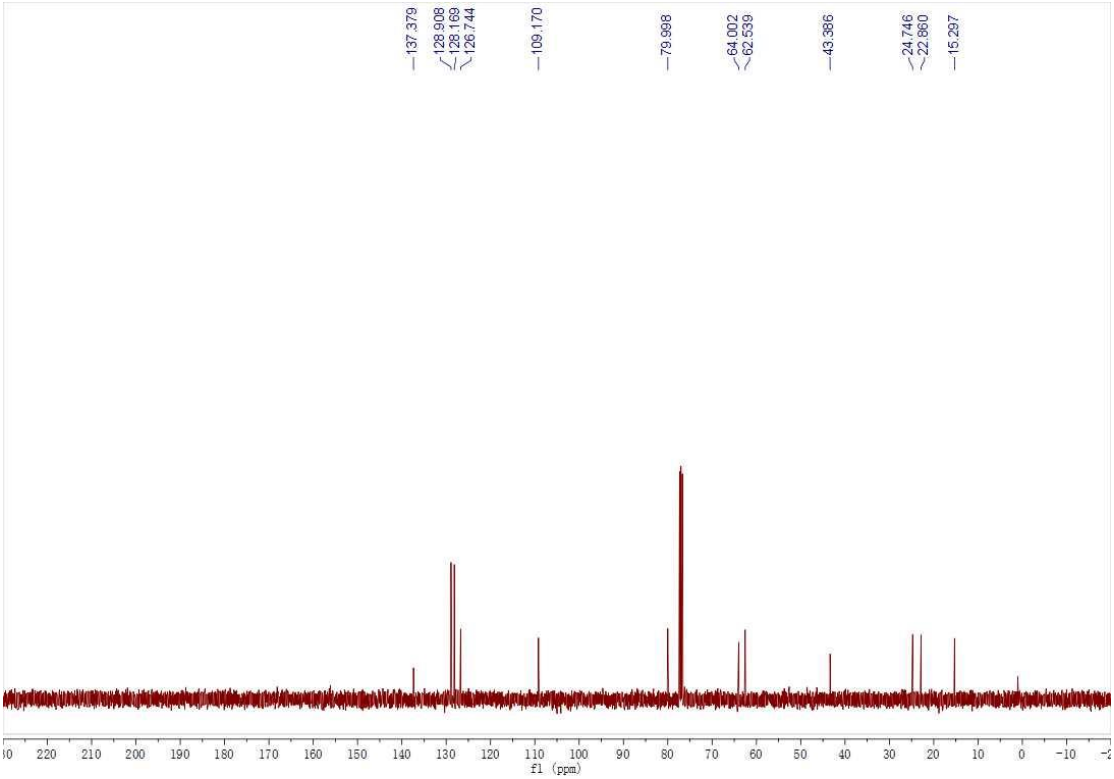

7.327
7.323
7.309
7.304
7.292
7.286
7.275
7.270
7.259
7.254
7.250
7.240
7.235
7.231
7.227
7.223
7.219
7.215
7.210
5.006
4.950
4.944
4.216
4.187
4.167
4.147
3.800
3.788
3.785
3.779
3.775
3.761
3.754
3.734
3.728
3.716
3.709
3.692
3.407
3.389
3.383
3.365
3.308
3.290
3.026
3.020
3.008
3.001
2.118
2.096
2.093
2.071
1.763
1.746
1.741
1.262
1.240
1.222
1.205
1.198
1.189
1.180
1.171
1.162
1.153
0.870
0.862
0.853
0.843
0.826
0.775
0.759
7.76
0.96
1.00
0.39
1.05
3.07
1.54
0.40
1.04
0.39
1.08
1.15
4.44
0.45
7.35
1.13
f1 (ppm)


137.379
128.908
128.169
126.744
109.170
79.998
64.002
62.539
43.386
24.746
22.860
15.297
f1 (ppm)

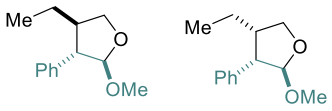
(**35**)

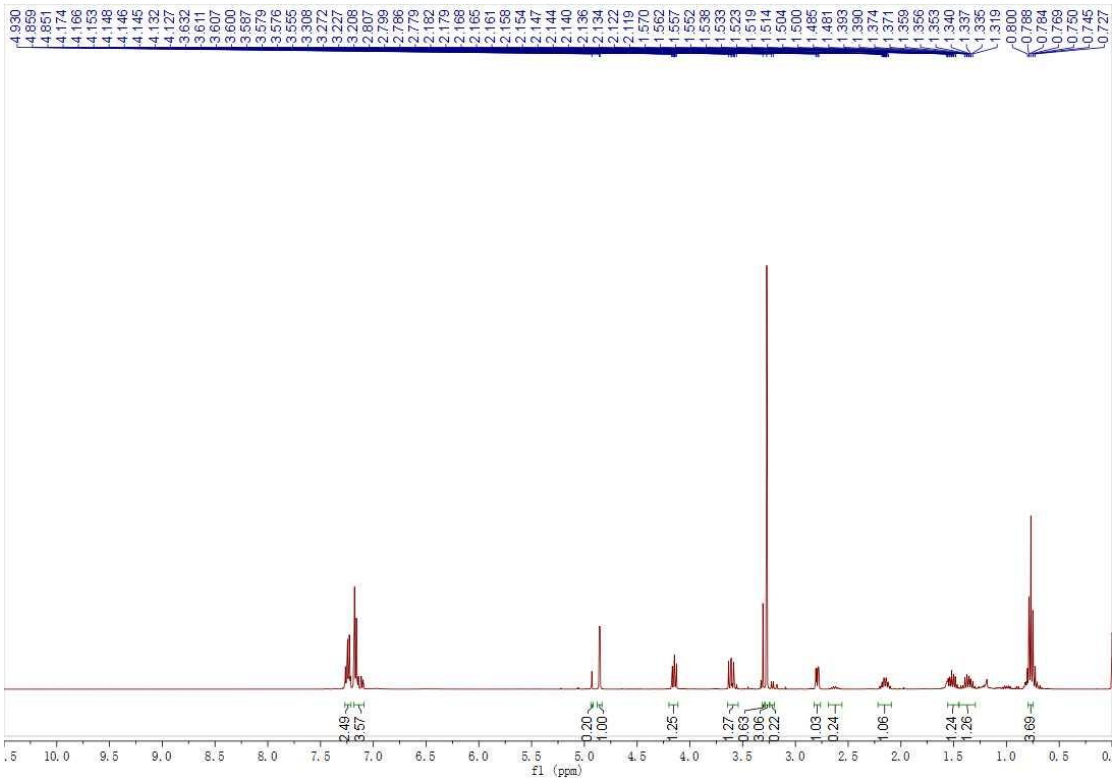

Me
Me
O
Ph
OEt

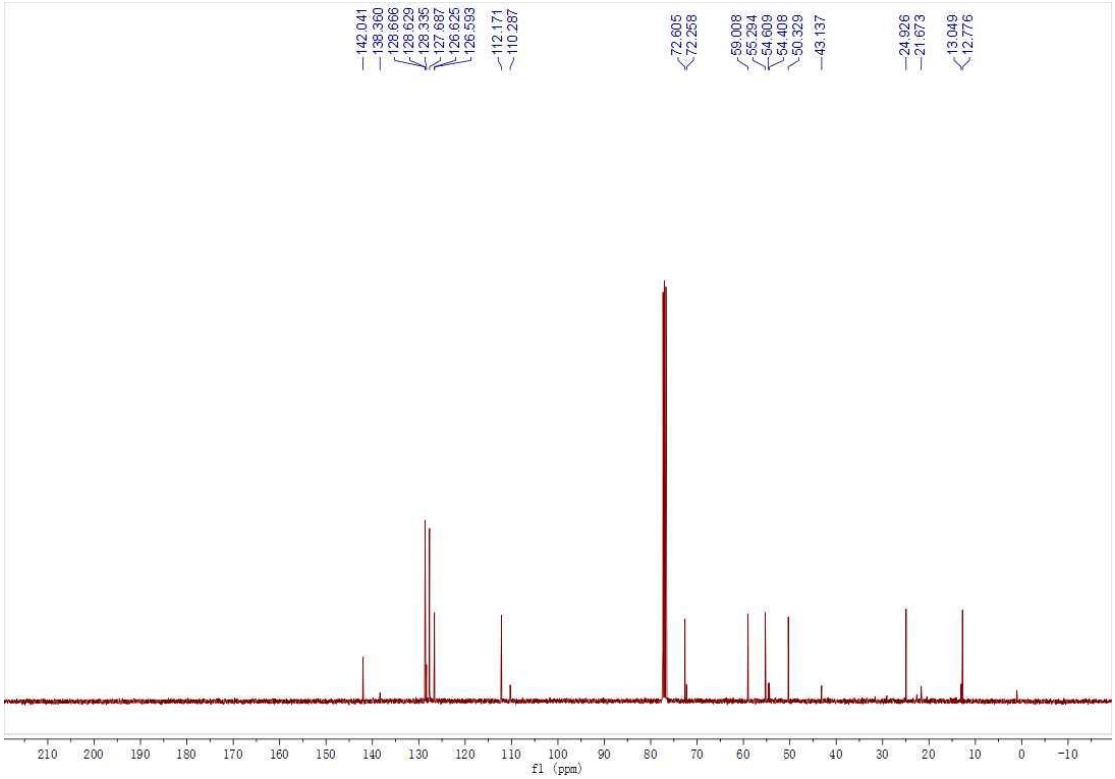

7.274
7.270
7.266
7.258
7.253
7.249
7.238
7.234
7.232
7.229
7.207
7.203
7.200
7.189
7.185
7.179
7.171
7.167
7.131
7.127
7.122
7.114
7.110
7.107
5.344
5.332
3.835
3.833
3.815
3.813
3.767
3.749
3.743
3.732
3.726
3.714
3.708
3.690
3.672
3.651
3.426
3.408
3.402
3.391
3.384
3.373
3.367
3.349
2.940
2.928
1.519
1.125
1.107
1.090
1.027
0.687
2.03
1.41
2.04
1.00
1.06
1.06
1.03
1.06
1.00
3.11
3.14
3.13
f1 (ppm)

