Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Sandmeyer Cyanation of Arenediazonium Tetrafluoroborate Using Acetonitrile as Cyanide Source

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Contents

General:

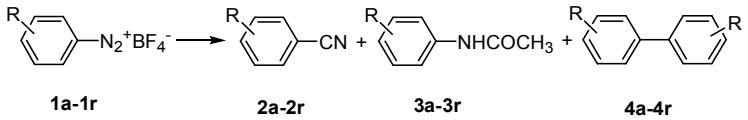
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Acetonitrile was dried and newly distilled. NMR spectra were obtained on a Bruker AMX 400 system using chloroform-d as deuterated solvents, with proton and carbon resonances at 400 MHz and 100 MHz, respectively. Mass spectra were measured on an Agilent1290-micrOTOF Q II system spectrometer. IR (KBr pellets) spectra were recorded in the 400-4000 cm^{-1} range on a Nicolet360 spectrophotometer.

General synthesis of arenediazonium tetrafluoroborates

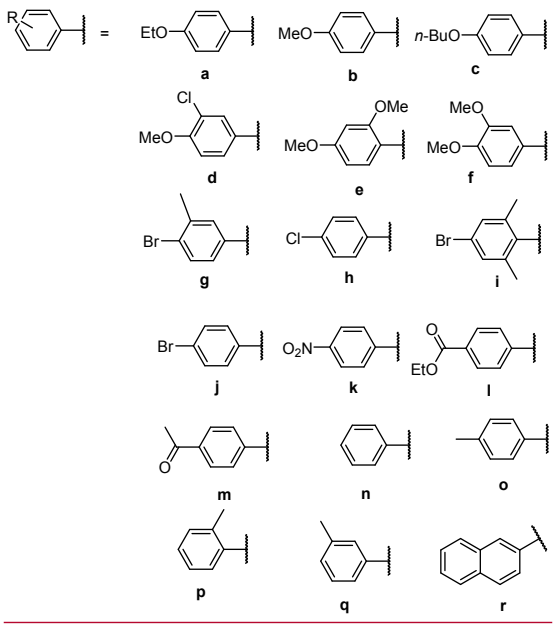
In an Erlenmeyer flask, the aniline (10 mmol) was dissolved in an aqueous solution of HBF_4 (50%, 5.0 mL, 40 mmol) and a saturated solution of sodium nitrite (760 mg, 11 mmol) was added dropwise at 0°C. The excess of oxidant was removed by the addition of urea. Then, the precipitated diazonium salt was filtered off and dissolved in the less amount of acetone. Diethyl ether was added to the clear solution, causing the precipitation of the arenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3×10 mL). The arenediazonium tetrafluoroborate was dried in vacuo (10^{-3} mbar) for 10 minutes and then directly used without further purification.

General synthesis of aryl nitriles from the corresponding arenediazonium salts.

To a solution of arenediazonium tetrafluoroborate (0.5 mmol) in MeCN (3.0 mL) was added $PdCl_2$ (8.8mg, 0.05mmol) and Ag_2O (116 mg, 0.5 mmol). The mixture was stirred at 55℃ for 24 h under air. Then the reaction mixture was cooled to room temperature and filtered through a pad of celite (1.0 g) and rinsed with CH_2Cl_2 (10 mL). The resulting organic solution was concentrated under reduced pressure and further purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate gradient), yielding the corresponding aryl nitriles **2a-2r**. The byproducts **3a-3r** and **4a-4r** sometimes were also isolated depending on the substrates.

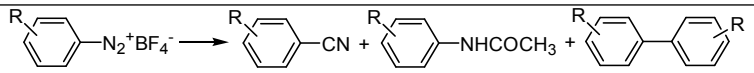


Scheme 1 Scope of the Sandmeyer reaction using CH_3CN as cyanide source.



Scheme 2. Scope of the Sandmeyer reaction using CH_3CN as cyanide source

Table 1 Pd-Catalyzed Sandmeyer cyanation of aryldiazonium tetrafluoroborate in acetonitrile: products distribution [a, b].



1a-1r 2a-2r 3a-3r 4a-4r

1	Yield (%) **2**	Yield (%) **3**	Yield (%) **4**	(**1**)	Yield (%) **2**	Yield (%) **3**	Yield (%) **4**
a	64	nd	24	**j**	30	nd	28
b	61	nd	12	**k**	38	nd	trace
c	61	nd	26	**l**	32	nd	16
d	50	nd	20	**m**	35	nd	trace
e	62	nd	trace	**n**	nd	83	nd
f	55	nd	18	**o**	nd	92	nd
g	35	nd	12	**p**	nd	92	nd
h	31	nd	15	**q**	nd	85	nd
i	45	nd	13	**r**	nd	87	nd

[a] isolated yields. [b] under the optimized conditions. nd: not detected.

4-Ethoxybenzonitrile (2a). Yield: 64%; White solid; m.p. 55-57 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.47 (t, J = 7.2 Hz, 3H), 4.01-4.14 (m, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.6, 93.9, 103.7, 115.2,

119.3, 133.9, 162.3; IR (KBr, cm^{-1}): υ = 2978, 2936, 2225, 1609, 1506, 1264, 1036, 842, 545; HRMS (ESI-TOF): calcd for C_9H_9NO 148.0757 $(M+H)^+$, found 148.0759.

4-Methoxybenzonitrile (2b)[1]. Yield: 61%; White solid; m.p.51-53 ºC; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.88 (s, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 55.6, 103.9, 114.8, 119.2, 113.9, 162.9; IR (KBr, cm^{-1}): υ = 2919, 2844, 2216, 1603, 1506, 1260, 1027, 825, 549.

4-Butoxybenzonitrile(2c)[2]. Yield: 61%； Yellow liquid; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.98 (t, *J*=7.2, 3H), 1.44-1.51(m, 2H), 1.74-1.82 (m, 2H), 4.00 (t, *J*=6.4, 2H), 6.93(d, *J*=8.0,2H), 7.56 (d, *J*=8.0, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 13.7, 19.1, 31.0, 68.1, 103.7, 115.2, 119.3, 133.9, 162.5; IR (KBr, cm^{-1}): υ =2960, 2226, 1609, 1504, 1255, 1169, 833.

3-Chloride- 4-Methoxybenzonitrile (2d). Yield: 50%; Yellow solid; m.p. 108-110 ºC; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.00 (s, 3H), 6.99-7.02 (m, 1H), 7.57-7.60 (m, 1H), 7.68-7.69 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 56.6, 104.7, 112.3, 117.9, 123.5, 132.5, 133.5, 158.6; IR (KBr, cm^{-1}): υ = 2854, 2232, 1596, 1499, 1298, 1063, 814, 717, 594; HRMS (ESI-TOF): calcd for C_8H_6NClO 168.0211 $(M+H)^+$, found 168.0223.

2, 4-Dimethoxybenzonitrile (2e)[3]. Yield: 62%; Yellow solid; m.p. 92-94 ºC; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.88 (s, 3H), 3.92 (s, 3H), 6.48 (s, 1H), 6.52-6.55 (m, 1H), 7.50 (d, *J* = 8.0, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 55.7, 56.0, 93.9, 98.5, 105.8, 117.0, 134.9, 162.9, 164.7; IR (KBr, cm^{-1}): υ = 2923, 2847, 2225, 1602, 1506, 1215, 1022, 842, 517.

3, 4-Dimethoxybenzonitrile (2f)[4]. Yield: 55%; White solid; m.p. 56-58 ºC; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.92 (s, 3H), 3.95 (s, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 7.09-7.10 (m, 1H), 7.29-7.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 56.1, 56.2, 103.9, 111.3, 113.9, 119.2, 126.5, 149.2, 152.9; IR (KBr, cm^{-1}): υ = 2936, 2840, 2218, 1596, 1513, 1271, 1139, 1022, 759, 614.

3-Methyl-4-Bromide benzonitrile (2g). Yield: 35%; Brown solid; m.p. 47-49 ºC; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.46 (s, 3H), 7.34-7.37 (m, 1H), 7.54 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 22.9, 111.4, 118.2, 130.5, 130.6, 133,4, 133.8, 139.7; IR (KBr, cm^{-1}): υ = 2232, 1589, 1471, 1029, 822, 586.

4-Chloride benzonitrile (2h)[3]. Yield: 31%; Yellow solid; m.p. 84-86 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.49 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 110.8, 117.9, 129.7, 113.4, 139.6; IR (KBr, cm^{-1}): υ = 3089, 3033, 2923, 2225, 1596, 1485, 1091, 828, 538.

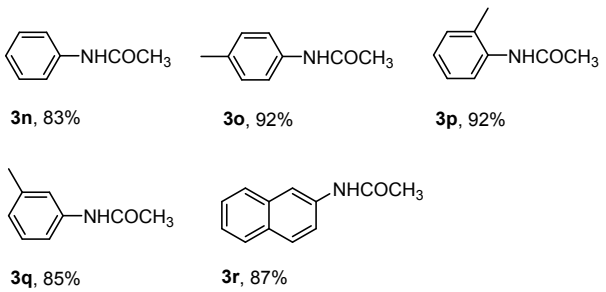
2, 6-Dimethyl-4-Bromide benzonitrile (2i)[5]. Yield: 45%; Yellow solid; m.p. 133-136 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.53 (s, 6H), 7.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 20.6, 112.4, 116.6, 127.1, 130.6, 143.8; IR (KBr, cm^{-1}): υ = 2916, 2854, 2218, 1581, 1464, 1257, 1174, 856, 738, 580.

4-Bromide benzonitrile (2j)[1]. Yield: 30%; Yellow solid; m.p. 106-108 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 111.3, 118.1, 128.0, 132.7, 133.4; IR (KBr, cm^{-1}): υ = 2923, 2847, 2218, 1581, 1478, 1063, 821, 538.

4-Nitro benzonitrile (2k)[1]. Yield: 38%; Yellow solid; m.p. 133-135 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91 (d ,*J* = 8.0 Hz, 2H), 8.38 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR, ($CDCl_3$, 100 MHz, ppm): δ 116.8, 118.4, 124.3, 133.5, 150.1; IR (KBr, cm^{-1}): υ = 3109, 2234, 1602, 1527, 1347, 863, 746, 684, 538.

Ethyl 4-cyanobenzoateate (2l)[6]. Yield: 32%; Yellow solid; m.p. 48-50 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.43 (t, *J*=7.2 Hz, 3H), 4.41-4.46 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J*=8.0 Hz, 2H); ^{13}C NMR, ($CDCl_3$, 100 MHz, ppm): δ 14.2, 61.8, 116.3, 118.0, 130.1, 132.2, 134.3, 164.9; IR (KBr, cm^{-1}): υ =3096, 2958, 2902, 2225, 1727, 1277, 1105, 870, 766, 690, 545.

4-Acetylbenzonitrile (2m)[3]. Yield: 35%; White solid; m.p. 49-51 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.67 (s, 3H), 7.80 (d, *J* = 8.0 Hz, 2H),8.06 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 26.8, 116.4, 117.9, 128.7, 132.5, 139.9, 196.5; IR (KBr, cm^{-1}): υ = 2923, 2232, 1685, 1402, 1246, 828, 594, 538.



3n, 83% **3o**, 92% **3p**, 92%

3q, 85% **3r**, 87%

Scheme 3. Unexpected byproducts of substrates under the standard conditions

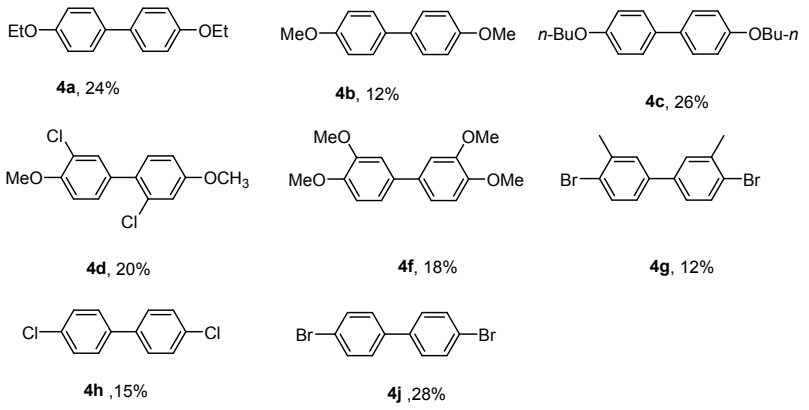
Acetanilide (3n)[7]. Yield: 83%; Yellow solid; m.p. 110-112 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.20 (s, 3H), 7.11-7.15 (m, 1H), 7.25 (s, 1H), 7.73-7.36 (m, 2H), 7.51-7.53 (m, 2H); IR (KBr, cm^{-1}): υ = 3289, 1665, 1430, 1430, 1319, 745, 690, 510.

4-Methylacetanilide (3o)[8]. Yield: 92%; White solid; M.P. 145-147 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.18 (s, 3H), 2.33 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H); IR (KBr, cm^{-1}): υ = 3289, 3117, 2943, 1665, 1506, 1319, 821, 510.

2-Methylacetanilide (3p)[9]. Yield: 92%; White solid; m.p. 104-106 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.24 (s, 3H), 2.29 (s, 3H), 6.96 (s, 1H), 7.09-7.13 (m, 1H), 7.20-7.26 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H); IR (KBr, cm^{-1}): υ = 3283, 3033, 1658, 1527, 1458, 1271, 752.

3-Methylacetanilide (3q)[10]. Yield: 85%; White solid; m.p. 235-237 ºC; ^{1}H NMR ($CDCl^3$, 400 MHz, ppm): δ 2.13 (s, 3H), 2.16 (s, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.17-7.21 (m, 1H), 7.29-7.32 (m, 1H), 7.38 (s, 1H), 7.89 (s, 1H); IR (KBr, cm^{-1}): υ = 3289, 2916, 1665, 1547, 1492, 1367, 780, 690.

N-Acetyl-2-aminonaphthalene (3r)[11]. Yield: 87%; White solid; m.p. 127-129 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.26 (s, 3H), 7.41-7.48 (m, 4H), 7.81 (d, *J* = 8.0 Hz, 3H), 8.20 (s, 1H); IR (KBr, cm^{-1}): υ = 3283, 1671, 1561, 1277, 814, 745, 476.



Scheme 4. Biaryls products

4, 4'-Diethoxybiphenyl (4a)[12]. Yield: 24%; white solid; ^{1}H NMR ($CDCl_3$, 400 MHz,

ppm): δ 1.55-1.59 (t, *J*=7.2Hz, 6H), 4.17-4.23 (m, 4H), 7.06-7.09 (d, *J*=8.0Hz, 4H), 7.58-7.61 (d, *J*=8.0Hz, 4H)； IR (KBr, cm^{-1}): υ = 2976, 2928, 1604, 1500, 1272, 1252, 1051, 817, 796, 590, 521.

4, 4'-Dimethoxybiphenyl (4b)[13]. Yield: 12%; white solid; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ3.87 (s, 6H), 6.97-7.01 (d, *J*=8.Hz, 4H), 7.49-7.52 (d, *J*=8.0Hz, 4H); IR (KBr, cm^{-1}): υ =2960, 2834, 1605, 1504, 1277, 1251, 1182, 1037, 823, 810, 514.

4, 4'-Dibutoxybiphenyl (4c)[14]. Yield: 26%; white solid; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ0.96-1.01 (t, *J*=7.2Hz, 6H), 1.48-1.52 (m, 4H), 1.71-1.84 (m, 4H), 3.97-4.02 (t, *J*=6.8Hz, 4H), 6.93-6.96 (d, *J*=8.0Hz, 4H), 7.44-7.47 (d, *J*=8.0Hz, 4H); IR (KBr, cm^{-1}): υ = 2955, 2929, 1617, 1498, 1277, 1251, 1037, 817, 804.

3, 3'-Dichloro-4, 4'-Dimethoxybiphenyl (4d). Yield: 20%; white solid; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.94 (s, 6H), 6.96-6.99 (d, *J*=8.0Hz, 2H), 7.36-7.39 (d, *J*=8.0Hz, 2H), 7.54 (s, 2H), IR (KBr, cm^{-1}): υ = 2923, 1561, 1491, 1251, 1069, 1019, 873, 811, 728.

3, 3'-4, 4'-Tetramethoxybiphenyl (4f)[14]. Yield: 18%; white solid; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ3.85 (s, 6H), 3.86 (s, 6H), 6.76-6.80 (m, 2H), 6.80-6,93(m, 4H); IR (KBr, cm^{-1}): υ = 2929, 2828, 1511, 1460, 1258, 1220, 1119, 1025, 956, 741.

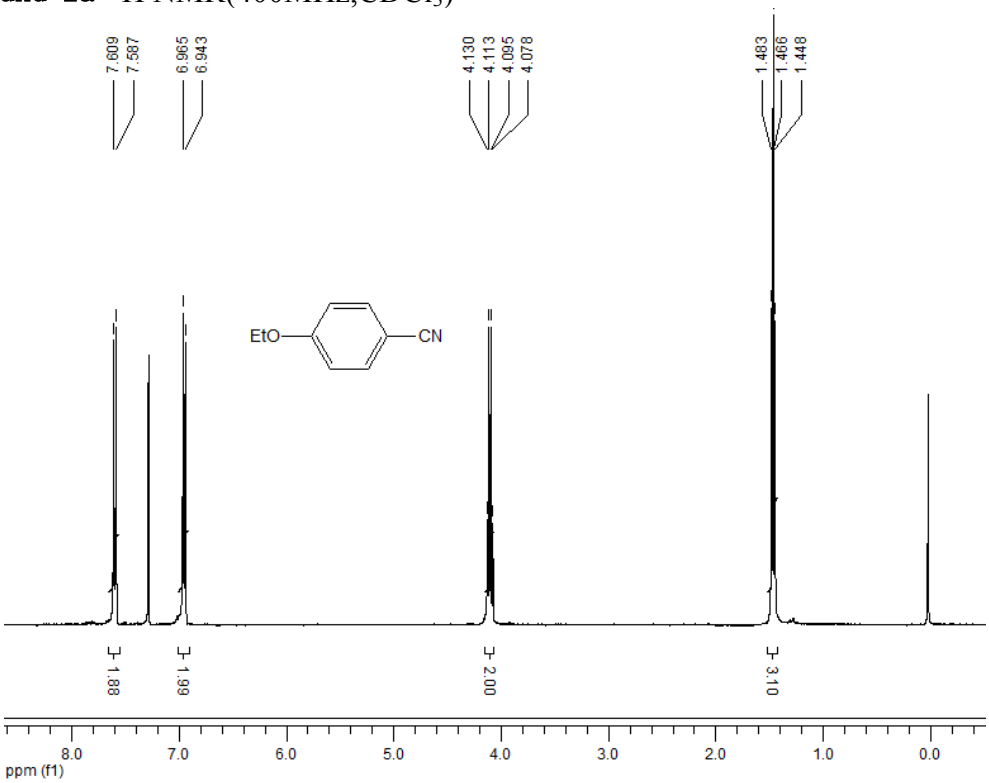
3, 3'-Dimethyl-4, 4'-Dibromobiphenyl (4g). Yield: 12%, white solid; ^1H NMR ($CDCl_3$, 400MHz, ppm): δ 2.46 (s, 6H), 7.20-7.26 (m, 2H), 7.45 (s, 2H), 7.56-7.59 (d, *J*=8.0Hz, 2H); IR (KBr, cm^{-1}): υ = 2918, 2855, 1557, 1469, 1025, 804.

4, 4'-Dichlorobiphenyl (4h)[15]. Yield:15%, white solid; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ7.39-7.42 (d, *J*=8.0Hz, 4H), 7.46-7.49 (d, *J*=8.0Hz, 4H); IR (KBr, cm^{-1}): υ = 1564, 1095, 1000, 817, 506.

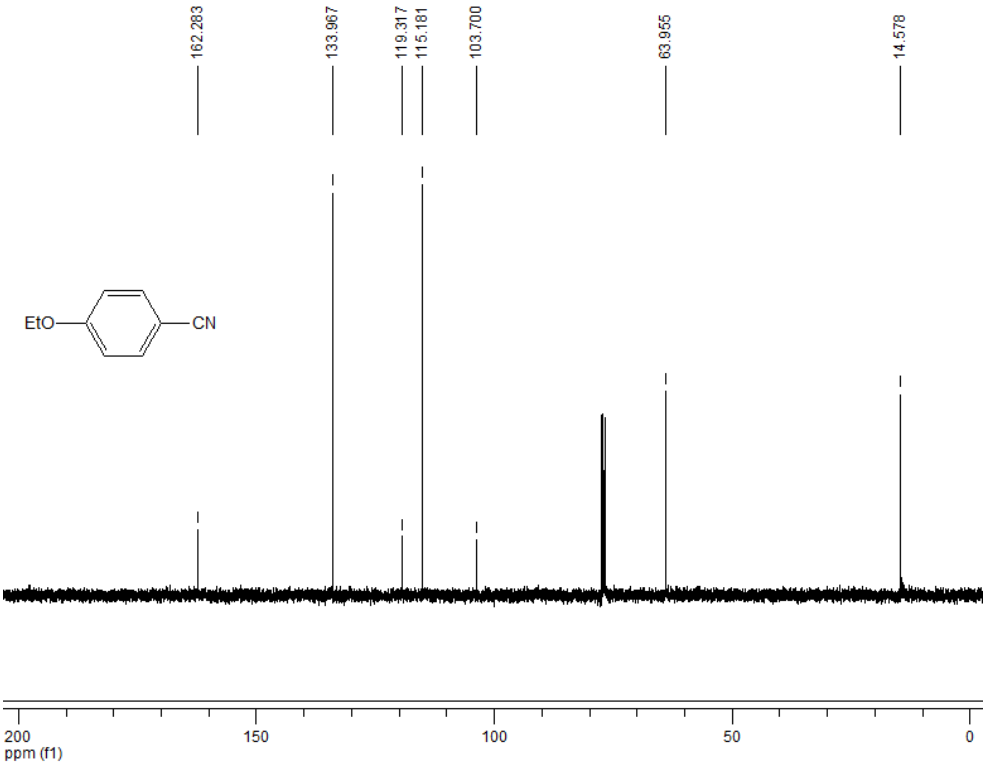
4, 4'-Dibromobiphenyl (4j)[16]. Yield: 28%, white solid; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.42-7.45 (d, *J*=8.0Hz, 4H), 7.57-7.60 (d, *J*=8.0Hz, 4H); IR (KBr, cm^{-1}): υ = 1664, 1627, 1475, 1380, 1101, 1000, 804, 538, 500.

