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Supporting Information

$B(C_6F_5)_3$ Catalyzed Direct Nucleophilic Substitution of Benzylic Alcohols: An Effective Method of Constructing C-O, C-S and C-C Bonds from Benzylic Alcohols

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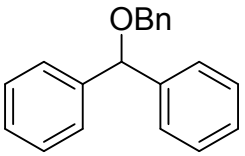
General Information

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).

Experiment section

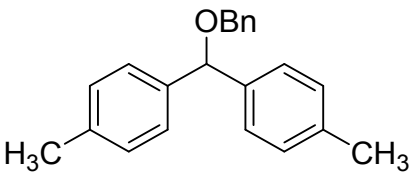
General procedure for alcohol etherification

To a 25ml Schlenk tube was added alcohol **1** (0.2 mmol) and BnOH (25.9 mg, 0.4mmol) and **$B(C_6F_5)_3$** (5.5 mg, 0.05 eq), then 1ml DCE was added. The mixture was stirred at 60 ^oC until the alcohol was disapperaed (monitored by TLC). Then the solvent was removed and the residue was purified by silica gel column chromatography (PE:EA=100:1) to afford product **2**.



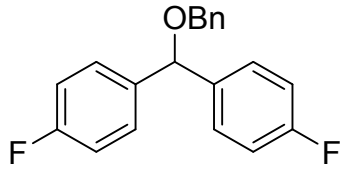
((benzyloxy)methylene)dibenzene **2a**

Colourless oil, 95% yield. Analytical data for **2a**: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 6.85 (m, 15H), 5.44 (s, 1H), 4.54 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.16, 138.41, 128.42, 128.38, 127.72, 127.55, 127.48, 127.15, 82.49, 70.52. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{20}H_{18}ONa$: 297.1255. Found: 297.1253.



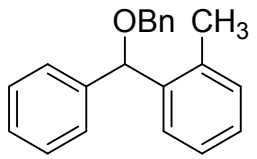
4,4'-((benzyloxy)methylene)bis(methylbenzene) **2b**

Colourless oil, 99% yield. Analytical data for **2b**: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.29 (m, 4H), 7.25 (m, 5H), 7.11 (d, J = 8.0 Hz, 4H), 5.38 (s, 1H), 4.52 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 139.47, 138.65, 137.06, 129.14, 128.39, 127.74, 127.51, 127.10, 82.24, 70.40, 21.21. HRMS (ESI) m/z [M+Na]$^{+}$: Calcd for $C_{22}H_{22}ONa$: 325.1568. Found: 325.1560.



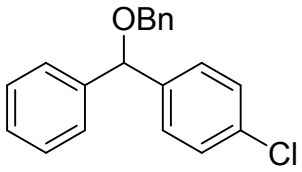
4,4'-((benzyloxy)methylene)bis(fluorobenzene) **2c**

Colourless oil, 95% yield. Analytical data for **2c**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.12 (m, 9H), 7.02 – 6.76 (m, 5H), 5.31 (s, 1H), 4.42 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.39, 159.94, 136.82 (d, *J* = 30.0 Hz), 127.72, 127.64, 127.40, 126.68, 114.29 (d, *J* = 21.4 Hz), 79.99, 69.47. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.82. HRMS (ESI) m/z [M+Na]$^{+}$: Calcd for $C_{20}H_{16}F_2ONa$: 333.1067. Found: 333.1058.



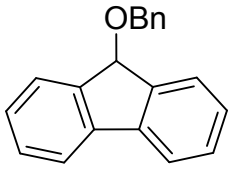
1-((benzyloxy)(phenyl)methyl)-2-methylbenzene **2d**

Colourless oil, 97% yield. Analytical data for **2d**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.26 (m, 9H), 7.20 (dt, *J* = 15.3, 7.0 Hz, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 5.60 (s, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.21, 139.62, 138.47, 136.15, 130.66, 128.42, 128.37, 127.88, 127.69, 127.62, 127.57, 127.48, 127.41, 126.12, 79.94, 70.72, 19.52. HRMS (ESI) m/z [M+Na]$^{+}$: Calcd for $C_{21}H_{20}ONa$: 311.1412. Found: 311.1417.



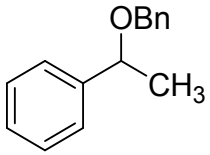
1-((benzyloxy)(phenyl)methyl)-4-chlorobenzene **2e**

Colourless oil, 98% yield. Analytical data for **2e**: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.22 (m, 14H), 5.40 (s, 1H), 4.59 – 4.44 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.65, 140.80, 138.14, 133.23, 128.60, 128.58, 128.47, 128.46, 127.78, 127.76, 127.71, 127.13, 81.74, 70.55.HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{21}H_{20}ClONa$: 331.0866. Found: 331.0864.



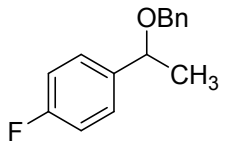
9-(benzyloxy)-9H-fluorene **2f**

Colourless oil, 88% yield. Analytical data for **2f**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 12.6, 7.5 Hz, 4H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.36 – 7.23 (m, 7H), 5.79 (s, 1H), 4.20 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.79 , 140.94 , 138.58 , 129.08 , 128.33 , 127.84 , 127.63 , 127.56 , 125.56 , 120.02 , 80.80 , 66.62 . HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{20}H_{16}ONa$: 295.1099. Found: 295.1090.



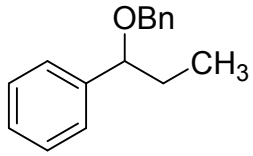
(1-(benzyloxy)ethyl)benzene **2g**

Colourless oil, 96% yield. Analytical data for **2g**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 4.4 Hz, 4H), 7.29 (m, 6H), 4.57 – 4.39 (m, 2H), 4.29 (d, *J* = 11.9 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.78, 138.70, 128.55, 128.40, 127.74, 127.55, 127.51, 126.39, 77.28, 70.36, 24.27. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{15}H_{16}ONa$: 235.1099. Found: 235.1098.



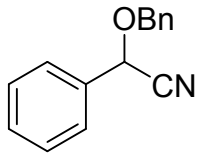
1-(1-(benzyloxy)ethyl)-4-fluorobenzene **2h**

Colourless oil, 93% yield. Analytical data for **2h**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.18 (m, 7H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.53 – 4.38 (m, 2H), 4.28 (d, *J* = 11.8 Hz, 1H), 1.45 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.24 (d, *J* = 245.1 Hz), 139.47 (d, *J* = 3.0 Hz), 138.50, 128.44, 127.96 (d, *J* = 8.0 Hz), 127.72, 127.60, 115.37 (d, *J* = 21.3 Hz), 76.55, 70.31, 24.23. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.16. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{15}H_{16}FO$: 231.1185. Found: 231.1190.



(1-(benzyloxy)propyl)benzene **2i**

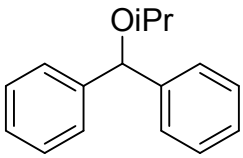
Colourless oil, 94% yield. Analytical data for **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.15 (m, 10H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.23 (dd, *J* = 17.4, 9.4 Hz, 2H), 1.96 – 1.81 (m, 1H), 1.79 – 1.60 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 142.49, 138.75, 128.38, 128.34, 127.76, 127.51, 127.46, 126.93, 82.99, 70.40, 31.20, 10.41. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{16}H_{18}ONa$: 249.1255. Found: 249.1256.



2-(benzyloxy)-2-phenylacetonitrile **2j**

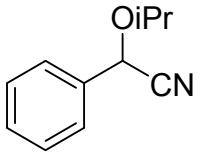
Colourless oil, 94% yield. Analytical data for **2j**:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.46 – 7.31 (m, 8H), 5.26 (s, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

135.74, 133.41, 129.84, 129.06, 128.75, 128.58, 128.38, 127.41, 117.19, 71.65, 69.42. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{15}H_{13}NOK$: 262.0634. Found: 262.0630.



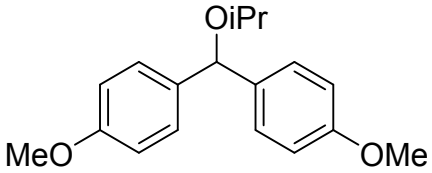
(isopropoxymethylene)dibenzene **2k**

Colourless oil, 96% yield. Analytical data for **2k**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (m, 10H), 5.40 (s, 1H), 3.58 (dt, *J* = 12.2, 6.1 Hz, 1H), 1.13 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.04, 128.37, 127.30, 127.14, 80.52, 69.15, 22.33. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{16}H_{18}ONa$: 249.1255. Found: 249.1253.



2-isopropoxy-2-phenylacetonitrile **2l**

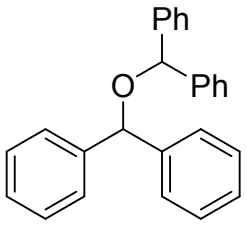
Colourless oil, 92% yield. Analytical data for **2l**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.46 – 7.33 (m, 3H), 5.27 (s, 1H), 4.03 (q, *J* = 6.1 Hz, 1H), 1.29 (dd, *J* = 14.6, 6.1 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 134.30, 129.58, 128.99, 127.16, 118.13, 72.32, 68.30, 22.56, 21.24. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{11}H_{13}NOK$: 214.0634. Found: 214.0644.



4,4'-(isopropoxymethylene)bis(methoxybenzene) **2m**

Colourless oil, 91% yield. Analytical data for **2m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 4H), 6.87 (d, *J* = 8.6 Hz, 4H), 5.43 (s, 1H), 3.81 (s, 6H), 3.66 (dt, *J* = 12.2, 6.1 Hz, 1H), 1.23 (d, *J* = 6.1 Hz,

6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.74, 135.40, 128.25, 113.67, 79.53, 68.77, 55.26, 22.29. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{18}H_{22}O_3Na$: 309.1467. Found: 309.1470.

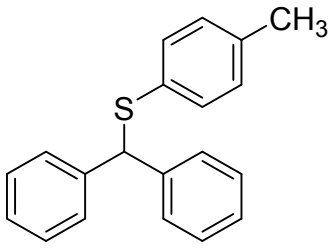


(oxybis(methanetriyl))tetrabenzene **2n**

Colourless oil, 95% yield. Analytical data for **2n**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 6.92 (m, 20H), 5.40 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.23, 128.41, 127.45, 127.29, 80.02. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{26}H_{22}ONa$: 373.1568. Found: 373.1567.

General procedure for alcohol thioetherification

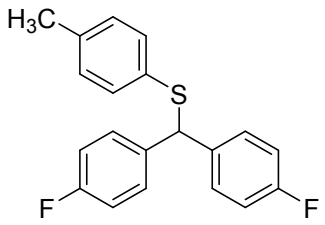
To a 25ml Schlenk tube was added alcohol **1** (0.2 mmol) and 4-methylbenzenethiol (29.7 mg, 0.24 mmol) and **$B(C_6F_5)_3$** (5.5 mg, 0.05 eq), then 1ml DCE was added. The mixture was stirred at 60 ^{o}C until the alcohol was disapperaed (monitored by TLC). Then the solvent was removed and the residue was purified by silica gel column chromatography (PE:EA=100:1) to afford product **3**.



Benzhydryl(p-tolyl)sulfane **3a**

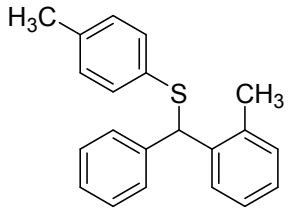
Colourless oil, 97% yield. Analytical data for **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 4H), 7.32 – 7.24 (m, 4H), 7.24 – 7.15 (m, 2H), 7.16 – 7.08 (m, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 5.46 (s, 1H), 2.24 (s,

3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.25, 136.86, 132.31, 131.38, 129.55, 128.52, 128.46, 127.20, 58.08, 21.09. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_0H_{18}SK$: 329.0766. Found: 329.0771.



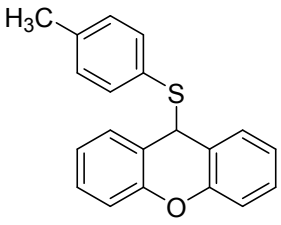
(bis(4-fluorophenyl)methyl)(p-tolyl)sulfane **3b**

Colourless oil, 94% yield. Analytical data for **3b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 3H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.04 – 6.92 (m, 5H), 5.42 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.89 (d, *J* = 246.3 Hz), 137.33, 56.62, 21.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.14. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{20}H_{16}F_2KS$: 365.0578. Found: 365.0634.



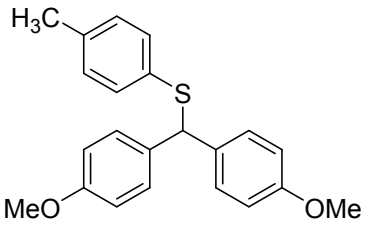
(phenyl(o-tolyl)methyl)(p-tolyl)sulfane **3c**

Colourless oil, 95% yield. Analytical data for **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.08 (m, 6H), 6.97 (d, *J* = 7.9 Hz, 2H), 5.65 (s, 1H), 2.32 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.59, 139.06, 136.63, 135.88, 132.87, 130.69, 130.57, 129.59, 128.80, 128.59, 128.45, 127.19, 127.09, 126.30, 54.39, 21.07, 19.68. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{21}H_{20}KS$: 343.0923. Found: 343.1022.



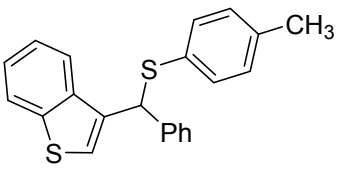
9-(p-tolylthio)-9H-xanthene **3d**

Colourless oil, 96% yield. Analytical data for **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.11 (m, 2H), 7.04 (td, *J* = 7.5, 1.1 Hz, 2H), 6.94 – 6.86 (m, 4H), 6.79 (d, *J* = 8.1 Hz, 2H), 5.44 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.12, 138.99, 136.28, 129.52, 129.23, 128.42, 127.84, 123.07, 121.39, 116.22, 47.68, 21.29. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{20}H_{16}OKS$: 343.0559. Found: 343.0567.



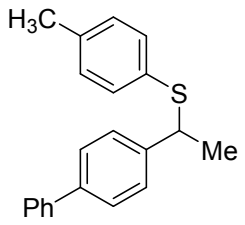
(bis(40methoxyphenyl)methyl)(p-tolyl)sulfane **3e**

Colourless oil, 92% yield. Analytical data for **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 4H), 7.13 (s, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.84 – 6.74 (m, 4H), 5.42 (s, 1H), 3.74 (s, 6H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.62, 136.60, 133.62, 132.66, 131.13, 129.52, 129.48, 113.86, 56.67, 55.26, 21.09. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{22}H_{22}O_2KS$: 389.0978. Found: 389.0980.



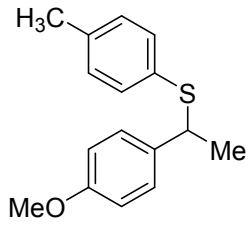
3-(phenyl(p-tolylthio)methyl)benzo[b]thiophene **3f**

Colourless oil, 99% yield. Analytical data for **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 1H), 7.78 – 7.69 (m, 1H), 7.45 (d, *J* = 0.8 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.30 (m, 4H), 7.23 (m 1H), 7.17 (m, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 5.74 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.90, 140.11, 137.65, 137.06, 135.29, 132.22, 131.27, 129.66, 128.60, 128.51, 127.50, 125.50, 124.45, 124.06, 122.94, 122.47, 52.36, 21.10. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{22}H_{18}KS_2$: 385.0487. Found: 385.0510.



(1-([1,1'-biphenyl]-4-yl)ethyl)(p-tolyl)sulfane **3g**

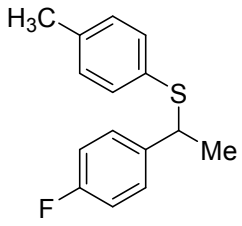
Colourless oil, 95% yield. Analytical data for **3g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 4.31 (q, *J* = 7.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.45, 140.83, 139.92, 137.46, 133.27, 131.23, 129.53, 128.76, 127.73, 127.22, 127.07, 127.03, 48.11, 22.15, 21.14. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{21}H_{29}KS$: 343.0923. Found: 343.1062.



(1-(4-methoxyphenyl)ethyl)(p-tolyl)sulfane **3h**

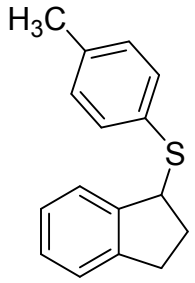
Colourless oil, 99% yield. Analytical data for **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.12 (m, 4H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.89 – 6.61 (m, 2H), 4.24 (q, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 2.29 (s, 3H), 1.57 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.59, 137.28, 135.41, 133.18, 131.49, 129.48, 128.37,

113.72, 55.29, 47.76, 22.33, 21.15. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{16}H_{18}OSK$: 297.0715. Found: 297.0703.



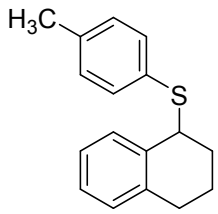
(1-(4-fluorophenyl)ethyl)(p-tolyl)sulfane **3i**

Colourless oil, 94% yield. Analytical data for **3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.07 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 8.7 Hz, 2H), 4.24 (q, *J* = 7.0 Hz, 1H), 2.29 (s, 3H), 1.58 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.75 (d, *J* = 245.2 Hz), 139.13, 137.61, 133.43, 130.88, 129.51, 128.81 (d, *J* = 8.1 Hz), 115.09 (d, *J* = 21.3 Hz), 47.70, 22.21, 21.12. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_5H_{16}FS$: 247.0957. Found: 247.0956.



(2,3-dihydro-1H-inden-1-yl)(p-tolyl)sulfane **3j**

Colourless oil, 93% yield. Analytical data for **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.12 (m, 6H), 7.09 (d, *J* = 8.1 Hz, 2H), 4.68 (dd, *J* = 7.4, 4.0 Hz, 1H), 2.99 (dt, *J* = 15.7, 7.8 Hz, 1H), 2.82 (ddd, *J* = 15.8, 8.4, 4.4 Hz, 1H), 2.49 (ddd, *J* = 15.8, 13.5, 7.5 Hz, 1H), 2.33 (s, 3H), 2.18 (ddd, *J* = 17.4, 8.3, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.80, 143.09, 137.05, 132.29, 132.01, 129.63, 127.68, 126.46, 124.96, 124.69, 52.43, 33.55, 30.79, 21.14. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{16}H_{16}OK$: 279.0610. Found: 279.0600.

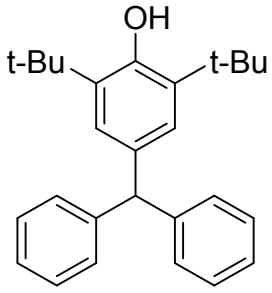


(1,2,3,4-tetrahydronaphthalen-1-yl)(p-tolyl)sulfane **3k**

Colourless oil, 95% yield. Analytical data for **3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 3H), 7.18 – 7.11 (m, 4H), 7.11 – 7.03 (m, 1H), 4.49 (t, *J* = 4.0 Hz, 1H), 2.94 – 2.52 (m, 2H), 2.36 (s, 3H), 2.30 – 2.14 (m, 1H), 2.10 – 1.86 (m, 2H), 1.83 – 1.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.57, 137.31, 135.72, 132.79, 132.32, 130.54, 129.74, 129.25, 127.02, 125.69, 48.23, 29.16, 28.43, 21.16, 18.56. HRMS (ESI) m/z $[M+K]^+$: Calcd for $C_{17}H_{18}KS$: 293.0766. Found: 293.0753.

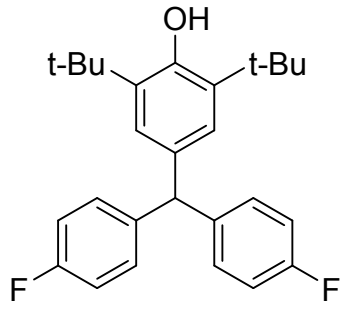
General procedure for alcohol arylation

To a 25ml Schlenk tube was added alcohol **1** (0.2 mmol) and **phenol** or **indole** (0.4mmol) and **$B(C_6F_5)_3$** (11mg, 0.1 eq), then 1ml DCE was added. The mixture was stirred at 60 °C until the alcohol was disapperaed (monitored by TLC). Then the solvent was removed and the residue was purified by silica gel column chromatography (PE:EA=100:1) to afford product **4**.



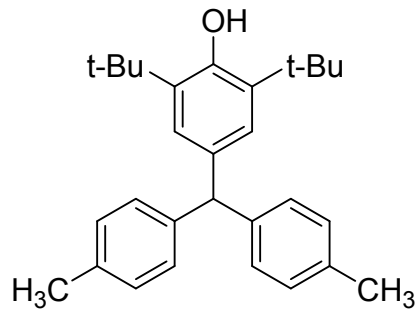
4-benzhydryl-2,6-di-tert-butylphenol **4a**

Colourless oil, 95% yield. Analytical data for **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 4H), 6.90 (s, 2H), 5.44 (s, 1H), 5.07 (s, 1H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.09, 144.84, 135.42, 134.12, 129.43, 128.14, 126.07, 126.02, 56.83, 34.35, 30.33. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{27}H_{31}O$: 371.2375. Found: 371.2374.



