

Electronic Supplementary Material

Construction of 4*H*-pyrido[4,3,2-*gh*]phenanthridin-5(6*H*)-one skeleton via a catalyst-free radical cascade addition/cyclization using azo compounds as radical resources

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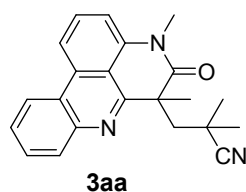
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1. General remarks

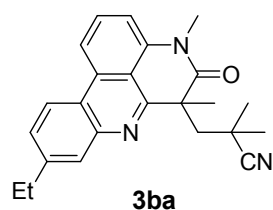
^1H NMR (400MHz) spectra were recorded on a Bruker Avance 400 spectrometers in CDCl_3 [using $(\text{CH}_3)_4\text{Si}$ (for ^1H , $\delta = 0.00$) as internal standard]. ^{13}C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometers in CDCl_3 [using CDCl_3 (for ^{13}C , $\delta = 77.00$) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet, ddd = doublet of doublet of doublet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. *N*-Arylacrylamides **1** were prepared according to our previous procedures.¹

2. General procedure for the synthesis of products **3**

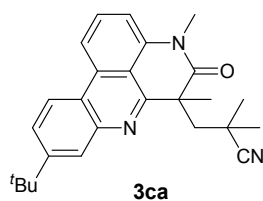
N-Arylacrylamides **1** (0.2 mmol) and azo compounds **2** (0.4 mmol, 2.0 equiv.) were added to a 25 mL sealed tube with a Teflon lined cap, and the internal atmosphere were exchanged with argon gas *via* three repeated cycle of vacuum-refill. Then 1,4-dioxane (2 mL) was added. The mixture was heated at 60 °C under vigorous stirring for 24 h. After the reaction was completed, the reaction mixture was cooled to room temperature and extracted with EtOAc (15 × 3 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4 , filtered and concentrated in *vacuo*. The residue was purified by silica gel chromatography using hexane/ethyl acetate (5:1) as eluent to afford the pure products **3**.



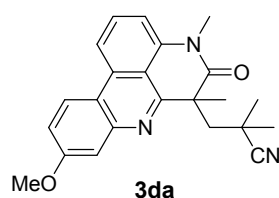
3-(4,6-Dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3aa). Yellow solid (55.6 mg, 81% yield); mp 200–201 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.56 (dd, $J = 8.2, 1.1$ Hz, 1H), 8.31 (d, $J = 8.2$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 7.86 (t, $J = 8.1$ Hz, 1H), 7.78 (ddd, $J = 8.3, 7.1, 1.3$ Hz, 1H), 7.68 (ddd, $J = 8.3, 7.1, 1.3$ Hz, 1H), 7.30–7.26 (m, 1H), 3.64 (s, 3H), 3.02 (d, $J = 13.7$ Hz, 1H), 2.81 (d, $J = 13.7$ Hz, 1H), 1.78 (s, 3H), 1.32 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.1, 158.1, 144.5, 138.6, 133.5, 132.1, 129.6, 129.3, 126.9, 124.2, 123.0, 122.7, 116.4, 112.4, 111.1, 50.1, 49.6, 32.9, 30.8, 29.9, 29.3, 29.2; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{22}\text{N}_3\text{O}$ [$\text{M} + \text{H}$]⁺ 344.1757, found 344.1758.



3-(9-Ethyl-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ba). Yellow solid (46.8 mg, 63% yield); mp 125–126 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.47 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.96 (s, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 3.63 (s, 3H), 3.00 (d, *J* = 13.8 Hz, 1H), 2.93 (q, *J* = 7.6 Hz, 2H), 2.81 (d, *J* = 13.7 Hz, 1H), 1.78 (s, 3H), 1.42 (t, *J* = 7.6 Hz, 3H), 1.32 (s, 3H), 1.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.1, 158.0, 145.8, 144.7, 138.5, 133.5, 132.0, 127.8, 127.7, 124.3, 122.6, 120.9, 116.3, 112.1, 110.7, 50.1, 49.7, 32.9, 30.8, 29.9, 29.2, 29.2, 28.9, 15.4; HRMS (ESI) *m/z*: calcd for C₂₄H₂₆N₃O [M + H]⁺ 372.2070, found 372.2070.

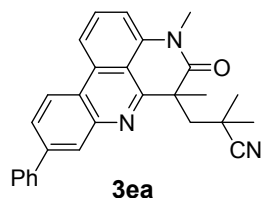


3-(9-(*tert*-Butyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ca). Yellow solid (52.7 mg, 66% yield); mp 123–124 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.50 (d, *J* = 8.7 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.10 (s, 1H), 7.85 (t, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 3.64 (s, 3H), 3.00 (d, *J* = 13.0 Hz, 1H), 2.81 (d, *J* = 13.7 Hz, 1H), 1.78 (s, 3H), 1.51 (s, 9H), 1.34 (s, 3H), 1.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.1, 158.0, 152.7, 144.6, 138.6, 133.4, 132.0, 125.4, 124.3, 122.4, 120.6, 116.3, 112.2, 110.7, 50.1, 49.7, 35.1, 32.9, 31.3, 30.9, 29.9, 29.4, 29.1; HRMS (ESI) *m/z*: calcd for C₂₆H₃₀N₃O [M + H]⁺ 400.2383, found 400.2381.

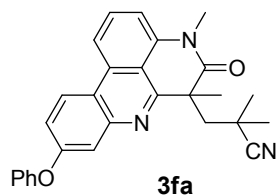


3-(9-Methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3da). Yellow solid (47.8 mg, 64% yield); mp 147–149 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.44 (d, *J* = 9.1 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.53

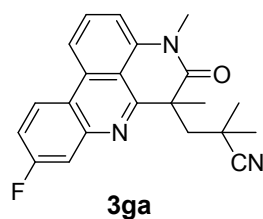
(d, $J = 11.8$ Hz, 1H), 7.36–7.29 (m, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 4.03 (s, 3H), 3.63 (s, 3H), 2.97 (d, $J = 13.6$ Hz, 1H), 2.80 (d, $J = 13.7$ Hz, 1H), 1.78 (s, 3H), 1.30 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.1, 160.6, 158.4, 146.3, 138.5, 133.6, 132.1, 124.2, 123.9, 118.2, 117.1, 116.0, 111.6, 110.0, 109.1, 55.6, 49.9, 32.9, 30.8, 29.7, 29.2, 29.0; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_2$ $[\text{M} + \text{H}]^+$ 374.1863, found 374.1861.



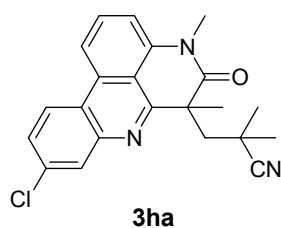
3-(4,6-Dimethyl-5-oxo-9-phenyl-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ea). Yellow solid (58.7 mg, 70% yield); mp 261–262 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.63 (d, $J = 8.6$ Hz, 1H), 8.39 (s, 1H), 8.33 (d, $J = 8.3$ Hz, 1H), 7.96 (dd, $J = 8.5$, 1.4 Hz, 1H), 7.93–7.82 (m, 3H), 7.55 (t, $J = 7.6$ Hz, 2H), 7.45 (t, $J = 7.3$ Hz, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 3.65 (s, 3H), 3.03 (d, $J = 13.5$ Hz, 1H), 2.82 (d, $J = 13.7$ Hz, 1H), 1.80 (s, 3H), 1.34 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.1, 158.6, 144.9, 142.0, 140.2, 138.7, 133.3, 132.2, 129.0, 127.9, 127.5, 126.1, 124.2, 123.3, 122.1, 116.4, 112.3, 111.1, 50.2, 49.6, 33.0, 30.8, 29.9, 29.3, 29.3; HRMS (ESI) m/z : calcd for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$ 420.2070, found 420.2070.



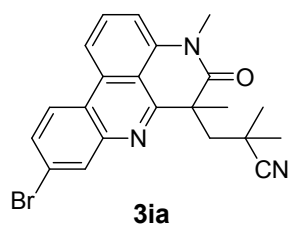
3-(4,6-Dimethyl-5-oxo-9-phenoxy-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3fa). Brown solid (56.6 mg, 65% yield); mp 156–157 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 9.18 (d, $J = 1.7$ Hz, 1H), 8.59 (d, $J = 9.1$ Hz, 1H), 8.33 (d, $J = 8.1$ Hz, 1H), 8.20 (t, $J = 7.8$ Hz, 1H), 7.56 (dd, $J = 8.9$, 1.6 Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 7.8$ Hz, 2H), 4.29 (d, $J = 15.0$ Hz, 1H), 3.65 (s, 3H), 2.95 (d, $J = 15.0$ Hz, 1H), 2.31 (s, 3H), 1.31 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 170.2, 161.0, 159.8, 154.6, 141.8, 139.1, 136.9, 135.6, 130.5, 125.6, 124.9, 123.5, 121.6, 120.4, 119.0, 116.4, 112.2, 110.0, 109.0, 50.4, 48.6, 32.3, 30.7, 30.5, 28.4, 28.4; HRMS (ESI) m/z : calcd for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}_2$ $[\text{M} + \text{H}]^+$ 436.2020, found 436.2018.



3-(9-Fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ga). Yellow solid (52.8 mg, 73% yield); mp 170–171 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.53 (dd, $J = 9.1, 5.9$ Hz, 1H), 8.23 (d, $J = 8.3$ Hz, 1H), 7.86 (t, $J = 8.1$ Hz, 1H), 7.79 (dd, $J = 9.7, 1.9$ Hz, 1H), 7.43 (ddd, $J = 9.0, 8.2, 2.7$ Hz, 1H), 7.29–7.25 (m, 1H), 3.63 (s, 3H), 3.00 (d, $J = 13.7$ Hz, 1H), 2.79 (d, $J = 13.7$ Hz, 1H), 1.77 (s, 3H), 1.31 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.0, 163.0 (d, $J = 247.4$ Hz), 159.5, 145.8 (d, $J = 12.1$ Hz), 138.7, 133.3, 132.5, 124.8 (d, $J = 9.7$ Hz), 124.2, 119.7 (d, $J = 1.9$ Hz), 116.2, 116.1 (d, $J = 23.8$ Hz), 114.0 (d, $J = 20.2$ Hz), 112.1 (d, $J = 1.1$ Hz), 110.9, 50.2, 49.6, 32.9, 30.8, 29.9, 29.4, 29.0; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{21}\text{FN}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 362.1663, found 362.1661.

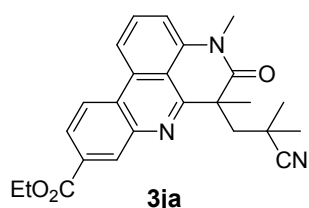


3-(9-Chloro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ha). Yellow solid (54.4 mg, 72% yield); mp 192–193 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.47 (d, $J = 8.8$ Hz, 1H), 8.25 (d, $J = 8.3$ Hz, 1H), 8.15 (s, 1H), 7.88 (t, $J = 8.1$ Hz, 1H), 7.62 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.29 (d, $J = 7.8$ Hz, 1H), 3.63 (s, 3H), 2.99 (d, $J = 13.7$ Hz, 1H), 2.79 (d, $J = 13.7$ Hz, 1H), 1.76 (s, 3H), 1.32 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.9, 159.6, 145.1, 138.7, 135.0, 133.1, 132.6, 128.8, 127.5, 124.2, 121.5, 116.3, 112.4, 111.4, 50.2, 49.6, 33.0, 30.8, 29.9, 29.5, 29.0; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{21}\text{ClN}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 378.1368, found 378.1368.



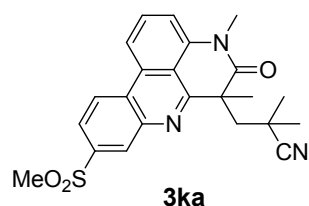
3-(9-Bromo-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-

dimethylpropanenitrile (3ia). Yellow solid (43.1 mg, 51% yield); mp 210–211 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.41 (d, $J = 8.8$ Hz, 1H), 8.33 (s, 1H), 8.25 (d, $J = 8.3$ Hz, 1H), 7.88 (t, $J = 8.1$ Hz, 1H), 7.76 (dd, $J = 8.8, 1.3$ Hz, 1H), 7.32–7.29 (m, 1H), 3.63 (s, 3H), 2.99 (d, $J = 13.7$ Hz, 1H), 2.78 (d, $J = 13.7$ Hz, 1H), 1.76 (s, 3H), 1.32 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.9, 159.6, 145.3, 138.8, 133.1, 132.6, 131.9, 130.1, 124.2, 124.1, 123.2, 121.9, 116.2, 112.4, 111.5, 50.2, 49.6, 32.9, 30.7, 29.9, 29.5, 29.1; HRMS (ESI) m/z : calcd for $\text{C}_{22}\text{H}_{21}\text{BrN}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 422.0863, found 422.0862.



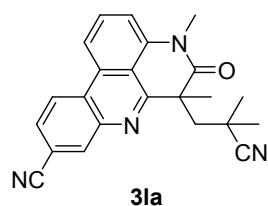
Ethyl 6-(2-cyano-2-methylpropyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]

phenanthridine-9-carboxylate (3ja). Yellow solid (61.5 mg, 74% yield); mp 198–199 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.80 (d, $J = 1.0$ Hz, 1H), 8.53 (d, $J = 8.6$ Hz, 1H), 8.29–8.21 (m, 2H), 7.84 (t, $J = 8.1$ Hz, 1H), 7.31 (d, $J = 7.9$ Hz, 1H), 4.51–4.43 (m, 2H), 3.61 (s, 3H), 3.01 (d, $J = 13.7$ Hz, 1H), 2.78 (d, $J = 13.7$ Hz, 1H), 1.77 (s, 3H), 1.47 (t, $J = 7.1$ Hz, 3H), 1.31 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.9, 166.3, 159.2, 143.9, 138.7, 132.8, 132.5, 131.5, 131.0, 126.7, 126.2, 124.1, 123.0, 116.9, 112.9, 112.9, 61.4, 50.2, 49.7, 32.9, 30.8, 29.9, 29.5, 29.1, 14.5; HRMS (ESI) m/z : calcd for $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}_3$ [$\text{M} + \text{H}$] $^+$ 416.1969, found 416.1968.

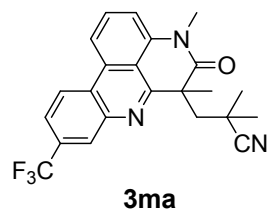


3-(4,6-Dimethyl-9-(methylsulfonyl)-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ka). Yellow solid (44.7 mg, 53% yield); mp 213–214 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.74–8.70 (m, 2H), 8.33 (d, $J = 8.3$ Hz, 1H), 8.12 (dd, $J = 8.6, 2.0$ Hz, 1H), 7.95 (t, $J = 8.1$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 3.64 (s, 3H), 3.21 (s, 3H), 3.02 (d, $J = 13.7$ Hz, 1H), 2.78 (d, $J = 13.7$ Hz, 1H), 1.75 (s, 3H), 1.33 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.7, 160.8, 143.9, 140.6, 138.9, 133.1, 132.4, 129.7, 126.8, 124.6, 124.1, 123.7, 116.9, 113.2, 112.9, 50.4, 49.5, 44.6, 33.0, 30.7, 30.0, 29.7, 29.0; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}_3\text{S}$ [$\text{M} +$

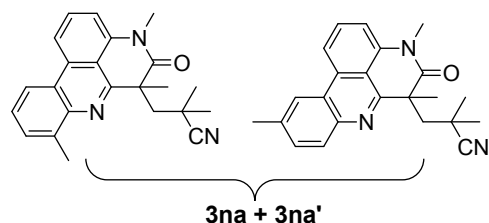
H]⁺ 422.1533, found 422.1533.



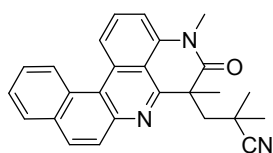
6-(2-Cyano-2-methylpropyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridine-9-carbonitrile (3a). Yellow solid (37.6 mg, 51% yield); mp 225–226 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.60 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 1.5 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.94 (t, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 3.64 (s, 3H), 3.01 (d, *J* = 13.8 Hz, 1H), 2.78 (d, *J* = 13.8 Hz, 1H), 1.76 (s, 3H), 1.31 (s, 3H), 1.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.8, 160.6, 143.7, 138.9, 134.7, 133.1, 132.4, 128.2, 126.3, 124.2, 124.1, 118.6, 116.8, 113.1, 112.8, 112.5, 50.4, 49.5, 33.0, 30.7, 30.0, 29.7, 28.7; HRMS (ESI) *m/z*: calcd for C₂₃H₂₁N₄O [M + H]⁺ 369.1710, found 369.1709.



3-(4,6-Dimethyl-5-oxo-9-(trifluoromethyl)-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ma). White solid (46.1 mg, 56% yield); mp 169–170 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.65 (d, *J* = 8.6 Hz, 1H), 8.44 (s, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 7.92 (dd, *J* = 10.2, 6.0 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 3.65 (s, 3H), 3.02 (d, *J* = 13.7 Hz, 1H), 2.80 (d, *J* = 13.7 Hz, 1H), 1.78 (s, 3H), 1.34 (s, 3H), 1.11 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.9, 160.0, 143.8, 138.8, 132.8, 132.7, 131.0 (q, *J* = 32.6 Hz), 127.1 (q, *J* = 4.1 Hz), 125.3, 124.1, 124.0 (q, *J* = 274.7 Hz), 123.9, 122.6 (q, *J* = 3.3 Hz), 116.6, 113.0, 112.2, 50.3, 49.6, 32.9, 30.7, 30.0, 29.5, 29.1; HRMS (ESI) *m/z*: calcd for C₂₃H₂₁F₃N₃O [M + H]⁺ 412.1631, found 412.1632.

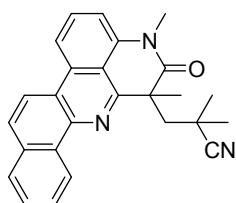


2,2-Dimethyl-3-(4,6,8-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile (3na) and **2,2-dimethyl-3-(4,6,10-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile (3na')**. Yellow solid (40.8 mg, 57% yield); mp 147–148 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.41 (d, *J* = 8.1 Hz, 0.67H), 8.34 (s, 0.33H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 0.3H), 7.82 (t, *J* = 8.1 Hz, 1H), 7.66–7.59 (m, 1H), 7.58–7.54 (m, 0.67H), 7.25 (d, *J* = 7.9 Hz, 1H), 3.64 (d, *J* = 3.8 Hz, 3H), 3.08–2.97 (m, 1H), 2.90 (s, 2H), 2.83 (t, *J* = 13.8 Hz, 1H), 2.64 (s, 1H), 1.78 (d, *J* = 7.0 Hz, 3H), 1.32 (d, *J* = 9.2 Hz, 3H), 1.06 (d, *J* = 9.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.3, 173.2, 156.9, 156.4, 143.1, 142.9, 138.6, 138.5, 137.4, 136.8, 133.8, 133.2, 131.8, 131.1, 129.8, 129.4, 126.5, 124.2, 122.8, 122.8, 122.3, 120.6, 116.7, 116.4, 112.5, 112.2, 111.0, 110.9, 50.4, 50.0, 49.8, 49.7, 33.6, 32.9, 30.8, 30.8, 29.9, 29.9, 29.6, 29.3, 29.3, 29.1, 22.0, 18.4; HRMS (ESI) *m/z*: calcd for C₂₃H₂₄N₃O [M + H]⁺ 358.1914, found 358.1914.



3oa

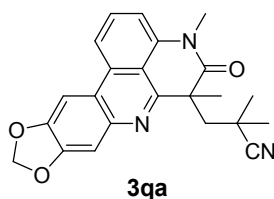
3-(4,6-Dimethyl-5-oxo-5,6-dihydro-4H-benzo[*a*]pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3oa). Yellow solid (59.0 mg, 75% yield); mp 136–137 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.09 (d, *J* = 8.4 Hz, 1H), 8.81 (d, *J* = 8.6 Hz, 1H), 8.12–8.02 (m, 3H), 7.89 (t, *J* = 8.2 Hz, 1H), 7.77–7.66 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.68 (s, 3H), 3.00 (d, *J* = 13.7 Hz, 1H), 2.85 (d, *J* = 13.8 Hz, 1H), 1.85 (s, 3H), 1.31 (s, 3H), 1.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.0, 157.2, 144.5, 138.4, 133.5, 133.2, 131.7, 130.3, 129.9, 128.8, 128.0, 127.6, 126.7, 126.4, 124.2, 121.1, 119.6, 113.7, 110.3, 50.0, 49.8, 32.8, 30.8, 30.0, 29.2, 29.0; HRMS (ESI) *m/z*: calcd for C₂₆H₂₄N₃O [M + H]⁺ 394.1914, found 394.1913.



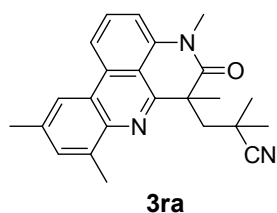
3pa

3-(4,6-Dimethyl-5-oxo-5,6-dihydro-4H-benzo[*c*]pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3pa). Brown solid (41.7 mg, 53% yield); mp 209–210 °C; ¹H NMR (400

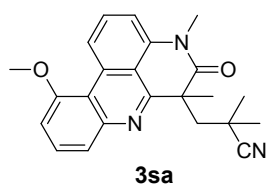
MHz, CDCl₃) δ (ppm) 9.43 (d, J = 8.1 Hz, 1H), 8.54 (d, J = 9.0 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.06–8.00 (m, 2H), 7.90 (t, J = 8.1 Hz, 1H), 7.83–7.71 (m, 2H), 7.29 (t, J = 3.9 Hz, 1H), 3.67 (s, 3H), 3.14 (d, J = 13.7 Hz, 1H), 2.93 (d, J = 13.7 Hz, 1H), 1.88 (s, 3H), 1.34 (s, 3H), 0.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.2, 156.7, 141.6, 138.6, 133.7, 133.6, 132.0, 131.6, 127.7, 127.7, 127.0, 124.8, 124.1, 120.3, 119.9, 116.7, 113.1, 110.4, 50.3, 50.3, 33.5, 30.9, 29.9, 29.5, 29.3; HRMS (ESI) m/z : calcd for C₂₆H₂₄N₃O [M + H]⁺ 394.1914, found 394.1918.



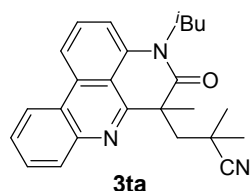
3-(4,6-Dimethyl-5-oxo-5,6-dihydro-4H-[1,3]dioxolo[4,5-*b*]pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3qa). Brown solid (51.9 mg, 67% yield); mp 199–200 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.08 (d, J = 8.4 Hz, 1H), 7.85 (s, 1H), 7.79 (t, J = 8.1 Hz, 1H), 7.50 (s, 1H), 7.18 (d, J = 7.9 Hz, 1H), 6.17 (d, J = 6.5 Hz, 2H), 3.61 (s, 3H), 2.95 (d, J = 12.0 Hz, 1H), 2.77 (d, J = 13.7 Hz, 1H), 1.77 (s, 3H), 1.27 (s, 3H), 1.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.2, 155.4, 149.9, 148.2, 138.5, 133.3, 131.5, 124.7, 124.1, 119.0, 116.2, 111.8, 109.9, 107.1, 101.9, 99.7, 49.9, 49.6, 32.9, 30.8, 29.8, 29.3, 28.7; HRMS (ESI) m/z : calcd for C₂₃H₂₂N₃O₃ [M + H]⁺ 388.1656, found 388.1654.



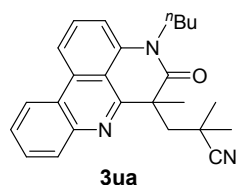
2,2-Dimethyl-3-(4,6,8,10-tetramethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanenitrile (3ra). Yellow solid (52.0 mg, 70% yield); mp 149–150 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.30 (d, J = 8.3 Hz, 1H), 8.21 (s, 1H), 7.82 (dd, J = 10.1, 6.2 Hz, 1H), 7.49 (s, 1H), 7.25 (d, J = 7.8 Hz, 1H), 3.64 (s, 3H), 3.03 (d, J = 13.6 Hz, 1H), 2.85 (s, 3H), 2.82 (d, J = 13.7 Hz, 1H), 2.60 (s, 3H), 1.77 (s, 3H), 1.31 (s, 3H), 1.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.3, 155.2, 141.4, 138.5, 137.0, 136.3, 133.5, 131.7, 131.6, 124.2, 122.7, 120.0, 116.7, 112.2, 110.7, 50.1, 49.8, 33.6, 30.8, 29.9, 29.5, 29.2, 22.0, 18.3; HRMS (ESI) m/z : calcd for C₂₄H₂₆N₃O [M + H]⁺ 372.2070, found 372.2074.



3-(11-Methoxy-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3sa). Yellow solid (62.0 mg, 83% yield); mp 115–116 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.30 (d, *J* = 8.3 Hz, 1H), 7.84–7.78 (m, 2H), 7.69 (t, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.15–7.11 (m, 1H), 4.12 (s, 3H), 3.63 (s, 3H), 3.00 (d, *J* = 13.7 Hz, 1H), 2.80 (d, *J* = 13.7 Hz, 1H), 1.77 (s, 3H), 1.31 (s, 3H), 1.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.9, 158.4, 158.3, 146.5, 137.9, 133.4, 131.8, 128.8, 124.3, 122.5, 122.4, 114.0, 112.8, 111.0, 107.8, 55.9, 49.9, 49.5, 32.9, 30.8, 30.0, 29.3, 29.2; HRMS (ESI) *m/z*: calcd for C₂₃H₂₄N₃O₂ [M + H]⁺ 374.1863, found 374.1865.

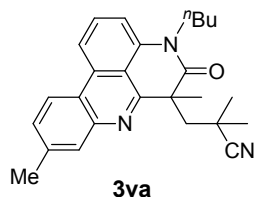


3-(4-Isobutyl-6-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ta). Yellow solid (46.3 mg, 60% yield); mp 139–140 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.56 (d, *J* = 7.5 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.84 (t, *J* = 8.1 Hz, 1H), 7.81–7.75 (m, 1H), 7.71–7.65 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 4.48 (dd, *J* = 14.1, 9.4 Hz, 1H), 3.74 (dd, *J* = 14.3, 5.4 Hz, 1H), 3.10 (d, *J* = 13.6 Hz, 1H), 2.80 (d, *J* = 13.7 Hz, 1H), 2.40–2.25 (m, 1H), 1.73 (s, 3H), 1.35 (s, 3H), 1.22 (s, 3H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.5, 158.2, 144.4, 138.2, 133.7, 131.9, 129.6, 129.3, 126.8, 124.5, 123.1, 122.7, 116.2, 112.6, 111.6, 50.7, 49.3, 47.9, 33.6, 30.7, 29.8, 29.3, 26.6, 20.6, 20.2; HRMS (ESI) *m/z*: calcd for C₂₅H₂₈N₃O [M + H]⁺ 386.2227, found 386.2229.

