Iron-catalyzed Regioselective Carboazidation of Alkenes for the Synthesis of Multi-substituted Cyclobutylamines

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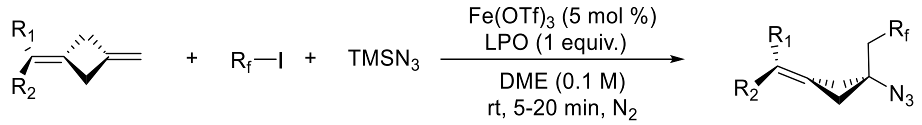
Materials and methods

All reactions were carried out under an atmosphere of nitrogen in quartz tube or glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Photoreactor was obtained from Wuhan JinboTianhua Instrument Equipment Co., Ltd. (blue LEDs, λ_{max} = 450 nm, light intensity = 64.8 mw/cm^2, 5 W for every light bulb; the distance between the lamp (without filter) and the test tube (borosilicate glass) is around 0.8 cm; every test tube was irradiated by one light bulb from the bottom). Solvents were dried by Inert PureSolv MD5. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD, JEOL ECZ400S or JEOL ECZ600S. Data for ^{1}H NMR spectra are reported relative to $CDCl_3$ as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to $CDCl_3$ as an internal standard (77.0 ppm) and are reported in terms of chemical shift (ppm). GC-MS data were recorded on Thermo ISQ QD. HRMS data were recorded on Bruker Impact II UHR-TOF, Waters Micromass GCT Premier, or Thermo Fisher Scientific LTQ FT Ultra. IR data were obtained from Bruker VERTEX 70.

Synthesis of 1,3-dimethylenecyclobutanes

All the 1,3-dimethylenecyclobutanes were synthesized according to literatures or minor modification of the reported methods.[1-4]

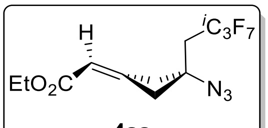
General procedure for the synthesis of products



General Procedure: In a flame-dried Schlenk tube, $Fe(OTf)_3$ (5 mol %) and LPO (0.2 mmol, 1.0 equiv) were added, then the reaction vessel was degassed and filled with N_2 for 3 times. The reaction was then added with DME (2 mL) stock of alkene (0.2 mmol), $TMSN_3$ (0.3 mmol, 1.5 equiv), and alkyl halide (0.3 mmol, 1.5 equiv). The reaction was stirred at r.t. and was monitored by TLC for completion (5-20 min). After the reaction completion, the reaction mixture was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the carboazidation product.

Characterization data for the products

Ethyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2 (trifluoromethyl)propyl)cyclobutylidene)acetate (4aa)



4aa

Following the general procedure, **4aa** was obtained as a liquid (45 mg, 62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.81 (t, *J* = 2.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.32 (m, 2H), 3.20 – 3.02 (m, 2H), 2.50 (d, *J* = 17.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

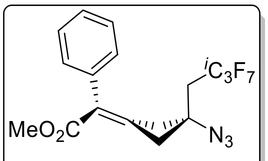
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 153.3, 116.5, 60.3, 58.9, 58.8, 45.6, 43.6, 35.8 (d, *J* = 19.3 Hz), 14.4. *(NOTE: The signals for carbons corresponding to* $^{i}C_3F_7$ *are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.07 (d, *J* = 31.0 Hz), -186.83.

HRMS (ESI) m/z calcd for $[C_{12}H_{12}F_7N_3NaO_2]^+$($[M+Na]^+$): 386.0710, found: 386.0707.

IR (KBr, v/cm^{-1}): 2112, 1718, 1222, 1162.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-phenylacetate (4ba)



4ba

Following the general procedure, **4ba** was obtained as a liquid (65 mg, 74% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 3H), 7.24 – 7.16 (m, 2H), 3.75 (s, 3H), 3.62 – 3.43 (m, 2H), 3.14 – 2.92 (m, 2H), 2.61 – 2.43 (m, 2H).

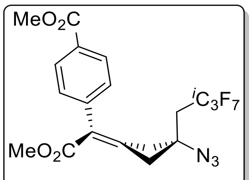
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 149.0, 134.5, 129.6, 129.0, 128.4, 127.9, 58.3, 58.2, 51.9, 46.2, 43.7, 35.90 (d, *J* = 19.3 Hz). *(NOTE: The signals for carbons corresponding to* $^{i}C_3F_7$ *are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.03 (d, *J* = 52.9 Hz), -186.72.

HRMS (ESI) m/z calcd for $[C_{17}H_{14}F_7N_3NaO_2]^+$($[M+Na]^+$): 448.0886, found: 448.0868.

IR (KBr, v/cm^{-1}): 2112, 1716, 1223, 1163, 698.

Methyl 4-(1-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-methoxy-2-oxoethyl)benzoate (4ca)



4ca

Following the general procedure, **4ca** was obtained as a liquid (57 mg, 90% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 8.03 (m, 2H), 7.30 – 7.28 (m, 2H), 3.93 (s, 3H), 3.76 (s, 3H), 3.57 – 3.48 (m, 2H), 3.13 – 2.94 (m, 2H), 2.55 – 2.46 (m, 2H).

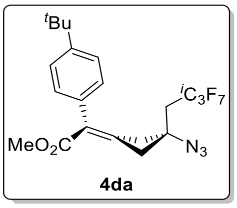
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 165.8, 150.5, 139.2, 125.7 – 113.9 (m), 94.8 – 86.5 (m), 58.2, 58.1, 52.2, 52.0, 46.2, 43.7, 35.8 (d, *J* = 19.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.06 (d, *J* = 48.7 Hz), -186.74.

HRMS (ESI) m/z calcd for $[C_{19}H_{16}F_7N_3NaO_4]^+$($[M+Na]^+$): 506.0921, found: 506.0921.

IR (KBr, v/cm^{-1}): 2112, 1719, 1278, 1223, 1163.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-(tert-butyl)phenyl)acetate (4da)



Following the general procedure, **4da** was obtained as a liquid (37 mg, 59% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 3H), 3.59 – 3.43 (m, 2H), 3.19 – 2.96 (m, 2H), 2.59 – 2.41 (m, 2H), 1.35 – 1.32 (m, 9H).

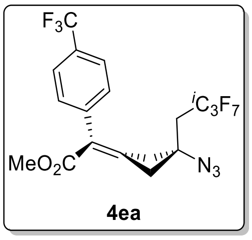
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 150.7, 148.3, 131.4, 129.4, 128.7, 125.3, 58.3, 58.3, 51.9, 46.2, 43.9, 35.9 (d, *J* = 19.2 Hz), 34.7, 31.4. *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.01 (d, *J* = 48.9 Hz), -186.67.

HRMS (ESI) m/z calcd for $[C_{21}H_{22}F_7N_3NaO_2]^+$($[M+Na]^+$): 504.1492, found: 504.1489.

IR (KBr, v/cm^{-1}): 2110, 1715, 1223, 1162.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-(trifluoromethyl)phenyl)acetate (4ea)



Following the general procedure, **4ea** was obtained as a liquid (55 mg, 84% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.75 (s, 3H), 3.62 – 3.46 (m, 2H), 3.12 – 2.92 (m, 2H), 2.61 – 2.44 (m, 2H).

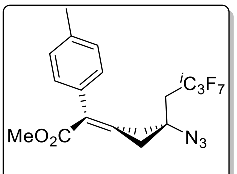
^{13}C NMR (101 MHz, Chloroform-d) δ 165.8, 150.9, 138.2, 131.2 – 129.7 (m), 129.5, 128.5, 125.4 – 125.3 (m), 124.1 (q, *J* = 272.0 Hz), 122.3 – 118.5 (m), 93.4 – 87.1 (m), 58.2, 58.2, 52.1, 46.3, 43.7, 35.9 (d, *J* = 19.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.75, -77.10 (d, *J* = 52.8 Hz), -186.74.

HRMS (ESI) m/z calcd for $[C_{18}H_{14}F_{10}NO_2]^+$($[M+H-N_2]^+$): 466.0856, found: 466.0859.

IR (KBr, v/cm^{-1}): 2111, 1717, 1326, 1224, 1163, 1126, 1068, 1018, 843.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(p-tolyl)acetate (4fa)



4fa

Following the general procedure, **4fa** was obtained as a liquid (44 mg, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.15 (m, 2H), 7.12 – 7.06 (m, 2H), 3.74 (s, 3H), 3.60 – 3.43 (m, 2H), 3.15 – 2.93 (m, 2H), 2.58 – 2.44 (m, 2H), 2.36 (s, 3H).

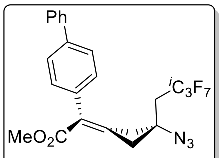
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 148.5, 137.7, 131.6, 129.4, 129.1, 128.9, 126.3 – 114.7 (m), 96.2 – 85.3 (m), 58.3, 58.2, 51.9, 46.2, 43.7, 35.9 (d, *J* = 19.3 Hz), 21.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.04 (d, *J* = 50.3 Hz), -186.71.

HRMS (ESI) m/z calcd for $[C_{18}H_{16}F_7N_3NaO_2]^+$($[M+Na]^+$): 462.1023, found: 462.1029.

IR (KBr, v/cm^{-1}): 2112, 1716, 1223, 1163, 698.

Methyl 2-([1,1'-biphenyl]-4-yl)-2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)acetate (4ga)



4ga

Following the general procedure, **4ga** was obtained as a liquid (55 mg, 82% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 4H), 7.48 – 7.42 (m, 2H), 7.39 – 7.34 (m, 1H), 7.32 – 7.27 (m, 2H), 3.79 (s, 3H), 3.64 – 3.49 (m, 2H), 3.22 – 3.00 (m, 2H), 2.54 (d, *J* = 17.2 Hz, 2H).

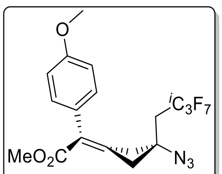
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 149.1, 140.7, 140.6, 133.4, 129.5, 129.2, 128.9, 127.6, 127.2, 127.1, 58.3, 58.3, 52.0, 46.2, 43.9, 35.9 (d, *J* = 19.3 Hz). *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*

^{19}F NMR (565 MHz, Chloroform-*d*) δ -76.84 – -77.14 (m), -186.45 – -186.77 (m).

HRMS (ESI) m/z calcd for $[C_{23}H_{18}F_7N_3NaO_2]^+$($[M+Na]^+$): 524.1179, found: 524.1178.

IR (KBr, v/cm^{-1}): 2111 1716, 1223, 1163.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-methoxyphenyl)acetate (4ha)

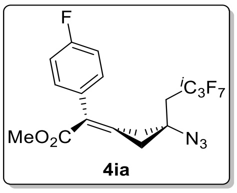


4ha

Following the general procedure, **4ha** was obtained as a liquid (45 mg, 78% yield).

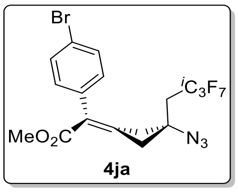
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.11 (m, 2H), 6.92 – 6.87 (m, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 3.60 – 3.40 (m, 2H), 3.16 – 2.93 (m, 2H), 2.60 – 2.43 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 159.2, 148.1, 130.3, 129.1, 126.8, 113.8, 58.3, 58.2, 55.3, 51.9, 46.2, 43.7, 35.9 (d, J = 19.2 Hz). *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.02 (d, J = 48.0 Hz), -186.72.
HRMS (ESI) m/z calcd for $[C_{18}H_{16}F_7N_3NaO_3]^+$($[M+Na]^+$): 478.0972, found: 478.0977.
IR (KBr, v/cm^{-1}): 2108, 1712, 1512, 1219, 1160, 1026, 831.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-fluorophenyl)acetate (4ia)



Following the general procedure, **4ia** was obtained as a liquid (43 mg, 78% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 2H), 7.09 – 7.02 (m, 2H), 3.75 (s, 3H), 3.61 – 3.43 (m, 2H), 3.14 – 2.92 (m, 2H), 2.61 – 2.43 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 162.3 (d, J = 247.4 Hz), 149.4, 130.8 (d, J = 8.0 Hz), 130.4 (d, J = 3.5 Hz), 128.6, 123.7 – 118.7 (m), 115.4 (d, J = 21.6 Hz), 92.8 – 88.9 (m), 58.2, 58.2, 52.0, 46.2, 43.7, 35.9 (d, J = 19.3 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.07 (d, J = 52.0 Hz), -113.82, -186.73.
HRMS (ESI) m/z calcd for $[C_{17}H_{13}F_8N_3NaO_2]^+$($[M+Na]^+$): 466.0772, found: 466.0759.
IR (KBr, v/cm^{-1}): 2111, 1717, 1510, 1223, 1161.

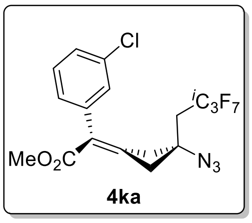
Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ja)



Following the general procedure, **4ja** was obtained as a liquid (41 mg, 61% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 3.74 (s, 3H), 3.59 – 3.42 (m, 2H), 3.13 – 2.89 (m, 2H), 2.60 – 2.43 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 149.9, 133.4, 131.6, 130.8, 128.6, 122.1, 58.2, 58.2, 52.0, 46.2, 43.7, 35.9 (d, J = 19.3 Hz). *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.03 (d, J = 48.3 Hz), -186.70.
HRMS (ESI) m/z calcd for $[C_{17}H_{14}BrF_7NO_2]^+$($[M+H-N_2]^+$): 476.0091, found: 476.0089.
IR (KBr, v/cm^{-1}): 2108, 1713, 1219, 1160, 773.

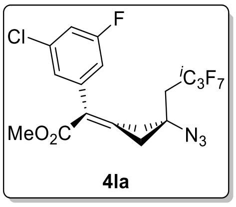
Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-

(trifluoromethyl)propyl)cyclobutylidene)-2-(3-chlorophenyl)acetate (4ka)



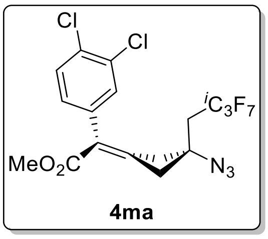
Following the general procedure, **4ka** was obtained as a liquid (48 mg, 82% yield).
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.06 (m, 1H), 3.76 (s, 3H), 3.60 – 3.44 (m, 2H), 3.15 – 2.90 (m, 2H), 2.59 – 2.45 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 150.4, 136.2, 134.2, 129.7, 129.2, 128.4, 128.1, 127.3, 58.2, 58.2, 52.1, 46.1, 43.8, 35.9 (d, *J* = 19.2 Hz). *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*
^{19}F NMR (565 MHz, Chloroform-*d*) δ -76.38 – -77.73 (m), -185.98 – -187.34 (m).
HRMS (ESI) m/z calcd for $[C_{17}H_{13}ClF_7N_3NaO_2]^+$($[M+Na]^+$): 482.0477, found: 482.0481.
IR (KBr, v/cm^{-1}): 2110, 1717, 1221, 1161, 773.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(3-chloro-5-fluorophenyl)acetate (4la)



Following the general procedure, **4la** was obtained as a liquid (53 mg, 85% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 7.03 (m, 1H), 7.03 – 6.96 (m, 1H), 6.90 – 6.79 (m, 1H), 3.77 (d, *J* = 1.7 Hz, 3H), 3.61 – 3.44 (m, 2H), 3.17 – 2.94 (m, 2H), 2.62 – 2.48 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 162.4 (d, *J* = 249.8 Hz), 151.4, 137.6 (d, *J* = 9.1 Hz), 135.0 (d, *J* = 11.0 Hz), 127.5 (d, *J* = 2.2 Hz), 125.2 (d, *J* = 3.2 Hz), 122.9 – 118.7 (m), 115.8 (d, *J* = 24.7 Hz), 114.8 (d, *J* = 22.0 Hz), δ 94.1 – 88.1 (m), 58.2, 58.2, 52.1, 46.1, 43.8, 35.8 (d, *J* = 19.3 Hz).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.05 (d, *J* = 52.6 Hz), -110.69, -186.69.
HRMS (ESI) m/z calcd for $[C_{17}H_{13}ClF_8NO_2]^+$($[M+H-N_2]^+$): 450.0500, found: 450.0502.
IR (KBr, v/cm^{-1}): 2112, 1718, 1223, 1162, 772.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(3,4-dichlorophenyl)acetate (4ma)



Following the general procedure, **4ma** was obtained as a liquid (55 mg, 84% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.75 (s, 3H), 3.58 – 3.43 (m, 2H), 3.12 – 2.90 (m, 2H), 2.59 – 2.43 (m, 2H).

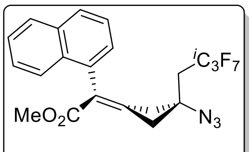
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.6, 151.0, 134.4, 132.5, 132.2, 131.0, 130.4, 128.5, 127.6, 58.2, 58.2, 52.1, 46.2, 43.8, 35.80 (d, *J* = 19.3 Hz). *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.11 (d, *J* = 49.0 Hz), -186.72.

HRMS (ESI) m/z calcd for $[C_{17}H_{13}Cl_2F_7NO_2]^+$($[M+H-N_2]^+$): 466.0203, found: 466.0206.

IR (KBr, v/cm^{-1}): 2110, 1700, 1223, 936.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(naphthalen-1-yl)acetate (4na)



4na

Following the general procedure, **4na** was obtained as a liquid (54 mg, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.81 (m, 2H), 7.72 – 7.65 (m, 1H), 7.52 – 7.44 (m, 3H), 7.29 – 7.25 (m, 1H), 3.74 – 3.59 (m, 5H), 2.95 – 2.65 (m, 2H), 2.60 – 2.43 (m, 2H).

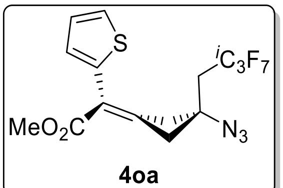
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.6, 151.4, 133.8, 132.1, 131.7, 128.7, 128.6, 128.1, 127.2, 126.6, 126.1, 125.5, 124.7, 122.7 – 116.6 (m), 96.0 – 88.4 (m), 58.3, 58.3, 52.0, 46.2, 43.4, 35.90 (d, *J* = 19.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.0 (d, *J* = 44.3 Hz), -186.7.

HRMS (ESI) m/z calcd for $[C_{21}H_{16}F_7N_3NaO_2]^+$($[M+Na]^+$): 498.1030, found: 498.1023.

IR (KBr, v/cm^{-1}): 2112, 1716, 1231, 1162, 779.

Methyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(thiophen-2-yl)acetate (4oa)



4oa

Following the general procedure, **4oa** was obtained as a liquid (60 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.31 (m, 1H), 7.13 – 7.08 (m, 1H), 7.07 – 7.02 (m, 1H), 3.83 (s, 3H), 3.59 – 3.41 (m, 2H), 3.38 – 3.19 (m, 2H), 2.59 – 2.49 (m, 2H).

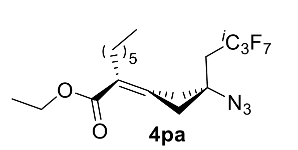
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 147.5, 135.6, 127.4, 126.9, 126.3, 123.3, 58.3, 58.3, 52.1, 46.3, 45.1, 35.9 (d, *J* = 19.2 Hz). *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.01, -186.65.

HRMS (ESI) m/z calcd for $[C_{15}H_{12}F_7N_3NaO_2]^+$($[M+Na]^+$): 454.0431, found: 454.0430.

IR (KBr, v/cm^{-1}): 2112, 1718, 1223, 1162, 771, 703.

Ethyl (*S*,*E*)-2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)octanoate (4pa)



4pa

Following the general procedure, **4pa** was obtained as a liquid (176 mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.21 – 4.16 (m, 2H), 3.44 – 3.23 (m, 2H), 3.15 – 2.97 (m, 2H), 2.58 – 2.44 (m, 2H), 2.17 – 2.11 (m, 2H), 1.31 – 1.27 (m, 9H), 0.90 – 0.86 (m, 3H).

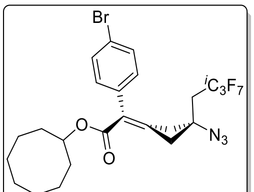
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 145.0, 128.7, 60.3, 57.9 (d, *J* = 3.5 Hz), 45.9, 42.3, 36.0 (d, *J* = 19.3 Hz), 31.7, 29.2, 28.8, 28.4, 22.7, 14.4, 14.1. *(NOTE: The signals for carbons corresponding to* $^{i}C_3F_7$ *are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.92 – -77.17 (m), -186.67 – -186.97 (m).

HRMS (ESI) m/z calcd for $[C_{18}H_{24}F_7N_3NaO_2]^+$($[M+Na]^+$): 470.1649, found: 470.1650.

IR (KBr, v/cm^{-1}): 3459, 2927, 2860, 2109, 1669, 1570, 1230, 739.

Cyclooctyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4qa)



4qa

Following the general procedure, **4qa** was obtained as a liquid (45 mg, 52% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.12 – 4.97 (m, 1H), 3.56 – 3.40 (m, 2H), 3.14 – 2.89 (m, 2H), 2.60 – 2.42 (m, 2H), 1.87 – 1.78 (m, 2H), 1.78 – 1.71 (m, 2H), 1.72 – 1.61 (m, 2H), 1.56 – 1.43 (m, 8H).

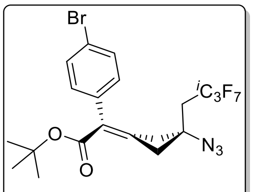
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.9, 148.3, 133.5, 131.3, 130.7, 129.2, 121.8, 58.2, 58.1, 46.2, 43.7, 35.8 (d, *J* = 19.4 Hz), 31.5, 31.5, 27.0, 27.0, 25.3, 22.9, 22.9, 21.1, 14.2. *(NOTE: The signals for carbons corresponding to* $^{i}C_3F_7$ *are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.02 (d, *J* = 60.5 Hz), -186.74.

HRMS (ESI) m/z calcd for $[C_{24}H_{26}BrF_7NO_2]^+$($[M-N_2+H]^+$): 572.1032, found: 572.1030.

IR (KBr, v/cm^{-1}): 2109, 1706, 1221, 1163, 773, 745.

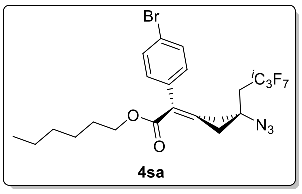
Tert-butyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ra)



4ra

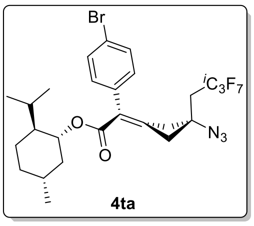
Following the general procedure, **4ra** was obtained as a liquid (50 mg, 66% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.44 (m, 2H), 7.13 – 7.03 (m, 2H), 3.55 – 3.39 (m, 2H), 3.13 – 2.89 (m, 2H), 2.57 – 2.45 (m, 2H), 1.49 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 147.3, 133.8, 131.4, 130.8, 130.2, 121.8, 81.8, 58.2, 58.1, 46.2, 43.7, 35.9 (d, *J* = 19.3 Hz), 28.3. *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.03 (d, *J* = 53.8 Hz), -186.79.
HRMS (ESI) m/z calcd for $[C_{20}H_{19}BrF_7N_3NaO_2]^+$($[M+Na]^+$): 568.0441, found: 568.0434.
IR (KBr, v/cm^{-1}): 2110, 1708, 1222, 1163, 773.

Hexyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4sa)



Following the general procedure, **4sa** was obtained as a liquid (74 mg, 94% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.11 – 7.06 (m, 2H), 4.15 (t, *J* = 6.7 Hz, 2H), 3.60 – 3.42 (m, 2H), 3.19 – 2.87 (m, 2H), 2.52 (d, *J* = 17.1 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.36 – 1.23 (m, 6H), 0.92 – 0.85 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 149.2, 133.5, 131.5, 130.8, 128.9, 122.0, 65.3, 58.2, 58.2, 46.2, 43.8, 35.9 (d, *J* = 19.3 Hz), 31.4, 28.6, 25.7, 22.6, 14.0. *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.03 (d, *J* = 54.2 Hz), -186.73.
HRMS (ESI) m/z calcd for $[C_{22}H_{24}BrF_7N_3O_2]^+$($[M+H]^+$): 574.0935, found: 574.0936.
IR (KBr, v/cm^{-1}): 2111, 1712, 1222, 1163, 1073, 1011, 773.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-(3-azido-3-(2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ta)



Following the general procedure, **4ta** was obtained as a liquid (66 mg, 71% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 7.11 – 7.03 (m, 2H), 4.85 – 4.69 (m, 1H), 3.59 – 3.35 (m, 2H), 3.15 – 2.91 (m, 2H), 2.59 – 2.41 (m, 2H), 2.11 – 1.99 (m, 1H), 1.87 – 1.74 (m, 1H), 1.75 – 1.65 (m, 2H), 1.57 – 1.41 (m, 1H), 1.40 – 1.21 (m, 2H), 1.14 – 0.94 (m, 2H), 0.92 – 0.85 (m, 6H), 0.78 – 0.72 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2, 148.5, 133.6, 133.6, 131.5, 131.4, 130.9, 130.8, 129.2, 121.9, 75.2, 58.3, 58.2, 58.2, 47.2, 46.2, 46.0, 44.0, 43.8, 41.2, 41.2, 36.0, 36.0, 35.8, 34.2, 31.5, 26.4, 23.3, 22.1, 20.9, 20.9, 16.3. *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the*

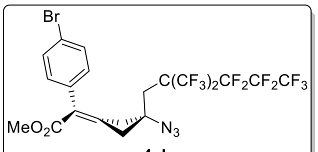
spectrum).

[19]F NMR (376 MHz, Chloroform-*d*) δ -77.04 (d, *J* = 40.7 Hz), -186.78.

HRMS (ESI) m/z calcd for $[C_{26}H_{29}BrF_7N_3NaO_2]^+$($[M+Na]^+$): 650.1224, found: 650.1223.

IR (KBr, v/cm^{-1}): 2110, 1708, 1224, 1163.

Methyl 2-(3-azido-3-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ab)



4ab

Following the general procedure, **4ab** was obtained as a liquid (75 mg, 57% yield).

[1]H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.44 (m, 2H), 7.14 – 7.02 (m, 2H), 3.75 (s, 3H), 3.63 – 3.38 (m, 2H), 3.09 – 2.91 (m, 2H), 2.74 – 2.59 (m, 2H).

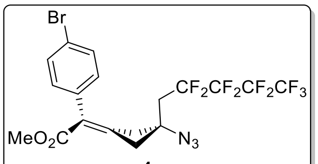
[13]C NMR (101 MHz, Chloroform-*d*) δ 166.0, 149.8, 133.3, 131.6, 130.7, 128.3, 122.1, 58.9, 52.0, 46.9, 44.4, 36.2. *(NOTE: The signals for carbons corresponding to* $C(CF_3)_2CF_2CF_2CF_3$ *are not shown in the spectrum).*

[19]F NMR (376 MHz, Chloroform-*d*) δ -61.97, -79.93 (d, *J* = 18.2 Hz), -105.78 – -106.16 (m), -122.41.

HRMS (ESI) m/z calcd for $[C_{20}H_{14}BrF_{13}NO_2]^+$($[M-N_2+H]^+$): 625.9995, found: 626.0001.

IR (KBr, v/cm^{-1}): 2112, 1715, 1253, 1218, 773.

Methyl 2-(3-azido-3-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ac)



4ac

Following the general procedure, **4ac** was obtained as a liquid (67 mg, 60% yield).

[1]H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 2H), 7.14 – 7.03 (m, 2H), 3.76 (s, 3H), 3.62 – 3.46 (m, 2H), 3.21 – 2.90 (m, 2H), 2.66 – 2.41 (m, 2H).

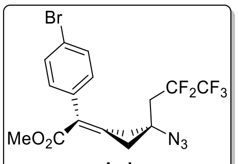
[13]C NMR (101 MHz, Chloroform-*d*) δ 165.9, 150.1, 133.3, 131.5, 130.7, 128.4, 122.0, 57.6, 52.0, 46.0, 43.7, 37.6 (t, *J* = 20.8 Hz). *(NOTE: The signals for carbons corresponding to* $CF_2CF_2CF_2CF_3$ *are not shown in the spectrum).*

[19]F NMR (376 MHz, Chloroform-*d*) δ -80.90, -112.98 (d, *J* = 17.8 Hz), -124.46, -125.61 – -125.88 (m).

HRMS (ESI) m/z calcd for $[C_{18}H_{14}BrF_9NO_2]^+$($[M-N_2+H]^+$): 526.0059, found: 526.0059.

IR (KBr, v/cm^{-1}): 2110, 1715, 1221, 1134, 1011.

Methyl 2-(3-azido-3-(2,2,3,3,3-pentafluoropropyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ad)



4ad

Following the general procedure, **4ad** was obtained as a liquid (56 mg, 61% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.13 – 7.02 (m, 2H), 3.75 (s, 3H), 3.62 – 3.46 (m, 2H), 3.16 – 2.91 (m, 2H), 2.58 – 2.37 (m, 2H).

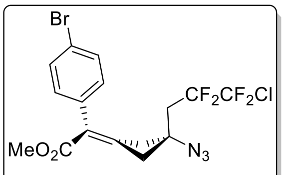
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 150.0, 133.3, 131.5, 130.7, 128.4, 122.0, 57.5, 52.0, 45.9, 43.7, 37.6 (t, *J* = 20.7 Hz). *(NOTE: The signals for carbons corresponding to CF_2CF_3 are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -86.10, -116.86 (d, *J* = 17.8 Hz).

HRMS (ESI) m/z calcd for $[C_{16}H_{14}BrF_5NO_2]^+$($[M-N_2+H]^+$): 426.0123, found: 426.0120.

IR (KBr, v/cm^{-1}): 2108, 1715, 1333, 1199, 1011.

Methyl 2-(3-azido-3-(3-chloro-2,2,3,3-tetrafluoropropyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ae)



4ae

Following the general procedure, **4ae** was obtained as a liquid (58 mg, 55% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.45 (m, 2H), 7.14 – 7.05 (m, 2H), 3.75 (s, 3H), 3.61 – 3.46 (m, 2H), 3.18 – 2.93 (m, 2H), 2.60 – 2.44 (m, 2H).

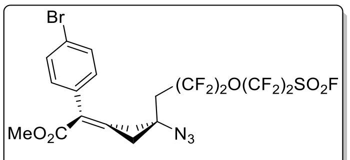
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 150.3, 133.4, 131.6, 130.8, 128.5, 122.1, 57.8, 52.0, 46.0, 43.8, 37.6 (t, *J* = 21.1 Hz). *(NOTE: The signals for carbons corresponding to CF_2CF_2Cl are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.17 (d, *J* = 2.6 Hz), -112.72 (d, *J* = 11.7 Hz).

HRMS (ESI) m/z calcd for $[C_{16}H_{14}BrClF_4NO_2]^+$($[M-N_2+H]^+$): 441.9827, found: 441.9823.

IR (KBr, v/cm^{-1}): 2106, 1714, 1217, 1150, 1095, 1010, 772.

Methyl 2-(3-azido-3-(2,2,3,3-tetrafluoro-3-(1,1,2,2-tetrafluoro-2-(fluorosulfonyl)ethoxy)propyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4af)



4af

Following the general procedure, **4af** was obtained as a liquid (75 mg, 59% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.45 (m, 2H), 7.15 – 7.00 (m, 2H), 3.75 (s, 3H), 3.61 – 3.45 (m, 2H), 3.17 – 2.91 (m, 2H), 2.56 – 2.35 (m, 2H).

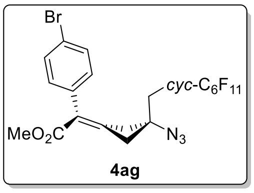
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 149.9, 133.4, 131.6, 130.8, 128.5, 122.1, 57.5, 52.0, 46.0, 43.8, 37.3 (t, J = 20.5 Hz). *(NOTE: The signals for carbons corresponding to $(CF_2)_2O(CF_2)_2SO_2F$ are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ 45.51, -82.10 (d, J = 17.1 Hz), -88.37 (d, J = 12.2 Hz), -112.09, -116.75 (t, J = 20.8 Hz).

HRMS (ESI) m/z calcd for $[C_{18}H_{14}BrF_9NO_5S]^+$($[M-N_2+H]^+$): 605.9627, found: 605.9633.

IR (KBr, v/cm^{-1}): 2108, 1715, 1461, 1208, 1011, 824.

Methyl 2-(3-azido-3-((perfluorocyclohexyl)methyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ag)



Following the general procedure, **4ag** was obtained as a liquid (72 mg, 58% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.45 (m, 2H), 7.12 – 7.02 (m, 2H), 3.75 (s, 3H), 3.61 – 3.44 (m, 2H), 3.14 – 2.90 (m, 2H), 2.71 – 2.48 (m, 2H).

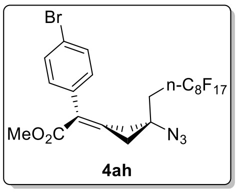
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 149.8, 133.4, 131.6, 130.8, 128.6, 122.1, 58.1, 58.1, 52.1, 46.4, 43.9, 33.3 (d, J = 19.8 Hz). *(NOTE: The signals for carbons corresponding to cyc-C_6F_{11} are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.47 (d, J = 297.0 Hz), -122.90 (dd, J = 553.6, 284.9 Hz), -133.35 (dd, J = 298.1, 69.7 Hz), -138.75 (d, J = 284.7 Hz), -141.97 (d, J = 285.9 Hz), -185.79.

HRMS (ESI) m/z calcd for $[C_{20}H_{14}BrF_{11}NO_2]^+$($[M-N_2+H]^+$): 588.0027, found: 588.0024.

IR (KBr, v/cm^{-1}): 2112, 1716, 1224, 1179, 1025, 965.

Methyl 2-(3-azido-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)cyclobutylidene)-2-(4-bromophenyl)acetate (4ah)



Following the general procedure, **4ah** was obtained as a solid (120 mg, 80% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 3.74 (s, 3H), 3.62 – 3.44 (m, 2H), 3.14 – 2.93 (m, 2H), 2.60 – 2.37 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 150.2, 133.4, 131.6, 130.8, 128.5, 122.1, 57.7, 52.0, 46.1, 43.8, 37.8 (t, J = 20.8 Hz). *(NOTE: The signals for carbons corresponding to n-C_8F_{17} are not shown in the spectrum).*

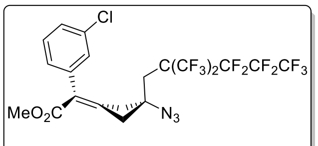
^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.67, -112.73 (d, J = 23.1 Hz), -121.40, -121.82, -122.64, -123.51, -126.05 (d, J = 13.6 Hz).

HRMS (ESI) m/z calcd for $[C_{22}H_{14}BrF_{17}NO_2]^+$($[M-N_2+H]^+$): 725.9931, found: 725.9943.

IR (KBr, v/cm^{-1}): 2110, 1715, 1217, 1150, 773.

Methyl 2-(3-azido-3-(3,3,4,4,5,5,5-heptafluoro-2,2-

bis(trifluoromethyl)pentyl)cyclobutylidene)-2-(3-chlorophenyl)acetate (4bi)



4bi

Following the general procedure, **4bi** was obtained as a liquid (28 mg, 28% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 2H), 7.24 – 7.16 (m, 1H), 7.12 – 7.05 (m, 1H), 3.76 (s, 3H), 3.65 – 3.42 (m, 2H), 3.12 – 2.93 (m, 2H), 2.77 – 2.57 (m, 2H).

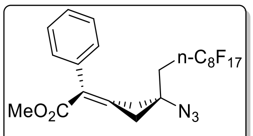
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 150.3, 136.2, 134.2, 129.7, 129.2, 128.2, 128.1, 127.3, 58.9, 52.1, 46.8, 44.5, 36.2. *(NOTE: The signals for carbons corresponding to $C(CF_3)_2CF_2CF_2CF_3$ are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.99, -79.97, -106.01, -122.41.

HRMS (ESI) m/z calcd for $[C_{20}H_{14}ClF_{13}NO_2]^+$($[M-N_2+H]^+$): 582.0500, found: 582.0497.

IR (KBr, v/cm^{-1}): 2112, 1716, 1218, 913, 772.

Methyl 2-(3-azido-3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)cyclobutylidene)-2-phenylacetate (4dj)



4dj

Following the general procedure, **4dj** was obtained as a liquid (71 mg, 52% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.29 (m, 3H), 7.24 – 7.14 (m, 2H), 3.75 (s, 3H), 3.63 – 3.48 (m, 2H), 3.19 – 2.96 (m, 2H), 2.63 – 2.41 (m, 2H).

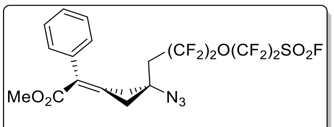
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 149.2, 134.5, 129.4, 129.0, 128.3, 127.8, 57.6, 51.8, 46.0, 43.7, 37.7 (t, J = 20.9 Hz). *(NOTE: The signals for carbons corresponding to n-C_8F_{17} are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.80 (t, J = 10.0 Hz), -112.87 (d, J = 9.2 Hz), -121.51, -121.94, -122.77, -123.66, 126.15.

HRMS (ESI) m/z calcd for $[C_{22}H_{15}F_{17}NO_2]^+$($[M-N_2+H]^+$): 648.0826, found: 648.0822.

IR (KBr, v/cm^{-1}): 2110, 1714, 1219, 1150, 773.

Methyl 2-(3-azido-3-(2,2,3,3-tetrafluoro-3-(1,1,2,2-tetrafluoro-2-(fluorosulfonyl)ethoxy)propyl)cyclobutylidene)-2-phenylacetate (4dk)



4dk

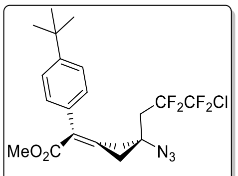
Following the general procedure, **4dk** was obtained as a liquid (55 mg, 49% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 3H), 7.24 – 7.16 (m, 2H), 3.75 (s, 3H), 3.62 – 3.47 (m, 2H), 3.18 – 2.93 (m, 2H), 2.55 – 2.36 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.5, 149.1, 134.5, 129.5, 129.1, 128.4, 127.9, 57.5, 51.9, 45.9,

43.8, 37.4 (t, J = 20.5 Hz). *(NOTE: The signals for carbons corresponding to $(CF_2)_2O(CF_2)_2SO_2F$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ 45.5, -82.1 (d, J = 16.8 Hz), -88.4 (d, J = 23.8 Hz), -112.1, -116.7 (t, J = 20.7 Hz).
HRMS (ESI) m/z calcd for $[C_{18}H_{15}F_9NO_5S]^+$($[M-N_2+H]^+$): 528.0522, found: 528.0521.
IR (KBr, v/cm^{-1}): 2105, 1714, 1461, 1217, 1146, 1111, 773.

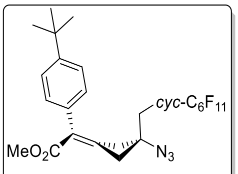
Methyl 2-(3-azido-3-(3-chloro-2,2,3,3-tetrafluoropropyl)cyclobutylidene)-2-(4-(tert-butyl)phenyl)acetate (4cl)



4cl

Following the general procedure, **4cl** was obtained as a liquid (48 mg, 53% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.18 – 7.11 (m, 2H), 3.75 (s, 3H), 3.61 – 3.46 (m, 2H), 3.23 – 2.98 (m, 2H), 2.62 – 2.43 (m, 2H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 150.7, 148.7, 131.5, 129.3, 128.7, 125.3, 57.8, 51.9, 46.0, 43.9, 37.6, 37.7 (t, J = 21.0 Hz), 31.4. *(NOTE: The signals for carbons corresponding to $CF_2CF_2\underline{Cl}$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -72.05, -112.62.
HRMS (ESI) m/z calcd for $[C_{20}H_{23}ClF_4NO_2]^+$($[M-N_2+H]^+$): 420.1348, found: 420.1345.
IR (KBr, v/cm^{-1}): 2107, 1715, 1271, 1218, 1152, 1096.

Methyl 2-(3-azido-3-((perfluorocyclohexyl)methyl)cyclobutylidene)-2-(4-(tert-butyl)phenyl)acetate (4cm)

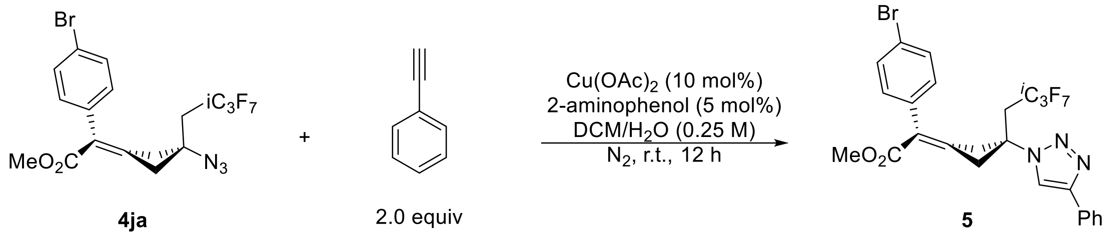


4cm

Following the general procedure, **4cm** was obtained as a liquid (29 mg, 24% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.18 – 7.11 (m, 2H), 3.76 (s, 3H), 3.62 – 3.46 (m, 2H), 3.23 – 2.97 (m, 2H), 2.69 – 2.55 (m, 2H), 1.33 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 150.7, 148.2, 131.4, 129.4, 128.7, 125.3, 58.2, 58.2, 51.9, 46.3, 44.0, 34.7, 33.3 (d, J = 20.1 Hz), 31.4. *(NOTE: The signals for carbons corresponding to cyc-C_6F_{11} are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.5 (d, J = 297.1 Hz), -122.2 (d, J = 283.5 Hz), -123.6 (d, J = 286.1 Hz), -133.3 (dd, J = 298.1, 70.1 Hz), -138.8 (d, J = 285.3 Hz), -142.0 (d, J = 285.8 Hz), -185.8.
HRMS (ESI) m/z calcd for $[C_{24}H_{23}F_{11}NO_2]^+$($[M-N_2+H]^+$): 566.1548, found: 566.1544.
IR (KBr, v/cm^{-1}): 2110, 1715, 1223, 1180, 1026, 965, 774.

Synthetic applications

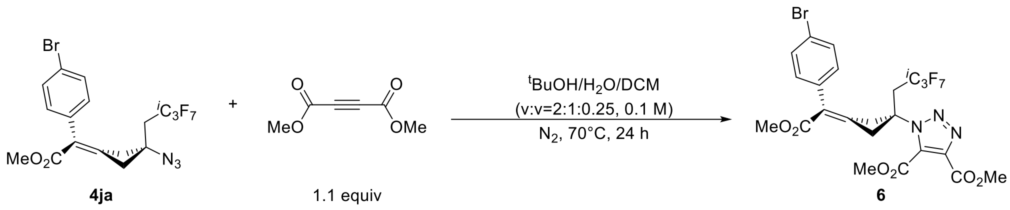
a) Transformation of the azide to triazole 5



In a flame-dried Schlenk tube, $Cu(OAc)_2$ (10 mol%), **4ja** (0.2 mmol, 1.0 equiv), 2-aminophenol (5 mol%), and phenylacetylene (2.0 equiv) were dissolved in a mixture of DCM (0.4 mL) and water (0.4 mL) under the atmosphere of nitrogen. The mixture was stirred at rt for 12 h. After completion, the reaction mixture was extracted with DCM and brine. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product as a colorless oil (120 mg, 99% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 3H), 7.53 – 7.48 (m, 2H), 7.47 – 7.40 (m, 2H), 7.39 – 7.32 (m, 1H), 7.10 – 7.05 (m, 2H), 4.11 – 3.89 (m, 2H), 3.76 (s, 3H), 3.74 – 3.37 (m, 2H), 3.18 – 3.00 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 149.1, 147.6, 132.9, 131.7, 130.7, 130.3, 129.0, 128.9, 128.5, 125.9, 122.3, 118.9, 118.9, 58.4, 58.3, 52.1, 47.4, 45.2, 37.4 (d, J = 18.4 Hz). *(NOTE: The signals for carbons corresponding to $^{i}C_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.88 (d, J = 35.4 Hz), -189.10.
HRMS (ESI) m/z calcd for $[C_{25}H_{20}BrF_7N_3O_2]^+$($[M+H]^+$): 606.0622, found: 606.0624.
IR (KBr, v/cm^{-1}): 1715, 1224, 1164, 1026, 764, 695.

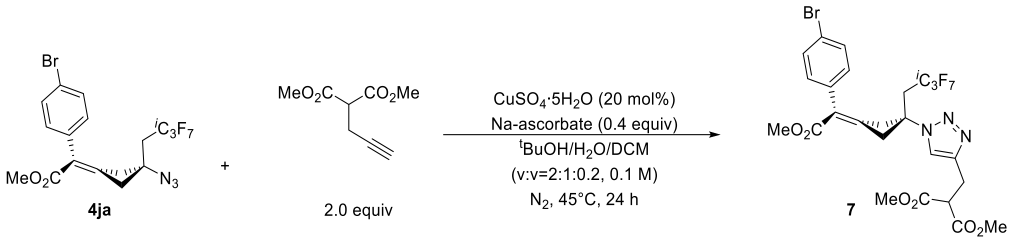
b) Transformation of the azide to triazole 6



In a flame-dried Schlenk tube, a mixture of **4ja** (0.2 mmol, 1.0 equiv) and dimethyl but-2-ynedioate (1.1 equiv) in t-BuOH/H_2O/DCM (2:1:0.25, v/v, 3.25 mL) was heated at 70 °C for 18 h. The resulting mixture was cooled to rt and extracted with DCM and brine. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the corresponding product as a colorless oil (101 mg, 78% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.44 (m, 2H), 7.07 – 7.01 (m, 2H), 4.13 – 4.04 (m, 1H), 3.99 – 3.94 (m, 6H), 3.94 – 3.84 (m, 2H), 3.72 (s, 3H), 3.39 – 3.20 (m, 2H), 3.12 – 3.01 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 160.4, 159.6, 149.1, 141.3, 132.9, 131.7, 130.7, 130.0, 128.6, 122.3, 60.7, 60.7, 54.0, 53.0, 52.1, 48.0, 44.9, 35.10 (d, J = 18.2 Hz). *(NOTE: The signals for carbons corresponding to $^{i}C_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.93 (m), -190.25 – -190.62 (m).
HRMS (ESI) m/z calcd for $[C_{23}H_{20}BrF_7N_3O_6]^+$($[M+H]^+$): 646.0418, found: 646.0417.
IR (KBr, v/cm^{-1}): 1734, 1221, 773.

c) Transformation of the azide to triazole 7, 8



In a flame-dried Schlenk tube, azide **4ja** (0.2 mmol, 1.0 equiv), $CuSO_4$•$5H_2O$ (20 mol% mmol), sodium ascorbate (0.4 equiv) and dimethyl (prop-2-yn-1-yl) malonate (2.0 equiv) were dissolved in t-BuOH/H_2O/DCM (2:1:0.2, v/v, 3.2 mL) under the atmosphere of nitrogen. The mixture was stirred at 45℃ for 24 h. After completion, the reaction mixture was quenched with H_2O and extracted with DCM. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the corresponding product as a colorless oil (133 mg, 99% yield).

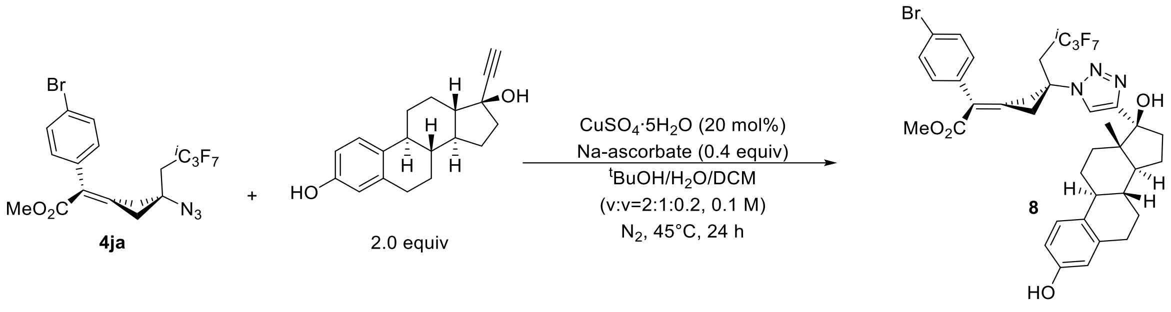
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.41 (m, 3H), 7.08 – 6.98 (m, 2H), 3.99 – 3.79 (m, 3H), 3.74 – 3.71 (m, 3H), 3.69 (d, *J* = 1.3 Hz, 6H), 3.63 – 3.55 (m, 1H), 3.37 – 3.26 (m, 3H), 3.05 – 2.94 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 165.7, 149.0, 143.7, 132.9, 131.5, 130.6, 128.7, 122.2, 121.9, 121.5, 77.3, 58.0, 58.0, 52.7, 52.6, 52.0, 51.4, 47.3, 44.9, 37.3 (d, *J* = 18.5 Hz), 24.9. *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -78.04 – -78.24 (m), -187.15 – -192.61 (m).

HRMS (ESI) m/z calcd for $[C_{25}H_{24}BrF_7N_3O_6]^+$($[M+H]^+$): 674.0731, found: 674.0732.

IR (KBr, v/cm^{-1}): 1753, 1736, 1718, 1224, 1163.



Following the same procedure for compound **7**, compound **8** was prepared from ethinyl estradiol as a colorless oil (153 mg, 96% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 1H), 7.44 – 7.37 (m, 2H), 7.02 – 6.91 (m, 3H), 6.55 – 6.49 (m, 1H), 6.49 – 6.41 (m, 1H), 6.30 (s, 1H), 4.02 – 3.75 (m, 2H), 3.72 – 3.64 (m, 3H), 3.64 – 3.52 (m, 1H), 3.38 – 3.17 (m, 1H), 3.06 – 2.92 (m, 2H), 2.92 – 2.77 (m, 1H), 2.79 – 2.57 (m, 2H), 2.40 – 2.24 (m, 1H), 2.13 – 1.93 (m, 3H), 1.92 – 1.67 (m, 3H), 1.57 – 1.24 (m, 5H), 1.24 – 1.06 (m, 2H), 0.95 (s, 3H), 0.66 – 0.53 (m, 1H).

