Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Radical Anti-Markovnikov Addition of Alkyl Nitriles to Simple Alkenes via Selective sp^3C-H Bond Functionalization

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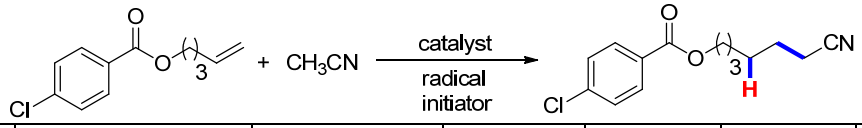
General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. Electron paramagnetic resonance (EPR) data were measured on a Bruker A300 EPR spectrometer (X-band). All products were identified by ^{1}H and ^{13}C NMR, ^{31}P NMR, MS, HRMS, and Element Analysis. The starting materials were purchased from Energy Chemicals, Alfa Aesar, Acros Organics, J&K Chemicals, Adamas, or Aldrich and used without further purification.

Optimization of the typical reaction conditions

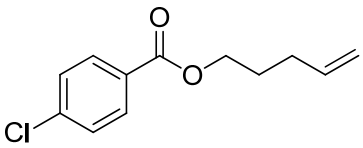
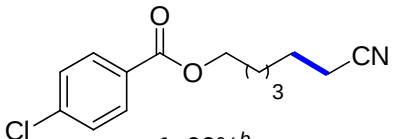
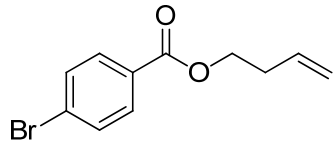
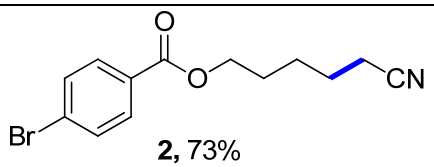
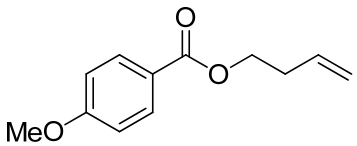
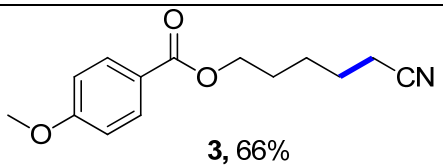
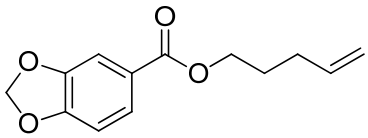
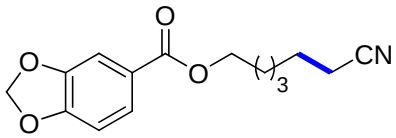
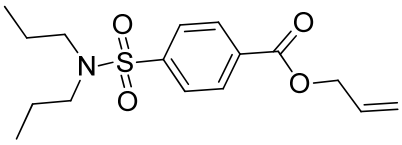
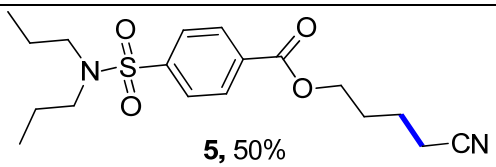
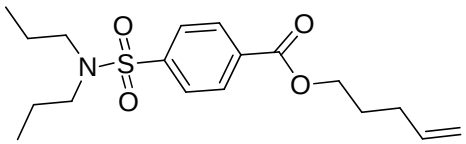
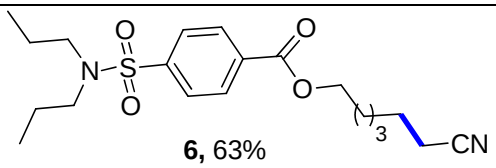
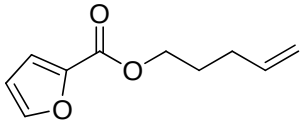
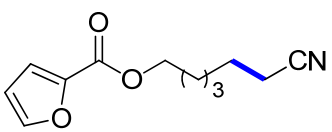


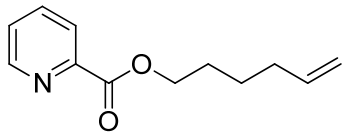
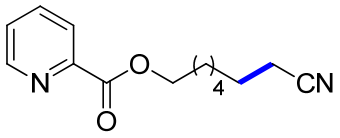
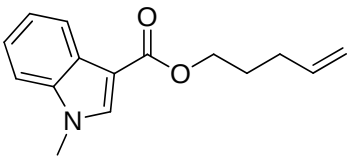
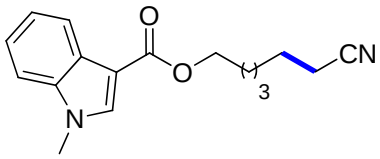
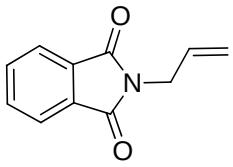
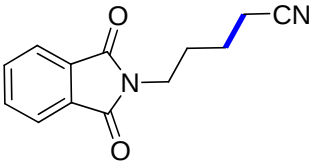
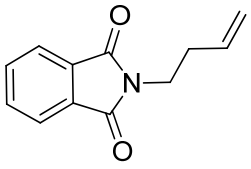
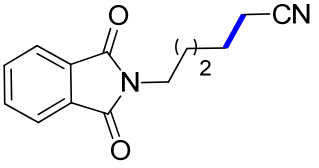
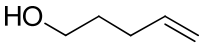
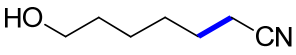
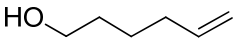
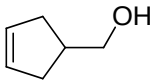
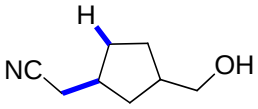
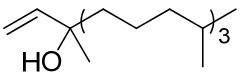
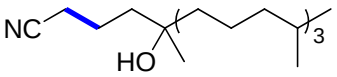
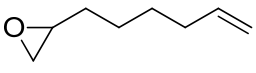
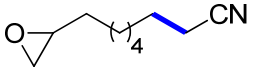
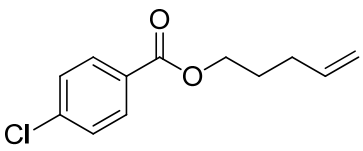
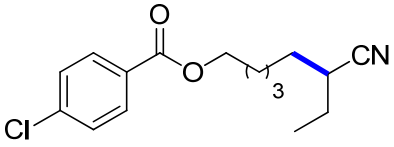
Entry	CH_3CN(mL)	catalyst (mol %)	Oxidant (equiv)	T (°C)	t (h)	Yield (%)
1	5	CuI(10)	DCP(3)	110	2	36
2	5	CuI (10)	DCP(3)	110	5	80
3	5	CuI (10)	DCP(3)	110	7	86
4	**5**	**CuI (10)**	**DCP(3)**	**110**	**10**	**90**
5	5	CuI (10)	DCP(3)	110	12	89
6	5	CuI (10)	DCP(3)	110	15	86
7	5	CuI (10)	DCP(3)	110	24	80
8	5	CuI (10)	DTBP(3)	110	10	Trace
9	5	CuI (10)	BPO(3)	110	10	10
10	5	CuI (10)	TBHP(3)	110	10	Trace
11	5	CuI(10)	TBPB(3)	110	10	22
12	5	CuI(10)	TBCP(3)	110	10	11
13	5	CuI(10)	DCP(3)	50	10	Trace
14	5	CuI(10)	DCP(3)	80	10	Trace
15	5	CuI(10)	DCP(0.2)	110	10	Trace
16	5	CuI(10)	DCP(0.5)	110	10	Trace
17	5	CuI(10)	DCP(1)	110	10	22
18	5	CuI(10)	DCP(2)	110	10	80
19	5	-	DCP(3)	110	10	76
20	5	CuI(2)	DCP(3)	110	10	79
21	5	CuI(5)	DCP(3)	110	10	81
22	5	CuCl(10)	DCP(3)	110	10	75
23	5	CuBr(10)	DCP(3)	110	10	70
24	5	Cu_2O(10)	DCP(3)	110	10	78
25	0.5	CuI (10)	DCP(3)	110	10	18
26	1	CuI (10)	DCP(3)	110	10	53
27	2	CuI(10)	DCP(3)	110	10	62
28	3	CuI (10)	DCP(3)	110	10	69
29	10eq+*t*-Butanol(5)	CuI (10)	DCP(3)	110	10	Trace
30	10eq+TFE(5)	CuI (10)	DCP(3)	110	10	Trace
31	10eq+Benzene(5)	CuI (10)	DCP(3)	110	10	Trace
32	5	-	DCP(0.2)	110	10	Trace
33	5	-	DCP(0.5)	110	10	Trace
34	5	-	DCP(1)	110	10	20
35	5	-	DCP(2)	110	10	68

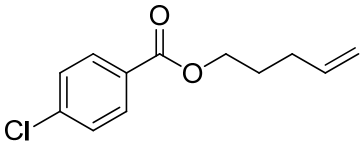
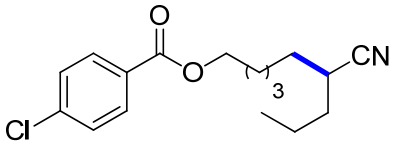
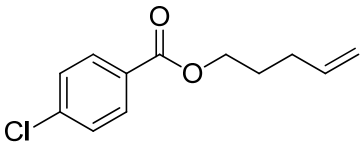
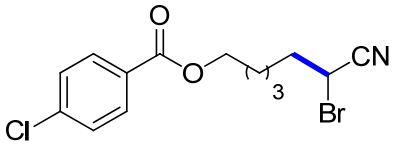
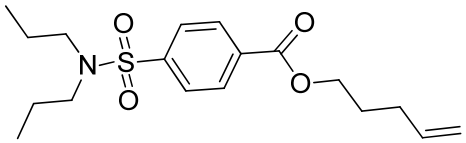
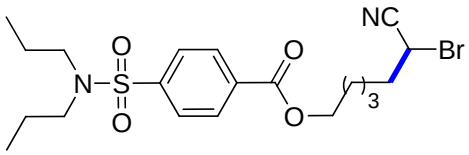
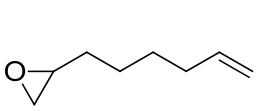
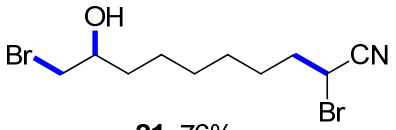
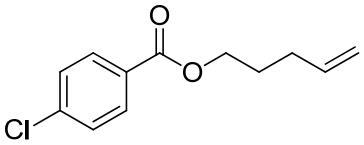
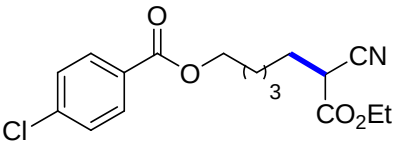
Typical procedure

Reaction of Acetonitriles with alkenes: A mixture of alkenes (1 equiv., 0.20 mmol), acetonitriles (5 mL), CuI (10 mol%, 0.02 mmol), and DCP (3 eq, 0.60 mmol) was heated at 110 ^{o}C (the measured temperature of the oil bath) under nitrogen condition for 10 h in a sealed tube (15 mL). After the reaction finished, the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product.

Substrate scope [a]

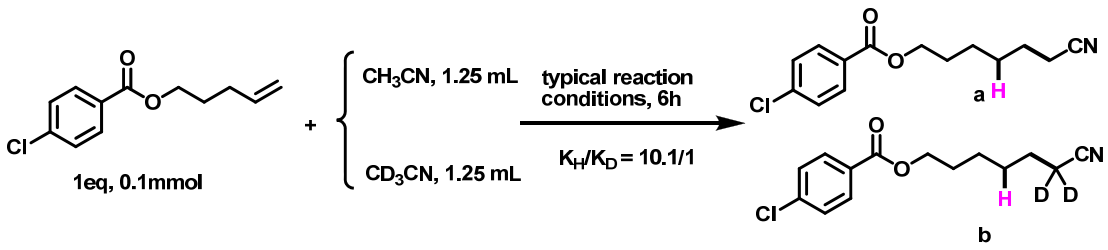
Starting alkene	Product
	 **1,** 90%[b]
	 **2,** 73%
	 **3,** 66%
	 **4,** 76%
	 **5,** 50%
	 **6,** 63%
	 **7,** 58%, (rsm 23%)

	 **8,** 56%, (rsm 26%)
	 **9,** 28%,(rsm 58%)
	 **10,** 60%
	 **11,** 62%
	 **12,** 46%, (rsm 43%)
	 **13,** 50%, (rsm 36%)
	 **14,** 46%, (rsm 36%) d.r. = 2.5/1[c]
	 **15,** 60%, (rsm 24%)
	 **16,** 72%
	 **17,** 40%, (rsm51%)

	 **18,** 46%,(rsm38%)
	 **19,** 73%, (rsm18%)
	 **20,** 88%
	 **21,** 76%
	 **22,** 70%

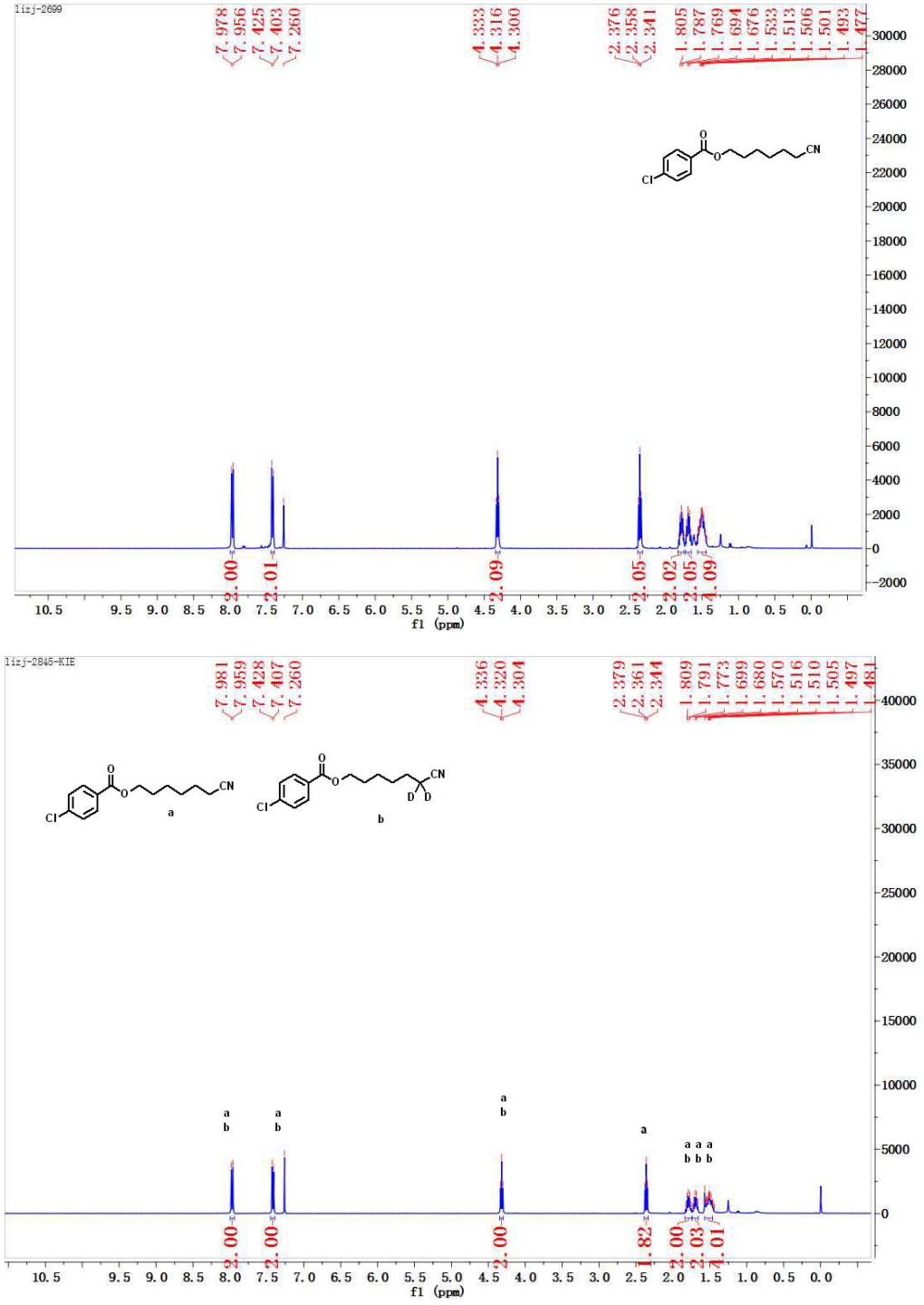
[a] Reaction conditions: Alkenes (1 equiv, 0.20 mmol), CuI (0.02 mmol), DCP (3 equiv, 0.60 mmol), 5 mL of nitriles as solvent, N_2, 110 ^oC, sealed tube, 10 h. [b] Isolated yields. [c] Obtained as a mixture of diastereoisomers and the diastereomeric ratio determined by ^1H NMR spectroscopy.

Competing Kinetic Isotope Effect (KIE) Experiment:



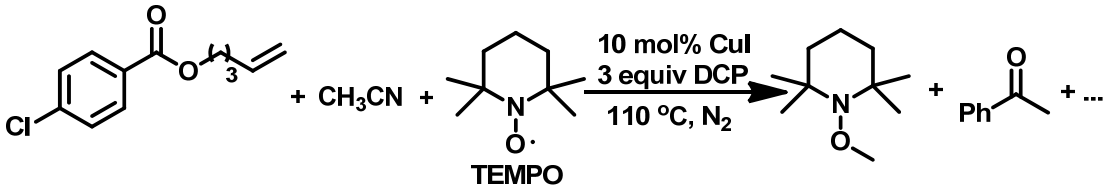
Conversion 23%, a(yield, 20%), b(yield, 2%)

