A novel type of donor-acceptor cyclopropanes with fluorine as donor: (3+2)-cycloadditions with carbonyls

Haidong Liu,[a] Lifang Tian,[a] Hui Wang,[a] Zhi-Qiang Li,[a] Chi Zhang,[a] Fei Xue,[b] and Chao Feng*[a]

[a]Technical Institute of Fluorochemistry (TIF), Institute of Advanced Synthesis (IAS), School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, P. R. China.

[b]Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China

iamcfeng@njtech.edu.cn

Table of Contents

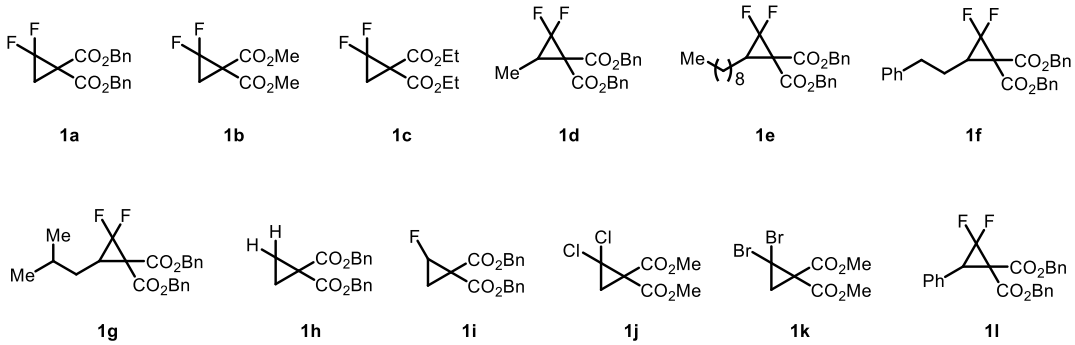
1. General Information

Unless otherwise noted, all reactions were carried out under dry nitrogen atmosphere. $AlCl_3$ (Energy Chemical), $In(OTf)_3$ (Bidepharm), $FSO_2CF_2CO_2SiMe_3$ (Shang Fluoro). All commercial reagents were used directly without further purification. All solvent dried by passage through a column of neutral alumina under nitrogen prior to use. Organic solutions were concentrated under reduced pressure on an IKA RV 10 rotary evaporator. Flash chromatography was performed using Huanghai flash silica gel (200–300 mesh). Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates visualized under UV light (254 nm).

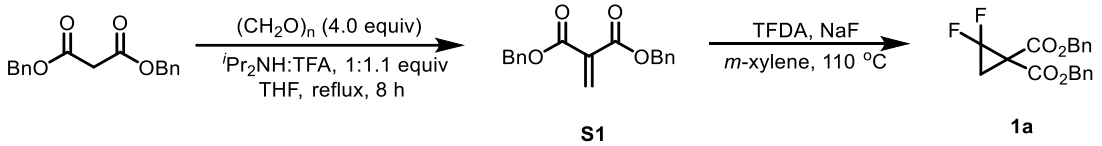
HRMS spectra were recorded on a Xevo G2-XS QTof (Waters Corporation). The NMR spectra were recorded using JEOL 400 MHz Fourier-transform NMR spectrometer. Chemical shifts were reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplet) and etc. Coupling constants are reported as a J value in Hz. IR spectra were recorded on a NICOLET IS10 (Thermo Fisher Scientific).

2. Preparation of Substrates

Scheme S1. Structure of Trifluoromethyl Alkenes

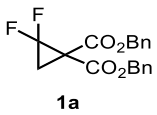


General Procedure A*: Preparation of gem-Difluorocyclopropanes* (**1a-1c**).



Dibenzyl 2-methylenemalonate (**S1**) was prepared by a modified reported procedure.[1] To a 250 mL round bottom flask equipped with a stir bar were added dibenzyl malonate (1.0 equiv, 10 mmol, 2.84 g), paraformaldehyde (2.0 equiv, 20 mmol, 0.6 g), Diisopropylamine (10 mmol, 1.0 equiv, 1.4 mL), trifluoroacetic acid（11 mmol, 1.1 equiv, 0.82 mL）and dry THF (100 mL). The reaction mixture was stirred, open to the atmosphere, at reflux for 2 h. The mixture would become clear, then the reaction mixture was cooled down to room temperature and a second addition of paraformaldehyde (2.0 equiv, 20 mmol, 0.6 g) was performed. Next, the reaction mixture was stirred at reflux for an additional 6 h open to the atmosphere. The reaction mixture was cooled down and the solvent was removed under reduced pressure, dissolved in Et_2O and washed with brine. The solution mixture was dried (Na_2SO_4) and concentrated under vacuum to get the **S1** as a clear liquid (90% yield) which was carried on directly to the next step. (*Note: purification of this compound led to extensive loss of material on silica*).

Dibenzyl 2,2-difluorocyclopropane-1,1-dicarboxylate (**1a**) was prepared by a modified reported procedure.[2] Under N_2 atmosphere, to a 50 mL two neck round bottom flask equipped with a stir bar were added NaF (20 mol%, 1.8 mmol, 76 mg), dibenzyl 2-methylenemalonate (**S1**, 9 mmol, 1.0 equiv, 2.67 g) and m-xylene (0.5 mL). The mixture was heated to 110 ºC and stirred for 5 min. TFDA ($FSO_2CF_2CO_2SiMe_3$, 18 mmol) was added dropwise in 15 min. Then the mixture was stirred for further 30 min at 110ºC. When the substrate was completely conversed detected by TLC, the mixture was cooled to room temperature. After removal of the solvent under reduced pressure, the residue was subjected to column chromatography (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.20, CAM solution, UV) to afford the pure product **1a** (2.31 g, 6.7 mmol, 74% yield) as a colorless oil.



^{1}H NMR (401 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 6H), 7.23 – 7.19 (m, 4H), 5.13 (s, 4H), 2.27 (t, *J* = 9.3 Hz, 2H)

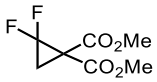
ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 , 134.7 , 128.5 , 128.4 , 128.1 , 109.2 (t, *J* = 291.6 Hz), 68.1 , 39.0 (t, *J* = 11.6 Hz), 21.5 (t, *J* = 9.9 Hz) ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ -131.74 (t, *J* = 9.3 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{19}H_{16}F_2NaO_4^+$ $[M+Na]^+$: 369.0914, found: 369.0910.

IR (film) ν_{max} 3035, 1743, 1499, 1447, 1380, 1274, 1116, 977, 913, 750, 697 cm^{-1}.



1b

dimethyl 2,2-difluorocyclopropane-1,1-dicarboxylate (1b) was prepared from dimethyl malonate (1.0 equiv, 10 mmol, 1.3 g**)** according to the *general procedure A*. **1b** was obtained as a colorless oil (47% yield over two steps) after flash chromatography (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.20, 10% phosphomolybdic acid hydrate in EtOH solution);

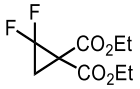
^{1}H NMR (401 MHz, $CDCl_3$) δ 3.81 (s, 6H), 2.32 (t, *J* = 9.3 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 109.1 (t, *J* = 291.3 Hz), 53.4, 38.8 (t, *J* = 11.7 Hz), 21.5 (t, *J* = 9.9 Hz) ppm;

^{19}F NMR (377 MHz, $CDCl_3$) δ -132.12 (t, *J* = 9.3 Hz, 3F) ppm;

HRMS (ESI, m/z): calculated for $C_7H_8F_2NaO_4^+$ $[M+Na]^+$: 217.0288, found: 217.0279.

IR (film) ν_{max} 2957, 1743, 1438, 1276, 1163 cm^{-1}.



1c

diethyl 2,2-difluorocyclopropane-1,1-dicarboxylate (1c): was prepared from diethyl malonate (1.0 equiv, 10 mmol, 1.6 g**)** according to the *general procedure A*. **1c** was obtained as a colorless oil (50% yield over two steps) after flash chromatography (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.20, 10% phosphomolybdic acid hydrate in EtOH solution);

^{1}H NMR (401 MHz, $CDCl_3$) δ 4.21 (qd, *J* = 7.1, 1.3 Hz, 5H), 2.23 (t, *J* = 9.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 6H) ppm.

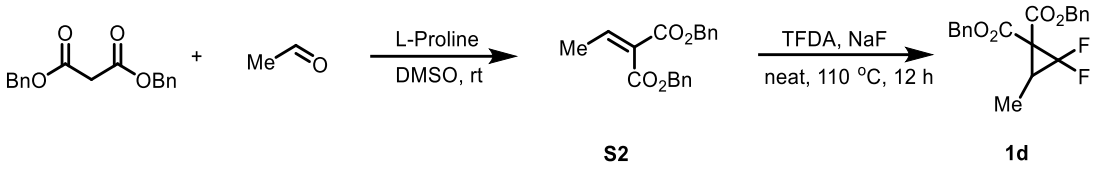
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 , 109.1 (t, *J* = 290.9 Hz), 62.4 , 38.9 (t, *J* = 11.5 Hz), 21.1 (t, *J* = 10.0 Hz), 13.7 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ -132.53 (t, *J* = 9.4 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_9H_{12}F_2NaO_4^+$ $[M+Na]^+$: 245.0601, found: 245.0602.

IR (film) ν_{max} 2986, 1739, 1447, 1371, 1259, 1176, 1033 cm^{-1}.

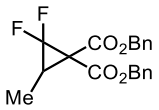
***General Procedure B**: Preparation of gem-Difluorocyclopropanes* (**1d-1g**).



S2 **1d**

dibenzyl 2-ethylidenemalonate(S2). To an over dried 50 mL round-bottom flask under N_2 was charged with anhydrous DMSO (6 mL), L-Proline (0.15 g, 1.3 mmol), and acetaldehyde (5.0 M in THF, 12.0 mmol, 1.2 equiv). The suspension was stirred for 5 minutes after which dimethylmalonate (10 mmol, 1.0 equiv) was added. After 18 h, the reaction was diluted with ethyl acetate (30 mL) and washed with water (2*30 mL), dried over sodium sulfate and concentrated in vacuo. The desire product **S2** was obtained after column chromatography as a colorless oil. The analytical data obtained matched those reported in the literature.[3]

dibenzyl 2,2-difluoro-3-methylcyclopropane-1,1-dicarboxylate (1d) was prepared by a modified reported procedure. Under N_2 atmosphere, to a 50 mL two neck round bottom flask equipped with a stir bar were added NaF (20 mol%), dibenzyl 2-ethylidenemalonate (**S2**, 1.0 equiv, 5.0 mmol). The mixture was heated to 110 °C and stirred for 5 min. TFDA ($FSO_2CF_2CO_2SiMe_3$, 2.0 equiv. 10.0 mmol) was added dropwise in 15 min and the mixture was stirred for further 15 h at 110 °C. Then the mixture was cooled to room temperature and the reaction mixture was subjected to column chromatography directly (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.25, CAM solution, UV) to afford the pure product **1d** (0.36 g, 1.0 mmol, 20% yield) as a colorless oil.



1d

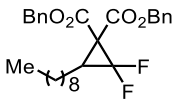
^{1}H NMR (401 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 6H), 7.28 – 7.23 (m, 4H), 5.21 – 5.12 (m, 4H), 2.65 (dqd, *J* = 13.5, 6.7, 4.0 Hz, 1H), 1.22 (dd, *J* = 6.8, 1.9 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 , 162.4 , 134.8 (d, *J* = 9.0 Hz), 128.6 , 128.5 , 128.5 , 128.4 , 128.1 , 110.4 (dd, *J* = 295.1, 292.3 Hz), 68.1 , 67.7 , 41.7 (dd, *J* = 13.1, 9.9 Hz), 27.9 (t, *J* = 10.0 Hz), 6.9 (d, *J* = 5.1 Hz) ppm;

^{19}F NMR (377 MHz, $CDCl_3$) δ -131.02 (dd, *J* = 154.0, 13.5 Hz), -141.15 (dd, *J* = 154.1, 3.7 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{20}H_{18}F_2NaO_4^+$ $[M+Na]^+$: 383.1071, found: 383.1078.

IR (film) ν_{max} 2960, 1739, 1499, 1455, 1380, 1166, 750, 698 cm^{-1}.



1e

dibenzyl 2,2-difluoro-3-nonylcyclopropane-1,1-dicarboxylate (1e) was prepared from dibenzyl malonate (1.0 equiv, 10 mmol, 2.84 g) and decanal (1.2 equiv, 12 mmol, 1.87 g) according to the *general procedure B.* **1e** was obtained as a colorless oil (15% yield over two steps) after flash chromatography (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.25, CAM solution, UV);

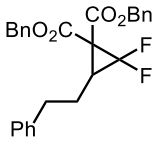
^{1}H NMR (401 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 8H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.00 (d, *J* = 2.7 Hz, 1H), 5.25 (d, *J* = 12.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.38 (d, *J* = 12.1 Hz, 1H), 3.53 – 3.40 (m, 1H), 2.32 (s, 3H), 1.41 – 1.14 (m, 16H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 , 162.5 , 134.8 (d, *J* = 4.1 Hz), 128.6 , 128.5 , 128.5 , 128.4 , 128.0 , 110.4 (q, *J* = 294.8. 292.9 Hz), 68.1 , 67.6 , 41.8 (dd, *J* = 13.0, 9.3 Hz), 33.0 (t, *J* = 9.4 Hz), 31.8 , 29.4 , 29.3 , 29.3 , 28.9 , 28.1 , 22.7 , 22.3 (d, *J* = 2.6 Hz), 14.1 ppm;

^{19}F NMR (377 MHz, $CDCl_3$) δ -129.77 (ddd, *J* = 154.6, 13.7, 3.6 Hz, 1F), -141.17 (dd, *J* = 154.6, 4.2 Hz 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{28}H_{34}F_2NaO_4^+$ $[M+H]^+$: 357.1853, found: 357.1847.

IR (film) ν_{max} 2927, 2856, 1741, 1499, 1456, 1377, 1262, 1088, 749, 697 cm^{-1}.



1f

dibenzyl 2,2-difluoro-3-phenethylcyclopropane-1,1-dicarboxylate (1f) was prepared from dibenzyl malonate (1.0 equiv, 10 mmol, 2.84 g) and 3-phenylpropanal (1.2 equiv, 12 mmol, 1.6 g) according to the *general procedure B.* **1f** was obtained as a colorless oil (27% yield over two steps) after flash chromatography (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.20, CAM solution, UV);

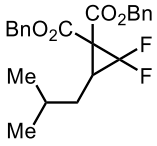
^{1}H NMR (401 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 3H), 7.32 – 7.25 (m, 9H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 6.9 Hz, 3H), 5.26 – 5.11 (m, 4H), 2.73 (h, *J* = 7.3 Hz, 2H), 2.69 – 2.54 (m, 1H), 2.04 – 1.88 (m, 1H), 1.80 (dq, *J* = 15.0, 8.1 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 162.4, 140.1, 134.7 (d, *J* = 1.3 Hz), 128.6, 128.5, 128.5, 128.4, 128.4, 128.0, 126.3, 110.2 (dd, *J* = 295.3, 292.3 Hz), 41.9 (dd, *J* = 13.1, 9.4 Hz), 34.2, 32.3 (t, *J* = 9.3 Hz), 24.3 (d, *J* = 2.3 Hz) ppm;

^{19}F NMR (377 MHz, $CDCl_3$) δ -129.89 (ddd, *J* = 154.4, 13.5, 3.8 Hz, 1F), -139.74 (dd, *J* = 154.7, 4.6 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{27}H_{24}F_2NaO_4^+$ $[M+Na]^+$: 473.1540, found: 473.1543.

IR (film) ν_{max} 3032, 1739, 1498, 1455, 1378, 1263, 1166, 1090, 950, 750, 698 cm^{-1}.



1g

dibenzyl 2,2-difluoro-3-isobutylcyclopropane-1,1-dicarboxylate (1g) was prepared from dibenzyl malonate (1.0 equiv, 10 mmol, 2.84 g**)** and 3-methylbutanal (1.2 equiv, 12 mmol, 1.0 g) according to the *general procedure B.* **1g** was obtained as a colorless oil (15% yield over two steps) after flash chromatography (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.20, CAM solution, UV);

^{1}H NMR (401 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 10H), 5.23 – 5.11 (m, 4H), 2.58 (ddt, *J* = 14.1, 9.4, 4.7 Hz, 1H), 1.74 – 1.59 (m, 2H), 1.29 – 1.21 (m, 1H), 0.90 (dd, *J* = 10.1, 6.4 Hz, 6H) ppm;

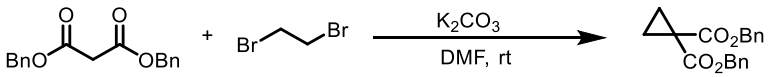
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 162.6, 134.8 (d, *J* = 5.1 Hz), 128.6, 128.5, 128.5, 128.0, 110.4 (t, *J* = 294.0 Hz), 68.1, 67.6, 41.6 (dd, *J* = 13.5, 9.7 Hz), 31.7 (t, *J* = 9.5 Hz), 30.7, 27.4, 22.3, 21.5 ppm;

^{19}F NMR (377 MHz, $CDCl_3$) δ -129.89 (ddd, *J* = 154.4, 13.5, 3.8 Hz, 1F), -139.74 (dd, *J* = 154.7, 4.6 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{23}H_{24}F_2NaO_4^+$ $[M+Na]^+$: 425.1540, found: 425.1542.

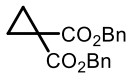
IR (film) ν_{max} 2960, 1740, 1499, 1456, 1377, 1264, 1189, 1143, 1074, 965, 749, 697 cm^{-1}.

General Procedure C*: Preparation of dibenzyl cyclopropane-1,1-dicarboxylate* (**1h**)



1h

To a solution of dibenzyl malonate (1.0 equiv, 4 mmol, 1.0 g) in DMF (20 mL) was added K_2CO_3 (9.0 equiv, 36 mmol, 5.0 g) and 1,2-dibromoethane (3.0 equiv, 12 mmol, 1.0 mL). The reaction mixture was stirred at room temperature for 24 h. The reaction was diluted with ethyl acetate (30 mL) and washed with water (2 x 30 mL), dried over sodium sulfate and concentrated in vacuo. The desire product **1h** was obtained after column chromatography (Petroleum ether/EtOAc = 5 : 1, TLC Rf = 0.30, UV) as a colorless oil(0.96 g, 3.1 mmol, 78% yield).



1h

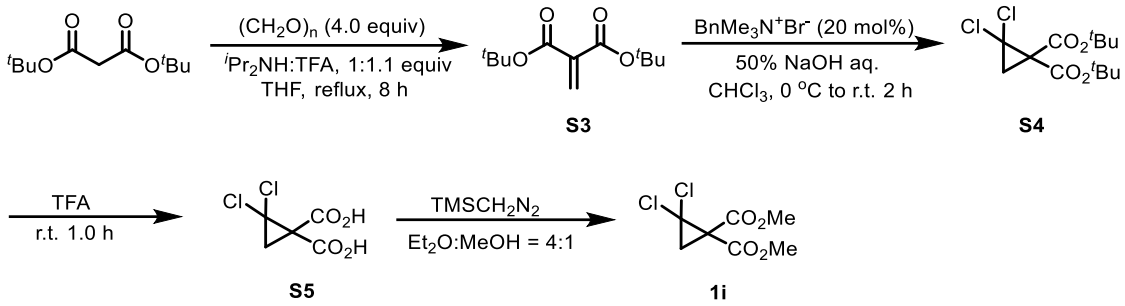
^{1}H NMR (401 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 10H), 5.15 (s, 4H), 1.49 (s, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7 , 135.6 , 128.6 , 128.3 , 128.2 , 67.3 , 28.3 , 17.1 ppm;

HRMS (ESI, m/z): calculated for $C_{19}H_{19}O_4^+$ $[M+H]^+$: 311.1283, found: 311.1288.

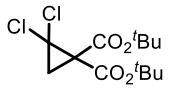
IR (film) ν_{max} 3034, 1731, 1498, 1456, 1383, 1318, 1199, 1128, 751, 697 cm^{-1}.

General Procedure D *Preparation of dimethyl 2,2-dichlorocyclopropane-1,1-dicarboxylate* (**1i**)



di-tert-butyl 2-methylenemalonate (**S3**) was prepared by a modified reported procedure.[1] To a 250 mL round bottom flask equipped with a stir bar were added di-tert-butyl malonate (1.0 equiv, 10 mmol, 2.84 g), paraformaldehyde (2.0 equiv, 20 mmol, 0.6 g), Diisopropylamine (10 mmol, 1.0 equiv, 1.4 mL), trifluoroacetic acid （11 mmol, 1.1 equiv, 0.82 mL） and dry THF (100 mL). The reaction mixture was stirred, open to the atmosphere, at reflux for 2 h. The mixture would become clear, then the reaction mixture was cooled down to room temperature and a second addition of paraformaldehyde (2.0 equiv, 20 mmol, 0.6 g) was performed. Next, the reaction mixture was stirred at reflux for an additional 6 h open to the atmosphere. The reaction mixture was cooled down and the solvent was removed under reduced pressure, dissolved in Et_2O and washed with brine. The solution mixture was dried (Na_2SO_4) and concentrated under vacuum to get the **S3** as a clear liquid (90% yield) which was carried on directly to the next step. Spectral data matched that previously reported[1].

di-tert-butyl 2,2-dichlorocyclopropane-1,1-dicarboxylate (**S4**) di-tert-butyl 2-methylenemalonate (**S3**, 2.0 g, 9.0 mmol), chloroform (5.0 mL), benzyltrimethylammonium bromide (0.41 g, 1.8 mmol, 2 mol%) were put in a flask equipped with a magnetic stirrer and thermometer. A 50% solution of sodium hydroxide (1.1 g, 27.0 mmol, 3.0 equiv) was added dropwise with cooling in an ice-salt bath (T<5 ºC). The mixture was stirred for 2.0 h under ambient temperature and quenched with water. The organic layer was separated and washed with water. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried and the solvent was removed in vacuo. The **S4** was obtained after column chromatography (DCM = 100% to DCM/EA = 20 : 1, TLC (DCM) Rf = 0.15, 10% phosphomolybdic acid hydrate in EtOH solution) as a white solid(0.98 g, 0.34 mmol, 35% yield).



S4

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 1H), 1.50 (s, 9H) ppm;

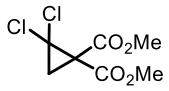
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 , 83.4 , 59.4 , 44.9 , 30.3 , 27.9 ppm;

HRMS (ESI, m/z): calculated for $C_{13}H_{20}Cl_2NaO_4^+$ $[M+Na]^+$: 369.0272, found: 369.0280.

IR (film) ν_{max} 2979, 1740, 1728, 1369, 1324, 1288, 1251, 1169, 1128, 843, 760 cm^{-1}.

2,2-dichlorocyclopropane-1,1-dicarboxylic acid (**S5**): Ester **S4** (310 mg, 1.0 mmol) and trifluoroacetic acid (1.0 mL) were allowed to stand for 1.0 h at ambient temperature. The reaction mixture was washed with hexane (5x5.0 mL) to give 2,2-dichlorocyclopropane-1,1-dicarboxylic acid (**S5**) as a sticky solid which was direct used in the next step without further purification.

dimethyl 2,2-dichlorocyclopropane-1,1-dicarboxylate (**1i**): The acid **S5** was dissolved in Et_2O (8.0 mL) and MeOH (2.0 mL). The mixture was cooled to 0 °C, The Et_2O solution of $TMSCHN_2$ (2.0 mmol, 2.0 equiv) was added at 0 °C. The mixture was stirred at 0 °C for 30 min. The volatile was removed under reduced pressure and the crude residue was purified by column chromatography (PE/EA = 20:1. Rf = 0.27, 10% phosphomolybdic acid hydrate in EtOH solution) to afford the **1i** as a colourless liquid (0.14 g, 60%).



1i

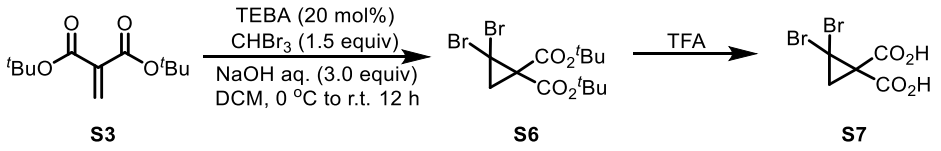
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 6H), 2.37 (s, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 , 59.4 , 53.6 , 43.6 , 30.9 ;ppm;

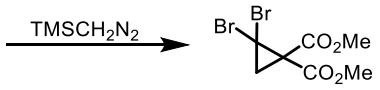
HRMS (ESI, m/z): calculated for $C_7H_8Cl_2NaO_4^+$ $[M+Na]^+$: 248.9697, found: 348.9702.

IR (film) ν_{max} 2925, 2854, 1743, 1437, 1324, 1291, 1254, 1126, 1054 cm^{-1}.

***General Procedure E**: Preparation of dimethyl 2,2-dibromocyclopropane-1,1-dicarboxylate* **(1j)**



S3 **S6** **S7**

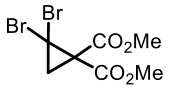


1j

di-tert-butyl 2,2-dibromocyclopropane-1,1-dicarboxylate (S6): di-tert-butyl 2-methylenemalonate (2.0 g, 9.0 mmol), bromoform (1.1 mL, 13.5 mmol, 1.5 equiv), Benzyltriethylammonium chloride (TEBA, 0.4 g, 1.8 mmol, 2 mol%) and dichloromethane (20 mL) were put in a flask equipped with a magnetic stirrer and thermometer. A 50% solution of sodium hydroxide (1.1 g, 27.0 mmol, 3.0 equiv) was added dropwise with cooling in an ice-salt bath (T<5 °C). The mixture was stirred for 12 h under ambient temperature and quenched with water. The organic layer was separated and washed with water. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried. The solvent was removed and the residue was crystallised from hexane giving ester **S6** as a colourless solid (0.9 g, 25%). Spectral data matched that previously reported[5].

2,2-dibromocyclopropane-1,1-dicarboxylic acid (S7): Ester S4 (0.79 g, 2.0 mmol) and trifluoroacetic acid (1.0 mL) were allowed to stand for 1 h at ambient temperature. The product was filtered and washed with hexane to give acid **S7** as a white solid (0.57 mg, 99%). Spectral data matched that previously reported[5].

dimethyl 2,2-dibromocyclopropane-1,1-dicarboxylate (1j): The acid **S7** (0.5 mmol, 0.14 g) was dissolved in Et_2O (4.0 mL) and MeOH (1.0 mL). The mixture was cooled to 0 °C, The Et_2O solution of $TMSCHN_2$ (1.0 mmol, 2.0 equiv) was added at 0 °C. The mixture was stirred at 0 °C for 30 min. The volatile was removed under reduced pressure and the crude residue was purified by column chromatography (PE/EA = 20:1. Rf = 0.25, UV) to afford the **1j** as a colourless liquid (0.25g, 80%).



1j

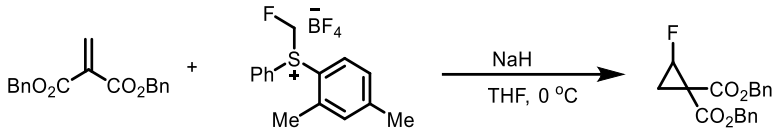
^{1}H NMR (401 MHz, $CDCl_3$) δ 2.32 (s, 2H), 1.52 (s, 18H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 , 83.6 , 44.0 , 32.2 , 27.9 , 22.9 ppm;

HRMS (ESI, m/z): calculated for $C_7H_8Br_2O_4^+$ $[M+H]^+$: 314.8868, found: 314. 8867.

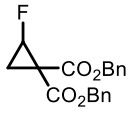
IR (film) ν_{max} 2955, 1747, 1436, 1315, 1238, 1123, 1039, 874, 696 cm^{-1}.

General Procedure F *Preparation of dibenzyl 2-fluorocyclopropane-1,1-dicarboxylate* (**1k**)



S1 **S8** **1k**

dibenzyl 2-fluorocyclopropane-1,1-dicarboxylate (**1k**) and (2,4-dimethylphenyl)(fluoromethyl)(phenyl)sulfonium tetrafluoroborate (**S8**) was prepared by a reported procedure.[4] To a solution of dibenzyl 2-methylenemalonate (**S1**, 296 mg, 1.0 mmol, 1.0 equiv) in anhydrous THF (100 mL) cooled in ice bath under N_2 atmosphere was added (2,4-dimethylphenyl)(fluoromethyl)(phenyl)sulfonium tetrafluoroborate (**S8**, 668 mg, 2.0 mmol, 2.0 equiv) followed by NaH (60% in mineral oil, 400 mg, 10 mmol, 10 equiv). The reaction mixture was stirred for 15 min at 0 °C. When the substrate was completely conversed detected by TLC, the reaction was quenched with water, exacted with EA (15 x 3 mL), dried over sodium sulfate and concentrated in vacuo. The desire product **1k** was obtained after column chromatography (Petroleum ether/EtOAc = 20 : 1, TLC Rf = 0.15, CAM solution, UV) as a colorless oil(0.11 g, 0.34 mmol, 34% yield).



1k

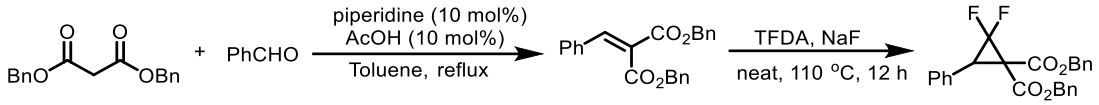
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 10H), 5.28 – 5.01 (m, 5H), 2.24 (ddd, *J* = 22.3, 7.4, 4.2 Hz, 1H), 1.64 (dt, *J* = 13.7, 6.7 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6 , 164.4 (d, *J* = 3.2 Hz), 135.1 , 134.9 , 128.6 , 128.5 , 128.4 , 128.3 , 128.1 , 128.1 , 75.1 (d, *J* = 235.5 Hz), 67.9 , 67.5 , 34.4 (d, *J* = 12.5 Hz), 20.3 (d, *J* = 9.1 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -211.59 (ddd, *J* = 63.4, 22.4, 15.0 Hz) ppm;

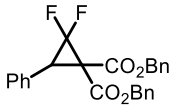
HRMS (ESI, m/z): calculated for C19H17FNaO4$^+$ $[M+Na]^+$: 351.1009, found: 351.1014.

IR (film) ν_{max} 3035, 1738, 1498, 1455, 1381, 1317, 1282, 1215, 1124, 1074, 1027, 750, 697 cm^{-1}.



dibenzyl 2-benzylidenemalonate (S9). To an over dried 100 mL round-bottom flask was charged with anhydrous toluene (30 mL), dibenzyl malonate (1.0 equiv, 10 mmol, 2.84 g), benzaldehyde (1.0 equiv, 10 mmol, 1.06 g), piperidine (10 mol%, 1 mmol, 85 mg) and glacial acetic acid (10 mol%, 1 mmol, 60 mg). The reaction mixture was refluxed under Dean-Stark condition until water collection ceased. The reaction mixture was then sequentially washed with water, 5% aqueous HCl, saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The desire product **S9** was obtained after column chromatography as a colorless oil. The analytical data obtained matched those reported in the literature.[6]

dibenzyl 2,2-difluoro-3-phenylcyclopropane-1,1-dicarboxylate (1l). was prepared by a modified reported procedure. Under N_2 atmosphere, to a 50 mL two neck round bottom flask equipped with a stir bar were added NaF (20 mol%) and dibenzyl 2-benzylidenemalonate (**S9**, 1.0 equiv). The mixture was heated to 130 °C and stirred for 5 min. TFDA ($FSO_2CF_2CO_2SiMe_3$, 2.0 equiv) was added dropwise in 15 min and the mixture was stirred for further 15 h at 130 °C. Then the mixture was cooled to room temperature and the reaction mixture was subjected to column chromatography directly (Petroleum ether/EtOAc = 50 : 1, TLC Rf = 0.20, CAM solution, UV) to afford the pure product **1l** (0.29 g, 0.7 mmol, 27% yield over two steps) as a colorless oil.



1l

^{1}H NMR (401 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 13H), 6.98 (d, *J* = 7.6 Hz, 2H), 5.34 – 5.16 (m, 2H), 4.98 – 4.84 (m, 2H), 3.87 (dd, *J* = 14.3, 3.9 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 , 161.8 , 134.8 , 134.6 , 129.3 , 128.7 , 128.7 , 128.6 , 128.5 , 128.5 , 128.2 , 109.6 (dd, *J* = 298.0, 291.4 Hz), 68.6 , 67.7 , 44.7 (dd, *J* = 12.5, 8.0 Hz), 36.3 (dd, *J* = 12.4, 7.9 Hz) ppm;

^{19}F NMR (377 MHz, $CDCl_3$) δ -124.79 (dd, *J* = 158.5, 14.4 Hz, 1F), -138.41 (dd, *J* = 158.4, 3.9 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{25}H_{20}F_2NaO_4^+$ $[M+Na]^+$: 321.0984, found: 321.0992.

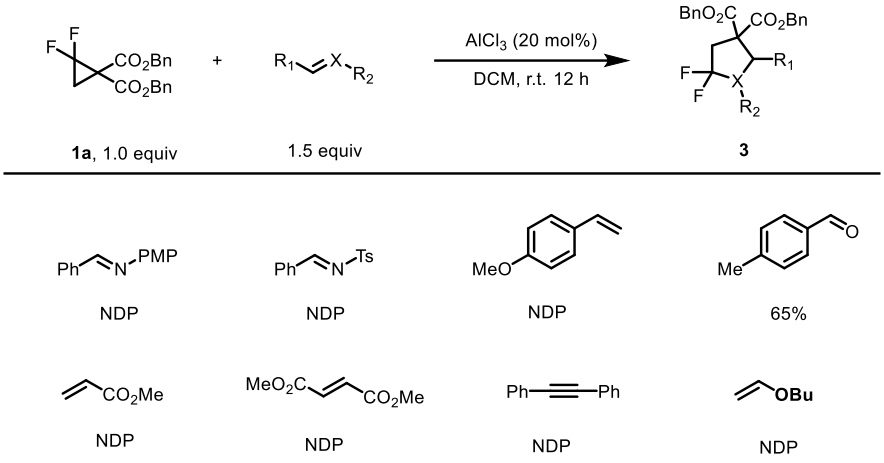
IR (film) ν_{max}, 1741, 1500, 1456, 1436, 1379, 1263, 1090, 971, 747, 697 cm^{-1}.

3. Reaction Optimization

General Procedure for Screening of Unsaturated Systems

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $AlCl_3$ (20 mol%,0.02 mmol, 2.7 mg) and DCE (1.0 mL) in a glove box. Then, the unsaturated systems (1.5 equiv, 0.15 mmol) and dibenzyl 2,2-difluorocyclopropane-1,1-dicarboxylate (1.0 equiv, 0.1 mmol) was added. Then., the reaction mixture was stirred at room temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The 1-iodo-4-(trifluoromethyl)benzene (0.1 mmol, 27.2 mg) was added to the crude residue and the mixture was dissolved with $CDCl_3$. Then the reaction mixture was analyzed by ^{19}F NMR.

Table S1. Screening of Unsaturated Systems

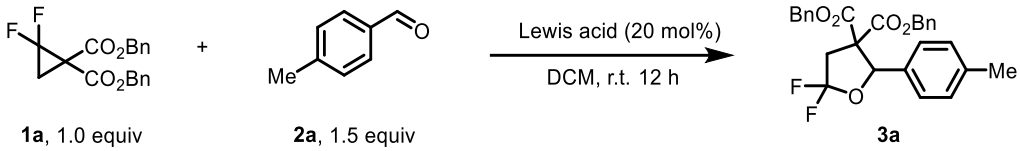


[a] Yields determined by ^{19}F NMR.

General Procedure for optimization of Lewis acids

To an over dried 10 mL Schlenk tube equipped with a stir bar was added appropriate Lewis acid (20 mol%,0.02 mmol) and DCM (1.0 mL) in a glove box. The tube was sealed with a cap and then charged with 4-methylbenzaldehyde (1.5 equiv, 0.15 mmol) followed by dibenzyl 2,2-difluorocyclopropane-1,1-dicarboxylate (1.0 equiv, 0.1 mmol) by microinjector. The reaction mixture was stirred at room temperature for 12 h. After 12 h, the solvent was removed *in vacuo* by rotary evaporation. The 1-iodo-4-(trifluoromethyl)benzene (0.1 mmol, 27.2 mg) was added to the crude residue and the mixture was dissolved with $CDCl_3$. Then the reaction mixture was analyzed by ^{19}F NMR.

Table S2. Screening of Lewis Acids[a]



1a, 1.0 equiv **2a**, 1.5 equiv **3a**

Entry	LA (20 mol%)	Yield of 3a (%)	Conversion of 1a (%)	Entry	LA (20 mol%)	Yield of 3a (%)	Conversion of 1a (%)
1	$Sn(OTf)_2$	0	100	13	MgI_2	0	65
2	$Zn(OTf)_2$	11	12	14	TMSOTf	trace	33
3	$Yb(OTf)_2$	34	47	15	BF_3 OEt	0	40
4	$SnCl_2$	0	100	16	$Ni(OTf)_2$	0	2
5	$AlCl_3$	65	97	17	$Fe(OTf)_3$	14	60
6	$Cu(OTf)_2$	6	26	18	TfOH	0	15
7	$Bi(OTf)_2$	4	52	19	$In(OTf)_3$	62	100
8	$La(OTf)_3$	0	10	20	$Ga(OTf)_3$	12	35
9	$NbCl_5$	0	100	21	$MgCl_2$	0	8
10	$Eu(OTf)_3$	7	31	22	$Ti(OEt)_4$	0	7
11	$Sc(OTf)_3$	0	100	23	$TiCl_4$	0	100
12	$AgSbF_6$	12	99	24	PPh_3 AuCl	0	7

[a] Yields determined by ^{19}F NMR.

General Procedure for optimization of equivalent of Lewis acid

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $AlCl_3$ in appropriate equivalent and DCM (1.0 mL) in a glove box. The tube was sealed with a cap and then charged with 4-methylbenzaldehyde (1.5 equiv, 0.15 mmol) followed by dibenzyl 2,2-difluorocyclopropane-1,1-dicarboxylate (1.0 equiv, 0.1 mmol) by microinjector. The reaction mixture was stirred at this temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The 1-iodo-4-(trifluoromethyl)benzene (0.1 mmol, 27.2 mg) was added to the crude residue and the mixture was dissolved with $CDCl_3$. Then the reaction mixture was analyzed by ^{19}F NMR.

Table S3. Screening of Equivalent of Lewis Acid[a]

1a, 1.0 equiv **2a**, 1.5 equiv **3a**

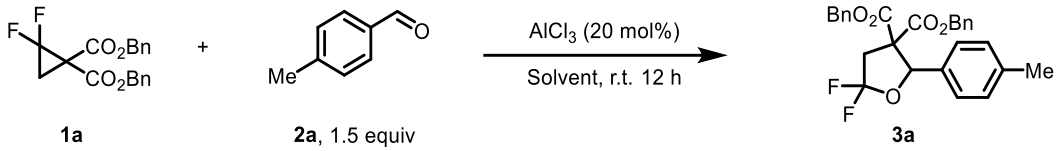
Entry	Equivalent of Catalyst (n)	Yield of 3a (%)	Conversion of 1a (%)
1	1	0	5
2	2	0	6
3	5	trace	9
4	10	56	71
5	20	65	97
6	50	33	100

[a] Yields determined by ^{19}F NMR.

General Procedure for optimization of solvent and temperature

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $AlCl_3$ (20 mol%, 0.02 mmol) appropriate Solvent (1.0 mL) in a glove box. The tube was sealed with a cap and the mixture was cooled to appropriate temperature. The tube was then charged with 4-methylbenzaldehyde (1.5 equiv, 0.15 mmol) followed by dibenzyl 2,2-difluorocyclopropane-1,1-dicarboxylate (1.0 equiv, 0.1 mmol) by microinjector. The reaction mixture was stirred at the indicated temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The 1-iodo-4-(trifluoromethyl)benzene (0.1 mmol, 27.2 mg) was added to the crude residue and the mixture was dissolved with $CDCl_3$. Then the reaction mixture was analyzed by ^{19}F NMR.

Table S4. Screening of Solvent and Temperature



1a **2a**, 1.5 equiv **3a**

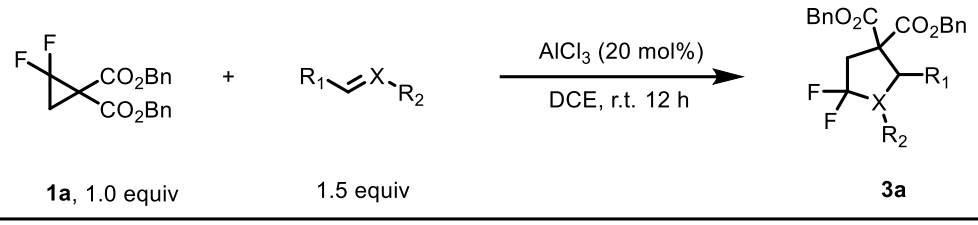
Entry	Solvent	T (ºC)	Yield of 3a (%)	Conversion of 1a (%)
1	DCM	25	65	97
2	DCM	0	77	98
3	DCM	-20	82	99
4	DCE	25	52	100
5	DCE	-20	95	100

[a]Yields determined by ^{19}F NMR.

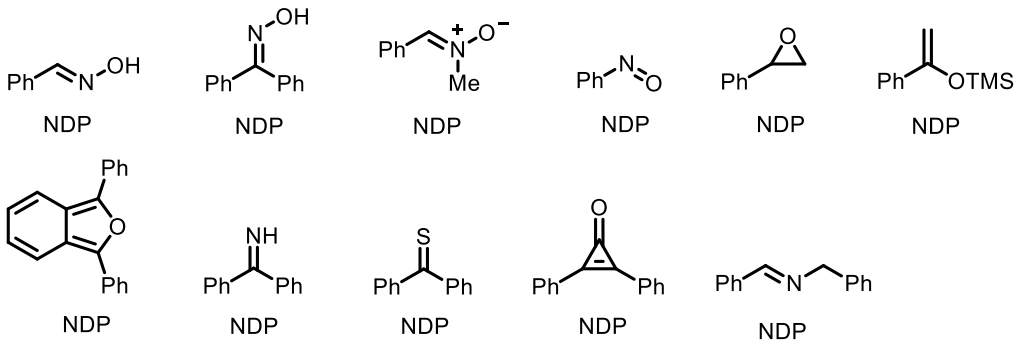
General Procedure for Screening of Other Unsaturated Systems

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $AlCl_3$ (20 mol%,0.02 mmol, 2.7 mg) and DCE (1.0 mL) in a glove box. Then, the unsaturated systems (1.5 equiv, 0.15 mmol) and dibenzyl 2,2-difluorocyclopropane-1,1-dicarboxylate (1.0 equiv, 0.1 mmol) was added. Then, the reaction mixture was stirred at room temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The 1-iodo-4-(trifluoromethyl)benzene (0.1 mmol, 27.2 mg) was added to the crude residue and the mixture was dissolved with $CDCl_3$. Then the reaction mixture was analyzed by ^{19}F NMR.

Table S5. Screening of Other Unsaturated Systems



1a, 1.0 equiv | 1.5 equiv | **3a**



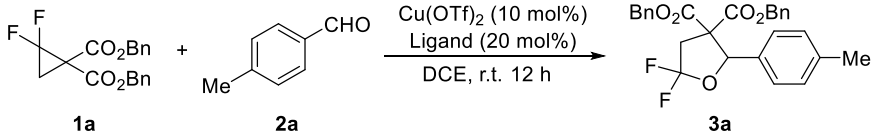
NDP | NDP | NDP | NDP | NDP | NDP

NDP | NDP | NDP | NDP | NDP

General Procedure for Enantioselective reaction

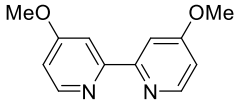
To an over dried 10 mL Schlenk tube equipped with a stir bar was added Lewis acid (10 mol%,0.01 mmol) and solvent (1.0 mL) in a glove box. The reaction mixture was stirred for 10 min. Then, dibenzyl 2,2-difluorocyclopropane-1,1-dicarboxylate **1a** (1.0 equiv, 0.1 mmol) and 4-methylbenzaldehyde 2a (1.5 equiv, 0.1 mmol) was added. The tube was sealed and stirred at room temperature for 12 h. Then, the solvent was removed *in vacuo* by rotary evaporation. The 1-iodo-4-(trifluoromethyl)benzene (0.1 mmol, 27.2 mg) was added to the crude residue and the mixture was dissolved with $CDCl_3$. Then the reaction mixture was analyzed by ^{19}F NMR.

Table S6 Screening of Ligand

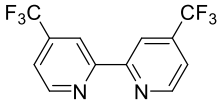


1a **2a** **3a**

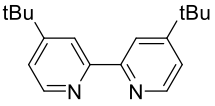
Entry	Ligand	Yield(%)	Conversion(%)
1	-	39	40
2	**L1**	0	7
3	**L2**	0	9
4	**L3**	0	3
5	**L4**	0	6
6	**L5**	0	0
7	**L6**	0	2
8	**L7**	0	2
9	**L8**	0	8
10	**L9**	0	9
11	**L10**	0	4
12	**L11**	0	0



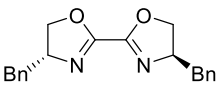
L1



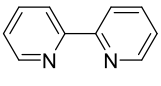
L2



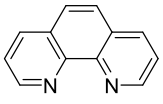
L3



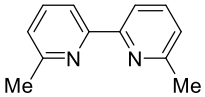
L4



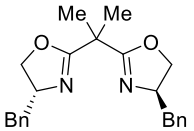
L5



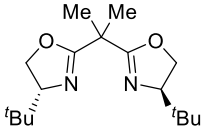
L6



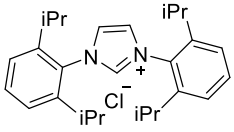
L7



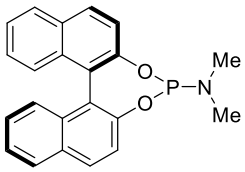
L8



L9

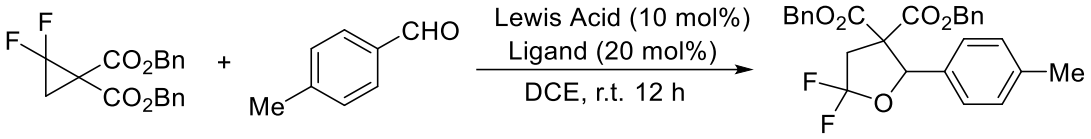


L10



L11

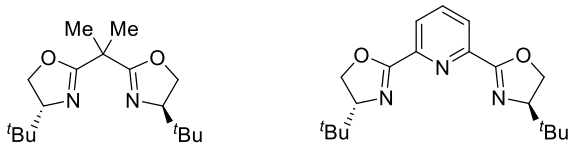
Table S6 Screening of the Combinations of Lewis acid and Ligand



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

Entry	Leiws Acid	Ligand	Yield of **3a**(%)	Conversion of **1a**(%)
1	$In(OTf)_3$	L9	0	4
2	$In(OTf)_3$	L12	0	7
3	MgI_2	L12	0	0
4	$Sc(OTf)_3$	L9	0	3
5	$Sc(OTf)_3$	-	56	99
6[a]	$Sc(OTf)_3$	L9	0	0
7	$Cu(ClO_4)_2$	L9	0	0

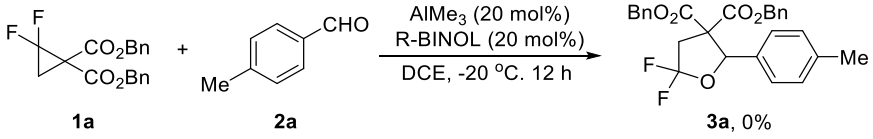
[a] DCM was used as solvent.



L9 **L12**

General Procedure for Enantioselective Reaction

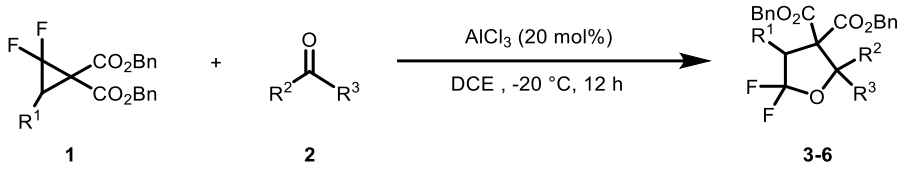
To an over dried 10 mL Schlenk tube equipped with a stir bar was added R-BINOL (20 mol%,0.01 mmol) and DCE (1.0 mL) in a glove box. The tube was sealed with a cap and the mixture was cooled to -20 ºC. Then, AlMe3 in hexane (20 mol%) was added with the help of micro-syringe. The reaction mixture was vigorously stirred for 30 min. Then, the reaction mixture was stirred at this temperature for 12 h. Then, the solvent was removed *in vacuo* by rotary evaporation. The 1-iodo-4-(trifluoromethyl)benzene (0.1 mmol, 27.2 mg) was added to the crude residue and the mixture was dissolved with $CDCl_3$. Then the reaction mixture was analyzed by ^{19}F NMR.



1a **2a** **3a**, 0%

4. General Procedures

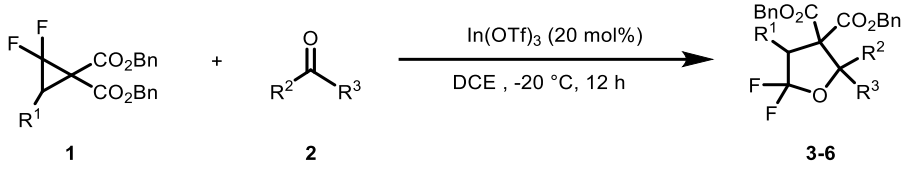
General Procedure (GP1)**: Preparation of gem-Difluorotetrahydrofuran Derivatives **3-6



1 **2** **3-6**

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $AlCl_3$ (20 mol%,0.04 mmol, 5.3 mg) and DCE (1.0 mL) in a glove box. The tube was sealed with a cap and the mixture was cooled to -20 °C. The tube was then charged with aldehydes or ketones (1.5 equiv, 0.3 mmol in 0.5 mL DCE) followed by *gem*-difluorocyclopropanes (1.0 equiv, 0.2 mmol in 0.5 mL DCE) by syringe. The reaction mixture was stirred at this temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The crude residue was further purified by column chromatography on silica gel (Petroleum ether/EtOAc = 50:1 to 5:1) to afford the desired product.

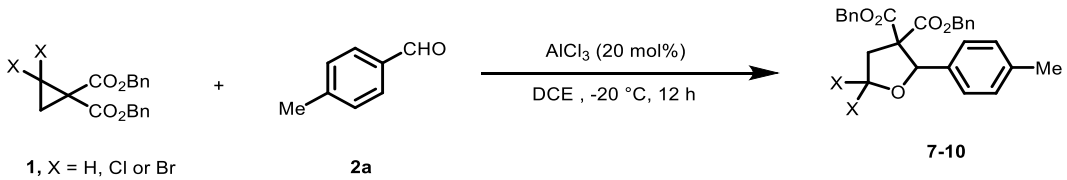
General Procedure (GP2)**: Preparation of gem-Difluorotetrahydrofuran Derivatives **3-6



1 **2** **3-6**

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $In(OTf)_3$ (20 mol%,0.04 mmol, 22.5 mg) and DCE (1.0 mL) in a glove box. The tube was sealed with a cap and the mixture was cooled to -20 °C. The tube was then charged with aldehydes or ketones (1.5 equiv, 0.3 mmol in 0.5 mL DCE) followed by *gem*-difluorocyclopropanes (1.0 equiv, 0.2 mmol in 0.5 mL DCE) by syringe. The reaction mixture was stirred at this temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The crude residue was further purified by column chromatography on silica gel (Petroleum ether/EtOAc = 50:1 to 5:1) to afford the desired product.

General Procedure (GP3)**: Preparation of Tetrahydrofuran Derivatives **7-10



1, X = H, Cl or Br **2a** **7-10**

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $AlCl_3$ (20 mol%,0.04 mmol, 5.3 mg) and DCE (1.0 mL) in a glove box. The tube was sealed with a cap and the mixture was cooled to -20 °C. The tube was then charged with *p*-Tolualdehyde (1.5 equiv, 0.3 mmol in 0.5 mL DCE) followed by cyclopropanes (1.0 equiv, 0.2 mmol in 0.5 mL DCE) by syringe. The reaction mixture was stirred at this temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The crude residue was further purified by column chromatography on silica gel (Petroleum ether/EtOAc = 50:1) to afford the desired product.

General Procedure (GP4)**: Preparation of gem-Difluorotetrahydrofuran Derivatives **11

1j **2a** **11,** 72 %, d.r. > 100:1

To an over dried 10 mL Schlenk tube equipped with a stir bar was added $AlCl_3$ (20 mol%,0.04 mmol, 5.3 mg) and DCE (1.0 mL) in a glove box. The tube was sealed with a cap and the mixture was cooled to -20 ºC. The tube was then charged with *p*-Tolualdehyde (1.5 equiv, 0.3 mmol in 0.5 mL DCE) followed by dibenzyl 2,2-difluoro-3-phenylcyclopropane-1,1-dicarboxylate (**1j**, 1.0 equiv, 0.2 mmol in 0.5 mL DCE). The reaction mixture was stirred at this temperature for 12 h. After this time, the solvent was removed *in vacuo* by rotary evaporation. The crude residue was further purified by column chromatography on silica gel (Petroleum ether/EtOAc = 20:1) to afford the desired product **5ja**.

5. DFT Study

The DFT calculations were performed with the Gaussian 09 program.[7] Geometries of the minimum energy structures and the transition states were optimized at the B3-LYP level of theory with the 6-31G(d, p) basis set in MeCN implicitly.[8] Harmonic vibrational frequency calculations were performed for all stationary points to confirm whether they are local minima or transition structures, and to derive the thermochemical corrections for the enthalpies and free energies. Solvent effects in CH_2Cl_2 were considered implicitly using the SMD polarizable continuum model.[9] The single-point energies were obtained using the M06-2X functional with the 6-311G (d, p) basis set with more accurate energy information.[10]

Scheme S2. DFT Study: Gibbs Free Energy (kcal/mol) Profile for [3+2] Cycloaddition of *gem*-Difluorocyclopropane 1b and Aldehyde 2a

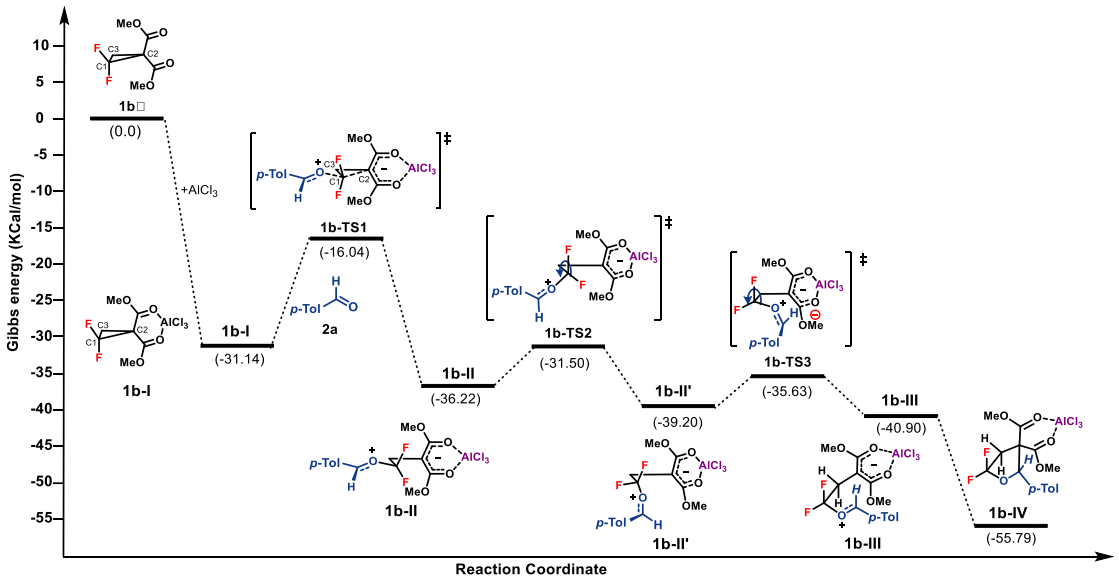
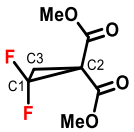


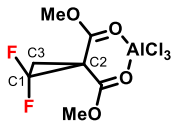
Table S5. The calculated Mulliken charge distribution of the *gem*-difluorocyclopropane 1b



1b

Atom	value
C1	0.610
C2	-0.205
C3	-0.271

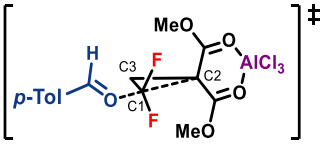
Table S6. The calculated Mulliken charge distribution of the intermediate 1b-I



1b-I

Atom	value
C1	0.649
C2	-0.270
C3	-0.240

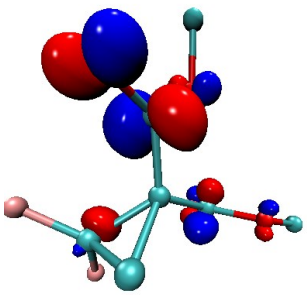
Table S7. The Calculated Mulliken Charge Distribution of the 1b-TS1



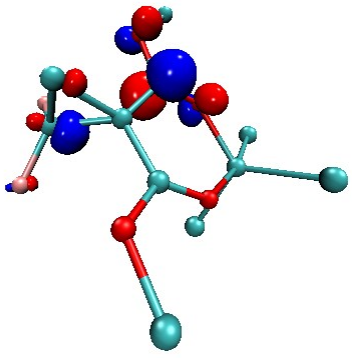
1b-TS1

Atom	value
C1	0.712
C2	-0.285
C3	-0.214

Scheme S3. LUMO Orbital of 1b and 1b-I with the Isovalue of 0.1 Atomic Units



1b



1b-I

Table S8 B3-LYP Calculated Energies, Enthalpies, and Free Energies

Geometry	$E_{(elec\text{-}B3LYP)}$[a]	$G_{(Corr\text{-}B3LYP)}$[b]	$H_{(Corr\text{-}B3LYP)}$[c]	$E_{(solv\text{-}M06)}$[d]	G from shermo	IF[e]
1b	-772.12403131	0.10786	0.16549	-772.05448621	-771.94955630	-
2a	-384.91694252	0.10339	0.14646	-384.83179625	-384.73107380	-

$AlCl_3$	-1623.24196790	-0.02493	0.01095	-1623.22504785	-1623.25006630	-
1b-I	-2395.42490186	0.10771	0.17902	-2395.35088227	-2395.24624210	-
1b-TS1	-2780.33660540	0.22977	0.32658	-2780.17426519	-2779.950234	-299.74
1b-II	-2780.37261839	0.23677	0.32940	-2780.21334222	-2779.98238620	-
1b-TS2	-2780.36676157	0.23807	0.32837	-2780.20712432	-2779.97486630	-21.43
1b-II'	-2780.37418279	0.23707	0.32950	-2780.21839224	-2779.98713890	-
1b-TS3	-2780.36994498	0.23915	0.32831	-2780.21478403	-2779.98145020	-17.34
1b-III	-2780.37691501	0.23811	0.32931	-2780.22214567	-2779.98985640	-
1b-IV	-2780.38934716	0.24188	0.33027	-2780.24961471	-2780.01358710	-

Relative energies (kcal/mol) for the studied complexes of at B3LYP/6-311G(d,p) level of theory. [a]The electronic energy calculated by B3-LYP in CH_2Cl_2. [b]The thermal correction to Gibbs free energy calculated by B3-LYP in CH_2Cl_2 . [c]The thermal correction to enthalpy calculated by B3-LYP in CH_2Cl_2. [d]The electronic energy calculated by M06 in CH_2Cl_2. [e]The B3-LYP calculated imaginary frequencies for the transition states.

B3-LYP Geometries for All the Optimized Species and Transition State

1b

0 1

C	-0.47438100	-1.37601200	1.35954400
C	-0.16565100	-0.33182500	0.25343500
C	-0.85421600	-1.64147300	-0.03259300
H	0.37089500	-1.92026600	1.76761400
H	-1.26194500	-1.09096200	2.04937900
F	-0.17846100	-2.57130300	-0.74323900
F	-2.14885300	-1.64134300	-0.41331600
C	-1.02251200	0.90714900	0.27249800
O	-2.07336300	1.00253900	0.87094800
O	-0.47275200	1.88057300	-0.46539600
C	1.25535500	-0.15254400	-0.23628900
O	1.62433700	-0.35585400	-1.37206700
O	2.04471700	0.27721500	0.75843400
C	-1.20903900	3.12362900	-0.52793700
H	-1.34134300	3.53864100	0.47356500
H	-0.59991400	3.78870900	-1.13896500
H	-2.18360900	2.96412900	-0.99456300
C	3.42098600	0.53573800	0.40020200
H	3.90443000	0.86683400	1.31875800
H	3.89584800	-0.37409600	0.02620500

H	3.47471200	1.31707200	-0.36151100

2a

0 1

C	1.75586200	-0.06378600	-0.00770800
C	1.16103300	1.20619300	-0.00625700
C	-0.22550000	1.34424900	-0.00164900
C	-1.04816000	0.20980700	0.00020300
C	-0.46077500	-1.06737400	-0.00302000
C	0.92065400	-1.19787100	-0.00778200
H	1.79192300	2.09080700	-0.00899200
H	-0.67622000	2.33387000	-0.00158000
H	-1.10475300	-1.94152700	-0.00395000
H	1.36928500	-2.18793200	-0.01255300
C	-2.51232700	0.37121200	0.00358000
O	-3.31708500	-0.54872100	0.00483300
H	-2.86082800	1.42553400	0.00548900
C	3.25466200	-0.22217800	0.00938100
H	3.76154000	0.71898400	-0.21986500
H	3.59984300	-0.55544100	0.99620400
H	3.58320400	-0.97604500	-0.71390200

1b-I

0 1

C	3.16144100	0.34247800	-0.83596500
C	1.67093900	0.15909800	-0.40334500
C	2.86814100	0.34911800	0.58481300
H	3.62372900	-0.54475900	-1.25351300
H	3.39096300	1.29010700	-1.30991900
F	3.17655800	-0.68885800	1.36840600
F	2.89553900	1.48528600	1.29132100
C	0.72889500	1.29529200	-0.53957900
O	-0.50606200	1.20083200	-0.37587800
O	1.28328600	2.43313300	-0.82948400
C	1.04593400	-1.19125400	-0.47893800
O	-0.16991200	-1.38261100	-0.36983500
O	1.90024100	-2.16381500	-0.66749900
C	0.43294300	3.62343800	-0.90761400
H	-0.07519400	3.76912600	0.04562100
H	1.12344900	4.43721200	-1.11612400
H	-0.28695500	3.49946600	-1.71677400
C	1.37979000	-3.52721000	-0.70684600
H	2.25905900	-4.15345900	-0.84101900
H	0.87600000	-3.75472500	0.23305300

H	0.69284300	-3.63190300	-1.54725300
Al	-1.77094800	-0.16248800	0.11619400
Cl	-1.64216100	-1.08010000	2.10315200
Cl	-3.23842500	1.45446800	0.58875700
Cl	-2.82643500	-1.13746400	-1.53165800

1b-TS1

0 1

C	0.43252300	0.28462900	-1.25719400
C	-1.01202200	0.13407800	-0.78797300
C	0.77353900	0.21742500	0.14088500
H	0.79770300	-0.56185500	-1.83316200
H	0.65603400	1.24603500	-1.71329200
F	0.98418200	-0.89464400	0.77247700
F	0.81895000	1.25030300	0.91723100
C	-1.82275500	1.28248500	-0.53121500
O	-3.04233400	1.25148600	-0.19315200
O	-1.21849700	2.44566300	-0.66653500
C	-1.63789600	-1.16260800	-0.71359000
O	-2.83107400	-1.35241100	-0.39712000
O	-0.84443900	-2.17946900	-1.01332300
C	-1.98036400	3.65374900	-0.38877400
H	-2.32294900	3.64915600	0.64668800
H	-1.27890600	4.46795700	-0.56091400
H	-2.83008100	3.72391800	-1.06866600
C	-1.40765600	-3.51603800	-0.93082000
H	-0.58166900	-4.18255500	-1.17311500
H	-1.77547000	-3.70656900	0.07838400
H	-2.21686200	-3.62573800	-1.65430700
Al	-4.29324200	-0.11416300	0.21347700
Cl	-4.13957300	-1.10551600	2.18104500
Cl	-5.74925000	1.50203100	0.82488500
Cl	-5.52322000	-0.98639400	-1.39781900
O	3.17189500	0.48611800	-0.21520300
C	3.97393500	-0.25026500	0.35978300
C	5.42677100	-0.13982200	0.24519600
H	3.60960200	-1.06147200	1.01749900
C	6.02252900	0.84769500	-0.56255700
C	6.24172700	-1.03398300	0.95621100
C	7.40327700	0.92987500	-0.65039600
H	5.38765100	1.53830000	-1.10861600
C	7.62777600	-0.94372500	0.86256300
H	5.78453800	-1.79610800	1.58219900
C	8.23005200	0.03613000	0.05970000

H	7.86014100	1.69382500	-1.27392300
H	8.25321900	-1.63776700	1.41662900
C	9.72850600	0.13579100	-0.05430700
H	10.05882400	-0.10218400	-1.07281200
H	10.07273000	1.15332900	0.16208700
H	10.23011600	-0.55072200	0.63247200

1b-II

0 1

C	-0.68678600	-0.24749600	-0.66135100
C	0.80222100	-0.11112800	-0.49141000
C	-1.41175600	-0.34085100	0.66827200
H	-1.10233700	0.60985900	-1.19698500
H	-0.93821000	-1.15099400	-1.22106900
F	-1.28033000	0.76876000	1.42285600
F	-1.03466100	-1.39058500	1.40749200
C	1.62950400	-1.24060700	-0.42400600
O	2.90212800	-1.23729700	-0.27044400
O	1.02689600	-2.42594900	-0.54574800
C	1.41955700	1.15814200	-0.37465900
O	2.65660100	1.36435300	-0.22595500
O	0.59441900	2.21040200	-0.44965800
C	1.85130200	-3.61153600	-0.50354500
H	2.33967100	-3.70645000	0.46844500
H	1.16116300	-4.43992900	-0.66185800
H	2.60489800	-3.58919900	-1.29287800
C	1.18707700	3.52368000	-0.35488300
H	0.35100300	4.21909800	-0.42848000
H	1.69890700	3.64826000	0.60143500
H	1.89004000	3.69074300	-1.17371800
Al	4.15962300	0.12322800	-0.02448600
Cl	4.49915700	0.99714600	1.99571800
Cl	5.74561000	-1.51363100	0.18196700
Cl	5.10315300	1.10759100	-1.78443300
O	-2.84022500	-0.57449800	0.46837800
C	-3.65877200	0.42930900	0.37049500
C	-5.02287400	0.22601700	0.13209300
H	-3.25476700	1.43267600	0.49060100
C	-5.59015400	-1.07133400	-0.02404900
C	-5.85647000	1.37498800	0.06050500
C	-6.94249200	-1.19571800	-0.24313800
H	-4.95454600	-1.94835800	0.03109800
C	-7.21251600	1.22718100	-0.15766800
H	-5.41913900	2.36159800	0.18005700

C	-7.77865200	-0.05361500	-0.31153800
H	-7.38330300	-2.18027600	-0.36387900
H	-7.85200900	2.10179900	-0.21121200
C	-9.24943200	-0.22374900	-0.53603700
H	-9.43478900	-0.82954700	-1.43022100
H	-9.69869300	-0.76450800	0.30626000
H	-9.75982100	0.73508000	-0.64475100

1b-TS2

0 1

C	-0.51827300	1.37741100	-0.66786000
C	0.83527200	0.76233800	-0.45070700
C	-1.35025000	1.56253200	0.61494500
H	-0.41046000	2.37300500	-1.10025500
H	-1.11167900	0.77703800	-1.36194900
F	-1.74143000	2.84398100	0.79014800
F	-0.73965800	1.16592500	1.73409000
C	0.96799400	-0.61467800	-0.23936400
O	2.05989500	-1.25839500	-0.04983200
O	-0.17271900	-1.31343600	-0.23210400
C	2.01284500	1.54638800	-0.39960700
O	3.18333100	1.09971700	-0.23747900
O	1.84028100	2.86614400	-0.54186100
C	-0.08761100	-2.74374400	-0.04405200
H	0.35376400	-2.97942800	0.92619300
H	-1.11832600	-3.09525900	-0.08644300
H	0.50266200	-3.20359100	-0.83897100
C	3.02288100	3.69465000	-0.52702200
H	2.65553400	4.71489900	-0.63686700
H	3.55961100	3.58477100	0.41721700
H	3.68330200	3.43871800	-1.35830800
Al	3.85306500	-0.72765200	-0.01898900
Cl	4.83133800	-0.03879200	1.85932800
Cl	4.40613900	-2.93068400	0.27037000
Cl	4.93143000	-0.48968800	-1.95110100
O	-2.55727100	0.74072100	0.59745000
C	-3.66246500	1.19979000	0.09417100
C	-4.79947800	0.38774500	0.00191500
H	-3.68445100	2.23257100	-0.24929100
C	-4.80931700	-0.97116200	0.42843600
C	-5.97763800	0.96445500	-0.54378700
C	-5.96362800	-1.70979900	0.30668600
H	-3.90946700	-1.41194100	0.84312200
C	-7.12652900	0.20571000	-0.65579100

H	-5.96430800	2.00031500	-0.86842900
C	-7.14201800	-1.13826500	-0.23393000
H	-5.97992700	-2.74643300	0.62817400
H	-8.02790000	0.64315600	-1.07207300
C	-8.38565100	-1.96497600	-0.34302400
H	-8.19389500	-2.87166000	-0.92868500
H	-8.70748900	-2.29739600	0.65149300
H	-9.20337600	-1.41103900	-0.80778600

1b-II'

0 1

C	0.01503900	2.56978300	-1.04452400
C	0.88704400	1.38974700	-0.70602300
C	-0.98879500	2.92275200	0.03451200
H	0.61160400	3.47409400	-1.19277700
H	-0.54627400	2.39255600	-1.96462500
F	-1.81270900	3.92215200	-0.35085800
F	-0.42387500	3.27092800	1.19551200
C	0.53747800	0.09443500	-1.09956500
O	1.20692900	-0.97600200	-0.87996300
O	-0.61243000	-0.03139300	-1.78009200
C	2.09896300	1.54721300	0.01321000
O	2.88879200	0.61637100	0.33612400
O	2.40500000	2.80345600	0.35224000
C	-0.97753800	-1.35037700	-2.24495600
H	-1.11630600	-2.03224200	-1.40409300
H	-1.91633100	-1.21168500	-2.78063300
H	-0.21558600	-1.74676000	-2.91849600
C	3.64484900	3.01922600	1.06013000
H	3.67652900	4.09095900	1.25529300
H	3.65531400	2.46260800	1.99914300
H	4.49632500	2.72076100	0.44495400
Al	2.77817600	-1.32321500	0.07292900
Cl	2.66069500	-1.54881500	2.28452600
Cl	2.45526800	-3.54204300	-0.39210300
Cl	4.77746600	-1.20977100	-0.89611100
O	-1.82726700	1.79038200	0.41529800
C	-2.86786800	1.48479100	-0.29896200
C	-3.66656400	0.38348900	0.02943700
H	-3.11290800	2.11850400	-1.15013400
C	-3.37585900	-0.47178400	1.13095600
C	-4.80015900	0.12304500	-0.78743600
C	-4.19705100	-1.54497500	1.38905900
H	-2.51010100	-0.27456400	1.75346000

C	-5.61232800	-0.95916400	-0.50973600
H	-5.01860400	0.77982800	-1.62402300
C	-5.32687500	-1.81054600	0.57617500
H	-3.98020300	-2.20298700	2.22454100
H	-6.47873300	-1.16101300	-1.13070300
C	-6.19831400	-2.98962300	0.87991100
H	-5.61395300	-3.91639200	0.83056900
H	-6.58896400	-2.92201700	1.90218400
H	-7.03745900	-3.06747300	0.18609700

1b-TS3

0 1

C	0.22597700	2.98295500	0.89234200
C	-0.58267400	1.75313600	0.57345800
C	1.55642400	3.14907900	0.14214700
H	-0.32778800	3.90250100	0.67786000
H	0.47160700	2.99331600	1.95497900
F	2.47900600	3.75647100	0.92436900
F	1.45043800	3.86431200	-0.98438600
C	-0.75833000	0.72466500	1.51070000
O	-1.45401200	-0.33796100	1.34397900
O	-0.13860500	0.87012000	2.69001400
C	-1.27385100	1.62477400	-0.66179400
O	-1.99573900	0.65142300	-1.00924900
O	-1.11697700	2.65251300	-1.49996500
C	-0.36240900	-0.13995900	3.70078300
H	-0.03059900	-1.11946000	3.35209900
H	0.23178800	0.18263200	4.55544900
H	-1.41911100	-0.18315600	3.97099400
C	-1.79218100	2.58406100	-2.77578400
H	-1.49605600	3.49140700	-3.30128200
H	-1.47346200	1.70078700	-3.33248800
H	-2.87484100	2.56205000	-2.63574800
Al	-2.38333500	-1.05278000	-0.11447300
Cl	-1.26224400	-2.05775900	-1.75755900
Cl	-2.69419700	-2.95025700	1.12161800
Cl	-4.54211300	-0.60686600	-0.38308100
O	2.15052700	1.91591400	-0.32521600
C	2.39242600	0.96094900	0.52840800
C	2.85108300	-0.28769300	0.09985800
H	2.25643900	1.16388000	1.59012900
C	3.03943200	-0.60832700	-1.27589200
C	3.10874400	-1.27022800	1.09571800
C	3.46309500	-1.86989200	-1.62351600

H	2.84324600	0.13940500	-2.03622400
C	3.53155200	-2.53048600	0.72463800
H	2.96859800	-1.01853700	2.14260000
C	3.70820200	-2.85564600	-0.63549600
H	3.60421300	-2.12436000	-2.66913900
H	3.72393300	-3.28405100	1.48082800
C	4.12559600	-4.23319000	-1.04514000
H	3.26818000	-4.76125100	-1.48319000
H	4.90084800	-4.19629900	-1.81746600
H	4.48672200	-4.81802700	-0.19681400

1b-III

0 1

C	0.02501700	2.86657300	0.98905600
C	0.69969100	1.56218600	0.66470800
C	-1.11194600	3.23245900	0.04791000
H	-0.39996600	2.84683900	1.99414300
H	0.72777600	3.70305800	0.93637900
F	-0.70271600	3.42912300	-1.22329300
F	-1.76628700	4.33255500	0.44815100
C	1.77109100	1.50274900	-0.24724500
O	2.45232700	0.46098200	-0.54295200
O	2.09612300	2.64625400	-0.84697000
C	0.38169400	0.36845200	1.36732600
O	0.95110800	-0.74695300	1.21776500
O	-0.61253000	0.47463600	2.25726300
C	3.23854300	2.64685400	-1.73434800
H	3.08963600	1.94483100	-2.55652400
H	3.29954600	3.66709200	-2.11176900
H	4.14772000	2.38885600	-1.18764800
C	-0.94044800	-0.70059500	3.03186400
H	-1.77277500	-0.39837500	3.66691700
H	-1.23809600	-1.52385500	2.38038100
H	-0.08950900	-1.00491600	3.64452400
Al	2.41943400	-1.31868200	0.04503800
Cl	1.00013700	-2.76593200	-0.87939400
Cl	4.12909600	-1.73145000	-1.40856300
Cl	3.52670200	-1.93158200	1.87018300
O	-2.12986600	2.20945900	0.03267400
C	-2.00524000	1.19401000	-0.77601000
C	-2.86173800	0.09058900	-0.66726400
H	-1.25429300	1.24875600	-1.56000900
C	-3.84197600	-0.02151100	0.35961300
C	-2.72499500	-0.94613700	-1.62789700

C	-4.65288600	-1.13272200	0.40185000
H	-3.94192600	0.76687300	1.09745100
C	-3.55163800	-2.05197700	-1.56932300
H	-1.96944800	-0.86049800	-2.40277100
C	-4.52598500	-2.16603400	-0.55921500
H	-5.40340500	-1.22588200	1.18079400
H	-3.44956500	-2.84437400	-2.30335500
C	-5.42839000	-3.35973400	-0.49032100
H	-5.28704500	-3.89129500	0.45862600
H	-6.47865600	-3.04669900	-0.52046000
H	-5.24454400	-4.05624600	-1.31020300

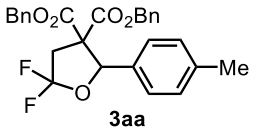
1b-IV

0 1

C	1.20818200	0.91087500	0.87707800
O	1.83672500	2.19227500	1.00930300
C	1.79729500	2.94405300	-0.13978700
C	0.95542600	2.21674300	-1.18619100
C	0.22619900	1.10807500	-0.39943500
H	0.59864000	0.76269300	1.77173800
H	0.27825800	2.90117600	-1.69556400
H	1.62661100	1.77260200	-1.91879200
F	3.07377000	3.15968100	-0.59443300
F	1.33229200	4.18427200	0.16968000
C	0.03573000	-0.18910100	-1.17822000
O	-0.89377000	-0.97872700	-0.98919800
O	0.96860300	-0.41019200	-2.06422900
C	-1.11316300	1.57370300	0.15454900
O	-2.09109500	0.83873300	0.39401200
O	-1.14312500	2.83697200	0.44071400
C	0.90839400	-1.65755300	-2.82184100
H	-0.04317300	-1.72159000	-3.34990600
H	1.74058300	-1.59694100	-3.51985300
H	1.02965900	-2.50007500	-2.14014700
C	-2.34819200	3.39316800	1.06271700
H	-2.10621200	4.43960900	1.23248000
H	-3.18786200	3.28611800	0.37599700
H	-2.54387300	2.87261600	2.00037800
C	2.20272900	-0.22388300	0.77712100
C	1.84745300	-1.47034500	1.30602900
C	3.46207600	-0.07326700	0.18081000
C	2.72294600	-2.55235900	1.21741200
H	0.88321800	-1.59975100	1.78987600
C	4.33436400	-1.15671300	0.10636000

H	3.76941200	0.88929300	-0.21191100
C	3.98062500	-2.41607400	0.61530100
H	2.42628300	-3.51278300	1.62994800
H	5.30907400	-1.02269700	-0.35587300
C	4.94018800	-3.57748900	0.54370600
H	5.69245100	-3.51728300	1.34040800
H	4.41937000	-4.53248300	0.65641700
H	5.48160600	-3.59052400	-0.40761600
Al	-2.68624400	-0.96006900	0.04189400
Cl	-1.91121700	-2.72232500	1.08642800
Cl	-3.66574300	-1.17402000	-1.89930700
Cl	-4.45172600	-0.55990000	1.34594400

6. Compound Data of Products



3aa

dibenzyl 5,5-difluoro-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate (3aa): Follow the general procedure (***GP1)***, **3aa** was obtained as a colorless oil (85.7 mg, 0.18 mmol, yield: 92%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.19;

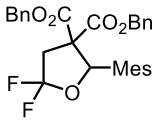
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 10H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 6.9 Hz, 2H), 6.11 (d, *J* = 3.6 Hz, 1H), 5.18 (s, 2H), 4.71 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.44 (ddd, *J* = 16.8, 14.9, 7.6 Hz, 1H), 2.92 (ddd, *J* = 14.9, 8.5, 3.0 Hz, 1H), 2.30 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2 , 166.1 , 138.8 , 134.5 , 134.1 , 131.8 (d, *J* = 1.5 Hz), 130.2 (dd, *J* = 256.7, 254.0 Hz), 128.9 , 128.6 , 128.6 , 128.4 , 128.2 , 126.4 , 84.4 , 68.3 , 68.0 , 63.6 (d, *J* = 3.0 Hz), 40.3 (dd, *J* = 34.2, 30.4 Hz), 21.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.77 – -59.24 (m, 1F), -71.73 – -72.21 (m, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{27}H_{24}F_2NaO_5^+$ $[M+Na]^+$: 489.1489, found: 489.1495.