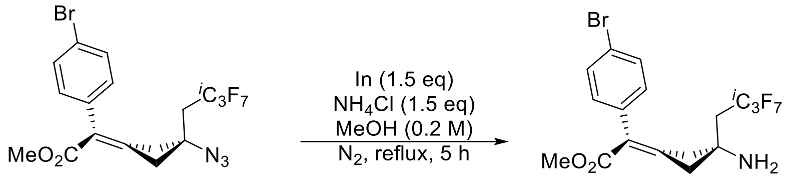
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 165.9, 153.9, 153.3, 149.1, 149.1, 138.2, 132.9, 132.9, 131.7, 130.7, 128.8, 126.4, 122.3, 121.1, 115.5, 112.9, 82.7, 82.6, 58.2, 58.2, 52.2, 47.4, 45.2, 43.3, 39.5, 38.0, 37.9, δ 37.3 (d, J = 18.0 Hz), 32.5, 29.7, 27.3, 26.3, 23.4, 14.3. *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.43 – -78.04 (m), -189.11 (td, J = 15.1, 14.5, 7.1 Hz).

HRMS (ESI) m/z calcd for $[C_{37}H_{38}BrF_7N_3O_4]^+$($[M+H]^+$): 800.1928, found: 800.1927.

IR (KBr, v/cm^{-1}): 1717, 1225, 1164, 1029.

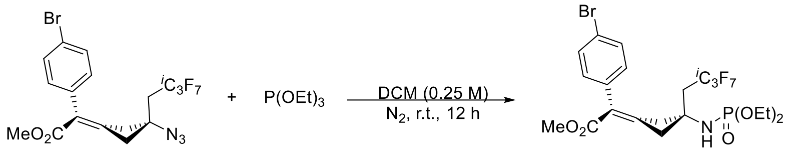
d) Reduction of the azide to amine 9



In a flame-dried Schlenk tube, the mixture of azide **4ja** (0.2 mmol, 1.0 equiv), NH_4Cl (1.5 equiv), and indium powder (1.5 equiv) was refluxed in MeOH (1 mL) for 5 h under the atmosphere of nitrogen. After completion, the mixture was filtered, and the solvent was evaporated. The residue was purified by flash chromatography on Al_2O_3 to afford the corresponding product as a light-yellow oil (32 mg, 34% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 2H), 7.13 – 7.02 (m, 2H), 3.73 (s, 3H), 3.41 – 3.14 (m, 2H), 2.95 – 2.65 (m, 2H), 2.59 – 2.29 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 153.9, 134.0, 131.3, 130.8, 127.7, 121.6, 51.7, 51.4, 51.4, 49.5, 47.2, 47.2, 38.5 (d, J = 18.8 Hz). *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.01 (d, J = 8.1 Hz), -187.92 (td, J = 17.4, 16.3, 8.2 Hz).
HRMS (ESI) m/z calcd for $[C_{17}H_{16}BrF_7NO_2]^+$($[M+H]^+$): 478.0247, found: 478.0266.
IR (KBr, v/cm^{-1}): 1712, 1220, 773.

e) Transformation of the azide to phosphoramide 10



In a flame-dried Schlenk tube, the mixture solution of azide **4ja** (0.2 mmol, 1.0 equiv) and $P(OEt)_3$ (1.5 equiv) in DCM (1 mL) was stirred at rt for 12 h. After completion, the organic solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the corresponding product as colorless oil (108 mg, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 2H), 7.08 – 7.02 (m, 2H), 4.09 – 3.98 (m, 4H), 3.72 (s, 3H), 3.64 – 3.30 (m, 2H), 3.25 – 3.16 (m, 1H), 3.14 – 3.06 (m, 1H), 2.88 – 2.78 (m, 1H), 2.72 – 2.51 (m, 2H), 1.30 – 1.25 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 153.1, 133.7, 131.5, 130.8, 127.4, 121.8, 62.9, 62.8, 51.9, 47.6, 45.4, 37.4 (d, *J* = 18.2 Hz), 29.8, 16.3, 16.2. *(NOTE: The signals for carbons corresponding to $^iC_3F_7$ are not shown in the spectrum).*

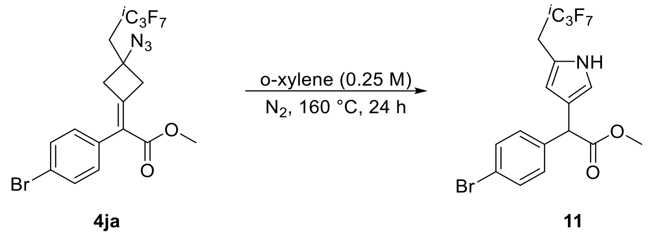
^{19}F NMR (376 MHz, Chloroform-*d*) δ -76.88 (d, *J* = 57.8 Hz), -187.66.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 5.6.

HRMS (ESI) m/z calcd for $[C_{21}H_{25}BrF_7NO_5P]^+$($[M+H]^+$): 614.0537, found: 614.0561.

IR (KBr, v/cm^{-1}): 1716, 1222, 1031, 966.

f) Transformation of the azide to pyrrole 11

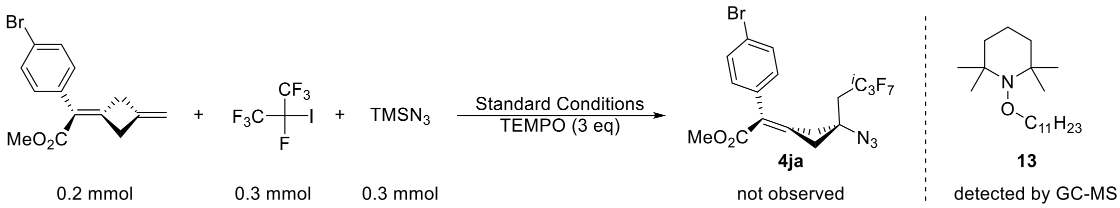


In a flame-dried Schlenk tube, the azide **4ja** (0.2 mmol, 1.0 equiv) was dissolved in o-xylene and stirred at 160 ℃ for 24 h. After completion, the organic solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the corresponding product as colorless oil (74 mg, 78% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.0 (s, 1H), 7.5 – 7.4 (m, 2H), 7.2 – 7.2 (m, 2H), 6.7 – 6.6 (m, 1H), 6.1 – 6.0 (m, 1H), 4.8 (s, 1H), 3.7 (s, 3H), 3.4 (d, J = 22.9 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 138.5, 131.6, 130.2, 121.3, 121.1, 119.9, 117.8, 110.8, 52.4, 49.5, 27.9, 27.7. *(NOTE: The signals for carbons corresponding to $^{i}C_3F_7$ are not shown in the spectrum).*
^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.83 (d, J = 7.3 Hz), -180.74 (dq, J = 22.6, 14.9, 10.7 Hz).
HRMS (ESI) m/z calcd for $[C_{17}H_{14}BrF_7NO_2]^+$($[M+H]^+$): 476.0091, found: 476.0096.
IR (KBr, v/cm^{-1}): 1728, 1225, 1163.

Preliminary mechanism study

Radical trapping experiment with TEMPO



In a flame-dried Schlenk tube, $Fe(OTf)_3$ (5 mol %), LPO (0.2 mmol, 1.0 equiv) and TEMPO (3.0 equiv) were added, then the reaction vessel was degassed and filled with N_2 for 3 times. The reaction was then added with DME (2 mL) stock of alkene (0.2 mmol), $TMSN_3$ (0.3 mmol, 1.5 equiv), and alkyl halide (0.3 mmol, 1.5 equiv). After the reaction completion, the reaction mixture was evaporated under reduced pressure. The solution was filtrated with ethyl acetate on silica gel, and then detected by GC-MS. No desired coupling product was detected, but compound **13** was detected by GC-MS analysis.

Single crystal data of 4dj

X-ray diffractions for single crystals of **4dj** was carried out on XtaLAB Synergy R, Hypix diffractometer equipped with PhotonJet R (Cu) X-ray source (λ = 1.54184 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CrysAlisPro. The structure was solved with the SHELXT and refined with the SHELXL using least-squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. CCDC 2298823 **4dj** contains the supplementary crystallographic data. Crystal data and structure refinements of **4dj** is listed in Table S1. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/

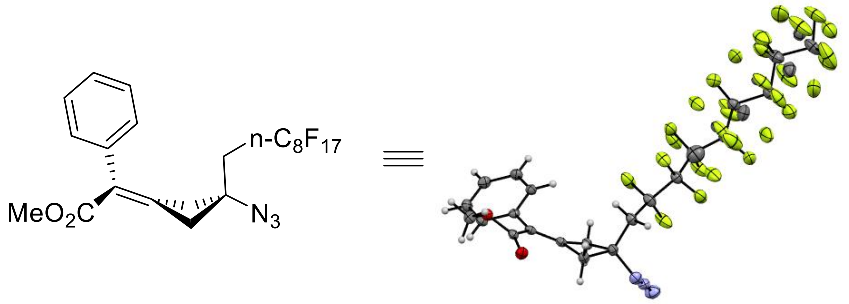


Table S1. Crystal data and structure refinement for **4dj**.

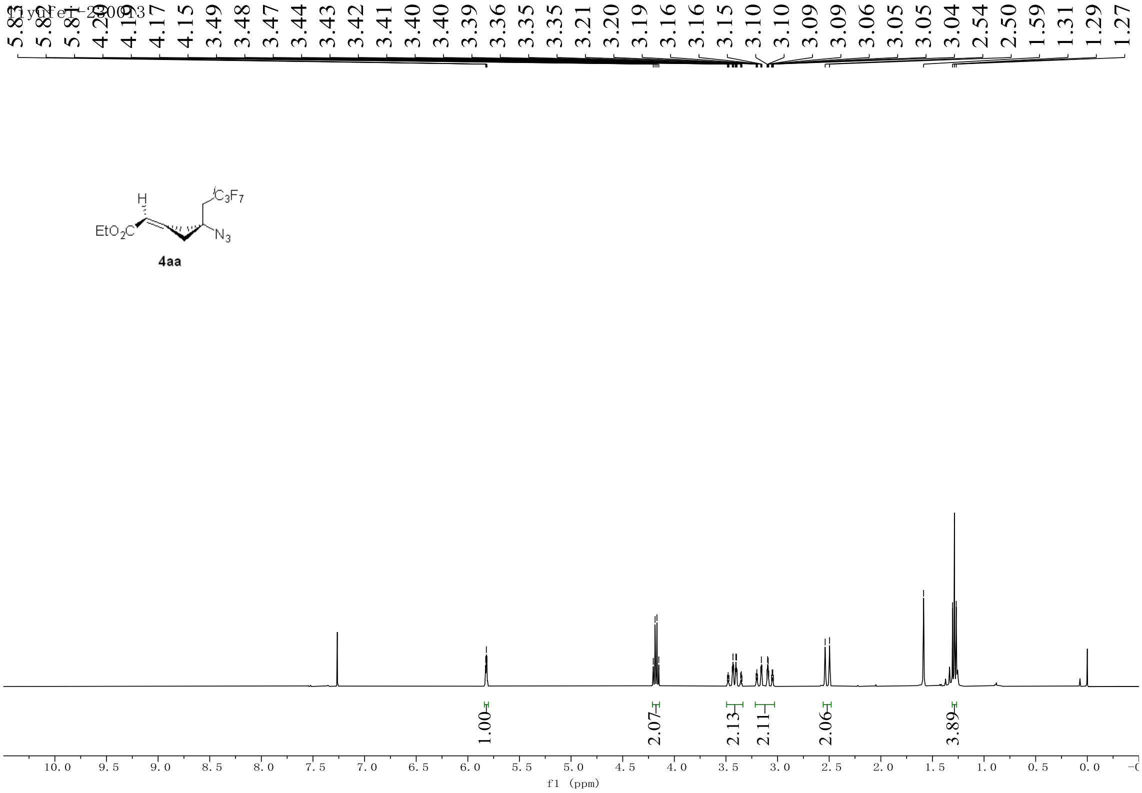
Identification code	Compound-**4dj**	
Empirical formula	$C_{22}H_{14}F_{17}N_3O_2$	
Formula weight	675.36	
Temperature (K)	100(2)	
Wavelength (Å)	1.54184	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions (Å, °)	*a* = 19.5389(4)	α = 90
	b = 6.30440(10)	β = 100.111(2)
	c = 20.8222(4)	γ = 90
Volume (Å)	2525.07(8)	
Z	4	
Calculated density (g cm^{-3})	1.777	
Absorption coefficient (mm^{-1})	1.834	
F_{000}	1344	
Crystal size (mm^3)	0.4 ´ 0.1 ´ 0.05	

θ range for data collection (°)	2.297 to 76.091
Miller index ranges	$-24 \leq h \leq 24$, $-7 \leq k \leq 5$, $-23 \leq l \leq 25$
Reflections collected	22301
Independent reflections	5053 [R_{int} = 0.0364]
Completeness to θ_{max} (%)	0.958
Max. and min. transmission	0.67409 and 1.00000
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5053 / 133 / 569
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0460, $wR2$ = 0.1240
R indices (all data)	$R1$ = 0.0542, $wR2$ = 0.1298
Largest diff. peak and hole (e Å^{-3})	0.598 and -0.312

Reference

1. I. D. Jurberg, H. M. L. Davies, Blue light-promoted photolysis of aryldiazoacetates, *Chem. Sci.* 2018**, 9**, 5112-5118.
2. F. He, R. M. Koenigs, Visible light mediated, metal-free carbene transfer reactions of diazoalkanes with propargylic alcohols, *Chem. Commun.* 2019**, 55**, 4881-4884.
3. R. Cheng, C. Qi, L. Wang, W. Xiong, H. Liu, H. Jiang, Visible light-promoted synthesis of organic carbamates from carbon dioxide under catalyst- and additive-free conditions, *Green Chem.* 2020**, 22**, 4890-4895.
4. J. Hu, X. Yuan, Y. Li, X. Chen, Z. Nie, M.-F. Chiou, Y. Li and H. Bao, Photocatalyzed Dual Strain Release of [1.1.1]Propellane with Diazo Compounds, *ACS Catal.*, 2024, **14**, 5481.

NMR spectra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N3
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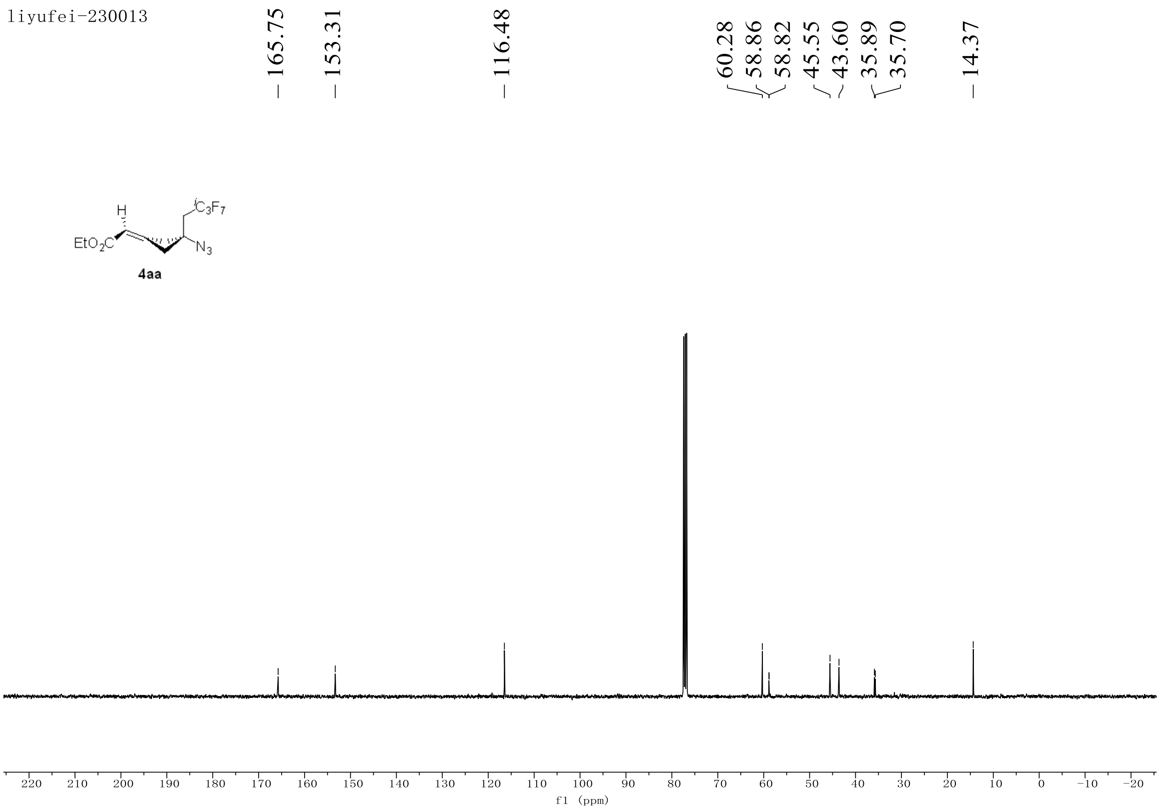
2.13
2.11
2.06
3.89
f1 (ppm)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H
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N3
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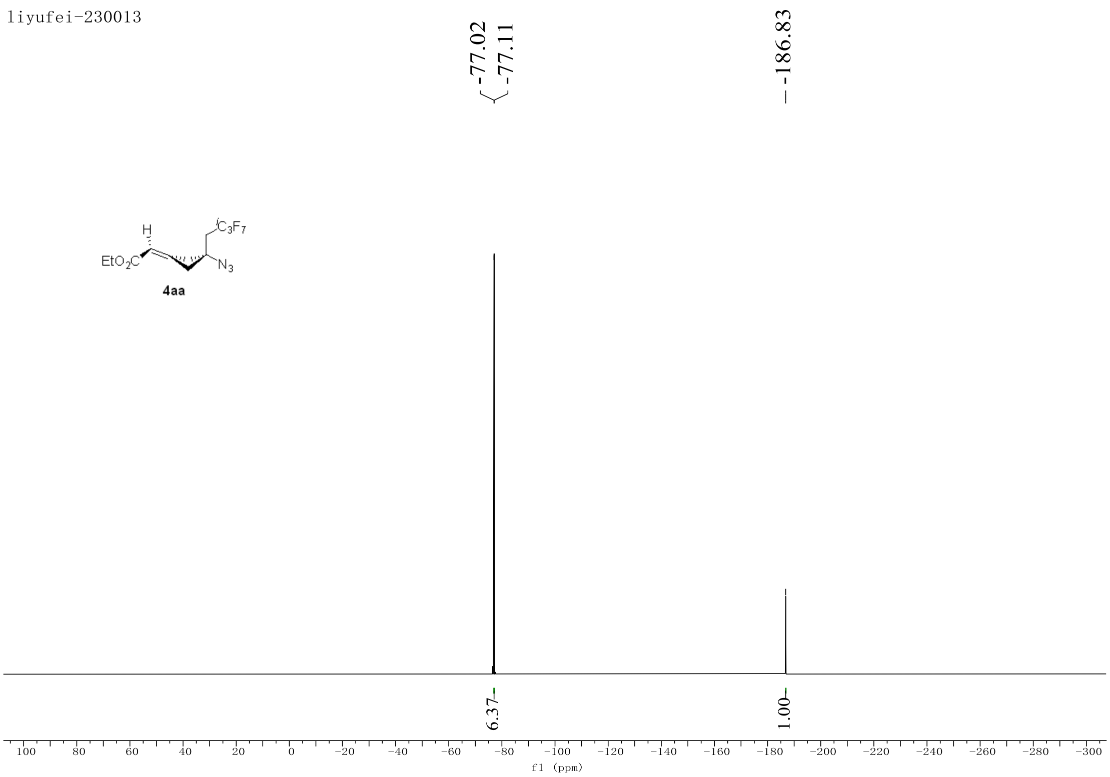
f1 (ppm)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-186.83
EtO_2C
H
$^iC_3F_7$
N_3
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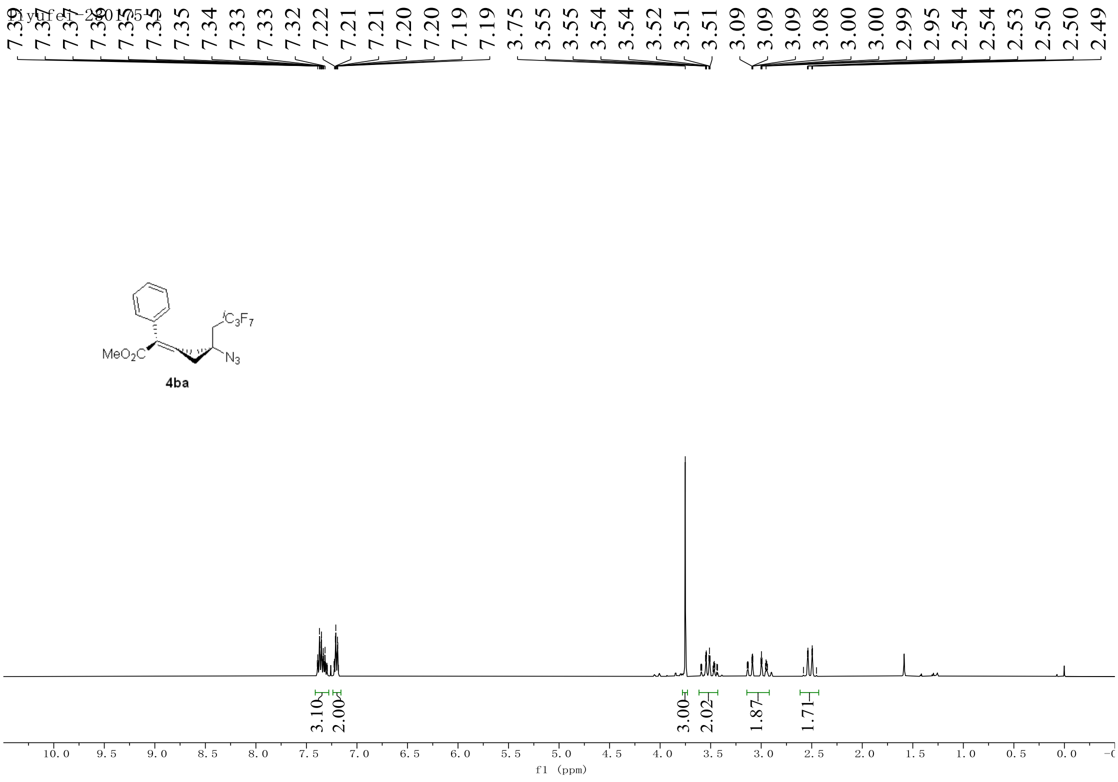
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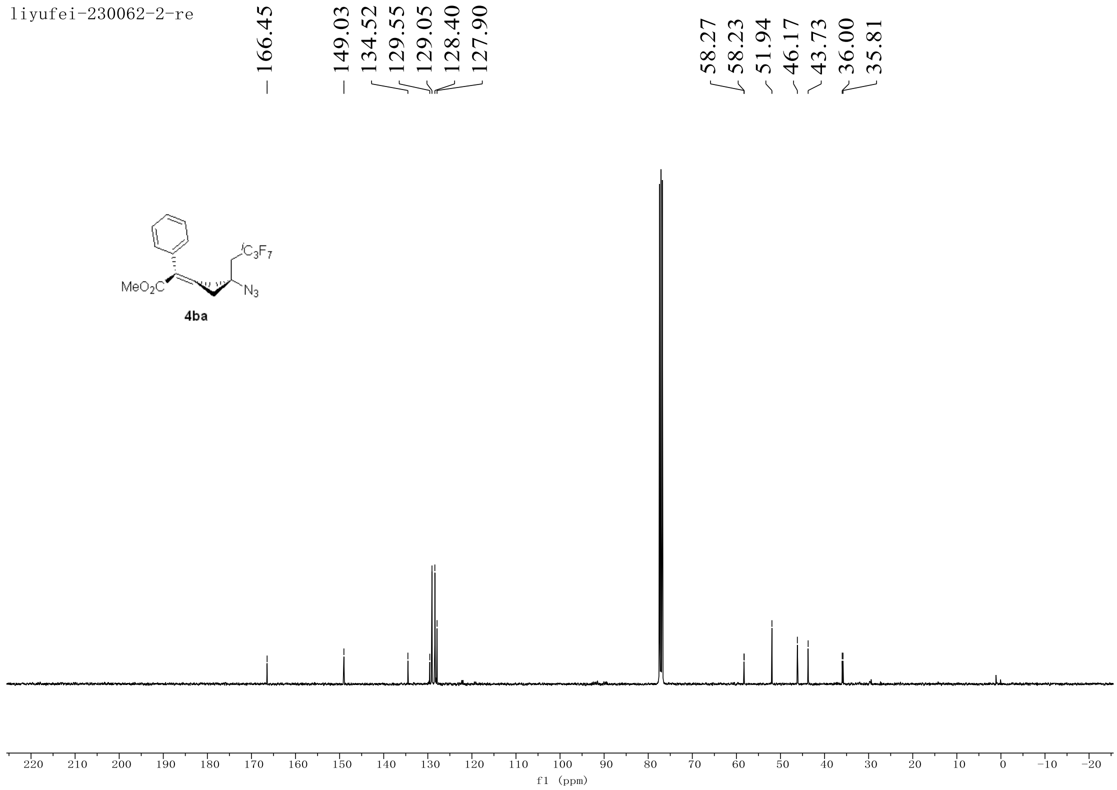
MeO_2C
$^iC_3F_7$
N_3
4ba
3.10
2.00
3.00
2.02
1.87
1.71
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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43.73
36.00
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N3
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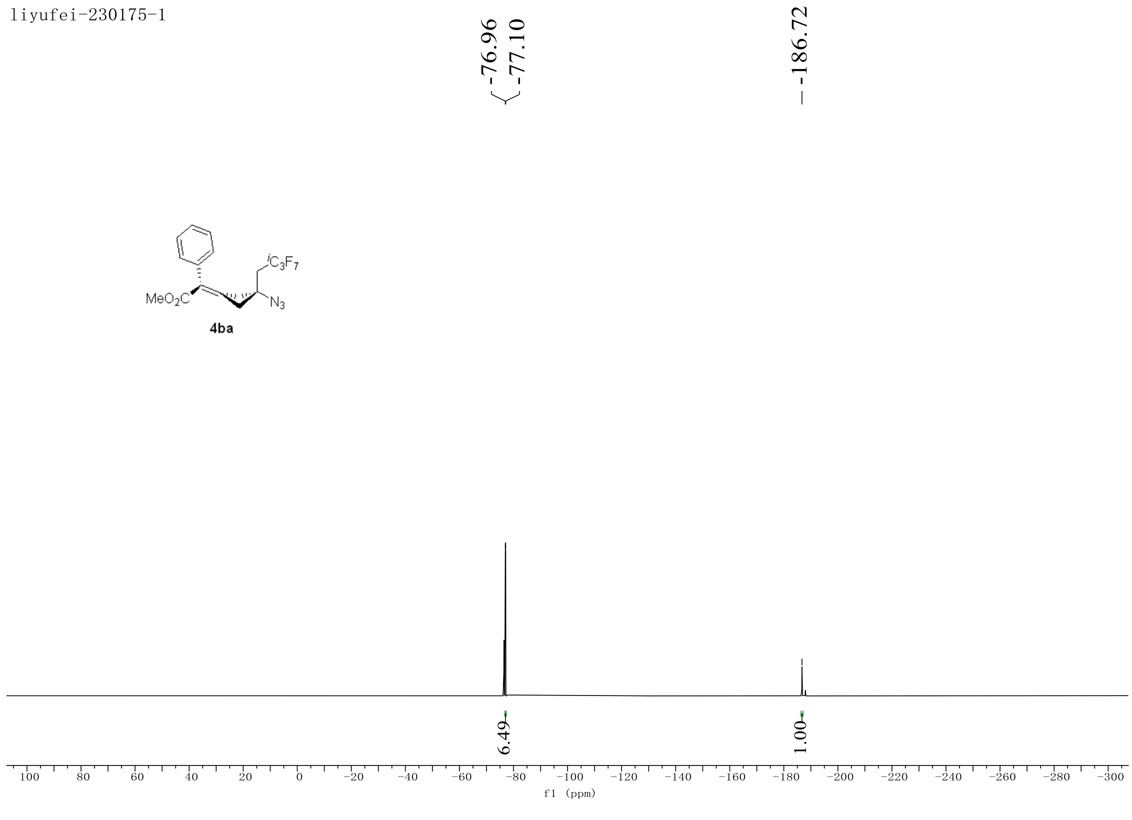
f1 (ppm)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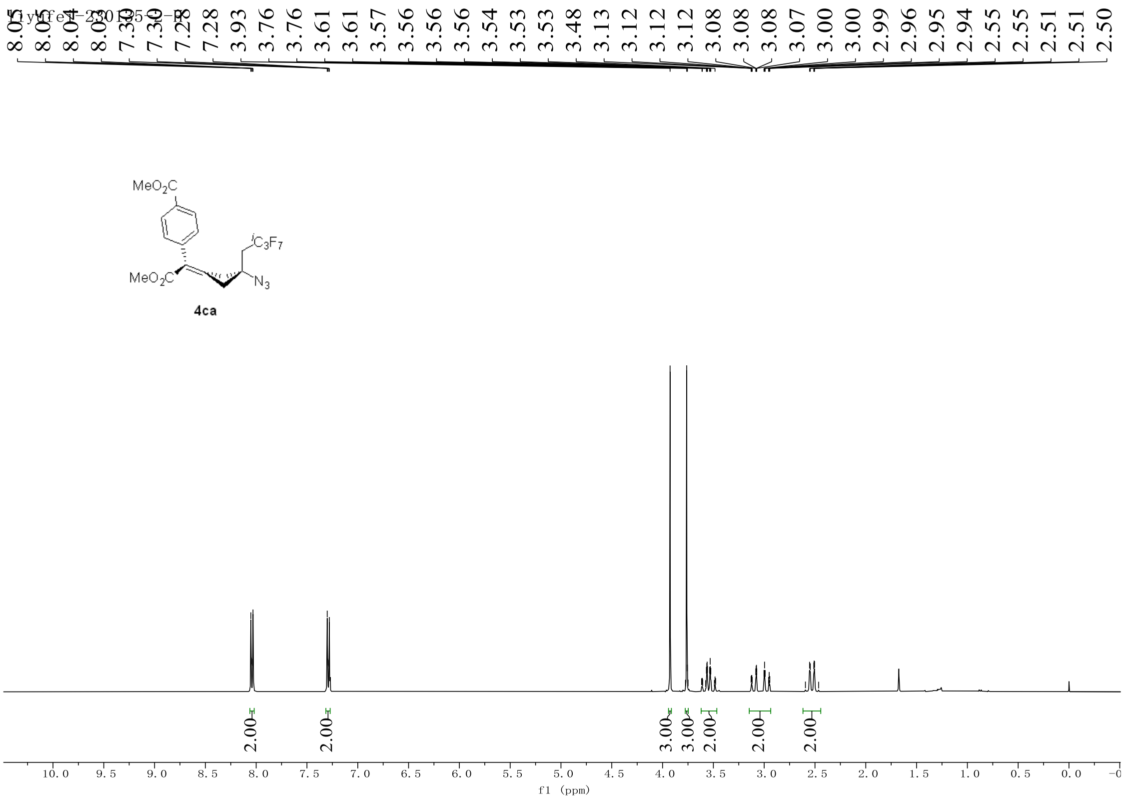
f1 (ppm)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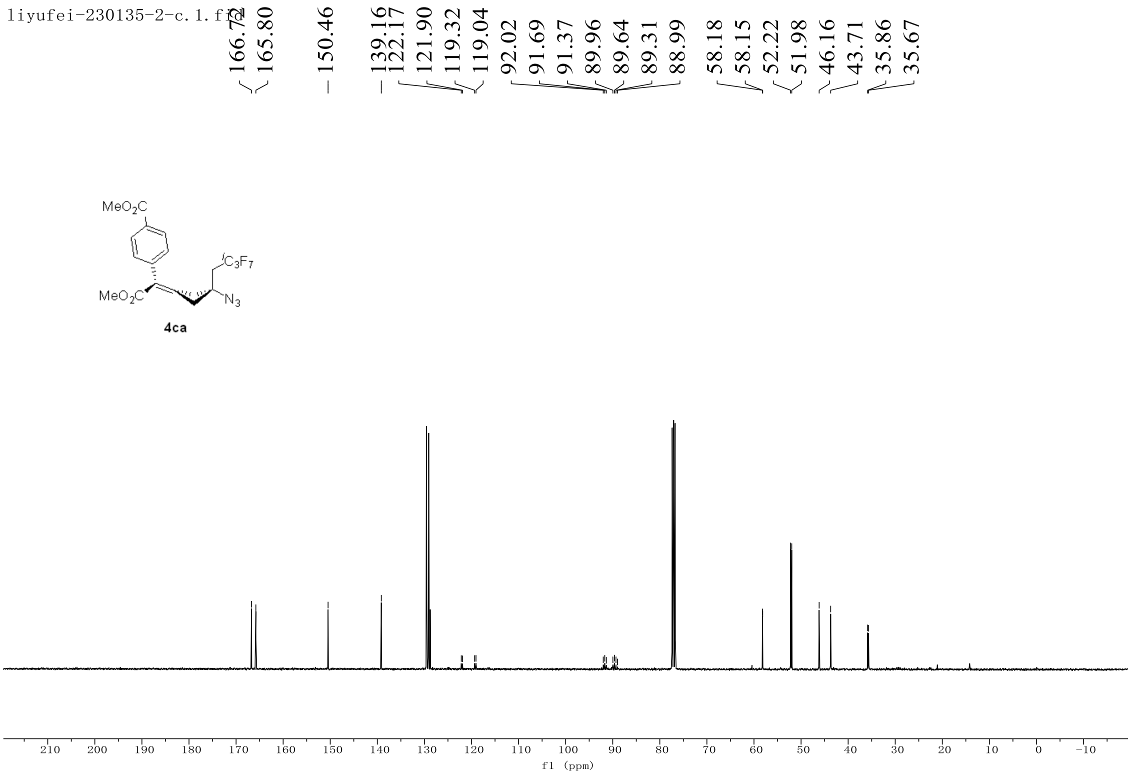
MeO2C
iC3F7
MeO2C
N3
4ca
2.00 2.00 3.00 3.00 2.00 2.00 2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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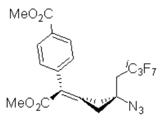
MeO2C
iC3F7
MeO2C
N3
4ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

liyufei-230135-2-HF

-76.99
-77.12
-186.74



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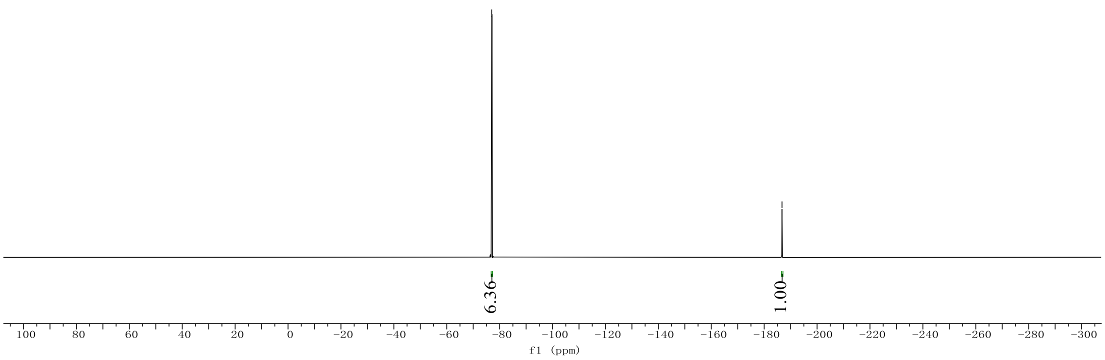

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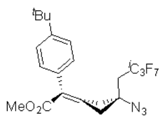

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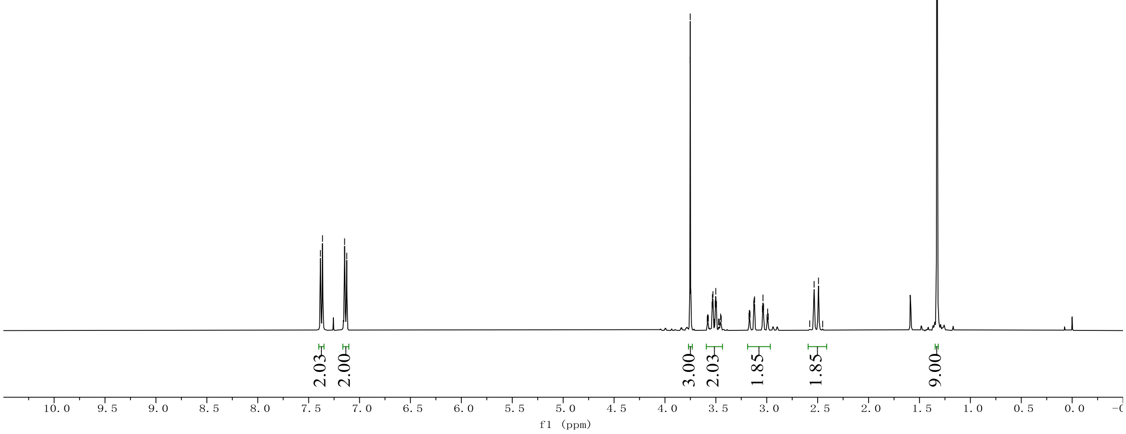

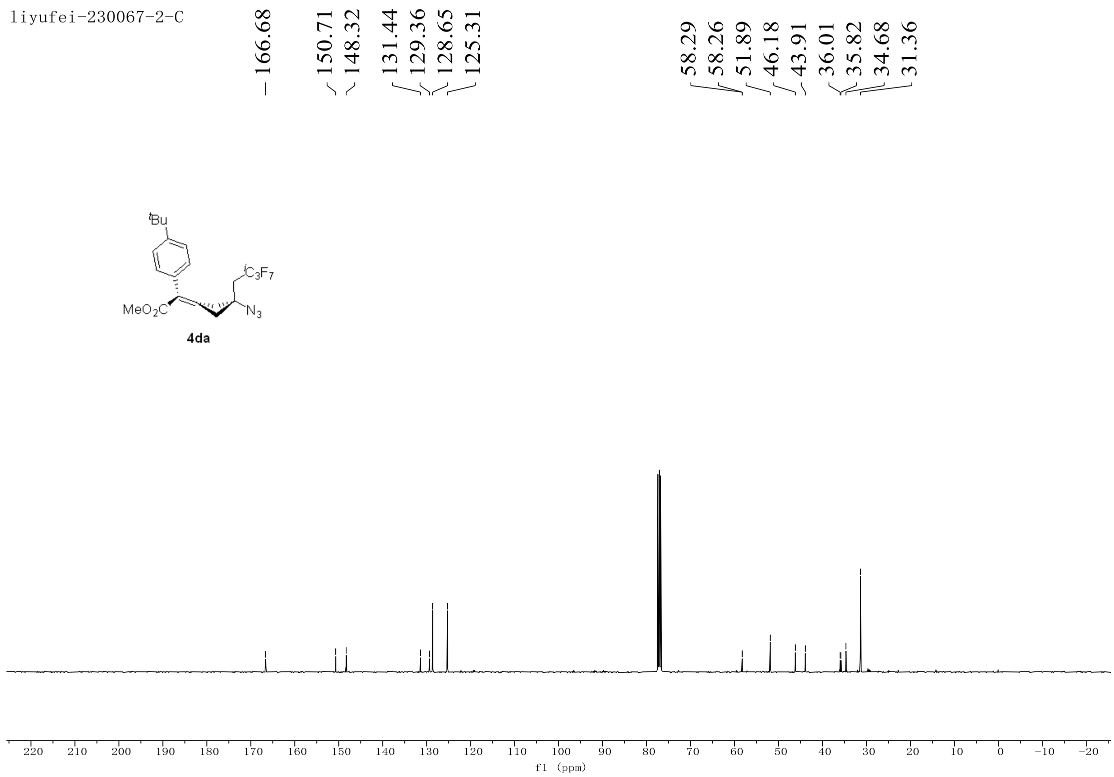
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46.18
43.91
36.01
35.82
34.68
31.36
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C3F7
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N3
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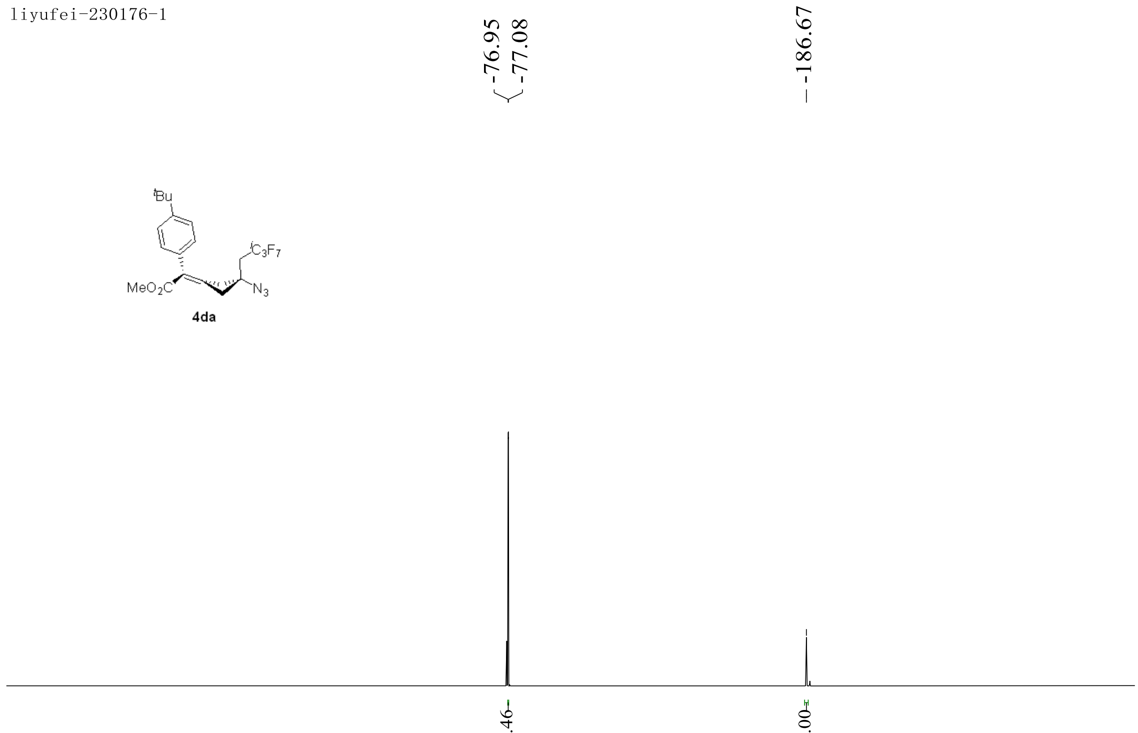
f1 (ppm)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C3F7
MeO2C
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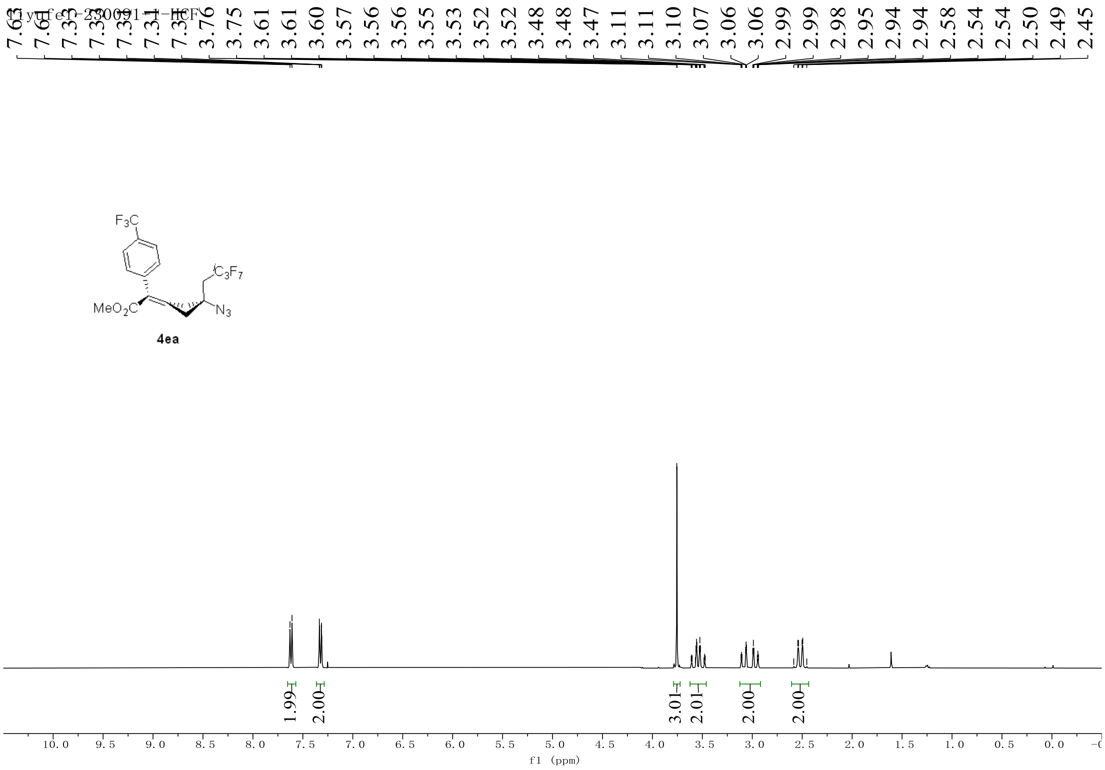
f1 (ppm)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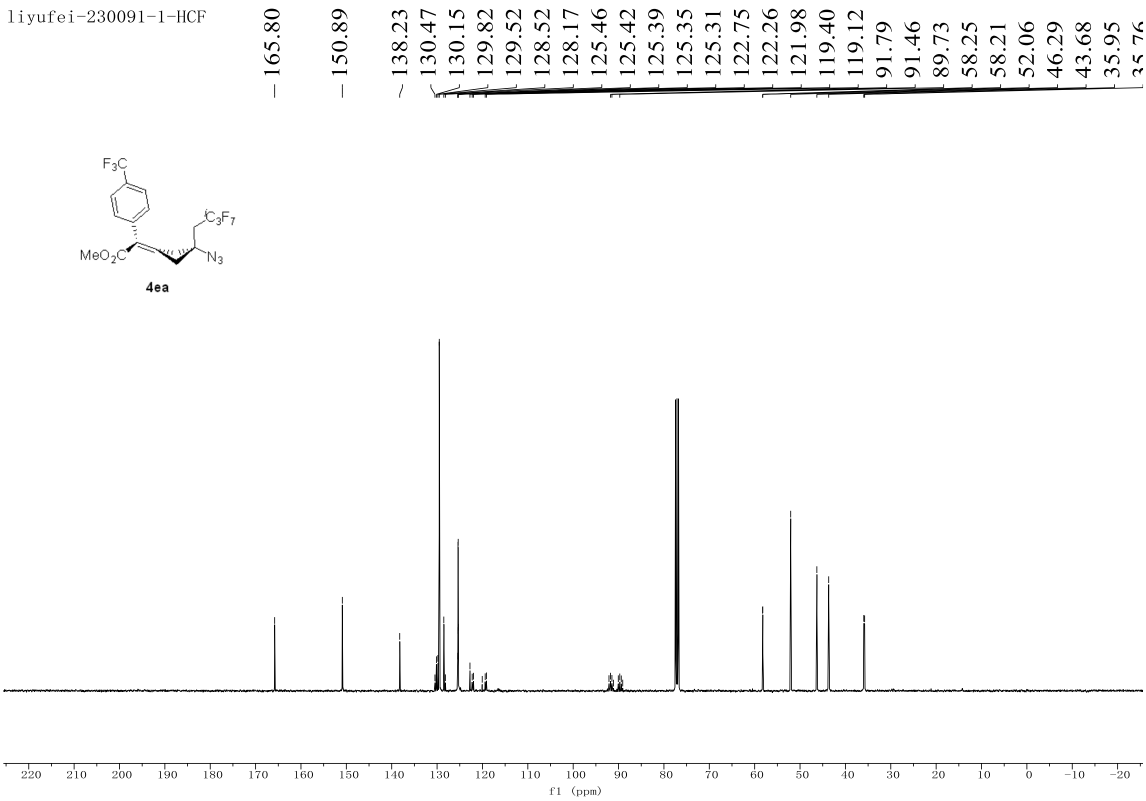
F3C
C3F7
MeO2C
N3
4ea
1.99
2.00
3.01
2.01
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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F3C
C3F7
MeO2C
N3
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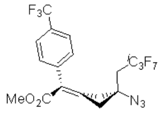
f1 (ppm)

liyufei-230091-1-HCF



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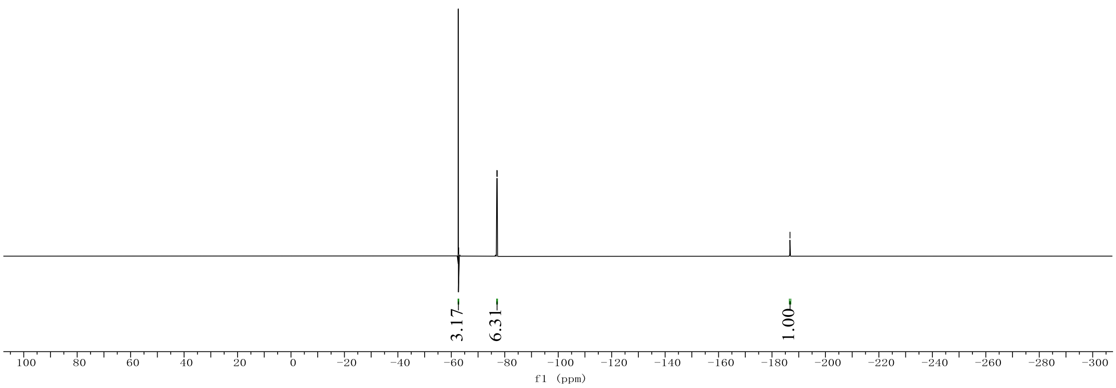

