Supporting Information for

Aerobic Oxidation of Alcohols with Air Catalyzed by Decacarbonyldimanganese

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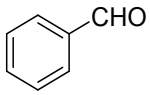
General Information

Unless stated otherwise, all reactions were carried out in glassware under air . All solvents were directly used without any pretreatment. NMR spectras were recorded on a Bruker Avance III 400, or Ascend TM 500 spectrometer and were recorded in ppm (δ) downfield of TMS (δ = 0) in deuterated solvent. Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz. Mass spectra were conducted at LCMS-IT-TOF(ESI). EPR spectra was detected by Bruker A300. Operando IR analysis was conducted by Mettler-Toledo ReactIR 15 equipped with a 6.35 mm diameter DiComp probe.

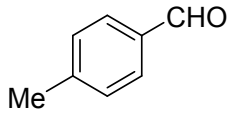
General Procedure for the oxidation of alcohols

To a solution of alcohols (primary alcohols, secondary alcohols, 1,2-diols, 1,2-amino alcohols et al) (0.2mmol) in 1ml toluene in 15 ml pressure tube was added $Mn_2(CO)_{10}$ (0.01mmol, 3.68mg), the color of the solution was orange, and the solution was stirred at 120°C under air and the color became light yellow. After 8-12h, black sediment appeared and the solution was cooled to room temperature，the product **2** or **4** was isolated by silica gel column chromatography (PE:EA=50:1). (Caution: The solvent should be removed under low temperature.)



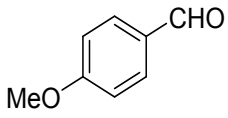
Benzaldehyde **2a**

Colorless oil, 95% yield. Analytical data for **2a**:^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.94 – 7.82 (m, 2H), 7.67 – 7.58 (m, 1H), 7.53 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.42, 136.40, 134.48, 129.75, 129.01.



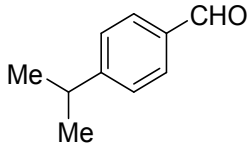
4-methylbenzaldehyde **2b**

Colorless oil, 96% yield. Analytical data for **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.98, 145.55, 134.21, 129.84, 129.71, 21.85.



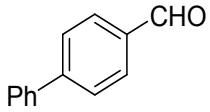
4-methoxybenzaldehyde **2c**

Colorless oil, 98% yield. Analytical data for **2c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.84, 164.62, 132.00, 129.96, 114.32, 55.59.



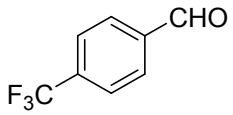
4-isopropylbenzaldehyde **2d**

Colorless oil, 95% yield. Analytical data for **2d:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 2.99 (hept, *J* = 6.9 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.04, 156.25, 134.60, 130.02, 127.15, 34.48, 23.63.



[1,1'-biphenyl]-4-carbaldehyde **2e**

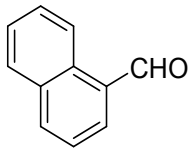
Colorless oil, 92% yield. Analytical data for **2e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.53 – 7.45 (m, 2H), 7.46 – 7.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.96, 147.22, 139.74, 135.22, 130.30, 129.04, 128.50, 127.71, 127.39.



4-(trifluoromethyl)benzaldehyde **2f**

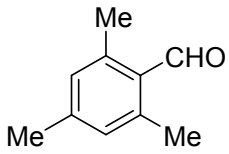
Colorless oil, 91% yield. Analytical data for **2f:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.12, 138.64, 135.60 (q, *J* = 32.7 Hz), 129.92, 126.11 (q, *J* = 3.7 Hz), 123.43 (d, *J*

= 272.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.26.



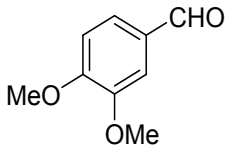
1-naphthaldehyde **2g**

Colorless oil, 94% yield. Analytical data for **2g:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 9.26 (d, *J* = 8.7 Hz, 1H), 8.09 (s, 1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.61 (ddd, *J* = 10.4, 8.0, 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.58, 136.70, 135.33, 133.76, 131.44, 130.57, 129.10, 128.50, 126.99, 124.90.



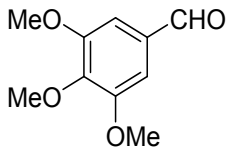
2,4,6-trimethylbenzaldehyde **2h**

Colorless oil, 95% yield. Analytical data for **2h:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 6.89 (s, 2H), 2.57 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.98, 143.83, 141.49, 130.53, 129.98, 21.46, 20.49.



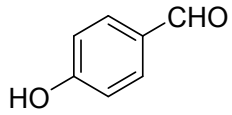
3,4-dimethoxybenzaldehyde **2i**

Colorless oil, 96% yield. Analytical data for **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.55 – 7.38 (m, 2H), 7.00 (t, *J* = 11.3 Hz, 1H), 3.95 (d, *J* = 10.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.83, 154.44, 149.57, 130.09, 126.80, 110.38, 108.90, 56.13, 55.94.



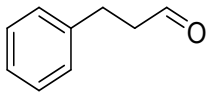
3,4,5-trimethoxybenzaldehyde **2j**

Colorless solid, 98% yield. Analytical data for **2j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.14 (s, 2H), 3.95 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.07, 153.63, 143.57, 131.71, 106.69, 60.98, 56.26.



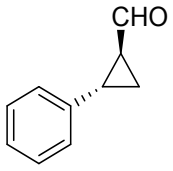
4-hydroxybenzaldehyde **2k**

Colorless solid, 96% yield. Analytical data for **2k**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.39, 161.80, 132.59, 129.75, 116.06.



3-phenylpropanal **2l**

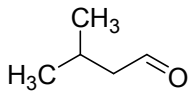
Colorless oil, 69% NMR yield using 0.2mmol CH_3NO_2 as standard. Analytical data for **2l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.19 (t, J = 7.9 Hz, 3H), 2.95 (t, J = 7.5 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.61, 140.38, 128.64, 128.33, 126.34, 45.29, 28.14.



(Rac)-Trans-2-phenylcylcopropane-1-carbaldehyde **2m**

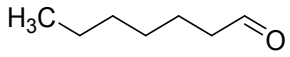
Colorless oil, 63% yield. Analytical data for **2m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, J = 4.6 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 7.8 Hz, 2H), 2.63 (t, J = 9.9 Hz, 1H), 2.18 (dd, J = 10.6, 6.5 Hz, 1H), 1.73 (dt, J = 9.8, 5.0

Hz, 1H), 1.53 (dd, J = 12.5, 7.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.73, 138.97, 128.62, 126.86, 126.28, 33.81, 26.61, 16.47.



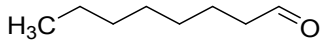
3-methylbutanal **2n**

Colorless oil, 32% NMR yield using 0.2mmol CH_3NO_2 as standard. Analytical data for **2n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 – 9.68 (m, 1H), 2.30 (ddd, J = 6.7, 4.7, 2.2 Hz, 2H), 2.27 – 2.15 (m, 1H), 0.98 (t, J = 5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.94, 52.56, 23.44, 22.54.



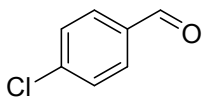
Heptanal **2o**

Colorless oil, 50% NMR yield using 0.2mmol CH_3NO_2 as standard. Analytical data for **2o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 – 9.68 (m, 1H), 2.49 – 2.36 (m, 2H), 1.71 – 1.56 (m, 2H), 1.30 (s, 6H), 0.92 – 0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.91, 43.88, 31.51, 28.80, 22.42, 22.01, 13.95.



Octanal **2p**

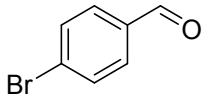
Colorless oil, 36% NMR yield using 0.2mmol CH_3NO_2 as standard. Analytical data for **2p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (m, 1H), 2.42 (td, J = 7.4, 1.5 Hz, 2H), 1.70 – 1.57 (m, 2H), 1.33 – 1.26 (m, 8H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.94, 43.89, 31.60, 29.10, 29.00, 22.56, 22.05, 14.01.



4-chlorobenzaldehyde **2q**

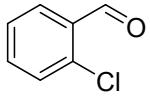
Colorless oil, 91% yield. Analytical data for **2q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s,

1H), 7.83 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.90, 141.07, 134.73, 130.93, 129.49.



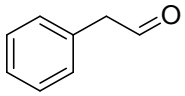
4-bromobenzaldehyde **2r**

Colorless oil, 92% yield. Analytical data for **2r**: ^{1}H NMR (400 MHz, CDCl3) δ 9.98 (s, 1H), 7.75 (dd, J = 8.5, 2.0 Hz, 2H), 7.69 (dd, J = 7.7, 2.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 191.08, 135.09, 132.46, 130.99, 129.80.



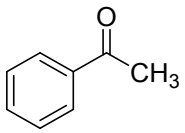
2-chlorobenzaldehyde **2s**

Colorless oil, 92% yield. Analytical data for **2s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.93 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.3, 1.8 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 – 7.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.84, 137.96, 135.14, 132.47, 130.62, 129.38, 127.30.



2-phenylacetaldehyde **2t**

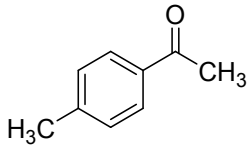
Colorless oil, 94% yield. Analytical data for **2t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 2.4 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 2H), 3.68 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.51, 131.88, 129.66, 129.04, 127.45, 50.60.



Acetophenone **4a**

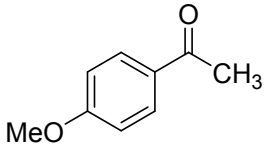
Colorless oil, 97% yield. Analytical data for **4a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d,

J = 8.0 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.14, 137.10, 133.11, 128.57, 128.30, 26.58.



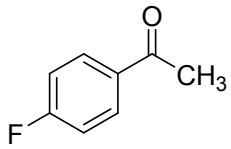
1-(p-tolyl)ethan-1-one **4b**

Colorless oil, 94% yield. Analytical data for **4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 2.57 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.86, 143.88, 134.72, 129.25, 128.45, 26.53, 21.63.



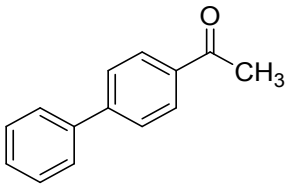
1-(4-methoxyphenyl)ethan-1-one **4c**

Colorless oil, 89% yield. Analytical data for **4c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.81, 163.49, 130.60, 130.34, 113.69, 55.47, 26.35.



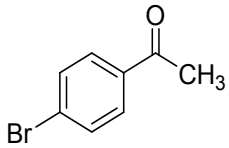
1-(4-fluorophenyl)ethan-1-one **4d**

Colorless oil, 91% yield. Analytical data for **4d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (ddd, J = 6.9, 5.4, 2.1 Hz, 2H), 7.13 (t, J = 8.7 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.47, 165.75 (d, J = 254.6 Hz), 133.58 (d, J = 2.9 Hz), 130.94 (d, J = 9.3 Hz), 115.63 (d, J = 21.9 Hz), 26.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.37.



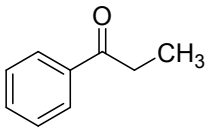
1-([1,1'-biphenyl]-4-yl)ethan-1-one **4e**

White solid, 93% yield. Analytical data for **4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.83, 145.81, 139.89, 135.86, 128.98, 128.94, 128.26, 127.30, 127.25, 26.70.



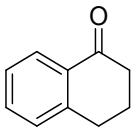
1-(4-bromophenyl)ethan-1-one **4f**

Colorless oil, 97% yield. Analytical data for **4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 2H), 7.71 – 7.40 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.00, 135.82, 131.90, 129.85, 128.31, 26.55.



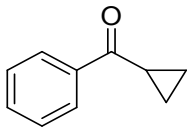
Propiophenone **4g**

Colorless oil, 91% yield. Analytical data for **4g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.54 (q, *J* = 6.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 3.09 – 2.89 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.81, 136.91, 132.88, 128.55, 127.97, 31.77, 8.23.



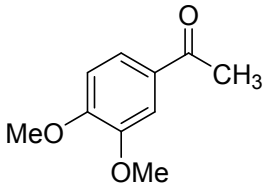
3,4-dihrdronaphthalen-1(2H)-one **4h**

Colorless oil, 92% yield. Analytical data for **4h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 – 7.13 (m, 2H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.78 – 2.54 (m, 2H), 2.14 (dt, *J* = 12.6, 6.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.50, 144.52, 133.42, 132.63, 128.79, 127.19, 126.65, 39.19, 29.72, 23.30.



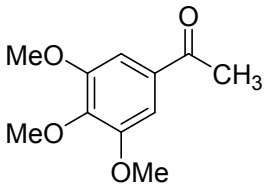
Cyclopropyl(phenyl)methanone **4i**

Colorless oil, 86% yield. Analytical data for **4i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.60 – 7.52 (m, 1H), 7.52 – 7.38 (m, 2H), 2.68 (tt, *J* = 7.8, 4.6 Hz, 1H), 1.29 – 1.21 (m, 2H), 1.05 (dq, *J* = 7.2, 3.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.74, 138.01, 132.75, 128.52, 128.03, 17.16, 11.69.



1-(3,4-dimethoxyphenyl)ethan-1-one **4j**

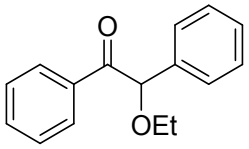
Colorless oil, 93% yield. Analytical data for **4j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 5.8 Hz, 6H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.85, 153.30, 149.00, 130.51, 123.31, 110.06, 109.94, 56.08, 56.00, 26.23.



1-(3,4,5-trimethoxyphenyl)ethan-1-one **4k**

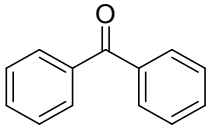
Colorless oil, 96% yield. Analytical data for **4k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 2H), 3.92 (d, *J* = 1.8 Hz, 9H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.93,

153.04, 142.63, 132.45, 105.84, 60.95, 56.31, 26.44.



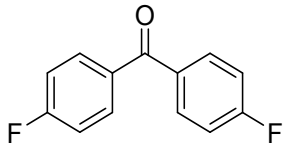
2-ethoxy-1,2-diphenylethan-1-one **4l**

Colorless solid, 76% yield. Analytical data for **4l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.51 (dd, *J* = 13.0, 7.2 Hz, 3H), 7.39 (dt, *J* = 21.4, 7.7 Hz, 4H), 7.33 – 7.28 (m, 1H), 5.61 (s, 1H), 3.77 – 3.46 (m, 2H), 1.30 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.71, 136.61, 135.01, 133.17, 129.19, 128.78, 128.41, 128.34, 127.36, 85.32, 65.51, 15.29.



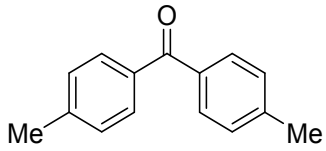
Benzophenone **4m**

White solid, 96% yield. Analytical data for **4m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.79, 137.61, 132.45, 130.08, 128.31.



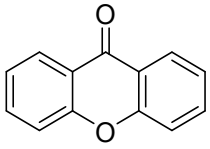
Bis(4-fluorophenyl)methanone **4n**

White solid, 91% yield. Analytical data for **4n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, 4H), 7.23 – 7.07 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.83, 165.41 (d, *J* = 254.4 Hz), 133.70 (d, *J* = 3.0 Hz), 132.51 (d, *J* = 9.1 Hz), 115.57 (d, *J* = 21.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.75.



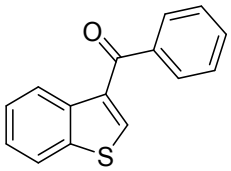
di-p-tolylmethanone **4o**

White solid, 97% yield. Analytical data for **4o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 4H), 2.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.32, 142.94, 135.23, 130.20, 128.92, 21.64.



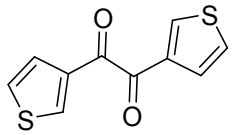
9H-xanthen-9-one **4p**

White solid, 99% yield. Analytical data for **4p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.50 (dt, *J* = 14.2, 7.3 Hz, 4H), 7.34 – 7.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.97, 144.46, 134.71, 134.17, 129.10, 124.35, 120.33.



Benzo[b]thiophen-3-yl(phenyl)methanone **4q**

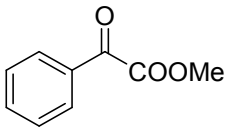
Yellow solid, 98% yield. Analytical data for **4q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.95 – 7.79 (m, 3H), 7.65 – 7.55 (m, 1H), 7.53 – 7.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.92, 140.08, 139.31, 138.35, 137.47, 134.82, 132.39, 129.54, 128.49, 125.72, 125.63, 125.22, 122.39.



1,2-di(thiophen-3-yl)ethane-1,2-dione **4r**

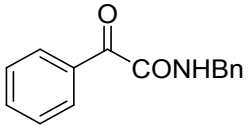
Yellow oil, 91% yield. Analytical data for **4r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd,

J = 3.9, 0.9 Hz, 2H), 7.85 (dd, *J* = 4.9, 0.9 Hz, 2H), 7.21 (dd, *J* = 4.7, 4.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.44, 138.62, 137.52, 137.29, 128.70.



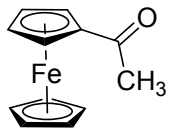
Methyl 2-oxo-2-phenylacetate **4s**

Colorless oil, 93% yield. Analytical data for **4s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.93 (m, 2H), 7.73 – 7.64 (m, 1H), 7.52 (dd, *J* = 10.7, 4.8 Hz, 2H), 3.99 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.06, 164.05, 135.01, 132.44, 130.11, 128.92, 52.80.



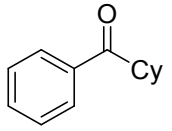
N-benzyl-2-oxo-2-phenylacetamide **4t**

Colorless oil, 96% yield. Analytical data for **4t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.68 – 7.59 (m, 1H), 7.48 (dd, *J* = 10.8, 4.8 Hz, 2H), 7.40 – 7.28 (m, 5H), 4.58 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.66, 161.54, 137.11, 134.49, 133.34, 131.30, 128.89, 128.54, 127.93, 127.89, 43.49.



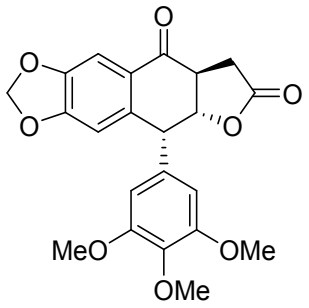
Acetylferrocene **4u**

Yellow solid, 86% yield. Analytical data for **4u**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 – 4.70 (m, 2H), 4.55 – 4.42 (m, 2H), 4.20 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.24, 79.29, 72.37, 69.89, 69.63, 27.45.



Cyclohexyl(phenyl)methanone **4v**

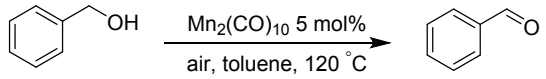
Yellow oil, 86% yield. Analytical data for **4v**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 6H), 7.54 (t, *J* = 7.3 Hz, 3H), 7.46 (t, *J* = 7.6 Hz, 5H), 3.29 (t, *J* = 3.0 Hz, 1H), 1.97 – 1.77 (m, 13H), 1.74 (d, *J* = 12.8 Hz, 4H), 1.57 – 1.33 (m, 14H), 1.33 – 1.27 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.91, 136.37, 132.73, 128.59 128.26, 45.64, 29.43, 25.98, 25.87.



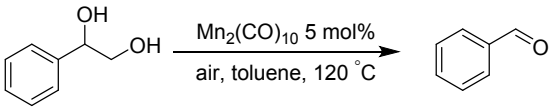
(5R, 5Ar, 8As)-5-(3,4,5-trimethoxyphenyl)-5,5a,8,8a-tetrahydrofuro[2',3':6,7]naphtha[2,3-d][1,3]dioxole-7,9-dione **8a**

Colorless oil, 43% yield. Analytical data for **8a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 6.71 (s, 1H), 6.39 (s, 2H), 6.10 (dd, *J* = 7.5, 1.1 Hz, 2H), 4.85 (d, *J* = 4.3 Hz, 1H), 4.57 (dd, *J* = 9.2, 7.6 Hz, 1H), 4.36 (dd, *J* = 10.4, 9.4 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 6H), 3.58 – 3.47 (m, 1H), 3.28 (dd, *J* = 15.5, 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.48, 153.23, 153.10, 148.15, 141.55, 137.68, 132.13, 128.21, 109.68, 107.65, 106.13, 102.42, 67.02, 60.80, 56.30, 46.72, 44.68, 43.47, 29.71.

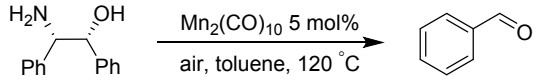
Large-scale experiments



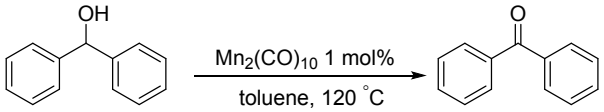
1a, 10 mmol ***2a, 0.95g, 89% yield***



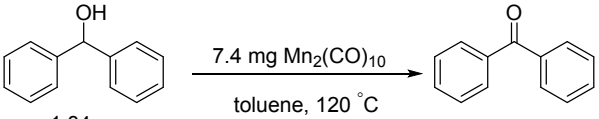
5a, 5 mmol ***2a, 0.42g, 80% yield***



6h, 5 mmol ***2a, 0.80g, 76% yield***



0.92g 5 mmol ***0.81 g, 89% yield***



1.84 g

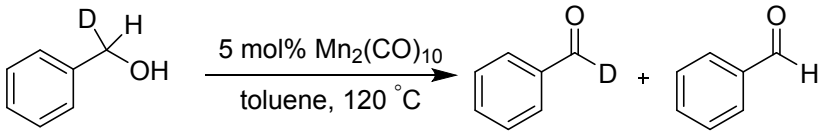
Under air: ***4m, 0.41g, 22.6% yield***

Under O_2: ***4m, 0.35g, 19.2% yield***

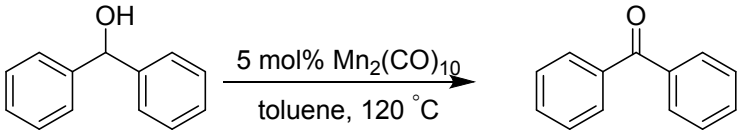
To a solution of alcohols in 10ml toluene in 500 ml pressure tube was added $Mn_2(CO)_{10}$ (x mol%), the color of the solution was orange, and the solution was stirred at 120°C under air, after 3h, opened the sealed tube replacing the fresh air. After 8-12h, black sediment appeared and the solution was cooled to room temperature，the product was isolated by silica gel column chromatography (PE:EA=50:1). (Caution: The solvent should be removed under low temperature.)

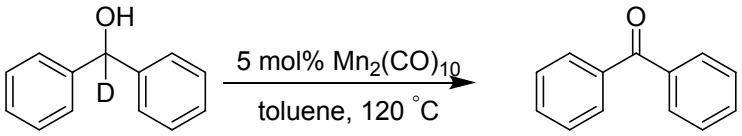
Mechanism experiments

KIE experiments



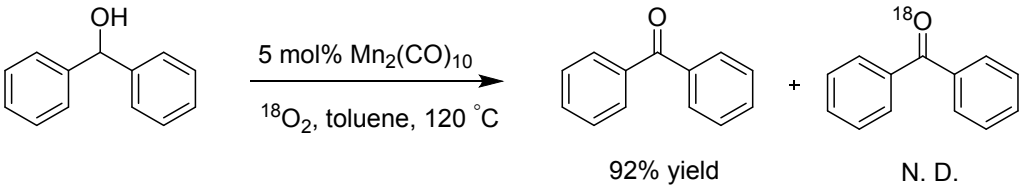
KIE = 9.9:1

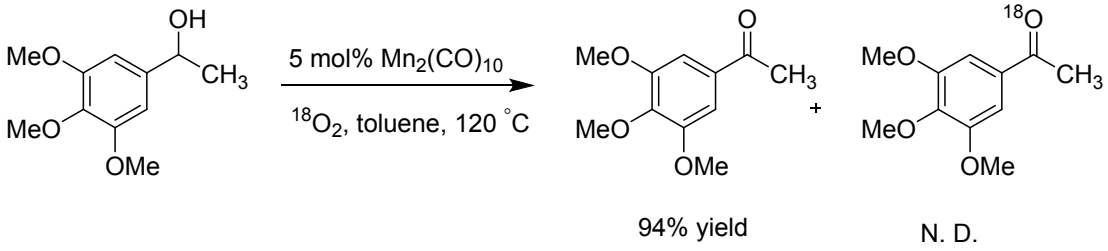




KIE = 2.3

^{18}O-labeled experiments.

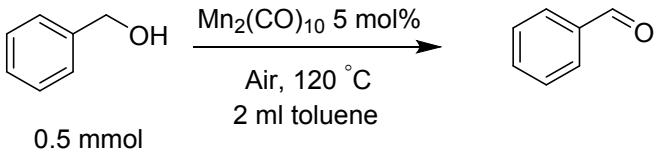


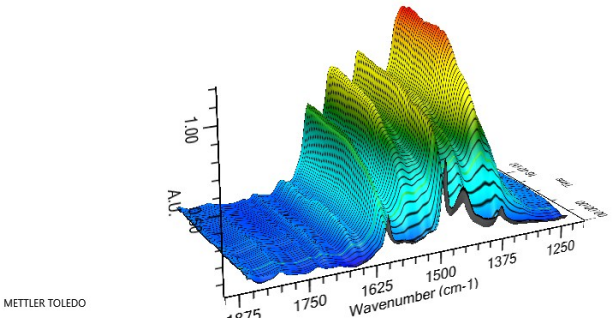


To a solution of alcohols (0.2mmol) in 1ml degassed toluene in 10 ml Schlenk tube was added $Mn_2(CO)_{10}$ (0.01mmol, 3.68mg), and the tube was filled with $^{18}O_2$, and the solution was stirred at 120°C until the substrate was disappeared, the product was isolated by silica gel column chromatography (PE:EA=10:1). The molecule weight was detected by HPLC-MS.

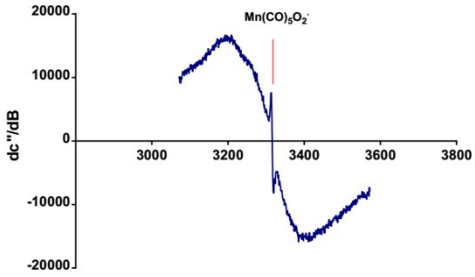
Operando IR analysis

The model reaction was monitored by Mettler-Toledo ReactIR 15 equipped with a 6.35 mm diameter DiComp probe.

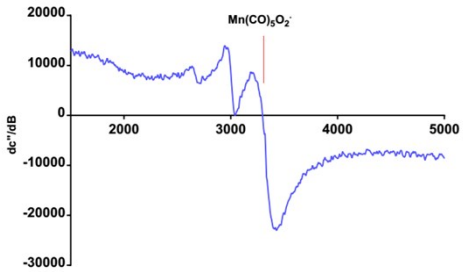




EPR test

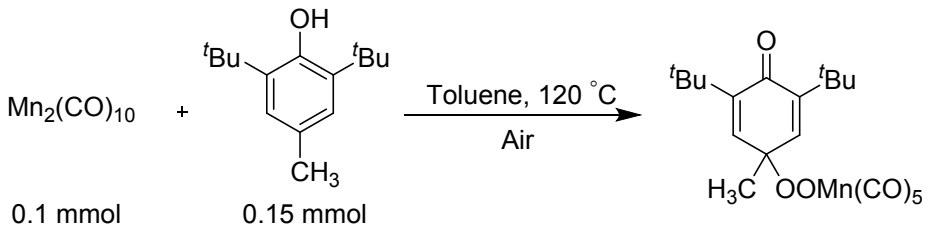


EPR spectra for the oxidation of **catalyst**. Conditions: $Mn_2(CO)_{10}$ (12 mg), at 363K, under air. The signal was collected after heating 0.5h.

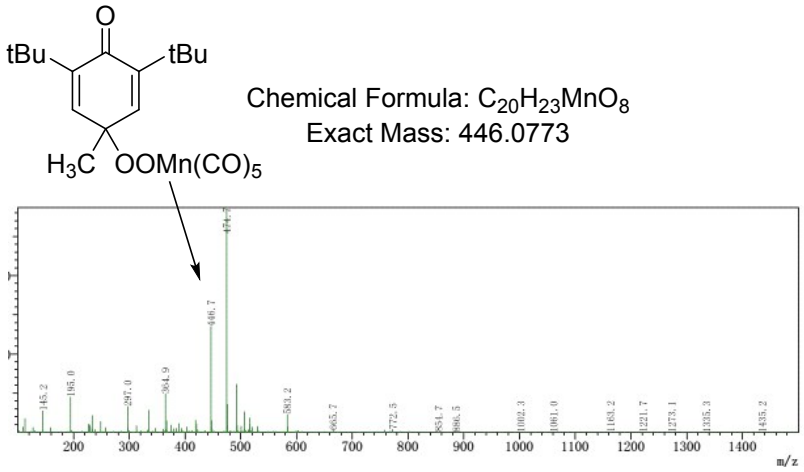


EPR spectra for the oxidation of **3m**. Conditions: **3m** (55.2 mg), $Mn_2(CO)_{10}$ (12 mg), at 363K, under air. The signal was collected after heating 1h.

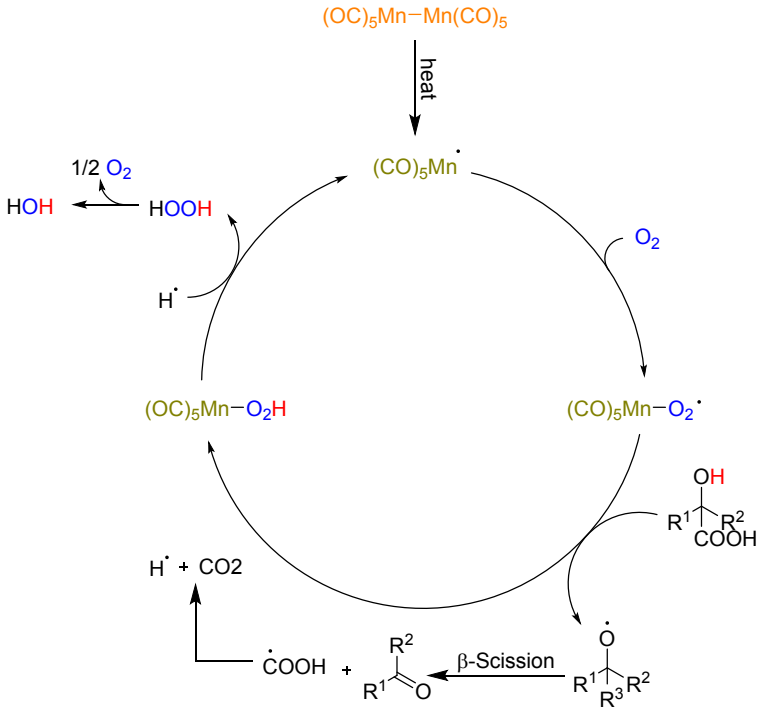
Radical-trapping experiment.



$Mn_2(CO)_{10}$ (38.9 mg, 0.1 mmol) and BHT (33.0 mg, 0.15 mmol) in 1 ml toluene were added to 15 ml sealed tube, then the solution was stirred at 120 °C, after 45 min, the reaction was detected by HPLC-MS.

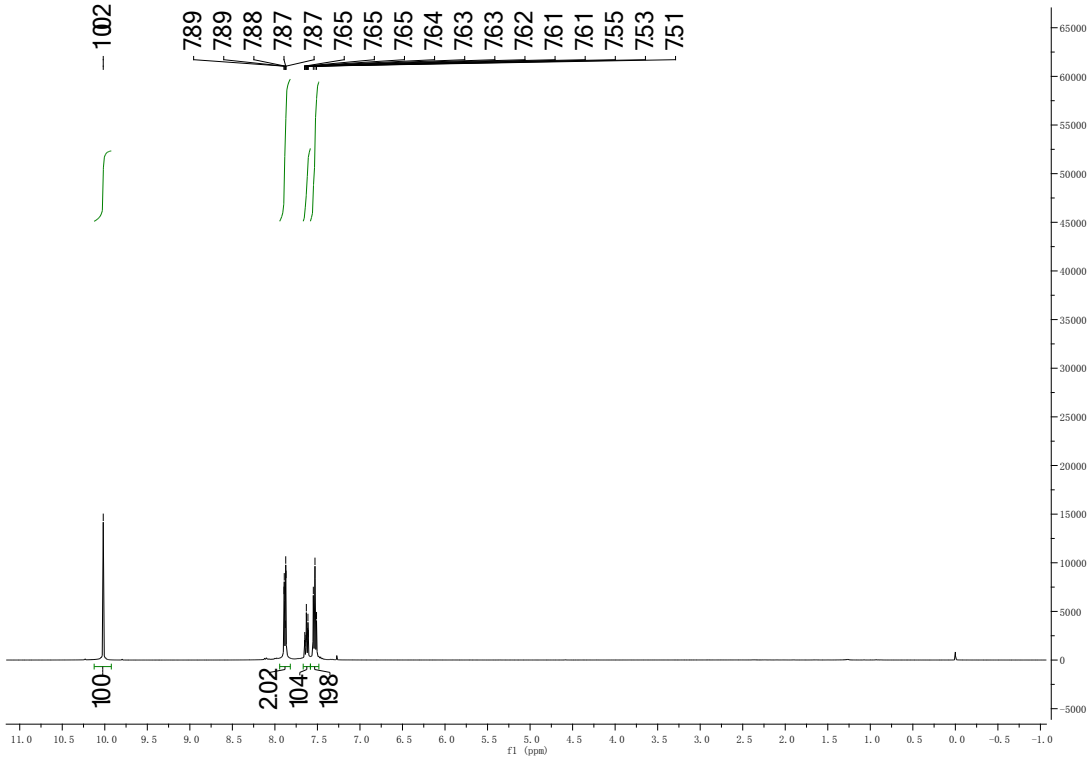


Proposed mechanism (R^3 = COOH).