IR (film) ν_{max} 1741, 1500, 1436, 1379, 1263, 1090, 971, 747, 697 cm^{-1}.



3ab

dibenzyl 5,5-difluoro-2-mesityldihydrofuran-3,3(2H)-dicarboxylate (3ab): Follow the general procedure (***GP1)***, **3ab** was obtained as a colorless oil (74.1 mg, 0.15 mmol, yield: 75%) after flash chromatography (Petroleum ether/EtOAc = 20:1, CAM solution, UV): TLC Rf = 0.25;

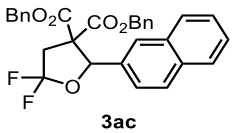
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 7.26 – 7.21 (m, 4H), 6.87 – 6.82 (m, 2H), 6.63 (s, 1H), 5.21 (s, 2H), 4.64 (d, *J* = 11.9 Hz, 1H), 4.19 (d, *J* = 12.0 Hz, 1H), 3.65 (ddd, *J* = 24.5, 14.9, 6.1 Hz, 1H), 2.94 (ddd, *J* = 14.8, 6.9, 1.0 Hz, 1H), 2.34 (s, 3H), 2.22 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0 , 166.5 , 138.1 , 134.6 , 133.9 , 131.4 , 129.5 (dd, *J* = 259.8, 251.0 Hz), 129.4 , 128.7 , 128.6 , 128.4 , 128.4 , 128.4 , 128.3 , 128.0 , 81.7 , 68.4 , 68.1 , 62.6 (d, *J* = 4.1 Hz), 41.5 (dd, *J* = 35.1, 29.6 Hz), 20.8 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -56.08 – -56.59 (m, 1F), -80.28 (dd, *J* = 145.5, 5.1 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{29}H_{28}F_2NaO_5^+$ $[M+Na]^+$: 517.1803, found: 517.1799.

IR (film) ν_{max} 2979, 1749, 1725, 1457, 1378, 1324, 1276, 1220, 1195, 1116, 1049, 987, 910, 862, 753, 699 cm^{-1}.



3ac

dibenzyl 5,5-difluoro-2-(naphthalen-2-yl)dihydrofuran-3,3(2H)-dicarboxylate (3ac): Follow the general procedure (***GP1)***, **3ac** was obtained as a colorless oil (85.3 mg, 0.17 mmol, yield: 85%) after flash chromatography (Petroleum ether/EtOAc = 20:1, CAM solution, UV): TLC Rf = 0.25;

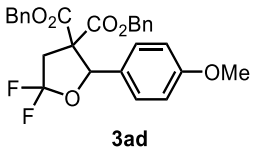
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.73 (t, *J* = 8.0 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.42 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.22 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.23 – 7.12 (m, 1H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.30 (d, *J* = 3.4 Hz, 1H), 5.21 (s, 2H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 12.1 Hz, 1H), 3.53 (ddd, *J* = 16.4, 15.1, 7.7 Hz, 1H), 2.98 (ddd, *J* = 15.0, 8.7, 3.6 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2 , 166.2 , 134.4 , 133.7 , 133.4 , 132.7 , 132.1, 130.4 (dd, *J* = 258.6, 255.5 Hz), 128.7 , 128.7 , 128.4 , 128.3 , 128.3 , 128.2 , 128.1 , 127.7 , 126.6 , 126.4 , 126.2 , 123.7 , 84.5 , 68.4 , 68.1 , 63.7 (d, *J* = 3.0 Hz), 40.51 (dd, *J* = 34.2, 30.4 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.19 (ddd, *J* = 143.8, 16.3, 8.8 Hz, 1F), -71.58 – -72.08 (m, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{30}H_{24}F_2NaO_5^+$ $[M+Na]^+$: 525.1489, found: 525.1498.

IR (film) ν_{max} 3036, 1735, 1456, 1337, 1271, 1249, 1199, 1156, 1114, 1055, 912, 743, 700 cm^{-1}.



3ad

dibenzyl 5,5-difluoro-2-(4-methoxyphenyl)dihydrofuran-3,3(2H)-dicarboxylate (3ad): Follow the general procedure (***GP1)***, **3ad** was obtained as a colorless oil (38.6 mg, 0.08 mmol, yield: 40%) after flash chromatography (Petroleum ether/EtOAc = 20:1, CAM solution, UV): TLC Rf = 0.25;

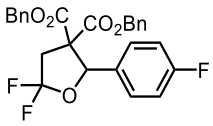
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 10H), 6.95 – 6.90 (m, 2H), 6.79 – 6.73 (m, 2H), 6.09 (d, *J* = 3.5 Hz, 1H), 5.18 (d, *J* = 1.0 Hz, 2H), 4.72 (d, *J* = 12.2 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.76 (s, 3H), 3.43 (ddd, *J* = 16.8, 15.0, 7.6 Hz, 1H), 2.91 (ddd, *J* = 14.8, 8.6, 3.2 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2 , 166.2 , 160.0 , 134.5 , 134.1 , 130.1 (dd, *J* = 256.8, 253.9 Hz), 128.7 , 128.6 , 128.4 , 128.2 , 127.9 , 126.8 , 126.8 , 113.6 , 84.3 , 68.3 , 68.0 , 63.6 (d, *J* = 2.8 Hz), 55.2, 40.3 (dd, *J* = 34.3, 30.4 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.19 (ddd, *J* = 144.4, 17.0, 8.5 Hz, 1F), -71.67 – -72.12 (m,1F) ppm.

HRMS (ESI, m/z): calculated for $C_{27}H_{24}F_2NaO_6^+$ $[M+Na]^+$: 505.1439, found: 505.1434.

IR (film) ν_{max} 1739, 1615, 1516, 1456, 1337, 1255, 1159, 1109, 1052, 1030, 944, 910, 748, 697 cm^{-1}.



3ae

dibenzyl 5,5-difluoro-2-(4-fluorophenyl)dihydrofuran-3,3(2H)-dicarboxylate (3ae): Follow the general procedure (***GP1)***, **3ae** was obtained as a white solid (57.3 mg, 0.12 mmol, yield: 61%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.20;

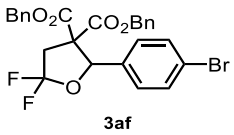
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 10H), 6.95 – 6.85 (m, 4H), 6.09 (d, *J* = 3.4 Hz, 1H), 5.19 (s, 2H), 4.70 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 3.48 – 3.37 (m, 1H), 2.93 (ddd, *J* = 14.9, 8.8, 3.8 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1 , 166.1 , 162.9 (d, *J* = 248.0 Hz), 134.4 , 133.9 , 130.5 , 130.0 (dd, *J* = 257.3, 254.4 Hz), 128.8 , 128.7 , 128.6 , 128.5 , 128.4 , 128.3 , 115.3 , 83.7 , 68.4 , 68.1 , 63.5 , 40.4 (dd, *J* = 34.3, 30.3 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.51 (ddd, *J* = 143.2, 16.2, 8.9 Hz, 1F), -71.73 (ddt, *J* = 143.2, 7.1, 3.6 Hz, 1F), -112.09 (ddd, *J* = 13.5, 8.8, 5.6 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{26}H_{21}F_3NaO_5^+$ $[M+Na]^+$: 493.1239, found: 493.1237.

IR (film) ν_{max} 1737, 1609, 1513, 1456, 1384, 1337, 1272, 1158, 1115, 1055, 948, 913, 851, 747, 700 cm^{-1}.



3af

dibenzyl 2-(4-bromophenyl)-5,5-difluorodihydrofuran-3,3(2H)-dicarboxylate (3af): Follow the general procedure (***GP1)***, **3af** was obtained as a white solid (71.0 mg, 0.13 mmol, yield: 67%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.20;

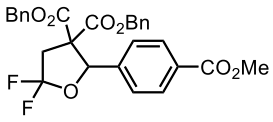
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 10H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 6.8 Hz, 2H), 6.05 (d, *J* = 3.4 Hz, 1H), 5.19 (s, 2H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 3.42 (td, *J* = 15.4, 7.7 Hz, 1H), 2.92 (ddd, *J* = 15.0, 8.9, 4.0 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0 , 166.0 , 134.4 , 133.8 , 133.7 , 131.4 , 130.0 (dd, *J* = 257.4, 255.0 Hz), 128.8 , 128.7 , 128.5 , 128.5 , 128.2 , 123.2 , 83.6 , 68.4 , 68.2 , 63.4 (d, *J* = 2.7 Hz), 40.5 (dd, *J* = 34.4, 30.3 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.61 (ddd, *J* = 143.0, 14.9, 8.7 Hz), -71.66 (dd, *J* = 142.0, 9.6 Hz) ppm.

HRMS (ESI, m/z): calculated for $C_{26}H_{21}BrF_2NaO_5^+$ $[M+Na]^+$: 553.0438, found: 553.0443.

IR (film) ν_{max} 3028, 1738, 1491, 1456, 1384, 1328, 1269, 1214, 1165, 1117, 1056, 1029, 980, 944, 912, 749, 701 cm^{-1}.



3ag

dibenzyl 5,5-difluoro-2-(4-(methoxycarbonyl)phenyl)dihydrofuran-3,3(2H)-dicarboxylate (3ag): Follow the general procedure (***GP1)***, **3ag** was obtained as a colorless oil (79.5 mg, 0.16 mmol, yield: 78%) after flash chromatography (Petroleum ether/EtOAc = 20:1, CAM solution, UV): TLC Rf = 0.25;

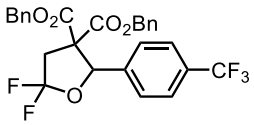
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.27 – 7.20 (m, 5H), 6.88 (d, *J* = 6.9 Hz, 2H), 6.15 (d, *J* = 3.4 Hz, 1H), 5.20 (s, 2H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.92 (s, 3H), 3.44 (td, *J* = 15.4, 7.6 Hz, 1H), 2.95 (ddd, *J* = 14.9, 8.8, 3.9 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1 , 166.6 , 166.0 , 139.7 , 134.5 , 133.9 , 130.8 , 130.2 (dd, *J* = 257.5, 254.9 Hz), 129.6 , 128.9 , 128.8 , 128.7 , 128.6 , 128.6 , 128.5 , 126.6 , 83.8 , 68.6 , 68.2 , 63.7 (d, *J* = 2.7 Hz), 52.3 , 40.6 (dd, *J* = 34.2, 30.3 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.34 – -59.86 (m, 1F), -71.55 – -72.01 (m, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{28}H_{24}F_2NaO_7^+$ $[M+Na]^+$: 533.1388, found: 533.1390.

IR (film) ν_{max} 2953, 1739, 1723, 1457, 1438, 1383, 1326, 1271, 1216, 1199, 1113, 1054, 982, 947, 913, 750, 701 cm^{-1}.



3ah

dibenzyl 5,5-difluoro-2-(4-(trifluoromethyl)phenyl)dihydrofuran-3,3(2H)-dicarboxylate (3ah): Follow the general procedure (***GP1)***, **3ah** was obtained as a colorless oil (72.8 mg, 0.14 mmol, yield: 70%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

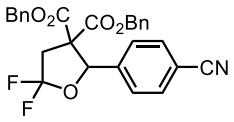
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 4H), 7.35 – 7.28 (m, 4H), 7.26 – 7.21 (m, 4H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.12 (d, *J* = 3.3 Hz, 1H), 5.20 (s, 2H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 3.43 (td, *J* = 15.2, 7.7 Hz, 1H), 2.94 (ddd, *J* = 15.0, 9.0, 4.3 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9 , 166.0 , 138.6 , 134.3 , 133.6 , 131.0 (q, *J* = 32.7 Hz), 130.2 (dd, *J* = 258.6, 255.5 Hz), 128.8 , 128.7 , 128.7 , 128.5 , 128.4 , 127.0 , 125.2 , 125.1 , 123.7 (q, *J* = 273.7 Hz), 83.4 , 68.5 , 68.3 , 63.4 (d, *J* = 2.4 Hz), 40.6 (dd, *J* = 34.2, 30.3 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.71 (ddd, *J* = 143.2, 15.6, 8.7 Hz, 1F), -62.52 (s, 3F), -71.54 (ddt, *J* = 144.2, 8.1, 3.8 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{27}H_{21}F_5NaO_5^+$ $[M+Na]^+$: 543.1207, found: 543.1210.

IR (film) ν_{max} 1739, 1457, 1383, 1333, 1270, 1217, 1162, 1130, 1071, 982, 944, 913, 856, 750, 701 cm^{-1}.



3ai

dibenzyl 2-(4-cyanophenyl)-5,5-difluorodihydrofuran-3,3(2H)-dicarboxylate (3ai): Follow the general procedure (***GP1)***, **3ai** was obtained as a colorless oil (33.5 mg, 0.07 mmol, yield: 35%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

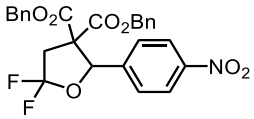
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 8H), 7.31 – 7.25 (m, 4H), 6.88 (d, *J* = 7.3 Hz, 2H), 6.07 (d, *J* = 3.3 Hz, 1H), 5.22 (d, *J* = 5.2 Hz, 2H), 4.59 (s, 2H), 3.42 (td, *J* = 15.0, 7.8 Hz, 1H), 2.94 (ddd, *J* = 15.0, 9.1, 4.9 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 , 165.9 , 139.6 (d, *J* = 1.2 Hz), 134.3 , 133.5 , 131.8 , 129.9 (dd, *J* = 258.4, 255.9 Hz), 128.9 , 128.7 , 128.6 , 127.2 , 118.3 , 112.8 , 83.1 , 68.6 , 68.2 , 63.4 (d, *J* = 2.5 Hz), 40.7 (dd, *J* = 34.4, 30.0 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -60.10 (ddd, *J* = 143.1, 14.6, 8.9 Hz, 1F), -71.32 (ddt, *J* = 143.4, 8.4, 4.5 Hz, 1F).

HRMS (ESI, m/z): calculated for $C_{27}H_{21}F_2NO_5^+$ $[M+H]^+$: 478.1466, found: 478.1469.

IR (film) ν_{max} 2230, 1738, 1498, 1456, 1378, 1275, 1197, 1158, 1113, 1052, 946, 910, 751, 698 cm^{-1}.



3aj

dibenzyl 5,5-difluoro-2-(4-nitrophenyl)dihydrofuran-3,3(2H)-dicarboxylate (3aj) : Follow the general procedure (***GP1)***, **3aj** was obtained as a colorless oil (52.7 mg, 0.11 mmol, yield: 53%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

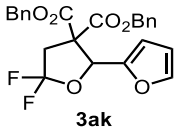
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.11 (d, *J* = 3.3 Hz, 1H), 5.28 (d, *J* = 12.0 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 3.45 (td, *J* = 14.8, 7.8 Hz, 1H), 2.96 (ddd, *J* = 14.7, 9.2, 5.1 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7 , 165.9 , 147.9 , 141.4 , 134.3 , 133.4 , 129.9 (dd, *J* = 258.6, 256.5 Hz), 128.9 , 128.9 , 128.7 , 128.7 , 128.6 , 128.4 , 127.3 , 123.2 , 82.9 , 68.6 , 68.2 , 63.4 (d, *J* = 2.0 Hz), 40.8 (dd, *J* = 34.4, 30.1 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -60.18 (ddd, *J* = 143.1, 14.7, 9.1 Hz, 1F), -71.09 (ddt, *J* = 143.2, 8.3, 4.1 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{26}H_{21}F_2NNaO_7^+$ $[M+Na]^+$: 520.1184, found: 520.1193.

IR (film) ν_{max} 1749, 1729, 1608, 1514, 1456, 1432, 1351, 1269, 1150, 1129, 1100, 1039, 1006, 911, 758, 702 cm^{-1}.



3ak

dibenzyl 5,5-difluoro-2-(furan-2-yl)dihydrofuran-3,3(2H)-dicarboxylate (3ak): Follow the general procedure (***GP1)***, **3ak** was obtained as a colorless oil (62.8 mg, 0.14 mmol, yield: 71%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

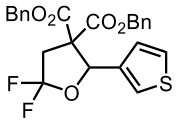
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 7H), 7.26 – 7.17 (m, 3H), 7.05 – 6.95 (m, 3H), 6.19 (d, *J* = 3.5 Hz, 1H), 5.19 (d, *J* = 1.4 Hz, 2H), 4.81 (d, *J* = 12.2 Hz, 1H), 4.56 (d, *J* = 12.2 Hz, 1H), 3.48 – 3.36 (m, 1H), 2.93 (ddd, *J* = 15.0, 8.8, 3.3 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0 , 166.0 , 135.9 (d, *J* = 1.7 Hz) , 134.4 , 134.1 , 130.1 (dd, *J* = 256.9, 254.6 Hz), 128.7 , 128.6 , 128.5 , 128.4 , 128.3 , 126.2 , 125.8 , 123.7 , 81.3 , 68.4 , 68.1 , 63.3 (d, *J* = 2.7 Hz), 40.2 (dd, *J* = 33.8, 30.7 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.17 (ddd, *J* = 144.3, 16.0, 8.7 Hz, 1F), -70.58 (ddt, *J* = 144.2, 7.7, 3.4 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{24}H_{20}F_2NaO_6^+$ $[M+Na]^+$: 443.1306, found: 443.1308.

IR (film) ν_{max} 3108, 2968, 1758, 1735, 1457, 1338, 1274, 1195, 1160, 1112, 1056, 1033, 938, 898, 795, 752, 697 cm^{-1}.



3al

dibenzyl 5,5-difluoro-2-(thiophen-3-yl)dihydrofuran-3,3(2H)-dicarboxylate (3al): Follow the general procedure (***GP1)***, **3al** was obtained as a colorless oil (49.4 mg, 0.11 mmol, yield: 54%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

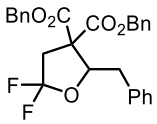
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 7H), 7.07 (dd, *J* = 7.7, 17 Hz, 3H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.24 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.12 (d, *J* = 3.8 Hz, 1H), 5.25 – 5.16 (m, 2H), 4.83 (q, *J* = 12.0 Hz, 2H), 3.56 (ddd, *J* = 18.9, 14.8, 7.6 Hz, 1H), 3.00 (dd, *J* = 14.9, 7.8 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 , 165.0 , 147.9 (d, *J* = 3.2 Hz), 143.7 , 134.5 , 134.2 , 128.7 , 128.6 , 128.6 , 128.5 , 128.4 , 128.4 , 110.8 , 110.4 , 78.2 , 68.6 , 68.2 , 62.6 (d, *J* = 2.9 Hz), 39.7 (t, *J* = 31.6 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.45 (ddd, *J* = 143.0, 18.0, 7.4 Hz, 1F), -70.30 (dd, *J* = 142.6, 10.4 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{24}H_{20}F_2NaO_5S^+$ $[M+Na]^+$: 481.0897, found: 481.0892.

IR (film) ν_{max} 1743, 1500, 1456, 1376, 1334, 1273, 1197, 1153, 1114, 1059,1014, 937, 748, 698 cm^{-1}.



3am

dibenzyl 2-benzyl-5,5-difluorodihydrofuran-3,3(2H)-dicarboxylate (3am): Follow the general procedure (***GP1)***, **3am** was obtained as a colorless oil (49.4 mg, 0.11 mmol, yield: 53%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.22;

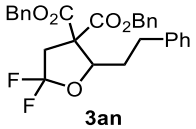
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 6H), 7.30 – 7.22 (m, 7H), 7.12 (d, J = 6.7 Hz, 2H), 5.18 – 5.06 (m, 5H), 3.39 – 3.23 (m, 1H), 2.95 – 2.81 (m, 2H), 2.70 (dd, J = 14.2, 10.3 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 , 166.6 , 136.4 , 134.5 , 134.3 , 130.0 (t, *J* = 130.5 Hz), 129.2 , 128.8 , 128.7 , 128.7 , 128.5 , 128.4 , 128.4 , 126.9 , 84.1 , 68.3 , 68.2 , 61.3 (d, *J* = 1.8 Hz), 40.8 (dd, *J* = 34.2, 31.5 Hz), 37.3 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.72 (ddd, *J* = 144.3, 13.2, 9.5 Hz, 1F), -66.89 (ddt, *J* = 144.4, 8.8, 4.9 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{27}H_{24}F_2NaO_5^+$ $[M+Na]^+$: 489.1489, found: 489.1492.

IR (film) ν_{max} 3034, 1739, 1498, 1456, 1377, 1334, 1270, 1198, 1169, 1114, 1074, 748, 698 cm^{-1}.



3an

dibenzyl 5,5-difluoro-2-phenethyldihydrofuran-3,3(2H)-dicarboxylate (3an): Follow the general procedure (***GP1)***, **3an** was obtained as a colorless oil (62.4 mg, 0.13 mmol, yield: 65%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

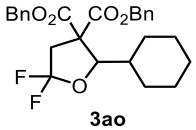
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 13H), 7.04 (d, *J* = 7.0 Hz, 2H), 5.19 – 5.09 (m, 3H), 5.02 (d, *J* = 12.0 Hz, 1H), 4.87 (dt, *J* = 10.1, 3.7 Hz, 1H), 3.26 (td, *J* = 14.4, 13.9, 8.2 Hz, 1H), 2.84 (dddd, *J* = 19.4, 14.4, 9.4, 5.4 Hz, 2H), 2.61 (ddd, *J* = 13.9, 9.3, 7.6 Hz, 1H), 1.81 – 1.64 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9 , 166.6 , 140.4 , 134.6 , 134.3 , 130.0 (t, *J* = 255.4 Hz), 128.8 , 128.6 , 128.4 , 128.3 , 126.1 , 82.7 , 68.1 , 61.4 (d, *J* = 2.2 Hz), 40.8 (dd, *J* = 33.9, 31.8 Hz), 32.8 , 32.0 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.31 – -59.82 (m, 1F), -67.16 (dd, *J* = 149.0, 7.8 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{28}H_{26}F_2O_5^+$ $[M+Na]^+$: 503.1646, found: 503.1649.

IR (film) ν_{max} 2960, 2926, 2855, 1742, 1502, 1456, 1263, 1171, 1113, 1031, 995, 909, 803, 751, 698 cm^{-1}.



3ao

dibenzyl 2-cyclohexyl-5,5-difluorodihydrofuran-3,3(2H)-dicarboxylate (3ao): Follow the general procedure, **3ao** was obtained as a colorless oil (53.1 mg, 0.12 mmol, yield: 58%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

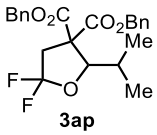
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 6H), 7.29 – 7.23 (m, 4H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.15 (s, 2H), 5.05 (d, *J* = 11.9 Hz, 1H), 4.73 (dd, *J* = 6.1, 3.8 Hz, 1H), 3.24 (td, *J* = 14.5, 7.8 Hz, 1H), 2.80 (ddd, *J* = 14.6, 9.2, 5.0 Hz, 1H), 1.72 – 1.50 (m, 5H), 1.42 (m, 1H), 1.12 – 0.99 (m, 3H), 0.98 – 0.84 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 , 166.9 , 134.6 , 134.3 , 129.8 (t, *J* = 254.5 Hz), 128.89 , 128.8 , 128.7 , 128.6 , 128.4 , 88.0 , 68.1 , 68.12, 61.0 (d, *J* = 2.3 Hz), 42.1 (dd, *J* = 34.8, 30.8 Hz), 39.1 , 29.9 , 27.7 , 25.8 , 25.6 , 25.4 . ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.95 (ddd, *J* = 144.2, 14.1, 9.1 Hz, 1F), -70.04 (ddt, *J* = 144.2, 8.3, 4.7 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{26}H_{28}F_2NaO_5^+$ $[M+Na]^+$: 481.1803, found: 481.1809.

IR (film) ν_{max} 2930, 2855, 1739, 1498, 1455, 1335, 1269, 1213, 1113, 1028, 972, 909, 751, 698 cm^{-1}.



3ap

dibenzyl 5,5-difluoro-2-isopropyldihydrofuran-3,3(2H)-dicarboxylate(3ap): Follow the general procedure (***GP1)***, **3ap** was obtained as a colorless oil (52.7 mg, 0.13 mmol, yield: 64%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.30;

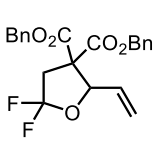
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 6H), 7.26 – 7.21 (m, 4H), 5.14 (t, *J* = 5.6 Hz, 4H), 4.76 (dd, *J* = 6.2, 3.9 Hz, 1H), 3.26 (td, *J* = 14.7, 7.8 Hz, 1H), 2.89 – 2.77 (m, 1H), 1.85 (h, *J* = 6.6 Hz, 1H), 0.90 (d, *J* = 6.6 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 , 134.4 , 129.8 (t, *J* = 250.3 Hz), 128.6 , 128.6 , 99.0 , 68.0 , 67.1 , 43.2 (t, *J* = 31.8 Hz), 34.2 , 19.2 , 17.9 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.18 (ddd, *J* = 144.2, 14.5, 9.1 Hz, 1F), -70.08 (ddt, *J* = 144.2, 8.2, 4.3 Hz, 1F).

HRMS (ESI, m/z): calculated for $C_{23}H_{24}F_2NaO_5^+$ $[M+Na]^+$: 441.1489, found: 481.1495.

IR (film) ν_{max} 3055, 2969, 1739, 1498, 1456, 1373, 1334, 1269, 1169, 1127, 1087, 1060, 909, 751, 698 cm^{-1}.



3aq

dibenzyl 5,5-difluoro-2-vinyldihydrofuran-3,3(2H)-dicarboxylate (3aq): Follow the general procedure (***GP1)***, **3aq** was obtained as a colorless oil (61.1 mg, 0.15 mmol, yield: 76%) after flash chromatography (Petroleum ether/EtOAc = 50:1, $KMnO_4$, UV): TLC Rf = 0.25;

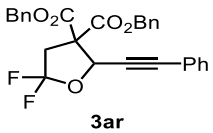
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 5H), 7.27 – 7.20 (m, 4H), 5.66 (ddd, *J* = 16.9, 10.5, 6.2 Hz, 1H), 5.48 – 5.44 (m, 1zH), 5.40 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.23 – 5.14 (m, 3H), 5.05 (dd, *J* = 21.4, 12.0 Hz, 2H), 3.24 (ddd, *J* = 16.3, 15.0, 7.8 Hz, 1H), 2.89 (ddd, *J* = 14.9, 8.4, 3.2 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7 , 165.9 , 134.5 , 134.3 , 130.7 (d, *J* = 2.1 Hz), 130.2 (t, *J* = 255.6 Hz), 128.70 , 128.67 , 128.62 , 128.58 , 128.54 , 128.35 , 120.1 , 83.3 , 68.3 , 68.2 , 62.3 (d, *J* = 2.7 Hz), 39.8 (t, *J* = 32.1 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.00 (ddd, *J* = 144.4, 16.4, 8.4 Hz, 1F), -68.83 (ddt, *J* = 144.5, 7.3, 3.3 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{22}H_{20}F_2NaO_5^+$ $[M+Na]^+$: 425.1176, found: 425.1174.

IR (film) ν_{max} 1741, 1499, 1456, 1377, 1334, 1271, 1199, 1166, 1105, 1058, 948, 910, 750, 697 cm^{-1}.



3ar

dibenzyl 5,5-difluoro-2-(phenylethynyl)dihydrofuran-3,3(2H)-dicarboxylate (3ar): Follow the general procedure (***GP1)***, **3ar** was obtained as a white solid (85.7 mg, 0.18 mmol, yield: 90%) after flash chromatography (Petroleum ether/EtOAc = 20:1, $KMnO_4$, UV): TLC Rf = 0.25;

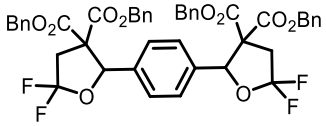
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 15H), 5.97 (d, *J* = 3.6 Hz, 1H), 5.22 (q, *J* = 12.1 Hz, 2H), 5.12 (s, 2H), 3.47 (ddd, *J* = 17.8, 14.9, 8.1 Hz, 1H), 3.03 (ddd, *J* = 14.8, 8.1, 1.5 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9 , 165.0 , 134.4 , 134.3 , 131.9 , 130.6 (dd, *J* = 259.1, 255.4 Hz), 129.3 , 128.7 , 128.6 , 128.5 , 128.4 , 128.3 , 128.2 , 120.9 , 89.7 , 81.3 (d, *J* = 4.0 Hz), 73.4 , 68.6 , 68.4 , 63.9 (d, *J* = 2.4 Hz), 39.5 (t, *J* = 31.7 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.12 (ddd, *J* = 143.1, 17.9, 9.0 Hz, 1F), -66.71 – -67.41 (m, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{28}H_{22}F_2NaO_5^+$ $[M+Na]^+$: 499.1333, found: 499.1336.

IR (film) ν_{max} 3035, 2235, 1745, 1491, 1456, 1332, 1308, 1274, 1195, 1159, 1117, 1057, 757, 696 cm^{-1}.



3as

tetrabenzyl 2,2'-(1,4-phenylene)bis(5,5-difluorodihydrofuran-3,3(2H)-dicarboxylate)(3as):

Follow the general procedure (***GP1)***, **3as** was obtained as a white solid (85.7 mg, 0.18 mmol, yield: 90%) after flash chromatography (Petroleum ether/EtOAc = 20:1, CAM solution, UV): TLC Rf = 0.25;

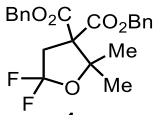
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.18 (m, 20H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.09 (dd, *J* = 6.1, 3.5 Hz, 2H), 5.20 (d, *J* = 8.7 Hz, 4H), 4.70 (dd, *J* = 16.8, 12.1 Hz, 2H), 4.47 (t, *J* = 11.6 Hz, 2H), 3.49 – 3.33 (m, 2H), 2.95 (dd, *J* = 14.8, 8.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3 , 168.2 , 166.1 , 165.8 , 135.9 , 135.7 , 134.6 , 134.5 , 134.1 , 134.0 , 130.4 (dd, J = 261.9, 254.8 Hz), 130.3 (dd, J = 261.9, 254.8 Hz), 126.7 , 126.6 , 84.0 , 84.0 , 68.6 , 68.6 , 68.3 , 68.3 , 63.7 (t, *J* = 3.2 Hz), 41.0 – 39.8 (m) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.53 – -59.88 (m), -71.47 – -72.78 (m) ppm;

HRMS (ESI, m/z): calculated for $C_{46}H_{38}F_4NaO_{10}^+$ $[M+Na]^+$: 849.2299, found: 849.2302.

IR (film) ν_{max} 3035, 1739, 1499, 1456, 1337, 1273, 1198, 1159, 1111, 1053, 700, 697 cm^{-1}.



4aa

benzyl 3-((benzylperoxy)-l2-methyl)-5,5-difluoro-2,2-dimethyltetrahydrofuran-3-carboxylate (4aa): Follow the general procedure (***GP1)***, **4aa** was obtained as a colorless oil (72.7 mg, 0.18 mmol, yield: 90%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.30;

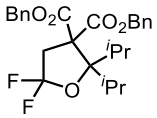
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 6H), 7.30 – 7.26 (m, 4H), 5.19 (d, *J* = 12.2 Hz, 2H), 5.14 (d, *J* = 12.2 Hz, 2H), 3.11 (t, *J* = 9.1 Hz, 2H), 1.43 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 , 134.6 , 129.6 (t, *J* = 253.9 Hz), 128.6 , 128.4 , 87.8 , 67.9 , 65.3 , 41.5 (t, *J* = 32.8 Hz), 24.8 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.35 (t, *J* = 9.1 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{22}H_{22}F_2NaO_5^+$ $[M+Na]^+$: 427.1333, found: 427.1330.

IR (film) ν_{max} 3035, 2986, 1742, 1456, 1390, 1272， 1100, 1029, 907, 750, 697 cm^{-1}.



4ab

benzyl 3-((benzylperoxy)-l2-methyl)-5,5-difluoro-2,2-diisopropyltetrahydrofuran-3-carboxylate (**4ab**): Follow the general procedure (***GP2)***, **4ab** was obtained as a colorless oil (62.7 mg, 0.14 mmol, yield: 68%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.30;

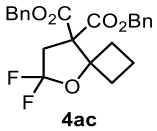
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 6H), 7.31 – 7.26 (m, 4H), 5.13 (d, *J* = 2.8 Hz, 4H), 3.13 (t, *J* = 8.7 Hz, 2H), 2.39 (hept, *J* = 7.0 Hz, 2H), 0.97 (d, *J* = 6.9 Hz, 6H), 0.92 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 , 134.4 , 129.8 (t, *J* = 250.3 Hz), 128.6 , 128.6 , 99.0 , 68.0 , 67.1 , 43.2 (t, *J* = 31.8 Hz), 34.2 , 19.2 , 17.9 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.11 (t, *J* = 8.5 Hz, 2F) ppm;

HRMS (ESI, m/z): calculated for $C_{26}H_{30}F_2NaO_5^+$ $[M+Na]^+$: 483.1959, found: 483.1958.

IR (film) ν_{max} 2978, 1741, 1456, 1395, 1344, 1256, 1139, 1041, 1013, 907, 752, 697 cm^{-1}.



4ac

dibenzyl 6,6-difluoro-5-oxaspiro[3.4]octane-8,8-dicarboxylate (4ac): Follow the general procedure (***GP1)***, **4ac** was obtained as a colorless oil (57.4 mg, 0.14 mmol, yield: 69%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

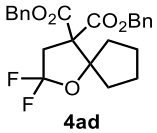
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 6H), 7.30 – 7.26 (m, 4H), 5.20 (d, *J* = 12.1 Hz, 2H), 5.14 (d, *J* = 12.1 Hz, 2H), 3.01 (t, *J* = 9.1 Hz, 2H), 2.48 – 2.29 (m, 4H), 2.02 – 1.89 (m, 1H), 1.55 – 1.44 (m, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7 , 134.6 , 129.3 (t, *J* = 255.2 Hz), 128.7 , 128.6 , 128.4 , 90.6 , 67.9 , 63.6 , 40.7 (t, *J* = 32.6 Hz), 31.4 , 14.1 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.0 (t, *J* = 9.3 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{23}H_{22}F_2NaO_5^+$ $[M+Na]^+$: 439.1333, found: 439.1337.

IR (film) ν_{max} 2957, 1742, 1456,1267, 1149, 1116, 1092, 1029, 908, 750, 697 cm^{-1}.



4ad

dibenzyl 2,2-difluoro-1-oxaspiro[4.4]nonane-4,4-dicarboxylate (4ad): Follow the general procedure (***GP1)***, **4ad** was obtained as a colorless oil (73.1 mg, 0.17 mmol, yield: 85%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

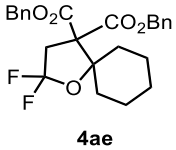
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 6H), 7.27 – 7.24 (m, 4H), 5.17 (d, *J* = 12.2 Hz, 2H), 5.12 (d, *J* = 12.2 Hz, 2H), 3.09 (t, *J* = 9.1 Hz, 2H), 2.09 – 1.97 (m, 2H), 1.84 – 1.65 (m, 4H), 1.55 – 1.46 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2 , 134.6 , 129.4 (t, *J* = 253.7 Hz), 128.6 , 128.4 , 97.8 , 67.8 , 64.0 , 42.2 (t, *J* = 32.7 Hz), 35.2 , 23.7 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -60.08 (t, *J* = 8.9 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{24}H_{24}F_2NaO_5^+$ $[M+Na]^+$: 453.1489, found: 453.1492.

IR (film) ν_{max} 2962, 1742, 1455,1331, 1266, 1157, 1095, 1030, 1013, 975, 908, 750, 697 cm^{-1}.



4ae

dibenzyl 2,2-difluoro-1-oxaspiro[4.5]decane-4,4-dicarboxylate (4ae): Follow the general procedure (***GP1)***, **4ae** was obtained as a colorless oil (63.9 mg, 0.14 mmol, yield: 72%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV).

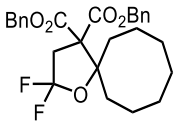
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 6H), 7.28 (dd, *J* = 6.7, 3.1 Hz, 4H), 5.20 (d, *J* = 12.2 Hz, 2H), 5.13 (d, *J* = 12.2 Hz, 2H), 3.10 (t, *J* = 9.1 Hz, 2H), 1.80 (d, *J* = 9.5 Hz, 2H), 1.69 – 1.49 (m, 7H), 1.16 – 1.01 (m, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 , 134.6 , 129.6 (t, *J* = 253.7 Hz), 128.6 , 128.5 , 128.3 , 89.8 , 67.7 , 65.7 , 41.3 (t, *J* = 32.9 Hz), 32.0 , 24.8 , 21.9 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.92 (t, *J* = 9.1 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{25}H_{26}F_2NaO_5^+$ $[M+Na]^+$: 467.1646, found: 467.1644.

IR (film) ν_{max} 3035, 2939, 2866, 1743, 1455, 1339, 1263, 1105, 1015, 958, 916, 833, 750, 697 cm^{-1}.



4af

dibenzyl 2,2-difluoro-1-oxaspiro[4.7]dodecane-4,4-dicarboxylate (4af): Follow the general procedure (***GP1)***, **4af** was obtained as a colorless oil (53.6 mg, 0.11 mmol, yield: 57%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

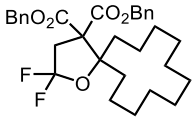
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 10H), 5.20 (d, *J* = 12.1 Hz, 2H), 5.12 (d, *J* = 12.1 Hz, 2H), 3.10 (t, *J* = 9.2 Hz, 2H), 1.85 (t, *J* = 5.5 Hz, 4H), 1.70 – 1.57 (m, 3H), 1.56 – 1.43 (m, 3H), 1.43 – 1.28 (m, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 , 134.5 , 129.5 (t, *J* = 253.4 Hz), 128.6 , 128.6 , 128.5 , 93.0 , 67.8 , 67.3 , 42.2 (t, *J* = 32.7 Hz), 32.0 , 27.5 , 23.7 , 21.0 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.91 (t, *J* = 9.2 Hz, 2F) ppm;

HRMS (ESI, m/z): calculated for $C_{27}H_{30}F_2NaO_5^+$ $[M+Na]^+$: 495.1959, found: 495.1961.

IR (film) ν_{max} 3034, 2925, 1740, 1455, 1337, 1269, 1164, 1094, 1029, 908, 751, 697 cm^{-1}.



4ag

dibenzyl 2,2-difluoro-1-oxaspiro[4.11]hexadecane-4,4-dicarboxylate (**4ag**): Follow the general procedure (***GP2)***, **4ag** was obtained as a colorless oil (70.7 mg, 0.13 mmol, yield: 67%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25);

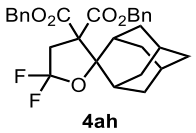
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 10H), 7.31 – 7.27 (m, 5H), 5.24 (d, *J* = 11.9 Hz, 2H), 5.06 (d, *J* = 11.9 Hz, 2H), 3.14 (t, *J* = 9.3 Hz, 2H), 1.69 – 1.61 (m, 6H), 1.37 – 1.23 (m, 5H), 1.22 – 1.10 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7 , 134.47 , 129.12 (t, *J* = 252.9 Hz), 128.85 , 128.71 , 128.62 , 93.52 , 67.88 , 66.12 , 42.85 (t, *J* = 33.0 Hz), 31.04 , 26.18 , 25.80 , 22.45 , 21.87 , 19.46 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.79 (s, 2F) ppm;

HRMS (ESI, m/z): calculated for $C_{31}H_{38}F_2NaO_5^+$ $[M+Na]^+$: 551.2585, found: 551.2593.

IR (film) ν_{max} 2930, 2892, 1747,1729,1473, 1331, 1263, 1198, 1150, 1098, 1029, 945, 907, 752, 698 cm^{-1}.



4ah

dibenzyl (1r,3r,5r,7r)-5',5'-difluorodihydro-3'H-spiro[adamantane-2,2'-furan]-3',3'-dicarboxylate (4ah): Follow the general procedure (***GP1)***, **4ah** was obtained as a white solid (70.4 mg, 0.14 mmol, yield: 71%) after flash chromatography (Petroleum ether/EtOAc = 50:1, CAM solution, UV): TLC Rf = 0.25;

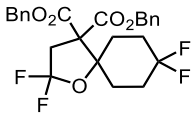
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 6H), 7.28 – 7.22 (m, 4H), 5.11 (s, 4H), 3.38 (t, *J* = 9.2 Hz, 2H), 2.61 (s, 2H), 2.26 (d, *J* = 11.4 Hz, 2H), 1.77 (d, *J* = 10.5 Hz, 3H), 1.64 (s, 2H), 1.62 – 1.53 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 , 134.3 , 128.6 , 128.5, 128.3 (t, *J* = 277.5 Hz) , 95.7 , 68.1 , 64.3 , 43.5 (t, *J* = 32.2 Hz), 37.8 , 34.7 , 33.9 , 33.3 , 26.4 , 25.9 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.28 (t, *J* = 9.2 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{29}H_{30}F_2NaO_5^+$ $[M+Na]^+$: 519.1959, found: 519.1960.

IR (film) ν_{max} 2923, 1731, 1455, 1330, 1248, 1223, 1188, 1056, 1027, 1005, 899, 749, 694 cm^{-1}.



4ai

dibenzyl 2,2,8,8-tetrafluoro-1-oxaspiro[4.5]decane-4,4-dicarboxylate (**4ai**): Follow the general procedure (***GP2)***, **4ai** was obtained as a colorless oil (68.2 mg, 0.14 mmol, yield: 71%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

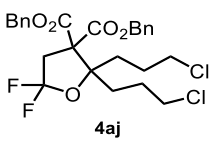
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.29 – 7.25 (m, 3H), 5.20 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 3.12 (t, *J* = 9.2 Hz, 1H), 2.16 – 1.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.84 , 134.27 , 129.42 (t, *J* = 255.2 Hz), 128.73 , 128.66 , 128.45 , 122.01 (dd, *J* = 243.4, 238.5 Hz), 87.22 , 68.11 , 64.58 , 41.34 (t, *J* = 32.6 Hz), 29.67 (t, *J* = 25.0 Hz), 28.69 , 28.59 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.64 (t, *J* = 9.2 Hz), -93.52 (d, *J* = 237.4 Hz), -103.33 – -104.27 (m).

HRMS (ESI, m/z): calculated for $C_{25}H_{24}F_4NaO_5^+$ $[M+Na]^+$: 503.1458, found: 503.1463.

IR (film) ν_{max} 3035, 2951, 1742, 1456, 1390, 1266, 1171, 1111, 1078, 992, 911, 750, 698 cm^{-1}.



4aj

dibenzyl 2,2-bis(3-chloropropyl)-5,5-difluorodihydrofuran-3,3(2H)-dicarboxylate (4aj):

Follow the general procedure (***GP1)***, **4aj** was obtained as a colorless oil (82.4 mg, 0.16 mmol, yield: 78%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.20, CAM solution, UV);

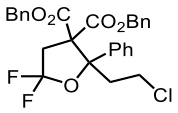
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 7H), 7.31 – 7.26 (m, 4H), 5.20 (d, *J* = 12.0 Hz, 2H), 5.11 (d, *J* = 12.0 Hz, 2H), 3.31 (t, *J* = 5.7 Hz, 4H), 3.14 (t, *J* = 9.2 Hz, 2H), 1.94 – 1.71 (m, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 , 134.3 , 129.1 (t, *J* = 254.0 Hz), 128.8 , 128.8 , 128.7 , 91.4 , 68.2 , 66.2 , 44.8 , 42.1 (t, *J* = 32.5 Hz), 32.1 , 26.4 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.83 (s, 2F) ppm;

HRMS (ESI, m/z): calculated for $C_{26}H_{28}Cl_2F_2NaO_5^+$ $[M+Na]^+$: 551.1180, found: 551.1176.

IR (film) ν_{max} 3714, 3034, 2961, 1741, 1456, 1264, 1215, 1153, 1099, 752, 698 cm^{-1}.



4ak

dibenzyl 2-(2-chloroethyl)-5,5-difluoro-2-phenyldihydrofuran-3,3(2H)-dicarboxylate (4ak): Follow the general procedure (***GP1)***, **4ak** was obtained as a colorless oil (86.4 mg, 0.17 mmol, yield: 84%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

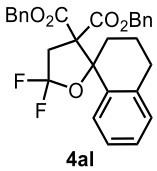
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.34 – 7.19 (m, 11H), 6.93 (d, *J* = 6.4 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.2 Hz, 1H), 4.29 (d, *J* = 12.2 Hz, 1H), 3.58 (td, *J* = 11.3, 4.9 Hz, 1H), 3.35 (ddd, *J* = 15.4, 9.5, 5.8 Hz, 1H), 3.22 – 3.10 (m, 2H), 3.03 (td, *J* = 11.2, 4.4 Hz, 1H), 2.42 (td, *J* = 12.7, 4.3 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 , 166.3 , 136.0 , 134.2 , 134.0 , 129.3 (t, *J* = 254.8 Hz), 128.8 , 128.7 , 128.6 , 128.5 , 128.4 , 128.2 , 128.2 , 126.1 , 91.7 , 68.2 , 67.9 , 67.4 , 41.7 (dd, *J* = 35.0, 29.3 Hz), 40.4 , 39.0 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -54.40 (ddd, *J* = 145.9, 11.4, 5.6 Hz, 1F), -65.17 (dt, *J* = 145.8, 10.4 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{28}H_{25}ClF_2NaO_5^+$ $[M+Na]^+$: 537.1256, found: 537.1258.

IR (film) ν_{max} 3034, 1740, 1498, 1456, 1342, 1269, 1168, 1108, 1049, 1029, 947, 909, 750, 696 cm^{-1}.



4al

dibenzyl 5,5-difluoro-3',4,4',5-tetrahydro-2'H,3H-spiro[furan-2,1'-naphthalene]-3,3-dicarboxylate (4al): Follow the general procedure (***GP1)***, **4al** was obtained as a colorless oil (68.9 mg, 0.14 mmol, yield: 70%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 5H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.25 – 7.10 (m, 4H), 6.99 (d, *J*

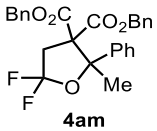
= 7.2 Hz, 1H), 6.85 (d, *J* = 6.9 Hz, 2H), 5.30 (d, *J* = 12.1 Hz, 1H), 5.15 (d, *J* = 12.2 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 3.72 (ddd, *J* = 15.8, 13.7, 9.7 Hz, 1H), 3.25 (ddd, *J* = 15.9, 8.9, 2.6 Hz, 1H), 2.63 (dt, *J* = 16.7, 5.5 Hz, 1H), 2.37 – 2.24 (m, 2H), 2.21 – 2.13 (m, 1H), 1.90 – 1.79 (m, 1H), 1.74 – 1.62 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 , 167.3 , 138.3 , 136.4 (d, *J* = 2.0 Hz), 134.4 , 134.1 , 130.4 (dd, *J* = 252.3, 255.5 Hz), 129.5 , 128.7 , 128.6 , 128.5 , 128.4 , 128.4 , 128.3 , 126.2 , 125.8 , 90.5 , 68.1 , 68.0 , 68.0 , 43.4 (t, *J* = 32.2 Hz), 34.4 , 29.3 , 19.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.24 (ddd, *J* = 145.9, 14.0, 9.1 Hz, 1F), -59.58 (dd, *J* = 145.7, 9.2 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{29}H_{26}F_2NaO_5^+$ $[M+Na]^+$: 515.1646, found: 515.1646.

IR (film) ν_{max} 3726, 3034, 2943, 1741, 1455, 1274, 1109, 1045, 909, 752, 697 cm^{-1}.



4am

dibenzyl 5,5-difluoro-2-methyl-2-phenyldihydrofuran-3,3(2H)-dicarboxylate (4am): Follow the general procedure (***GP1)***, **4am** was obtained as a colorless oil (65.2 mg, 0.14 mmol, yield: 72%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

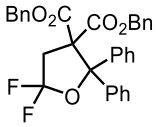
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.34 – 7.20 (m, 11H), 6.95 (dd, *J* = 7.6, 1.5 Hz, 2H), 5.18 (d, *J* = 12.1 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.36 (d, *J* = 12.2 Hz, 1H), 3.34 (ddd, *J* = 15.2, 9.4, 5.7 Hz, 1H), 3.19 (dt, *J* = 15.4, 10.8 Hz, 1H), 1.89 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 , 166.9 , 139.5 , 134.4 , 134.2 , 129.4 (t, *J* = 253.5 Hz), 128.7 , 128.6 , 128.5 , 128.3 , 128.3 , 128.1 , 127.8 , 125.8 , 91.0 , 68.0 , 67.8 , 67.2 , 42.0 (dd, *J* = 35.4, 29.6 Hz), 26.1 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -53.48 – -54.01 (m, 1F), -64.46 (dt, *J* = 145.8, 10.8 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{27}H_{24}F_2NaO_5^+$ $[M+Na]^+$: 489.1489, found: 489.1492.

IR (film) ν_{max} 3034, 1741, 1456, 1343, 1243, 1169, 1110, 1025, 908, 765, 740, 697 cm^{-1}.



4an

dibenzyl 5,5-difluoro-2,2-diphenyldihydrofuran-3,3(2H)-dicarboxylate (4an): Follow the general procedure (***GP1)***, **4an** was obtained as a colorless oil (53.9 mg, 0.10 mmol, yield: 51%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.34 – 7.25 (m, 6H), 7.24 – 7.17 (m, 6H), 7.08 – 7.03 (m, 4H), 4.85 (d, *J* = 12.0 Hz, 2H), 4.80 (d, *J* = 12.0 Hz, 2H), 3.40 (t, *J* = 8.8 Hz, 2H) ppm;

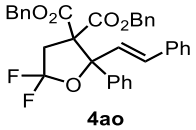
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 , 140.6 , 134.1 , 130.0 (t, *J* = 253.6 Hz), 128.5 , 128.5 , 128.0 , 127.9 ,

127.1 , 95.2 , 68.3 , 68.2 , 42.9 (t, J = 31.3 Hz) ppm;

^{19}F NMR (376 MHz, CDCl$_3$) δ -59.71 (t, J = 8.9 Hz, 2F) ppm.

HRMS (ESI, m/z): calculated for $C_{32}H_{26}F_2NaO_5^+$ $[M+Na]^+$: 551.1646, found: 551.1651.

IR (film) ν_{max} 3066, 3034, 2957, 1741, 1722, 1497, 1448, 1379, 1347, 1292, 1146, 1055, 935, 898, 750, 697, 624 cm^{-1}.



4ao

dibenzyl (E)-5,5-difluoro-2-phenyl-2-styryldihydrofuran-3,3(2H)-dicarboxylate (4ao): Follow the general procedure (***GP1)***, **4ao** was obtained as a colorless oil (33.2 mg, 0.06 mmol, yield: 30%) after flash chromatography (Petroleum ether/EtOAc = 20:1, TLC Rf = 0.30, $KMnO_4$, UV);

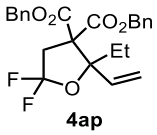
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.64 (m, 2H), 7.32 – 7.20 (m, 16H), 7.00 (dd, J = 7.6, 1.8 Hz, 2H), 6.83 (s, 2H), 5.22 (d, J = 12.0 Hz, 1H), 5.12 (d, J = 12.0 Hz, 1H), 4.71 (d, J = 12.2 Hz, 1H), 4.50 (d, J = 12.1 Hz, 1H), 3.29 – 3.14 (m, 2H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.2 , 166.7 , 138.8 (d, J = 2.5 Hz), 136.0 , 134.4 , 134.2 , 131.4 , 129.7 (dd, J = 255.2, 252.8 Hz), 128.7 , 128.7 , 128.6 , 128.5 , 128.4 , 128.4 , 128.2 , 128.1 , 128.1 , 128.0 , 127.85 , 127.8 , 126.9 , 126.0 , 92.3 , 68.2 , 67.9 , 41.1 (dd, J = 33.3, 29.3 Hz) ppm;

^{19}F NMR (376 MHz, CDCl$_3$) δ -57.55 (dd, J = 140.6, 8.4 Hz, 1F), -60.89 – -61.48 (m, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{34}H_{28}F_2NaO_5^+$ $[M+Na]^+$: 577.1803, found: 577.1808.

IR (film) ν_{max} 3062, 3032, 1742, 1449, 1344, 1263, 1241, 1161, 1111, 746, 695 cm^{-1}.



4ap

benzyl 3-((benzylperoxy)-l2-methyl)-2-ethyl-5,5-difluoro-2-vinyltetrahydrofuran-3-carboxylate (4ap): Follow the general procedure (***GP1)***, **4ap** was obtained as a colorless oil (55.0 mg, 0.13 mmol, yield: 64%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, $KMnO_4$, UV);

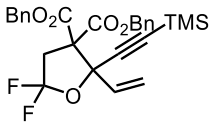
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.30 (m, 6H), 7.28 – 7.24 (m, 4H), 5.76 (dd, J = 17.2, 11.1 Hz, 1H), 5.39 (dd, J = 17.1, 1.2 Hz, 1H), 5.20 – 5.02 (m, 5H), 3.08 (td, J = 9.1, 1.4 Hz, 2H), 1.86 – 1.68 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.3 , 167.0 , 134.6 (d, J = 3.8 Hz), 134.0 (d, J = 1.6 Hz), 129.7 (t, J = 255.3 Hz), 128.6 , 128.5 , 128.5 , 128.4 , 128.4 , 117.5 , 91.9 , 67.9 , 67.9 , 66.3 , 40.8 (dd, J = 33.8, 30.7 Hz), 28.1 , 7.5 .

^{19}F NMR (376 MHz, CDCl$_3$) δ -56.43 (dt, J = 146.1, 9.0 Hz, 1F), -62.92 (dt, J = 146.1, 8.9 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{24}H_{24}F_2NaO_5^+$ $[M+Na]^+$: 453.1489, found: 453.1494.

IR (film) ν_{max} 2939, 1742, 1456, 1282, 1266, 1102, 1041, 939, 907,698 cm^{-1}.



4aq

dibenzyl 5,5-difluoro-2-((trimethylsilyl)ethynyl)-2-vinyldihydrofuran-3,3(2H)-dicarboxylate (4aq): Follow the general procedure (***GP1)***, **4aq** was obtained as a colorless oil (64.7 mg, 0.13 mmol, yield: 65%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, $KMnO_4$, UV);

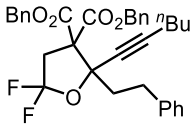
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 10H), 6.05 (dd, *J* = 17.0, 10.6 Hz, 1H), 5.61 (d, *J* = 17.0 Hz, 1H), 5.24 – 5.05 (m, 5H), 3.35 (ddd, *J* = 15.2, 12.6, 10.5 Hz, 1H), 3.13 – 3.03 (m, 1H), 0.14 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 , 166.1 , 134.5 , 134.4 , 131.6 , 129.7 (dd, *J* = 259.1, 255.4 Hz), 128.5 , 128.5 , 128.3 , 128.1 , 119.5 , 99.1 , 95.4 , 84.0 (d, *J* = 2.4 Hz), 68.1 , 68.0 , 67.6 , 41.2 (dd, *J* = 34.5, 29.3 Hz), -0.6 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.77 (ddd, *J* = 142.1, 10.4, 4.5 Hz, 1F), -62.20 (ddd, *J* = 142.6, 12.7, 9.6 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{27}H_{28}F_2NaO_5Si^+$ $[M+Na]^+$: 521.1572, found: 521.1575.

IR (film) ν_{max} 2961, 1745, 1456, 1336, 1272, 1238, 1157, 1112, 948, 849, 750, 697 cm^{-1}.



4ar

benzyl 3-((benzylperoxy)-l2-methyl)-5,5-difluoro-2-(hex-1-yn-1-yl)-2-phenethyltetrahydrofuran-3-carboxylate (4ar): Follow the general procedure (***GP1)***, **4ar** was obtained as a colorless oil (104.2 mg, 0.19 mmol, yield: 93%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, $KMnO_4$, UV);

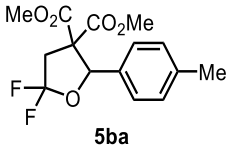
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.16 (m, 15H), 7.05 (d, *J* = 7.0 Hz, 2H), 5.23 – 5.15 (m, 3H), 5.10 (d, *J* = 12.1 Hz, 1H), 3.36 (ddd, *J* = 15.1, 12.6, 10.6 Hz, 1H), 3.12 – 2.94 (m, 2H), 2.81 (td, *J* = 13.2, 4.8 Hz, 1H), 2.32 (td, *J* = 13.0, 4.2 Hz, 1H), 2.17 – 2.07 (m, 3H), 1.47 – 1.34 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 , 166.4 , 141.2 , 134.7 , 134.4 , 129.9 (dd, *J* = 258.6, 254.1 Hz), 128.6 , 128.5 , 128.45 , 128.4 , 128.4 , 128.3 , 128.3 , 125.9 , 90.8 , 85.4 (d, *J* = 2.0 Hz), 75.7 (d, *J* = 2.5 Hz), 68.0 , 66.9 , 41.5 (dd, *J* = 34.6, 29.8 Hz), 38.0 , 31.2 , 30.2 , 21.8 , 18.2 , 13.5 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.51 – -59.07 (m), -61.92 (dt, *J* = 143.1, 10.7 Hz) ppm.

HRMS (ESI, m/z): calculated for $C_{34}H_{34}F_2NaO_5^+$ $[M+Na]^+$: 583.2272, found: 583.2277.

IR (film) ν_{max} 2958, 2245, 1746, 1498, 1455, 1270, 1240, 1158, 1112, 1039, 950, 749, 698 cm^{-1}.



5ba

dimethyl 5,5-difluoro-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate (5ba): Follow the general procedure (***GP1)***, **5ba** was obtained as a colorless oil (59.7 mg, 0.19 mmol, yield: 95%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, UV);

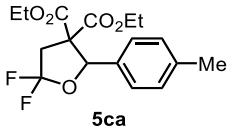
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.09 (d, *J* = 3.6 Hz, 1H), 3.83 (s, 3H), 3.39 (ddd, *J* = 17.2, 14.9, 7.5 Hz, 1H), 3.26 (s, 3H), 2.90 (ddd, *J* = 14.9, 8.4, 2.8 Hz, 1H), 2.32 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 166.7, 138.9, 131.9 (d, *J* = 1.6 Hz), 130.2 (dd, *J* = 253.3, 256.5 Hz), 128.9, 126.3, 84.4, 53.6, 52.9, 40.1 (dd, *J* = 34.3, 30.2 Hz), 21.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.09 (ddd, *J* = 24.3, 18.0, 9.0 Hz, 1F), -72.08 – -72.56 (m, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{15}H_{16}F_2NaO_5^+$ $[M+Na]^+$: 337.0863, found: 337.0867.

IR (film) ν_{max} 2957, 1743, 1518, 1437, 1337, 1280, 1256, 1209, 1161, 1115, 1060, 944, 800 cm^{-1}.



5ca

diethyl 5,5-difluoro-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate (5ca): Follow the general procedure (***GP1)***, **5ca** was obtained as a colorless oil (49.2 mg, 0.14 mmol, yield: 72%) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, UV);

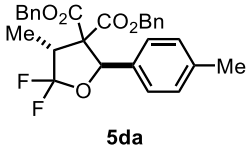
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.10 (d, *J* = 3.7 Hz, 1H), 4.37 – 4.21 (m, 2H), 3.80 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.58 (dq, *J* = 10.7, 7.2 Hz, 1H), 3.40 (ddd, *J* = 17.4, 14.9, 7.6 Hz, 1H), 2.89 (ddd, *J* = 14.9, 8.4, 2.8 Hz, 1H), 2.31 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 , 166.3 , 138.8 , 132.0 (d, *J* = 2.0 Hz), 130.3 (d, *J* = 256.8, 253.7 Hz), 128.8 , 126.5 , 84.4 , 63.4 (d, *J* = 2.8 Hz), 62.6 , 62.2 , 40.1 (dd, *J* = 33.8, 30.2 Hz), 21.1 , 13.9 , 13.3 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.06 (ddd, *J* = 144.0, 17.5, 8.4 Hz, 1F), -72.27 (ddt, *J* = 143.1, 6.2, 2.7 Hz, 1F) ppm.

HRMS (ESI, m/z): calculated for $C_{17}H_{20}F_2NaO_5^+$ $[M+Na]^+$: 365.1176, found: 365.1173.

IR (film) ν_{max} 2985, 1740, 1518, 1447, 1369, 1336, 1271, 1204, 1161,1109, 1059, 1019, 990, 863, 807 cm^{-1}.



5da

dibenzyl 5,5-difluoro-4-methyl-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate (5da): Follow the general procedure (***GP1)***, **5da** was obtained as a white solid (70.0 mg, 0.15 mmol, yield: 73%, d.r.=8:1) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

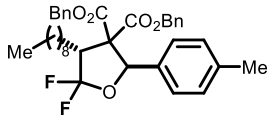
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 8H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 6.9 Hz, 2H), 6.03 (d, *J* = 3.9 Hz, 1H), 5.18 (s, 2H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.36 (d, *J* = 12.1 Hz, 1H), 3.60 (dp, *J* = 14.8, 7.3 Hz, 1H), 2.31 (s, 3H), 1.18 (d, *J* = 7.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 , 166.3 , 138.9 , 134.4 , 134.2 , 132.4 (d, *J* = 2.7 Hz), 130.5 (dd, *J* = 260.8, 252.2 Hz), 129.0 , 128.6 , 128.6 , 128.6 , 128.4 , 128.4 , 126.8 , 83.8 (d, *J* = 1.0 Hz), 68.1 , 67.8 , 66.70 (d, *J* = 3.9 Hz), 43.9 (t, *J* = 30.0 Hz), 21.2 , 9.4 (d, *J* = 4.8 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -71.64 (dd, *J* = 143.5, 14.8 Hz, 1F), -76.45 – -76.92 (m, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{28}H_{26}F_2NaO_5^+$ $[M+Na]^+$: 503.1646, found: 503.1646.

IR (film) ν_{max} 3032, 1735, 1456, 1387, 1338, 1269, 1246, 1203, 1135, 1058, 1016, 978, 906, 746, 696 cm^{-1}.



