Supporting Information

Selective C(sp^2) –H Bond Radical Thiocyanation of Cyclic *α*, *β*-Unsaturated Ketones

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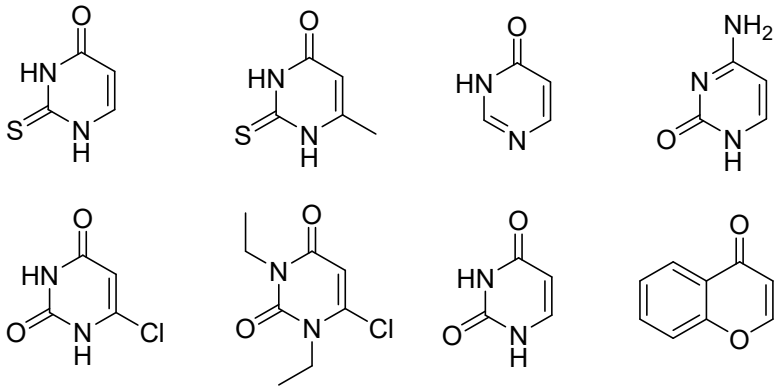
1. General Experimental Information

All reactions were carried out under air atmosphere, unless otherwise stated. All chemicals were purchased from commercial companies or synthesized according to the literature method. ^{1}H NMR spectra were recorded on 400 MHz or 600 MHz in $CDCl_3$ or DMSO-d_6. $^{13}C\{^1H\}$ NMR spectra were recorded on 100 MHz or 150 MHz in $CDCl_3$ or DMSO-d_6. The data is reported as (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet or unresolved, coupling constant(s) in Hz, integration, assignment).

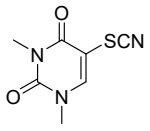
2. General procedure for synthesis of 2

To a glass tube with substrate (0.1 mmol, 1.0 equiv), NTS (0.15 mmol, 1.5 equiv) and AIBN (0.05 mmol, 0.5 equiv) was added dry DMSO (1.0 mL) under air atmosphere, and it was stirred 5 h at 80 °C. The reaction mixture was purified by column chromatography on silica gel with eluent to afford the pure desired product.

3. Failed substrates

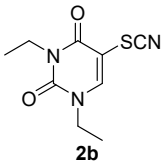


4. Analytical data of the target compounds



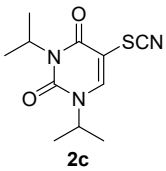
2a

1,3-dimethyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2a)[1]: white solid, (18 mg, 91% yield), mp: 98 – 100 °C, eluent EtOAc. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.55 (s, 1H), 3.36 (s, 3H), 3.22 (s, 3H). $^{13}C\{_1H\}$ NMR (150 MHz, DMSO-d_6) δ: 160.2, 151.5, 150.9, 111.1, 93.5, 37.0, 28.4.



2b

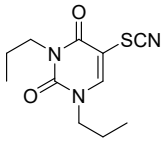
1,3-dimethyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2b)[1]: yellow solid, (16 mg, 71% yield), mp: 123 – 125 °C. eluent PE/EtOAc (2:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 1H), 4.08 – 4.03 (m, 2H), 3.92 – 3.87(m, 2H), 1.38 (t, J = 8.0 Hz, 3H), 1.25 (t, J = 8.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 159.7, 150.1, 146.2, 109.7, 97.5, 46.1, 37.9, 14.6, 12.7.



2c

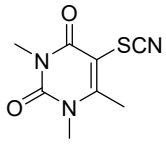
1,3-diisopropyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2c)[1]: yellow oil, (20 mg, 79% yield), eluent

PE/EtOAc (1:1, v/v). 1H NMR (400 MHz, $CDCl_3$) δ: 7.66 (s, 1H), 5.24 – 5.17 (m, 1H), 4.92 – 4.86 (m, 1H), 1.47 (d, J = 4.0 Hz, 6H), 1.38 (d, J = 4.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 159.8, 150.2, 142.4, 110.0, 97.8, 49.5, 47.8, 21.7, 19.2.



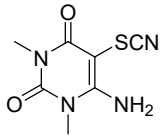
2d

1,3-dipropyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2d): yellow oil, (14 mg, 55% yield), eluent PE/EtOAc (2:1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H), 3.94 (t, J = 8.0 Hz, 3H), 3.78 (t, J = 8.0 Hz, 3H), 1.81 – 1.71 (m, 2H), 1.71 – 1.61 (m, 2H), 1.00 – 0.92 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 159.8, 150.5, 146.1, 109.7, 97.6, 52.4, 44.2, 22.5, 20.8, 11.3, 11.0. HRMS (ESI) m/z: calcd. for $C_{11}H_{16}N_3O_2S$ $[M + H]^+$ 254.0958, found 254.0940.



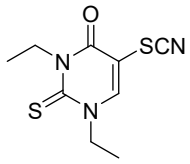
2e

1,3,6-trimethyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2e): white solid, (21 mg, 99% yield), mp: 131 – 133 °C, eluent EtOAc. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.54 (s, 3H), 3.41 (s, 3H), 2.71 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 159.8, 159.1, 151.1, 110.0, 95.6, 33.8, 29.4, 20.0. HRMS (ESI) m/z: calcd. for $C_8H_8N_3O_2S$ $[M - H]^-$ 210.0343, found 210.0335.



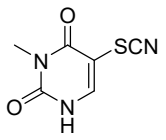
2f

6-amino-1,3-dimethyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2f)[1]: white solid, (14 mg, 66% yield), mp: > 280 °C, eluent EtOAc. ^1H NMR (400 MHz, DMSO-d_6) δ: 7.87 (s, 2H), 3.34 (s, 3H), 3.15 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ: 160.2, 157.3, 150.3, 112.4, 66. 2, 31.0, 28.3.



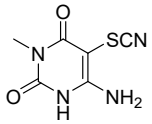
2g

1,3-diethyl-5-thiocyanato-2-thioxo-2,3-dihydropyrimidin-4(1H)-one (2g): yellow oil, (10 mg, 41% yield), eluent PE/EtOAc (8:1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.08 (s, 1H), 4.14 (q, J = 8.0 Hz, 2H), 3.21 (q, J = 8.0 Hz, 2H), 1.41 – 1.33 (m, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 164.6, 158.7, 152.3, 109.3, 109.0, 41.1, 27.1, 14.0, 12.3. HRMS (ESI) m/z: calcd. for $C_9H_{12}N_3OS_2$ $[M + H]^+$ 242.0416, found 242.0396.



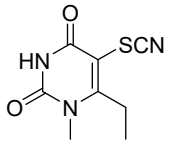
2h

3-methyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2h): colorless oil, (17 mg, 93% yield), eluent PE/EtOAc (1:1, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.44 (s, 1H), 8.23 (s, 1H), 3.17 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ: 160.9, 151.4, 148.7, 111.5, 93.7, 27.7. HRMS (ESI) m/z: calcd. for $C_6H_6N_3O_2S$ $[M + H]^+$ 184.0175, found 184.0160.



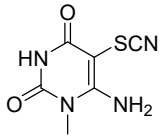
2i

6-amino-3-methyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2i): white solid, (18 mg, 91% yeild), mp: 270 – 272 °C, eluent DCM/CH_3OH (8:1, v/v). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.00 (s, 1H), 7.23 (s, 2H), 3.09 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ: 162.0, 156.7, 150.2, 112.9, 66.4, 27.6. HRMS (ESI) m/z: calcd. for $C_6H_7N_4O_2S$ $[M + H]^-$ 199.0284, found 199.0289.



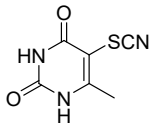
2j

6-ethyl-1-methyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2j): colorless oil, (16 mg, 76% yeild), eluent PE/EtOAc (1:3, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 10.86 (s, 1H), 3.39 (s, 3H), 2.90 (q, J = 6.0 Hz, 2H), 1.39 (t, J = 6.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ: 162.2, 160.7, 152.4, 109.9, 95.4, 28.5, 26.7, 12,2. HRMS (ESI) m/z: calcd. for $C_8H_8N_3O_2S$ $[M - H]^-$ 210.0343, found 210.0333.



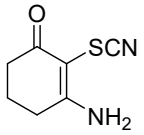
2k

6-amino-1-methyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2k): white solid, (16 mg, 81% yield), mp: > 280 °C. eluent DCM/CH_3OH (5:1, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.07 (s, 1H), 7.90 (s, 2H), 3.27 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ: 160.6, 158.6, 149.9, 112.5, 66.0, 30.0.



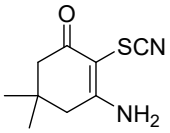
2l

6-methyl-5-thiocyanatopyrimidine-2,4(1H,3H)-dione (2l): white solid, (14 mg, 76% yield), mp: 219 – 221 °C, eluent EtOAc, ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.71 (s, 1H), 11.61 (s, 1H), 2.36(s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ: 161.3, 160.7, 150.1, 111.4, 93.3, 18.7. HRMS (ESI) m/z: calcd. for $C_6H_6N_3O_2S$ $[M + H]^+$ 184.0175, found 184.0186.



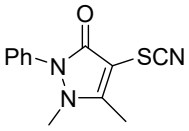
2m

3-amino-2-thiocyanatocyclohex-2-en-1-one (2m) [2]: white solid, (14 mg, 83% yield), mp: 165 – 167 °C, eluent DCM/CH_3OH (15:1, v/v). ^1H NMR (600 MHz, DMSO-d_6) δ: 8.20 (s, 1H), 7.79 (s, 1H), 2.60 (t, J = 6.0 Hz, 2H), 2.30 (t, J = 6.0 Hz, 2H), 1.82 – 1.78 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ: 189.9, 171.2, 112.5, 86.2, 36.7, 29.9, 20.1.



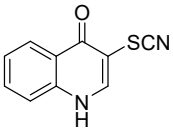
2n

3-amino-5,5-dimethyl-2-thiocyanatocyclohex-2-en-1-one (2n) [2]: white solid, (14 mg, 71% yield), mp: 149 – 151°C, eluent DCM/CH_3OH (15:1, v/v). ^1H NMR (400 MHz, DMSO-d_6) δ: 8.23 (s, 1H), 7.88 (s, 1H), 2.47 (s, 2H), 2.20 (s, 2H), 0.94 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ: 189.4, 169.6, 112.6, 85.0, 50.1, 42.9, 31.4, 27.4.



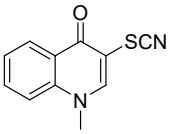
2o

1-methyl-2-phenyl-4-thiocyanato-1,2-dihydro-3H-pyrazol-3-one (2o): white solid, (19 mg, 77% yield), mp: 120 – 122 °C, eluent EtOAc. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.49 (t, J = 7.68 Hz, 2H), 7.39 (t, J = 7.36 Hz, 2H), 7.30 (d, J = 7.8 Hz, 1H), 3.29 (s, 3H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 163.1, 157.0, 133.7, 129.7, 128.6, 126.1, 110.9, 86.5, 35.1, 12.1. HRMS (ESI) m/z: calcd. for $C_{12}H_{10}N_3OS$ $[M - H]^-$ 244.0550, found 244.0558.



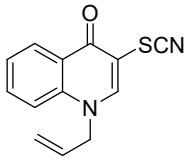
2p

3-thiocyanatoquinolin-4(1H)-one (2p)[3]: white solid, (20 mg, 99% yield), mp: 219 – 221 °C, eluent PE/Acetone (2:1, v/v). ^1H NMR (400 MHz, DMSO-d_6) δ: 12.64 (s, 1H), 8.59 (s, 1H), 8.16 (d, J = 7.2 Hz, 1H), 7.75 (t, J = 8.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 6.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (400 MHz, DMSO-d_6) δ: 173.2, 144.2, 139.6, 132.8, 125.2, 125.0, 124.5, 118.9, 111.8, 101.9.



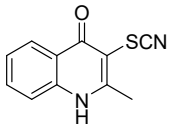
2q

1-methyl-3-thiocyanatoquinolin-4(1H)-one (2q): white solid, (20 mg, 92% yield), mp: 235 – 237 °C. eluent DCM/CH_3OH (15:1, v/v). ^1H NMR (400 MHz, DMSO-d_6) δ: 8.76 (s, 1H), 8.37 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 3.92 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ: 172.8, 149.5, 140.4, 133.1, 125.8, 125.3, 125.3, 117.5, 111.7, 101.2, 40.7. HRMS (ESI) m/z: calcd. for $C_{11}H_9N_2OS$ $[M + H]^+$ 217.0430, found 217.0423.



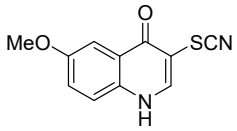
2r

1-allyl-3-thiocyanatoquinolin-4(1H)-one (2r): white solid, (16 mg, 66% yield), mp: 78 – 80 °C. eluent PE/Acetone (2:1, v/v). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.76 (s, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.81 (t, J = 7.2 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 6.08 – 6.02 (m, 1H), 5.25 (d, J = 10.8 Hz, 1H), 5.16 (d, J = 17.4 Hz, 1H), 5.03 (d, J = 4.8 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ: 172.8, 148.8, 139.5, 133.0, 132.5, 126.0, 125.5, 125.2, 118.2, 117.8, 111.6, 102.1, 54.5. HRMS (ESI) m/z: calcd. for $C_{13}H_{11}N_2OS$ [M + H]$^+$ 243.0587, found 243.0583.



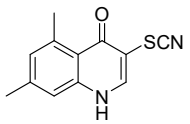
2s

2-methyl-3-thiocyanatoquinolin-4(1H)-one (2s)[3]: yellow solid, (21 mg, 97% yield), mp: 252 – 254 °C, eluent DCM/CH_3OH (15:1, v/v). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 12.42 (s, 1H), 8.11 (d, J = 12.0 Hz, 1H), 7.73 (t, J = 12.0 Hz, 1H), 7.57 (d, J = 12.0 Hz, 1H), 7.42 (t, J = 12.0 Hz, 1H), 2.67 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ: 173.6, 155.8, 139.4, 133.3, 125.8, 125.2, 124.1, 118.7, 112.2, 101.4, 20.6.



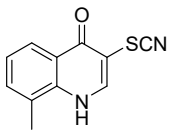
2t

6-methoxy-3-thiocyanatoquinolin-4(1H)-one (2t): yellow solid, (22 mg, 94% yield), mp: 240 – 242 °C, eluent DCM/CH_3OH (10:1, v/v). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 12.85 (s, 1H), 8.5 (s, 1H), 7.65 (d, J = 9.0 Hz,1H), 7.53 (d, J = 3.0 Hz, 1H), 7.38 (dd, J = 9.0, 3.0 Hz, 1H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ: 172.6, 156.7, 142.8, 134.2, 125.7, 123.0, 120.8, 111.9, 104.5, 100.7, 55.5. HRMS (ESI) m/z: calcd. for $C_{11}H_9N_2O_2S$ [M + H]$^+$ 233.0379, found 233.0370.



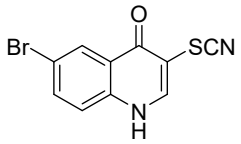
2u

5,7-dimethyl-3-thiocyanatoquinolin-4(1H)-one (2u): yellow solid, (21 mg, 91% yield), mp: > 260 °C. eluent PE/Acetone (1:1, v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.28 (s, 1H), 8.25 (s, 1H), 7.18 (s, 1H), 6.97 (s, 1H), 2.77, (s, 3H), 2.35(s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ: 174.9, 142.1, 141.8, 141.5, 139.3, 128,8, 120.7, 116.2, 112.1, 103.6, 23.0, 21.1. HRMS (ESI) m/z: calcd. for $C_{12}H_9N_2OS$ [M - H]$^-$ 229.0441, found 229.0435.



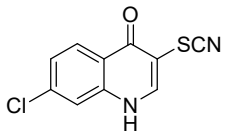
2v

7-methyl-3-thiocyanatoquinolin-4(1H)-one (2v): white solid, (18 mg, 83% yield), mp: > 280 °C. eluent DCM/CH_3OH (15:1, v/v). 1H NMR (400 MHz, DMSO-d_6) δ: 11.93 (s, 1H), 8.37 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 4.0 Hz, 1H), 7.36 (t, J = 8.0 HZ, 1H), 3.36 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ: 173.5, 143.4, 138.2, 133.6, 127.3, 124.7, 124.6, 123.1, 111.9, 102.5, 17.3. HRMS (ESI) m/z: calcd. for $C_{11}H_7N_2OS$ $[M - H]^-$ 215.0285, found 215.0281.



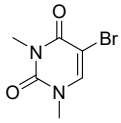
2w

6-bromo-3-thiocyanatoquinolin-4(1H)-one (2w): white solid, (28 mg, 99% yield), mp: 223 – 225 °C. eluent PE/Acetone (2:1, v/v). 1H NMR (600 MHz, DMSO-d_6) δ: 12.77 (s, 1H), 8.61 (s, 1H), 8.20 (d, J = 2.4 Hz, 1H), 7.87 (dd, J = 9.0, 2.4 Hz, 1H), 7.59 (d, J = 9.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ: 172.0, 144.5, 138.5, 135.5, 127.2, 125.8, 121.5, 117.6, 111.6, 102.6. HRMS (ESI) m/z: calcd. for $C_{10}H_4BrN_2OS$ $[M - H]^-$ 278.9233, found 278.9232.



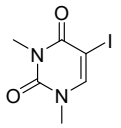
2x

7-chloro-3-thiocyanatoquinolin-4(1H)-one (2x): yellow solid, (20 mg, 85% yield), mp: 242 – 244 °C, eluent PE/Acetone (2:1, v/v). 1H NMR (400 MHz, DMSO-d_6) δ: 12.66 (s, 1H), 8.63 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.66 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ: 173.2, 145.4, 140.9, 137.9, 128.0, 125.9, 123.7, 118.7, 112.2, 103.4. HRMS (ESI) m/z: calcd. for $C_{10}H_4ClN_2OS$ $[M - H]^-$ 234.9738, found 234.9731.



3a

5-bromo-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (3a)[4]: white solid, (20 mg, 91% yield), mp: 179 – 180 °C, eluent EtOAc. 1H NMR (400 MHz, $CDCl^3$) δ: 7.53 (s, 1H), 3.42 (s, 3H), 3.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 159.7, 151.2, 124.5, 95.9, 37.4, 29.3.



4a

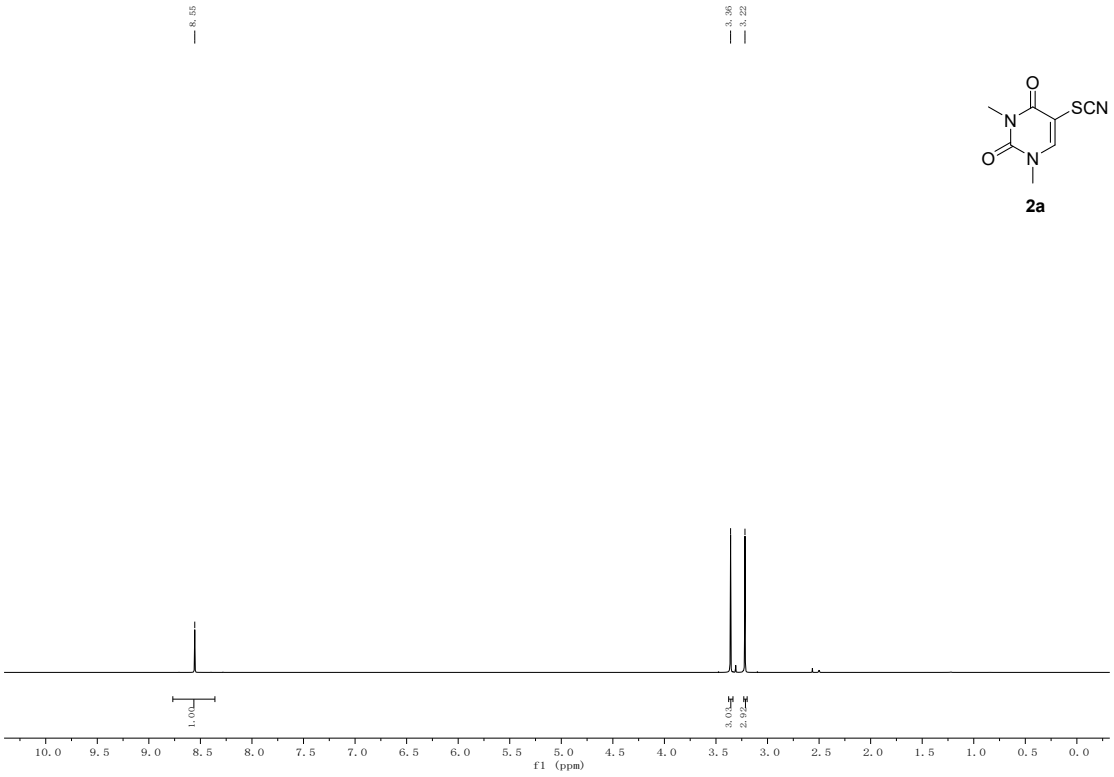
5-iodo-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (4a)[4]: white solid, (22 mg, 83% yield), mp: 140 – 142 °C, eluent EtOAc,. 1H NMR (400 MHz, DMSO-d_6) δ: 8.25 (s, 1H), 3.29 (s, 3H), 3.20 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ: 160.4, 151.2, 149.0, 66.3, 36.5, 28.8.

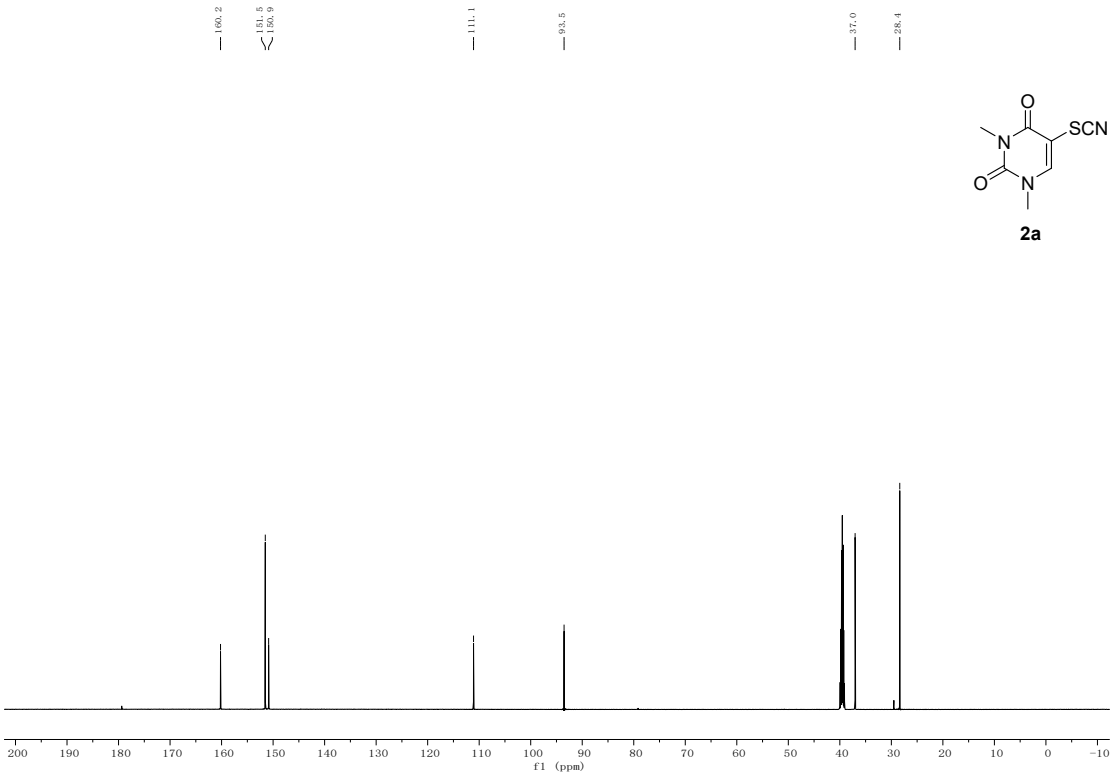
5. References

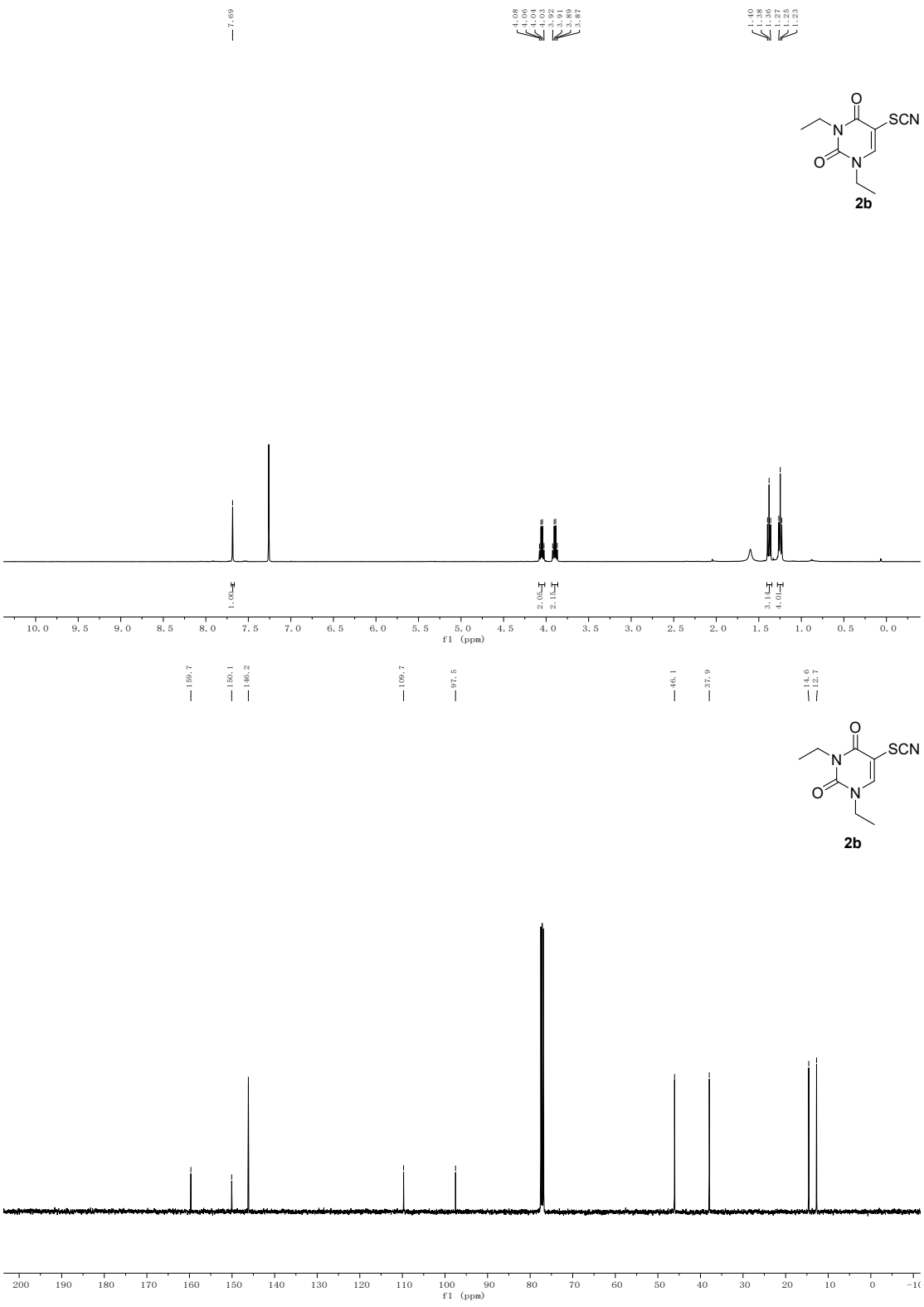
1. M. Noikham and S. Yotphan, *Eur. J. Org. Chem.*, 2019, 2759–2766.
2. P. Chauhan, R. Preeti, S. Kumar and N. Jain, *Eur. J. Org. Chem.*, 2019, 4334-4340.
3. D. Ail, A. K. Panday and L. H. Choudhury, *J. Org. Chem.*, 2020, **85**, 13610-13620.

4. J. Asakura and M. J. Robins, *J. Org. Chem.*, 1990, **55**, 4928-4933.

6. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra



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4.03
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3.91
3.89
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1.40
1.38
1.36
1.27
1.25
1.23
O
N
SCN
O
N
2b
1.00
2.05
2.15
3.14
4.01
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)
159.7
150.1
146.2
109.7
97.5
46.1
37.9
14.6
12.7
O
N
SCN
O
N
2b
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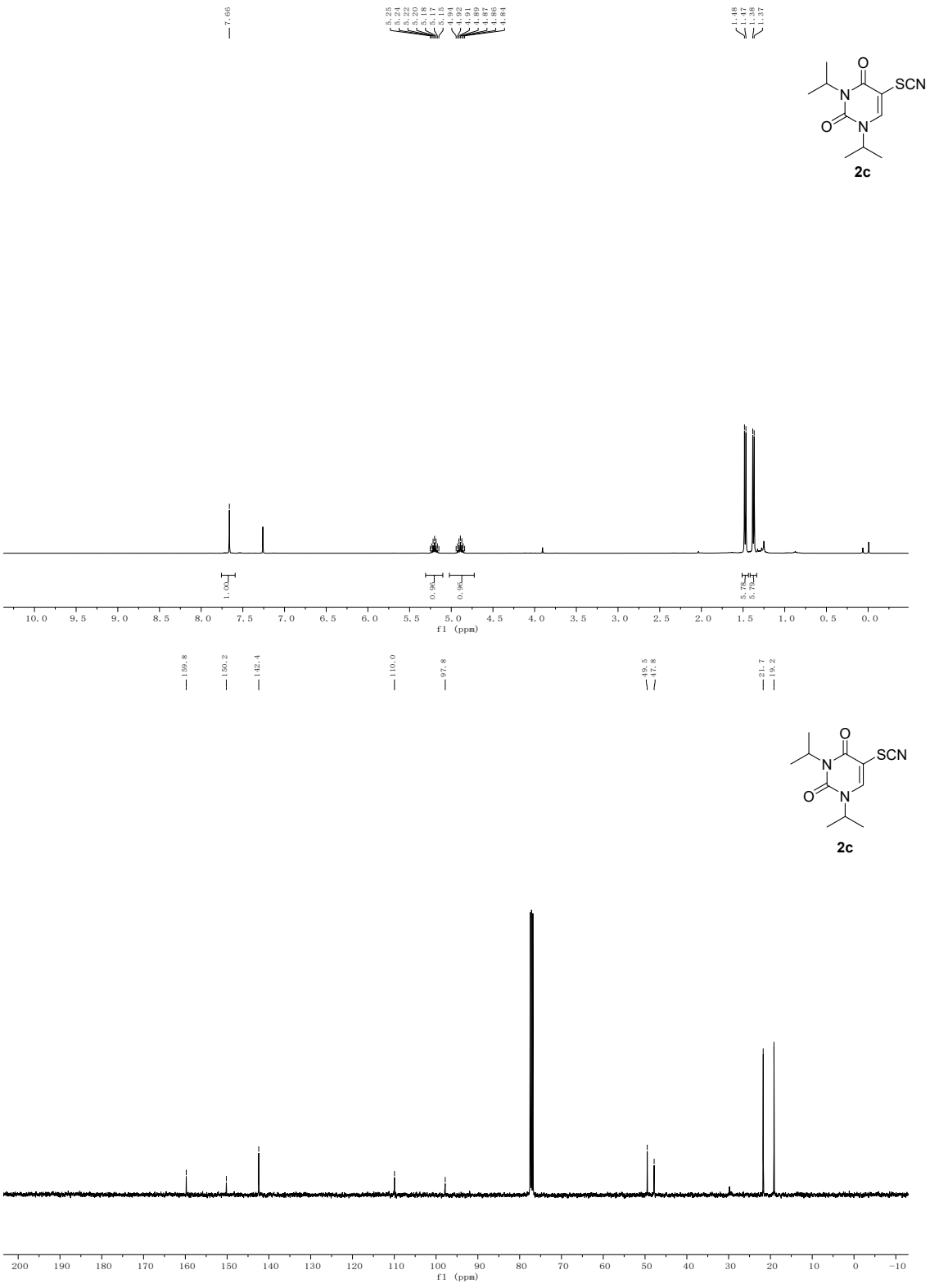
f1 (ppm)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5.15
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4.91
4.89
4.87
4.86
4.84
1.48
1.47
1.38
1.37
SCN
2c
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0.98
5.74
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f1 (ppm)
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142.4
110.0
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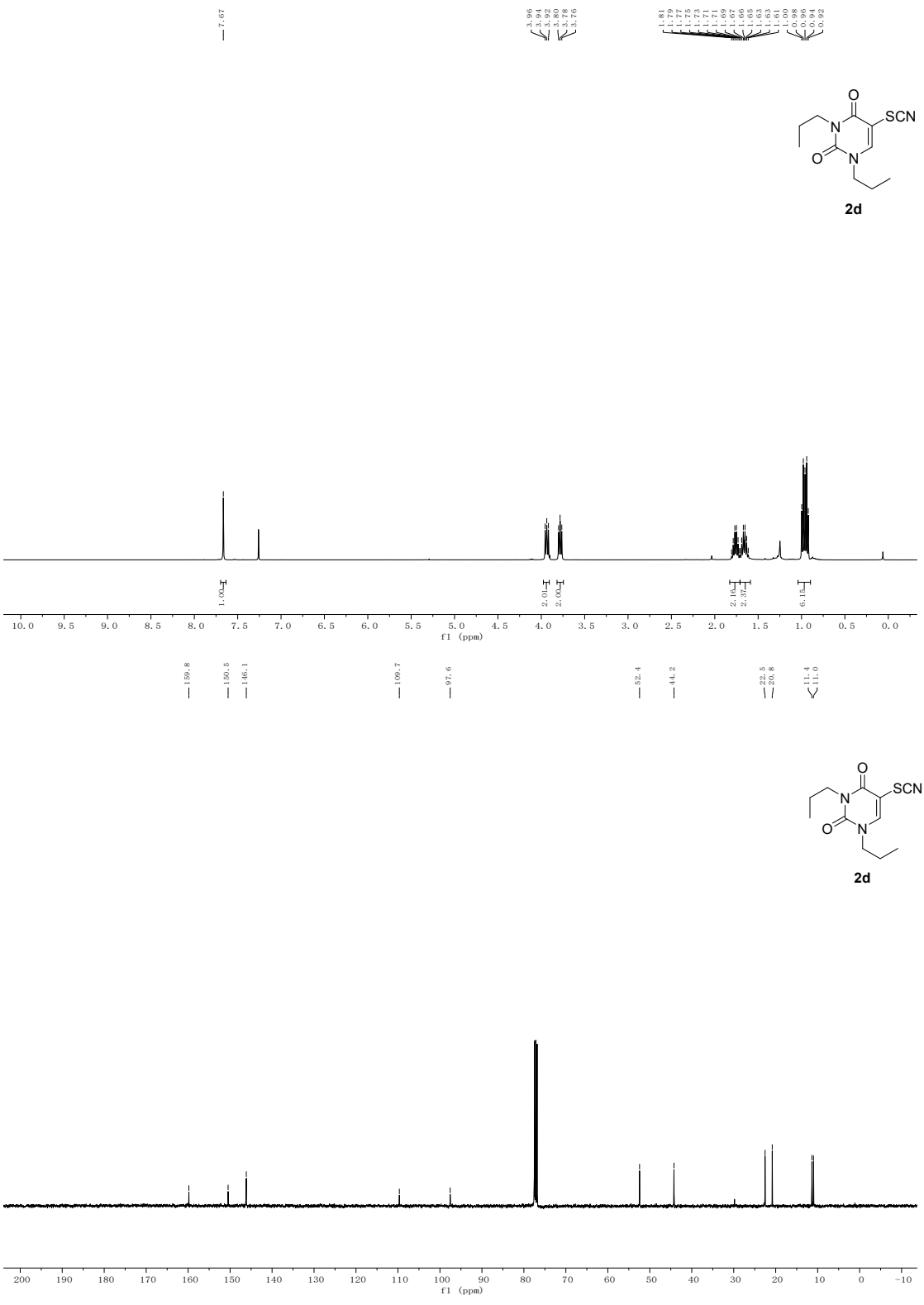
21.7
19.2
SCN
2c
f1 (ppm)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1.71
1.69
1.67
1.65
1.63
1.61
1.00
0.98
0.96
0.94
0.92
O
SCN
N
O
N
1.00
2.01
2.00
2.18
2.37
6.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
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150.5
146.1
109.7
97.6
52.4
44.2
22.5
20.8
11.4
11.0
2d
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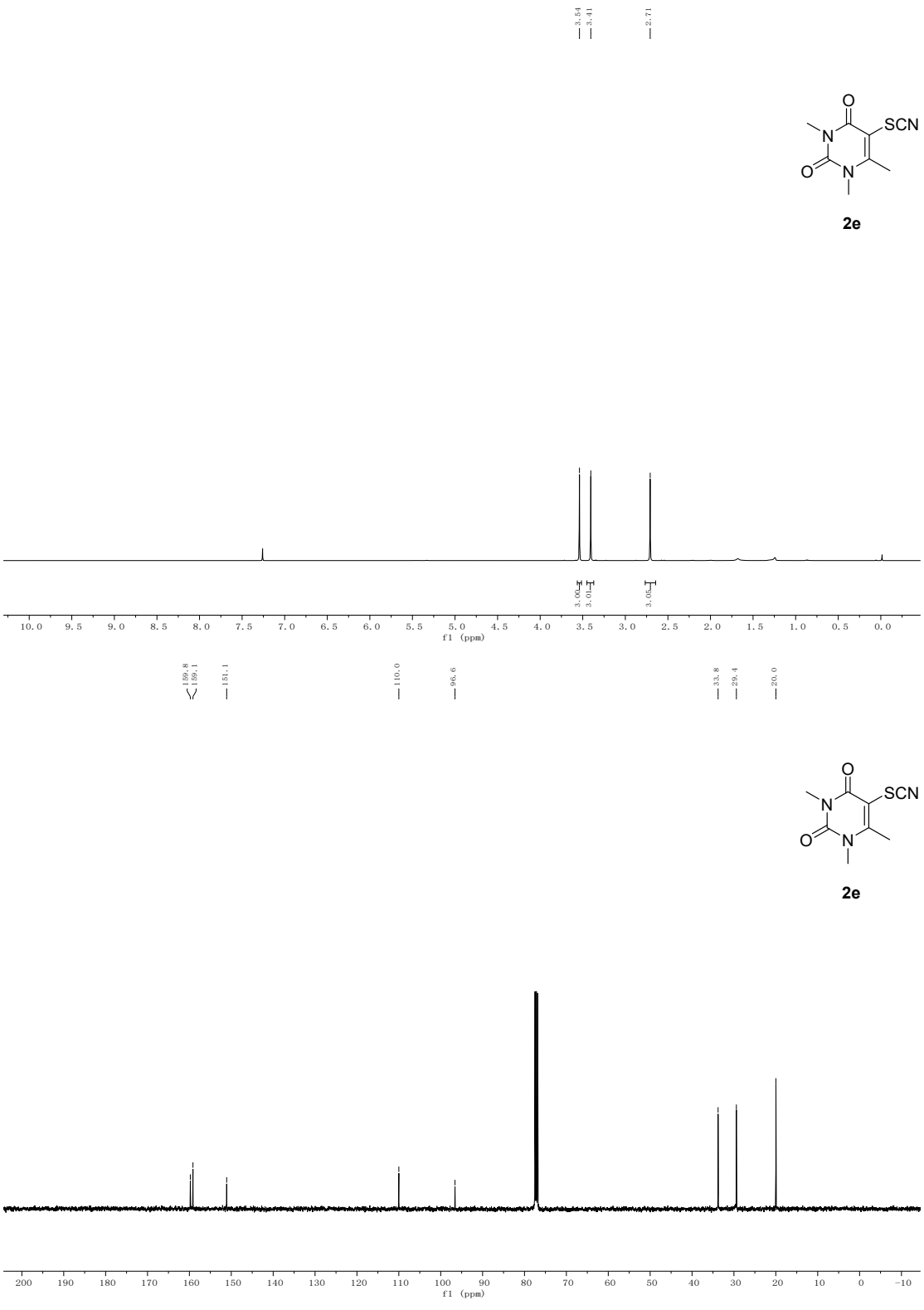
f1 (ppm)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3.01
3.04
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159.1
151.1
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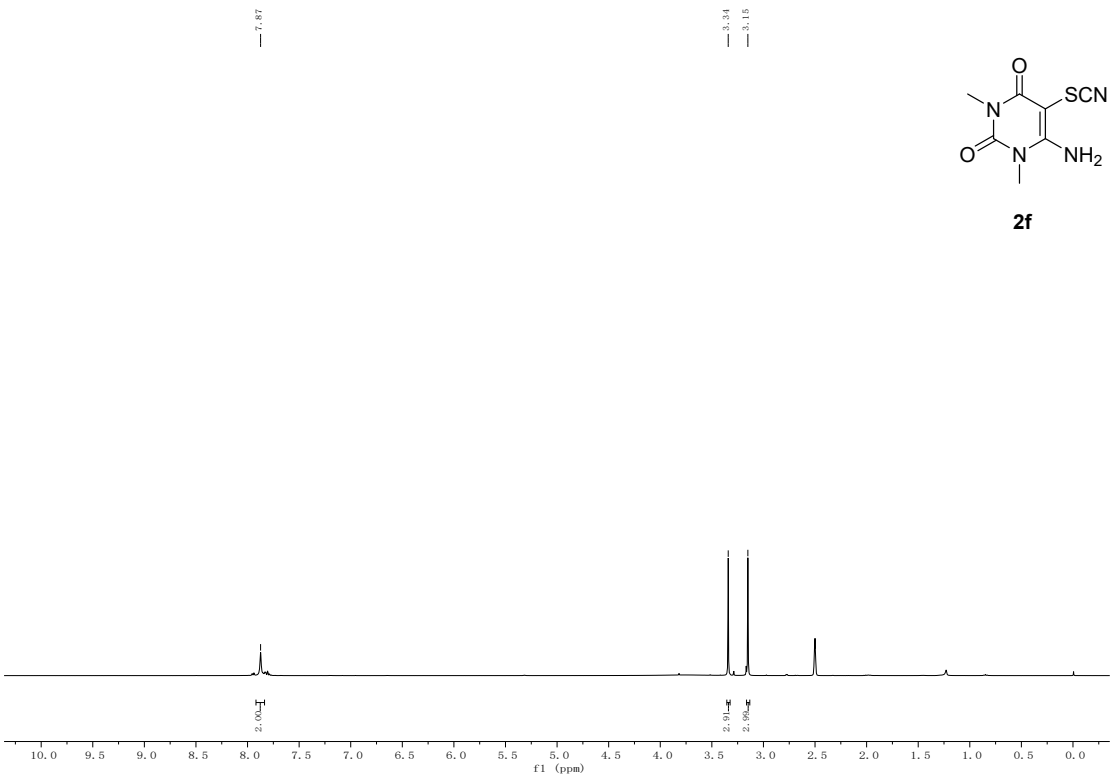
96.6
33.8
29.4
20.0
SCN
2e
f1 (ppm)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f1 (ppm)
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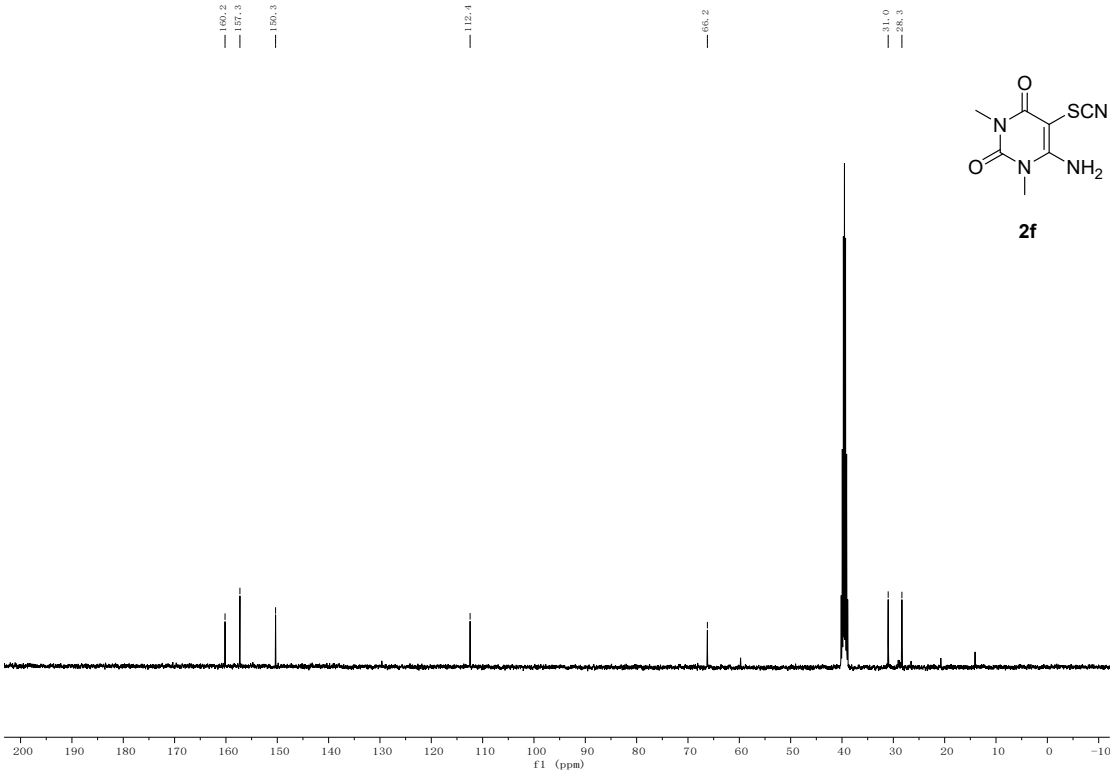
O
N
NH2

2f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f1 (ppm)
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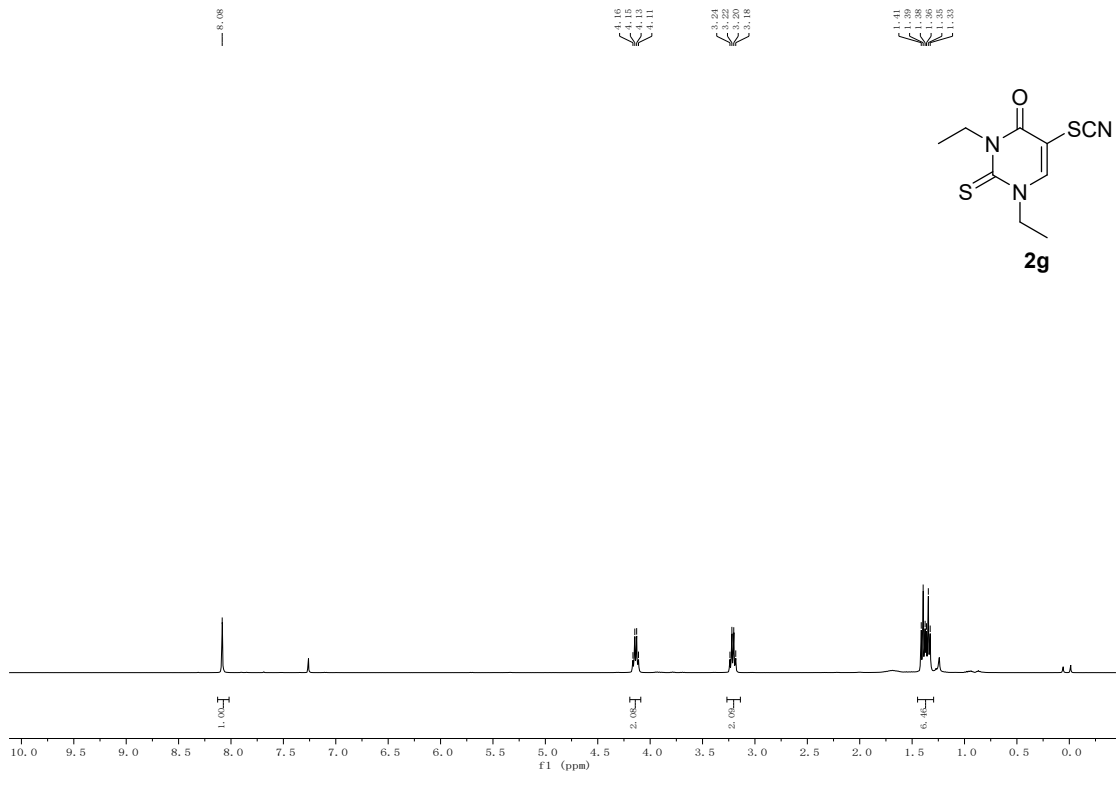
SCN
N
O
N
NH2

2f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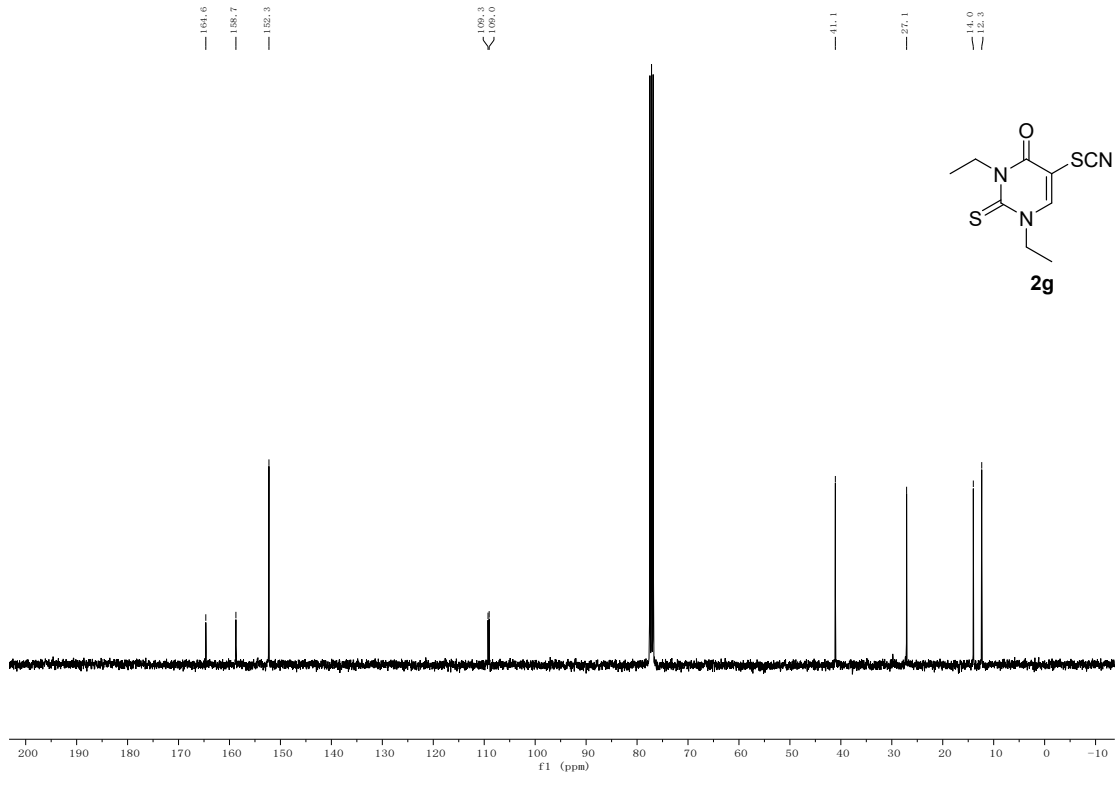
1.36
1.35
1.33
O
SCN
N
S
N
2g
1.00
2.08
2.09
6.46
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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27.1
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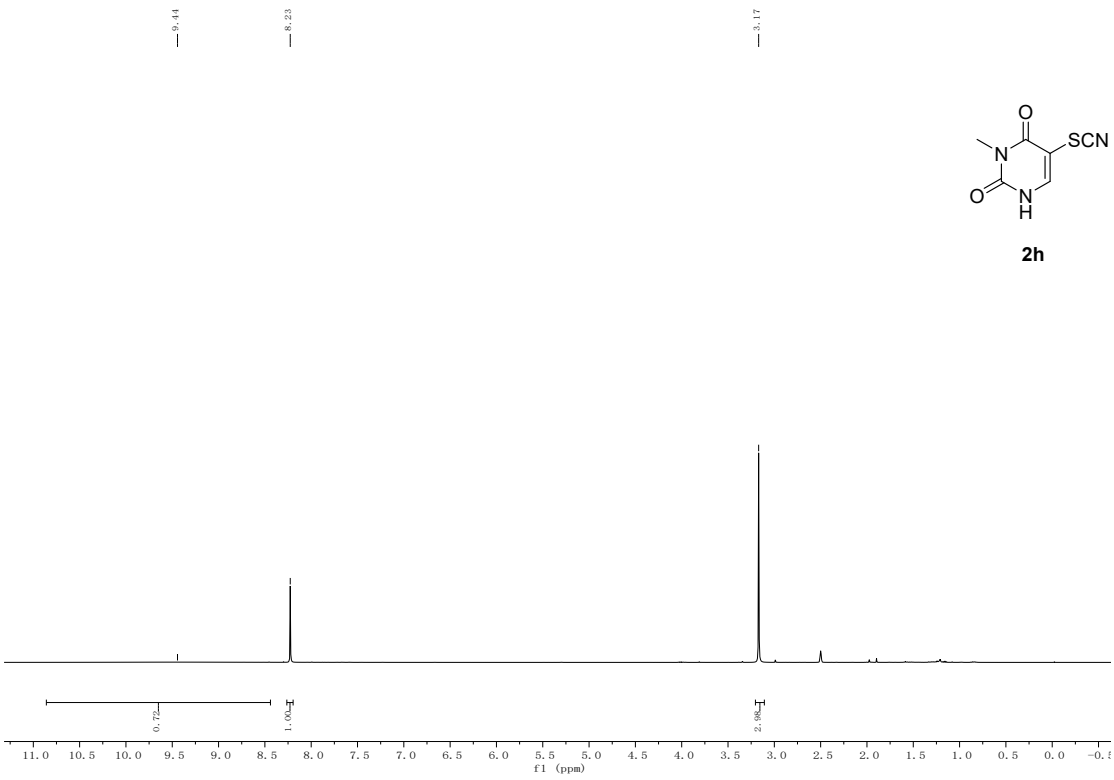
SCN
N
S
N
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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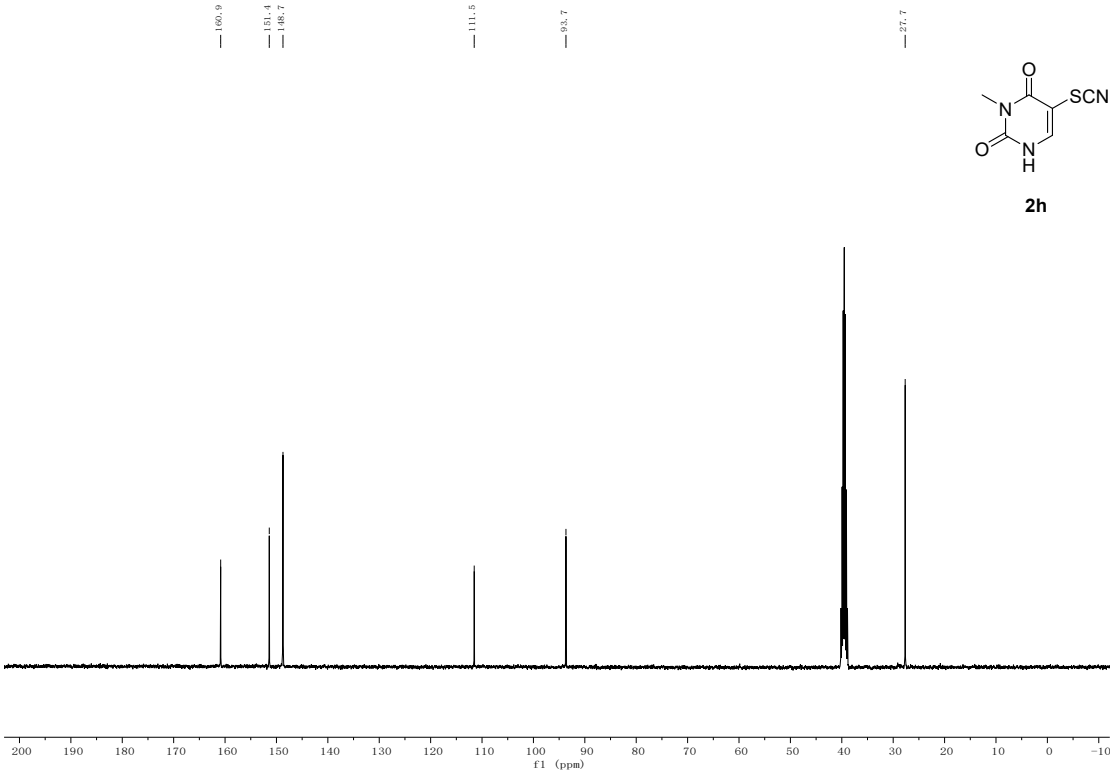
f1 (ppm)

2h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SCN
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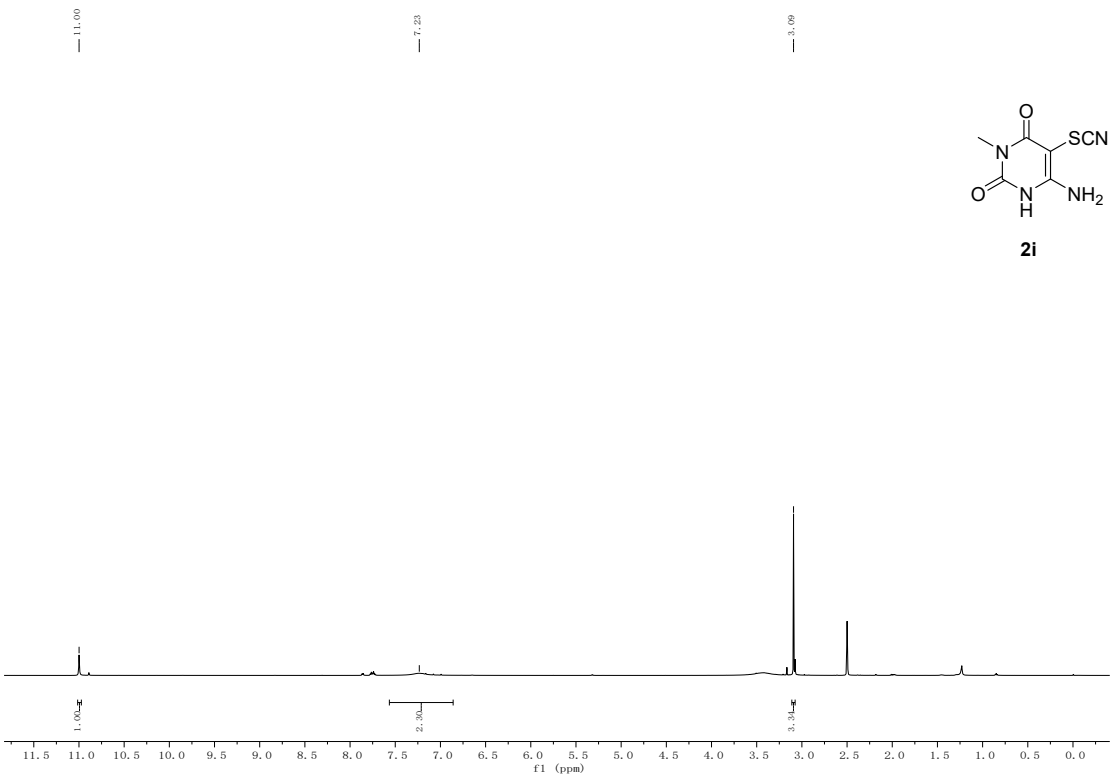
f1 (ppm)

2h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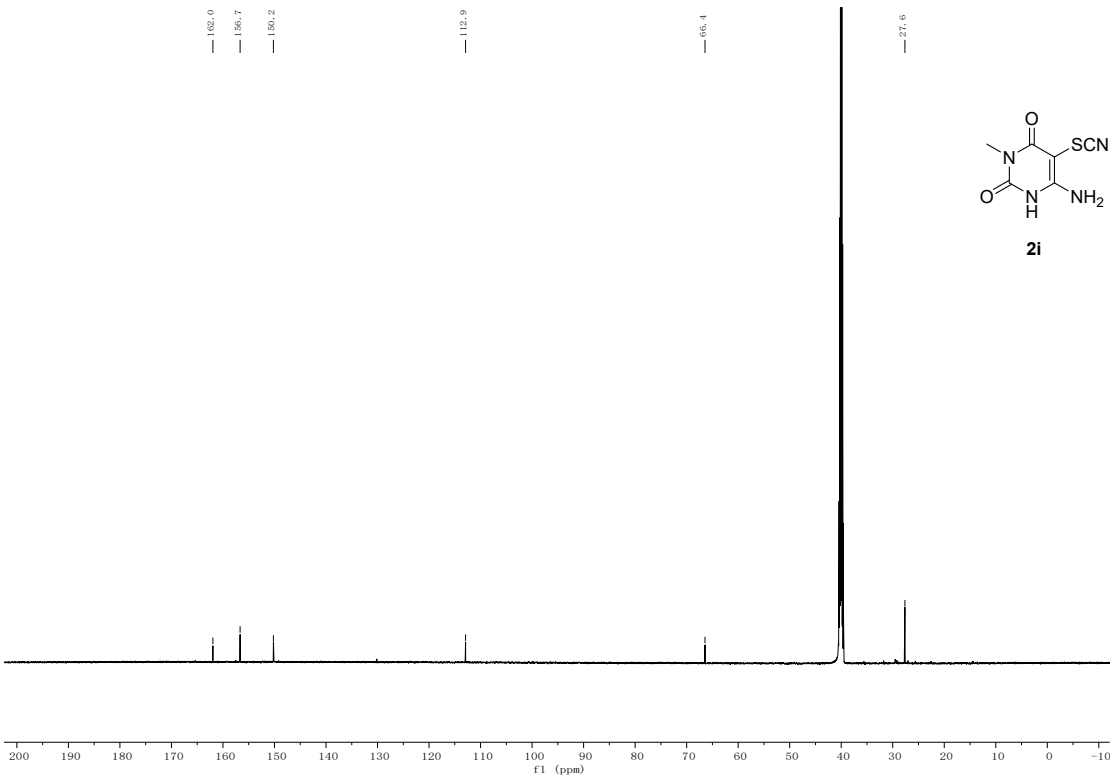
N
O
N
H
NH2

2i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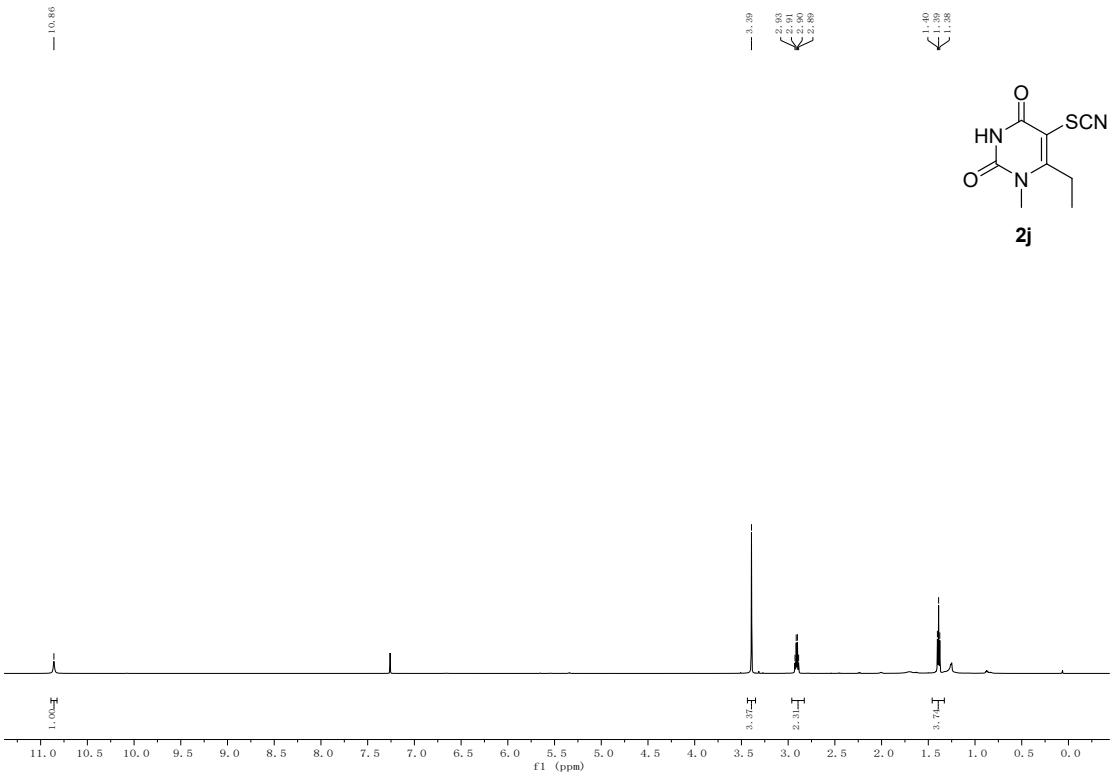
SCN
N
O
N
H
NH2

2i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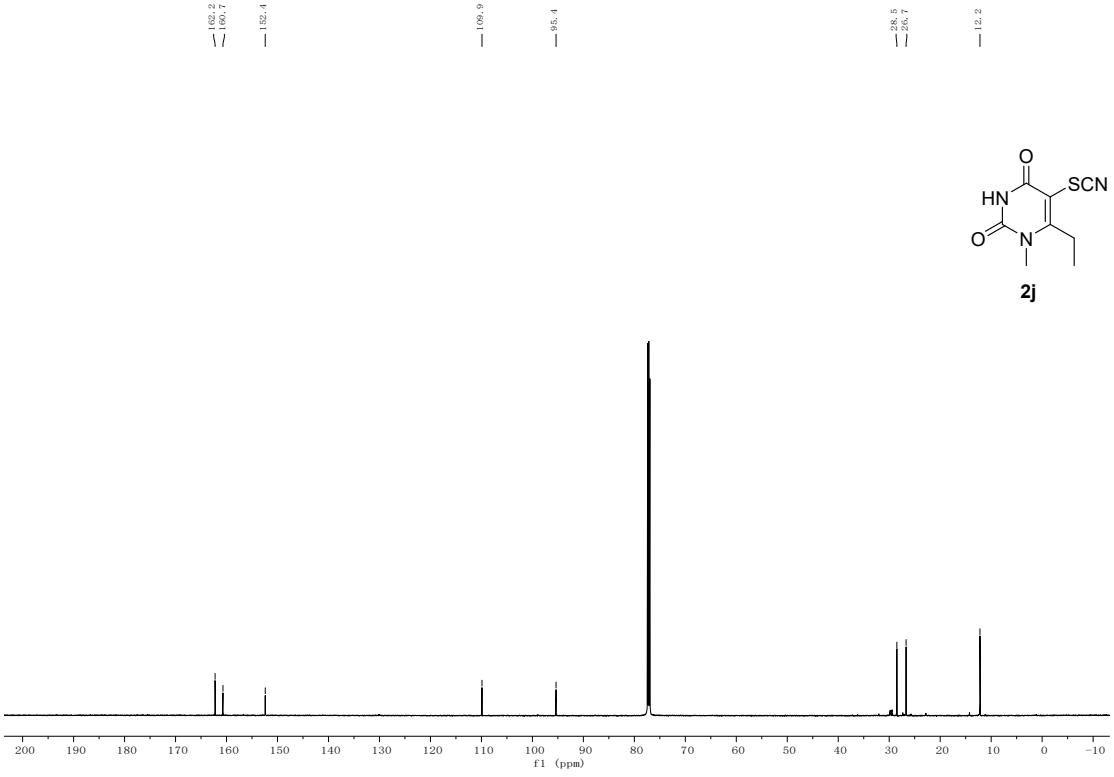
f1 (ppm)

2j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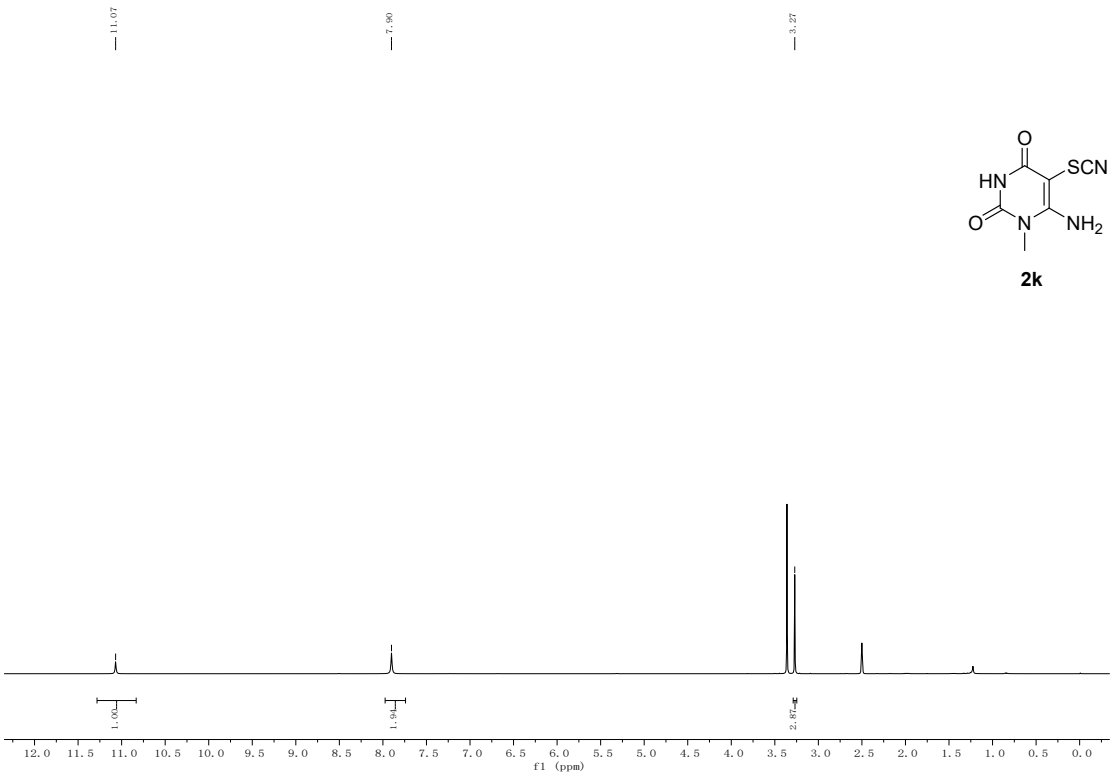
f1 (ppm)

2j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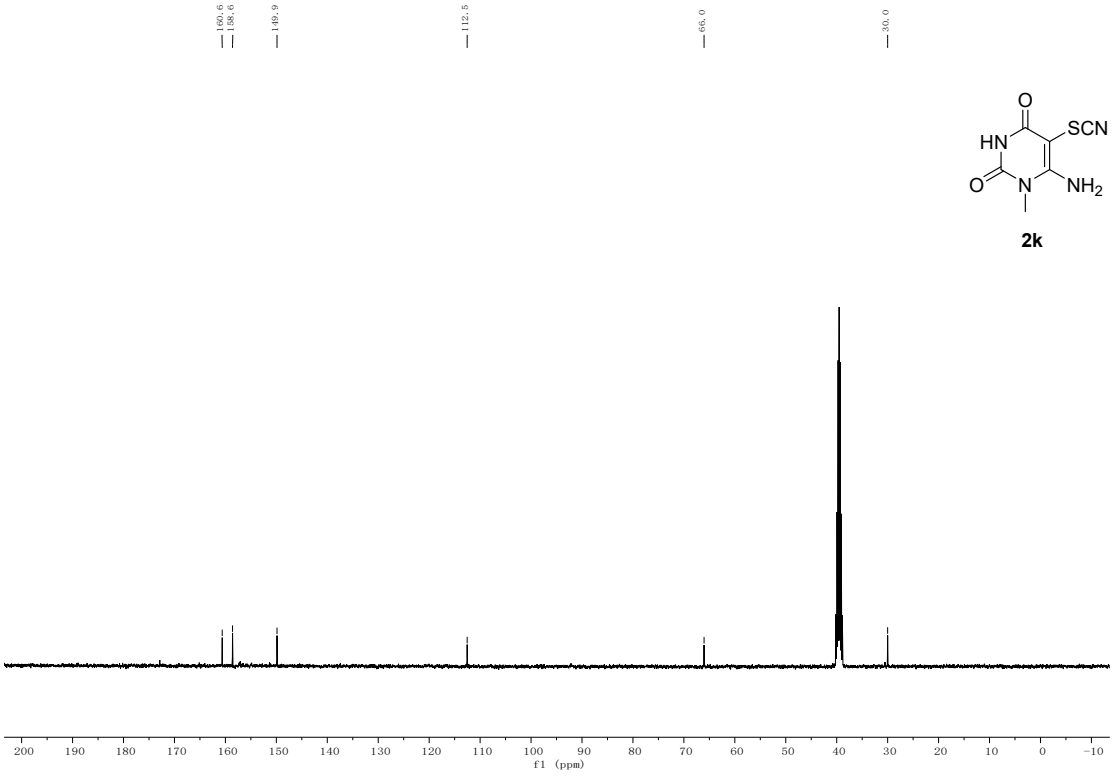
f1 (ppm)

O
HN
O
N
SCN
NH2

2k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f1 (ppm)

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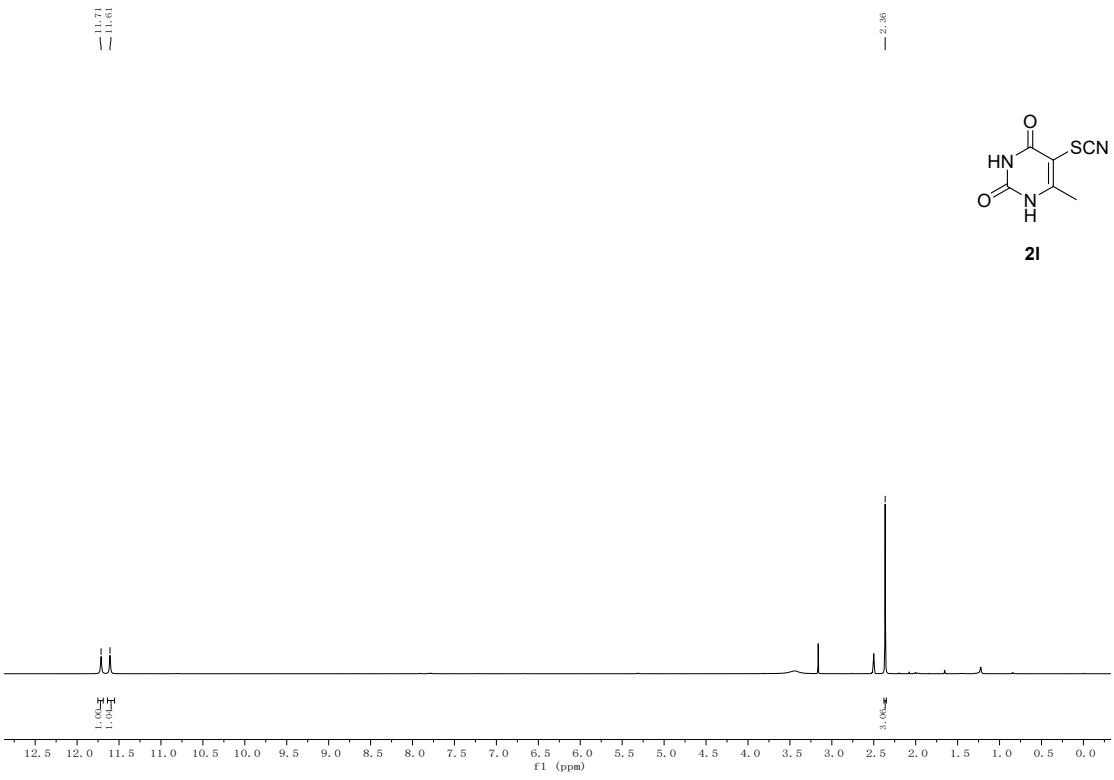
HN
O
N
SCN
NH2

2k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3.06
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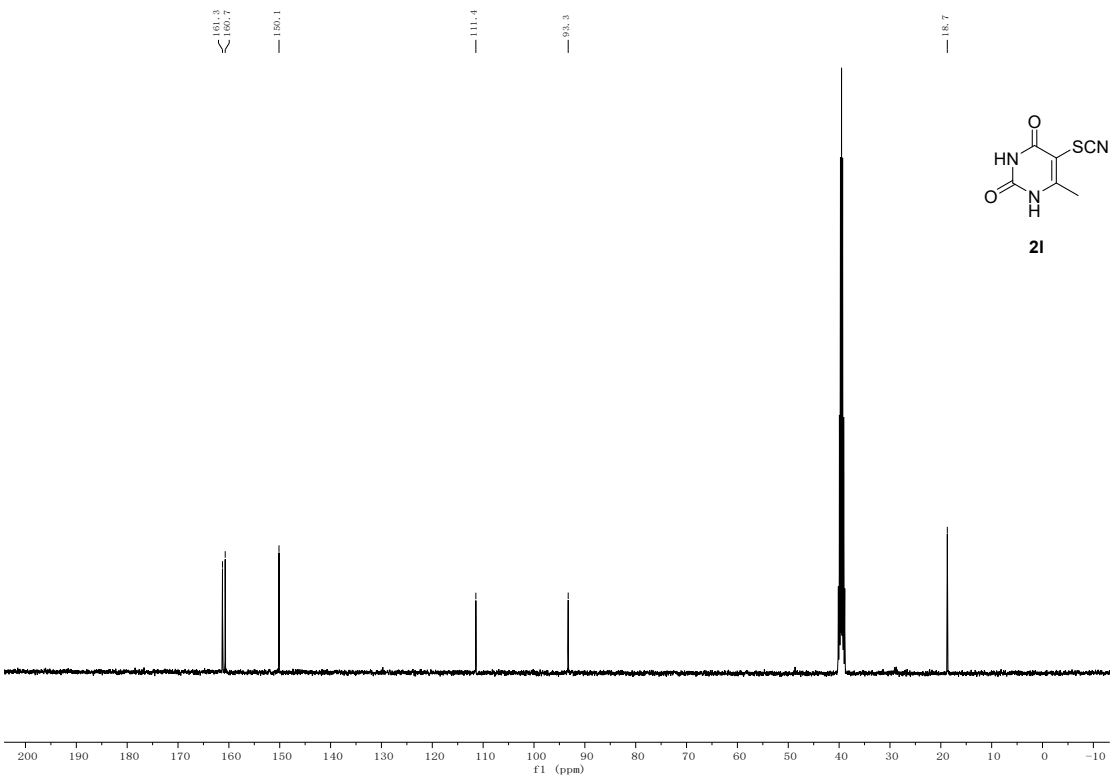
f1 (ppm)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111.4
93.3
18.7
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HN
O
N
H
SCN
2l
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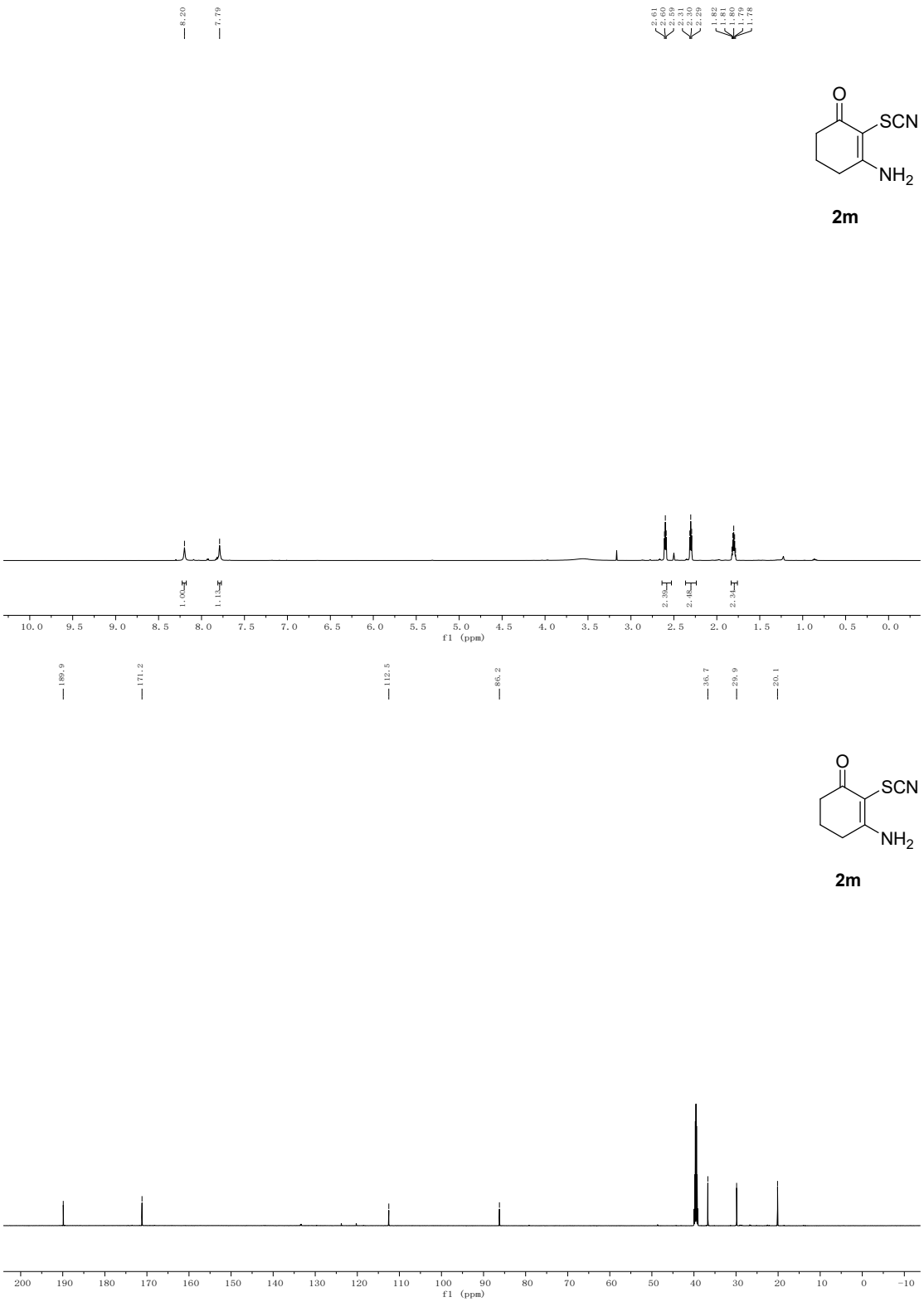
f1 (ppm)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O
SCN
NH2
1.00
1.13
2.38
2.40
2.34
f1 (ppm)
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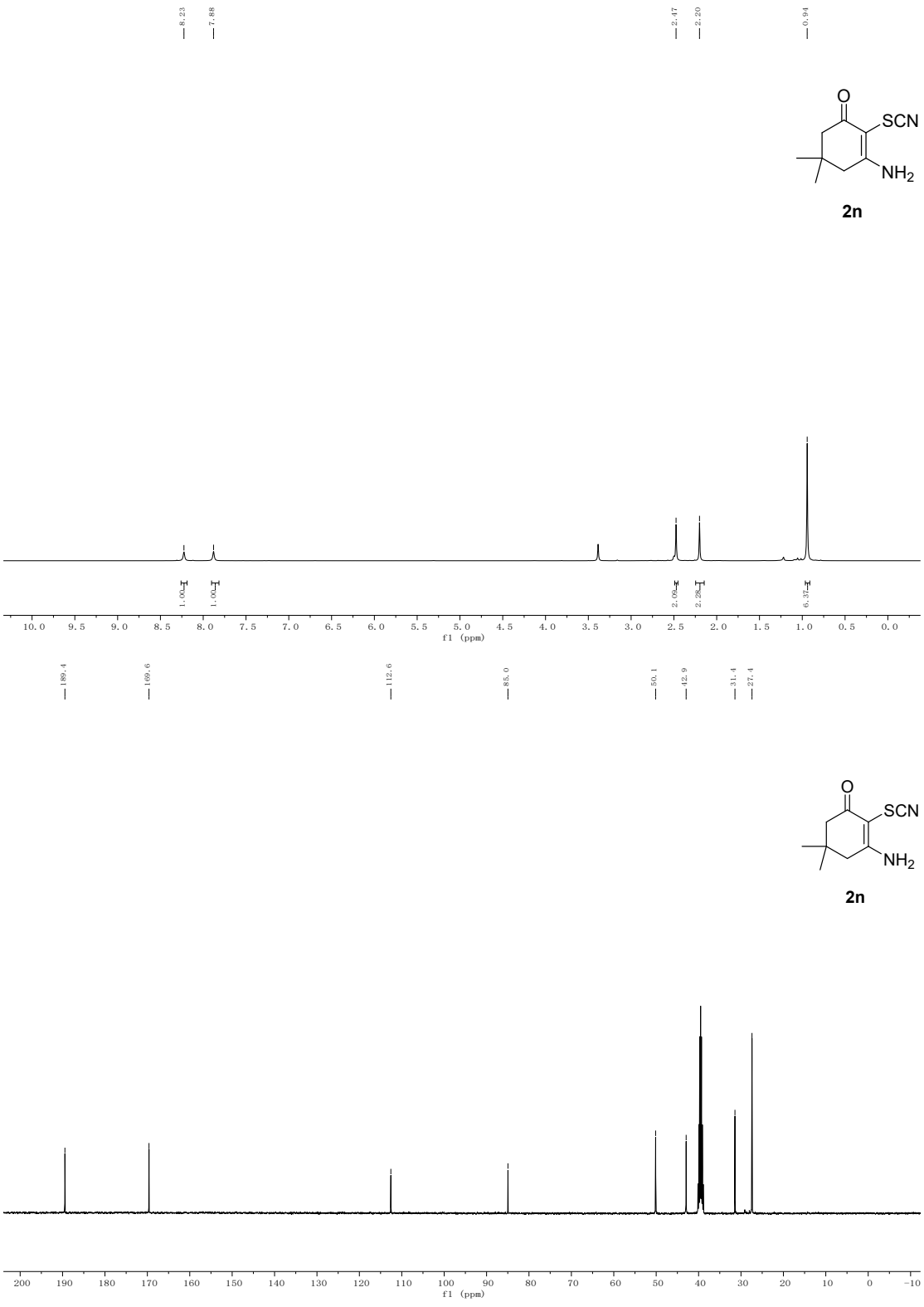
112.5
86.2
36.7
29.9
20.1
O
SCN
NH2
f1 (ppm)

2m

2m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f1 (ppm)
189.4
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50.1
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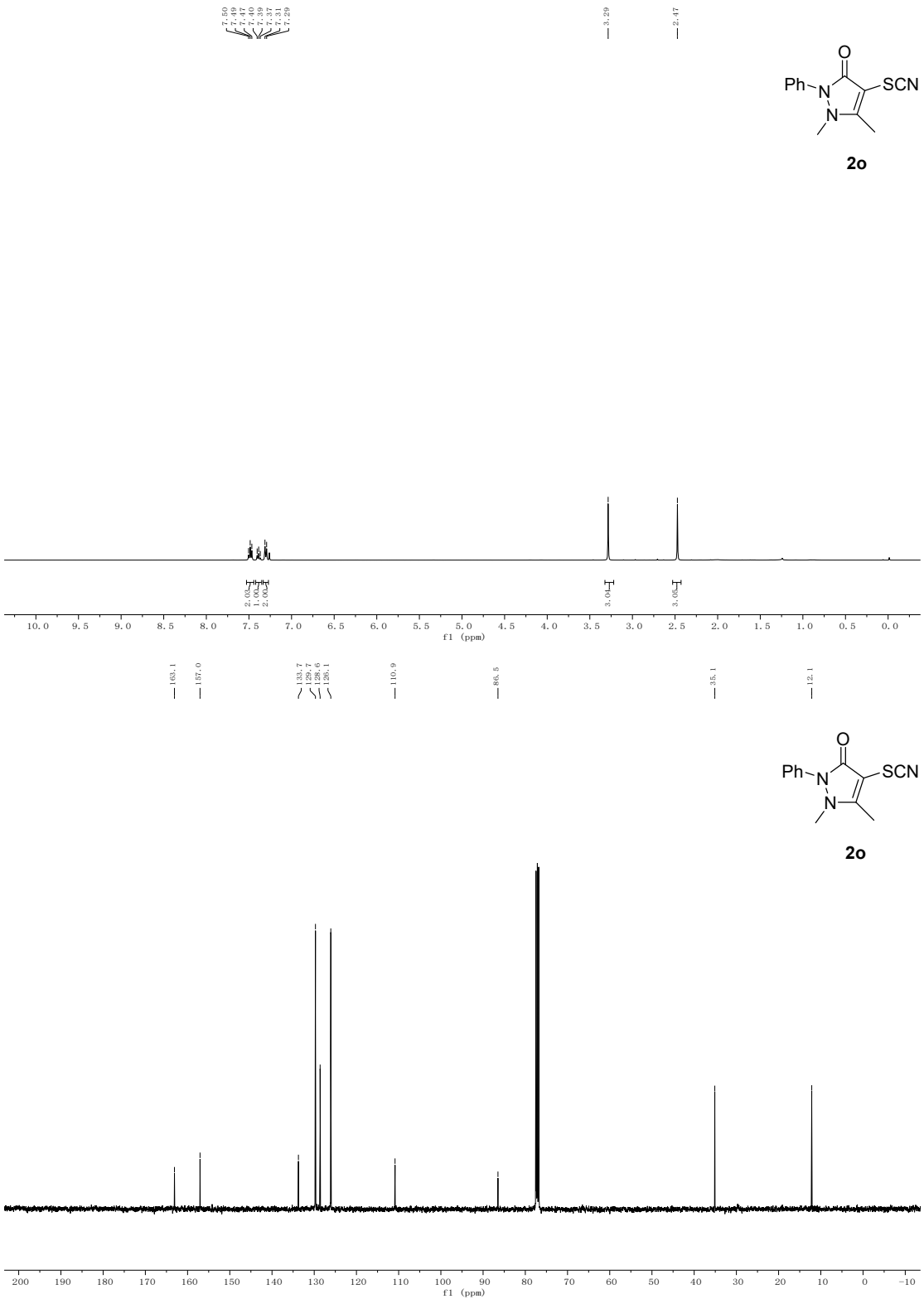
27.4
O
SCN
NH2
f1 (ppm)

2n

2n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7.37
7.31
7.29
3.29
2.47
Ph
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2.03
2.00
3.04
3.06
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)
163.1
157.0
133.7
129.7
126.6
126.1
110.9
86.5
35.1
12.1
Ph
N
N
O
SCN
2o
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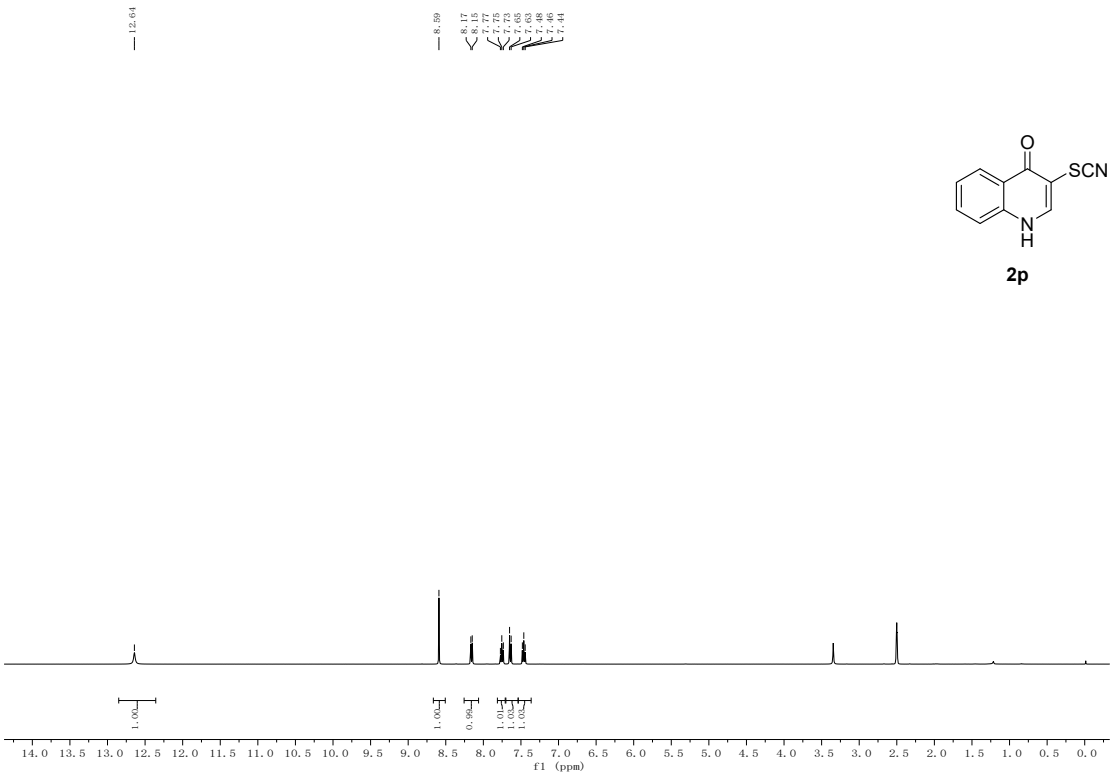
f1 (ppm)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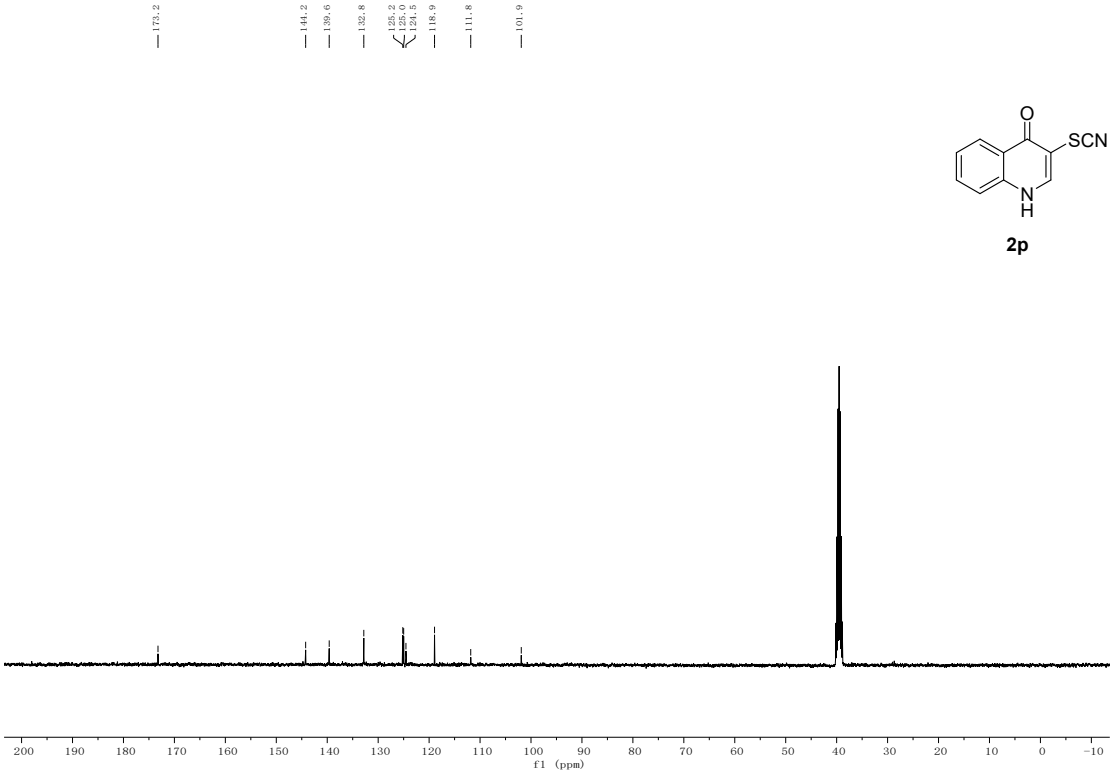
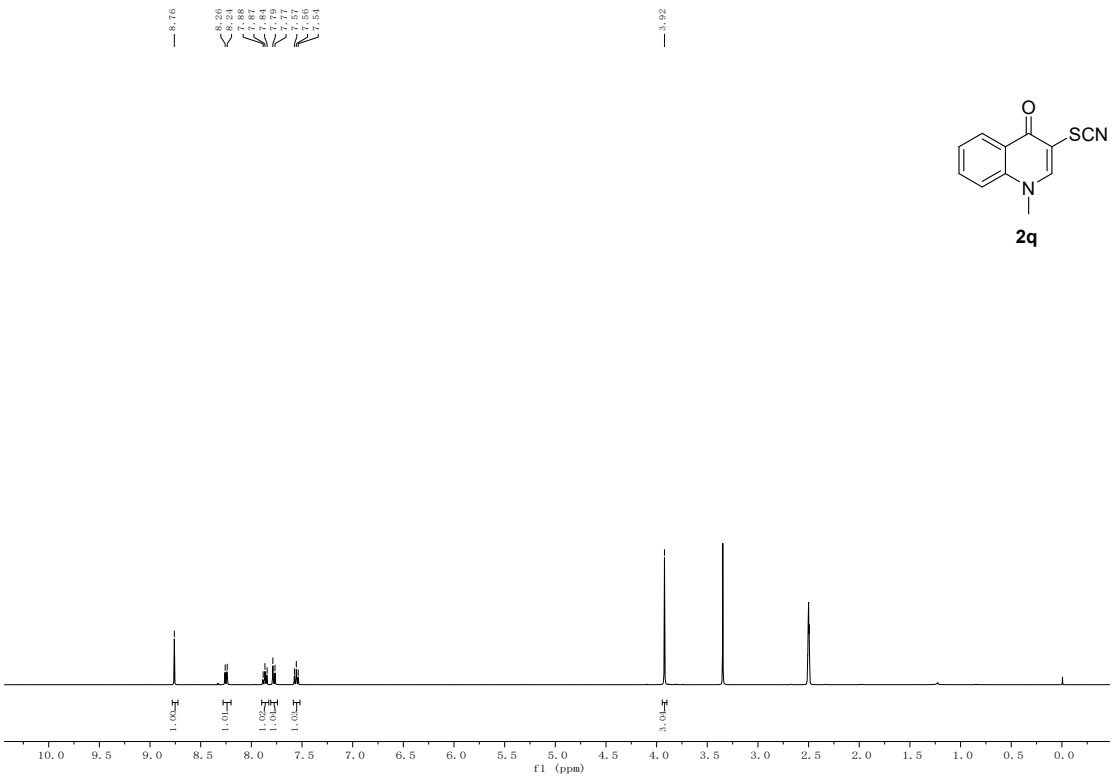
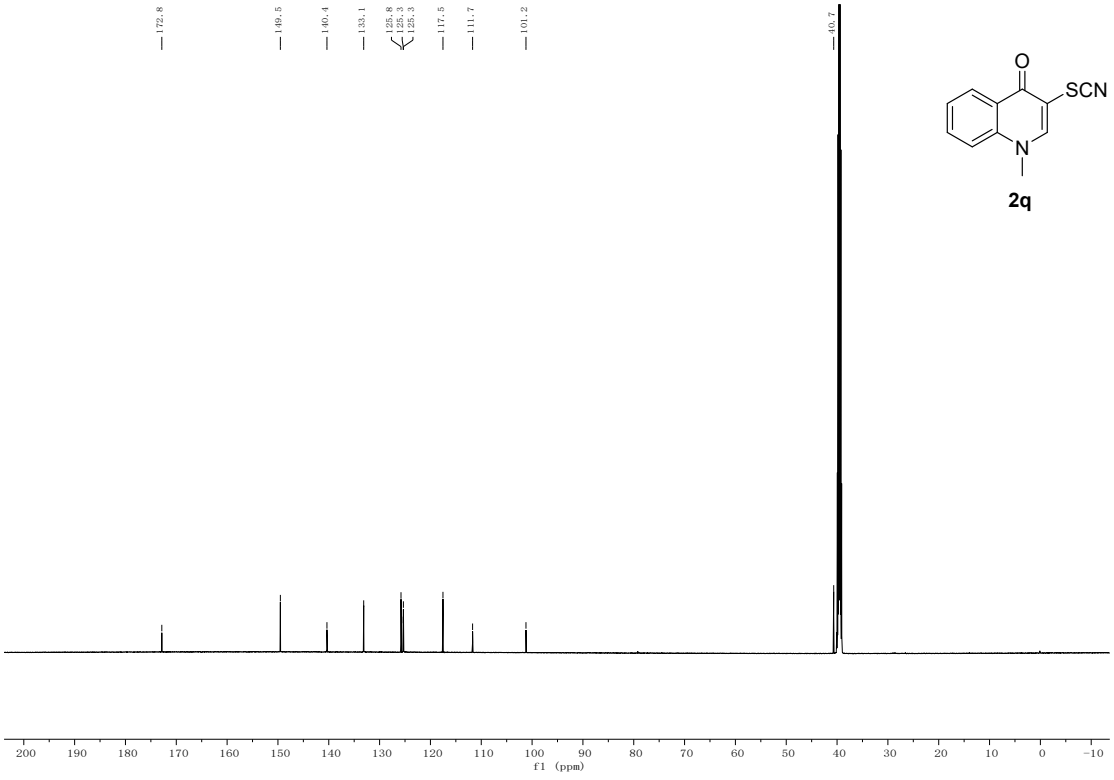
7.48
7.46
7.44
O
SCN
N
H
1.00
1.00
0.96
1.01
1.03
1.02
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2p

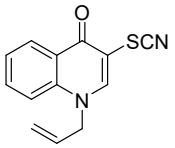

173.2
144.2
139.6
132.8
125.2
125.0
124.5
118.9
111.8
101.9
O
SCN
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2p

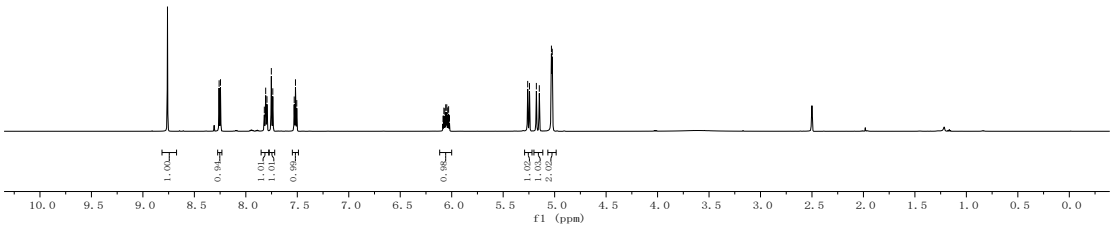

8.76
8.26
8.24
7.88
7.87
7.84
7.79
7.77
7.77
7.57
7.56
7.54
3.92
O
SCN
N
2q
1.00
1.01
1.02
1.04
1.03
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.8
149.5
140.4
133.1
125.8
125.3
125.3
117.5
111.7
101.2
40.7
O
SCN
N
2q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

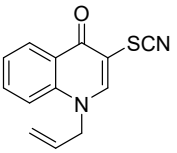

8.761
8.260
8.246
7.820
7.807
7.795
7.752
7.738
7.520
7.518
7.505
6.084
6.076
6.067
6.058
6.048
6.039
6.030
6.021
5.262
5.244
5.178
5.149
5.031
5.023


O
SCN
N

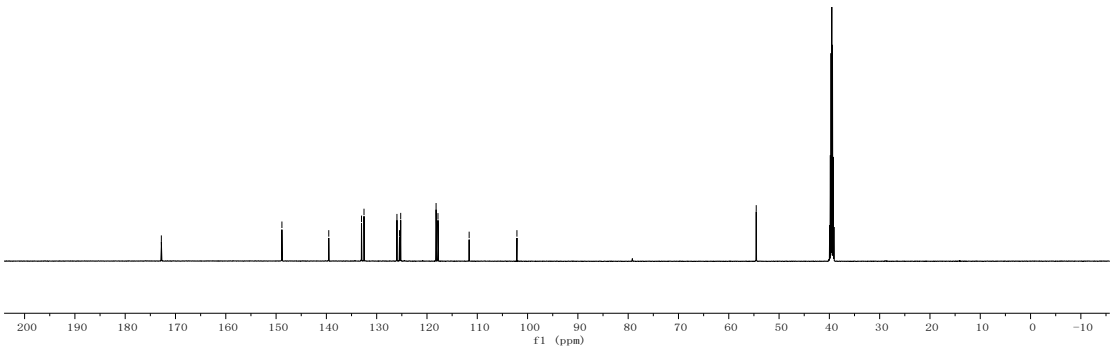
2r

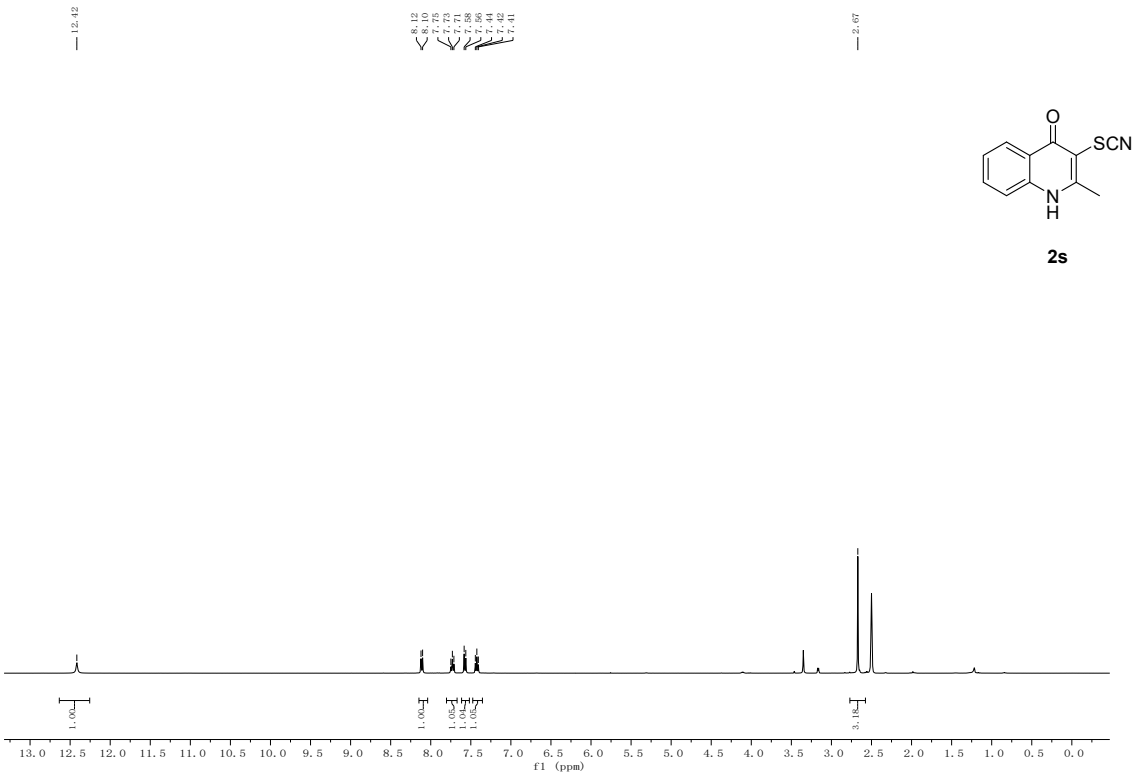

1.00
0.94
1.01
1.01
0.99
0.98
1.02
1.02
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.8
148.8
139.5
133.0
132.5
126.0
125.5
125.2
118.2
117.8
111.6
102.1
54.5

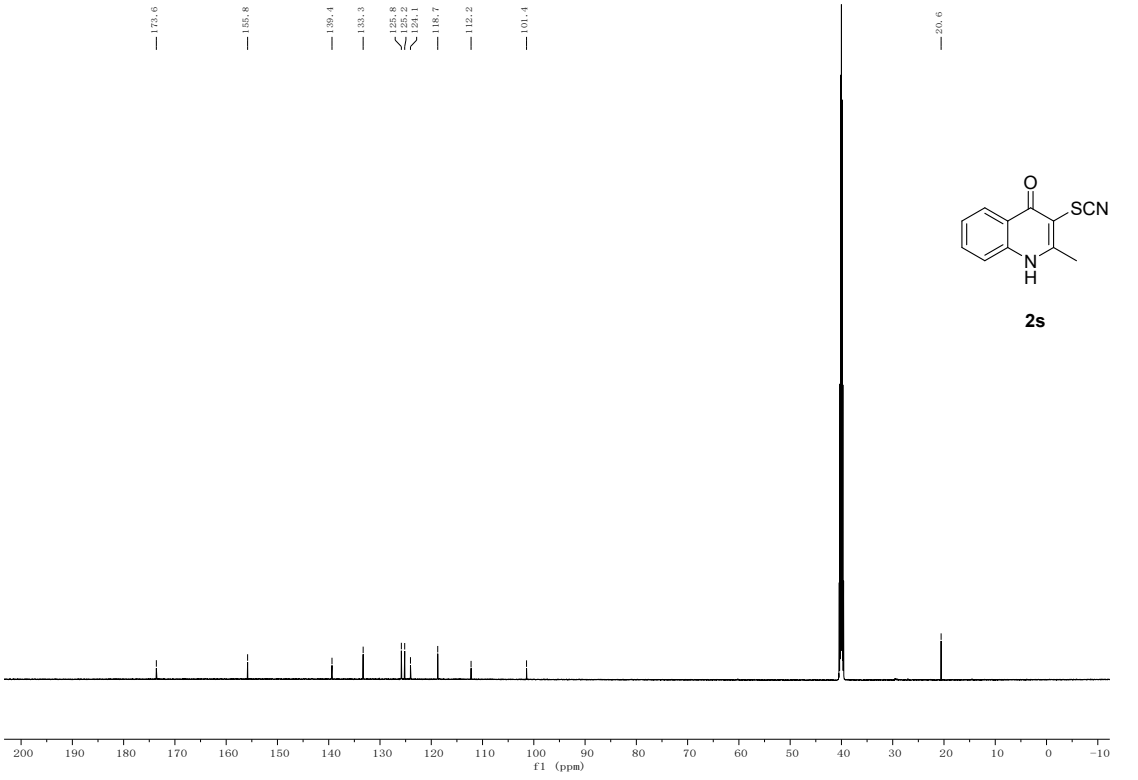

O
SCN
N

2r

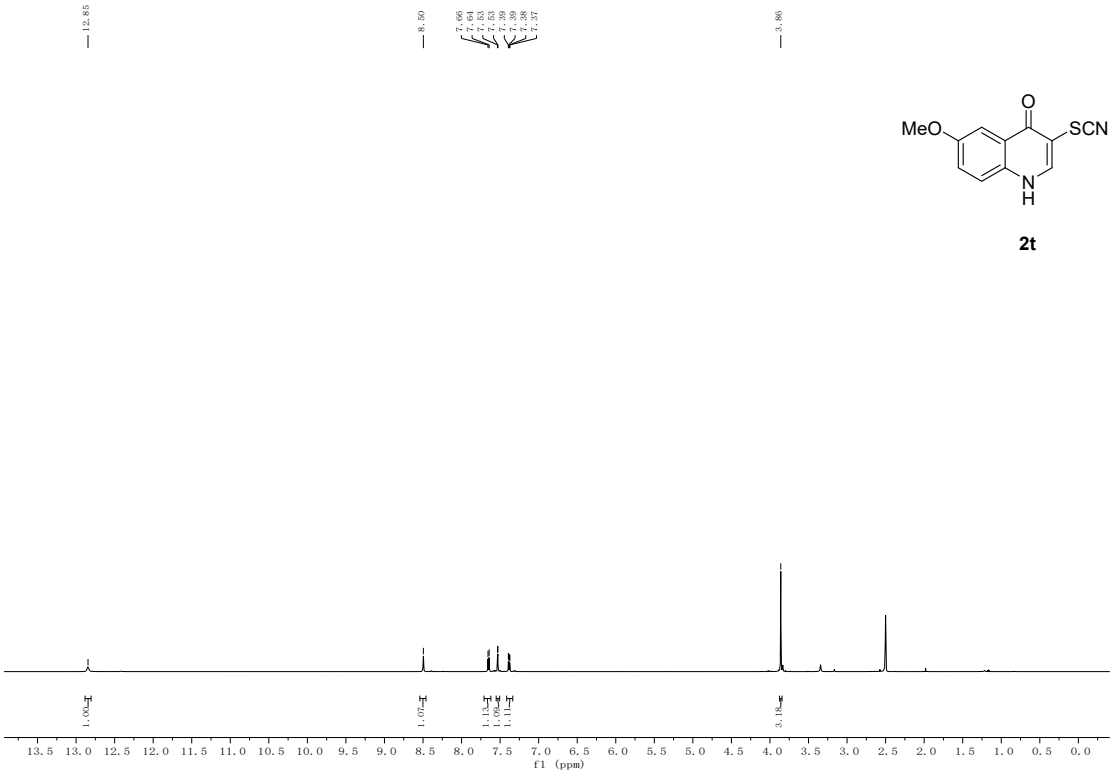

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


12.42
8.12
8.10
7.75
7.73
7.71
7.58
7.56
7.44
7.42
7.41
2.67
O
SCN
N
H
1.00
1.00
1.02
1.04
1.00
3.18
13.0 12.5 12.0 11.5 11.0 10.5 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)

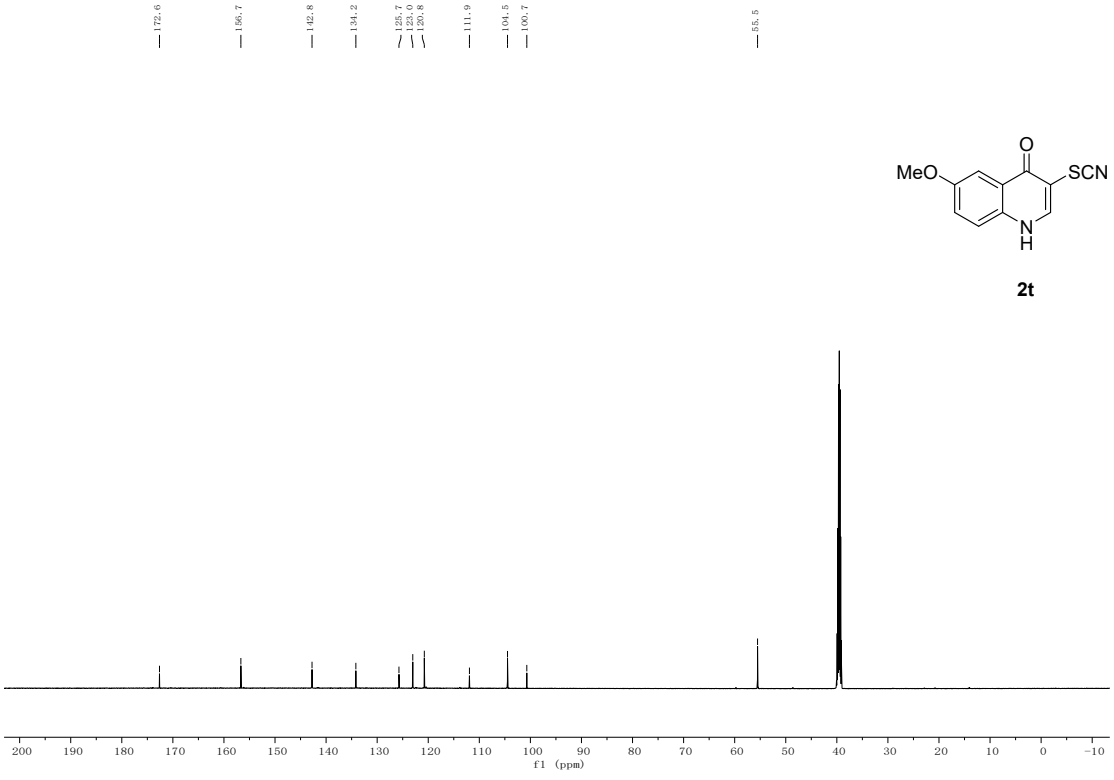
2s


173.6
155.8
139.4
133.3
125.8
125.2
124.1
118.7
112.2
101.4
20.6
O
SCN
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

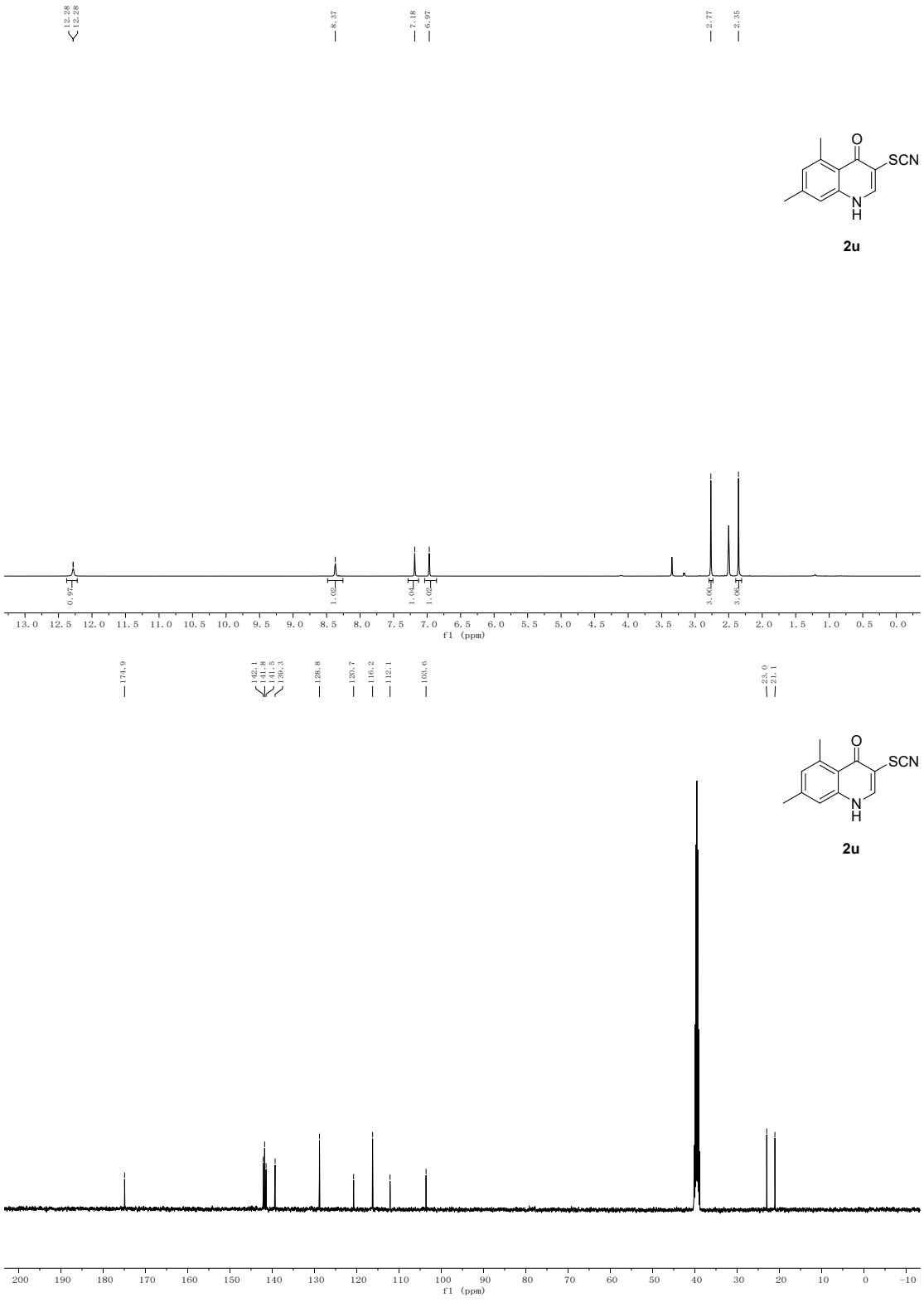
2s

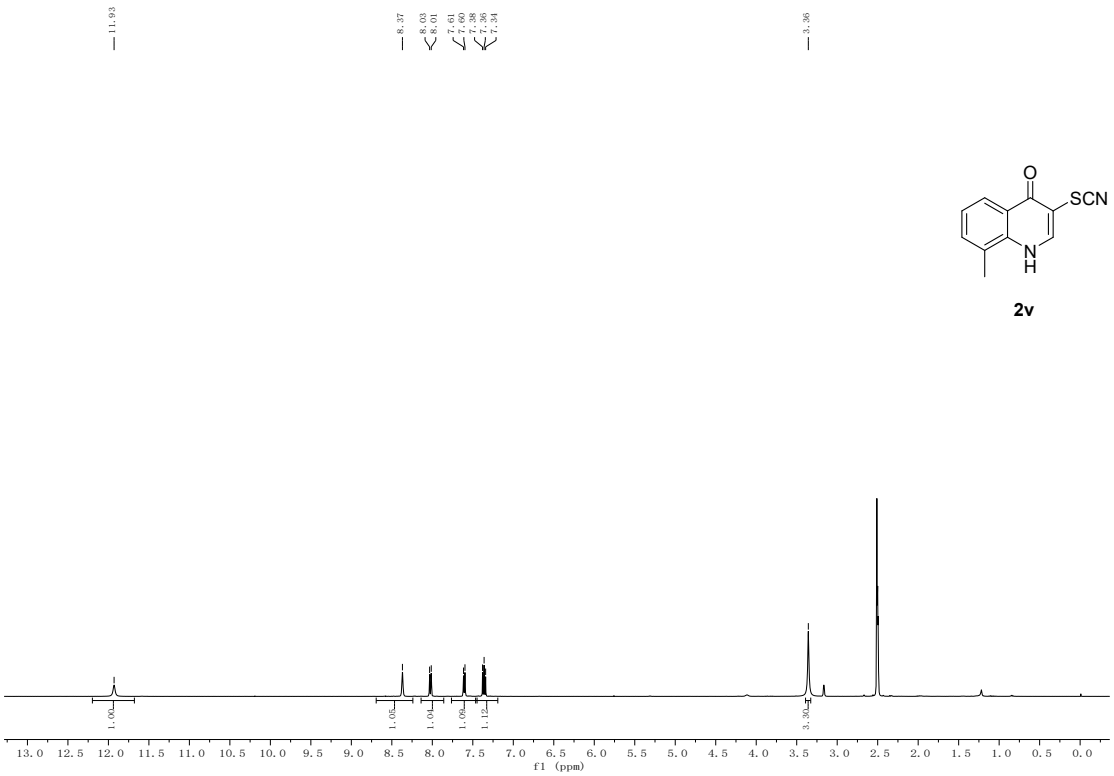

12.85
8.50
7.66
7.64
7.53
7.53
7.39
7.38
7.37
3.86
MeO
SCN
O
N
H
1.00
1.07
1.13
1.09
1.11
3.18
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2t

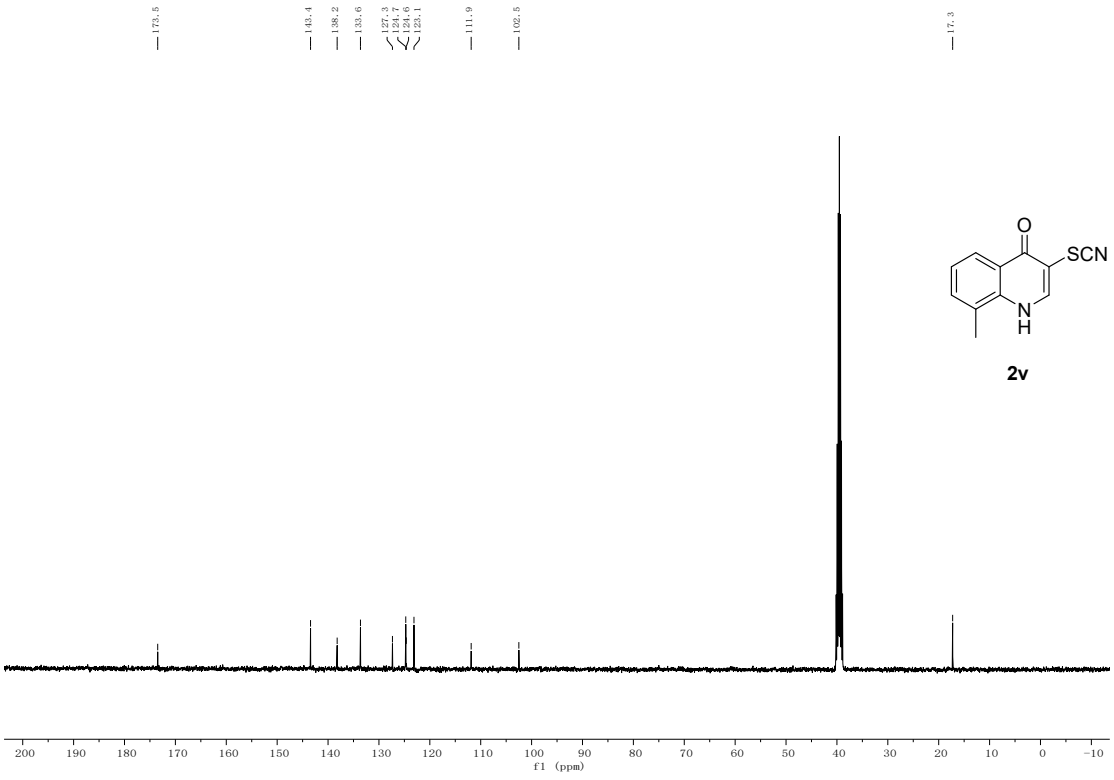

172.6
156.7
142.8
134.2
125.7
123.0
120.8
111.9
104.5
100.7
55.5
MeO
SCN
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2t

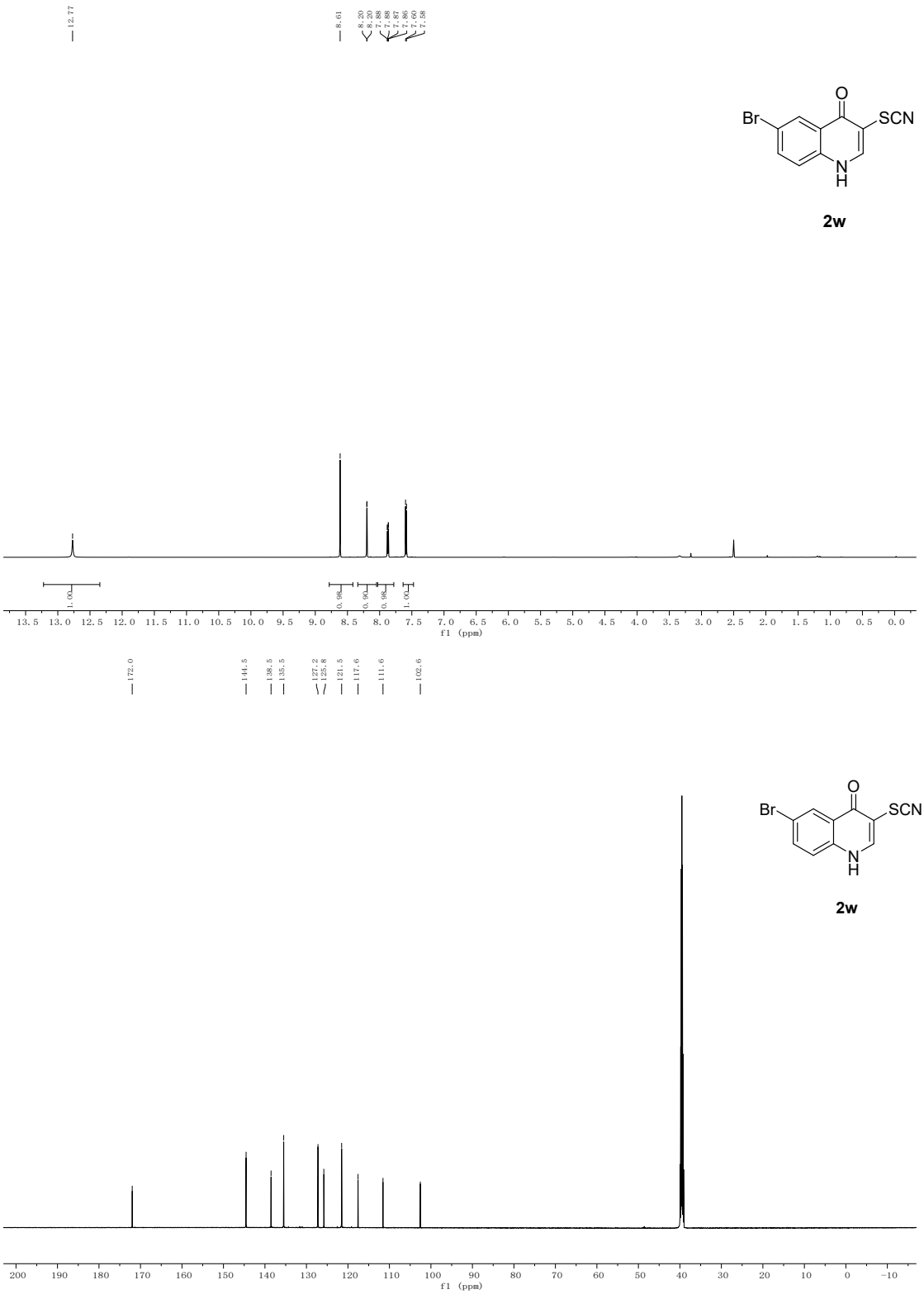

12.28
12.28
8.37
7.18
6.97
2.77
2.35
SCN
O
N
H
2u
0.97
1.02
1.04
1.02
3.00
3.06
f1 (ppm)
174.9
142.1
141.8
141.5
139.3
128.8
120.7
116.2
112.1
103.6
23.0
21.1
SCN
O
N
H
2u
f1 (ppm)

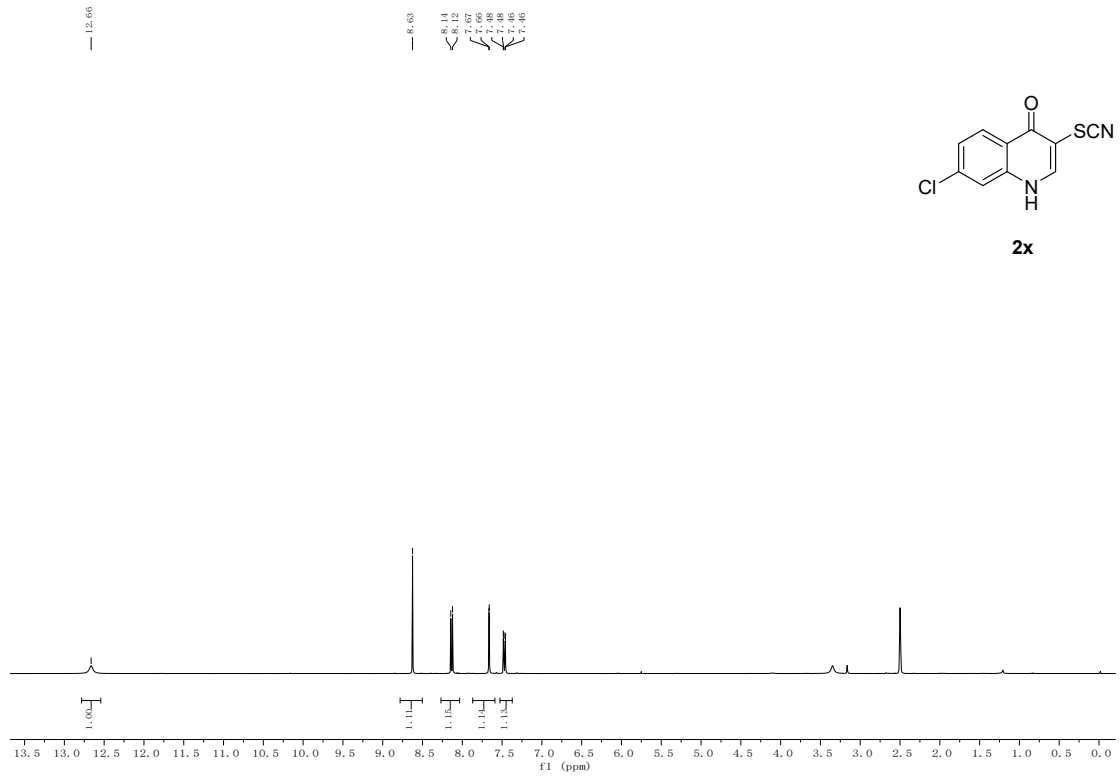

11.93
8.37
8.03
8.01
7.61
7.60
7.38
7.36
7.34
3.36
O
SCN
N
H
1.00
1.05
1.04
1.06
1.12
3.30
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2v

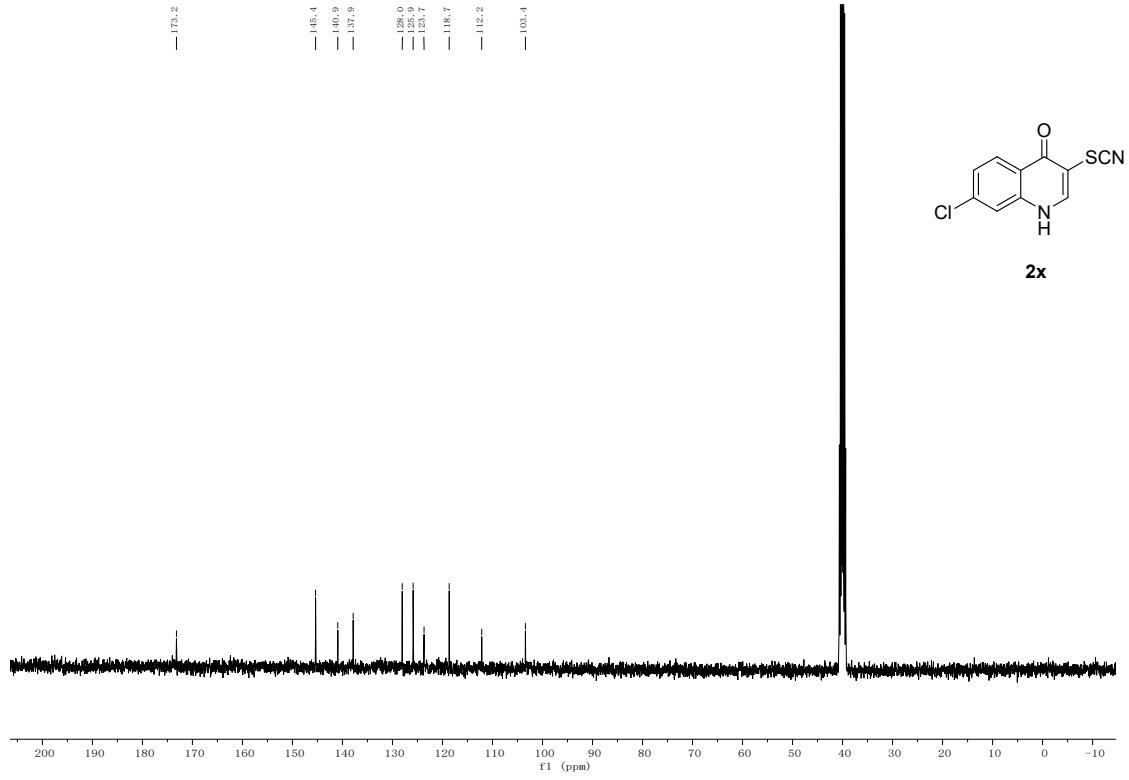

173.5
143.4
138.2
133.6
127.3
124.7
124.6
123.1
111.9
102.5
17.3
O
SCN
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2v

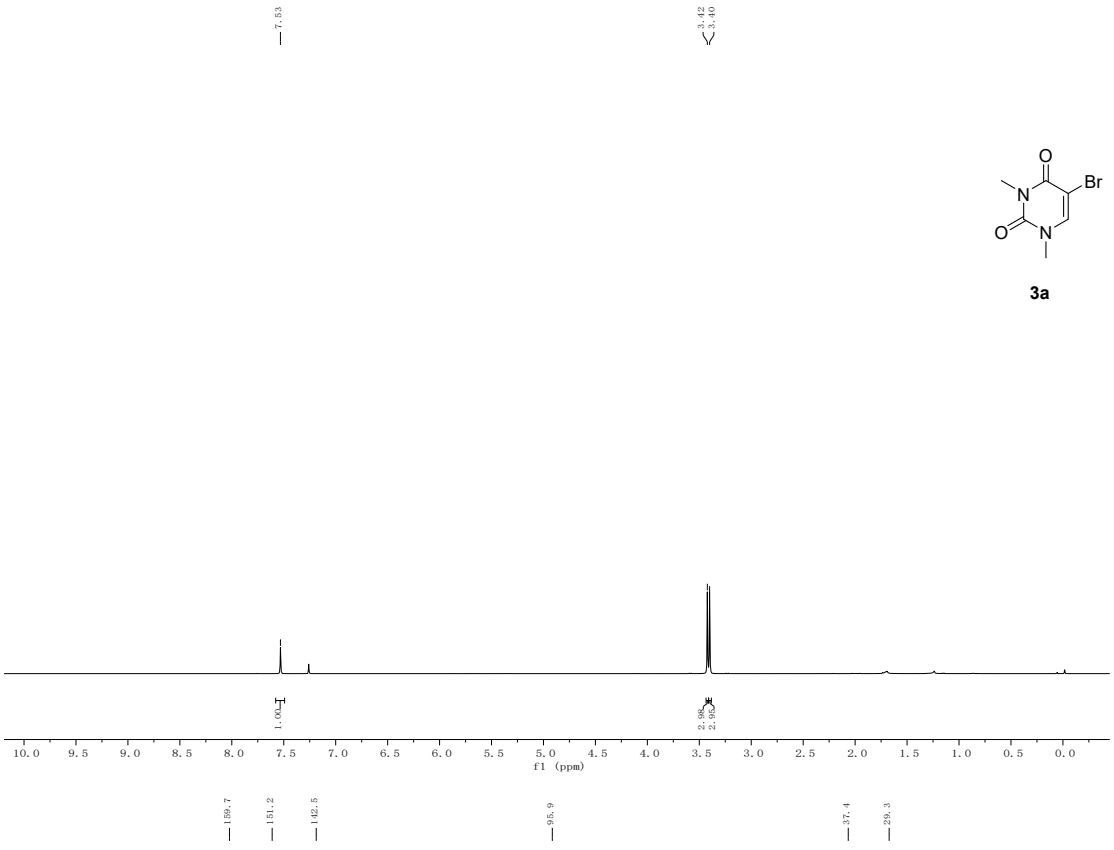

12.77
8.61
8.20
8.20
7.88
7.88
7.87
7.87
7.86
7.86
7.60
7.58
Br
O
SCN
N
H
2w
1.00
0.98
0.94
0.98
1.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
172.0
144.5
138.5
135.5
127.2
125.8
121.5
117.6
111.6
102.6
Br
O
SCN
N
H
2w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

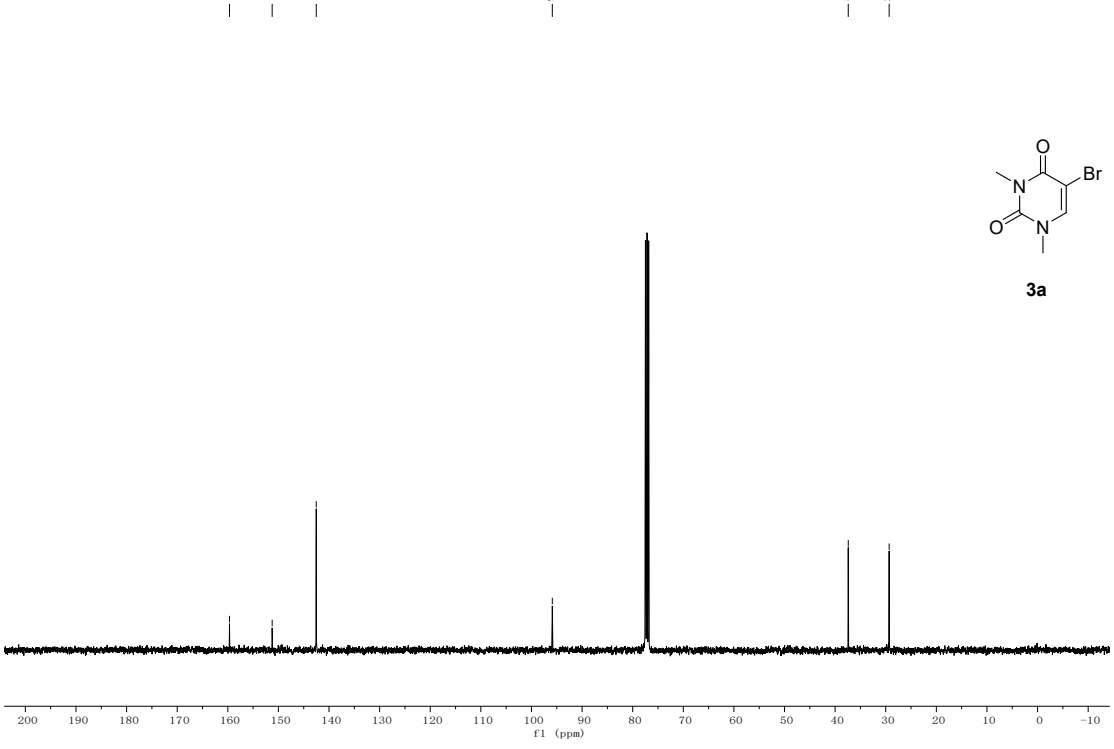

12.66
8.63
8.14
8.12
7.67
7.66
7.48
7.46
7.46
7.45
O
SCN
Cl
N
H
1.00
1.11
1.16
1.14
1.13
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

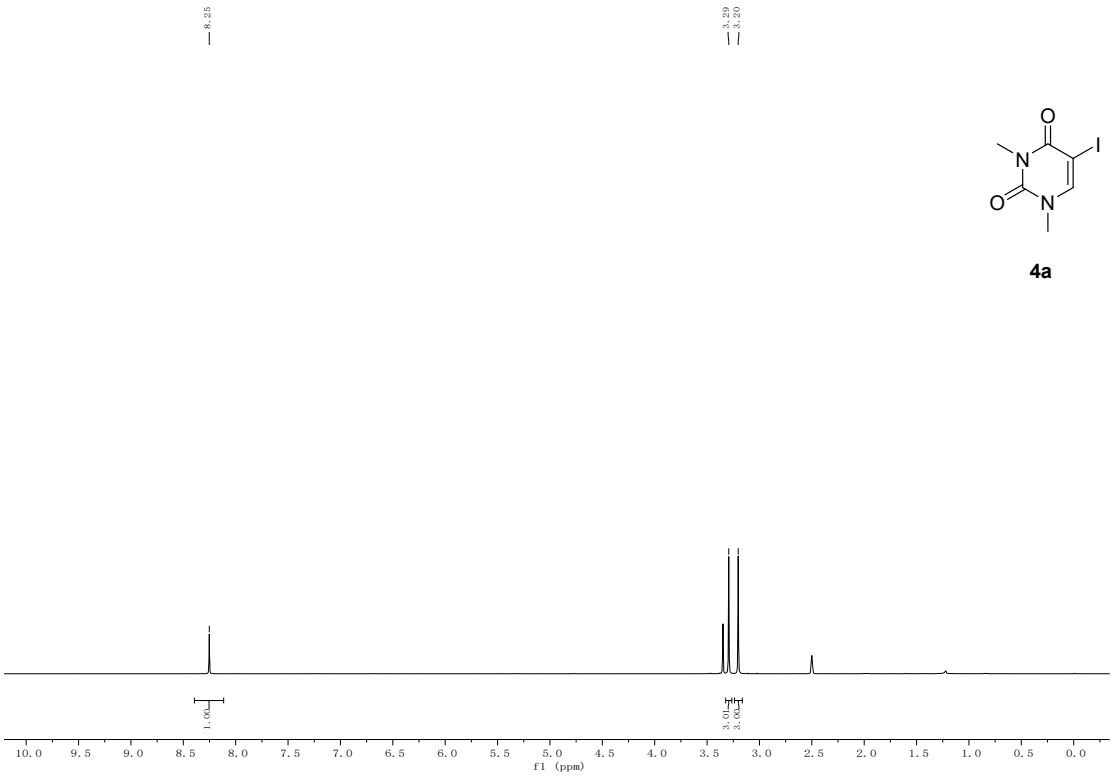
2x

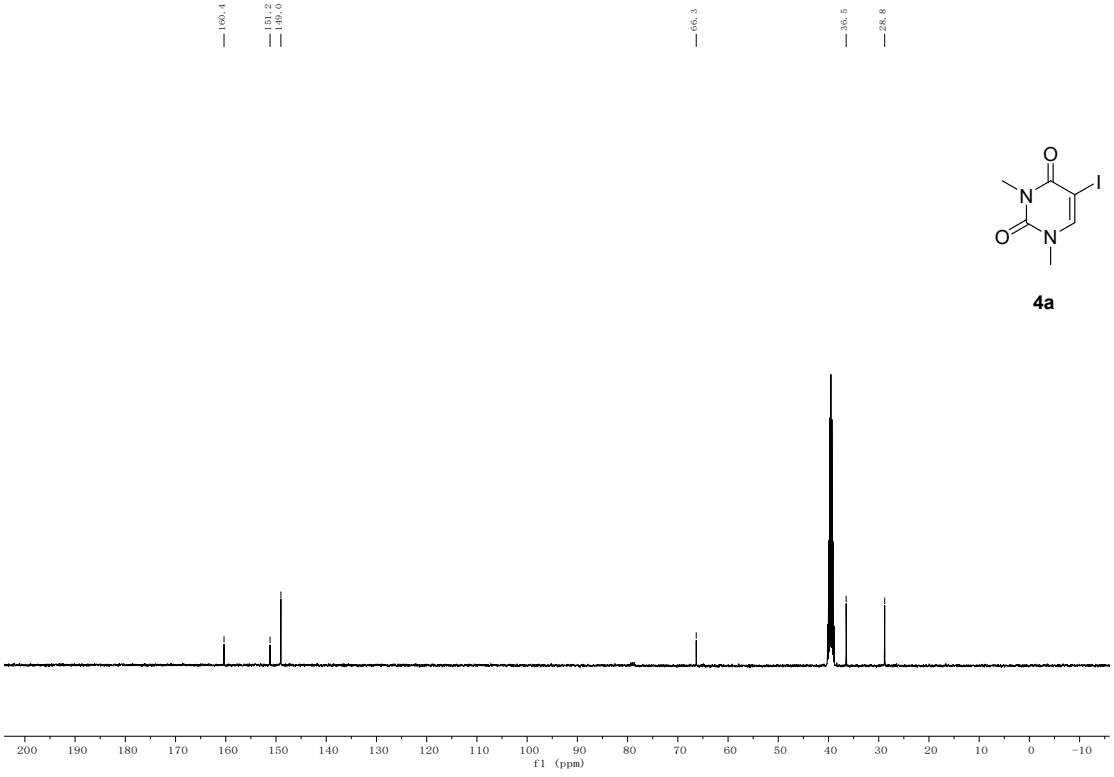

173.2
145.4
140.9
137.9
128.0
125.9
123.7
118.7
112.2
103.4
O
SCN
Cl
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2x


7.53
3.42
3.40
Br
3a
1.00
2.98
2.92
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)


159.7
151.2
142.5
95.9
37.4
29.3
Br
3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)





1. References

1 M. Noikham and S. Yotphan, Eur. *J. Org. Chem*., 2019, 2759-2766.

2 D. Ail, A. K. Panday and L. H. Choudhury, *J. Org. Chem.*, 2020, **85**, 13610-13620.

3 P. Chauhan, R. Preeti, S. Kumar and N. Jain, *Eur. J. Org. Chem.*, 2019, 4334-4340.

4 J. Asakura and M. J. Robins, *J. Org. Chem.*, 1990, **55**, 4928-4933.