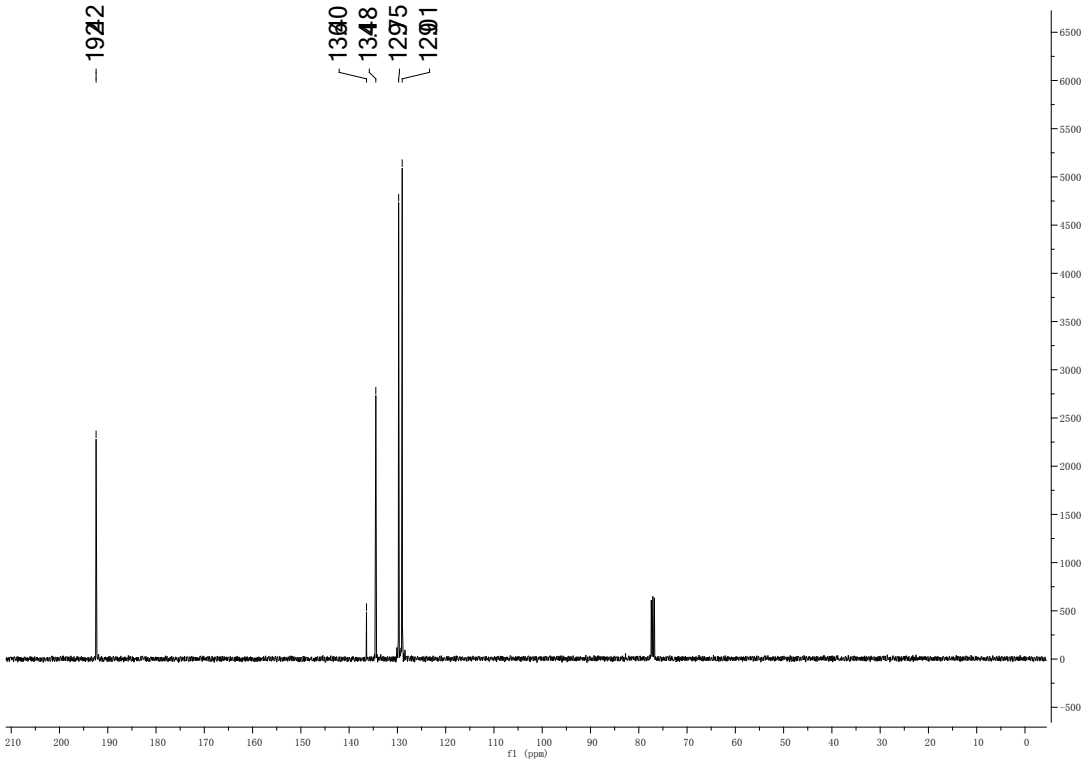


NMR spectra

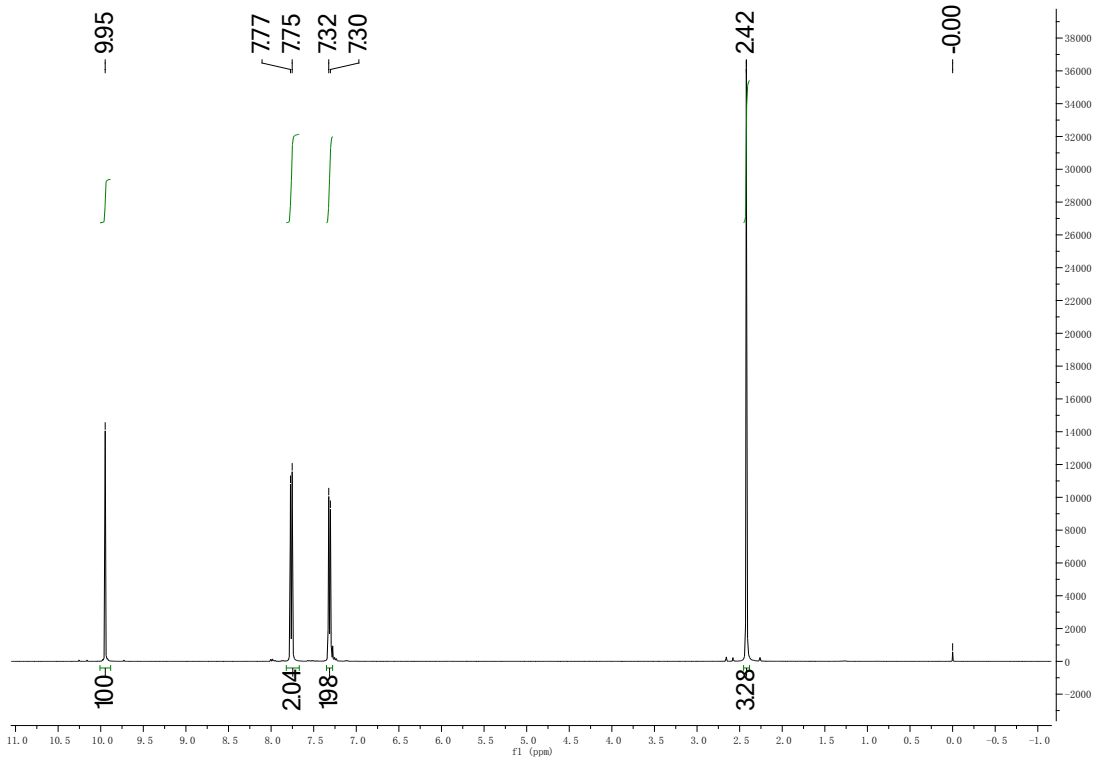
2a ^{1}H NMR



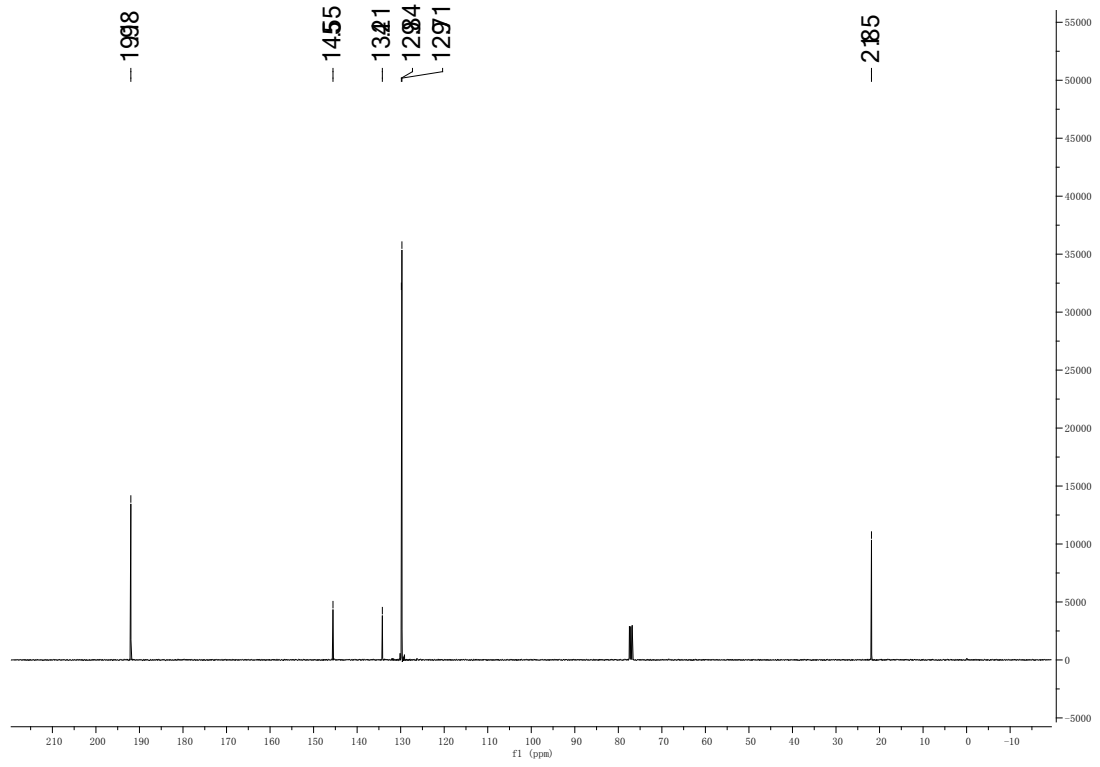
2a ^{13}C NMR



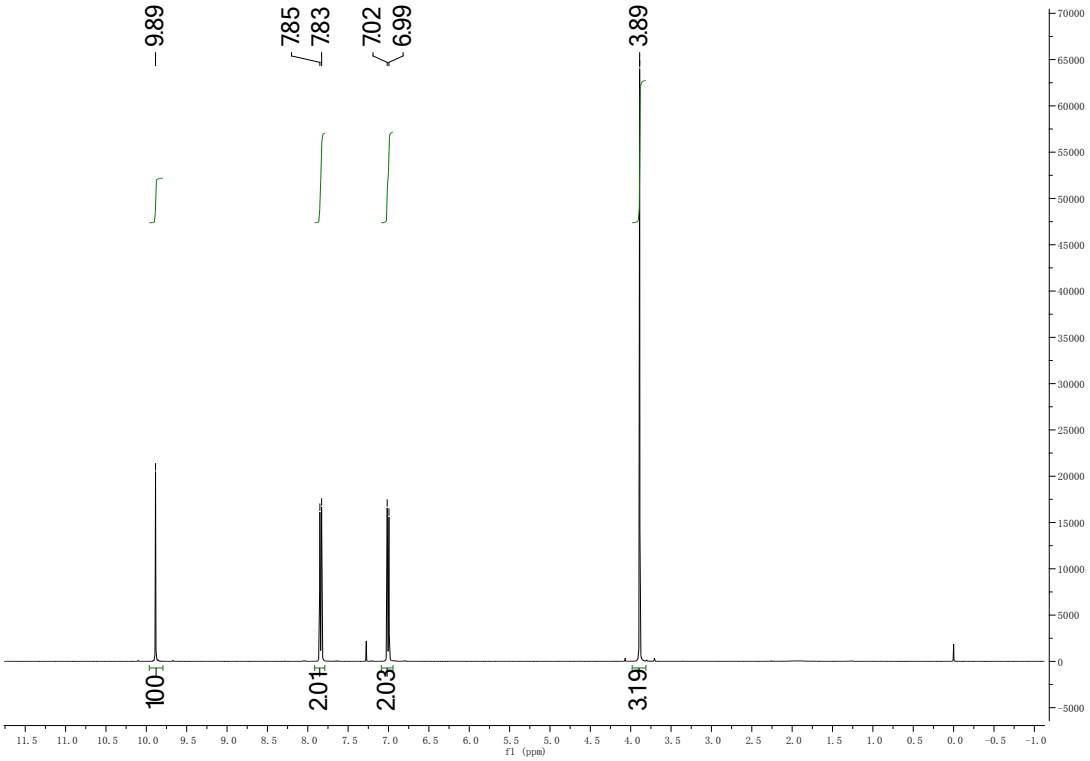
2b ^{1}H NMR



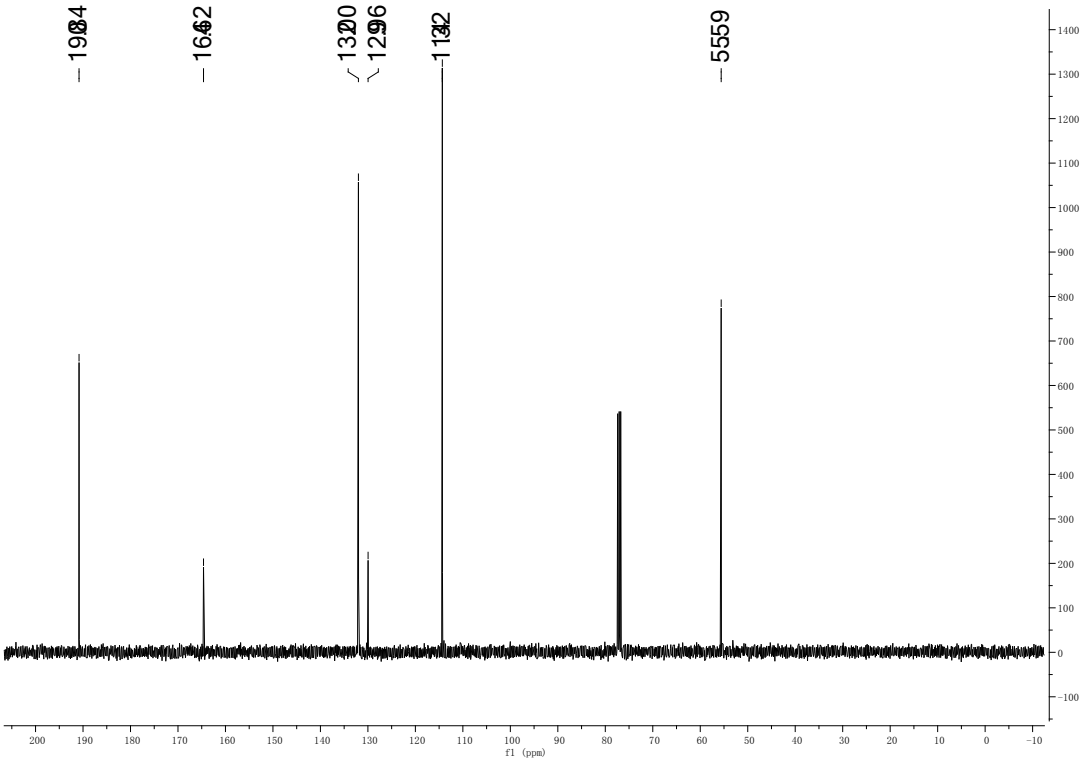
2b ^{13}C NMR



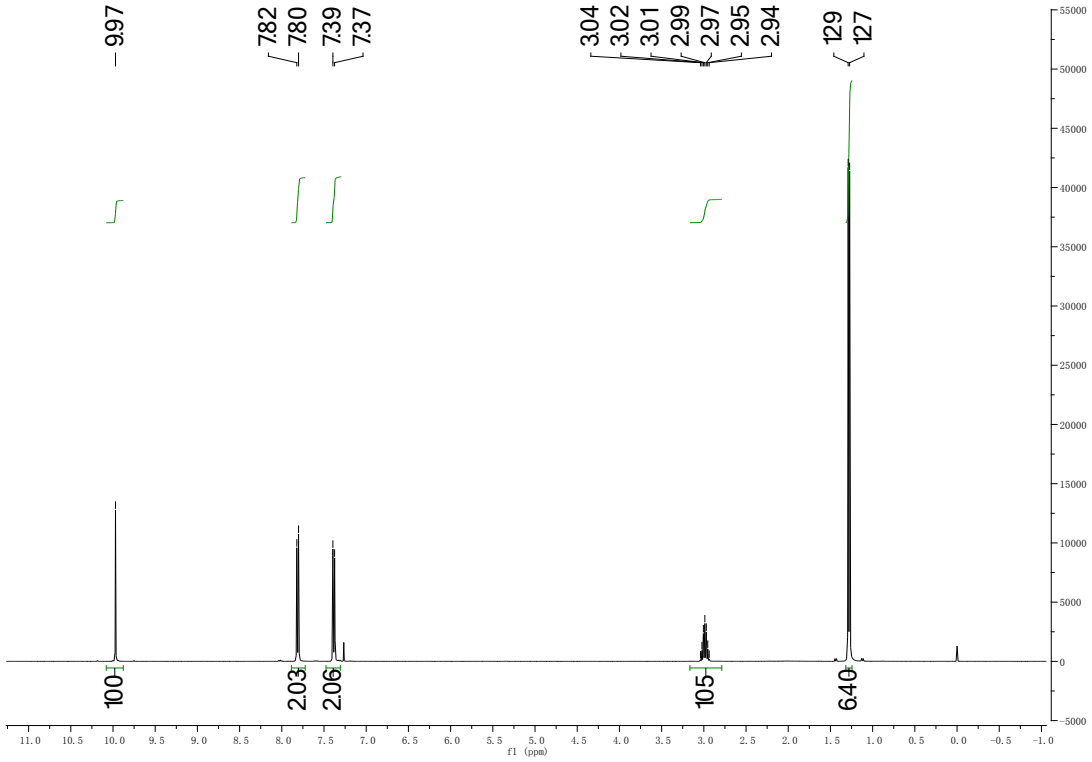
2c ^{1}H NMR



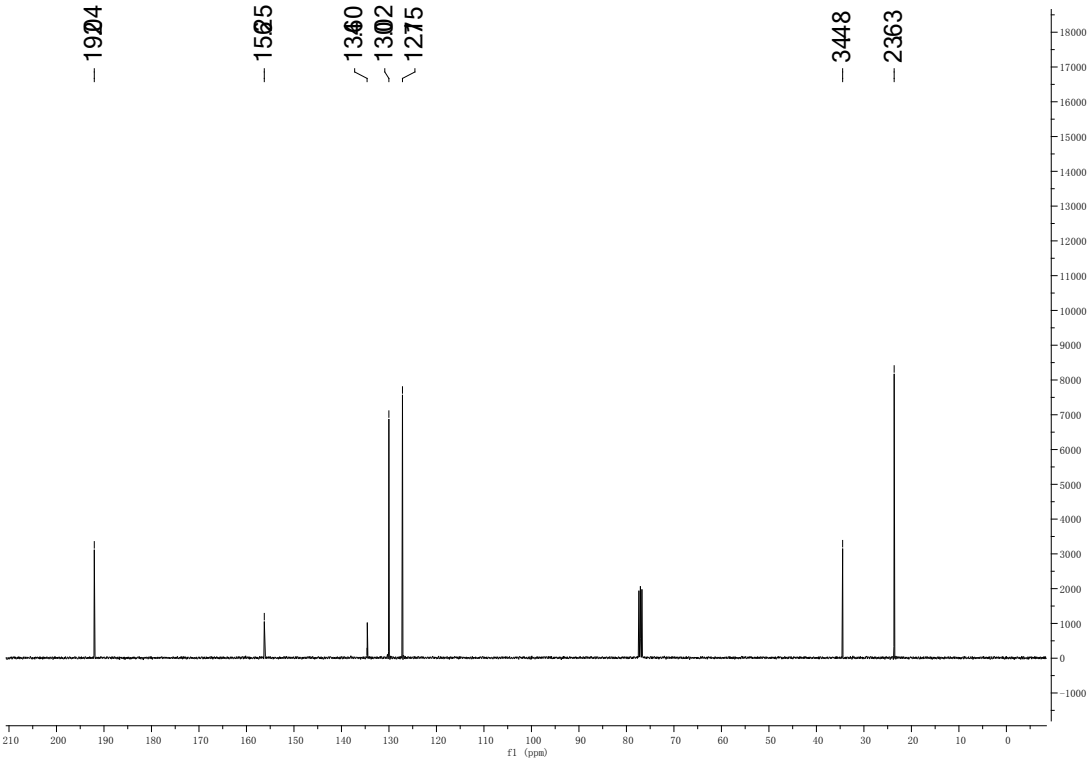
2c ^{13}C NMR



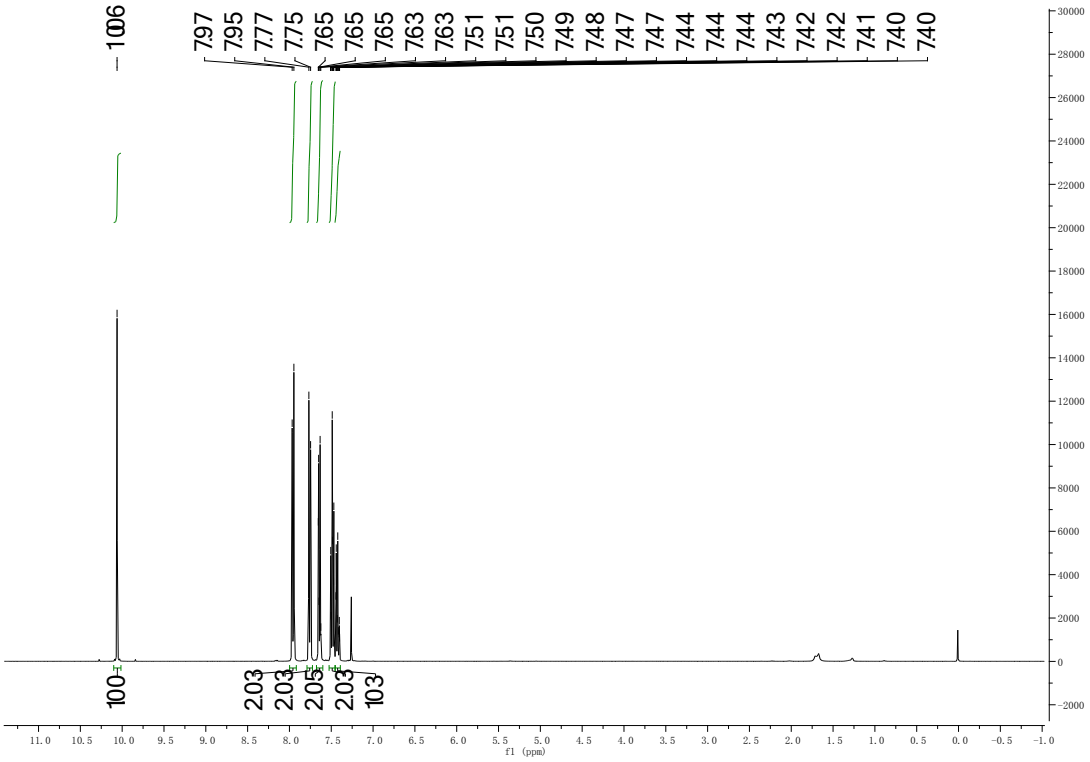
2d ^{1}H NMR



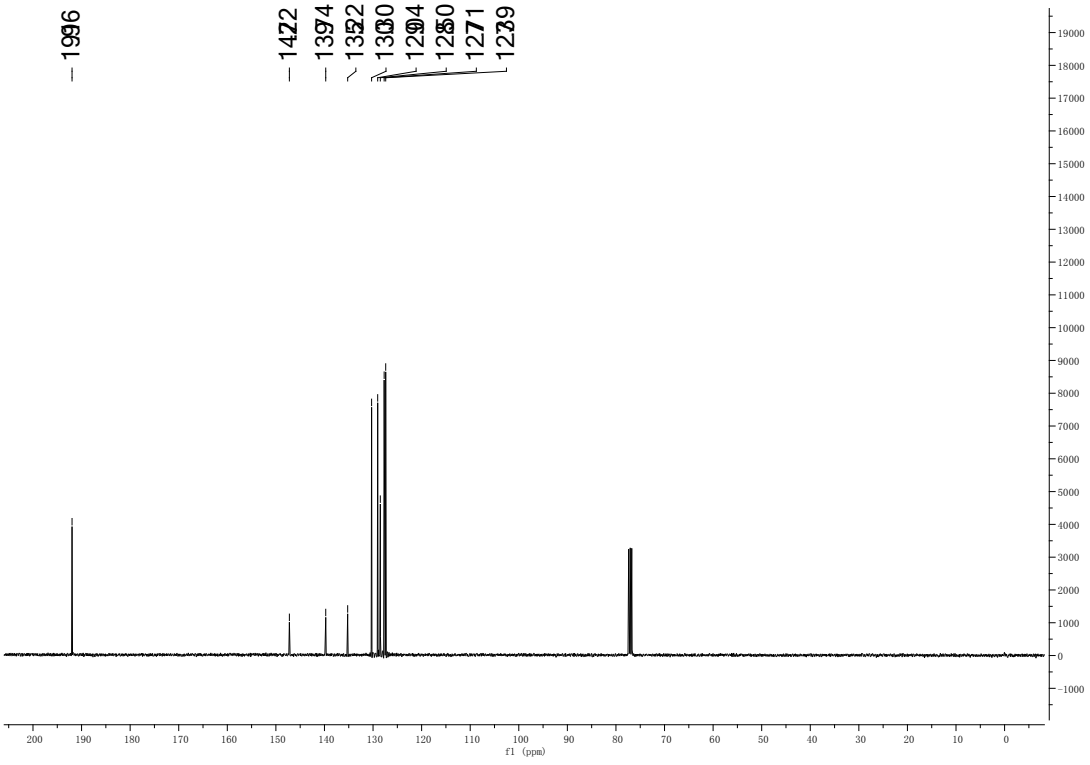
2d ^{13}C NMR



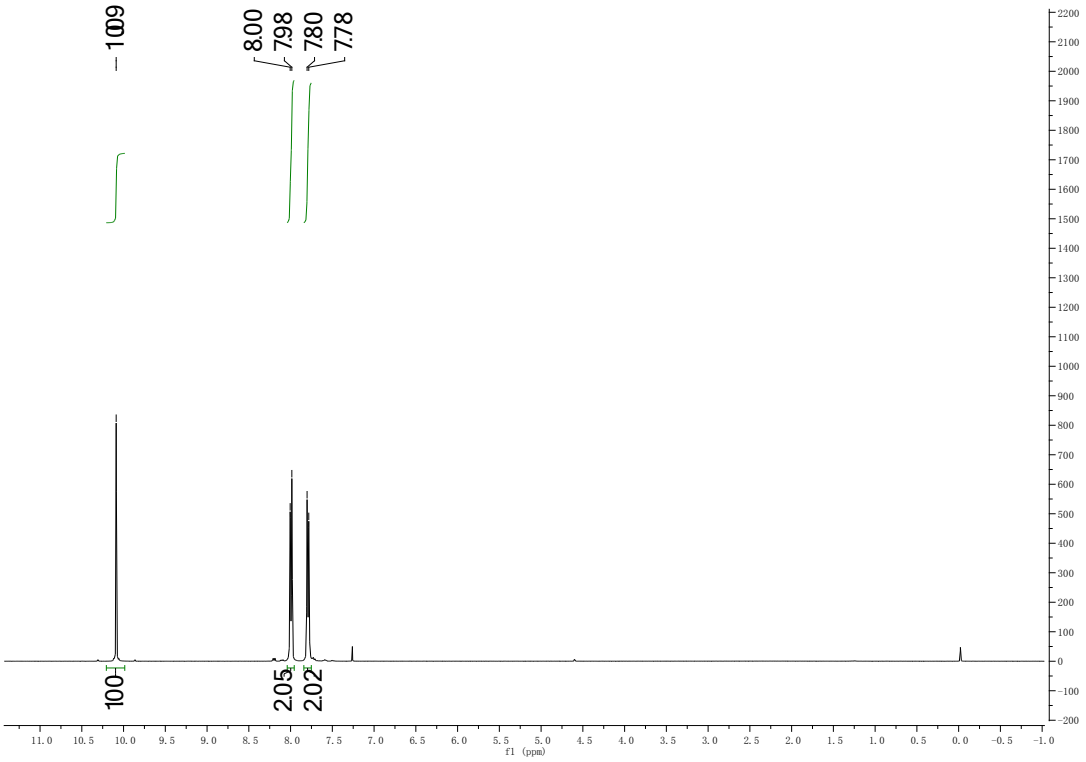
2e ^{1}H NMR



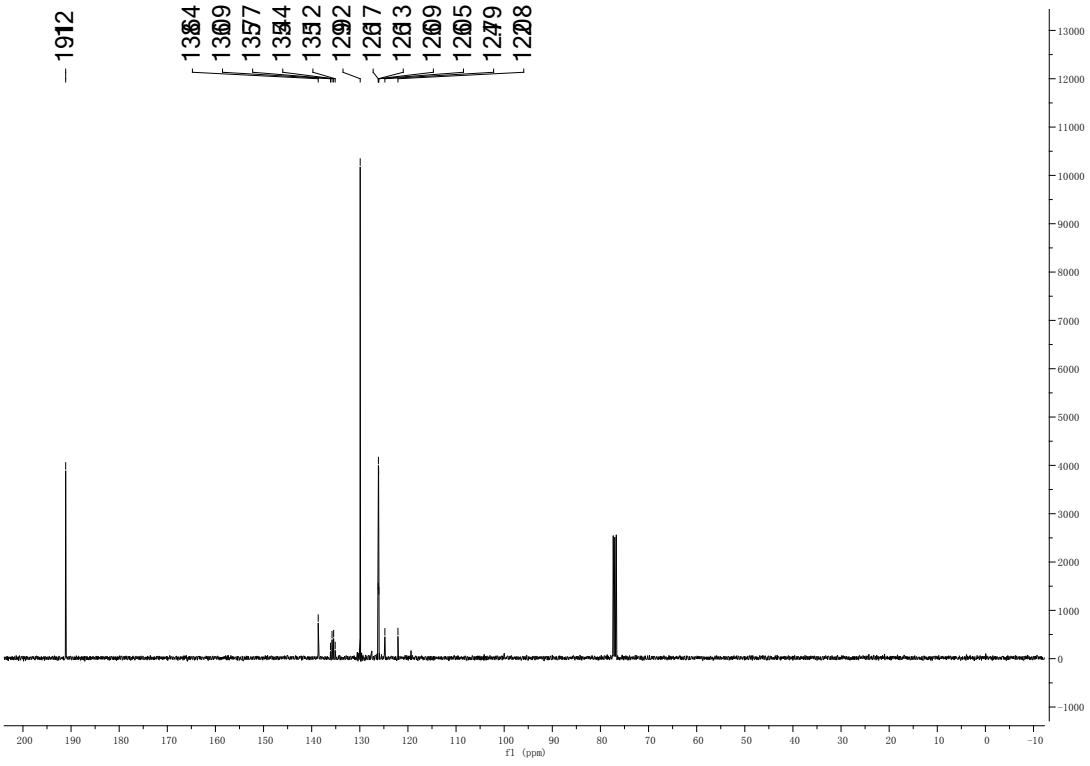
2e ^{13}C NMR



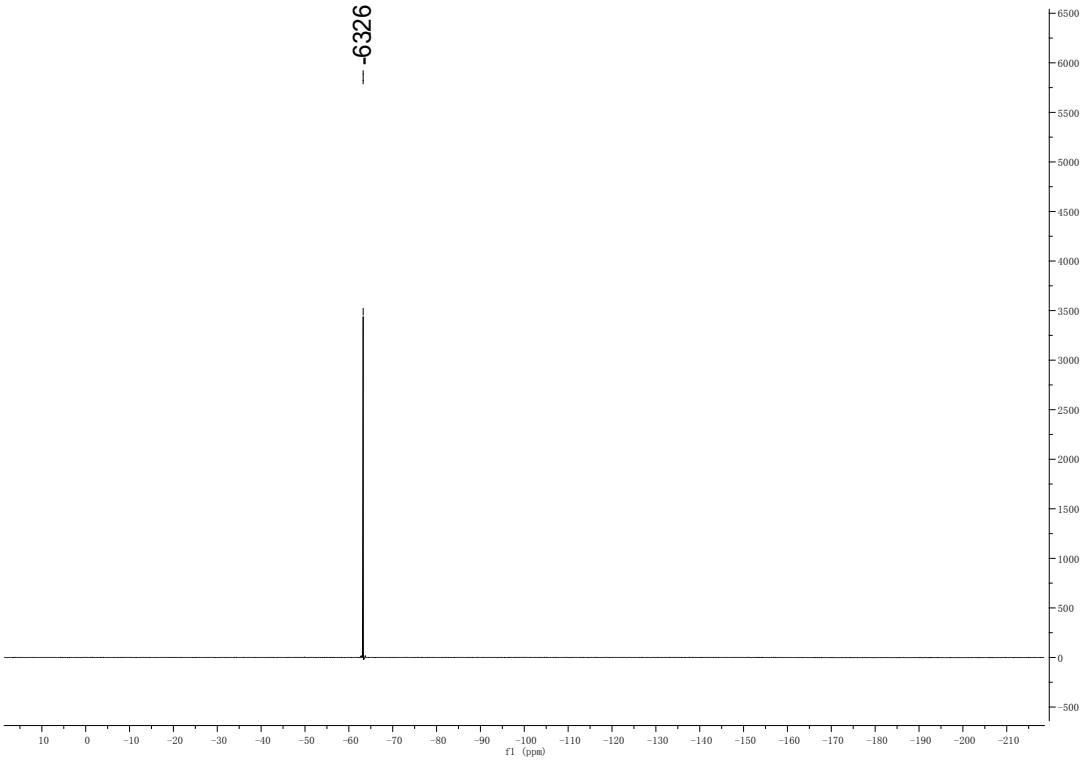
2f ^{1}H NMR



2f ^{13}C NMR



2f ^{19}F NMR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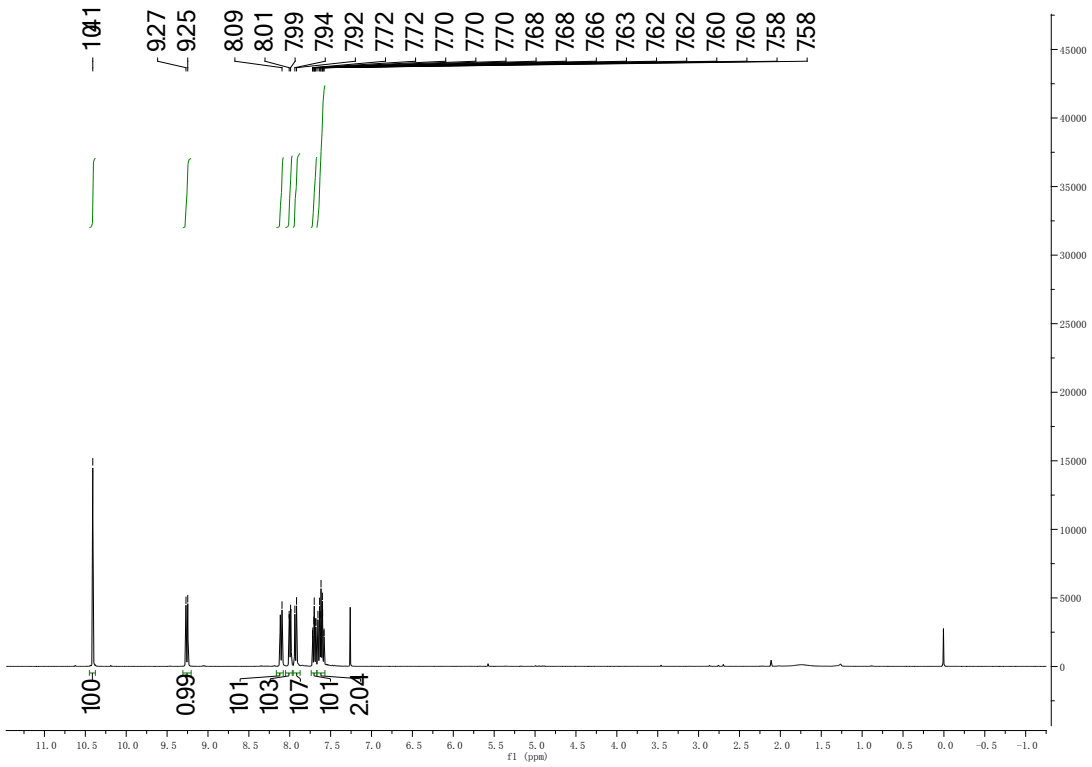
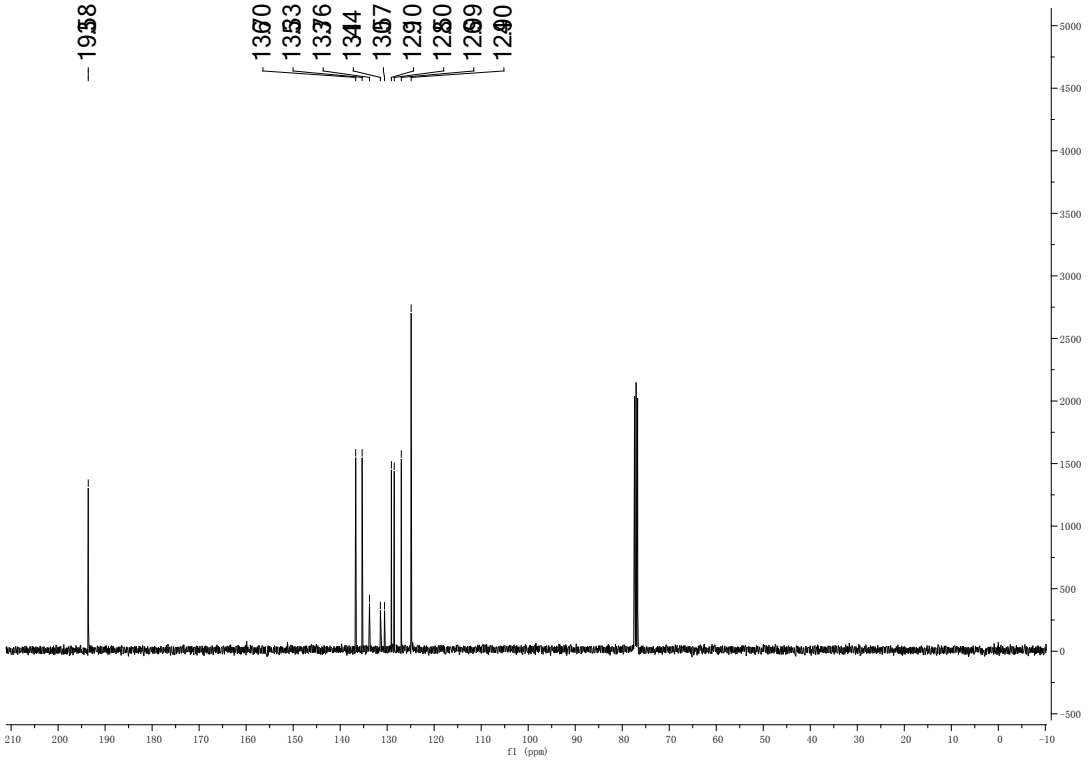
-200
-210
f1 (ppm)