Spectroscopic data

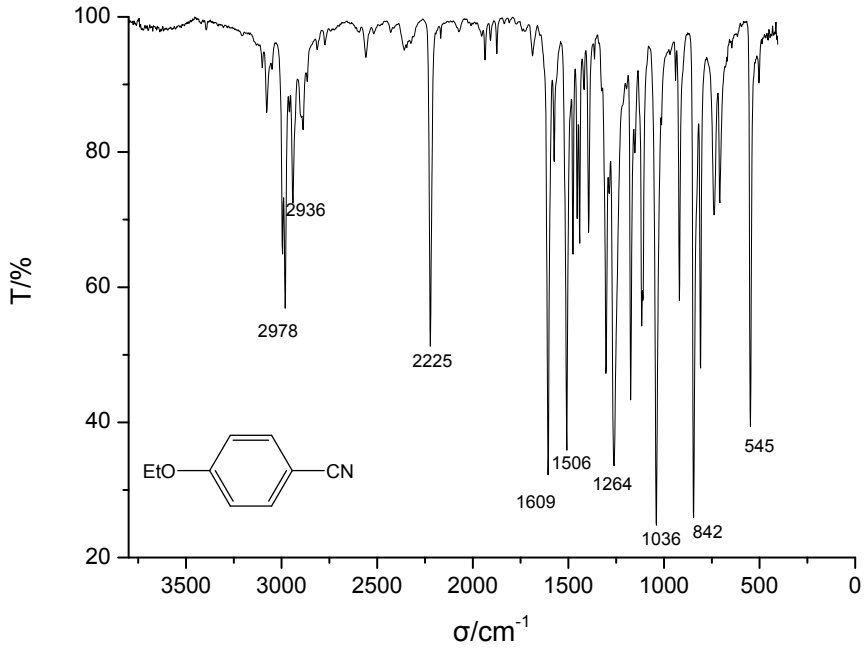
Compound 2a ^{1}H NMR(400MHz,$CDCl_3$)



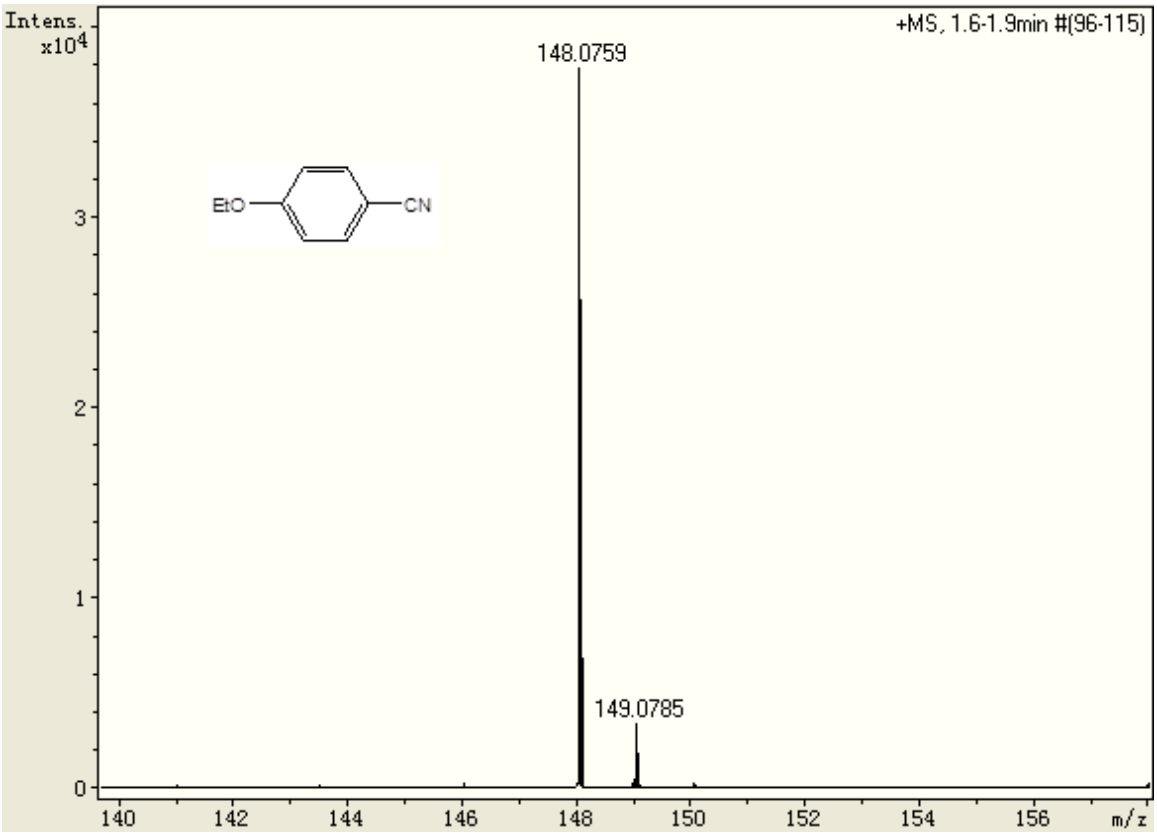
Compound 2a ^{13}C NMR(100MHz,$CDCl_3$)



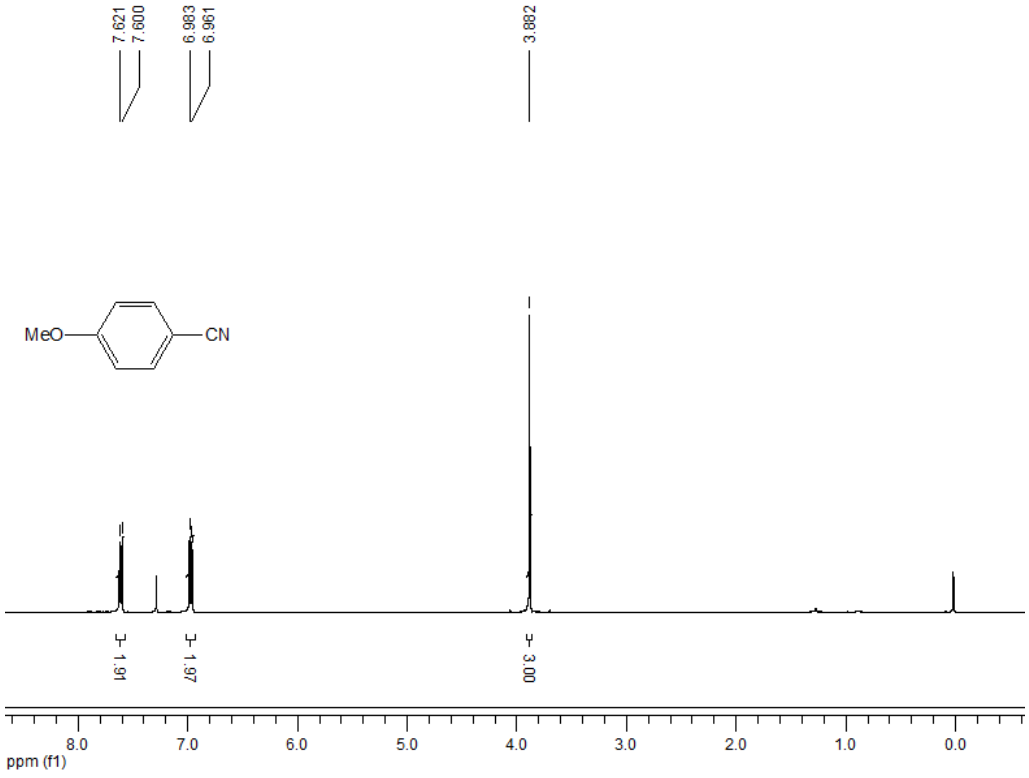
Compound 2a IR (KBr, cm^{-1})



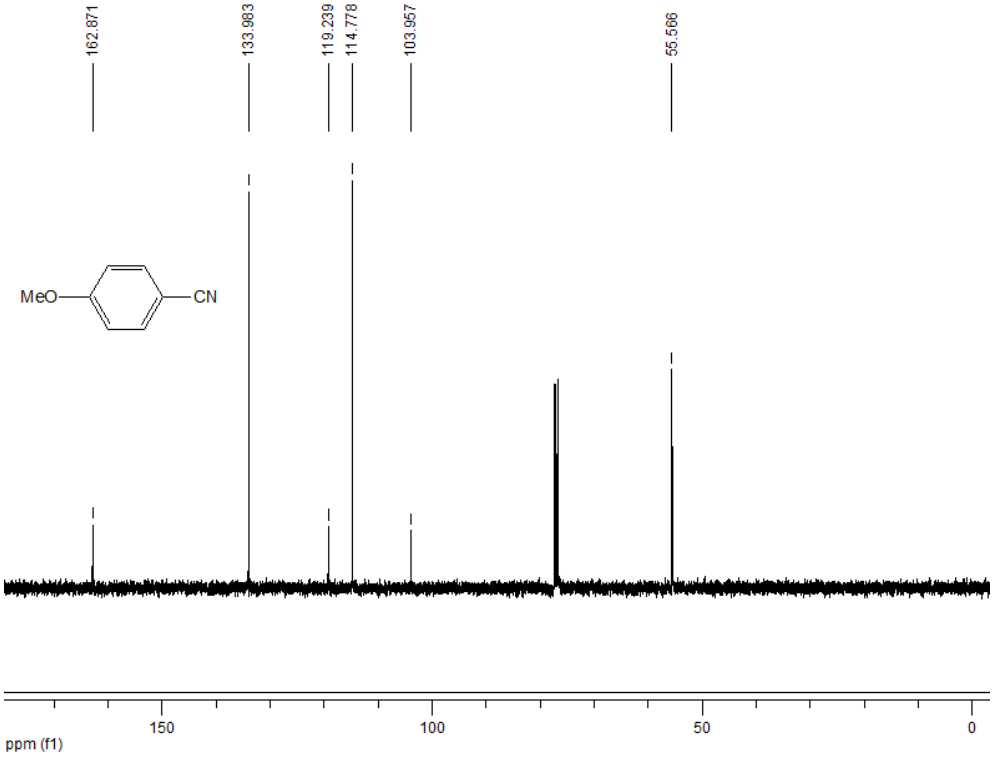
Compound 2a HRMS



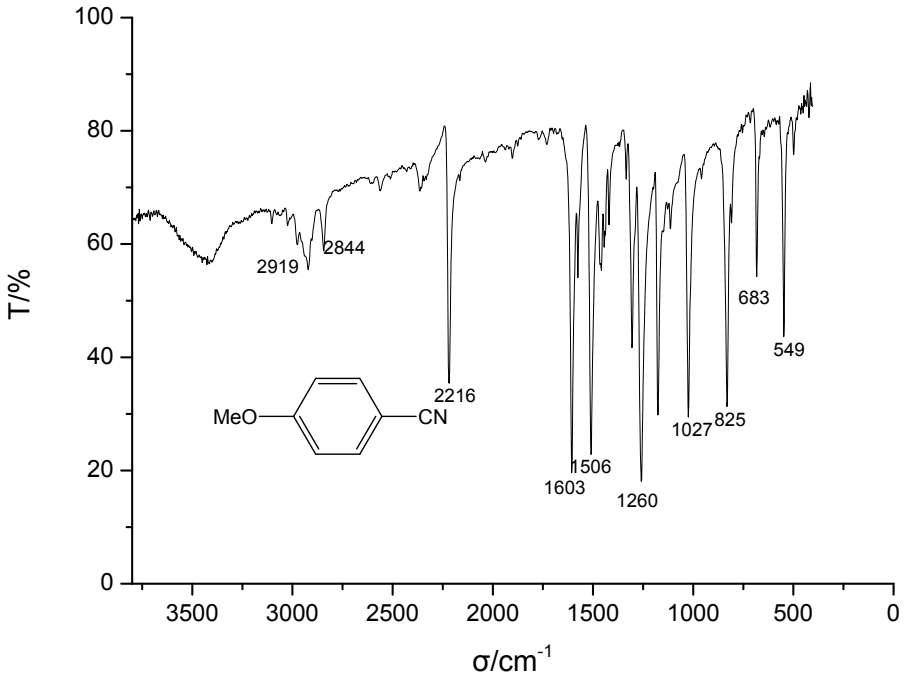
Compound 2b ^{1}H NMR(400MHz, $CDCl_3$)



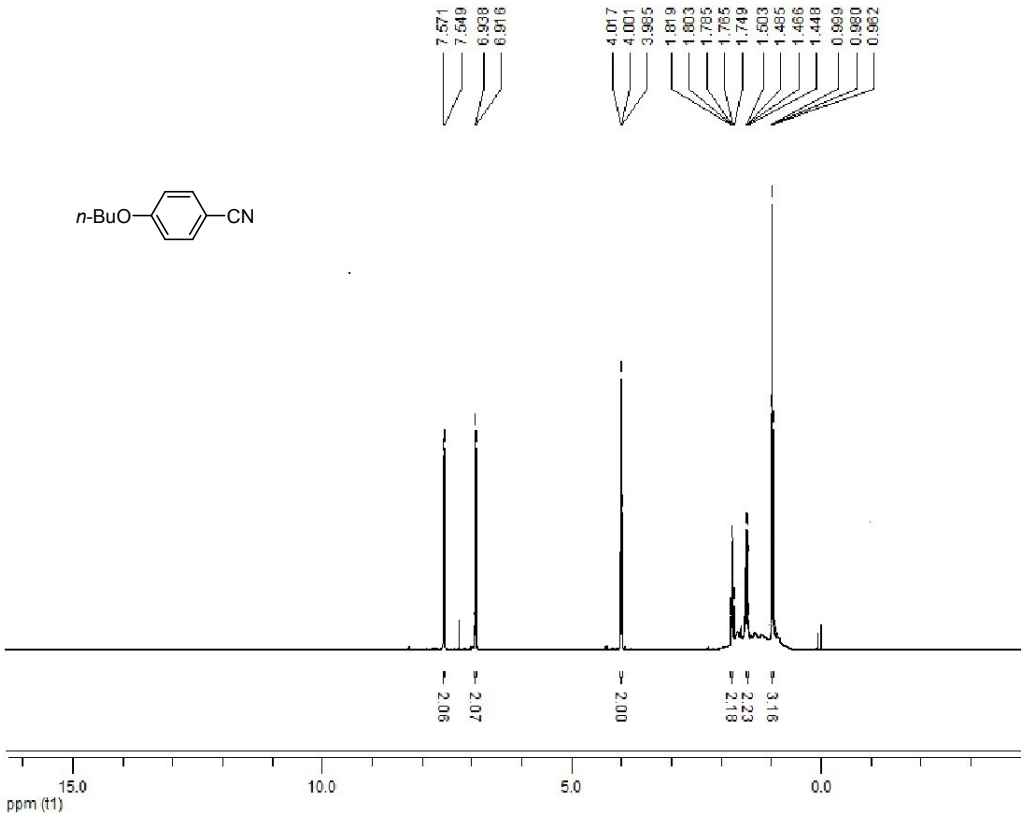
Compound 2b ^{13}C NMR(100MHz, $CDCl_3$)



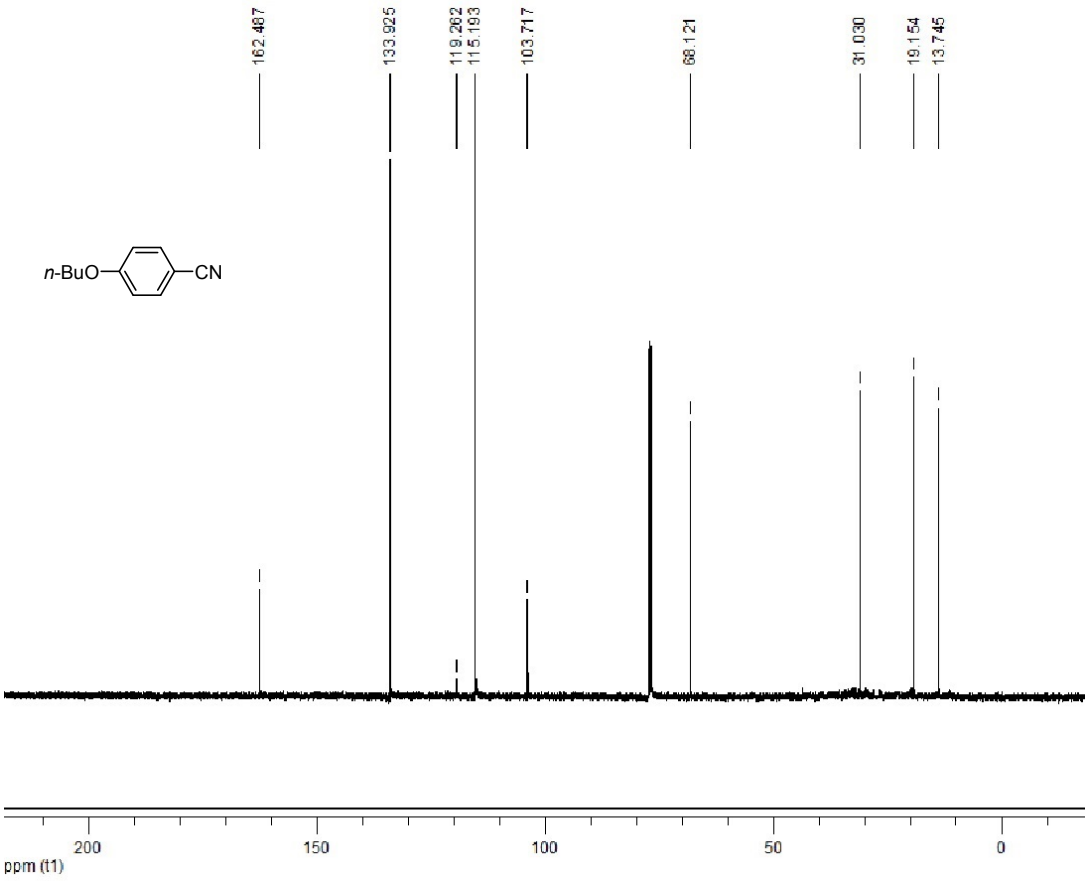
Compound 2b IR (KBr, cm^{-1})



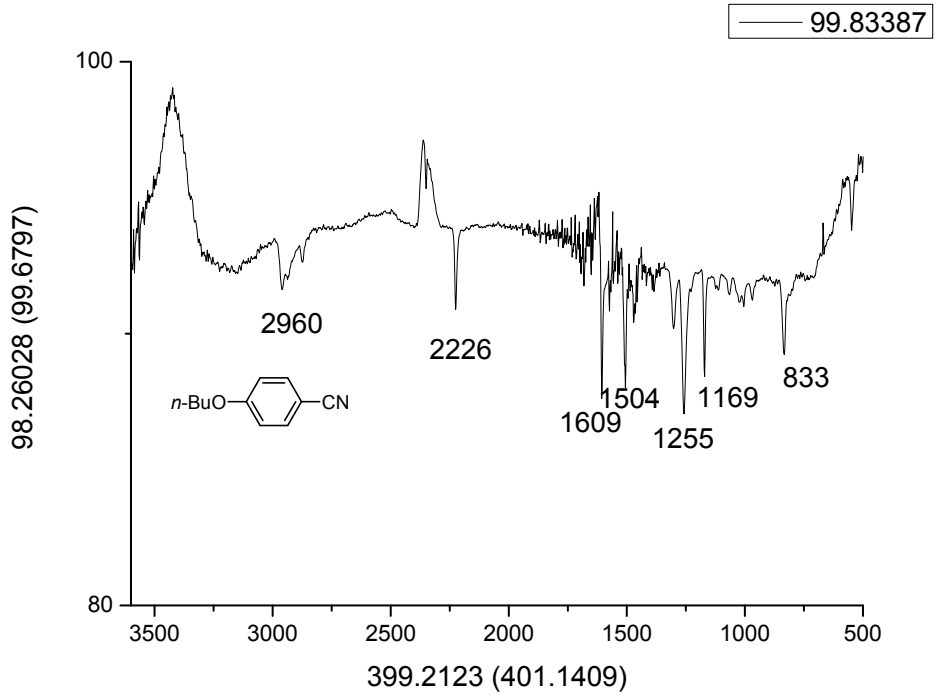
Compound 2c ^{1}H NMR(400MHz, $CDCl_3$)



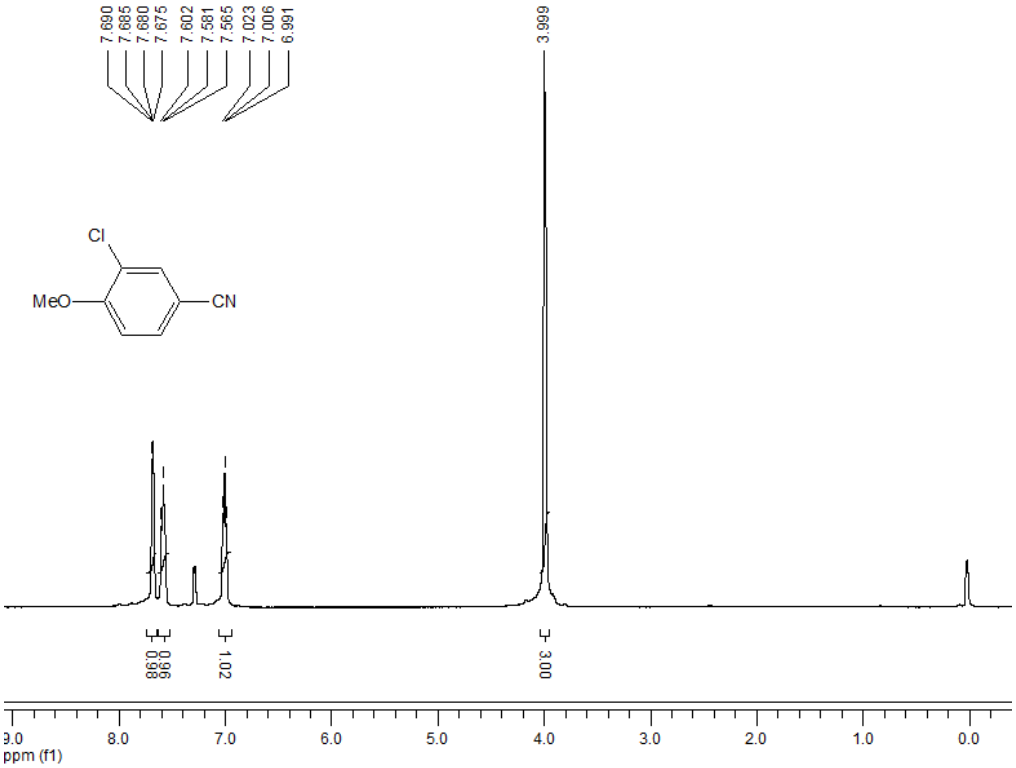
Compound 2c ^{13}C NMR(100MHz, $CDCl_3$)