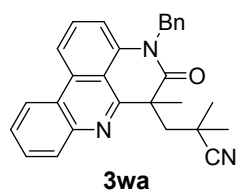


3-(4-Butyl-6-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ua). Yellow solid (44.7 mg, 58% yield); mp 98–99 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.56 (d, *J* = 7.7 Hz, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 4.8 Hz, 1H), 7.86 (t, *J* =

8.0 Hz, 1H), 7.78 (t, $J = 7.4$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 4.33–4.24 (m, 1H), 4.15–4.05 (m, 1H), 3.08 (d, $J = 13.0$ Hz, 1H), 2.79 (d, $J = 13.7$ Hz, 1H), 1.85–1.69 (m, 5H), 1.58–1.51 (m, 2H), 1.32 (s, 3H), 1.20 (s, 3H), 1.06 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.9, 158.1, 144.4, 137.7, 133.8, 132.0, 129.6, 129.3, 126.8, 124.4, 123.1, 122.7, 116.2, 112.5, 111.1, 50.2, 48.5, 42.7, 33.3, 30.8, 29.7, 29.0, 28.4, 20.4, 13.9; HRMS (ESI) m/z : calcd for $\text{C}_{25}\text{H}_{28}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$ 386.2227, found 386.2226.

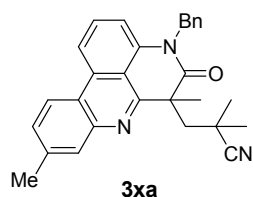


3-(4-Butyl-6,9-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3va). Yellow solid (66.3 mg, 83% yield); mp 115–116 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.44 (d, $J = 8.4$ Hz, 1H), 8.25 (d, $J = 8.3$ Hz, 1H), 7.95 (s, 1H), 7.82 (t, $J = 8.1$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 4.33–4.24(m, 1H), 4.14–4.05 (m, 1H), 3.07 (d, $J = 13.6$ Hz, 1H), 2.79 (d, $J = 13.7$ Hz, 1H), 2.62 (s, 3H), 1.83–1.76 (m, 2H), 1.72 (s, 3H), 1.54 (ddd, $J = 8.9, 7.1, 1.9$ Hz, 2H), 1.32 (s, 3H), 1.20 (s, 3H), 1.06 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.9, 158.0, 144.6, 139.5, 137.6, 133.8, 131.9, 129.1, 128.7, 124.4, 122.5, 120.7, 116.1, 112.3, 110.6, 50.2, 48.6, 42.7, 33.3, 30.8, 29.7, 29.0, 28.4, 21.6, 20.4, 13.9; HRMS (ESI) m/z : calcd for $\text{C}_{26}\text{H}_{30}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$ 400.2383, found 400.2385.

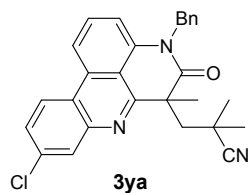


3-(4-Benzyl-6-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3wa). Yellow solid (64.6 mg, 77% yield); mp 159–160 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.57–8.53 (m, 1H), 8.28 (d, $J = 8.3$ Hz, 1H), 8.17 (d, $J = 6.4$ Hz, 1H), 7.82–7.76 (m, 1H), 7.75–7.66 (m, 2H), 7.39–7.35 (m, 4H), 7.33–7.29 (m, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 5.97 (d, $J = 16.4$ Hz, 1H), 5.02 (d, $J = 16.5$ Hz, 1H), 3.16 (d, $J = 13.3$ Hz, 1H), 2.87 (d, $J = 13.7$ Hz, 1H), 1.82 (s, 3H), 1.40 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.6, 158.1, 144.4, 137.8, 136.3, 133.6, 132.0, 129.6, 129.3, 128.9, 127.3, 126.9, 126.5, 124.6, 123.1, 122.7, 116.5, 112.5, 112.3, 50.8, 48.2, 46.6, 33.5, 30.8, 29.8, 29.4; HRMS (ESI) m/z : calcd for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$

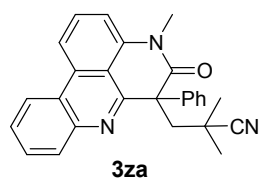
420.2070, found 420.2074.



3-(4-Benzyl-6,9-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3xa). Yellow solid (61.6 mg, 71% yield); mp 156–157 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.43 (d, $J = 8.4$ Hz, 1H), 8.22 (d, $J = 8.3$ Hz, 1H), 7.99 (s, 1H), 7.68 (t, $J = 8.1$ Hz, 1H), 7.51 (dd, $J = 8.4, 1.5$ Hz, 1H), 7.41–7.35 (m, 4H), 7.30 (dt, $J = 8.3, 2.9$ Hz, 1H), 7.15 (d, $J = 7.9$ Hz, 1H), 5.97 (d, $J = 16.4$ Hz, 1H), 5.03 (d, $J = 16.5$ Hz, 1H), 3.17 (d, $J = 13.6$ Hz, 1H), 2.88 (d, $J = 13.7$ Hz, 1H), 2.64 (s, 3H), 1.83 (s, 3H), 1.41 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.6, 157.9, 144.6, 139.5, 137.8, 136.4, 133.6, 131.9, 129.1, 128.9, 128.7, 127.3, 126.5, 124.6, 122.5, 120.8, 116.4, 112.2, 111.8, 50.7, 48.3, 46.6, 33.5, 30.8, 29.8, 29.5, 21.7; HRMS (ESI) m/z : calcd for $\text{C}_{29}\text{H}_{28}\text{N}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 434.2227, found 434.2227.

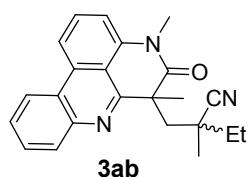


3-(4-Benzyl-9-chloro-6-methyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (3ya). White solid (31.8 mg, 35% yield); mp 154–155 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.45 (d, $J = 8.8$ Hz, 1H), 8.20 (d, $J = 8.3$ Hz, 1H), 8.16 (d, $J = 2.1$ Hz, 1H), 7.72 (t, $J = 8.2$ Hz, 1H), 7.62 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.36 (d, $J = 4.4$ Hz, 4H), 7.31–7.29 (m, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 5.94 (d, $J = 16.4$ Hz, 1H), 5.02 (d, $J = 16.4$ Hz, 1H), 3.12 (d, $J = 13.7$ Hz, 1H), 2.84 (d, $J = 13.7$ Hz, 1H), 1.80 (s, 3H), 1.40 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.4, 159.5, 145.1, 138.0, 136.2, 135.0, 133.2, 132.4, 128.9, 128.8, 127.5, 127.4, 126.4, 124.5, 124.1, 121.6, 116.4, 112.5, 50.9, 48.2, 46.6, 33.5, 30.7, 29.9, 29.4; HRMS (ESI) m/z : calcd for $\text{C}_{28}\text{H}_{25}\text{ClN}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 454.1681, found 454.1680.

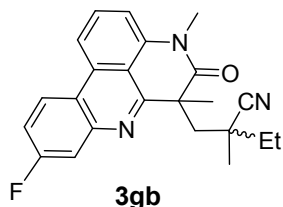


2,2-Dimethyl-3-(4-methyl-5-oxo-6-phenyl-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-

yl)propanenitrile (3za). White solid (43.8 mg, 54% yield); mp 224–225 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.60 (dd, $J = 8.2, 1.1$ Hz, 1H), 8.32 (d, $J = 8.2$ Hz, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 7.86–7.79 (m, 2H), 7.75–7.70 (m, 1H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.19–7.12 (m, 5H), 3.67 (s, 3H), 3.50 (d, $J = 13.4$ Hz, 1H), 3.16 (d, $J = 13.4$ Hz, 1H), 1.58 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.3, 156.6, 144.2, 143.1, 138.7, 133.3, 132.1, 129.9, 129.3, 128.6, 127.4, 127.2, 126.6, 125.0, 123.3, 122.8, 116.5, 113.5, 111.5, 59.9, 47.2, 30.9, 30.7, 30.4, 30.4; HRMS (ESI) m/z : calcd for $\text{C}_{27}\text{H}_{24}\text{N}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 406.1914, found 406.1914.

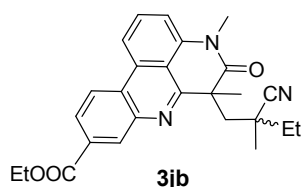


2-((4,6-Dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)methyl)-2-methylbutanenitrile (3ab), two inseparable diastereoisomers, d.r. = 1:1). Brown solid (55.8 mg, 78% yield); mp 123–124 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.56 (d, $J = 7.7$ Hz, 1H), 8.30 (dd, $J = 8.3, 4.1$ Hz, 1H), 8.15 (t, $J = 8.5$ Hz, 1H), 7.84 (td, $J = 8.1, 3.5$ Hz, 1H), 7.80–7.75 (m, 1H), 7.70–7.64 (m, 1H), 7.27 (dd, $J = 7.7, 3.7$ Hz, 1H), 3.64 (d, $J = 1.2$ Hz, 3H), 3.18 (d, $J = 13.7$ Hz, 0.5H), 2.91 (q, $J = 13.7$ Hz, 1H), 2.69 (d, $J = 13.8$ Hz, 0.5H), 1.76 (d, $J = 6.9$ Hz, 3H), 1.69 (dt, $J = 13.2, 6.6$ Hz, 0.5H), 1.62–1.50 (m, 1H), 1.45–1.35 (m, 0.5H), 1.25 (s, 1.5H), 1.02 (t, $J = 7.4$ Hz, 1.5H), 0.96–0.90 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.4, 173.0, 158.5, 158.0, 144.5, 144.4, 138.8, 138.5, 133.5, 133.4, 132.2, 131.9, 129.7, 129.5, 129.3, 126.9, 126.8, 123.4, 123.4, 123.0, 122.8, 122.7, 116.5, 116.2, 112.4, 112.4, 111.2, 111.1, 50.3, 50.1, 47.9, 47.3, 35.7, 35.5, 35.1, 34.8, 33.2, 33.1, 29.9, 25.8, 25.3, 9.2, 9.1; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{24}\text{N}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 358.1914, found 358.1912.



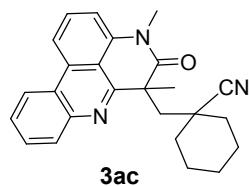
2-((9-Fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)methyl)-2-methylbutanenitrile (3gb), two inseparable diastereoisomers, d.r. = 1:1). White solid (56.3 mg, 75% yield); mp 157–158 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.55–8.49 (m, 1H), 8.21 (dd, $J = 8.3, 3.5$ Hz, 1H), 7.85 (td, $J = 8.1, 3.6$ Hz, 1H), 7.78 (ddd, $J = 9.9, 7.6, 2.6$ Hz, 1H), 7.45–7.37 (m, 1H),

7.26 (dd, $J = 7.9, 3.3$ Hz, 1H), 3.63 (s, 3H), 3.13 (d, $J = 13.8$ Hz, 0.5H), 2.93–2.83 (m, 1H), 2.67 (d, $J = 13.8$ Hz, 0.5H), 1.75 (d, $J = 3.9$ Hz, 3H), 1.71–1.66 (m, 0.5H), 1.60–1.51 (m, 1H), 1.41 (dd, $J = 13.8, 7.4$ Hz, 0.5H), 1.24 (s, 1.5H), 1.01 (t, $J = 7.4$ Hz, 1.5H), 0.96–0.91 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.3, 172.9, 163.0 (d, $J = 247.2$ Hz), 160.0, 159.5, 145.9 (d, $J = 12.9$ Hz), 145.7 (d, $J = 12.5$ Hz), 138.9, 138.6, 133.3, 133.2, 132.6, 132.4, 124.8 (d, $J = 9.6$ Hz), 124.8 (d, $J = 9.6$ Hz), 123.4, 123.3, 119.8 (d, $J = 1.6$ Hz), 119.8 (d, $J = 1.6$ Hz), 116.3, 116.0 (d, $J = 23.8$ Hz), 116.0 (d, $J = 23.8$ Hz), 116.0, 114.0 (d, $J = 20.2$ Hz), 113.9 (d, $J = 20.0$ Hz), 112.1 (d, $J = 0.9$ Hz), 112.0 (d, $J = 0.9$ Hz), 111.0, 110.9, 50.4, 50.1, 47.9, 47.4, 35.7, 35.4, 35.0, 34.0, 33.2, 33.1, 29.9, 25.8, 25.2, 9.2, 9.0; HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{23}\text{FN}_3\text{O}$ [$\text{M} + \text{H}$] $^+$ 376.1820, found 376.1818.



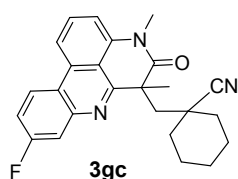
Ethyl 6-(2-cyano-2-methylbutyl)-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]

phenanthridine-9-carboxylate (3jb), two inseparable diastereoisomers, d.r. = 1:1). White solid (60.1 mg, 70% yield); mp 180–181 °C; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.82 (dd, $J = 5.9, 1.2$ Hz, 1H), 8.59 (dd, $J = 8.6, 3.4$ Hz, 1H), 8.35–8.26 (m, 2H), 7.90 (td, $J = 8.1, 4.0$ Hz, 1H), 7.34 (dd, $J = 7.9, 3.6$ Hz, 1H), 4.55–4.46 (m, 2H), 3.64 (s, 3H), 3.17 (d, $J = 13.8$ Hz, 0.5H), 2.90 (q, $J = 13.7$ Hz, 1H), 2.68 (d, $J = 13.8$ Hz, 0.5H), 1.77 (d, $J = 2.0$ Hz, 3H), 1.72–1.68 (m, 0.5H), 1.61–1.53 (m, 1H), 1.53–1.47 (m, 3H), 1.41 (dd, $J = 13.9, 7.3$ Hz, 0.5H), 1.26 (s, 1.5H), 1.01 (t, $J = 7.4$ Hz, 1.5H), 0.95–0.90 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.2, 172.8, 166.4, 166.3, 159.8, 159.2, 143.9, 143.8, 139.0, 138.7, 132.9, 132.8, 132.6, 132.4, 131.6, 131.4, 131.1, 131.1, 126.7, 126.2, 123.3, 123.0, 123.0, 116.9, 116.7, 113.1, 112.9, 112.2, 112.0, 61.4, 61.3, 50.4, 50.2, 48.0, 47.7, 35.7, 35.5, 35.1, 34.9, 33.2, 33.1, 29.9, 25.9, 25.3, 14.4, 9.1, 9.0; HRMS (ESI) m/z : calcd for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_3$ [$\text{M} + \text{H}$] $^+$ 430.2125, found 430.2124.

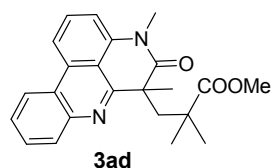


1-((4,6-Dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)methyl)cyclohexane-1-carbonitrile (3ac). White solid (44.5 mg, 58% yield); mp 143–144 °C; ^1H

NMR (400 MHz, CDCl₃) δ (ppm) 8.57 (d, J = 7.5 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 7.9 Hz, 1H), 7.86 (t, J = 8.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.70–7.65 (m, 1H), 7.30–7.26 (m, 1H), 3.64 (s, 3H), 3.07 (d, J = 13.6 Hz, 1H), 2.76 (d, J = 13.7 Hz, 1H), 1.98–1.92 (m, 1H), 1.73 (s, 3H), 1.55 (dt, J = 6.9, 4.7 Hz, 3H), 1.47–1.39 (m, 3H), 1.30–1.16 (m, 2H), 1.06 (ddd, J = 15.7, 12.0, 5.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.3, 158.5, 144.5, 138.8, 133.4, 132.0, 129.6, 129.2, 126.7, 123.1, 122.7, 122.5, 116.3, 112.4, 111.1, 50.2, 48.9, 37.8, 37.7, 37.1, 33.1, 29.9, 24.9, 23.0, 22.8; HRMS (ESI) m/z : calcd for C₂₅H₂₆N₃O [M + H]⁺ 384.2070, found 384.2072.

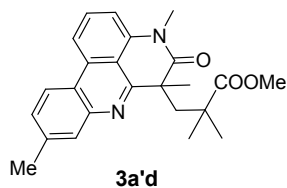


1-((9-Fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)methyl)cyclohexane-1-carbonitrile (3gc). White solid (37.7 mg, 47% yield); mp 198–199 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.53 (dd, J = 8.9, 6.0 Hz, 1H), 8.22 (d, J = 8.3 Hz, 1H), 7.85 (t, J = 8.1 Hz, 1H), 7.78 (d, J = 9.7 Hz, 1H), 7.46–7.38 (m, 1H), 7.30–7.24 (m, 1H), 3.63 (d, J = 1.4 Hz, 3H), 3.05 (d, J = 13.7 Hz, 1H), 2.75 (d, J = 13.7 Hz, 1H), 1.96–1.90 (m, 1H), 1.73 (s, 3H), 1.58 (dd, J = 23.8, 10.4 Hz, 3H), 1.45 (dd, J = 13.9, 5.1 Hz, 3H), 1.31–1.18 (m, 2H), 1.13–1.03 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.2, 163.0 (d, J = 247.2 Hz), 160.0, 145.8 (d, J = 12.1 Hz), 138.9, 133.3, 132.4, 124.7 (d, J = 9.6 Hz), 122.4, 119.8 (d, J = 1.8 Hz), 116.0, 116.0 (d, J = 23.7 Hz), 113.9 (d, J = 20.3 Hz), 112.1, 110.9, 50.3, 49.0, 37.9, 37.6, 37.1, 33.1, 29.9, 24.9, 22.9, 22.8; HRMS (ESI) m/z : calcd for C₂₅H₂₅FN₃O [M + H]⁺ 402.1976, found 402.1974.

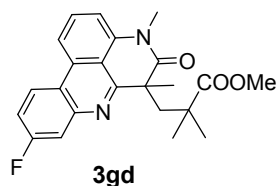


Methyl 3-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-gh]phenanthridin-6-yl)-2,2-dimethylpropanoate (3ad). Yellow oil (55.0 mg, 73% yield); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.53 (d, J = 7.7 Hz, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.13 (d, J = 6.6 Hz, 1H), 7.83 (t, J = 8.1 Hz, 1H), 7.77–7.72 (m, 1H), 7.66–7.61 (m, 1H), 7.23 (d, J = 7.9 Hz, 1H), 3.57 (s, 3H), 3.18 (s, 3H), 3.12 (d, J = 13.9 Hz, 1H), 2.83 (d, J = 14.0 Hz, 1H), 1.76 (s, 3H), 1.02 (s, 3H), 0.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 177.6, 173.6, 159.2, 144.5, 138.8, 133.3, 131.9, 129.6, 129.1, 126.6, 122.8, 122.6, 116.1,

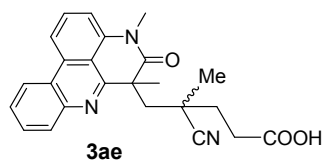
112.3, 110.8, 51.5, 50.8, 49.6, 41.7, 33.3, 29.7, 27.1, 25.7; HRMS (ESI) m/z : calcd for $C_{23}H_{25}N_2O_3$ [M + H]⁺ 377.1860, found 377.1860;



Methyl 2,2-dimethyl-3-(4,6,9-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)propanoate (3a'd). Yellow oil (55.4 mg, 71% yield); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.39 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.92 (s, 1H), 7.78 (t, J = 8.1 Hz, 1H), 7.45 (dd, J = 8.4, 1.5 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 3.56 (s, 3H), 3.18 (s, 3H), 3.09 (d, J = 14.0 Hz, 1H), 2.82 (d, J = 14.0 Hz, 1H), 2.59 (s, 3H), 1.74 (s, 3H), 1.02 (s, 3H), 0.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 177.6, 173.7, 159.1, 144.7, 139.3, 138.7, 133.3, 131.7, 129.1, 128.4, 122.4, 120.4, 115.9, 112.0, 110.3, 51.5, 50.9, 49.6, 41.7, 33.3, 29.7, 27.0, 25.9, 21.6; HRMS (ESI) m/z : calcd for $C_{24}H_{27}N_2O_3$ [M + H]⁺ 391.2016, found 391.2015.

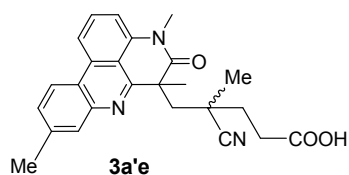


Methyl 3-(9-fluoro-4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanoate (3gd). White solid (60.0 mg, 76% yield); mp 140–141 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.49 (dd, J = 9.1, 5.9 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H), 7.82 (t, J = 8.1 Hz, 1H), 7.75 (dd, J = 9.9, 2.6 Hz, 1H), 7.38 (ddd, J = 9.0, 8.1, 2.7 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H), 3.57 (s, 3H), 3.21 (s, 3H), 3.07 (d, J = 14.0 Hz, 1H), 2.82 (d, J = 14.0 Hz, 1H), 1.73 (s, 3H), 1.01 (s, 3H), 0.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 177.6, 173.5, 162.9 (d, J = 247.2 Hz), 160.7, 145.8 (d, J = 12.0 Hz), 138.9, 133.1, 132.3, 124.7 (d, J = 9.6 Hz), 119.5 (d, J = 1.9 Hz), 115.8, 115.8 (d, J = 23.8 Hz), 113.9 (d, J = 20.1 Hz), 111.9 (d, J = 0.9 Hz), 110.6, 51.5, 50.8, 49.7, 41.7, 33.3, 29.7, 27.1, 25.8; HRMS (ESI) m/z : calcd for $C_{23}H_{24}FN_2O_3$ [M + H]⁺ 395.1765, found 395.1763.



4-Cyano-5-(4,6-dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-4-

methylpentanoic acid (3ae, two inseparable diastereoisomers, d.r. = 1.25:1). White solid (50.0 mg, 61% yield); mp 202–203 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.57 (dd, *J* = 7.8, 3.7 Hz, 1H), 8.33 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.20–8.11 (m, 1H), 7.87 (td, *J* = 8.1, 3.2 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.69 (dt, *J* = 11.0, 5.5 Hz, 1H), 7.29 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.64 (s, 3H), 3.19 (d, *J* = 13.7 Hz, 0.54H), 3.02 (d, *J* = 13.6 Hz, 0.43H), 2.88 (d, *J* = 13.7 Hz, 0.44H), 2.74 (d, *J* = 13.8 Hz, 0.53H), 2.68–2.38 (m, 2.22H), 2.04–1.79 (m, 1.78H), 1.74 (d, *J* = 9.6 Hz, 3H), 1.32 (s, 1.62H), 1.07 (s, 1.30H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 177.8, 177.8, 173.2, 173.1, 158.0, 157.8, 144.3, 138.7, 138.5, 133.6, 133.5, 132.3, 132.1, 129.5, 129.5, 129.4, 129.3, 127.0, 123.1, 122.8, 122.7, 122.6, 116.6, 116.4, 112.4, 112.3, 111.3, 111.2, 50.4, 50.4, 47.2, 46.4, 36.0, 34.6, 34.4, 33.3, 33.2, 30.0, 29.7, 29.5, 26.6, 26.3; HRMS (ESI) *m/z*: calcd for C₂₄H₂₄N₃O₃ [M + H]⁺ 402.1812, found 402.1810.

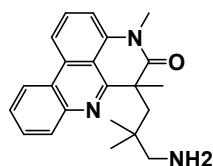


4-Cyano-4-methyl-5-(4,6,9-trimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)pentanoic acid (3a'e, two inseparable diastereoisomers, d.r. = 1:1). White solid (47.4 mg, 57% yield); mp 189–190 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.44 (dd, *J* = 8.3, 4.1 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 13.7 Hz, 1H), 7.84 (td, *J* = 8.1, 3.3 Hz, 1H), 7.51 (dd, *J* = 7.0, 4.0 Hz, 1H), 7.25 (dd, *J* = 7.8, 3.6 Hz, 1H), 3.63 (s, 3H), 3.17 (d, *J* = 13.7 Hz, 0.5H), 3.00 (d, *J* = 13.7 Hz, 0.5H), 2.88 (d, *J* = 13.7 Hz, 0.5H), 2.77–2.39 (m, 5.5H), 1.96 (ddd, *J* = 15.7, 10.3, 4.7 Hz, 1H), 1.90–1.66 (m, 4H), 1.31 (s, 1.5H), 1.06 (s, 1.5H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 177.9, 177.8, 173.3, 173.1, 157.9, 157.6, 144.5, 139.6, 138.6, 138.4, 133.6, 133.5, 132.1, 132.0, 129.0, 128.9, 128.8, 122.7, 122.6, 122.5, 122.5, 120.8, 116.5, 116.3, 112.1, 112.0, 110.9, 110.7, 50.3, 50.3, 47.2, 46.5, 36.0, 35.9, 34.6, 34.4, 33.2, 33.1, 30.0, 29.7, 29.5, 26.5, 26.2, 21.6; HRMS (ESI) *m/z*: calcd for C₂₅H₂₆N₃O₃ [M + H]⁺ 416.1969, found 416.1968.

3. Reduction of the product 3aa

3-(4,6-Dimethyl-5-oxo-5,6-dihydro-4H-pyrido[4,3,2-*gh*]phenanthridin-6-yl)-2,2-dimethylpropanenitrile (**3aa**) (0.2 mmol) was added to a 25 mL sealed tube with a Teflon lined cap, and the internal atmosphere were exchanged with argon gas for three times. Then methanol (4 mL) was added. The mixture was cooled to 0 °C and NaBH₄ (0.6 mmol) was added in

portions. The mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was quenched by water and extracted with EtOAc (15 × 3 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na₂SO₄, filtered and concentrated in *vacuo*. The residue was purified by silica gel chromatography using hexane/ethyl acetate (2:1) as eluent to afford the pure product **4aa**.