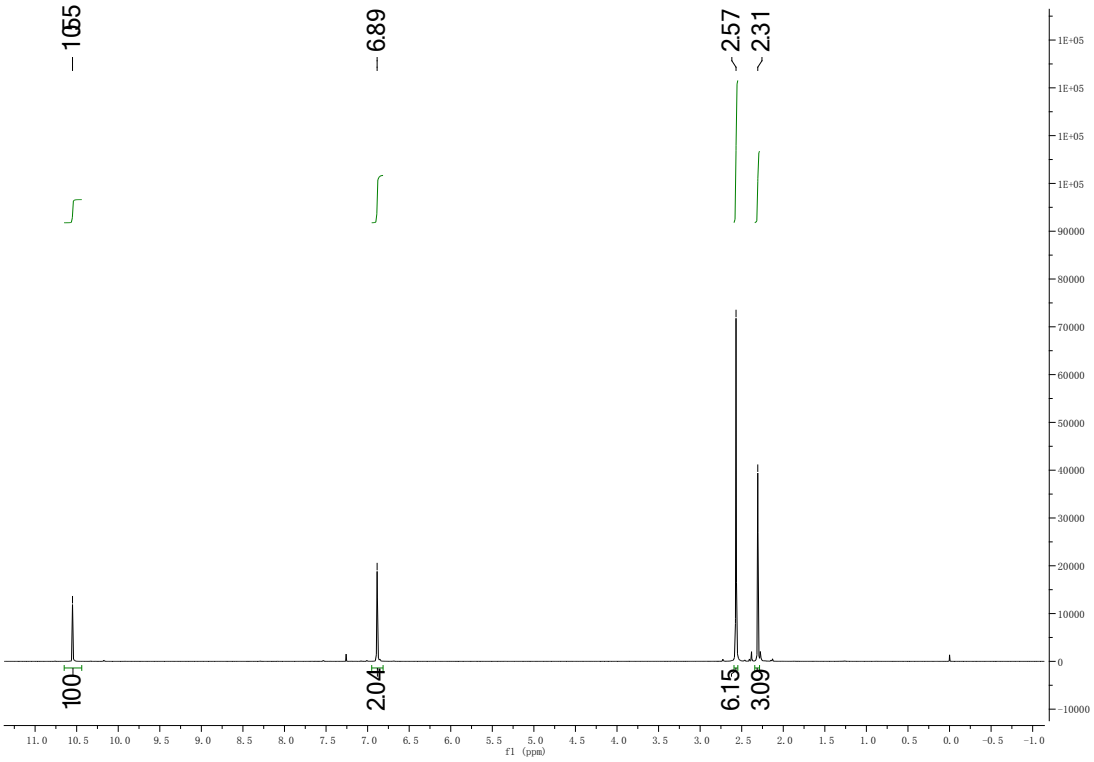
2g ^{1}H NMR



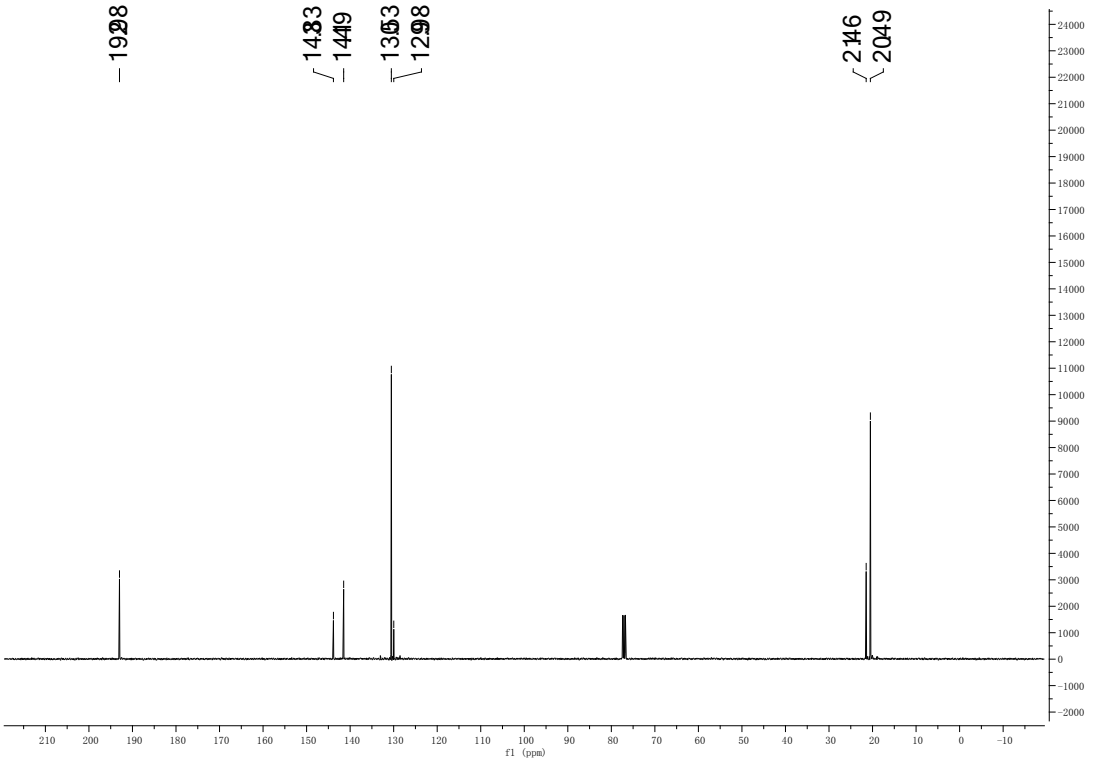
2g ^{13}C NMR



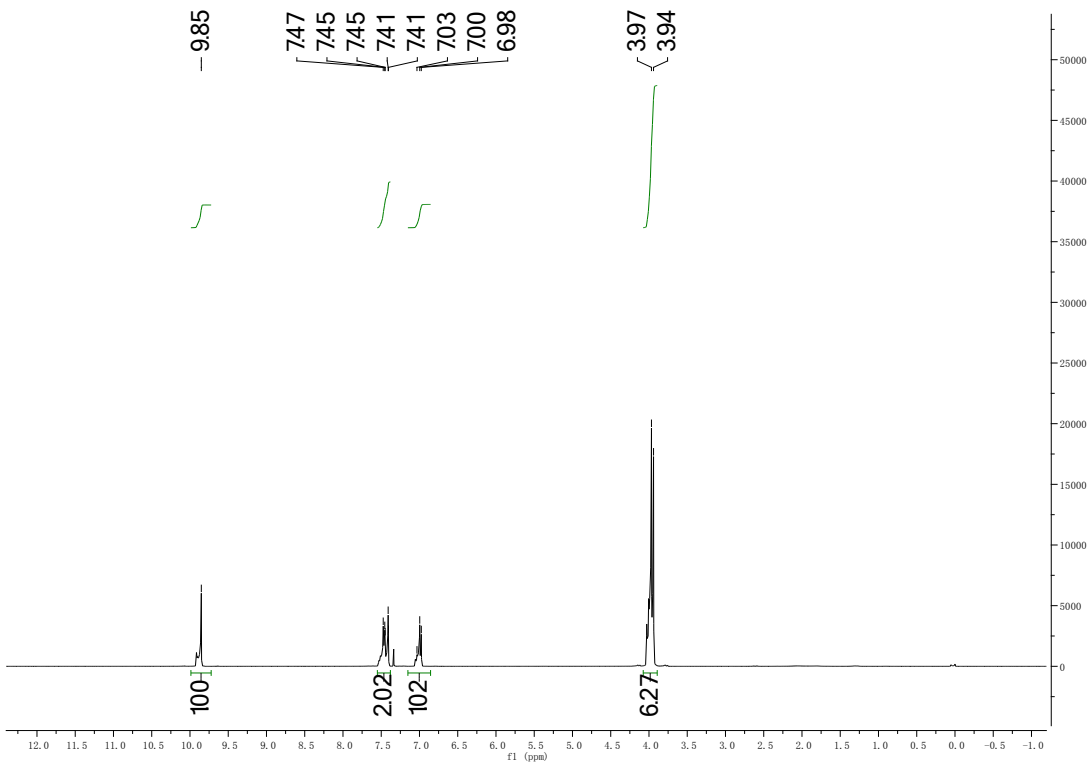
2h ^{1}H NMR



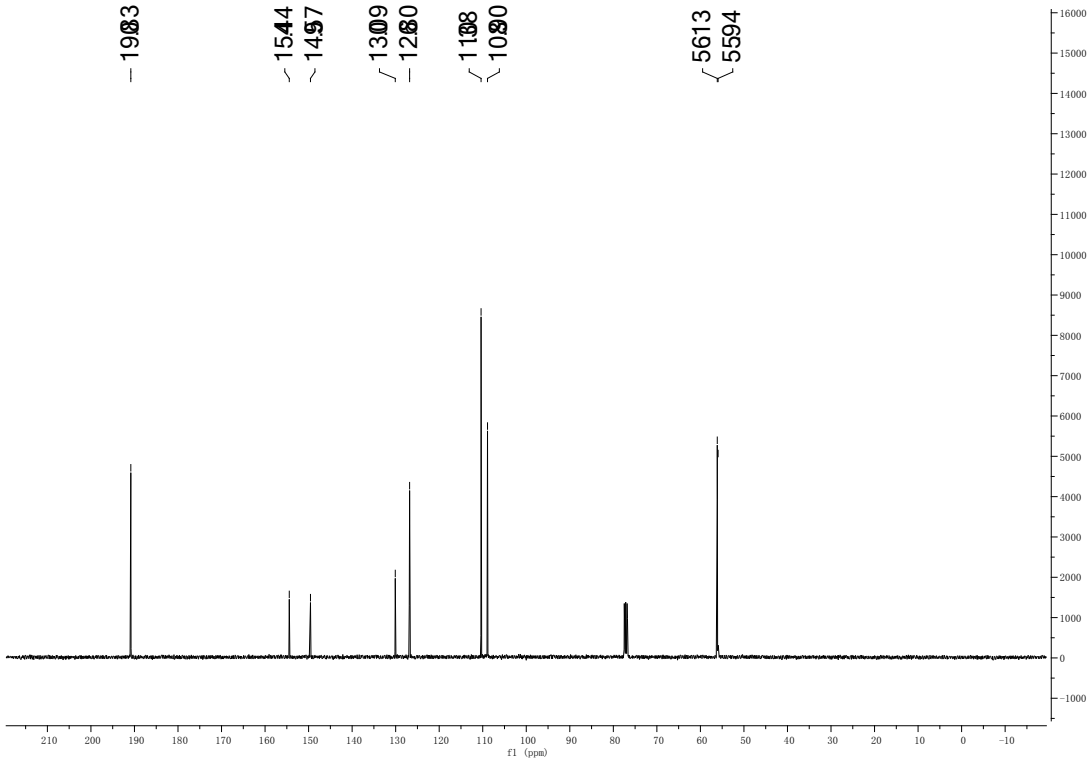
2h ^{13}C NMR



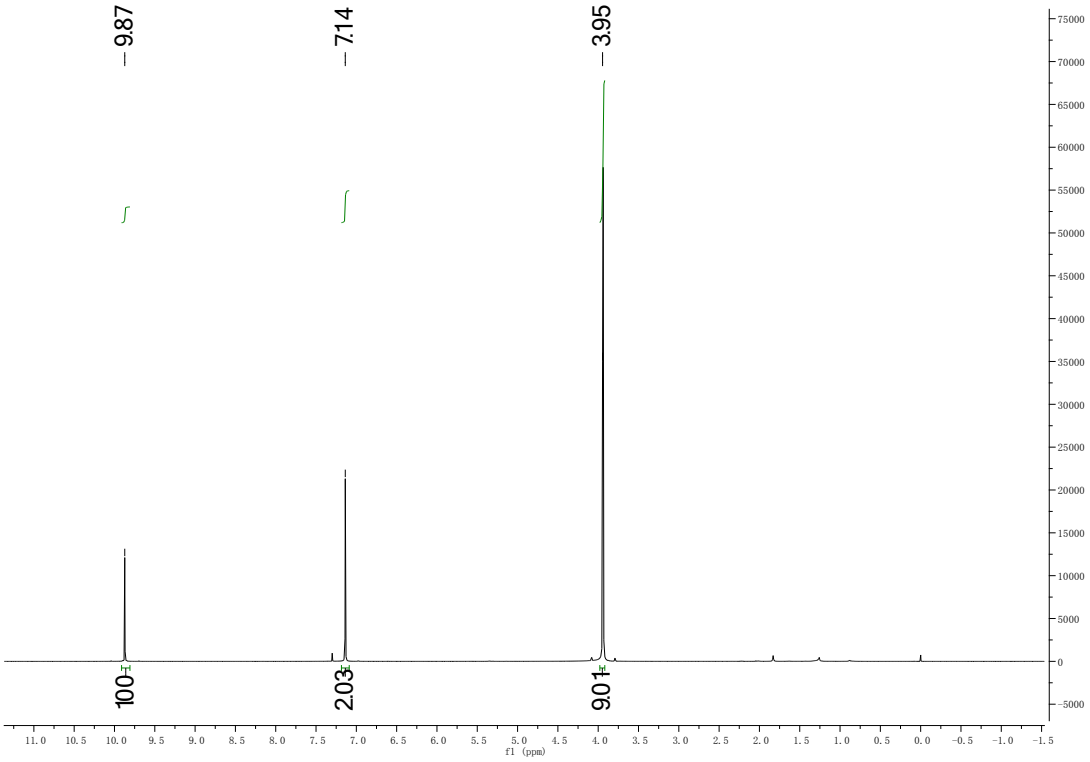
2i ^{1}H NMR



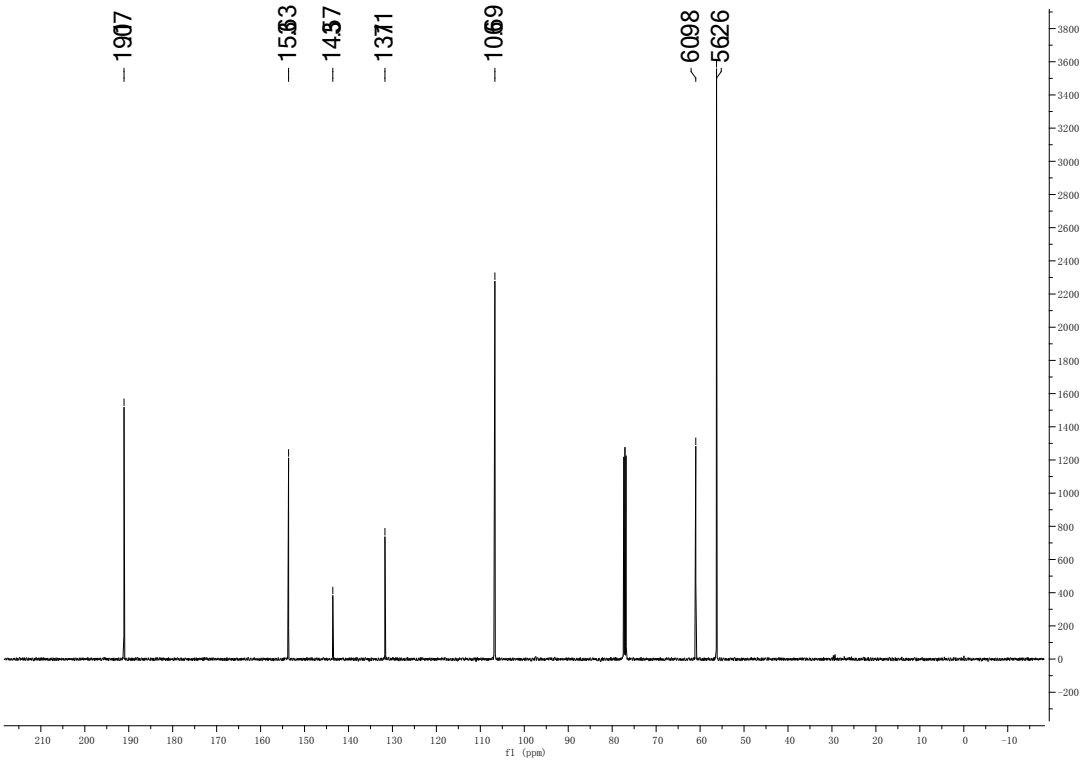
2i ^{13}C NMR



2j ^{1}H NMR



2j ^{13}C NMR



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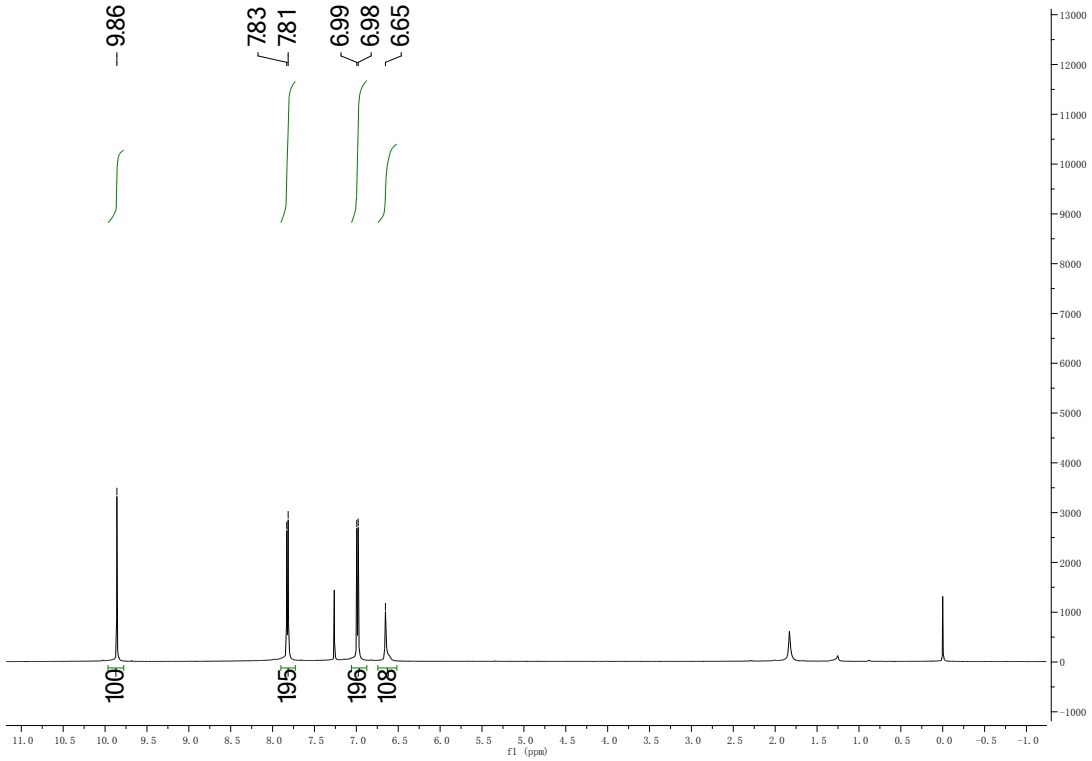

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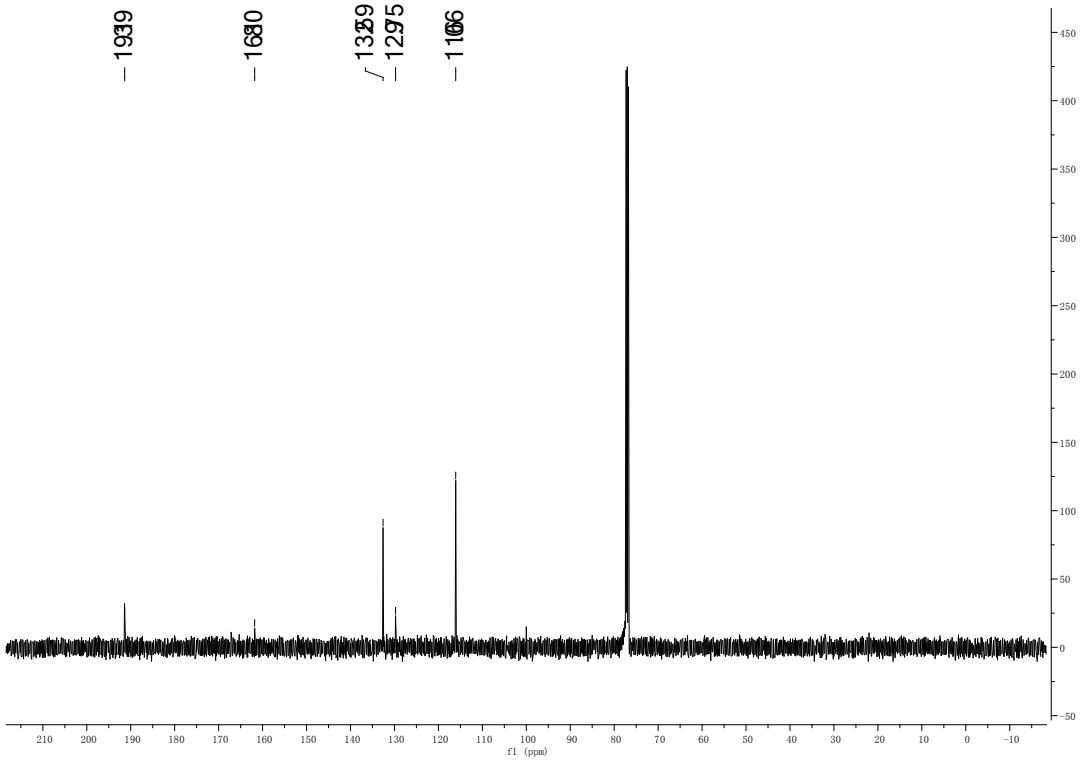
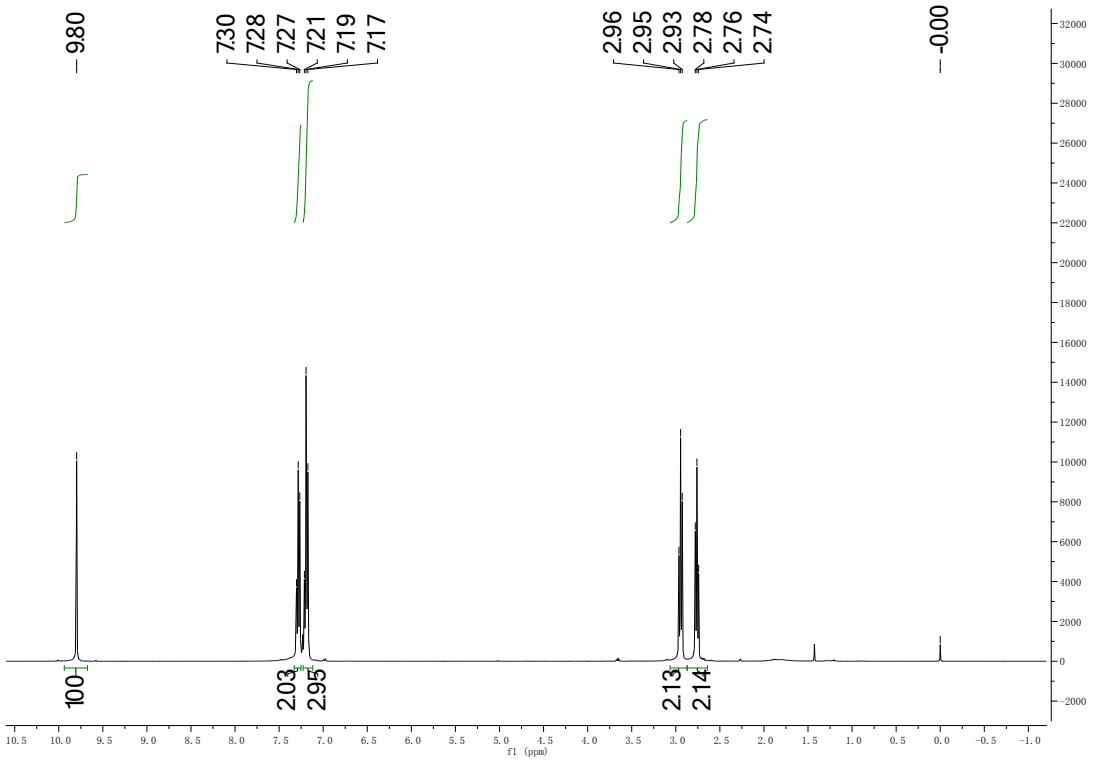


2l ^{1}H NMR



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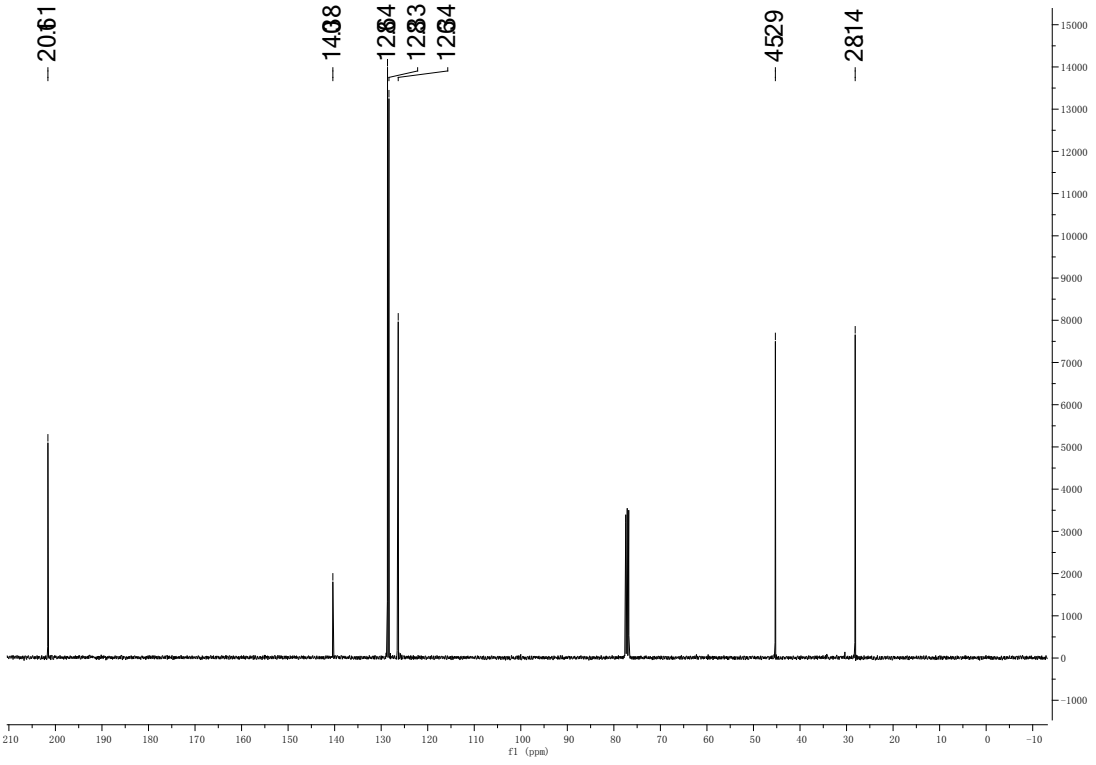
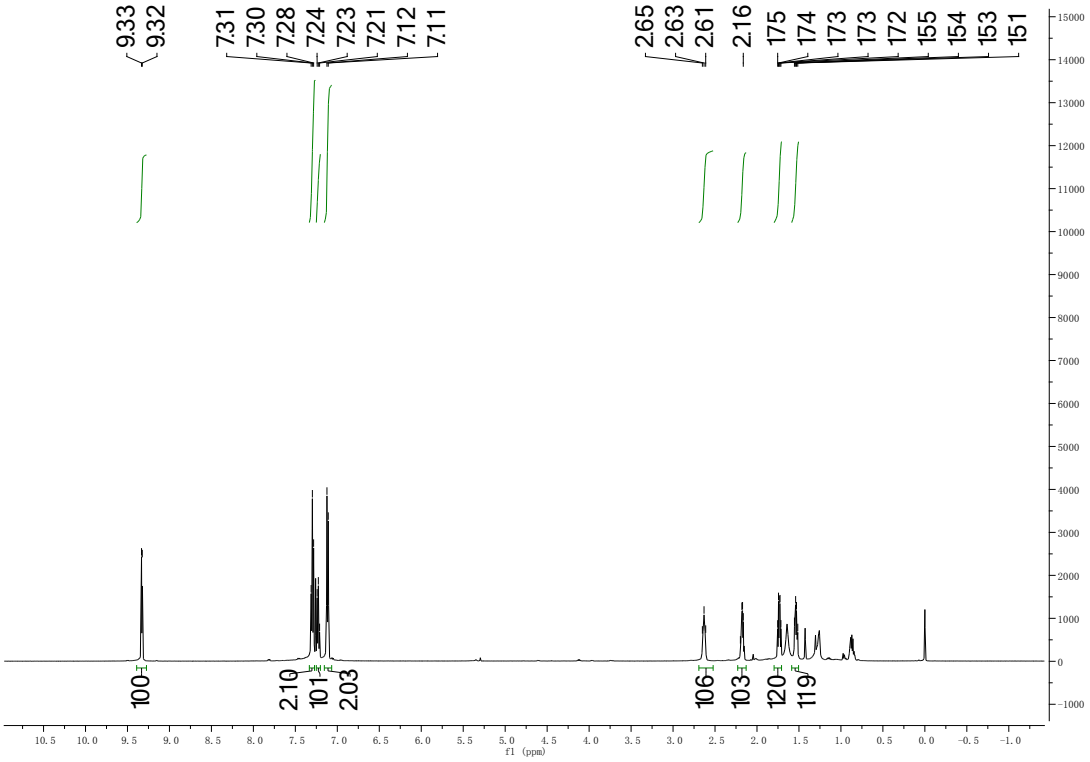
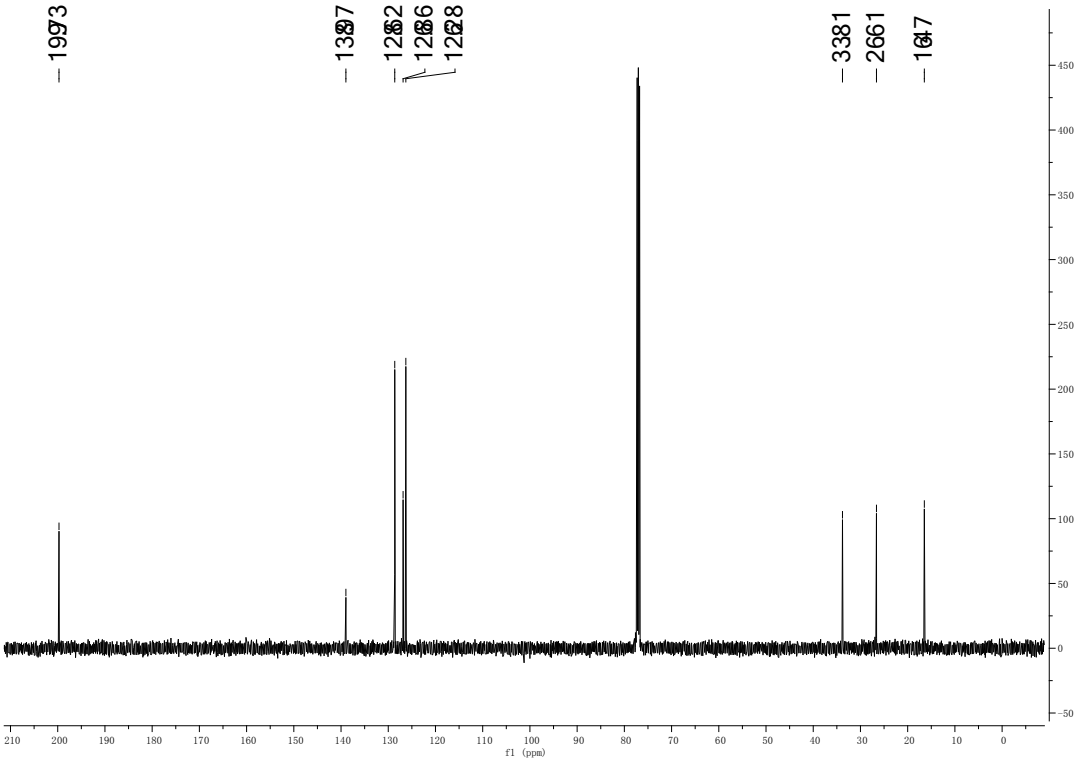