5ea

dibenzyl 5,5-difluoro-4-nonyl-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate(5ea) : Follow the general procedure (***GP1)***, **5ea** was obtained as a white solid (92.3 mg, 0.16 mmol, yield: 78%, d.r.=10:1) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

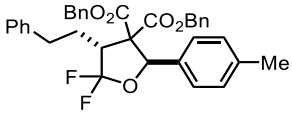
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 8H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 5.99 (d, *J* = 2.7 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.37 (d, *J* = 12.1 Hz, 1H), 3.52 – 3.40 (m, 1H), 2.31 (s, 3H), 1.40 – 1.16 (m, 16H). 0.88 (t, *J* = 6.9 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 , 166.2 , 138.9 , 134.5 , 134.2 , 132.6 , 130.8 (dd. *J* = 260.0. 255.5 Hz), 129.0 , 128.7 , 128.6 , 128.6 , 128.4 , 126.9 , 83.9 , 68.1 , 67.8 , 66.7 , 66.6 , 48.2 (t, *J* = 28.4 Hz), 31.9 , 29.6 , 29.5 , 29.3 , 26.9 , 25.5 , 22.7 , 21.2 , 14.1 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.62 – -71.54 (m) ppm;

HRMS (ESI, m/z): calculated for $C_{36}H_{43}F_2O_5^+$ $[M+H]^+$: 593.3079, found: 593.3069.

IR (film) ν_{max} 2919. 2851, 1734, 1499, 1262, 1233, 1201, 1037, 744, 698 cm^{-1}



5fa

dibenzyl 5,5-difluoro-4-phenethyl-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate (5fa) : Follow the general procedure (***GP1)***, **5fa** was obtained as a white solid (100.0 mg, 0.18 mmol, yield: 88%, d.r.=7:1) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.20, CAM solution, UV);

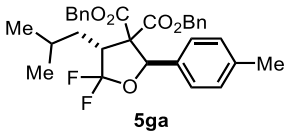
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 7H), 7.19 (t, *J* = 7.3 Hz, 4H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 4H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.03 (s, 1H), 5.22 (d, *J* = 11.9 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.76 (d, *J* = 12.1 Hz, 1H), 4.39 (d, *J* = 12.1 Hz, 1H), 3.57 (ddt, *J* = 15.0, 10.3, 4.9 Hz, 1H), 2.84 (td, *J* = 13.1, 4.7 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.31 (s, 3H), 1.93 (ddd, *J* = 17.3, 11.3, 5.5 Hz, 1H), 1.82 – 1.68 (m, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6 , 166.1 , 141.1 , 138.9 , 134.3 , 134.14, 132.4 , 130.7 (dd, *J* = 255.8, 258.3 Hz), 129.0 , 128.8 , 128.7 , 128.6 , 128.5 , 128.4 , 128.3 , 128.3 , 126.8 , 126.0 , 84.0 , 68.3 , 67.8 , 66.6 , 48.0 (t, *J* = 28.5 Hz), 33.1 , 27.3 , 21.2 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.69 (dd, *J* = 11.1, 6.7 Hz, 2F) ppm;

HRMS (ESI, m/z): calculated for $C_{35}H_{32}F_2NaO_5^+$ $[M+Na]^+$: 593.2116, found: 593.2123.

IR (film) ν_{max} 3031, 1735, 1456, 1335, 1272, 1259, 1226, 1201, 1103, 1033, 975, 909, 752, 699 cm^{-1}.



5ga

dibenzyl 5,5-difluoro-4-isobutyl-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate (5ga) : Follow the general procedure (***GP1)***, **5ga** was obtained as a white solid (41.8 mg, 0.08 mmol, yield: 40%, d.r.=50:1) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

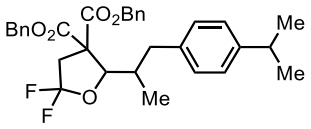
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m), 7.14 (d, *J* = 8.1 Hz), 7.07 (d, *J* = 8.0 Hz), 6.99 (d, *J* = 7.2 Hz), 5.99 (d, *J* = 3.6 Hz), 5.26 (d, *J* = 12.0 Hz), 5.15 (d, *J* = 12.0 Hz), 4.75 (d, *J* = 12.1 Hz), 4.38 (d, *J* = 12.1 Hz), 3.68 – 3.54 (m), 2.32 (s), 1.85 – 1.70 (m), 1.43 – 1.24 (m), 0.87 (dd, *J* = 13.9, 6.6 Hz) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.3, 138.9, 134.5, 134.2, 132.6 (d, *J* = 2.6 Hz), 130.8 (dd, *J* = 253.2, 261.1 Hz), 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 126.9, 84.0, 68.1, 67.8, 66.7 (d, *J* = 4.2 Hz), 45.9 (t, *J* = 28.5 Hz), 34.2, 24.8, 23.5, 21.2, 21.1 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.84 (dd, *J* = 144.6, 15.0 Hz, 1F), -71.56 (ddd, *J* = 144.8, 8.1, 2.7 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{31}H_{32}F_2NaO_5^+$ $[M+Na]^+$: 545.2116, found: 545.2121.

IR (film) ν_{max} 3037, 2961, 1735, 1500, 1469, 1379, 1279, 1231, 1200, 1166, 1123, 1089, 1053, 1040, 1020, 941, 902, 805, 744, 697, cm^{-1}.



6aa

dibenzyl 5,5-difluoro-2-(1-(4-isopropylphenyl)propan-2-yl)dihydrofuran-3,3(2H)-dicarboxylate (6aa): Follow the general procedure, **6aa** was obtained as a colorless oil (69.7 mg, 0.13 mmol, yield: 65%, d.r.=1:1) after flash chromatography (Petroleum ether/EtOAc = 50:1, TLC Rf = 0.25, CAM solution, UV);

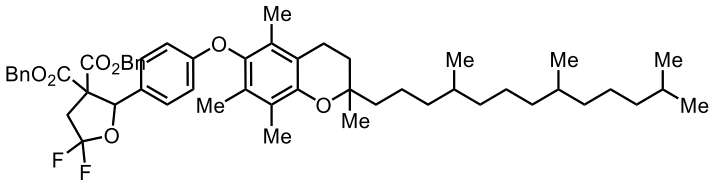
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 6H), 7.25 – 7.20 (m, 4H), 7.10 (d, *J* = 5.8 Hz, 2H), 6.94 (dd, *J* = 17.7, 7.1 Hz, 2H), 5.23 – 5.01 (m, 4.5H), 4.79 (dd, *J* = 7.5, 3.0 Hz, 0.5H), 3.42 – 3.20 (m, 1H), 2.96 – 2.81 (m, 2.5H), 2.73 (dd, *J* = 13.6, 5.5 Hz, 0.5H), 2.41 – 2.27 (m, 1H), 2.08 – 1.90 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 6H), 0.76 (d, *J* = 6.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 , 168.3 , 167.0 , 166.6 , 146.6 , 146.5 , 136.7 , 136.5 , 134.6 , 134.6 , 134.3 , 134.3 , 130.1 (t, *J* = 254.5 Hz) , 129.6 (t, *J* = 24.5 Hz) , 129.3 , 129.0 , 128.8 , 128.7 , 128.6 , 128.5 , 128.3 , 128.3 , 126.3 , 126.2 , 87.8 , 86.6 , 68.2 , 68.2 , 68.2 , 61.2 , 61.2 , 42.6 (dd, *J* = 35.1, 30.5 Hz), 41.4 (dd, *J* = 33.9, 31.3 Hz), 40.4 , 37.9 , 36.4 , 33.7 , 24.0 , 15.7 , 13.3 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.96 (ddd, *J* = 144.5, 16.6, 8.5 Hz, 0.5F), -59.98 (ddd, *J* = 143.9, 12.5, 10.4 Hz, 0.5F), -68.72 – -69.80 (m, 0.5F), -70.36 – -71.46 (m, 0.5F) ppm;

HRMS (ESI, m/z): calculated for $C_{31}H_{32}F_2NaO_5^+$ $[M+Na]^+$: 545.2116, found: 545.2114.

IR (film) ν_{max} 2961, 1740, 1456, 1266, 1242, 1213, 1120, 1058, 750, 697 cm^{-1}.



6ab

dibenzyl 5,5-difluoro-2-(4-((2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)oxy)phenyl)dihydrofuran-3,3(2H)-dicarboxylate (6ab): Follow the general procedure (***GP2)***, **6ab** was obtained as a colorless(143.8 mg, 0.16 mmol, yield: 82%) after flash chromatography (Petroleum ether/EtOAc = 20:1, TLC Rf =0.30, UV);

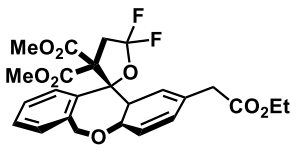
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (ddd, *J* = 21.1, 14.7, 7.0 Hz, 10H), 6.98 (d, *J* = 6.4 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.11 (d, *J* = 3.3 Hz, 1H), 5.18 (d, *J* = 2.6 Hz, 2H), 4.79 (d, *J* = 12.2 Hz, 1H), 4.36 (d, *J* = 12.2 Hz, 1H), 3.53 – 3.37 (m, 1H), 2.92 (ddd, *J* = 14.9, 8.5, 2.9 Hz, 1H), 2.59 (t, *J* = 6.7 Hz, 2H), 2.12 (s, 3H), 1.95 (s, 3H), 1.91 (s, 3H), 1.89 – 1.78 (m, 2H), 1.66 – 1.37 (m, 7H), 1.34 – 1.22 (m, 11H), 1.19 – 1.04 (m, 7H), 0.88 (t, *J* = 6.6 Hz, 12H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2 , 166.2 , 159.4 , 148.8 , 143.1 , 134.5 , 134.1 , 130.0 (dd, *J* = 256.9, 253.9 Hz), 128.6 , 128.6 , 128.5 , 128.4 , 128.4 , 128.1 , 128.0 , 127.9 , 127.0 , 126.0 , 123.3 , 117.9 , 114.5 , 84.3 , 75.0 , 68.3 , 67.9 , 63.6 , 63.5 , 40.3 (dd, *J* = 34.1, 30.5 Hz), 39.96 , 39.33 , 37.6 , 37.4 , 37.4 , 37.3 , 32.8 , 32.7 , 31.2 , 31.2 , 27.95 , 24.79 , 24.42 , 23.8 , 23.8 .22.7 , 22.6 , 21.0 , 20.6 , 19.7 (t, *J* = 6.9 Hz), 12.8 , 11.9 , 11.8 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.19 (ddd, *J* = 144.0, 16.9, 8.6 Hz, 1F), -71.75 – -72.23 (m, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{55}H_{70}F_2NaO_7^+$ $[M+Na]^+$: 903.4987, found: 903.4991.

IR (film) ν_{max} 2927, 2867, 1740, 1611, 1507, 1456, 1411, 1378, 1251, 1161, 1110, 1052, 939, 911, 737, 696 cm^{-1}.



6bc

dimethyl 2-(2-ethoxy-2-oxoethyl)-5',5'-difluoro-4',5'-dihydro-3'H,6H-spiro[dibenzo[b,e]oxepine-11,2'-furan]-3',3'-dicarboxylate (6bc): Follow the general procedure (***GP1)***, **6bc** was obtained as a colorless oil (29.4 mg, 0.06 mmol, yield: 30%) after flash chromatography (Petroleum ether/EtOAc = 5:1, TLC Rf = 0.10, CAM solution, UV);

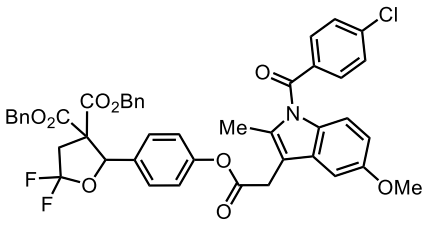
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.51 (d, *J* = 2.1 Hz, 1H), 7.27 – 7.19 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.91 – 6.87 (m, 1H), 5.40 (d, *J* = 15.5 Hz, 1H), 4.94 (d, *J* = 15.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.58 (d, *J* = 3.5 Hz, 2H), 3.55 (s, 3H), 3.48 (s, 3H), 3.31 (dt, *J* = 14.5, 7.4 Hz, 1H), 3.18 (dt, *J* = 14.3, 9.4 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4 , 167.4 , 167.2 , 152.9 , 136.8 , 136.6 , 135.1 , 131.0 , 130.7 , 129.7 (t, *J* = 253.7 Hz), 128.5 , 126.6 , 126.4 , 126.1 , 125.3 , 121.1 , 94.0 , 73.0 , 67.1 , 60.9 , 53.0 , 52.9 , 42.3 (t, *J* = 29.9 Hz), 41.0 , 14.1 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.14 – -64.23 (m, 2F) ppm;

HRMS (ESI, m/z): calculated for $C_{25}H_{24}F_2NaO_8^+$ $[M+Na]^+$: 513.1337, found: 513.1335.

IR (film) ν_{max} 2953, 1739, 1499, 1434, 1340, 1251, 1146, 1103, 1031, 946, 772,756 cm^{-1}.



6ad

dibenzyl 2-(4-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxy)phenyl)-5,5-difluorodihydrofuran-3,3(2H)-dicarboxylate (6ad): Follow the general procedure (***GP1)***, **6ad** was obtained as a coless oil (114.6 mg, 0.14 mmol, yield: 71%) after flash chromatography (Petroleum ether/EtOAc = 5:1, TLC Rf = 0.25, UV);

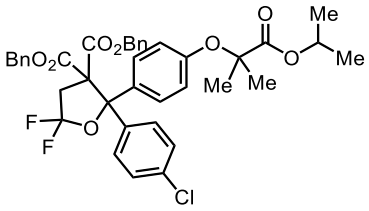
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.22 – 7.17 (m, 5H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 6.3 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.11 (d, *J* = 3.3 Hz, 1H), 5.22 – 5.12 (m, 2H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 3.91 (s, 2H), 3.83 (s, 3H), 3.43 (td, *J* = 15.6, 7.7 Hz, 1H), 2.92 (ddd, *J* = 14.9, 8.8, 3.7 Hz, 1H), 2.47 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9 , 168.2 , 168.0 , 166.1 , 156.1 , 151.1 , 139.3 , 136.2 , 134.4 , 134.0 , 133.7 , 132.4 , 131.2 , 130.8 , 130.4 , 130.0 (dd, *J* = 257.6 254.8 Hz), 129.1 , 128.7 , 128.6 , 128.4 , 127.7 , 121.3 , 115.0 , 111.8 , 111.7 , 101.2 , 83.7 , 68.4 , 68.1 , 63.6 , 63.5 , 55.7 , 40.4 (dd, *J* = 34.4, 30.2 Hz), 30.5 , 13.4 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.47 (ddd, *J* = 143.8, 16.1, 8.8 Hz, 1F), -71.73 (ddt, *J* = 143.5, 7.3, 3.0 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{45}H_{36}ClF_2NNaO_9^+$ $[M+Na]^+$: 830.1944, found: 830.1949.

IR (film) ν_{max} 3034, 2957, 1738, 1683, 1508, 1478, 1456, 1323, 1122, 1014, 926, 834, 753, 697 cm^{-1}.



6ae

dibenzyl 2-(4-chlorophenyl)-5,5-difluoro-2-(4-((1-isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)dihydrofuran-3,3(2H)-dicarboxylate(6ae): Follow the general procedure (***GP1)***, **6ae** was obtained as a coless oil (64.9 mg, 0.09 mmol, yield: 46%) after flash chromatography (Petroleum ether/EtOAc = 20:1, TLC Rf = 0.2, CAM solution, UV);

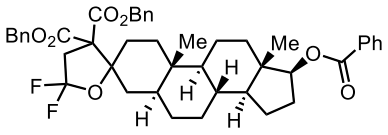
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 8H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.11 – 7.02 (m, 6H), 6.66 (d, *J* = 9.0 Hz, 2H), 5.04 (hept, *J* = 6.3 Hz, 1H), 4.90 – 4.77 (m, 4H), 3.44 (dt, *J* = 15.5, 9.9 Hz, 1H), 3.28 (ddd, *J* = 15.5, 8.8, 6.5 Hz, 1H), 1.55 (s, 6H), 1.16 (d, *J* = 6.7 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3 , 167.5 , 167.0 , 155.5 , 139.2 , 129.9 (t, *J* = 253.7 Hz), 128.7 , 128.6 , 128.6 , 128.5 , 128.5 , 128.5 , 128.2 , 127.8 , 117.7 , 94.5 , 79.1 , 69.0 , 68.4 , 68.3 , 42.9 (t, *J* = 31.4 Hz), 25.3 , 21.5 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.89 – -60.48 (m, 2F) ppm;

HRMS (ESI, m/z): calculated for $C_{39}H_{37}ClF_2NaO_8^+$ $[M+Na]^+$: 729.2043, found: 729.2045.

IR (film) ν_{max} 2983, 1731, 1608, 1509, 1289, 1148, 1105, 1010, 934, 829, 750, 697 cm^{-1}.



6af

dibenzyl (5S,8R,9S,10S,13S,14S,17S)-17-(benzoyloxy)-5',5'-difluoro-10,13-dimethyloctadecahydro-3'H-spiro[cyclopenta[a]phenanthrene-3,2'-furan]-3',3'-dicarboxylate (6af): Follow the general procedure (***GP1)***, **6af** was obtained as a colorless oil (85.9 mg, 0.12 mmol, yield: 58%) after flash chromatography (Petroleum ether/EtOAc = 5:1, TLC Rf = 0.25, CAM solution, UV);

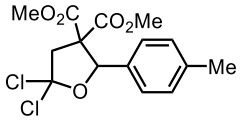
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.27 (m, 10H), 5.23 (dd, *J* = 14.7, 12.1 Hz, 2H), 5.10 (t, *J* = 12.1 Hz, 2H), 4.81 (t, *J* = 8.3 Hz, 1H), 3.09 (t, *J* = 9.0 Hz, 2H), 2.34 – 2.21 (m, 1H), 1.86 – 1.73 (m, 2H), 1.71 – 1.58 (m, 5H), 1.55 – 1.43 (m, 3H), 1.38 – 1.24 (m, 5H), 1.23 – 1.14 (m, 2H), 1.14 – 0.97 (m, 3H), 0.90 (s, 3H), 0.76 (m, 1H), 0.57 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 , 167.4 , 166.5 , 134.6 , 134.5 , 132.7 , 130.7 , 129.6 (t, *J* = 254.5 Hz) , 129.5 , 128.7 , 128.6 , 128.6 , 128.5 , 128.3 , 90.2 , 83.3 , 67.8 , 65.5 , 53.4 , 50.6 , 43.0 , 41.2 (t, J = 32.8 Hz) , 41.2 , 36.9 , 35.2 , 35.1 , 34.6 , 34.0 , 31.2 , 28.0 , 27.9 , 27.67 , 23.6 , 20.4 , 12.4 , 11.3 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.07 (dt, *J* = 146.6, 8.8 Hz, 1F), -59.00 (dt, *J* = 146.6, 9.0 Hz, 1F) ppm;

HRMS (ESI, m/z): calculated for $C_{45}H_{50}F_2NaO_7^+$ $[M+Na]^+$: 763.3422, found: 763.3428.

IR (film) ν_{max} 2029, 1741, 1716, 1451, 1276, 1115, 1099, 907, 7751, 712, 697 cm^{-1}.



9

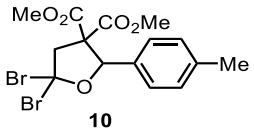
dimethyl 5,5-dichloro-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate (9) : Follow the general procedure (***GP3)***, **9** was obtained as a white solid (38.0 mg, 0.11 mmol, yield: 55%) after flash chromatography (Petroleum ether/EtOAc = 5:1, TLC Rf = 0.20, UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 6.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 3.82 (s, 3H), 3.62 (s, 3H), 3.25 (d, *J* = 17.5 Hz, 1H), 3.05 (d, *J* = 17.5 Hz, 1H), 2.32 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9 , 168.1 , 167.7 , 139.1 , 133.1 , 128.8 , 128.4 , 63.4 , 62.3 , 53.3 , 52.9 , 35.3 , 21.1 ppm;

HRMS (ESI, m/z): calculated for $C_{15}H_{16}Cl_2NaO_5^+$ $[M+Na]^+$: 369.0272, found: 369.0280.

IR (film) ν_{max} 2952, 1742, 1714, 1500, 1430, 1413, 1309, 1288, 1249, 1195, 1065, 953, 889 cm^{-1}.



10

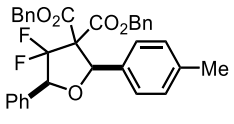
dimethyl 5,5-dibromo-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate(10): Follow the general procedure (***GP3)***, **10** was obtained as a white solid (13.0 mg, 0.03 mmol, yield: 15%) after flash chromatography (Petroleum ether/EtOAc = 10:1, TLC Rf = 0.30, UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 3.84 (s, 3H), 3.48 (d, *J* = 18.0 Hz, 1H), 3.29 (s, 3H), 2.96 (d, *J* = 18.0 Hz, 1H), 2.33 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7 , 168.8 , 167.2 , 139.1 , 131.3 , 129.0 , 126.1 , 82.4 , 61.9 , 53.6 , 52.9 , 36.2 , 21.2 ppm;

HRMS (ESI, m/z): calculated for $C_{15}H_{16}Br_2NaO_5^+$ $[M+Na]^+$: 456.9260, found: 456.9260.

IR (film) ν_{max} 2956, 1795, 1738, 1436, 1400, 1270, 1207, 1181, 1071, 1031, cm^{-1}.



11

dibenzyl 4,4-difluoro-5-phenyl-2-(p-tolyl)dihydrofuran-3,3(2H)-dicarboxylate(11) : Follow the general procedure (***GP4)***, **11** was obtained as a white solid (78.0 mg, 0.14 mmol, yield: 72%, d.r.> 50:1) after flash chromatography (Petroleum ether/EtOAc = 20:1, TLC Rf = 0.25, CAM solution, UV);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.28 – 7.17 (m, 8H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 5.80 (s, 1H), 5.28 – 5.14 (m, 3H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 2.33 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (d, *J* = 3.9 Hz), 163.0 (d, *J* = 6.7 Hz), 138.7 , 134.7 , 134.1 , 132.7 , 131.7 , 128.9 , 128.8 , 128.4 , 128.3 , 128.2 , 128.0 , 127.8 , 126.9 , 126.5 (dd, *J* = 279.8, 249.2 Hz), 85.3 (dd, *J* = 35.2, 24.6 Hz), 81.6 (d, *J* = 2.9 Hz), 70.6 (dd, *J* = 24.7, 19.1 Hz), 67.9 , 67.6 , 21.3 ppm;

^{19}F NMR (376 MHz, $CDCl_3$) δ -88.24 (dd, *J* = 241.1, 20.4 Hz), -108.95 (dd, *J* = 241.0, 8.9 Hz) ppm;

HRMS (ESI, m/z): calculated for $C_{33}H_{28}F_2NaO_5^+$ $[M+Na]^+$: 565.1803, found: 565.1809.

IR (film) ν_{max} 3034, 1739, 1517, 1498, 1456, 1379, 1313, 1270, 1231, 1120, 1068, 1038, 997, 907, 749, 696 cm^{-1}.

7. References:

(1) A. Bugarin, K. D. Jones, B. T. Connell, *Chem. Commun.* 2010, **46**, 1715-1717.

(2) F. Tian, V. Kruger, O. Bautista, J.-X. Duan, A.-R. Li, W. R. Dolbier and Q.-Y. Chen, *Org. Lett.*, 2000, **2**, 563-564.

(3) F. de Nanteuil, J. Waser, *Angew. Chem. Int. Ed.* 2013, **52**, 9009-9013.

(4) (a) A. Kazia, R. Melngaile, A. Mishnev and J. Veliks, *Org. Biomol. Chem.*, 2020, **18**, 1384-1388. (b) A. Sperga, R. Melngaile, A. Kazia, S. Belyakov and J. Veliks, *J. Org. Chem.*, 2021, **86**, 3196-3212.

(5) M. S. Baird, V. M. Boitsov, A. V. Stepakov, A. P. Molchanov, J. Kopf, M. Rajaratnam, R. R. Kostikov, *Tetrahedron* 2007, **63**, 7717-7726.

(6) S. Hajra, S. M. Aziz, R. Maji, *RSC Advances* 2013, **3**, 10185-10188.

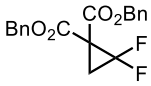
(7) Frischi, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucii, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian 09, Revision D.01;

(8) (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652. (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789. (*c*) R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2011, **2**, 2810-2817.

(9) (*a*) M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* 1996, **255**, 327-335. (*b*) B. Mennucci, E. Cancès, J. Tomasi, *J. Phys. Chem. B* 1997, **101**, 10506-10517.

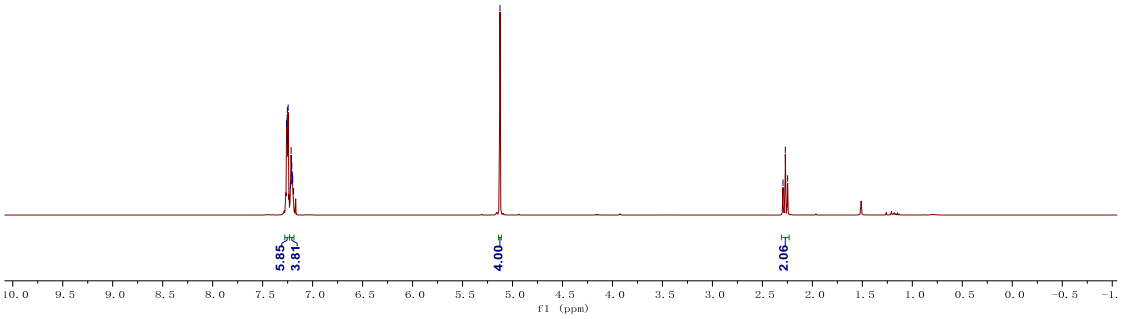
(10) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215-241.

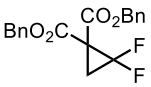
8. NMR-Spectra of New Compounds



1a

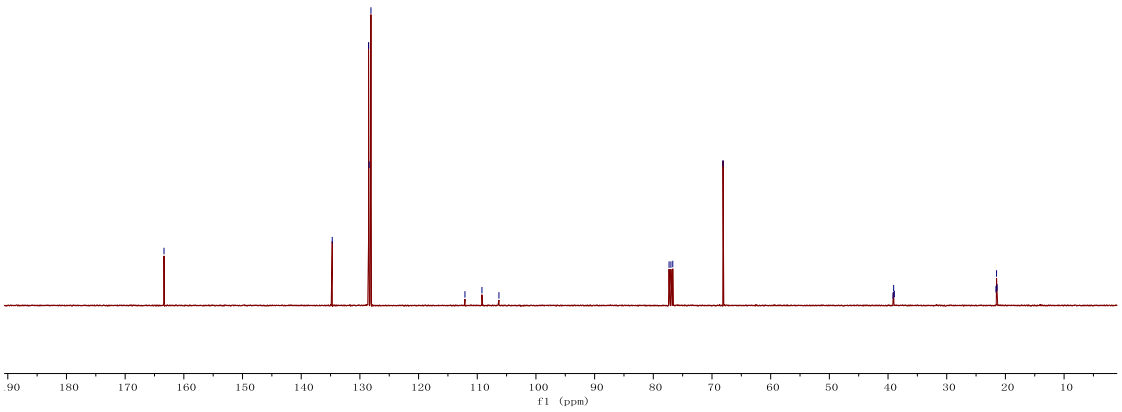
^{1}H NMR (400 MHz, $CDCl_3$)

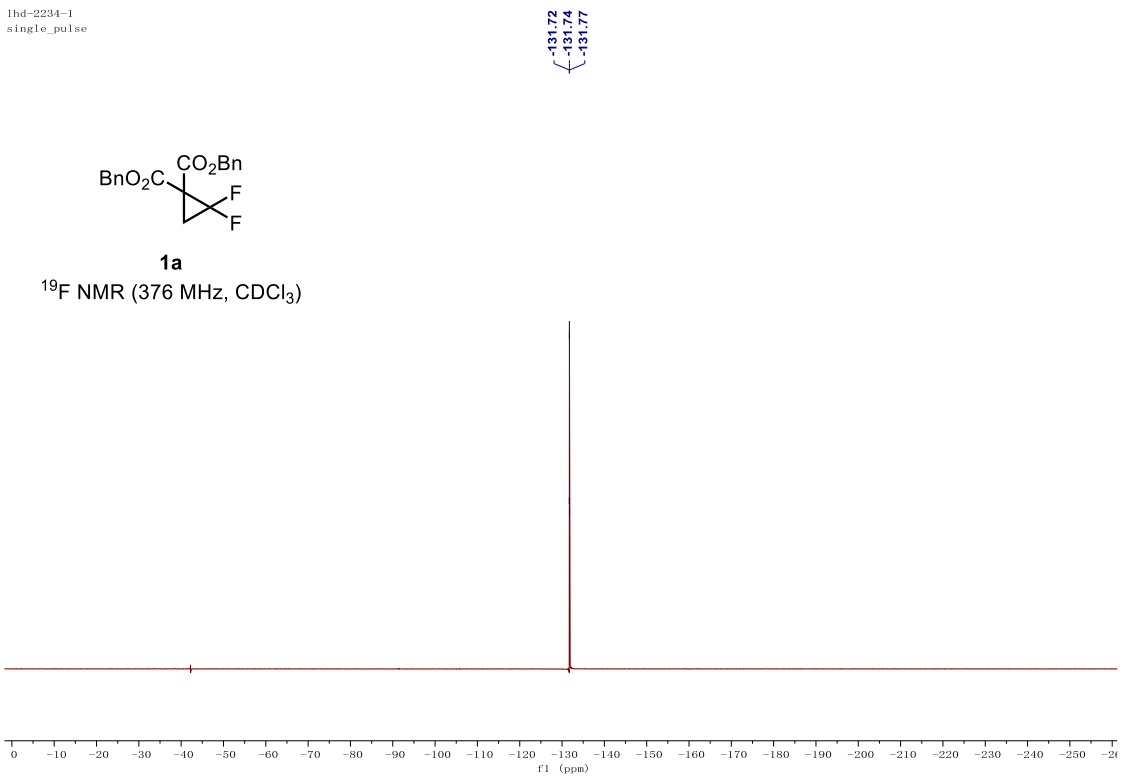


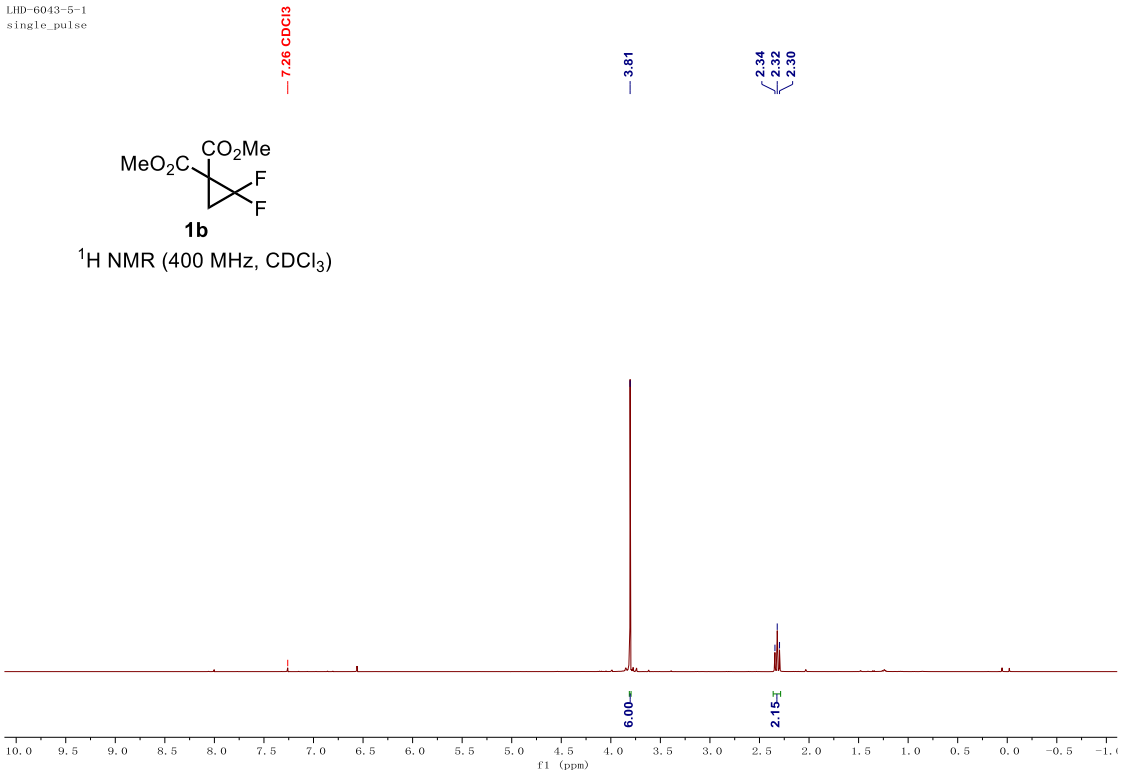


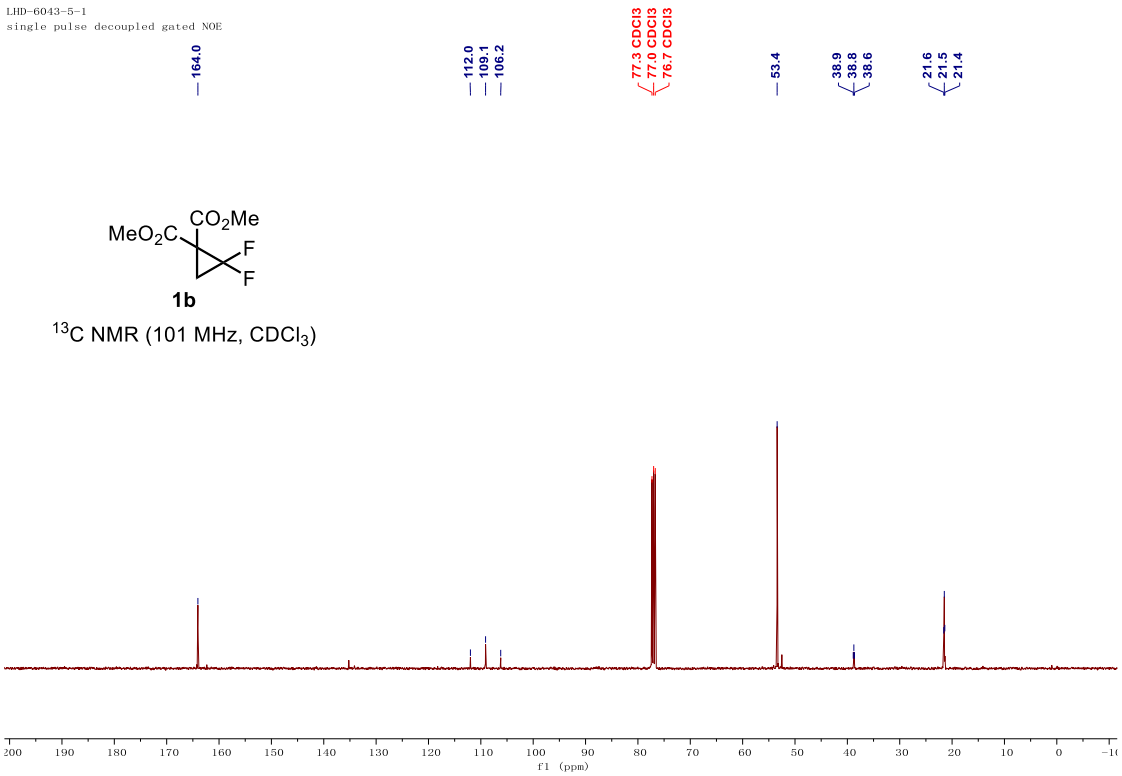
1a

^{13}C NMR (101 MHz, $CDCl_3$)



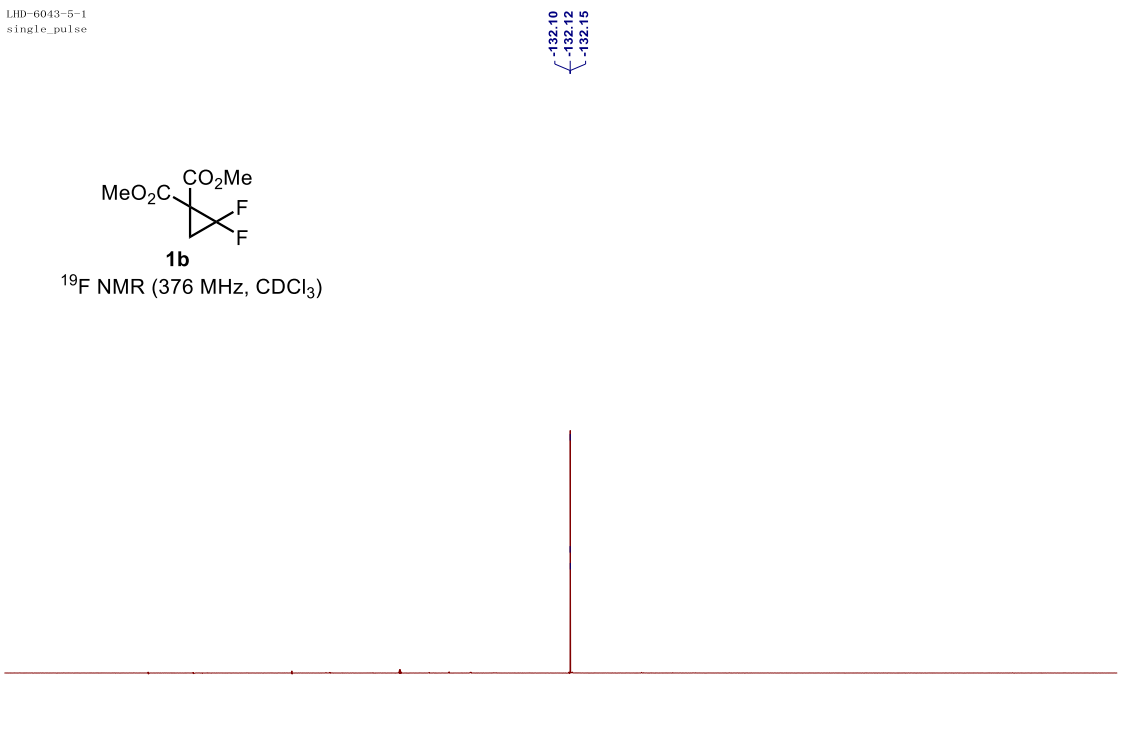

lhd-2234-1
single_pulse
-131.72
-131.74
-131.77
BnO2C
CO2Bn
F
F
1a
19F NMR (376 MHz, CDCl3)
f1 (ppm)


LHD-6043-5-1
single_pulse
7.26 CDCl3
3.81
2.34
2.32
2.30
MeO2C
CO2Me
F
F
1b
1H NMR (400 MHz, CDCl3)
6.00
2.15
f1 (ppm)



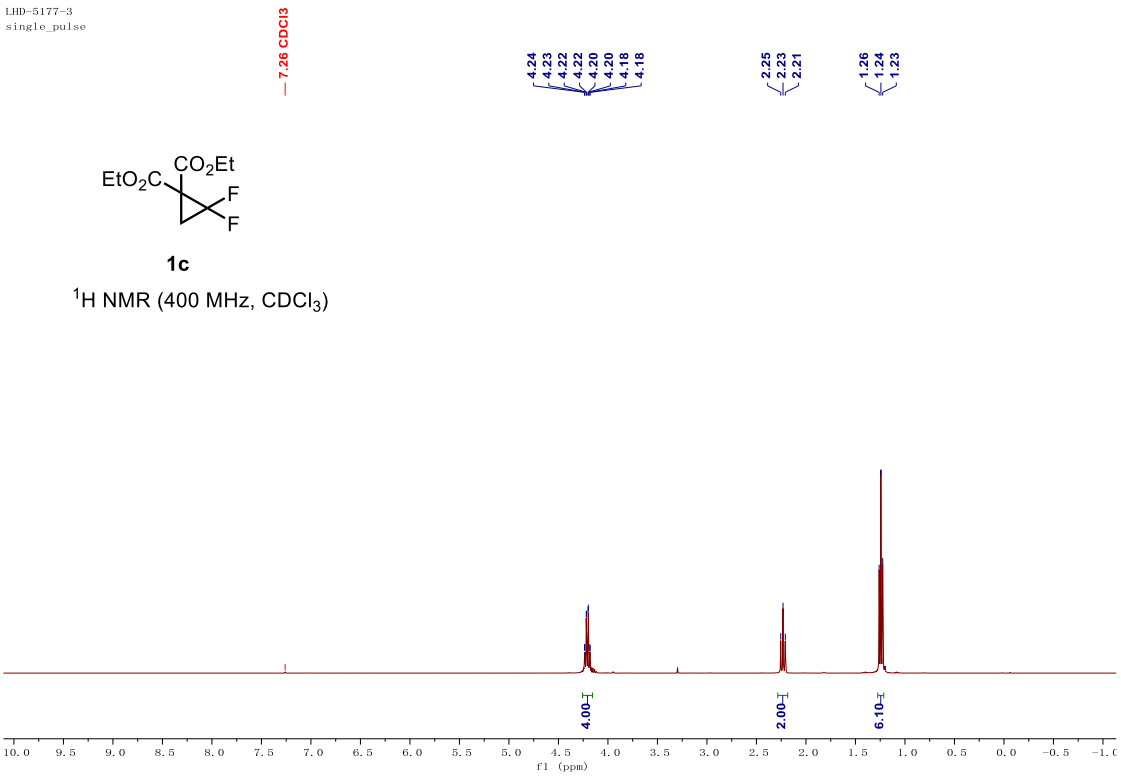
1b

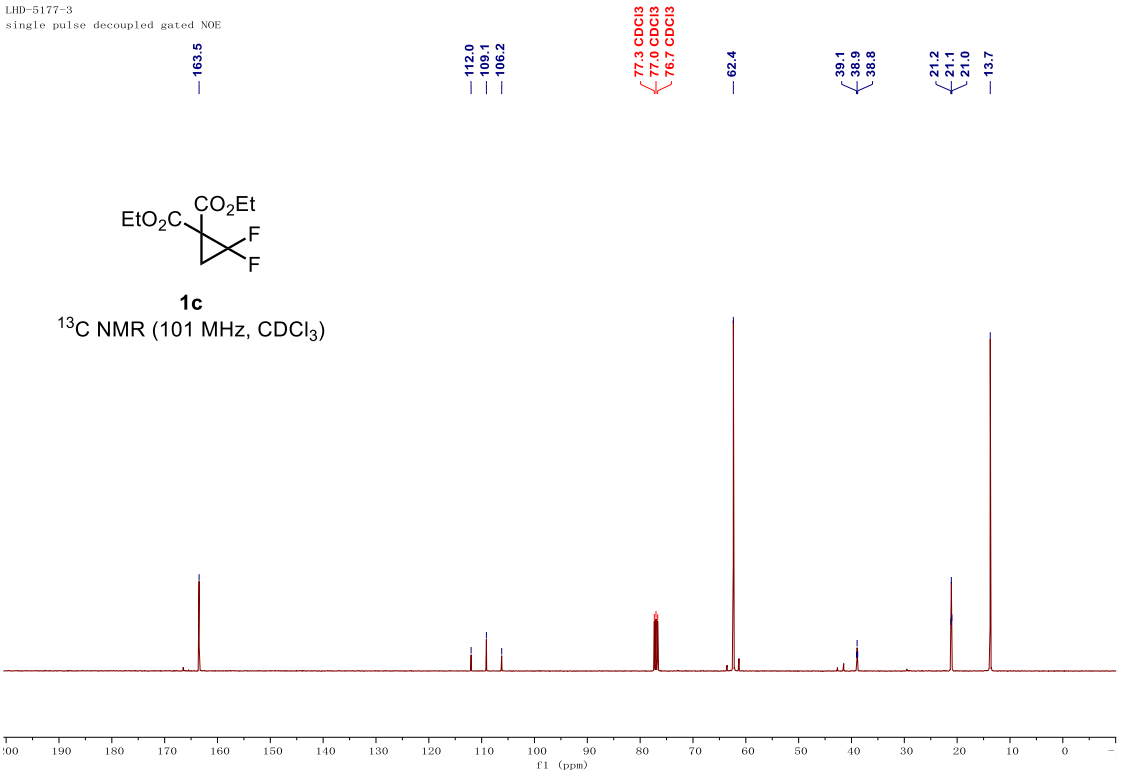
^{13}C NMR (101 MHz, $CDCl_3$)



1b

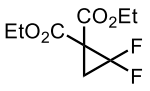
^{19}F NMR (376 MHz, $CDCl_3$)


LHD-5177-3
single_pulse
7.26 CDCl3
4.24
4.23
4.22
4.22
4.20
4.20
4.18
4.18
2.25
2.23
2.21
1.26
1.24
1.23
EtO2C
CO2Et
F
F
1c
1H NMR (400 MHz, CDCl3)
4.00
2.00
6.10
f1 (ppm)


LHD-5177-3
single pulse decoupled gated NOE
163.5
112.0
109.1
106.2
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
62.4
39.1
38.9
38.8
21.2
21.1
21.0
13.7
EtO2C
CO2Et
F
F
1c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

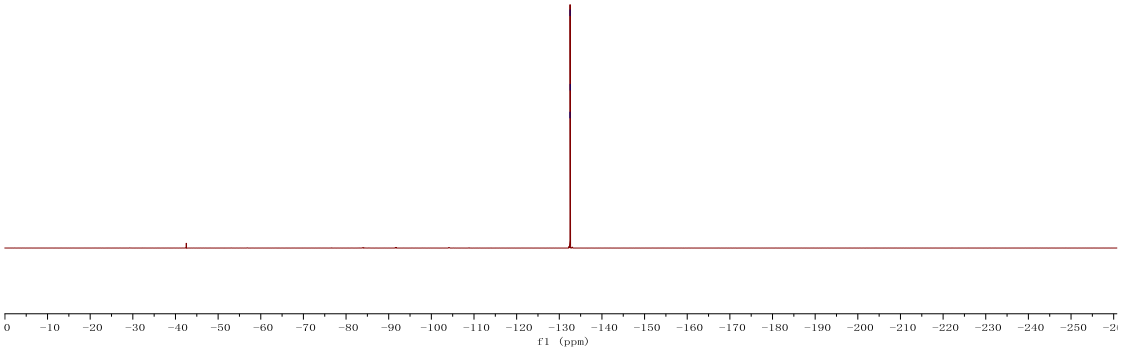
LHD-5177-3
single_pulse

-132.50
-132.53
-132.55



1c

^{19}F NMR (376 MHz, $CDCl_3$)



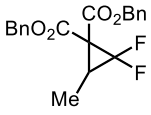
LHD-6021-1
single_pulse

7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.25
7.24

5.21
5.18
5.17
5.17
5.13

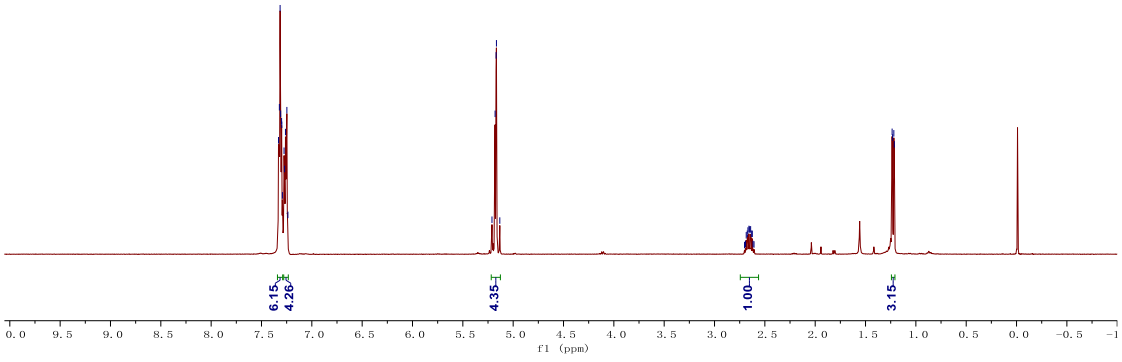
2.70
2.69
2.68
2.67
2.67
2.66
2.65
2.64
2.63
2.62
2.62
2.61

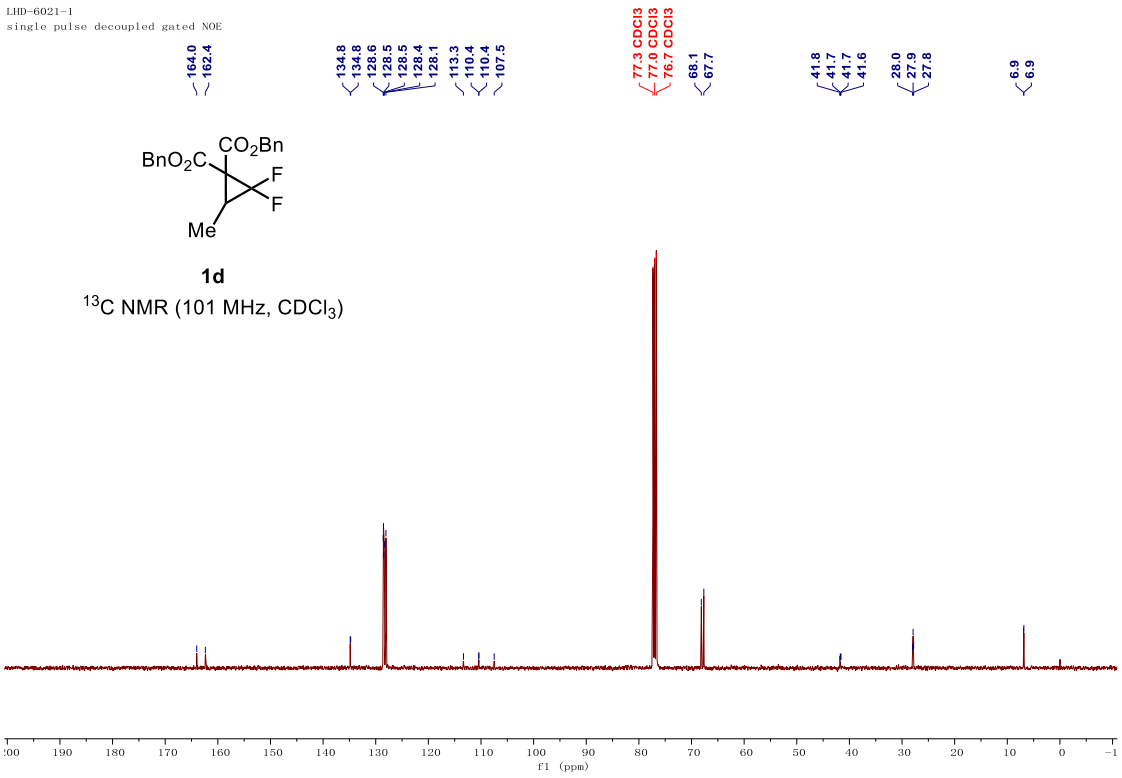
1.24
1.23
1.22
1.21



1d

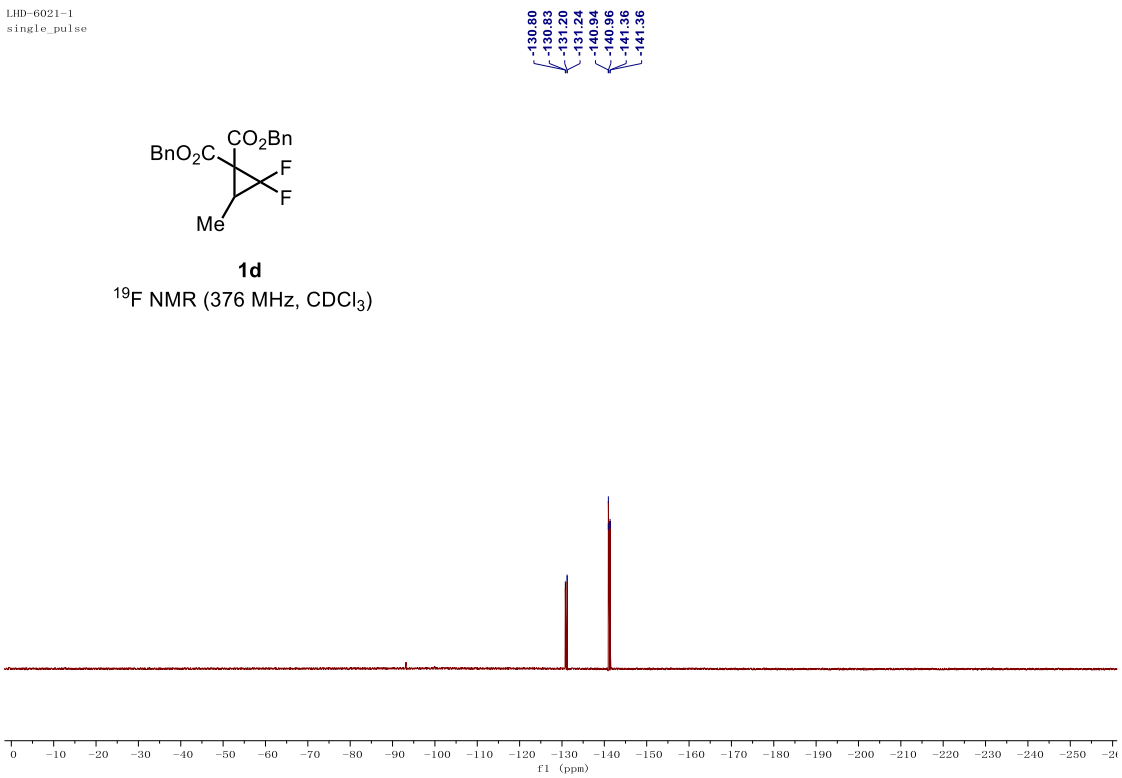
^{1}H NMR (400 MHz, $CDCl_3$)





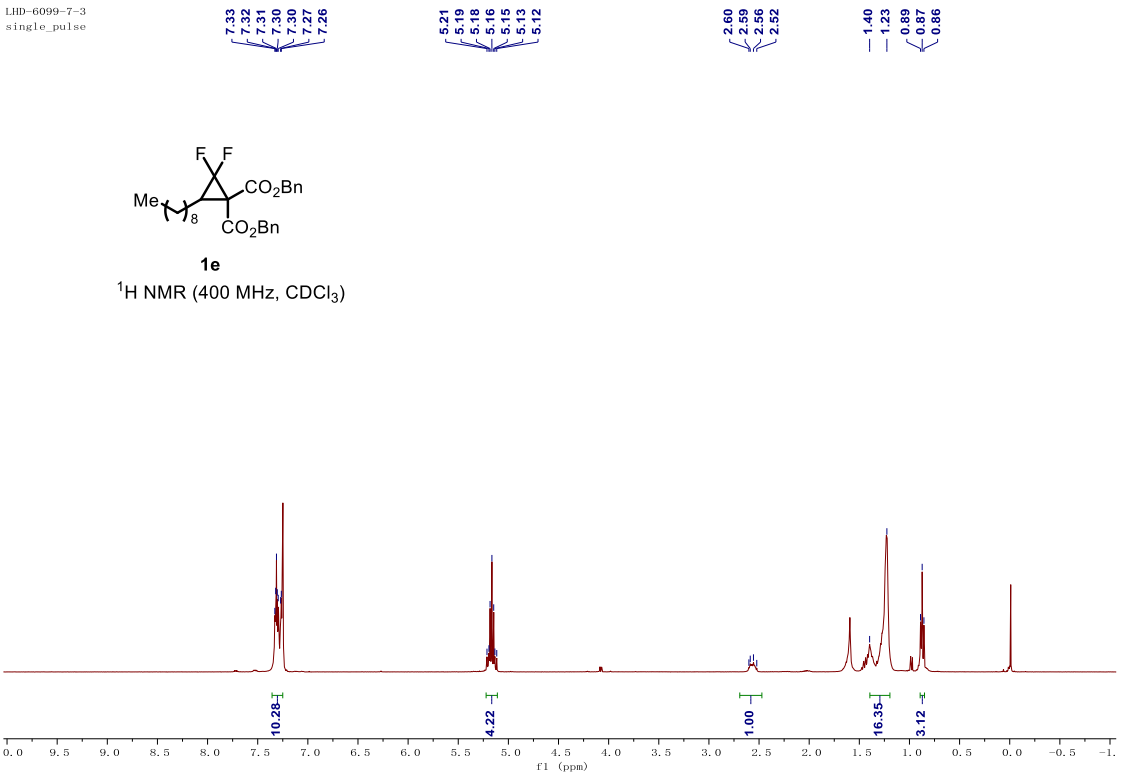
1d

^{13}C NMR (101 MHz, $CDCl_3$)



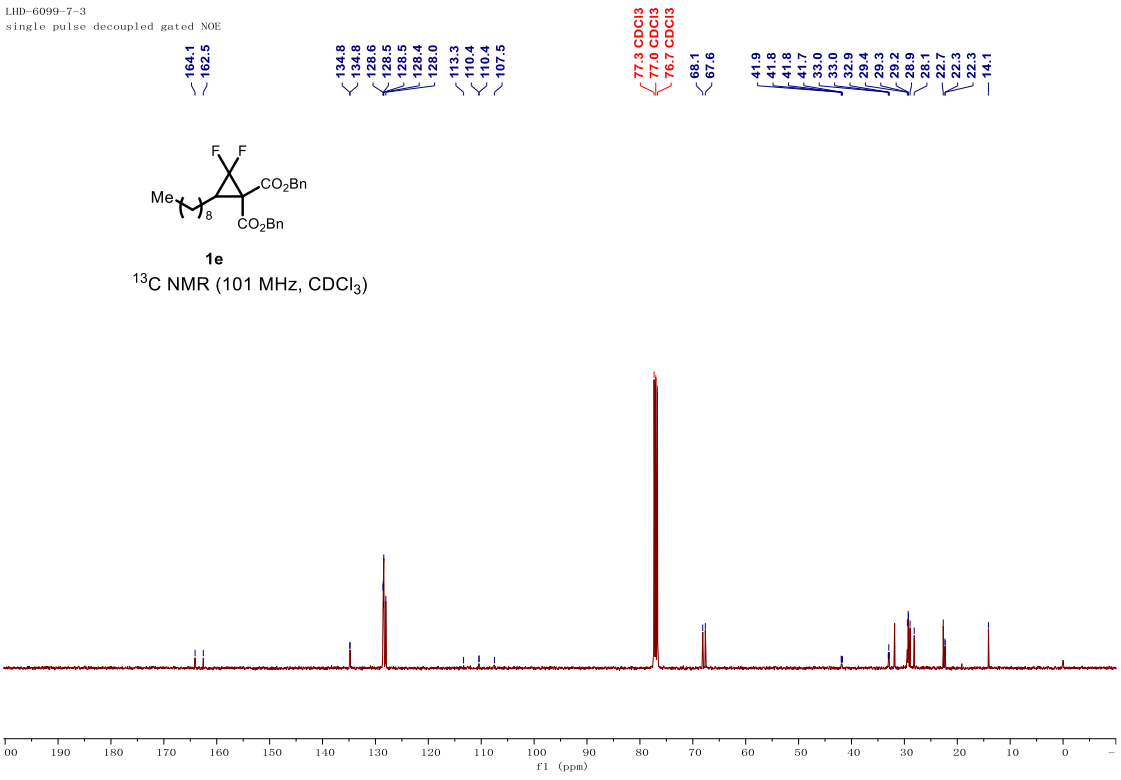
1d

^{19}F NMR (376 MHz, $CDCl_3$)



1e

^{1}H NMR (400 MHz, $CDCl_3$)

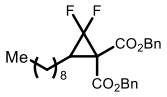


1e

^{13}C NMR (101 MHz, $CDCl_3$)

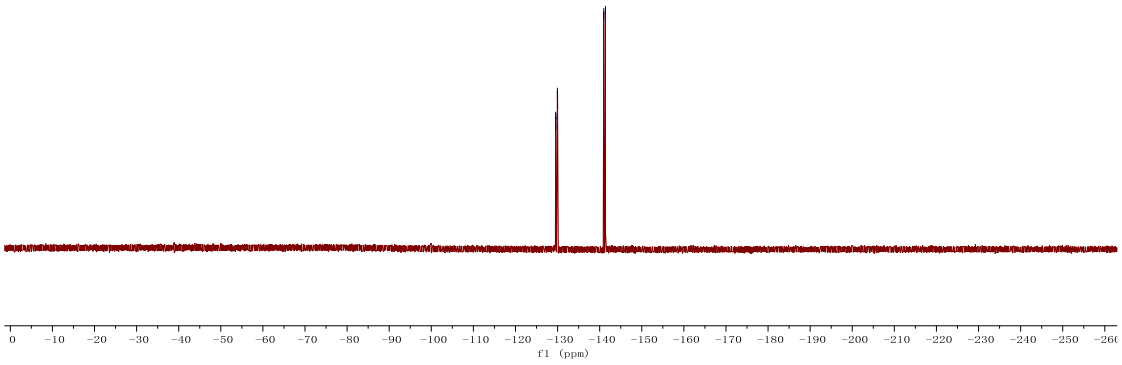
LHD-6099-7-3
single_pulse

-129.54
-129.55
-129.58
-129.59
-129.95
-129.96
-129.99
-130.00
-140.96
-140.97
-141.37
-141.38



1e

^{19}F NMR (376 MHz, $CDCl_3$)



LHD-6073-3-4
single_pulse

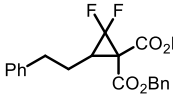
7.33
7.32
7.32
7.30
7.29
7.28
7.26
7.24
7.23
7.21
7.19
7.17
7.10
7.09

5.21
5.19
5.17
5.17
5.16
5.14
5.13

2.75
2.74
2.71
2.70
2.68
2.66
2.64
2.62
2.61
2.59
2.58
2.57
2.56

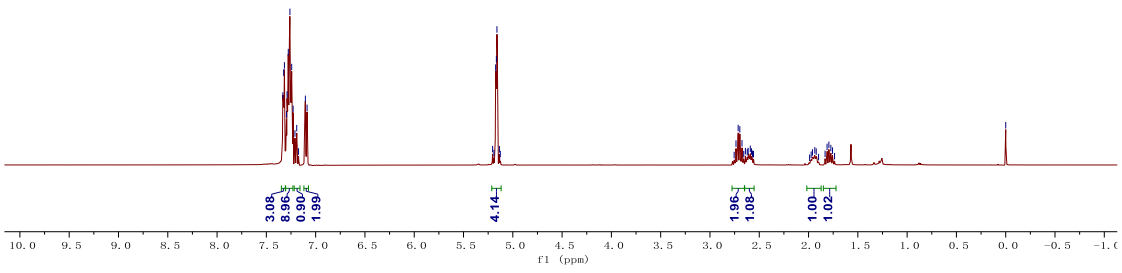
1.99
1.97
1.96
1.94
1.92
1.90
1.83
1.81
1.79
1.77
1.76
1.74

-0.00



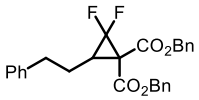
1f

^{1}H NMR (400 MHz, $CDCl_3$)



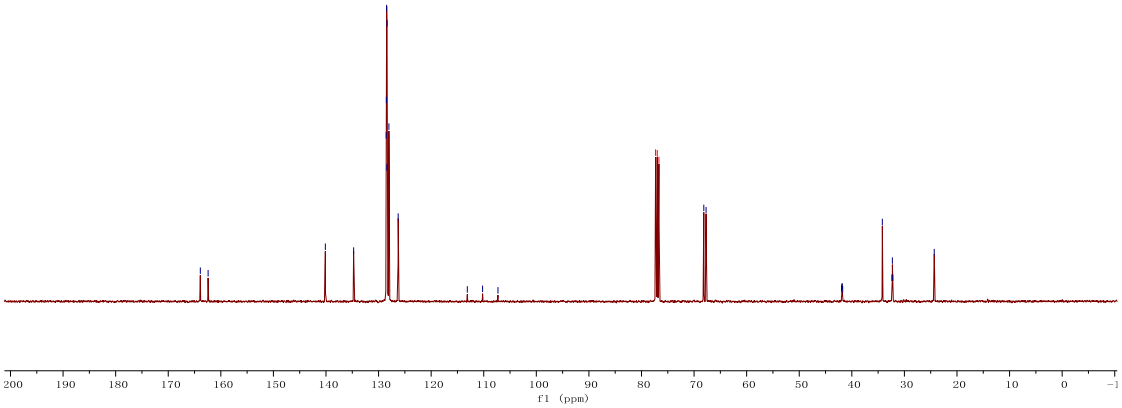
LHD-6073-3-2
single pulse decoupled gated NOE

163.9
162.4
140.1
134.7
128.6
128.5
128.5
128.4
128.4
128.0
126.3
113.1
110.2
107.3
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
68.1
67.7
42.0
41.9
41.8
41.7
34.2
32.4
32.3
32.2
24.3



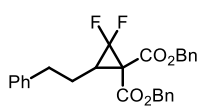
1f

^{13}C NMR (101 MHz, $CDCl_3$)



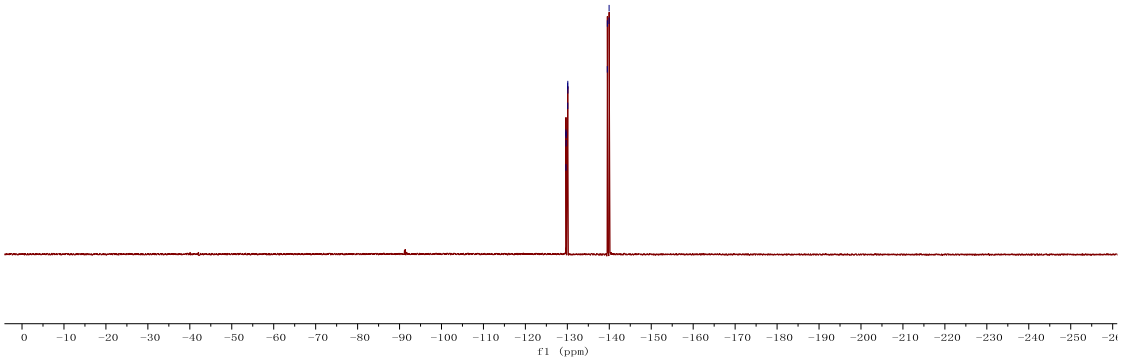
LHD-6071-3-5
single_pulse

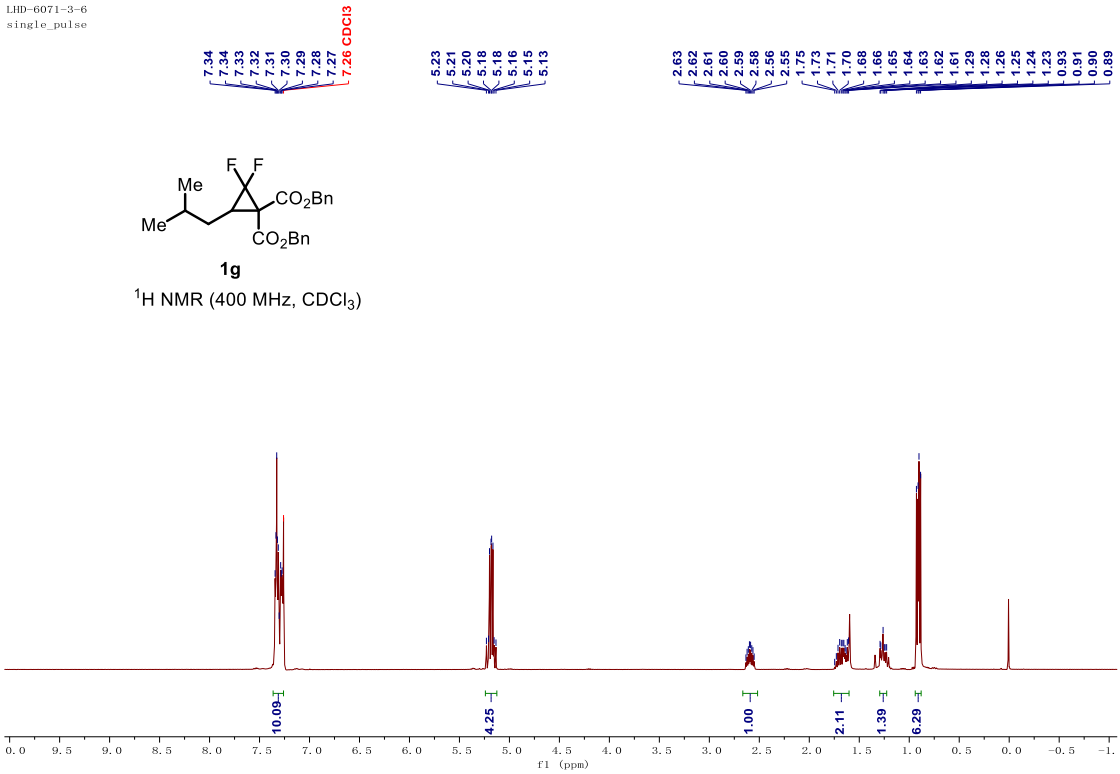
-129.66
-129.67
-129.70
-129.71
-130.07
-130.09
-130.11
-130.12
-139.53
-139.54
-139.94
-139.95



1f

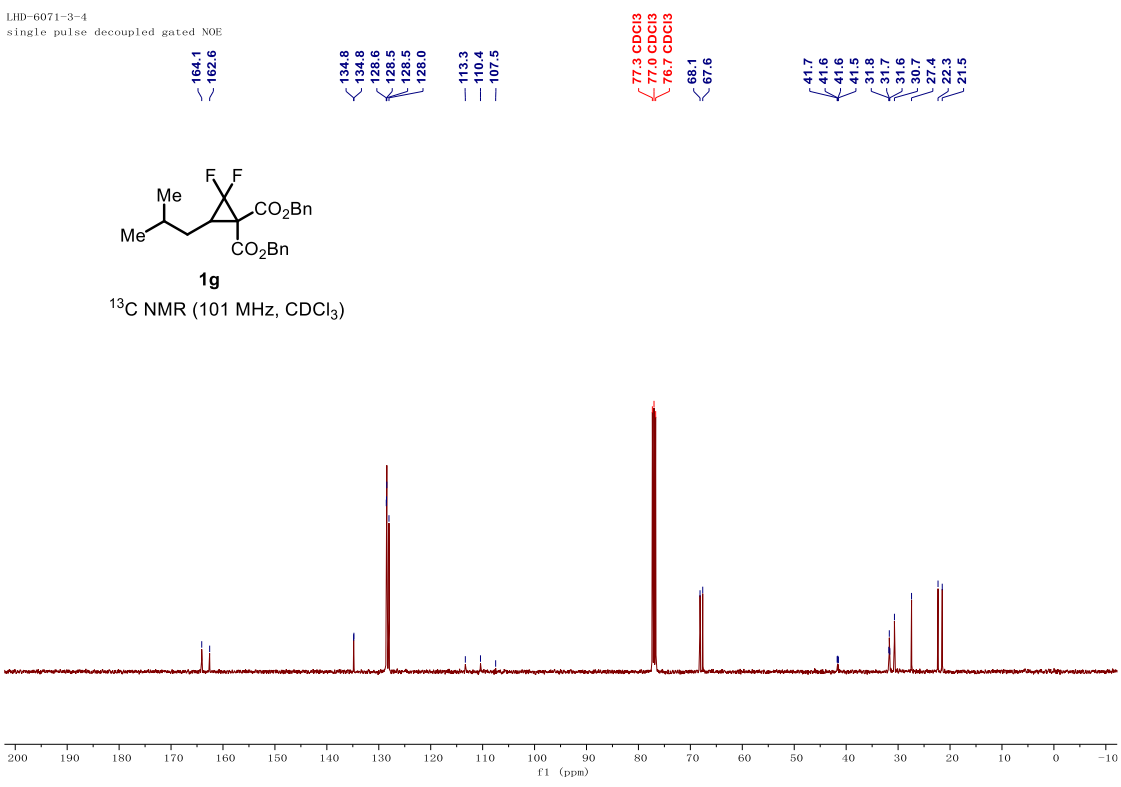
^{19}F NMR (376 MHz, $CDCl_3$)