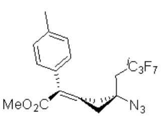

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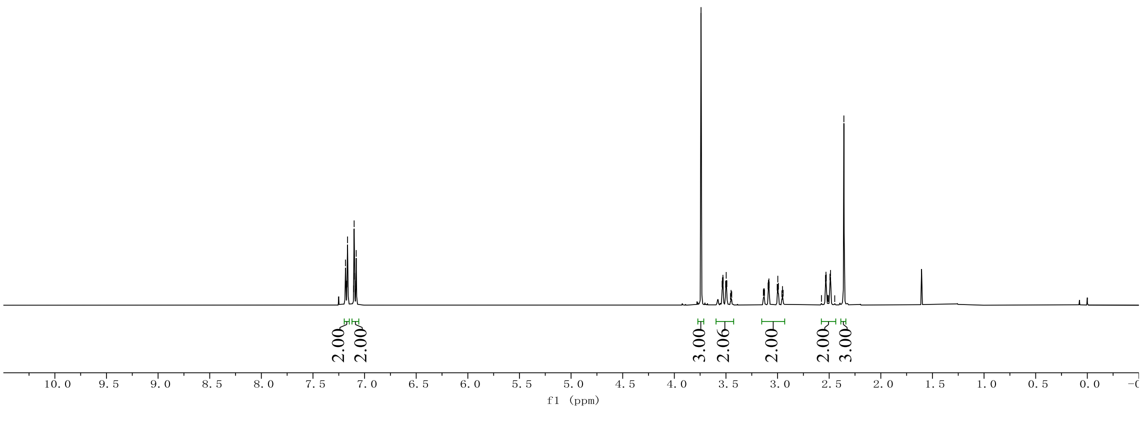

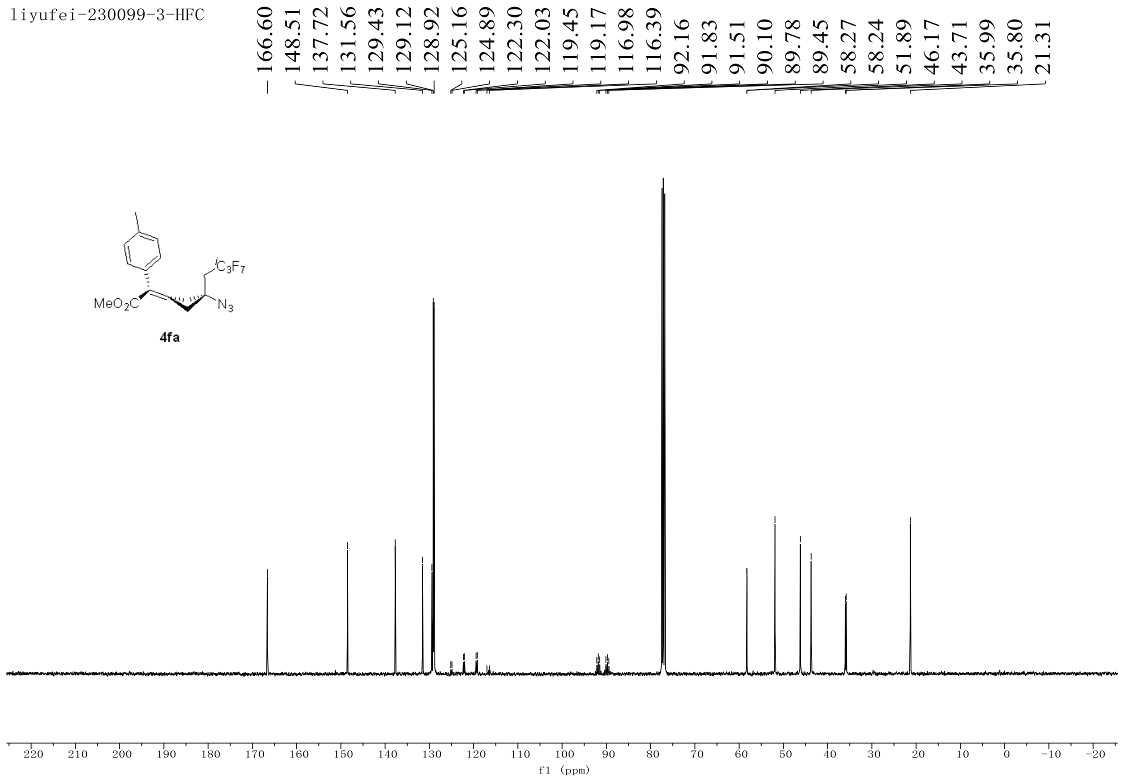
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122.03
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116.98
116.39
92.16
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90.10
89.78
89.45
58.27
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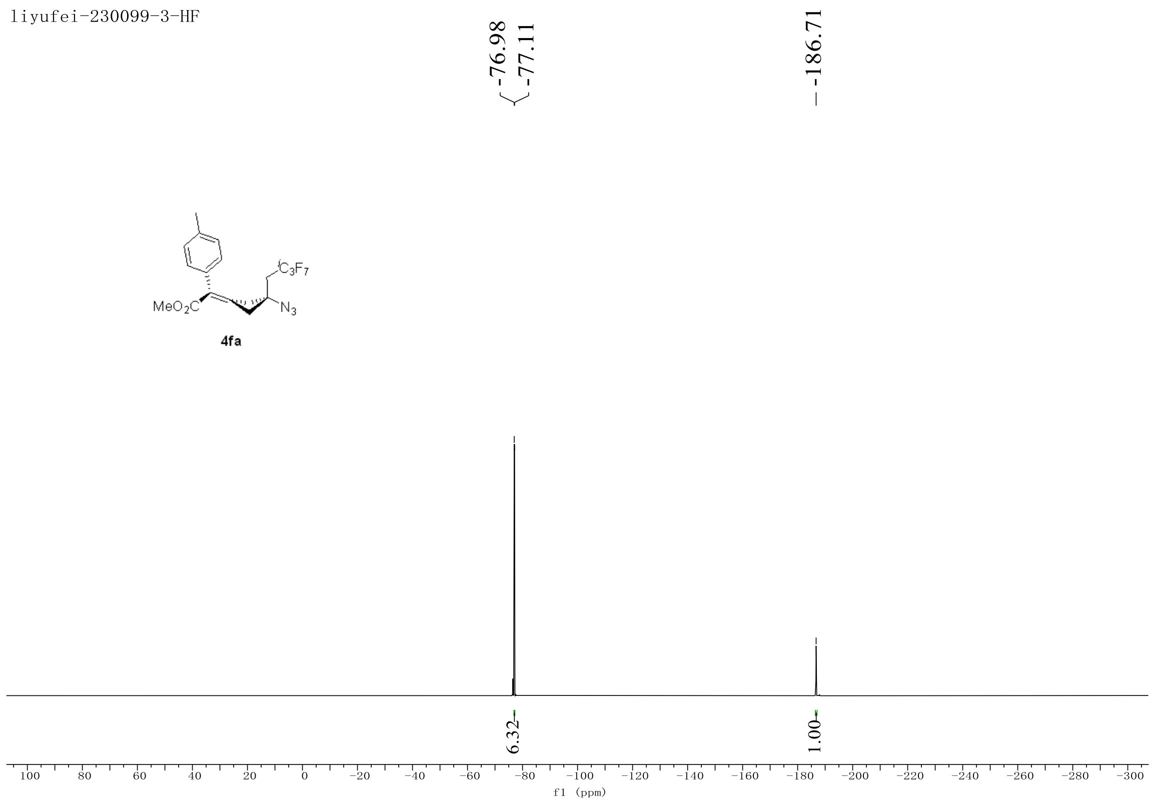
N3
4fa
f1 (ppm)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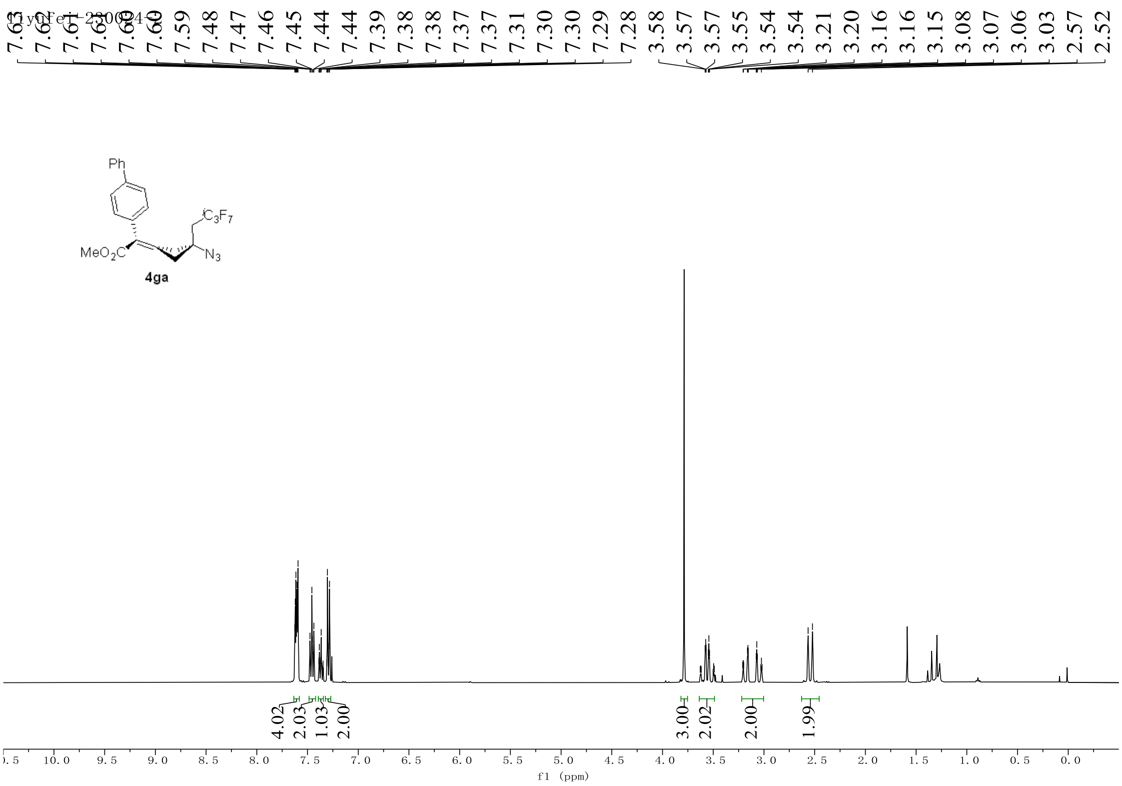
f1 (ppm)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7.30
7.30
7.29
7.28
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3.57
3.57
3.55
3.54
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3.20
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3.16
3.15
3.08
3.07
3.06
3.03
2.57
2.52
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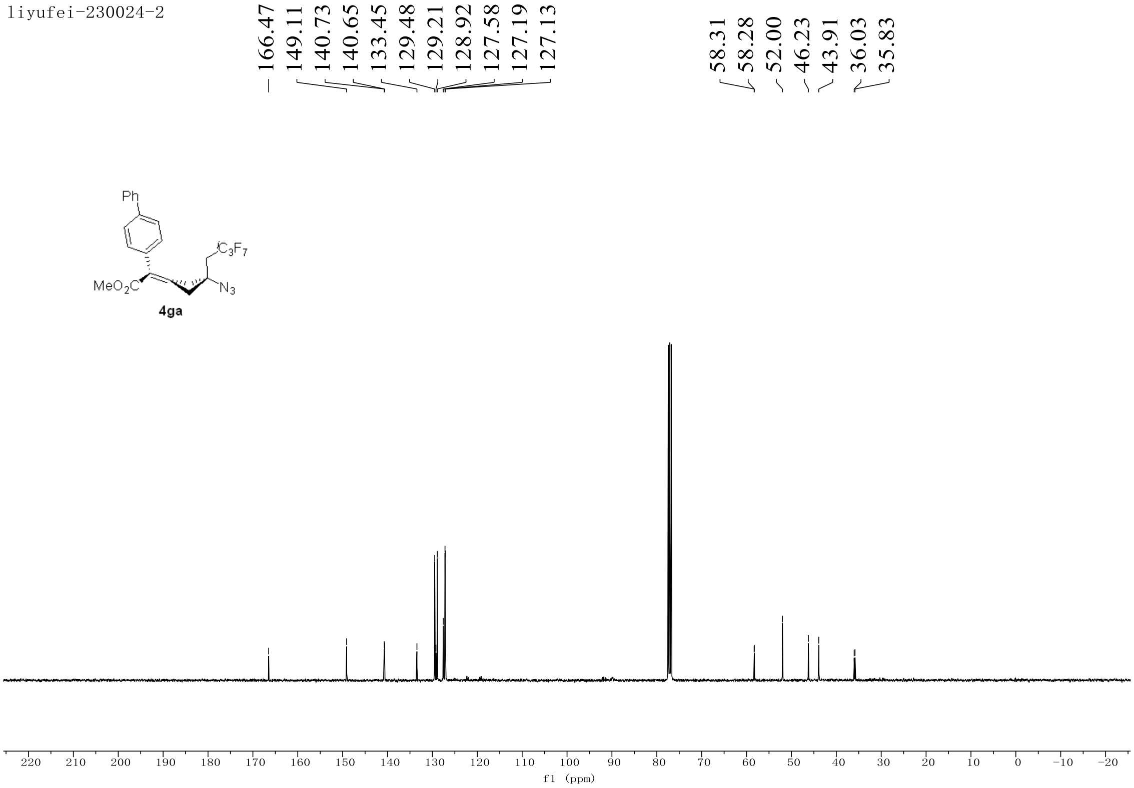
f1 (ppm)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Ph
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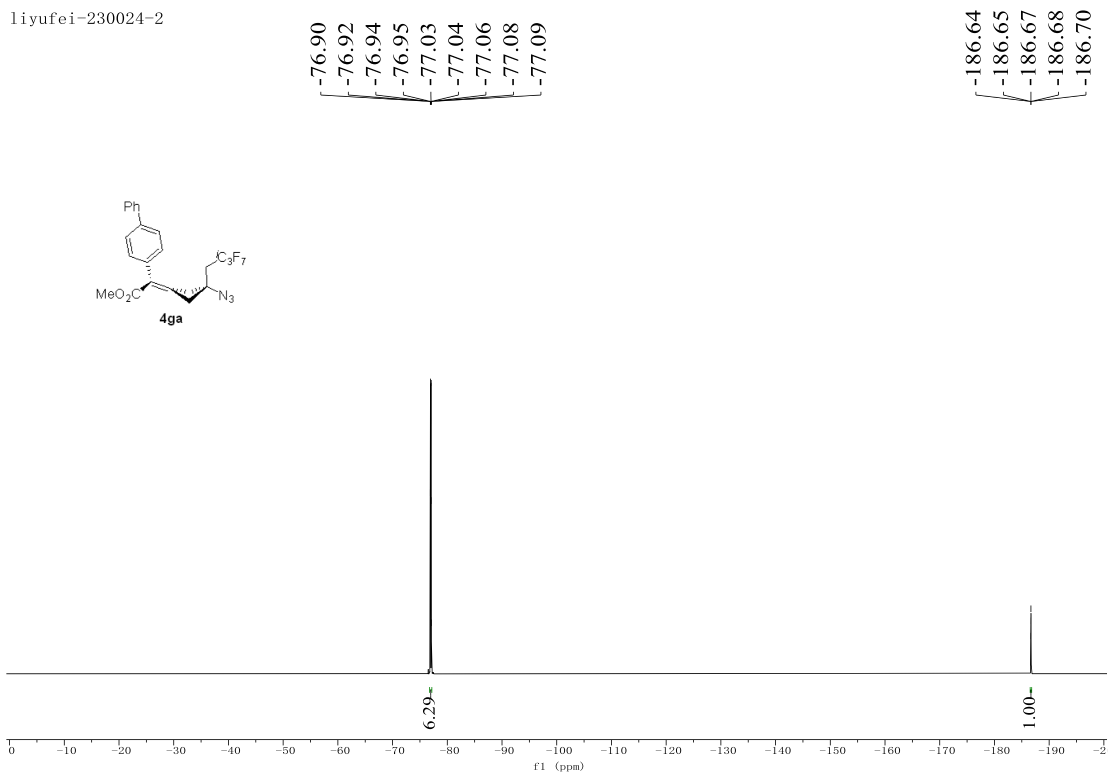
N3
4ga
f1 (ppm)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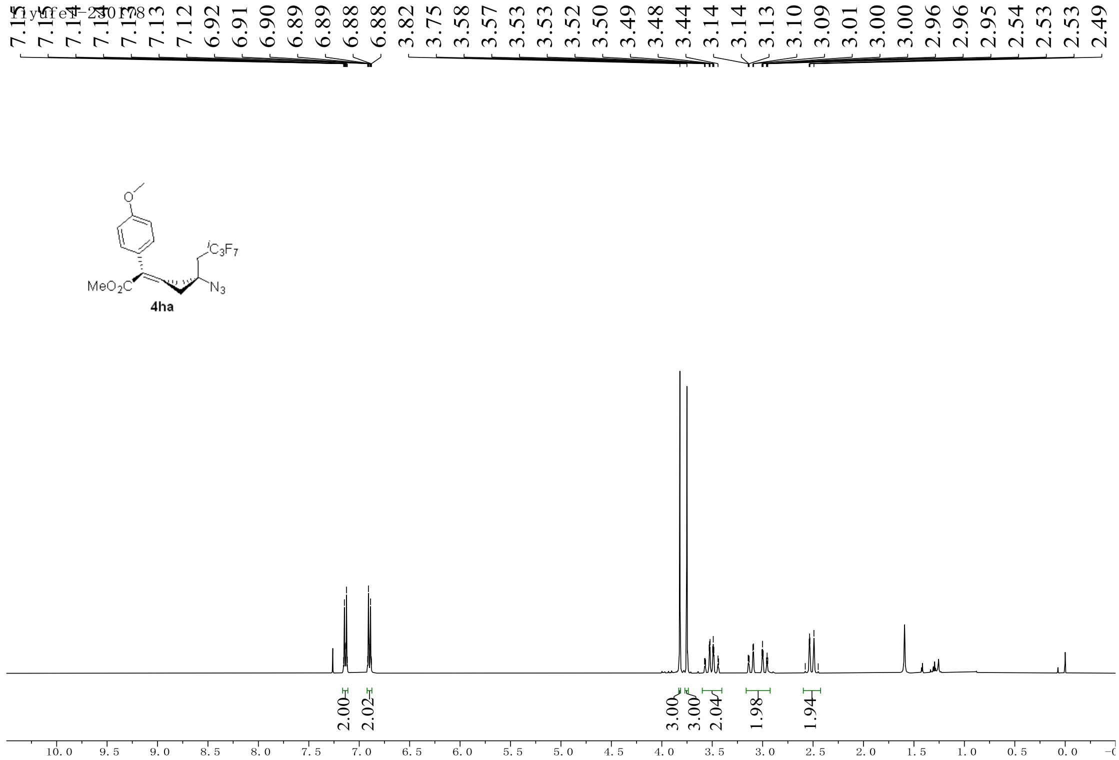
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3.09
3.01
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2.95
2.54
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2.49
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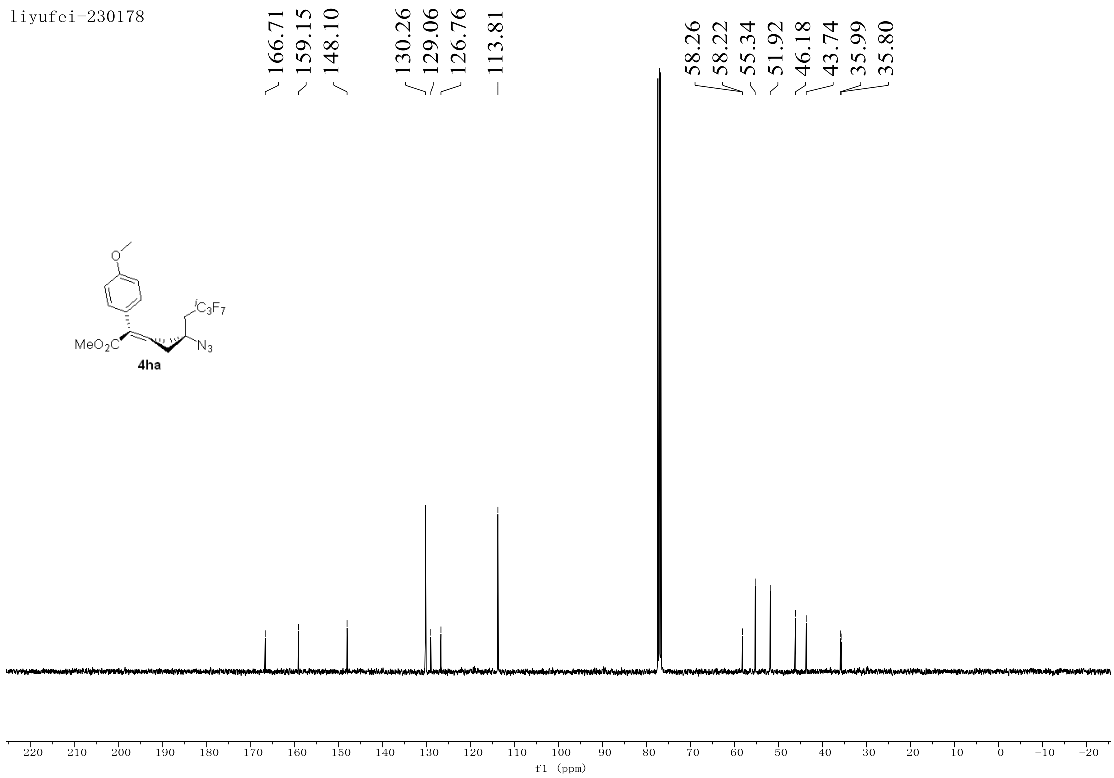
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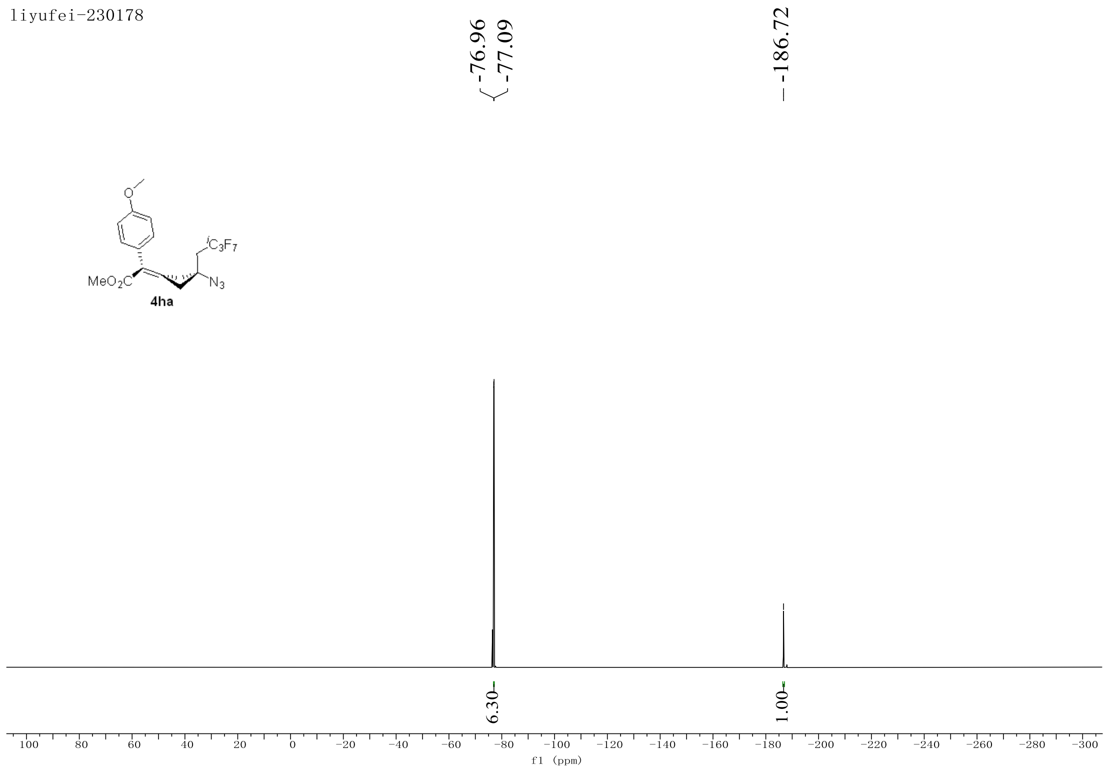
4ha
f1 (ppm)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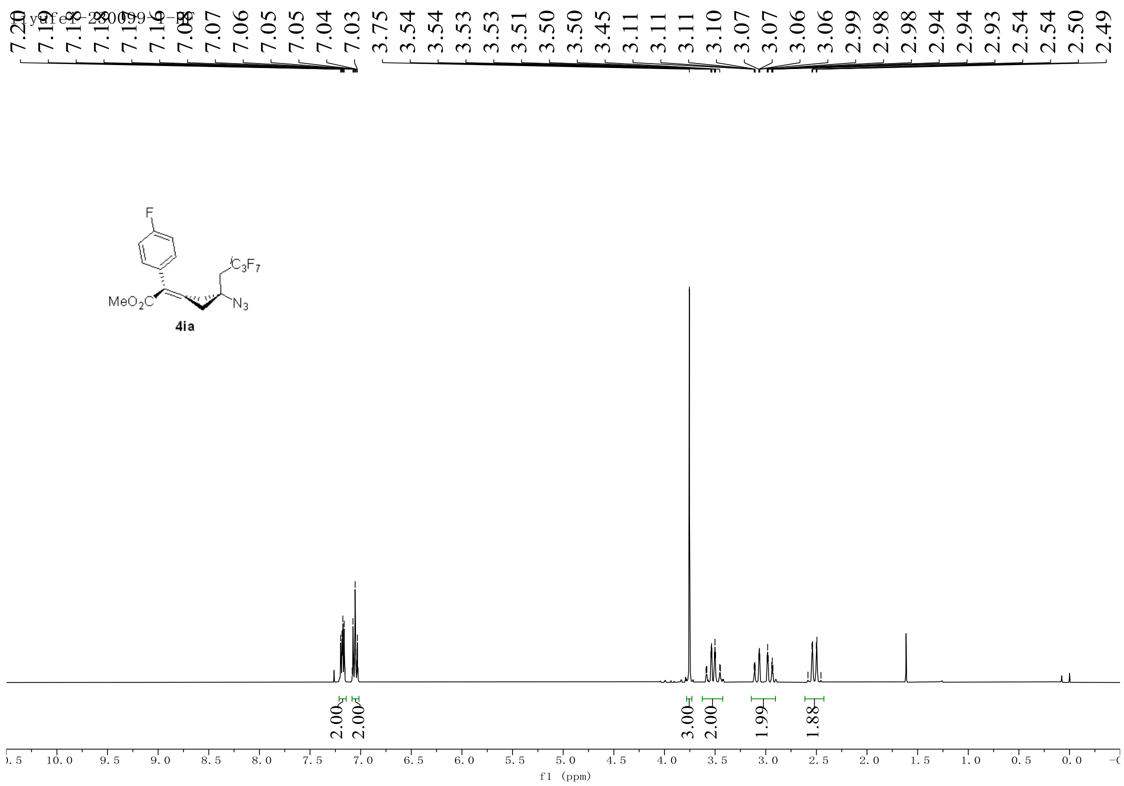
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3.53
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2.98
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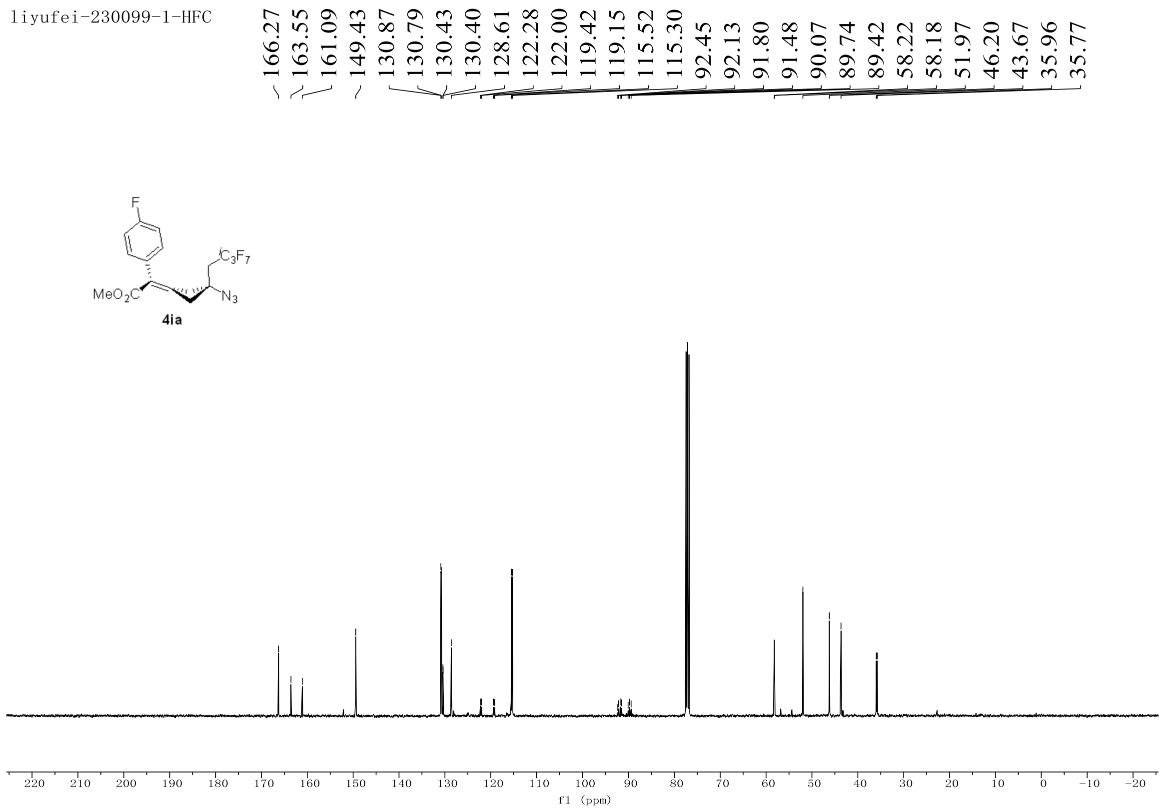
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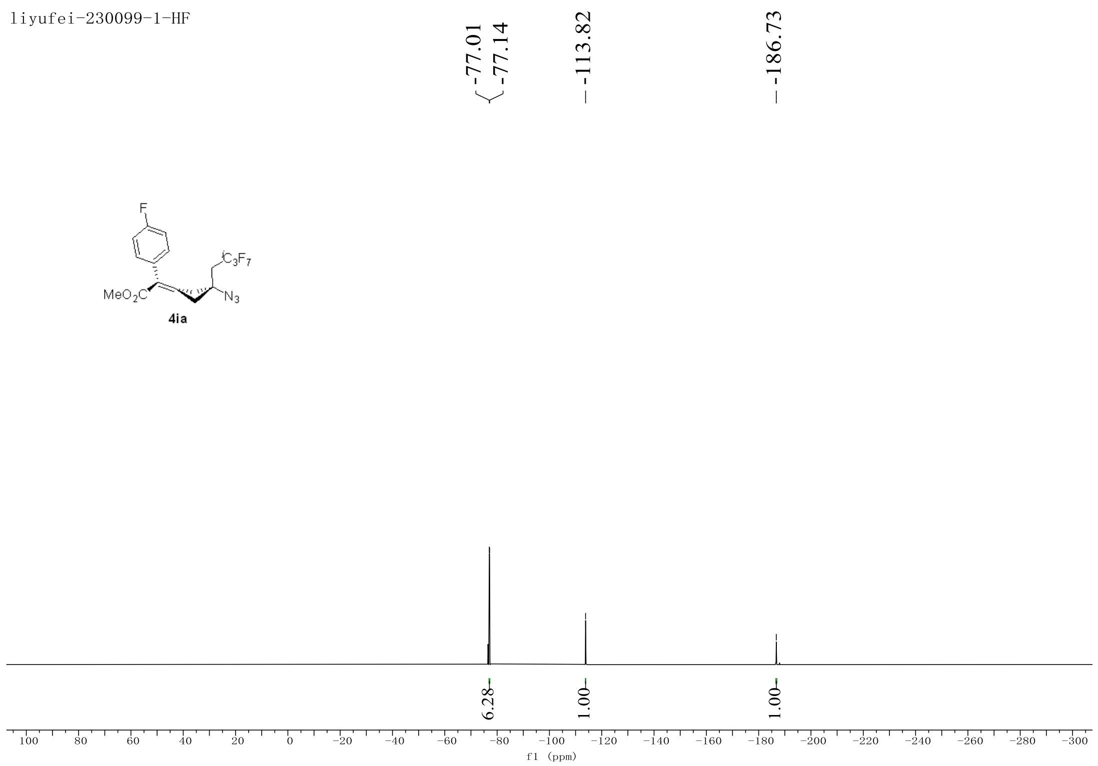
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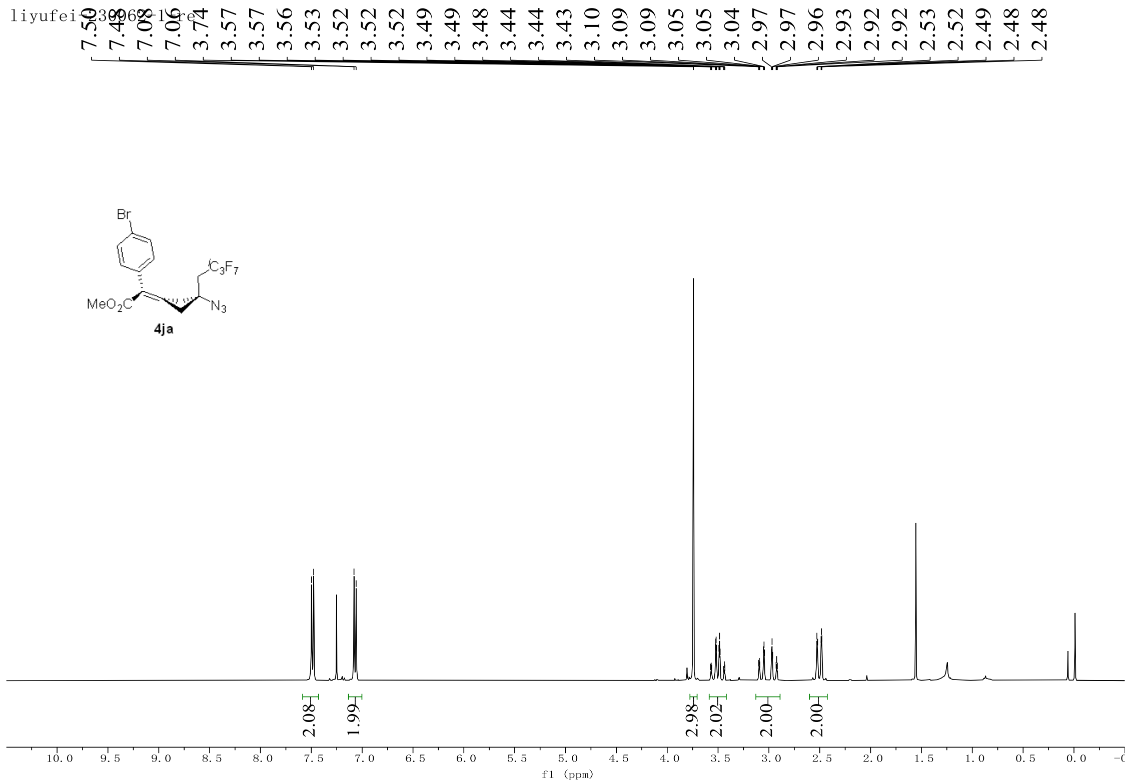
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N_3
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2.02
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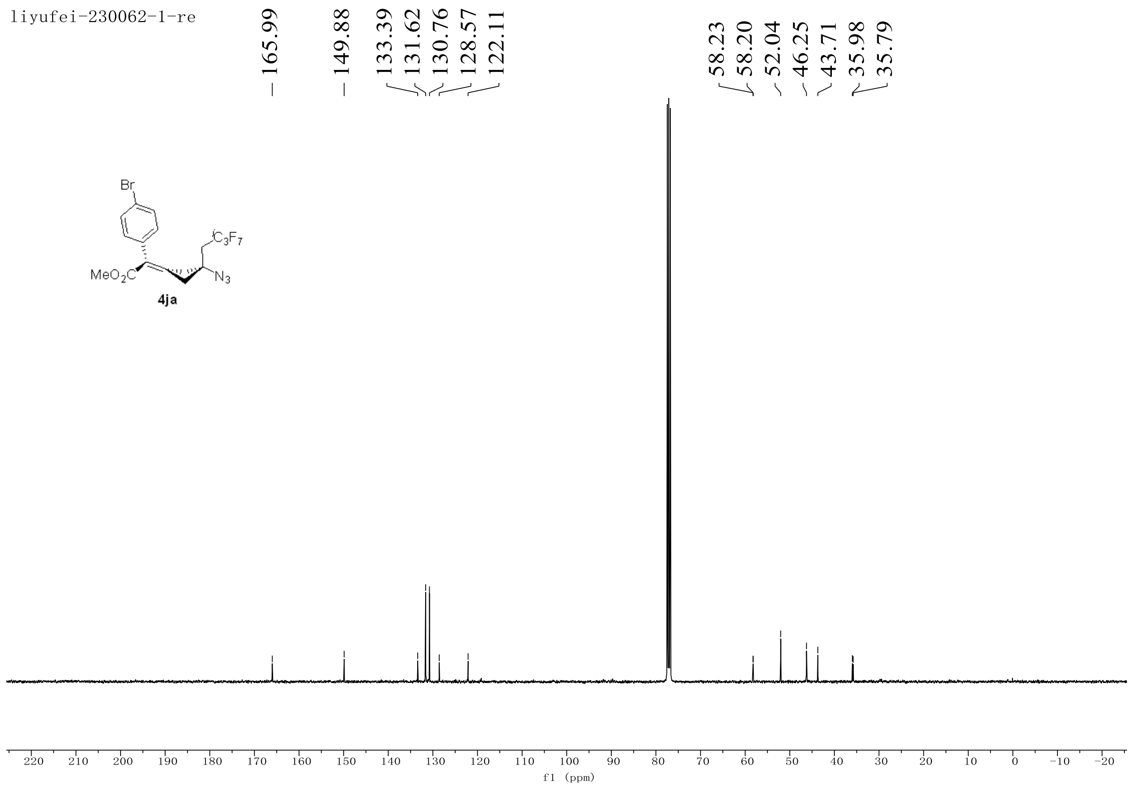
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52.04
46.25
43.71
35.98
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N3
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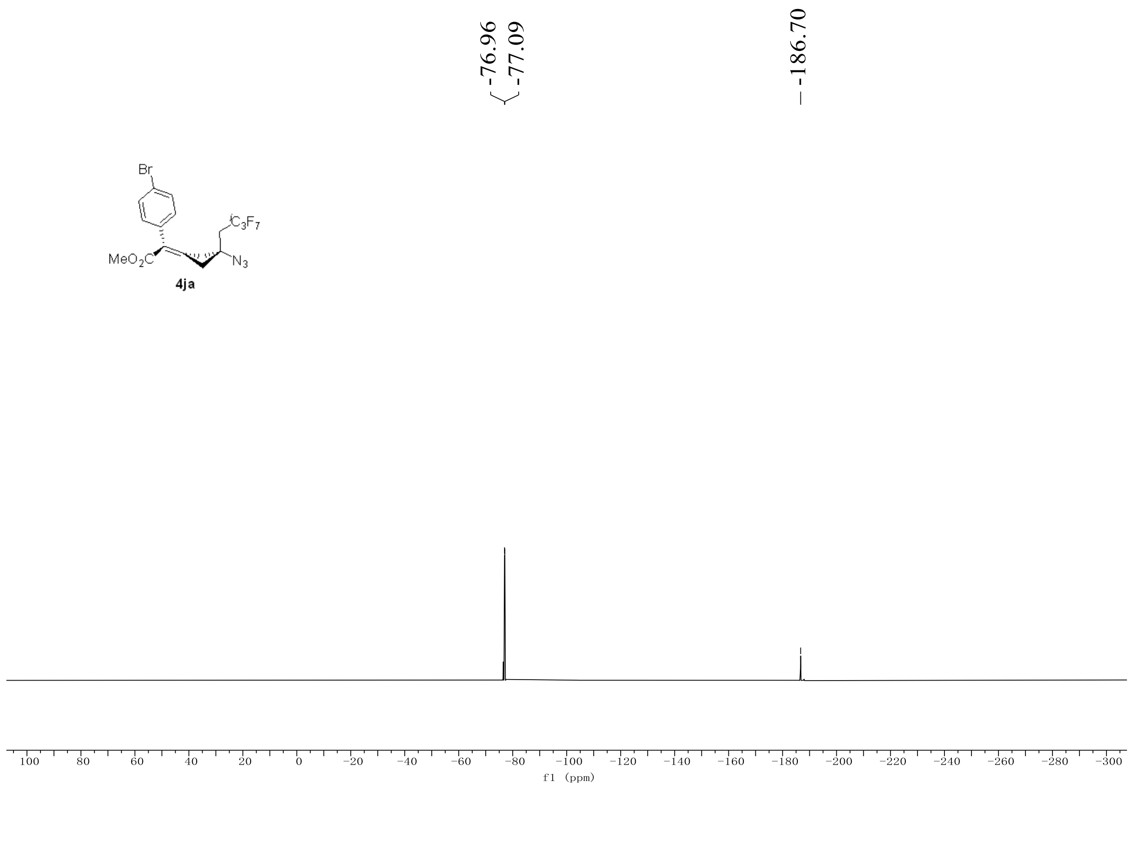
f1 (ppm)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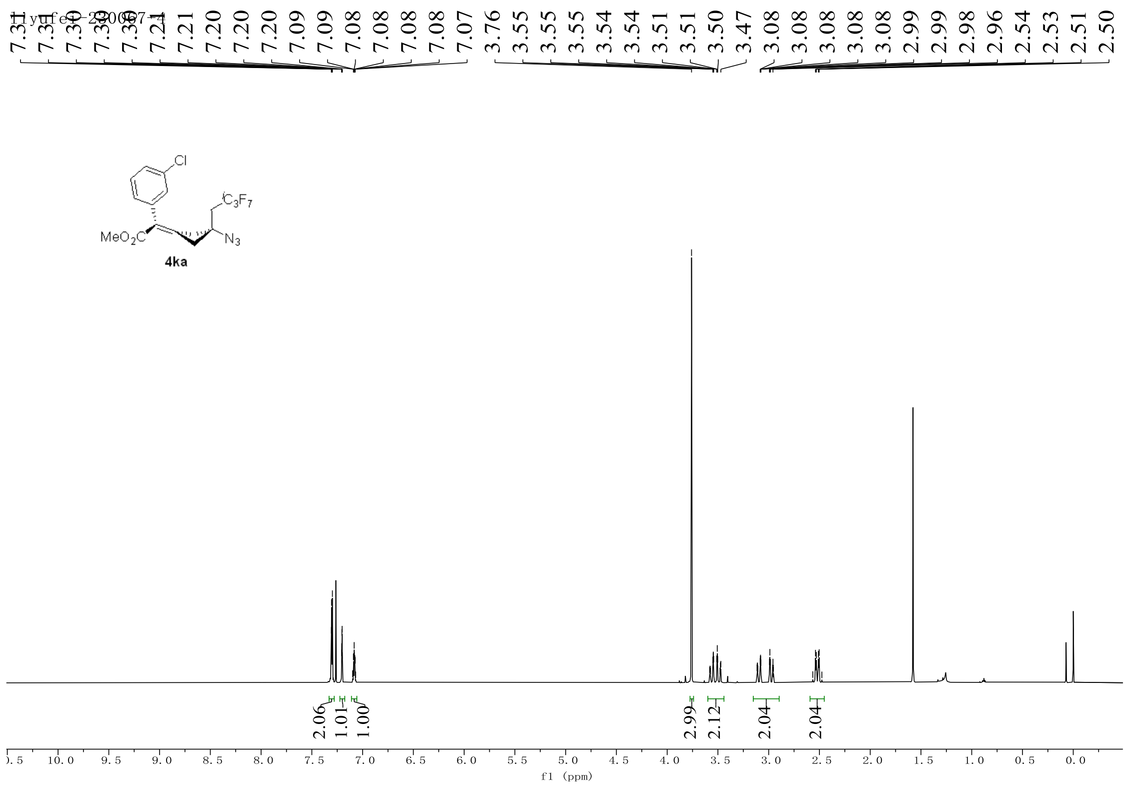
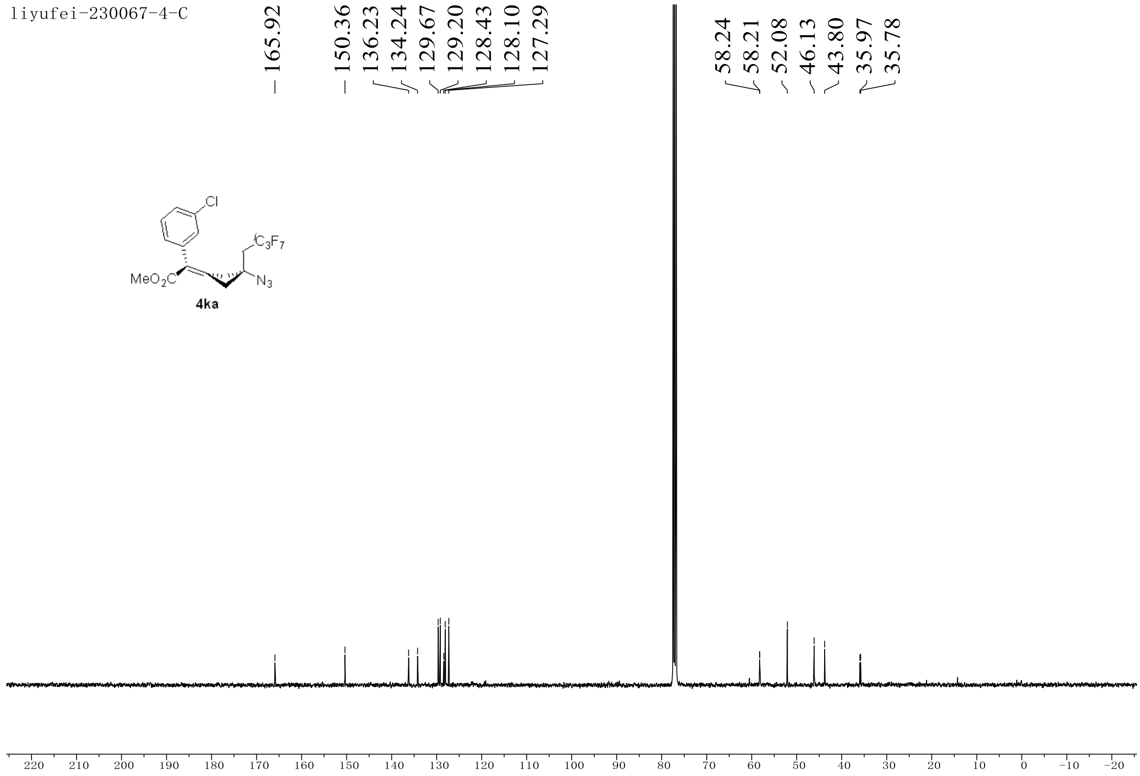
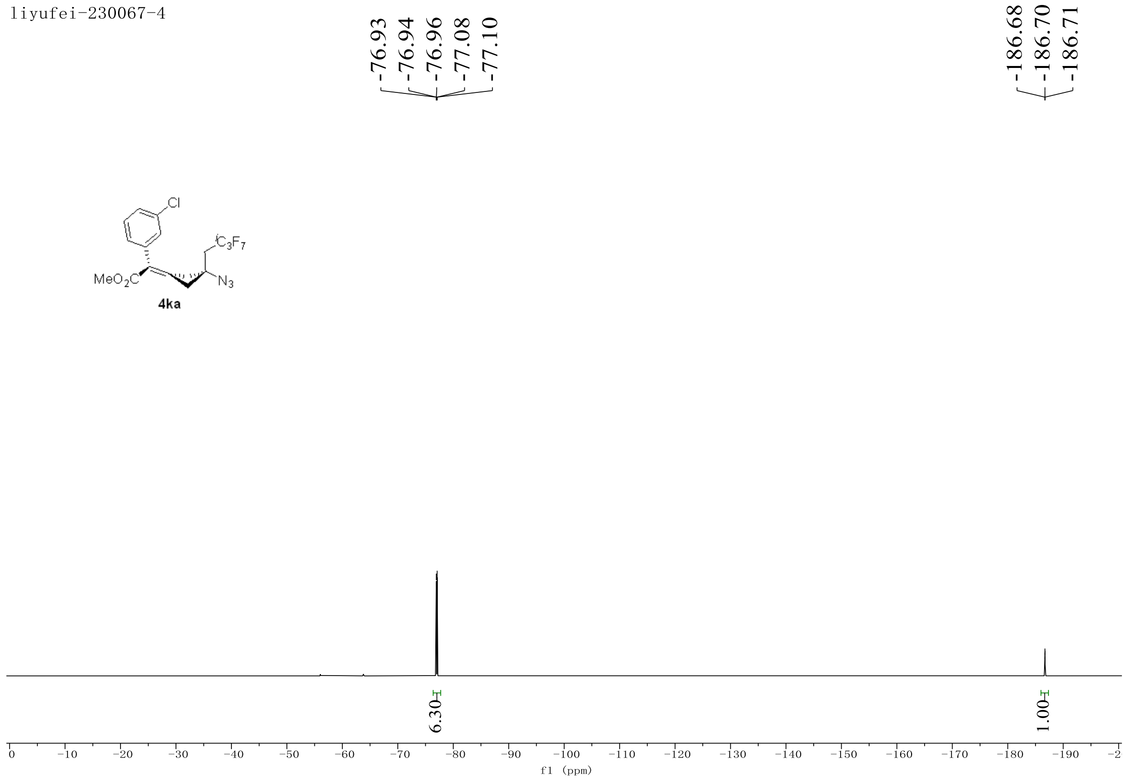
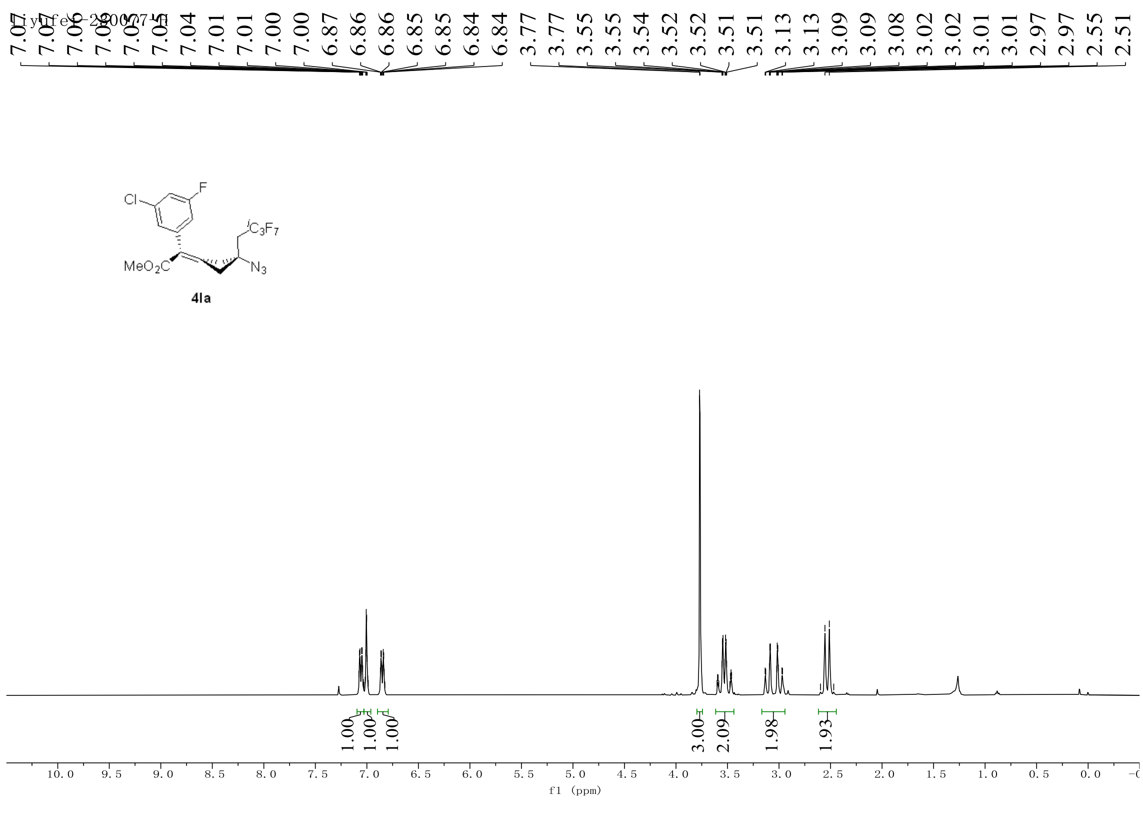

liyufei-230067-4
7.31 7.31 7.30 7.30 7.30 7.21 7.21 7.20 7.20 7.20 7.09 7.09 7.08 7.08 7.08 7.08 7.07 3.76 3.55 3.55 3.55 3.54 3.54 3.51 3.51 3.50 3.47 3.08 3.08 3.08 3.08 3.08 2.99 2.99 2.98 2.96 2.54 2.53 2.51 2.50
Cl
C3F7
MeO2C
N3
4ka
2.06 1.01 1.00 2.99 2.12 2.04 2.04
f1 (ppm)