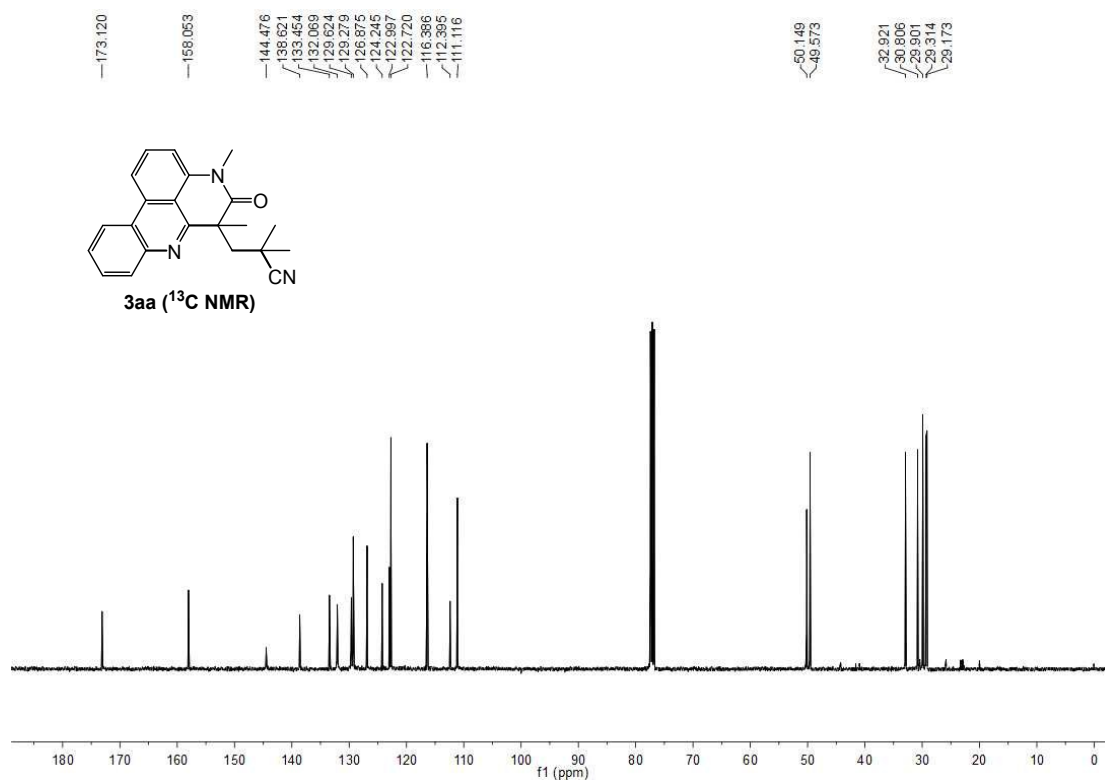
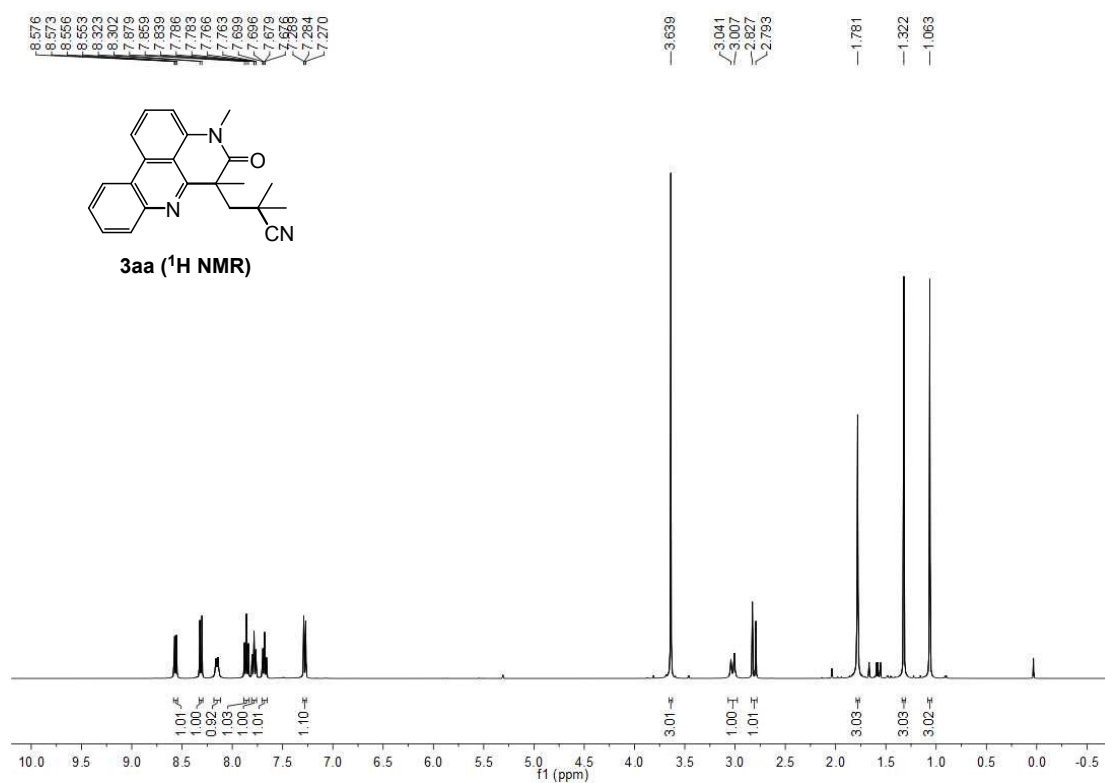
4aa

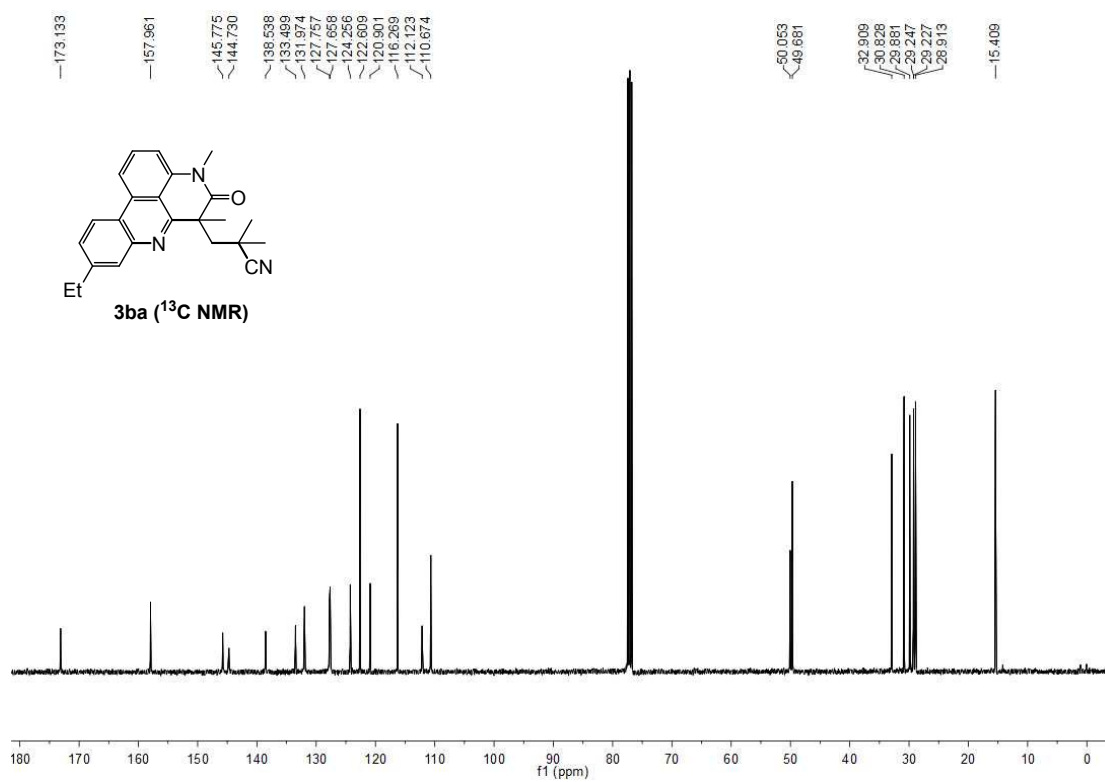
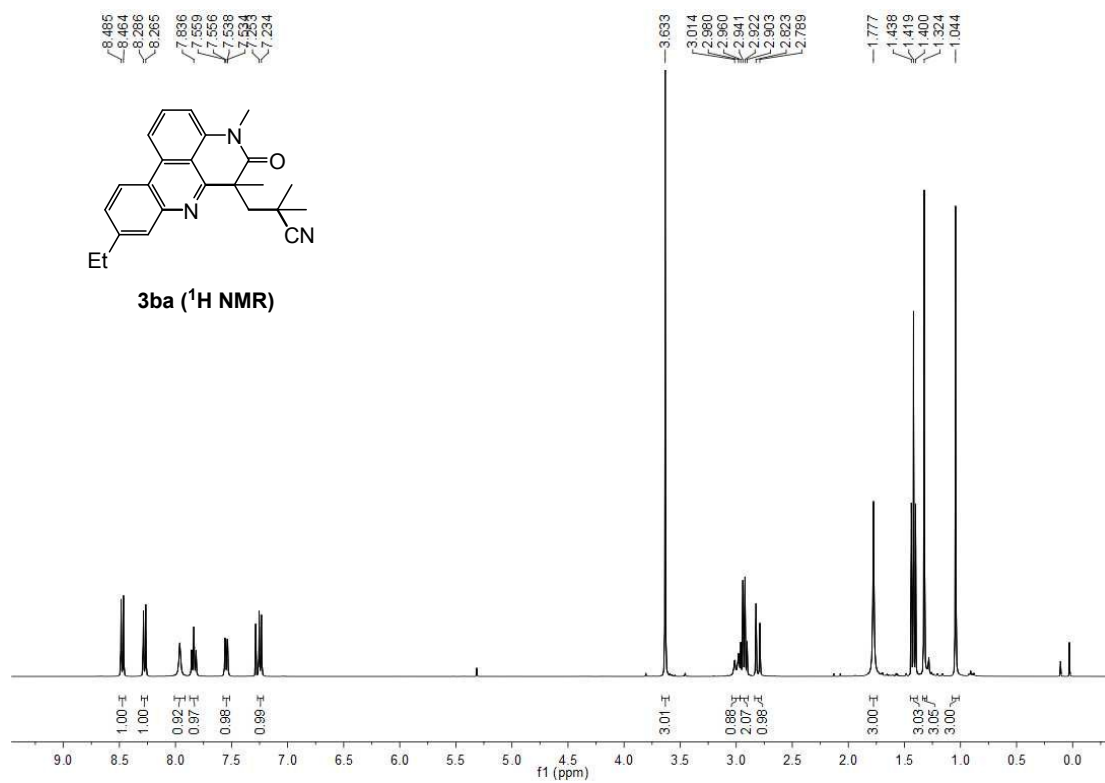
6-(3-Amino-2,2-dimethylpropyl)-4,6-dimethyl-4H-pyrido[4,3,2-*gh*]phenanthridin-5(6H)-one (4aa). Yellow oil (38.2 mg, 55% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.19–8.04 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.77–7.54 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.05 (s, 1H), 5.48 (s, 1H), 3.44 (d, *J* = 11.6 Hz, 1H), 3.34–3.26 (m, 1H), 3.10 (s, 3H), 2.46 (s, 2H), 1.55 (s, 3H), 1.14 (s, 3H), 1.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.1, 162.0, 157.5, 147.8, 134.2, 128.7, 128.6, 126.3, 123.8, 122.7, 111.9, 109.9, 109.1, 107.9, 61.7, 46.7, 41.9, 41.8, 39.6, 30.0, 29.7, 26.2; HRMS (ESI) *m/z*: calcd for C₂₂H₂₆N₃O [M + H]⁺ 348.2070, found 348.2072.

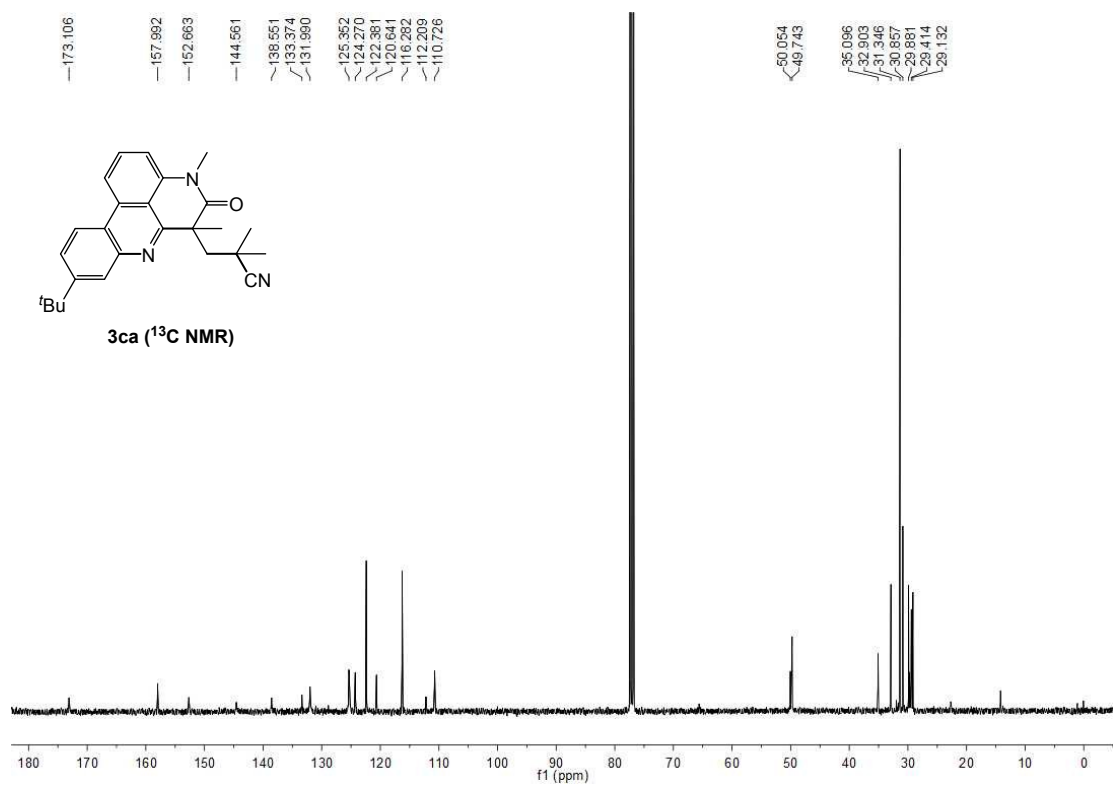
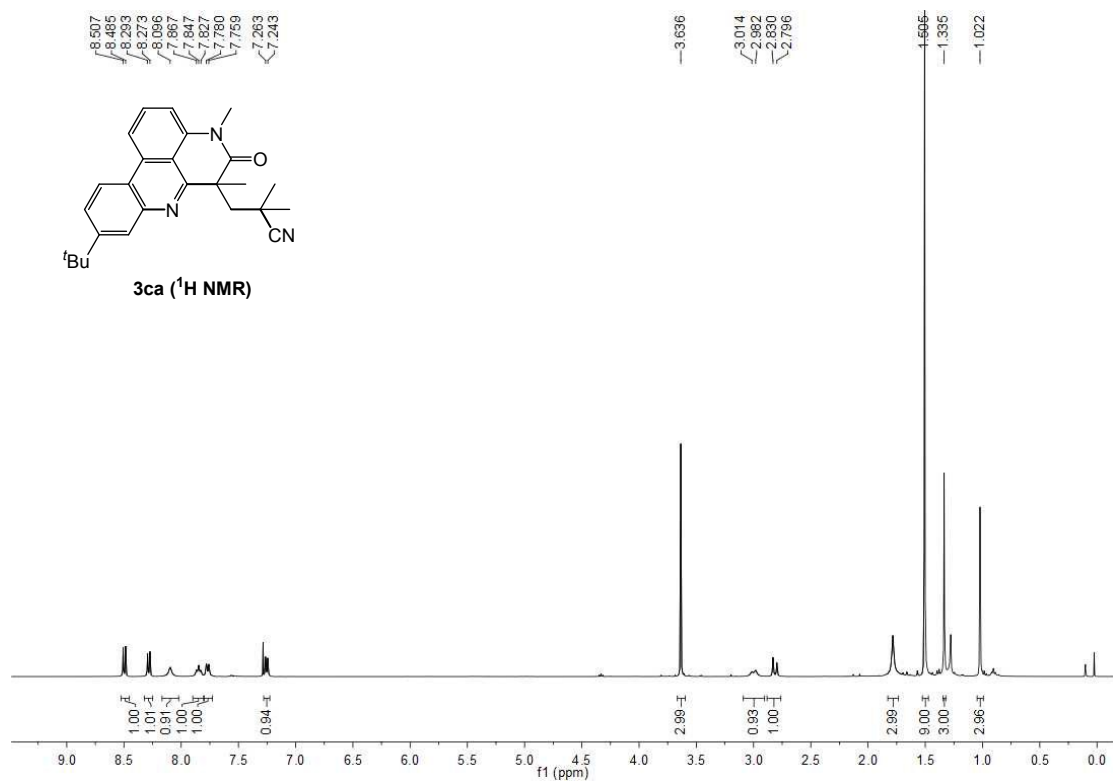
4. References

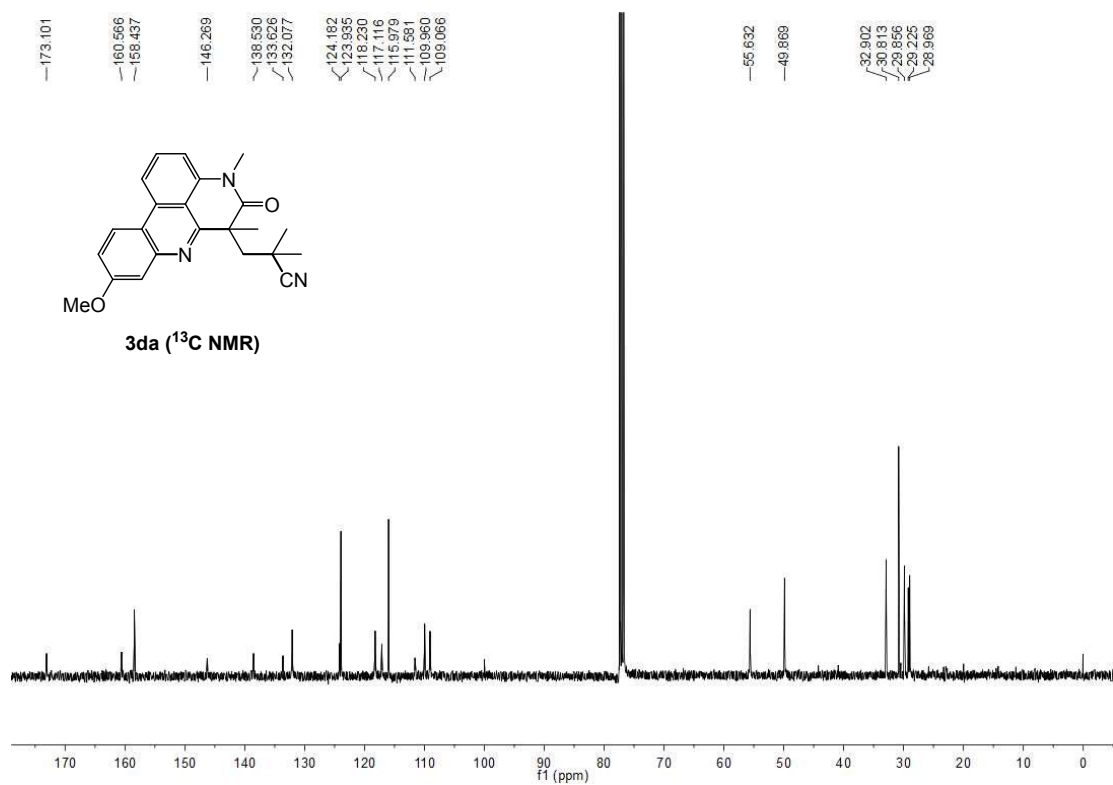
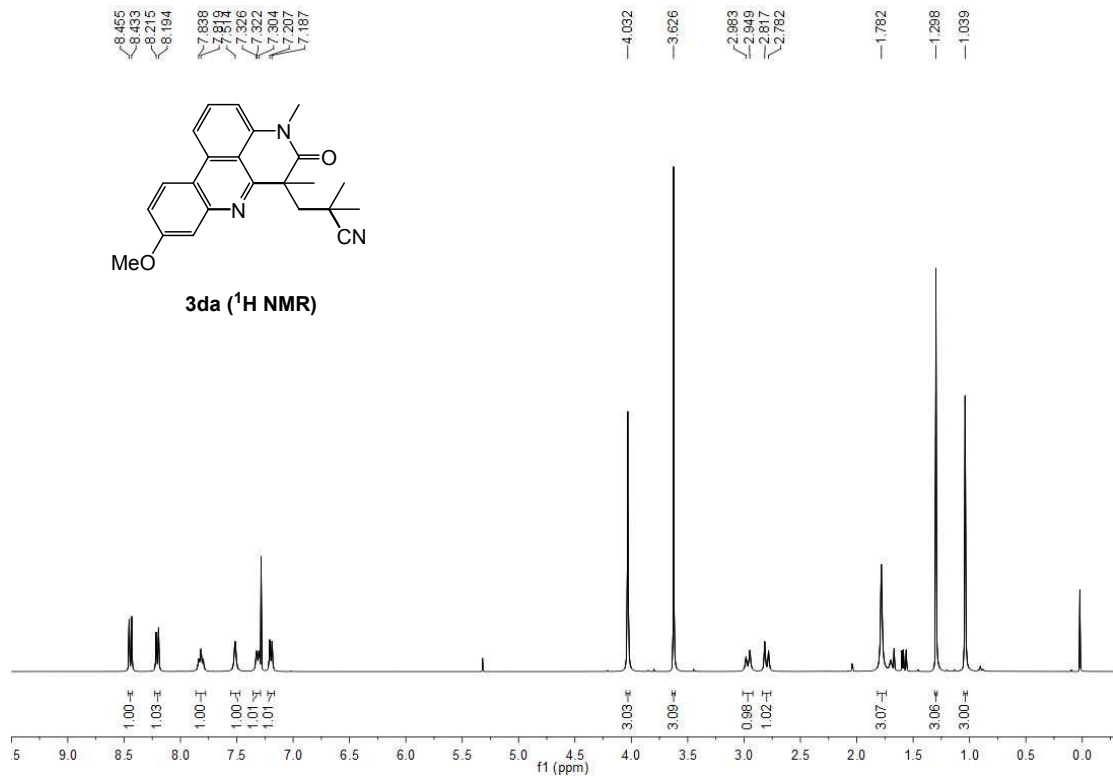
- 1 X. Li, X. Fang, S. Zhuang, P. Liu and P. Sun, *Org. Lett.*, 2017, **19**, 3580.

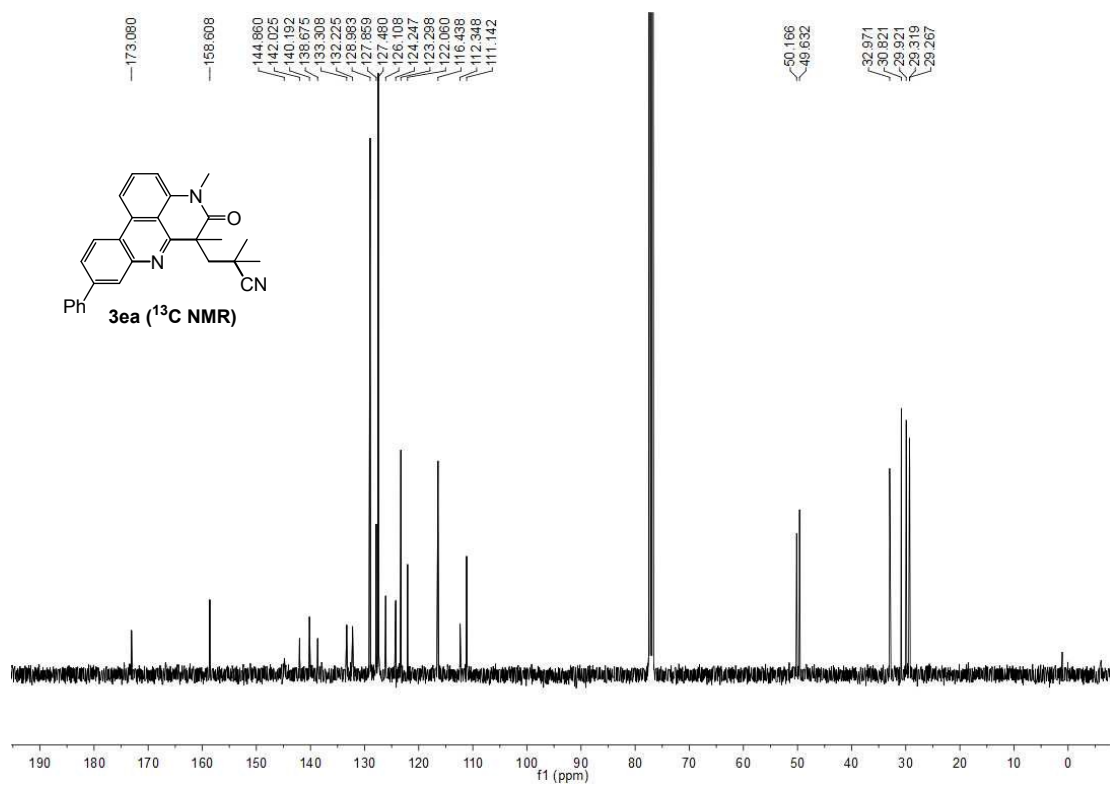
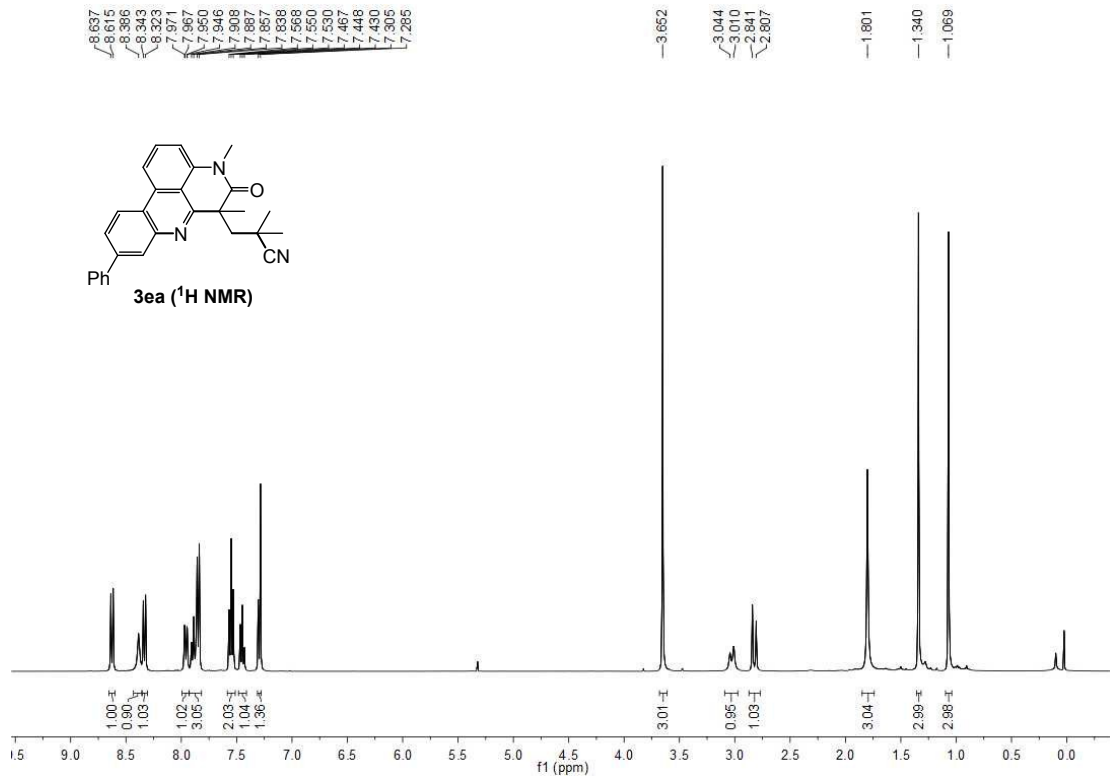
5. NMR spectra of the products 3 and 4aa