1g

^{1}H NMR (400 MHz, $CDCl_3$)

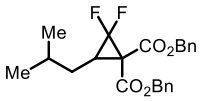


1g

^{13}C NMR (101 MHz, $CDCl_3$)

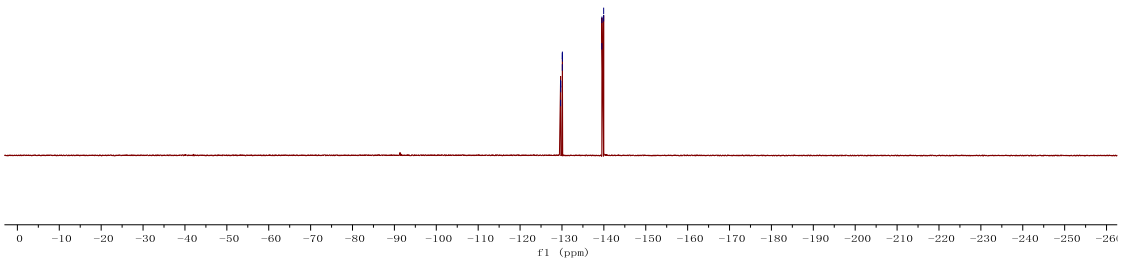
LHD-6071-3-5
single_pulse

-129.66
-129.67
-129.70
-129.71
-130.07
-130.09
-130.11
-130.12
-139.53
-139.54
-139.94
-139.95



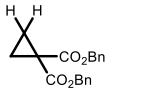
1g

^{19}F NMR (376 MHz, $CDCl_3$)



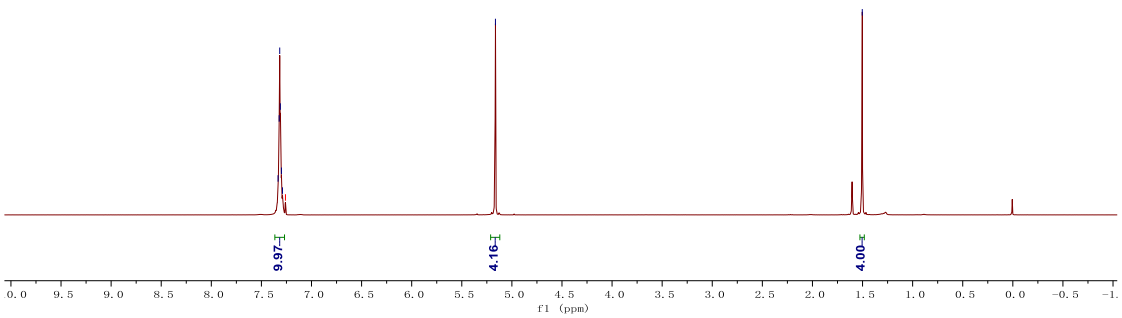
LHD-6085-1
single_pulse

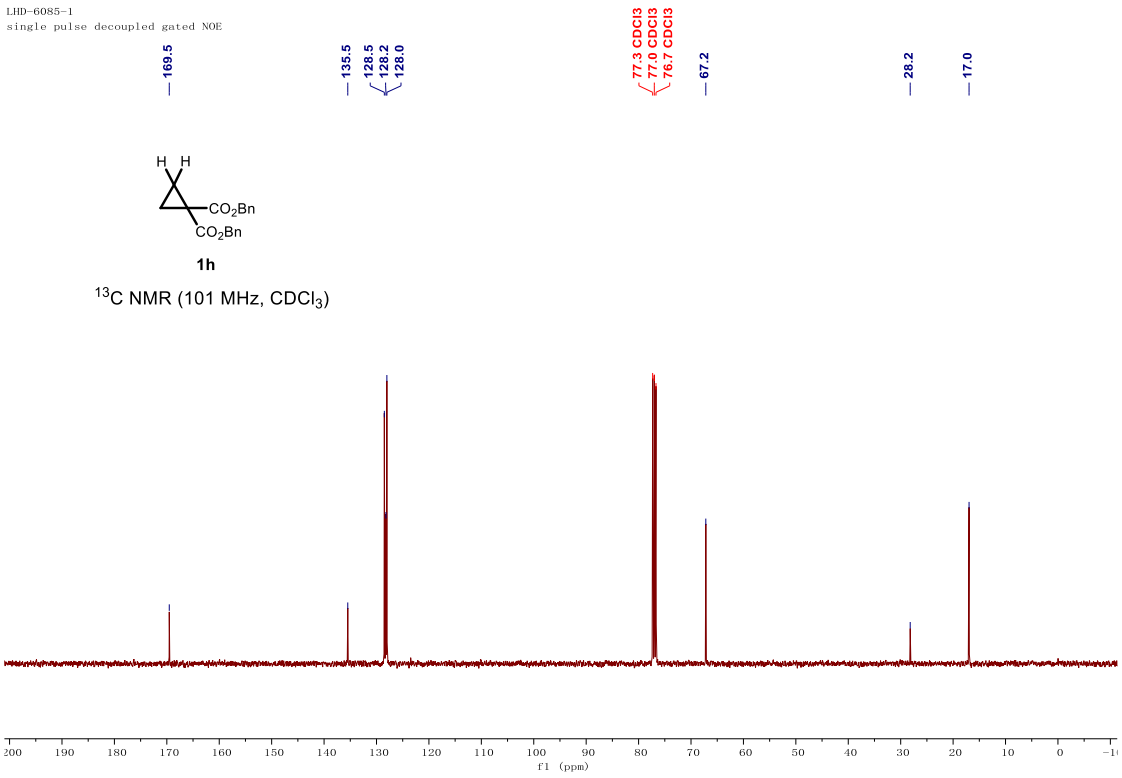
7.33
7.32
7.32
7.31
7.30
7.29
7.26 CDCl3
5.16
1.50



1h

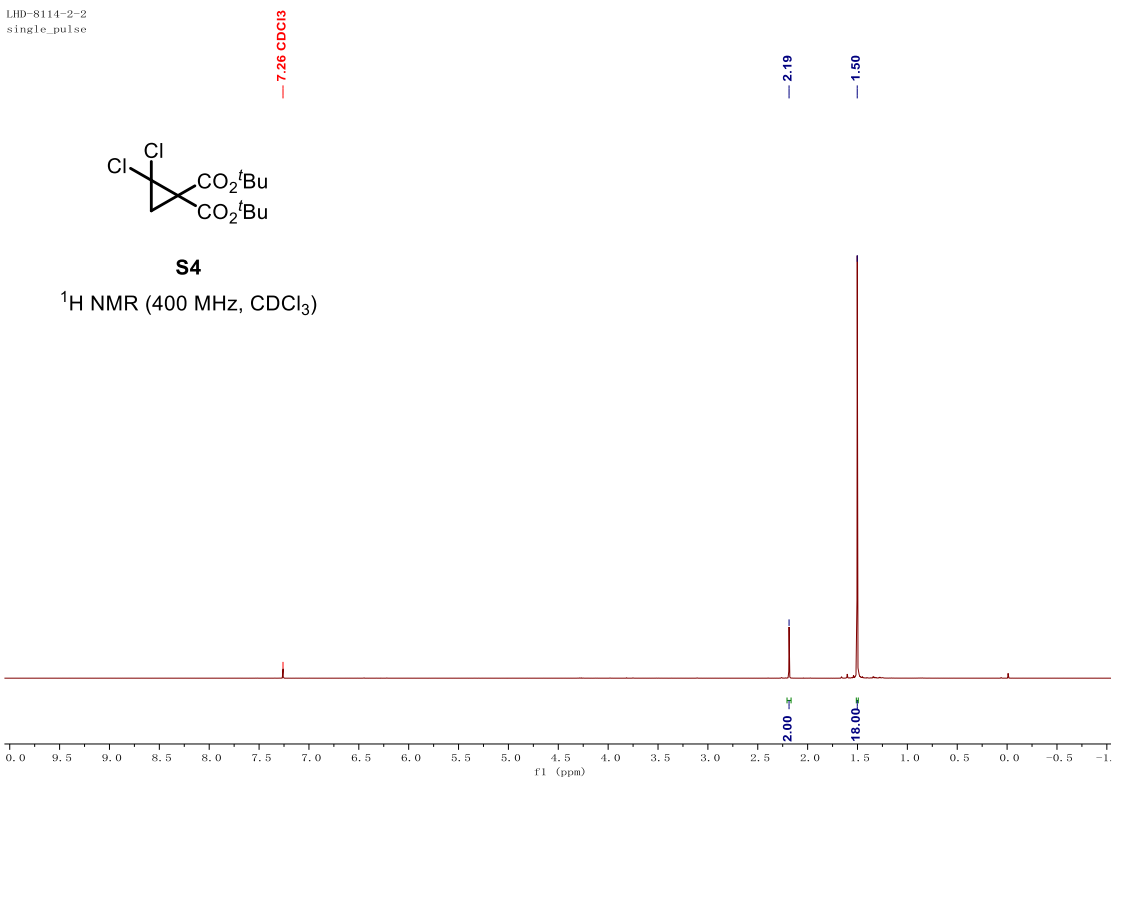
^{1}H NMR (400 MHz, $CDCl_3$)





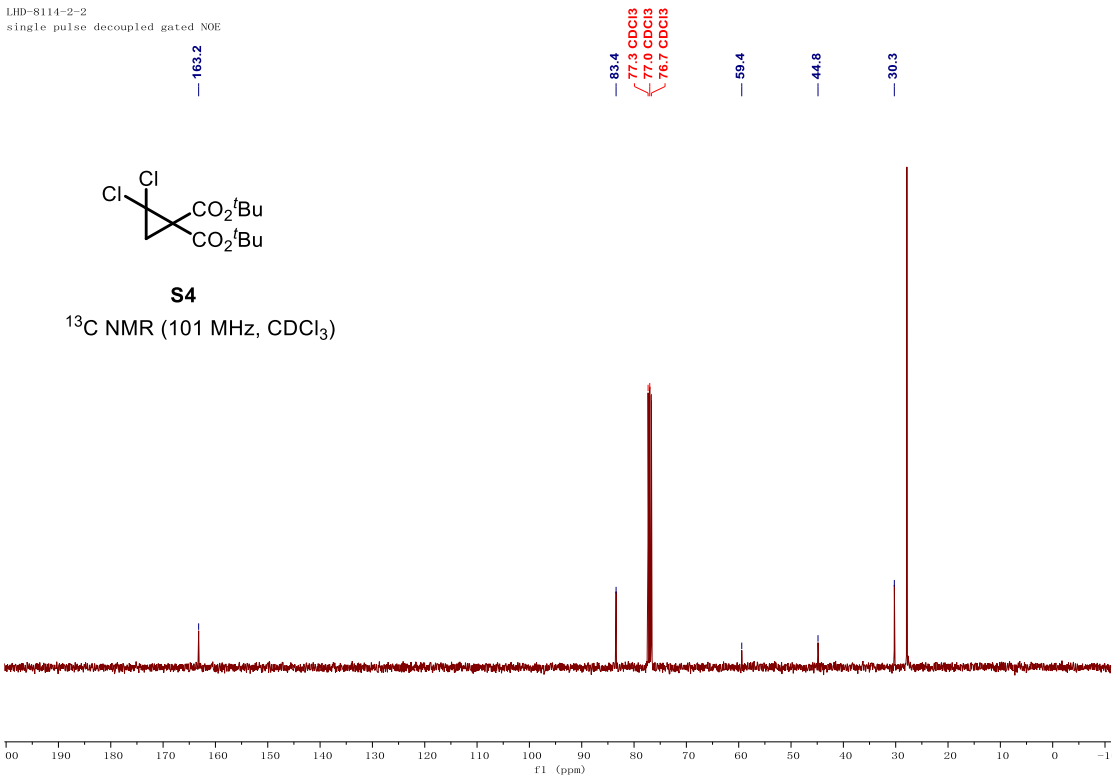
1h

^{13}C NMR (101 MHz, $CDCl_3$)



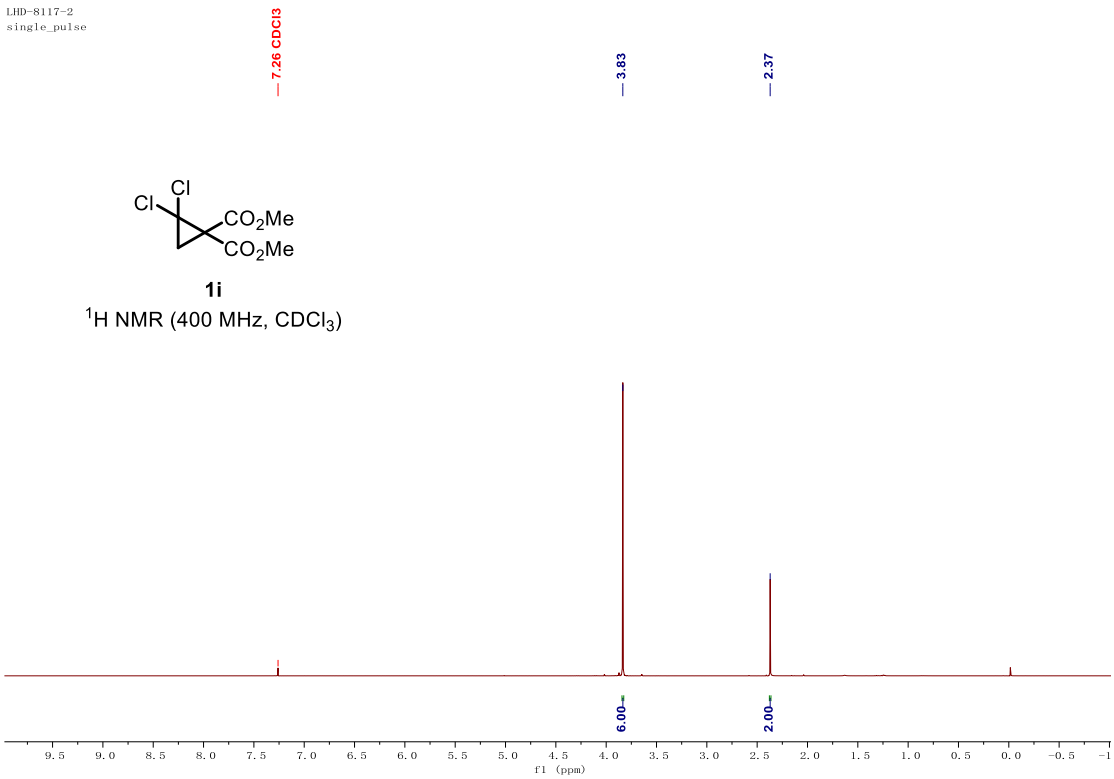
S4

^{1}H NMR (400 MHz, $CDCl_3$)



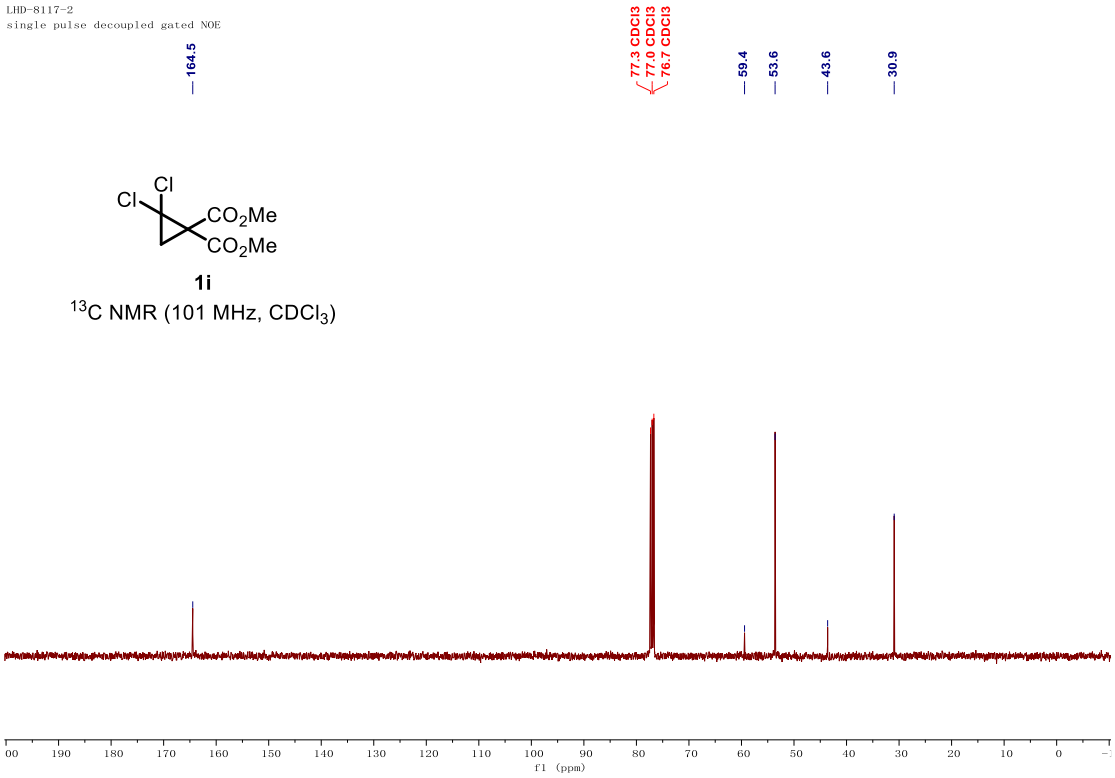
S4

^{13}C NMR (101 MHz, $CDCl_3$)



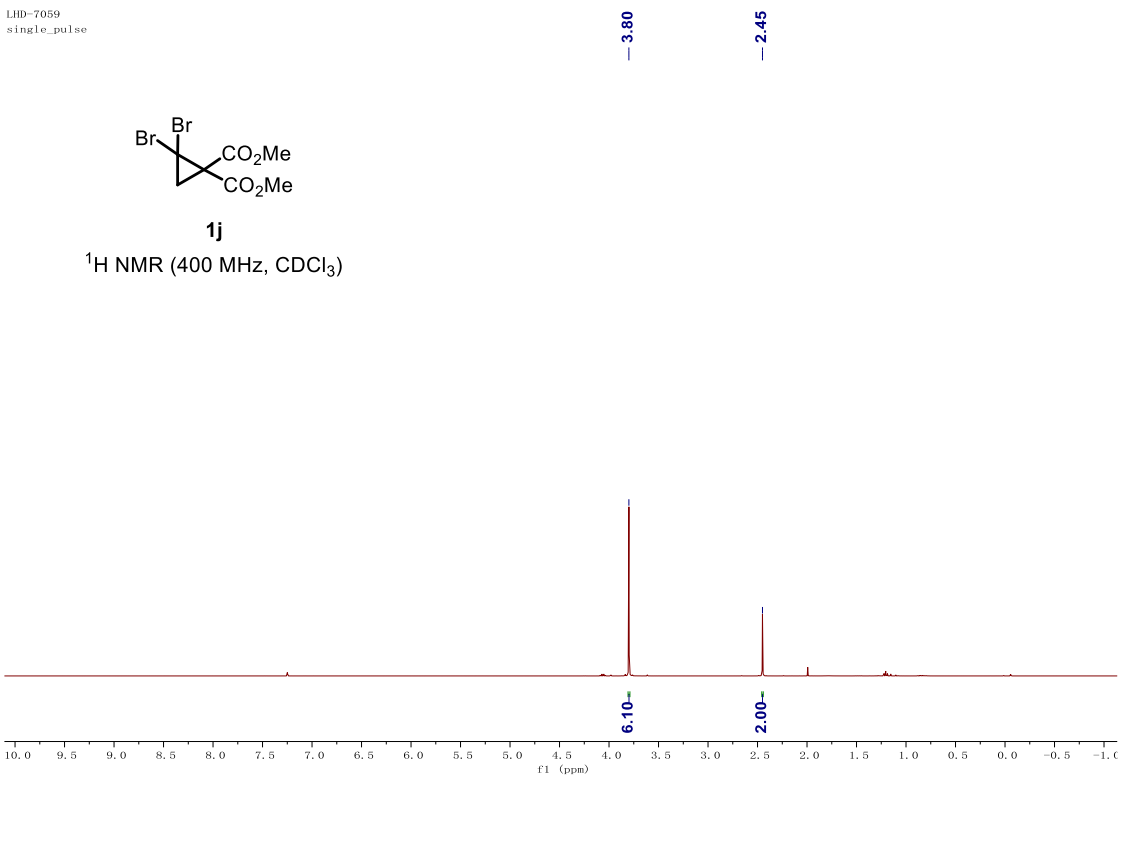
1i

^{1}H NMR (400 MHz, $CDCl_3$)



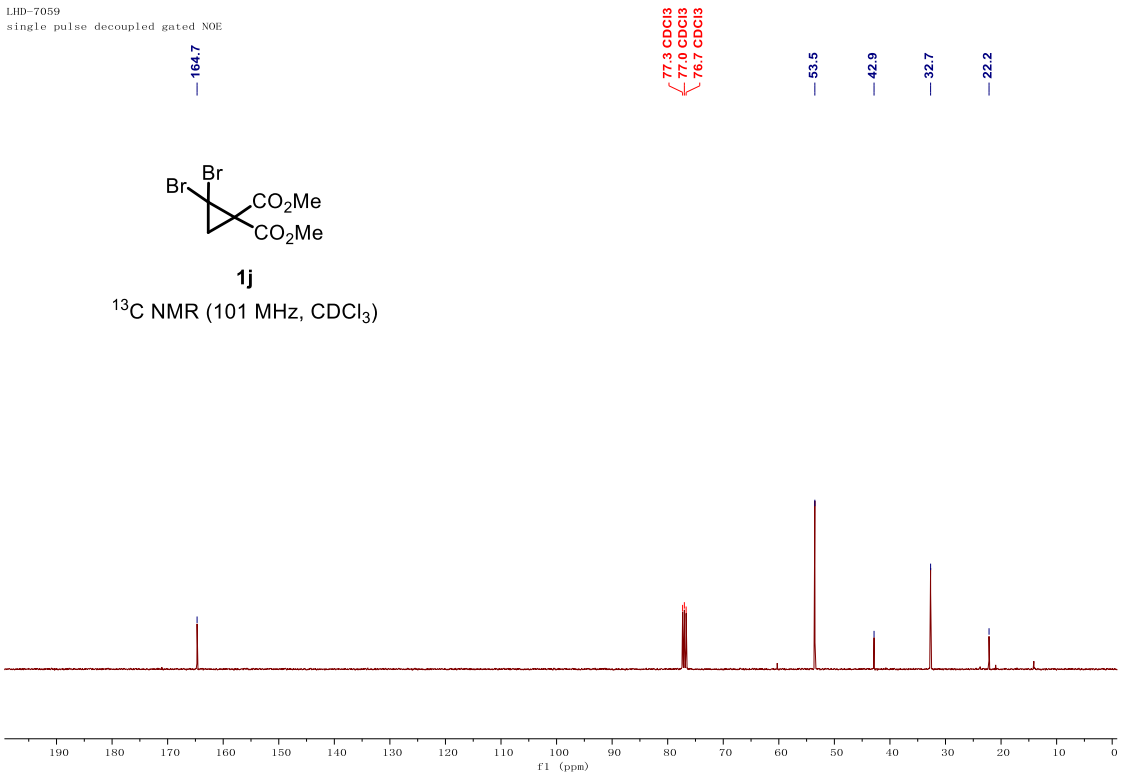
1i

^{13}C NMR (101 MHz, $CDCl_3$)



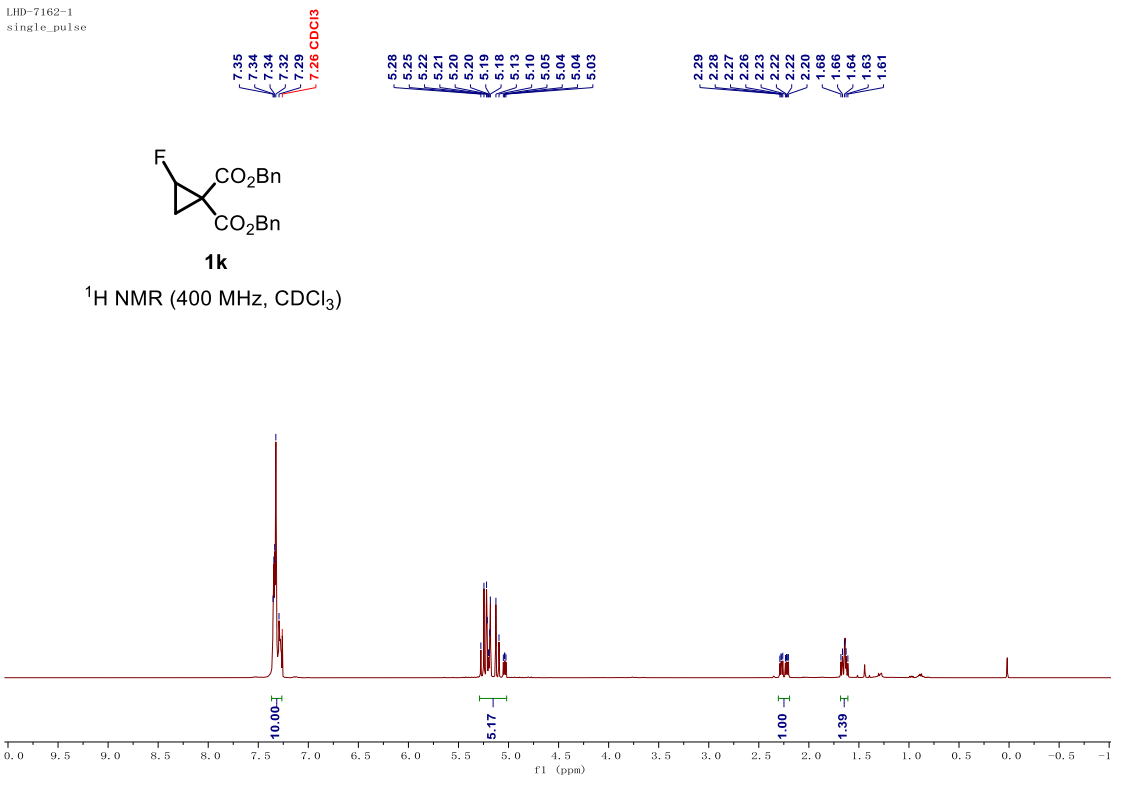
1j

^{1}H NMR (400 MHz, $CDCl_3$)



1j

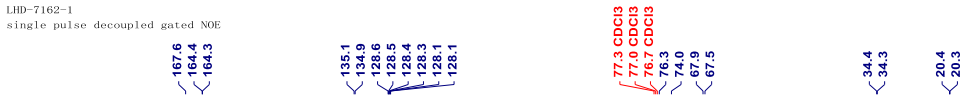
^{13}C NMR (101 MHz, $CDCl_3$)

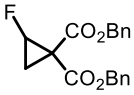


1k

^{1}H NMR (400 MHz, $CDCl_3$)

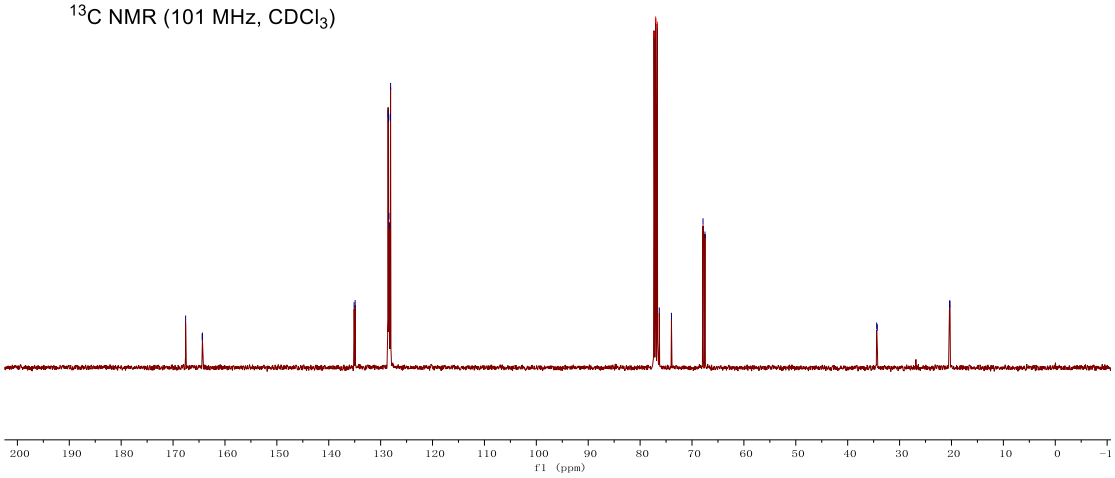
LHD-7162-1
single pulse decoupled gated NOE



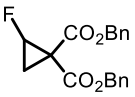


1k

^{13}C NMR (101 MHz, $CDCl_3$)

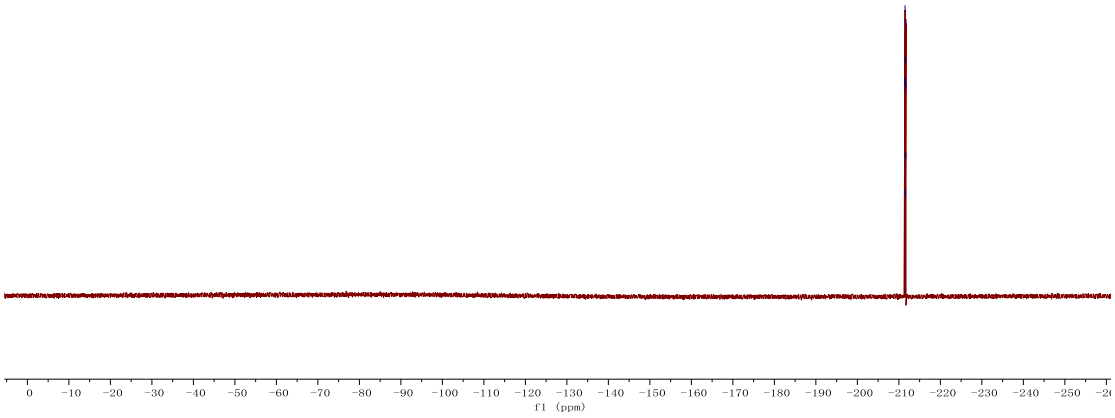


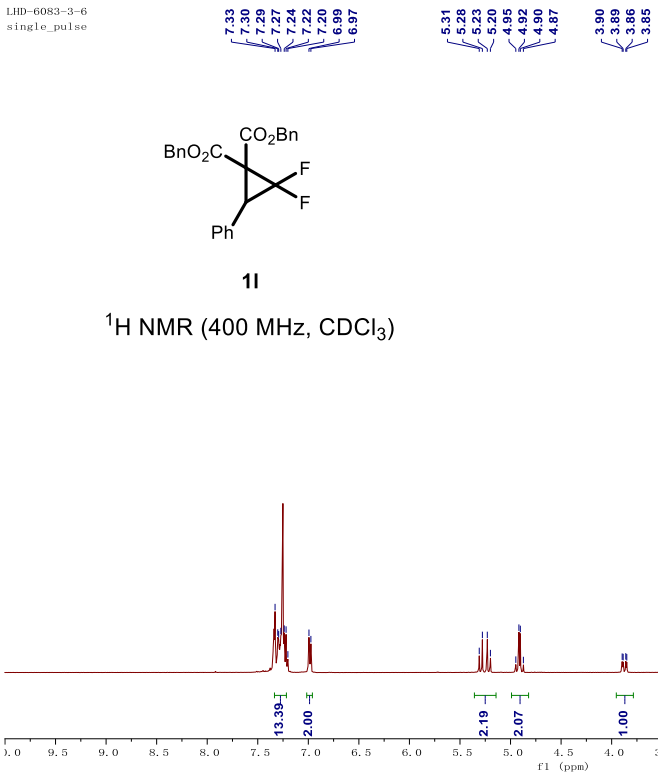
LHD-8117-3
single_pulse



1k

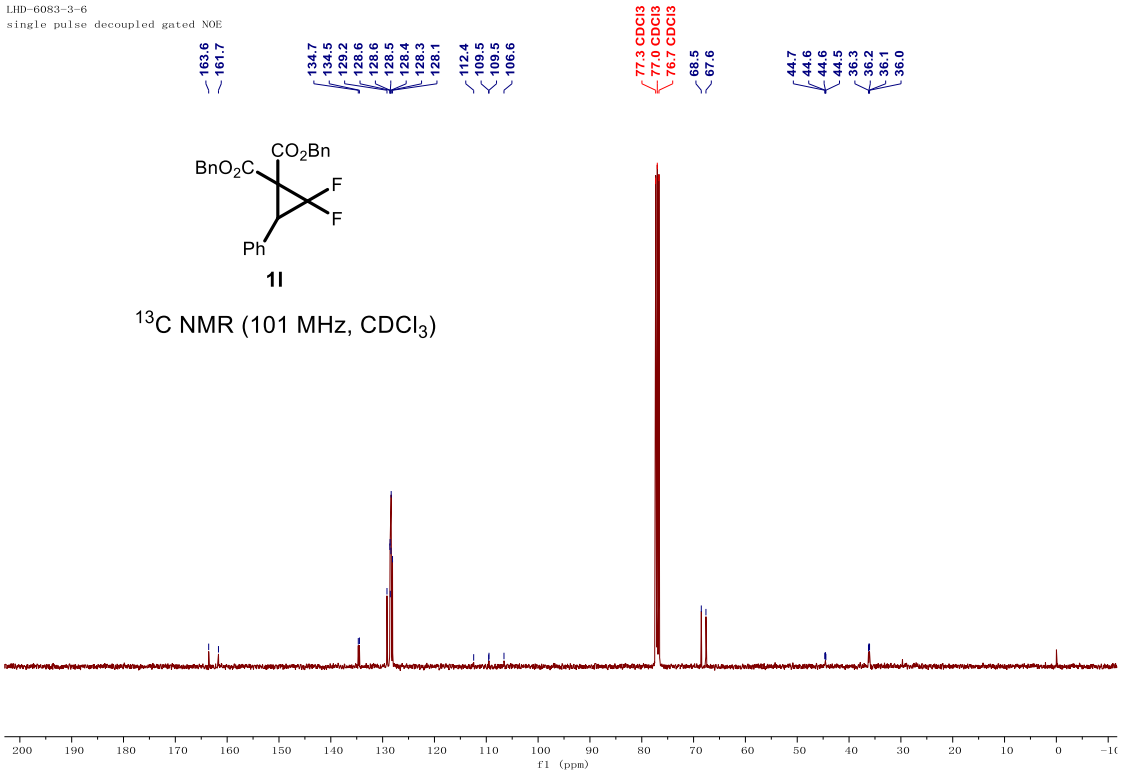
^{19}F NMR (376 MHz, $CDCl_3$)





1l

^{1}H NMR (400 MHz, $CDCl_3$)

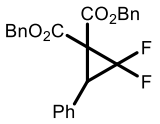


1l

^{13}C NMR (101 MHz, $CDCl_3$)

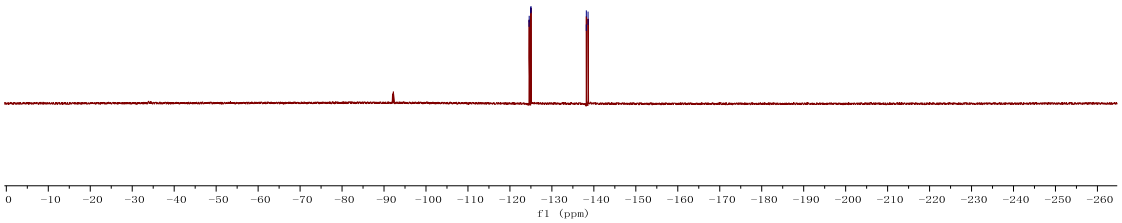
LHD-6083-3-6
single_pulse

-124.56
-124.59
-124.98
-125.01
-138.20
-138.21
-138.62
-138.63



1l

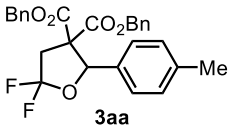
^{19}F NMR (376 MHz, $CDCl_3$)



LHD-5181-4-2
single_pulse

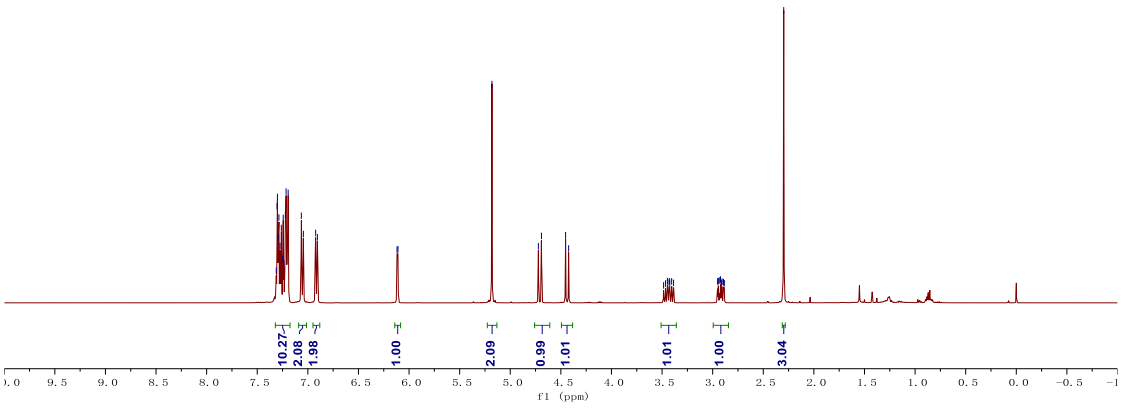
7.31
7.30
7.30
7.29
7.29
7.28
7.26
7.25
7.24
7.24
7.22
7.22
7.19
7.06
7.04
6.92
6.91
6.12
6.11

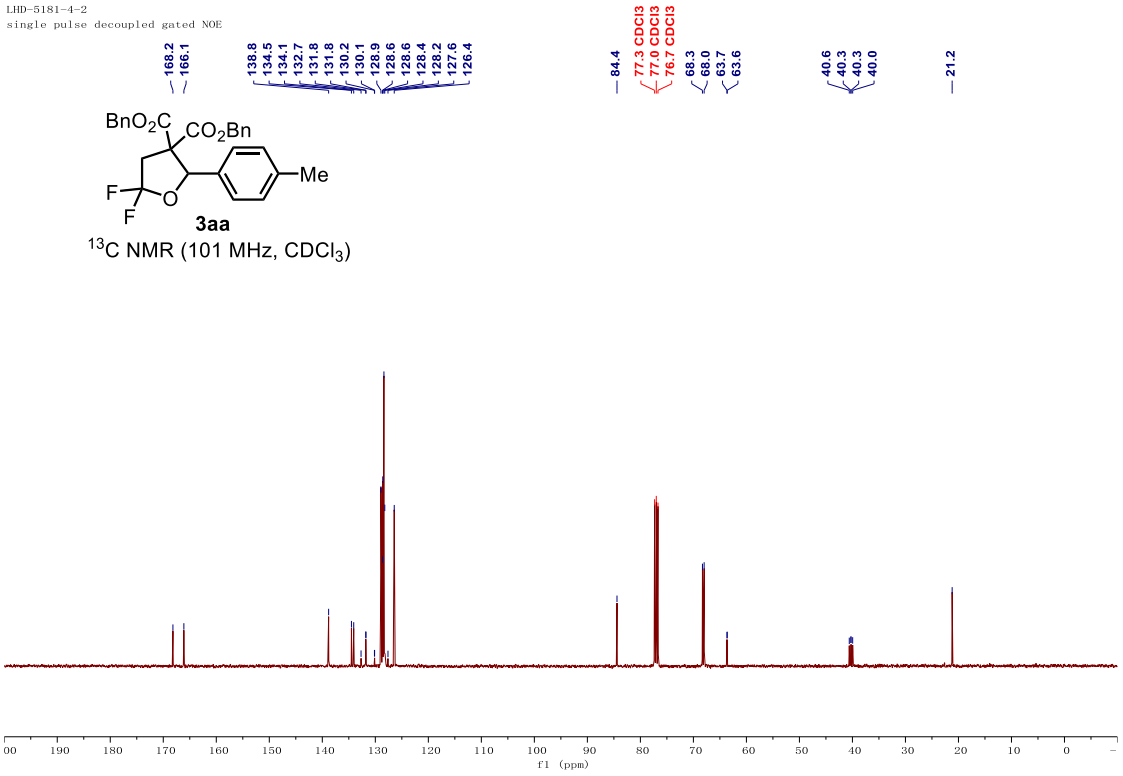
5.18
4.72
4.69
4.45
4.42
3.48
3.47
3.45
3.44
3.43
3.42
3.41
3.39
2.95
2.94
2.93
2.92
2.91
2.91
2.89
2.89
2.30



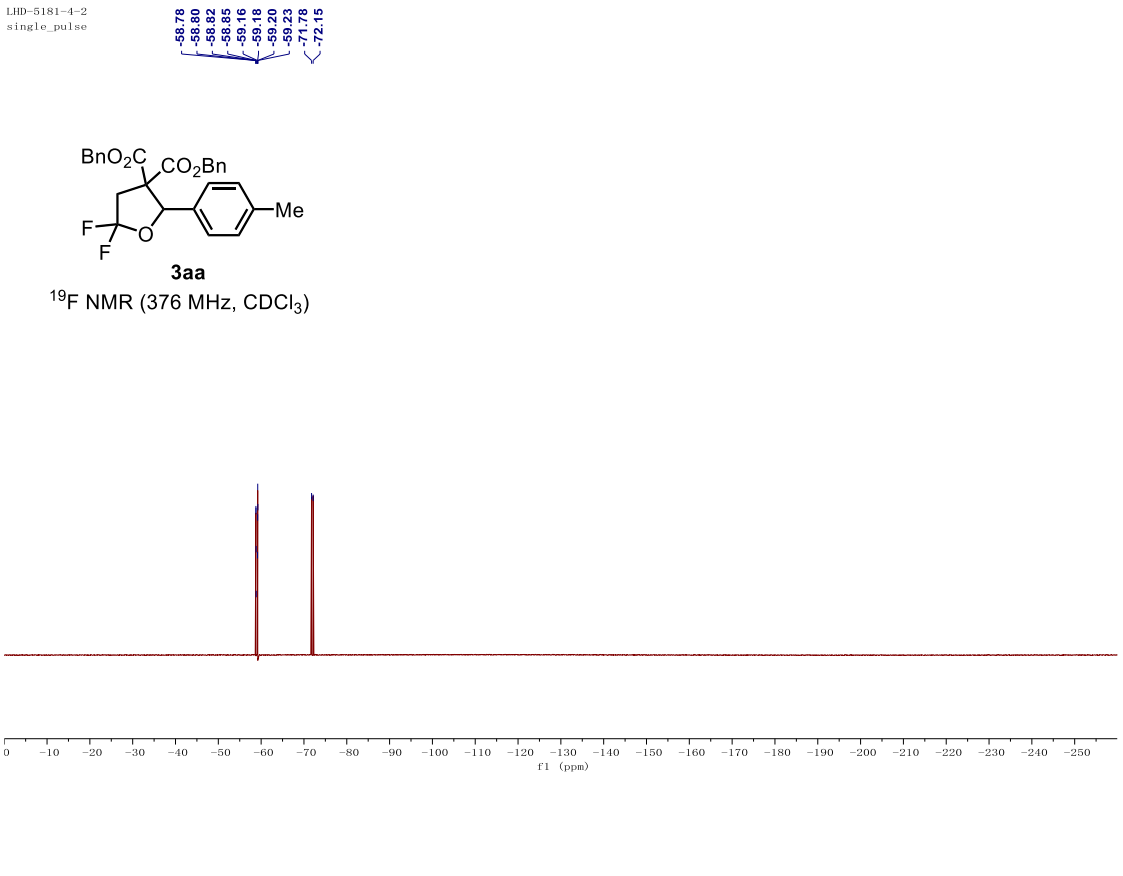
3aa

^{1}H NMR (400 MHz, $CDCl_3$)

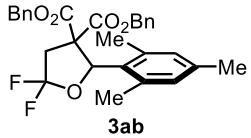




^{13}C NMR (101 MHz, $CDCl_3$)

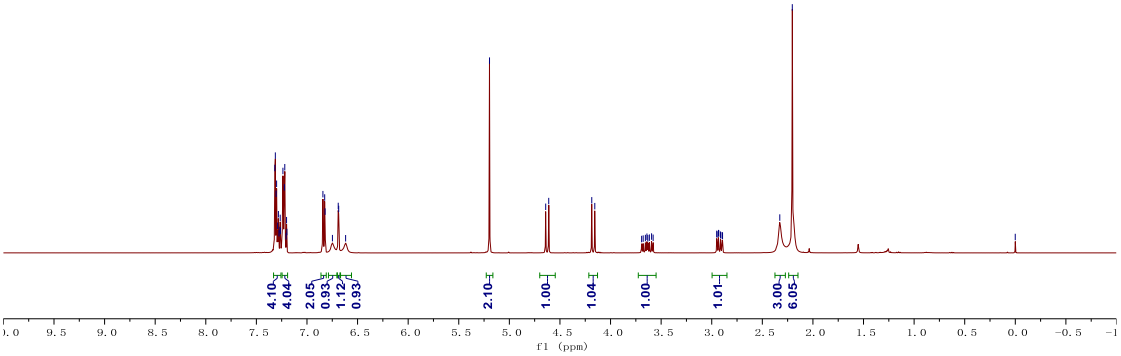


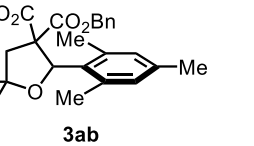
^{19}F NMR (376 MHz, $CDCl_3$)



3ab

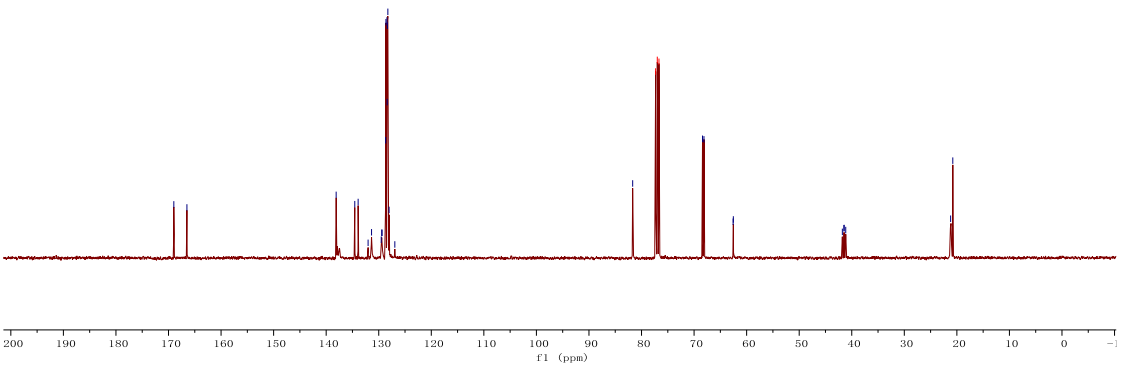
^{1}H NMR (400 MHz, $CDCl_3$)





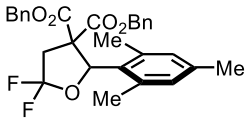
3ab

^{13}C NMR (101 MHz, $CDCl_3$)



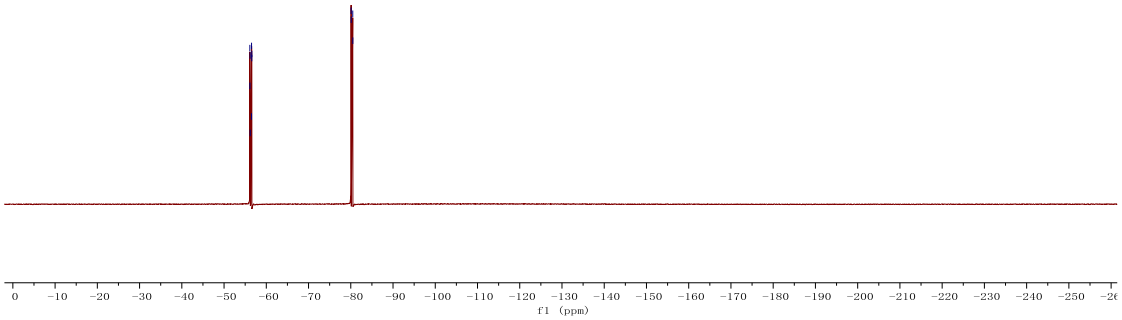
LHD-5193-4
single_pulse

-56.11
-56.12
-56.17
-56.19
-56.49
-56.51
-56.56
-56.57
-80.08
-80.09
-80.47
-80.48



3ab

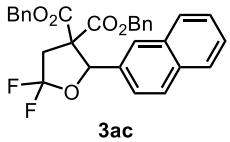
^{19}F NMR (376 MHz, $CDCl_3$)



LHD-6033-3
single_pulse

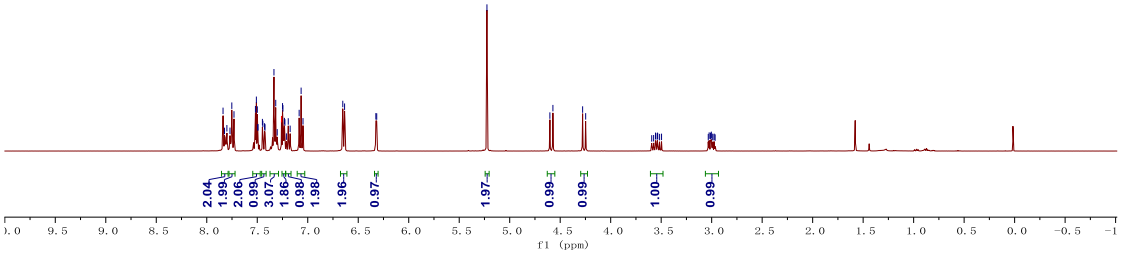
7.84
7.75
7.73
7.52
7.51
7.50
7.49
7.45
7.44
7.43
7.33
7.32
7.26 CDCl3
7.25
7.25
7.23
7.23
7.19
7.09
7.07
6.65
6.64
6.33
6.32

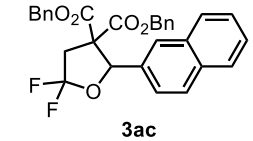
5.23
4.60
4.57
4.28
4.25
3.59
3.57
3.56
3.55
3.54
3.53
3.52
3.50
3.03
3.03
3.01
3.00
3.00
2.99
2.97
2.97



3ac

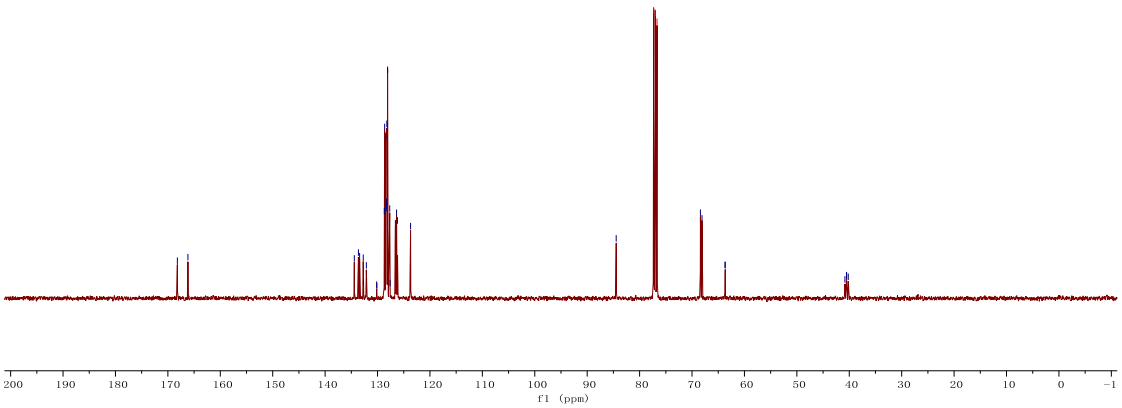
^{1}H NMR (400 MHz, $CDCl_3$)

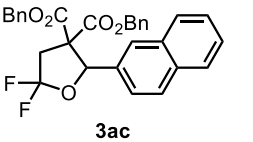




3ac

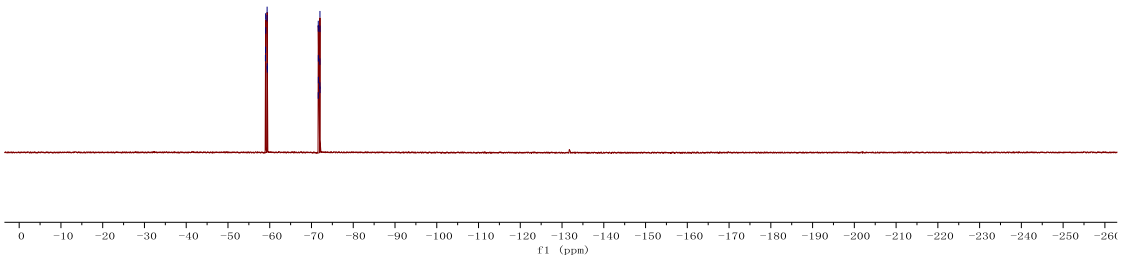
^{13}C NMR (101 MHz, $CDCl_3$)

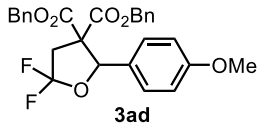




3ac

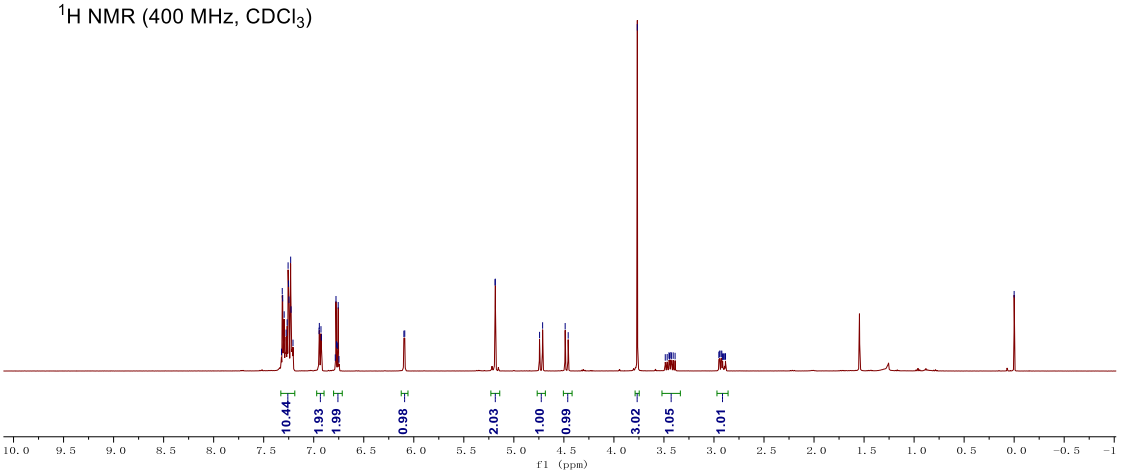
^{19}F NMR (376 MHz, $CDCl_3$)

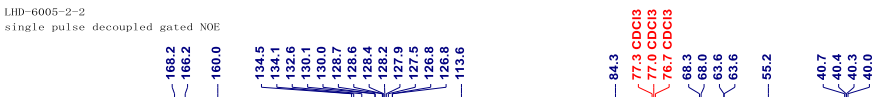


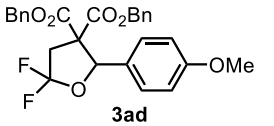


3ad

^{1}H NMR (400 MHz, $CDCl_3$)

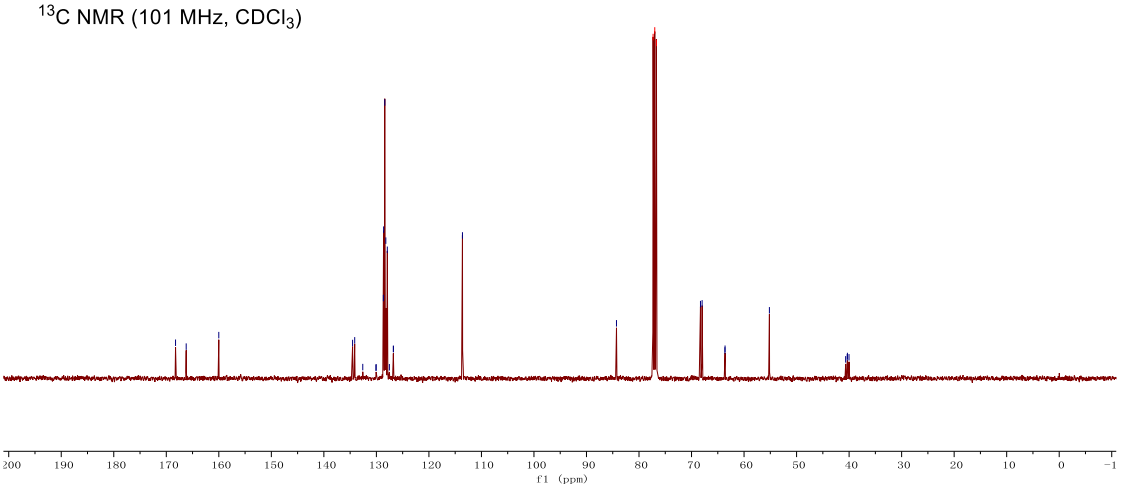






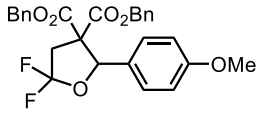
3ad

^{13}C NMR (101 MHz, $CDCl_3$)



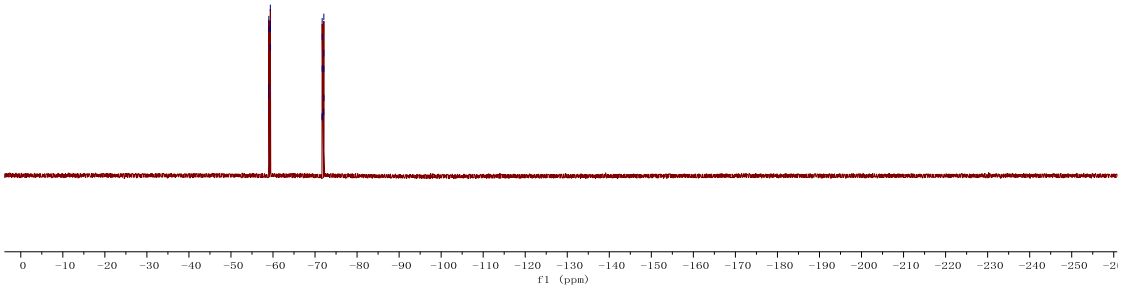
LHD-6005-2
single_pulse

-58.97
-58.99
-59.01
-59.03
-59.35
-59.37
-59.39
-59.42
-71.69
-71.69
-71.70
-71.71
-71.72
-72.07
-72.08
-72.09
-72.10
-72.10



3ad

^{19}F NMR (376 MHz, $CDCl_3$)



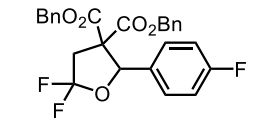
LHD-6027-7
single_pulse

7.33
7.32
7.31
7.29
7.28
7.26
7.24
7.21
6.93
6.91
6.89
6.87
6.09
6.09

5.19

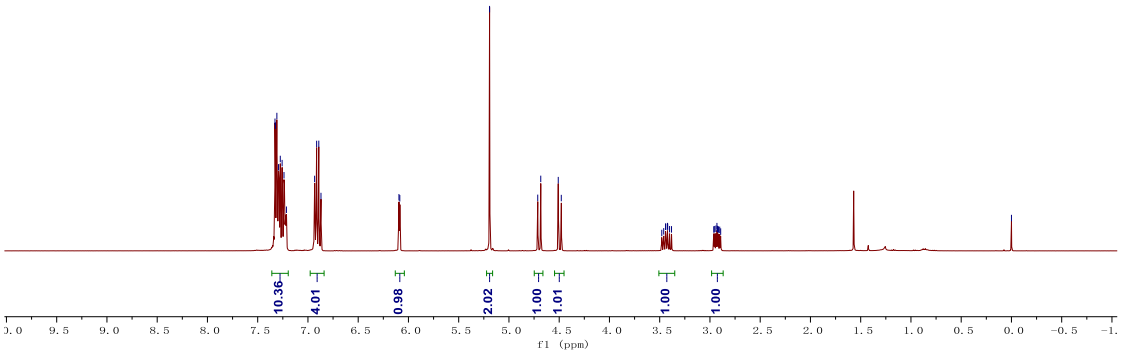
4.71
4.68
4.51
4.48
3.48
3.46
3.44
3.44
3.42
3.42
3.40
3.38
2.96
2.95
2.94
2.93
2.92
2.92
2.90
2.89

-0.00

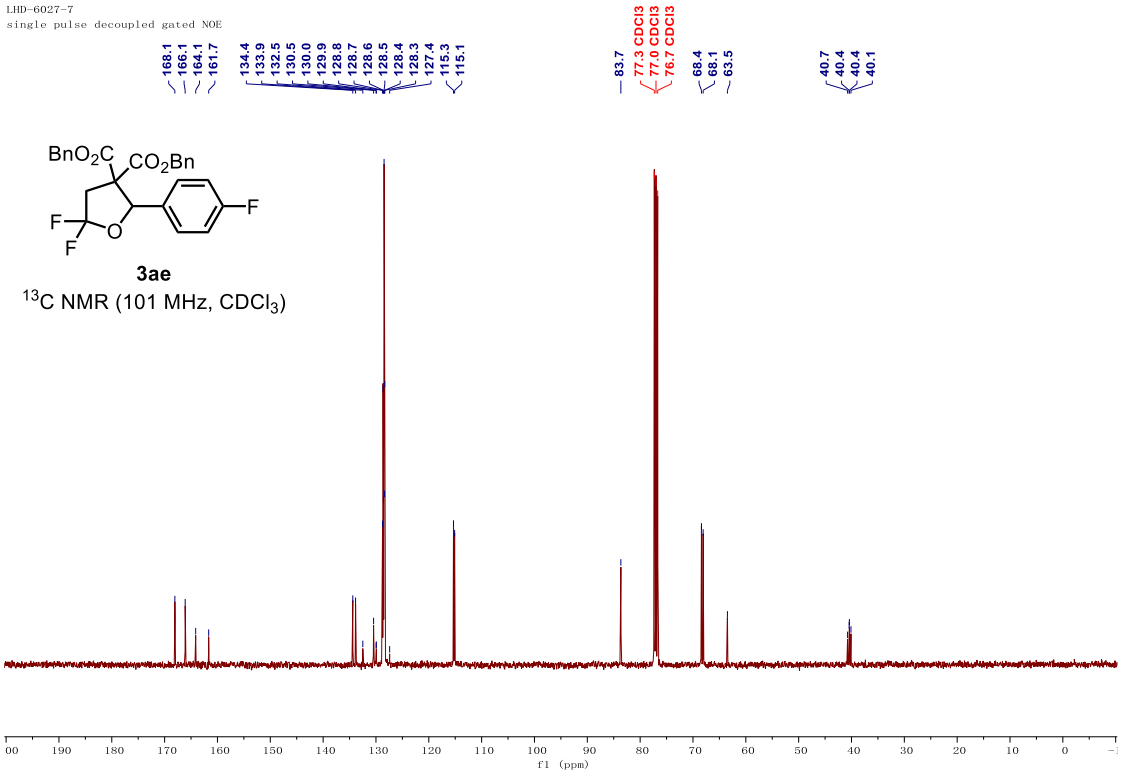


3ae

^{1}H NMR (400 MHz, $CDCl_3$)



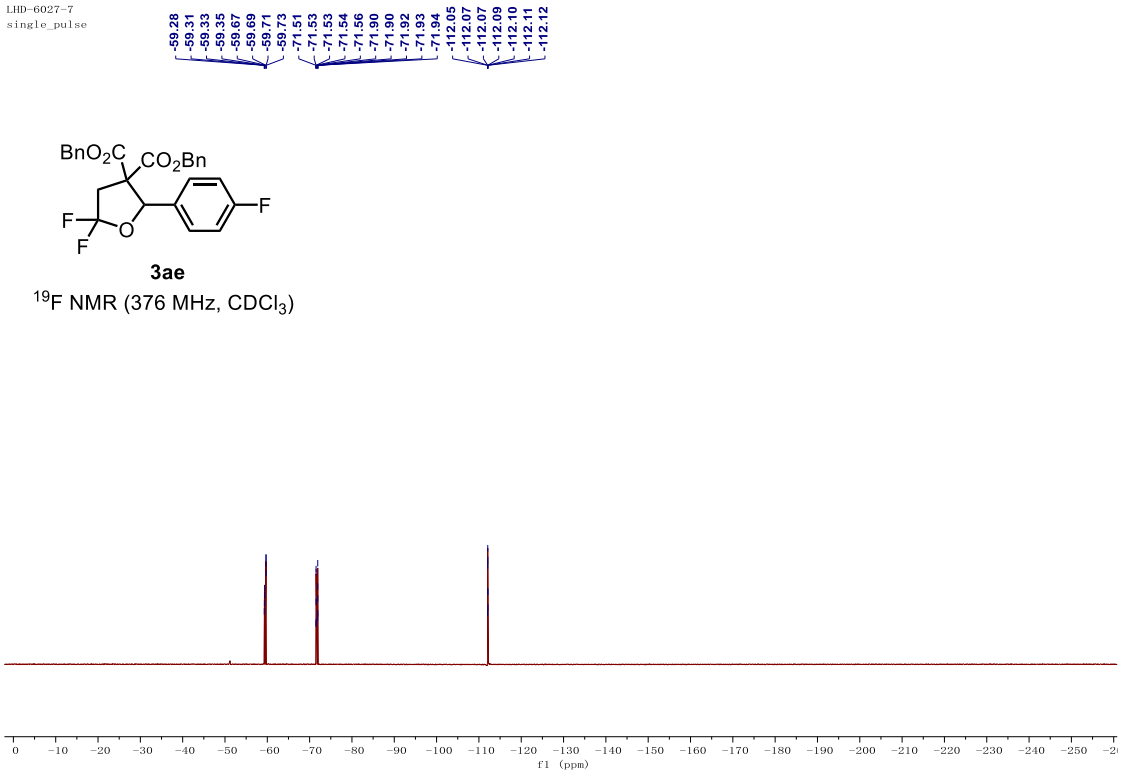
LHD-6027-7
single pulse decoupled gated NOE



3ae

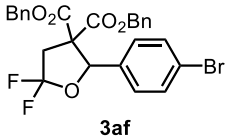
^{13}C NMR (101 MHz, $CDCl_3$)

LHD-6027-7
single_pulse



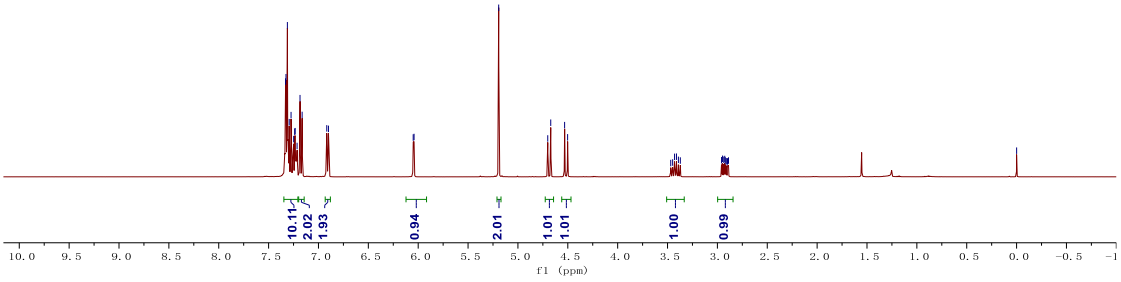
3ae

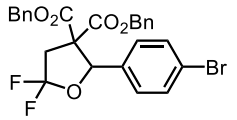
^{19}F NMR (376 MHz, $CDCl_3$)



3af

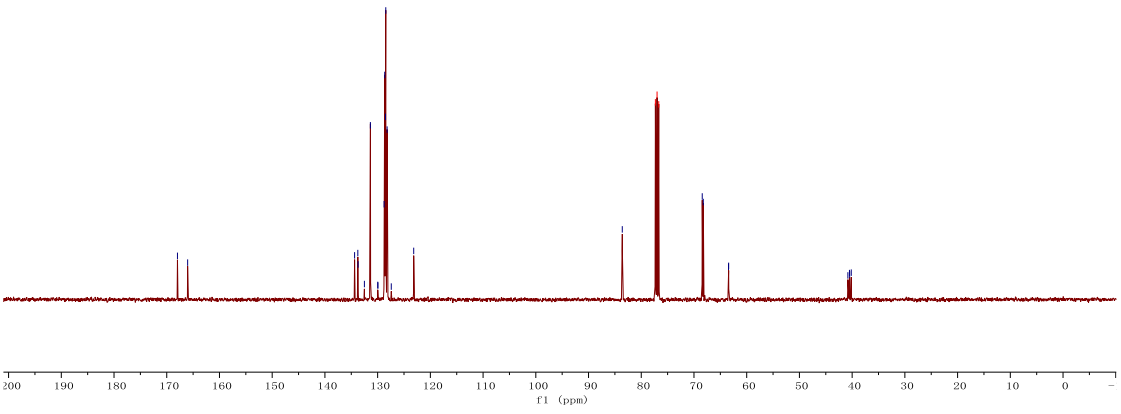
^{1}H NMR (400 MHz, $CDCl_3$)





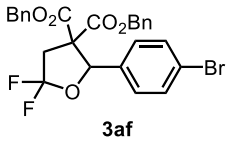
3af

^{13}C NMR (101 MHz, $CDCl_3$)



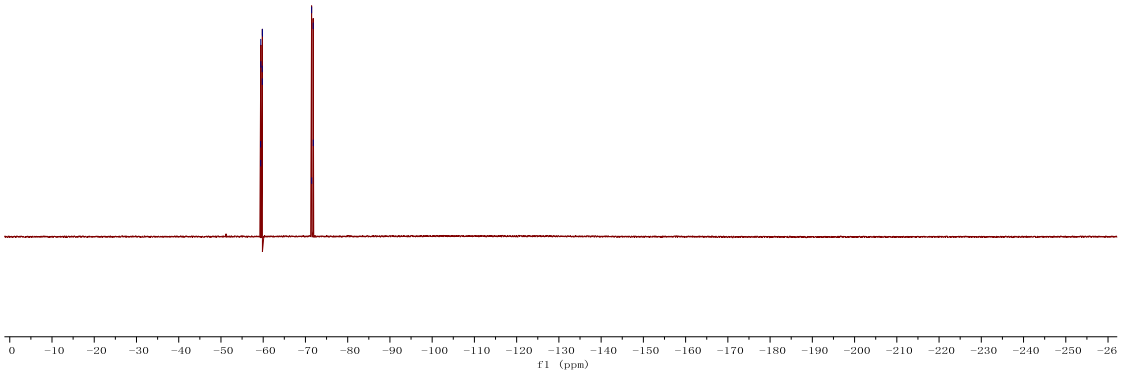
LHD-5193-3-2
single_pulse

-59.39
-59.41
-59.43
-59.45
-59.77
-59.79
-59.81
-59.83
-71.46
-71.48
-71.83
-71.86