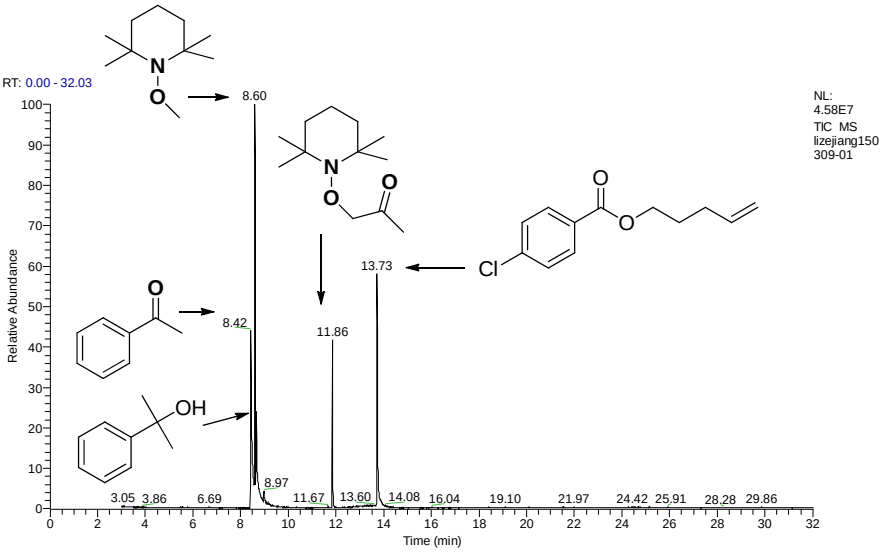
^1H NMR

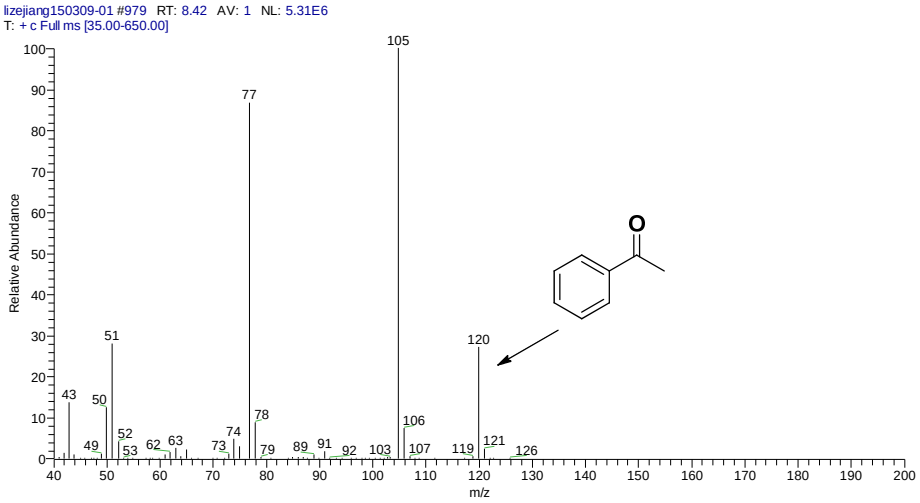


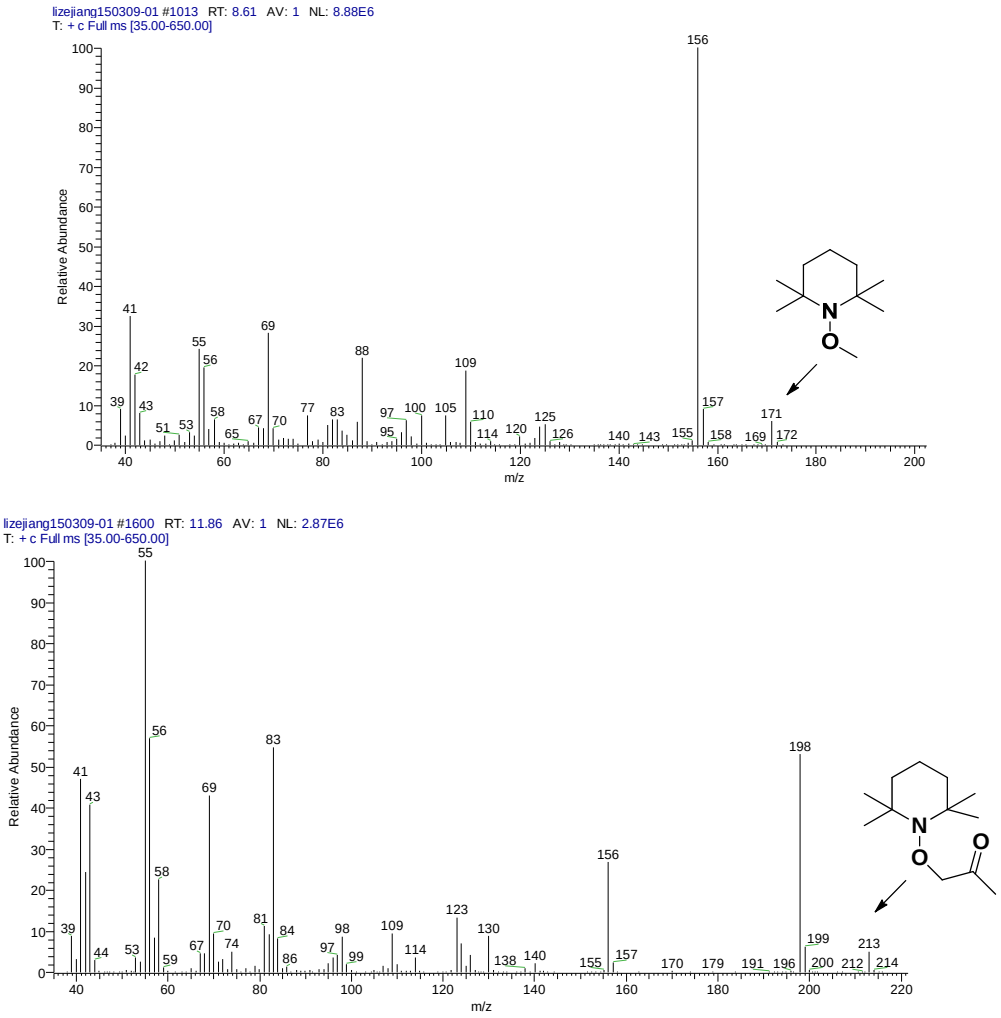
Note: The value of k_H/k_D was calculated from the ^{1}H NMR spectra above which should be the mixture of compound **a** and **b** (the KIE scheme). The sum of the integral of **a** and **b** at chemical shift 4.30 – 4.34 was integrated as 2.00 (both **a** and **b** keep the same double bond hydrogen). Compound **a** has 2 hydrogen atoms at chemical shift 2.34 – 2.38, while **b** has no H atoms. The amount of **a** could be defined as 1.82, on the other hand, the sum of **a** and **b** is 2.00, so the amount of **b** is 0.18 (2.00 – 1.82 = 0.18). As a result, k_H / k_D=1.82 / 0.18 = 10.1.

The Experiment by Addition of TEMPO :









Physical data and references for the following products:

All known compounds are determined by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

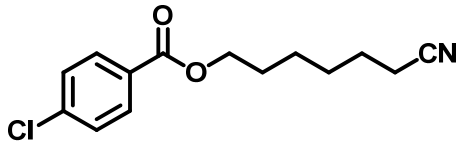
References:

1. J. W. Bruno, T. J. Marks, F. D. Lewis, *J. Am. Chem. Soc.*, 1982, **104**, 5580.
2. T. Kamitanaka, T. Hikida, S. Hayashi, N. Kishida, T. Matsuda, T. Harada, *Tetrahedron Lett.* 2007, **48**, 8460.
3. J. Li, Z. Wang, N. Wu, G. Gao, J. You, *Chem. Commun.* 2014, **50**, 15049.
4. Y. Li, B. Liu, H.-B. Li, Q. Wang, J.-H. Li, *Chem. Commun.* 2015, **51**, 1024.
5. A. Bunescu, Q. Wang, J.-P. Zhu, *Angew. Chem. Int. Ed.* 2015, **54**, 3132.
6. C. C. Sazepin, Q. Wang, G. M. Sammis, J.-P. Zhu, *Angew. Chem. Int. Ed.* 2015, DOI: 10.1002/anie.201412357.

Physical data for the following products:

1. 6-cyanohexyl 4-chlorobenzoate

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



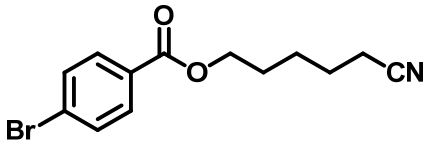
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.73 – 1.66 (m, 2H), 1.59 – 1.44 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 139.3, 130.9, 128.7, 128.6, 119.6, 64.9, 28.4, 28.3, 25.3, 25.2, 17.1.

HRMS (ESI, m/z): Calculated for $C_{14}H_{17}ClNO_2$ $(M+H)^+$ 266.0942, found 266.0939.

2. 5-cyanopentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.71 (m, 4H), 1.65 – 1.57 (m, 2H).

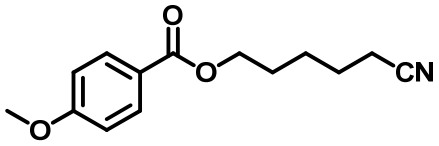
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 131.7, 131.0, 129.0, 128.1, 119.4, 64.6, 27.9, 25.2, 25.0, 17.1.

HRMS (ESI, m/z): Calculated for $C_{13}H_{14}BrNO_2NH_4(M+NH_4)^+$ 313.0546, found 313.0542.

3. 5-cyanopentyl 4-methoxybenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl

acetate = 10/1)



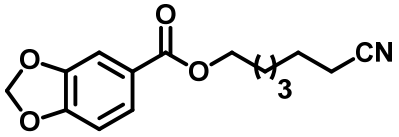
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.71 (m, 4H), 1.65 – 1.57 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 163.3, 131.5, 122.6, 119.5, 113.6, 64.0, 55.4, 28.0, 25.3, 25.0, 17.1.

HRMS (ESI, m/z): Calculated for $C_{14}H_{18}NO_3$ $(M+H)^+$ 248.1281, found 248.1278.

4. 4-cyanobutyl benzo[d][1,3]dioxole-5-carboxylate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



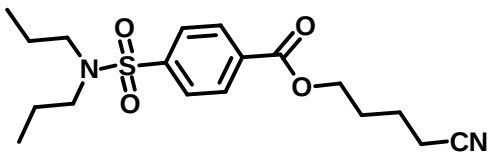
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.45 (d, *J* = 1.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.04 (s, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.73 – 1.66 (m, 2H), 1.56 – 1.45 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 151.5, 147.7, 125.2, 124.3, 119.6, 109.4, 107.9, 101.8, 64.6, 28.5, 28.3, 25.3, 25.2, 17.1.

HRMS (ESI, m/z): Calculated for $C_{15}H_{18}NO_4$ $(M+H)^+$ 276.1230, found 276.1229.

5. 4-cyanobutyl 4-(N,N-dipropylsulfamoyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H),

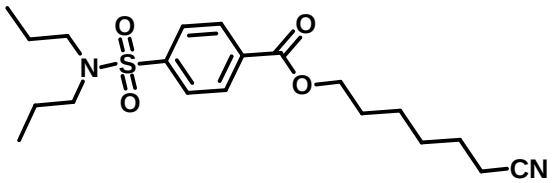
4.40 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 4H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.00 – 1.94 (m, 2H), 1.88 – 1.81 (m, 2H), 1.59 – 1.52 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 144.4, 133.2, 130.2, 127.0, 119.1, 64.3, 49.9, 27.7, 22.3, 21.9, 16.9, 11.1.

HRMS (ESI, m/z): Calculated for $C_{18}H_{27}N_2O_4S$ $(M+H)^+$ 367.1686, found 367.1690.

6. 6-cyanohexyl 4-(N,N-dipropylsulfamoyl)benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



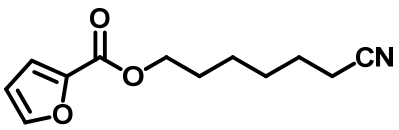
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 4.35 (t, *J* = 6.4 Hz, 2H), 3.11 – 3.07 (m, 4H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.73 – 1.66 (m, 2H), 1.58 – 1.49 (m, 8H), 0.86 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 144.2, 133.5, 130.1, 126.9, 119.6, 65.3, 49.9, 28.4, 28.3, 25.3, 25.2, 21.9, 17.1, 11.1.

HRMS (ESI, m/z): Calculated for $C_{20}H_{31}N_2O_4S$ $(M+H)^+$ 395.1999, found 395.2000.

7. 6-cyanohexyl furan-2-carboxylate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 0.8 Hz, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 6.51 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.73 – 1.65 (m, 2H), 1.57 – 1.44 (m, 4H).

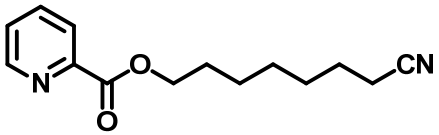
^{13}C NMR (151 MHz, $cdcl_3$): δ 158.8, 146.2, 144.7, 119.6, 117.8, 111.8, 64.6, 28.4,

28.3, 25.3, 25.2, 17.1.

HRMS (ESI, m/z): Calculated for $C_{12}H_{15}NO_3NH_4(M+NH_4)^+$ 239.1390, found 239.1392.

8. 7-cyanoheptyl picolinate

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 2/1)



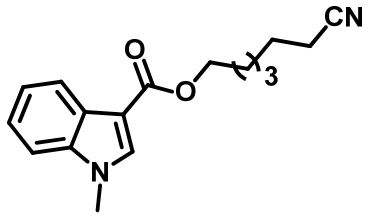
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.84 (td, *J* = 7.6, 1.6 Hz, 1H), 7.47 (dd, *J* = 7.6, 5.6 Hz, 1H), 4.40 (t, *J* = 6.8 Hz, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.68 – 1.61 (m, 2H), 1.50 – 1.38 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 149.8, 148.1, 136.9, 126.8, 125.0, 119.7, 65.7, 28.5, 28.4, 28.3, 25.6, 25.2, 17.1.

HRMS (ESI, m/z): Calculated for $C_{14}H_{19}N_2O_2$ $(M+H)^+$ 247.1441, found 247.1439.

9. 4-cyanobutyl 1-methyl-1H-indole-3-carboxylate

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



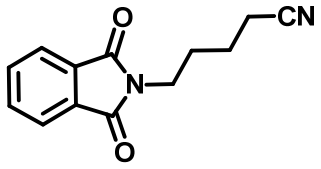
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 6.4, 3.2 Hz, 1H), 7.80 (s, 1H), 7.37 – 7.34 (m, 1H), 7.33 – 7.28 (m, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.79 (m, 2H), 1.75 – 1.66 (m, 2H), 1.59 – 1.53 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 137.2, 135.2, 126.5, 122.7, 121.8, 121.6, 119.7, 109.8, 107.0, 63.4, 33.4, 28.7, 28.4, 25.5, 25.3, 17.1.

HRMS (ESI, m/z): Calculated for $C_{17}H_{21}N_2O_2$ $(M+H)^+$ 285.1598, found 285.1600.

10. 5-(1,3-dioxoisoindolin-2-yl)pentanenitrile

A light yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



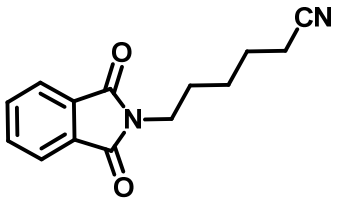
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.73 (dd, *J* = 5.2, 3.2 Hz, 2H), 3.73 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.75 – 1.67 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 134.1, 131.9, 123.3, 119.2, 36.6, 27.6, 22.6, 16.6.

HRMS (ESI, m/z): Calculated for $C_{13}H_{12}N_2O_2NH_4(M+NH_4)^+$ 246.1237, found 246.1236.

11. 6-(1, 3-dioxoisoindolin-2-yl)hexanenitrile

A light yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



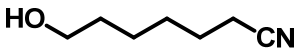
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.71 (dd, *J* = 5.2, 3.2 Hz, 2H), 3.69 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.75 – 1.68 (m, 4H), 1.53 – 1.47 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 133.9, 132.0, 123.2, 119.4, 37.3, 27.7, 25.8, 24.8, 17.0.

HRMS (ESI, m/z): Calculated for $C_{14}H_{14}N_2O_2NH_4(M+NH_4)^+$ 260.1394, found 260.1391.

12. 7-hydroxyheptanenitrile

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (t, *J* = 6.4 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.61 – 1.54 (m, 2H), 1.52 – 1.36 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.7, 62.6, 32.3, 28.4, 25.3, 24.9, 17.0.

HRMS (ESI, m/z): Calculated for $C_7H_{13}NONH_4(M+NH_4)^+$ 145.1335, found 145.1331.

13. 8-hydroxyoctanenitrile

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).

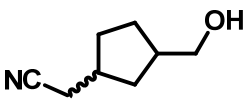
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (t, *J* = 6.4 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.61 – 1.54 (m, 2H), 1.51 – 1.42 (m, 2H), 1.38 – 1.31 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.7, 62.8, 32.5, 28.6, 28.5, 25.4, 25.3, 17.1.

HRMS (ESI, m/z): Calculated for $C_8H_{15}NONH_4(M+NH_4)^+$ 159.1492, found 159.1488.

14. 2-(3-(hydroxymethyl)cyclopentyl)acetonitrile

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



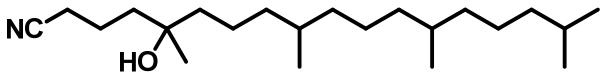
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.51 (d, *J* = 6.4 Hz, 2H), 2.36 (d, *J* = 6.8 Hz, 2H), 2.30 – 2.21 (m, 2H), 2.00 – 1.87 (m, 2H), 1.74 – 1.67 (m, 1H), 1.58 – 1.52 (m, 1H), 1.39 – 1.30 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.1, 66.7, 40.8, 35.5, 34.4, 32.1, 28.6, 22.8.

HRMS (ESI, m/z): Calculated for $C_8H_{13}NONH_4(M+NH_4)^+$ 157.1335, found 157.1332.

15. 5-hydroxy-5,9,13,17-tetramethyloctadecanenitrile

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 2/1).



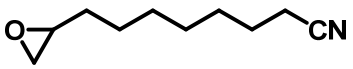
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (t, *J* = 7.2 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.60 – 1.45 (m, 4H), 1.43 – 1.25 (m, 13H), 1.18 (s, 3H), 1.16 – 1.02 (m, 6H), 0.87 – 0.83 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.7, 72.4, 42.6, 40.5, 39.3, 37.4, 37.3, 37.2, 32.8, 32.7, 28.0, 26.8, 26.7, 24.8, 24.5, 22.7, 22.6, 21.3, 20.1, 19.7, 19.6, 17.7.

HRMS (ESI, m/z): Calculated for $C_{22}H_{43}NONH_4(M+NH_4)^+$ 355.3683, found 355.3679.

16. 8-(oxiran-2-yl)octanenitrile

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



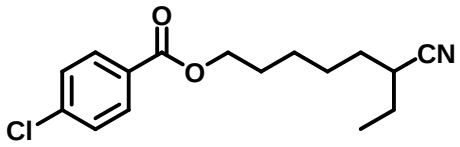
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (d, *J* = 8.8 Hz, 1H), 2.75 (t, *J* = 4.4 Hz, 1H), 2.47 – 2.45 (m, 1H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.57 – 1.42 (m, 6H), 1.40 – 1.35 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.8, 52.3, 47.0, 32.4, 29.1, 28.7, 28.5, 25.8, 25.3, 17.1.

HRMS (ESI, m/z): Calculated for $C_{10}H_{17}NONH_4(M+NH_4)^+$ 185.1648, found 185.1645.

17. 6-cyanooctyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



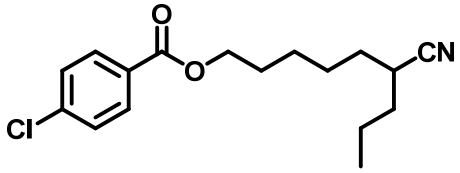
^{1}H NMR (400 MHz, $CDCl_3$): 7.97 (d, *J* = 8.8Hz, 2H), 7.42 (d, *J* = 8.8Hz, 2H), 4.32 (t, *J* = 6.4Hz, 2H), 2.52 – 2.44 (m, 1H), 1.83 – 1.76 (m, 1H), 1.67 – 1.45 (m, 8H), 1.26 – 1.22 (m, 1H), 1.08 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 139.3, 130.9, 128.8, 128.7, 122.1, 65.0, 33.3, 31.8, 28.5, 26.9, 25.7, 25.6, 11.6.

HRMS (ESI, m/z): Calculated for $C_{16}H_{20}ClNO_2NH_4(M+NH_4)^+$ 311.1521, found 311.1525.

18. 6-cyanononyl 4-chlorobenzoate

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 2.55 – 2.50 (m, 1H), 1.84 – 1.75 (m, 2H), 1.65 – 1.41 (m, 10H), 0.95 (t, *J* = 7.2 Hz, 3H).

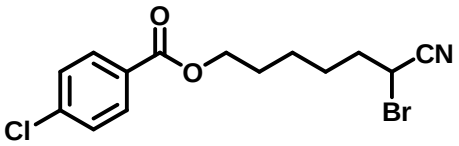
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 139.3, 130.9, 128.8, 128.7, 122.2, 65.0, 34.3, 32.2, 31.4, 28.5, 26.9, 25.7, 20.4, 13.6.

HRMS (ESI, m/z): Calculated for $C_{17}H_{22}ClNO_2NH_4(M+NH_4)^+$ 325.1677, found 325.1674.

19. 6-bromo-6-cyanohexyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl

acetate = 10/1)



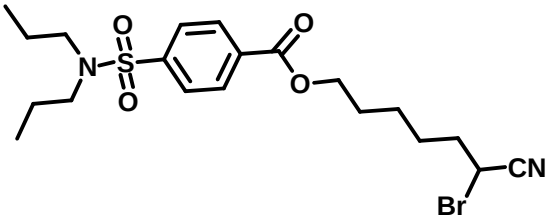
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.41 – 4.31 (m, 2H), 4.15 – 4.09 (m, 1H), 2.66 – 2.62 (m, 2H), 2.25 – 1.89 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 139.5, 130.9, 128.8, 128.5, 118.6, 64.1, 53.9, 35.5, 34.7, 26.9, 16.1.

HRMS (ESI, m/z): Calculated for $C_{14}H_{15}BrClNO_2NH_4(M+NH_4)^+$ 361.0313, found 361.0317.

20. 6-bromo-6-cyanohexyl 4-(N,N-dipropylsulfamoyl)benzoate

A light yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



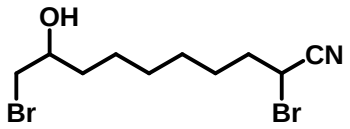
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 4.44 – 4.35 (m, 2H), 4.15 – 4.09 (m, 1H), 3.08 (t, *J* = 7.6 Hz, 4H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.25 – 1.92 (m, 6H), 1.58 – 1.48 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 144.2, 133.2, 130.1, 126.9, 118.5, 64.5, 53.9, 49.8, 35.4, 34.6, 26.8, 21.8, 16.0, 11.1.

HRMS (ESI, m/z): Calculated for $C_{20}H_{29}BrN_2O_4SNa(M+Na)^+$ 495.0924, found 495.0918.

21. 2,10-dibromo-9-hydroxydecanenitrile

A yellow liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



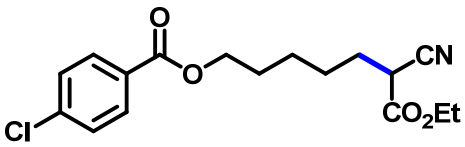
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 – 4.02 (m, 1H), 3.78 (s, 1H), 3.55 – 3.51 (m, 1H), 3.38 (dd, *J* = 10.0, 6.8 Hz, 1H), 2.63 – 2.59 (m, 2H), 2.21 – 2.02 (m, 3H), 1.93 – 1.79 (m, 2H), 1.63 – 1.35 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 118.7, 70.8, 54.6, 40.4, 38.6, 34.7, 34.5, 27.3, 24.9, 16.0.

