Supporting Information

Synthesis of Aza-Fused Polycyclic Quinolines through Copper-Catalyzed Cascade Reactions

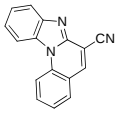
Qian Cai, Zhengqiu Li, Jiajia Wei, Liangbin Fu, Chengyong Ha, Duanqing Pei and Ke Ding**

Key Laboratory of Regenerative Biology and Institute of Chemical Biology, Guangzhou Institutes of Biomedicine and Health, Chinese Academy of Sciences
No. 190 Kaiyuan Avenue, Science Park, Guangzhou, China, 510530
Fax: (+) 86-20-32015299
E-mail: cai_qian@gibh.ac.cn, ding_ke@gibh.ac.cn

Content:

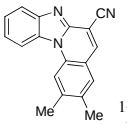
Typical procedure for the preparation of Aza-Fused Polycyclic Quinolines: The substrates, base, copper salt, ligand and solvent were added together and reacted at appointed temperature under nitrogen atmosphere. The reactions were monitored by TLC and final products were obtained after workup. .

1. Benzimidazo[1,2-a]quinoline-6-carbonitrile



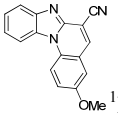
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (d, *J* = 8.8 Hz, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 8.18 (s, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 7.94-7.90 (m, 2H), 7.64-7.55 (m, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.9, 144.2, 141.2, 136.3, 134.2, 131.7, 131.0, 125.7, 125.6, 124.2, 121.7, 120.8, 116.4, 115.9, 115.4, 101.8; ESI-MS *m/z* 244.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{16}H_{10}N_3$ $(M+H)^+$ requires 244.0875, found 244.0875.

2a. 2,3-Dimethyl-benzimidazo[1,2-a]quinoline-6-carbonitrile



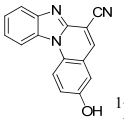
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.39 (d, *J* = 7.6 Hz, 1H), 8.36 (s, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.10 (s, 1H), 7.62 (s, 1H),7.60-7.54 (m, 2H), 2.61 (s, 3H), 2.46 (s, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.9, 144.6, 143.7, 138.5, 135.0, 134.3, 130.9, 130.7, 125.2, 123.5, 121.4, 119.6, 116.1, 115.2, 113.9, 101.8, 21.3, 19.3; ESI-MS *m/z* 272.1 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{18}H_{14}N_3$ $(M+H)^+$ requires 272.1188, found 272.1189.

2b. 3-Methoxy-benzimidazo[1,2-a]quinoline-6-carbonitrile



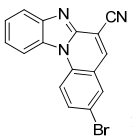
^{1}H NMR (DMSO, 400 MHz) δ 8.62 (d, *J* = 9.2 Hz, 1H), 8.55 (d, *J* = 9.2 Hz, 1H), 8.35-8.33 (m, 2H), 7.69-7.49 (m, 3H), 7.31 (s, 1H), 3.98 (s, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.5, 144.5, 144.3, 138.3, 131.1, 130.9, 125.2, 123.8, 122.6, 121.6, 121.5, 116.8, 114.9, 113.7, 112.1, 103.7, 55.9; ESI-MS *m/z* 274.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{17}H_{12}N_3O$ $(M+H)^+$ requires 274.0980, found 274.0985.

2c. 3-Hydroxy-benzimidazo[1,2-a]quinoline-6-carbonitrile



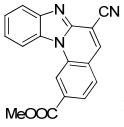
^{1}H NMR (DMSO, 400 MHz) δ 10.24 (s, 1H), 8.71-8.68 (m, 2H), 8.65 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.58-7.50 (m, 2H), 7.44-7.43 (m, 2H) , ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.8, 144.5, 144.2, 140.6, 130.9, 129.7, 125.2, 123.8, 123.1, 122.7, 120.6, 117.7, 115.9, 115.4, 114.9, 101.8; ESI-MS *m/z* 260.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{16}H_{10}N_3O$ $(M+H)^+$ requires 260.0824, found 260.0827.

2d. 3-Bromo-benzimidazo[1,2-a]quinoline-6-carbonitrile



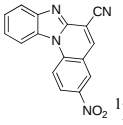
^{1}H NMR (DMSO, 400 MHz) δ 8.76 (d, *J* = 9.2 Hz, 1H), 8.70 (s, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.36 (s, 1H), 8.06-7.99 (m, 2H), 7.63-7.55 (m, 2H), ^{13}C NMR (DMSO, 75 MHz) δ 144.6, 144.2, 139.8, 136.1, 135.2, 133.3, 130.9, 125.8, 124.4, 123.5, 120.9, 118.5, 117.5, 115.6, 115.2, 103.0; ESI-MS *m/z* 321.0, 323.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{16}H_9BrN_3$ $(M+H)^+$ requires 321.9980, 323.9959, found 321.9971, 323.9948.

2e. Methyl ester 6-cyano-benzimidazo[1,2-a]quinoline-2-carboxylic acid



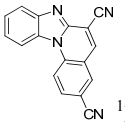
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.29 (s, 1H), 8.48 (s, 1H), 8.24-8.20 (m, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.66-7.64 (m, 2H); ESI-MS *m/z* 302.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{18}H_{12}N_3O_2$ $(M+H)^+$ requires 302.0930, found 302.0925.

2f. 3-Nitro-benzimidazo[1,2-a]quinoline-6-carbonitrile



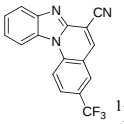
^{1}H NMR (DMSO, 400 MHz) δ 8.84 (s, 1H), 8.76-8.74 (m, 2H), 8.41 (d, *J* = 7.2 Hz, 1H), 8.28 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 7.71-7.66 (m, 2H); ESI-MS *m/z* 289.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{16}H_9N_4O_2$ $(M+H)^+$ requires 289.0726, found 289.0729.

2g. 3-Nitrile-benzimidazo[1,2-a]quinoline-6-carbonitrile



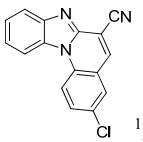
^{1}H NMR (DMSO, 400 MHz) δ 8.86 (s, 1H), 8.37-8.34 (m, 1H), 8.21-8.19 (m, 2H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.69-7.67 (m, 2H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.7, 143.6, 138.2, 135.4, 131.8, 130.3, 127.3, 125.4, 124.4, 124.0, 120.6, 119.1, 117.4, 115.1, 114.3, 114.1; ESI-MS *m/z* 269.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{17}H_9N_4$ $(M+H)^+$ requires 269.0827, found 269.0825.

2h. 3- Trifluoromethyl -benzimidazo[1,2-a]quinoline-6-carbonitrile



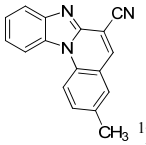
^{1}H NMR (DMSO, 400 MHz) δ 8.96 (d, *J* = 9.2 Hz, 1H), 8.83 (s, 1H), 8.68 (d, *J* = 7.6 Hz, 1H), 8.57 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 6.8 Hz, 1H), 7.64-7.57 (m, 2H), ^{13}C NMR (DMSO, 75 MHz) δ 144.9, 144.3, 140.5, 138.4, 130.9, 129.7, 128.8, 126.1, 125.6, 124.7, 122.9, 121.8, 121.1, 117.6, 115.5, 115.3, 103.4; ESI-MS *m/z* 312.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{17}H_9F_3N_3$ $(M+H)^+$ requires 312.0749, found 312.0747.

2i. 3-Chloro-benzimidazo[1,2-a]quinoline-6-carbonitrile



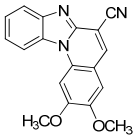
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.57 (d, *J* = 9.2 Hz, 1H), 8.34 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 7.91 (s, 1H), 8.88 (d, *J* = 9.2 Hz, 1H), 7.65-7.57 (m, 2H), ^{13}C NMR (DMSO, 75 MHz) δ 144.7, 144.3, 139.8, 135.0, 133.4, 131.0, 130.4, 129.6, 125.8, 124.4, 123.2, 121.0, 118.4, 115.5, 115.2, 103.2; ESI-MS *m/z* 278.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{16}H_9ClN_3$ $(M+H)^+$ requires 278.0485, found 278.0487.

2j. 3-Methyl-benzimidazo[1,2-a]quinoline-6-carbonitrile



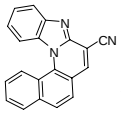
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.40-8.38 (m, 2H), 8.16-8.14 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.63-7.55 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 2.71 (s, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.0, 144.6, 144.5, 138.8, 136.8, 131.0, 130.6, 126.4, 125.3, 123.7, 121.4, 119.3, 115.7, 115.1, 114.0, 102.0, 22.7; ESI-MS *m/z* 258.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{17}H_{12}N_3$ $(M+H)^+$ requires 258.1031, found 258.1030.

2k. 2,3-Dimethoxy-benzimidazo[1,2-a]quinoline-6-carbonitrile



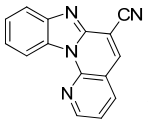
^{1}H NMR (DMSO, 400 MHz) δ 8.67-8.64 (m, 2H), 8.08 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.64-7.75 (m, 2H), 4.18 (s, 3H), 3.92 (s, 3H) ; ESI-MS *m/z* 304.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{17}H_{12}N_3$ $(M+H)^+$ requires 304.1086, found 304.1089.

2l. Benzimidazo[1,2-a]benzo[h]quinoline-8-carbonitrile



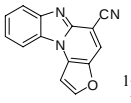
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.75 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.77 (m, 2H), 7.63-7.56 (m, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.5, 144.8, 138.0, 135.5, 133.9, 132.7, 129.6, 128.7, 128.2, 126.8, 125.9, 125.4, 125.1, 124.4, 122.4, 121.4, 121.2, 120.1, 115.7, 114.9, 102.5; ESI-MS *m/z* 294.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{20}H_{12}N_3$ $(M+H)^+$ requires 294.1031, found 294.1036.

2m. Benzimidazo[1,2-a][1,8]naphthyridine-6-carbonitrile



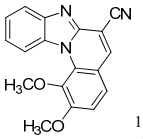
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.18 (d, *J* = 7.2 Hz, 1H), 8.97 (d, *J* = 4.4 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.16 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.65-7.54 (m, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.9, 147.4, 144.7, 144.1, 138.0, 136.9, 130.7, 126.0, 124.6, 120.8, 120.7, 117.2, 116.1, 114.4, 104.5; ESI-MS *m/z* 245.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{15}H_9N_4$ $(M+H)^+$ requires 245.0827, found 245.0821.

2n. Furo[2',3':5,6]pyrido[1,2-a]benzimidazole-6-carbonitrile



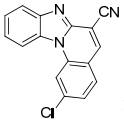
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.07 (m, 2H), 7.66-7.62 (m, 1H), 7.57-7.53 (m, 1H), 7.49-7.47 (m, 1H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 149.7, 145.1, 144.6, 140.2, 130.5, 129.1, 126.1, 123.4, 123.0, 121.1, 115.4, 111.7, 101.9, 96.7; ESI-MS *m/z* 234.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{14}H_8N_3O$ $(M+H)^+$ requires 234.0667, found 234.0669.

2o. 1,2-Dimethoxy-benzimidazo[1,2-a]quinoline-6-carbonitrile



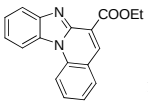
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.03 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 4.11 (s, 3H), 3.57 (s, 3H), ^{13}C NMR (DMSO, 75 MHz) δ 157.1, 146.2, 144.5, 141.0, 137.9, 132.6, 130.5, 128.2, 125.1, 123.2, 120.0, 118.5, 117.7, 116.2, 111.6, 99.0, 61.9, 57.3; ESI-MS *m/z* 304.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{18}H_{14}N_3O_2$ $(M+H)^+$ requires 304.1086, found 304.1081.

2p. 2-Chloro-benzimidazo[1,2-a]quinoline-6-carbonitrile



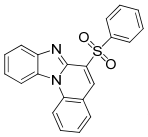
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.60 (s, 1H), 8.34 (d, *J* = 7.6 Hz, 1H), 8.17-8.15 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.66-7.60 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.7, 144.5, 139.4, 137.8, 137.0, 131.7, 130.8, 125.8, 125.6, 124.4, 121.8, 119.9, 115.8, 114.6, 113.7, 103.5; ESI-MS *m/z* 278.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{16}H_9ClN_3$ $(M+H)^+$ requires 278.0485, found 278.0481.

4a. Ethyl ester benzimidazo[1,2-a]quinoline-6-carboxylic acid



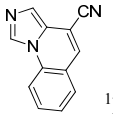
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.44 (s, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H),7.96 (d, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 8.8 Hz, 1H), 7.59-7.50 (m, 3H), 4.50 (q, *J* = 7.2 Hz, 2H), 1.53 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.9, 145.3, 145.1, 136.9, 135.4, 131.9, 131.1, 130.6, 124.7, 124.5, 123.2, 121.9, 121.7, 120.3, 115.2, 113.7, 61.8, 14.4; ESI-MS *m/z* 291.1 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{18}H_{15}N_2O_2$ $(M+H)^+$ requires 291.1134, found 291.1131.

4b. 6-(Phenylsulfonyl)-benzimidazo[1,2-a]quinoline



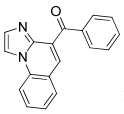
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (s, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.44-8.42 (m, 2H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 8.8 Hz, 1H), 7.58-7.48 (m, 6H) , ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.4, 142.1, 139.6, 137.1, 134.8, 133.8, 133.0, 131.9, 130.4, 129.5, 129.3, 128.7, 125.0, 124.9, 123.7, 121.8, 121.1, 115.3, 113.8; ESI-MS *m/z* 359.1 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{21}H_{15}N_2O_2S$ $(M+H)^+$ requires 359.0854, found 359.0860.

4c. 4-Carbonitrile imidazo[1,5-a]quinoline



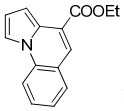
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.67 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.75-7.71 (m, 2H), 7.70 (s, 1H), 7.53-7.49 (m, 2H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.0, 131.7, 130.2, 130.1, 129.3, 126.5, 125.4, 123.6, 122.1, 115.3, 114.9, 102.3; ESI-MS *m/z* 194.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{12}H_8N_3$ $(M+H)^+$ requires 194.0718, found 194.0715.

4d. 4-Benzoyl-imidazo[1,2-a]quinoline



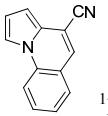
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.11 (s, 1H), 7.99-7.92 (m, 3H), 7.87 (m, 1H), 7.73-7.67 (m, 3H), 7.59 (m, 1H), 7.51-7.43 (m, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 193.2, 141.3, 136.9, 133.5, 133.2, 133.1, 130.5, 130.2, 128.4, 127.9, 127.8, 125.3, 122.2, 115.3, 111.4; ESI-MS *m/z* 273.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{18}H_{13}N_2O$ $(M+H)^+$ requires 273.1028, found 273.1029.