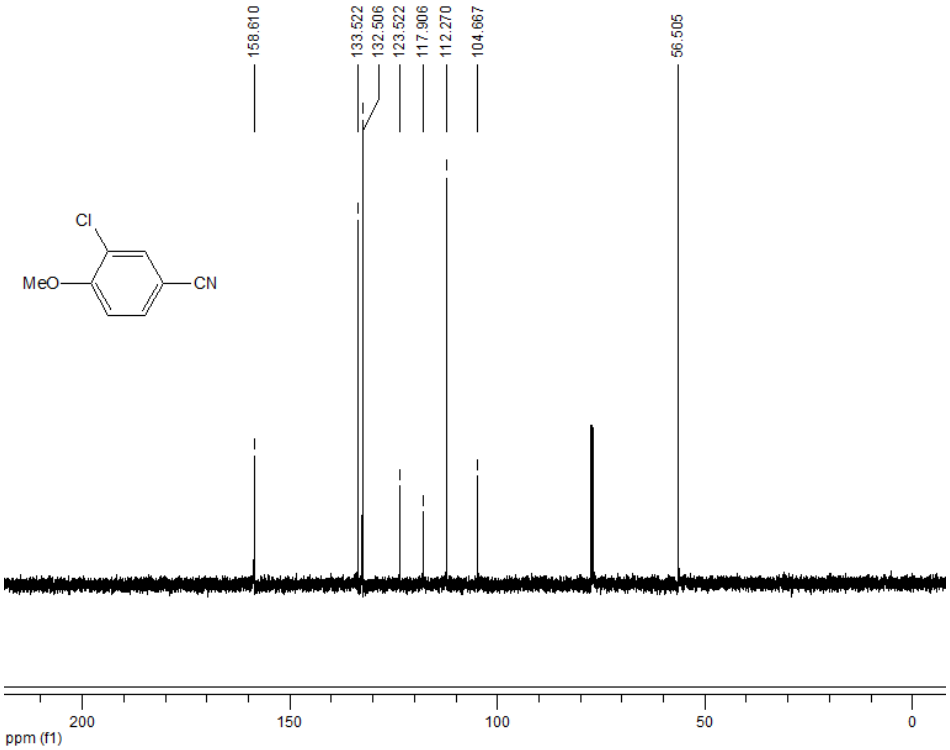
Compound 2c IR (KBr, cm^{-1})



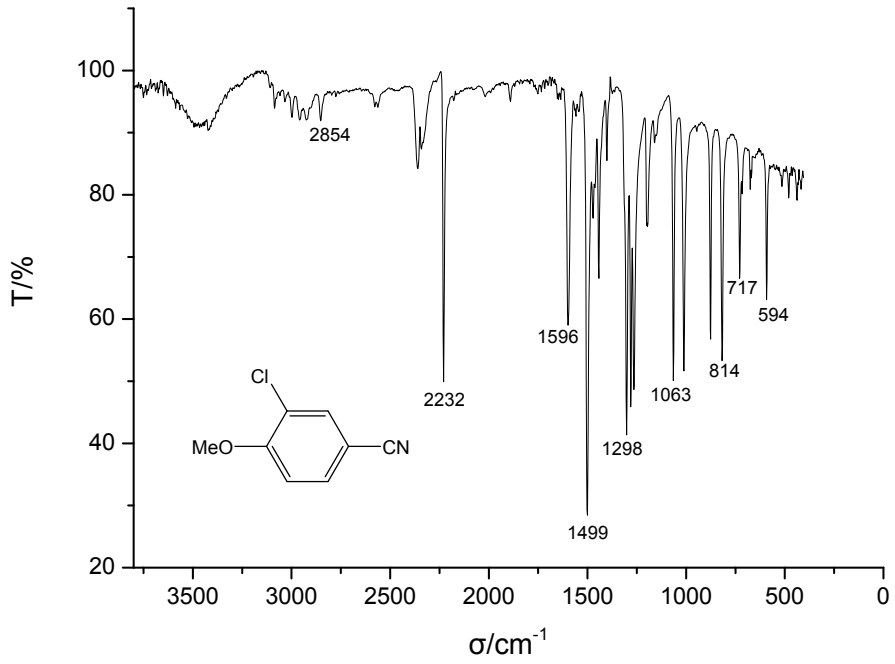
Compound 2d ^{1}H NMR(400MHz, $CDCl_3$)



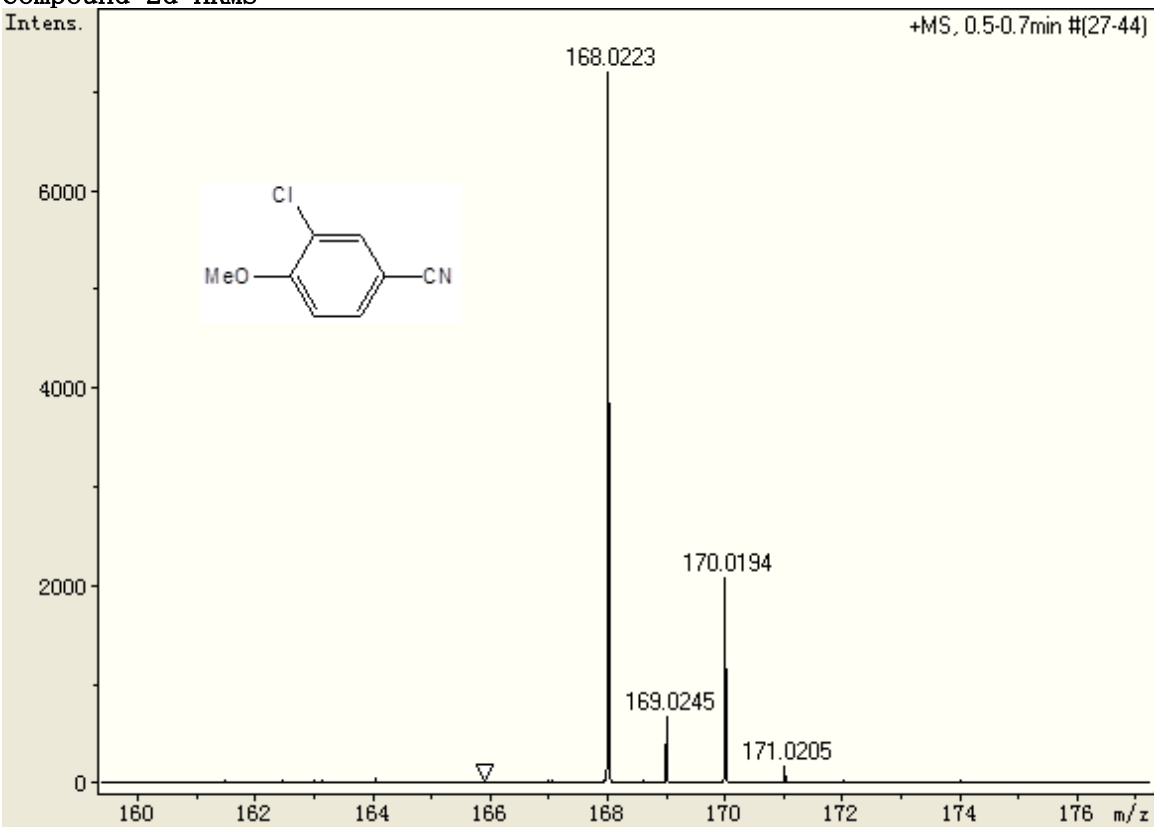
Compound 2d ^{13}C NMR(100MHz, $CDCl_3$)



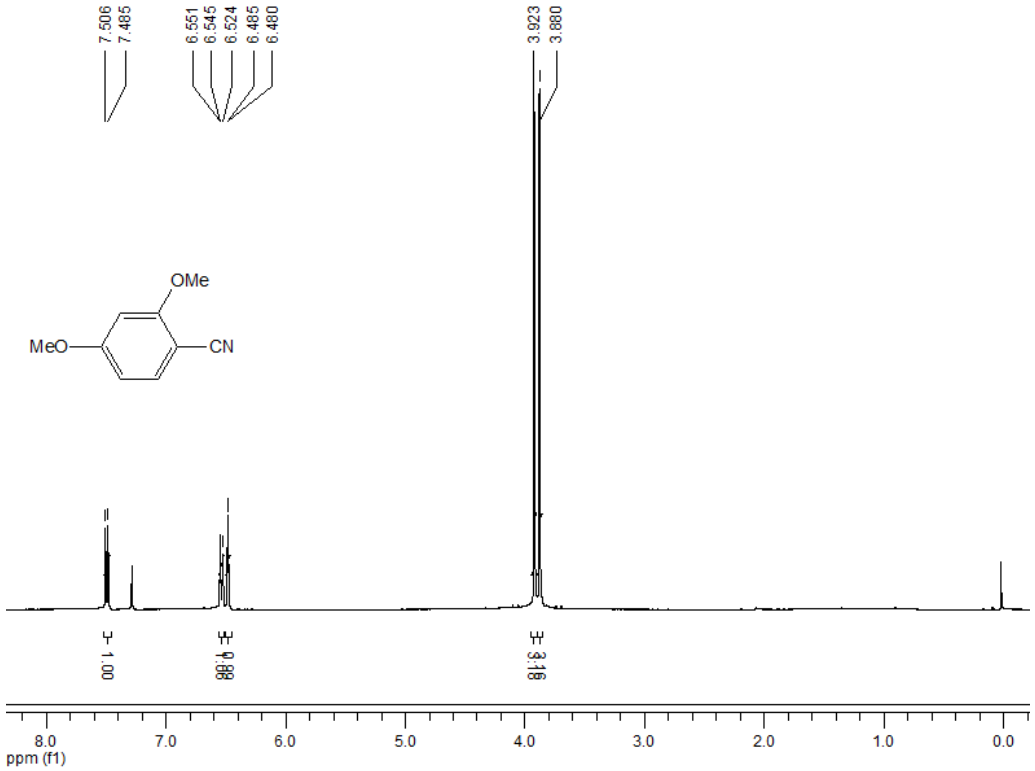
Compound 2d IR (KBr, cm^{-1})



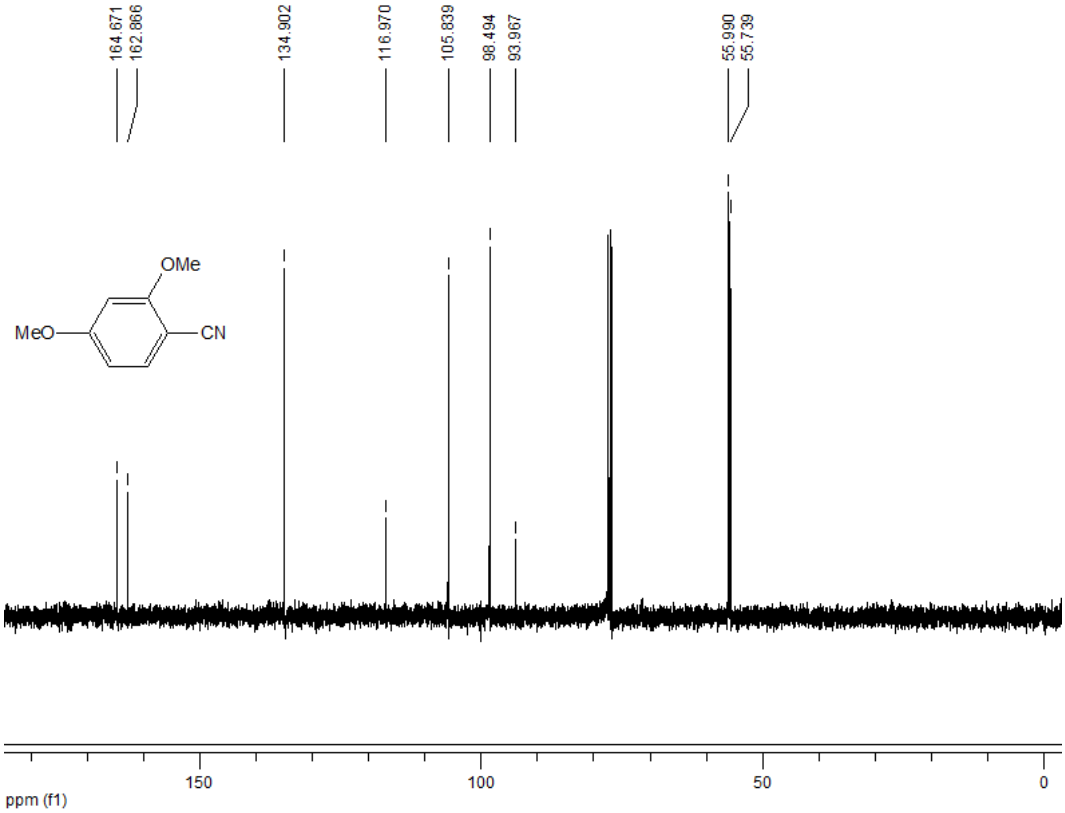
Compound 2d HRMS



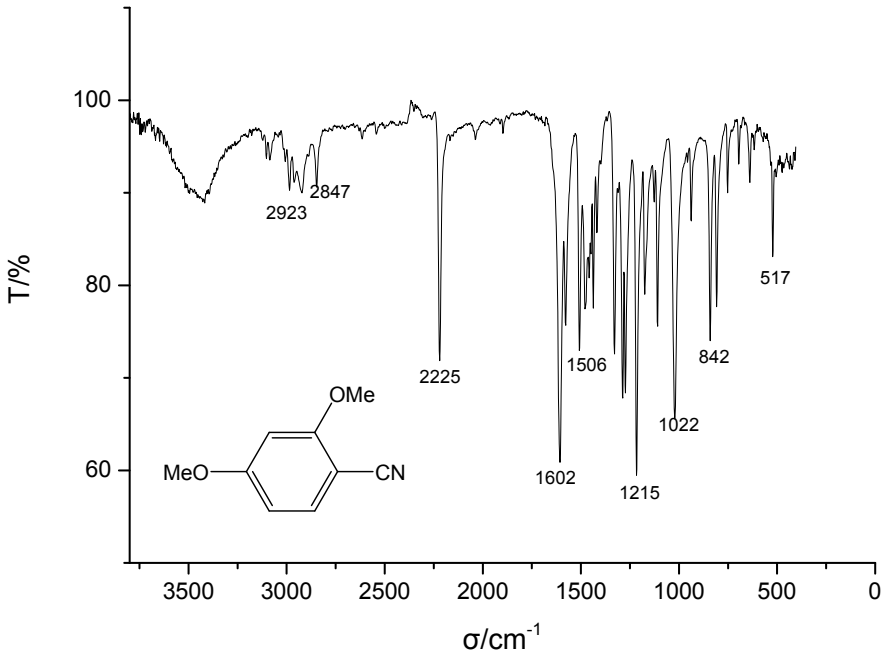
Compound 2e ^{1}H NMR(400MHz, $CDCl_3$)



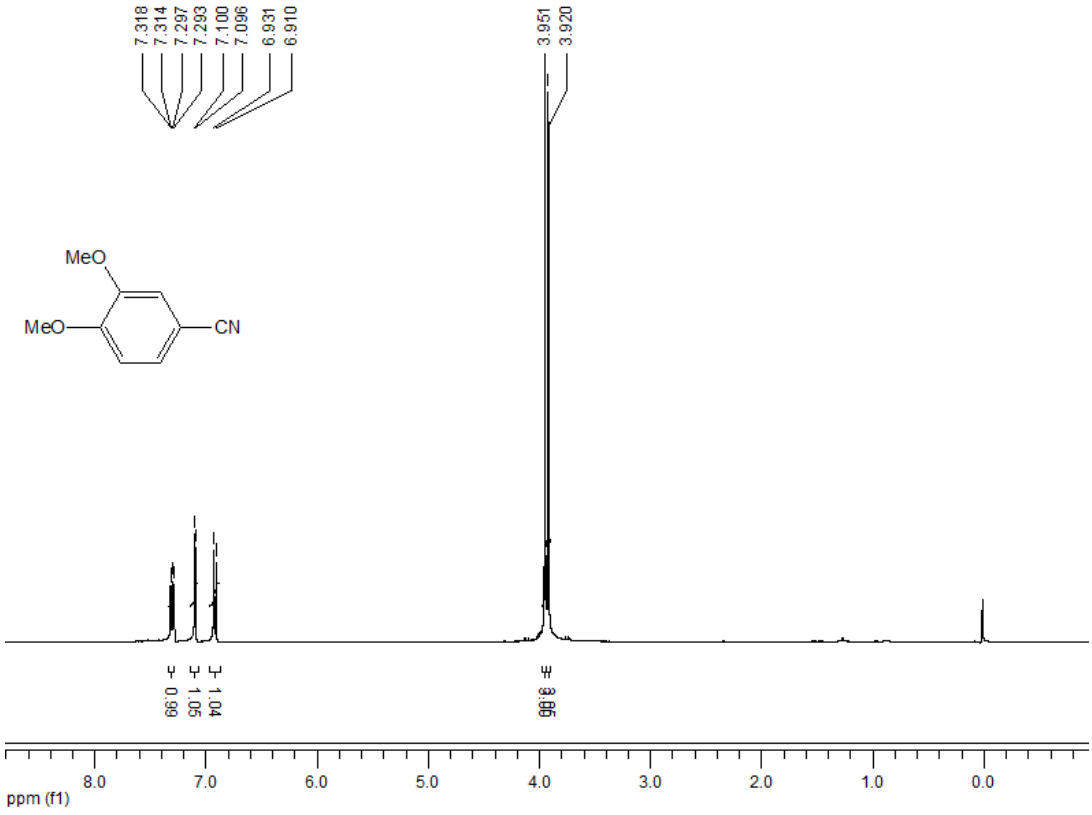
Compound 2e ^{13}C NMR(100MHz, $CDCl_3$)



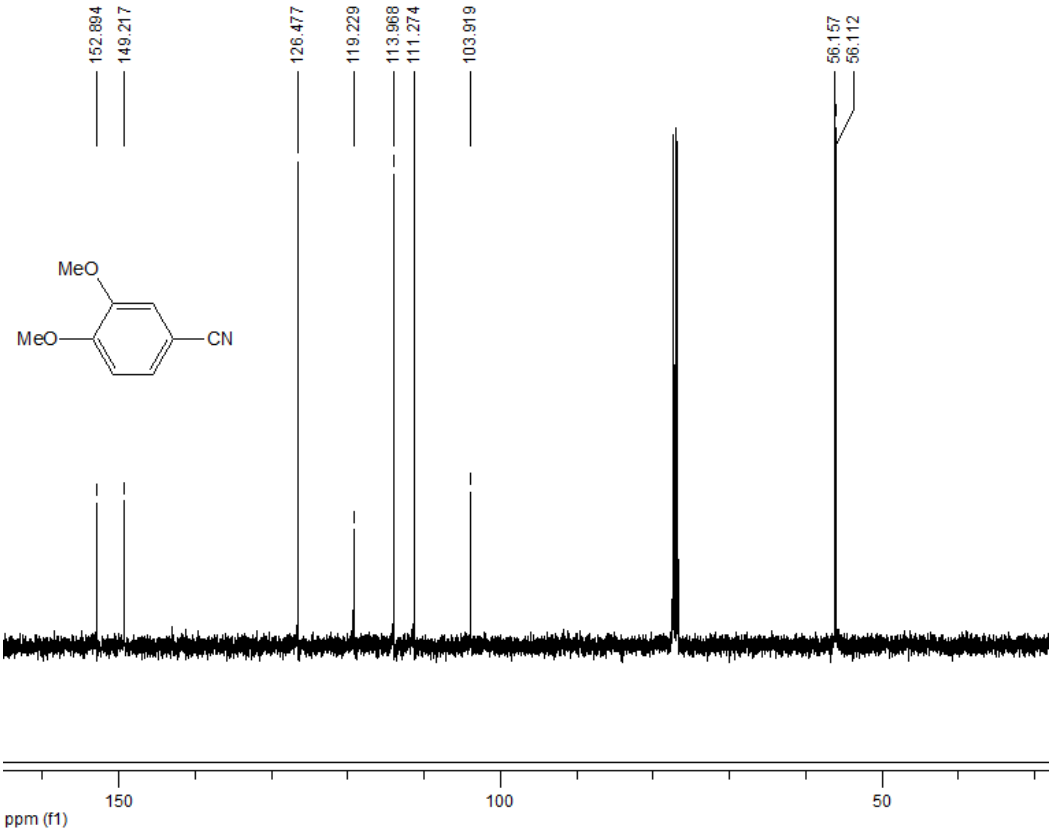
Compound 2e IR (KBr, cm^{-1})



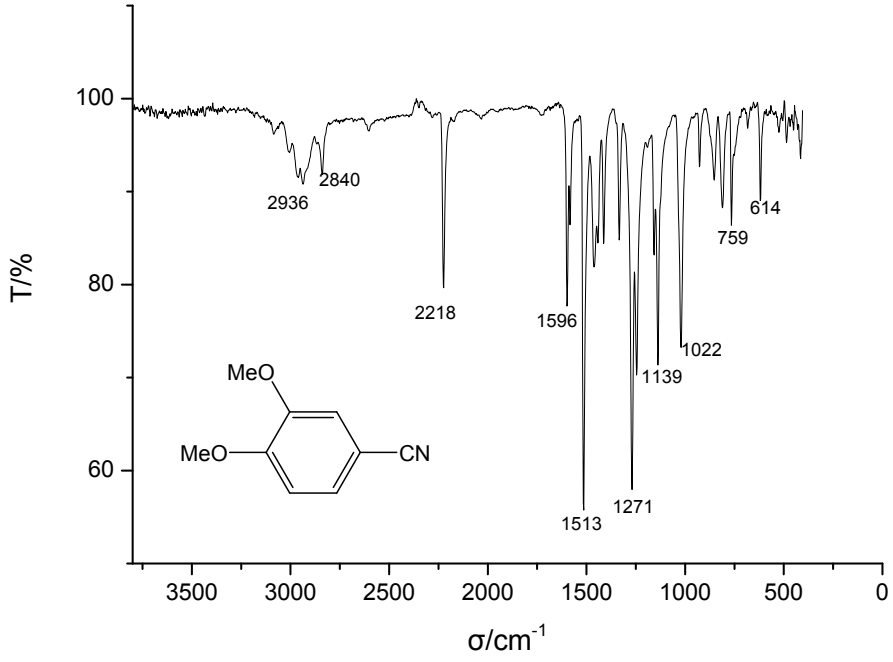
Compound 2f ^1H NMR(400MHz, $CDCl_3$)