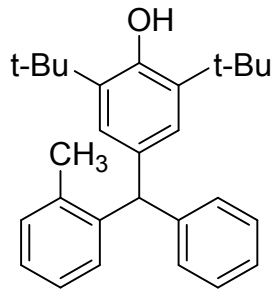
4-(bis(4-fluorophenyl)methyl)-2,6-di-tert-butylphenol **4b**

Colourless oil, 93% yield. Analytical data for **4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 8.5, 5.6 Hz, 4H), 6.96 (t, *J* = 8.7 Hz, 4H), 6.84 (s, 2H), 5.40 (s, 1H), 5.11 (s, 1H), 1.36 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.36 (d, *J* = 244.6 Hz), 152.28, 140.39, 135.67, 133.86, 130.72 (d, *J* = 7.9 Hz), 125.83, 115.01 (d, *J* = 21.1 Hz), 55.23, 34.37, 30.31. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.08. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{27}H_{29}F_2O$: 407.2186. Found: 407.2179.



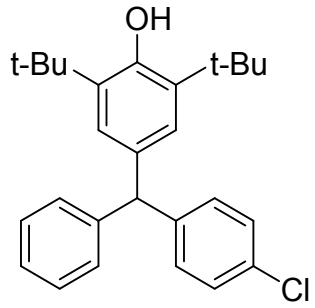
2,6-di-tert-butyl-4-(di-p-tolylmethyl)phenol **4c**

Colourless oil, 98% yield. Analytical data for **4c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.0 Hz, 4H), 6.99 (d, *J* = 8.1 Hz, 4H), 6.92 (s, 2H), 5.35 (s, 1H), 5.05 (s, 1H), 2.30 (s, 6H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.03, 142.15, 135.37, 135.36, 134.50, 129.25, 128.84, 126.02, 56.16, 34.38, 30.39, 21.07. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{29}H_{35}O$: 399.2688. Found: 399.2694.



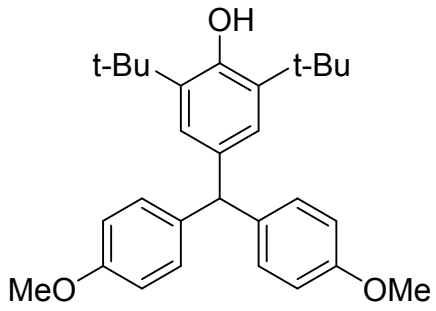
2,6-di-tert-butyl-4-(phenyl(o-tolyl)methyl)phenol **4d**

Colourless oil, 98% yield. Analytical data for **4d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.21 – 6.98 (m, 6H), 6.82 (m, 3H), 5.56 (s, 1H), 5.06 (s, 1H), 2.22 (s, 3H), 1.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.02, 144.18, 143.28, 136.60, 135.40, 133.67, 130.27, 129.54, 129.31, 128.12, 126.29, 126.09, 125.95, 125.63, 53.46, 34.35, 30.37, 20.06. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{28}H_{33}O$: 385.2531. Found: 385.2538.



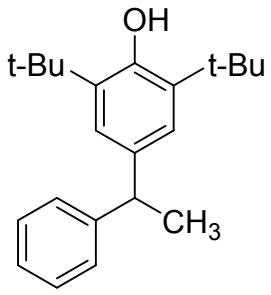
2,6-di-tert-butyl-4-((4-chlorophenyl)(phenyl)methyl)phenol **4e**

Colourless oil, 91% yield. Analytical data for **4e**:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 5H), 7.06 (dd, *J* = 19.1, 7.8 Hz, 4H), 6.87 (s, 2H), 5.41 (s, 1H), 5.10 (s, 1H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.26, 144.26, 143.47, 135.61, 133.65, 131.80, 130.77, 129.33, 128.27, 126.27, 125.94, 56.19, 34.37, 30.32. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{27}H_{30}ClO$: 405.1985. Found: 405.1981.



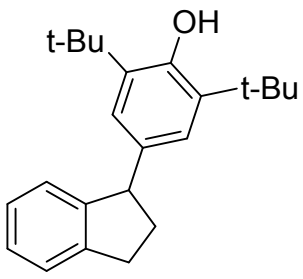
4-(bis(4-methoxyphenyl)methyl)-2,6-di-tert-butylhenol **4f**

Colourless oil, 99% yield. Analytical data for **4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.6 Hz, 4H), 6.82 (s, 2H), 6.73 (d, *J* = 8.7 Hz, 4H), 5.26 (s, 1H), 4.98 (s, 1H), 3.71 (s, 6H), 1.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.69, 150.92, 136.38, 134.32, 133.72, 129.17, 124.83, 112.41, 54.18, 54.12, 33.29, 29.30. HRMS (ESI) m/z $[M+Na]^+$: Calcd for $C_{29}H_{36}O_3Na$: 455.2562. Found: 455.2557.



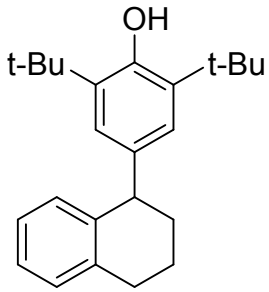
2,6-di-tert-butyl-4-(1-phenylethyl)phenol **4g**

Colorless oil, 92% yield. Analytical data for **4g**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 20.3, 12.9 Hz, 4H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.06 (s, 2H), 5.06 (s, 1H), 4.10 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.3 Hz, 3H), 1.45 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.91, 147.10, 136.78, 135.57, 128.24, 127.58, 125.77, 124.11, 44.83, 34.39, 30.37, 22.40. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{22}H_{29}O$: 309.2218. Found: 309.2218.



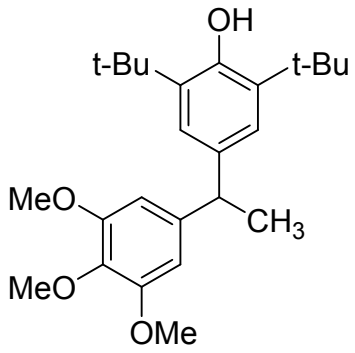
2,6-di-tert-butyl-4-(2,3-dihydro-1H-inden-1-yl)phenol **4h**

Colorless oil, 91% yield. Analytical data for **4h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 1H), 7.21 – 7.06 (m, 2H), 6.99 (d, *J* = 7.4 Hz, 3H), 5.07 (s, 1H), 4.24 (t, *J* = 8.3 Hz, 1H), 3.02 (dd, *J* = 18.9, 8.4 Hz, 1H), 2.98 – 2.84 (m, 1H), 2.64 – 2.42 (m, 1H), 2.04 (td, *J* = 17.9, 8.9 Hz, 1H), 1.41 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.17, 147.37, 144.25, 135.69, 135.49, 126.26, 126.15, 124.91, 124.58, 124.26, 51.64, 36.74, 34.38, 31.81, 30.40. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{23}H_{29}O$: 321.2218. Found: 321.2208.



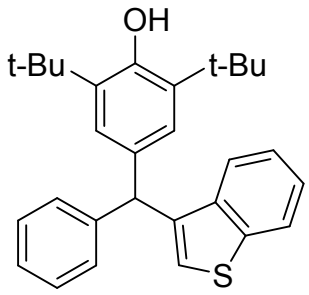
2,6-di-tert-butyl-4-(1,2,3,4-tetrahydronaphthalen-1-yl)phenol **4i**

Colorless oil, 94% yield. Analytical data for **4i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 2H), 7.05 – 6.95 (m, 1H), 6.86 (d, *J* = 6.7 Hz, 3H), 5.04 (s, 1H), 4.09 – 3.86 (m, 1H), 3.01 – 2.56 (m, 2H), 2.13 (ddd, *J* = 12.2, 10.6, 4.8 Hz, 1H), 1.96 – 1.69 (m, 3H), 1.39 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.84, 140.16, 137.82, 137.42, 135.35, 130.10, 128.77, 125.63, 125.43, 125.36, 45.63, 34.34, 33.26, 30.42, 29.82, 21.33. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{24}H_{31}O$: 335.2375. Found: 335.2371.



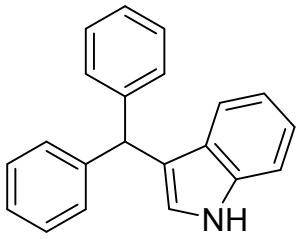
2,6-di-tert-butyl-4-(1-(3,4,5-trimethoxyphenyl)ethyl)phenol **4j**

Colourless oil, 91% yield. Analytical data for **4j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.47 (s, 2H), 5.07 (s, 1H), 3.99 (q, *J* = 7.2 Hz, 1H), 3.82 (s, 9H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.42 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.95, 152.02, 142.74, 136.44, 136.06, 135.55, 123.98, 104.64, 60.88, 56.05, 45.15, 34.42, 30.36, 22.79. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{25}H_{37}O_4$: 401.2692. Found: 401.2691.



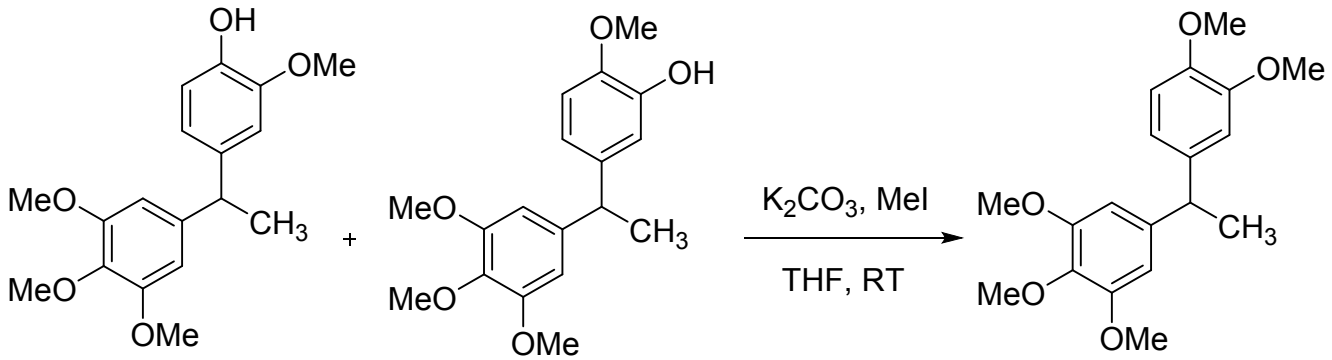
4-(benzo[*b*]thiophen-3-yl(phenyl)methyl)-2,6-di-tert-butylphenol **4k**

Yellow oil, 88% yield. Analytical data for **4k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.35 – 7.11 (m, 7H), 6.96 (s, 2H), 6.74 (s, 1H), 5.65 (s, 1H), 5.09 (s, 1H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.30, 143.22, 140.68, 140.10, 138.68, 135.61, 133.23, 128.99, 128.34, 126.34, 125.69, 124.70, 124.11, 123.81, 122.86, 122.71, 51.35, 34.35, 30.34. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{29}H_{31}OS$: 427.2096. Found: 427.2094.

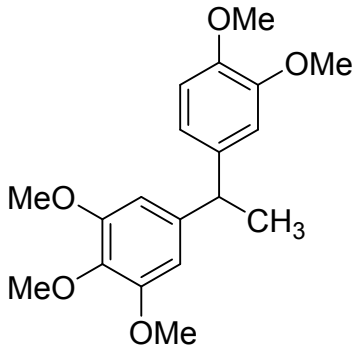


3-benzhydryl-1H-indole **4l**

Colourless oil, 88% yield. Analytical data for **4l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (br, 1H), 7.30 – 7.04 (m, 13H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 1.4 Hz, 1H), 5.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.88, 135.65, 127.96, 127.23, 125.94, 125.18, 123.01, 121.06, 118.88, 118.35, 109.99, 98.93, 47.76. HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{21}H_{18}N$: 284.1439. Found: 284.1445.



To a solution of **4m** and **4n** in THF was added K_2CO_3 (2 equiv) and MeI (2.5 equiv), and the reaction was stired at room temperature until the starting compounds were disappeared. Then 30ml water was added to the solution and extracted with EA. And the extracts were evaporated, then the residue was purified by by silica gel column chromatography to afford **4o**.

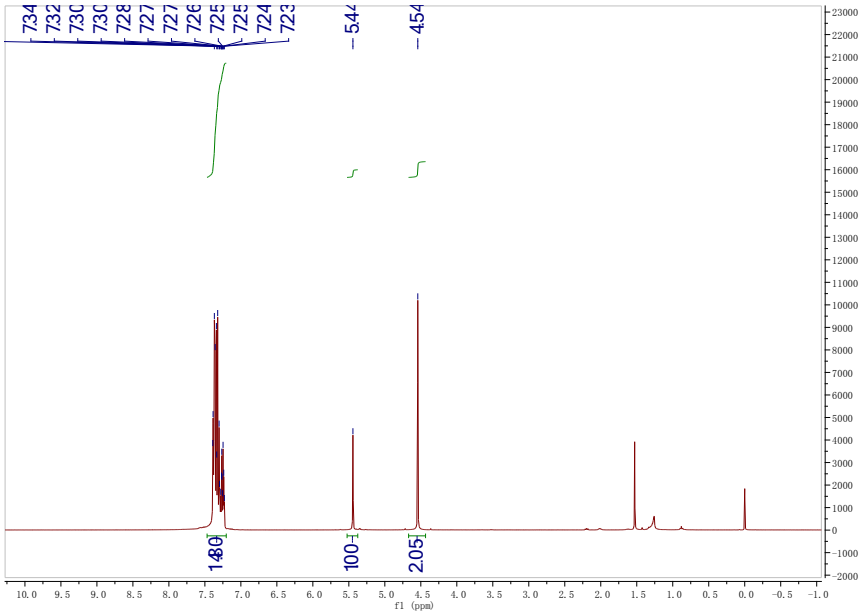


5-(1-(3,4-dimethoxyphenyl)ethyl)-1,2,3-trimethoxybenzene **4o**

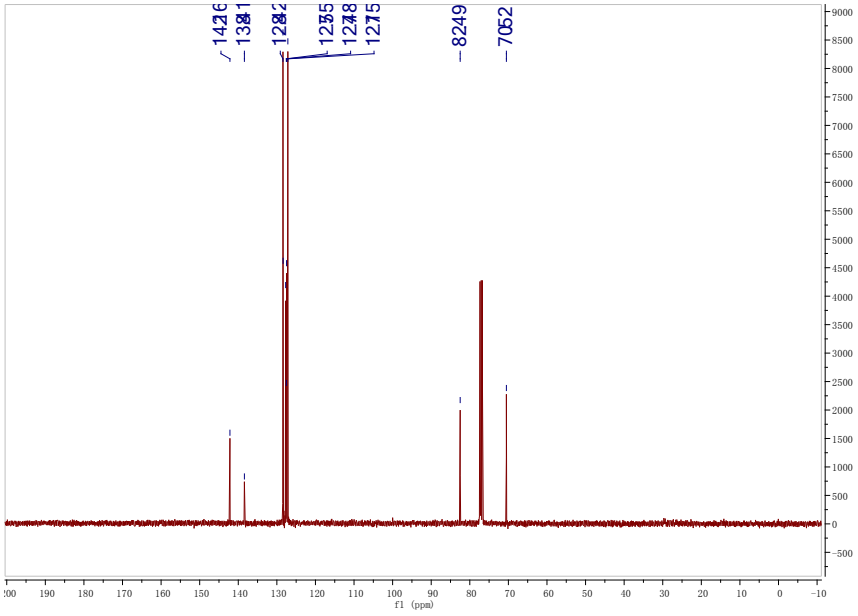
Colorless oil, 92% yield. Analytical data for **4o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (dt, *J* = 8.3, 5.0 Hz, 2H), 6.66 (d, *J* = 1.6 Hz, 1H), 6.35 (s, 2H), 3.96 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 3.74 (s, 6H), 1.53 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.01, 147.73, 146.35, 141.31, 137.72, 135.18, 118.23, 110.12, 109.99, 103.59, 59.81, 55.05, 54.85, 43.53, 21.25. HRMS (ESI) m/z $[M-H]^-$: Calcd for $C_{19}H_{24}O_5Na$: 355.1521. Found: 355.1510.