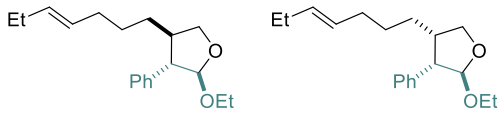

137.379
128.908
128.169
126.744
109.170
79.998
64.002
62.539
43.386
24.746
22.860
15.297
f1 (ppm)

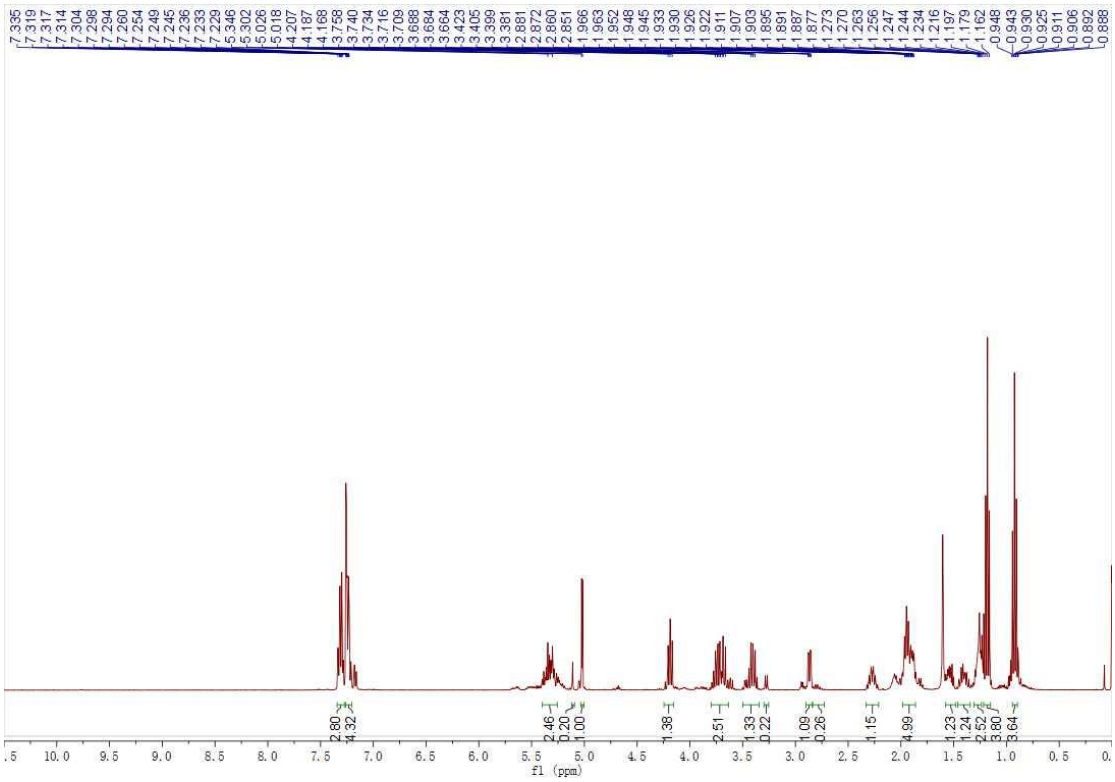
(**36**)







(**37**) 
Et
Ph
O
OEt
Et
Ph
O
OEt


7.335
7.319
7.317
7.314
7.304
7.298
7.294
7.260
7.254
7.249
7.245
7.236
7.233
7.229
5.346
5.302
5.026
5.018
4.207
4.187
4.168
3.758
3.740
3.734
3.716
3.709
3.688
3.684
3.664
3.423
3.405
3.399
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2.860
2.851
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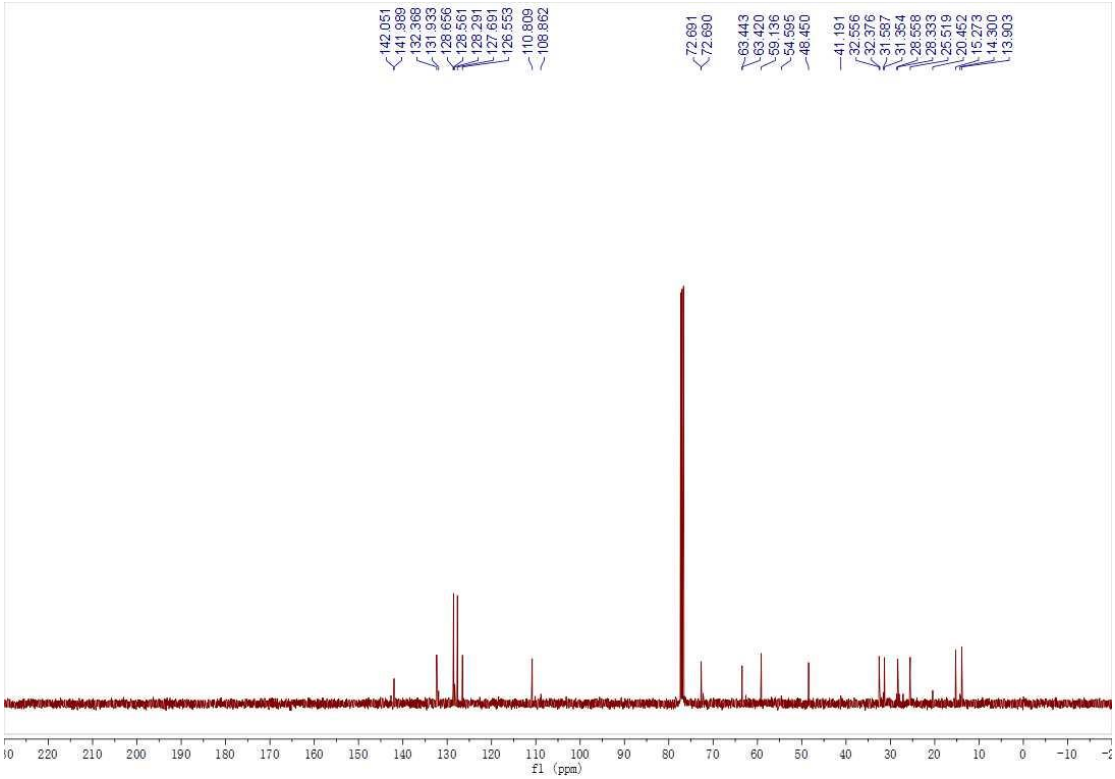
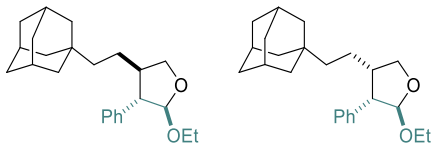
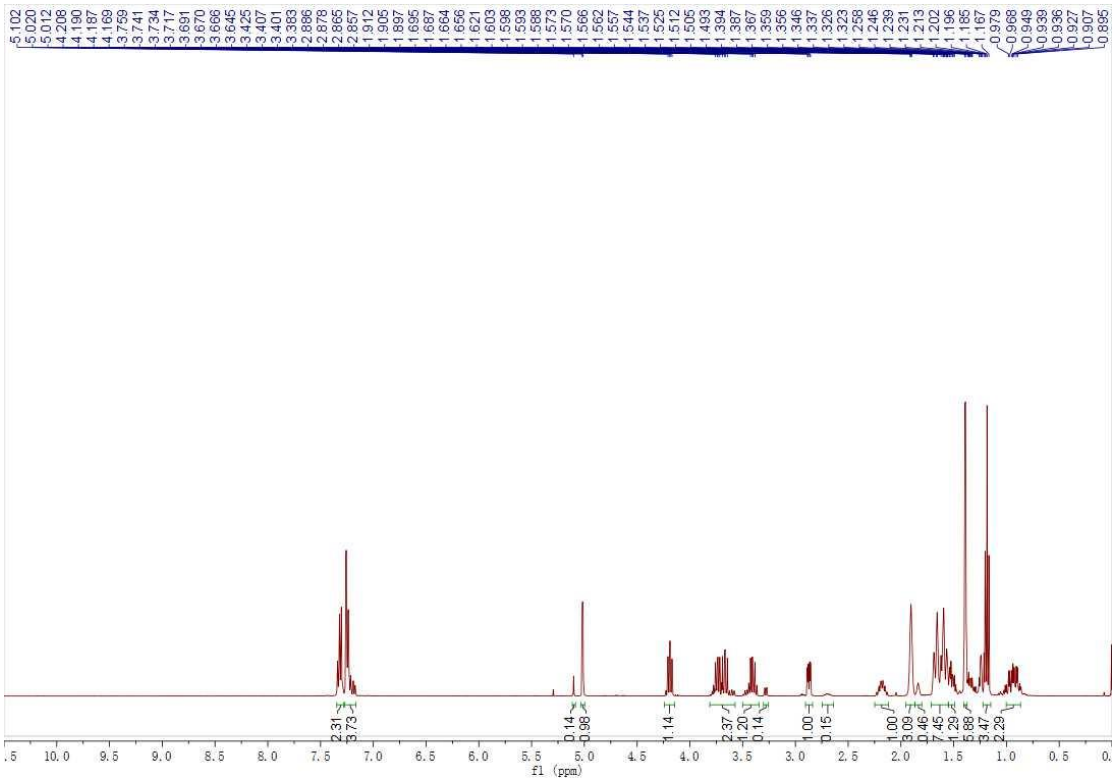
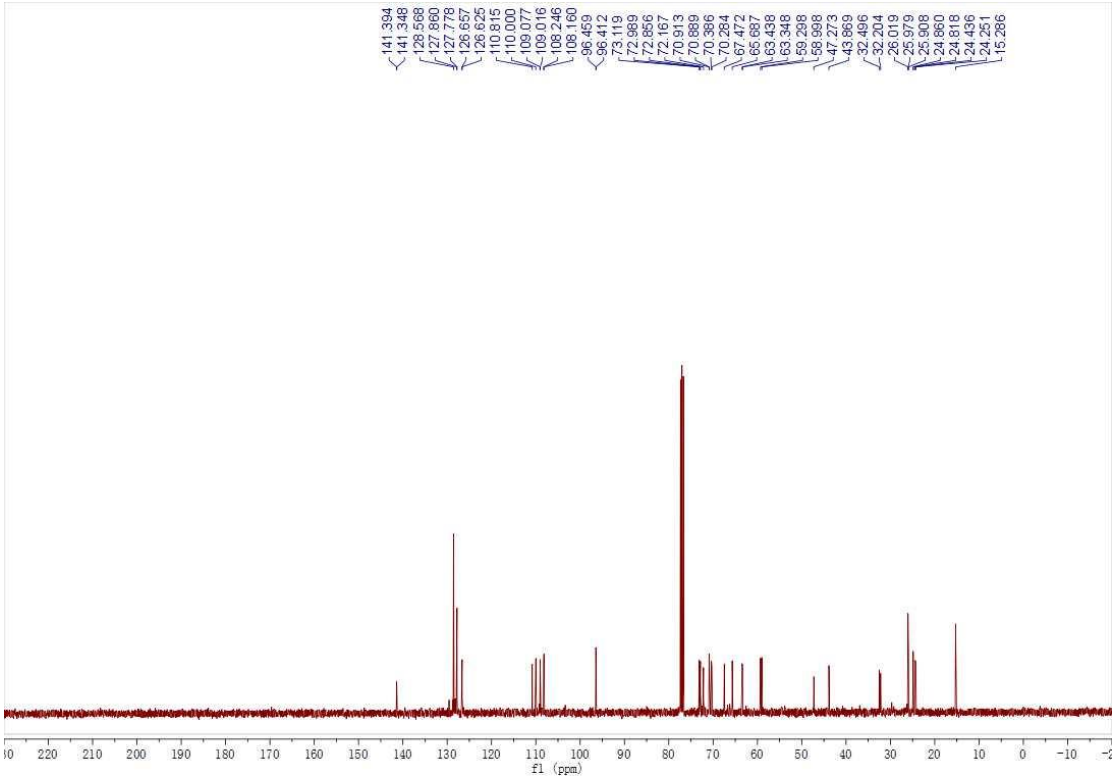
1.963
1.952
1.948
1.945
1.933
1.930
1.926
1.922
1.911
1.907
1.903
1.895
1.891
1.887
1.877
1.273
1.270
1.263
1.256
1.247
1.244
1.234
1.216
1.197
1.179
1.162
0.948
0.943
0.930
0.925
0.911
0.906
0.892
0.888
2.80
4.32
2.46
0.20
1.00
1.38
2.51
1.33
0.22
1.09
0.26
1.15
4.99
1.23
1.24
2.52
3.60
3.64
f1 (ppm)


