Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 699–700

Magnetically recyclable Cu-BTC@Fe_3O_4-catalyzed synthesis of cyano functionalized chroman-4-ones

Yongsheng Zhou and Liang Wang

Contents

General Experimental

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin) and used without further purification. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ at ambient temperature on a 500 MHz NMR spectrometer. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). Substrates **1** were prepared according to the literature.[S1-S4]

Preparation of Cu-BTC@Fe_3O_4 composite

Cu-BTC@Fe_3O_4 was prepared through a secondary growth strategy according to the literature.[S5] PVP (0.2 g, 0.005 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.1 g, 0.5 mmol) were uniformly dissolved in a mixed solution of EtOH/H_2O (2:1, 90 ml) in a 150 mL round-bottom flask under mechanical stirring (600 rpm). Then 0.2 g carboxyl functionalized Fe_3O_4 was gradually added to the mixed solution with high-speed mechanical stirring of 900 rpm and kept for 10 min. The reaction system was stirred for another 12 h upon the addition of trimesic acid (0.3 g, 1.428 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (0.1 g, 0.5 mmol). The product was obtained by centrifugation and then washed with C_2H_5OH/H_2O (2:1, 3×20 ml) and EtOH (3×20 ml). Finally, the obtained product was dried at 60 °C under vacuum for 10 h and stored in a desiccator. This composite was fully characterized and the data was reported in our previous report.[S5]

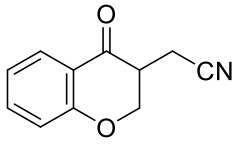
Experimental Procedures, Spectral and Analytical data

*General procedure for the synthesis of **2a~o***

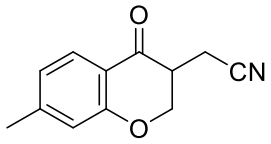
A sealed tube equipped with a magnetic stirrer bar was charged with *o*-(allyloxy)benzaldehyde **1** (0.2 mmol), TMSCN (0.4 mmol), Bu^{t}OOH (0.4 mmol, 70% in water), Cu-BTC@Fe_3O_4 composite (20 mg) and acetonitrile (2 ml). The reaction mixture was stirred at 80 ^{o}C overnight. After reaction, the Cu-BTC@Fe_3O_4 was recovered with an external magnet, and washed with EtOAc and water. The reaction mixture was

extracted with EtOAc (3×5 ml) and dried over Na_2SO_4. The organic phase was then concentrated under reduced pressure to give the crude product, which was further purified by column chromatography using petroleum ether/ethyl acetate (8:1, v/v) as eluent to afford products **2a**~**o**.

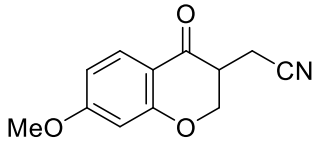
Characterization data



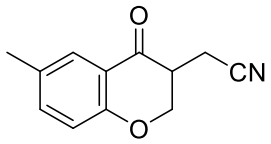
2-(4-Oxochroman-3-yl)acetonitrile 2a.[S6] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.09 – 6.99 (m, 2H), 4.74 (dd, *J* = 11.4, 5.2 Hz, 1H), 4.34 (t, *J* = 11.7 Hz, 1H), 3.24 – 3.14 (m, 1H), 2.99 (dd, *J* = 17.3, 4.6 Hz, 1H), 2.60 (dd, *J* = 17.3, 9.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 161.7, 136.7, 127.5, 122.1, 119.9, 118.1, 117.1, 69.5, 42.1, 14.2.



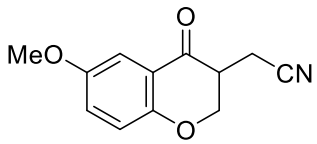
2-(7-Methyl-4-oxochroman-3-yl)acetonitrile 2b.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.83 (s, 1H), 4.73 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.33 (t, *J* = 11.6 Hz, 1H), 3.20 – 3.14 (m, 1H), 3.00 (dd, *J* = 17.3, 4.5 Hz, 1H), 2.60 (dd, *J* = 17.3, 9.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 161.7, 148.5, 127.4, 123.5, 118.0, 117.6, 117.2, 69.5, 42.0, 22.0, 14.2.



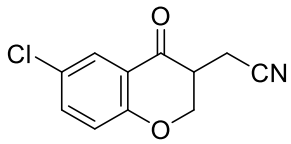
2-(7-Methoxy-4-oxochroman-3-yl)acetonitrile 2c.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 1H), 6.62 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.44 (d, *J* = 1.7 Hz, 1H), 4.72 (dd, *J* = 11.3, 5.1 Hz, 1H), 4.33 (t, *J* = 11.5 Hz, 1H), 3.86 (s, 3H), 3.16 – 3.10 (m, 1H), 2.99 (dd, *J* = 17.3, 4.4 Hz, 1H), 2.59 (dd, *J* = 17.3, 9.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 166.5, 163.7, 129.2, 117.3, 113.7, 110.8, 100.8, 69.8, 55.8, 41.6, 14.2.



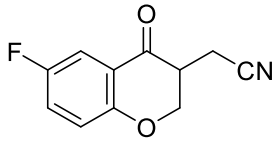
2-(6-Methyl-4-oxochroman-3-yl)acetonitrile 2d.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.5 Hz, 1H), 7.36 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.73 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.33 (t, *J* = 11.7 Hz, 1H), 3.21 – 3.15 (m, 1H), 3.00 (dd, *J* = 17.3, 4.5 Hz, 1H), 2.61 (dd, *J* = 17.3, 9.2 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 159.7, 137.8, 131.6, 127.0, 119.5, 117.8, 117.2, 69.5, 42.1, 20.4, 14.2.



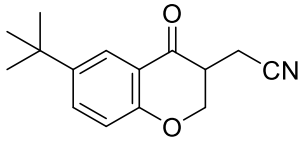
2-(6-Methoxy-4-oxochroman-3-yl)acetonitrile 2e.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 3.2 Hz, 1H), 7.16 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.97 (d, *J* = 9.1 Hz, 1H), 4.72 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.34 (t, *J* = 11.6 Hz, 1H), 3.83 (s, 3H), 3.21 – 3.15 (m, 1H), 3.00 (dd, *J* = 17.3, 4.6 Hz, 1H), 2.63 (dd, *J* = 17.3, 9.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 156.4, 154.5, 126.1, 119.7, 119.4, 117.1, 107.6, 69.6, 55.9, 42.1, 14.3.



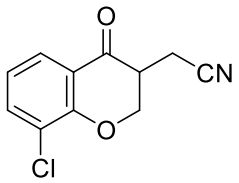
2-(6-Chloro-4-oxochroman-3-yl)acetonitrile 2f.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.6 Hz, 1H), 7.49 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.78 (dd, *J* = 11.5, 5.2 Hz, 1H), 4.36 (t, *J* = 11.9 Hz, 1H), 3.24 – 3.18 (m, 1H), 3.01 (dd, *J* = 17.4, 4.6 Hz, 1H), 2.63 (dd, *J* = 17.4, 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.1, 160.1, 136.6, 127.7, 126.7, 120.6, 119.8, 116.8, 69.6, 41.9, 14.1.



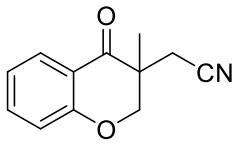
2-(6-Fluoro-4-oxochroman-3-yl)acetonitrile 2g.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.1, 3.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.03 (dd, *J* = 9.1, 4.1 Hz, 1H), 4.76 (dd, *J* = 11.5, 5.2 Hz, 1H), 4.36 (t, *J* = 11.8 Hz, 1H), 3.25 – 3.16 (m, 1H), 3.01 (dd, *J* = 17.3, 4.6 Hz, 1H), 2.64 (dd, *J* = 17.3, 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 158.0 (d, *J* = 1.1 Hz), 156.5 (d, *J* = 241.7 Hz), 124.5 (d, *J* = 24.6 Hz), 120.2 (d, *J* = 6.6 Hz), 119.8 (d, *J* = 7.4 Hz), 116.9, 112.5 (d, *J* = 23.5 Hz), 69.6, 41.9, 14.1.



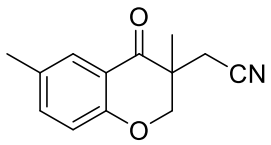
2-(6-*tert*-Butyl-4-oxochroman-3-yl)acetonitrile 2h.[S7] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.63 – 7.59 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 4.73 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.35 (t, *J* = 11.6 Hz, 1H), 3.22 – 3.15 (m, 1H), 3.00 (dd, *J* = 17.3, 4.6 Hz, 1H), 2.63 (dd, *J* = 17.3, 9.2 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 159.7, 145.1, 134.5, 123.4, 119.1, 117.7, 117.2, 69.5, 42.1, 34.4, 31.2, 14.3.



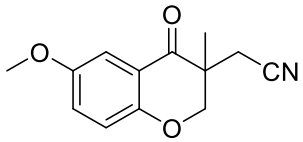
2-(8-Chloro-4-oxochroman-3-yl)acetonitrile 2i.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 1H), 7.63 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 4.90 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.50 – 4.41 (m, 1H), 3.29 – 3.23 (m, 1H), 3.00 (dd, *J* = 17.3, 4.7 Hz, 1H), 2.67 (dd, *J* = 17.3, 8.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.4, 157.1, 136.8, 126.1, 122.9, 122.2, 121.2, 116.8, 69.9, 41.8, 14.1.



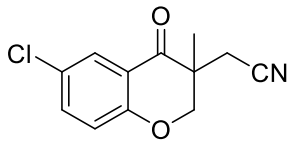
2-(3-Methyl-4-oxochroman-3-yl)acetonitrile 2j.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ7.91 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.55 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 4.38 (dd, *J* = 28.5, 11.7 Hz, 2H), 2.71 (dd, *J* = 43.0, 17.1 Hz, 2H), 1.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 161.0, 136.6, 128.0, 122.2, 118.7, 118.0, 116.4, 73.7, 43.1, 22.2, 18.4.