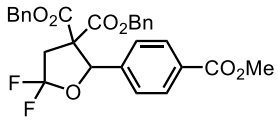
3af

^{19}F NMR (376 MHz, $CDCl_3$)



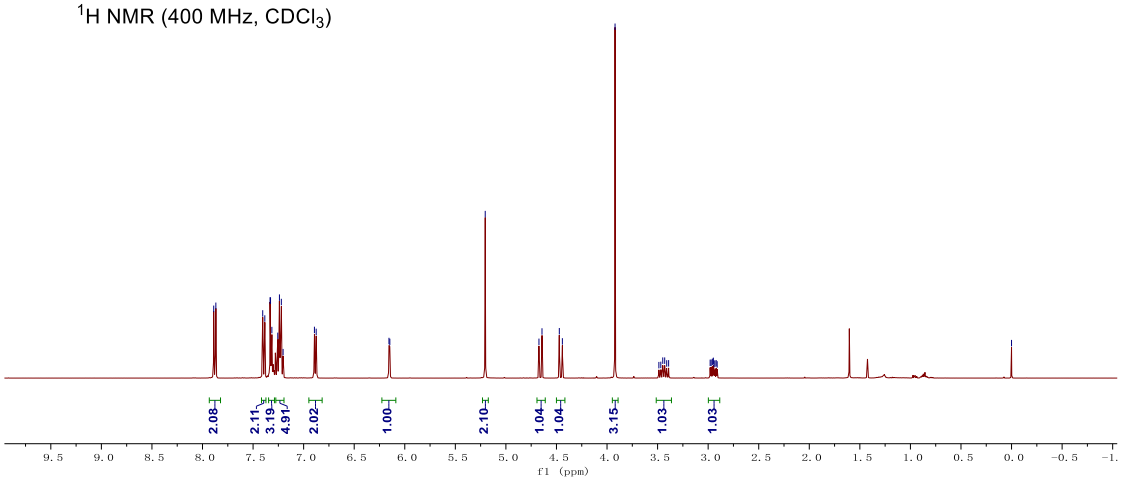
LHD-6027-6
single_pulse

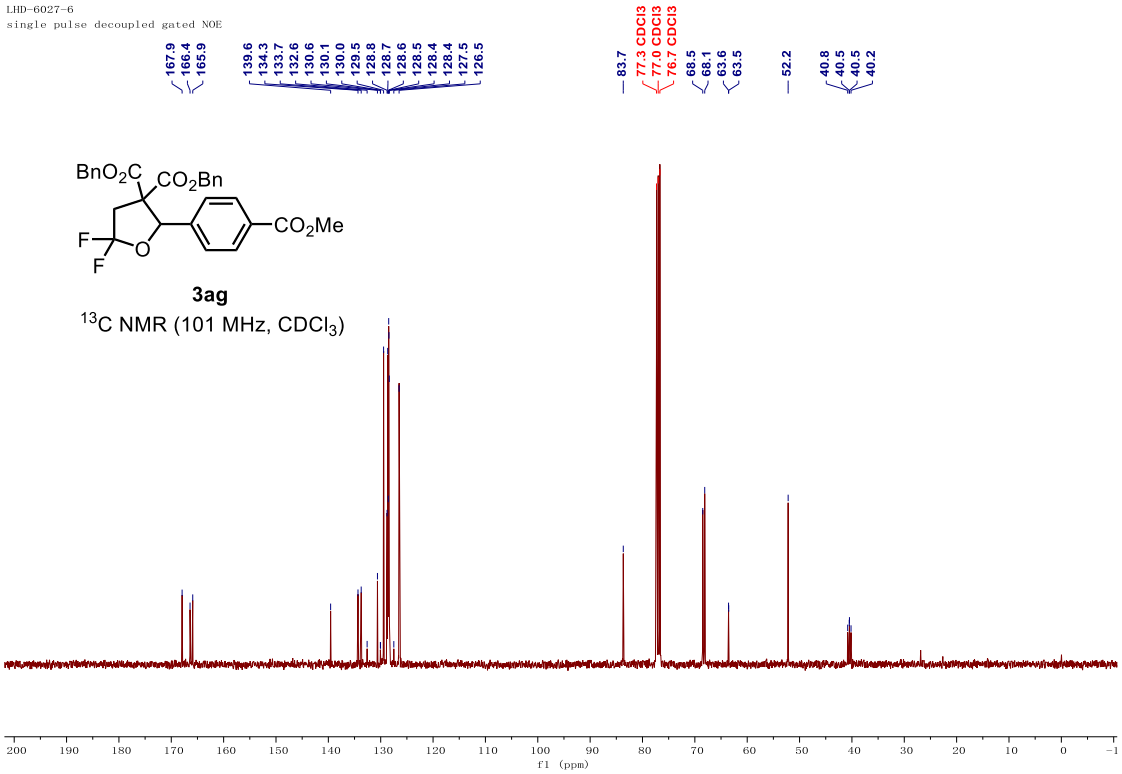
7.89
7.87
7.40
7.38
7.33
7.33
7.31
7.26
7.24
7.22
7.20
6.89
6.88
6.16
6.15
5.20
4.67
4.64
4.47
4.44
3.92
3.49
3.47
3.45
3.43
3.41
3.39
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.91
0.00

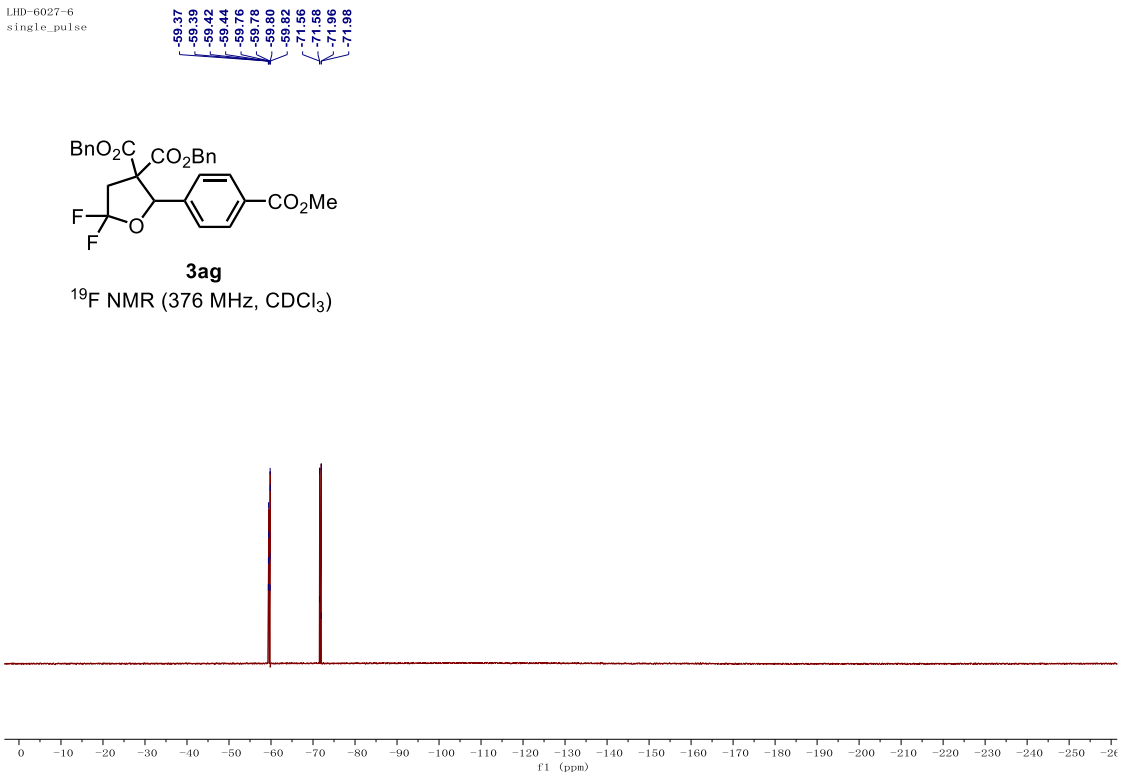


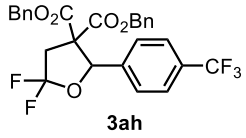
3ag

^{1}H NMR (400 MHz, $CDCl_3$)



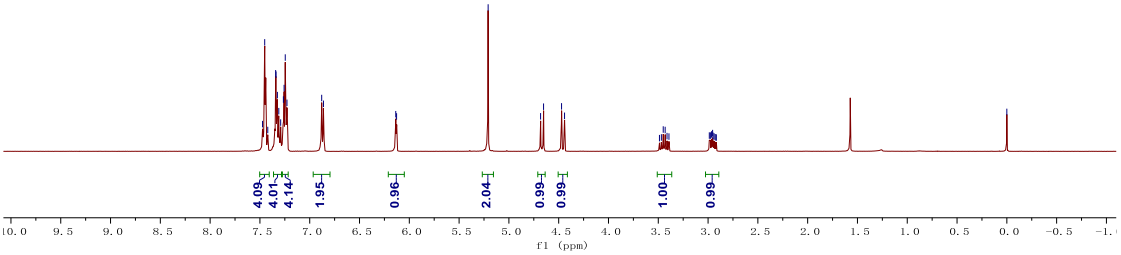

LHD-6027-6
single pulse decoupled gated NOE
167.9
166.4
165.9
139.6
134.3
133.7
132.6
130.6
130.1
130.0
129.5
128.8
128.7
128.6
128.5
128.4
128.4
127.5
126.5
83.7
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
68.5
68.1
63.6
63.5
52.2
40.8
40.5
40.5
40.2
BnO2C
CO2Bn
CO2Me
F
F
O
3ag
13C NMR (101 MHz, CDCl3)
f1 (ppm)

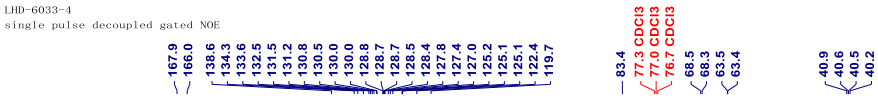

LHD-6027-6
single_pulse
-59.37
-59.39
-59.42
-59.44
-59.76
-59.78
-59.80
-59.82
-71.56
-71.58
-71.96
-71.98
BnO2C
CO2Bn
CO2Me
F
F
O
3ag
19F NMR (376 MHz, CDCl3)
f1 (ppm)

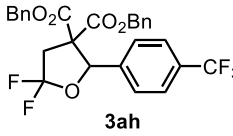


3ah

^{1}H NMR (400 MHz, $CDCl_3$)

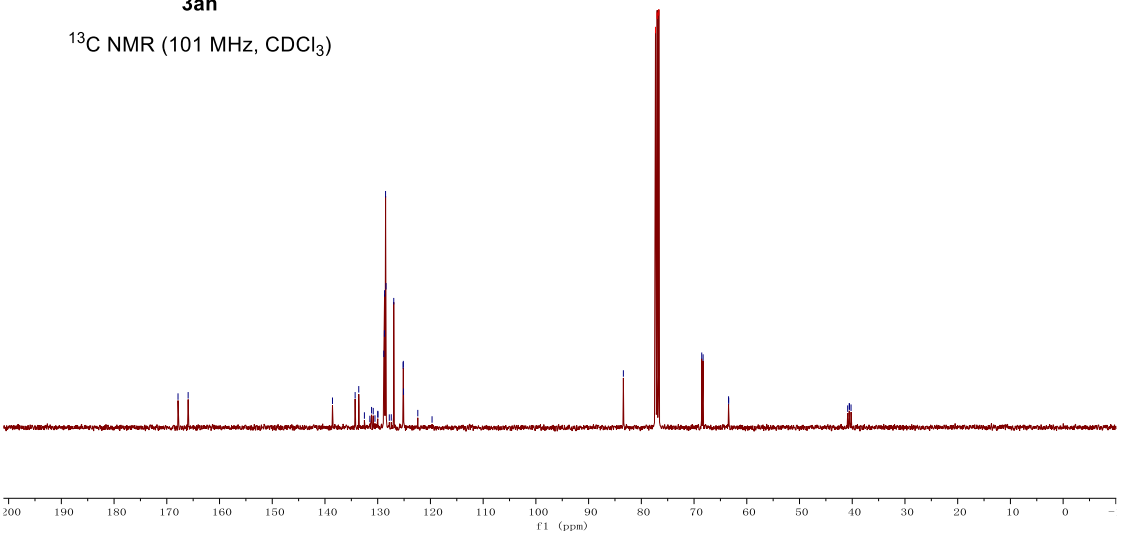






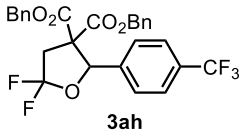
3ah

^{13}C NMR (101 MHz, $CDCl_3$)



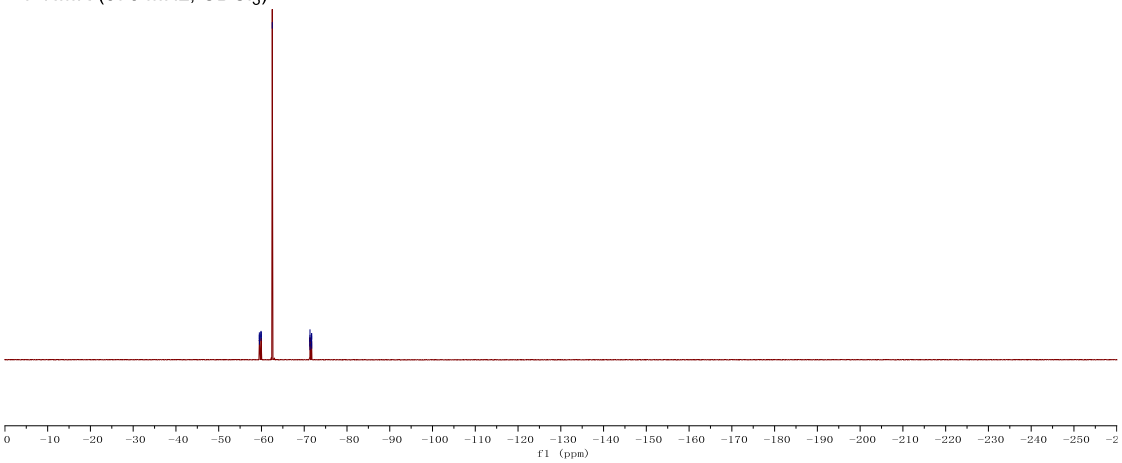
LHD-6033-4
single_pulse

-59.49
-59.51
-59.53
-59.55
-59.87
-59.89
-59.91
-59.93
-62.52
-71.33
-71.34
-71.35
-71.36
-71.37
-71.71
-71.72
-71.73
-71.74
-71.75



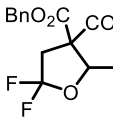
3ah

^{19}F NMR (376 MHz, $CDCl_3$)



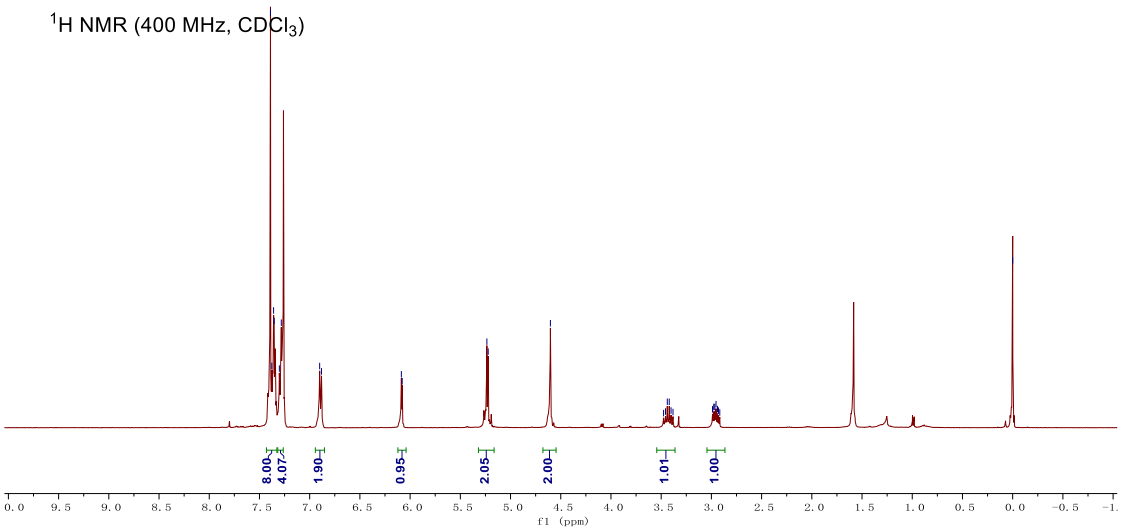
LHD-6105-8
single_pulse

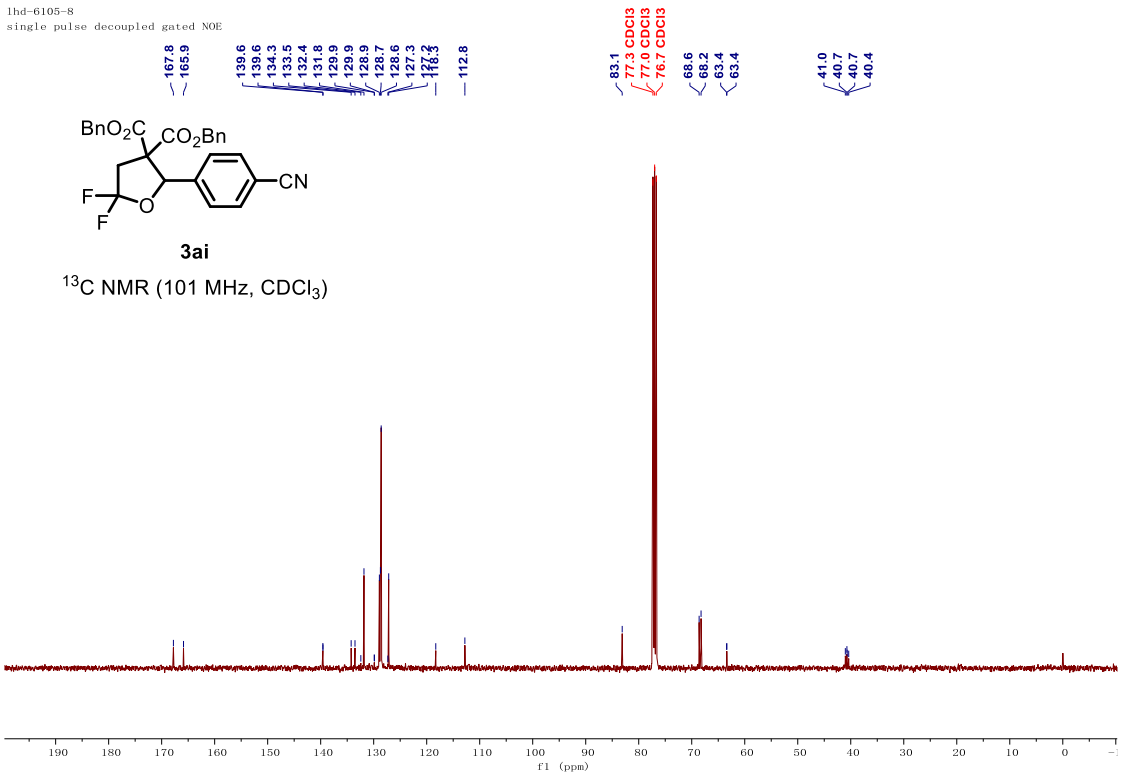
7.39
7.38
7.36
7.35
7.30
7.28
6.90
6.88
6.09
6.08
5.24
5.22
4.60
3.48
3.46
3.44
3.42
3.40
3.38
2.99
2.98
2.97
2.95
2.94
2.93
2.92
-0.00



3ai

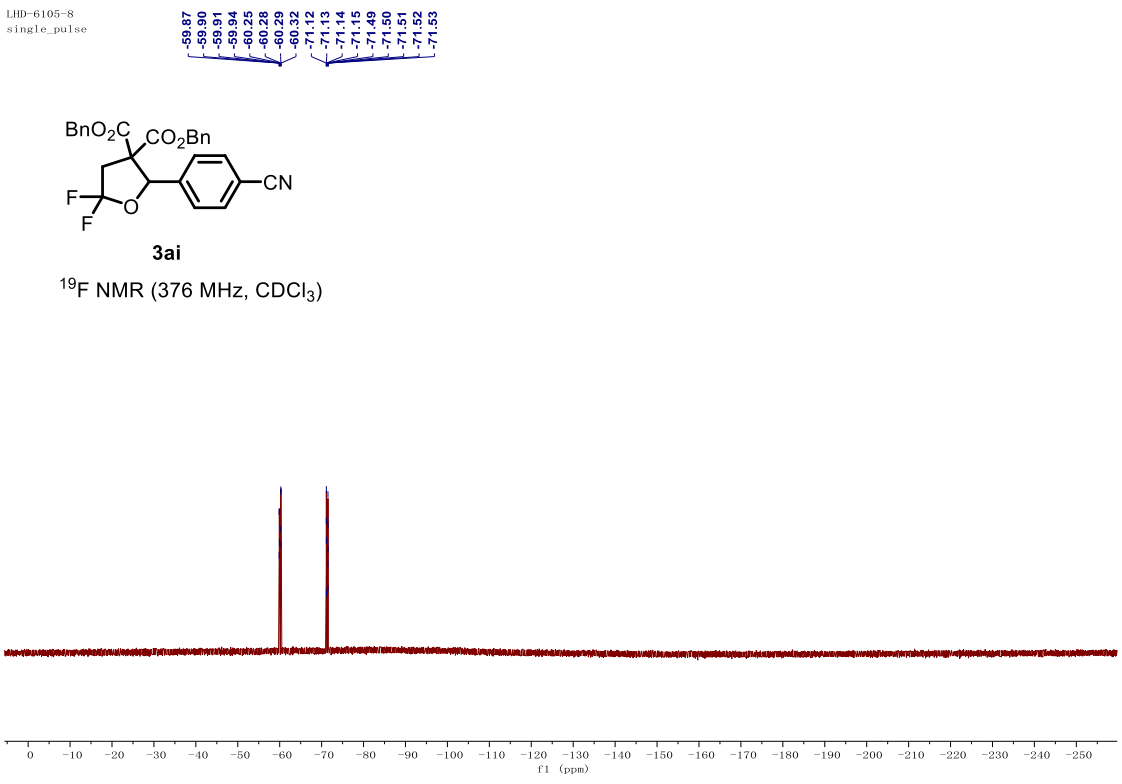
^{1}H NMR (400 MHz, $CDCl_3$)





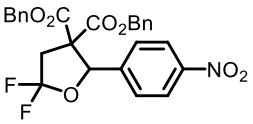
3ai

^{13}C NMR (101 MHz, $CDCl_3$)



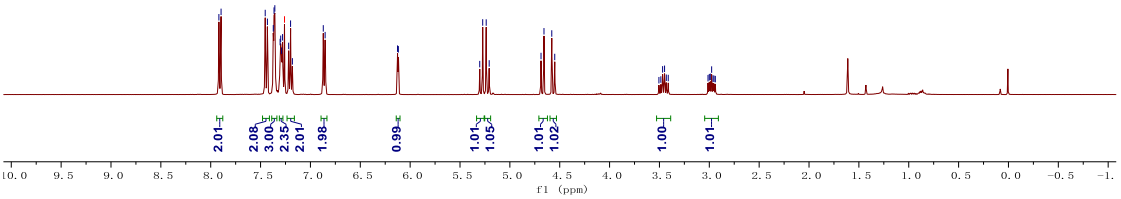
3ai

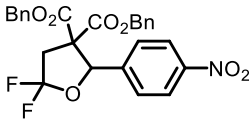
^{19}F NMR (376 MHz, $CDCl_3$)



3aj

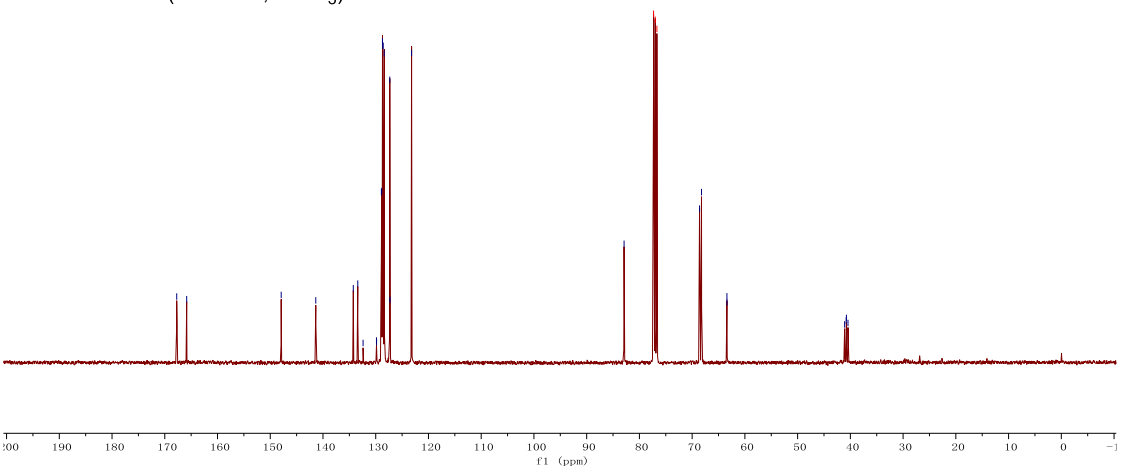
^{1}H NMR (400 MHz, $CDCl_3$)





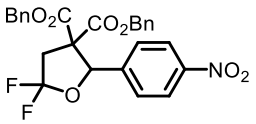
3aj

^{13}C NMR (101 MHz, $CDCl_3$)



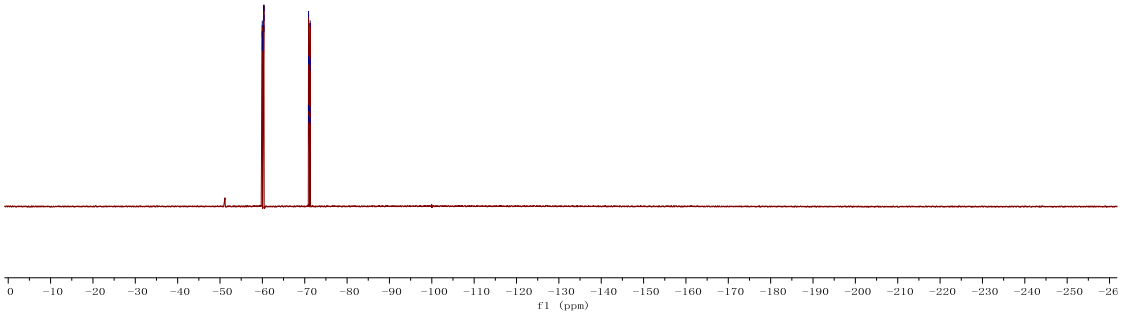
LHD-6105-7
single_pulse

-59.96
-59.98
-59.99
-60.02
-60.34
-60.36
-60.37
-60.40
-70.88
-70.89
-70.90
-70.91
-70.92
-71.26
-71.27
-71.28
-71.29
-71.30



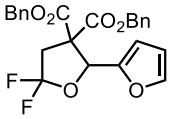
3aj

^{19}F NMR (376 MHz, $CDCl_3$)



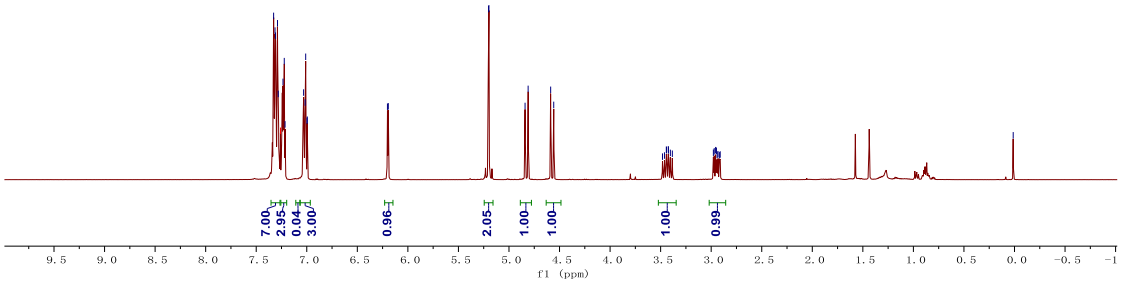
LHD-6013-8
single_pulse

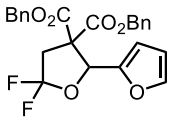
7.33
7.31
7.31
7.29
7.28
7.26 CDCl3
7.24
7.22
7.21
7.03
7.02
7.01
7.00
6.99
6.20
6.19
5.20
5.20
4.84
4.81
4.59
4.56
3.48
3.46
3.44
3.44
3.42
3.42
3.40
3.38
2.98
2.97
2.96
2.95
2.94
2.93
2.92
2.91
0.01



3ak

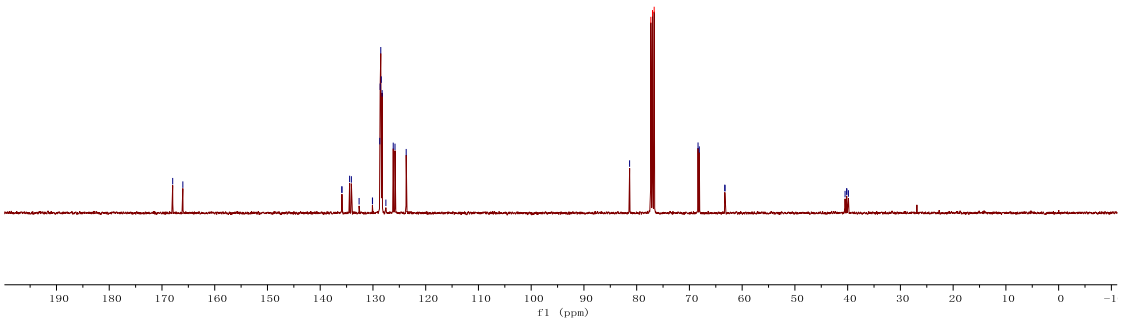
^{1}H NMR (400 MHz, $CDCl_3$)

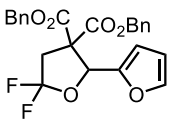




3ak

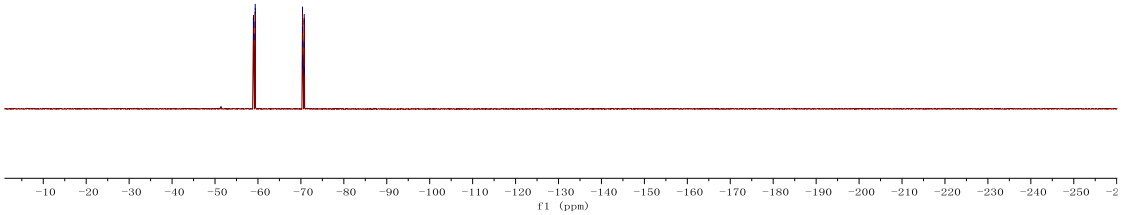
^{13}C NMR (101 MHz, $CDCl_3$)

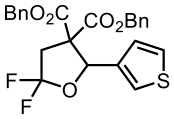




3ak

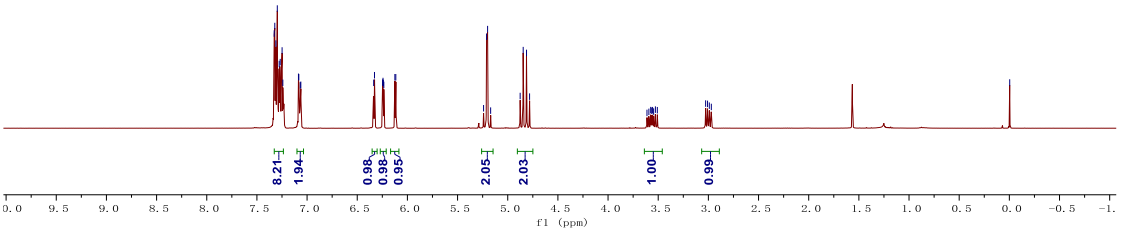
^{19}F NMR (376 MHz, $CDCl_3$)

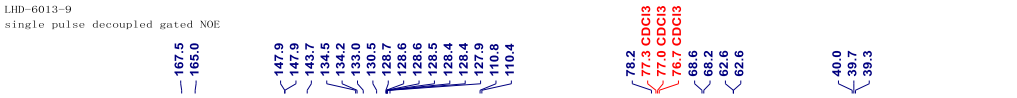


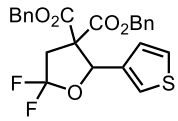


3al

^{1}H NMR (400 MHz, $CDCl_3$)

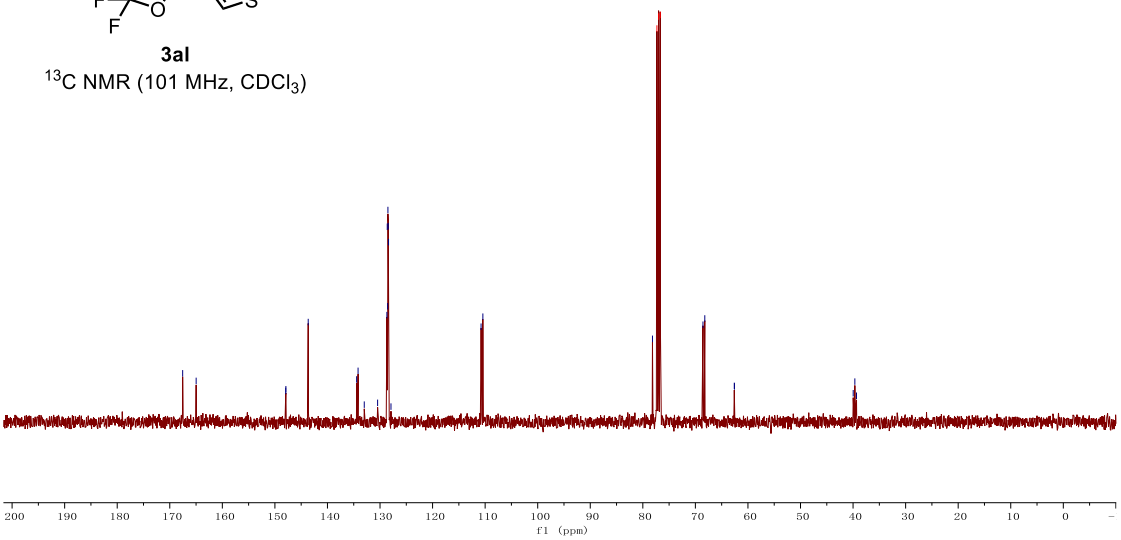






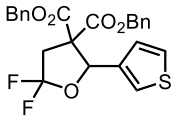
3al

^{13}C NMR (101 MHz, $CDCl_3$)



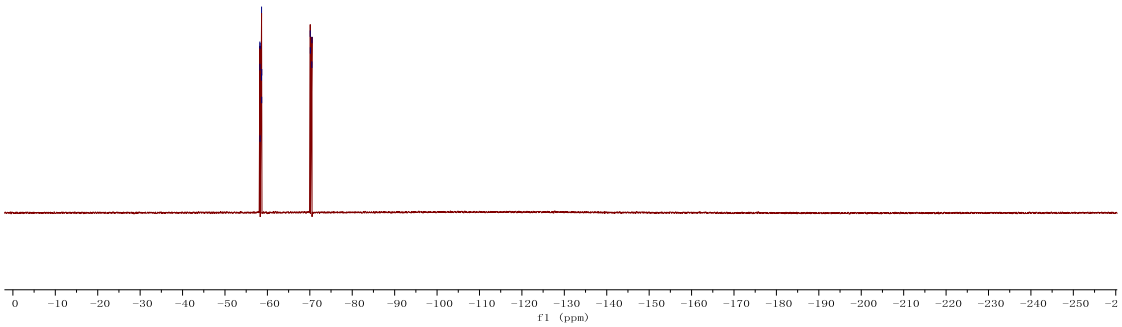
LHD-6013-9
single_pulse

-58.22
-58.25
-58.27
-58.29
-58.60
-58.63
-58.66
-58.67
-70.10
-70.13
-70.48
-70.51



3al

^{19}F NMR (376 MHz, $CDCl_3$)

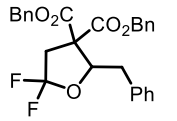


LHD-6087-3-2
single_pulse

7.34
7.33
7.32
7.27
7.25
7.25
7.13
7.12

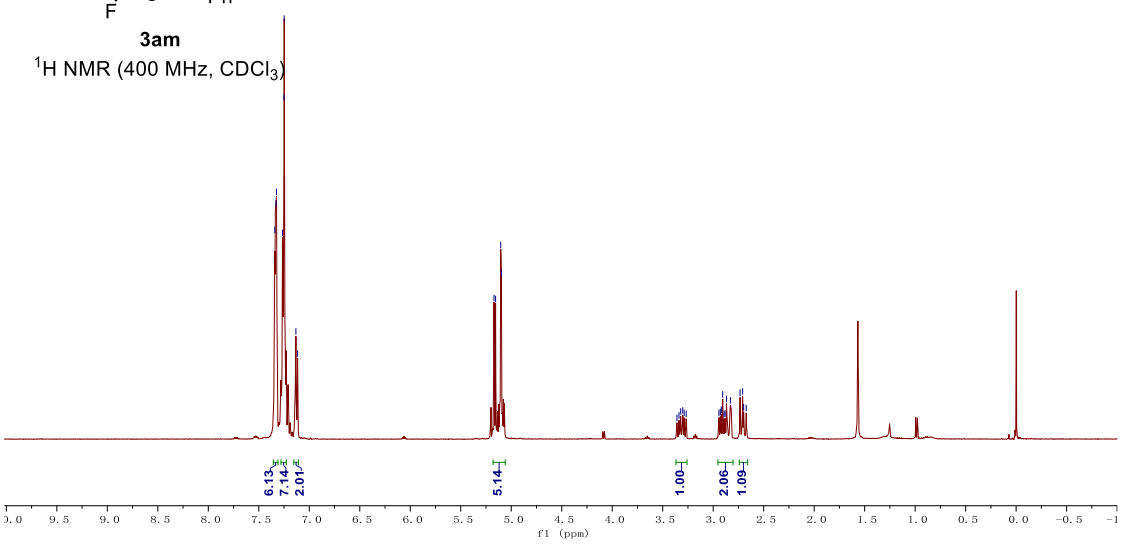
5.17
5.16
5.10
5.10

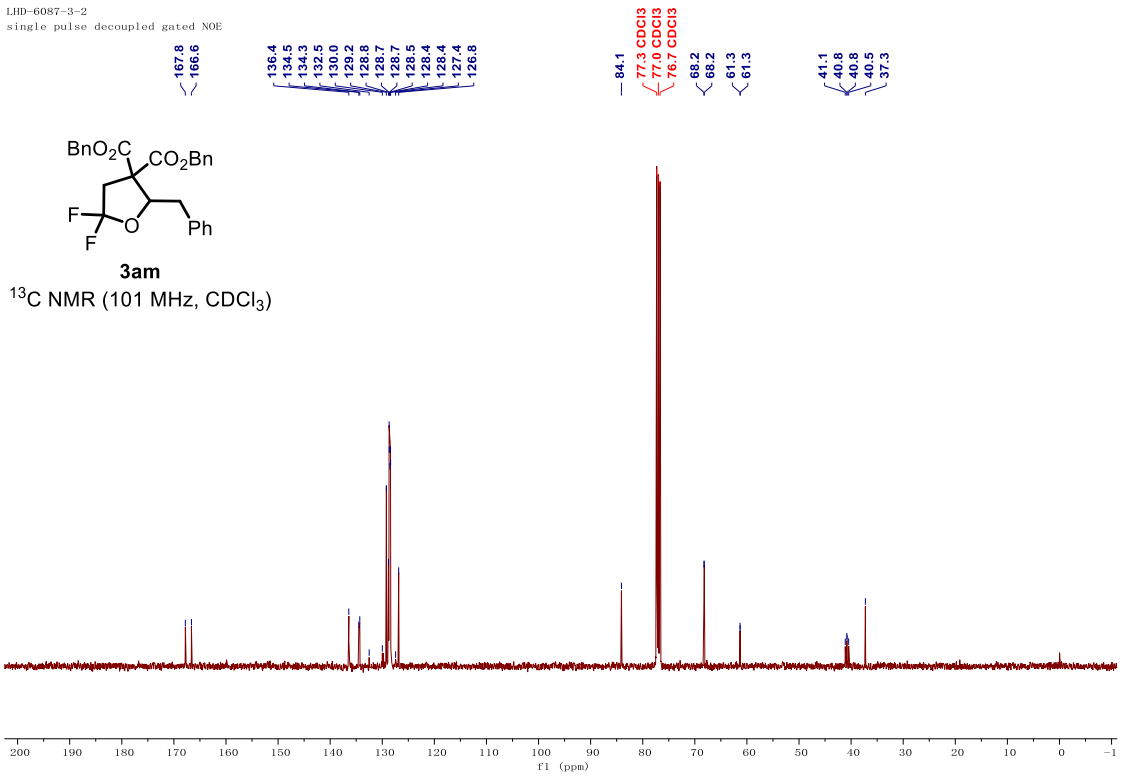
3.36
3.34
3.32
3.30
3.29
3.27
2.94
2.93
2.92
2.91
2.89
2.88
2.87
2.83
2.73
2.71
2.70
2.67



3am

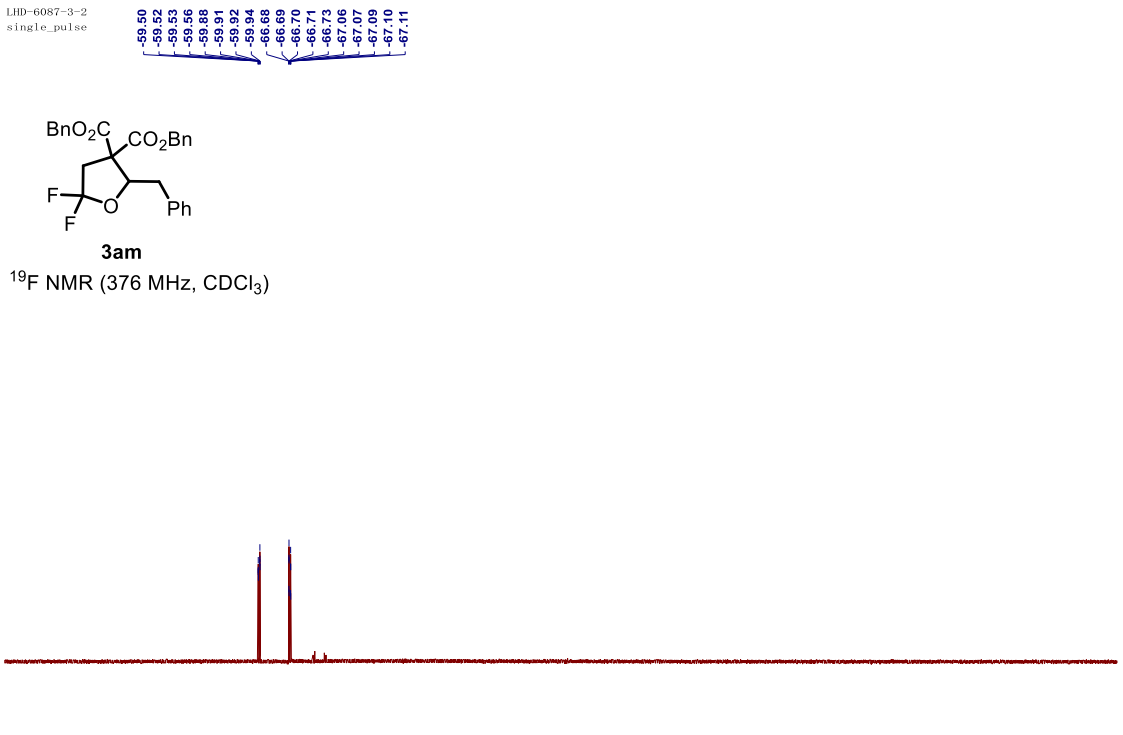
^{1}H NMR (400 MHz, $CDCl_3$)





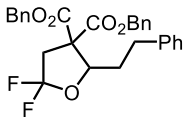
3am

^{13}C NMR (101 MHz, $CDCl_3$)



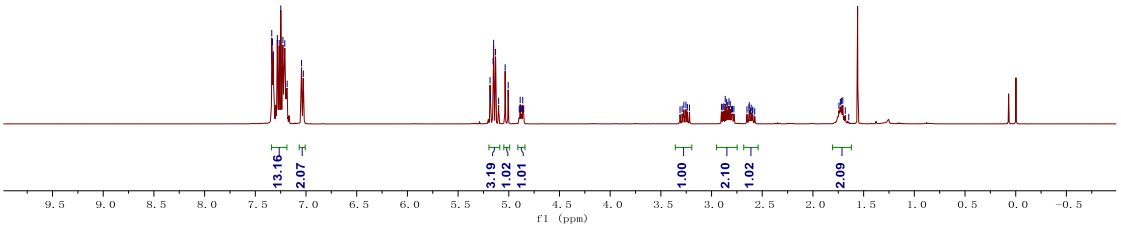
3am

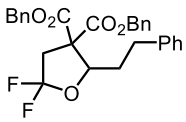
^{19}F NMR (376 MHz, $CDCl_3$)



3an

^{1}H NMR (400 MHz, $CDCl_3$)



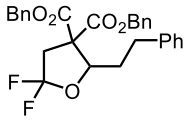


3an

^{13}C NMR (101 MHz, $CDCl_3$)

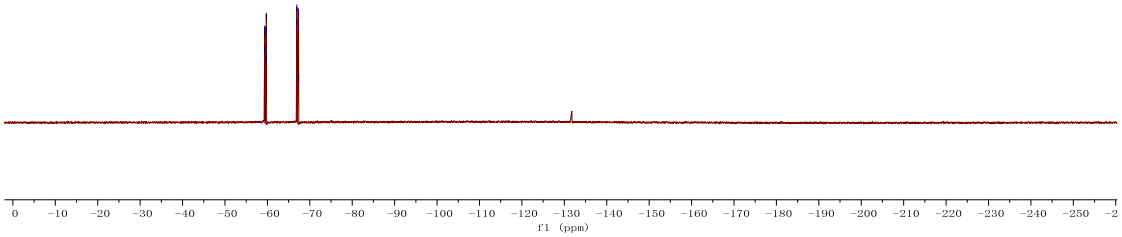
LHD-5191-5-2
single_pulse

-59.34
-59.38
-59.40
-59.73
-59.75
-59.79
-66.95
-66.97
-67.35
-67.37



3an

^{19}F NMR (376 MHz, $CDCl_3$)

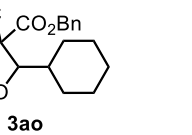


LHD-6035-3-3
single_pulse

7.34
7.33
7.32
7.28
7.27
7.26
7.25

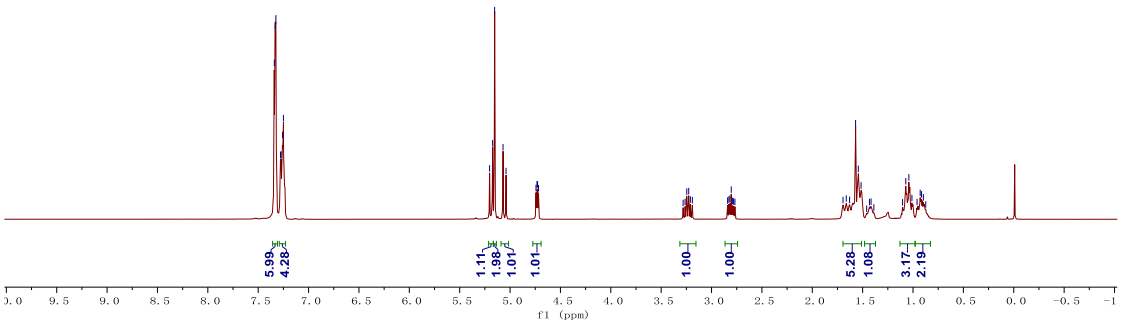
5.20
5.17
5.15
5.07
5.04
4.74
4.73
4.72

3.28
3.26
3.25
3.23
3.21
3.19
2.84
2.83
2.82
2.80
2.79
2.78
2.77
1.69
1.66
1.63
1.57
1.54
1.52
1.46
1.43
1.42
1.39
1.10
1.07
1.04
1.01
0.96
0.93
0.92
0.90
0.87



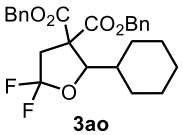
3ao

^{1}H NMR (400 MHz, $CDCl_3$)



LHD-6035-3-2
single pulse decoupled gated NOE

168.4
166.9
134.6
134.3
132.2
129.7
128.9
128.8
128.7
128.6
128.4
127.2
88.0
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
68.1
68.1
61.0
61.0
42.4
42.1
42.0
41.7
39.1
29.9
27.7
25.8
25.6
25.3

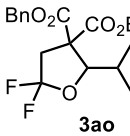


3ao

^{13}C NMR (101 MHz, $CDCl_3$)

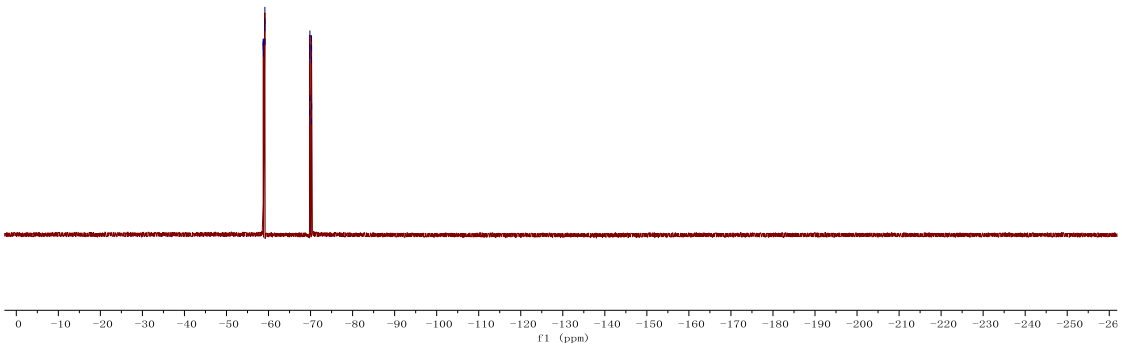
LHD-6035-3-2
single_pulse

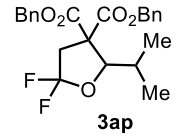
-58.73
-58.75
-58.76
-58.79
-59.11
-59.13
-59.15
-59.17
-69.82
-69.84
-69.85
-69.86
-69.87
-70.21
-70.22
-70.23
-70.24
-70.25



3ao

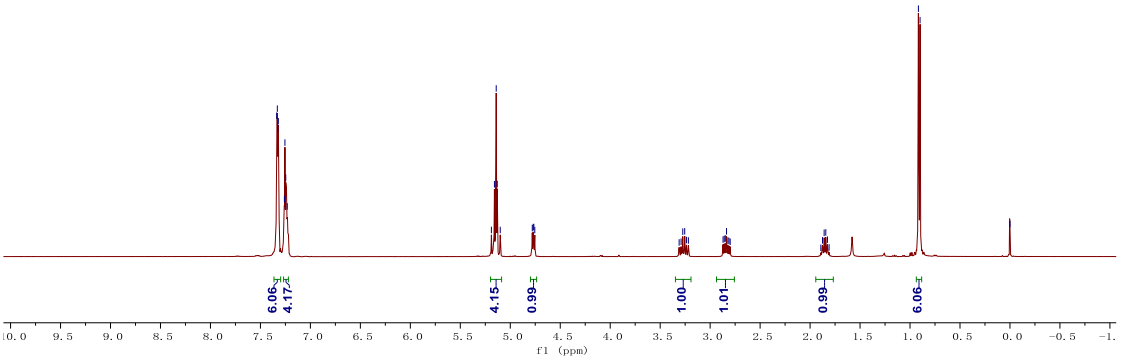
^{19}F NMR (376 MHz, $CDCl_3$)

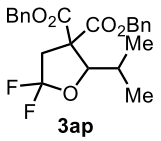




3ap

^{1}H NMR (400 MHz, $CDCl_3$)



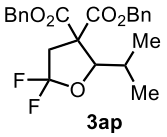


3ap

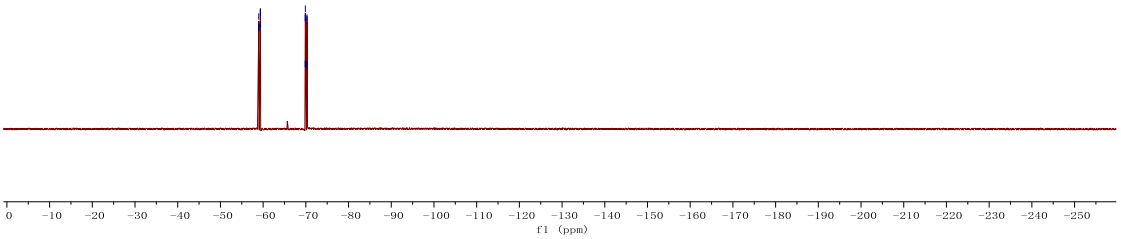
^{13}C NMR (101 MHz, $CDCl_3$)

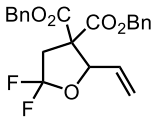
LHD-6097-3
single_pulse

-58.96
-58.98
-59.00
-59.02
-59.34
-59.37
-59.38
-59.40
-69.87
-69.88
-69.89
-69.90
-69.91
-70.25
-70.26
-70.27
-70.28
-70.29



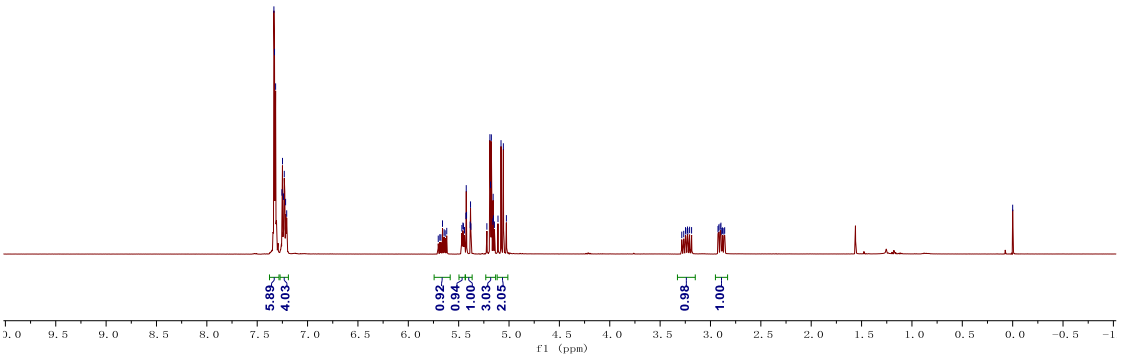
3ap

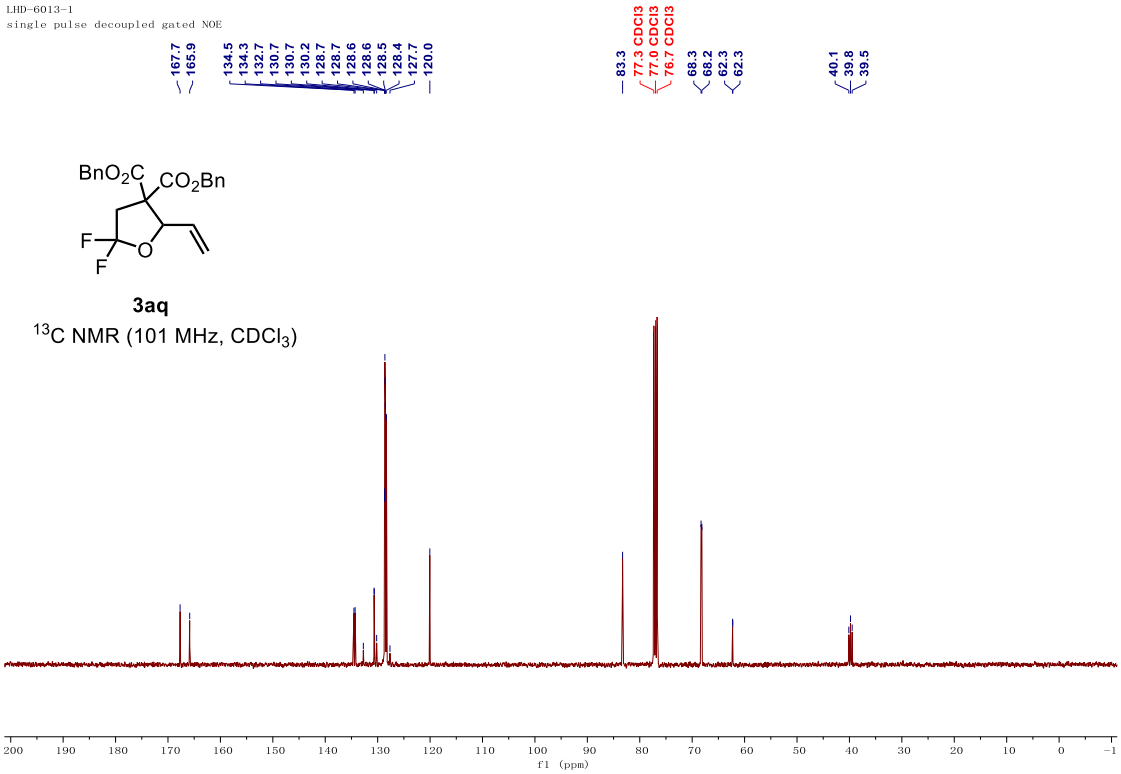




3aq

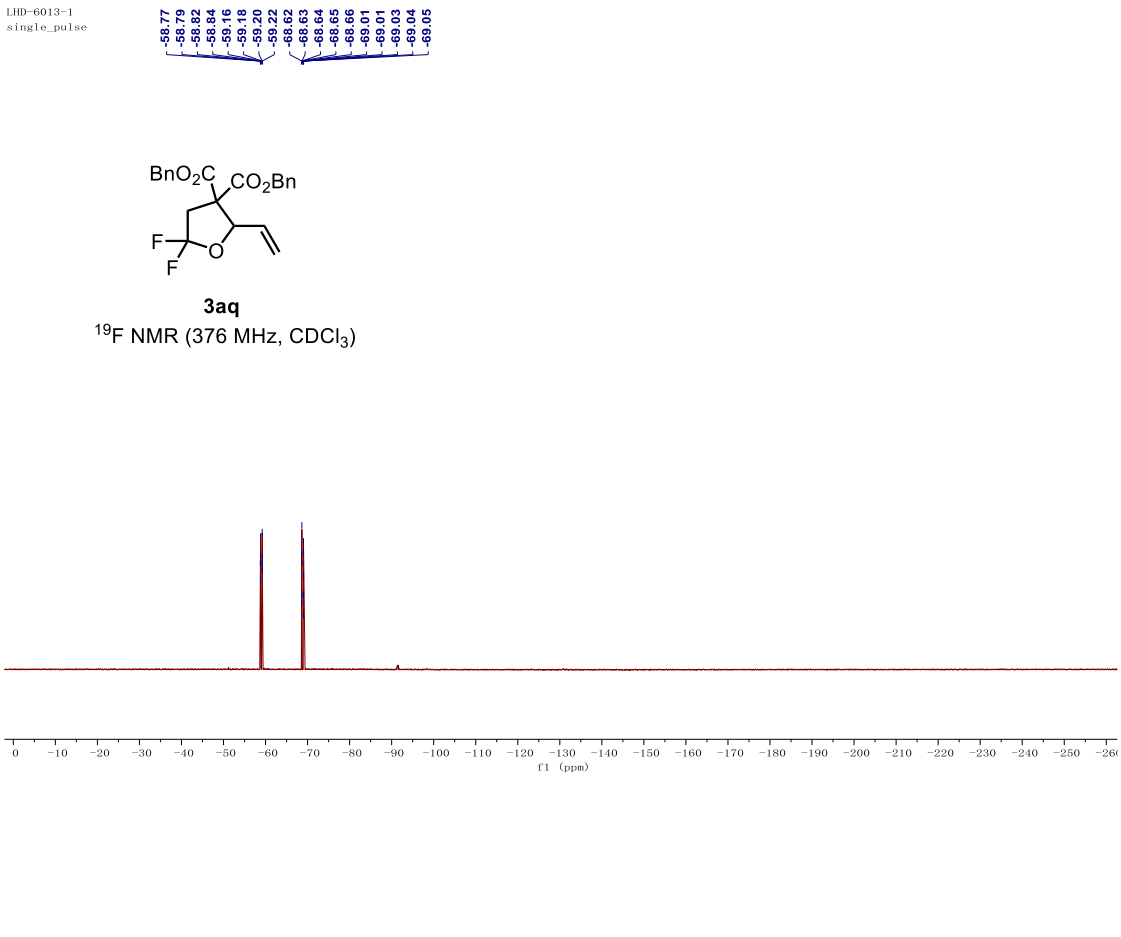
^{1}H NMR (400 MHz, $CDCl_3$)





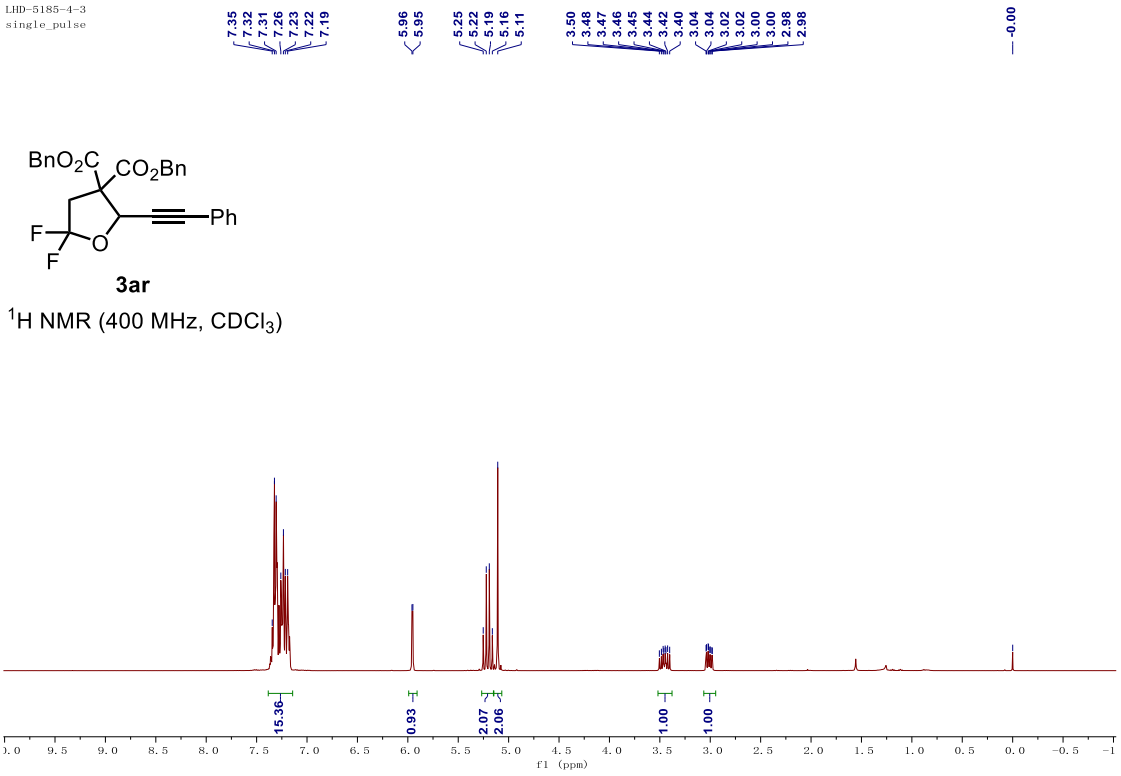
3aq

^{13}C NMR (101 MHz, $CDCl_3$)



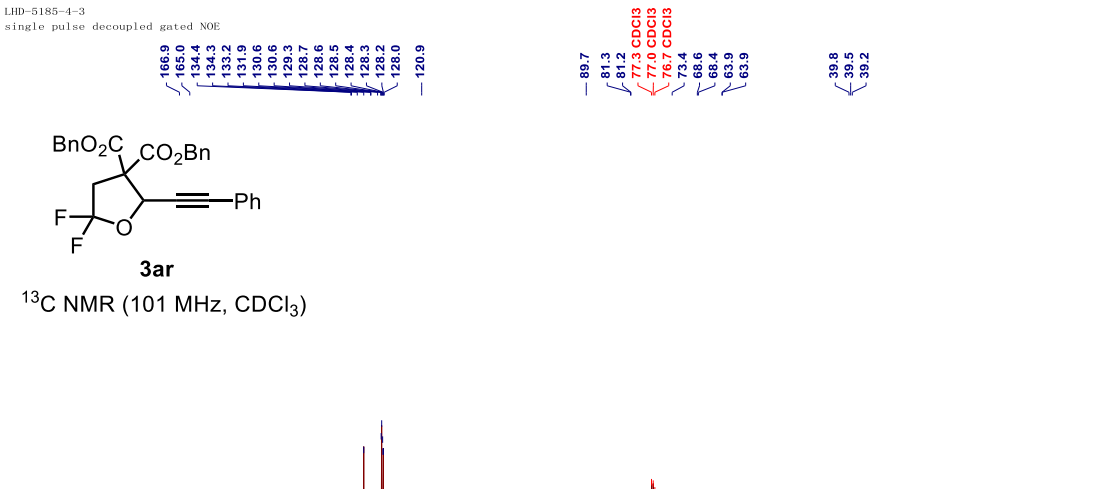
3aq

^{19}F NMR (376 MHz, $CDCl_3$)



3ar

^{1}H NMR (400 MHz, $CDCl_3$)

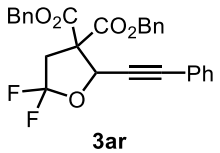


3ar

^{13}C NMR (101 MHz, $CDCl_3$)

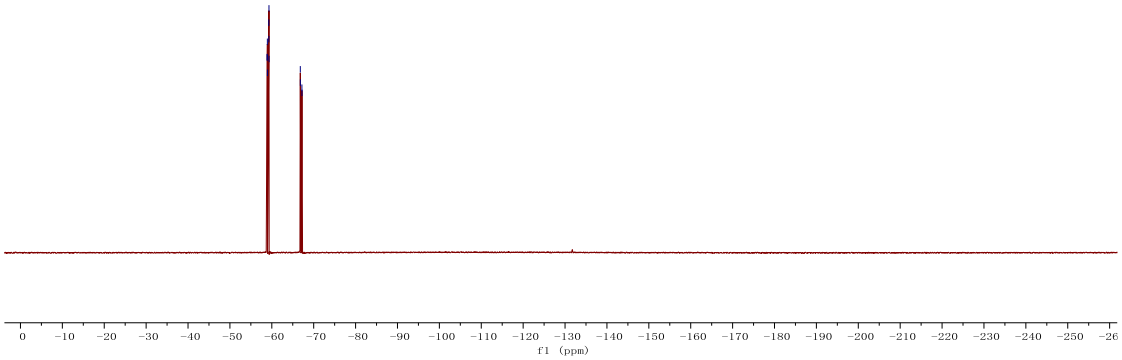
LHD-5185-4-3
single_pulse

-58.89
-58.92
-58.94
-58.97
-59.27
-59.30
-59.32
-59.35
-66.80
-66.82
-67.18
-67.20



3ar

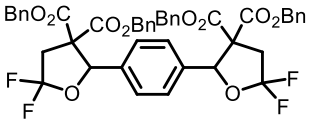
^{19}F NMR (376 MHz, $CDCl_3$)



LHD-6087-5-2
single_pulse

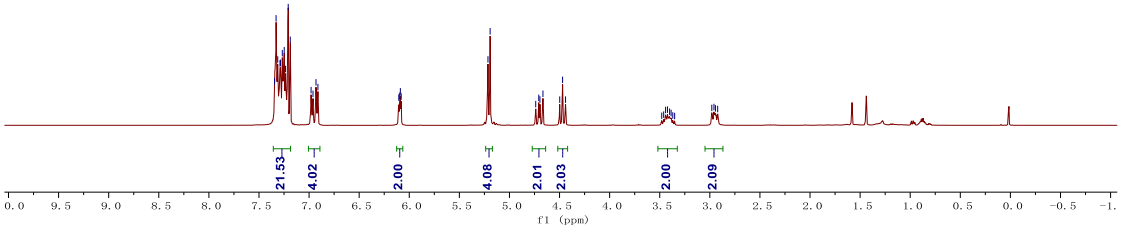
7.34
7.33
7.31
7.29
7.29
7.27
7.25
7.23
7.21
7.19
6.98
6.96
6.93
6.91
6.10
6.10
6.09
6.08

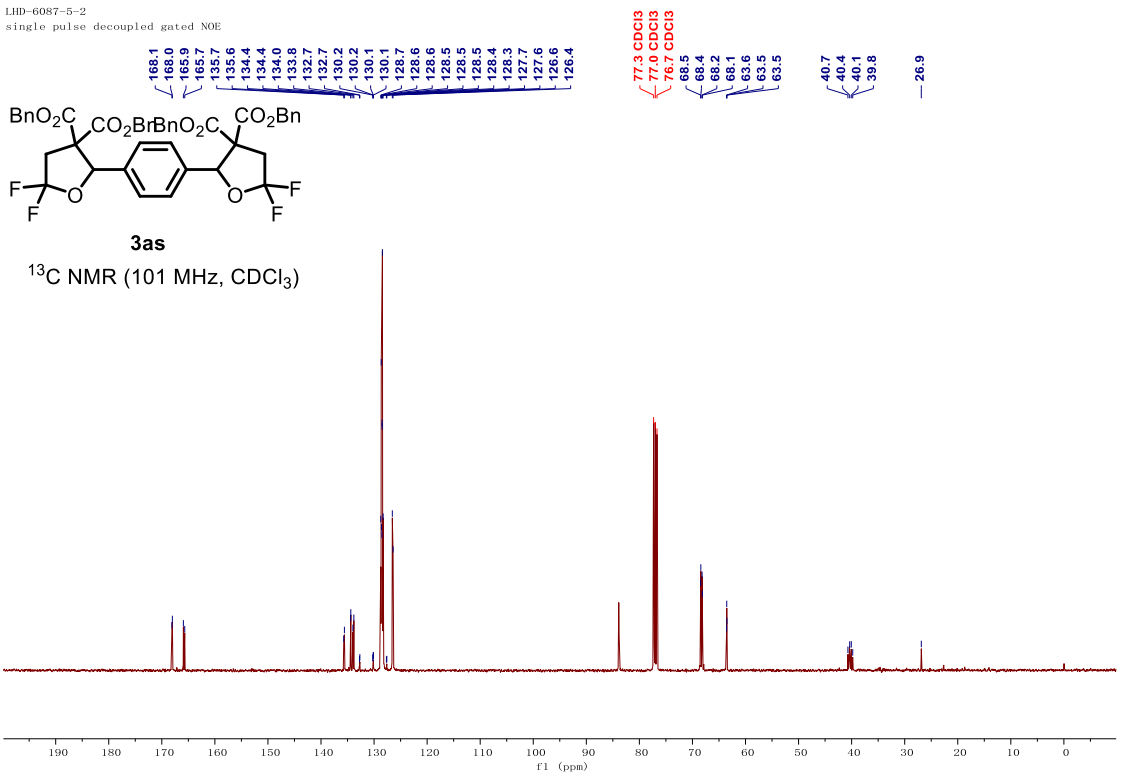
5.21
5.19
4.74
4.71
4.70
4.67
4.50
4.47
4.44
3.48
3.46
3.44
3.42
3.40
3.39
3.37
3.35
2.98
2.96
2.94
2.92