142.051
141.980
132.368
131.933
128.656
128.561
128.291
127.691
126.553
110.809
108.862
72.691
72.690
63.443
63.420
59.136
54.595
48.450
41.191
32.556
32.376
31.887
31.354
28.558
28.333
25.519
20.452
15.273
14.300
13.903
f1 (ppm)

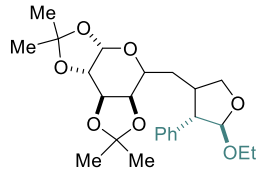
(**38**)



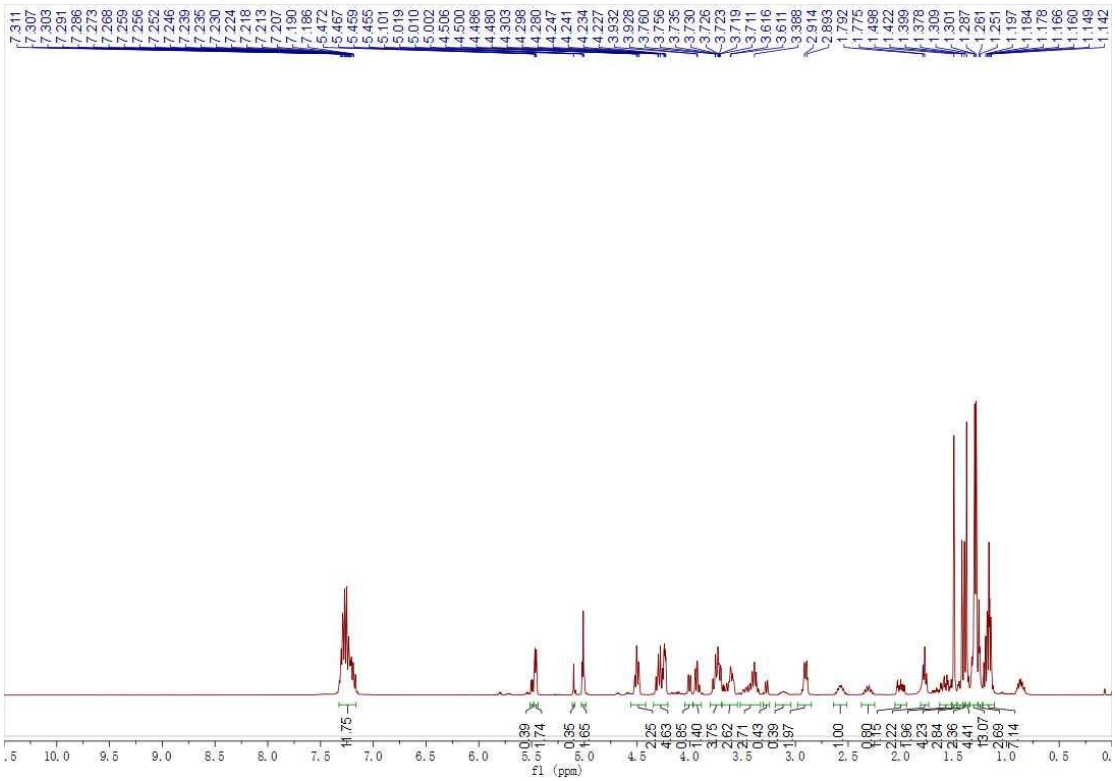


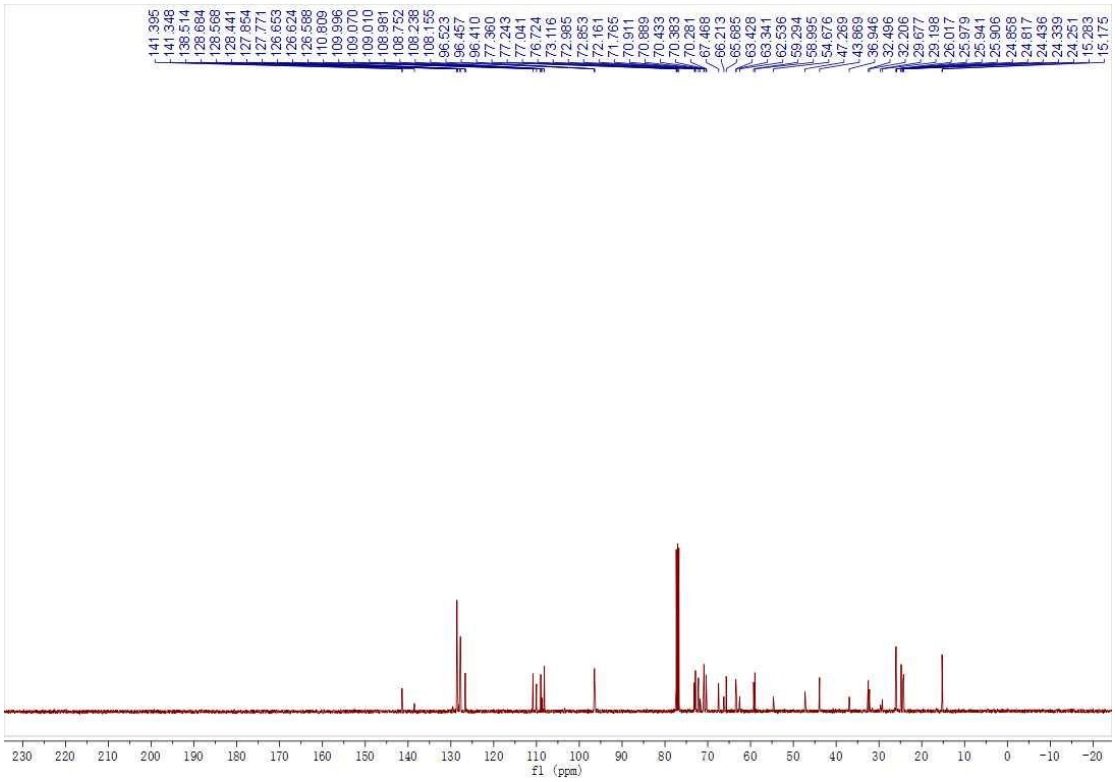


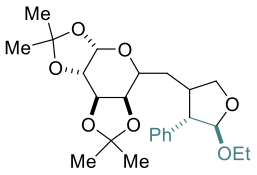
(**39**)