NMR Spectra

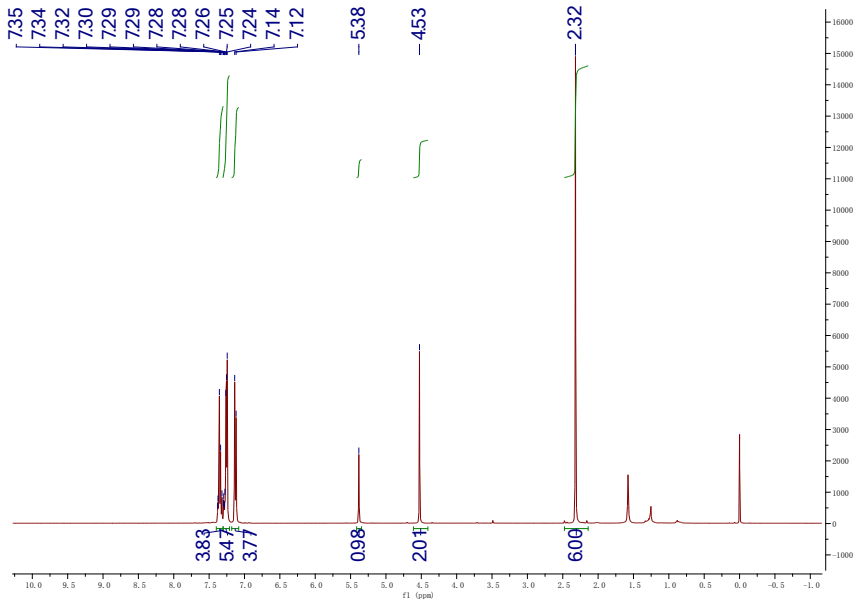
2a ^{1}H NMR



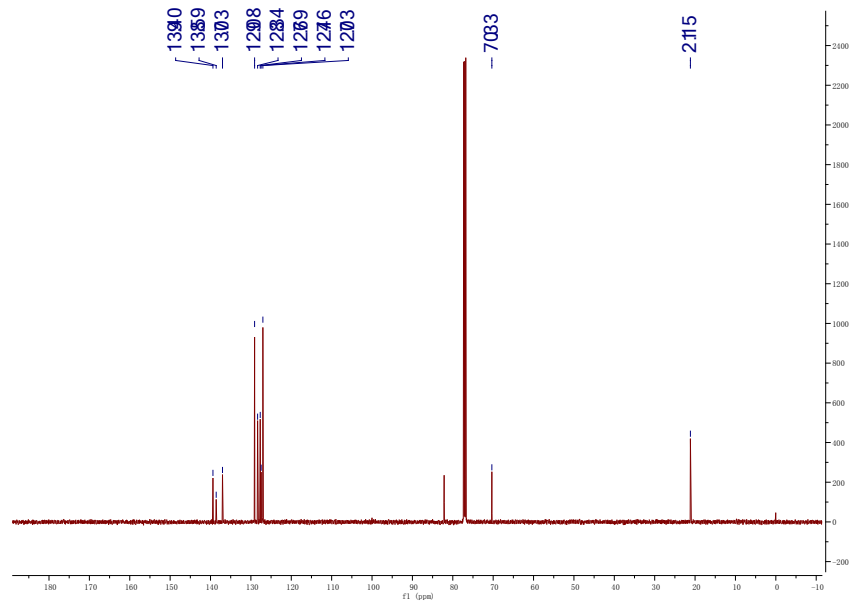
2a ^{13}C NMR



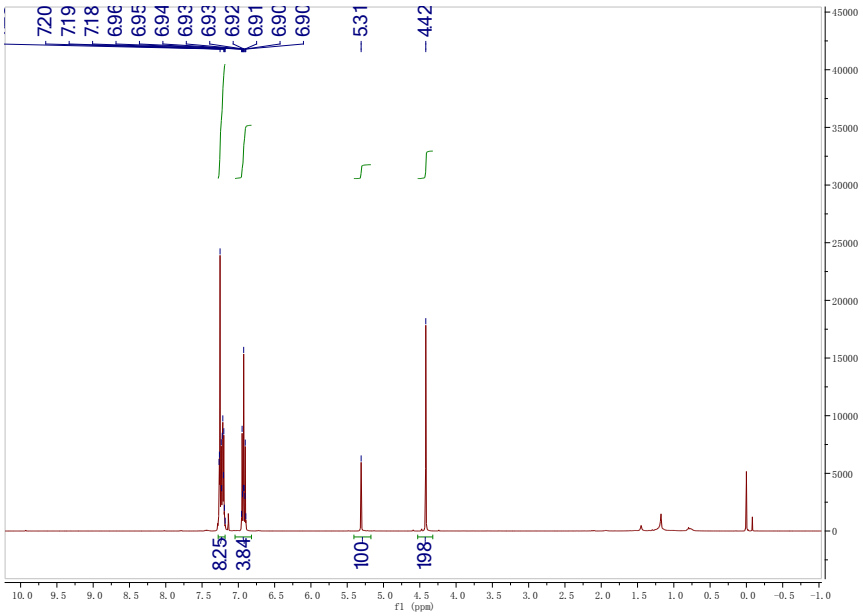
2b ^{1}H NMR



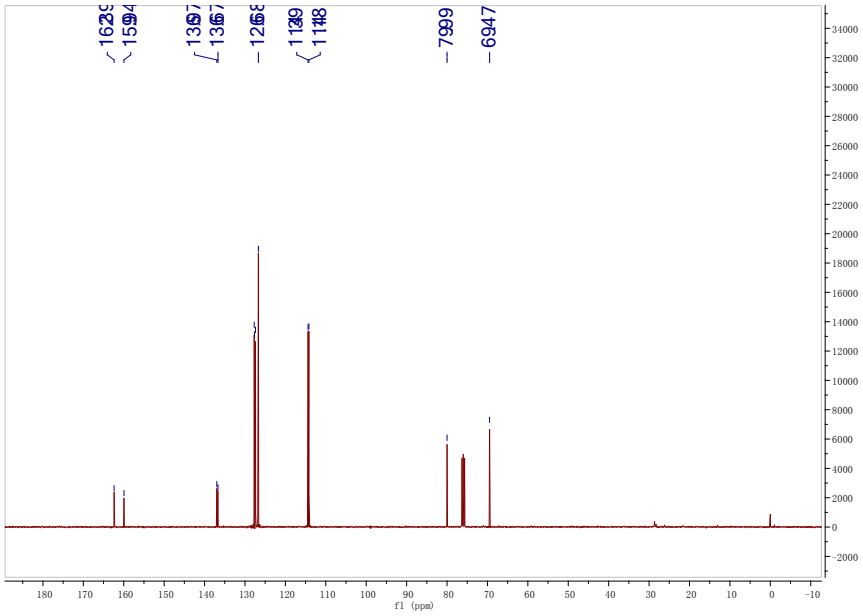
2b ^{13}C NMR



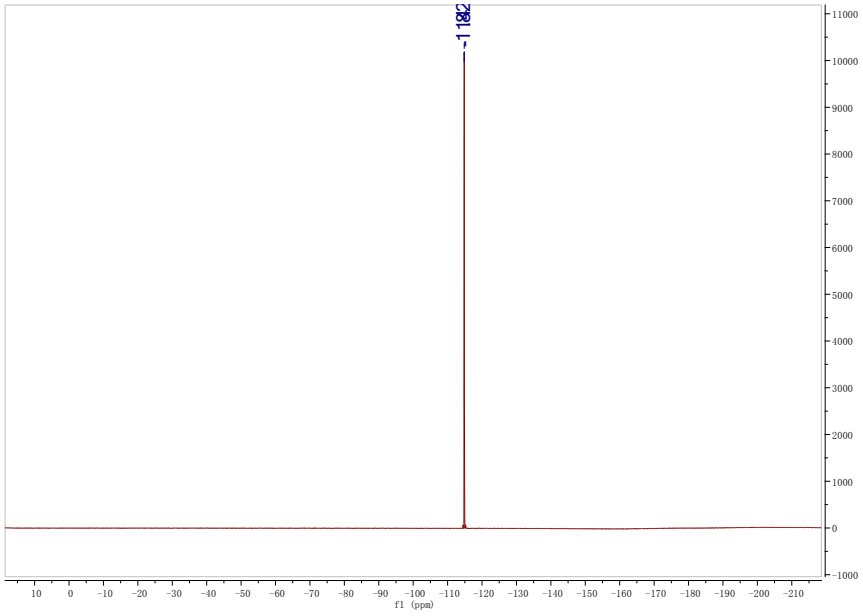
2c ^{1}H NMR



2c ^{13}C NMR



2c ^{19}F NMR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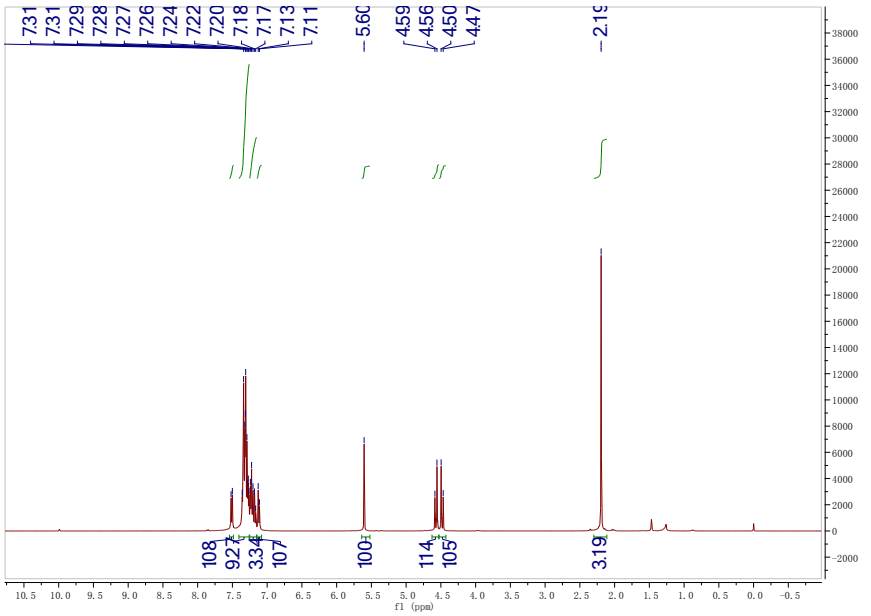
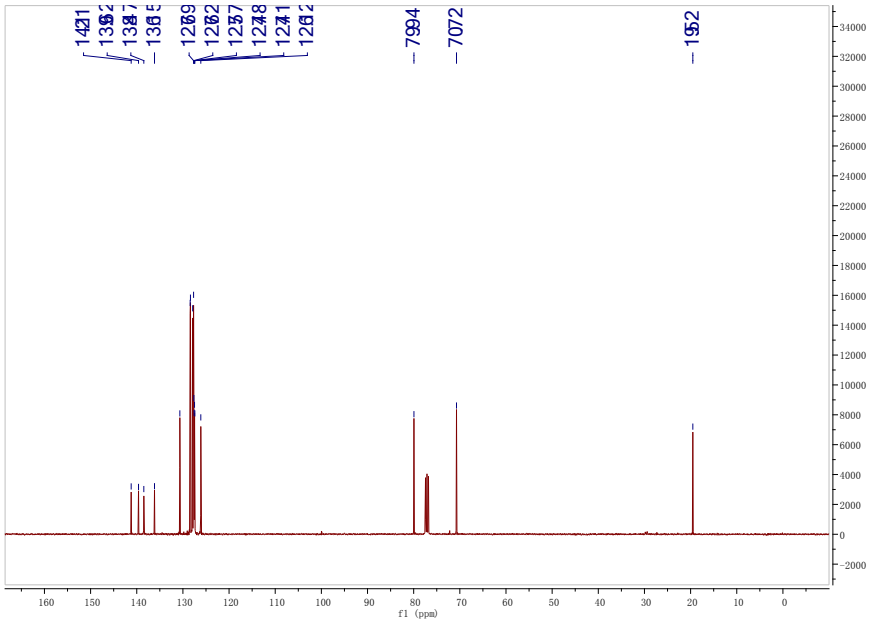
f1 (ppm)

2d ^{1}H NMR



2d ^{13}C NMR



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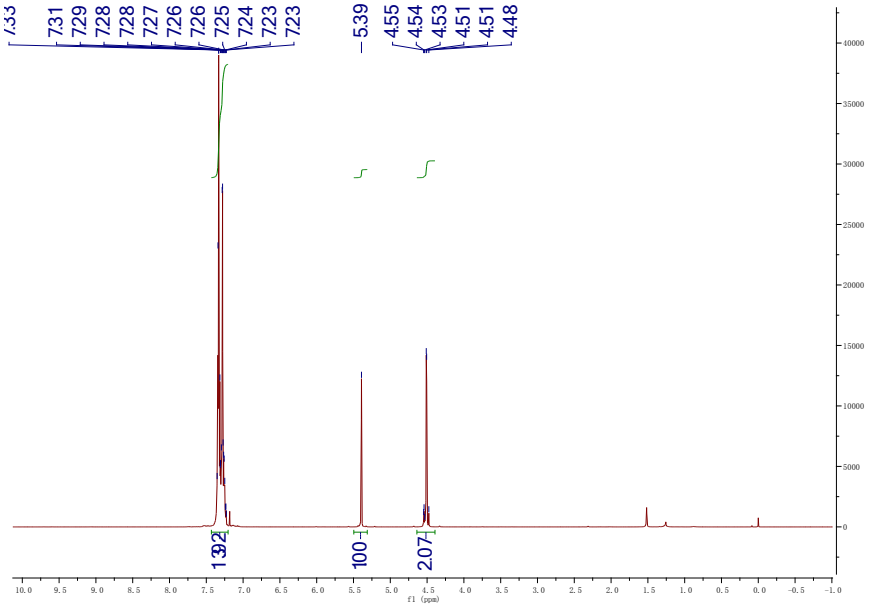

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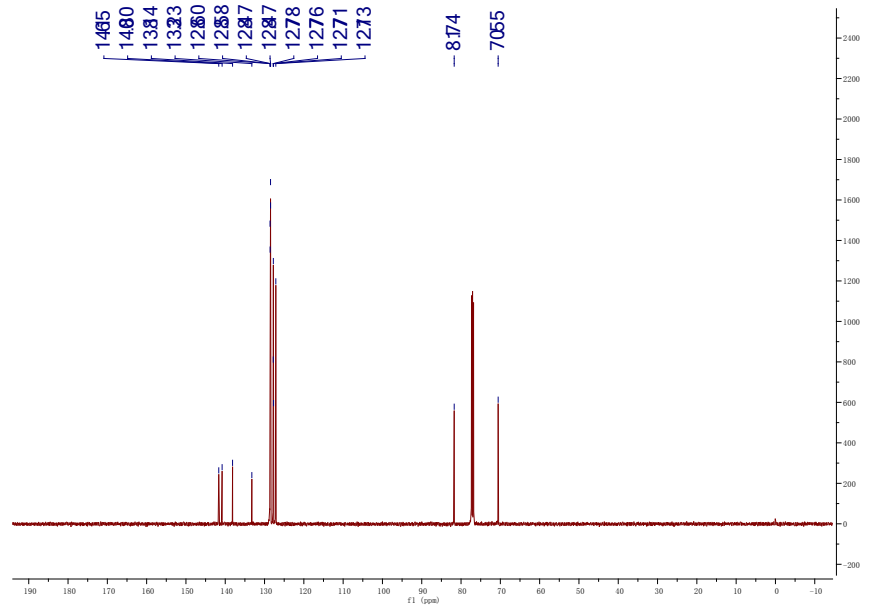

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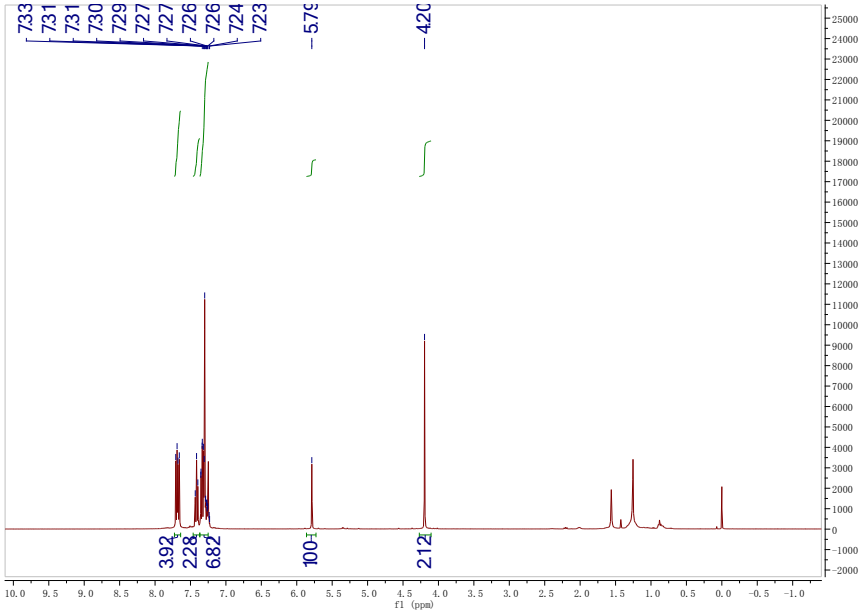
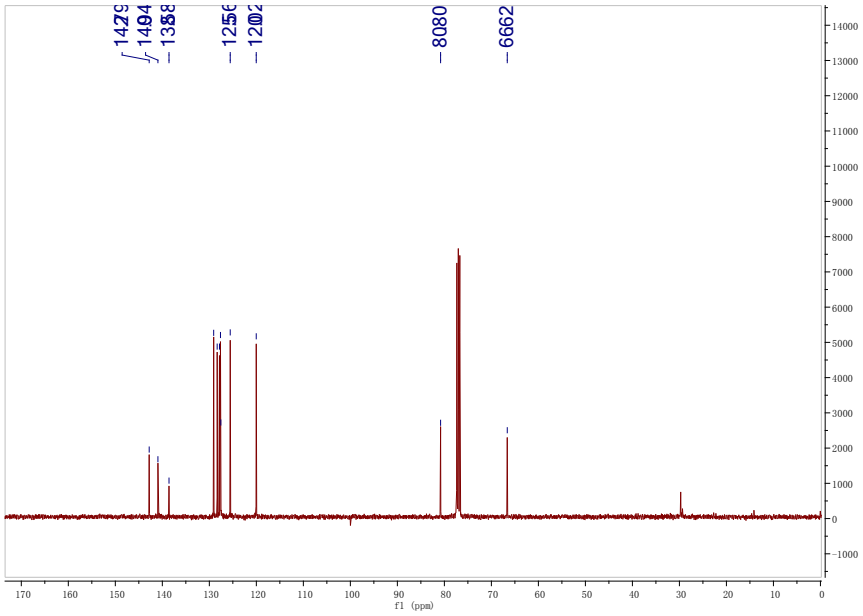
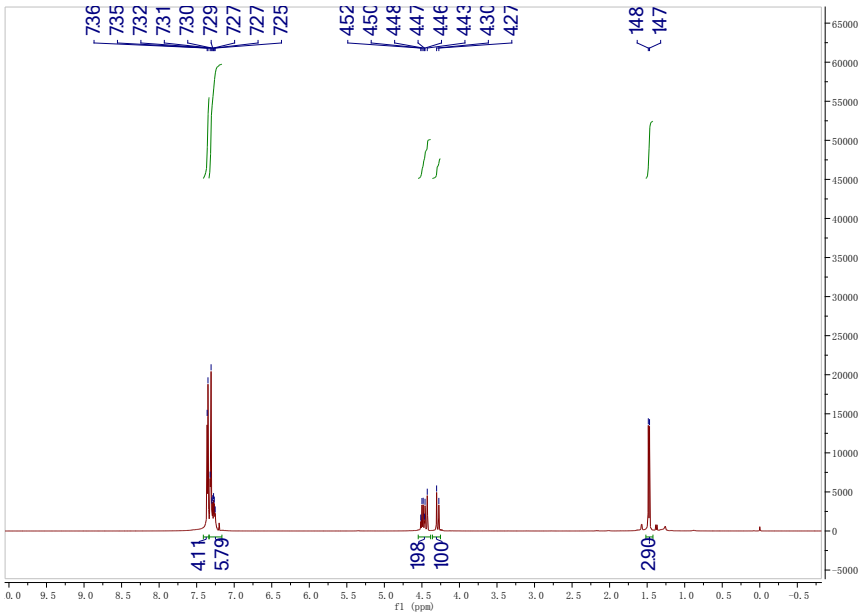


2f ^{13}C NMR



2g ^{1}H NMR



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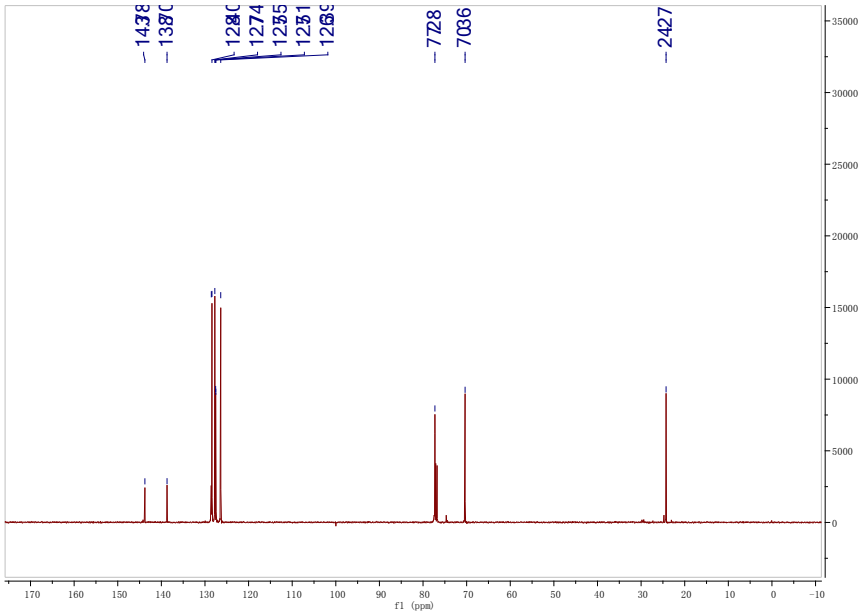

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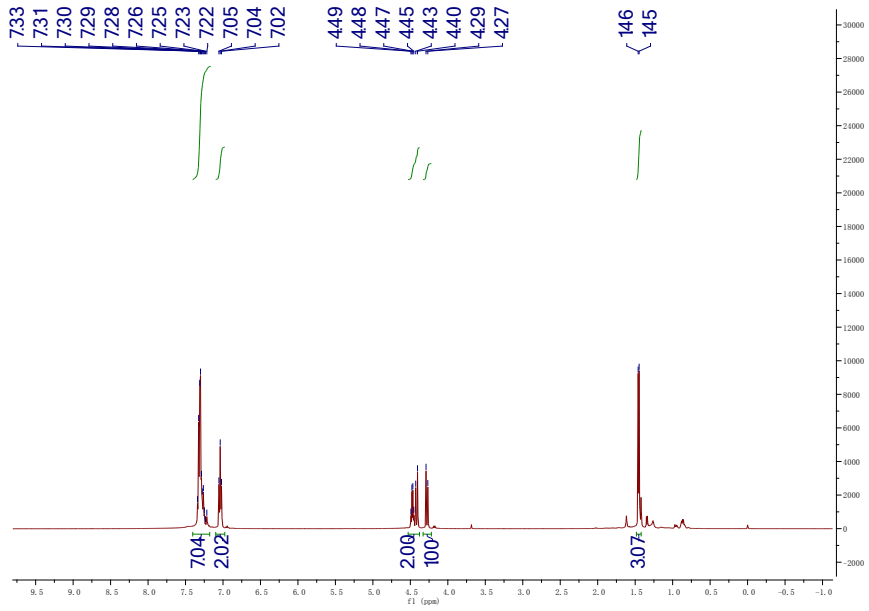

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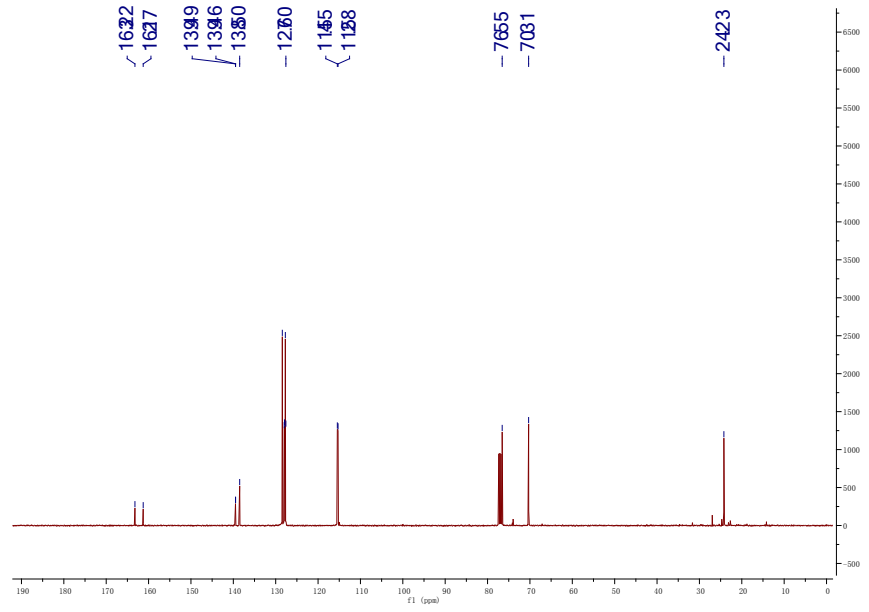
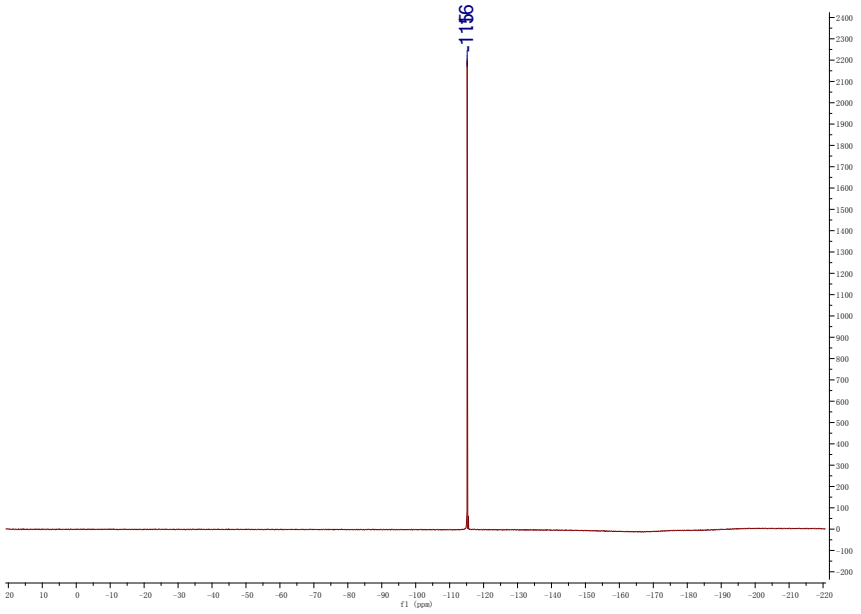