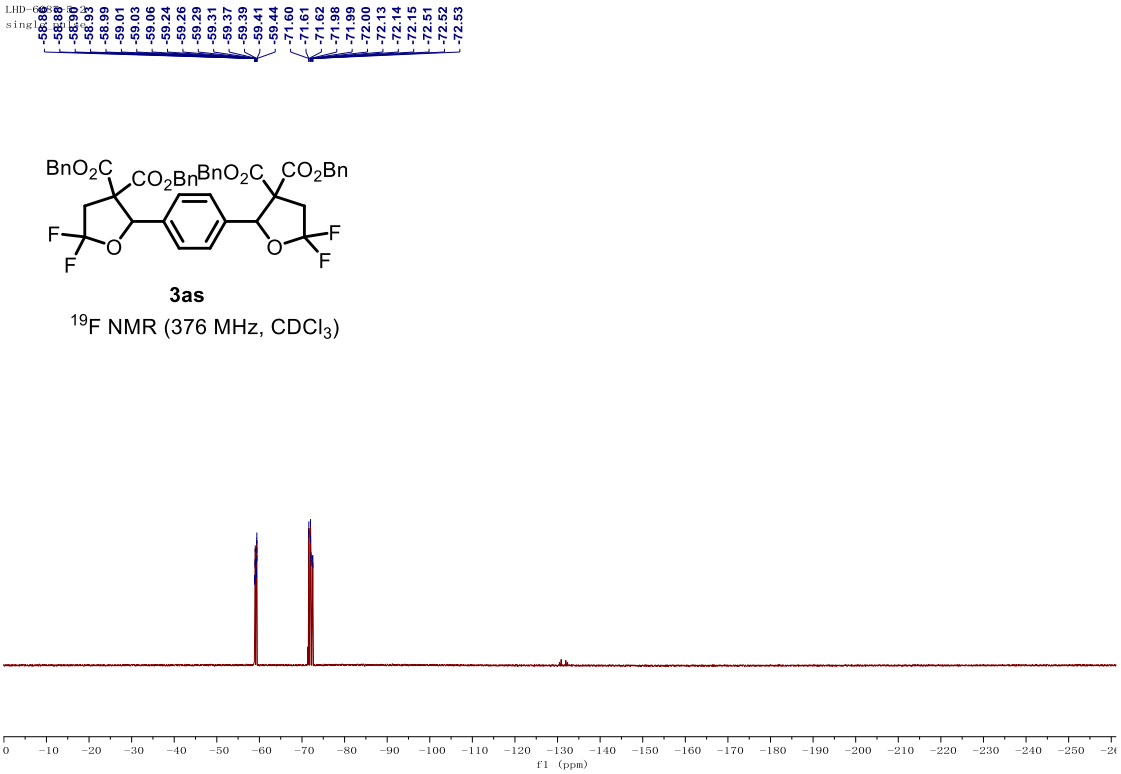


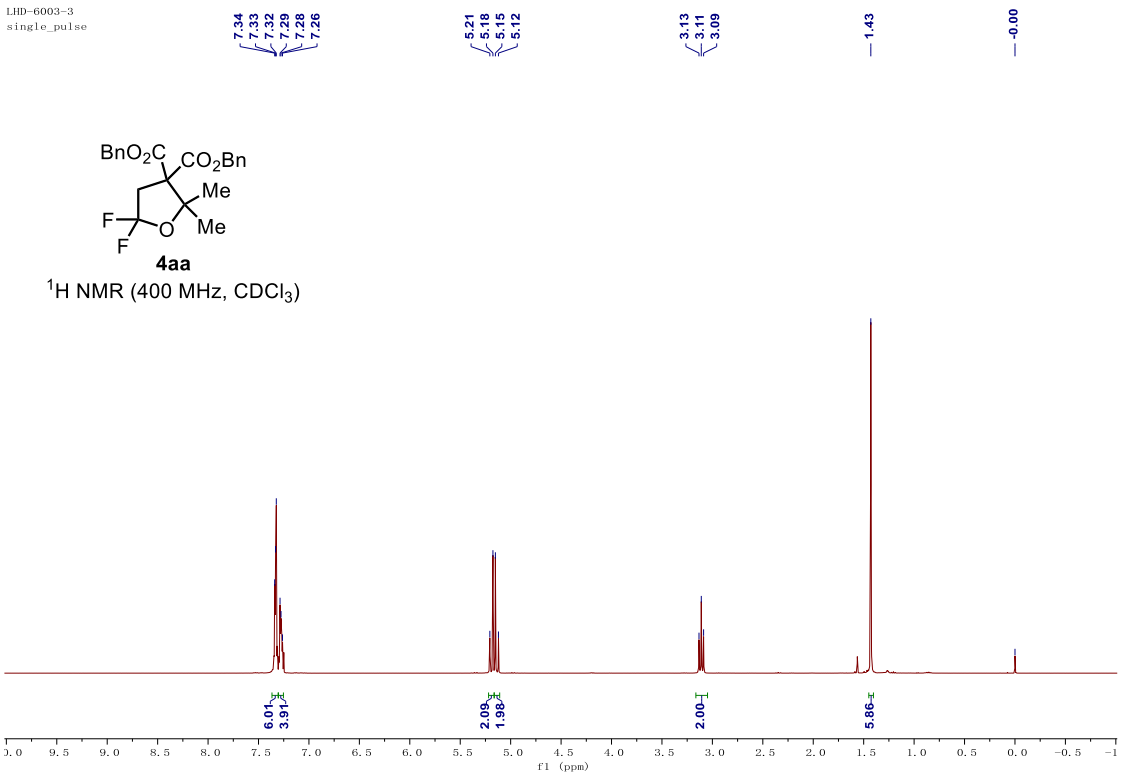
3as

^{1}H NMR (400 MHz, $CDCl_3$)



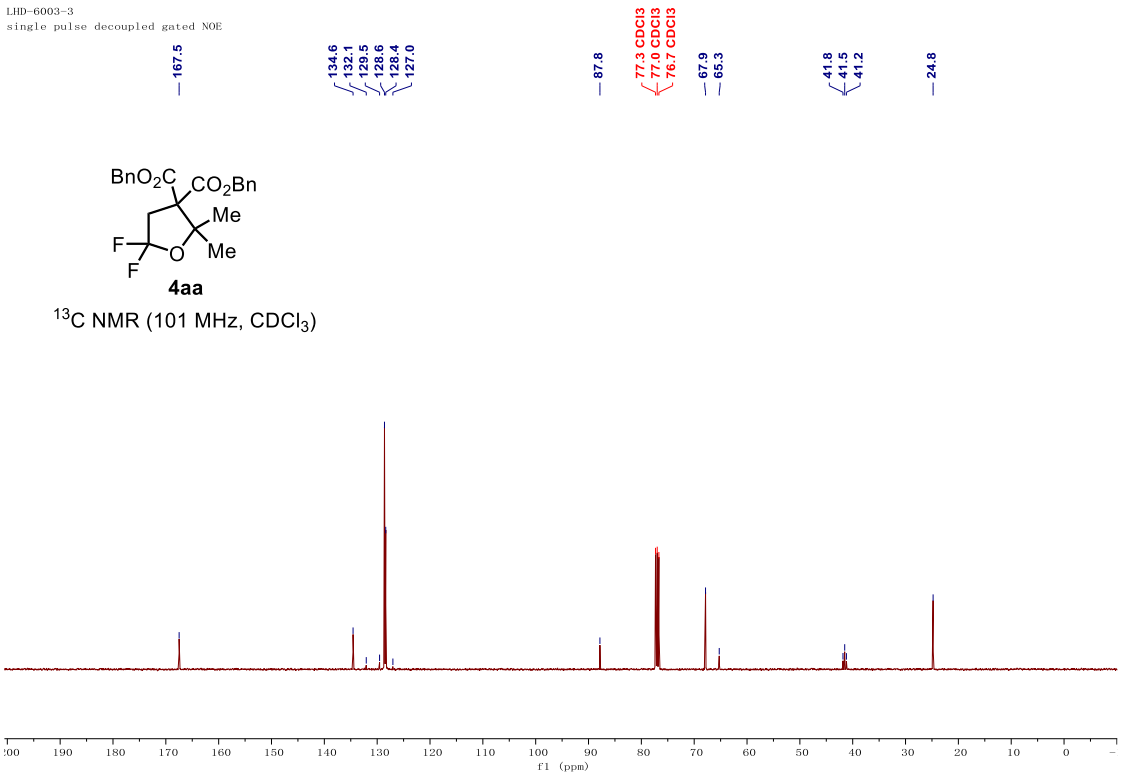

LHD-6087-5-2
single pulse decoupled gated NOE
168.1
168.0
165.9
165.7
135.7
135.6
134.4
134.4
134.0
133.8
132.7
132.7
130.2
130.2
130.1
130.1
128.7
128.6
128.6
128.5
128.5
128.5
128.4
128.3
127.7
127.6
126.6
126.4
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
68.5
68.4
68.2
68.1
63.6
63.5
63.5
40.7
40.4
40.1
39.8
26.9
BnO2C
CO2Bn
BnO2C
CO2Bn
F
O
F
F
O
F
3as
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-58.88
-58.90
-58.93
-58.99
-59.01
-59.03
-59.06
-59.24
-59.26
-59.29
-59.31
-59.37
-59.39
-59.41
-59.44
-71.60
-71.61
-71.62
-71.98
-71.99
-72.00
-72.13
-72.14
-72.15
-72.51
-72.52
-72.53
BnO2C
CO2Bn
BnO2C
CO2Bn
F
O
F
F
O
F
3as
19F NMR (376 MHz, CDCl3)
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
−230
−240
−250
f1 (ppm)



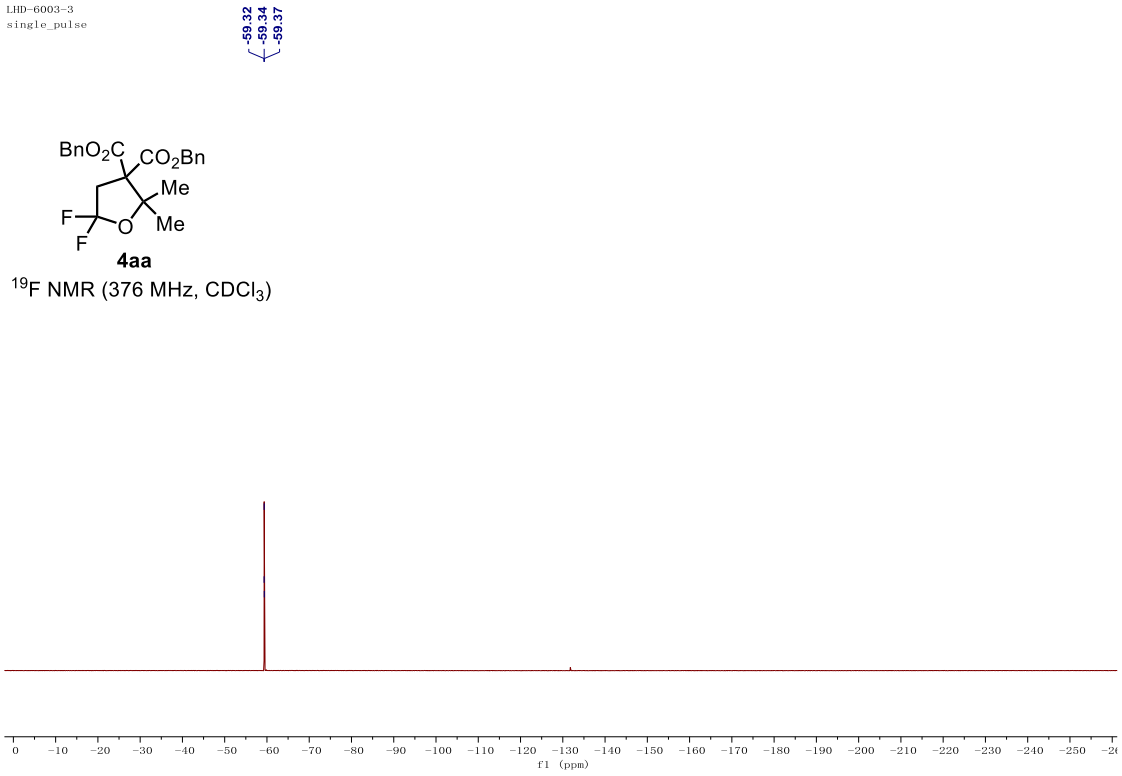
4aa

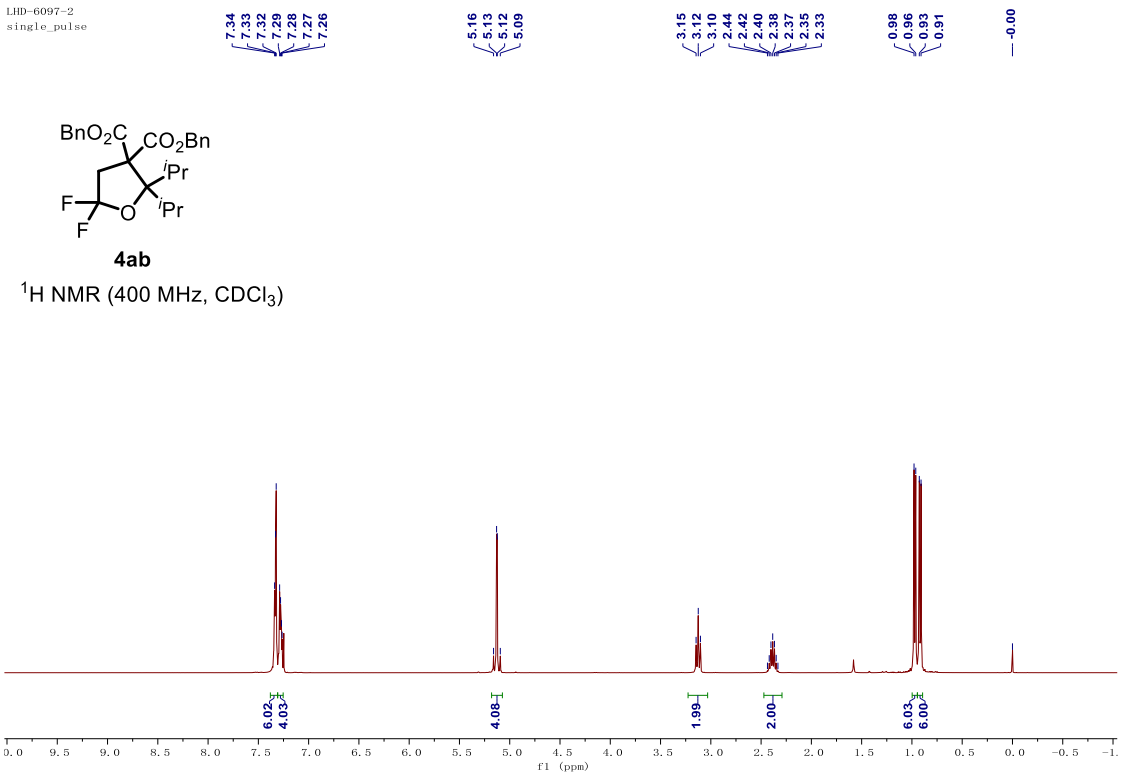
^{1}H NMR (400 MHz, $CDCl_3$)

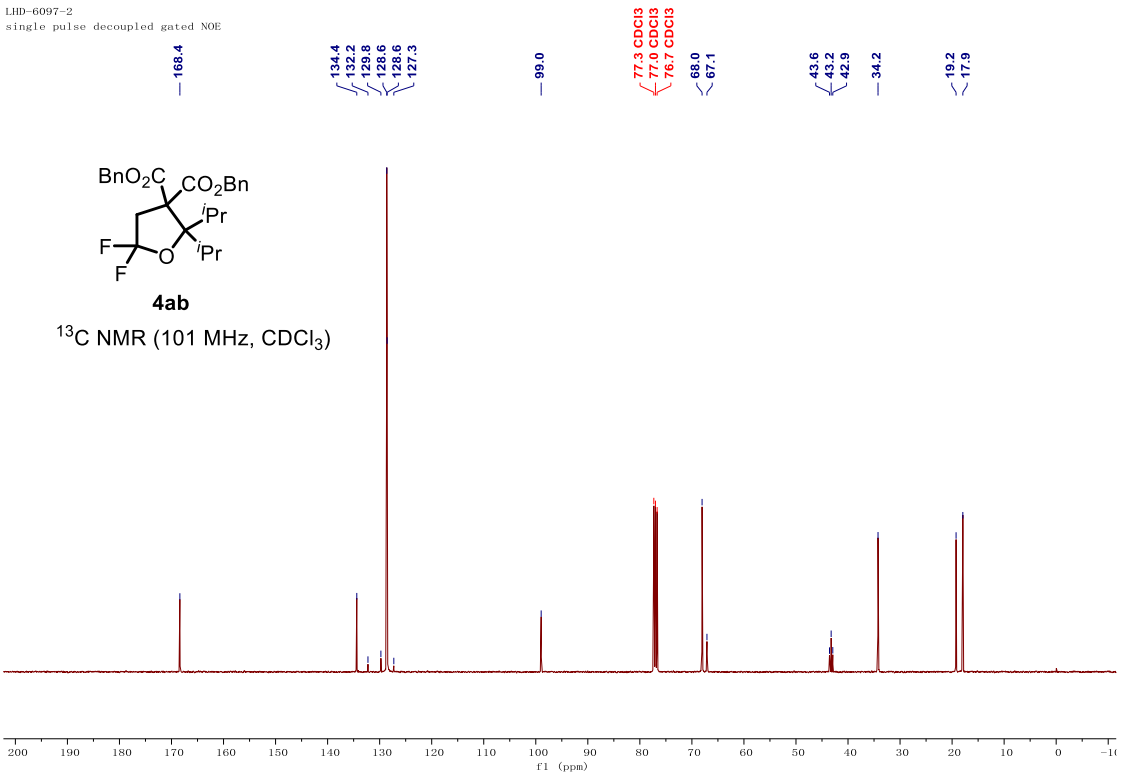


4aa

^{13}C NMR (101 MHz, $CDCl_3$)

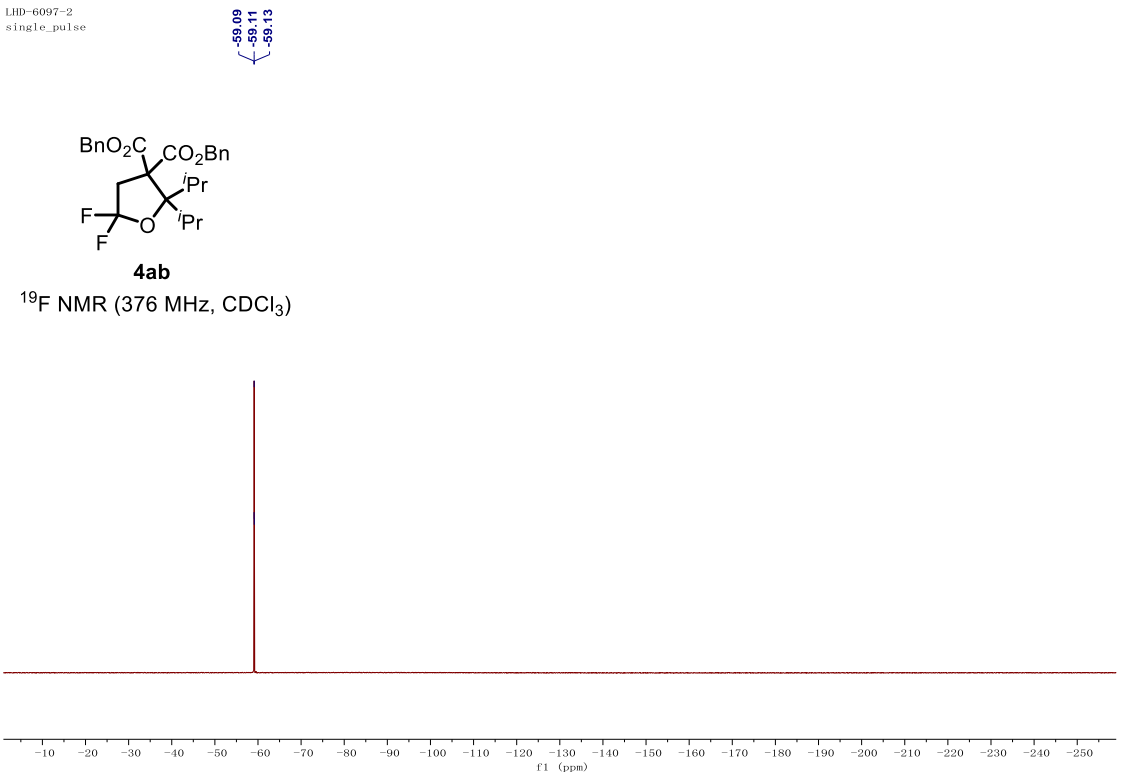

LHD-6003-3
single_pulse
-59.32
-59.34
-59.37
BnO2C
CO2Bn
Me
F
O
Me
F
4aa
19F NMR (376 MHz, CDCl3)
f1 (ppm)


LHD-6097-2
single_pulse
7.34
7.33
7.32
7.29
7.28
7.27
7.26
5.16
5.13
5.12
5.09
3.15
3.12
3.10
2.44
2.42
2.40
2.38
2.37
2.35
2.33
0.98
0.96
0.93
0.91
-0.00
BnO2C
CO2Bn
iPr
F
O
iPr
F
4ab
1H NMR (400 MHz, CDCl3)
6.02
4.03
4.08
1.99
2.00
6.03
6.00
f1 (ppm)



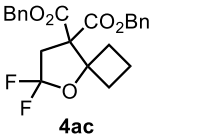
4ab

^{13}C NMR (101 MHz, $CDCl_3$)



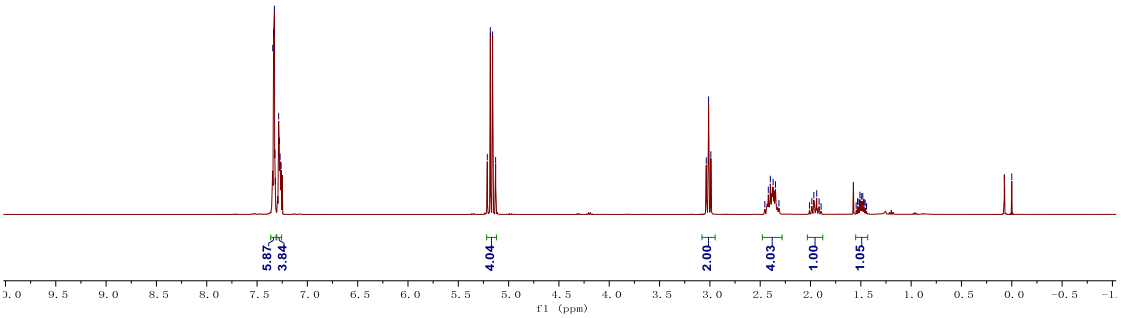
4ab

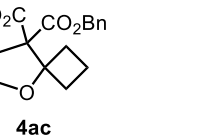
^{19}F NMR (376 MHz, $CDCl_3$)



4ac

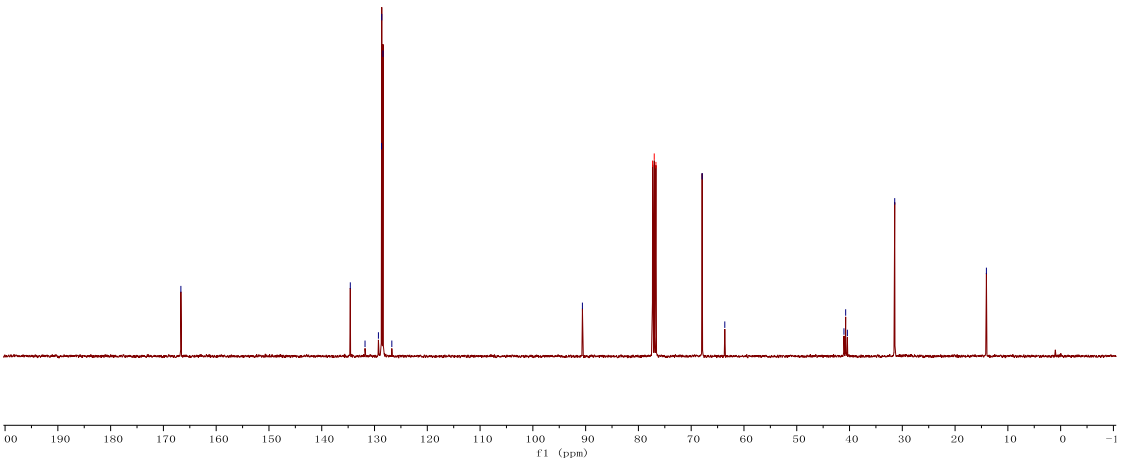
^{1}H NMR (400 MHz, $CDCl_3$)





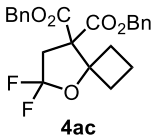
4ac

^{13}C NMR (101 MHz, $CDCl_3$)



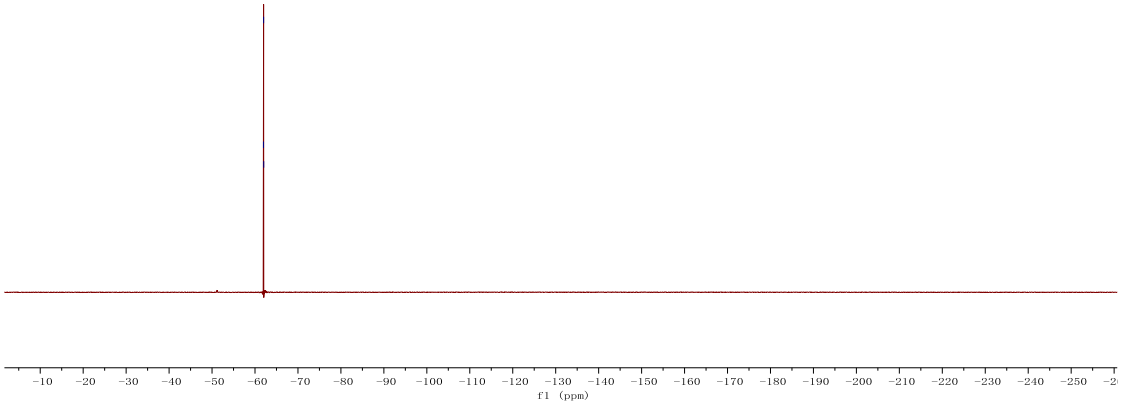
LHD-6009-2
single_pulse

-61.98
-62.00
-62.03



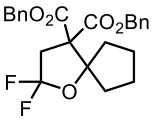
4ac

^{19}F NMR (376 MHz, $CDCl_3$)



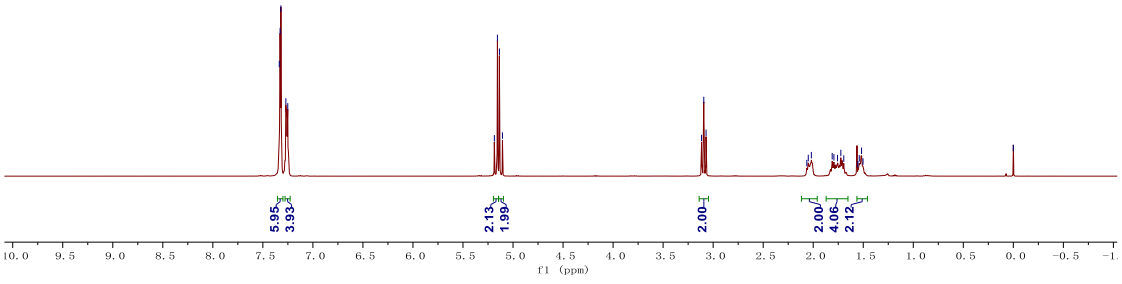
LHD-6003-2
single_pulse

7.34
7.33
7.32
7.27
7.25
5.19
5.16
5.14
5.11
3.12
3.09
3.07
2.06
2.05
2.02
1.81
1.79
1.76
1.72
1.69
1.55
1.54
1.52
1.50
-0.00



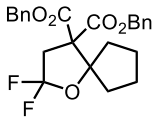
4ad

^{1}H NMR (400 MHz, $CDCl_3$)



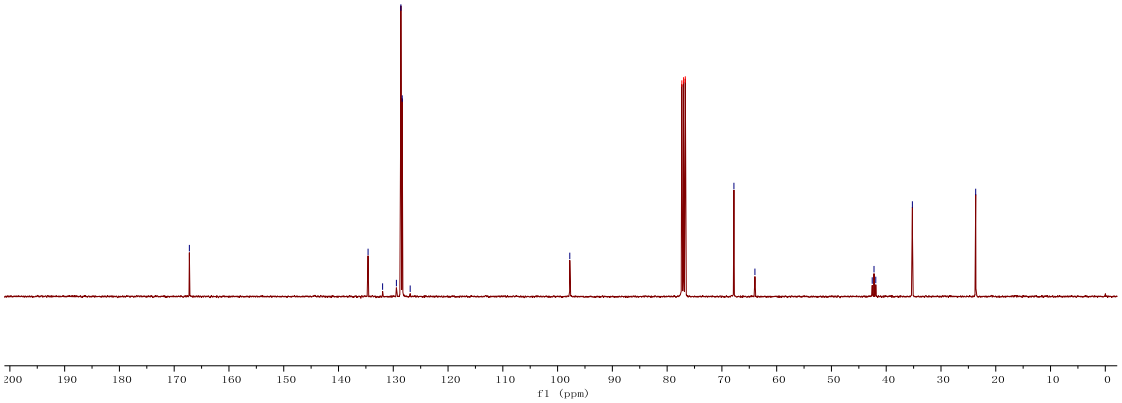
LHD-6003-2
single pulse decoupled gated NOE

167.2
134.6
131.9
129.4
128.6
128.4
126.9
97.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
67.8
64.0
42.6
42.2
41.9
35.2
23.7



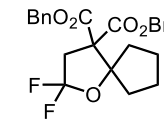
4ad

^{13}C NMR (101 MHz, $CDCl_3$)



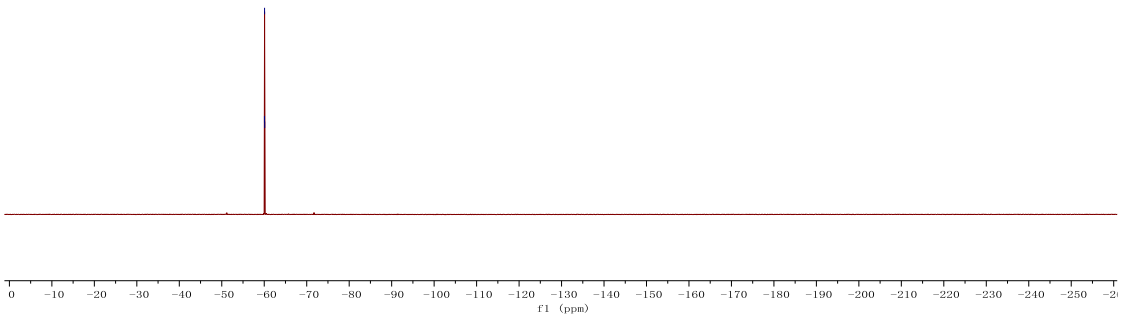
LHD-6003-2
single_pulse

-60.05
-60.08
-60.10

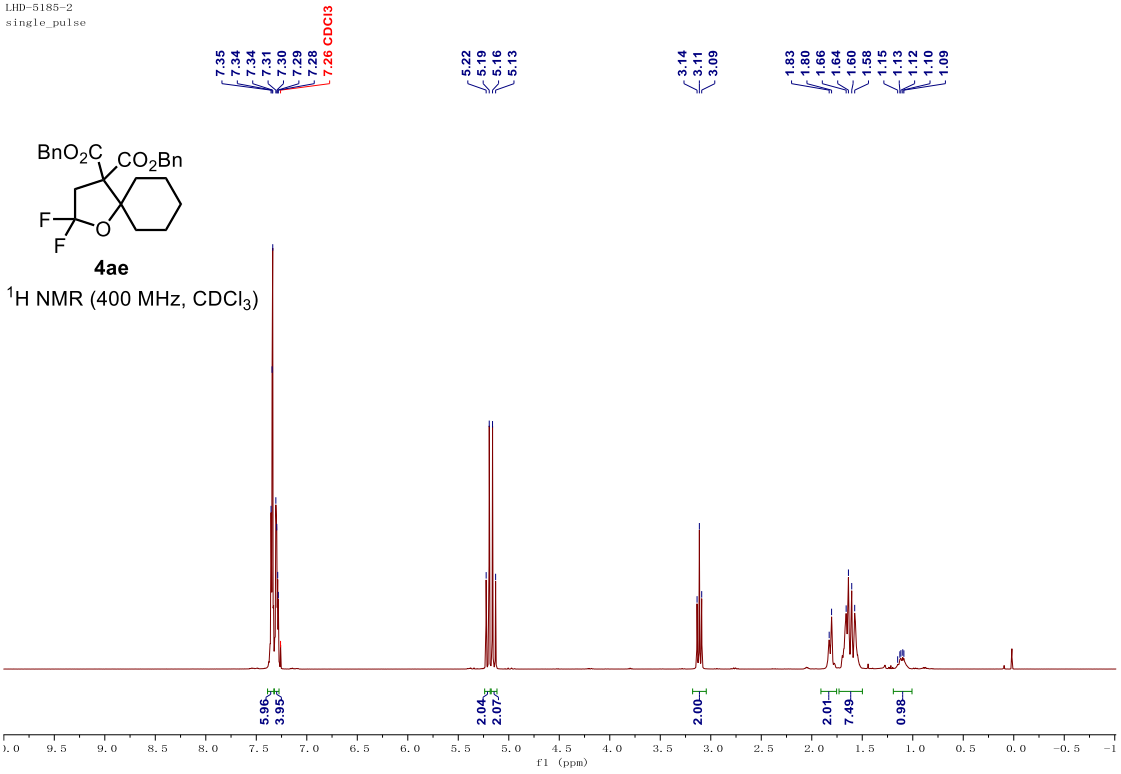


4ad

^{19}F NMR (376 MHz, $CDCl_3$)



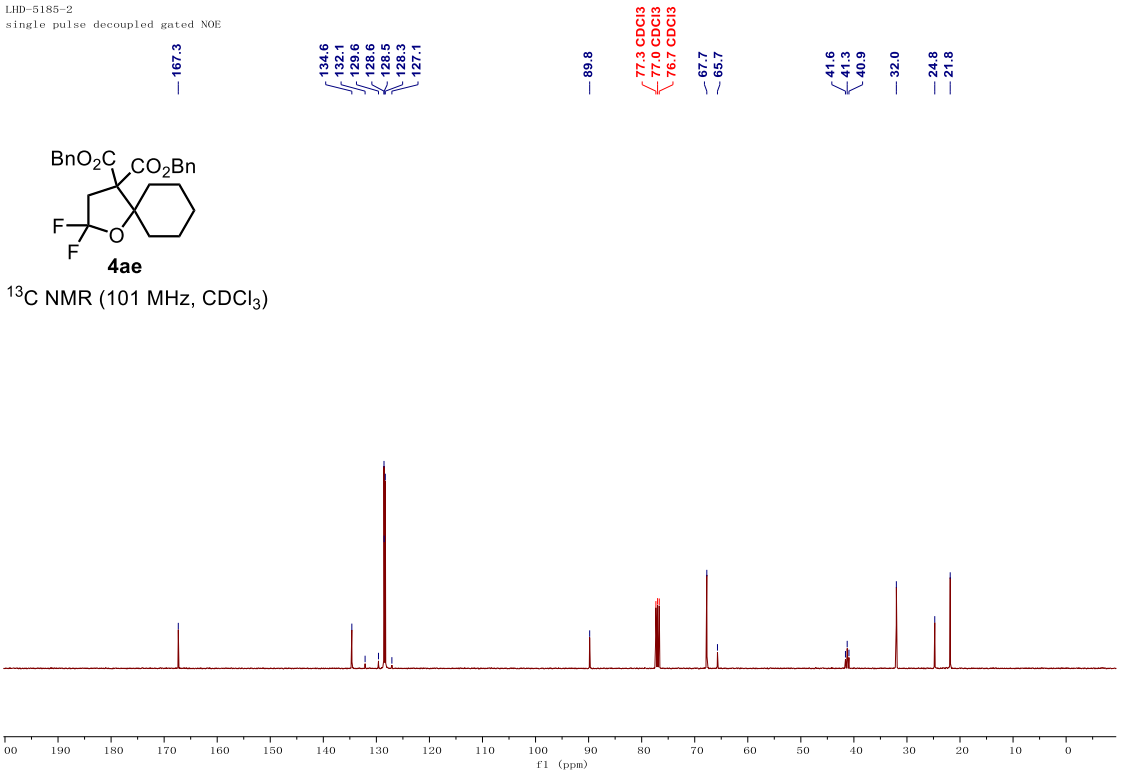
LHD-5185-2
single_pulse



4ae

^{1}H NMR (400 MHz, $CDCl_3$)

LHD-5185-2
single pulse decoupled gated NOE

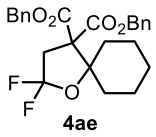


4ae

^{13}C NMR (101 MHz, $CDCl_3$)

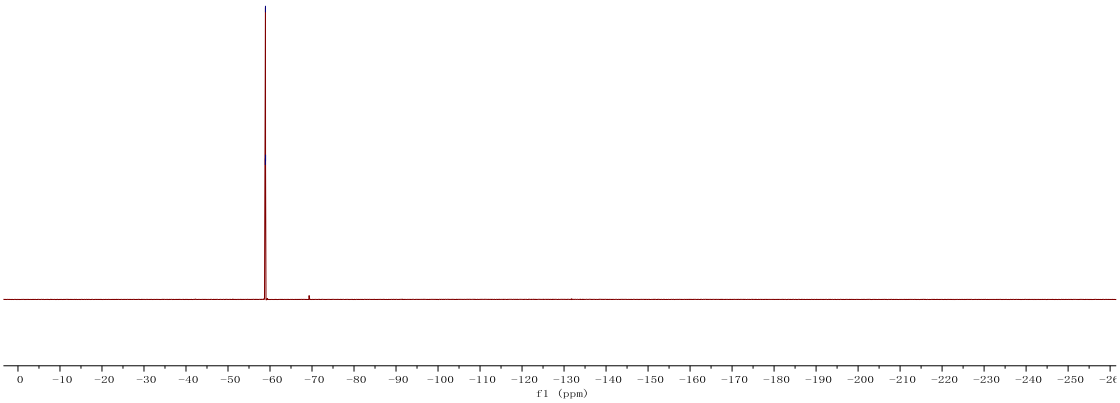
LHD-5185-2
single_pulse

-58.89
-58.92
-58.94



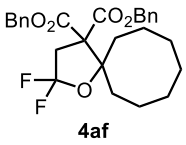
4ae

^{19}F NMR (376 MHz, $CDCl_3$)



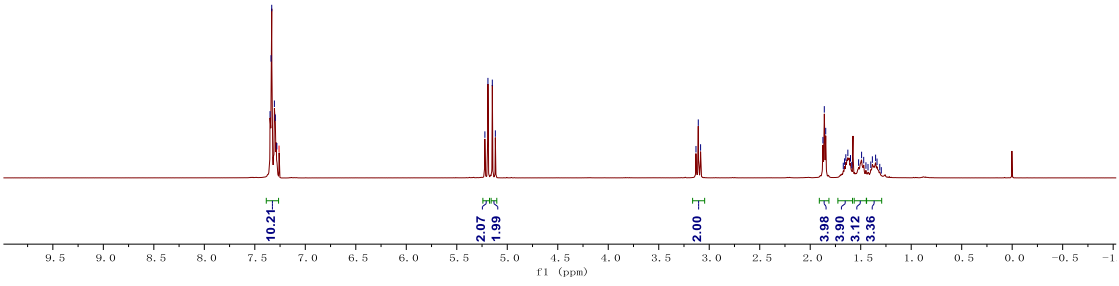
LHD-6029-2
single_pulse

7.35
7.34
7.33
7.31
7.30
7.28
7.26 CDCl3
5.22
5.19
5.15
5.12
3.13
3.11
3.09
1.87
1.86
1.85
1.67
1.66
1.65
1.63
1.60
1.59
1.52
1.49
1.47
1.45
1.43
1.40
1.38
1.35
1.34
1.31
1.30

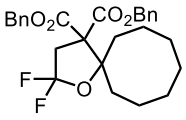


4af

^{1}H NMR (400 MHz, $CDCl_3$)

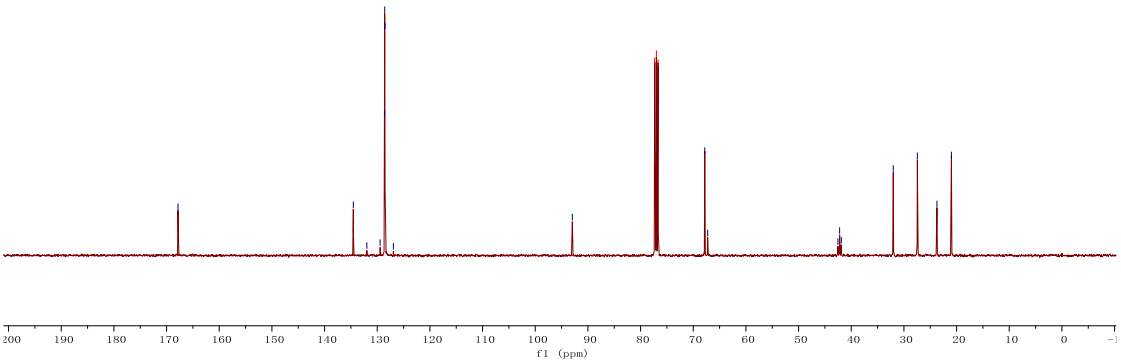


LHD-6029-2
single pulse decoupled gated NOE

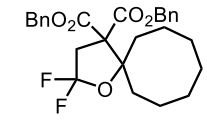


4af

^{13}C NMR (101 MHz, $CDCl_3$)

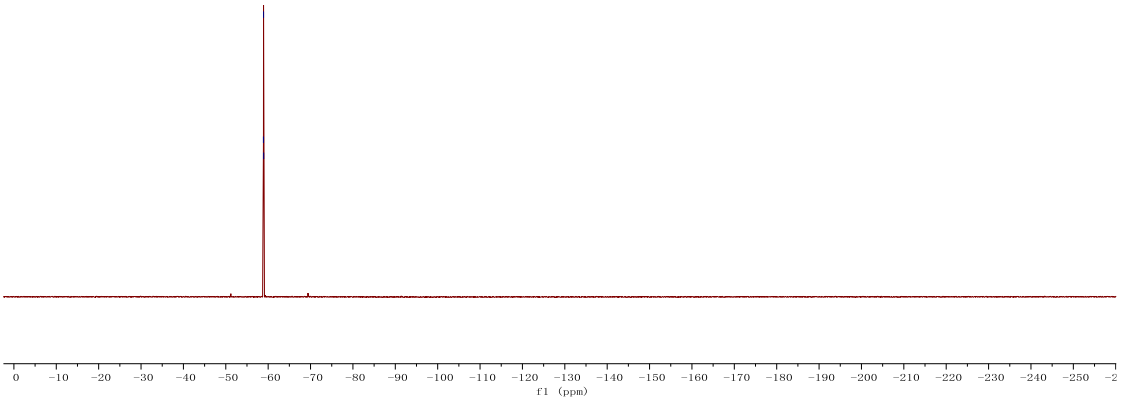


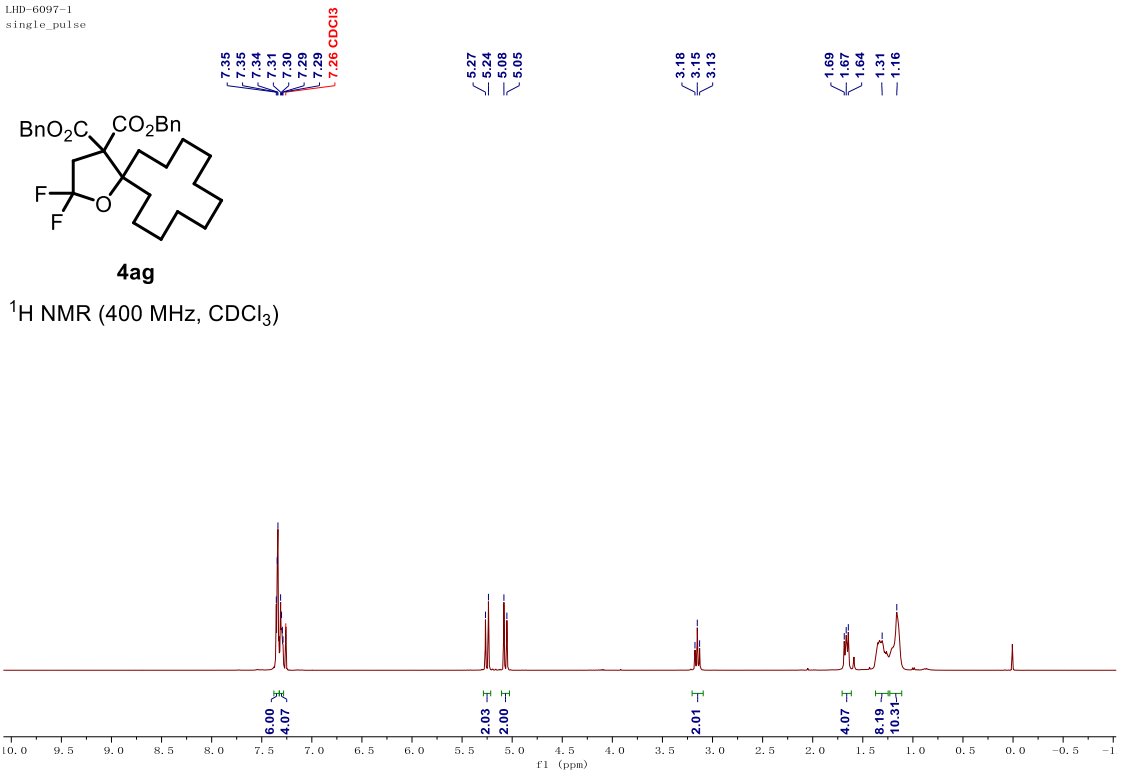
LHD-6029-2
single_pulse



4af

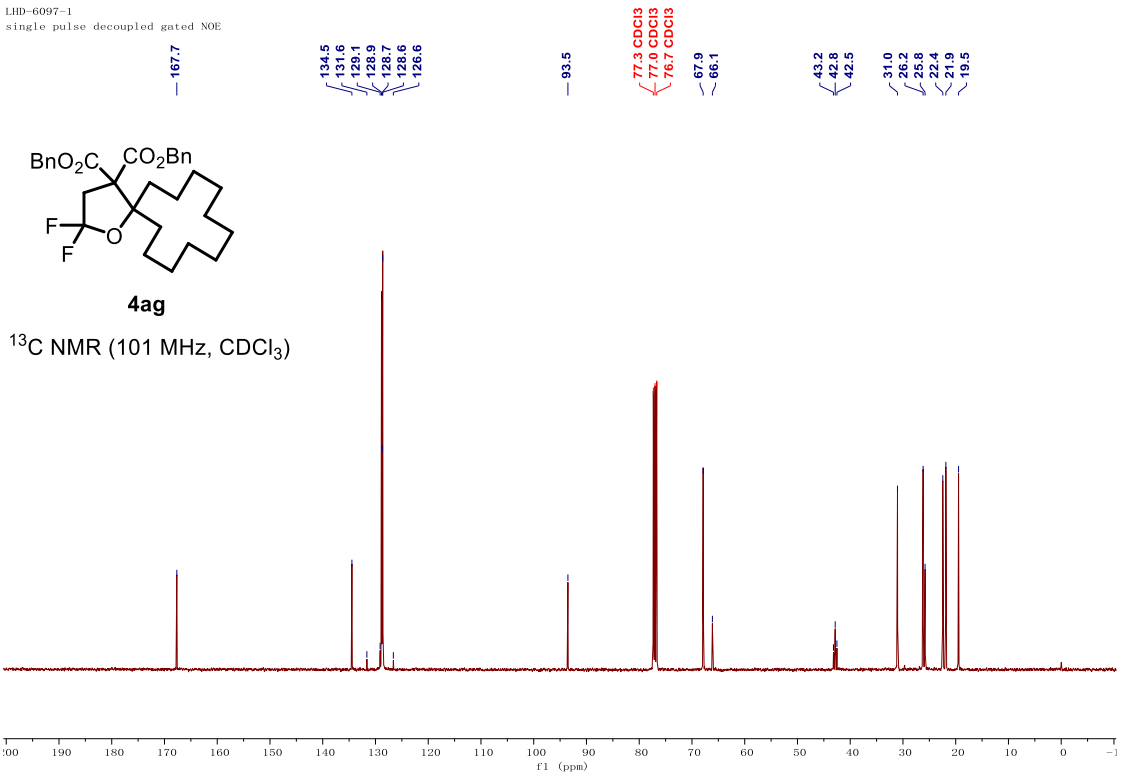
^{19}F NMR (376 MHz, $CDCl_3$)





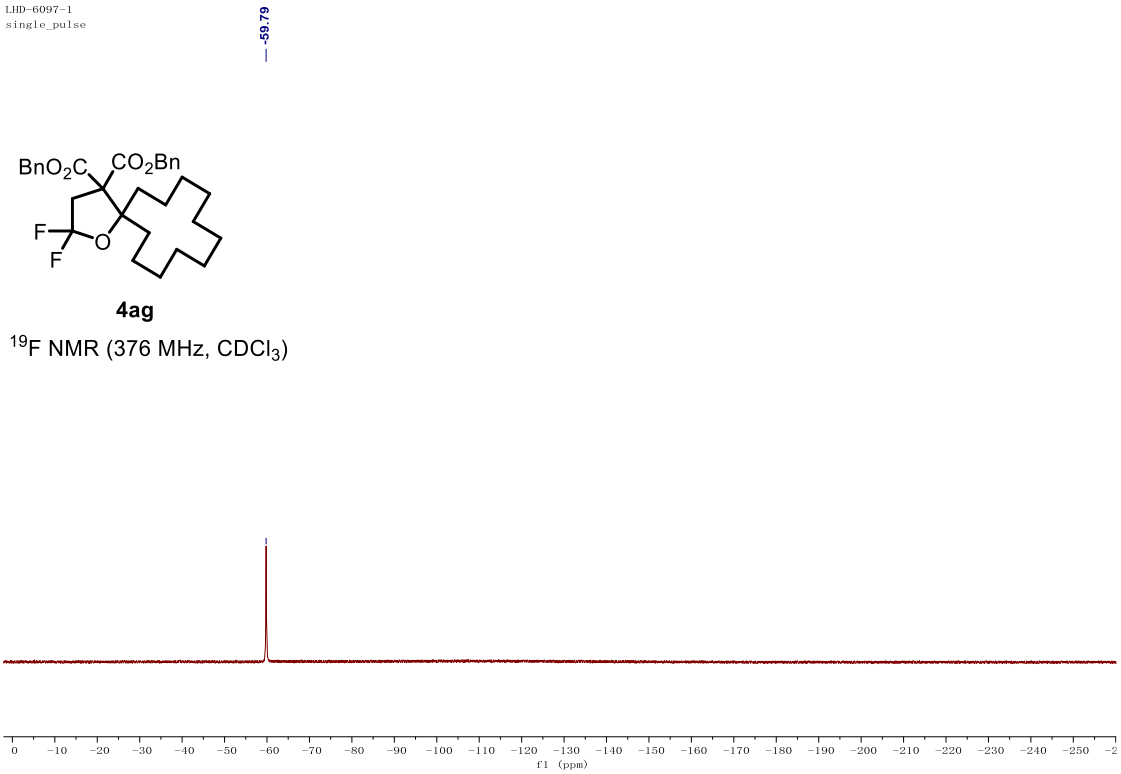
4ag

^{1}H NMR (400 MHz, $CDCl_3$)



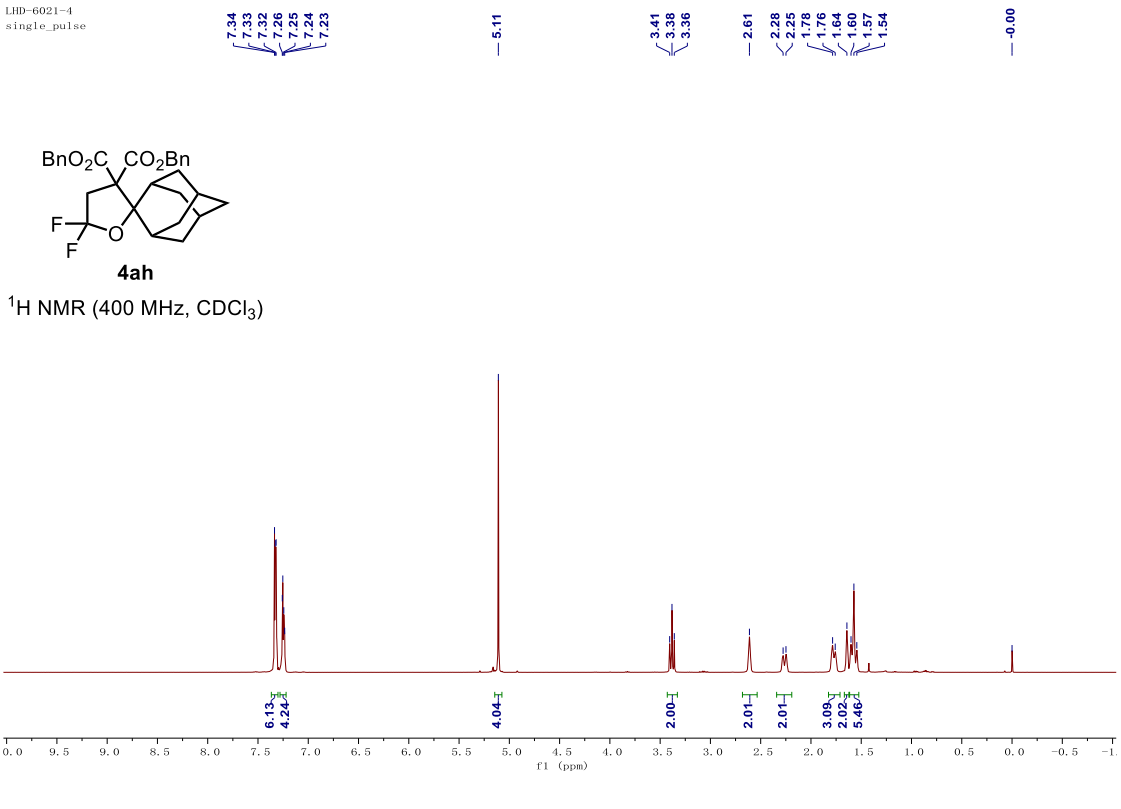
4ag

^{13}C NMR (101 MHz, $CDCl_3$)



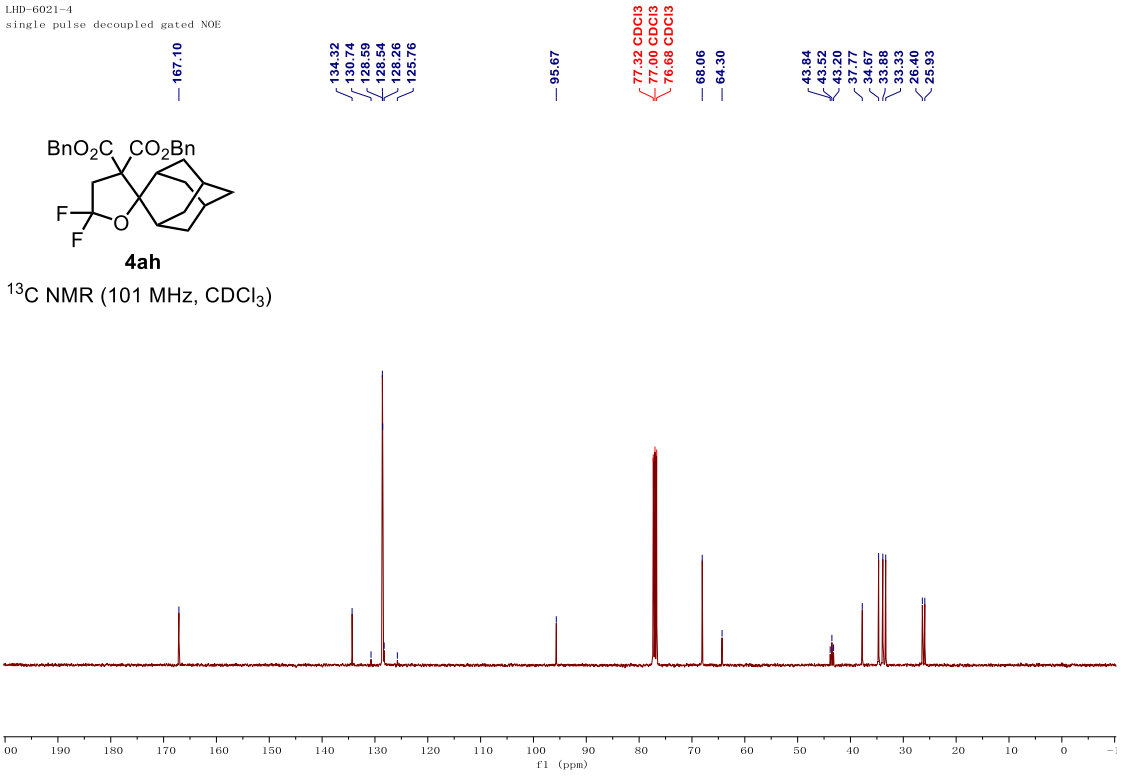
4ag

^{19}F NMR (376 MHz, $CDCl_3$)



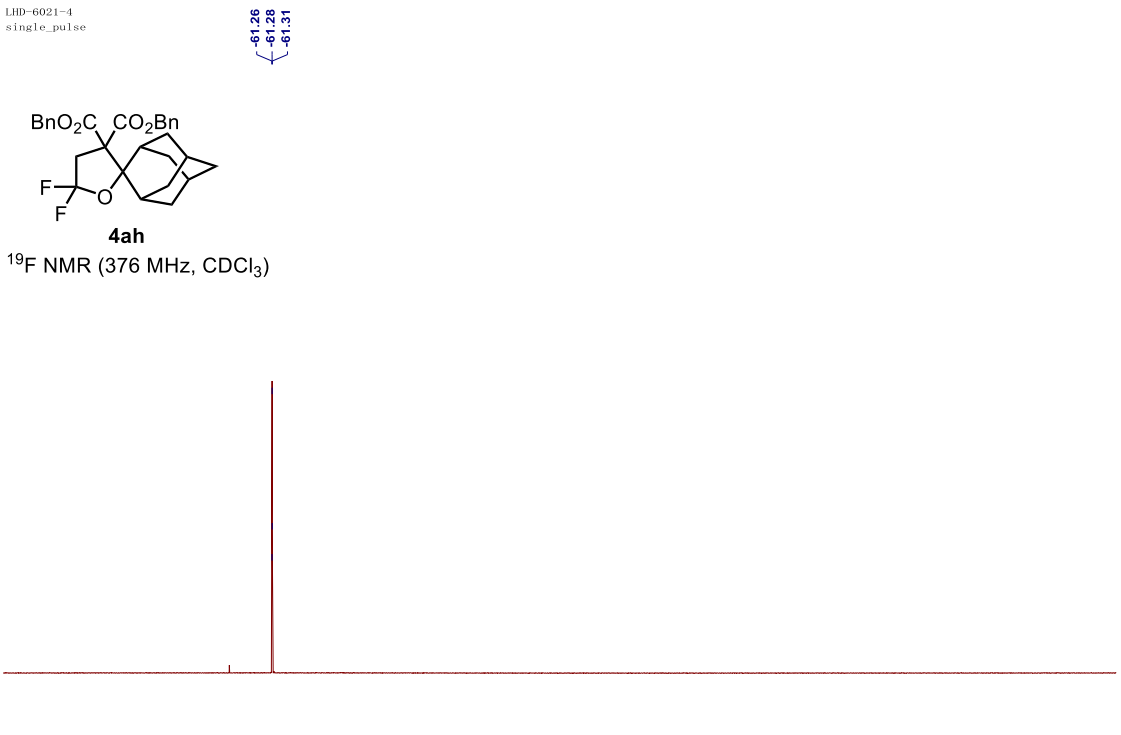
4ah

^{1}H NMR (400 MHz, $CDCl_3$)



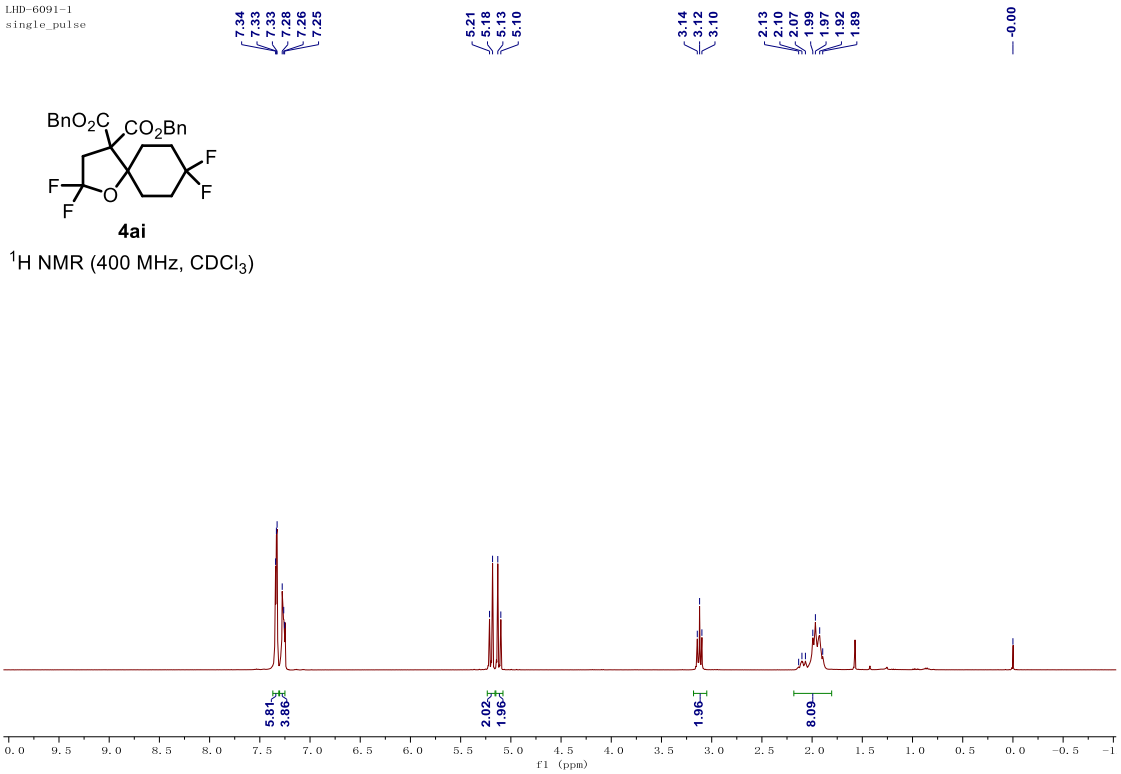
4ah

^{13}C NMR (101 MHz, $CDCl_3$)



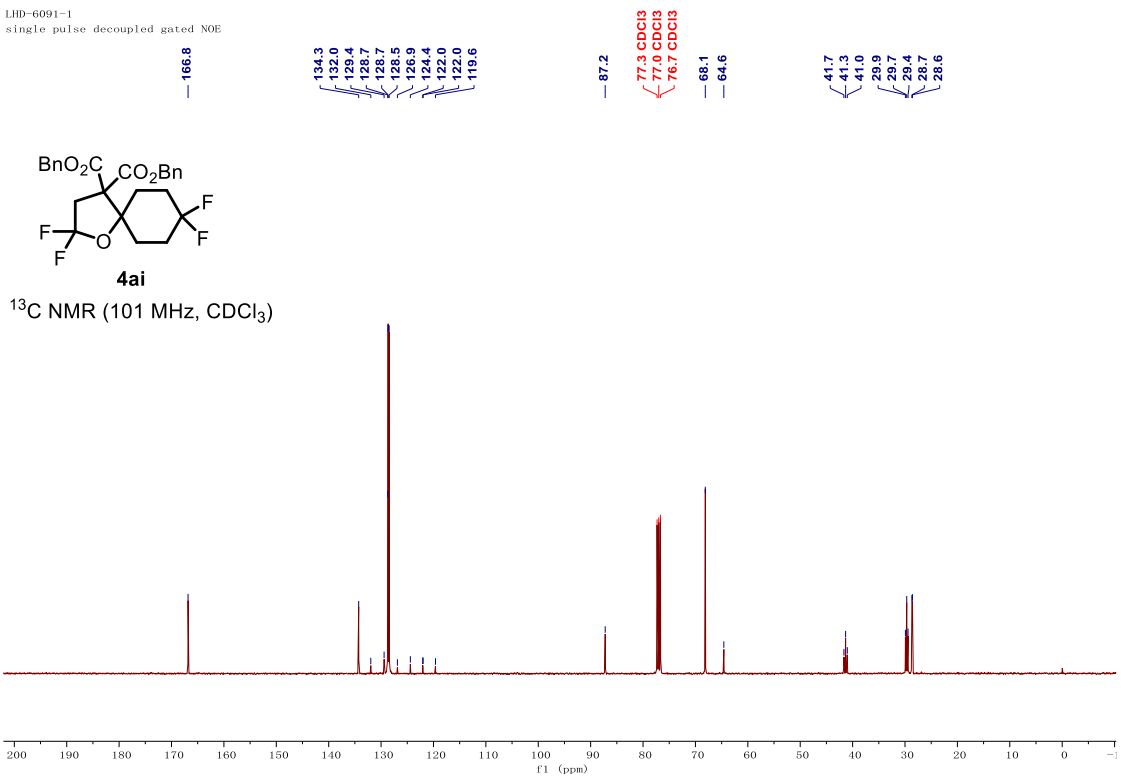
4ah

^{19}F NMR (376 MHz, $CDCl_3$)



4ai

^{1}H NMR (400 MHz, $CDCl_3$)



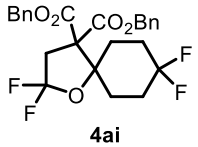
4ai

^{13}C NMR (101 MHz, $CDCl_3$)

LHD-6091-1
single_pulse

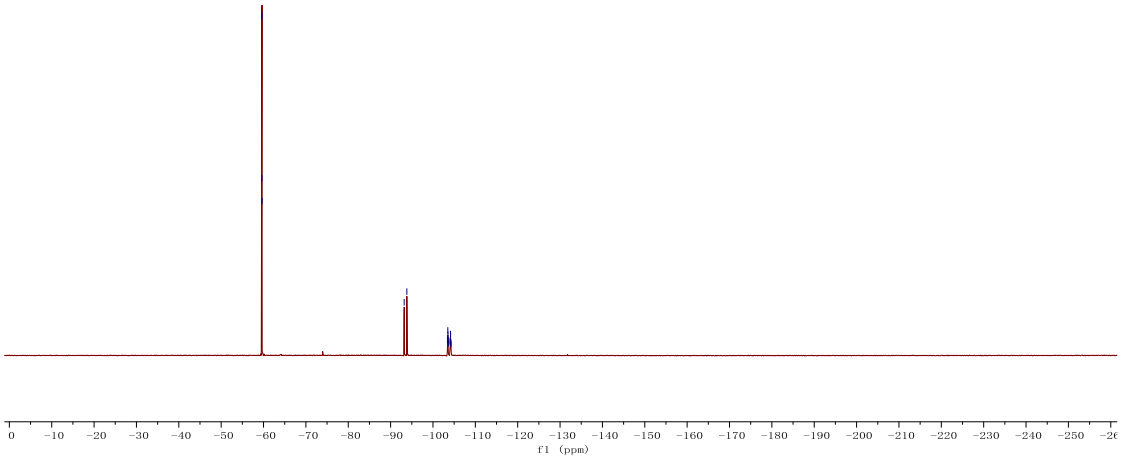
-59.61
-59.64
-59.66

-93.20
-93.83
-103.42
-103.44
-103.50
-103.53
-103.59
-103.62
-104.04
-104.07
-104.13
-104.16
-104.23
-104.25



4ai

^{19}F NMR (376 MHz, $CDCl_3$)



LHD-7081-2-2
single_pulse

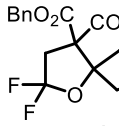
7.36
7.35
7.34
7.33
7.30
7.29
7.28
7.27

5.22
5.19
5.13
5.10

3.33
3.31
3.30
3.17
3.14
3.12

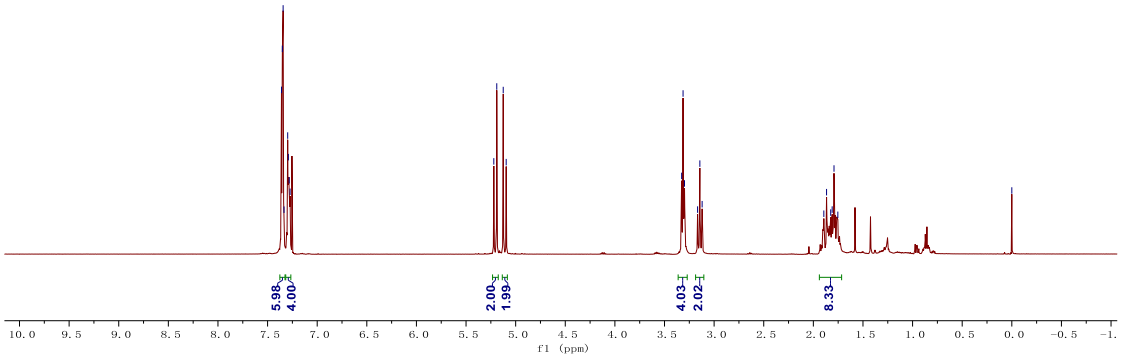
1.89
1.87
1.83
1.81
1.79
1.75

-0.00

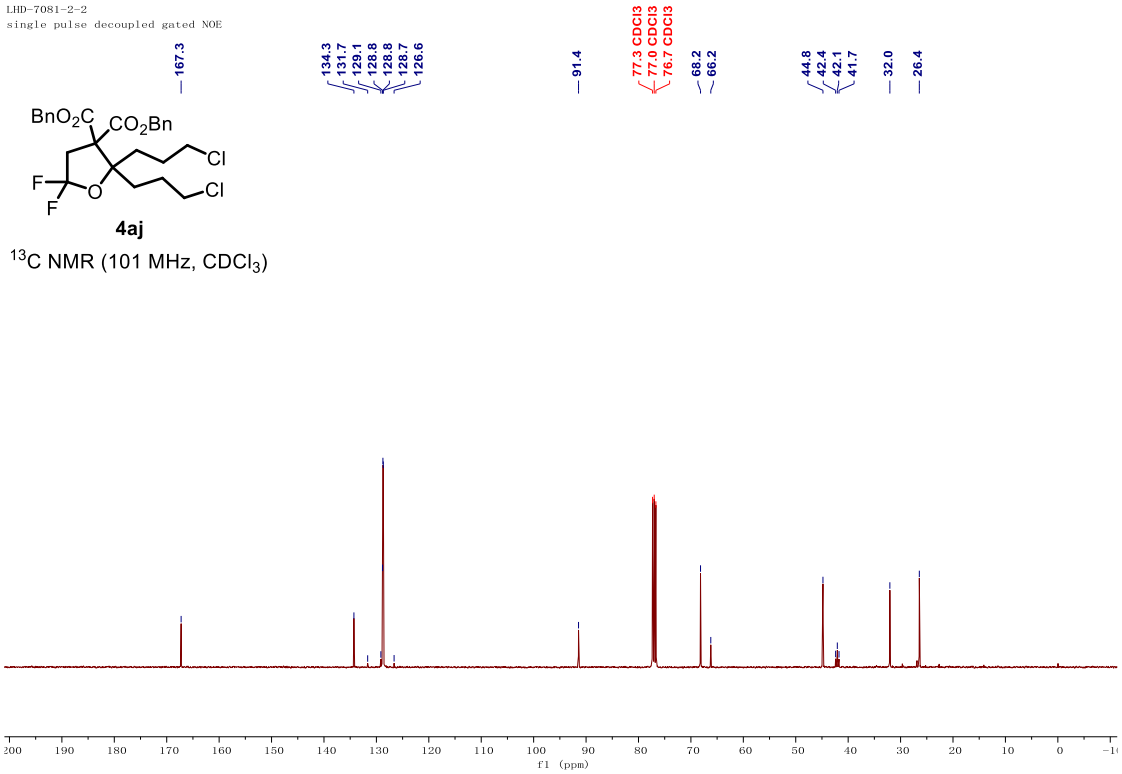


4aj

^{1}H NMR (400 MHz, $CDCl_3$)