HRMS (ESI, m/z): Calculated for $C_{10}H_{17}Br_2NONH_4$ $(M+NH_4)^+$ 343.0015, found 343.0016.

22. 6-cyano-7-ethoxy-7-oxoheptyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



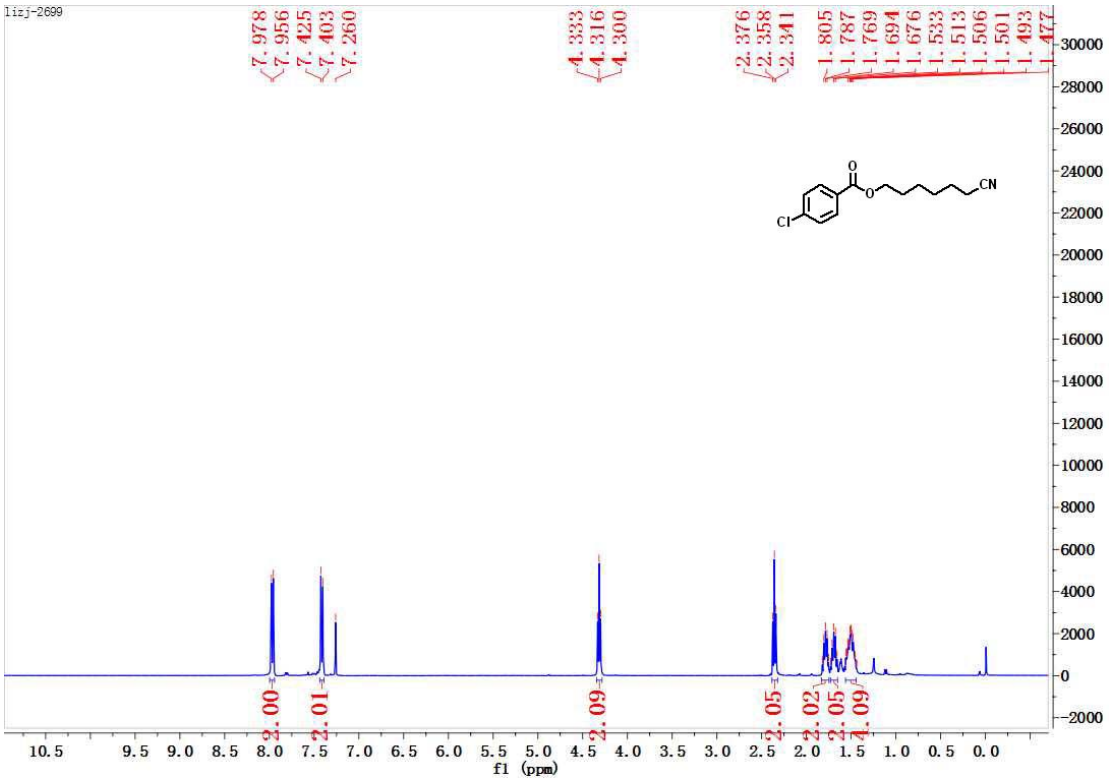
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.50 (t, *J* = 6.8 Hz, 1H), 1.98 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.62 – 1.49 (m, 4H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $cdcl_3$): δ 166.0, 165.7, 139.4, 130.9, 128.7, 116.4, 110.0, 64.8, 62.8, 37.5, 29.7, 28.4, 26.5, 25.4, 14.0.

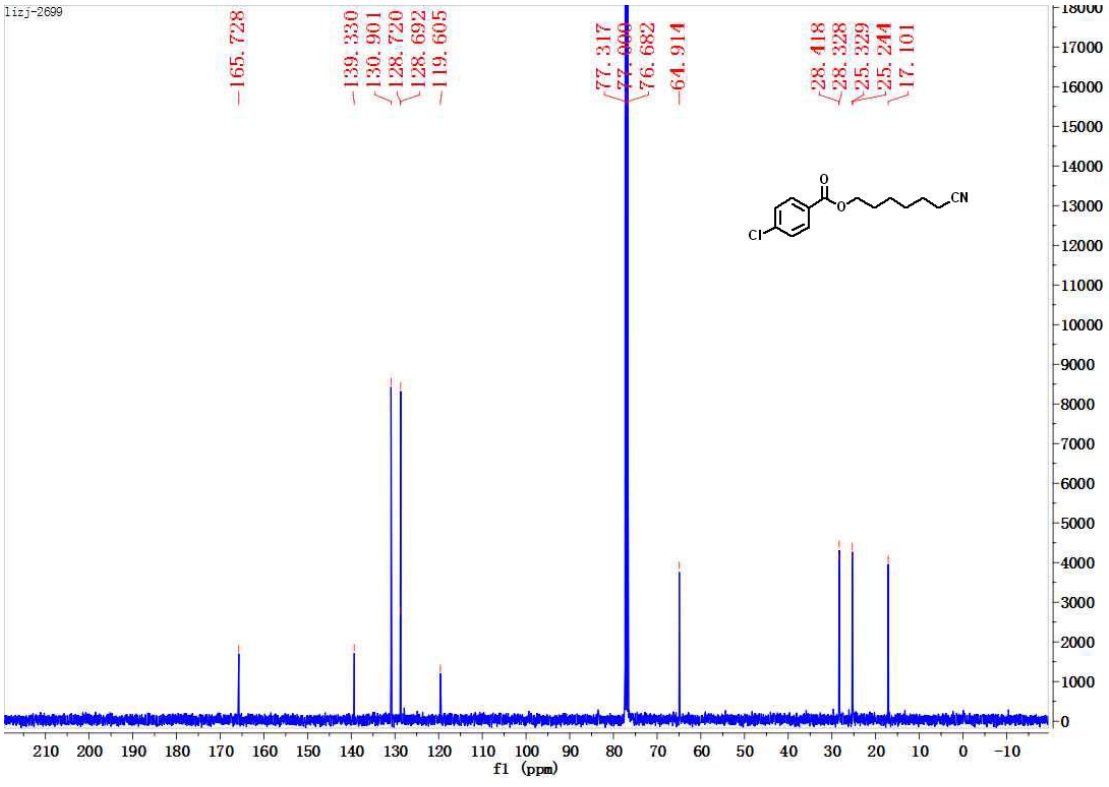
HRMS (ESI, m/z): Calculated for $C_{17}H_{20}ClNO_4Na(M+Na)^+$ 360.0973, found 360.0977.