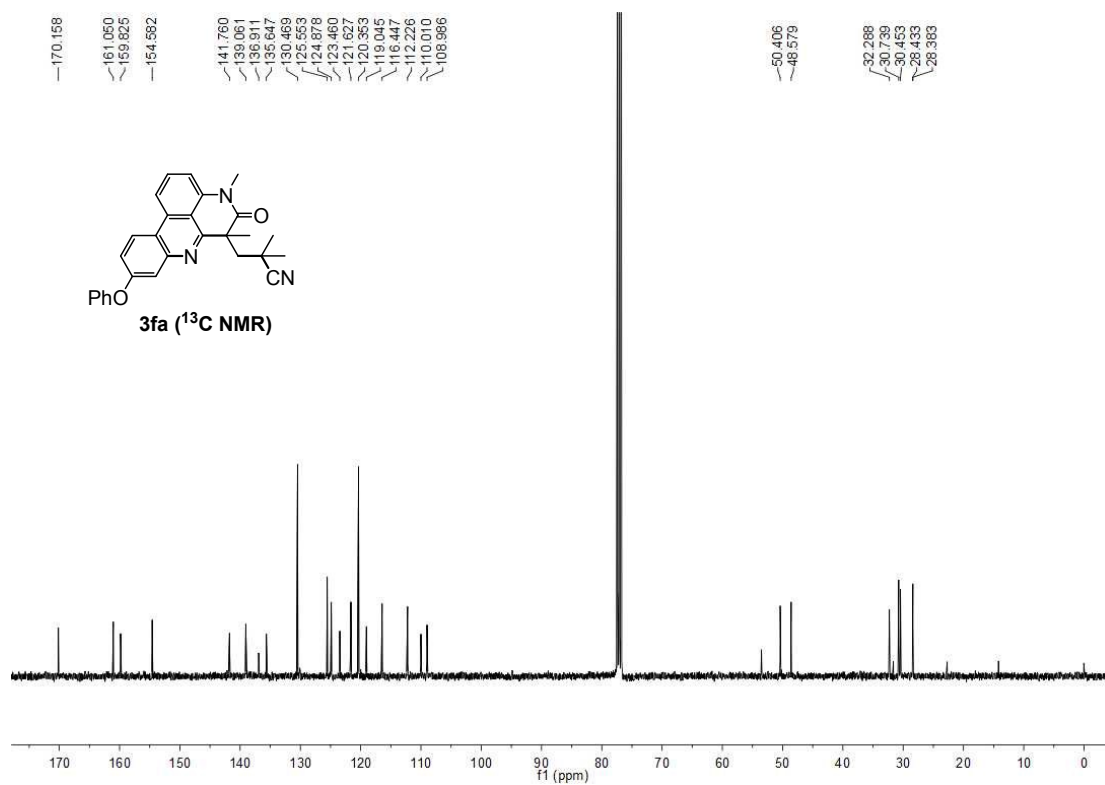
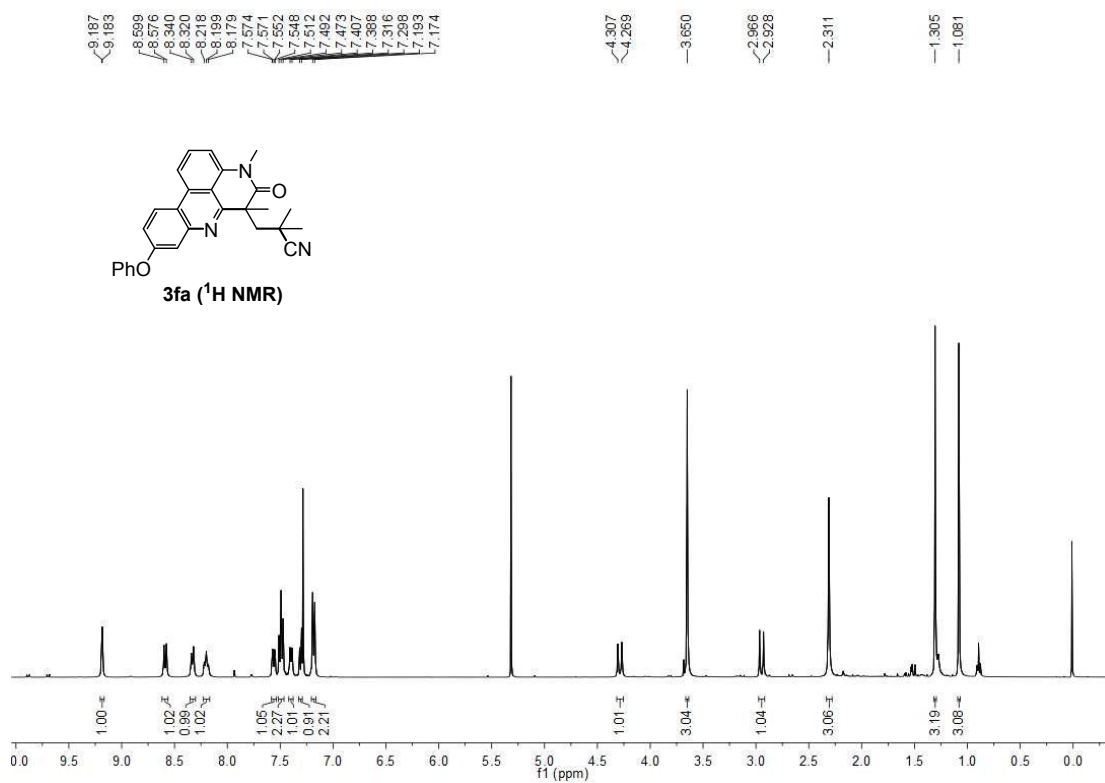


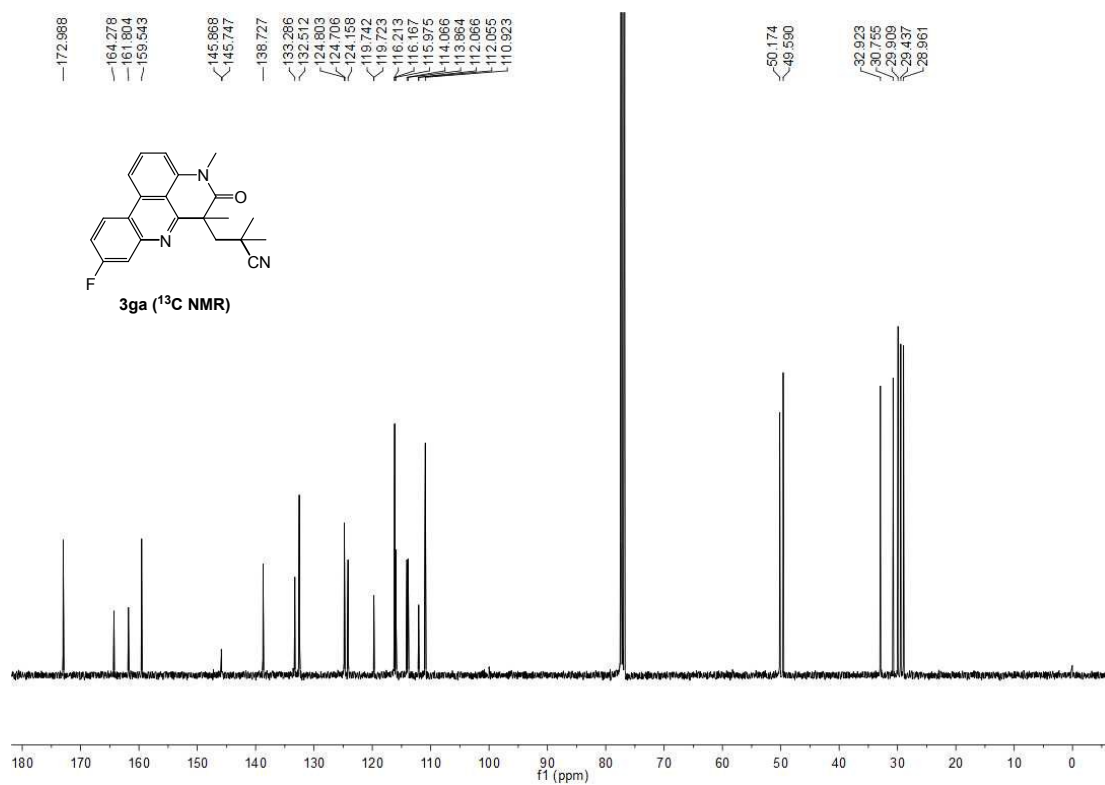
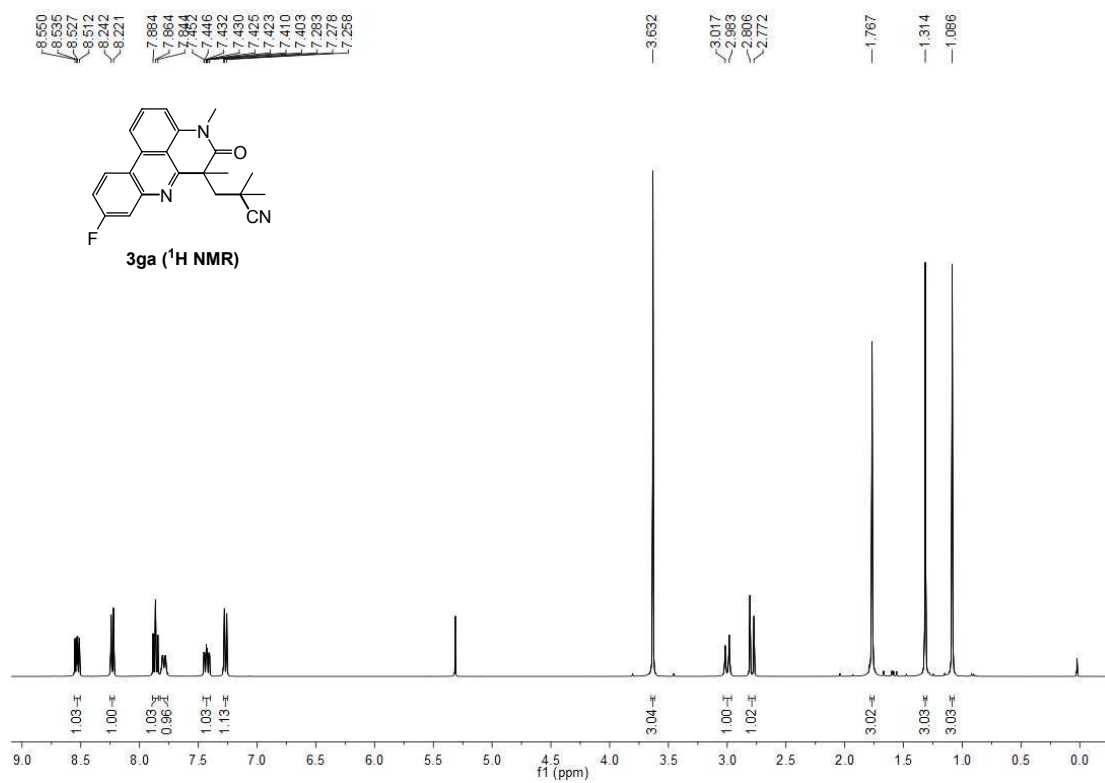


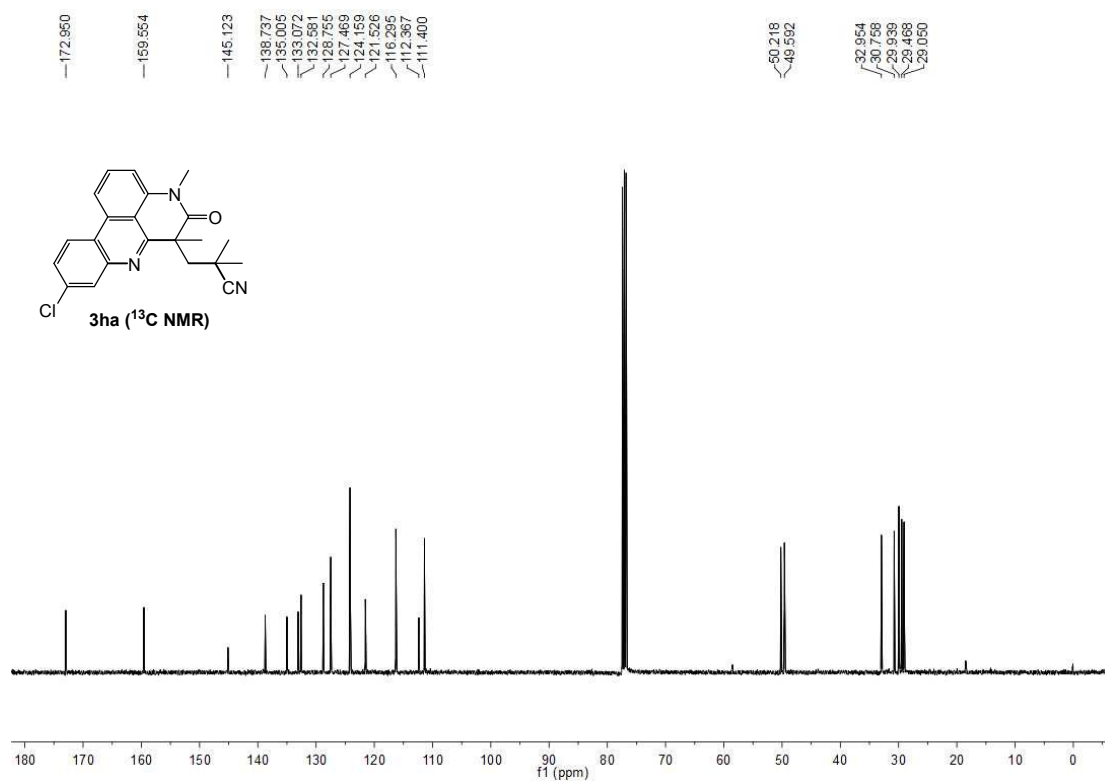
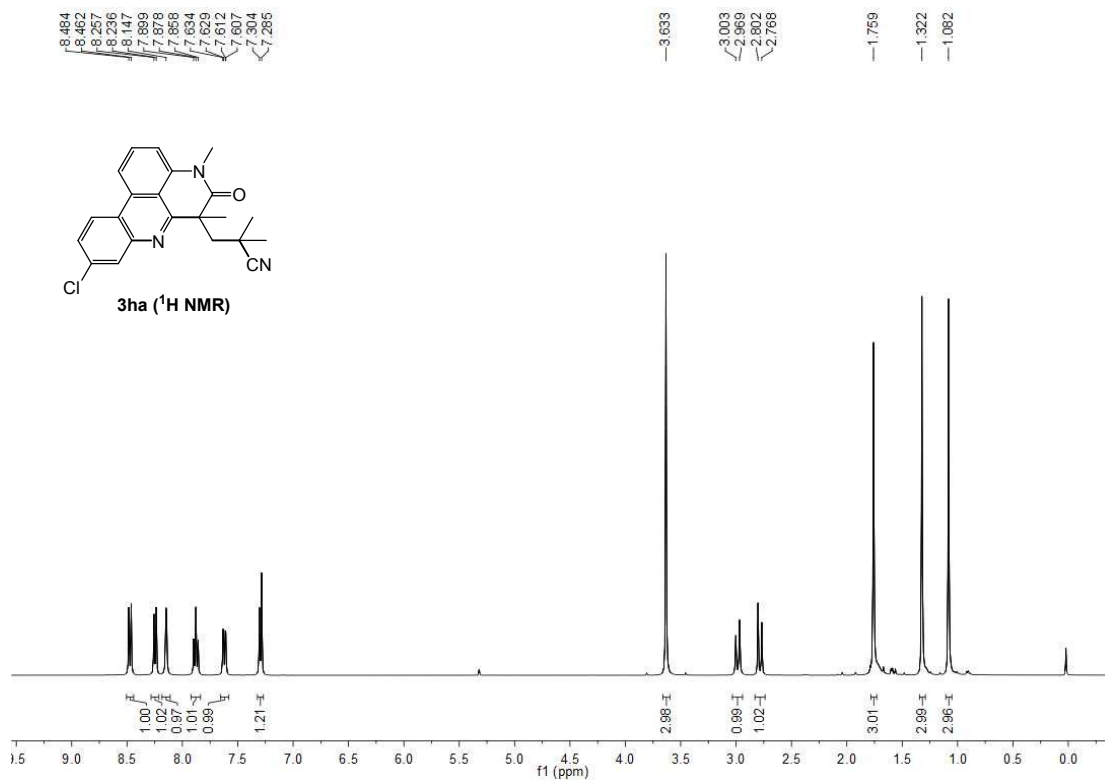


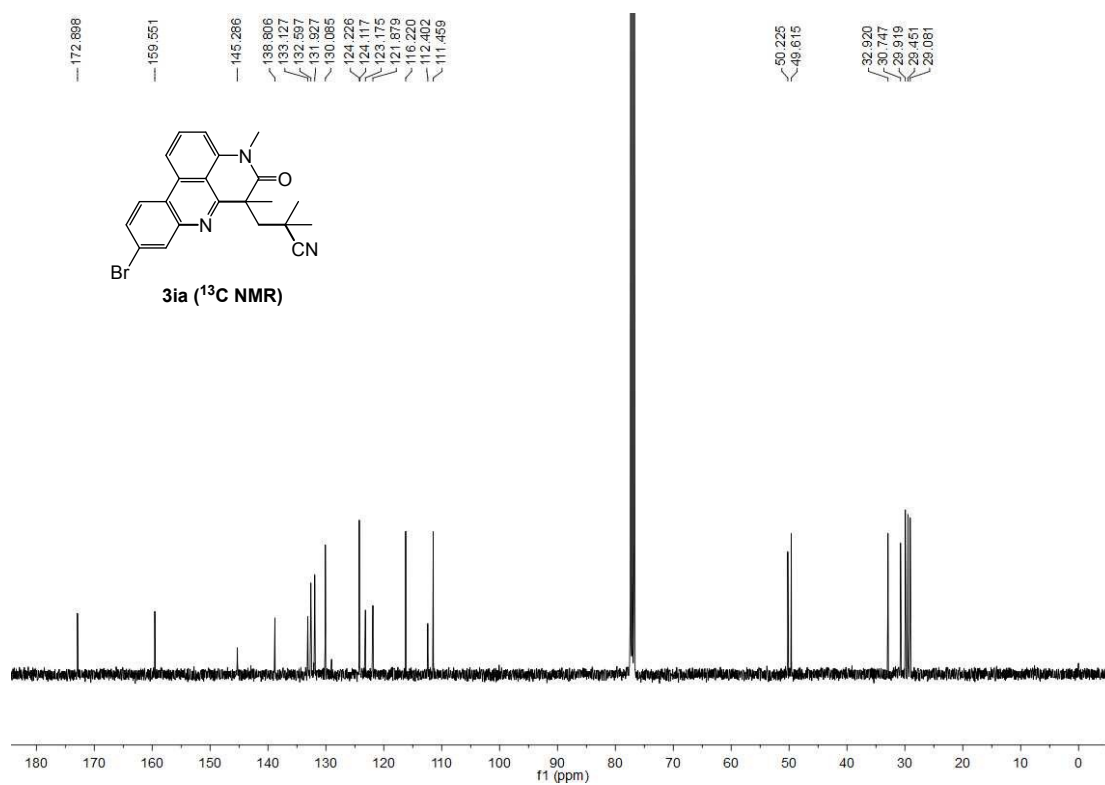
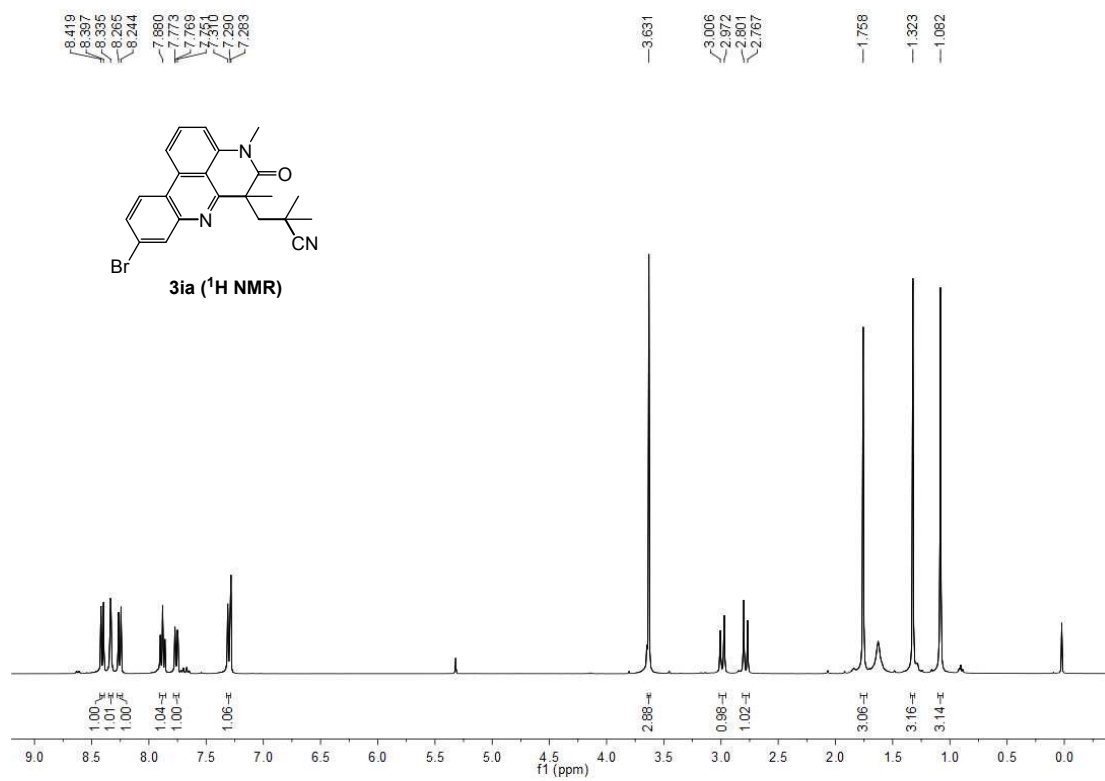


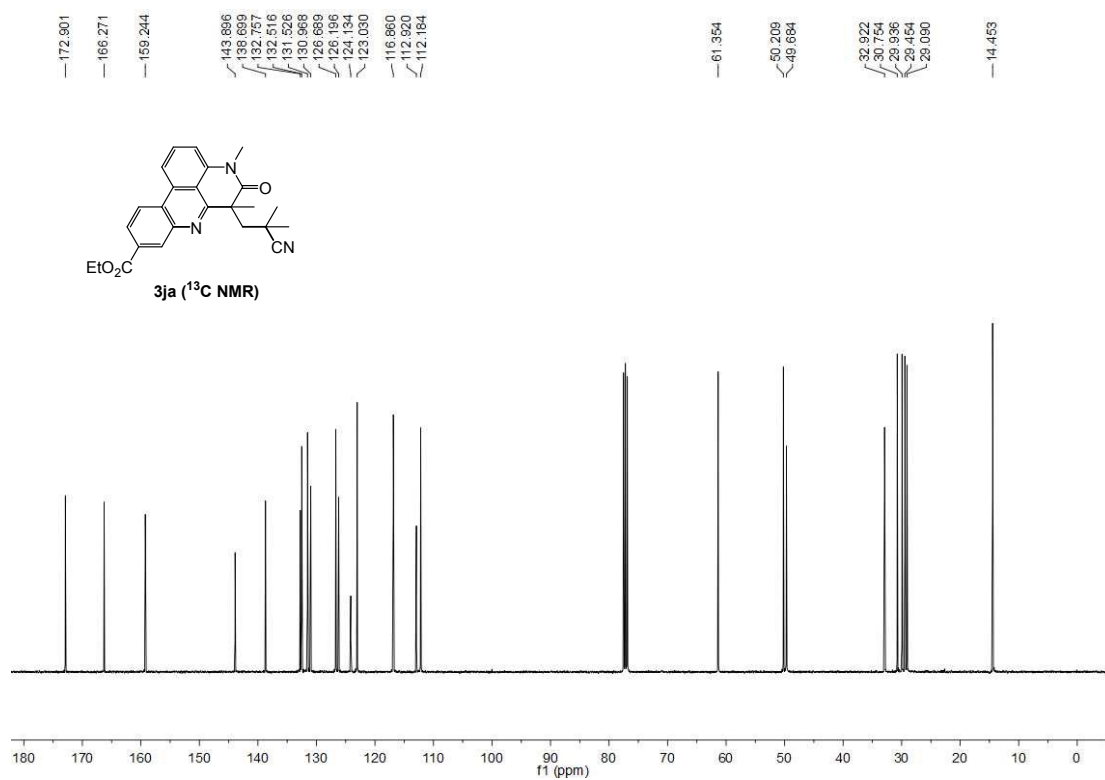
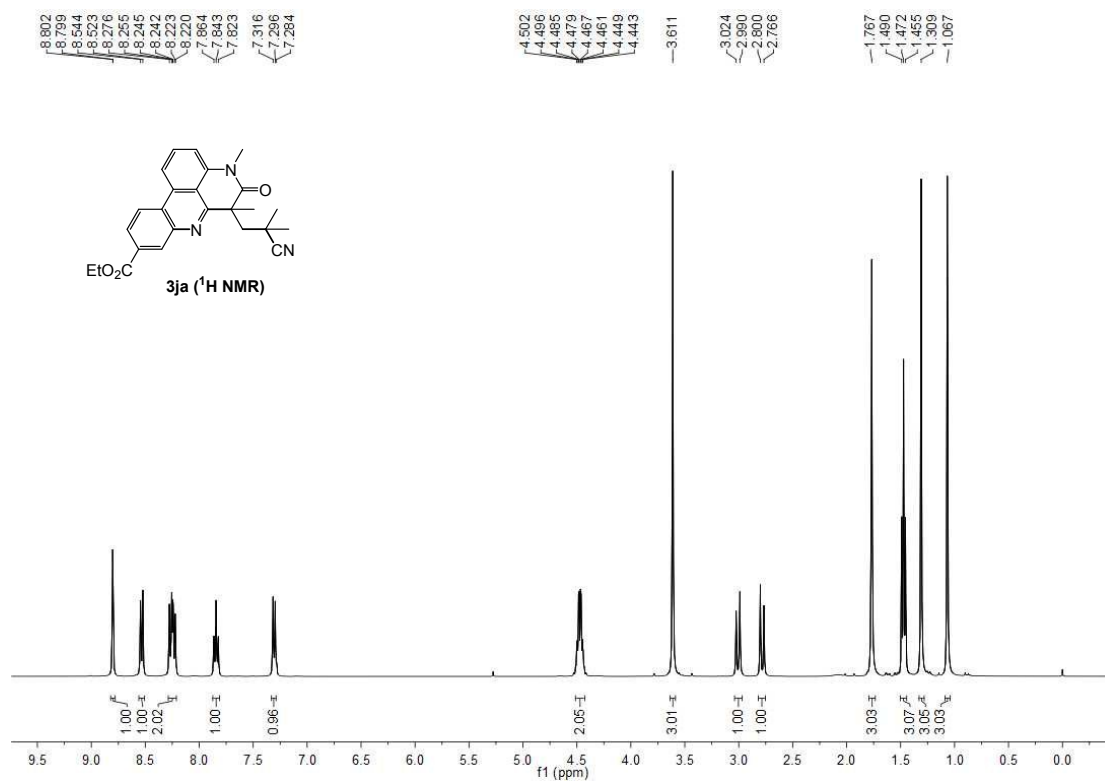