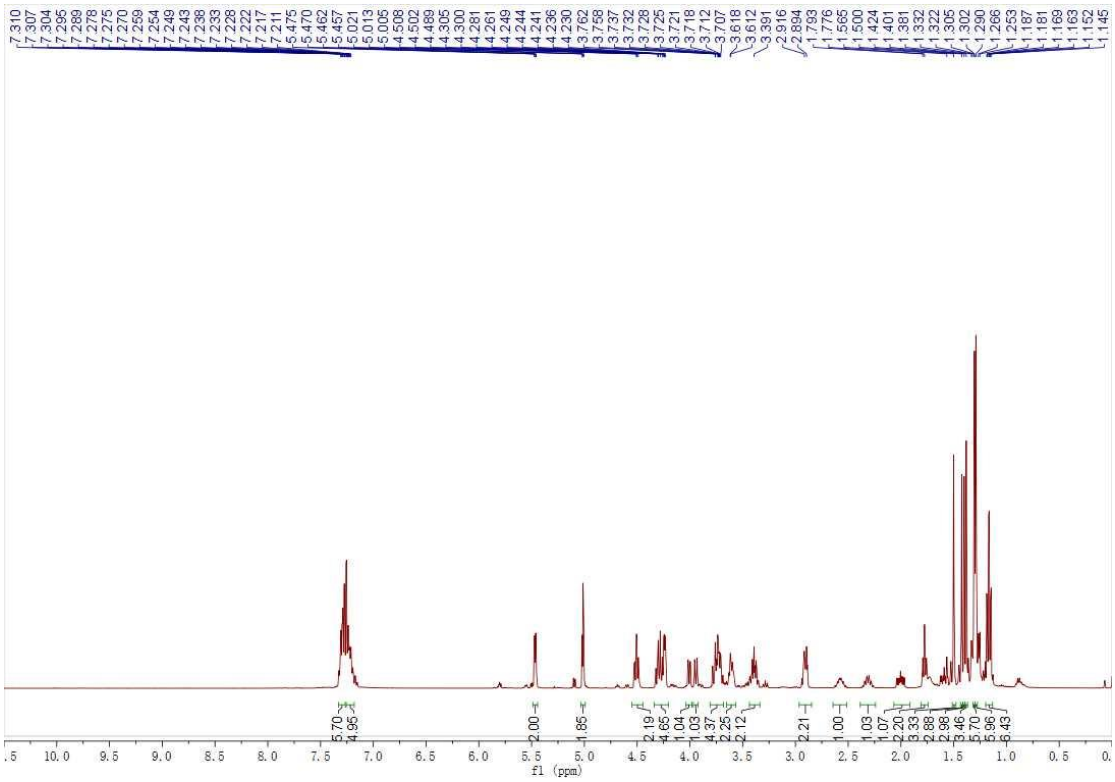
(from **Z-SM**, dr = 2.6:2:1)

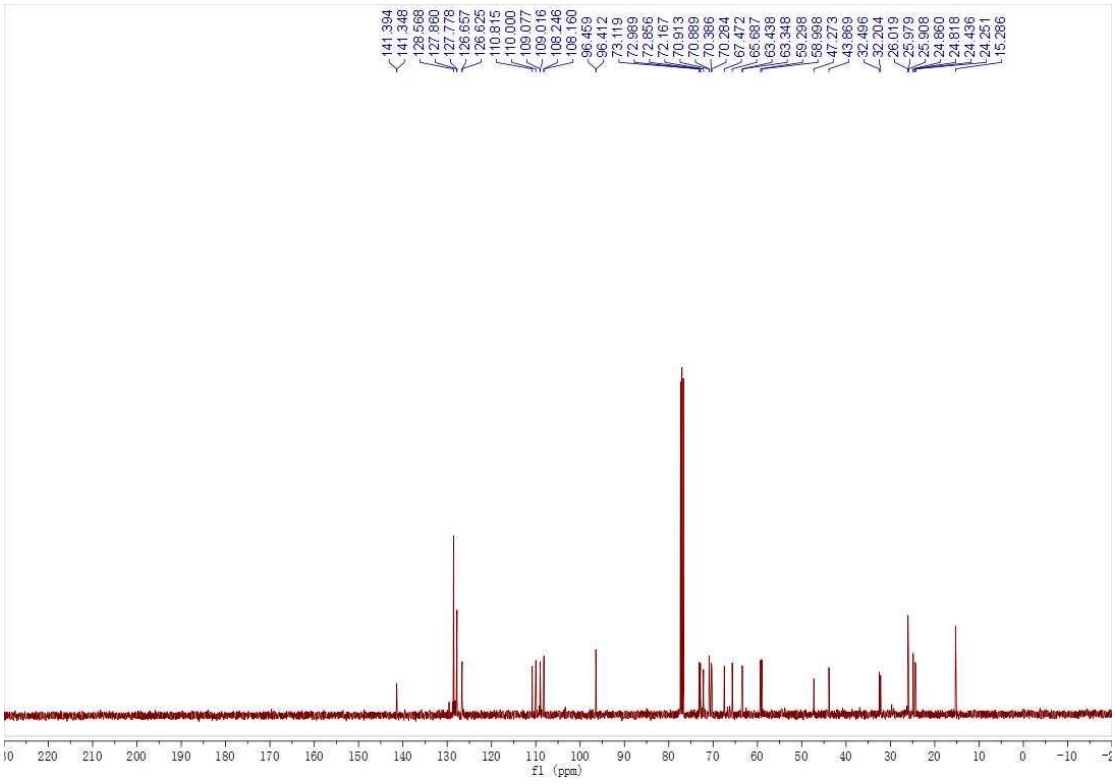




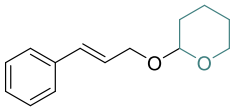


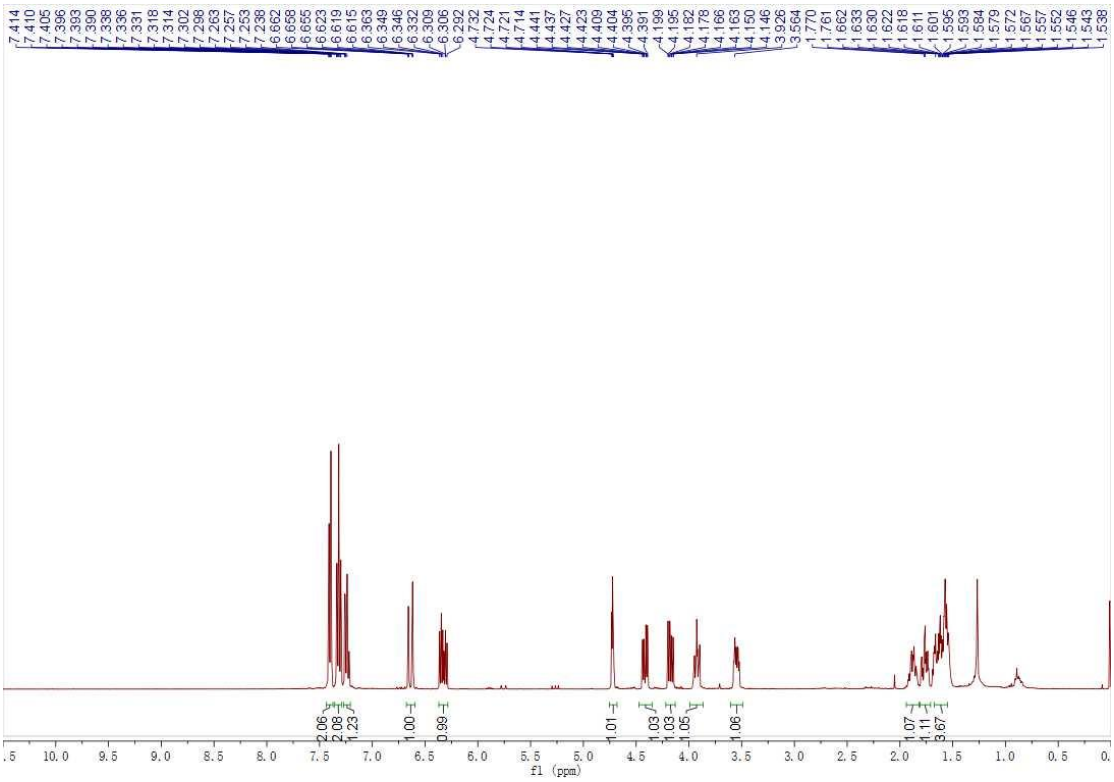
(from **E-SM**, dr = 1.1:1)





(**40**)