Copies of the ^{1}H NMR, ^{13}C NMR, ^{135}DEPT

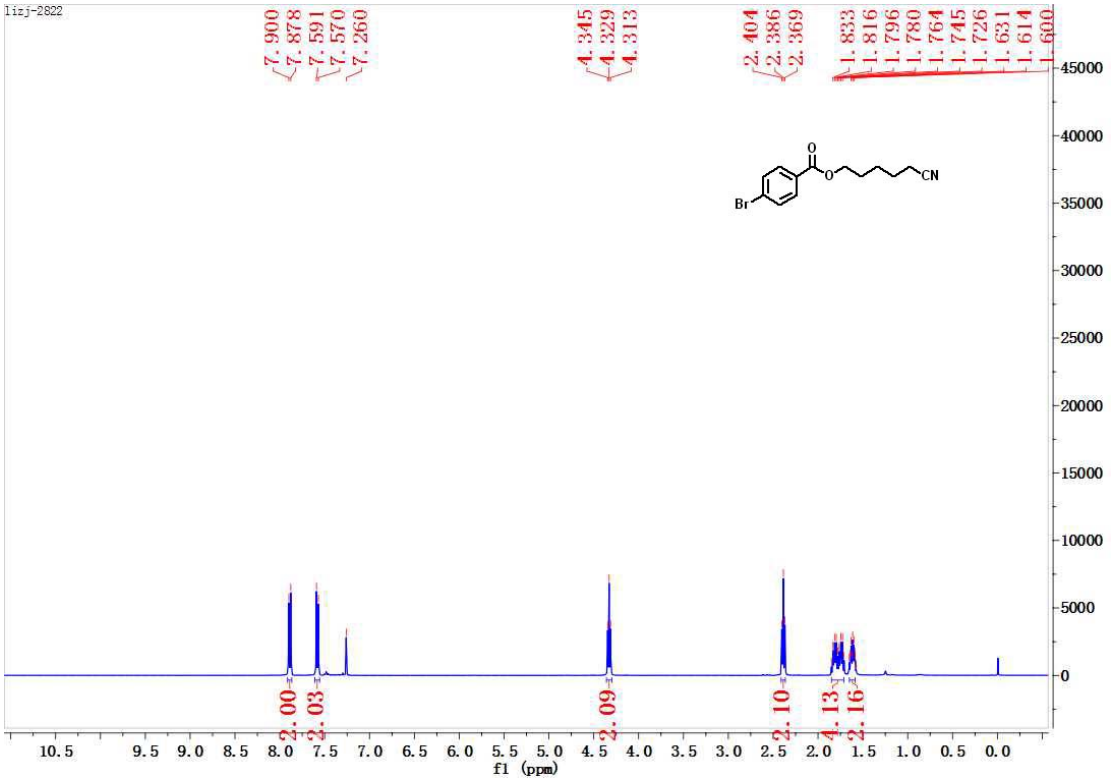
1-^{1}H NMR



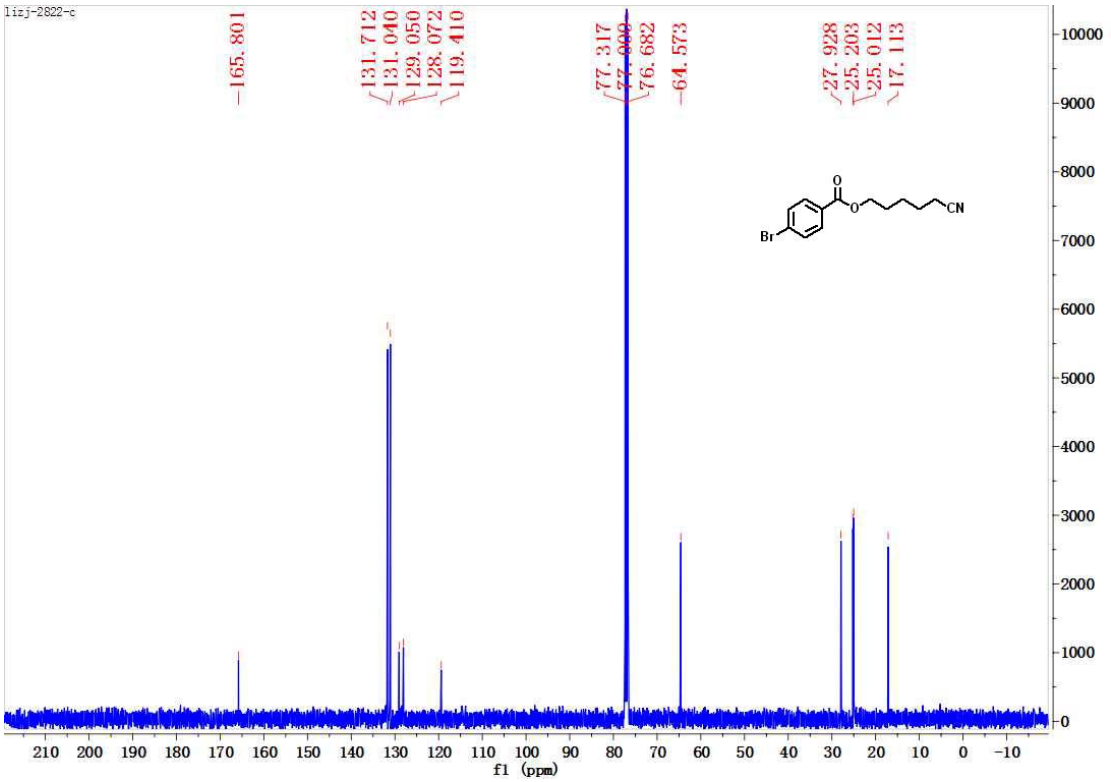
1-^{13}C NMR



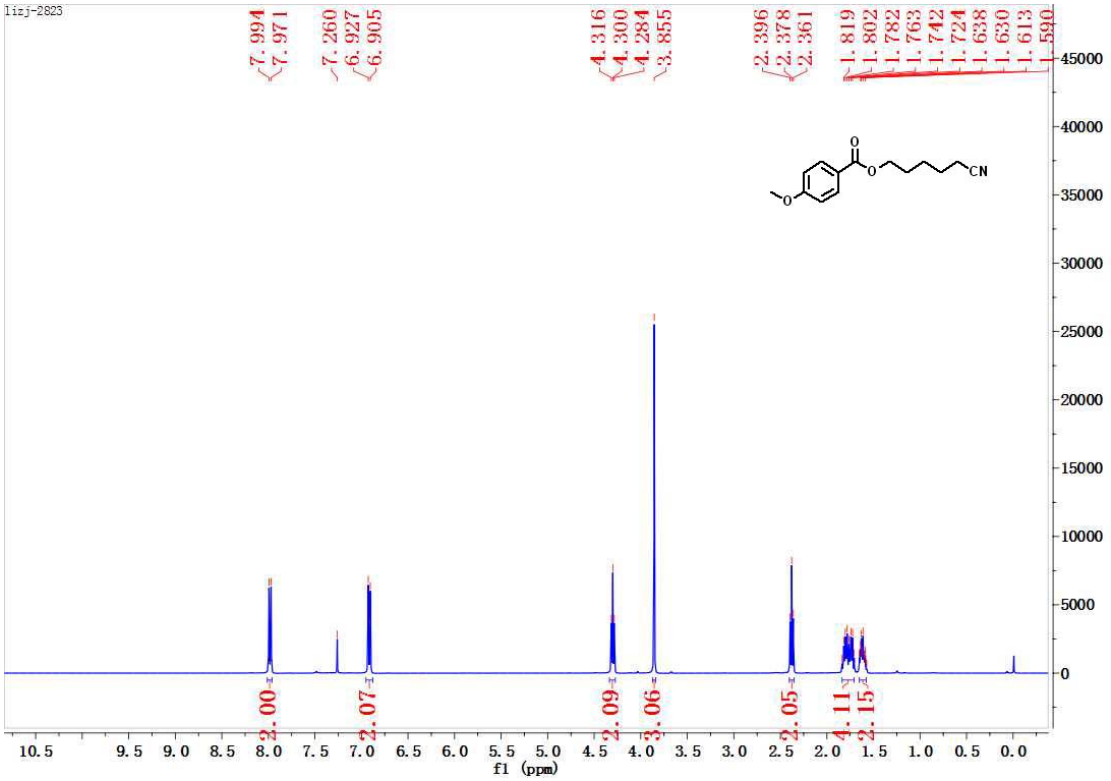
2-^{1}H NMR



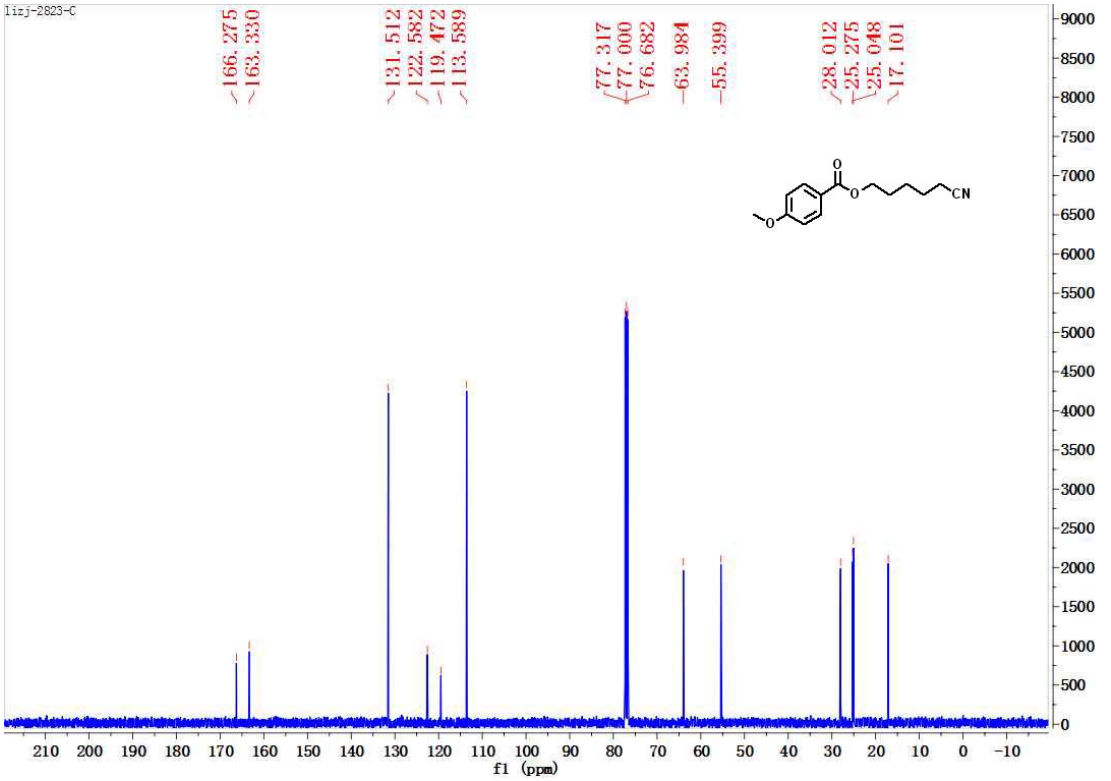
2-^{13}C NMR



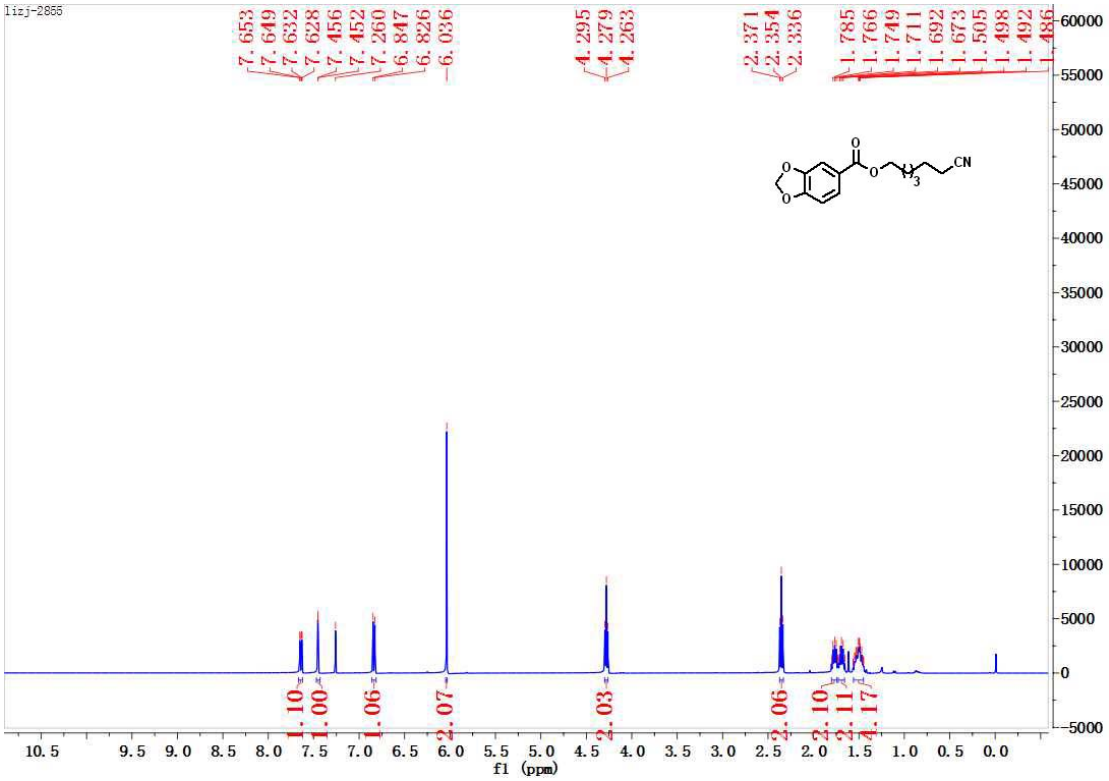
3-^{1}H NMR



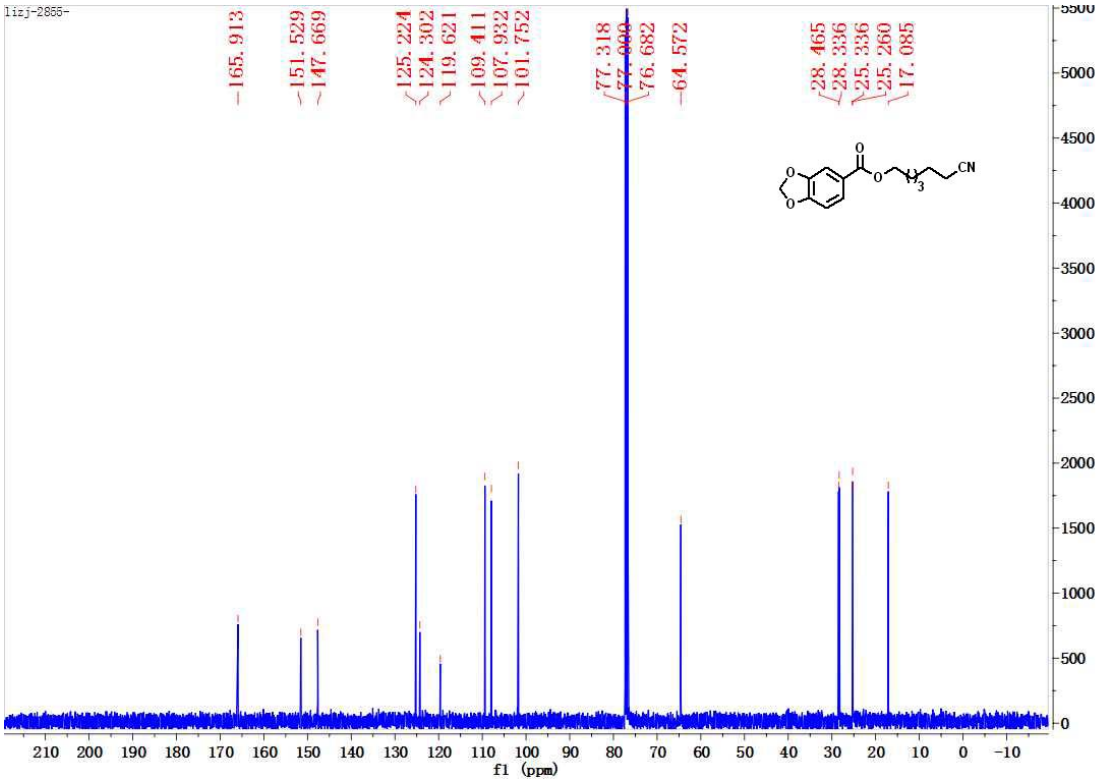
3-^{13}C NMR



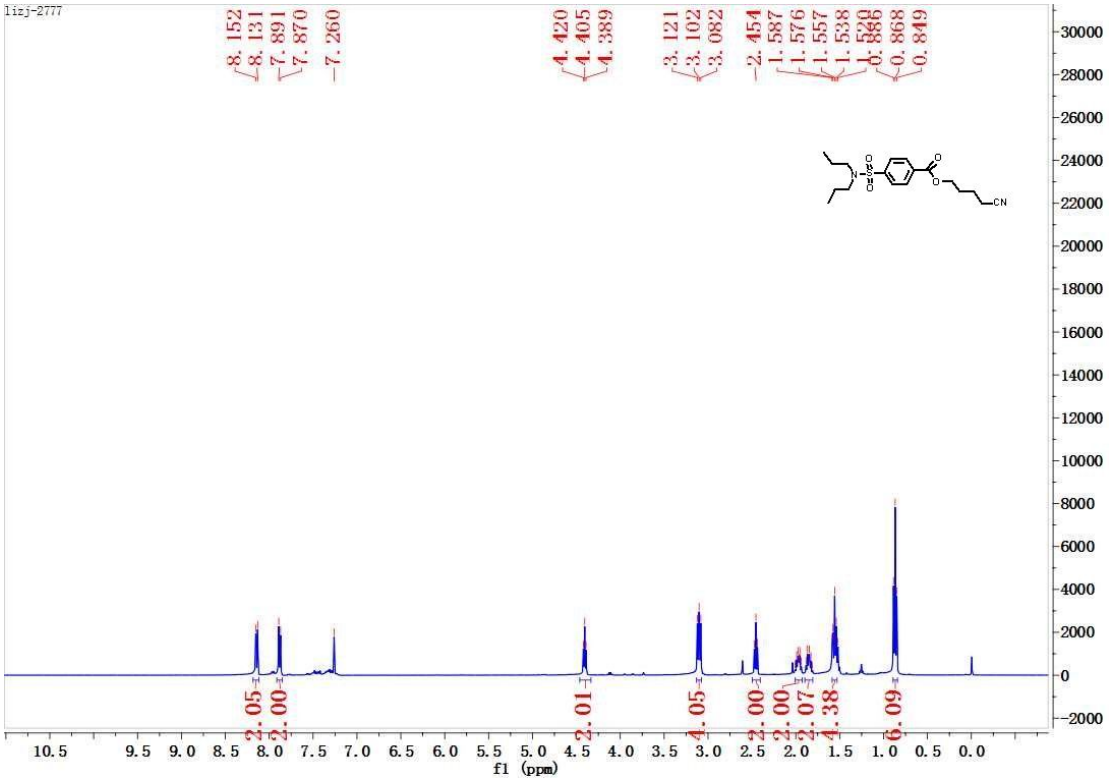
4-^{1}H NMR



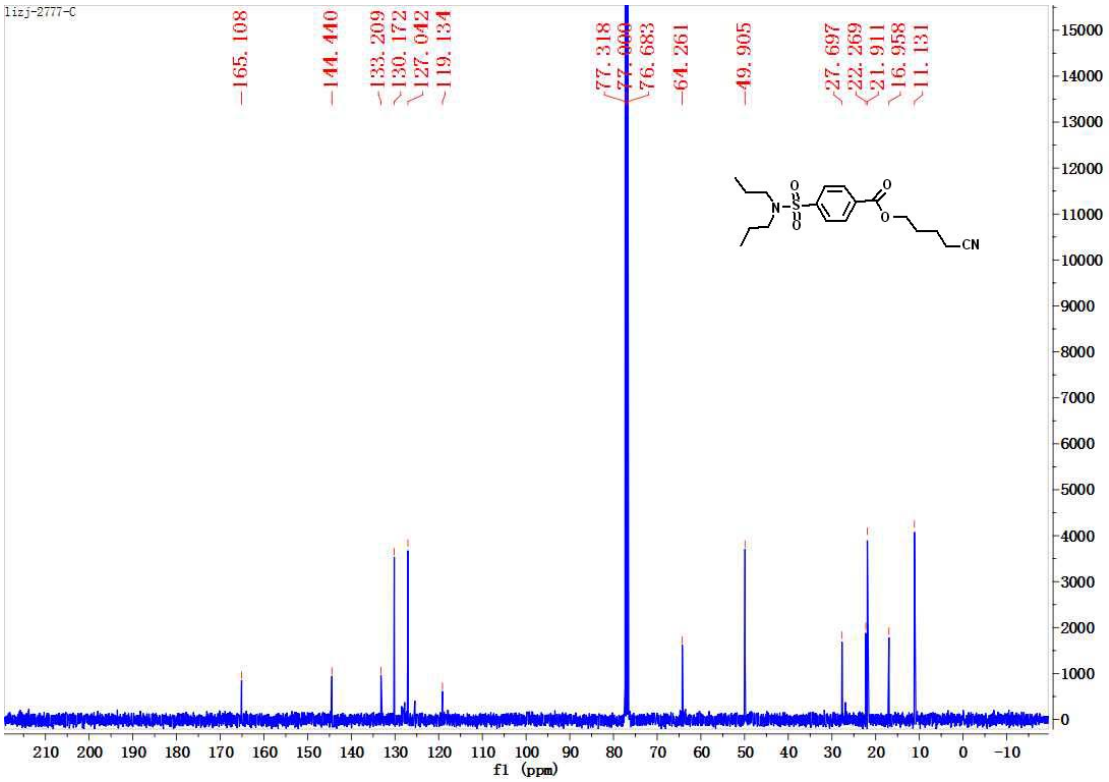
4-^{13}C NMR



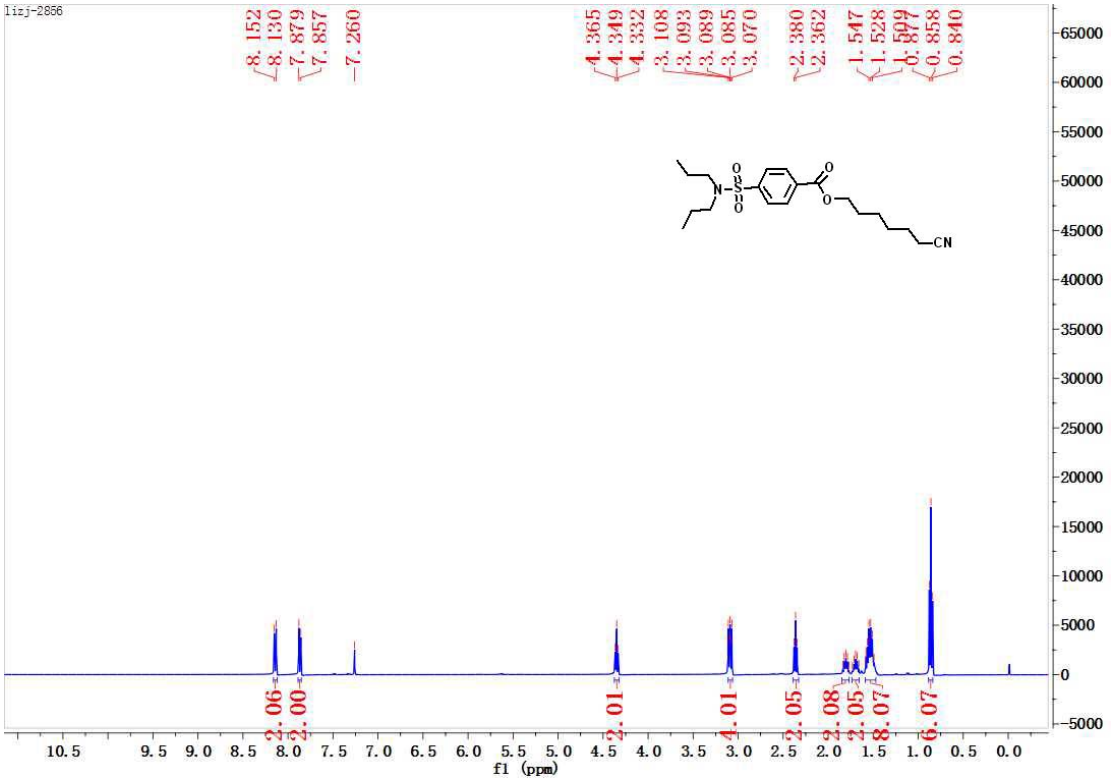