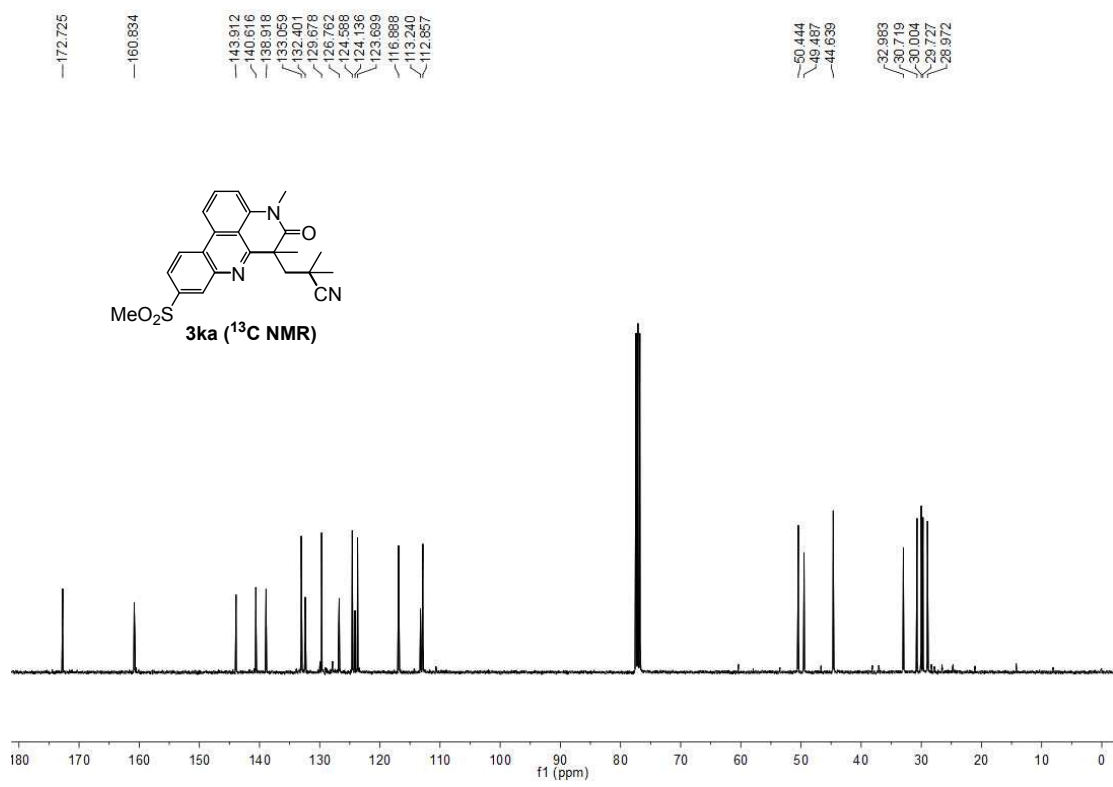
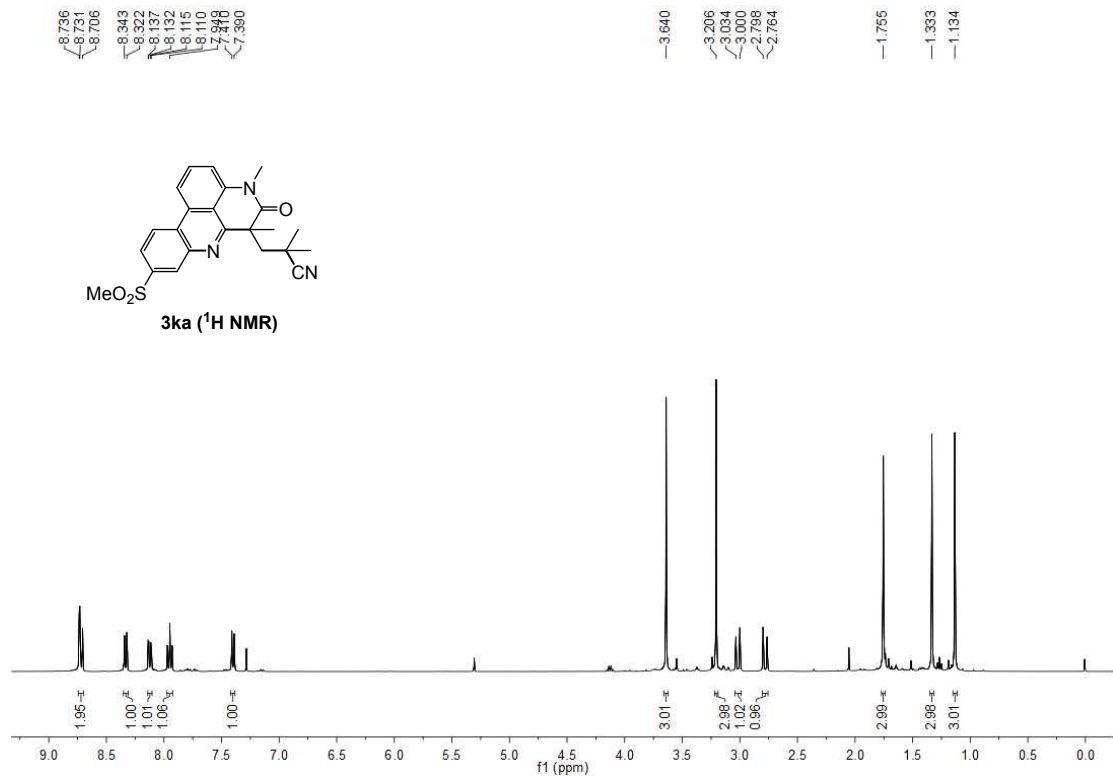


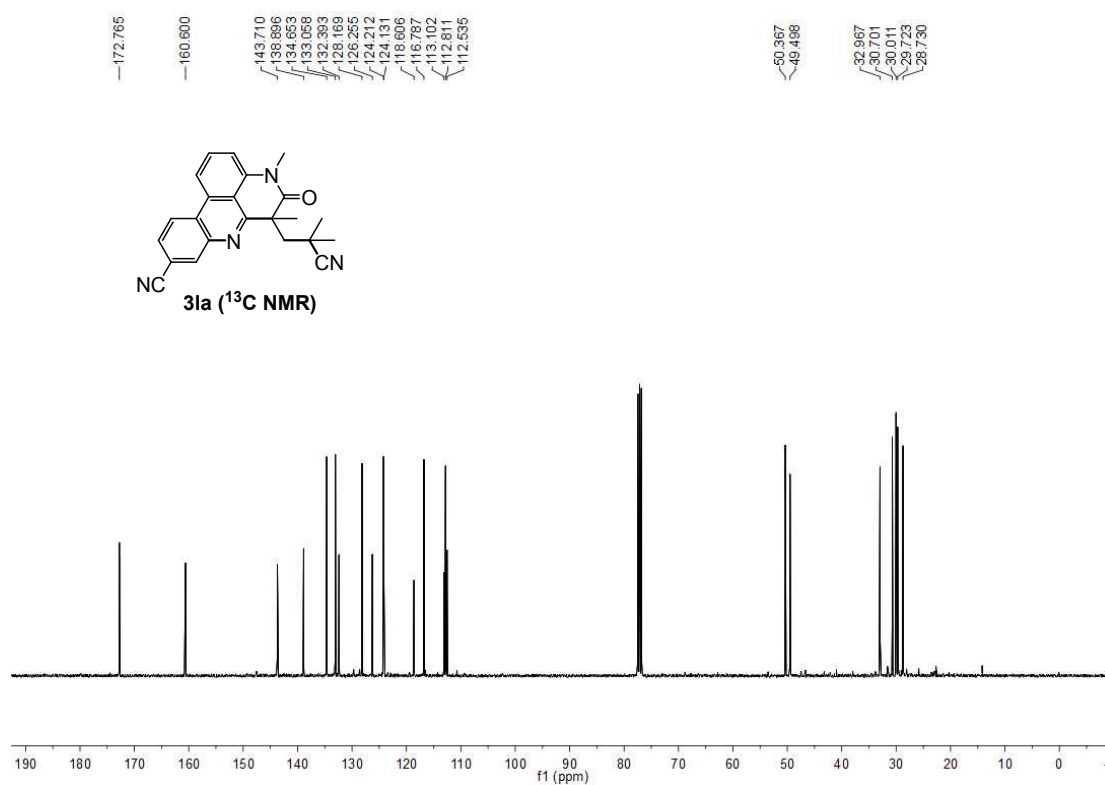
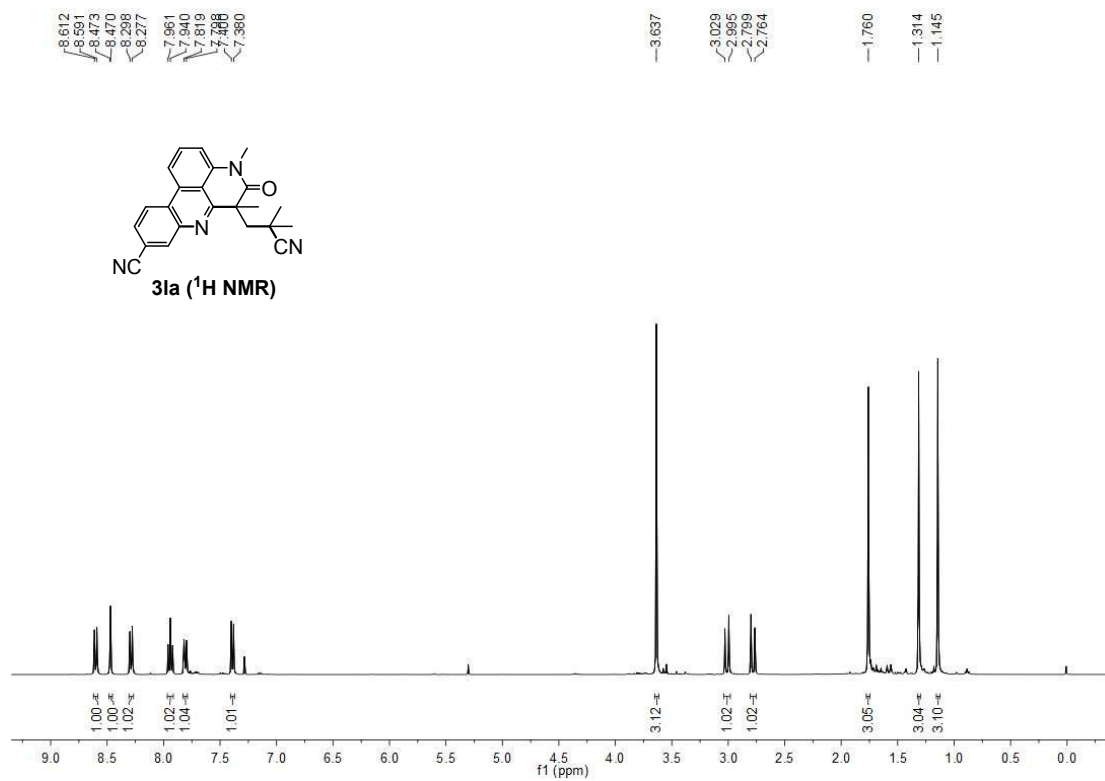






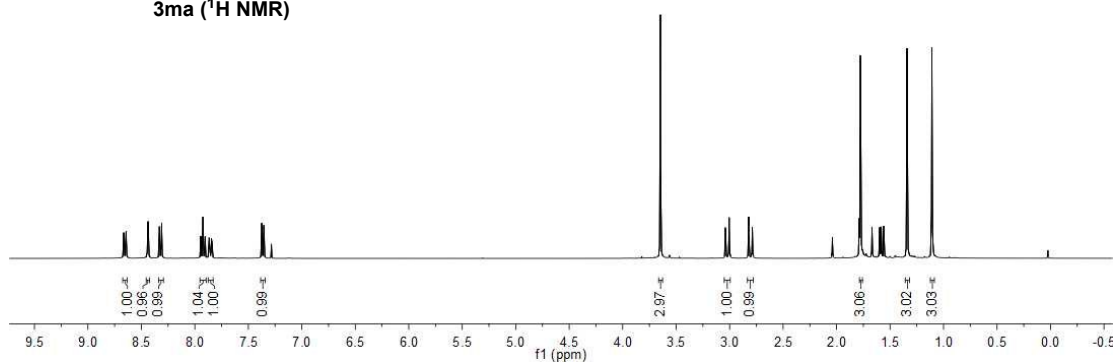
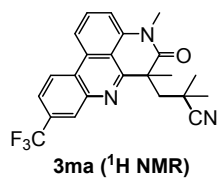




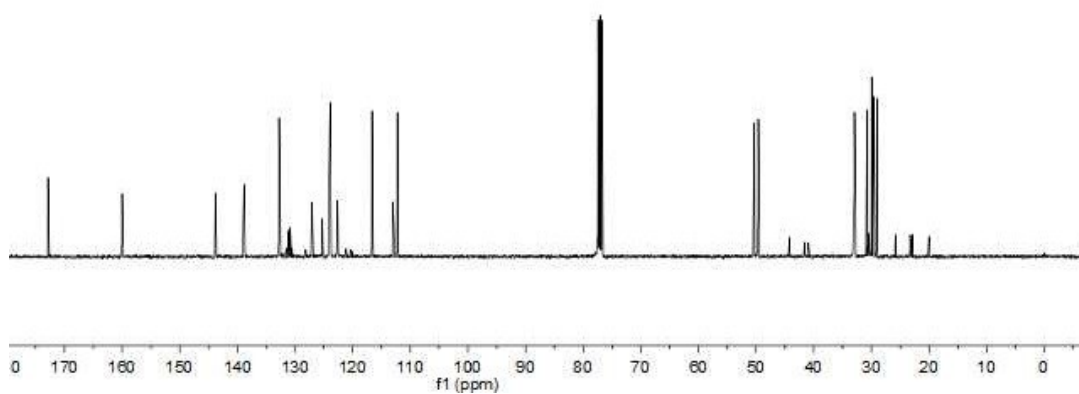
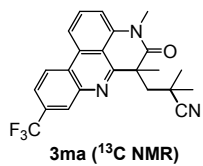


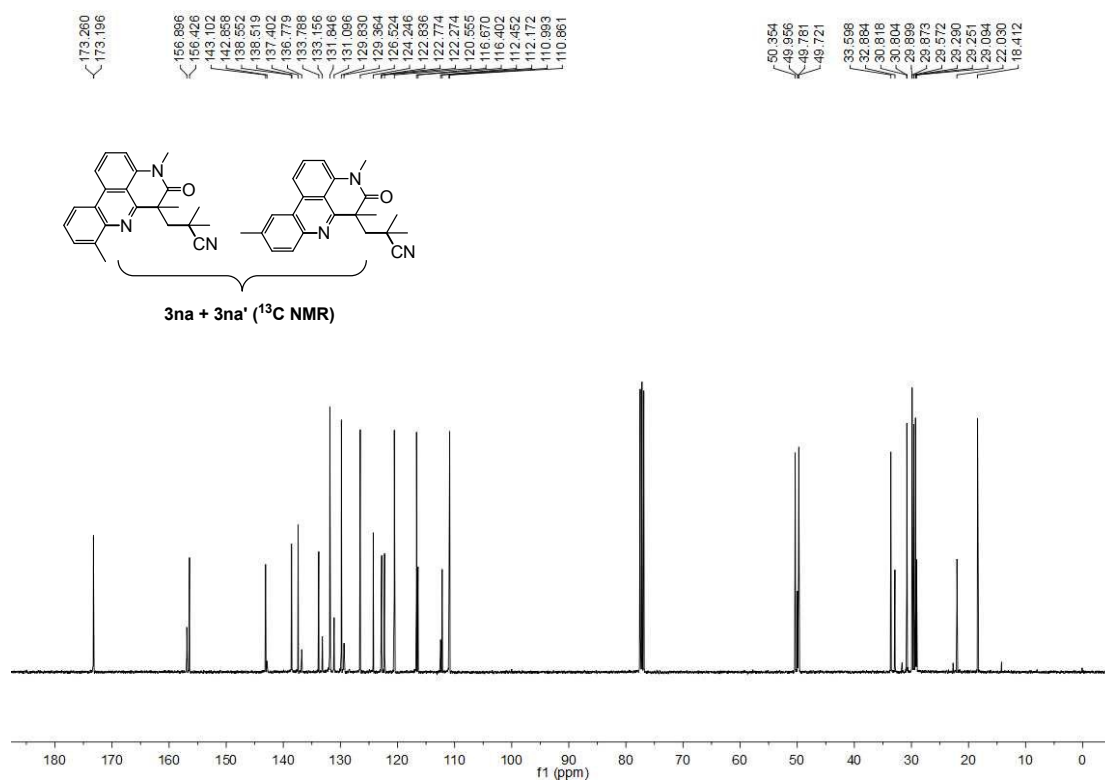
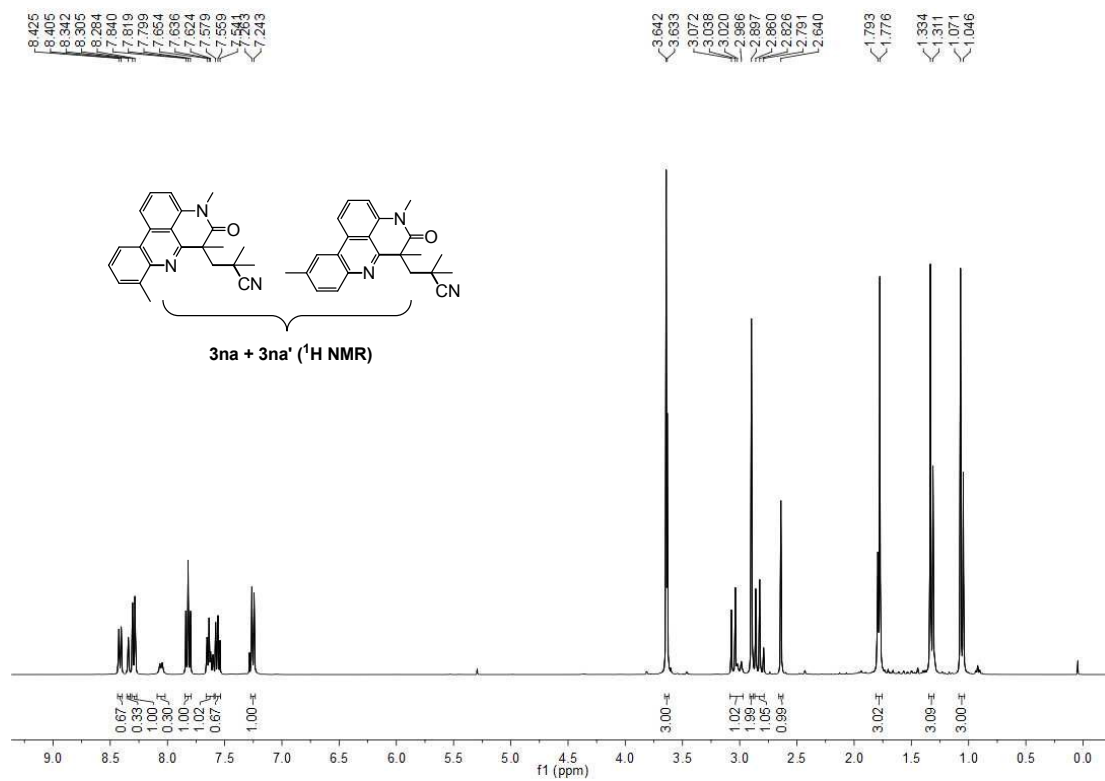
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7.504
7.392
7.354

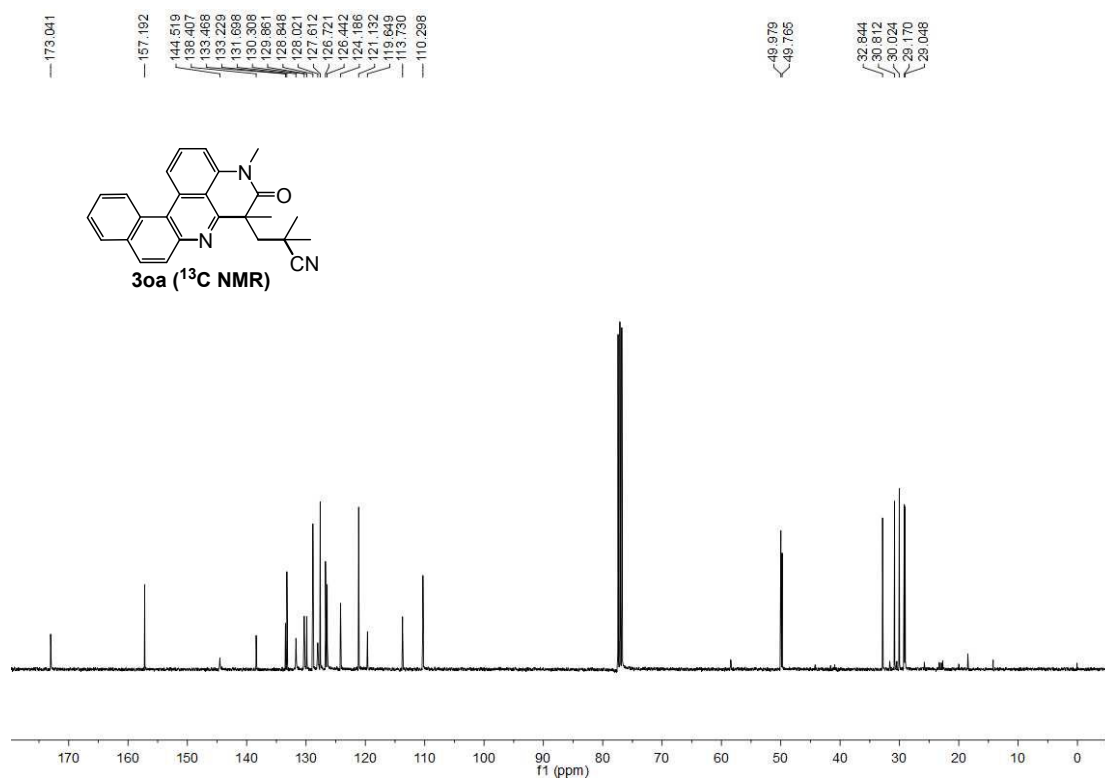
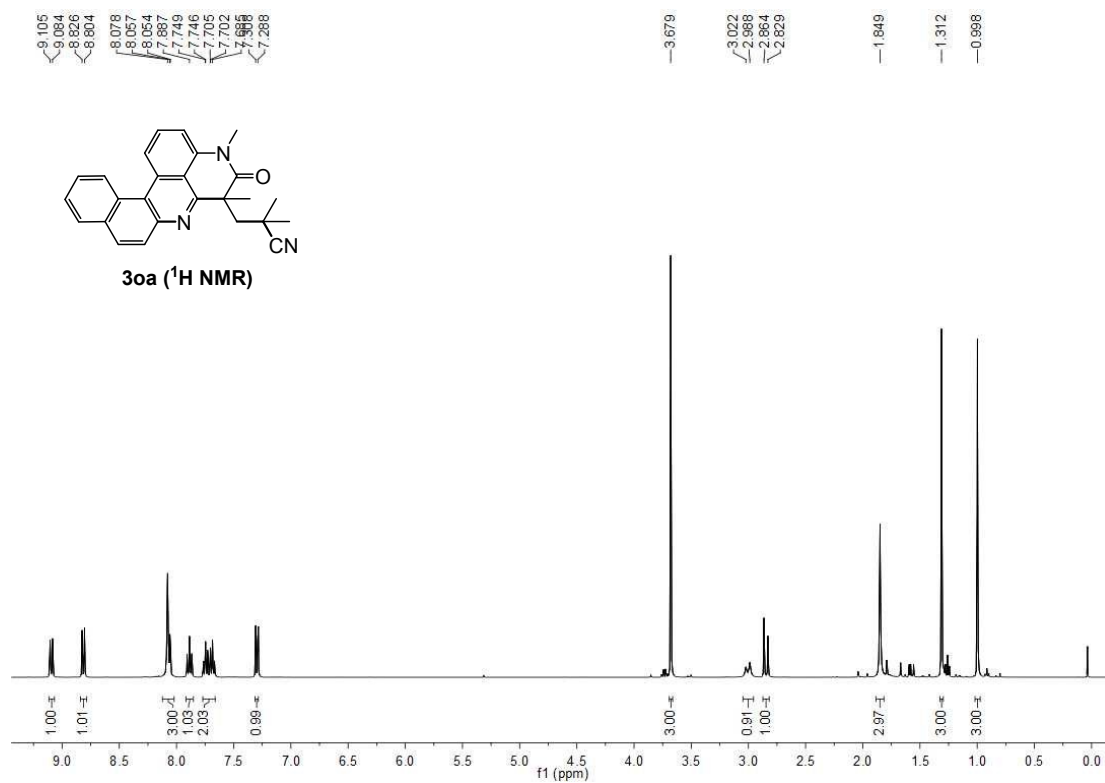
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3.039
3.005
2.822
2.788
1.777
1.341
1.109



172.851
159.986
143.794
138.829
132.756
132.685
131.495
131.170
130.844
130.518
128.142
127.144
127.103
127.062
127.020
127.020
125.305
125.297
124.125
123.893
122.728
122.694
122.662
122.629
122.586
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29.536
29.055

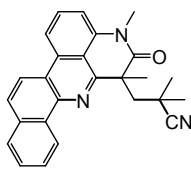




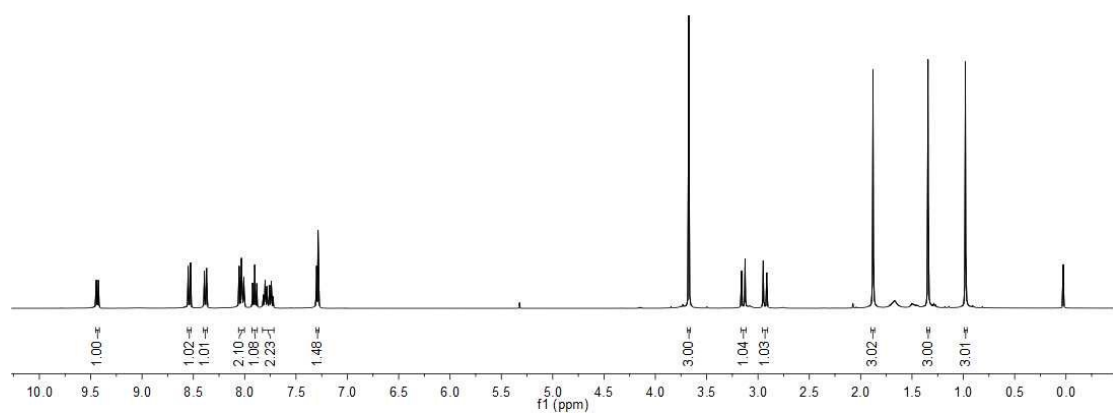


9.444
9.424
8.560
8.528
8.382
8.371
8.054
8.031
8.009
7.896
7.285
7.280

3.674
3.160
3.126
2.949
2.915
1.880
1.344
0.980

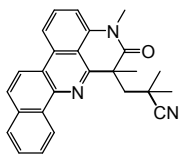


3pa (¹H NMR)