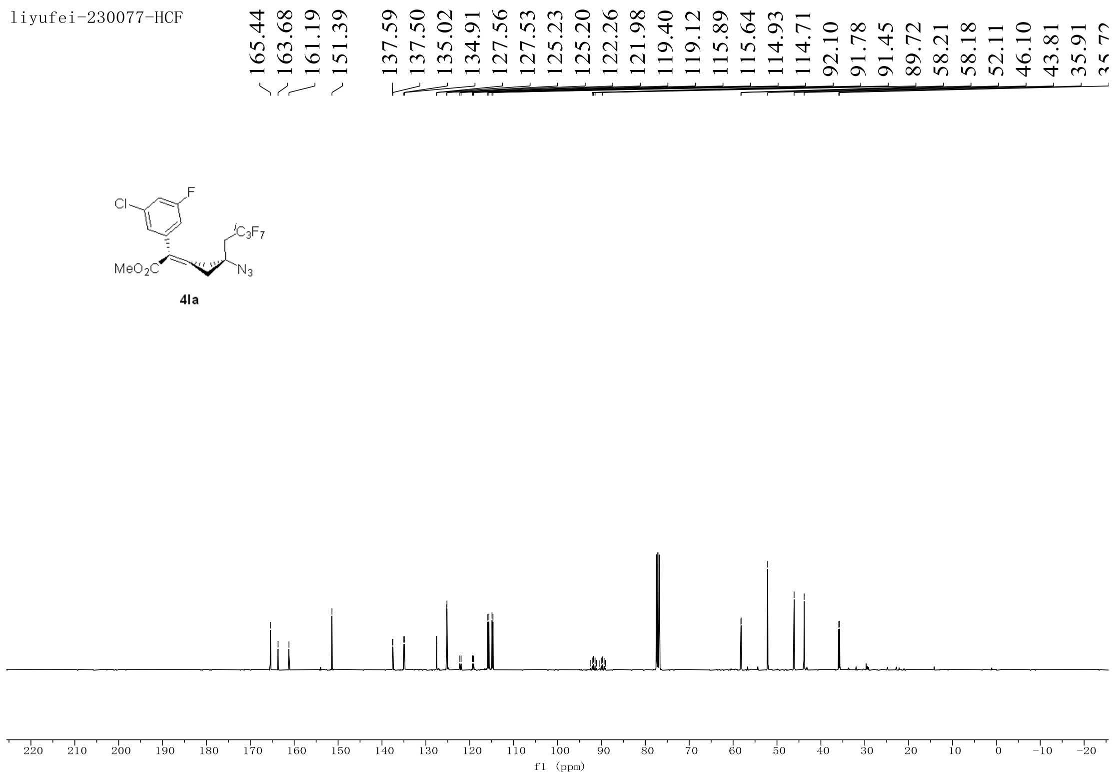

liyufei-230067-4-C
165.92 150.36 136.23 134.24 129.67 129.20 128.43 128.10 127.29 58.24 58.21 52.08 46.13 43.80 35.97 35.78
Cl
C3F7
MeO2C
N3
4ka
f1 (ppm)

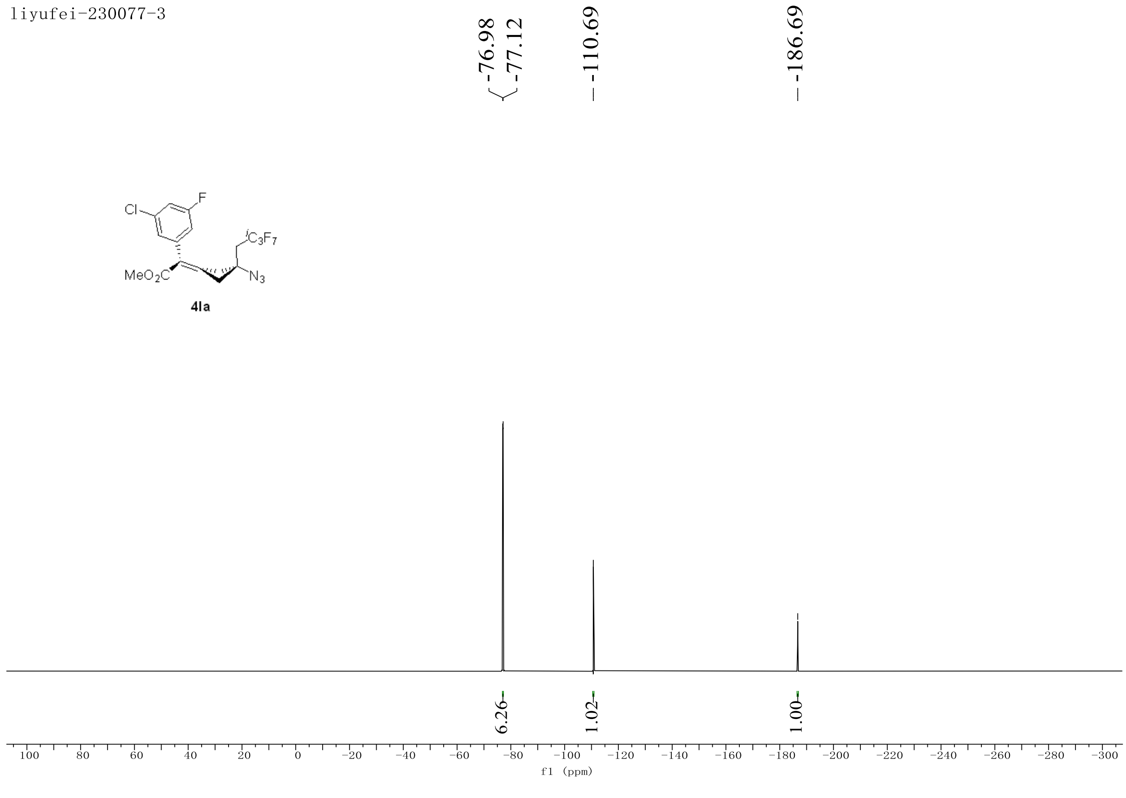


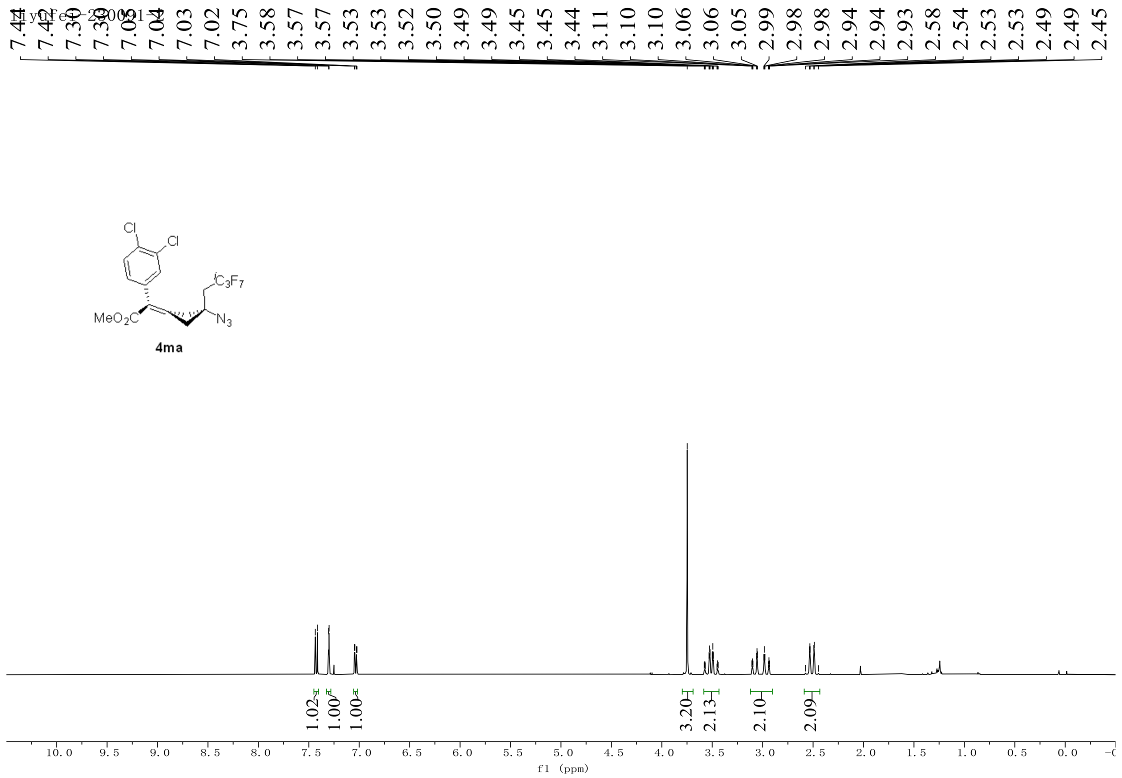
liyufei-230067-4
-76.93
-76.94
-76.96
-77.08
-77.10
-186.68
-186.70
-186.71
Cl
C3F7
MeO2C
N3
4ka
6.30
1.00
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

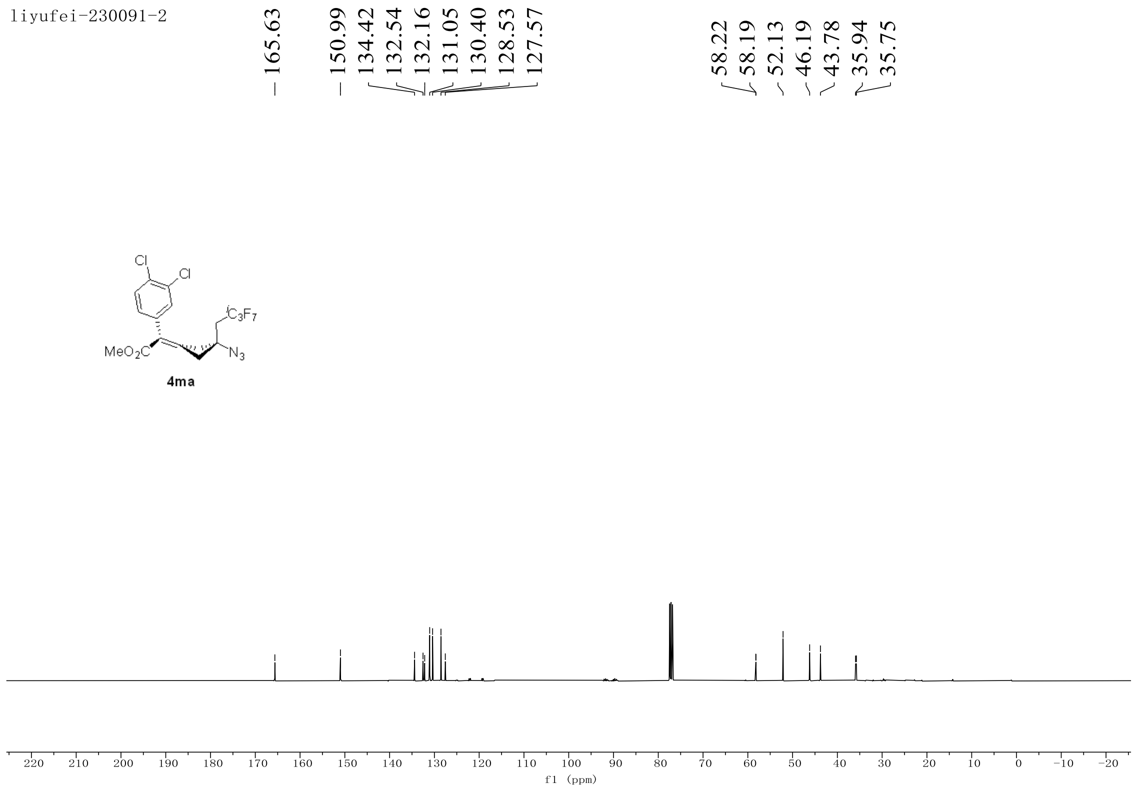


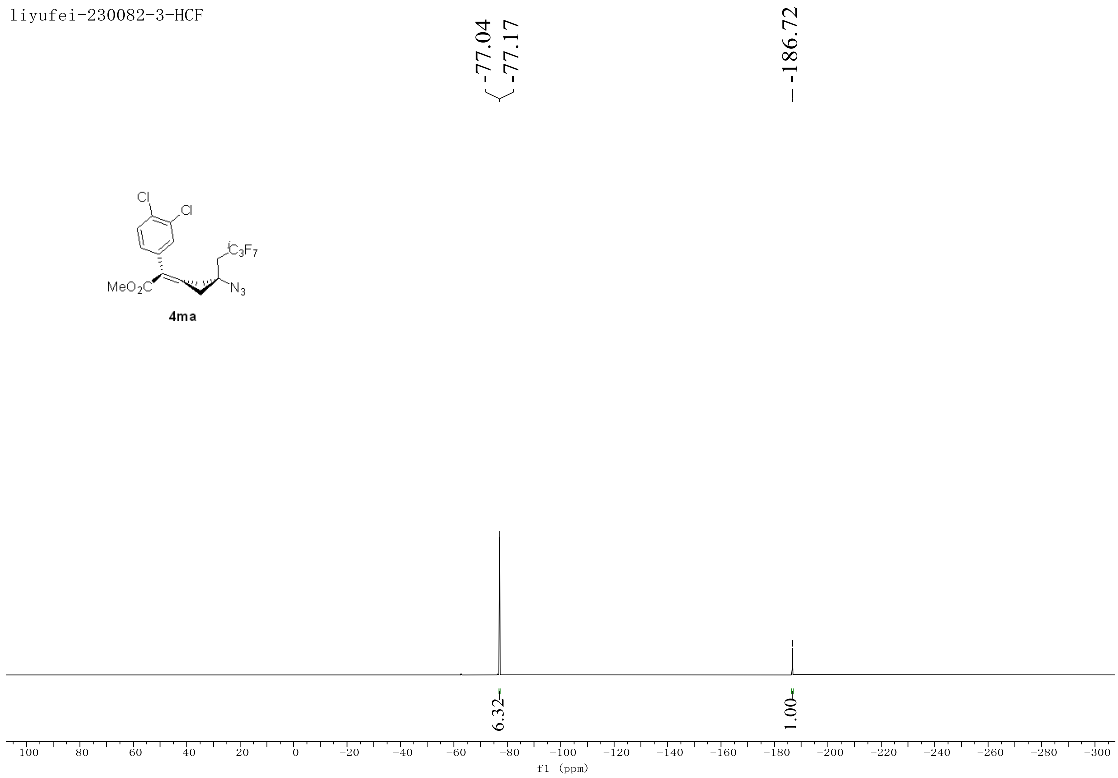
7.04
7.01
7.01
7.00
7.00
6.87
6.86
6.86
6.85
6.85
6.84
6.84
3.77
3.77
3.55
3.55
3.54
3.52
3.52
3.51
3.51
3.13
3.13
3.09
3.09
3.08
3.02
3.02
3.01
3.01
2.97
2.97
2.55
2.51
Cl
F
C3F7
MeO2C
N3
4la
1.00
1.00
1.00
3.00
2.09
1.98
1.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

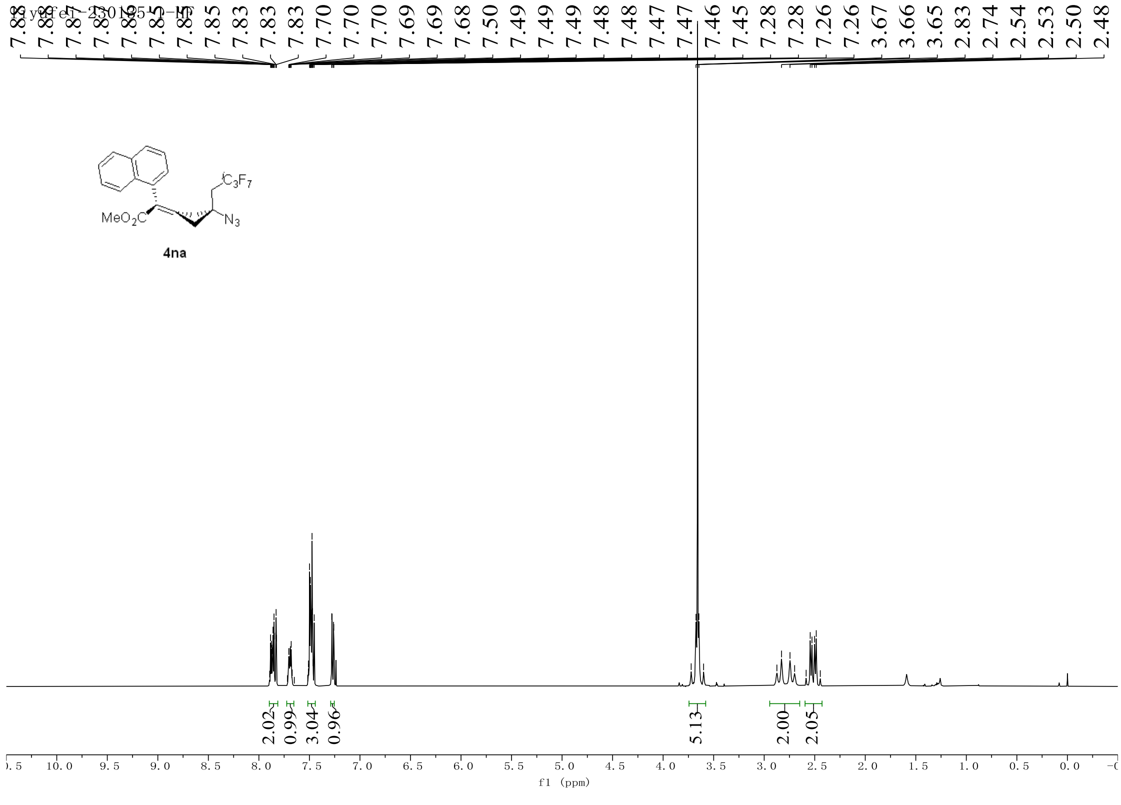

liyufei-230077-HCF
165.44
163.68
161.19
151.39
137.59
137.50
135.02
134.91
127.56
127.53
125.23
125.20
122.26
121.98
119.40
119.12
115.89
115.64
114.93
114.71
92.10
91.78
91.45
89.72
58.21
58.18
52.11
46.10
43.81
35.91
Cl
F
C3F7
MeO2C
N3
4la
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

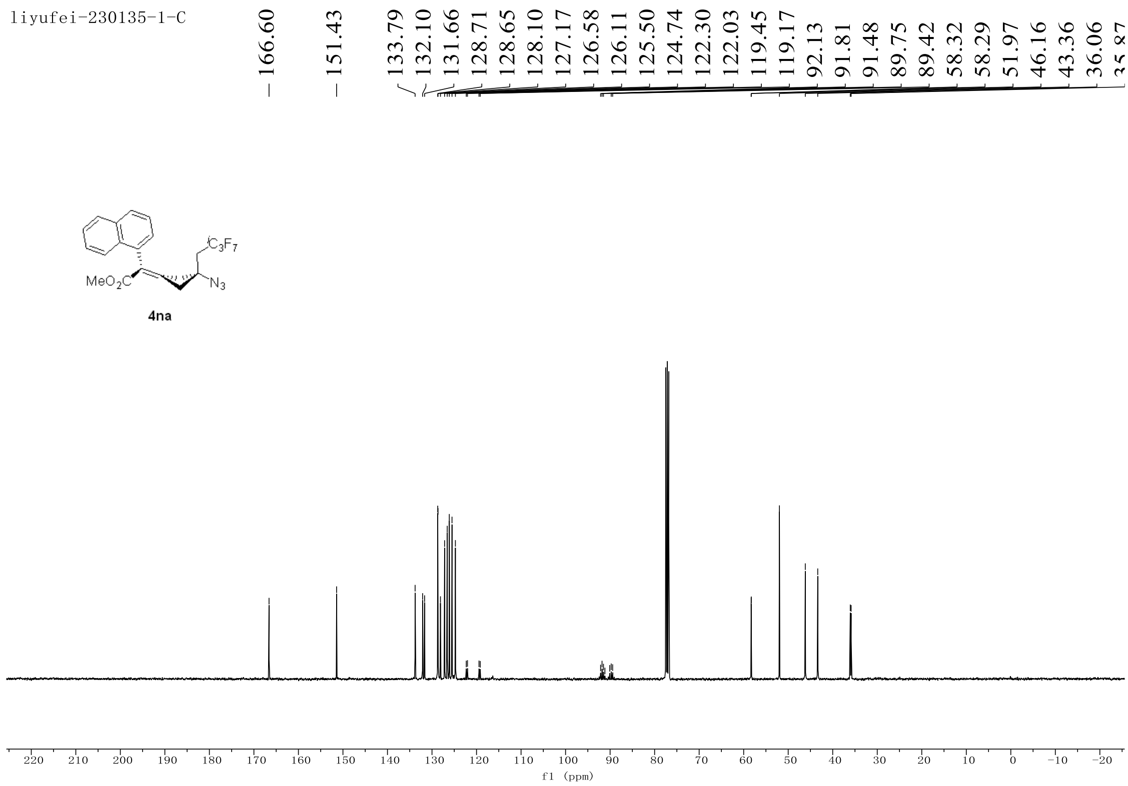

liyufei-230077-3
-76.98
-77.12
-110.69
-186.69
Cl
F
C3F7
MeO2C
N3
4la
6.26
1.02
1.00
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

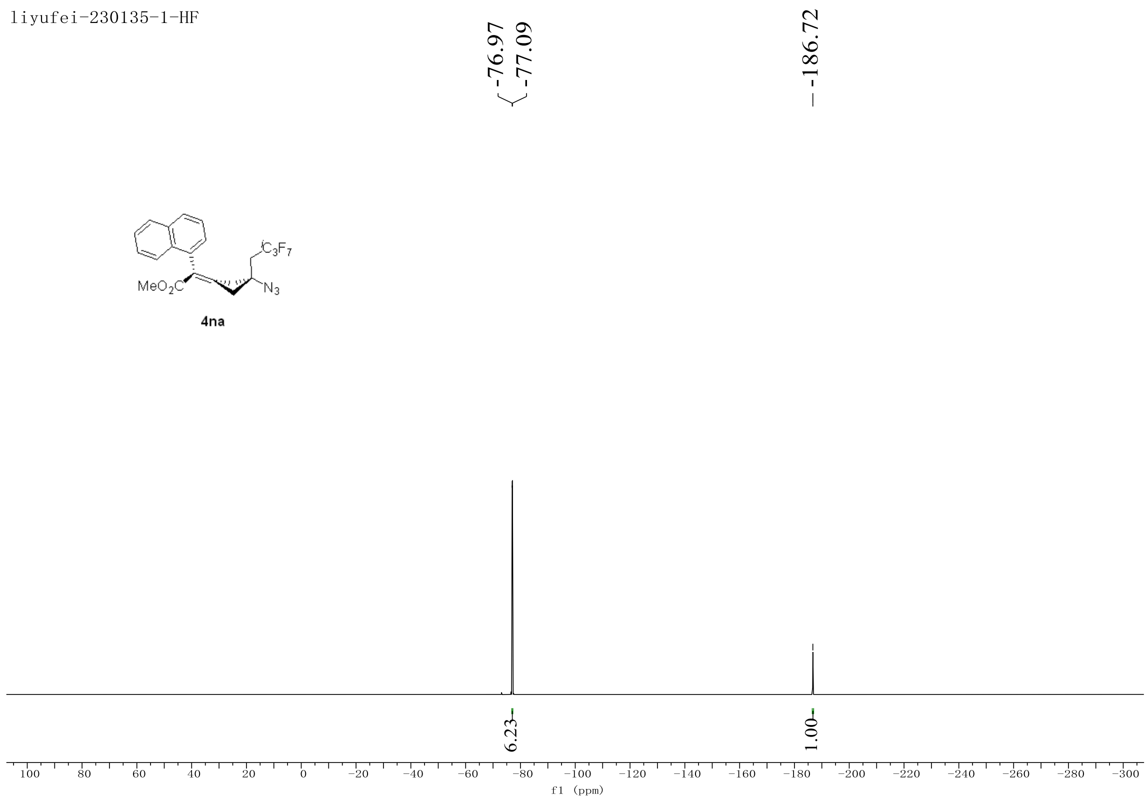

liyufei-230091-1
7.44 7.42 7.31 7.30 7.05 7.04 7.03 7.02 3.75 3.58 3.57 3.57 3.53 3.53 3.52 3.50 3.49 3.49 3.45 3.45 3.44 3.11 3.10 3.10 3.06 3.06 3.05 2.99 2.98 2.98 2.94 2.94 2.93 2.58 2.54 2.53 2.53 2.49 2.49 2.45
Cl
Cl
C3F7
MeO2C
N3
4ma
1.02
1.00
1.00
3.20
2.13
2.10
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

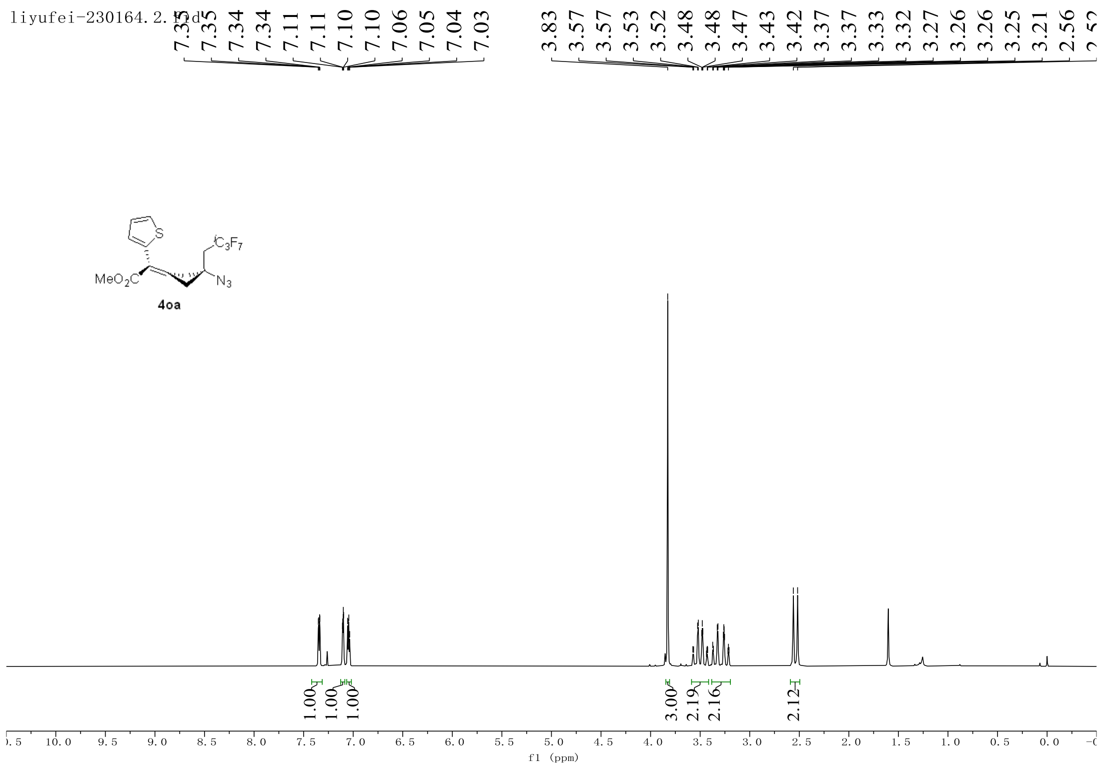

liyufei-230091-2
165.63
150.99 134.42 132.54 132.16 131.05 130.40 128.53 127.57
58.22 58.19 52.13 46.19 43.78 35.94 35.75
Cl
Cl
C3F7
MeO2C
N3
4ma
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

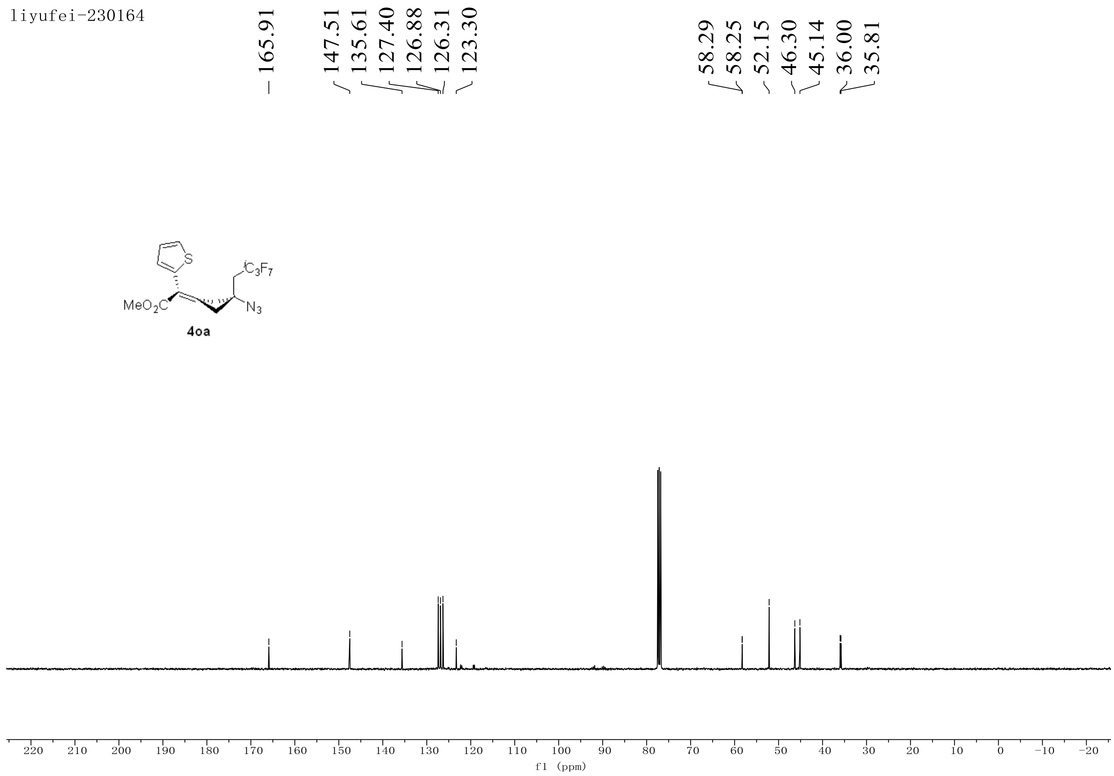

liyufei-230082-3-HCF
-77.04
-77.17
-186.72
4ma
6.32
1.00
f1 (ppm)

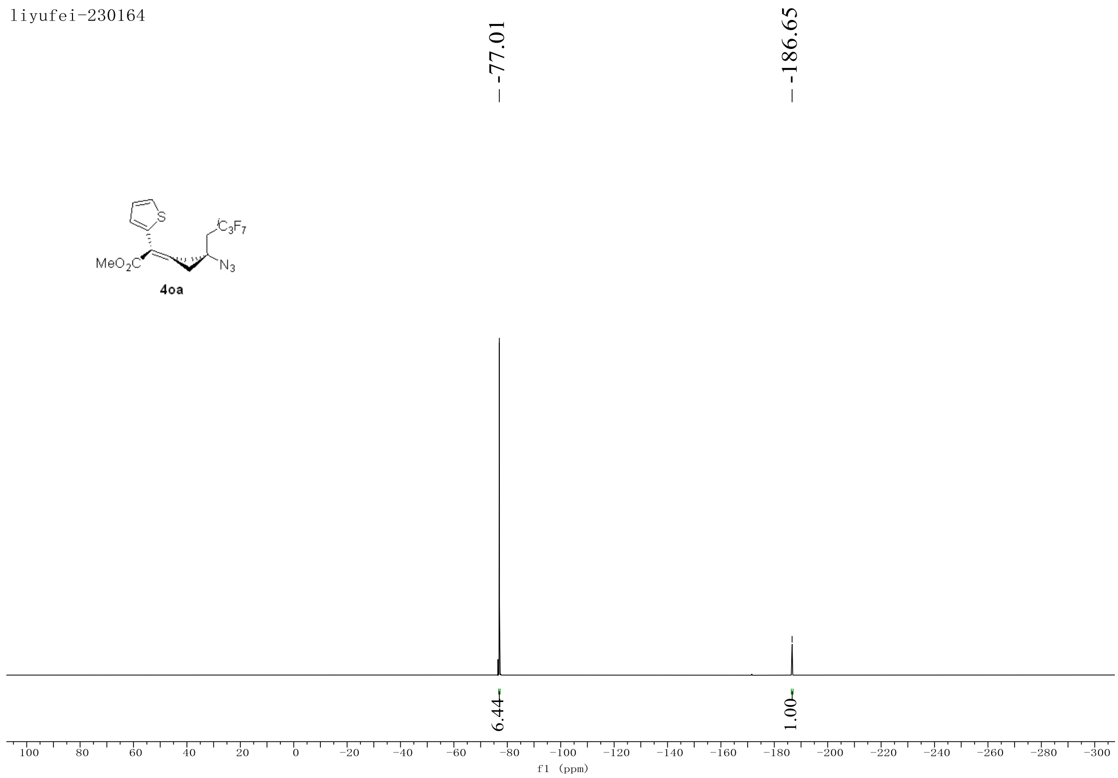

7.88 7.88 7.87 7.86 7.85 7.85 7.85 7.85 7.83 7.83 7.83 7.70 7.70 7.70 7.69 7.69 7.68 7.50 7.49 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.45 7.28 7.28 7.26 7.26 3.67 3.66 3.65 2.83 2.74 2.54 2.53 2.50 2.48
4na
2.02
0.99
3.04
0.96
5.13
2.00
2.05
f1 (ppm)


liyufei-230135-1-C
166.60
151.43
133.79
132.10
131.66
128.71
128.65
128.10
127.17
126.58
126.11
125.50
124.74
122.30
122.03
119.45
119.17
92.13
91.81
91.48
89.75
89.42
58.32
58.29
51.97
46.16
43.36
36.06
MeO2C
C3F7
N3
4na
f1 (ppm)

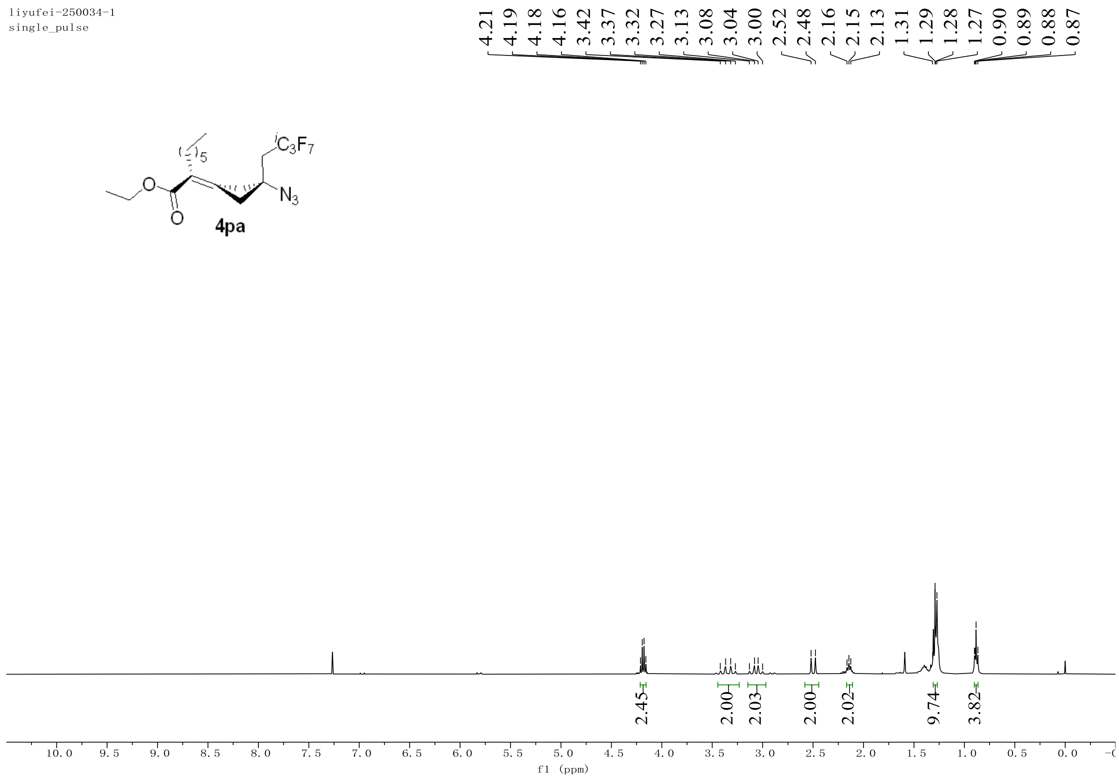

liyufei-230135-1-HF
-76.97
-77.09
-186.72
MeO2C
C3F7
N3
4na
6.23
1.00
f1 (ppm)


liyufei-230164.2.fid
7.35 7.35 7.34 7.34 7.11 7.11 7.10 7.10 7.06 7.05 7.04 7.03
3.83 3.57 3.57 3.53 3.52 3.48 3.48 3.47 3.43 3.42 3.37 3.37 3.33 3.32 3.27 3.26 3.26 3.25 3.21 2.56
S
C3F7
MeO2C
N3
4oa
1.00 1.00 1.00 3.00 2.19 2.16 2.12
f1 (ppm)

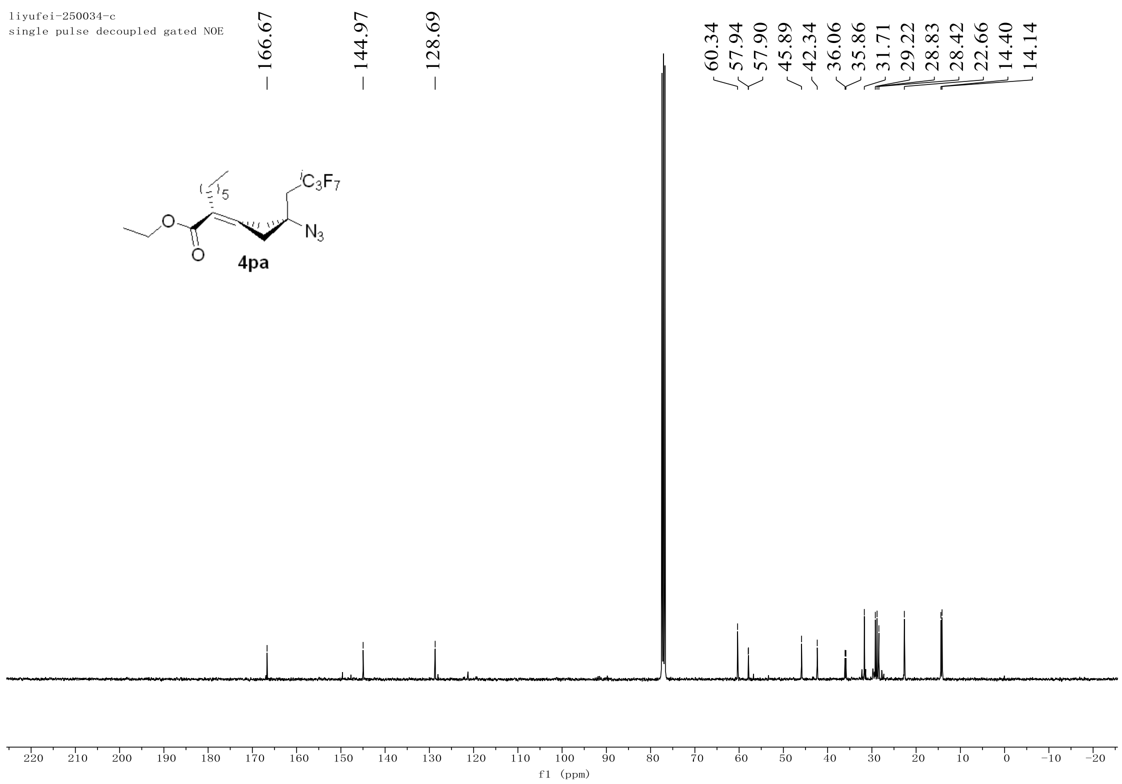

liyufei-230164
165.91 147.51 135.61 127.40 126.88 126.31 123.30
58.29 58.25 52.15 46.30 45.14 36.00 35.81
S
C3F7
MeO2C
N3
4oa
f1 (ppm)

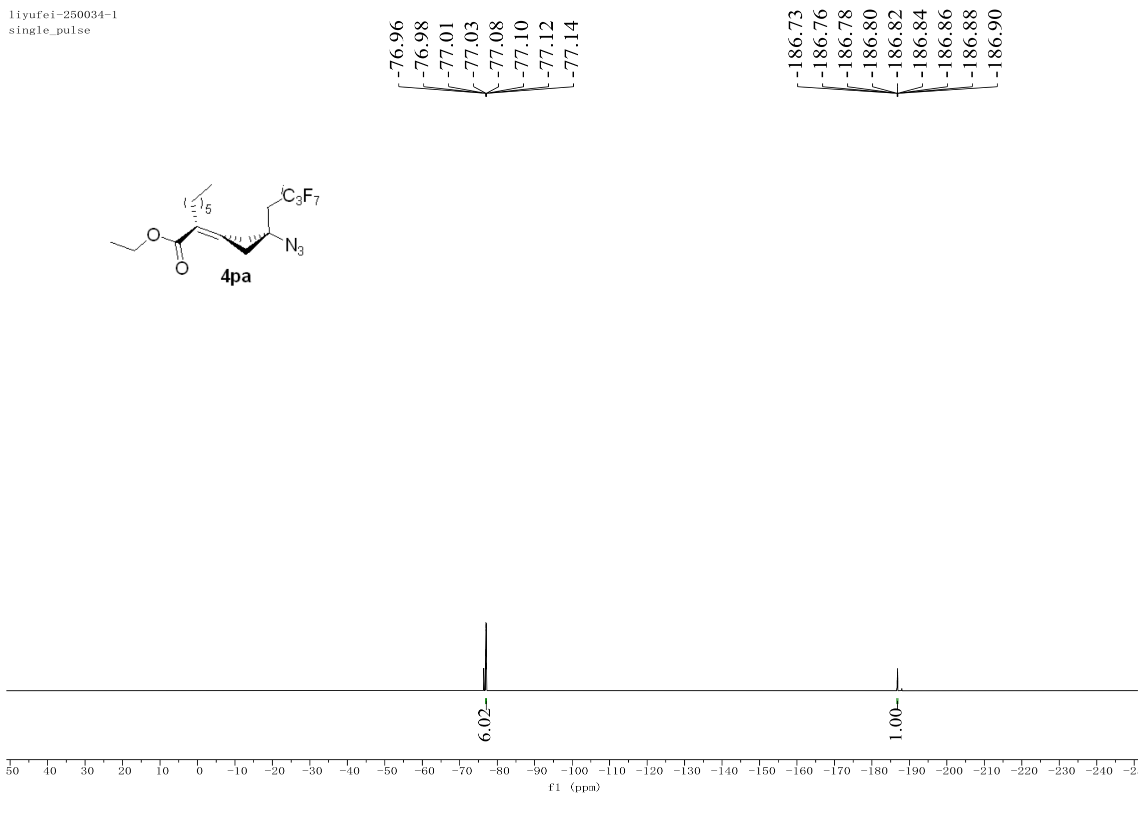


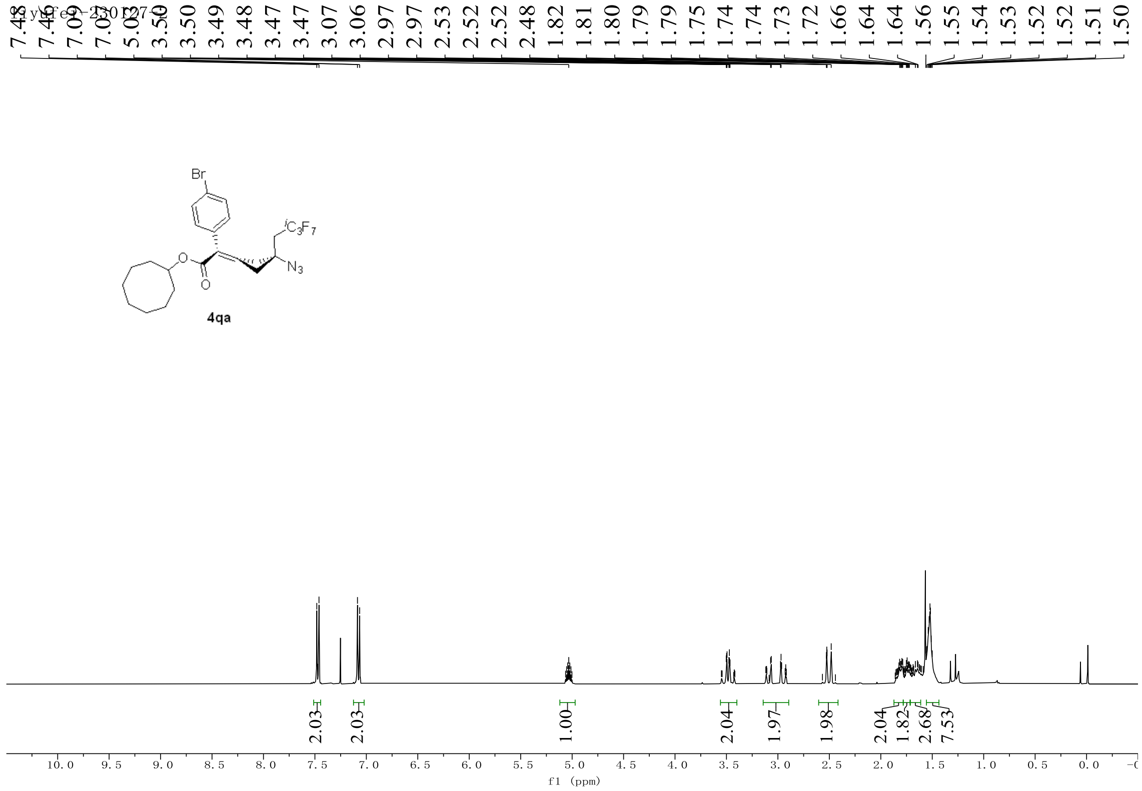
liyufei-230164
-77.01
-186.65
4oa
6.44
1.00
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300
f1 (ppm)