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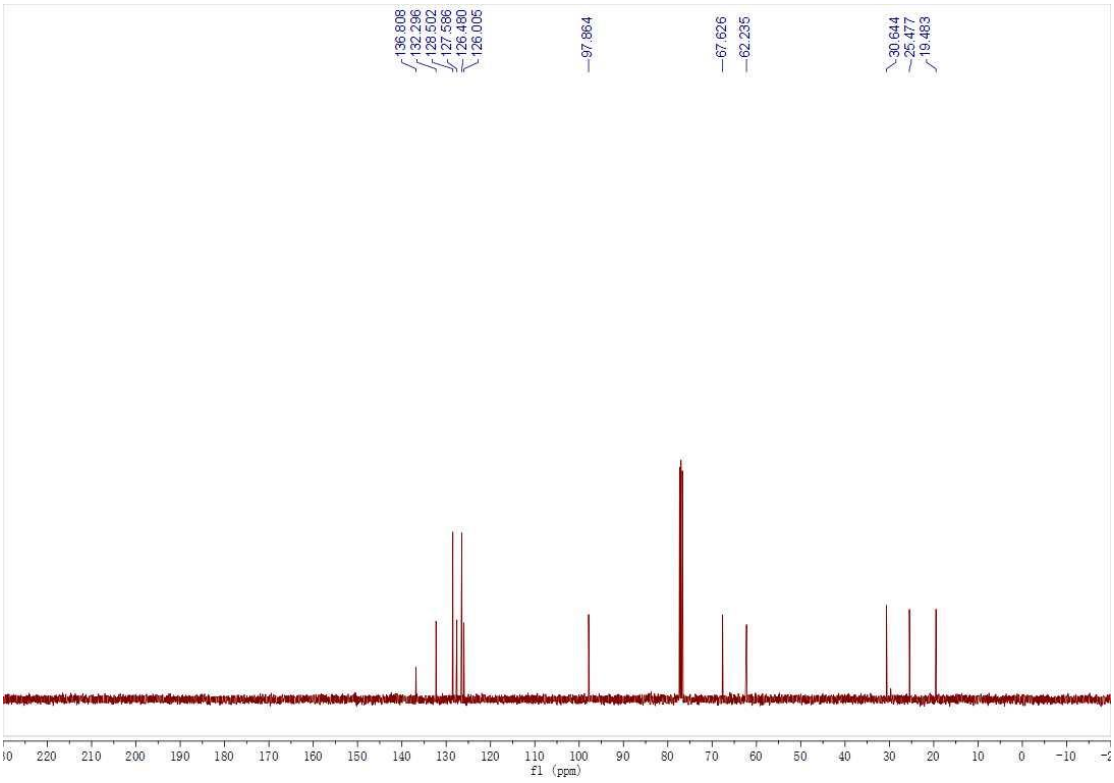
7.410
7.405
7.396
7.393
7.390
7.338
7.336
7.331
7.318
7.314
7.302
7.298
7.263
7.257
7.253
7.238
6.662
6.658
6.655
6.623
6.619
6.615
6.363
6.349
6.346
6.332
6.309
6.306
6.292
4.732
4.724
4.721
4.714
4.441
4.437
4.427
4.423
4.409
4.404
4.395
4.391
4.199
4.195
4.182
4.178
4.166
4.163
4.150
4.146
3.926
3.564
1.770
1.761
1.662
1.633
1.630
1.622
1.618
1.611
1.601
1.595
1.593
1.584
1.579
1.572
1.567
1.557
1.552
1.546
1.543
1.538
2.06
2.08
1.23
1.00
0.99
1.01
1.03
1.03
1.05
1.06
1.07
1.11
3.67
f1 (ppm)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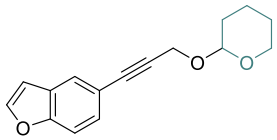
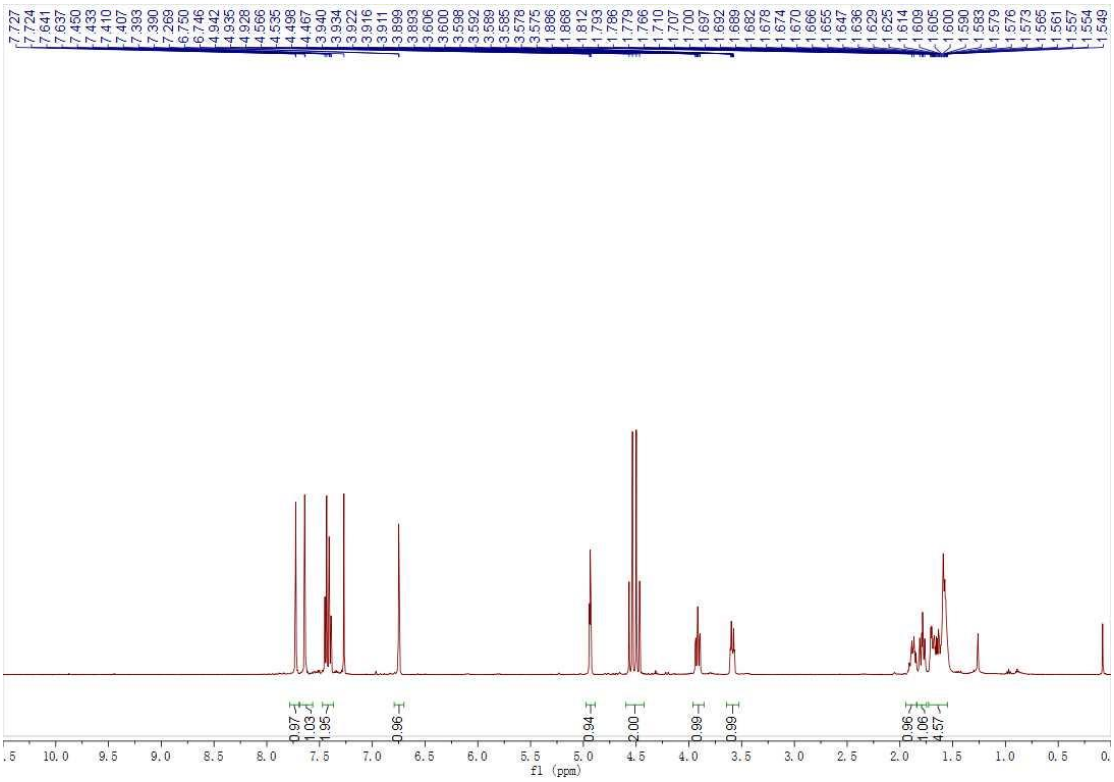
132.296
128.502
127.586
126.480
126.005
97.864
67.626
62.235
30.644
25.477
19.483
f1 (ppm)