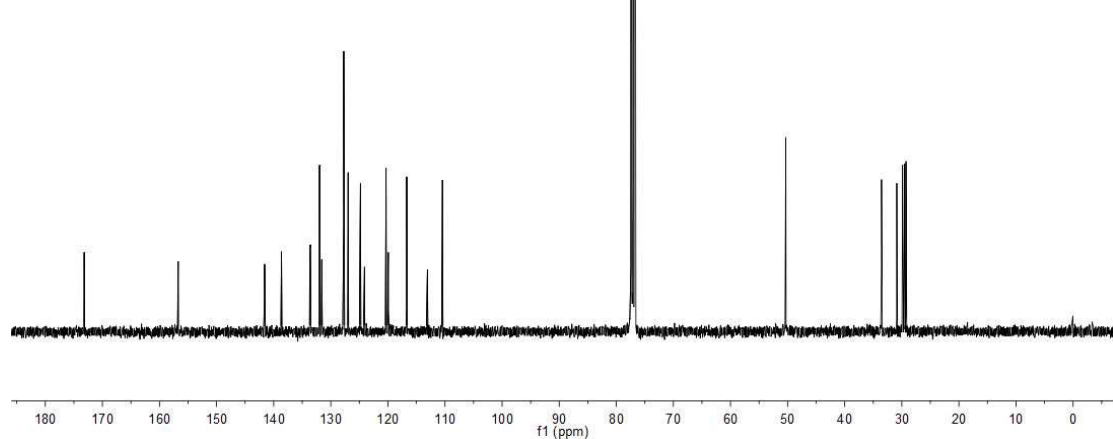


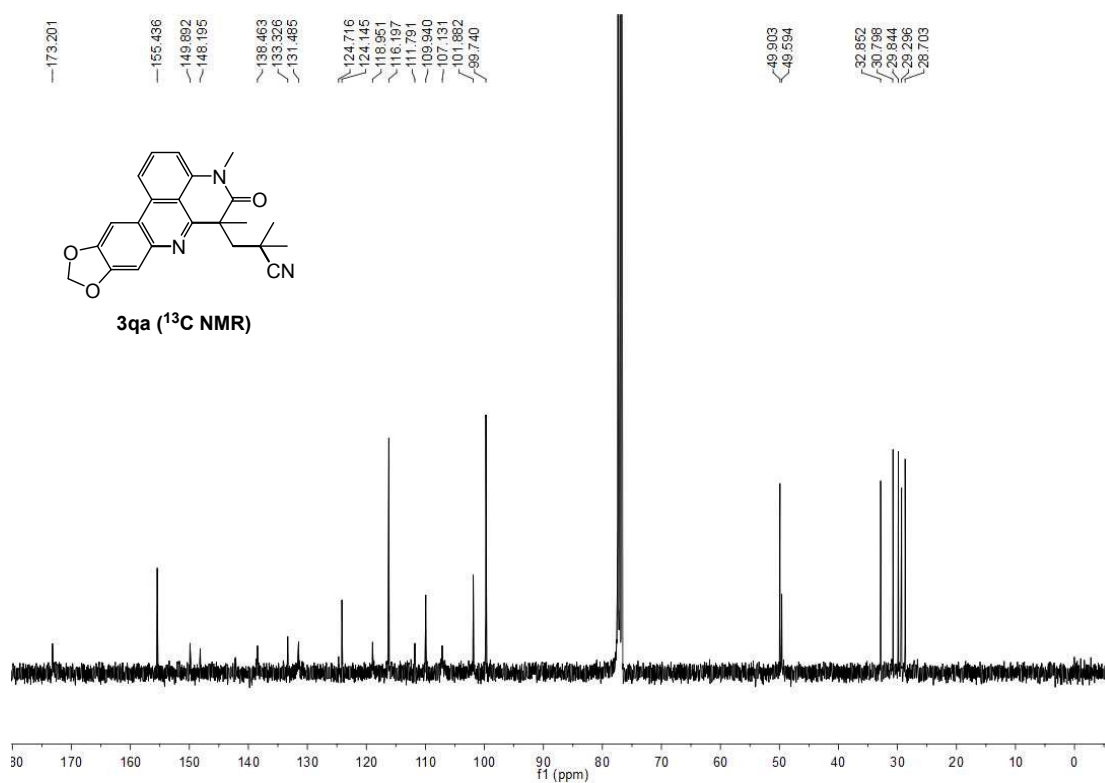
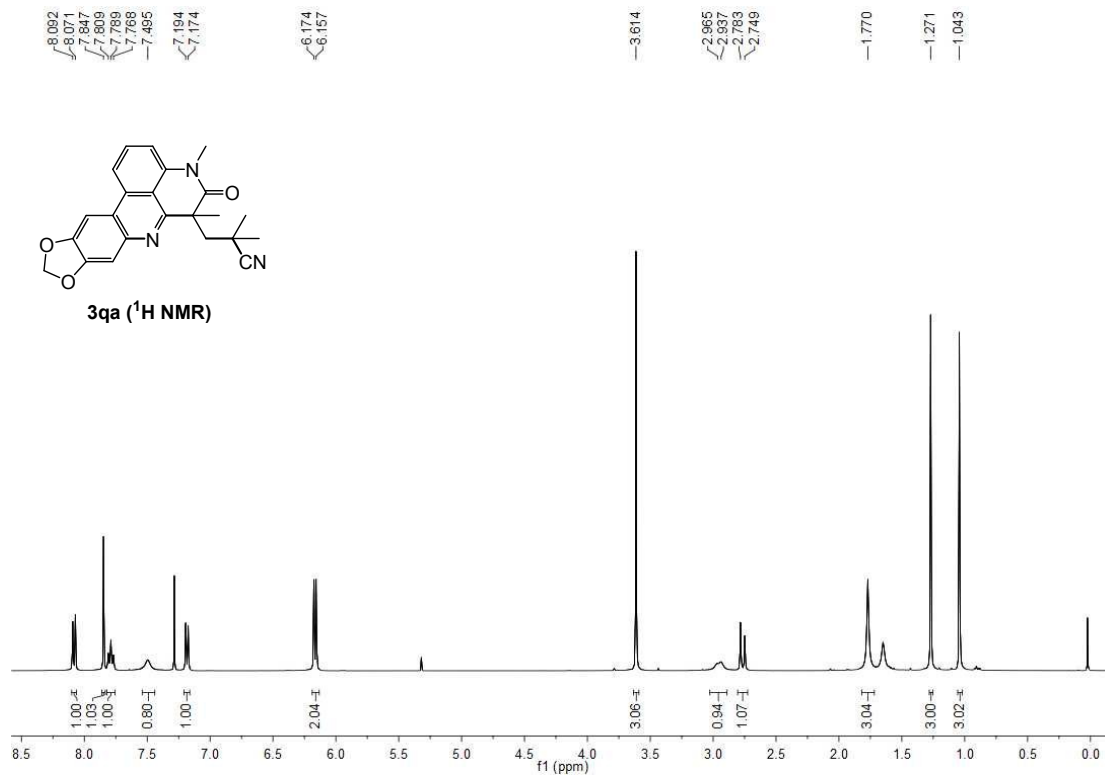
173.183
156.726
141.598
138.638
133.685
133.561
131.967
131.581
127.732
127.694
120.960
124.809
124.103
119.838
118.703
113.075
110.440

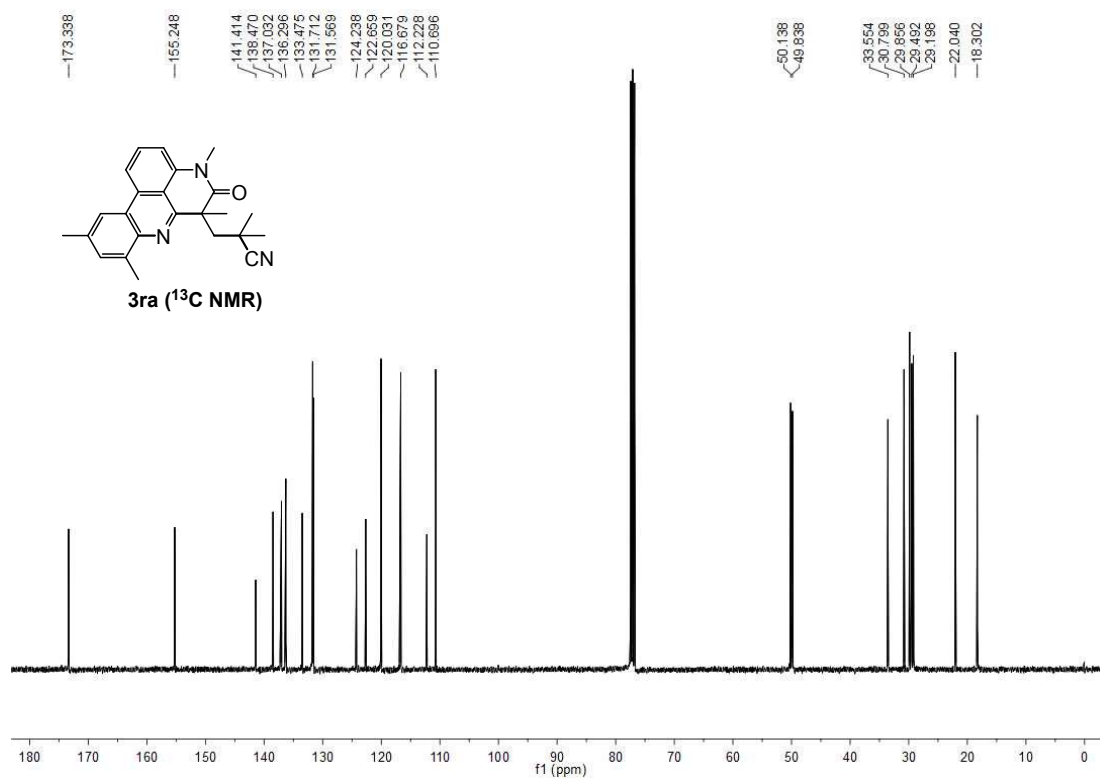
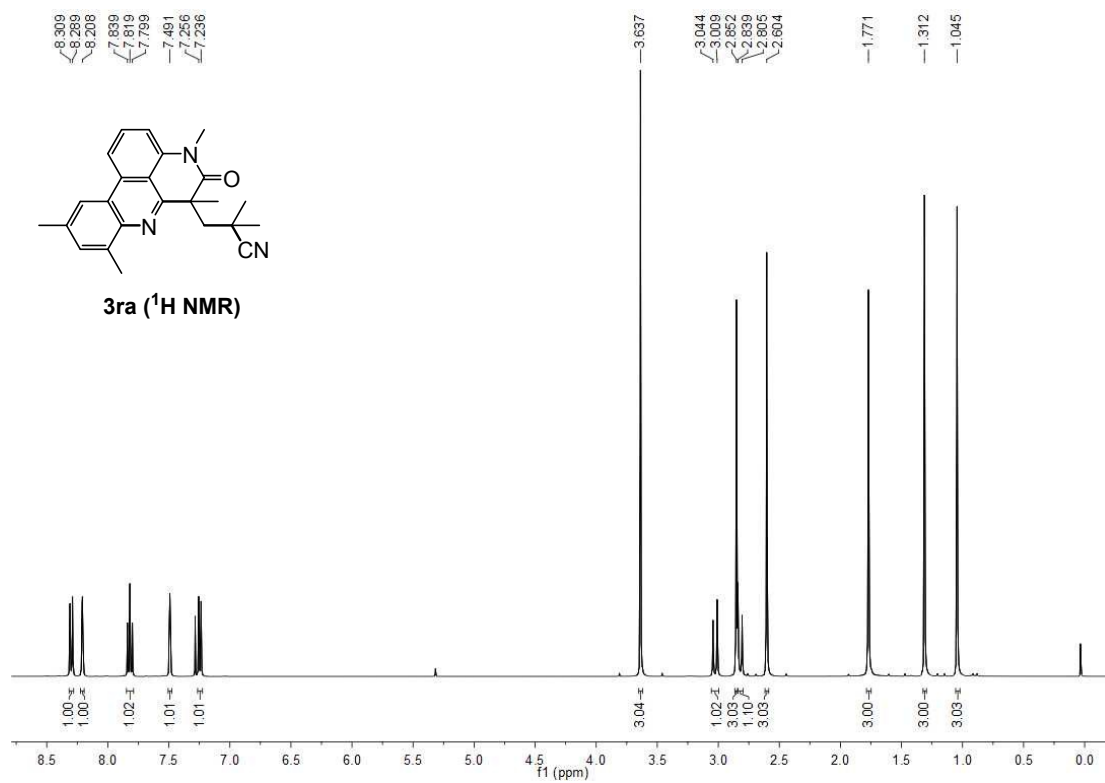
50.318
50.308
33.547
30.871
29.868
29.504
29.265

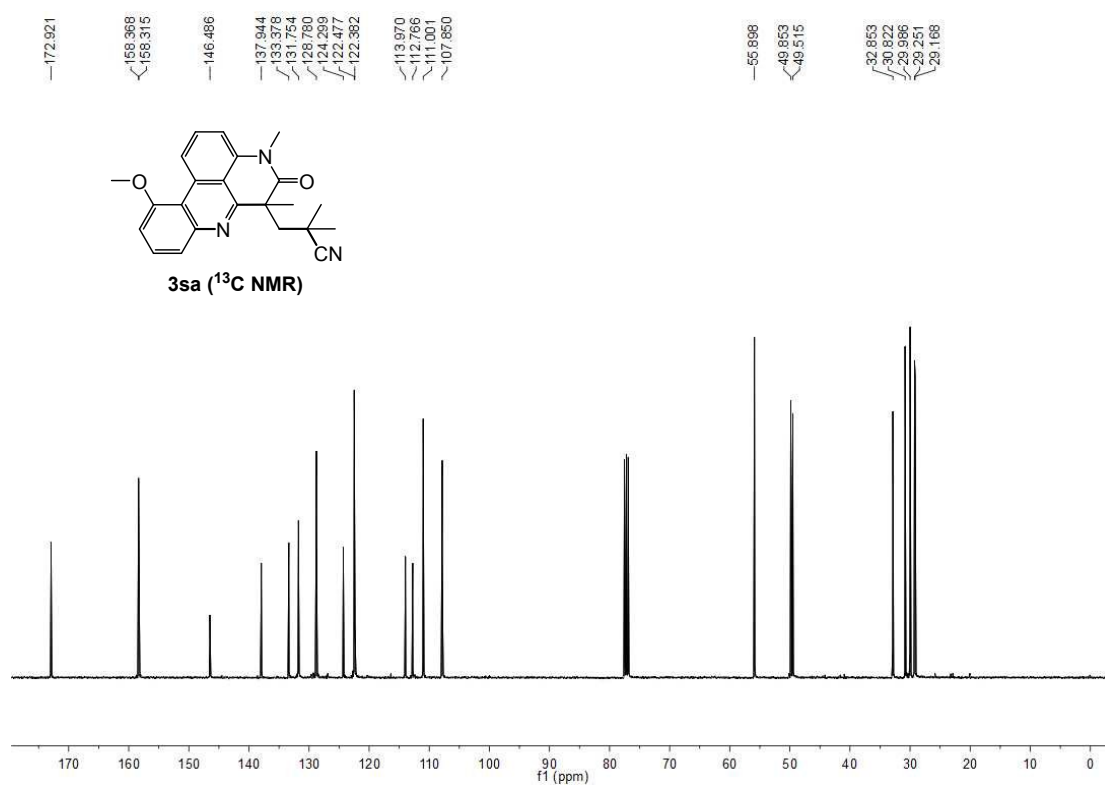
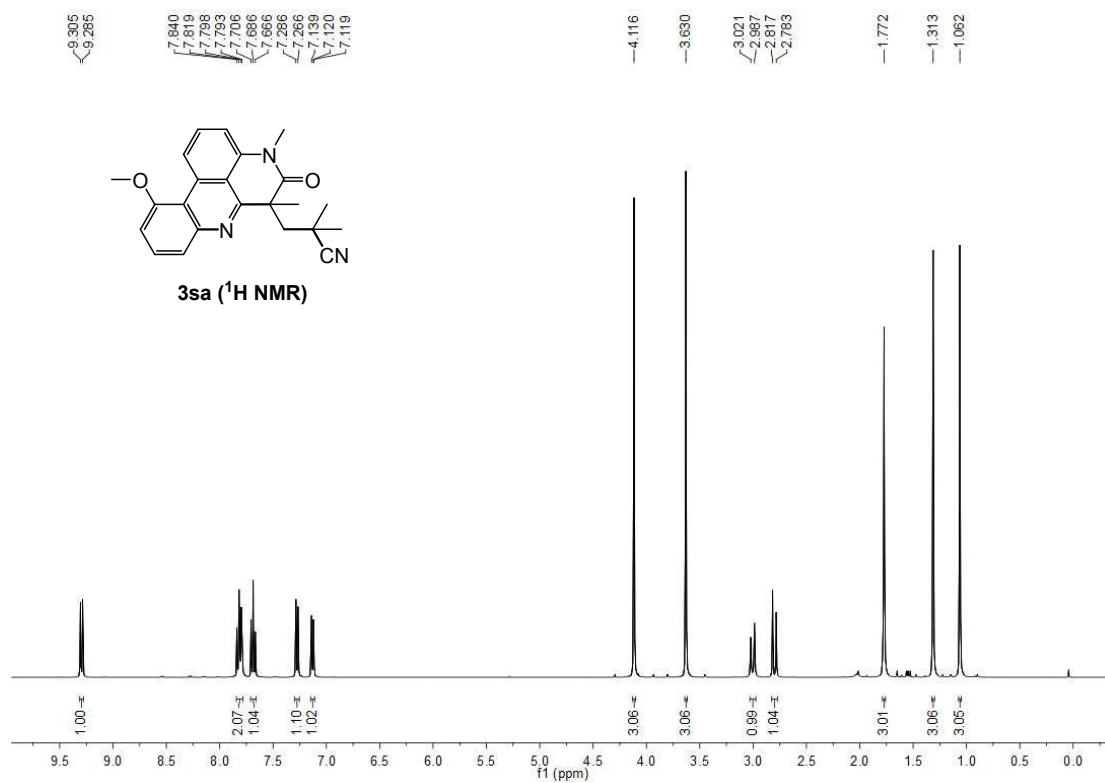


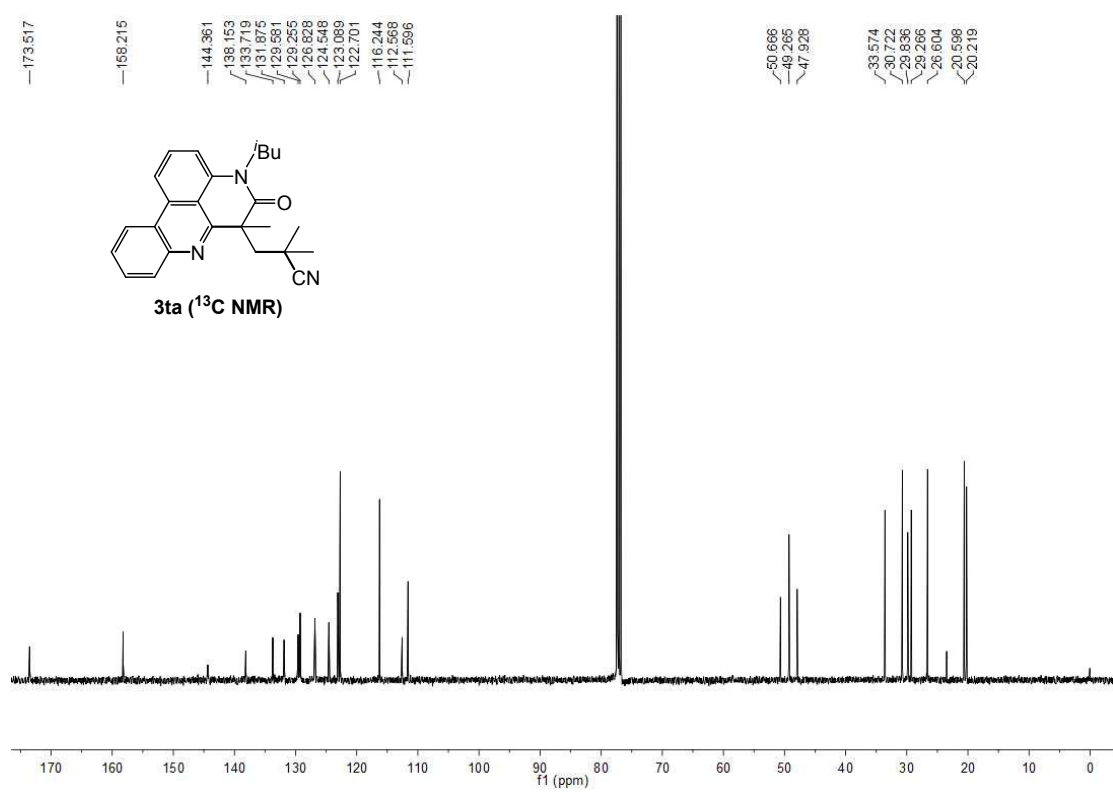
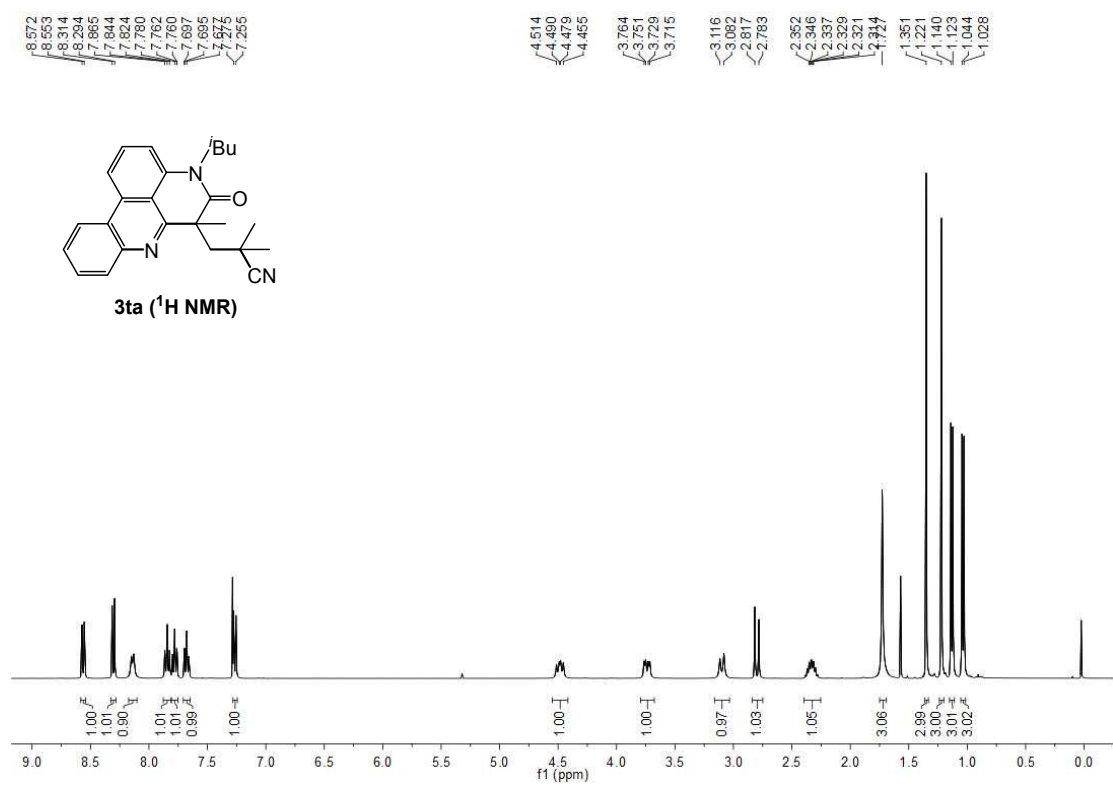
3pa (¹³C NMR)

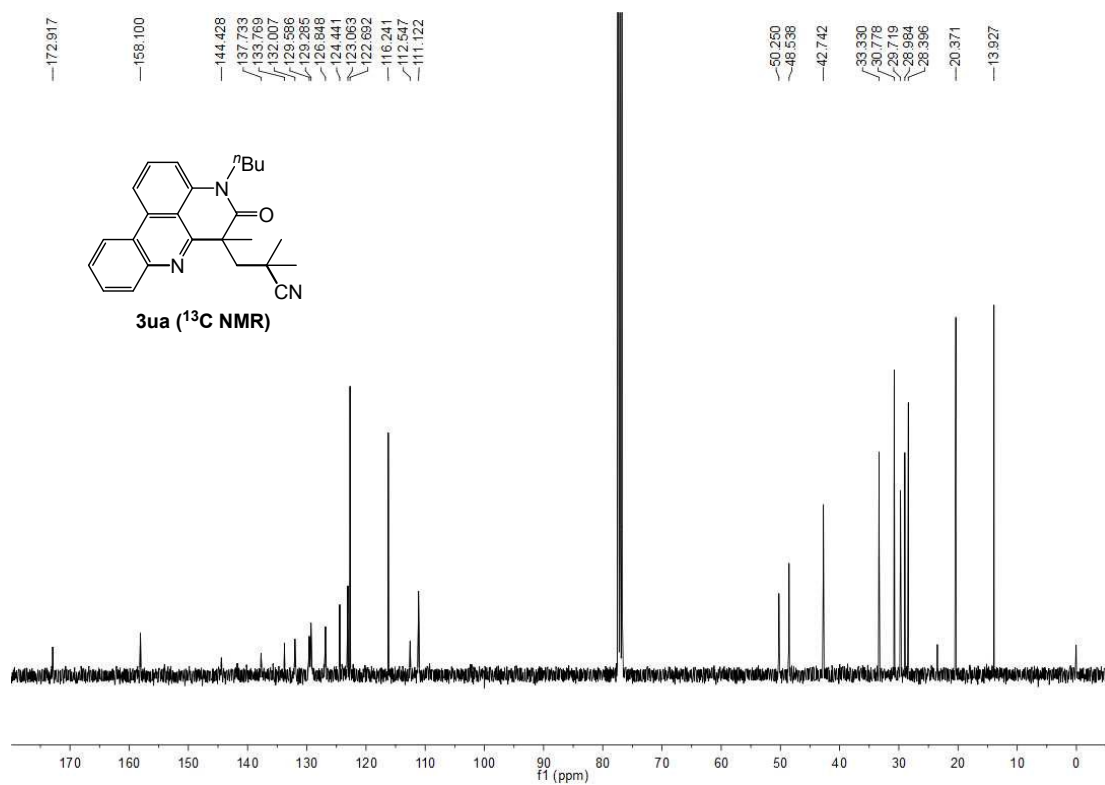
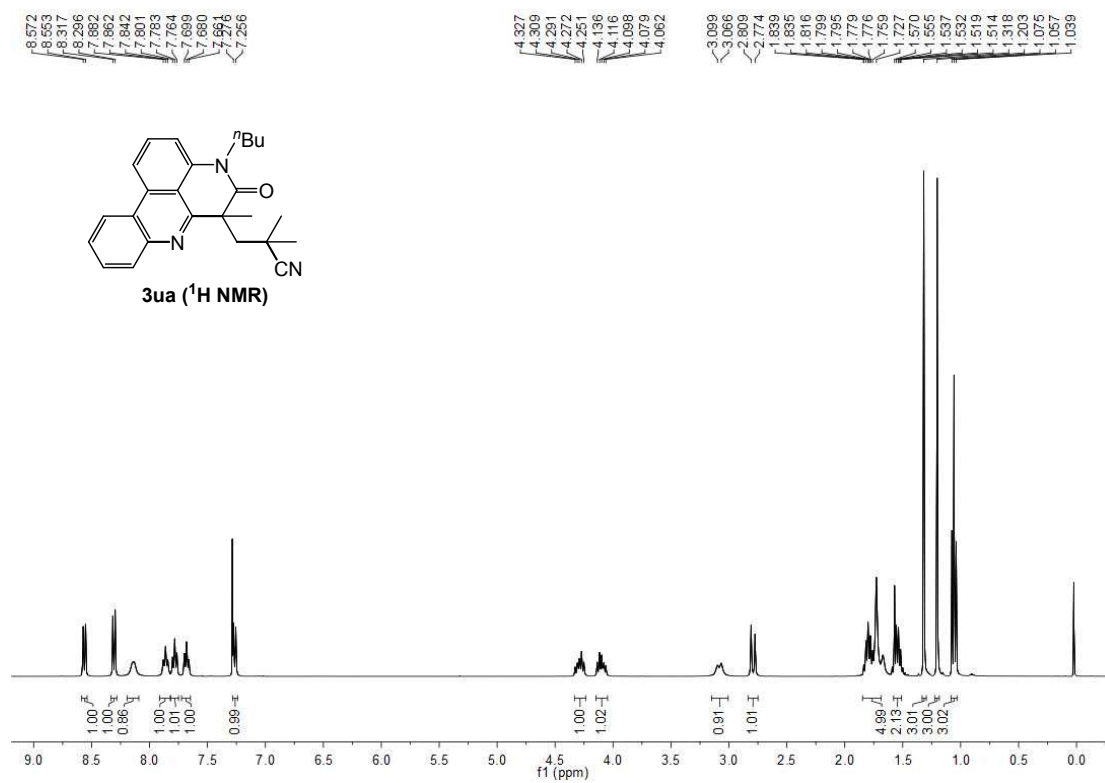


