Supporting Information

Controllable syntheses of tetrahydroquinolines and 1,2-dihydroquinolines via vinylogous cascade hydride transfer/ cyclization

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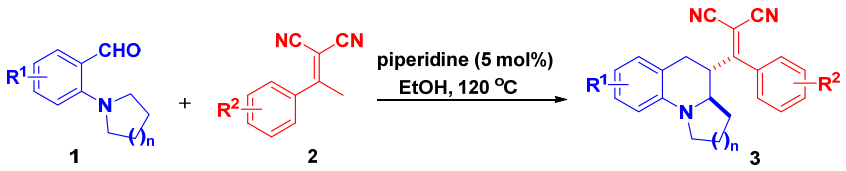
1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 500 MHz NMR spectrometer ($CDCl_3$ or DMSO-d_6 solvent). The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d_6 (δ 2.54, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. All substituted benzaldehydes, and all aryl ketones were purchased from adamas-beta. All substituted 2-(1-phenylethylidene)malononitrile[1] and 4-methyl-2-oxo-2*H*-chromene-3-carbonitrile[2] were prepared according to literature, respectively.

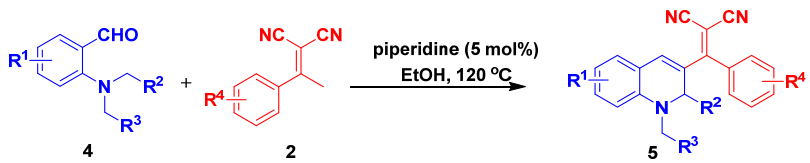
2. General Procedure

2.1. Procedure for the Synthesis of 3



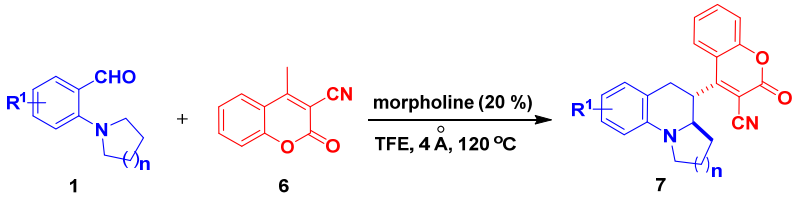
A reaction tube was charged with 2-(pyrrolidin-1-yl)benzaldehyde **1** (0.12 mmol), α,α-dicyanoolefin **2** (0.1 mmol), piperidine (5 mol%) and EtOH (1.0 mL). The mixture was stirred at 120 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography for purification to afford product **3**.

2.2. General Procedure for the Synthesis of 5



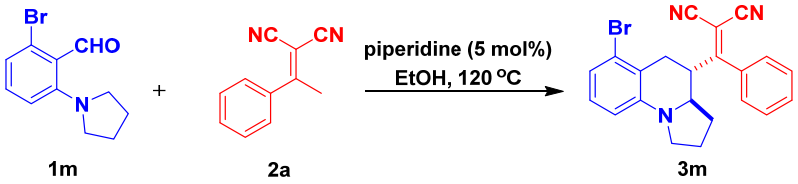
A reaction tube was charged with 2-(dialkylamino)benzaldehyde **4** (0.12 mmol), α,α-dicyanoolefin **2** (0.1 mmol), piperidine (5 mol%) and EtOH (1.0 mL). The mixture was stirred at 120 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography for purification to afford product **5**.

2.3. General Procedure for the Synthesis of 7



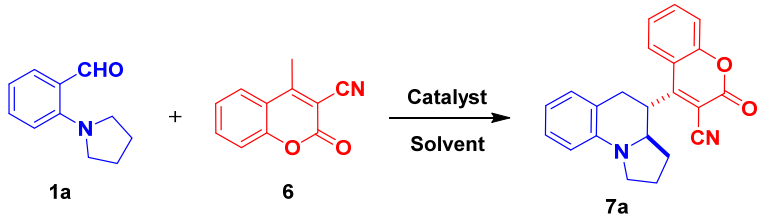
A reaction tube was charged with 2-(pyrrolidin-1-yl)benzaldehyde **1** (0.1 mmol), 4-methyl-2-oxo-2*H*-chromene-3-carbonitrile **6** (0.3 mmol), morpholine (20 mol%) , 4 Å molecular sieves (70 mg) and TFE (1.0 mL). The mixture was stirred at 120 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography for purification to afford product **7.**

2.4. Large-scale synthesis.



A reaction tube was charged with 2-bromo-6-(pyrrolidin-1-yl)benzaldehyde **1m** (1.2 equiv, 1.2 mmol), α,α-dicyanoolefin **2a** (1.0 equiv, 1 mmol), piperidine (5 mol%) and EtOH (3.0 mL). The mixture was stirred at 120 °C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography for purification to afford product **3m** in 64% yield (256 mg) with excellent diastereoselectivity.

2.5. Optimization of reaction conditions[a]

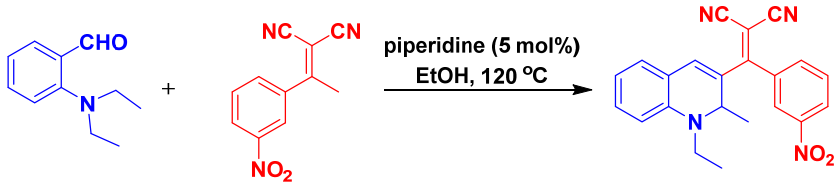


Entry	Catalyst	Solvent	Add.	Tem. (˚C)	Yield[b]
1	Piperidine	EtOH	-	120	60
2	Morpholine	EtOH	-	120	63
3	Morpholine	EtOH	4Å	120	70
4	Morpholine	DMF	4Å	120	39
5	Morphoilne	Tol.	4Å	120	NR
6	Morpholine	CH_3CN	4Å	120	44
7	Morpholine	Diox.	4Å	120	NR
8	Morpholine	TFE	4Å	120	70
9[c]	Morpholine	TFE	4Å	120	26

10[d]	Morpholine	TFE	4Å	120	65
11	-	TFE	4Å	120	NR
12[e]	Morpholine	TFE	4Å	120	74

[a] Reaction conditions (unless otherwise noted): **1a** (0.12 mmol), **6** (0.10 mmol), catalyst (20 mol%), solvent (1 mL); [b] Isolated yield after column chromatography; [c] Morpholine (10 mol%); [d] Morpholine (40 mol%); [e] **1a** (0.10 mmol), **6** (0.30 mmol).

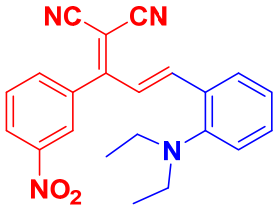
2.6. Mechanism verified deoxygenation



4 2c 5c

A schlenk tube was charged with 2-(diethylamino)benzaldehyde **4** (1.2 equiv, 0.12 mmol), α,α-dicyanoolefin **2a** (1.0 equiv, 0.1 mmol), piperidine (5 mol%) and EtOH (2.0 mL) under nitrogen atmosphere. At room temperature, the mixture was pumped at the same time with ultrasound for 15 minutes. The mixture was stirred at 120 °C under a nitrogen atmosphere for 2d. The mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography for purification to afford product **5c** in 15% yield (5.5 mg) and the intermediate, i.e. (E)-2-(1-(3-nitrophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)allylidene)malononitrile in 50% yield (18.6 mg) (see below).

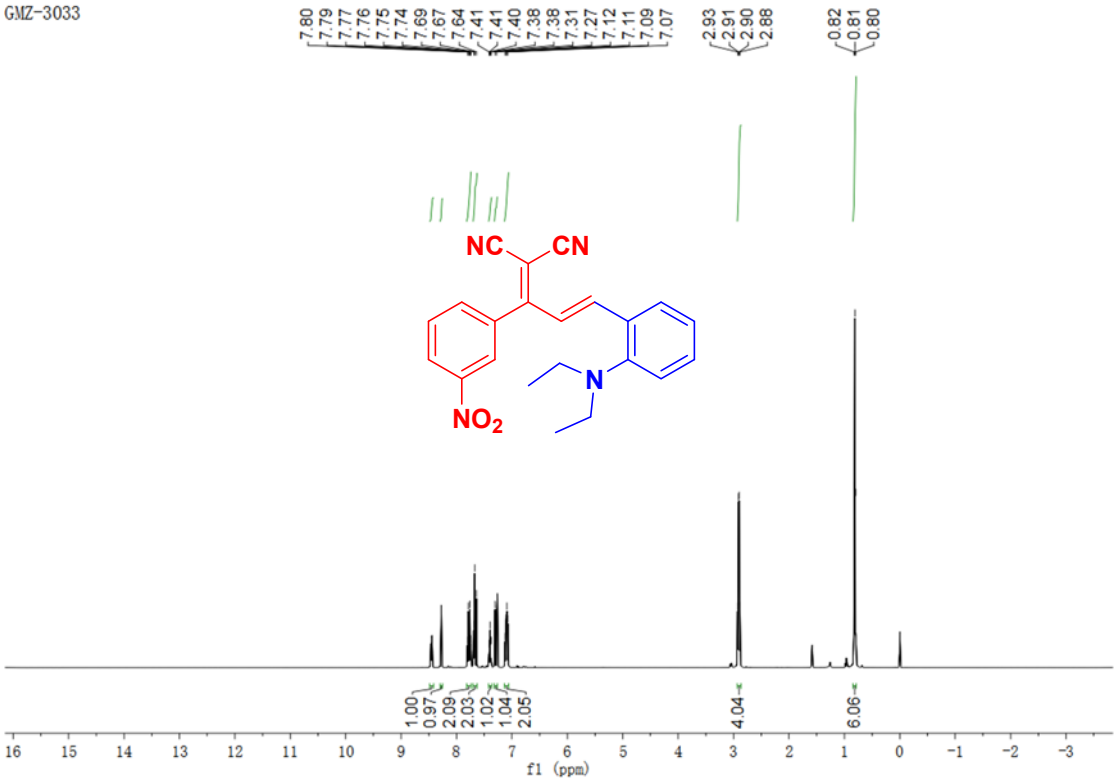
(E)-2-(1-(3-nitrophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)allylidene)malononitrile

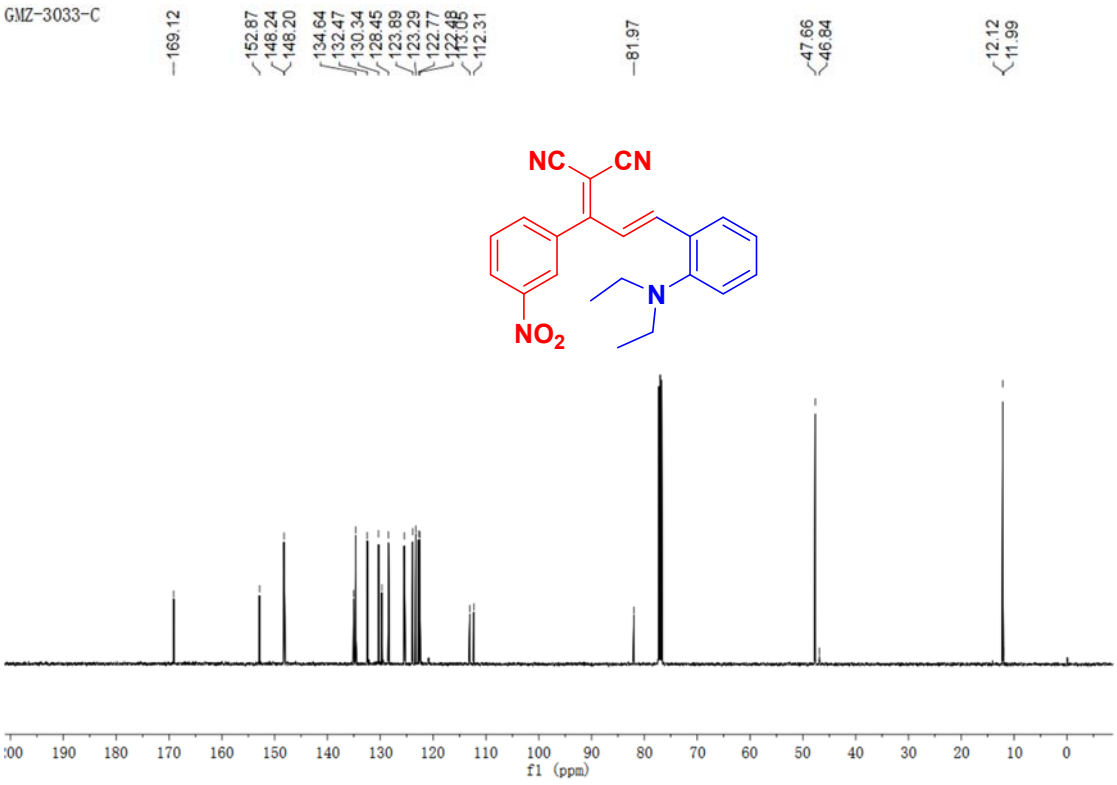


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1.5:40) afforded the product (18.6 mg, 50% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 – 8.41 (m, 1H), 8.28 (d, *J* = 1.6 Hz, 1H), 7.80-7.74 (m, 2H), 7.67 (t, *J* = 11.9 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.29 (d, *J* = 15.8 Hz, 1H), 7.10 (dd, *J* = 16.9, 8.0 Hz, 2H), 2.91 (q, *J* = 7.1 Hz, 4H), 0.81 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.1, 152.9, 148.2, 148.3, 135.0, 134.6, 132.5, 130.3, 129.7, 128.4, 125, 123.9, 123.3, 122.8, 122.5, 113.1, 112.3, 81.9, 47.7, 46.8, 12.1, 11.9 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{20}N_4O_2$ $[M+H]^+$: 373.1659, found: 373.1655.

(E)-2-(1-(3-nitrophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)allylidene)malononitrile

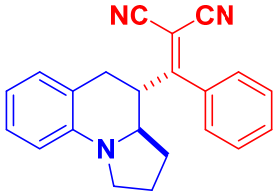




3. Characterization of All Compounds

Compounds 3:

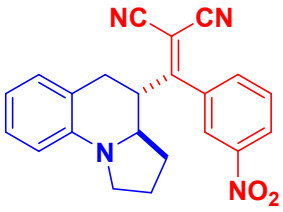
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)malononitrile (3a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (26 mg, 80% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 3H), 7.25 (t, *J* = 3.8 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 3.48-3,41 (m, 2H), 3.27 (dd, *J* = 16.5, 9.0 Hz, 1H), 3.21 – 3.12 (m, 1H), 3.01 (t, *J* = 13.7 Hz, 1H), 2.89 (dd, *J* = 15.2, 3.7 Hz, 1H), 2.20 – 2.10 (m, 2H), 1.99 – 1.90 (m, 1H), 1.74-1.66(m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 182.3, 143.1, 134.1, 130.8, 129.1, 128.4, 128.1, 126.5, 118.4, 115.9, 111.9, 111.8, 110.8, 88.2, 59.6, 47.3, 46.6, 32.9, 31.5, 23.6 ppm. **HRMS (ESI):** calcd. for $C_{22}H_{19}N_3$ $[M+H]^+$: 326.1652, found: 326.1657.

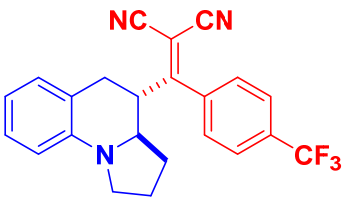
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(3-nitrophenyl)methylene)malononitrile (3b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1.5:40) afforded the product (10 mg, 25% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.36 (m, 1H), 8.14 (t, *J* = 1.8 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 11.2, 4.2 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.64 (t, *J* = 7.1 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 3.51 – 3.37 (m, 2H), 3.32-3.27 (m, 1H), 3.26-3.20 (m, 1H), 2.98 – 2.89 (m, 2H), 2.25 – 2.14 (m, 2H), 2.04-1.94 (m, 1H), 1.80-1.72 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.2, 148.3, 142.9, 135.3, 132.6, 130.7, 128.5, 128.3, 125.5, 121.7, 117.6, 116.2, 111.2, 111.1, 111.0, 89.9, 59.6, 47.3, 46.6, 32.9, 31.6, 23.6 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}N_4O_2$ $[M+H]^+$: 371.1503, found: 371.1506.

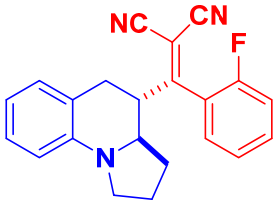
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(4-(trifluoromethyl)phenyl)methylene)-malononitrile (3c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (13 mg, 33% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 3.46-3.37 (m, 2H), 3.28 (dd, *J* = 16.5, 9.0 Hz, 1H), 3.23-3.17 (m, 1H), 2.99 – 2.85 (m, 2H), 2.22 – 2.12 (m, 2H), 2.03 – 1.90 (m, 1H), 1.73 (tt, *J* = 19.4, 9.7 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.5, 143.0, 137.4, 132.8 (q, *J* = 32.8 Hz), 128.4, 138.2, 127.2, 126.2 (q, *J* = 3.8 Hz), 123.3 (q, *J* = 273.4 Hz), 117.9, 116.1, 111.4 (d, *J* = 18.9 Hz), 110.9, 89.3, 59.5, 47.3, 46.5, 32.8, 31.5, 23.6 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{18}F_3N_3$ $[M+H]^+$: 394.1526, found: 394.1526.

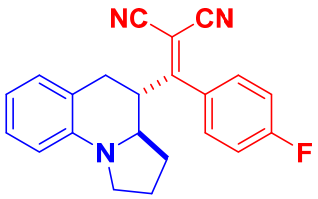
2-((2-fluorophenyl)(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile (3d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (14.4 mg, 42% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 13.4, 6.9 Hz, 1H), 7.30-7.23 (m, 2H), 7.13 (dd, *J* = 20.0, 12.4 Hz, 2H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 3.44 (t, *J* = 8.3 Hz, 2H), 3.29-3.17 (m, 2H), 2.95 (d, *J* = 11.7 Hz, 2H), 2.28-2.23 (m, 1H), 2.19 – 2.09 (m, 1H), 1.96 (d, *J* = 7.6 Hz, 1H), 1.74 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.9, 157.6 (d, *J* = 250.7 Hz), 143.1, 132.8 (d, *J* = 7.6 Hz), 128.4, 128.1, 124.8, 124.7, 121.6 (d, *J* = 16.4 Hz), 118.2, 116.8 (d, *J* = 21.4 Hz), 115.9, 111.5, 111.2, 110.8, 90.6, 59.8, 47.4, 46.8, 32.5, 31.5, 23.6 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}FN_3$ $[M+H]^+$: 344.1558, found: 344.1550.

2-((4-fluorophenyl)(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile (3e)

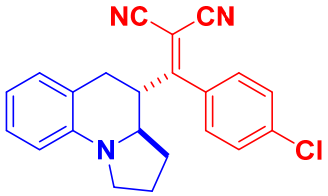


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (14.4 mg, 42% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.24 – 7.18 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 3.47-3.41 (m, 2H), 3.30-3.25 (m, 1H), 3.18-3.13 (m, 1H), 3.07 – 2.98 (m, 1H), 2.89 (dd, *J* = 15.1, 3.8 Hz, 1H), 2.19 – 2.09 (m, 2H), 2.00 – 1.89 (m, 1H), 1.73 – 1.63 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 181.2, 163.9 (d, *J* = 254.5 Hz), 143.1, 130.0, 128.9 (d, *J* = 8.8 Hz), 128.4, 128.1, 118.2, 116.7, 116.5, 115.9, 111.8 (d, *J* = 2.5 Hz), 110.9, 88.54, 59.6, 47.3, 46.7, 32.9, 31.4, 23.6 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}FN_3$ $[M+H]^+$: 344.1558, found: 344.1553.

2-((4-chlorophenyl)(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile

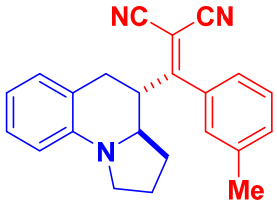
(3f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (18.7 mg, 52% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 3.44 (dd, *J* = 8.7, 6.9 Hz, 2H), 3.32 – 3.23 (m, 1H), 3.19 – 3.10 (m, 1H), 3.05 – 2.96 (m, 1H), 2.88 (dd, *J* = 15.1, 3.8 Hz, 1H), 2.18 – 2.08 (m, 2H), 2.01 – 1.88 (m, 1H), 1.67 (qd, *J* = 11.7, 7.9 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.9, 143.1, 137.4, 132.3, 129.5, 128.4, 128.1, 128.0, 118.1, 115.9, 111.7, 111.6, 110.9, 88.6, 59.6, 47.3, 46.59, 32.9, 31.4, 23.6 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}ClN_3$ $[M+H]^+$: 360.1262, found: 360.1268.

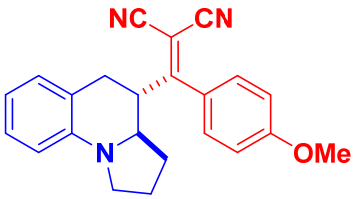
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(m-tolyl)methylene)malononitrile (3g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (21.7 mg, 64% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.03 (dd, *J* = 17.8, 8.0 Hz, 3H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 3.51 – 3.40 (m, 2H), 3.27 (dd, *J* = 16.4, 9.1 Hz, 1H), 3.18-3.12 (m, 1H), 3.08 – 2.99 (m, 1H), 2.88 (dd, *J* = 15.1, 3.7 Hz, 1H), 2.41 (s, 3H), 2.18-2.10 (m, 2H), 1.99 – 1.90 (m, 1H), 1.68 (qd, *J* = 11.7, 7.6 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 182.5, 143.2, 139.1, 134.1, 131.7, 128.9, 128.4, 128.0, 126.9, 123.7, 118.5, 115.8, 112.09, 111.9, 110.8, 87.9, 59.6, 47.3, 46.6, 32.9, 31.5, 23.6, 21.5 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{21}N_3$ $[M+H]^+$: 340.1808, found: 340.1803.

2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(4-methoxyphenyl)methylene)-malononitrile (3h)

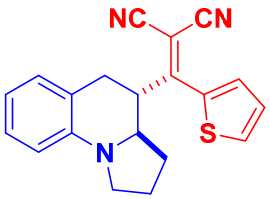


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (25.6 mg, 72% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 2H), 7.14 – 7.09 (m, 1H), 7.00 (dd, *J* = 11.9, 8.6 Hz, 3H), 6.62 (t, *J* = 7.1 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H), 3.53 (d, *J* = 4.8 Hz, 1H), 3.44-3.40 (m, 1H), 3.26 (dd, *J* = 16.5, 9.1 Hz, 1H), 3.15 (dd, *J* = 17.3, 9.2 Hz, 2H), 2.90 (d, *J* = 11.5 Hz, 1H), 2.13-2.04 (m, 2H), 1.98 – 1.85 (m, 1H), 1.66 – 1.57 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 181.8, 161.8, 143.2,

128.8, 128.4, 127.9, 126.5, 118.7, 115.8, 114.5, 112.6, 112.4, 110.8, 86.6, 59.7, 55.4, 47.2, 46.9, 33.1 31.3, 23.6 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{21}N_3O$ $[M+H]^+$: 356.1757, found: 357.1753.

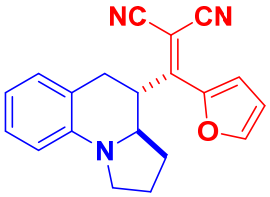
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(thiophen-2-yl)methylene)malononitrile (3i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (22.5 mg, 68% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 5.0 Hz, 2H), 7.22 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 3.80 (s, 1H), 3.50 – 3.35 (m, 2H), 3.30 (dd, *J* = 16.6, 8.9 Hz, 1H), 3.21 (d, *J* = 9.1 Hz, 1H), 2.92 (dd, *J* = 15.3, 3.5 Hz, 1H), 2.19 – 2.06 (m, 1H), 2.05-2.00 (m, 1H), 1.98 – 1.86 (m, 1H), 1.65 – 1.50 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.8, 143.2, 133.1, 132.8, 128.5, 128.4, 128.0, 118.0, 115.8, 113.5, 112.9, 110.9, 59.6, 47.5, 47.2, 33.0, 31.1, 23.5 ppm. **HRMS (ESI):** calcd. for: $C_{20}H_{17}N_3S$ $[M+H]^+$: 332.1216, found: 332.1210.

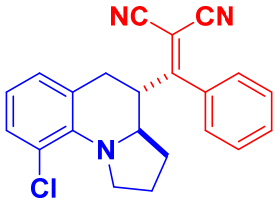
2-(furan-2-yl(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile (3j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (24 mg, 76% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.53 (d, *J* = 41.7 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 2.3 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 4.00 (s, 1H), 3.48 (t, *J* = 8.5 Hz, 2H), 3.33 (dd, *J* = 16.3, 8.3 Hz, 1H), 3.23 (s, 1H), 2.93 (dd, *J* = 15.5, 3.9 Hz, 1H), 2.12 (dd, *J* = 11.0, 6.0 Hz, 1H), 1.97 (s, 2H), 1.52 (d, *J* = 75.6 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.2, 148.0, 147.7, 143.4, 128.4, 127.9, 121.2, 120.3, 119.3, 115.8, 113.9, 113.8, 111.1, 59.8, 47.2, 33.2, 31.1, 23.5, 19.3 ppm. **HRMS (ESI):** calcd. for: $C_{20}H_{17}N_3O$ $[M+H]^+$: 316.1444, found: 316.1447.

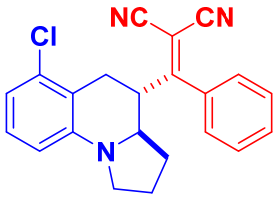
2-((9-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3k)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (19.4 mg, 54% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.23 – 7.15 (m, 3H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.7 Hz, 1H), 4.21 (dd, *J* = 17.6, 7.6 Hz, 1H), 3.53 (dd, *J* = 9.2, 7.8 Hz, 1H), 3.33 – 3.21 (m, 1H), 3.10-3.05 (m, 1H), 2.95-2.81 (m, 2H), 2.34 – 2.21 (m, 1H), 2.15 – 1.98 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 182.6, 142.3, 133.6, 130.8, 129.3, 129.2, 127.3, 126.4, 124.9, 124.7, 121.1, 111.9, 111.6, 89.1, 59.6, 52.7, 42.3, 32.4, 29.1, 23.5 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}ClN_3$ $[M+H]^+$: 360.1262 found: 360.1266.

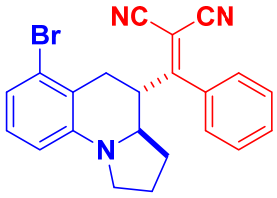
2-((6-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3l)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (14.4 mg, 40% yield) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 5.1, 1.4 Hz, 3H), 7.33 – 7.26 (m, 2H), 7.02 (t, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 1H), 3.44-3.37 (m, 2H), 3.33-3.22 (m, 2H), 3.17 – 3.11 (m, 1H), 2.78 (dd, *J* = 15.9, 12.5 Hz, 1H), 2.22 – 2.11 (m, 2H), 2.02 – 1.90 (m, 1H), 1.77 – 1.66 (m, 1H); **^{13}C NMR (**126 MHz, $CDCl_3$) δ 181.5, 144.4, 133.9, 130.9, 129.2, 128.3, 126.6, 116.6, 116.3, 111.9, 111.7, 109.3, 88.7, 58.9, 47.4, 46.4, 31.4, 30.1, 23.5 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}ClN_3$ $[M+H]^+$: 360.1262, found: 360.1268.

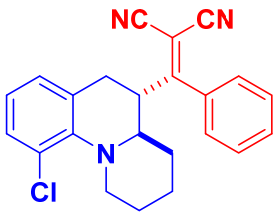
2-((6-bromo-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3m)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (35 mg, 87% yield) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.33 – 7.26 (m, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.39 (d, *J* = 8.1 Hz, 1H), 3.46 – 3.36 (m, 2H), 3.29 (dd, *J* = 16.8, 8.7 Hz, 1H), 3.22 (dd, *J* = 15.9, 4.1 Hz, 1H), 3.18 – 3.10 (m, 1H), 2.79 (dd, *J* = 15.8, 12.3 Hz, 1H), 2.23 – 2.11 (m, 2H), 2.00-1.92 (m, 1H), 1.76 – 1.66 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 181.3, 144.5, 133.9, 131.0, 129.2, 128.7, 126.6, 124.8, 119.8, 117.8, 111.9, 111.7, 109.9, 88.7, 58.9, 47.4, 46.7, 33.0, 31.3, 23.6 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}BrN_3$ $[M+H]^+$: 404.0757, found: 404.0753.

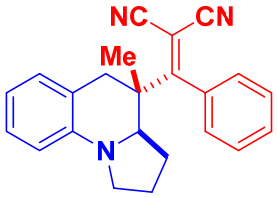
2-((10-chloro-2,3,4,4a,5,6-hexahydro-1*H*-pyrido[1,2-a]quinolin-5-yl)(phenyl)methylene)-malononitrile (3n)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (29.5 mg, 79% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 3H), 7.28 (d, *J* = 6.7 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 7.7 Hz, 1H), 3.78 (dd, *J* = 15.9, 10.5 Hz, 1H), 3.46 – 3.35 (m, 1H), 3.31 – 3.24 (m, 1H), 3.09 (s, 1H), 2.95 – 2.78 (m, 2H), 2.08-2.00 (m, 1H), 1.85-1.75 (m, 3H), 1.69 (d, *J* = 4.2 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 181.6, 144.4, 134.3, 131.2, 129.3, 129.1, 127.8, 127.4, 127.1, 127.0, 122.5, 112.1, 88.4, 57.9, 49.3, 41.5, 32.9, 28.5, 25.6, 21.1 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{20}ClN_3$ $[M+H]^+$: 374.1419, found: 374.1416.

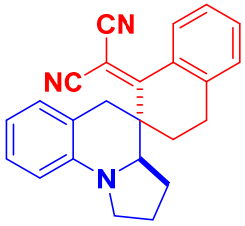
2-((4-methyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3o)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (21.4 mg, 63% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 3H), 7.14-7.09 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 4.01 (dd, *J* = 9.8, 5.3 Hz, 1H), 3.50-3.41 (m, 2H), 3.28 (q, *J* = 8.4 Hz, 1H), 2.82 (d, *J* = 15.4 Hz, 1H), 2.09-2.04 (m, 1H), 2.02 – 1.92 (m, 2H), 1.77 – 1.66 (m, 1H), 0.94 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.5, 142.4, 137.0, 129.8, 129.2, 128.9, 128.8, 127.8, 125.9, 125.7, 117.9 115.9, 112.8, 112.5, 110.4, 89.1, 62.2, 46.9, 42.3, 41.5, 27.5, 23.2, 17.4 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{21}N_3$ $[M+H]^+$: 340.1808, found: 340.1804.

2-(1',2',3,3',3a',4-hexahydro-1H,5'*H*-spiro[naphthalene-2,4'-pyrrolo[1,2-a]quinolin]-1-ylidene)-malononitrile (3p)



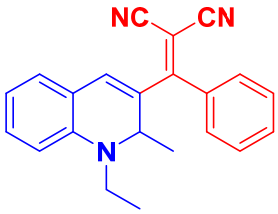
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (20.4 mg, 58% yield) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.25 (s, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.24 (dd, *J* = 9.3, 6.3 Hz, 1H), 4.01 (d, *J* = 16.0 Hz, 1H), 3.42-3.36 (m, 1H), 3.31 (dd, *J* = 16.5, 7.7 Hz,

1H), 3.04 (d, *J* = 16.1 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.62-2.56 (m, 1H), 2.04 – 1.88 (m, 2H), 1.85-1.79 (m, 1H), 1.53-1.48 (m, 1H), 1.36 – 1.26 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.5, 144.1, 143.1, 133.6, 132.4, 129.7, 129.3, 127.6, 126.8, 119.5, 116.3, 115.2, 114.6, 111.1, 82.2, 62.3, 46.6, 44.5, 36.4, 26.7, 26.2, 25.0, 23.0 ppm. **HRMS (ESI):** calcd. for: $C_{24}H_{21}N_3$ $[M+H]^+$: 352.1808, found: 352.1803.

Compounds 5:

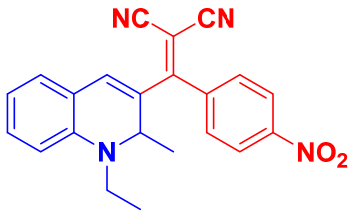
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (25.4 mg, 78% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.1 Hz, 1H), 7.54 – 7.45 (m, 4H), 7.29 – 7.24 (m, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.77 (s, 1H), 6.65 (dd, *J* = 13.9, 7.6 Hz, 2H), 4.62 (d, *J* = 6.3 Hz, 1H), 3.48 (dq, *J* = 14.2, 7.0 Hz, 1H), 3.31 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.9, 144.4, 138.2, 135.4, 133.2, 131.7, 131.0, 130.7, 129.5, 128.9, 120.1, 117.1, 114.5, 112.1, 78.2, 54.5, 44.3, 19.2, 13.7 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{19}N_3$ $[M+H]^+$: 326.1652, found: 326.1647.

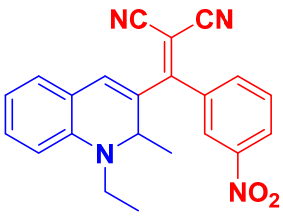
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-nitrophenyl)methylene)malononitrile (5b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (28.1 mg, 76% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.26 (m, 1H), 6.97 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.70 – 6.61 (m, 2H), 6.57 (s, 1H), 4.96 (q, *J* = 6.3 Hz, 1H), 3.54 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.39 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.1, 149.2, 145.1, 142.0, 141.0, 134.4, 131.6, 130.4, 129.1, 124.2, 119.9, 117.5, 114.1, 113.9, 112.4, 77.9, 53.8, 44.6, 19.4, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}N_4O_2$ $[M+H]^+$: 371.1503, found: 371.1500.

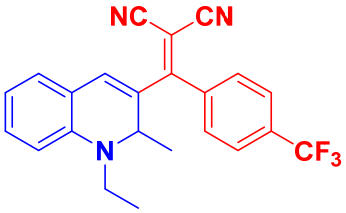
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(3-nitrophenyl)methylene)malononitrile (5c)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (24 mg, 65% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.40 (m, 1H), 8.26 (t, *J* = 1.7 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.31 – 7.26 (m, 1H), 6.98 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.71 – 6.58 (m, 3H), 4.94 (q, *J* = 6.3 Hz, 1H), 3.55 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.42-3.34 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.26 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.9, 148.4, 145.0, 141.0, 137.3, 135.0, 134.4, 131.7, 130.3, 129.2, 125.8, 124.3, 119.9, 117.5, 114.1, 113.9, 112.4, 78.2, 53.9, 44.6, 19.4, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}N_4O_2$ $[M+H]^+$: 371.1503, found: 371.1507.

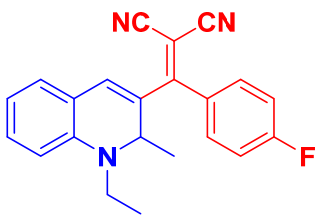
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-(trifluoromethyl)phenyl)methylene)-malononitrile (5d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (24 mg, 61% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.73 – 6.58 (m, 3H), 4.84 (q, *J* = 6.3 Hz, 1H), 3.52 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.37 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.23 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 144.8, 140.1, 139.2, 133.9, 133.1 (q, *J* = 34.0 Hz), 131.4, 129.8, 129.6, 126.0 (q, *J* = 3.8 Hz), 123.5 (q, *J* = 273.4 Hz), 119.9, 117.3, 114.1 (d, *J* = 6.3 Hz), 112.3, 78.2, 54.0, 44.5, 19.4, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{18}F_3N_3$ $[M+H]^+$: 392.1369, found: 392.1362.

2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-fluorophenyl)methylene)malononitrile (5e)

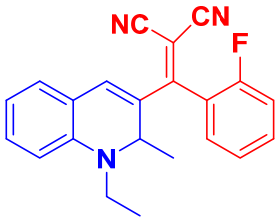


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (19.6 mg, 57% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.29 – 7.24 (m, 1H), 7.20 (t, *J* = 8.5 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.75 (s, 1H), 6.66 (dd, *J* = 12.9, 7.9 Hz, 2H), 4.62 (q, *J* = 6.3 Hz, 1H), 3.49 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.33 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126

MHz, $CDCl_3$) δ 171.7, 164.6 (d, *J* = 254.5 Hz), 144.3, 138.4, 133.3, 131.8 (d, *J* = 8.8 Hz), 131.3 (d, *J* = 2.5 Hz), 131.0, 130.4, 119.9, 117.1, 116.4, 116.3, 114.4 (d, *J* = 17.6 Hz), 112.1, 77.9, 54.5, 44.3, 19.3, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}FN_3$ $[M+H]^+$: 344.1558, found: 344.1555.

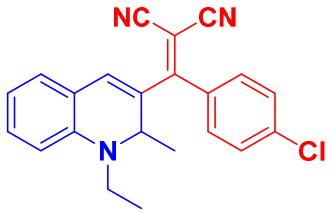
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(2-fluorophenyl)methylene)malononitrile (5f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (20.6 mg, 60% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 1H), 7.32 – 7.21 (m, 4H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.70 – 6.57 (m, 3H), 5.03 (q, *J* = 6.3 Hz, 1H), 3.53 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.36 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.6, 159.2 (d, *J* = 252.0 Hz), 145.1, 139.9, 133.9, 132.9 (d, *J* = 7.6 Hz), 131.5, 130.7(d, *J* = 1.3 Hz), 129.5, 124.7 (d, *J* = 3.8 Hz), 123.7 (d, *J* = 13.9 Hz), 120.1, 117.1, 116.6 (d, *J* = 20.2 Hz), 114.1 (d, *J* = 2.5 Hz), 112.2, 78.9, 53.6, 44.4, 19.3, 13.7 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}FN_3$ $[M+H]^+$: 344.1558, found: 344.1553.

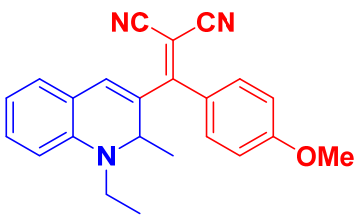
2-((4-chlorophenyl)(1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)methylene)malononitrile (5g)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (14.4 mg, 40% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.44 – 7.39 (m, 2H), 7.28-7.24 (m, 1H), 7.04 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.74 (s, 1H), 6.68 – 6.62 (m, 2H), 4.66 (q, *J* = 6.3 Hz, 1H), 3.50 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.34 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, CDCl3) δ 171.3, 144.4, 138.9, 138.1, 133.7, 133.5, 131.2, 130.9, 130.1, 129.4, 119.9, 117.2, 114.4, 114.3, 112.2, 77.9, 54.4, 44.4, 19.3, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}ClN_3$ $[M+H]^+$: 360.1262, found: 360.1266.

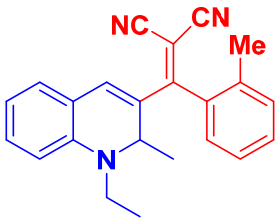
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-methoxyphenyl)methylene)malononitrile (5h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (19.9 mg, 56% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.26 – 7.22 (m, 1H), 7.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 6.69 – 6.63 (m, 2H), 4.42 (q, *J* = 6.4 Hz, 1H), 3.88 (d, *J* = 10.1 Hz, 3H), 3.47 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.31 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.8, 162.9, 143.9, 136.6, 132.7, 131.9, 131.2, 130.6, 126.9, 120.1, 116.9, 115.0, 114.8, 114.4, 111.9, 55.6, 55.3, 44.3, 19.2, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{21}N_3O$ $[M+H]^+$: 356.1757, found: 356.1754.

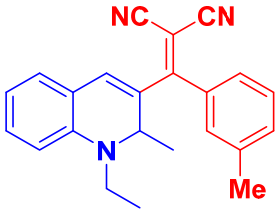
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(o-tolyl)methylene)malononitrile (5i)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (17.7 mg, 52% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 14.5, 7.1 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.63 (t, *J* = 8.6 Hz, 1H), 6.60 – 6.48 (m, 2H), 5.18 (dd, *J* = 13.8, 6.5 Hz, 1H), 3.58 – 3.47 (m, 1H), 3.36 (dq, *J* = 21.5, 7.2 Hz, 1H), 2.26 (s, 3H), 1.31 (t, *J* = 5.7 Hz, 3H), 1.28 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 145.3, 140.9, 135.9, 135.3, 134.0, 131.7, 131.0, 130.2, 129.4, 128.8, 128.2, 126.3, 120.4, 117.1, 114.3, 112.2, 89.9, 53.0, 44.2, 19.16, 18.8, 13.6 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{21}N_3$ $[M+H]^+$: 340.1808, found: 340.1805.

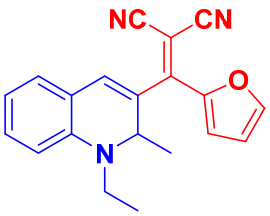
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(m-tolyl)methylene)malononitrile (5j)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (20 mg, 59% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.30 – 7.23 (m, 3H), 7.06 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.80 (s, 1H), 6.68 – 6.62 (m, 2H), 4.56 (q, *J* = 6.4 Hz, 1H), 3.52-3.44 (m, 1H), 3.29 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.41 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4, 144.2, 138.9, 137.8, 135.1, 133.1, 132.6, 130.9, 130.7, 129.9, 128.8, 126.6, 120.0, 117.0, 114.5, 114.4, 112.0, 77.9, 54.5, 44.2, 21.3, 19.2, 13.7 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{21}N_3$ $[M+H]^+$: 340.1808, found: 340.1803.

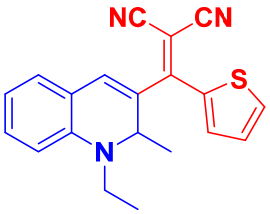
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(furan-2-yl)methylene)malononitrile (5k)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (16.4 mg, 52% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 1H), 7.27 (d, *J* = 3.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.11 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.77 (s, 1H), 6.72 – 6.66 (m, 3H), 4.45 (q, *J* = 6.4 Hz, 1H), 3.53 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.38 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.13 (d, *J* = 6.4 Hz, 3H);**^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.6, 149.1, 148.3, 143.5, 133.3, 131.9, 129.9, 128.5, 121.9, 120.1, 116.9, 114.4, 114.2, 113.8, 112.0, 74.7, 56.5, 44.5, 19.2, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{20}H_{17}N_3O$ $[M+H]^+$: 316.1444, found: 316.1448.

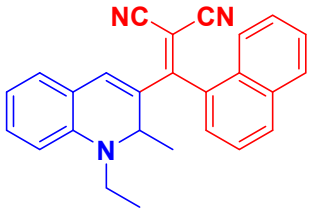
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(thiophen-2-yl)methylene)malononitrile(5l)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (16.9 mg, 51% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 3.8 Hz, 1H), 7.77 (d, *J* = 5.0 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.83 (s, 1H), 6.69 (t, *J* = 7.5 Hz, 2H), 4.45 (q, *J* = 6.4 Hz, 1H), 3.51 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.35 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.7, 143.6, 137.4, 134.6, 134.5, 134.4, 132.3, 131.0, 130.2, 128.9, 119.8, 116.9, 114.7, 114.4, 112.0, 76.3, 56.5, 44.5, 19.4, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{20}H_{17}N_3S$ $[M+H]^+$: 332.1216, found: 332.1219.

2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(naphthalen-1-yl)methylene)malononitrile (5m)

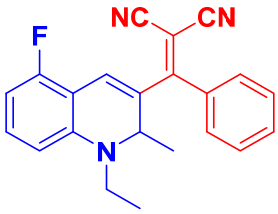


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (33 mg, 88% yield, dr 1:0.7) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.73 (s, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.51 (m, 2H), 7.45 (d, *J* = 6.8 Hz, 1H), 7.41 (d, *J* = 6.6 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 2H), 6.94 – 6.86 (m, 2H), 6.82 (d, *J* = 7.2 Hz, 1H), 6.64 (dd, *J* = 20.7, 8.4 Hz, 2H), 6.61 – 6.56 (m, 2H), 6.54 (d, *J* = 7.0 Hz, 1H), 5.28 (d, *J* = 5.7 Hz, 1H), 4.90 (d,

J = 6.0 Hz, 1H), 3.58 (dd, *J* = 13.9, 6.9 Hz, 1H), 3.45-3.37 (m, 2H), 3.27-3.19 (m, 1H), 1.35 (dd, *J* = 18.3, 6.4 Hz, 7H), 1.13 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.2, 168.8, 145.1, 145.0, 141.4, 140.2, 133.9, 133.7, 133.6, 133.4, 132.8, 131.5, 130.9, 130.8, 130.6, 130.2,129.9,128.7, 128.6, 127.8, 127.6, 127.5, 126.7, 126.6, 125.1, 124.2, 123.9, 120.2, 117.0, 114.7, 114.5, 114.3, 114.2, 112.2, 112.1, 78.9, 78.6, 53.4, 53.2, 44.3, 43.9, 19.3, 18.9, 13.7, 13.2 ppm. **HRMS (ESI):** calcd. for: $C_{26}H_{21}N_3$ $[M+H]^+$: 376.1808, found: 376.1803.

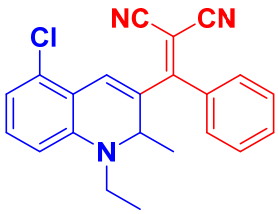
2-((1-ethyl-5-fluoro-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5n)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (27.5 mg, 80% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.1 Hz, 1H), 7.54 – 7.46 (m, 4H), 7.18 (dd, *J* = 15.0, 8.2 Hz, 1H), 7.03 (s, 1H), 6.45 (d, *J* = 8.5 Hz, 1H), 6.34 (t, *J* = 8.7 Hz, 1H), 4.62 (q, *J* = 6.4 Hz, 1H), 3.49 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.35 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.1, 161.1 (d, *J* = 252 Hz), 145.0 (d, *J* = 6.3 Hz), 135.1, 133.4, 133.3, 131.9, 130.4 (d, *J* = 6.3 Hz), 129.5, 129.0, 114.3, 114.2, 109.2, 109.1, 107.9 (d, *J* = 2.5 Hz), 102.7, 102.5, 78.7, 54.4, 44.9, 19.3, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}FN_3$ $[M+H]^+$: 344.1558, found: 344.1553.

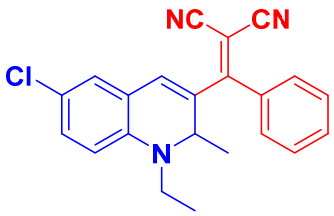
2-((5-chloro-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5o)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (25.5 mg, 71% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.9, 4.3 Hz, 1H), 7.54 – 7.48 (m, 4H), 7.27 (s, 1H), 7.14 (t, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 4.52 (q, *J* = 6.3 Hz, 1H), 3.50-3.44 (m, *J* = 14.2, 7.1 Hz, 1H), 3.37-3.31 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.3, 145.3, 135.2, 134.9, 133.6, 132.7, 132.0, 131.4, 129.5, 129.0, 117.9, 117.6, 114.3, 114.2, 110.9, 79.2, 54.5, 45.1, 19.2, 13.8 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}ClN_3$ $[M+H]^+$: 360.1262, found: 360.1265.

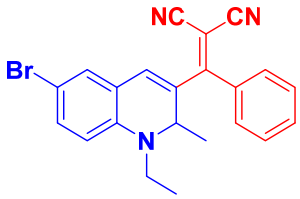
2-((6-chloro-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5p)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (24 mg, 67% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, *J* = 7.2 Hz, 1H), 7.54 – 7.46 (m, 4H), 7.18 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.69 (s, 1H), 6.60 (d, *J* = 8.9 Hz, 1H), 4.54 (q, *J* = 6.3 Hz, 1H), 3.45 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.29 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.9, 142.6, 136.2, 134.9, 132.6, 132.0, 131.9, 129.6, 129.4, 129.1, 121.8, 121.1, 114.2, 113.4, 79.2, 54.6, 44.5, 19.2, 13.6 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}ClN_3$ $[M+H]^+$: 360.1262, found: 360.1267.

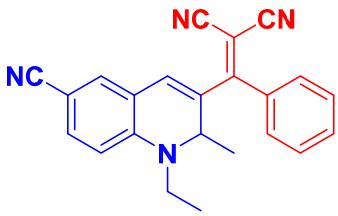
2-((6-bromo-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5q)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (31.4 mg, 78% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.1 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.22 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.10 (d, *J* = 1.9 Hz, 1H), 6.61 (s, 1H), 6.47 (d, *J* = 8.9 Hz, 1H), 4.47 (q, *J* = 6.3 Hz, 1H), 3.37 (dq, *J* = 14.2, 7.0 Hz, 1H), 3.20 (dq, *J* = 14.4, 7.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.9, 142.9, 136.0, 135.3, 134.8, 132.5, 132.0, 131.9, 129.4, 129.1, 121.6, 114.1, 114.0, 113.8, 108.6, 79.2, 54.6, 44.4, 19.3, 13.6 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}BrN_3$ $[M+H]^+$: 404.0757, found: 404.0753.

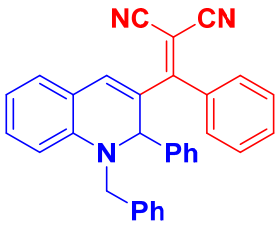
2-((6-cyano-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5r)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (28. 8 mg, 82% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 9.8, 4.3 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.44 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.33 (d, *J* = 1.8 Hz, 1H), 6.75 (s, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 4.51 (q, *J* = 6.4 Hz, 1H), 3.51 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.37-3.29 (m, 1H), 1.24 (dd, *J* = 15.2, 6.8 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.8, 146.3, 135.6, 134.8, 134.4, 134.1, 132.5, 132.2, 129.3, 129.2, 119.5, 119.3, 113.8, 113.7, 112.1, 99.1, 80.6, 55.4, 44.5, 20.4, 13.3 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{18}N_4$ $[M+H]^+$: 351.1604, found: 351.1601.

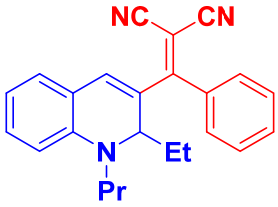
2-((1-benzyl-2-phenyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5s)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (29.2 mg, 65% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 10.1, 4.3 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.29 – 7.22 (m, 6H), 7.19-7.14 (m, 4H), 7.11 (s, 1H), 7.02 (d, *J* = 6.9 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 5.09 (s, 1H), 4.56 (d, *J* = 16.1 Hz, 1H), 4.05 (d, *J* = 16.1 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.9, 144.7, 140.2, 136.5, 134.7, 133.4, 133.1, 132.1, 130.5, 130.2, 129.2, 129.1, 129.0, 128.8, 128.6, 127.4, 127.1, 126.2, 119.2, 117.5, 113.8, 113.6, 111.3, 81.2, 63.4, 51.7 ppm. **HRMS (ESI):** calcd. for: $C_{32}H_{23}N_3$ $[M+H]^+$: 450.1965, found: 450.1969.

2-((2-ethyl-1-propyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5t)

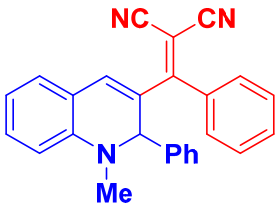


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (18.7 mg, 53% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.52 – 7.45 (m, 4H), 7.26 – 7.21 (m, 1H), 7.11 – 7.06 (m, 1H), 6.97 (s, 1H), 6.64 (t, *J* = 7.4 Hz, 2H), 4.26 (t, *J* = 6.3 Hz, 1H), 3.57-3.51 (m, 1H), 3.12 – 3.01 (m, 1H), 1.66-1.58 (m, 3H), 1.51-1.45 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.8, 144.7, 138.2, 135.1, 132.9, 131.8, 130.9, 129.5, 129.0, 128.9, 120.4, 116.9, 114.5, 114.4, 112.2, 78.2, 61.0, 52.6, 27.9, 21.1, 11.4, 9.3 ppm. **HRMS (ESI):** calcd. for: $C_{24}H_{23}N_3$ $[M+H]^+$: 354.1965, found: 354.1969.

.

2-((1-methyl-2-phenyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5u)



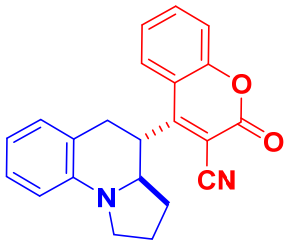
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product (12 mg, 32% yield) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.27 (dd, *J* = 12.0, 5.4 Hz, 4H), 7.10 (d, *J* = 7.3 Hz, 3H), 7.00 (s, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 5.22 (s, 1H), 2.75 (s, 3H); **^{13}C NMR (**126 MHz, $CDCl_3$) δ 173.7, 145.3, 139.6, 135.7, 134.1,

133.4, 132.1, 130.3, 130.2, 129.4, 129.2, 128.9, 128.8, 126.1, 119.1, 117.3, 113.9, 113.7, 110.7, 80.8, 65.3, 36.3 ppm. **HRMS (ESI):** calcd. for: $C_{26}H_{19}N_3$ $[M+H]^+$: 374.1652, found: 374.1657.

.Compounds 7:

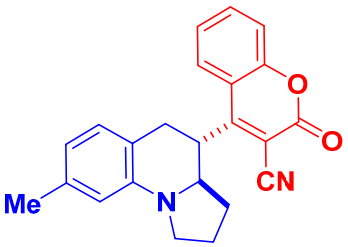
4-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7a)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (25.3 mg, 74% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.74-7.68 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40-7.35 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.69-6.63 (m, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 4.42-4.36 (m, 1H), 4.11 – 4.06 (m, 1H), 3.86 – 3.78 (m, 1H), 3.63 (d, *J* = 12.7 Hz, 1H), 3.59 – 3.50 (m, 1H), 3.49 – 3.37 (m, 1H), 3.37 – 3.33 (m, 1H), 3.12 (d, *J* = 11.7 Hz, 1H), 2.96 (dd, *J* = 15.5, 3.8 Hz, 1H), 2.15 (dd, *J* = 11.8, 7.7 Hz, 1H), 2.10 – 2.04 (m, 1H), 2.02 (dd, *J* = 13.9, 3.1 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.71 – 1.58 (m, 1H), 1.38 – 1.35 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 166.3, 157.2, 156.5, 153.8, 153.3, 143.6, 143.4, 135.3, 134.8, 128.6, 128.1, 128.0, 127.6, 125.5, 125.3, 125.2, 119.4, 118.9, 118.5, 118.2, 118.0, 116.4, 116.1, 115.7, 114.4, 113.6, 111.5, 110.9, 103.1, 100.4, 89.9, 59.7, 58.9, 47.6, 47.3, 47.2, 39.3, 32.7, 32.6, 31.5, 31.4, 23.5, 23.3 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{18}N_2O_2$ $[M+H]^+$: 343.1441, found: 343.1445.

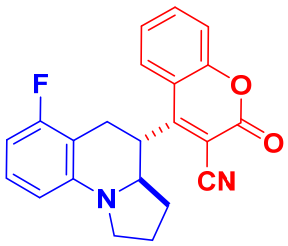
4-(8-methyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7b)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (18.9 mg, 53% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 12.0, 8.2 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.46 – 7.42 (m, 1H), 7.40-7.34 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.49 (t, *J* = 8.8 Hz, 1H), 6.40 (d, *J* = 14.5 Hz, 2H), 4.40-4.35 (m, 1H), 4.08-4.03 (m, 1H), 3.81 – 3.73 (m, 1H), 3.57 (s, 1H), 3.56 – 3.49 (m, 1H), 3.48 – 3.35 (m, 1H), 3.35 – 3.29 (m, 1H), 3.11 – 3.07 (m, 1H), 2.93 (dd, *J* = 15.4, 3.8 Hz, 1H), 2.32 (s, 4H), 2.13 (d, *J* = 1.8 Hz, 1H), 2.09 – 2.04 (m, 1H), 2.01 (dd, *J* = 9.3, 4.9 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.64 (dd, *J* = 9.7, 7.8 Hz, 1H), 1.37 – 1.34 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 166.4, 157.2, 156.6, 153.8, 153.3, 143.5, 143.3, 137.8, 137.7, 135.3, 134.8, 128.5, 128.4, 127.7, 125.5, 125.3, 125.1, 118.5, 118.2, 118.0, 117.0, 116.6, 116.5, 116.4, 116.1, 114.4, 113.6, 112.2, 111.6, 103.0, 100.3, 89.9, 59.7, 58.9, 47.8, 47.3, 47.2, 39.5, 32.4, 31.4, 31.3, 23.5, 23.3, 21.6, 21.5 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{20}N_2O_2$ $[M+H]^+$: 357.1598, found: 357.1595.

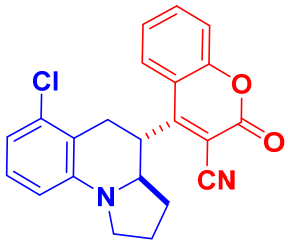
4-(6-fluoro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile（7c）



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (17.7 mg, 49% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.43-7.37 (m, 1H), 7.15 – 7.07 (m, 1H), 6.44 – 6.38 (m, 1H), 6.35 (dd, *J* = 16.2, 8.3 Hz, 2H), 4.39-4.34 (m, 1H), 4.09-4.03 (m, 1H), 3.55 – 3.50 (m, 1H), 3.48 (dd, *J* = 10.6, 6.0 Hz, 1H), 3.45 – 3.41 (m, 1H), 3.38 (d, *J* = 8.7 Hz, 1H), 3.33 (dd, *J* = 8.2, 6.2 Hz, 1H), 3.28 (d, *J* = 4.4 Hz, 1H), 3.21 (dd, *J* = 15.9, 3.4 Hz, 1H), 2.18 – 2.13 (m, 1H), 2.12 – 2.06 (m, 1H), 2.06 – 1.97 (m, 1H), 1.95 – 1.87 (m, 1H), 1.70 – 1.65 (m, 1H), 1.44 – 1.33 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.8, 165.8, 160.9 (d, *J* = 241.9 Hz), 160.8 (d, *J* = 241.9 Hz), 157.1, 156.5, 153.8, 153.4, 144.9 (d, *J* = 16.4 Hz), 144.8 (d, *J* = 16.4 Hz), 135.5, 134.9, 128.5 (d, *J* = 10.1 Hz), 128.4 (d, *J* = 11.3 Hz), 127.4, 125.6, 125.3, 125.2, 118.4 (d, *J* = 46.6 Hz),117.9, 116.3, 114.3, 113.6, 107.0 (d, *J* = 2.5 Hz), 106.7, 106.5 (d, *J* = 2.5 Hz), 106.2 (d, *J* = 20.2 Hz), 103.3,102.7, 102.5 (d, *J* = 6.3 Hz), 102.3, 100.6, 59.1, 58.2, 47.5, 47.4, 46.8, 38.6, 31.4, 31.3, 25.8, 25.5, 23.3, 23.2 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{17}FN_2O_2$ $[M+H]^+$: 362.1420, found: 362.1423.

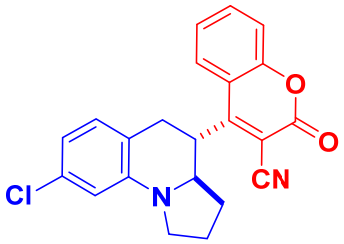
4-(6-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7d)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (20.7 mg, 55% yield, dr 2:1) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.76-7.69 (m, 2H), 7.49 – 7.44 (m, 2H), 7.43 – 7.37 (m, 1H), 7.09 (q, *J* = 8.2 Hz, 2H), 6.73 (dd, *J* = 14.0, 7.9 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 4.40-4.34 (m, 1H), 4.04 (dd, *J* = 10.0, 4.9 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.50 – 3.47 (m, 1H), 3.46 – 3.38 (m, 1H), 3.37 (d, *J* = 6.1 Hz, 1H), 3.35 – 3.34 (m, 1H), 3.30 (dd, *J* = 15.9, 4.0 Hz, 1H), 2.16 (dd, *J* = 11.6, 5.5 Hz, 1H), 2.13 – 2.07 (m, 1H), 2.07 – 1.98 (m, 1H), 1.96 – 1.87 (m, 1H), 1.70 – 1.65 (m, 1H), 1.46 – 1.34 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6, 165.6, 157.1, 153.9, 153.4, 144.9, 144.8, 135.5, 134.9, 134.2, 134.1, 128.4, 128.3, 127.4, 125.6, 125.3, 125.2, 118.7, 118.3, 117.9, 117.3, 116.9, 116.8, 116.5, 116.3, 114.3, 113.6, 109.9, 109.4, 103.4, 100.7, 59.1, 58.4, 58.1, 47.5, 47.4, 39.2, 31.4, 31.3, 30.6, 30.4, 23.5, 23.3, 18.4 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{17}ClN_2O_2$ $[M+H]^+$: 377.1051, found: 377.1056.

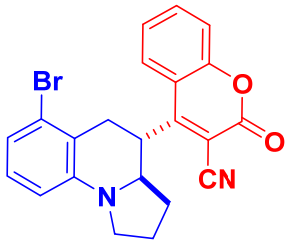
4-(8-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7e)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (15.8 mg, 42% yield, dr 2:1) as a yellow solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.76-7.69 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.40 (dd, *J* = 17.3, 9.0 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.61 (t, *J* = 9.6 Hz, 1H), 6.52 (d, *J* = 15.0 Hz, 2H), 4.40-4.35 (m, 1H), 4.13-4.08 (m, 1H), 3.82 – 3.71 (m, 1H), 3.61 – 3.49 (m, 1H), 3.46 (d, *J* = 9.5 Hz, 1H), 3.40 – 3.35 (m, 1H), 3.35 – 3.28 (m, 2H), 3.08 (dd, *J* = 14.6, 2.8 Hz, 1H), 2.93 (dd, *J* = 15.6, 3.7 Hz, 1H), 2.17 (dd, *J* = 12.6, 6.9 Hz, 1H), 2.14 – 2.05 (m, 1H), 2.05 – 1.99 (m, 1H), 1.97 – 1.86 (m, 1H), 1.66 (dd, *J* = 18.5, 10.3 Hz, 1H), 1.43 – 1.32 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 165.8, 157.1, 156.4, 153.8, 153.4, 144.4, 144.3, 135.5, 134.9, 133.5, 129.5, 129.4, 127.4, 125.6, 125.3, 118.6, 118.3, 117.9, 117.7, 117.3, 116.3, 115.8, 115.4, 114.3, 113.6, 111.1, 110.5, 103.3, 100.5, 59.5, 58.8, 47.4, 47.3, 47.2, 38.9, 32.3, 32.1, 31.5, 31.4, 23.5, 23.4 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{17}ClN_2O_2$ $[M+H]^+$: 377.1051, found: 377.1054.

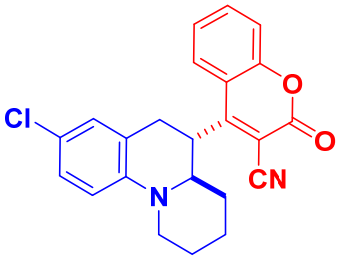
4-(6-bromo-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7f)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (16.8 mg, 40% yield, dr 1:0.7) as a yellow solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.84 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.49 – 7.44 (m, 2H), 7.43 – 7.36 (m, 2H), 7.02 (q, *J* = 8.2 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 4.41-4.35 (m, 1H), 4.07-4.01 (m, , 1H), 3.60 – 3.50 (m, 2H), 3.51 – 3.46 (m, 2H), 3.45 – 3.38 (m, 2H), 3.37 – 3.35 (m, 2H), 3.34-3.25 (m, 2H), 2.23 – 2.14 (m, 1H), 2.14 – 2.07 (m, 2H), 2.07 – 1.97 (m, 2H), 1.97 – 1.87 (m, 1H), 1.71 – 1.63 (m, 1H), 1.44 – 1.35 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 165.4, 157.1, 156.5, 153.9, 153.4, 145.1, 144.9, 135.5, 134.9, 128.8, 128.7, 127.4, 125.6, 125.3, 125.2, 125.1, 125.0, 120.1, 119.8, 118.8, 118.7, 118.5, 118.4, 117.9, 116.3, 114.3, 113.6, 110.6, 110.1, 103.4, 100.8, 59.2, 58.2, 47.6, 47.4, 47.3, 39.5, 33.5, 33.4, 31.3, 31.2, 23.5, 23.4 ppm. **HRMS (ESI):** calcd. for: $C_{22}H_{17}BrN_2O_2$ $[M+H]^+$: 420.0473, found: 420.0477.

4-(8-chloro-2,3,4,4a,5,6-hexahydro-1*H*-pyrido[1,2-a]quinolin-5-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7h)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (17.2 mg, 44% yield, dr 1:0.8) as a yellow solid.

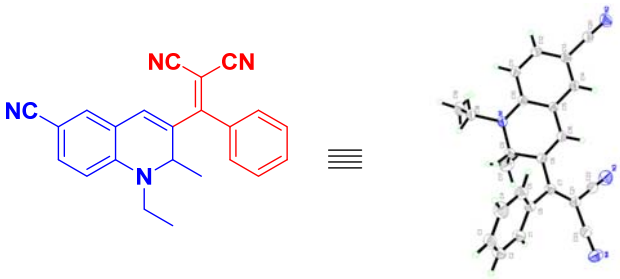
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 14.4, 7.7 Hz, 2H), 7.12 (dd, *J* = 18.1, 9.9 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 7.3 Hz, 2H), 3.95 (d, *J* = 13.3 Hz, 2H), 3.87 (dd, *J* = 26.9, 14.6 Hz, 2H), 3.72 (s, 1H), 3.59 (d, *J* = 8.4 Hz, 1H), 3.45 (t, *J* = 14.4 Hz, 1H), 3.29 (dd, *J* = 16.2, 5.9 Hz, 1H), 3.21 (t, *J* = 14.6 Hz, 2H), 2.88-2.81 (m, 2H), 1.84 (d, *J* = 13.3 Hz, 2H), 1.77 (s, 2H), 1.70 (s, 2H), 1.58 (d, *J* = 12.1 Hz, 2H), 1.49 – 1.40 (m, 2H), 1.36 (s, 1H), 1.19 (d, *J* = 11.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 165.7, 157.1, 156.5, 153.9, 153.5, 147.9, 147.7, 135.6, 135.0, 134.1, 134.0, 133.9, 128.0, 127.1, 125.7, 125.4, 125.3, 120.7, 119.9, 119.3, 118.8, 118.6, 118.2, 118.1, 116.1, 113.9, 113.4, 112.2, 112.1, 103.7, 100.9, 58.4, 56.7, 48.9, 48.3, 40.8, 31.5, 31.2, 29.8,29.9, 29.6, 25.3, 23.9, 23.6, 23.3 ppm. **HRMS (ESI):** calcd. for: $C_{23}H_{19}ClN_2O_2$ $[M+H]^+$: 391.1208, found: 391.1204.

Refference

1. Dong Xue, Ying-Chun Chen, et al. *J. Org. Chem.* **2005**, *70*, 3584

2. Chang-Yun Shi, Jun-Zhao Xiao, Liang Yin Xiao, *Chem. Commun.* **2018**, *54*, 11957

4. Crystal Structures and Data



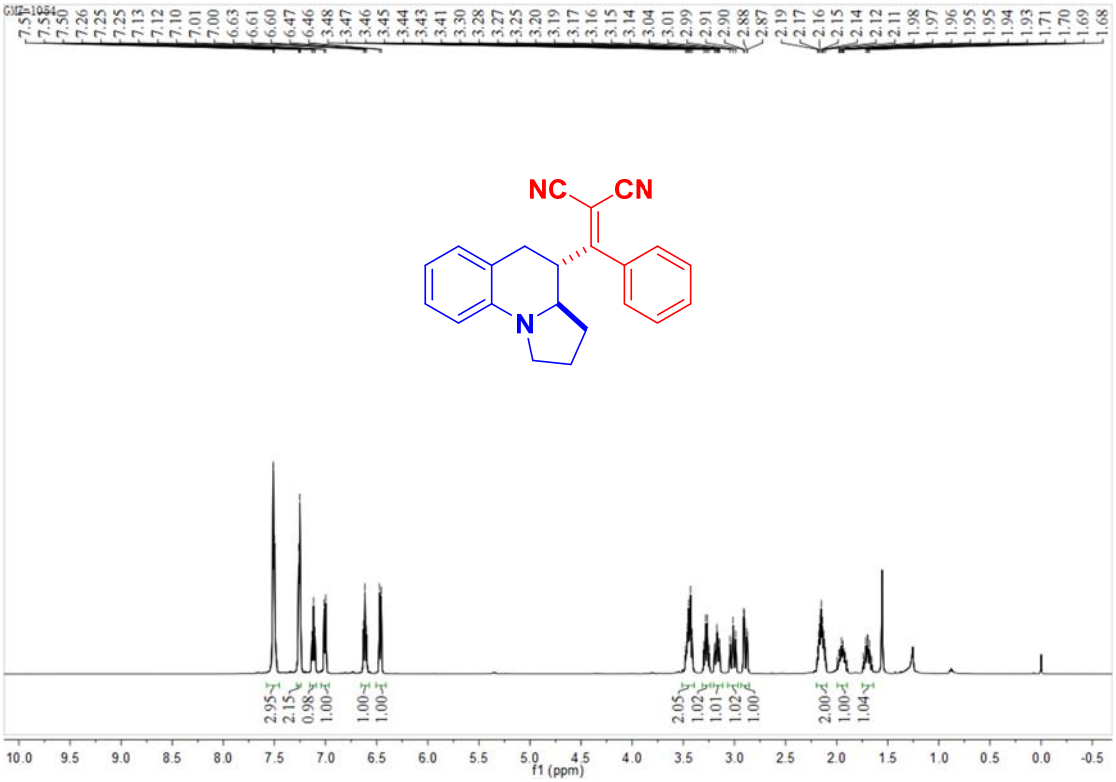
5r (CCDC 2041236)

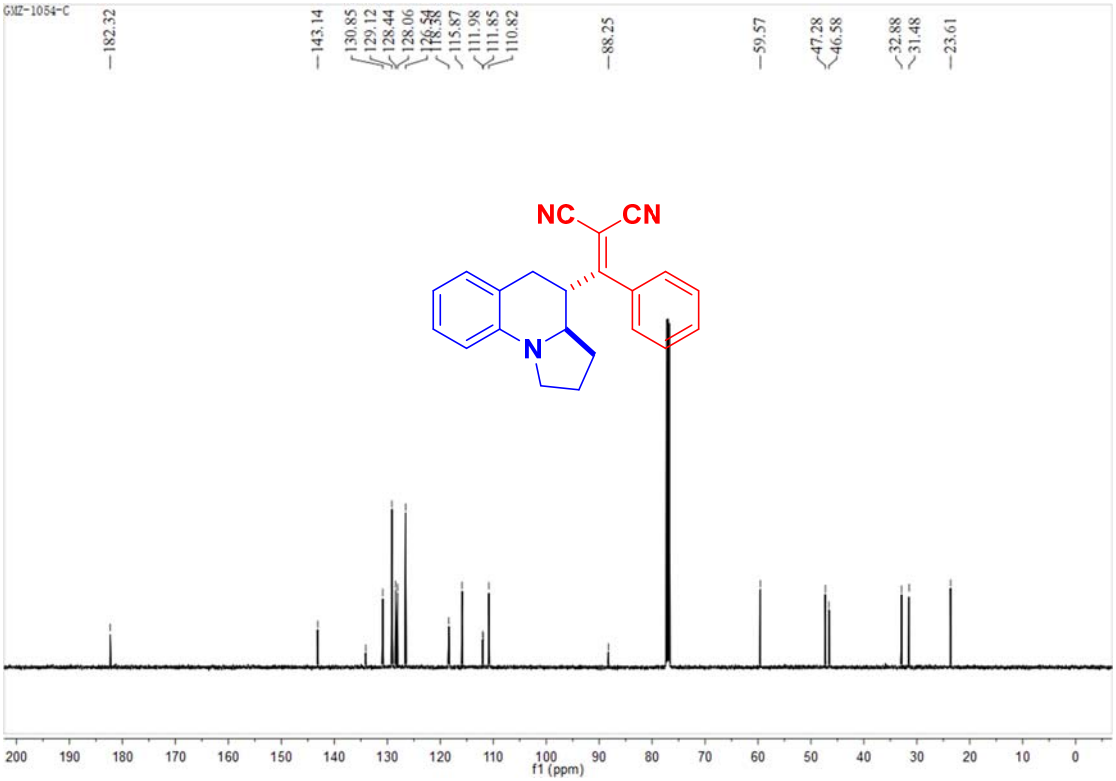
Table 1. Crystal data and structure refinement for **5r**.

Identification code	**5r**
Empirical formula	$C_{23}H_{18}N_4$
Formula weight	350.41
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 7.9882(4) A alpha = 93.836(4) deg.
	b = 10.1351(7) A beta = 96.860(4) deg.
	c = 11.5052(5) A gamma = 90.014(5) deg.
Volume	922.70(9) A^3
Z, Calculated density	2, 1.261 Mg/m^3
Absorption coefficient	0.601 mm^-1
F(000)	368
Crystal size	0.12 x 0.12 x 0.11 mm
Theta range for data collection	3.88 to 67.25 deg.
Limiting indices	-7<=h<=9, -12<=k<=11, -11<=l<=13
Reflections collected / unique	5652 / 3308 [R(int) = 0.0259]
Completeness to theta = 67.25	99.8 %
Max. and min. transmission	0.9369 and 0.9314
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3308 / 0 / 246
Goodness-of-fit on F^2	1.204
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1391
R indices (all data)	R1 = 0.0665, wR2 = 0.1485
Largest diff. peak and hole	0.130 and -0.182 e.A^-3

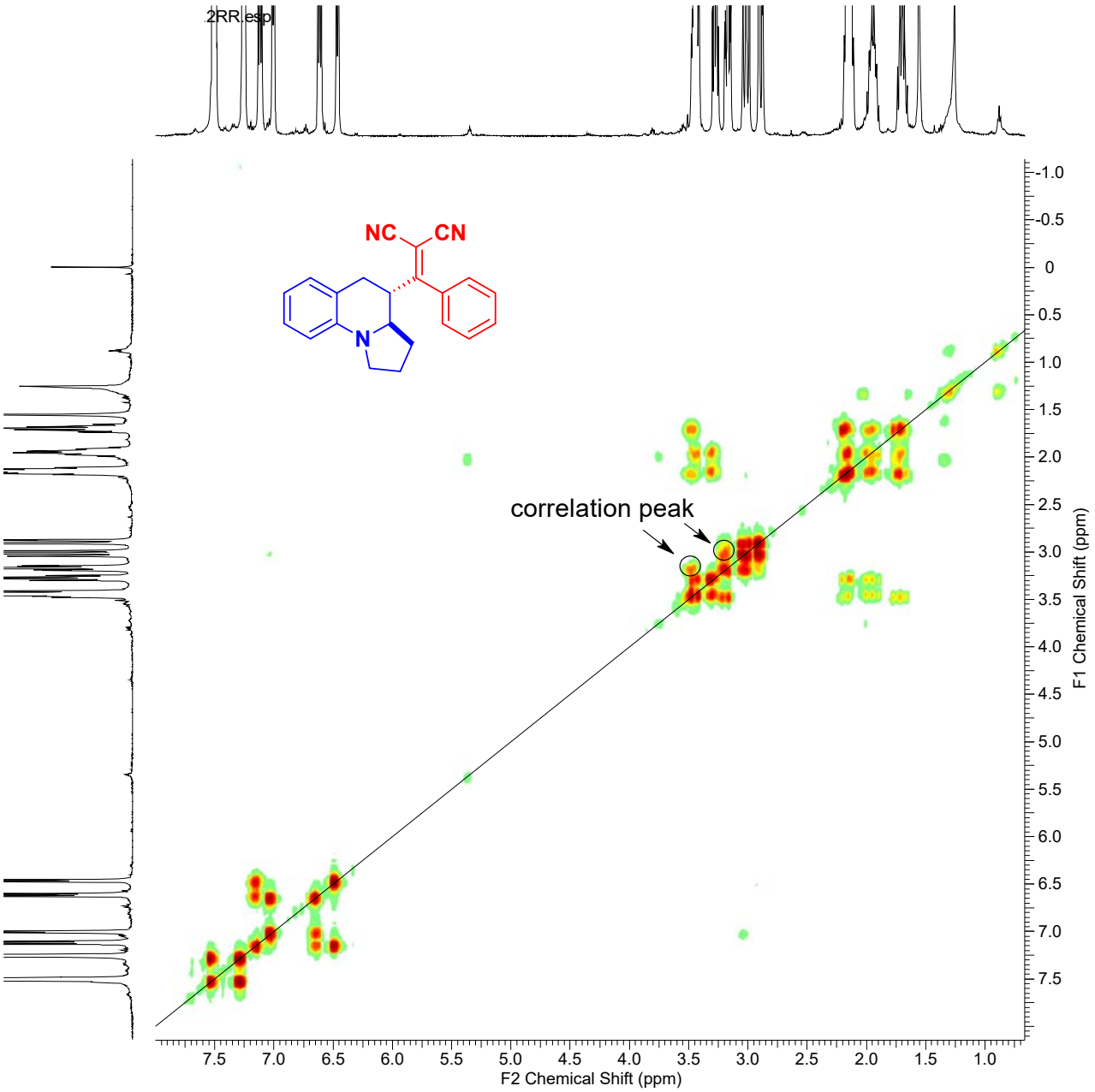
5. ^{1}H and ^{13}C NMR Spectra as well as H,H-Cosy and NOESY

2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)malononitrile (3a)

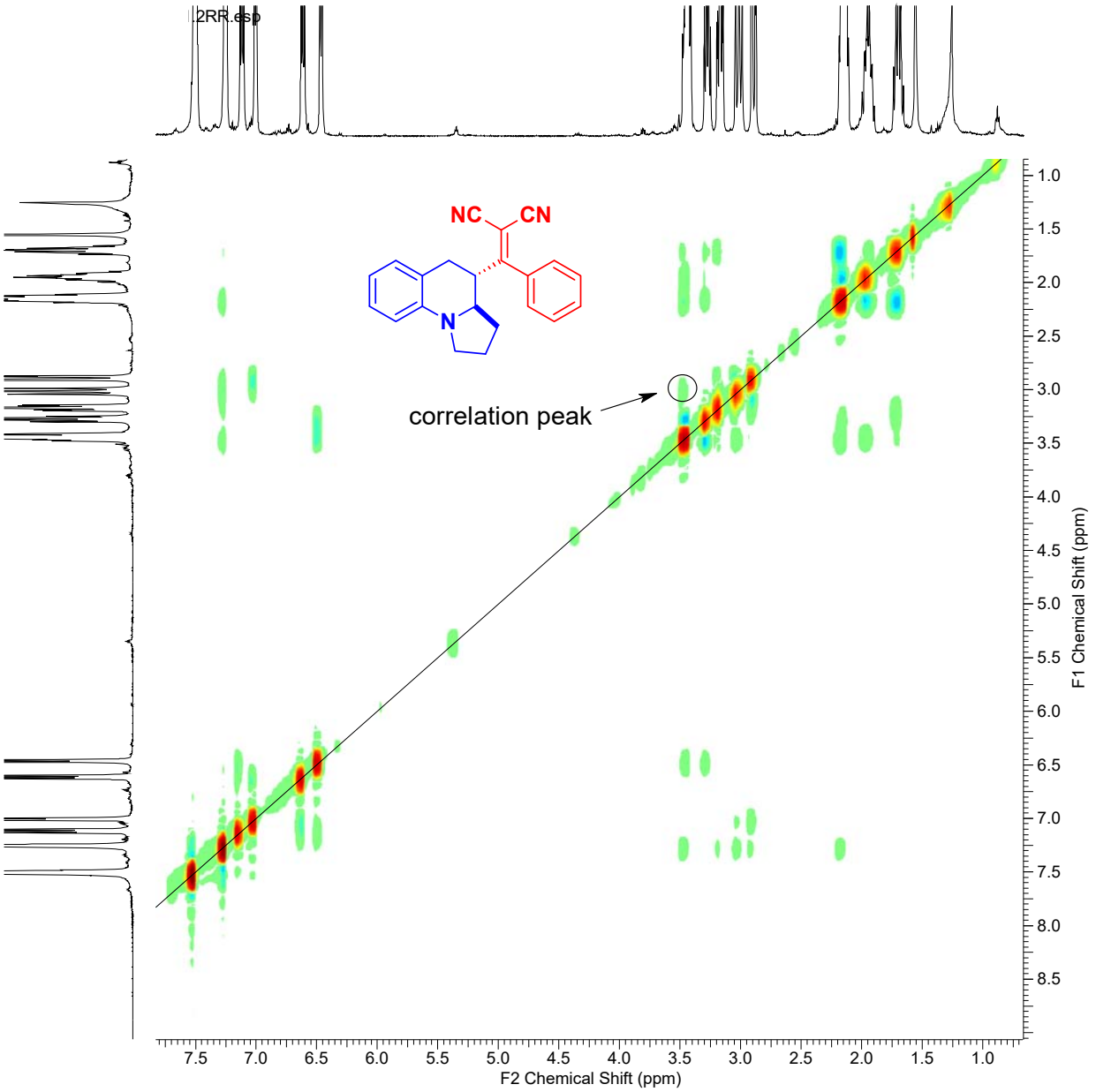




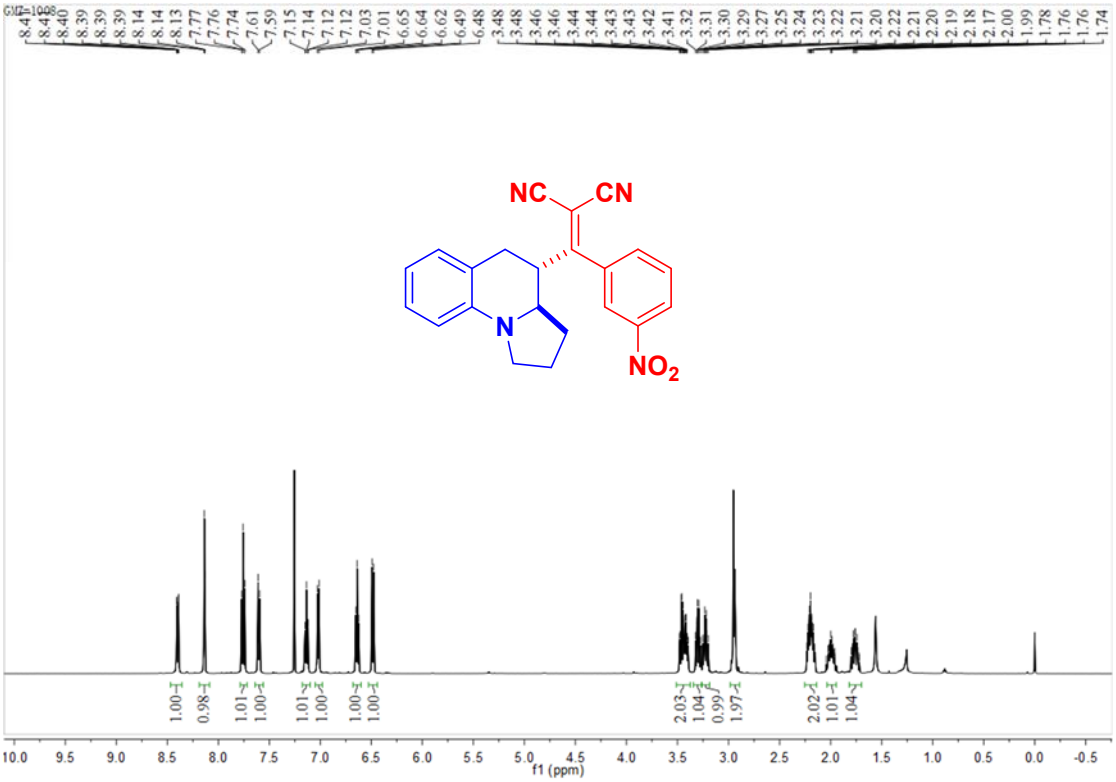
H,H-Cosy of ((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-yl)(phenyl)-ethylene)-alononitrile (3a)

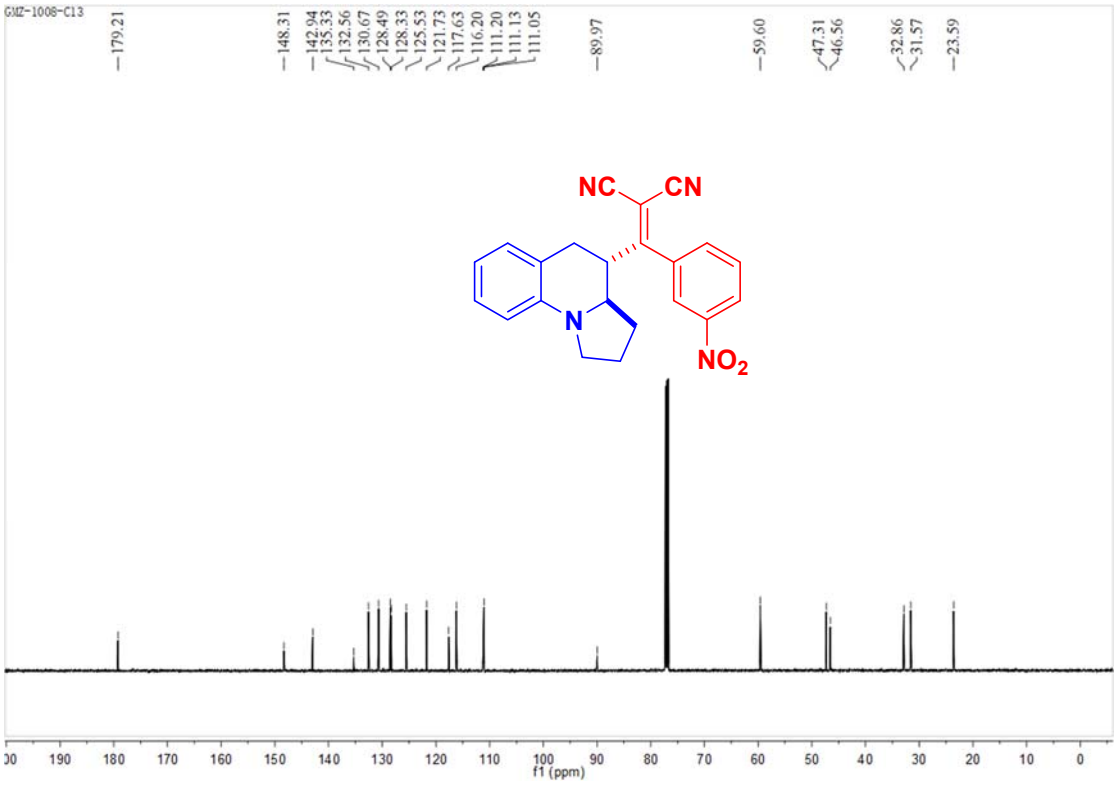


NOESY of ((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-yl)(phenyl)-ethylene)-alononitrile (3a)

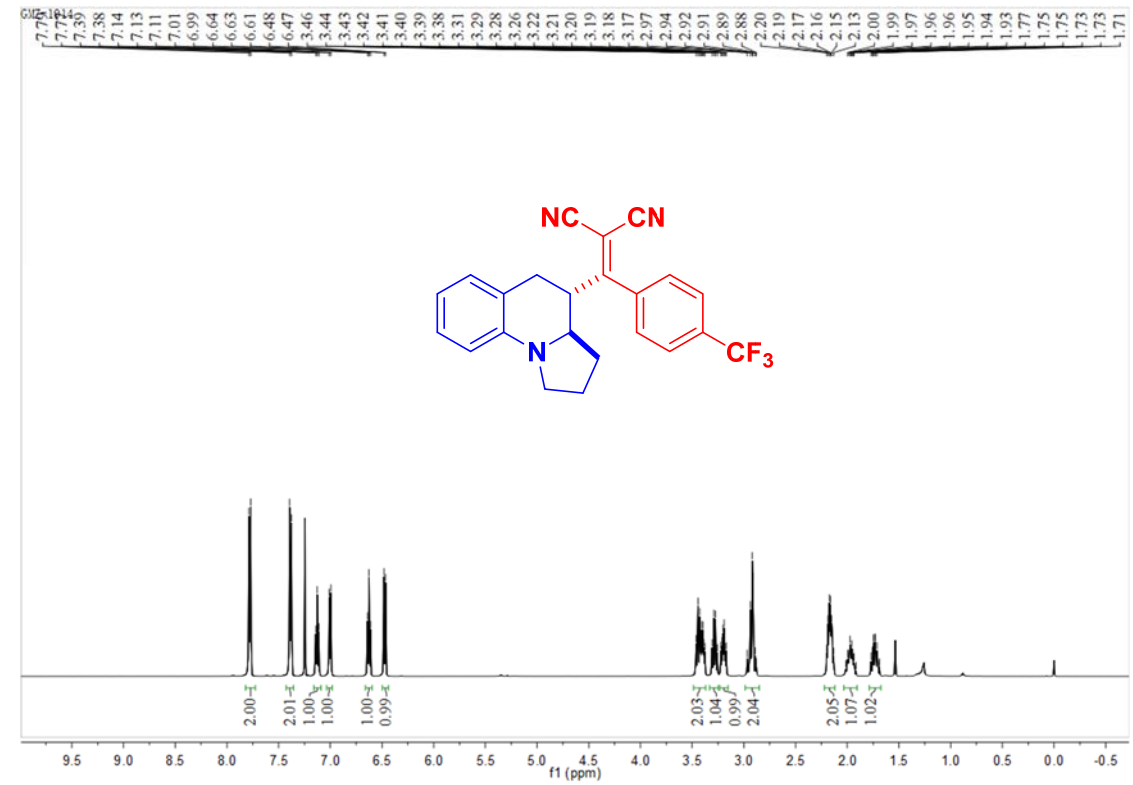


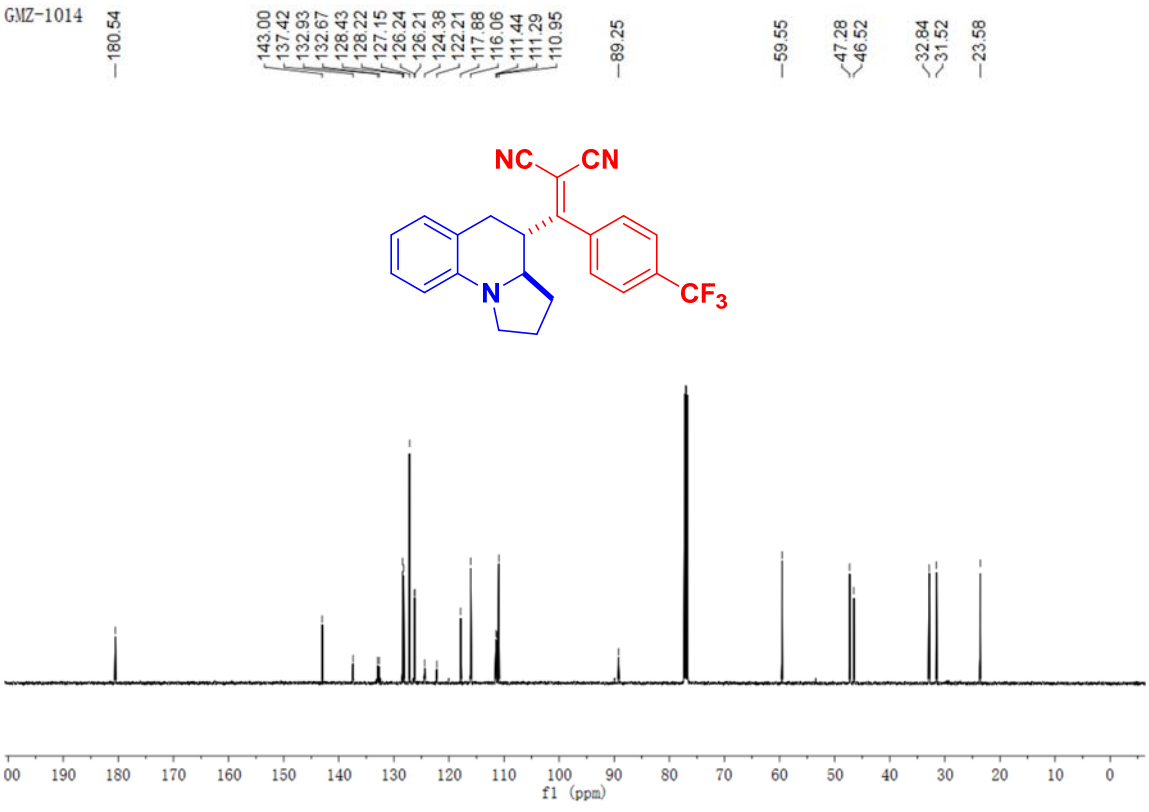
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(3-nitrophenyl)methylene)malononitrile (3b)



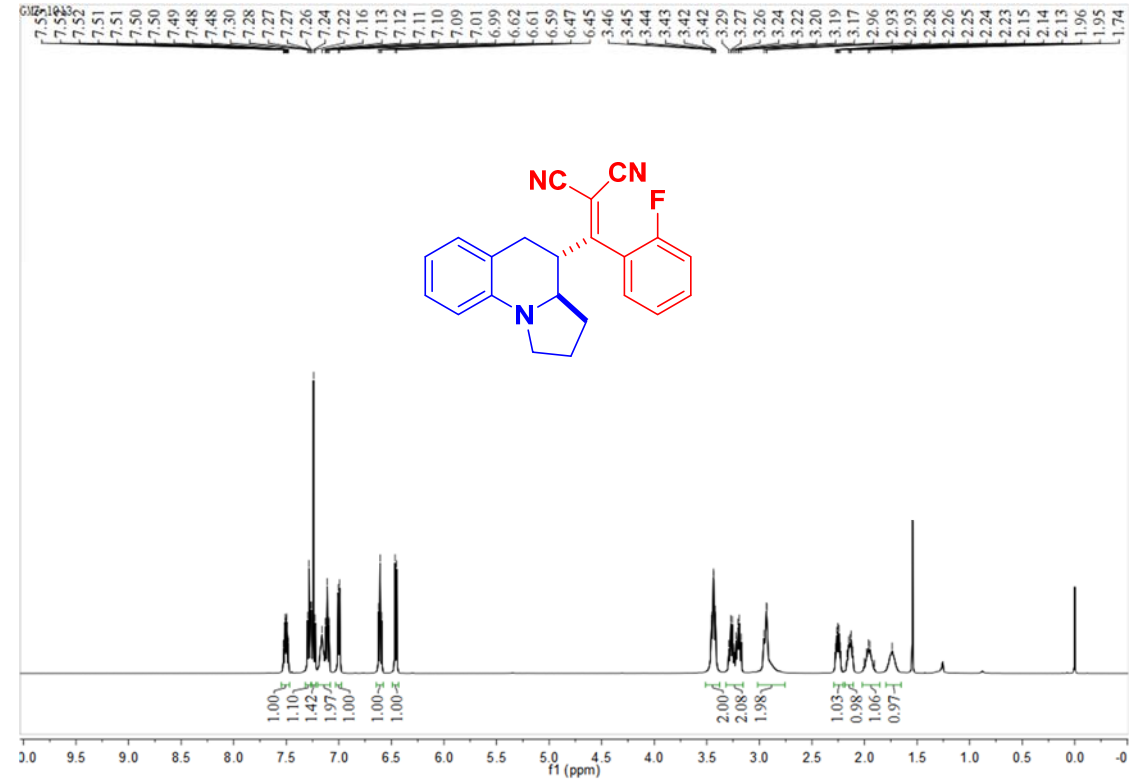


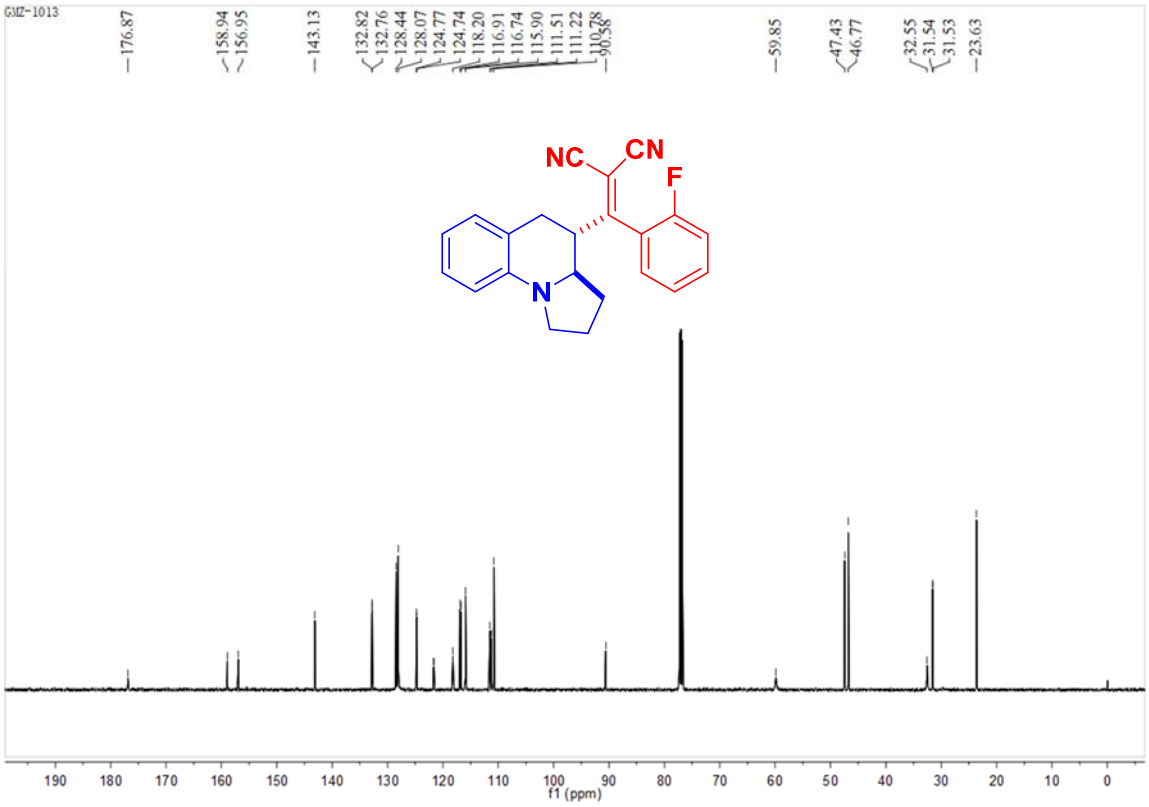
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(4-(trifluoromethyl)phenyl)methylene)-malononitrile (3c)



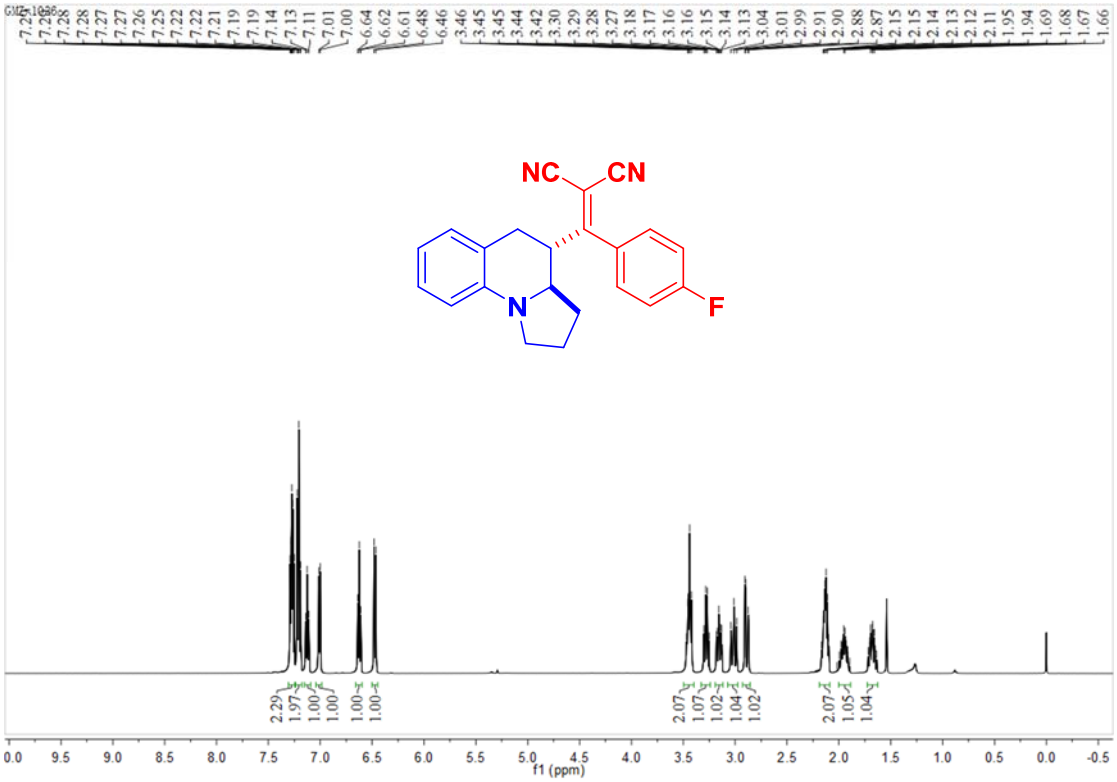


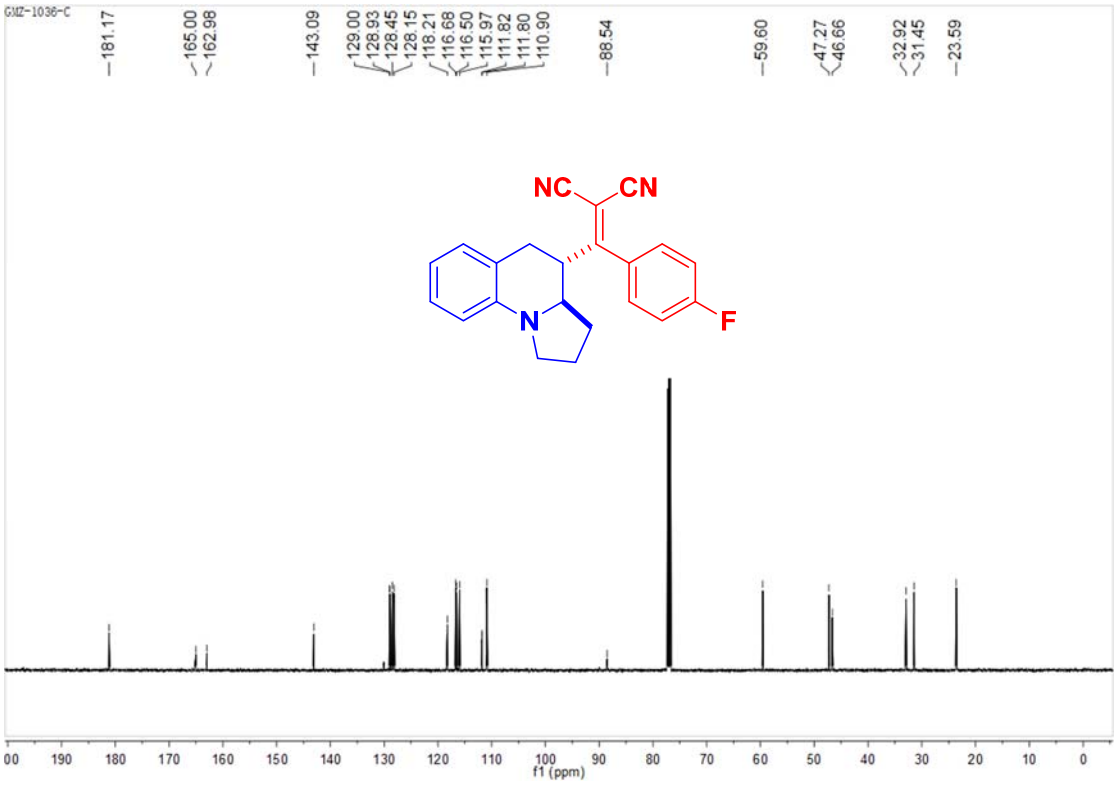
2-((2-fluorophenyl)(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile (3d)



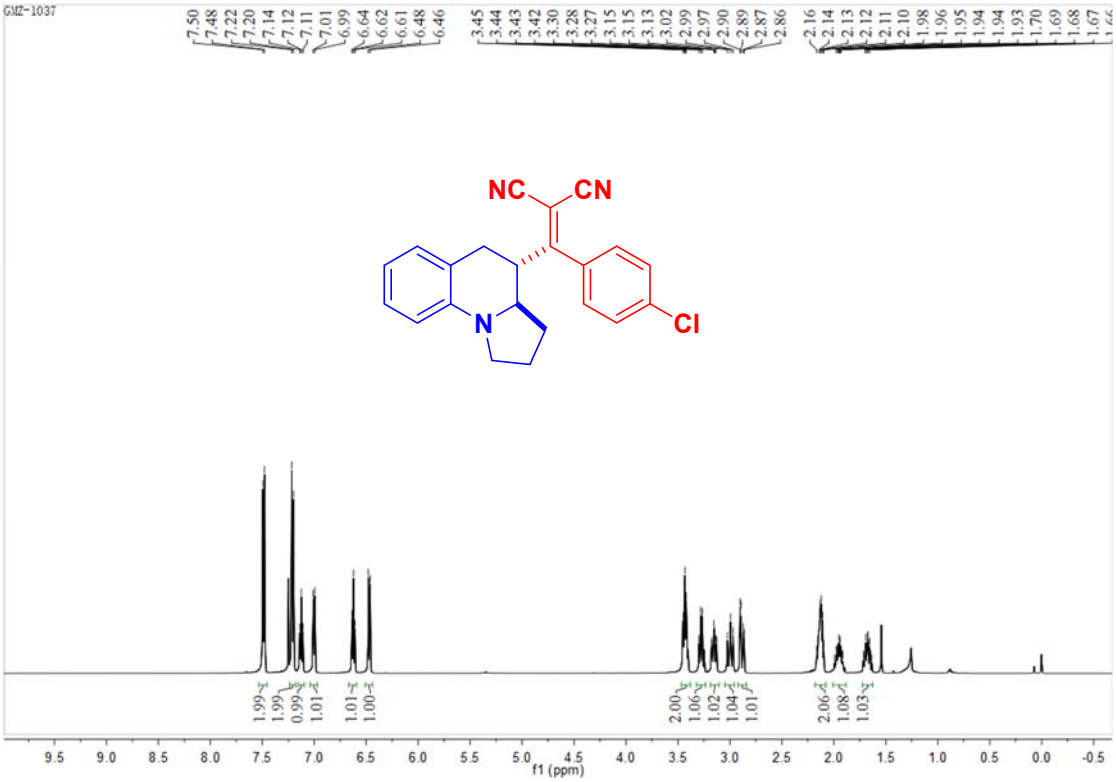


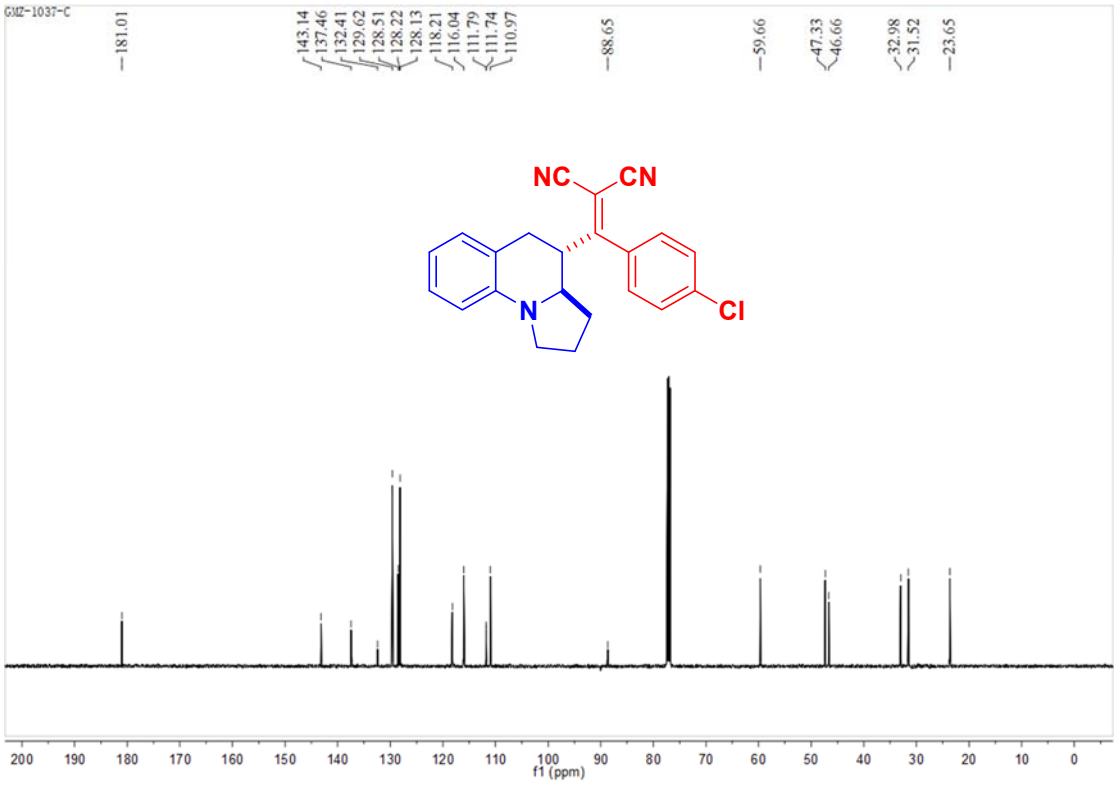
2-((4-fluorophenyl)(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile (3e)



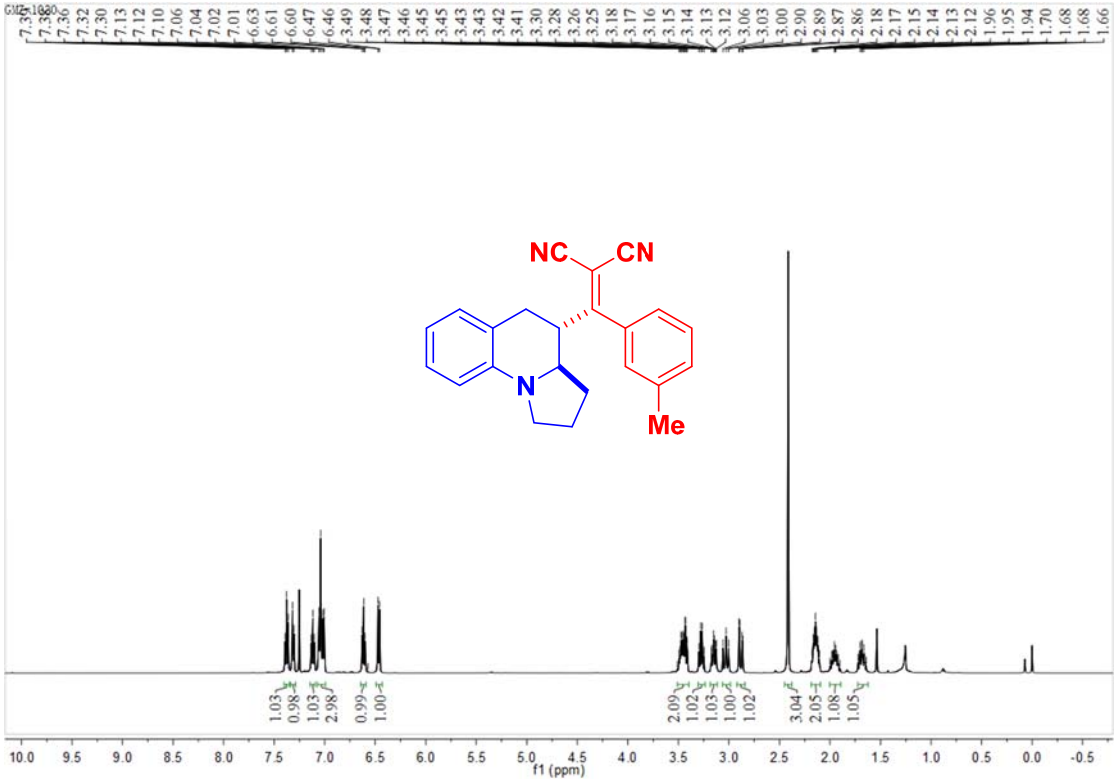


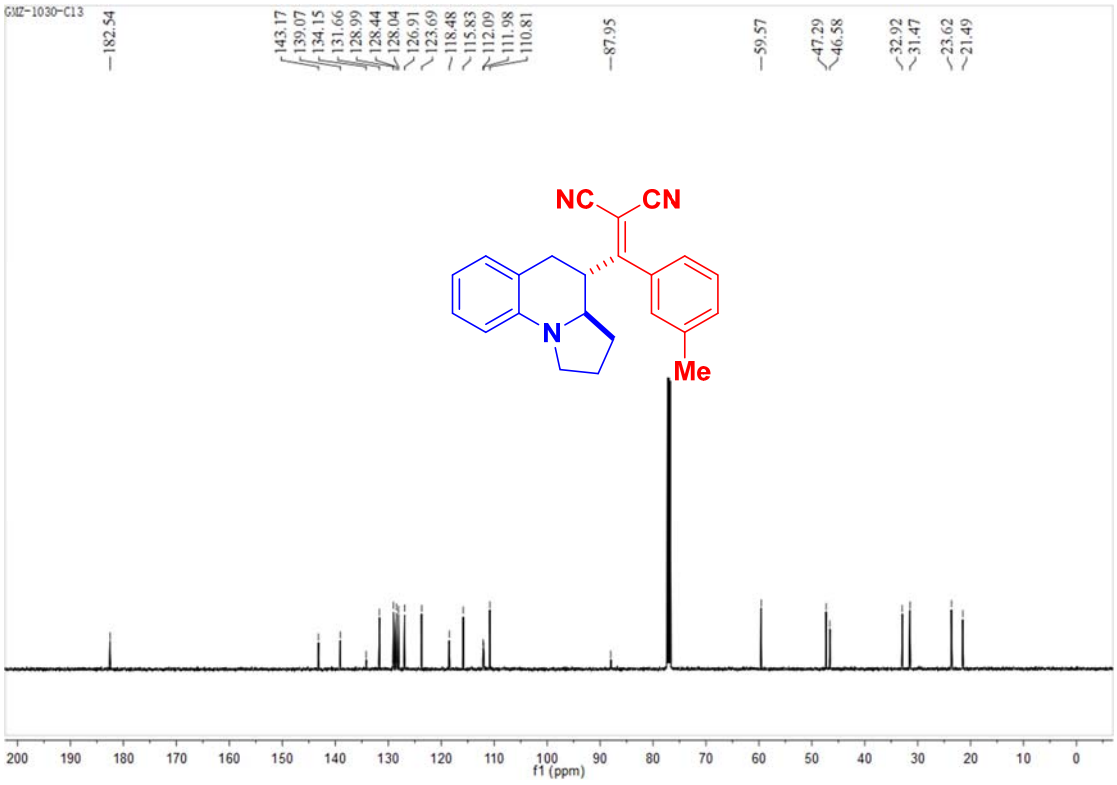
2-((4-chlorophenyl)(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile (3f)



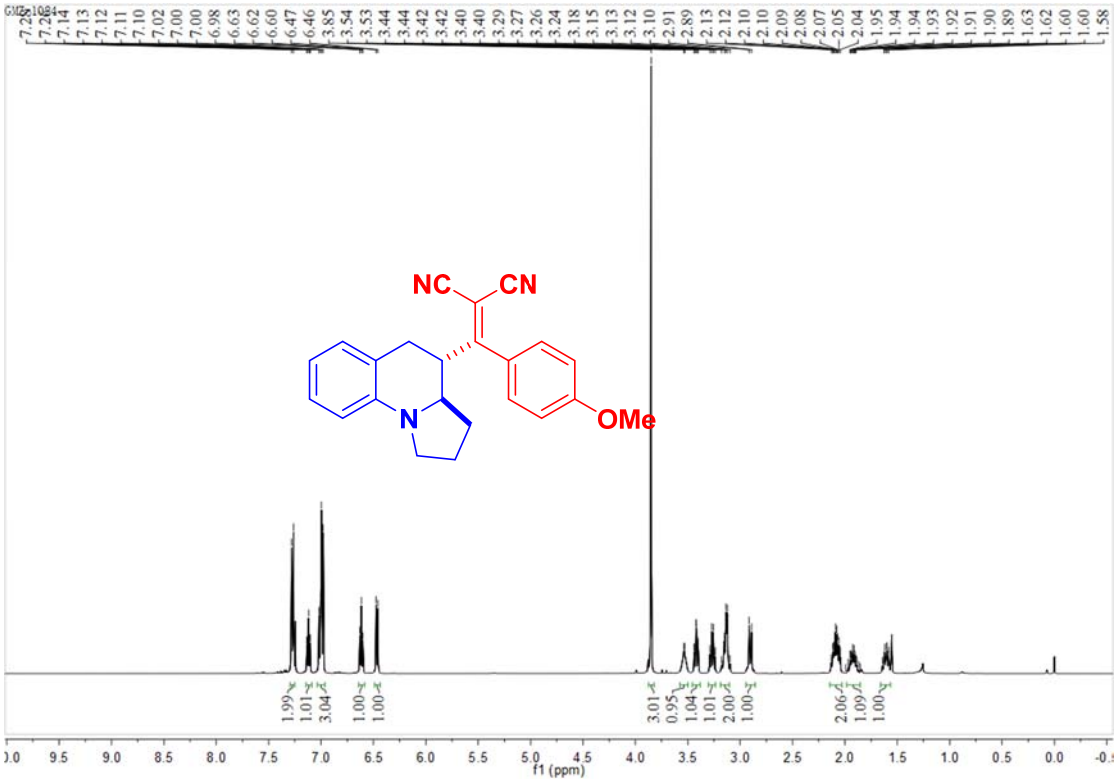


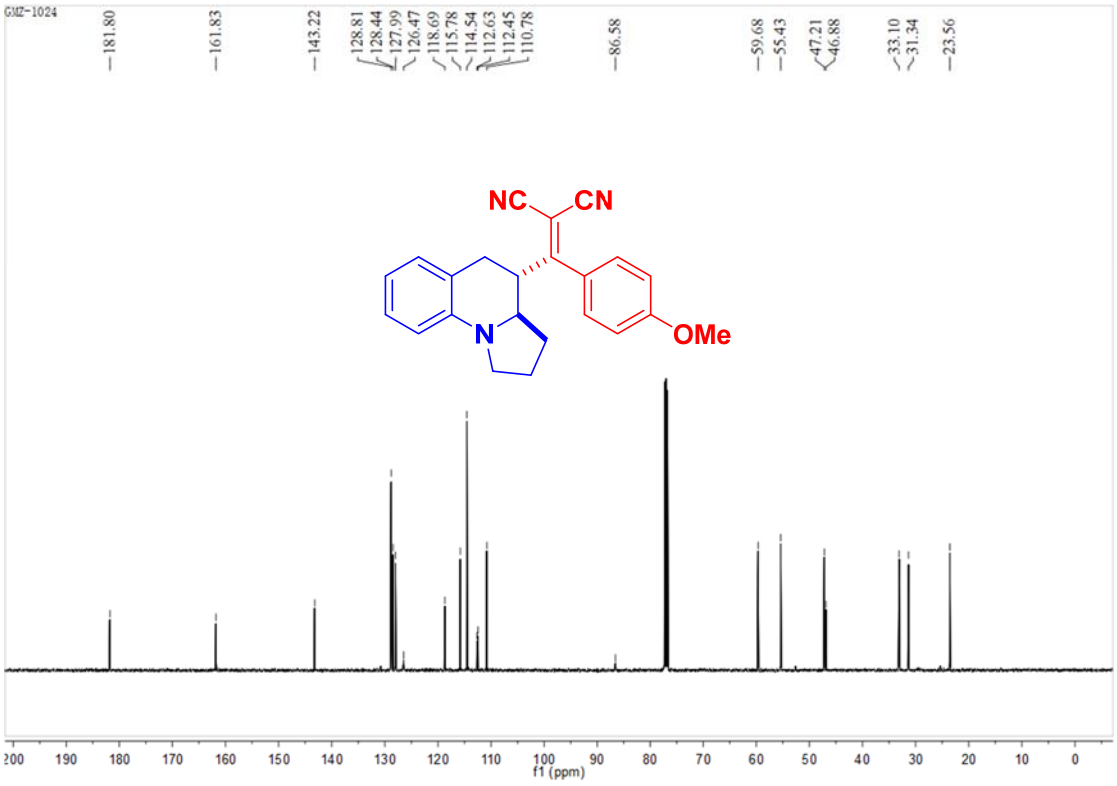
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(m-tolyl)methylene)malononitrile (3g)



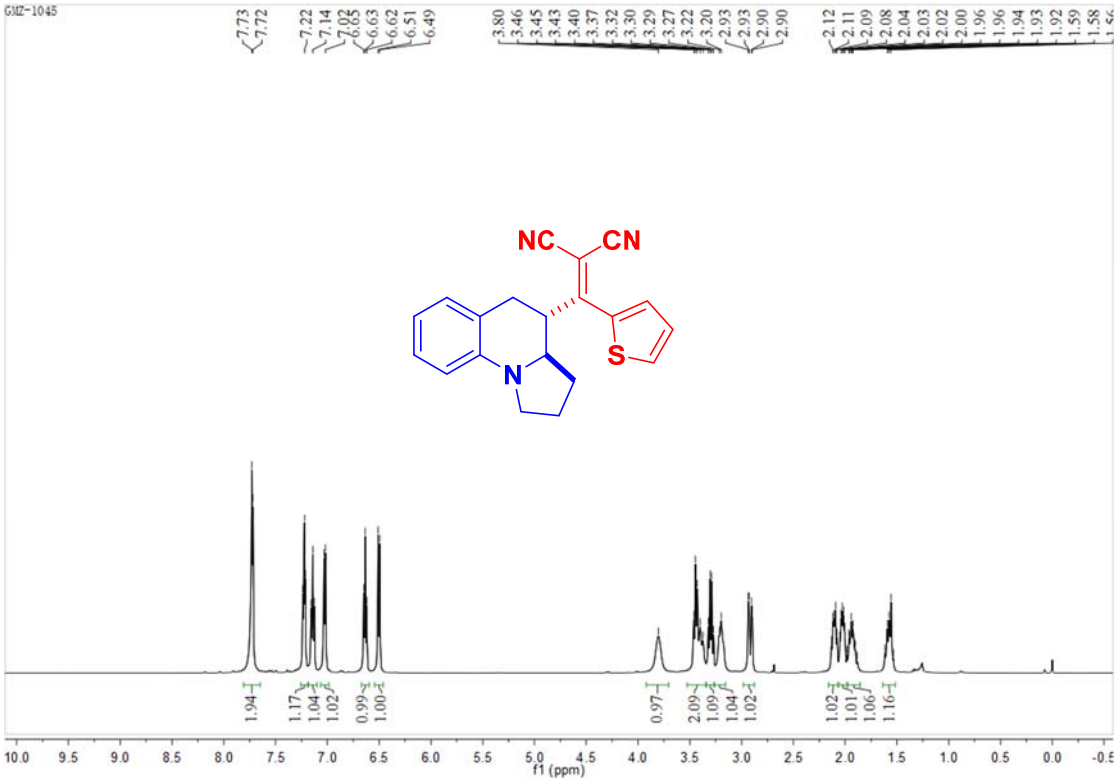


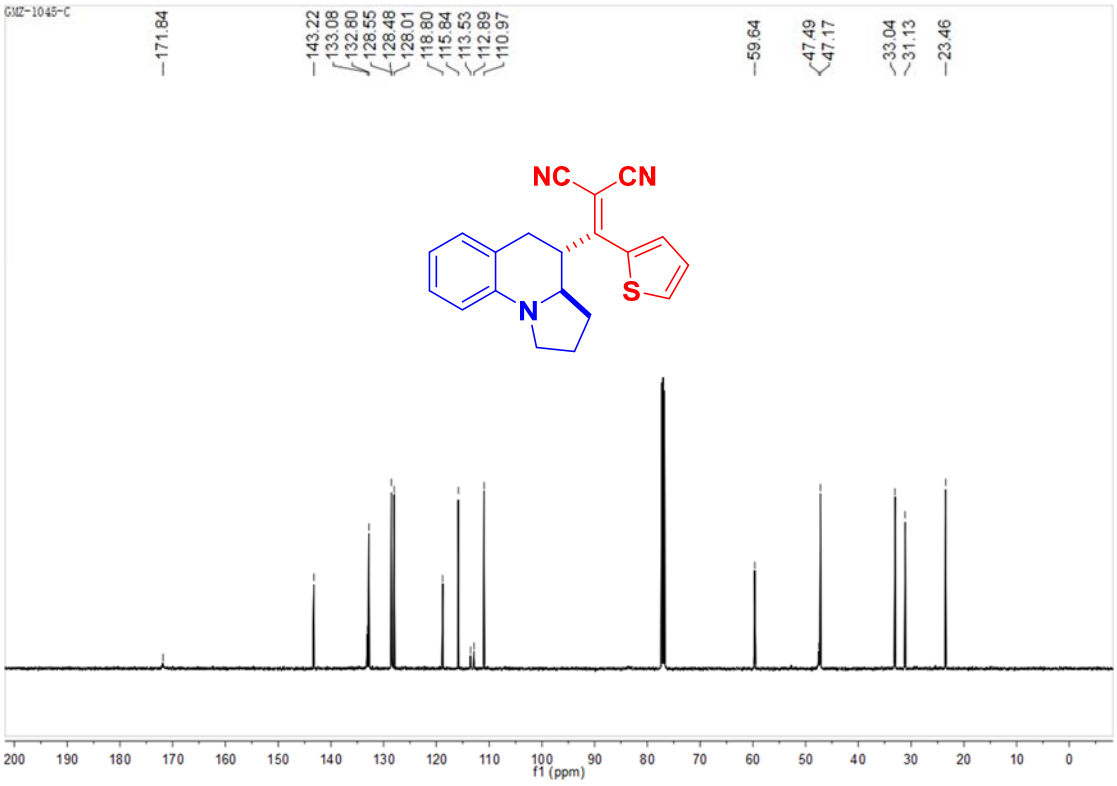
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(4-methoxyphenyl)methylene)-malononitrile (3h)



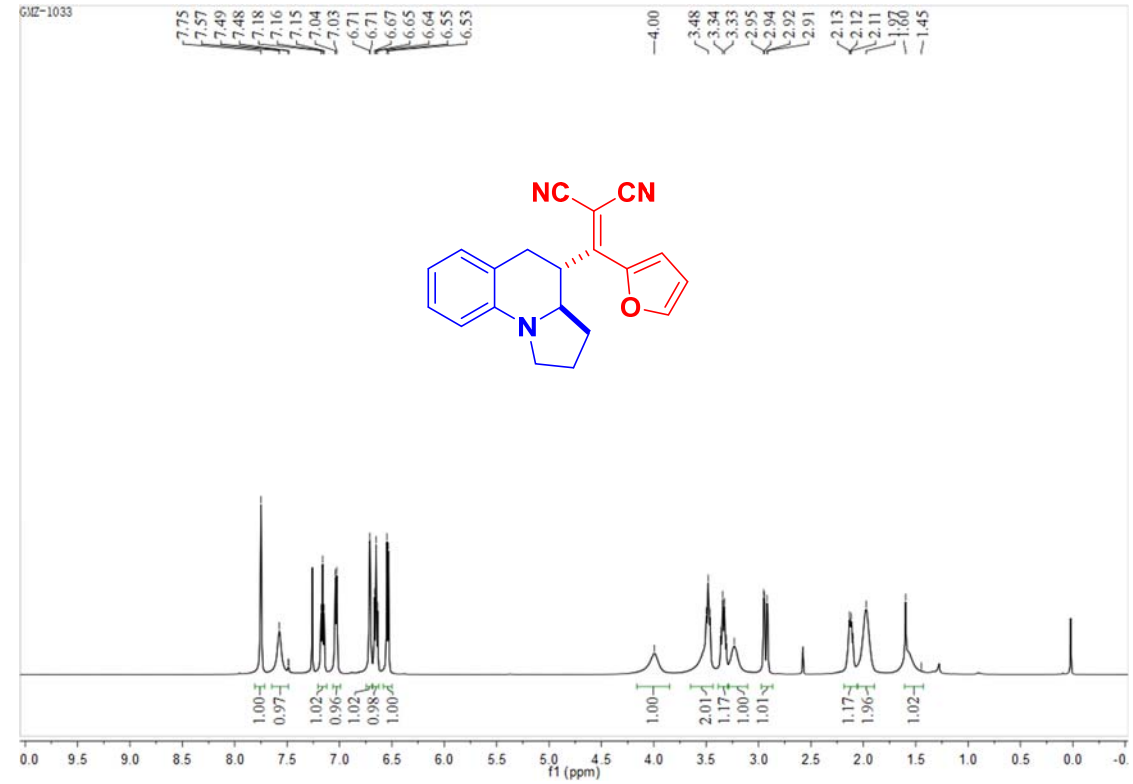


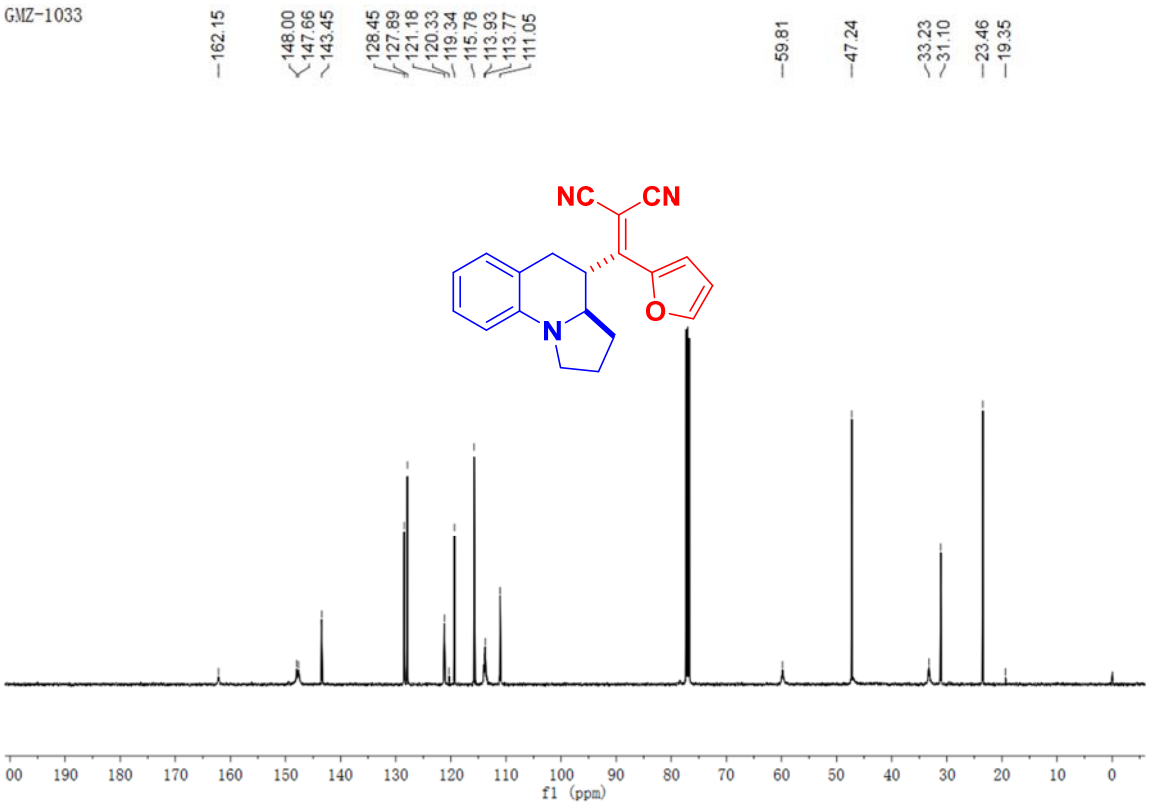
2-((1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(thiophen-2-yl)methylene)malononitrile (3i)



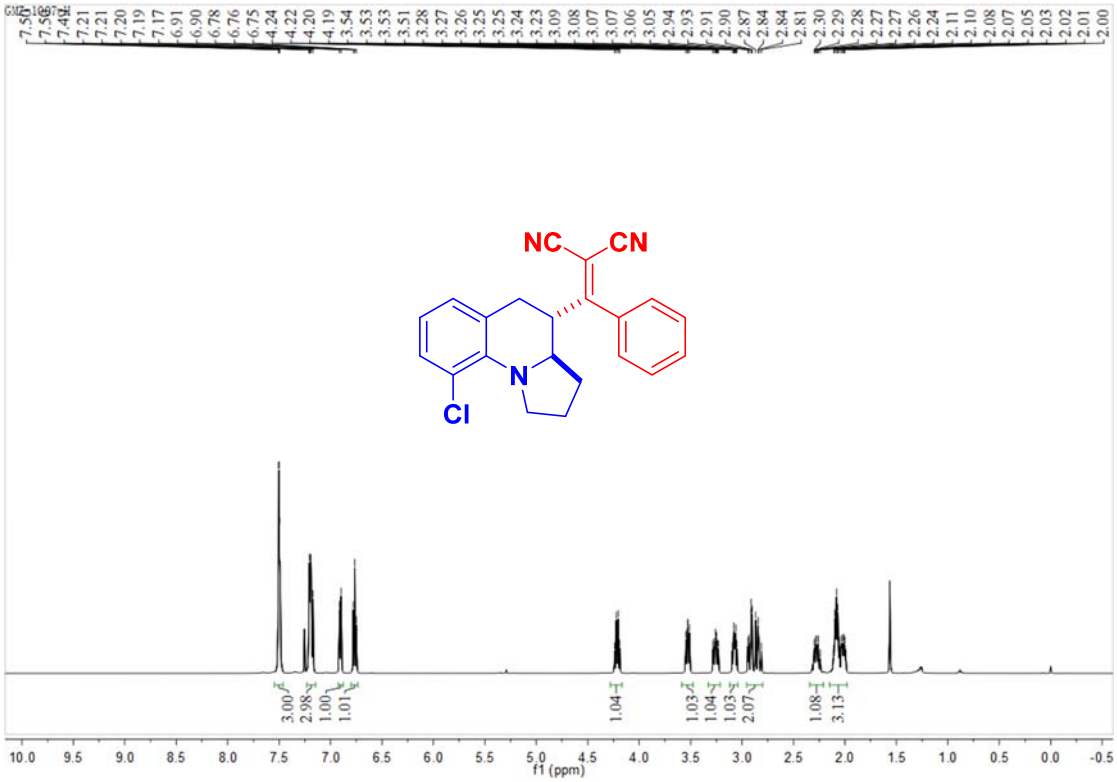


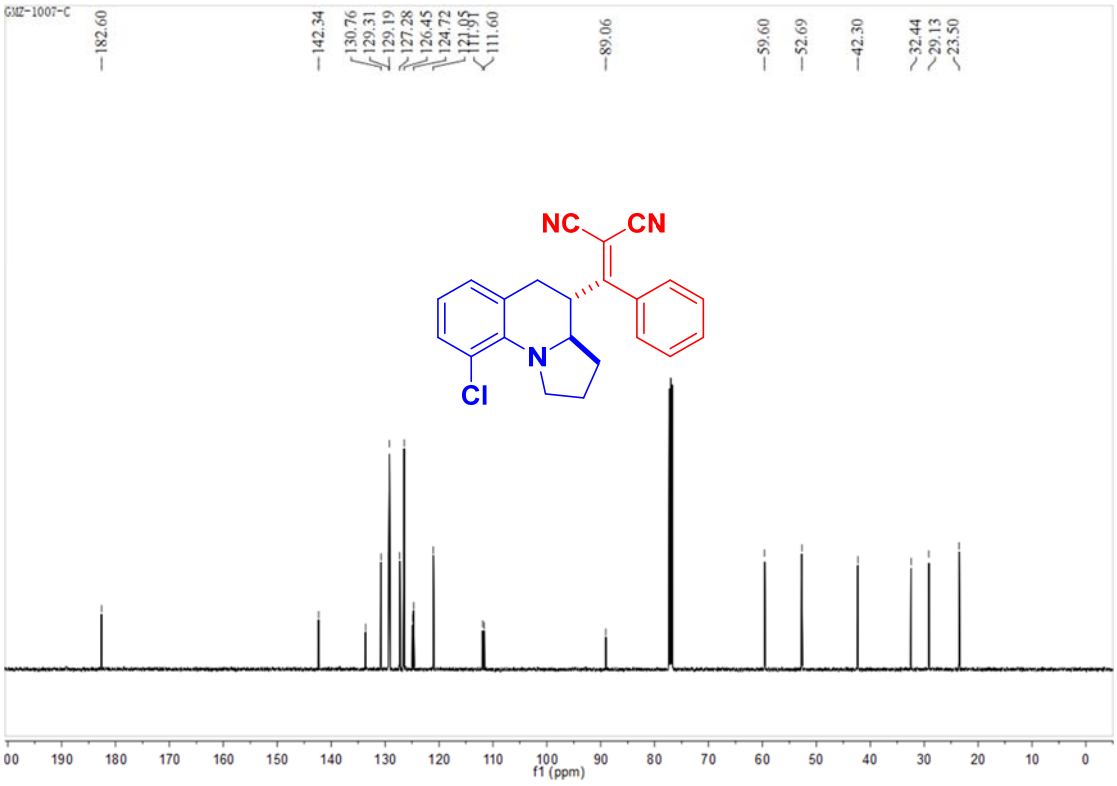
2-(furan-2-yl(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)methylene)malononitrile (3j)



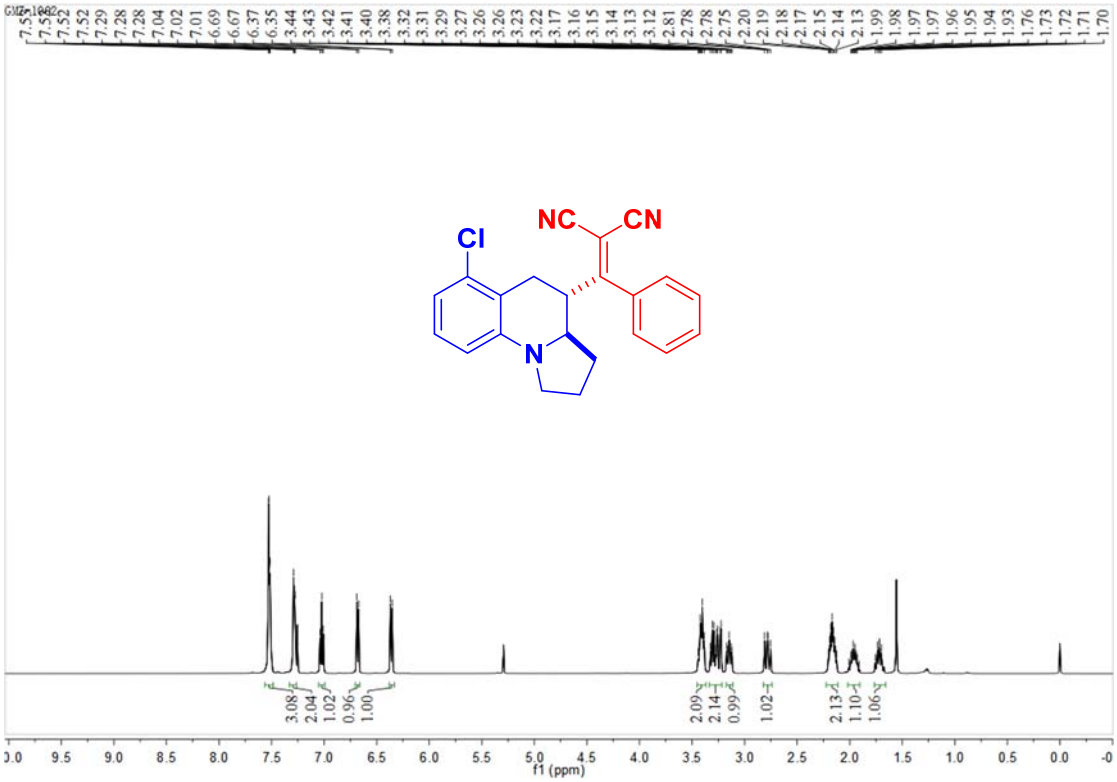


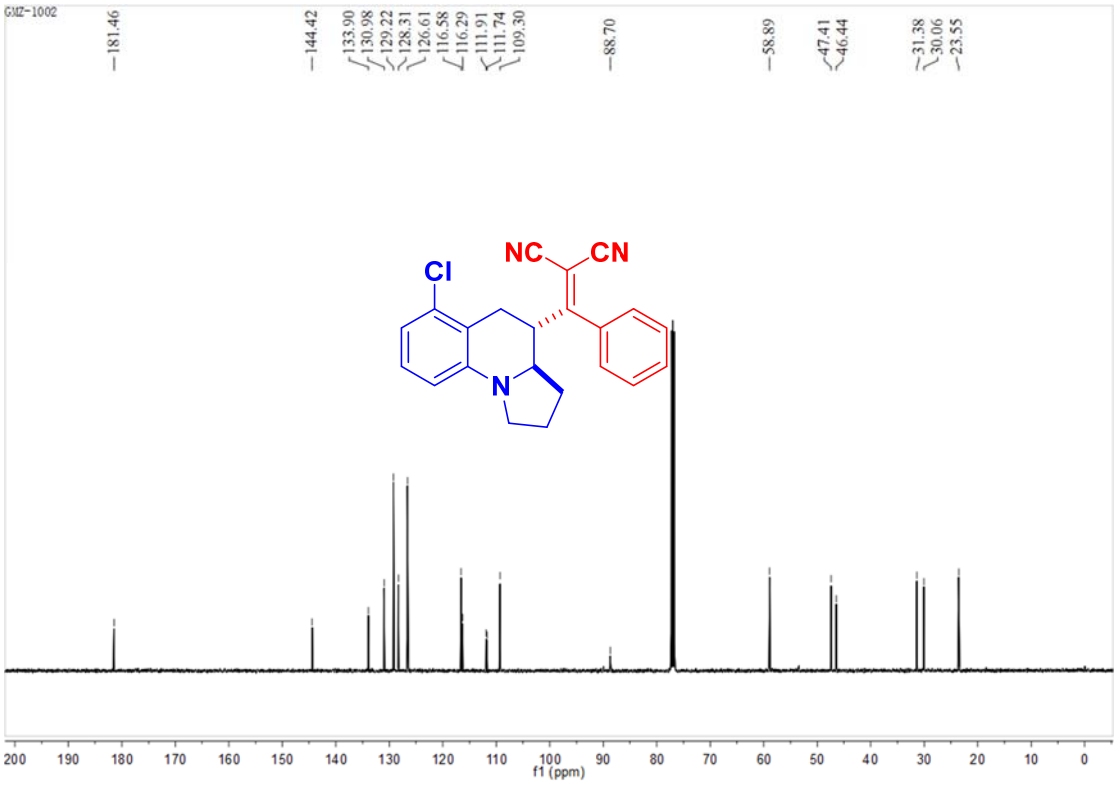
2-((9-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3k)



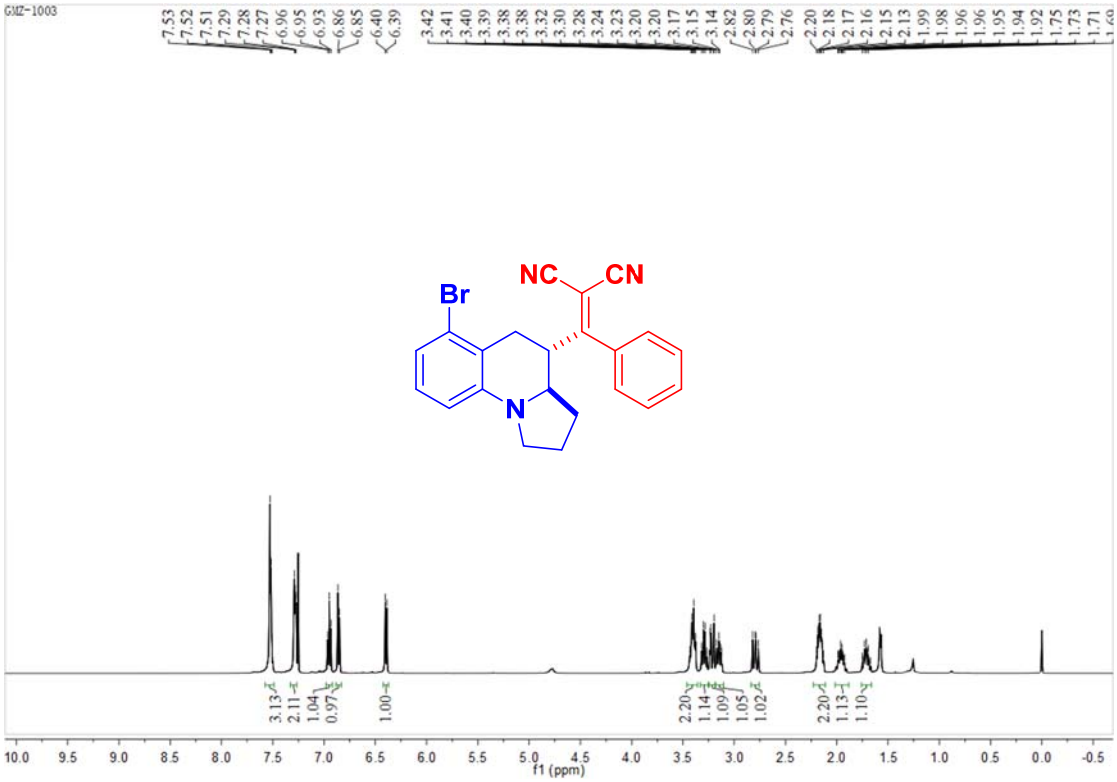


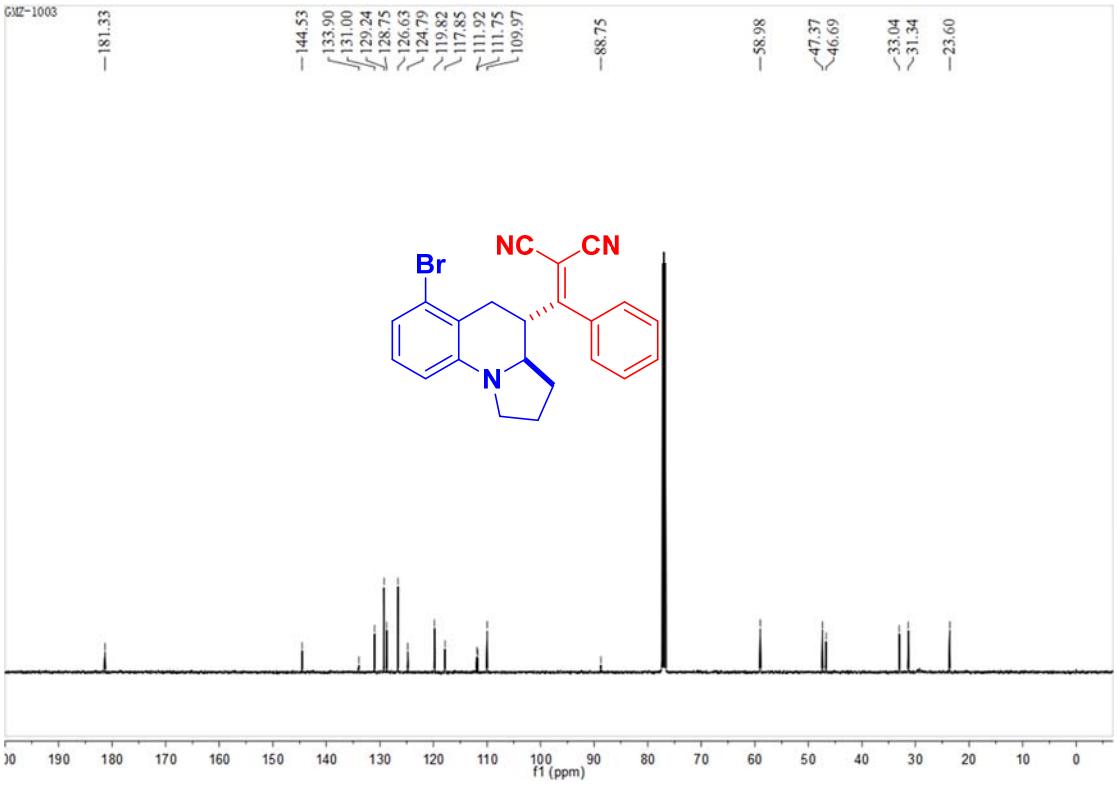
2-((6-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3l)



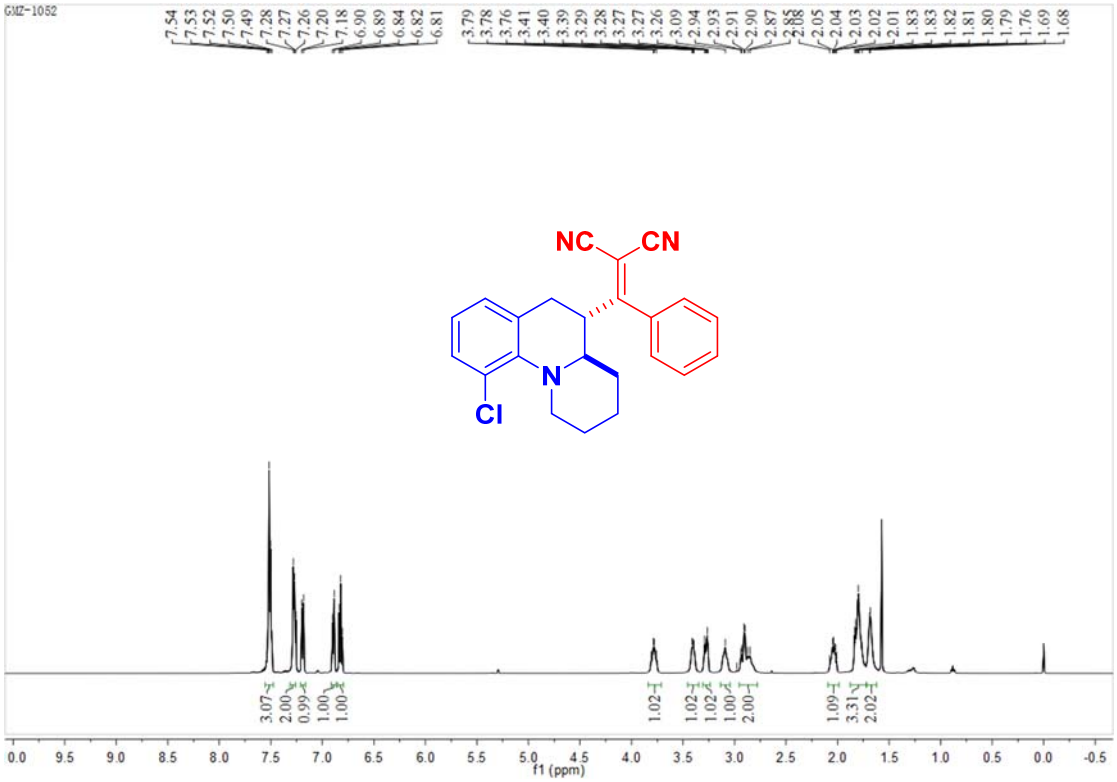


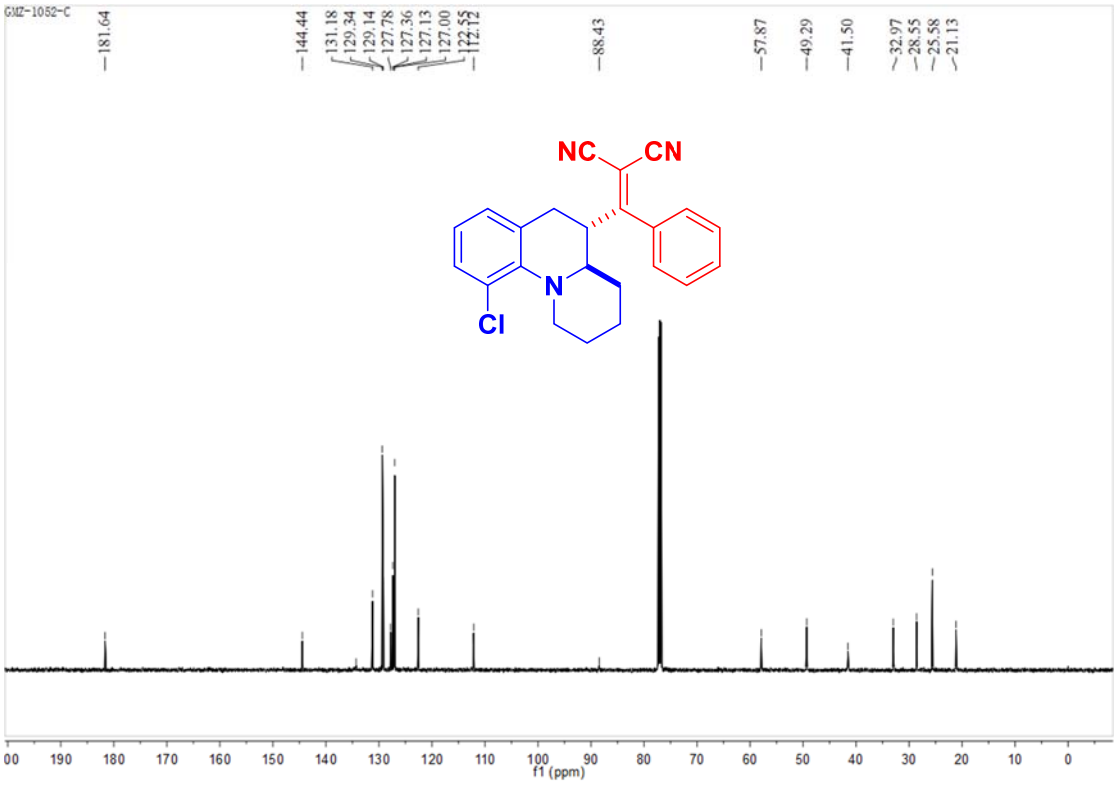
2-((6-bromo-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3m)



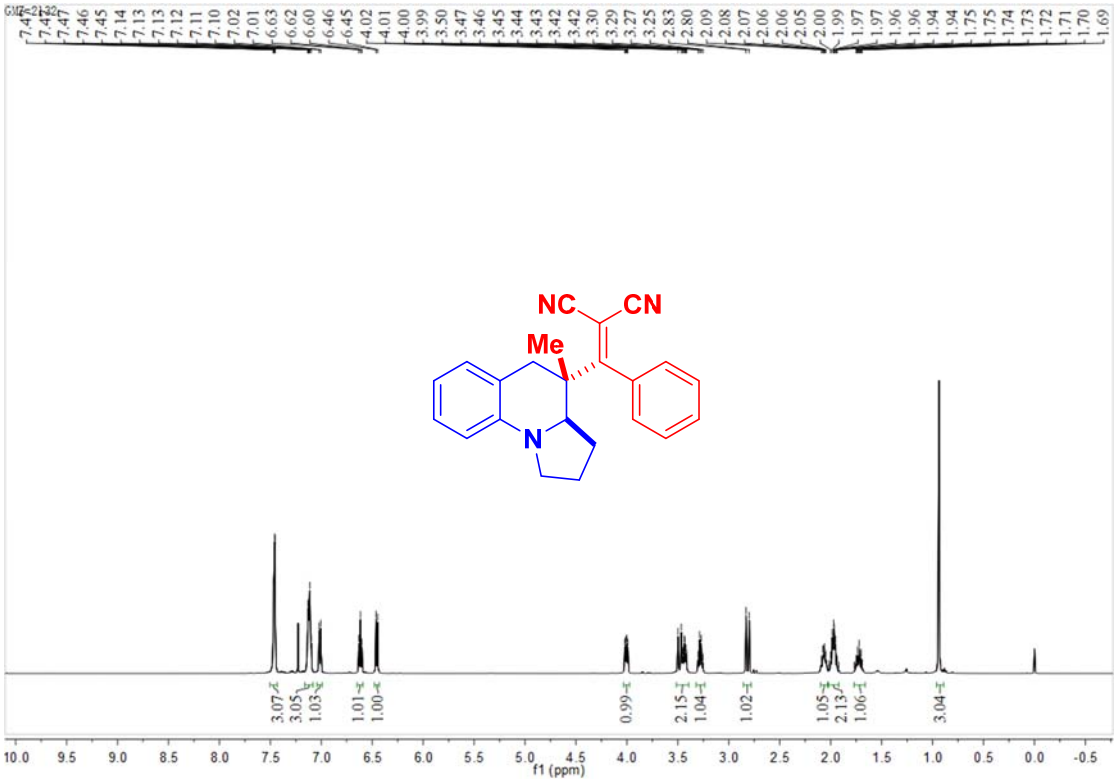


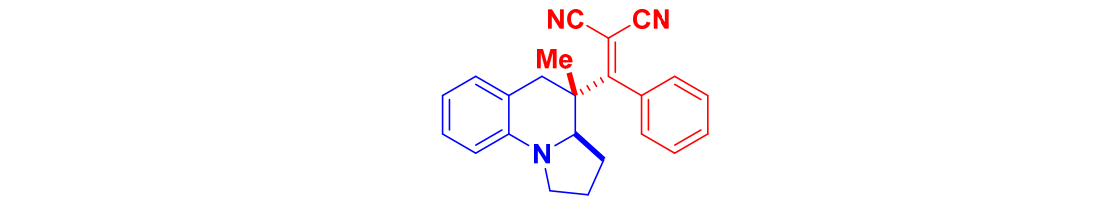
2-((10-chloro-2,3,4,4a,5,6-hexahydro-1*H*-pyrido[1,2-a]quinolin-5-yl)(phenyl)methylene)-malononitrile (3n)

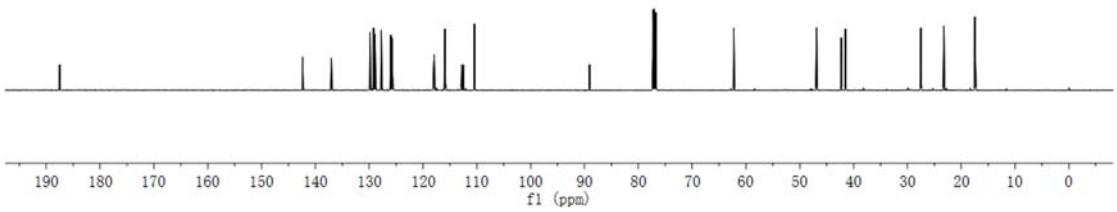




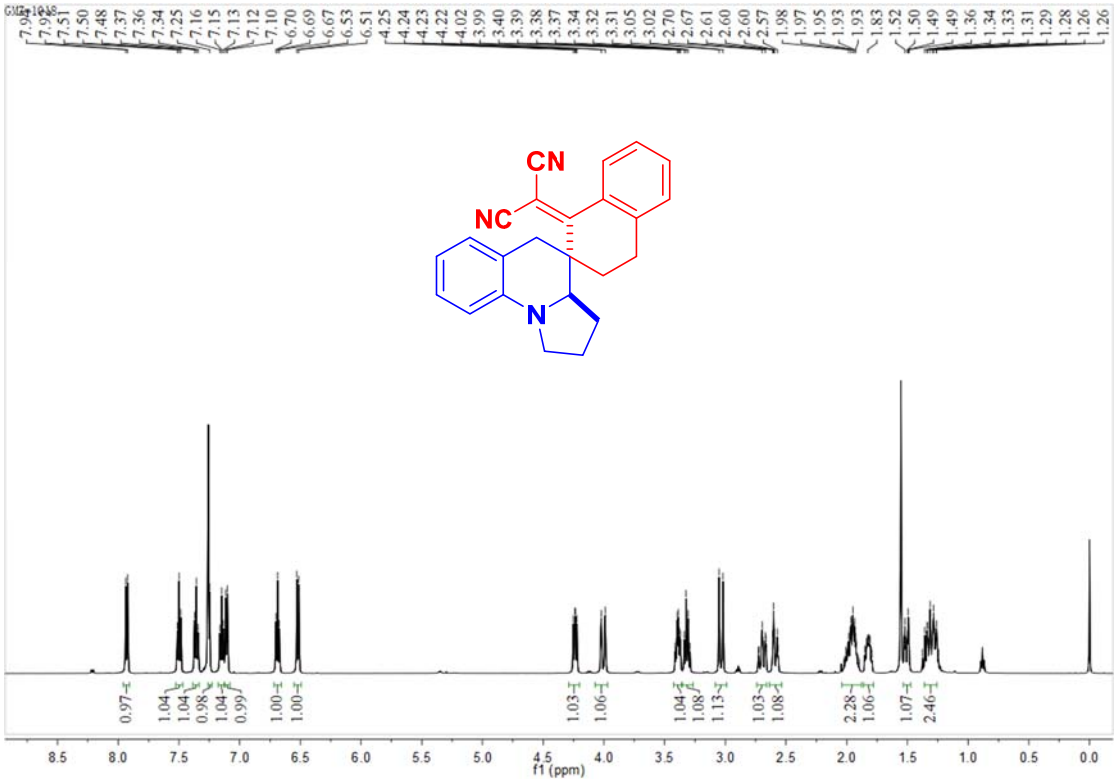
2-((4-methyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)(phenyl)methylene)-malononitrile (3o)

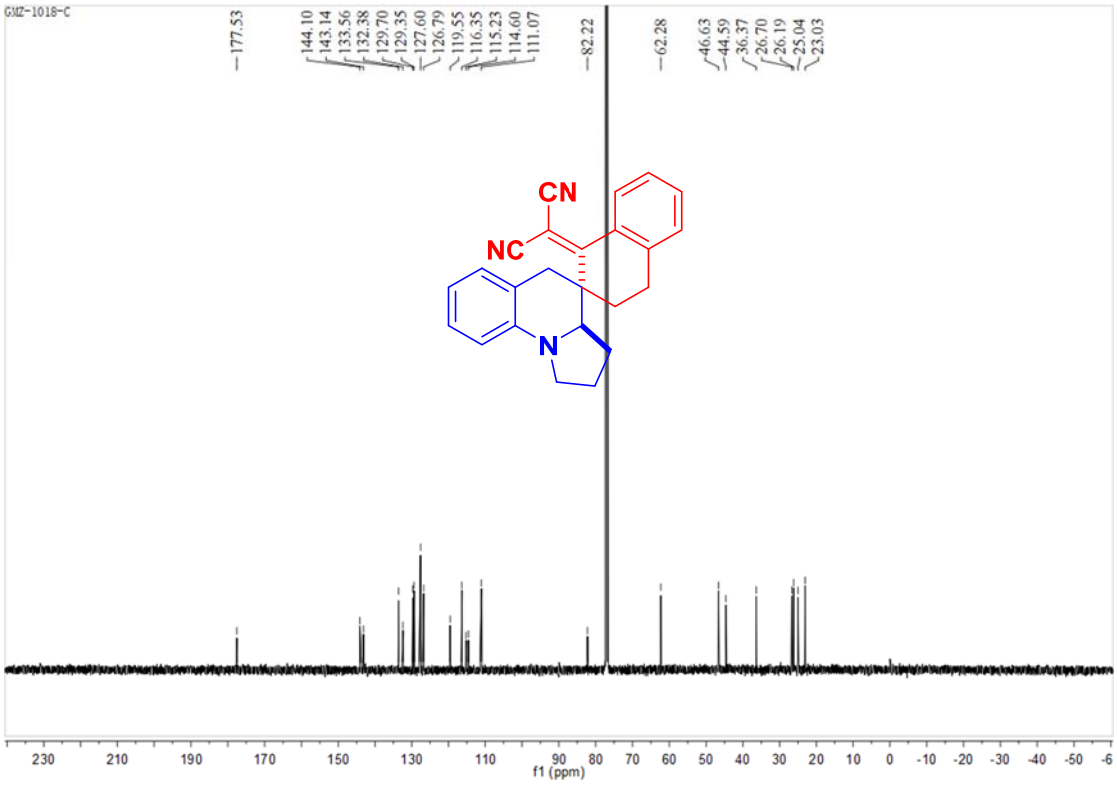




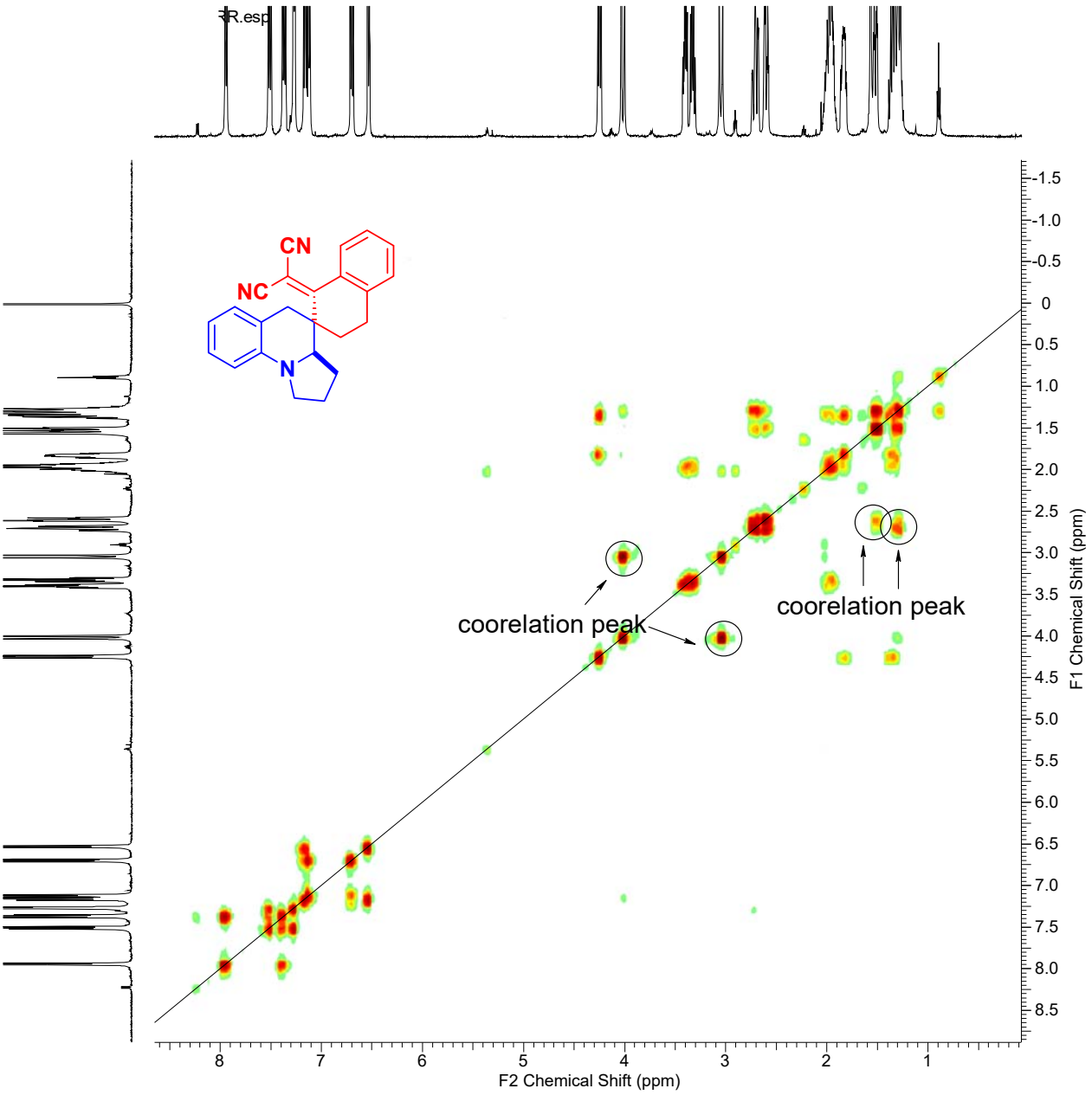


2-(1',2',3,3',3a',4-hexahydro-1H,5'*H*-spiro[naphthalene-2,4'-pyrrolo[1,2-a]quinolin]-1-ylidene)-malononitrile (3p)

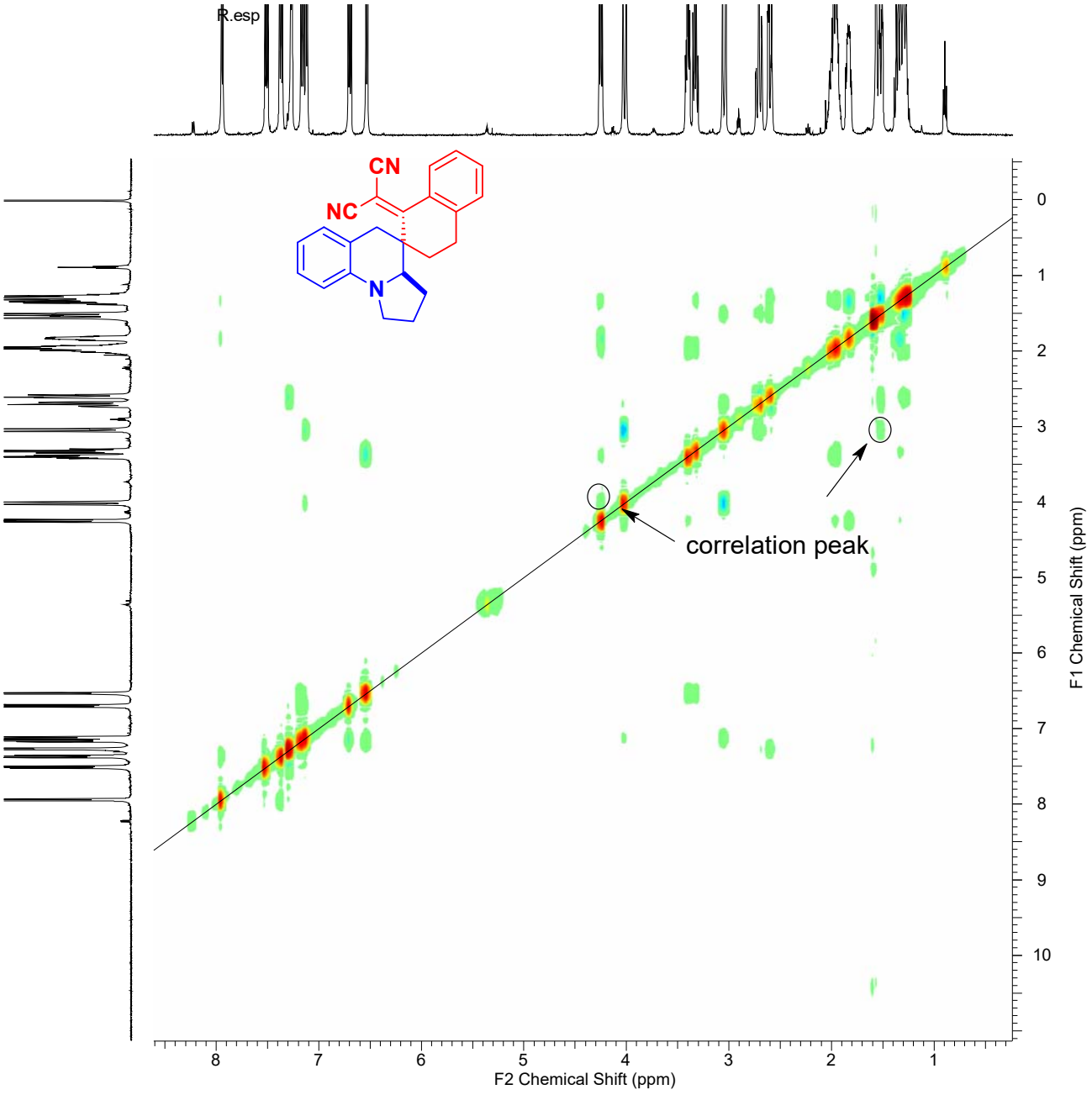




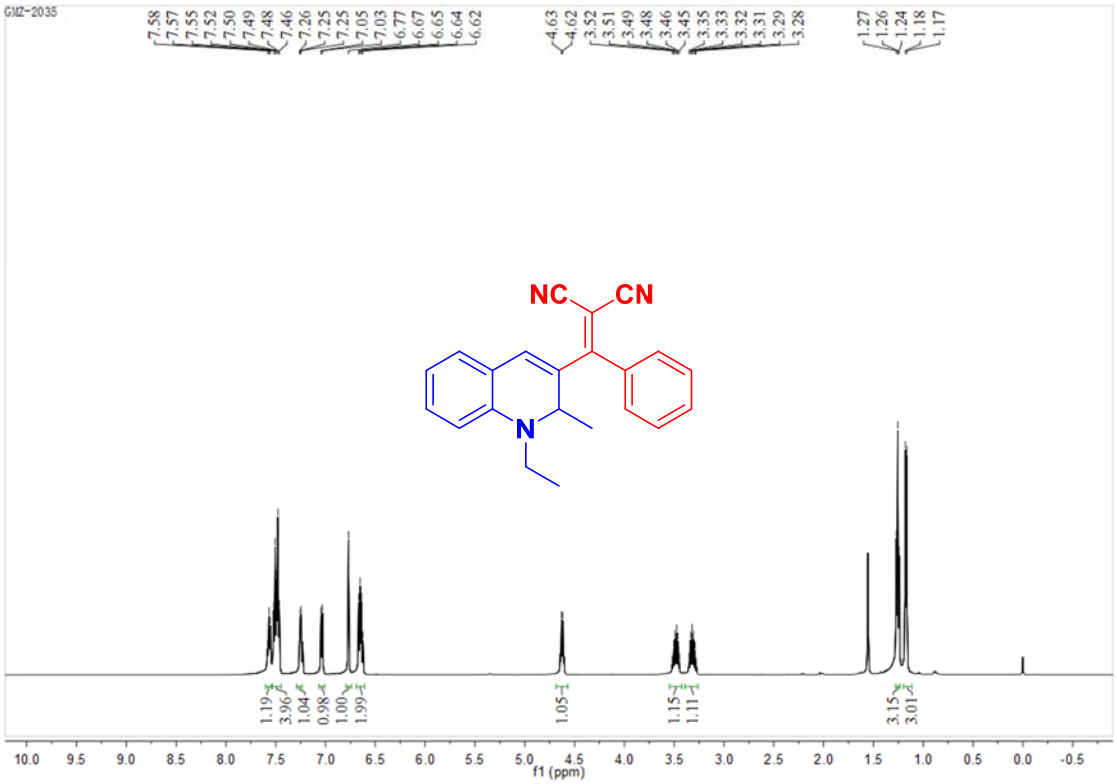
H,H-Cosy of 2-(1',2',3,3',3a',4-hexahydro-1H,5'*H*-spiro[naphthalene-2,4'-pyrrolo[1,2-a]quinolin]-1-ylidene)malononitrile (3p)

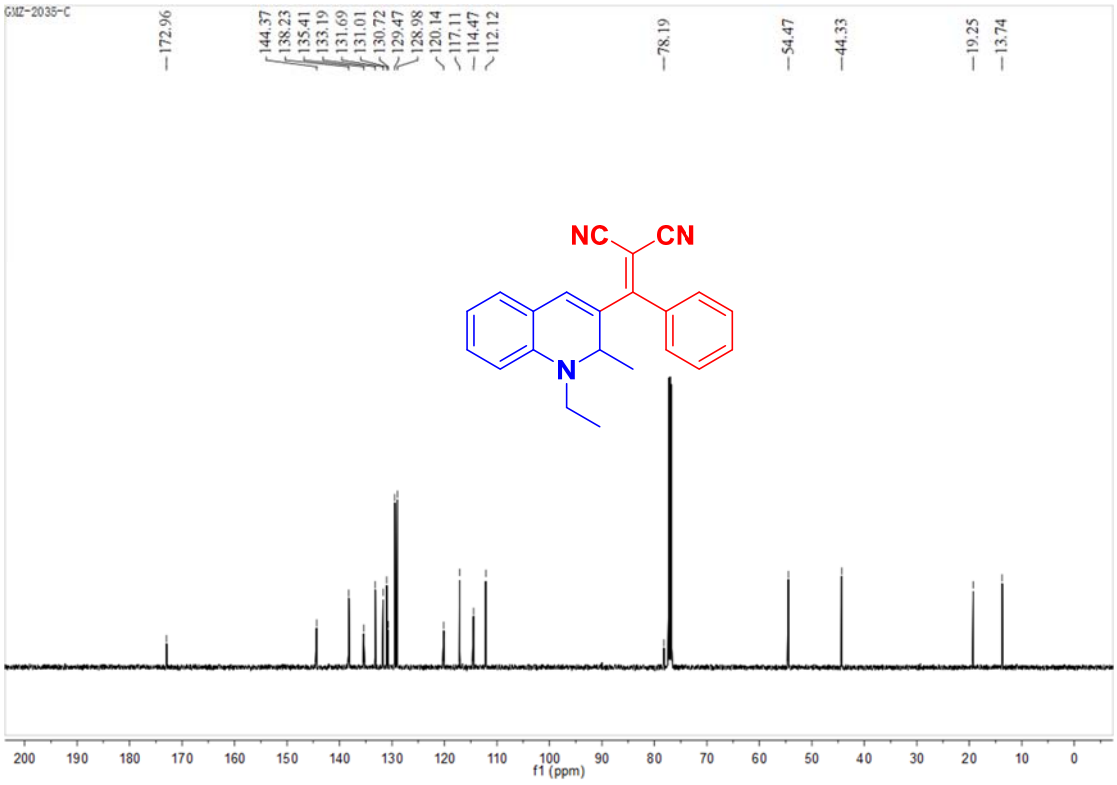


NOESY of 2-(1',2',3,3',3a',4-hexahydro-1H,5'*H*-spiro[naphthalene-2,4'-pyrrolo[1,2-a]quinolin]-1-ylidene)malononitrile (3p)

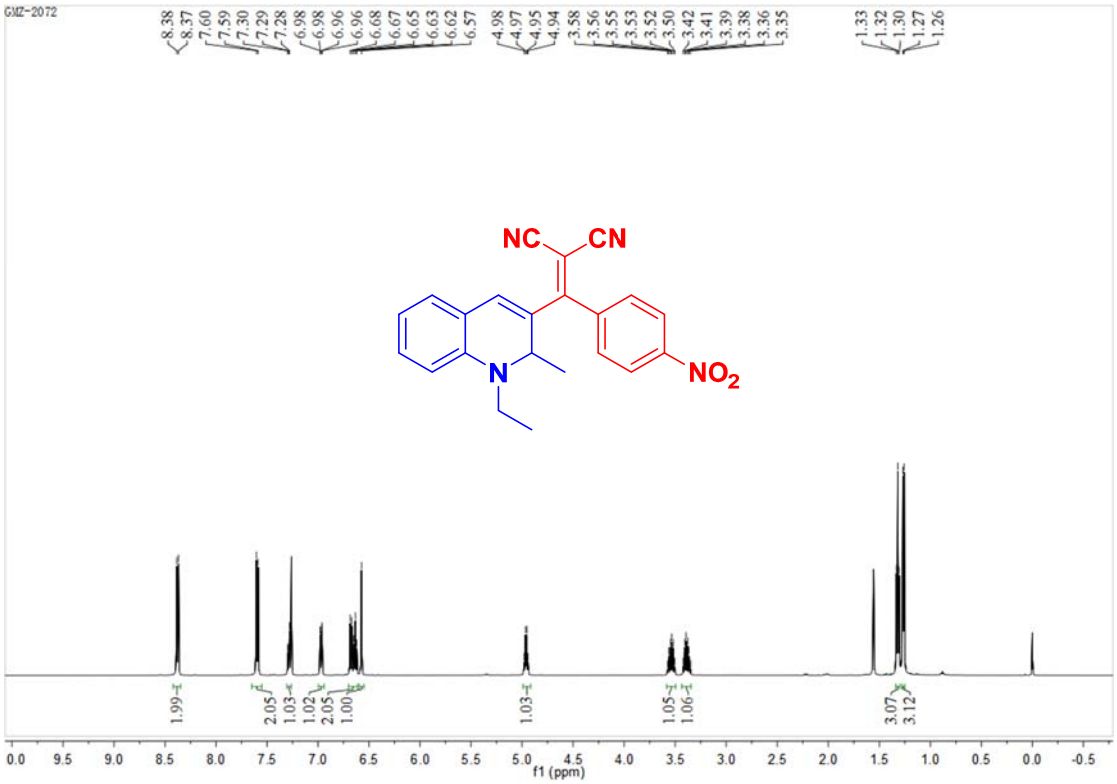


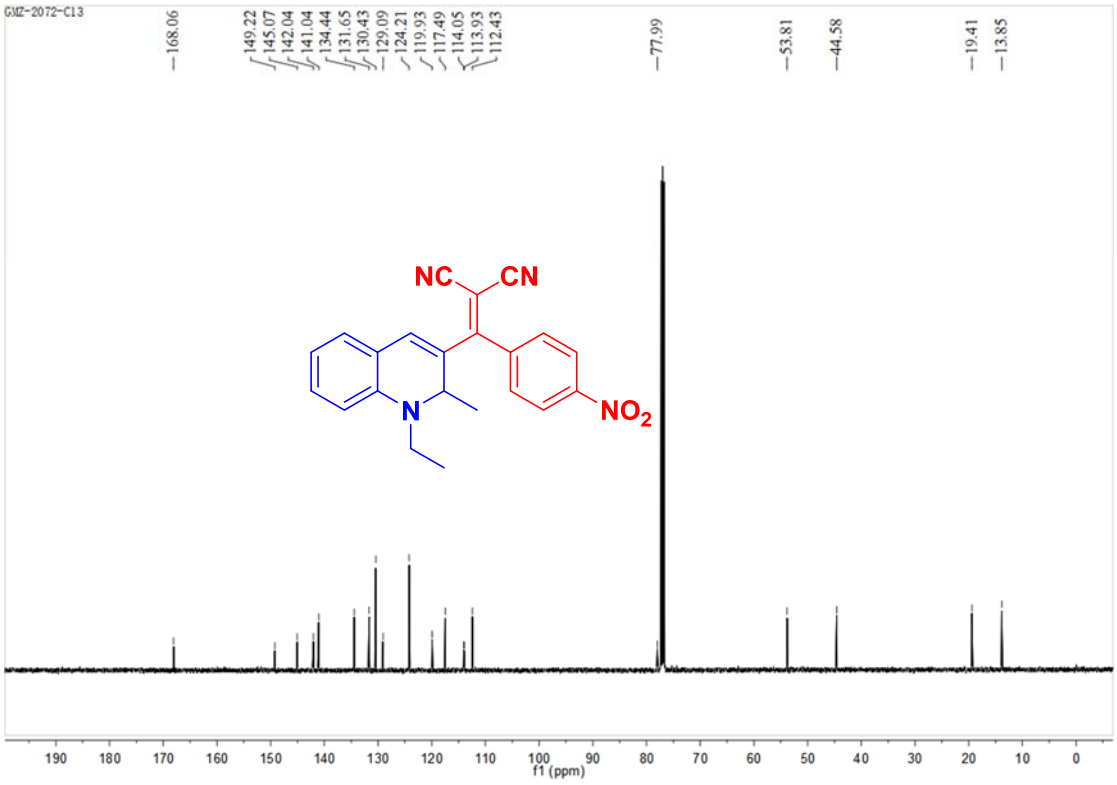
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5a)



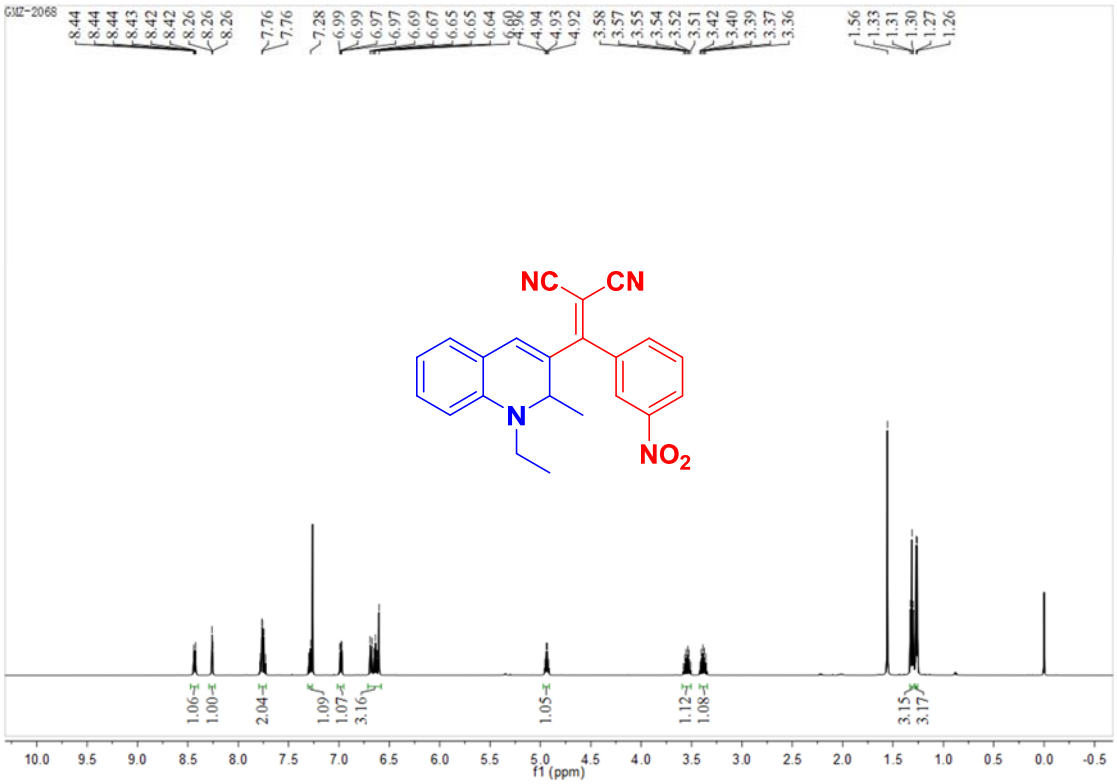


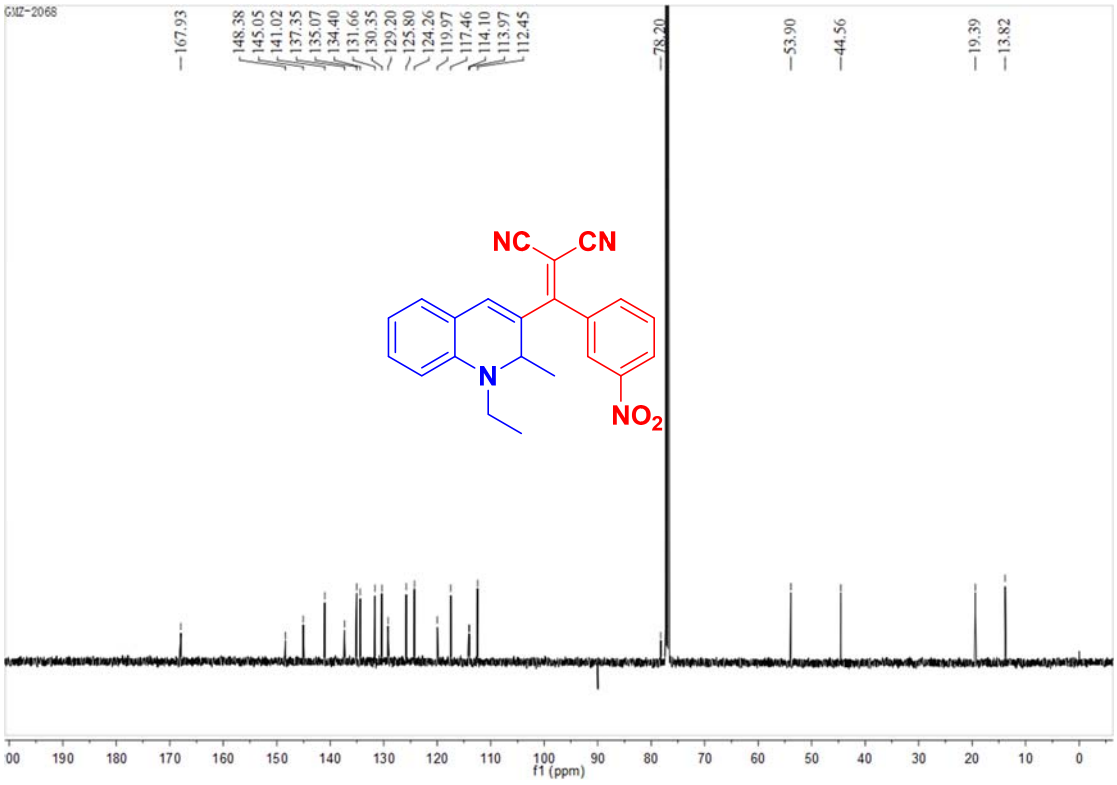
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-nitrophenyl)methylene)malononitrile (5b)



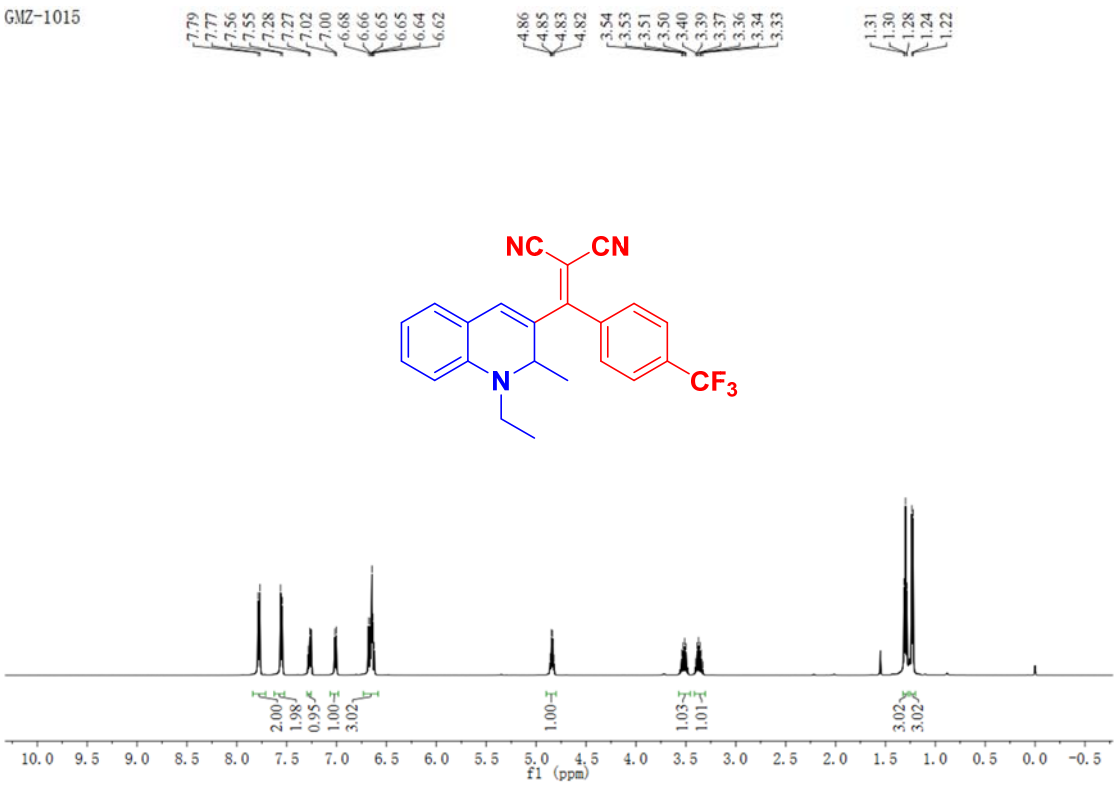


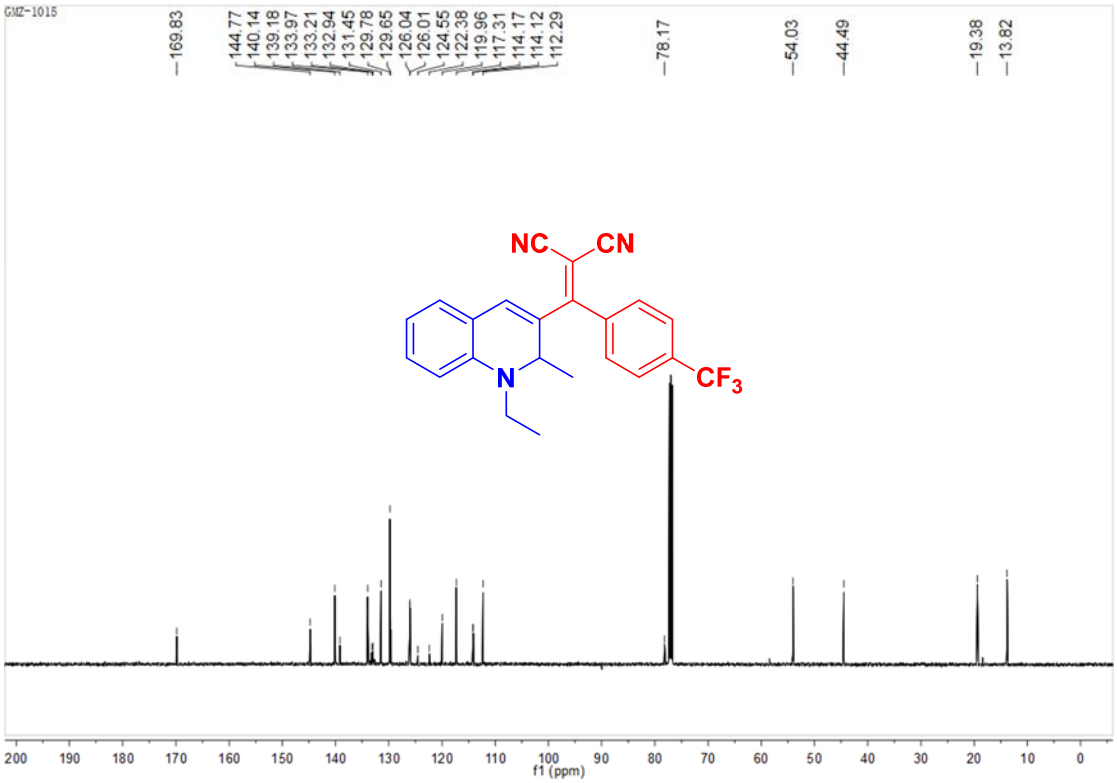
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(3-nitrophenyl)methylene)malononitrile (5c)



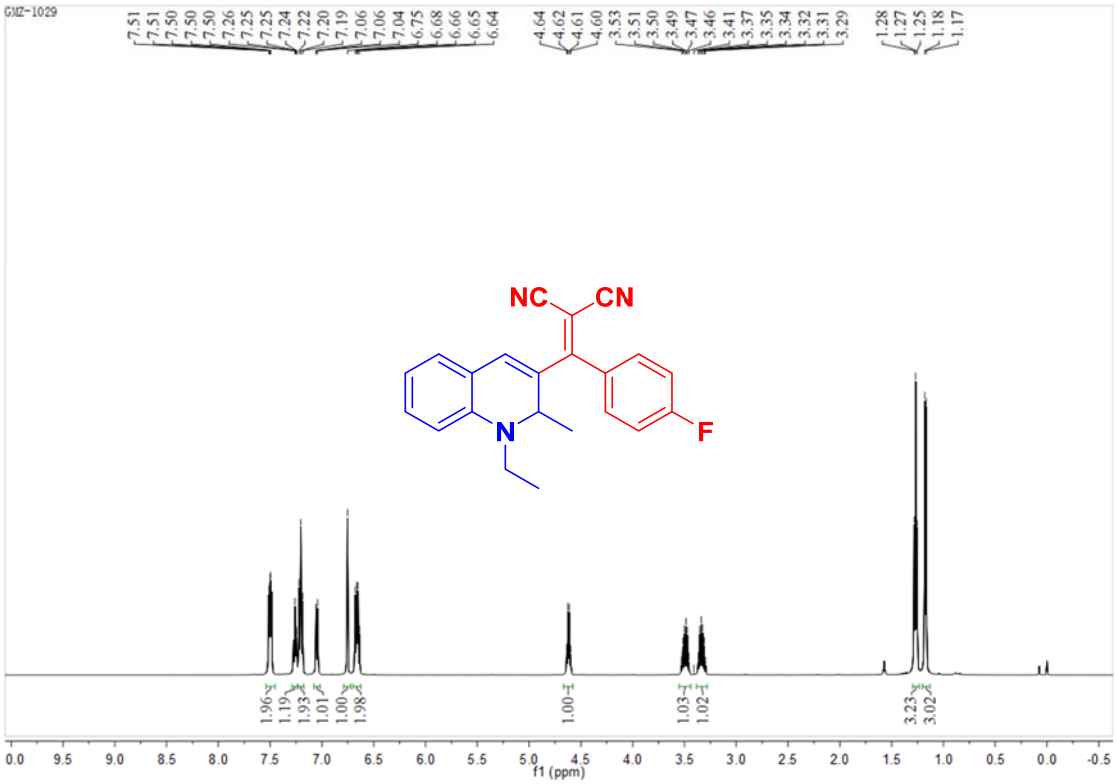


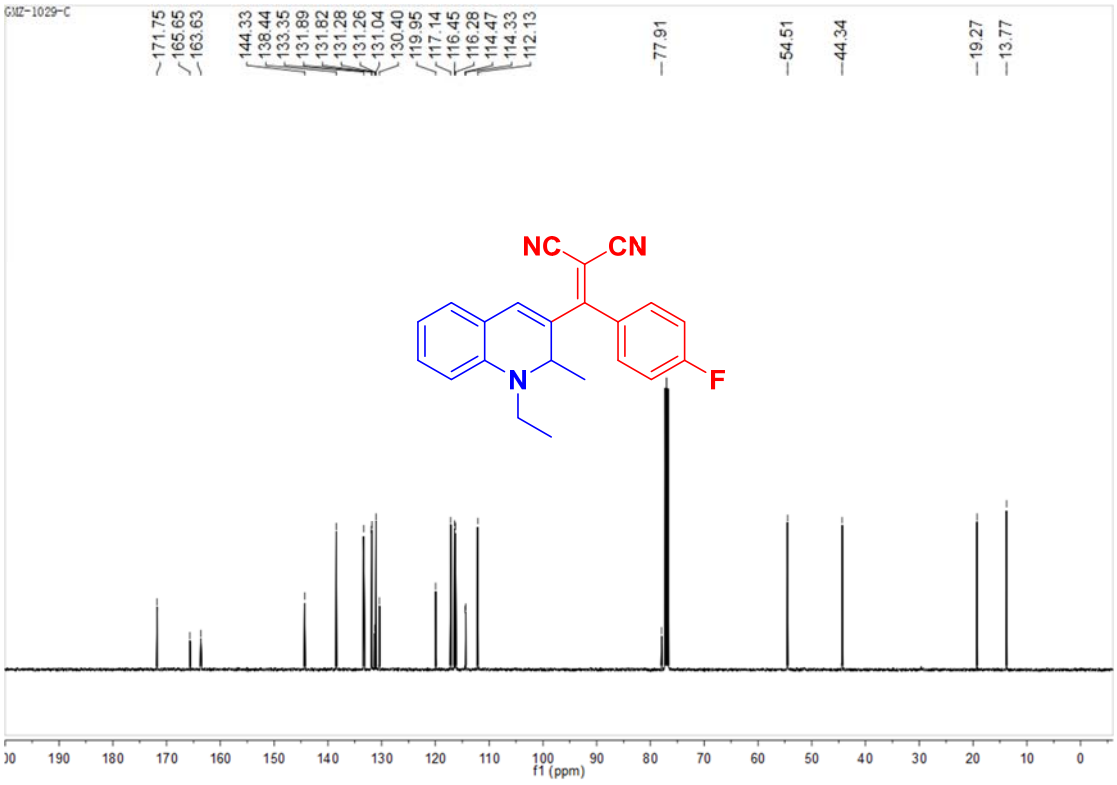
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-(trifluoromethyl)phenyl)methylene)-malononitrile (5d)



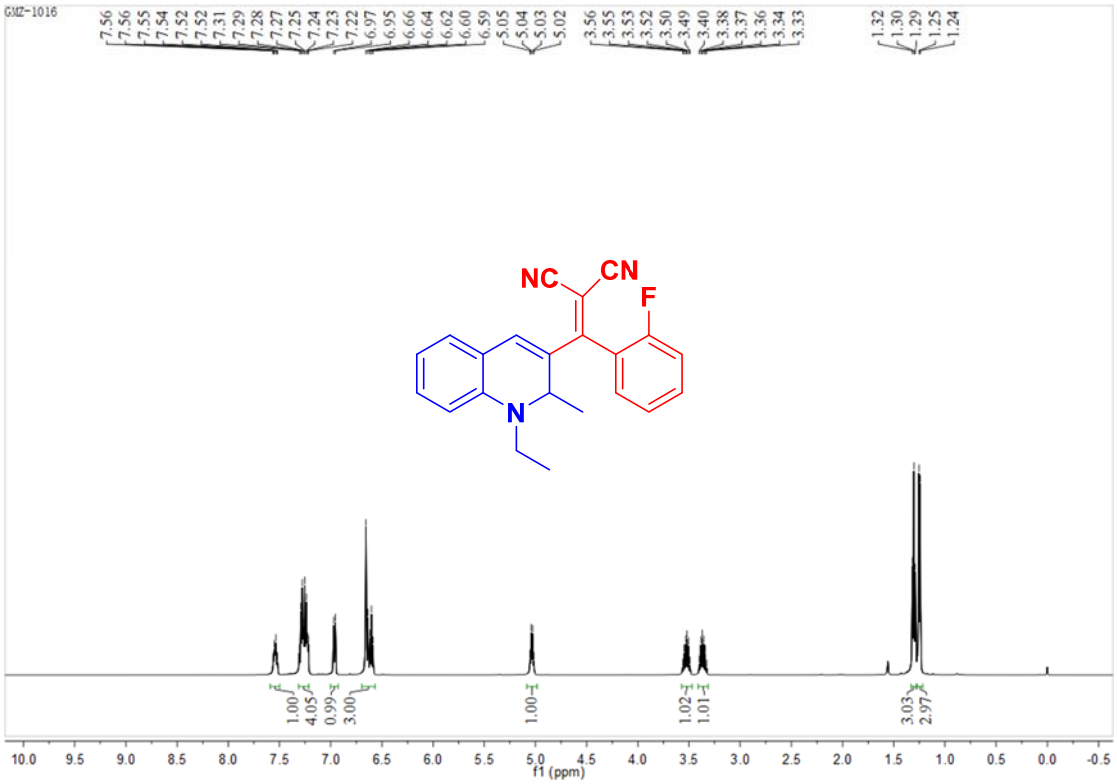


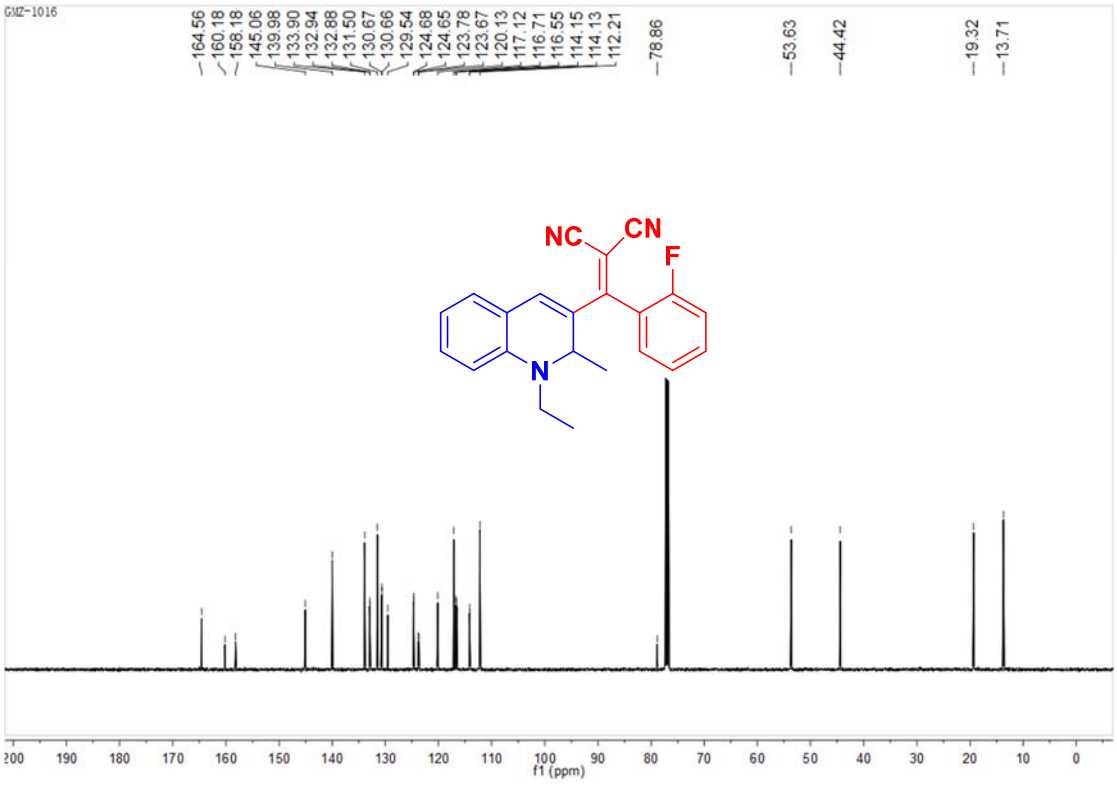
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-fluorophenyl)methylene)malononitrile (5e)



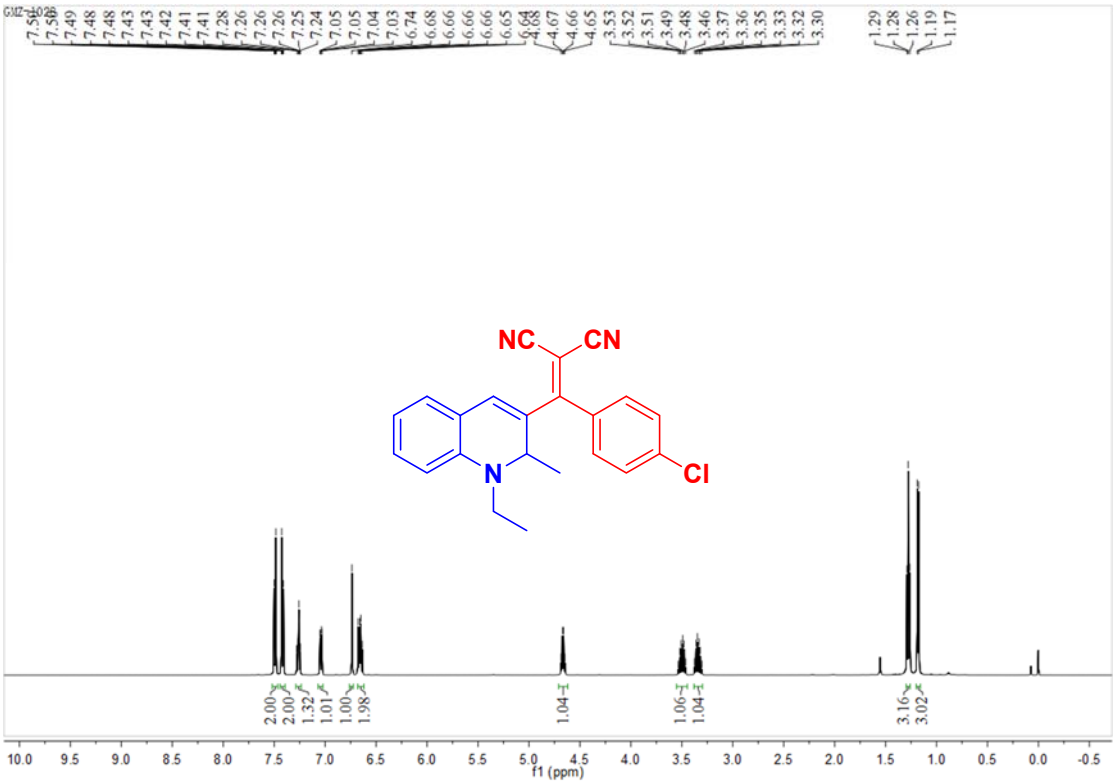


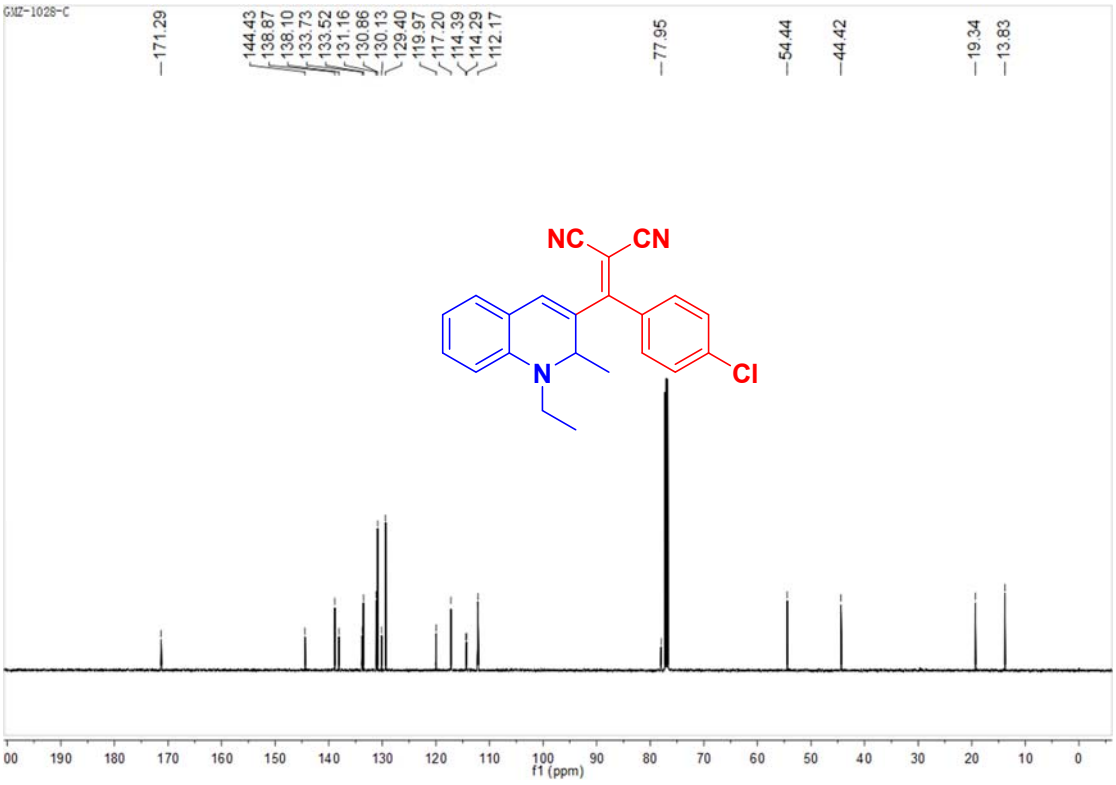
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(2-fluorophenyl)methylene)malononitrile (5f)



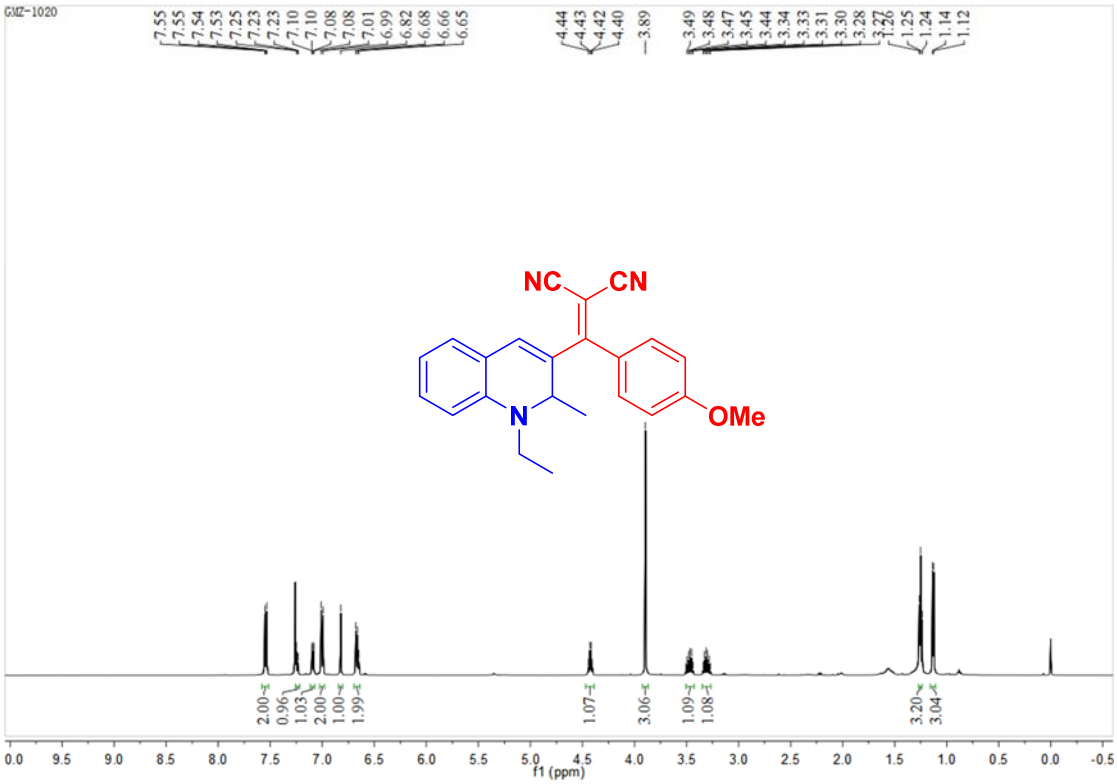


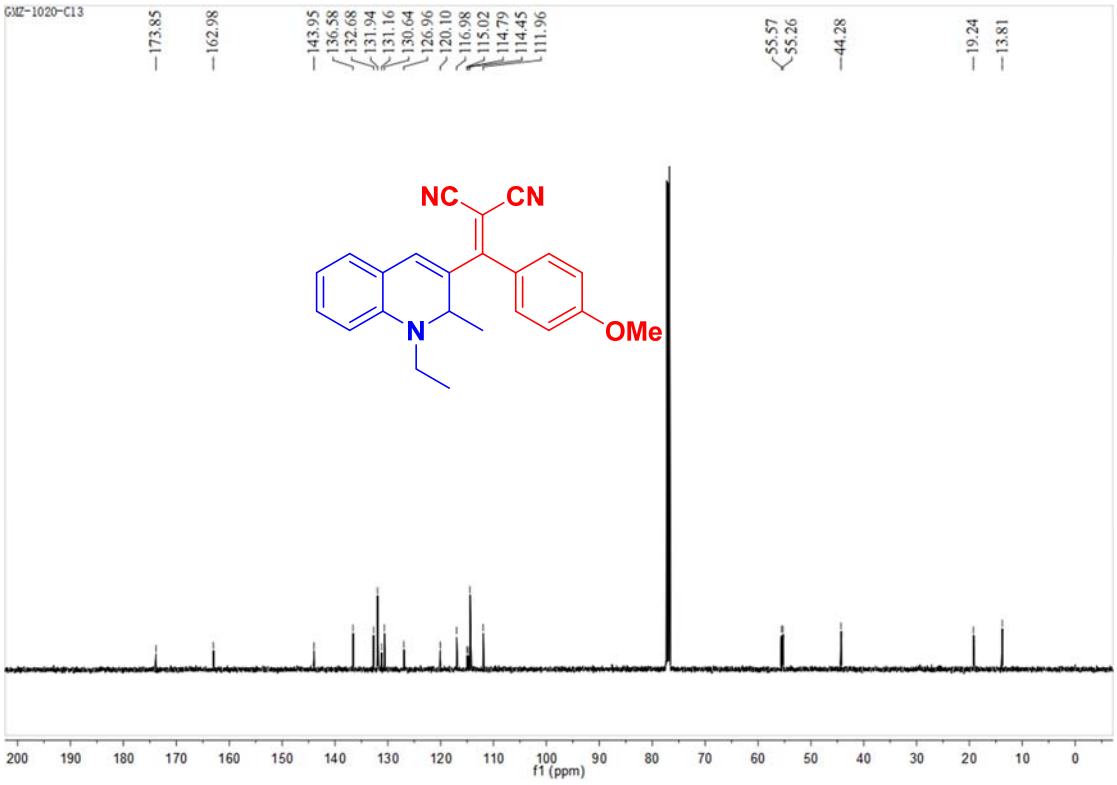
2-((4-chlorophenyl)(1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)methylene)malononitrile (5g)



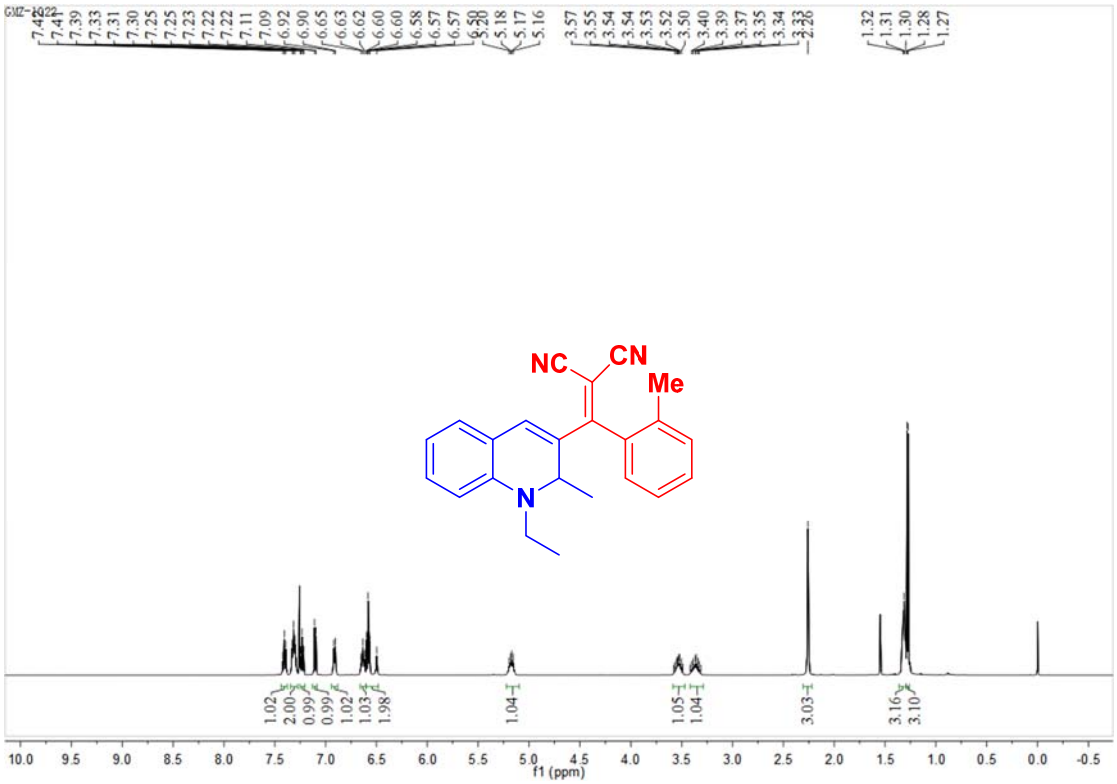


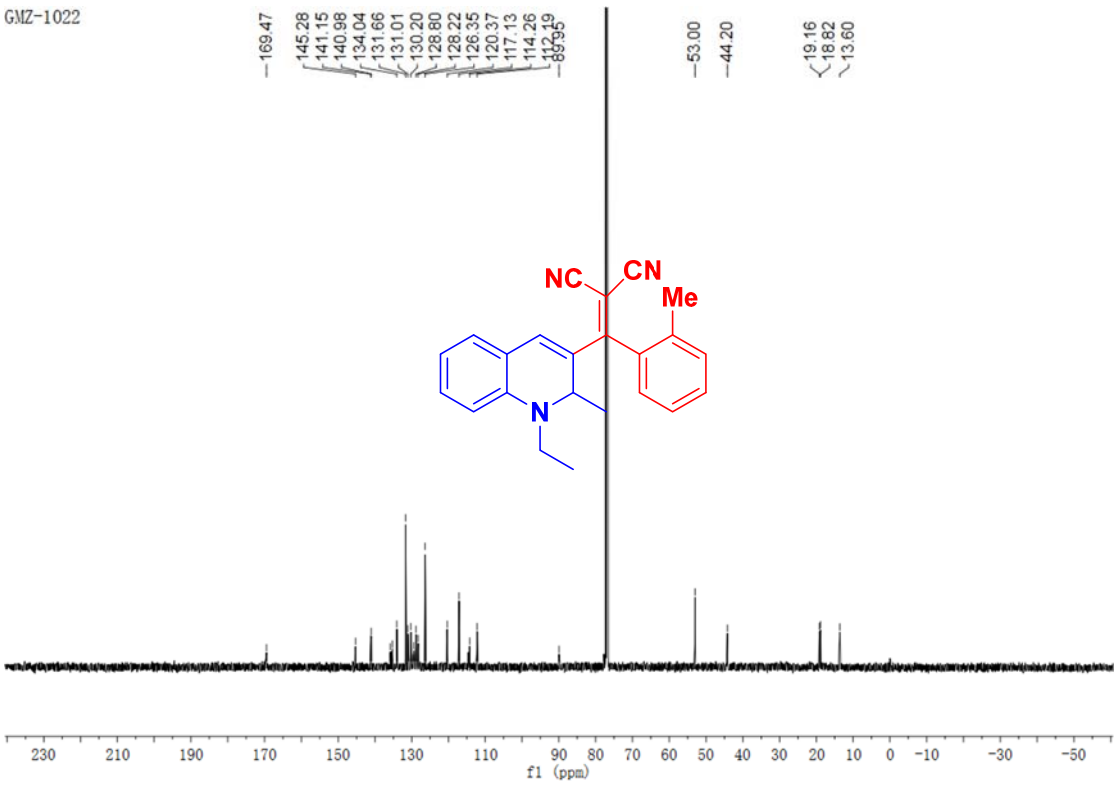
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(4-methoxyphenyl)methylene)malononitrile (5h)



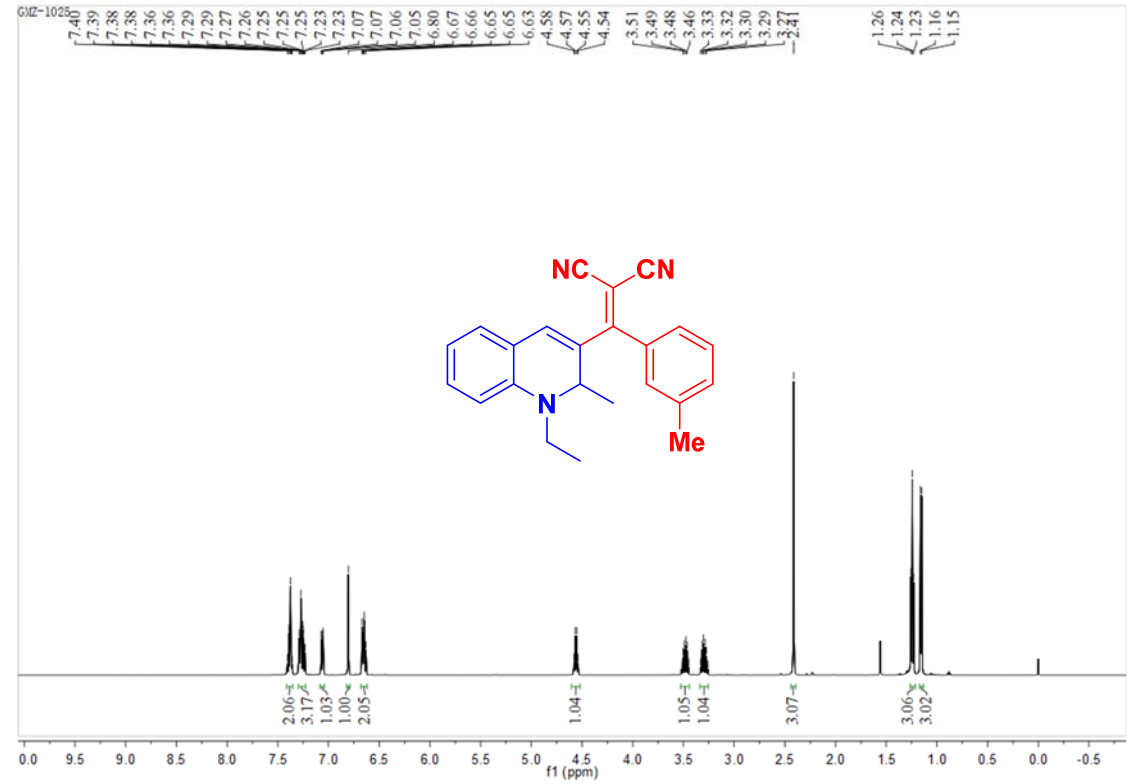


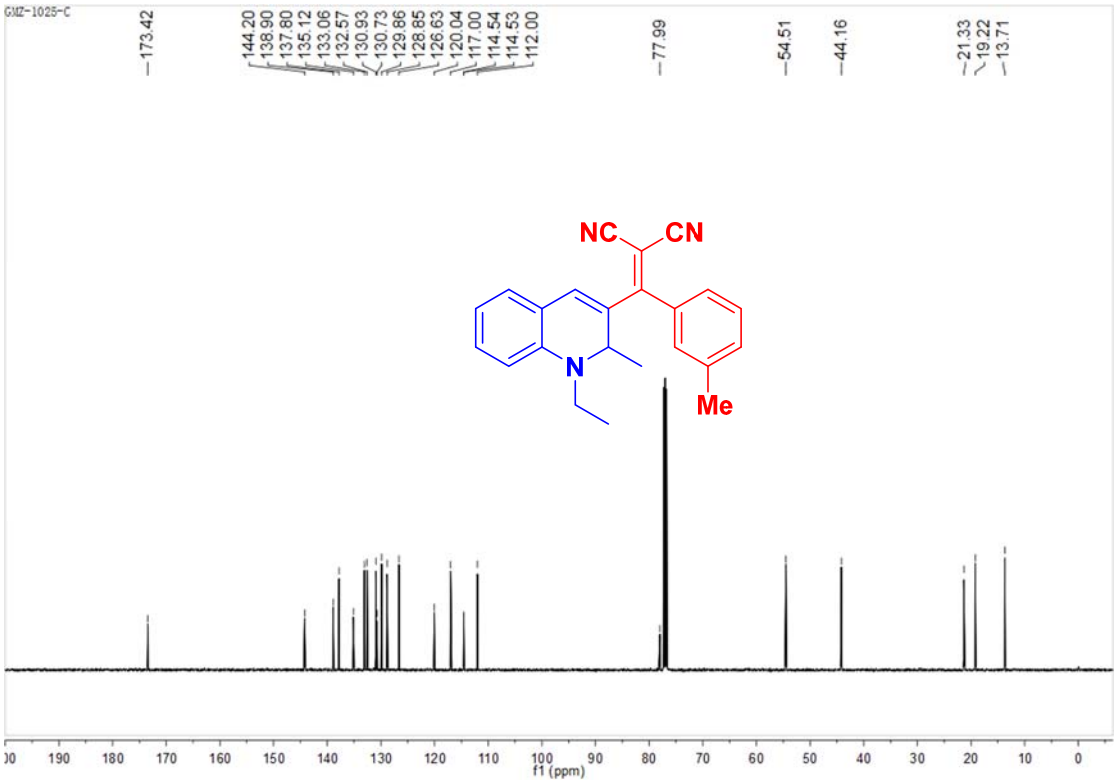
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(o-tolyl)methylene)malononitrile (5i)



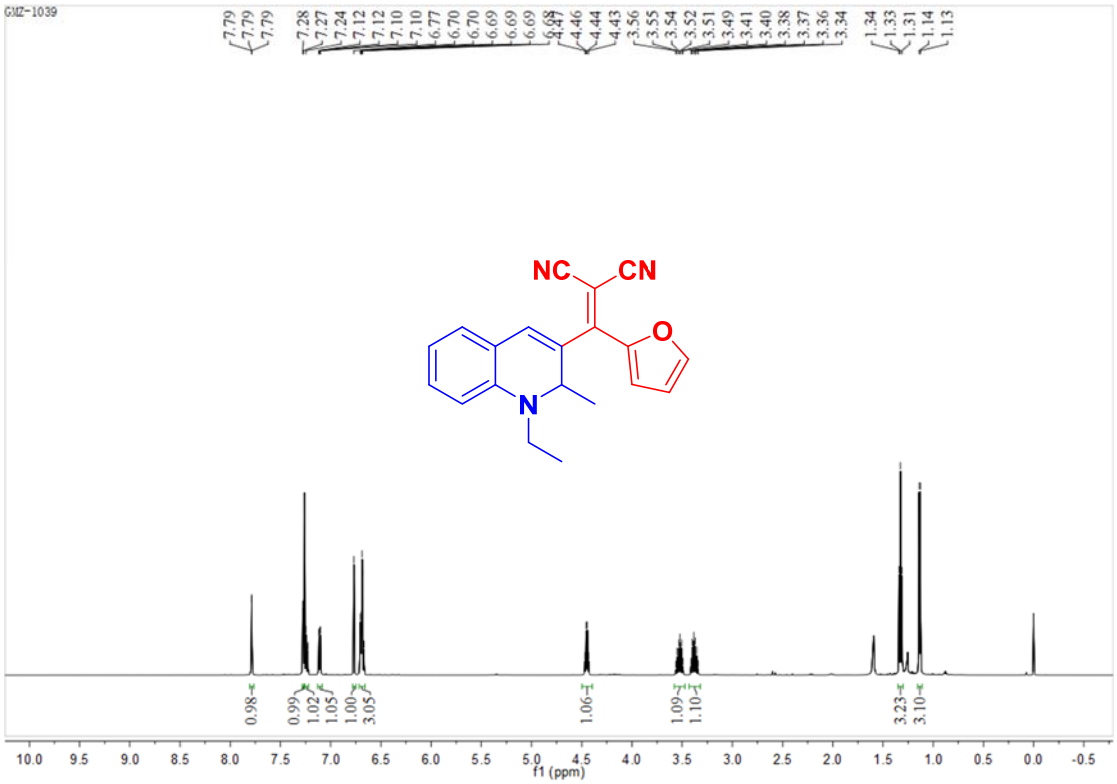


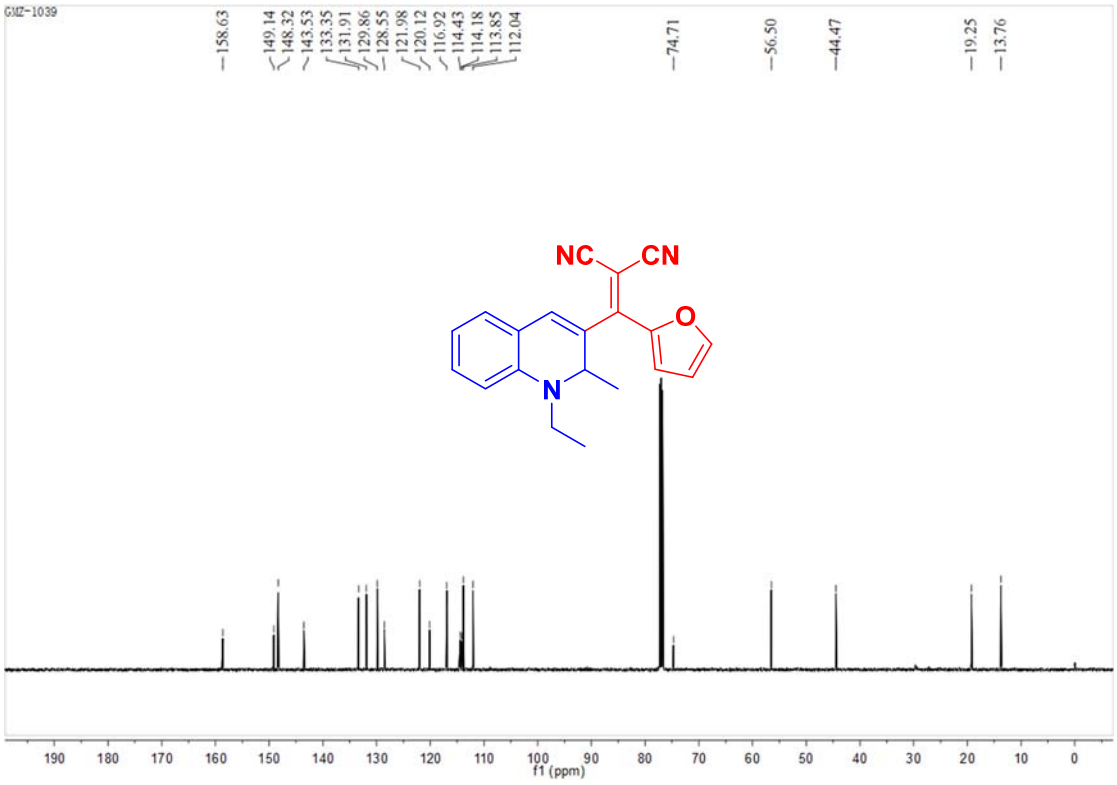
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(m-tolyl)methylene)malononitrile (5j)



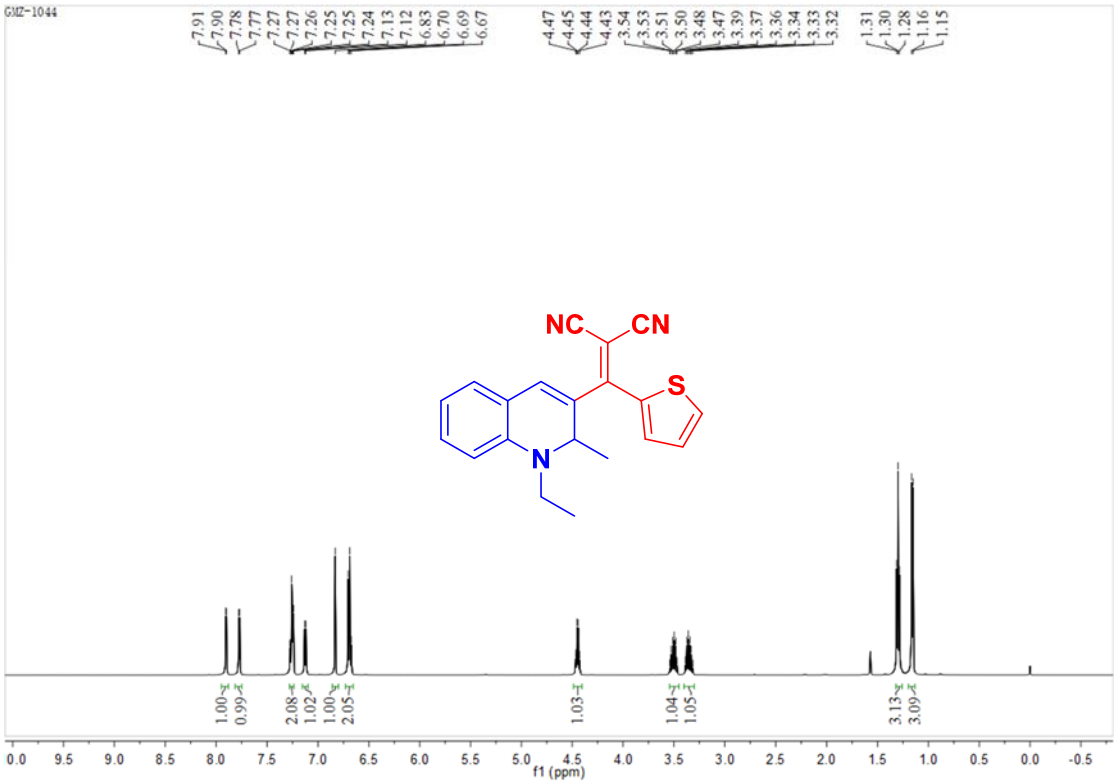


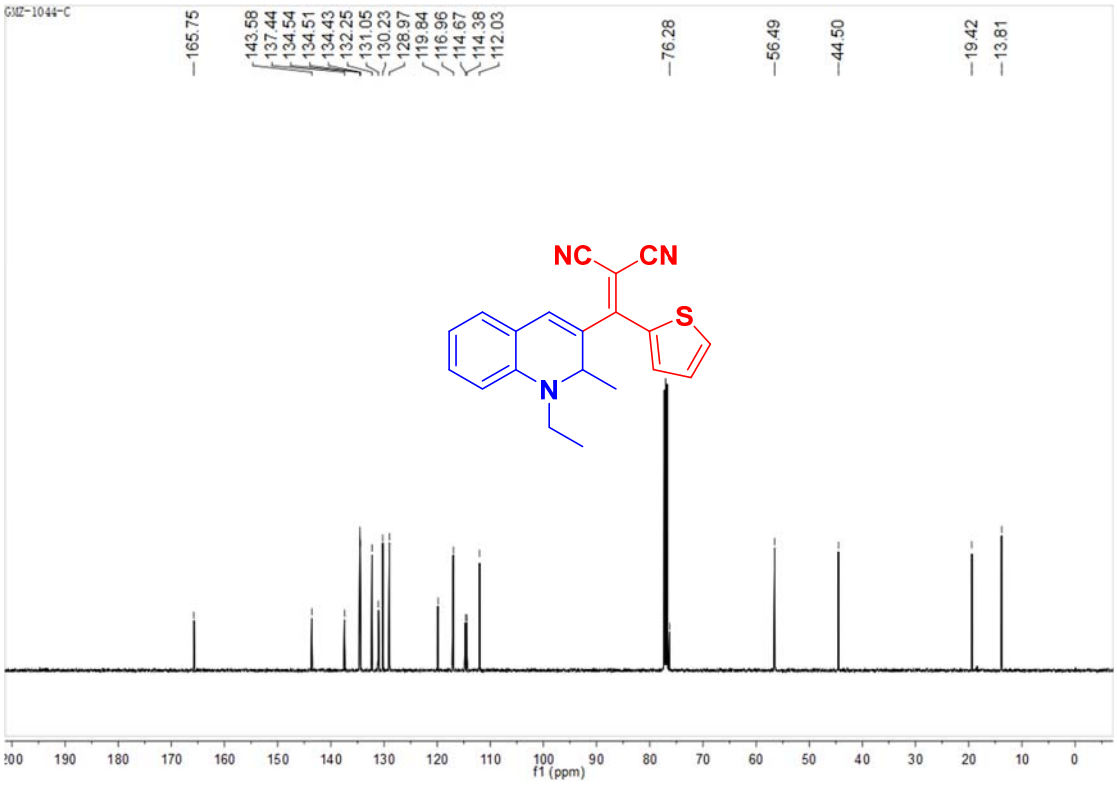
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(furan-2-yl)methylene)malononitrile (5k)



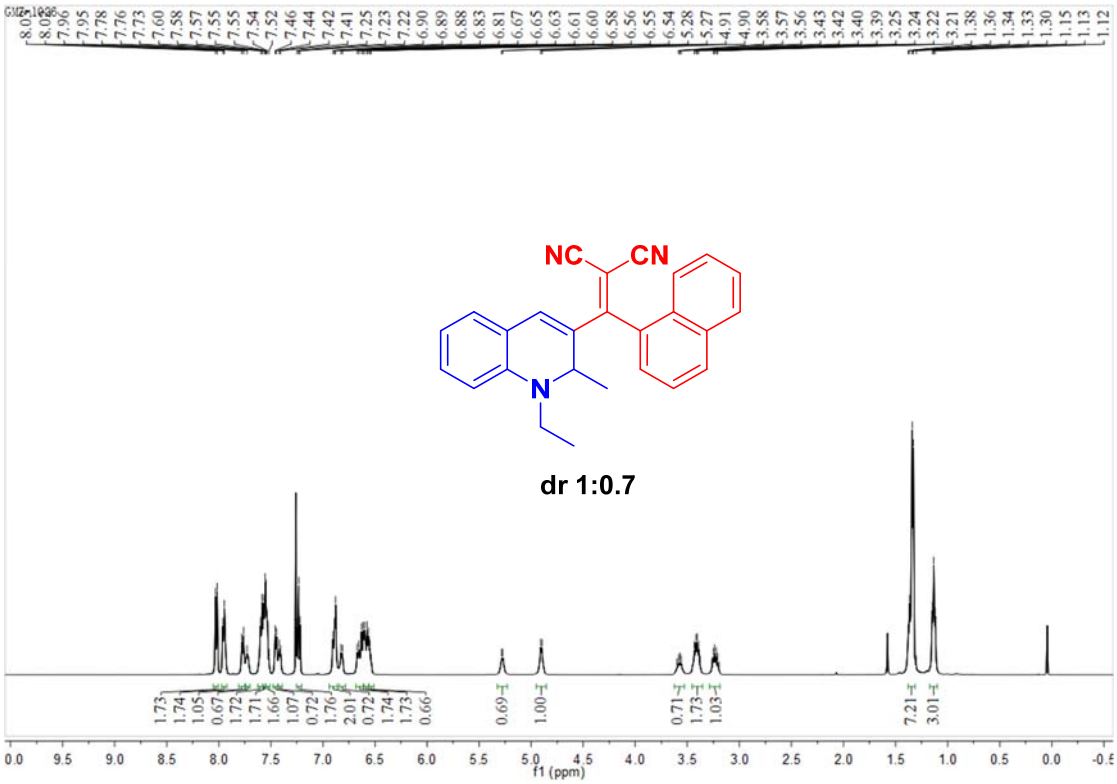


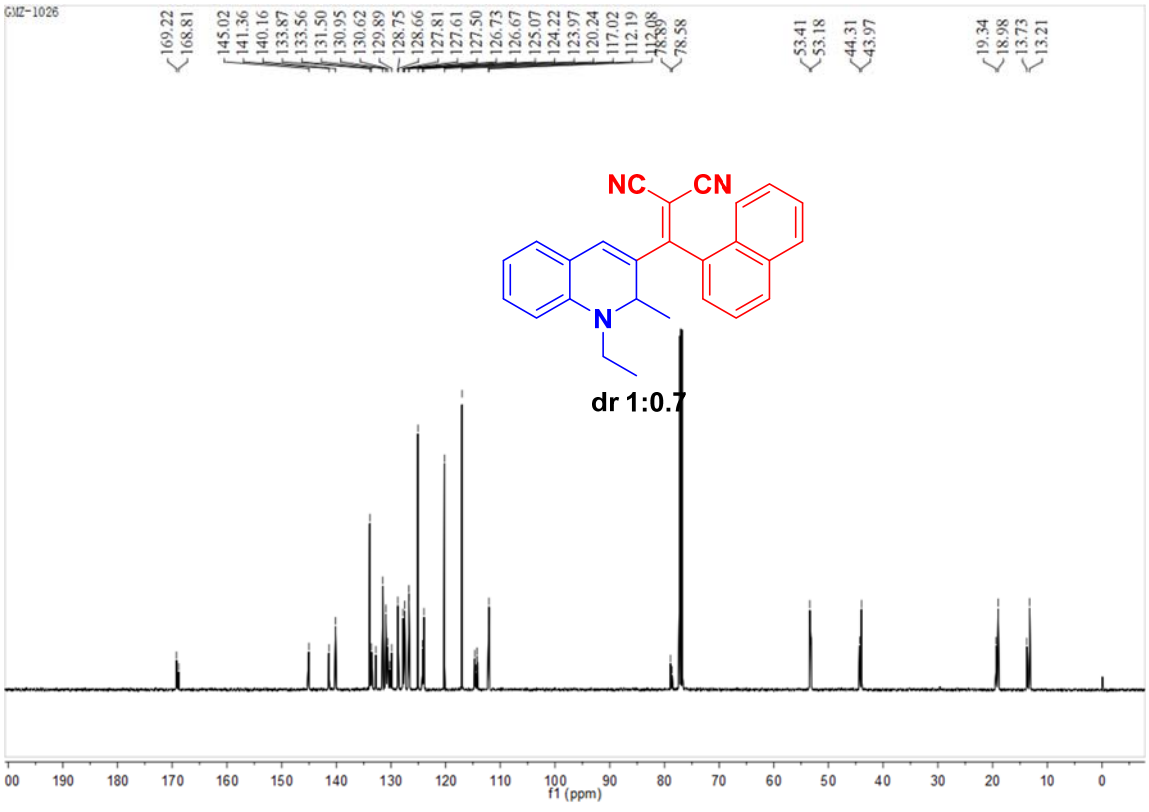
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(thiophen-2-yl)methylene)malononitrile (5l)



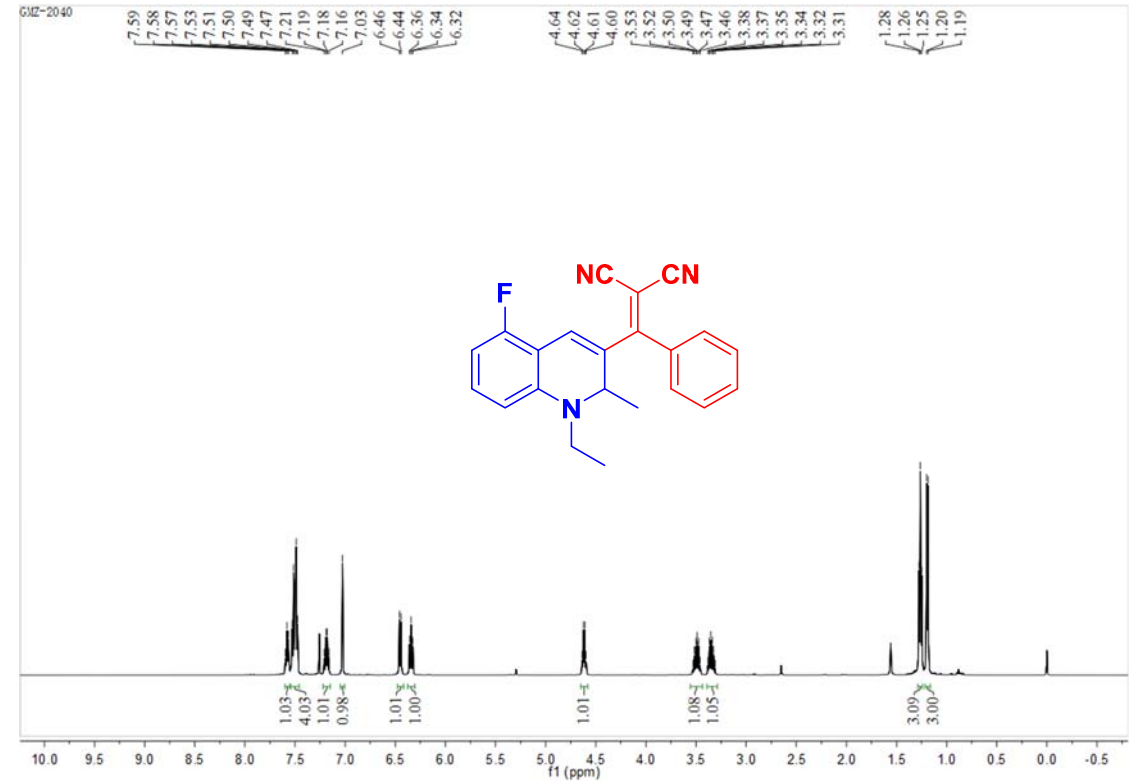


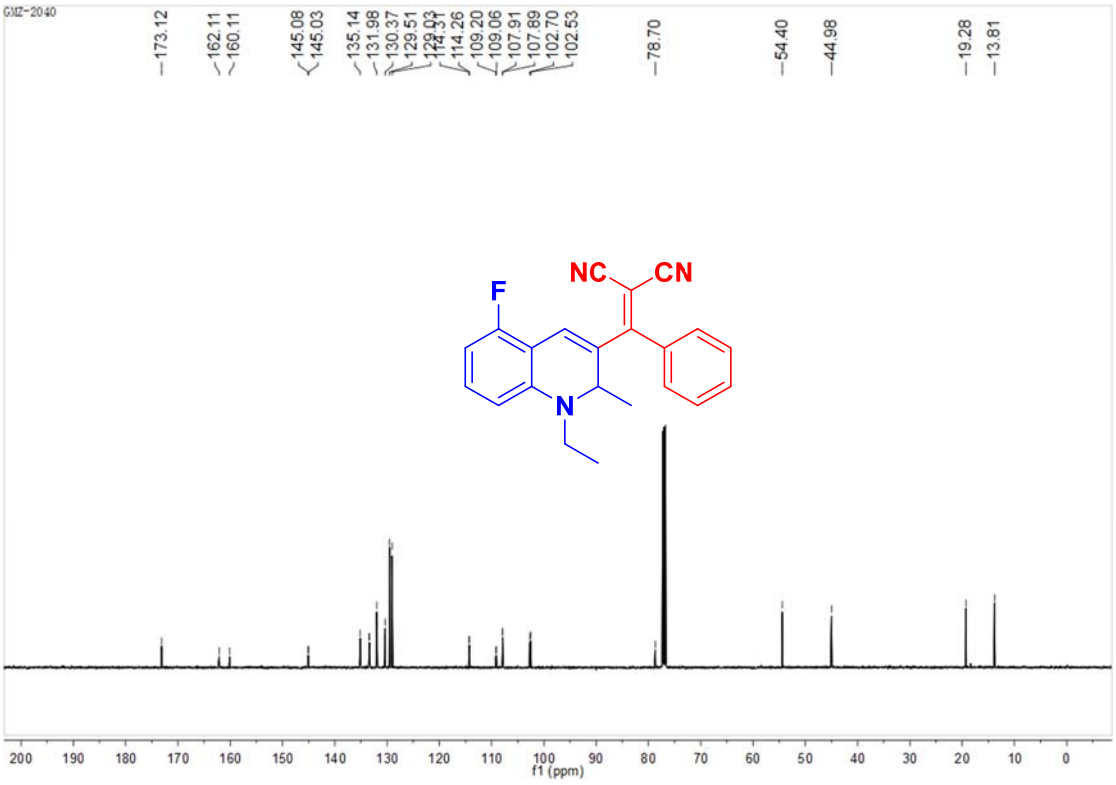
2-((1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(naphthalen-1-yl)methylene)malononitrile (5m)



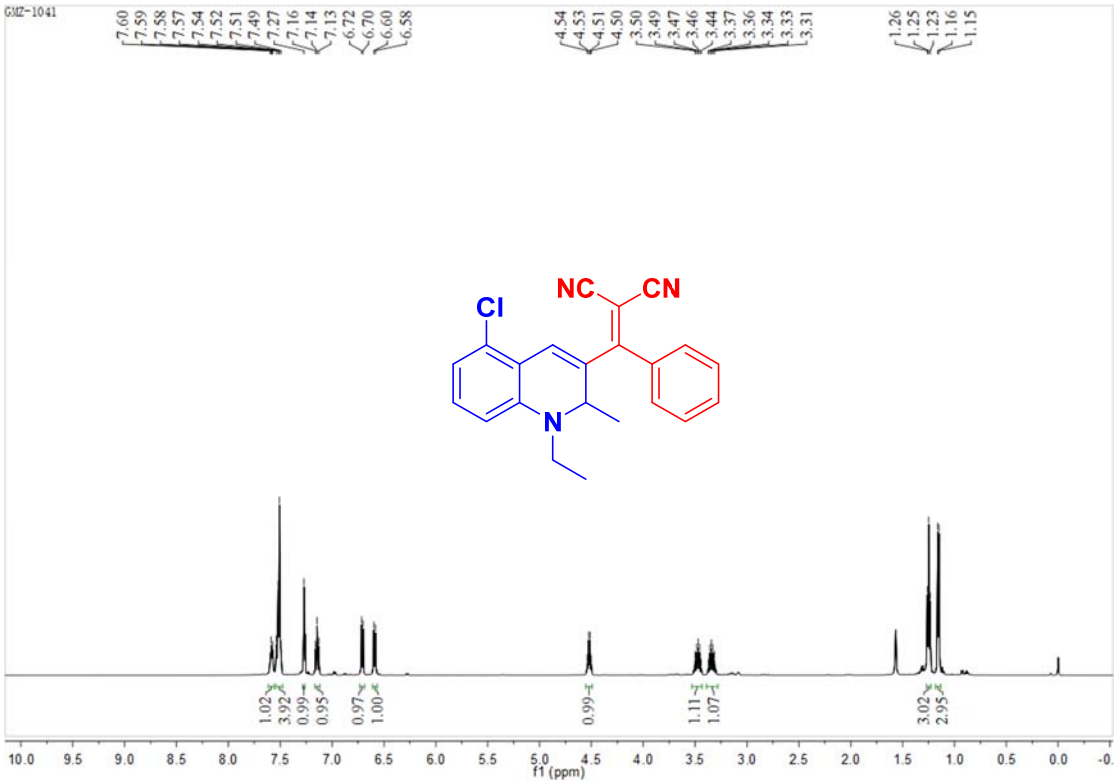


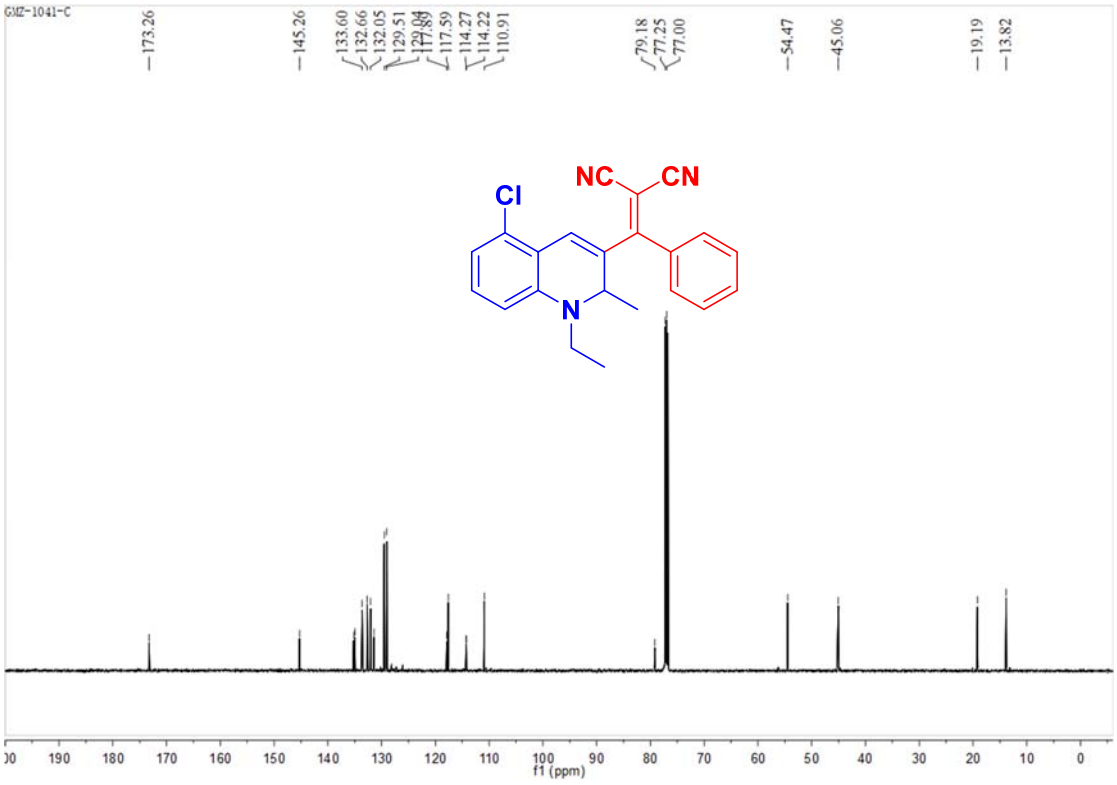
2-((1-ethyl-5-fluoro-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5n)



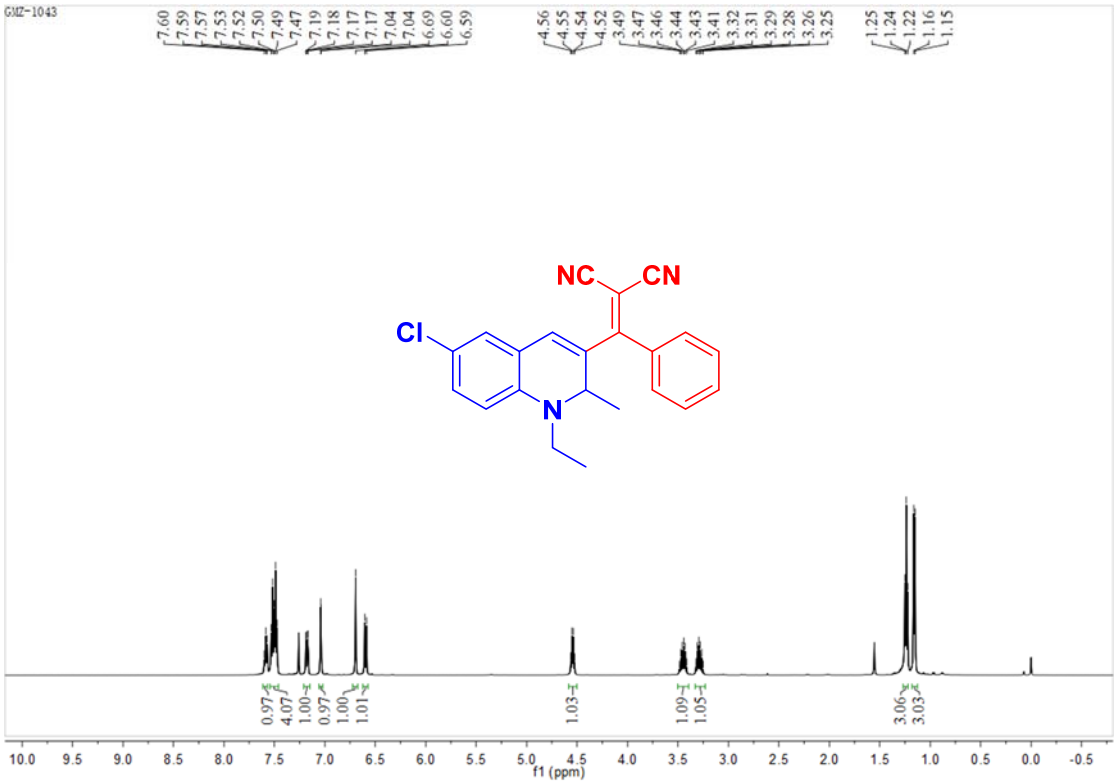


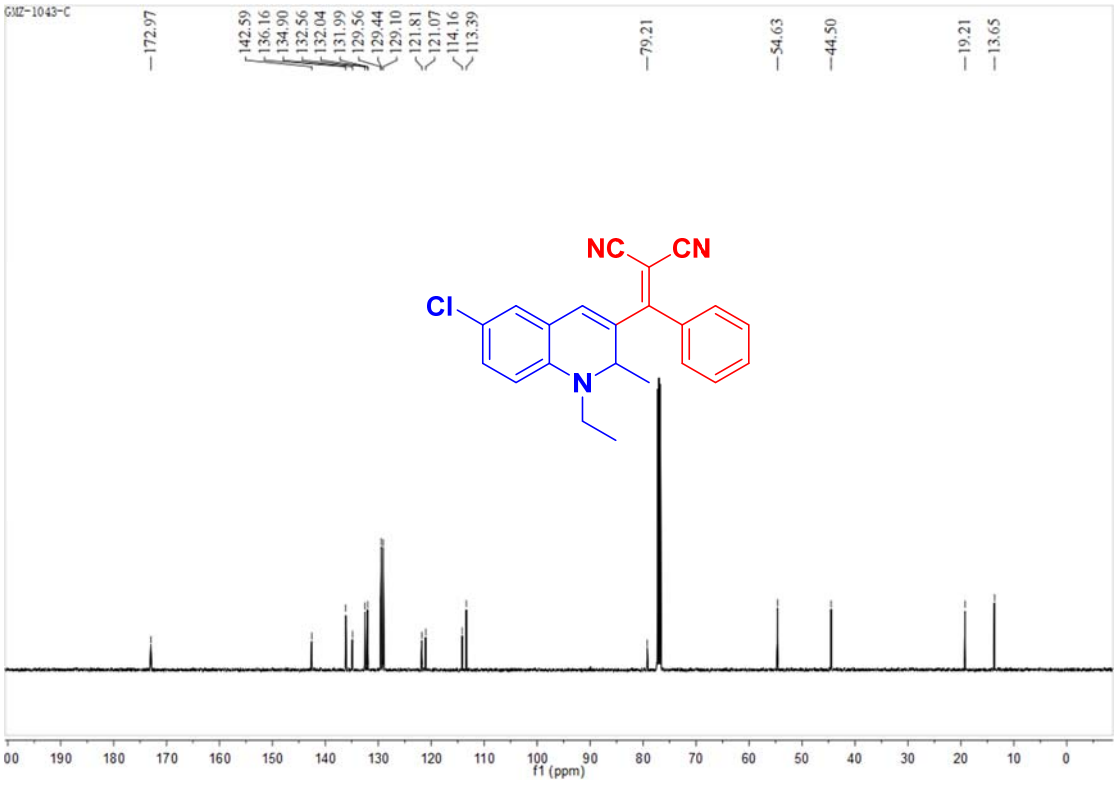
2-((5-chloro-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5o)



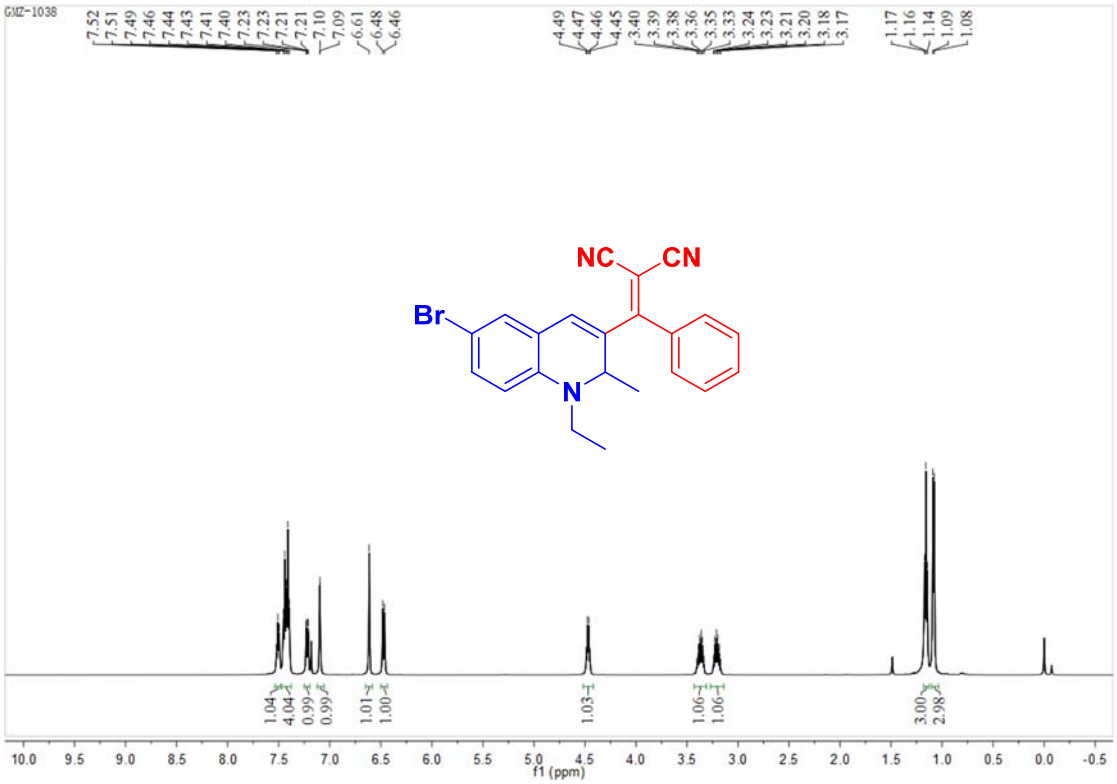


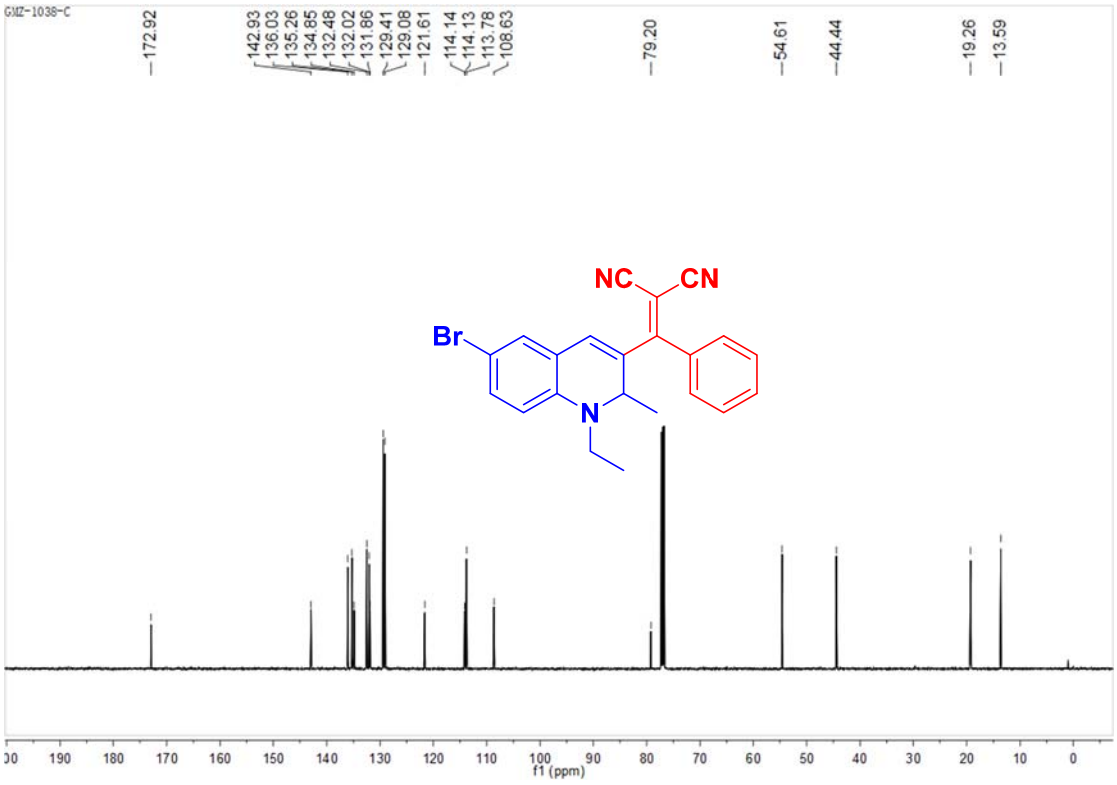
2-((6-chloro-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5p)



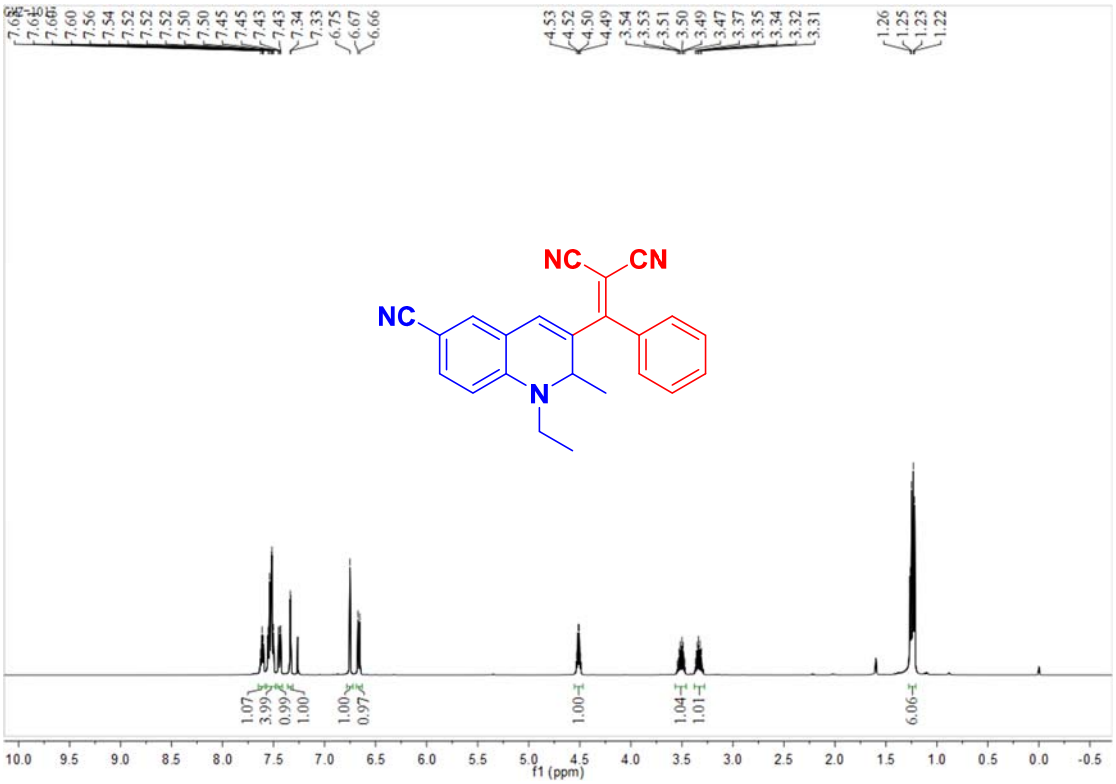


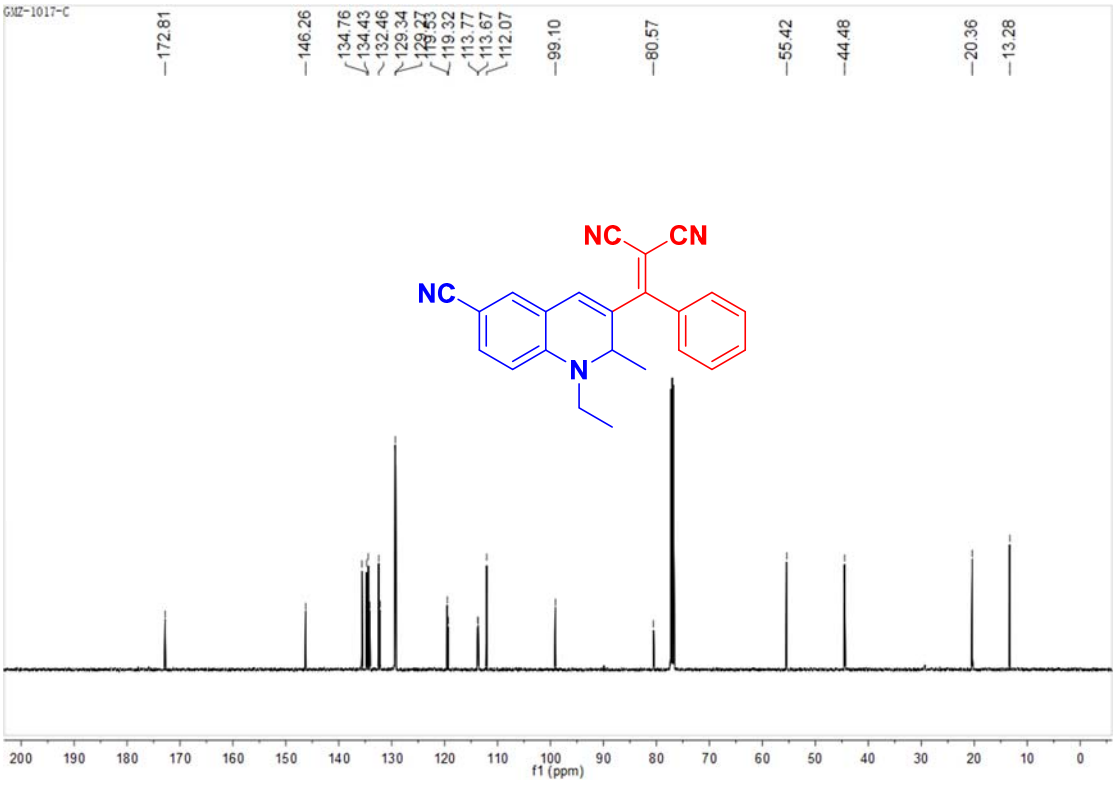
2-((6-bromo-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5q)



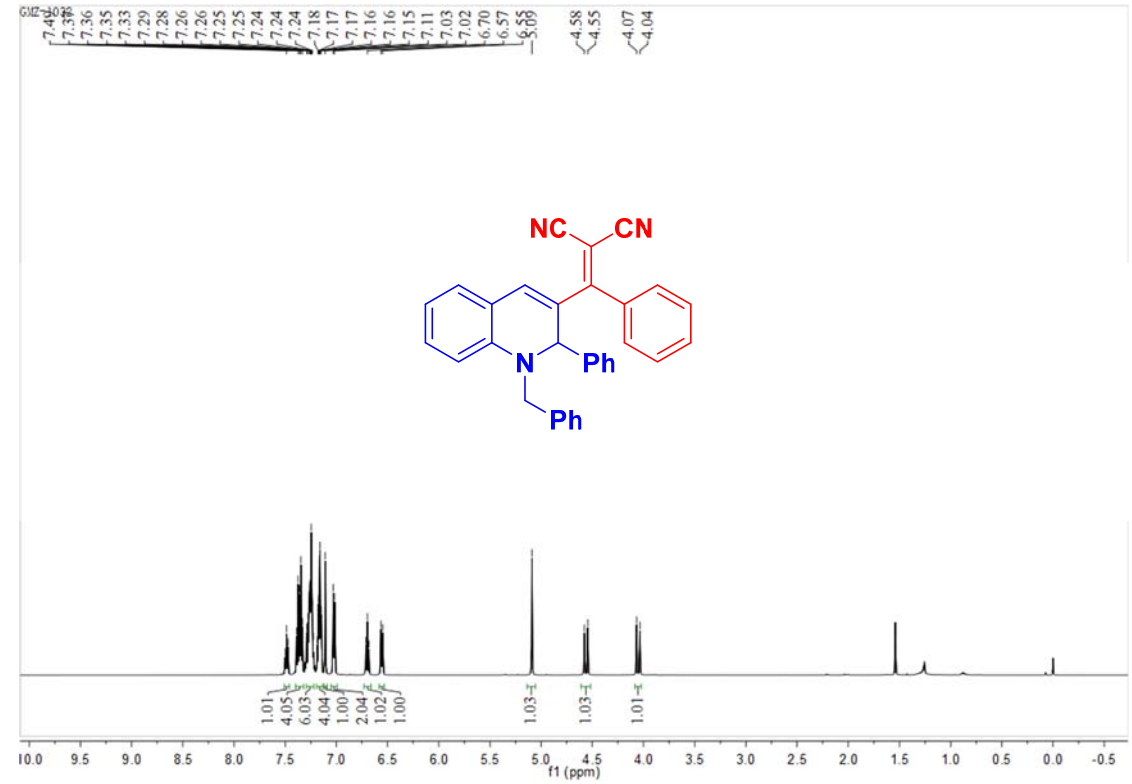


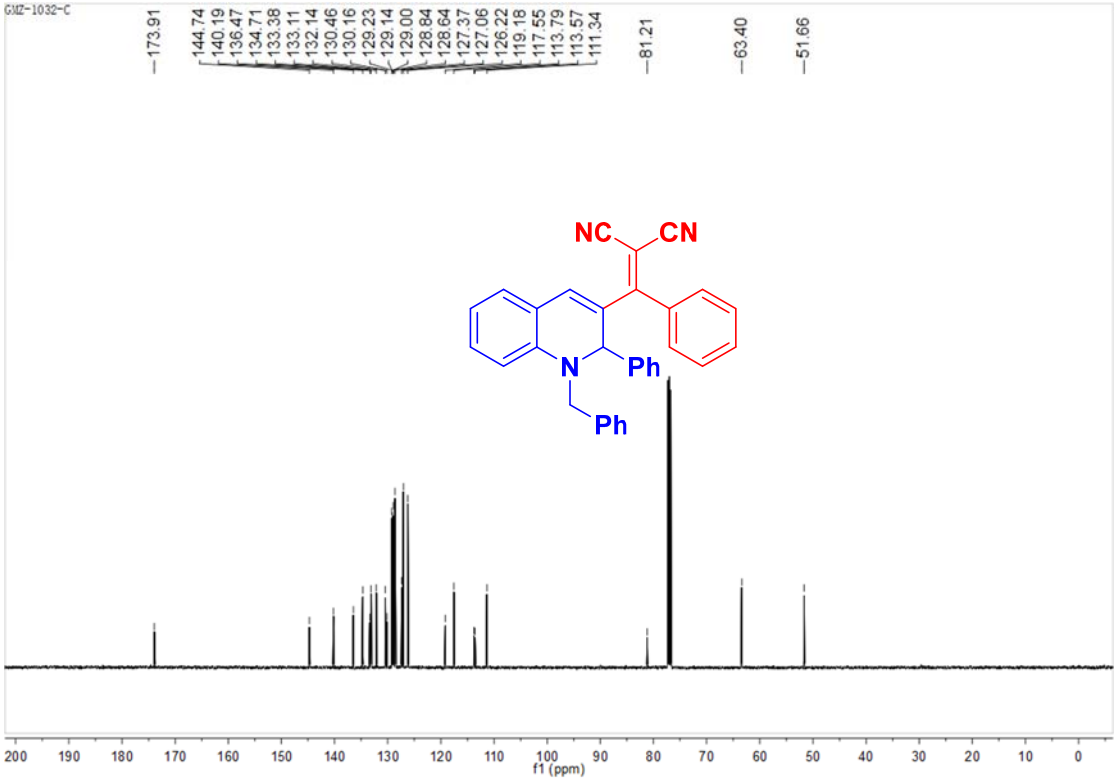
2-((6-cyano-1-ethyl-2-methyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5r)



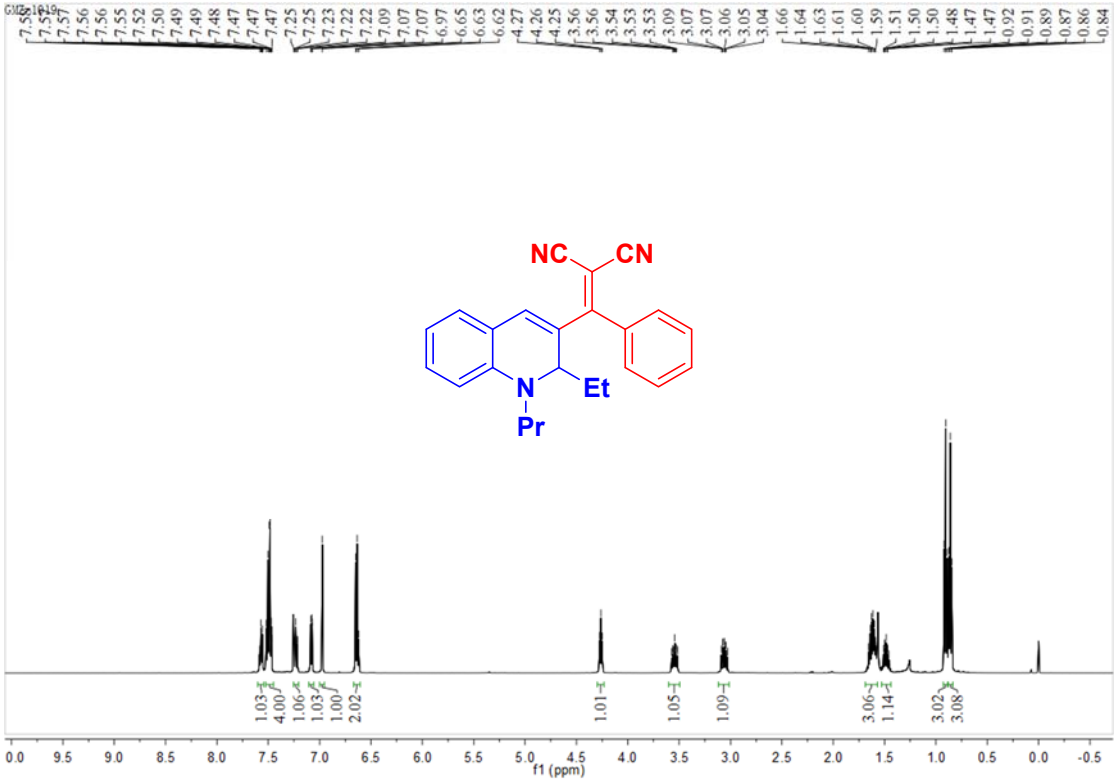


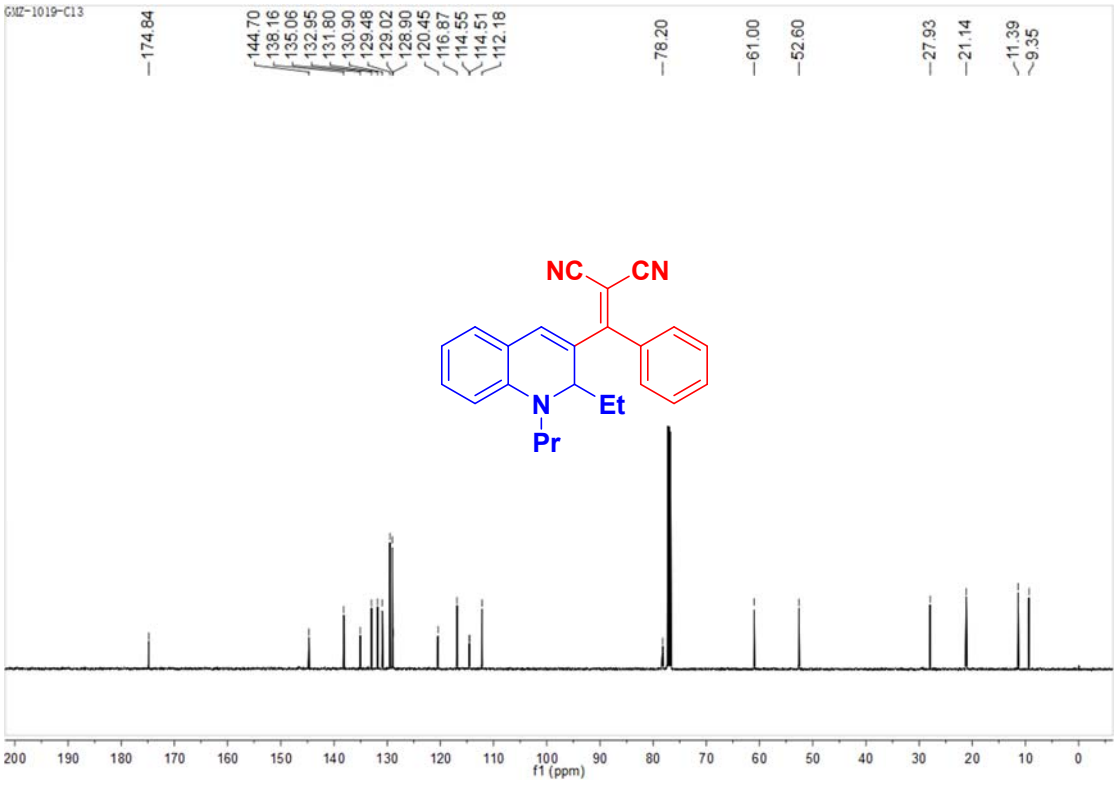
2-((1-benzyl-2-phenyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5s)



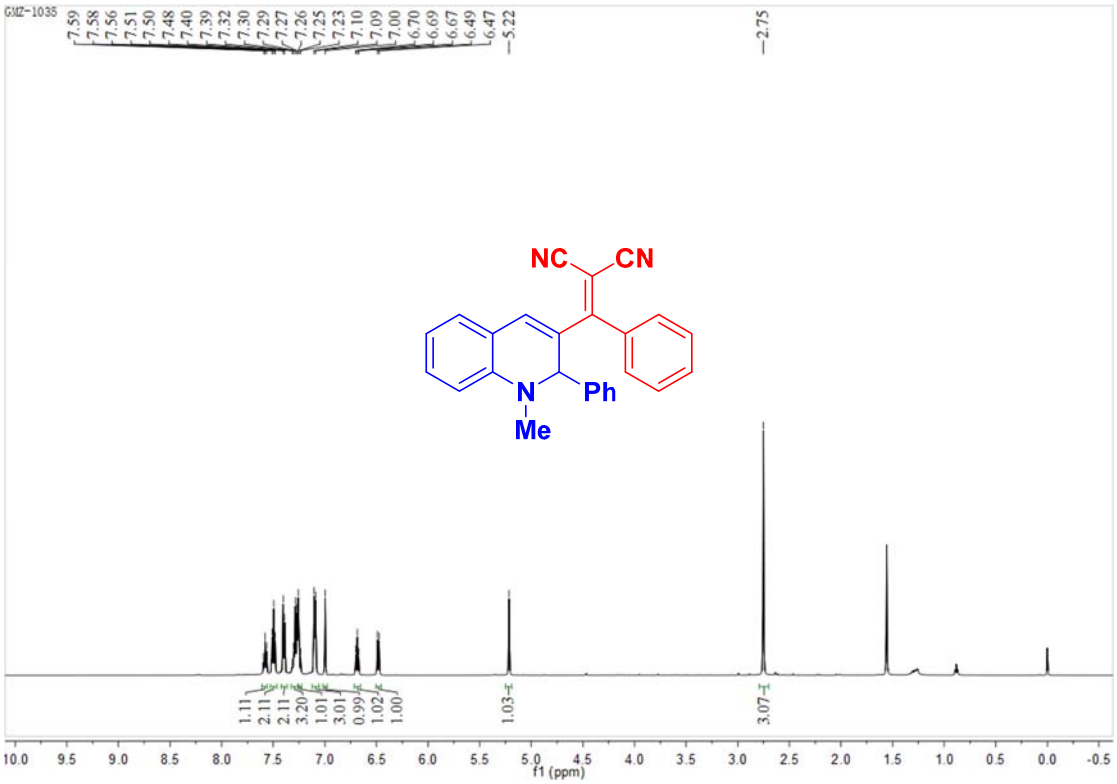


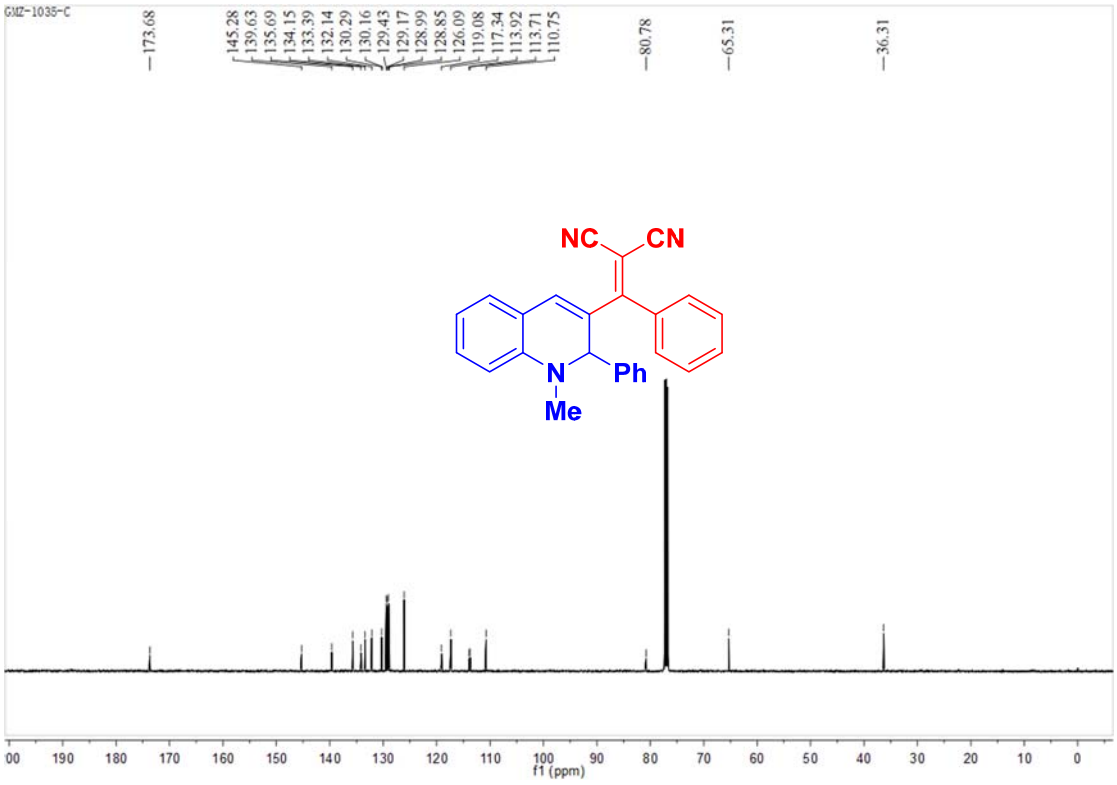
2-((2-ethyl-1-propyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5t)



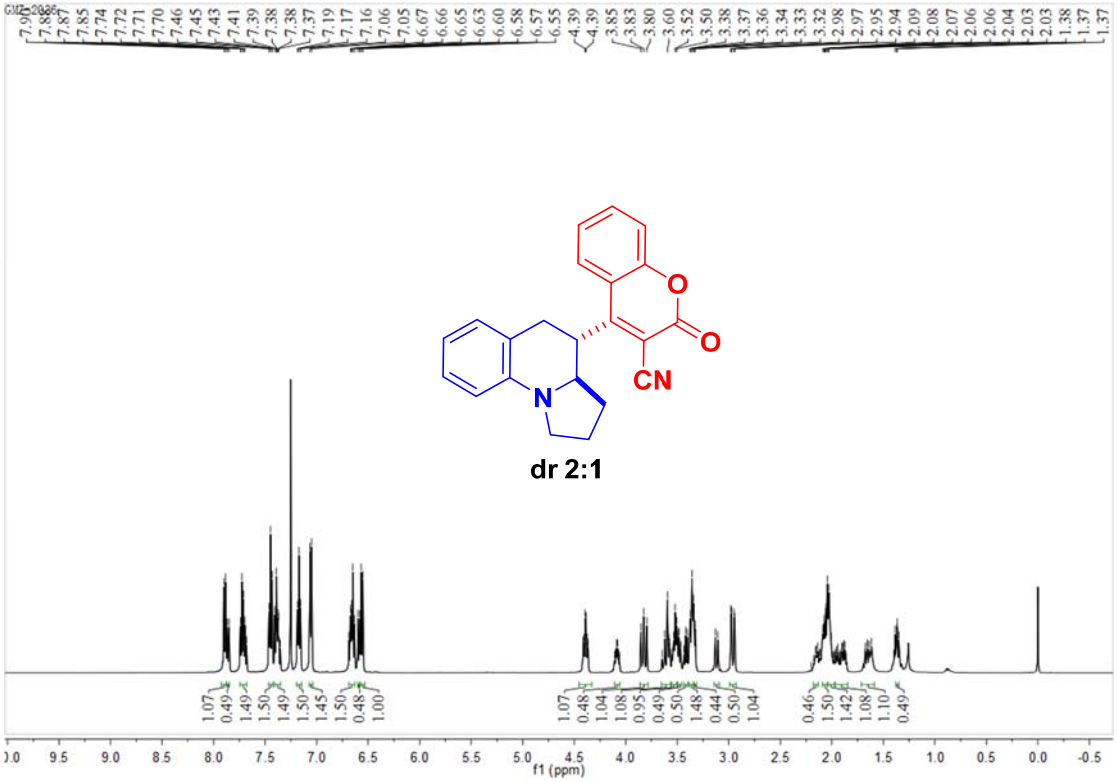


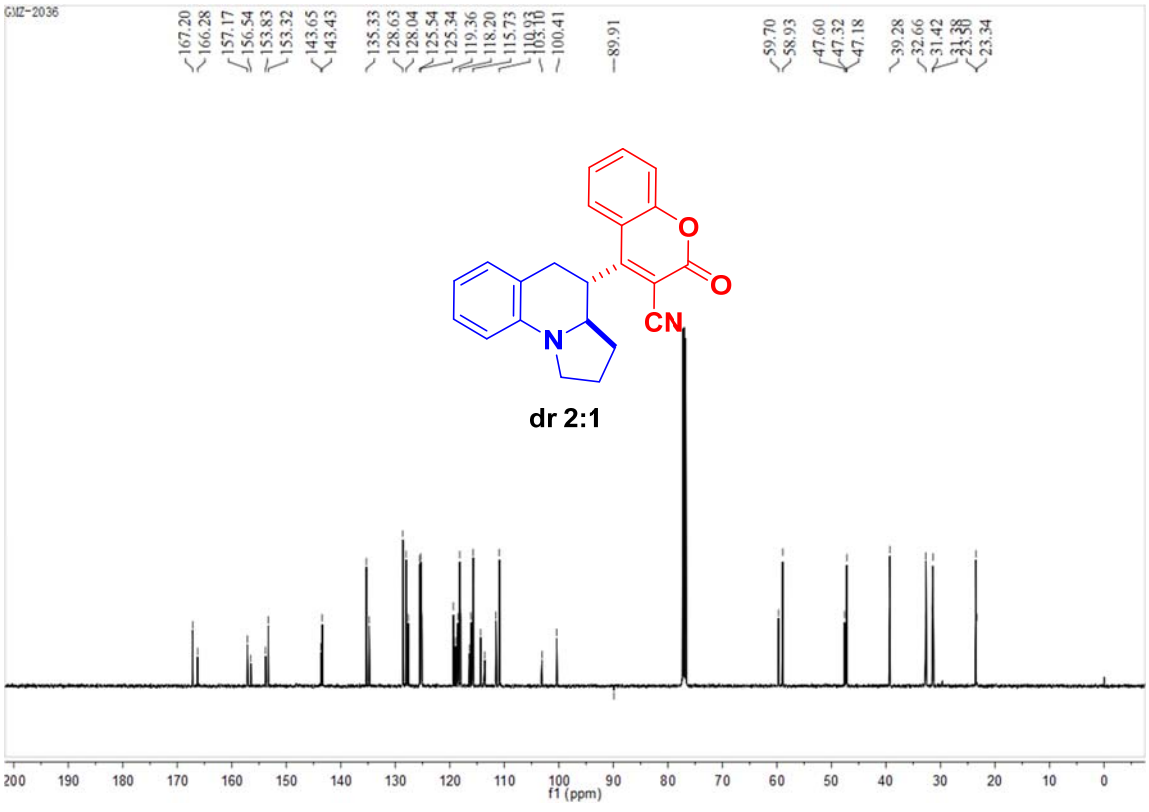
2-((1-methyl-2-phenyl-1,2-dihydroquinolin-3-yl)(phenyl)methylene)malononitrile (5u)



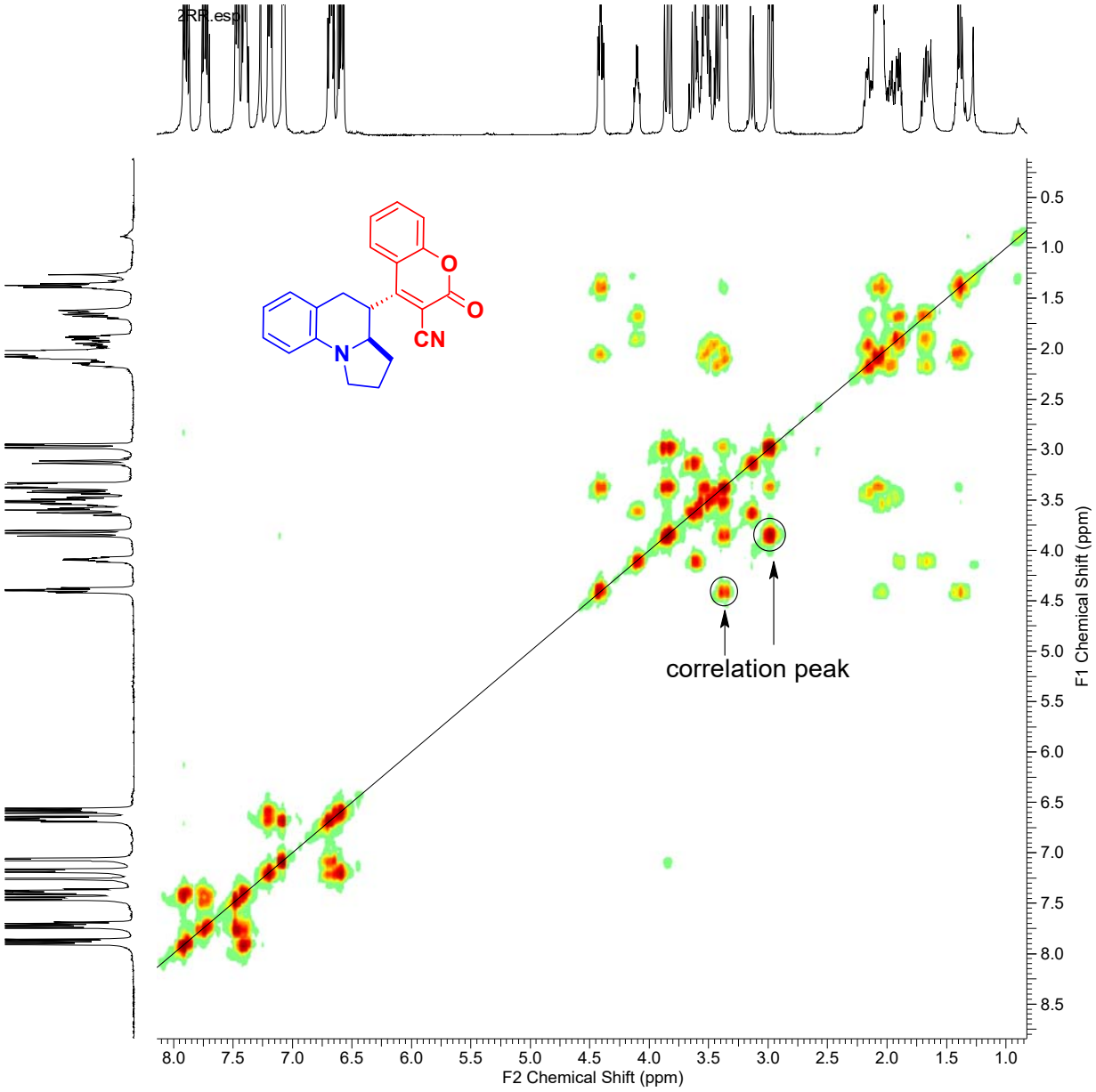


4-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7a)

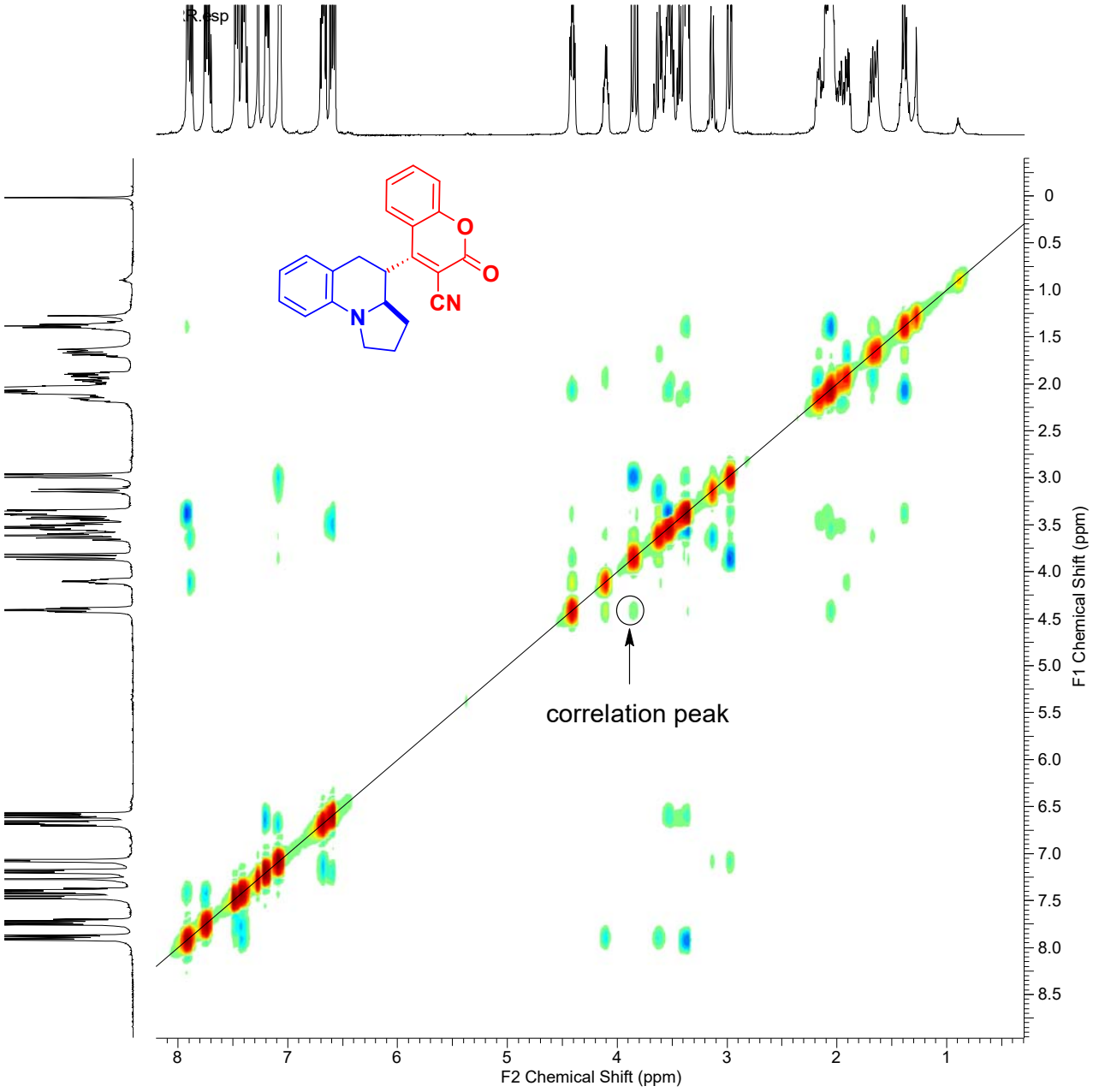




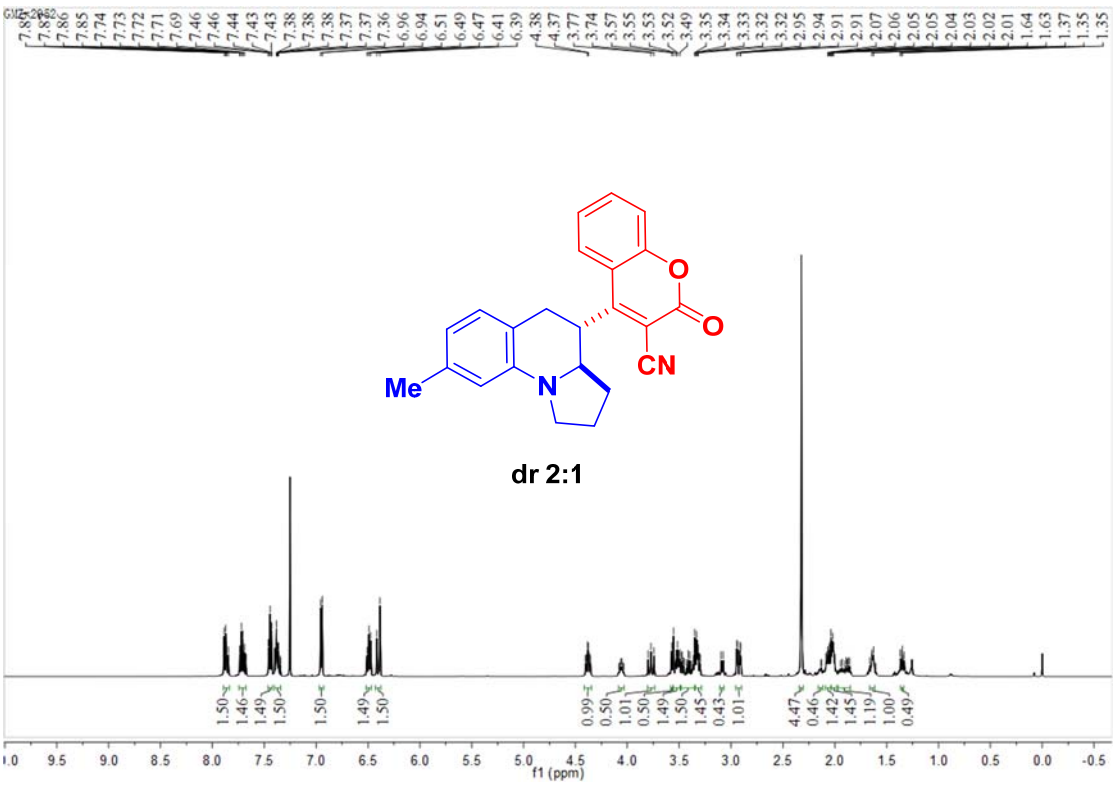
H,H-Cosy of 4-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7a)

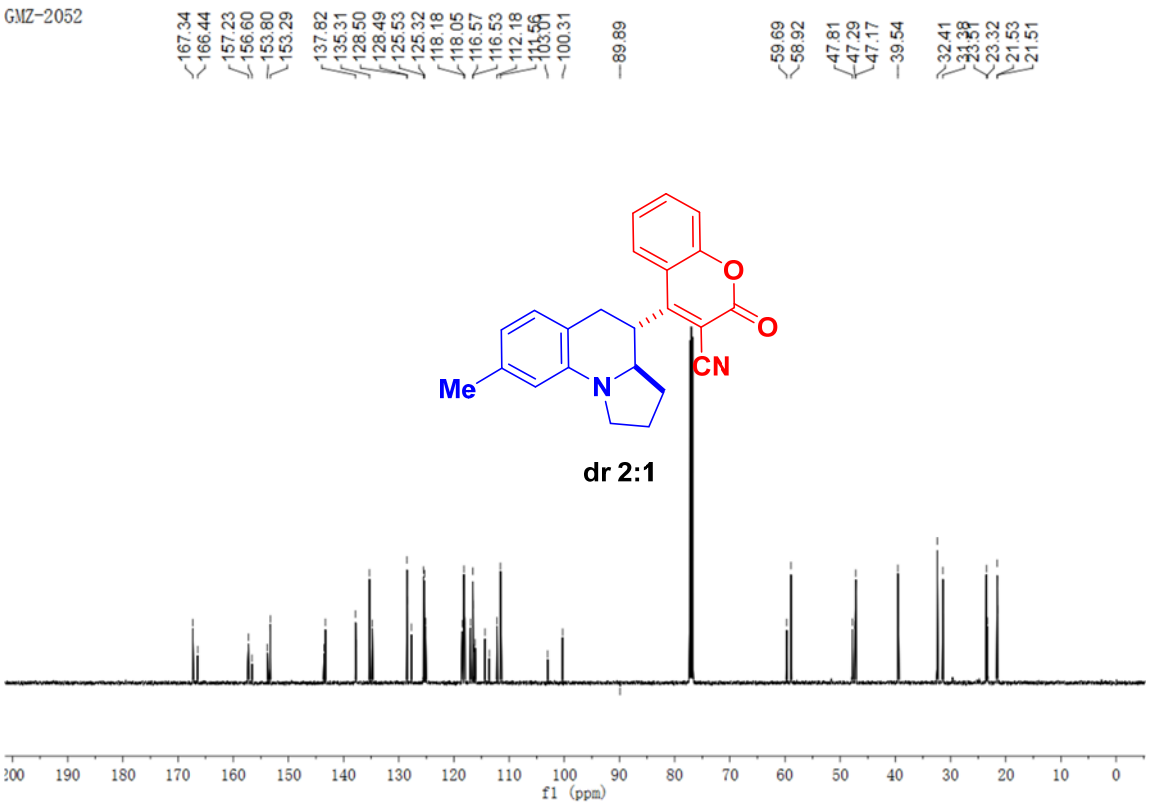


NOESY of 4-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7a)

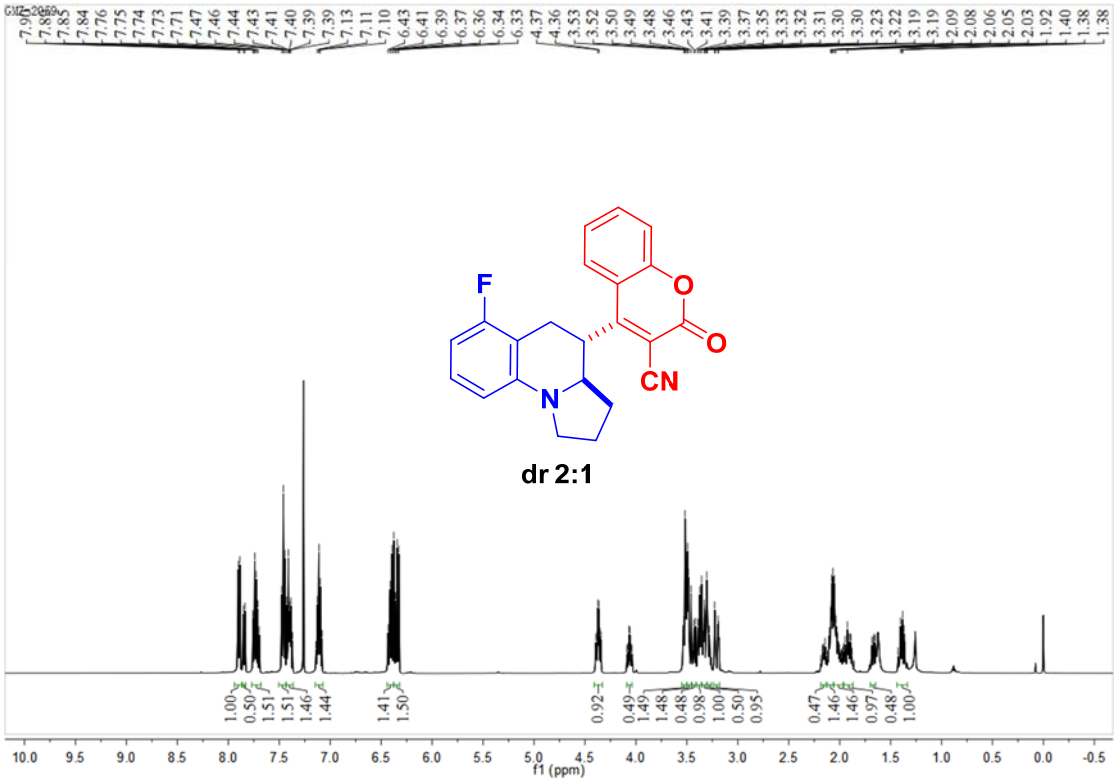


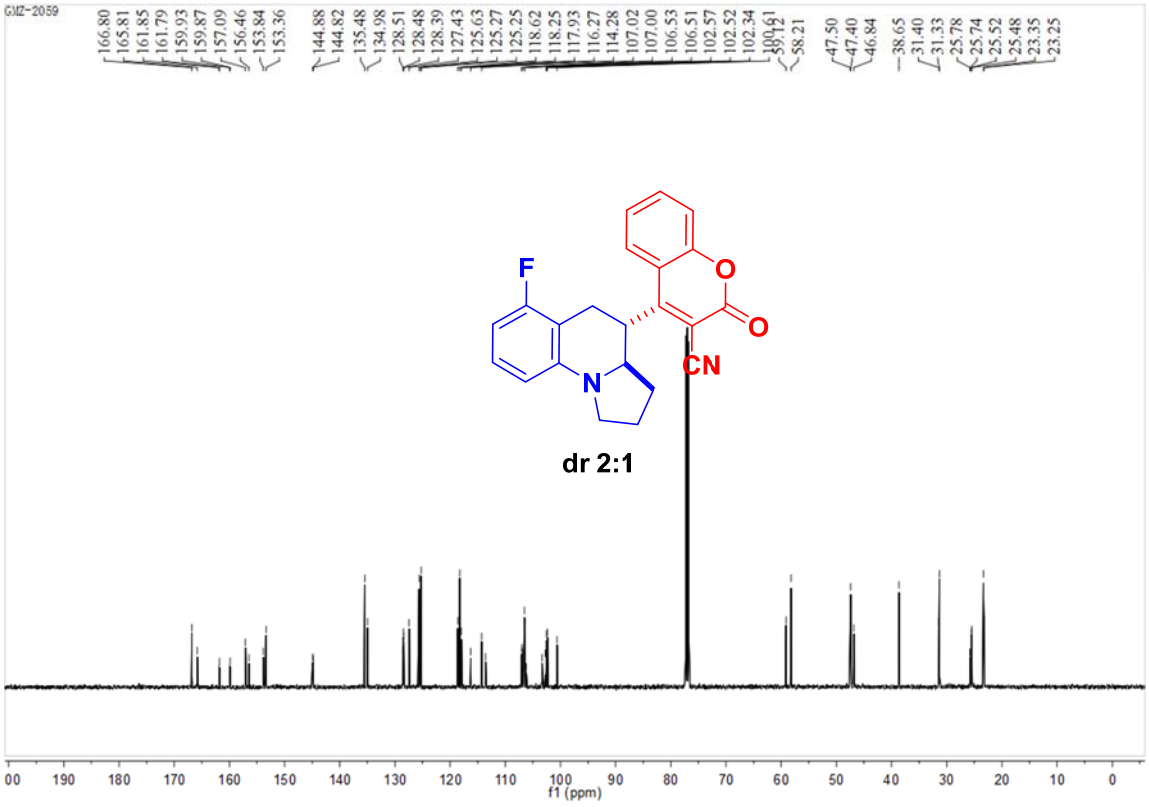
4-(8-methyl-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7b)



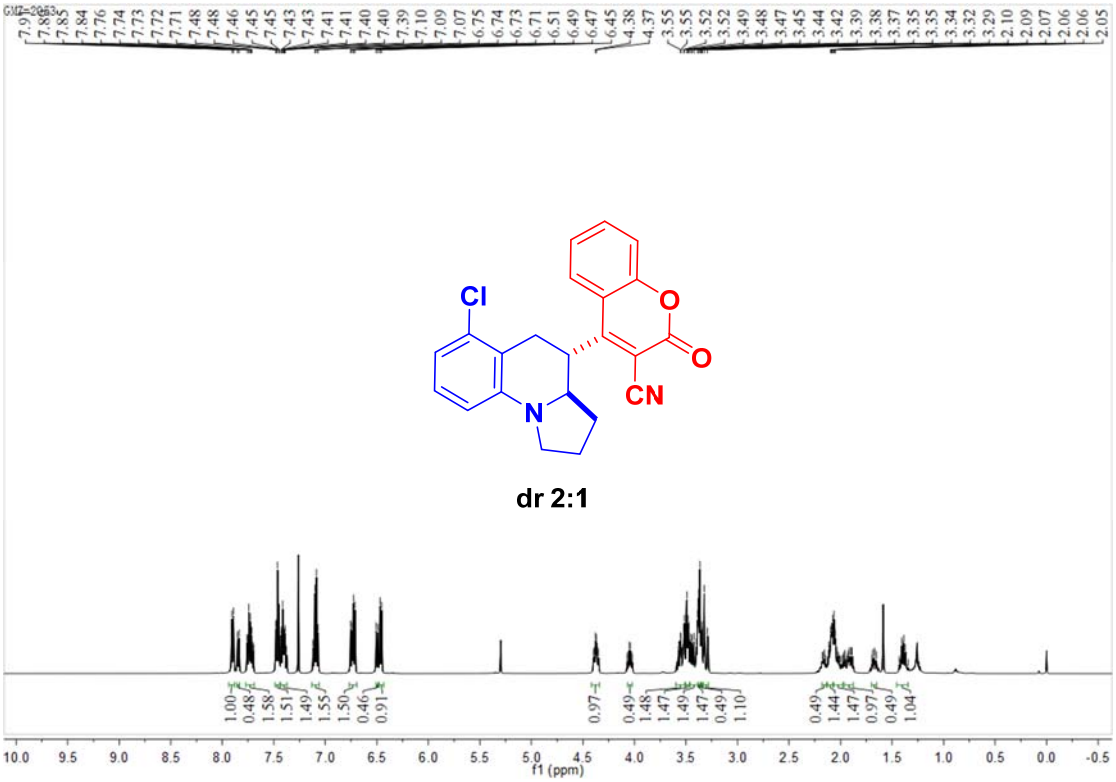


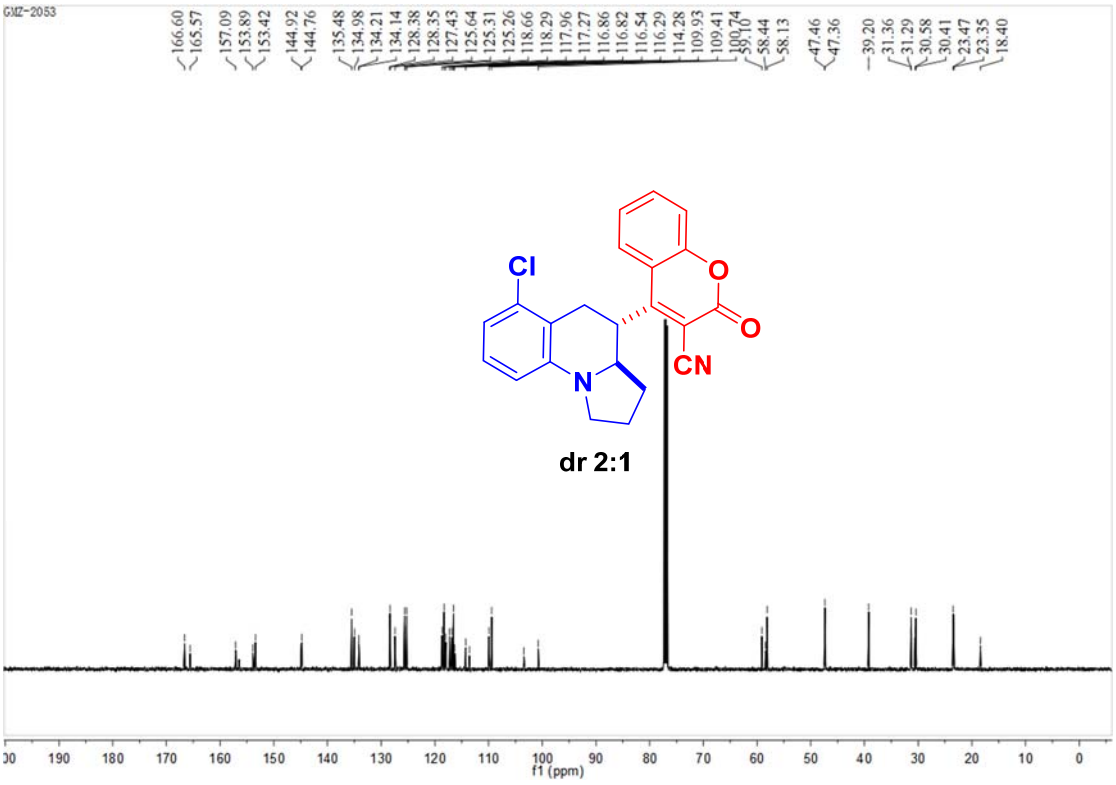
4-(6-fluoro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7c)



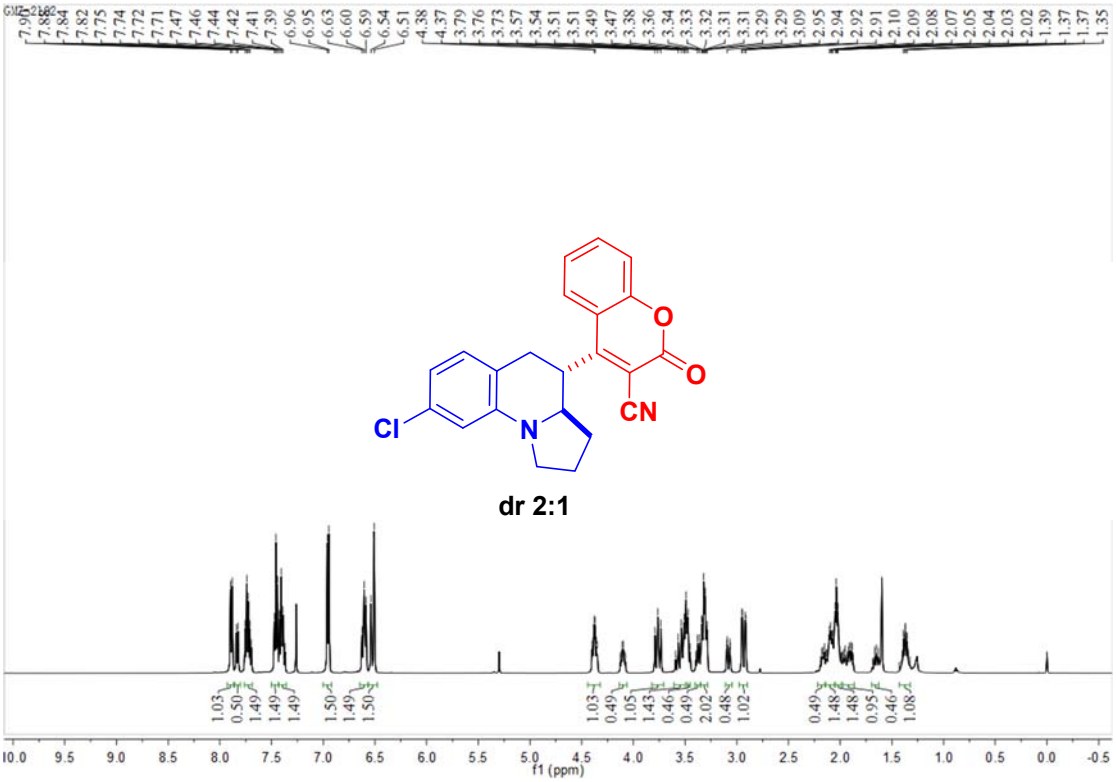


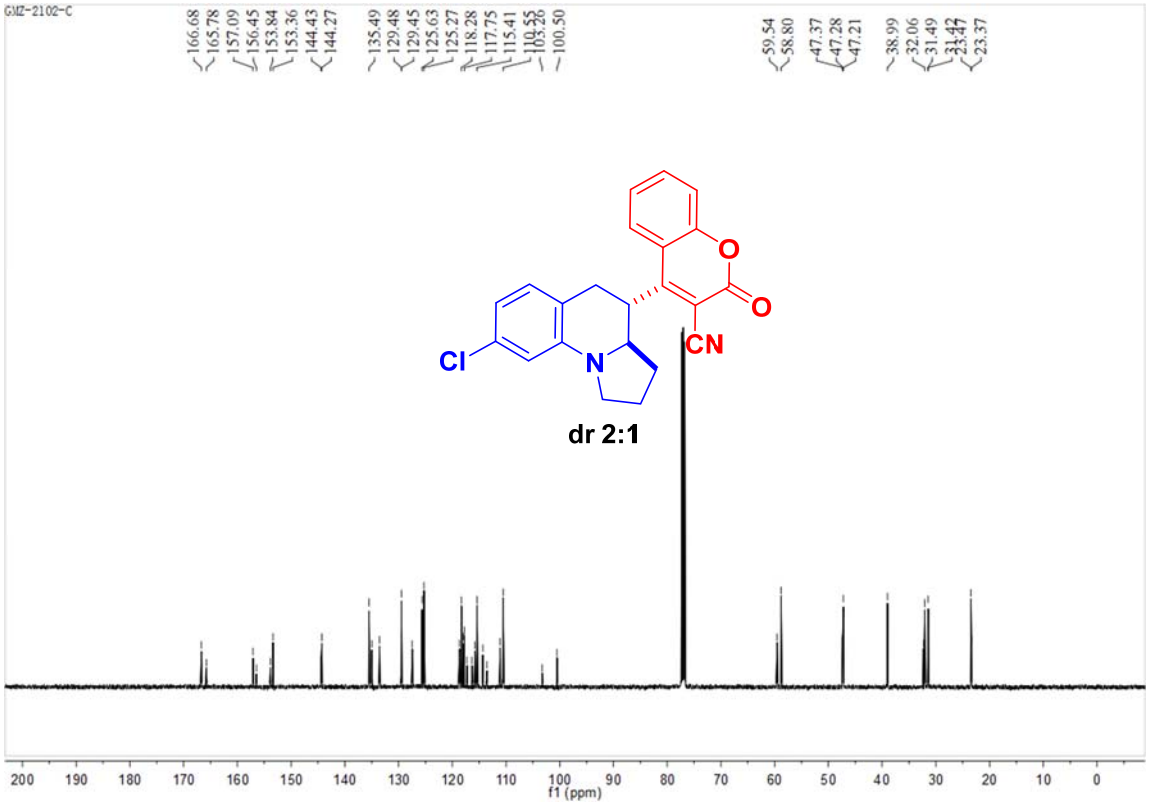
4-(6-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7d)



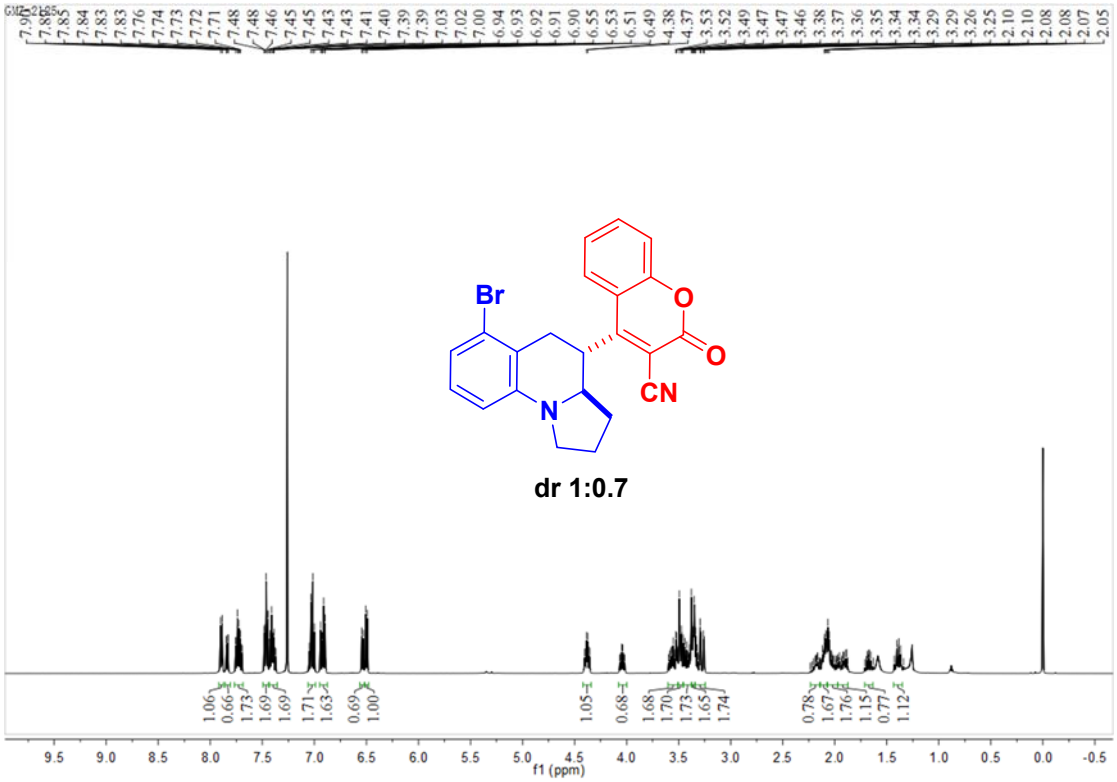


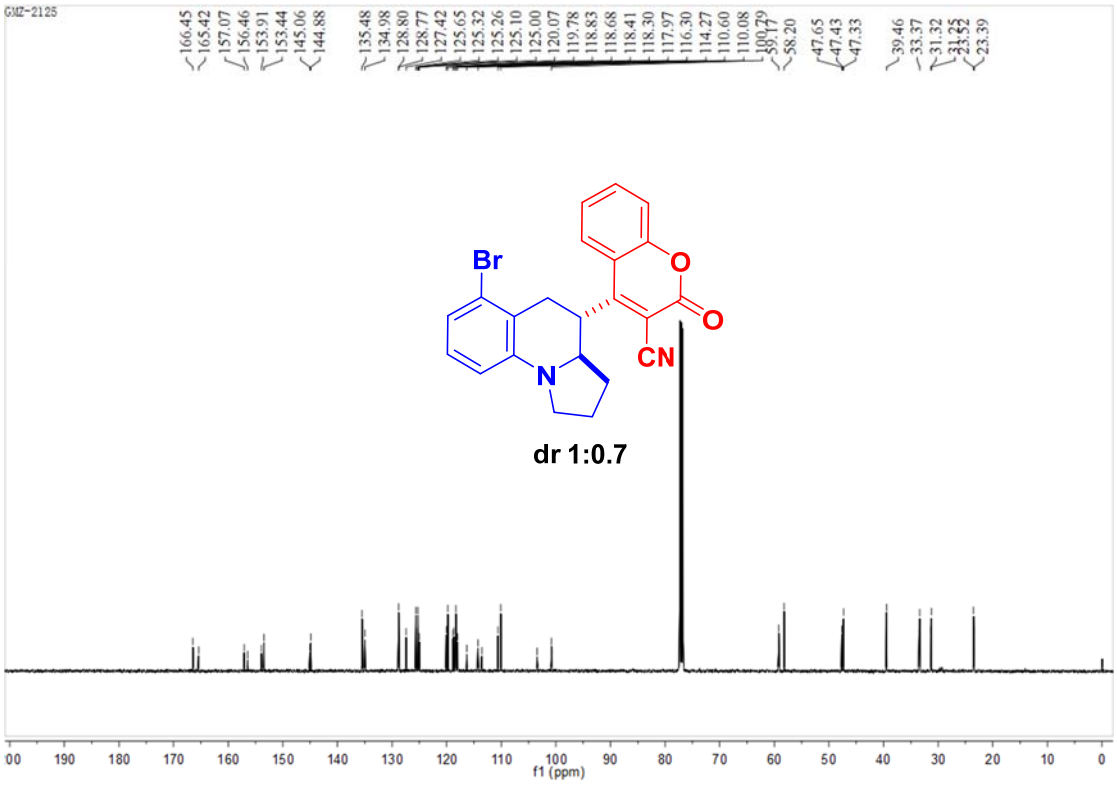
4-(8-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7e)





4-(6-bromo-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7f)





4-(8-chloro-2,3,4,4a,5,6-hexahydro-1H-pyrido[1,2-a]quinolin-5-yl)-2-oxo-2*H*-chromene-3-carbonitrile (7h)