5-^{1}H NMR



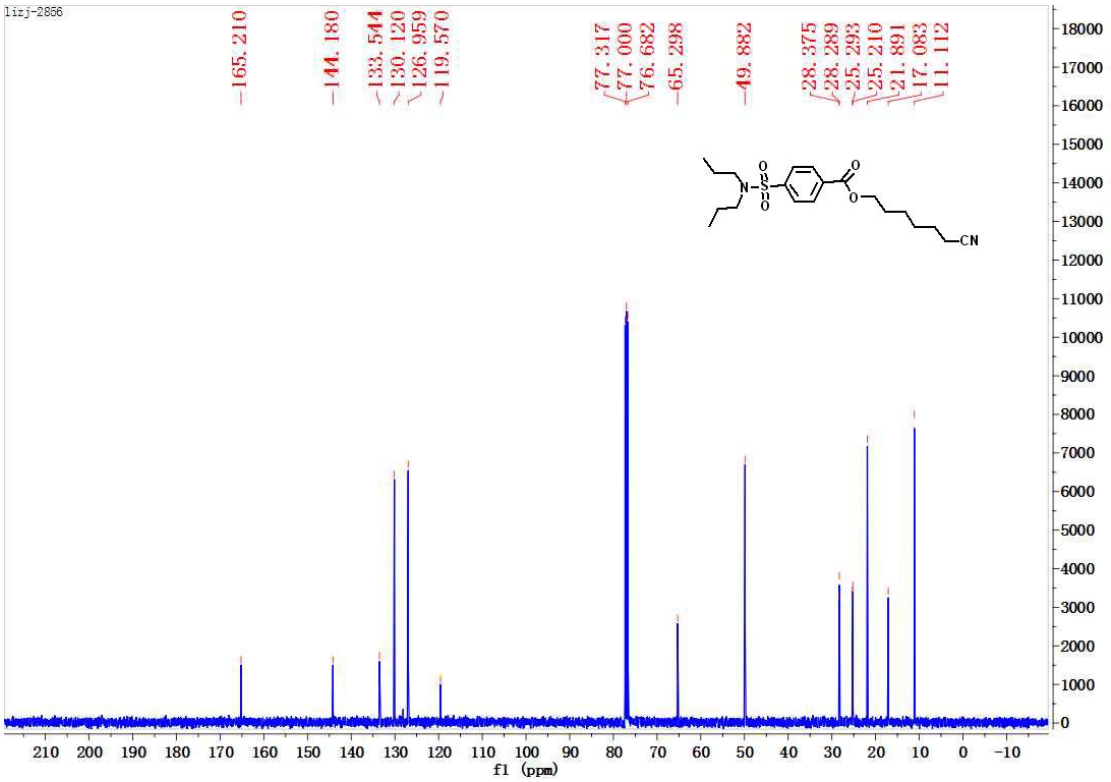
5-^{13}C NMR



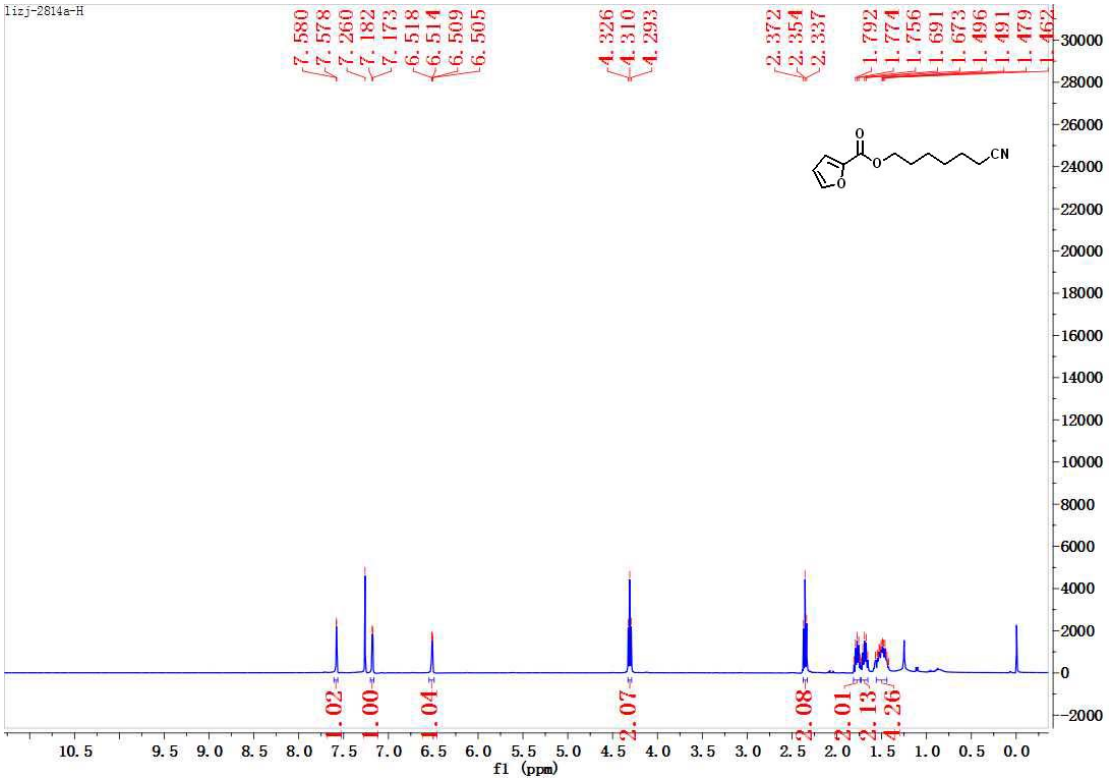
6-^{1}H NMR



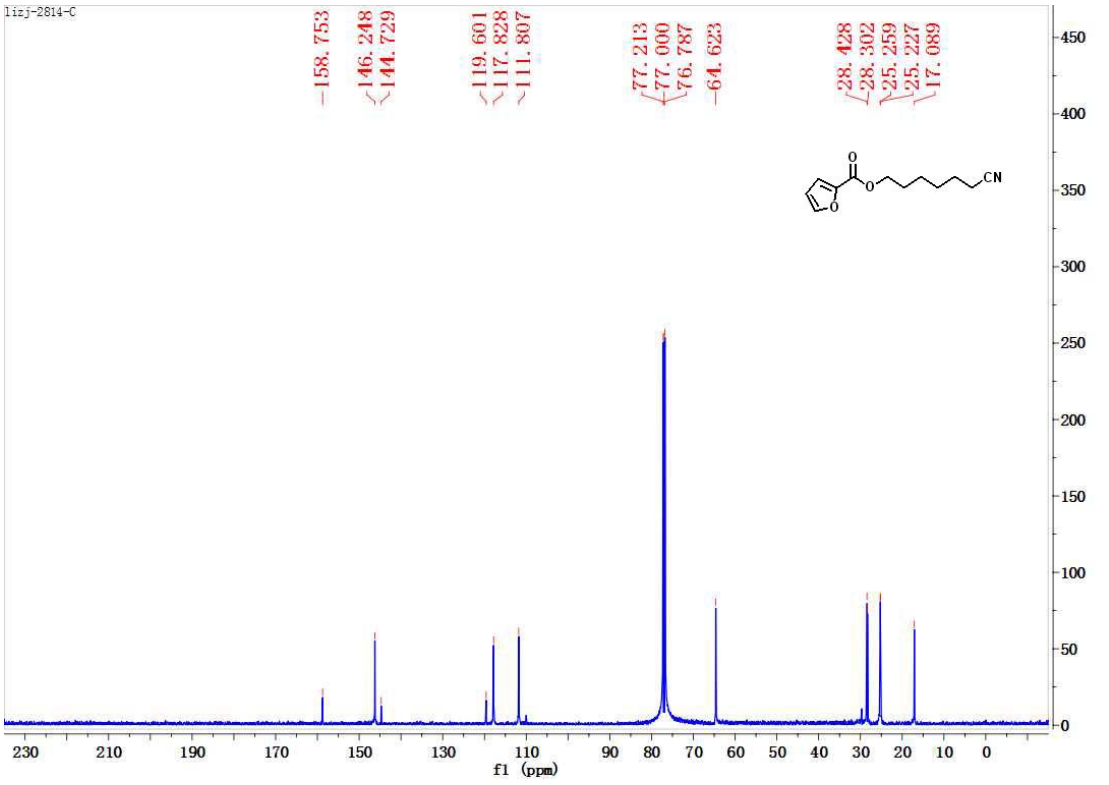
6-^{13}C NMR



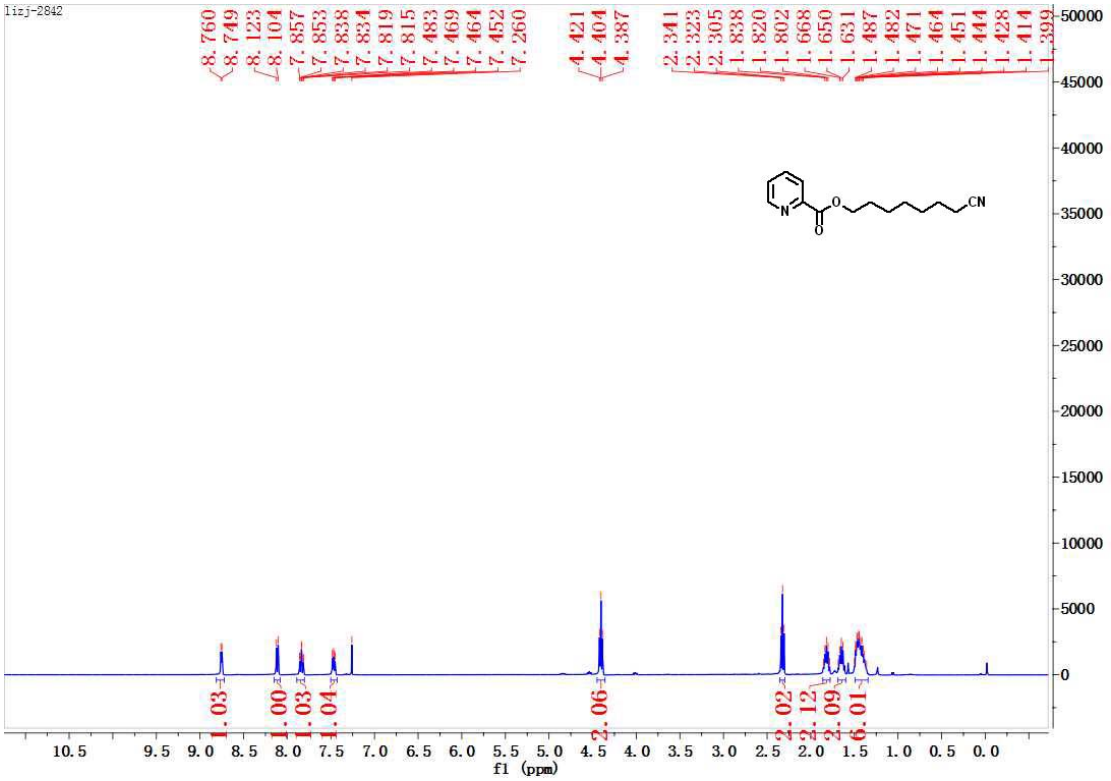
7-^{1}H NMR



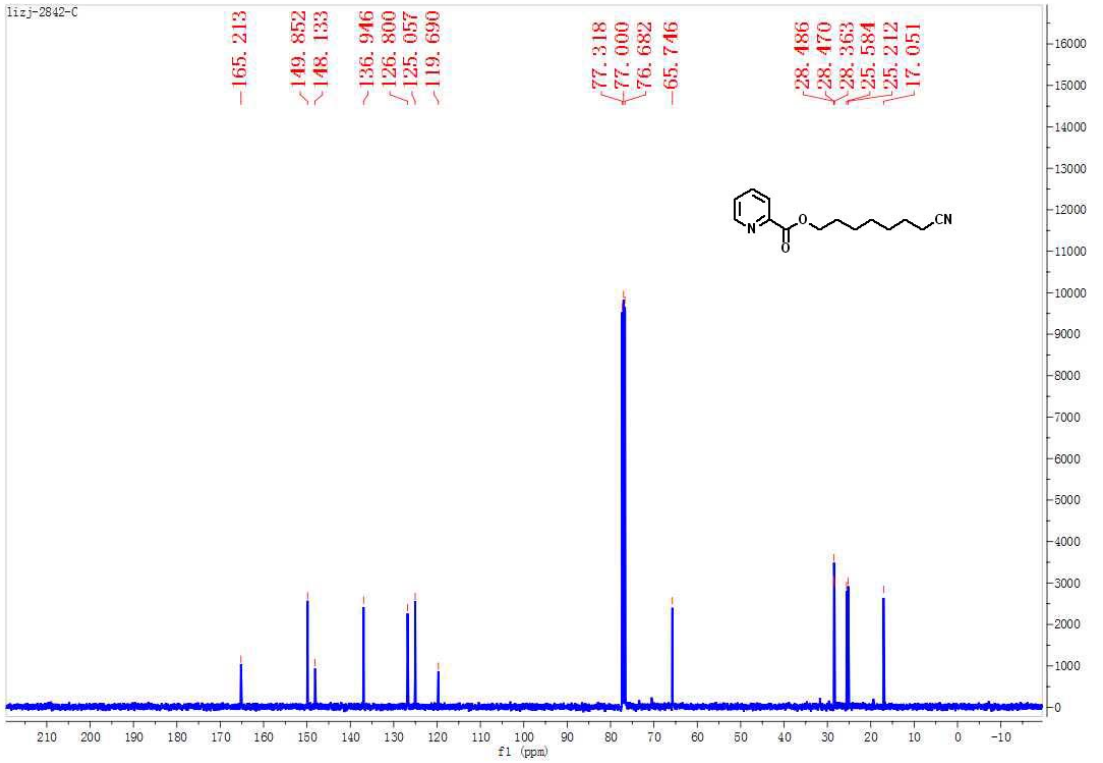
7-^{13}C NMR



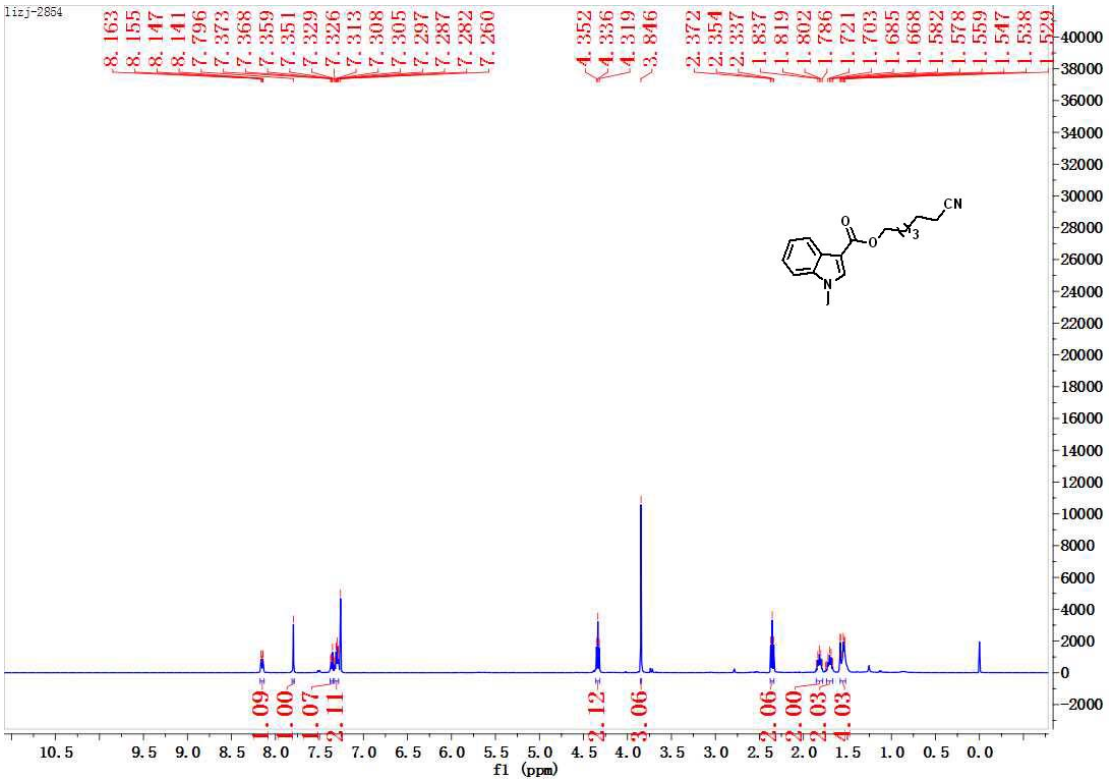
8-^{1}H NMR



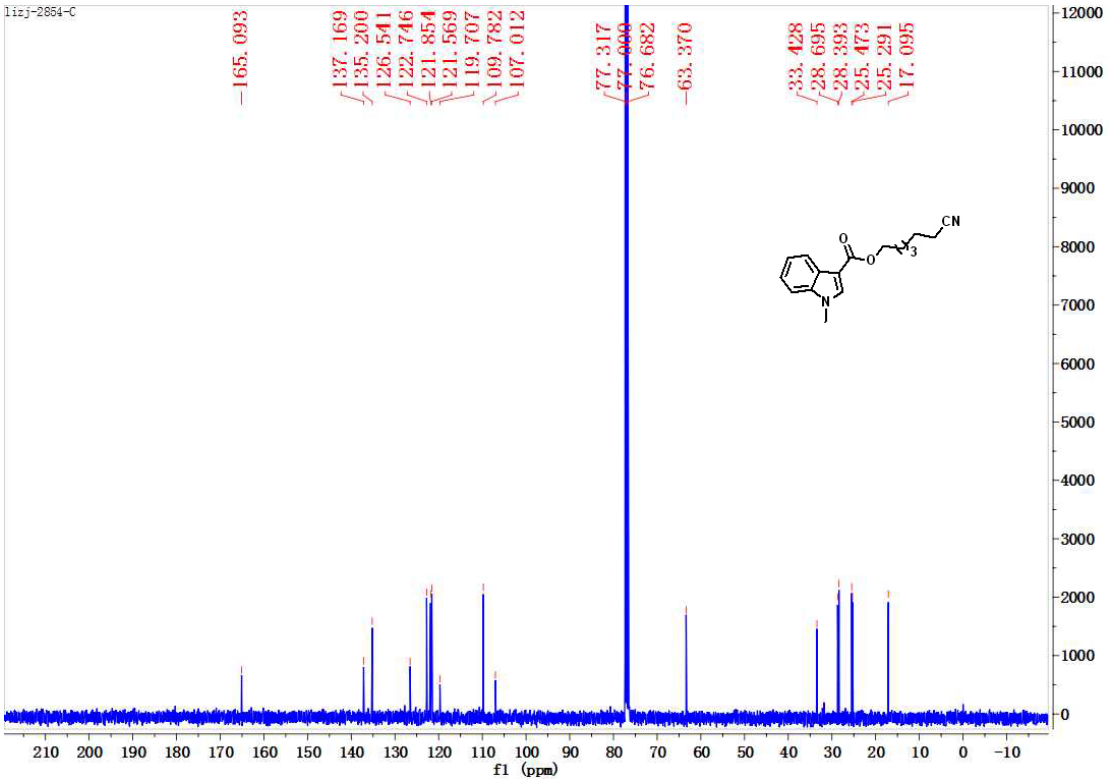
8-^{13}C NMR



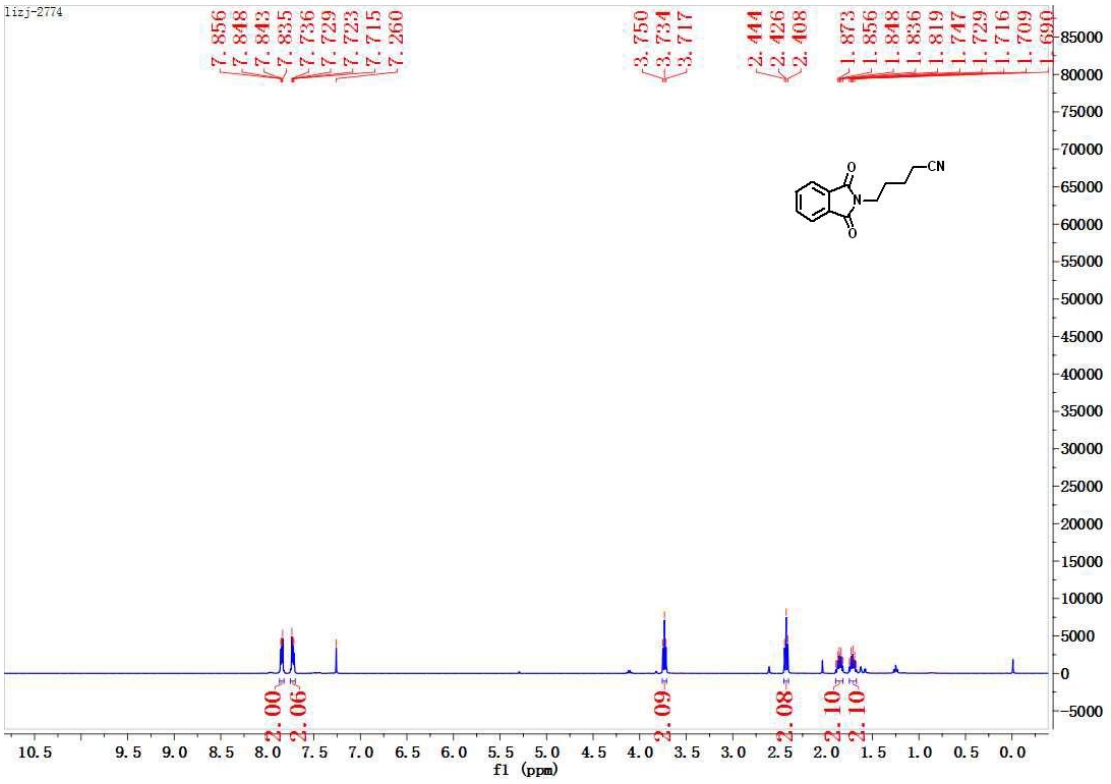
9-^{1}H NMR



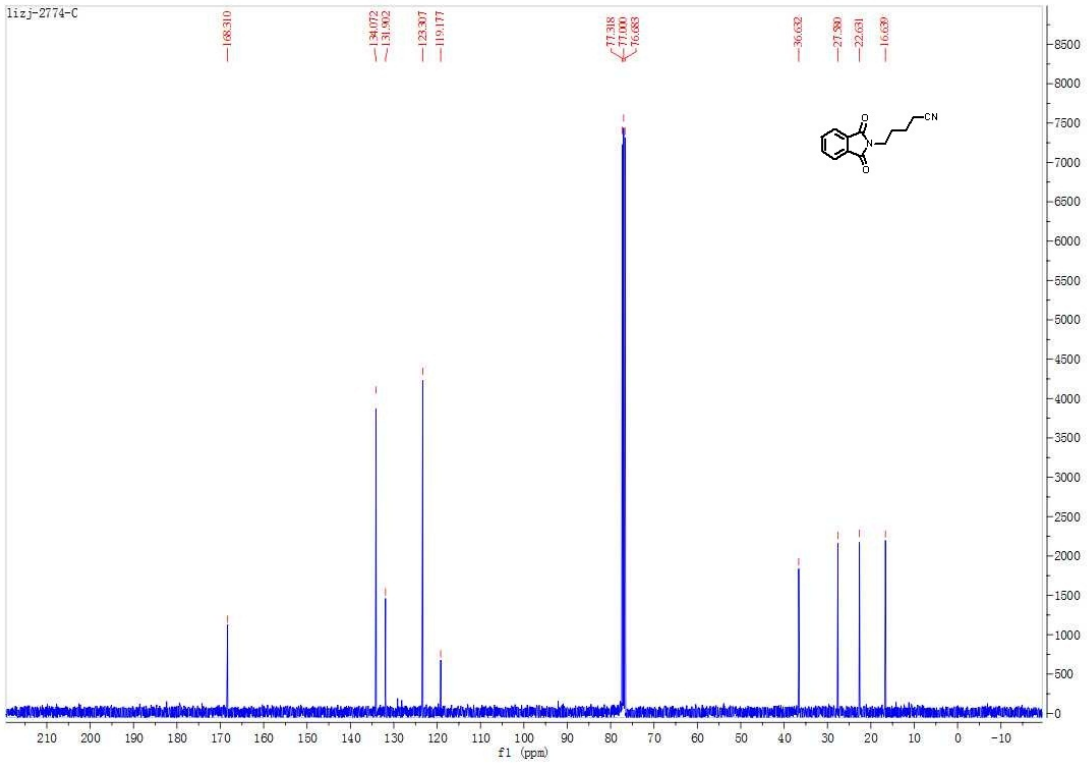
9-^{13}C NMR