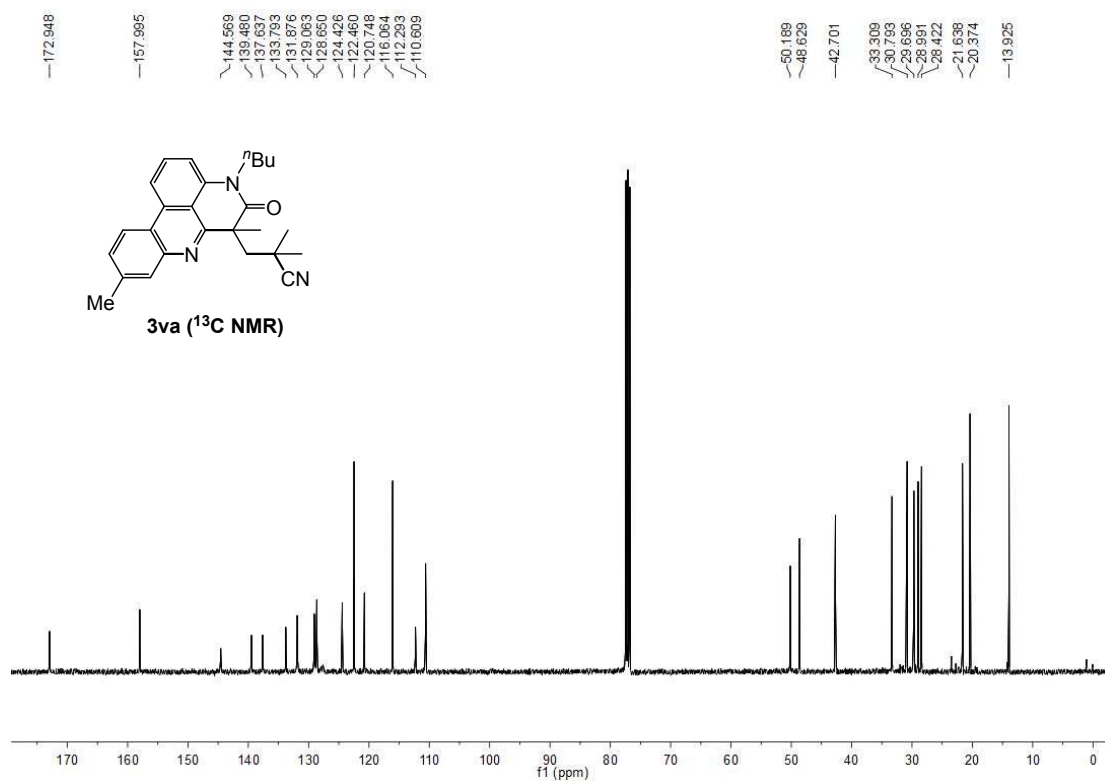
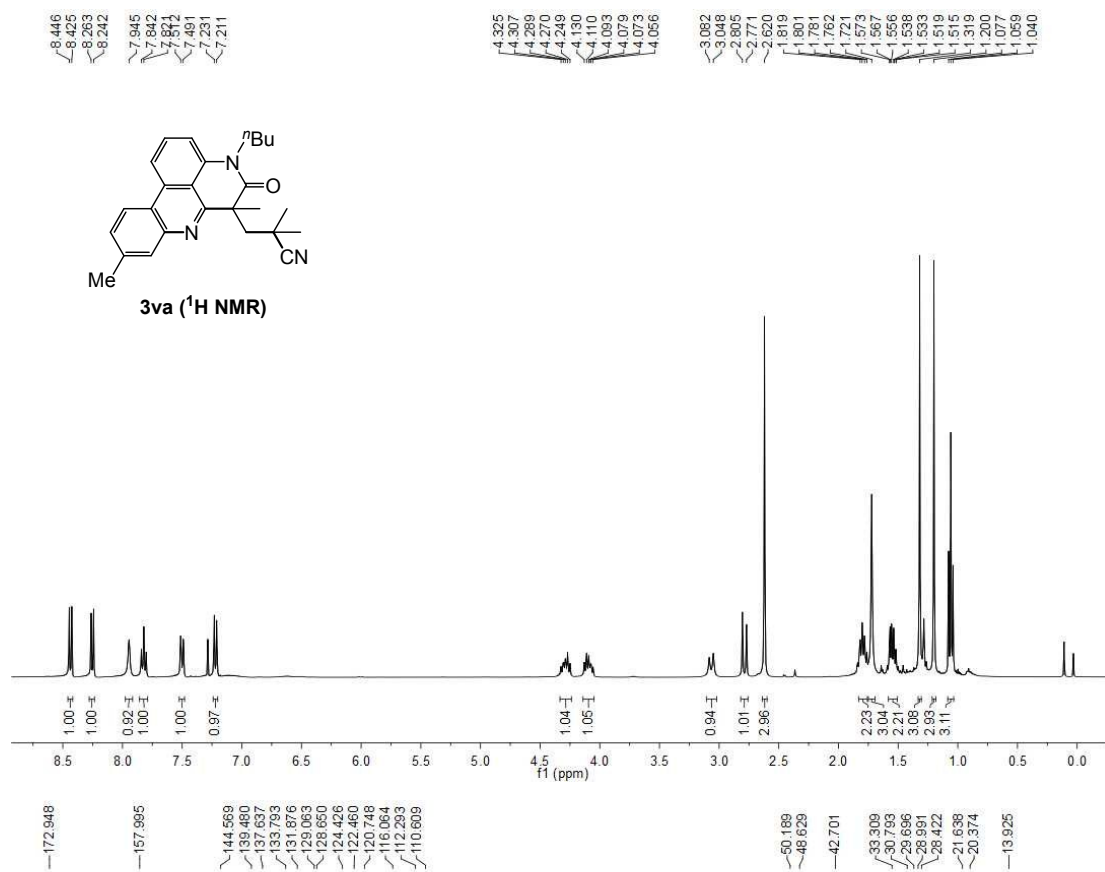


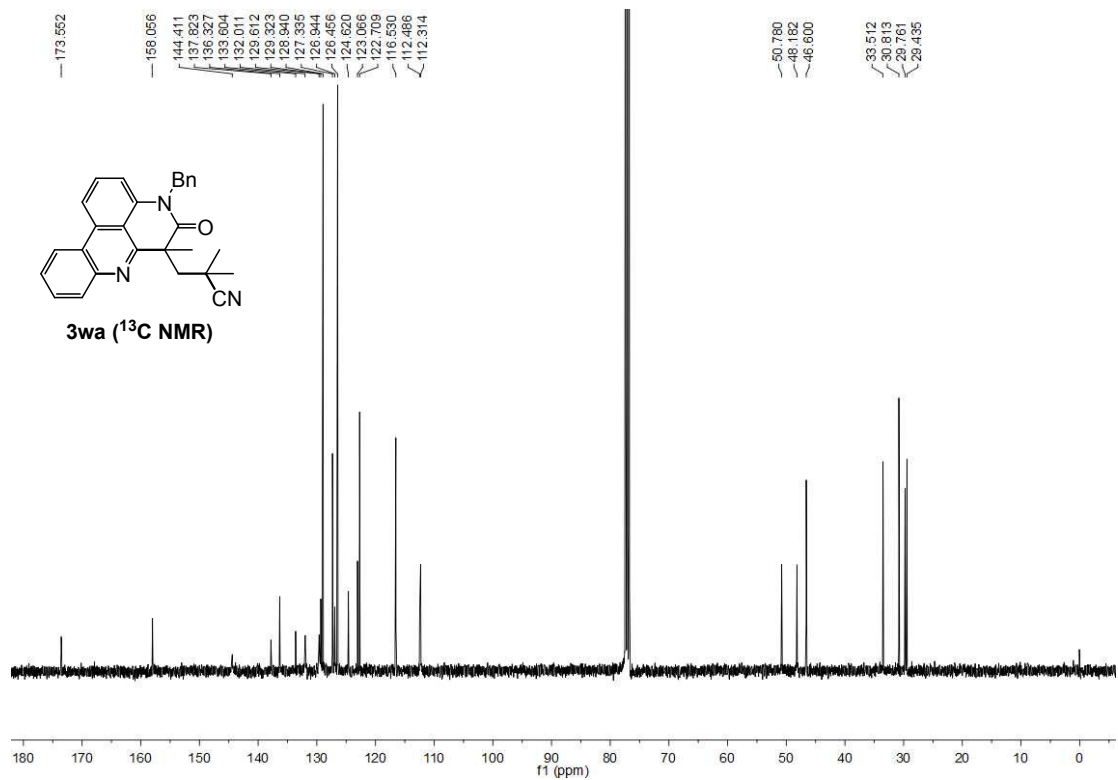
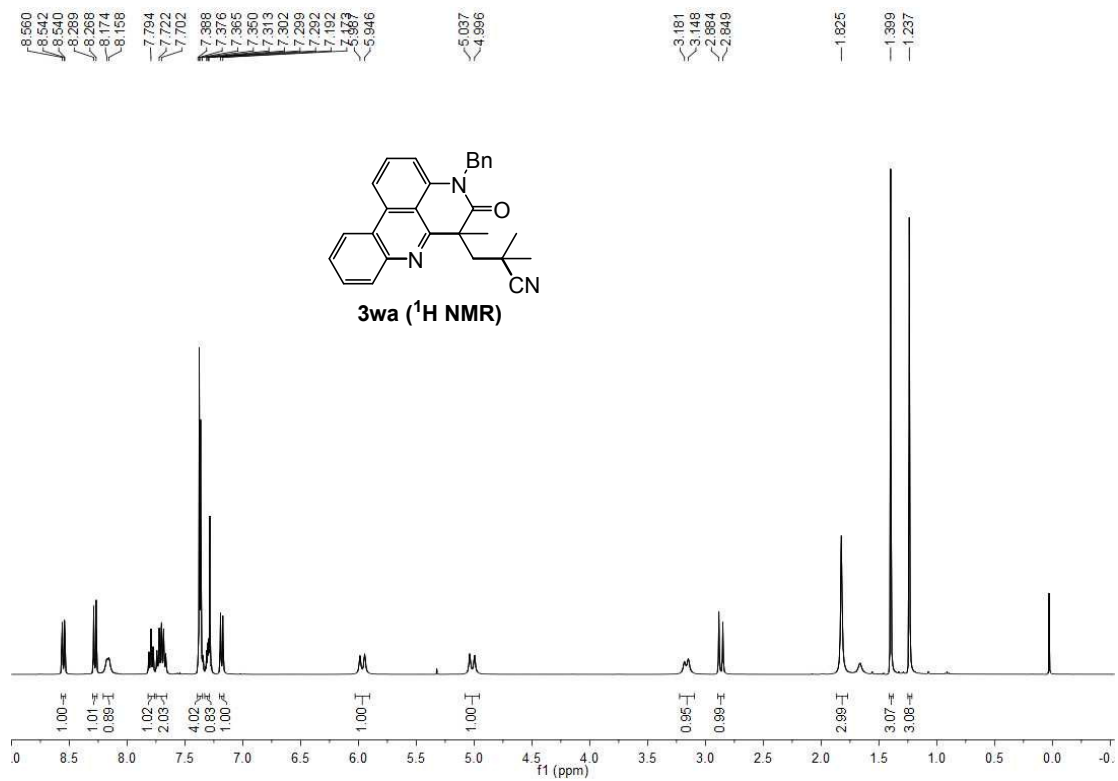


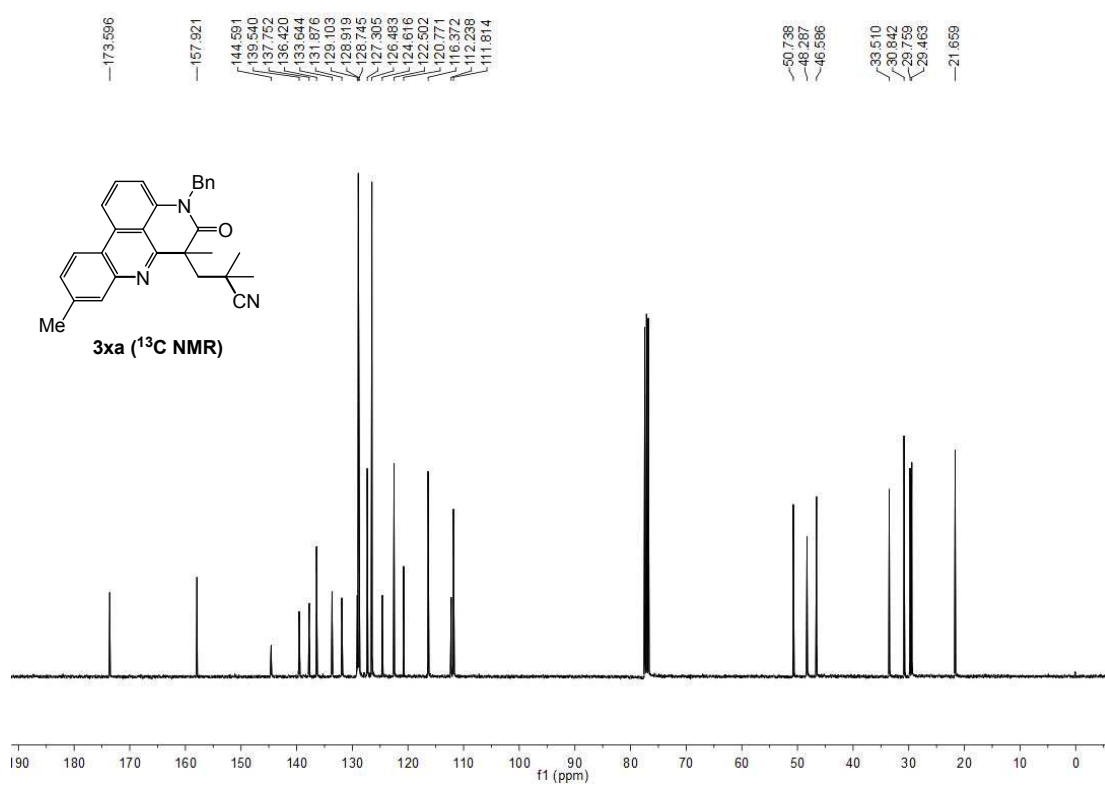
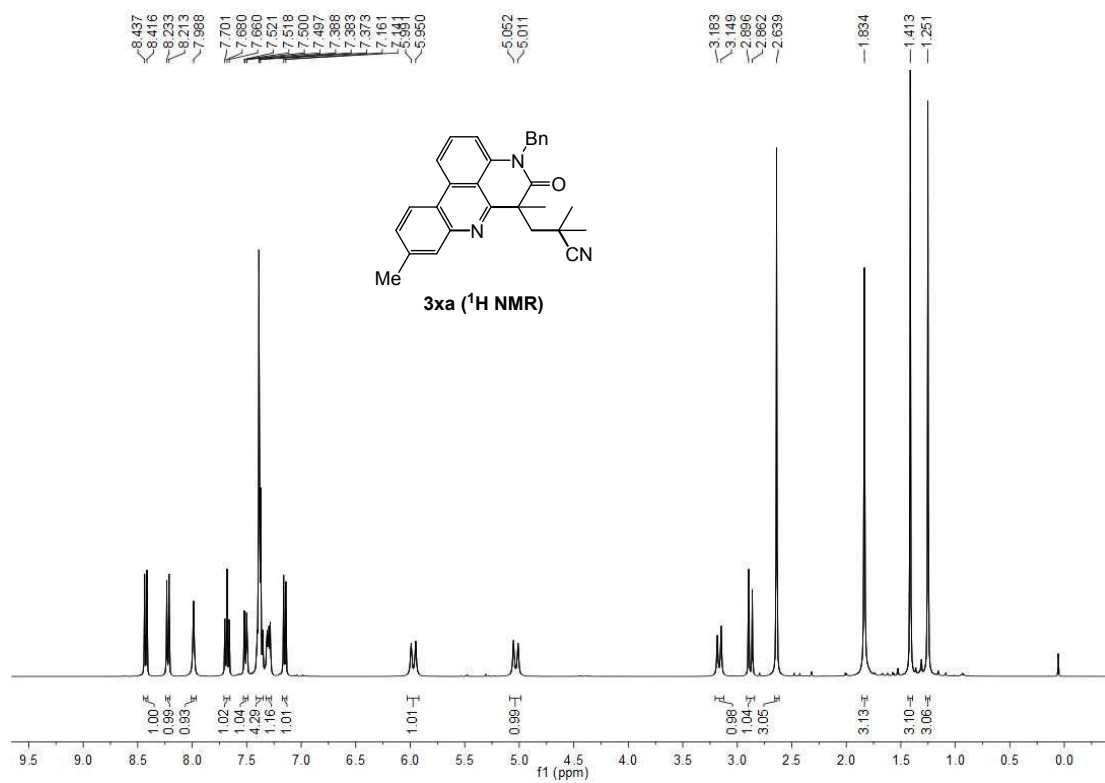


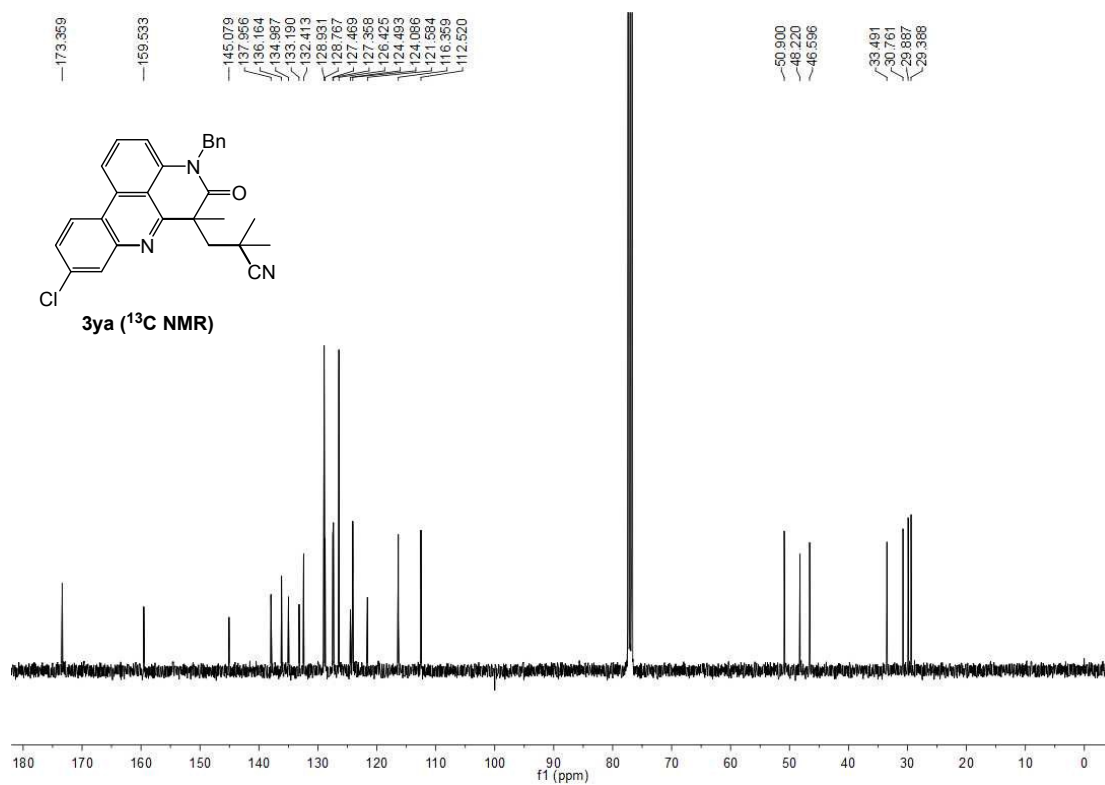
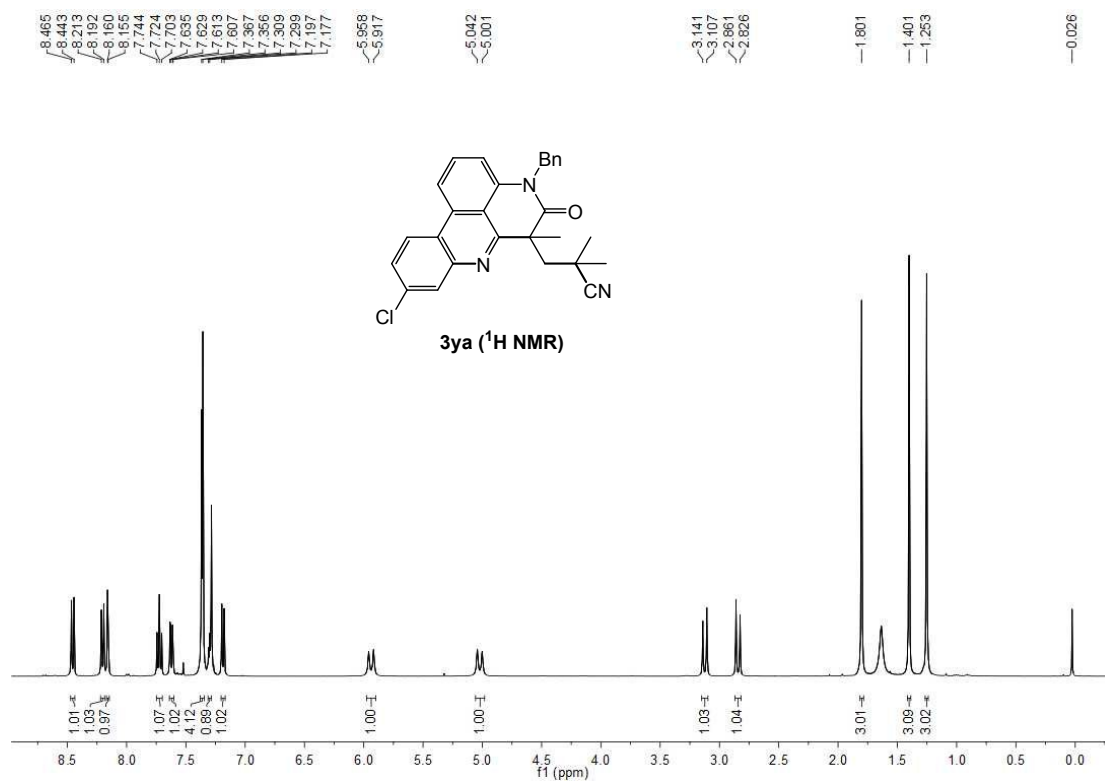


