Supporting Information

Hydrogen Isotope Exchange of Multisubstituted Alkenes Catalyzed by Zeolites

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Contents

1. General information

All glassware were oven dried at 110 °C for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Deuterium oxide (D_2O) was purchased from Energy Chemical®. 1,4-Dioxane was purchased from Leyan (Shanghai, China). HY and HZSM-5 zeolite were purchased from Nankai Catalyst Factory (Tianjin, China).

^1H, ^{13}C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane: δH = 0 ppm ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm; DMSO-d_6: δH = 2.50 ppm, δC = 39.52 ppm; D_2O: δH = 4.79 ppm).

High resolution mass spectra (HRMS) were measured with Waters Micromass GCT instrument and accurate masses were reported for the molecular hydrogen ion $(M+H)^+$ or $(M+Na)^+$.

The transmission electron microscopy (TEM) measurements were performed by JEM-2010 (HT) electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV.

The scanning electron microscope (SEM) measurements were performed by SIGMA electron microscope (Carl Zeiss, German).

The location and percentage of deuterium incorporation were determined by ^1H NMR. The following formula was used to determine the degree of deuterium incorporation. Calibrate peaks based on signals corresponding to unmarked locations. The label location was determined by ^1H NMR based on chemical shift and peak multiplicity. In addition, deuterium incorporation was confirmed using high-resolution MS by comparing labeled and unlabeled compounds.

$$\%\ \text{deuteration} = 100 - \left[\left(\frac{\text{residual integral}}{\text{number of labelling sites}} \times 100\right)\right]$$

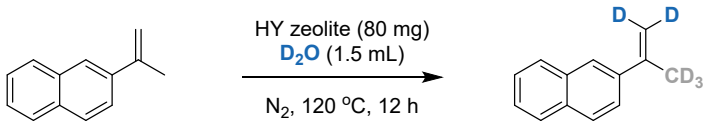
2. General procedure for reaction

In a 10 mL sealed tube, magnetic stirring bar (10 × 6 mm) and HY zeolite catalyst (80 mg) was fitted. The sealed tube was evacuated and inflated with N_2 three times. Then D_2O (1.5 mL) and alkene (0.20 mmol) were filled under N_2. The sealed tube was placed into heating module and heated to desired temperature (140 °C). At the end of reaction, the sealed tube was quickly cooled down at room temperature. The crude mixture was extracted with DCM (or EA) and collected organic phase for three times. After removal of all volatiles in vacuo, the desired product was obtained.

For gram scale reaction, alkene (10 mmol), HY zeolite (2.0 g), D_2O (25 mL) under N_2 at 140 °C for 48 h. At the end of reaction, the crude mixture was extracted with DCM (or EA) and collected organic phase for three times. After removal of all volatiles in vacuo, the desired product was obtained. And aqueous phase was centrifuged to remove zeolite catalyst for recovery of D_2O.

3. Reaction development and optimization

Table S1. Optimization of aryl alkenes.



8a 0.2 mmol **8b**

Entry	Variations[a]	Yield[b]	D-inc.[c]
1	D_2O	13%	97%
2	D_2O/1,4-dioxane	76%	88%
3	D_2O/THF	79%	83%
4	D_2O/MeCN	74%	70%
5	D_2O/DMF	95%	5%
6	D_2O/DMSO	99%	0

[a] D_2O/organic solvent (1.0/0.5 mL). [b] Yield was detected by GC-MS using mesitylene as internal standard. [c] D-incorporation was detected by GC-MS or ^1H NMR.

4. Characterization of catalyst

Table S2. Textural properties of the HY zeolite catalyst.

S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	D_{ave} (nm)
610	403	0.35	0.20	2.28

Table S3. Chemical composition of the HY zeolite catalyst.

catalyst	Si/Al
fresh HY zeolite	18.59
used HY zeolite	18.62

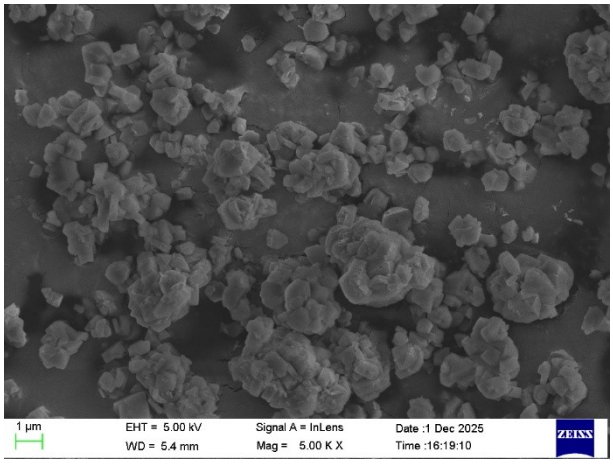


Figure S1. SEM of the HY zeolite catalyst.

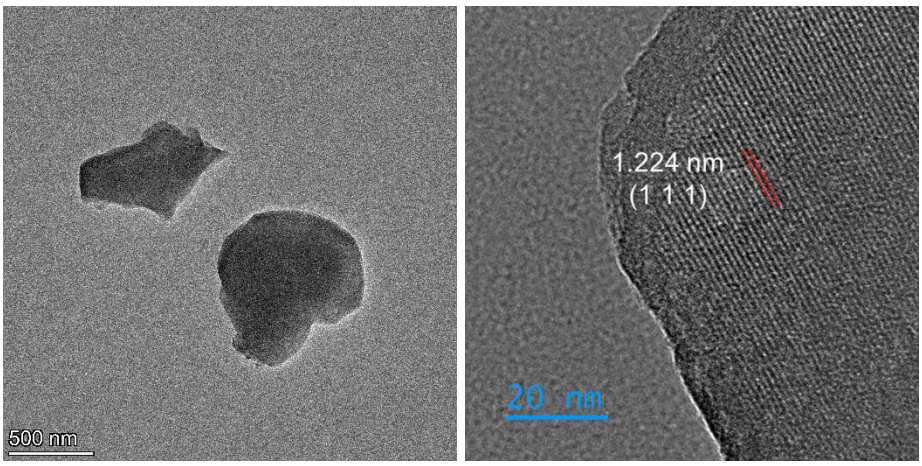


Figure S2. TEM of the HY zeolite catalyst

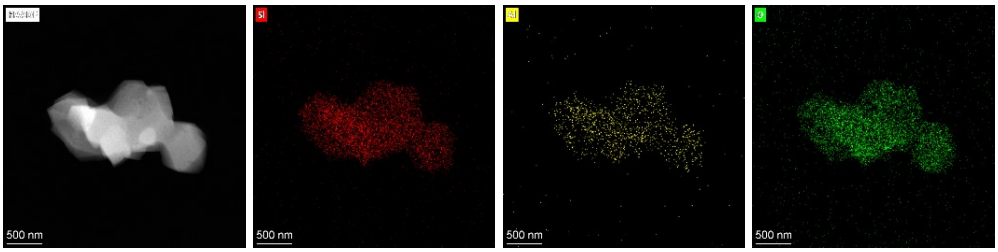


Figure S3. HAADF-STEM and EDS of the HY zeolite catalyst

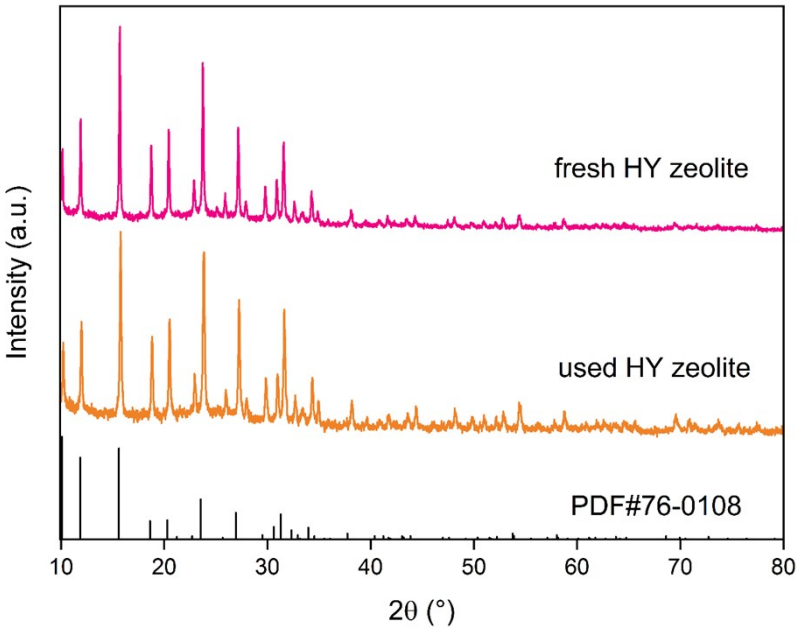


Figure S4. XRD of the HY zeolite catalyst

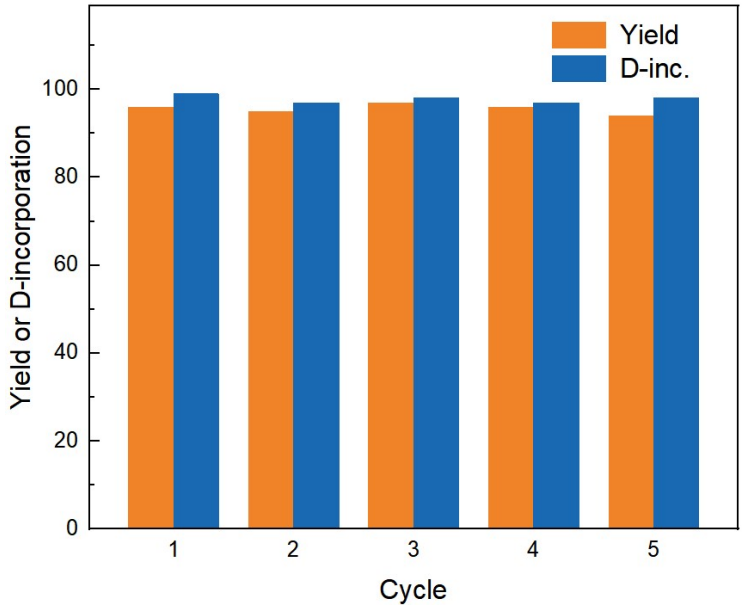
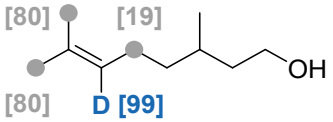
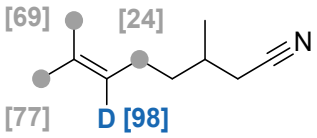


Figure S5. Recovery of the HY zeolite catalyst

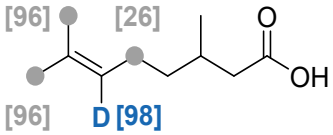
5. Characterization of products



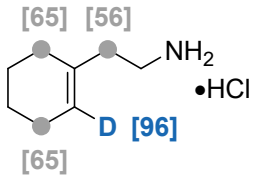
Citronellol-*d* (1b). According to the general procedure, the title product was obtained (30.4 mg, 96%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 – 5.02 (m, 0.01H), 3.85 – 3.54 (m, 2H), 2.06 – 1.87 (m, 1.62H), 1.72 – 1.49 (m, 3.23H), 1.46 – 1.24 (m, 2H), 1.22 – 1.09 (m, 1H), 0.89 (d, J = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.11, 124.73 (m, labeled), 61.25, 39.98, 37.31, 29.26, 25.42 (m, labeled), 24.80 (m, labeled), 19.62, 18.31 (m, labeled).
Deuterium incorporation: 6.2 D/molecule (^{1}H-NMR)



Agrunitrile-*d* (2b). According to the general procedure, the title product was obtained (28.7 mg, 94%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 – 4.98 (m, 0.02H), 2.27 (qd, J = 16.6, 6.4 Hz, 2H), 2.04 – 1.94 (m, 1.52H), 1.91 – 1.80 (m, 1H), 1.72 – 1.61 (m, 0.92H), 1.61 – 1.52 (m, 0.70H), 1.51 – 1.29 (m, 2H), 1.06 (d, J = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.34, 122.93 (m, labeled), 119.02, 35.94, 30.02, 25.72 (m, labeled), 25.22, 24.52 (m, labeled), 19.46, 17.19 (m, labeled).
Deuterium incorporation: 5.8 D/molecule (^{1}H-NMR)



Citronellic acid-*d* (3b). According to the general procedure, the title product was obtained (33.7 mg, 98%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 – 5.06 (m, 0.02H), 2.41 – 2.30 (m, 1H), 2.21 – 2.09 (m, 1H), 2.08 – 1.89 (m, 2.48H), 1.76 – 1.53 (m, 0.27H), 1.49 – 1.21 (m, 2H), 0.98 (d, J = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.71, 131.20, 123.96 (m, labeled), 41.66, 36.83, 29.96, 25.85 (m, labeled), 25.40 (m, labeled), 19.71, 18.18 (m, labeled).
Deuterium incorporation: 7.3 D/molecule (^{1}H-NMR)



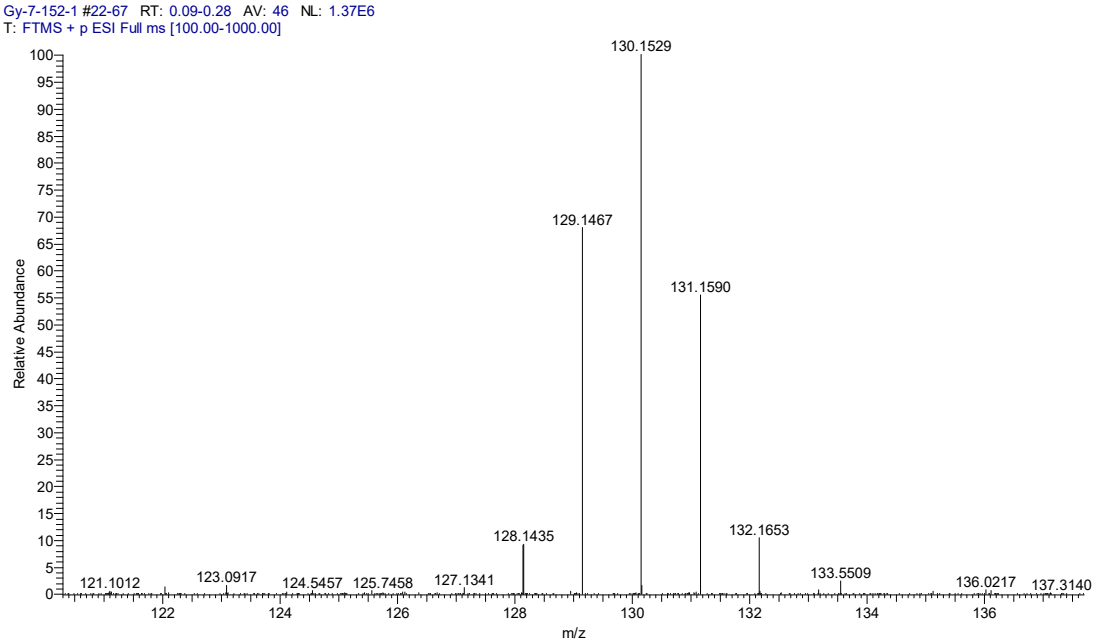
2-(Cyclohex-1-en-1-yl-2-*d*)ethan-1-amine hydrochloride (4b). According to the general procedure, the title product was obtained (30.7 mg, 94%).

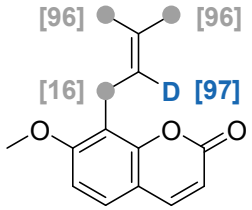
^{1}H NMR (400 MHz, DMSO-d_6) δ 5.45 – 5.41 (m, 0.04H), 2.90 – 2.79 (m, 2H), 2.17 – 2.07 (m, 0.88H), 1.89 – 1.82 (m, 1.40H), 1.50 – 1.35 (m, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 133.52, 125.63 (m, labeled), 38.26 (m, labeled), 35.87, 26.10 (m, labeled), 25.61, 23.06, 22.67 (m, labeled).

Deuterium incorporation: 4.7 D/molecule (^{1}H-NMR), 4.2 D/molecule [HRMS (ESI)].

HRMS (ESI) of **4b** $[M+H]^{+}$:





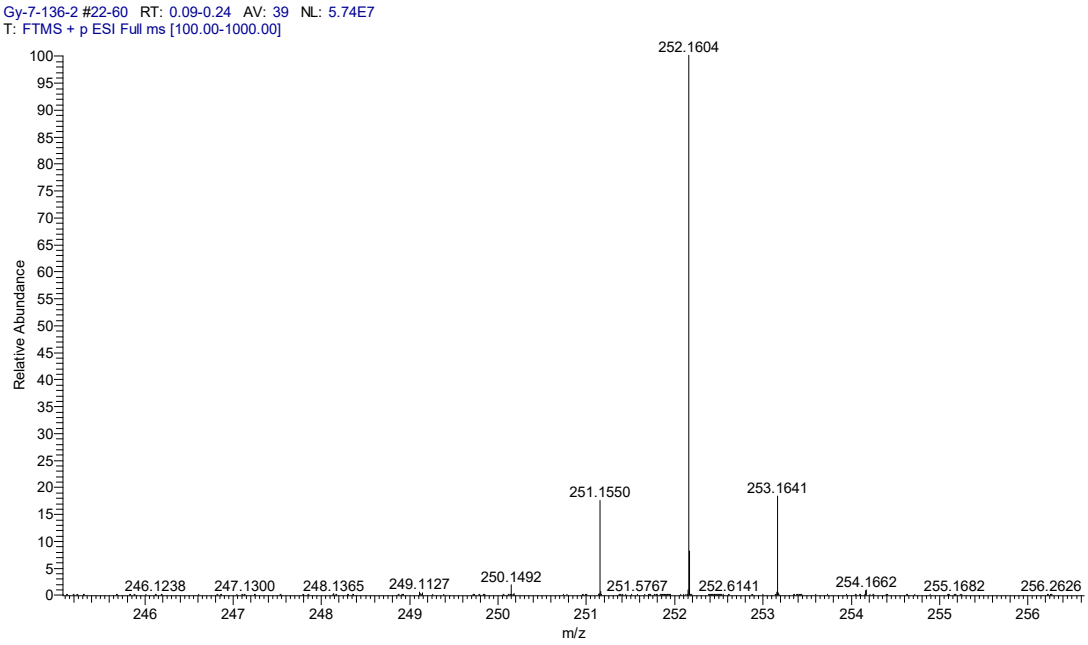
Osthol-*d* (5b). According to the general procedure, the title product was obtained (38.9 mg, 79%).

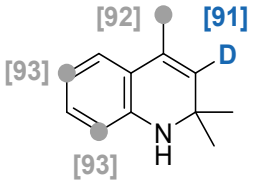
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 1H), 7.33 – 7.25 (m, 1H), 6.83 (d, J = 8.6 Hz, 1H), 6.23 (d, J = 9.4 Hz, 1H), 5.25 – 5.19 (m, 0.03H), 3.92 (s, 3H), 3.58 – 3.50 (m, 1.68H), 1.88 – 1.77 (m, 0.11H), 1.73 – 1.63 (m, 0.12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.55, 160.34, 152.95, 143.90, 132.60, 126.32, 121.05 (m, labeled), 118.12, 113.13, 113.08, 107.46, 56.18, 25.97 (m, labeled), 21.93, 18.10 (m, labeled).

Deuterium incorporation: 7.1 D/molecule (^{1}H-NMR), 7.0 D/molecule [HRMS (ESI)].

HRMS (ESI) of **5b** $[M+H]^+$:





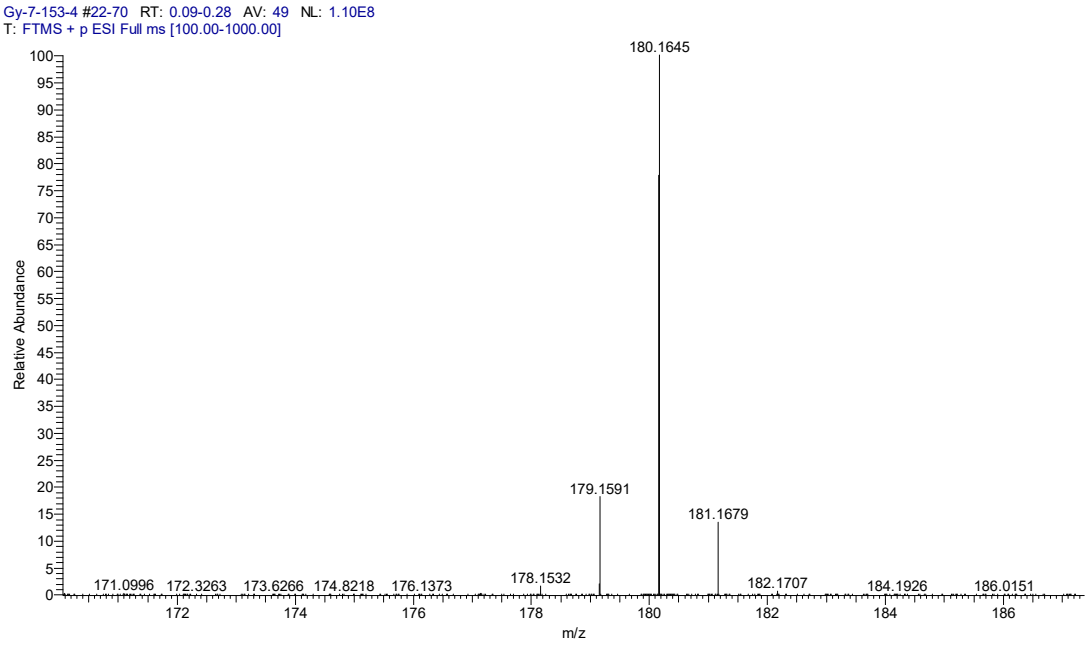
2,2,4-Trimethyl-1,2-dihydroquinoline-3-*d* (6b). According to the general procedure, the title product was obtained (33.6 mg, 96%).

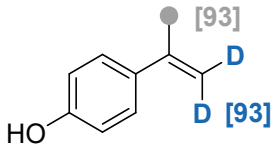
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.04 (m, 1H), 6.98 (s, 1H), 6.66 – 6.59 (m, 0.07H), 6.50 – 6.41 (m, 0.07H), 5.32 – 5.29 (m, 0.09H), 3.67 (s, 1H), 2.07 – 1.93 (m, 0.25H), 1.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.32, 129.49 (m, labeled), 128.22, 123.60, 121.77, 116.99 (m, labeled), 112.42 (m, labeled), 51.84, 31.14, 18.94 (m, labeled).

Deuterium incorporation: 5.5 D/molecule (^{1}H-NMR), 5.9 D/molecule [HRMS (ESI)].

HRMS (ESI) of **6b** $[M+H]^+$:





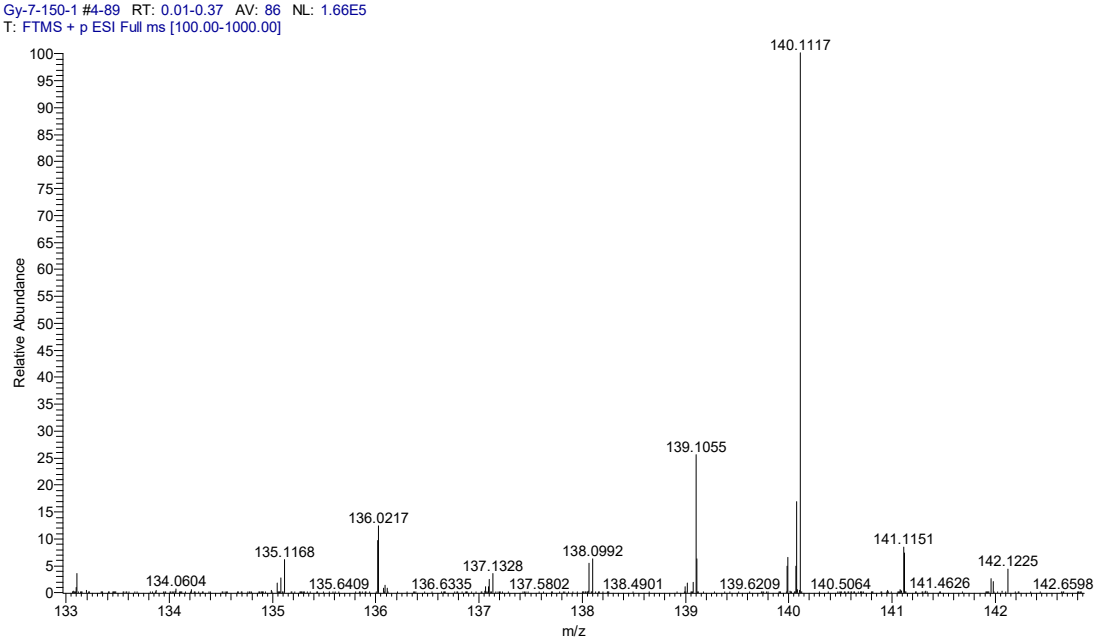
4-(Prop-1-en-2-yl-1,1-d_2)phenol (7b). According to the general procedure, the title product was obtained (14.3 mg, 52%).

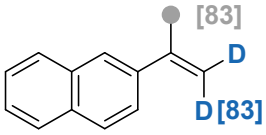
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 6.82 – 6.76 (m, 2H), 5.27 – 5.25 (m, 0.07H), 4.99 – 4.96 (m, 0.07H), 4.83 (s, 1H), 2.12 – 2.08 (m, 0.21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.78, 142.79, 134.36, 127.34, 115.04, 110.27 (m, labeled), 23.04 (m, labeled).

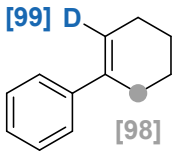
Deuterium incorporation: 4.7 D/molecule (^{1}H-NMR), 4.8 D/molecule [HRMS (ESI)].

HRMS (ESI) of **7b** $[M+H]^+$:

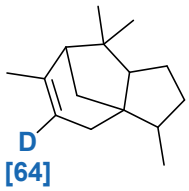




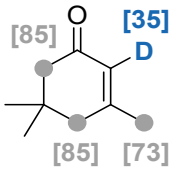
2-(Prop-1-en-2-yl-1,1-d_2)naphthalene (8b). According to the general procedure, the title product was obtained (24.3 mg, 71%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.77 (m, 4H), 7.69 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.54 – 7.42 (m, 2H), 5.59 – 5.53 (m, 0.17H), 5.24 – 5.18 (m, 0.17H), 2.32 – 2.22 (m, 0.52H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.86, 138.43, 133.52, 132.93, 128.37, 127.83, 127.64, 126.25, 125.95, 124.37, 124.01, 112.48 (m, labeled), 22.03 (m, labeled).
Deuterium incorporation: 4.2 D/molecule (^{1}H-NMR)



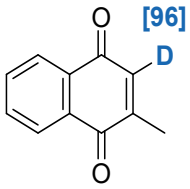
2,3,4,5-Tetrahydro-1,1'-biphenyl-6-*d* (9b). According to the general procedure, the title product was obtained (30.4 mg, 95%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.17 – 6.13 (m, 0.01H), 2.47 – 2.39 (m, 0.04H), 2.22 (t, *J* = 6.2 Hz, 2H), 1.82 – 1.76 (m, 2H), 1.73 – 1.64 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.78, 136.50, 128.32, 126.62, 125.04, 124.63 (m, labeled), 27.43 (m, labeled), 25.88, 22.99, 22.23.
Deuterium incorporation: 4.9 D/molecule (^{1}H-NMR)



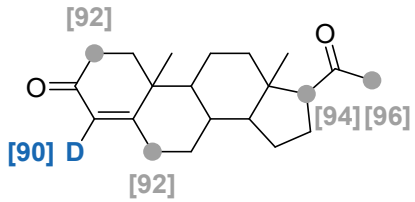
α-Cedrene-*d* (10b). According to the general procedure, the title product was obtained (39.2 mg, 95%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 – 5.19 (m, 0.36H), 2.16 (d, *J* = 16.8 Hz, 1H), 1.95 – 1.72 (m, 4H), 1.72 – 1.63 (m, 4H), 1.63 – 1.47 (m, 2H), 1.45 – 1.30 (m, 3H), 1.02 (s, 3H), 0.95 (s, 3H), 0.84 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.71, 119.34 (m, labeled), 59.08, 54.95, 53.98, 48.29, 41.59, 40.79, 38.94, 38.81, 36.20, 27.79, 25.73, 24.93, 15.57.
Deuterium incorporation: 0.6 D/molecule (^{1}H-NMR)



Lsophorone-*d* (11b). According to the general procedure, the title product was obtained (24.3 mg, 87%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.83 (m, 0.65H), 2.20 – 2.11 (m, 0.61H), 1.95 – 1.82 (m, 0.81H), 1.01 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.27, 160.47, 125.67 (m, labeled), 50.68 (m, labeled), 44.43 (m, labeled), 33.32, 28.31, 23.99 (m, labeled).
Deuterium incorporation: 7.6 D/molecule (^{1}H-NMR)



Menadione-*d* (12b). According to the general procedure, the title product was obtained (21.6 mg, 62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 7.99 (m, 2H), 7.73 (dd, J = 5.8, 3.2 Hz, 2H), 6.84 (d, J = 1.6 Hz, 0.04H), 2.20 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 185.82, 185.18, 148.24, 135.52 (m, labeled), 133.81, 133.76, 132.39, 132.31, 126.67, 126.23, 16.58.
Deuterium incorporation: 1.0 D/molecule (^{1}H-NMR)



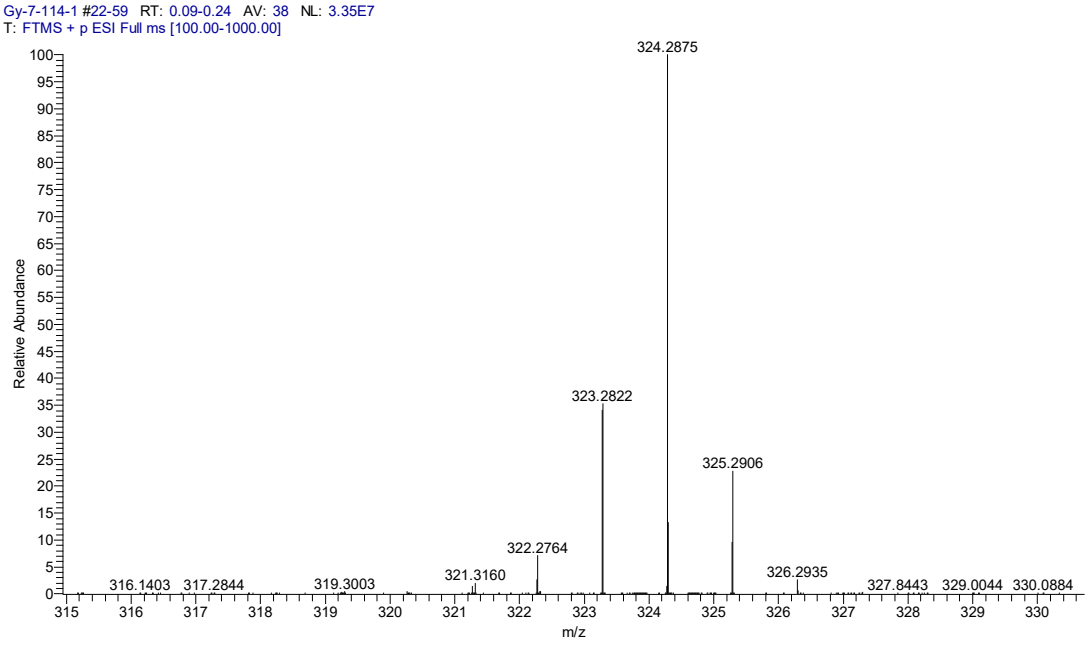
Progesterone-*d* (13b). According to the general procedure, the title product was obtained (57.6 mg, 91%).