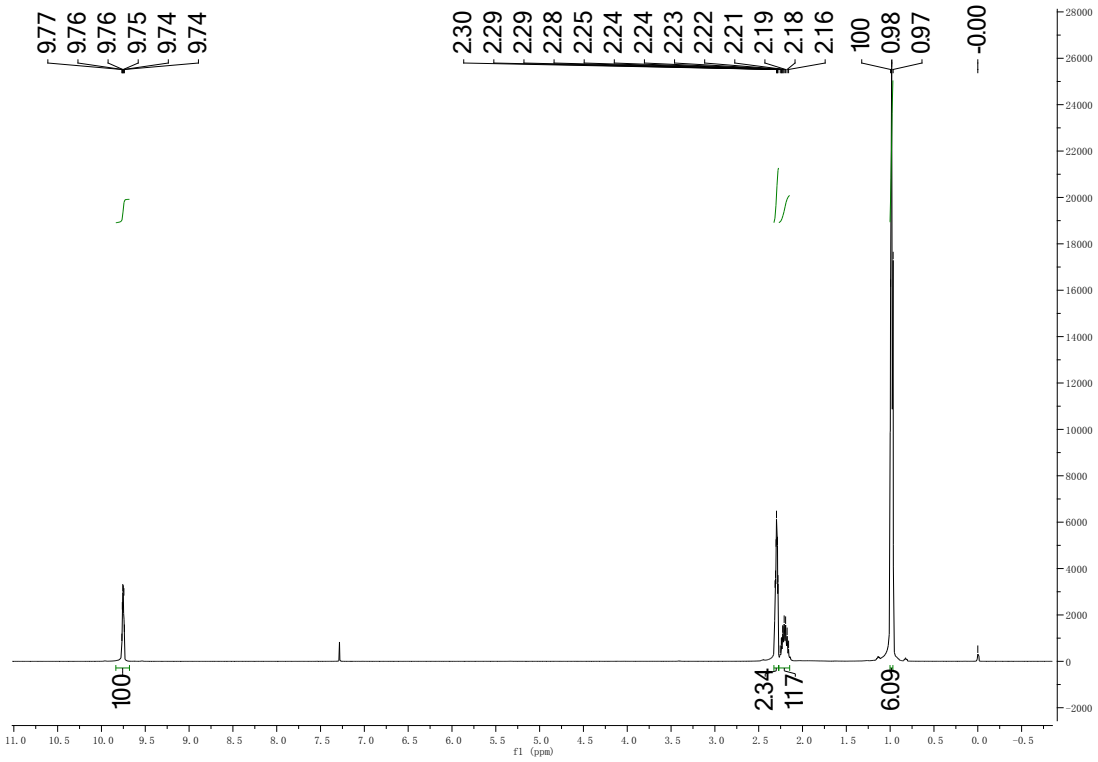
2m ^{1}H NMR



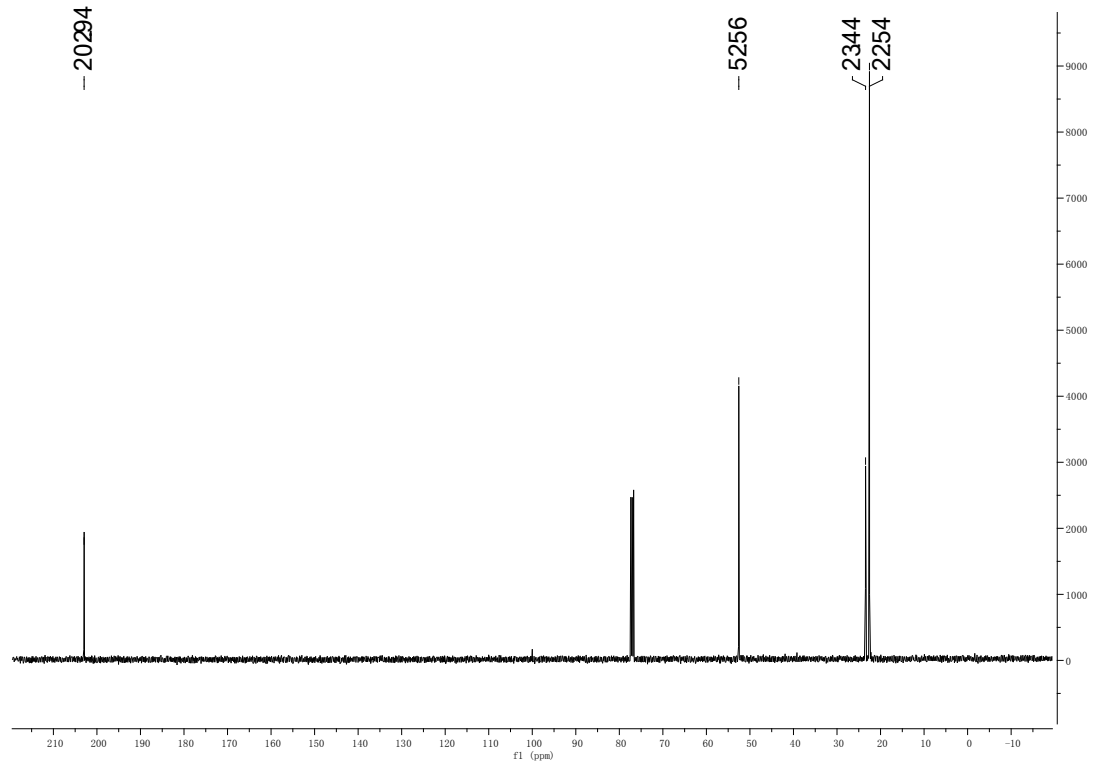
2m ^{13}C NMR



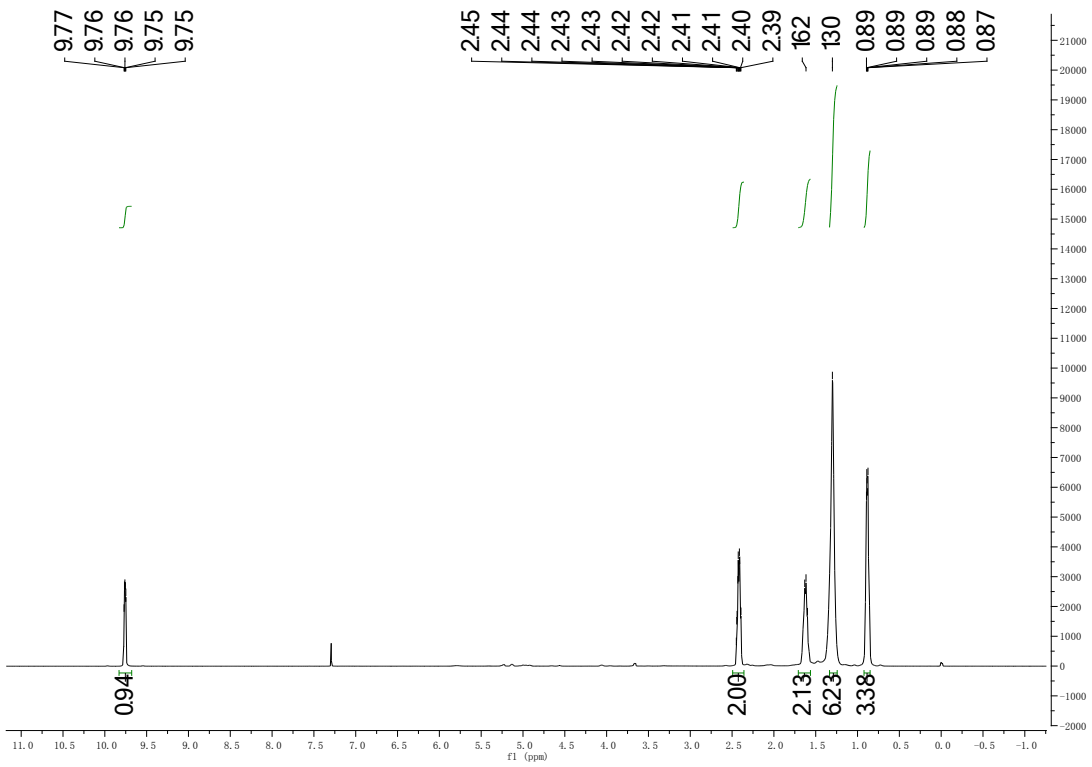
2n ^{1}H NMR



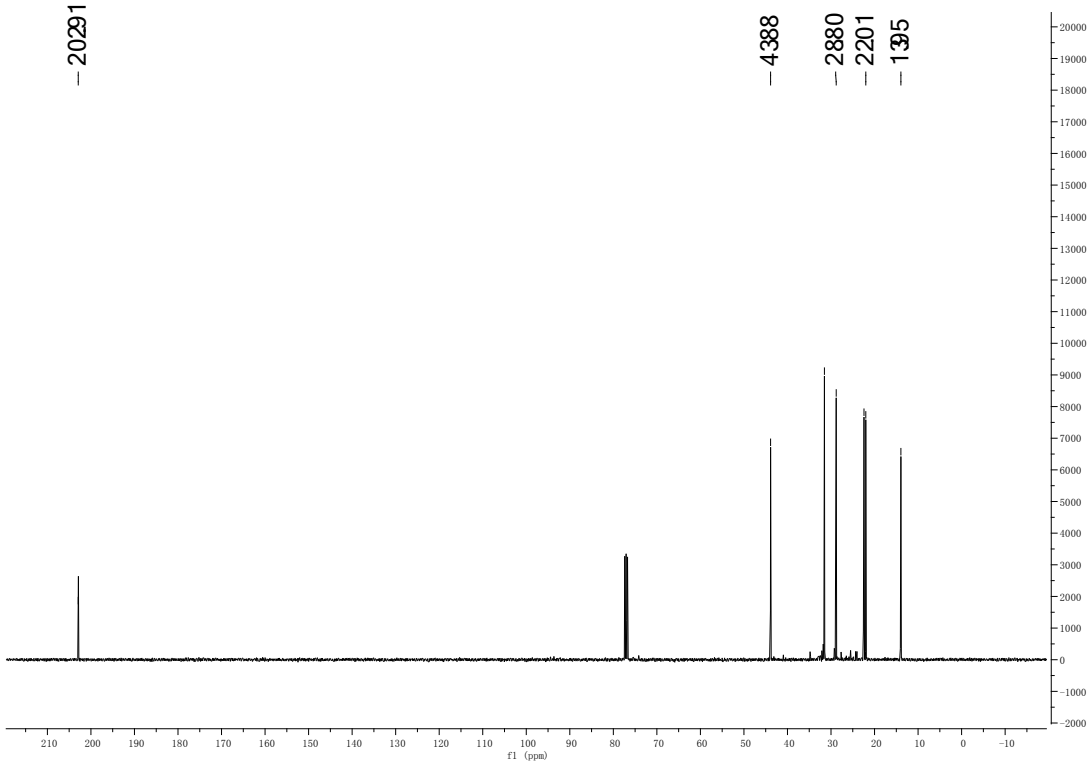
2n ^{13}C NMR



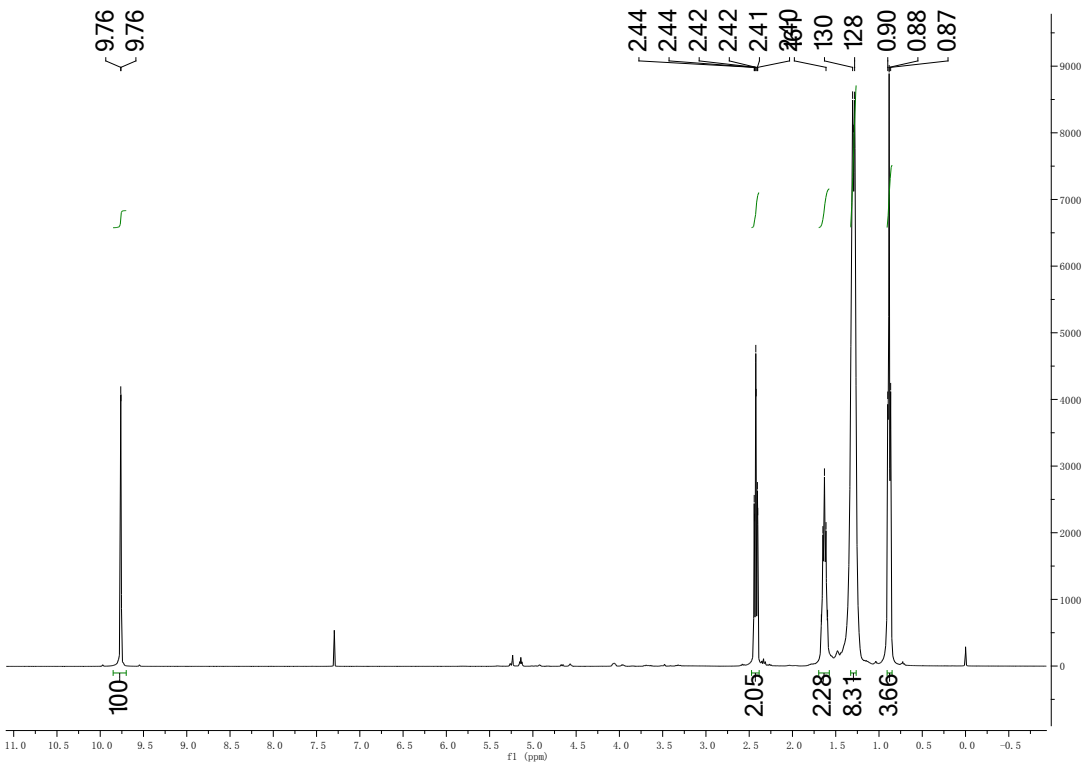
2o ^{1}H NMR



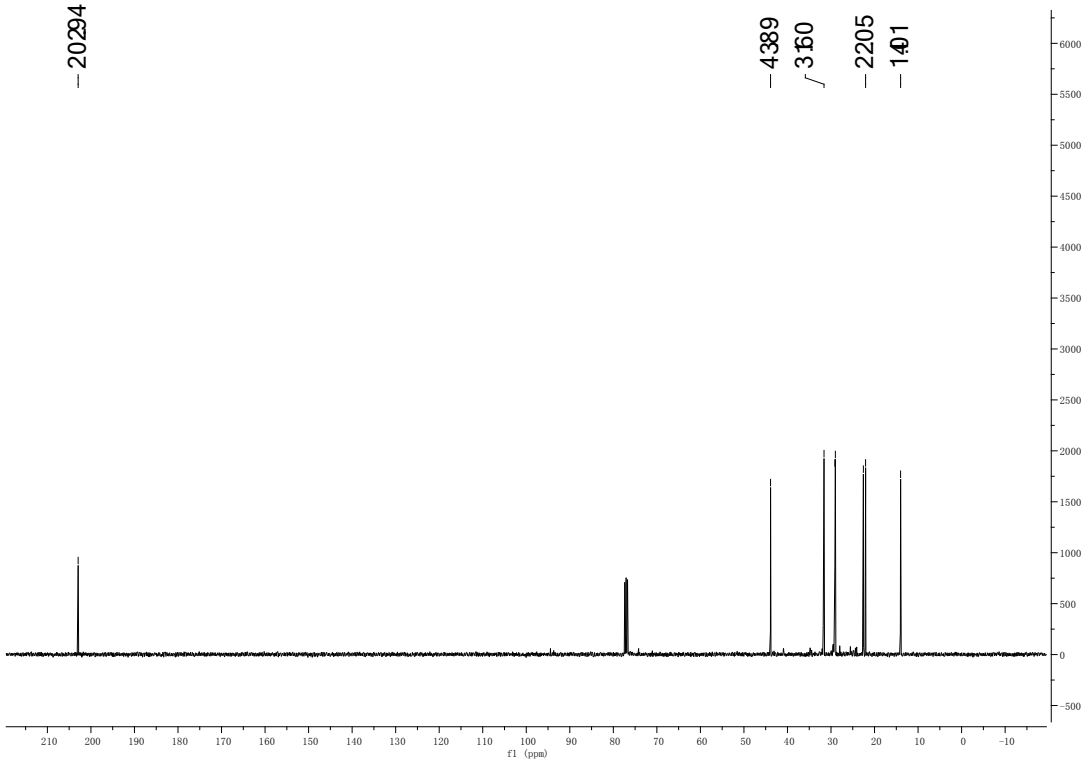
2o ^{13}C NMR



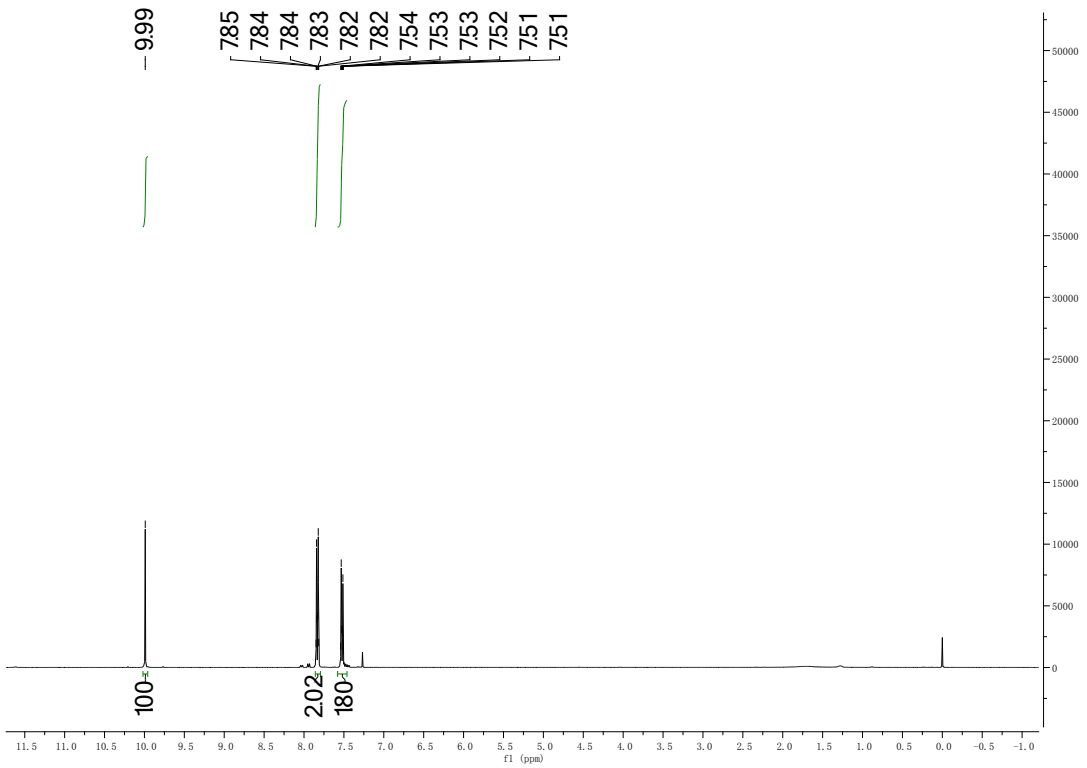
2p ^{1}H NMR



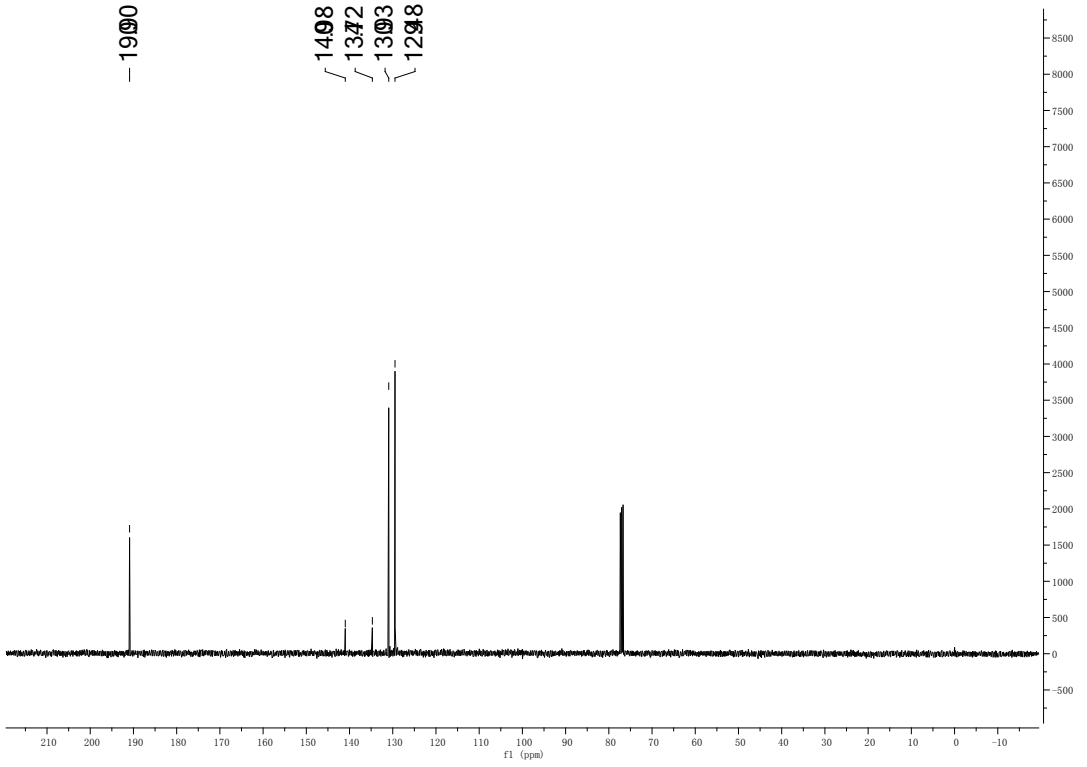
2p ^{13}C NMR



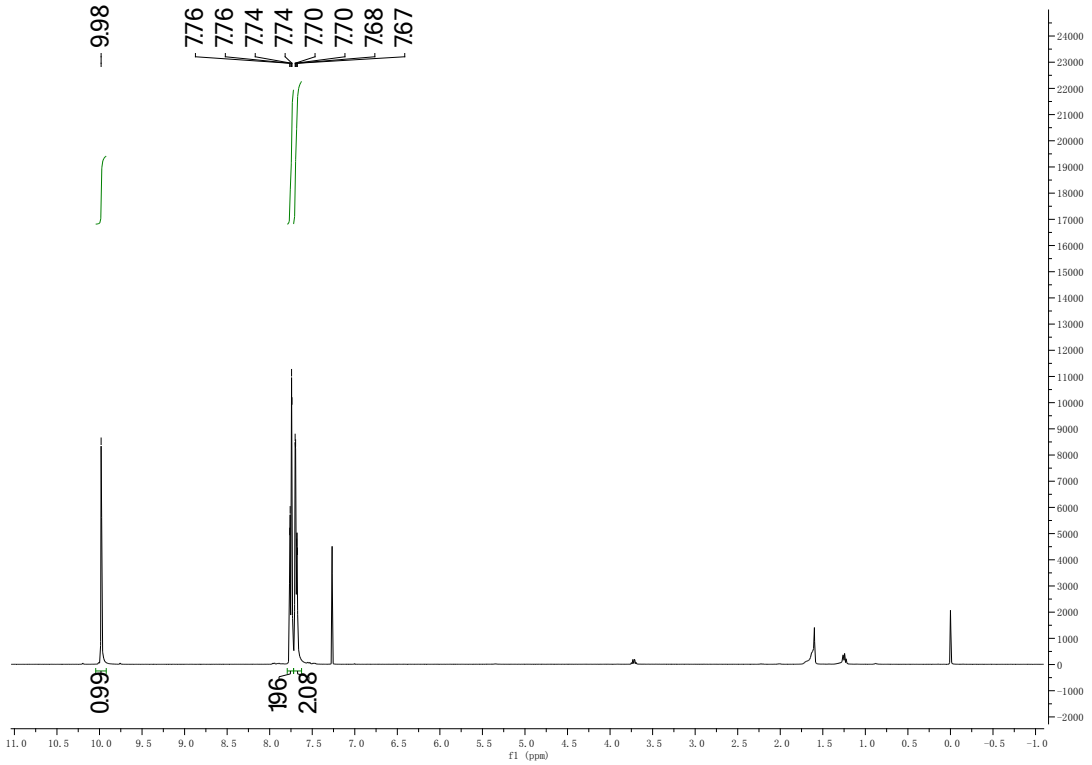
2q ^{1}H NMR



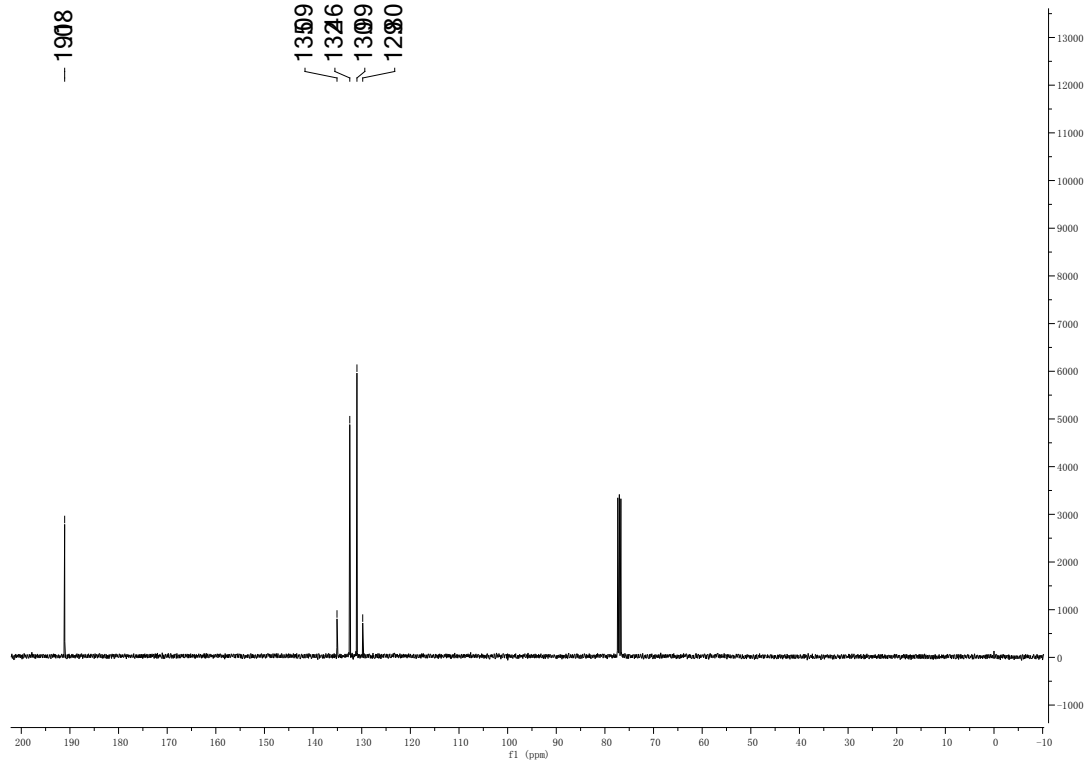
2q ^{13}C NMR



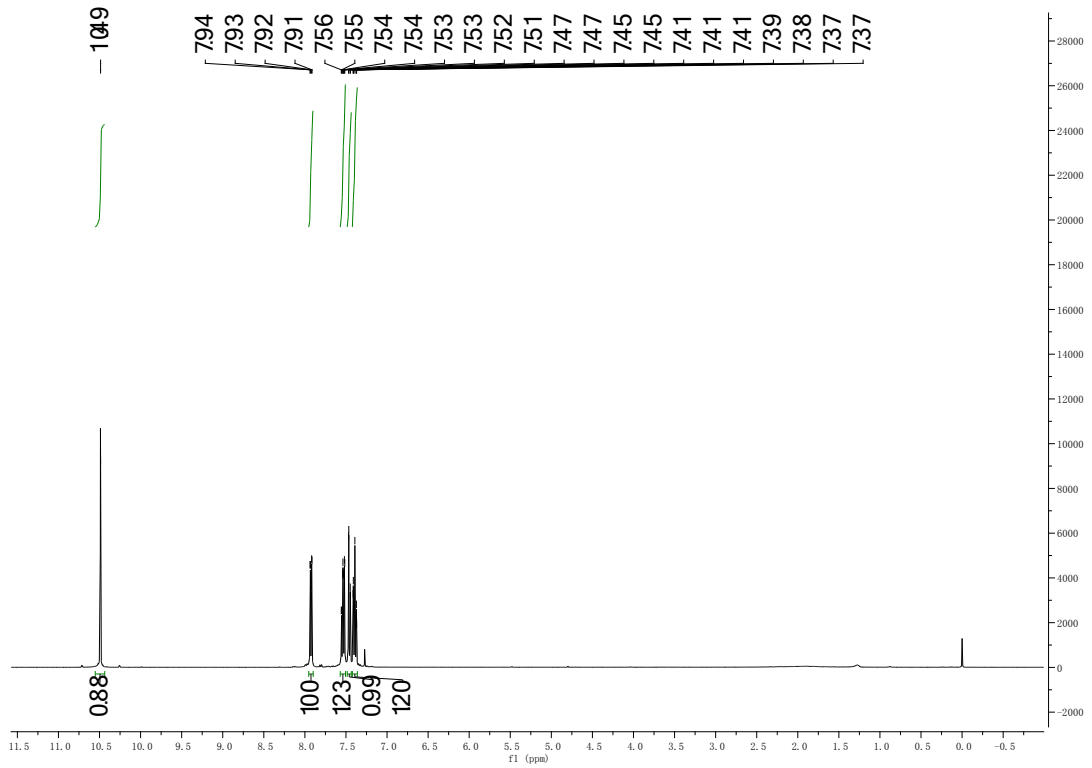
2r ^{1}H NMR



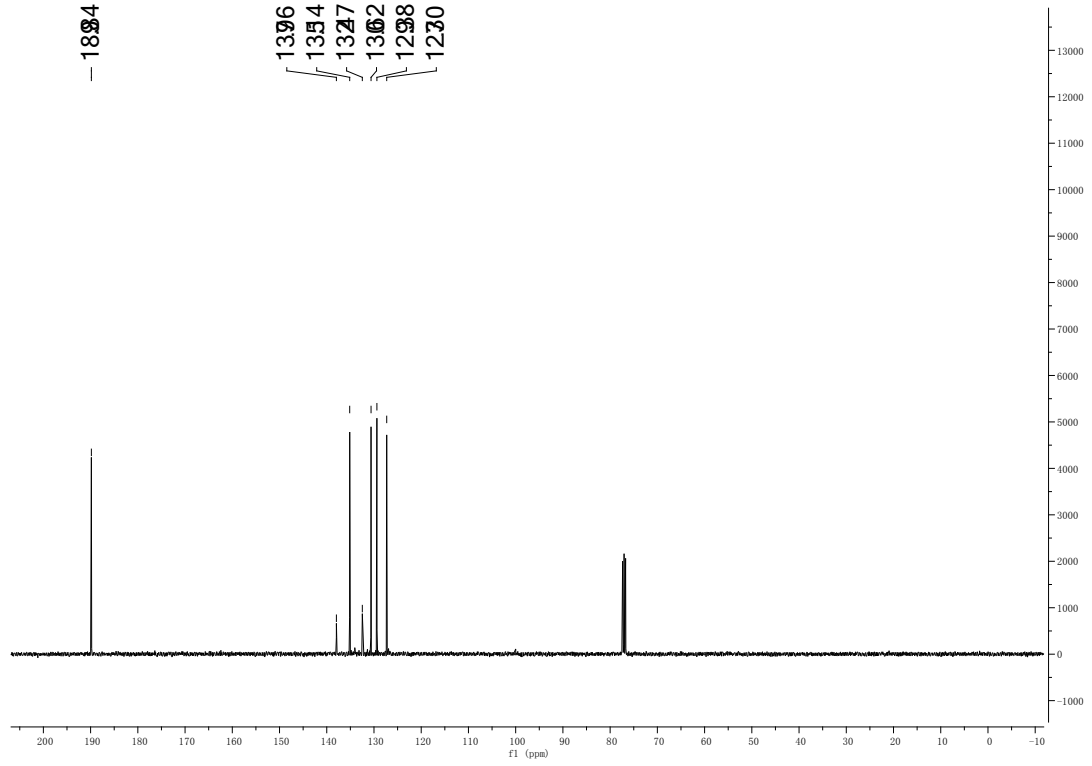
2r ^{13}C NMR



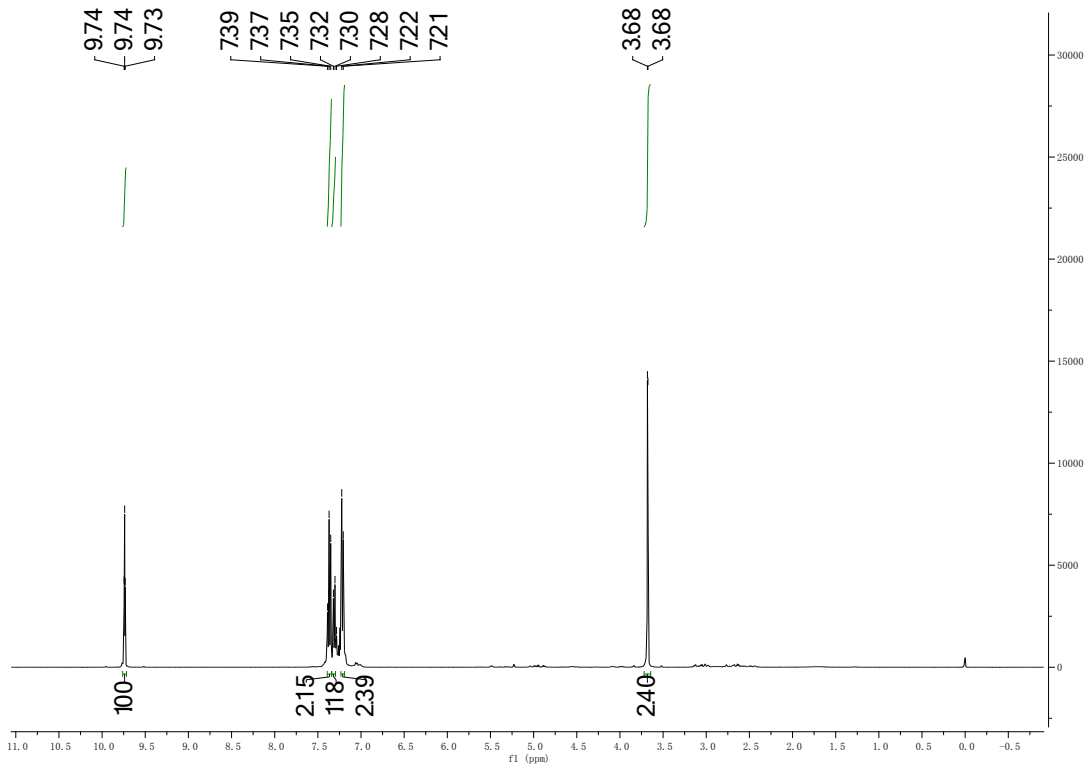
2s ^{1}H NMR