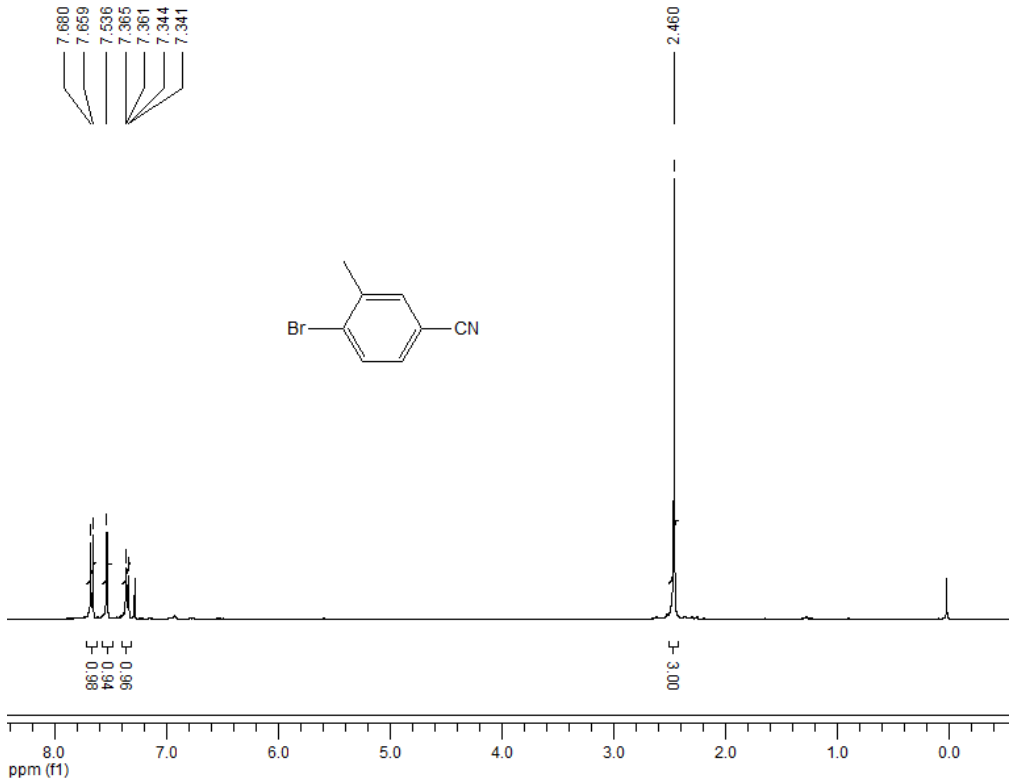
Compound 2f ^{13}C NMR(100MHz, $CDCl_3$)



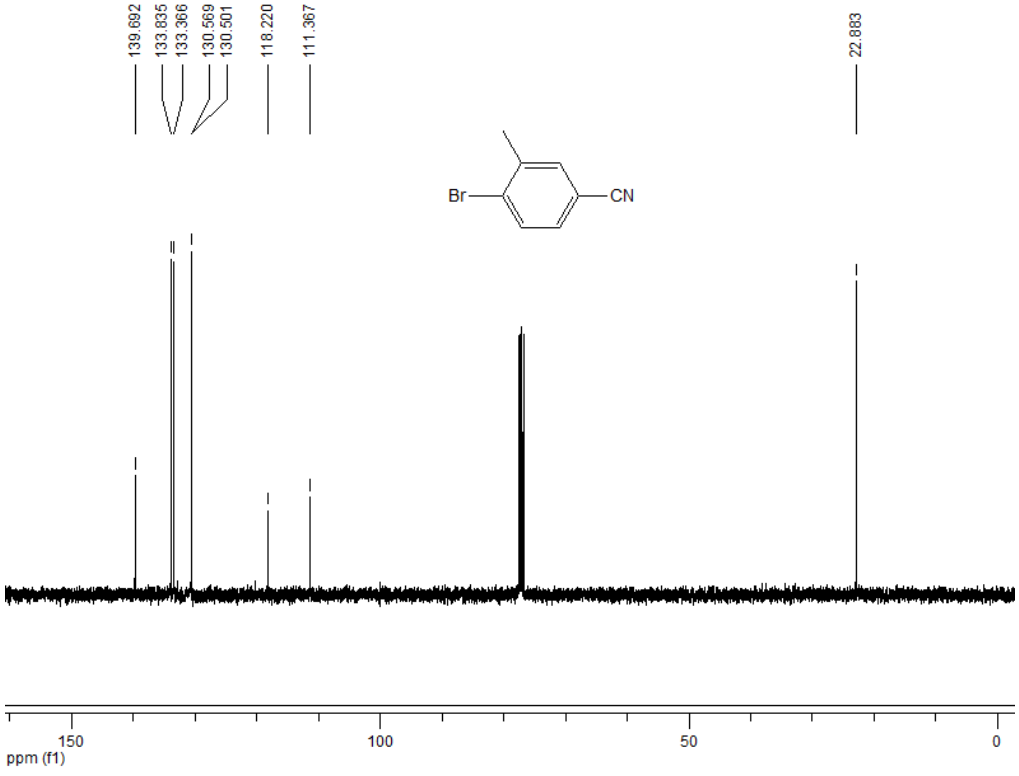
Compound 2f IR (KBr, cm^{-1})



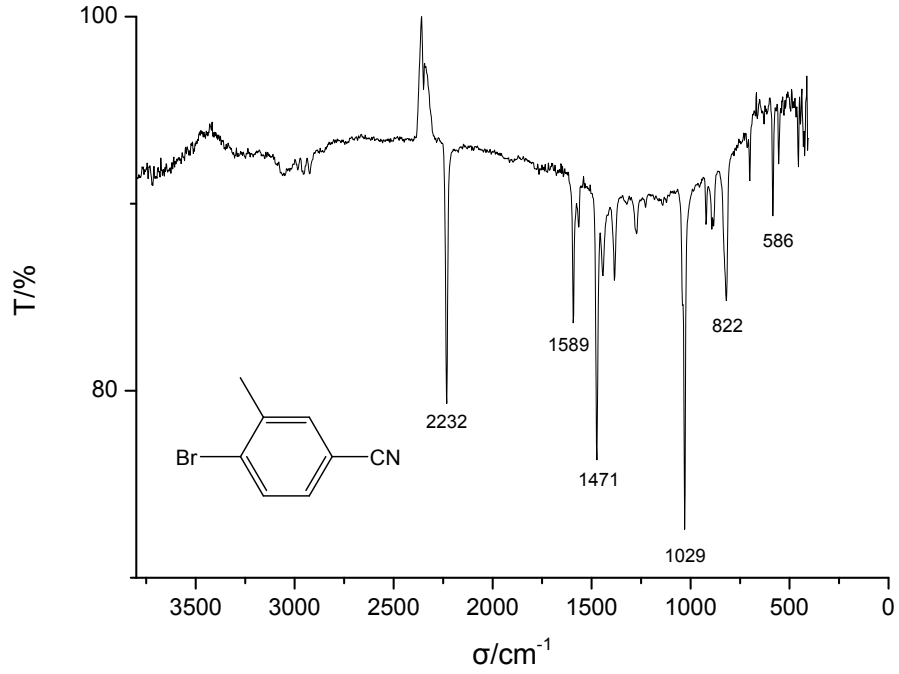
Compound 2g ^{1}H NMR(400MHz, $CDCl_3$)



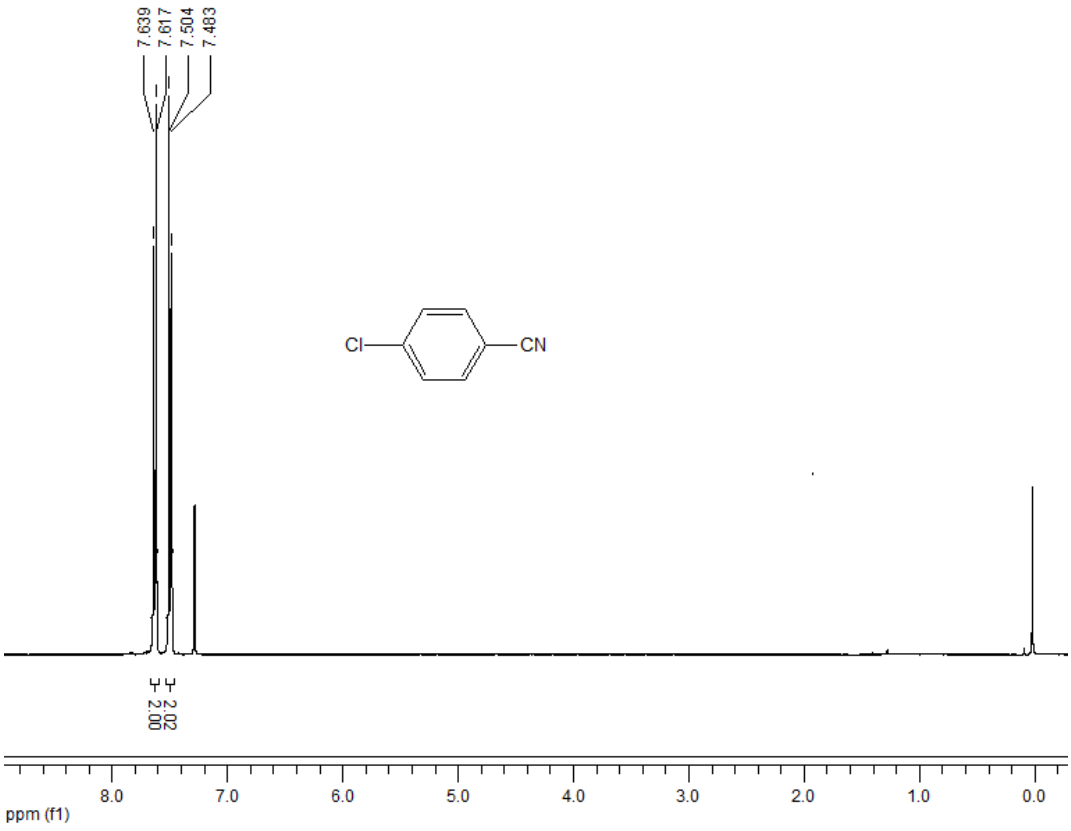
Compound 2g ^{13}C NMR(100MHz, $CDCl_3$)



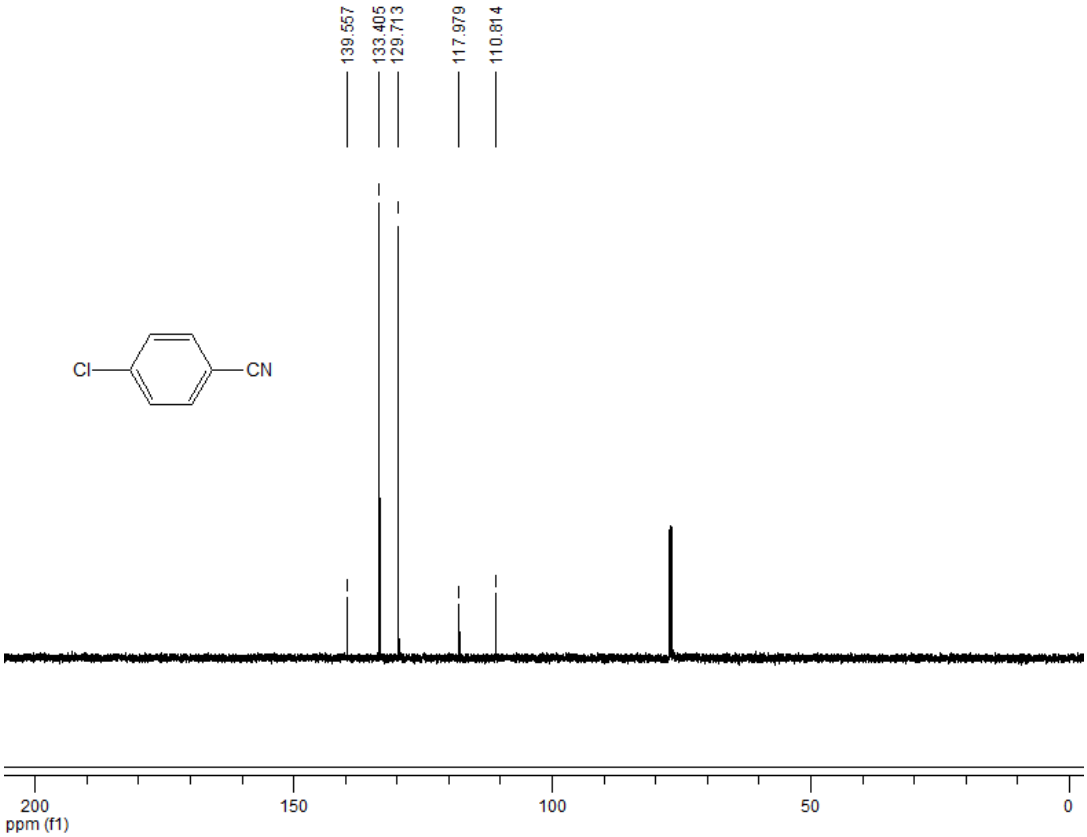
Compound 2g IR (KBr, cm^{-1})



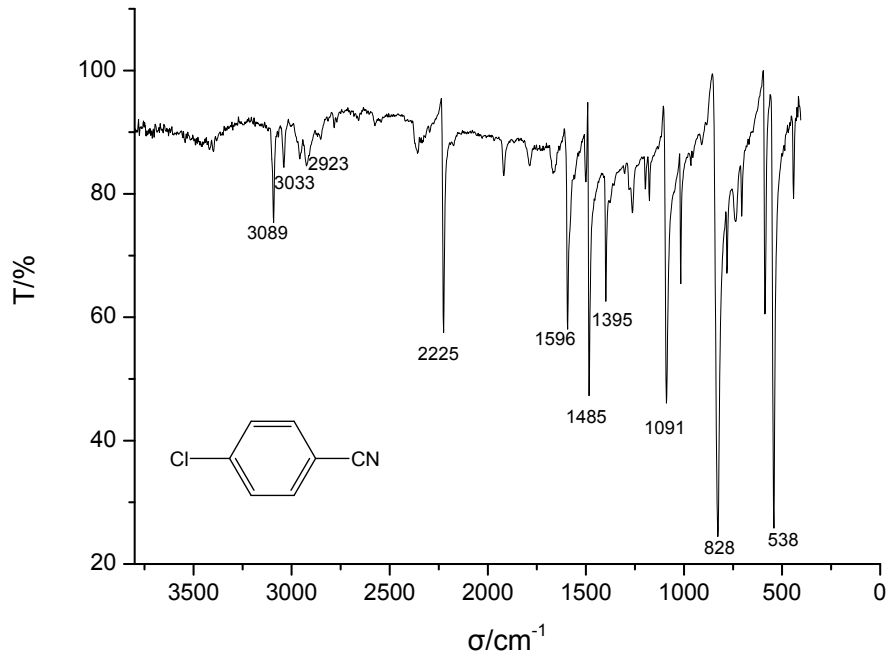
Compound 2h ^1H NMR(400MHz, $CDCl_3$)



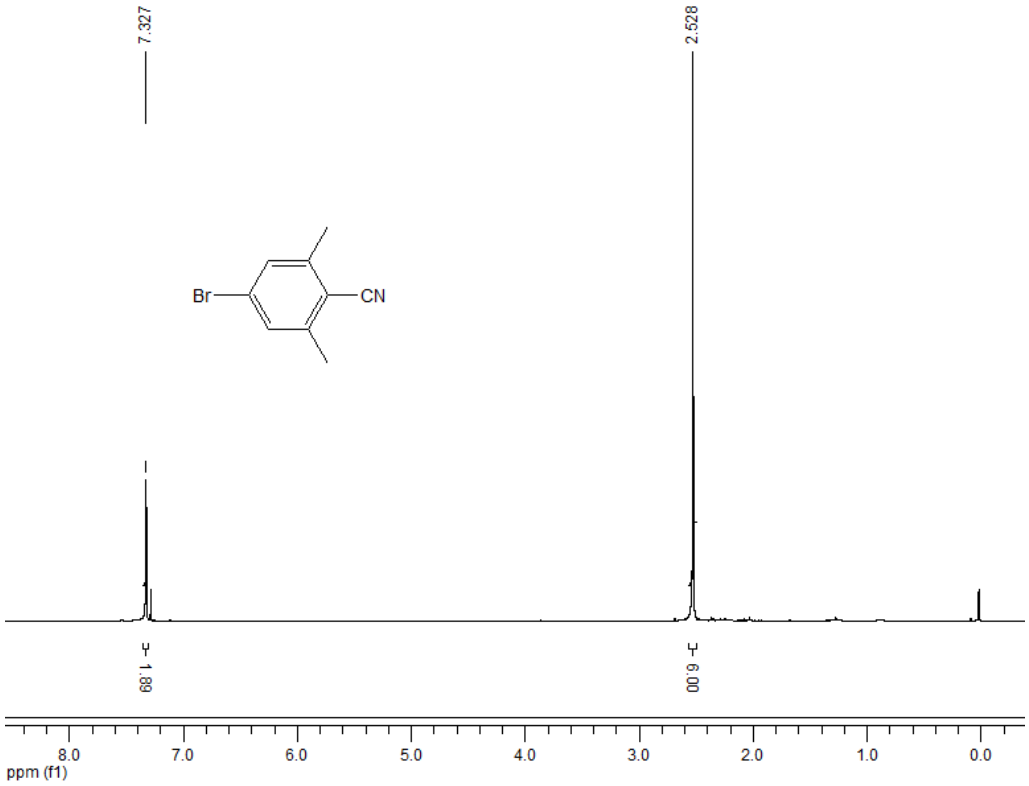
Compound 2h ^{13}C NMR(100MHz, $CDCl_3$)



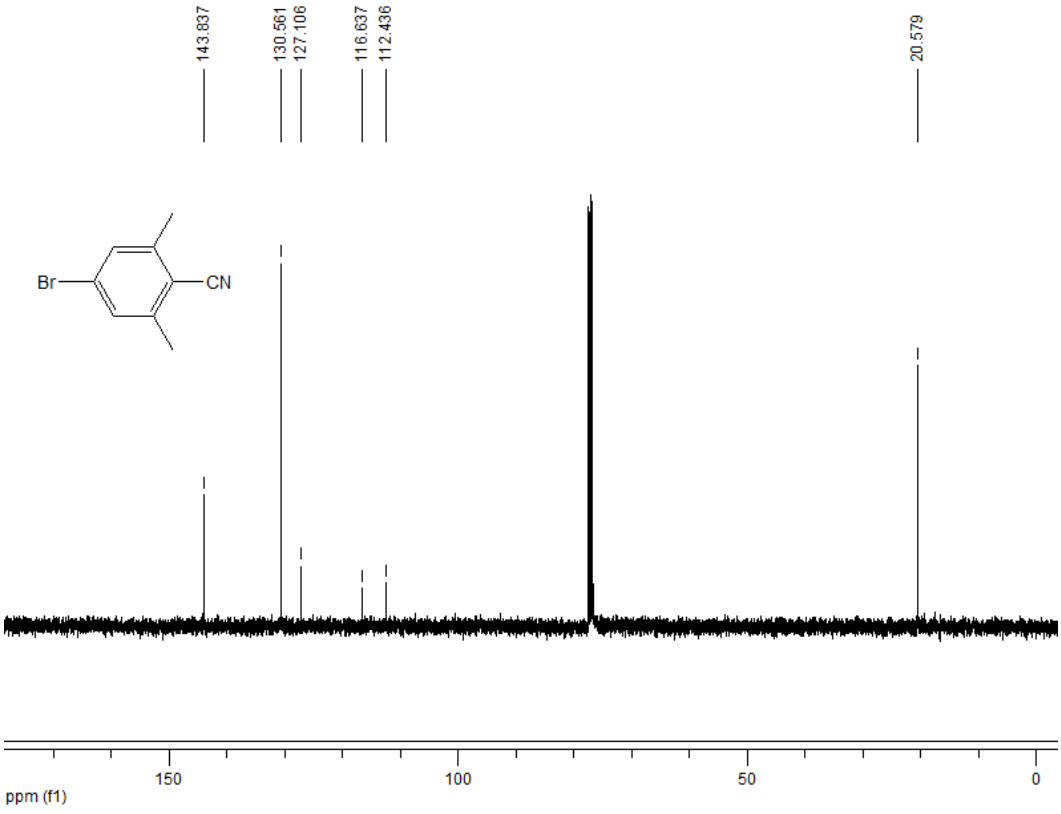
Compound 2h IR (KBr, cm^{-1})



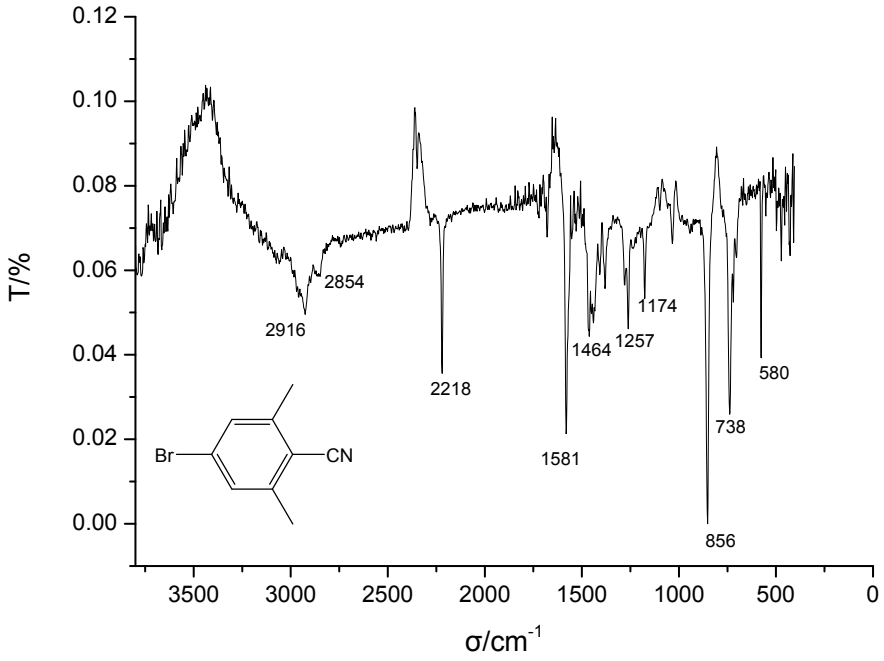
Compound 2i ^{1}H NMR(400MHz, $CDCl_3$)



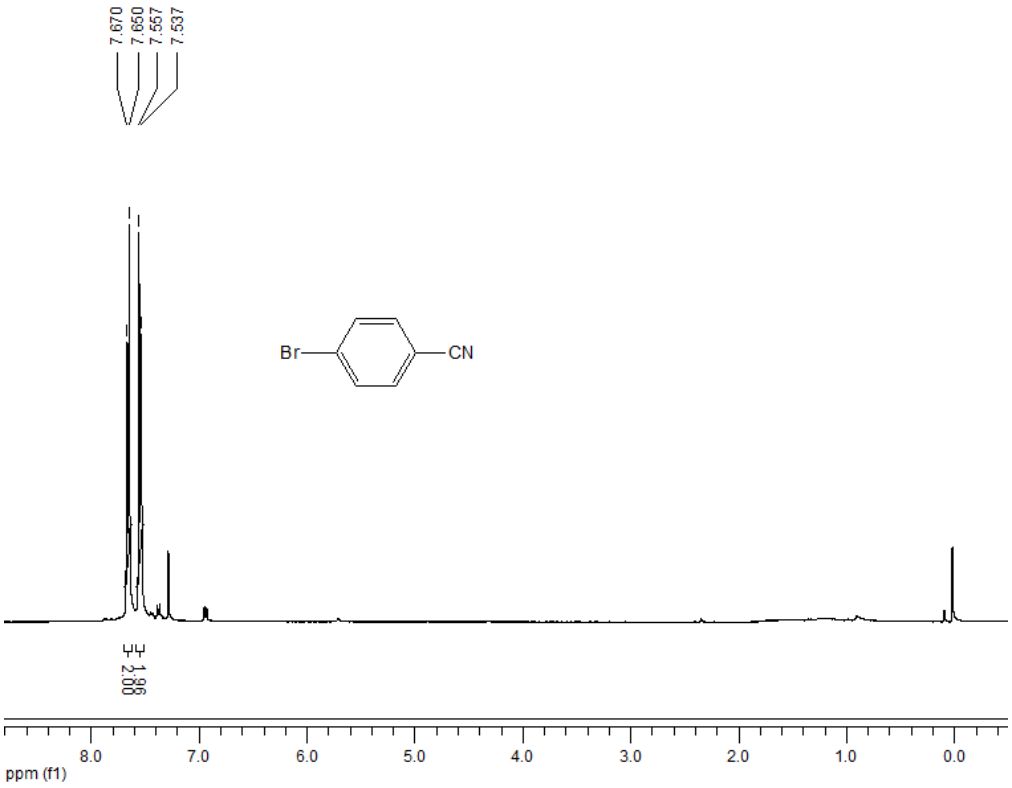
Compound 2i ^{13}C NMR(100MHz, $CDCl_3$)