4e. Ethyl ester pyrrolo[1,2-a]quinoline-4-carboxylic acid

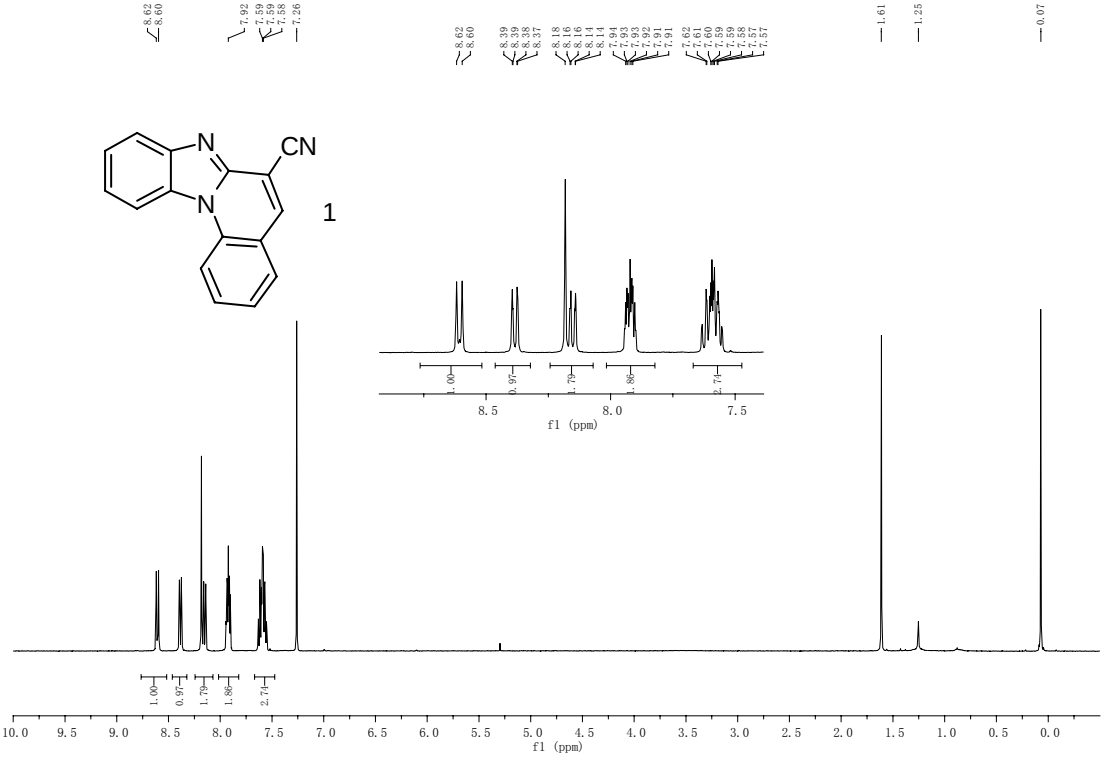


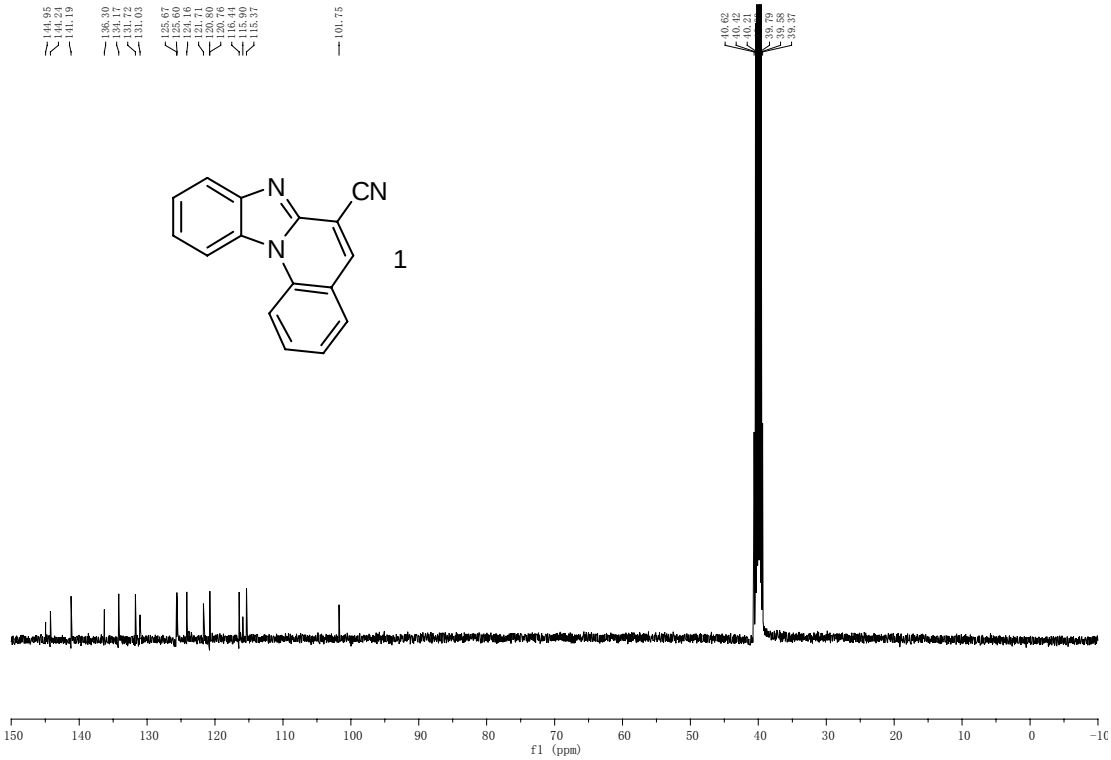
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91-7.88 (m, 3H), 7.77-7.74 (m, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.25-7.24 (m, 1H), 6.88-6.86 (m, 1H), 4.50 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.5, 134.7, 130.3, 128.0, 125.2, 123.8, 122.3, 121.2, 114.3, 113.5, 112.5, 105.2, 61.1, 14.4; ESI-MS *m/z* 240.1 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{15}H_{14}NO_2$ $(M+H)^+$ requires 240.1025, found 240.1025.

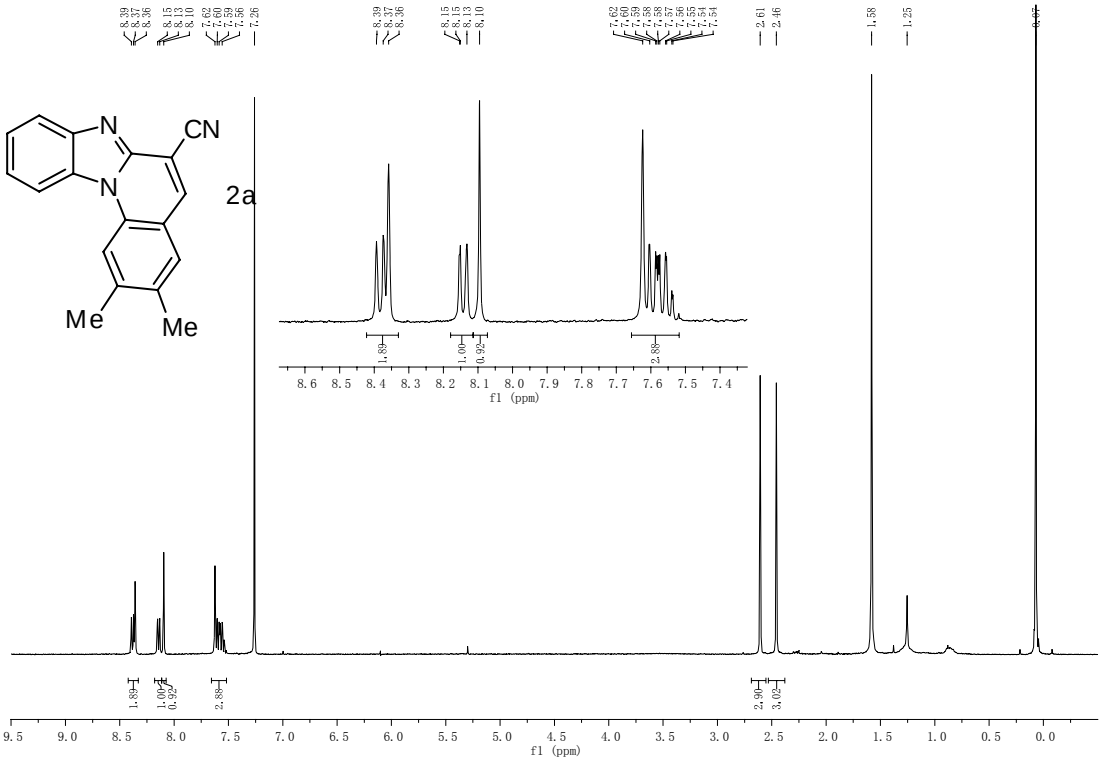
4f. Pyrrolo[1,2-a]quinoline-4-carbonitrile

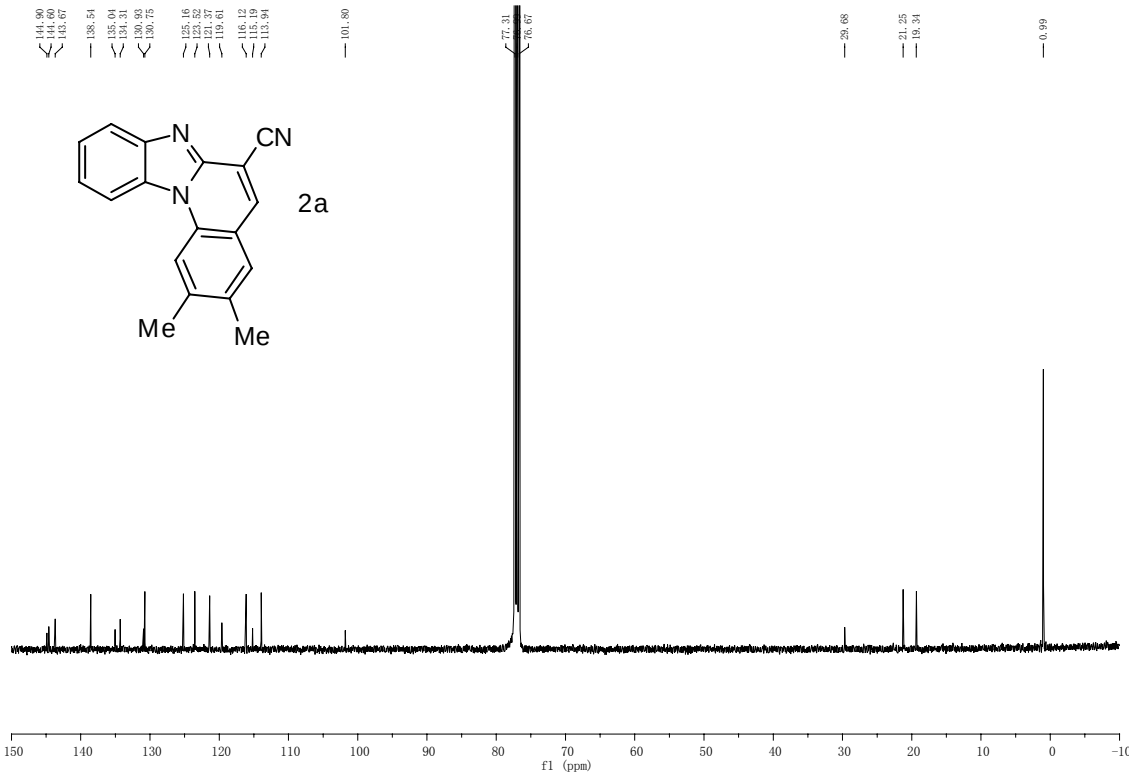


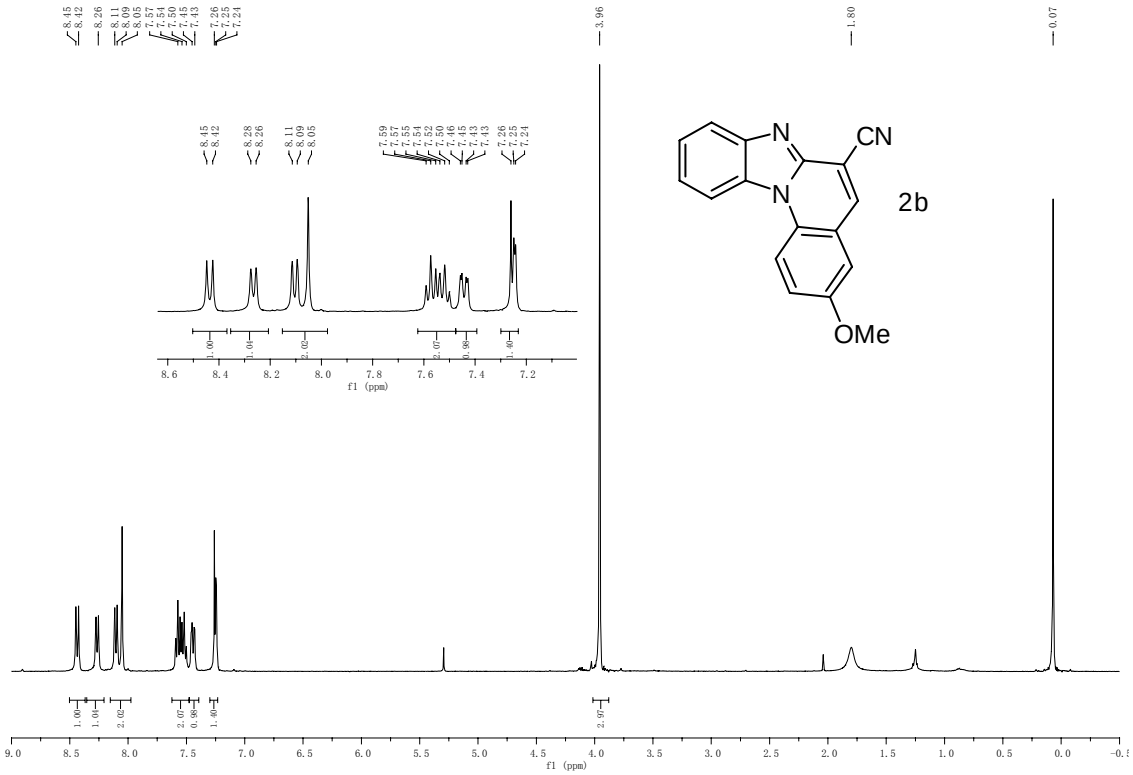
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91-7.88 (m, 2H), 7.71-7.63 (m, 2H), 7.49 (s, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 6.90-6.88 (m, 1H), 6.84-6.82 (m, 1H), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.1, 131.1, 129.8, 127.5, 127.3, 124.4, 121.7, 116.5, 114.5, 113.8, 113.7, 103.8, 103.7; ESI-MS *m/z* 193.0 $(M+H)^+$; HR-MS (ESI) calcd. for $C_{13}H_9N_2$ requires 193.0766, found 193.0764.

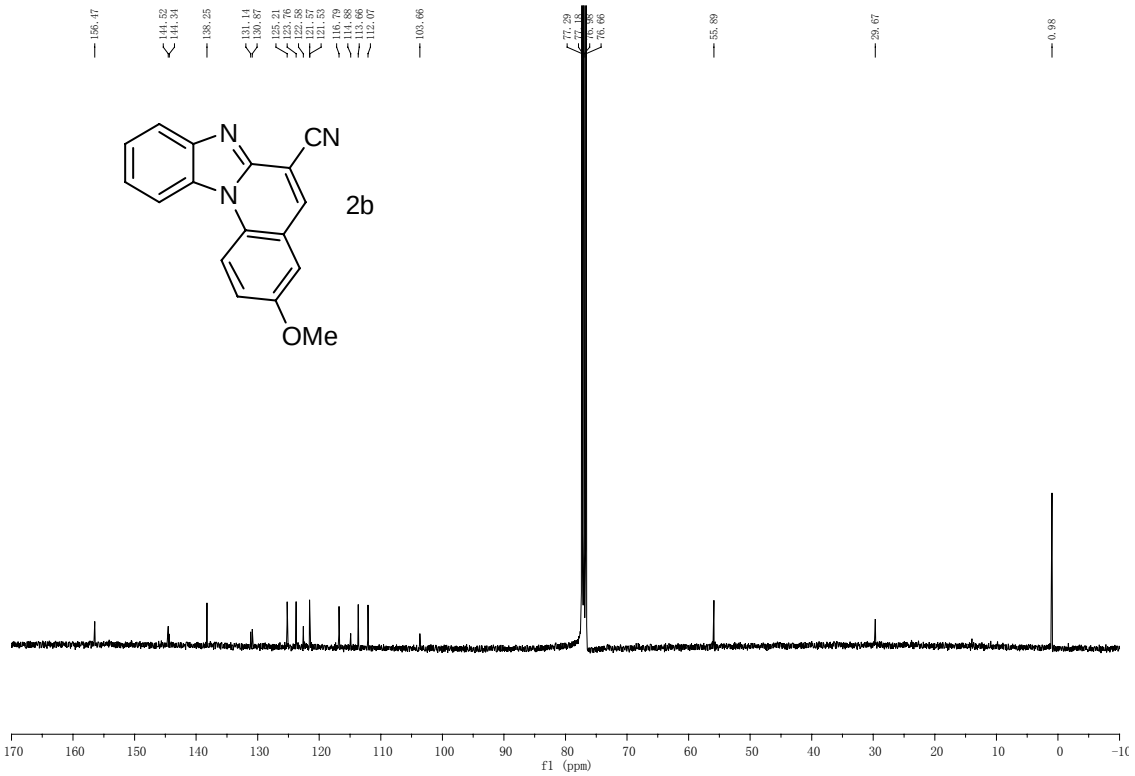


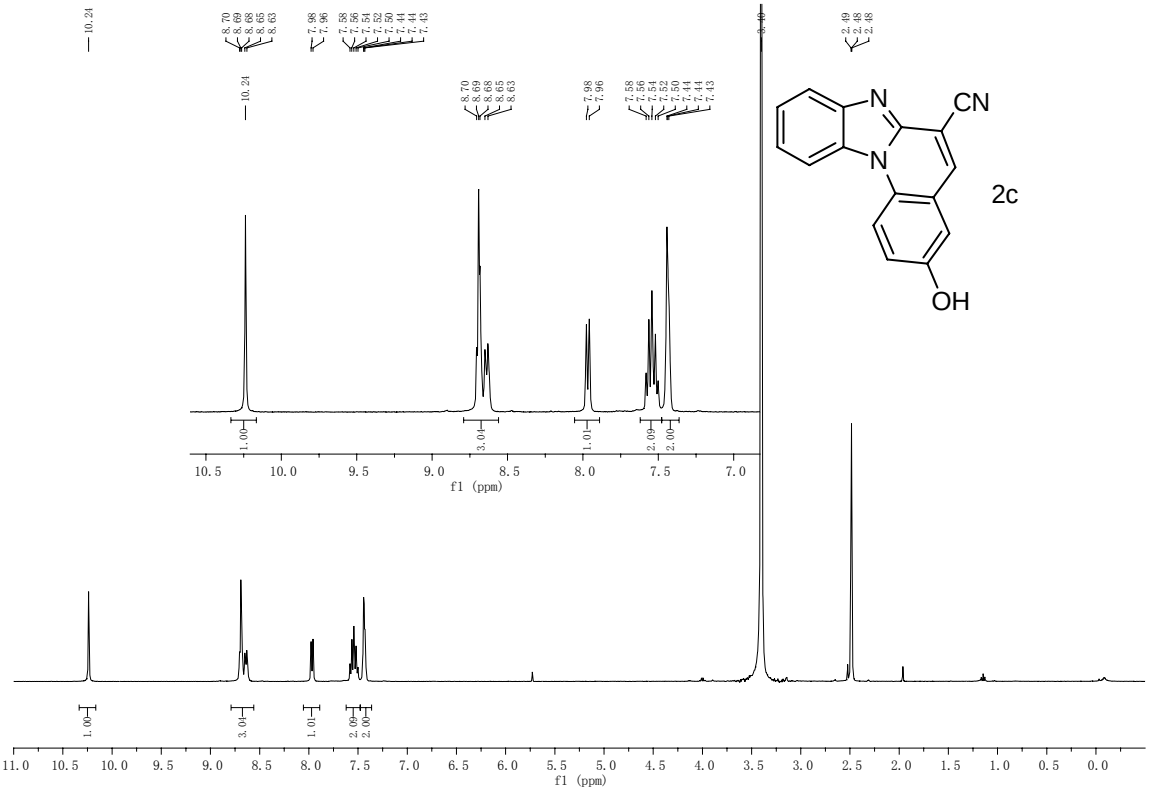

144.95
144.24
141.19
136.30
134.17
131.72
131.03
125.67
125.60
124.16
121.71
120.60
120.16
116.44
115.90
115.37
101.75
40.62
40.42
40.21
39.79
39.58
39.37
N
N
CN
1
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