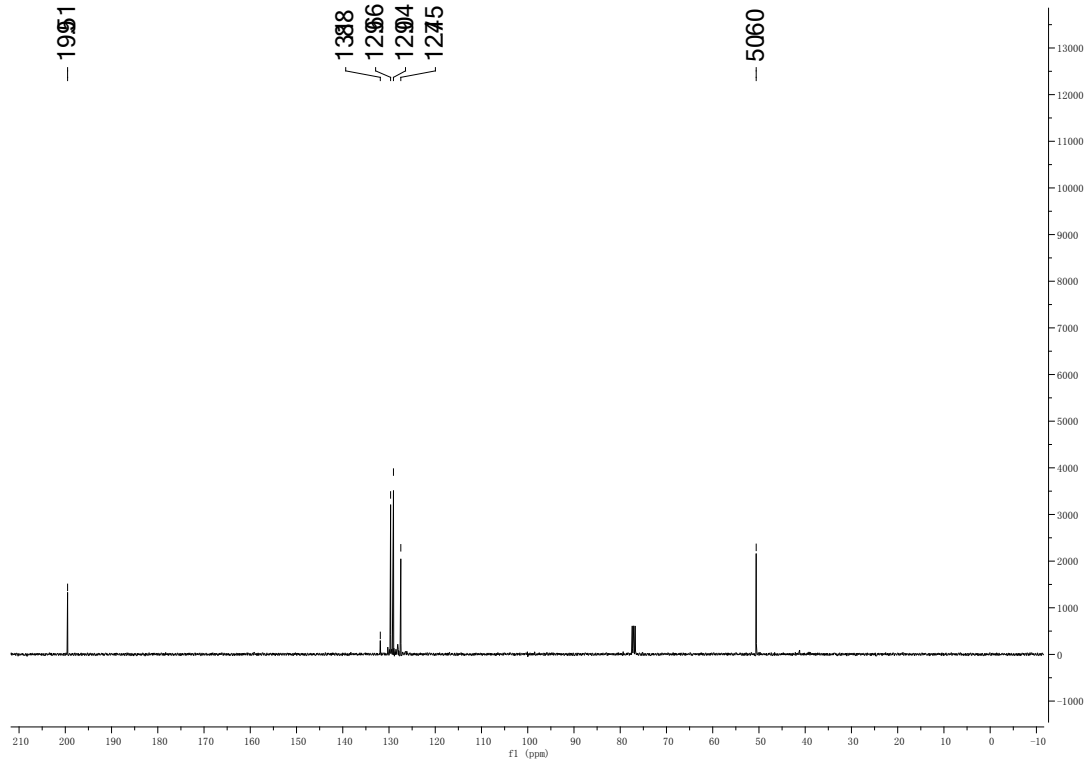
2s ^{13}C NMR



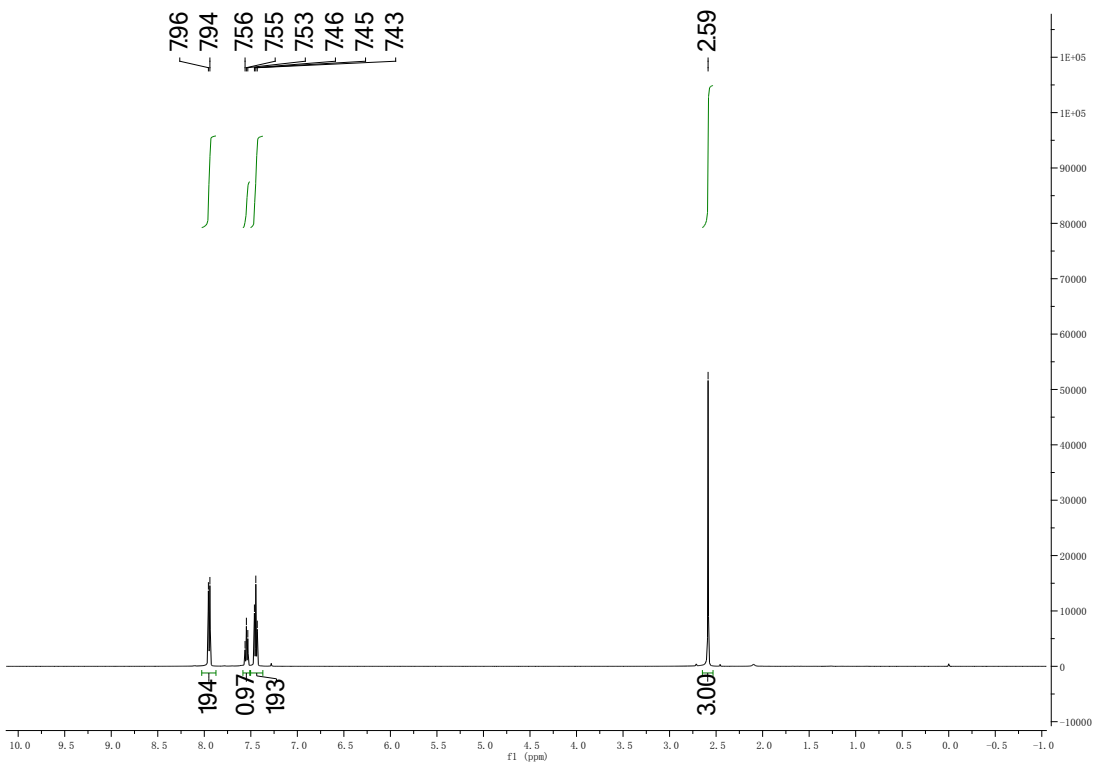
2t ^{1}H NMR



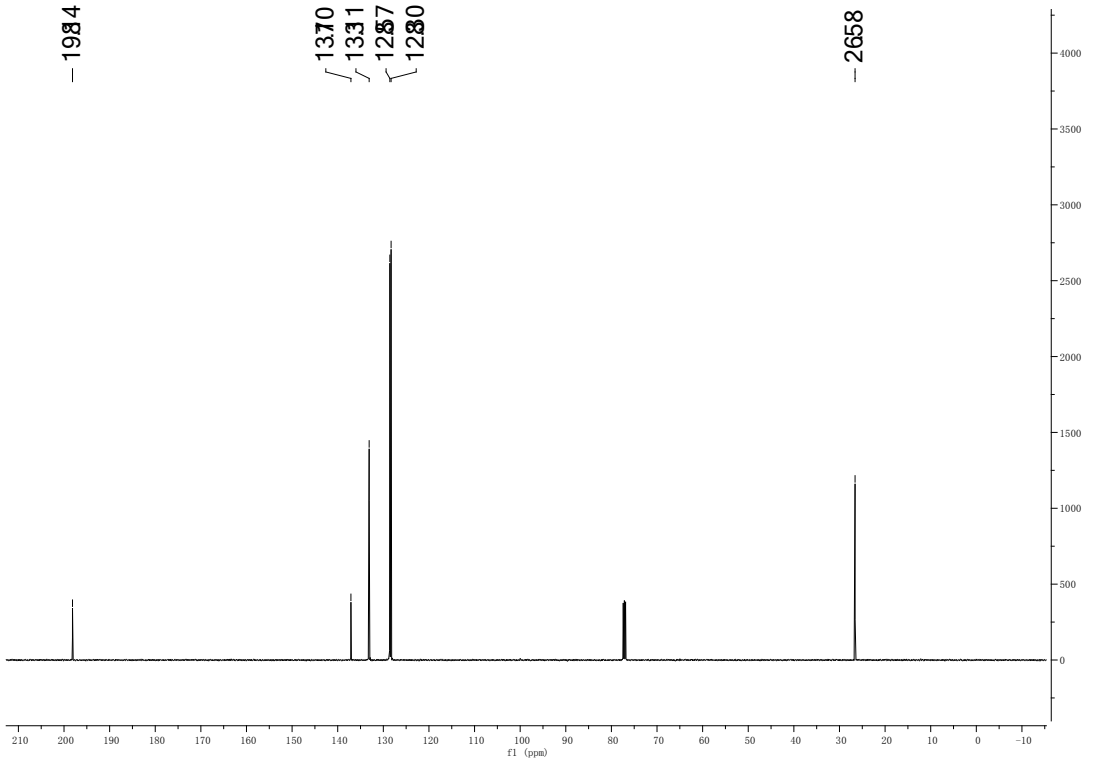
2t ^{13}C NMR



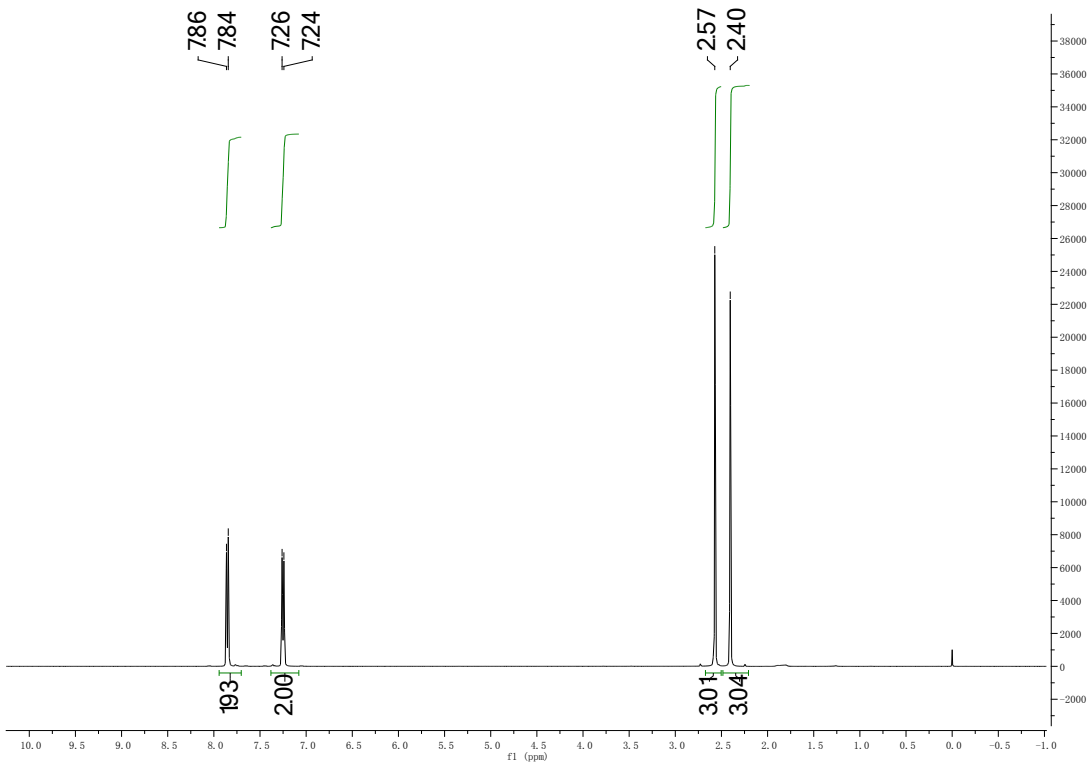
4a ^{1}H NMR



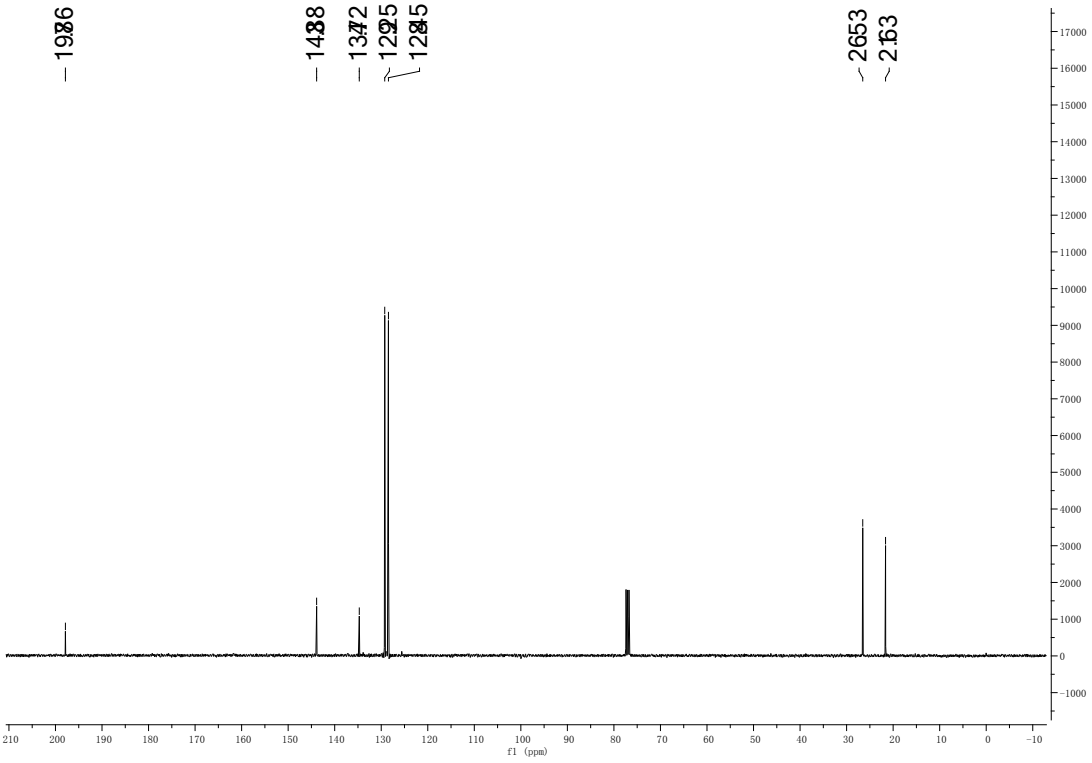
4a ^{13}C NMR



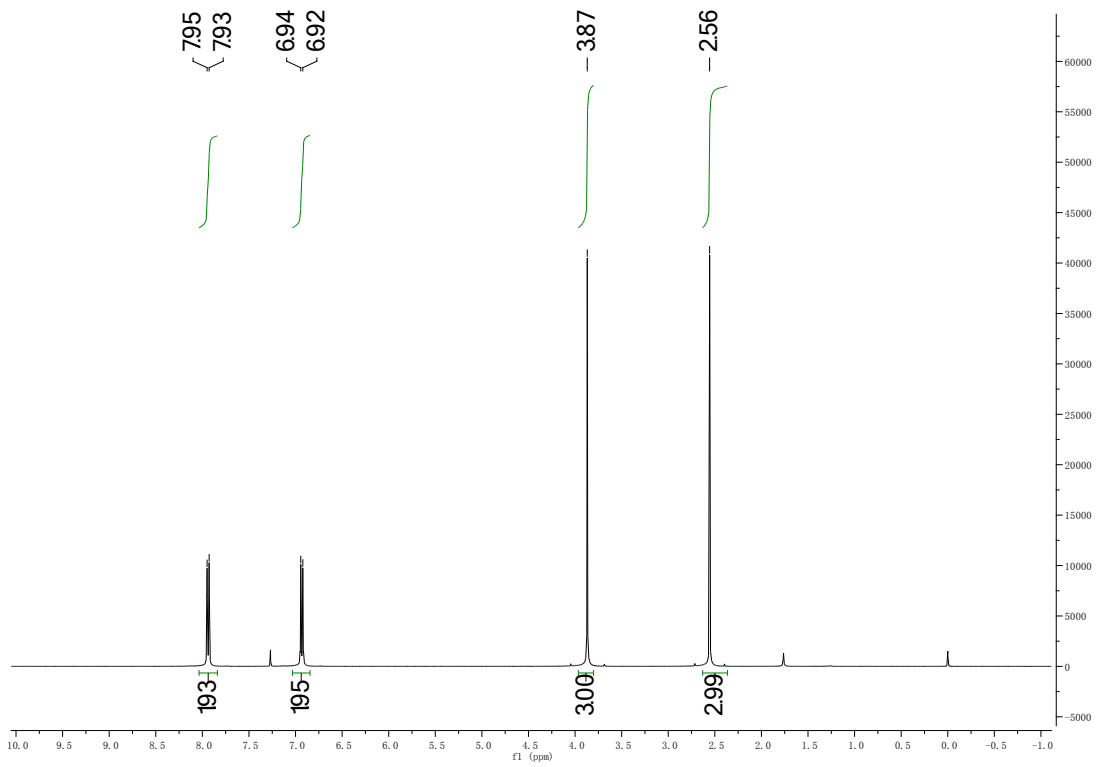
4b ^{1}H NMR



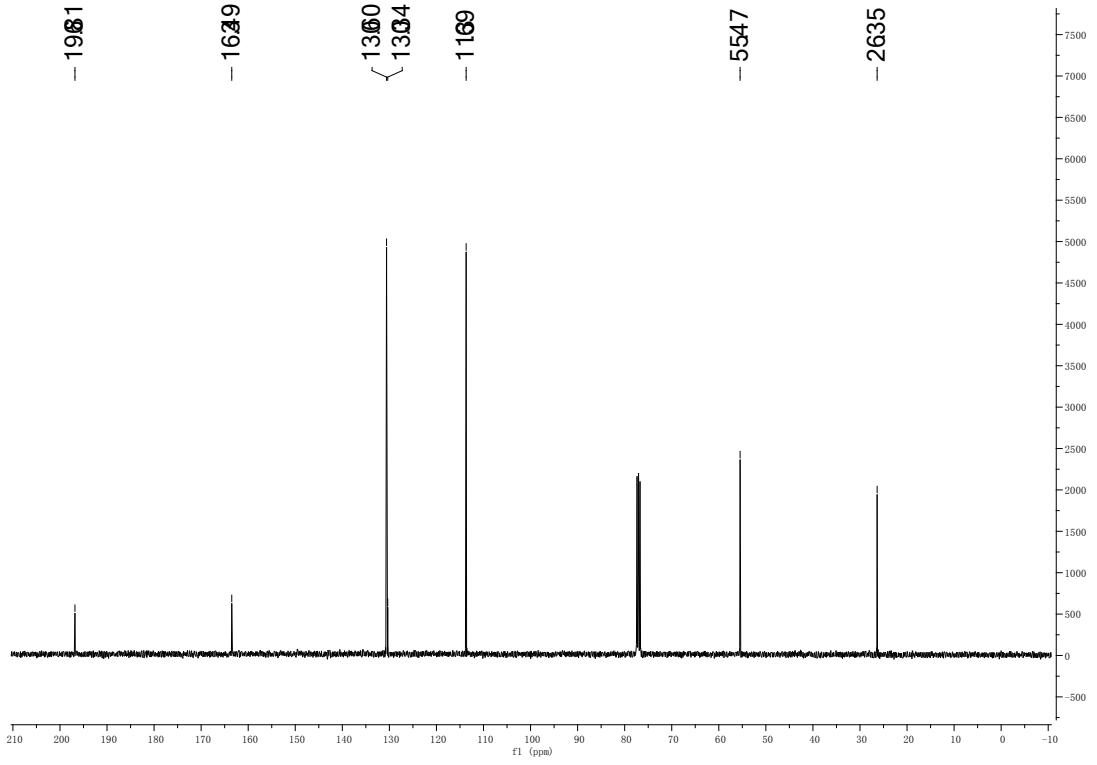
4b ^{13}C NMR



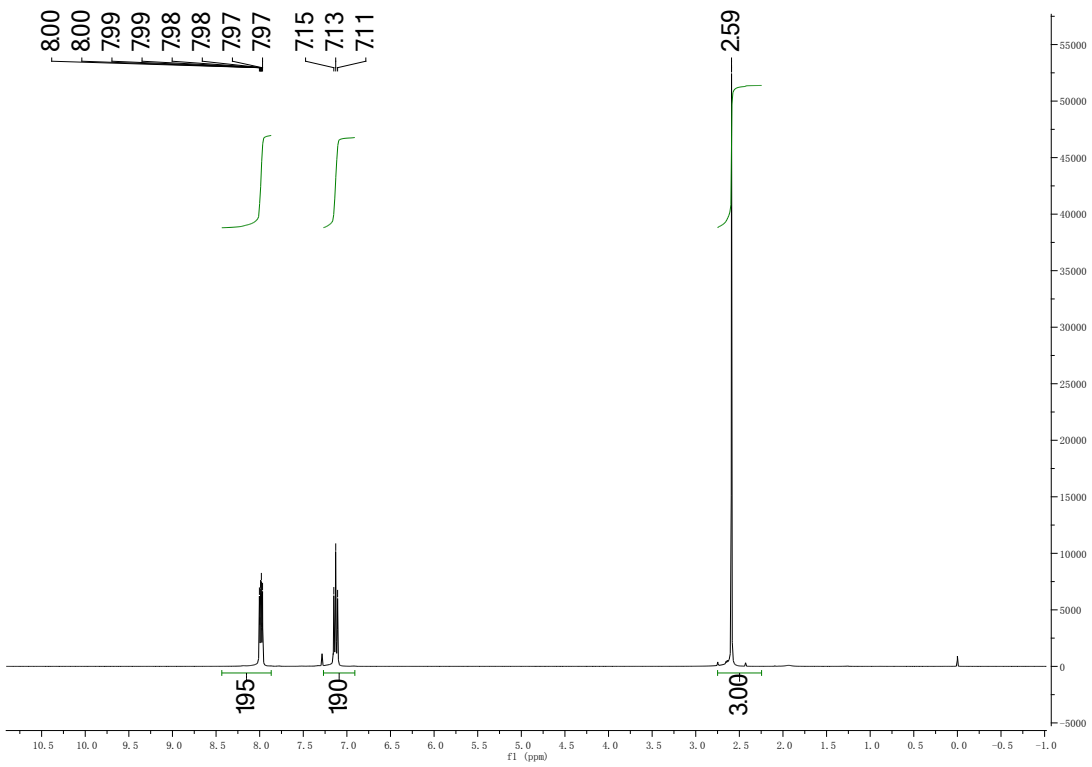
4c ^{1}H NMR



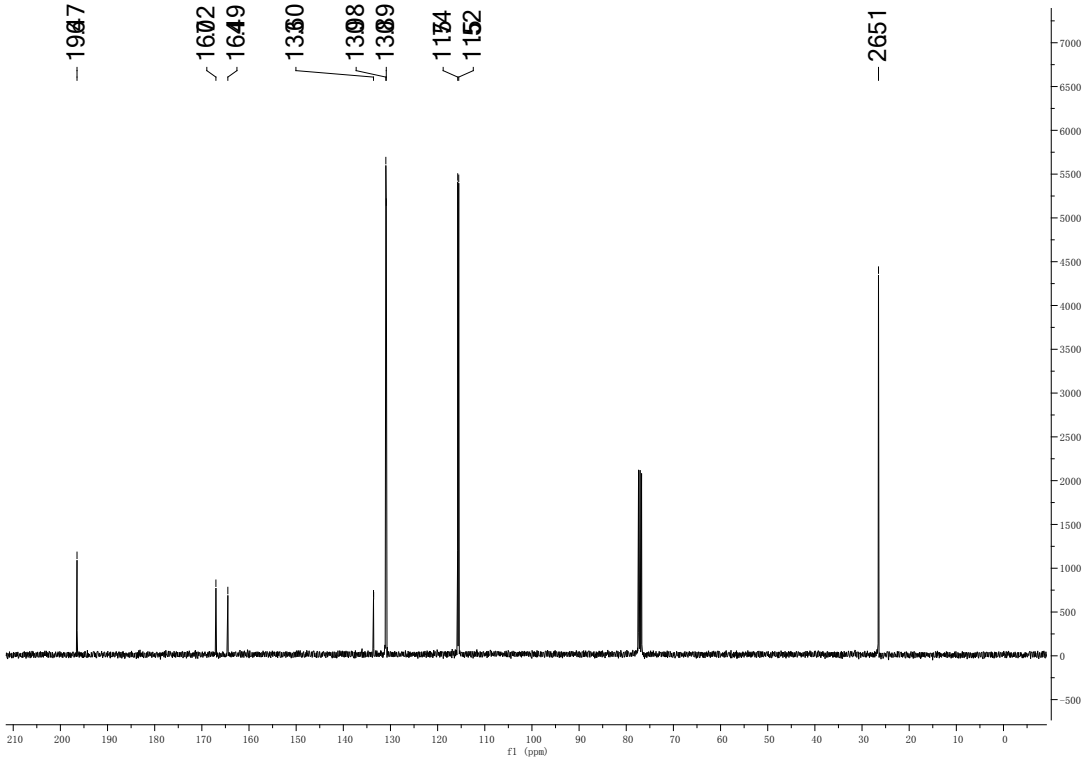
4c ^{13}C NMR



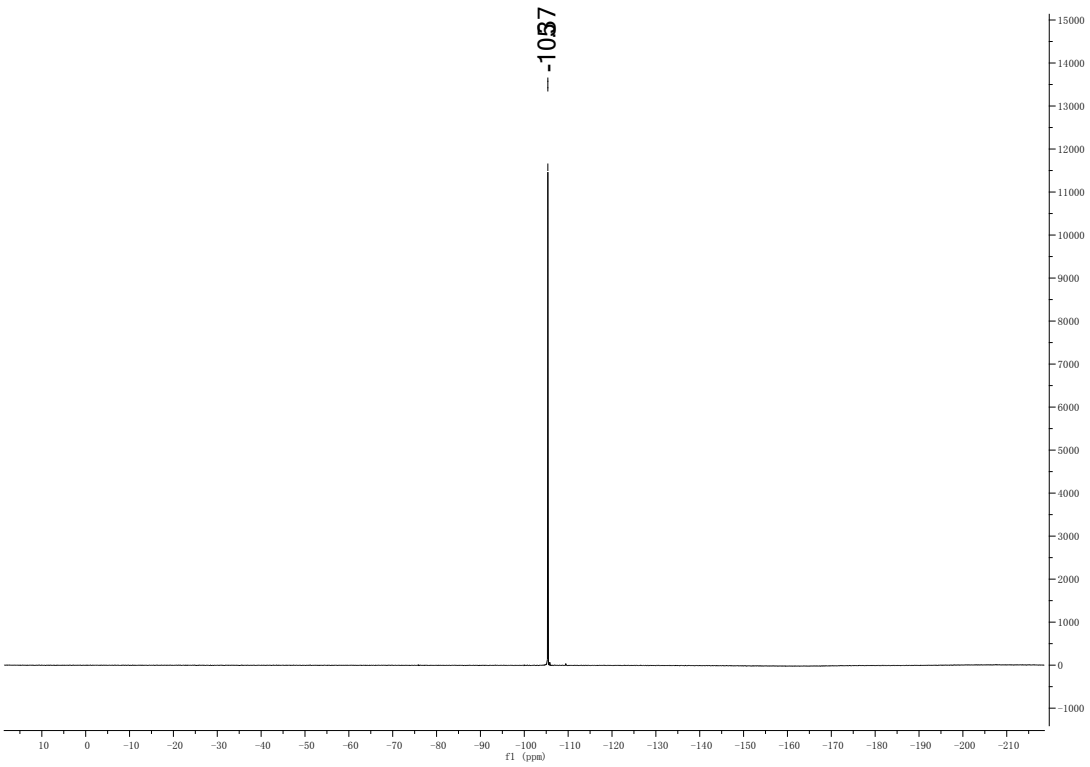
4d ^{1}H NMR



4d ^{13}C NMR



4d ^{19}F NMR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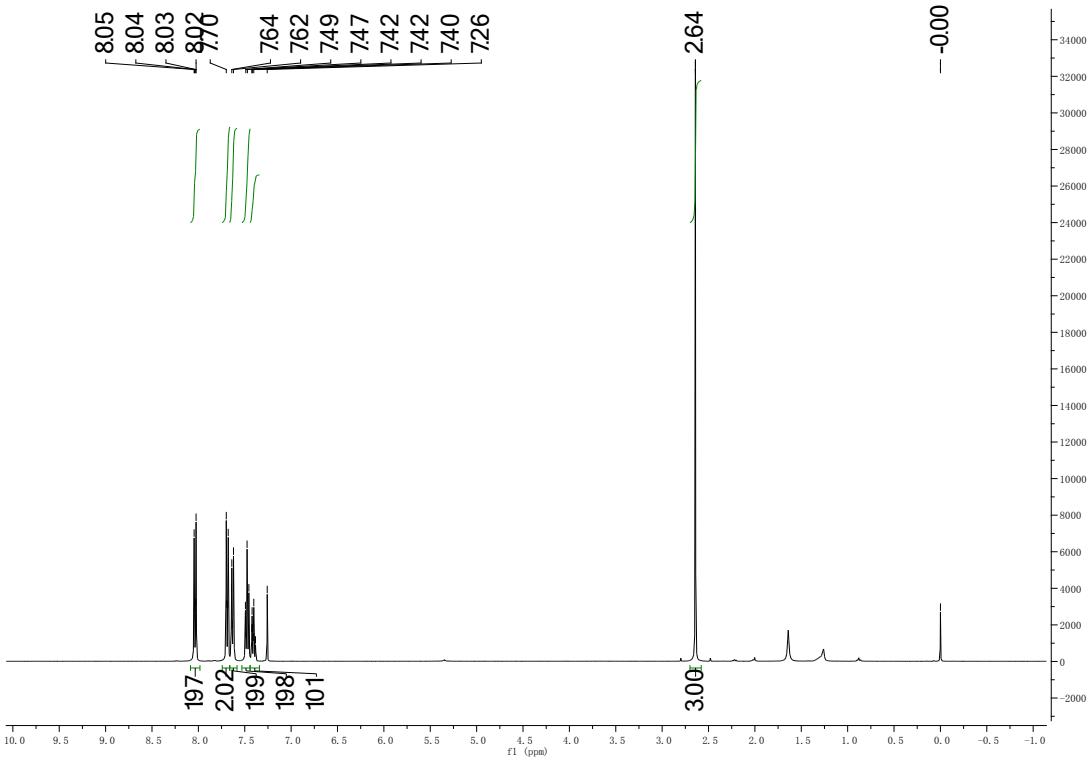
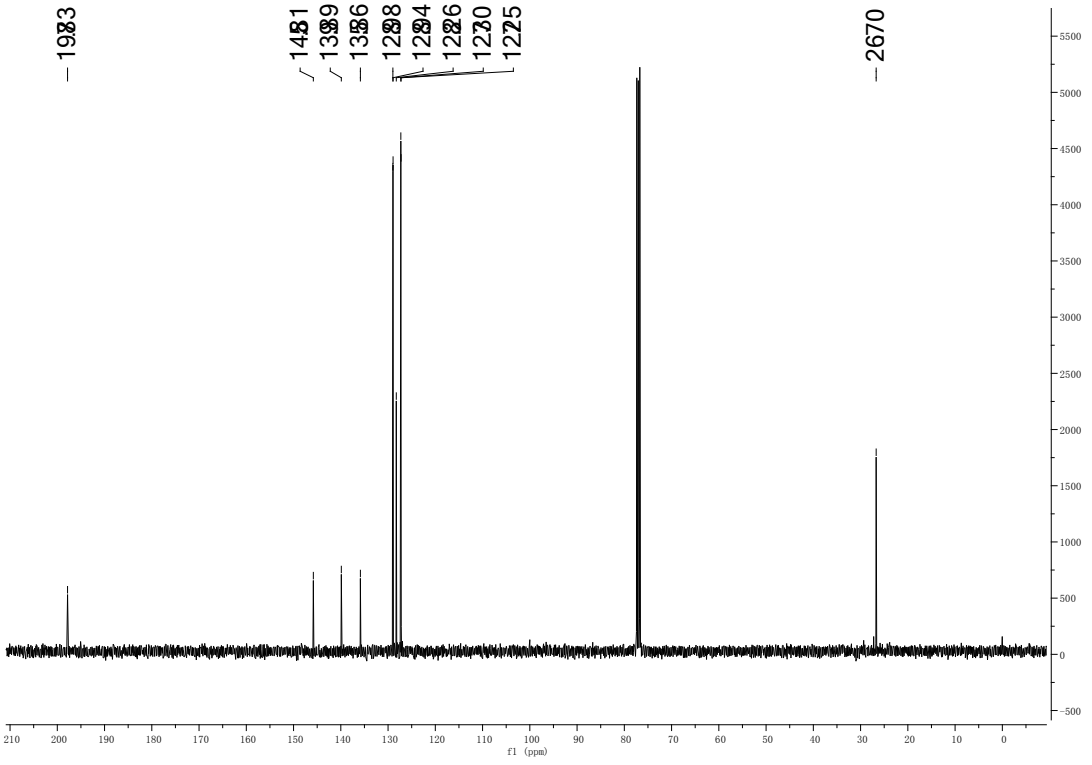
f1 (ppm)