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7.637
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7.390
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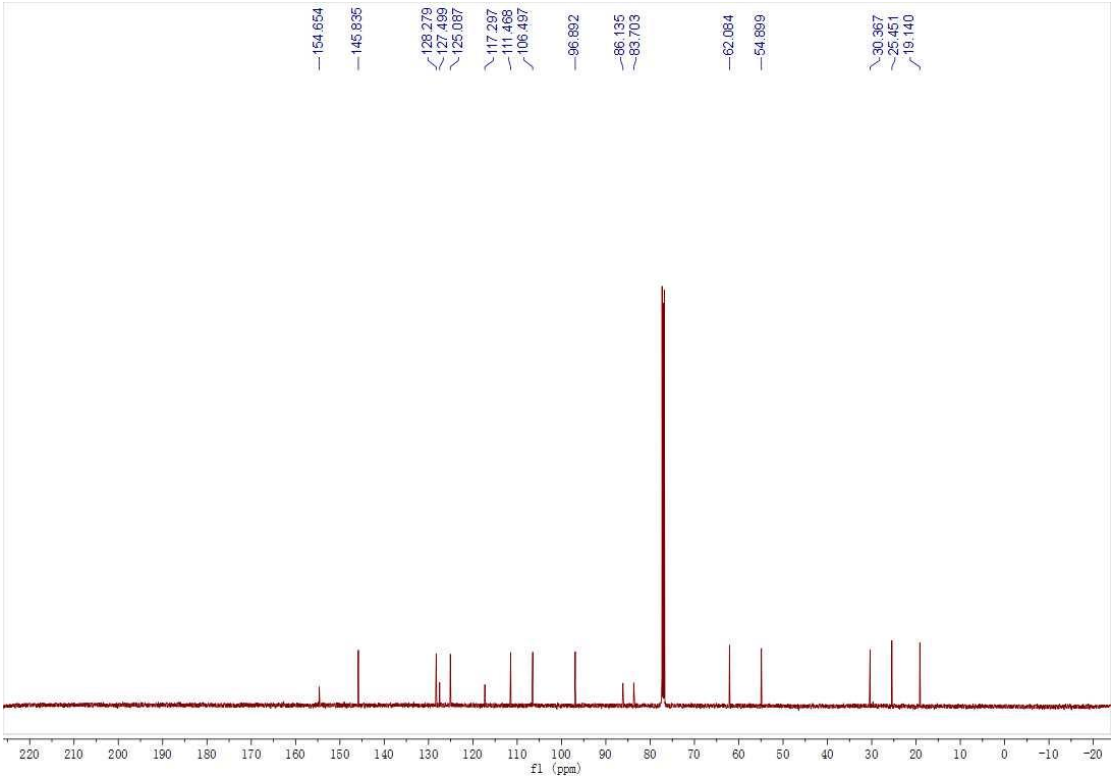
6.750
6.746
4.942
4.935
4.928
4.566
4.535
4.498
4.467
3.940
3.934
3.922
3.916
3.911
3.899
3.893
3.606
3.600
3.598
3.592
3.589
3.585
3.578
3.575
1.886
1.868
1.812
1.793
1.786
1.779
1.766
1.710
1.707
1.700
1.697
1.692
1.689
1.682
1.678
1.674
1.670
1.666
1.655
1.647
1.636
1.629
1.625
1.614
1.609
1.605
1.600
1.590
1.583
1.579
1.576
1.573
1.565
1.561
1.557
1.554
1.549
0.97
1.03
1.95
0.96
0.94
2.00
0.99
0.99
0.96
1.06
4.57
f1 (ppm)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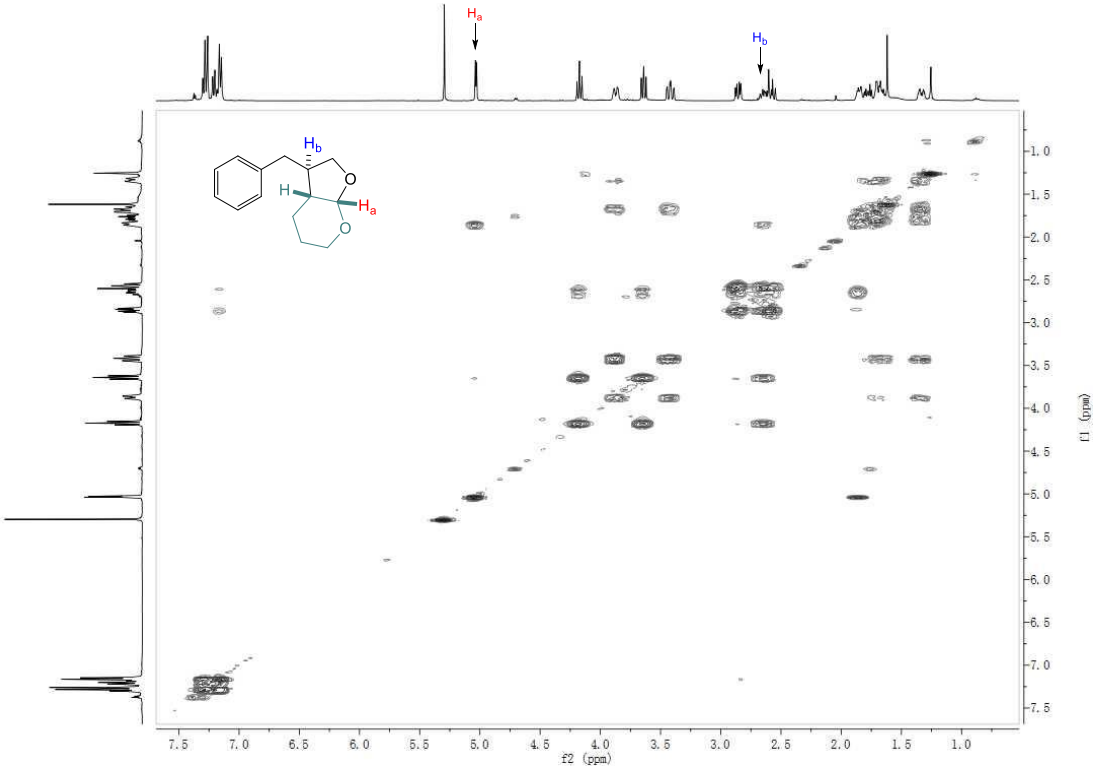
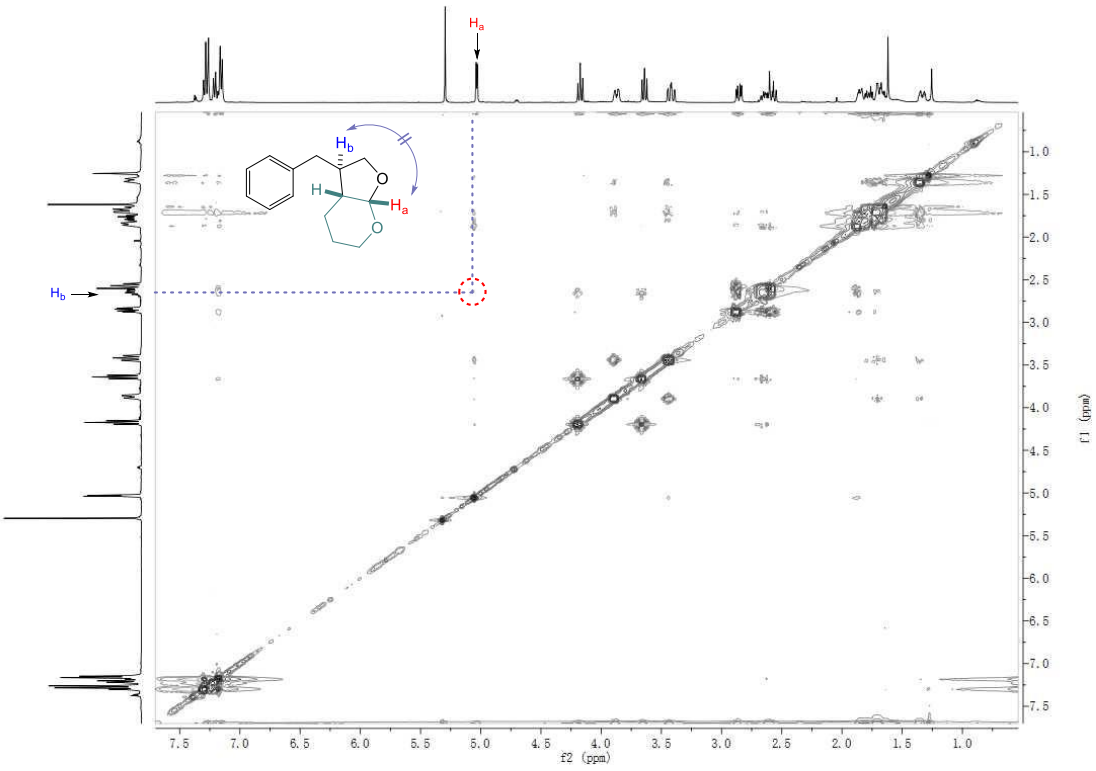
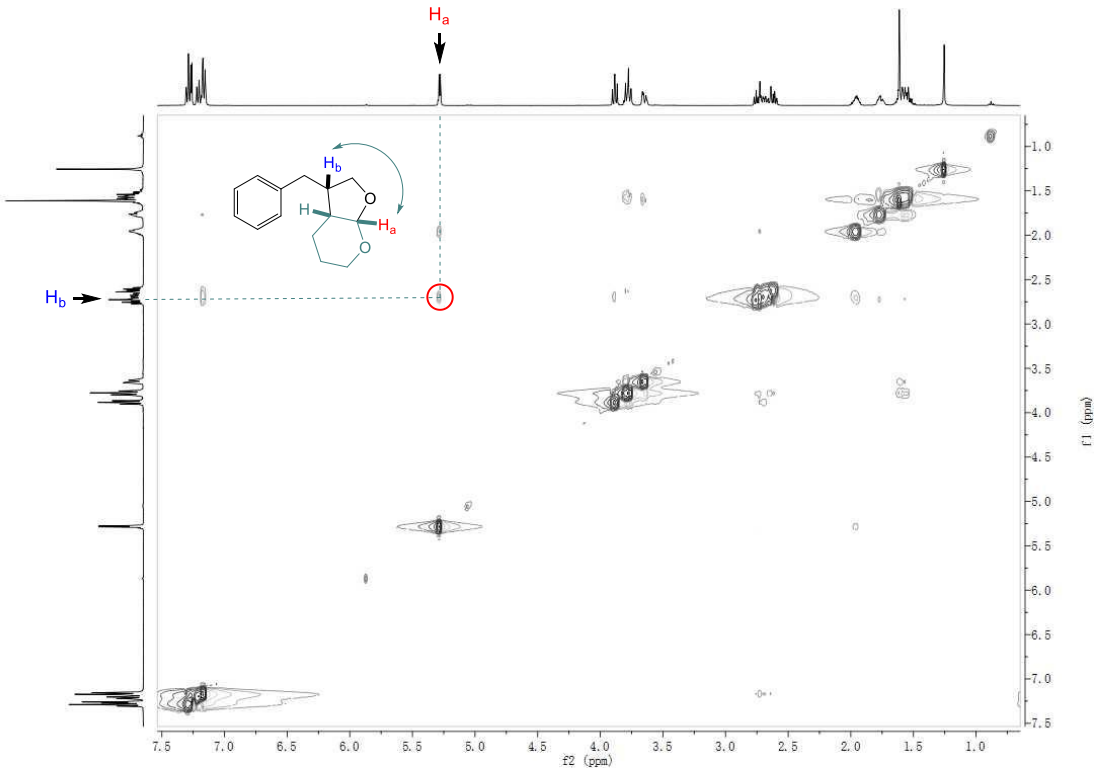
128.279
127.499
125.087
117.297
111.468
106.497
96.892
86.135
83.703
62.084
54.899
30.367
25.451
19.140
f1 (ppm)

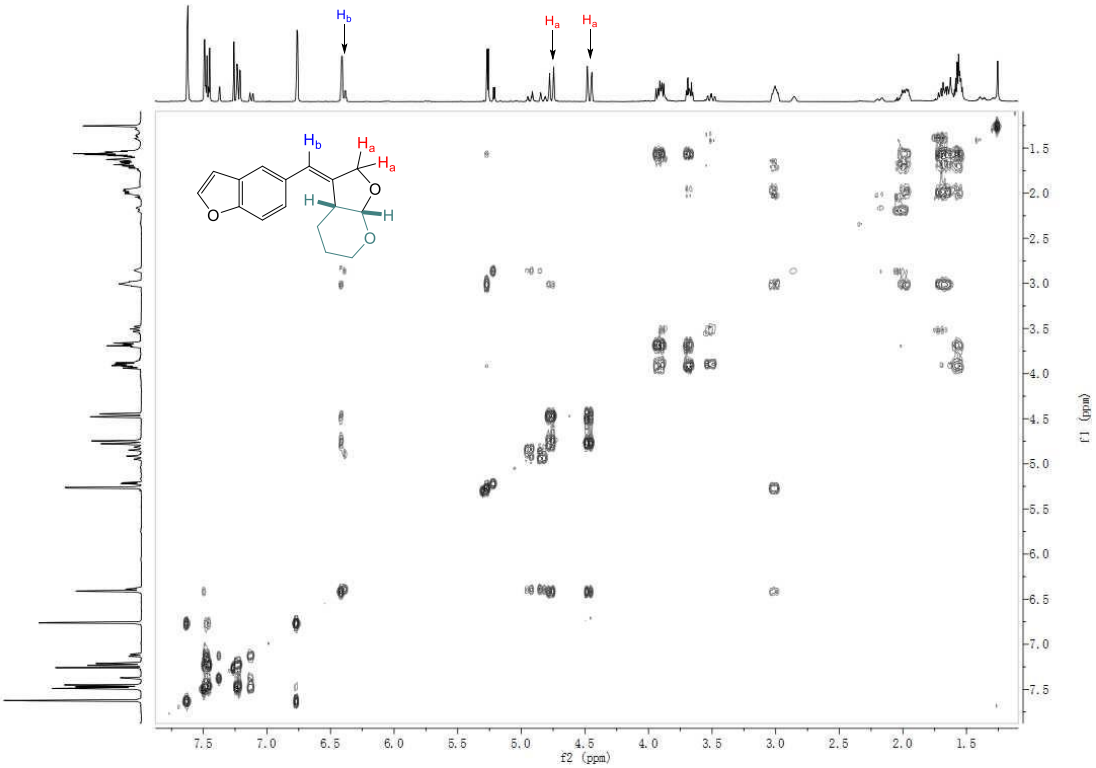
H^1-H^1 COSY and H^1-H^1 2D-NOESY NMR spectrums of product **1**