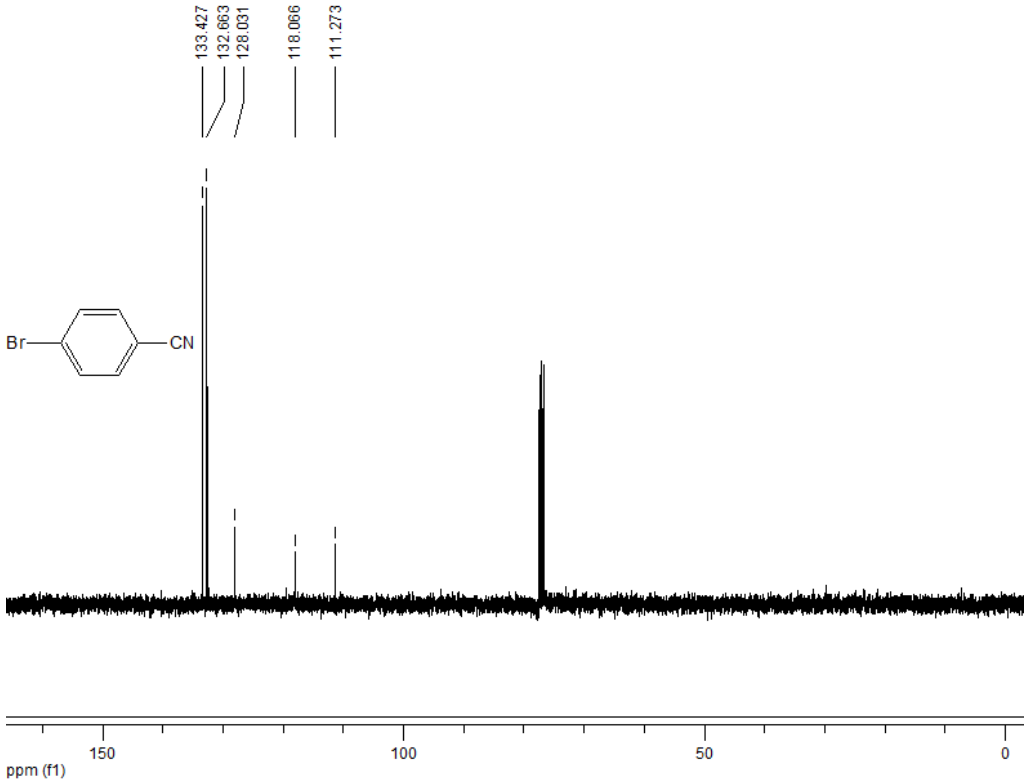
Compound 2i IR (KBr, cm^{-1})



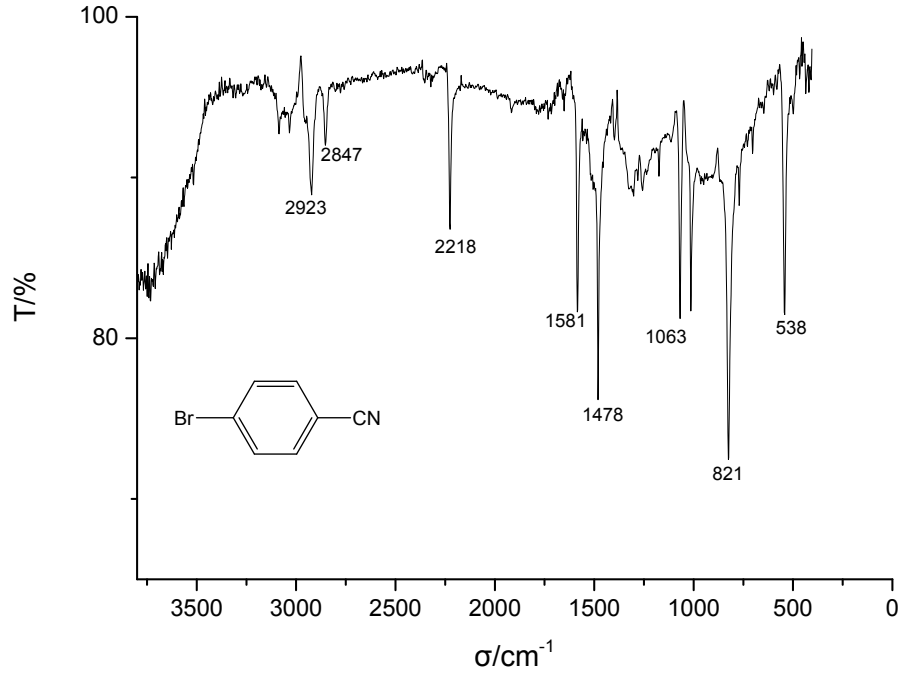
Compound 2j ^1H NMR(400MHz, $CDCl_3$)



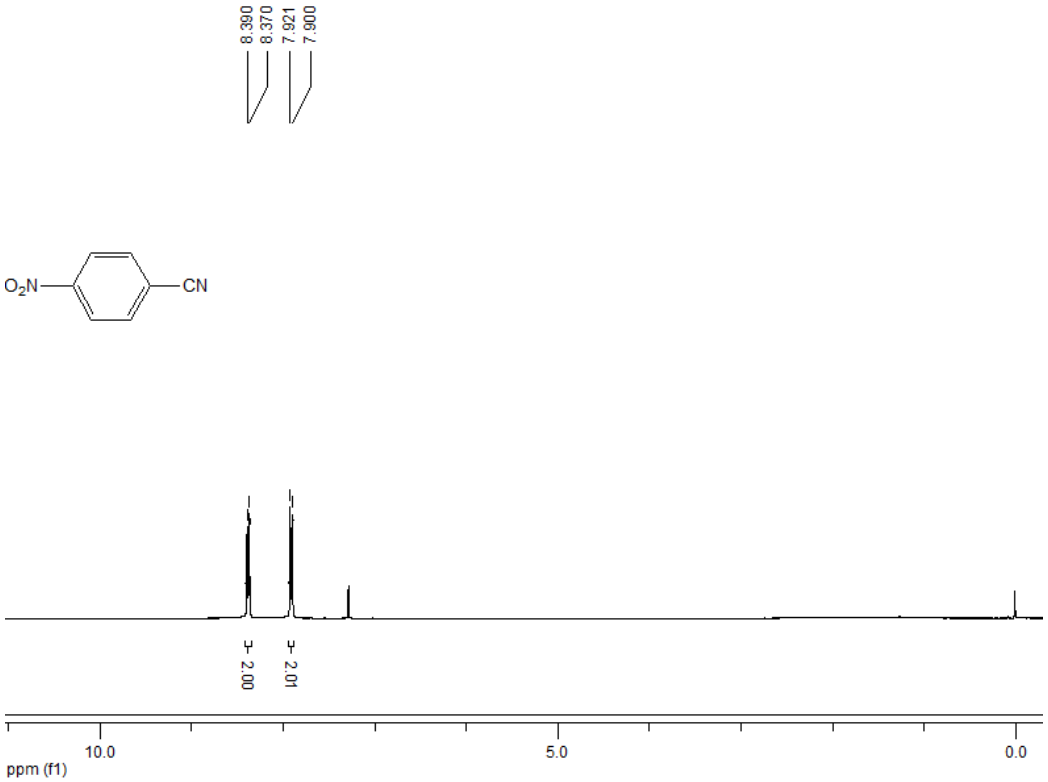
Compound 2j ^{13}C NMR(100MHz, $CDCl_3$)



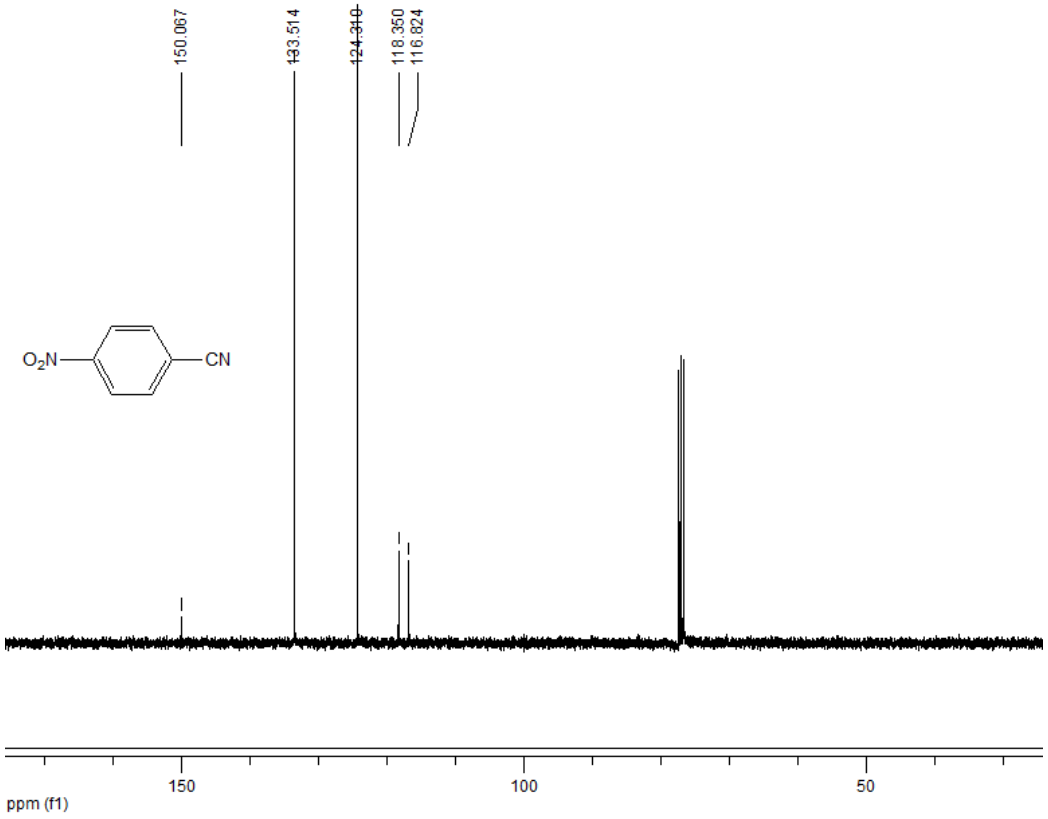
Compound 2j IR (KBr, cm^{-1})



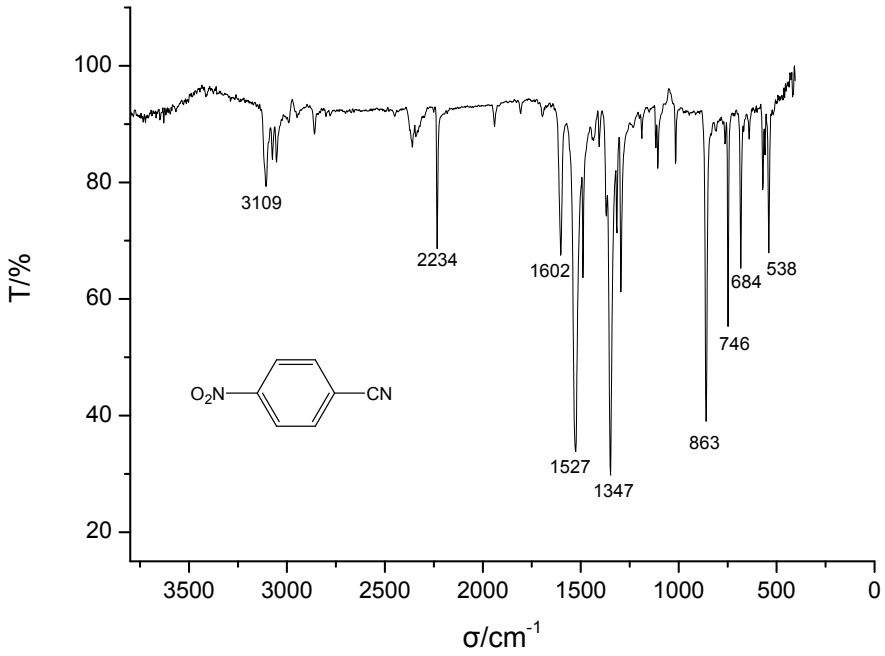
Compound 2k ^{1}H NMR(400MHz, $CDCl_3$)



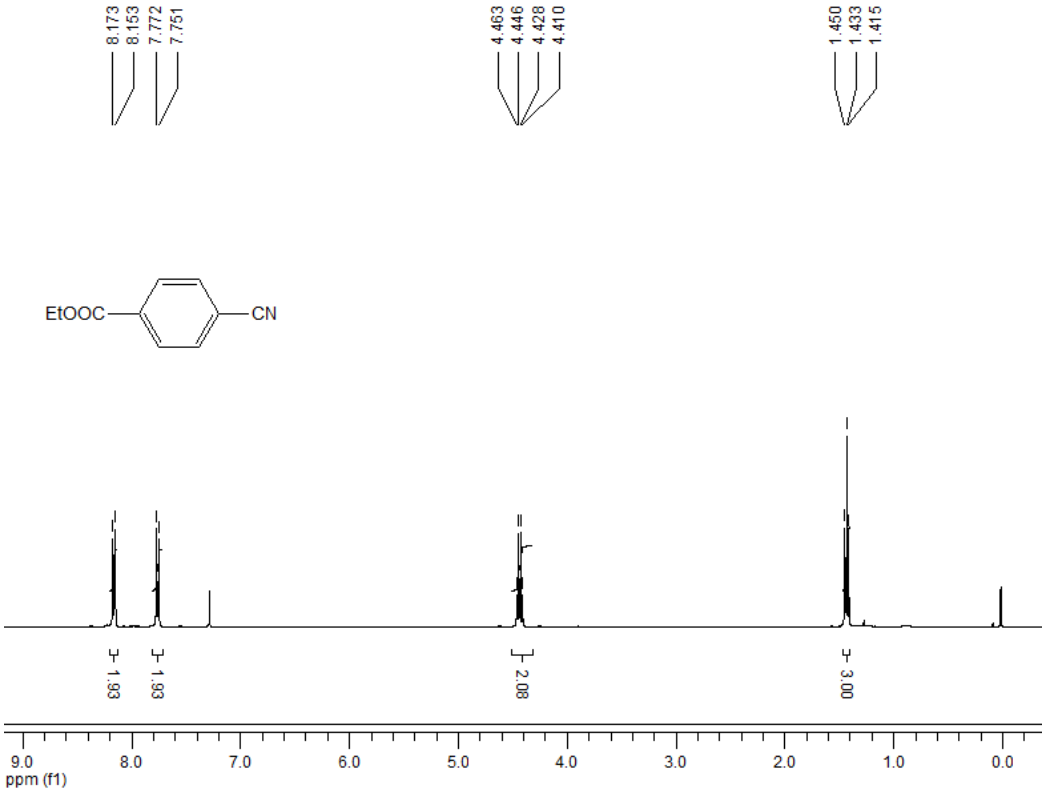
Compound 2k ^{13}C NMR(100MHz, $CDCl_3$)



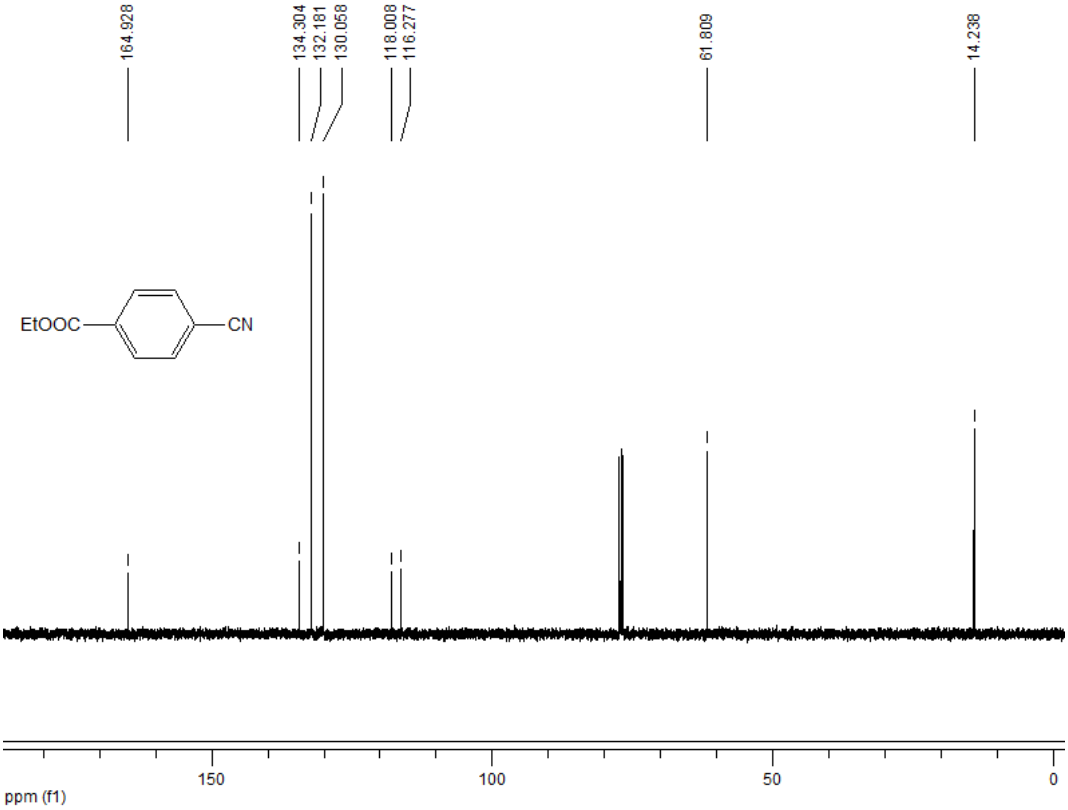
Compound 2k IR (KBr, cm^{-1})



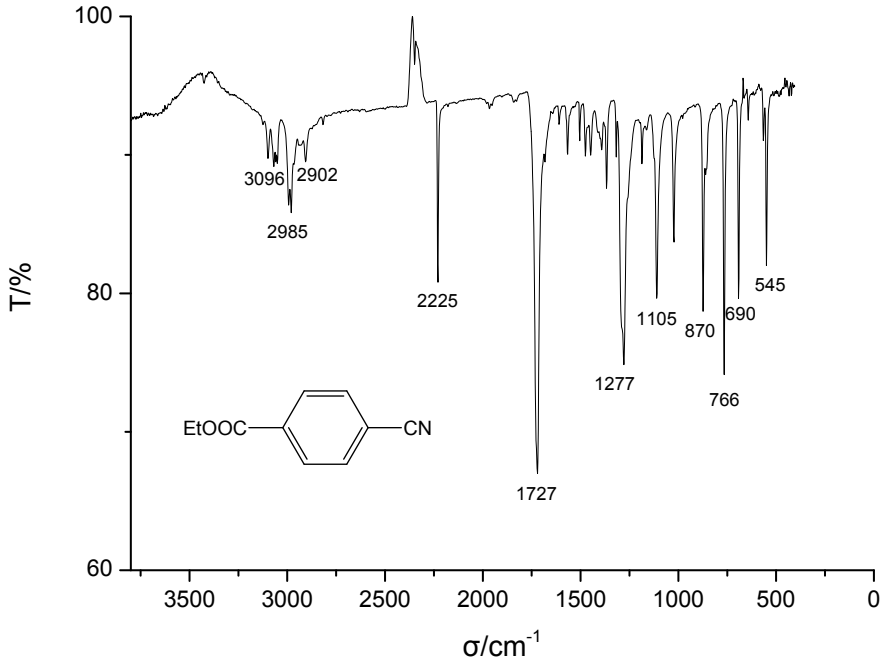
Compound 21 ^1H NMR(400MHz, $CDCl_3$)



Compound 21 ^{13}C NMR(100MHz, $CDCl_3$)



Compound 21 IR (KBr, cm^{-1})