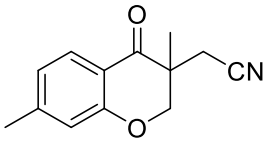
2-(3,6-Dimethyl-4-oxochroman-3-yl)acetonitrile 2k.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.6 Hz, 1H), 7.36 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.34 (dd, *J* = 28.6, 11.6 Hz, 2H), 2.70 (dd, *J* = 44.1, 17.1 Hz, 2H), 2.34 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 159.0, 137.7, 131.8, 127.4, 118.3, 117.7, 116.5, 73.8, 43.1, 22.2, 20.4, 18.4.



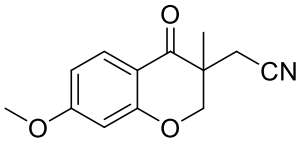
2-(6-Methoxy-3-methyl-4-oxochroman-3-yl)acetonitrile 2l.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 3.2 Hz, 1H), 7.16 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.97 (d, *J* = 9.1 Hz, 1H), 4.34 (dd, *J* = 31.8, 11.6 Hz, 2H), 3.82 (s, 3H), 2.71 (dd, *J* = 38.4, 17.1 Hz, 2H), 1.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 155.7, 154.7, 126.0, 119.3, 118.6, 116.4, 108.0, 74.0, 55.8, 43.0, 22.2, 18.4.



2-(6-Chloro-3-methyl-4-oxochroman-3-yl)acetonitrile 2m.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.7 Hz, 1H), 7.49 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.38 (q, *J* = 11.7 Hz, 2H), 2.71 (dd, *J* = 46.4, 17.1 Hz, 2H), 1.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.2, 159.4, 136.5, 127.9, 127.2, 119.7, 119.5, 116.2, 73.9, 43.0, 22.1, 18.4.



2-(3,7-Dimethyl-4-oxochroman-3-yl)acetonitrile 2n.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.83 (s, 1H), 4.40 – 4.30 (m, 2H), 2.69 (dd, *J* = 46.8, 17.1 Hz, 2H), 2.39 (s, 3H), 1.39 (s, 3H).. ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 161.0, 148.4, 127.8, 123.7, 117.9, 116.5, 116.4, 73.8, 43.0, 22.2, 22.0, 18.4.



2-(7-Methoxy-3-methyl-4-oxochroman-3-yl)acetonitrile 2o.[S5] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 1H), 6.65 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 4.36 (dd, *J* = 30.8, 11.6 Hz, 2H), 3.87 (s, 3H), 2.70 (dd, *J* = 50.6, 17.1 Hz, 2H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 166.7, 163.2, 129.8, 116.8, 112.6, 111.2, 100.8, 74.3, 55.9, 42.9, 22.4, 18.7.

References

S1. J. Zhao, P. Li, X. Li, C. Xia and F. Li, *Chem. Commun.*, 2016, **52**, 3661.
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S3. H. Hu, X. Chen, K. Sun, J. Wang, Y. Liu, H. Liu, B. Yu, Y. Sun, L. Qu, and Y. Zhao, *Org. Chem. Front.*, 2018, **5**, 2925.
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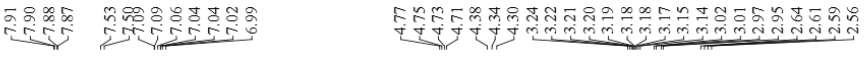
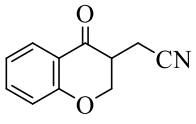
Copies of ^{1}H and ^{13}C NMR Spectra





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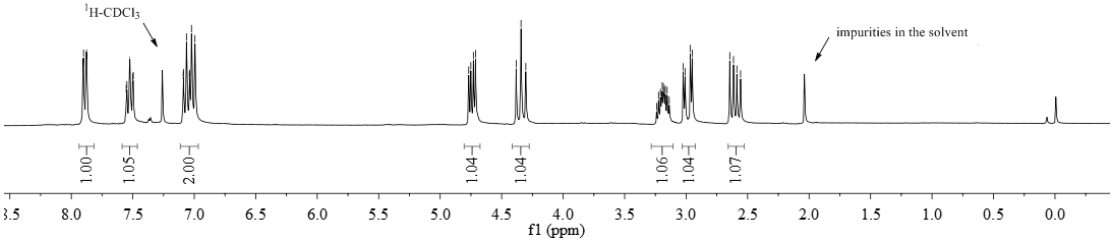

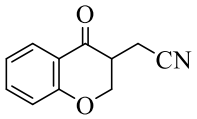

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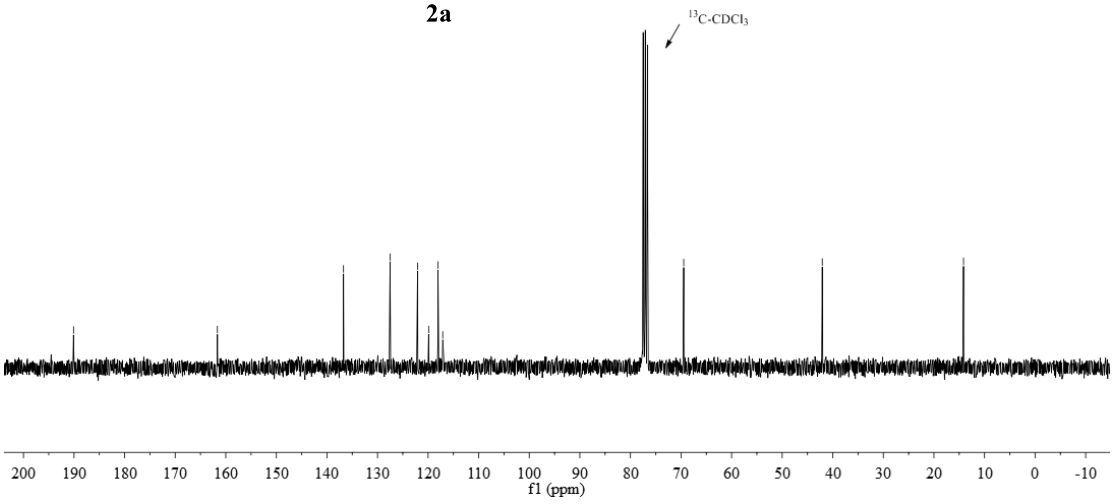

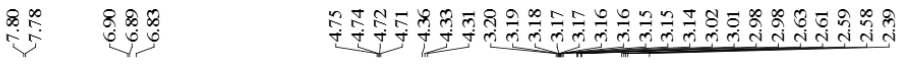
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7.78
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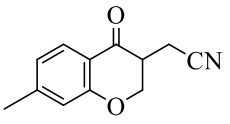
2.39


O
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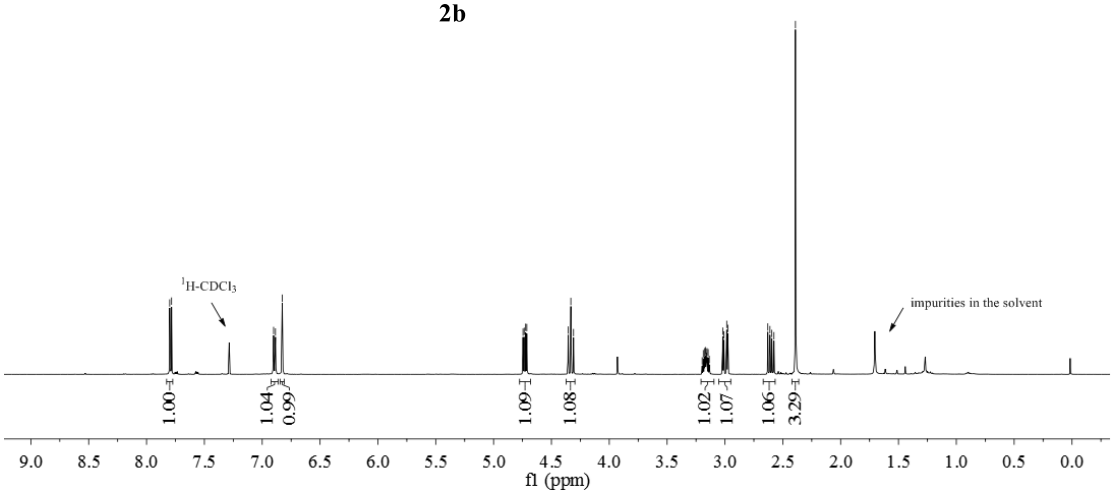
O

2b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impurities in the solvent
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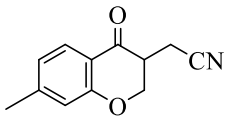
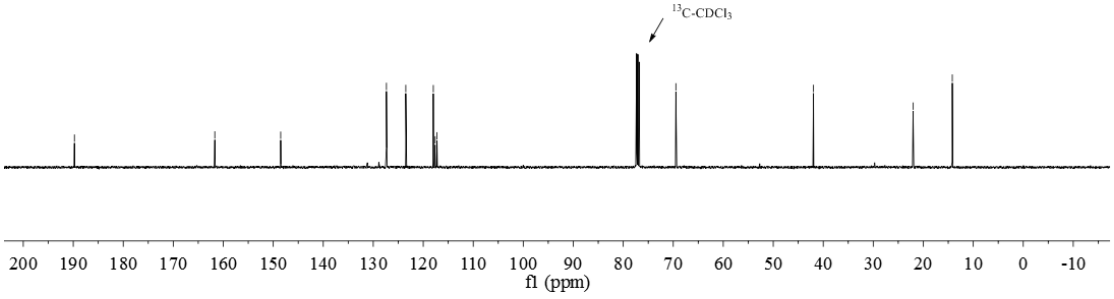
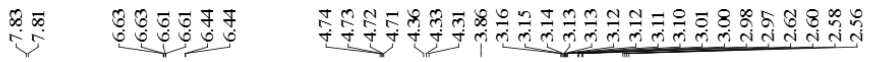
1.04
0.99
1.09
1.08
1.02
1.07
1.06
3.29
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