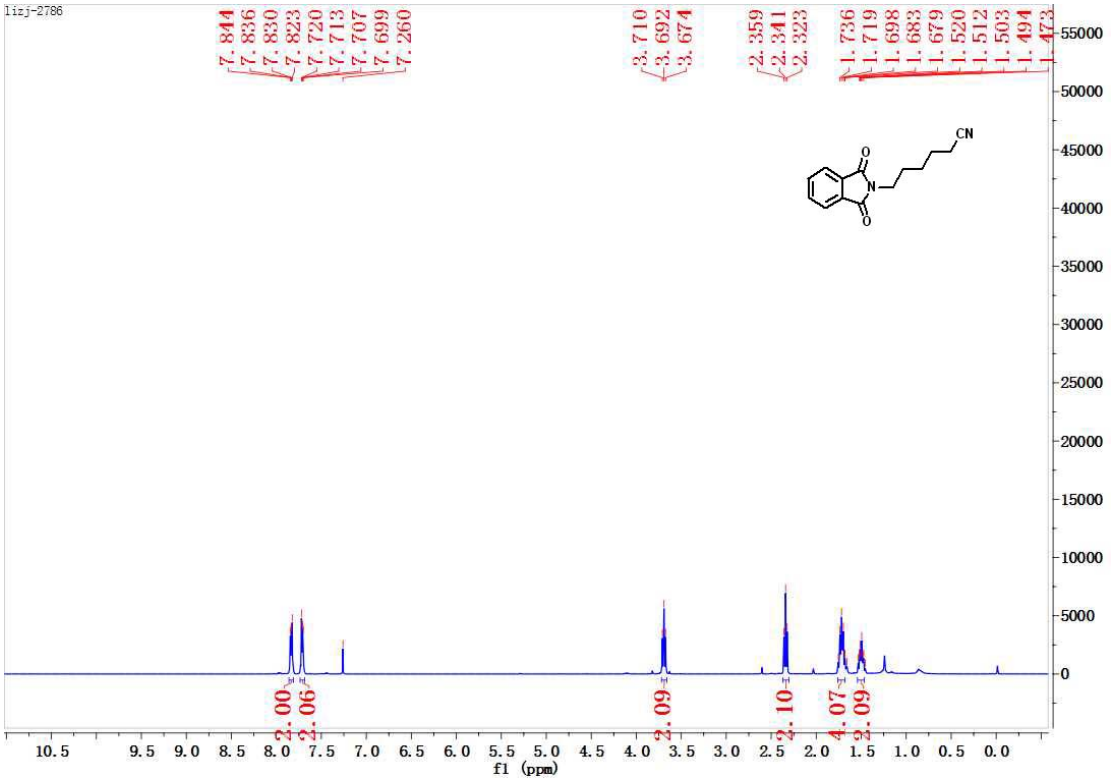
10-^{1}H NMR



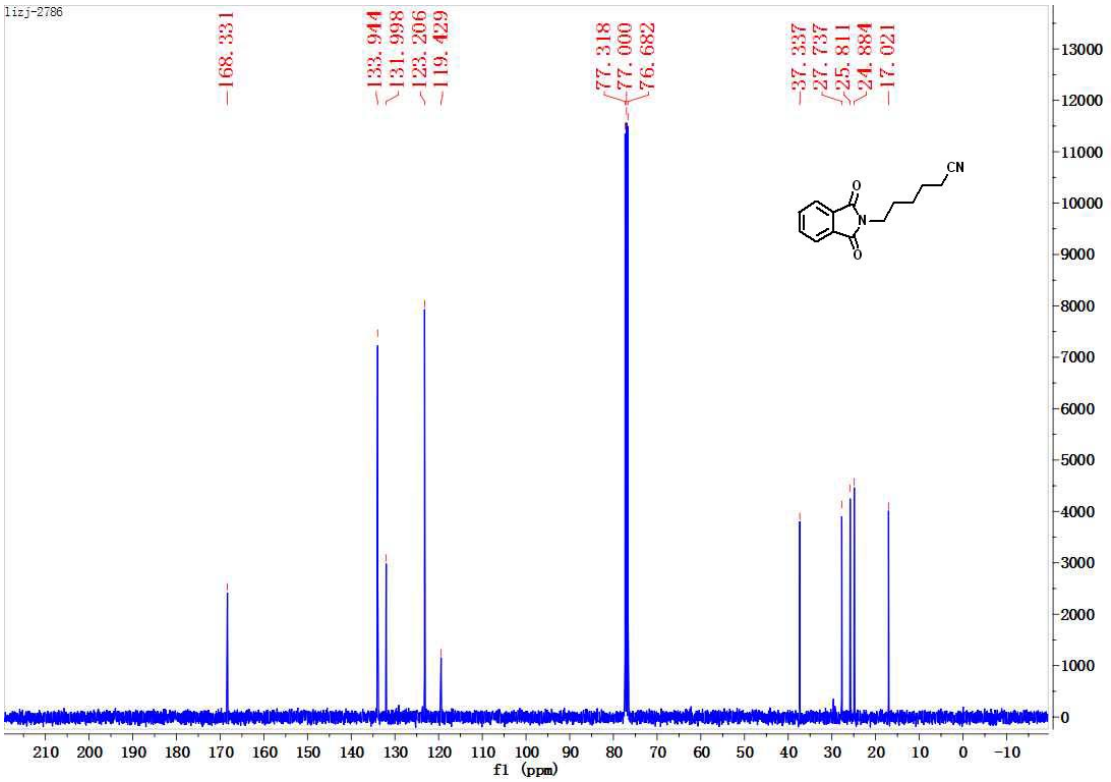
10-^{13}C NMR



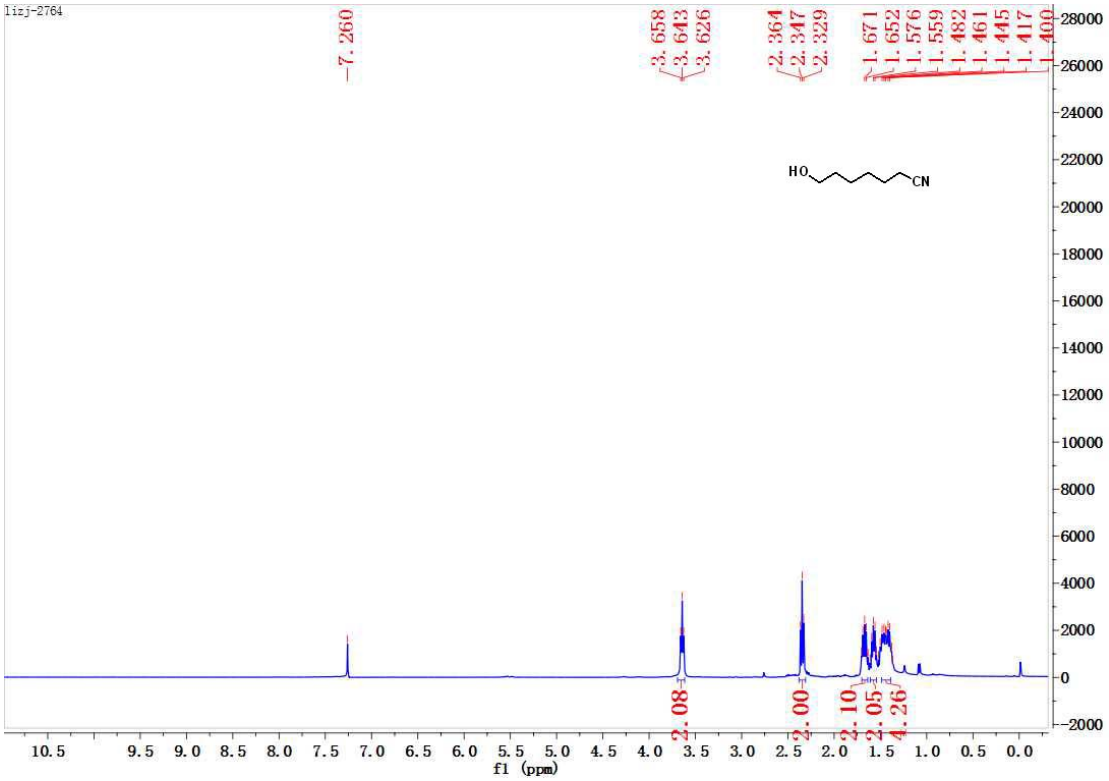
11-^{1}H NMR



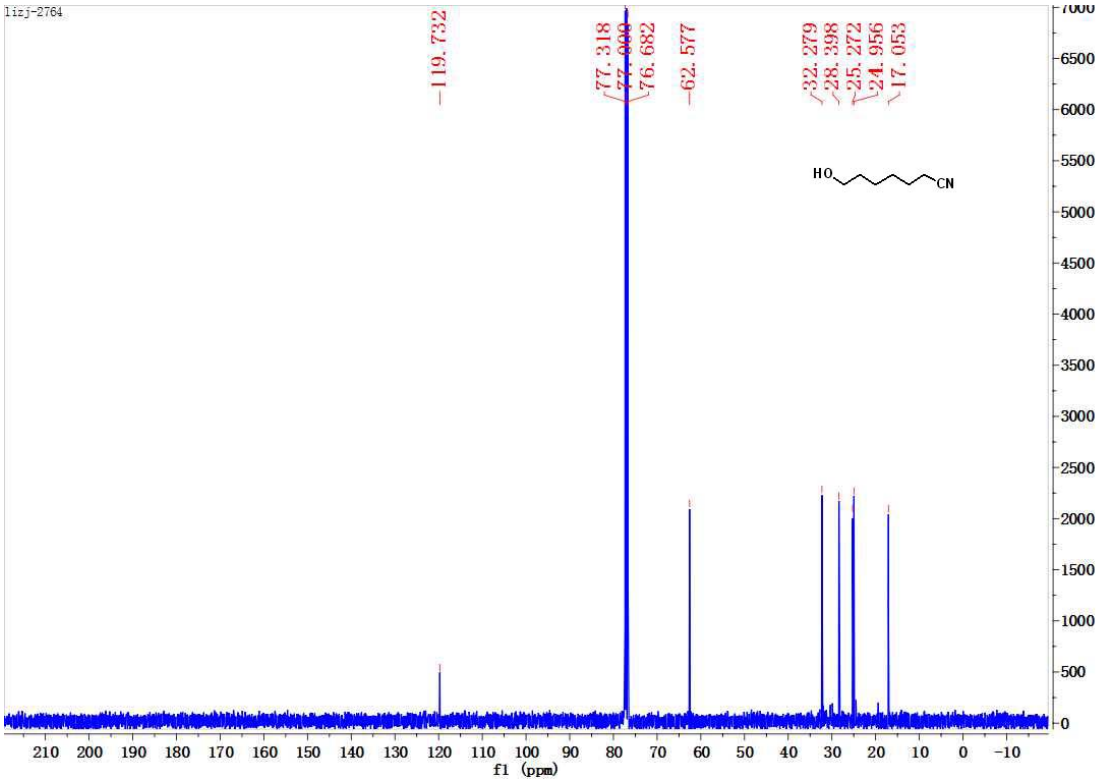
11-^{13}C NMR



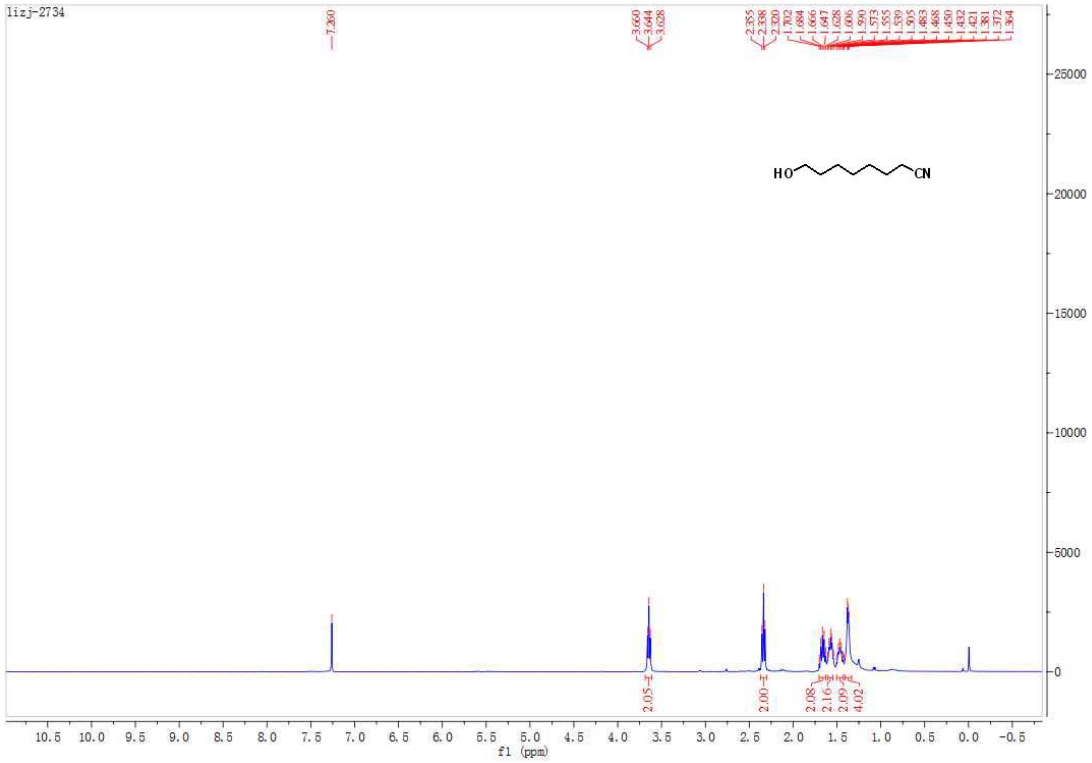
12-^{1}H NMR



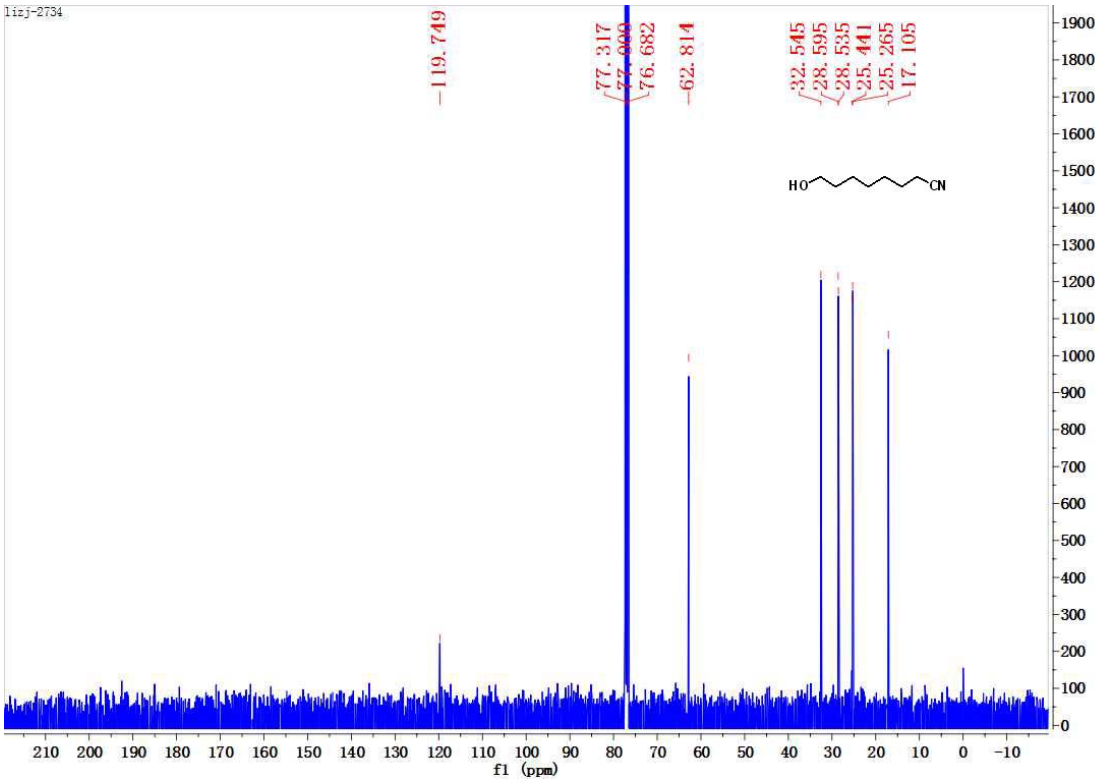
12-^{13}C NMR



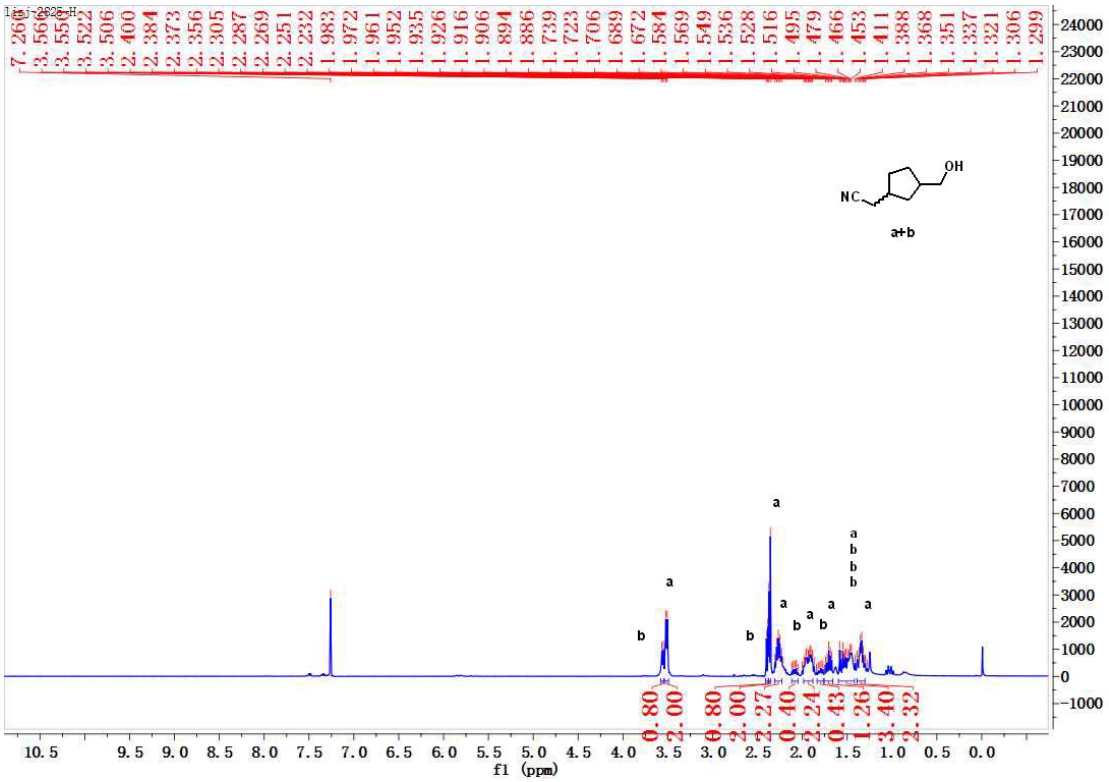
13-^{1}H NMR



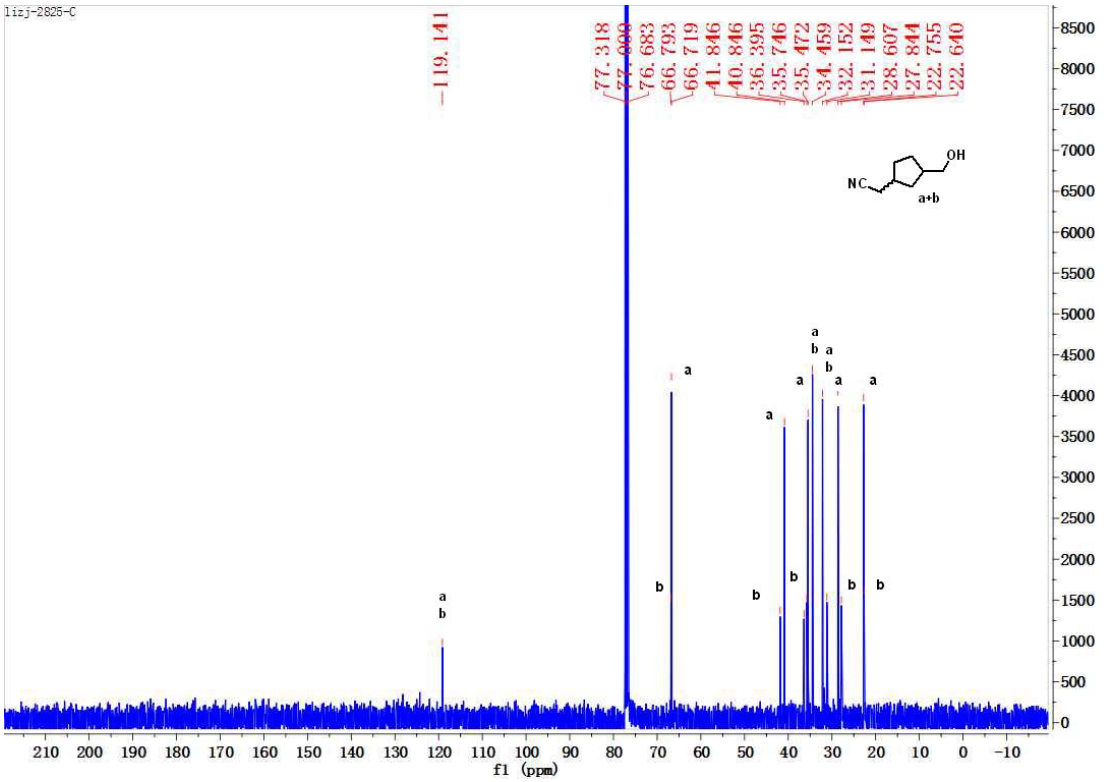
13-^{13}C NMR



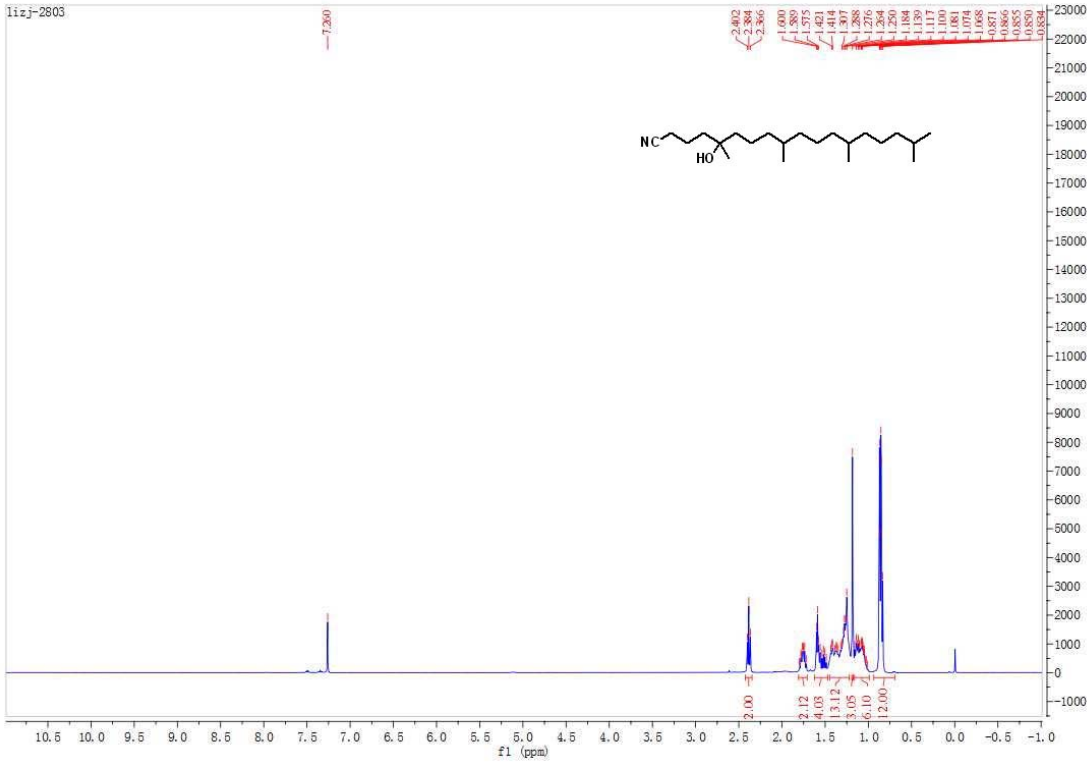
14-^{1}H NMR



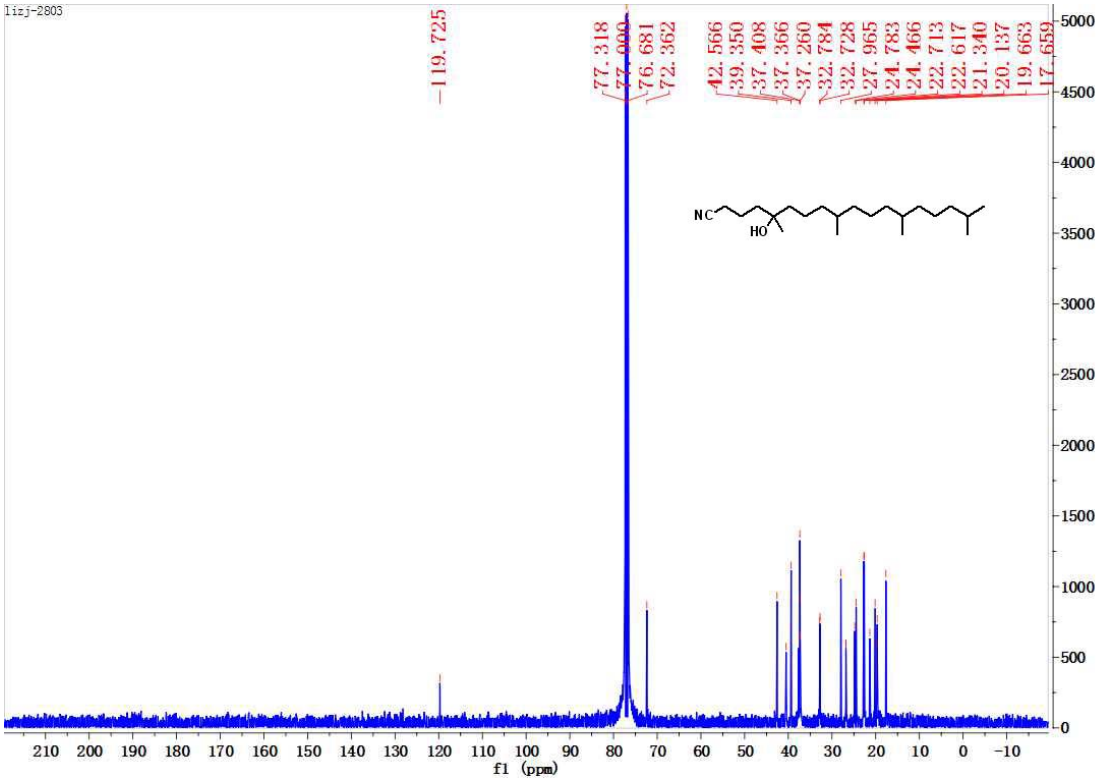
