Supporting Information

A Facile One-Pot Synthesis of *N*-Acyl-1-Cyano-1,2,3,4-Tetrahydroisoquinoline *via* Photoredox and Reissert-type Reaction from 1,2,3,4-Tetrahydroisoquinolines

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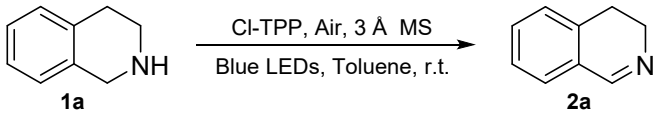
1. General Information

TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz Agilent DD2400-MR. Chemical shifts are reported in ppm versus tetramethylsilane with either tetramethylsilane or the residual solvent resonance used as an internal standard. Abbreviations were used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (*J*, Hz). Mass spectra were determined on a Waters Xevo G2-S QTOF or an Agilent 6520 QTOF., using electron spray ionization (ESI). Melting points are performed on a SGWX-4 digital visual melting point apparatus without correction. All other commercial chemicals were used without further purification.

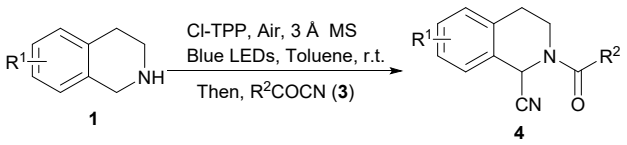
2. General procedure for the synthesis of 3,4-dihydroisoquinoline



1a **2a**

To a solution of 1,2,3,4-tetrahydroisoquinoline **1a** (0.067 g, 0.50 mmol) and 3 Å molecular sieve (0.250 g) in toluene (2.5 mL) was added *meso*-tetrakis(4-chlorophenyl)porphyrin (Cl-TPP, 0.008 g, 0.01 mmol). The mixture was stirred under an air atmosphere (air balloon) and irradiated with blue LEDs (12 W) at room temperature. After 24 hours, the solution was filtered through celite pad and the filtrate concentarted under vacuum. The residue was purified by column chromatography to give the 3,4-dihydroisoquinoline **2a** (63 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.40 – 7.33 (m, 1H), 7.32 – 7.25 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 1H), 3.77 (t, *J* = 6.8 Hz, 2H), 2.75 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 136.4, 131.2, 127.5, 127.3, 127.1, 47.3, 25.1. Analytical data are in agreement with those reported in the literature.[1]

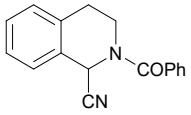
3. General procedure for the synthesis of *N*-acyl-1-cyano THIQs



1 4

To a solution of 1,2,3,4-tetrahydroisoquinoline **1** (0.50 mmol) and 3 Å molecular sieve (0.250 g) in toluene (2.5 mL) was added *meso*-tetrakis(4-chlorophenyl)-porphyrin (Cl-TPP, 0.008 g, 0.01 mmol). The mixture was stirred under an air atmosphere (air balloon) and irradiated with blue LEDs (12 W) at room temperature. After 24 hours, acyl cyanide **3** (0.55 mmol) was added and the reaction mixture was stirred at room temperature for another 12 hours. The solution was filtered through celite pad and the filtrate concentarted under vacuum. The residue was purified by column chromatography to give the corresponding product **4**.

2-benzoyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4a)

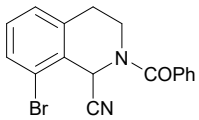


4a

4a was obtained as a reddish brown product (121 mg, 92%): mp 113-114 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.27 (m, 8H), 7.25 – 7.19 (m, 1H), 6.50 (brs, 1H), 4.04 (brs, 1H), 3.60 (brs, 1H), 3.14 – 3.03 (m, 1H), 2.95 – 2.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 134.0, 133.8, 131.9, 131.1, 129.7, 129.2, 129.0, 128.2, 127.7, 127.3, 117.9, 44.6, 43.4, 28.8; HRMS (ESI): calcd for $C_{17}H_{14}N_2NaO$ $[M+Na]^+$: 285.1004, found: 285.1000.

2-benzoyl-8-bromo-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4b)



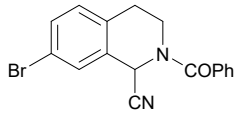
4b

4b was obtained as a light yellow solid (157 mg, 92%): mp 136-139 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.37 (m, 6H), 7.31 – 7.15 (m, 2H), 6.61 (s, 1H), 4.04 (s, 1H), 3.64 (s, 1H), 3.11 (s, 1H), 3.02 – 2.79 (m, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 171.0, 136.4, 133.7, 131.8, 131.2, 130.4, 129.0, 128.9, 127.9, 127.3, 123.4, 116.5, 45.8, 43.1, 28.8; HRMS (ESI): calcd for $C_{17}H_{14}BrN_2O$ $[M+H]^+$: 341.0284, found: 341.0286.

2-benzoyl-7-bromo-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4c)

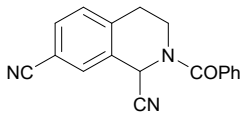


4c

4c was obtained as a white solid (119 mg, 70%): mp 188-191 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.43 (m, 7H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.46 (brs, 1H), 4.04 (brs, 1H), 3.56 (brs, 1H), 3.07 – 2.94 (m, 1H), 2.88 – 2.76 (m, 1H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 171.2, 133.6, 132.7, 132.4, 131.2, 130.4, 130.1, 129.0, 127.3, 121.0, 117.4, 110.1, 44.1, 43.1, 28.3; HRMS (ESI): calcd for $C_{17}H_{13}BrN_2NaO$ $[M+Na]^+$: 363.0103, found: 363.0107.

2-benzoyl-1,2,3,4-tetrahydroisoquinoline-1,7-dicarbonitrile (4d)

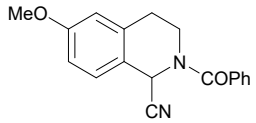


4d

4d was obtained as a white solid (81 mg, 56%): mp 202-205 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (brs, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.44 (m, 5H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.52 (brs, 1H), 4.11 (brs, 1H), 3.59 (brs, 1H), 3.21 – 3.03 (m, 1H), 2.95 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 139.5, 133.4, 132.4, 131.4, 131.3, 130.8, 129.9, 129.1, 127.3, 117.8, 117.0, 111.8, 44.2, 42.7, 28.0; HRMS (ESI): calcd for $C_{18}H_{13}N_3NaO$ $[M+Na]^+$: 310.0951, found: 310.0954.

2-benzoyl-6-methoxy-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4e)

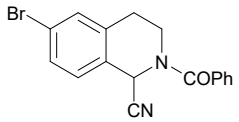


4e

4e was obtained as a white solid (132 mg, 90%): mp 96-99 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.39 (m, 5H), 7.26 (s, 1H), 6.84 (s, 1H), 6.71 (s, 1H), 6.38 (s, 1H), 3.97 (brs, 1H), 3.77 (s, 3H), 3.53 (brs, 1H), 3.02 (brs, 1H), 2.79 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 159.7, 135.1, 133.9, 130.8, 128.7, 128.5, 127.1, 120.0, 118.0, 113.9, 113.7, 55.3, 44.1, 43.2, 28.8; HRMS (ESI): calcd for $C_{18}H_{16}N_2NaO_2$ $[M+Na]^+$: 315.1104, found: 315.1102.

2-benzoyl-6-bromo-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4f)

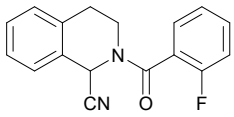


4f

4f was obtained as a light yellow solid (115 mg, 68%): mp 146-149 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.42 (m, 6H), 7.40 (s, 1H), 7.28 (s, 1H), 6.44 (brs, 1H), 4.04 (brs, 1H), 3.55 (brs, 1H), 3.05 (brs, 1H), 2.84 (d, *J* = 16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 135.9, 133.7, 132.5, 131.2, 130.82, 129.1, 129.0, 127.3, 127.2, 123.1, 117.4, 44.3, 43.0, 28.5; HRMS (ESI): calcd for $C_{17}H_{13}BrN_2NaO$ $[M+Na]^+$: 363.0103, found: 363.0103.

2-(2-fluorobenzoyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4g)

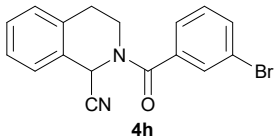


4g

4g was obtained as a reddish brown solid (99 mg, 71%): mp 139-141 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 4.4:1 mixture of amide rotamers at room temperature) δ 7.58 – 7.45 (m, 2H), 7.45 – 7.38 (m, 1H), 7.38 – 7.25 (m, 3H), 7.24 – 7.08 (m, 2H), 6.55 and 5.51 (2s, 1H), 4.93 – 4.83 and 3.91 – 3.77 (2m, 1H), 3.70 – 3.55 and 3.51 – 3.39 (2m, 1H), 3.21 – 3.02 (m, 1H), 3.00 – 2.91 and 2.90 – 2.79 (2m, 1H); ^{13}C NMR ((100 MHz, $CDCl_3$) δ 166.4, 158.5 (d, *J* = 248 Hz), 133.8, 132.5 (d, *J* = 8 Hz), 129.74, 129.53, 129.12, 127.89, 127.69, 127.58, 125.1 (d, *J* = 3 Hz), 122.4 (d, *J* = 16 Hz), 117.70, 116.1 (d, *J* = 21 Hz), 44.24, 42.82, 28.65; HRMS (ESI): calcd for $C_{17}H_{13}FN_2NaO$ $[M+Na]^+$: 303.0910, found: 303.0905.

2-(3-bromobenzoyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4h)

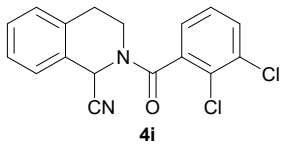


4h

4h was obtained as a yellow solid (124 mg, 73%): mp 156-159 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.60 (m, 2H), 7.54 – 7.29 (m, 5H), 7.26 – 7.16 (m, 1H), 6.46 (s, 1H), 3.99 (s, 1H), 3.63 (s, 1H), 3.16 – 2.99 (m, 1H), 2.89 (d, J = 16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4 135.8, 134.0, 133.4, 130.4, 130.2, 129.5, 129.1, 127.8, 127.6, 127.5, 125.6, 122.9, 117.5, 44.5, 43.3, 28.5; HRMS (ESI): calcd for $C_{17}H_{13}BrN_2NaO$ $[M+Na]^+$: 363.0103, found: 363.0101.

2-(2,3-dichlorobenzoyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4i)

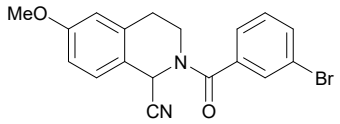


4i

4i was obtained as a light yellow solid (86 mg, 52%): mp 138-141 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 3.3:1 mixture of amide rotamers at room temperature) δ 7.62 and 7.58 (2d, 1H), 7.48 – 7.40 (m, 1H), 7.40 – 7.29 (m, 3H), 7.29 – 7.14 and 7.11 – 7.01 (2m, 2H), 6.61 and 5.40 (3d, 1H), 4.96 – 4.82 and 3.75 – 3.65 (2m, 1H), 3.65 – 3.39 (m, 1H), 3.21 – 3.07 and 3.04 – 2.90 (2m, 1H), 2.90 – 2.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 and 166.9, 136.3 and 136.2 and 136.1, 134.4 and 134.2 and 134.1, 133.5 and 133.42 and 133.39, 132.1 and 131.83 and 131.81, 129.9 and 129.8 and 129.7, 129.6 and 129.54 and 129.48, 129.3 and 129.0 and 128.9, 128.5 and 128.4, 127.9 and 127.81 and 127.77, 127.6 and 127.4, 126.9 and 126.7 and 126.3, 126.0 and 125.7 and 125.5, 117.7, and 117.2 and 117.0, 49.2 and 43.9 and 43.6, 42.8, 42.1 and 38.2, 28.7 and 28.5 and 27.7; HRMS (ESI): calcd for $C_{17}H_{12}Cl_2N_2NaO$ $[M+Na]^+$: 353.0219, found: 353.0217.

2-(3-bromobenzoyl)-6-methoxy-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4j)

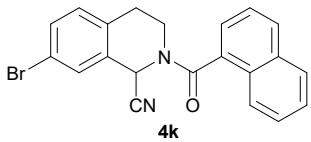


4j

4j was obtained as a light yellow solid (92 mg, 50%): mp 135-137 ℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 2H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.36 (t, *J* = 8.1 Hz, 1H), 7.31 (s, 1H), 6.88 (s, 1H), 6.73 (s, 1H), 6.40 (s, 1H), 3.93 (s, 1H), 3.82 (s, 3H), 3.61 (s, 1H), 3.03 (s, 1H), 2.85 (d, *J* = 17.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 159.9, 135.9, 134.8, 133.9, 130.4, 130.2, 128.6, 125.7, 122.9, 119.8, 117.7, 114.1, 113.9, 55.4, 44.2, 43.3, 28.8; HRMS (ESI): calcd for $C_{18}H_{15}BrN_2NaO_2$ $[M+Na]^+$: 393.0209, found: 393.0210.

2-(1-naphthoyl)-7-bromo-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4k)

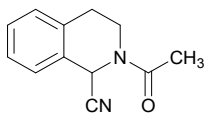


4k

4k was obtained as a green solid (69 mg, 35%): mp 209-211 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 3.6:1 mixture of amide rotamers at room temperature) δ 8.03 – 7.85 (m, 3H), 7.80 – 7.30 (m, 6H), 7.16 and 7.08 (2d, 1H), 6.85 – 6.70 and 5.47 – 5.33 (2m, 1H), 5.10 – 5.01 and 3.72 – 3.61 (2m, 1H), 3.58 – 3.44 (m, 1H), 3.21 – 2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 133.6, 132.7 (brs), 132.4, 131.9 (brs), 131.5 (brs), 131.3, 130.5 (brs), 129.7 (brs), 128.8 (brs), 128.1 (brs), 127.1 (brs), 125.1 (brs), 124.8 (brs), 124.4 (brs), 123.8 (brs), 121.2, 117.4, 49.2 and 43.4, 42.5 and 37.9, 28.4 and 27.5; HRMS (ESI): calcd for $C_{21}H_{16}BrN_2O$ $[M+H]^+$: 391.0441, found: 391.0443.

2-acetyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4l)

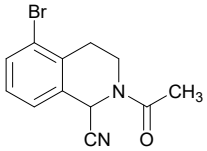


4l

4l was obtained as a white solid (71 mg, 71%): mp 103-106 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 5.2:1 mixture of amide rotamers at room temperature) δ 7.41 – 7.27 (m, 3H), 7.25 – 7.16 (m, 1H), 6.47 and 5.75 (2s, 1H), 4.73 – 4.63 and 3.98 – 3.90 (2m, 1H), 3.76 – 3.65 and 3.23 – 3.16 (2m, 1H), 3.07 – 2.87 (m, 2H), 2.31 and 2.22 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 133.9, 129.3, 129.1, 128.6, 127.7, 127.5, 117.9, 43.5, 42.3, 28.6, 21.5; HRMS (ESI): calcd for $C_{12}H_{12}N_2NaO$ $[M+Na]^+$: 223.0842, found: 223.0843.

2-acetyl-5-bromo-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4m)

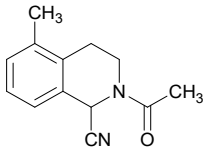


4m

4m was obtained as a light yellow solid (65 mg, 46%): mp 153-155 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 8.5:1 mixture of amide rotamers at room temperature) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.51 and 5.72 (2s, 1H), 4.85 – 4.80 and 4.09 – 4.02 (2m, 1H), 3.74 – 3.62 (m, 1H), 3.11 – 3.02 (m, 1H), 2.98 – 2.86 (m, 1H), 2.29 and 2.23 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 133.7, 133.1, 130.8, 128.8, 126.7, 125.5, 117.5, 43.4, 41.8, 29.4, 21.3; HRMS (ESI): calcd for $C_{12}H_{11}BrN_2NaO$ $[M+Na]^+$: 300.9947, found: 300.9946.

2-acetyl-5-methyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4n)



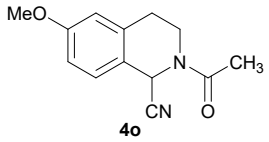
4n

4n was obtained as a reddish brown solid (28 mg, 25%): mp 137-139 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 6.8:1 mixture of amide rotamers at room temperature) δ 7.25 – 7.12 (m, 3H), 6.48 and 5.72 (2s, 1H), 4.81 – 4.76 and 4.07 – 3.99 (2m, 1H), 3.75 – 3.67 and 3.20 – 3.13 (2m, 1H), 2.91 – 2.82 and 2.81 – 2.74 (2m, 1H), 2.29 and 2.23 (2s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 137.1, 132.2, 130.4, 128.5,

127.3, 125.3, 118.1, 43.8, 42.0, 26.0, 21.3, 19.3; HRMS (ESI): calcd for $C_{13}H_{14}N_2NaO$ $[M+Na]^+$: 237.0998, found: 237.0998.

2-acetyl-6-methoxy-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4o)

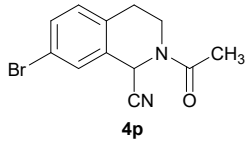


4o

4o was obtained as a reddish brown solid (52 mg, 44%): mp 92-94 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 8.3:1 mixture of amide rotamers at room temperature) δ 7.27 – 7.21 (m, 1H), 6.90 – 6.81 (m, 1H), 6.73 (s, 1H), 6.42 and 5.69 (2s, 1H), 4.67 – 4.59 and 3.95 – 3.87 (2m, 1H), 3.81 (s, 3H), 3.77 – 3.65 and 3.25 – 3.15 (2m, 1H), 3.05 – 2.81 (m, 2H), 2.31 and 2.22 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 159.9, 135.3, 128.7, 120.7, 118.1, 114.0, 113.7, 55.5, 43.2, 42.2, 28.9, 21.5; HRMS (ESI): calcd for $C_{13}H_{14}N_2NaO_2$ $[M+Na]^+$: 253.0947, found: 253.0947.

2-acetyl-7-bromo-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4p)

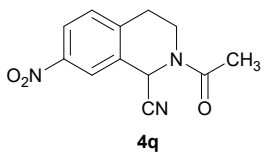


4p

4p was obtained as a white solid (85 mg, 61%): mp 172-174 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 7.8:1 mixture of amide rotamers at room temperature) δ 7.49 (s, 1H), 7.44 (dd, J = 8.2, 1.7 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 6.45 and 5.72 (2s, 1H), 4.73 – 4.67 and 4.00 – 3.91 (2m, 1H), 3.73 – 3.62 and 3.19 – 3.10 (2m, 1H), 3.01 – 2.81 (m, 2H), 2.29 and 2.22 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 132.8, 132.3, 130.9, 130.5, 130.4, 121.1, 117.4, 43.0, 41.9, 28.2, 21.5; HRMS (ESI): calcd for $C_{12}H_{11}BrN_2NaO$ $[M+Na]^+$: 300.9947, found: 300.9947.

2-acetyl-7-nitro-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4q)

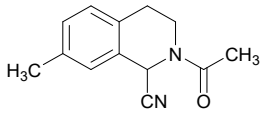


4q

4q was obtained as a light yellow solid (78 mg, 64%): mp 207-209 ℃

^{1}H NMR (400 MHz, $CDCl_3$, a 5.8:1 mixture of amide rotamers at room temperature) δ 8.27 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 6.63 and 5.87 (2s, 1H), 4.84 – 4.75 and 4.08 – 3.99 (2m, 1H), 3.82 – 3.67 (m, 1H), 3.15 – 3.01 (m, 2H), 2.34 and 2.26 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 141.3, 130.7, 130.6, 130.3, 124.0, 123.0, 116.9, 43.3, 43.2, 41.5, 28.9, 21.5; HRMS (ESI): calcd for $C_{12}H_{12}N_3O_3$ $[M+H]^+$: 246.0879, found: 246.0873.

2-acetyl-7-methyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4r)



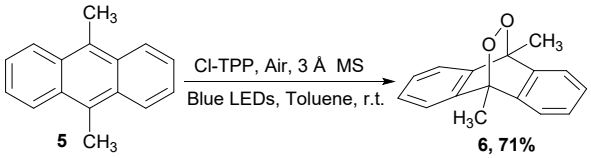
4r

4r was obtained as a light yellow solid (17 mg, 16%): mp 153-155 °C

^{1}H NMR (400 MHz, $CDCl_3$, a 6.5:1 mixture of amide rotamers at room temperature) δ 7.17 – 7.06 (m, 3H), 6.43 and 5.69 (s, 1H), 4.70 – 4.65 and 3.96 – 3.90 (2m, 1H), 3.72 – 3.64 and 3.21 – 3.13 (m, 1H), 3.01 – 2.83 (m, 2H), 2.36 and 2.35 (2s, 3H), 2.30 and 2.22 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 137.6, 130.7, 129.9, 129.1, 128.4, 127.8, 118.1, 43.6, 42.4, 28.2, 21.5, 21.1; HRMS (ESI): calcd for $C_{13}H_{14}N_2NaO$ $[M+Na]^+$: 237.0998, found: 237.0999.

4. Mechanistic studies

(1) Trapping experiments



To a solution of 9,10-dimethylanthracene **5** (0.103 g, 0.50 mmol) and 3 Å molecular sieve (0.250 g) in toluene (2.5 mL) was added *meso*-tetrakis(4-chlorophenyl)porphyrin (Cl-TPP, 0.008 g, 0.01 mmol). The mixture was stirred under an air atmosphere (air balloon) and irradiated with blue LEDs (12 W) at room temperature. After 24 hours, the solution was filtered through celite pad and the filtrate concentarted under vacuum. The residue was purified by column chromatography to give the the endoperoxide

product **6** (0.084 g, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 4H), 7.32 – 7.24 (m, 4H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 127.5, 120.8, 79.6, 13.9. Analytical data are in agreement with those reported in the literature.[2]

(2) Detection of H_2O_2

The formation of H_2O_2 in the reaction mixture was detected in a typical reaction with KI.[3]

Principle

H_2O_2 oxidizes iodide ion to iodine in the presence of an acid catalyst. The liberated iodine can be detected using starch solution as indicator.

$$H_2O_2 + 2KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2H_2O$$

Note: This method is less susceptible to interferences by organics, and is more suitable for measuring mg/L levels of H_2O_2.

The following reagents were prepared for the analysis.

Potassium iodide solution (1% w/v): In a 100 mL volumetric flask, 1.0 g of KI was dissolved in 100 mL water, stoppered and stored in a cool place away from light.

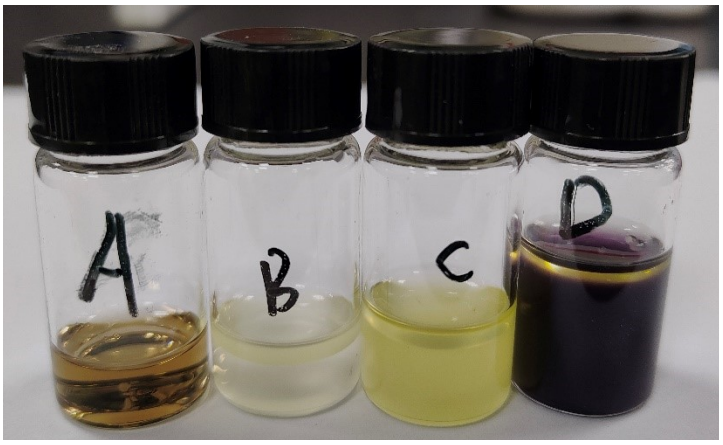
Sulfuric acid solution: Carefully 3.5 M H_2SO_4 solution was prepared by addition of concentrated H_2SO_4 to water.

Starch indicator: To 2.5 mL water 250 mg of corn starch was added, shaken well and was poured into a beaker containing 25 mL of boiling water. Boiling continued for further 2 minutes with stirring, cooled down to room temperature, the decanted supernatant was used as indicator.

Procedure:

To a 10 mL volumetric flask 0.5 mL of reaction mixture was taken, diluted with 5 mL of MeOH with stirring to give brown coloured solution (A). To it 1 mL of 3.5 M H_2SO_4 solution was added which decolourises the solution (B). To the colourless solution 2 mL of 1% KI solution was added. The colour of solution was changes to

yellow due to formation of molecular iodine (C). Finally to the solution 2 mL of freshly prepared starch solution was added and the colour changes to blue (D).



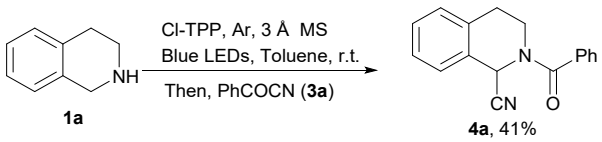
(A) Reaction mixture (under standard reaction conditions);

(B) Reaction mixture + dil. H_2SO_4;

(C) [Reaction mixture + dil. H_2SO_4] + KI;

(D) [Reaction mixture + dil. H_2SO_4 + KI] + Starch solution.

(3) Experiments in the absence of oxygen



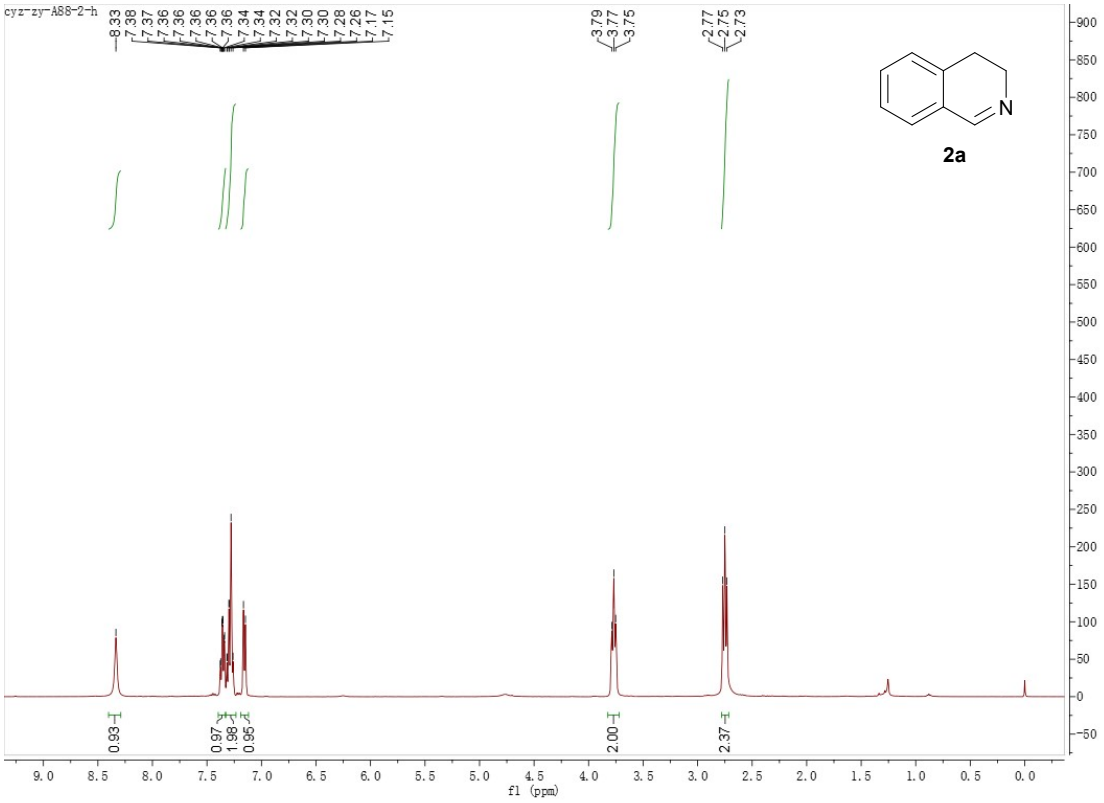
1a **4a**, 41%

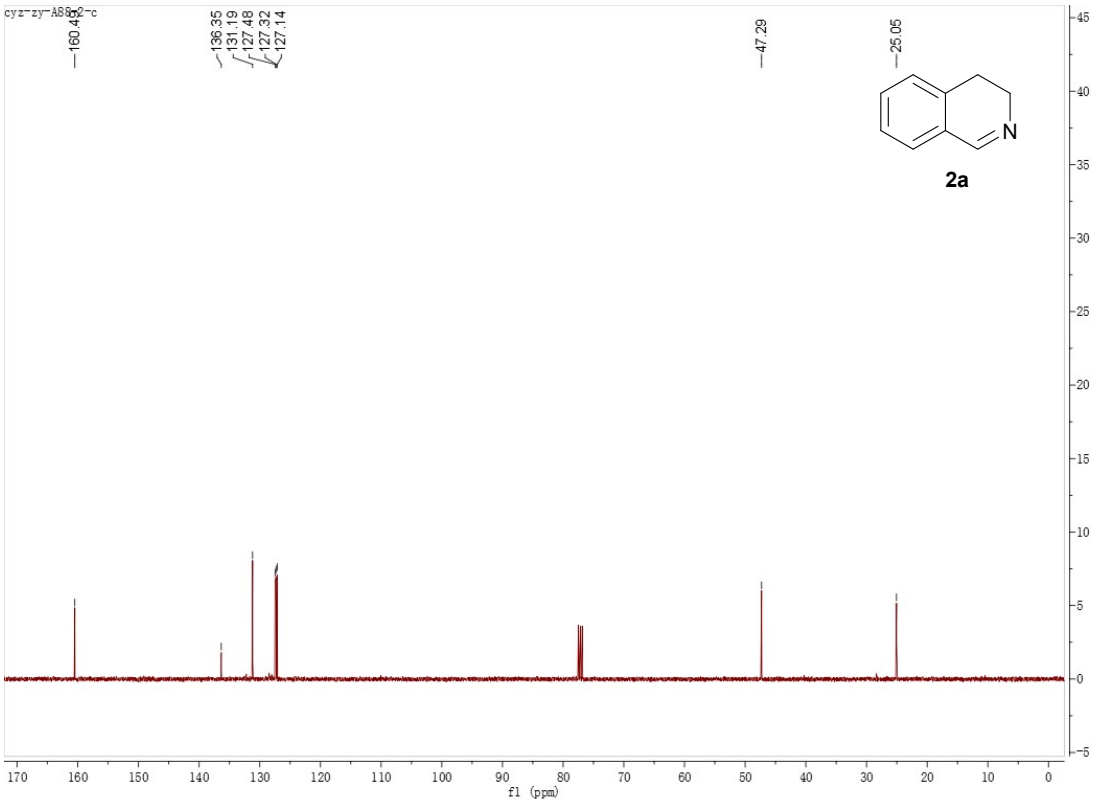
To a schlenk tube equipped with a magnetic stiring bar was charged 1,2,3,4-tetrahydroisoquinoline **1a** (0.067 g, 0.50 mmol), 3 Å molecular sieve (0.250 g) and *meso*-tetrakis(4-chlorophenyl)-porphyrin (Cl-TPP, 0.008 g, 0.01 mmol) under argon. Fresh degassed toluene (2.5 mL) was injected via syringe and the resulting mixture was stirred under argon and irradiated with blue LEDs (12 W) at room temperature. After 24 hours, benzoyl cyanide **3a** (0.072 g, 0.55 mmol) was injected via syringe and the reaction mixture was stirred at room temperature under argon for another 12 hours. The solution was filtered through celite pad and the filtrate concentarted under vacuum. The residue was purified by column chromatography to give the corresponding product **4a** (0.054 g, 41%).

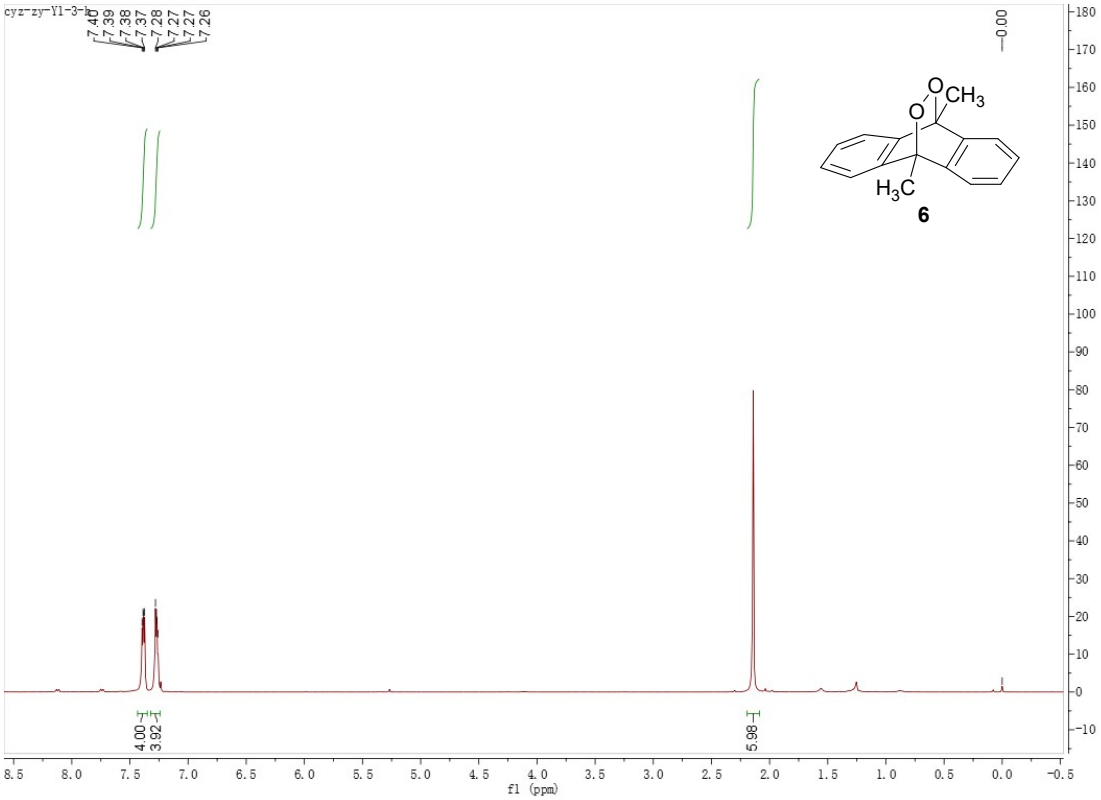
5. References

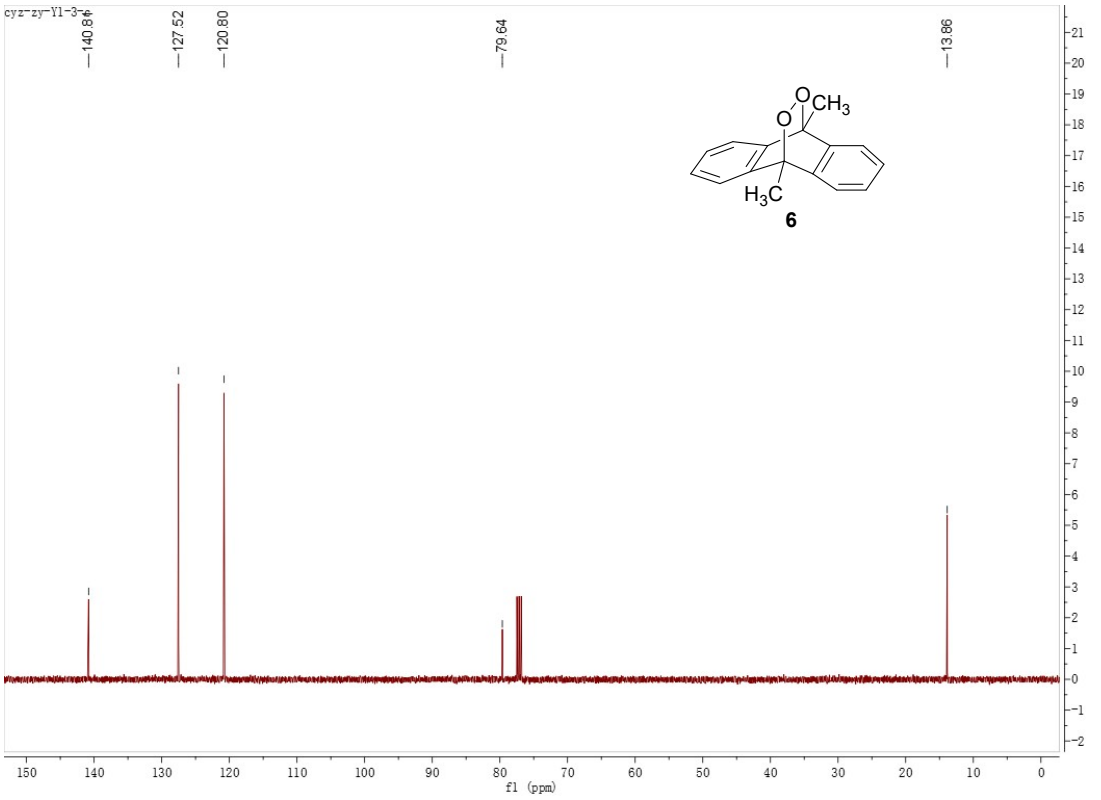
[1] J. M. Mbere, J. B. Bremner, B. W. Skelton, A. H. White, *Tetrahedron* 2011, **67**, 6895.
[2] a) W.-T. Xu, B. Huang, J.-J. Dai, J. Xu, H.-J. Xu, *Org. Lett.* 2016, **18**, 3114; b) J.-G. Sun, H. Yang, P. Li, B. Zhang, *Org. Lett.* 2016, **18**, 5114.
[3] a) M. K. Sahoo, G. Jaiswal, J. Rana, E. Balaraman, *Chem. Eur. J.* 2017, **23**, 14167; b) W.-Z. Weng, H. Liang, B. Zhang, *Org. Lett.* 2018, **20**, 4979.

6. Copies of ^{1}H and ^{13}C NMR spectra of 2a and 6

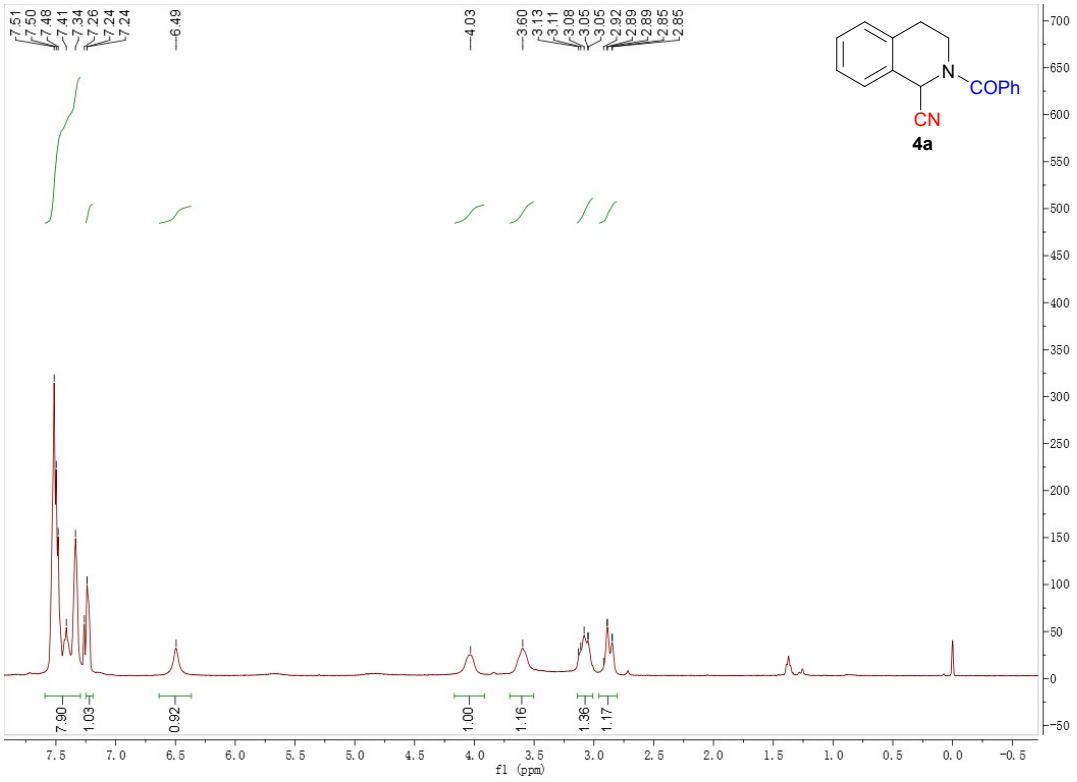


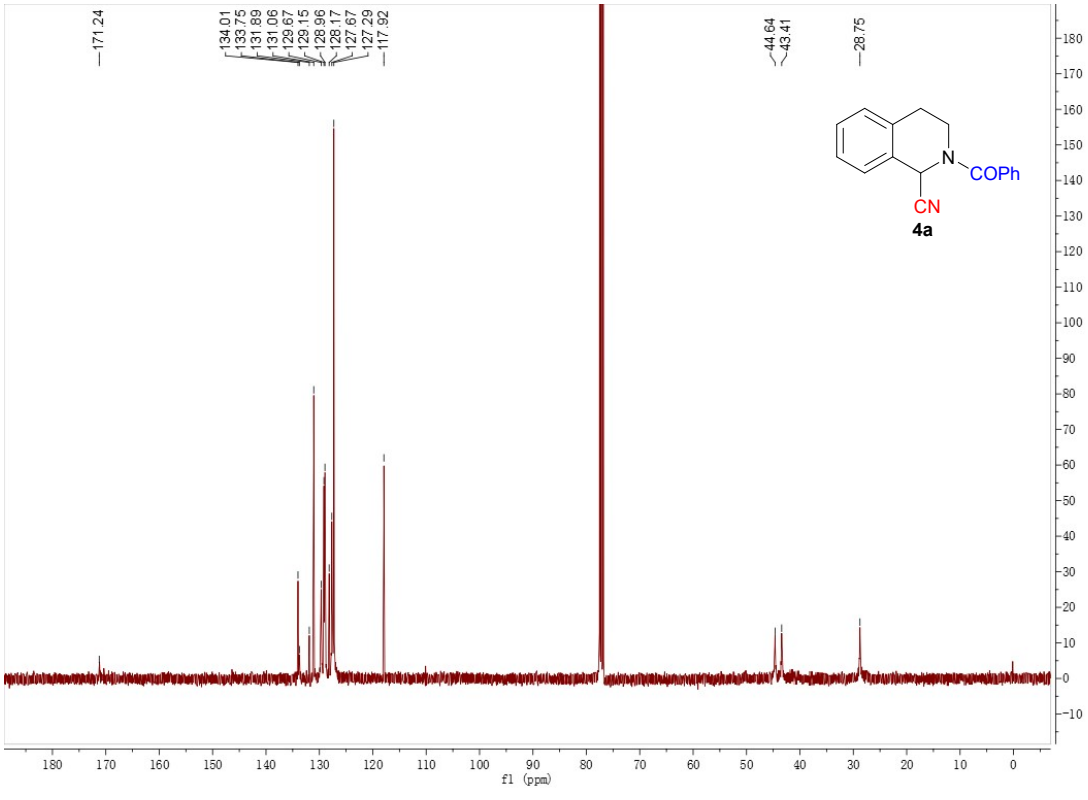


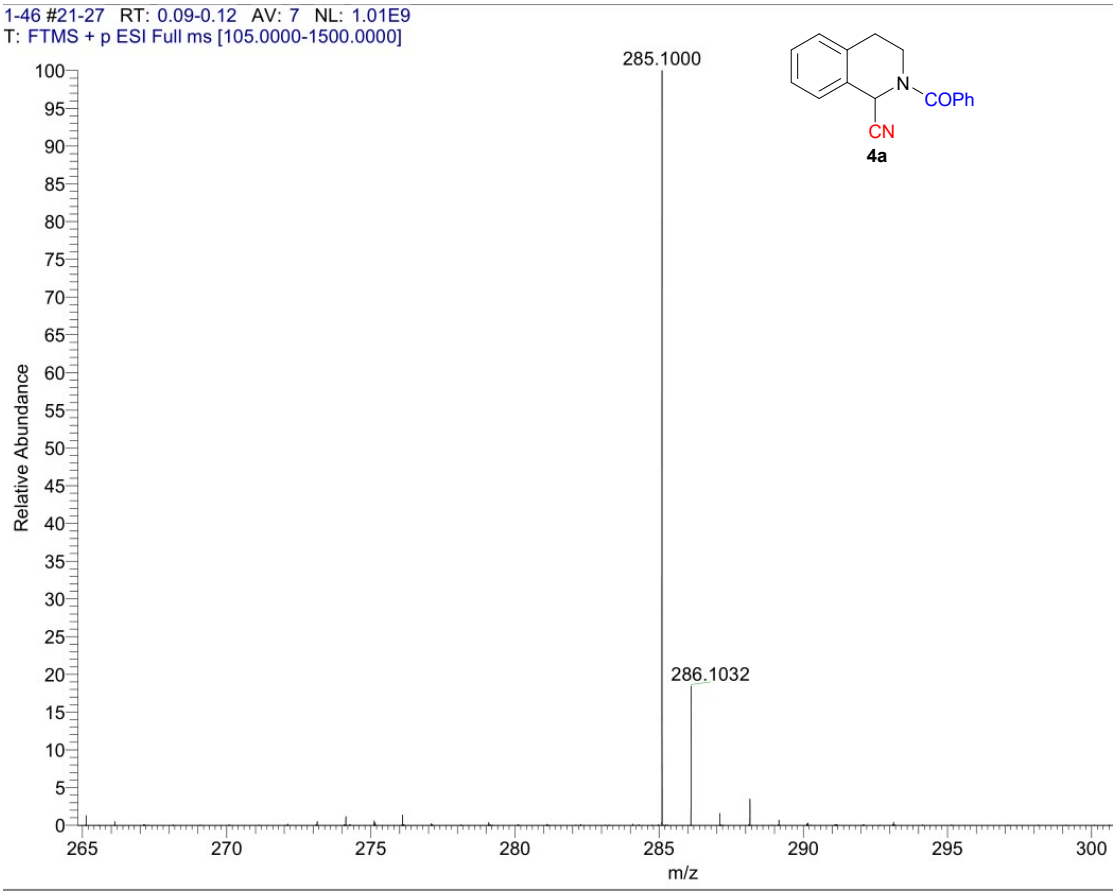

cyz-zy-Y1-3-H
7.40
7.39
7.38
7.37
7.28
7.27
7.27
7.26
0.00
4.00
3.92
5.98
f1 (ppm)
6

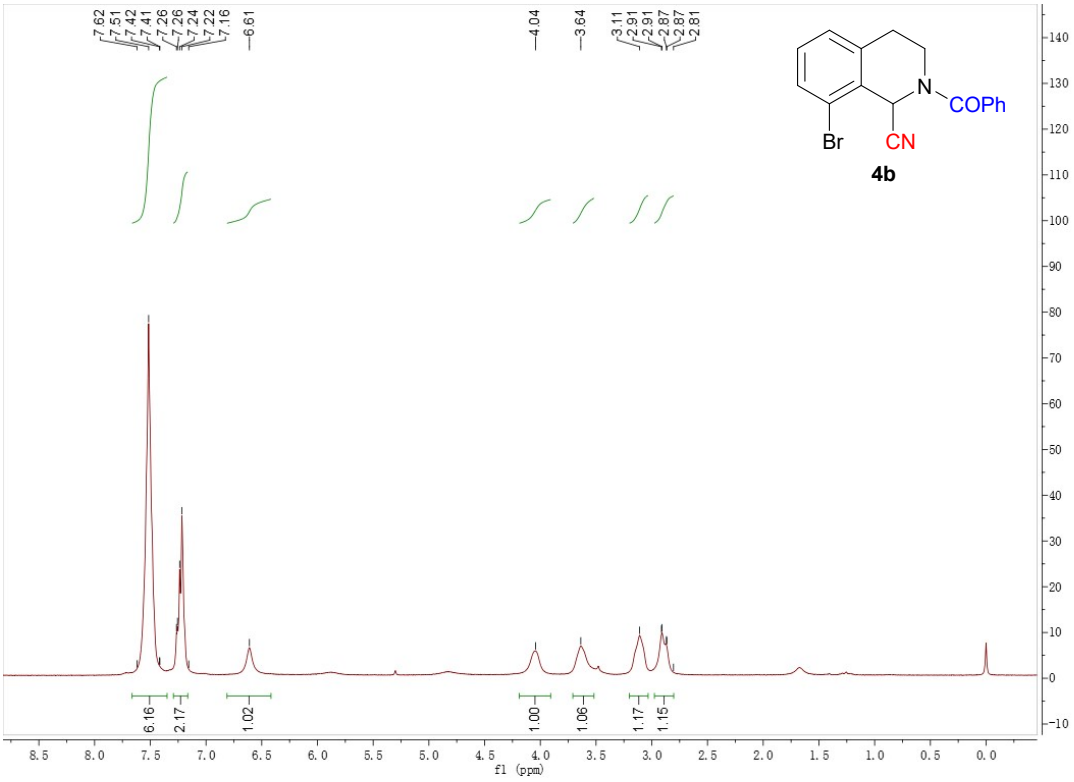

cyz-zy-Y1-3-C
140.84
127.52
120.80
79.64
13.86
f1 (ppm)
6

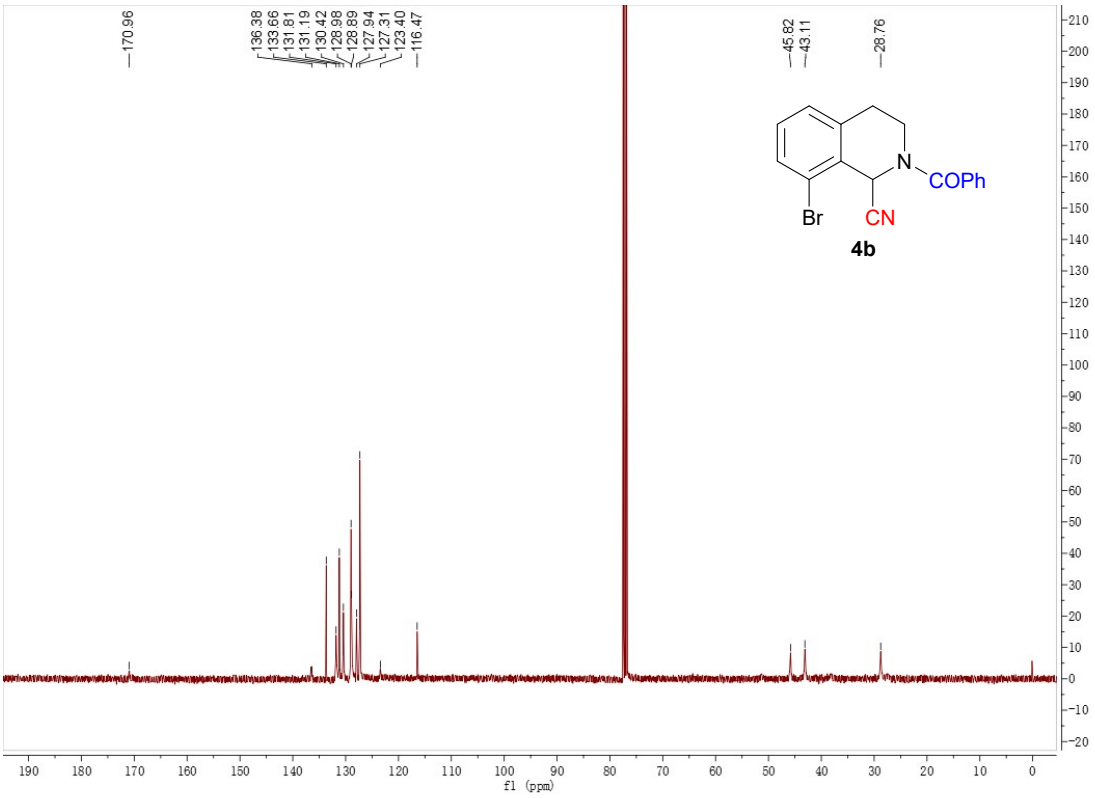
7. Copies of ^{1}H NMR, ^{13}C NMR and HRMS spectra of 4

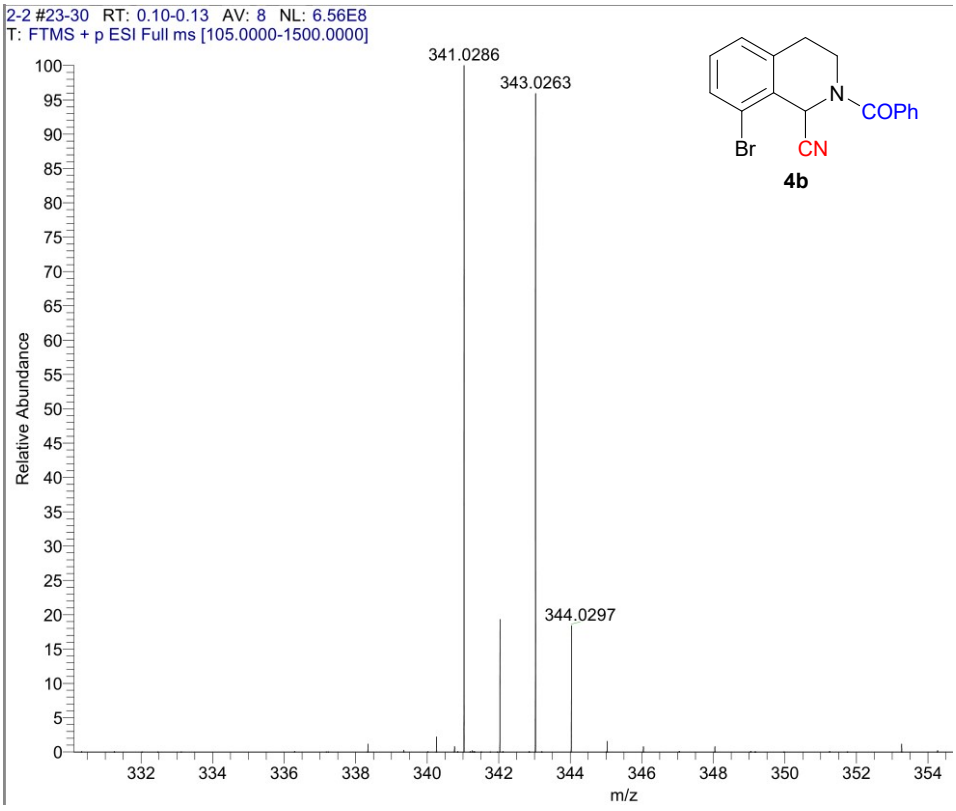


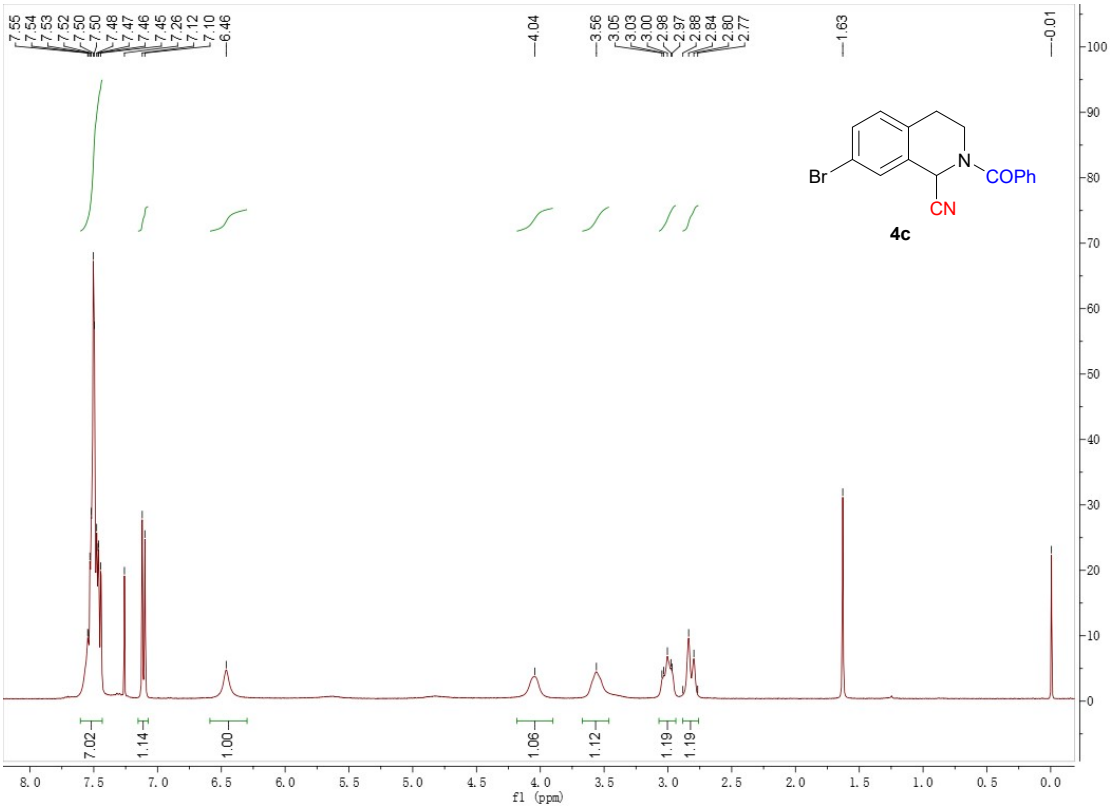


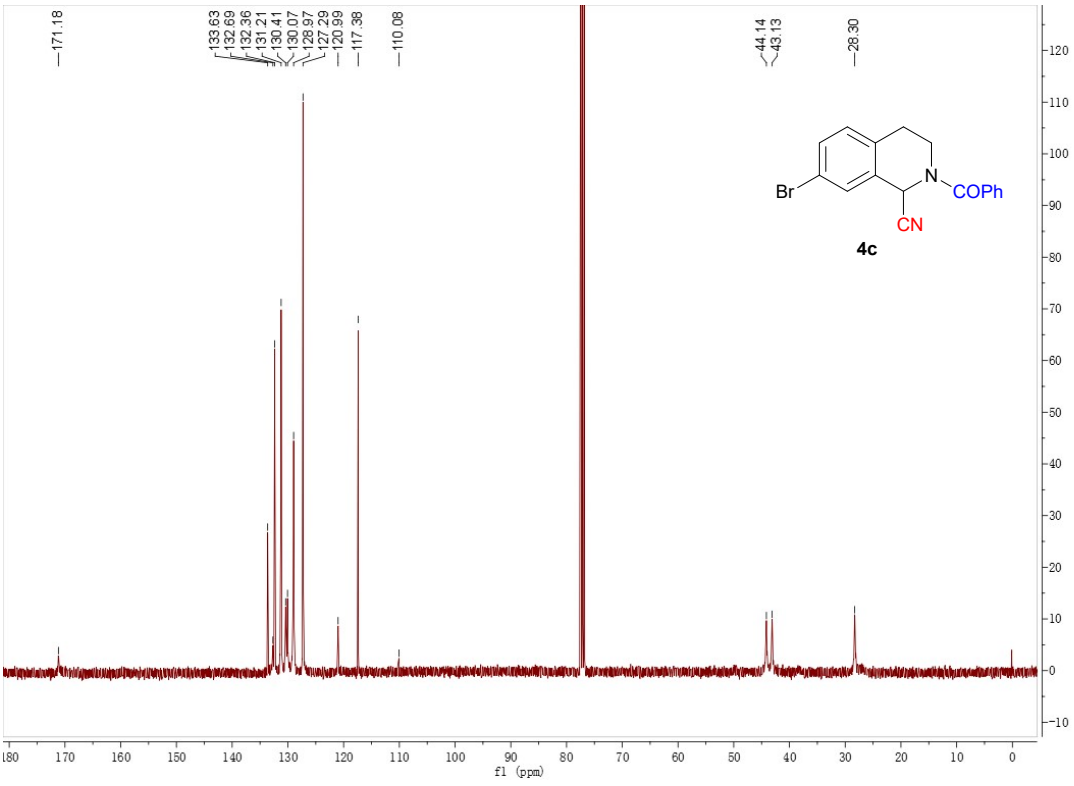

1-46 #21-27 RT: 0.09-0.12 AV: 7 NL: 1.01E9
T: FTMS + p ESI Full ms [105.0000-1500.0000]
285.1000
286.1032
Relative Abundance
m/z
N
COPh
CN
4a

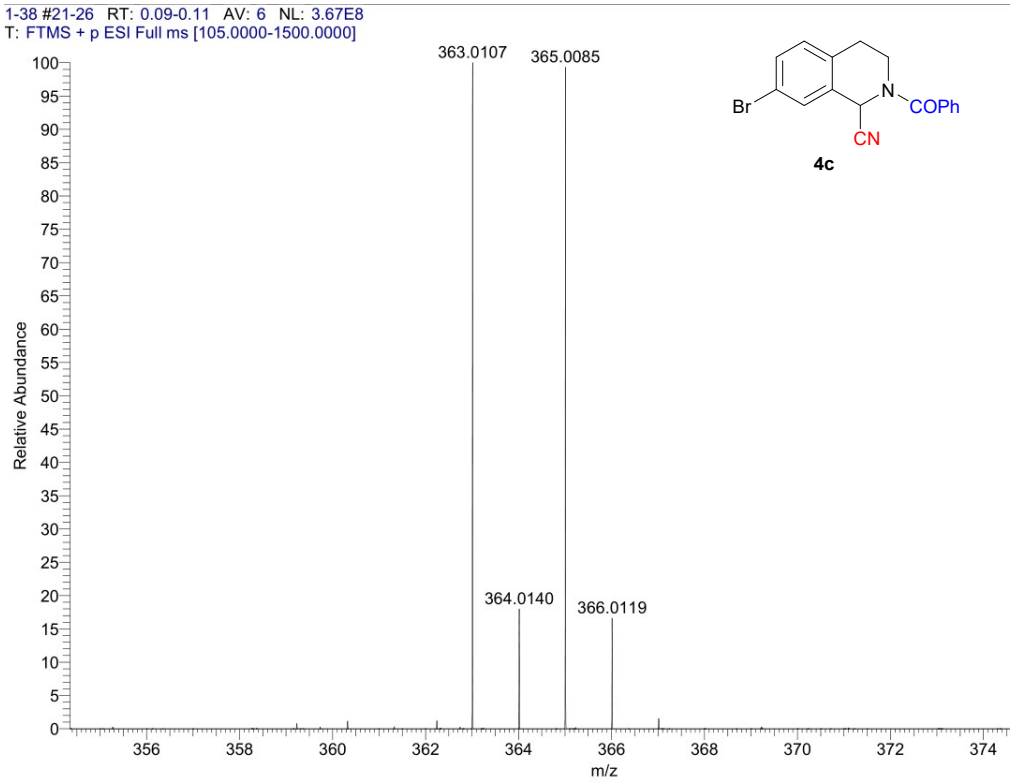

7.62
7.51
7.42
7.41
7.26
7.26
7.24
7.22
7.16
6.61
4.04
3.64
3.11
2.91
2.91
2.87
2.87
2.81
N
COPh
Br
CN
4b
6.16
2.17
1.02
1.00
1.06
1.17
1.15
f1 (ppm)

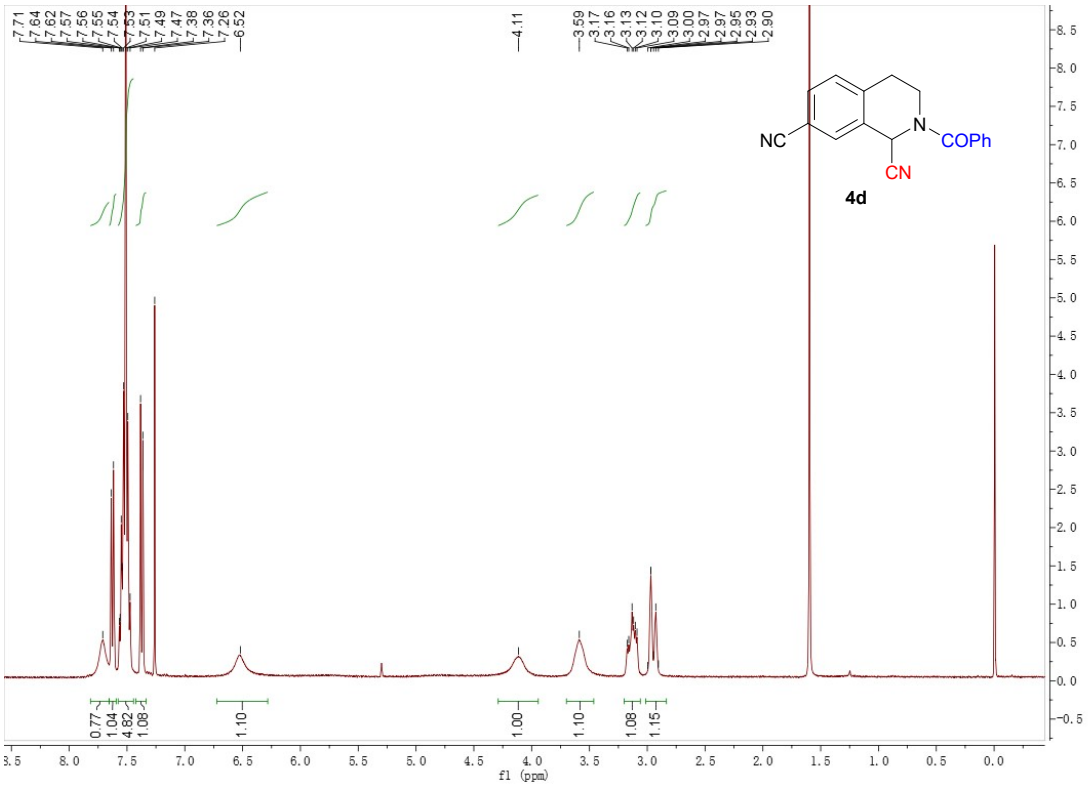

170.96
136.38
133.66
131.81
131.19
130.42
128.98
128.89
127.94
127.31
123.40
116.47
45.82
43.11
28.76
N
COPh
Br
CN
4b
f1 (ppm)

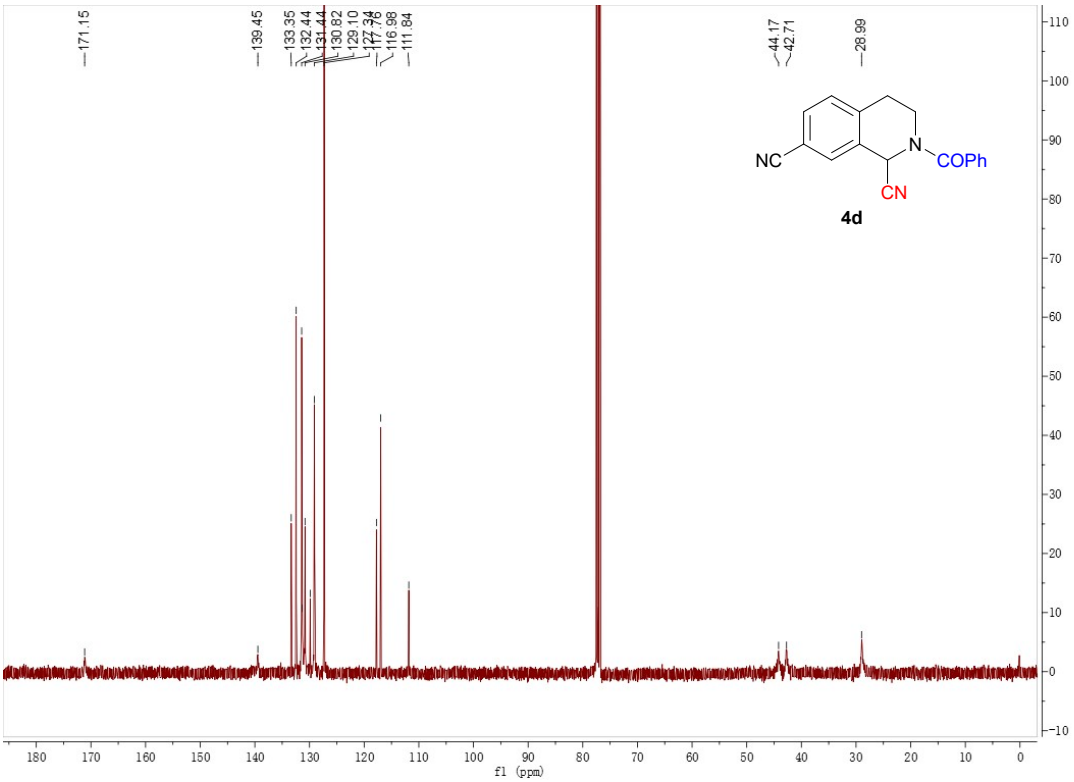

2-2 #23-30 RT: 0.10-0.13 AV: 8 NL: 6.56E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
341.0286
343.0263
344.0297
Relative Abundance
m/z
N
COPh
Br
CN
4b

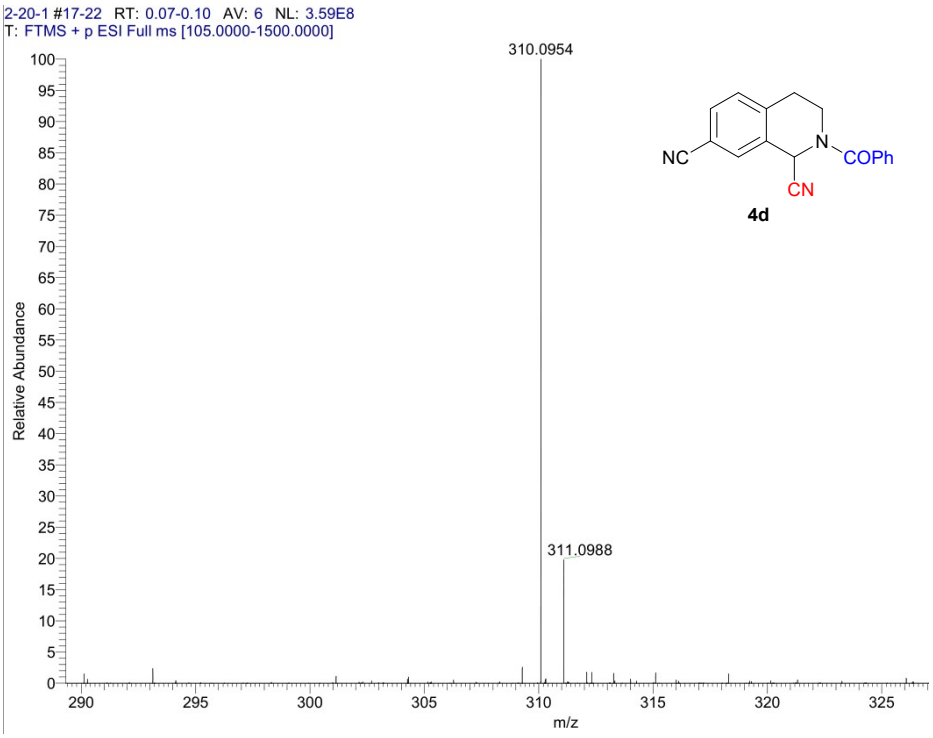

7.55
7.54
7.53
7.52
7.50
7.50
7.48
7.47
7.46
7.45
7.26
7.12
7.10
6.46
4.04
3.56
3.05
3.03
3.00
2.98
2.97
2.88
2.84
2.80
2.77
1.63
0.01
Br
N
COPh
CN
4c
7.02
1.14
1.00
1.06
1.12
1.19
1.19
f1 (ppm)


171.18
133.63
132.69
132.36
131.21
130.41
130.07
128.97
127.29
120.99
117.38
110.08
44.14
43.13
28.30
Br
N
COPh
CN
4c
f1 (ppm)


1-38 #21-26 RT: 0.09-0.11 AV: 6 NL: 3.67E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
363.0107
365.0085
364.0140
366.0119
Relative Abundance
m/z
Br
N
COPh
CN
4c


NC
N
COPh
CN
4d
f1 (ppm)


171.15
139.45
133.35
132.44
131.44
130.82
129.10
116.98
111.84
44.17
42.71
28.99
NC
N
COPh
CN
4d
f1 (ppm)


2-20-1 #17-22 RT: 0.07-0.10 AV: 6 NL: 3.59E8
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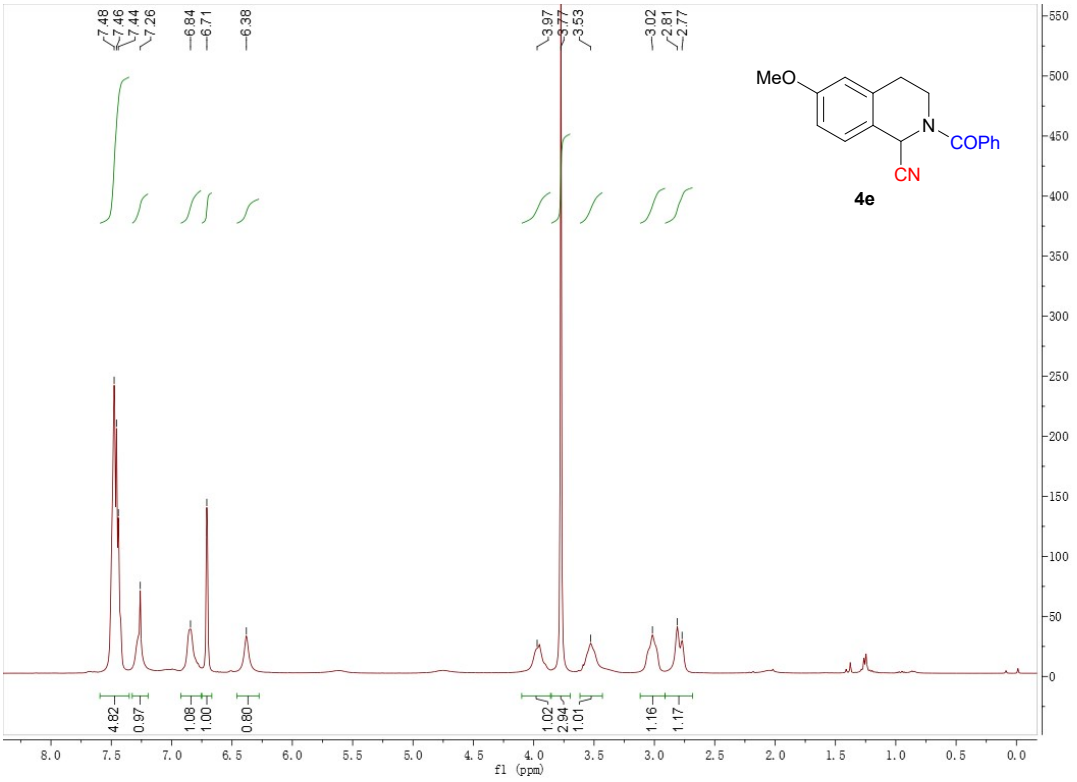
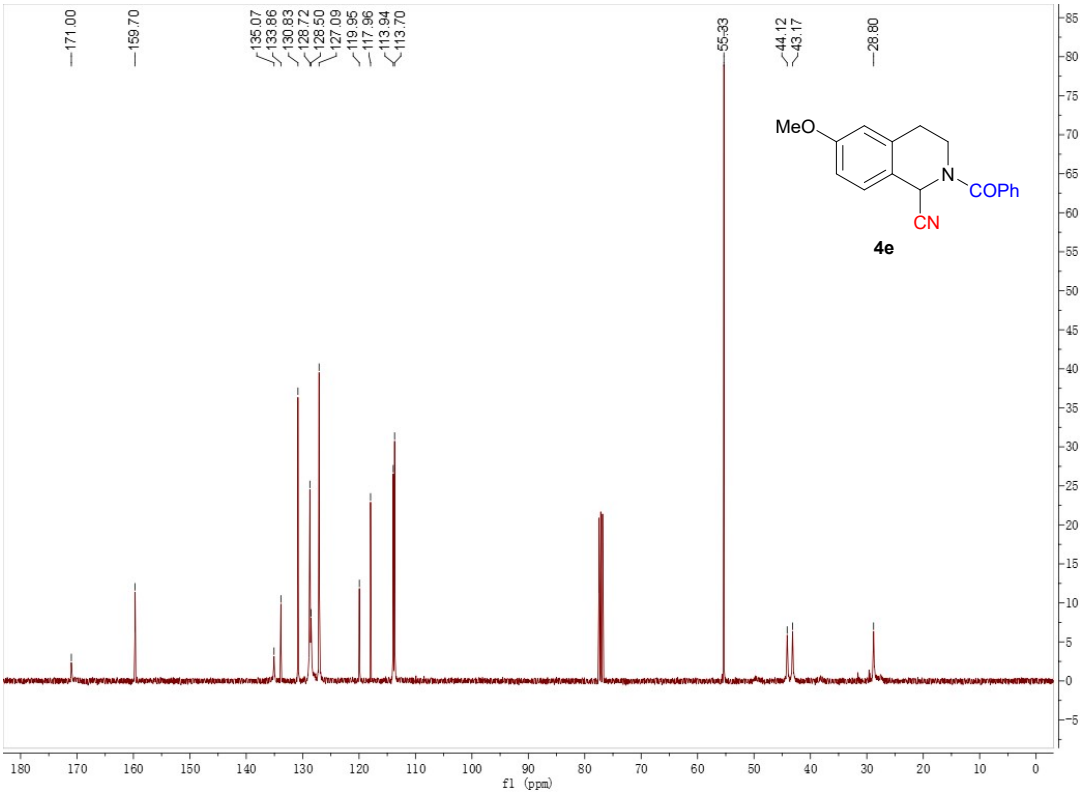
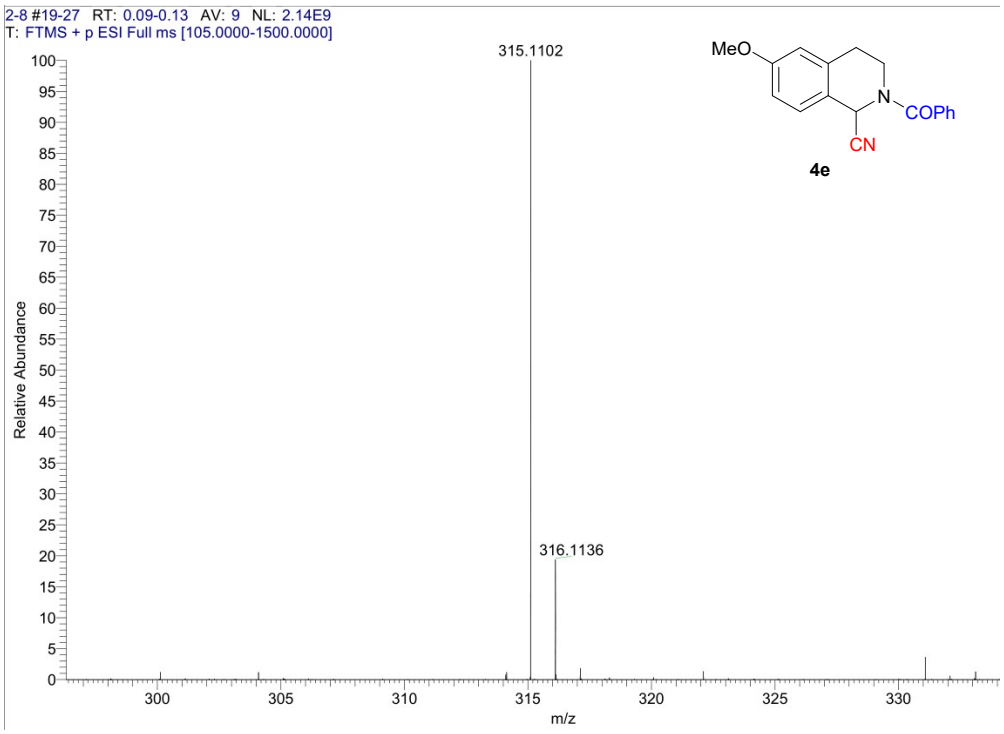
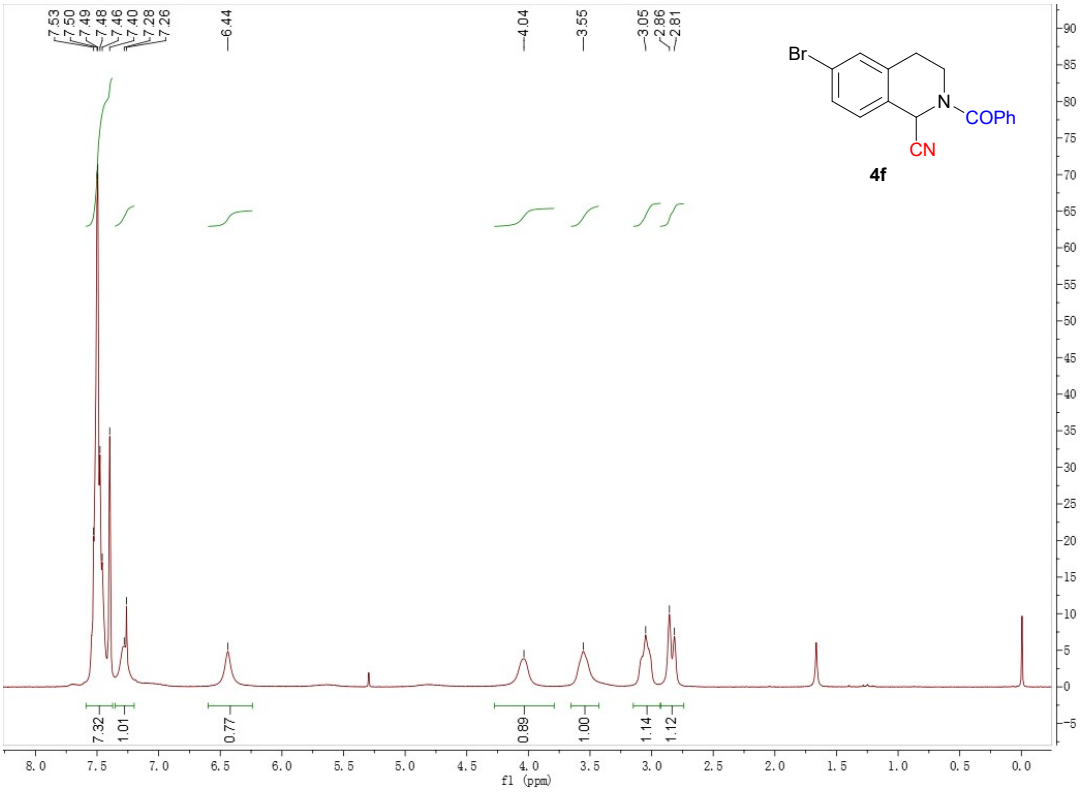
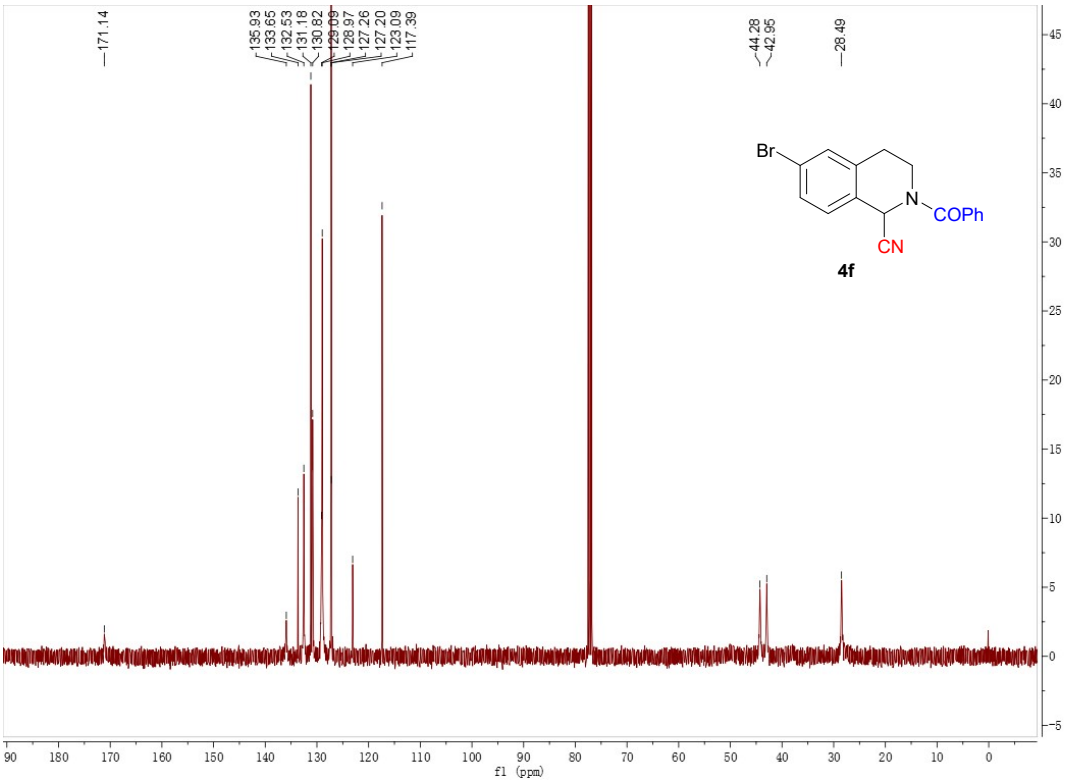
310.0954
311.0988
Relative Abundance
m/z
NC
N
COPh
CN
4d

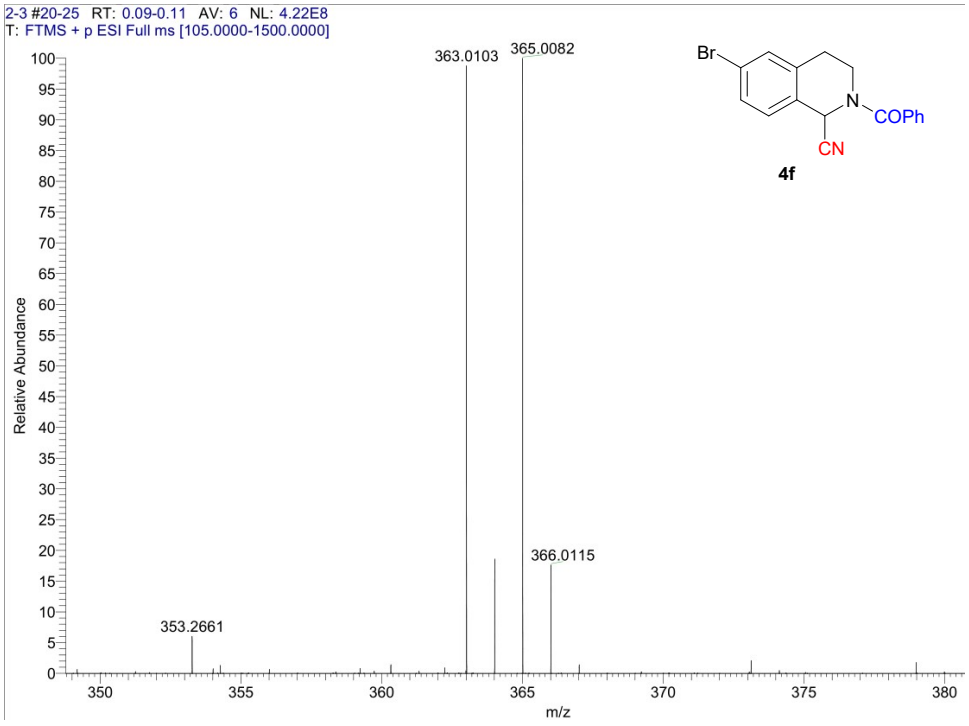

7.48
7.46
7.44
7.26
6.84
6.71
6.38
3.97
3.77
3.53
3.02
2.81
2.77
MeO
N
COPh
CN
4e
4.82
0.97
1.08
1.00
0.80
1.02
2.94
1.01
1.16
1.17
f1 (ppm)


171.00
159.70
135.07
133.86
130.83
128.72
128.50
127.09
119.95
117.96
113.94
113.70
55.33
44.12
43.17
28.80
MeO
N
COPh
CN
4e
f1 (ppm)


2-8 #19-27 RT: 0.09-0.13 AV: 9 NL: 2.14E9
T: FTMS + p ESI Full ms [105.0000-1500.0000]
315.1102
316.1136
Relative Abundance
m/z
MeO
N
COPh
CN
4e


7.53
7.50
7.49
7.48
7.46
7.40
7.28
7.26
6.44
4.04
3.55
3.05
2.86
2.81
Br
N
COPh
CN
4f
7.32
1.01
0.77
0.89
1.00
1.14
1.12
f1 (ppm)


171.14
135.93
133.65
132.53
131.18
130.82
129.09
128.97
127.26
127.20
123.09
117.39
44.28
42.95
28.49
Br
N
COPh
CN
4f
f1 (ppm)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T: FTMS + p ESI Full ms [105.0000-1500.0000]
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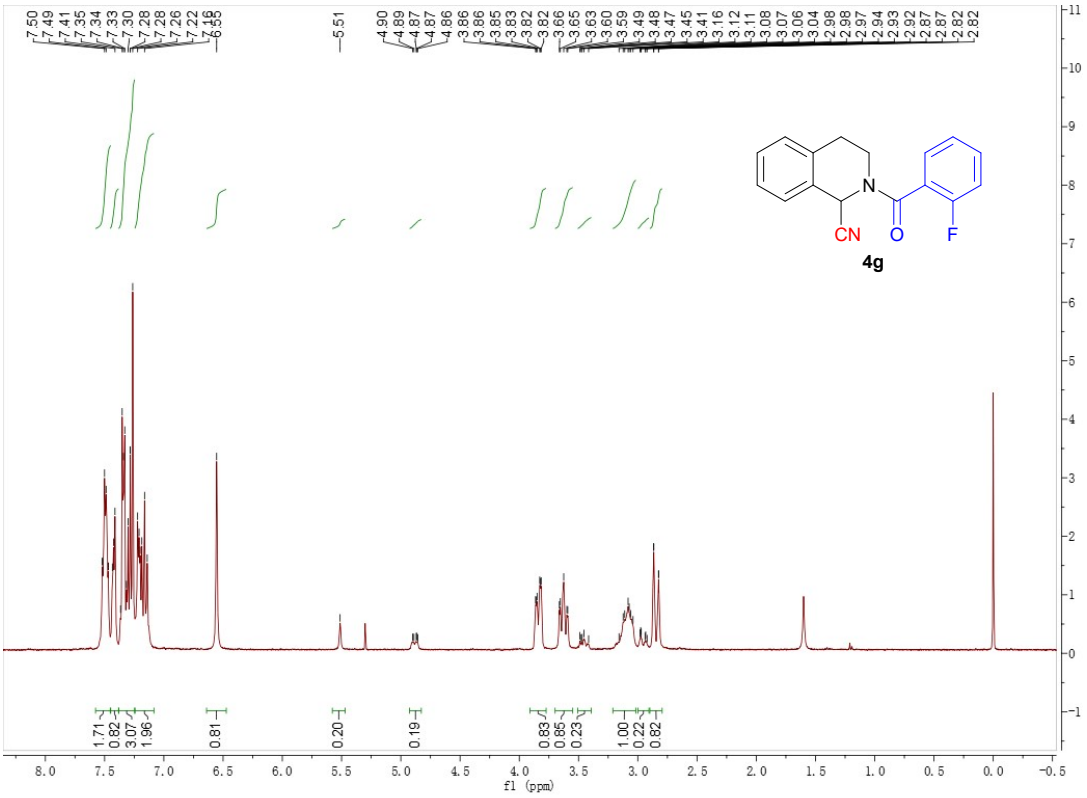
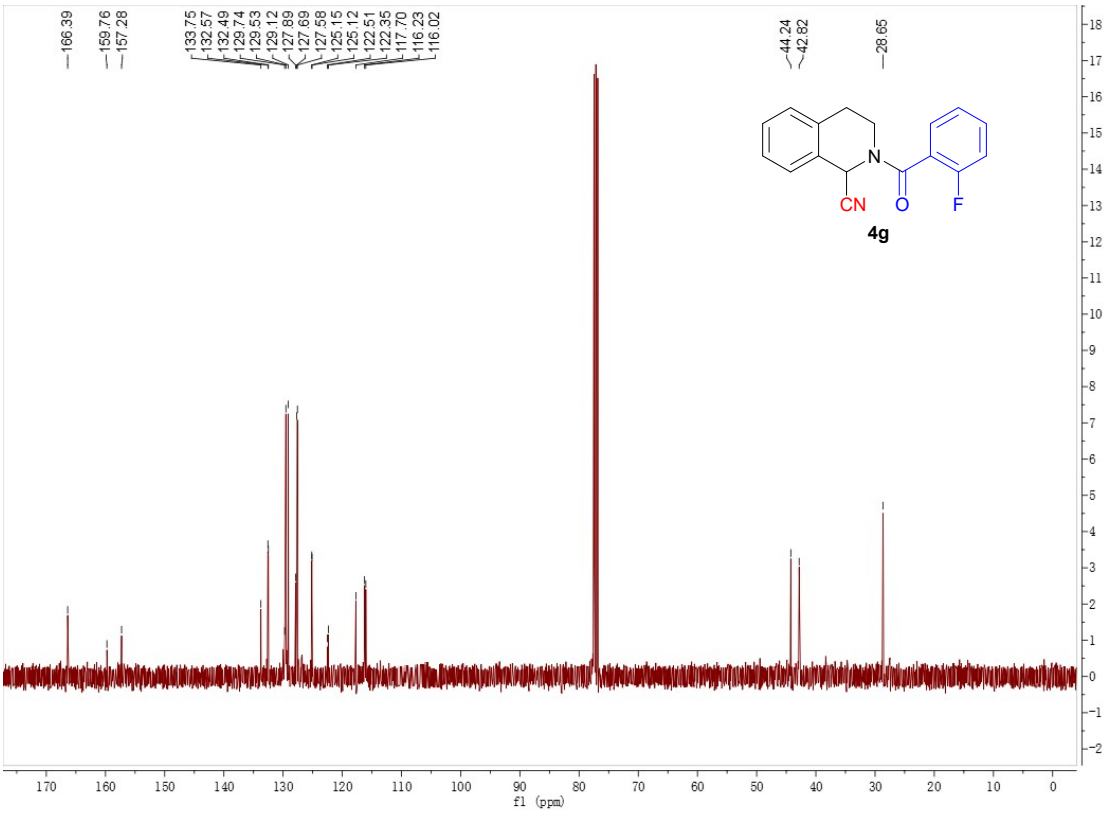
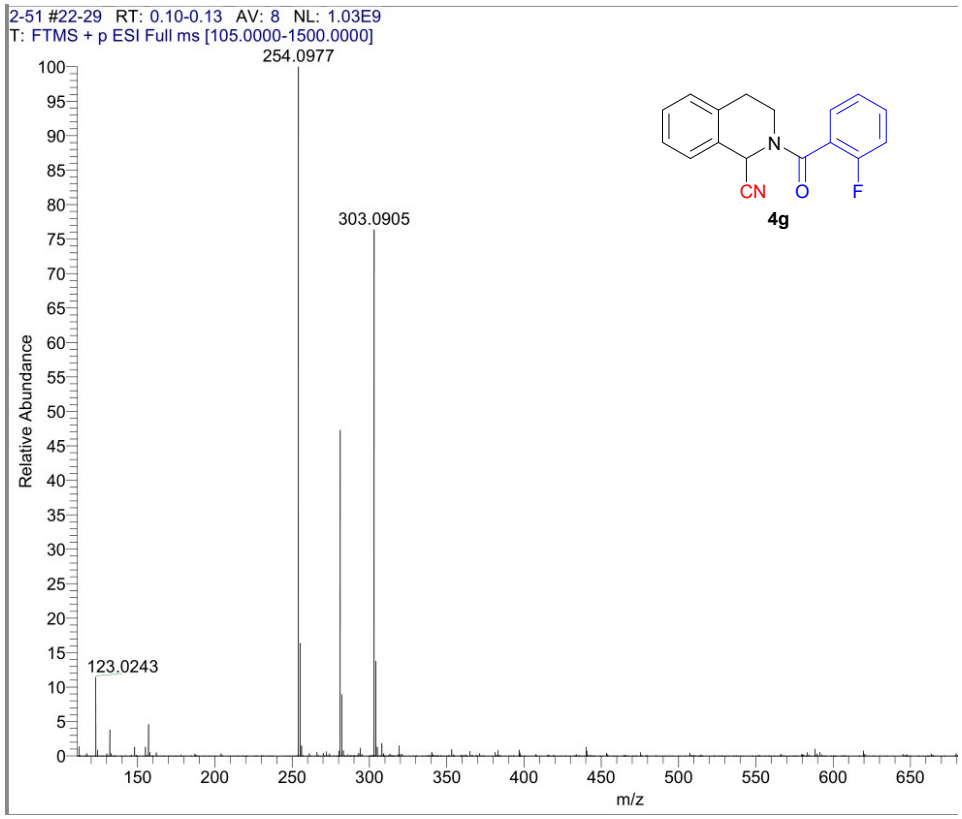
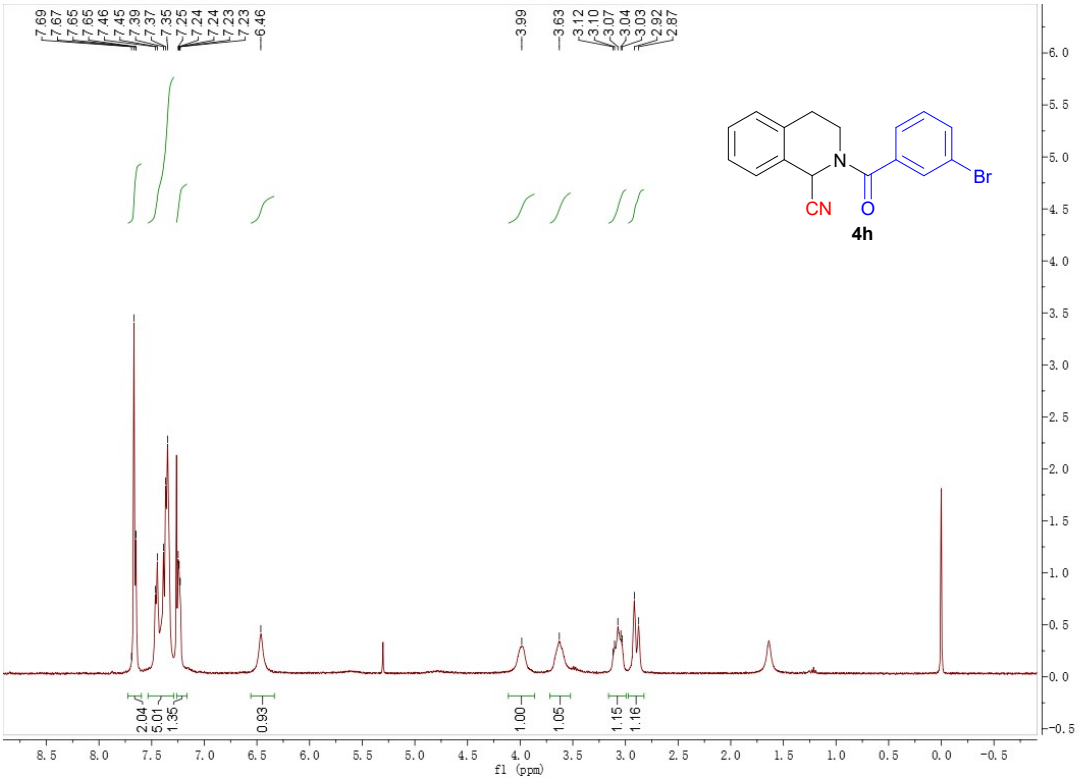
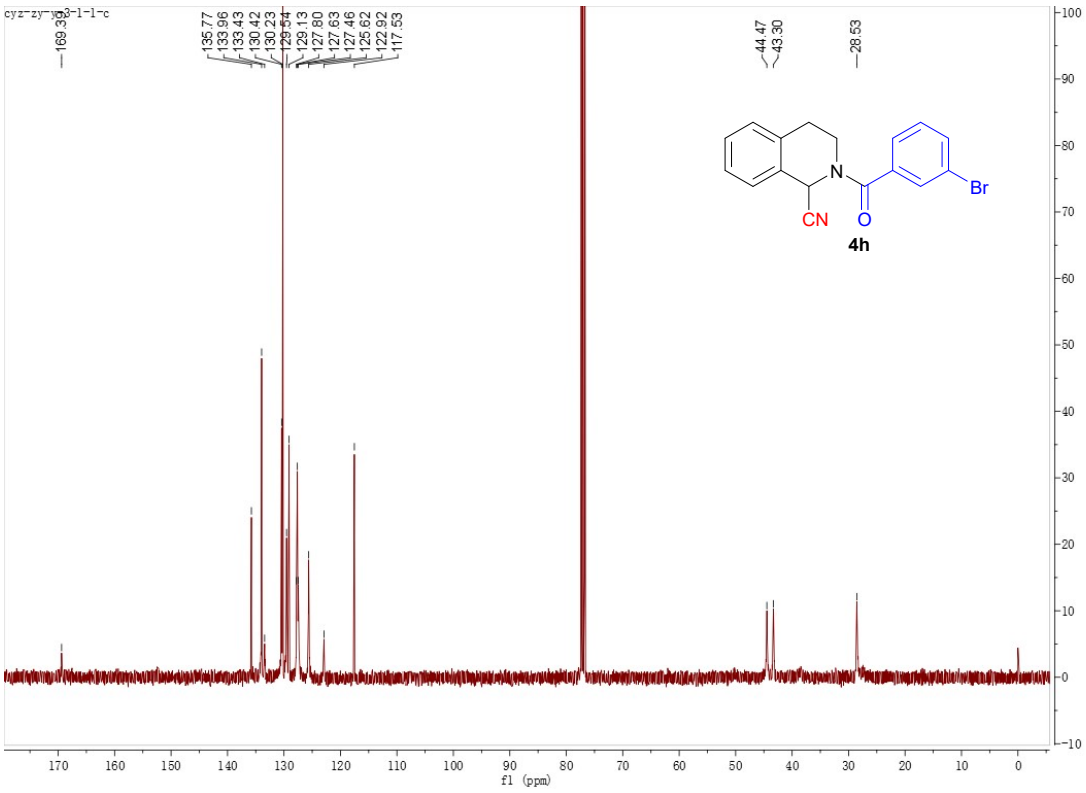
365.0082
366.0115
353.2661
Relative Abundance
m/z
Br
N
COPh
CN
4f

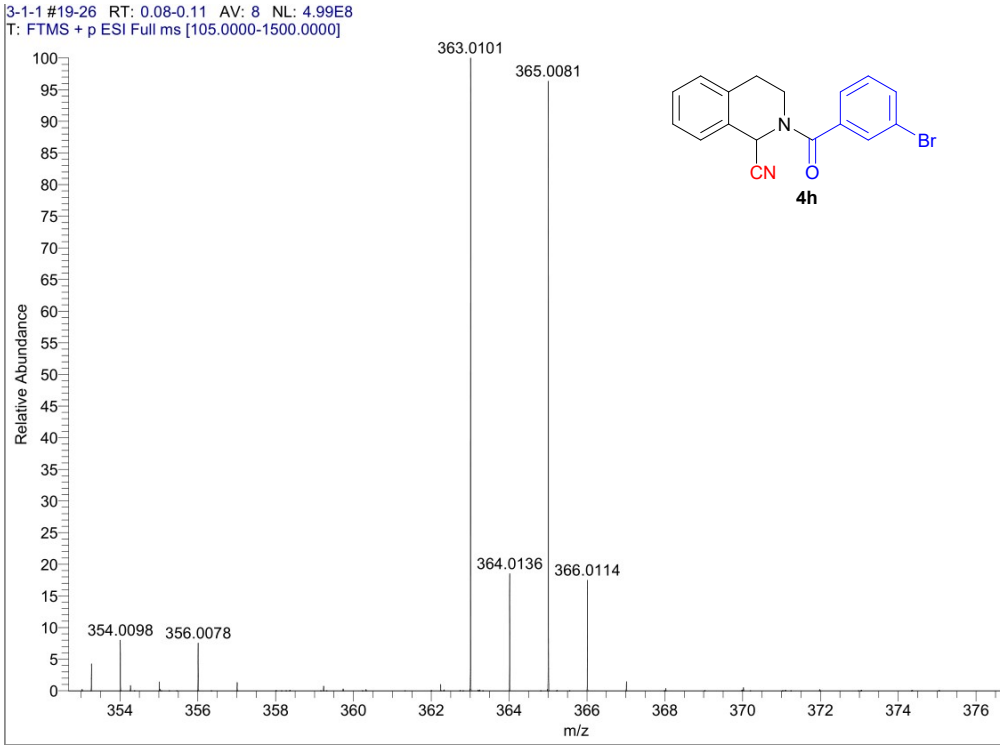

7.50
7.49
7.41
7.35
7.34
7.33
7.30
7.28
7.28
7.26
7.22
7.18
6.55
5.51
4.90
4.89
4.87
4.87
4.86
3.86
3.86
3.85
3.83
3.82
3.82
3.66
3.65
3.63
3.60
3.59
3.49
3.48
3.47
3.45
3.41
3.16
3.12
3.11
3.08
3.07
3.06
3.04
2.98
2.98
2.97
2.94
2.93
2.92
2.87
2.87
2.82
2.82
N
CN
O
F
4g
1.71
0.82
3.07
1.96
0.81
0.20
0.19
0.83
0.85
0.23
1.00
0.22
0.82
f1 (ppm)

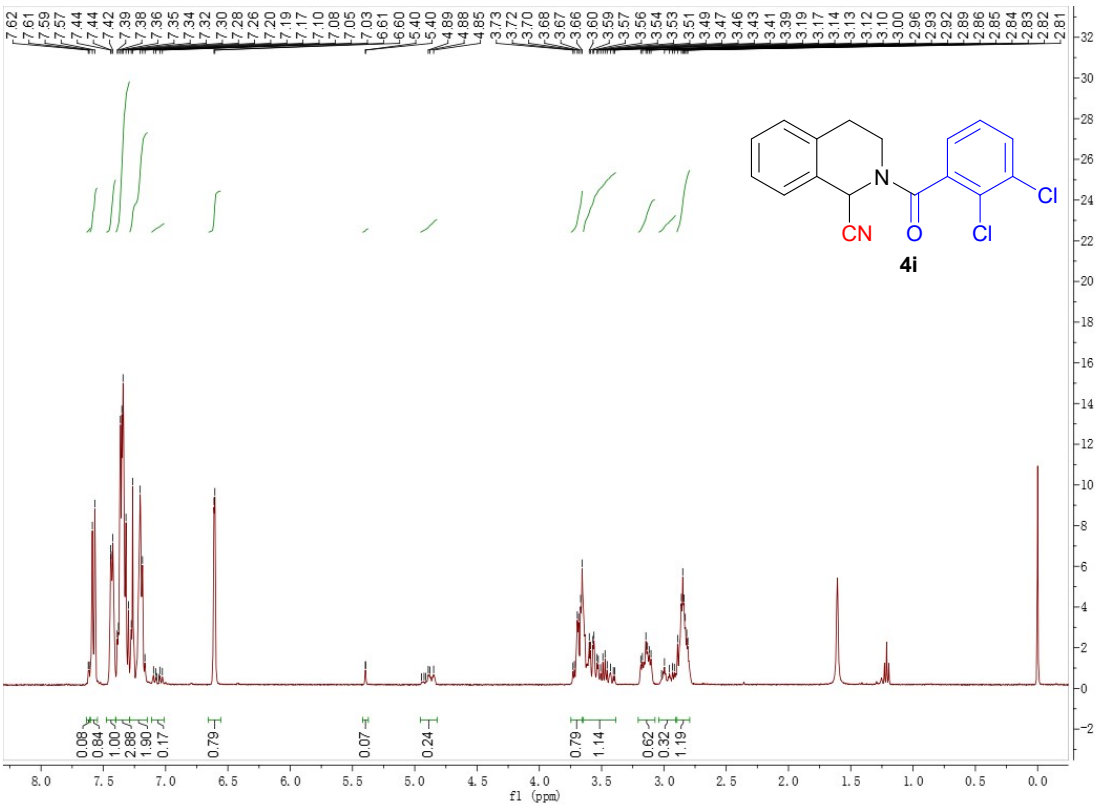

166.39
159.76
157.28
133.75
132.57
132.49
129.74
129.53
129.12
127.89
127.69
127.58
125.15
125.12
122.51
122.35
117.70
116.23
116.02
44.24
42.82
28.65
N
CN
O
F
4g
f1 (ppm)

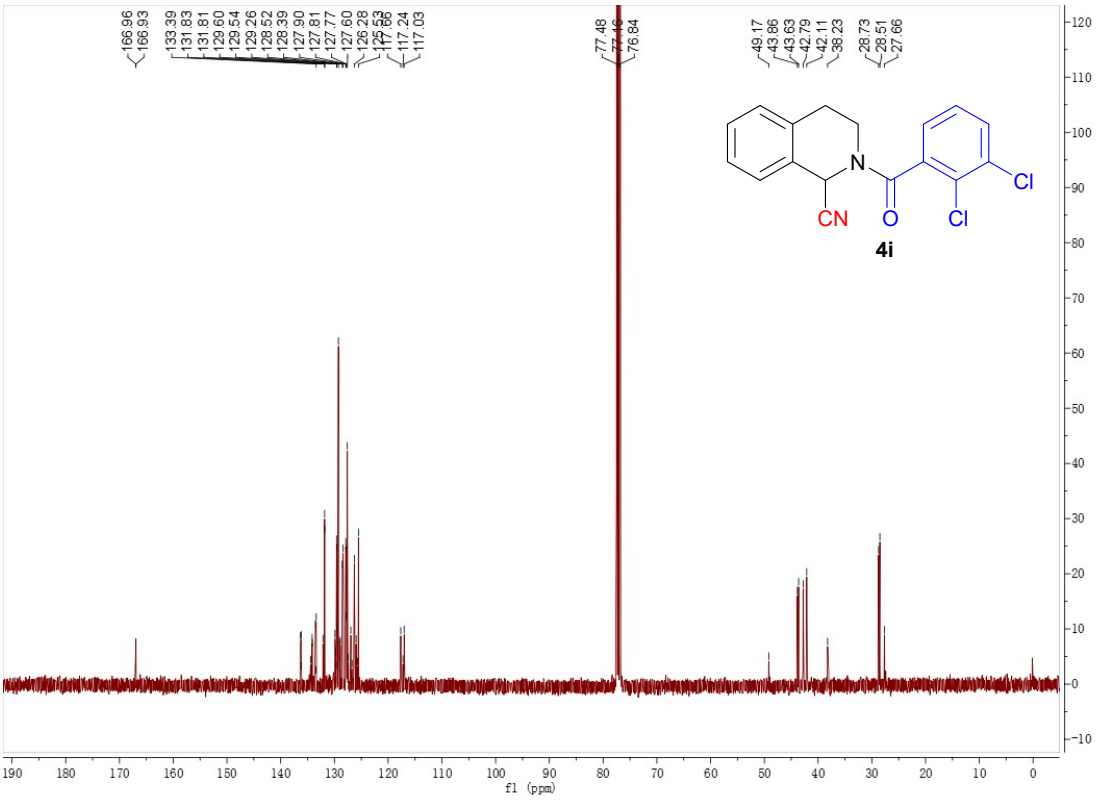

2-51 #22-29 RT: 0.10-0.13 AV: 8 NL: 1.03E9
T: FTMS + p ESI Full ms [105.0000-1500.0000]
254.0977
303.0905
123.0243
Relative Abundance
m/z
CN
O
F
4g

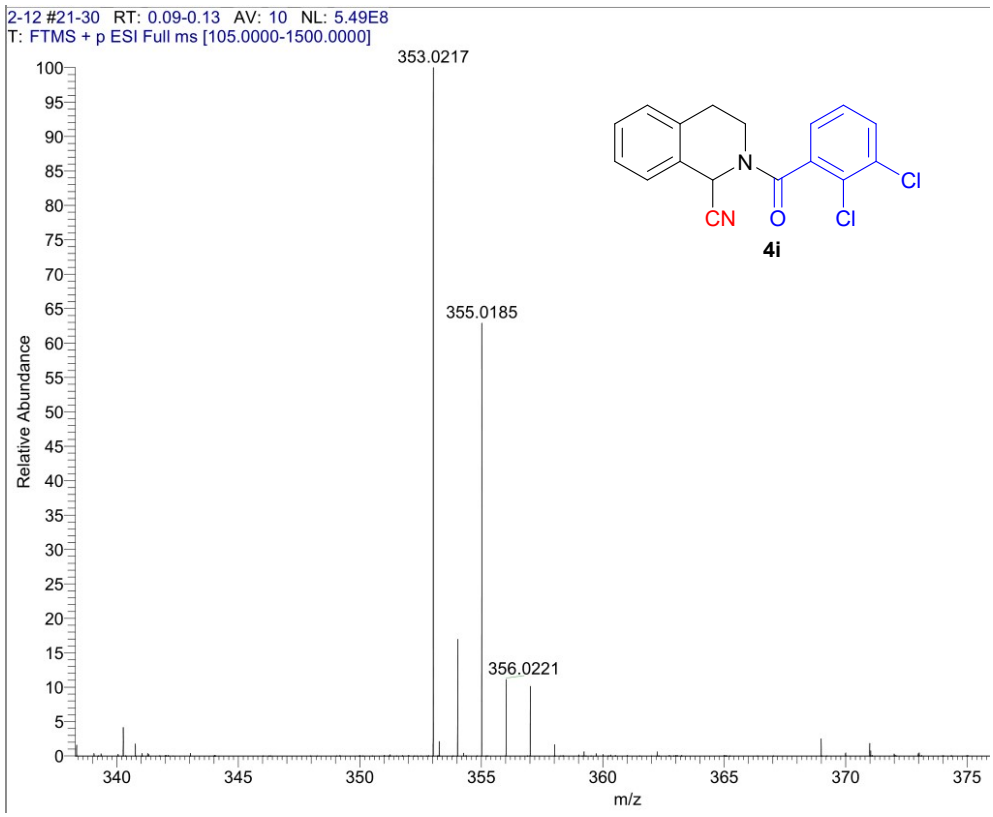

7.69
7.67
7.65
7.65
7.46
7.45
7.39
7.37
7.35
7.25
7.24
7.24
7.23
7.23
6.46
3.99
3.63
3.12
3.10
3.07
3.04
3.03
2.92
2.87
CN
O
Br
4h
2.04
5.01
1.35
0.93
1.00
1.05
1.15
1.16
f1 (ppm)

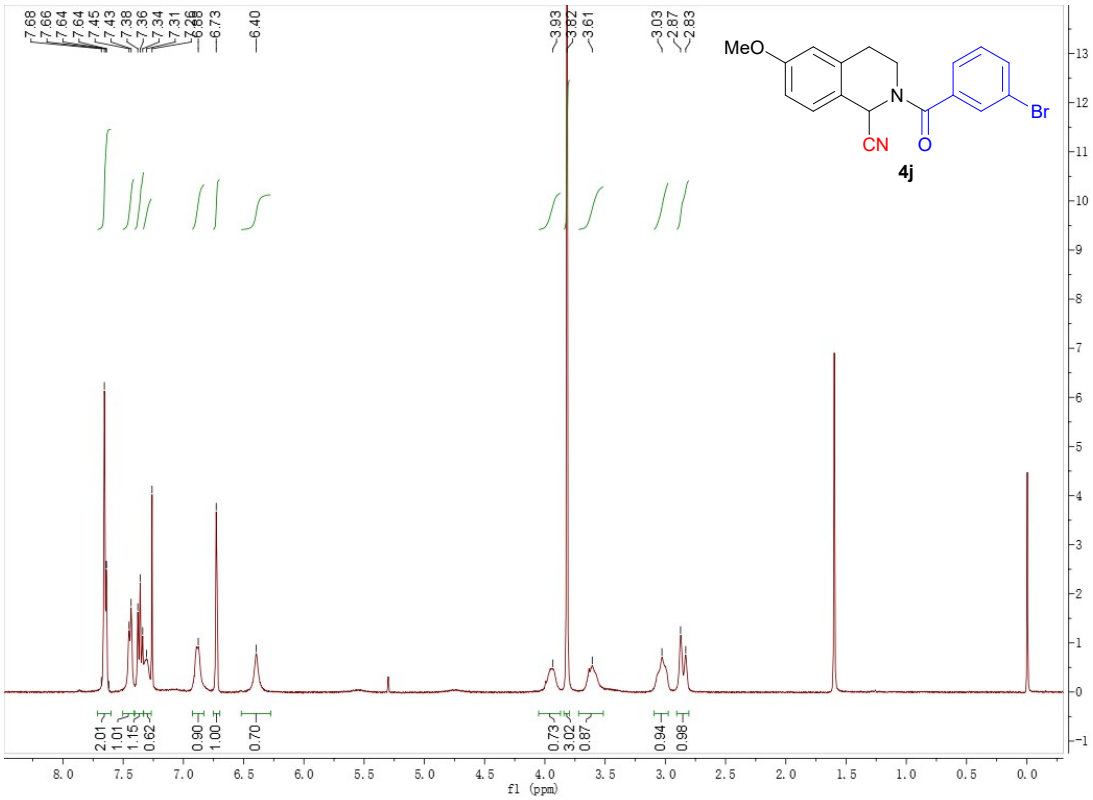

169.39
135.77
133.96
133.43
130.42
130.23
129.54
129.13
127.80
127.63
127.46
125.62
122.92
117.53
44.47
43.30
28.53
Br
CN
O
N
4h
f1 (ppm)

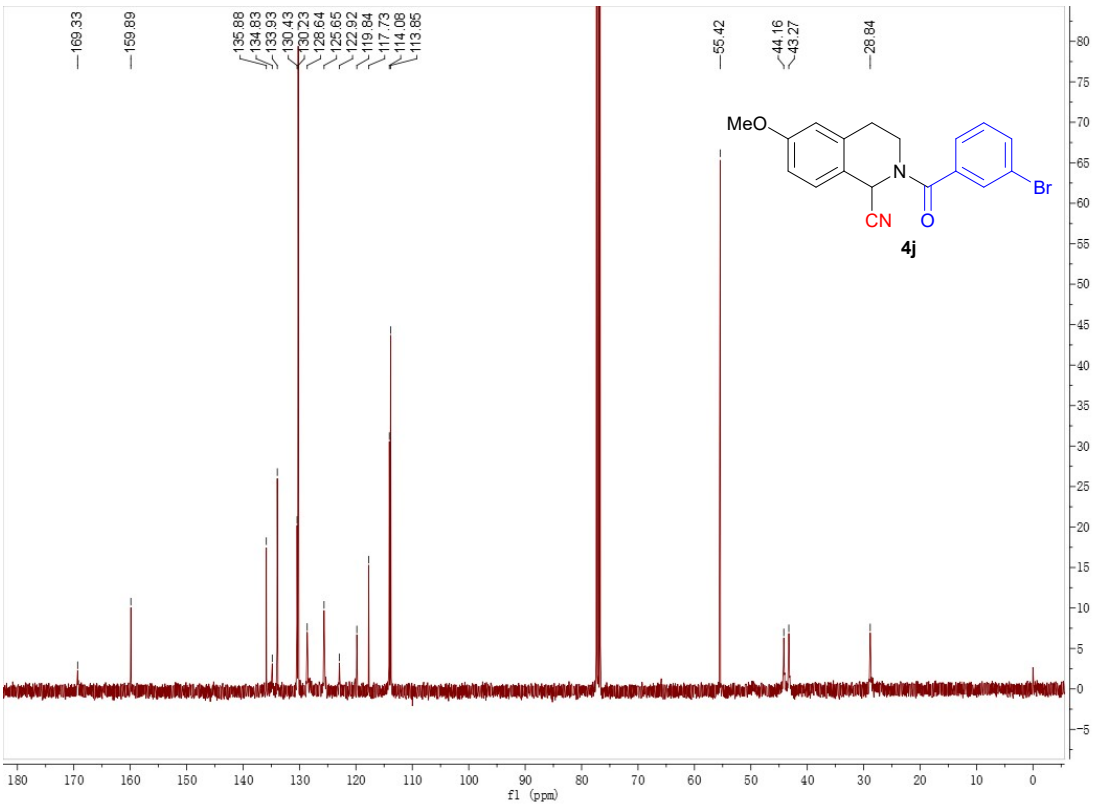

3-1-1 #19-26 RT: 0.08-0.11 AV: 8 NL: 4.99E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
363.0101
365.0081
364.0136
366.0114
354.0098
356.0078
Relative Abundance
m/z
Br
CN
O
N
4h

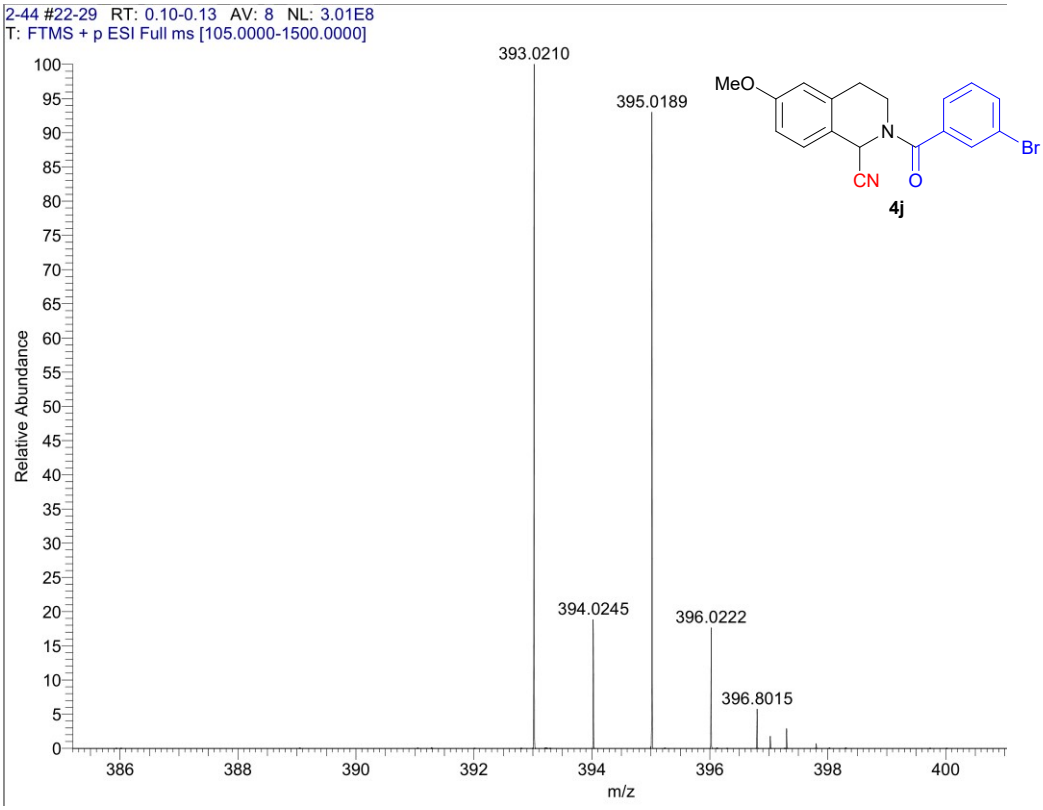

7.62 7.61 7.59 7.57 7.44 7.44 7.42 7.39 7.38 7.36 7.35 7.34 7.32 7.30 7.28 7.26 7.20 7.19 7.17 7.10 7.08 7.05 7.03 6.61 6.60 5.40 5.40 4.89 4.88 4.85 3.73 3.72 3.70 3.68 3.67 3.66 3.60 3.59 3.57 3.56 3.54 3.53 3.51 3.49 3.47 3.46 3.43 3.41 3.39 3.19 3.17 3.14 3.13 3.12 3.10 3.00 2.96 2.93 2.92 2.89 2.86 2.85 2.84 2.83 2.82 2.81
0.08 0.84 1.00 2.88 1.90 0.17 0.79 0.07 0.24 0.79 1.14 0.62 0.32 1.19
f1 (ppm)
N
CN
O
Cl
Cl
4i

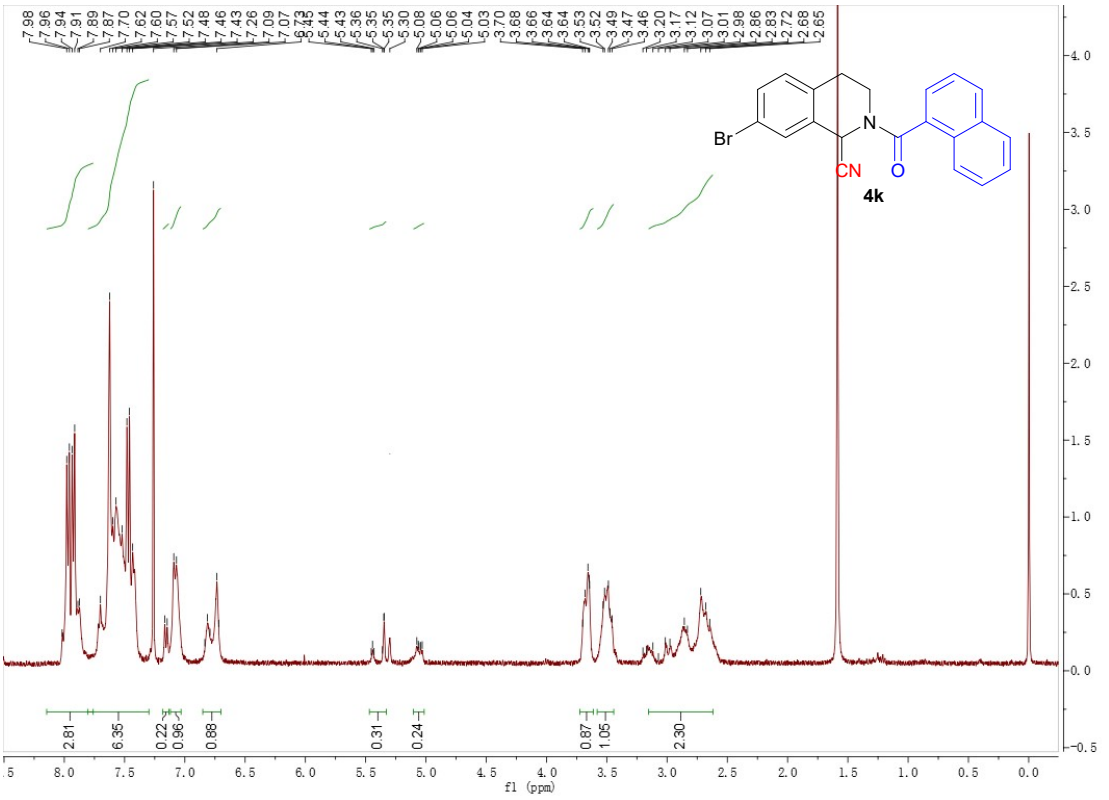

166.96 166.93 133.39 131.83 131.81 129.60 129.54 129.26 128.52 128.39 127.90 127.81 127.77 127.60 126.28 125.53 117.66 117.24 117.03
77.48 77.16 76.84
49.17 43.86 43.63 42.79 42.11 38.23 28.73 28.51 27.66
f1 (ppm)
N
CN
O
Cl
Cl
4i

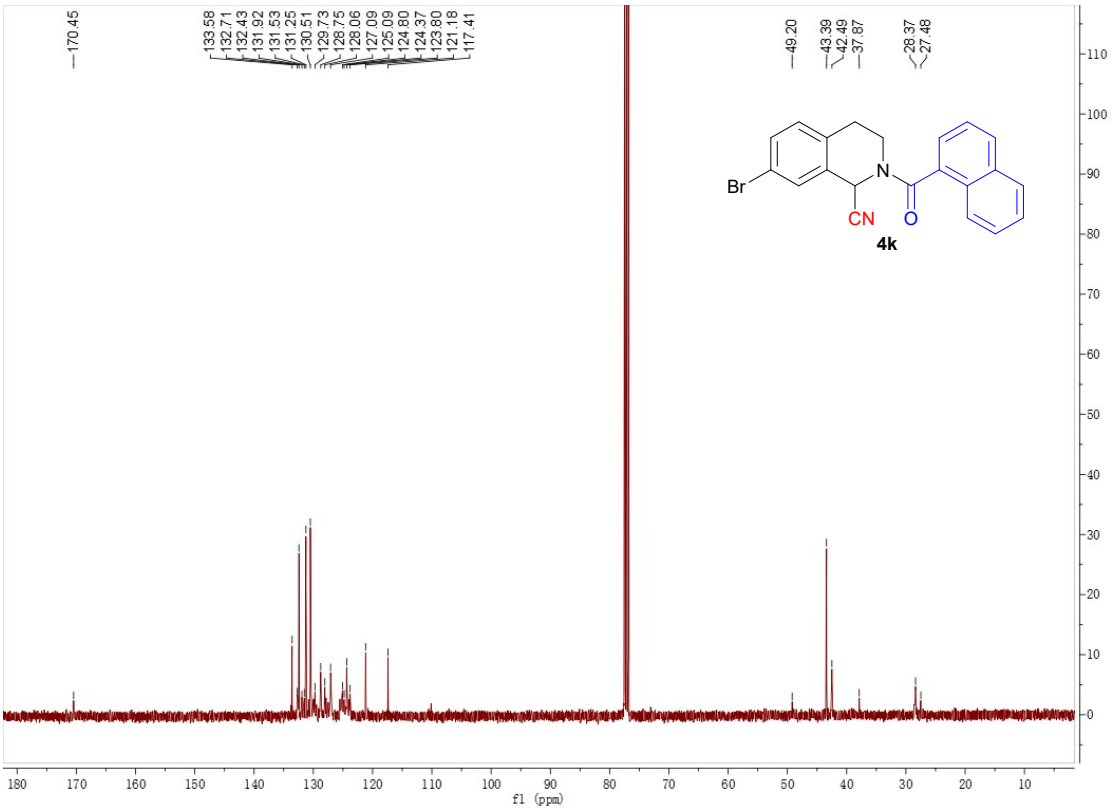

2-12 #21-30 RT: 0.09-0.13 AV: 10 NL: 5.49E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
353.0217
355.0185
356.0221
Relative Abundance
m/z
N
CN
O
Cl
Cl
4i

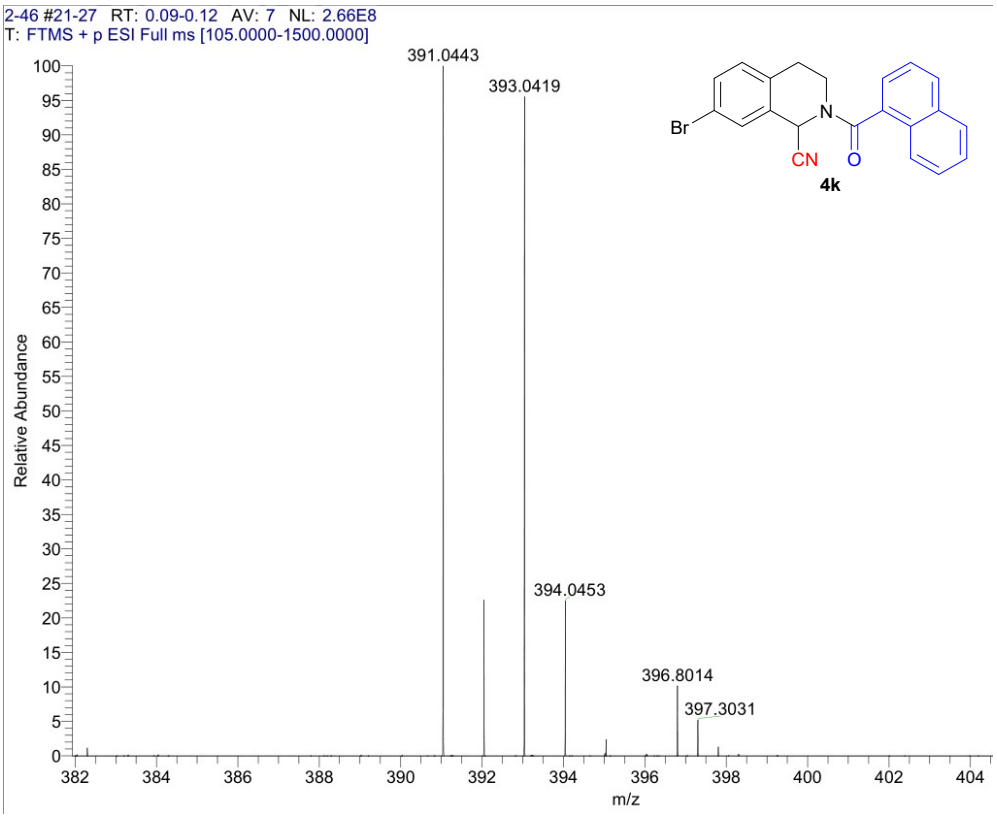

MeO
N
CN
O
Br
4j
f1 (ppm)

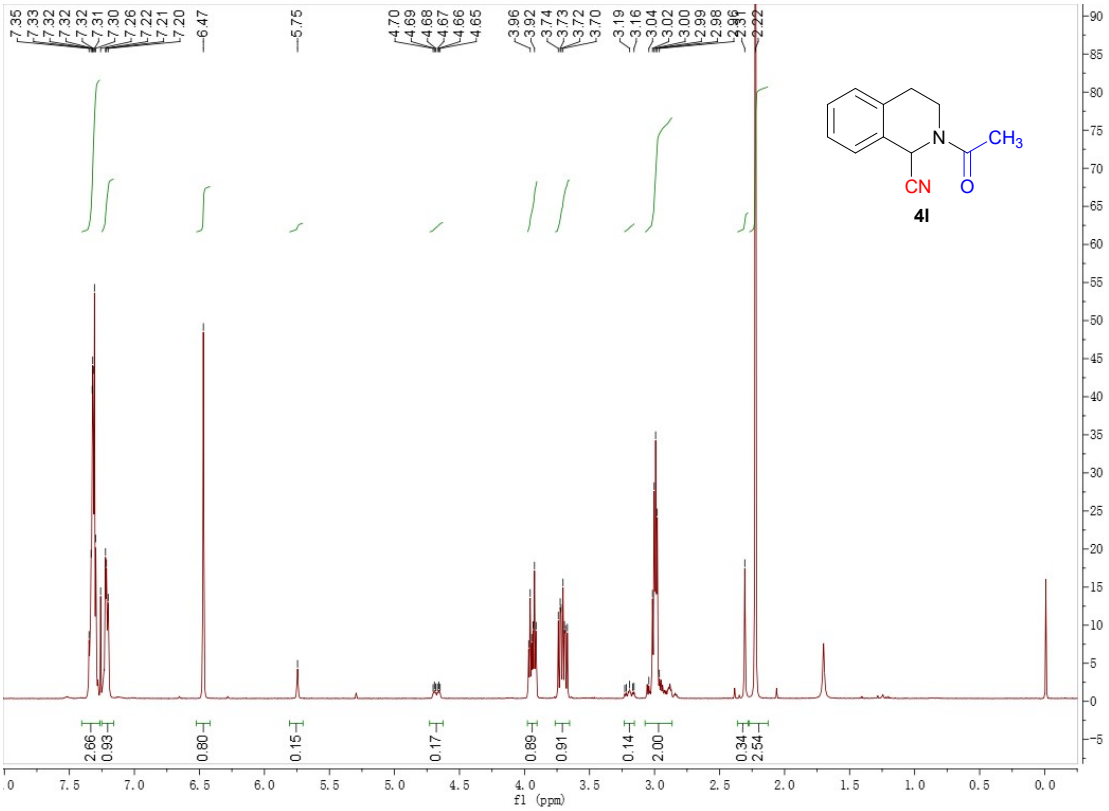

169.33
159.89
135.88
134.83
133.93
130.43
130.23
128.64
125.65
122.92
119.84
117.73
114.08
113.85
55.42
44.16
43.27
28.84
MeO
N
Br
CN
O
4j
f1 (ppm)

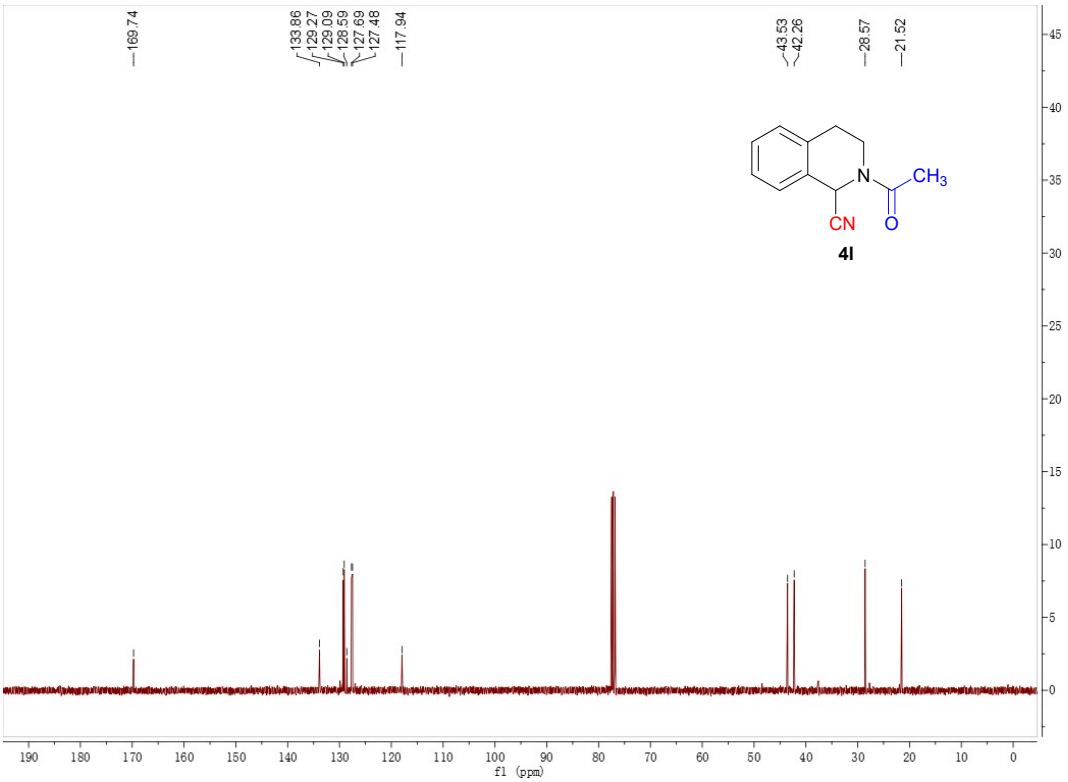

2-44 #22-29 RT: 0.10-0.13 AV: 8 NL: 3.01E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
393.0210
395.0189
394.0245
396.0222
396.8015
MeO
N
Br
CN
O
4j
Relative Abundance
m/z

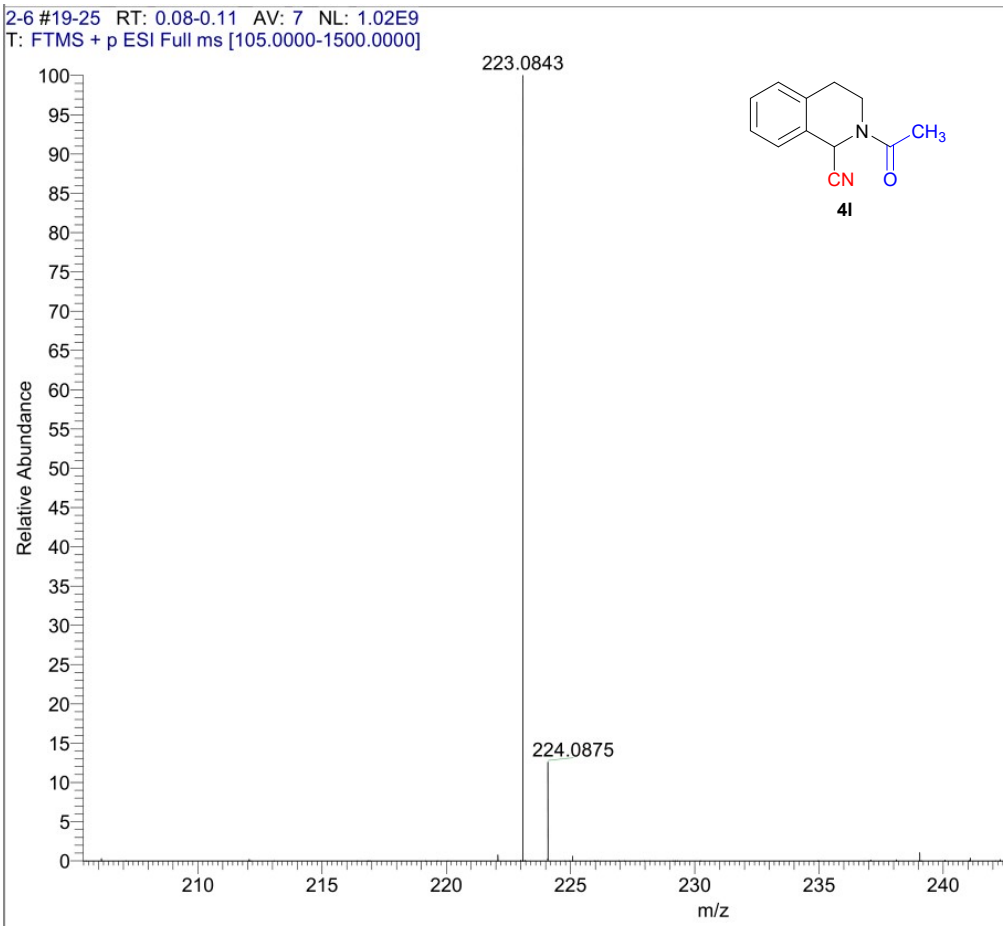

Br
N
CN
O
4k
f1 (ppm)

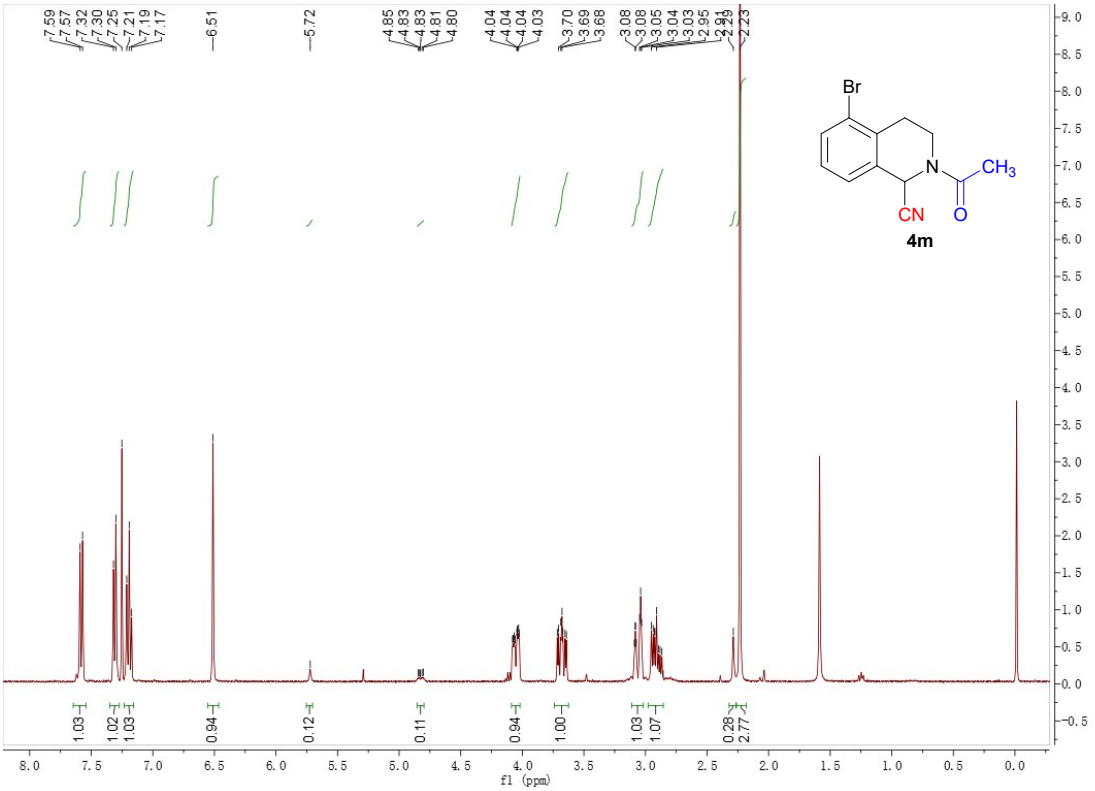

Br
N
CN
O
4k
f1 (ppm)

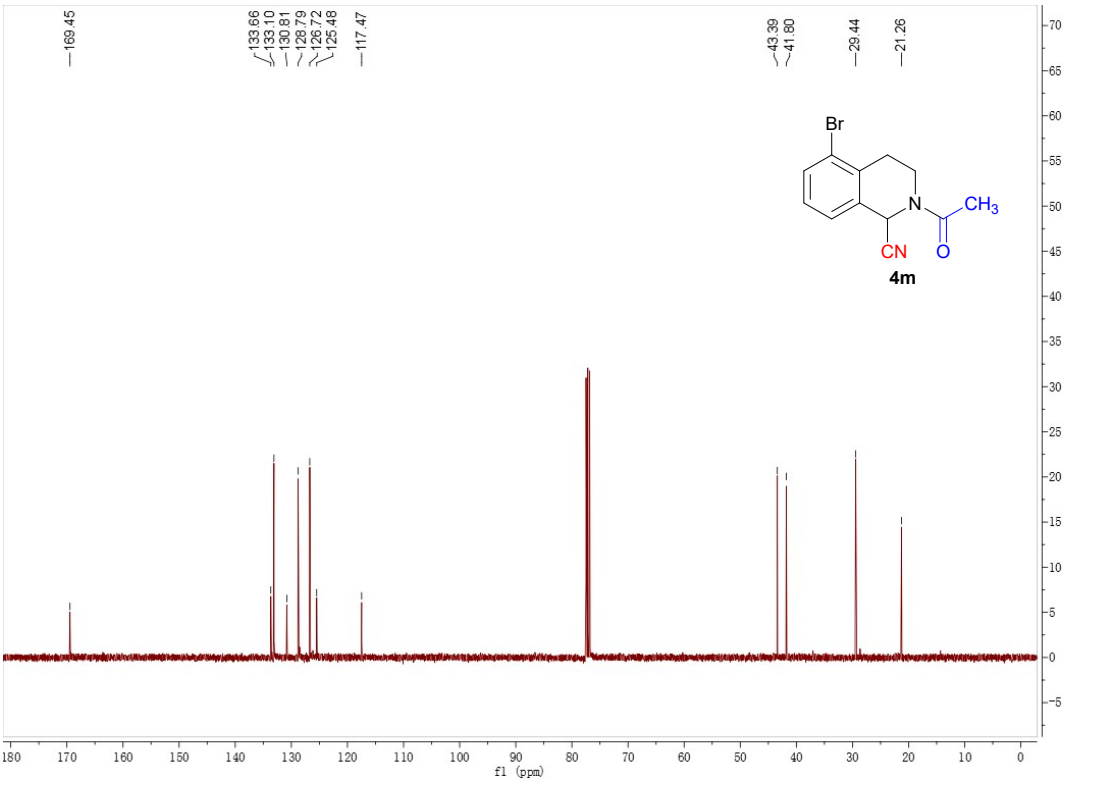

2-46 #21-27 RT: 0.09-0.12 AV: 7 NL: 2.66E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
391.0443
393.0419
394.0453
396.8014
397.3031
Relative Abundance
m/z
Br
N
CN
O
4k

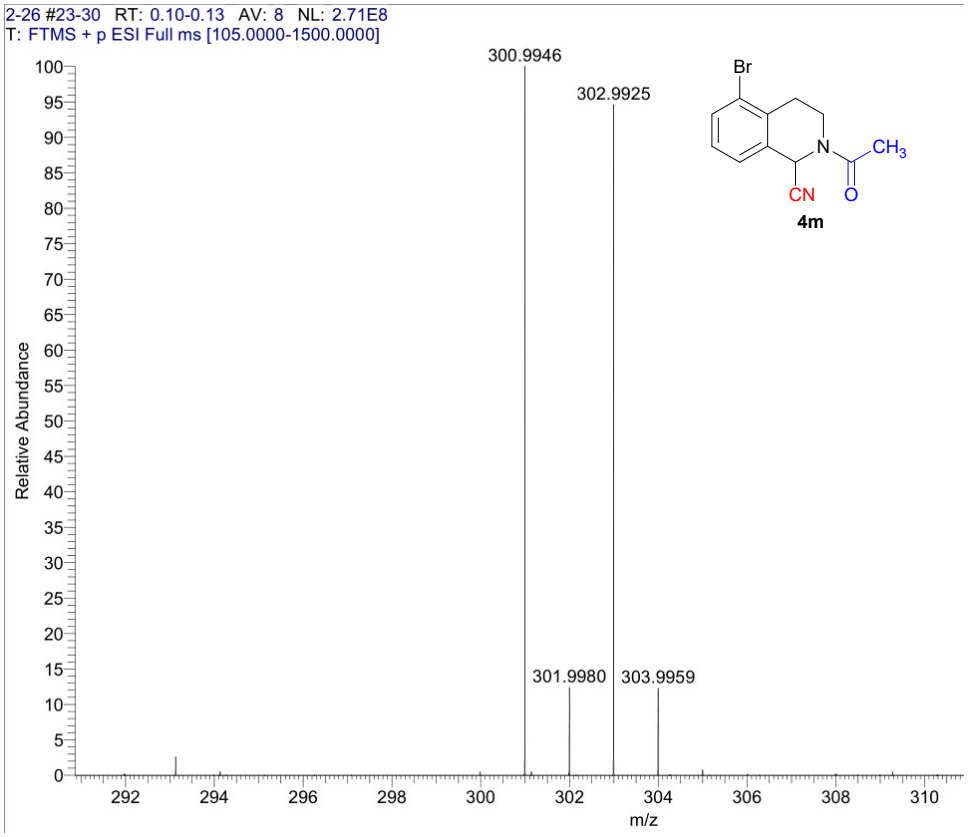

7.35
7.33
7.32
7.32
7.32
7.31
7.30
7.26
7.22
7.21
7.20
6.47
5.75
4.70
4.69
4.68
4.67
4.66
4.65
3.96
3.92
3.74
3.73
3.72
3.70
3.19
3.16
3.04
3.02
3.00
2.99
2.98
2.96
2.22
2.66
0.93
0.80
0.15
0.17
0.89
0.91
0.14
2.00
0.34
2.54
f1 (ppm)
N
CH3
CN
O
4l

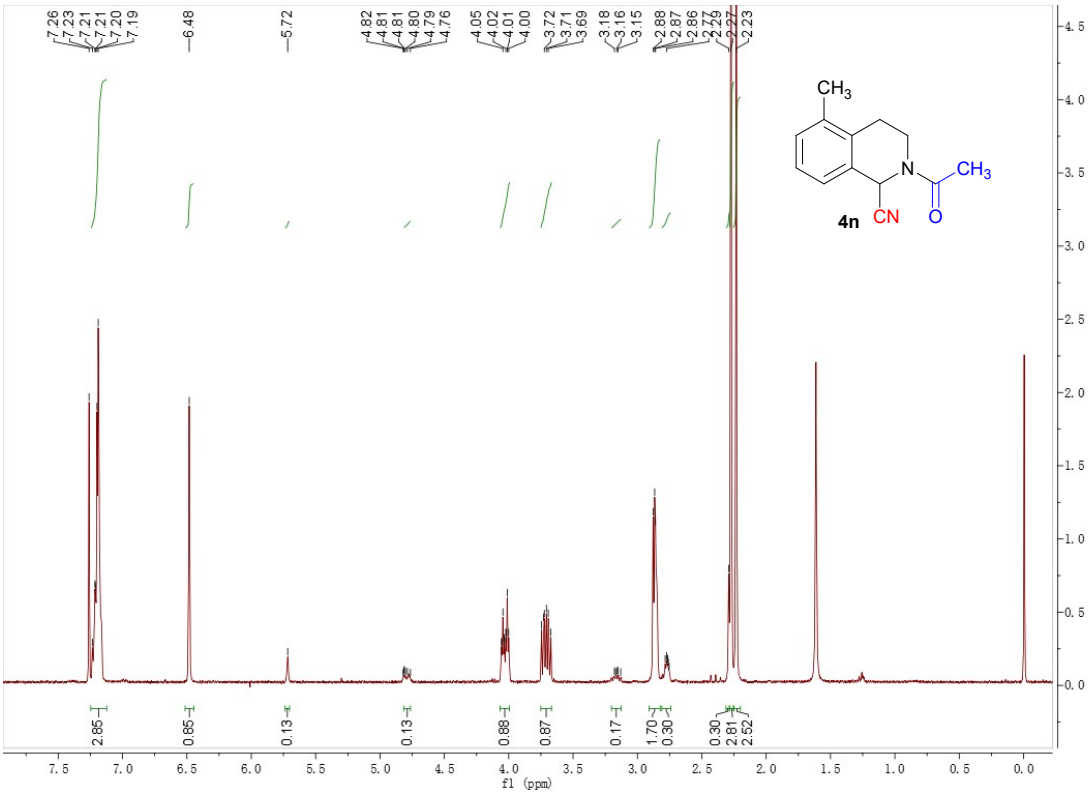

169.74
133.86
129.27
129.09
128.59
127.69
127.48
117.94
43.53
42.26
28.57
21.52
N
CH3
CN
O
4l
f1 (ppm)

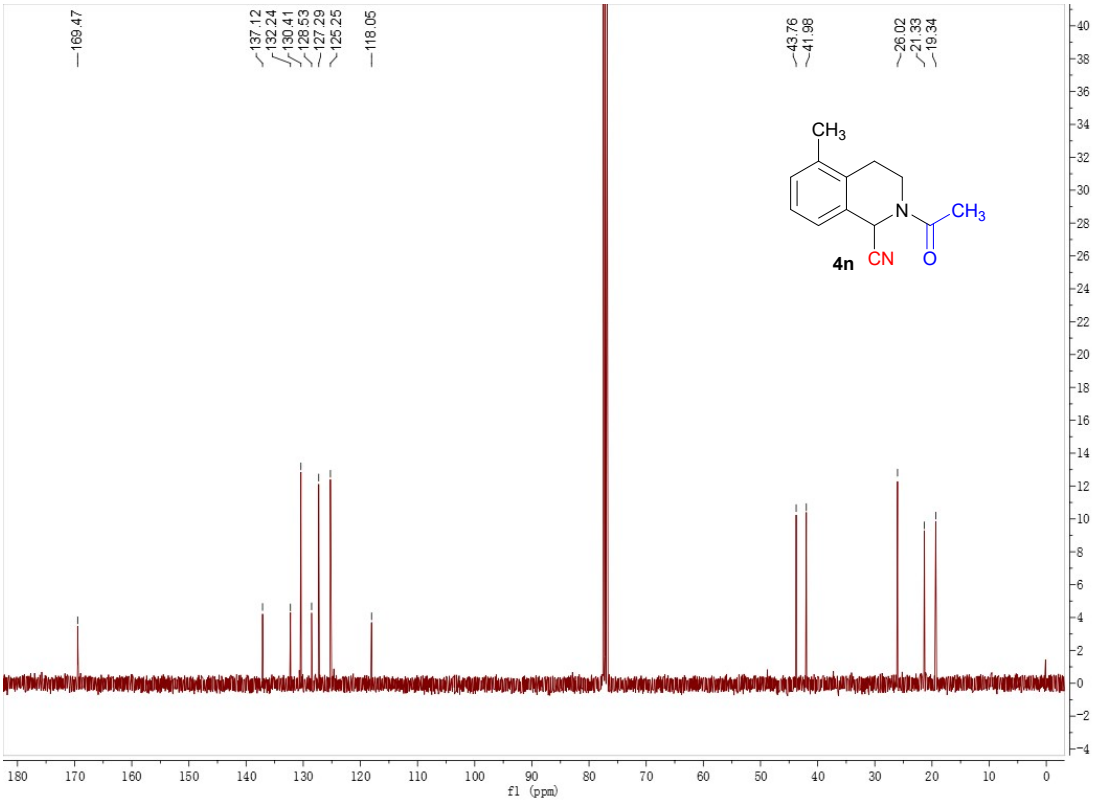

2-6 #19-25 RT: 0.08-0.11 AV: 7 NL: 1.02E9
T: FTMS + p ESI Full ms [105.0000-1500.0000]
223.0843
224.0875
Relative Abundance
m/z
N
CH3
CN
O
4l

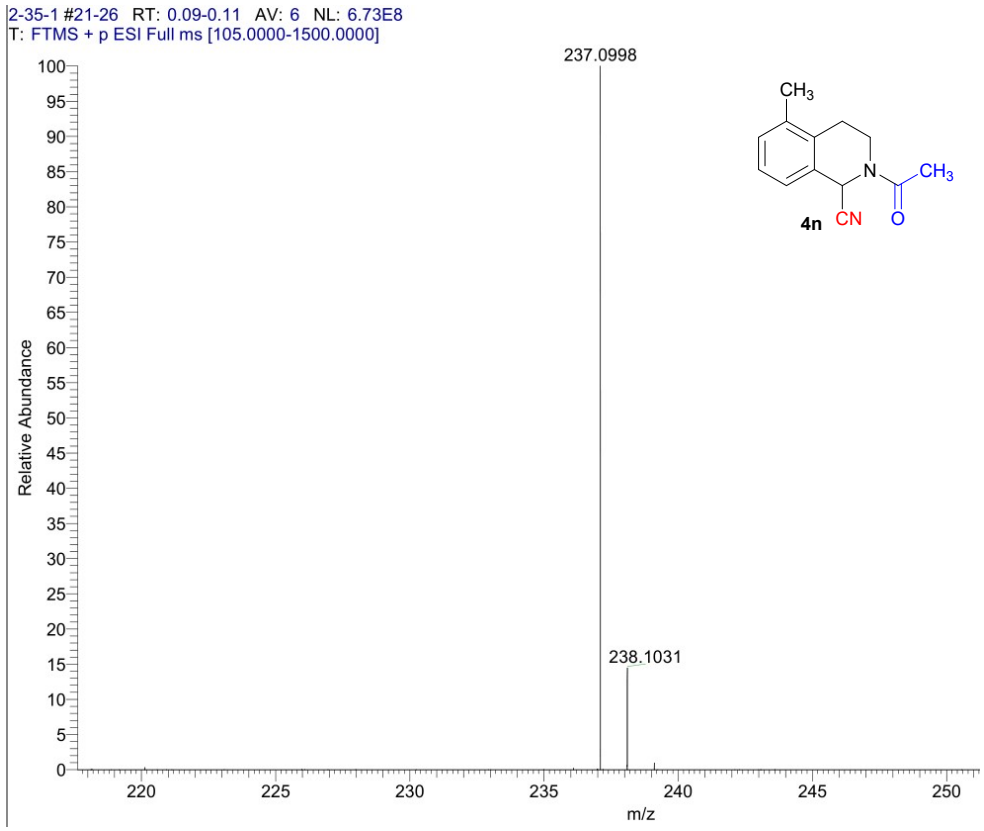

7.59
7.57
7.32
7.30
7.25
7.21
7.19
7.17
6.51
5.72
4.85
4.83
4.83
4.81
4.80
4.04
4.04
4.04
4.03
3.70
3.69
3.68
3.08
3.08
3.05
3.04
3.03
2.95
2.23
1.03
1.02
1.03
0.94
0.12
0.11
0.94
1.00
1.03
1.07
0.28
2.77
f1 (ppm)
Br
N
CH3
CN
O
4m

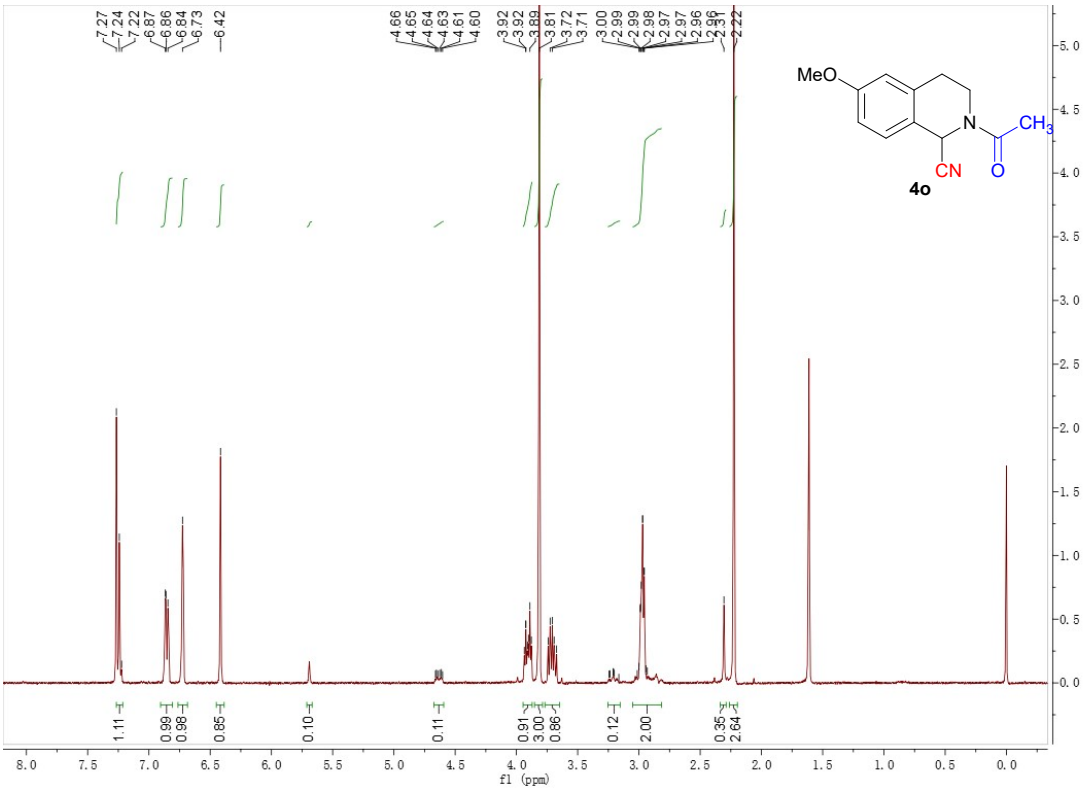

169.45
133.66
133.10
130.81
128.79
126.72
125.48
117.47
43.39
41.80
29.44
21.26
f1 (ppm)
Br
N
CH3
CN
O
4m

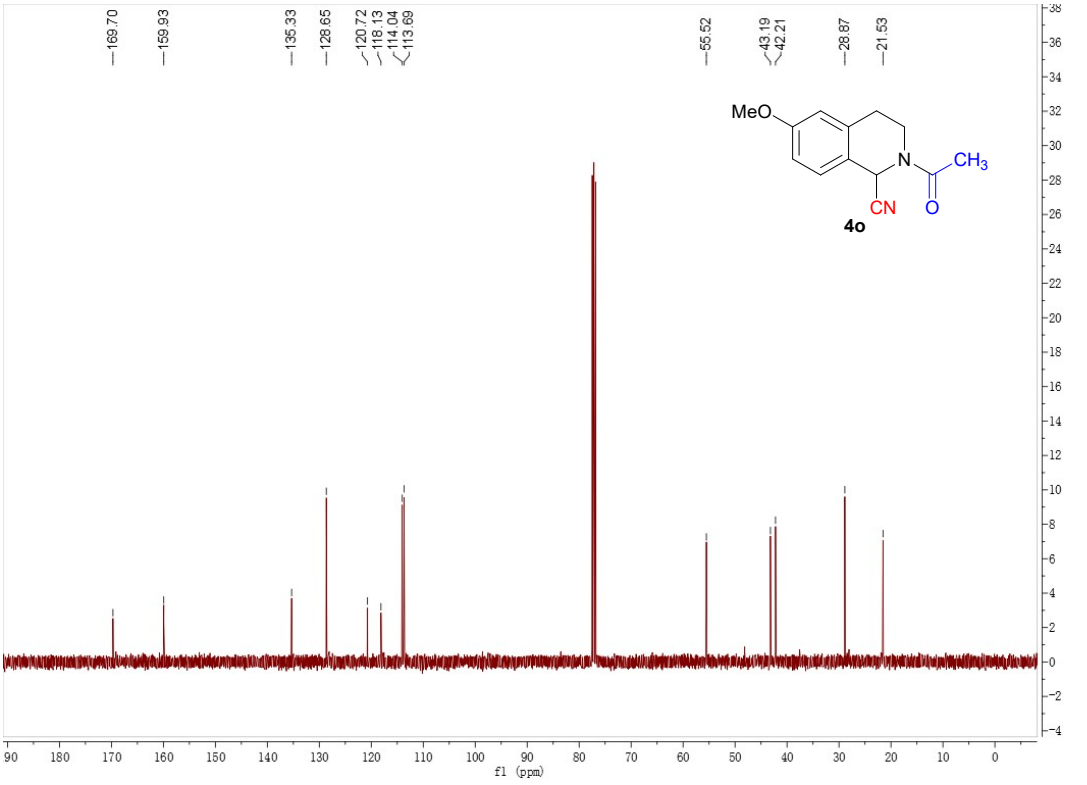

2-26 #23-30 RT: 0.10-0.13 AV: 8 NL: 2.71E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
300.9946
302.9925
301.9980
303.9959
Relative Abundance
m/z
Br
N
CH3
CN
O
4m

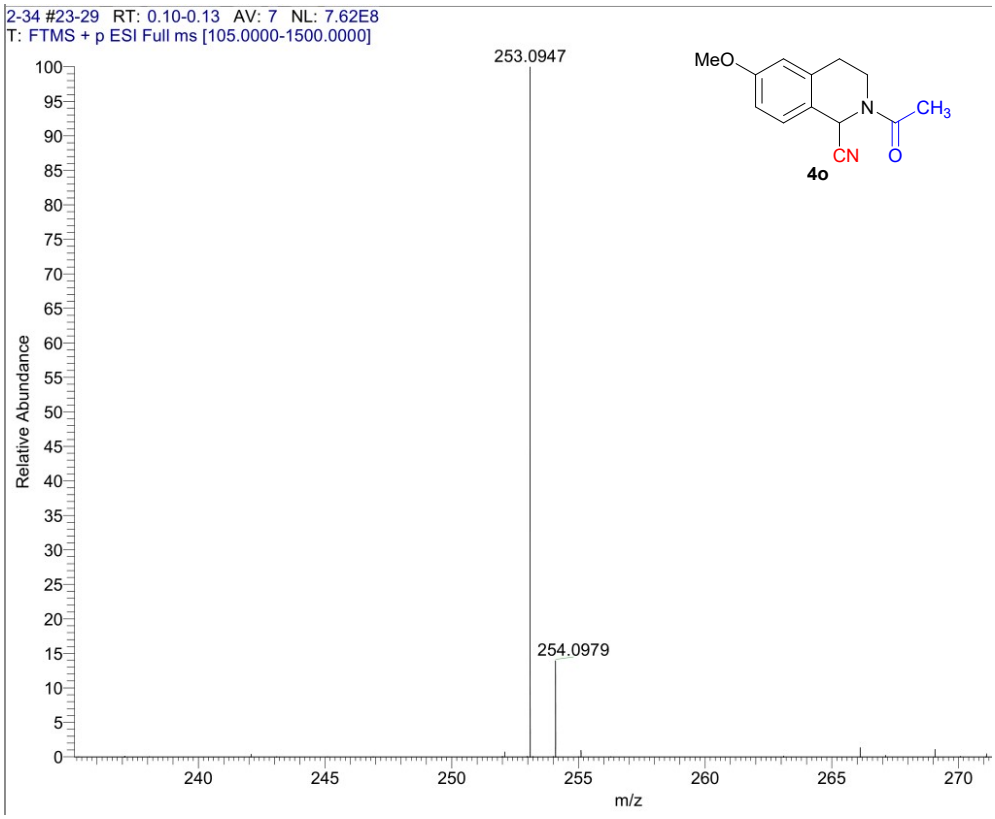

CH3
N
CH3
4n
CN
O
f1 (ppm)

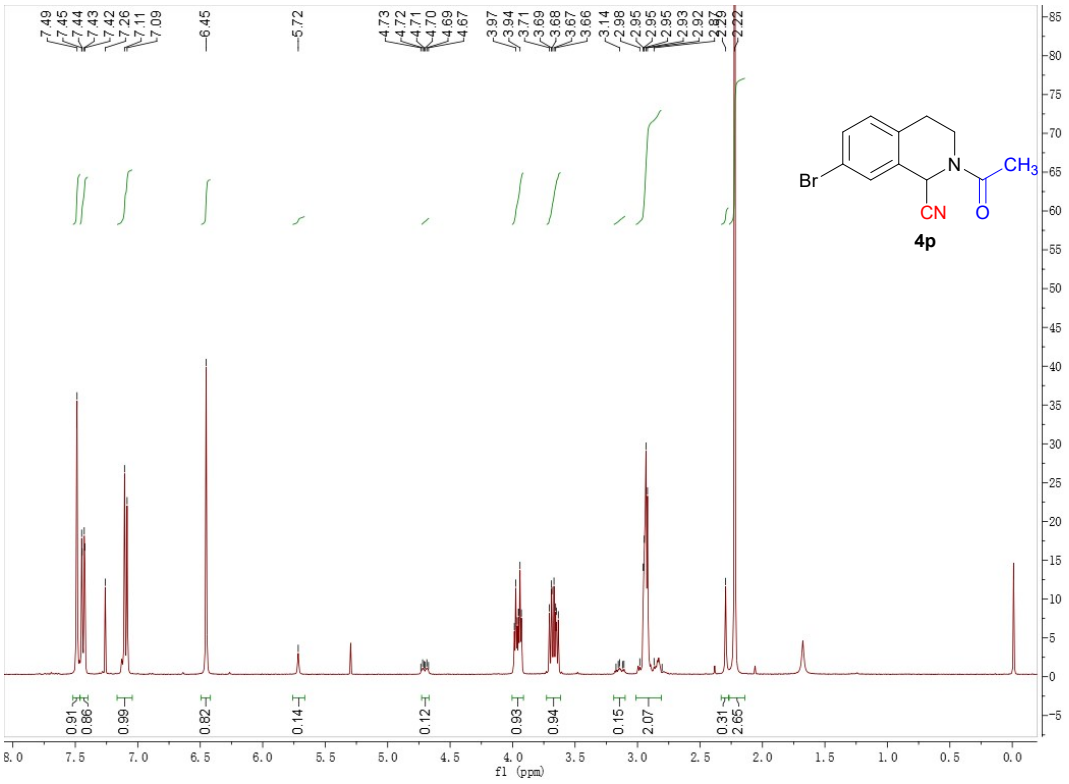

169.47
137.12
132.24
130.41
128.53
127.29
125.25
118.05
43.76
41.98
26.02
21.33
19.34
CH3
N
CH3
4n
CN
O
f1 (ppm)

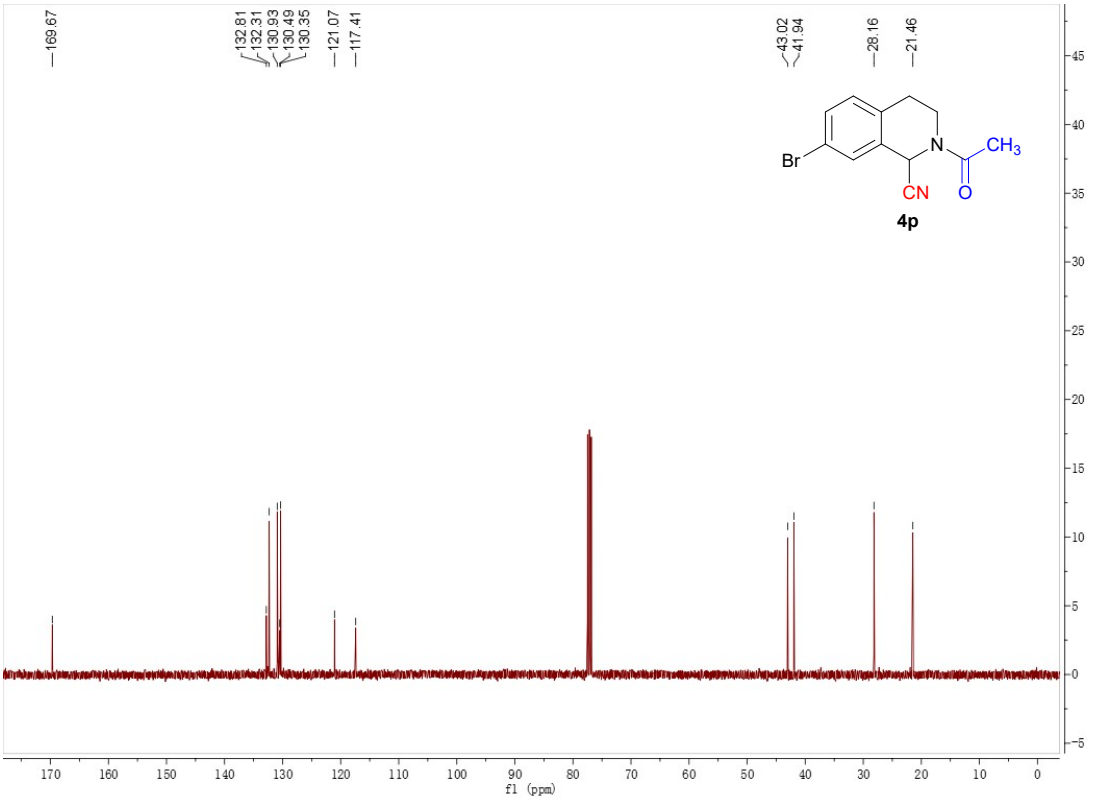

2-35-1 #21-26 RT: 0.09-0.11 AV: 6 NL: 6.73E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
237.0998
238.1031
Relative Abundance
m/z
CH3
N
CH3
4n
CN
O

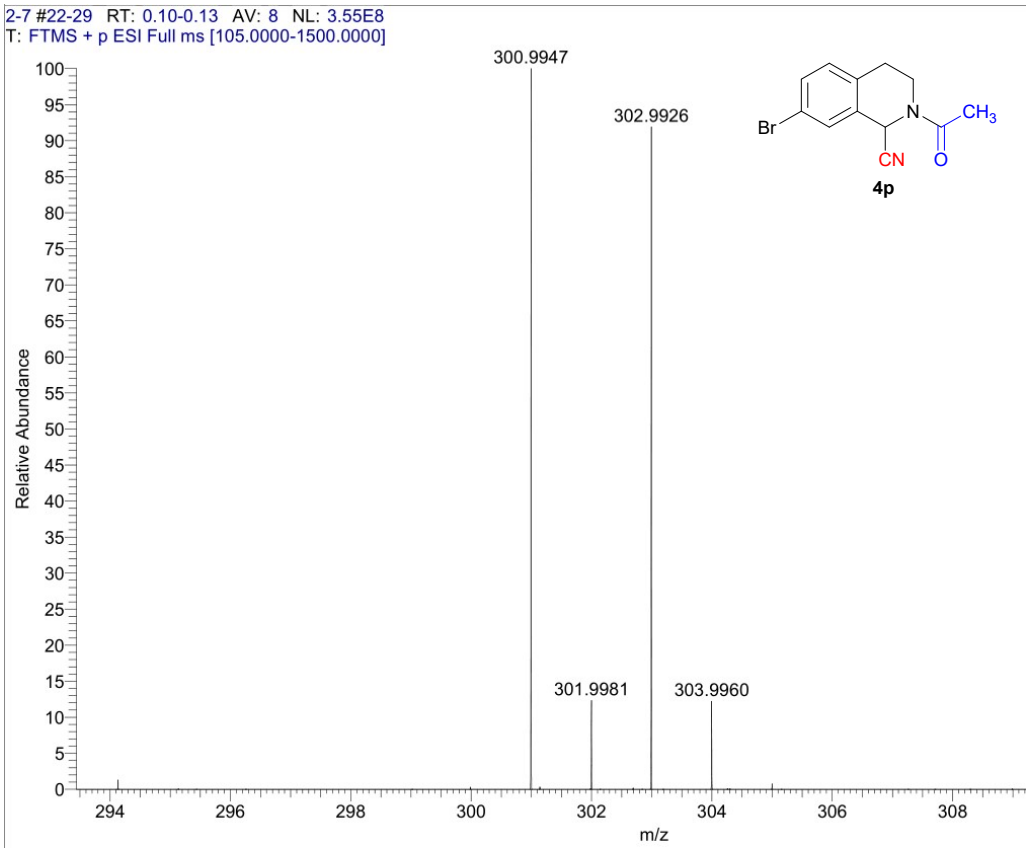

7.27
7.24
7.22
6.87
6.86
6.84
6.73
6.42
4.66
4.65
4.64
4.63
4.61
4.60
3.92
3.92
3.89
3.81
3.72
3.71
3.00
2.99
2.99
2.98
2.97
2.97
2.96
2.96
2.31
2.22
MeO
N
CH3
CN
O
4o
1.11
0.99
0.98
0.85
0.10
0.11
0.91
3.00
0.86
0.12
2.00
0.35
2.64
f1 (ppm)

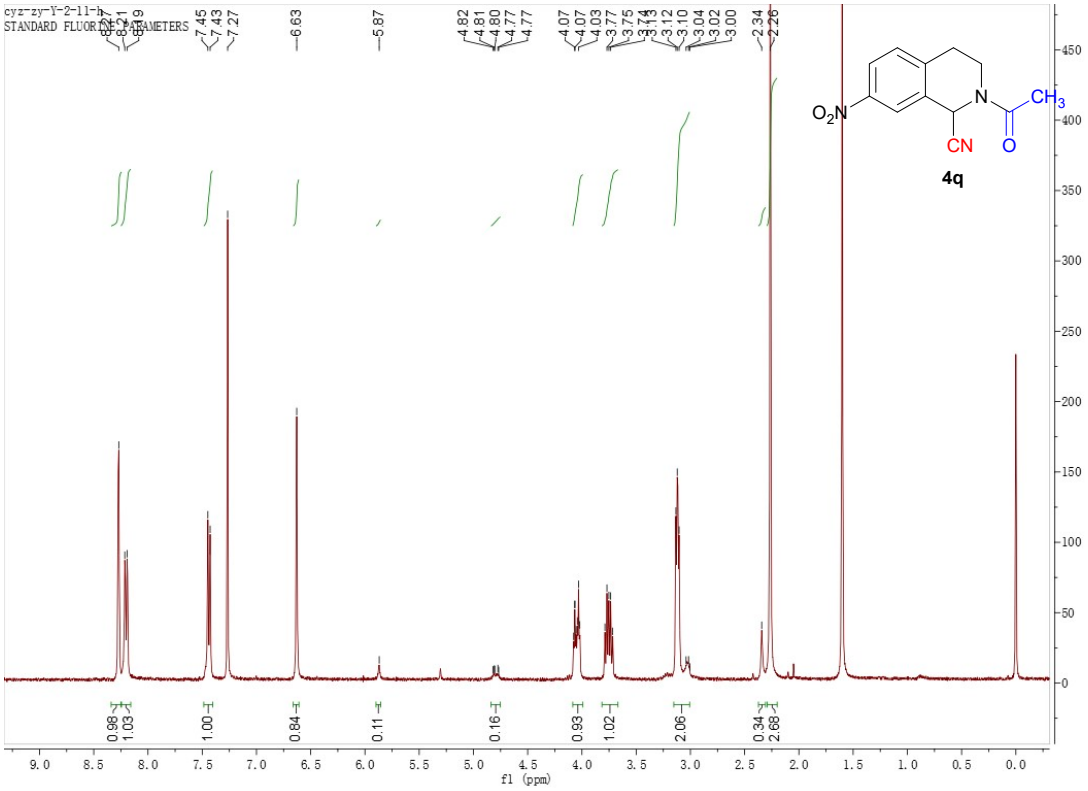

169.70
159.93
135.33
128.65
120.72
118.13
114.04
113.69
55.52
43.19
42.21
28.87
21.53
MeO
N
CH3
CN
O
4o
f1 (ppm)

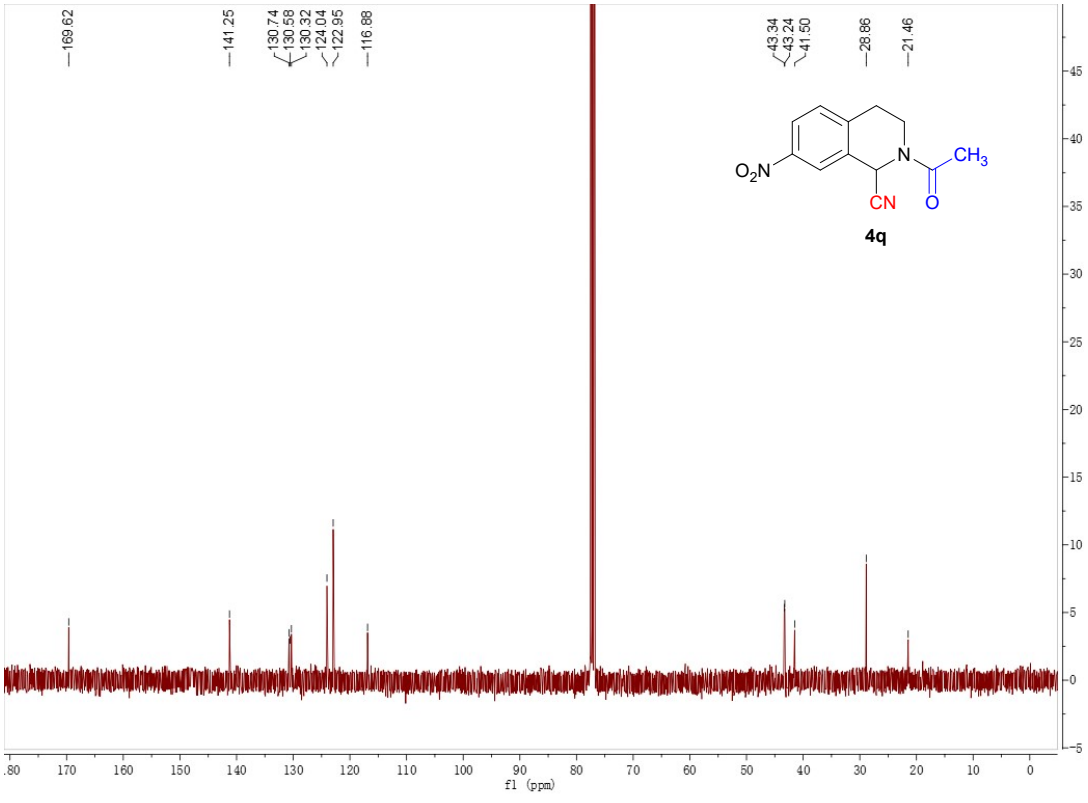

2-34 #23-29 RT: 0.10-0.13 AV: 7 NL: 7.62E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
253.0947
254.0979
Relative Abundance
m/z
MeO
N
CH3
CN
O
4o

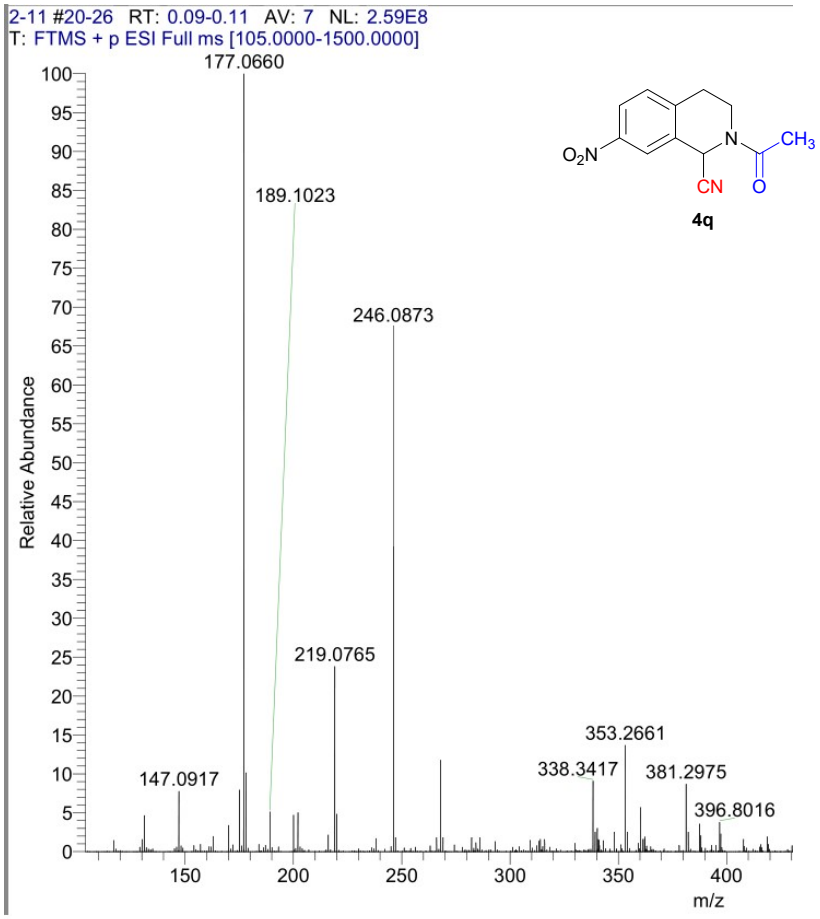

7.49
7.45
7.44
7.43
7.42
7.26
7.11
7.09
6.45
5.72
4.73
4.72
4.71
4.70
4.69
4.67
3.97
3.94
3.71
3.69
3.68
3.67
3.66
3.14
2.98
2.95
2.95
2.93
2.92
2.87
2.29
2.22
Br
N
CH3
CN
O
4p
0.91
0.86
0.99
0.82
0.14
0.12
0.93
0.94
0.15
2.07
0.31
2.65
f1 (ppm)

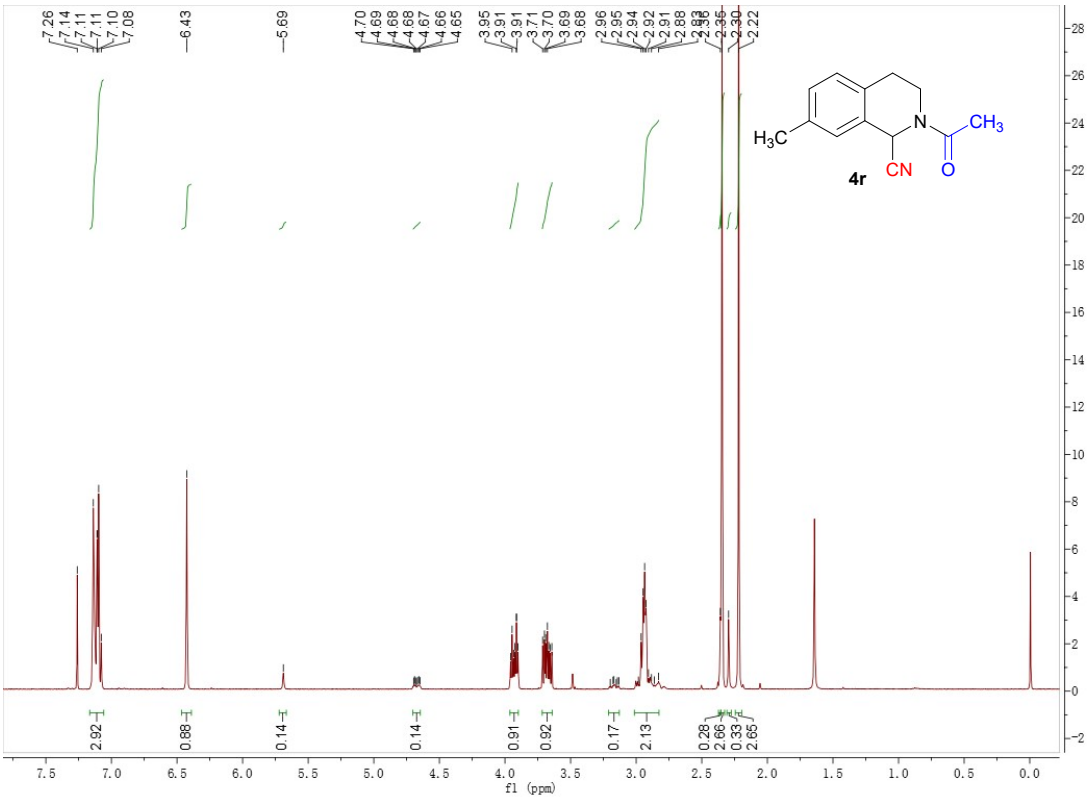

169.67
132.81
132.31
130.93
130.49
130.35
121.07
117.41
43.02
41.94
28.16
21.46
Br
N
CH3
CN
O
4p
f1 (ppm)

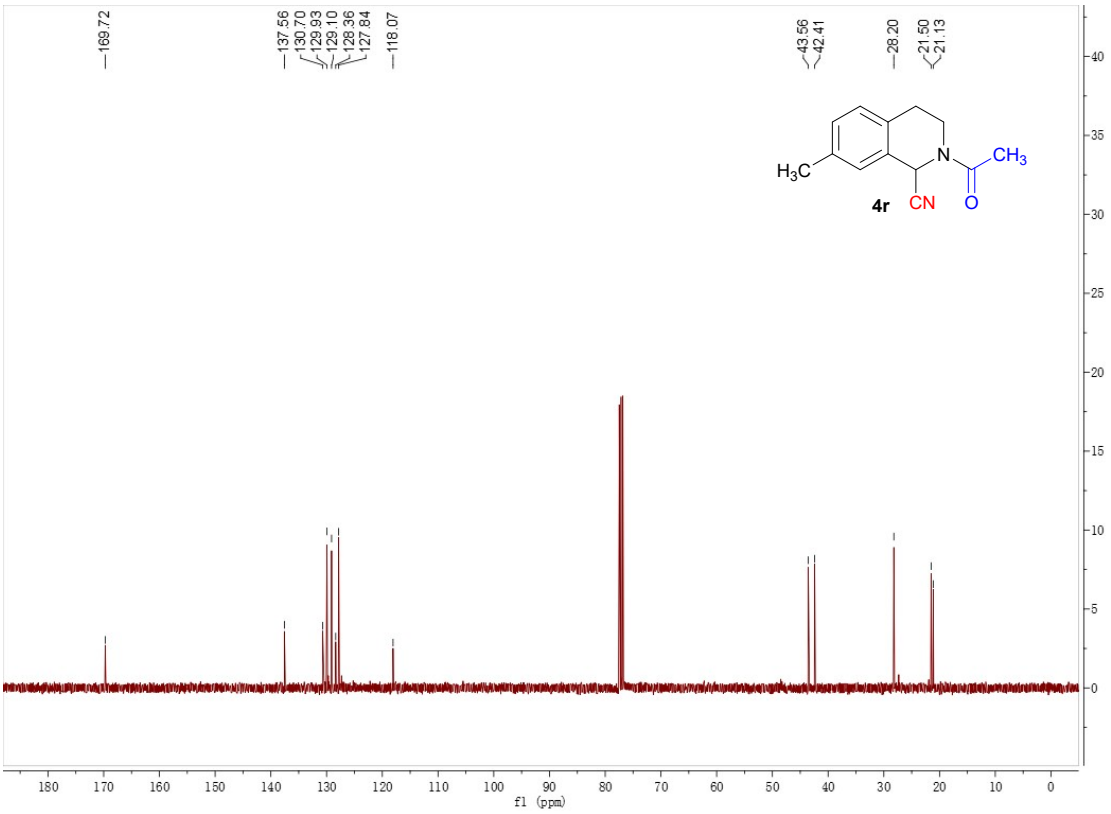

2-7 #22-29 RT: 0.10-0.13 AV: 8 NL: 3.55E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
300.9947
302.9926
301.9981
303.9960
Relative Abundance
m/z
Br
N
CH3
CN
O
4p

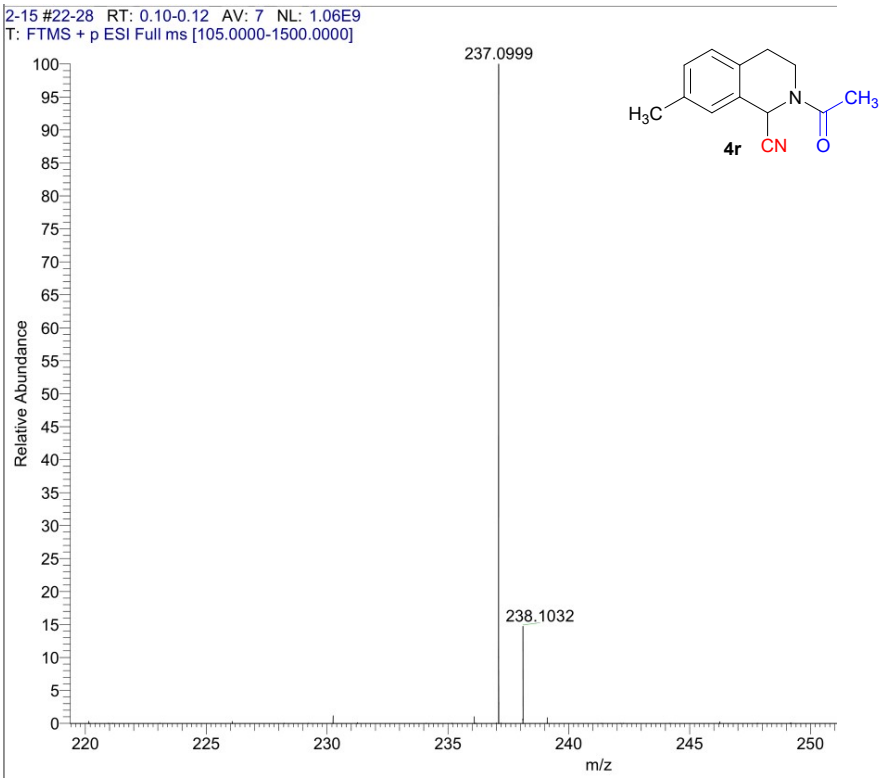

cyz-zy-Y-2-11-h
STANDARD FLUORINE PARAMETERS
8.17
8.21
8.19
7.45
7.43
7.27
6.63
5.87
4.82
4.81
4.80
4.77
4.77
4.07
4.07
4.03
3.77
3.75
3.74
3.13
3.12
3.10
3.04
3.02
3.00
2.34
2.26
0.98
1.03
1.00
0.84
0.11
0.16
0.93
1.02
2.06
0.34
2.68
f1 (ppm)
4q


169.62
141.25
130.74
130.58
130.32
124.04
122.95
116.88
43.34
43.24
41.50
28.86
21.46
f1 (ppm)
4q

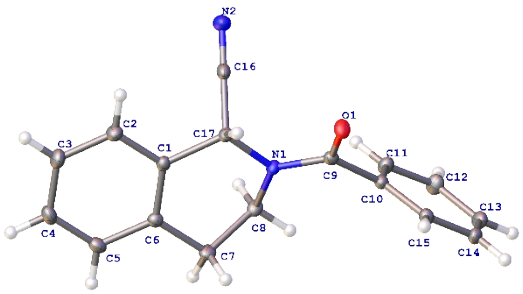

2-11 #20-26 RT: 0.09-0.11 AV: 7 NL: 2.59E8
T: FTMS + p ESI Full ms [105.0000-1500.0000]
177.0660
189.1023
246.0873
219.0765
147.0917
353.2661
338.3417
381.2975
396.8016
Relative Abundance
m/z
O2N
CH3
N
CN
O
4q

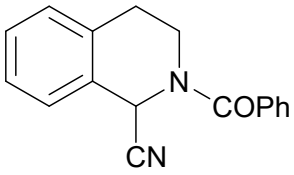

H3C
CH3
N
CN
O
4r
f1 (ppm)


169.72
137.56
130.70
129.93
129.10
128.36
127.84
118.07
43.56
42.41
28.20
21.50
21.13
H3C
N
CH3
CN
O
4r
f1 (ppm)


2-15 #22-28 RT: 0.10-0.12 AV: 7 NL: 1.06E9
T: FTMS + p ESI Full ms [105.0000-1500.0000]
237.0999
238.1032
Relative Abundance
m/z
H3C
N
CH3
CN
O
4r

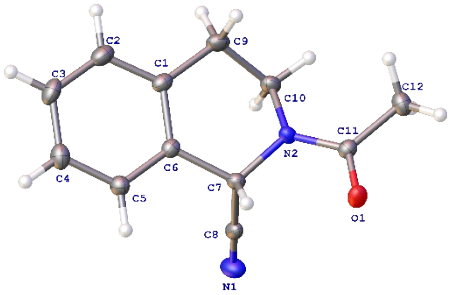
8. Crystal Structure

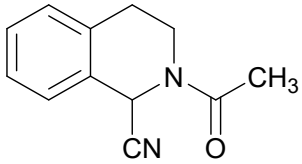




4a (CCDC: 2263510)

Identification code	**4a**
Empirical formula	$C_{17}H_{14}N_2O$
Formula weight	262.30
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5549(9)
b/Å	14.5492(13)
c/Å	8.7409(7)
α/°	90
β/°	94.492(6)
γ/°	90
Volume/Å^3	1338.2(2)
Z	4
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.082
F(000)	552.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.778 to 49.988
Index ranges	$-9 \le h \le 12$, $-12 \le k \le 17$, $-10 \le l \le 9$
Reflections collected	5811
Independent reflections	2359 [R_{int} = 0.0288, R_{sigma} = 0.0430]
Data/restraints/parameters	2359/0/181
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0430, wR_2 = 0.0906
Final R indexes [all data]	R_1 = 0.0569, wR_2 = 0.1006
Largest diff. peak/hole / e Å^{-3}	0.18/-0.22





4n (CCDC: 2263511)

Identification code	**4n**
Empirical formula	$C_{12}H_{12}N_2O$
Formula weight	200.24
Temperature/K	200.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.1562(12)
b/Å	8.1948(14)
c/Å	9.4259(17)
α/°	102.299(15)
β/°	97.775(15)
γ/°	99.273(14)
Volume/Å^3	524.71(16)
Z	2
ρ_{calc}g/cm^3	1.267
μ/mm^{-1}	0.083
F(000)	212.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.492 to 49.998
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 8, -9 ≤ l ≤ 11
Reflections collected	3302
Independent reflections	1845 [R_{int} = 0.0483, R_{sigma} = 0.0899]
Data/restraints/parameters	1845/0/138
Goodness-of-fit on F^2	0.965
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1193
Final R indexes [all data]	R_1 = 0.0844, wR_2 = 0.1435
Largest diff. peak/hole / e Å^{-3}	0.25/-0.31