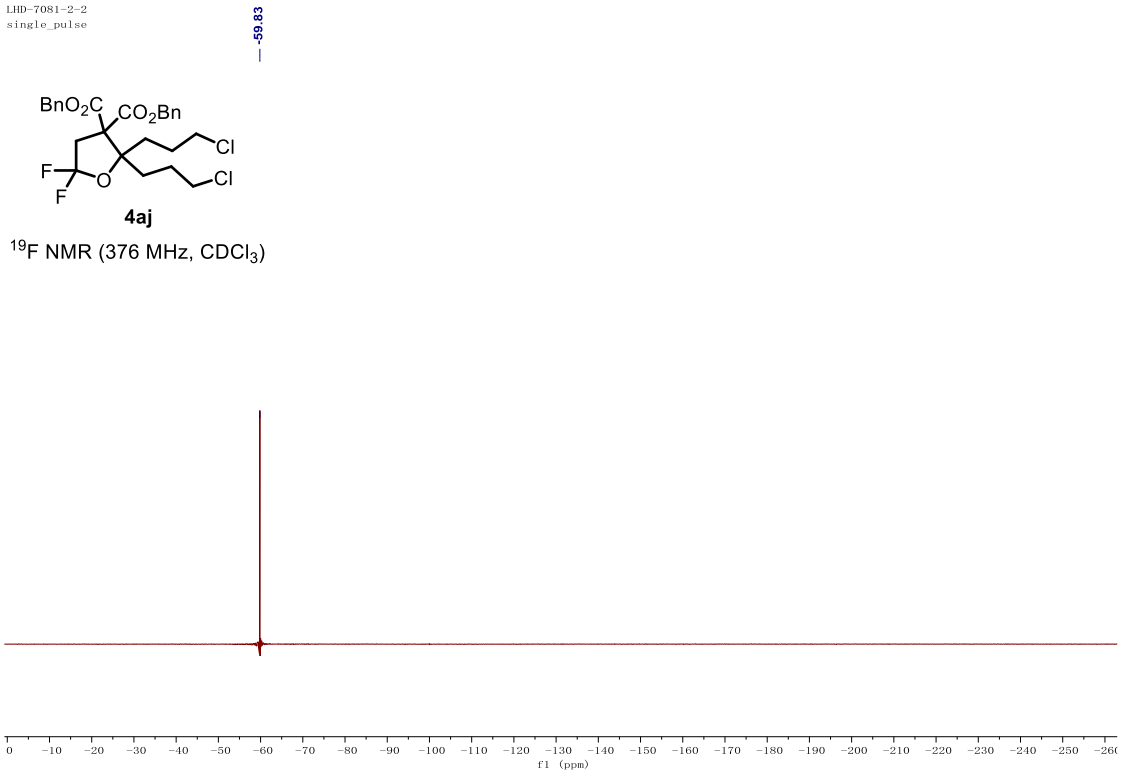
LHD-7081-2-2
single pulse decoupled gated NOE



4aj

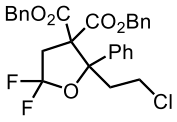
^{13}C NMR (101 MHz, $CDCl_3$)

LHD-7081-2-2
single_pulse



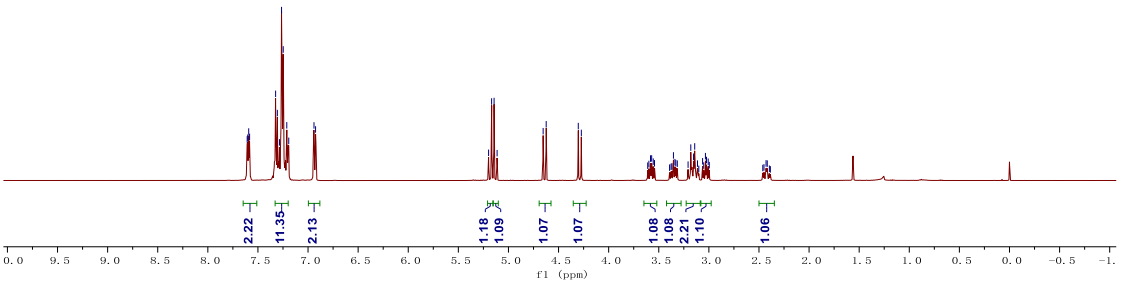
4aj

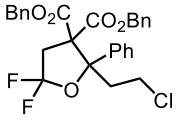
^{19}F NMR (376 MHz, $CDCl_3$)



4ak

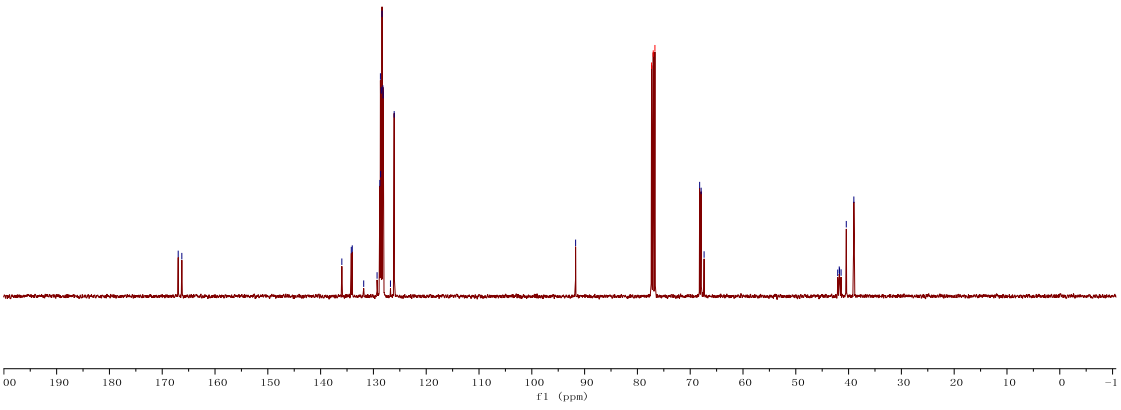
^{1}H NMR (400 MHz, $CDCl_3$)





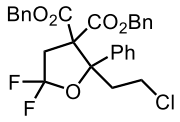
4ak

^{13}C NMR (101 MHz, $CDCl_3$)



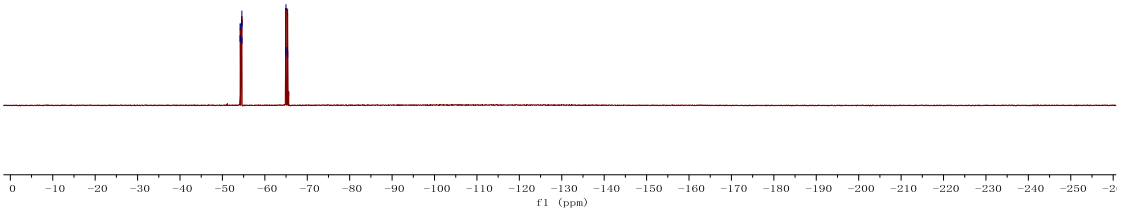
LHD-6029-1-2
single_pulse

-54.18
-54.20
-54.21
-54.23
-54.57
-54.59
-54.60
-54.62
-64.95
-64.98
-65.01
-65.34
-65.37
-65.39

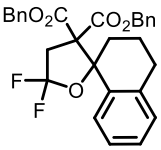


4ak

^{19}F NMR (376 MHz, $CDCl_3$)

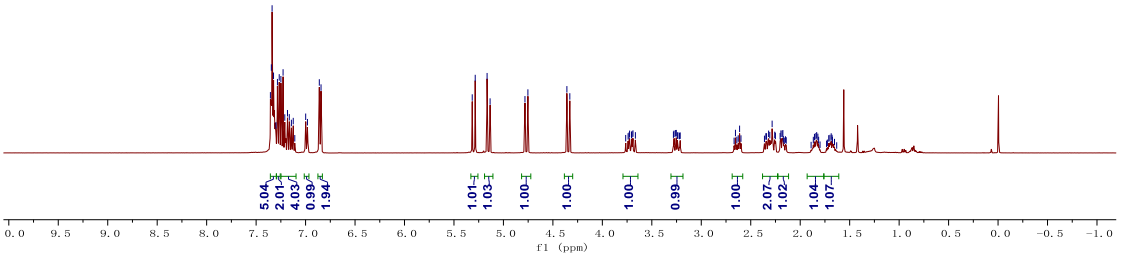


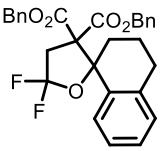
7.35
7.33
7.32
7.30
7.28
7.27
7.25
7.23
7.21
7.18
7.16
7.14
7.12
7.11
7.00
6.98
6.86
6.84
5.32
5.29
5.17
5.13
4.78
4.75
4.36
4.33
3.76
3.74
3.73
3.72
3.71
3.70
3.69
3.67
3.28
3.28
3.26
3.25
3.24
3.24
3.22
3.21
2.65
2.64
2.63
2.61
2.60
2.36
2.35
2.34
2.32
2.31
2.28
2.26
2.25
2.20
2.20
2.18
2.18
2.17
2.15
1.86
1.84
1.83
1.82
1.81
1.71
1.70
1.69
1.68
1.67



4al

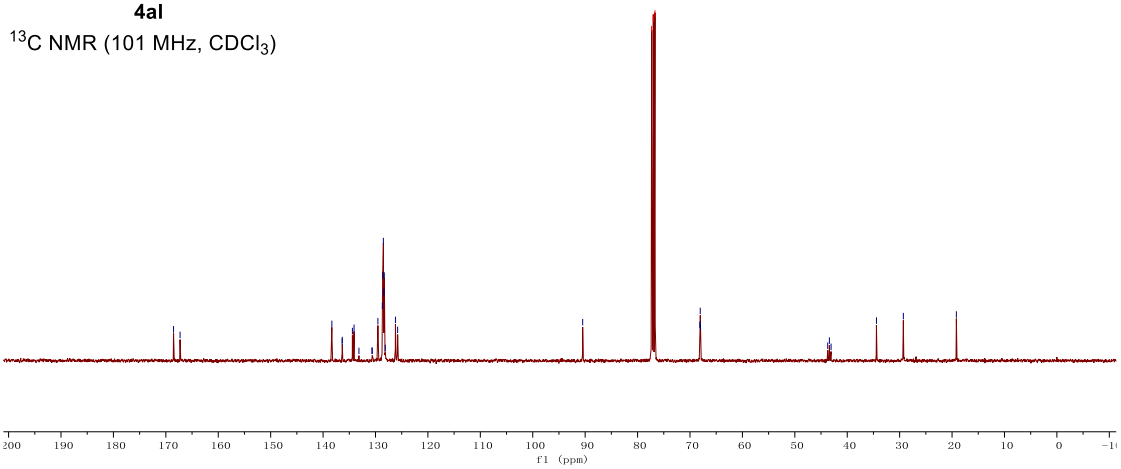
^{1}H NMR (400 MHz, $CDCl_3$)

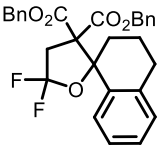




4al

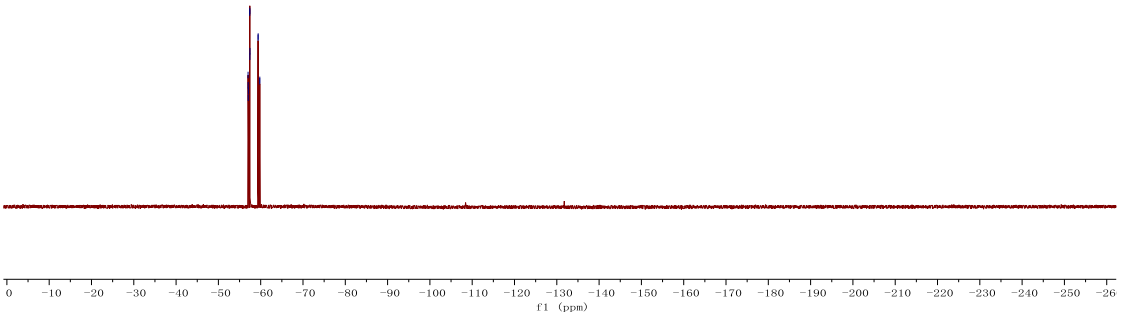
^{13}C NMR (101 MHz, $CDCl_3$)

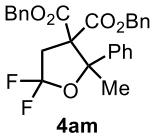




4al

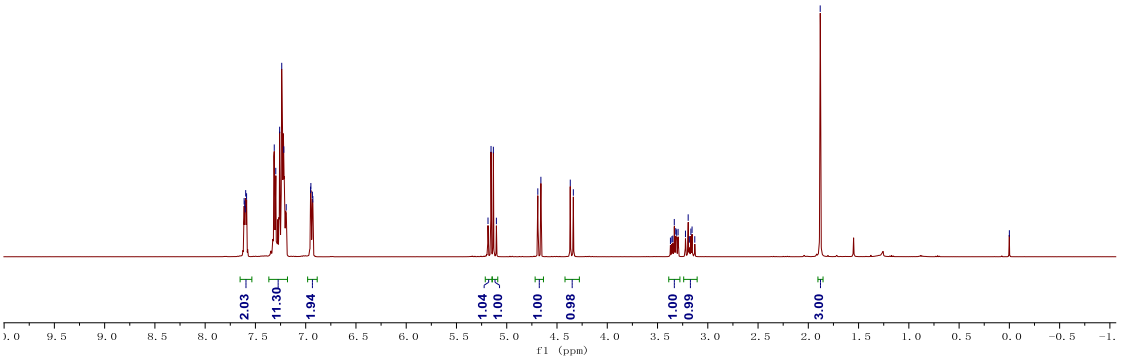
^{19}F NMR (376 MHz, $CDCl_3$)

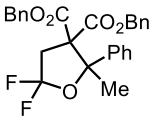




4am

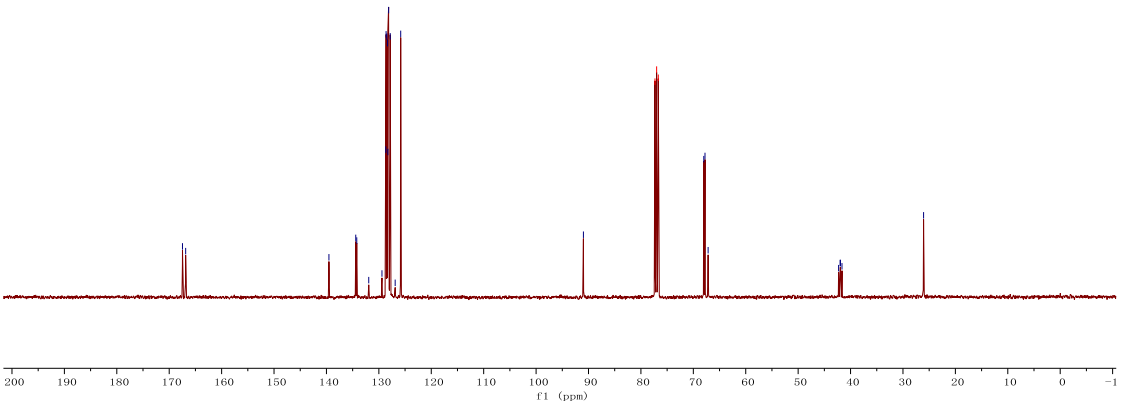
^{1}H NMR (400 MHz, $CDCl_3$)





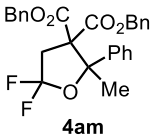
4am

^{13}C NMR (101 MHz, $CDCl_3$)



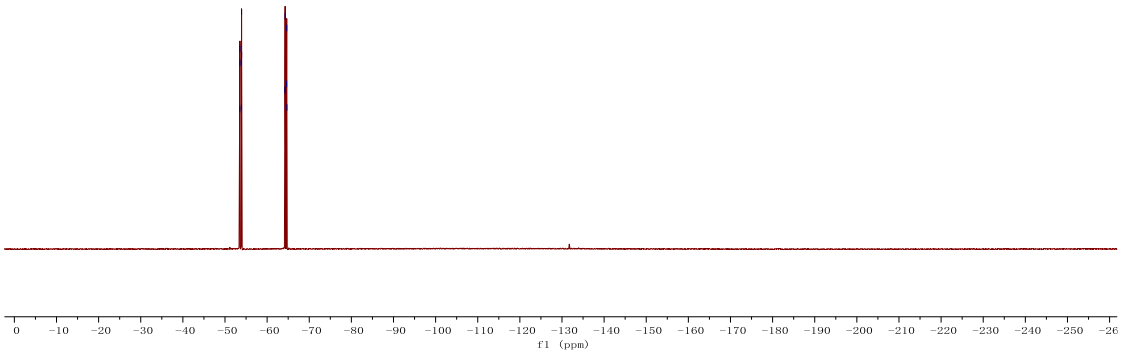
LHD-5185-1
single_pulse

-53.53
-53.55
-53.56
-53.91
-53.92
-53.93
-53.95
-64.24
-64.27
-64.30
-64.63
-64.66
-64.69



4am

^{19}F NMR (376 MHz, $CDCl_3$)



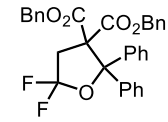
LHD-6007-7
single_pulse

7.44
7.44
7.43
7.42
7.31
7.30
7.28
7.23
7.22
7.20
7.18
7.06
7.06
7.04
7.04

4.86
4.83
4.81
4.78

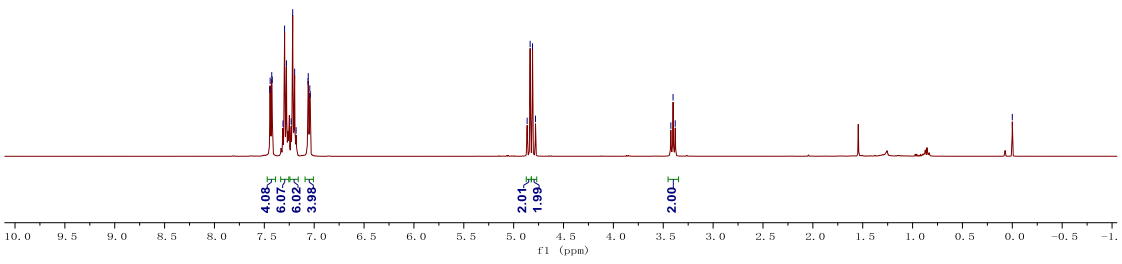
3.42
3.40
3.38

0.00

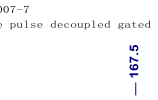


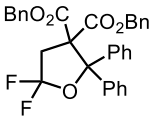
4an

^{1}H NMR (400 MHz, $CDCl_3$)



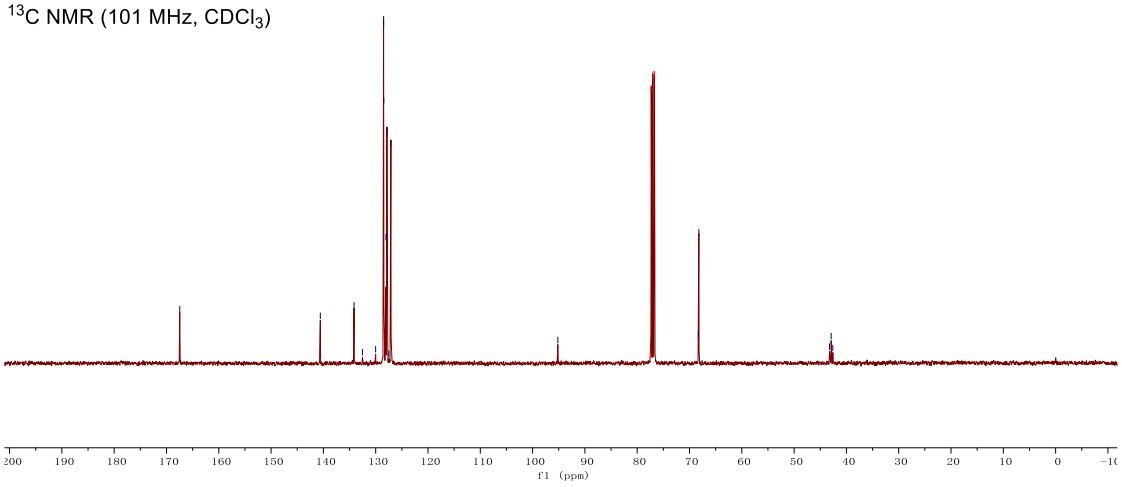
LHD-6007-7
single pulse decoupled gated NOE



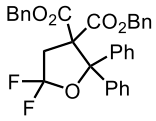


4an

^{13}C NMR (101 MHz, $CDCl_3$)

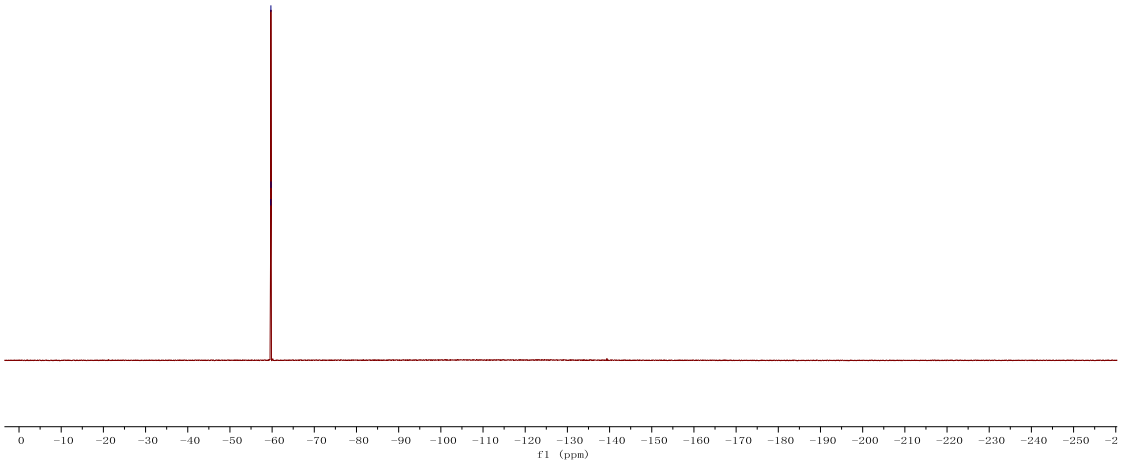


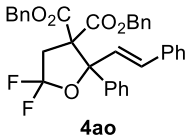
LHD-6007-7
single_pulse



4an

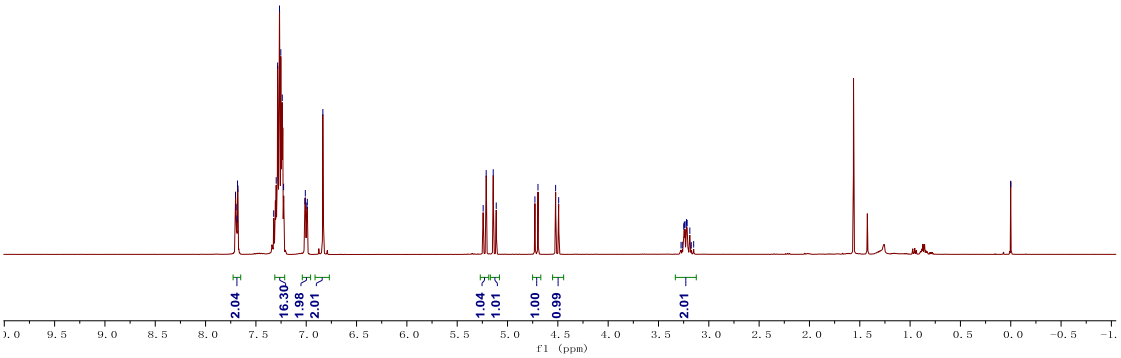
^{19}F NMR (376 MHz, $CDCl_3$)

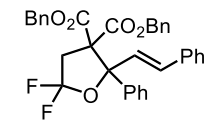




4ao

^{1}H NMR (400 MHz, $CDCl_3$)



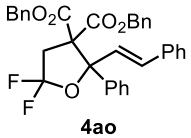


4ao

^{13}C NMR (101 MHz, $CDCl_3$)

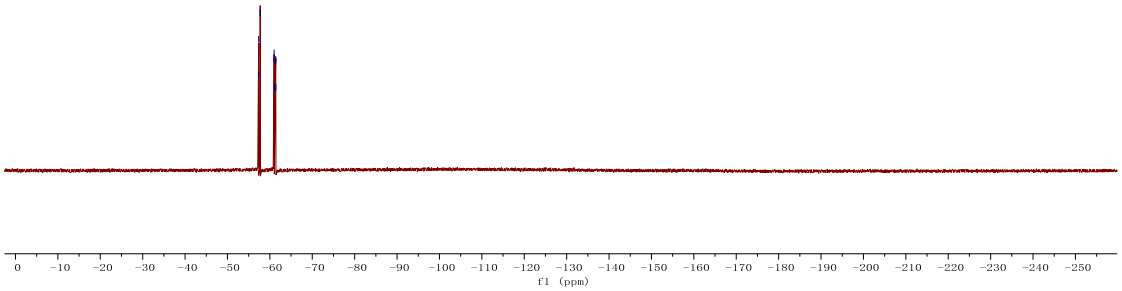
LHD-6019-3
single_pulse

-57.35
-57.37
-57.72
-57.75
-60.97
-61.00
-61.03
-61.36
-61.38
-61.41



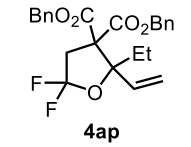
4ao

^{19}F NMR (376 MHz, $CDCl_3$)



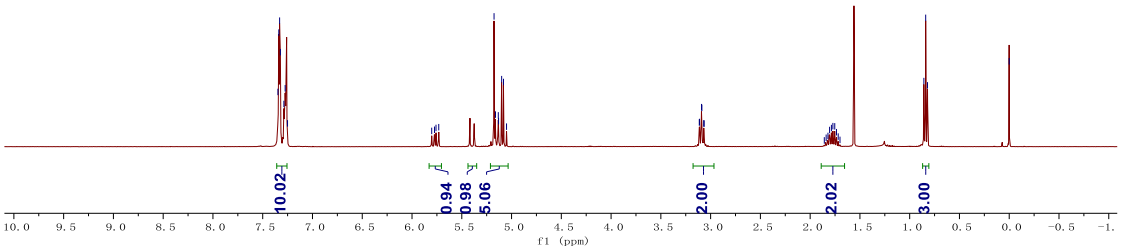
LHD-6003-6
single_pulse

7.35
7.34
7.33
7.32
7.29
7.27
7.25
5.80
5.77
5.76
5.73
5.18
5.16
5.13
5.13
5.10
5.08
5.05
3.11
3.11
3.09
3.09
3.07
3.06
1.86
1.84
1.82
1.80
1.79
1.77
1.75
1.74
1.72
1.70
0.86
0.84
0.82
-0.00

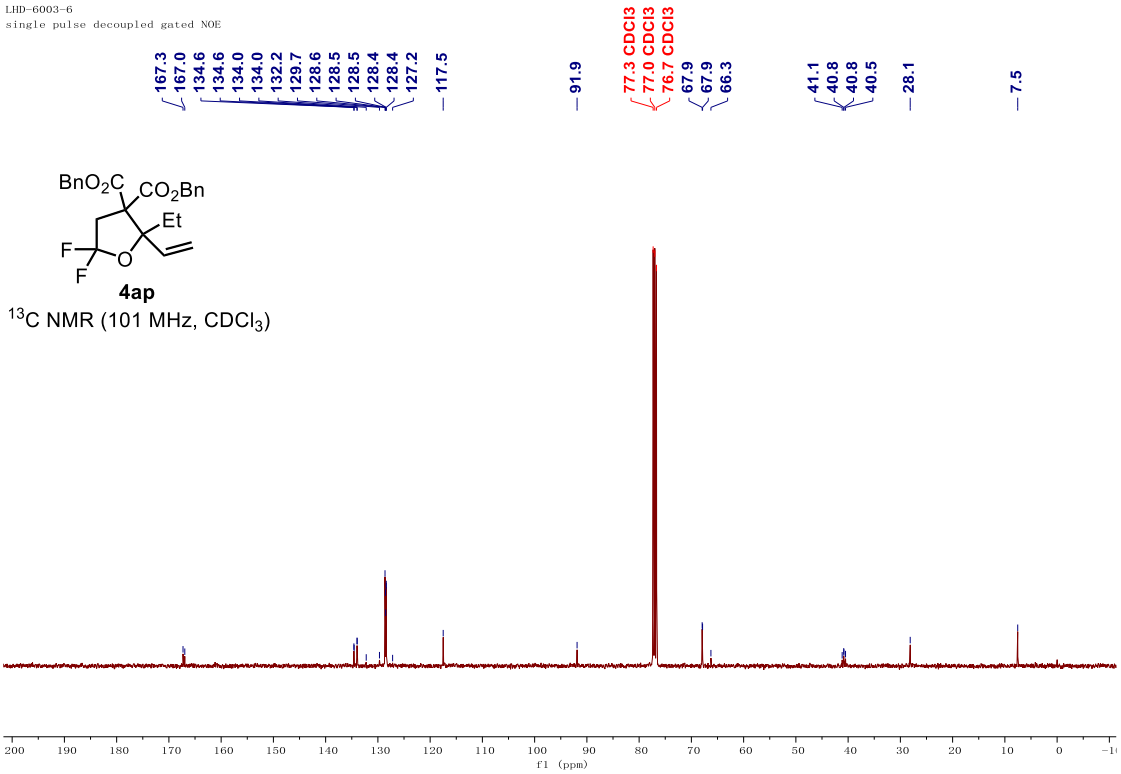


4ap

^{1}H NMR (400 MHz, $CDCl_3$)



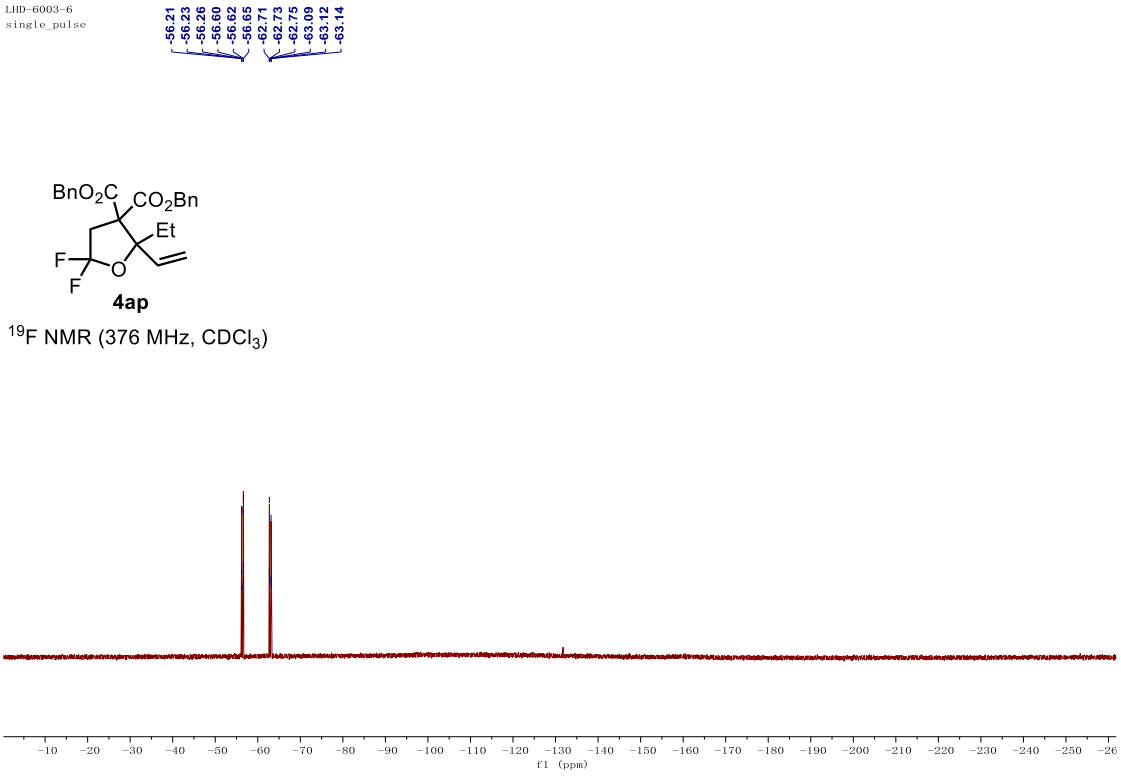
LHD-6003-6
single pulse decoupled gated NOE



4ap

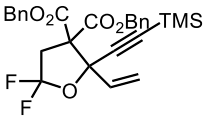
^{13}C NMR (101 MHz, $CDCl_3$)

LHD-6003-6
single_pulse



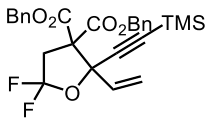
4ap

^{19}F NMR (376 MHz, $CDCl_3$)



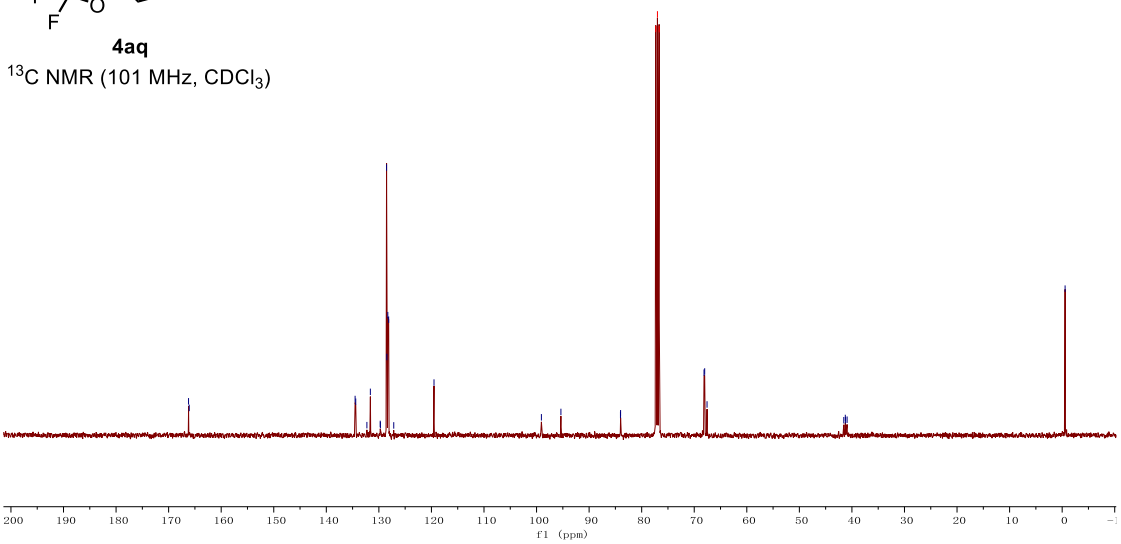
4aq

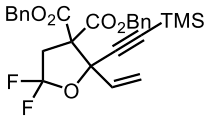
^{1}H NMR (400 MHz, $CDCl_3$)



4aq

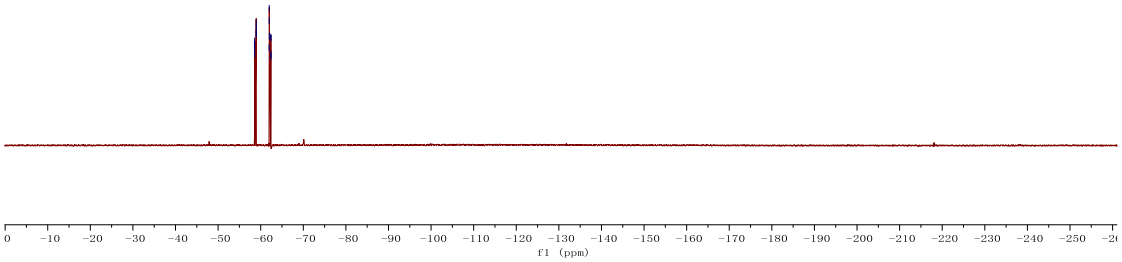
^{13}C NMR (101 MHz, $CDCl_3$)

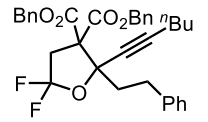




4aq

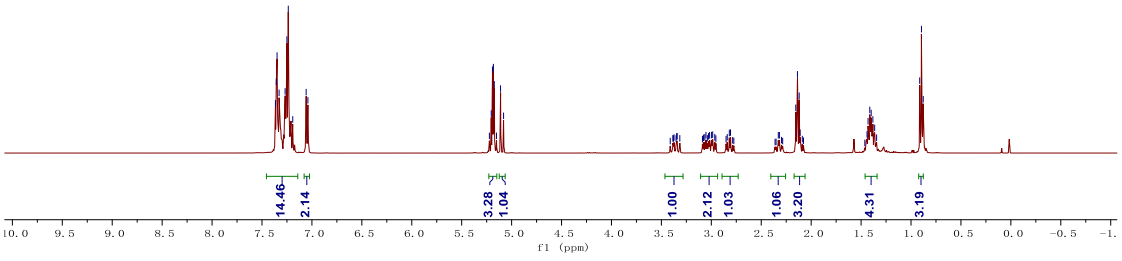
^{19}F NMR (376 MHz, $CDCl_3$)



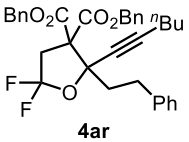


4ar

^{1}H NMR (400 MHz, $CDCl_3$)

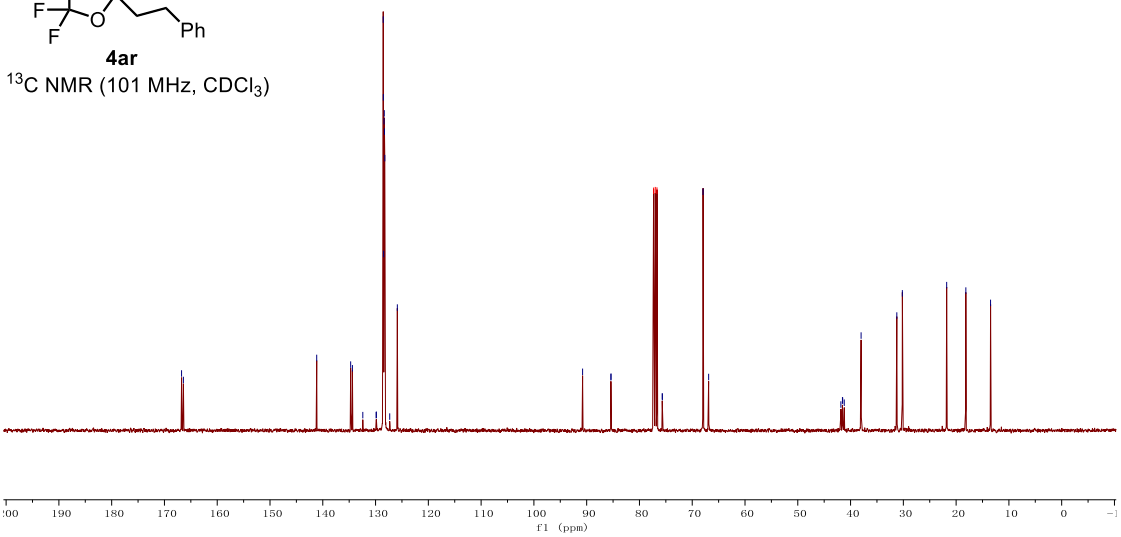


LHD-6013-3
single pulse decoupled gated NOE

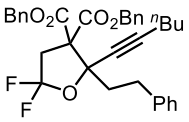


4ar

^{13}C NMR (101 MHz, $CDCl_3$)

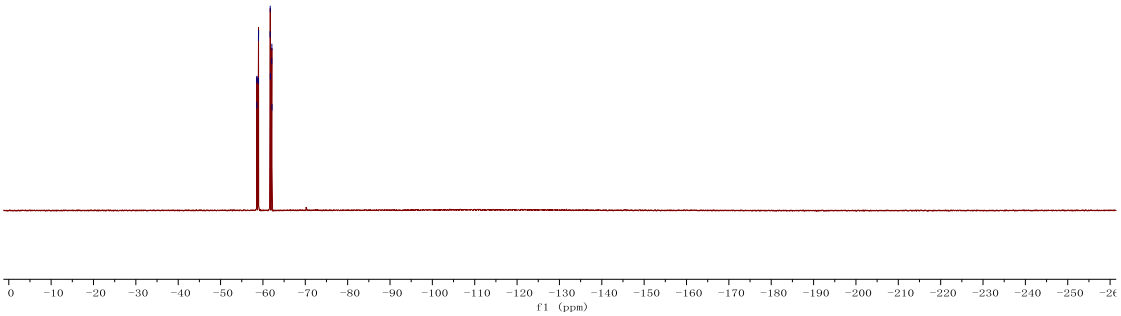


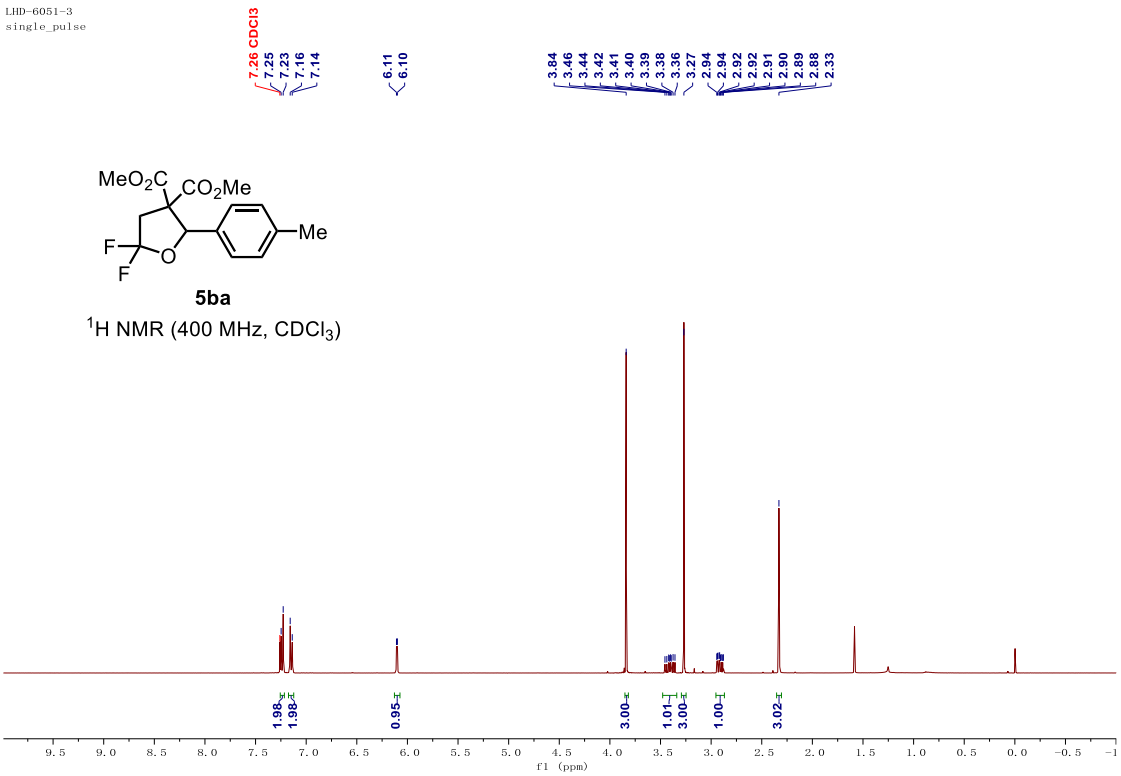
LHD-6013-3
single_pulse

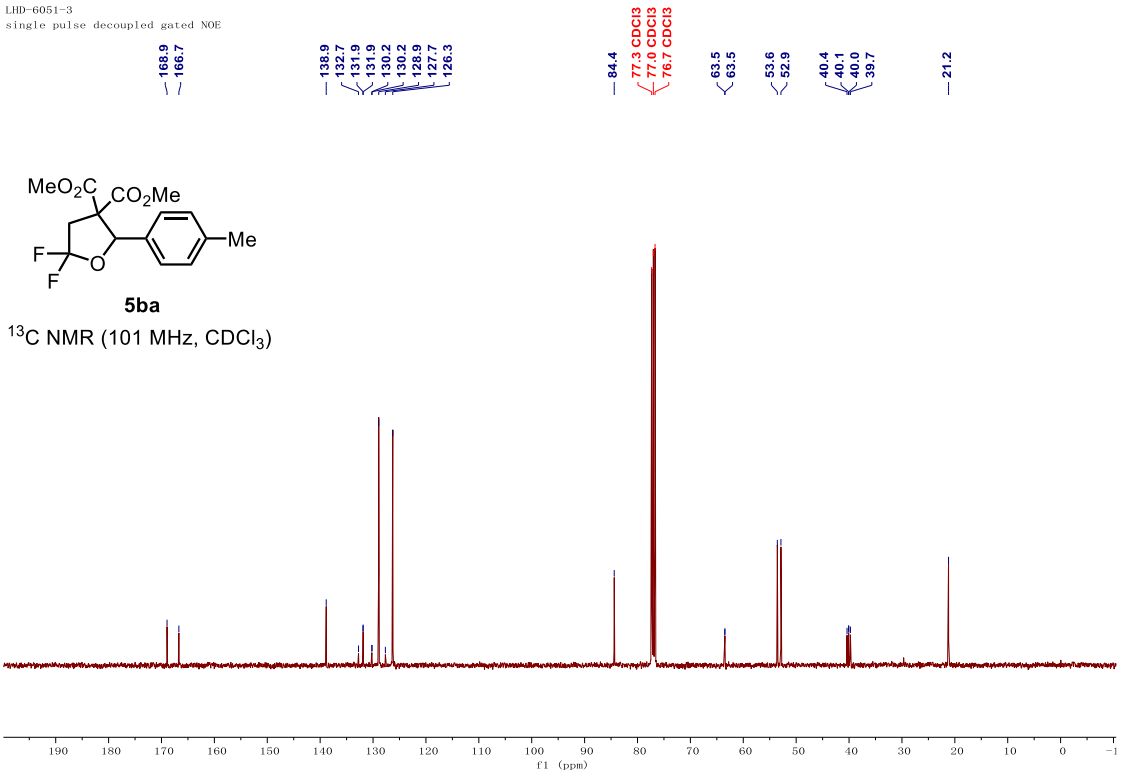


4ar

^{19}F NMR (376 MHz, $CDCl_3$)

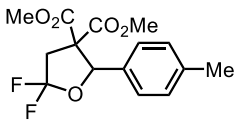



LHD-6051-3
single_pulse
7.26 CDCl3
7.25
7.23
7.16
7.14
6.11
6.10
3.84
3.46
3.44
3.42
3.41
3.40
3.39
3.38
3.36
3.27
2.94
2.94
2.92
2.92
2.91
2.90
2.89
2.88
2.33
MeO2C
CO2Me
F
F
O
Me
5ba
1H NMR (400 MHz, CDCl3)
1.98
1.98
0.95
3.00
1.01
3.00
1.00
3.02
f1 (ppm)


LHD-6051-3
single pulse decoupled gated NOE
168.9
166.7
138.9
132.7
131.9
131.9
130.2
130.2
128.9
127.7
126.3
84.4
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
63.5
63.5
53.6
52.9
40.4
40.1
40.0
39.7
21.2
MeO2C
CO2Me
F
F
O
Me
5ba
13C NMR (101 MHz, CDCl3)
f1 (ppm)

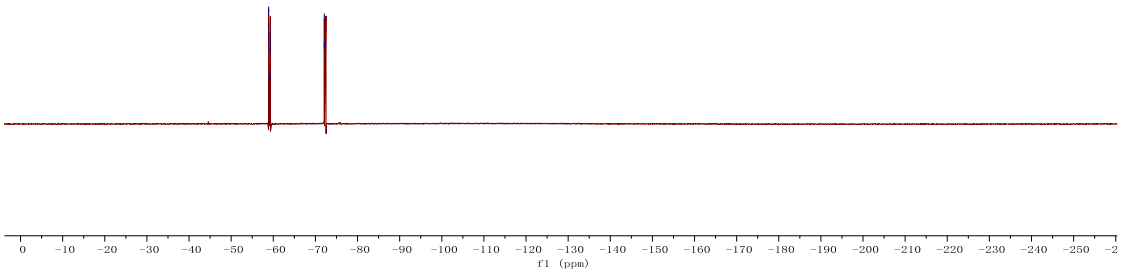
LHD-6051-3
single_pulse

-58.86
-58.89
-58.91
-58.93
-59.25
-59.27
-59.29
-72.11
-72.13



5ba

^{19}F NMR (376 MHz, $CDCl_3$)

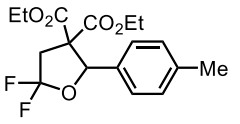


LHD-6035-4
single_pulse

7.25
7.23
7.14
7.12

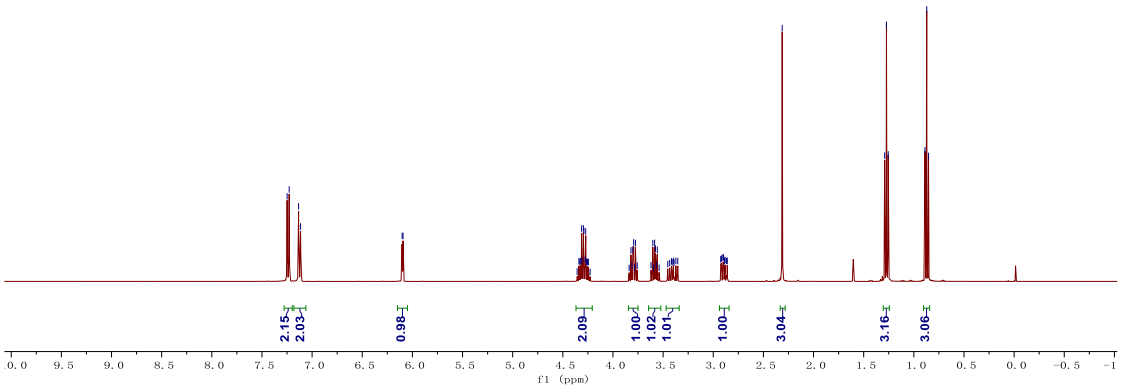
6.10
6.09
4.36
4.34
4.33
4.32
4.31
4.31
4.30
4.29
4.28
4.27
4.26
4.25
4.25
4.23

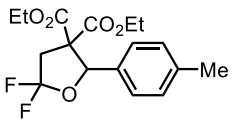
3.82
3.81
3.80
3.79
3.78
3.60
3.58
3.58
3.57
3.56
3.45
3.43
3.42
3.41
3.40
3.39
3.37
3.35
2.93
2.92
2.90
2.90
2.89
2.88
2.87
2.86
2.31
1.29
1.27
1.26
0.89
0.87



5ca

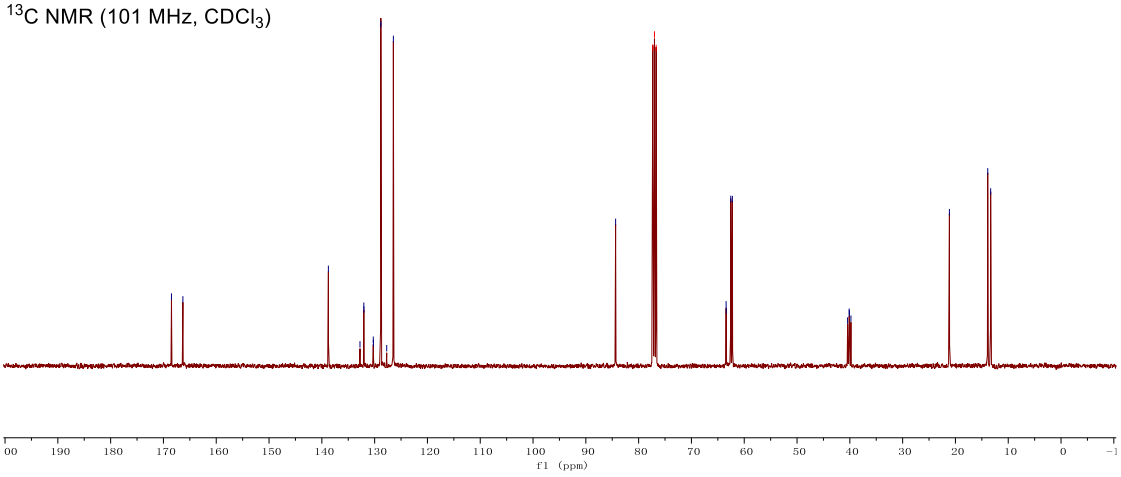
^{1}H NMR (400 MHz, $CDCl_3$)

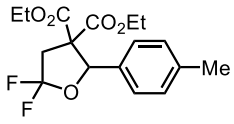




5ca

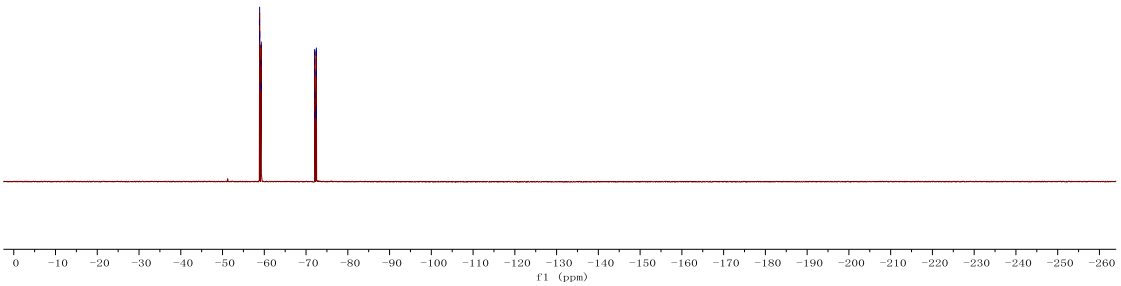
^{13}C NMR (101 MHz, $CDCl_3$)

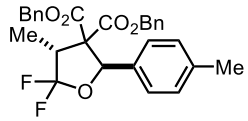




5ca

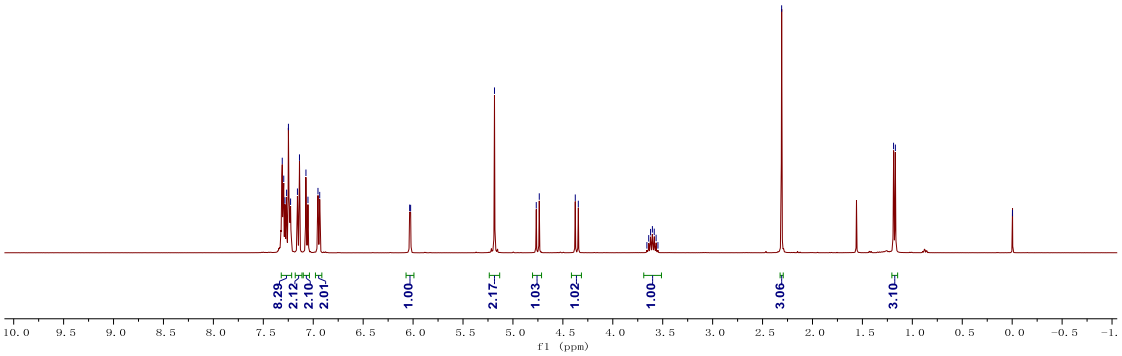
^{19}F NMR (376 MHz, $CDCl_3$)

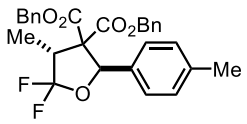




5da

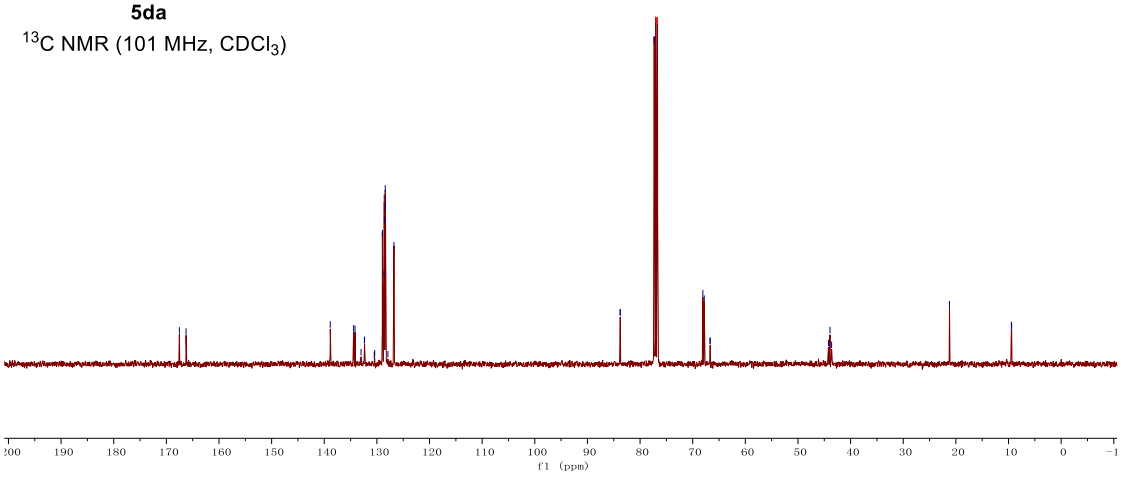
^{1}H NMR (400 MHz, $CDCl_3$)





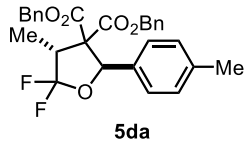
5da

^{13}C NMR (101 MHz, $CDCl_3$)



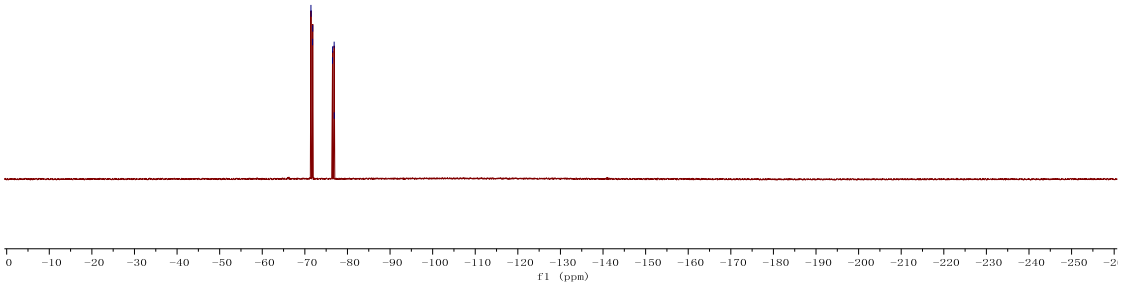
LHD-6021-5-2 1
single_pulse

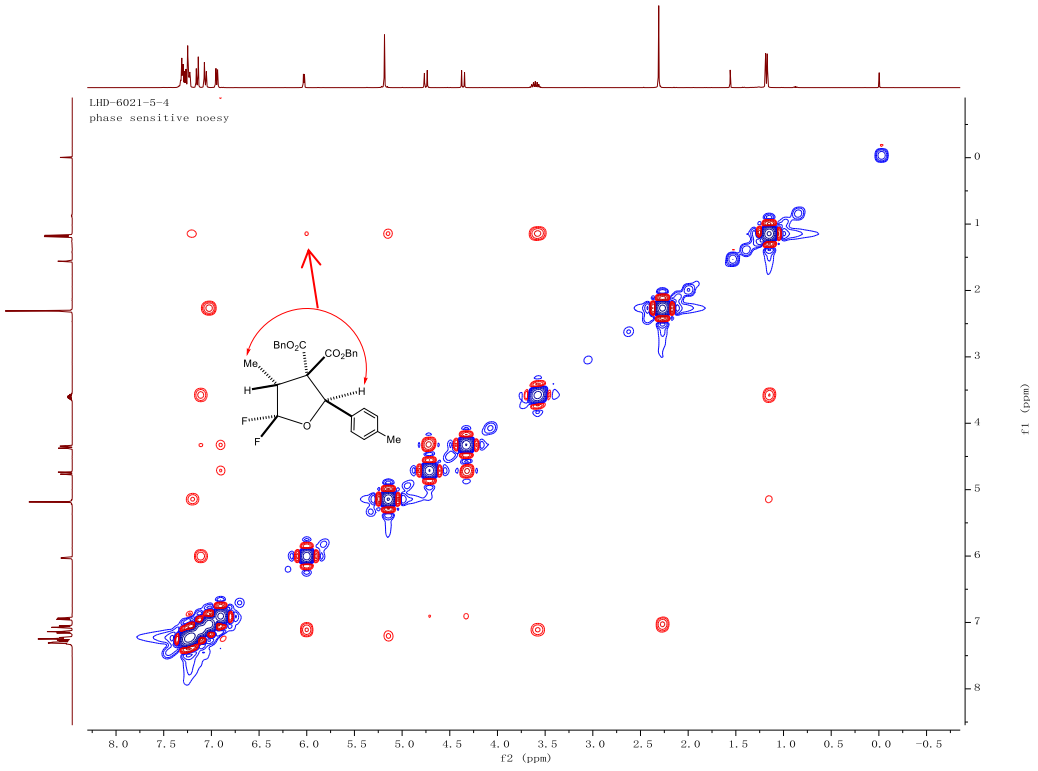
-71.43
-71.47
-71.81
-71.85
-76.48
-76.51
-76.88
-76.90

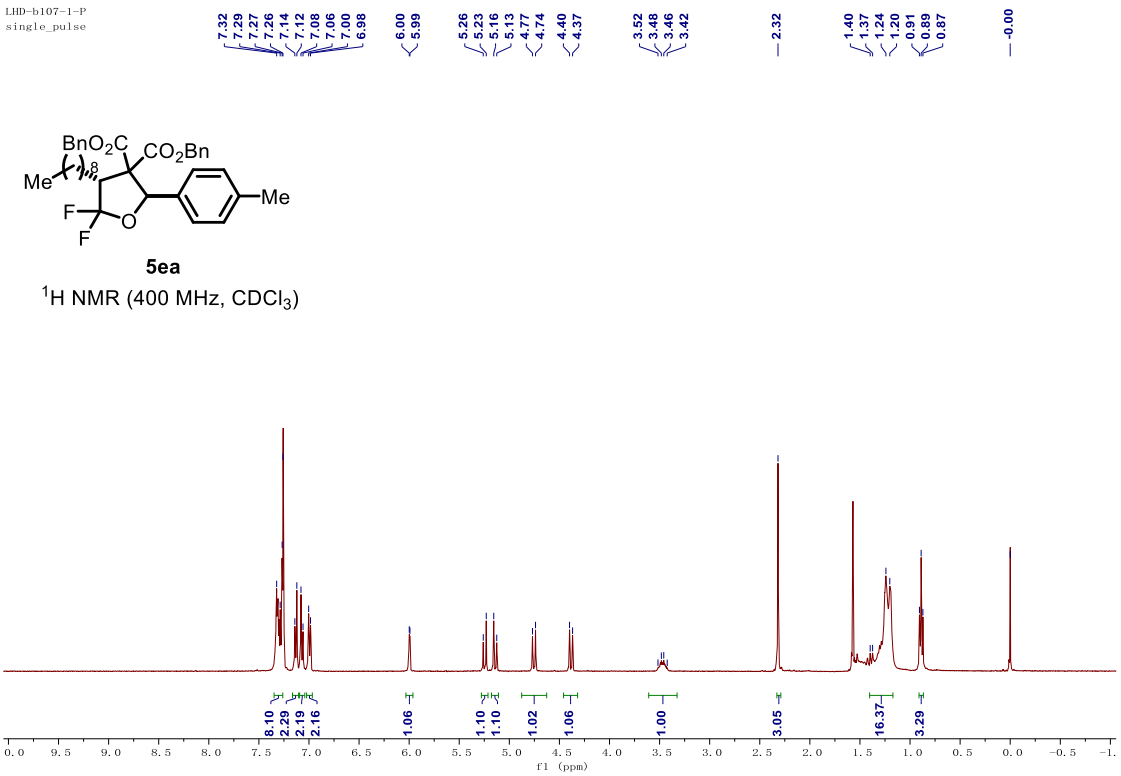


5da

^{19}F NMR (376 MHz, $CDCl_3$)

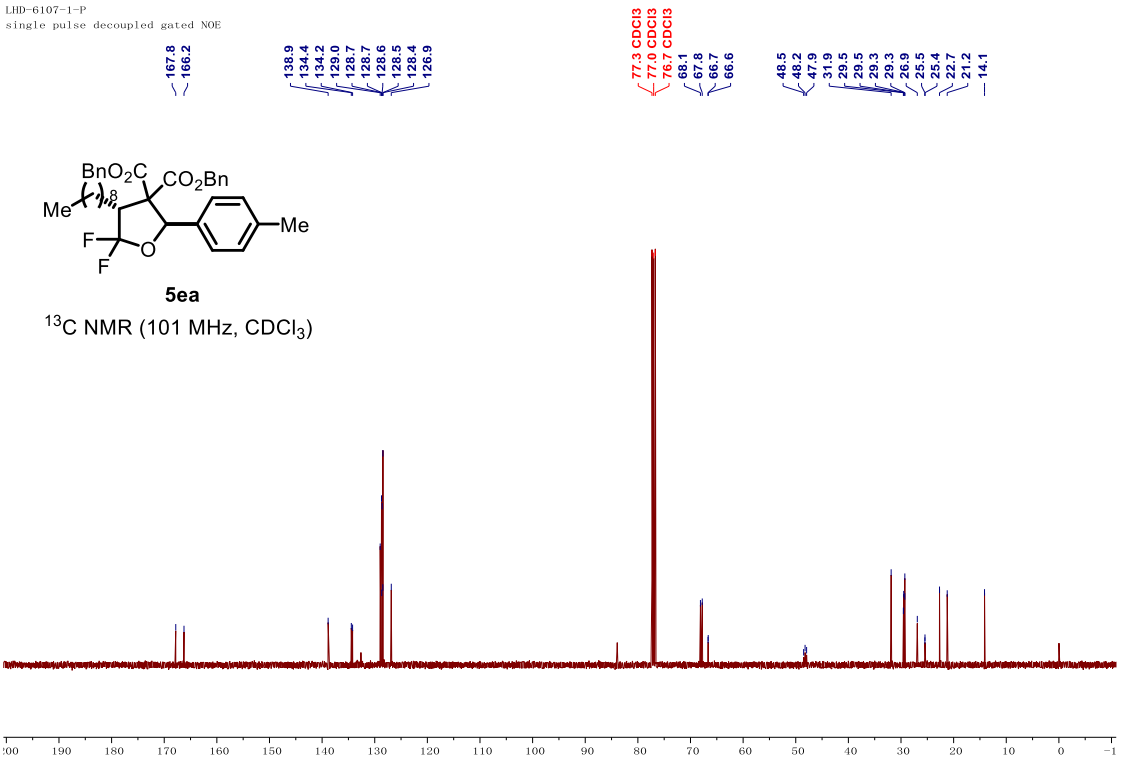






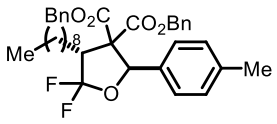
5ea

^{1}H NMR (400 MHz, $CDCl_3$)



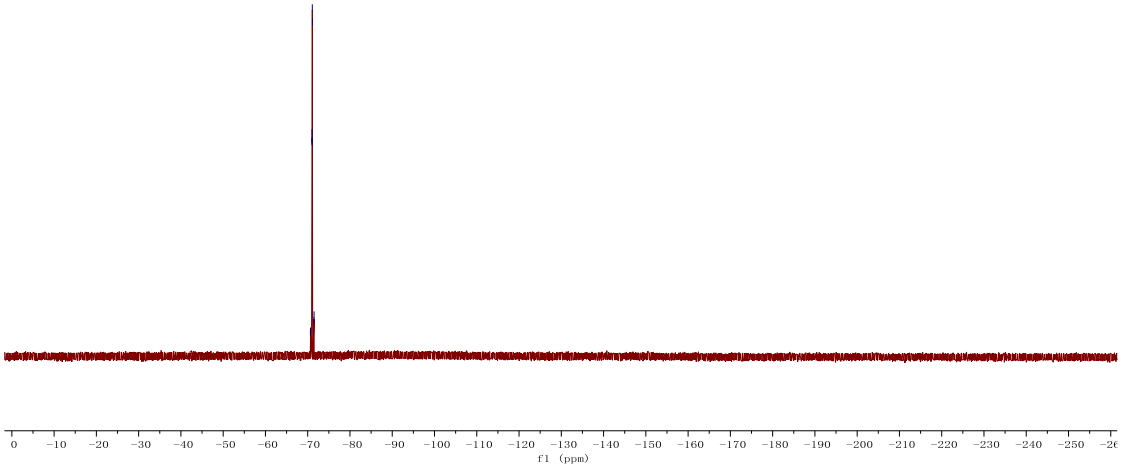
5ea

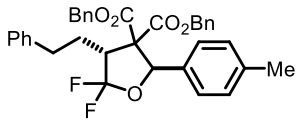
^{13}C NMR (101 MHz, $CDCl_3$)