14-^{13}C NMR



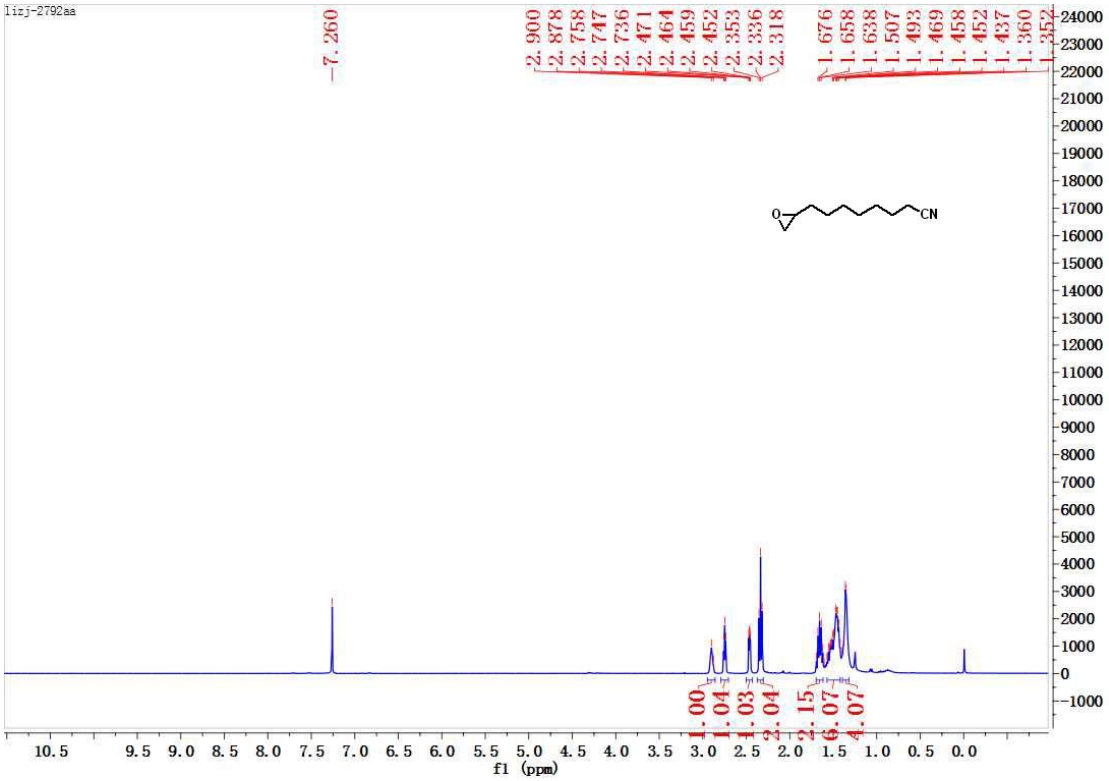
15-^{1}H NMR



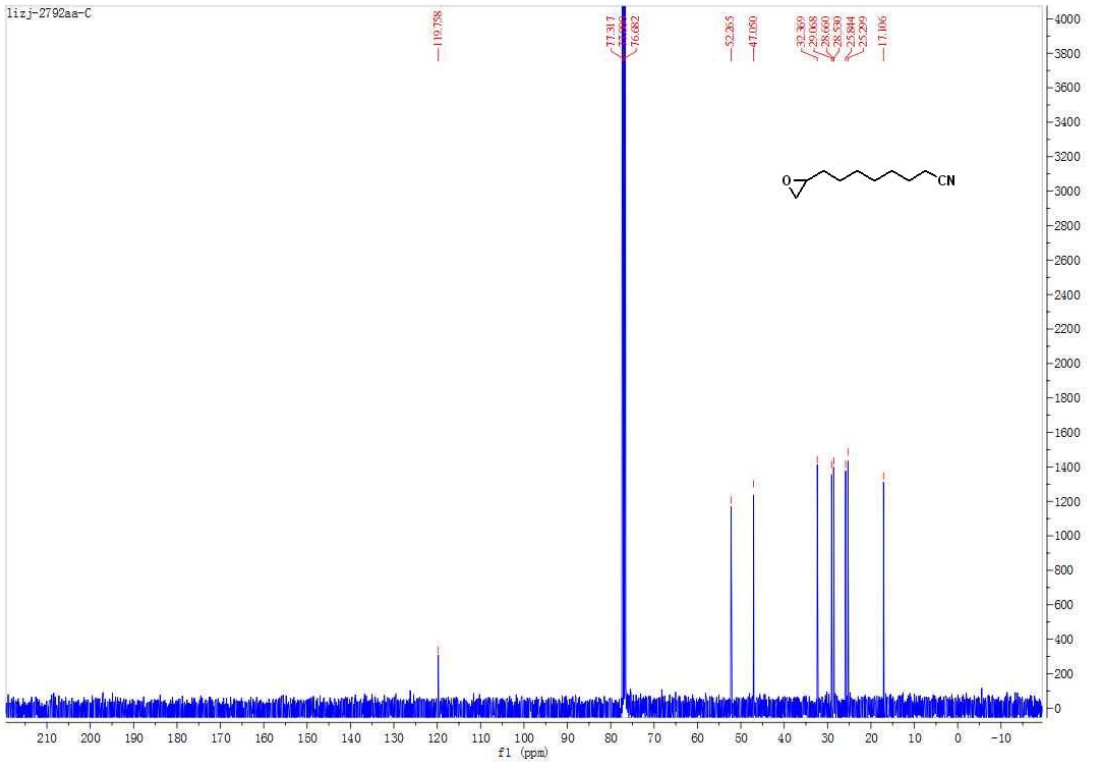
15-^{13}C NMR



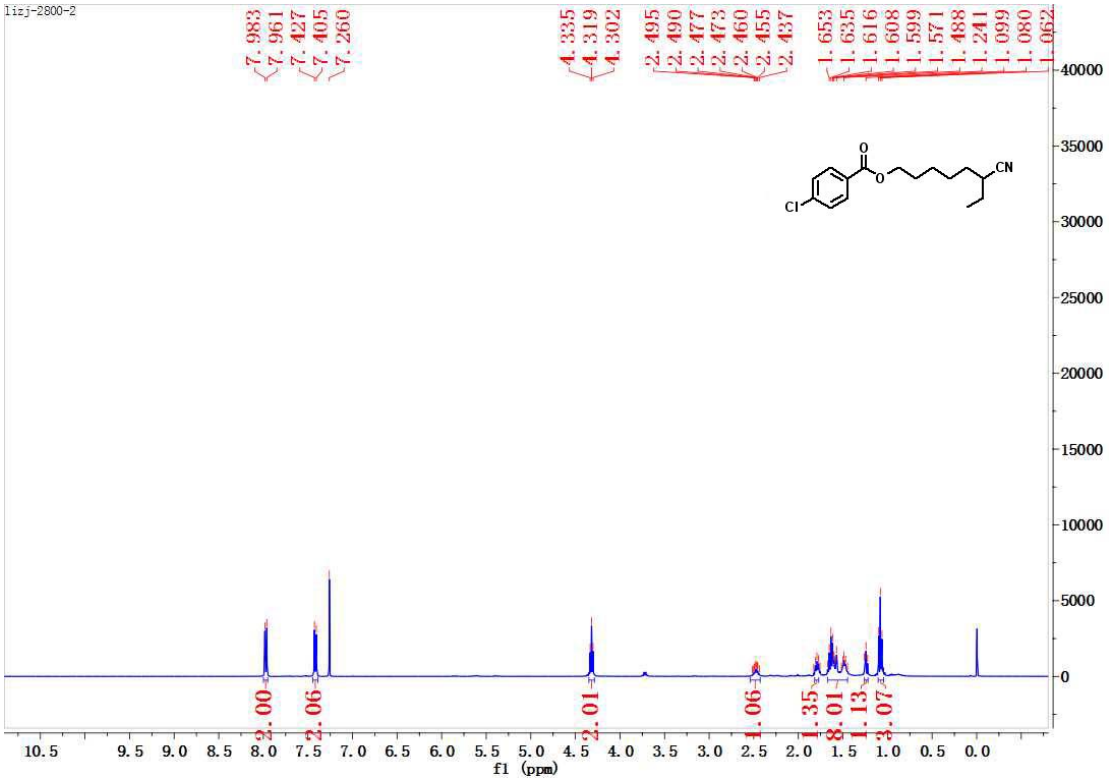
16-^{1}H NMR



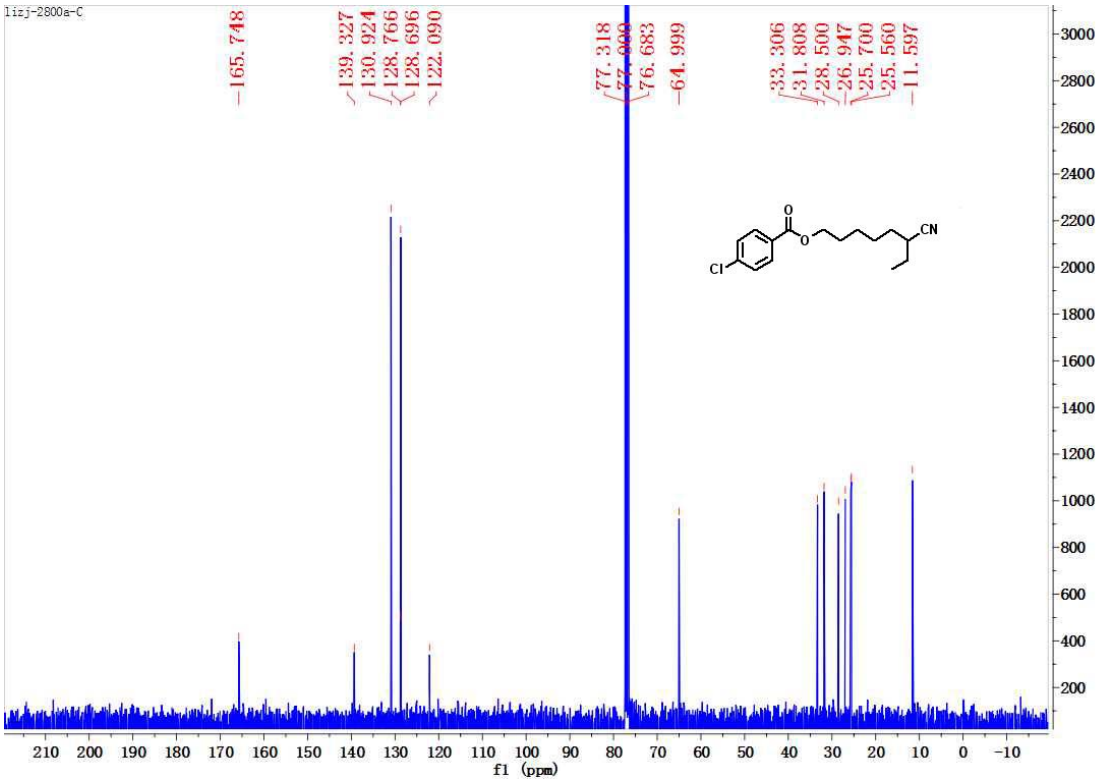
16-^{13}C NMR



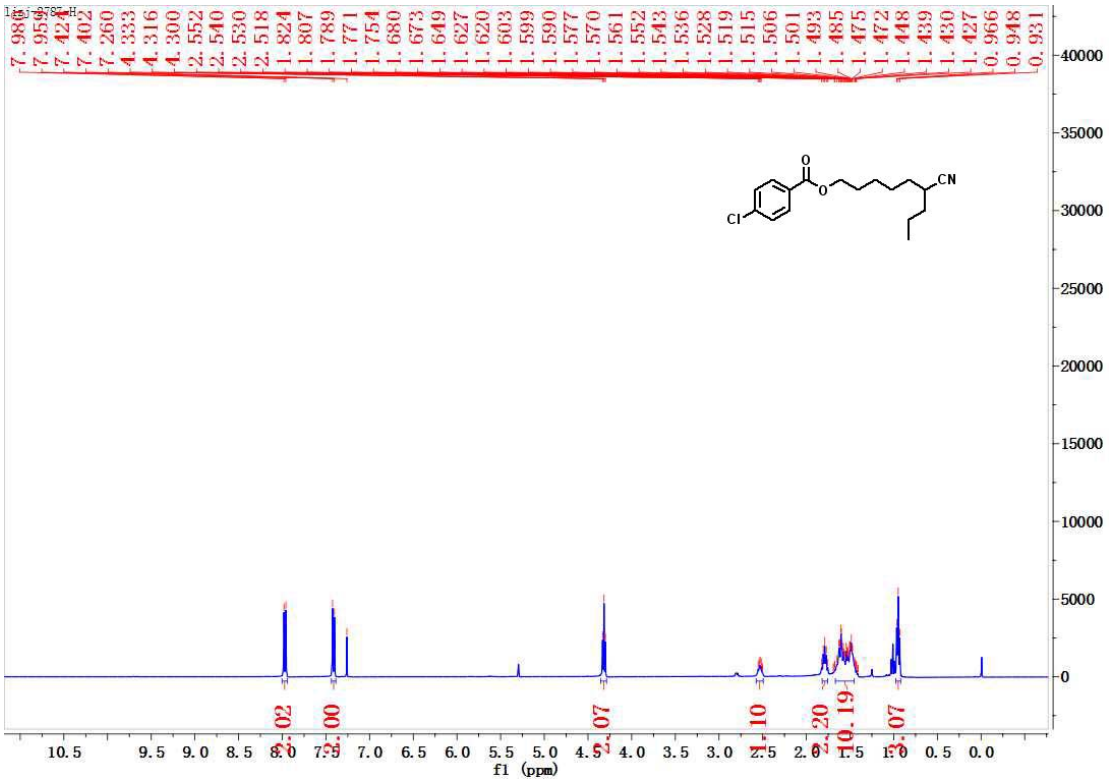
17-^{1}H NMR



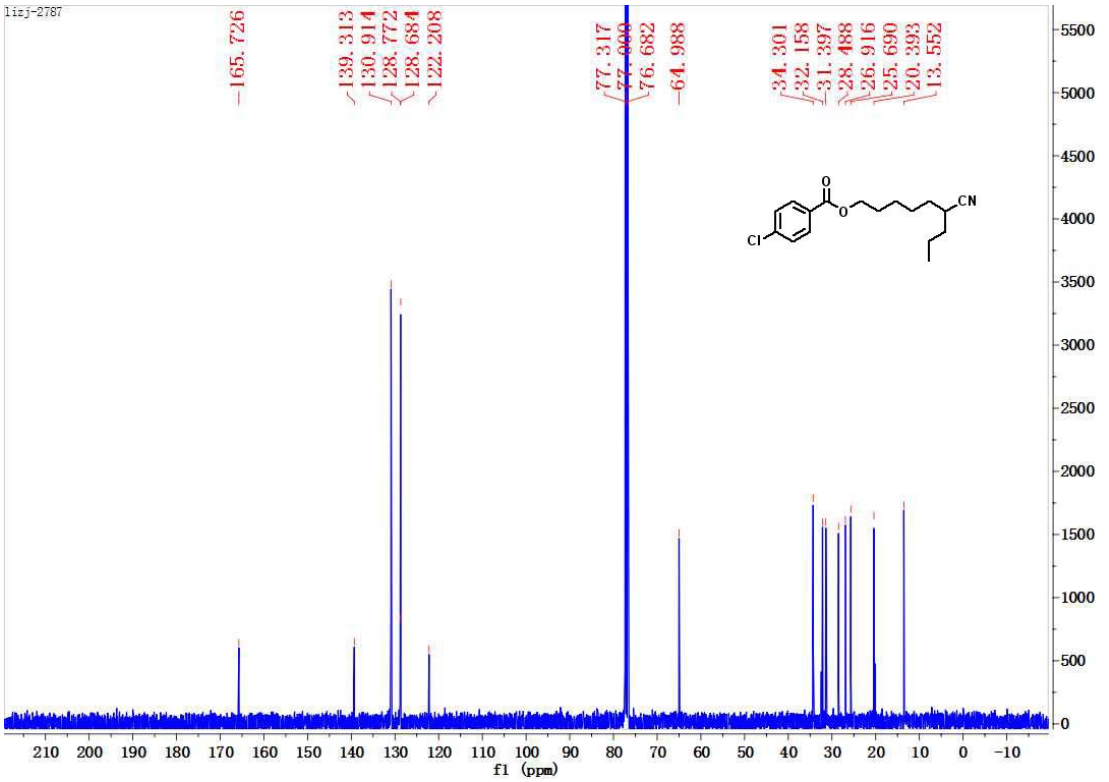
17-^{13}C NMR



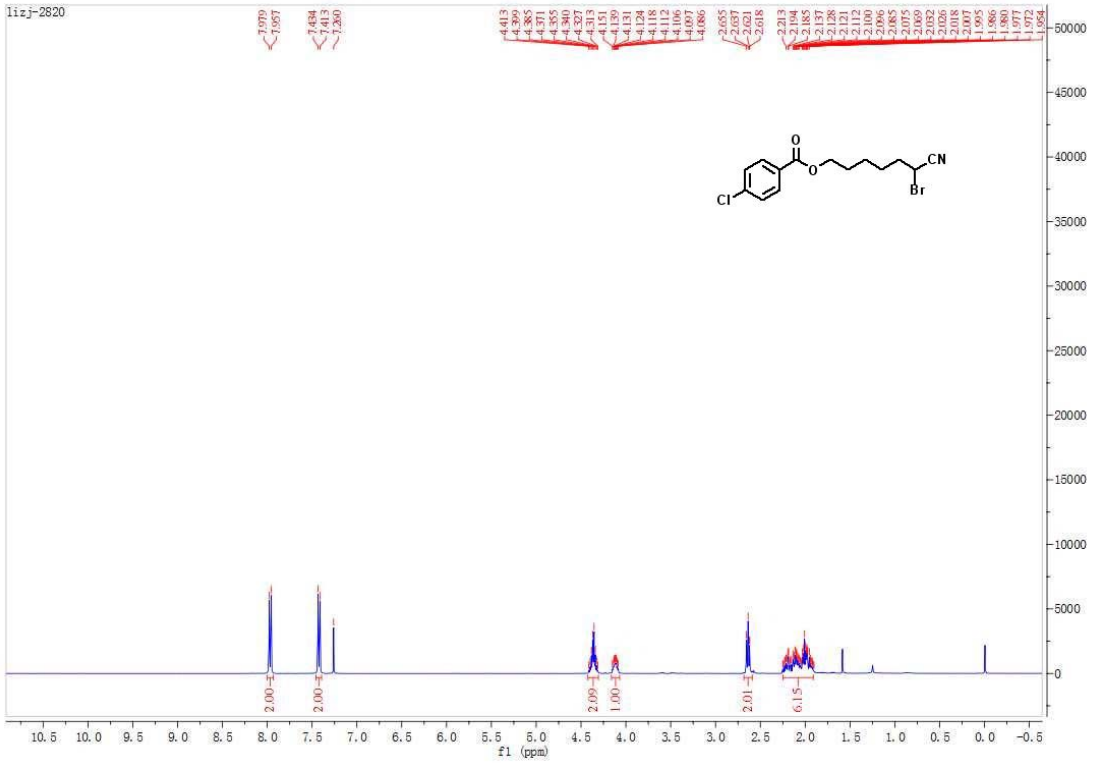
18-^{1}H NMR



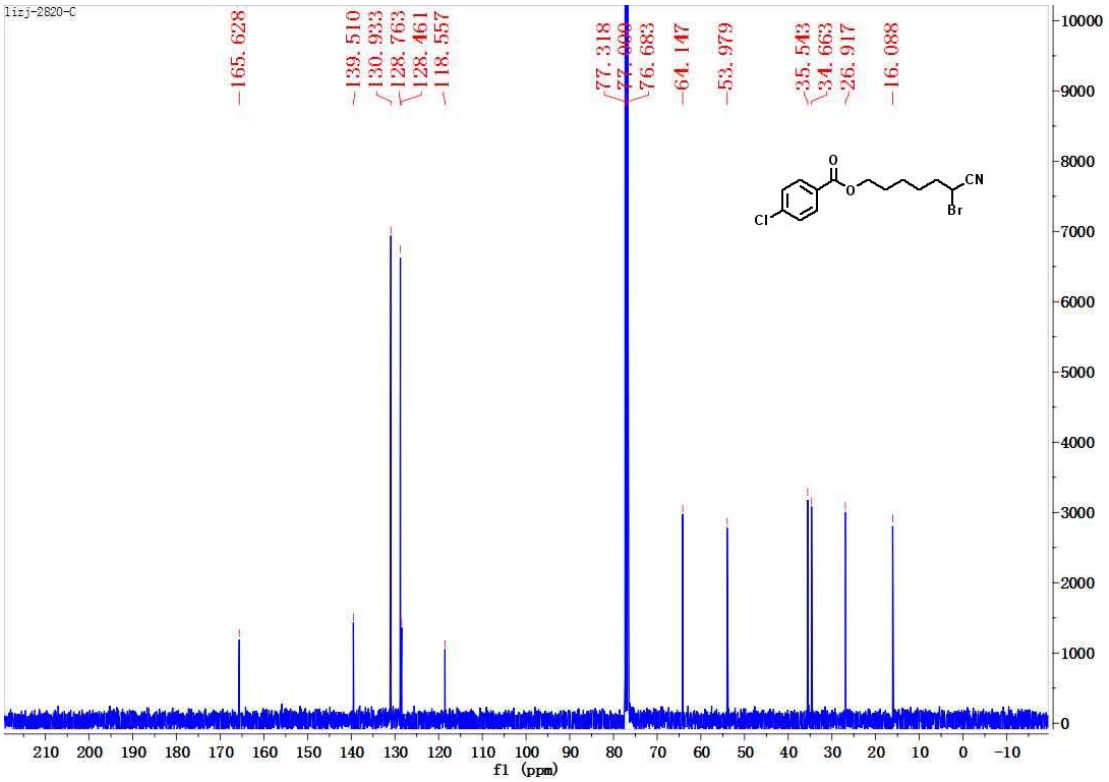
18-^{13}C NMR



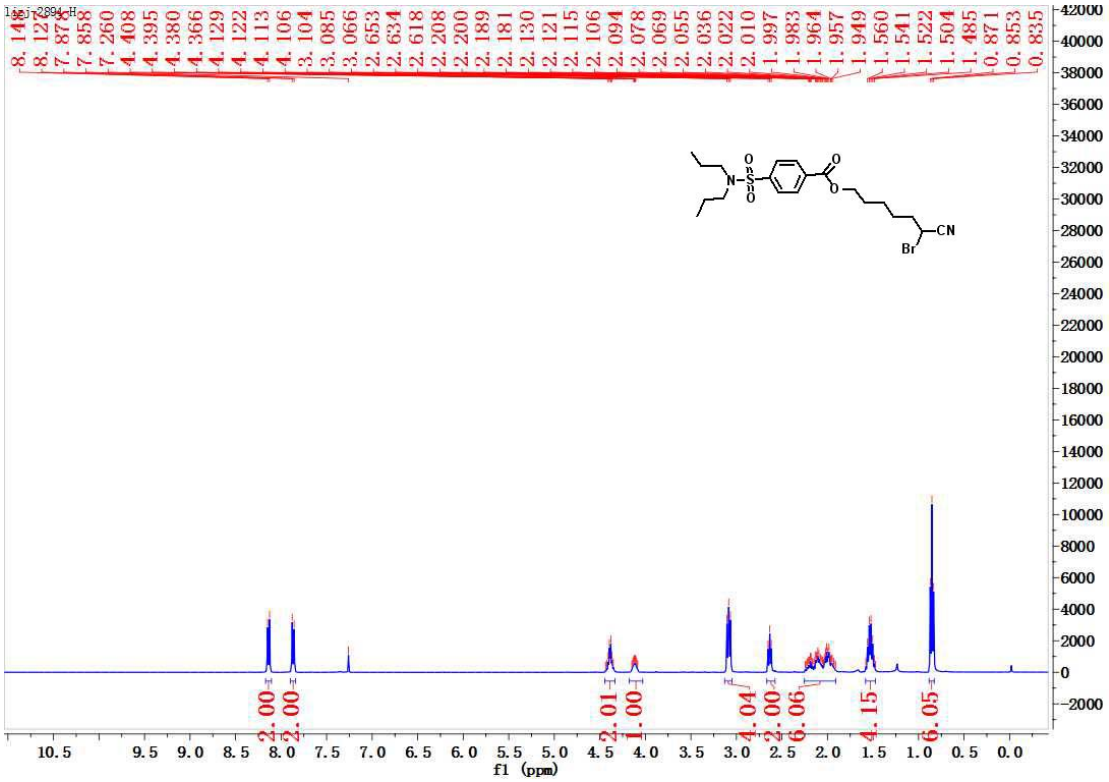
19-^{1}H NMR