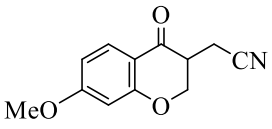

189.77
161.69
148.51
127.36
123.49
117.98
117.62
117.24
69.48
41.96
22.03
14.19


O
CN
O

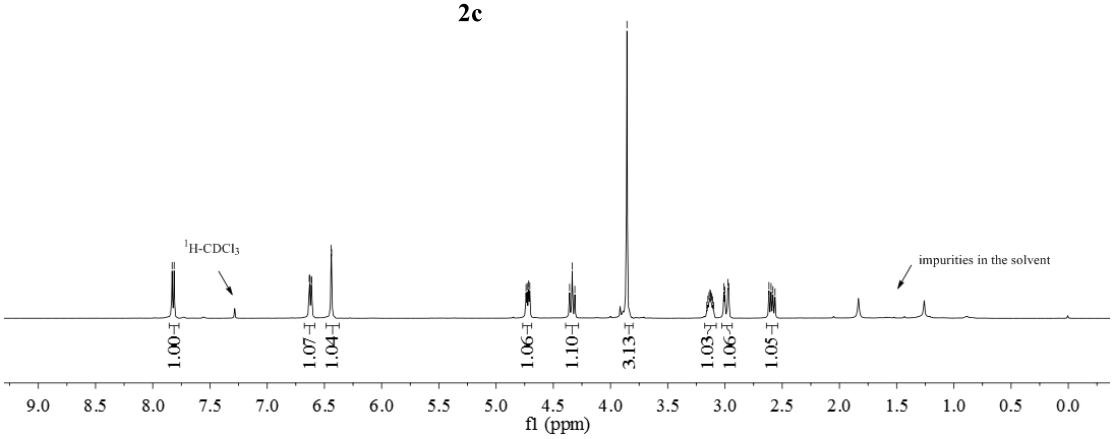
2b


^{13}C-CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

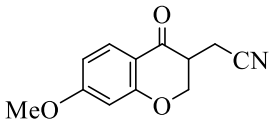

7.83
7.81
6.63
6.63
6.61
6.61
6.44
6.44
4.74
4.73
4.72
4.71
4.36
4.33
4.31
3.86
3.16
3.15
3.14
3.13
3.13
3.12
3.12
3.11
3.10
3.01
3.00
2.98
2.97
2.62
2.60
2.58
2.56


O
CN
MeO
O

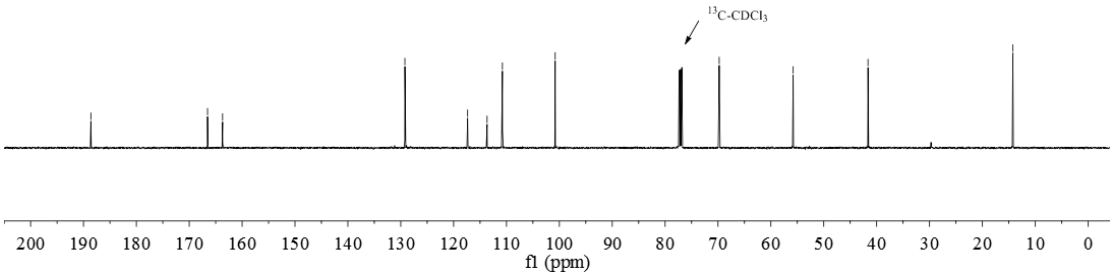
2c

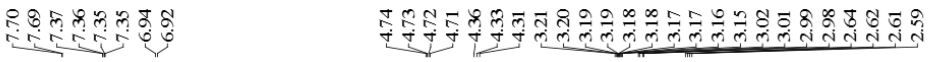

^{1}H-CDCl$_3$
impurities in the solvent
1.00
1.07
1.04
1.06
1.10
3.13
1.03
1.06
1.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

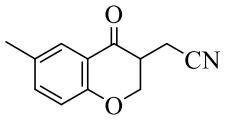

188.61
166.54
163.69
129.21
117.35
113.67
110.78
100.79
69.77
55.78
41.64
14.24


O
CN
MeO
O

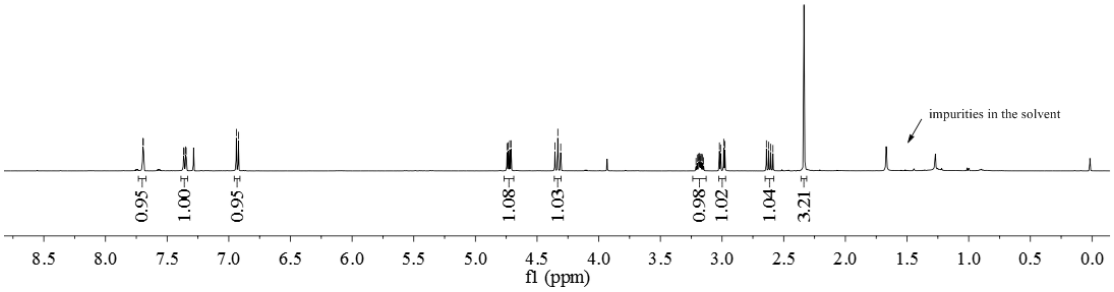
2c


^{13}C-CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

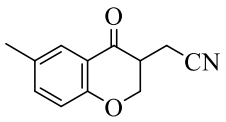

7.70
7.69
7.37
7.36
7.35
7.35
6.94
6.92
4.74
4.73
4.72
4.71
4.36
4.33
4.31
3.21
3.20
3.19
3.19
3.18
3.18
3.17
3.17
3.16
3.15
3.02
3.01
2.99
2.98
2.64
2.62
2.61
2.59


O
CN
O

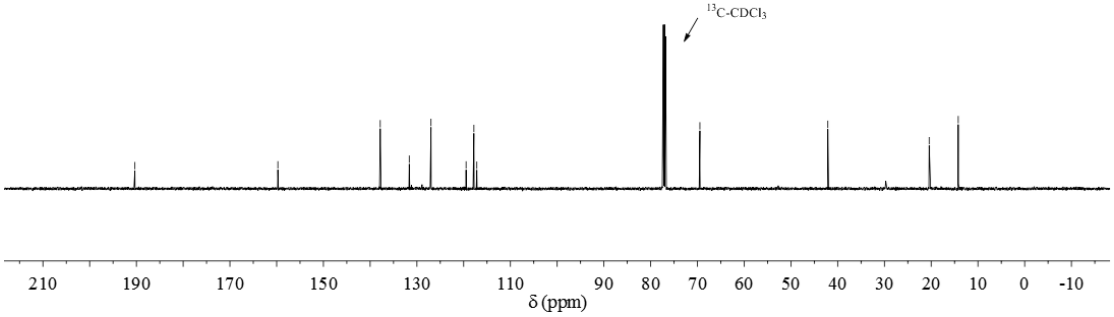
2d

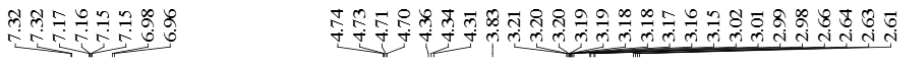

impurities in the solvent
0.95
1.00
0.95
1.08
1.03
0.98
1.02
1.04
3.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

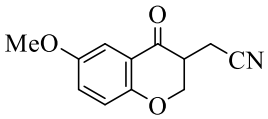

190.32
159.74
137.84
131.64
126.99
119.48
117.81
117.19
69.47
42.10
20.43
14.21


O
CN
O

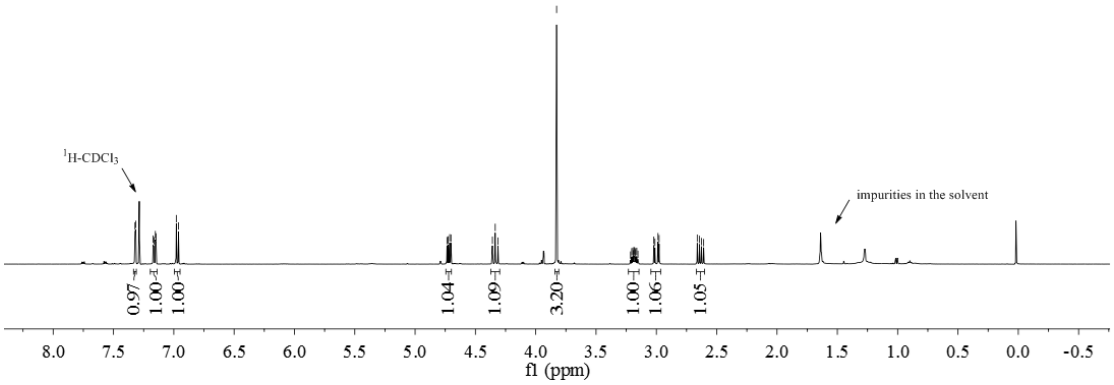
2d


13C-CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

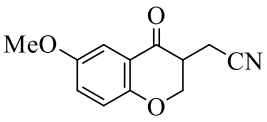

7.32
7.32
7.17
7.16
7.15
7.15
6.98
6.96
4.74
4.73
4.71
4.70
4.36
4.34
4.31
3.83
3.21
3.20
3.20
3.19
3.19
3.18
3.18
3.17
3.16
3.15
3.02
3.01
2.99
2.98
2.66
2.64
2.63
2.61