2h ^{19}F NMR



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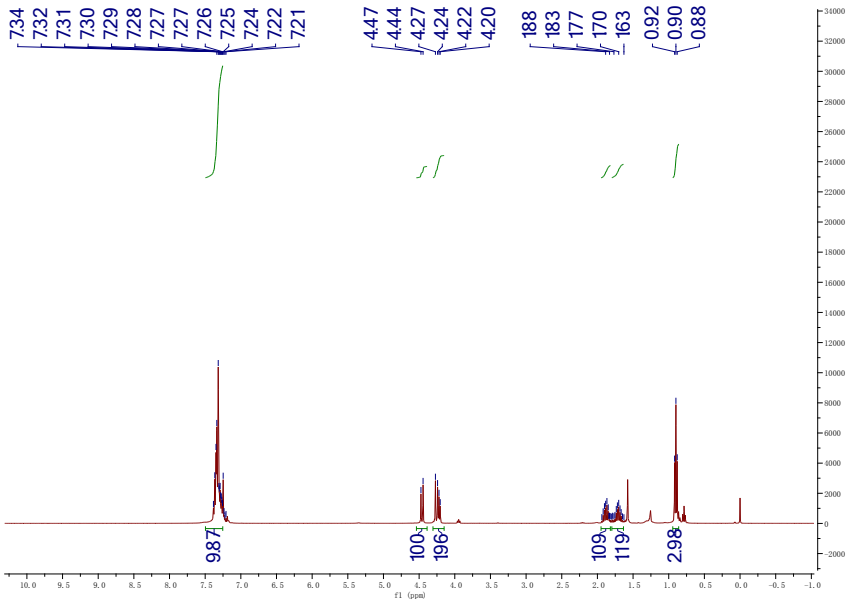

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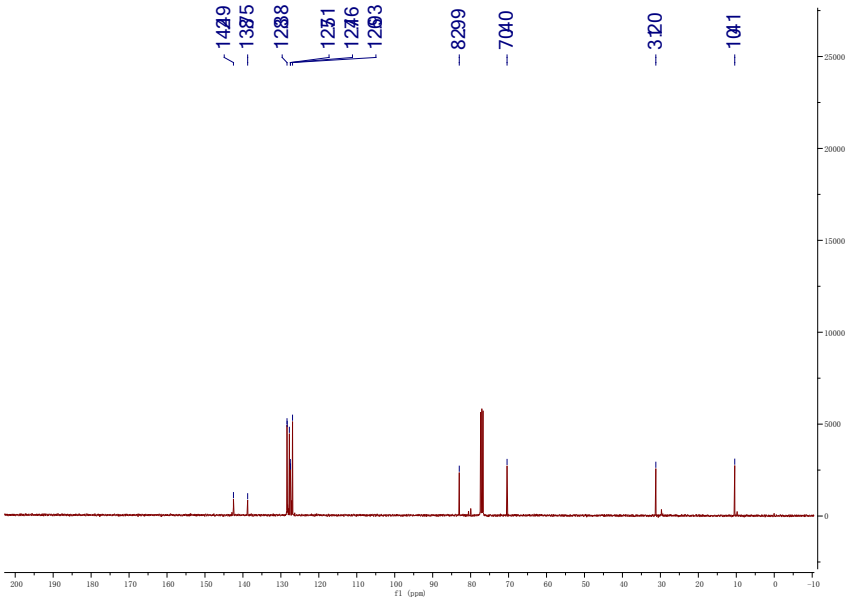

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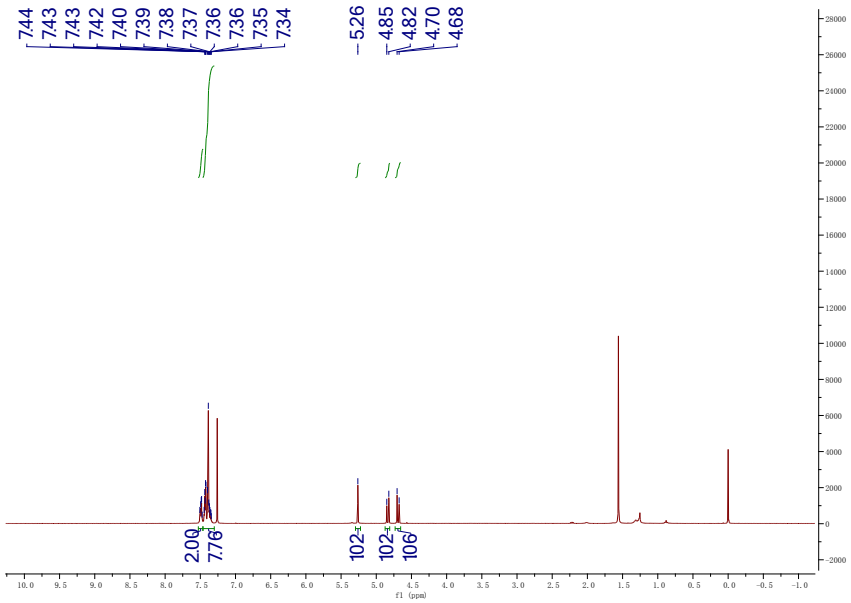

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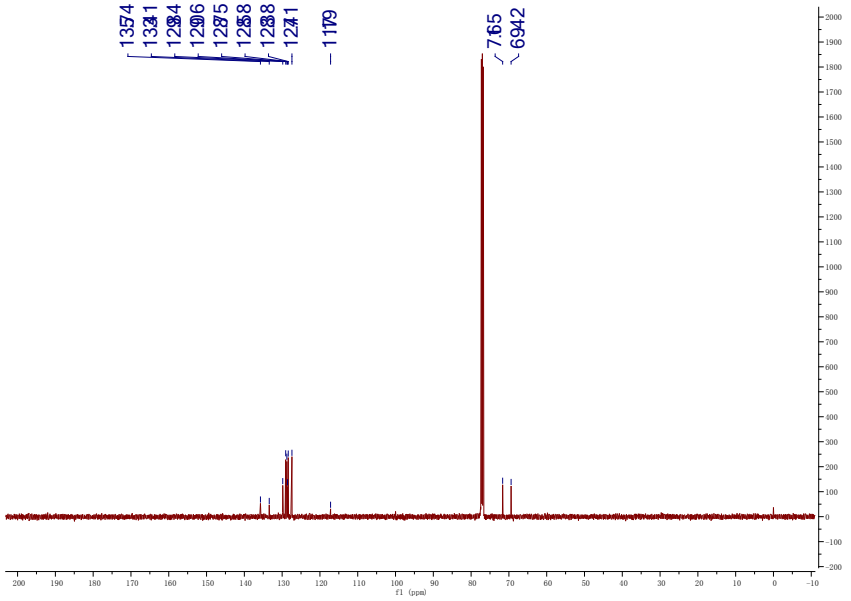
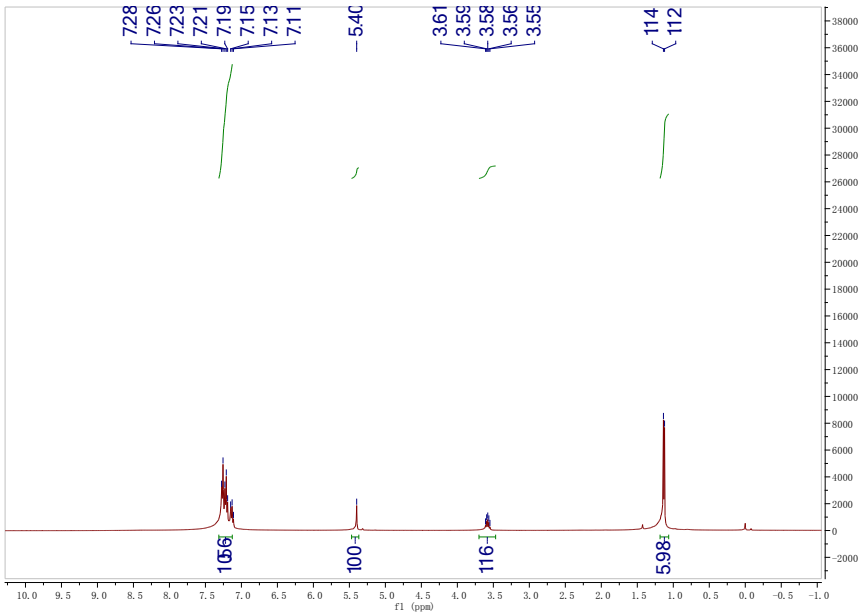


2k ^{1}H NMR



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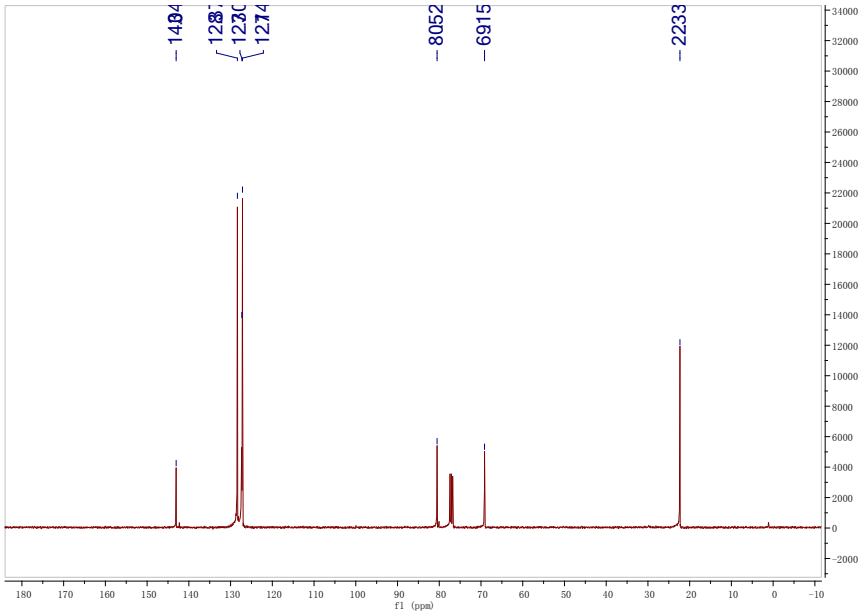

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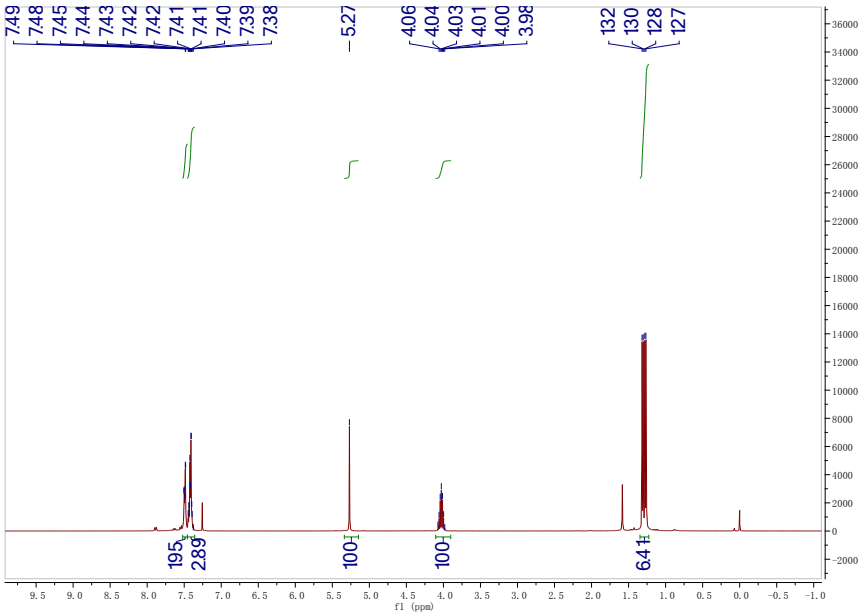

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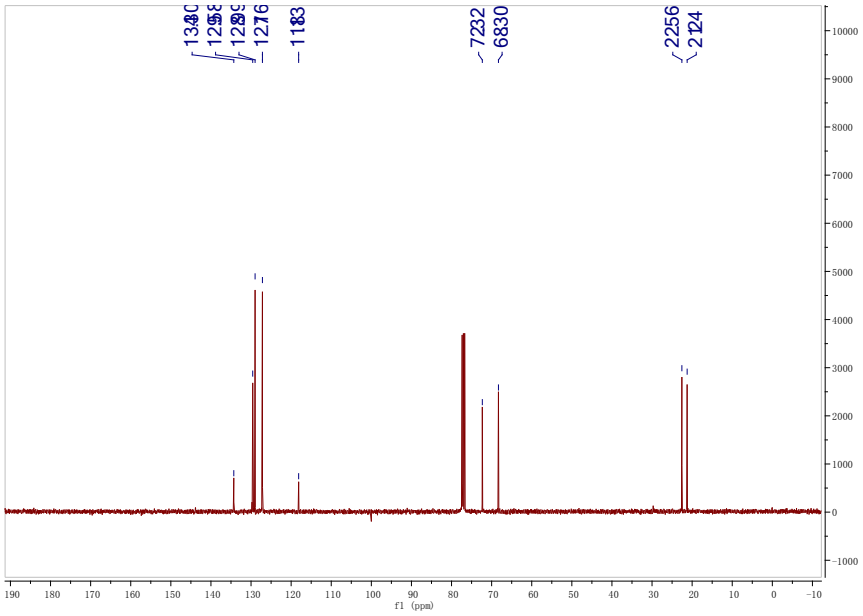
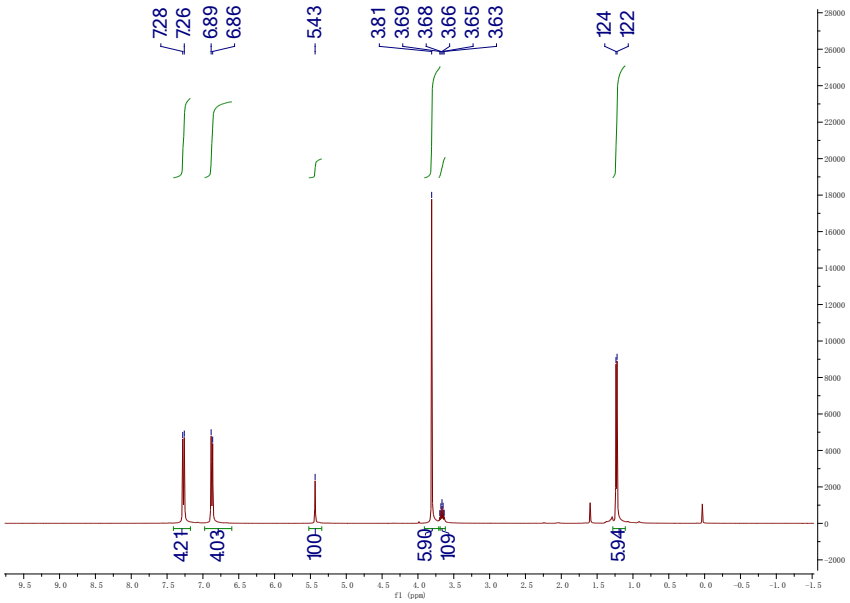


2m ^{1}H NMR



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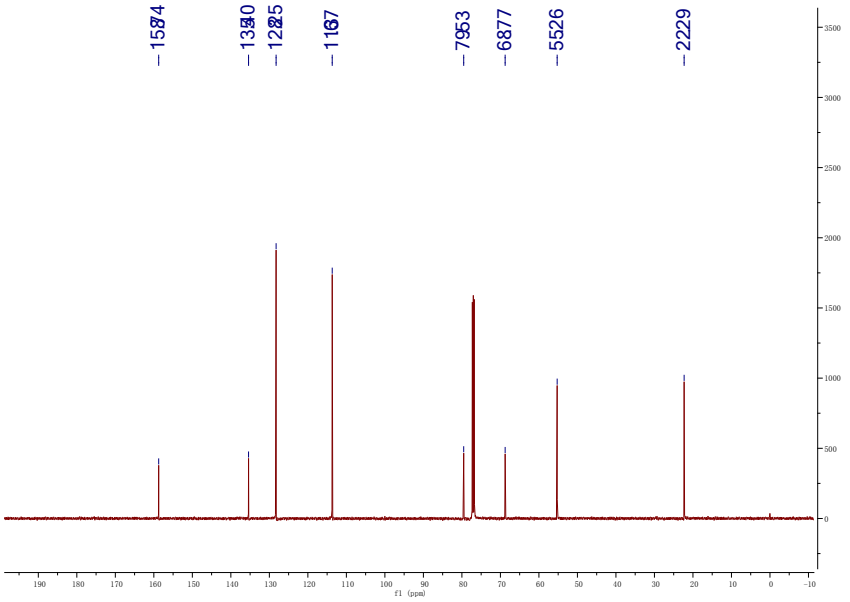

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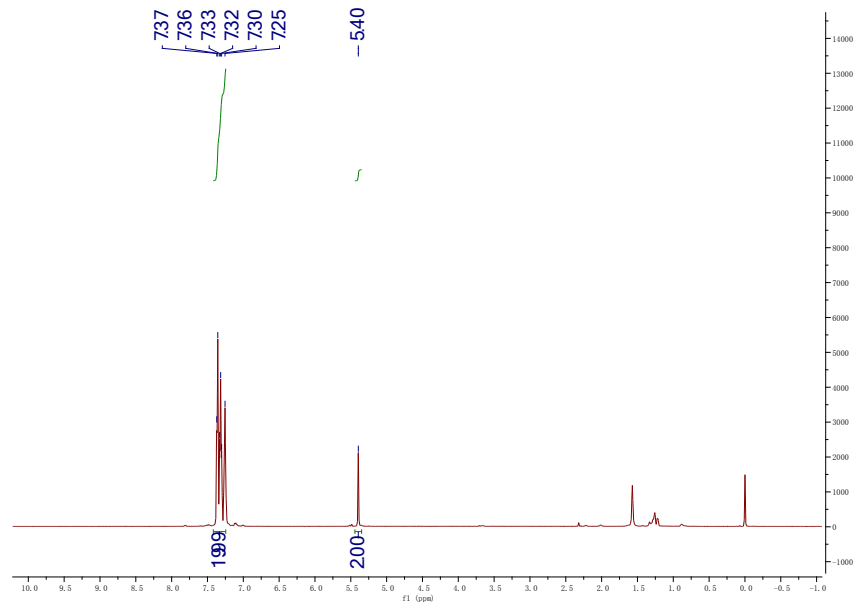