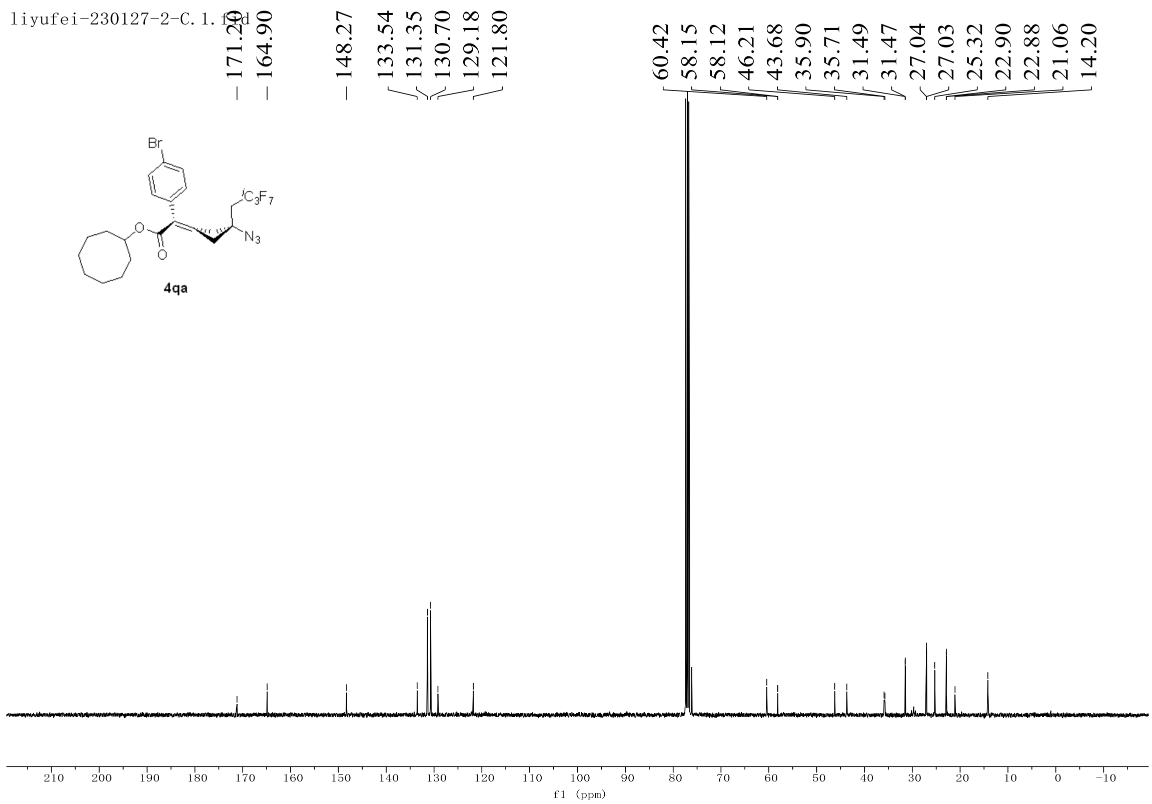


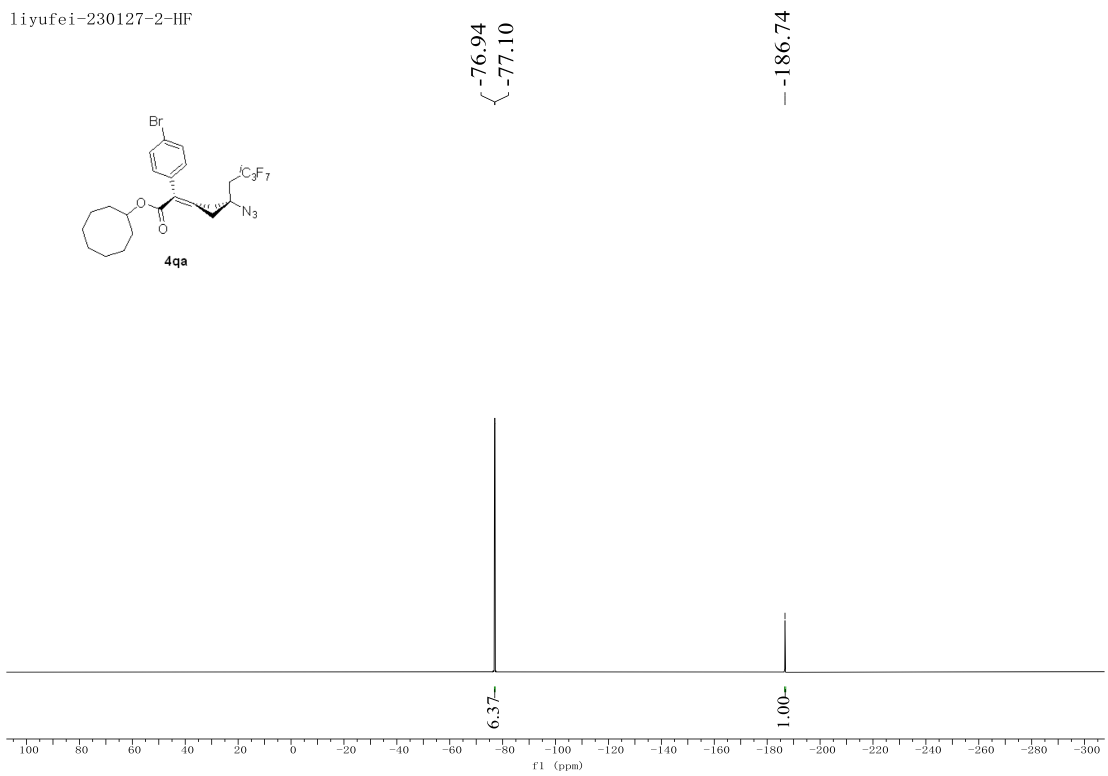
liyufei-250034-1
single_pulse
4.21 4.19 4.18 4.16 3.42 3.37 3.32 3.27 3.13 3.08 3.04 3.00 2.52 2.48 2.16 2.15 2.13 1.31 1.29 1.28 1.27 0.90 0.89 0.88 0.87
4pa
2.45 2.00 2.03 2.00 2.02 9.74 3.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

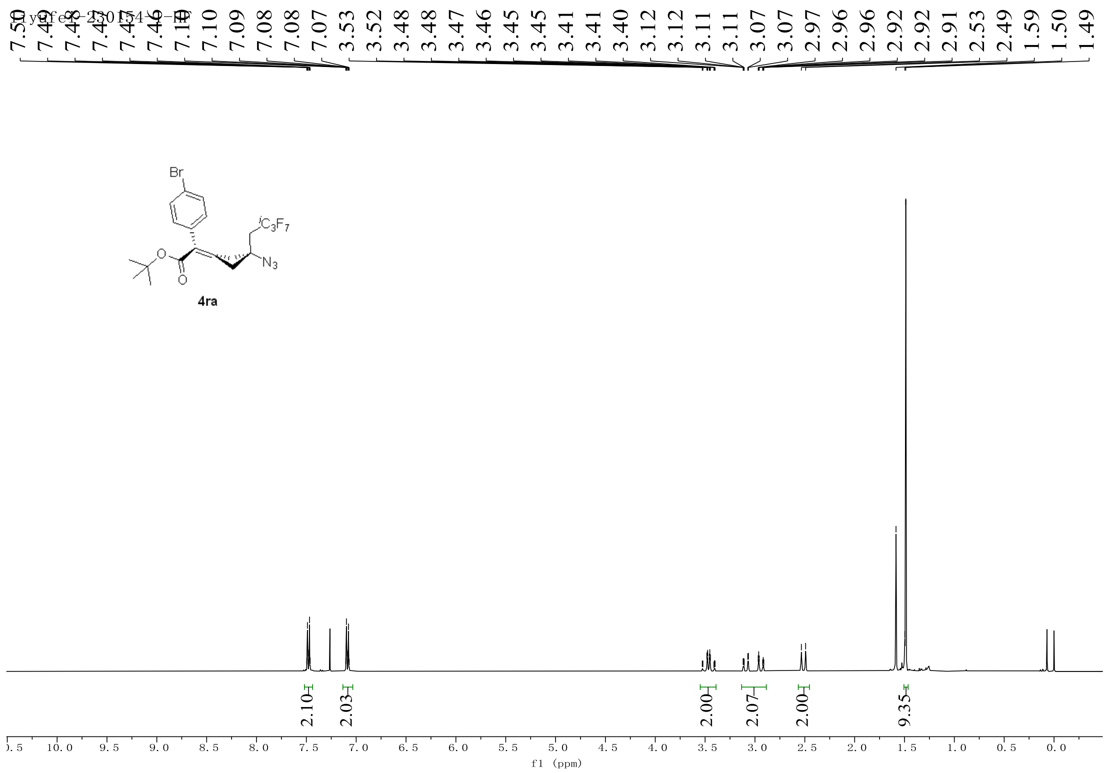

liyufei-250034-c
single pulse decoupled gated NOE
166.67
144.97
128.69
60.34
57.94
57.90
45.89
42.34
36.06
35.86
31.71
29.22
28.83
28.42
22.66
14.40
14.14
4pa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

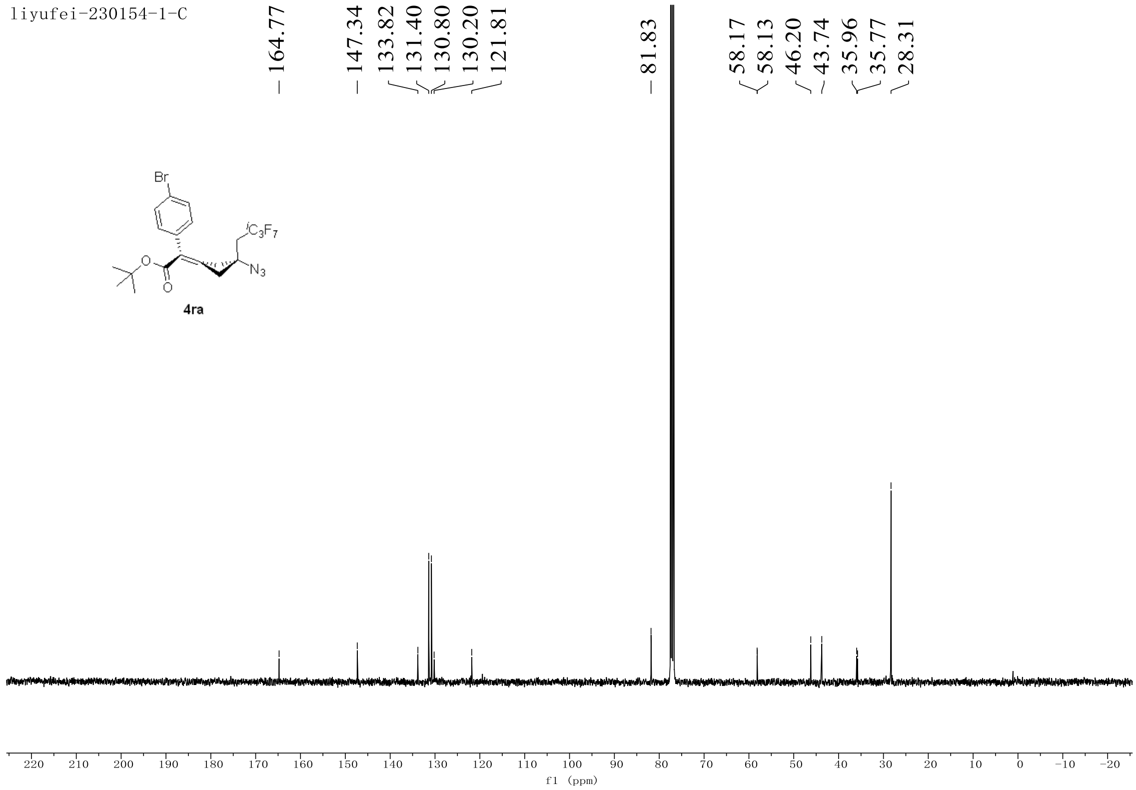

liyufei-250034-1
single_pulse
-76.96
-76.98
-77.01
-77.03
-77.08
-77.10
-77.12
-77.14
-186.73
-186.76
-186.78
-186.80
-186.82
-186.84
-186.86
-186.88
-186.90
4pa
6.02
1.00
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

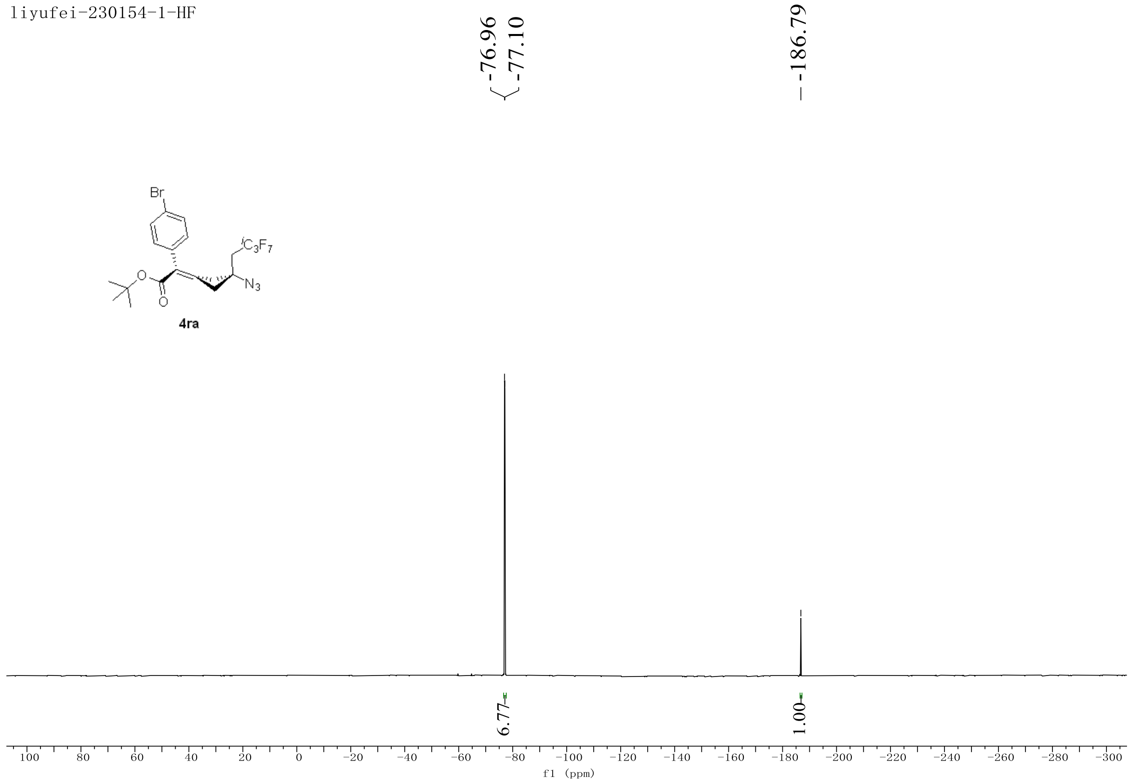

7.48 7.46 7.09 7.07 5.03 3.50 3.50 3.49 3.48 3.47 3.47 3.07 3.06 2.97 2.97 2.53 2.52 2.52 2.48 1.82 1.81 1.80 1.79 1.79 1.75 1.74 1.74 1.73 1.72 1.66 1.64 1.64 1.56 1.55 1.54 1.53 1.52 1.52 1.51 1.50
Br
$^iC_3F_7$
N_3
O
4qa
2.03 2.03 1.00 2.04 1.97 1.98 2.04 1.82 2.68 7.53
f1 (ppm)

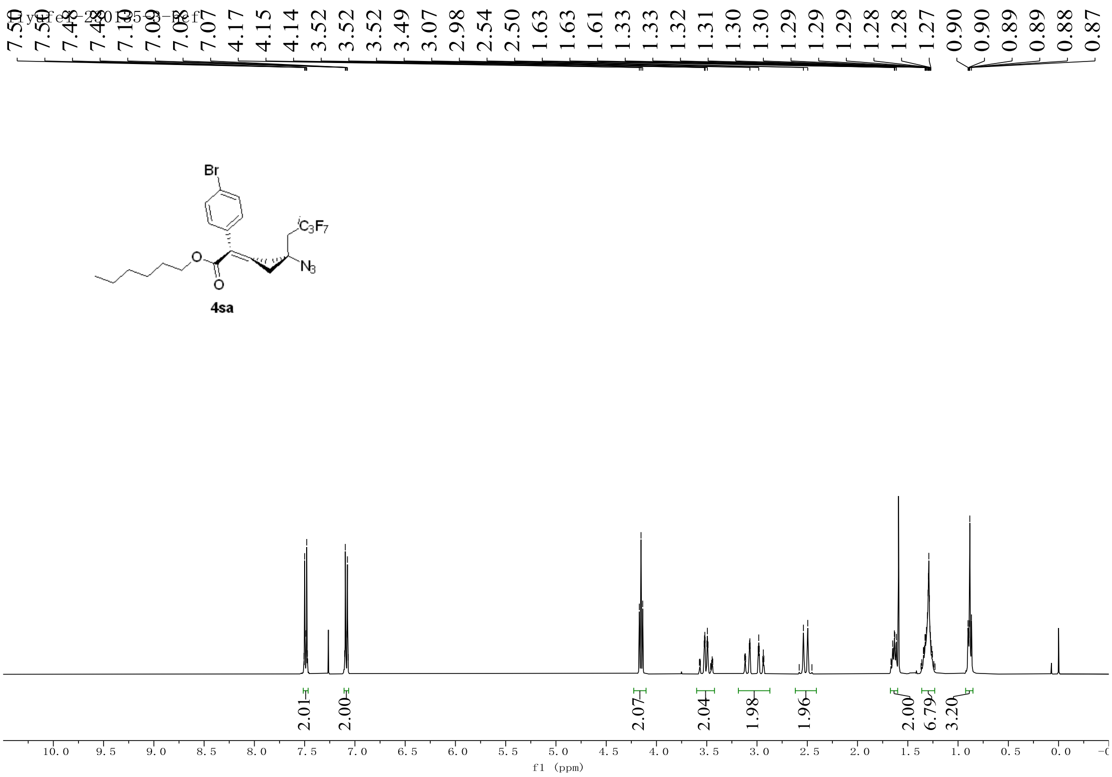

liyufei-230127-2-C.1.fid
171.20 164.90 148.27 133.54 131.35 130.70 129.18 121.80 60.42 58.15 58.12 46.21 43.68 35.90 35.71 31.49 31.47 27.04 27.03 25.32 22.90 22.88 21.06 14.20
Br
$^iC_3F_7$
N_3
O
4qa
f1 (ppm)

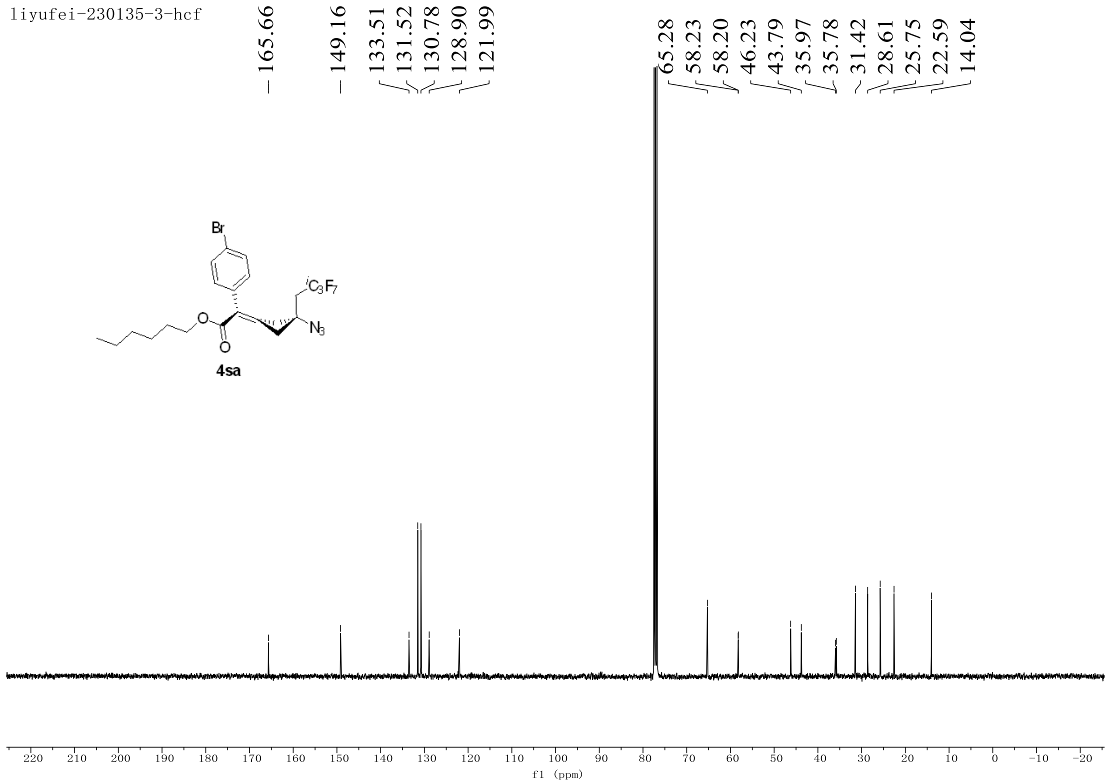

liyufei-230127-2-HF
-76.94
-77.10
-186.74
4qa
6.37
1.00
f1 (ppm)


7.50 7.49 7.48 7.47 7.46 7.46 7.10 7.10 7.09 7.08 7.08 7.07 3.53 3.52 3.48 3.48 3.47 3.46 3.45 3.45 3.41 3.41 3.40 3.12 3.12 3.11 3.11 3.07 3.07 2.97 2.96 2.96 2.92 2.92 2.91 2.53 2.49 1.59 1.50 1.49
4ra
2.10
2.03
2.00
2.07
2.00
9.35
f1 (ppm)

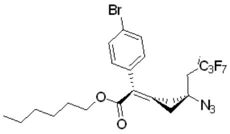

liyufei-230154-1-C
164.77
147.34
133.82
131.40
130.80
130.20
121.81
81.83
58.17
58.13
46.20
43.74
35.96
35.77
28.31
Br
iC3F7
N3
O
4ra
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


liyufei-230154-1-HF
-76.96
-77.10
-186.79
Br
iC3F7
N3
O
4ra
6.77
1.00
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

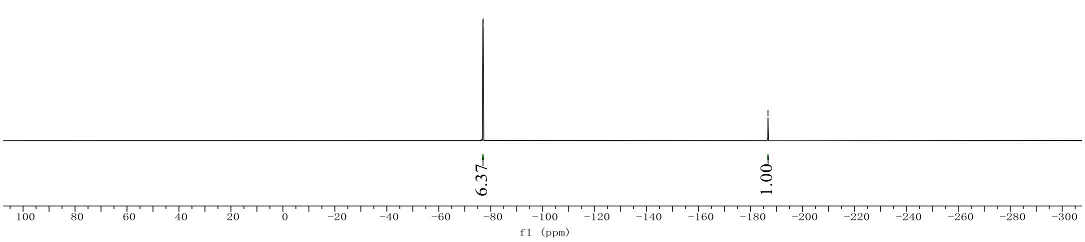

7.50
7.50
7.48
7.48
7.10
7.09
7.08
7.07
4.17
4.15
4.14
3.52
3.52
3.52
3.49
3.07
2.98
2.54
2.50
1.63
1.63
1.61
1.33
1.33
1.32
1.31
1.30
1.30
1.29
1.29
1.29
1.28
1.28
1.27
0.90
0.90
0.89
0.89
0.88
0.87
Br
$^{i}C_3F_7$
O
O
N_3
4sa
2.01
2.00
2.07
2.04
1.98
1.96
2.00
6.79
3.20
f1 (ppm)

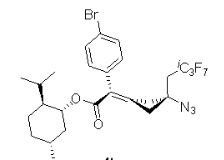

liyufei-230135-3-hcf
165.66
149.16
133.51
131.52
130.78
128.90
121.99
65.28
58.23
58.20
46.23
43.79
35.97
35.78
31.42
28.61
25.75
22.59
14.04
Br
$^{i}C_3F_7$
O
O
N_3
4sa
f1 (ppm)

liyufei-230135-3-hcf

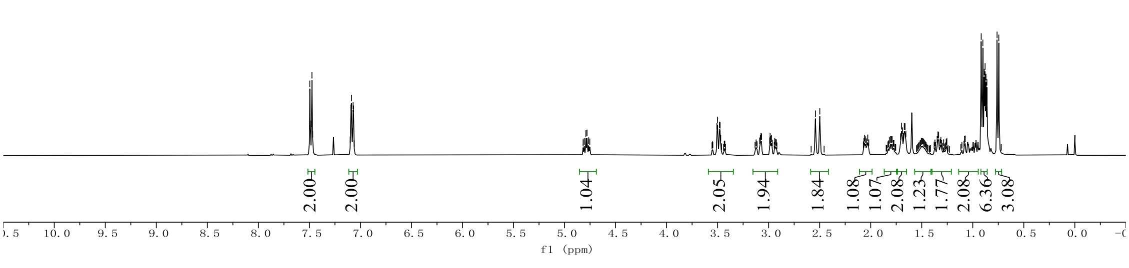


4sa

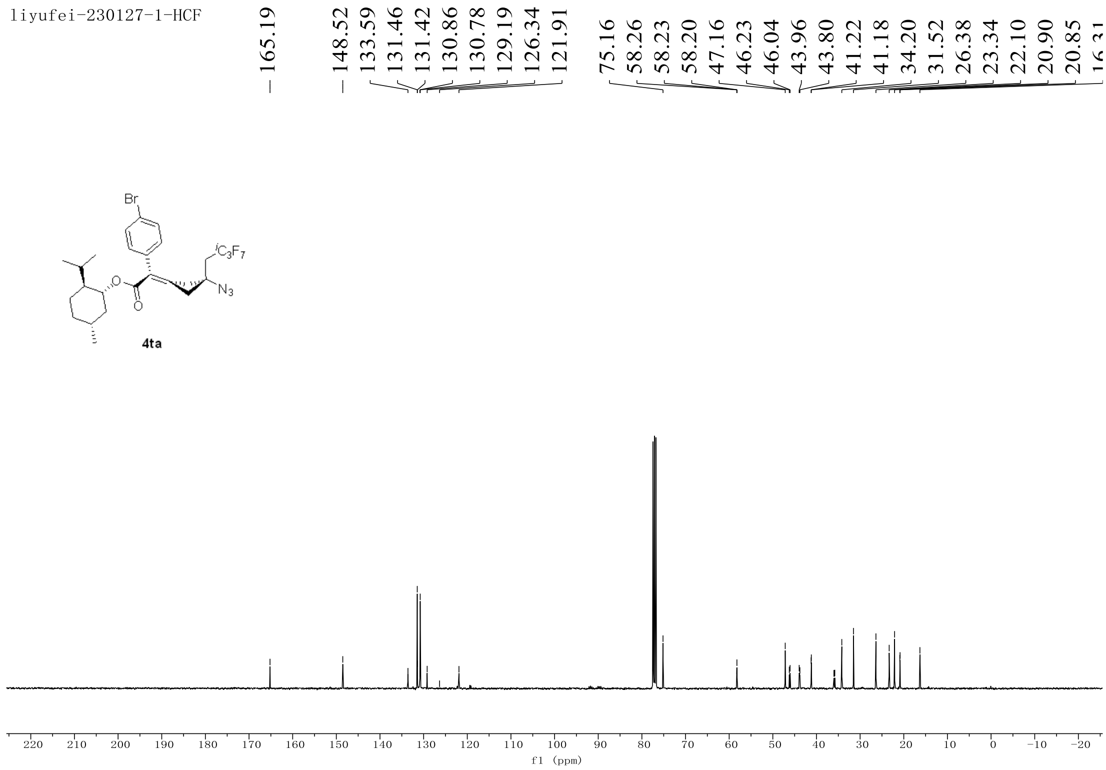




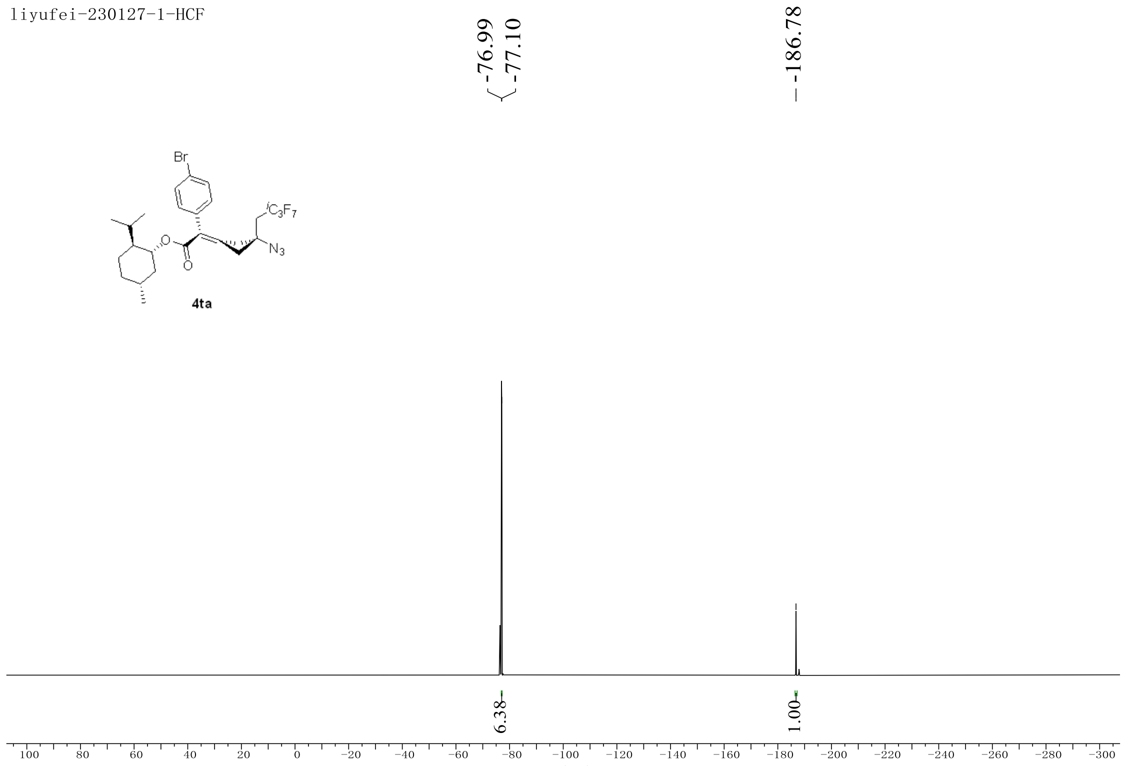
4ta

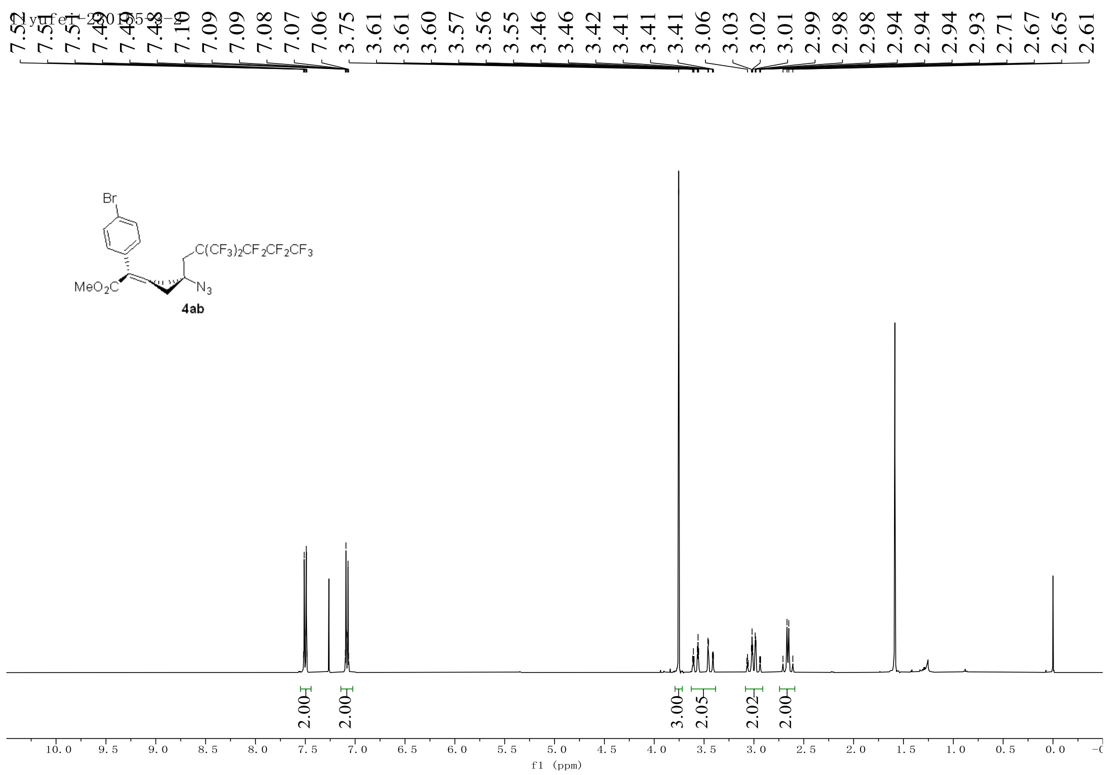


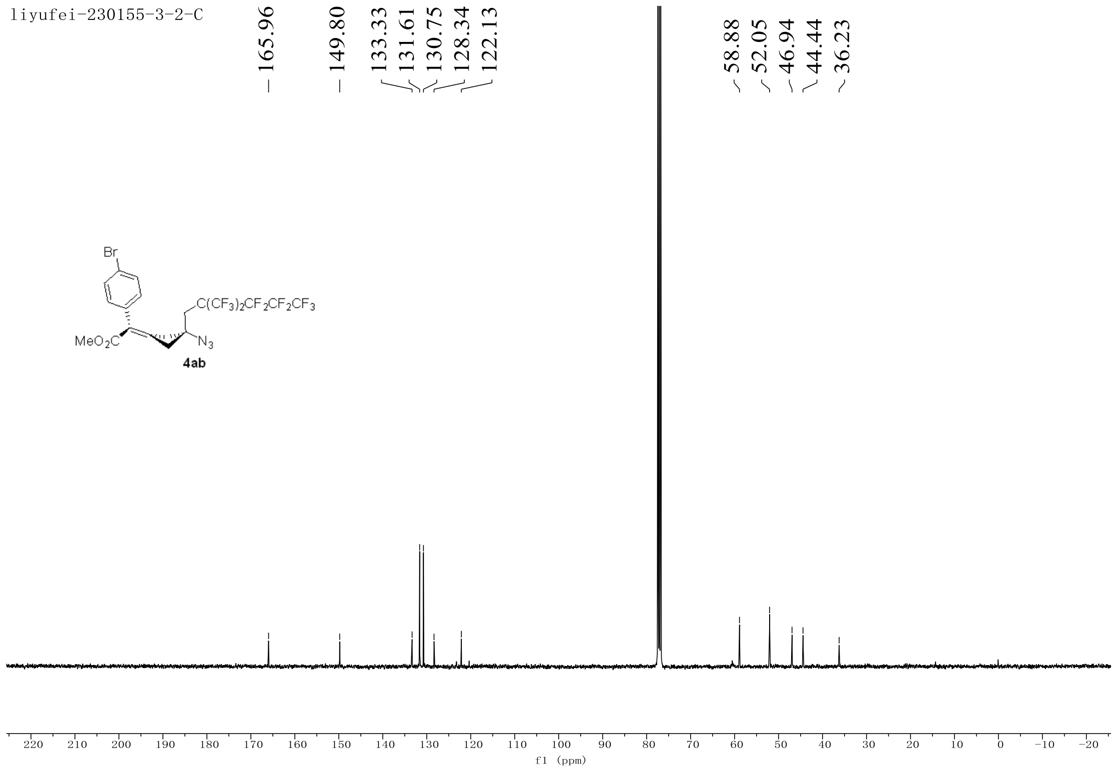
liyufei-230127-1-HCF

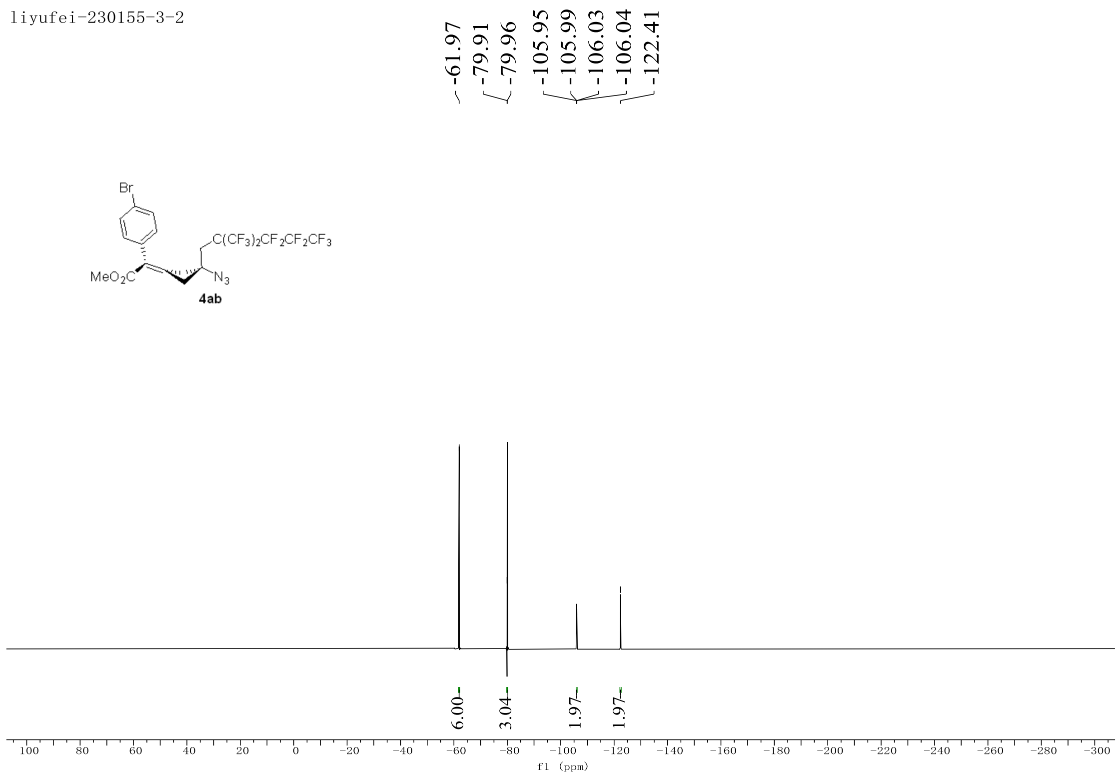


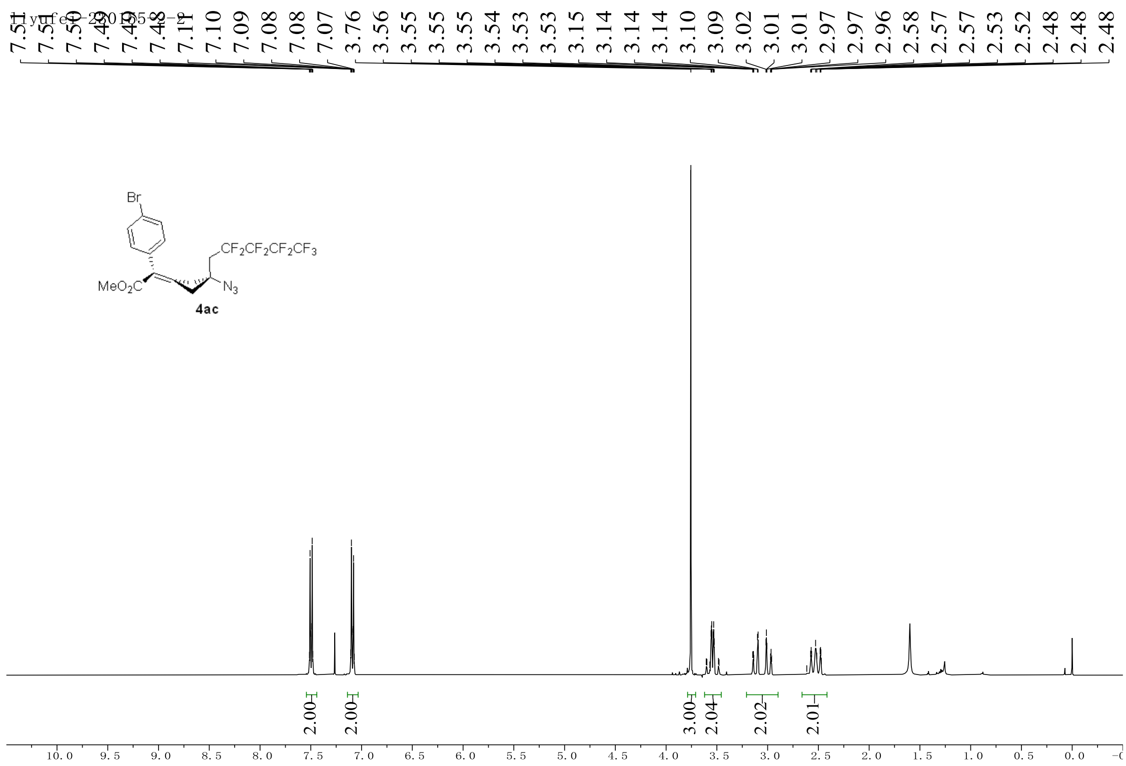
liyufei-230127-1-HCF

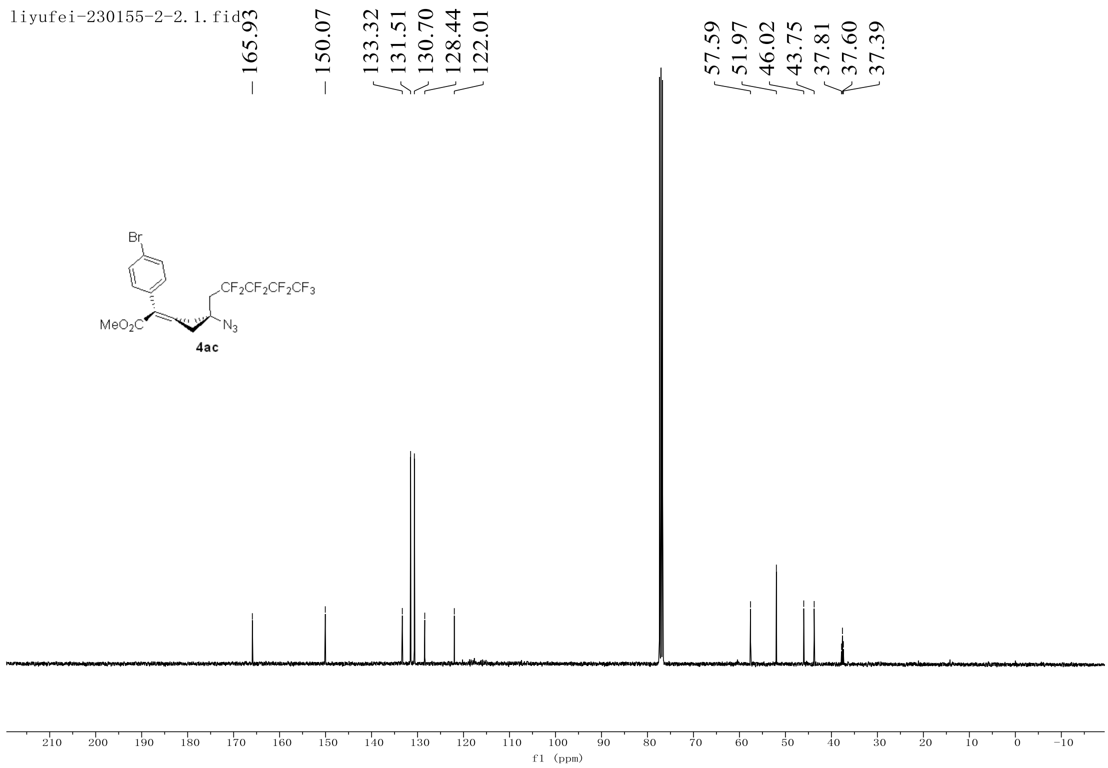


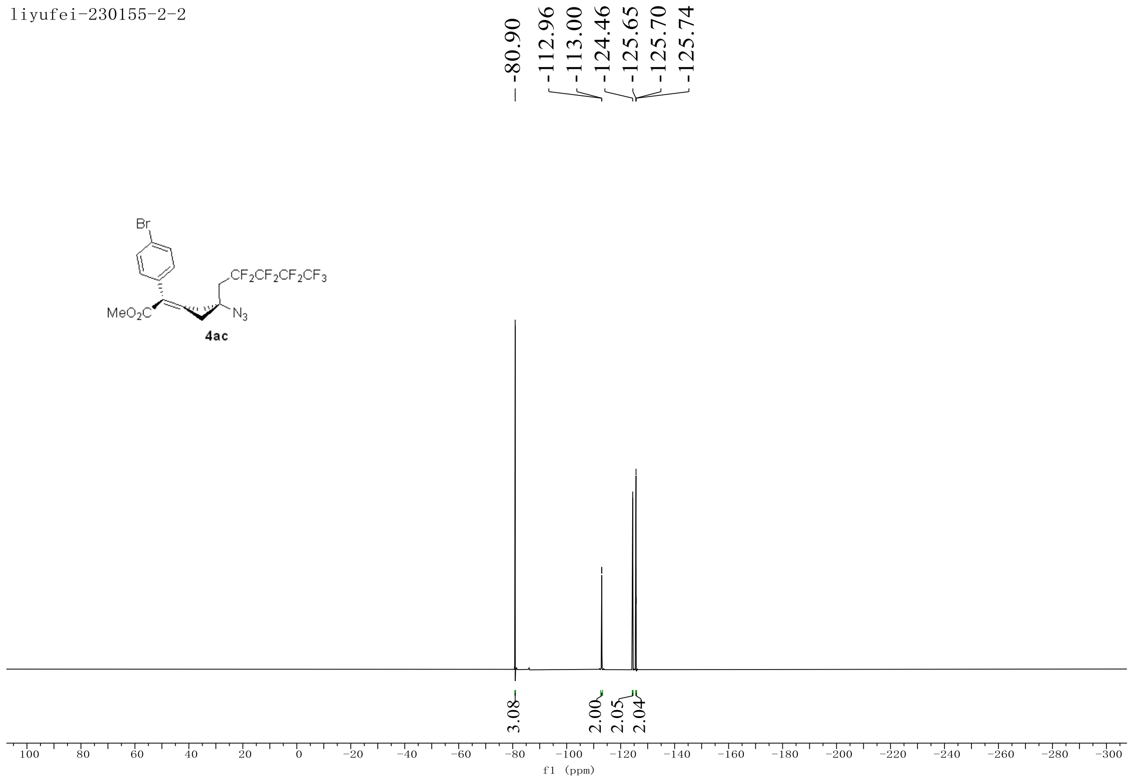

7.52 7.51 7.51 7.49 7.49 7.48 7.19 7.09 7.09 7.08 7.07 7.06 3.75 3.61 3.61 3.60 3.57 3.56 3.55 3.46 3.46 3.42 3.41 3.41 3.41 3.06 3.03 3.02 3.01 2.99 2.98 2.98 2.94 2.94 2.94 2.93 2.71 2.67 2.65 2.61
Br
C(CF3)2CF2CF2CF3
MeO2C
N3
4ab
2.00 2.00 3.00 2.05 2.02 2.00
f1 (ppm)

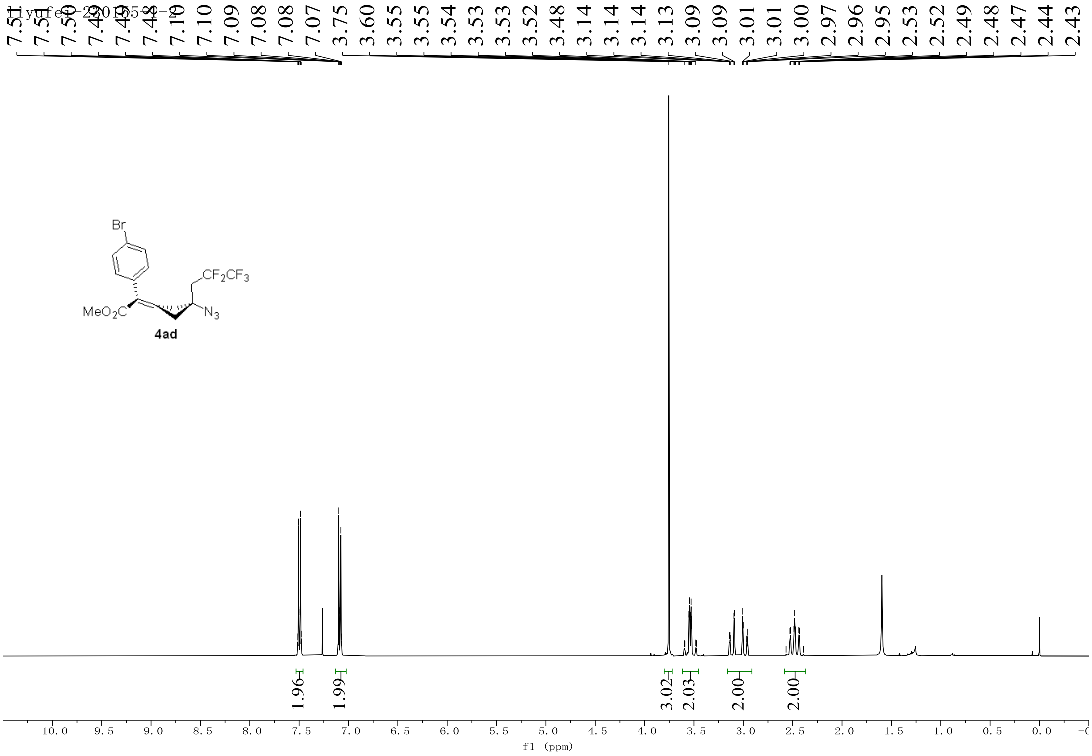

liyufei-230155-3-2-C
165.96
149.80
133.33 131.61 130.75 128.34 122.13
58.88 52.05 46.94 44.44 36.23
Br
C(CF3)2CF2CF2CF3
MeO2C
N3
4ab
f1 (ppm)