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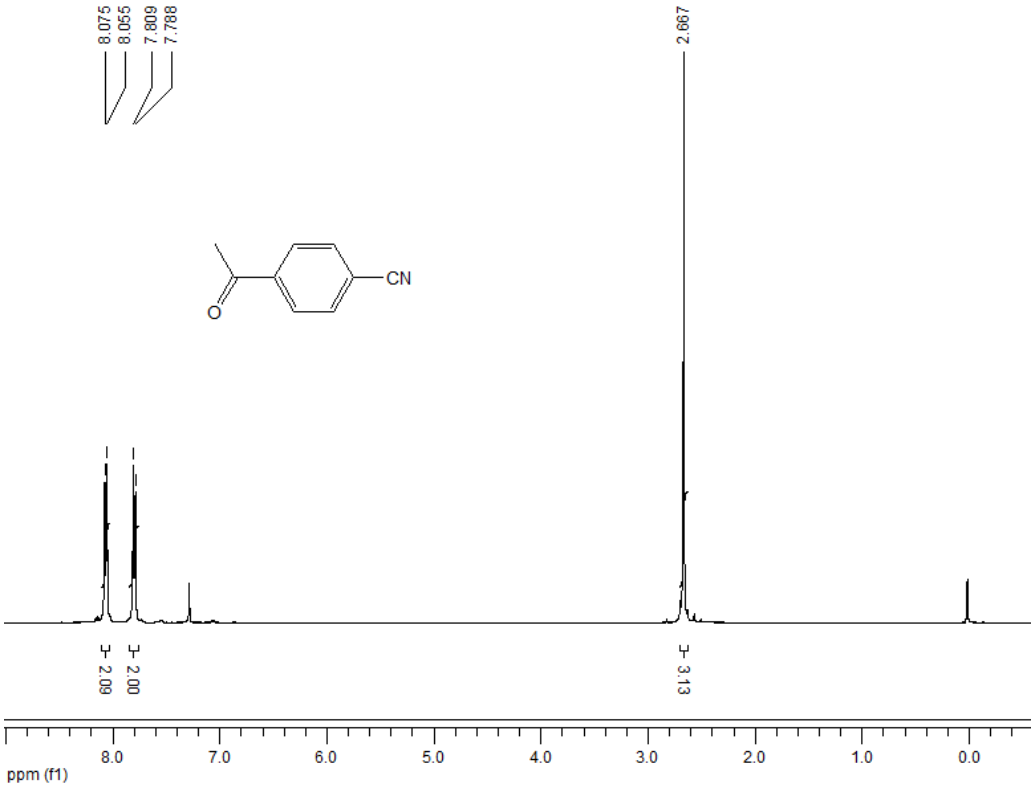
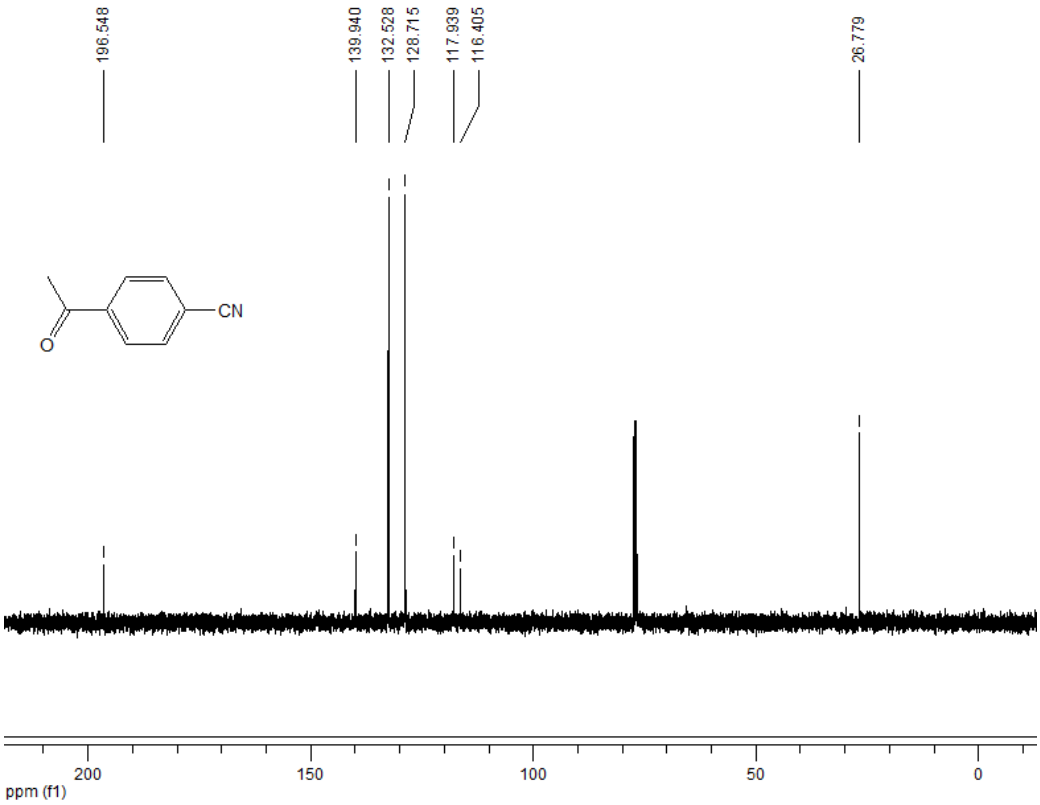
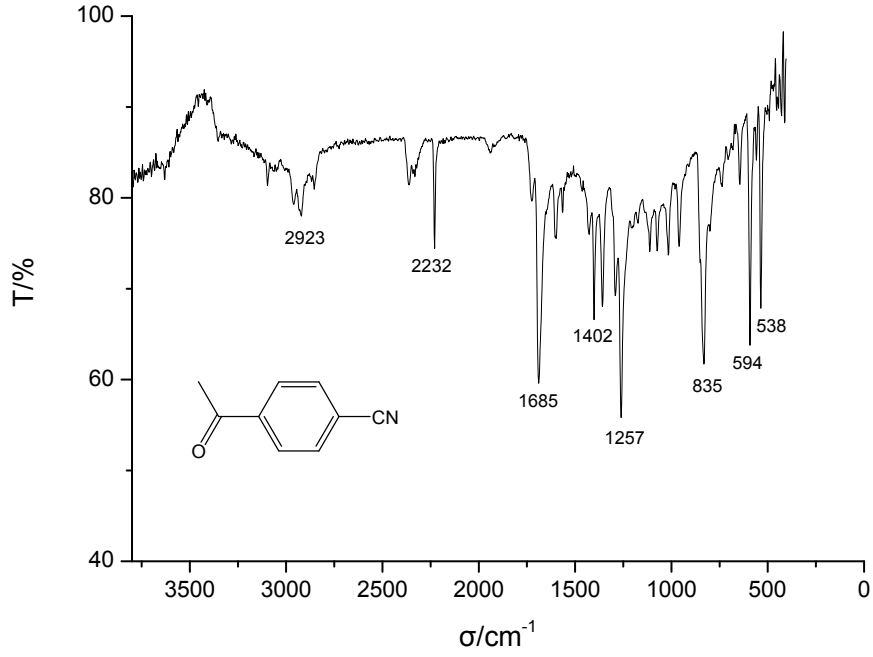


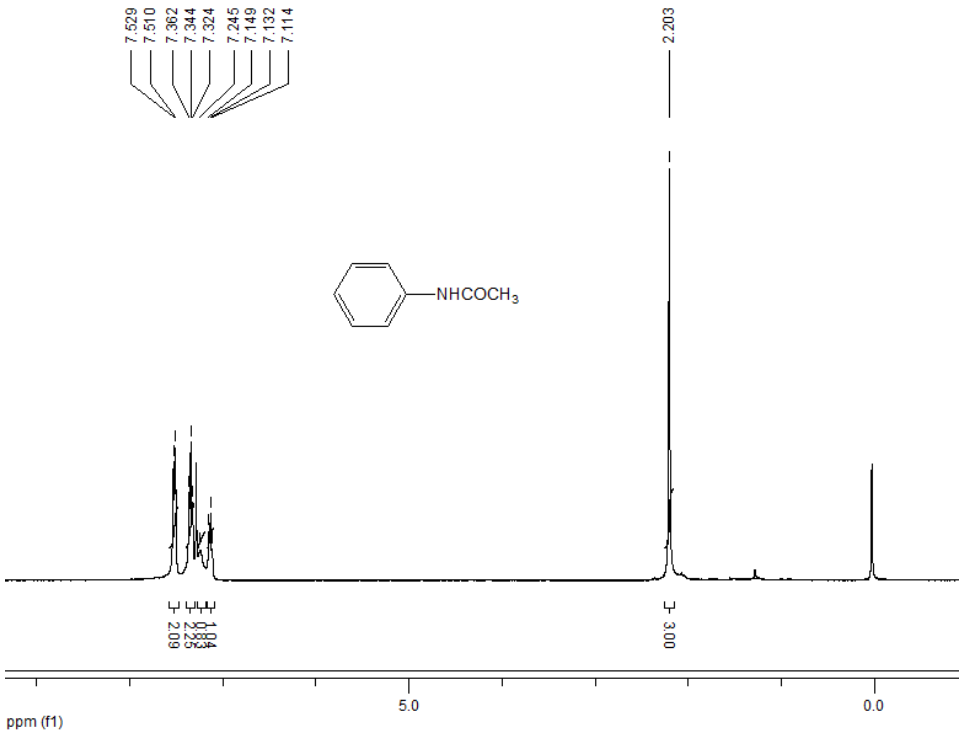
Compound 2m ^{13}C NMR(100MHz, $CDCl_3$)



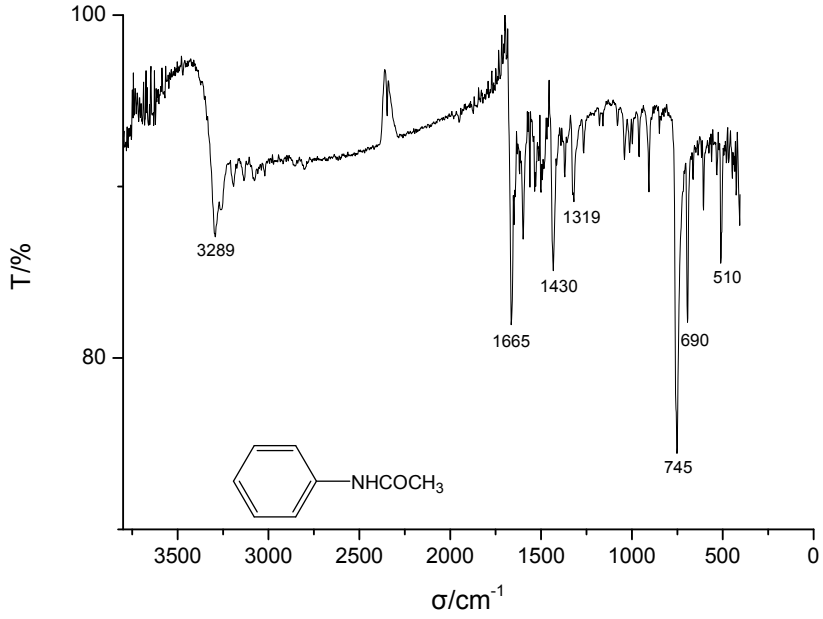
Compound 2m IR (KBr, cm^{-1})



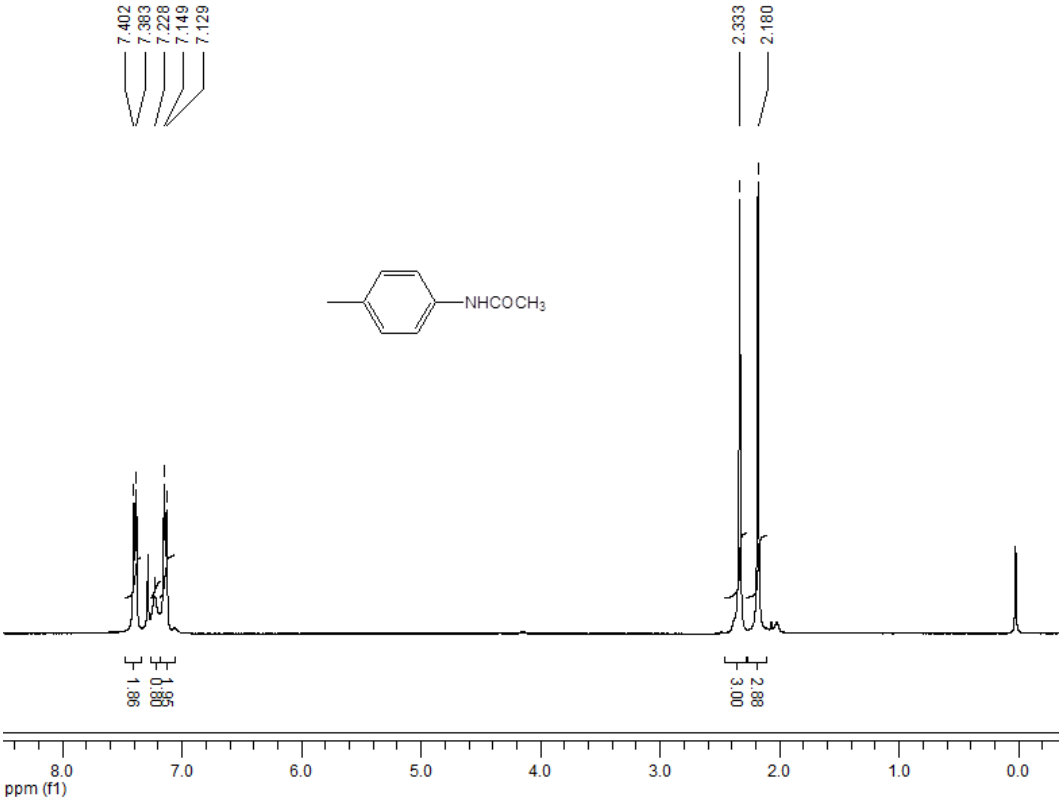
Compound 3n ^1H NMR(400MHz, $CDCl_3$)



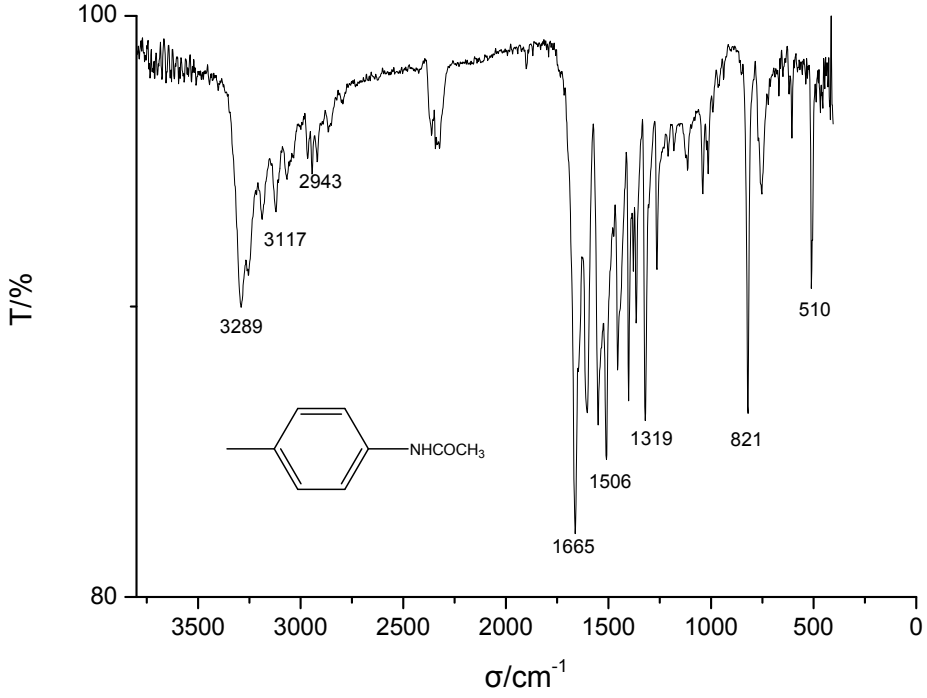
Compound 3n IR (KBr, cm^{-1})



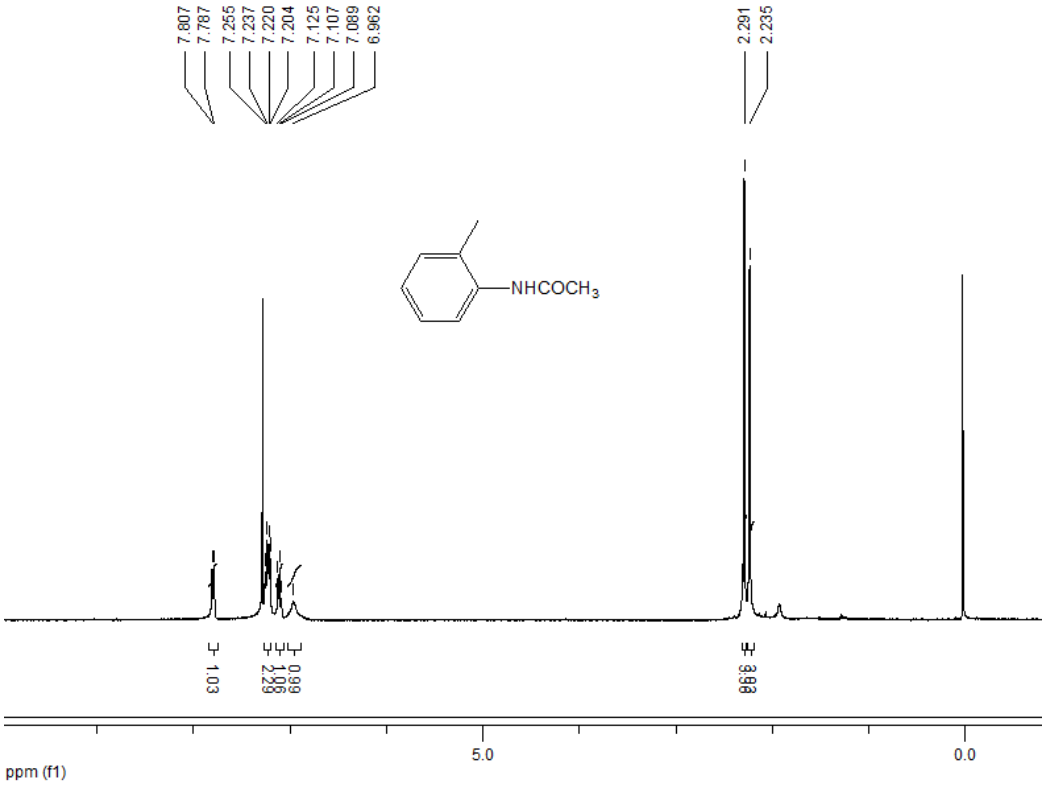
Compound 3o ^1H NMR(400MHz, $CDCl_3$)



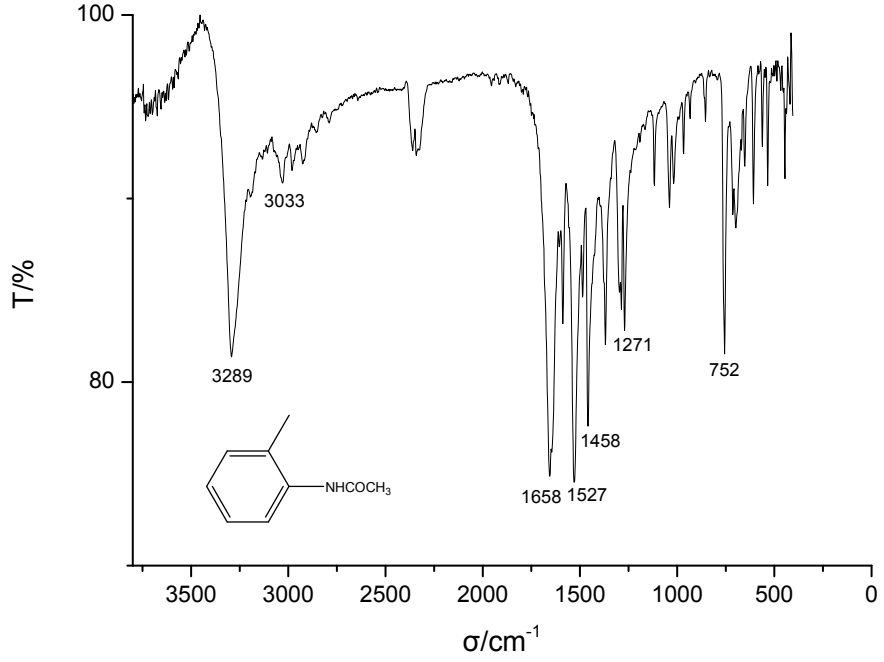
Compound 3o IR (KBr, cm^{-1})



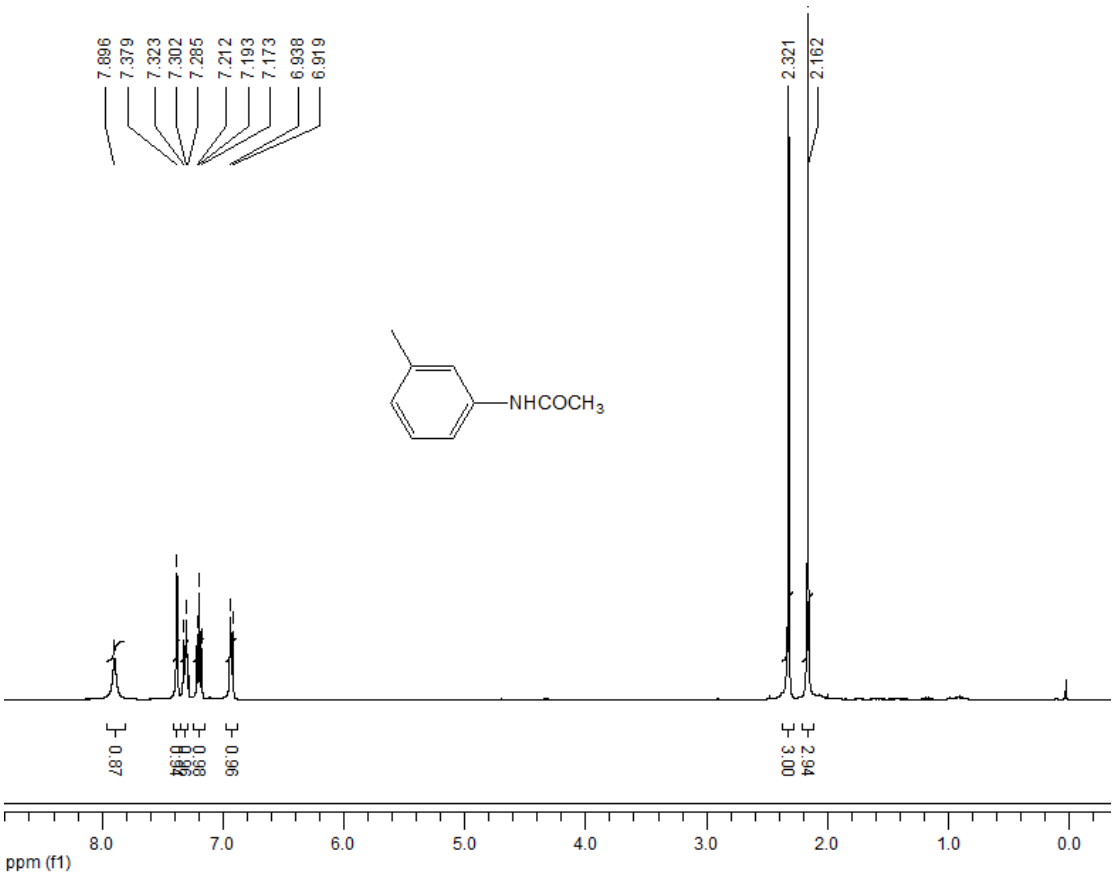
Compound 3p ^1H NMR(400MHz, $CDCl_3$)



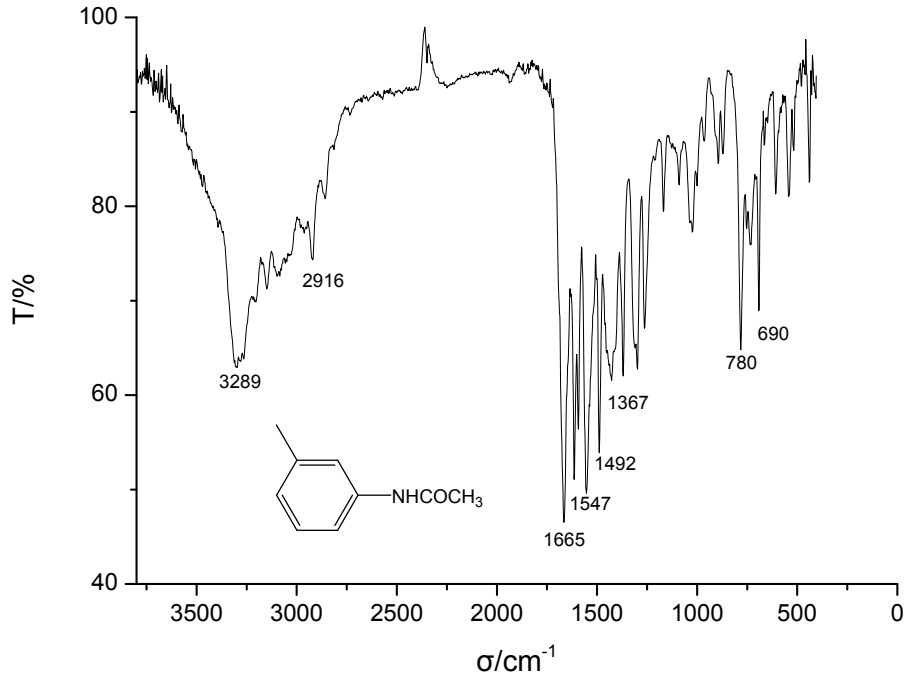
Compound 3p IR (KBr, cm^{-1})