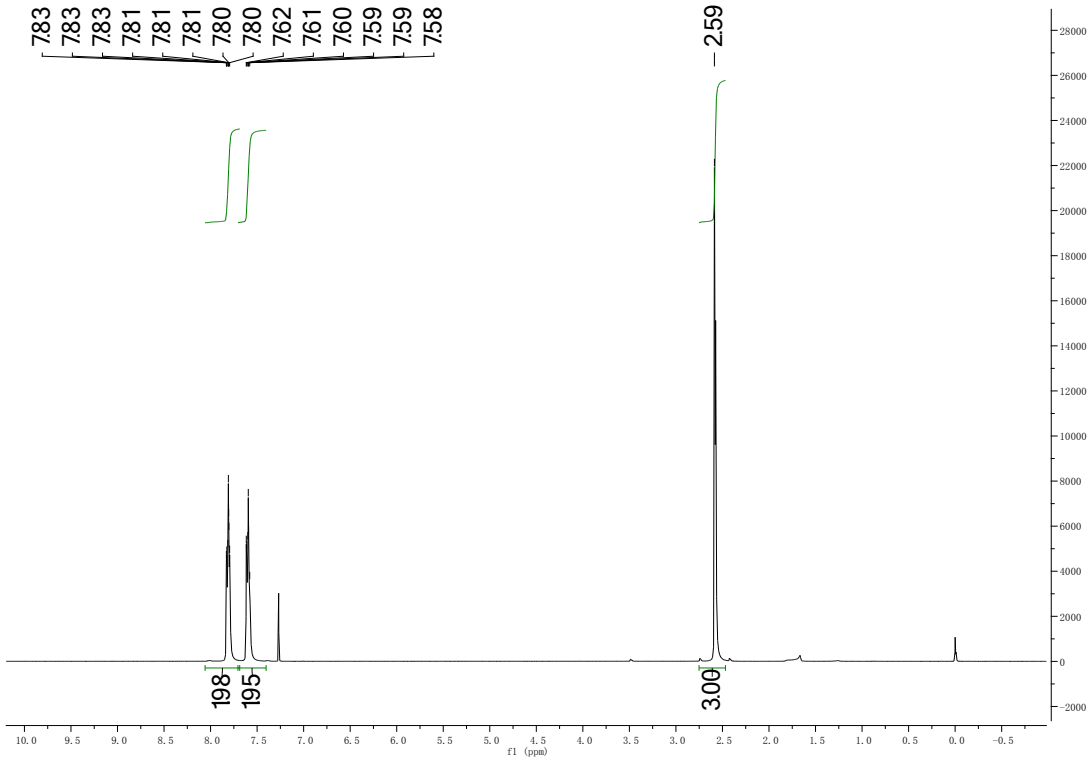
4e ^{1}H NMR



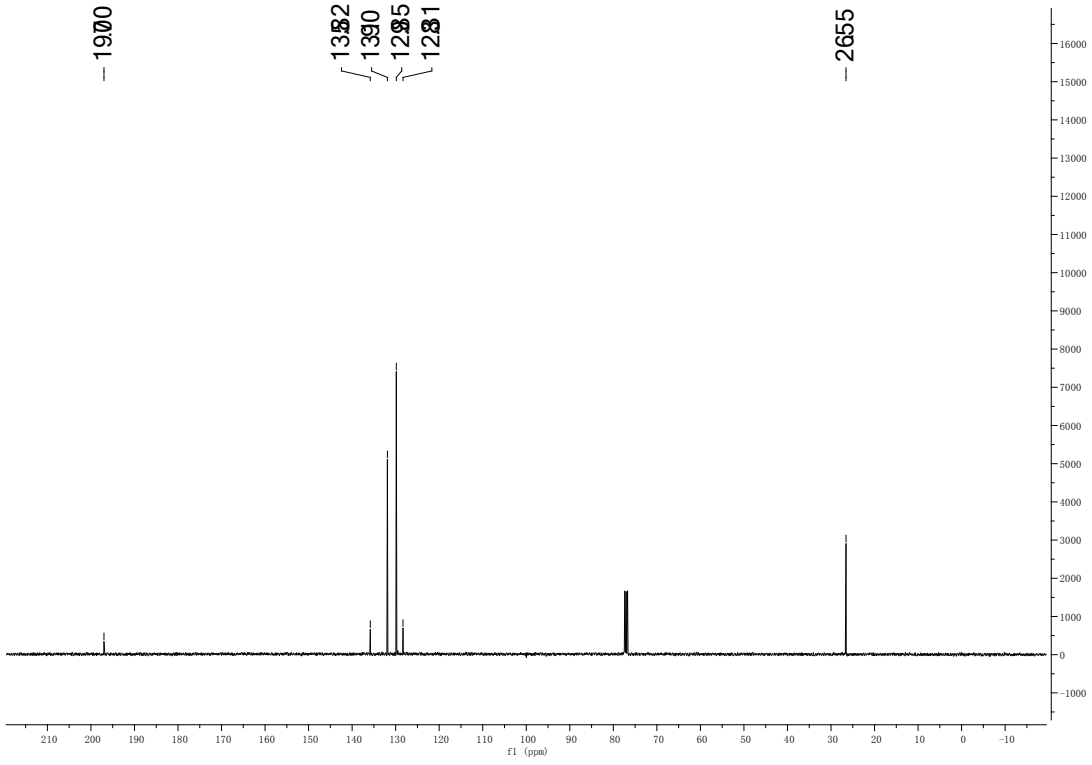
4e ^{13}C NMR



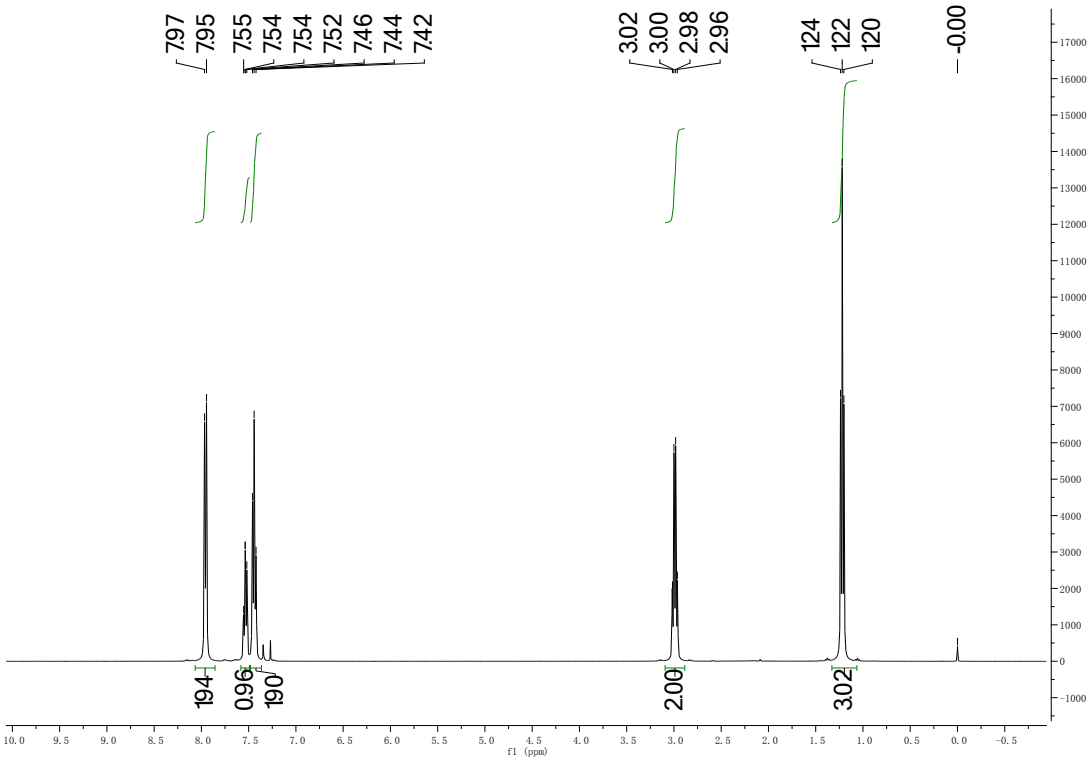
4f ^{1}H NMR



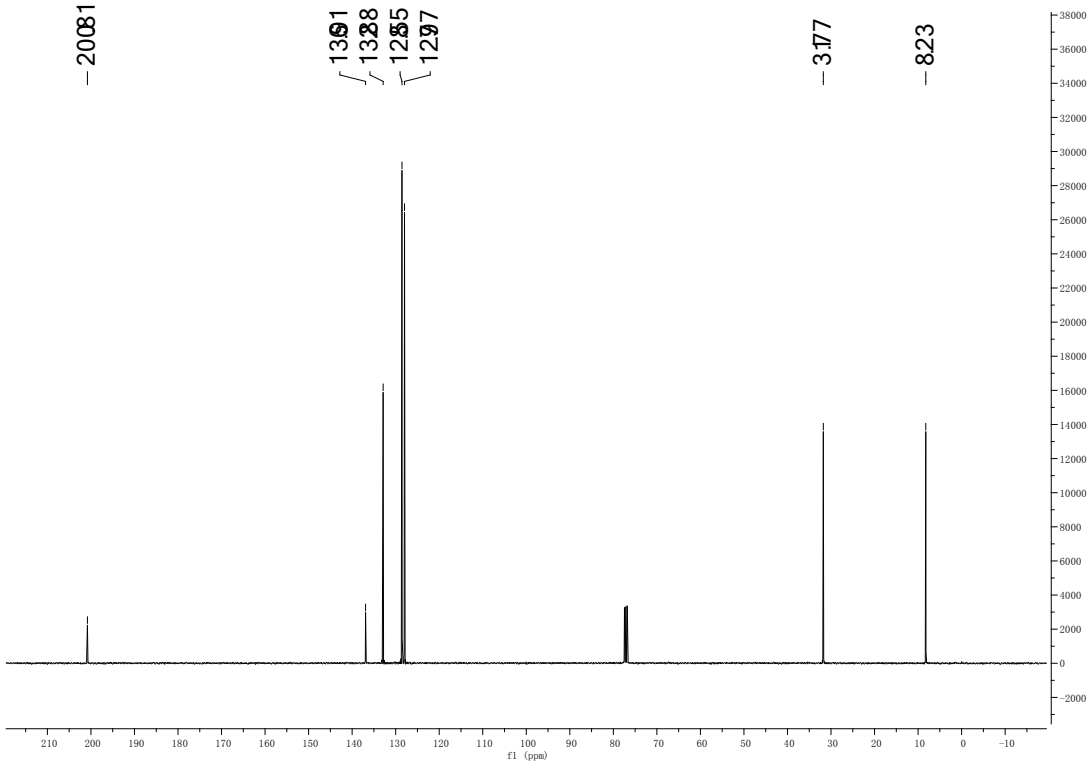
4f ^{13}C NMR



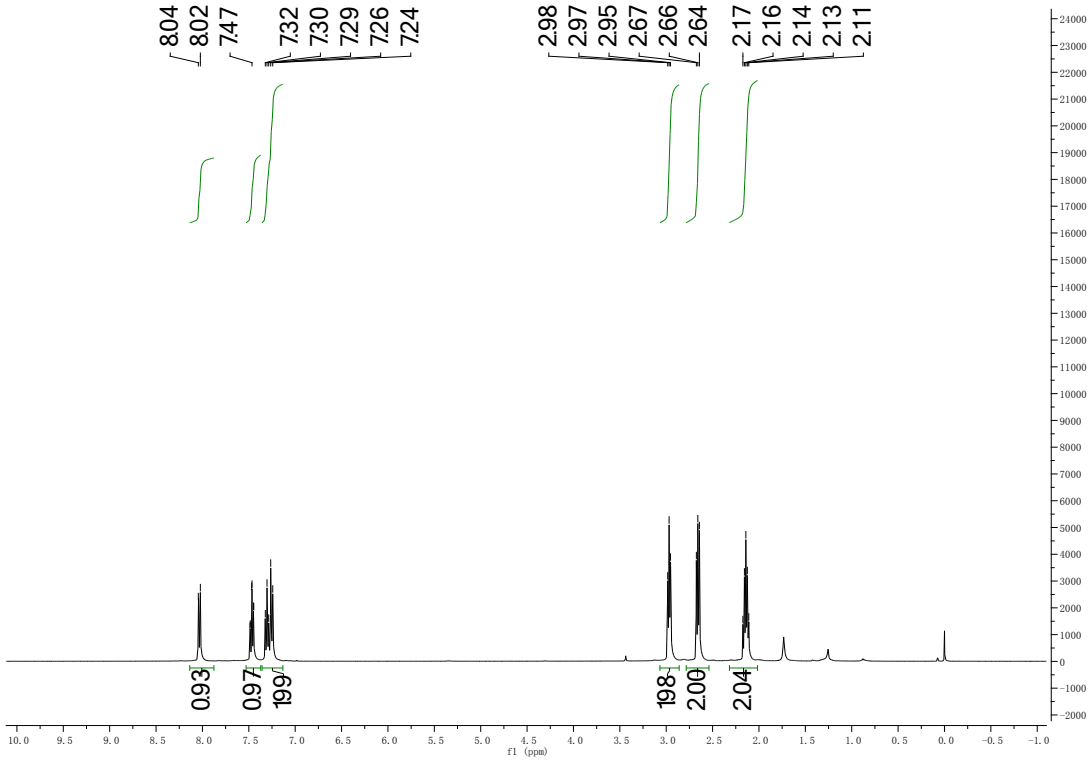
4g ^{1}H NMR



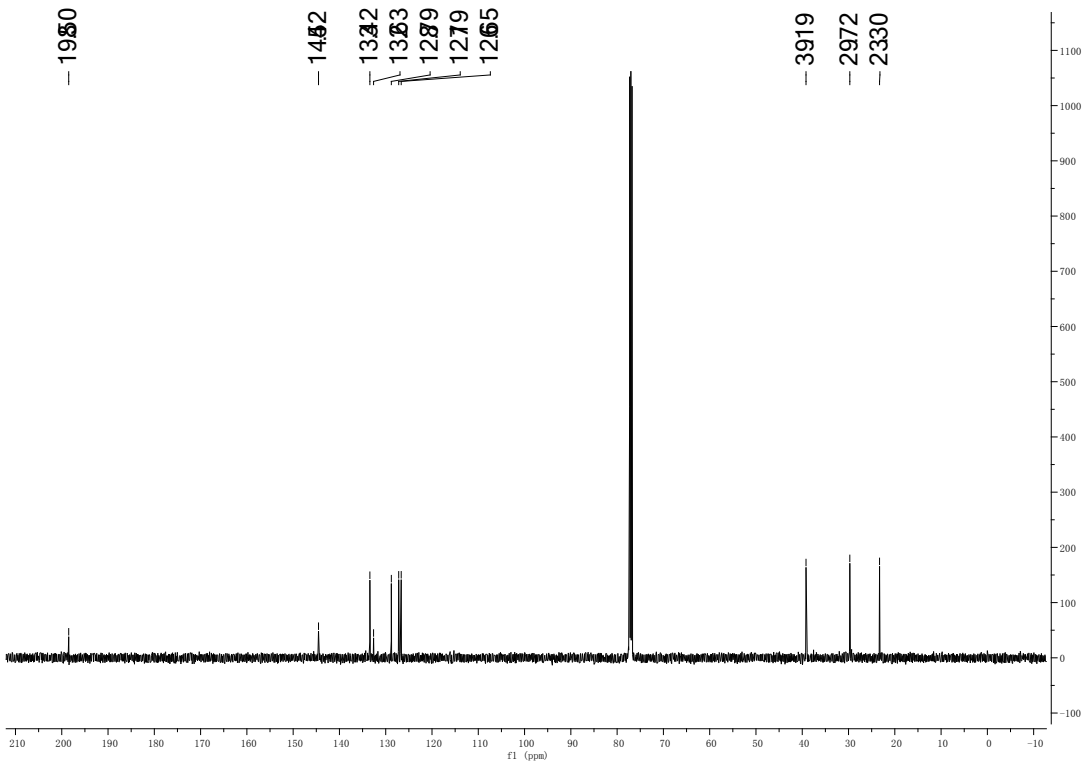
4g ^{13}C NMR



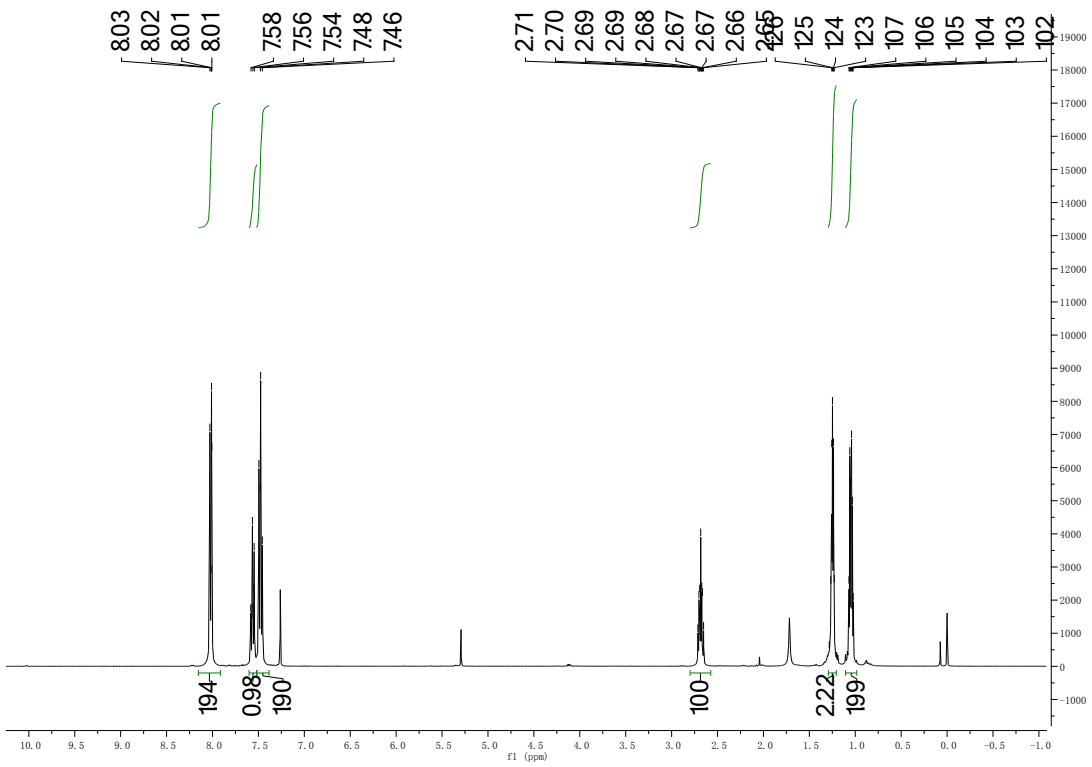
4h ^{1}H NMR



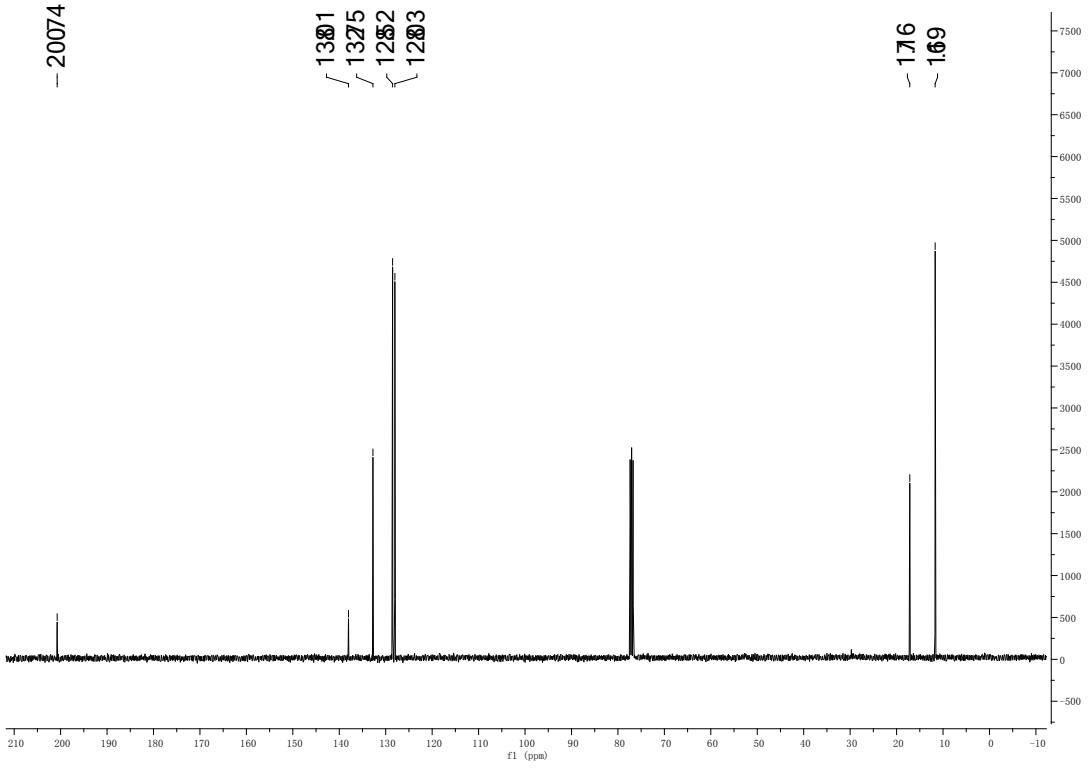
4h ^{13}C NMR



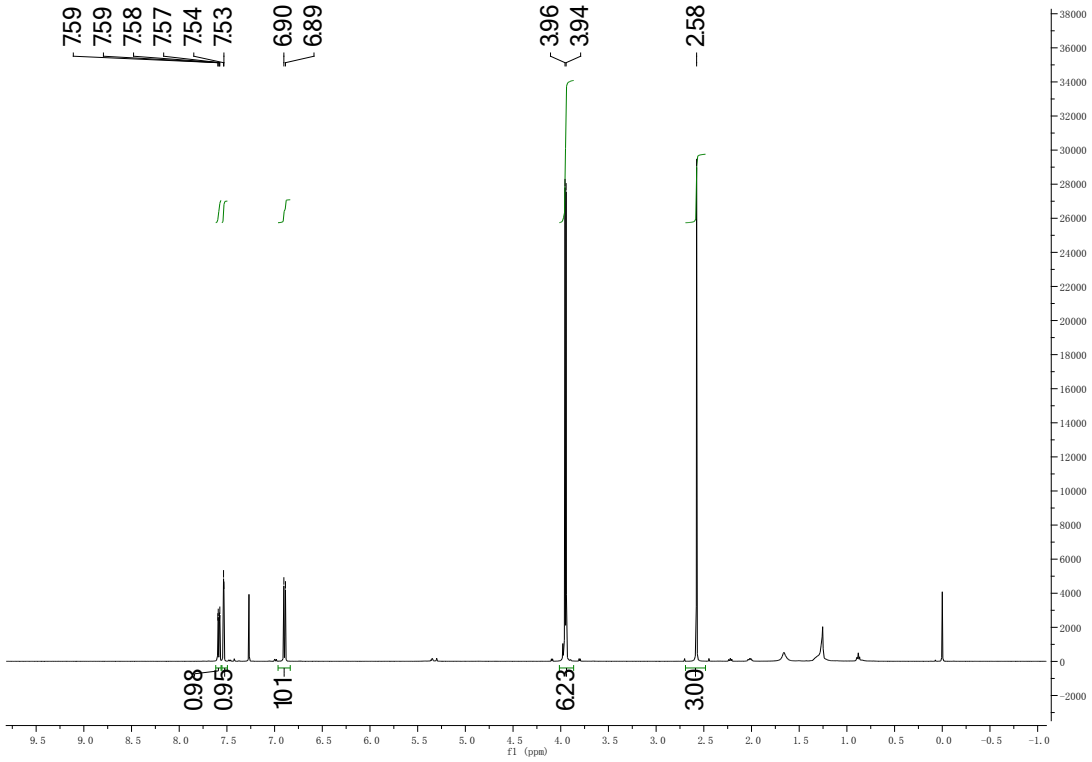
4i ^{1}H NMR



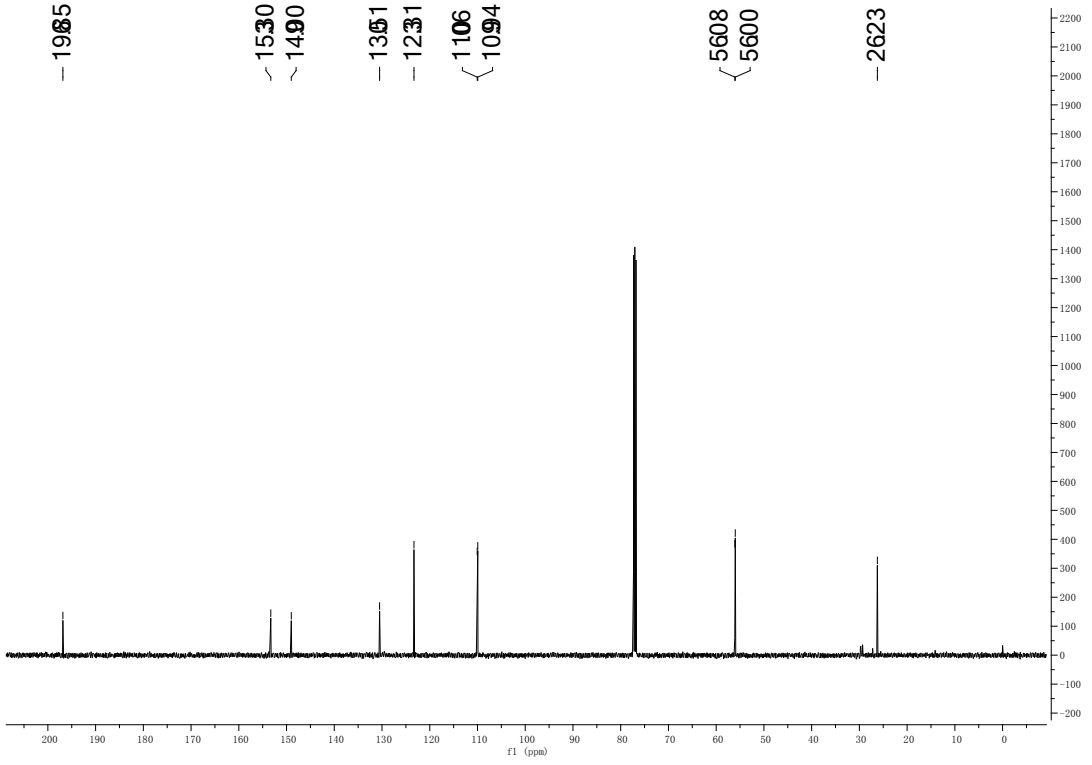
4i ^{13}C NMR



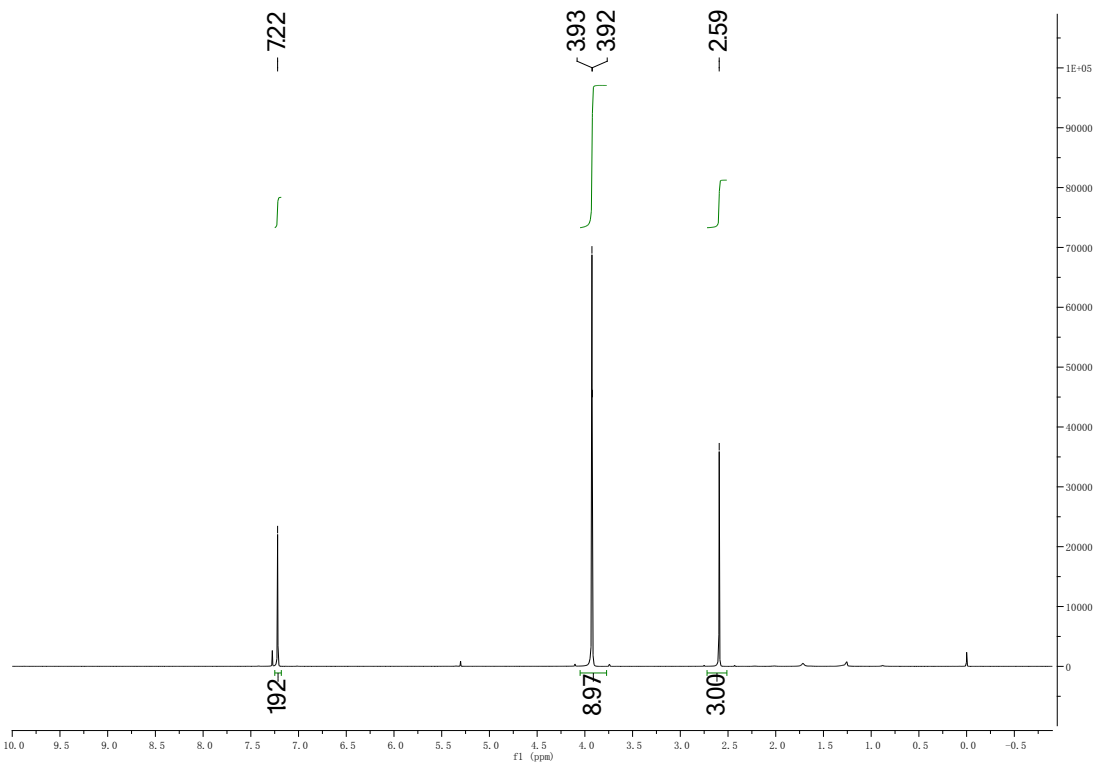
4j ^{1}H NMR