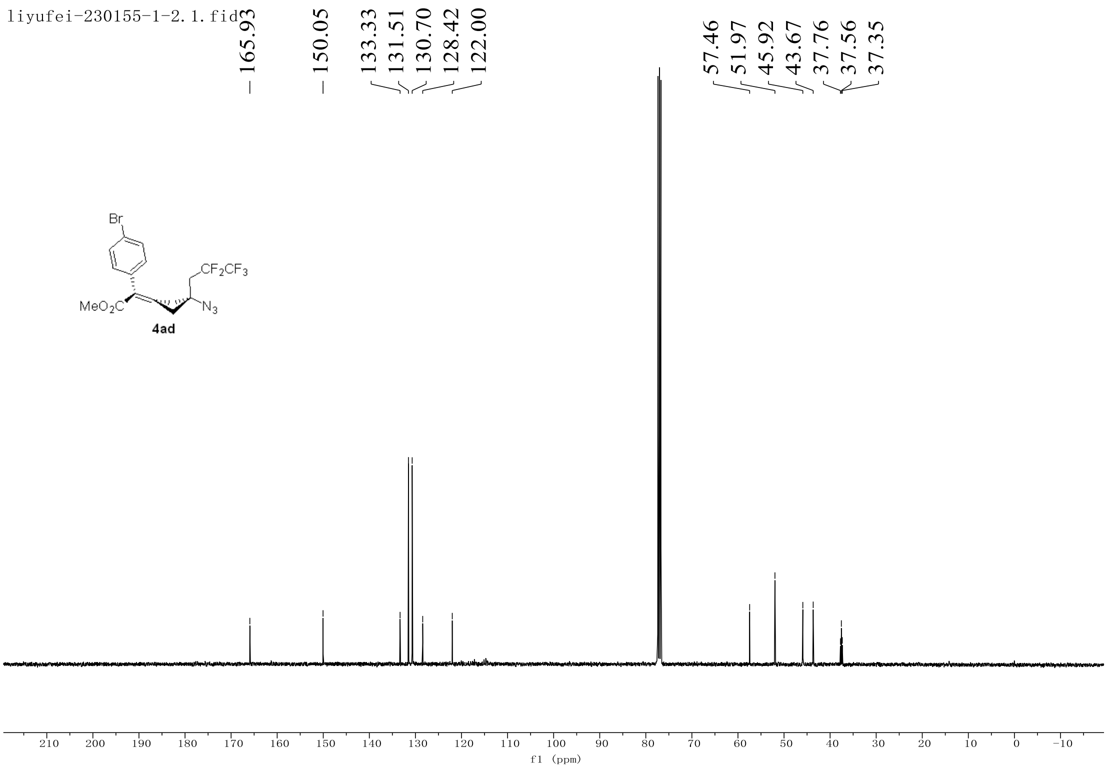

liyufei-230155-3-2
-61.97
-79.91
-79.96
-105.95
-105.99
-106.03
-106.04
-122.41
Br
C(CF3)2CF2CF2CF3
MeO2C
N3
4ab
6.00
3.04
1.97
1.97
f1 (ppm)

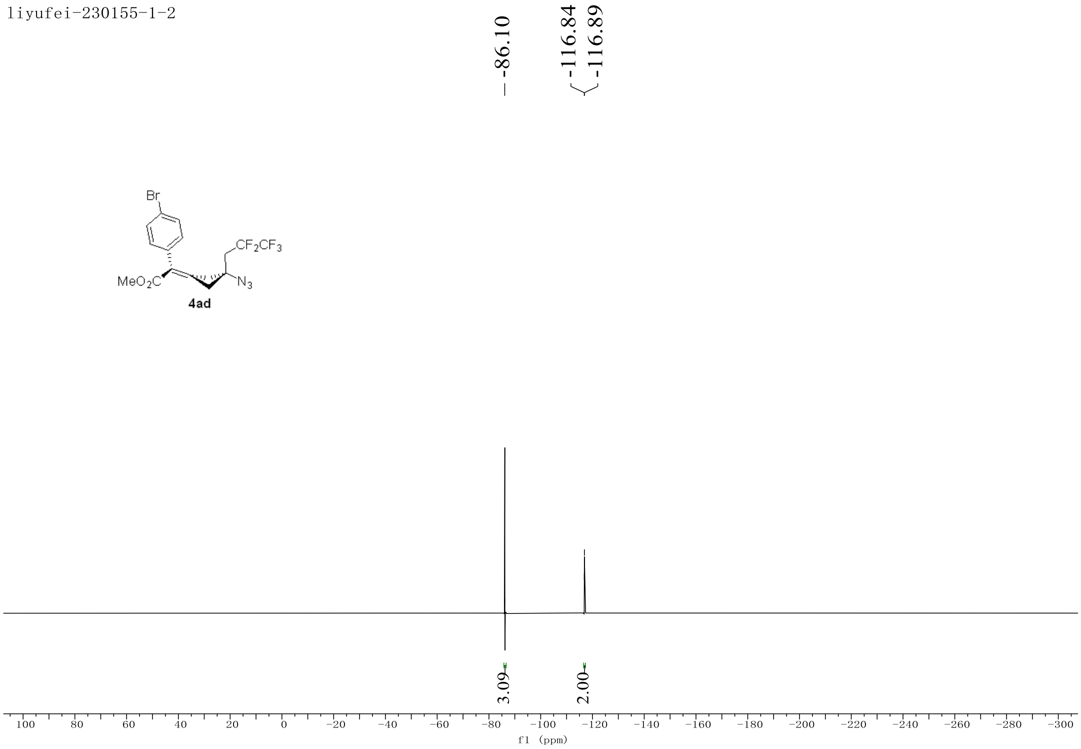

liyufei-230155-3-2
7.51
7.51
7.50
7.49
7.49
7.48
7.11
7.10
7.09
7.08
7.08
7.07
3.76
3.56
3.55
3.55
3.55
3.54
3.53
3.53
3.15
3.14
3.14
3.14
3.10
3.09
3.02
3.01
3.01
2.97
2.97
2.96
2.58
2.57
2.57
2.53
2.52
2.48
2.48
2.48
Br
CF2CF2CF2CF3
MeO2C
N3
4ac
2.00
2.00
3.00
2.04
2.02
2.01
f1 (ppm)


liyufei-230155-2-2.1.fid
165.93
150.07
133.32
131.51
130.70
128.44
122.01
57.59
51.97
46.02
43.75
37.81
37.60
37.39
Br
CF2CF2CF2CF3
MeO2C
N3
4ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

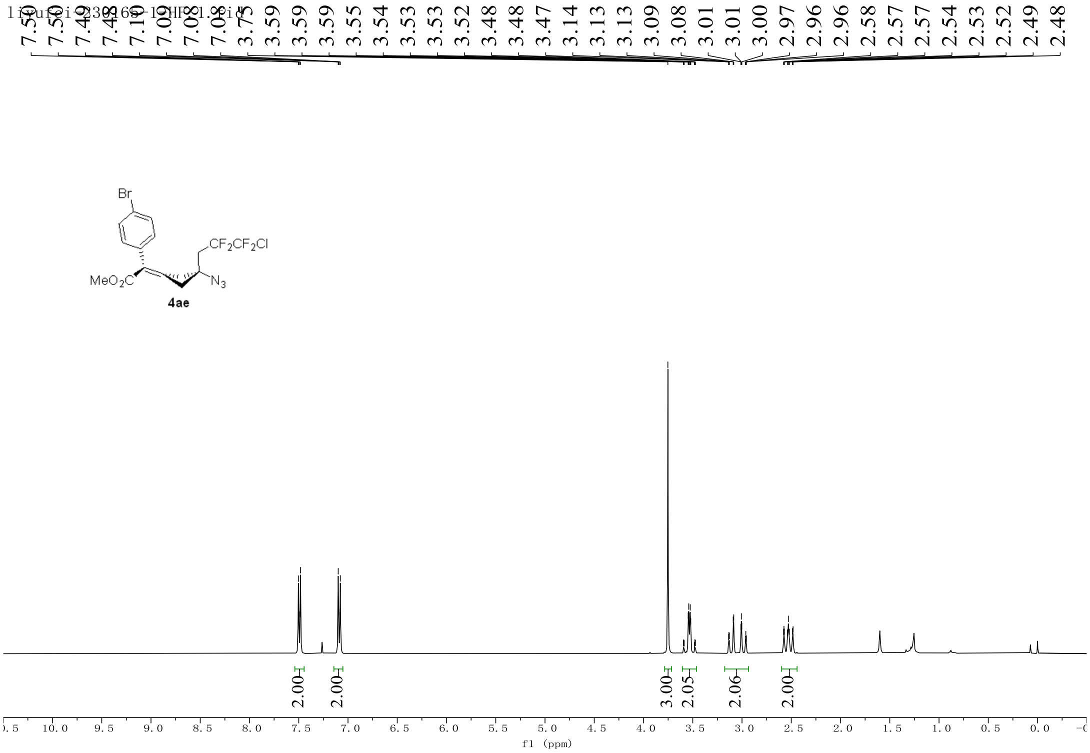

liyufei-230155-2-2
-80.90
-112.96
-113.00
-124.46
-125.65
-125.70
-125.74
Br
CF2CF2CF2CF3
MeO2C
N3
4ac
3.08
2.00
2.05
2.04
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


7.51 7.51 7.50 7.49 7.49 7.48 7.10 7.10 7.09 7.08 7.08 7.07 3.75 3.60 3.55 3.55 3.54 3.53 3.53 3.52 3.48 3.14 3.14 3.13 3.13 3.09 3.09 3.01 3.01 3.00 2.97 2.96 2.95 2.53 2.52 2.49 2.48 2.47 2.44 2.43
Br
CF_2CF_3
MeO_2C
N_3
4ad
1.96
1.99
3.02
2.03
2.00
2.00
f1 (ppm)

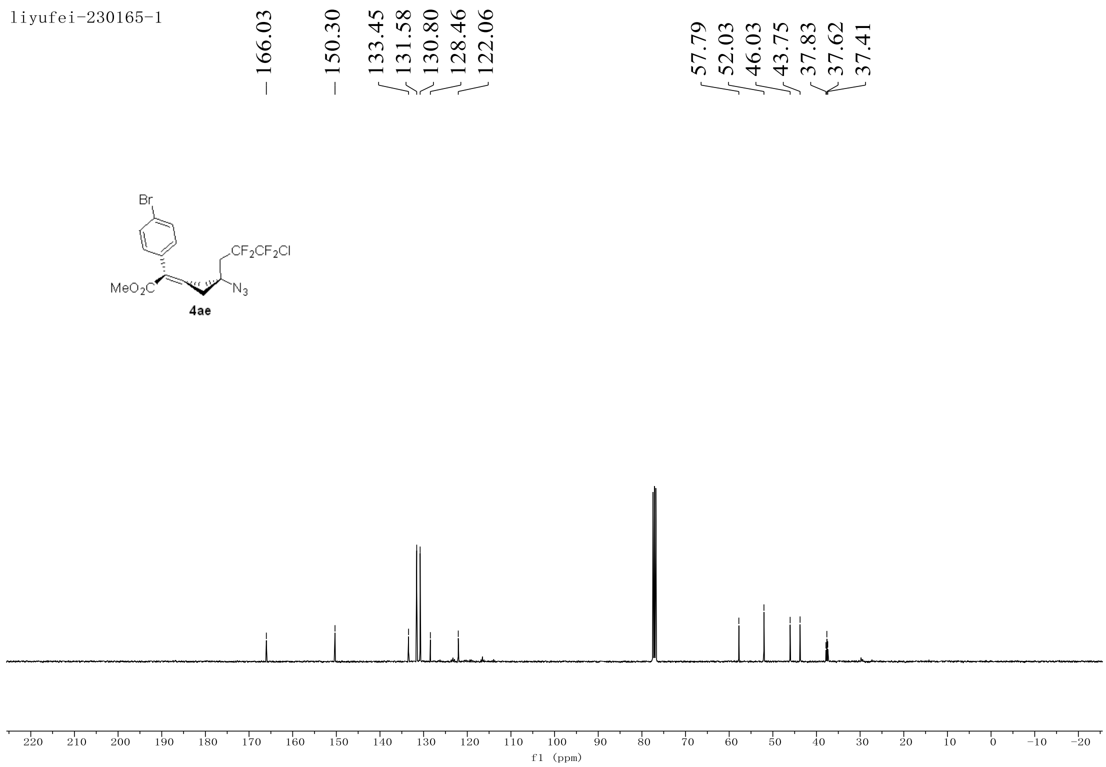

liyufei-230155-1-2.1.fid
165.93
150.05
133.33 131.51 130.70 128.42 122.00
57.46 51.97 45.92 43.67 37.76 37.56 37.35
Br
CF_2CF_3
MeO_2C
N_3
4ad
f1 (ppm)

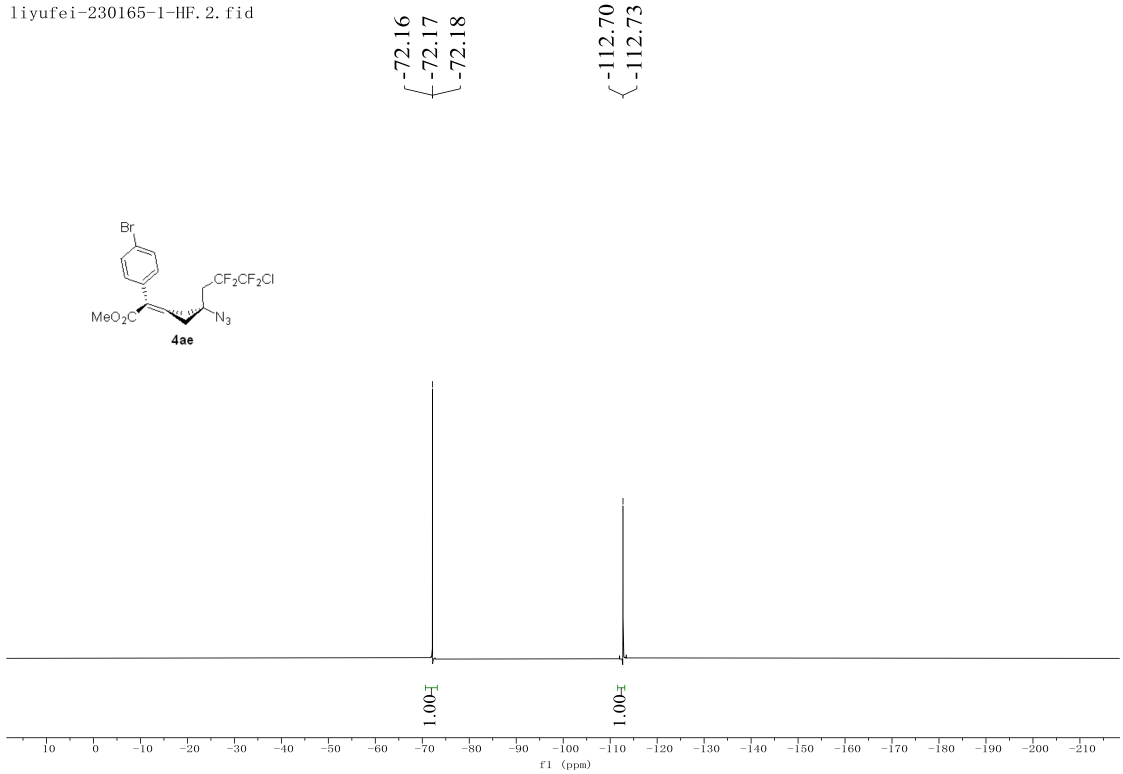


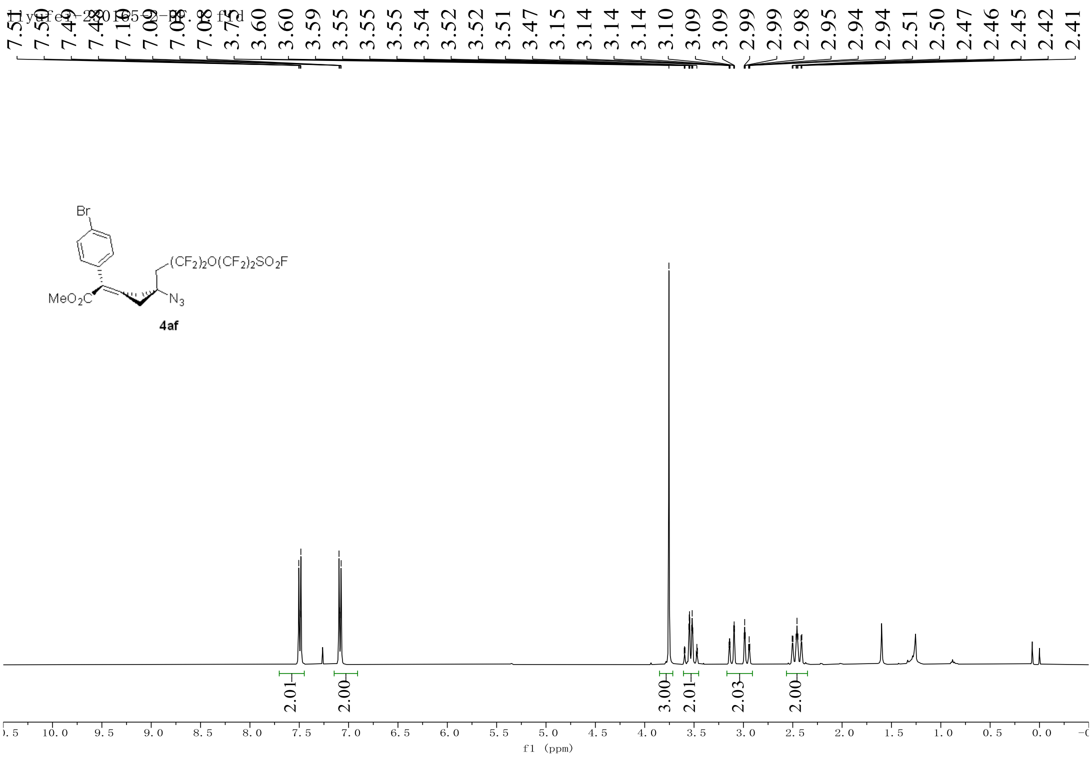
liyufei-230155-1-2
-86.10
-116.84
-116.89
Br
CF_2CF_3
MeO_2C
N_3
4ad
3.09
2.00
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300
f1 (ppm)

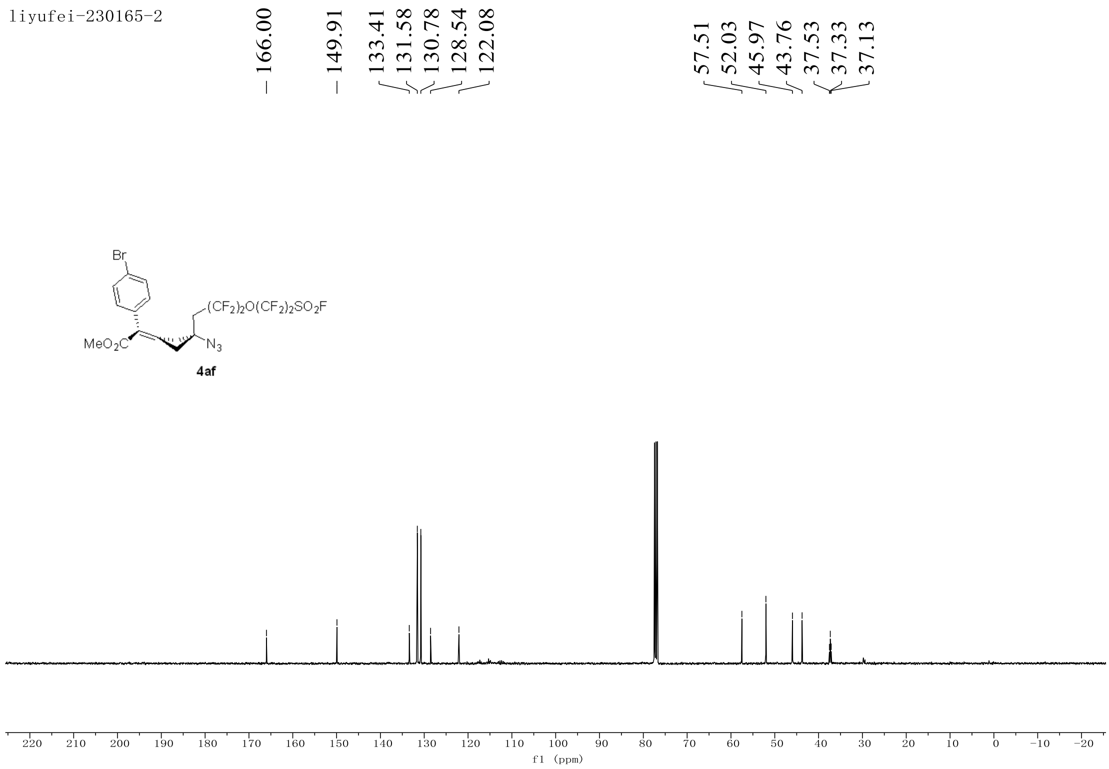


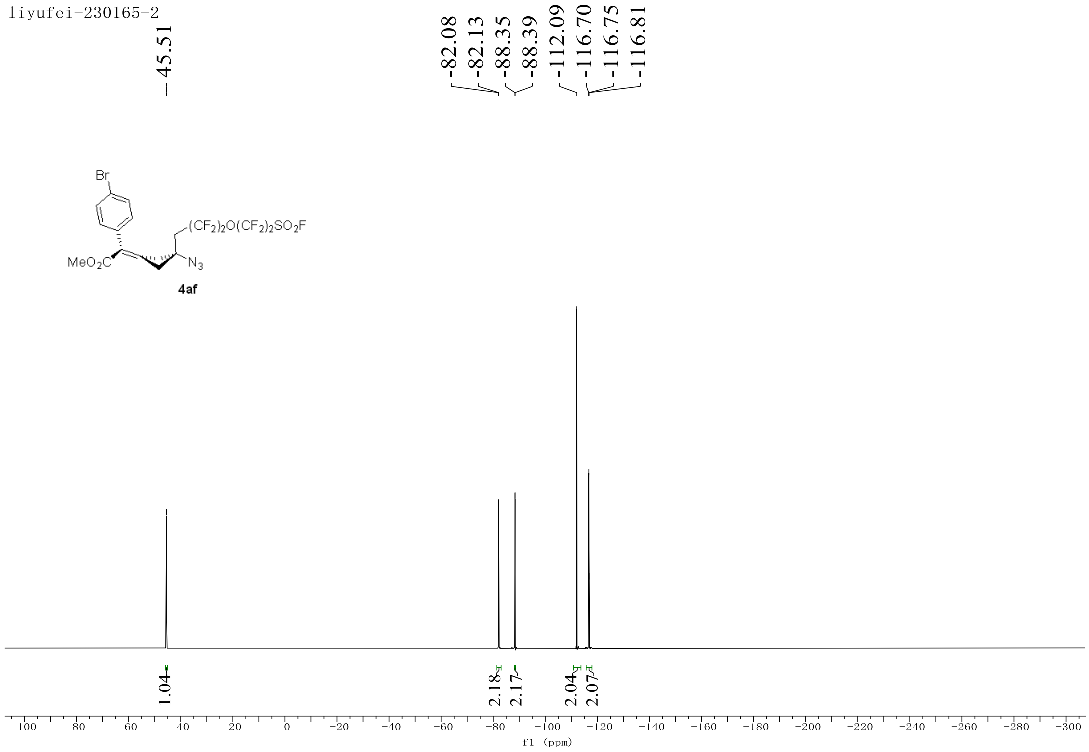
7.50 7.50 7.49 7.48 7.10 7.09 7.08 7.08 3.75 3.59 3.59 3.59 3.55 3.54 3.53 3.53 3.52 3.48 3.48 3.47 3.14 3.13 3.13 3.09 3.08 3.01 3.01 3.00 2.97 2.96 2.96 2.58 2.57 2.57 2.54 2.53 2.52 2.49 2.48
Br
CF_2CF_2Cl
MeO_2C
N_3
4ae
2.00
2.00
3.00
2.05
2.06
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

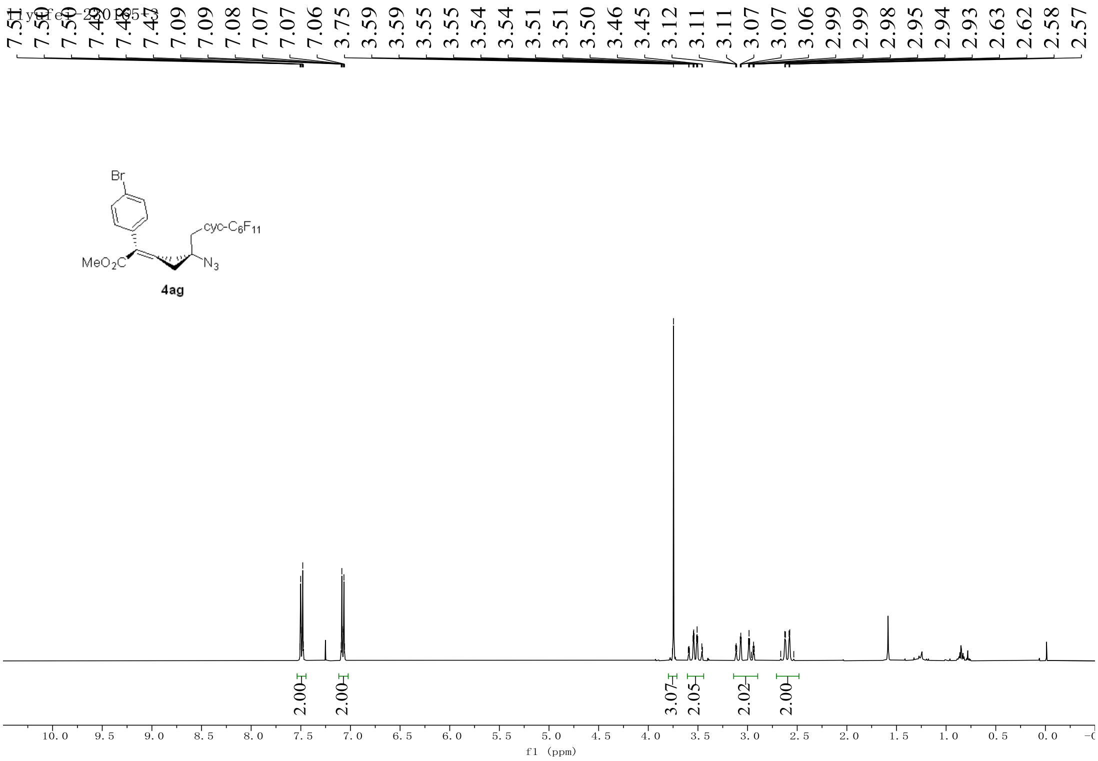

liyufei-230165-1
166.03
150.30
133.45
131.58
130.80
128.46
122.06
57.79
52.03
46.03
43.75
37.83
37.62
37.41
Br
CF2CF2Cl
MeO2C
N3
4ae
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


liyufei-230165-1-HF.2.fid
-72.16
-72.17
-72.18
-112.70
-112.73
Br
CF2CF2Cl
MeO2C
N3
4ae
1.00
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.51 7.50 7.49 7.48 7.10 7.09 7.08 7.08 3.75 3.60 3.60 3.59 3.55 3.55 3.55 3.54 3.52 3.52 3.51 3.47 3.15 3.14 3.14 3.14 3.10 3.09 3.09 2.99 2.99 2.98 2.95 2.94 2.94 2.51 2.50 2.47 2.46 2.45 2.42 2.41
Br
(CF2)2O(CF2)2SO2F
MeO2C
N3
4af
2.01
2.00
3.00
2.01
2.03
2.00
f1 (ppm)


liyufei-230165-2
166.00
149.91
133.41 131.58 130.78 128.54 122.08
57.51 52.03 45.97 43.76 37.53 37.33 37.13
Br
(CF2)2O(CF2)2SO2F
MeO2C
N3
4af
f1 (ppm)


liyufei-230165-2
-45.51
-82.08
-82.13
-88.35
-88.39
-112.09
-116.70
-116.75
-116.81
Br
(CF2)2O(CF2)2SO2F
MeO2C
N3
4af
1.04
2.18
2.17
2.04
2.07
f1 (ppm)


liyufei-230165-3
7.51
7.50
7.50
7.49
7.48
7.43
7.09
7.09
7.08
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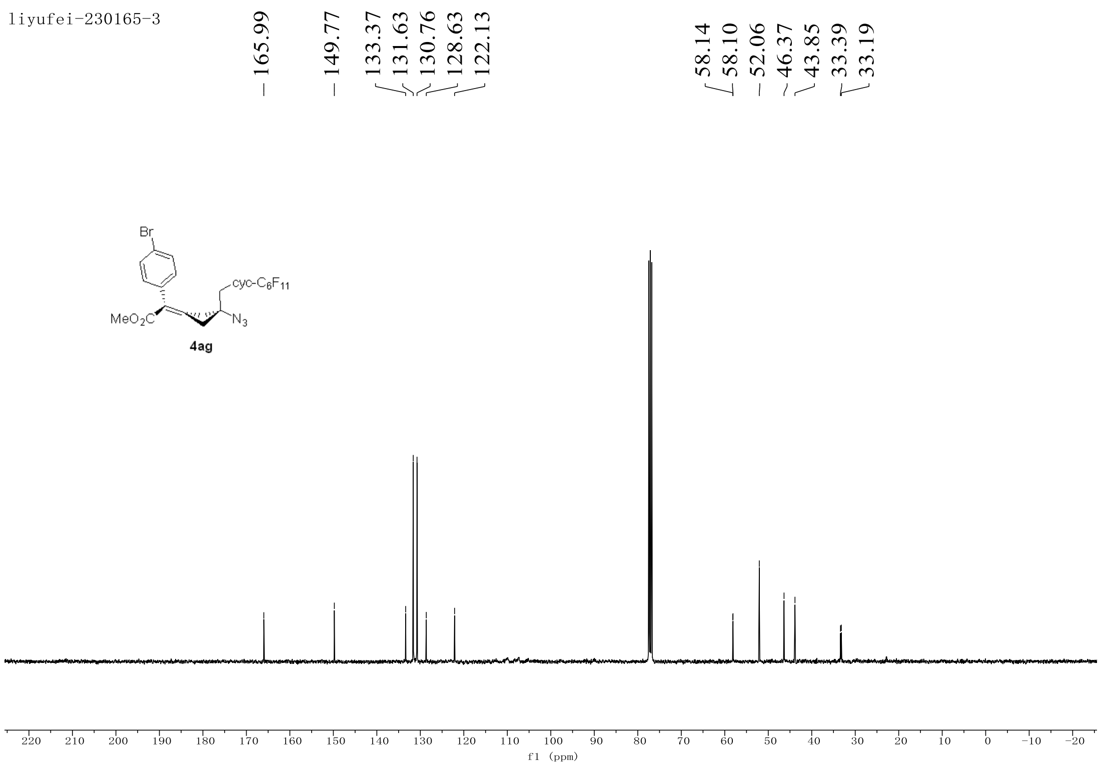
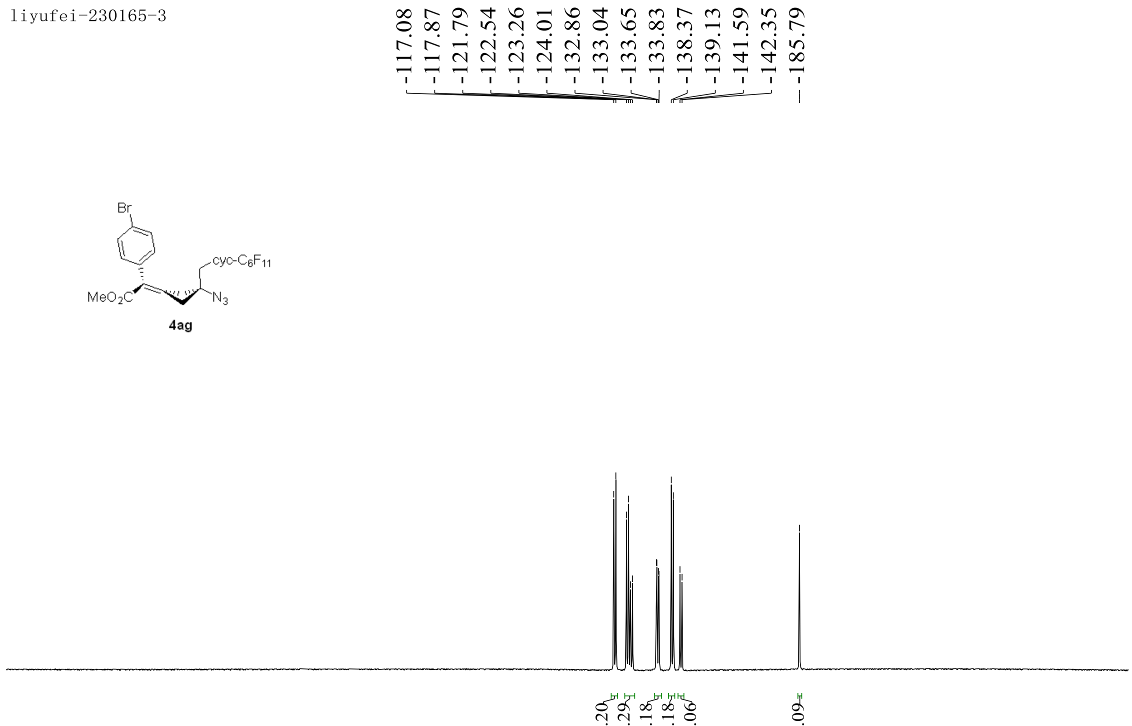
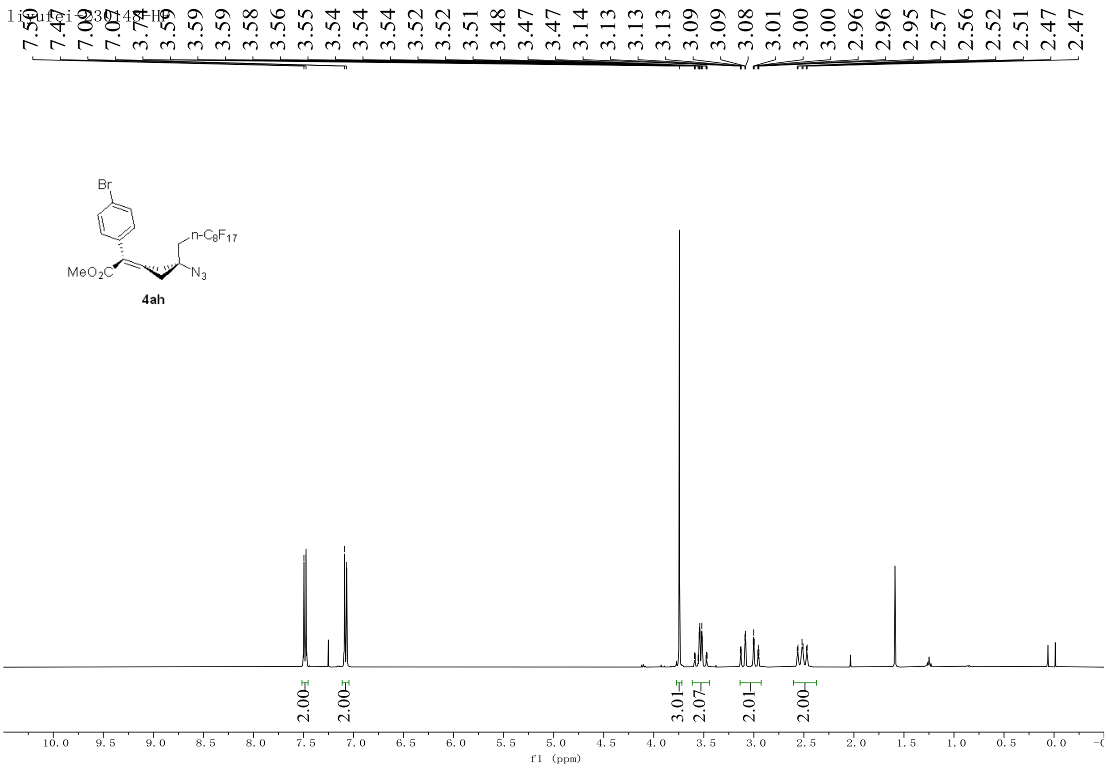
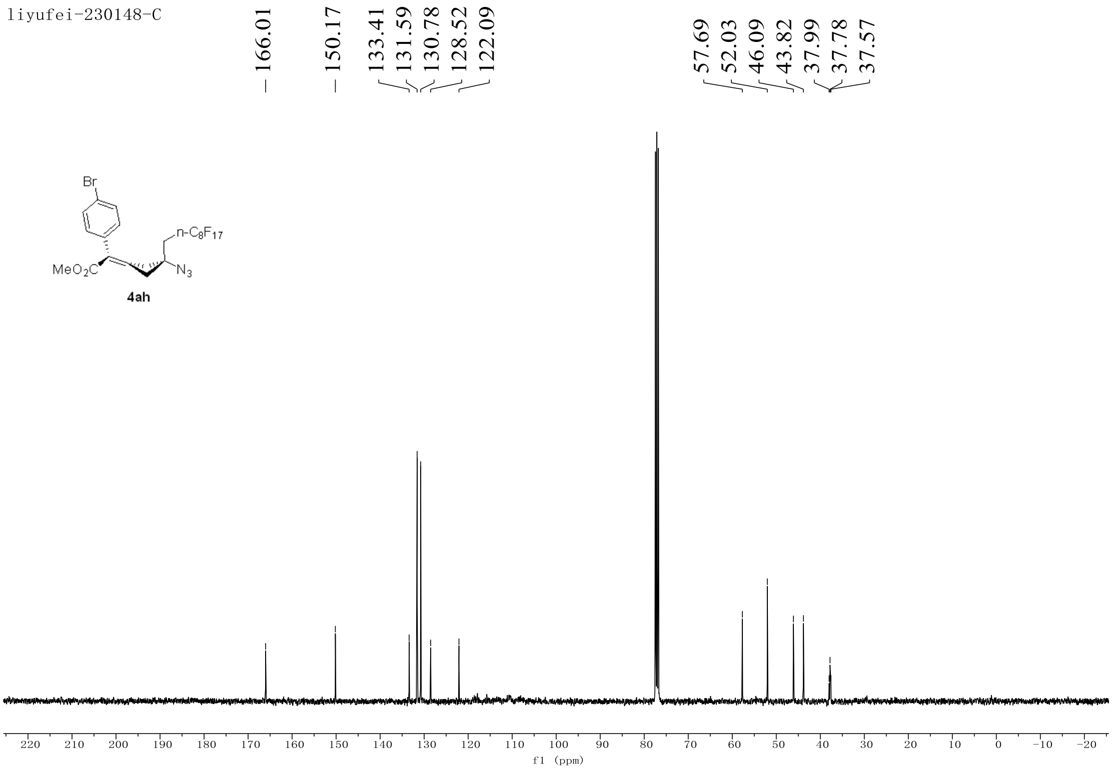
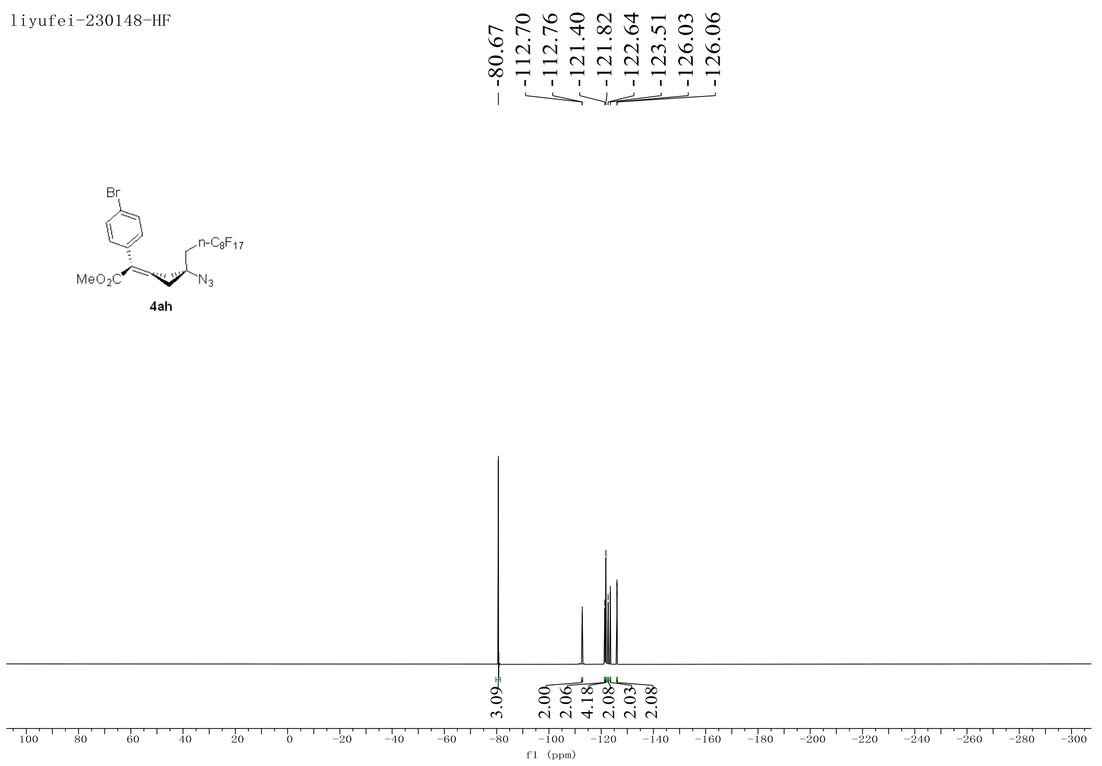
7.07
7.06
3.75
3.59
3.59
3.55
3.55
3.54
3.54
3.51
3.51
3.50
3.46
3.45
3.12
3.11
3.11
3.07
3.07
3.06
2.99
2.99
2.98
2.95
2.94
2.93
2.63
2.62
2.58
2.57
Br
cyc-C6F11
MeO2C
N3
4ag
2.00
2.00
3.07
2.05
2.02
2.00
f1 (ppm)


liyufei-230165-3
165.99
149.77
133.37
131.63
130.76
128.63
122.13
58.14
58.10
52.06
46.37
43.85
33.39
33.19
Br
cyc-C6F11
MeO2C
N3
4ag
f1 (ppm)

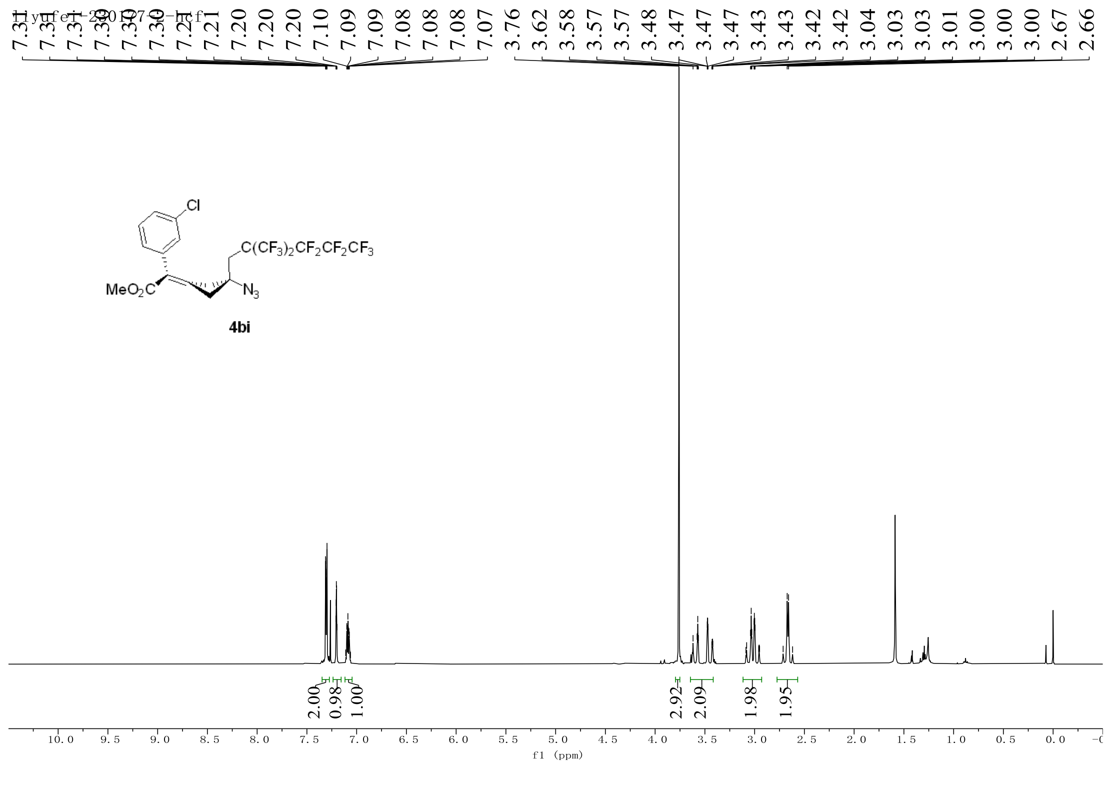

liyufei-230165-3
-117.08
-117.87
-121.79
-122.54
-123.26
-124.01
-132.86
-133.04
-133.65
-133.83
-138.37
-139.13
-141.59
-142.35
-185.79
Br
cyc-C6F11
MeO2C
N3
4ag
2.20
3.29
2.18
2.18
1.06
1.09
f1 (ppm)


liyufei-230148-H
7.50 7.47 7.09 7.07 3.74 3.59 3.59 3.59 3.58 3.56 3.55 3.54 3.54 3.54 3.52 3.52 3.51 3.48 3.47 3.47 3.14 3.13 3.13 3.13 3.09 3.09 3.08 3.01 3.00 3.00 2.96 2.96 2.95 2.57 2.56 2.52 2.51 2.47 2.47
Br
n-C_8F_{17}
MeO_2C
N_3
4ah
2.00
2.00
3.01
2.07
2.01
2.00
f1 (ppm)

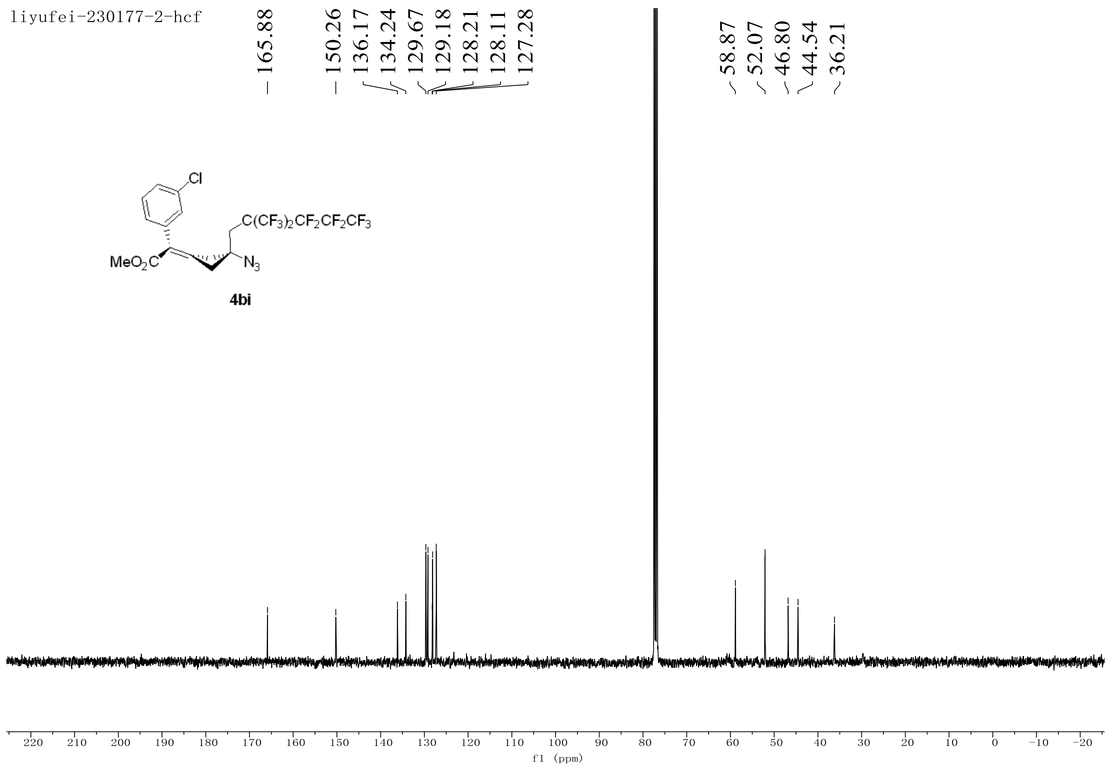

liyufei-230148-C
166.01
150.17
133.41 131.59 130.78 128.52 122.09
57.69 52.03 46.09 43.82 37.99 37.78 37.57
Br
n-C_8F_{17}
MeO_2C
N_3
4ah
f1 (ppm)



liyufei-230148-HF
-80.67
-112.70
-112.76
-121.40
-121.82
-122.64
-123.51
-126.03
-126.06
Br
n-C8F17
MeO2C
N3
4ah
3.09
2.00
2.06
4.18
2.08
2.03
2.08
f1 (ppm)