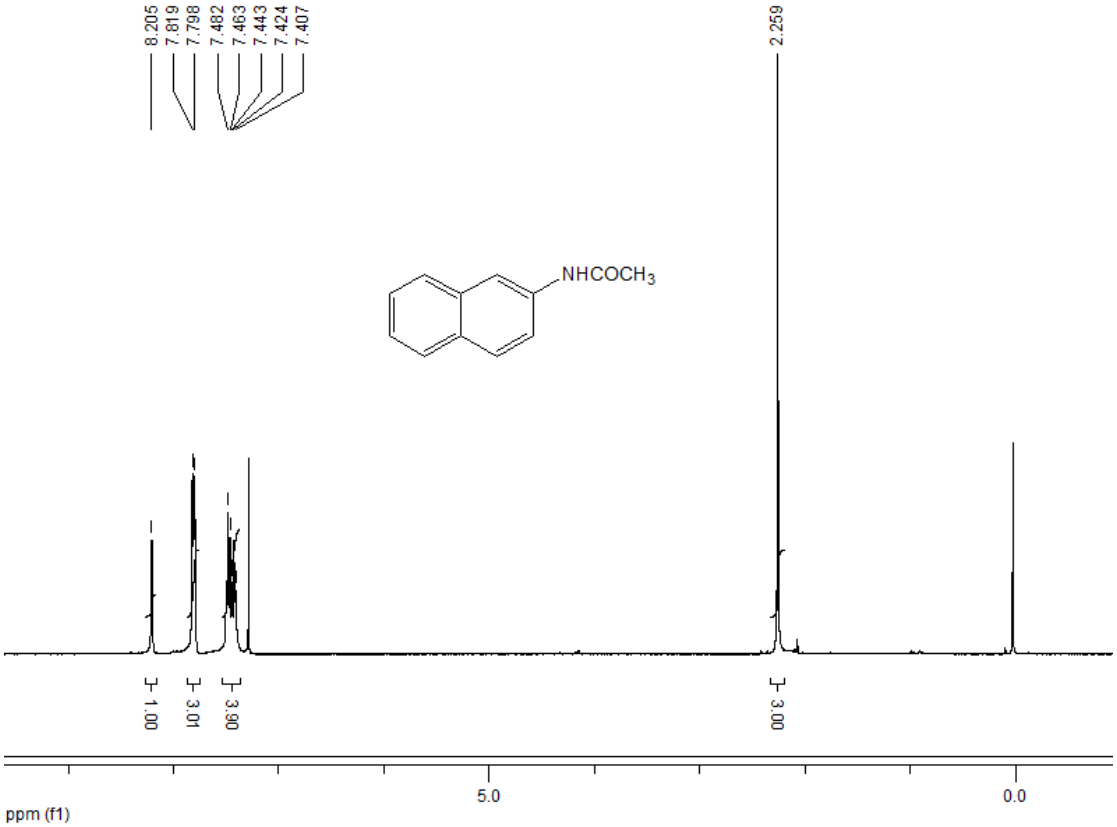
Compound 3q ^{1}H NMR(400MHz, $CDCl_3$)



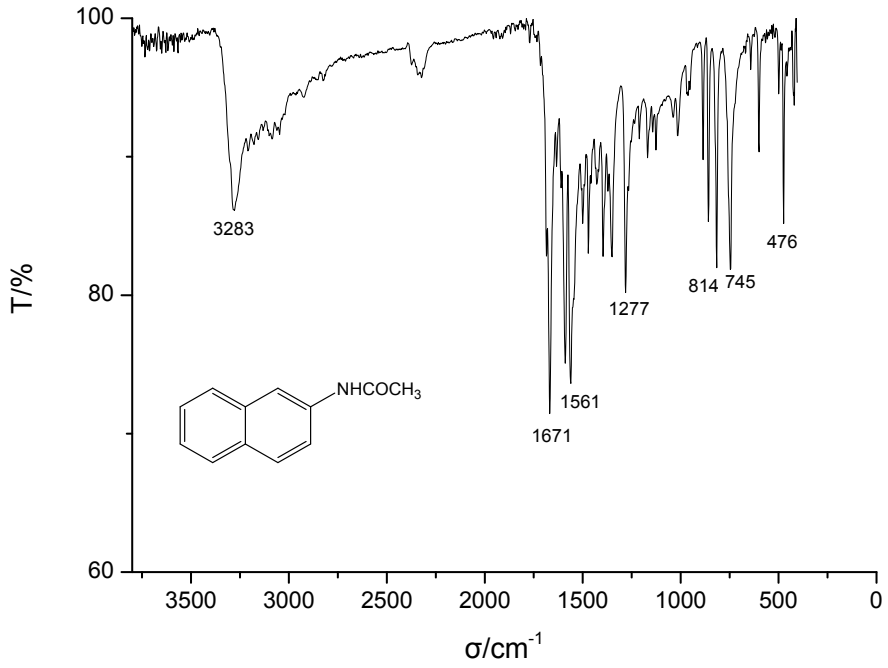
Compound 3q IR (KBr, cm^{-1})



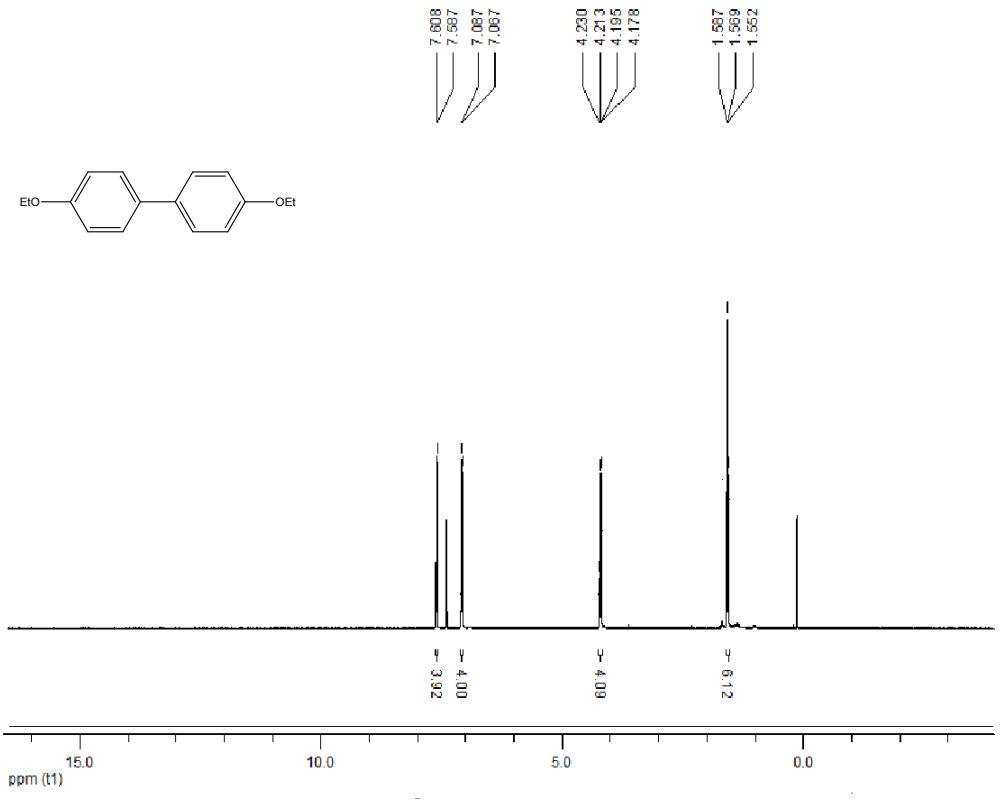
Compound 3r ^{1}H NMR(400MHz, $CDCl_3$)



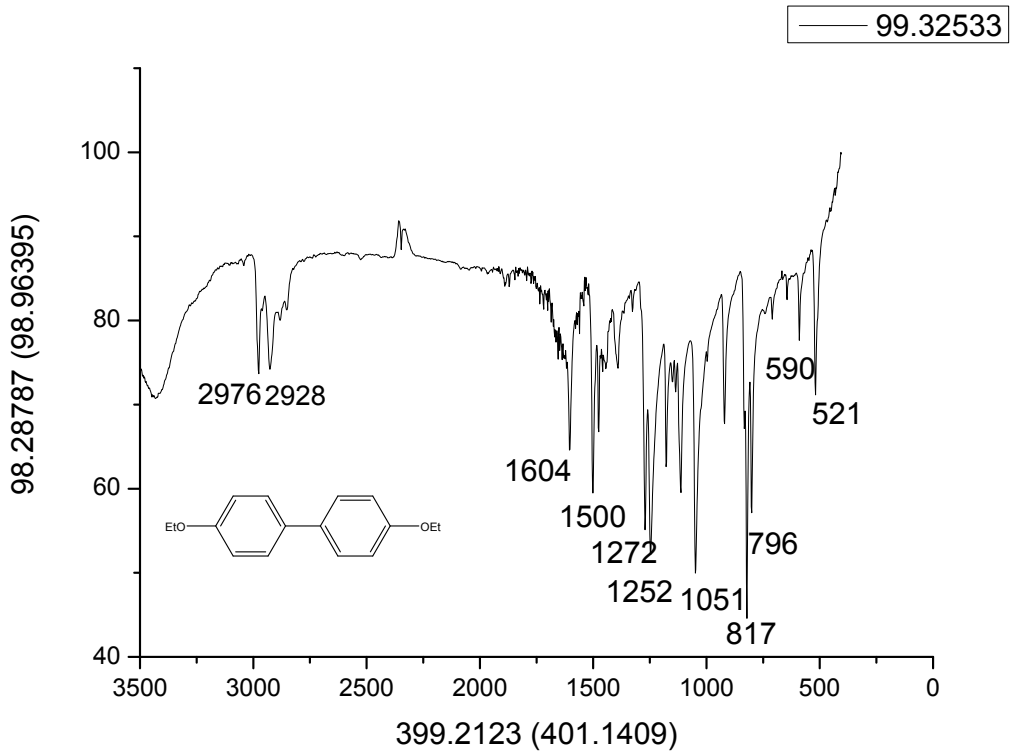
Compound 3r IR (KBr, cm^{-1})



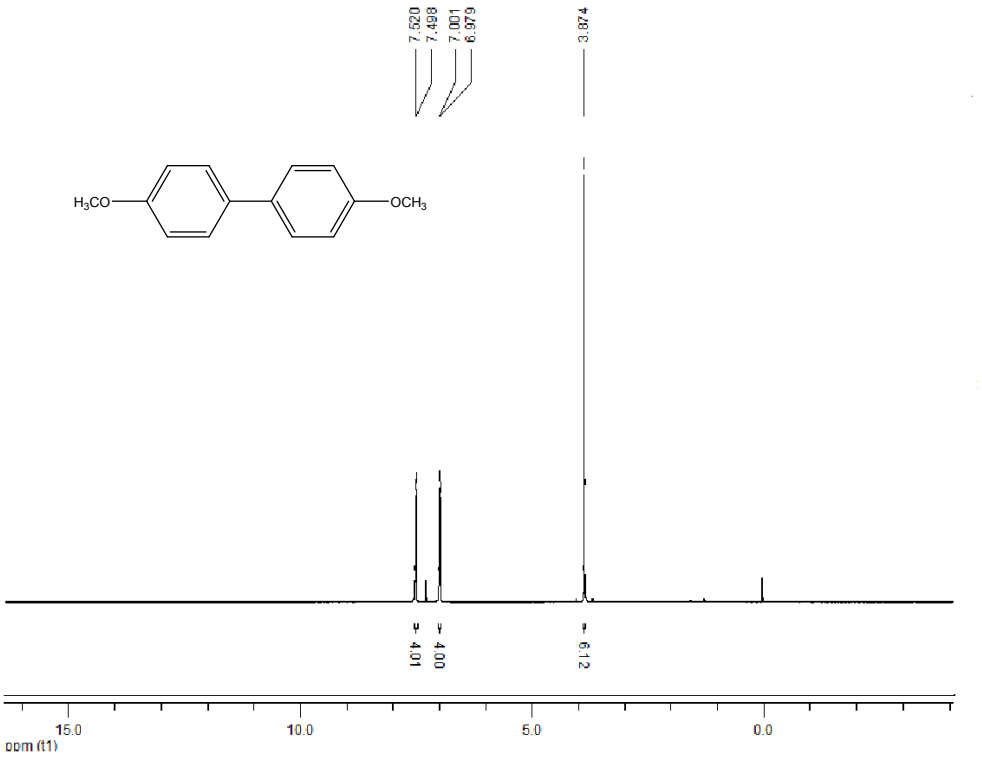
Compound 4a ^{1}H NMR(400MHz, $CDCl_3$)



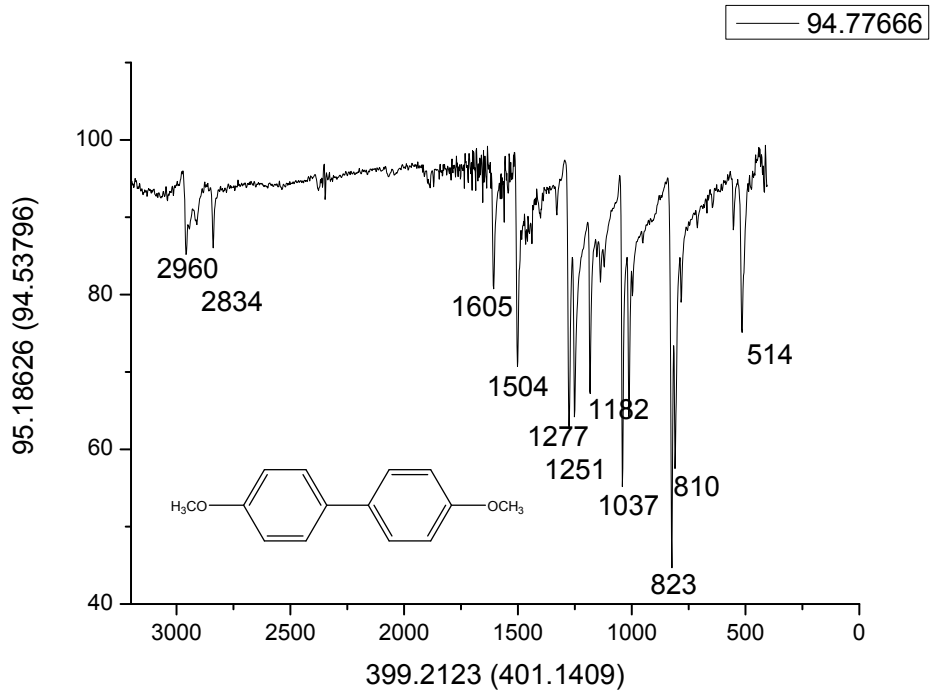
Compound 4a IR (KBr, cm^{-1})



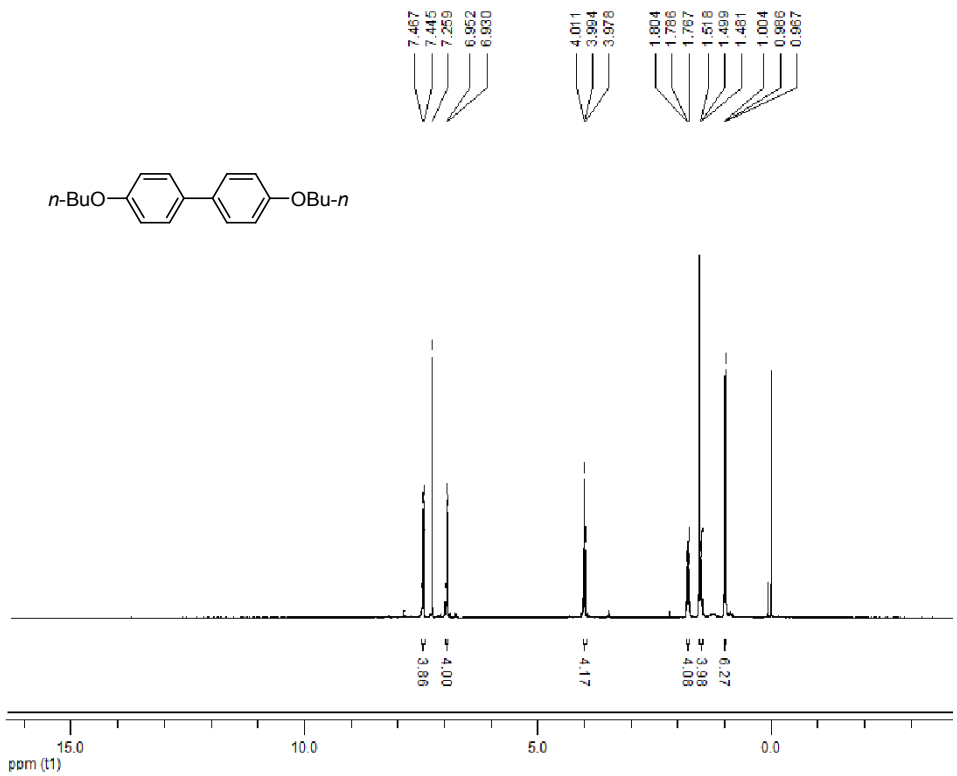
Compound 4b ^{1}H NMR(400MHz, $CDCl_3$)



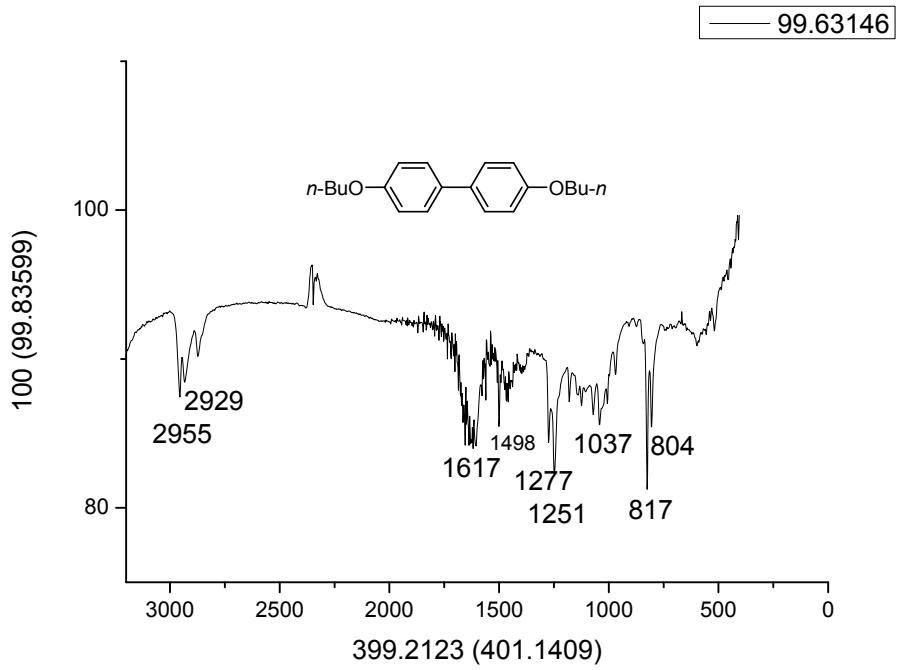
Compound 4b IR (KBr, cm^{-1})



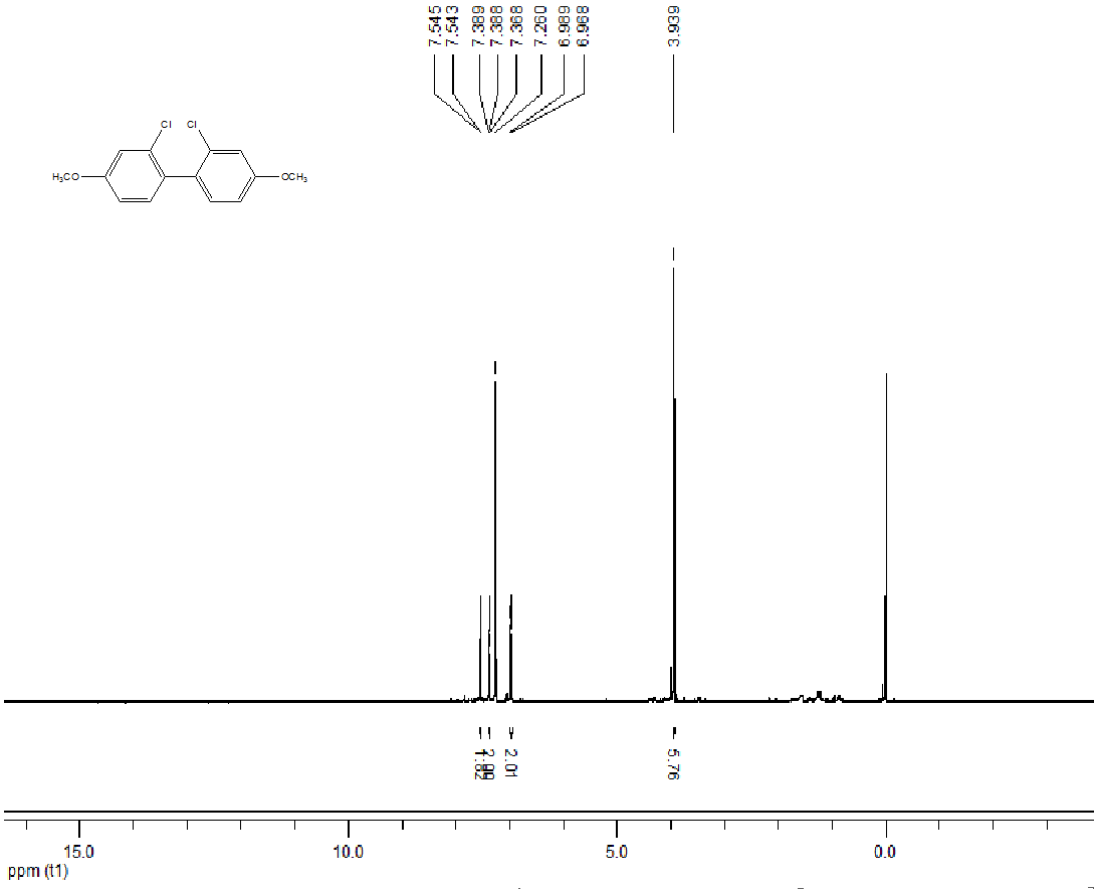
Compound 4c ^{1}H NMR(400MHz, $CDCl_3$)