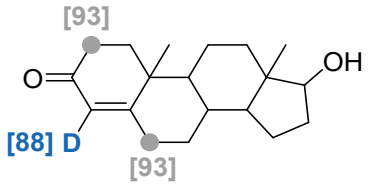
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 – 5.72 (m, 0.10H), 2.57 – 2.48 (m, 0.06H), 2.45 – 2.26 (m, 0.33H), 2.22 – 2.12 (m, 1H), 2.12 – 2.09 (m, 0.13H), 2.09 – 1.98 (m, 2H), 1.84 (dd, *J* = 12.8, 3.6 Hz, 1H), 1.76 – 1.65 (m, 3H), 1.65 – 1.58 (m, 2H), 1.58 – 1.51 (m, 1H), 1.51 – 1.42 (m, 2H), 1.28 – 1.24 (m, 1H), 1.20 – 1.16 (s, 3H), 1.07 – 0.95 (m, 2H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.73, 199.75, 171.09, 123.97 (m, labeled), 63.06 (m, labeled), 56.07, 53.71, 43.95, 38.66, 38.18, 35.58, 35.54, 34.78 (m, labeled), 33.58 (m, labeled), 32.40 (m, labeled), 31.77, 24.44, 22.74, 21.07, 17.42, 13.40.

Deuterium incorporation: 8.4 D/molecule (^{1}H-NMR), 8.8 D/molecule [HRMS (ESI)].

HRMS (ESI) of **13b** $[M+H]^+$:





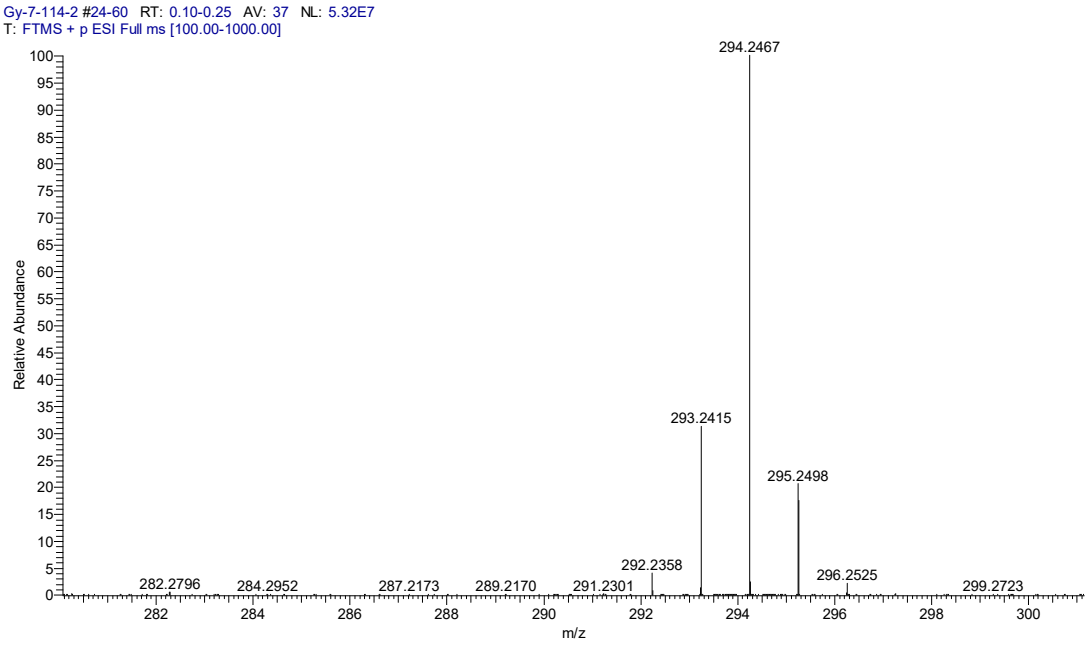
Testosterone-*d* (14b). According to the general procedure, the title product was obtained (55.7 mg, 96%).

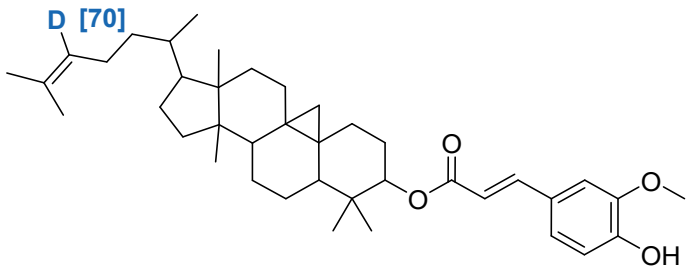
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.78 – 5.72 (m, 0.12H), 3.67 (t, *J* = 8.4 Hz, 1H), 2.48 – 2.21 (m, 0.29H), 2.16 – 2.00 (m, 2H), 1.91 – 1.82 (m, 2H), 1.71 – 1.51 (m, 5H), 1.50 – 1.37 (m, 2H), 1.33 – 1.25 (m, 1H), 1.21 (s, 3H), 1.17 – 0.89 (m, 4H), 0.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.94, 171.49, 123.91 (m, labeled), 81.65, 54.00, 50.56, 42.89, 38.66, 36.50, 35.69, 35.60, 33.34 (m, labeled), 32.06 (m, labeled), 31.44, 30.47, 23.42, 20.72, 17.48, 11.16.

Deuterium incorporation: 4.6 D/molecule (^{1}H-NMR), 4.9 D/molecule [HRMS (ESI)].

HRMS (ESI) of **14b** $[M+H]^+$:



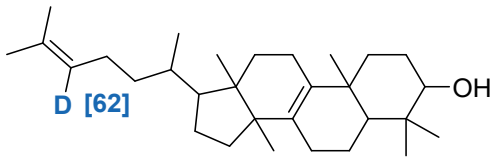


γ-Oryzanol-*d* (15b). According to the general procedure, the title product was obtained (113.5 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.14 – 6.99 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.09 (s, 1H), 4.75 – 4.63 (m, 1.29H), 3.91 (s, 3H), 2.31 – 1.78 (m, 6H) , 1.73 – 1.48 (m, 9H) , 1.47 – 1.24 (m, 8H) , 1.18 – 1.06 (m, 3H) , 1.05 – 1.00 (m, 3H) , 0.99 – 0.95 (m, 4H) , 0.93 – 0.73 (m, 11H) , 0.73 – 0.54 (m, 2H) , 0.42 – 0.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26, 156.93, 148.00, 146.93, 144.50, 130.94, 127.18, 125.36 (m, labeled), 123.11, 116.29, 114.87, 109.46, 106.06, 80.66, 56.03, 52.33, 48.90, 47.95, 47.29, 45.36, 39.79, 36.43, 36.21, 35.98, 35.63, 35.07, 33.88, 32.95, 31.72, 31.40, 29.88, 28.23, 27.04, 26.59, 26.07, 25.92, 25.83, 25.58, 25.03, 22.10, 21.96, 21.04, 20.23, 19.40, 18.40, 18.33, 18.08, 17.74, 15.44.

Deuterium incorporation: 0.7 D/molecule (^{1}H-NMR)

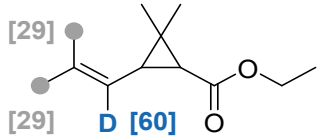


Lanosterol-*d* (16b). According to the general procedure, the title product was obtained (83.0 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 – 5.01 (m, 0.38H), 3.26 – 3.16 (m, 1H), 2.08 – 1.98 (m, 4H), 1.95 – 1.84 (m, 2H), 1.76 – 1.65 (m, 6H), 1.65 – 1.51 (m, 6H), 1.50 – 1.40 (m, 3H), 1.38 – 1.28 (m, 3H), 1.19 – 1.10 (m, 3H), 1.05 – 1.02 (m, 1H), 1.00 – 0.94 (m, 6H), 0.91 – 0.85 (m, 8H), 0.80 (s, 3H), 0.68 (s, 3H).

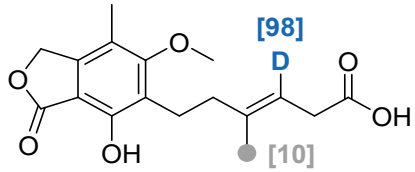
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.52, 130.99, 125.37 (m, labeled), 79.07, 50.62, 50.53, 49.92, 44.60, 39.64, 38.99, 37.13, 36.59, 36.47, 36.38, 35.72, 31.12, 30.97, 28.32, 28.09, 27.94, 26.62, 25.84, 25.04, 24.37, 24.22, 22.95, 22.67, 21.12, 19.26, 18.84, 18.76, 18.38, 17.75, 15.86, 15.55.

Deuterium incorporation: 0.6 D/molecule (^{1}H-NMR)



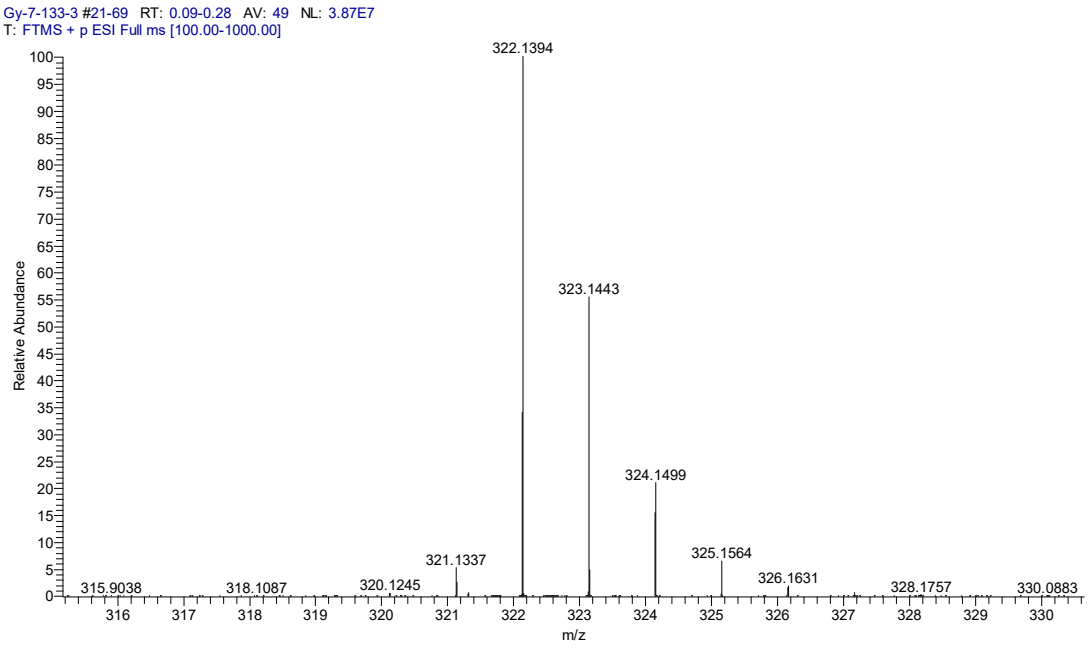
Ethyl chrysanthemate-*d* (17b). According to the general procedure, the title product

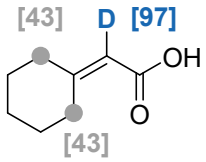
was obtained (36.0 mg, 91%, d.r. 1.5:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.29 (m, 0.08H), 4.91 – 4.82 (m, 0.32H), 4.21 – 4.02 (m, 2H), 2.06 – 2.00 (m, 0.8H), 1.87 – 1.81 (m, 0.2H), 1.76 – 1.60 (m, 4.29H), 1.53 (d, *J* = 7.8 Hz, 0.4H), 1.36 (d, *J* = 5.4 Hz, 0.6H), 1.29 – 1.22 (m, 6H), 1.20 (s, 1.2H), 1.12 (s, 1.8H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 171.24, 135.52, 121.35 (m, labeled), 60.31, 59.75, 34.98, 32.68, 32.15, 31.39, 28.98, 28.59, 27.51, 26.22, 25.70, 22.33, 20.53, 18.60, 18.12, 14.90, 14.52, 14.48.
Deuterium incorporation: 2.3 D/molecule (^{1}H-NMR)



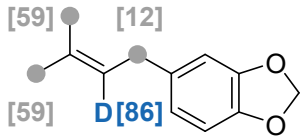
(E)-6-(4-hydroxy-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-3-enoic-3-*d* acid (18b). According to the general procedure, the title product was obtained (59.8 mg, 93%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 5.30 – 5.27 (m, 0.02H), 5.20 (s, 2H), 3.78 (s, 3H), 2.82 – 2.70 (m, 2H), 2.69 – 2.59 (m, 2H), 2.28 – 2.16 (m, 1H), 2.14 (s, 3H), 2.09 – 1.98 (m, 1H), 1.51 – 1.43 (m, 2.71H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.92, 172.98, 163.75, 153.60, 144.39, 123.27 (m, labeled), 122.09, 117.02, 106.50, 86.63, 70.21, 61.31, 32.85, 29.24, 25.53, 18.22, 11.70.
Deuterium incorporation: 1.3 D/molecule (^{1}H-NMR), 1.6 D/molecule [HRMS (ESI)].

HRMS (ESI) of **18b** $[M+H]^+$:





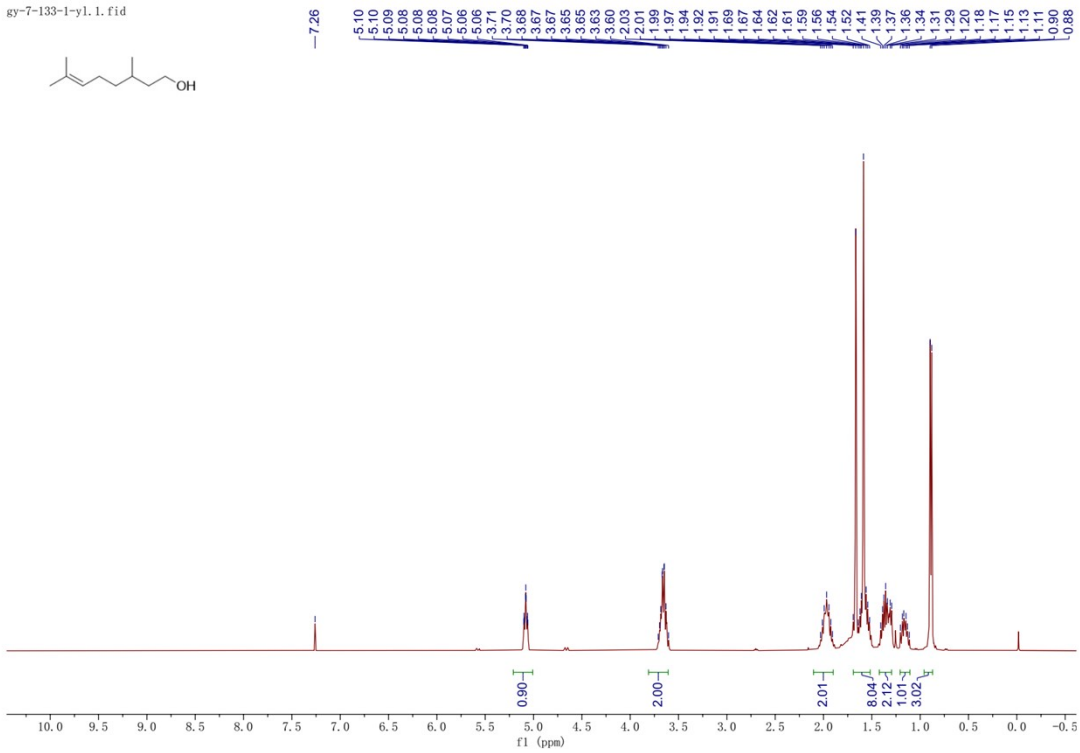
2-Cyclohexylideneacetic-2-*d* acid (19b). According to the general procedure, the title product was obtained (26.3 mg, 93%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 – 5.61 (m, 0.03H), 2.05 – 1.90 (m, 2.30H), 1.65 – 1.49 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.01, 120.96 (m, labeled), 29.79 (m, labeled), 25.28, 23.73 (m, labeled), 22.92, 22.46.
Deuterium incorporation: 3.6 D/molecule (^{1}H-NMR)



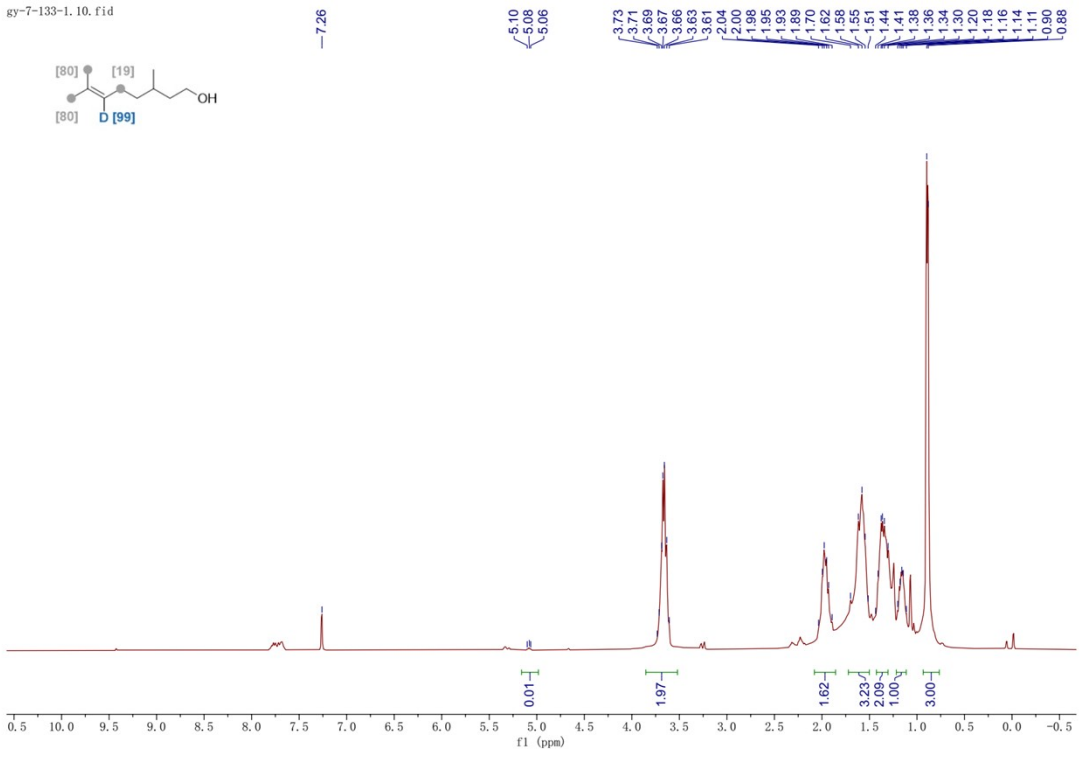
5-(3-Methylbut-2-en-1-yl-2-*d*)benzo[d][1,3]dioxole (20b). According to the general procedure, the title product was obtained (31.1 mg, 81%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.65 (m, 2H), 6.68 – 6.59 (m, 1H), 5.91 (s, 2H), 5.31 – 5.24 (m, 0.14H), 3.30 – 3.23 (m, 1.76H), 1.79 – 1.66 (m, 2.45H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.69, 145.63, 135.84, 132.59, 123.48 (m, labeled), 121.00, 108.97, 108.24, 100.86, 34.02, 29.85 (m, labeled).
Deuterium incorporation: 4.6 D/molecule (^{1}H-NMR)

6. NMR spectra of products

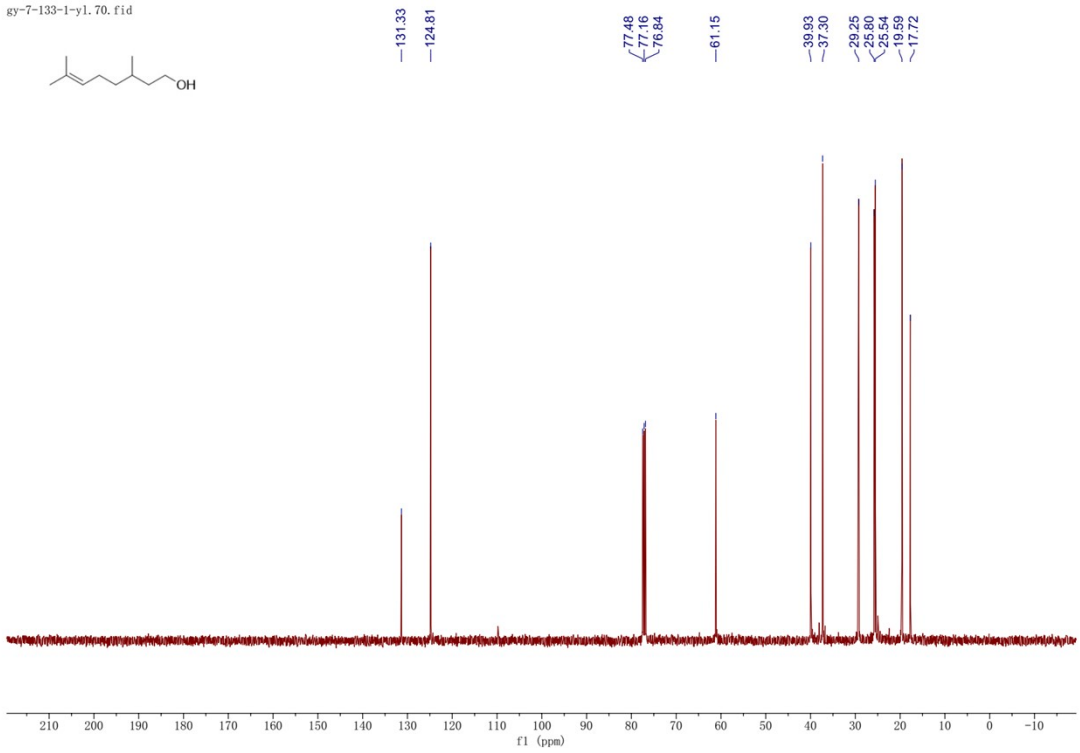
^{1}H NMR spectra of 1a:



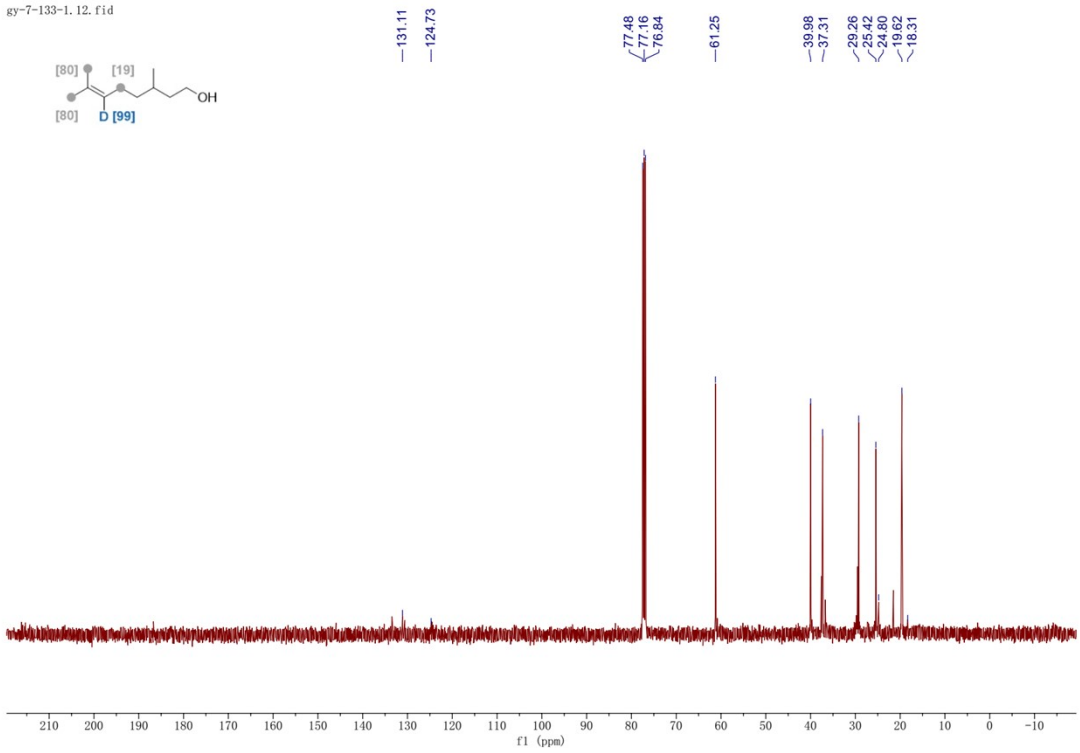
^{1}H NMR spectra of 1b:



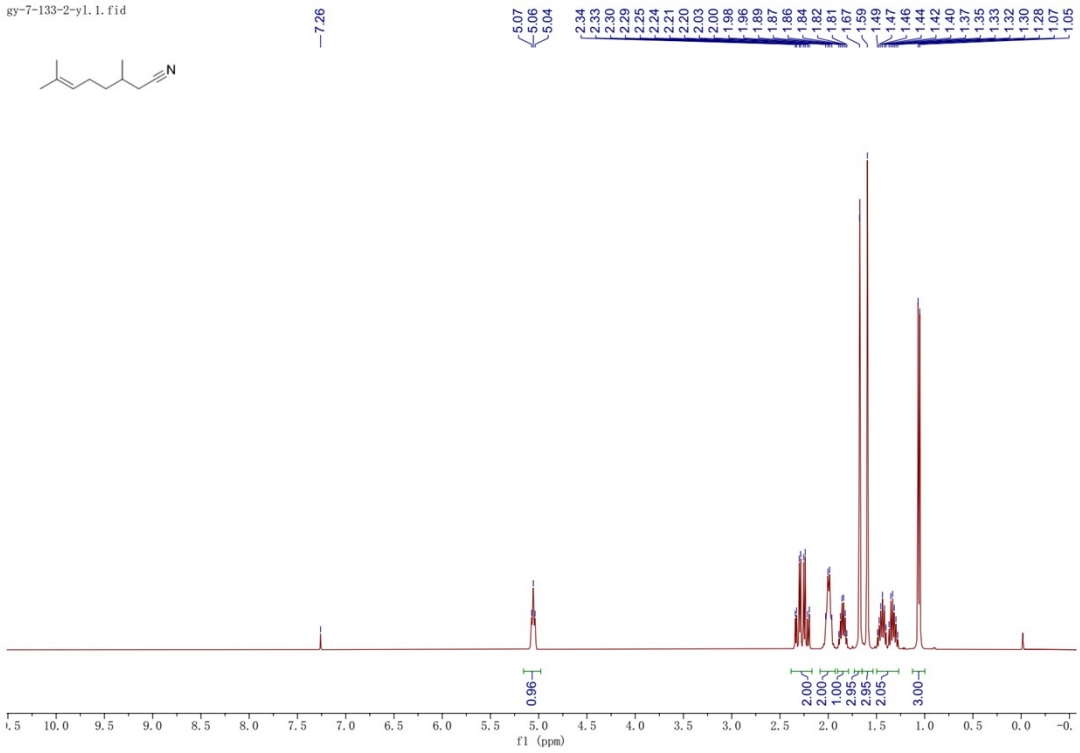
^{13}C NMR spectra of 1a:



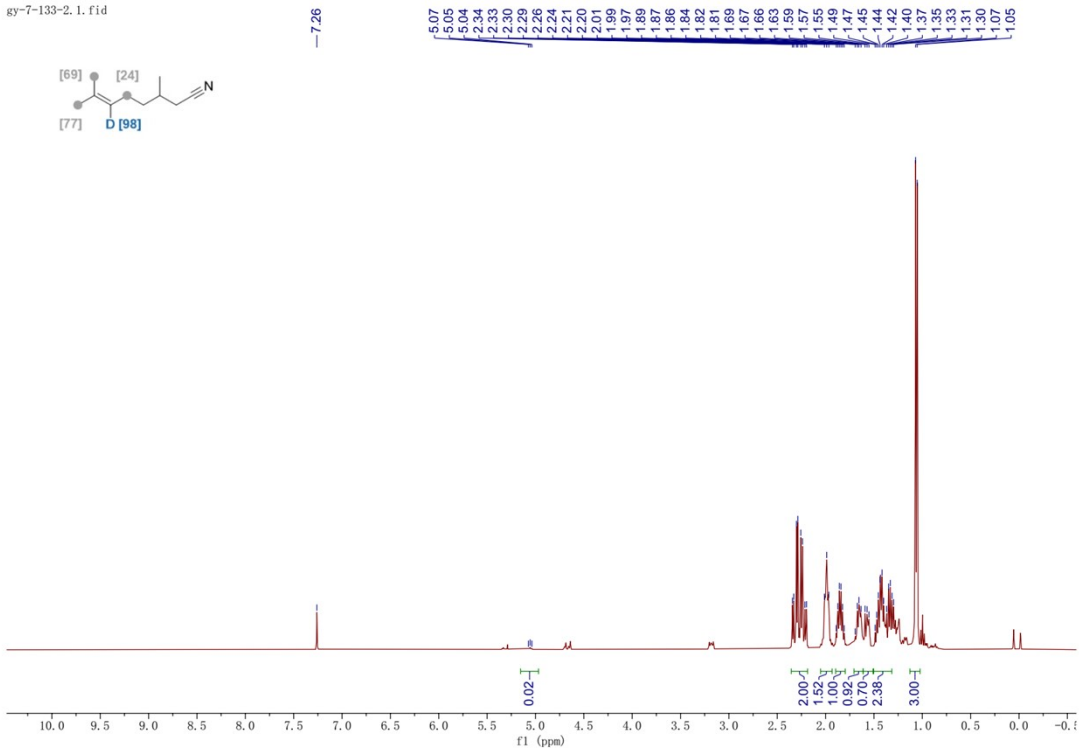
^{13}C NMR spectra of 1b:



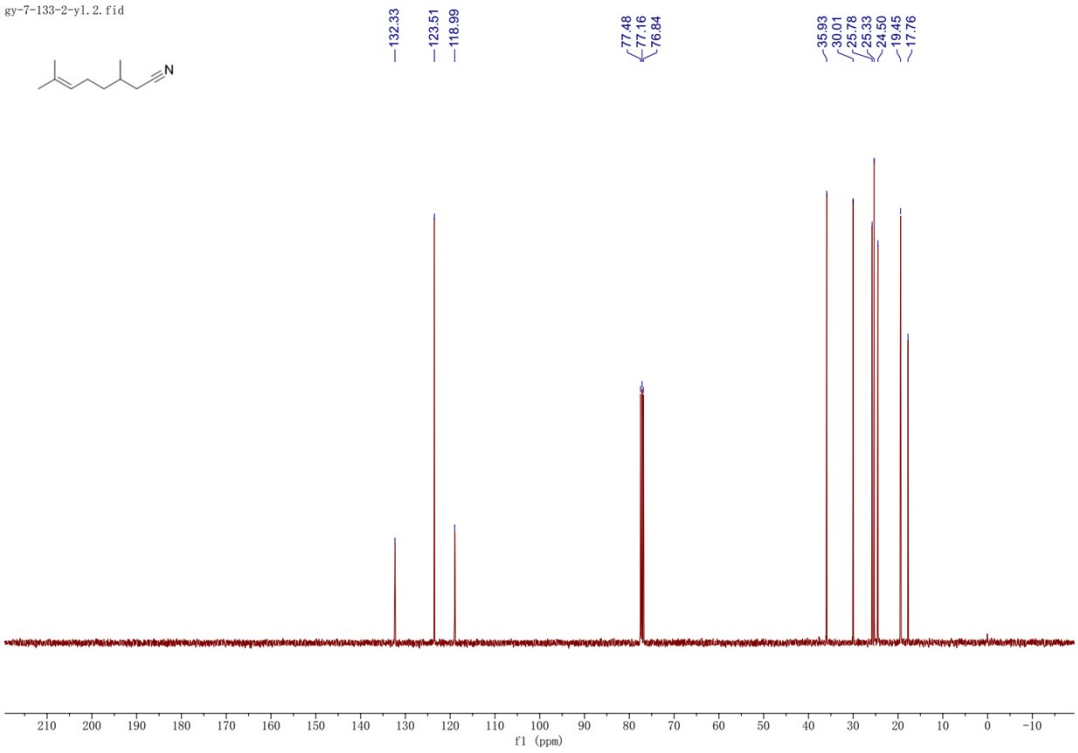
^{1}H NMR spectra of 2a:



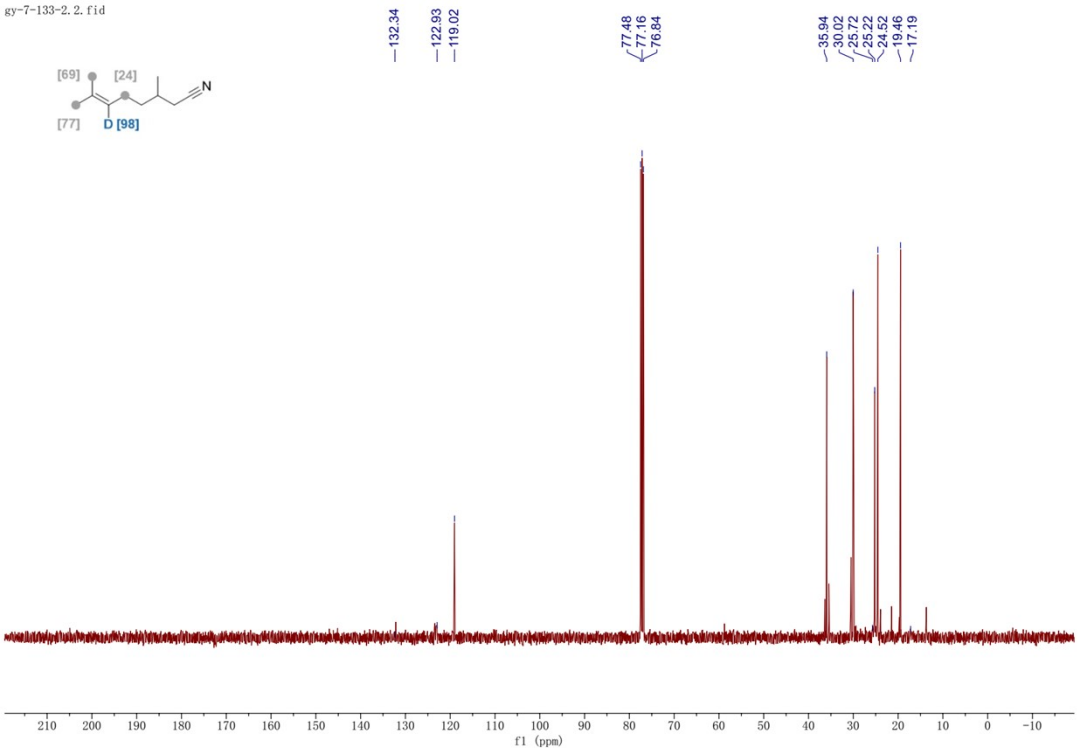
^{1}H NMR spectra of 2b:



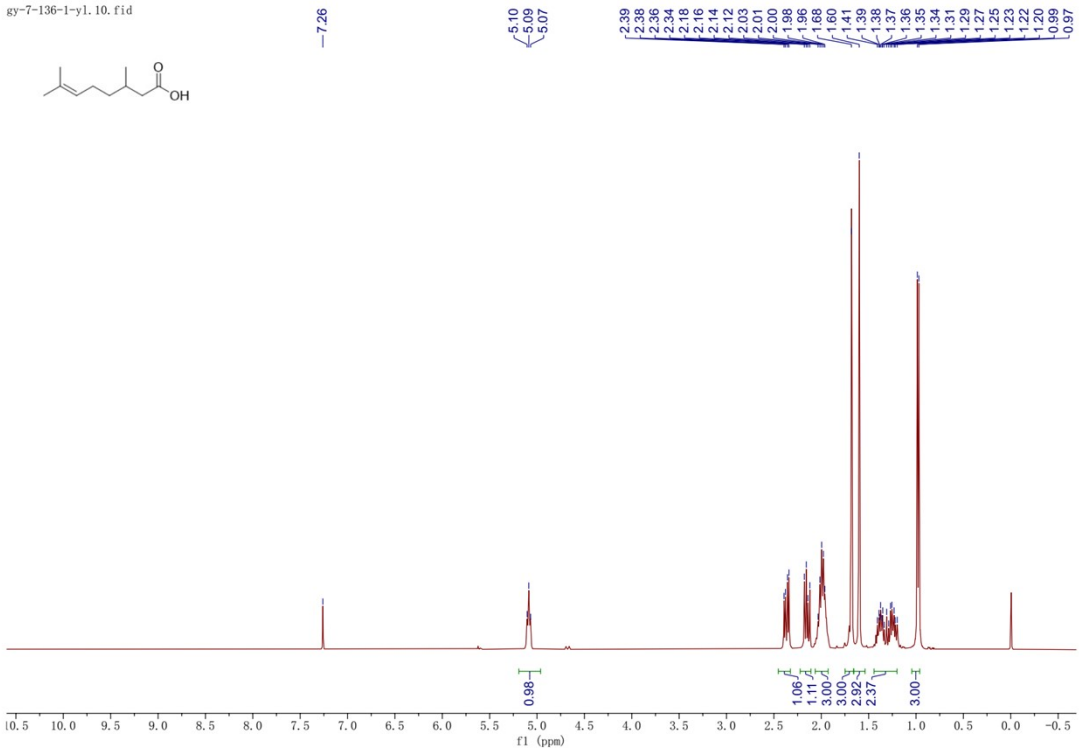
^{13}C NMR spectra of 2a:



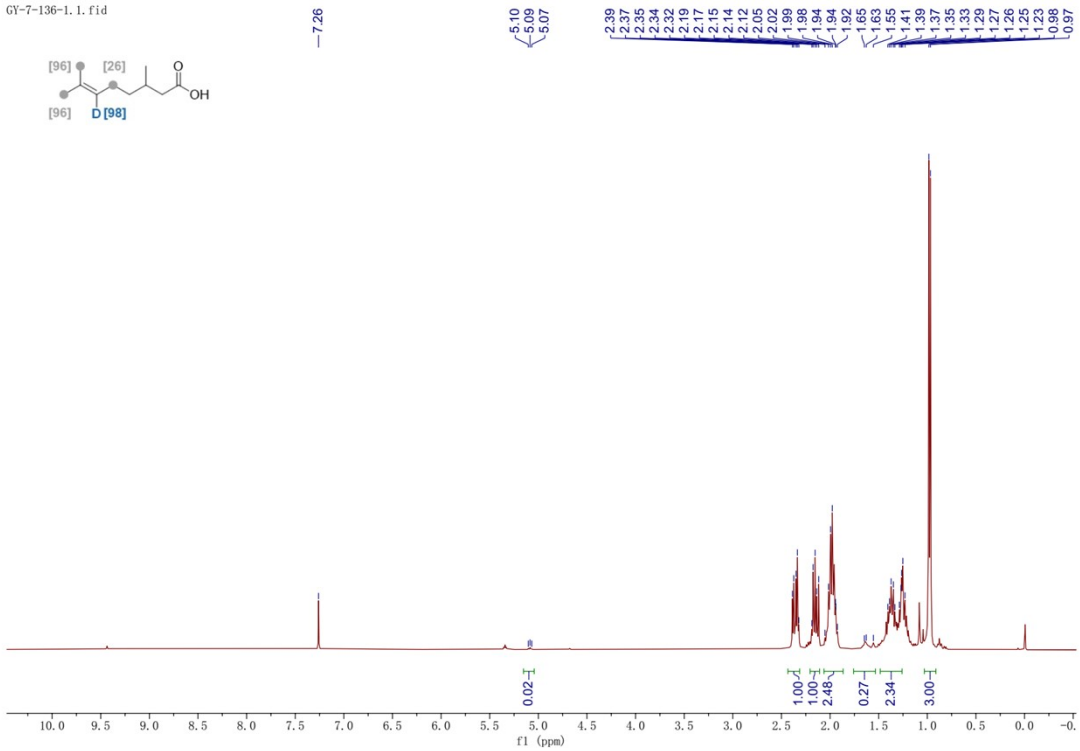
^{13}C NMR spectra of 2b:



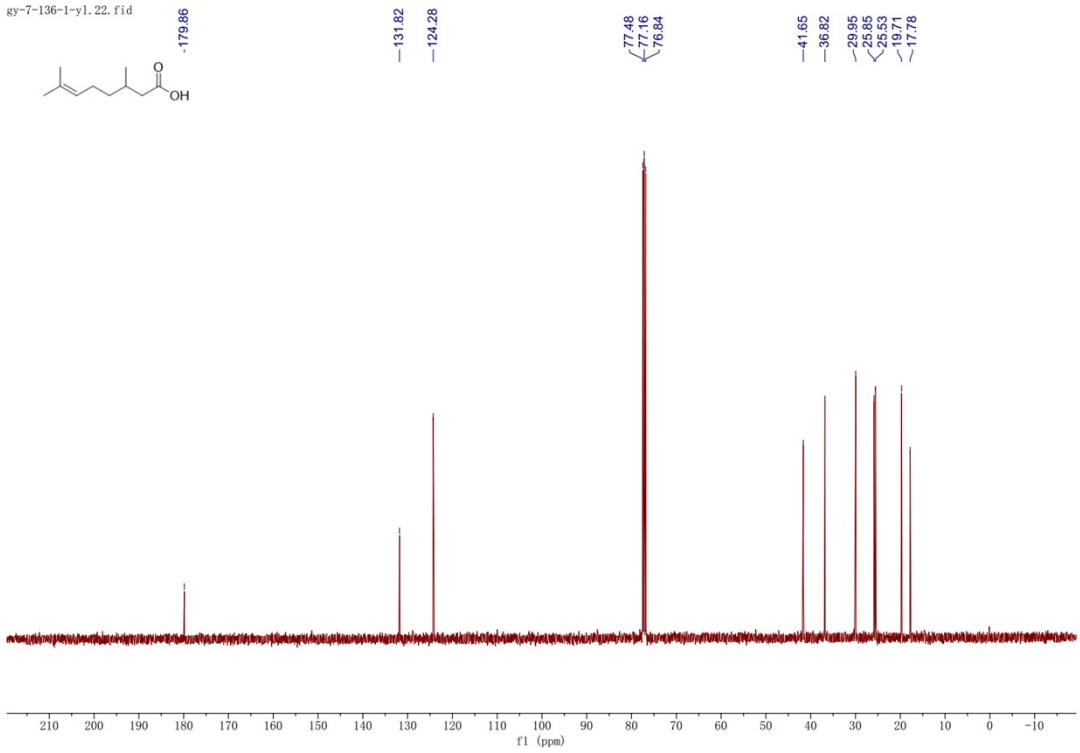
^{1}H NMR spectra of 3a:



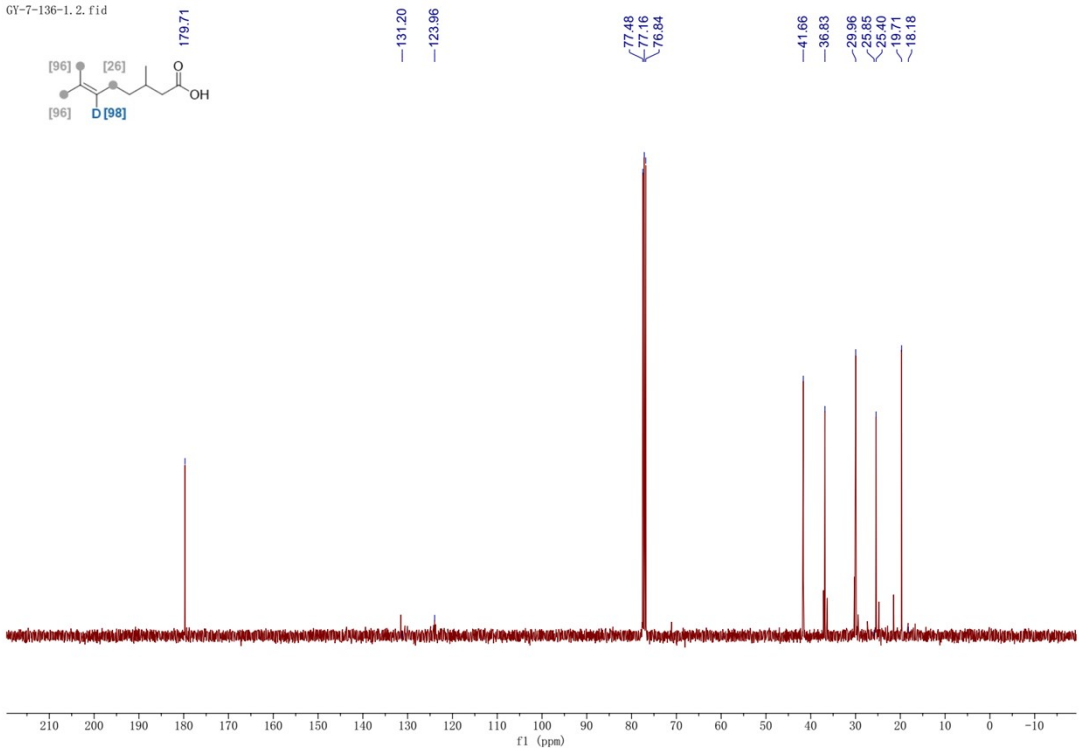
^{1}H NMR spectra of 3b:



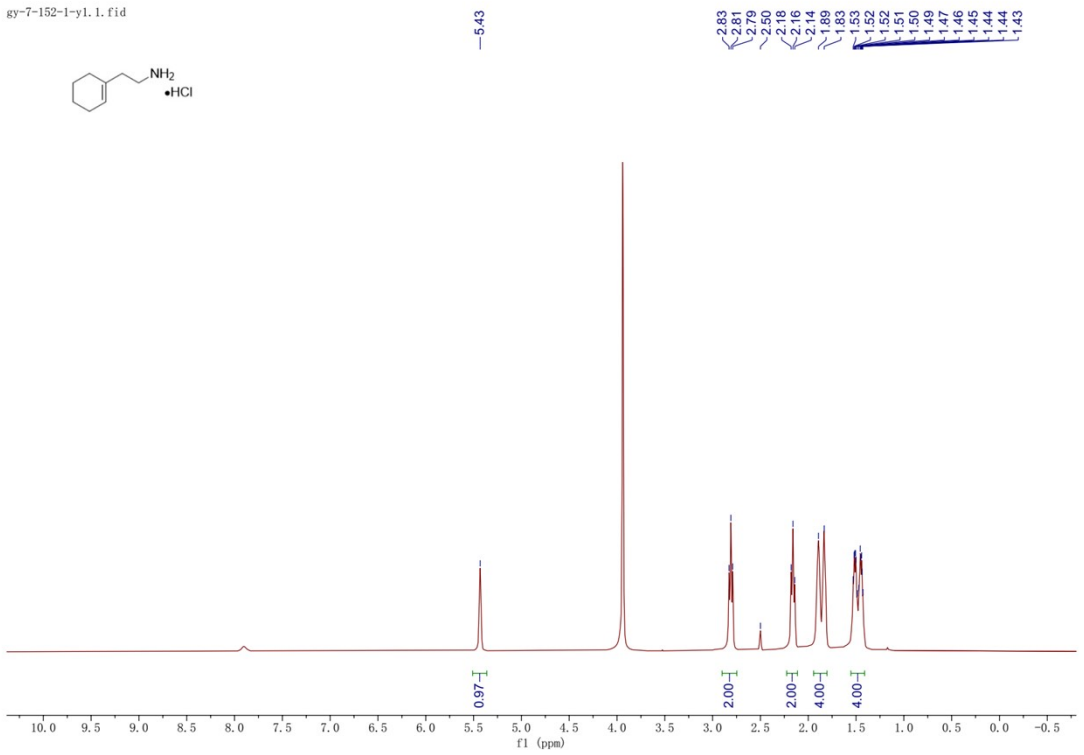
^{13}C NMR spectra of 3a:



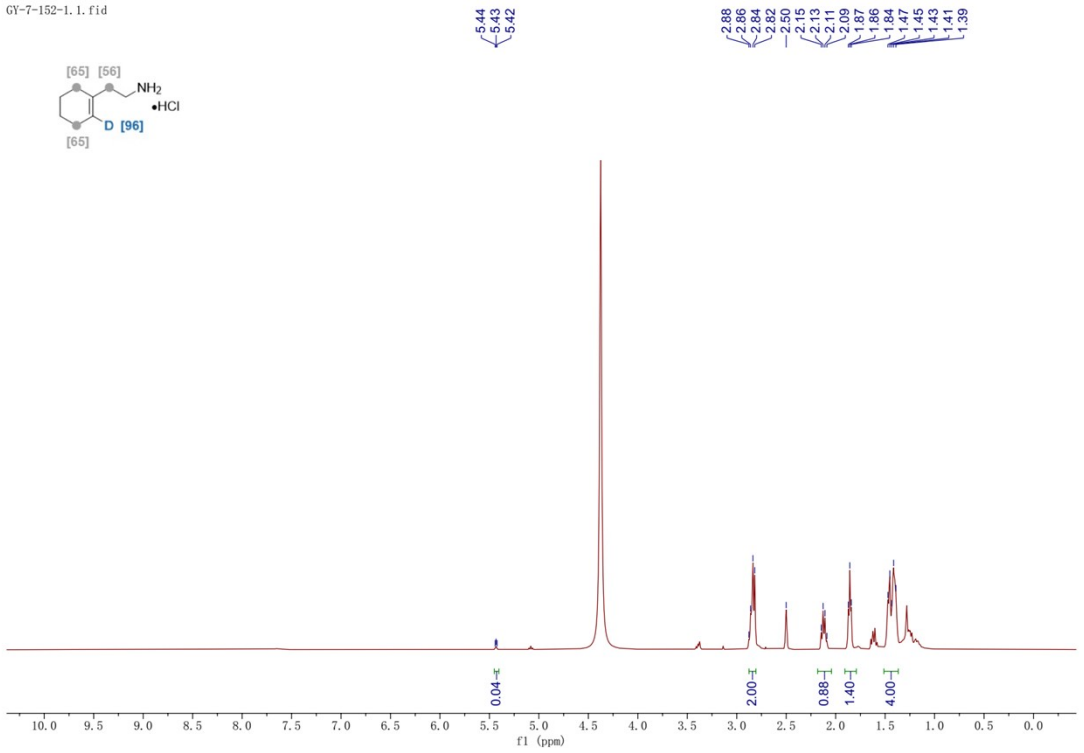
^{13}C NMR spectra of 3b:



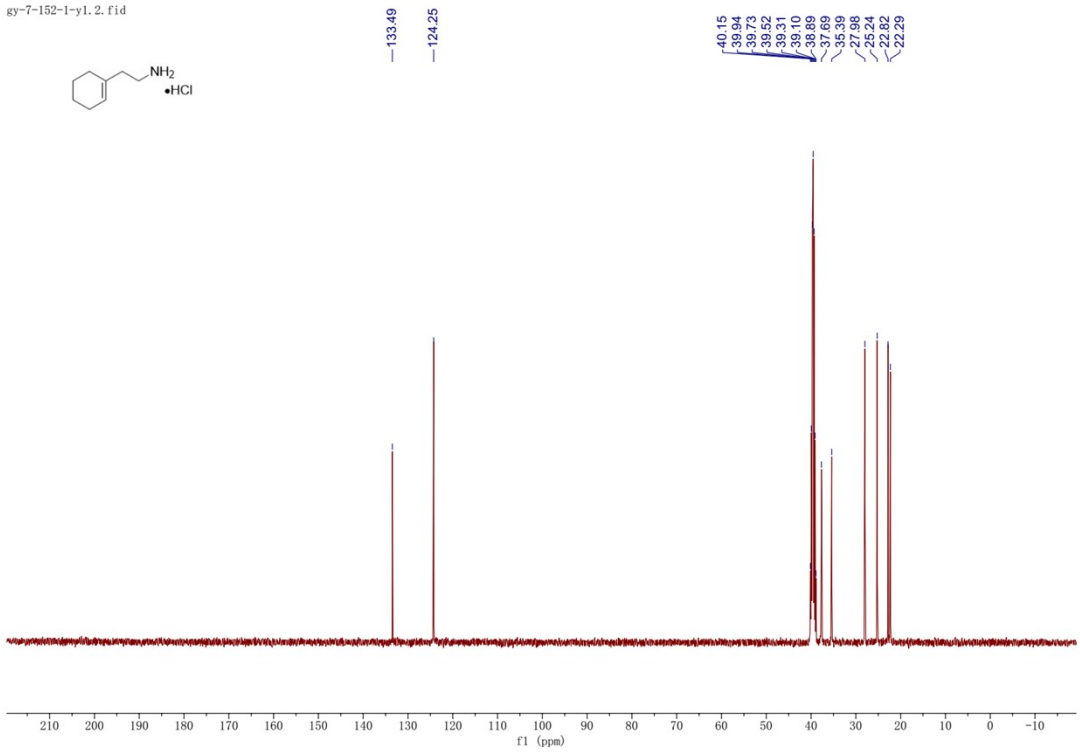
^{1}H NMR spectra of 4a:



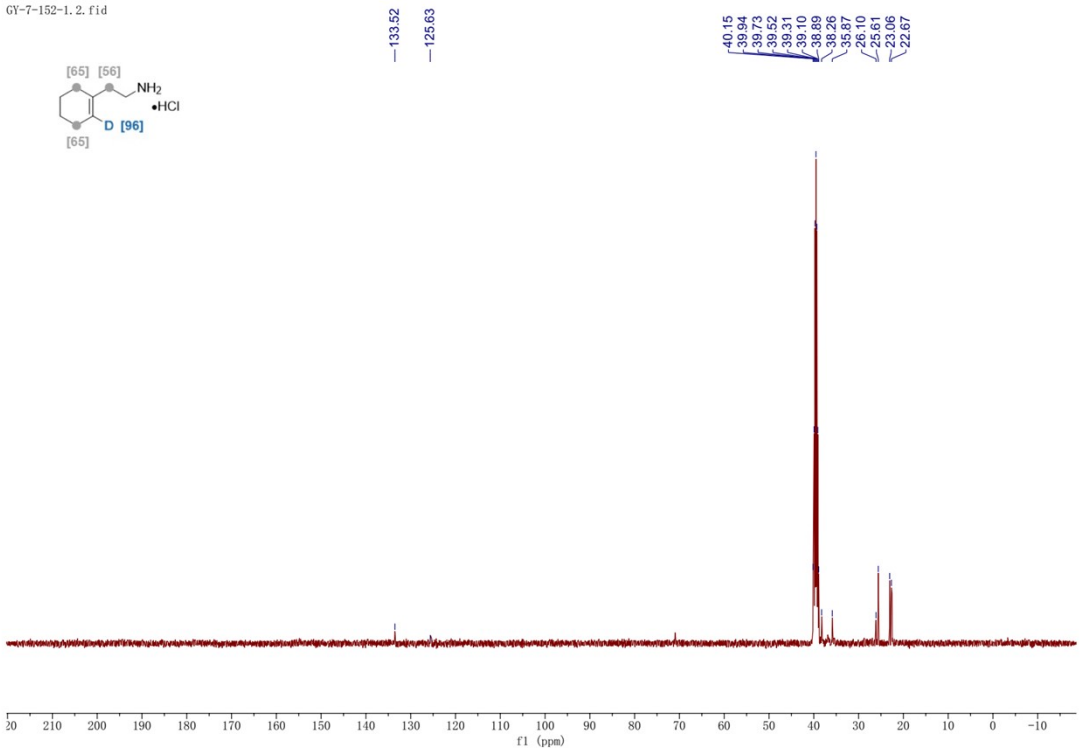
^{1}H NMR spectra of 4b:



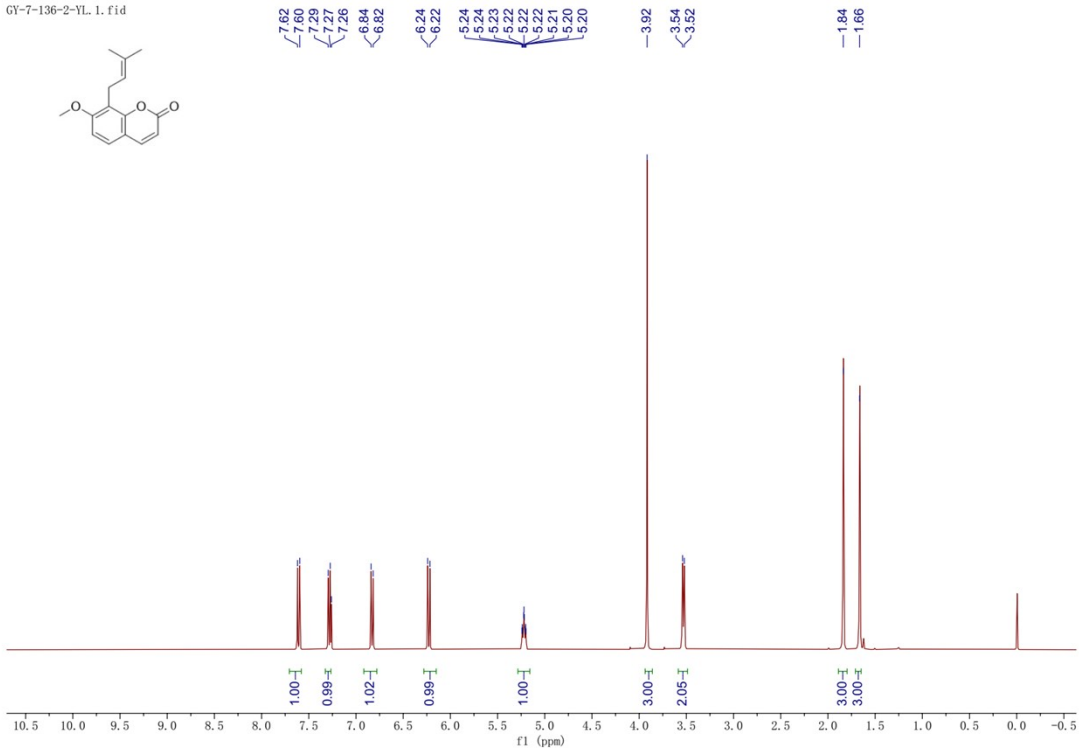
^{13}C NMR spectra of 4a:



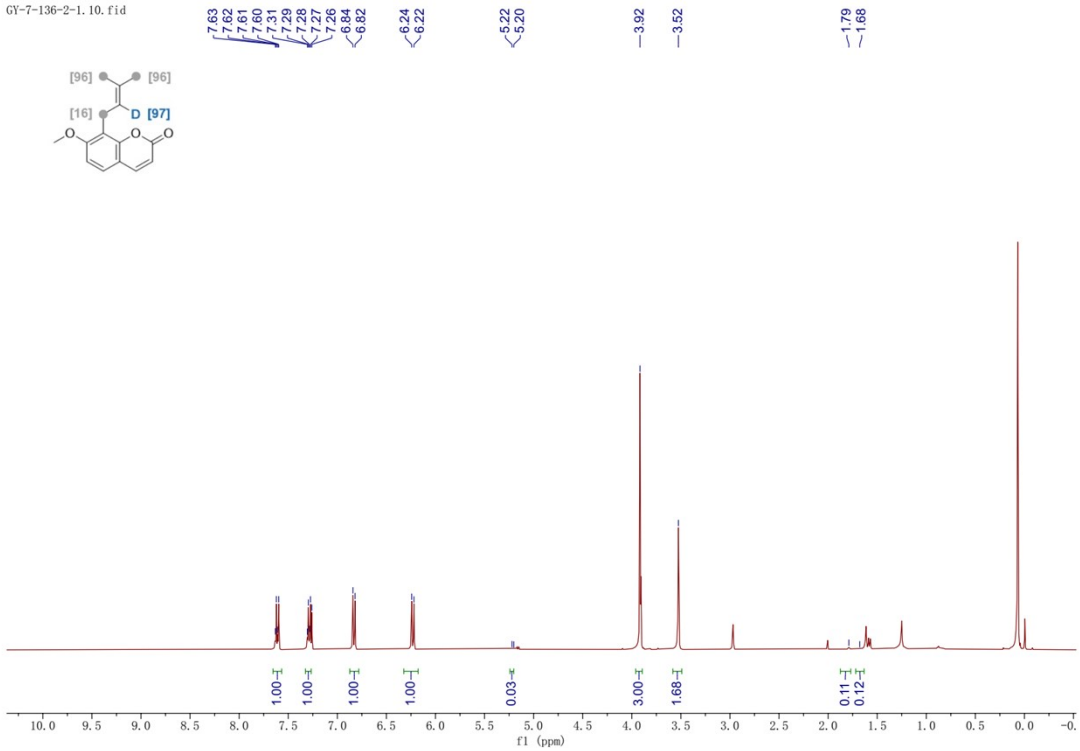
^{13}C NMR spectra of 4b:



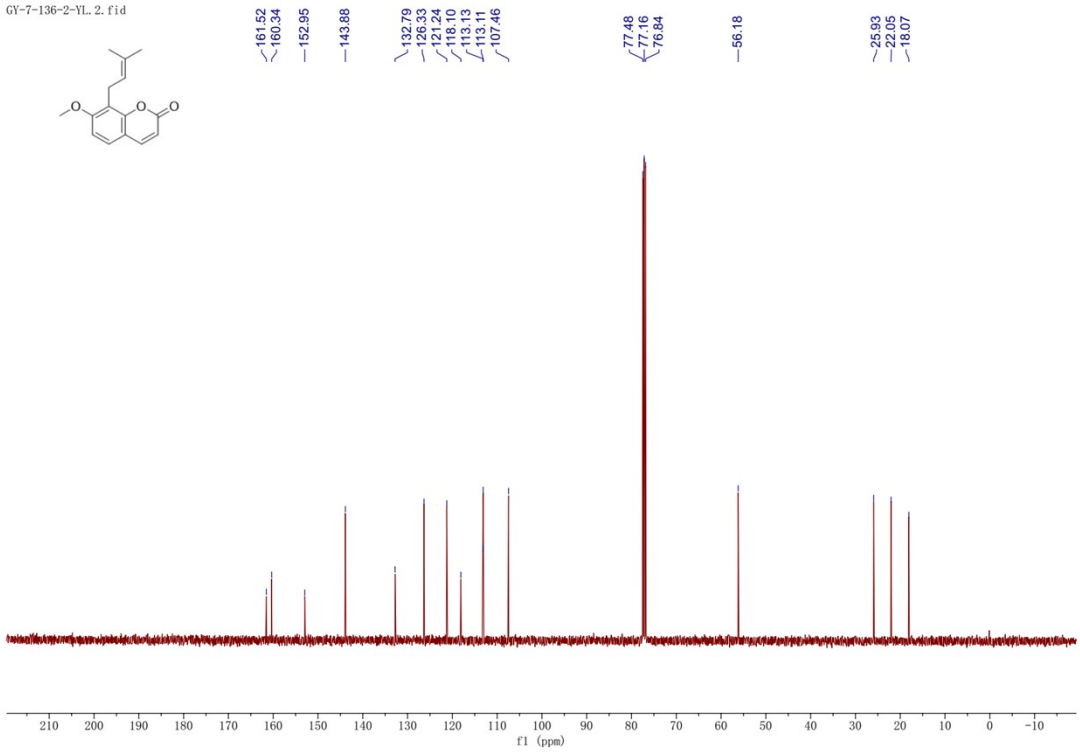
^{1}H NMR spectra of 5a:



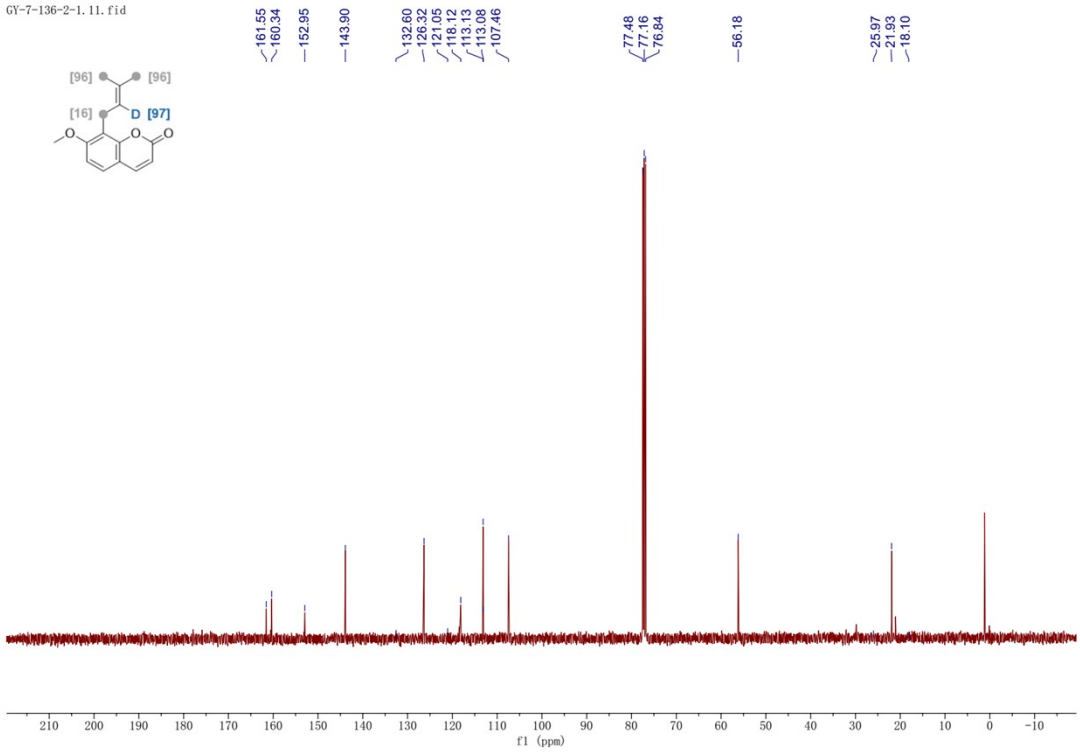
^{1}H NMR spectra of 5b:



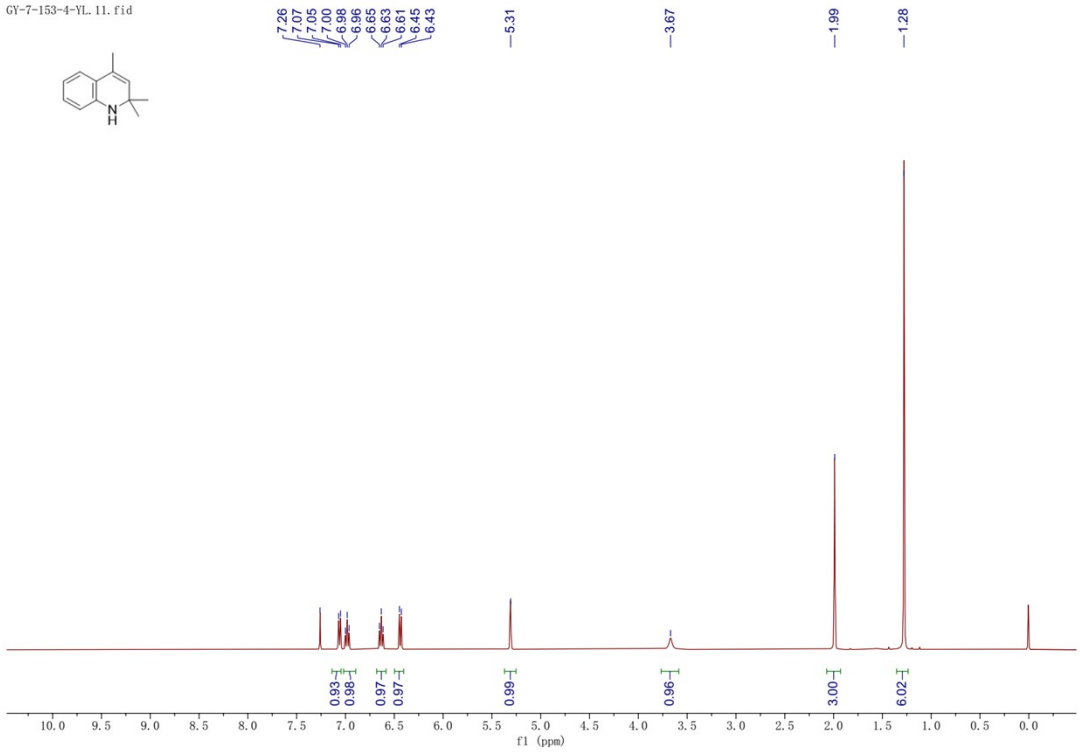
^{13}C NMR spectra of 5a:



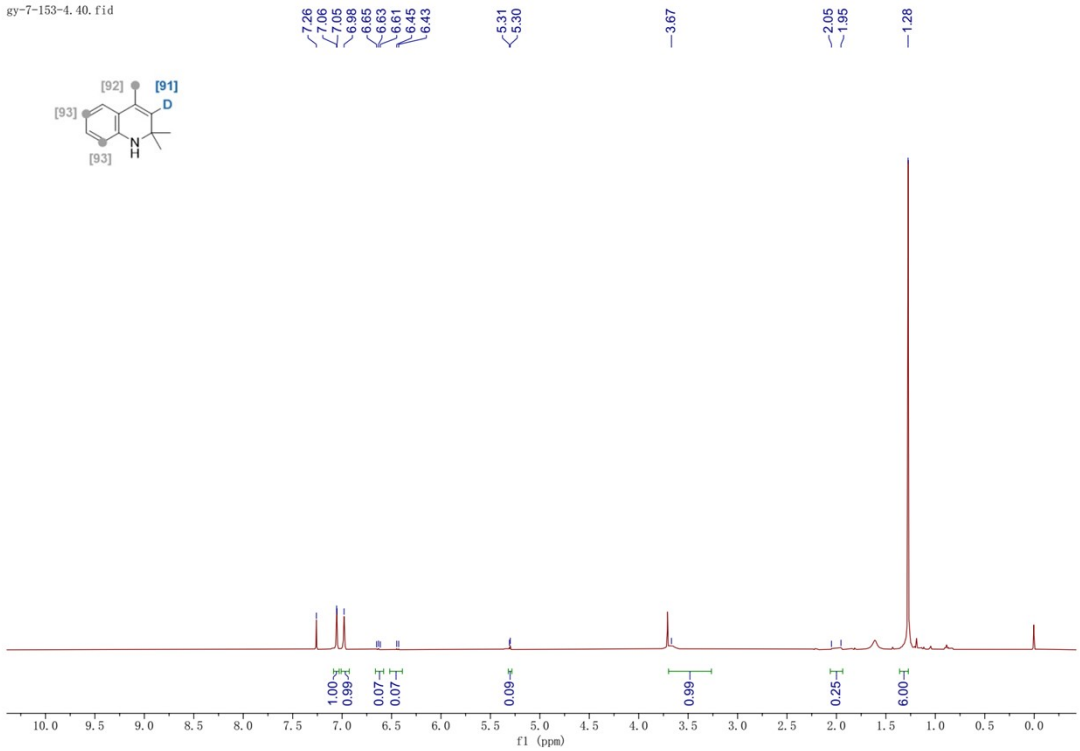
^{13}C NMR spectra of 5b:



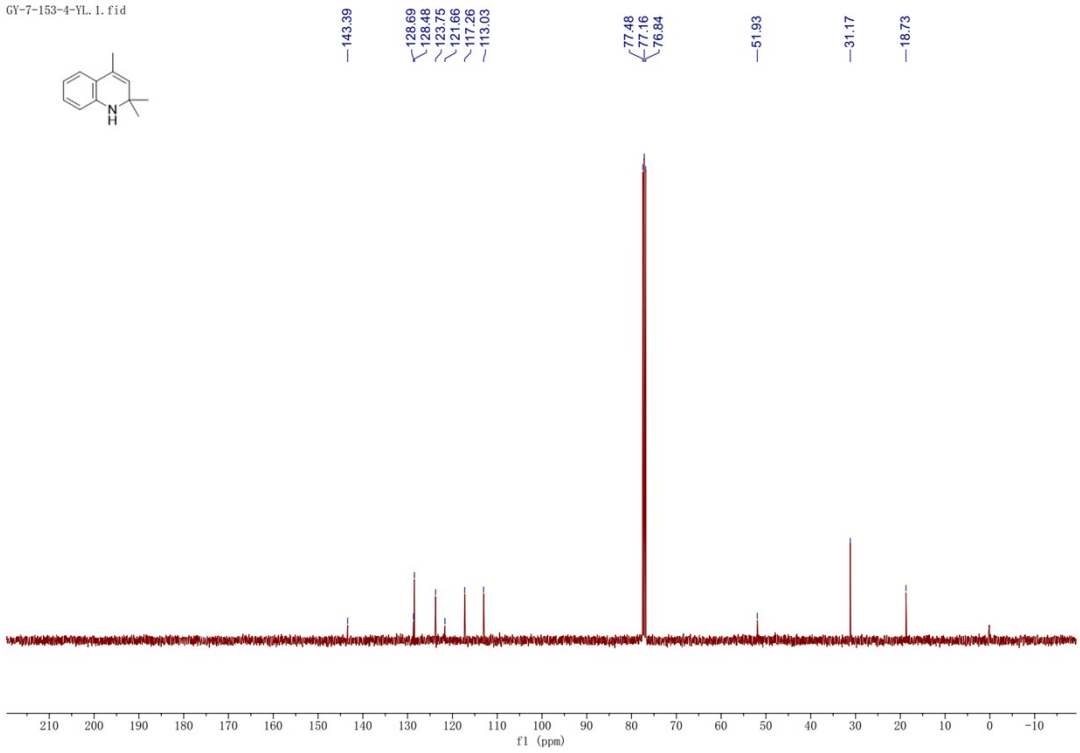
^{1}H NMR spectra of 6a:



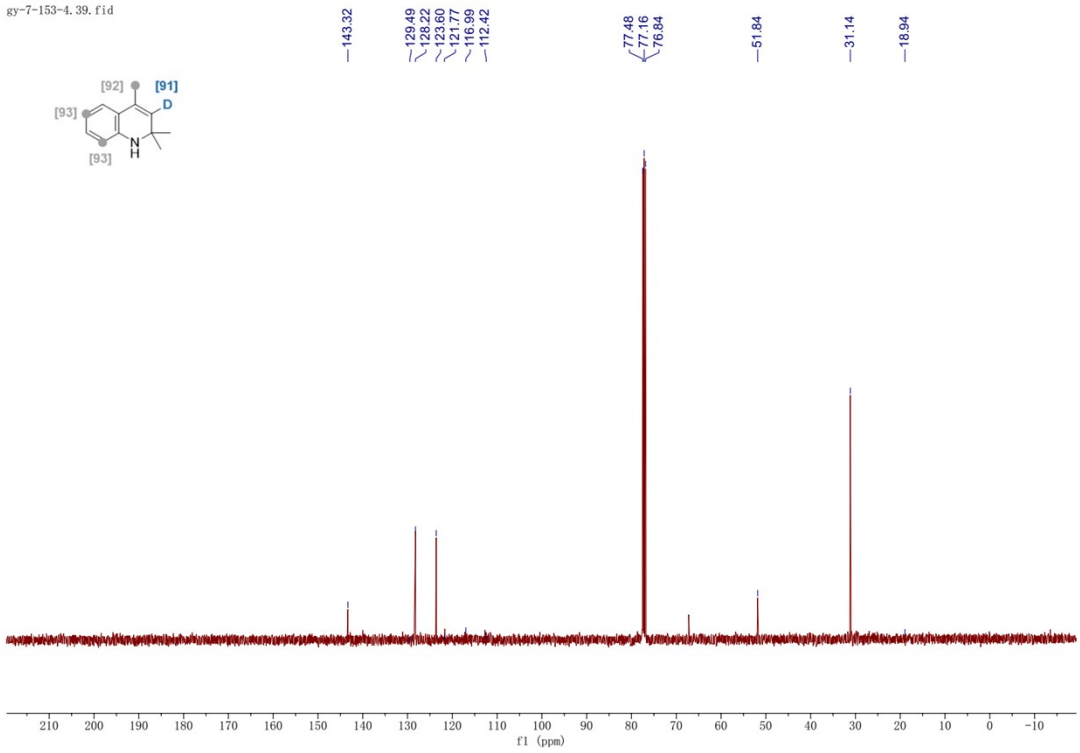
^{1}H NMR spectra of 6b:



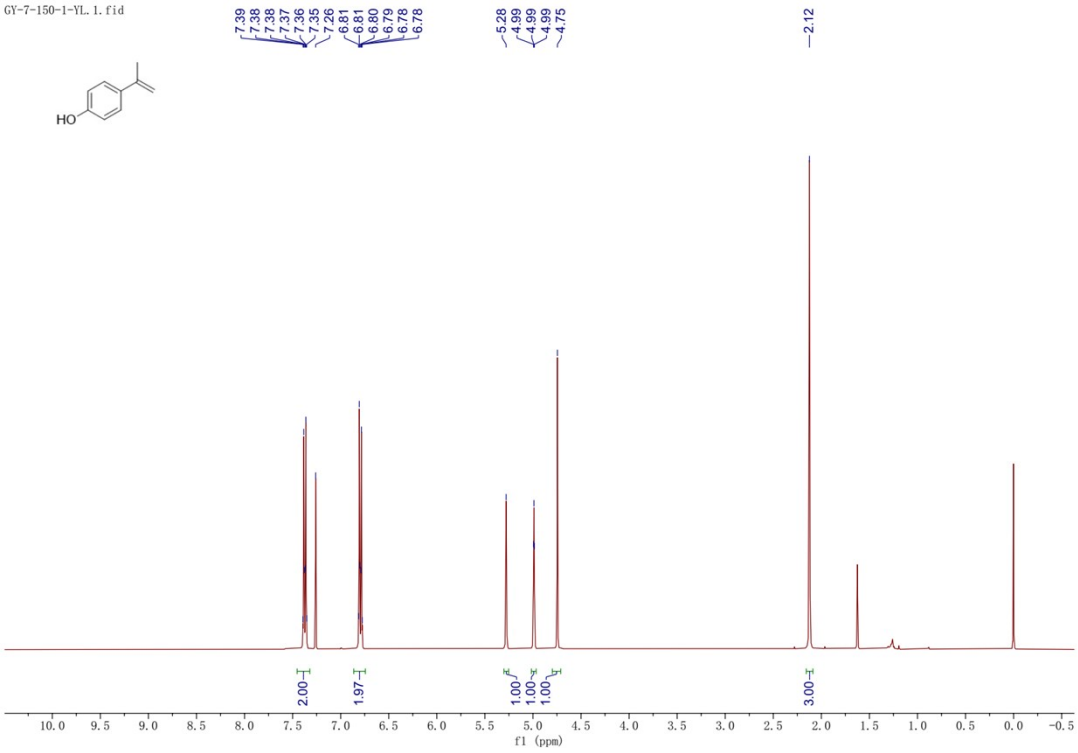
^{13}C NMR spectra of 6a:



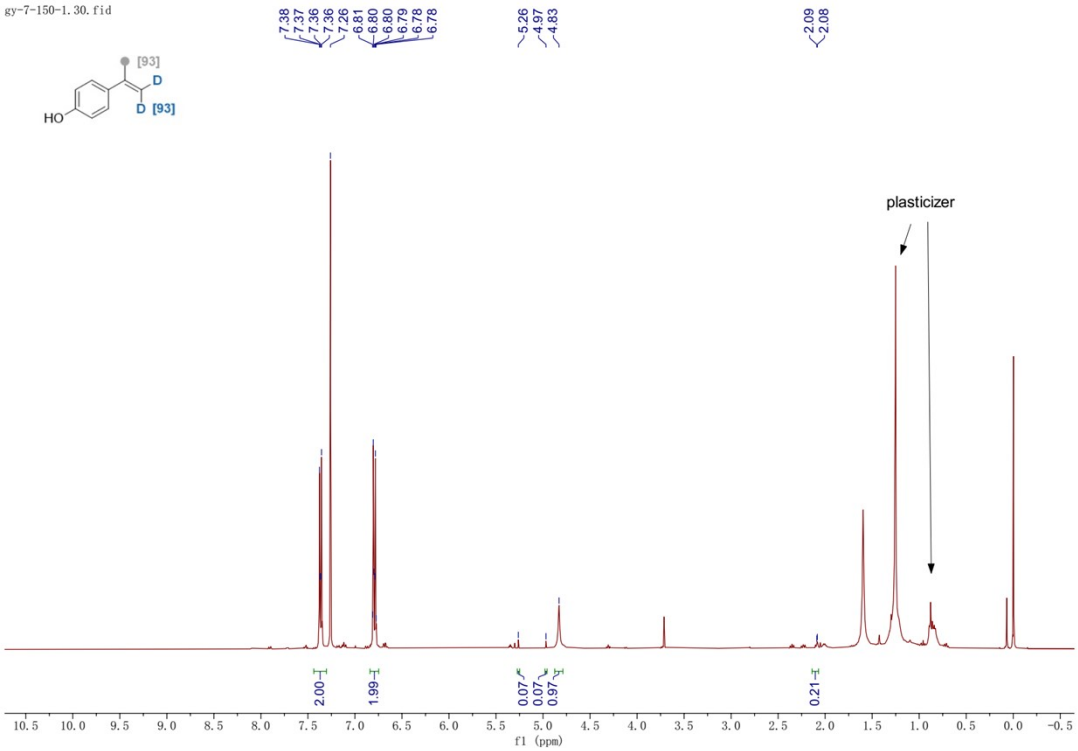
^{13}C NMR spectra of 6b:



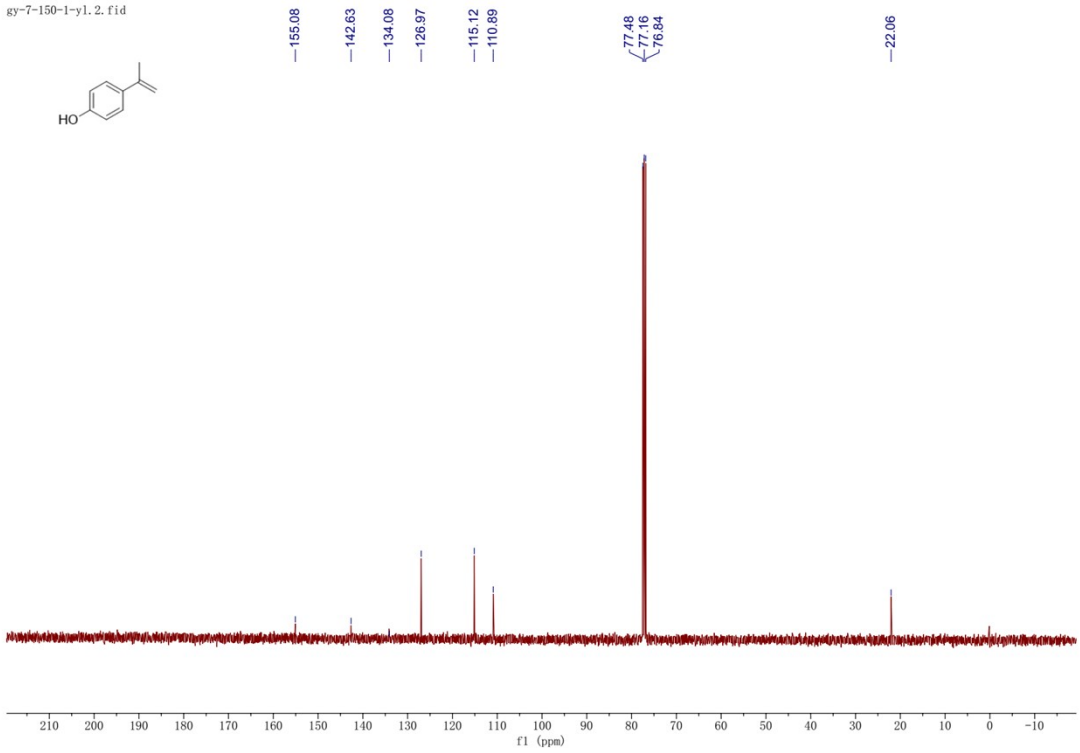
^{1}H NMR spectra of 7a:



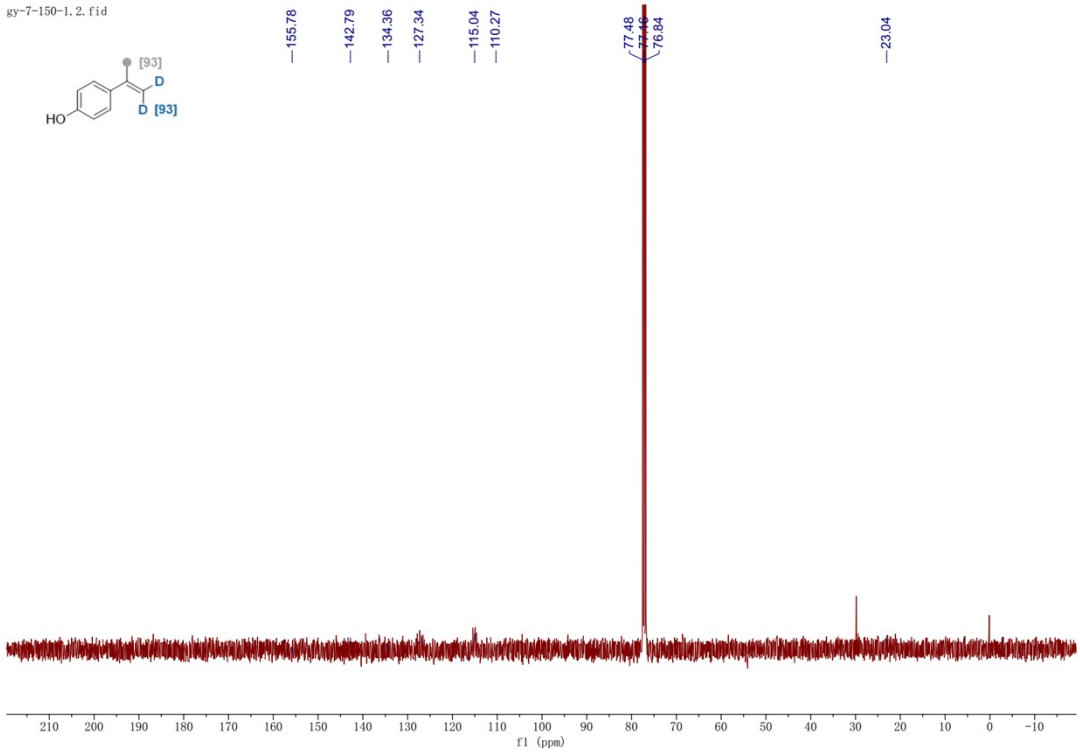
^{1}H NMR spectra of 7b:



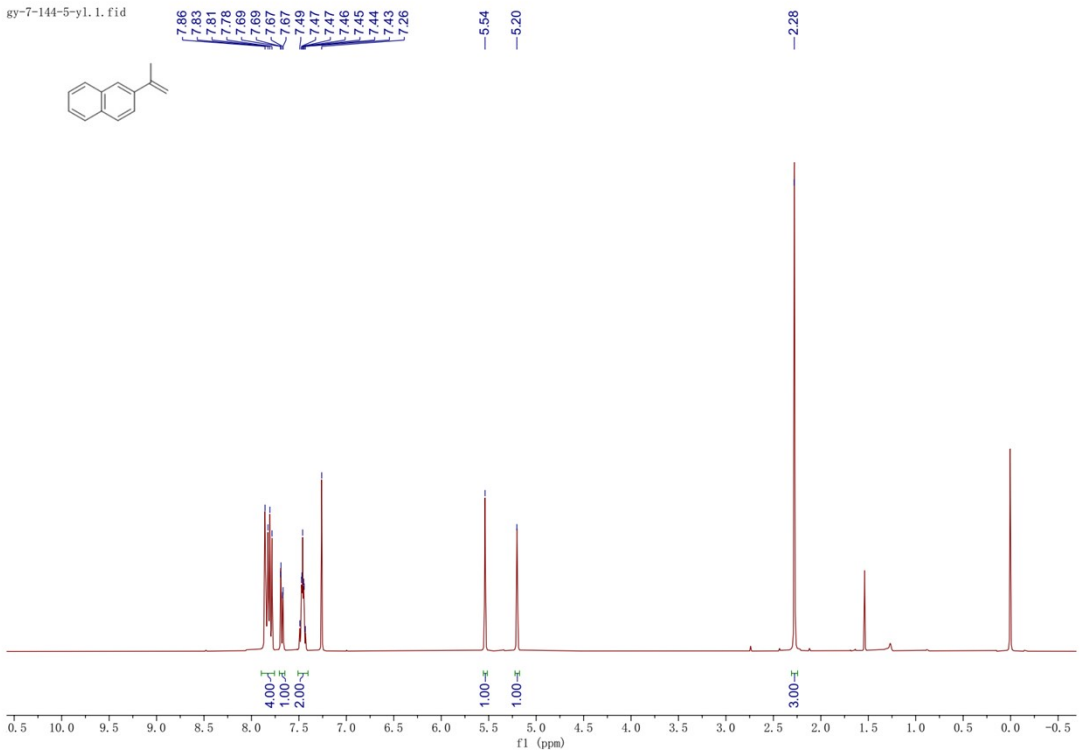
^{13}C NMR spectra of 7a:



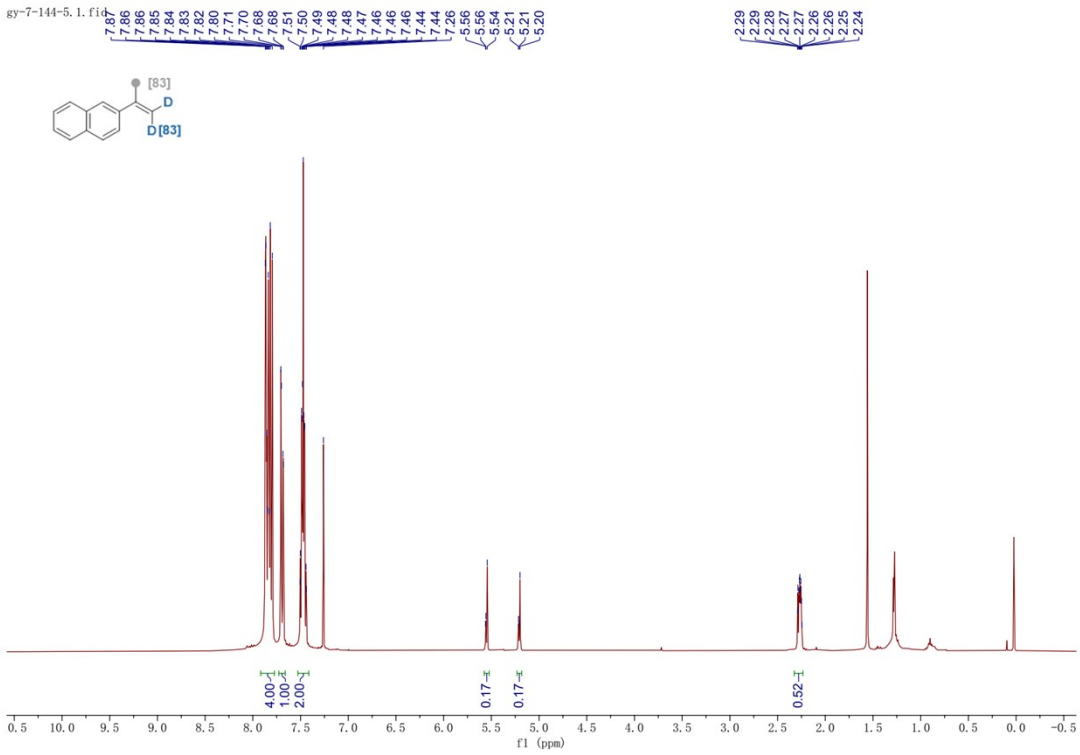
^{13}C NMR spectra of 7b:



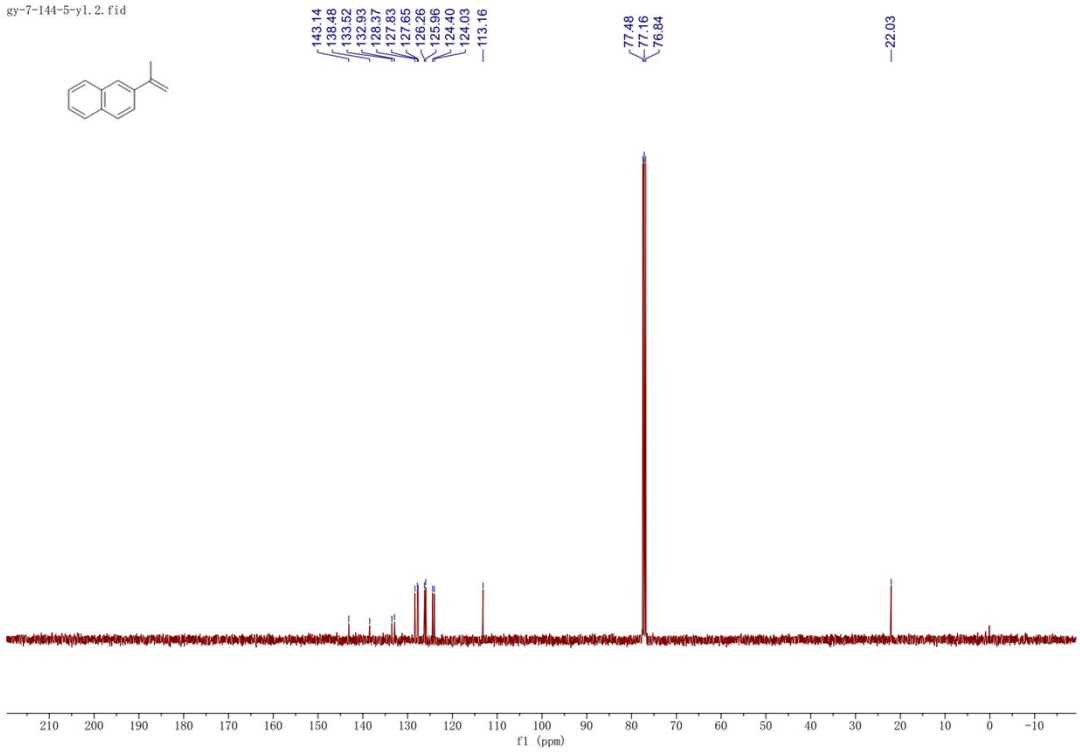
^{1}H NMR spectra of 8a:



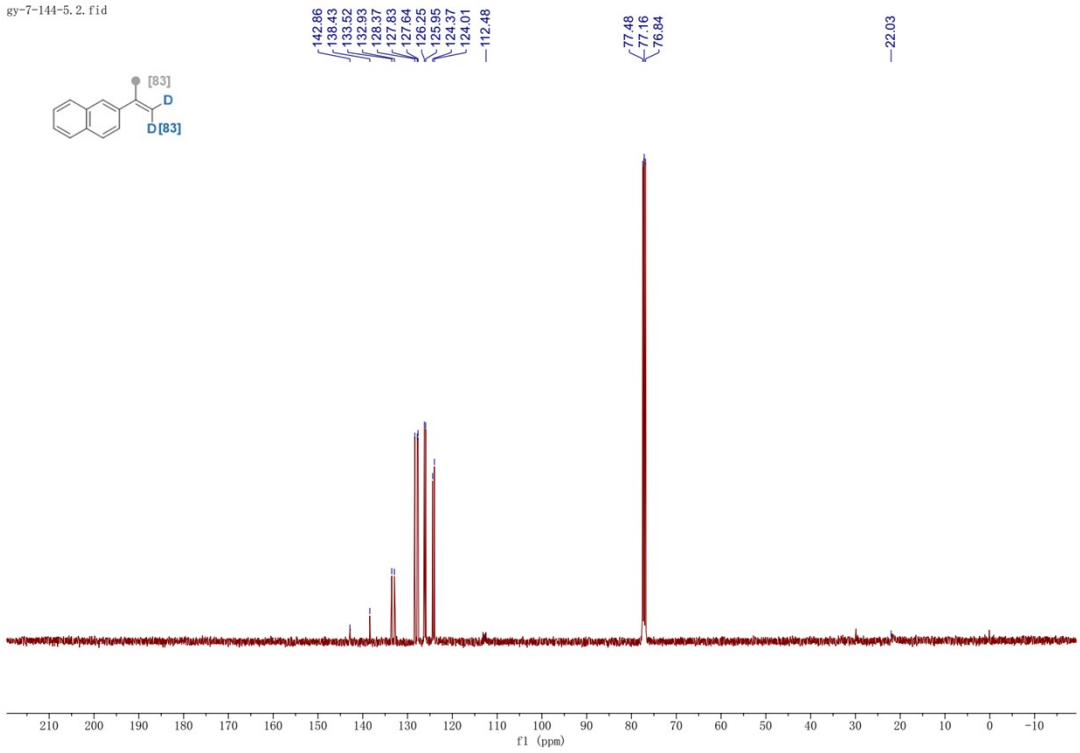
^{1}H NMR spectra of 8b:



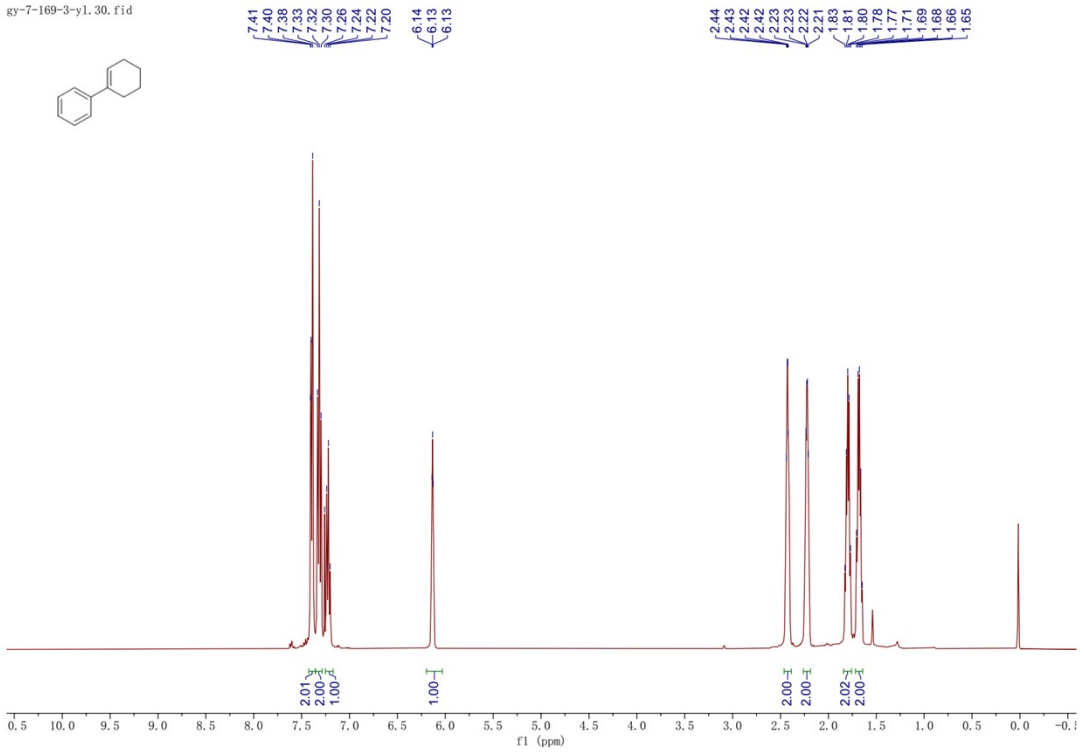
^{13}C NMR spectra of 8a:



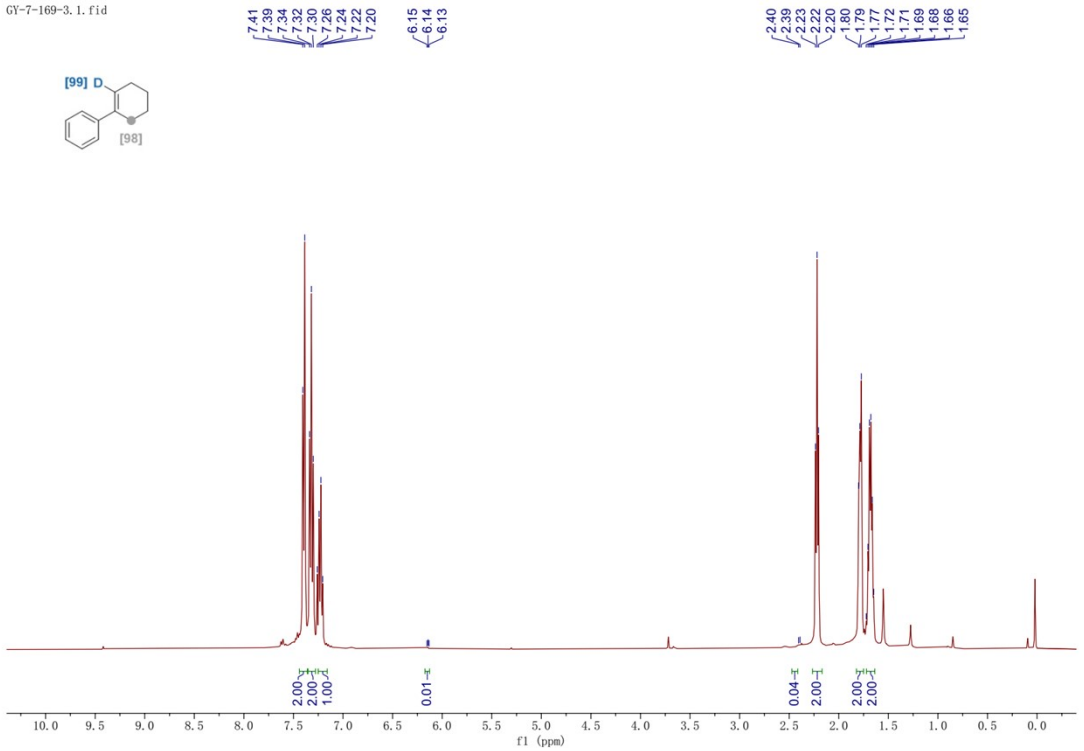
^{13}C NMR spectra of 8b:



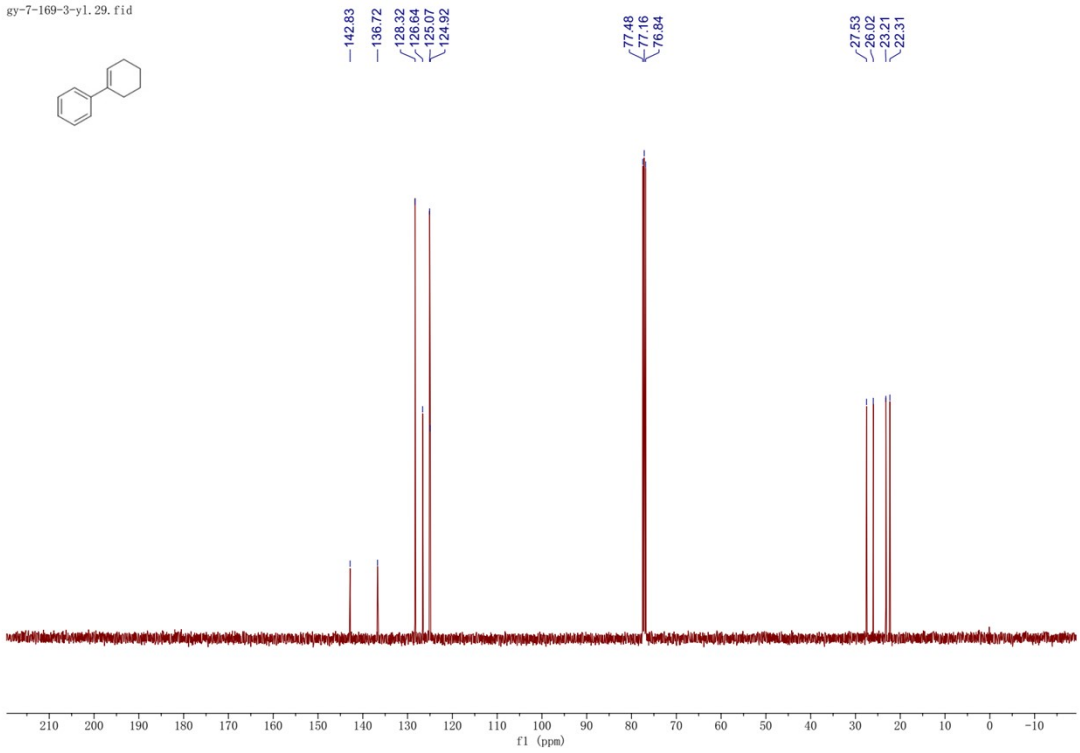
^{1}H NMR spectra of 9a:



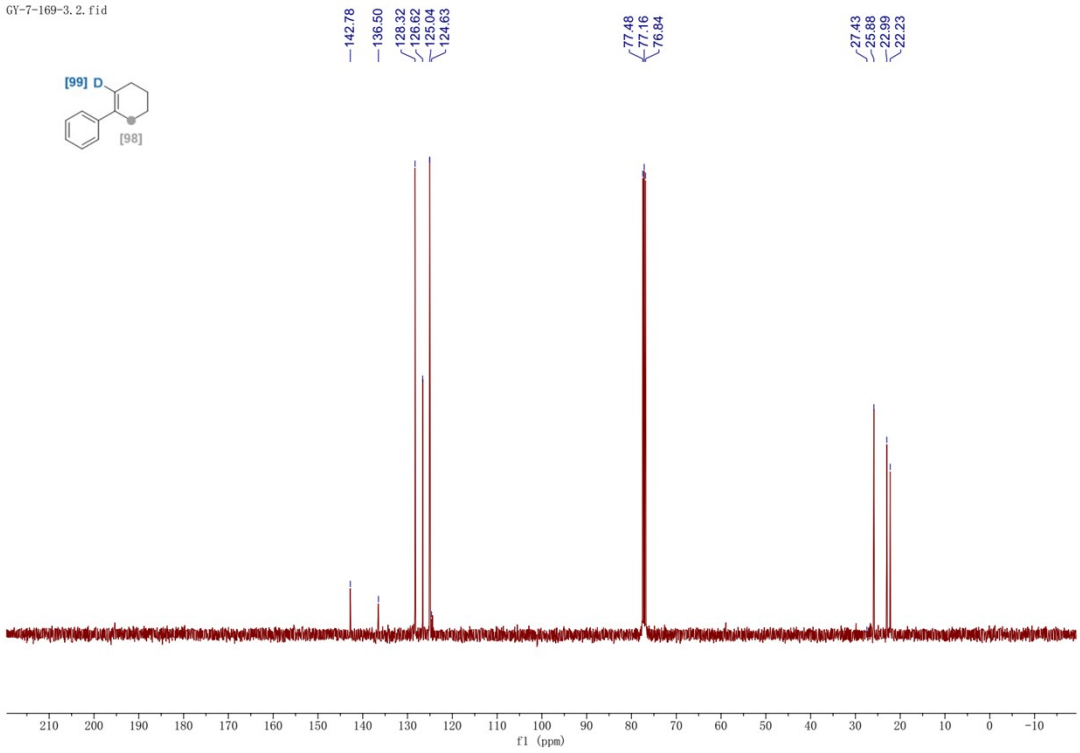
^{1}H NMR spectra of 9b:



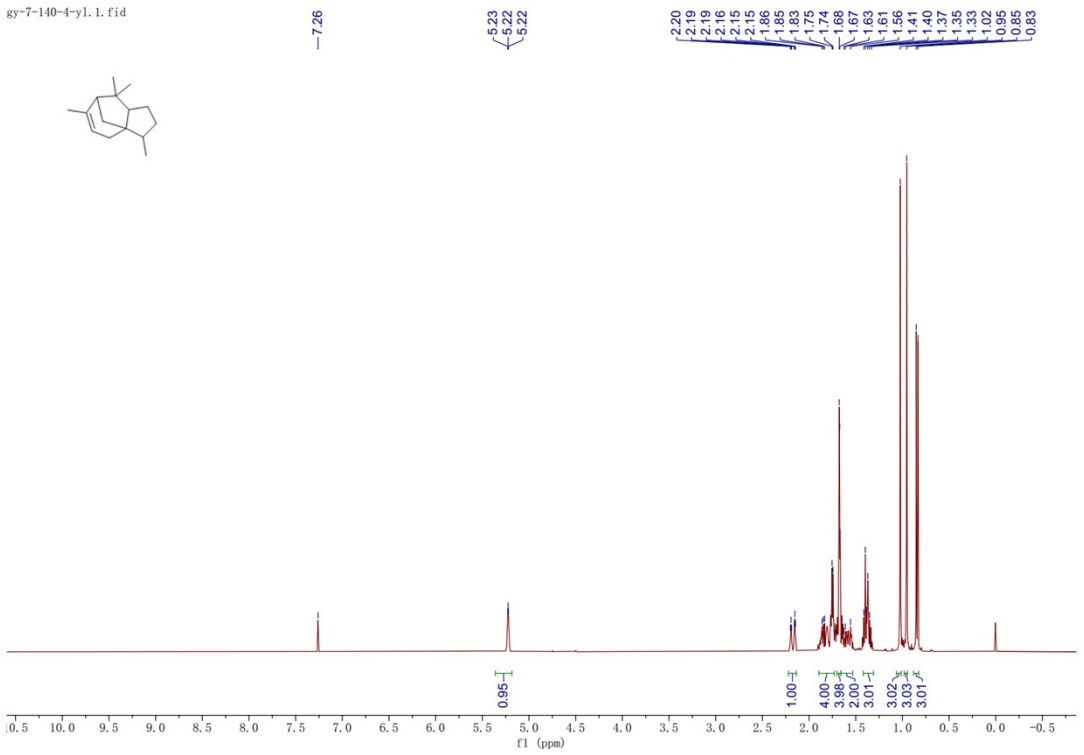
^{13}C NMR spectra of 9a:



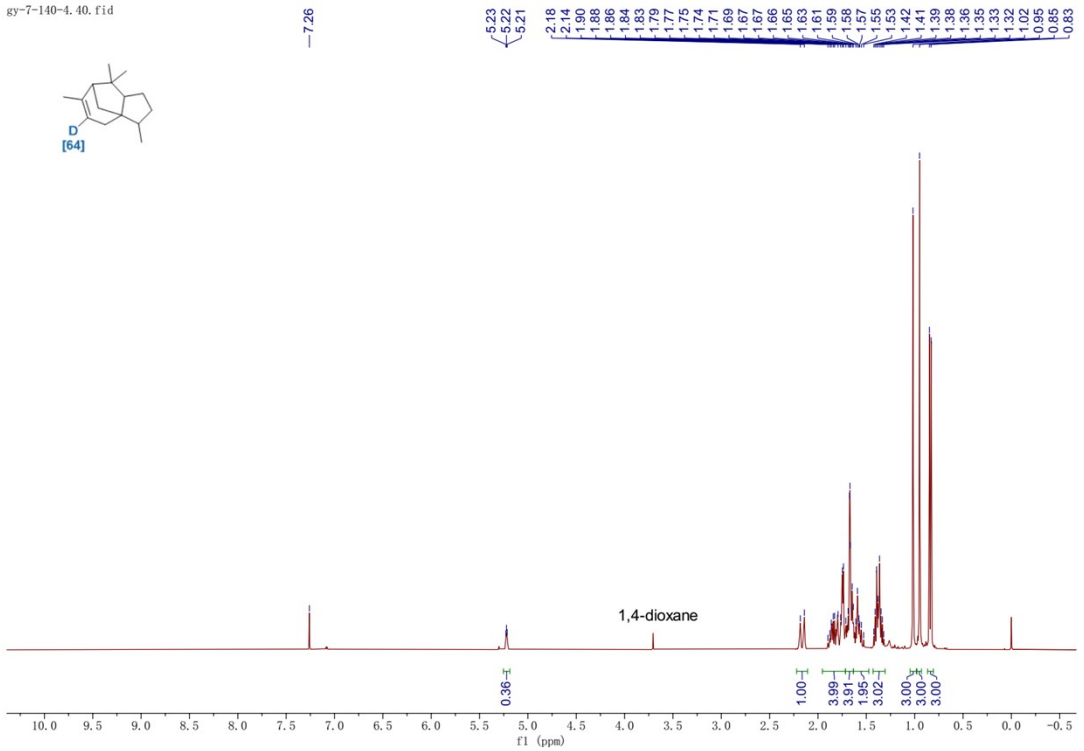
^{13}C NMR spectra of 9b:



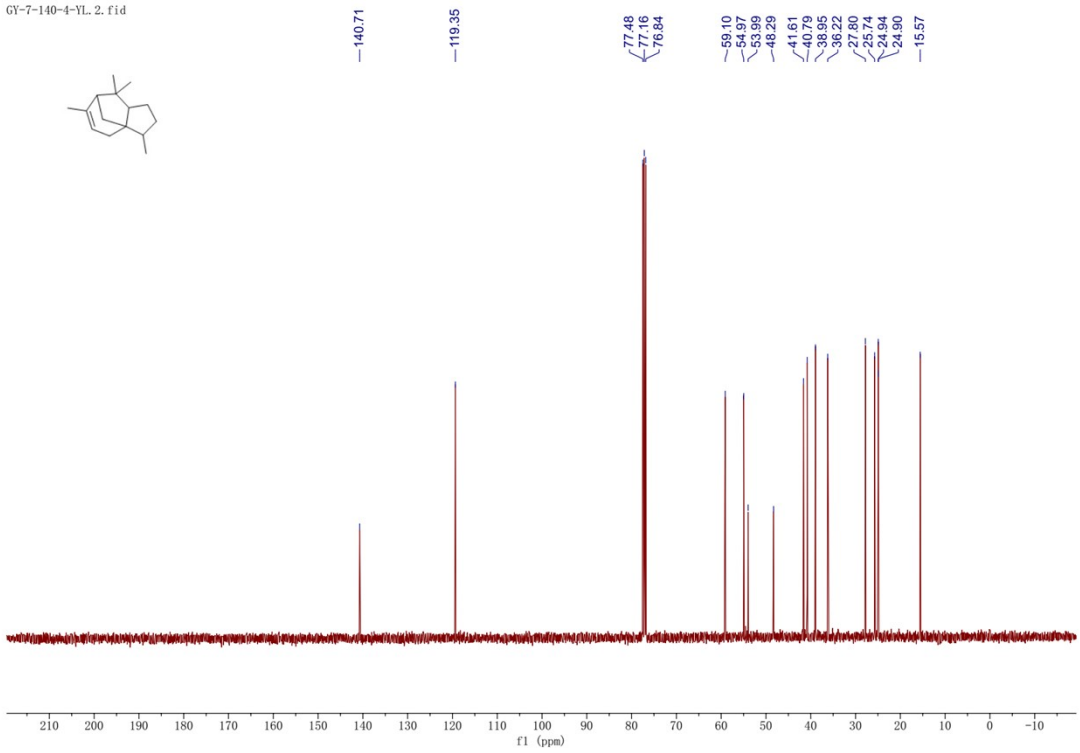
^{1}H NMR spectra of 10a:



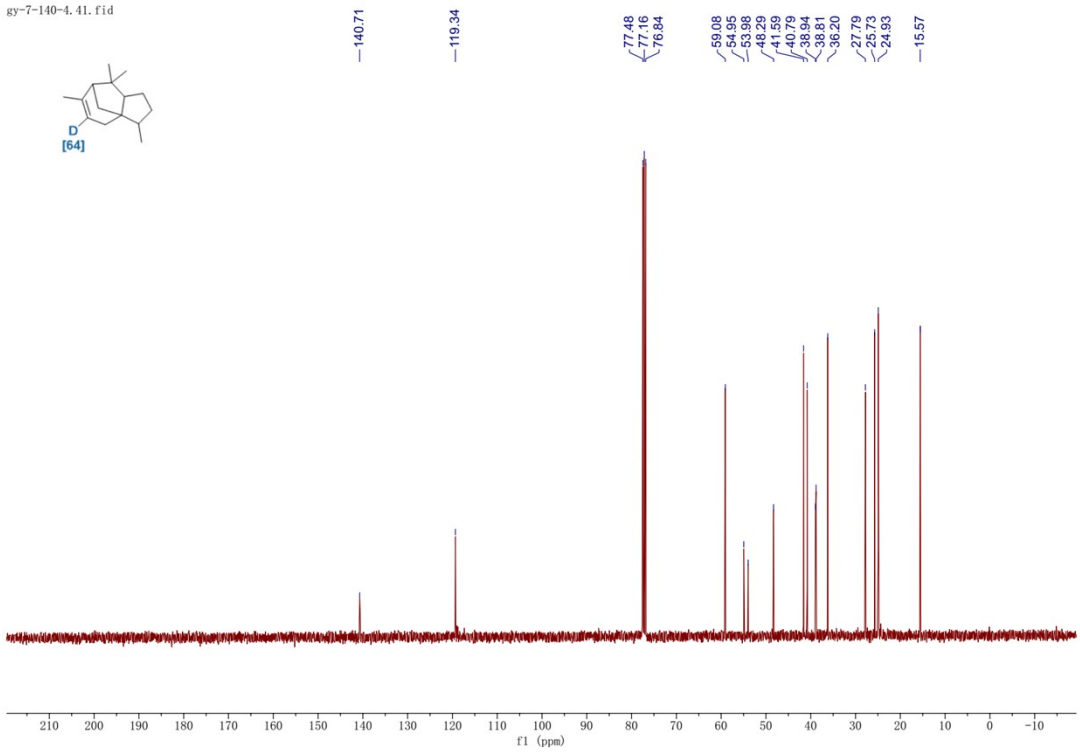
^{1}H NMR spectra of 10b:



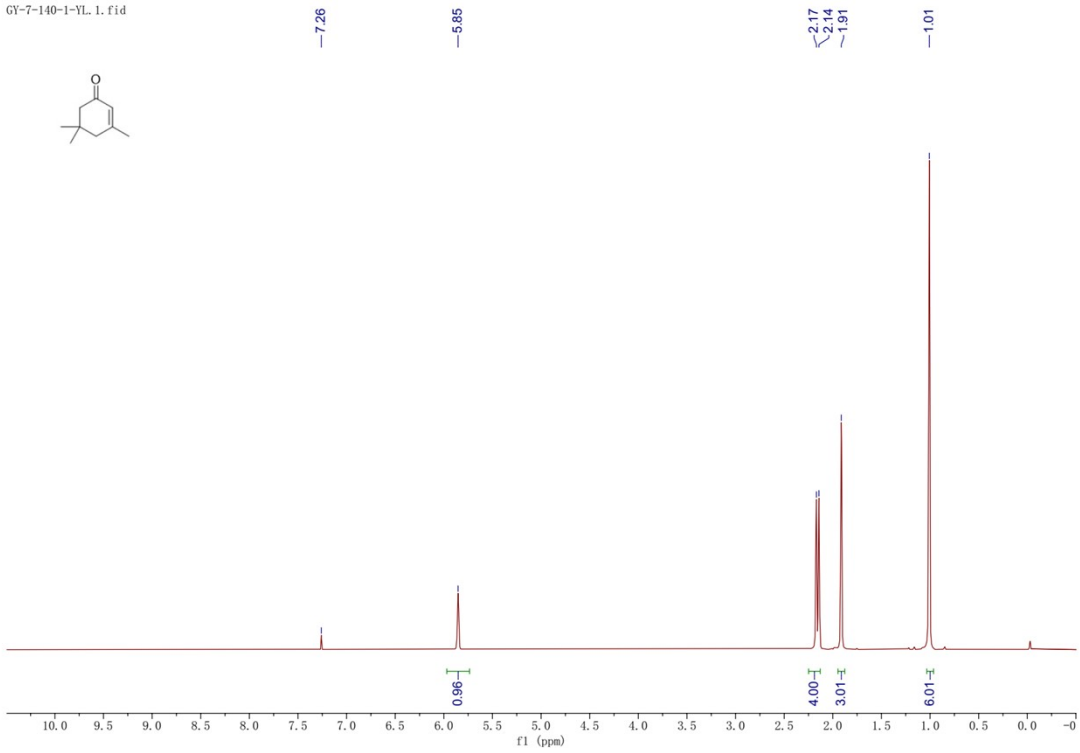
^{13}C NMR spectra of 10a:



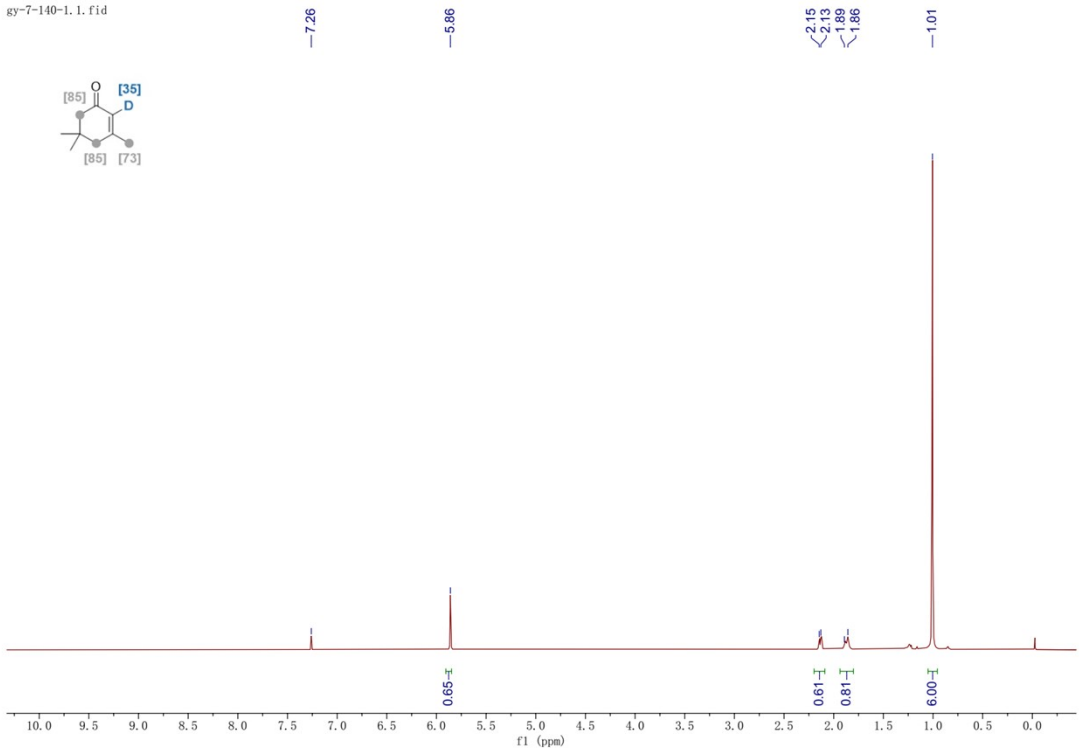
^{13}C NMR spectra of 10b:



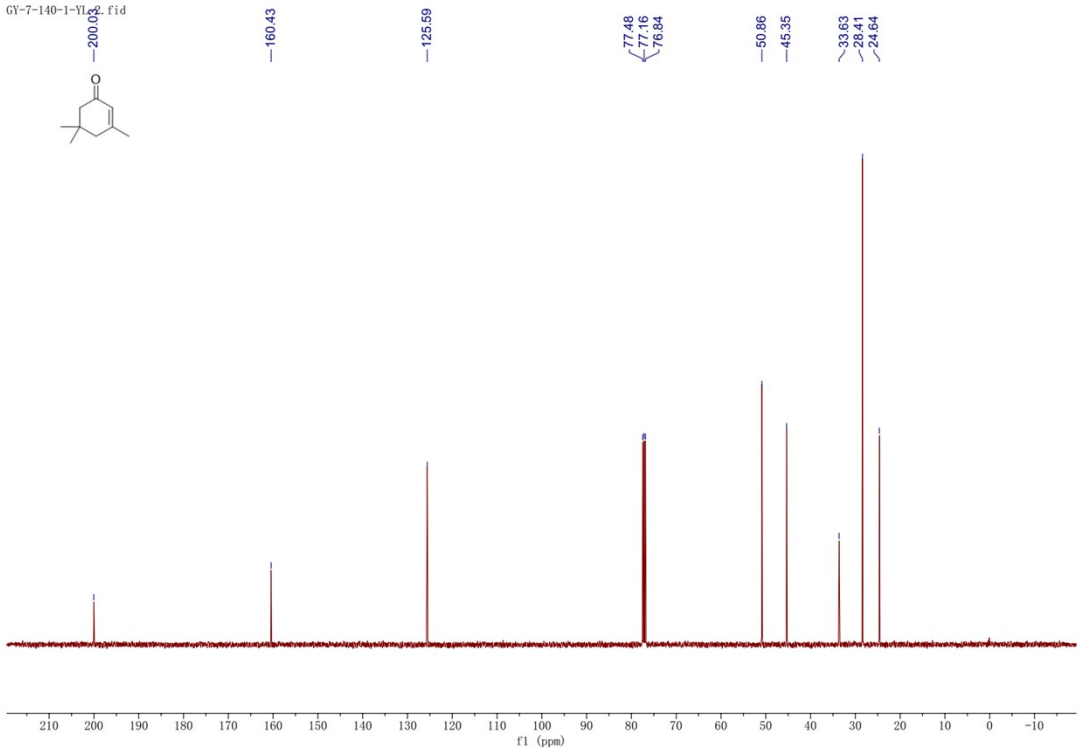
^{1}H NMR spectra of 11a:



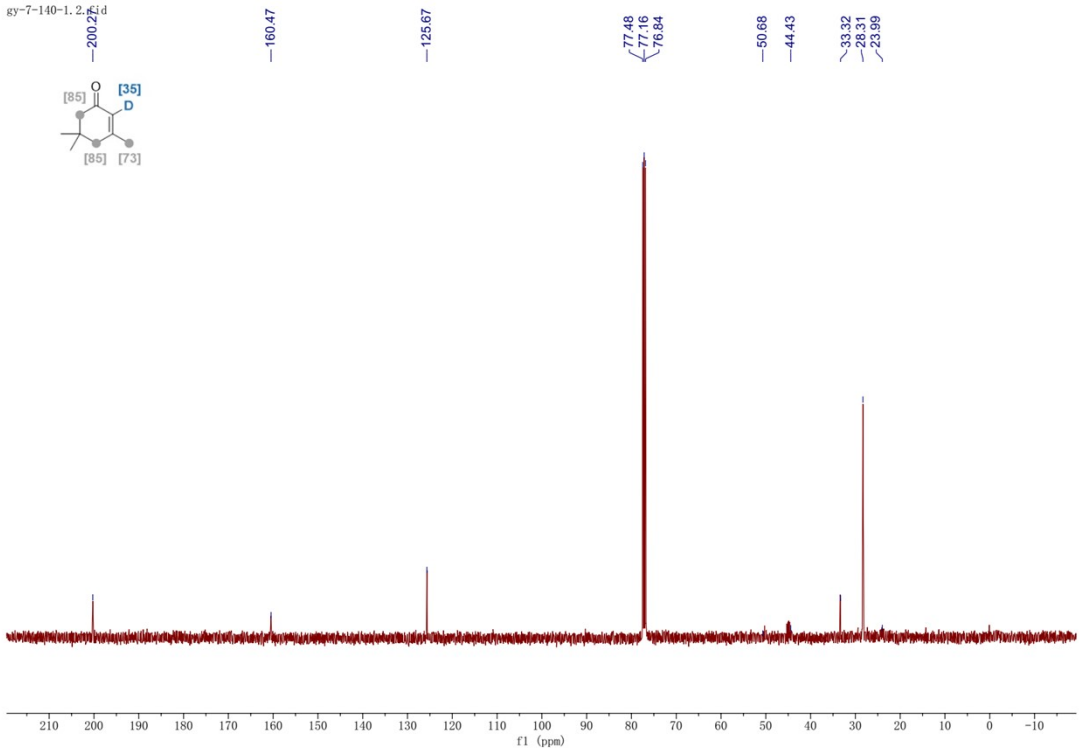
^{1}H NMR spectra of 11b:



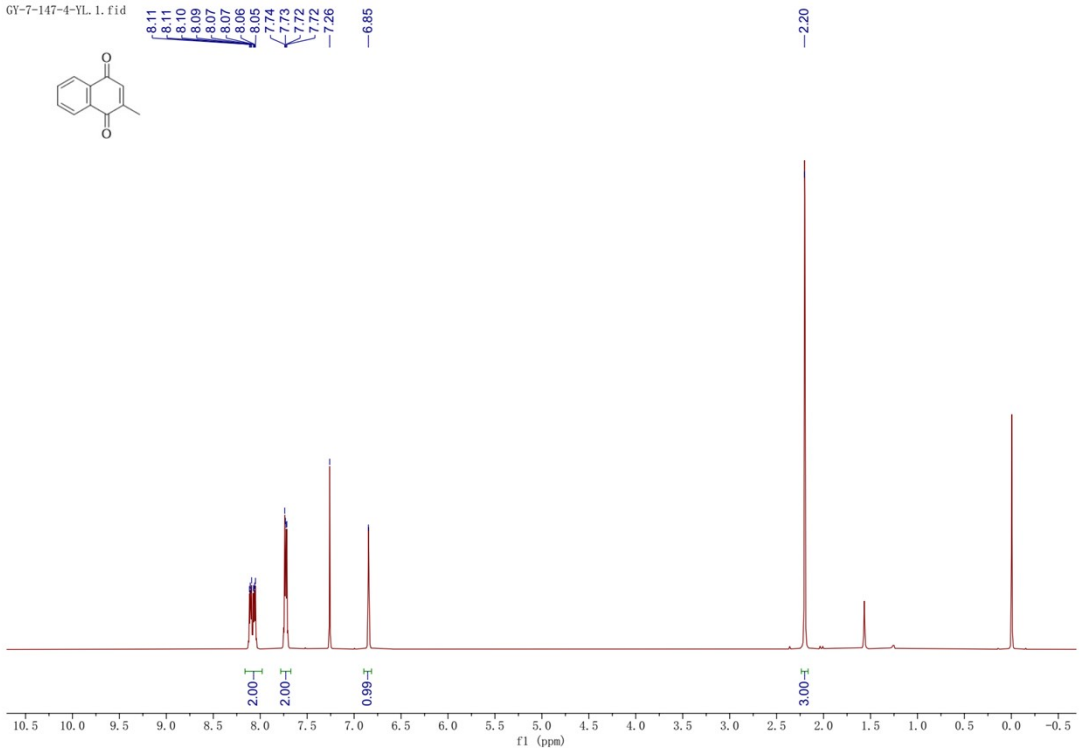
^{13}C NMR spectra of 11a:



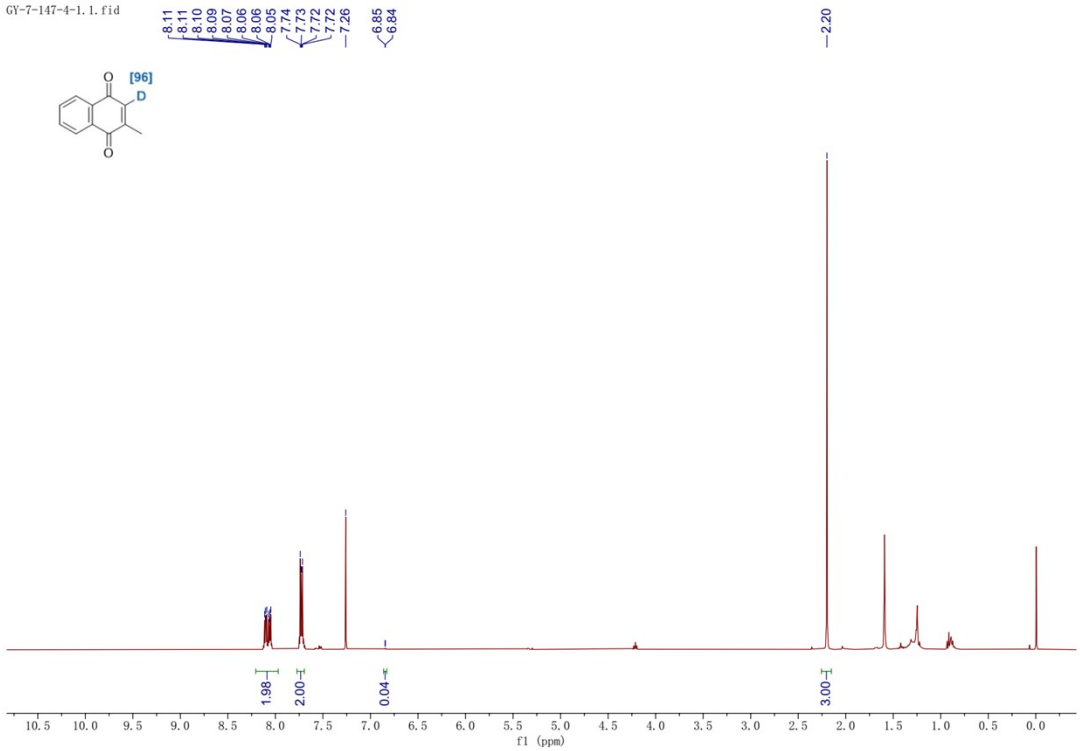
^{13}C NMR spectra of 11b:



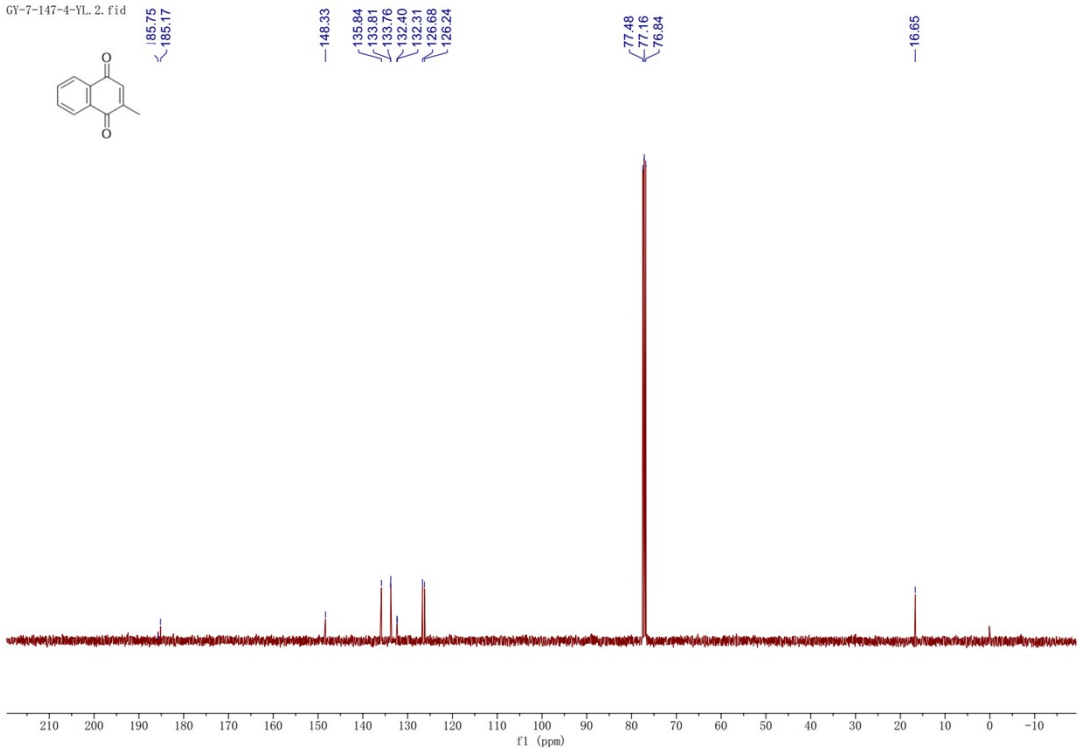
^{1}H NMR spectra of 12a:



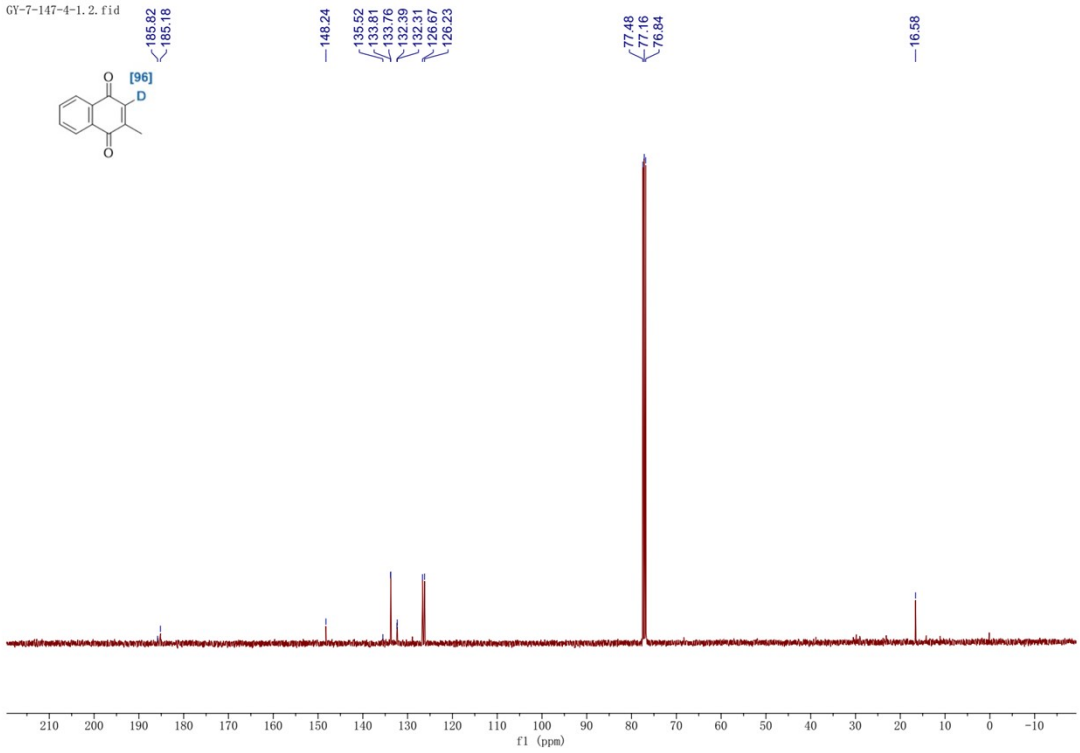
^{1}H NMR spectra of 12b:



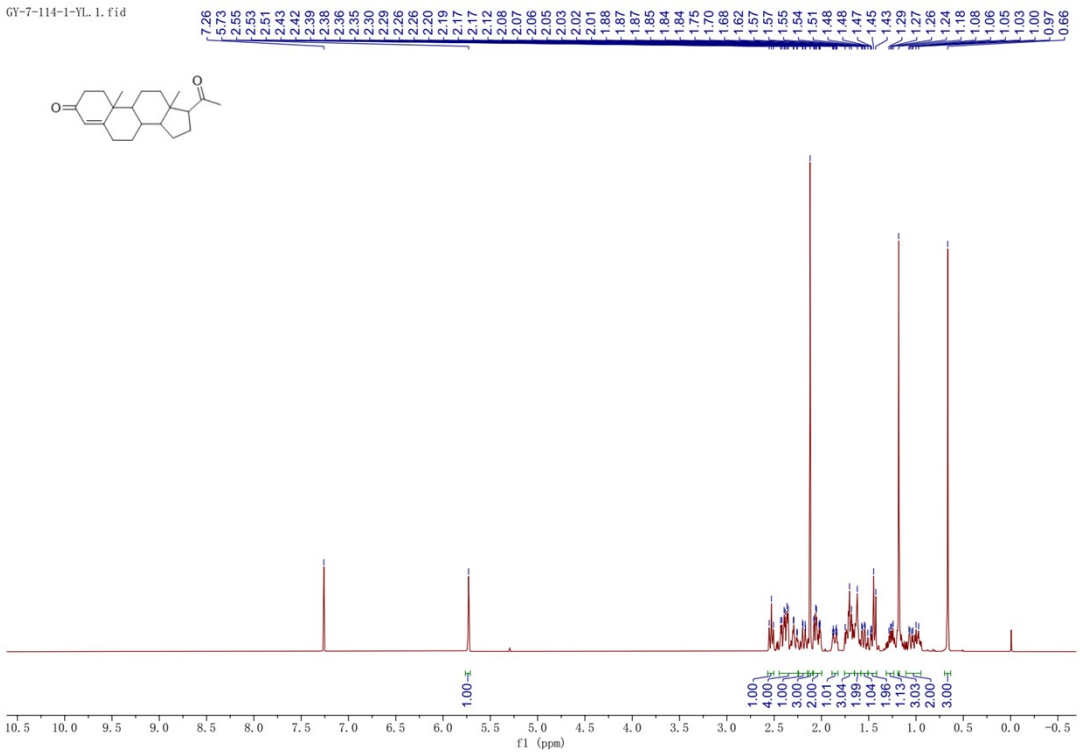
^{13}C NMR spectra of 12a:



^{13}C NMR spectra of 12b:



^{1}H NMR spectra of 13a:



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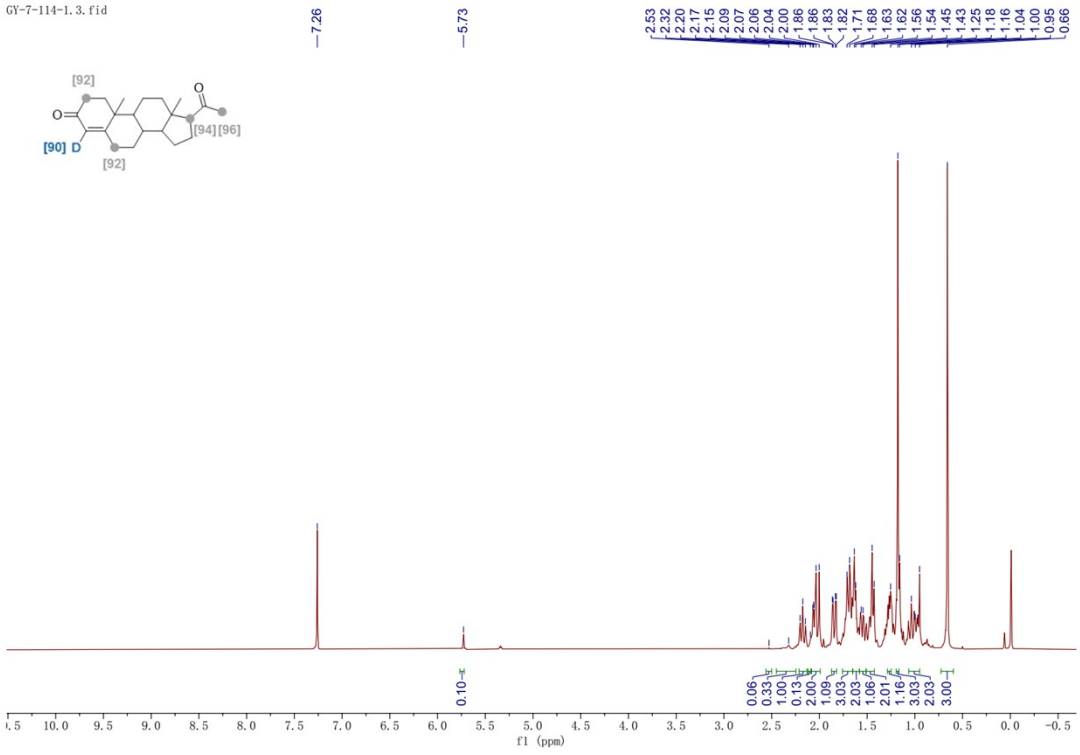
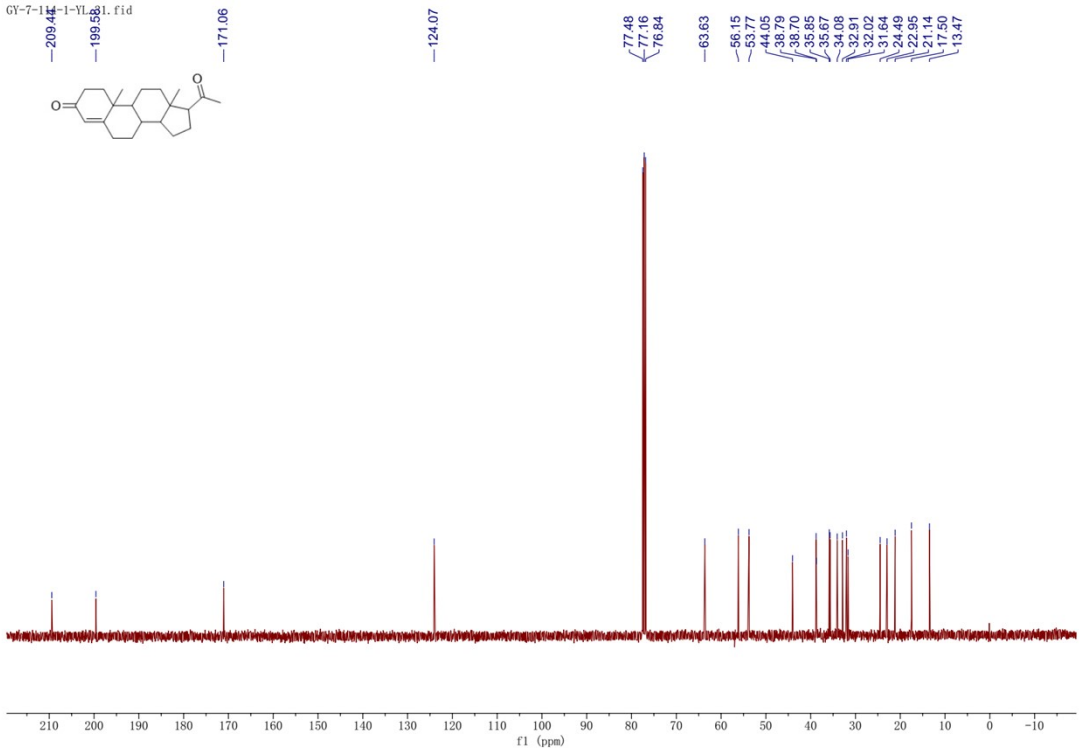
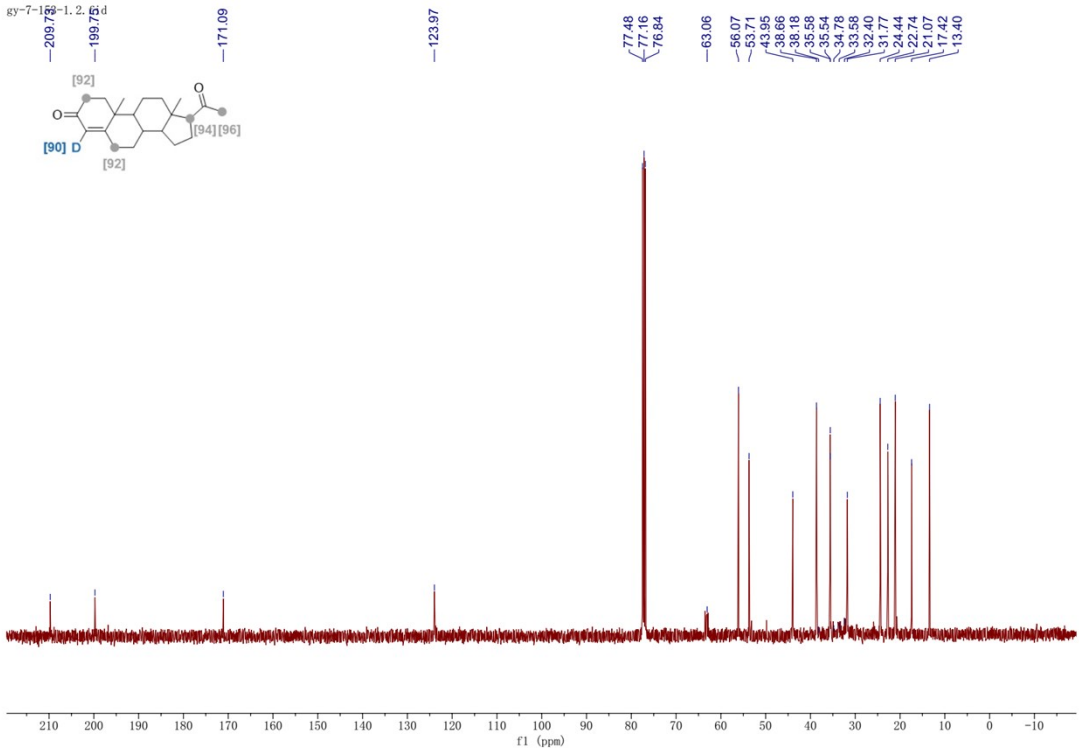


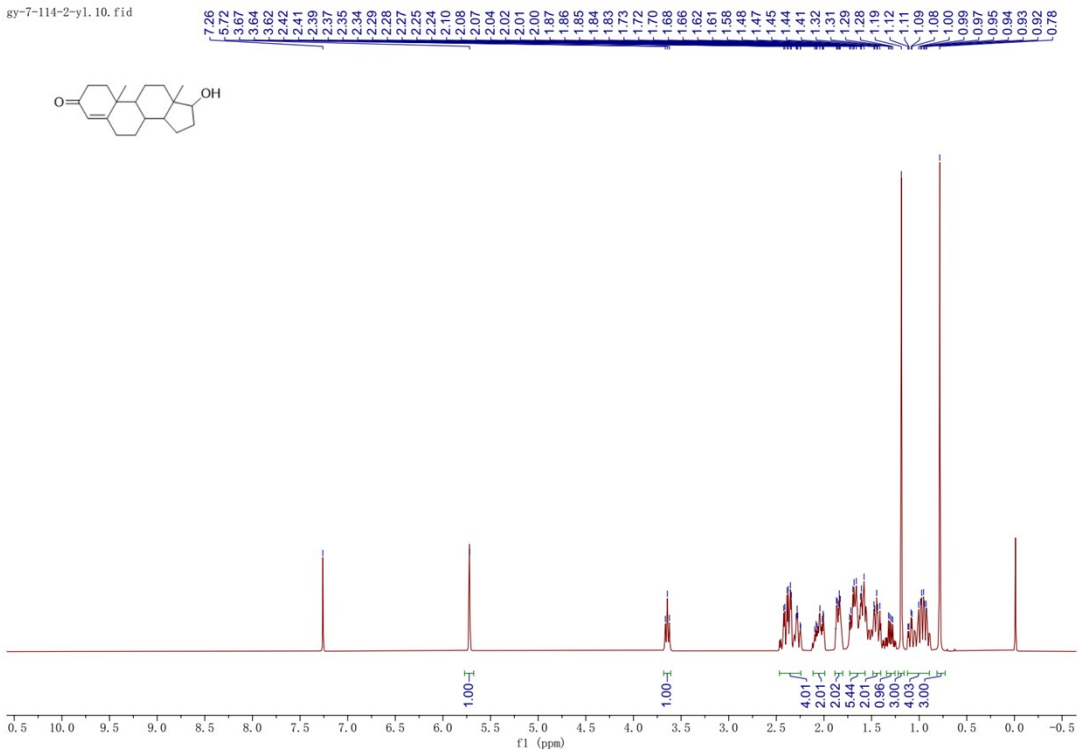
^{13}C NMR spectra of 13a:



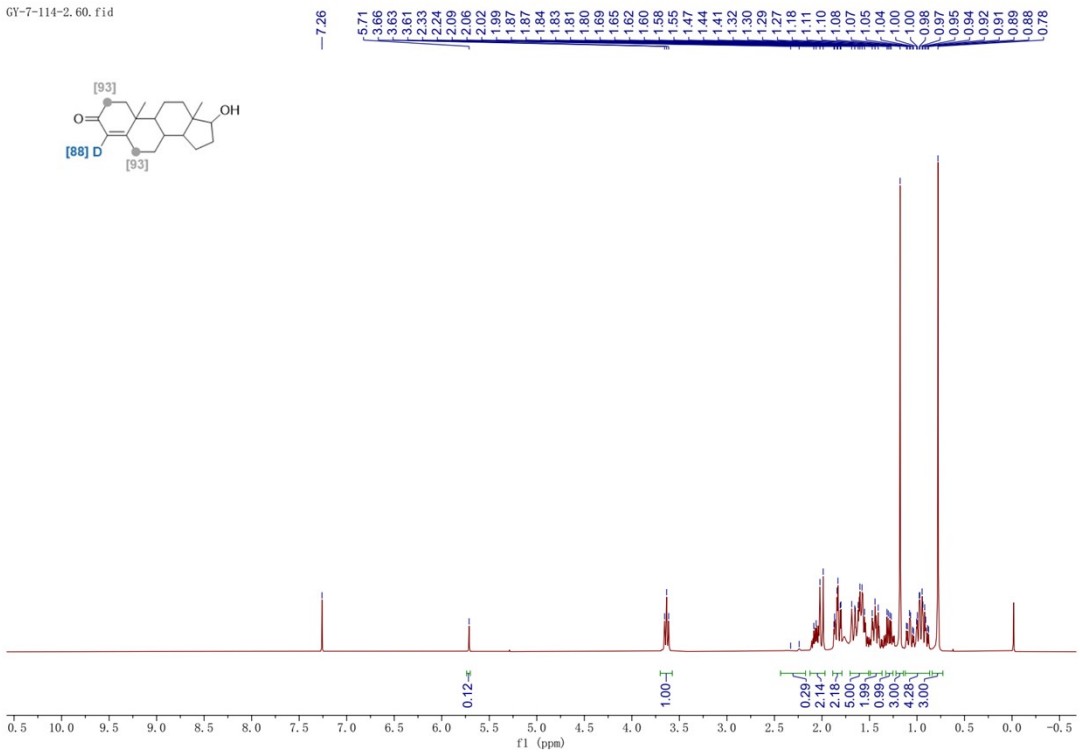
^{13}C NMR spectra of 13b:



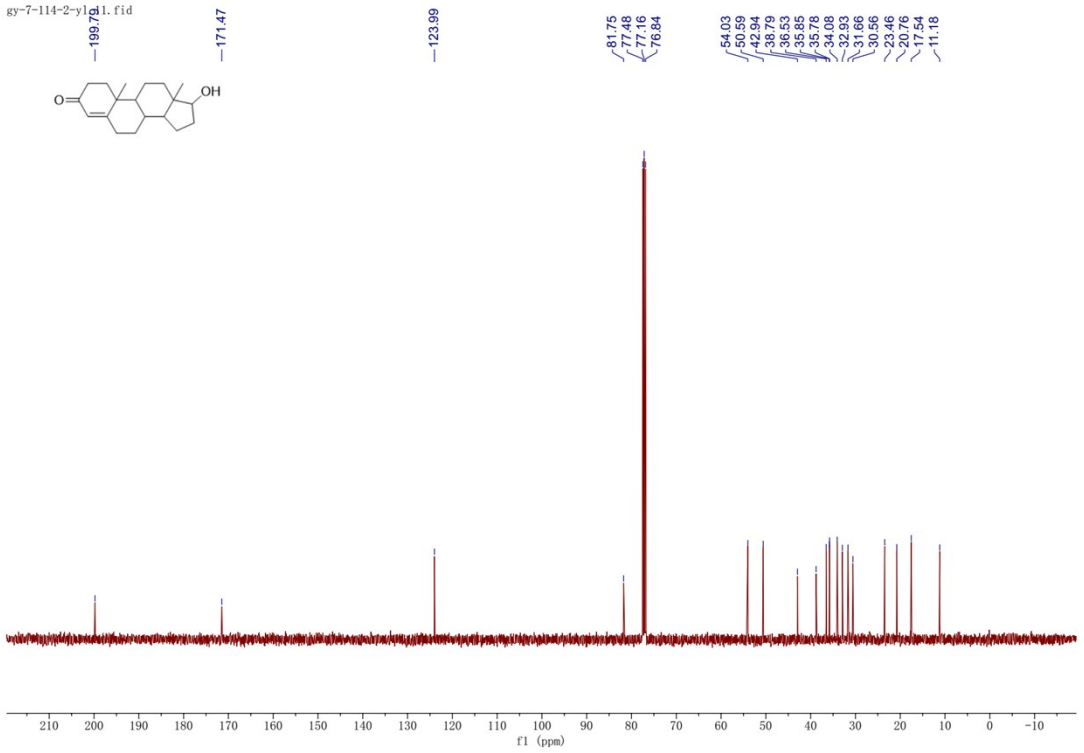
^{1}H NMR spectra of 14a:



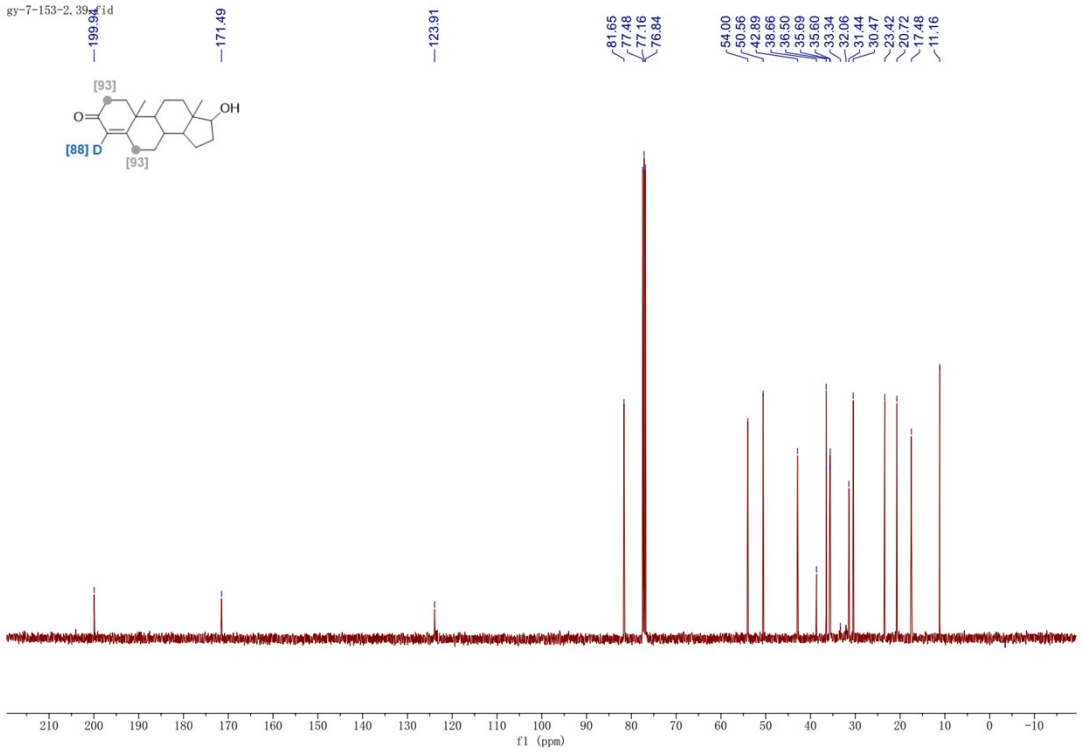
^{1}H NMR spectra of 14b:



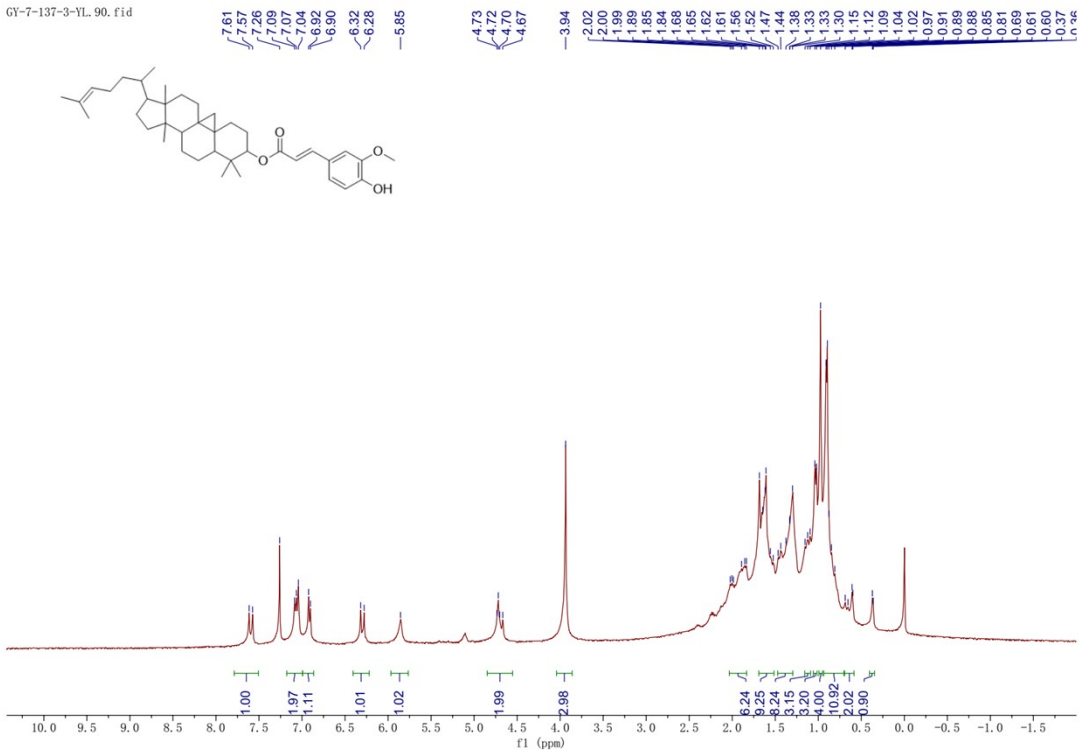
^{13}C NMR spectra of 14a:



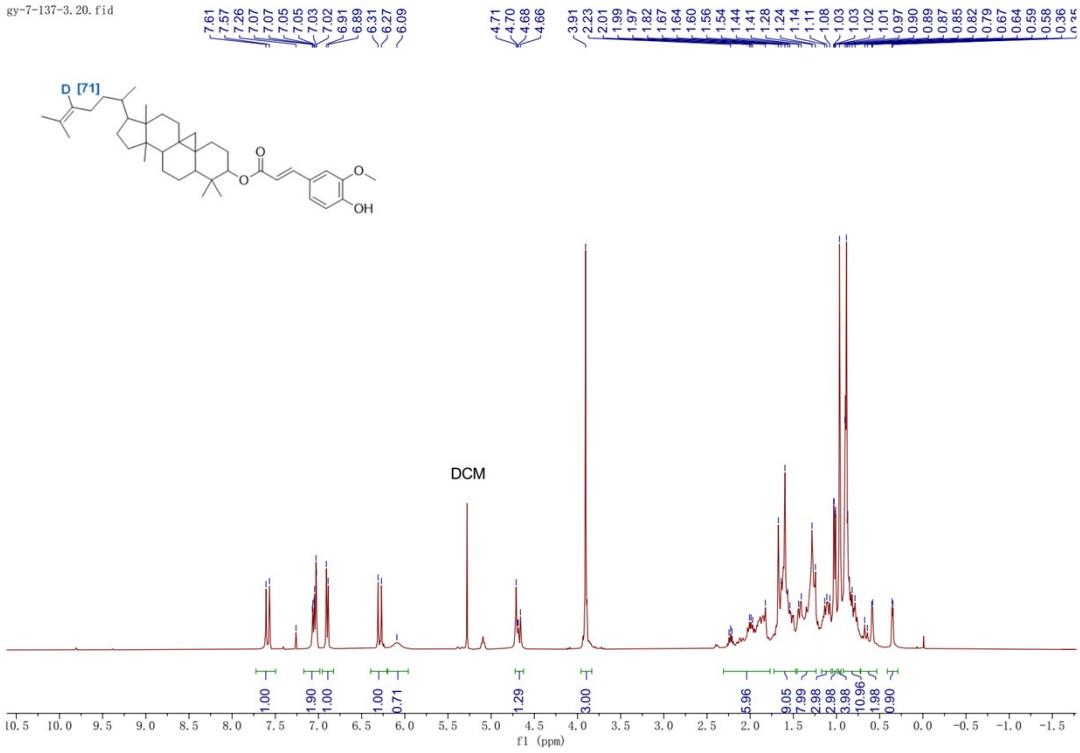
^{13}C NMR spectra of 14b:



^{1}H NMR spectra of 15a:



^{1}H NMR spectra of 15b:



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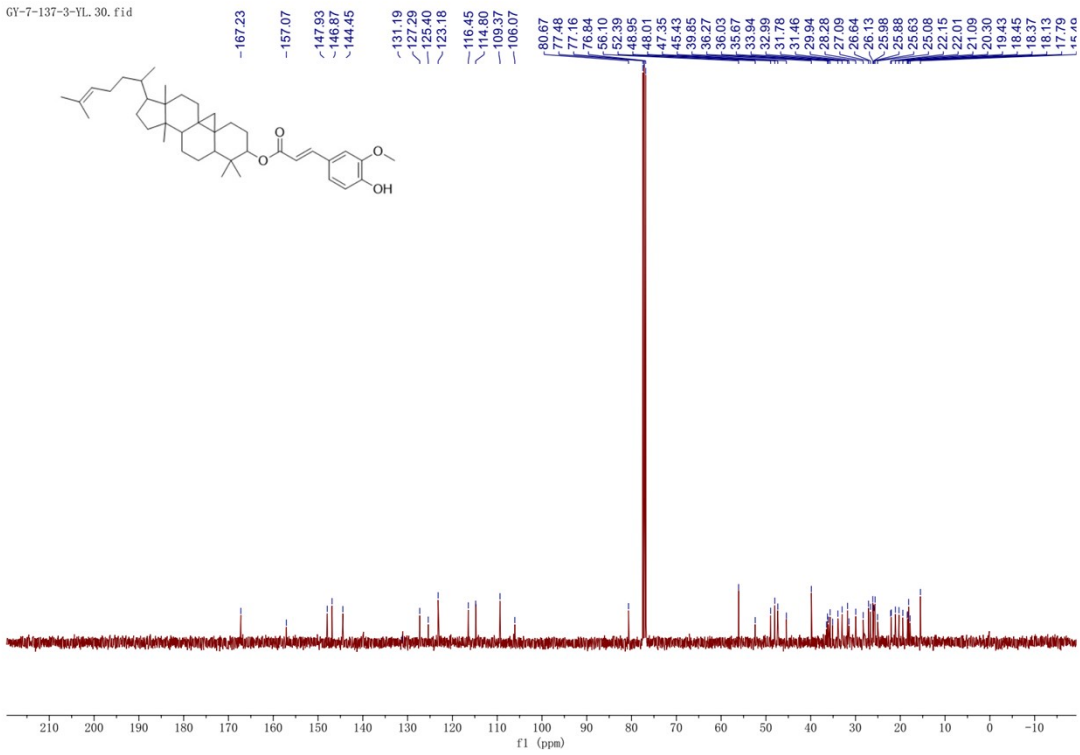

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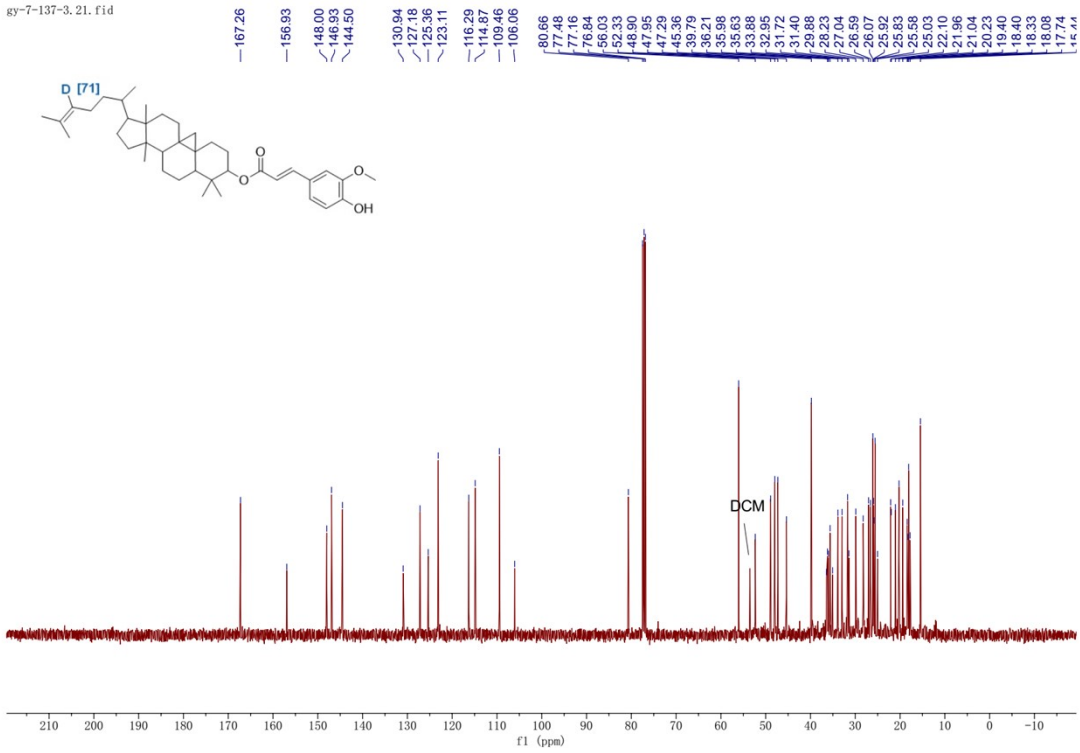
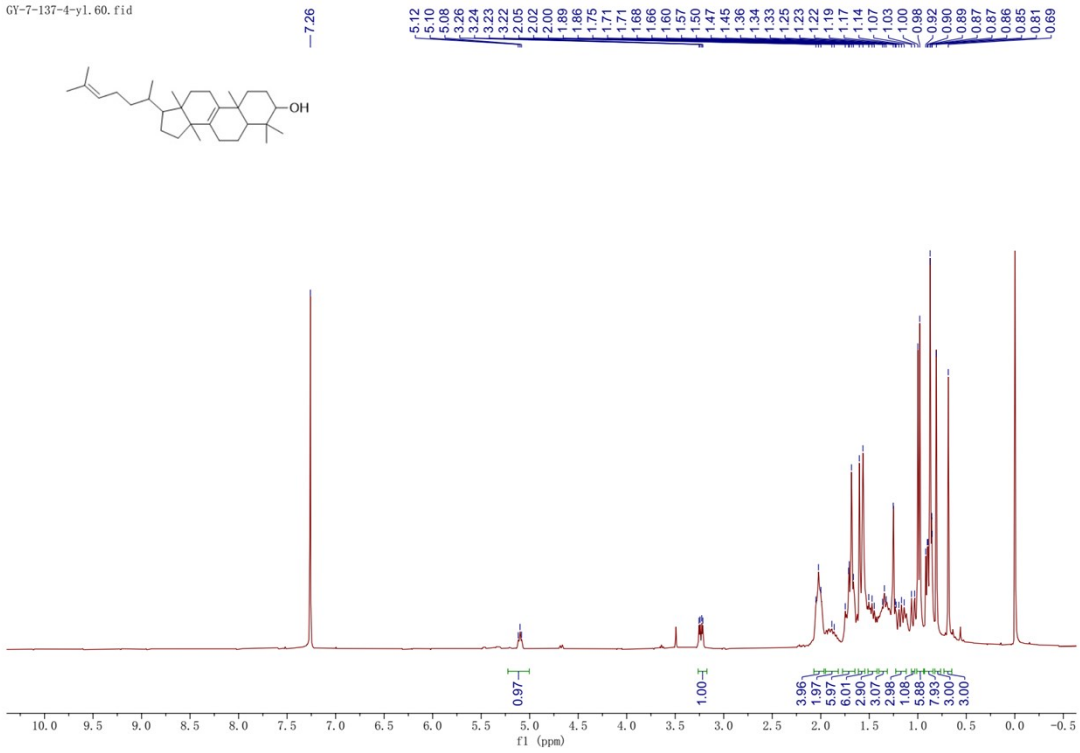
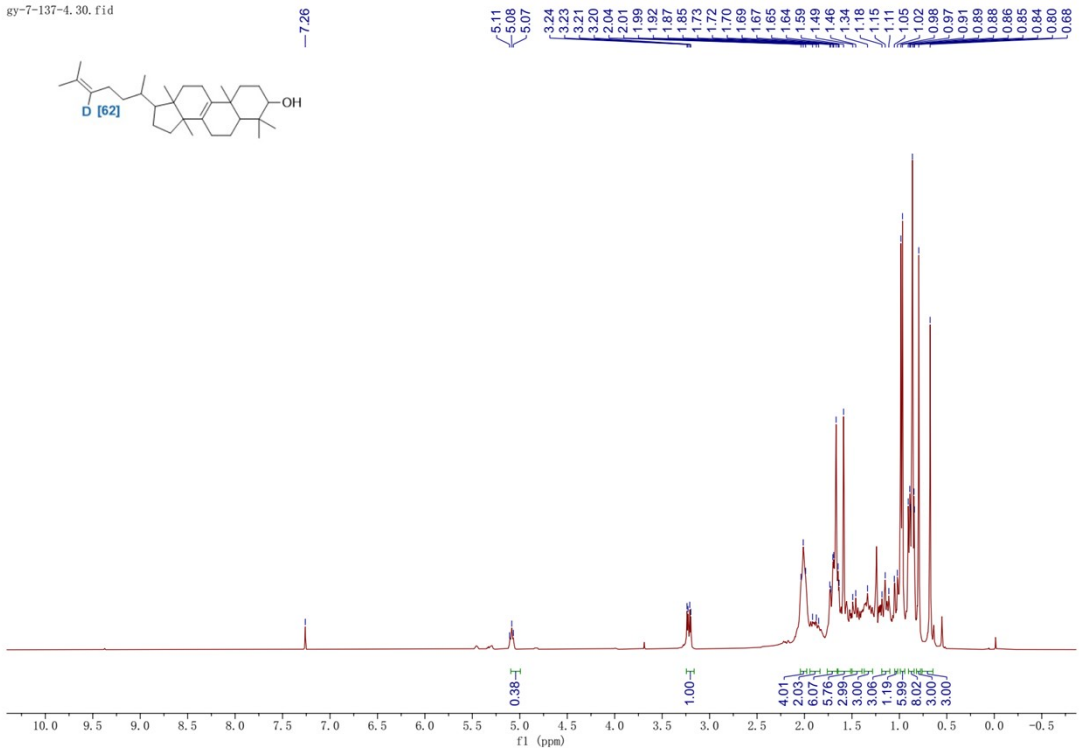


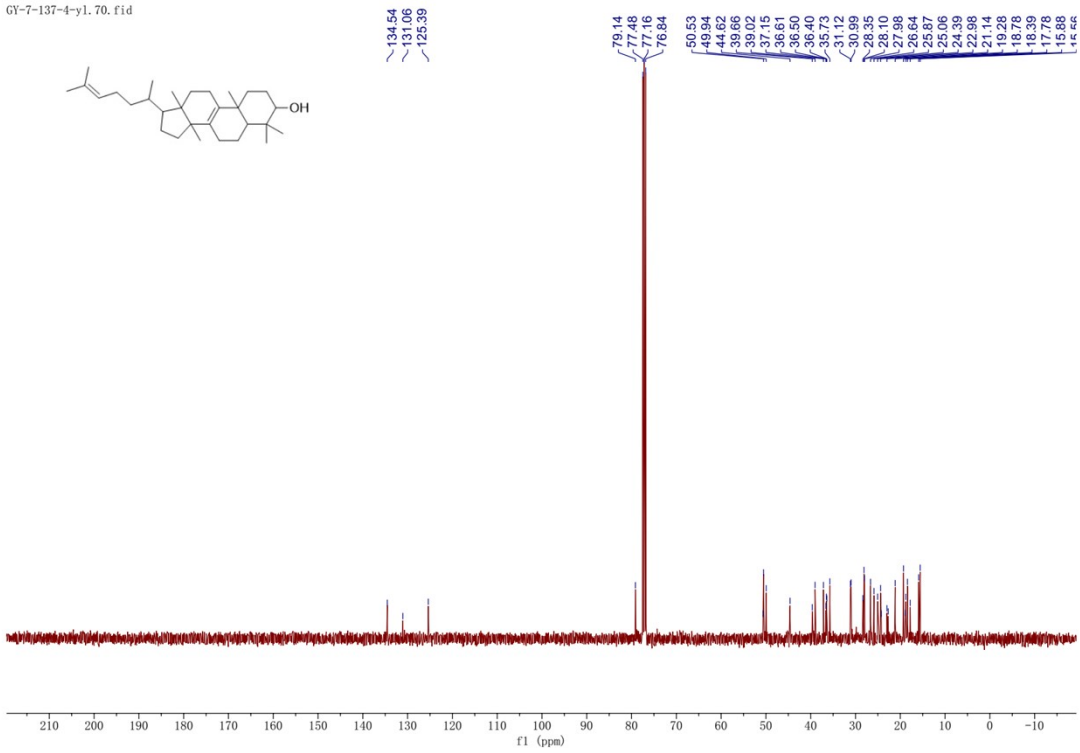
^{1}H NMR spectra of 16a:



^{1}H NMR spectra of 16b:



^{13}C NMR spectra of 16a:



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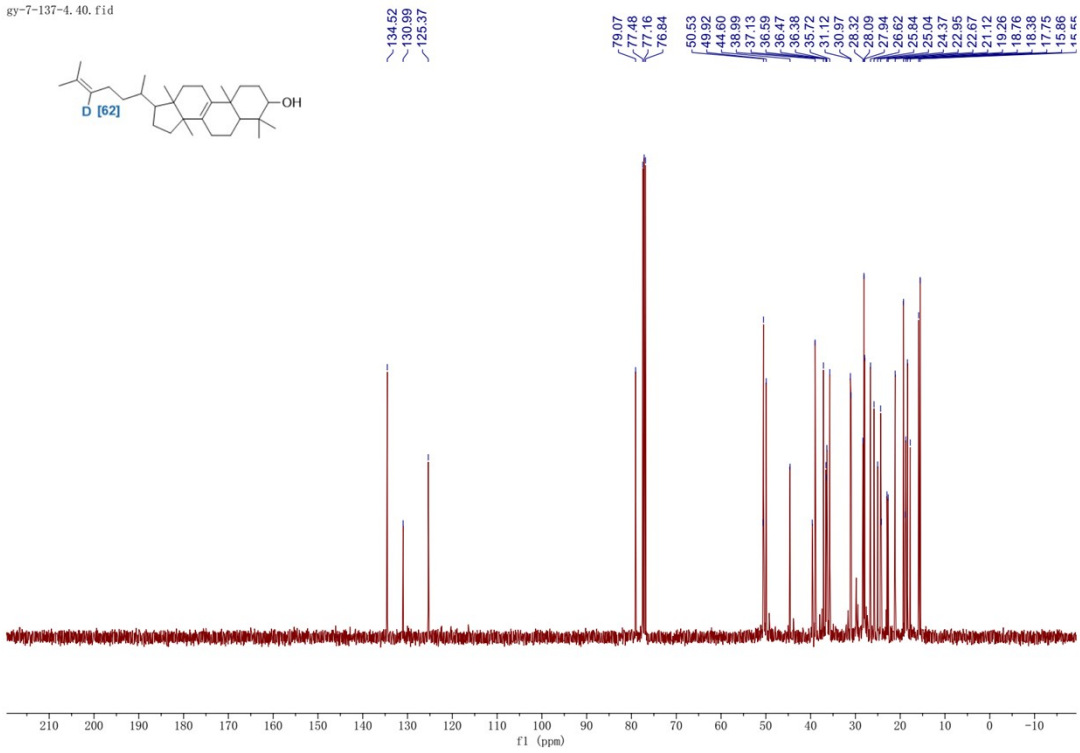
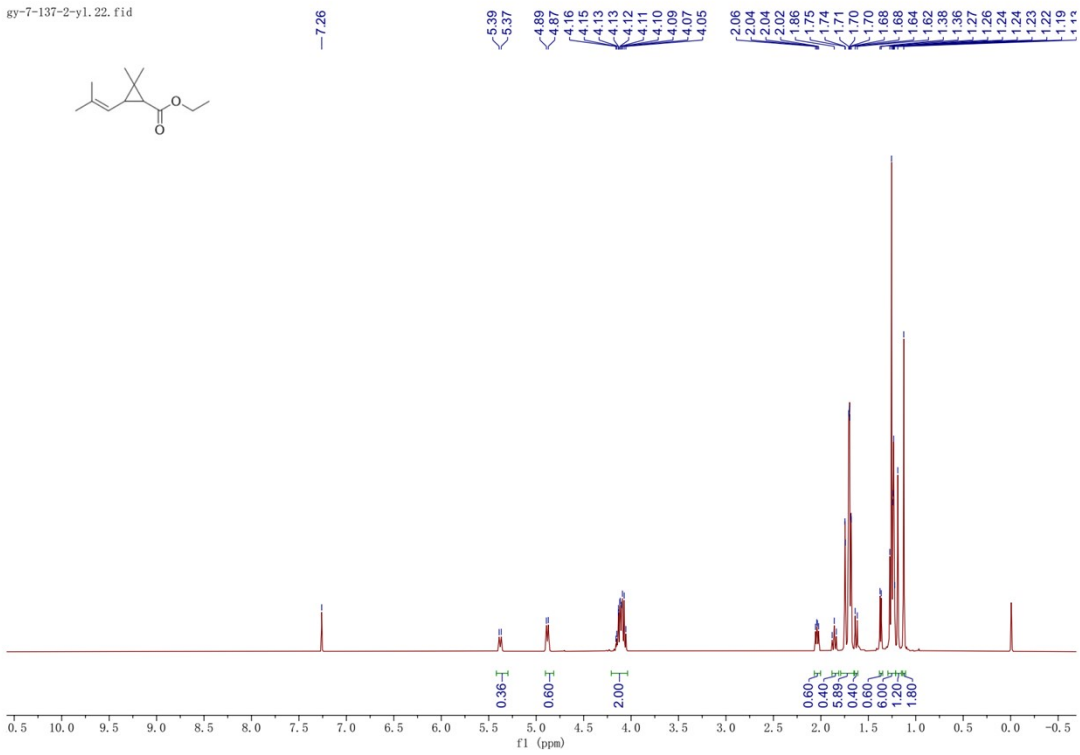


^{1}H NMR spectra of 17a:



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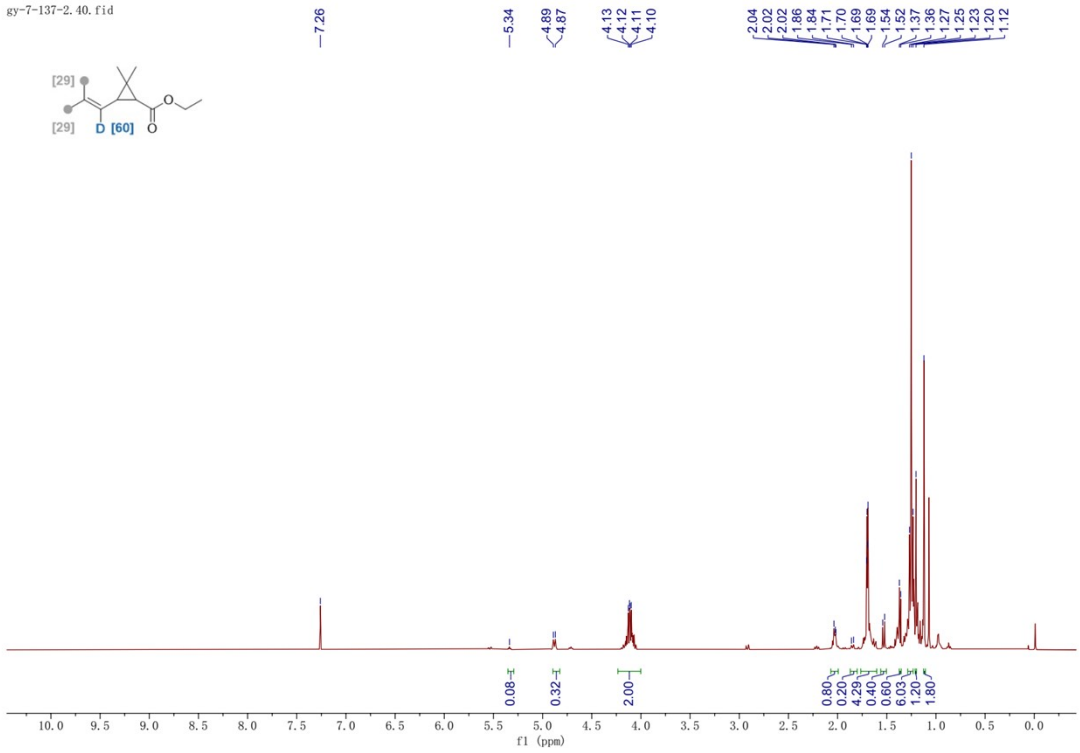
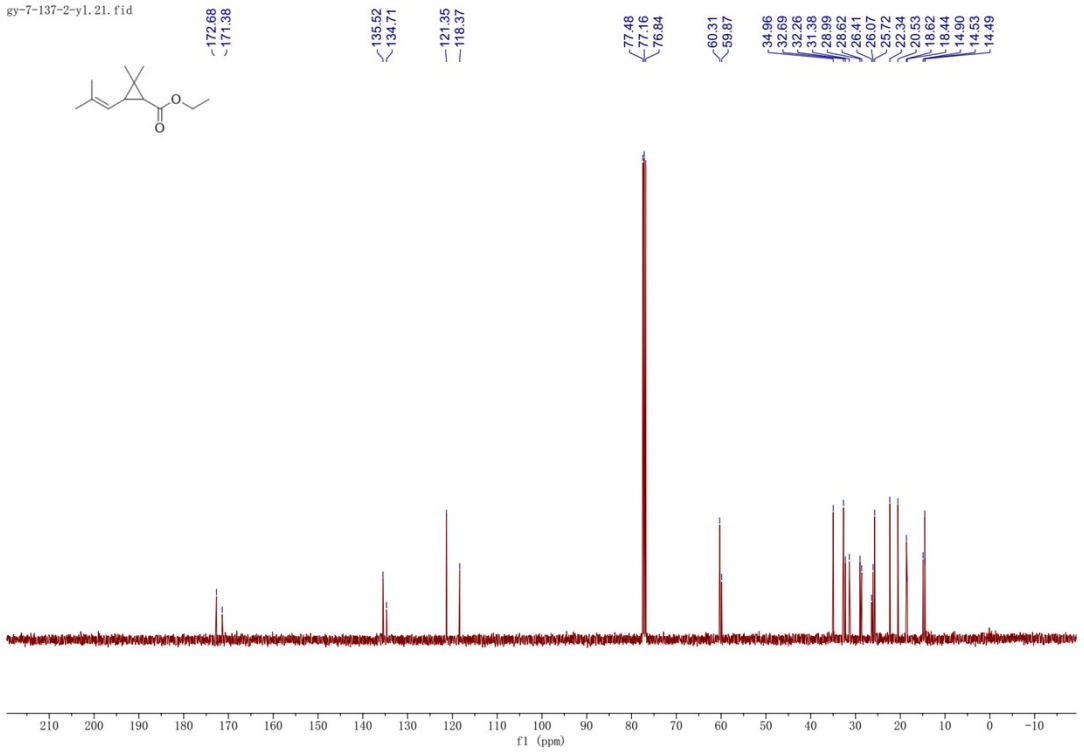