5ea

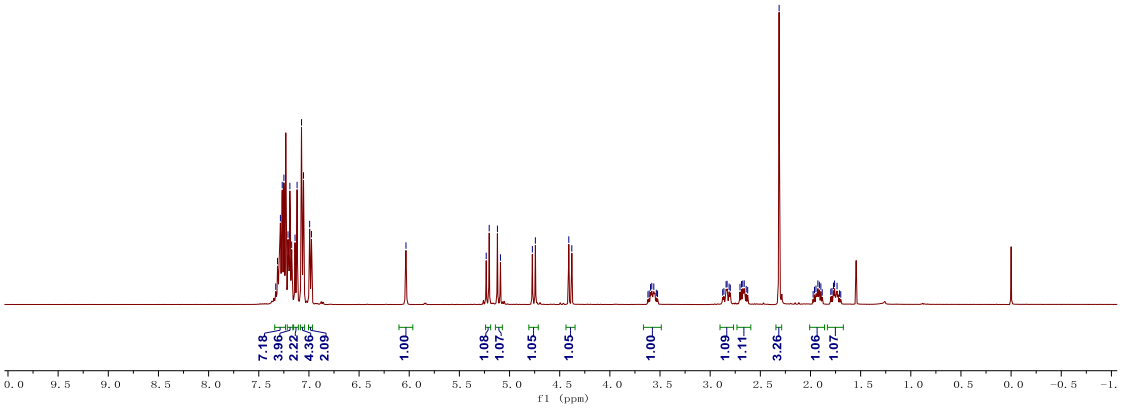
^{19}F NMR (376 MHz, $CDCl_3$)

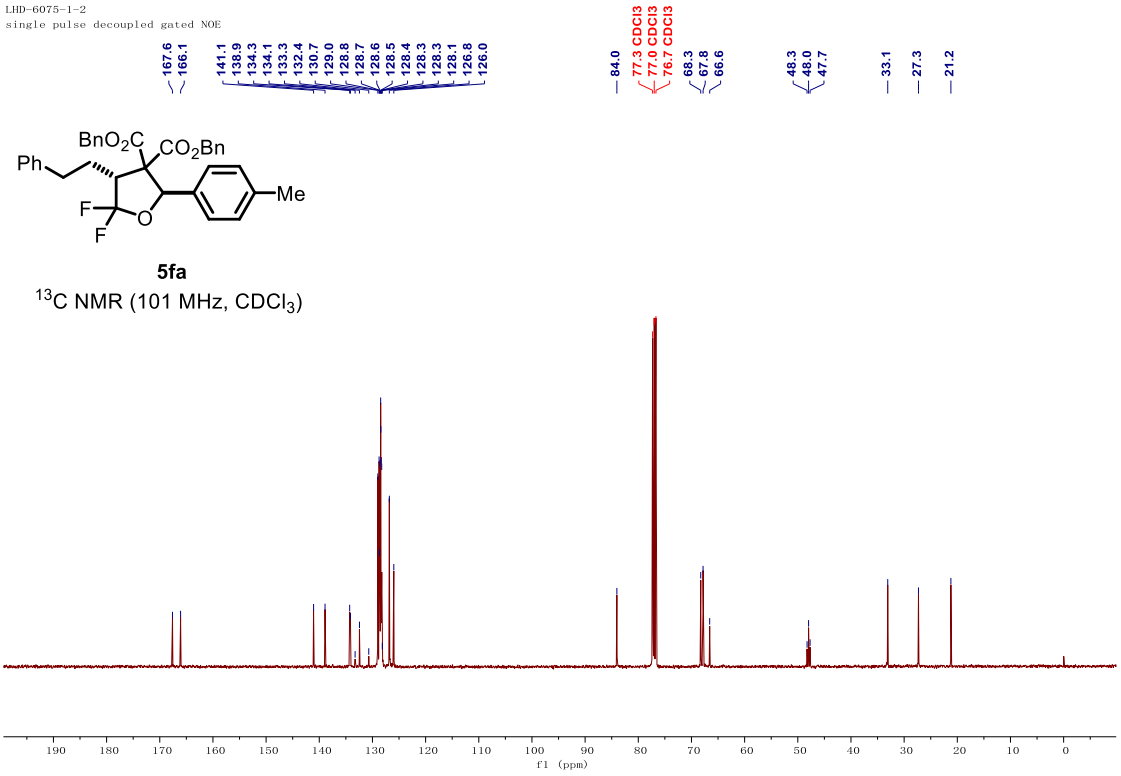




5fa

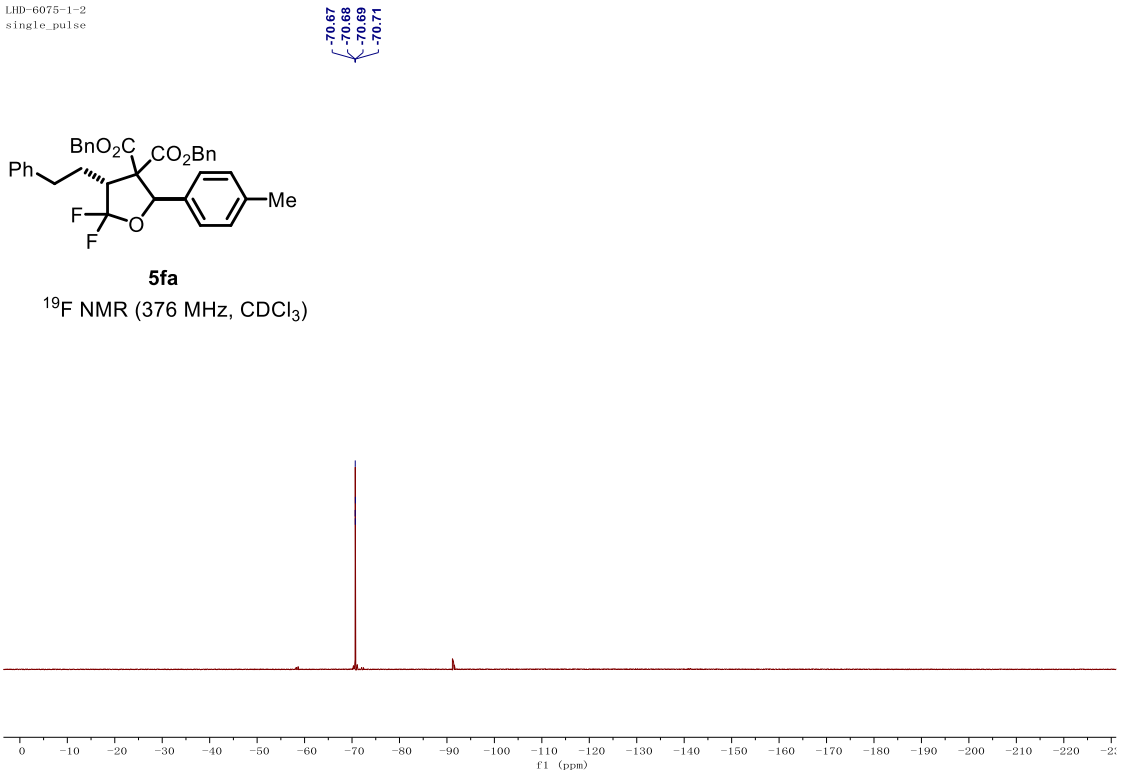
^{1}H NMR (400 MHz, $CDCl_3$)





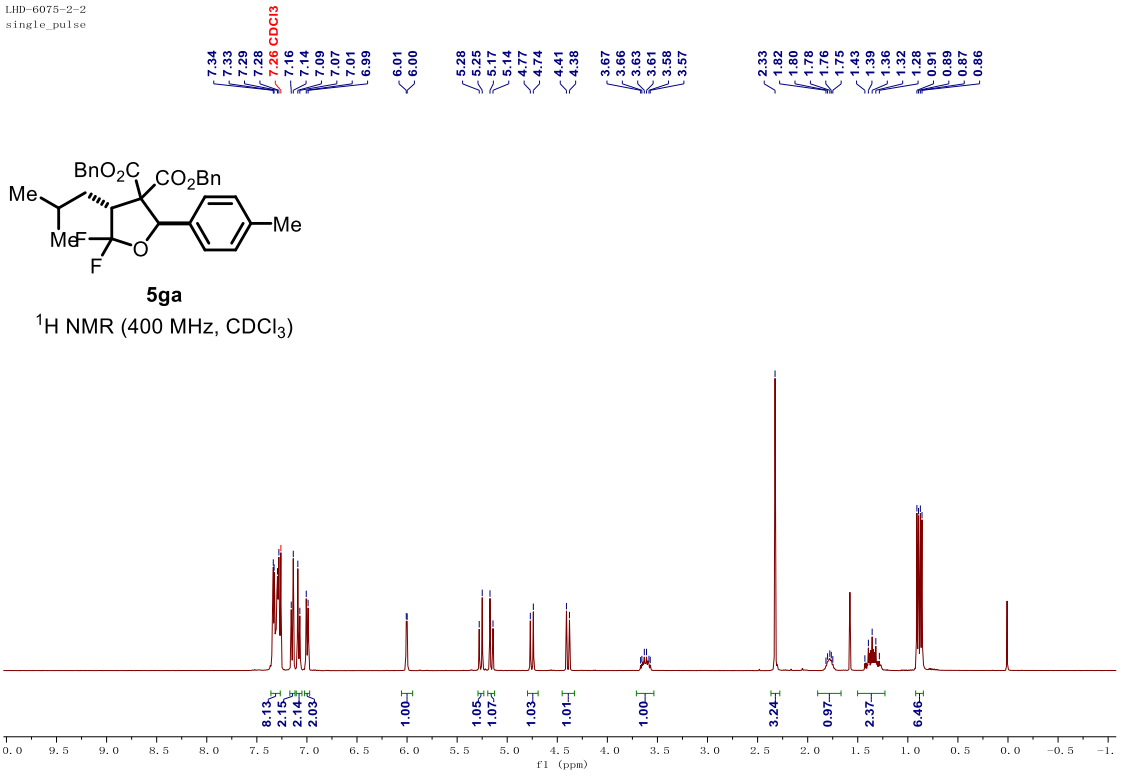
5fa

^{13}C NMR (101 MHz, $CDCl_3$)



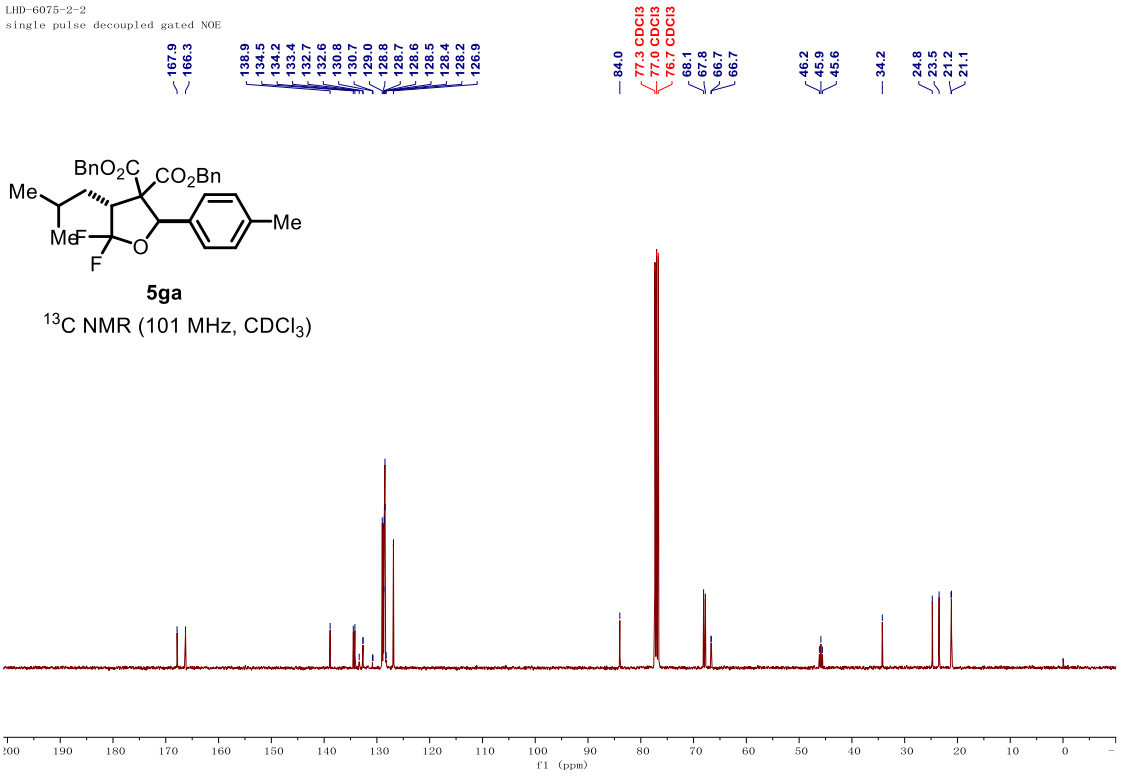
5fa

^{19}F NMR (376 MHz, $CDCl_3$)



5ga

^{1}H NMR (400 MHz, $CDCl_3$)

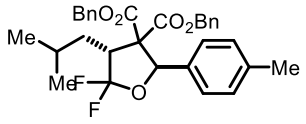


5ga

^{13}C NMR (101 MHz, $CDCl_3$)

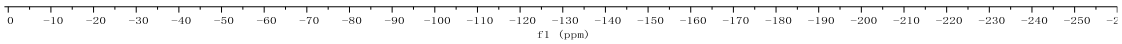
LHD-6075-2-2
single_pulse

-70.62
-70.66
-71.01
-71.05
-71.37
-71.38
-71.75
-71.76



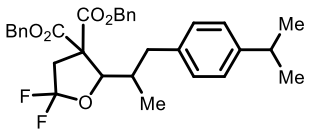
5ga

^{19}F NMR (376 MHz, $CDCl_3$)



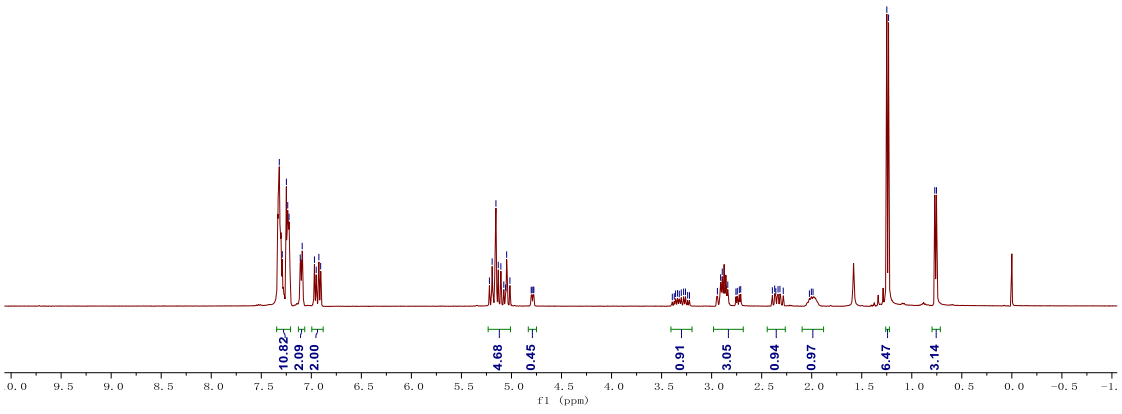
LHD-7130-2-3
single_pulse

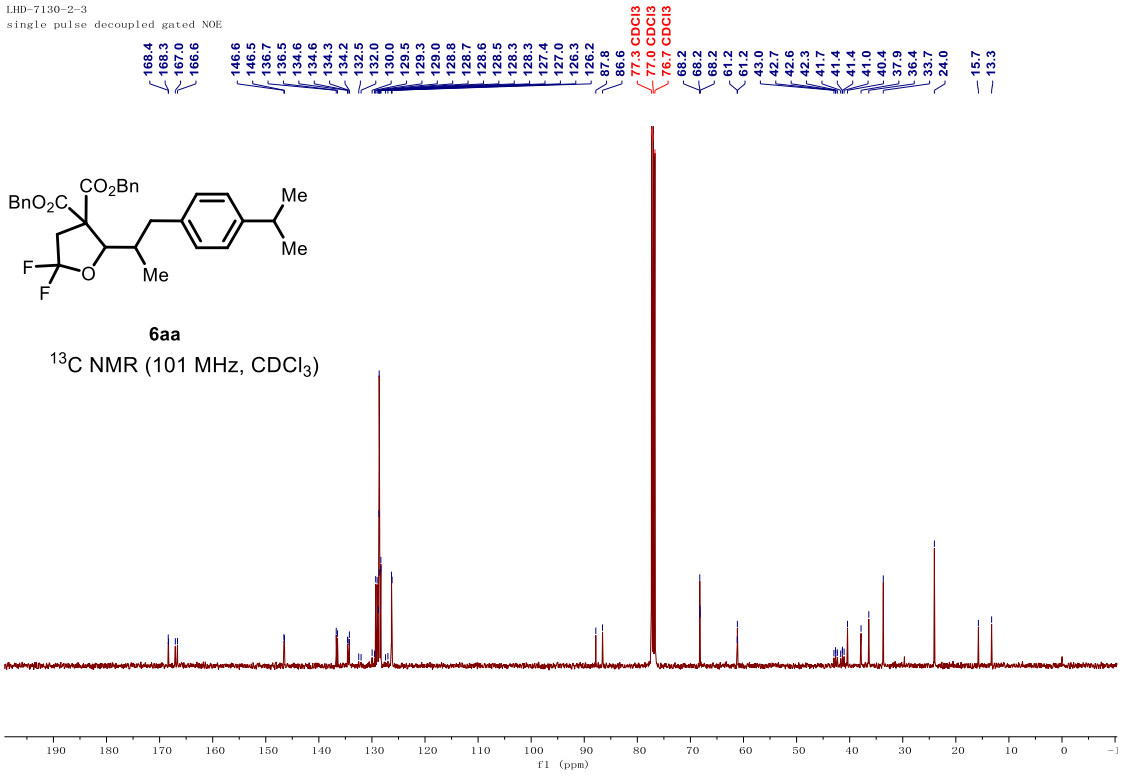
7.32
7.29
7.25
7.24
7.22
7.11
7.09
6.97
6.95
6.92
6.91
5.22
5.19
5.16
5.13
5.11
5.08
5.06
5.05
5.02
4.80
4.79
4.78
4.78
3.39
3.37
3.36
3.34
3.32
3.30
3.28
3.26
3.24
3.22
2.94
2.91
2.89
2.84
2.76
2.74
2.72
2.71
2.39
2.37
2.36
2.34
2.32
2.28
2.02
2.00
1.99
1.25
1.23
0.77
0.75



6aa

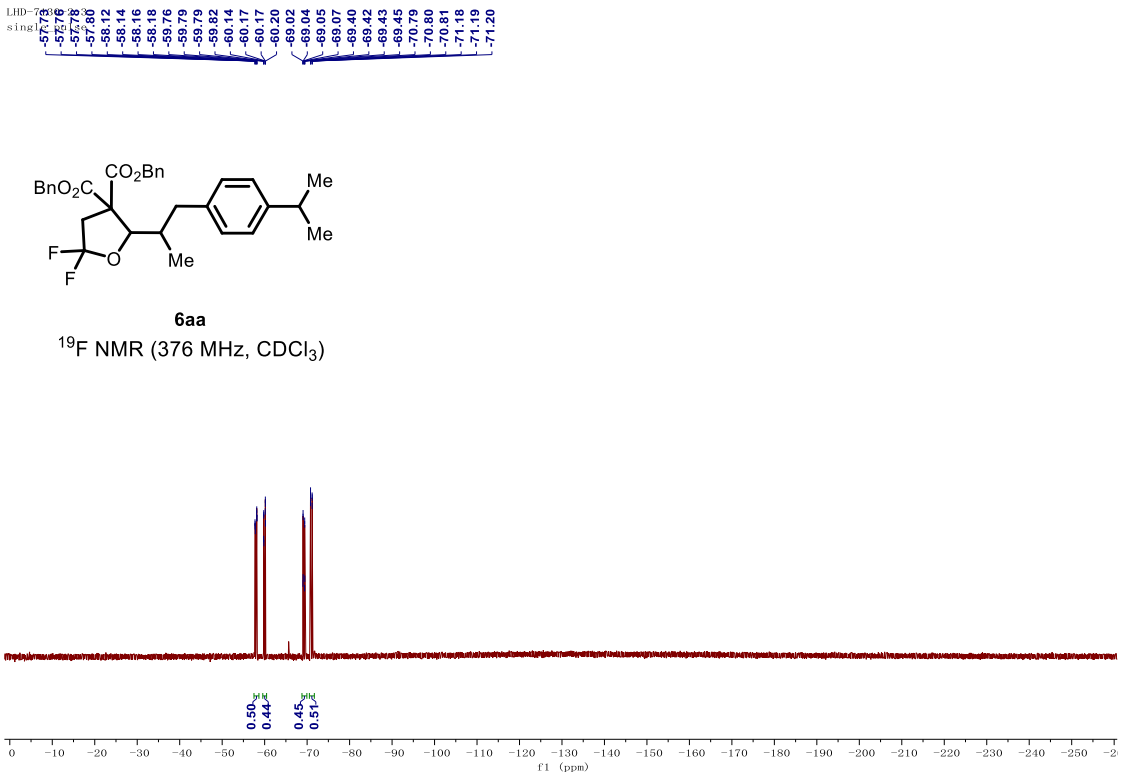
^{1}H NMR (400 MHz, $CDCl_3$)





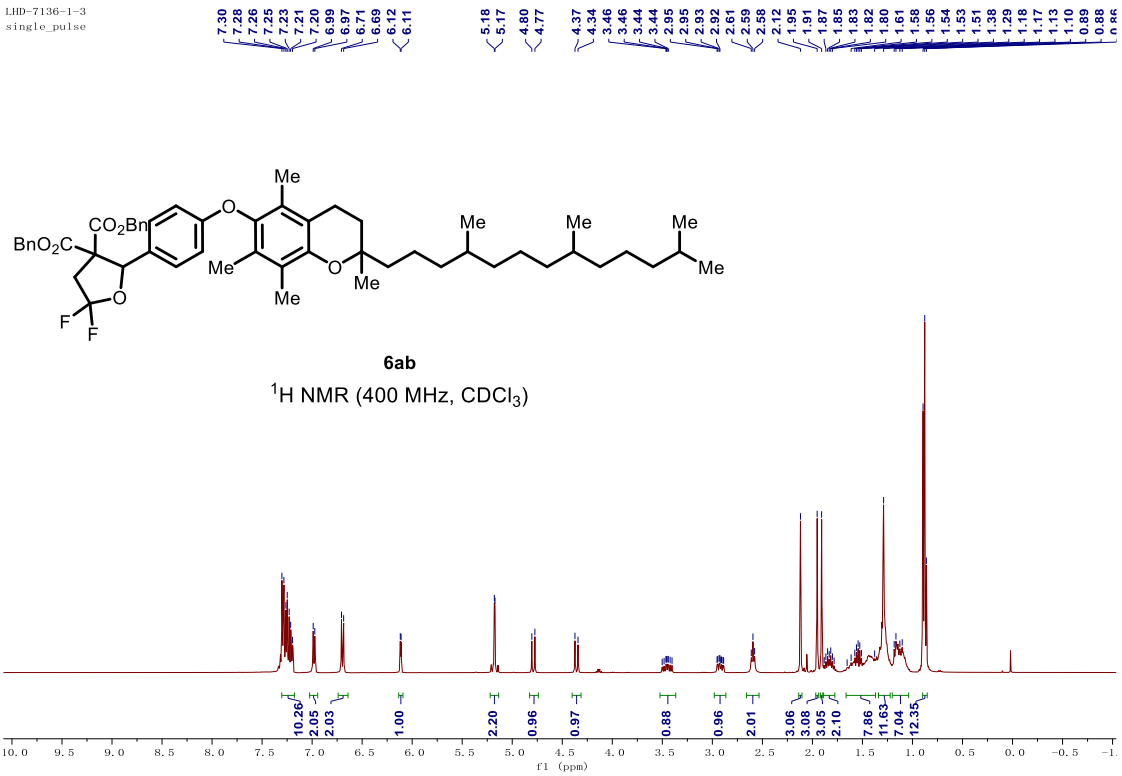
6aa

^{13}C NMR (101 MHz, $CDCl_3$)



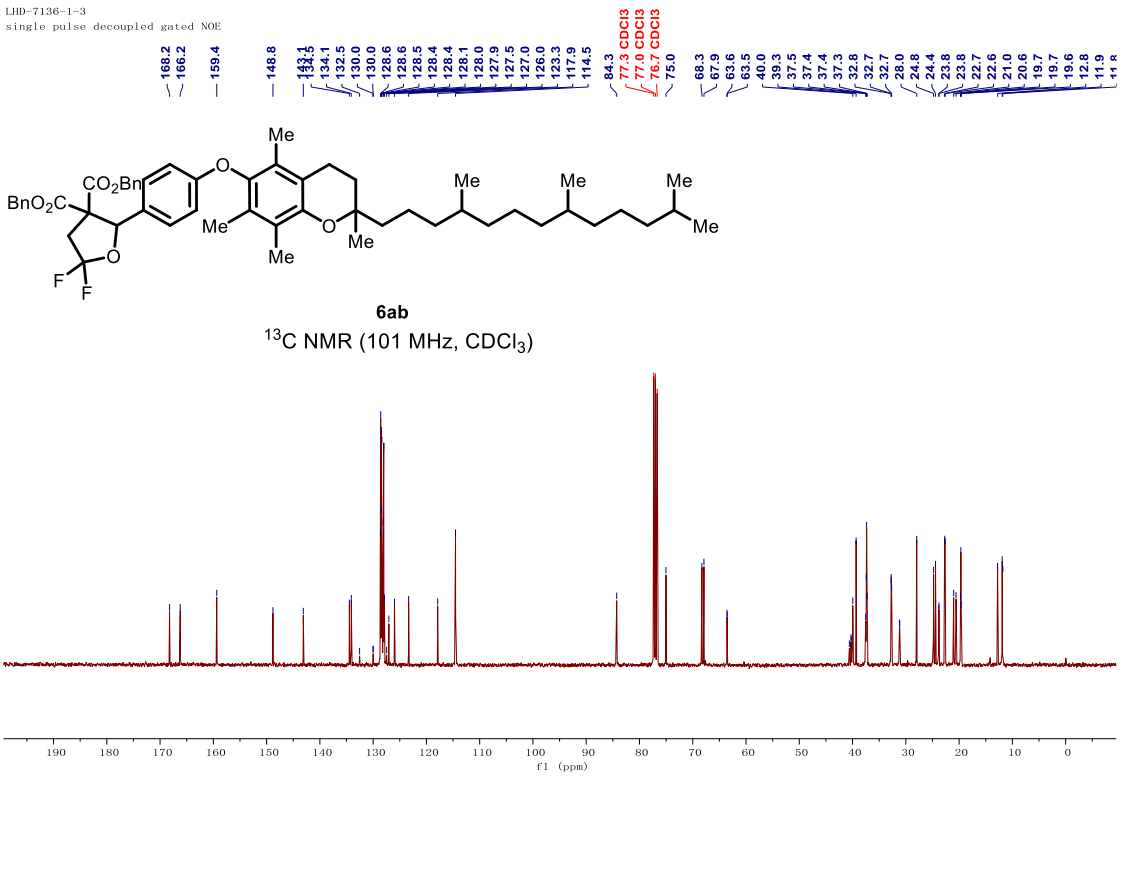
6aa

^{19}F NMR (376 MHz, $CDCl_3$)



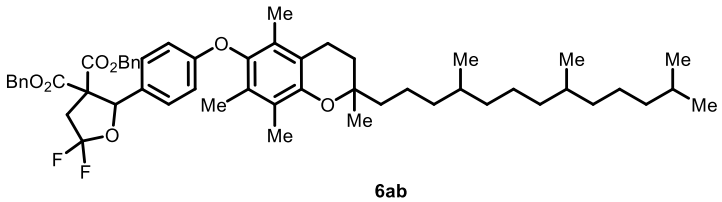
6ab

^{1}H NMR (400 MHz, $CDCl_3$)



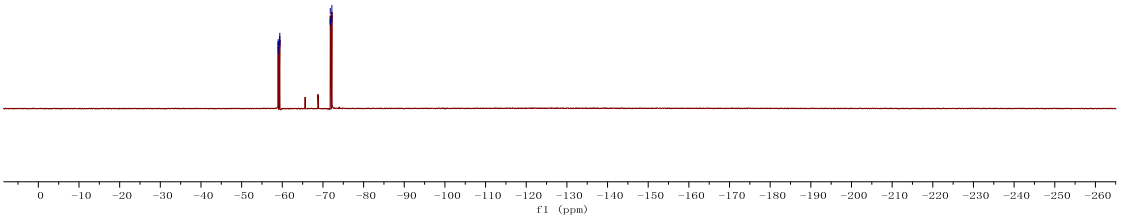
6ab

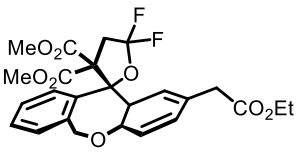
^{13}C NMR (101 MHz, $CDCl_3$)



6ab

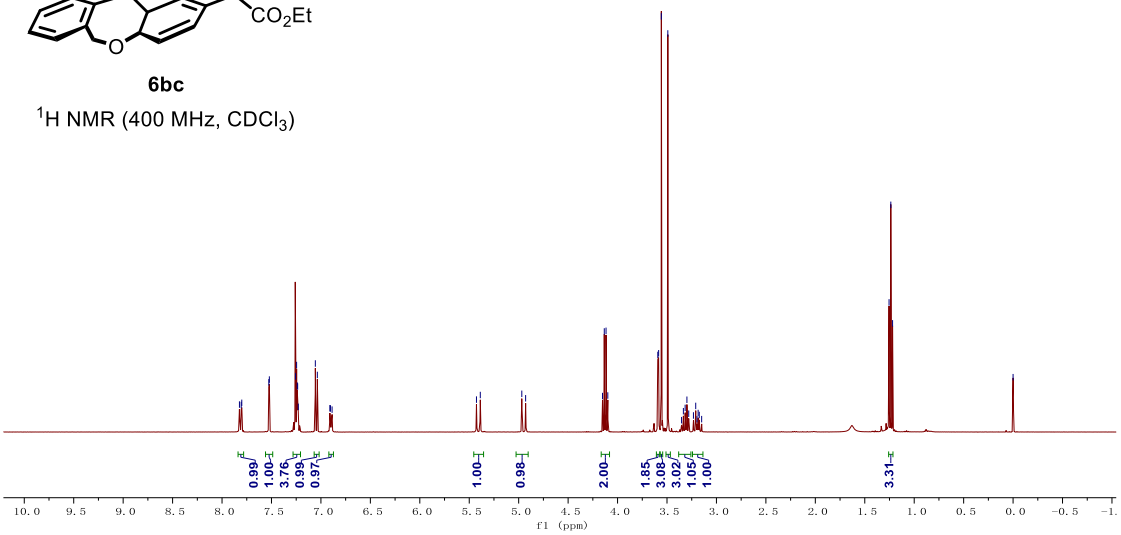
^{19}F NMR (376 MHz, $CDCl_3$)

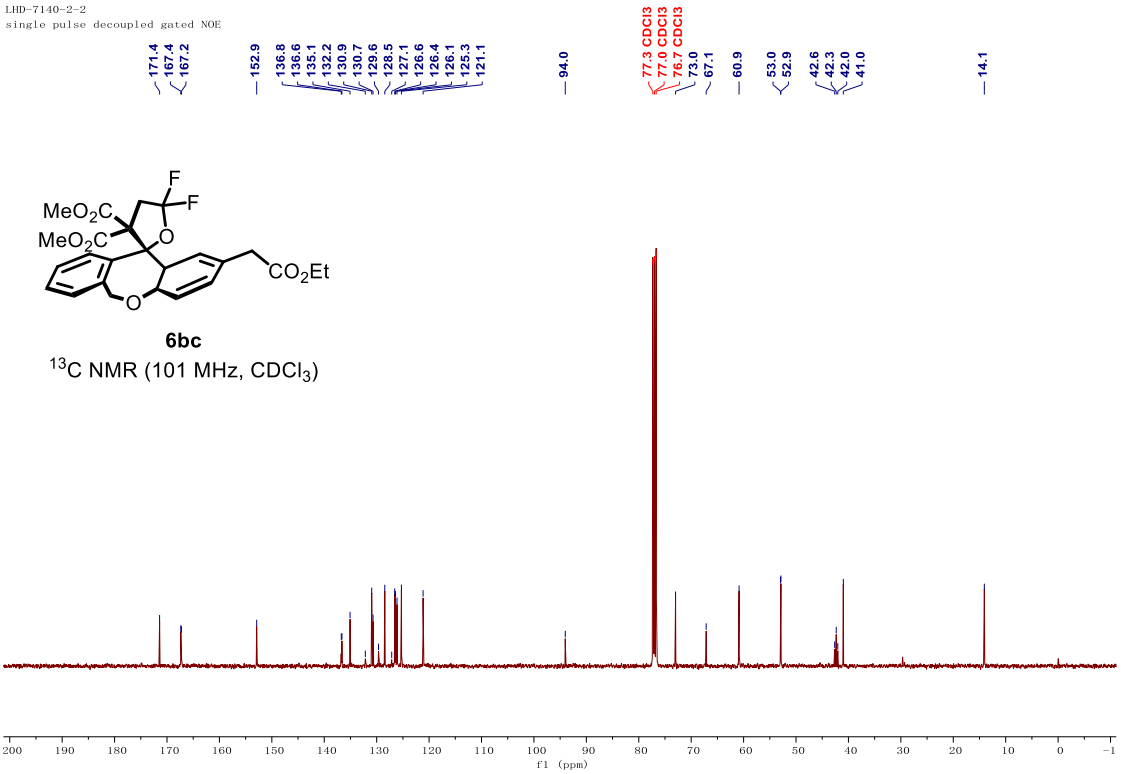




6bc

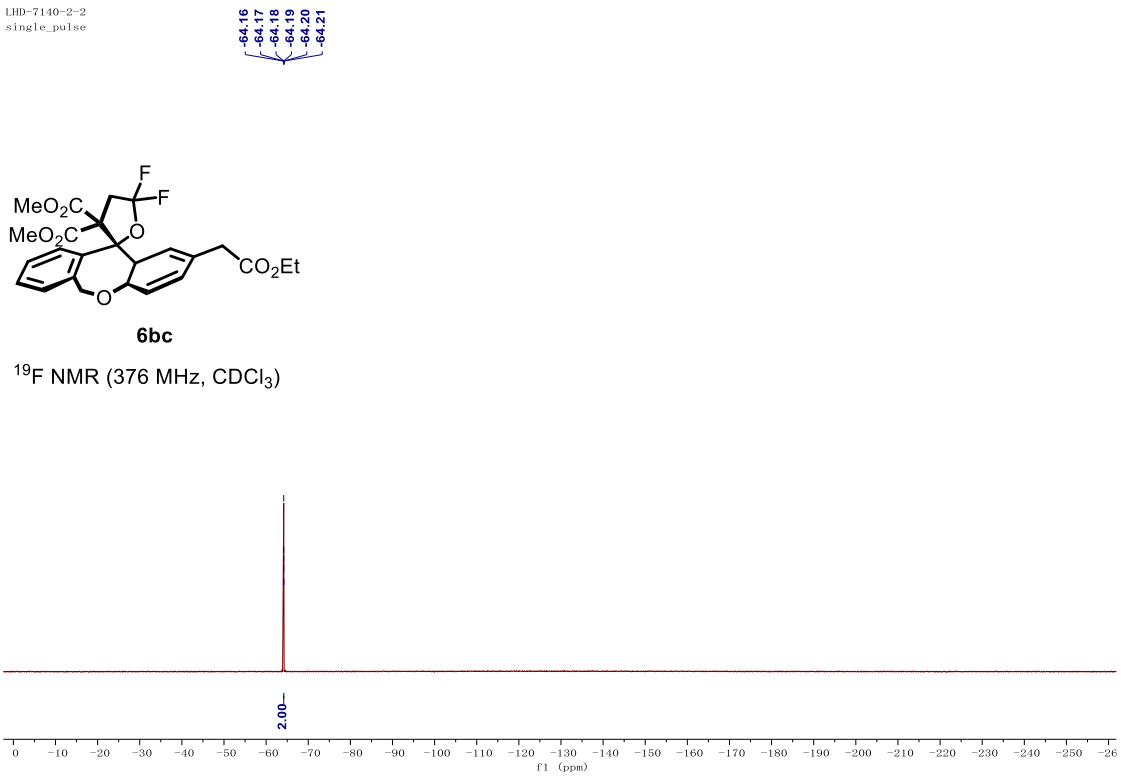
^{1}H NMR (400 MHz, $CDCl_3$)





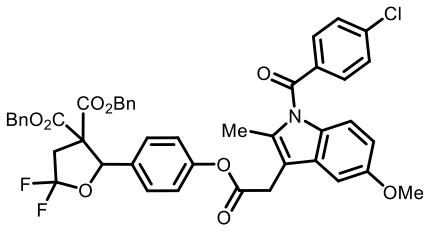
6bc

^{13}C NMR (101 MHz, $CDCl_3$)



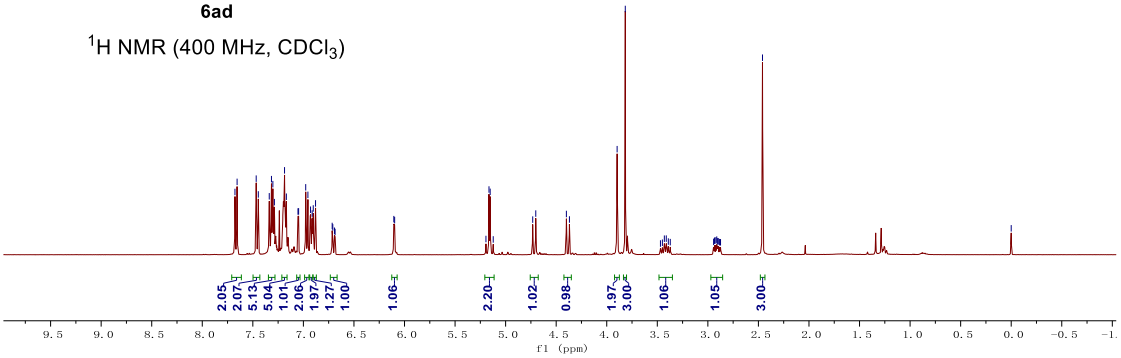
6bc

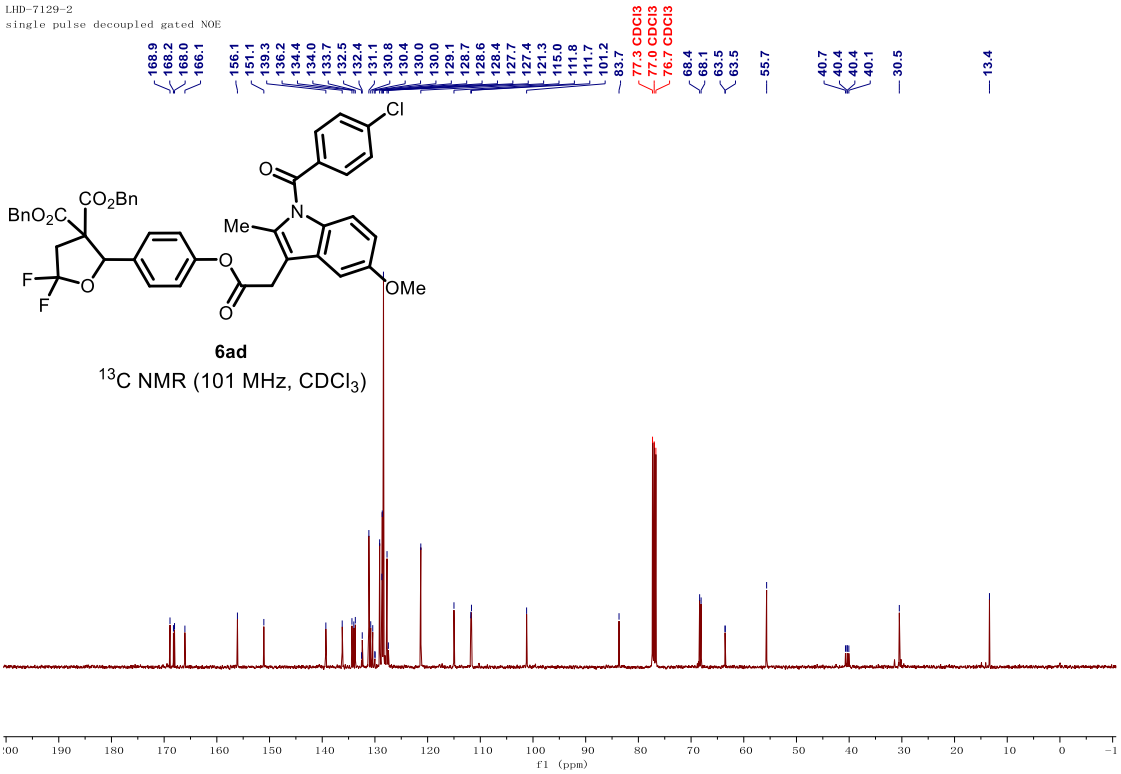
^{19}F NMR (376 MHz, $CDCl_3$)



6ad

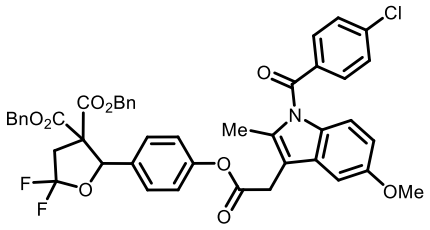
^{1}H NMR (400 MHz, $CDCl_3$)





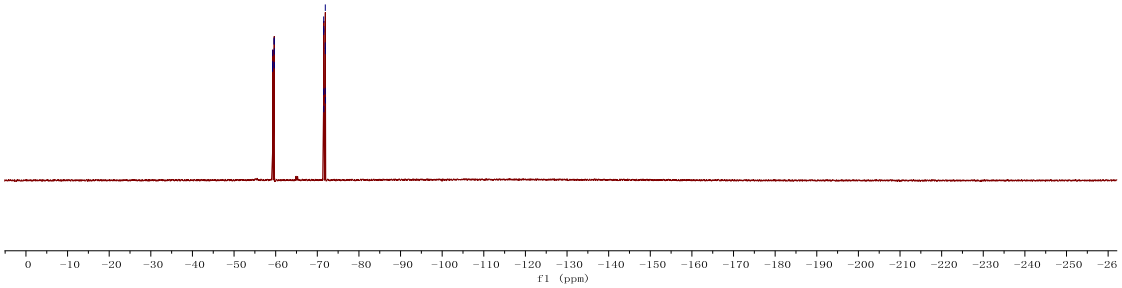
6ad

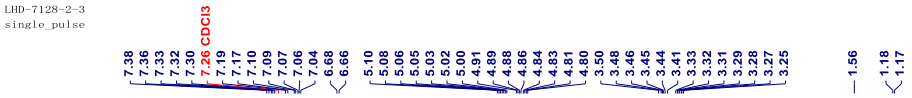
^{13}C NMR (101 MHz, $CDCl_3$)

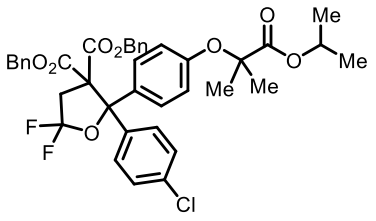


6ad

^{19}F NMR (376 MHz, $CDCl_3$)

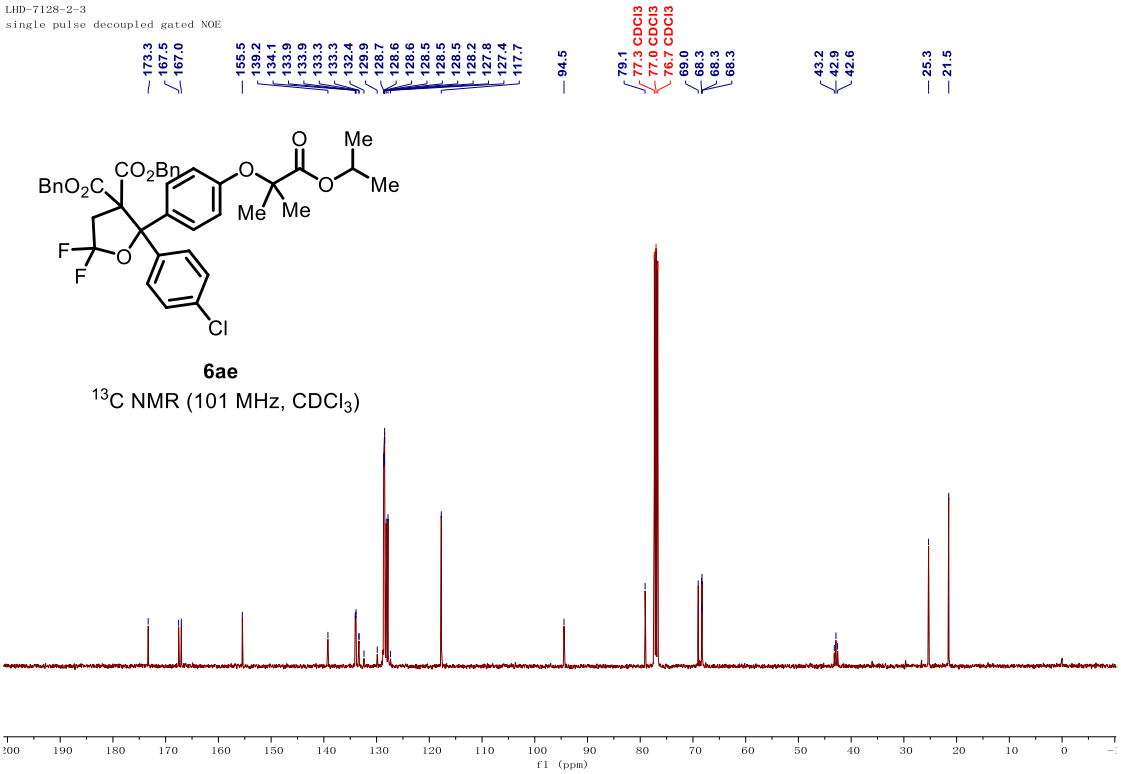






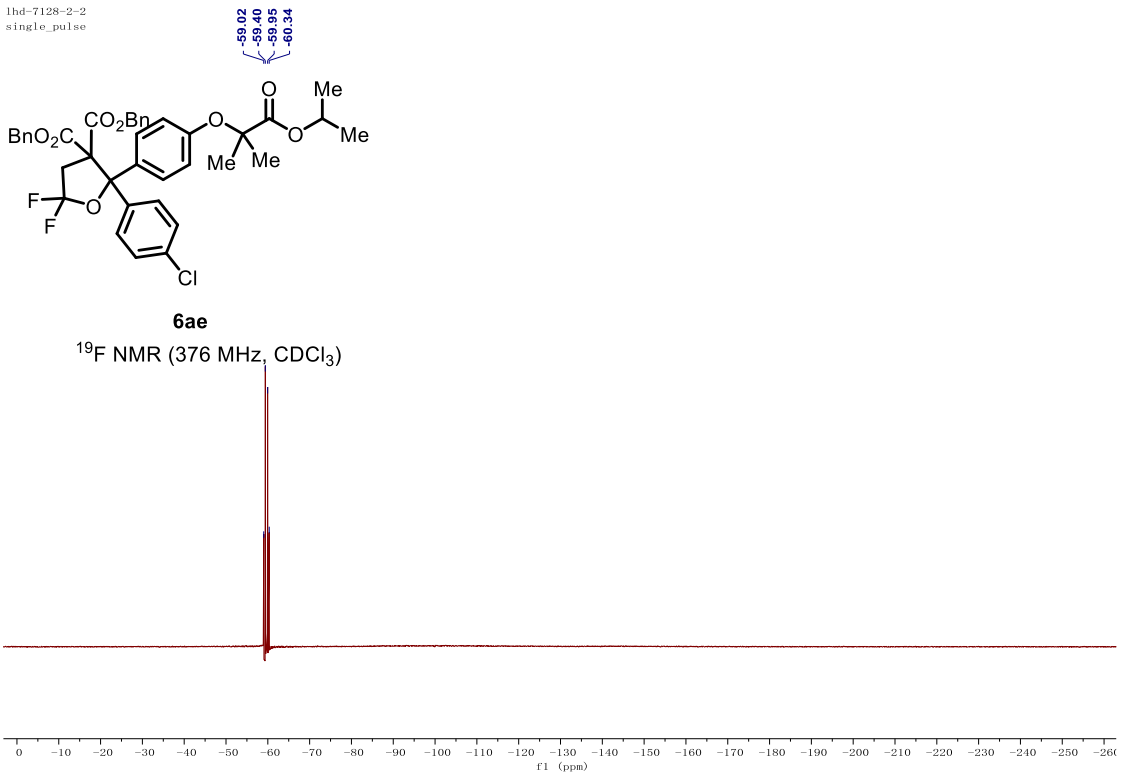
6ae

^{1}H NMR (400 MHz, $CDCl_3$)



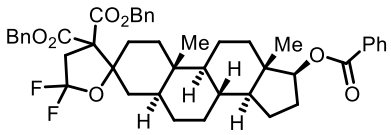
6ae

^{13}C NMR (101 MHz, $CDCl_3$)



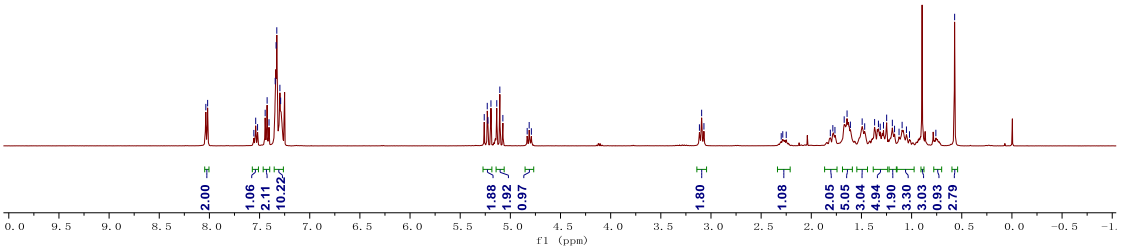
6ae

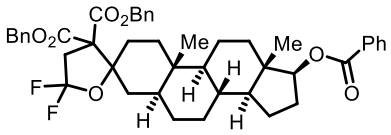
^{19}F NMR (376 MHz, $CDCl_3$)



6af

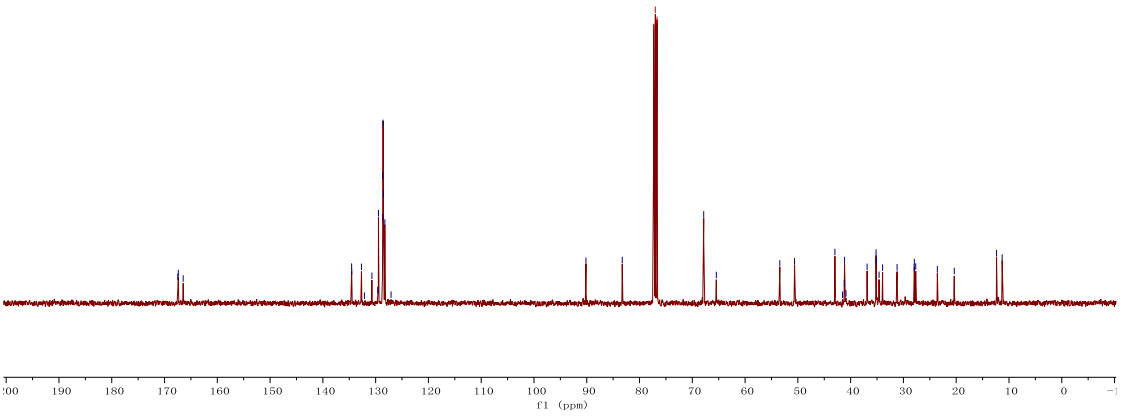
^{1}H NMR (400 MHz, $CDCl_3$)





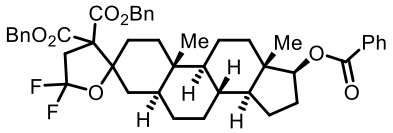
6af

^{13}C NMR (101 MHz, $CDCl_3$)



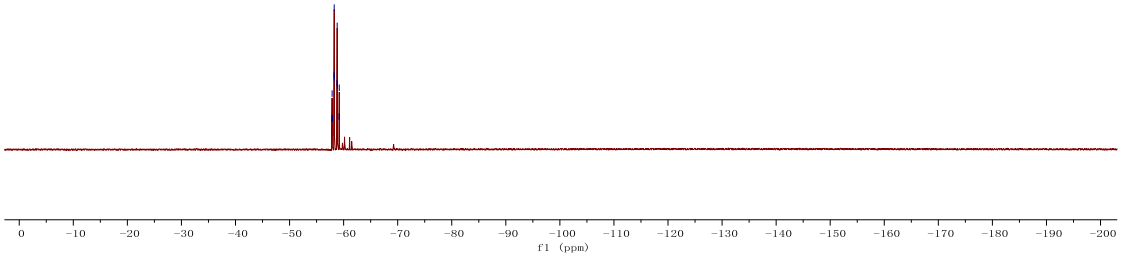
LHD-7136-3-4
single_pulse

-57.85
-57.87
-57.89
-58.24
-58.26
-58.28
-58.78
-58.81
-58.83
-59.17
-59.20
-59.22



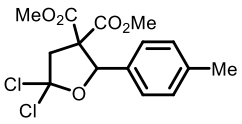
6af

^{19}F NMR (376 MHz, $CDCl_3$)



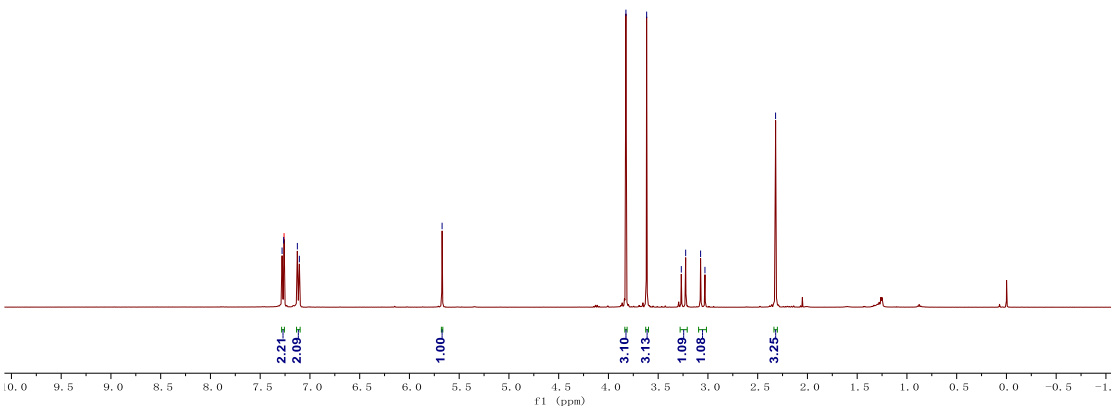
LHD-8118-2-2
single_pulse

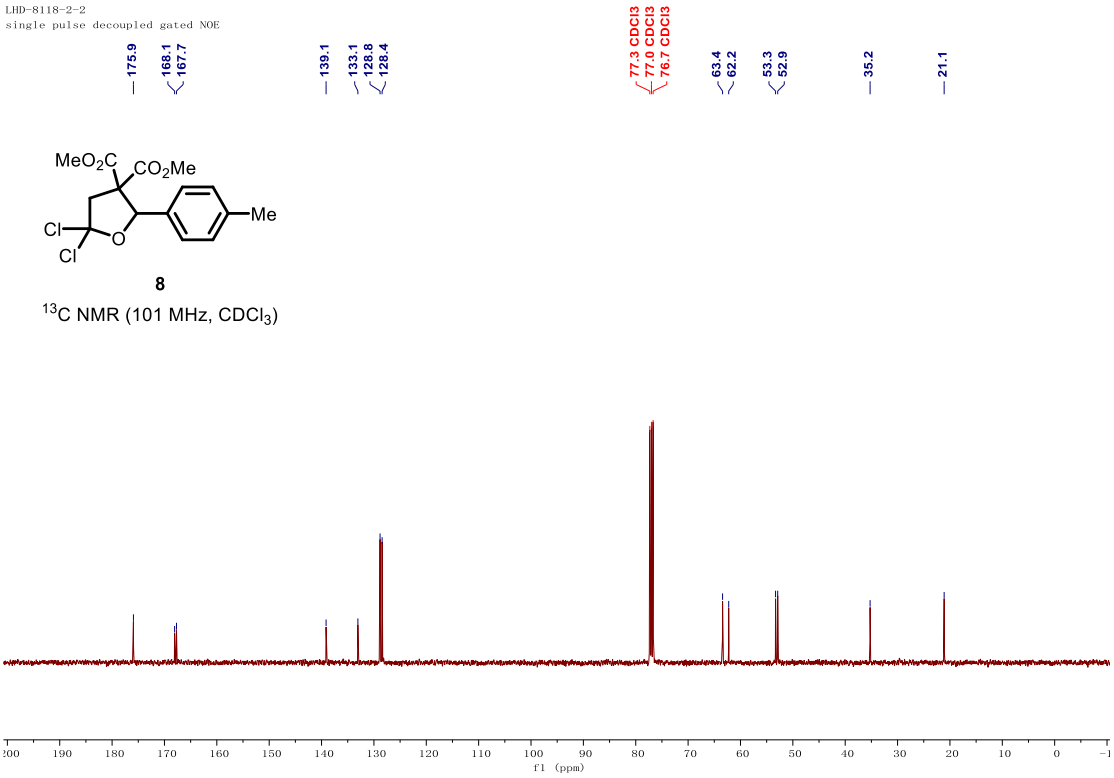
7.28
7.26
7.26 CDCl3
7.13
7.11
5.67
3.82
3.62
3.27
3.22
3.07
3.03
2.32



8

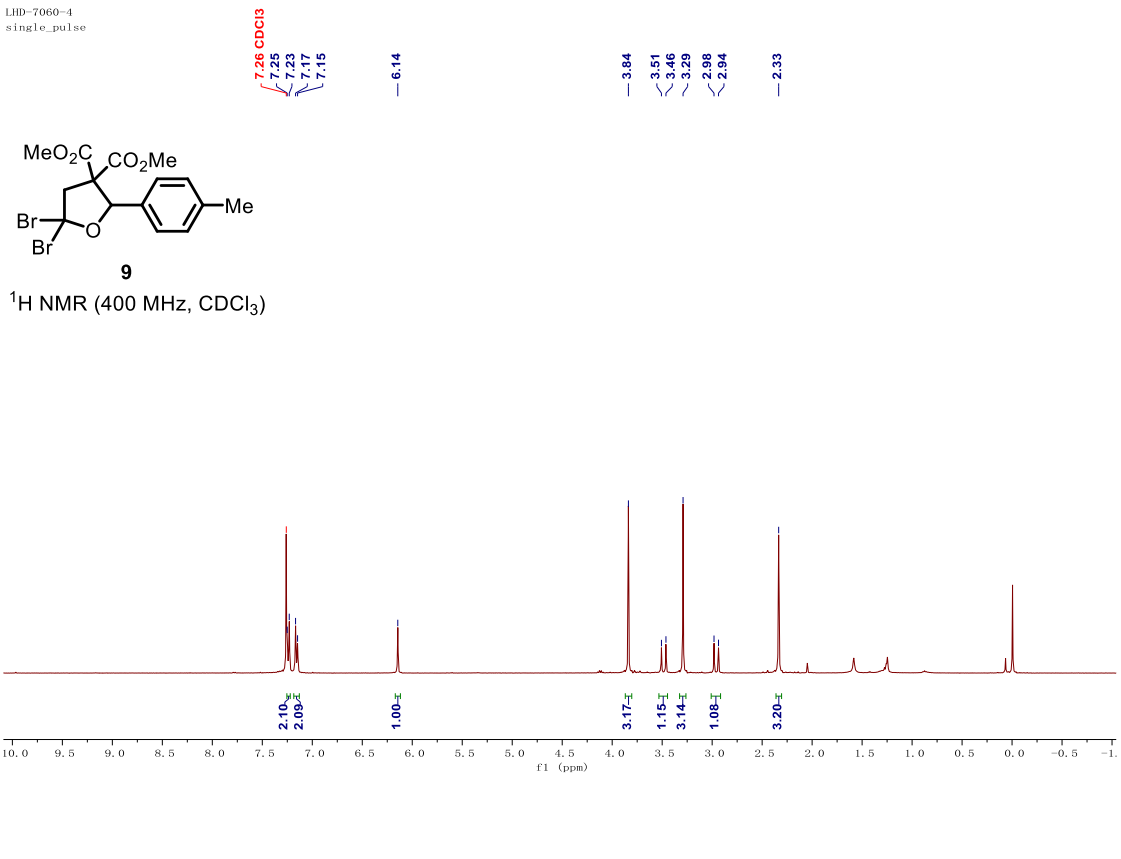
^{1}H NMR (400 MHz, $CDCl_3$)





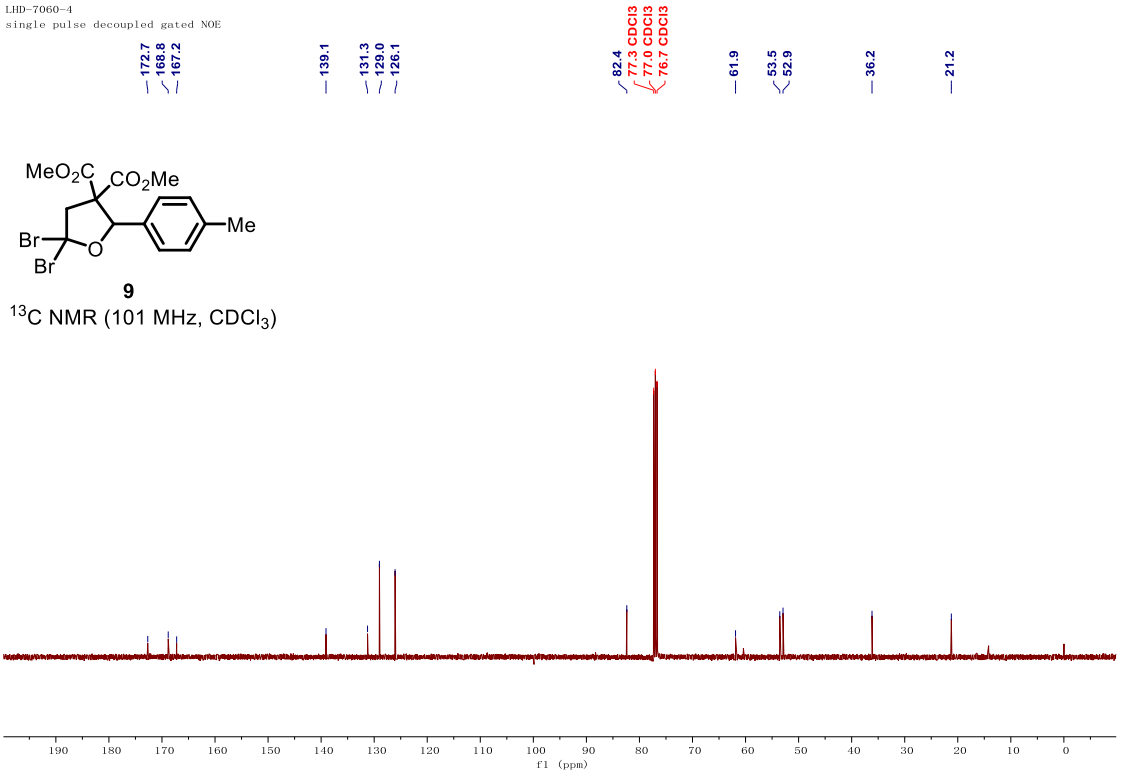
8

^{13}C NMR (101 MHz, $CDCl_3$)



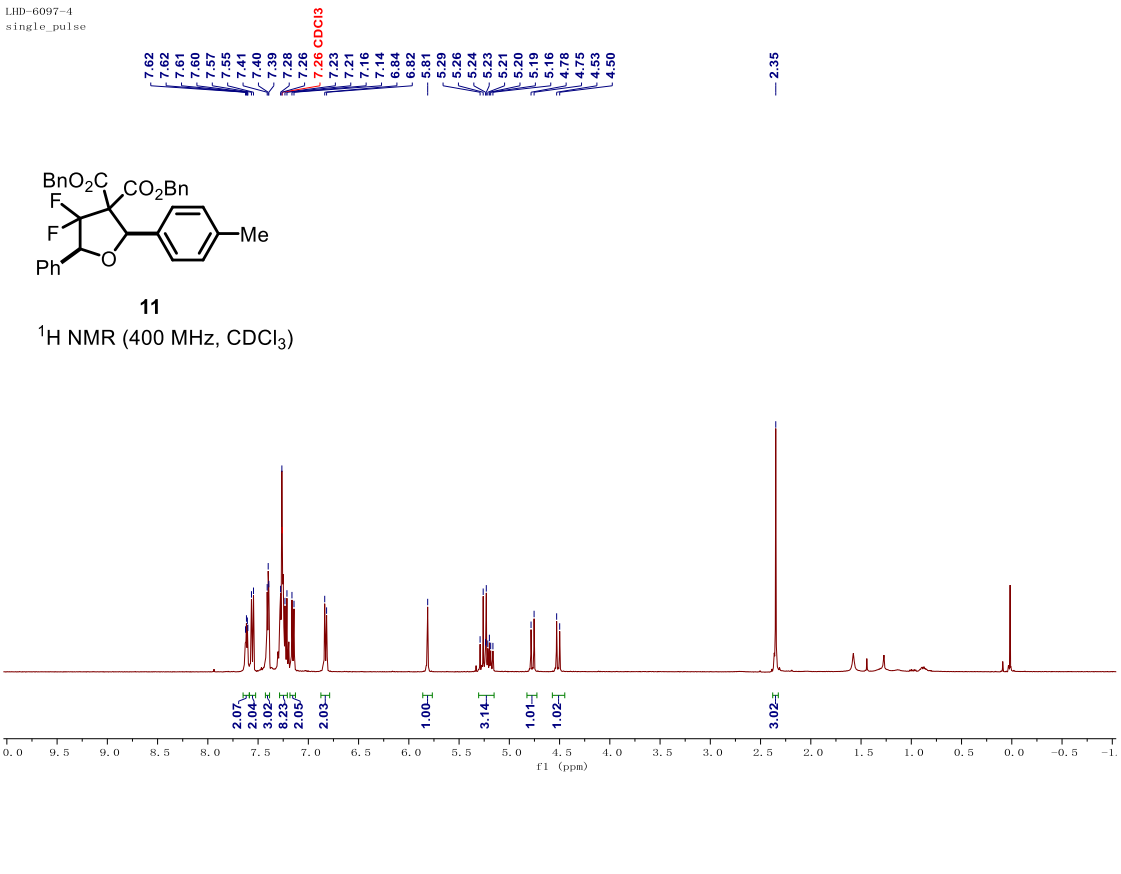
9

^{1}H NMR (400 MHz, $CDCl_3$)



9

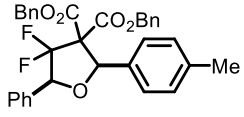
^{13}C NMR (101 MHz, $CDCl_3$)



11

^{1}H NMR (400 MHz, $CDCl_3$)

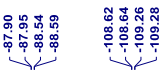
LHD-6097-4
single pulse decoupled gated NOE

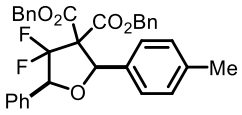


11

^{13}C NMR (101 MHz, $CDCl_3$)

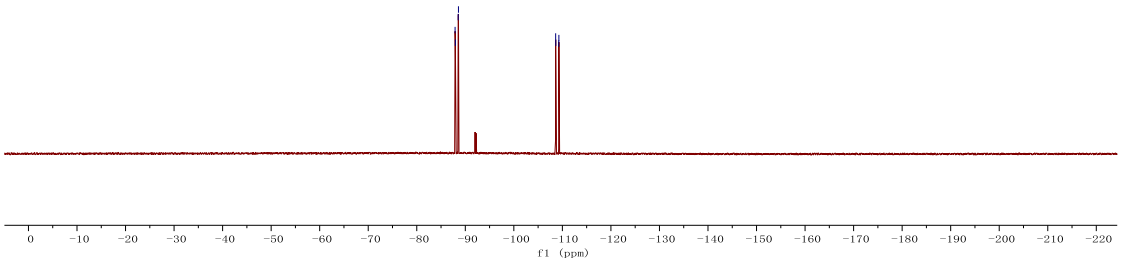
LHD-6097-4
single_pulse

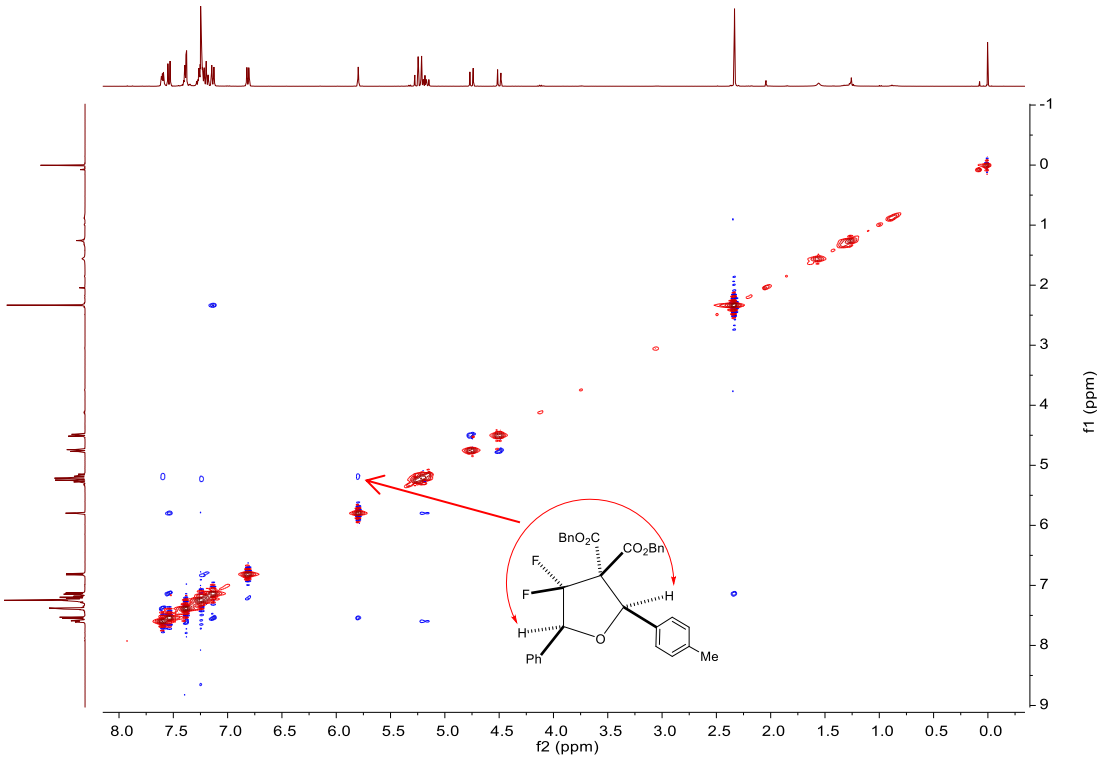




11

^{19}F NMR (376 MHz, $CDCl_3$)




f2 (ppm)
f1 (ppm)
BnO2C
CO2Bn
F
F
H
H
Ph
O
Me