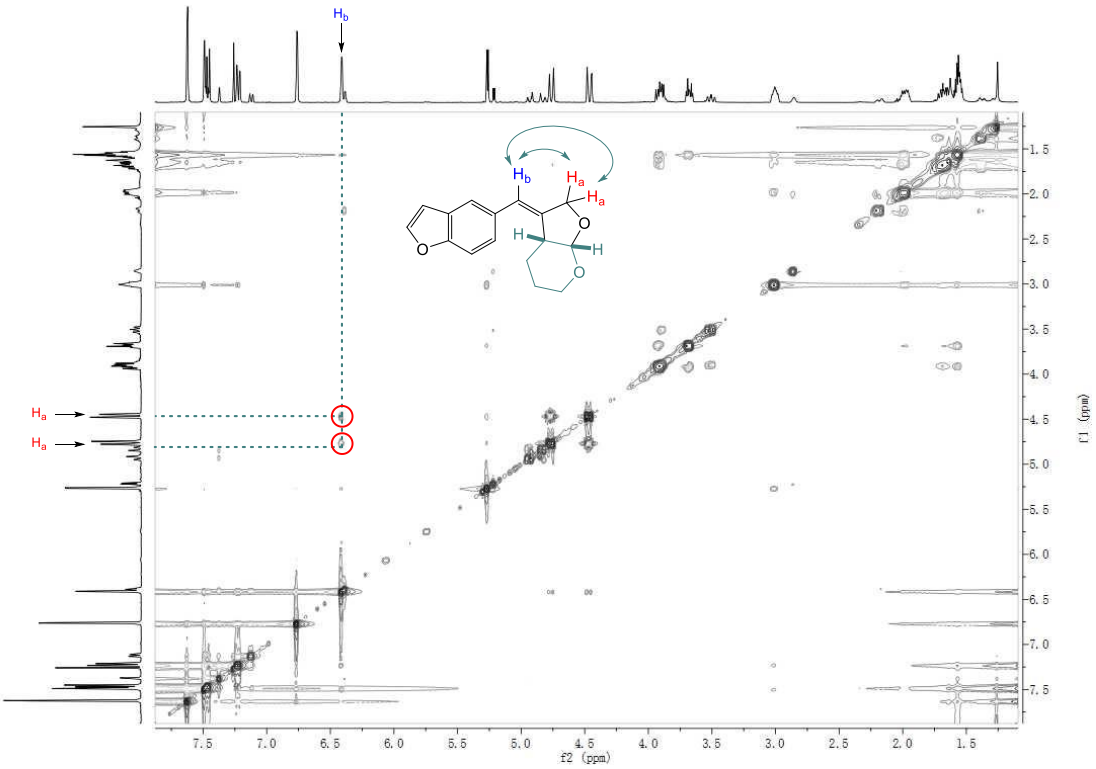




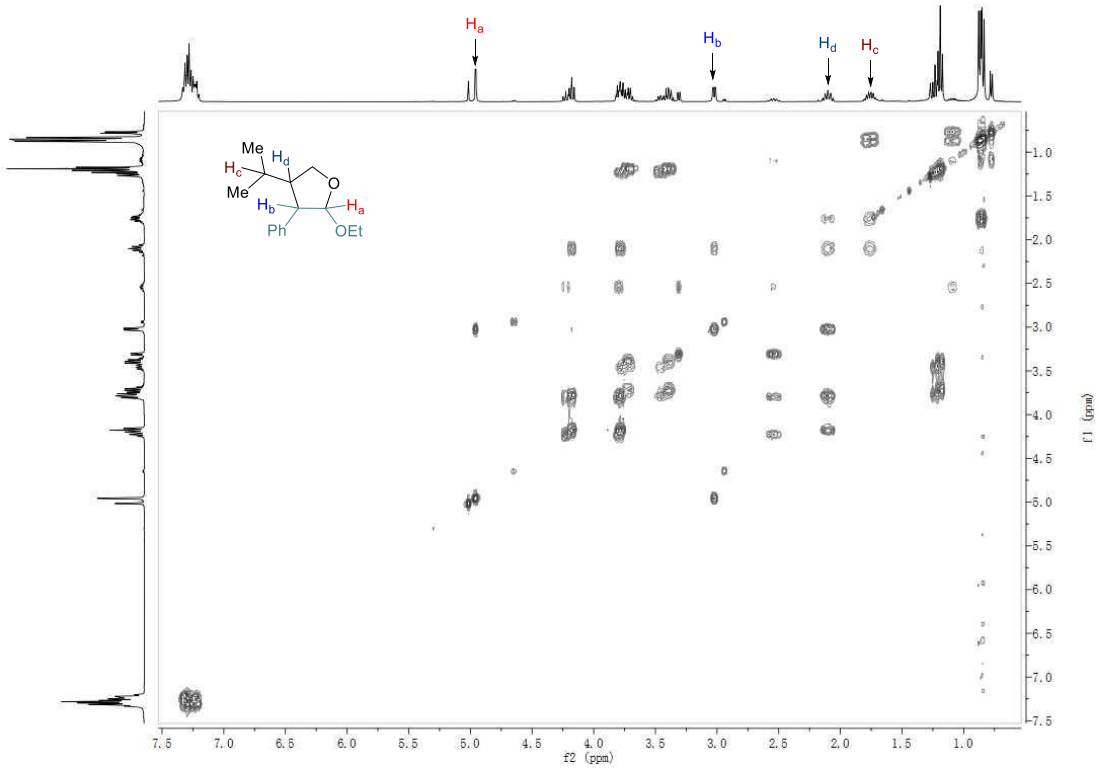

Ha
Hb
Hb
H
Ha
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)

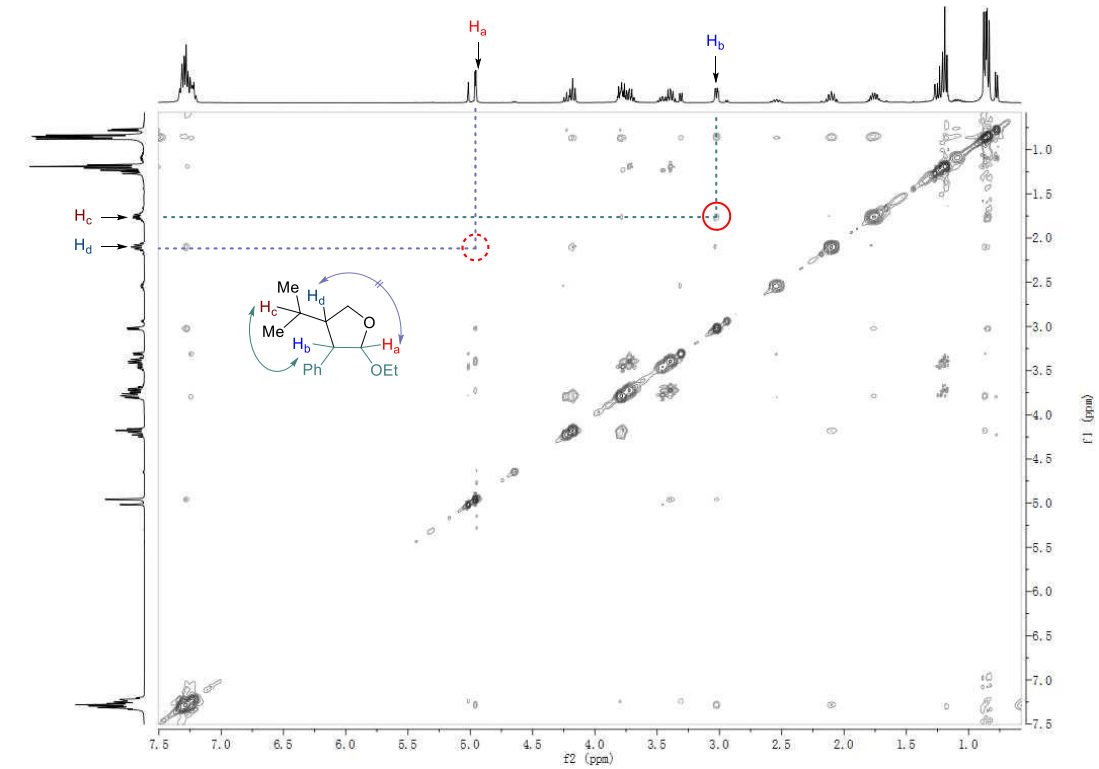
H^1-H^1 COSY and H^1-H^1 2D-NOESY NMR spectrums of compound **18**