7.31
7.31
7.31
7.30
7.30
7.30
7.22
7.21
7.20
7.20
7.20
7.10
7.09
7.09
7.08
7.08
7.08
7.07
3.76
3.62
3.58
3.57
3.57
3.48
3.47
3.47
3.47
3.43
3.43
3.42
3.42
3.04
3.03
3.03
3.01
3.00
3.00
3.00
2.67
2.66
Cl
C(CF3)2CF2CF2CF3
MeO2C
N3
4bi
2.00
0.98
1.00
2.92
2.09
1.98
1.95
f1 (ppm)


liyufei-230177-2-hcf
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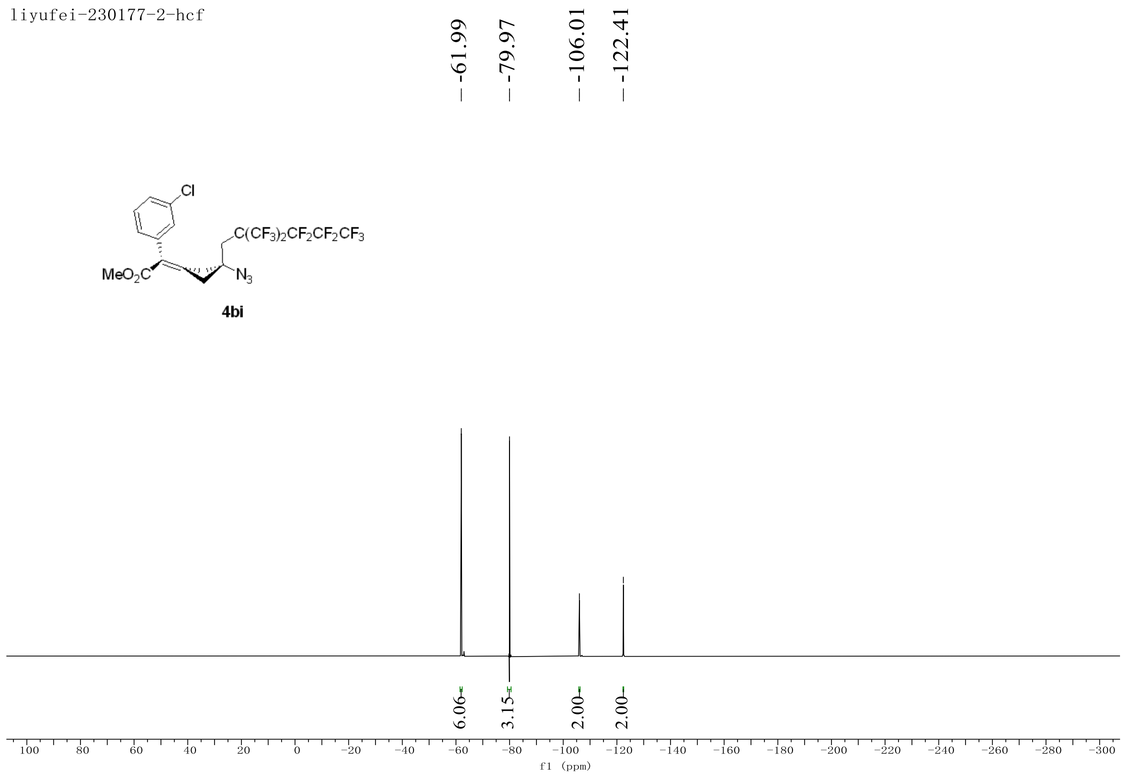
150.26
136.17
134.24
129.67
129.18
128.21
128.11
127.28
58.87
52.07
46.80
44.54
36.21
Cl
C(CF3)2CF2CF2CF3
MeO2C
N3
4bi
f1 (ppm)


liyufei-230177-2-hcf
-61.99
-79.97
-106.01
-122.41
Cl
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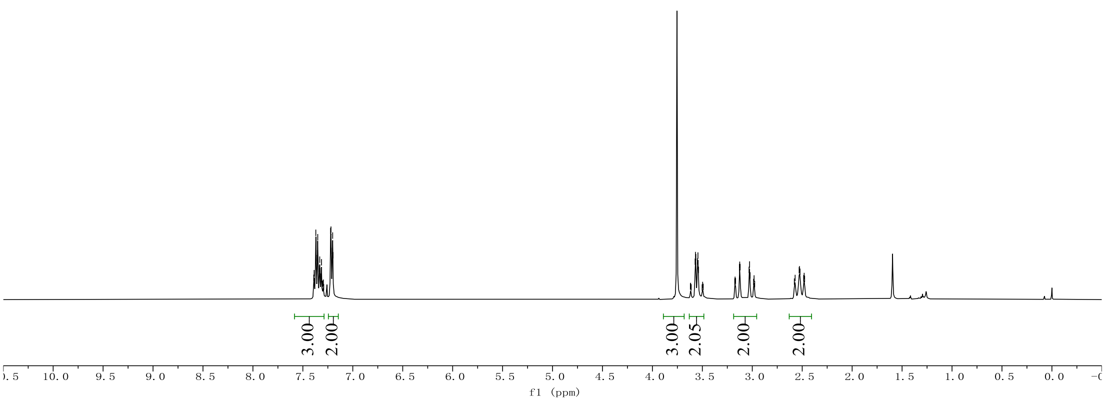
MeO2C
N3
4bi
6.06
3.15
2.00
2.00
f1 (ppm)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7.39
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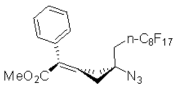
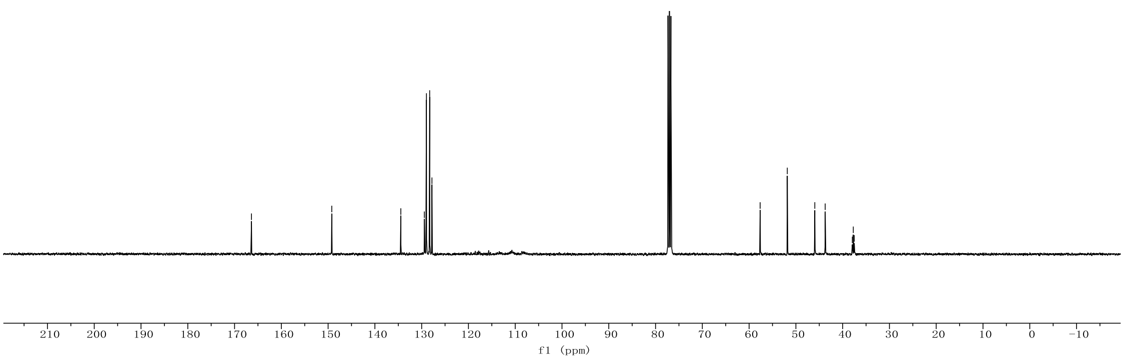
7.35
7.35
7.35
7.33
7.33
7.33
7.32
7.31
7.22
7.22
7.21
7.20
7.20
3.75
3.57
3.57
3.56
3.55
3.54
3.54
3.18
3.17
3.17
3.13
3.13
3.12
3.03
3.03
3.02
2.98
2.57
2.53
2.53
2.52
2.49
2.48
2.48
3.00
2.00
3.00
2.05
2.00
2.00
f1 (ppm)


n-C8F17
MeO2C
N3

4dj


liyufei-230175-2.2.fid
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149.22
134.45
129.43
128.98
128.29
127.80
57.64
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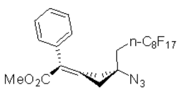
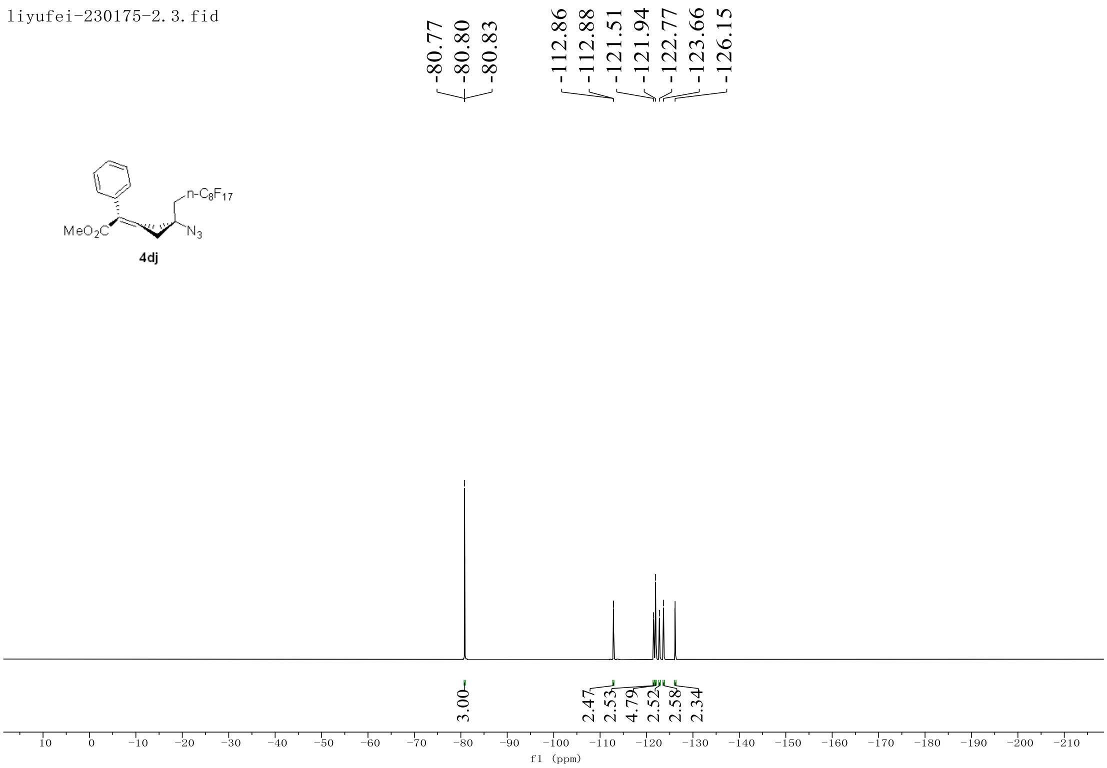
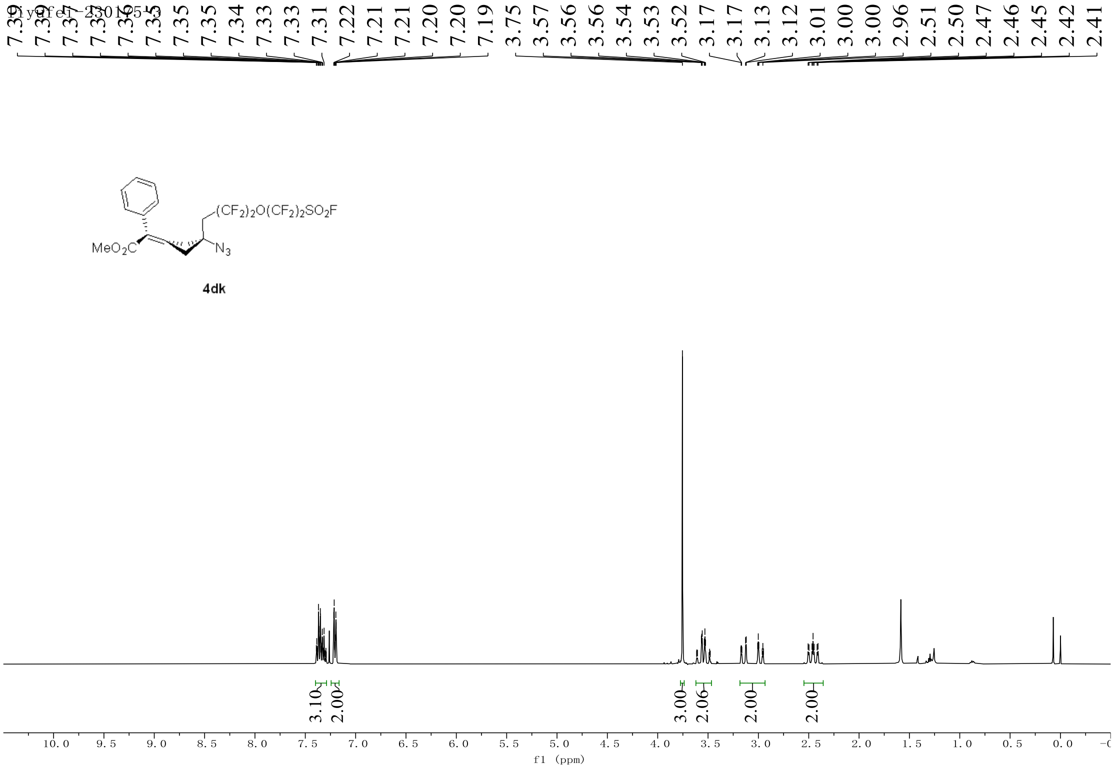
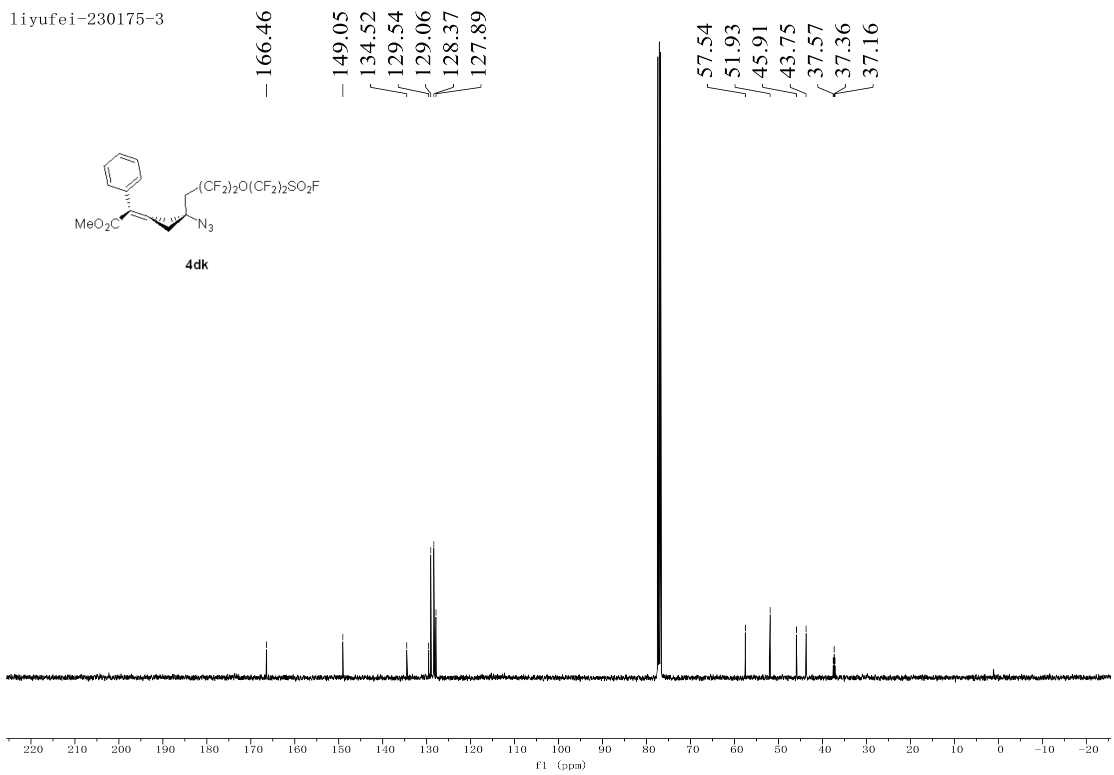
37.73
37.52
f1 (ppm)

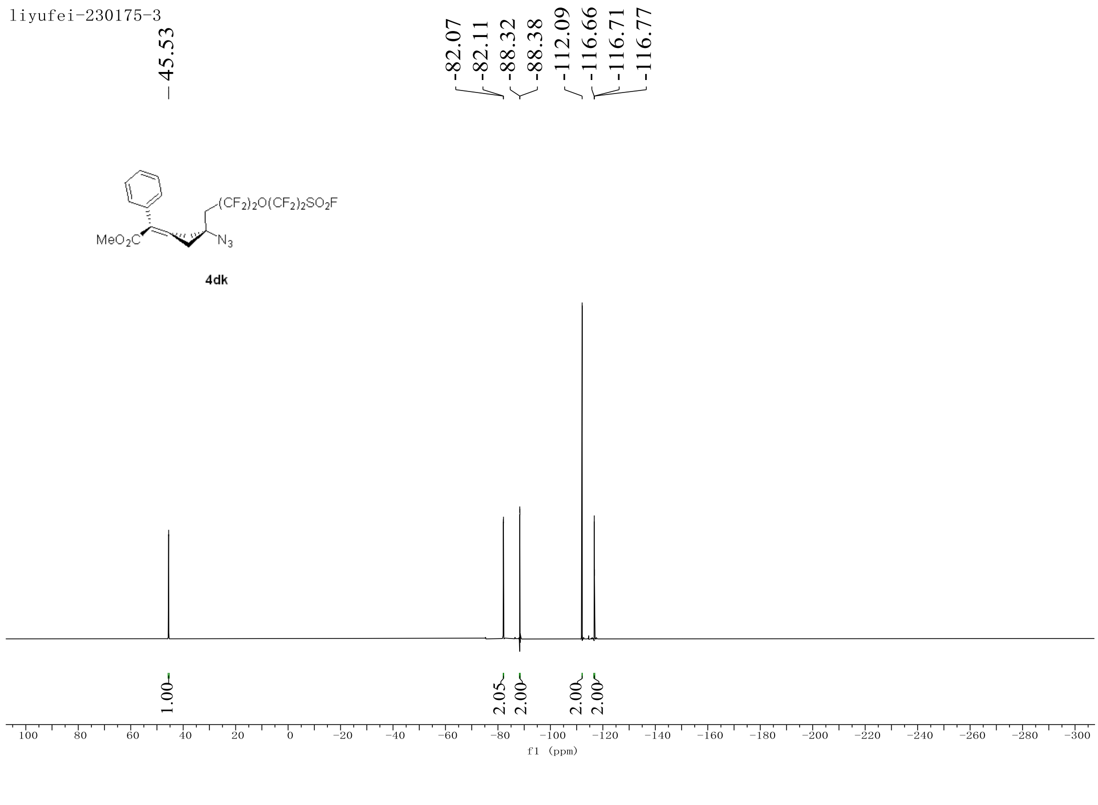

n-C8F17
MeO2C
N3

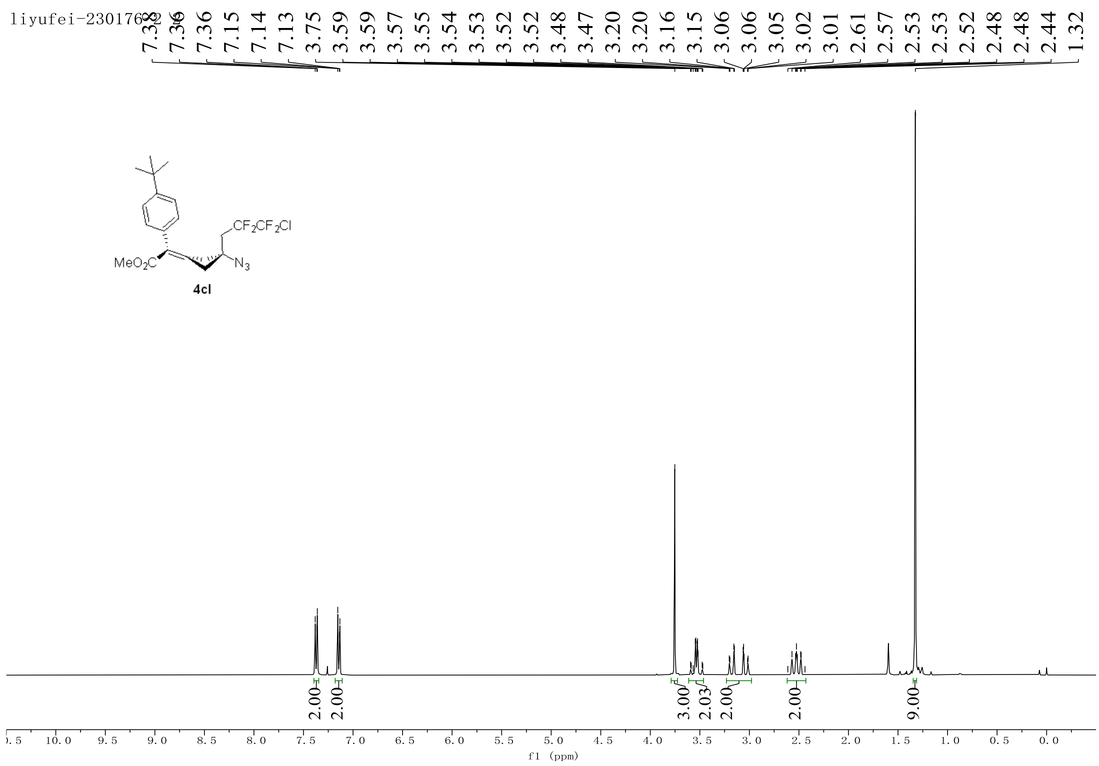
4dj


liyufei-230175-2.3.fid
-80.77
-80.80
-80.83
-112.86
-112.88
-121.51
-121.94
-122.77
-123.66
-126.15
n-C_8F_{17}
MeO_2C
N_3
4dj
3.00
2.47
2.53
4.79
2.52
2.58
2.34
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


liyufei-23017…
7.39 7.39 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.33 7.33 7.31 7.22 7.21 7.21 7.20 7.20 7.19 3.75 3.57 3.56 3.56 3.54 3.53 3.52 3.17 3.17 3.13 3.12 3.01 3.00 3.00 2.96 2.51 2.50 2.47 2.46 2.45 2.42 2.41
$(CF_2)_2O(CF_2)_2SO_2F$
MeO_2C
N_3
4dk
3.10
2.00
3.00
2.06
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


liyufei-230175-3
166.46
149.05
134.52
129.54
129.06
128.37
127.89
57.54
51.93
45.91
43.75
37.57
37.36
37.16
MeO2C
(CF2)2O(CF2)2SO2F
N3
4dk
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


liyufei-230175-3
45.53
-82.07
-82.11
-88.32
-88.38
-112.09
-116.66
-116.71
-116.77
MeO2C
(CF2)2O(CF2)2SO2F
N3
4dk
1.00
2.05
2.00
2.00
2.00
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300
f1 (ppm)


liyufei-230176-2
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CF2CF2Cl
MeO2C
N3
4cl
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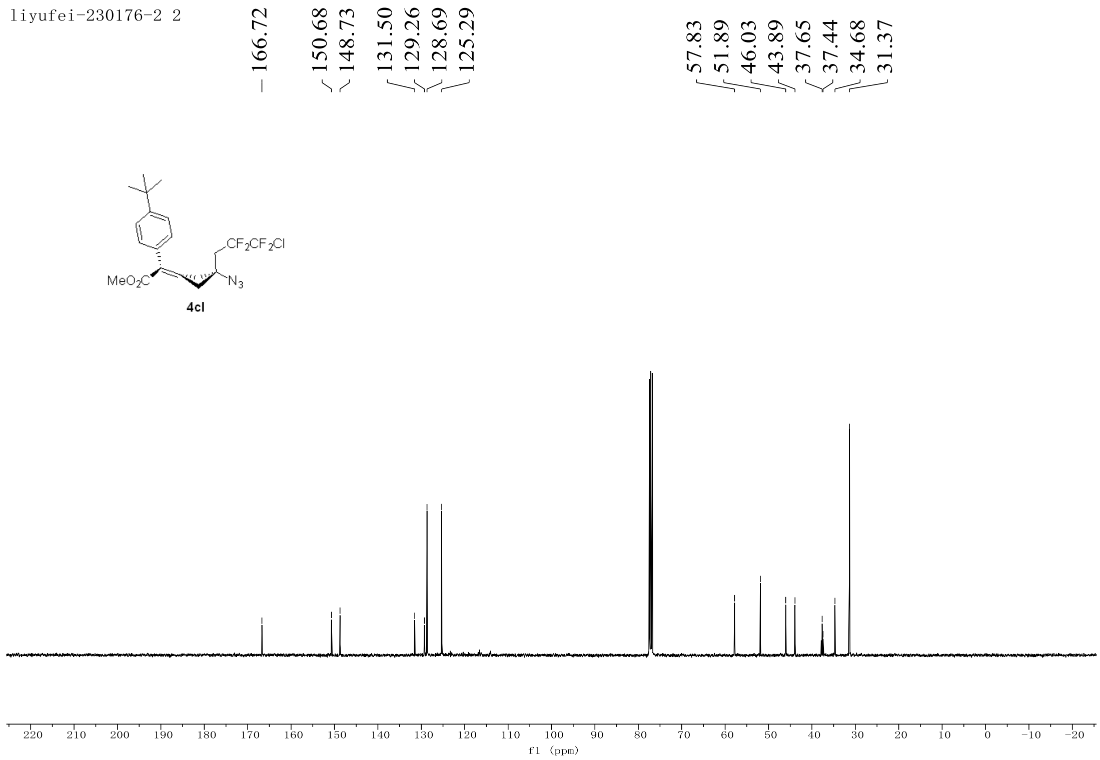
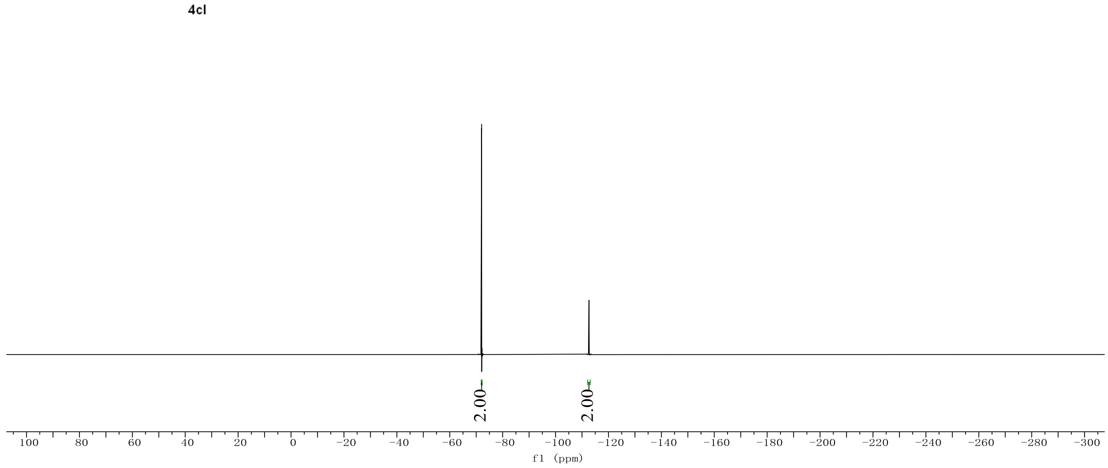
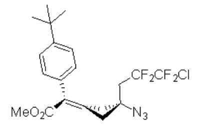
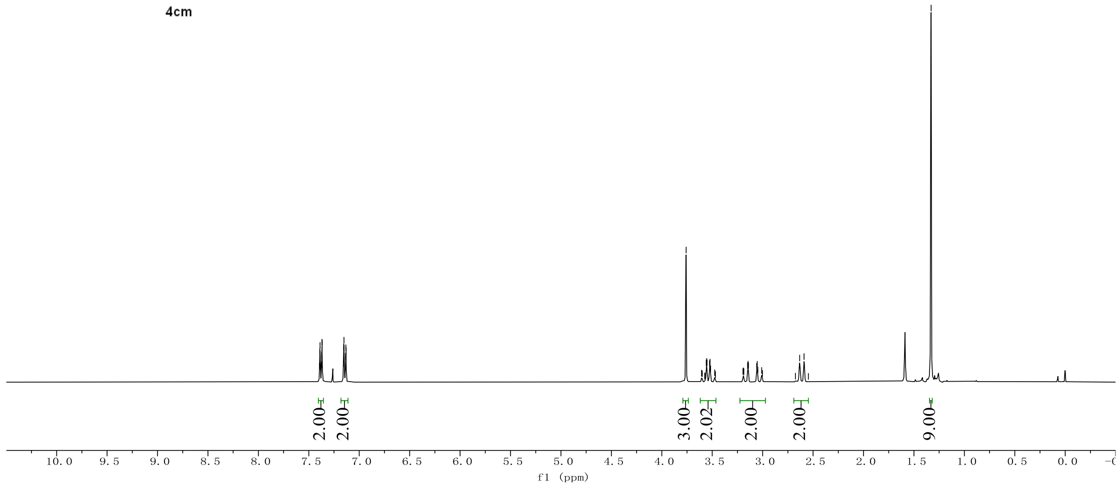
f1 (ppm)

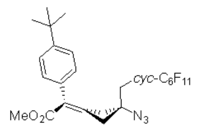

liyufei-230176-2 2
166.72 150.68 148.73 131.50 129.26 128.69 125.29 57.83 51.89 46.03 43.89 37.65 37.44 34.68 31.37
CF2CF2Cl
MeO2C
N3
4cl
f1 (ppm)


liyufei-230176-2 2
-72.05
-112.62
2.00
2.00
f1 (ppm)

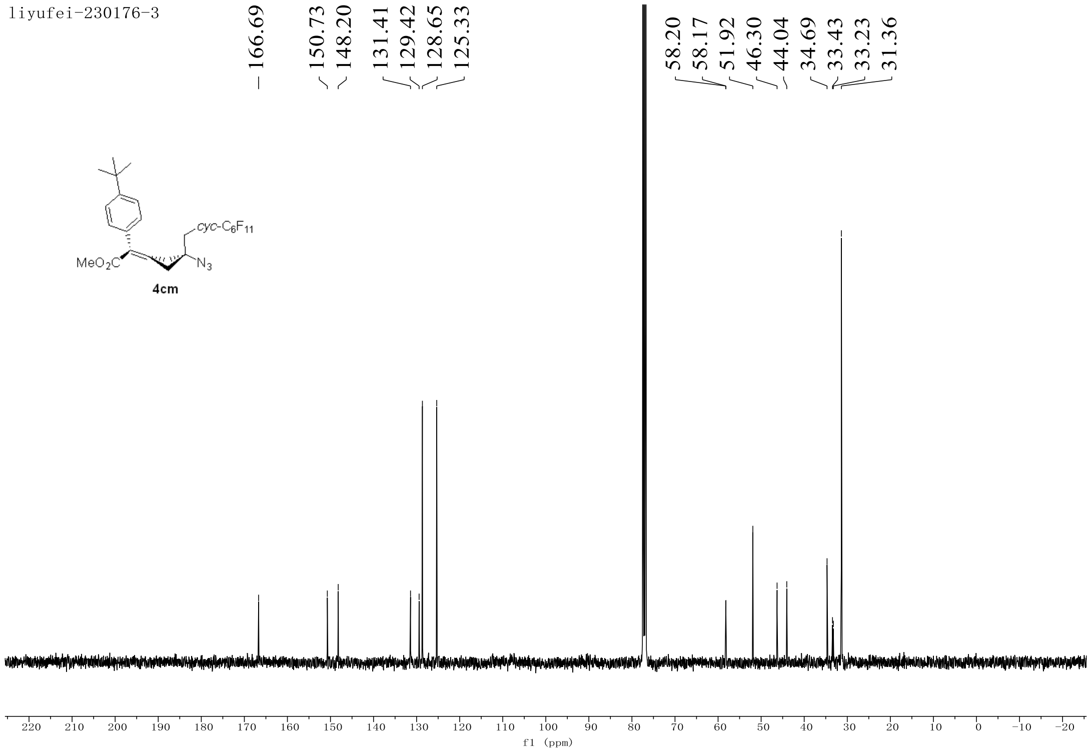

CF2CF2Cl
MeO2C
N3

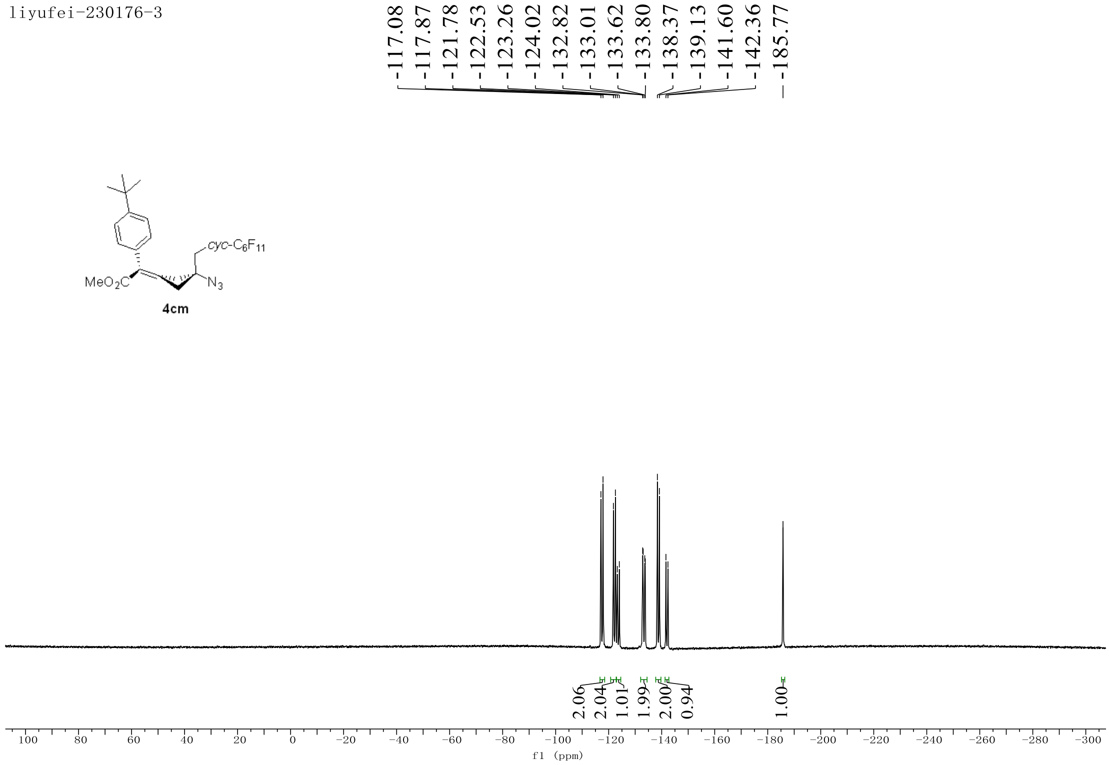
4cl

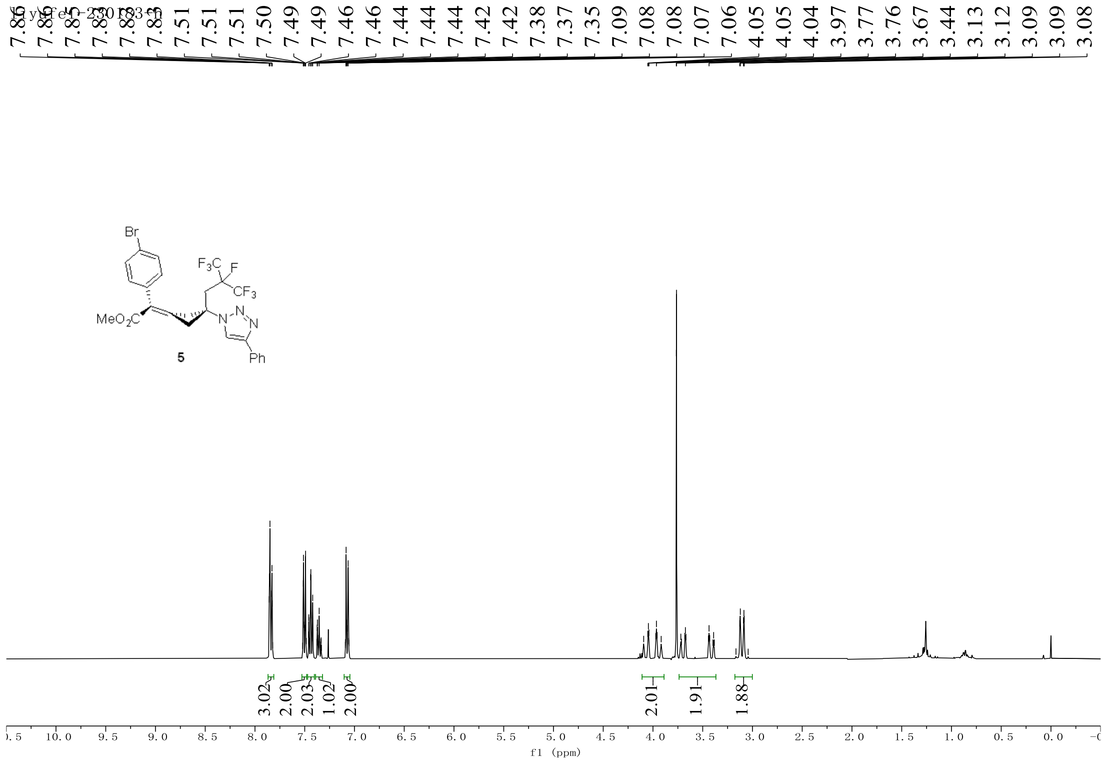

liyufei-230176-3
7.39
7.39
7.39
7.38
7.37
7.37
7.37
7.37
7.16
7.15
7.15
7.13
7.13
7.13
3.76
3.61
3.60
3.57
3.56
3.55
3.55
3.53
3.52
3.52
3.48
3.47
3.19
3.19
3.19
3.15
3.14
3.14
3.06
3.05
3.05
3.01
3.00
2.63
2.59
1.33
2.00
2.00
3.00
2.02
2.00
2.00
9.00
f1 (ppm)


cyc-C6F11
MeO2C
N3

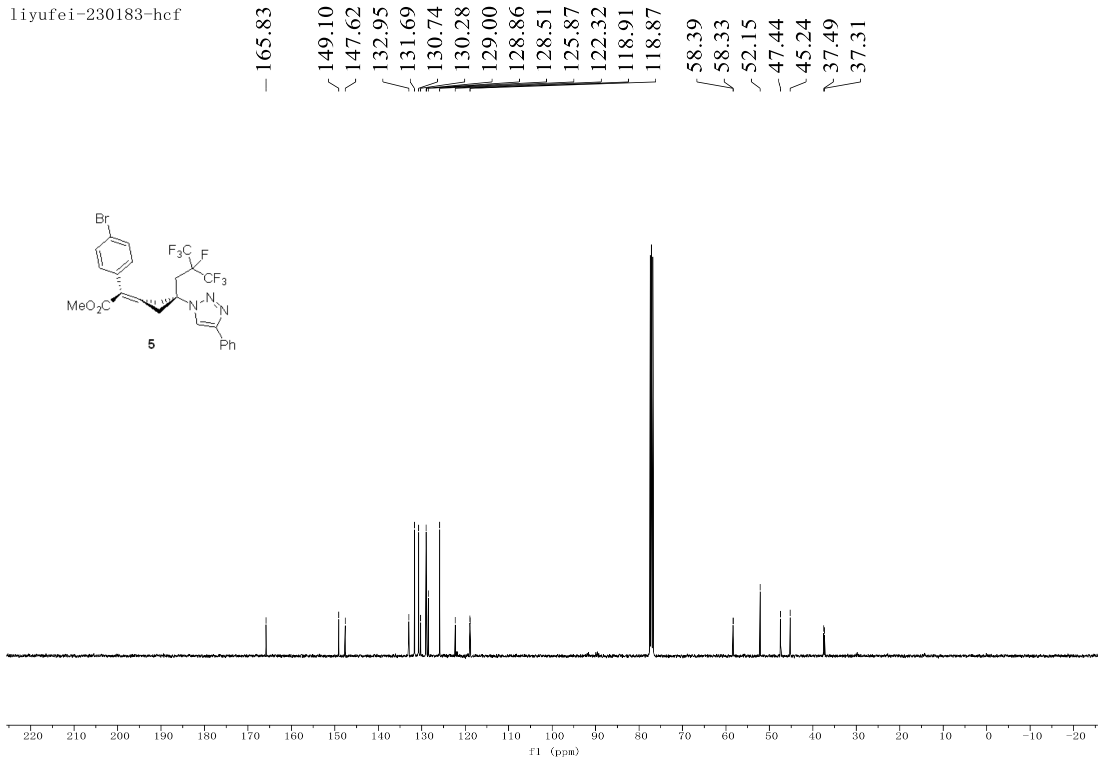
4cm


liyufei-230176-3
166.69
150.73
148.20
131.41
129.42
128.65
125.33
58.20
58.17
51.92
46.30
44.04
34.69
33.43
33.23
31.36
cyc-C6F11
MeO2C
N3
4cm
f1 (ppm)

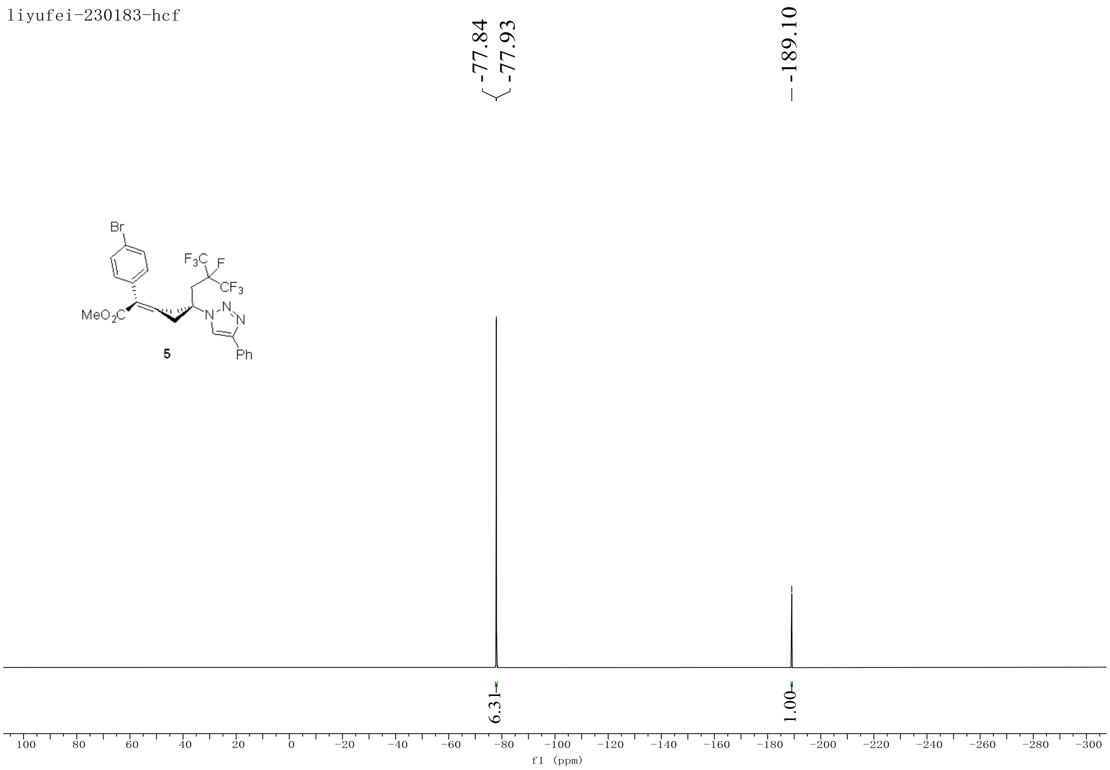

liyufei-230176-3
-117.08
-117.87
-121.78
-122.53
-123.26
-124.02
-132.82
-133.01
-133.62
-133.80
-138.37
-139.13
-141.60
-142.36
-185.77
cyc-C6F11
MeO2C
N3
4cm
2.06
2.04
1.01
1.99
2.00
0.94
1.00
f1 (ppm)

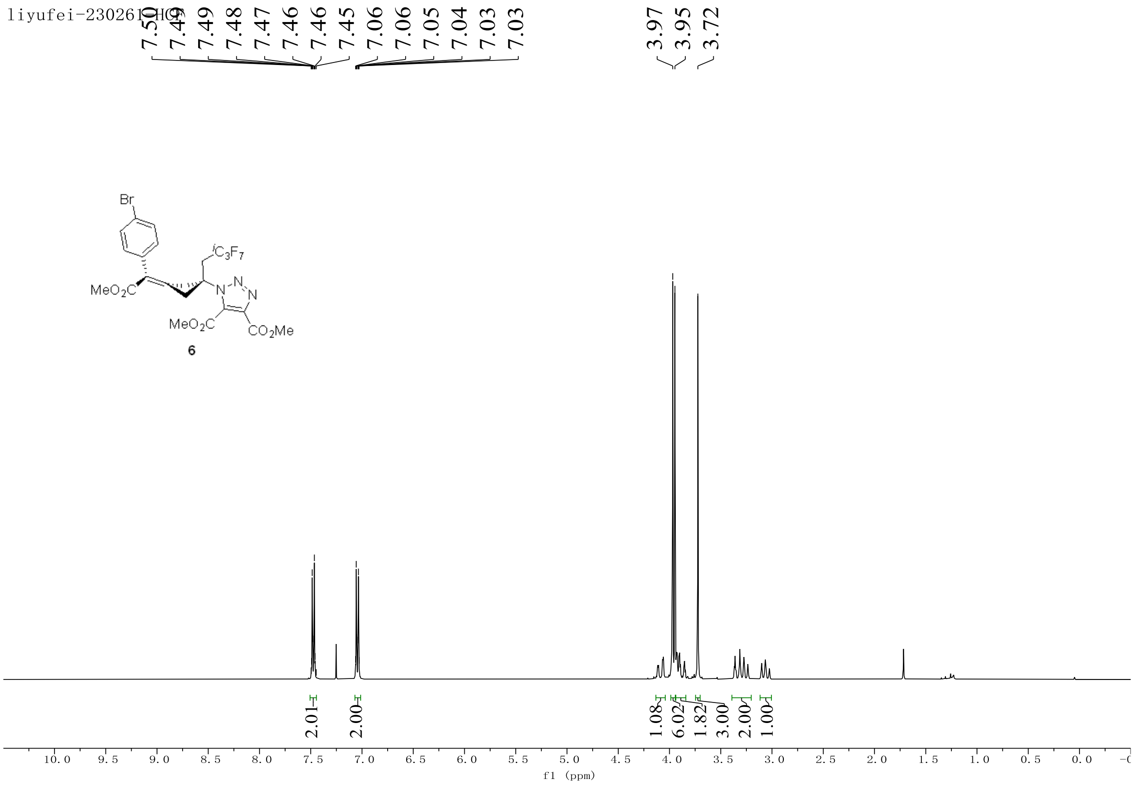


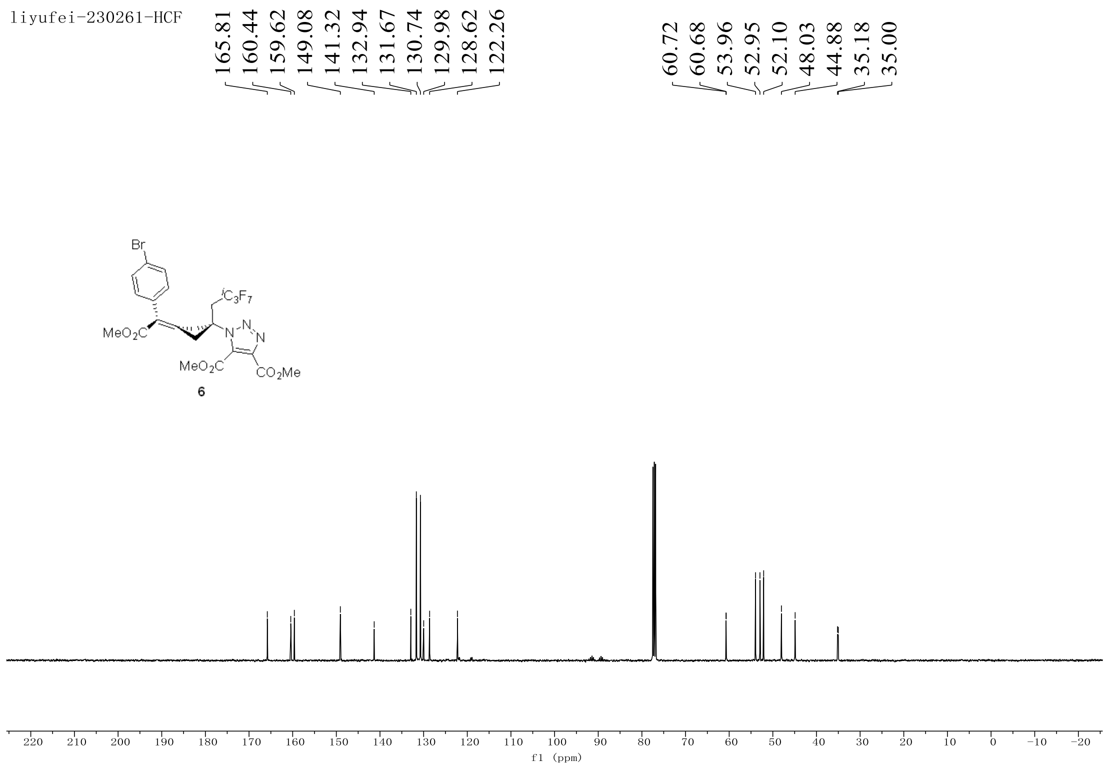
7.86 7.86 7.85 7.83 7.83 7.83 7.51 7.51 7.51 7.50 7.49 7.49 7.46 7.46 7.44 7.44 7.44 7.42 7.42 7.38 7.37 7.35 7.09 7.08 7.08 7.07 7.06 4.05 4.05 4.04 3.97 3.77 3.76 3.67 3.44 3.13 3.12 3.09 3.09 3.08
5
3.02 2.00 2.03 1.02 2.00 2.01 1.91 1.88
f1 (ppm)



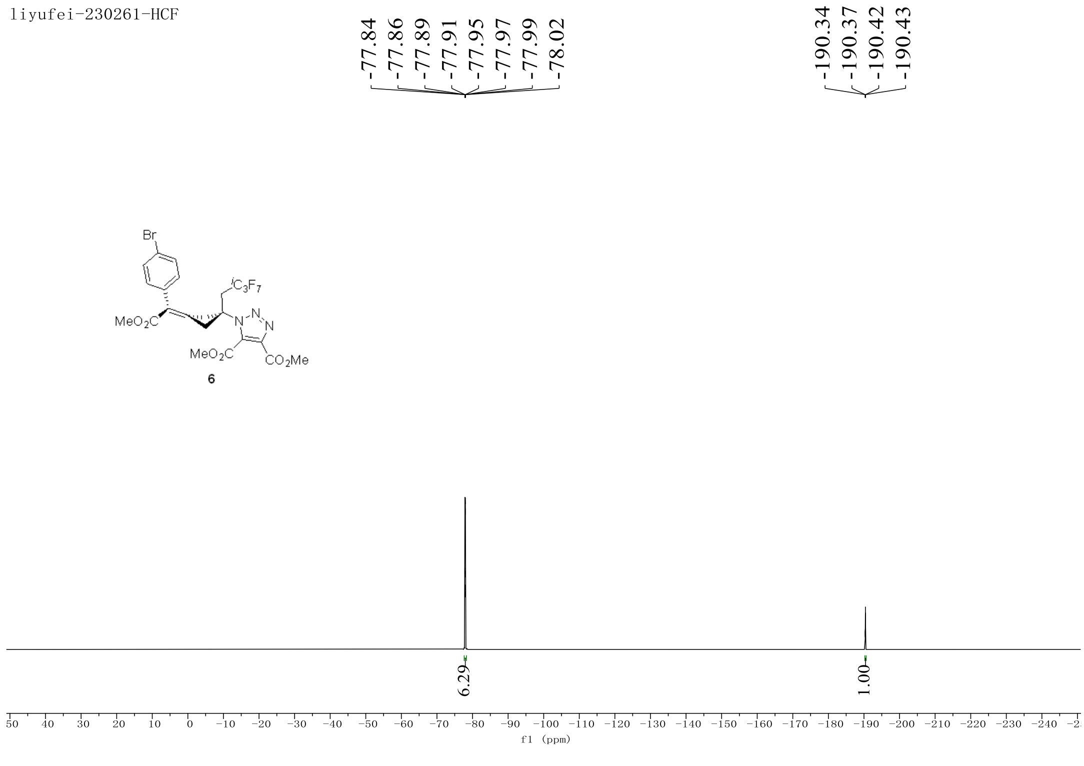
liyufei-230183-hcf
165.83 149.10 147.62 132.95 131.69 130.74 130.28 129.00 128.86 128.51 125.87 122.32 118.91 118.87 58.39 58.33 52.15 47.44 45.24 37.49 37.31
5
f1 (ppm)


liyufei-230183-hcf
-77.84
-77.93
-189.10
Br
F_3C F
CF_3
MeO_2C
N N N
Ph
5
6.31
1.00
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300
f1 (ppm)