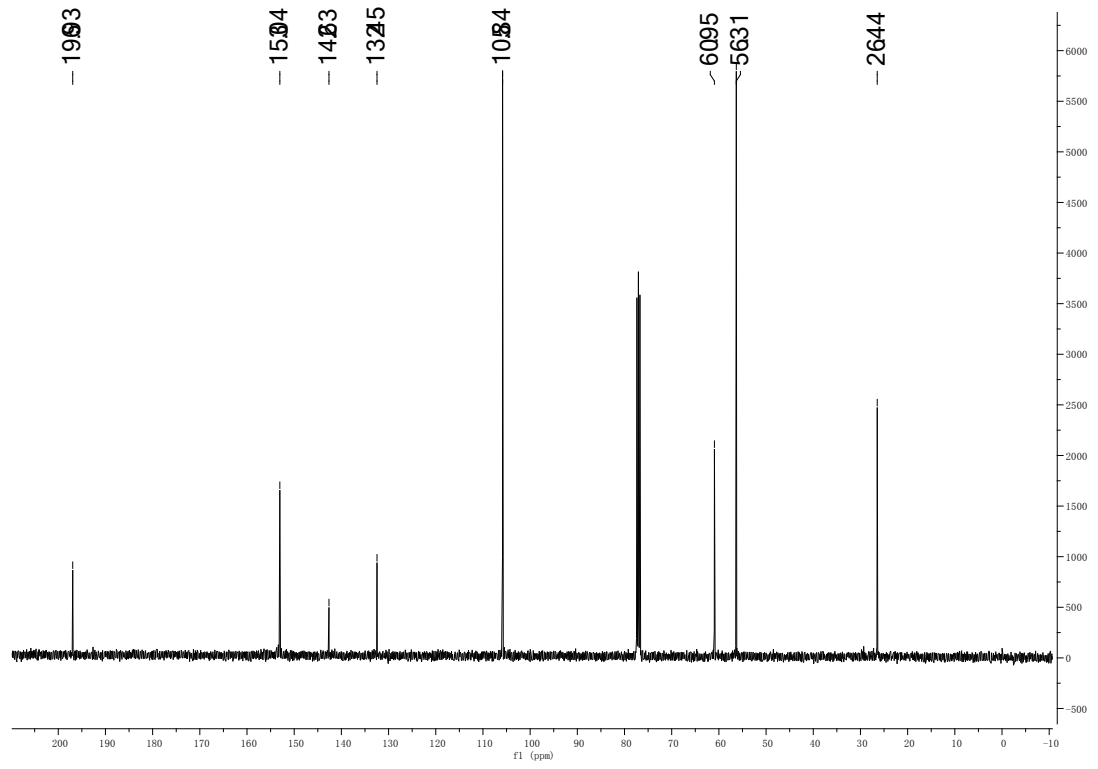
4j ^{13}C NMR



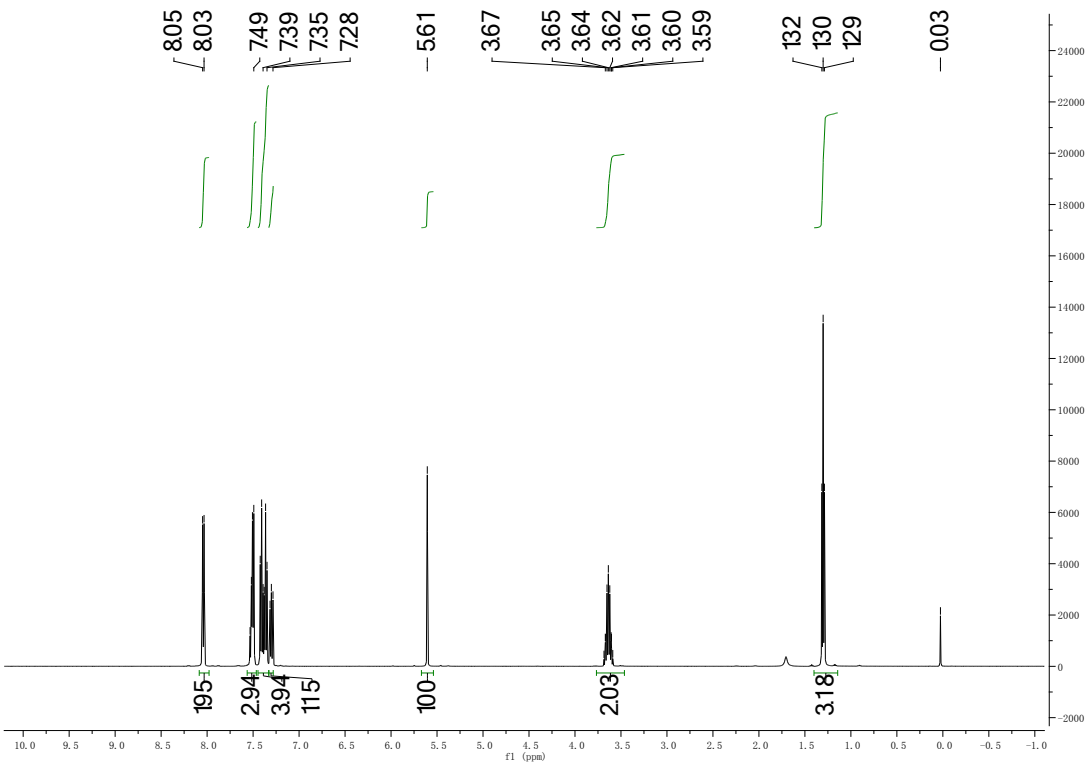
4k ^{1}H NMR



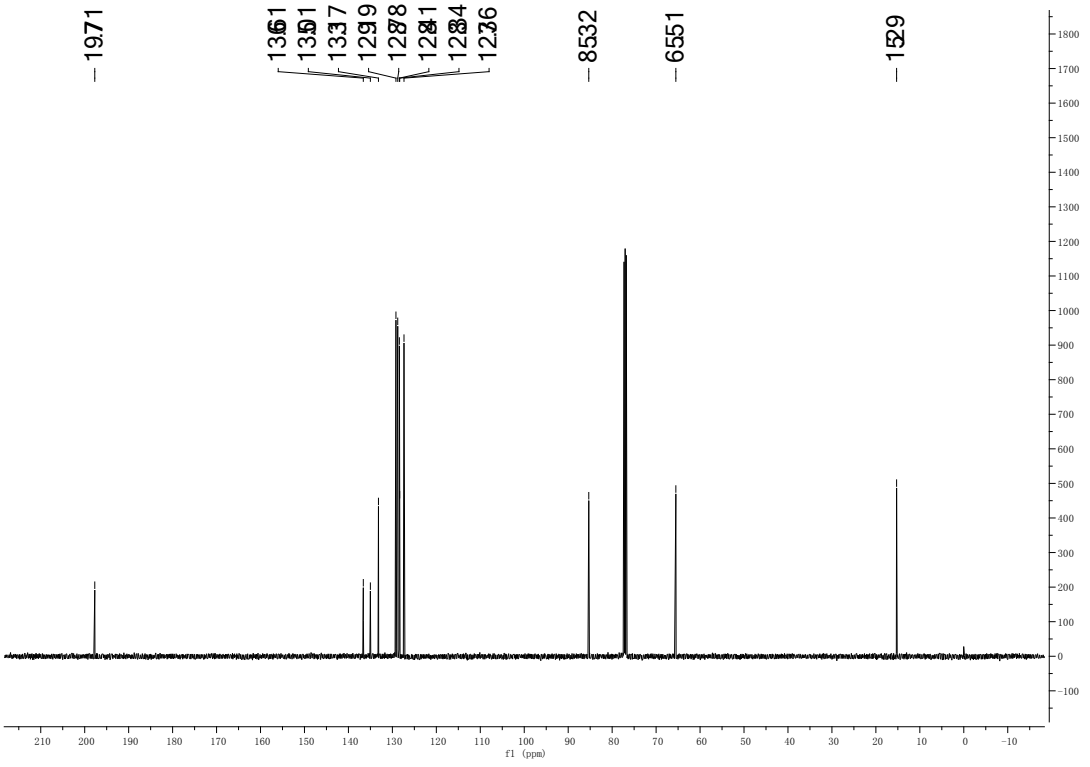
4k ^{13}C NMR



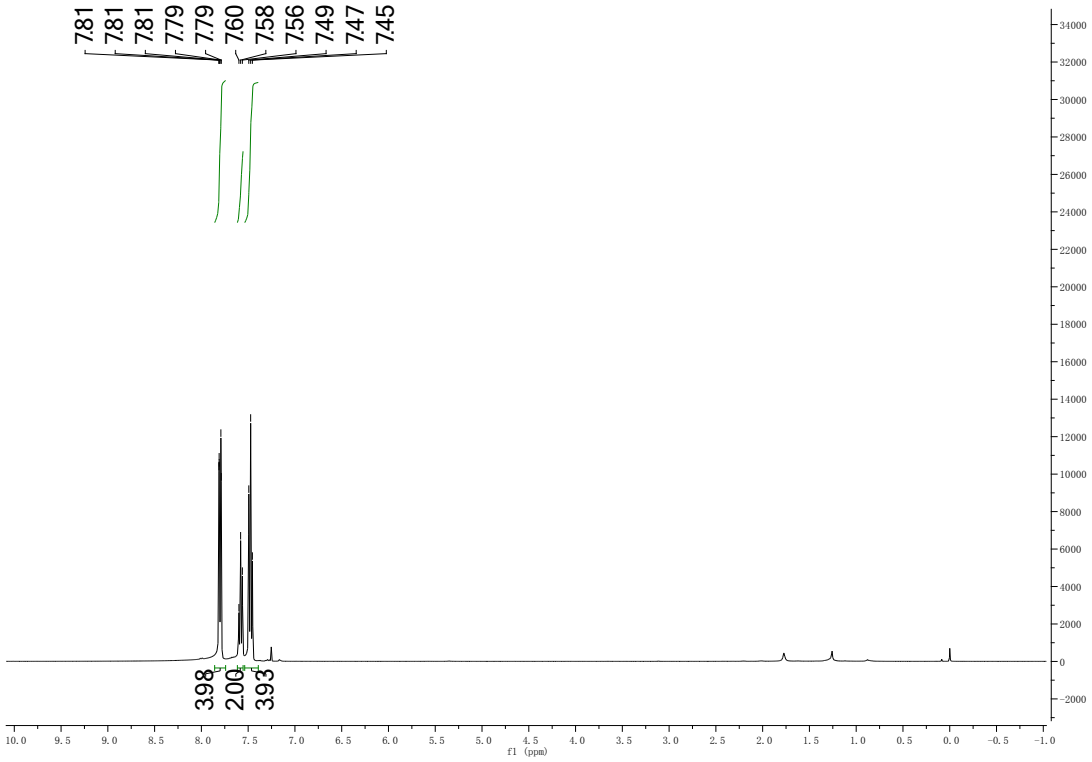
4l ^{1}H NMR



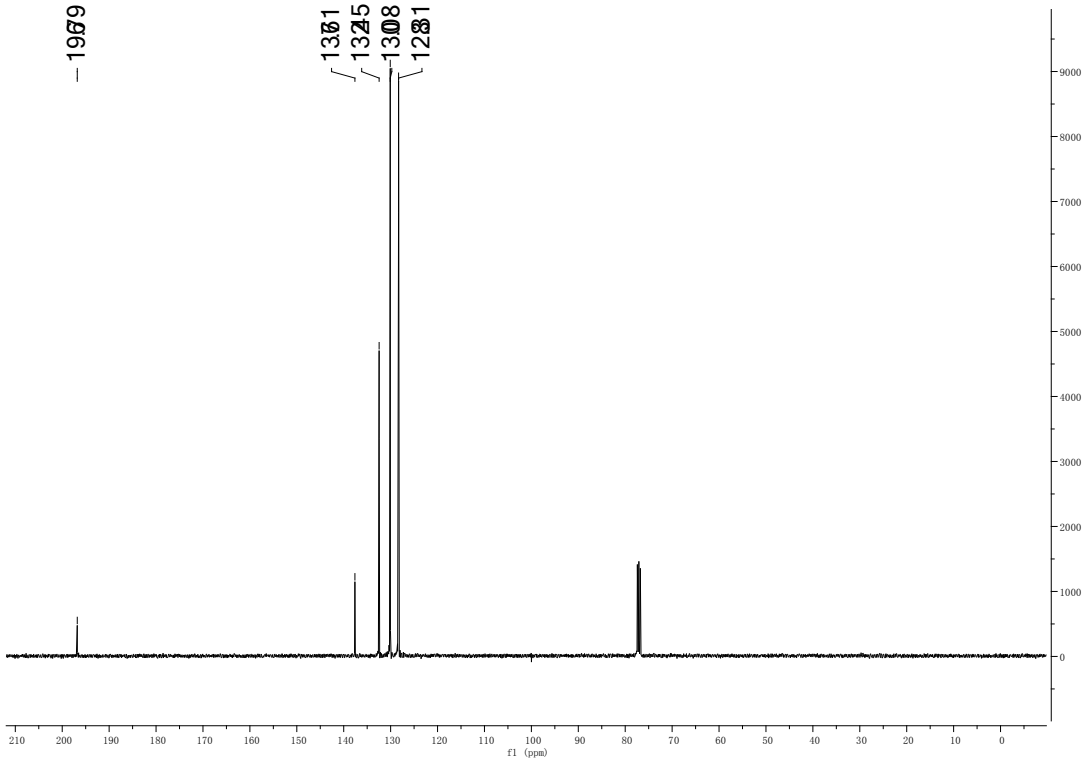
4l ^{13}C NMR



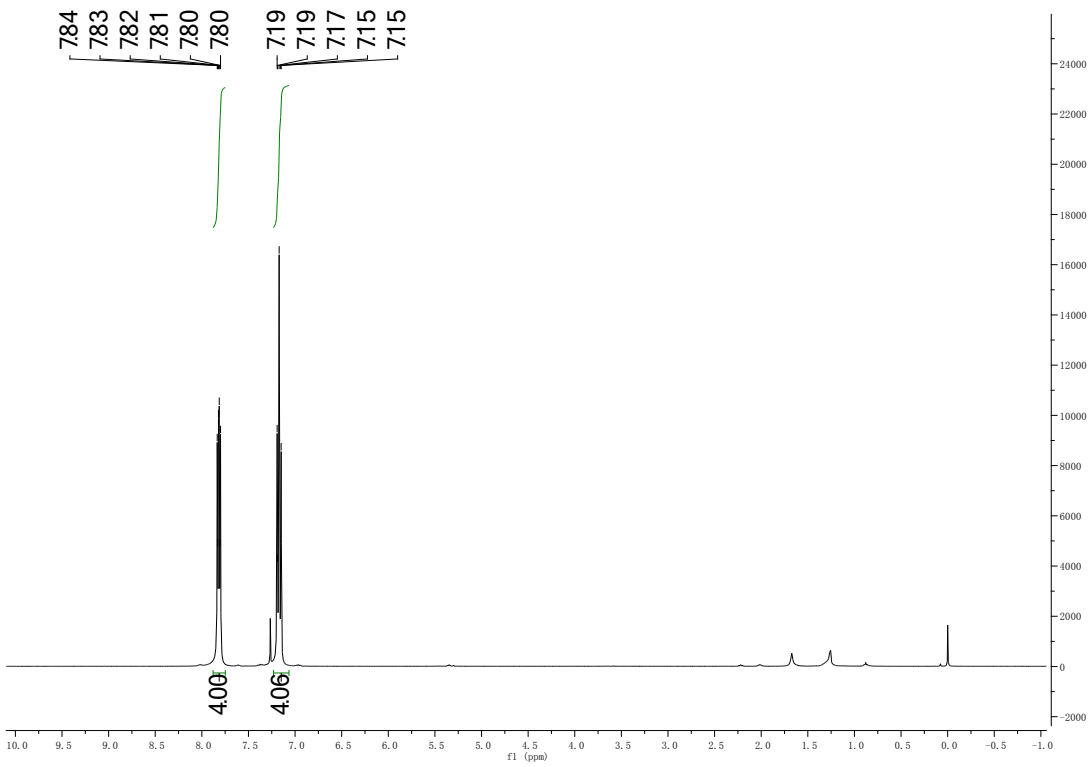
4m ^{1}H NMR (Without any purification)



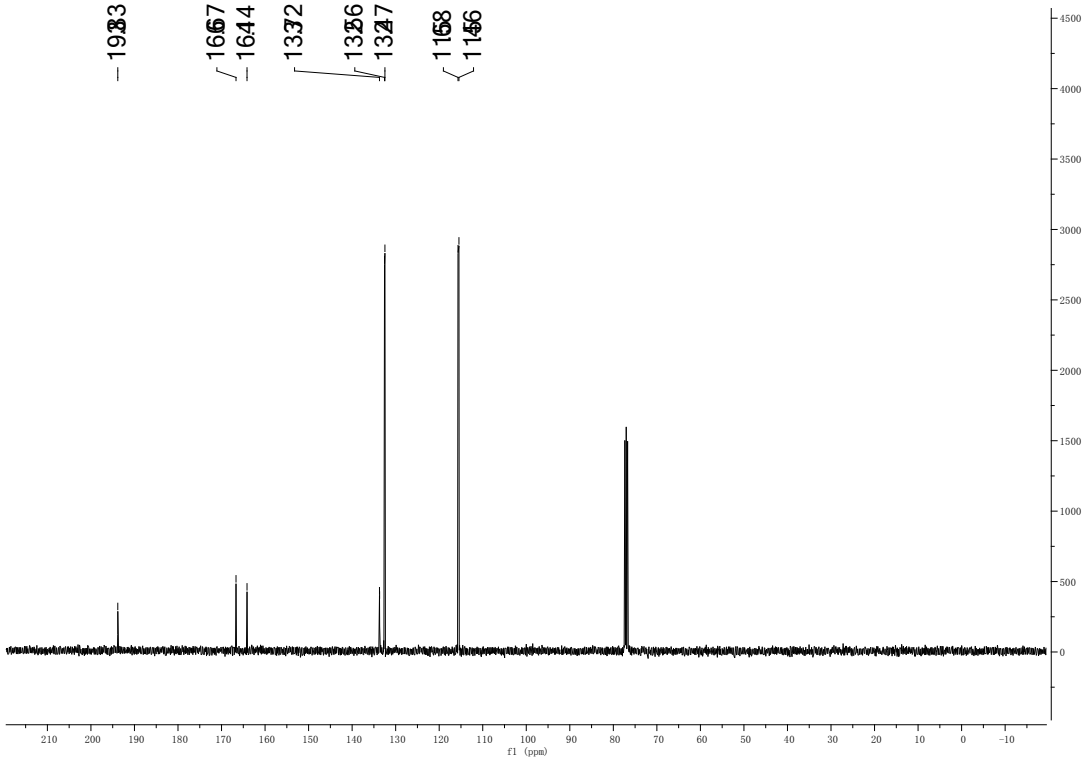
4m ^{13}C NMR



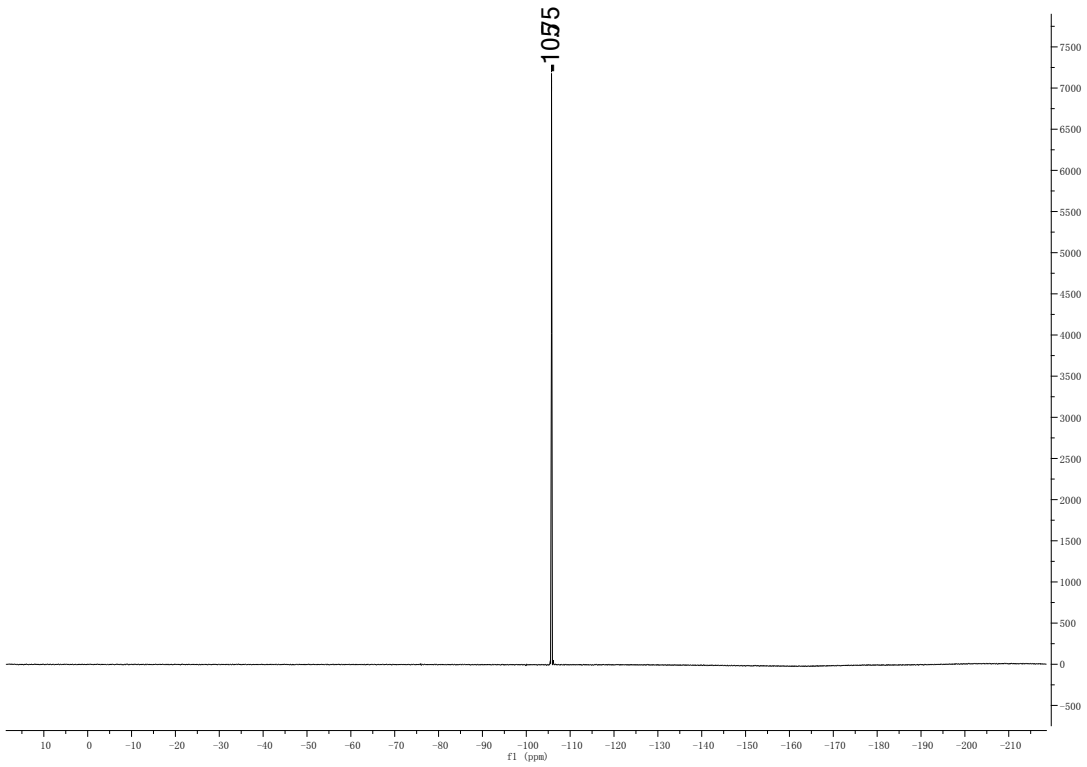
4n ^{1}H NMR



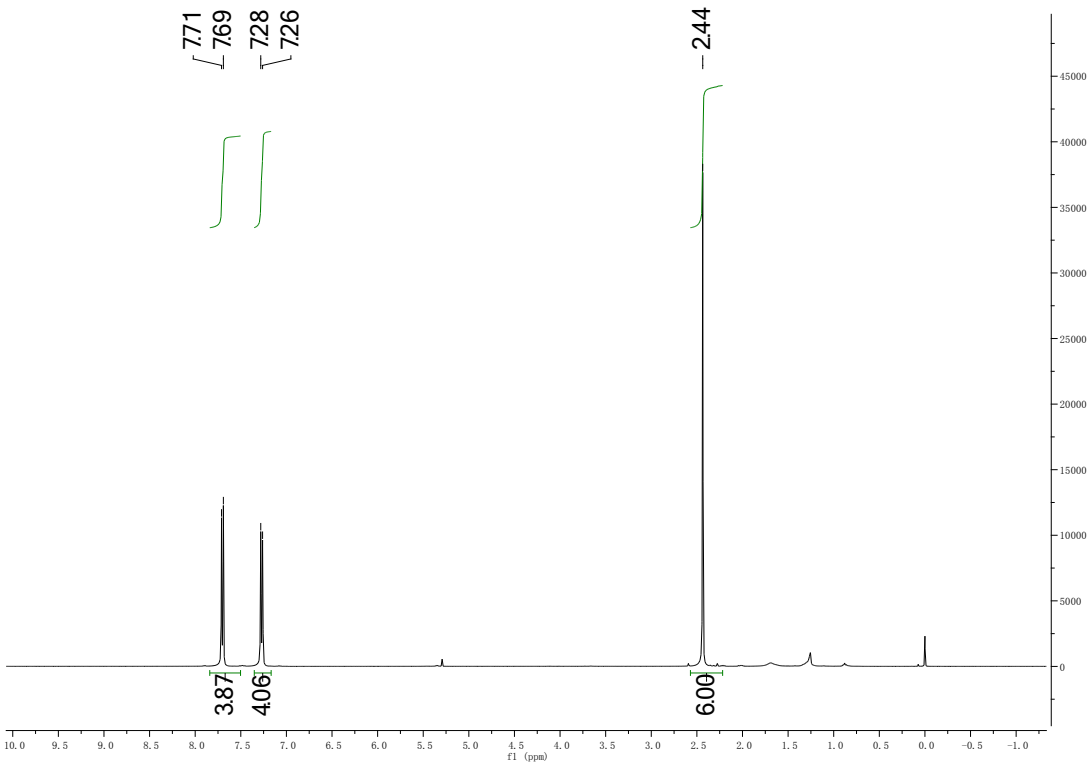
4n ^{13}C NMR



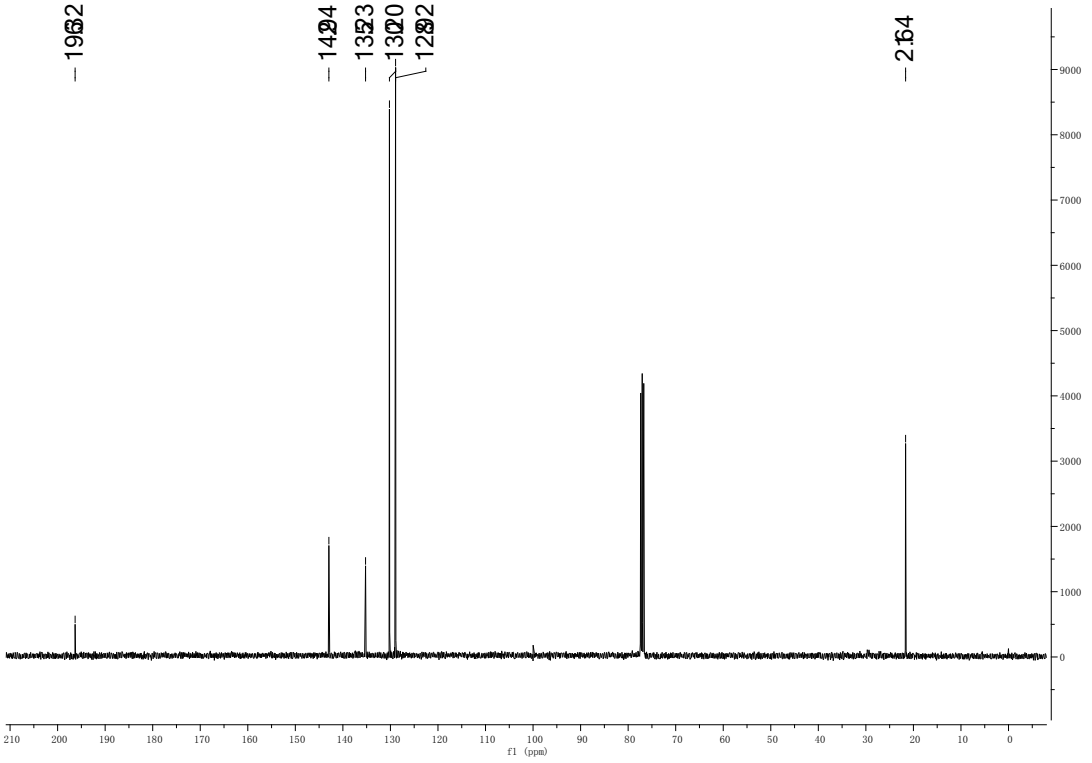
4n ^{19}F NMR


-105.75
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)