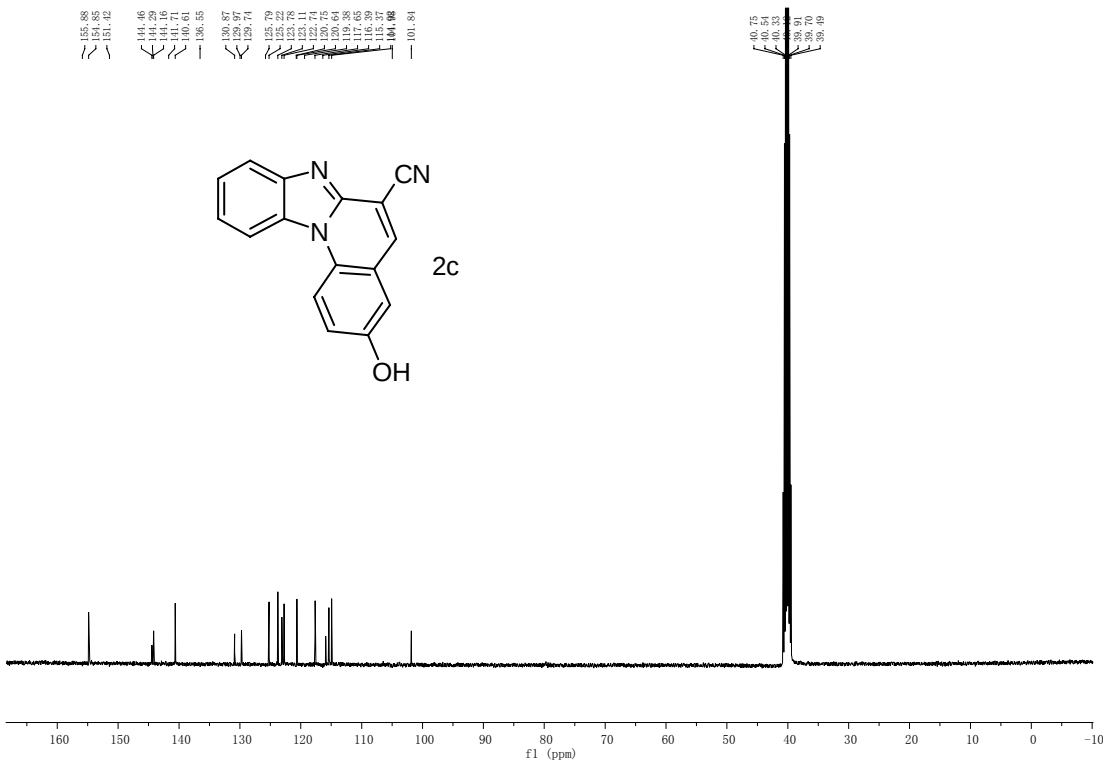

8.39
8.37
8.36
8.15
8.13
8.10
7.62
7.60
7.59
7.56
7.26
2.61
2.46
1.58
1.25
0.00
N
N
CN
Me
Me
2a
1.89
1.00
0.92
2.88
2.90
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

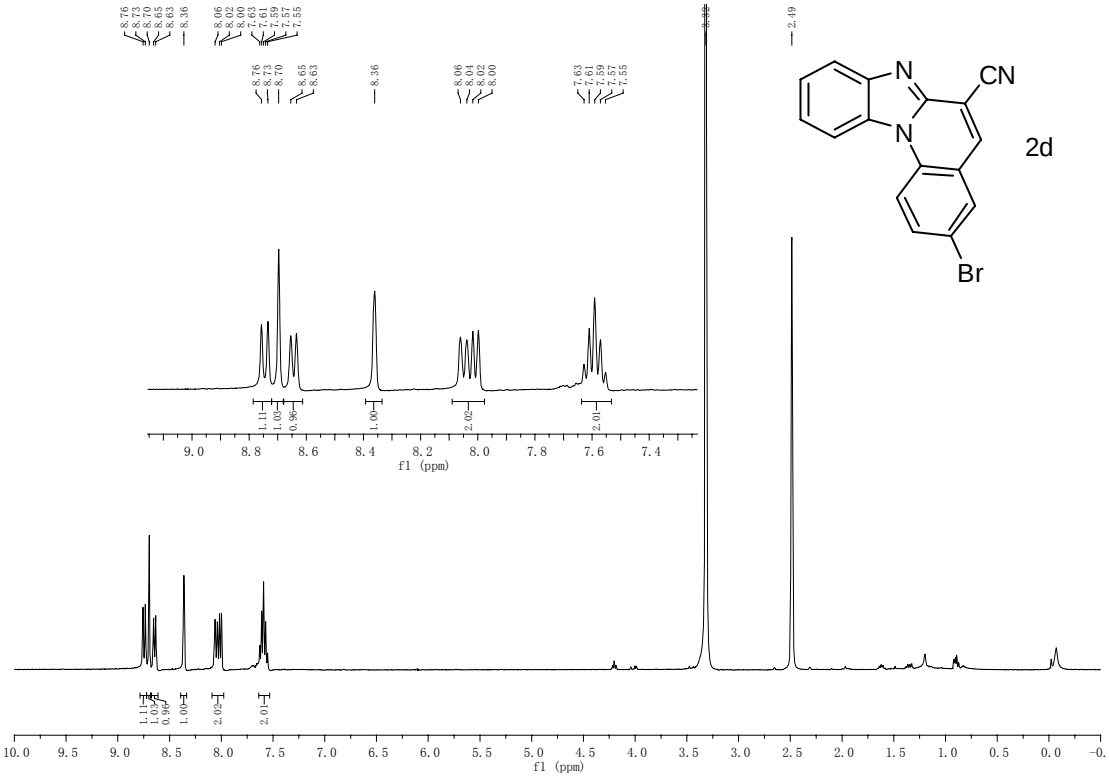

144.90
144.60
143.67
138.54
135.04
134.31
130.93
130.75
125.16
123.52
121.37
119.61
116.12
115.19
113.94
101.80
77.31
76.67
29.68
21.25
19.34
0.99
N
CN
N
2a
Me
Me
f1 (ppm)

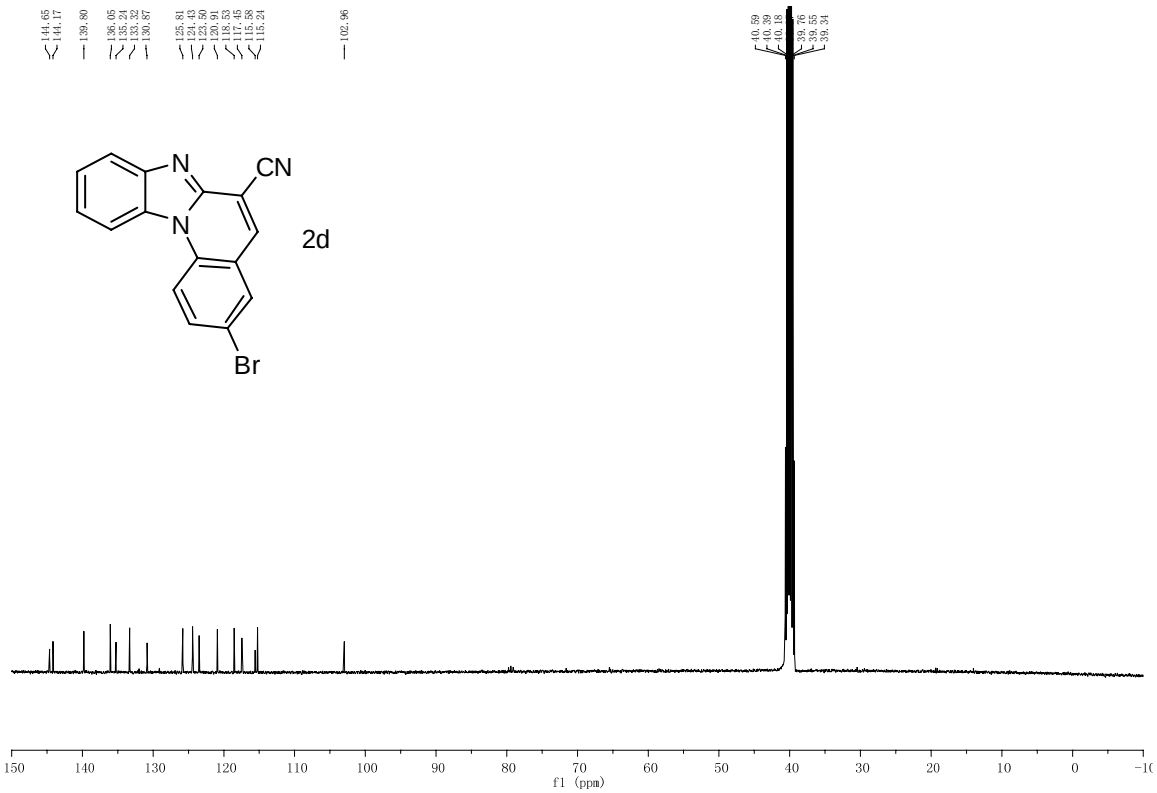

8.45
8.42
8.26
8.11
8.09
8.05
7.54
7.57
7.50
7.45
7.43
7.26
7.25
7.24
3.96
1.80
0.07
N
CN
N
2b
OMe
f1 (ppm)

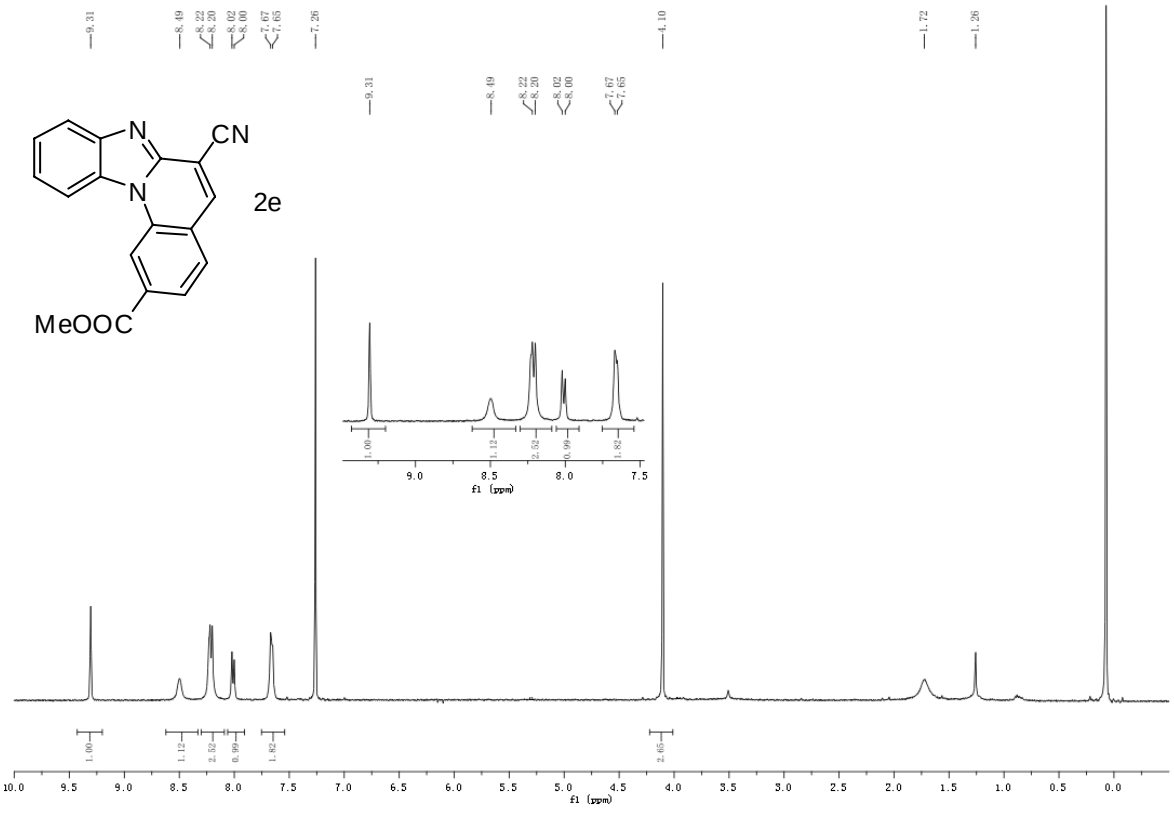

156.47
144.52
144.34
138.25
131.14
130.87
125.21
123.76
122.58
121.57
121.53
116.79
114.88
113.66
112.07
103.66
77.29
77.18
76.98
76.66
55.89
29.67
0.98
N
CN
N
2b
OMe
f1 (ppm)

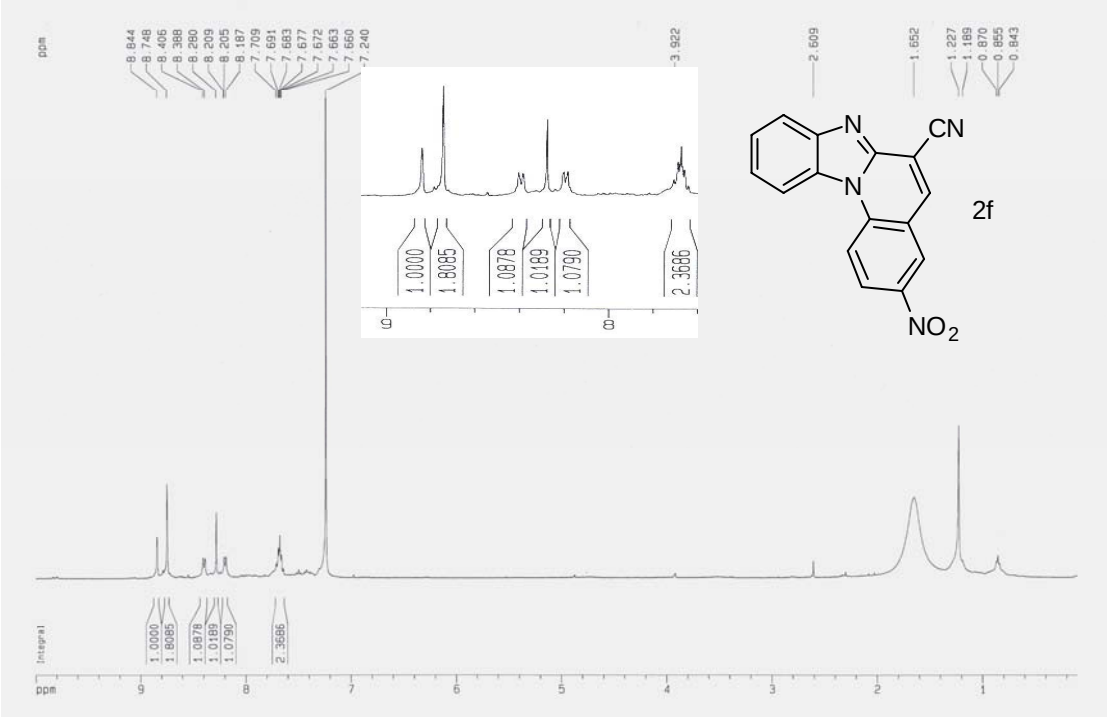

10.24
8.70
8.69
8.68
8.65
8.63
7.98
7.96
7.58
7.56
7.54
7.52
7.50
7.44
7.43
3.49
2.49
2.48
2.48
N
CN
N
2c
OH
1.00
3.04
1.01
2.09
2.00
f1 (ppm)


N
CN
N
OH
2c
f1 (ppm)

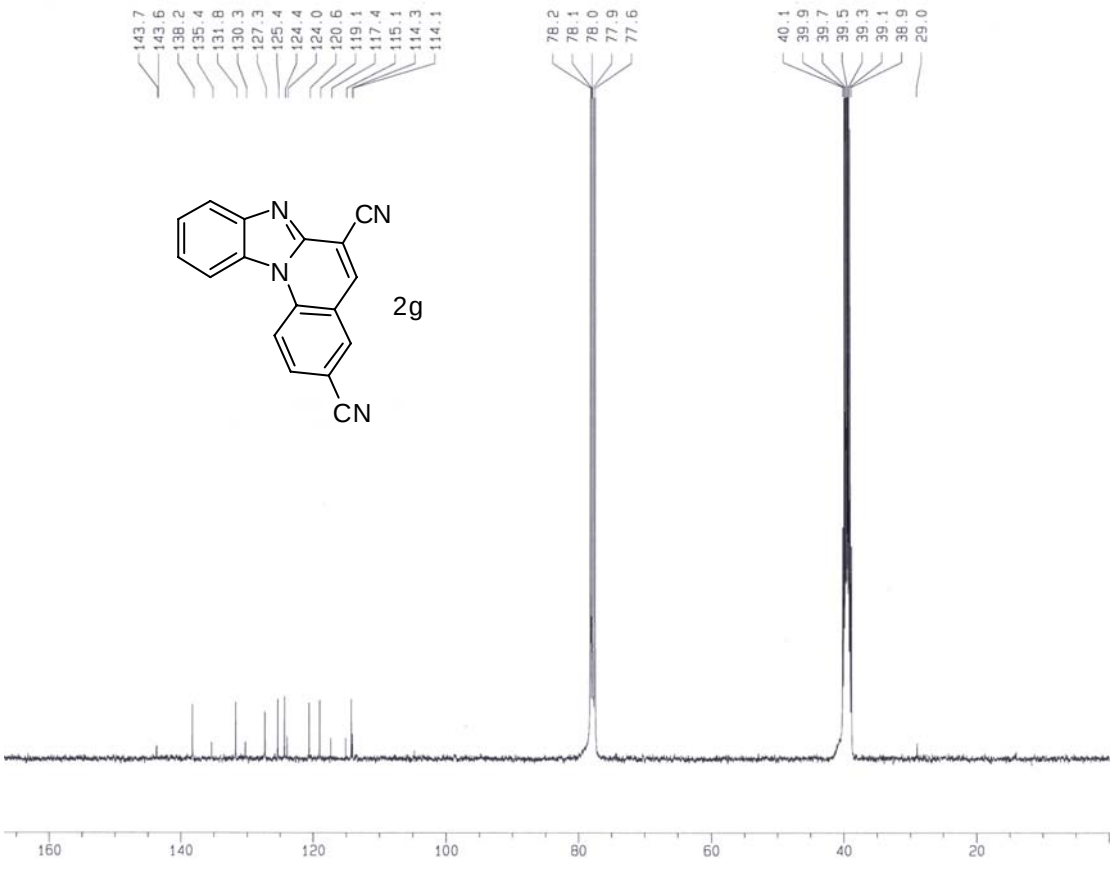

N
CN
N
Br
2d
f1 (ppm)

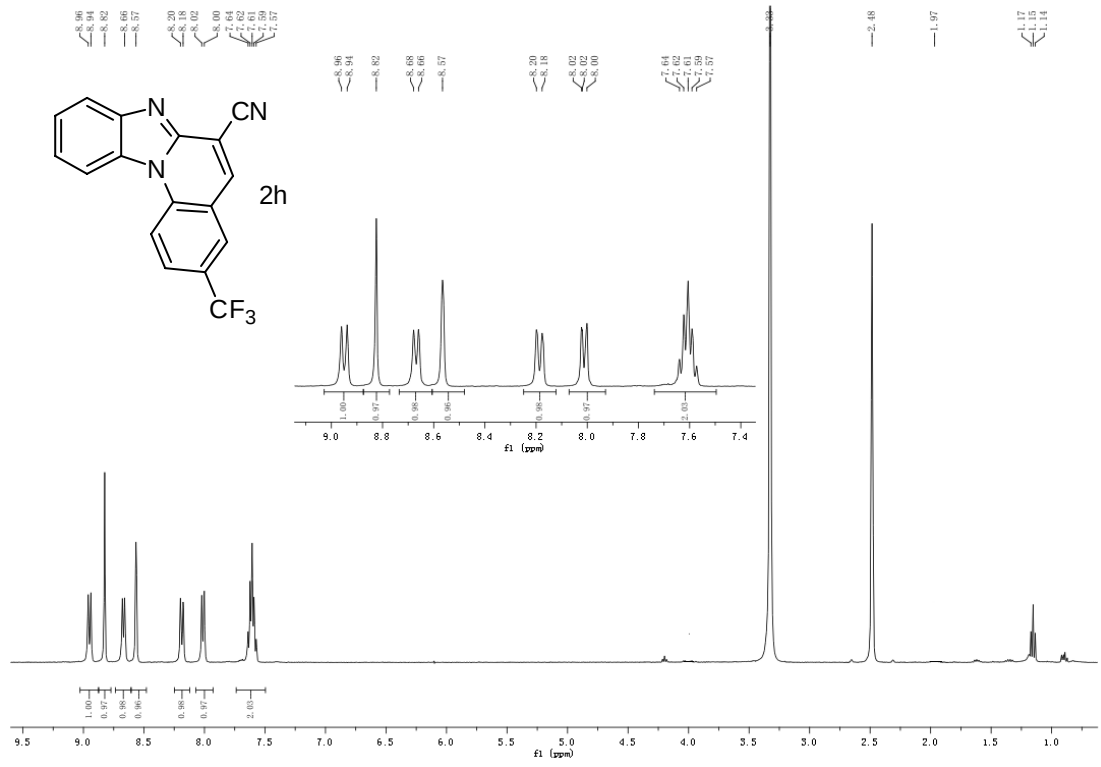

144.65
144.17
139.80
136.05
135.24
133.32
130.87
125.81
124.43
123.50
120.91
118.53
117.45
115.58
115.24
102.96
40.59
40.39
40.18
39.76
39.55
39.34
N
N
CN
Br
2d
f1 (ppm)

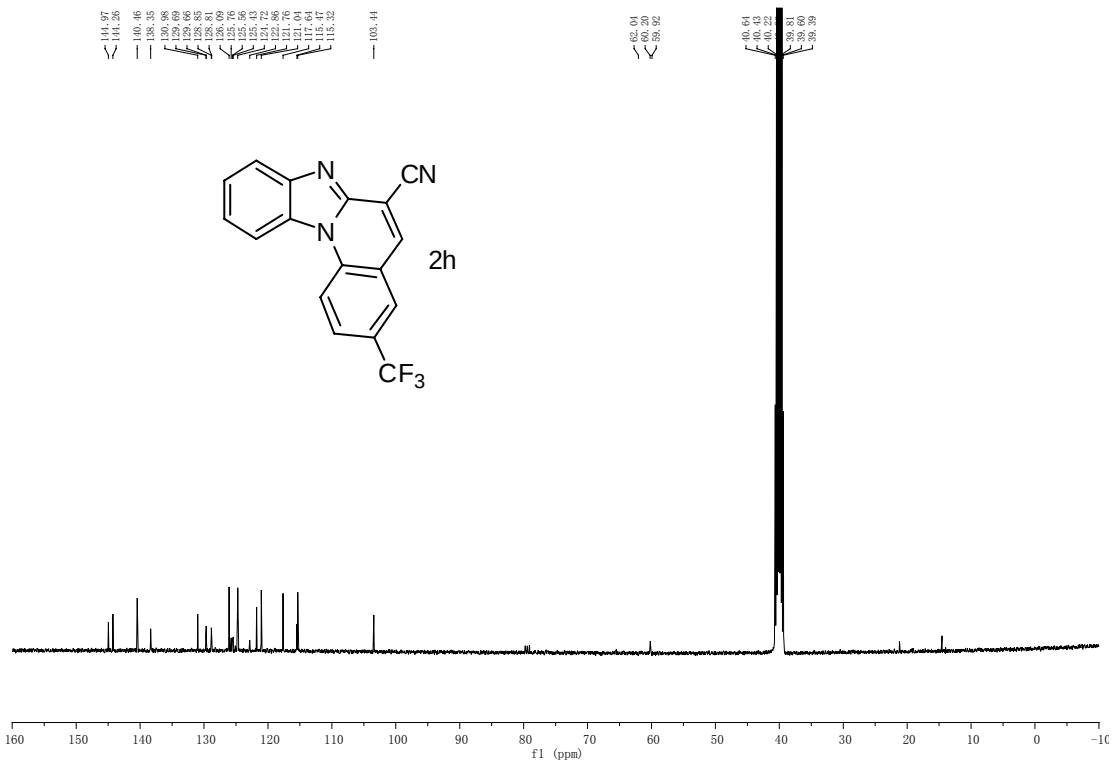

9.31
8.49
8.22
8.20
8.02
8.00
7.67
7.65
7.26
4.10
1.72
1.26
N
N
CN
MeOOC
2e
1.00
1.12
2.52
0.99
1.82
2.65
f1 (ppm)

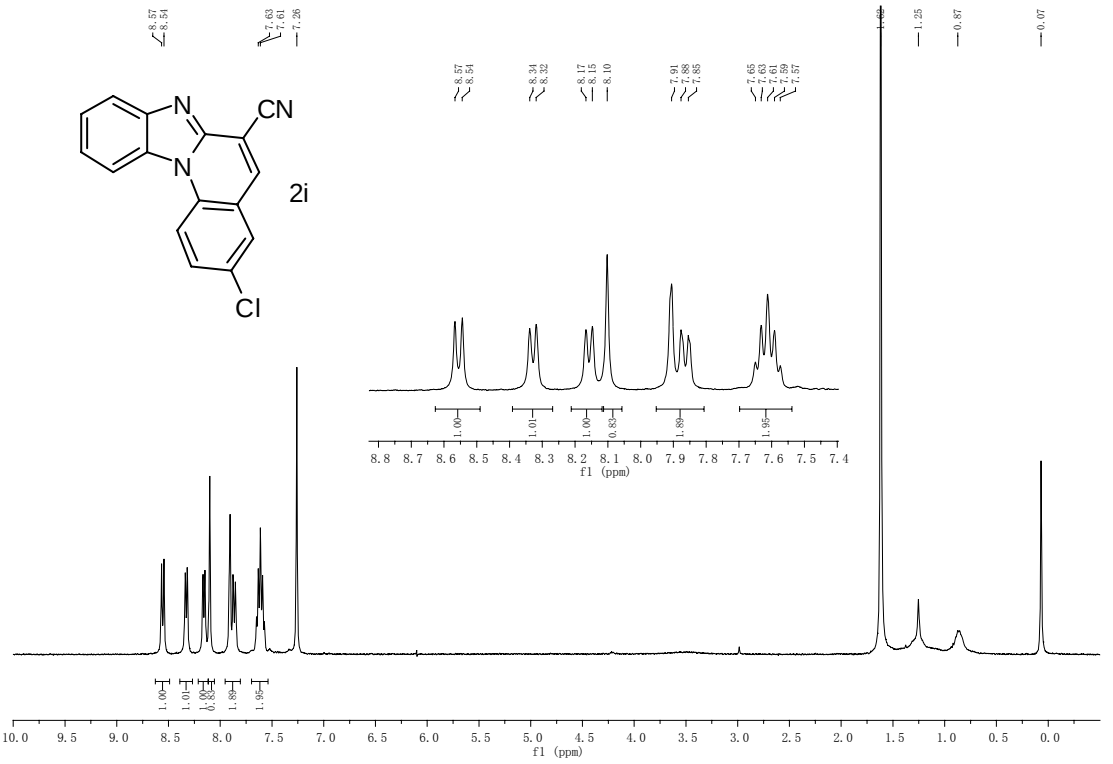

8.844
8.748
8.406
8.388
8.280
8.209
8.205
8.187
7.709
7.691
7.683
7.677
7.672
7.663
7.660
7.240
3.922
2.609
1.652
1.227
1.189
0.870
0.855
0.843
1.0000
1.8085
1.0878
1.0189
1.0790
2.3686
N
CN
N
NO2
2f
Integral
ppm

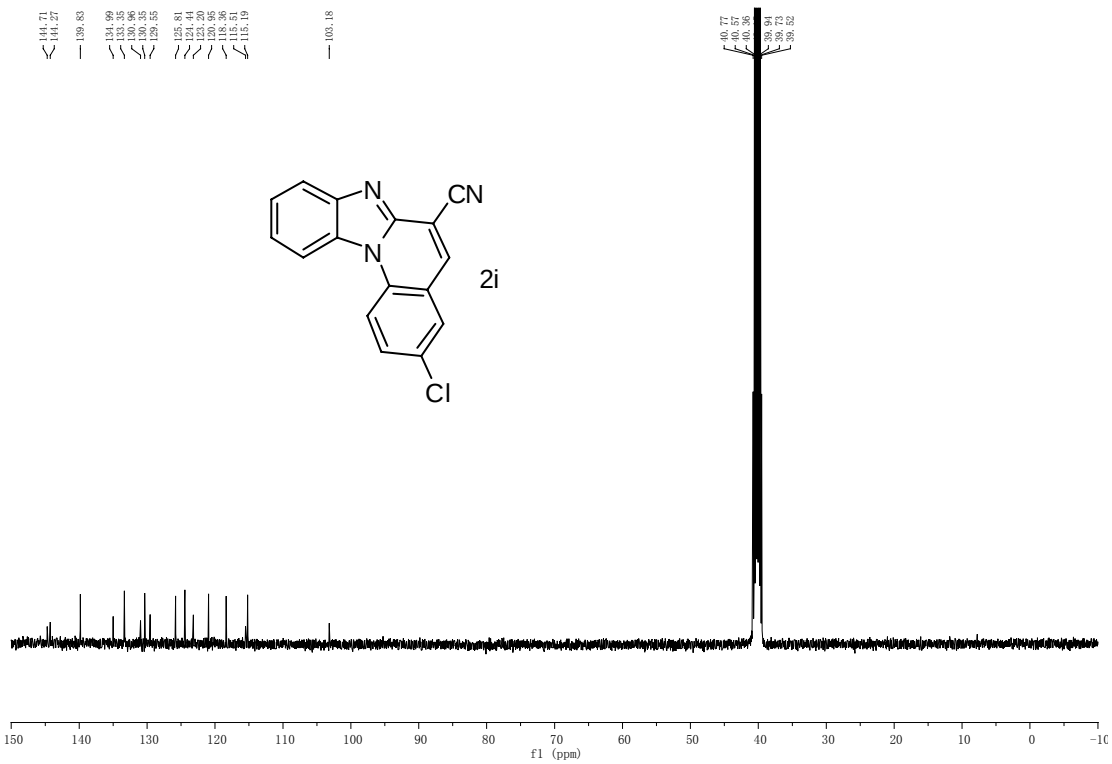

8.862
8.369
8.361
8.354
8.346
8.206
8.193
8.059
8.039
7.825
7.805
7.690
7.682
7.674
7.667
1.545
1.229
1.0138
1.0105
2.0213
1.0000
1.0137
2.0026
N
CN
N
CN
2g
Integral
ppm

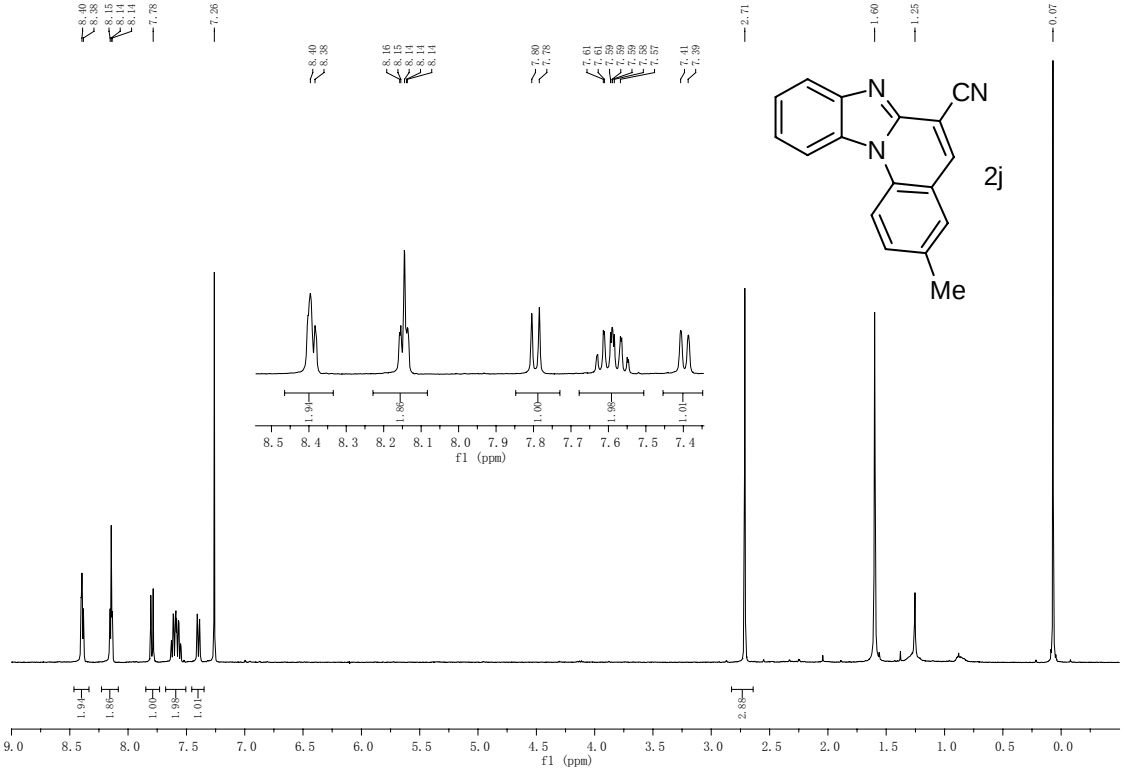

143.7
143.6
138.2
135.4
131.8
130.3
127.3
125.4
124.4
124.0
120.6
119.1
117.4
115.1
114.3
114.1
78.2
78.1
78.0
77.9
77.6
40.1
39.9
39.7
39.5
39.3
39.1
38.9
29.0
N
N
CN
CN
2g
160
140
120
100
80
60
40
20

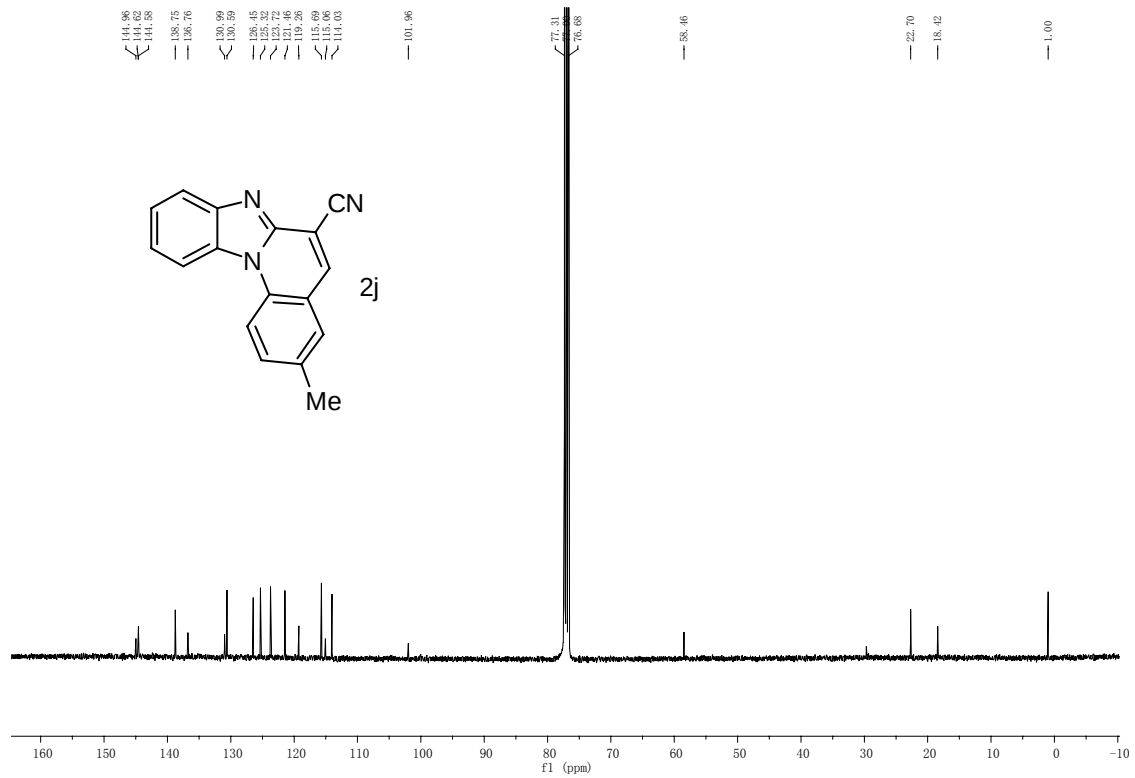

8.96
8.94
8.82
8.66
8.57
8.20
8.18
8.02
8.00
7.64
7.62
7.61
7.59
7.57
2.48
1.97
1.17
1.15
1.14
N
N
CN
CF3
2h
f1 (ppm)

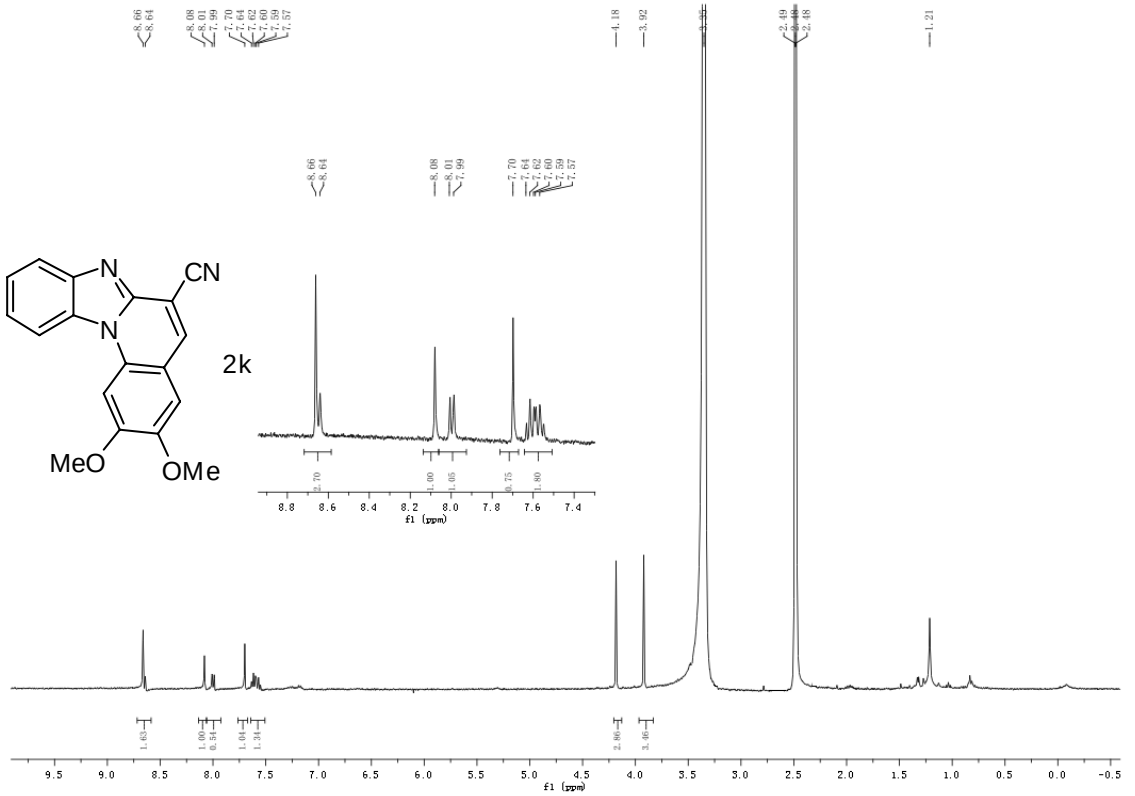

144.97
141.26
140.46
138.35
130.98
129.69
129.66
128.85
128.61
126.09
125.76
125.56
125.43
124.72
122.86
121.76
121.04
117.64
115.47
115.32
103.44
62.04
60.20
59.92
40.64
40.43
40.22
39.81
39.60
39.39
N
N
CN
2h
CF3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

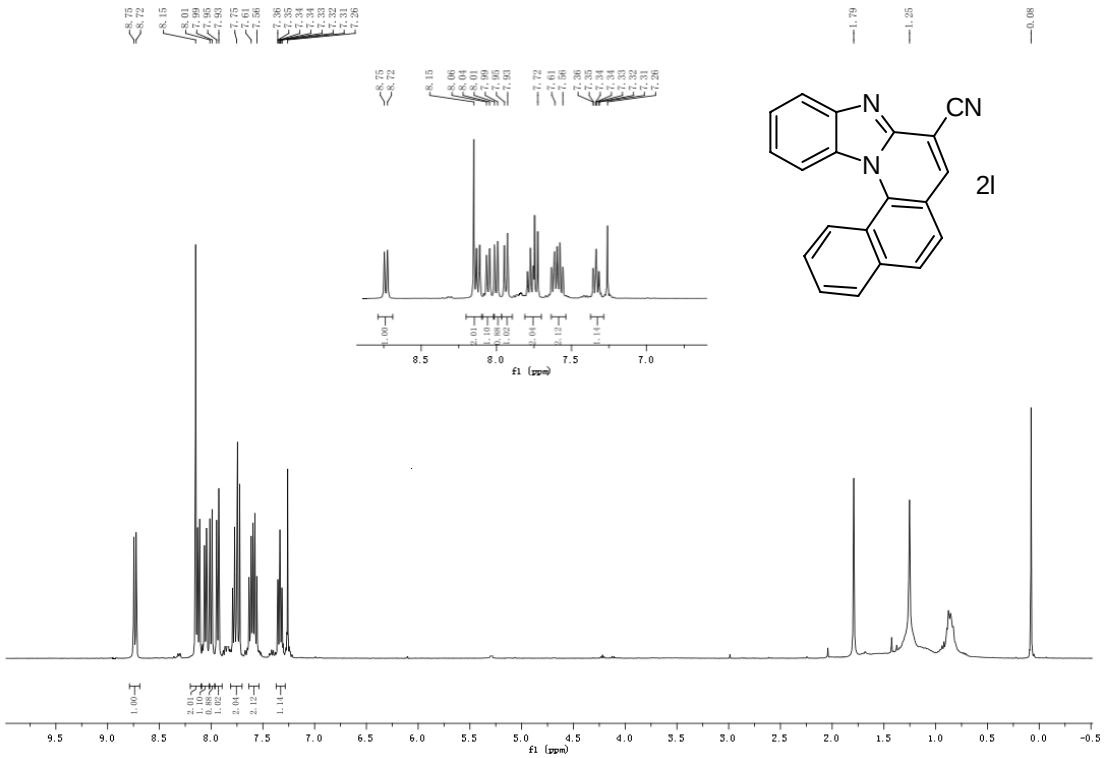

8.57
8.54
7.63
7.61
7.26
1.62
1.25
0.87
0.07
N
N
CN
2i
Cl
8.57
8.54
8.34
8.32
8.17
8.15
8.10
7.91
7.88
7.85
7.65
7.63
7.61
7.59
7.57
1.00
1.01
1.00
0.83
1.89
1.95
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

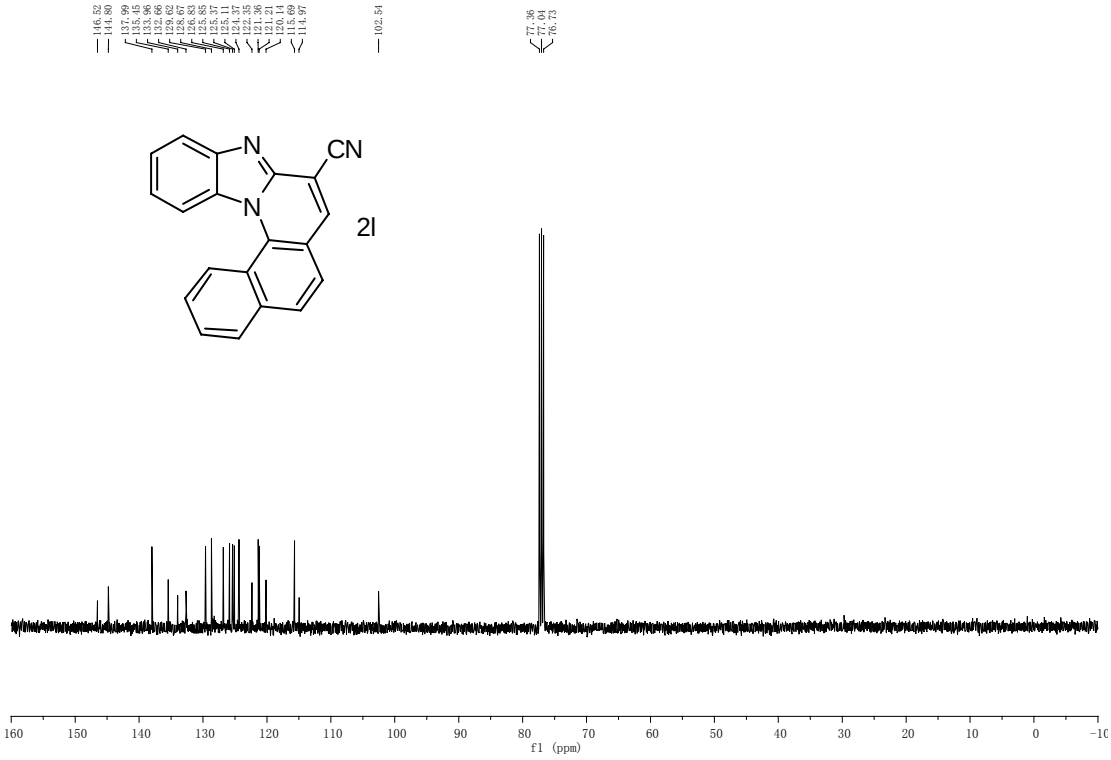

144.71
144.27
139.83
134.99
133.35
130.96
130.35
129.55
125.81
124.44
123.20
120.95
118.96
115.51
115.19
103.18
40.77
40.57
40.36
39.94
39.73
39.52
N
CN
N
2i
Cl
f1 (ppm)

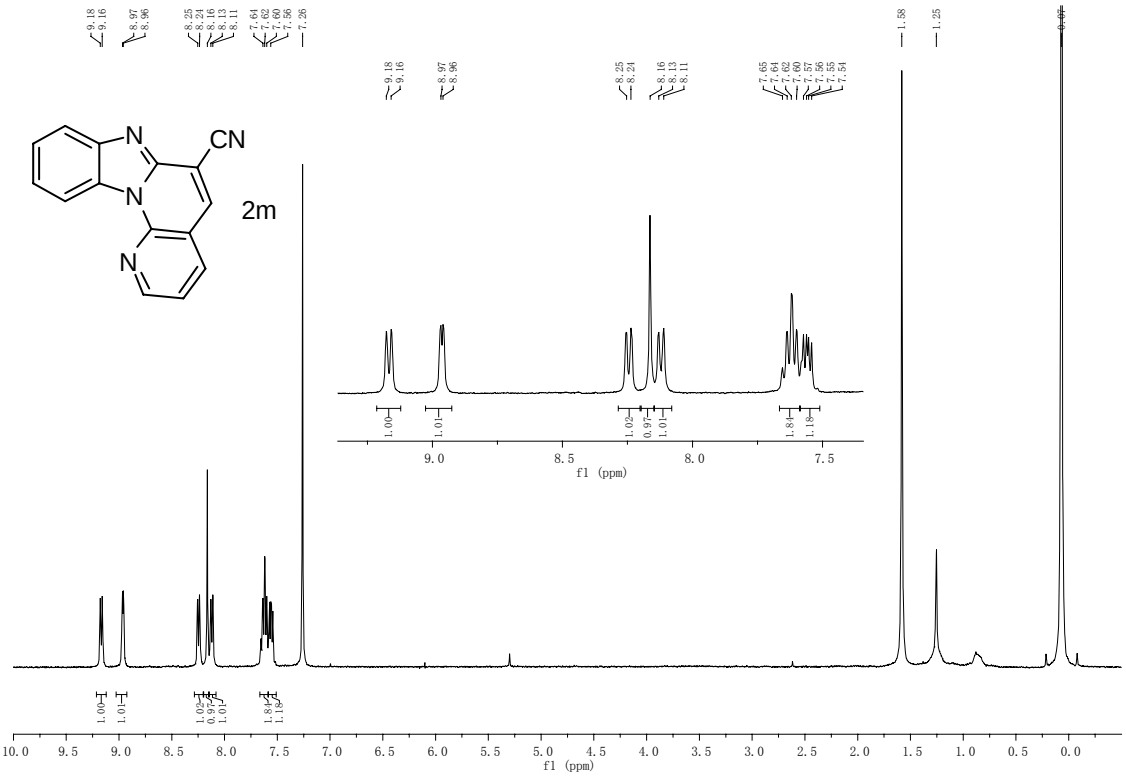

8.40
8.38
8.15
8.14
8.14
7.78
7.26
2.71
1.60
1.25
0.07
7.80
7.78
7.61
7.61
7.59
7.59
7.59
7.58
7.57
7.41
7.39
8.16
8.15
8.14
8.14
8.14
N
CN
N
2j
Me
1.91
1.88
1.00
1.98
1.01
f1 (ppm)
1.94
1.86
1.04
1.98
1.01
2.88
f1 (ppm)

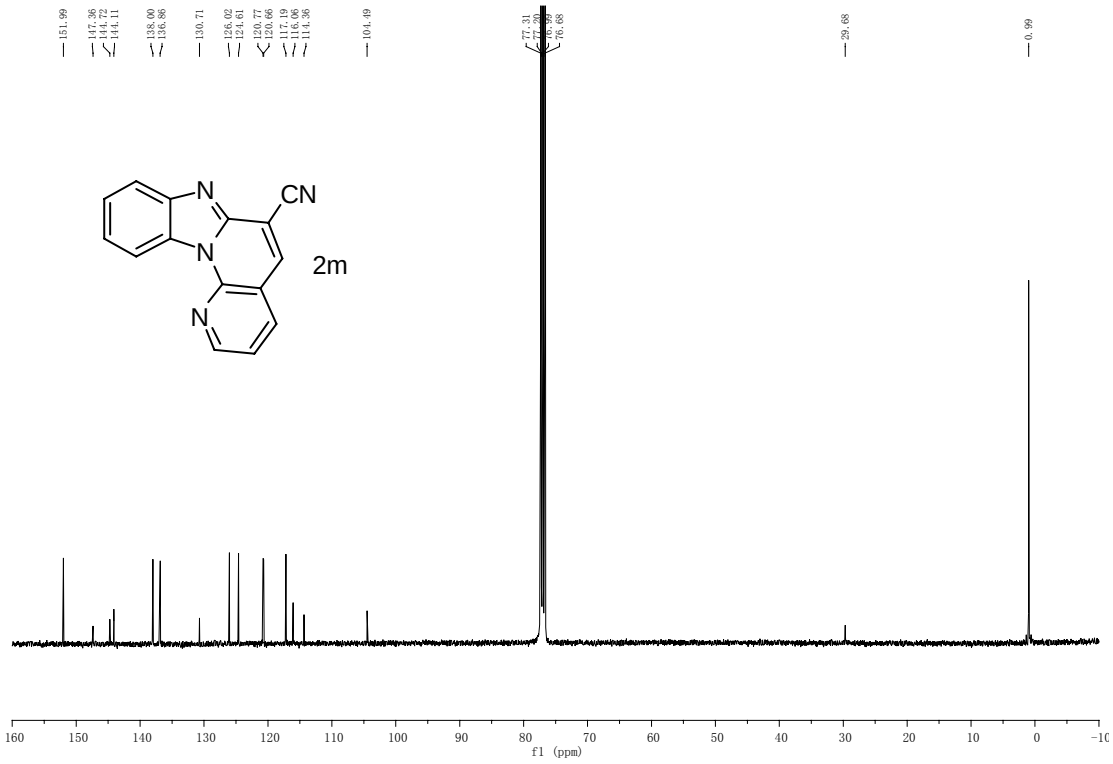

144.96
144.62
144.58
138.75
136.76
130.99
130.59
126.45
125.32
123.72
121.46
119.26
115.69
115.06
114.03
101.96
77.31
76.68
58.46
22.70
18.42
1.00
N
CN
N
2j
Me
f1 (ppm)

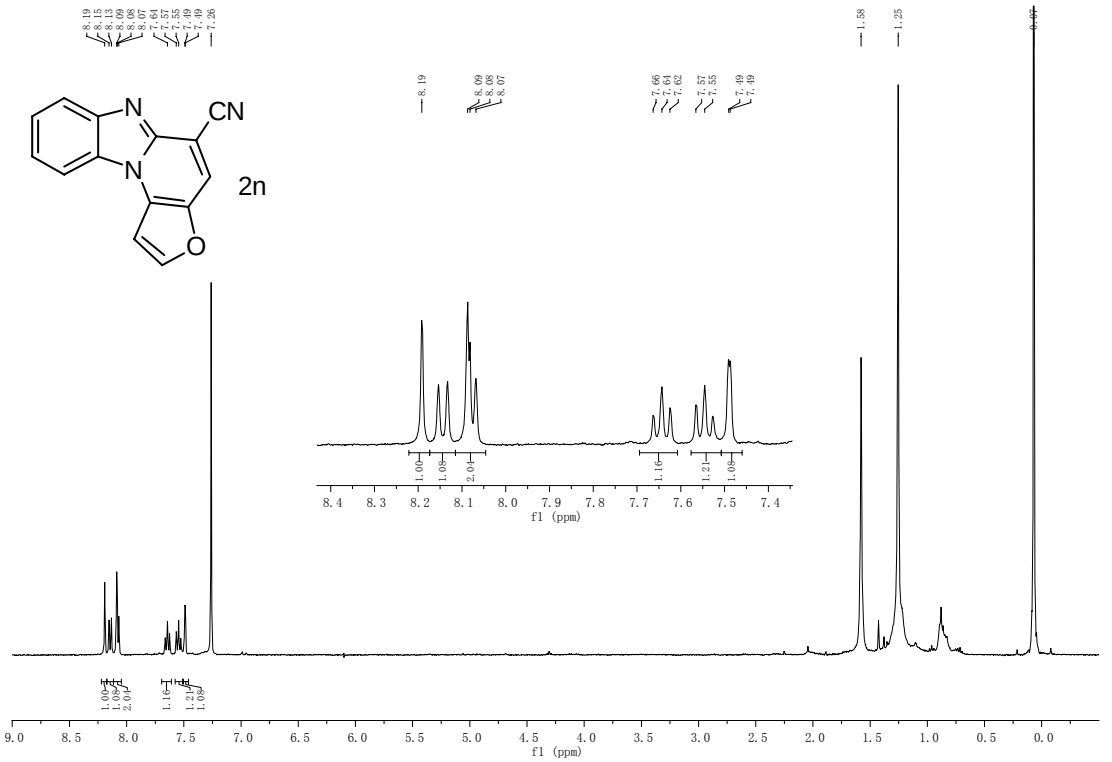

8.66
8.64
8.08
8.01
7.99
7.70
7.64
7.62
7.60
7.59
7.57
4.18
3.92
2.49
2.48
1.21
N
CN
N
2k
MeO
OMe
f1 (ppm)

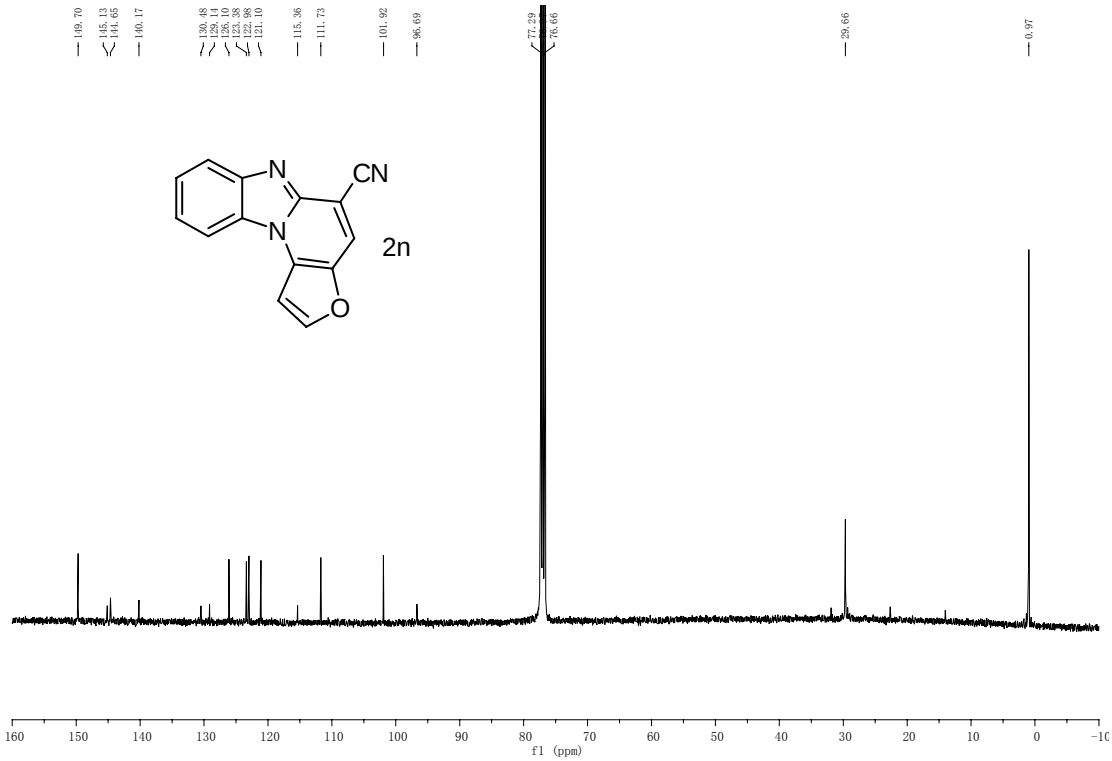

N
CN
N
2l
f1 (ppm)

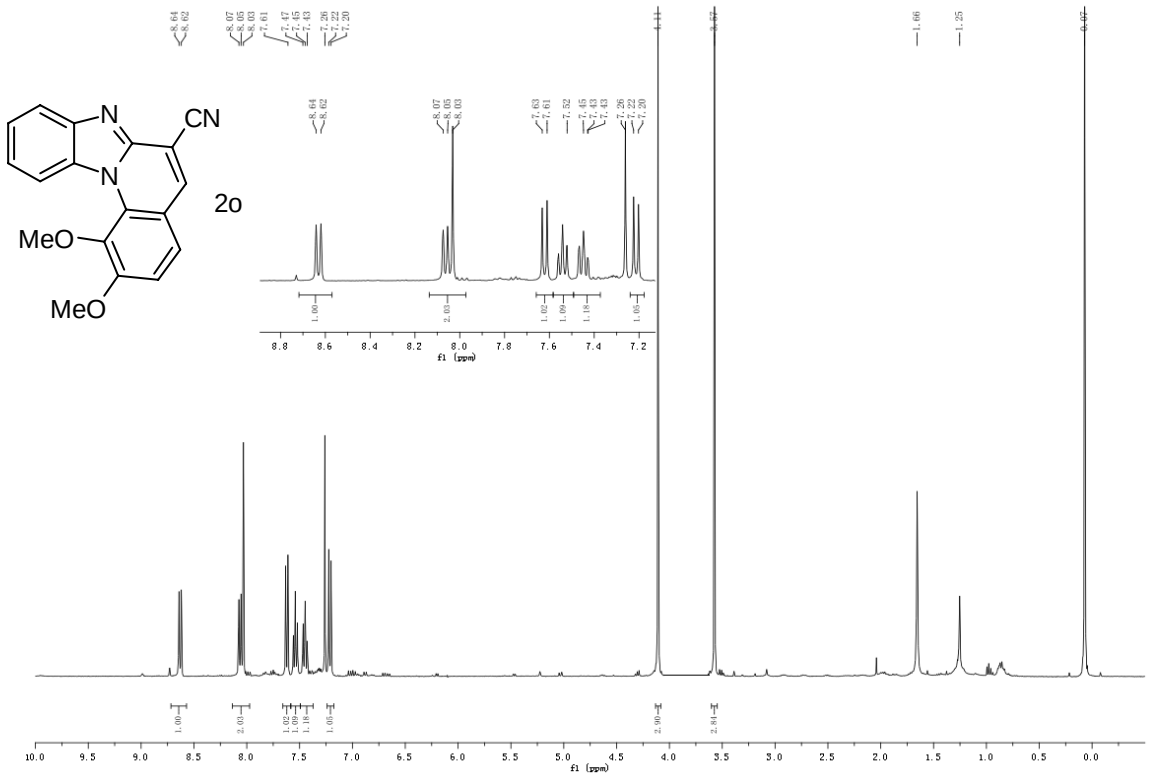

N
CN
N
2l
f1 (ppm)

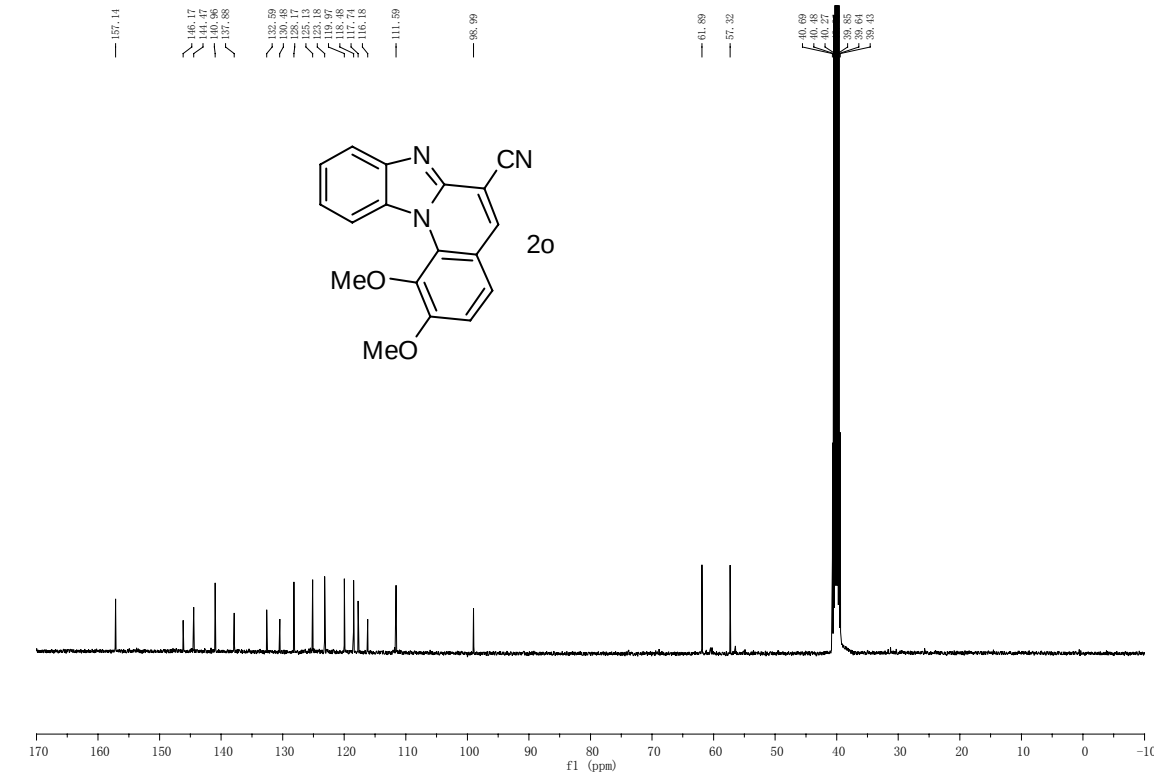

9.18
9.16
8.97
8.96
8.25
8.24
8.16
8.13
8.11
7.64
7.62
7.60
7.56
7.26
1.58
1.25
0.00
N
CN
N
N
2m
1.00
1.01
1.02
0.97
1.01
1.84
1.18
9.0
8.5
8.0
7.5
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

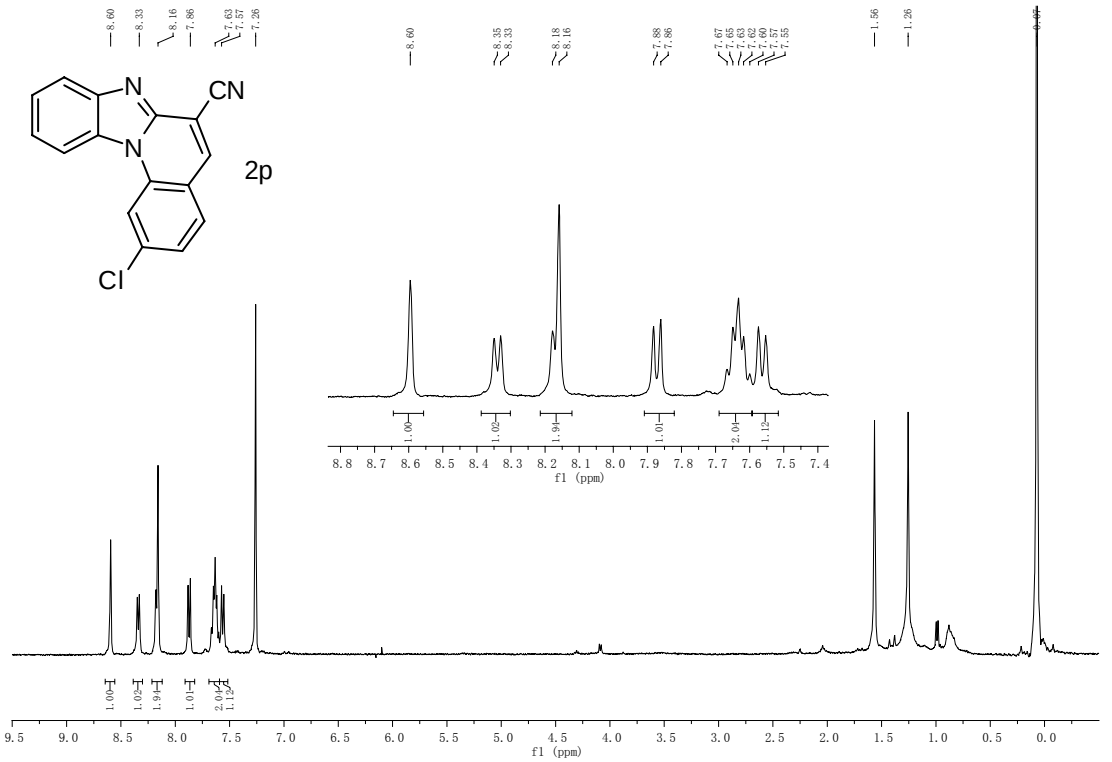

151.99
147.36
144.72
144.11
138.00
136.86
130.71
126.02
124.61
120.77
120.66
117.19
116.66
114.96
104.49
77.31
77.00
76.68
29.68
0.99
N
CN
N
N
2m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

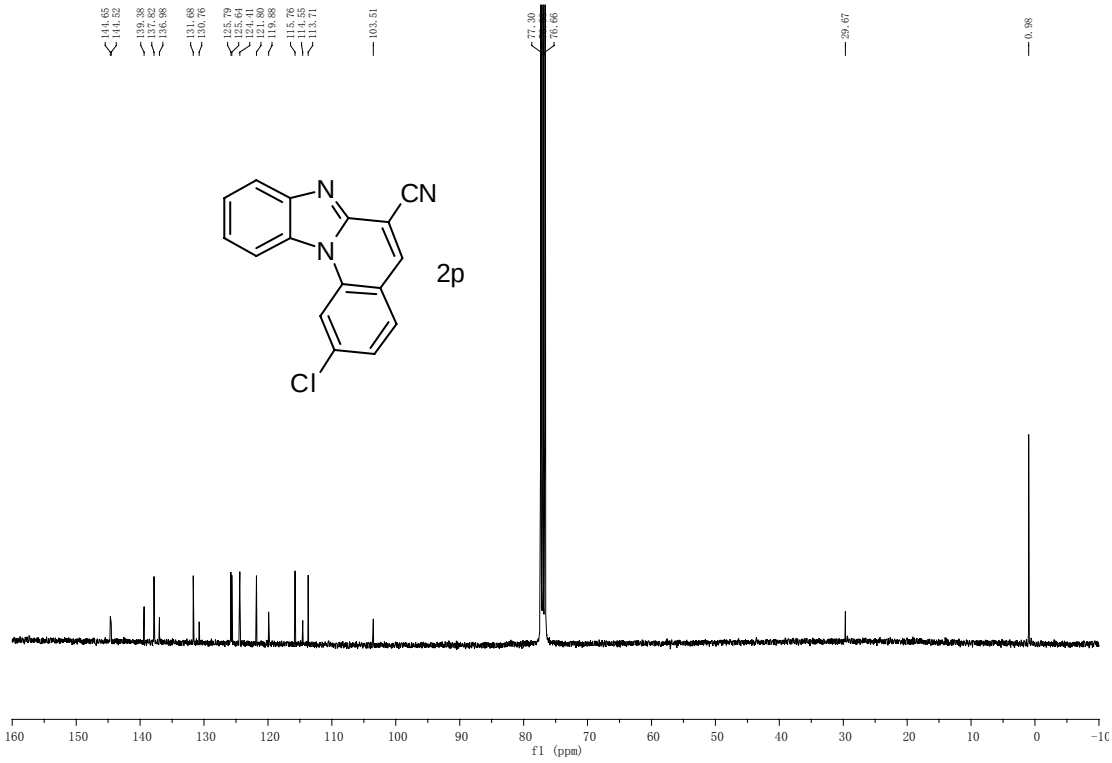

8.19
8.15
8.13
8.09
8.08
8.07
7.64
7.57
7.55
7.49
7.49
7.26
1.58
1.25
0.00
N
CN
N
O
2n
f1 (ppm)

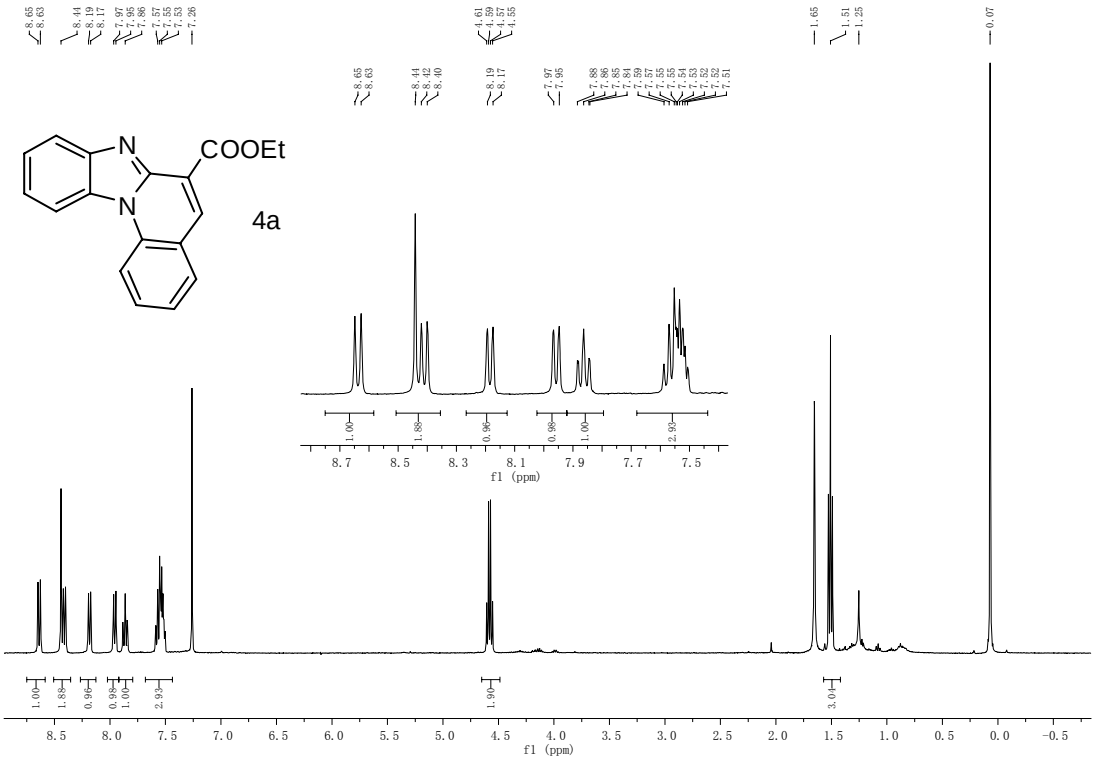

149.70
145.13
144.65
140.17
130.48
129.14
126.10
123.38
122.98
121.10
115.36
111.73
101.92
96.69
77.29
76.66
29.66
0.97
N
CN
N
O
2n
f1 (ppm)

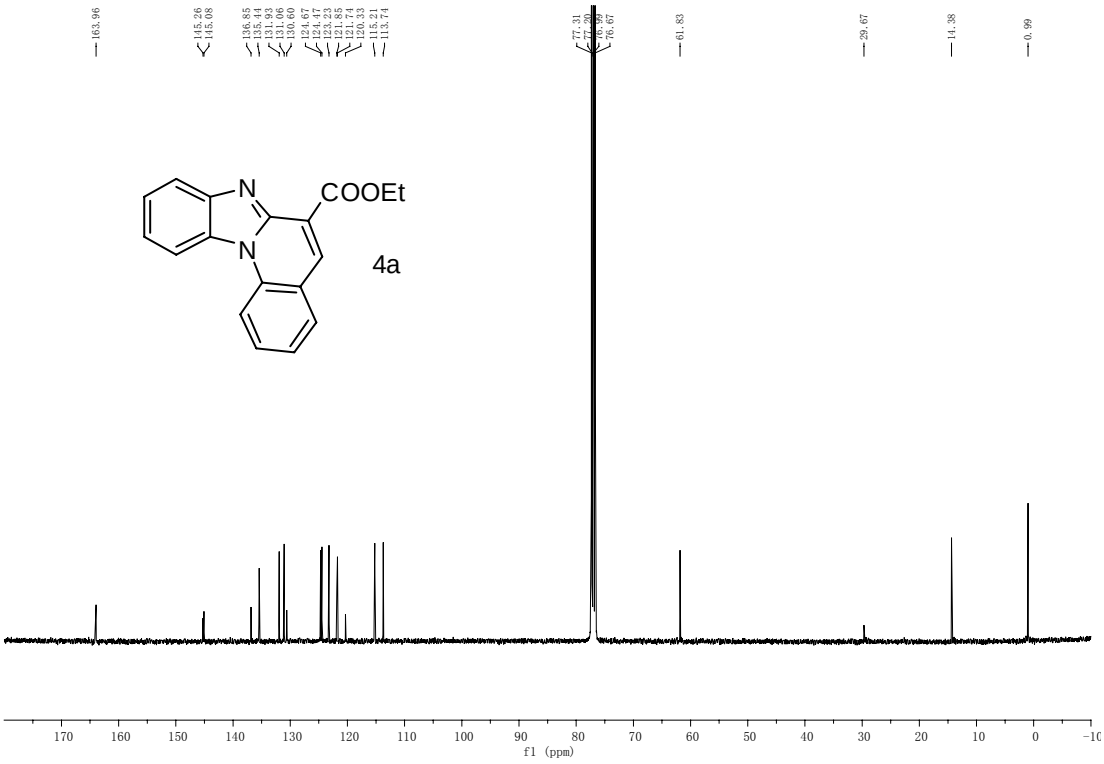

N
CN
N
2o
MeO
MeO
f1 (ppm)

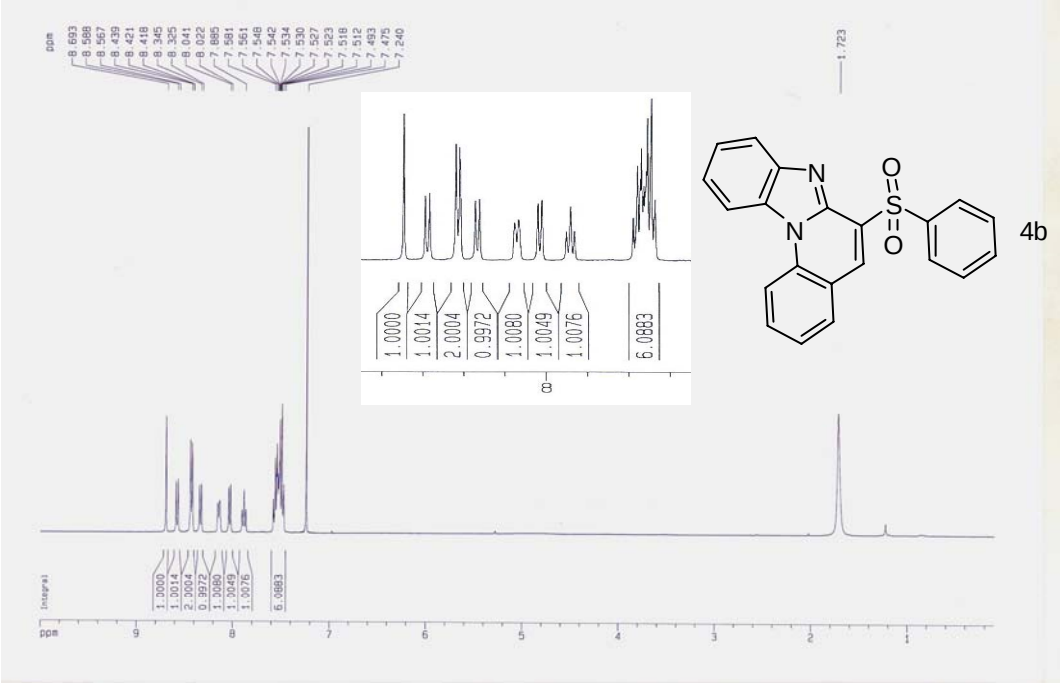

N
CN
N
2o
MeO
MeO
f1 (ppm)

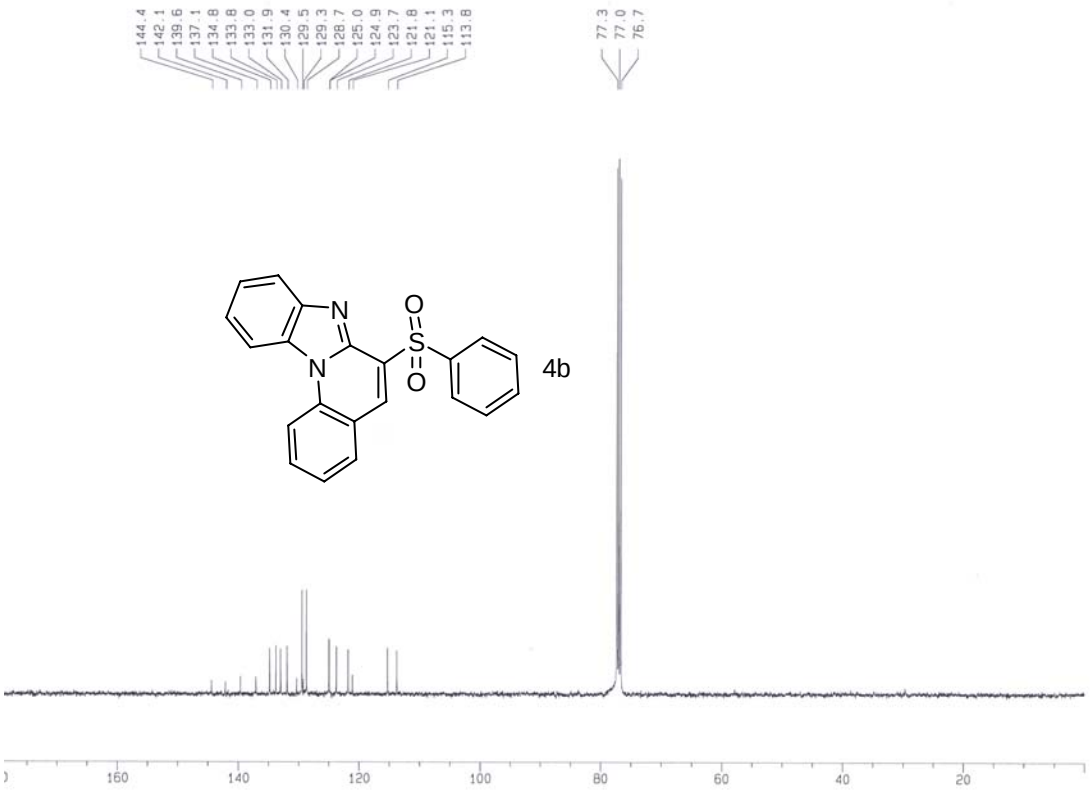

8.60
8.33
8.16
7.86
7.63
7.57
7.26
1.56
1.26
0.00
N
N
CN
Cl
2p
1.00
1.02
1.94
1.01
2.04
1.12
f1 (ppm)

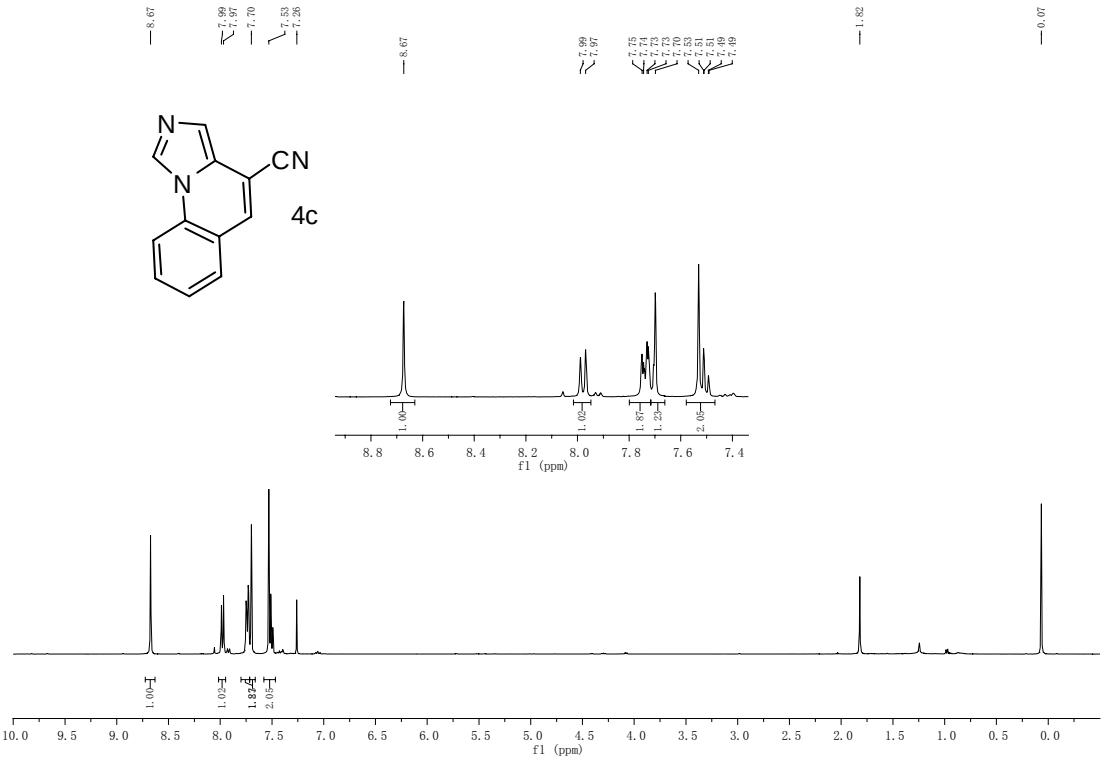

144.65
144.52
139.38
137.82
136.98
131.68
130.76
125.79
125.64
124.41
121.80
119.88
115.76
114.55
113.71
103.51
77.30
77.05
76.66
29.67
0.98
N
N
CN
Cl
2p
f1 (ppm)

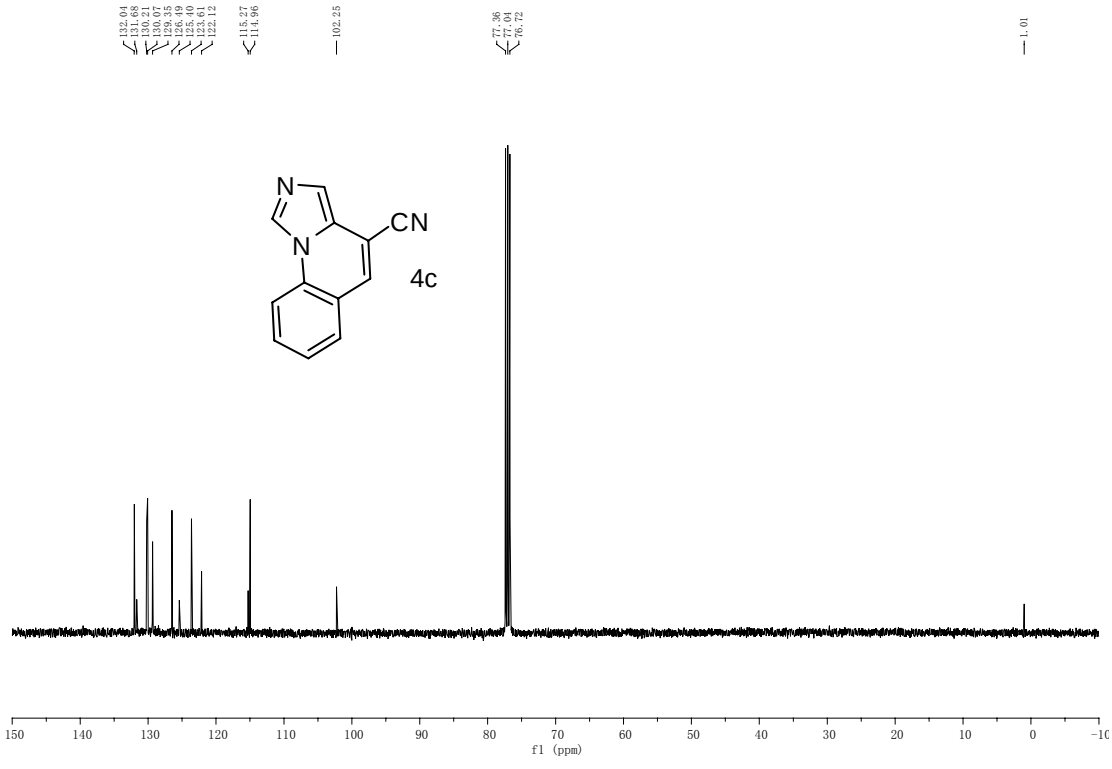

8.65
8.63
8.44
8.42
8.40
8.19
8.17
7.97
7.95
7.88
7.86
7.85
7.84
7.69
7.57
7.55
7.54
7.53
7.52
7.51
4.61
4.59
4.57
4.55
1.65
1.51
1.25
0.07
N
N
COOEt
4a
f1 (ppm)

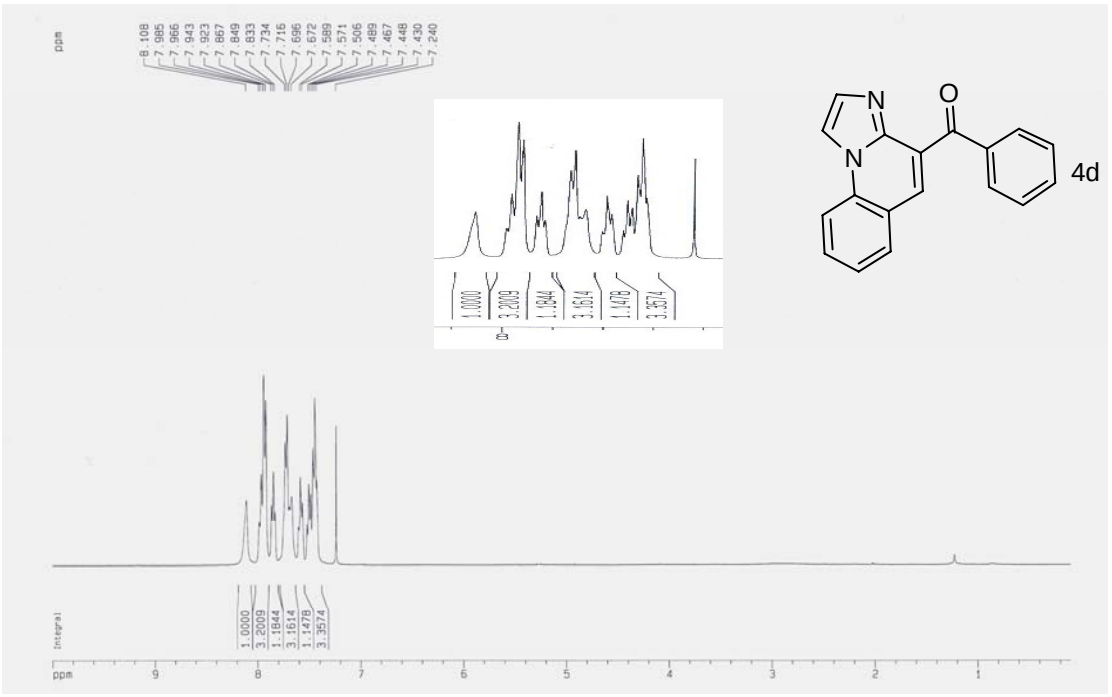

163.96
145.26
145.08
136.85
135.44
131.93
131.06
130.60
124.67
124.47
122.23
121.85
121.74
120.33
115.21
113.74
77.31
77.20
76.99
76.67
61.83
29.67
14.38
0.99
N
N
COOEt
4a
f1 (ppm)

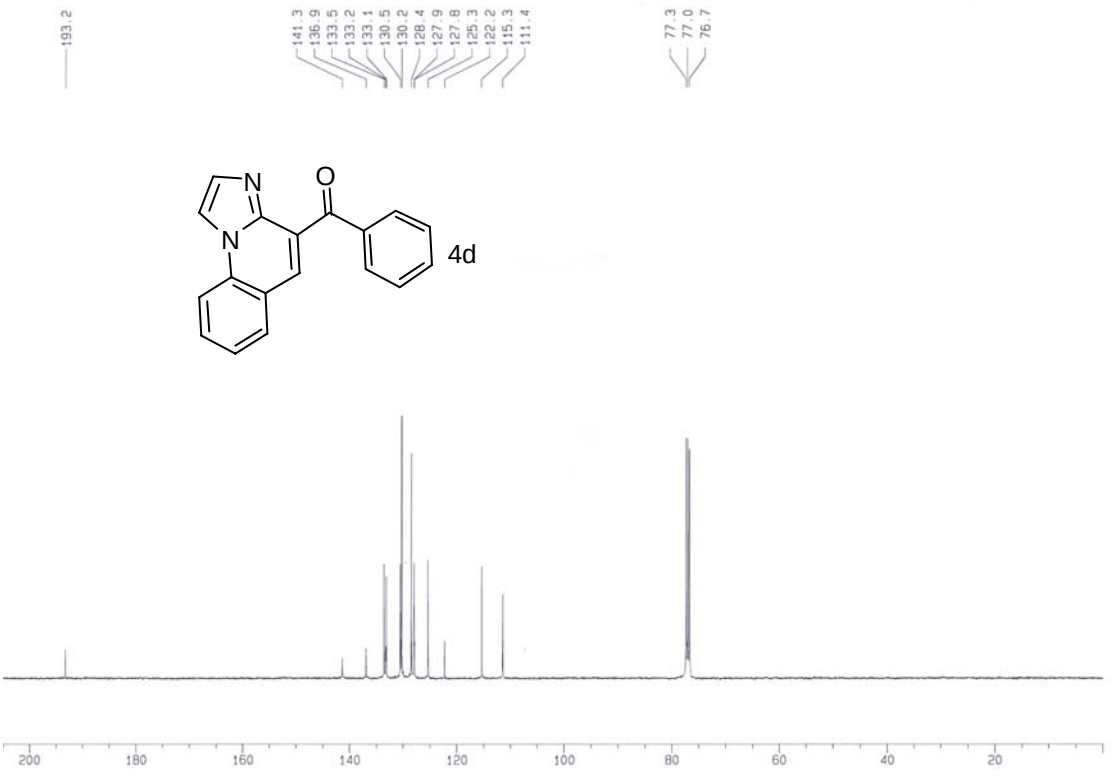

8.693
8.588
8.567
8.439
8.421
8.418
8.345
8.325
8.041
8.022
7.885
7.581
7.561
7.548
7.542
7.534
7.530
7.527
7.523
7.518
7.512
7.493
7.475
7.240
1.723
1.0000
1.0014
2.0004
0.9972
1.0080
1.0049
1.0076
6.0883
Integral
ppm
4b

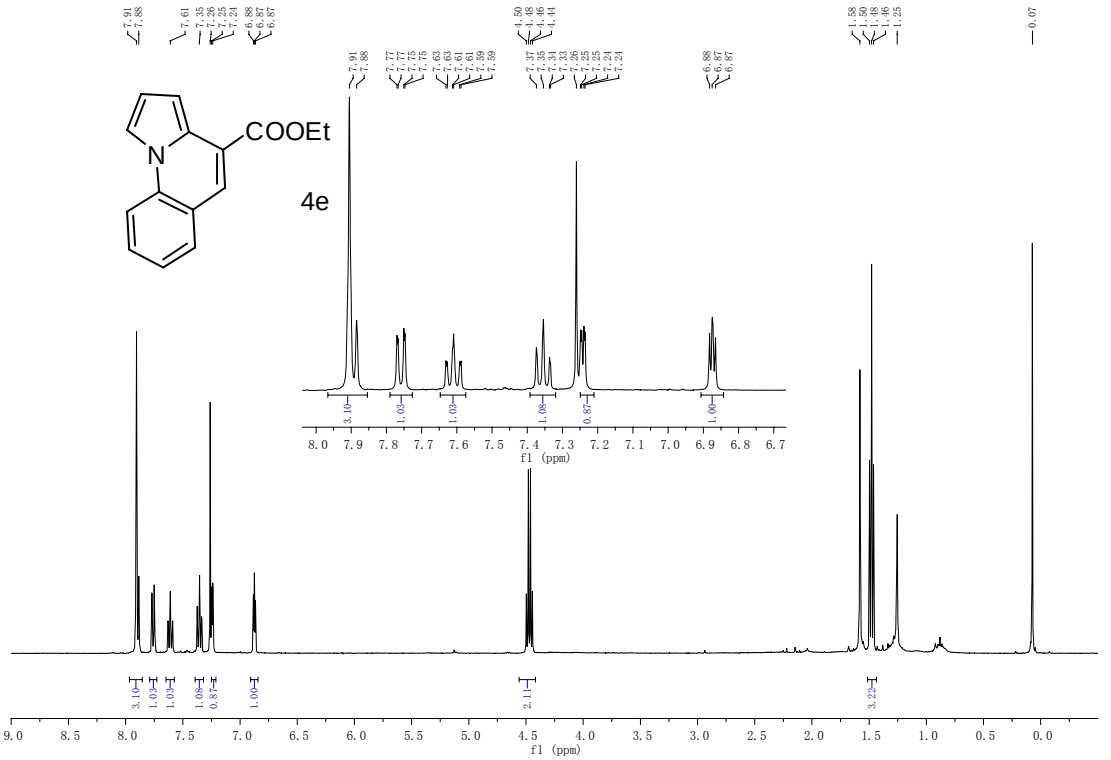

144.4
142.1
139.6
137.1
134.8
133.8
133.0
131.9
130.4
129.5
129.3
128.7
125.0
124.9
123.7
121.8
121.1
115.3
113.8
77.3
77.0
76.7
4b

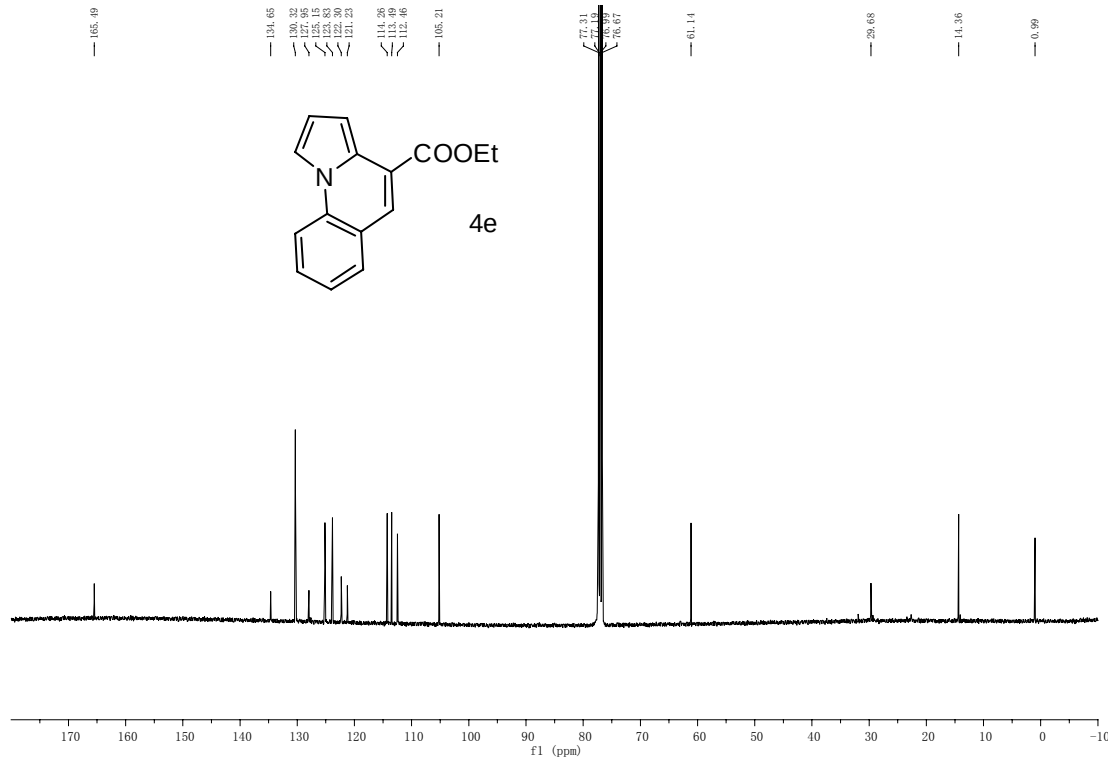

8.67
7.99
7.97
7.70
7.53
7.26
1.82
0.07
N
N
CN
4c
f1 (ppm)

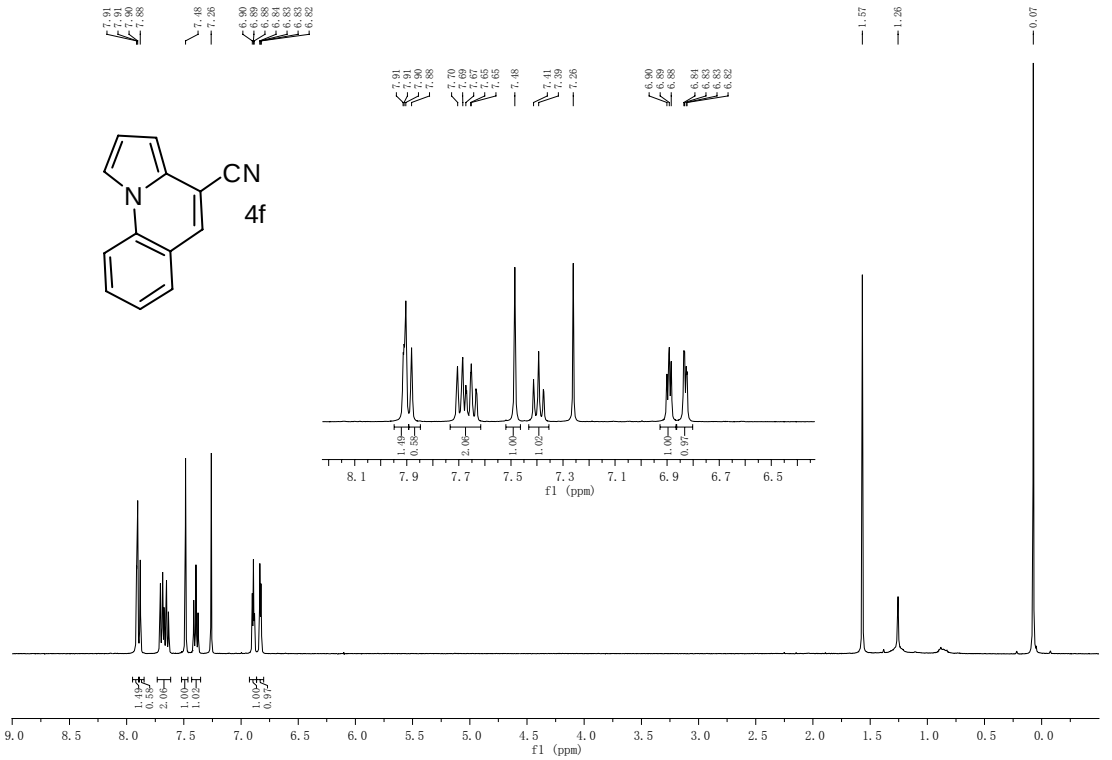

132.04
131.68
130.21
130.07
129.35
126.49
125.40
123.61
122.12
115.27
114.96
102.25
77.36
77.04
76.72
1.01
N
N
CN
4c
f1 (ppm)

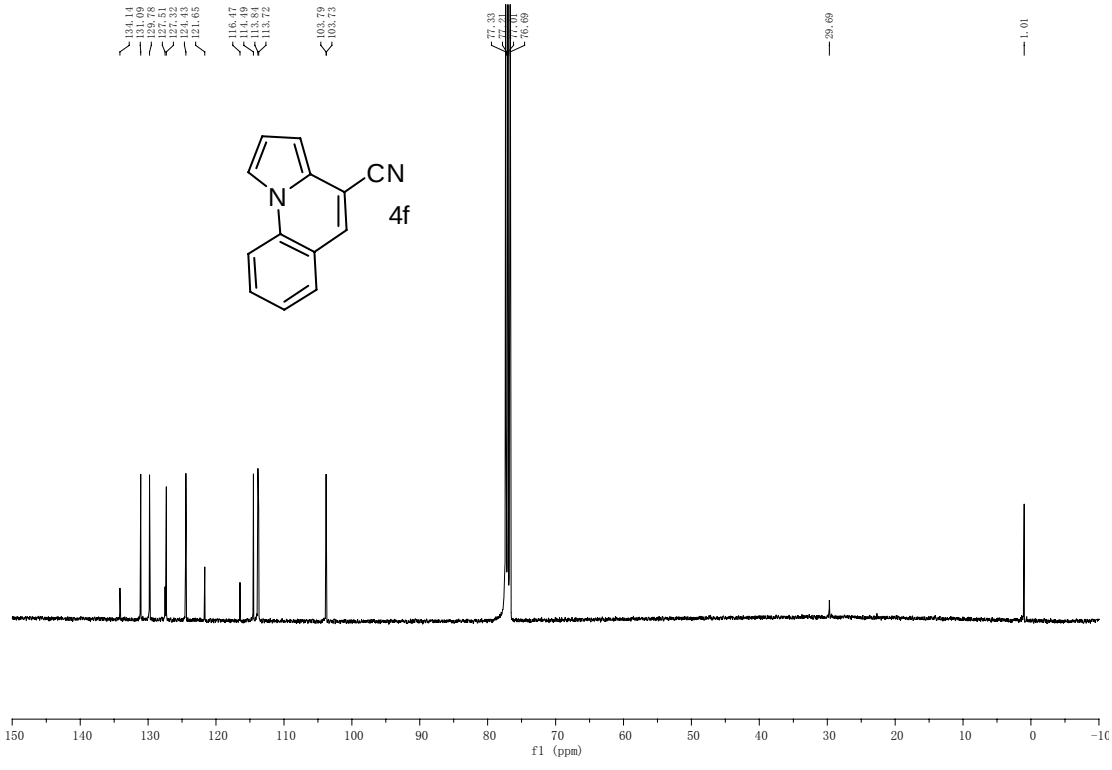

ppm
8.108
7.985
7.966
7.943
7.923
7.867
7.849
7.833
7.734
7.716
7.696
7.672
7.589
7.571
7.506
7.489
7.467
7.448
7.430
7.240
1.0000
3.2009
1.1844
3.1614
1.1478
3.3574
Integral
ppm
9
8
7
6
5
4
3
2
1
N
O
4d


193.2
141.3
136.9
133.5
133.2
133.1
130.5
130.2
128.4
127.9
127.8
125.3
122.2
115.3
111.4
77.3
77.0
76.7
N
O
4d
200
180
160
140
120
100
80
60
40
20


COOEt
4e
f1 (ppm)


COOEt
4e
f1 (ppm)


7.91
7.91
7.90
7.88
7.48
7.26
6.90
6.89
6.88
6.84
6.83
6.83
6.82
1.57
1.26
0.07
CN
N
4f
1.49
0.58
2.06
1.00
1.02
1.00
0.97
f1 (ppm)


134.14
131.09
129.78
127.51
127.32
124.43
121.65
116.47
114.49
113.84
113.72
103.79
103.73
77.33
77.21
77.01
76.69
29.69
1.01
CN
N
4f
f1 (ppm)