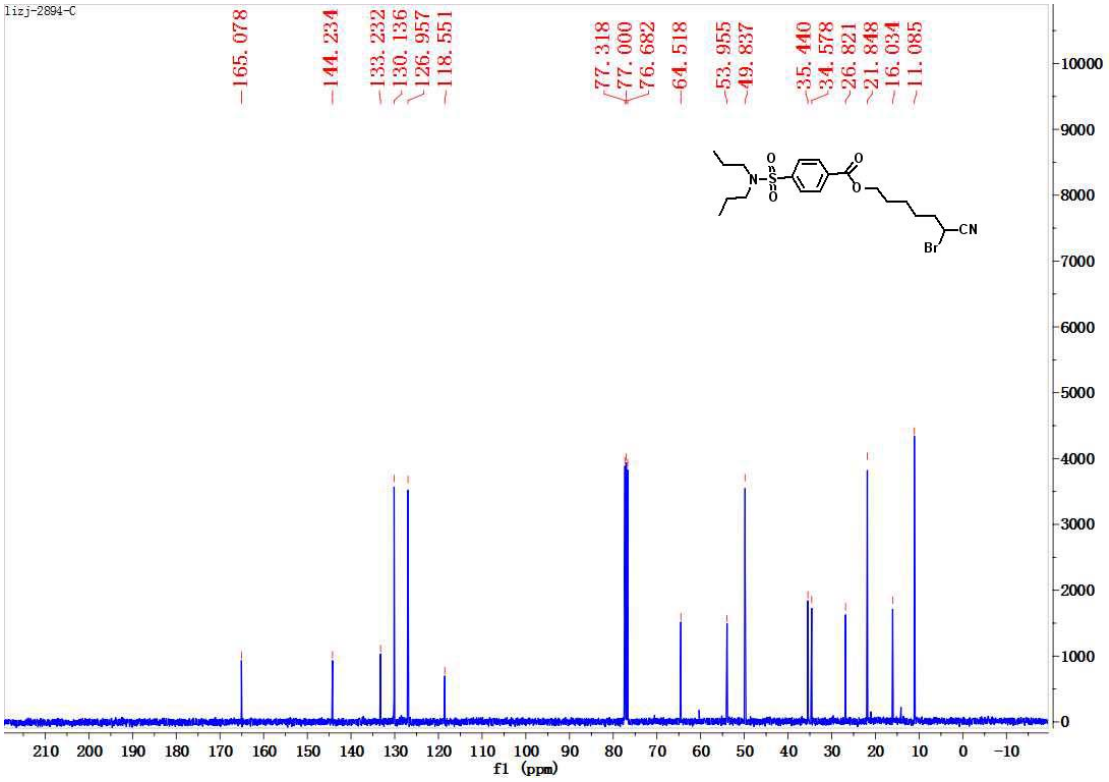
19-^{13}C NMR



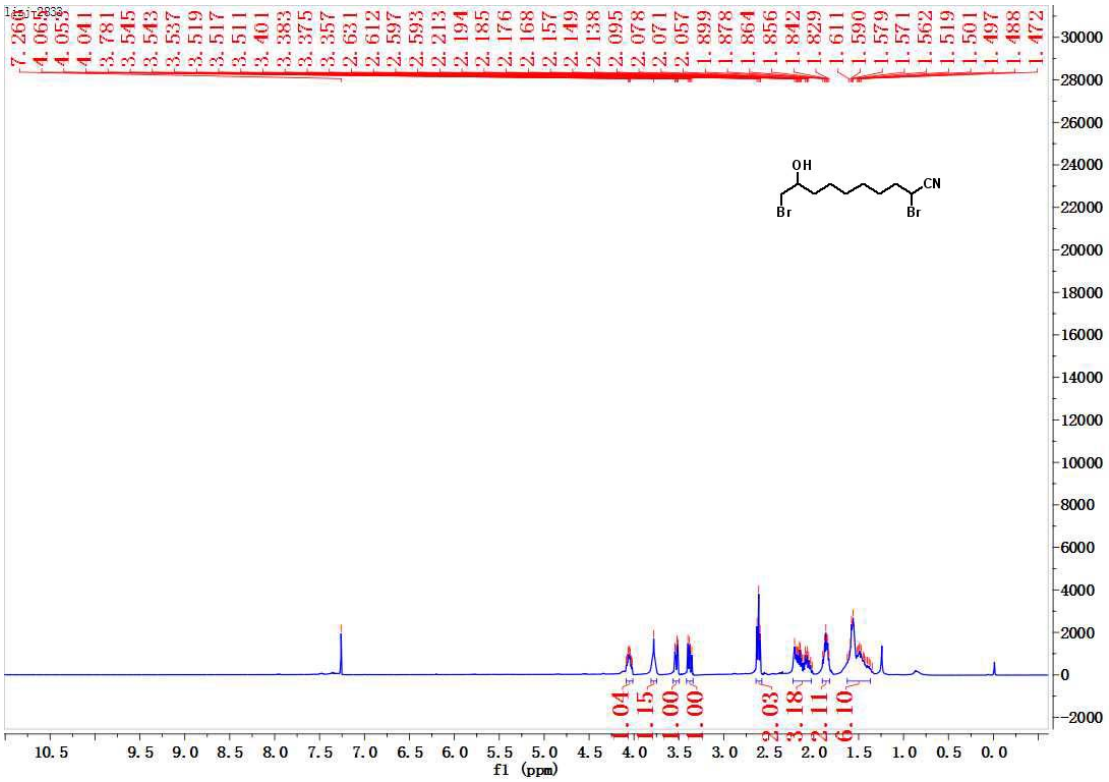
20-^{1}H NMR



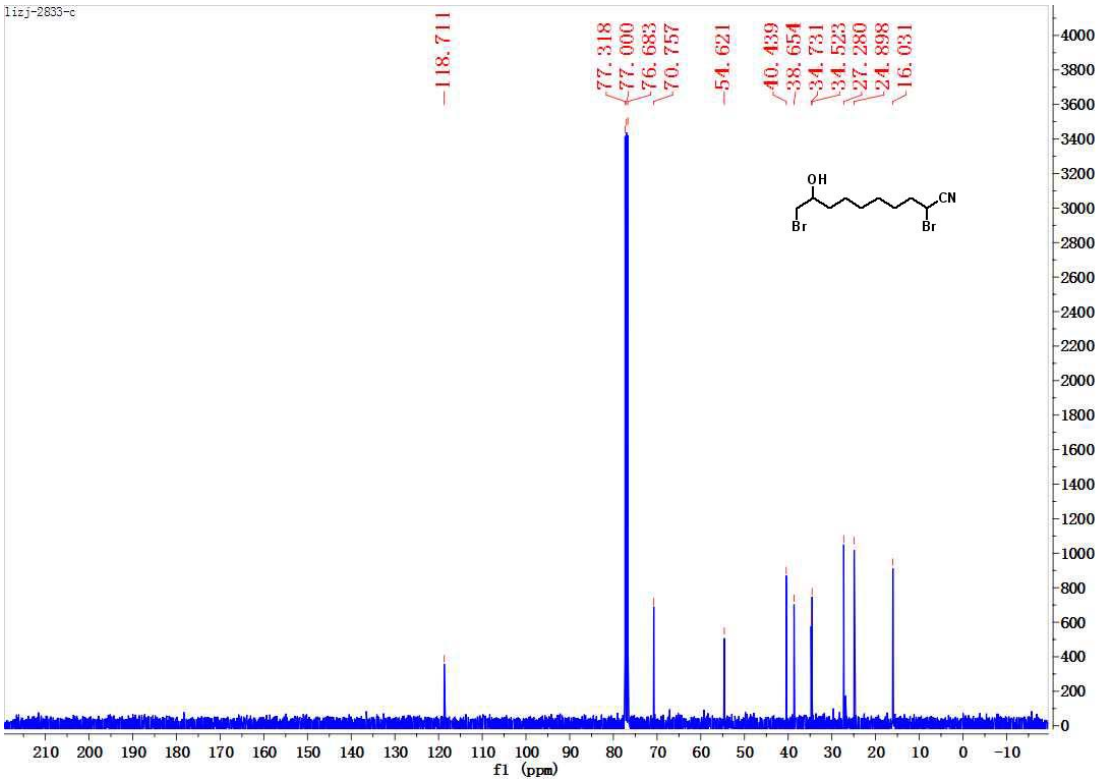
20-^{13}C NMR



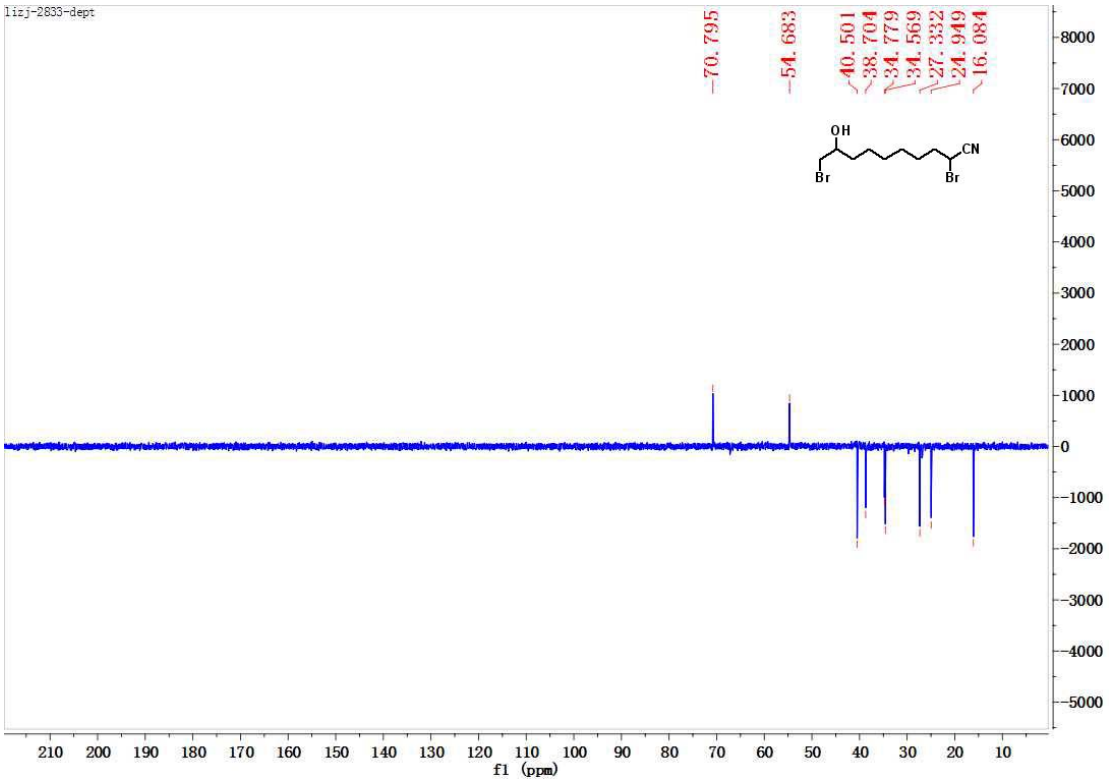
21-^{1}H NMR



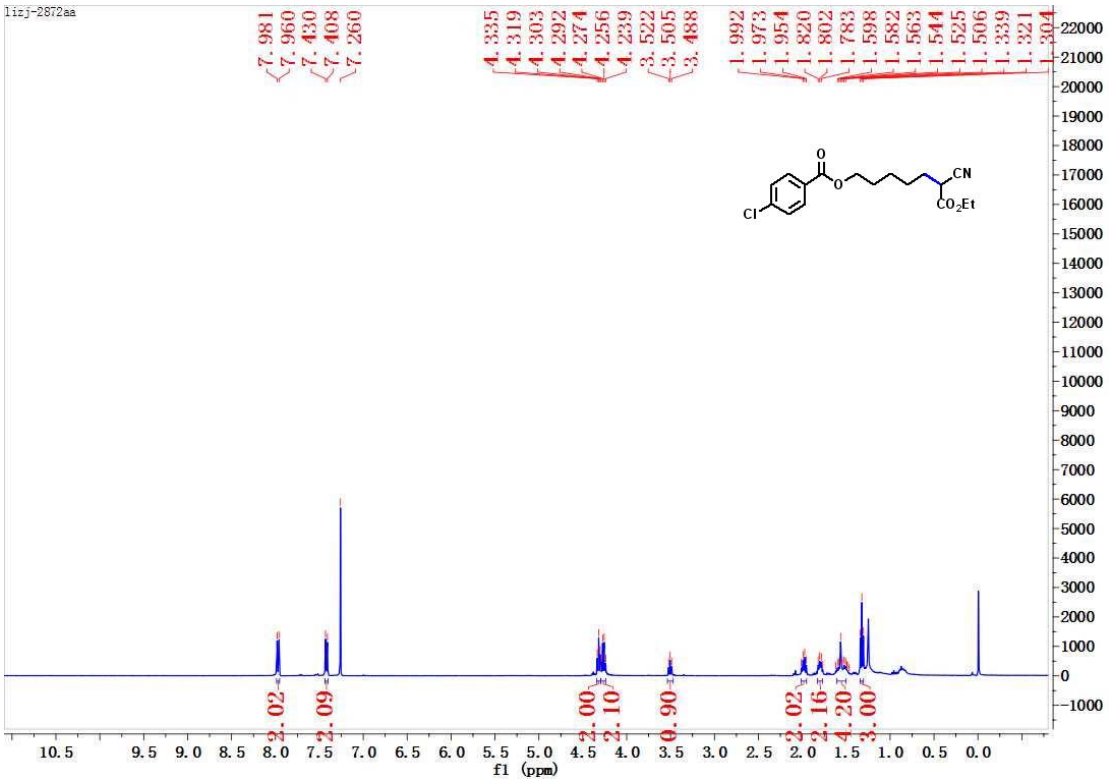
21-^{13}C NMR



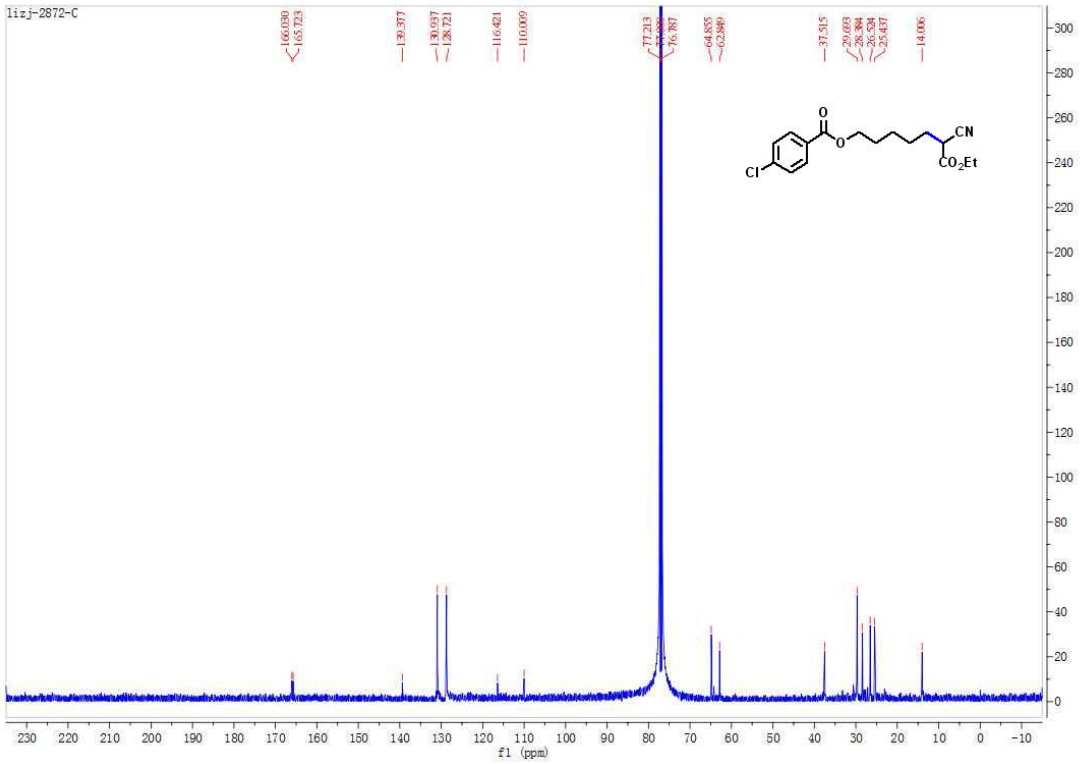
21-^{13}DEPT



22-^{1}H NMR



22-^{13}C NMR


lizj-2872-C
166.030
165.723
139.377
130.937
128.721
116.421
110.009
77.213
76.787
64.855
62.049
37.515
29.693
28.384
26.524
25.437
14.006
CN
CO2Et
Cl
f1 (ppm)