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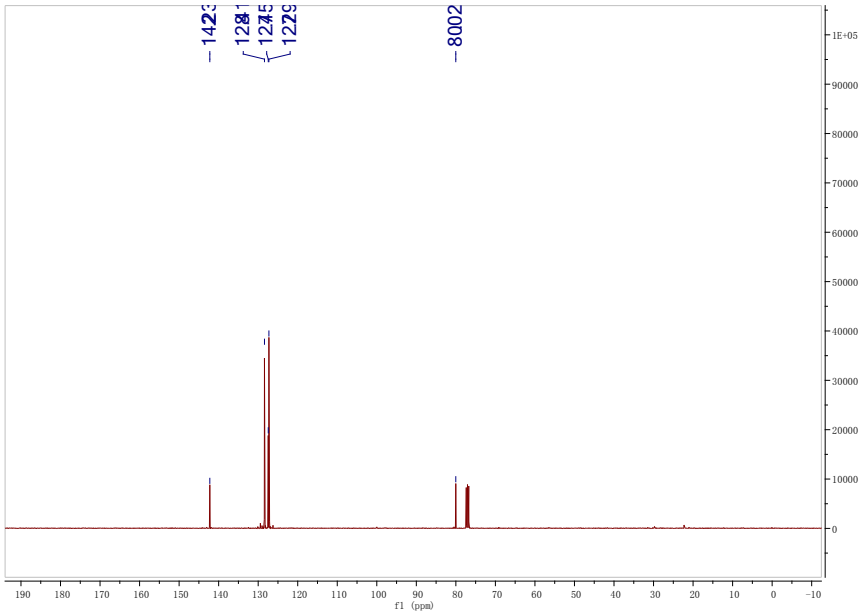
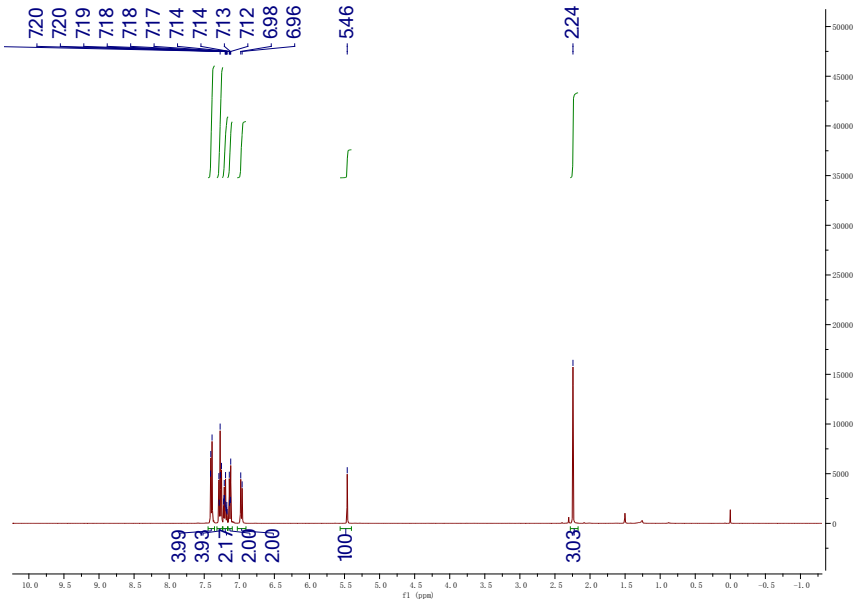
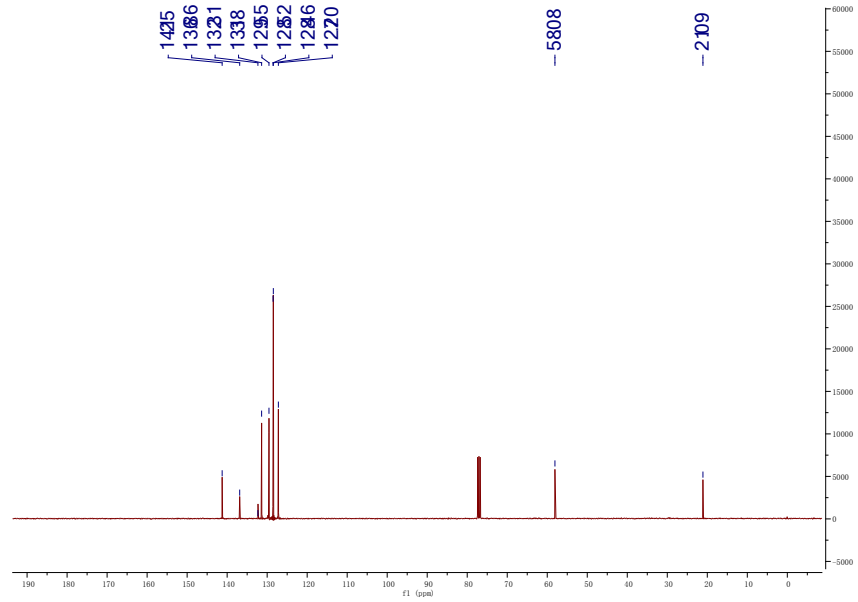


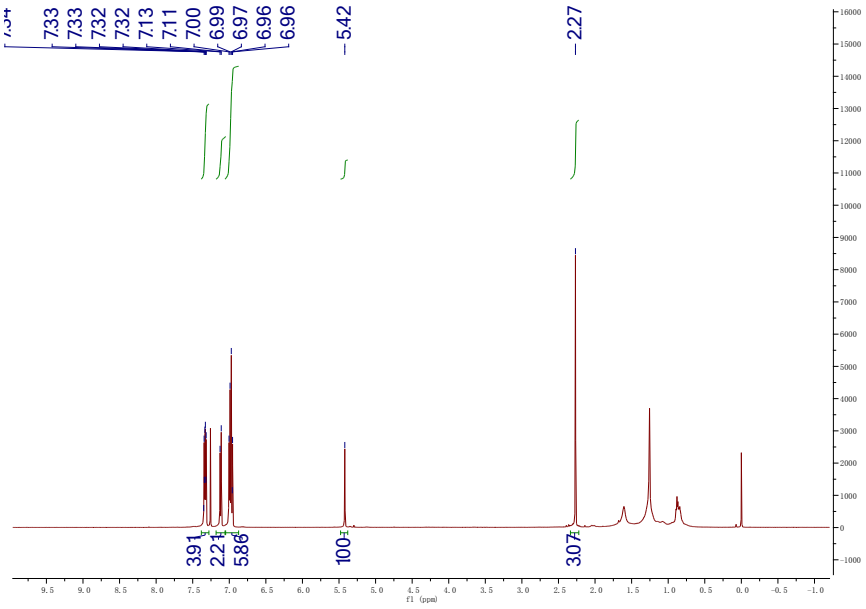
3a ^{1}H NMR



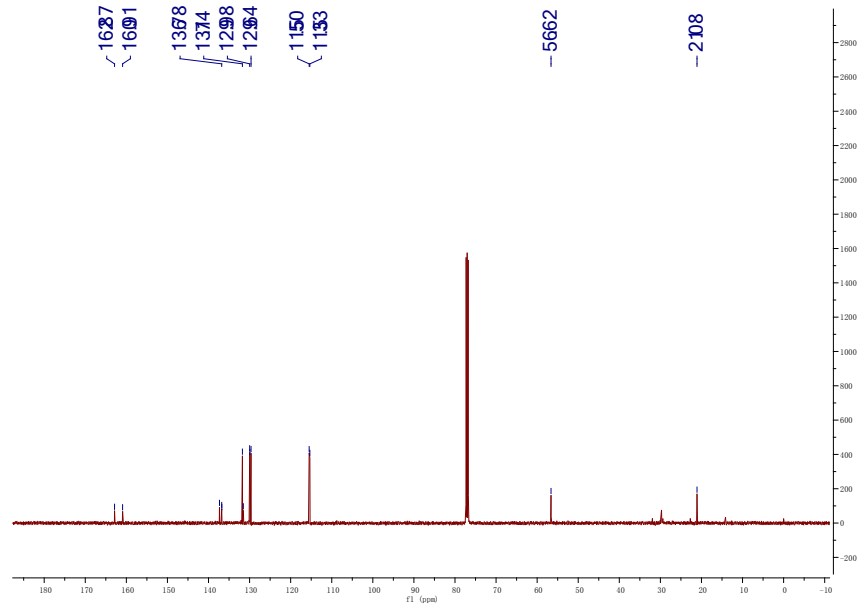
3a ^{13}C NMR



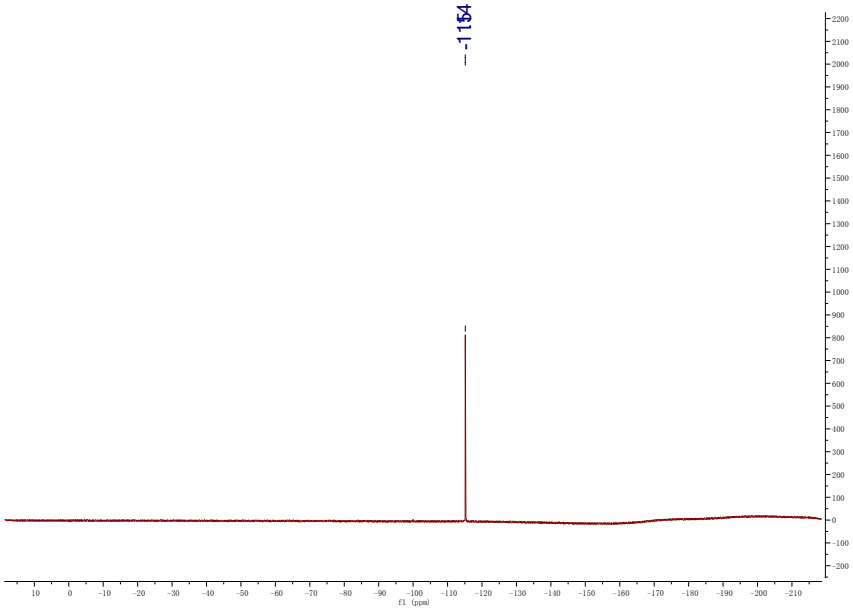
3b ^{1}H NMR



3b ^{13}C NMR



3b ^{19}F NMR



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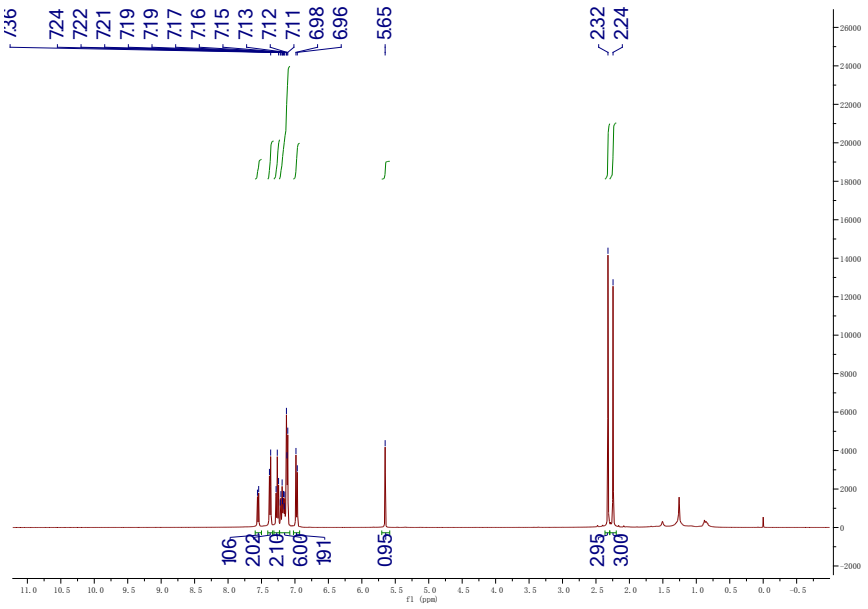

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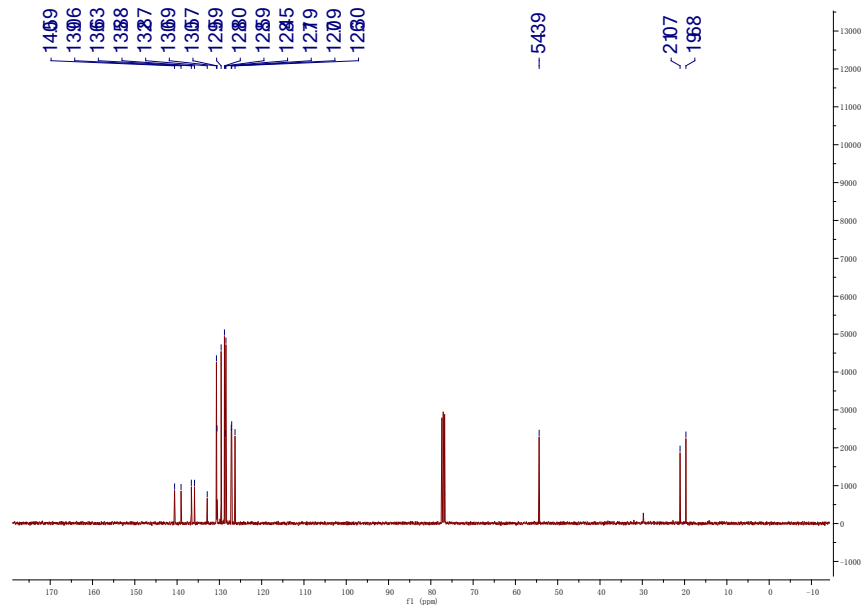
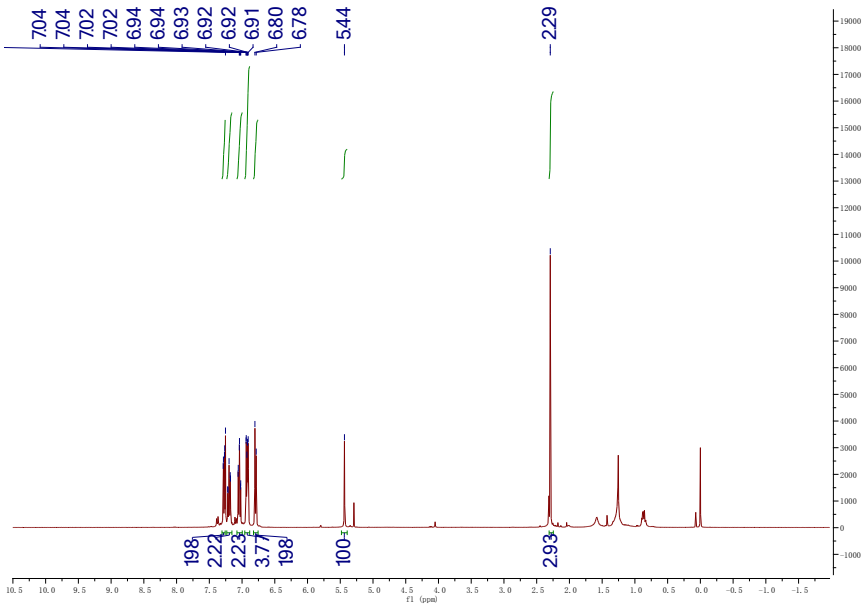


3d ^{1}H NMR



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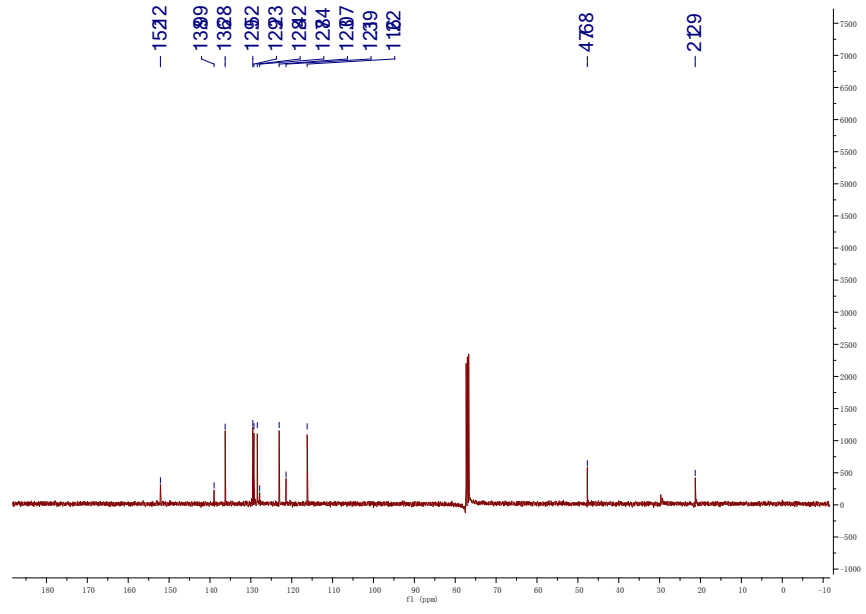

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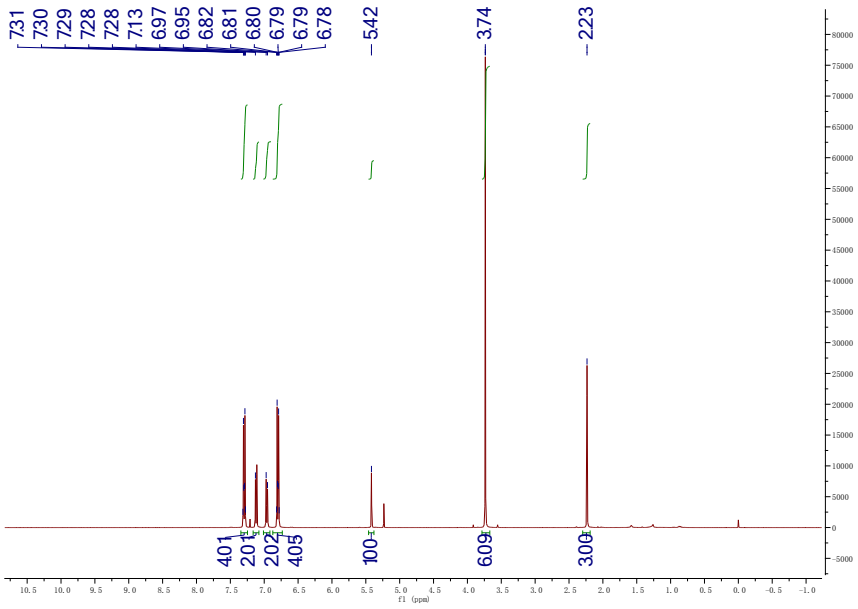

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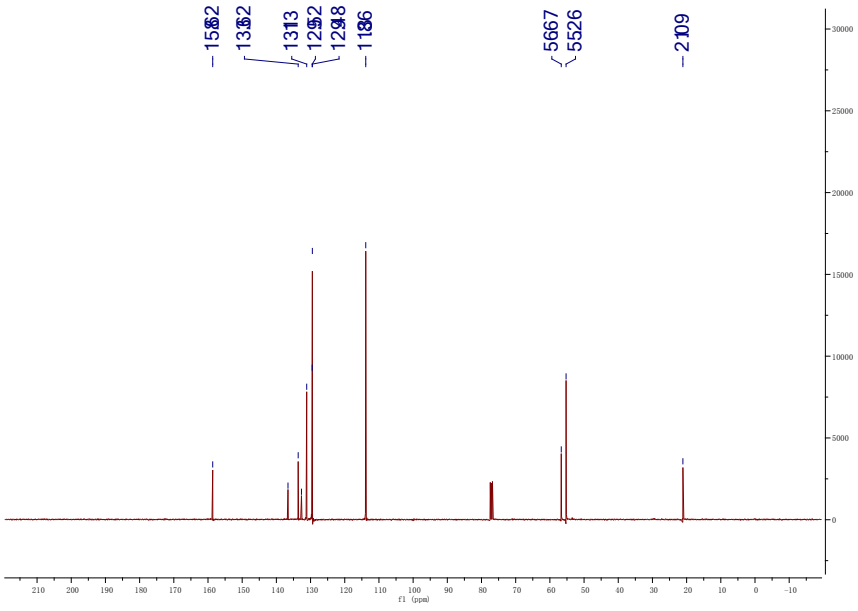
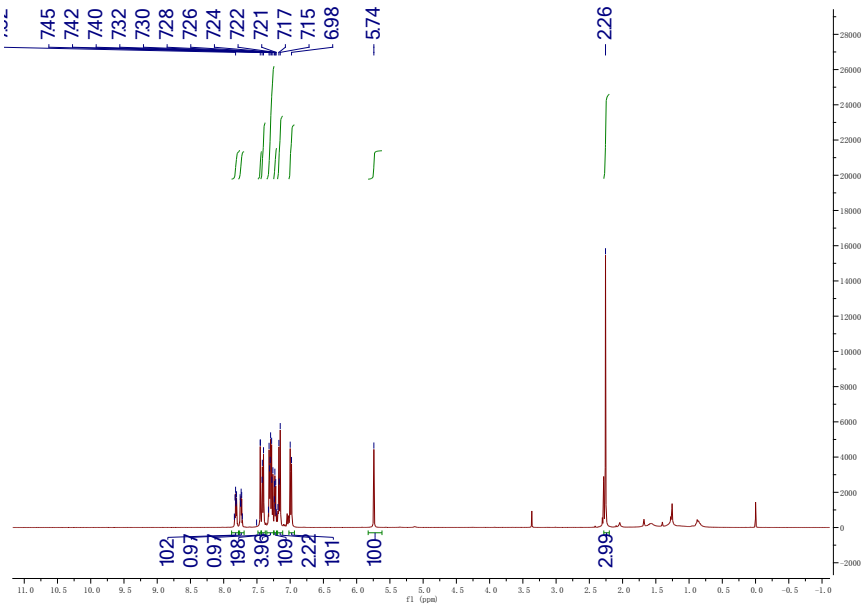
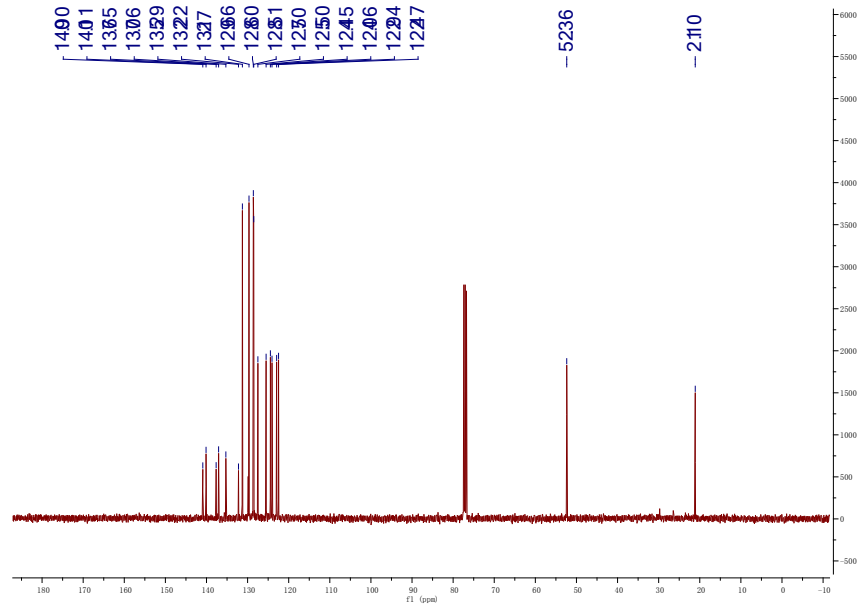