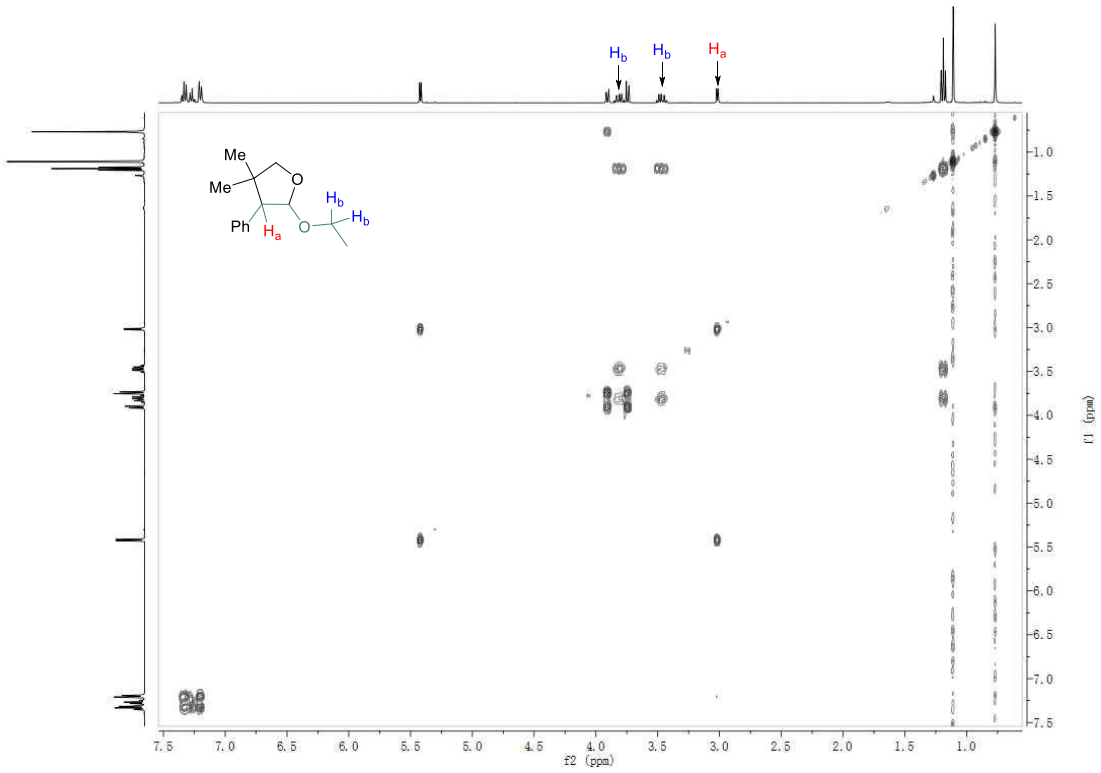


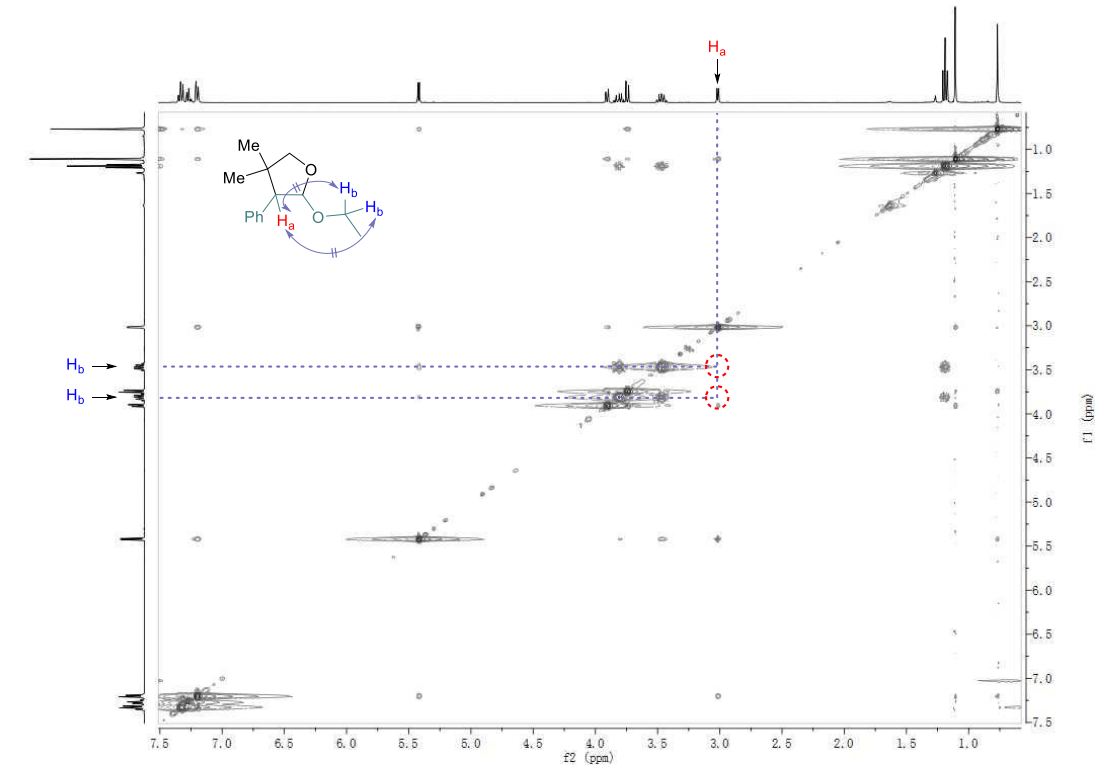
H^1-H^1 COSY and H^1-H^1 2D-NOESY NMR spectrums of compound **34**





H^1-H^1 COSY and H^1-H^1 2D-NOESY NMR spectrums of compound **35**





III. Date S2: Stability of cyclic acetals in simulated GI fluids (Related to Table 2)

Instruments and Equipments:
Agilent 1260 HPLC with DAD and 6420 Triple Quad MS
Waters Xbridge C8 (4.6 mm× 150 mm × 3.5 μm) column
Waters CSH C18 (4.6 mm× 150 mm × 3.5 μm) column
Eppendorf ThermoMixer C
Eppendorf Multipette Xstream
Mettler Toledo Seven Excellence pH meter

Reagents and Materials:
Purified water, Milli-Q HPLC grade
Acetonitrile, Sigma-Aldrich HPLC grade
Ammonium Bicarbonate, Sigma-Aldrich
Simulated Gastric Fluid USP without enzymes (SGF, pH 1.2)
Simulated Intestinal Fluid USP without enzymes (SIF, pH 6.8)
Compounds **1**, **15**, **27**, **35**.

Experiment:
HPLC method

Instrument	Agilent 1260 HPLC with DAD and 6420 Triple Quad MS
Column	Waters Xbridge C8 (4.6 mm× 150 mm × 3.5 μm) column for Compound A, B, C, E Waters CSH C18 (4.6 mm× 150 mm × 3.5 μm) column for Compound D
Column temperature	40 °C
Mobile phase	A: 10 mM NH4HCO3 in water B: ACN
Gradient program	Time (min) A% B% 0.00 95 5 15.00 5 95 20.00 5 95 20.10 95 5 25.00 95 5
Flow rate	0.7 mL/min
Detector	UV 214nm for Compound A, B, C, D UV 224nm for Compound E
Injection volume	10 μL

The solution stability of four compounds were evaluated in SGF and SIF at 37 °C. Detailed information is shown in Table S1.

Table S1 Stability testing plan, related to **Table 2**

Conditions	Time point	Test media	Testing items
37 °C	1 hr	SGF	Final pH,
	3 hr	SIF	% Purity,
			% Degradation.

Testing media:
Simulated Gastric Fluid USP without enzymes (SGF, pH 1.2)
Simulated Intestinal Fluid USP without enzymes (SIF, pH 6.8)

Initial solution:
Compound **35** was dissolved in ACN to make 2.5 mg/mL stock solutions. The solutions were diluted with ACN:water 1:1 to get 0.25 mg/mL initial solutions.
Compound **15** was dissolved in ACN to make a 5 mg/mL stock solution. The solution was diluted with ACN:water 1:1 to get 0.5 mg/mL initial solution.
Compounds **1** and **27** were dissolved in ACN and methanol to make a 2.5 mg/mL stock solution. The solution was diluted with ACN:water 1:1 to get 0.25 mg/mL initial solutions.

Sample solution:
100 µL of each stock solutions were diluted with 900 µL of SGF and 900 µL of SIF.

Testing procedure:
All the sample solutions were placed in Thermomixer according to Table S1 conditions respectively. The final pH values were measured by pH meter. The purities and concentrations were determined by HPLC-MS. Significant degradation (> 5 percent) of a compound in this study could suggest potential instability.

Table S2 Degradation studies in SIF and SGF at 37 °C (According to FDA: Waiver of In Vivo Bioavailability and Bioequivalence Studies)**,** related to **Table 2**

Classification	Degradation (%) after 1 h at 37 °C in SGF	Degradation (%) after 3 h at 37 °C in SIF
Fairly stable	< 5%	< 5%
Unstable	> 5%	> 5%

Results:
The stability results of five intermediates and final pH values are listed in **Table S3** – **S6** with stability classification remarks.

Table S3 Stability results of compound **35** (λ = 214 nm)**,** related to **Table 2**

Condition	Test Media	Time	Purity (%)	Conc. (mg/mL)	Recovery (%)	Degradation (%)	Classification	Final pH
Initial	ACN:water	0	95.74	0.25				

37 °C	SGF	1hr	0.56	0.0015	0.60	99.4151	Unstable	1.06
	SIF	3hrs	98.22	0.2381	95.23	-2.5903	/	6.92

Table S4 Stability results of compound **15** (λ = 214 nm), related to **Table 2**

Condition	Test Media	Time	Purity (%)	Conc. (mg/mL)	Recovery (%)	Degradation (%)	Classification	Final pH
Initial	ACN:water	0	93.70	0.5000				
37 °C	SGF	1hr	89.58	0.4585	91.71	4.3970	Fairly stable	1.08
	SIF	3hrs	93.61	0.4848	96.97	0.0961	Fairly stable	6.89

Table S5 Stability results of compound **1** (λ = 214 nm), related to **Table 2**

Condition	Test Media	Time	Purity (%)	Conc. (mg/mL)	Recovery (%)	Degradation (%)	Classification	Final pH
Initial	ACN:water	0	92.05	0.2500				
37 °C	SGF	1hr	80.65	0.2311	92.44	12.3846	Unstable	1.09
	SIF	3hrs	91.95	0.2618	104.73	0.1086	Fairly stable	6.88

Table S6 Stability results of compound **27** (λ = 224 nm), related to **Table 2**

Condition	Test Media	Time	Purity (%)	Conc. (mg/mL)	Recovery (%)	Degradation (%)	Classification	Final pH
Initial	ACN:water	0	99.78	0.2500				
37 °C	SGF	1hr	98.45	0.2598	103.90	1.3329	Fairly stable	1.07
	SIF	3hrs	99.27	0.2663	106.54	0.5111	Fairly stable	6.87

IV. Reference

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