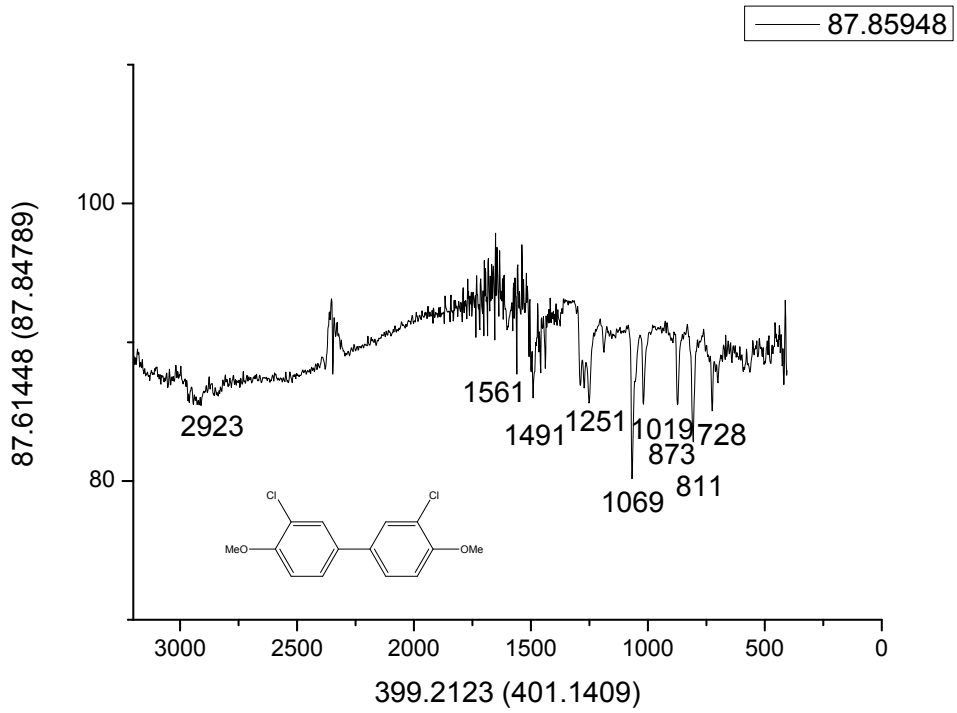
Compound 4c IR (KBr, cm^{-1})



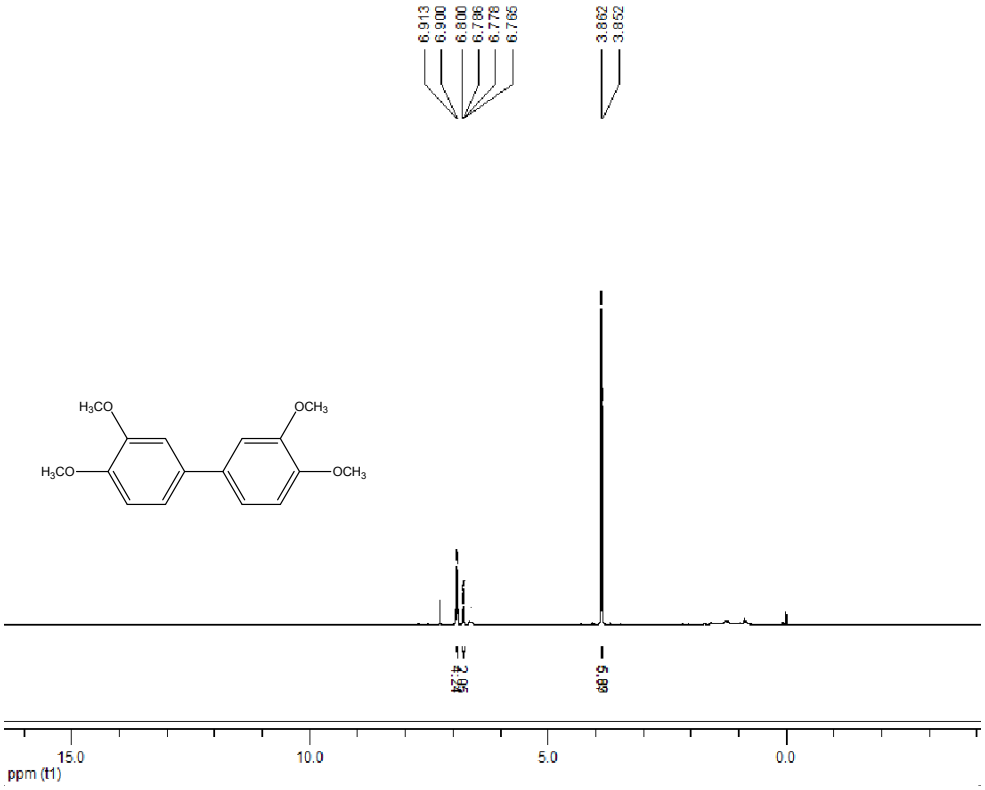
Compound 4d ^{1}H NMR(400MHz, $CDCl_3$)



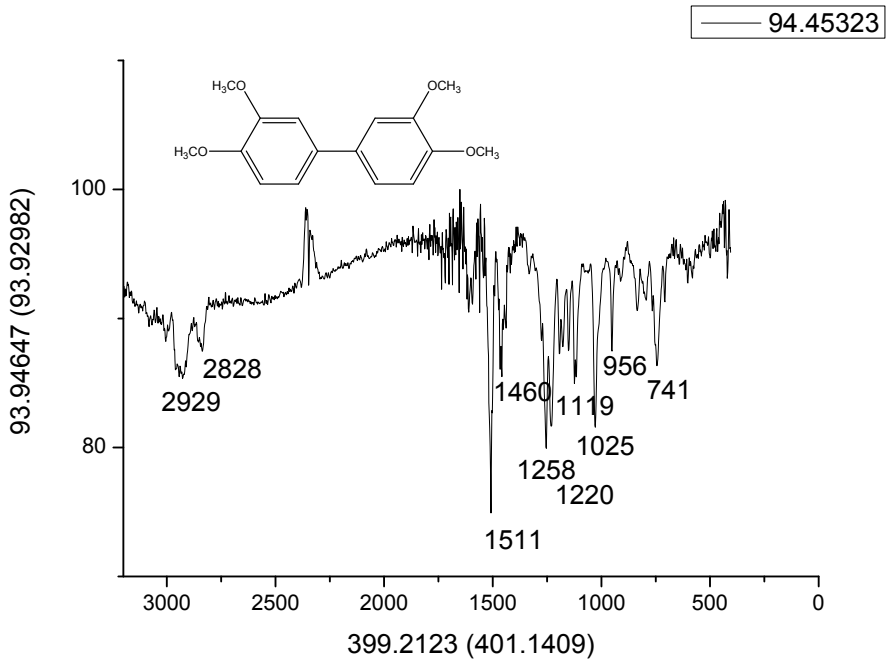
Compound 4d IR (KBr, cm^{-1})



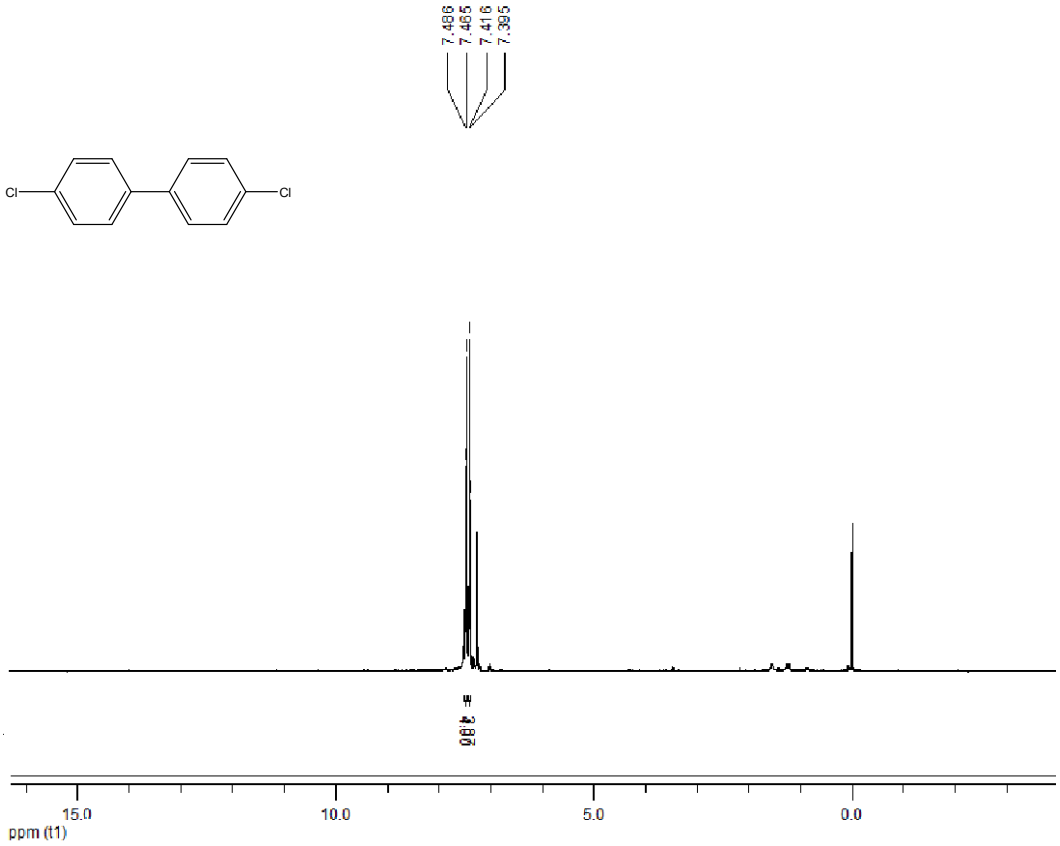
Compound 4e ^{1}H NMR(400MHz, $CDCl_3$)



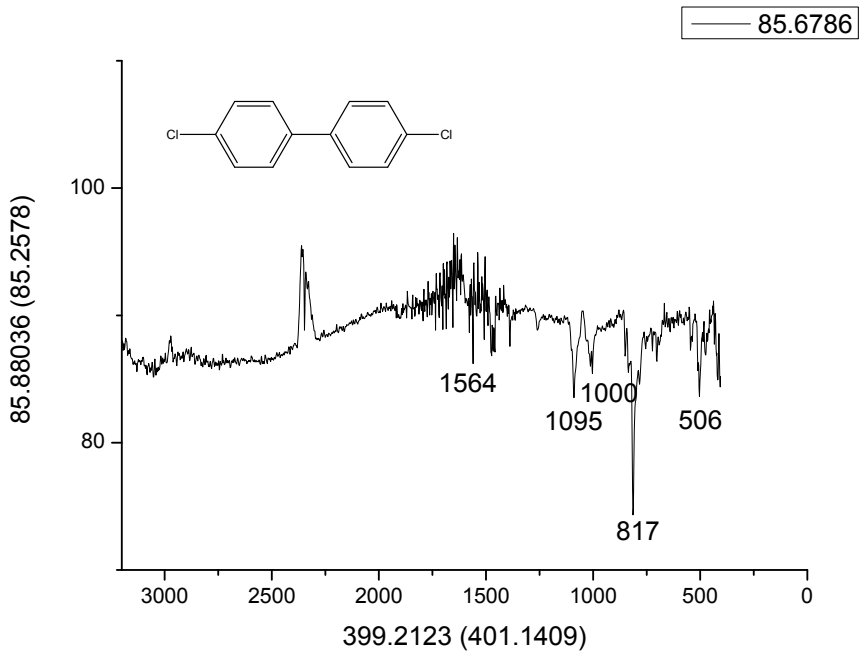
Compound 4e IR (KBr, cm^{-1})



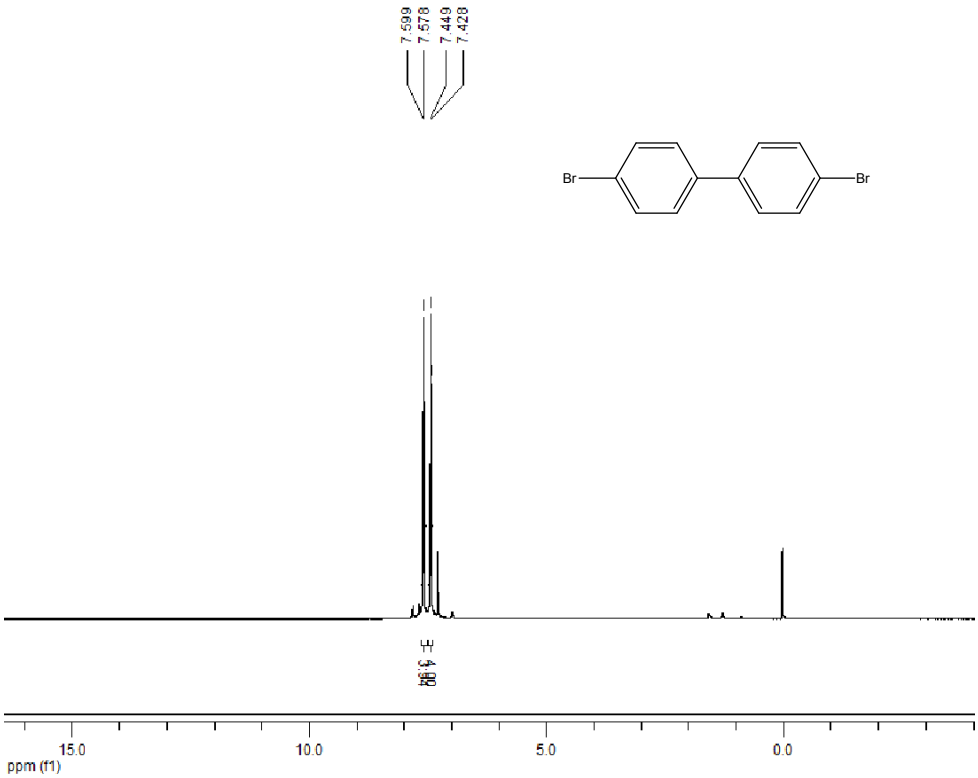
Compound 4h ^{1}H NMR(400MHz, $CDCl_3$)



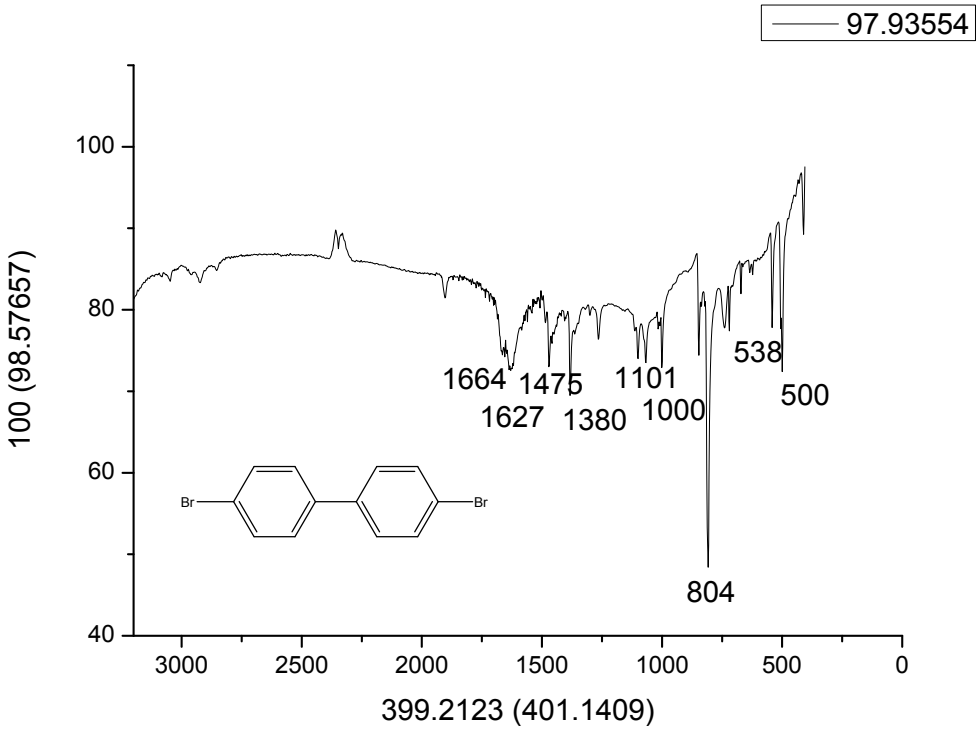
Compound 4h IR (KBr, cm^{-1})



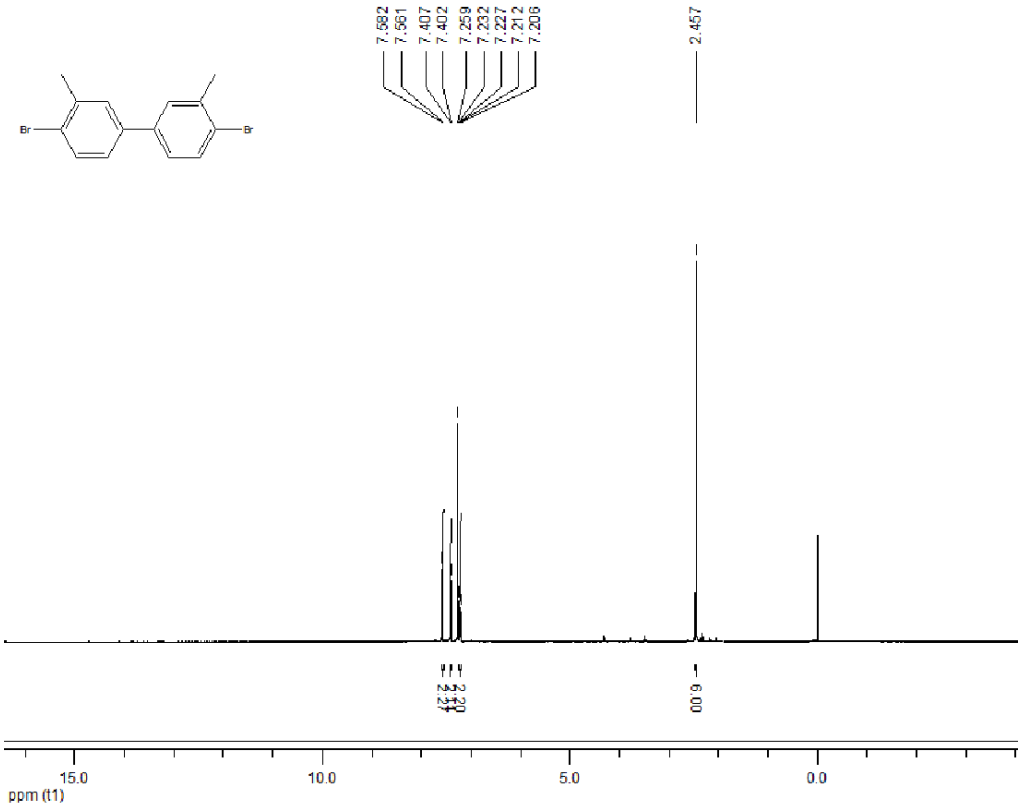
Compound 4j ^{1}H NMR(400MHz, $CDCl_3$)



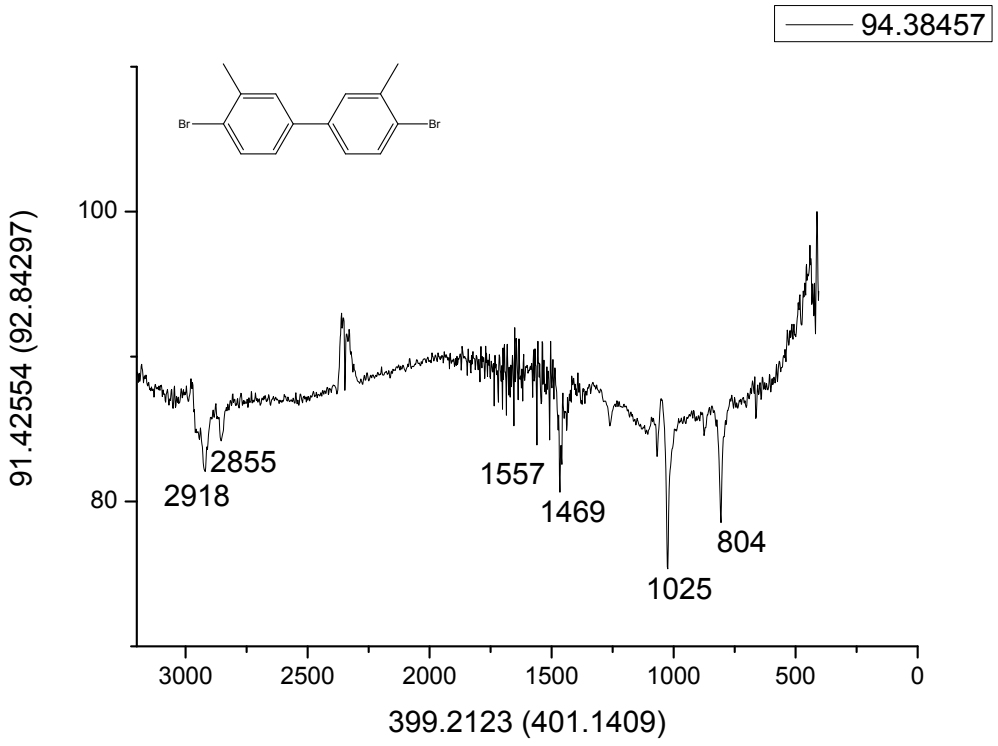
Compound 4j IR (KBr, cm^{-1})



Compound 4g ^{1}H NMR(400MHz, $CDCl_3$)



Compound 4g IR (KBr, cm^{-1})


94.38457
Br
Br
100
80
91.42554 (92.84297)
2855
2918
1557
1469
1025
804
3000
2500
2000
1500
1000
500
0
399.2123 (401.1409)

Reference

1. *Org. Lett* .**2013**,15(8), 1850-1853
2. *Eur. J. Org. Chem* .**2013**, 19, 4032-4036
3. *Syn. Lett*. **2012**,23(17), 2491-2496
4. *JACS*. **2012**, 134(5),2528-2531
5. *Chem. Eur. J.* **2010**, 16(9), 2830-2842
6. *JACS*. **2011**, 133(28), 10999-11005
7. *Chem. Eur. J.* **2011**, 17(19), 2763-2768
8. *Eur. J. Org. Chem.* **2012**, 31, 6127-6131
9. *Tetrahedton*. **2010**, 66(37), 7418-7422
10. *Tetra. Lett*. **2011**, 52, 4681-4685
11. *J. Org. Chem*. **2008,** 73, 2894-2897
12. *Synthesis*. **2013**, 45(4), 518-526
13. *Tetrahedron*. **2013**, 69(44), 9237-9244
14. *Eur. J. Org. Chem*. **2011**, 13, 2519-2523
15. *Chem. Cat. Chem*. **2014**, 6, 745-748
16. *Adv. Syn&Cat*. **2012**, 354, 2777-2778