^{13}C NMR spectra of 17a:



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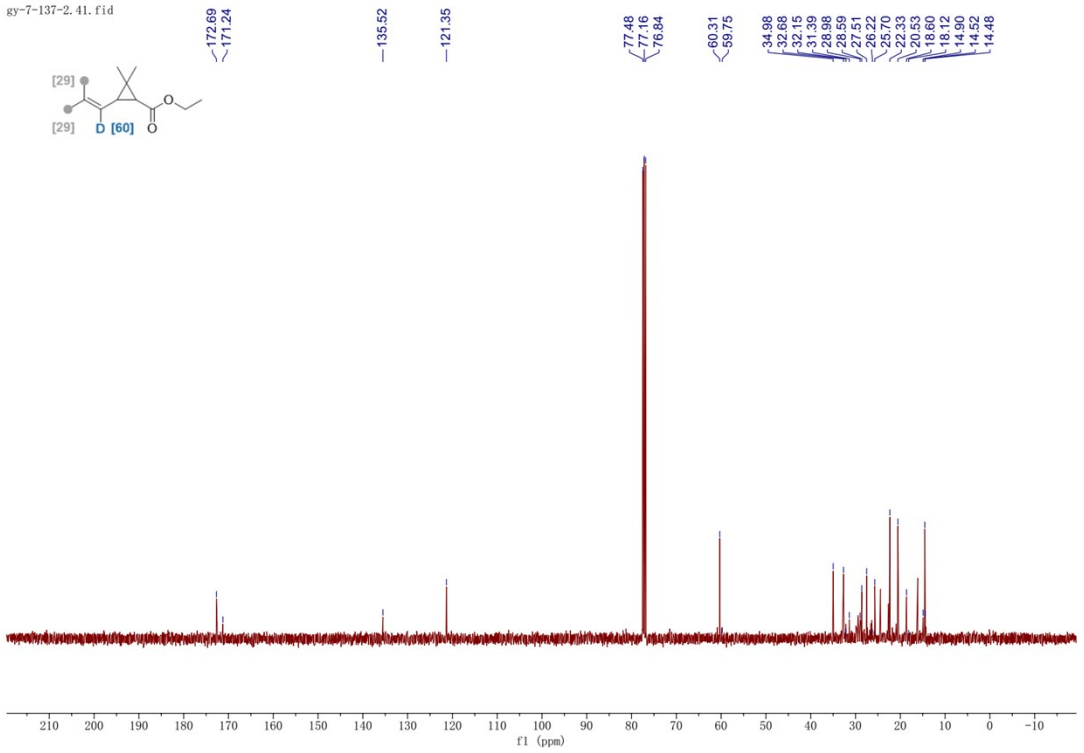
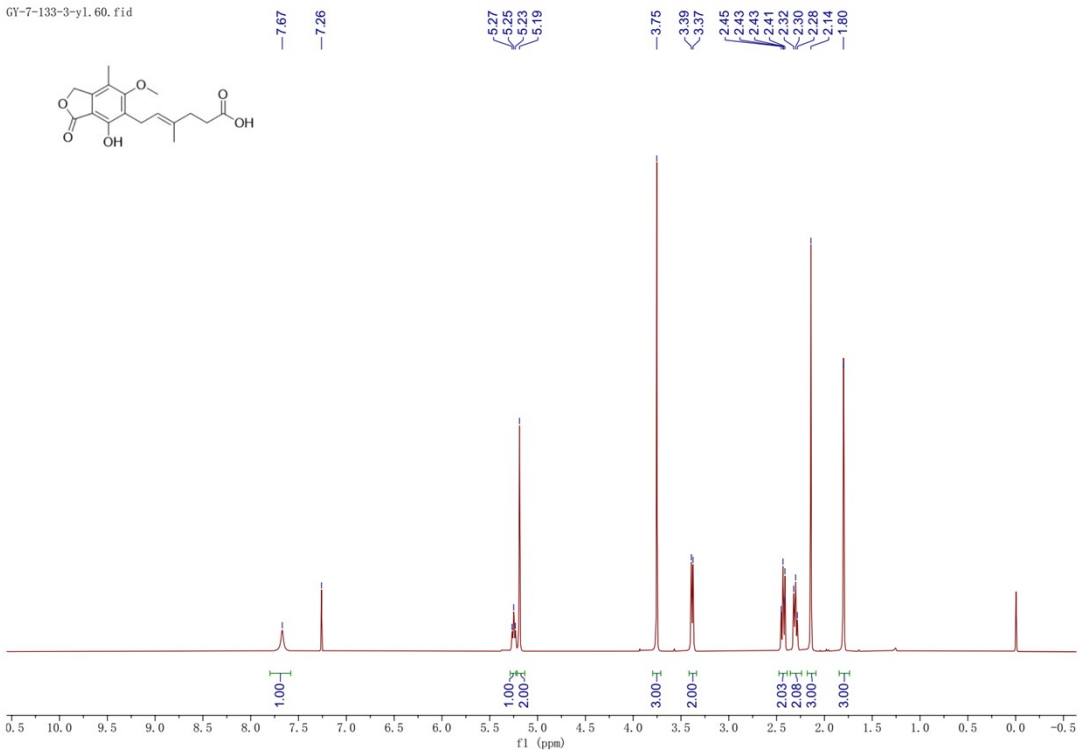
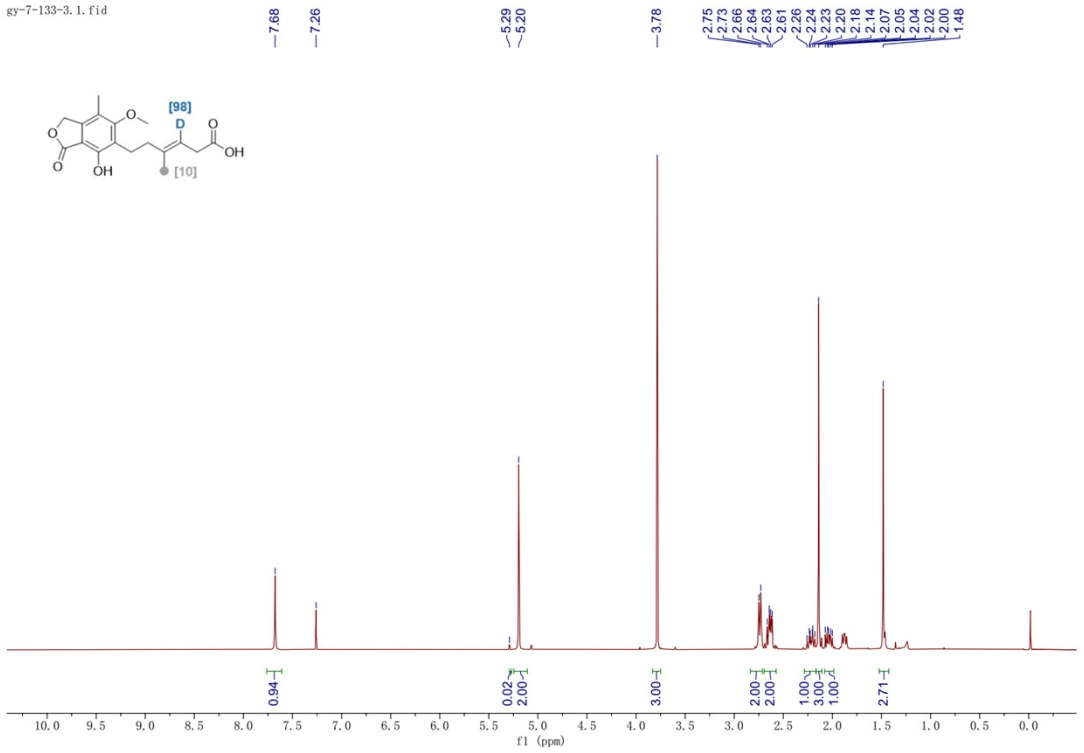


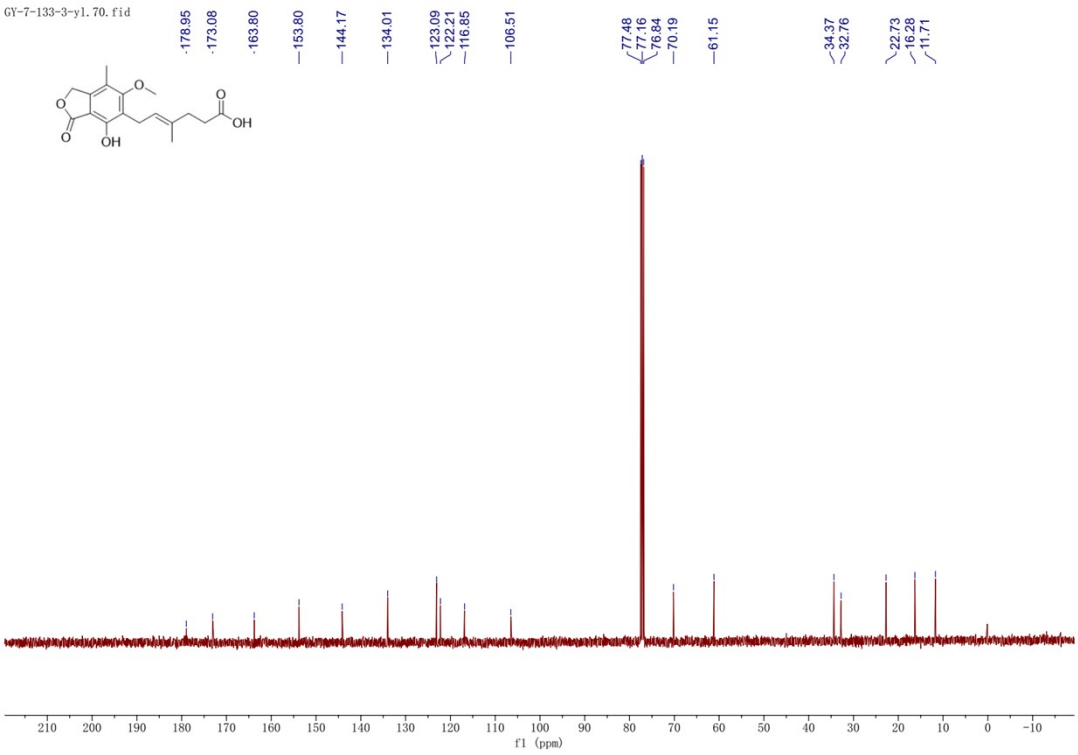
^{1}H NMR spectra of 18a:



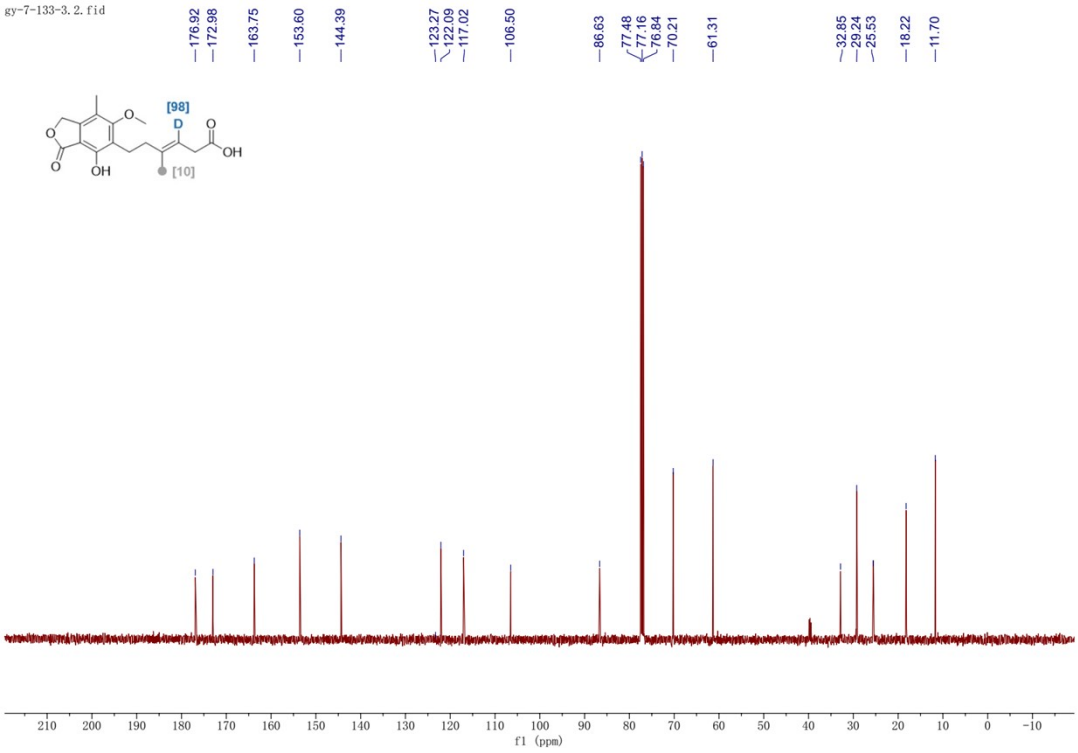
^{1}H NMR spectra of 18b:



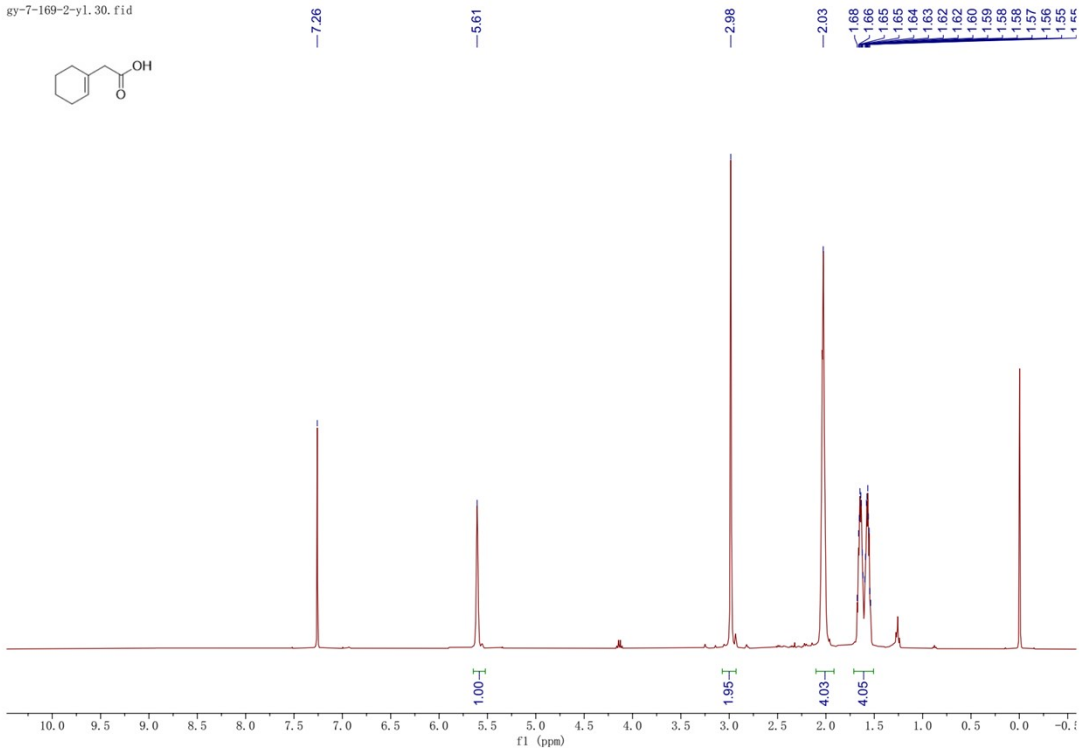
^{13}C NMR spectra of 18a:



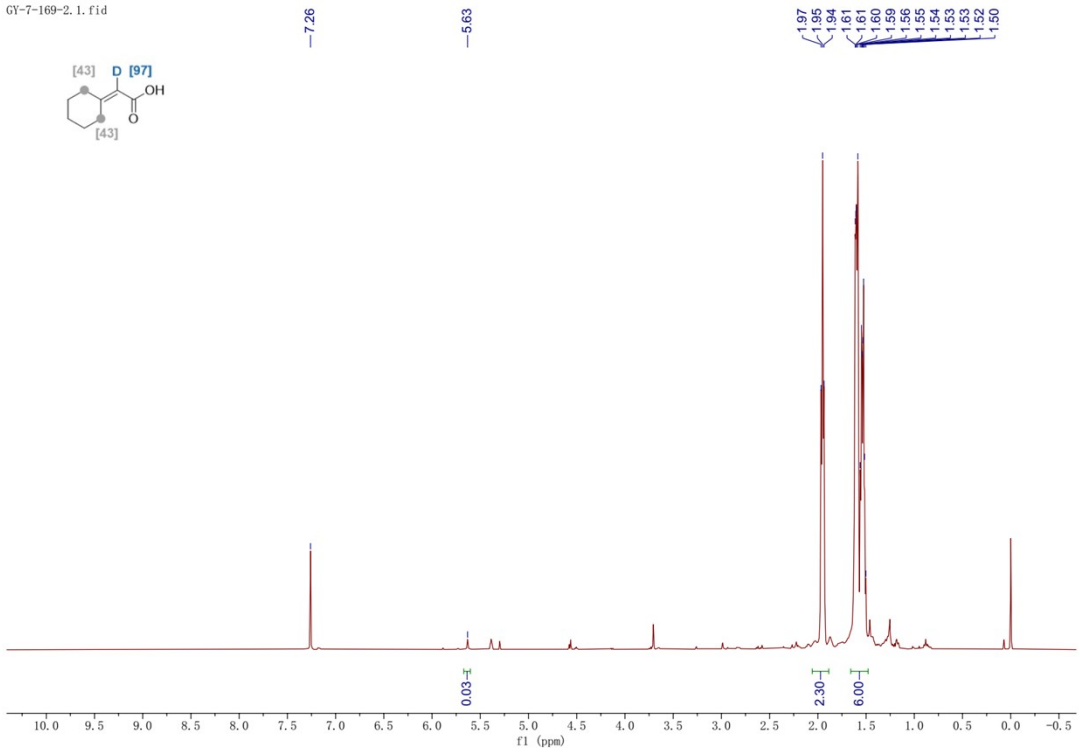
^{13}C NMR spectra of 18b:



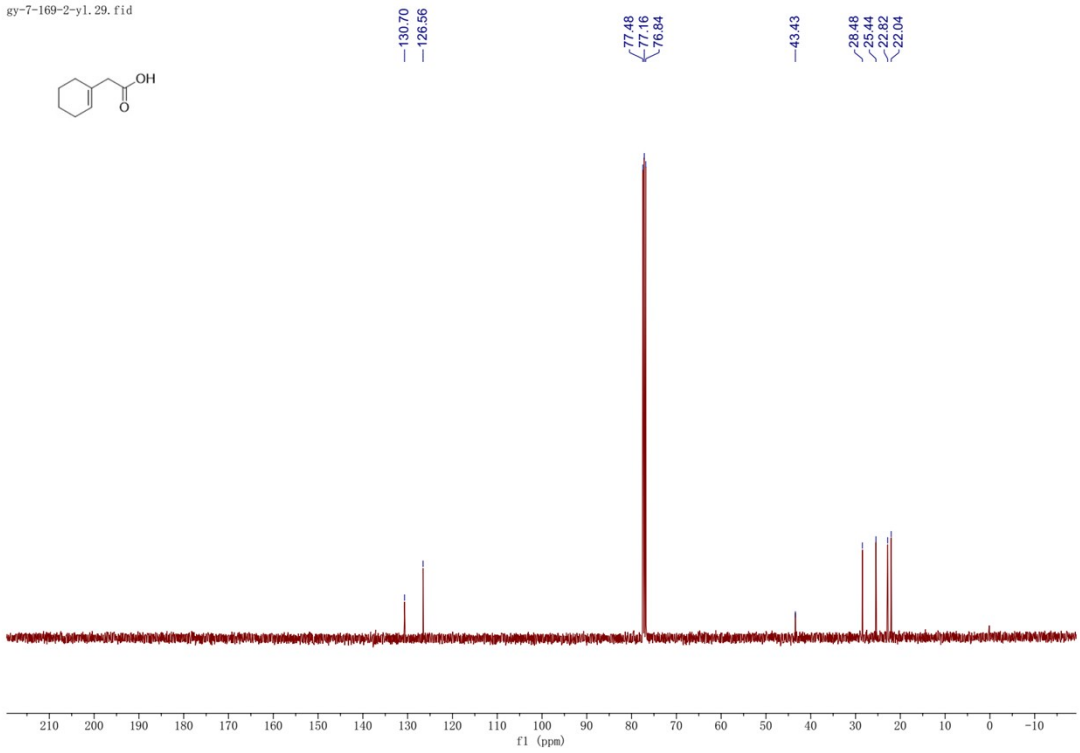
^{1}H NMR spectra of 19a:



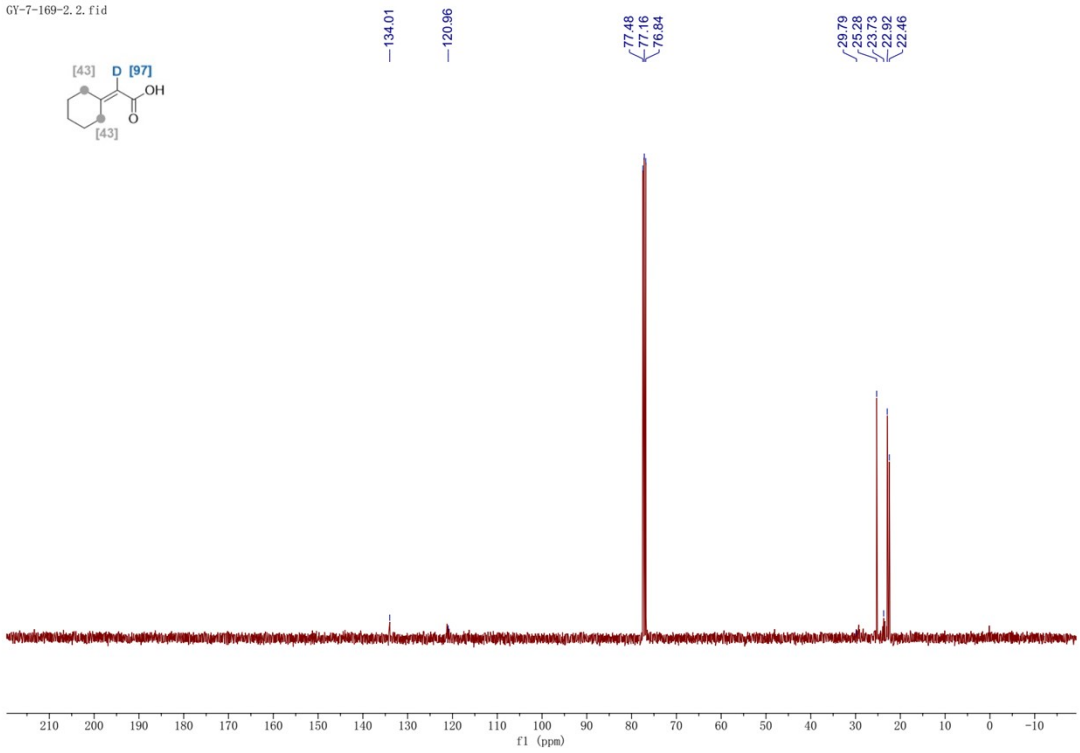
^{1}H NMR spectra of 19b:



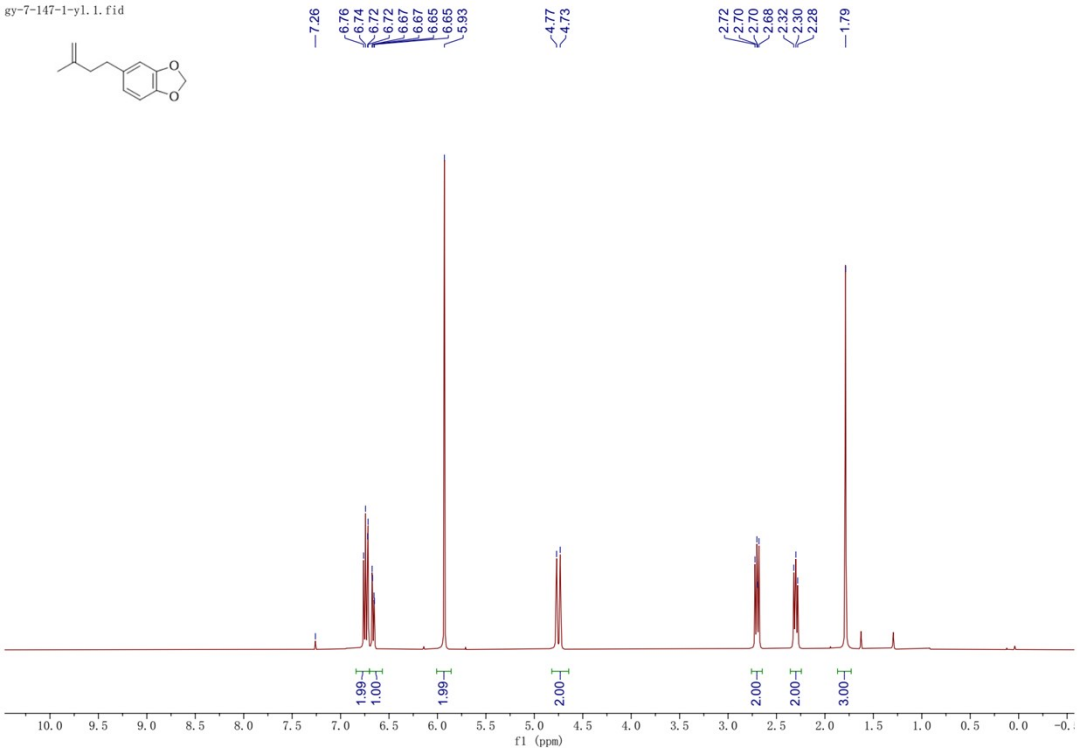
^{13}C NMR spectra of 19a:



^{13}C NMR spectra of 19b:



^{1}H NMR spectra of 20a:



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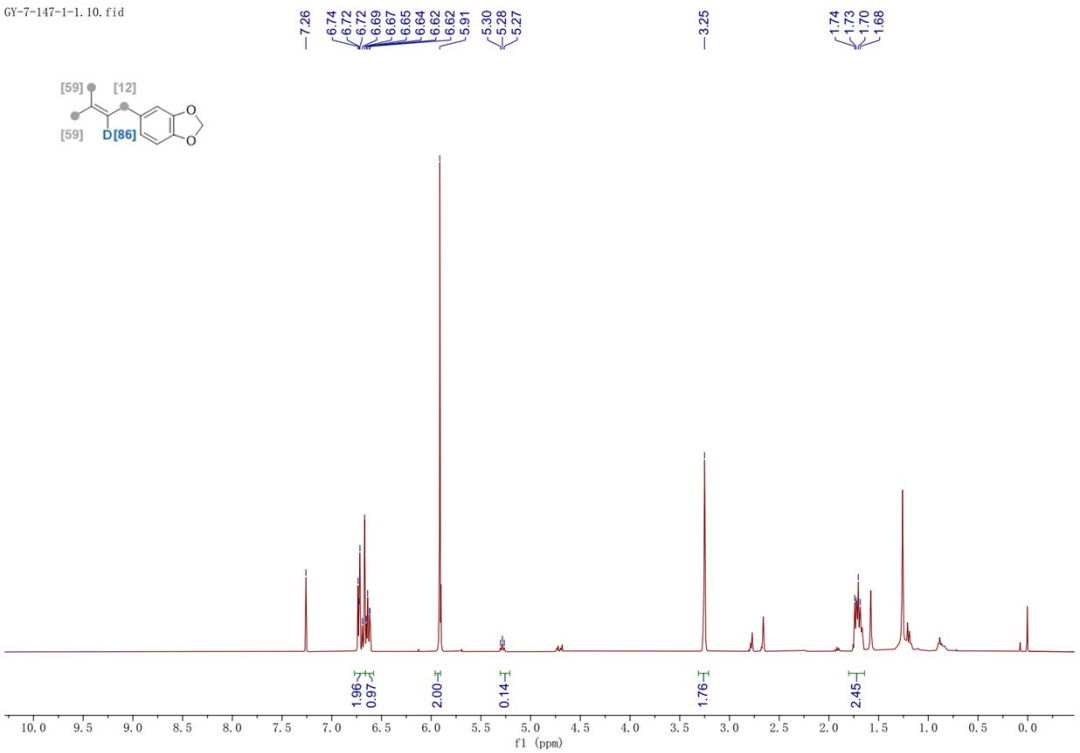

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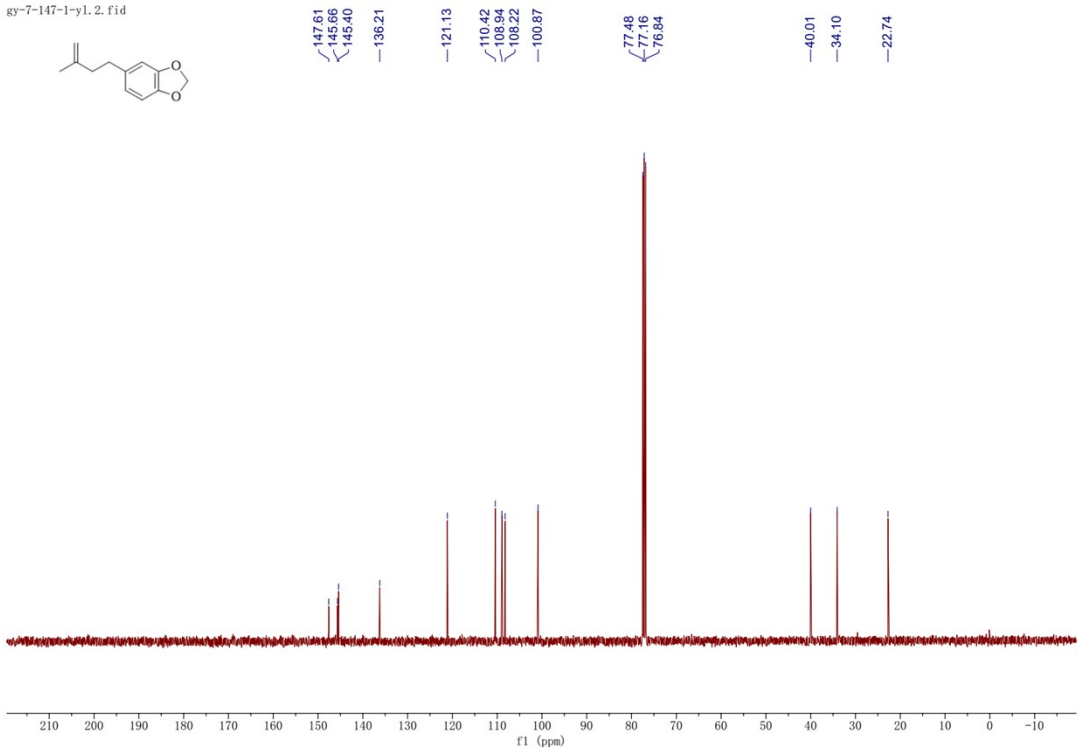

^{13}C NMR spectra of 20b: