Supporting Information

Chemoselective & Disastereoselective Construction of 4-Alkylidene-tetrahydroquinoline via Redox-Neutral Vinylogous Cascade [1,7]-Hydride Transfer/6-Endo-Trig Cyclization Strategy

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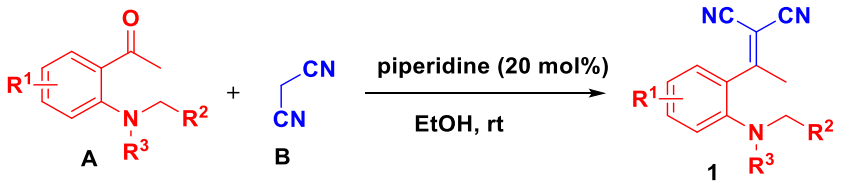
1. General Information

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 saturated and unsaturated aldehydes were purchased from adamas-beta. The substrates A in the following scheme can be readily accessed via the given references.

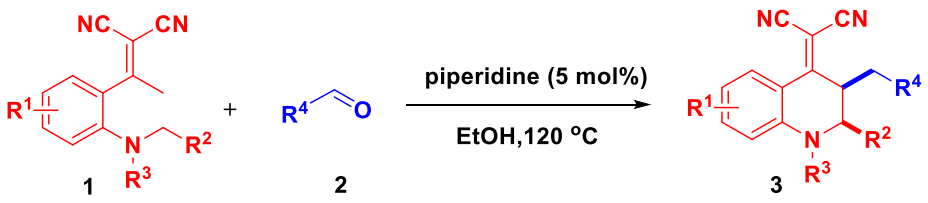
2. General Procedure

2.1 Procedure for the Synthesis of 3



The starting material **1** can be readily accessed as follows according to the references:[1] A reaction tube was charged with 2-(dialkylamino)acetophenone **A** (0.1 mmol), malononitrile **B** (0.15 mmol), piperidine (20 mol%) and EtOH (1.0 mL). The mixture was stirred at room temperature under an atmosphere for 8 h. 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 on silica gel (eluent: ethyl acetate/petroleum ether, 1:100) to afford product **1**.

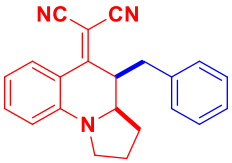
2.2 General Procedure for the Synthesis of 3/5



A sealed tube was charged with 2-(1-(2-(amino-1-yl)phenyl)ethylidene)malononitrile **1** (0.1 mmol), aldehyde **2** (0.2 mmol), piperidine (5 mol%) and EtOH (1.0 mL). The mixture was stirred at 120 °C for 24 h. 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 on silica gel (eluent: ethyl acetate/petroleum ether, 1:20) to afford product **3**.

3. Characterization of Products

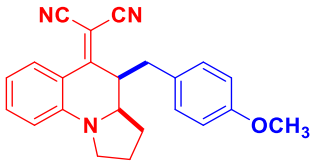
2-(4-benzyl-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1*H*)-ylidene)malononitrile 3a



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (20.7 mg, 76% yield) as a red solid, mp: 165-167 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.25 (d, *J* = 8.6 Hz, 4H), 6.95 – 6.90 (m, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 1H), 3.50 (d, *J* = 9.2 Hz, 1H), 3.44 – 3.36 (m, 2H), 2.95 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.36 (dd, *J* = 13.4, 10.6 Hz, 1H), 2.24 (dd, *J* = 6.8, 5.3 Hz, 1H), 2.15 (dd, *J* = 12.0, 5.8 Hz, 1H), 2.08 (dd, *J* = 11.0, 6.9 Hz, 1H), 2.02 – 1.93 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7, 145.5, 136.6, 136.1, 129.2, 129.2, 128.5, 127.0, 116.0, 114.5, 113.9, 113.0, 112.2, 75.4, 58.9, 46.7, 41.4, 32.8, 27.7, 23.4. **HRMS (ESI):** calcd. for $C_{22}H_{19}N_3$ $[M+H]^+$: 326.1652, found: 326.1650.

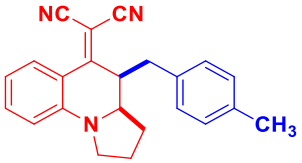
2-((3a*R*,4*R*)-4-(4-methoxybenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1*H*)-ylidene)malononitrile 3b



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (23.4 mg, 66% yield) as a red solid, mp: 177-179 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.43 – 7.37 (m, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.81 – 6.76 (m, 2H), 6.72 – 6.66 (m, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 3.82 (d, *J* = 3.9 Hz, 1H), 3.81 (s, 3H), 3.52 (dd, *J* = 13.4, 5.5 Hz, 1H), 3.44 – 3.36 (m, 2H), 2.91 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.32 (dd, *J* = 13.6, 10.6 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.20 – 2.12 (m, 1H), 2.11 – 2.04 (m, 1H), 2.03 – 1.93 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 158.529, 145.519, 136.0, 130.2, 129.2, 128.4, 115.9, 114.5, 113.9, 113.8, 113.0, 112.1, 75.5, 58.8, 55.2, 46.7, 41.5, 31.9, 27.7, 23.4. **HRMS (ESI):** calcd. for $C_{23}H_{21}N_3O$ $[M+H]^+$: 356.1757, found: 356.1755.

2-((3a*R*,4*R*)-4-(4-methylbenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3c

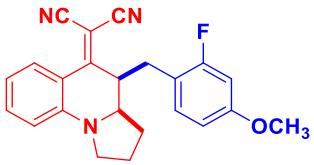


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (25.4 mg, 75% yield) as a red solid, mp: 163-165 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.52 (dd, *J* = 13.4, 5.3 Hz, 1H), 3.45 – 3.36 (m, 2H), 2.92 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.37 – 2.29 (m, 4H), 2.28 – 2.21 (m, 1H), 2.19 – 2.12 (m, 1H), 2.12 – 2.03 (m, 1H), 2.03 – 1.94 (m, 1H); **^{13}C NMR** (125 MHz,

$CDCl_3$) δ 170.8, 145.5, 136.4, 136.0, 133.36, 129.14, 129.1, 129.0, 115.8, 114.5, 113.9, 112.9, 112.1, 75.4, 58.8, 46.7, 41.4, 32.3, 27.7, 23.4, 21.0. **HRMS (ESI):** calcd. for $C_{23}H_{21}N_3$ $[M+H]^+$: 340.1808, found: 340.1808.

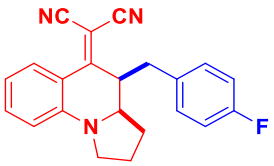
2-((3a*R*,4*R*)-4-(2-fluoro-4-methoxybenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1*H*)-ylidene)malononitrile 3d



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (28.0 mg,75% yield) as a red solid, mp: 178-181 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.66 – 6.59 (m, 2H), 6.58 – 6.53 (m, 2H), 3.85 – 3.81 (m, 1H), 3.80 (d, *J* = 5.5 Hz, 3H), 3.51 (t, *J* = 8.7 Hz, 1H), 3.42 (dd, *J* = 17.1, 9.0 Hz, 2H), 3.02 (dd, *J* = 13.7, 4.4 Hz, 1H), 2.28 (dd, *J* = 13.3, 10.8 Hz, 2H), 2.19 (dd, *J* = 12.2, 5.9 Hz, 1H), 2.13 (dd, *J* = 11.1, 7.2 Hz, 1H), 2.05 – 1.94 (m, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): -115.06 (s, 1F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.4, 161.7 (d, *J* = 243.8 Hz),160.1 (d, *J* = 11.3 Hz), 145.6, 136.1, 131.4 (d, *J* = 6.3 Hz), 129.2, 116.0, 115.5 (d, *J* = 16.3 Hz), 114.5, 113.2 (d, *J* = 66.3 Hz), 112.2, 109.8 (d, *J* = 1.3 Hz), 101.6, 101.6, 75.2, 58.8, 55.5, 46.7, 40.3, 27.6, 25.5, 23.3. **HRMS (ESI):** calcd. for $C_{23}H_{20}FN_3O$ $[M+H]^+$: 374.1663, found: 374.1665.

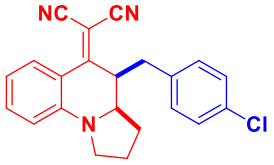
2-((3a*R*,4*R*)-4-(4-fluorobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3e



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (29.5mg, 86% yield) as a red solid, mp: 158-163 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 6.95 (t, *J* = 8.6 Hz, 2H), 6.89 (dd, *J* = 8.1, 5.6 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 3.88 – 3.78 (m, 1H), 3.52 (t, *J* = 8.8 Hz, 1H), 3.45 – 3.35 (m, 2H), 2.94 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.35 (dd, *J* = 13.4, 10.9 Hz, 1H), 2.29 – 2.22 (m, 1H), 2.21 – 2.14 (m, 1H), 2.12 – 2.04 (m, 1H), 2.04 – 1.94 (m, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): -115.58 (s, 1F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.3, 161.8 (d, *J* = 243.7 Hz), 145.5, 136.2, 132.2 (d, *J* = 3.75 Hz), 130.7 (d, *J* = 7.5 Hz), 129.0, 116.0, 115.3 (d, *J* = 21.3 Hz), 114.3, 113.9, 112.8, 112.2, 75.3, 58.7, 46.7, 41.3, 31.9, 27.6, 23.3. **HRMS (ESI):** calcd. for $C_{22}H_{18}FN_3$ $[M+H]^+$: 344.1558, found: 344.1557.

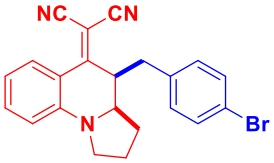
2-((3a*R*,4*R*)-4-(4-chlorobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3f



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (30.5mg, 85% yield) as a red solid, mp: 158-161 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 1H), 3.92 – 3.76 (m, 1H), 3.52 (t, *J* = 8.6 Hz, 1H), 3.47 – 3.35 (m, 2H), 2.93 (dd, *J* = 13.5, 5.2 Hz, 1H), 2.35 (dd, *J* = 13.4, 10.8 Hz, 1H), 2.30 – 2.20 (m, 1H), 2.21 – 2.13 (m, 1H), 2.12 – 2.03 (m, 1H), 2.03 – 1.94 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.2, 145.4, 136.2, 135.1, 132.8, 130.5, 129.1, 128.6, 116.1, 114.3, 113.9, 112.8, 112.2, 75.5, 58.8, 46.71, 41.1, 32.1, 27.7, 23.3. **HRMS (ESI):** calcd. for $C_{22}H_{18}{}^{35}ClN_3$ $[M+H]^+$: 360.1262, found: 360.1266; calcd. for $C_{22}H_{18}{}^{37}ClN_3$ $[M+H]^+$: 362.1233, found: 362.1236.

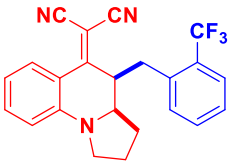
2-((3a*R*,4*R*)-4-(4-bromobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3g



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (32.2mg, 80% yield) as a red solid, mp: 161-163 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.40 – 7.36 (m, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 3.88 – 3.81 (m, 1H), 3.53 (dd, *J* = 13.2, 5.7 Hz, 1H), 3.42 (m, 2H), 2.91 (dd, *J* = 13.5, 5.2 Hz, 1H), 2.34 (dd, *J* = 13.5, 10.6 Hz, 1H), 2.26 (m, 1H), 2.21 – 2.15 (m, 1H), 2.11 – 2.03 (m, 1H), 2.03 – 1.95 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.2, 145.4, 136.2, 135.6, 131.6, 130.9, 129.1, 121.0, 116.1, 114.3, 113.9, 112.8, 112.2, 75.5, 58.8, 46.7, 41.0, 32.2, 27.7, 23.3. **HRMS (ESI):** calcd. for $C_{22}H_{18}{}^{79}BrN_3$ $[M+H]^+$: 404.0757, found: 404.0761; calcd. for $C_{22}H_{18}{}^{81}BrN_3$ $[M+H]^+$: 406.0737, found: 406.0739.

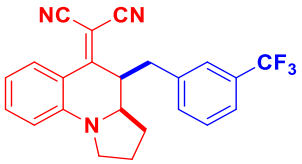
2-((3a*R*,4*R*)-4-(2-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3h



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (31.4 mg, 80% yield) as a red solid, mp: 172-174 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.41 – 7.37 (m, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 3.88 – 3.80 (m, 1H), 3.51 (dd, *J* = 9.3, 7.9 Hz, 1H), 3.48 – 3.42 (m, 1H), 3.42 – 3.37 (m, 1H), 3.34 (d, *J* = 14.0 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.32 – 2.24 (m, 1H), 2.23 – 2.11 (m, 2H), 2.06 – 1.95 (m, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -59.13 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 145.7, 136.3, 135.7, 131.7, 131.6, 129.1, 127.4, 126.7, 126.6, 116.3, 114.5, 113.1, 112.9, 112.6, 75.5, 59.0, 53.4, 46.7, 41.4, 29.6, 27.5, 23.2. **HRMS (ESI):** calcd. for $C_{23}H_{18}F_3N_3$ $[M+H]^+$: 394.1526, found: 394.1522.

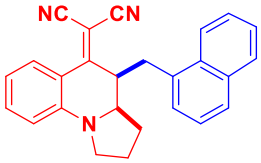
2-((3a*R*,4*R*)-4-(3-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3i



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (32.3mg, 82% yield) as a red solid, mp: 167-170 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 3.92 – 3.80 (m, 1H), 3.54 (t, *J* = 8.6 Hz, 1H), 3.47 – 3.38 (m, 2H), 3.03 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.45 (dd, *J* = 13.2, 11.0 Hz, 1H), 2.32-2.25 (m, 1H), 2.24 – 2.18 (m, 1H), 2.13 – 2.05 (m, 1H), 2.05 – 1.95 (m, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.70 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.8, 145.4, 137.5, 136.4, 132.6, 130.6 (d, *J* = 32.5 Hz), 139.0 (d, *J* = 10.0 Hz), 126.1 (q, *J* = 3.8 Hz), 125.0, 123.9 (d, *J* = 3.8 Hz), 122.8, 116.2, 114.1, 113.7, 112.7, 112.3, 75.4, 58.7, 46.7, 40.9, 32.5, 27.7, 23.3. **HRMS (ESI):** calcd. for $C_{23}H_{18}F_3N_3$ $[M+H]^+$: 394.1526, found: 394.1529.

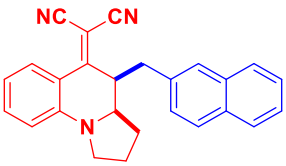
2-(4-(naphthalen-1-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3j



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (27.0 mg, 72% yield) as a red solid, mp: 177-179 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 6.9 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 3.88 (d, *J* = 6.4 Hz, 1H), 3.63 – 3.58 (m, 1H), 3.58 – 3.45 (m, 3H), 2.77 (dd, *J* = 13.4, 11.1 Hz, 1H), 2.35 – 2.22 (m, 3H), 2.04 (dd, *J* = 17.7, 8.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.4, 145.5, 136.1, 133.8, 132.8, 131.8, 129.5, 129.0, 127.9, 127.5, 126.1, 125.7, 125.1, 122.9, 116.0, 114.4, 113.0, 113.0, 112.3, 75.4, 59.0, 46.7, 40.9, 29.2, 27.8, 23.4. **HRMS (ESI):** calcd. for $C_{26}H_{21}N_3$ $[M+H]^+$: 376.1808, found: 376.1805.

2-((3a*R*,4*R*)-4-(naphthalen-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3k

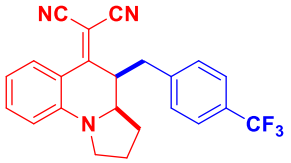


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (29.3 mg, 78% yield) as a red solid, mp: 174-176 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.47 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.43 (dd, *J* = 11.3, 4.1 Hz, 1H), 7.30 (s, 1H), 7.15 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.60 – 3.60 (m, 1H), 3.53 (d, *J* = 9.2 Hz, 1H), 3.44 (dd, *J* = 17.1, 9.5 Hz, 1H), 3.12 (dd, *J* = 13.5, 5.4 Hz, 1H), 2.55 (dd, *J* = 13.5, 10.4 Hz, 1H), 2.230 – 2.23 (m, 1H), 2.22 – 2.15 (m, 1H), 2.15 – 2.06 (m, 1H), 2.05 – 1.94 (m, 1H); **^{13}C**

NMR (125 MHz, $CDCl_3$) δ 170.7, 145.5, 136.1, 134.1, 133.2, 132.4, 129.2, 128.2, 127.9, 127.7, 127.5, 127.3, 126.2, 125.7, 116.0, 114.3, 113.8, 113.1, 112.2, 75.5, 58.9, 46.7, 41.1, 33.0, 27.8, 23.4. **HRMS (ESI):** calcd. for $C_{26}H_{22}N_3$ $[M+H]^+$: 376.1808, found: 376.1803.

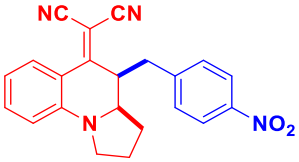
2-((3a*R*,4*R*)-4-(4-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3l



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product (35.4 mg, 90% yield) as a red solid, mp: 164-167 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 3.85 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.53 (t, *J* = 8.7 Hz, 1H), 3.49 – 3.45 (m, 1H), 3.42 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.02 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.45 (dd, *J* = 13.3, 10.7 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.23 – 2.16 (m, 1H), 2.2 – 2.04 (m, 1H), 2.04 – 1.95 (m, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.34 (s, *J* = 4.7, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.9, 145.5, 140.8, 136.3, 129.6, 129.3 (d, *J* = 31.3 Hz), 129.0, 125.3 (q, *J* = 3.8Hz), 125.2, 123.0, 116.2, 114.0 (d, *J* = 55.0 Hz), 112.7, 112.3, 75.3, 58.8, 46.7, 40.9, 32.6, 27.7, 23.3. **HRMS (ESI):** calcd. for $C_{23}H_{18}F_3N_3$ $[M+H]^+$: 394.1526, found: 394.1529.

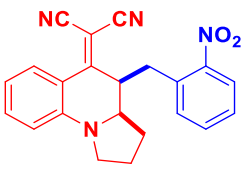
2-((3a*R*,4*R*)-4-(4-nitrobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3m



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (31.8 mg, 86% yield) as a red solid, mp: 177-180 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 3.90 – 3.81 (m, 1H), 3.53 (t, *J* = 8.6 Hz, 1H), 3.48 – 3.38 (m, 2H), 3.07 (dd, *J* = 13.4, 5.0 Hz, 1H), 2.49 (dd, *J* = 13.2, 10.9 Hz, 1H), 2.31 – 240 (m, 1H), 2.21 (dd, *J* = 11.4, 5.5 Hz, 1H), 2.12 – 2.03 (m, 1H), 2.03 – 1.96 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 146.9, 145.5, 144.6, 136.4, 130.1, 128.8, 123.5, 116.2, 114.0, 113.7, 112.5, 75.0, 58.7, 46.7, 40.7, 32.5, 27.7, 23.2. **HRMS (ESI):** calcd. for $C_{22}H_{18}N_4O_2$ $[M+H]^+$: 371.1503, found: 371.1505.

2-((3a*R*,4*R*)-4-(2-nitrobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3n

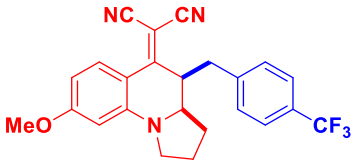


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product

(32.6 mg, 88% yield) as a red solid, mp: 182-184 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.46 – 7.41 (m, 1H), 6.78 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.70 – 3.65 (m, 1H), 3.63 (dd, *J* = 12.9, 3.3 Hz, 1H), 3.55 – 3.49 (m, 1H), 3.9 – 3.42 (m, 1H), 2.41 (dd, *J* = 12.7, 11.3 Hz, 1H), 2.35 – 2.20 (m, 3H), 2.08 – 1.98 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.4, 149.1, 145.8, 136.4, 133.2, 132.8, 132.8, 129.0, 128.6, 125.8, 116.3, 114.4, 113.2, 112.9, 112.7, 75.1, 59.0, 46.8, 40.3, 30.6, 27.6, 23.2. **HRMS (ESI):** calcd. for $C_{22}H_{18}N_4O_2$ $[M+H]^+$: 371.1503, found: 371.1501.

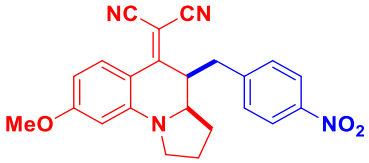
2-((3a*R*,4*R*)-8-methoxy-4-(4-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3o



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product (33.8 mg, 80% yield) as a red solid, mp: 178-181 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.1 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.33 (dd, *J* = 9.1, 2.2 Hz, 1H), 5.95 (d, *J* = 2.1 Hz, 1H), 3.89 (s, 3H), 3.85 – 3.79 (m, 1H), 3.50 (t, *J* = 8.5 Hz, 1H), 3.47 – 3.37 (m, 2H), 2.98 (dd, *J* = 13.5, 5.3 Hz, 1H), 2.45 (dd, *J* = 13.3, 10.2 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.21 – 2.14 (m, 1H), 2.11 – 2.02 (m, 1H), 2.02 – 1.94 (m, 6.6 Hz, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.34 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.4, 166.3, 147.6, 140.9, 131.1, 129.7, 129.3, 129.1, 125.3 (q, *J* = 3.8 Hz), 115.1, 114.6, 107.3, 105.0, 95.3, 71.6, 58.8, 55.5, 46.9, 41.1, 32.8, 27.8, 23.2. **HRMS (ESI):** calcd. for $C_{24}H_{20}F_3N_3O$ $[M+H]^+$: 424.1631, found: 424.1631.

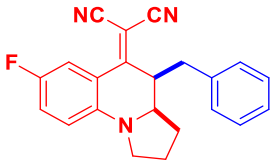
2-((3aR,4R)-8-methoxy-4-(4-nitrobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1H)-ylidene)malononitrile 3p



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:3) afforded the product (34.0 mg, 85% yield) as a yellow solid, mp: 175-178 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 9.1 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.34 (dd, *J* = 9.1, 1.9 Hz, 1H), 5.97 (d, *J* = 1.7 Hz, 1H), 3.89 (s, 3H), 3.86 – 3.78 (m, 1H), 3.52 (t, *J* = 9.1 Hz, 1H), 3.47 – 3.36 (m, 2H), 3.03 (dd, *J* = 13.3, 5.2 Hz, 1H), 2.50 (dd, *J* = 13.0, 10.7 Hz, 1H), 2.26 (d, *J* = 6.1 Hz, 1H), 2.21 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.09 – 1.96 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.8, 166.4, 147.6, 147.0, 144.6, 131.0, 130.2, 123.6, 114.9, 114.6, 107.1, 105.2, 95.3, 71.6, 58.8, 55.5, 46.9, 41.0, 32.8, 27.9, 23.2. **HRMS (ESI):** calcd. for $C_{23}H_{20}N_4O_3$ $[M+H]^+$:401.1608, found: 401.1606.

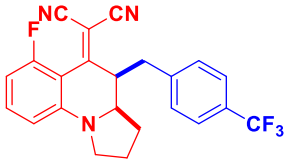
2-((3a*R*,4*R*)-4-benzyl-7-fluoro-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3q



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (**30.2 mg, 88% yield**) as a red solid, mp: 157-159 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 9.8, 2.7 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.28 – 7.23 (m, 2H), 7.23 – 7.16 (m, 1H), 7.00 – 6.88 (m, 2H), 6.53 (dd, *J* = 9.2, 4.5 Hz, 1H), 3.81 (dd, *J* = 8.6, 4.9 Hz, 1H), 3.50 (t, *J* = 9.1 Hz, 1H), 3.47 – 3.38 (m, 2H), 2.98 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.36 (dd, *J* = 13.2, 10.8 Hz, 1H), 2.30 – 2.23 (m, 1H), 2.22 – 2.15 (m, 1H), 2.15 – 2.04 (m, 1H), 2.05 – 1.94 (m, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -127.29 (s, 1F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.3, 153.7 (d, *J* = 235 Hz), 142.6, 136.4, 129.2, 128.5, 127.1, 124.1 (d, *J* = 22.5 Hz), 113.9 (d, *J* = 66.3 Hz), 113.7 (d, *J* = 58.8 Hz), 113.6 (d, *J* = 58.8 Hz), 112.3 (d, *J* = 7.5 Hz), 76.4, 58.9, 47.0, 41.5, 32.8, 27.7, 23.3. **HRMS (ESI):** calcd. for $C_{22}H_{18}FN_3$ $[M+H]^+$: 344.1558, found: 344.1561.

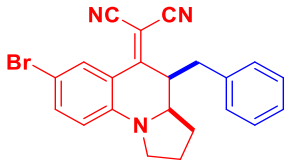
2-((3a*R*,4*R*)-6-fluoro-4-(4-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3r



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (32.9 mg, 80% yield) as a red solid, mp: 166-169 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 14.5, 8.2 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.44 (dd, *J* = 10.6, 8.3 Hz, 1H), 6.32 (d, *J* = 8.5 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.57 – 3.49 (m,, 2H), 3.34 (dd, *J* = 17.1, 9.5 Hz, 1H), 3.01 (dd, *J* = 13.4, 4.8 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.33 – 2.21 (m, 2H), 2.06 (dd, *J* = 20.5, 9.7 Hz, 2H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.36 (s, 3F); -101.23 (s, 1F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.1 (d, *J* = 2.5 Hz), 160.8 (d, *J* = 255.0 Hz), 145.9 (d, *J* = 5.0 Hz), 140.5, 136.1 (d, *J* = 11.3 Hz), 129.1, 125.4 (q, *J* = 6.3 Hz), 125.0, 122.9, 112.8, 112.5 (d, *J* = 2.5 Hz), 106.9 (d, *J* = 2.5 Hz), 102.9 (d, *J* = 22.5 Hz), 102.3 (d, *J* = 16.3 Hz), 81.6 (d, *J* = 3.8 Hz), 59.4, 46.9, 40.6, 32.5, 27.8, 23.5. **HRMS (ESI):** calcd. for $C_{23}H_{17}F_4N_3$ $[M+H]^+$: 412.1431, found: 412.1433.

2-((3a*R*,4*R*)-4-benzyl-7-bromo-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3s

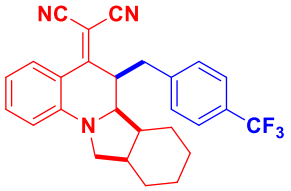


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (32.6 mg, 81% yield) as a red solid, mp: 182-184 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.38 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.19 (dd, *J* = 8.9, 5.7 Hz, 3H), 6.86 (d, *J* = 7.3 Hz, 2H), 6.39 (d, *J* = 9.0 Hz, 1H), 3.81 – 3.66 (m, 1H), 3.42 (t, *J* = 9.1 Hz, 1H), 3.38 – 3.33 (m, 1H), 3.32 – 3.26 (m, 1H), 2.89 (dd, *J* = 13.5, 5.0 Hz, 1H), 2.24 (dd, *J* = 13.3, 10.8 Hz, 1H), 2.21 – 2.15 (m, 1H), 2.14 – 2.07 (m, 1H), 2.06 – 1.98 (m, 1H), 1.98 – 1.88 (m, 1H); **^{13}C NMR**

(125 MHz, $CDCl_3$) δ 168.8, 144.3, 138.4, 136.3, 130.8, 129.1, 128.6, 127.2, 114.2, 113.9, 113.72, 113.3, 107.6, 58.9, 46.9, 41.2, 32.8, 27.7, 23.4. **HRMS (ESI):** calcd. for $C_{22}H_{18}{}^{79}BrN_3$ $[M+H]^+$: 404.0757, found: 404.0757; calcd. for $C_{22}H_{18}{}^{81}BrN_3$ $[M+H]^+$: 406.0737, found: 406.0740.

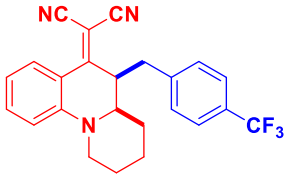
2-((6*R*,6a*R*,6b*S*)-6-(4-(trifluoromethyl)benzyl)-6a,6b,7,8,9,10,10a,11-octahydroisoindolo[2,1-*α*]quinolin-5(6H)-ylidene)malononitrile 3t



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:70) afforded the product (35.8 mg, 80% yield) as a red solid, mp: 168-171 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 3.94 (dd, *J* = 10.9, 2.8 Hz, 1H), 3.50 (dd, *J* = 9.8, 6.3 Hz, 1H), 3.39 – 3.30 (m, 1H), 3.23 (d, *J* = 9.9 Hz, 1H), 2.94 (dd, *J* = 13.5, 5.4 Hz, 1H), 2.48 (dd, *J* = 10.4, 4.9 Hz, 1H), 2.40 (dd, *J* = 13.5, 10.1 Hz, 2H), 1.83 (d, *J* = 14.0 Hz, 1H), 1.80 – 1.68 (m, 3H), 1.67 – 1.61 (m, 1H), 1.38 – 1.22 (m, 3H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.39 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.9, 145.9, 140.8, 136.3, 129.6, 129.3 (d, *J* = 32.5 Hz), 129.1, 125.3 (q, *J* = 3.8 Hz), 124.6 (d, *J* = 270.0 Hz), 116.0, 114.3, 113.7, 112.8, 111.9, 75.2, 57.1, 53.4, 39.2, 37.8, 36.3, 32.8, 28.5, 24.9, 23.4, 20.9. **HRMS (ESI):** calcd. for $C_{27}H_{24}F_3N_3$ $[M+H]^+$:448.1905, found: 448.1908.

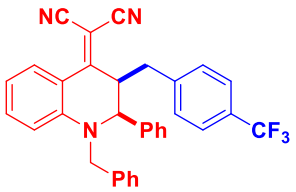
2-((5*R*)-5-(4-(trifluoromethyl)benzyl)-1,2,3,4,4a,5-hexahydro-6H-pyrido[1,2-*α*]quinolin-6-ylidene)malononitrile 3u



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (29.7 mg, 73% yield) as a red solid, mp: 176-178 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.31 – 7.26 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 4.27 (d, *J* = 14.3 Hz, 1H), 3.29 (d, *J* = 12.1 Hz, 1H), 3.20 – 3.13 (m, 1H), 3.11 – 3.02 (m, 1H), 2.89 – 2.78 (m, 2H), 1.88 (d, *J* = 13.1 Hz, 1H), 1.65 – 1.61 (m, 1H), 1.61 – 1.54 (m, 2H), 1.54 – 1.46 (m, 1H), 1.32 (dd, *J* = 12.9, 2.1 Hz, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.38 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.0, 145.3, 141.1, 136.6, 129.6, 129.4 (d, *J* = 32.5 Hz), 129.1, 127.3, 125.6 (q, *J* = 3.8 Hz), 125.1, 123.0, 120.8, 117.1, 114.4 (d, *J* = 2.5 Hz), 114.2, 114.0, 74.6, 60.8, 49.8, 46.3, 37.5, 28.3, 24.8, 24.1. **HRMS (ESI):** calcd. for $C_{24}H_{20}F_3N_3$ $[M+H]^+$: 408.1682, found: 408.1680.

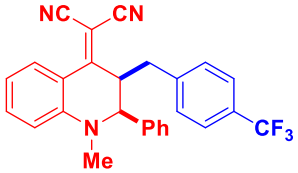
2-((2*S*,3*R*)-1-benzyl-2-phenyl-3-(4-(trifluoromethyl)benzyl)-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 3v



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:70) afforded the product (38.9 mg, 75% yield) as a orange solid, mp: 156-158 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 (q, *J* = 5.2 Hz, 3H), 7.37 – 7.32 (m, 3H), 7.31 (dd, *J* = 6.7, 4.9 Hz, 2H), 7.06 – 7.00 (m, 3H), 6.96 (dd, *J* = 6.4, 2.7 Hz, 2H), 6.87 (t, *J* = 7.6 Hz, 1H), 4.98 (d, *J* = 16.9 Hz, 1H), 4.52 (s, 1H), 4.12 (d, *J* = 16.9 Hz, 1H), 3.57 – 3.51 (m, 1H), 2.93 (dd, *J* = 7.4, 2.9 Hz, 2H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.47 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 146.3, 140.7, 138.0, 137.1, 136.8, 129.6, 129.4 (d, *J* = 10.0 Hz), 129.1, 128.9, 128.6, 128.1, 127.0, 125.7 (q, *J* = 3.8 Hz), 125.6, 125.1, 122.9, 117.3, 113.8, 113.6, 113.1, 112.1, 76.7, 62.7, 53.2, 48.9, 38.9.**HRMS (ESI):** calcd. for $C_{33}H_{24}F_3N_3$ $[M+H]^+$: 520.1995, found: 520.1995.

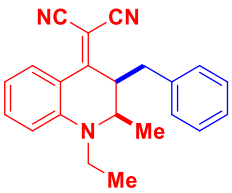
2-((2*S*,3*R*)-1-methyl-2-phenyl-3-(4-(trifluoromethyl)benzyl)-2,3-dihydroquinolin-4(1H)-ylidene)malononitrile 3w



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:75) afforded the product (30.6 mg, 69% yield) as a yellow solid, mp: 152-155 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.24 – 7.17 (m, 5H), 6.81 – 6.76 (m, 3H), 6.74 (t, *J* = 7.6 Hz, 1H), 4.25 (s, 1H), 3.49 – 3.42 (m, 1H), 3.01 (s, 3H), 2.85 (d, *J* = 8.3 Hz, 2H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -62.45 (s, 3F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 146.3, 140.9, 137.5, 136.8, 129.8, 129.5, 129.2, 128.6 (d, *J* = 3.8 Hz), 125.8 (q, *J* = 3.8 Hz), 125.2, 125.1, 122.9, 116.9, 113.9, 113.5, 113.3, 111.8, 76.0, 65.1, 48.2, 38.9, 38.4. **HRMS (ESI):** calcd. for $C_{27}H_{20}F_3N_3$ $[M+H]^+$: 4444.1682, found: 444.1684.

2-((2*R*,3*R*)-3-benzyl-1-ethyl-2-methyl-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 3x

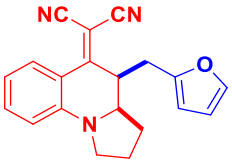


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:80) afforded the product (21.3 mg, 65% yield) as a red solid, mp: 156-158 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.14 (m, 1H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.60 (dd, *J* = 14.8, 8.1 Hz, 2H), 3.45 (dd, *J* = 14.8, 7.3 Hz, 1H), 3.29 (q, *J* = 6.4 Hz, 1H), 3.21 (dd, *J* = 14.9, 7.3 Hz, 1H), 3.06 (t, *J* = 7.6 Hz, 1H), 2.64 – 2.49 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 144.1,

136.8, 136.5, 129.0, 128.8, 128.6, 1267.0, 115.7, 114.6, 114.1, 112.4, 112.2, 74.24, 54.7, 46.23, 44.33, 38.2, 17.0, 12.7. **HRMS (ESI):** calcd. for $C_{22}H_{21}N_3$ $[M+H]^+$: 328.1808, found: 328.1800.

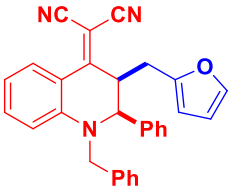
2-((3a*R*,4*R*)-4-(furan-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)-malononitrile 5a



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (19.2 mg, 61% yield) as a red solid, mp: 187-189 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.35 (d, *J* = 1.1 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 6.27 (dd, *J* = 2.9, 2.0 Hz, 1H), 5.85 (d, *J* = 3.0 Hz, 1H), 3.86 – 3.77 (m, 1H), 3.52 – 3.46 (m, 2H), 3.39 (dd, *J* = 17.0, 9.1 Hz, 1H), 2.95 (dd, *J* = 14.8, 4.8 Hz, 1H), 2.47 (dd, *J* = 14.8, 10.0 Hz, 1H), 2.70 – 2.20(m, *J* = 13.9, 8.8, 7.0 Hz, 1H), 2.19 – 2.12 (m, 1H), 2.06 – 1.93 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.1, 150.7, 145.4, 142.0, 136.0, 129.1, 116.0, 114.6, 113.5, 112.7, 112.2, 110.4, 107.5, 75.00, 58.5, 46.6, 39.4, 27.6, 25.1, 23.2. **HRMS (ESI):** calcd. for $C_{20}H_{17}N_3O$ $[M+H]^+$: 316.1444, found: 316.1442.

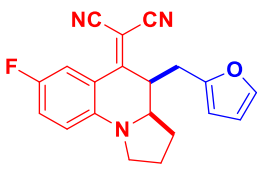
2-((2*S*,3*R*)-1-benzyl-3-(furan-2-ylmethyl)-2-phenyl-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 5b



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:70) afforded the product (24.3 mg, 55% yield) as a yellow solid, mp: 193-196 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.29 (s, 1H), 7.27 (d, *J* = 1.9 Hz, 2H), 7.27 – 7.23 (m, 4H), 7.18 (d, *J* = 5.7 Hz, 2H), 6.93 (dd, *J* = 7.1, 2.1 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.17 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.75 (d, *J* = 3.0 Hz, 1H), 4.79 (d, *J* = 17.0 Hz, 1H), 4.53 (d, *J* = 1.5 Hz, 1H), 4.10 (d, *J* = 17.0 Hz, 1H), 3.60 – 3.54 (m, 1H), 2.93 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.83 (dd, *J* = 14.8, 7.7 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 150.2, 146.2, 142.3, 138.2, 136.9, 136.5, 129.3, 129.0, 128.9, 128.5, 127.8, 126.5, 125.7, 117.1, 113.9, 113.6, 112.7, 112.1, 110.4, 107.9, 63.7, 53.6, 46.6, 32.0. **HRMS (ESI):** calcd. for $C_{30}H_{23}N_3O$ $[M+H]^+$: 442.1914, found: 442.1911.

2-((3a*R*,4*R*)-7-fluoro-4-(furan-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5c

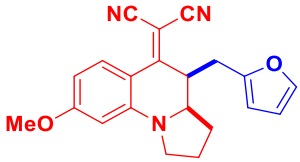


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:70) afforded the product

(25.6 mg, 77% yield) as a red solid, mp: 183-185 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 9.9, 2.8 Hz, 1H), 7.35 (d, *J* = 1.1 Hz, 1H), 7.21 – 7.09 (m,1H), 6.50 (dd, *J* = 9.2, 4.5 Hz, 1H), 6.27 (dd, *J* = 3.0, 1.9 Hz, 1H), 5.87 (d, *J* = 3.0 Hz, 1H), 3.85 – 3.71 (m, 1H), 3.52 – 3.48 (m, 1H), 3.48 – 3.44 (m, 1H), 3.39 (dd, *J* = 17.0, 8.9 Hz, 1H), 2.96 (dd, *J* = 14.9, 4.8 Hz, 1H), 2.47 (dd, *J* = 14.9, 10.0 Hz, 1H), 2.28 – 2.20 (m, 1H), 2.20 – 2.12 (m, 1H), 2.07 – 2.00 (m, 1H), 2.00 – 1.92 (m, 1H); **^{19}F NMR** (470 MHz, $CDCl_3$): δ -127.18 (s, 1F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.76, 153.71(d, *J* = 160.0 Hz), 150.5, 142.6, 142.1, 124.2(d, *J* = 88.8 Hz), 114.0, 113.9, 113.5, 113.2, 112.1, 110.5, 107.7(d, *J* = 5 Hz), 76.0, 58.6, 47.0, 39.5, 27.6, 25.2, 23.2. **HRMS (ESI):** calcd. for $C_{20}H_{16}FN_3O$ $[M+H]^+$: 334.1350, found: 334.1345.

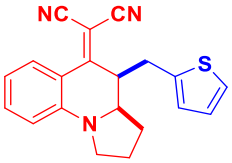
2-((3a*R*,4*R*)-4-(furan-2-ylmethyl)-8-methoxy-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5d



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (21.7 mg, 63% yield) as a yellow solid, mp: 185-187 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 9.1 Hz, 1H), 7.33 (d, *J* = 0.8 Hz, 1H), 6.32 – 6.22 (m, 2H), 5.92 (d, *J* = 2.2 Hz, 1H), 5.86 (d, *J* = 3.0 Hz, 1H), 3.86 (s, 3H), 3.80 – 3.74 (m, 1H), 3.49 – 3.42 (m, 2H), 3.38 (dd, *J* = 17.0, 8.9 Hz, 1H), 2.92 (dd, *J* = 14.8, 5.0 Hz, 1H), 2.45 (dd, *J* = 14.9, 9.5 Hz, 1H), 2.25 – 2.18 (m, 1H), 2.16 – 2.10 (m, 1H), 2.02 – 1.92 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.6, 166.1, 150.8, 147.6, 141.9, 131.1, 115.5, 114.2, 110.4, 107.5, 107.2, 104.8, 95.2, 71.2, 58.5, 55.4, 46.8, 39.8, 27.7, 25.4, 23.1. **HRMS (ESI):** calcd. for $C_{21}H_{19}N_3O_2$ $[M+H]^+$:346.1550, found: 346.1556.

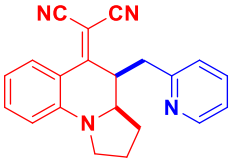
2-((3a*R*,4*R*)-4-(thiophen-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5e



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) afforded the product (21.5 mg, 65% yield) as a red solid, mp: 189-191 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.44 – 7.36 (m, 1H), 7.16 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.73 – 6.68 (m, 1H), 6.66 (d, *J* = 3.0 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 3.87 – 3.79 (m, 1H), 3.51 (dd, *J* = 13.2, 5.5 Hz, 1H), 3.47 – 3.42 (m, 1H), 3.42 – 3.34 (m, 1H), 3.16 (dd, *J* = 14.6, 5.0 Hz, 1H), 2.65 (dd, *J* = 14.6, 10.3 Hz, 1H), 2.80 – 2.22 (m, 1H), 2.21 – 2.14 (m, 1H), 2.10 – 2.03 (m, 1H), 2.02 – 1.93 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.3, 145.4, 138.5, 136.1, 129.4, 127.1, 126.5, 124.4, 116.0, 114.4, 113.8, 112.6, 112.2, 75.7, 58.8, 46.6, 41.7, 27.7, 26.6, 23.3. **HRMS (ESI):** calcd. for $C_{20}H_{17}N_3S$ $[M+H]^+$: 332.1216, found: 332.1215.

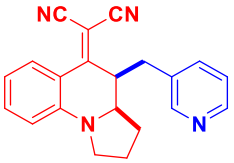
2-((3a*R*,4*R*)-4-(pyridin-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5f



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:5) afforded the product (28.0 mg, 86% yield) as a red solid, mp: 189-191 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 – 8.47 (m, 1H), 7.93 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.41 – 7.36 (m, 1H), 7.20 – 7.12 (m, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.68 (dd, *J* = 11.3, 3.9 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.67 – 3.62 (m, 1H), 3.52 – 3.46 (m, 1H), 3.40 (dd, *J* = 17.2, 9.5 Hz, 1H), 3.14 (dd, *J* = 13.4, 4.7 Hz, 1H), 2.54 (dd, *J* = 13.4, 9.9 Hz, 1H), 2.28 – 2.20 (m, 1H), 2.19 – 2.13 (m, 1H), 2.13 – 2.03 (m, 1H), 2.03 – 1.94 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.4, 157.3, 149.6, 145.5, 136.3, 136.1, 129.00, 123.4, 121.9, 115.9, 114.6, 113.5, 112.8, 112.3, 74.8, 58.9, 46.6, 40.3, 35.3, 27.8, 23.3. **HRMS (ESI):** calcd. for $C_{21}H_{18}N_4$ $[M+H]^+$: 327.1604, found: 327.1607.

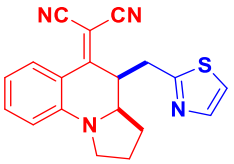
2-((3a*R*,4*R*)-4-(pyridin-3-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5g



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:3) afforded the product (27.4 mg, 84% yield) as a red solid, mp: 183-186 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 – 8.44 (m, 1H), 8.07 (d, *J* = 1.5 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.23 (dd, *J* = 7.7, 4.9 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 3.90 – 3.80 (m, 1H), 3.53 (t, *J* = 8.6 Hz, 1H), 3.47 – 3.35 (m, 2H), 2.95 (dd, *J* = 13.7, 5.1 Hz, 1H), 2.40 (dd, *J* = 13.6, 10.7 Hz, 1H), 2.30 – 2.24 (m, 1H), 2.23 – 2.17 (m, 1H), 2.13 – 2.05 (m, 1H), 2.05 – 1.95 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 150.0, 148.4, 145.4, 136.8, 136.4, 132.3, 129.0, 123.3, 116.3, 114.1, 113.8, 112.6, 112.3, 75.2, 58.7, 46.7, 40.8, 29.8, 27.7, 23.3. **HRMS (ESI):** calcd. for $C_{21}H_{18}N_4$ $[M+H]^+$: 326.1531, found: 326.1536.

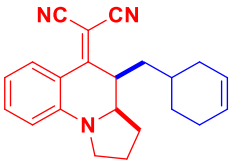
2-(4-(thiazol-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5h



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:5) afforded the product (26.6 mg, 80% yield) as a red solid, mp: 195-197 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 3.3 Hz, 1H), 7.44 – 7.35 (m, 1H), 7.24 (d, *J* = 3.3 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 3.89 – 3.80 (m, 1H), 3.71 – 3.62 (m, 1H), 3.50 (dd, *J* = 13.2, 5.5 Hz, 1H), 3.45 – 3.34 (m, 2H), 2.83 (dd, *J* = 14.7, 9.3 Hz, 1H), 2.28 – 2.21 (m, 1H), 2.21 – 2.14 (m, 1H), 2.10 – 2.01 (m, 1H), 2.01 – 1.92 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.3, 165.4, 145.4, 142.7, 136.3, 129.4, 119.3, 116.3, 114.4, 113.5, 112.6, 112.4, 75.4, 58.9, 46.6, 40.4, 30.1, 27.9, 23.2. **HRMS (ESI):** calcd. for $C_{19}H_{16}N_4S$ $[M+H]^+$: 333.1168, found: 333.1171.

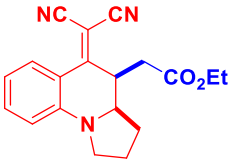
2-((3a*R*,4*R*)-4-(cyclohex-3-en-1-ylmethyl)-2,3,3*a*,4-tetrahydropyrrolo[1,2-a]quinolin-5(1H)-ylidene)malononitrile 5i



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:80) afforded the product (15.3 mg, 67% yield) as a red solid, mp: 198-201 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (t, *J* = 8.8 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 5.61 (d, *J* = 34.7 Hz, 2H), 3.78 (d, *J* = 4.2 Hz, 1H), 3.46 (t, *J* = 8.8 Hz, 1H), 3.32 (dd, *J* = 16.3, 7.8 Hz, 1H), 3.23 – 3.13 (m, 1H), 2.35 (d, *J* = 17.0 Hz, 1H), 2.27 – 1.85 (m, 8H), 1.71 – 1.56 (m, 2H), 1.55 – 1.44 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.3, 145.5, 136.0, 129.1, 127.0, 125.7, 115.7, 114.7, 114.5, 113.0, 112.0, 74.8, 59.5, 46.7, 37.5, 33.5, 31.8, 31.2, 29.8, 27.8, 24.7, 23.4. **HRMS (ESI):** calcd. for C22H23N3 $[M+H]^+$: 330.1965, found: 330.1962.

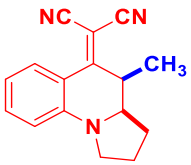
Ethyl 2-((3a*R*,4*R*)-5-(dicyanomethylene)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*α*]quinolin-4-yl) acetate 5j



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product (16.0 mg, 50% yield) as a red oily.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 4.21 – 4.05 (m, 2H), 3.82 – 3.73 (m, 1H), 3.68 – 3.61 (m, 1H), 3.46 (t, *J* = 9.0 Hz, 1H), 3.35 (dd, *J* = 17.5, 9.3 Hz, 1H), 2.56 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.22 (dd, *J* = 13.1, 6.7 Hz, 1H), 2.18 (d, *J* = 7.6 Hz, 1H), 2.17 – 2.13 (m, 1H), 2.01 – 1.90 (m, 1H), 1.86 – 1.77 (m, 1H), 1.26 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.5, 169.8, 145.3, 136.2, 129.1, 116.3, 114.5, 113.9, 112.8, 112.3, 75.3, 61.3, 58.7, 46.6, 36.1, 31.8, 28.0, 23.1, 14.0. **HRMS (ESI):** calcd. for $C_{19}H_{19}N_3O_2$ $[M+H]^+$: 322.1550, found: 322.1552.

2-((3a*R*,4*R*)-4-methyl-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5k

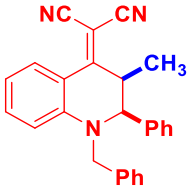


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:25) afforded the product (13.2 mg, 53% yield) as a red solid, mp: 129-131 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.42 – 7.31 (m, 1H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 8.5 Hz, 1H), 3.73 – 3.63 (m, 1H), 3.48 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.38 (dd, *J* = 17.4, 8.9 Hz, 1H), 3.24 – 3.17 (m, 1H), 2.25 – 2.18 (m, 1H), 2.12 – 2.05 (m, 1H), 2.02 – 1.94 (m, 1H), 1.94 – 1.86 (m, 1H), 0.99 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.9, 145.9, 136.3, 129.1, 115.9,

115.0, 114.4, 112.6, 112.5, 72.3, 58.2, 46.8, 35.0, 27.5, 23.1, 11.7. **HRMS (ESI):** calcd. for $C_{16}H_{15}N_3$ $[M+H]^+$: 250.1339, found: 250.1340.

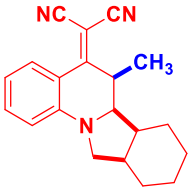
2-((2*S*,3*R*)-1-benzyl-3-methyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 5l



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:70) afforded the product ((19.2 mg, 51% yield) as a yellow solid, mp: 146-149 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.22 (dd, *J* = 12.5, 4.5 Hz, 3H), 7.17 – 7.13 (m, 2H), 6.95 (dd, *J* = 7.0, 2.1 Hz, 2H), 6.74 – 6.63 (m, 2H), 4.75 (d, *J* = 17.1 Hz, 1H), 4.43 (d, *J* = 1.4 Hz, 1H), 4.12 (d, *J* = 17.1 Hz, 1H), 3.35 (dd, *J* = 6.9, 1.8 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.1, 146.2, 138.6, 138.5, 136.9, 136.5, 136.4, 129.2, 129.2, 129.0, 128.9, 128.9, 128.5, 127.7, 126.2, 126.2, 125.6, 116.9, 114.1, 113.7, 113.6, 113.3, 112.1, 112.0, 75.3, 66.3, 53.7, 41.7, 19.7, 19.7. **HRMS (ESI):** calcd. for $C_{26}H_{21}N_3$ $[M+H]^+$: 376.1808, found: 376.1813.

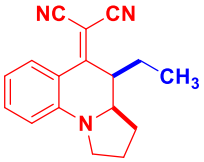
2-((6*R*,6a*R*,6b*S*)-6-methyl-6a,6b,7,8,9,10,10a,11-octahydroisoindolo[2,1-*α*]quinolin-5(6*H*)-ylidene)malononitrile 5m



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product (17.3 mg, 57% yield) as a red solid, mp: 137-139 ℃

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.39 – 7.30 (m, 1H), 6.69 – 6.59 (m, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 3.77 (dd, *J* = 10.6, 3.3 Hz, 1H), 3.44 (dd, *J* = 9.9, 6.2 Hz, 1H), 3.19 (d, *J* = 9.9 Hz, 1H), 3.09 (dd, *J* = 6.9, 3.4 Hz, 1H), 2.41 – 2.27 (m, 2H), 1.82 – 1.68 (m, 4H), 1.66 – 1.56 (m, 2H), 1.35 – 1.25 (m, 3H), 0.94 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.0, 146.4, 136.2, 129.2, 115.7, 115.1, 114.3, 112.7, 112.1, 72.4, 56.5, 53.5, 37.8, 36.3, 33.5, 28.7, 25.0, 23.5, 21.1, 11.9. **HRMS (ESI):** calcd. for $C_{20}H_{21}N_3$ $[M+H]^+$: 304.1808, found: 304.1806.

2-((3a*R*,4*R*)-4-ethyl-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5n



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:80) afforded the product (14.7 mg, 56% yield) as a red oily.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.37 – 7.32 (m, 1H), 6.68 – 6.60 (m, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 3.83 – 3.68 (m, 1H), 3.47 (dd, *J* = 13.3, 5.4 Hz, 1H), 3.30 (dd, *J* = 17.3, 9.2 Hz,

1H), 3.08 – 3.02 (m, 1H), 2.23 – 2.17 (m, 1H), 2.09 (dd, J = 11.2, 5.6 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.73 –1.62 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.9, 145.6, 136.1, 129.0, 115.7, 114.7, 114.6, 112.6, 112.1, 74.6, 58.8, 46.6, 41.1, 27.4, 23.3, 19.4, 10.9. **HRMS (ESI):** calcd. for $C_{17}H_{17}N_3$ $[M+H]^+$: 264.1495, found: 264.1495.

4. Crystal Structures and Data

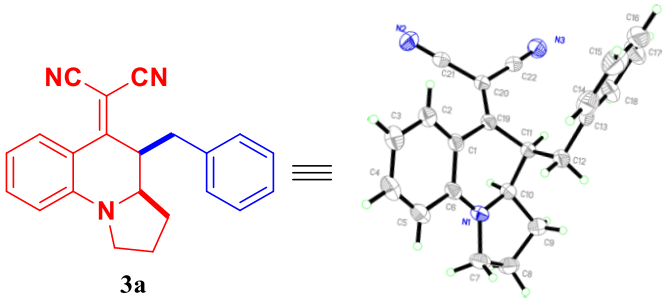


Table 1. Crystal data and structure refinement for 3a.

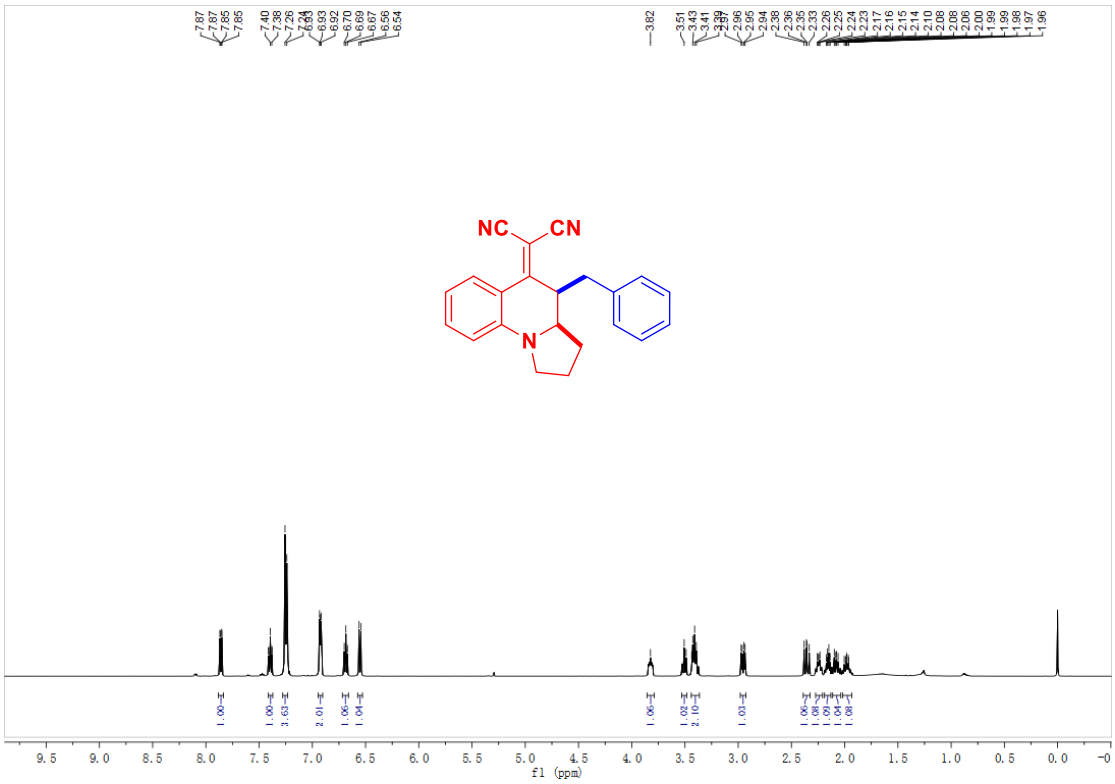
Identification code	3a
Empirical formula	$C_{22}H_{19}N_3$
Formula weight	325.40
Temperature	293(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.6563(6) A alpha = 90 deg.
	b = 9.6499(4) A beta = 104.392(5) deg.
	c = 14.6371(7) A gamma = 90 deg.
Volume	1731.55(13) A^3
Z, Calculated density	4, 1.248 Mg/m^3
Absorption coefficient	0.580 mm^-1
F(000)	688
Crystal size	0.230 x 0.210 x 0.180 mm
Theta range for data collection	4.140 to 67.219 deg.
Limiting indices	-15<=h<=11, -11<=k<=8, -13<=l<=17
Reflections collected / unique	5821 / 3076 [R(int) = 0.0300]
Completeness to theta = 67.219	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3076 / 0 / 227
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1287
R indices (all data)	R1 = 0.0690, wR2 = 0.1457
Extinction coefficient	0.0097(7)
Largest diff. peak and hole	0.169 and -0.209 e.A^-3

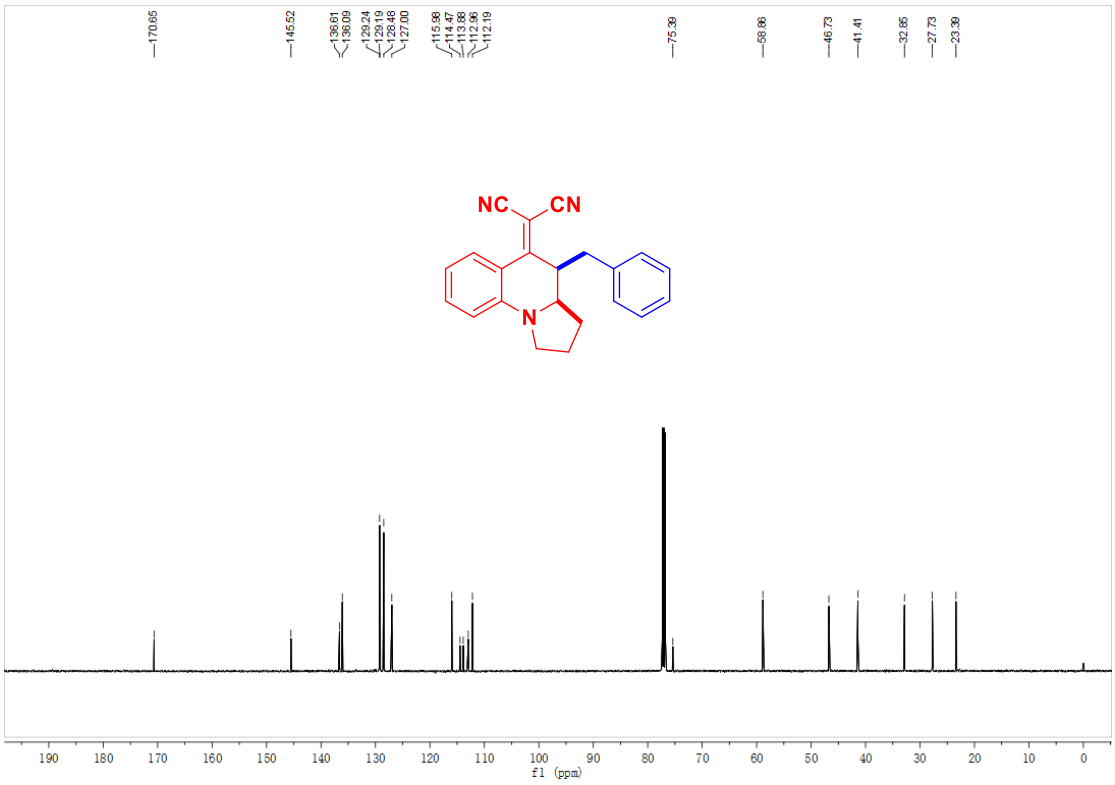
References:

1. (a) W. N. Nijhuis, W. Verboom and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1987, **109**, 3136-3138; (b) W. N. Nijhuis, W. Verboom, A. A. El-Fadl, S. Harkema and D. N. Reinhoudt, *J. Org. Chem.*, 1989, **54**, 199-209; (c) R. Deme, M. Schlich, Z. Mucsi, G. Karvaly, G. Tóth and P. Mátyus, *Arkivoc*, 2016, **2016**, 164-196.

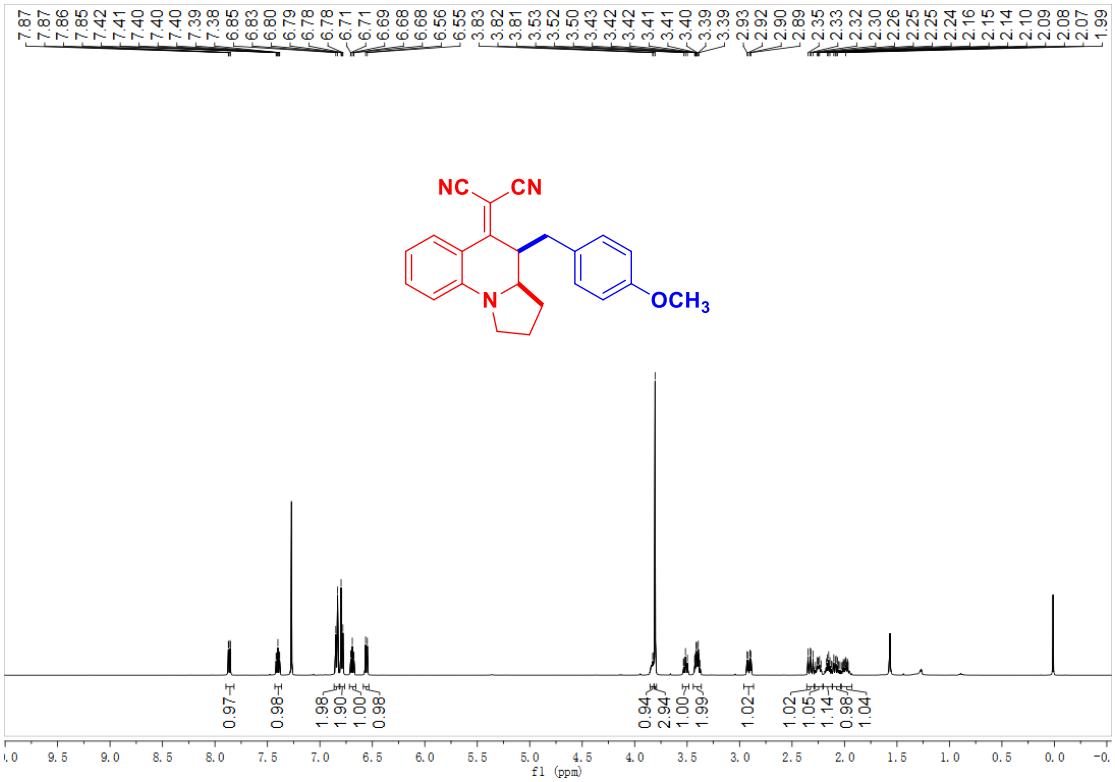
5. ^{1}H and ^{13}C NMR Spectra

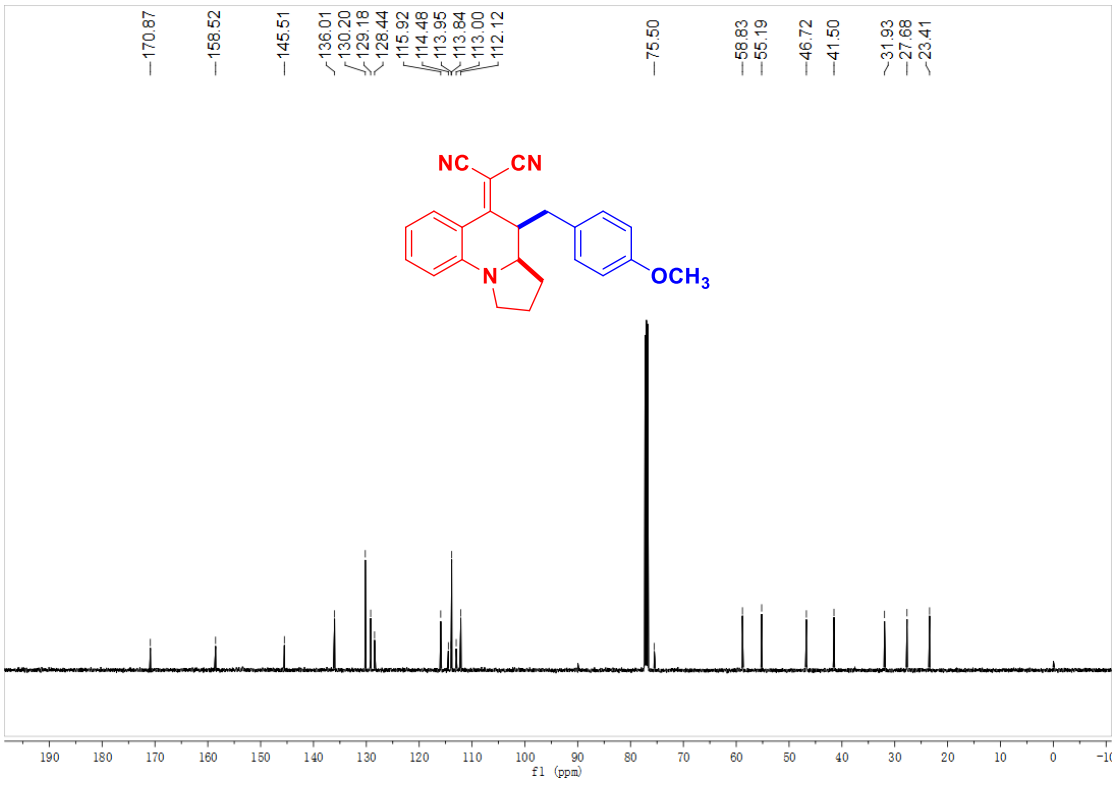
2-(4-benzyl-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1*H*)-ylidene)malononitrile 3a



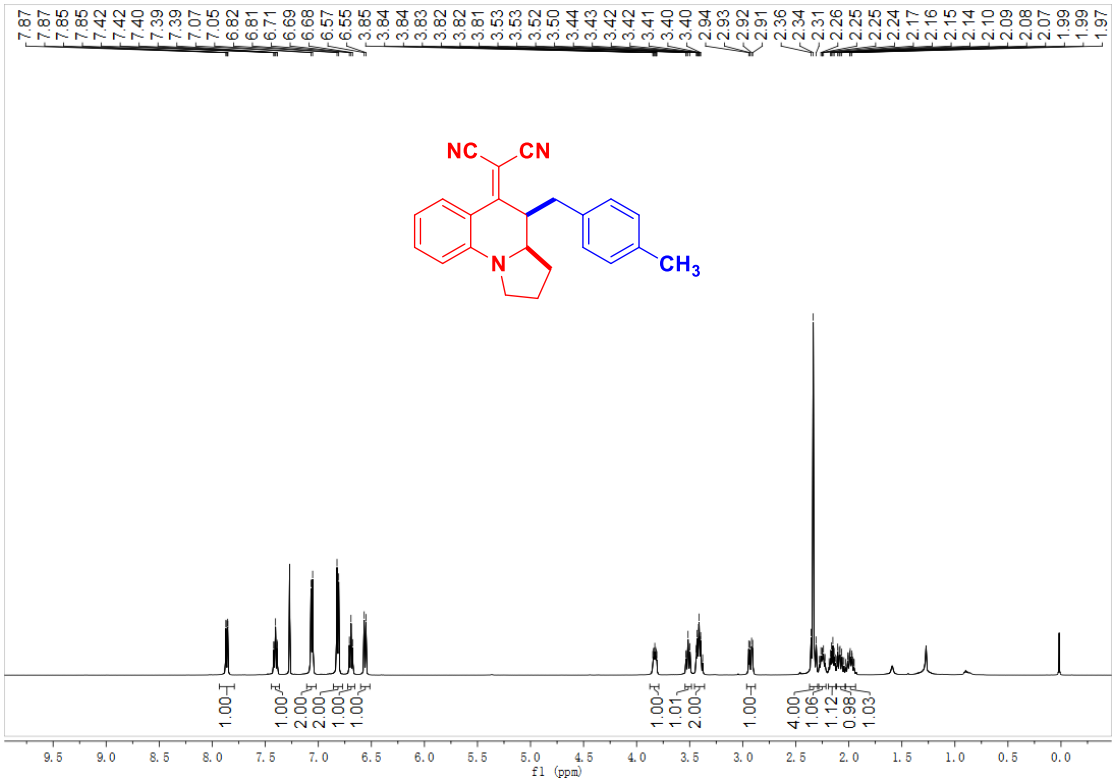


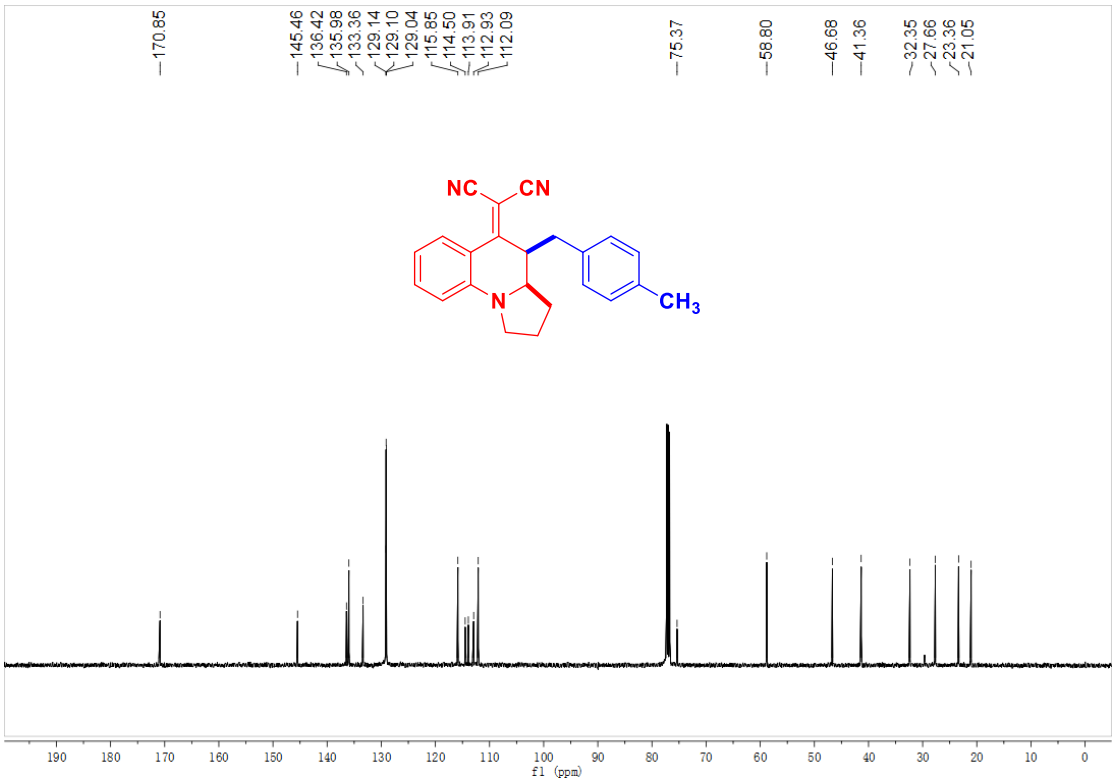
2-((3a*R*,4*R*)-4-(4-methoxybenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3b



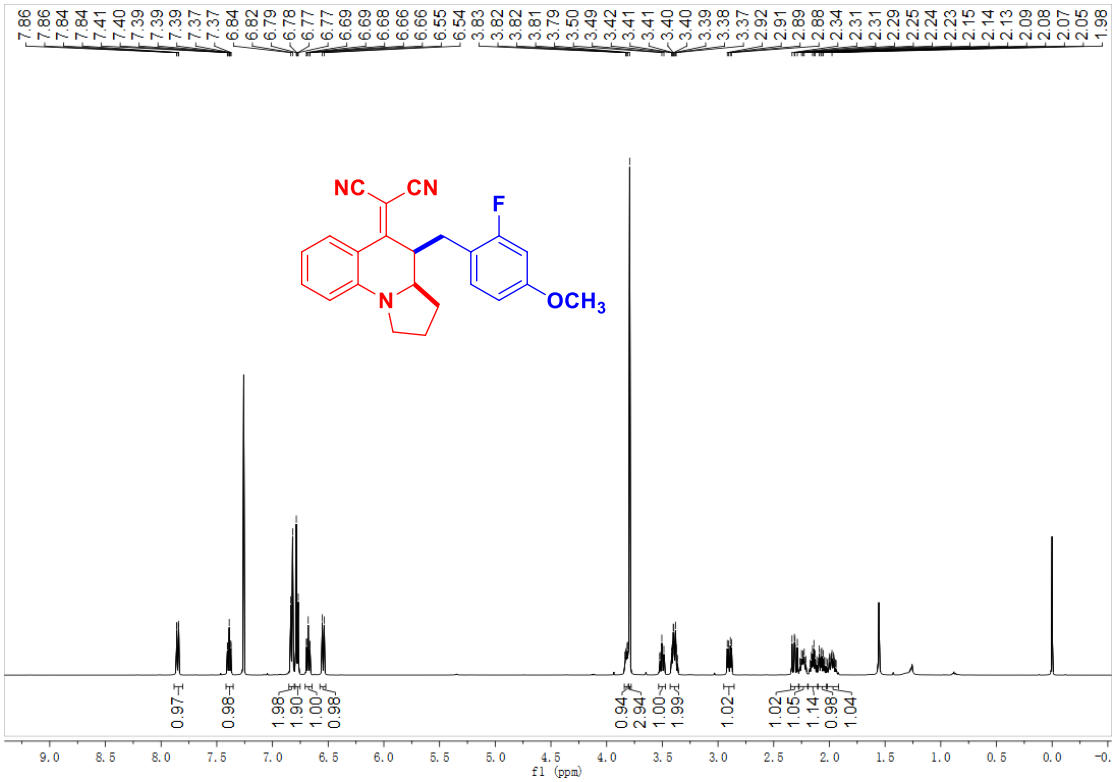


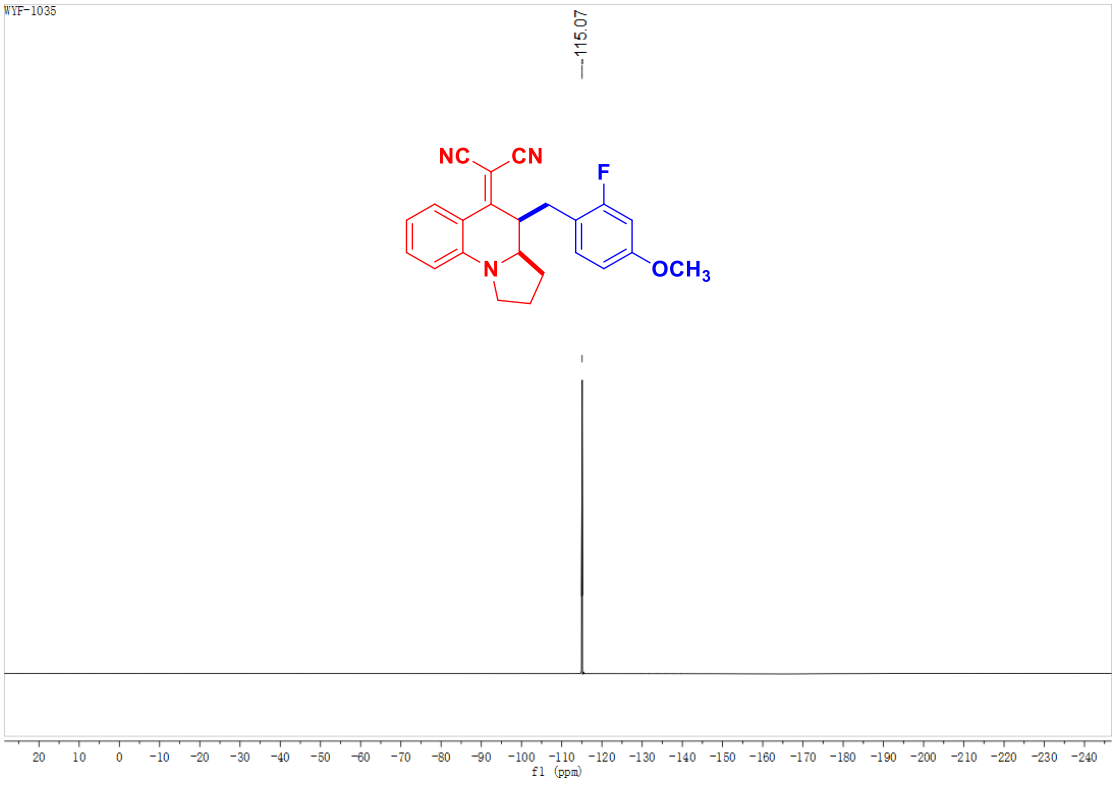
2-((3a*R*,4*R*)-4-(4-methylbenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3c

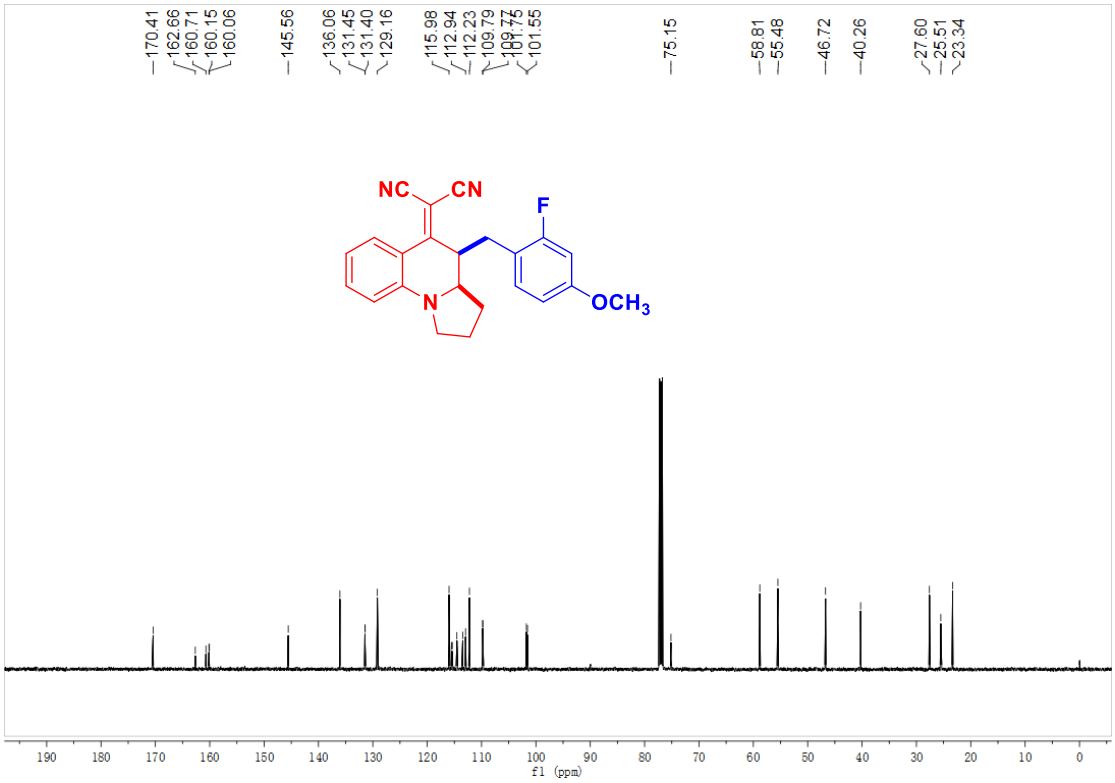




2-((3a*R*,4*R*)-4-(2-fluoro-4-methoxybenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1*H*)-ylidene)malononitrile 3d



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160.15
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136.06
131.45
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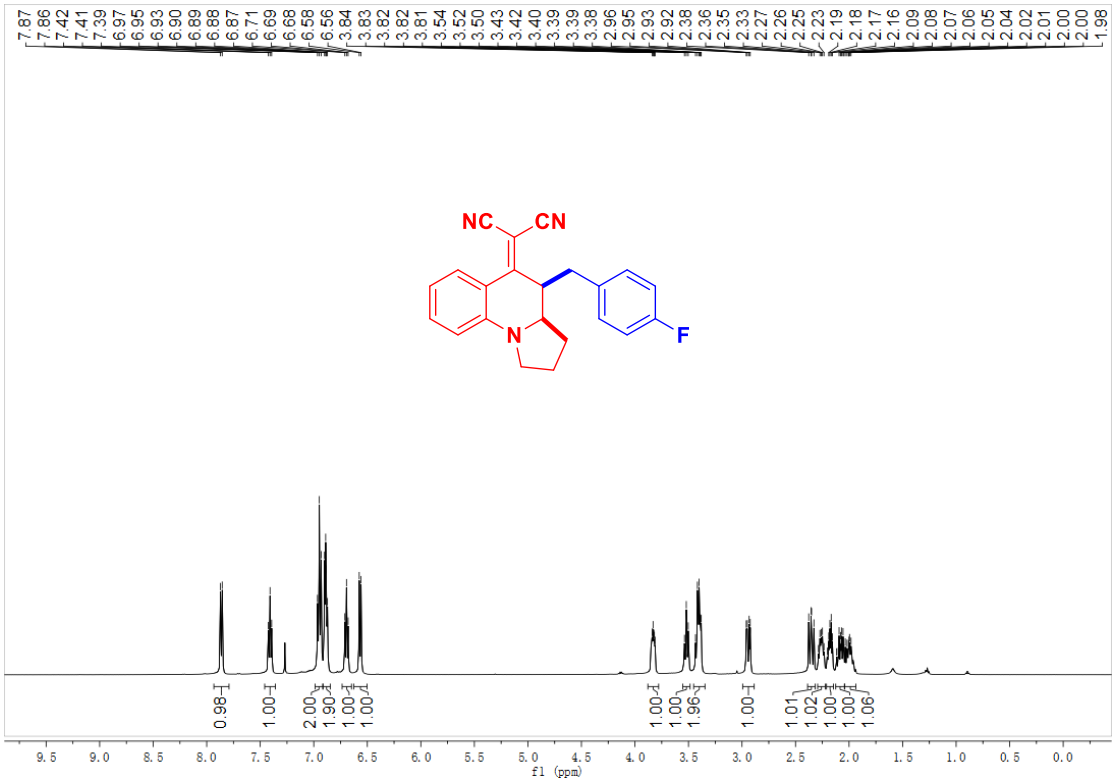
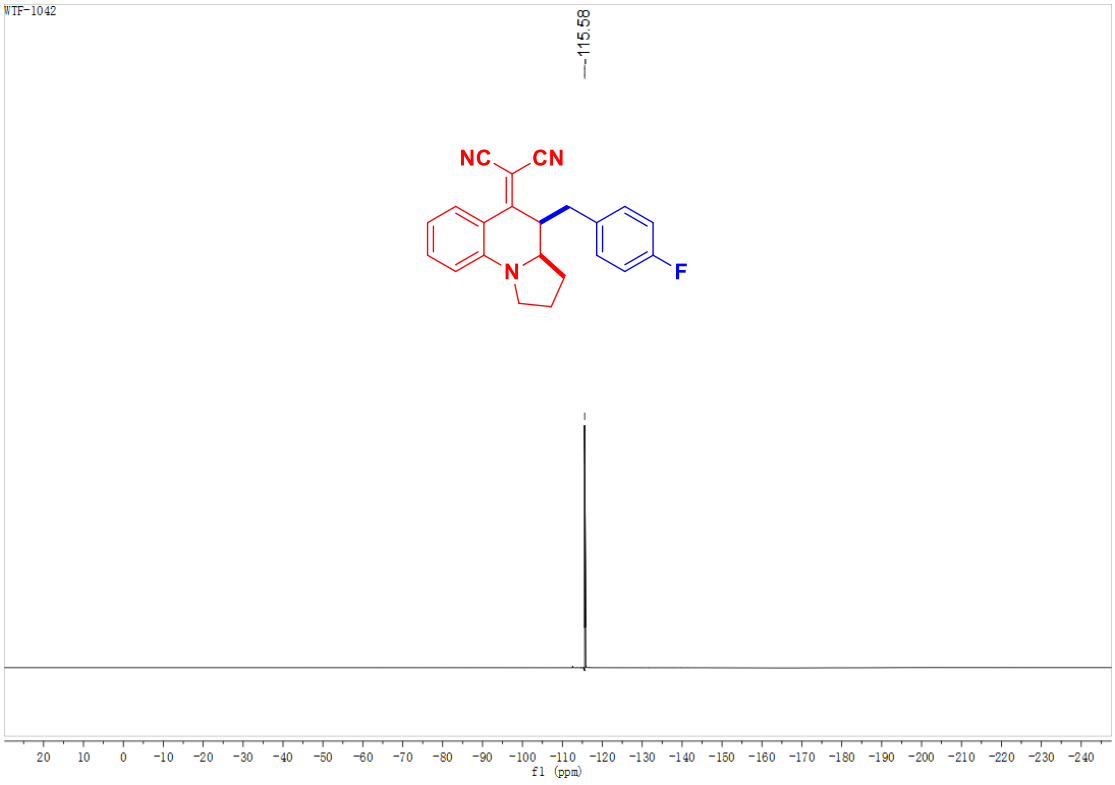
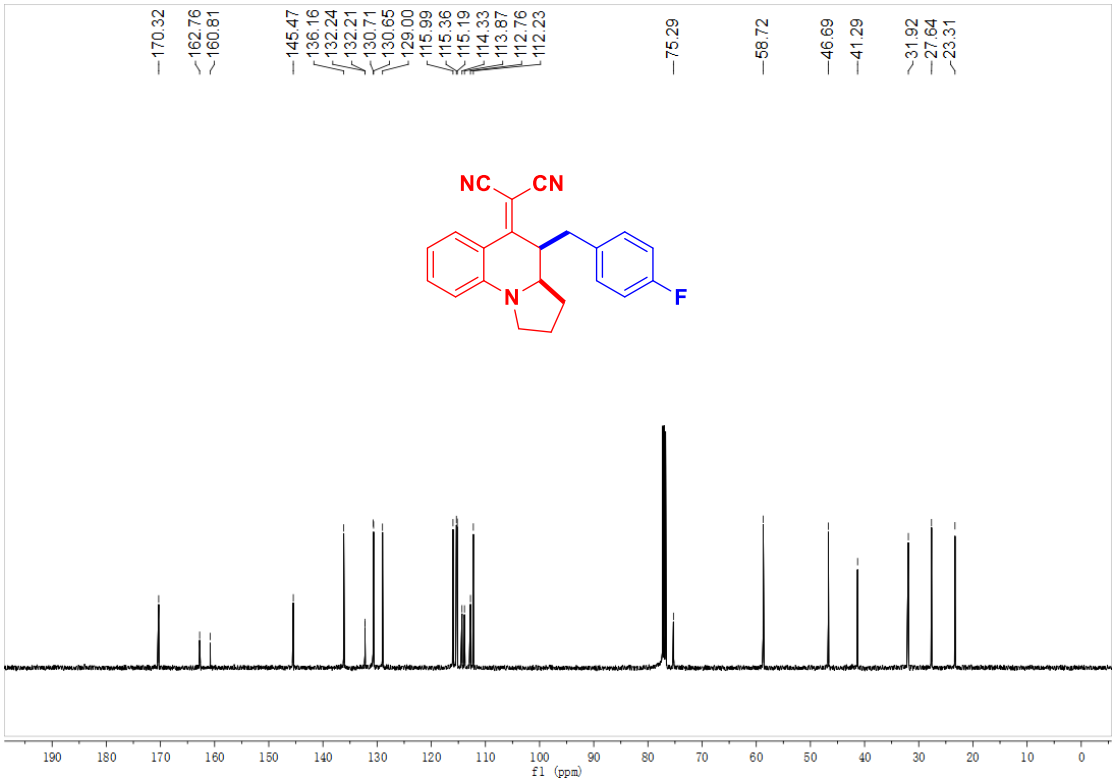
112.23
109.79
101.55
75.15
58.81
55.48
46.72
40.26
27.60
25.51
23.34
NC
CN
F
N
OCH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-((3a*R*,4*R*)-4-(4-fluorobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3e



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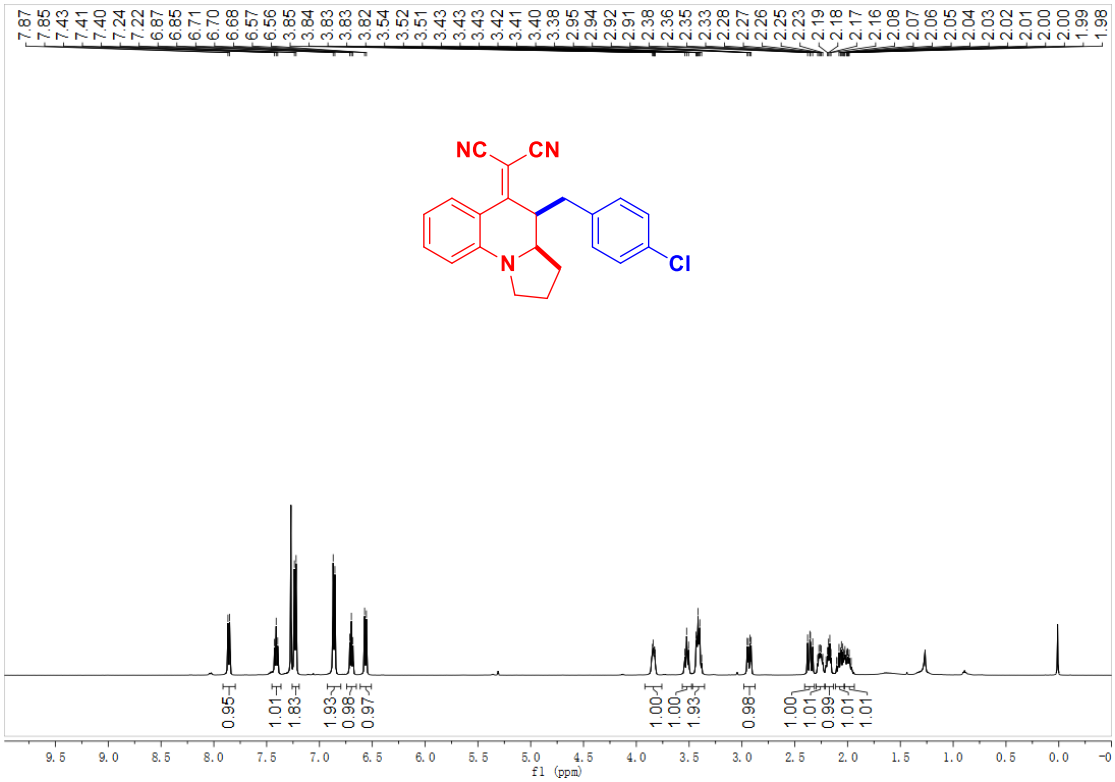
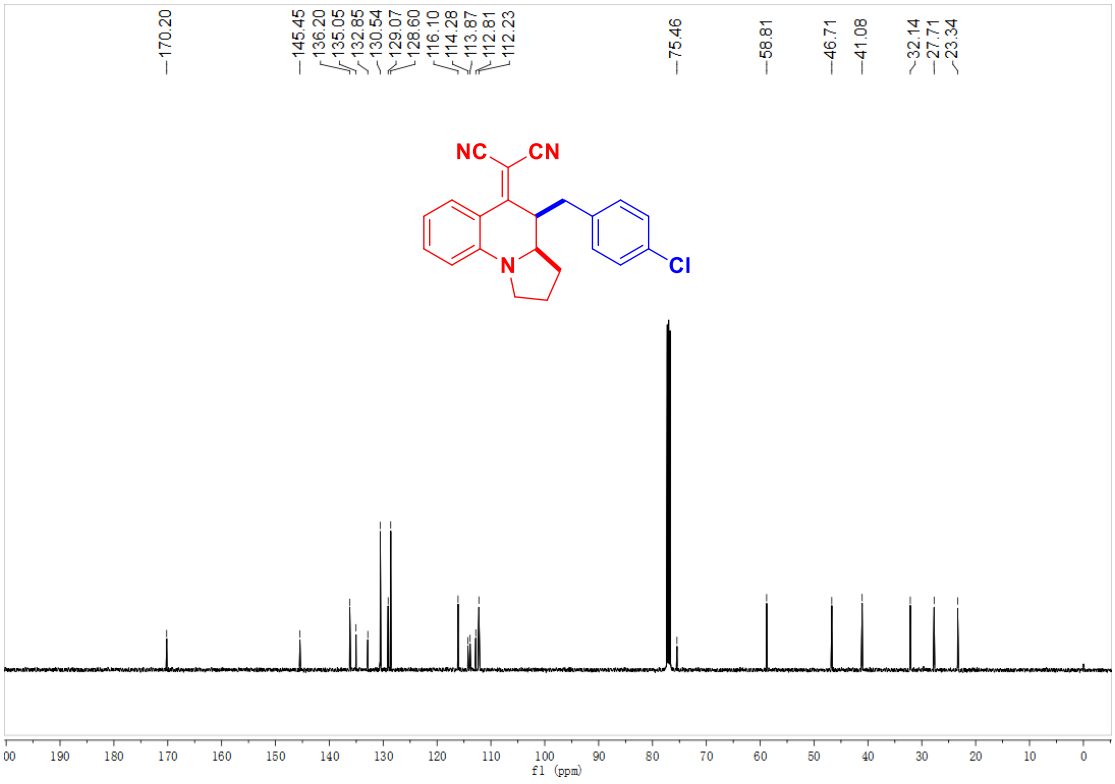
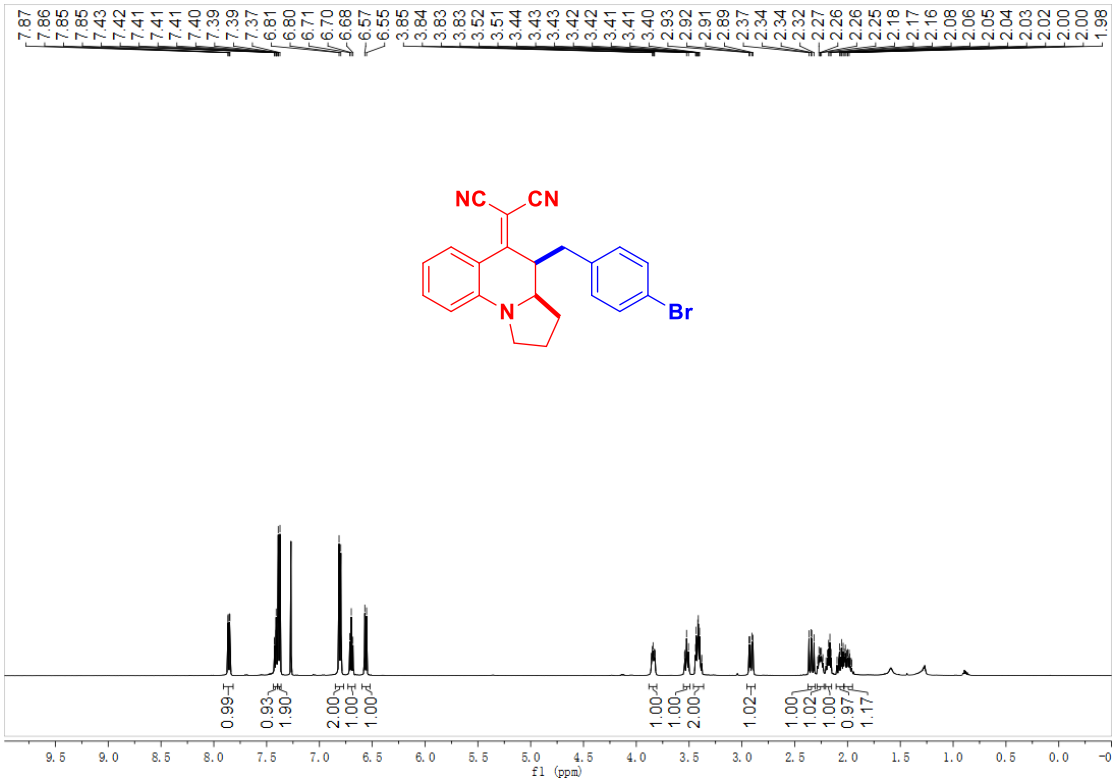
130.65
129.00
115.99
115.36
115.19
114.33
113.87
112.76
112.23
75.29
58.72
46.69
41.29
31.92
27.64
23.31
NC
CN
N
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

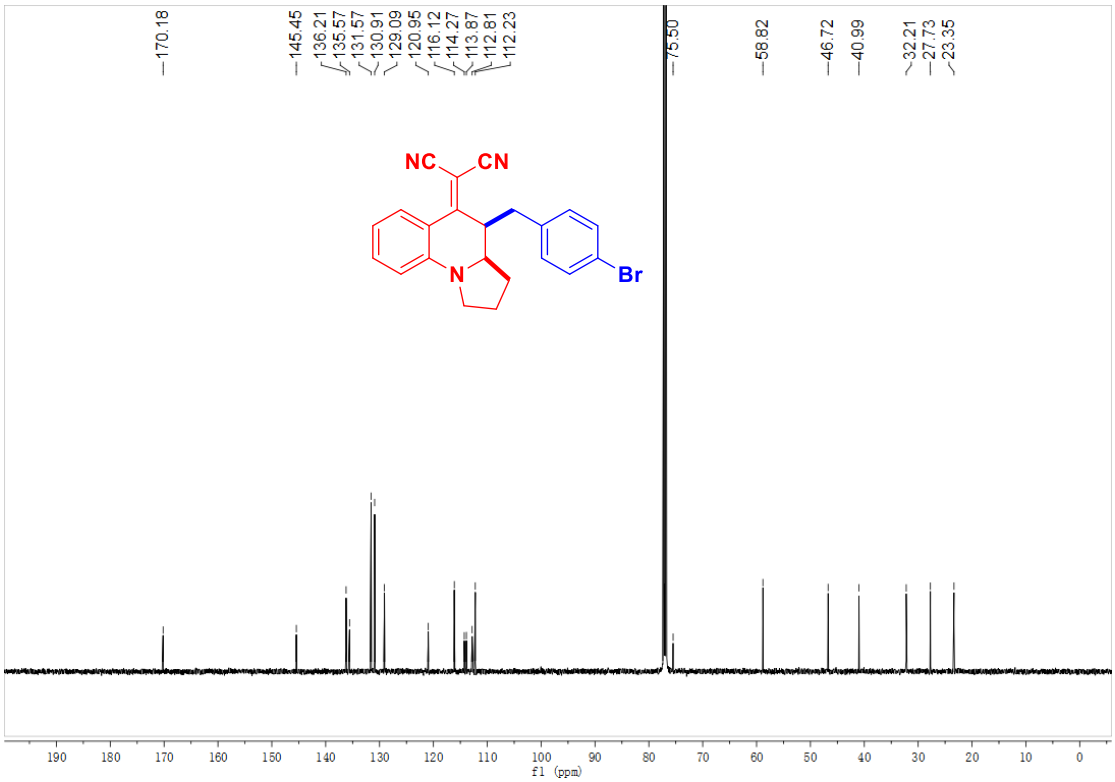
2-((3a*R*,4*R*)-4-(4-chlorobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3f



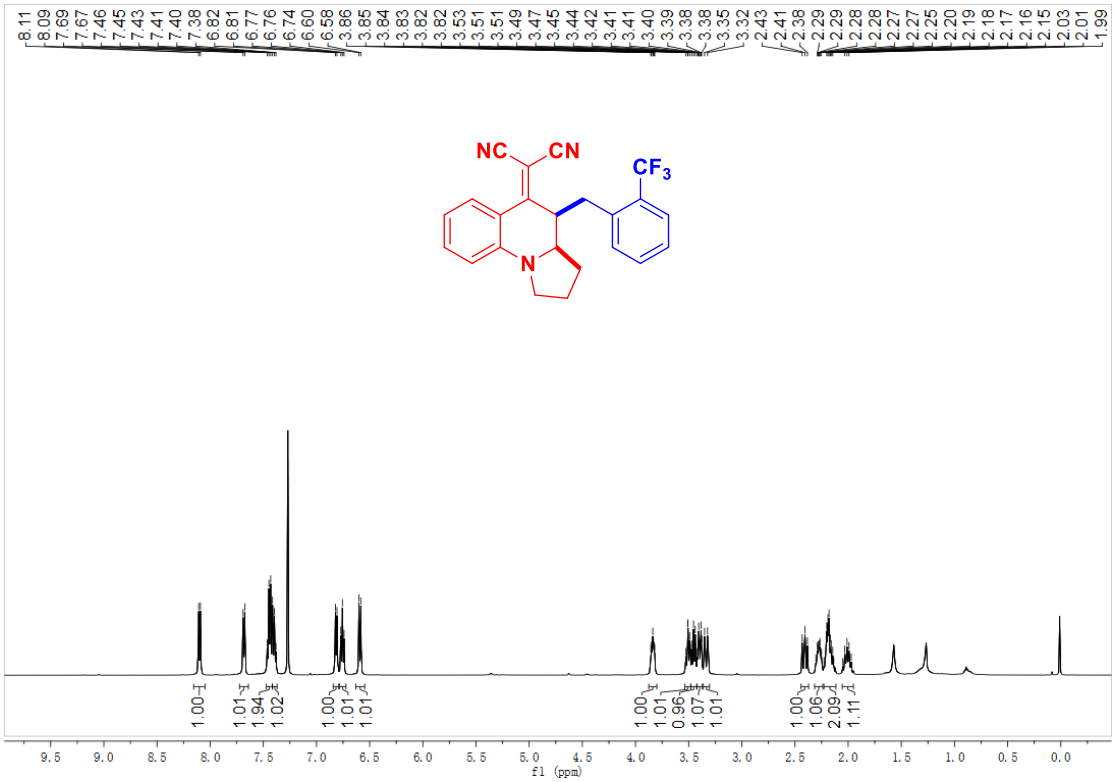


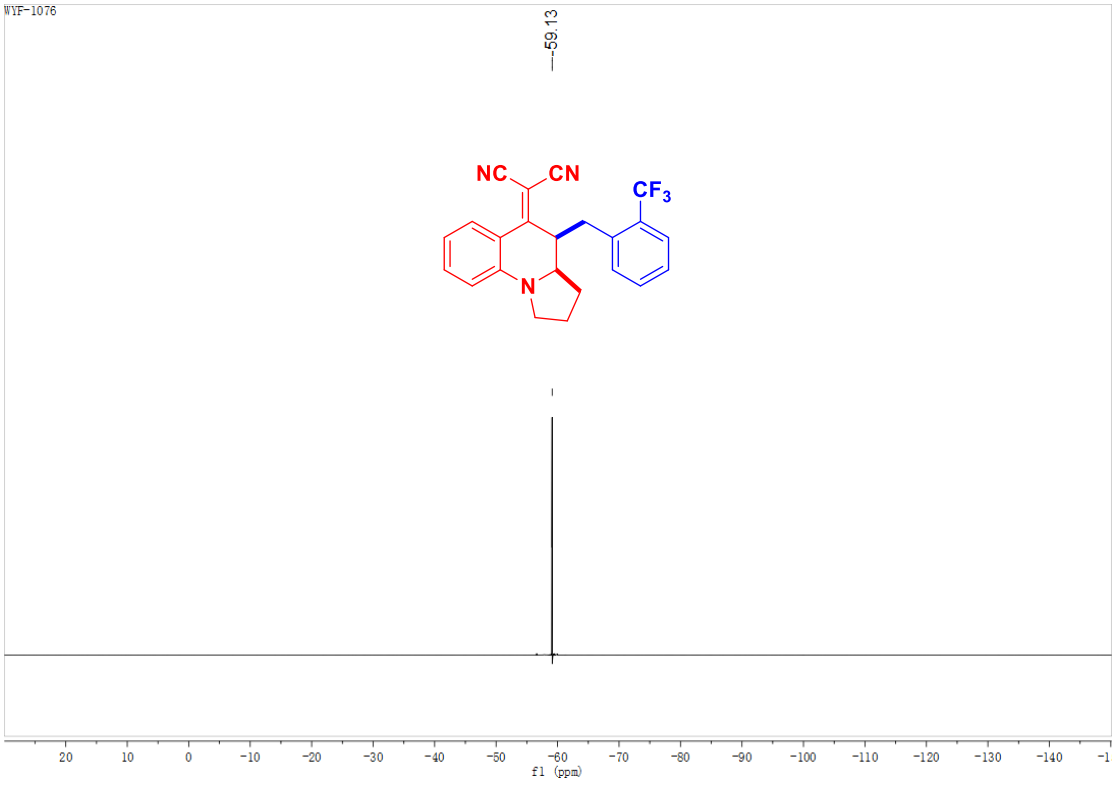
2-((3a*R*,4*R*)-4-(4-bromobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3g

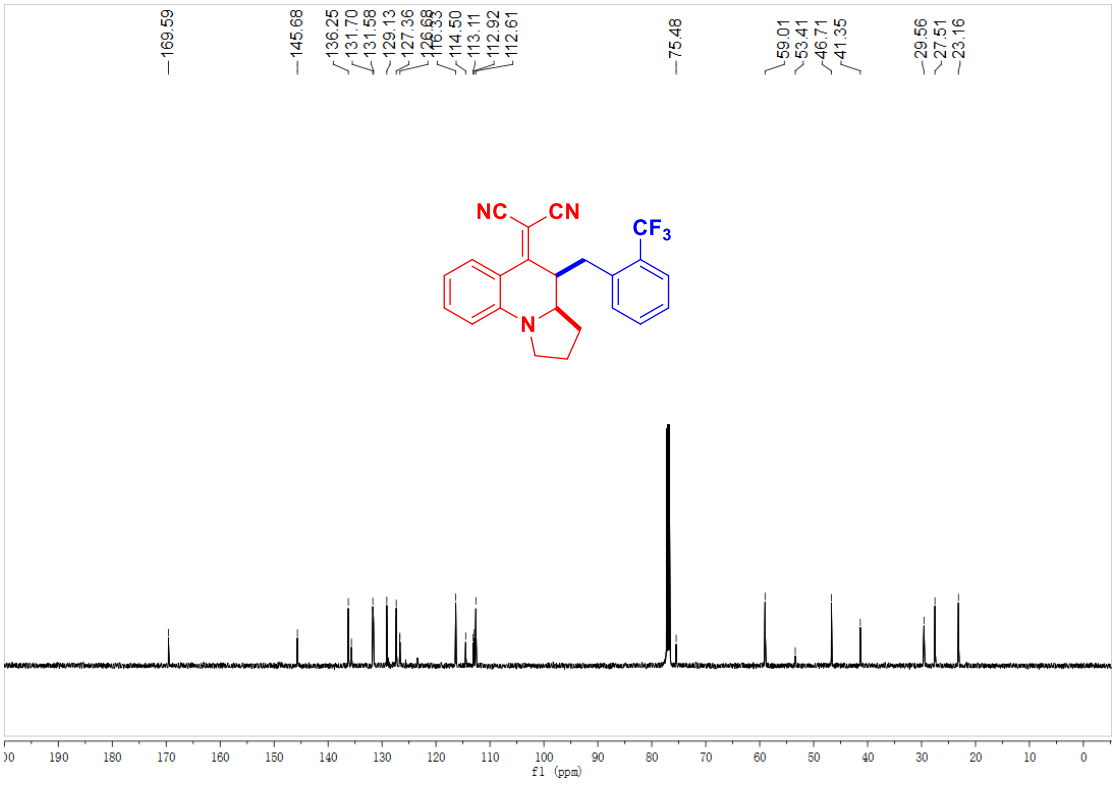




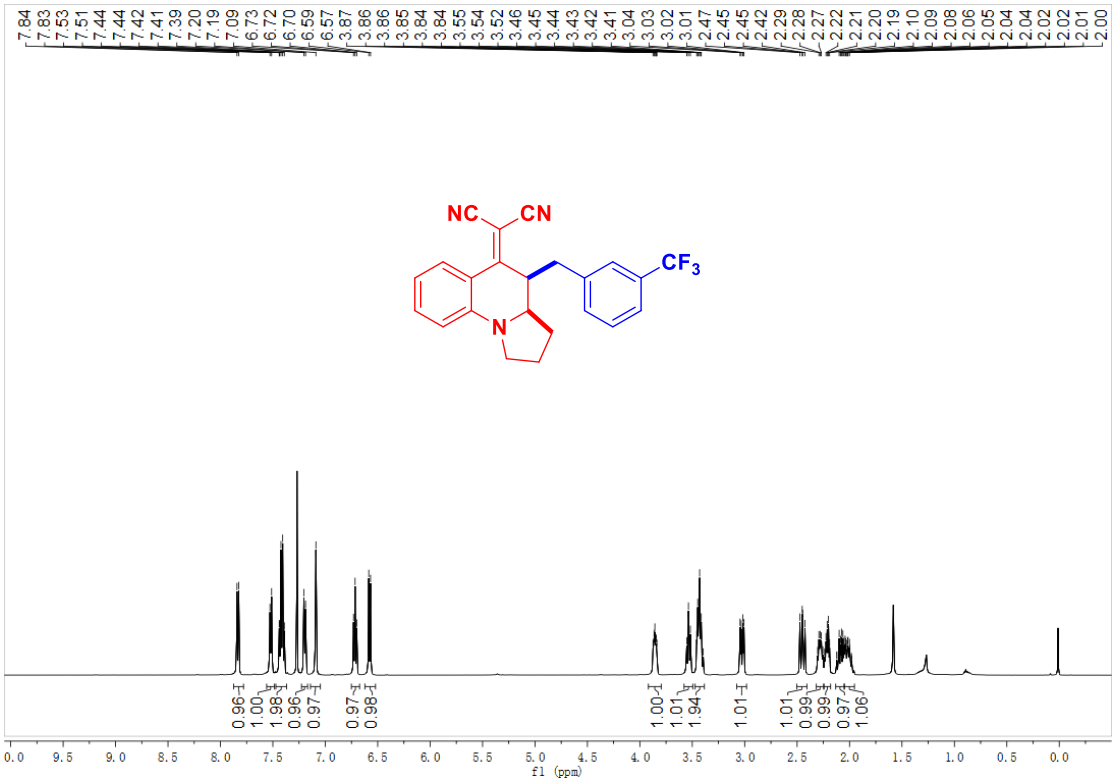
2-((3a*R*,4*R*)-4-(2-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1*H*)-ylidene)malononitrile 3h

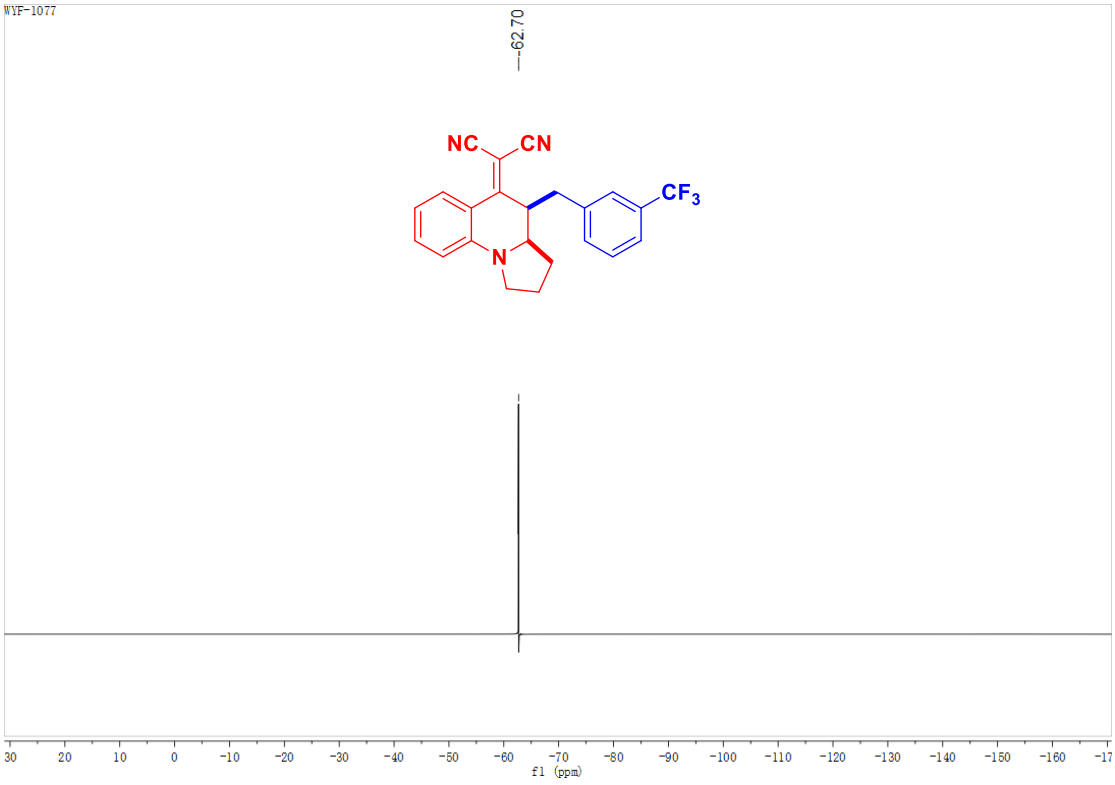


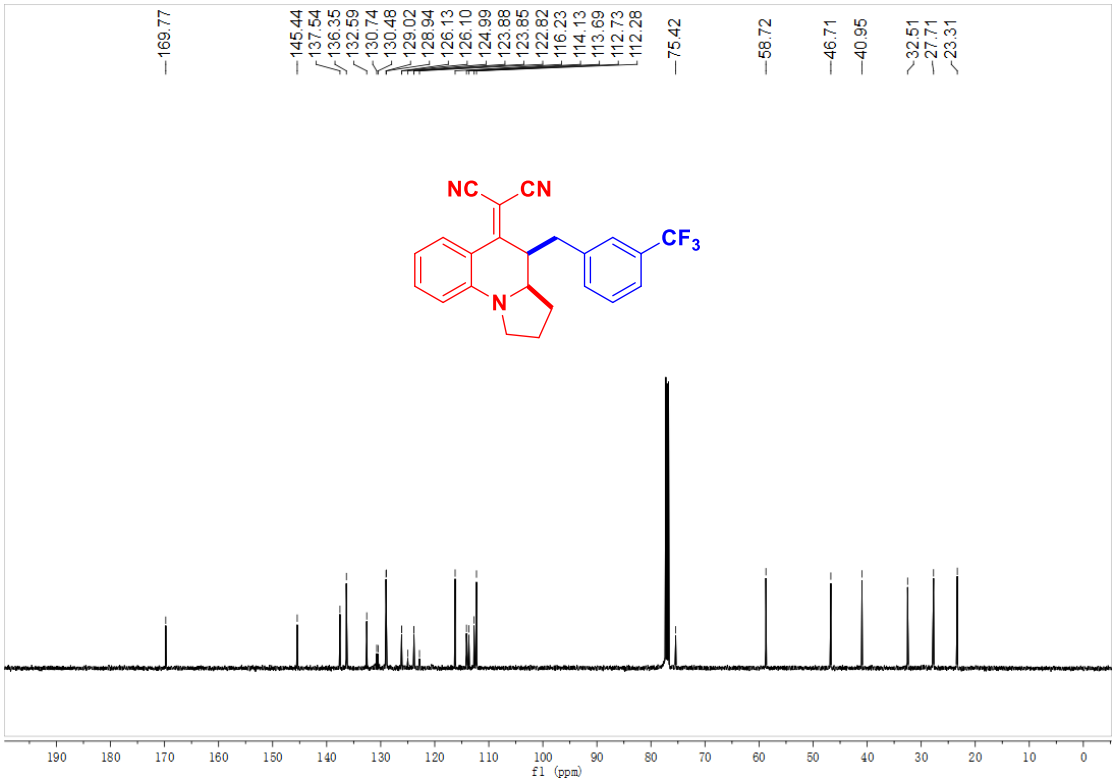



169.59
145.68
136.25
131.70
131.58
129.13
127.36
126.68
116.33
114.50
113.11
112.92
112.61
75.48
59.01
53.41
46.71
41.35
29.56
27.51
23.16
NC
CN
CF3
N
f1 (ppm)

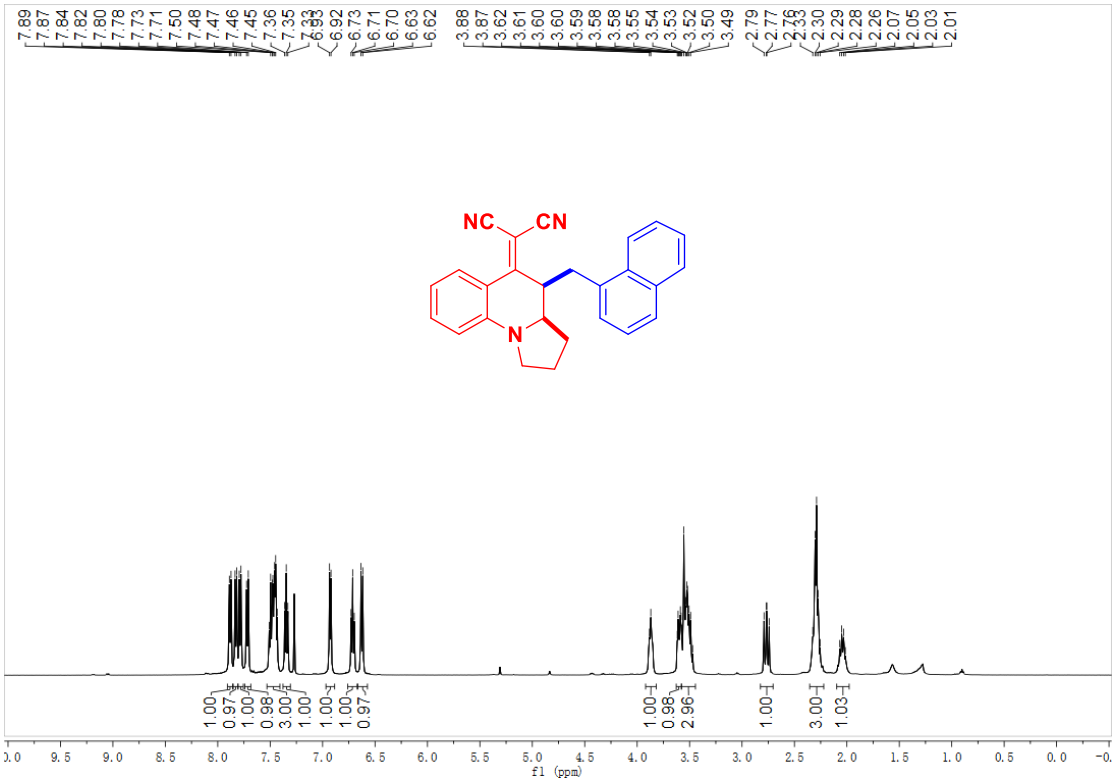
2-((3a*R*,4*R*)-4-(3-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3i

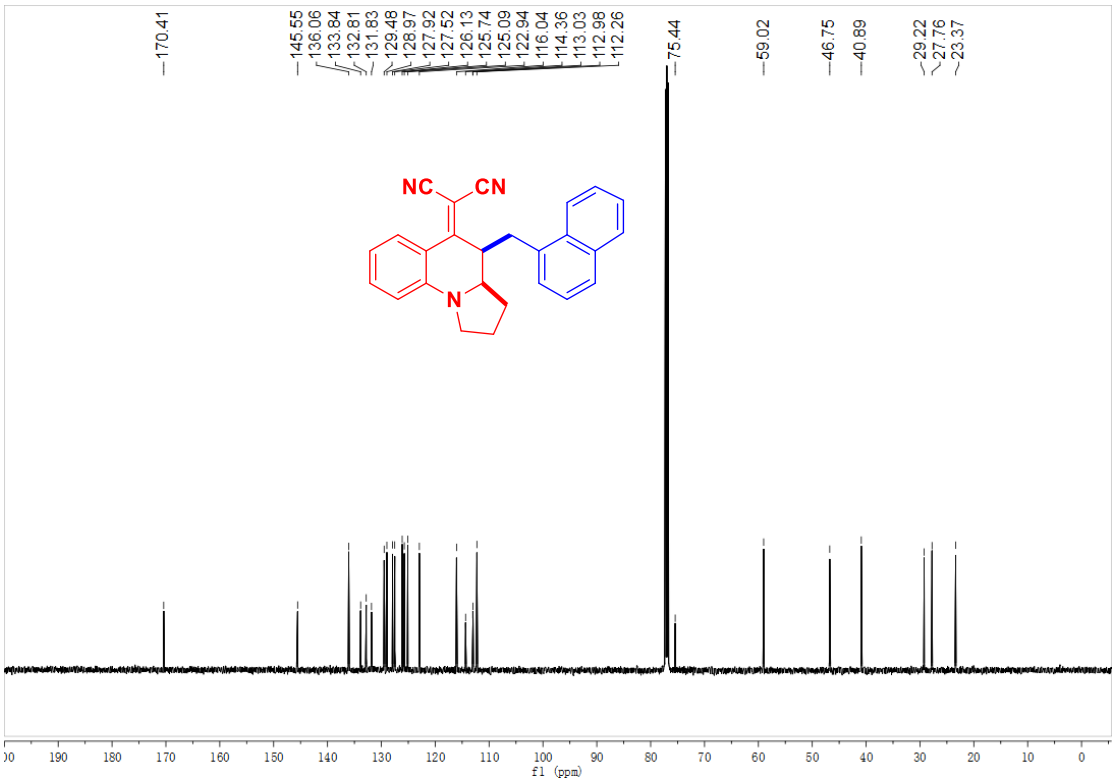




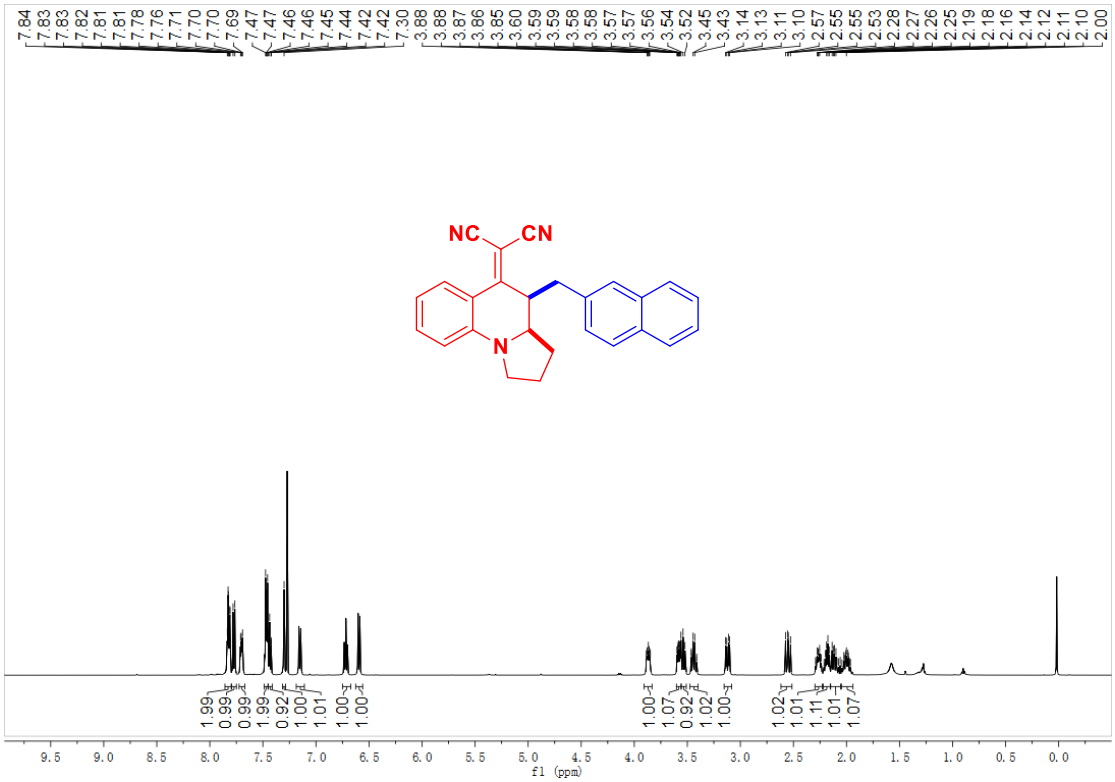

169.77
145.44
137.54
136.35
132.59
130.74
130.48
129.02
128.94
126.13
126.10
124.99
123.88
123.85
122.82
116.23
114.13
113.69
112.73
112.28
75.42
58.72
46.71
40.95
32.51
27.71
23.31
NC
CN
CF3
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

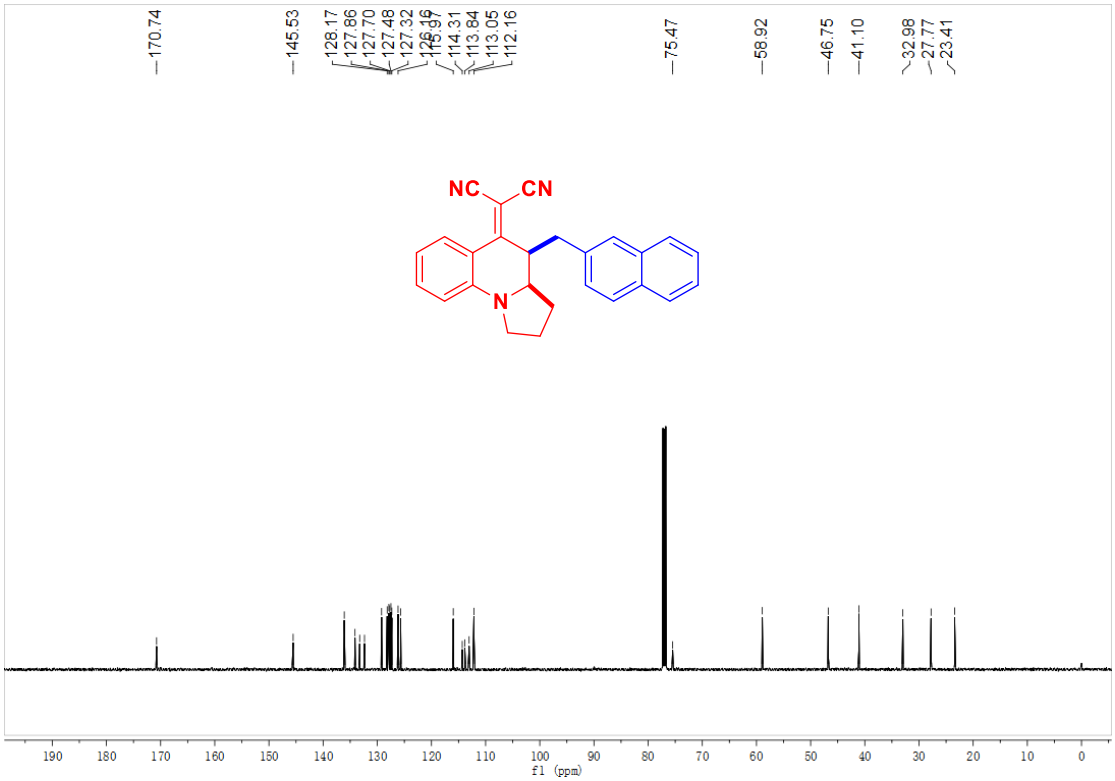
2-(4-(naphthalen-1-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3j



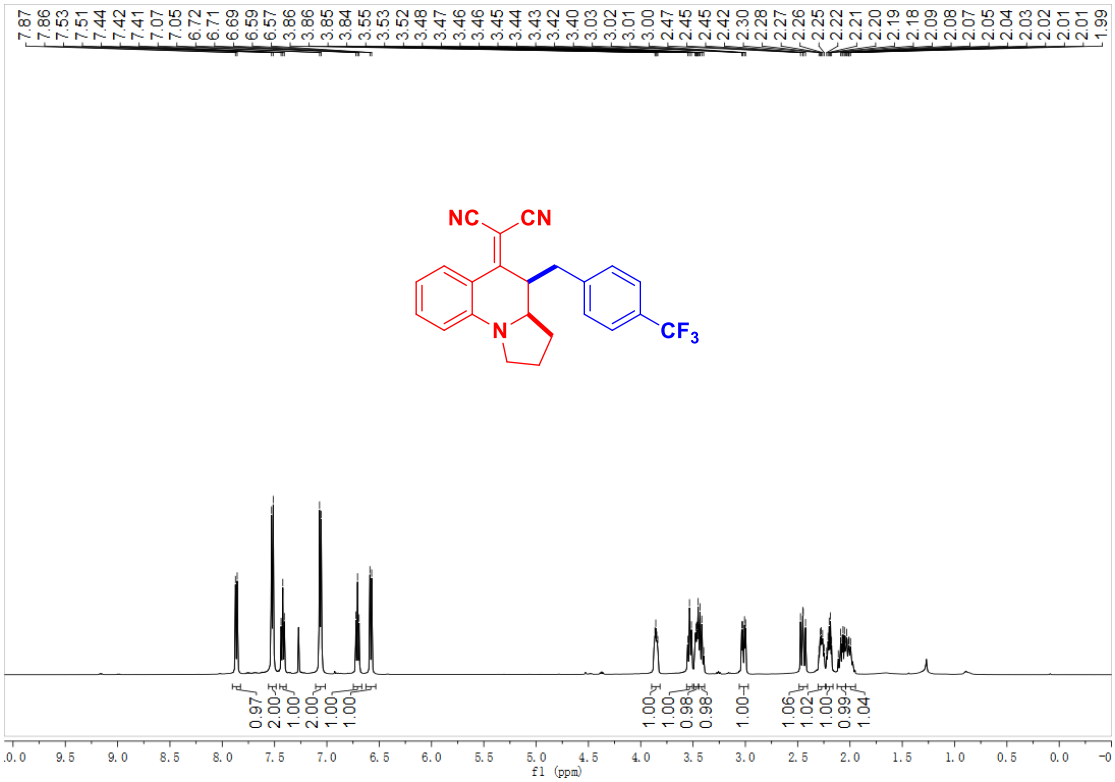


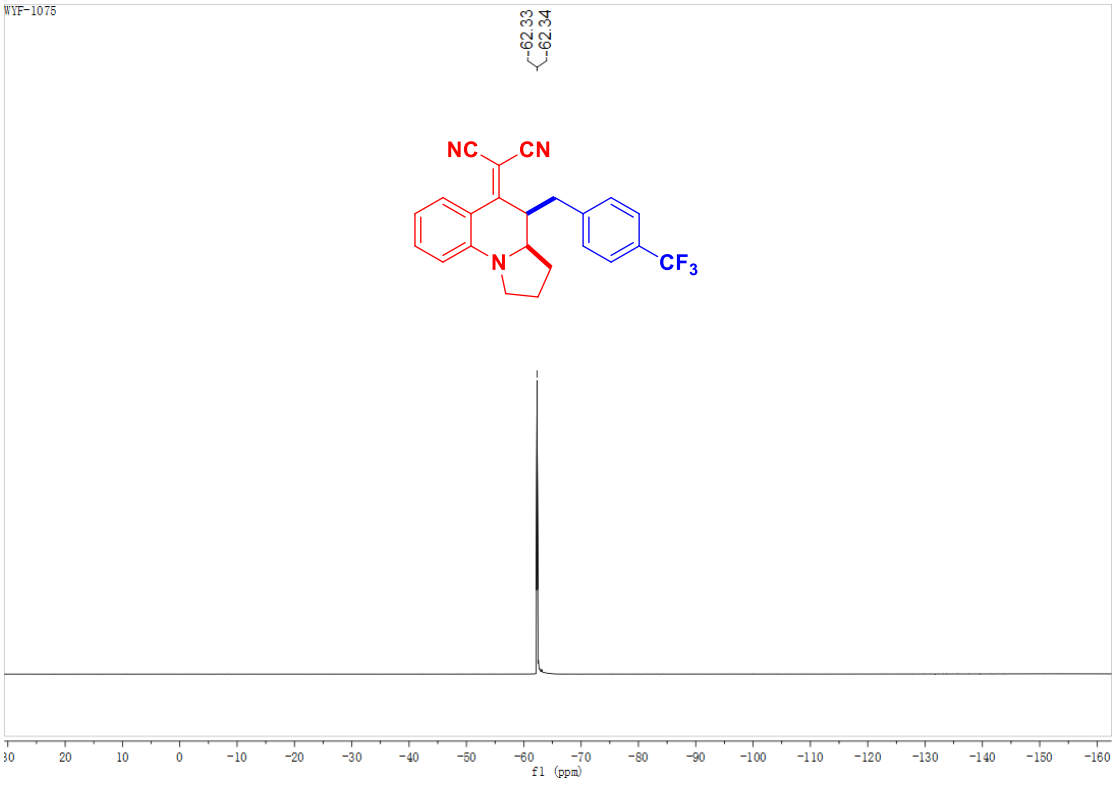
2-((3a*R*,4*R*)-4-(naphthalen-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3k

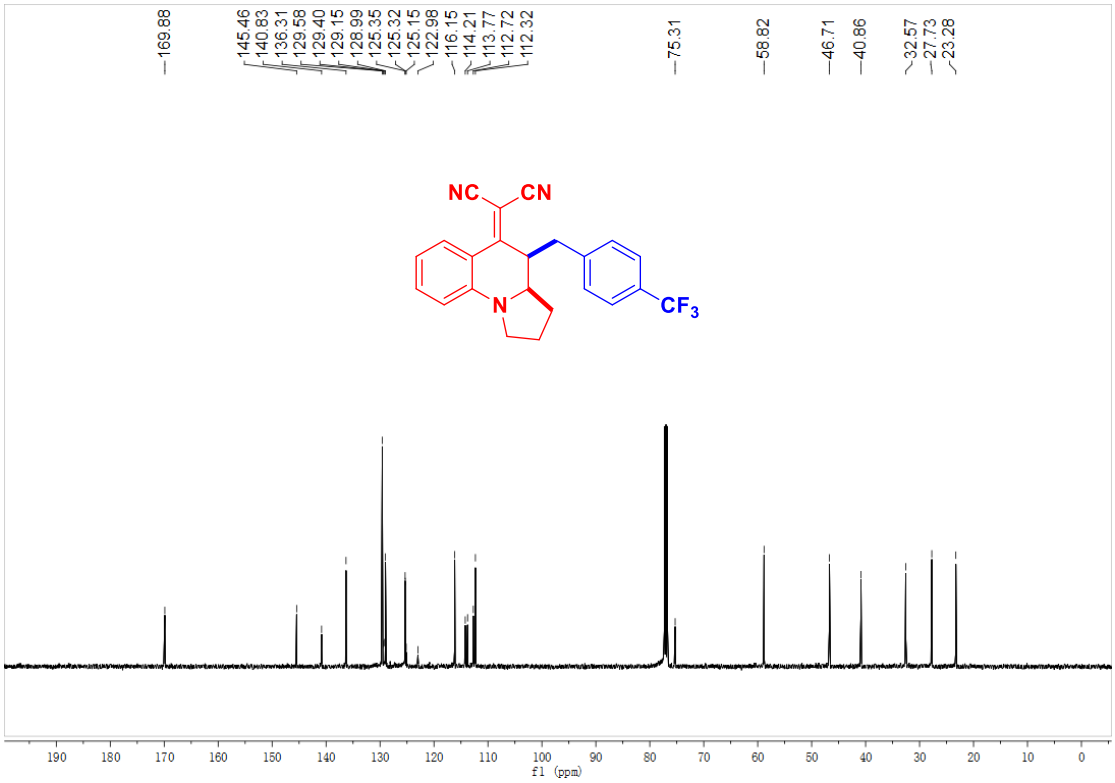




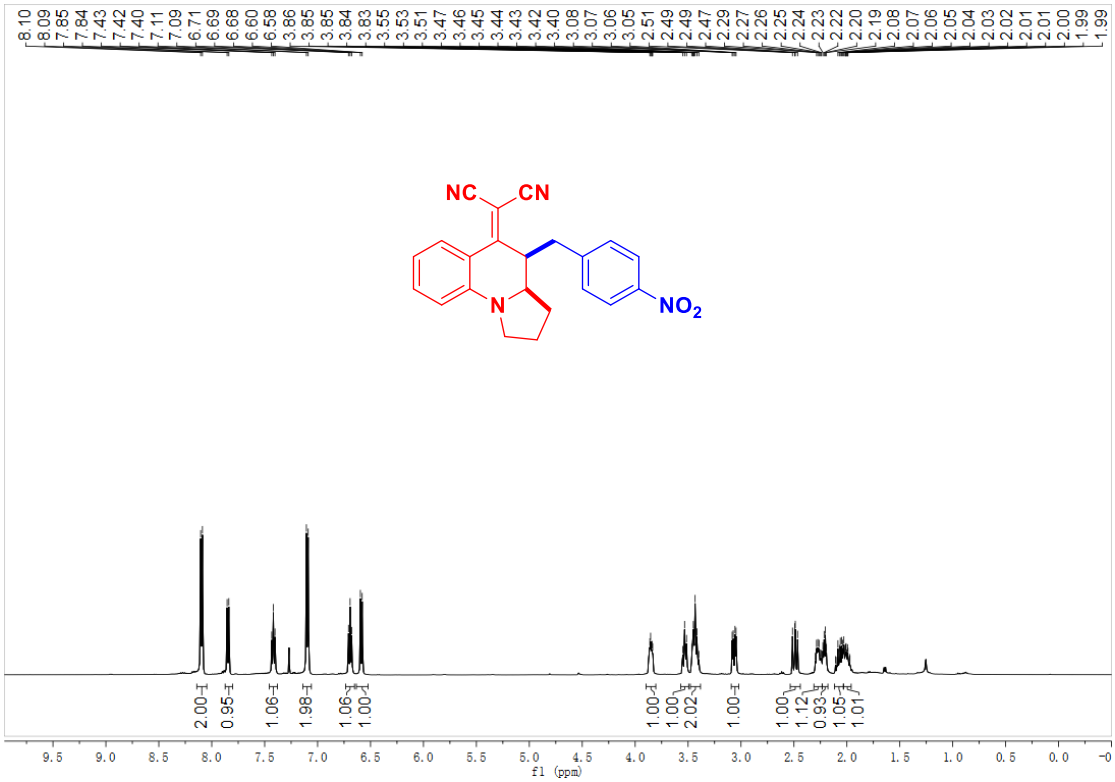
2-((3a*R*,4*R*)-4-(4-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3l

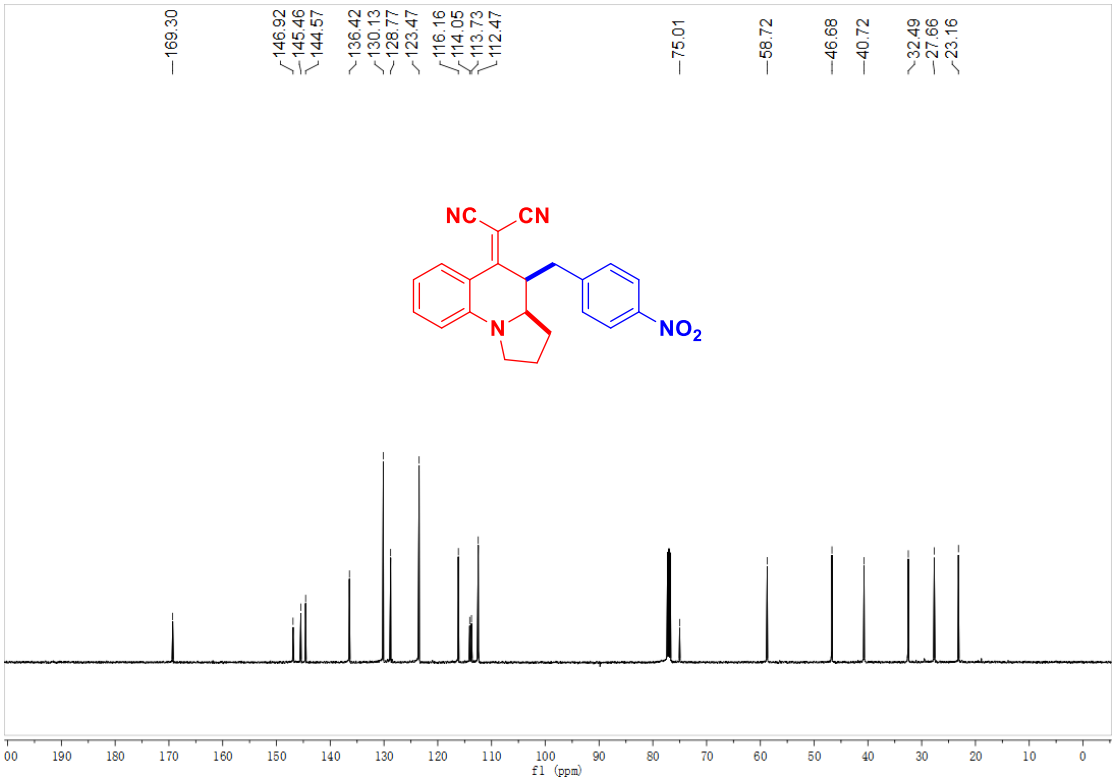




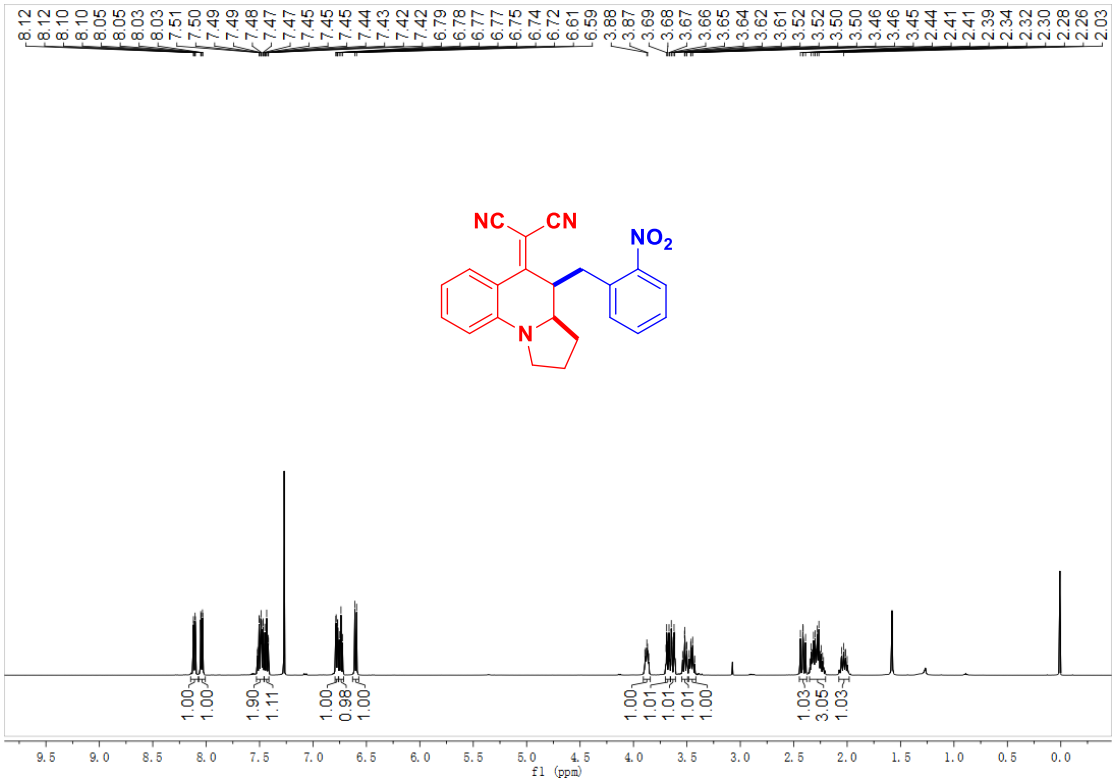

169.88
145.46
140.83
136.31
129.58
129.40
129.15
128.99
125.35
125.32
125.15
122.98
116.15
114.21
113.77
112.72
112.32
75.31
58.82
46.71
40.86
32.57
27.73
23.28
NC
CN
N
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

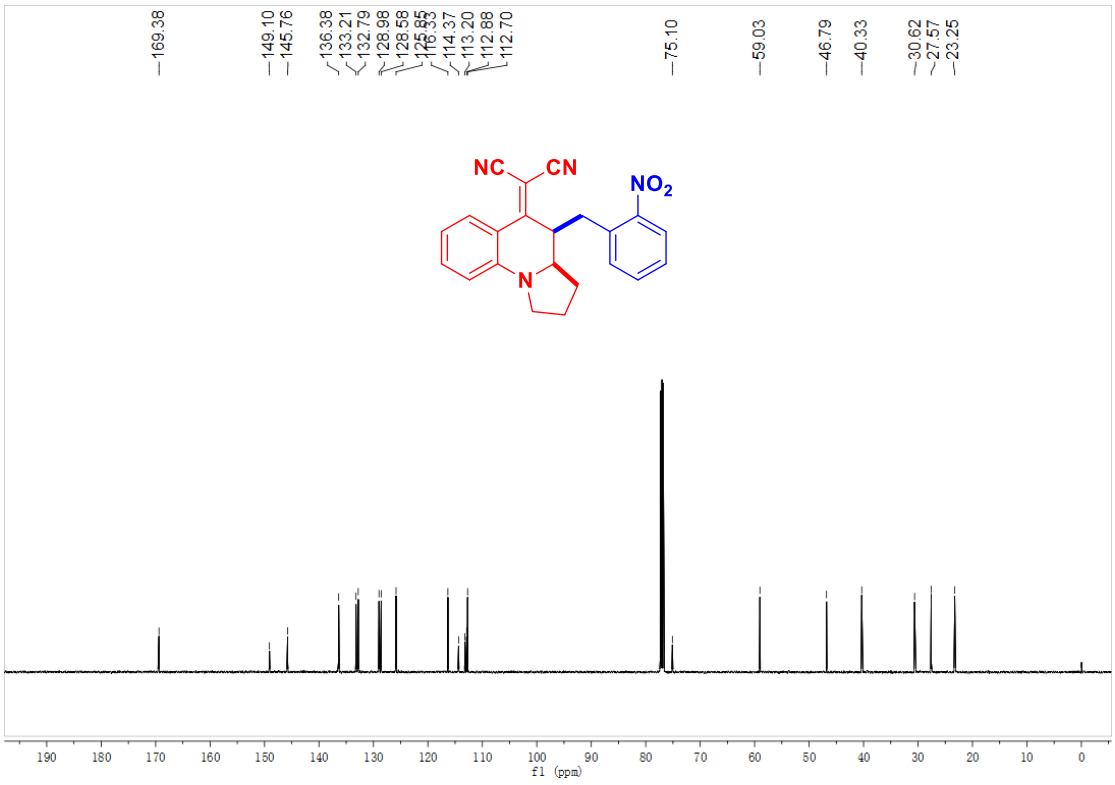
2-((3a*R*,4*R*)-4-(4-nitrobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3m



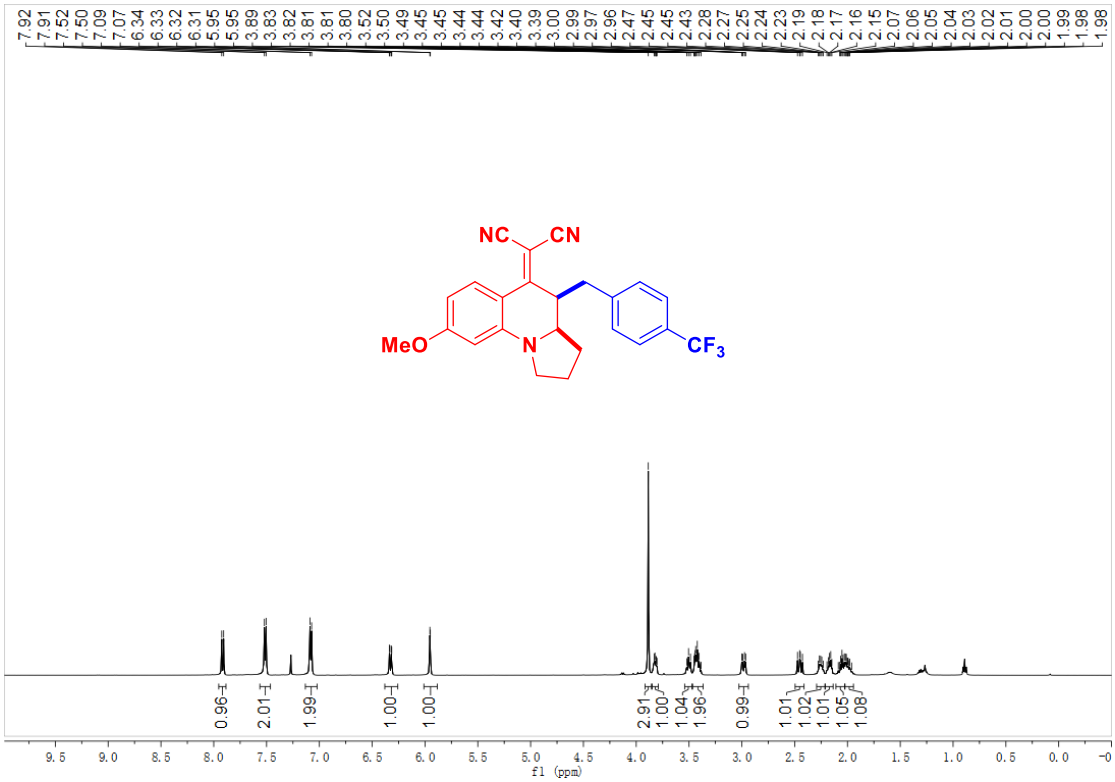


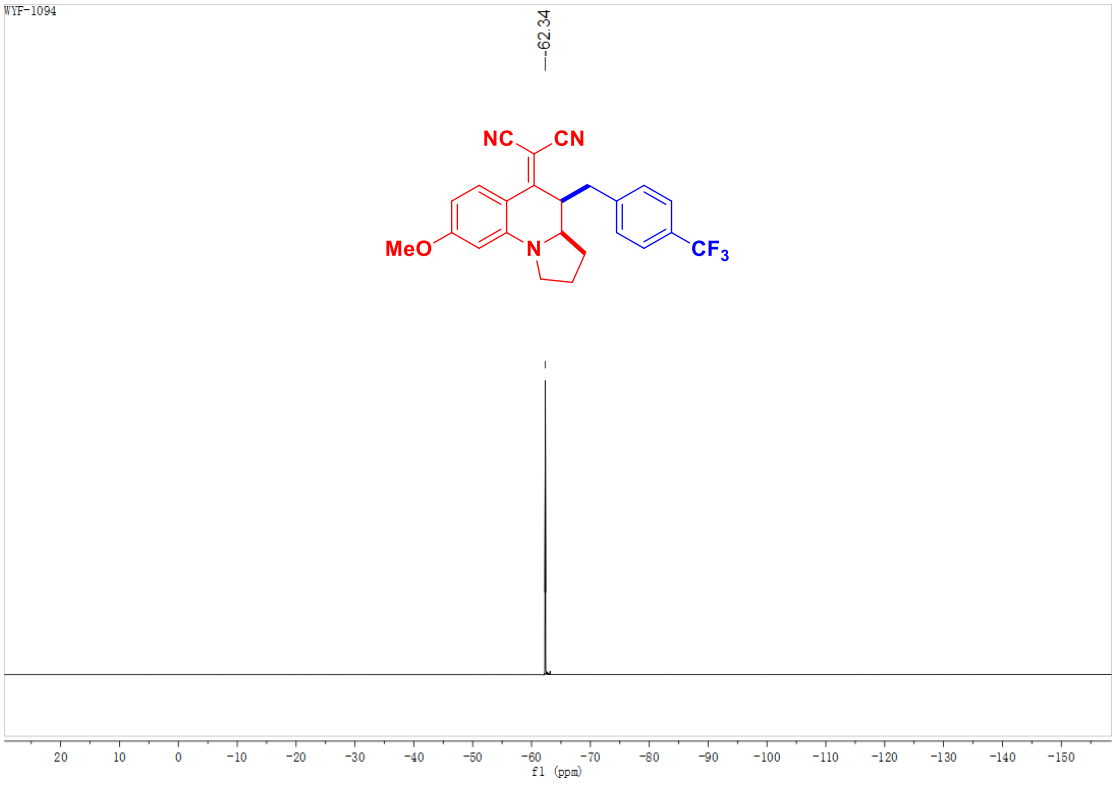
2-((3a*R*,4*R*)-4-(2-nitrobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3n

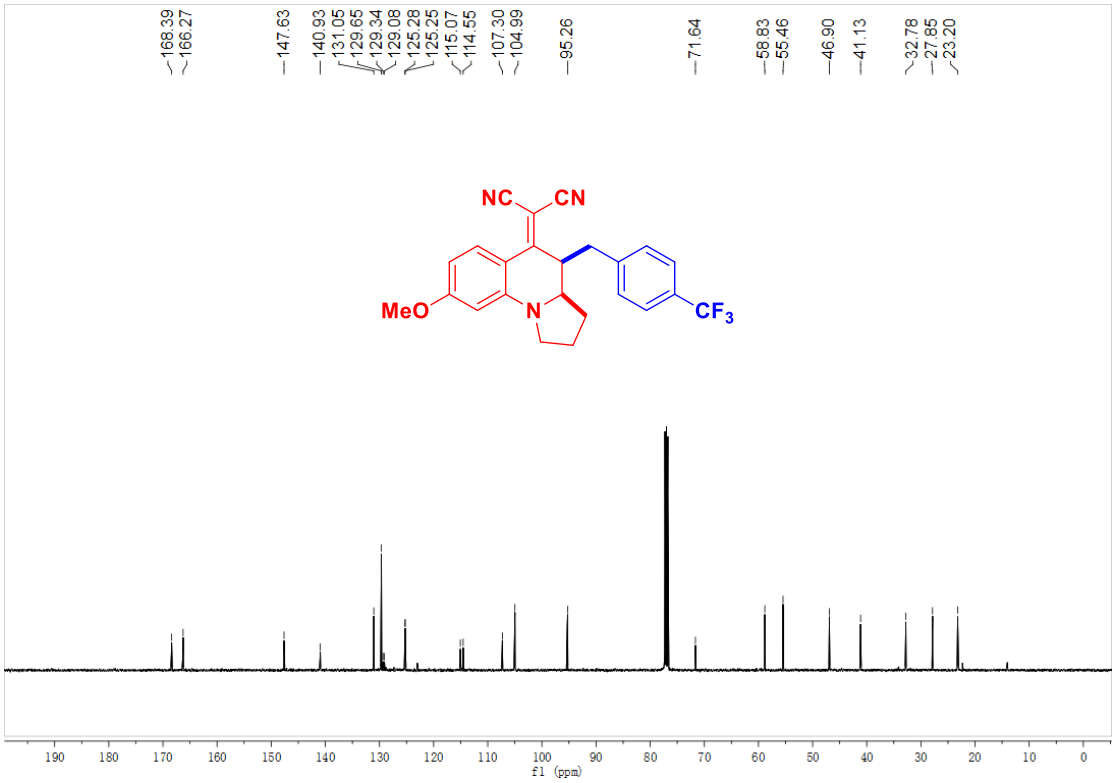




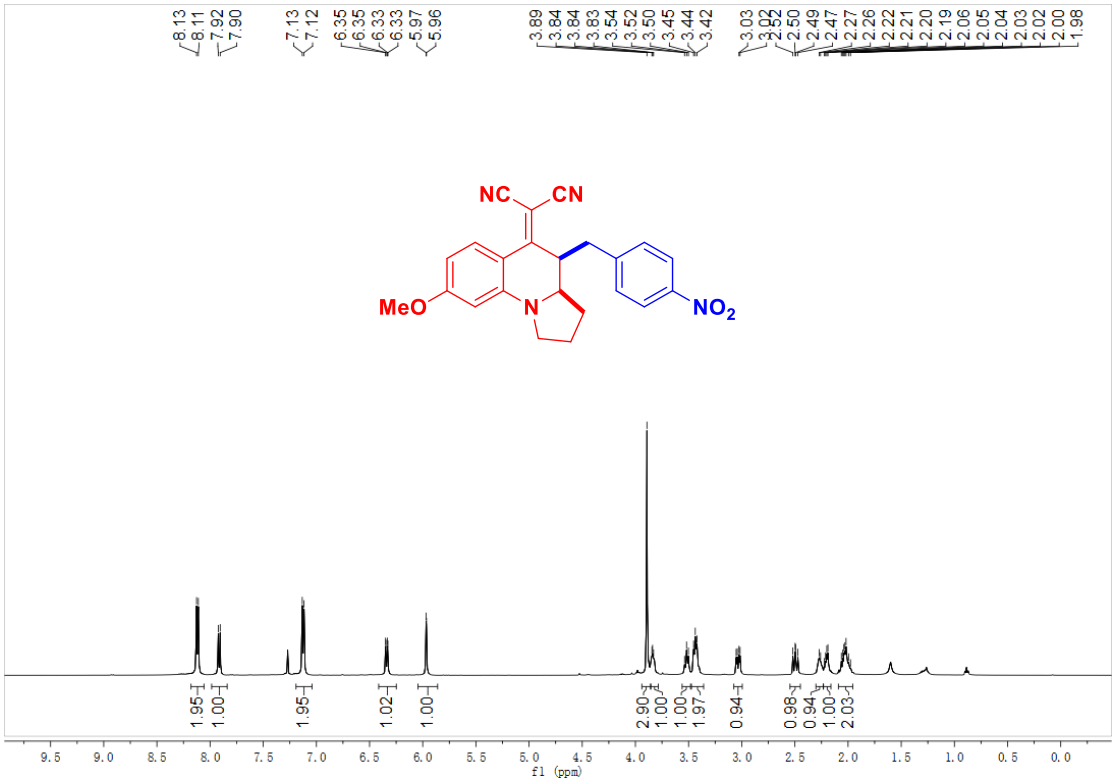
2-((3a*R*,4*R*)-8-methoxy-4-(4-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3o

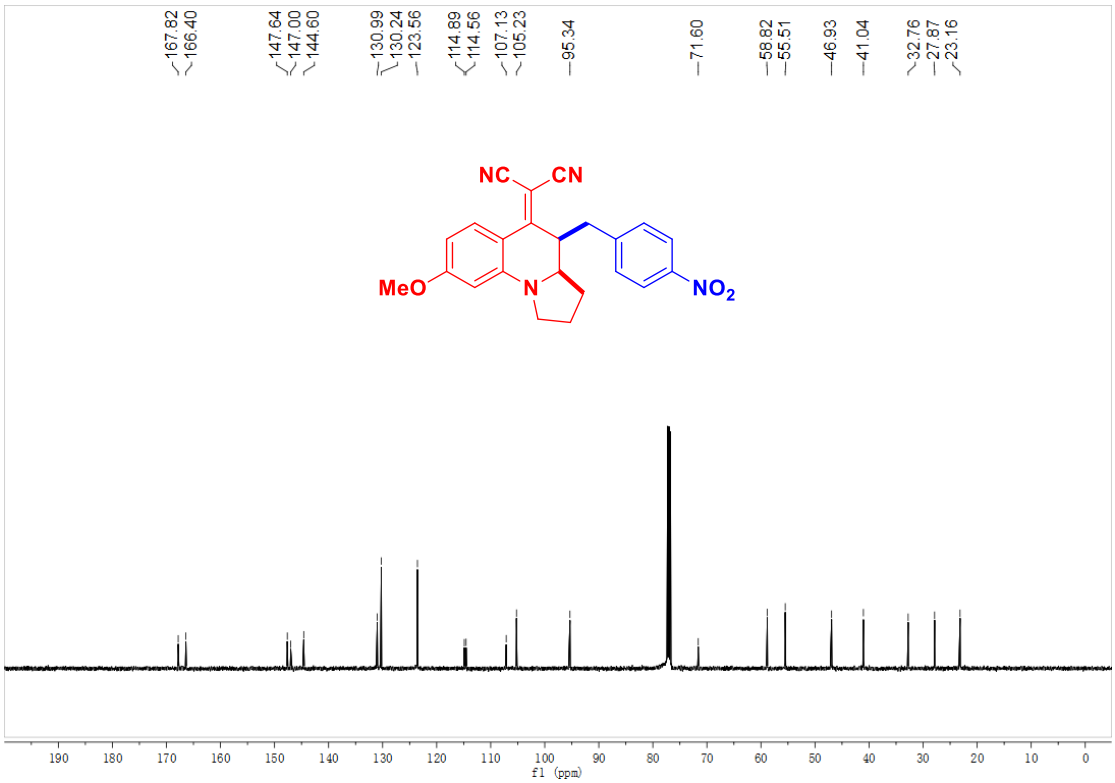




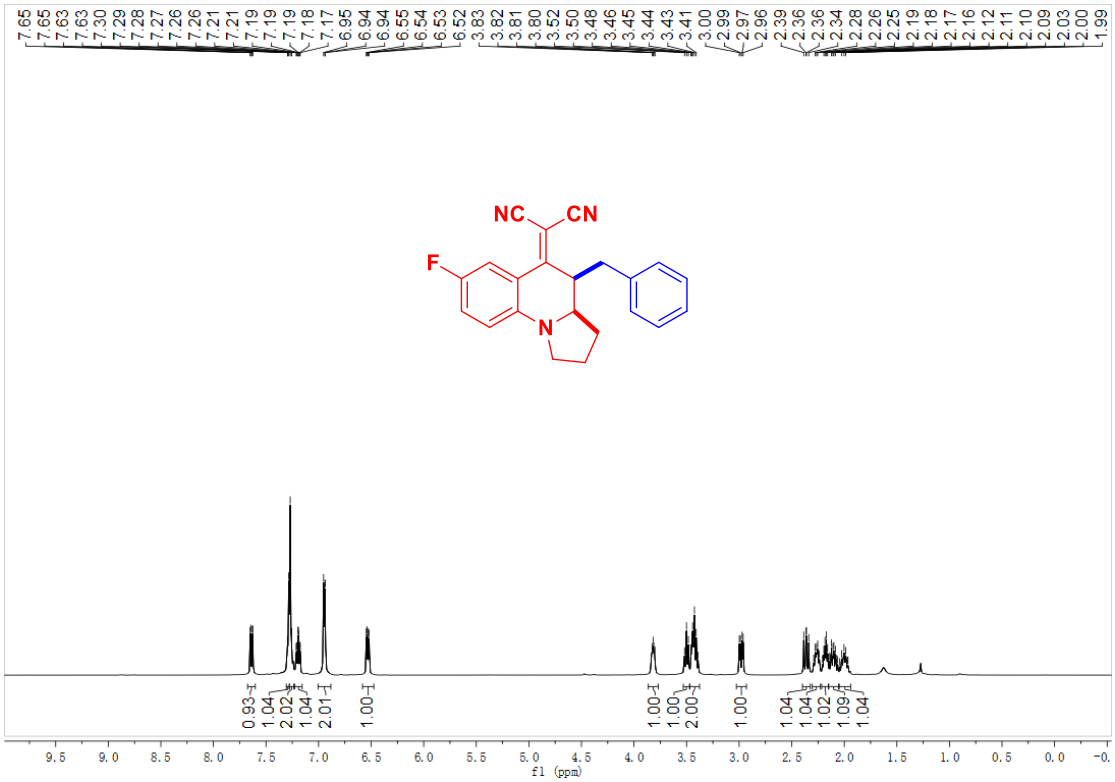

168.39
166.27
147.63
140.93
131.05
129.65
129.34
129.08
125.28
125.25
115.07
114.55
107.30
104.99
95.26
71.64
58.83
55.46
46.90
41.13
32.78
27.85
23.20
NC
CN
MeO
N
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

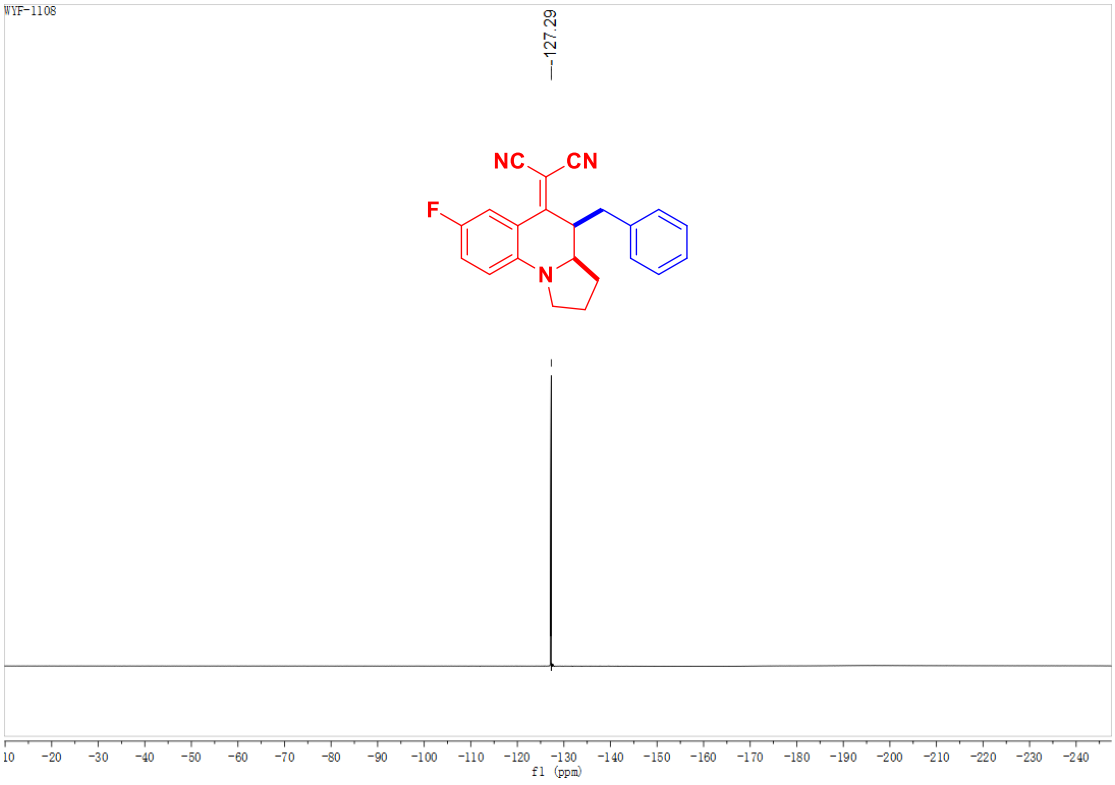
2-((3aR,4R)-8-methoxy-4-(4-nitrobenzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-α]quinolin-5(1H)-ylidene)malononitrile 3p

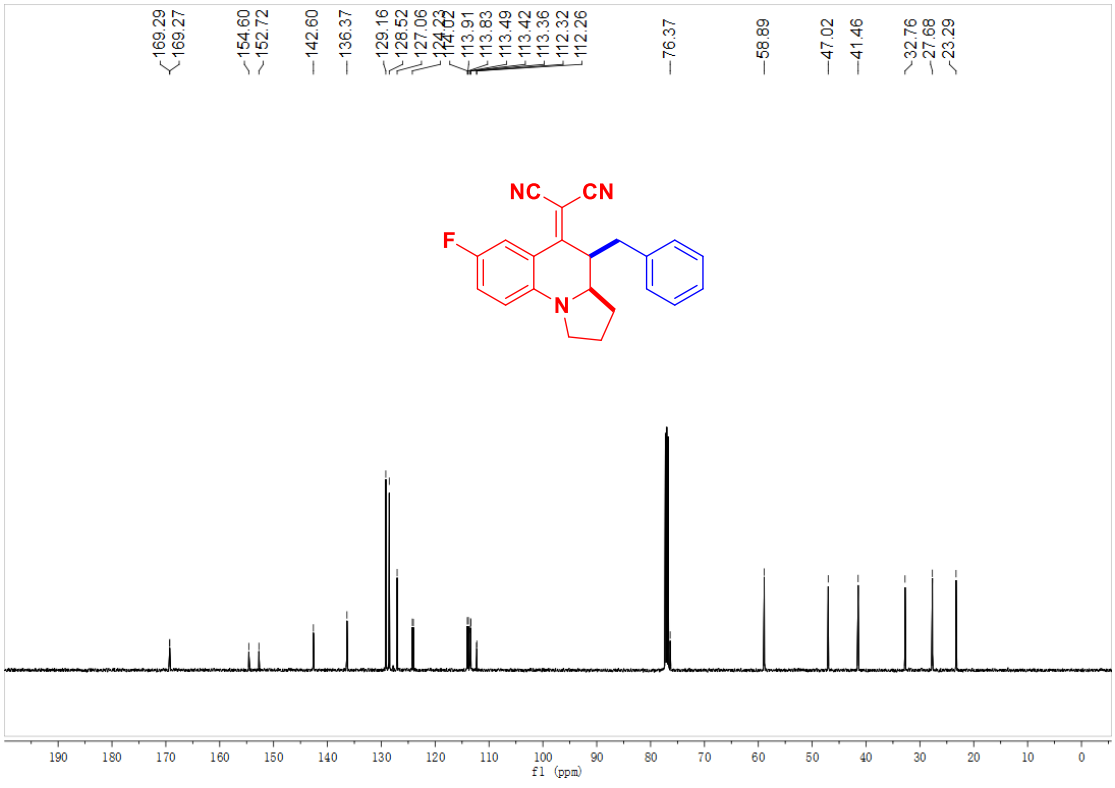




2-((3a*R*,4*R*)-4-benzyl-7-fluoro-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3q






169.29
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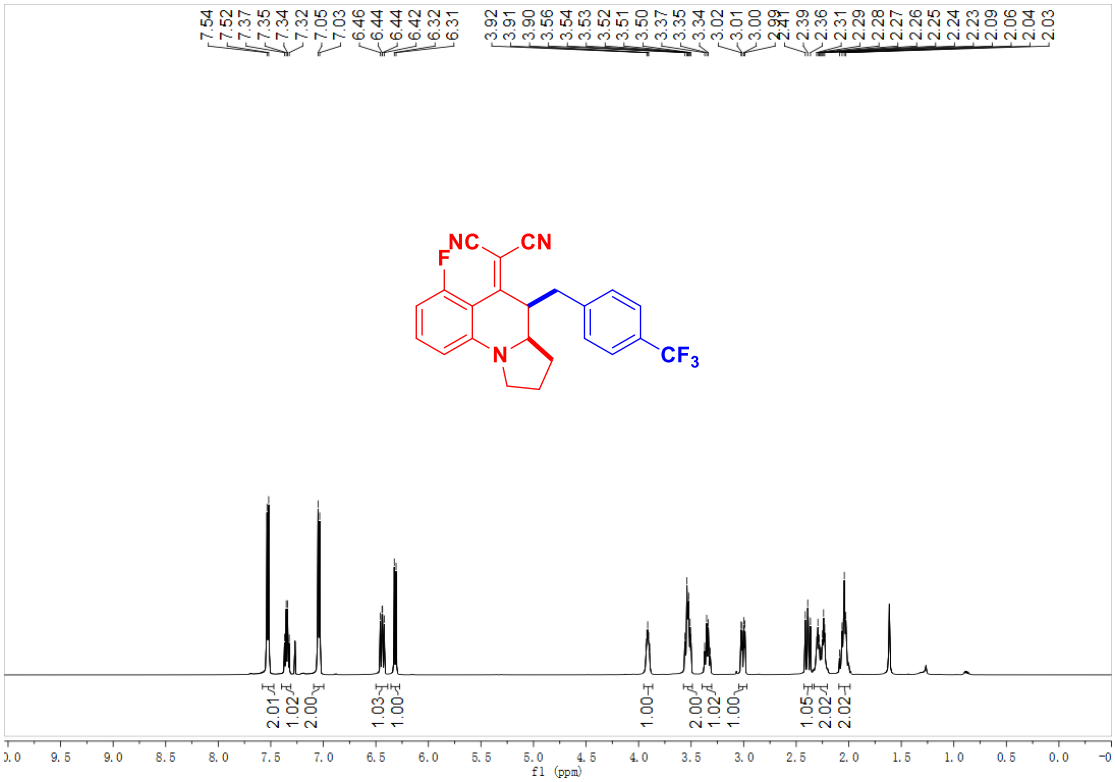
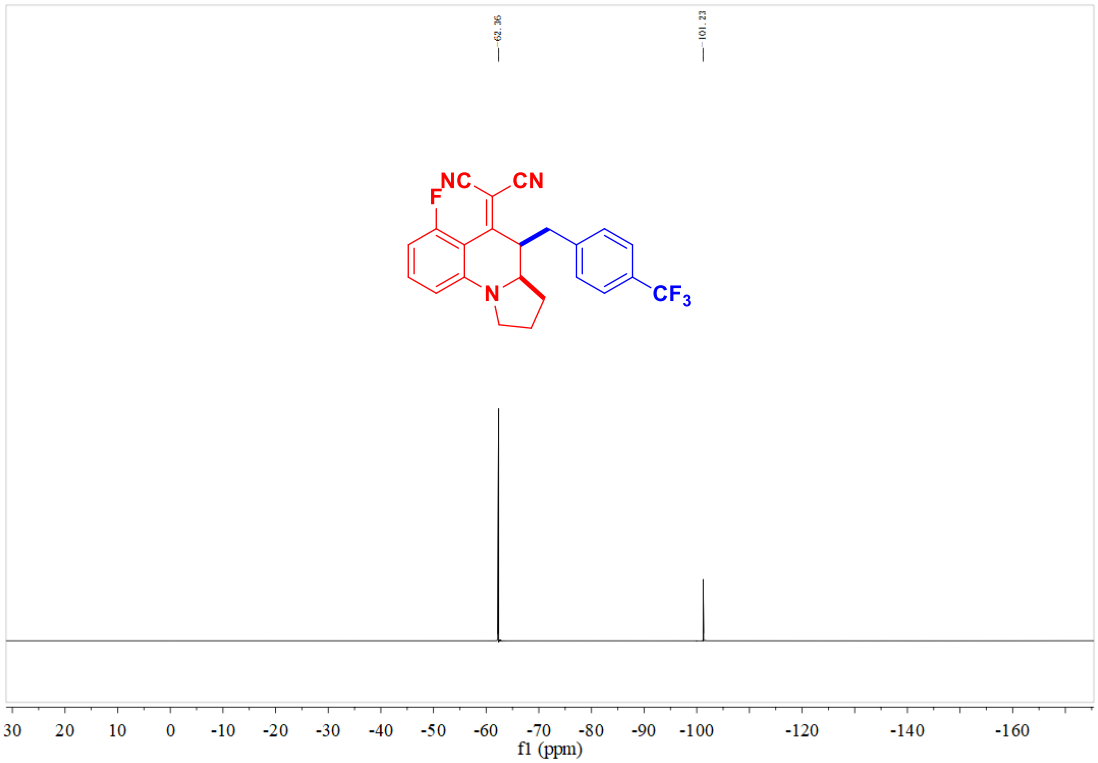
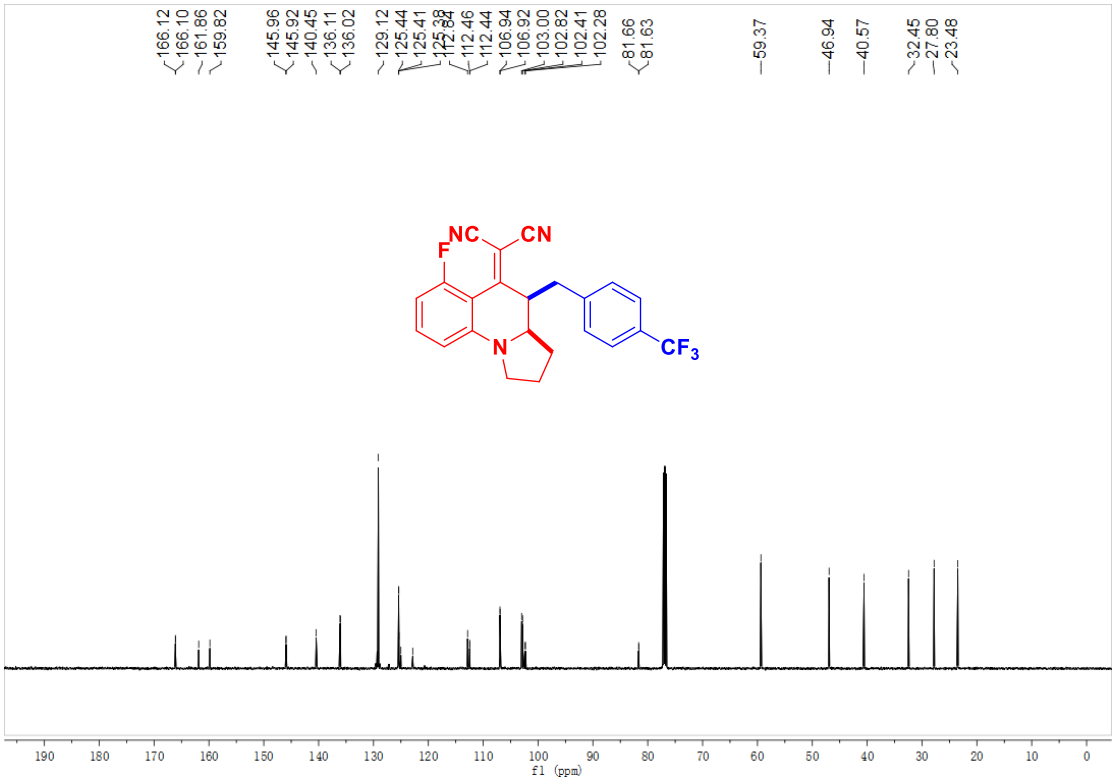
154.60
152.72
142.60
136.37
129.16
128.52
127.06
124.23
124.02
113.91
113.83
113.49
113.42
113.36
112.32
112.26
76.37
58.89
47.02
41.46
32.76
27.68
23.29
NC
CN
F
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

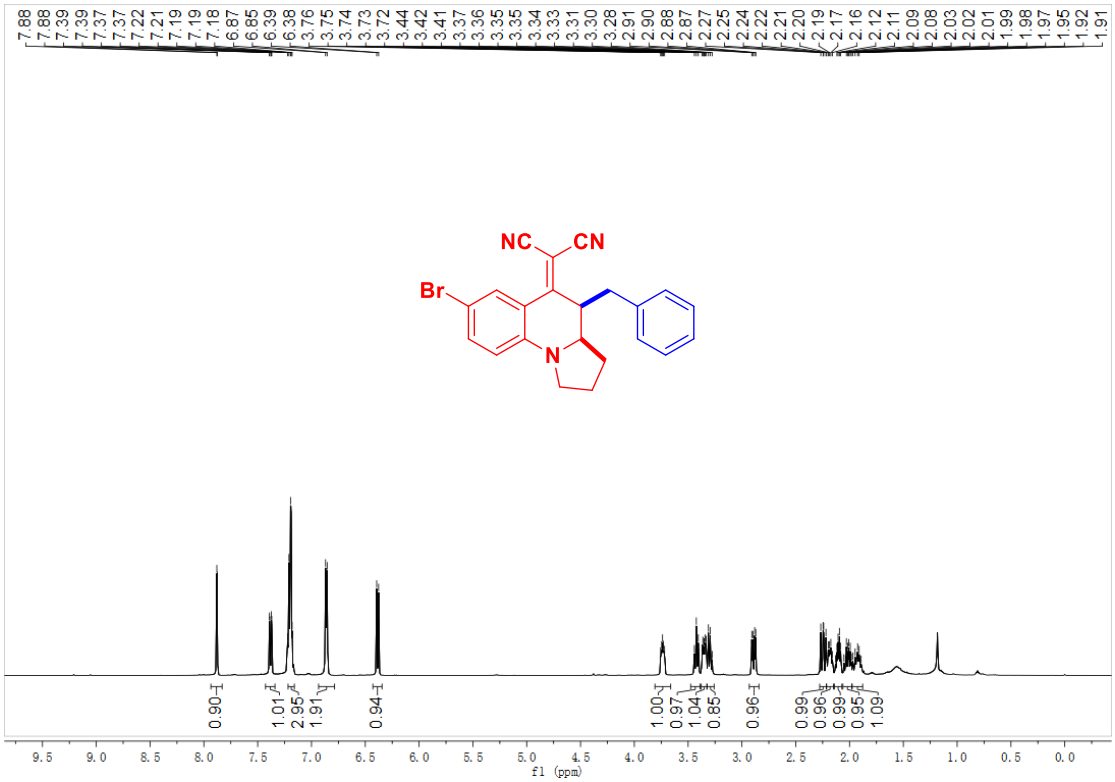
2-((3a*R*,4*R*)-6-fluoro-4-(4-(trifluoromethyl)benzyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 3r

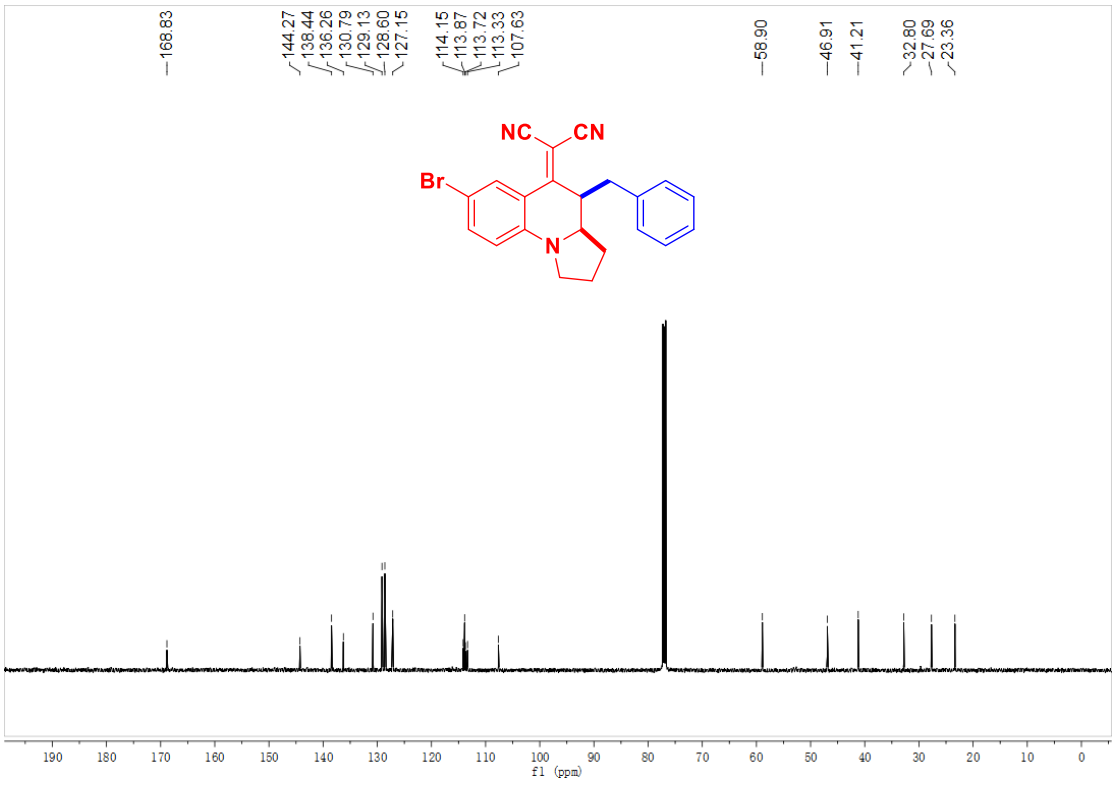




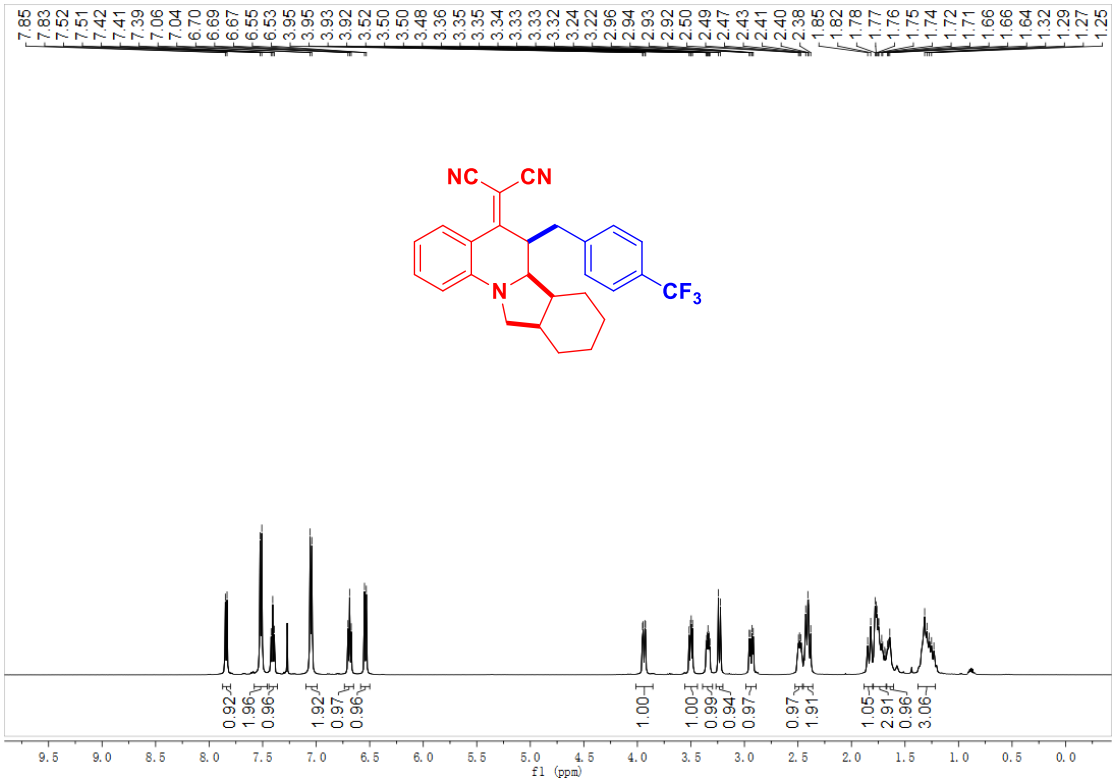

166.12
166.10
161.86
159.82
145.96
145.92
140.45
136.11
136.02
129.12
125.44
125.41
112.46
112.44
106.94
106.92
103.00
102.82
102.41
102.28
81.66
81.63
59.37
46.94
40.57
32.45
27.80
23.48
NC
CN
F
N
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

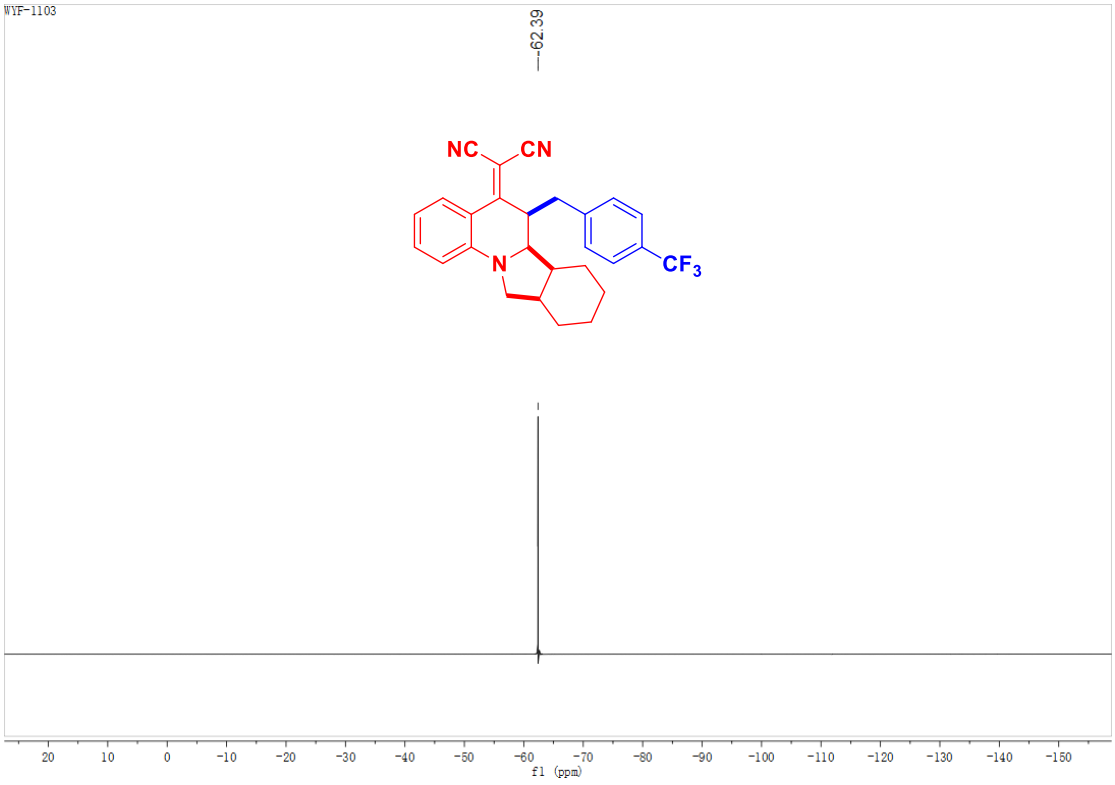
2-((3a*R*,4*R*)-4-benzyl-7-bromo-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 3s

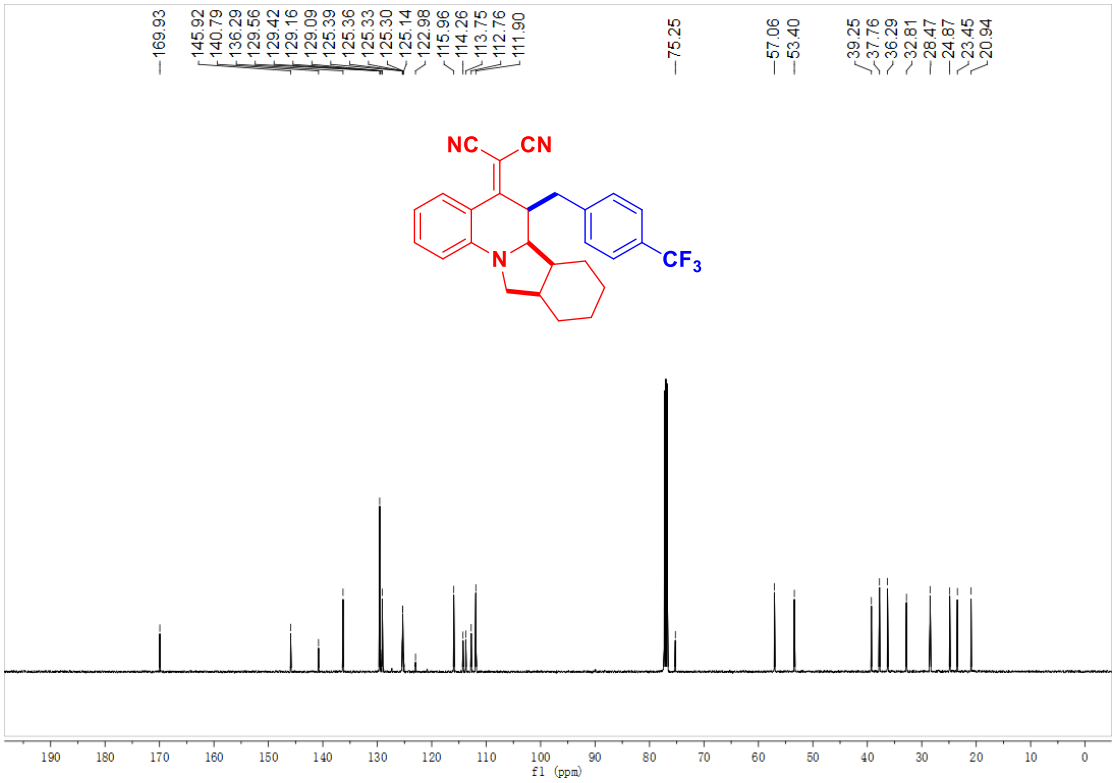




2-((6*R*,6a*R*,6b*S*)-6-(4-(trifluoromethyl)benzyl)-6a,6b,7,8,9,10,10a,11-octahydroisoindolo[2,1-*α*]quinolin-5(6H)-ylidene)malononitrile 3t



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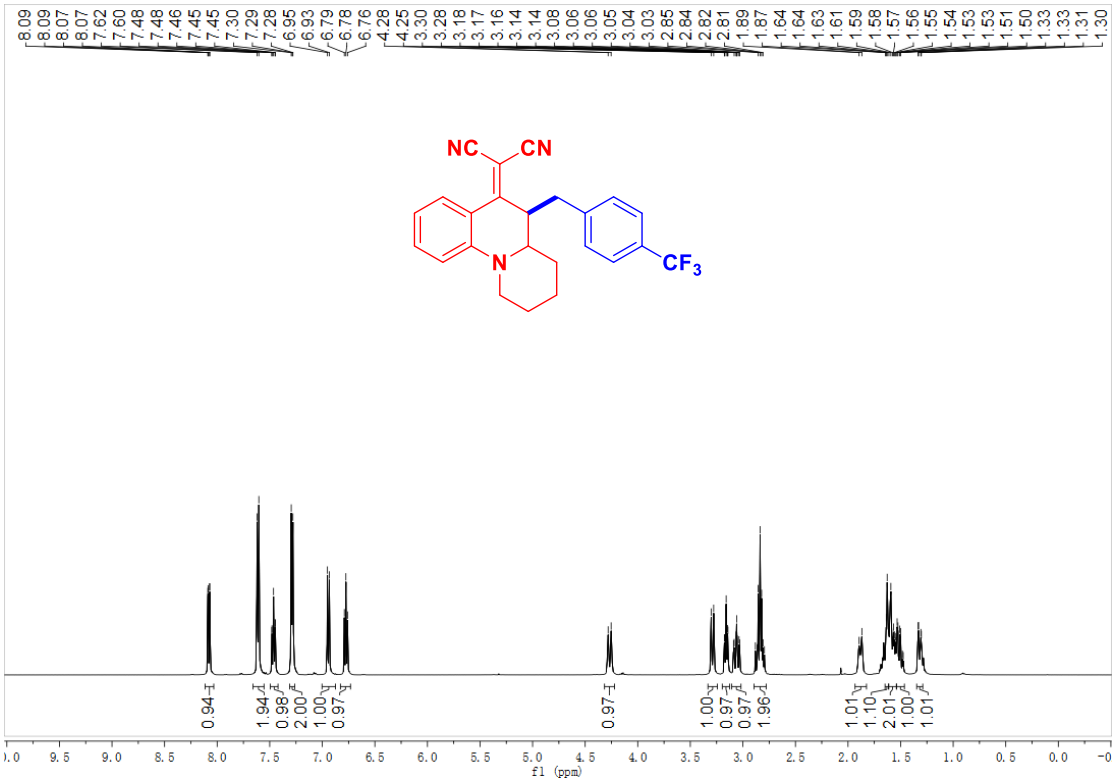
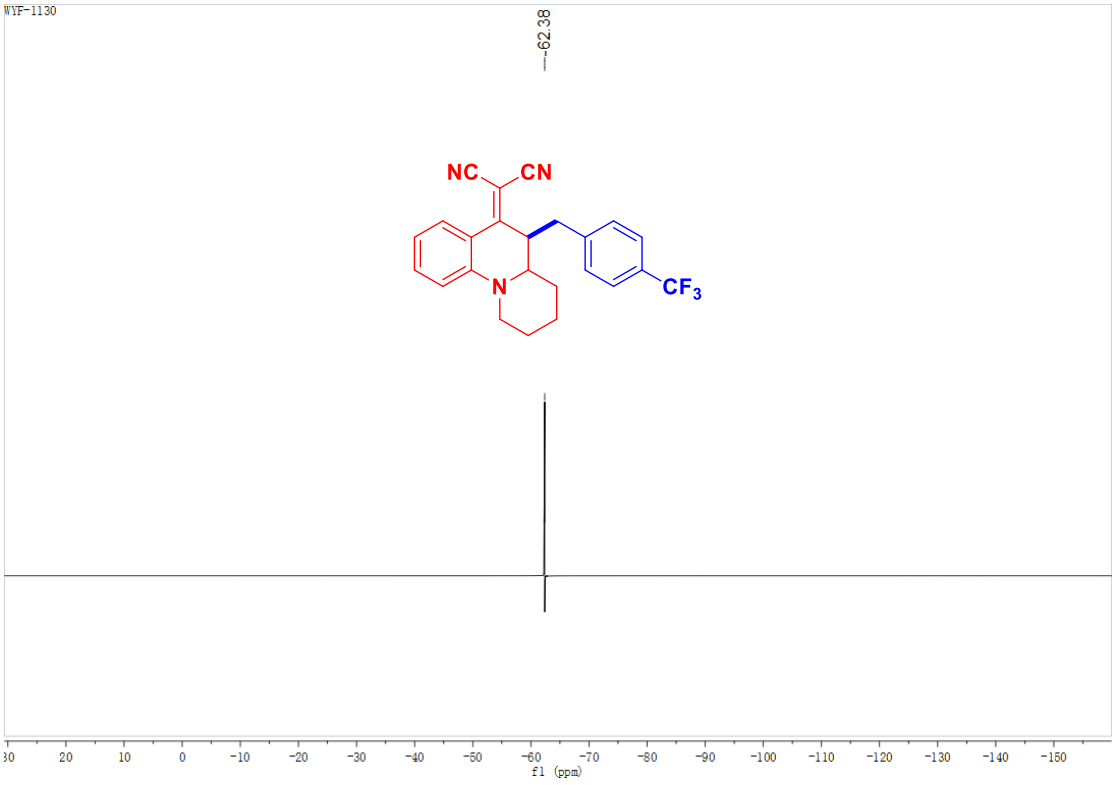
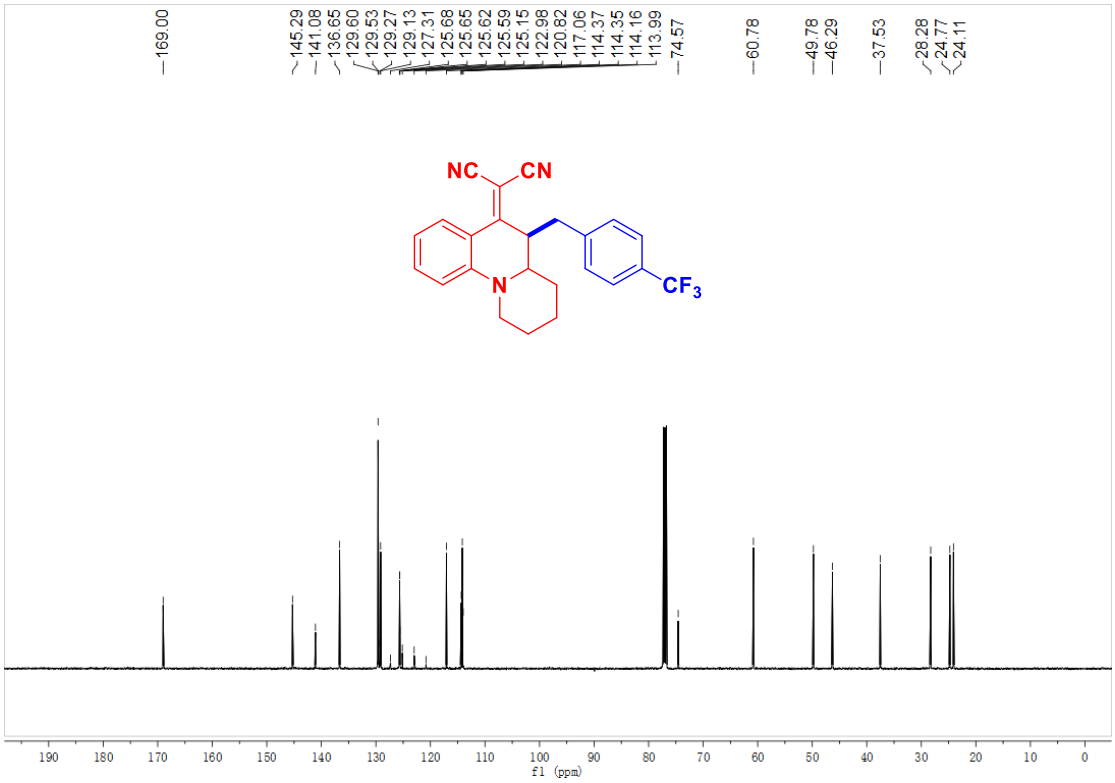
136.29
129.56
129.42
129.16
129.09
125.39
125.36
125.33
125.30
125.14
122.98
115.96
114.26
113.75
112.76
111.90
75.25
57.06
53.40
39.25
37.76
36.29
32.81
28.47
24.87
23.45
20.94
NC
CN
N
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-((5*R*)-5-(4-(trifluoromethyl)benzyl)-1,2,3,4,4a,5-hexahydro-6H-pyrido[1,2-*α*]quinolin-6-ylidene)malononitrile 3u



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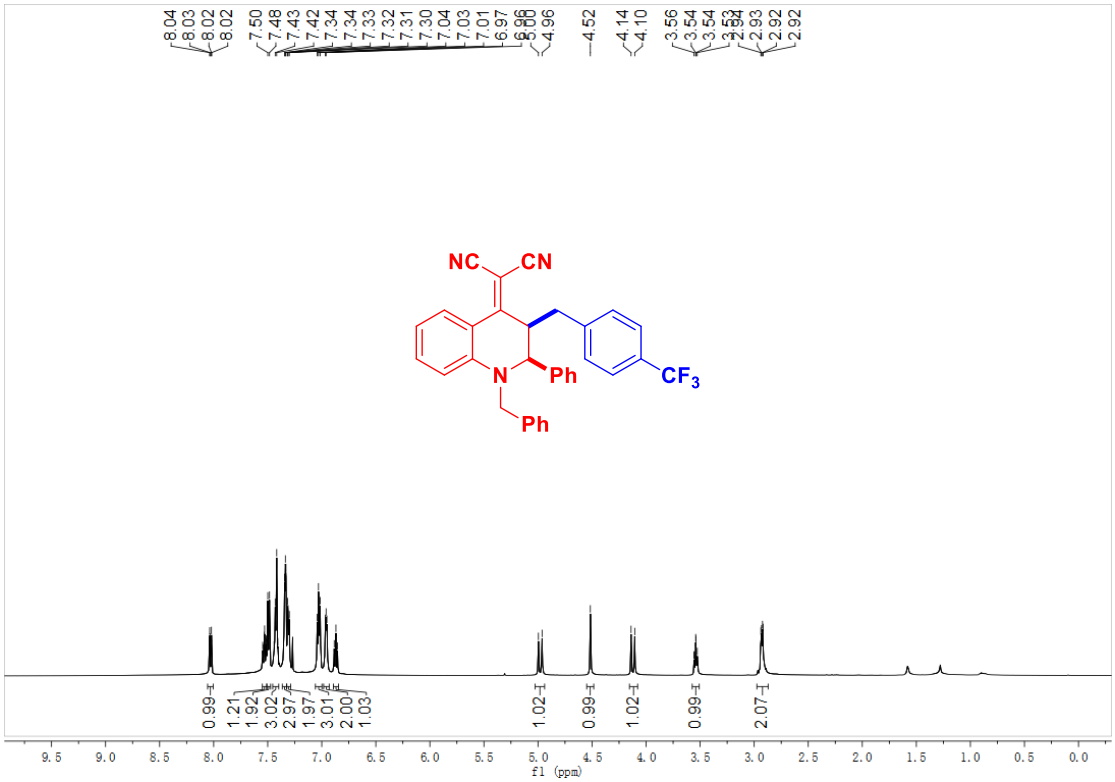
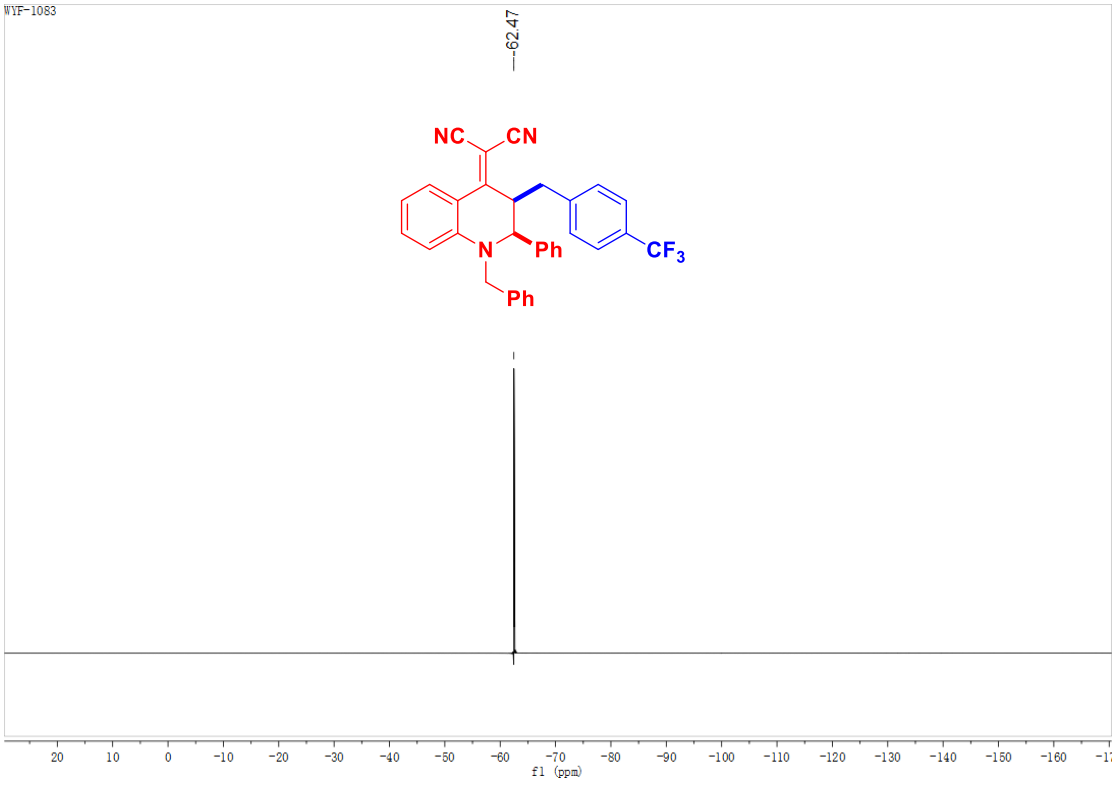
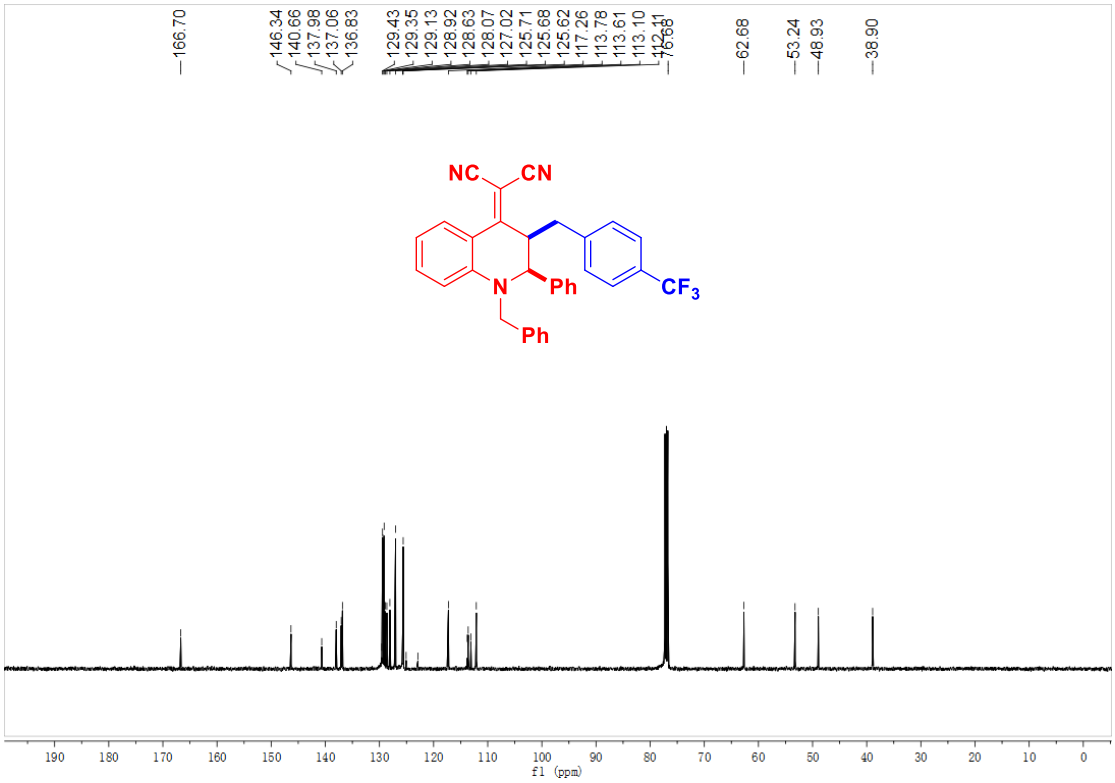
141.08
136.65
129.60
129.53
129.27
129.13
127.31
125.68
125.65
125.62
125.59
125.15
122.98
120.82
117.06
114.37
114.35
114.16
113.99
74.57
60.78
49.78
46.29
37.53
28.28
24.77
24.11
NC
CN
N
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-((2*S*,3*R*)-1-benzyl-2-phenyl-3-(4-(trifluoromethyl)benzyl)-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 3v






166.70
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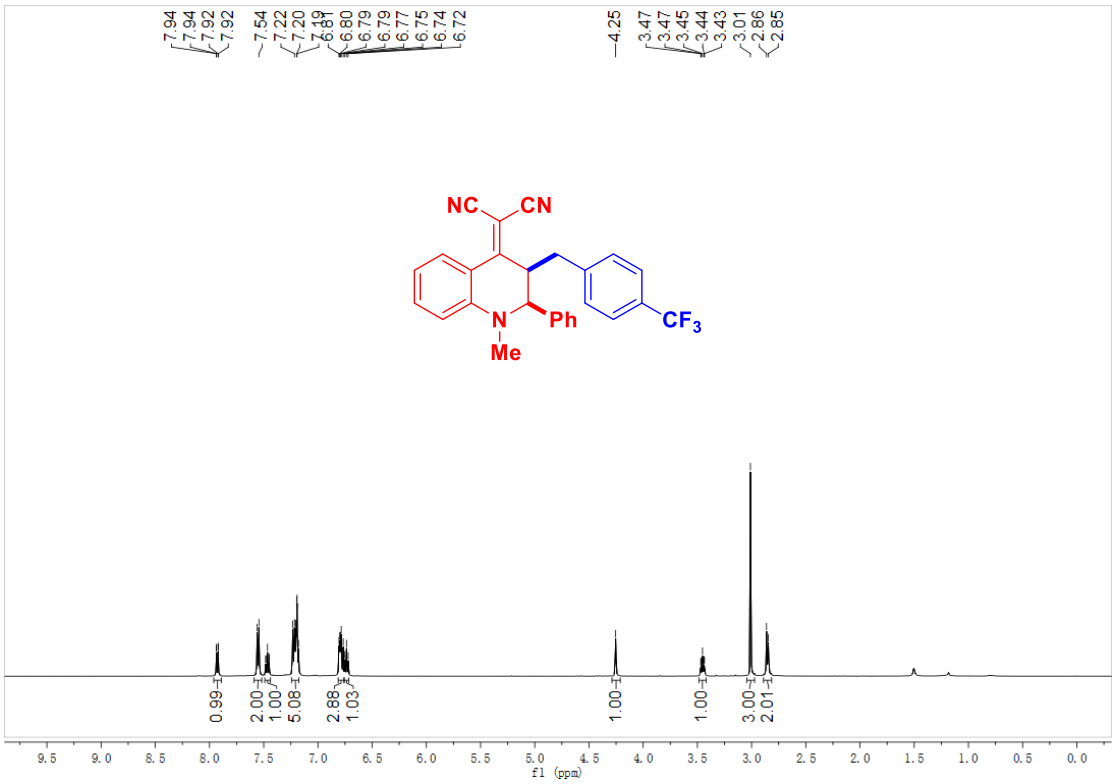
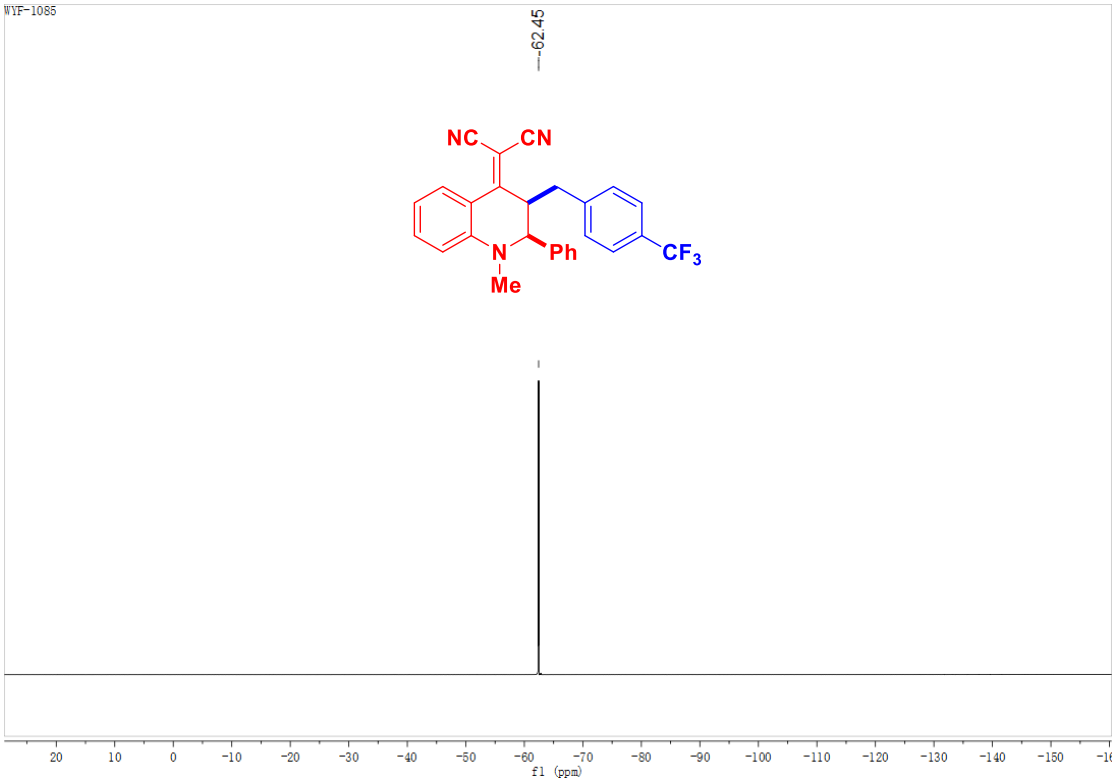
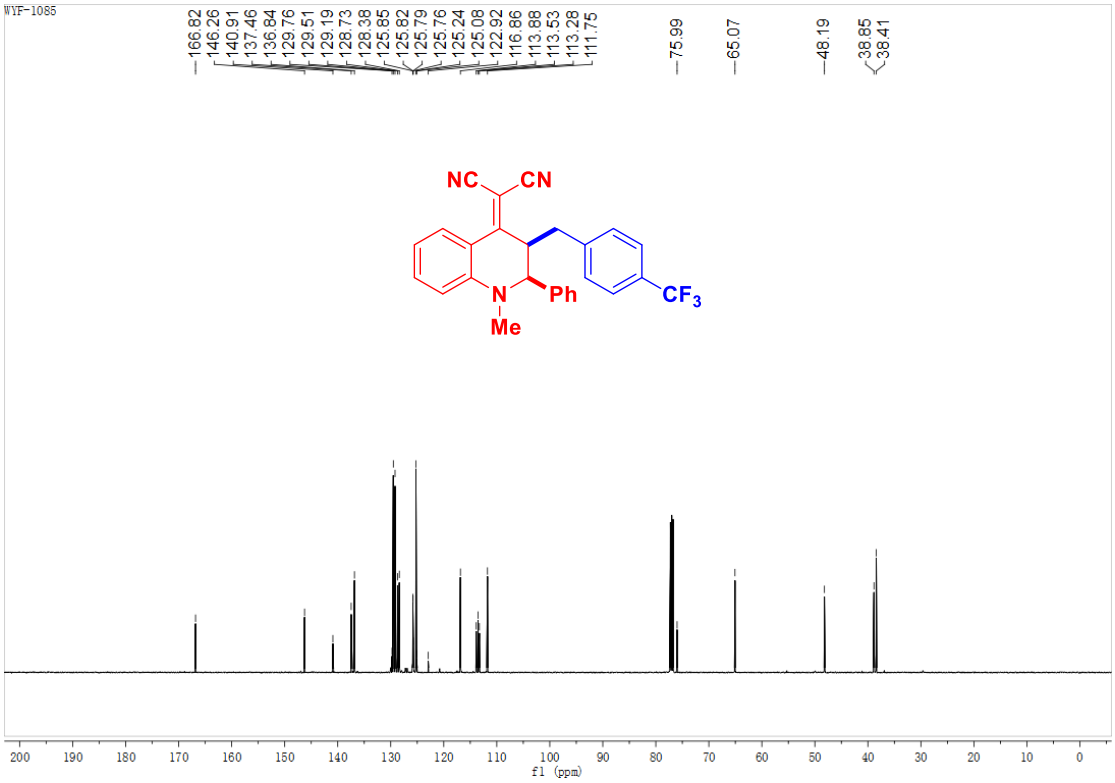
136.83
129.43
129.35
129.13
128.92
128.63
128.07
127.02
125.71
125.68
125.62
117.26
113.78
113.61
113.10
112.11
76.68
62.68
53.24
48.93
38.90
NC
CN
N
Ph
Ph
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

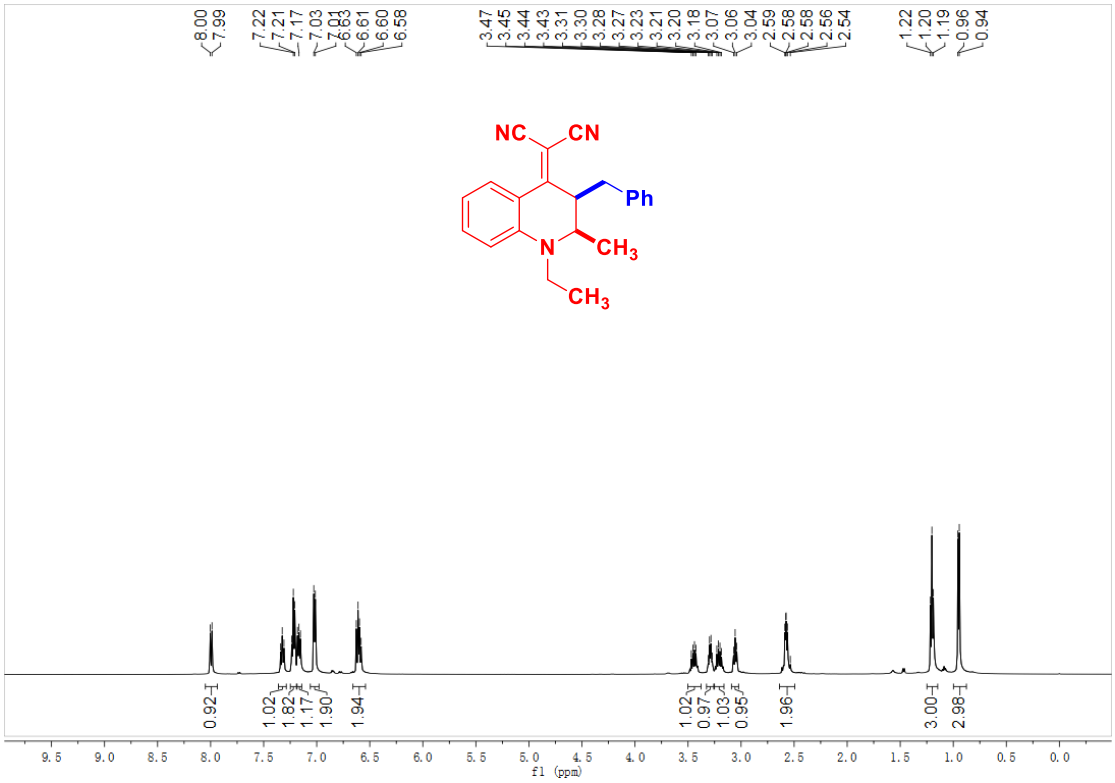
2-((2*S*,3*R*)-1-methyl-2-phenyl-3-(4-(trifluoromethyl)benzyl)-2,3-dihydroquinolin-4(1H)-ylidene)malononitrile 3w

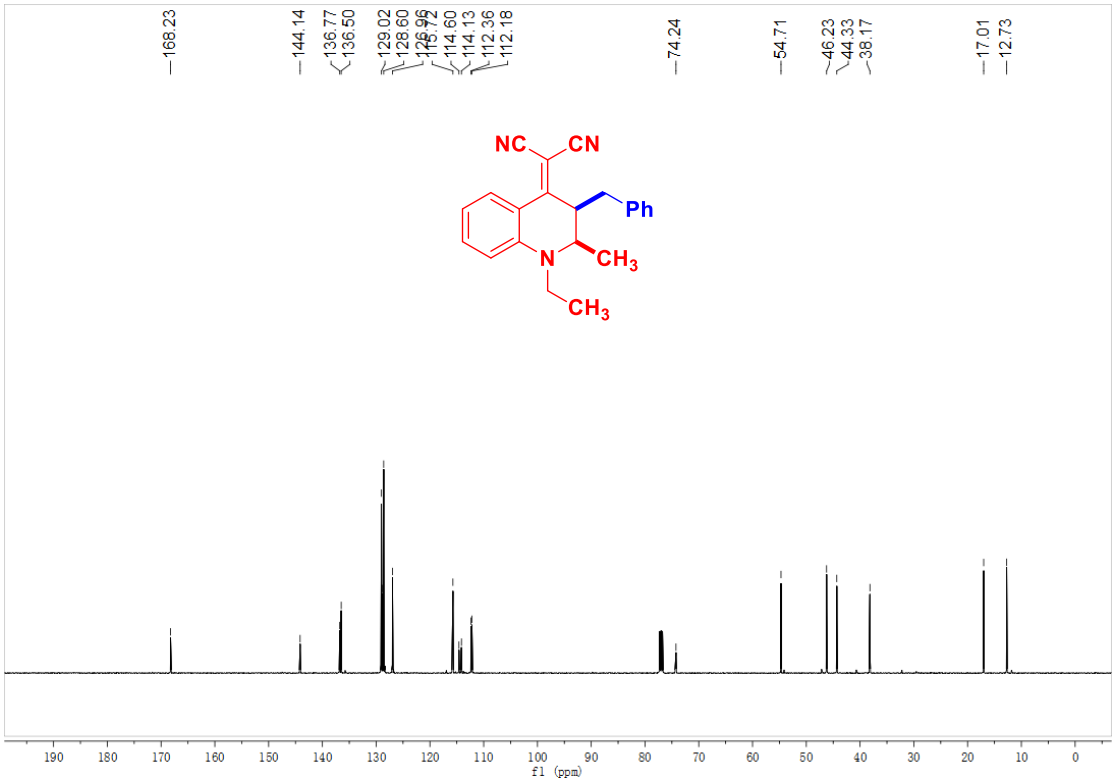




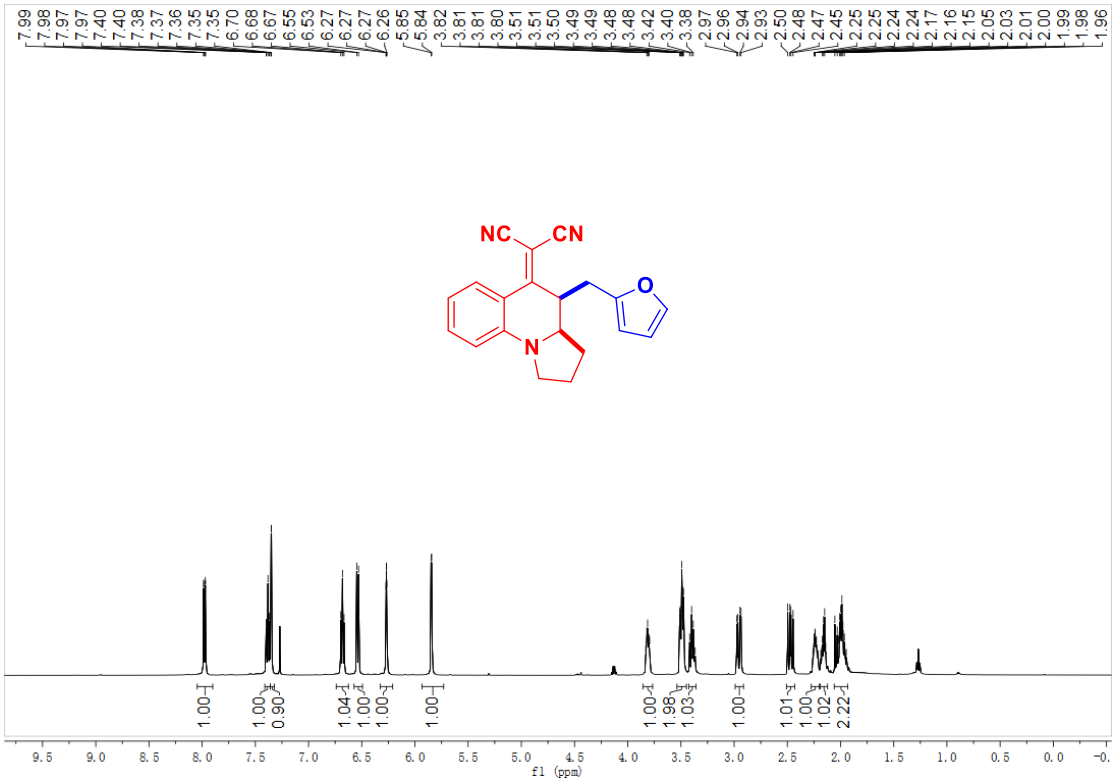

WYF-1085
166.82
146.26
140.91
137.46
136.84
129.76
129.51
129.19
128.73
128.38
125.85
125.82
125.79
125.76
125.24
125.08
122.92
116.86
113.88
113.53
113.28
111.75
75.99
65.07
48.19
38.85
38.41
NC
CN
N
Me
Ph
CF3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

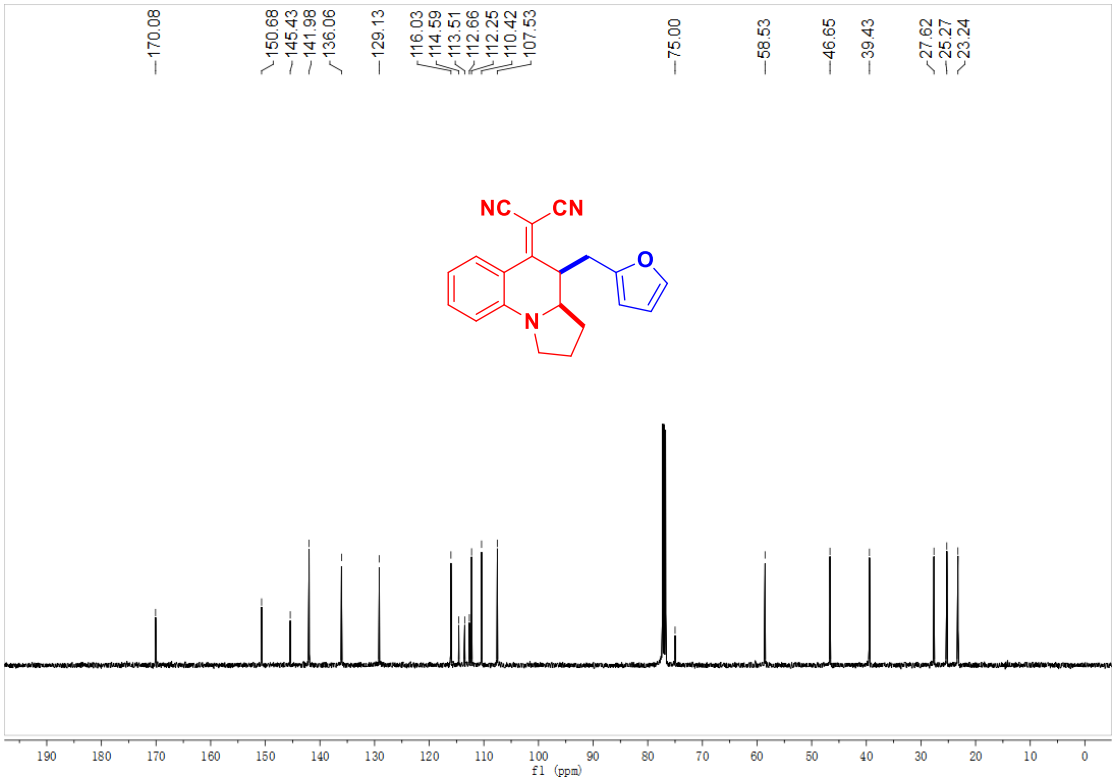
2-((2*R*,3*R*)-3-benzyl-1-ethyl-2-methyl-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 3x



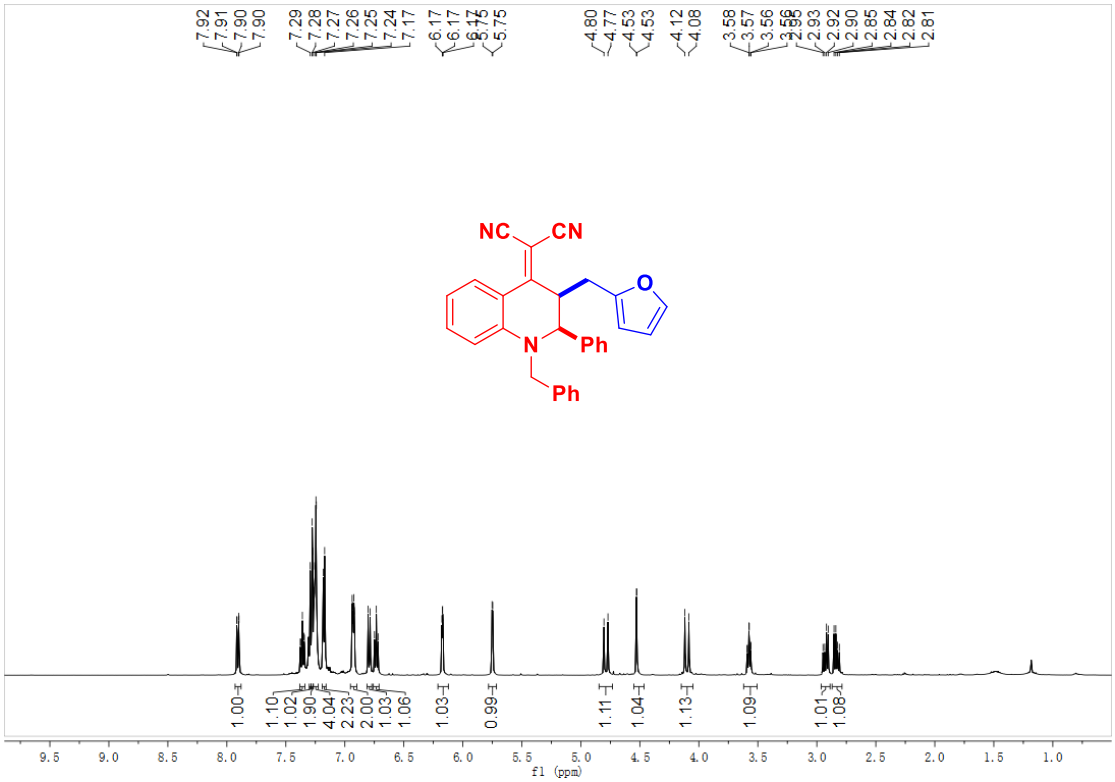


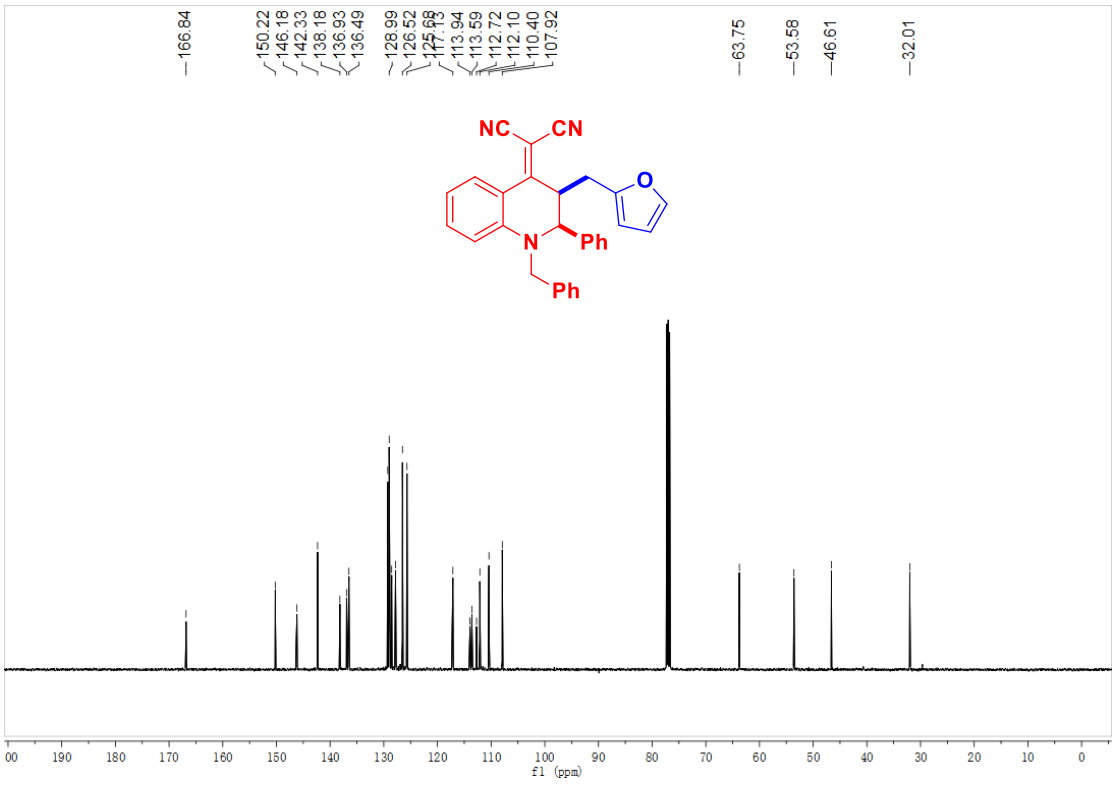
2-((3a*R*,4*R*)-4-(furan-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5a



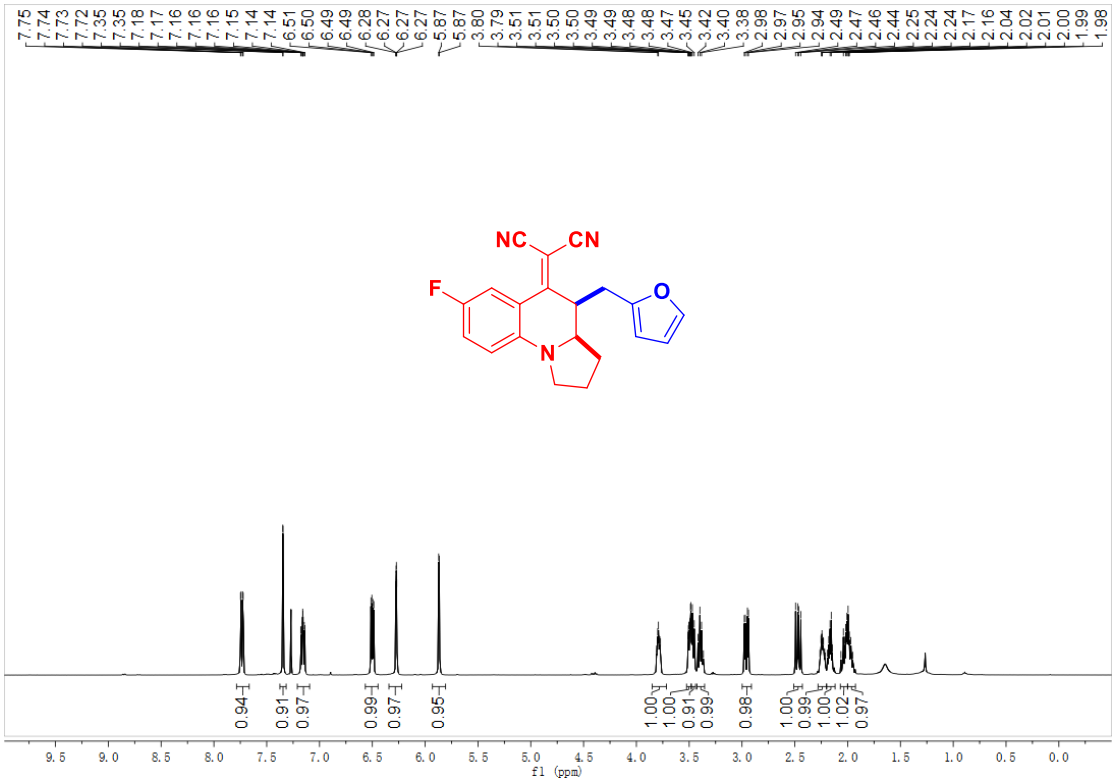


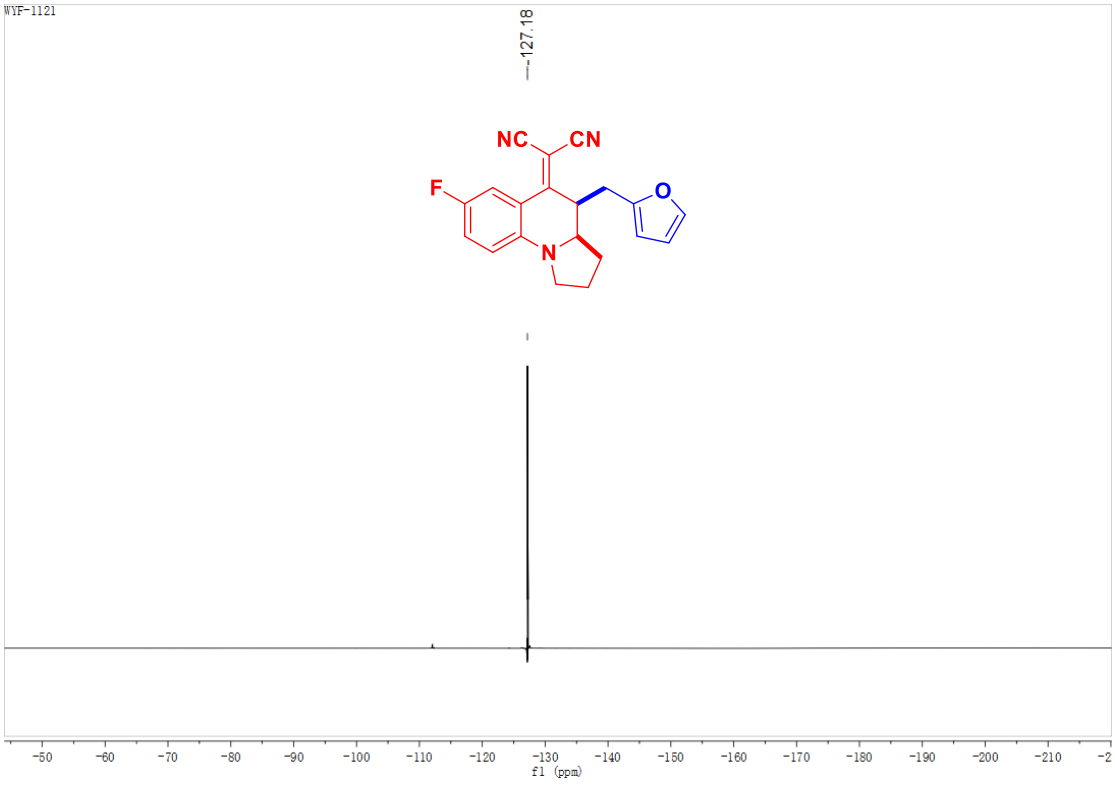
2-((2*S*,3*R*)-1-benzyl-3-(furan-2-ylmethyl)-2-phenyl-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 5b

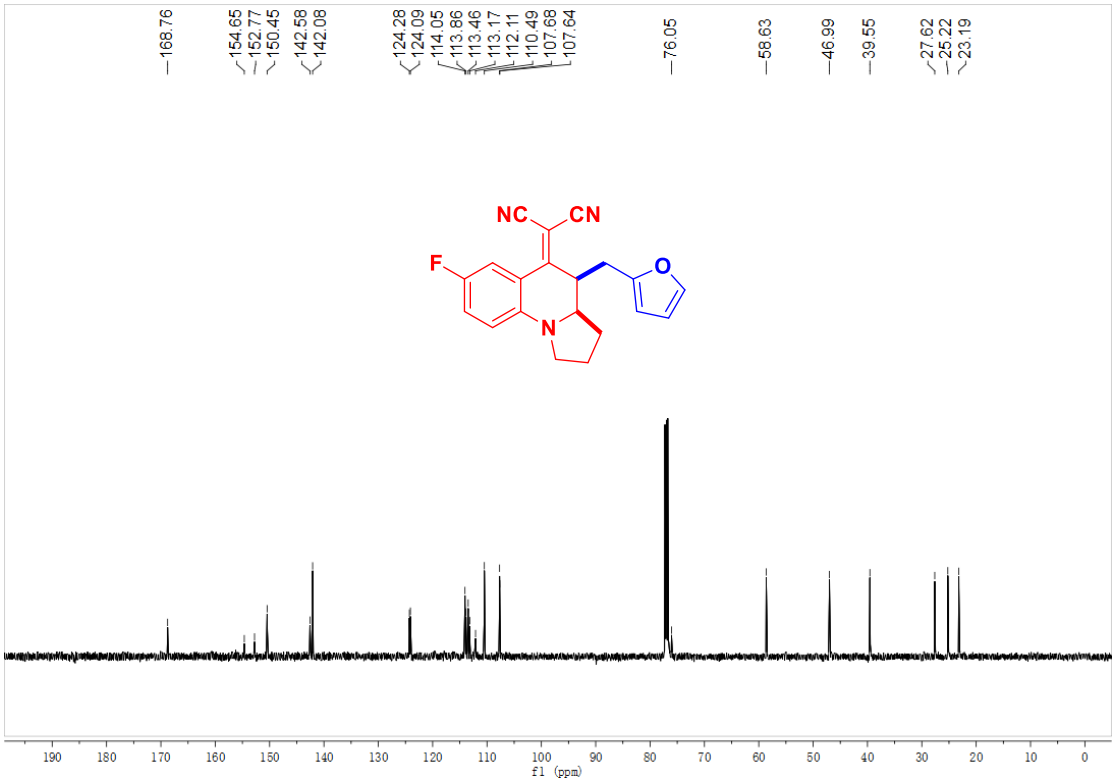




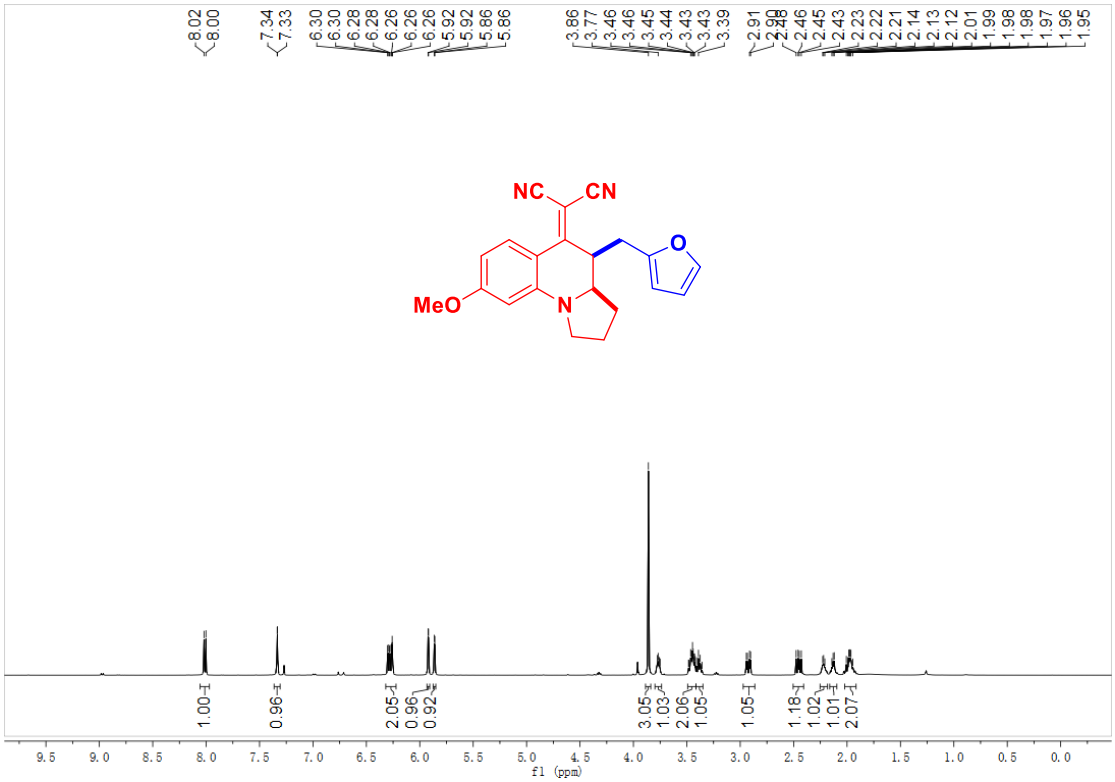
2-((3a*R*,4*R*)-7-fluoro-4-(furan-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5c

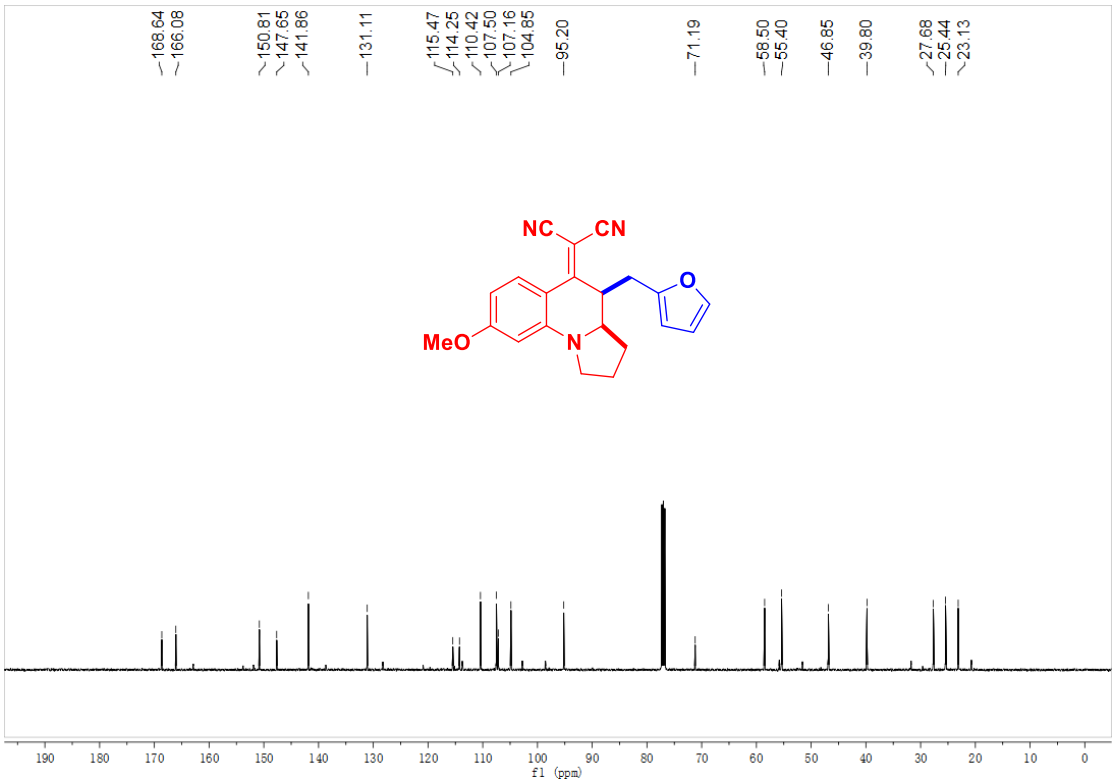




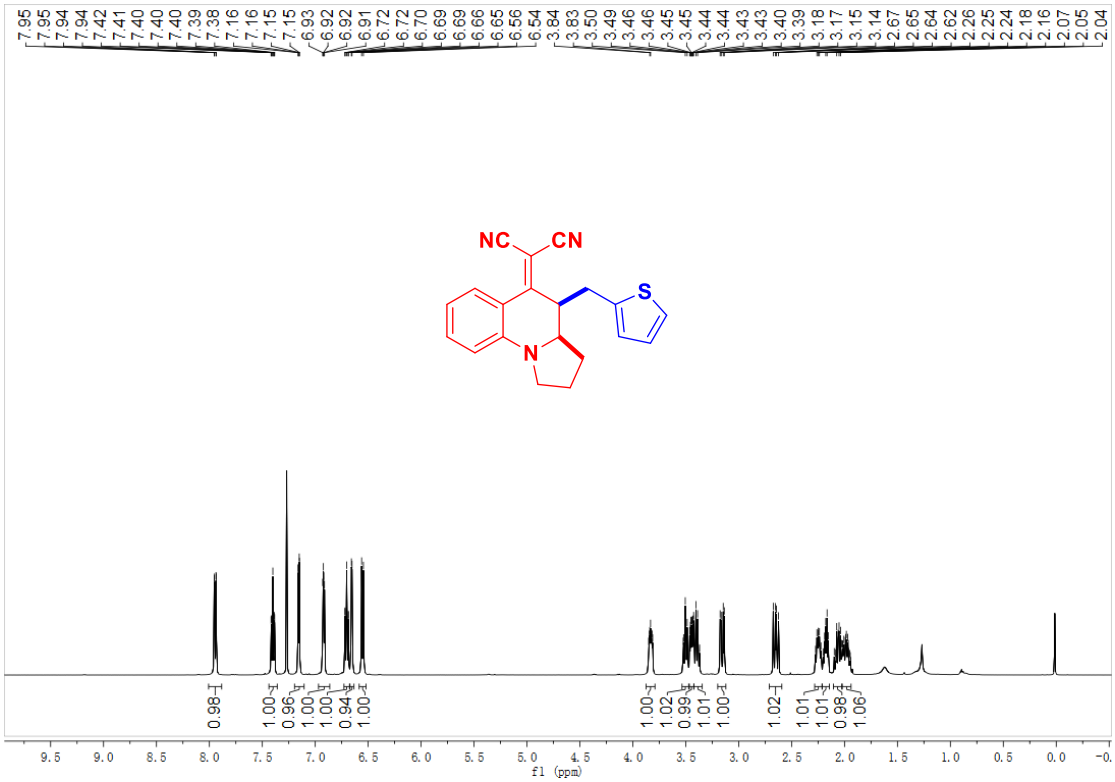

168.76
154.65
152.77
150.45
142.58
142.08
124.28
124.09
114.05
113.86
113.46
113.17
112.11
110.49
107.68
107.64
76.05
58.63
46.99
39.55
27.62
25.22
23.19
NC
CN
F
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

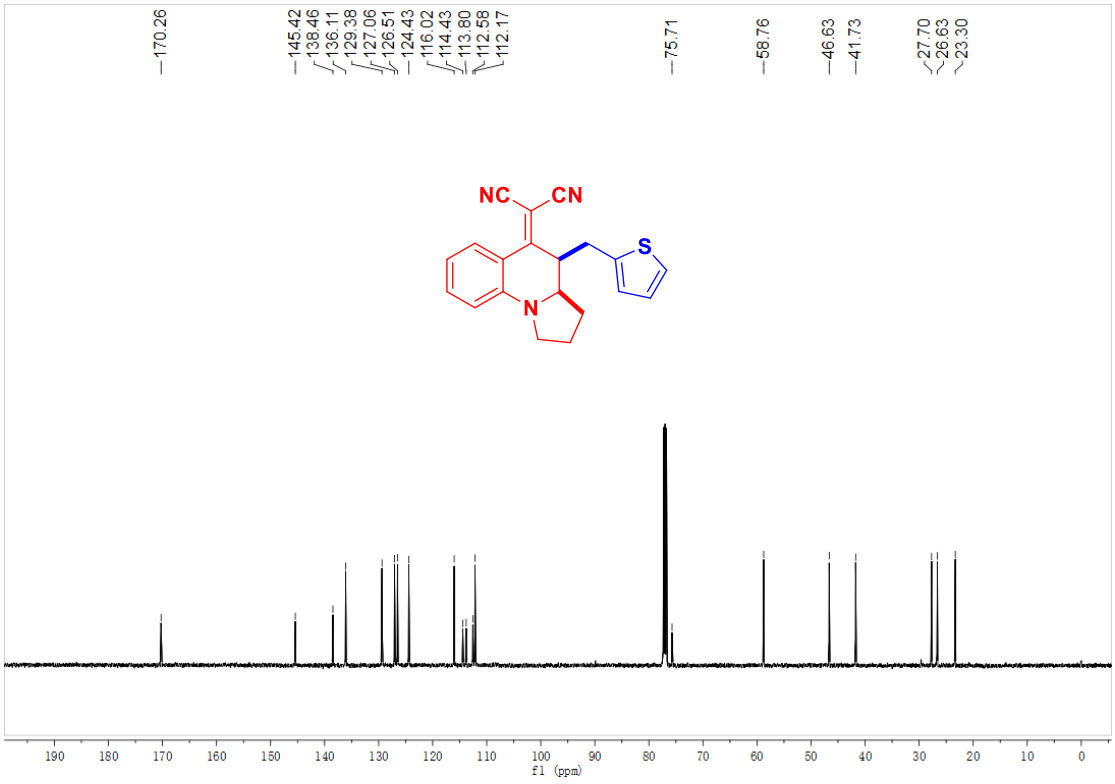
2-((3a*R*,4*R*)-4-(furan-2-ylmethyl)-8-methoxy-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5d



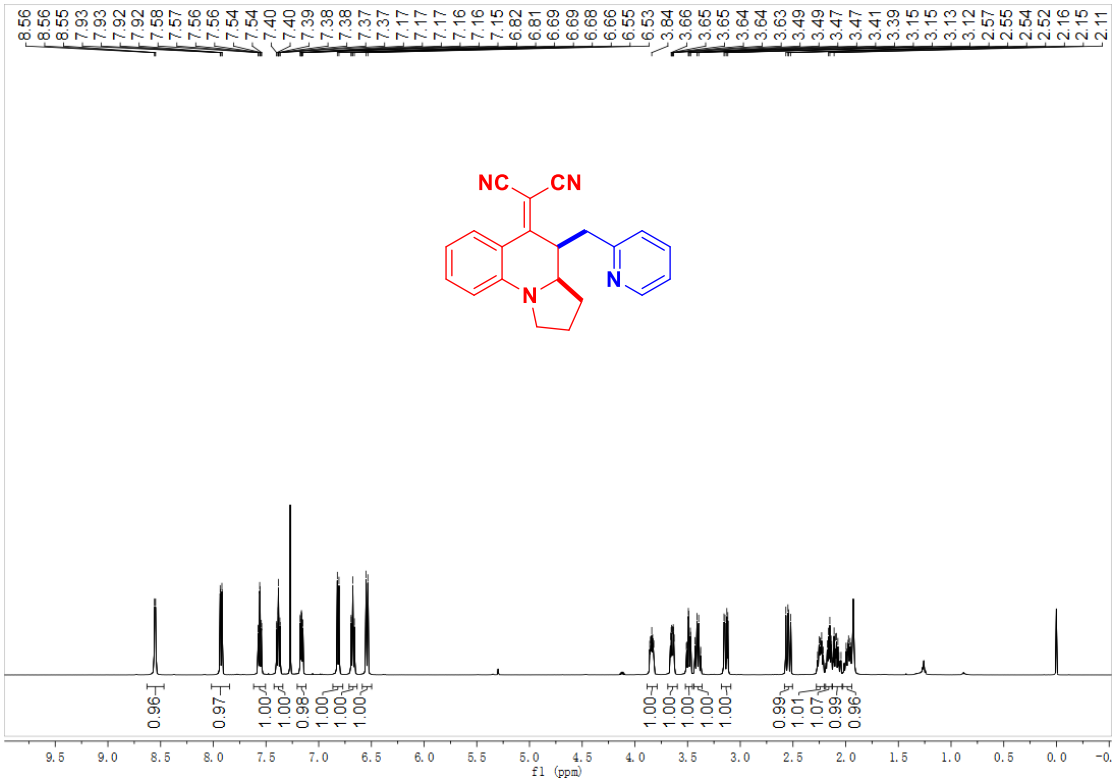


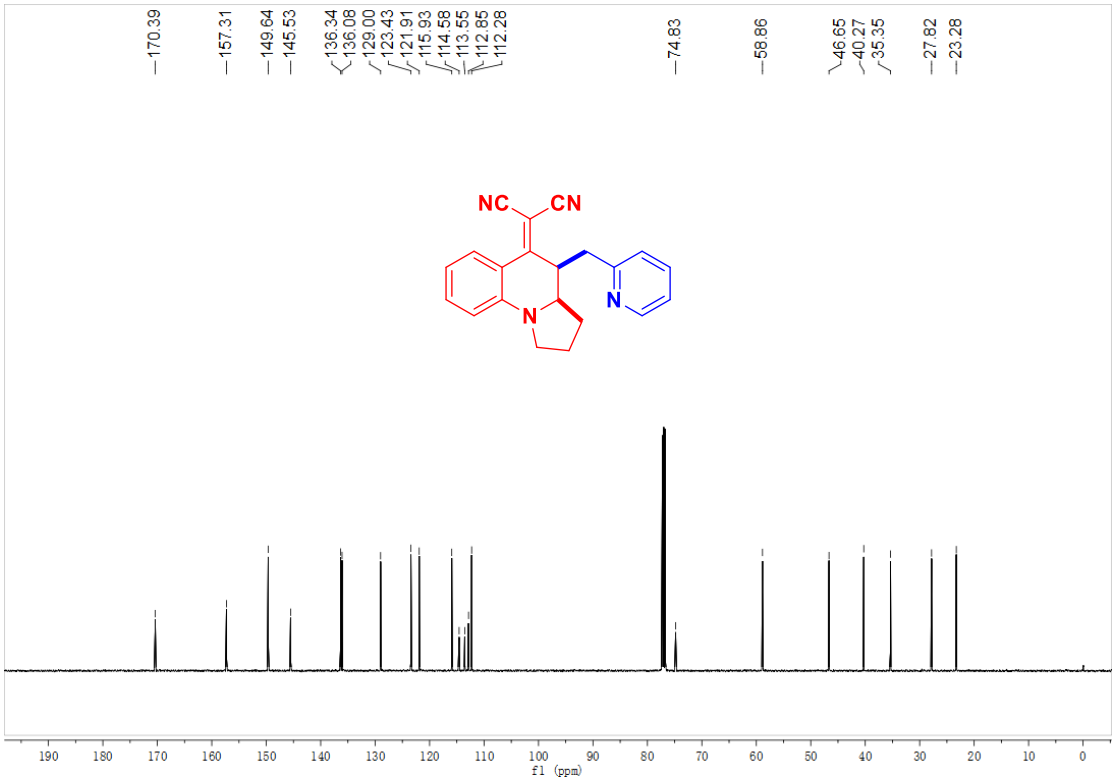
2-((3a*R*,4*R*)-4-(thiophen-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5e



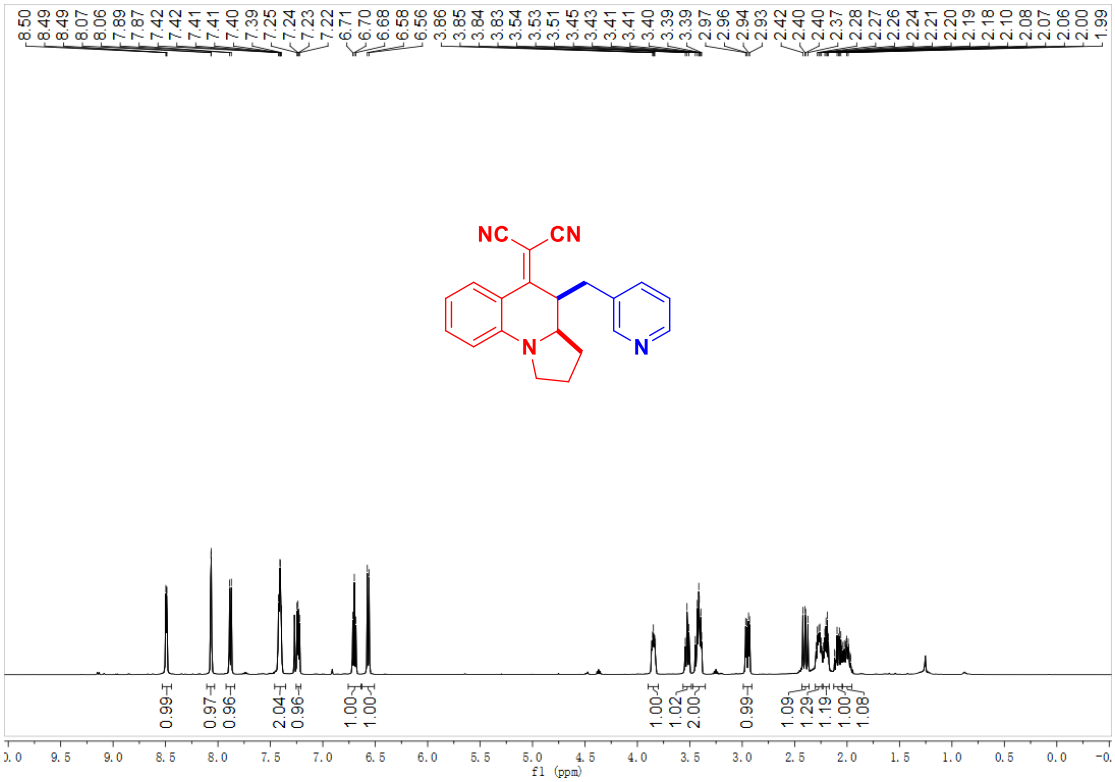


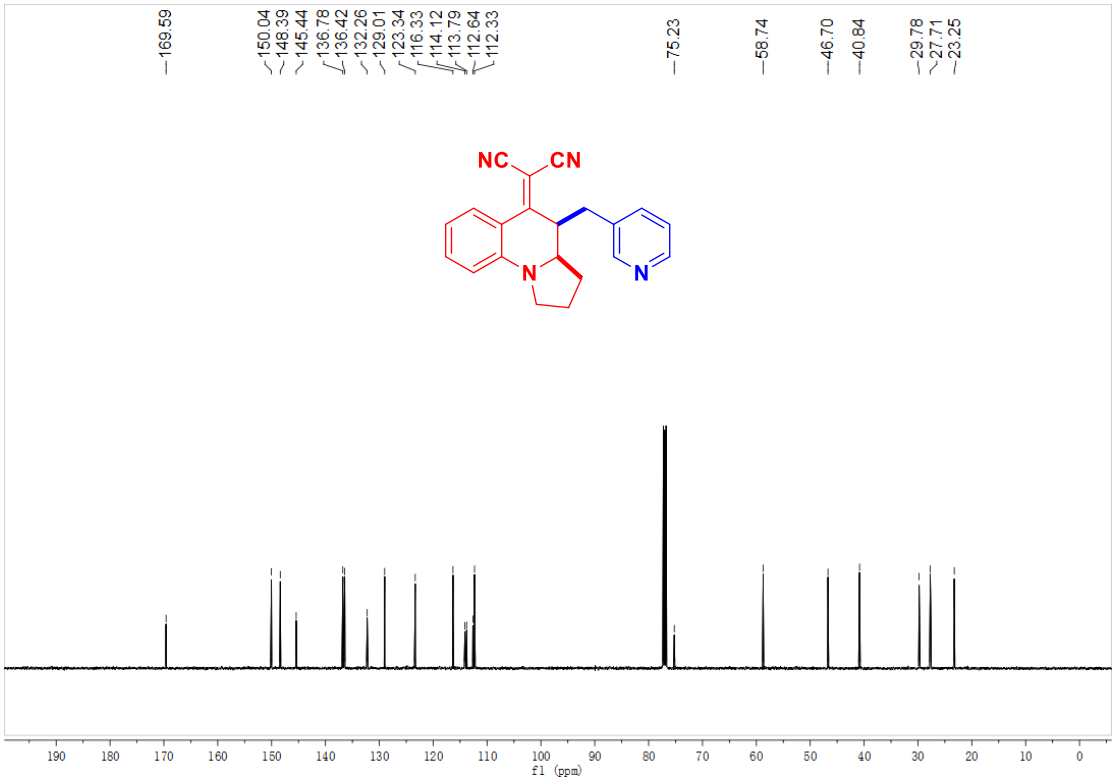
2-((3a*R*,4*R*)-4-(pyridin-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5f





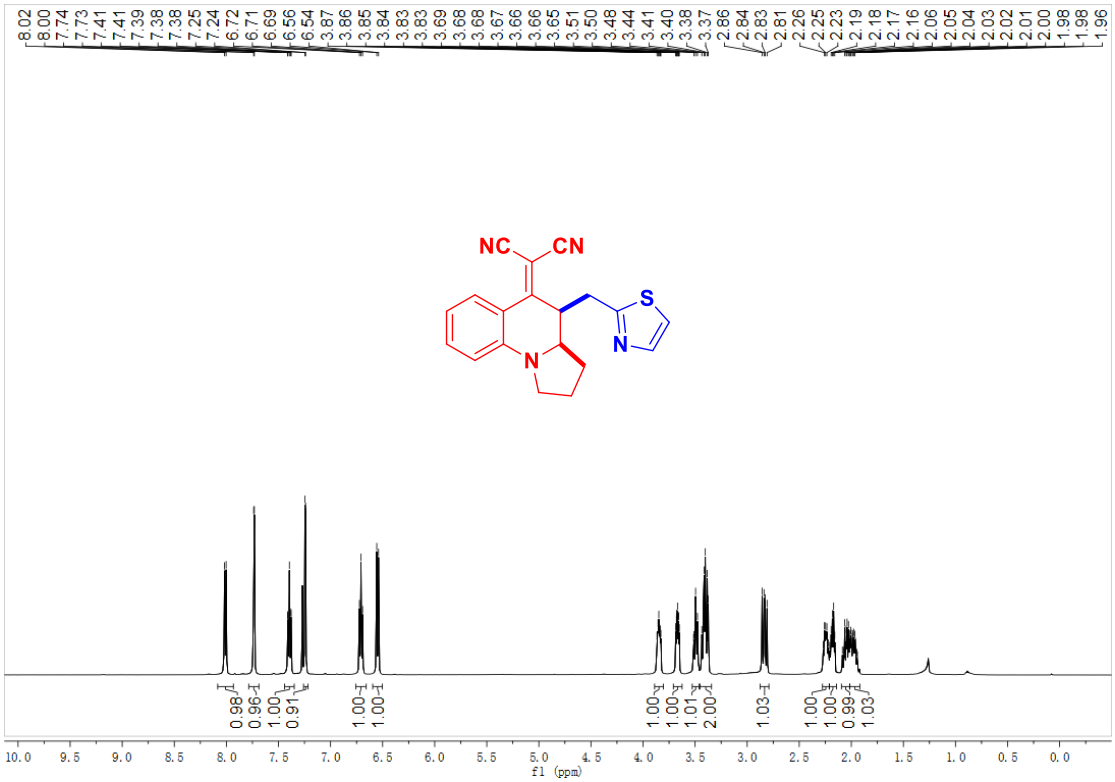
2-((3a*R*,4*R*)-4-(pyridin-3-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5g

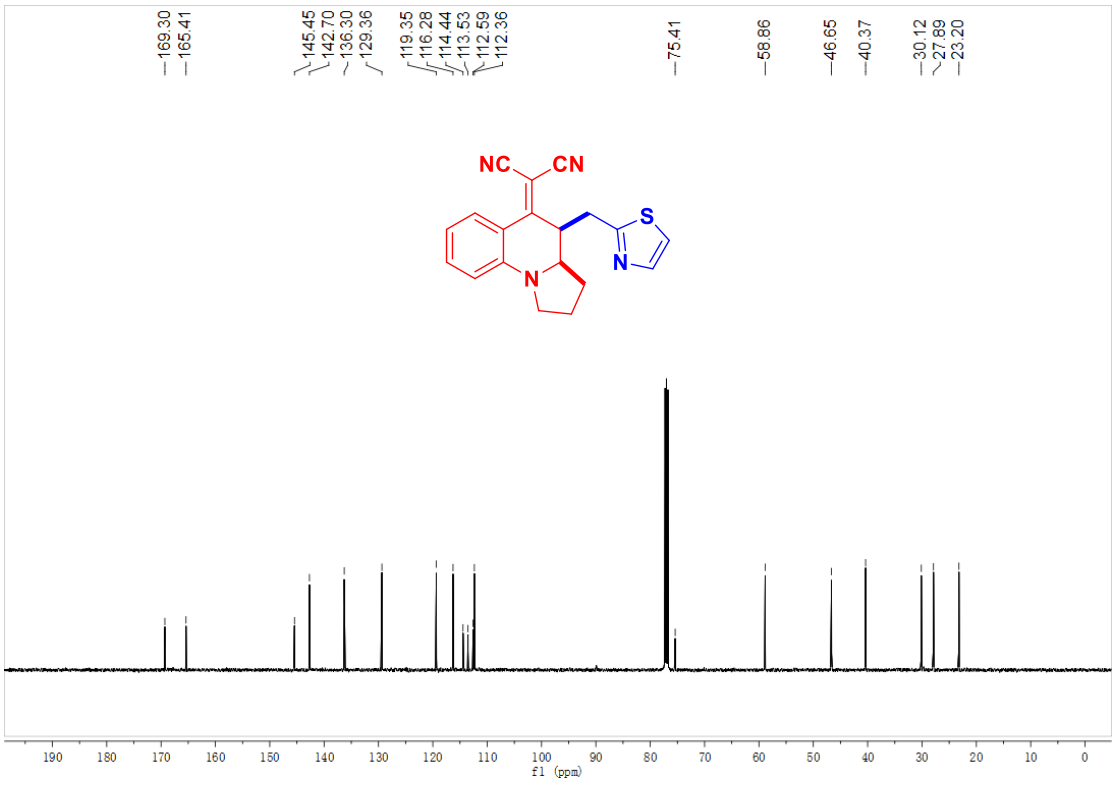




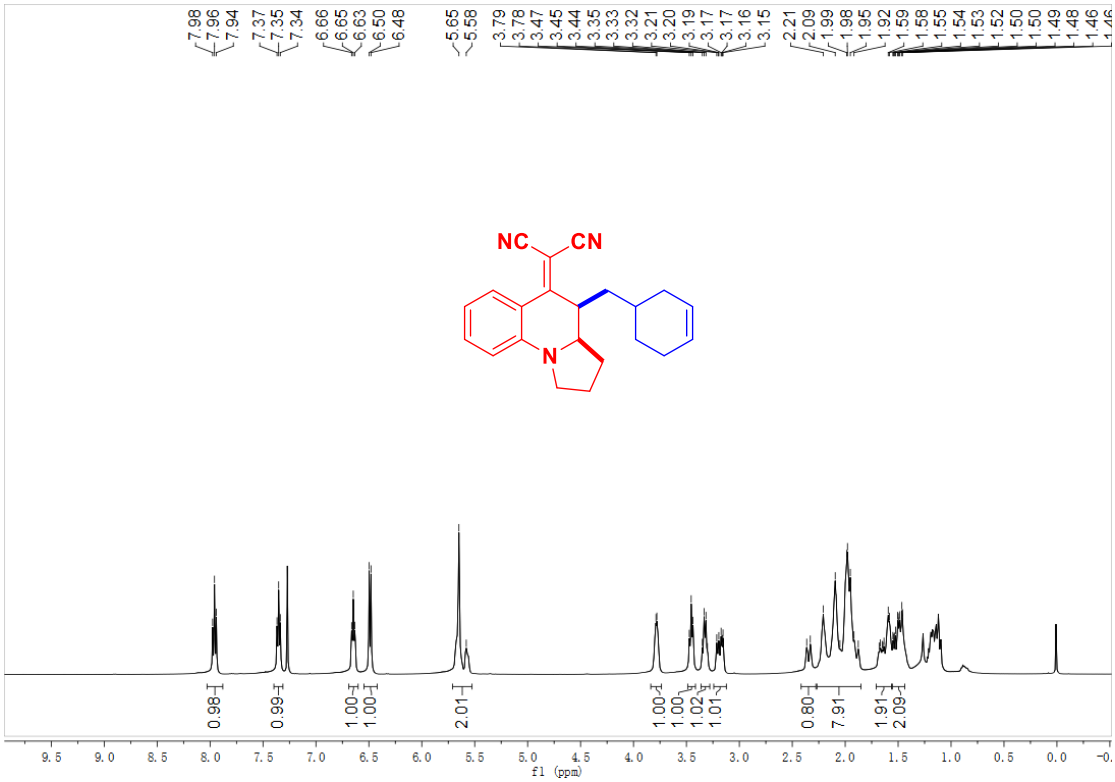
2-(4-(thiazol-2-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile

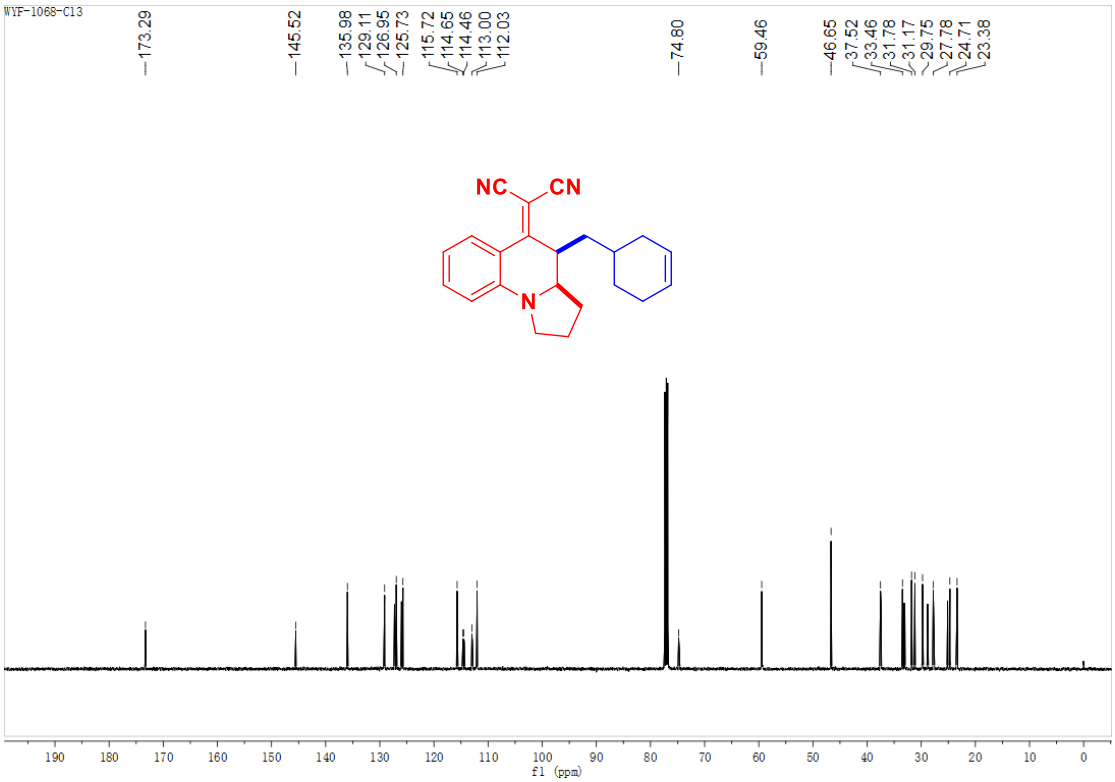
5h



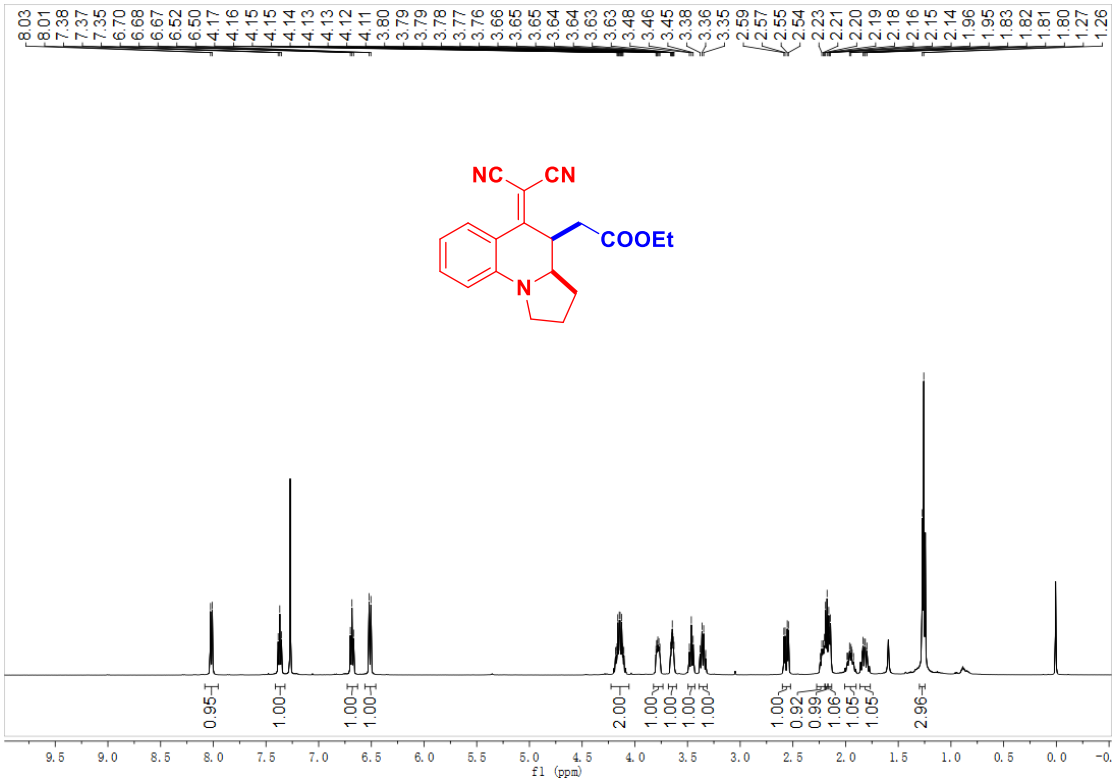


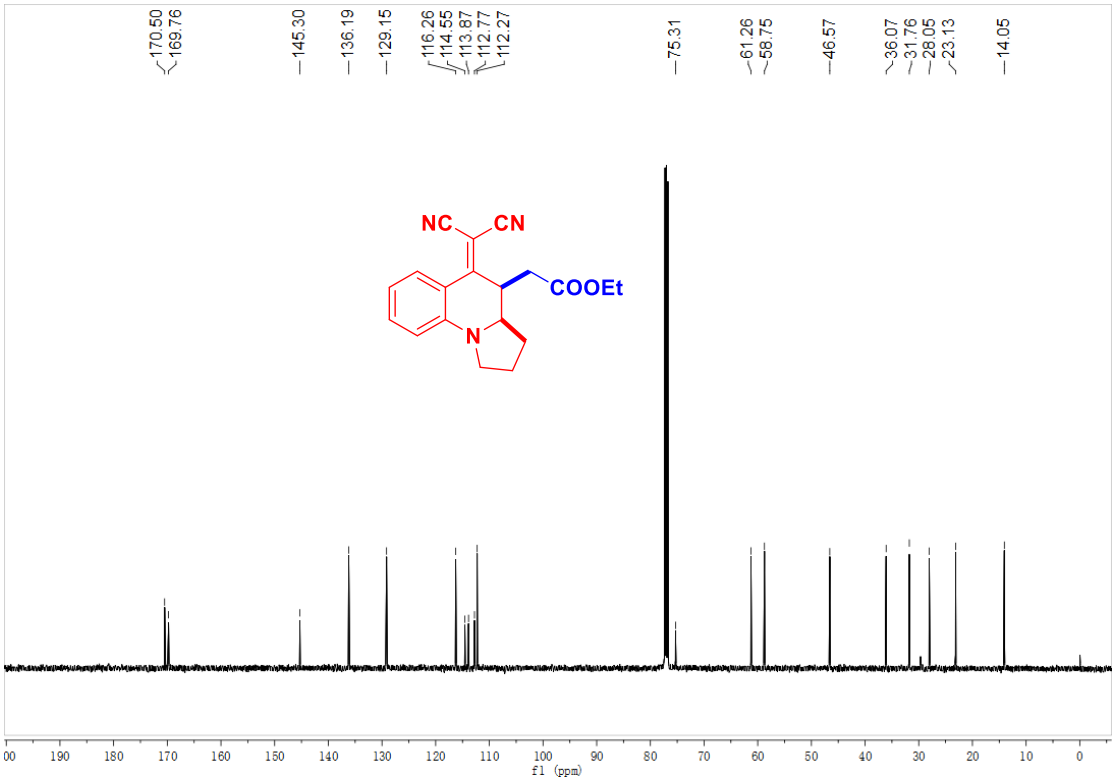
2-((3a*R*,4*R*)-4-(cyclohex-3-en-1-ylmethyl)-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1H)-ylidene)malononitrile 5i



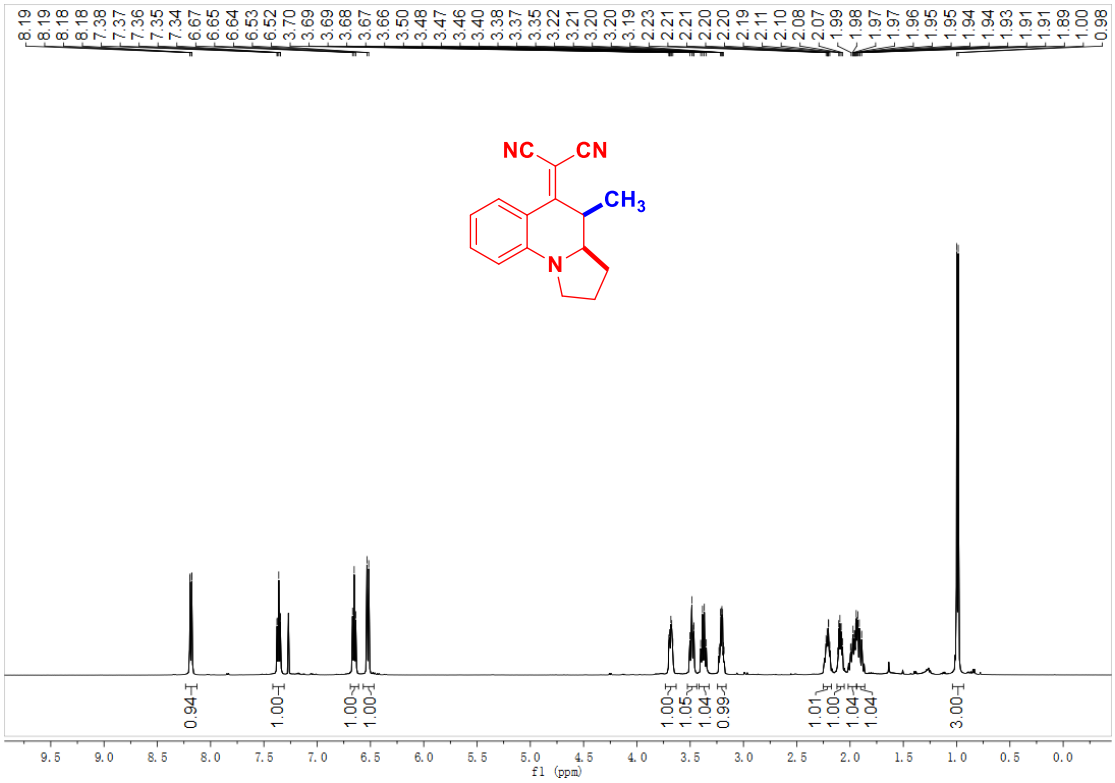


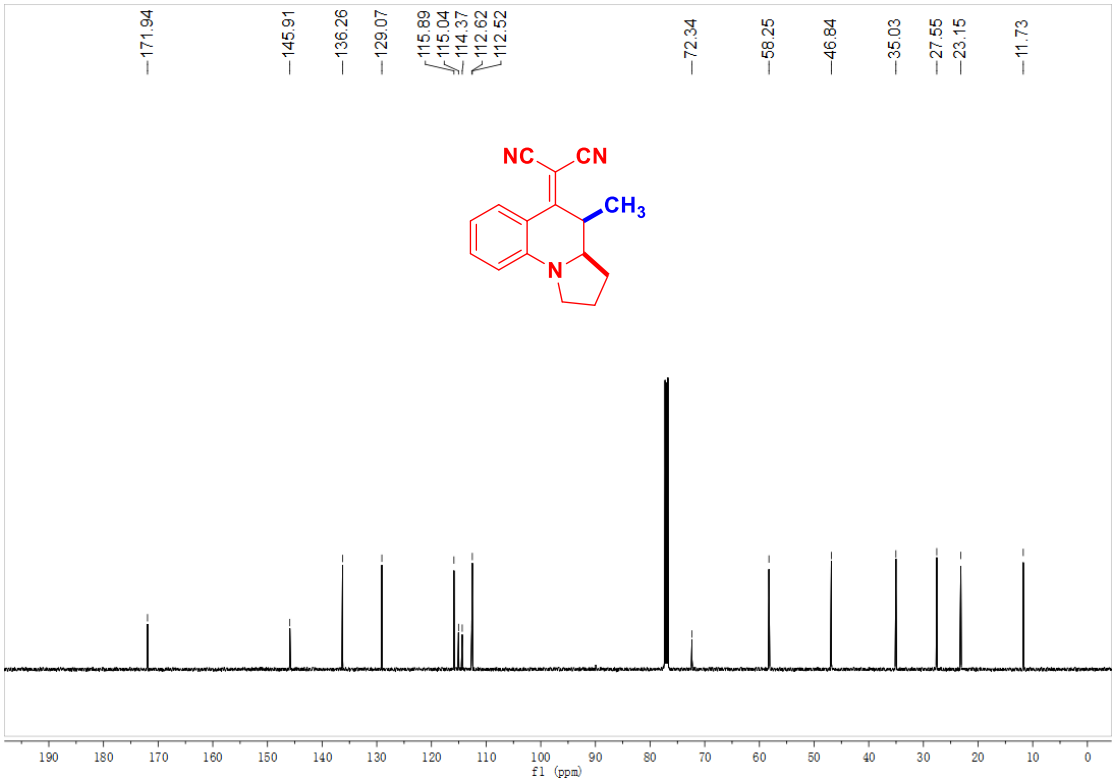
Ethyl 2-((3a*R*,4*R*)-5-(dicyanomethylene)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-*α*]quinolin-4-yl)acetate 5j



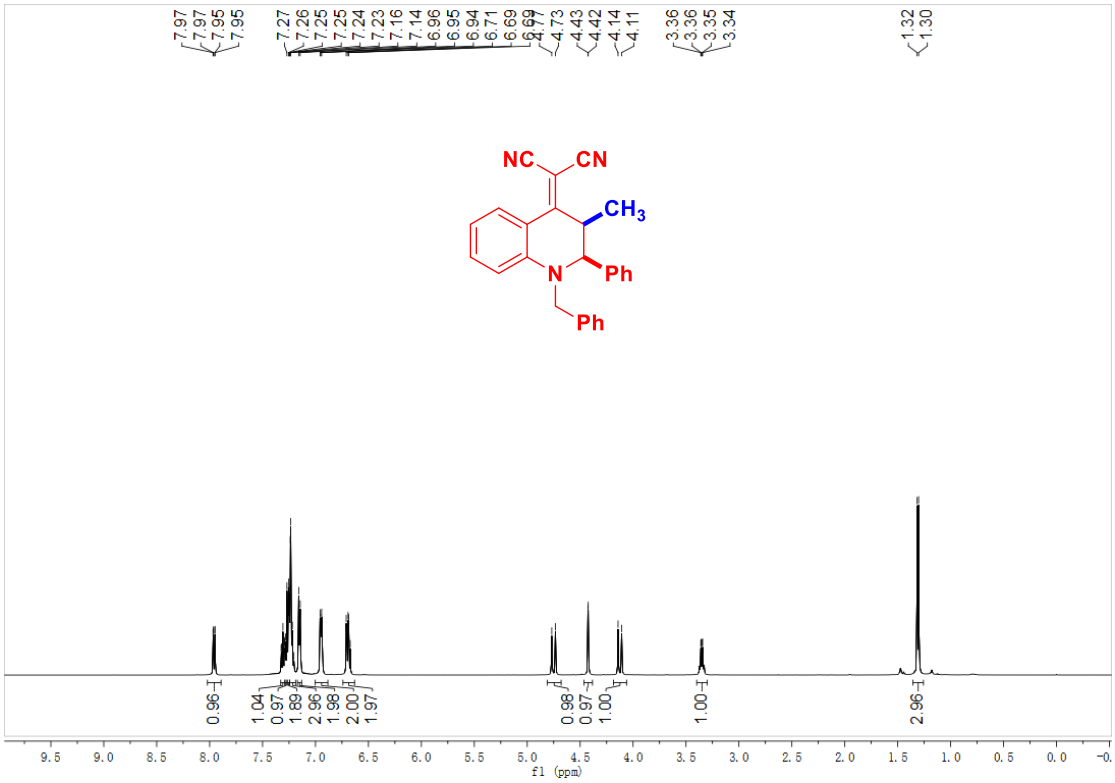


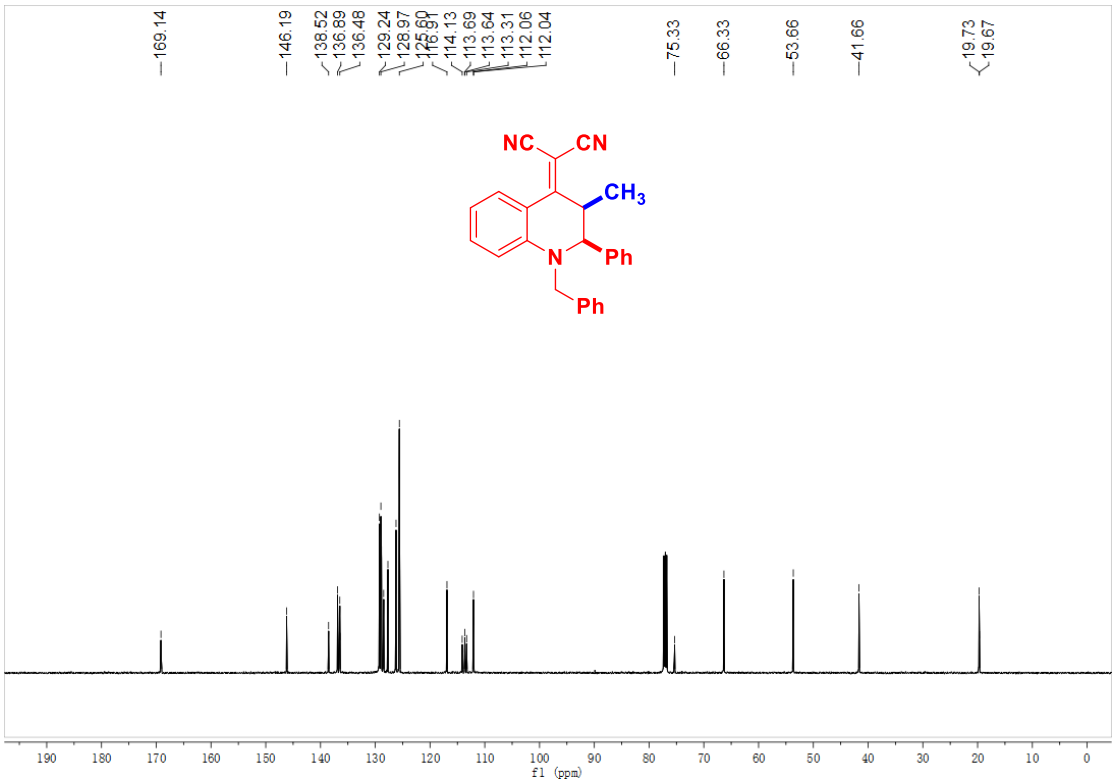
2-((3a*R*,4*R*)-4-methyl-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5k



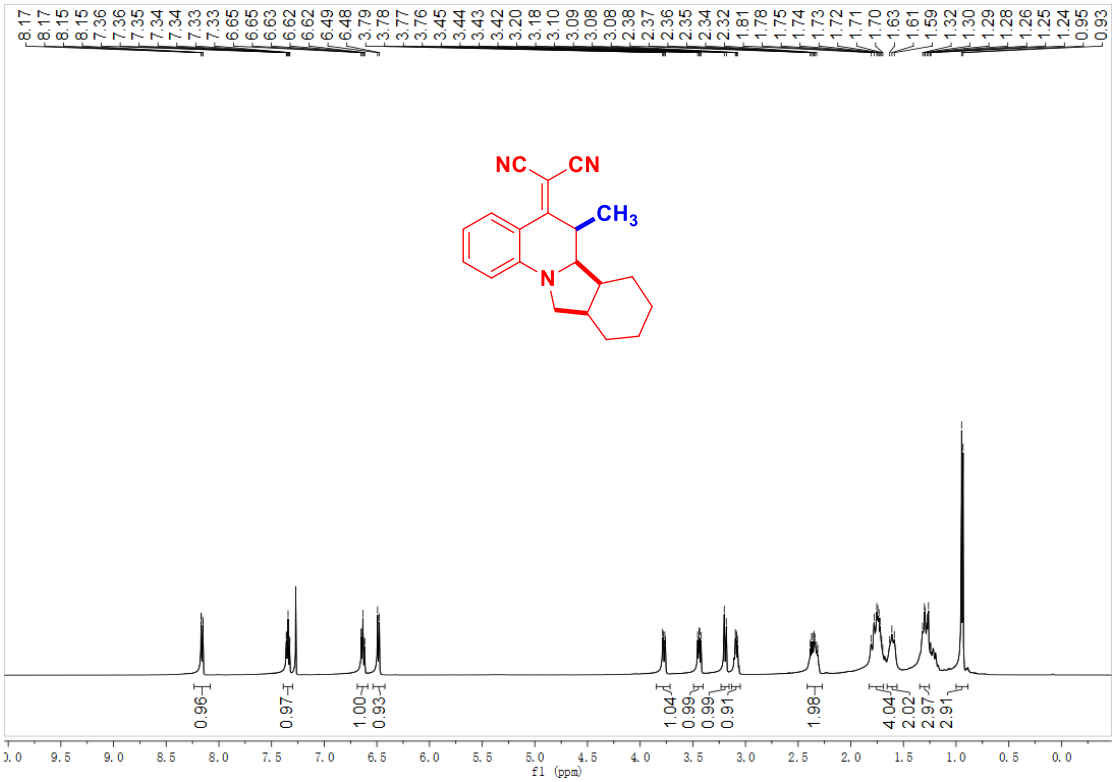


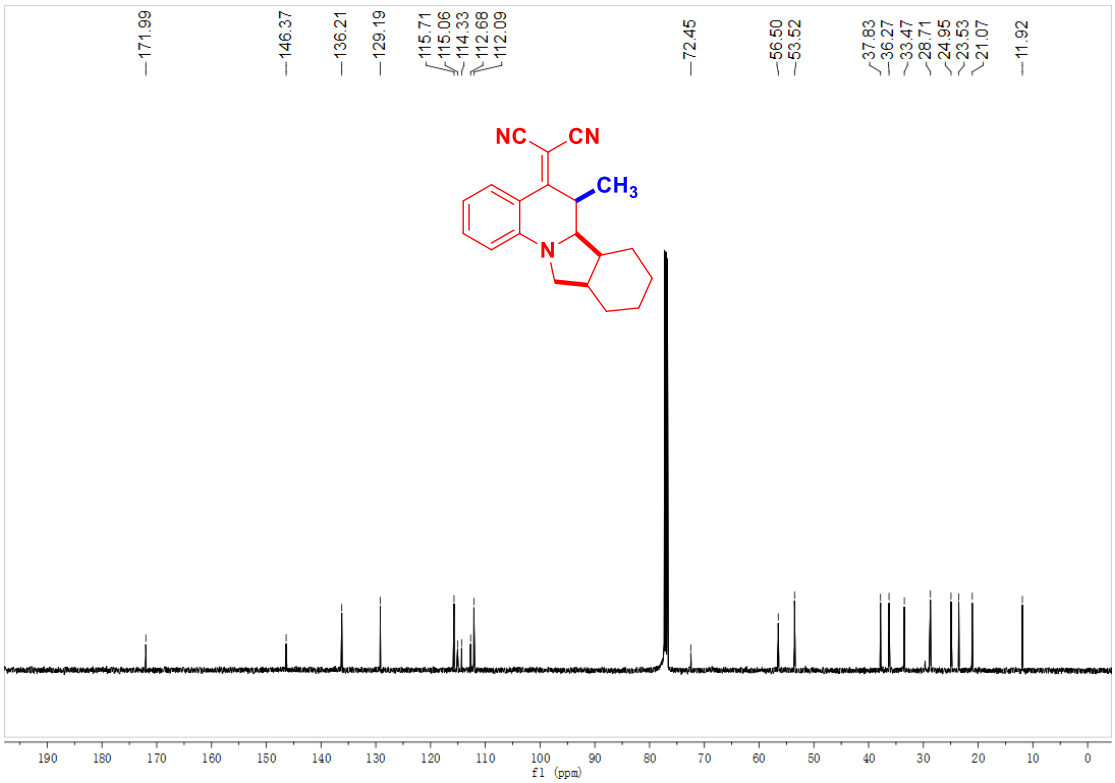
2-((2*S*,3*R*)-1-benzyl-3-methyl-2-phenyl-2,3-dihydroquinolin-4(1*H*)-ylidene)malononitrile 5l





2-((6*R*,6a*R*,6b*S*)-6-methyl-6a,6b,7,8,9,10,10a,11-octahydroisoindolo[2,1-α]quinolin-5(6*H*)-ylidene)malononitrile 5m





2-((3a*R*,4*R*)-4-ethyl-2,3,3a,4-tetrahydropyrrolo[1,2-*α*]quinolin-5(1*H*)-ylidene)malononitrile 5n