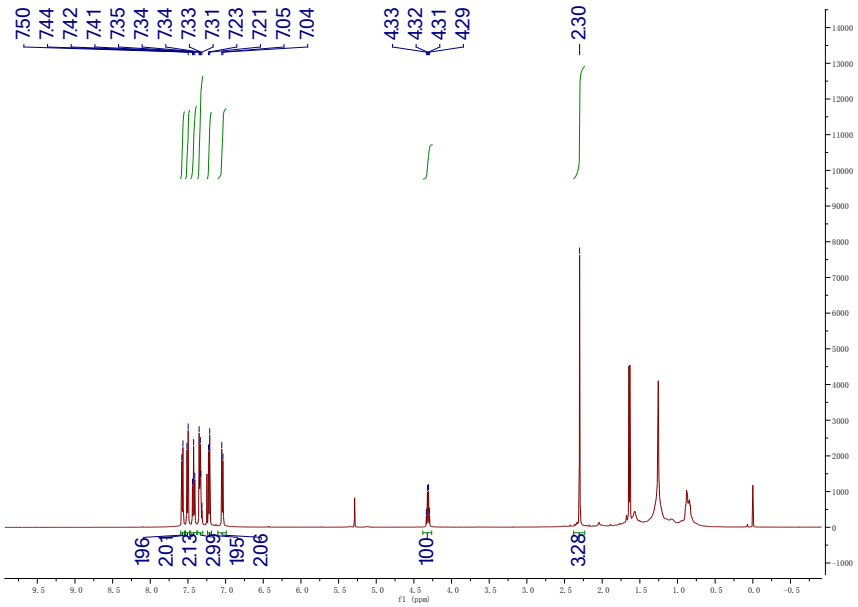
3f ^{1}H NMR



3f ^{13}C NMR



3g ^{1}H NMR



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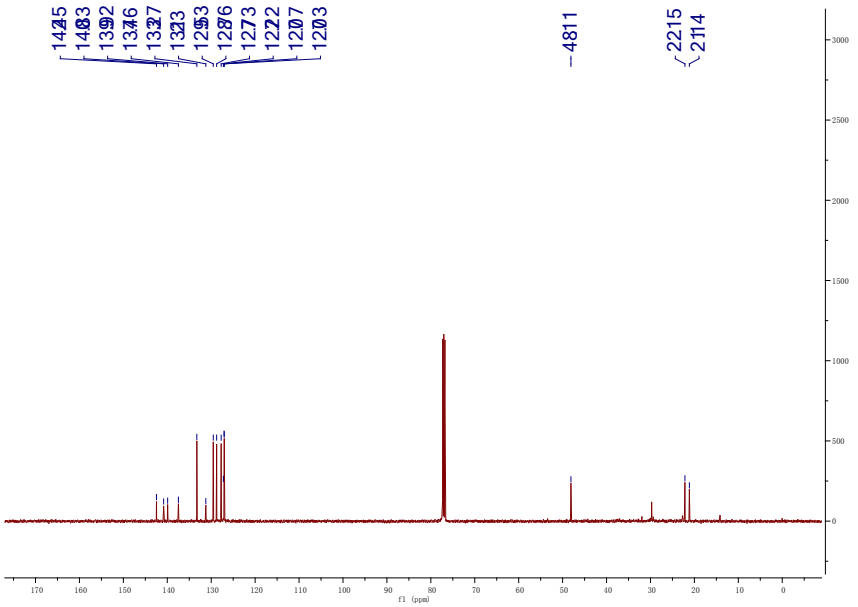
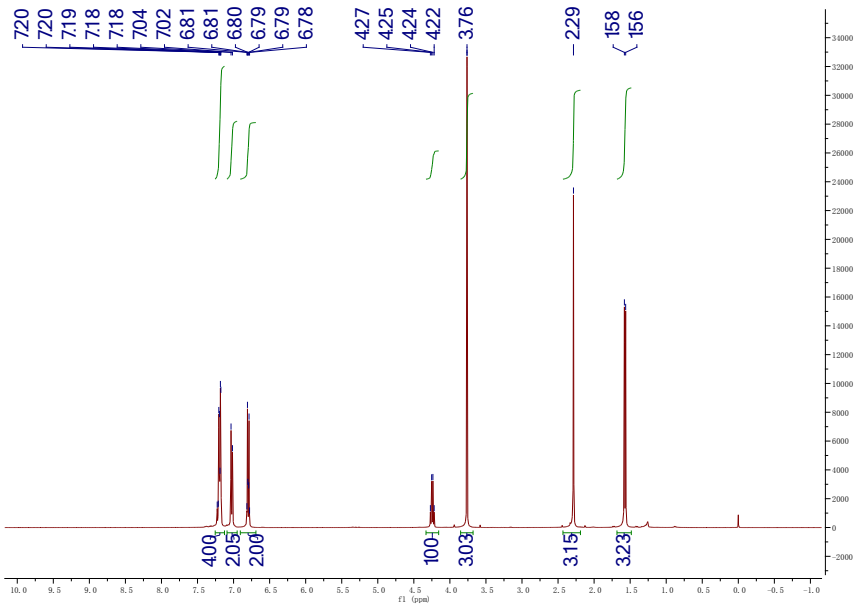
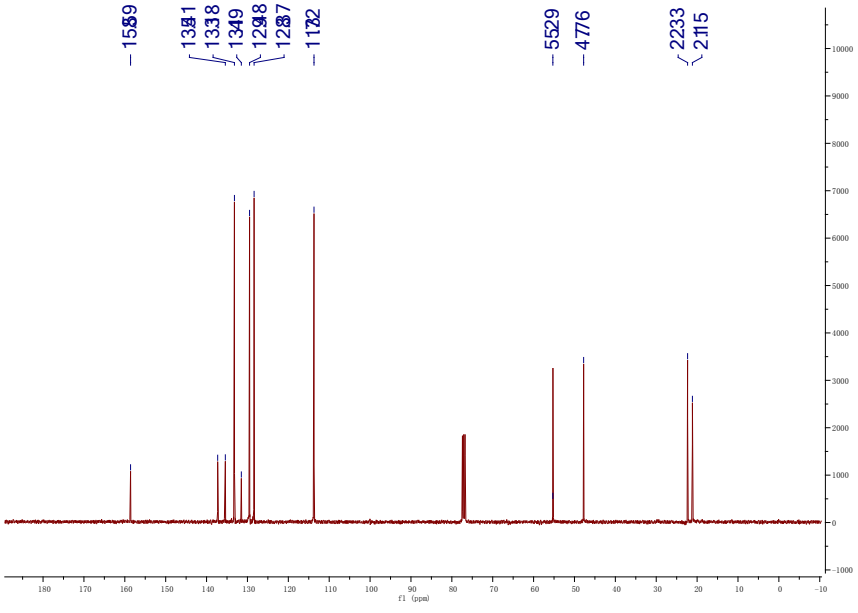


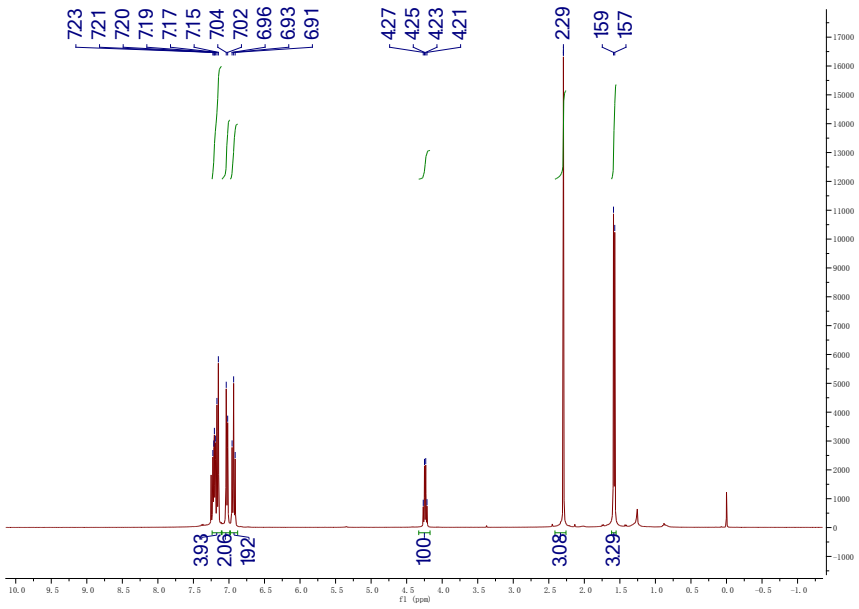
3h ^{1}H NMR



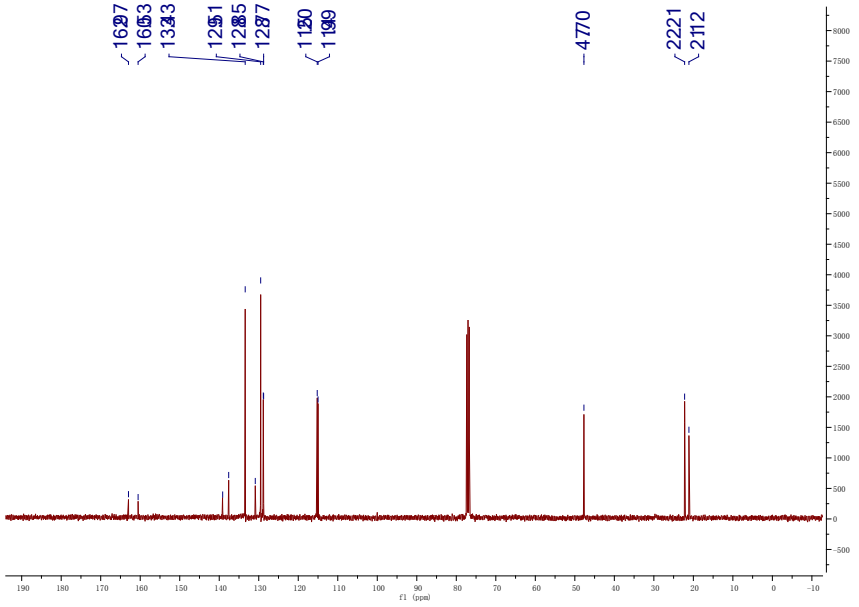
3h ^{13}C NMR



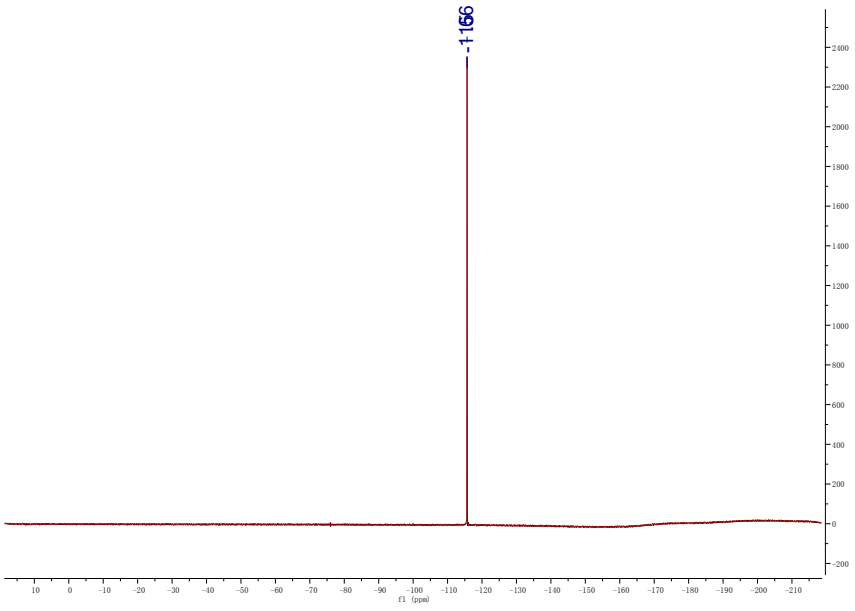
3i ^{1}H NMR



3i ^{13}C NMR



3i ^{19}F NMR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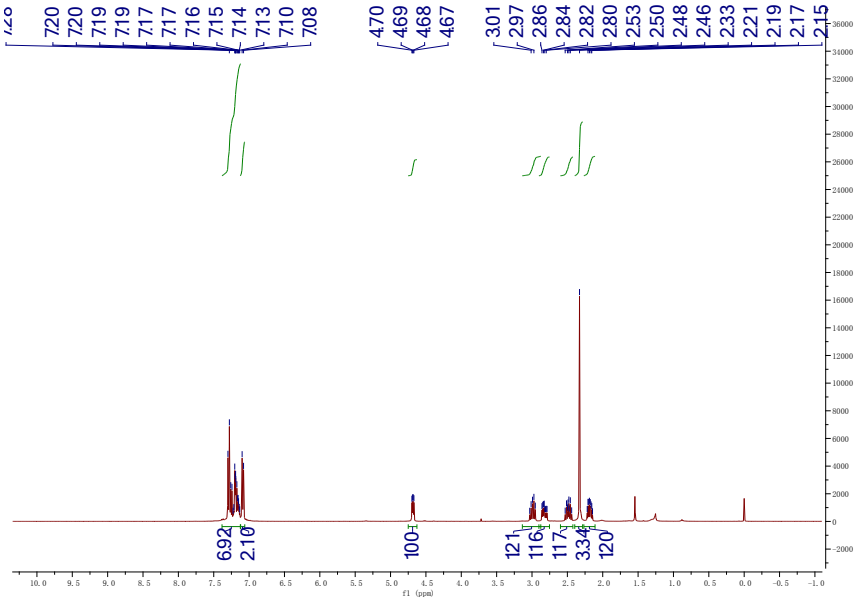
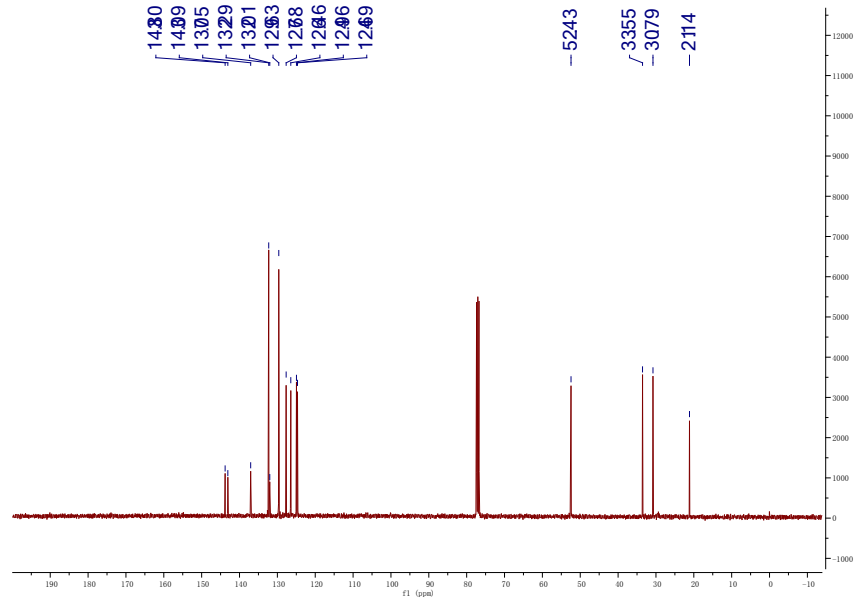
f1 (ppm)

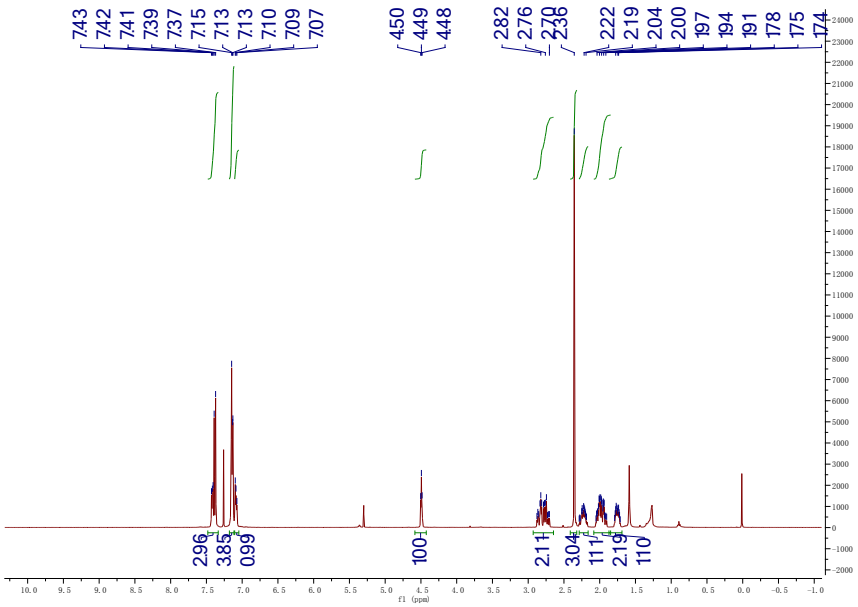
3j ^{1}H NMR



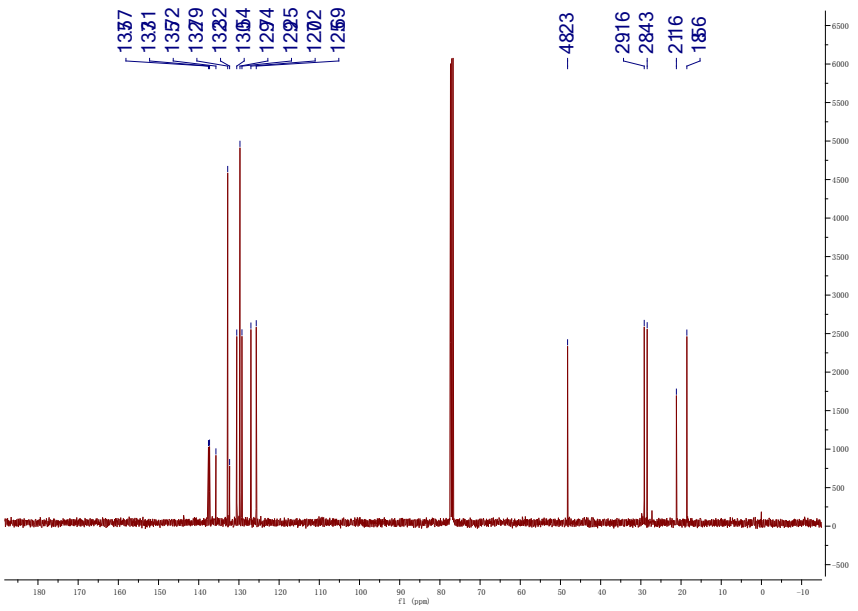
3j ^{13}C NMR



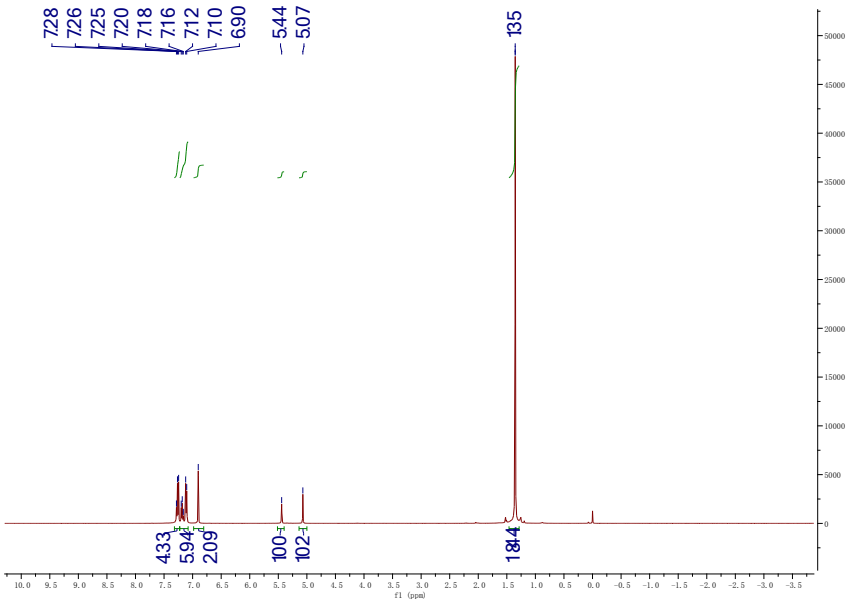
3k ^{1}H NMR



3k ^{13}C NMR



4a ^{1}H NMR



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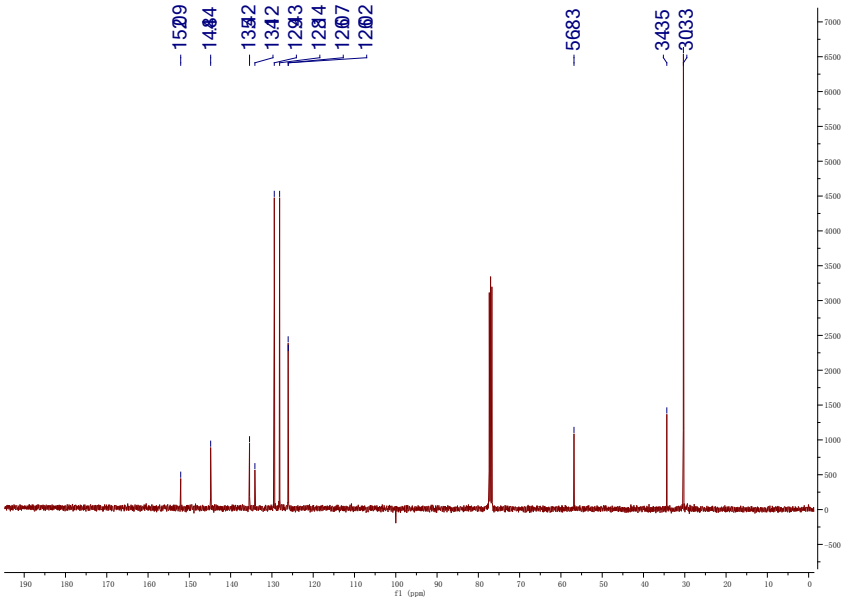

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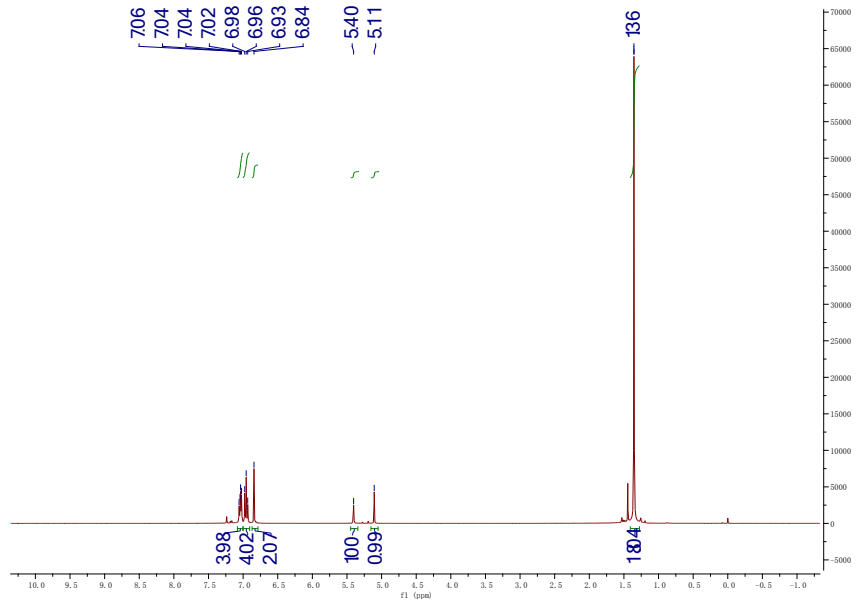
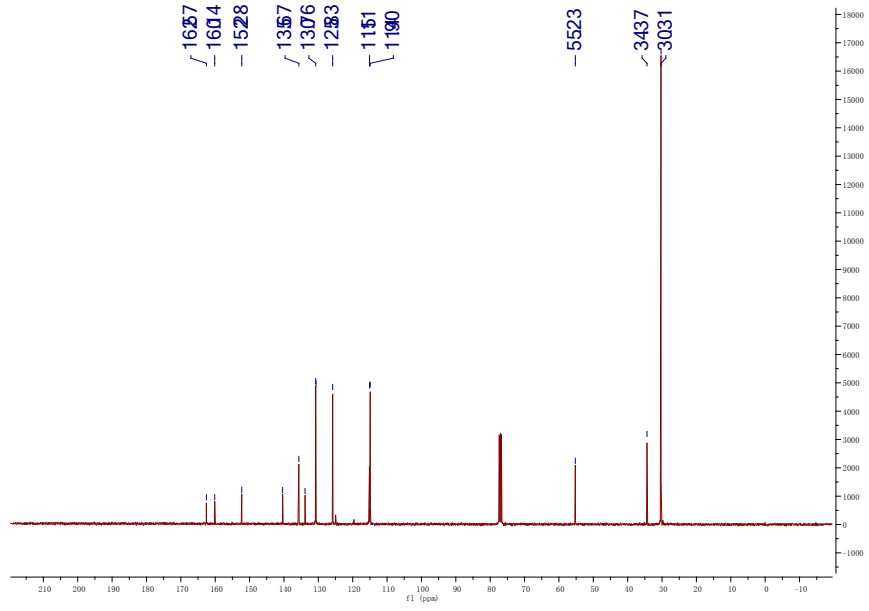
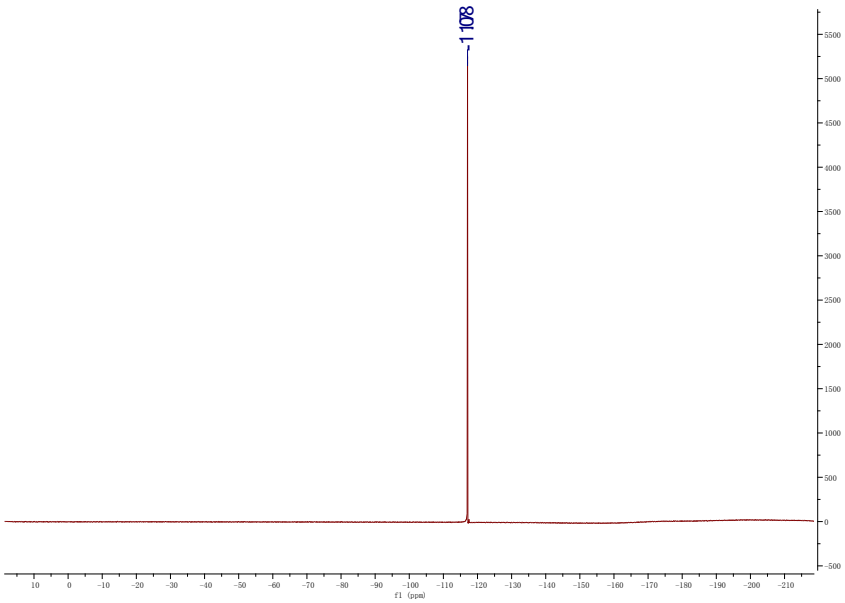


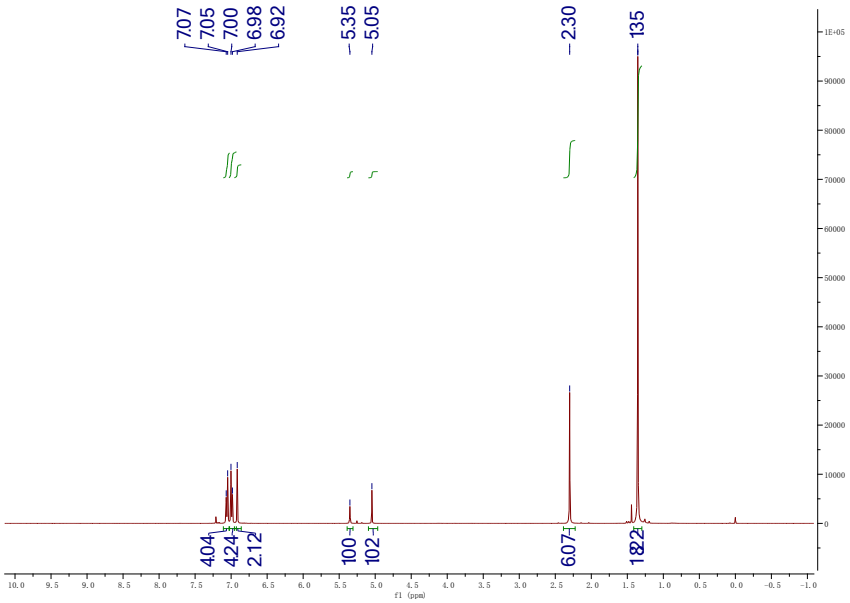
4b ^{13}C NMR



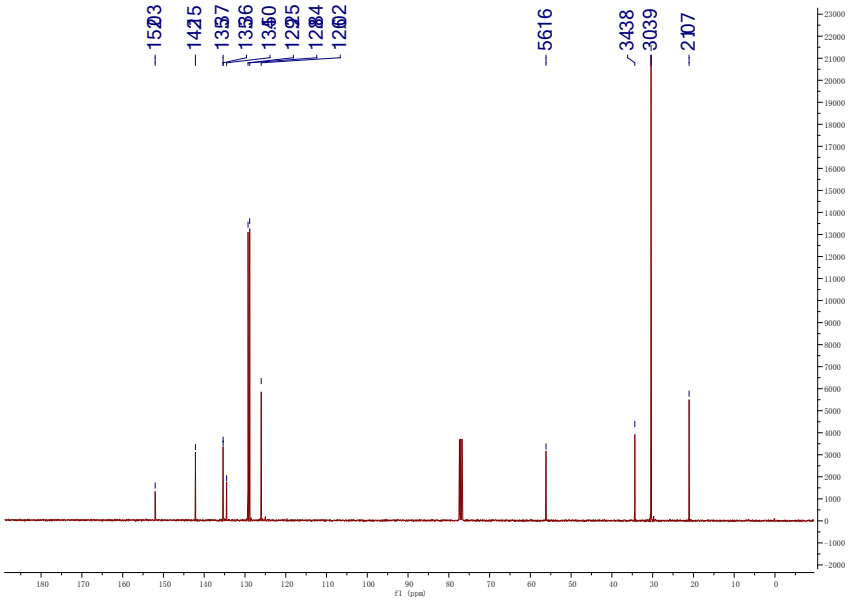
4b ^{19}F NMR


-110.78
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)

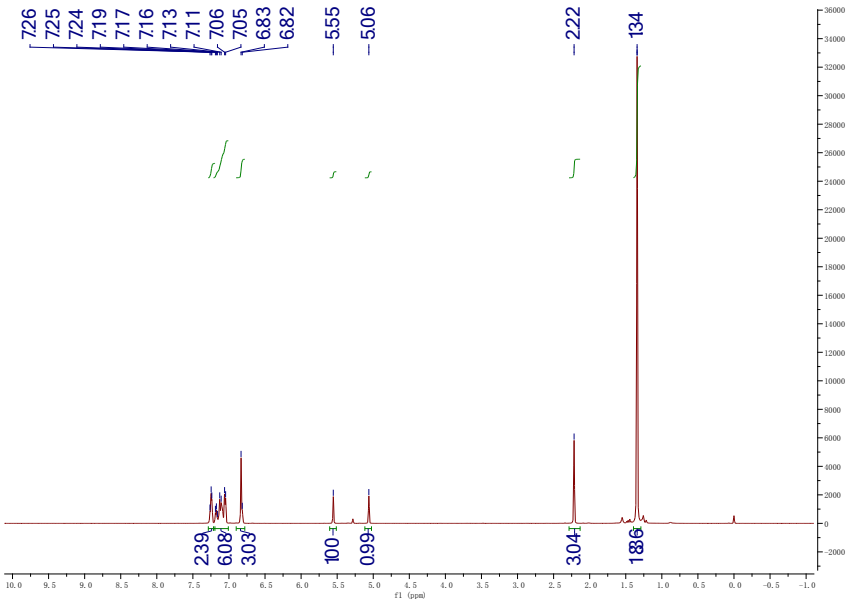
4c ^{1}H NMR



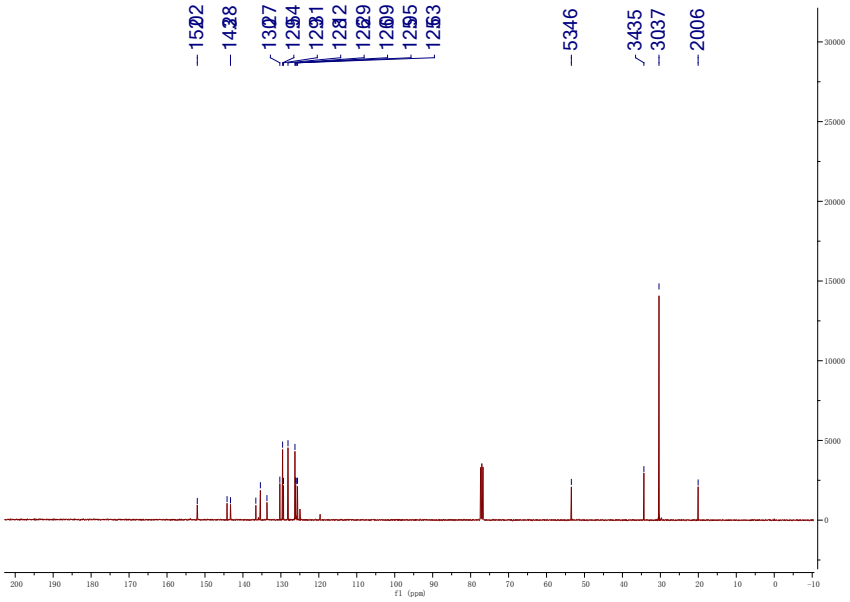
4c ^{13}C NMR



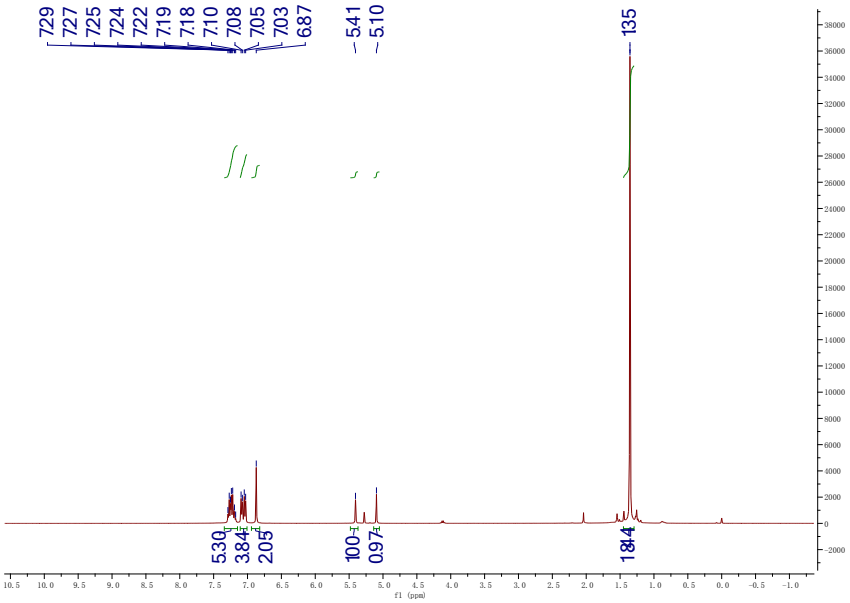
4d ^{1}H NMR



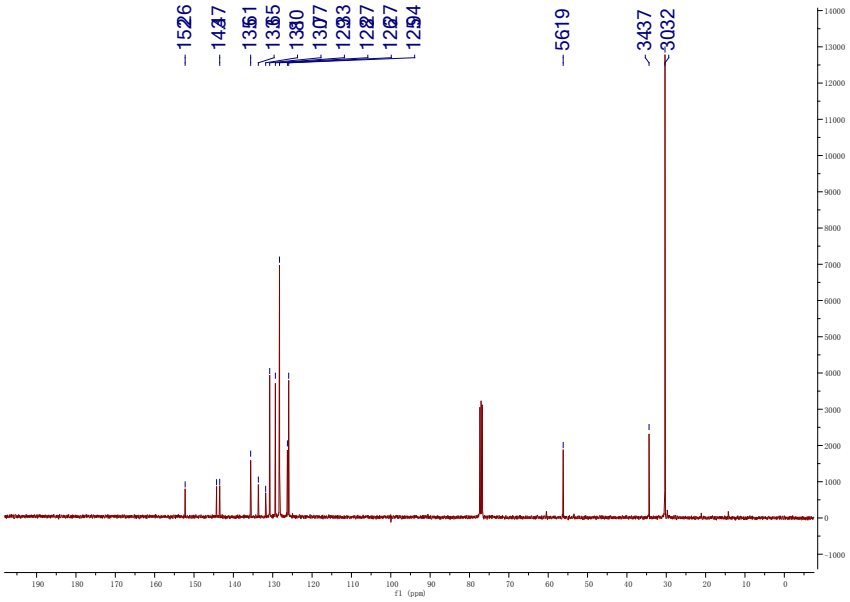
4d ^{13}C NMR



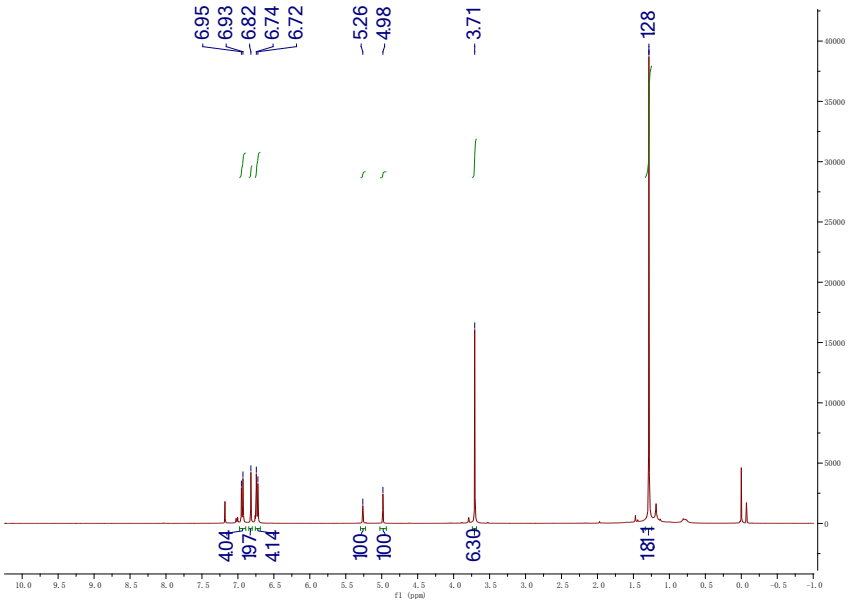
4e ^{1}H NMR



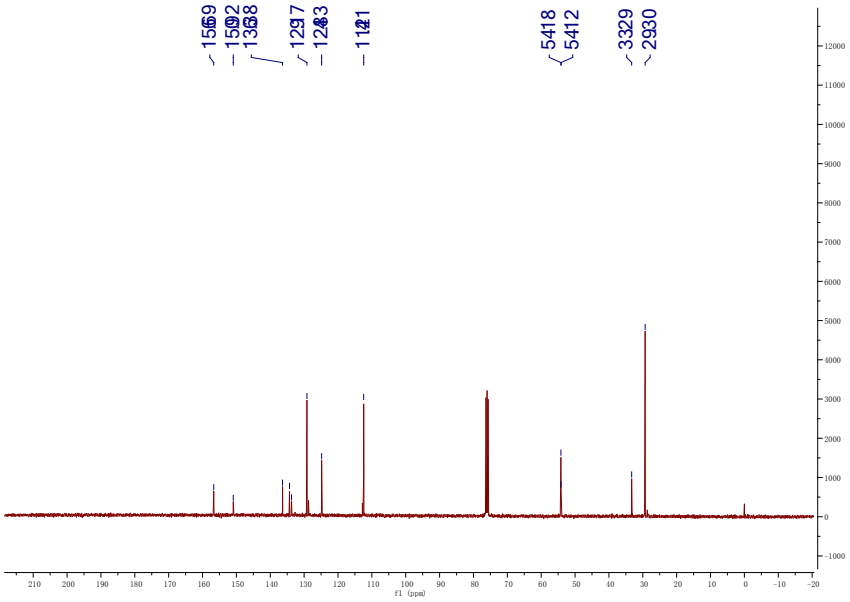
4e ^{13}C NMR



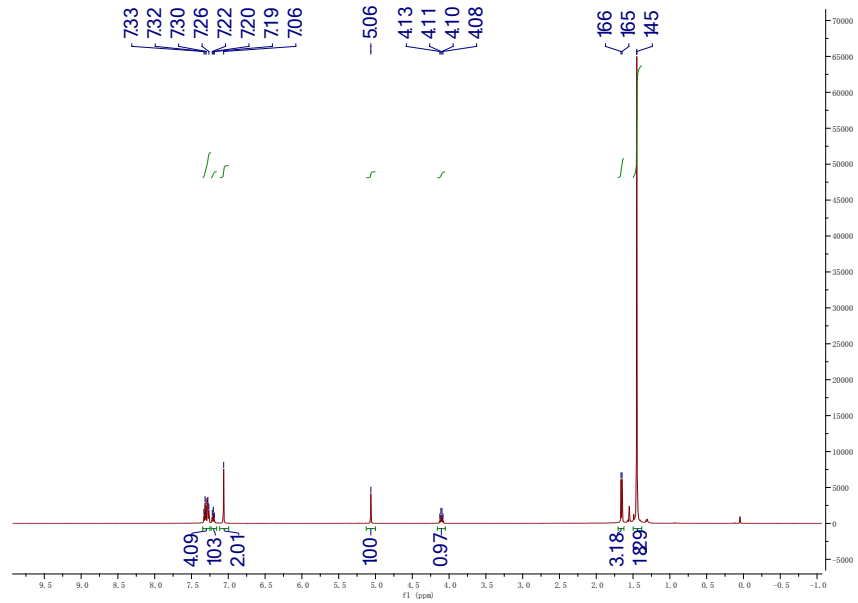
4f ^{1}H NMR



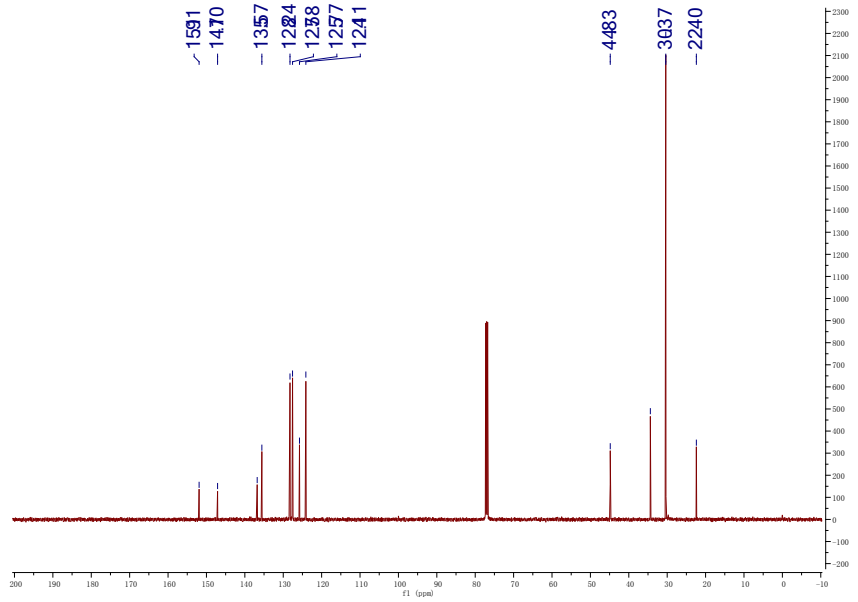
4f ^{13}C NMR



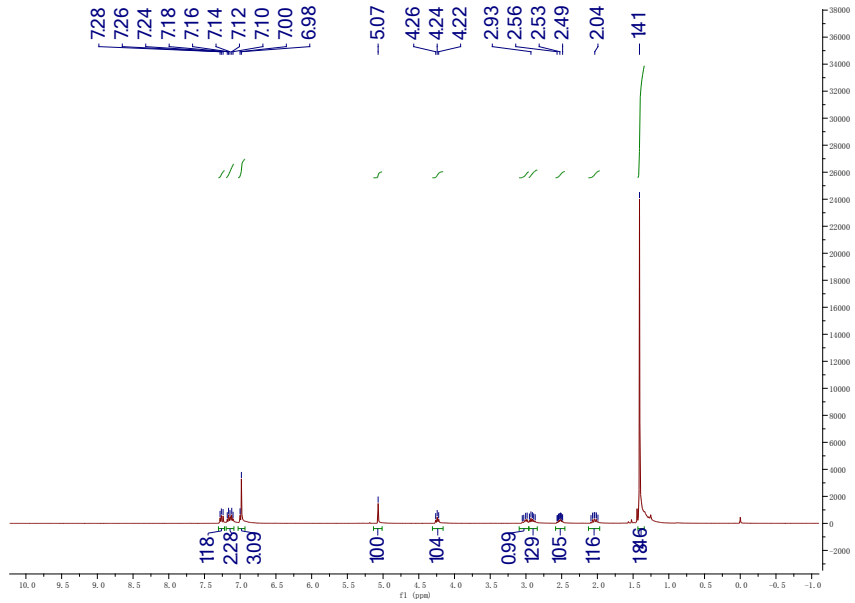
4g ^{1}H NMR



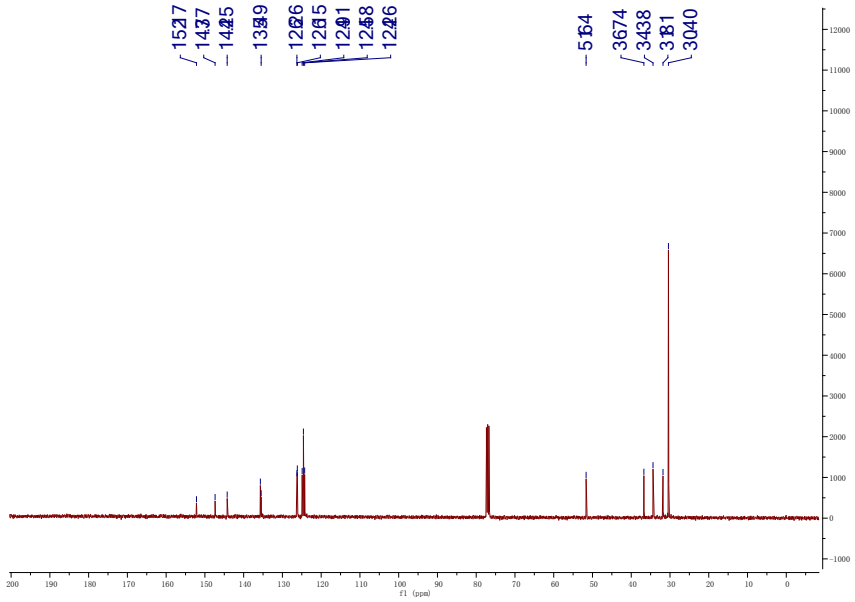
4g ^{13}C NMR



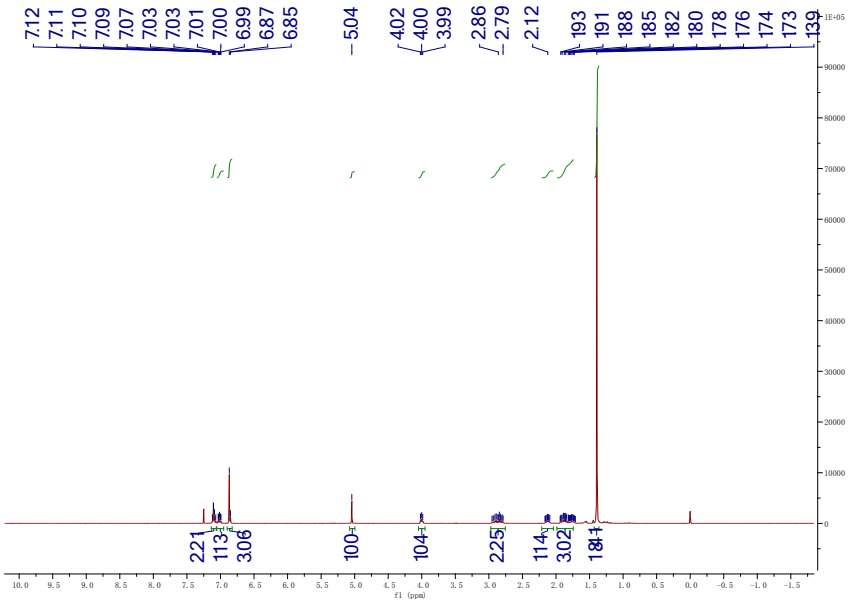
4h ^{1}H NMR



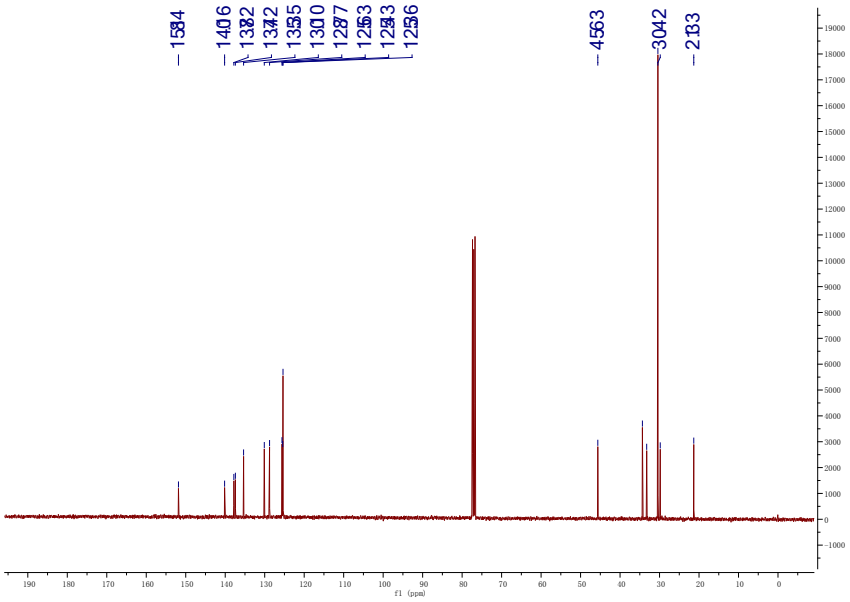
4h ^{13}C NMR



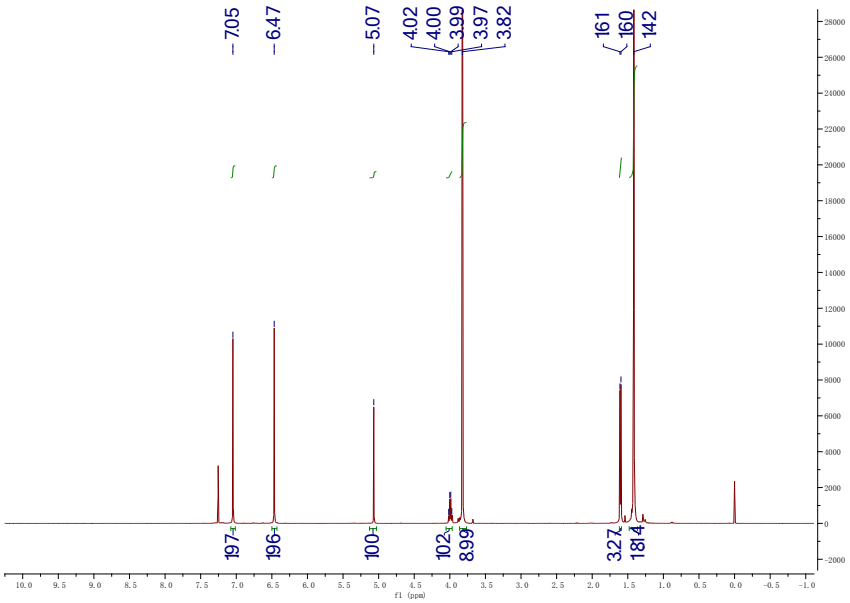
4i ^{1}H NMR



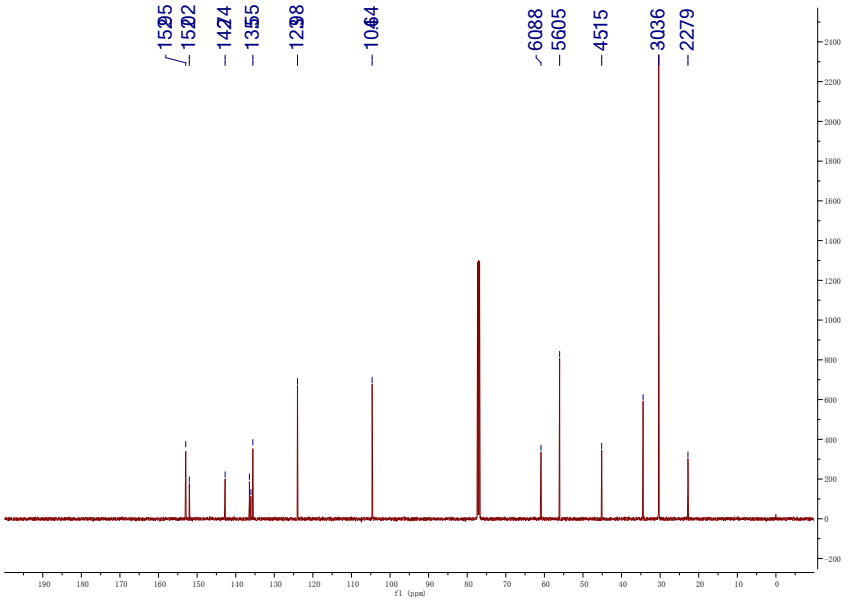
4i ^{13}C NMR



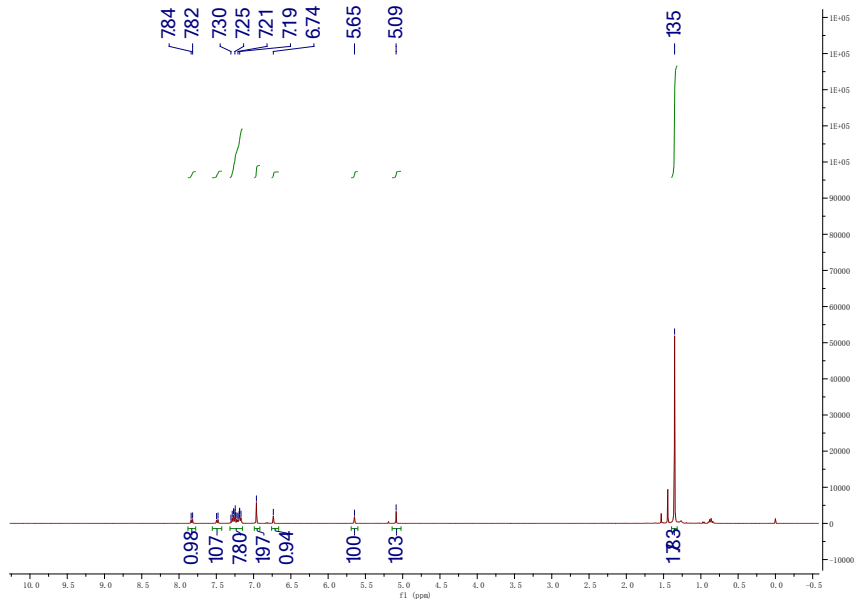
4j ^{1}H NMR



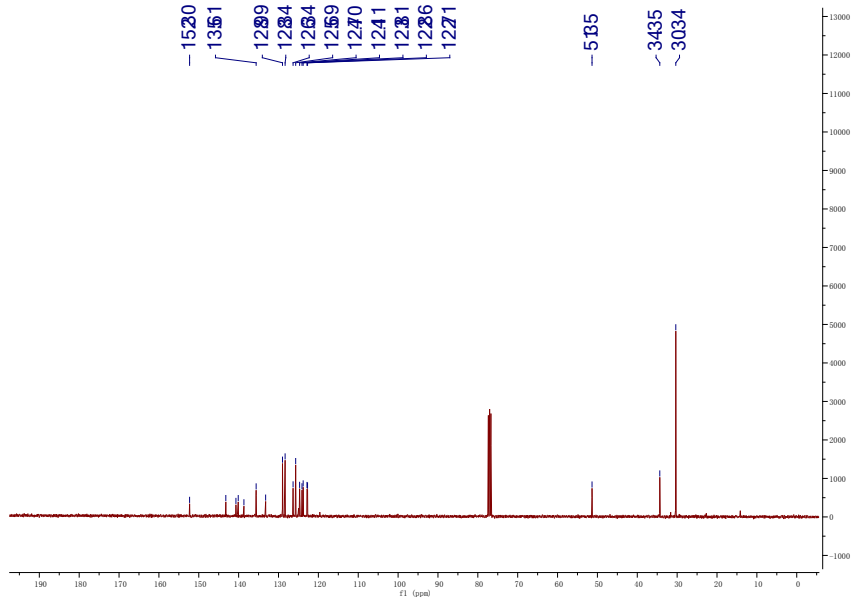
4j ^{13}C NMR



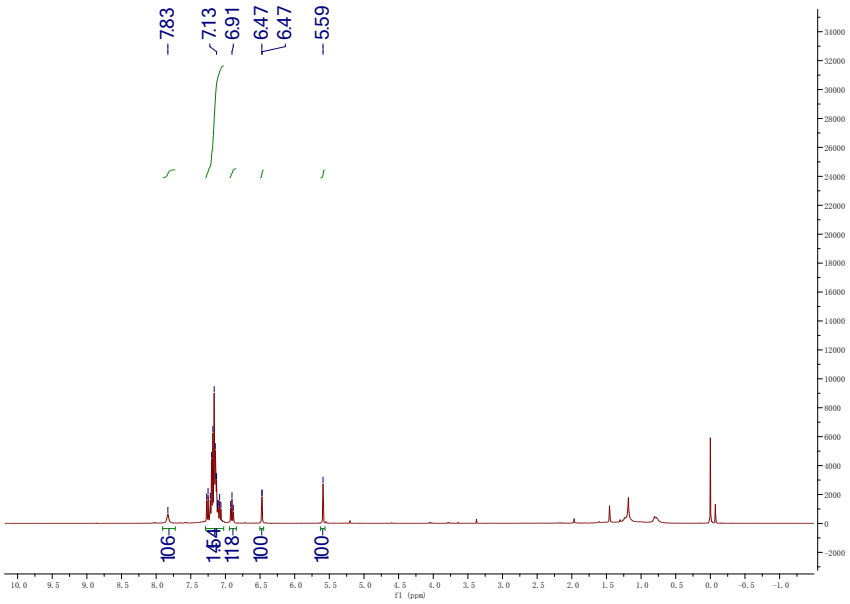
4k ^{1}H NMR



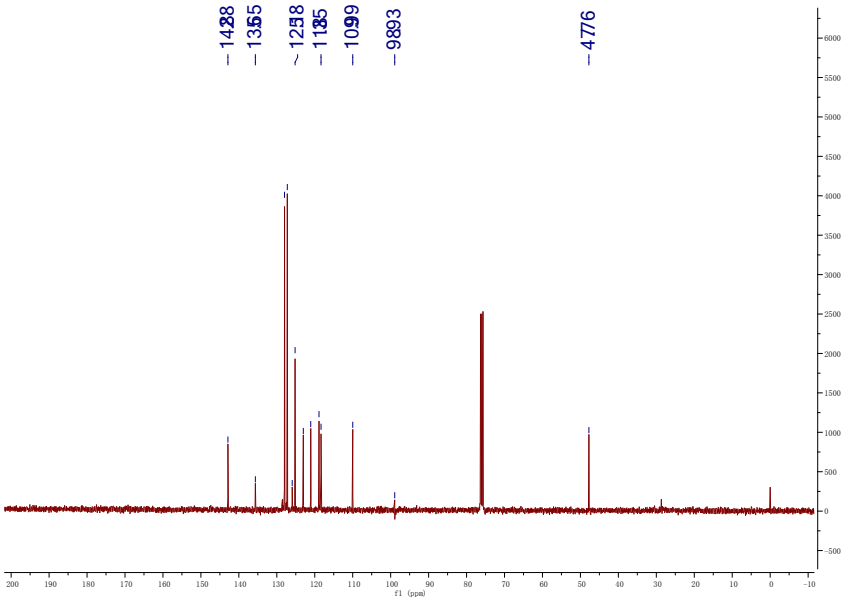
4k ^{13}C NMR



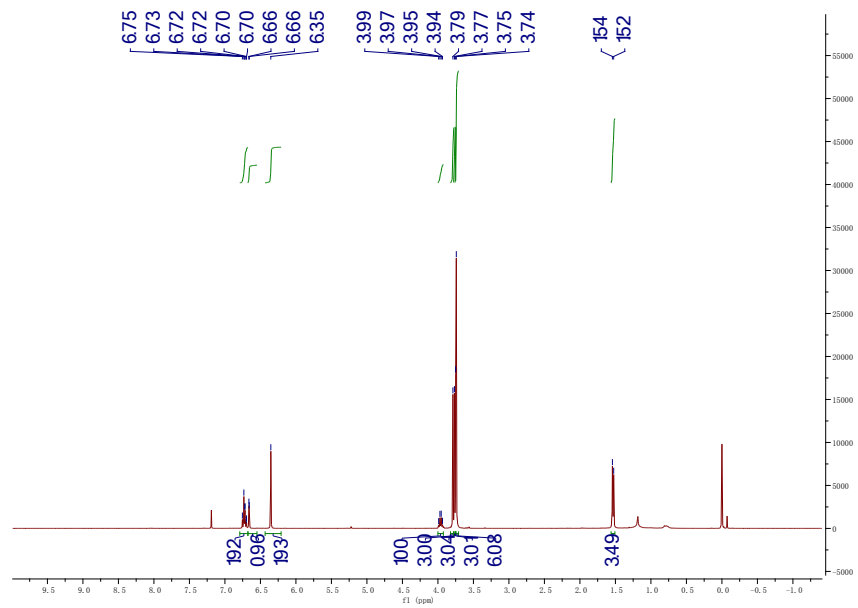
4l ^{1}H NMR



4l ^{13}C NMR



4o ^{1}H NMR



4o ^{13}C NMR