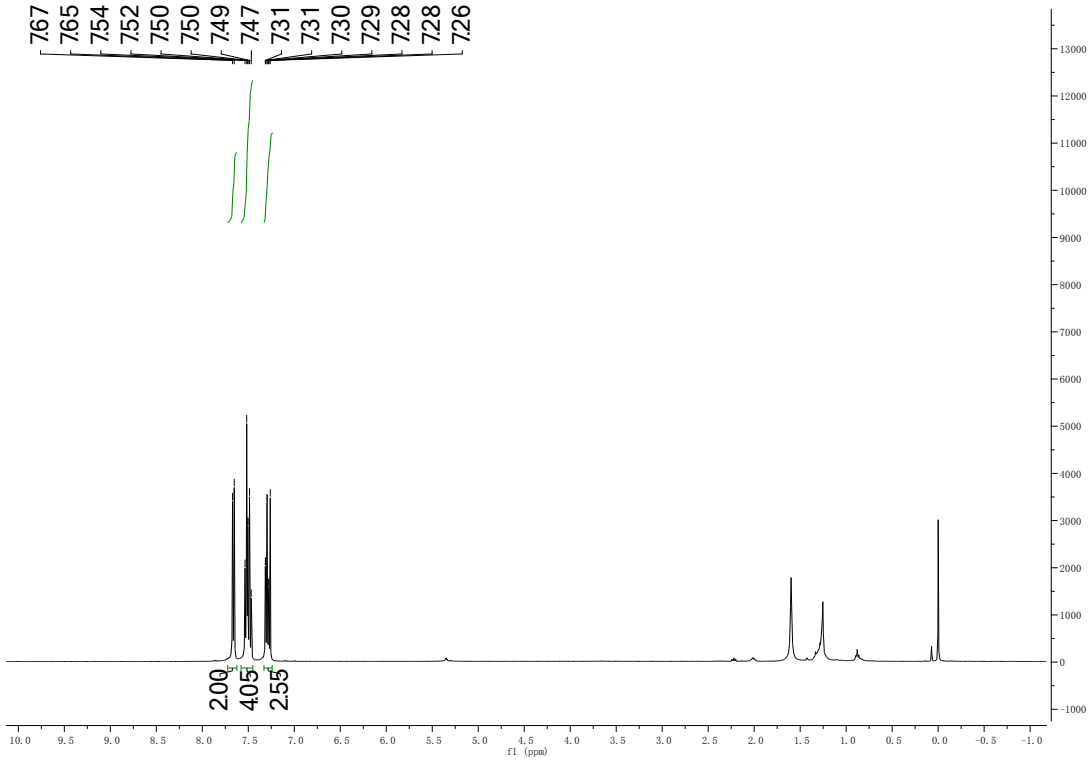
4o ^{1}H NMR



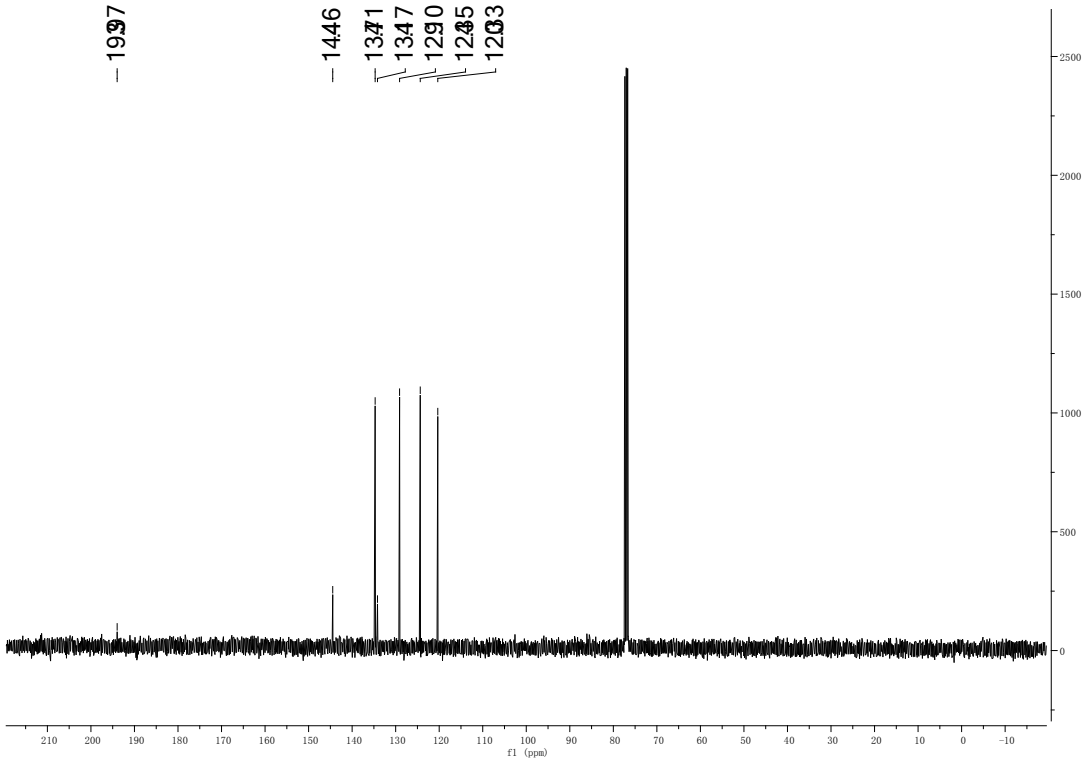
4o ^{13}C NMR



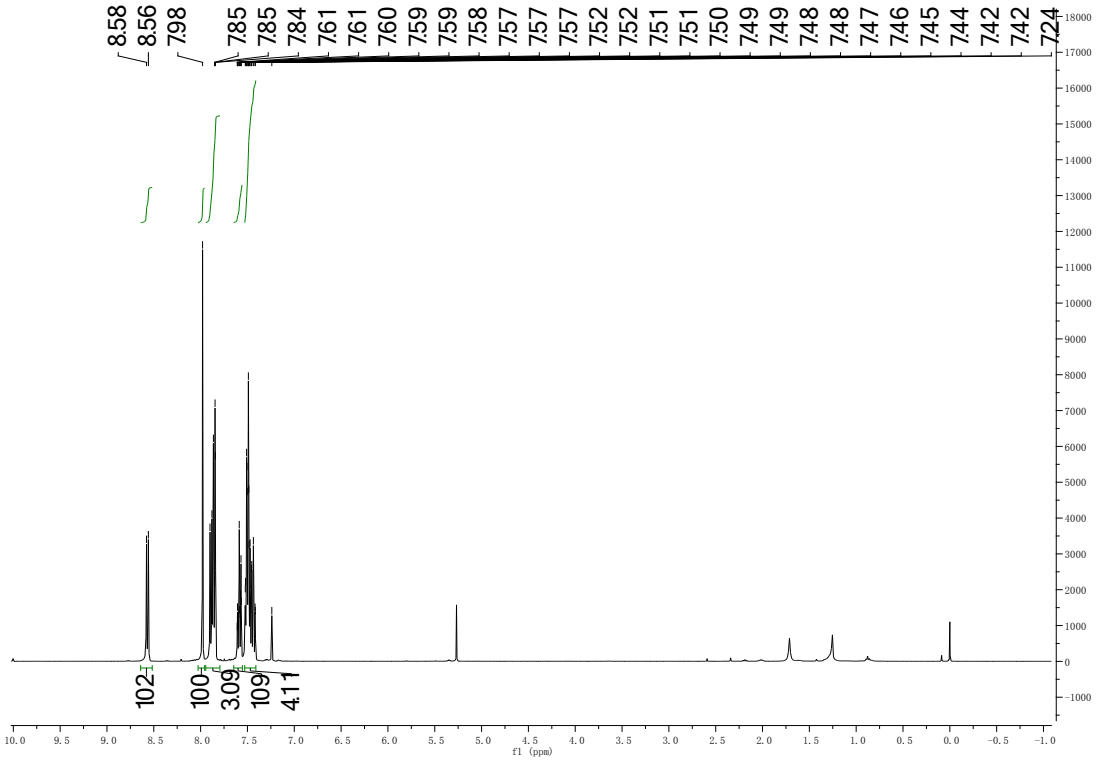
4p ^{1}H NMR



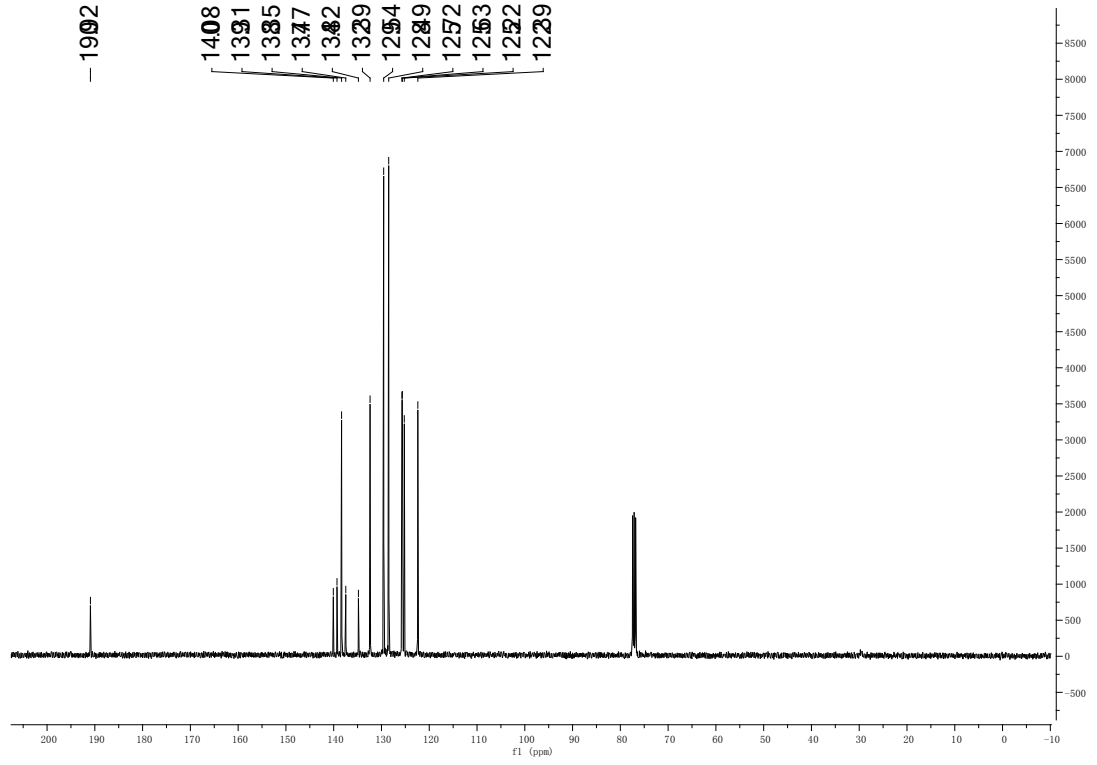
4p ^{13}C NMR



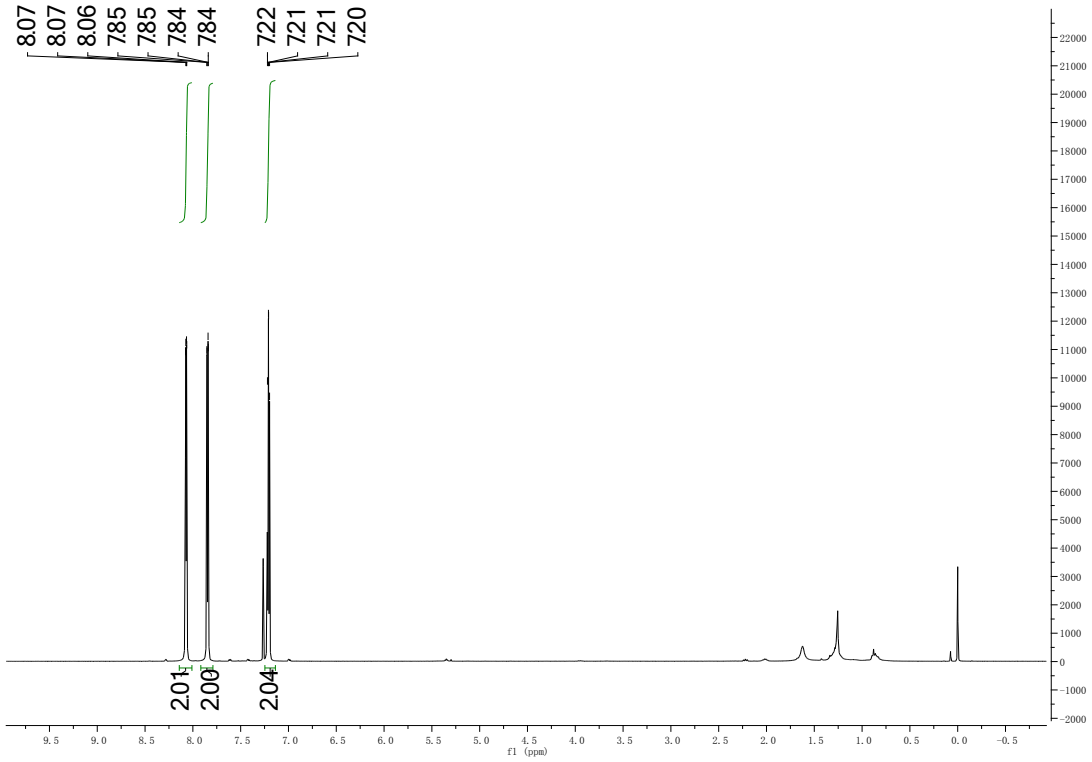
4q ^{1}H NMR



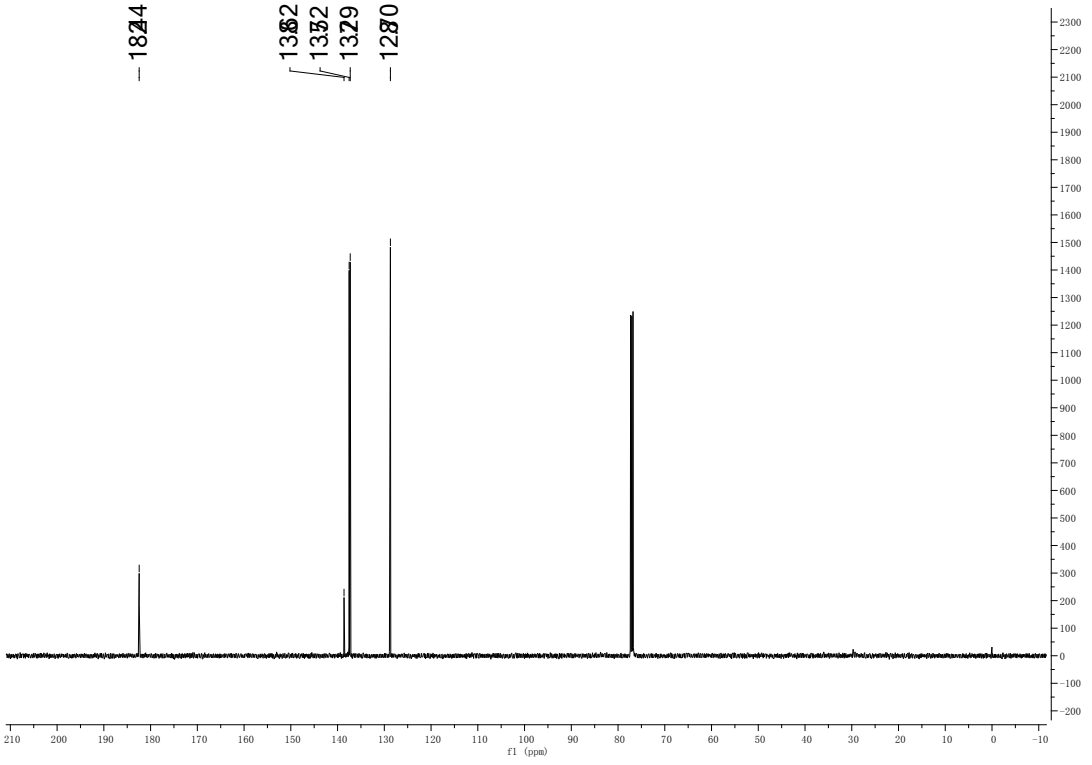
4q ^{13}C NMR



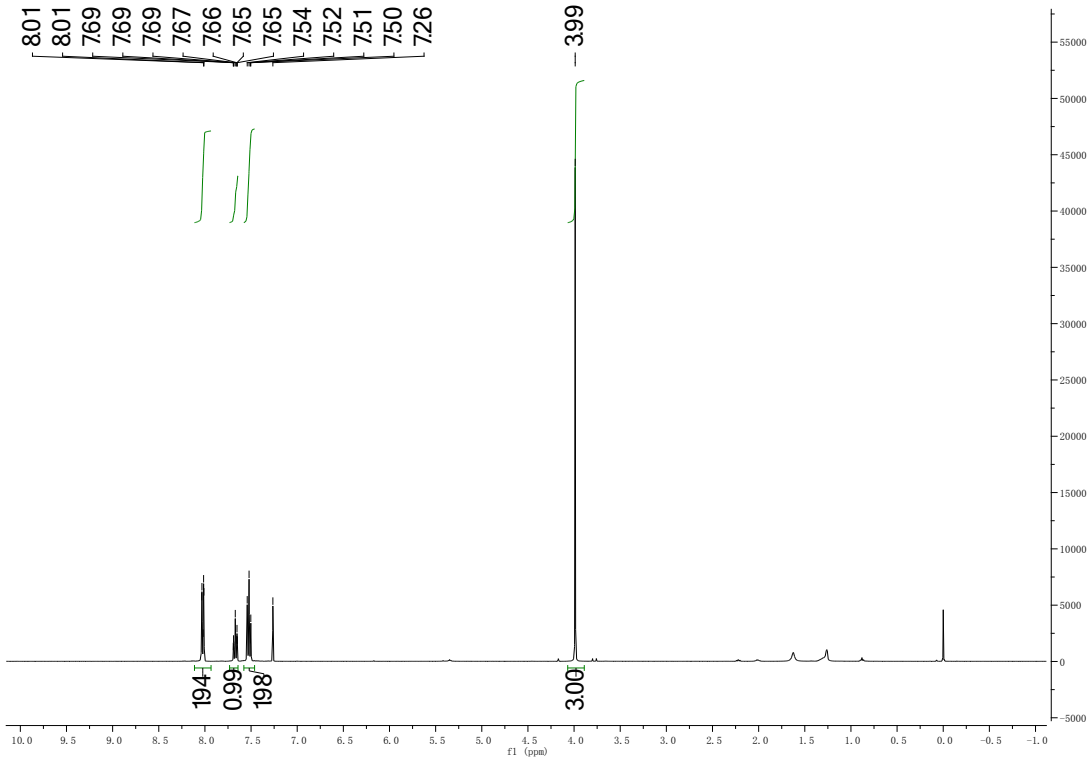
4r ^{1}H NMR



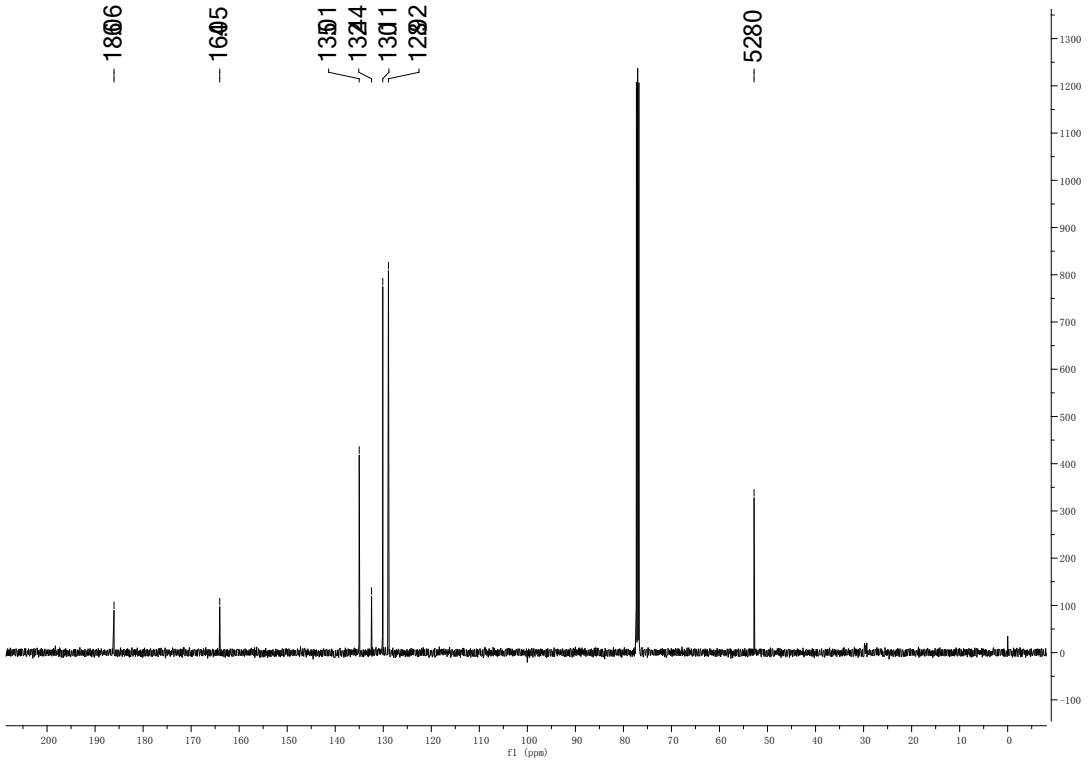
4r ^{13}C NMR



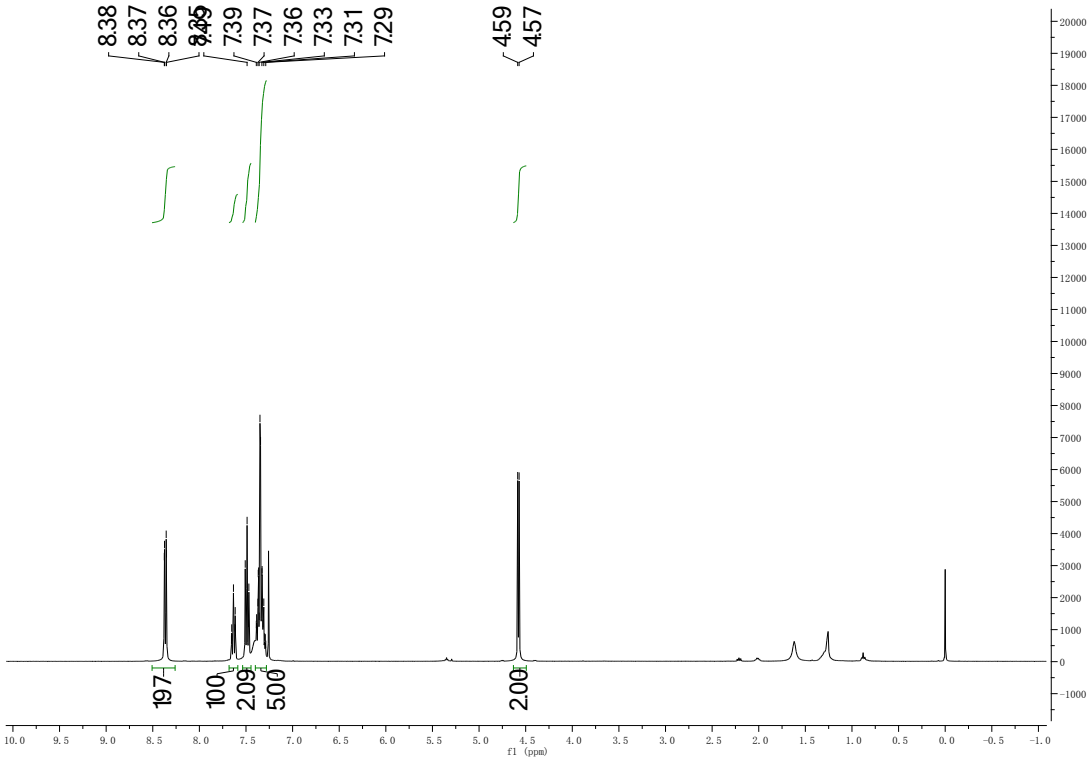
4s ^{1}H NMR



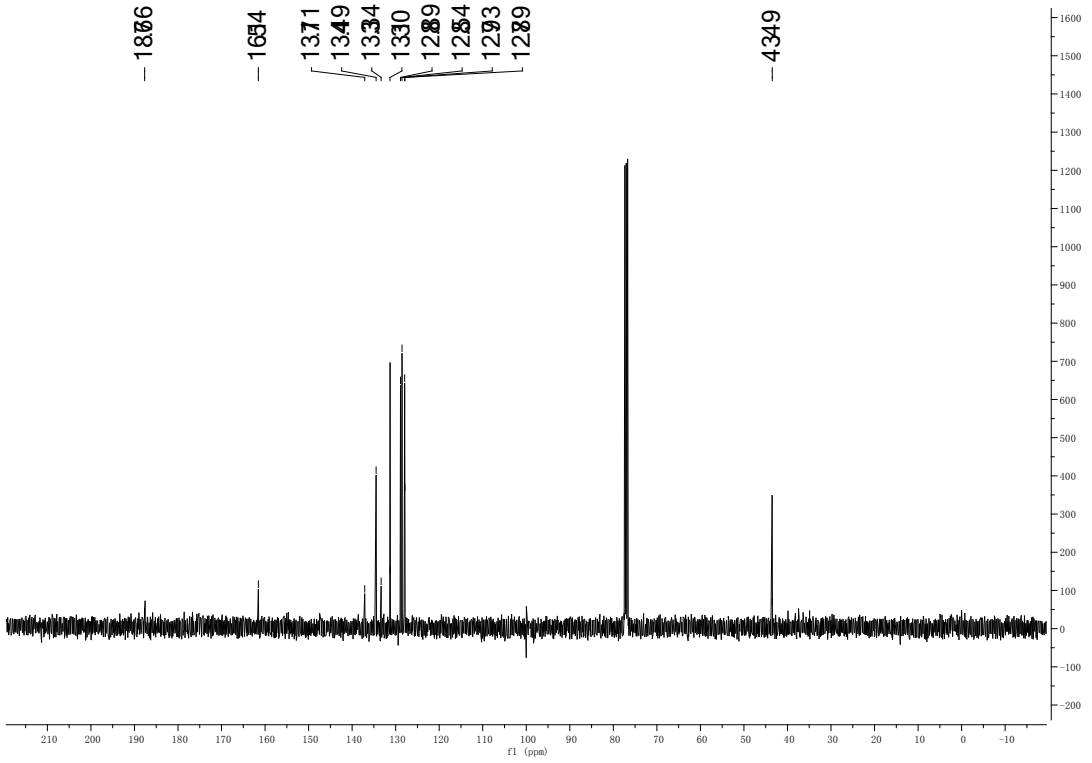
4s ^{13}C NMR



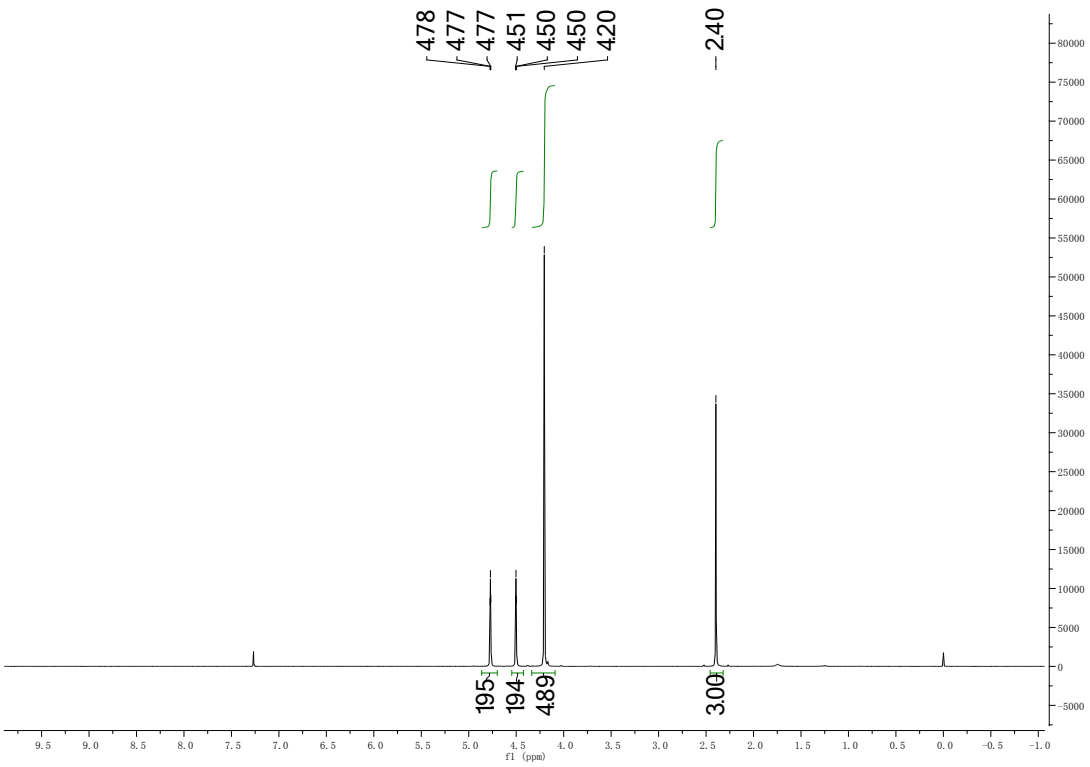
4t ^{1}H NMR



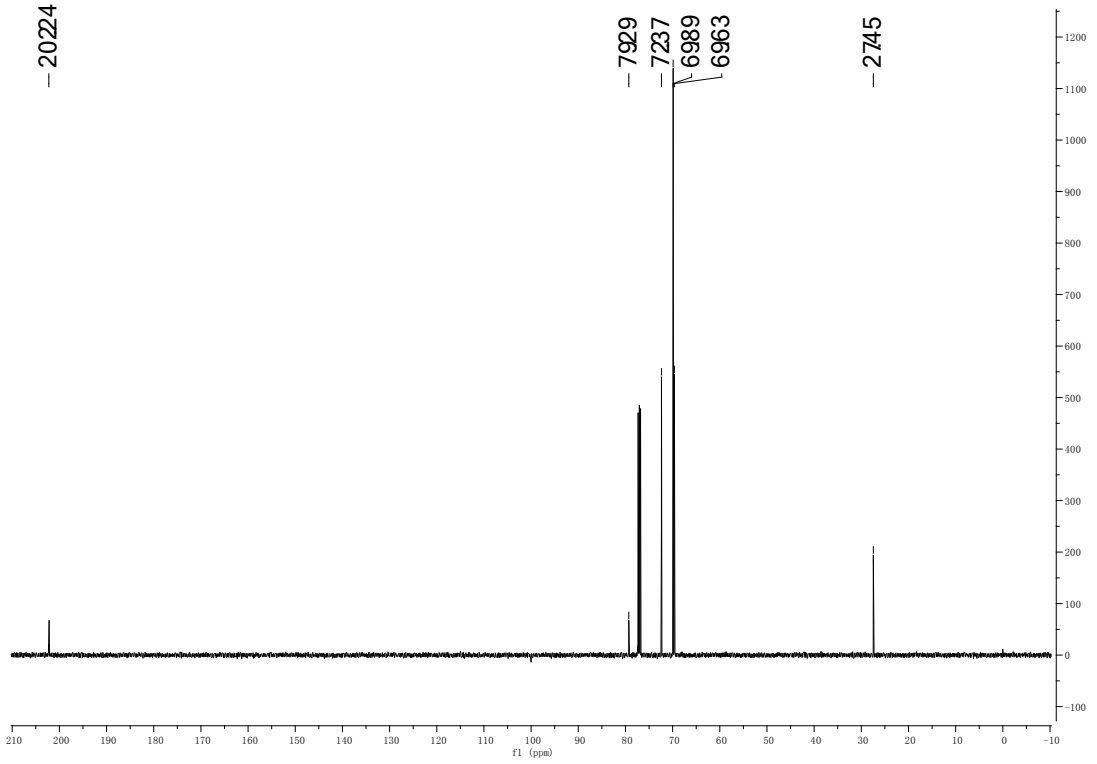
4t ^{13}C NMR



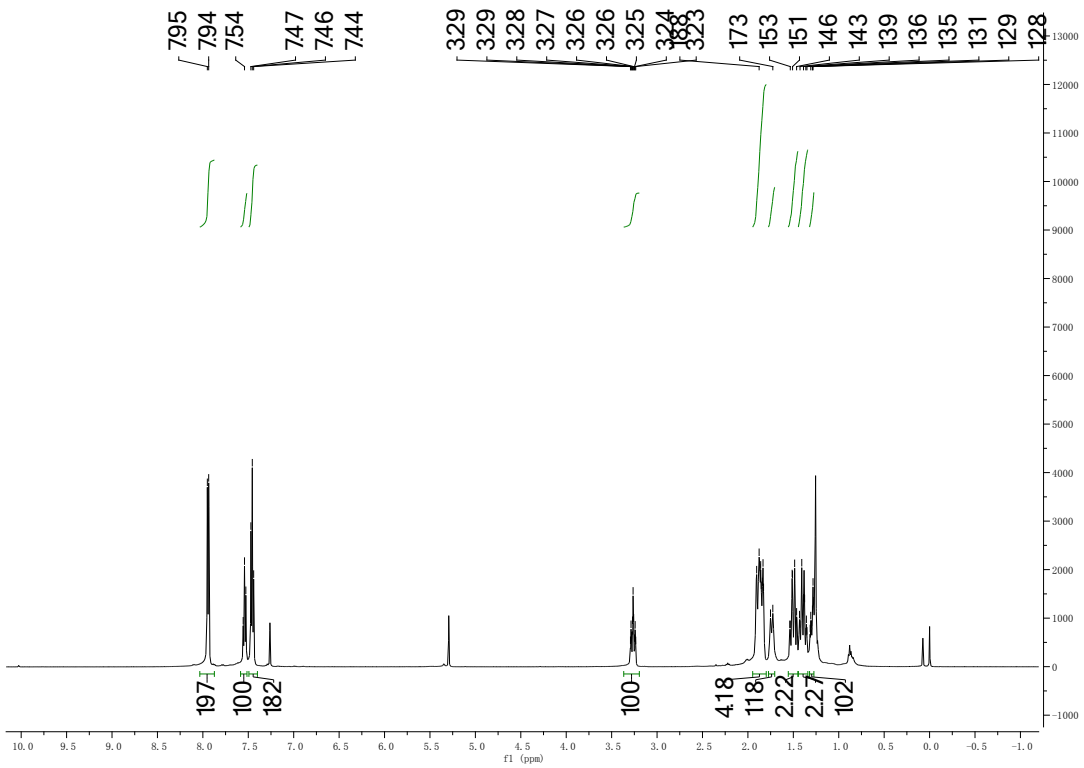
4u ^{1}H NMR



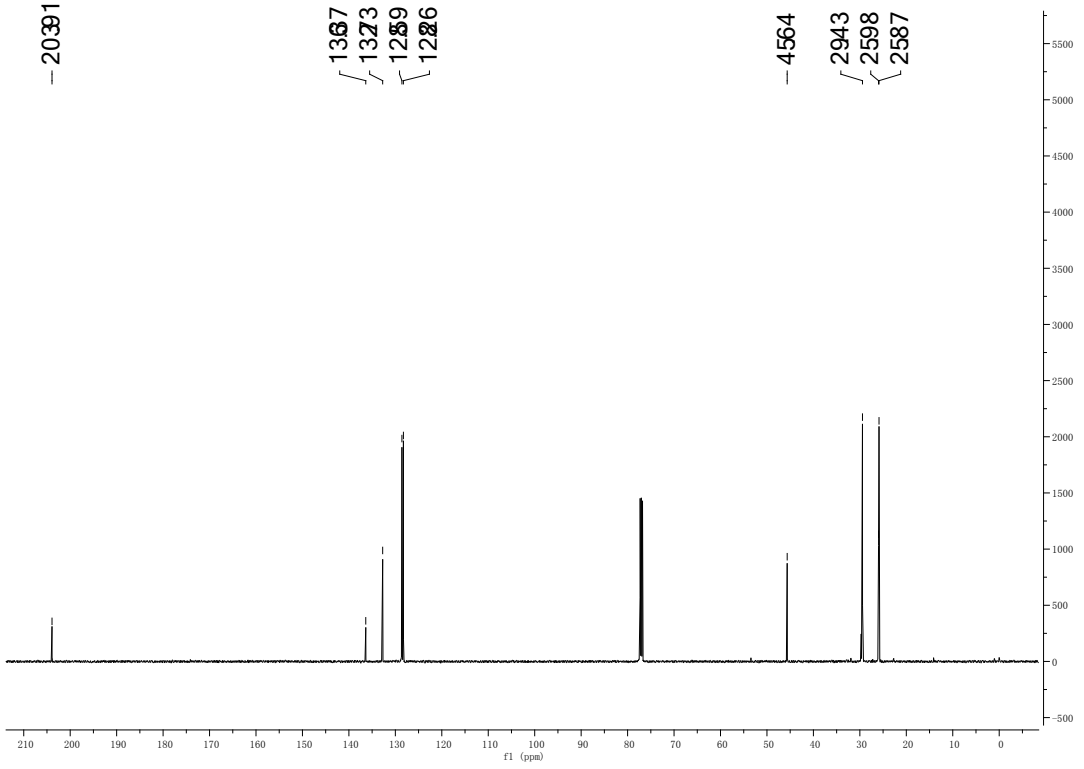
4u ^{13}C NMR



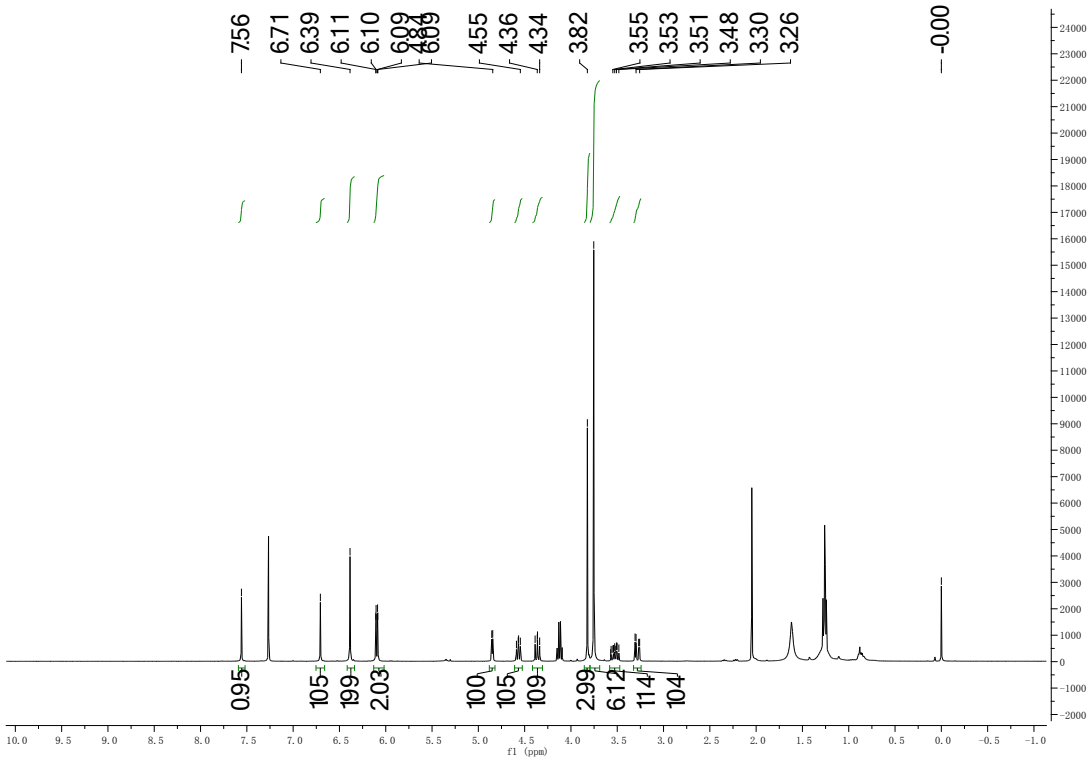
4v ^{1}H NMR



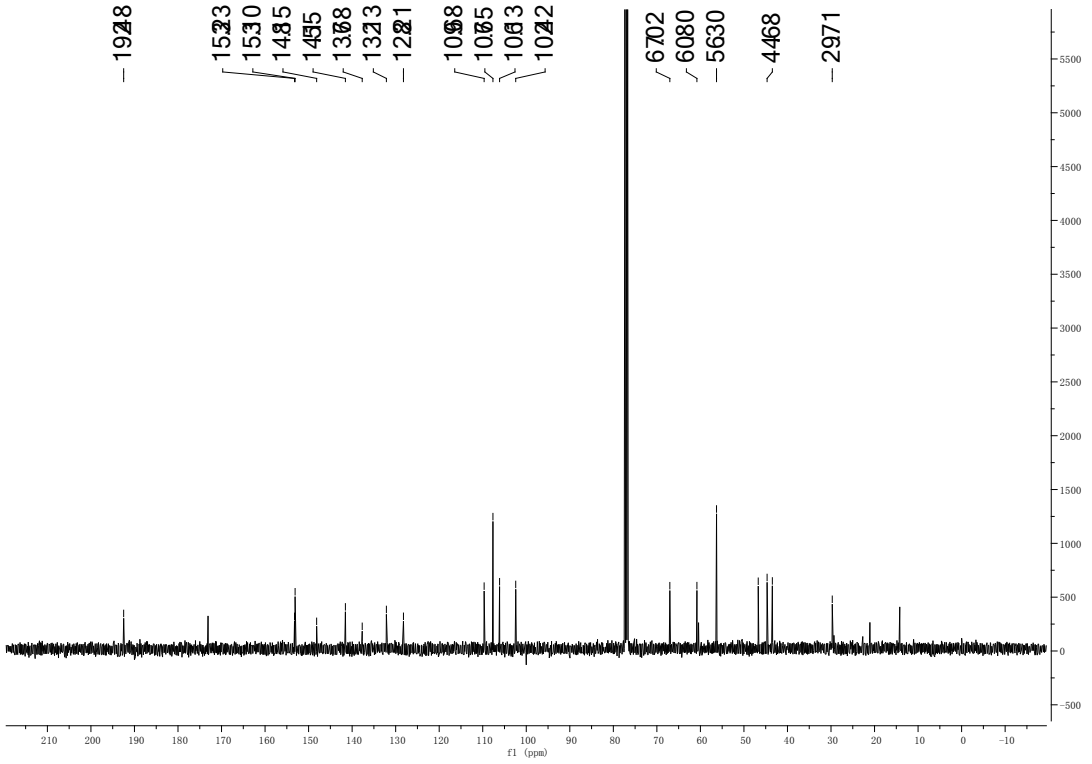
4v ^{13}C NMR



8a ^{1}H NMR


7.56
6.71
6.39
6.11
6.10
6.09
6.04
6.03
4.55
4.36
4.34
3.82
3.55
3.53
3.51
3.48
3.30
3.26
-0.00
0.95
1.05
1.99
2.03
1.00
1.05
1.09
2.99
6.12
1.14
1.04
f1 (ppm)

8a ^{13}C NMR


192.18
152.23
151.30
148.15
145.55
136.68
132.13
122.21
109.68
108.55
108.13
102.12
67.02
60.80
56.30
44.68
29.71
f1 (ppm)