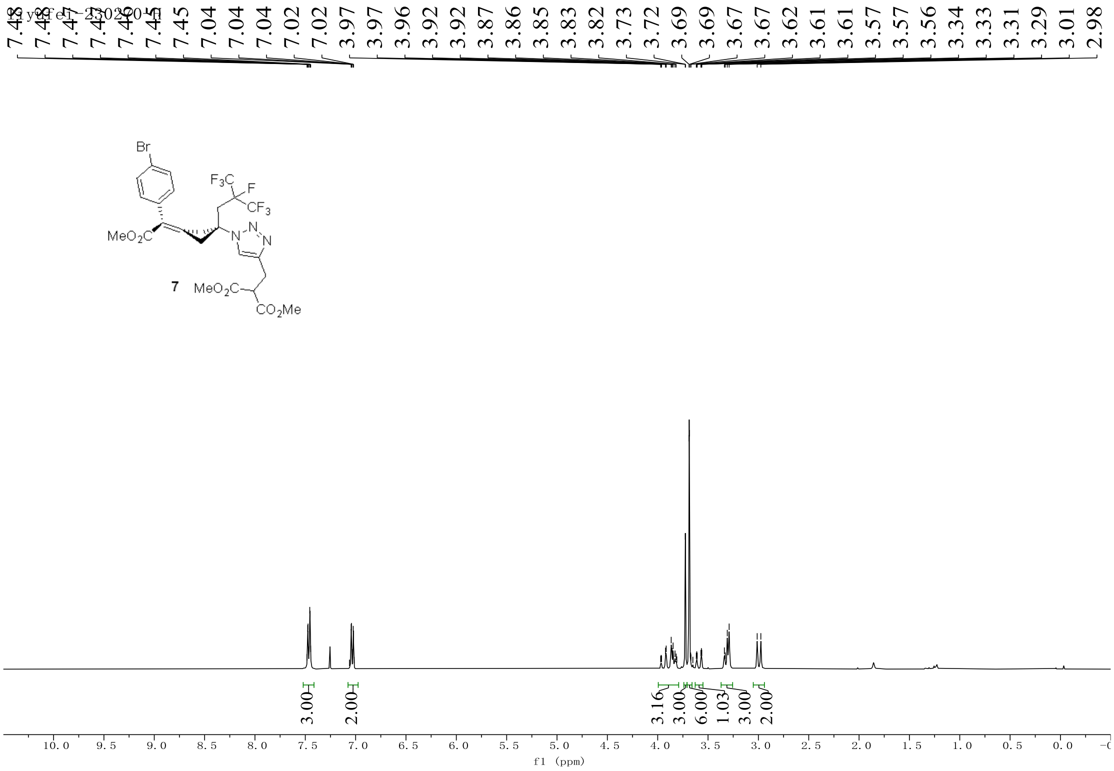

liyufei-230261
7.50 7.49 7.49 7.48 7.47 7.46 7.46 7.45 7.06 7.06 7.05 7.04 7.03 7.03
3.97 3.95 3.72
Br
$^iC_3F_7$
MeO_2C
N N N
MeO_2C
CO_2Me
6
2.01 2.00
1.08 6.02 1.82 3.00 2.00 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

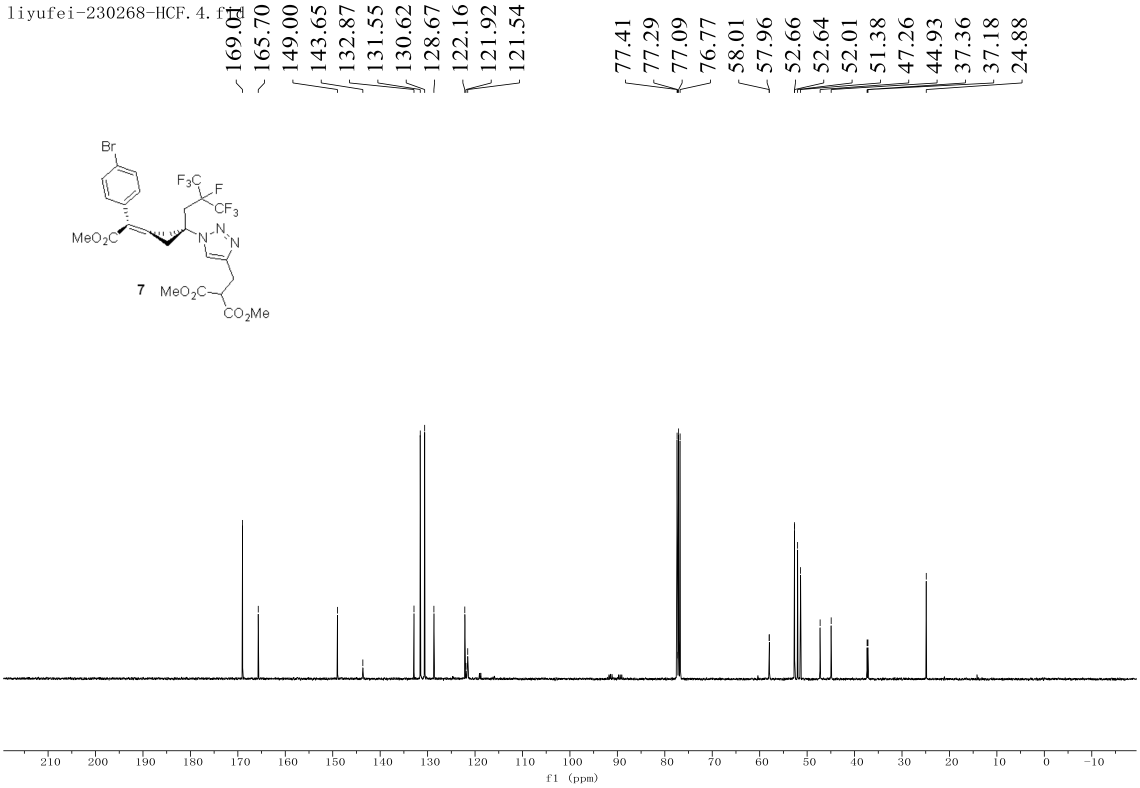


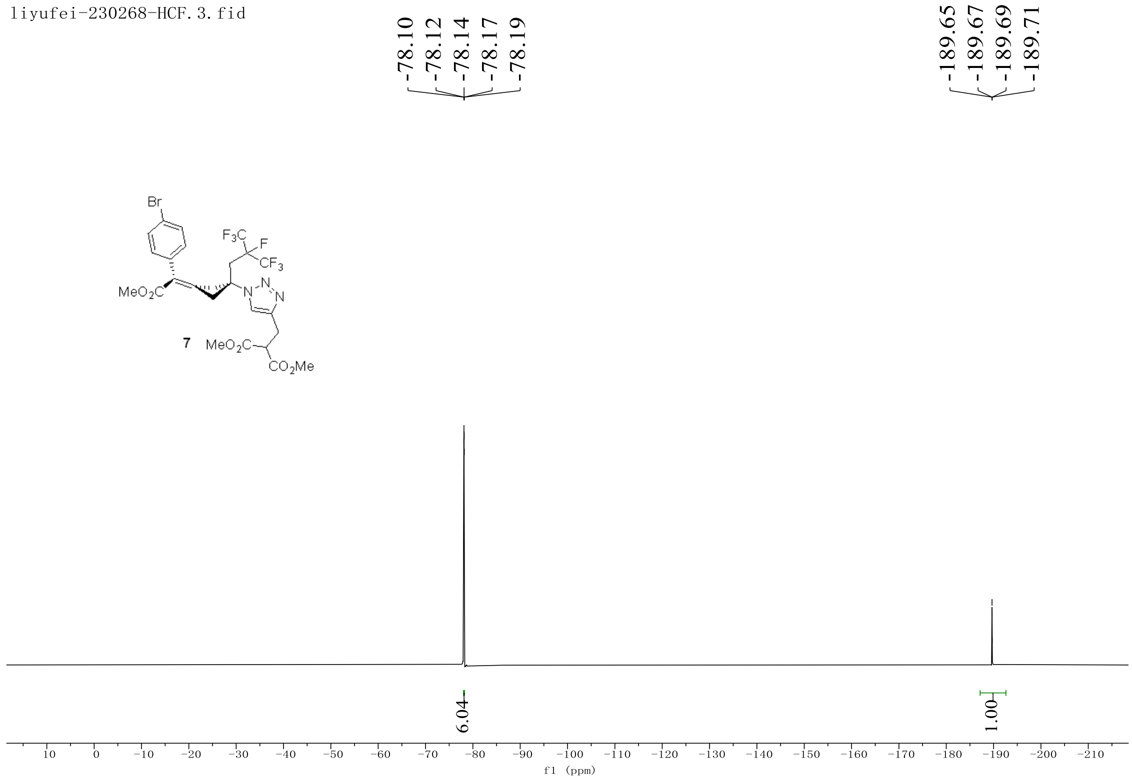
liyufei-230261-HCF
165.81
160.44
159.62
149.08
141.32
132.94
131.67
130.74
129.98
128.62
122.26
60.72
60.68
53.96
52.95
52.10
48.03
44.88
35.18
35.00
Br
$^{i}C_3F_7$
MeO_2C
N
N
N
MeO_2C
CO_2Me
6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



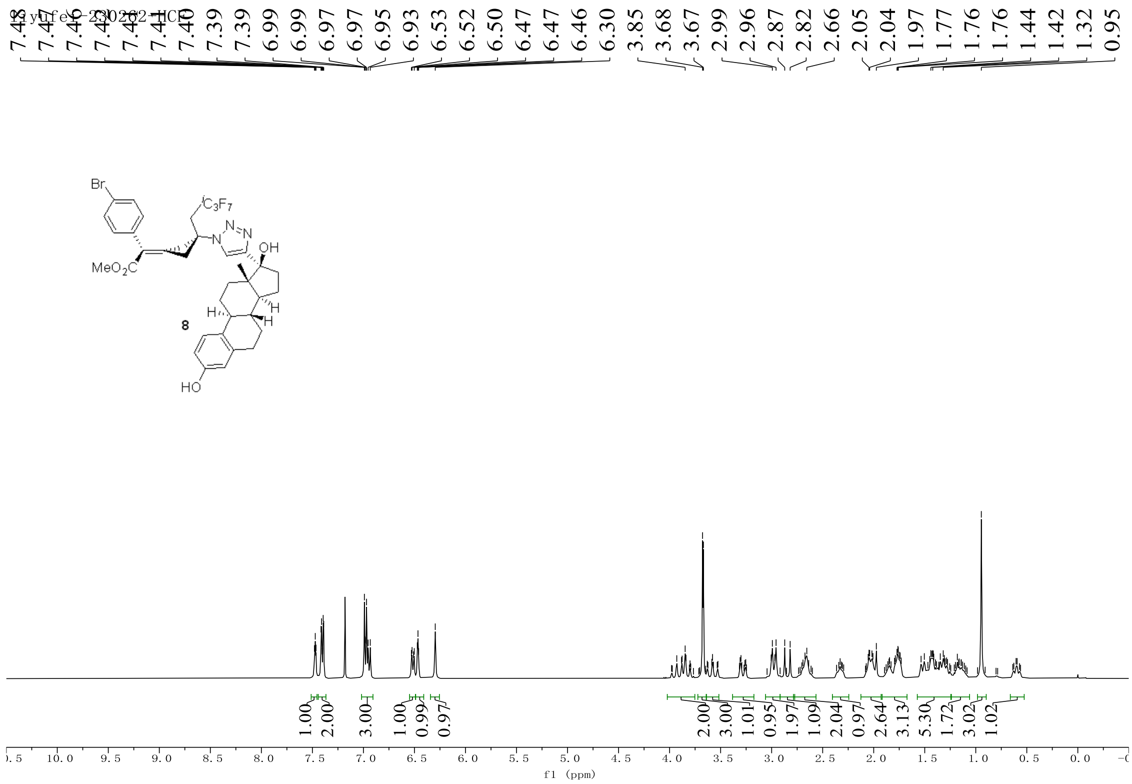
liyufei-230261-HCF
-77.84
-77.86
-77.89
-77.91
-77.95
-77.97
-77.99
-78.02
-190.34
-190.37
-190.42
-190.43
Br
$^{i}C_3F_7$
MeO_2C
N
N
N
MeO_2C
CO_2Me
6
6.29
1.00
50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240
f1 (ppm)


7.48 7.48 7.47 7.47 7.46 7.45 7.45 7.04 7.04 7.04 7.02 7.02 3.97 3.97 3.96 3.92 3.92 3.87 3.86 3.85 3.83 3.82 3.73 3.72 3.69 3.69 3.67 3.67 3.62 3.61 3.61 3.57 3.57 3.56 3.34 3.33 3.31 3.29 3.01 2.98
Br
F_3C
F
CF_3
MeO_2C
N
N
N
7
MeO_2C
CO_2Me
3.00
2.00
3.16
3.00
6.00
1.03
3.00
2.00
f1 (ppm)

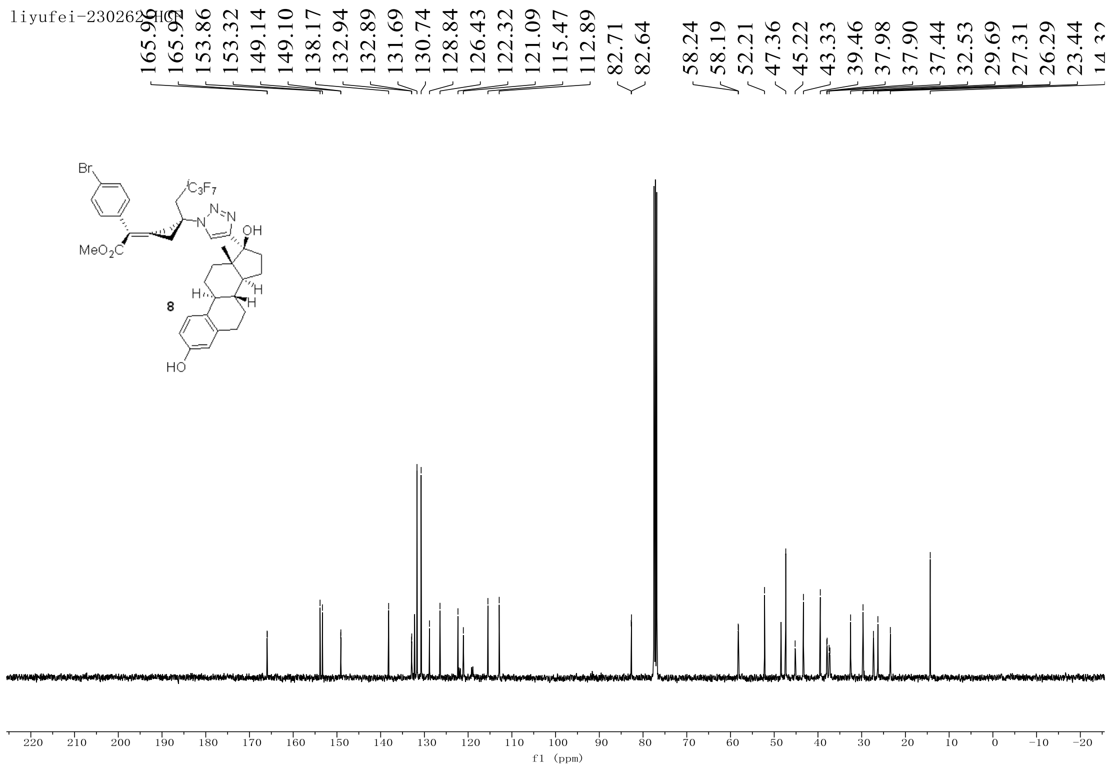

liyufei-230268-HCF.4.fid
169.01 165.70 149.00 143.65 132.87 131.55 130.62 128.67 122.16 121.92 121.54
77.41 77.29 77.09 76.77 58.01 57.96 52.66 52.64 52.01 51.38 47.26 44.93 37.36 37.18 24.88
Br
F_3C
F
CF_3
MeO_2C
N
N
N
7
MeO_2C
CO_2Me
f1 (ppm)

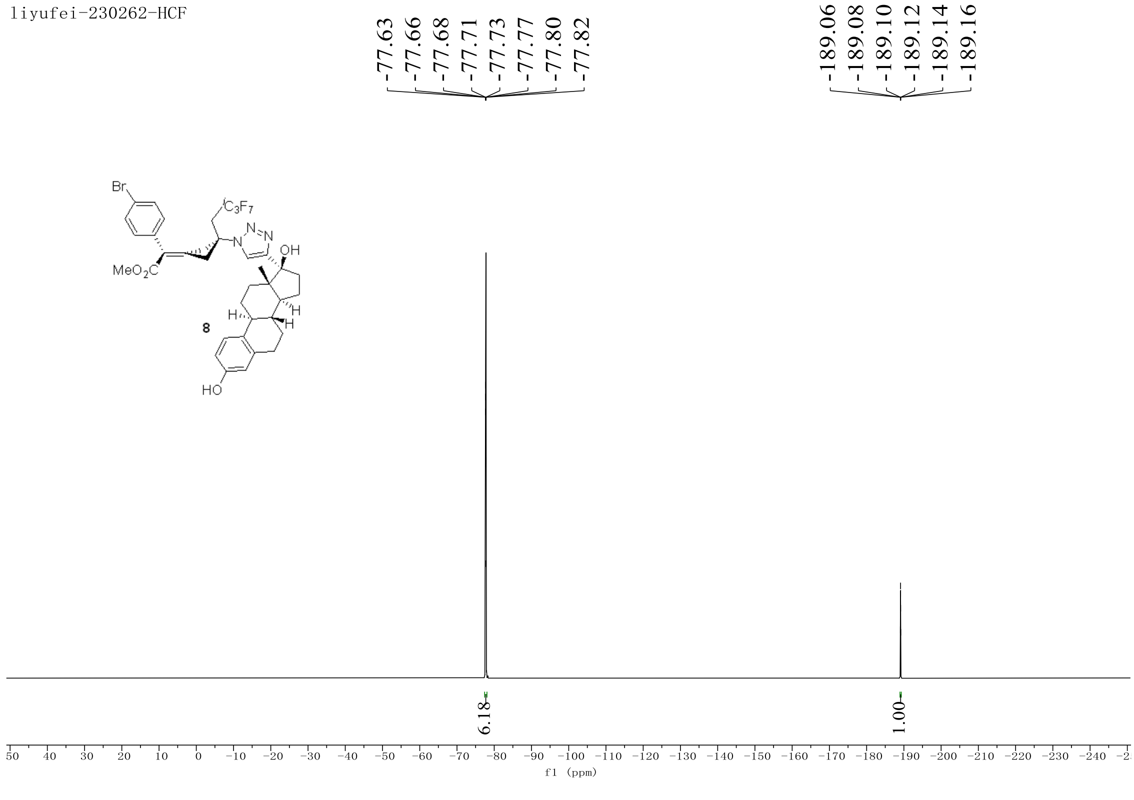


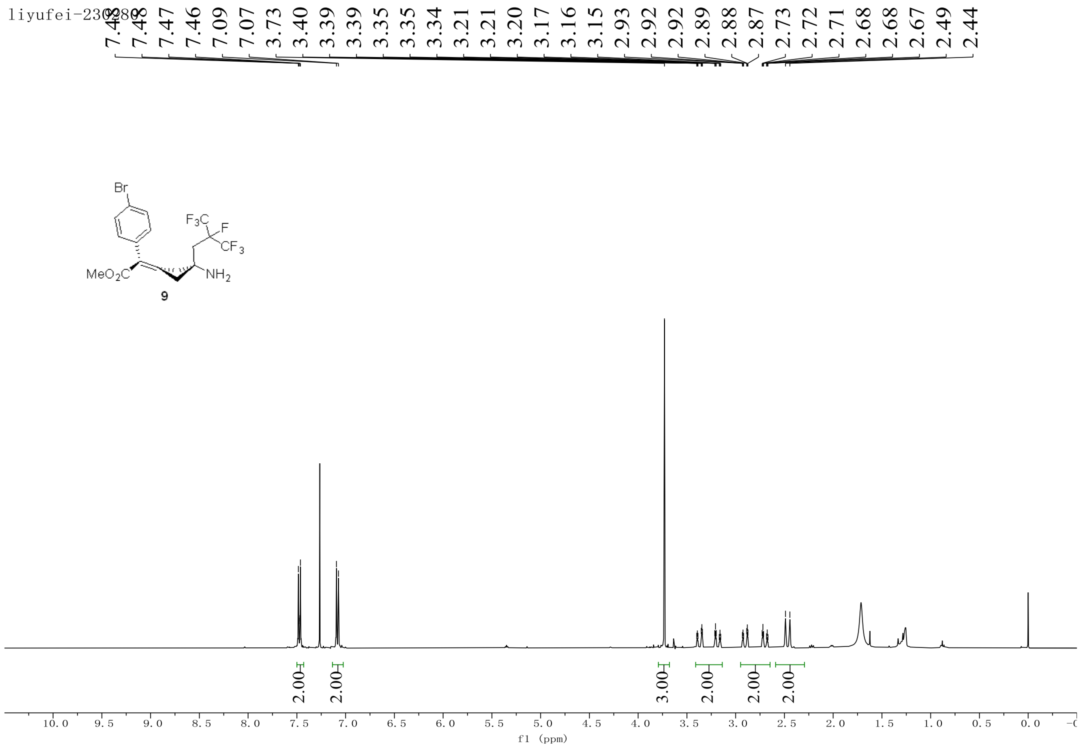
liyufei-230268-HCF.3.fid
-78.10
-78.12
-78.14
-78.17
-78.19
-189.65
-189.67
-189.69
-189.71
Br
F3C
F
CF3
MeO2C
N
N
N
7
MeO2C
CO2Me
6.04
1.00
f1 (ppm)

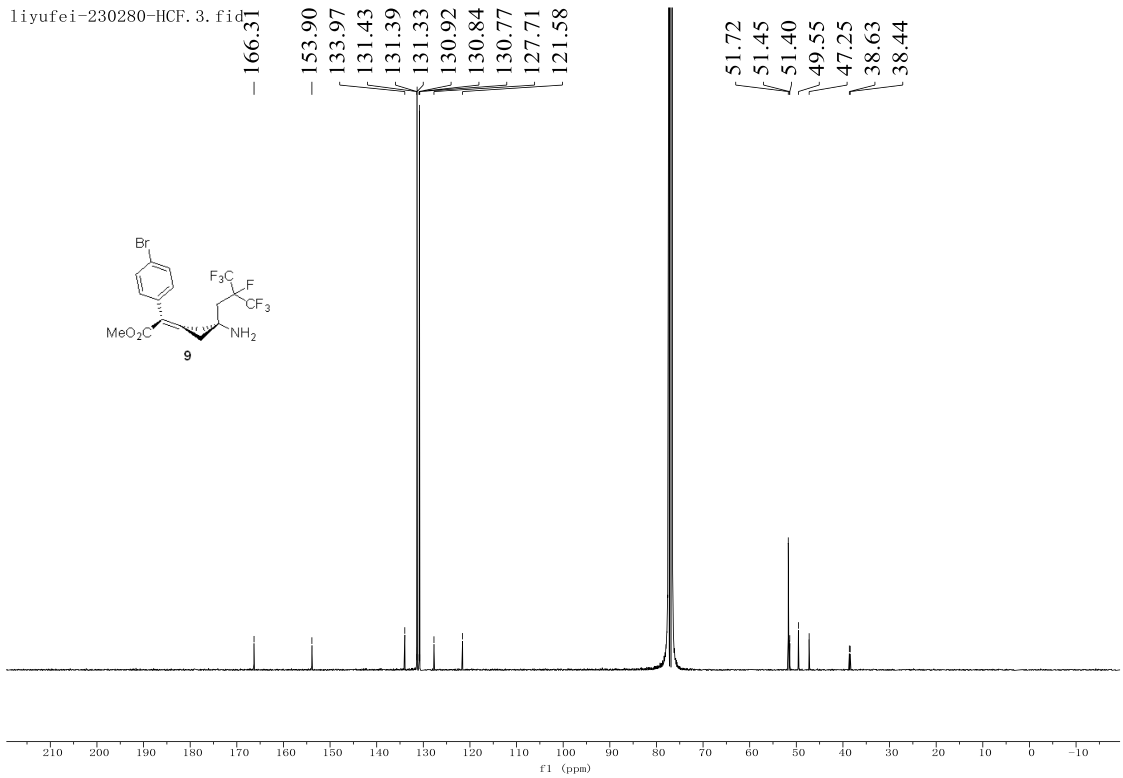


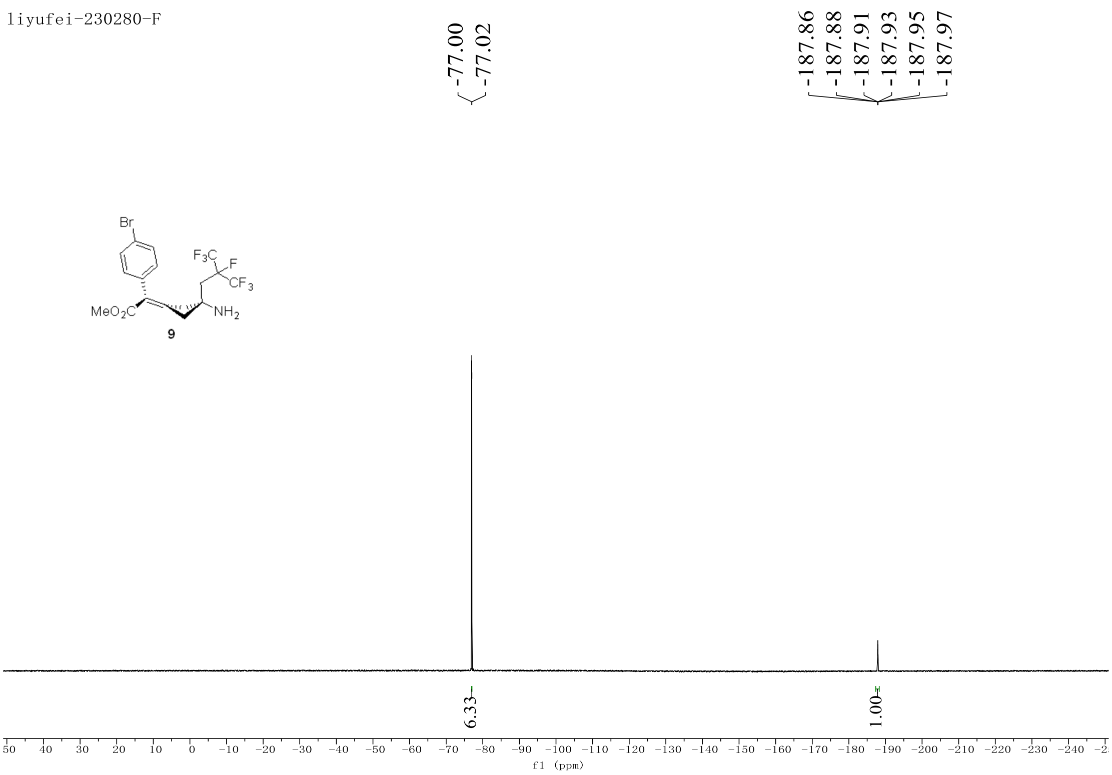
7.48
7.47
7.46
7.42
7.41
7.40
7.39
7.39
6.99
6.99
6.97
6.97
6.95
6.93
6.53
6.52
6.50
6.47
6.47
6.46
6.30
3.85
3.68
3.67
2.99
2.96
2.87
2.82
2.66
2.05
2.04
1.97
1.77
1.76
1.76
1.44
1.42
1.32
0.95
Br
C3F7
N
OH
MeO2C
H
H
8
HO
1.00
2.00
3.00
1.00
0.99
0.97
2.00
3.00
1.01
0.95
1.97
1.09
2.04
0.97
2.64
3.13
5.30
1.72
3.02
1.02
f1 (ppm)

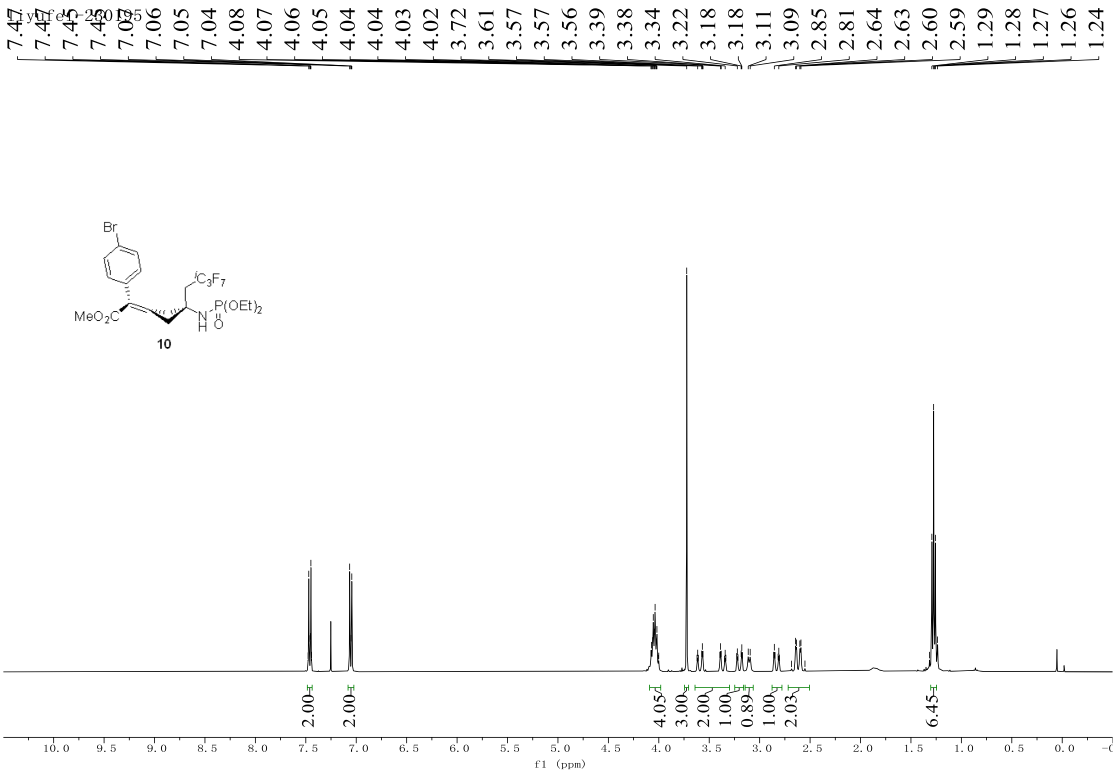

liyufei-230262-HCF
165.96
165.92
153.86
153.32
149.14
149.10
138.17
132.94
132.89
131.69
130.74
128.84
126.43
122.32
121.09
115.47
112.89
82.71
82.64
58.24
58.19
52.21
47.36
45.22
43.33
39.46
37.98
37.90
37.44
32.53
29.69
27.31
26.29
23.44
Br
C_3F_7
OH
MeO_2C
8
HO
f1 (ppm)


liyufei-230262-HCF
-77.63
-77.66
-77.68
-77.71
-77.73
-77.77
-77.80
-77.82
-189.06
-189.08
-189.10
-189.12
-189.14
-189.16
Br
C_3F_7
OH
MeO_2C
8
HO
6.18
1.00
f1 (ppm)

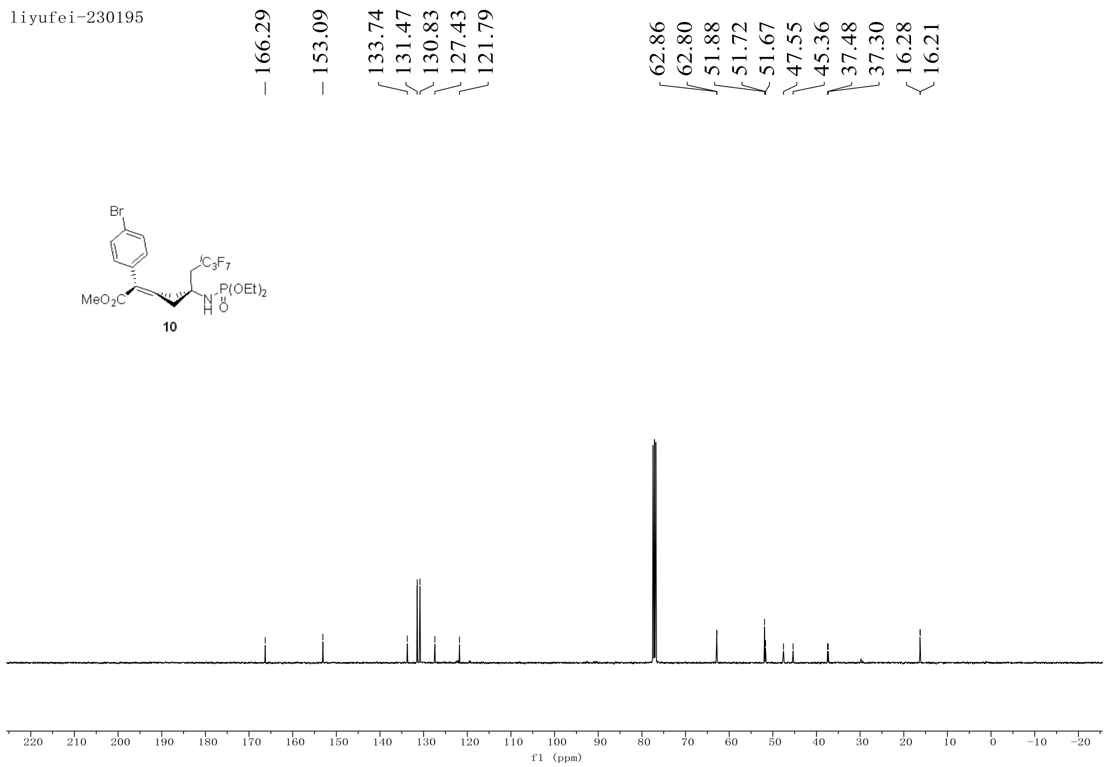

liyufei-230
7.48 7.48 7.47 7.46 7.09 7.07 3.73 3.40 3.39 3.39 3.35 3.35 3.34 3.21 3.21 3.20 3.17 3.16 3.15 2.93 2.92 2.92 2.89 2.88 2.87 2.73 2.72 2.71 2.68 2.68 2.67 2.49 2.44
Br
F_3C
F
CF_3
MeO_2C
NH_2
9
2.00 2.00 3.00 2.00 2.00 2.00
f1 (ppm)

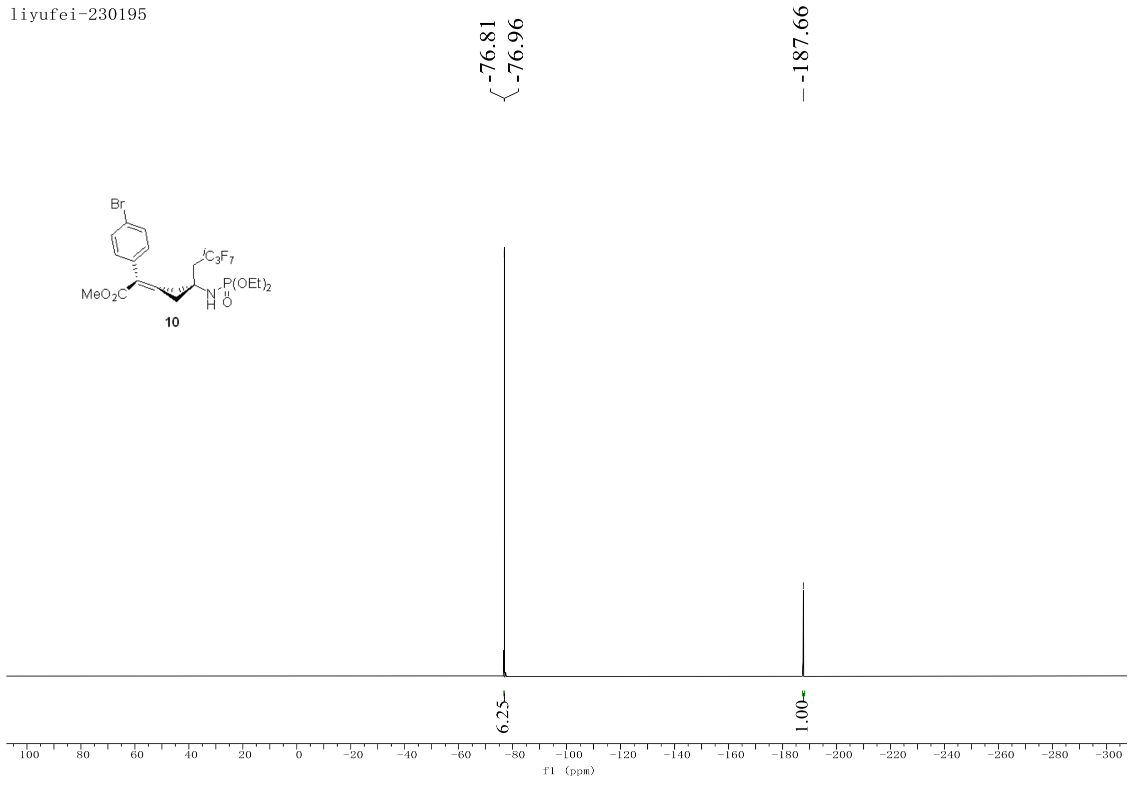

liyufei-230280-HCF.3.fid
166.31 153.90 133.97 131.43 131.39 131.33 130.92 130.84 130.77 127.71 121.58 51.72 51.45 51.40 49.55 47.25 38.63 38.44
Br
F_3C
F
CF_3
MeO_2C
NH_2
9
f1 (ppm)

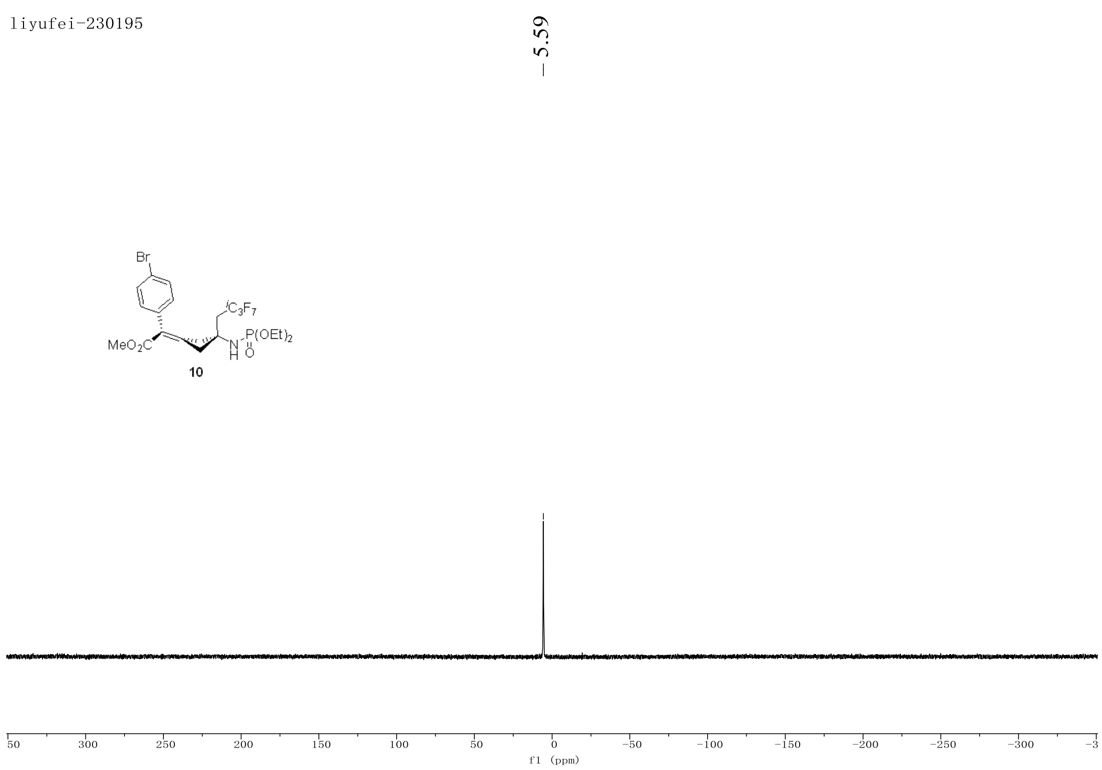

liyufei-230280-F
-77.00
-77.02
-187.86
-187.88
-187.91
-187.93
-187.95
-187.97
Br
F3C
F
CF3
MeO2C
NH2
9
6.33
1.00
f1 (ppm)

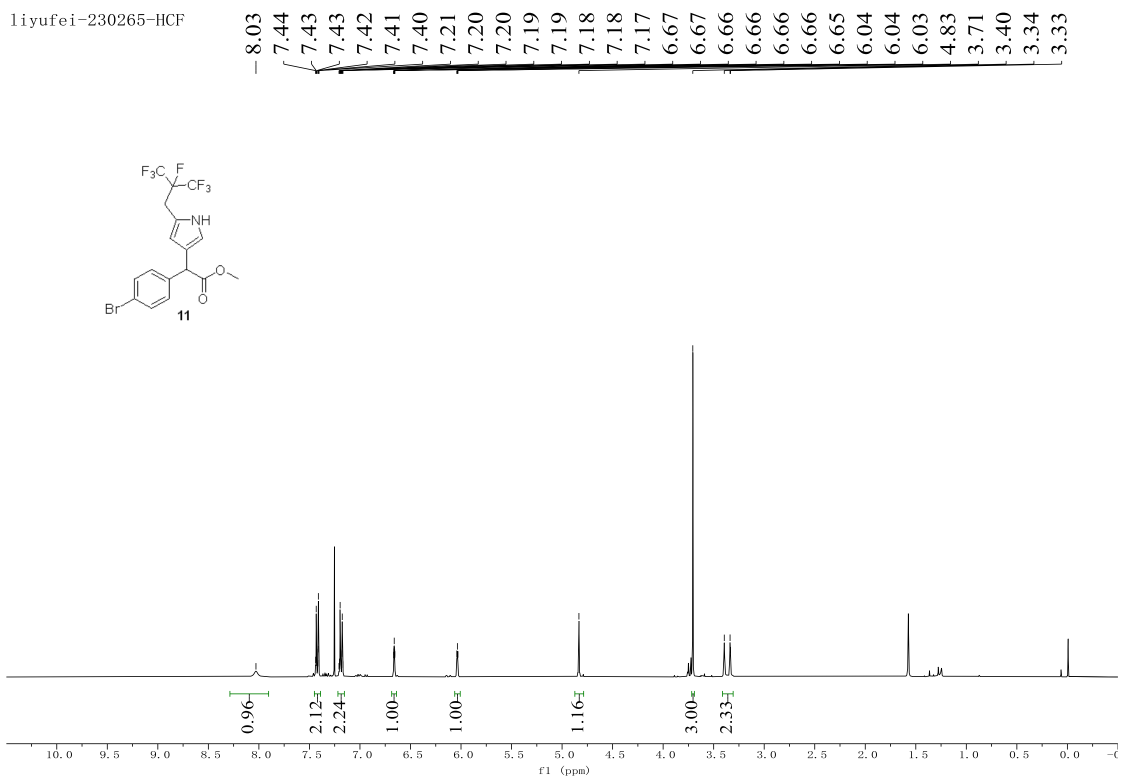

7.47
7.47
7.45
7.45
7.06
7.06
7.05
7.04
4.08
4.07
4.06
4.05
4.04
4.04
4.03
4.02
3.72
3.61
3.57
3.57
3.56
3.39
3.38
3.34
3.22
3.18
3.18
3.11
3.09
2.85
2.81
2.64
2.63
2.60
2.59
1.29
1.28
1.27
1.26
1.24
Br
iC3F7
MeO2C
N
H
P(OEt)2
O
10
2.00
2.00
4.05
3.00
2.00
1.00
0.89
1.00
2.03
6.45
f1 (ppm)

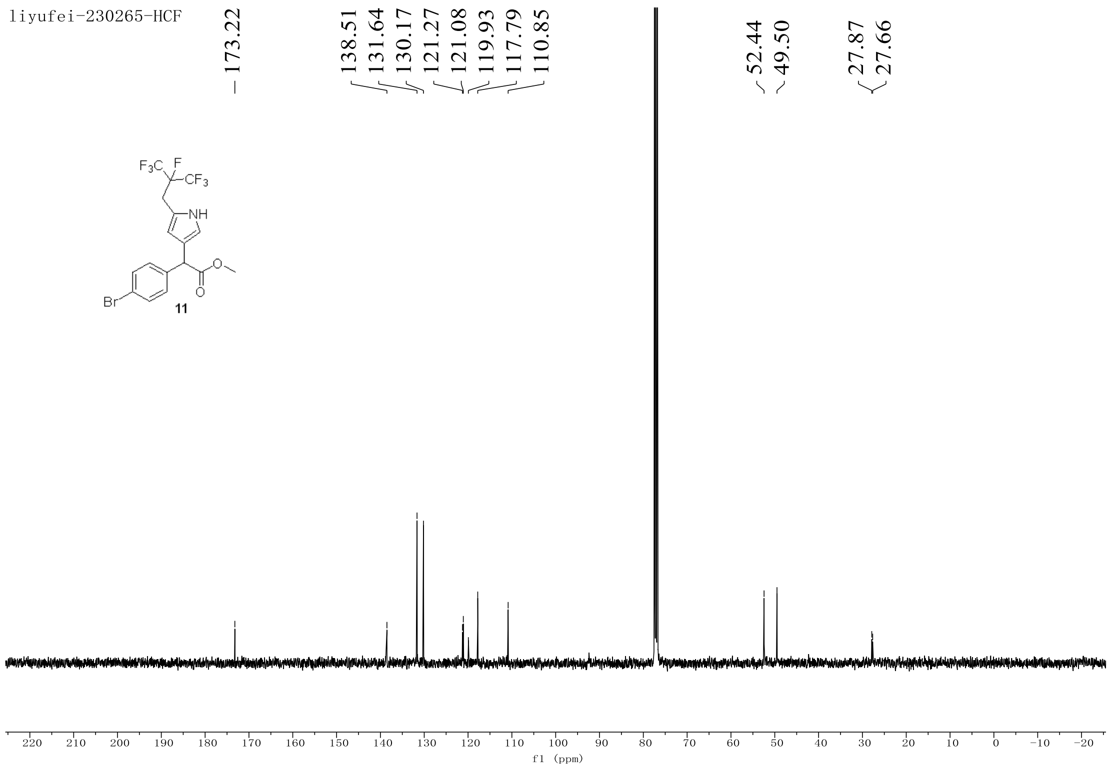
`

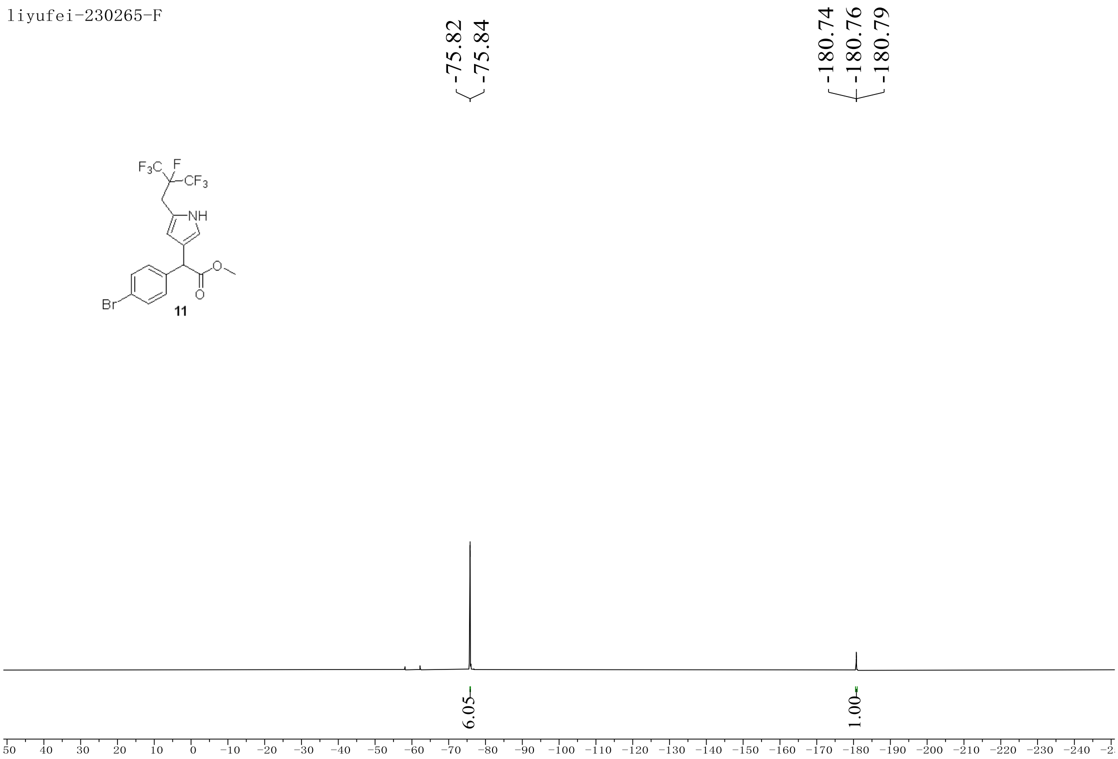

liyufei-230195
166.29
153.09
133.74
131.47
130.83
127.43
121.79
62.86
62.80
51.88
51.72
51.67
47.55
45.36
37.48
37.30
16.28
16.21
Br
^{i}C$_3$F$_7$
MeO$_2$C
N
H
P(OEt)$_2$
O
10
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)


liyufei-230195
-76.81
-76.96
-187.66
Br
^{i}C$_3$F$_7$
MeO$_2$C
N
H
P(OEt)$_2$
O
10
6.25
1.00
100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260 −280 −300
f1 (ppm)


liyufei-230195
5.59
Br
$^{i}C_3F_7$
MeO2C
NH
P(OEt)2
O
10
50
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


liyufei-230265-HCF
8.03
7.44
7.43
7.43
7.42
7.41
7.40
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
6.67
6.67
6.66
6.66
6.66
6.65
6.04
6.04
6.03
4.83
3.71
3.40
3.34
3.33
F3C
F
CF3
NH
O
O
Br
11
0.96
2.12
2.24
1.00
1.00
1.16
3.00
2.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


liyufei-230265-HCF
173.22
138.51
131.64
130.17
121.27
121.08
119.93
117.79
110.85
52.44
49.50
27.87
27.66
11
f1 (ppm)


liyufei-230265-F
-75.82
-75.84
-180.74
-180.76
-180.79
11
6.05
1.00
f1 (ppm)