MeO
O
CN
O

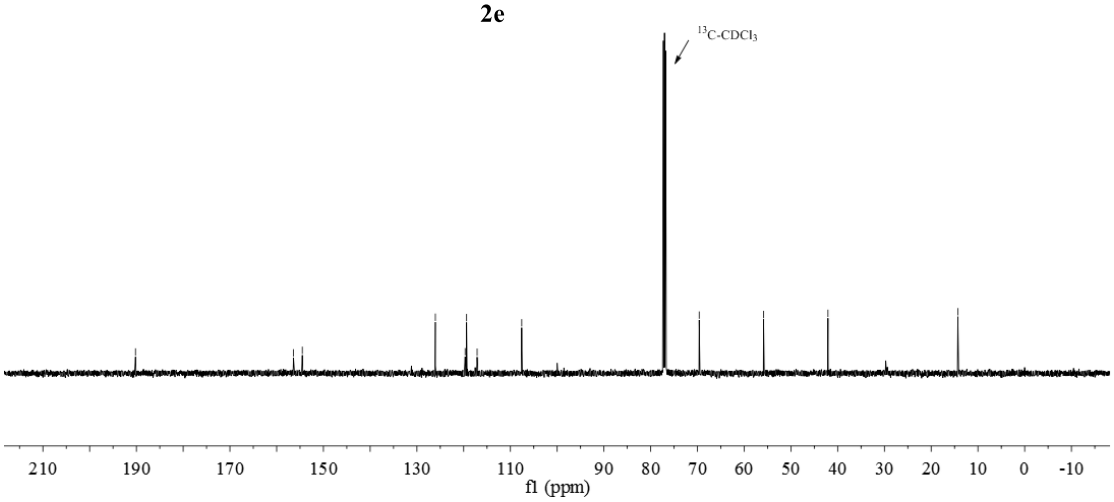
2e

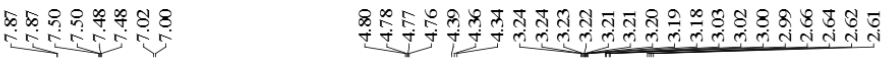

^{1}H-CDCl$_3$
impurities in the solvent
0.97
1.00
1.00
1.04
1.09
3.20
1.00
1.06
1.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

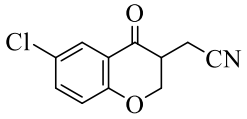

190.20
156.40
154.52
126.05
119.68
119.37
117.12
107.58
69.62
55.85
42.07
14.29


MeO
O
CN
O

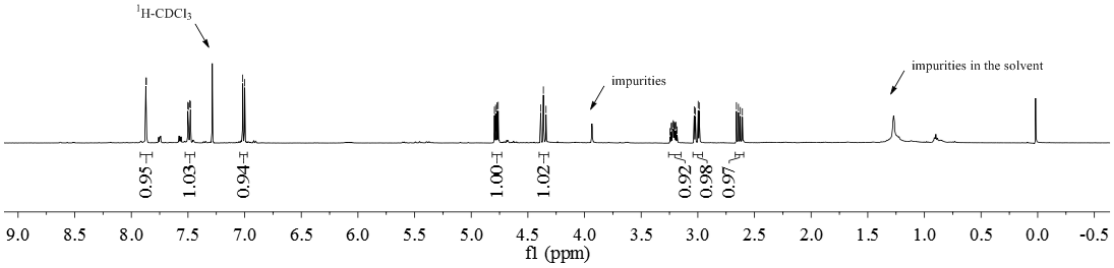
2e


^{13}C-CDCl$_3$
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

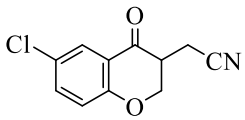

7.87
7.87
7.50
7.50
7.48
7.48
7.02
7.00
4.80
4.78
4.77
4.76
4.39
4.36
4.34
3.24
3.24
3.23
3.22
3.21
3.21
3.20
3.19
3.18
3.03
3.02
3.00
2.99
2.66
2.64
2.62
2.61


O
Cl
CN
O

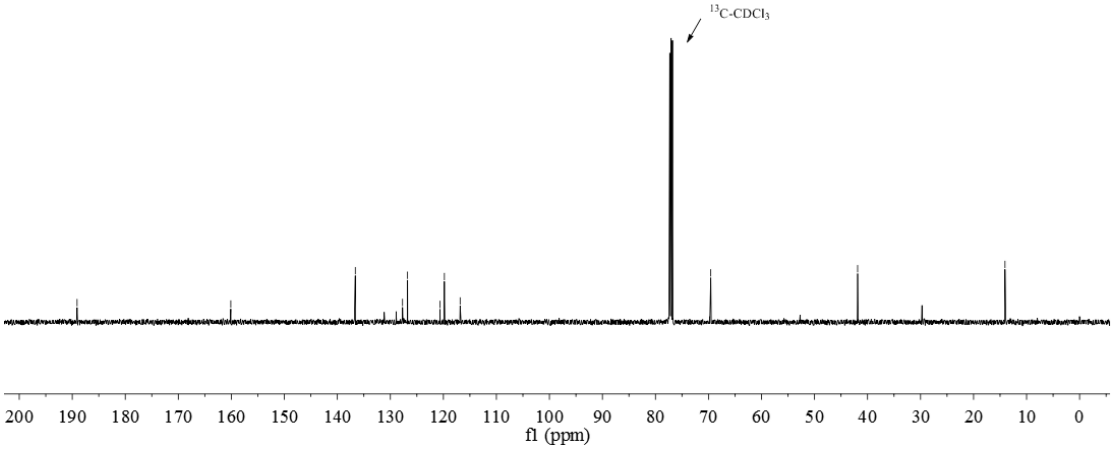
2f

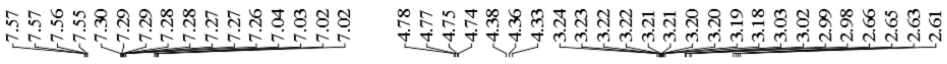

^{1}H-CDCl$_3$
impurities
impurities in the solvent
0.95
1.03
0.94
1.00
1.02
0.92
0.98
0.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

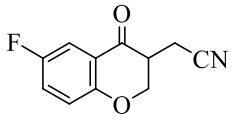

189.09
160.10
136.61
127.70
126.76
120.63
119.81
116.84
69.57
41.86
14.07


O
Cl
CN
O

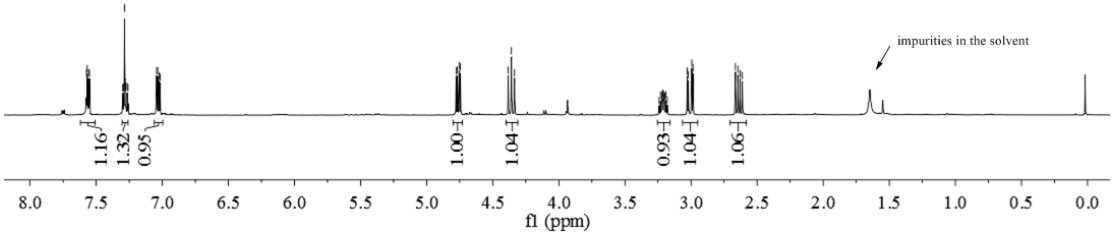
2f

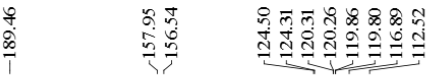

^{13}C-CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

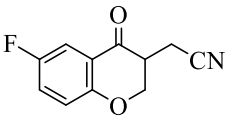

7.57
7.57
7.56
7.55
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.04
7.03
7.02
7.02
4.78
4.77
4.75
4.74
4.38
4.36
4.33
3.24
3.23
3.22
3.22
3.21
3.21
3.20
3.20
3.19
3.18
3.03
3.02
2.99
2.98
2.66
2.65
2.63
2.61


O
F
CN
O

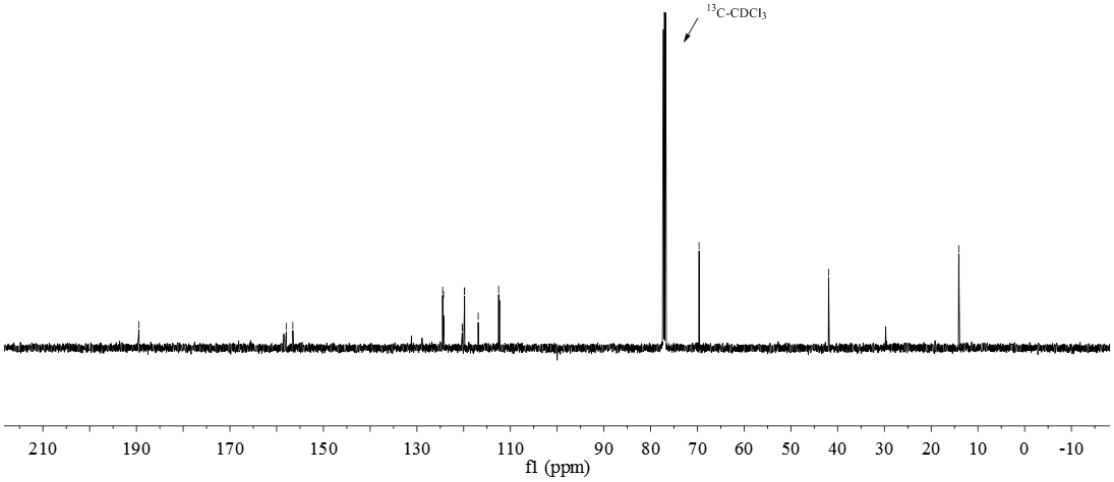
2g

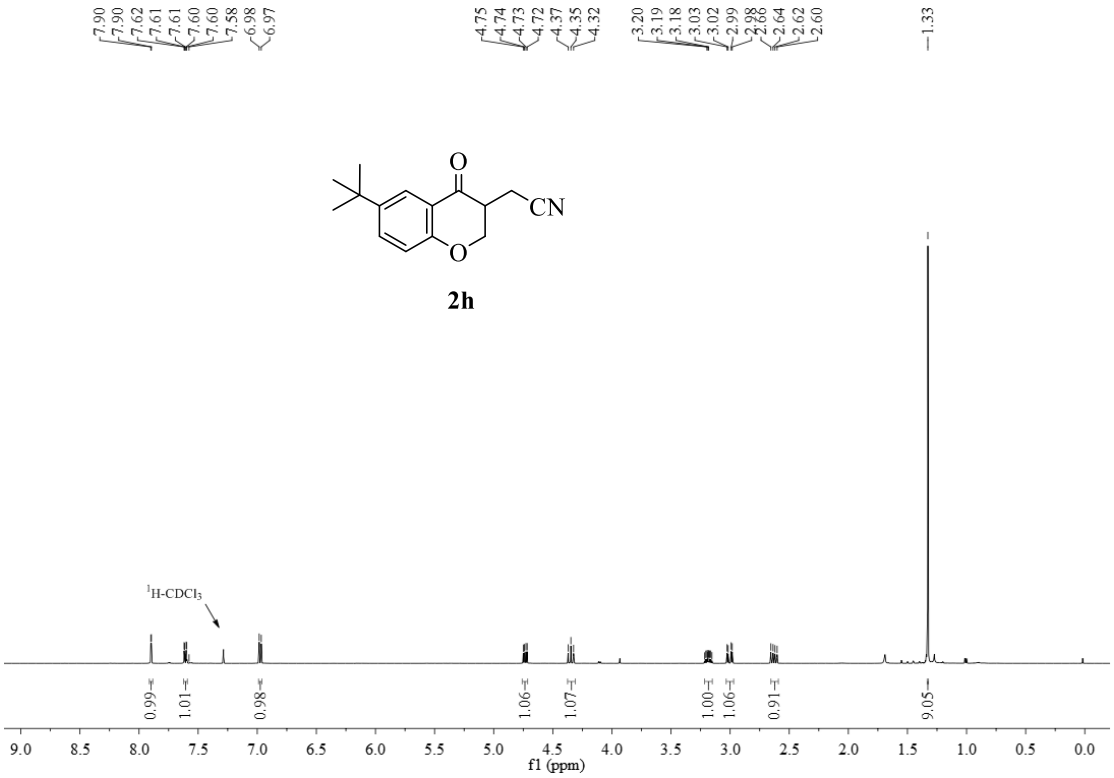

impurities in the solvent
1.16
1.32
0.95
1.00
1.04
0.93
1.04
1.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

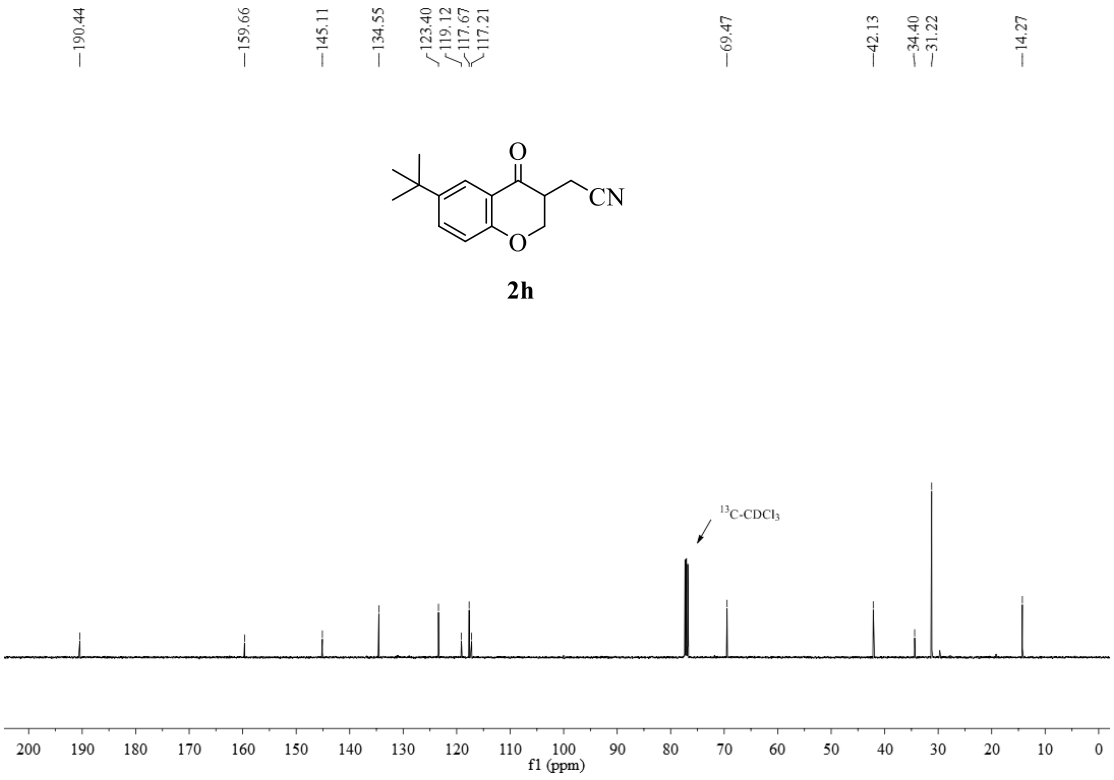

189.46
157.95
156.54
124.50
124.31
120.31
120.26
119.86
119.80
116.89
112.52
69.65
41.94
14.10

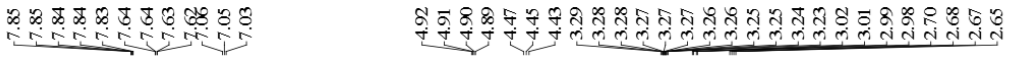

O
F
CN
O

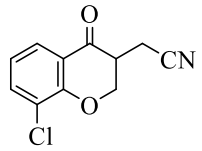
2g


13C-CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

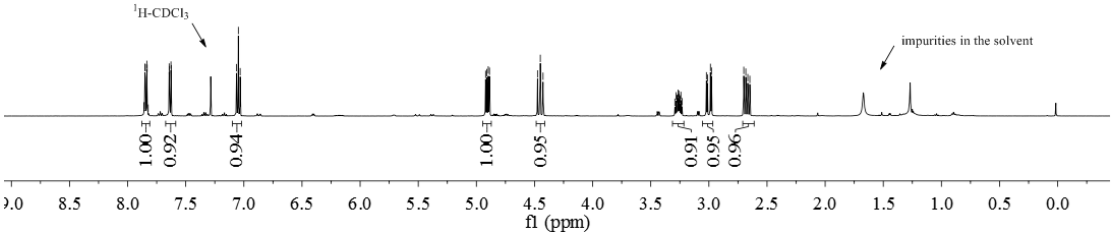

7.90
7.90
7.62
7.61
7.61
7.60
7.60
7.58
6.98
6.97
4.75
4.74
4.73
4.72
4.37
4.35
4.32
3.20
3.19
3.18
3.03
3.02
2.99
2.98
2.68
2.64
2.62
2.60
1.33
O
CN
O
2h
^{1}H-CDCl$_3$
0.99
1.01
0.98
1.06
1.07
1.00
1.06
0.91
9.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.44
159.66
145.11
134.55
123.40
119.12
117.67
117.21
69.47
42.13
34.40
31.22
14.27
O
CN
O
2h
^{13}C-CDCl$_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

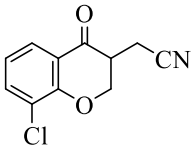

7.85
7.85
7.84
7.84
7.83
7.64
7.64
7.63
7.62
7.06
7.05
7.03
4.92
4.91
4.90
4.89
4.47
4.45
4.43
3.29
3.28
3.28
3.27
3.27
3.27
3.26
3.26
3.25
3.25
3.24
3.23
3.02
3.01
2.99
2.98
2.70
2.68
2.67
2.65


O
CN
O
Cl

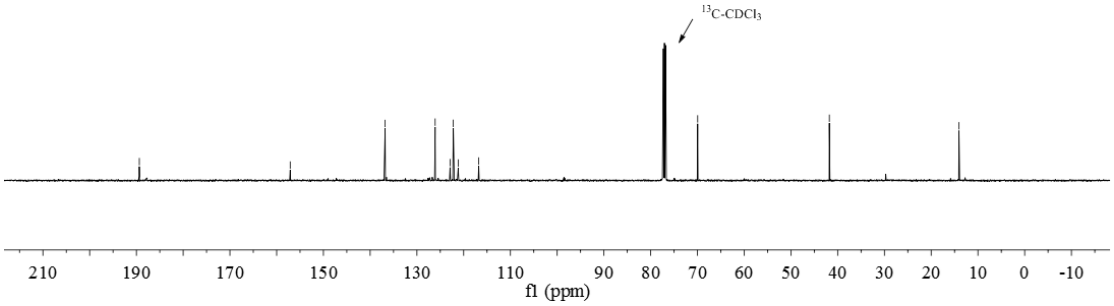
2i

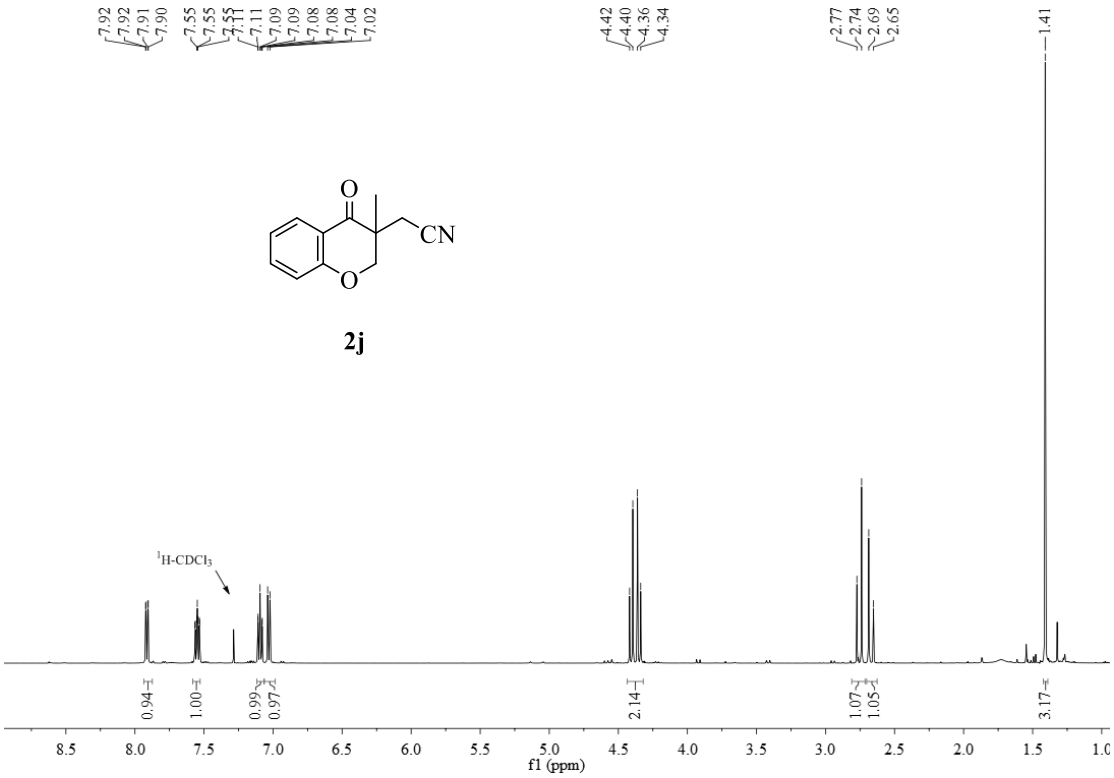

^{1}H-CDCl$_3$
impurities in the solvent
1.00
0.92
0.94
1.00
0.95
0.91
0.95
0.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


189.38
157.10
136.80
126.10
122.91
122.21
121.17
116.78
69.94
41.78
14.06

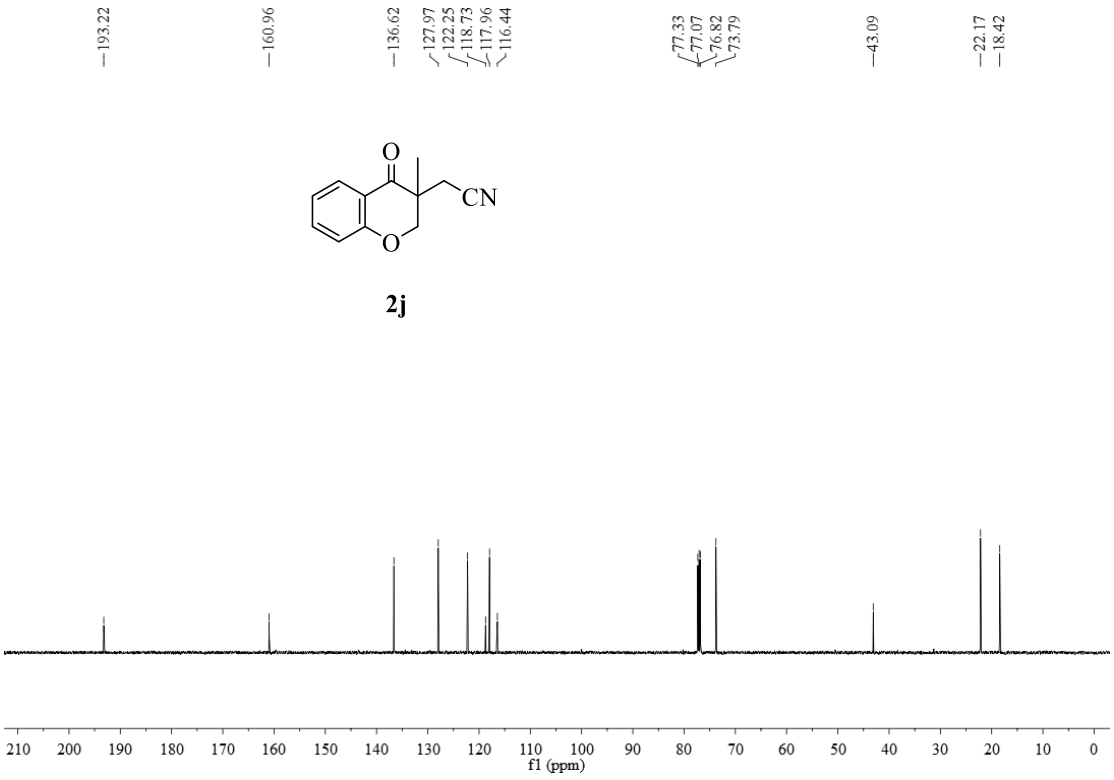

O
CN
O
Cl

2i

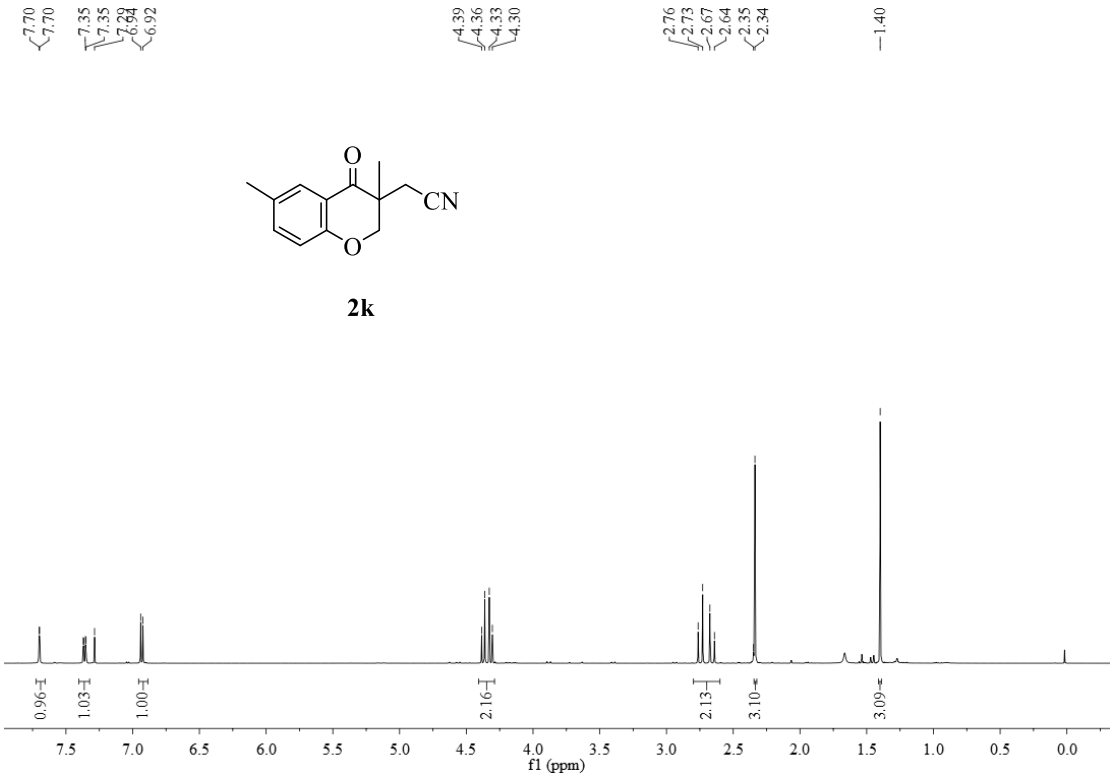

^{13}C-CDCl$_3$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.92
7.92
7.91
7.90
7.55
7.55
7.11
7.09
7.09
7.08
7.08
7.04
7.02
4.42
4.40
4.36
4.34
2.77
2.74
2.69
2.65
1.41
O
CN
O
^{1}H-CDCl$_3$
0.94
1.00
0.99
0.97
2.14
1.07
1.05
3.17
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
f1 (ppm)

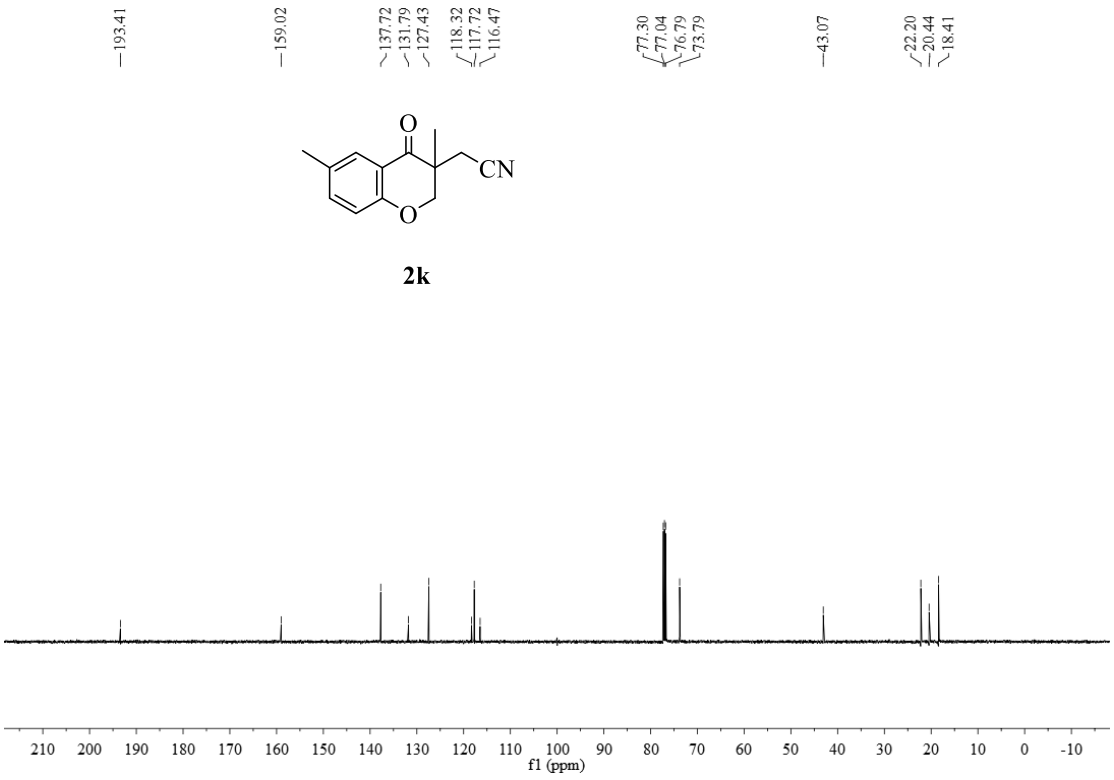
2j


193.22
160.96
136.62
127.97
122.25
118.73
117.96
116.44
77.33
77.07
76.82
73.79
43.09
22.17
18.42
O
CN
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

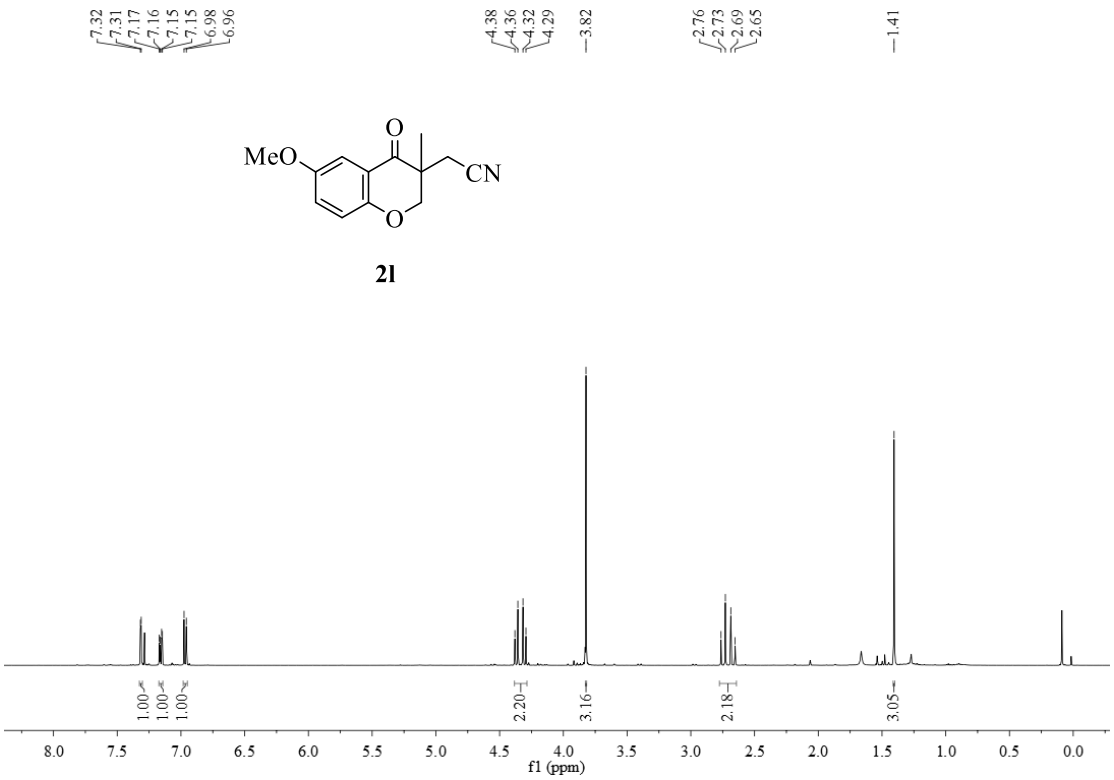
2j


7.70
7.70
7.35
7.35
7.29
6.94
6.92
4.39
4.36
4.33
4.30
2.76
2.73
2.67
2.64
2.35
2.34
1.40
O
CN
O
0.96
1.03
1.00
2.16
2.13
3.10
3.09
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)

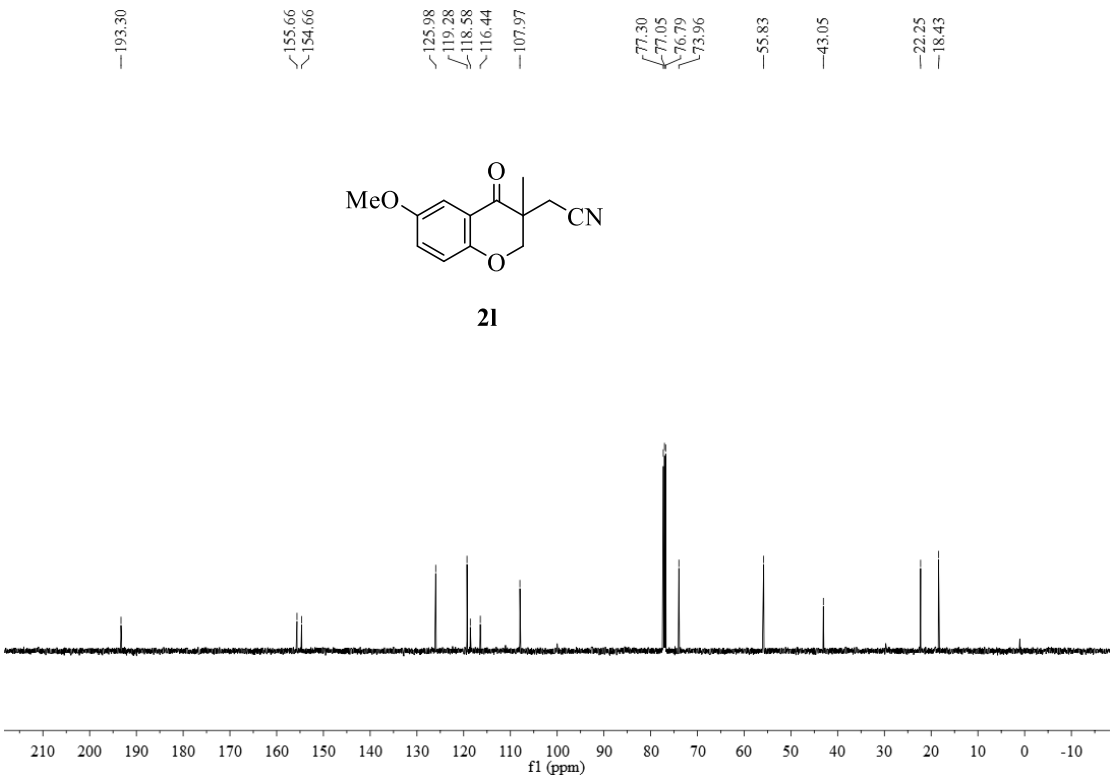
2k


193.41
159.02
137.72
131.79
127.43
118.32
117.72
116.47
77.30
77.04
76.79
73.79
43.07
22.20
20.44
18.41
O
CN
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

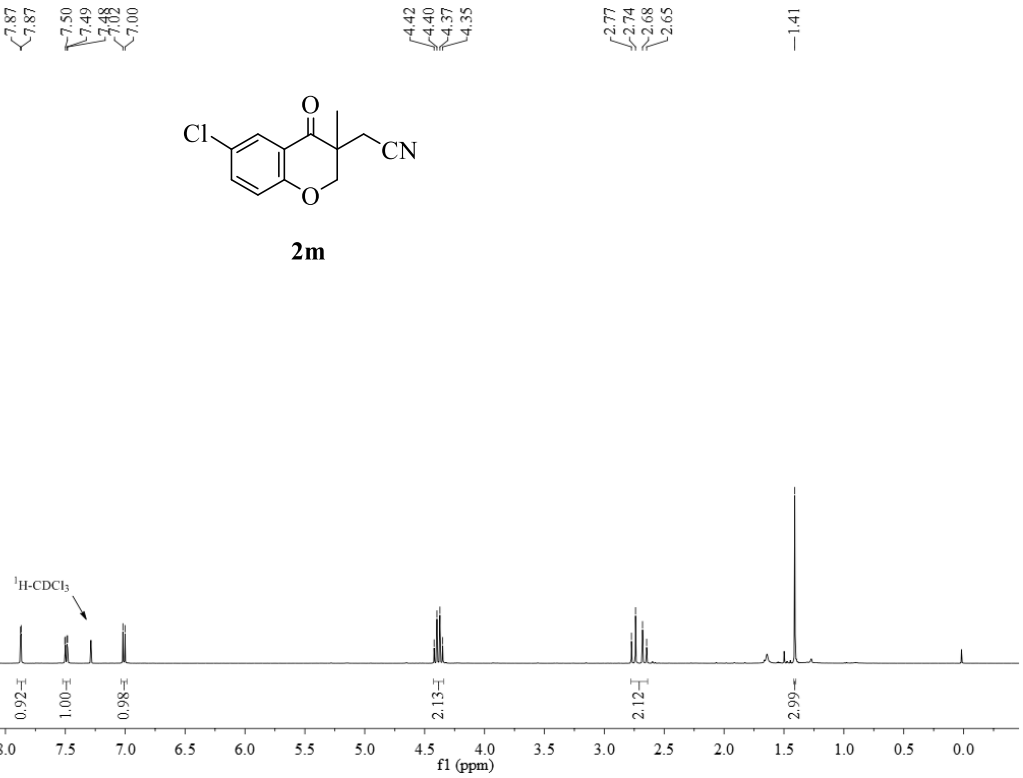
2k

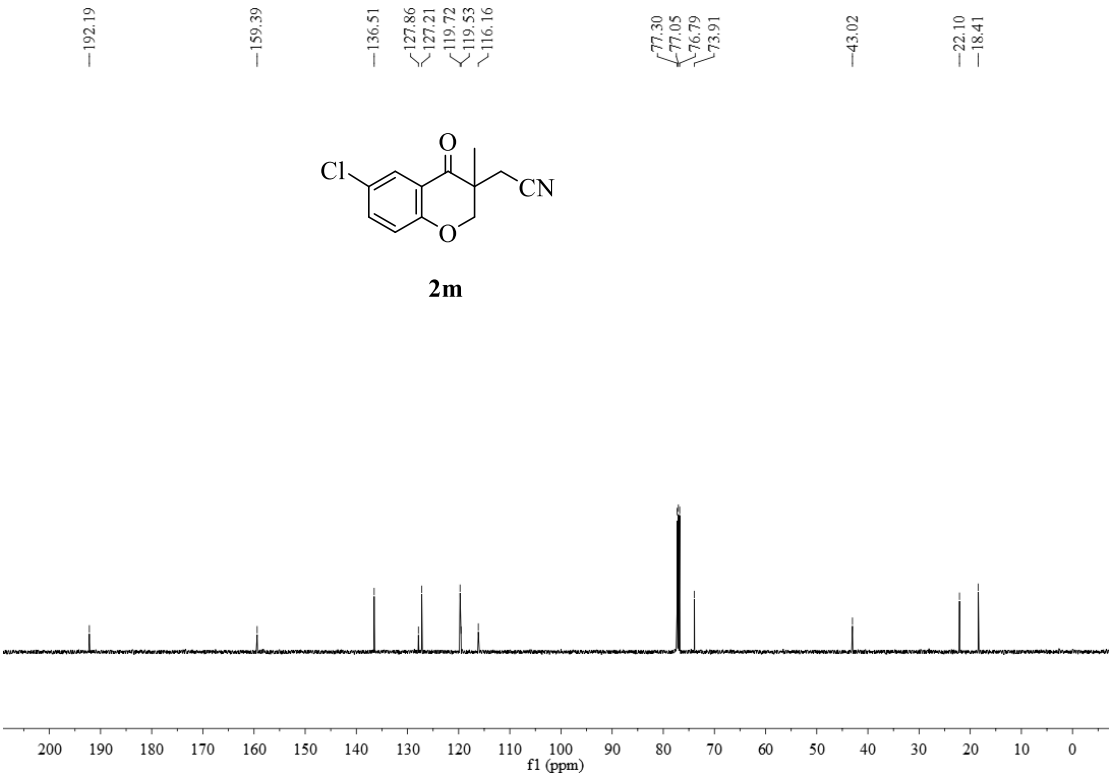

7.32
7.31
7.17
7.16
7.15
7.15
6.98
6.96
4.38
4.36
4.32
4.29
3.82
2.76
2.73
2.69
2.65
1.41
MeO
O
CN
O
1.00
1.00
1.00
2.20
3.16
2.18
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

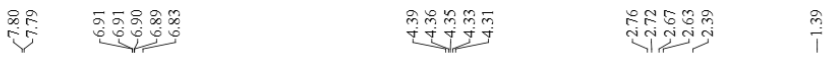
21

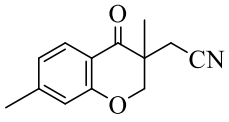

193.30
155.66
154.66
125.98
119.28
118.58
116.44
107.97
77.30
77.05
76.79
73.96
55.83
43.05
22.25
18.43
MeO
O
CN
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

21

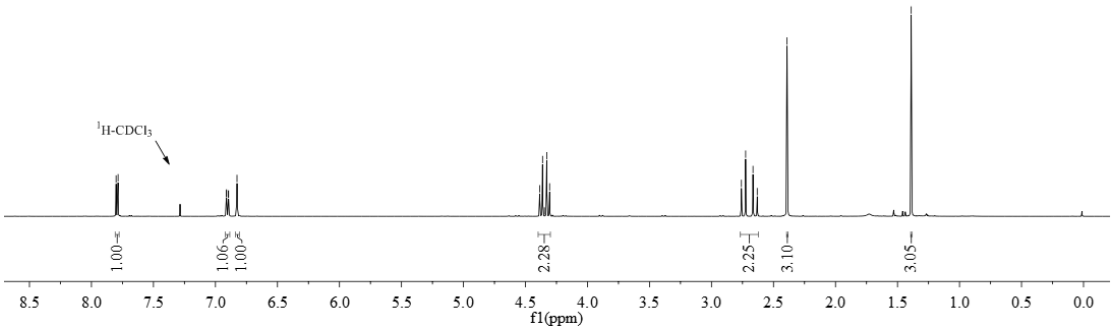

7.87
7.87
7.50
7.49
7.48
7.02
7.00
4.42
4.40
4.37
4.35
2.77
2.74
2.68
2.65
1.41
Cl
O
CN
O
2m
^{1}H-CDCl$_3$
0.92
1.00
0.98
2.13
2.12
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.19
159.39
136.51
127.86
127.21
119.72
119.53
116.16
77.30
77.05
76.79
73.91
43.02
22.10
18.41
Cl
O
CN
O
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

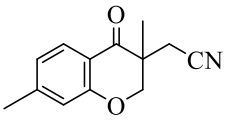

7.80
7.79
6.91
6.91
6.90
6.89
6.83
4.39
4.36
4.35
4.33
4.31
2.76
2.72
2.67
2.63
2.39
1.39


O
CN
O

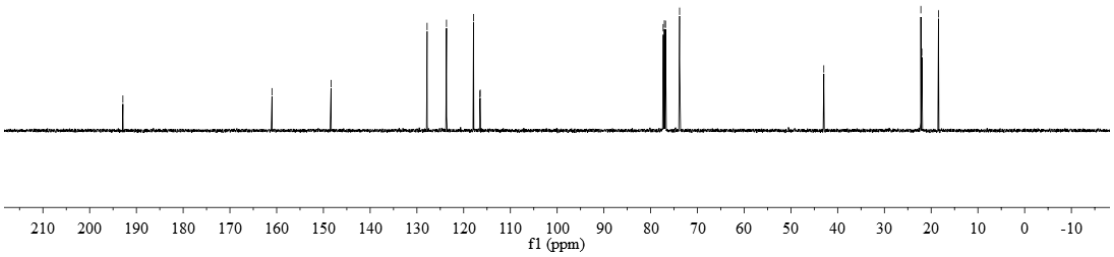
2n

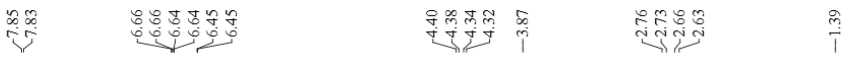

^{1}H-CDCl$_3$
1.00
1.06
1.00
2.28
2.25
3.10
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1(ppm)

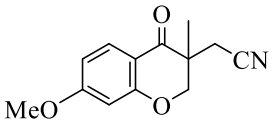

192.89
161.00
148.37
127.82
123.67
117.89
116.53
116.45
77.33
77.07
76.82
73.81
42.96
22.20
22.00
18.43


O
CN
O

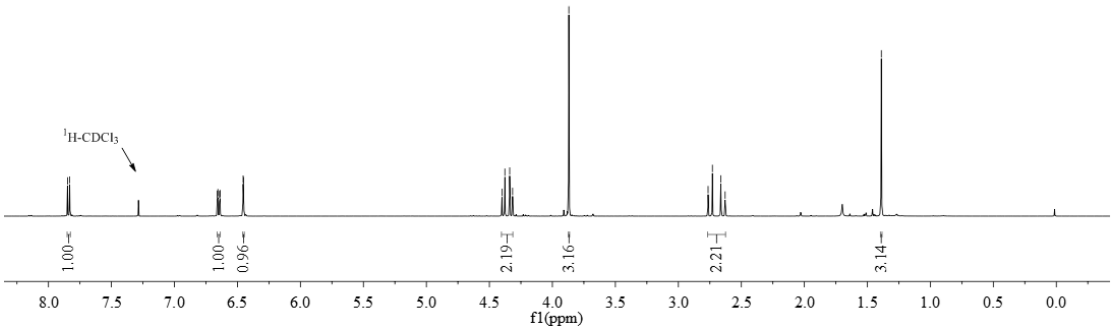
2n

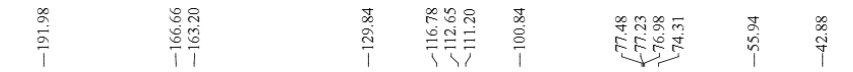

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

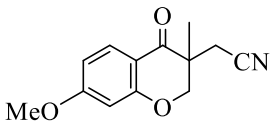

7.85
7.83
6.66
6.66
6.64
6.64
6.45
6.45
4.40
4.38
4.34
4.32
3.87
2.76
2.73
2.66
2.63
1.39


O
CN
MeO
O

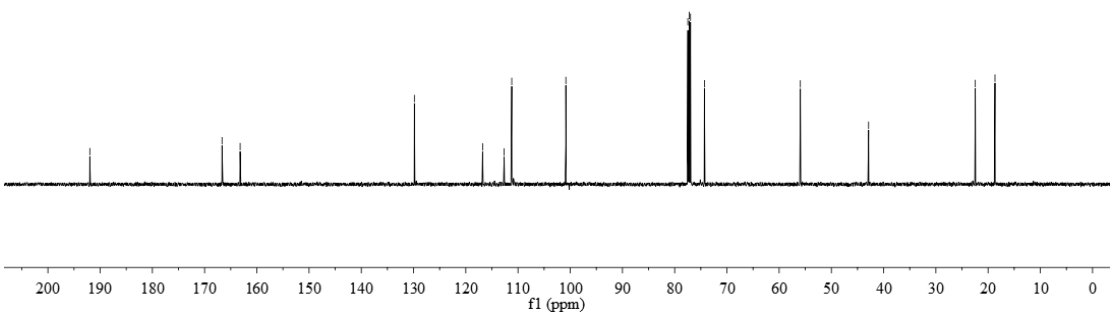
2o


^{1}H-CDCl$_3$
1.00
1.00
0.96
2.19
3.16
2.21
3.14
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)


191.98
166.66
163.20
129.84
116.78
112.65
111.20
100.84
77.48
77.23
76.98
74.31
55.94
42.88
22.45
18.68


O
CN
MeO
O

2o


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)