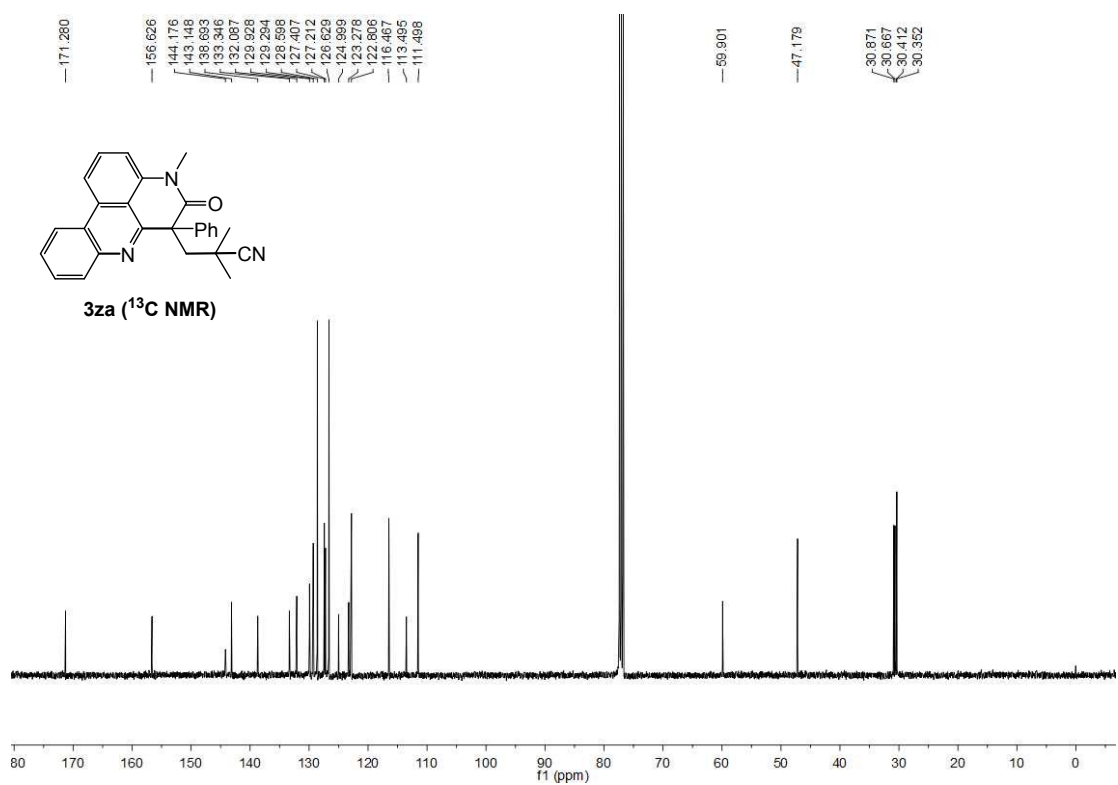
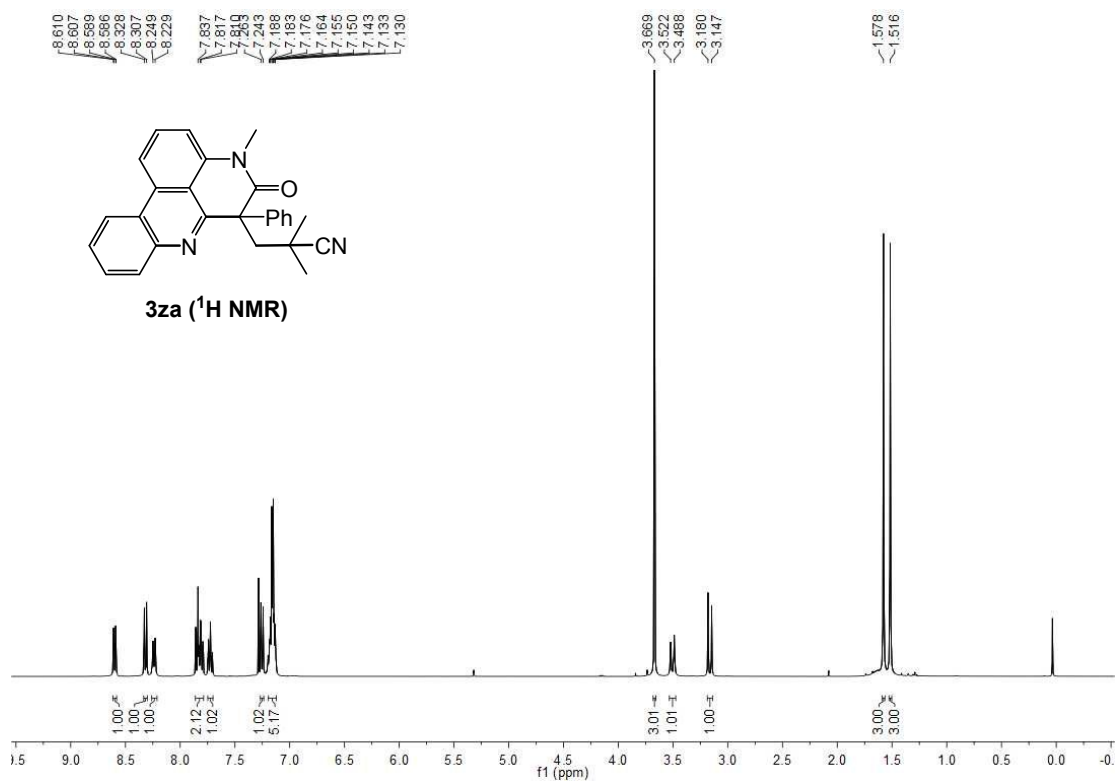


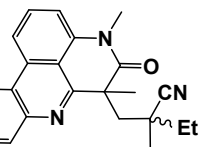
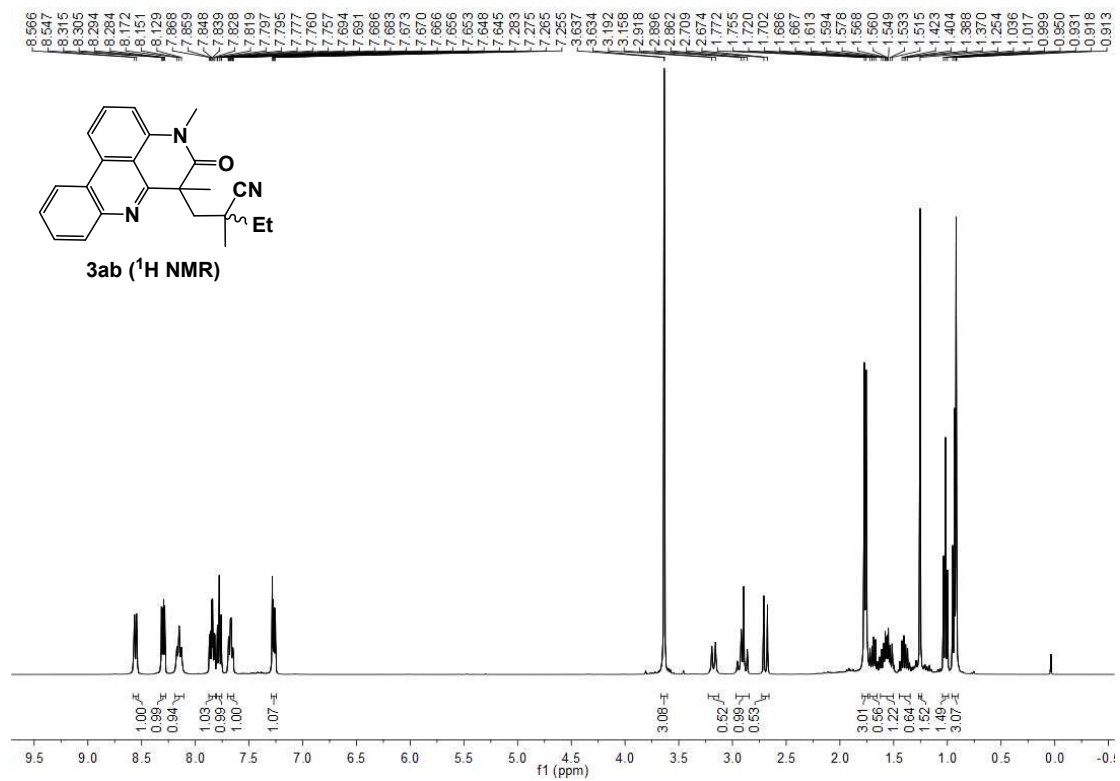




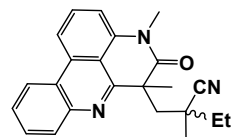




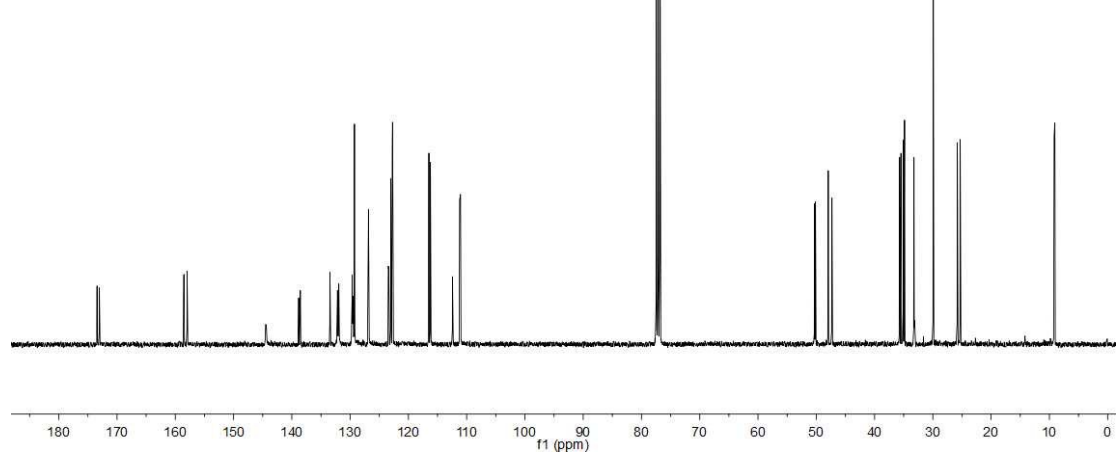


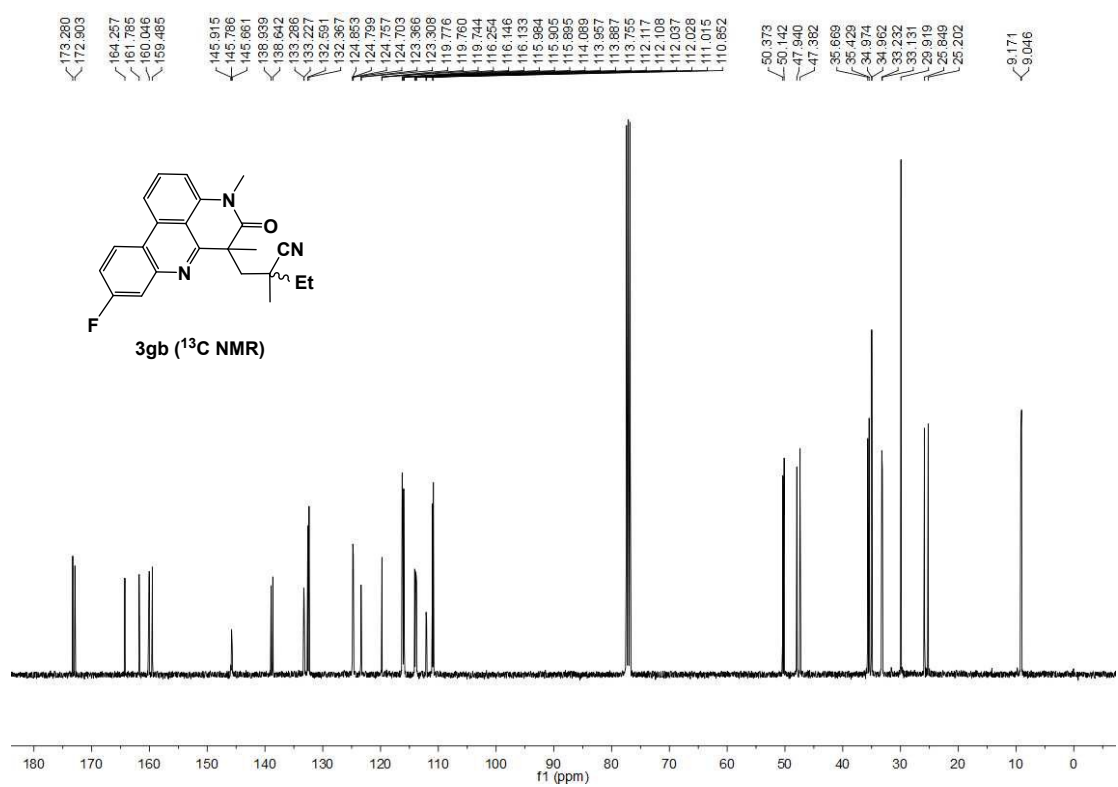
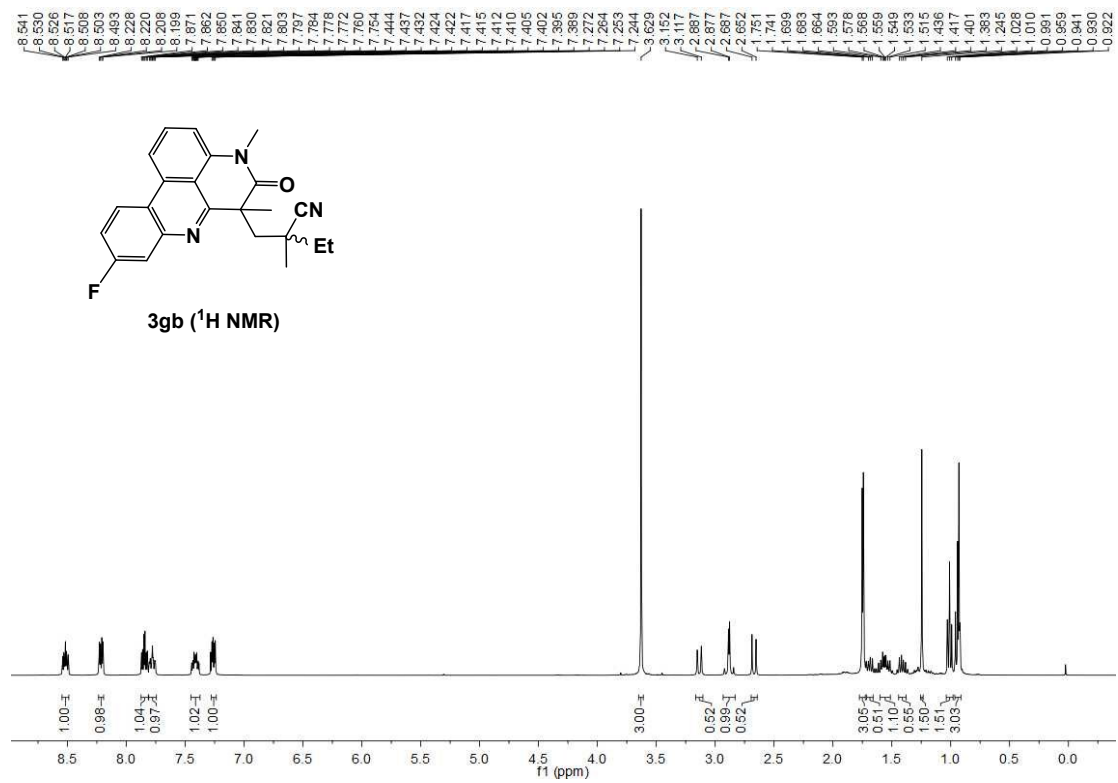


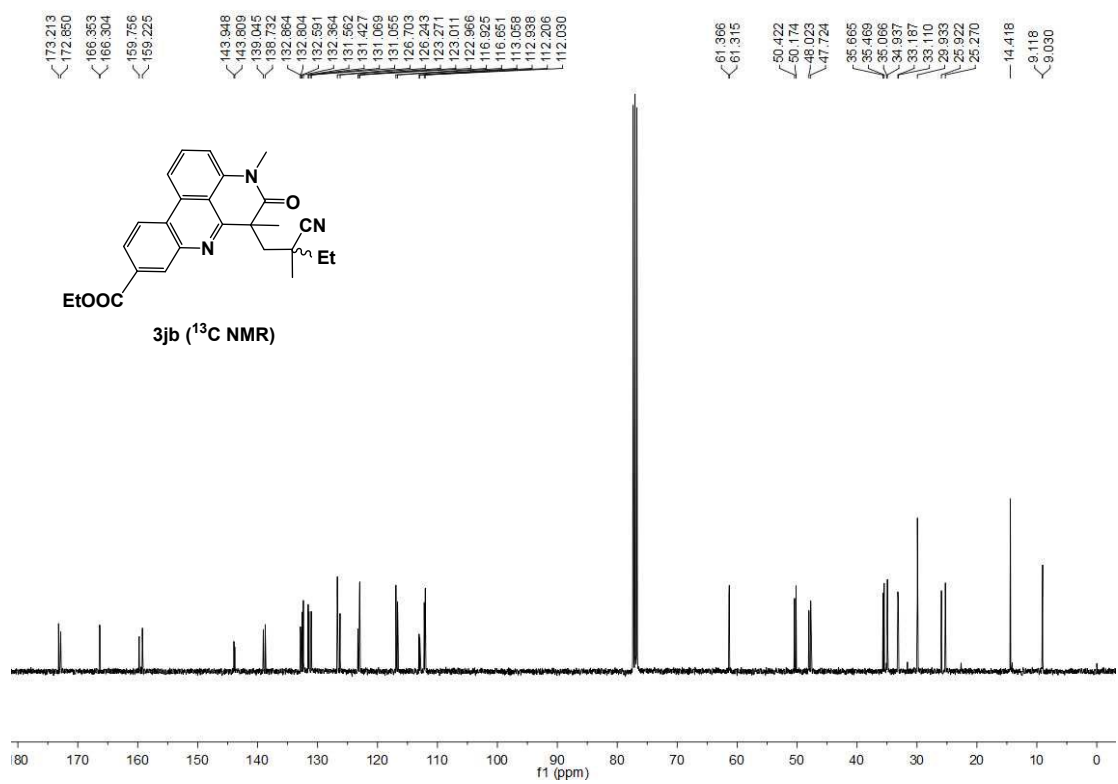
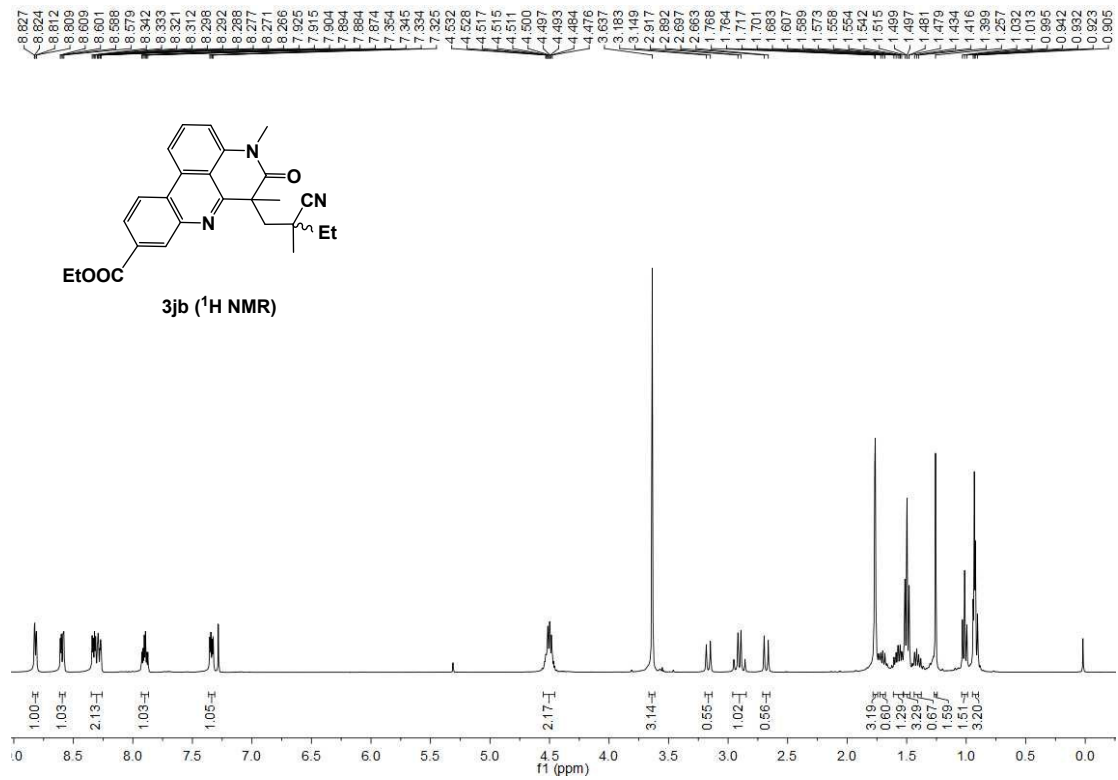
3ab (^1H NMR)

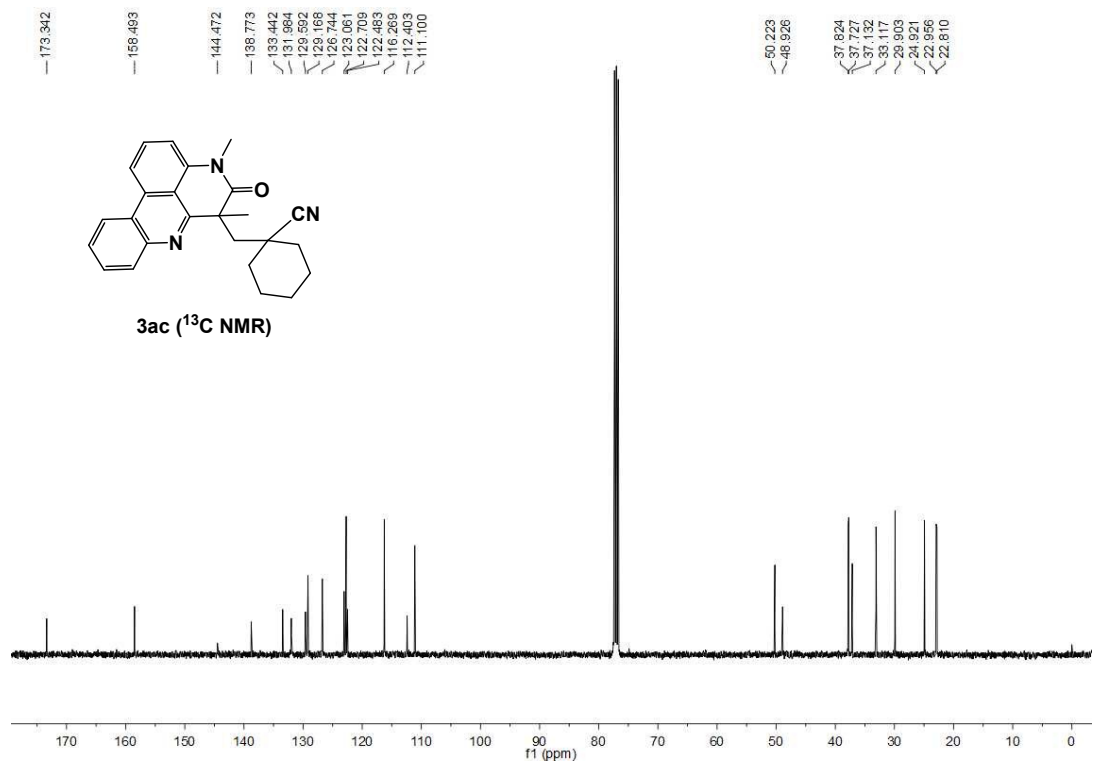
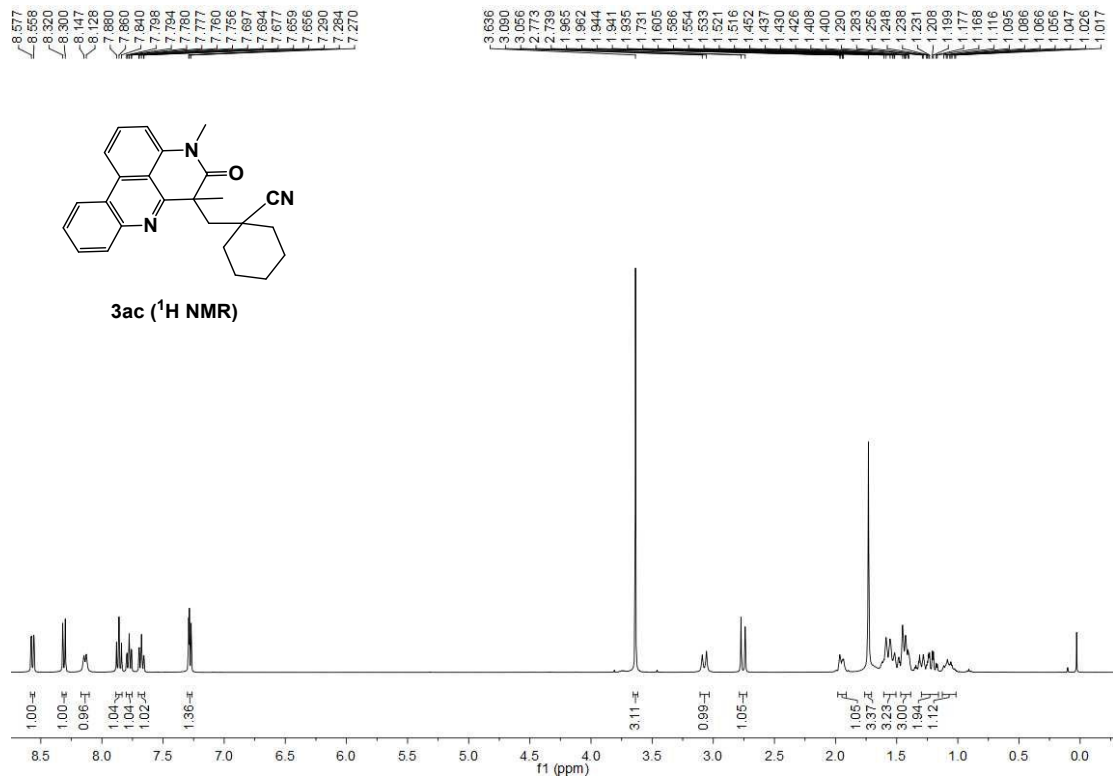


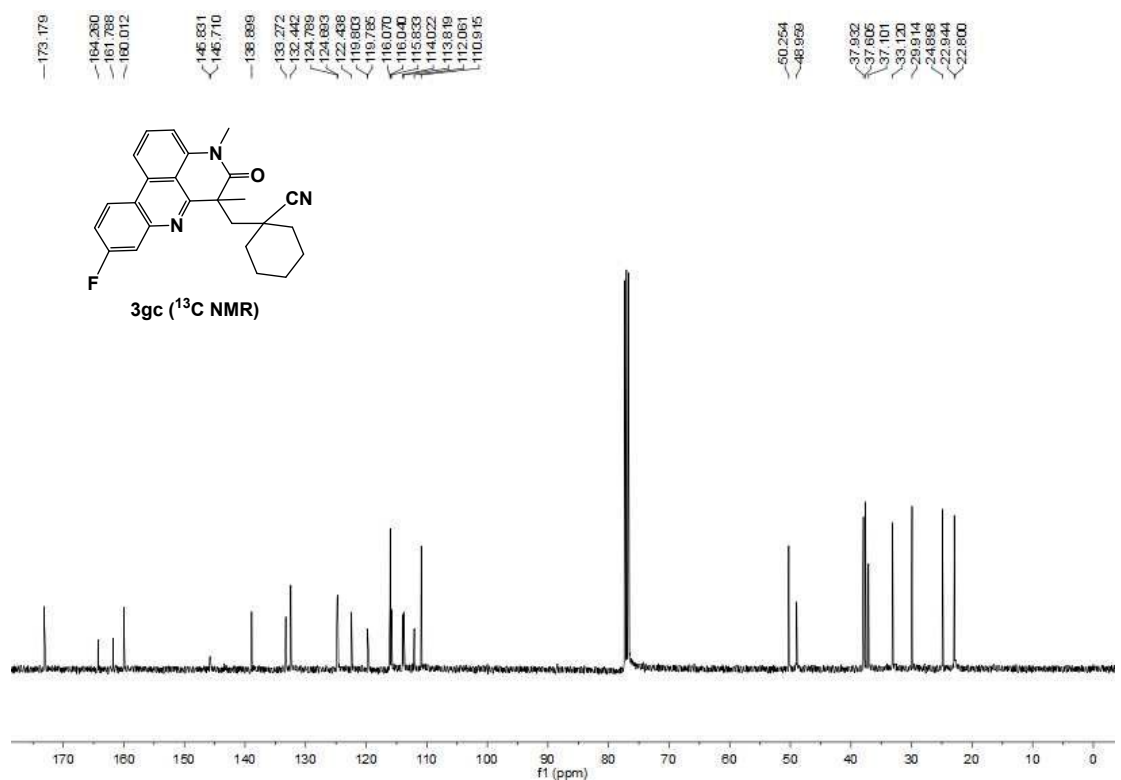
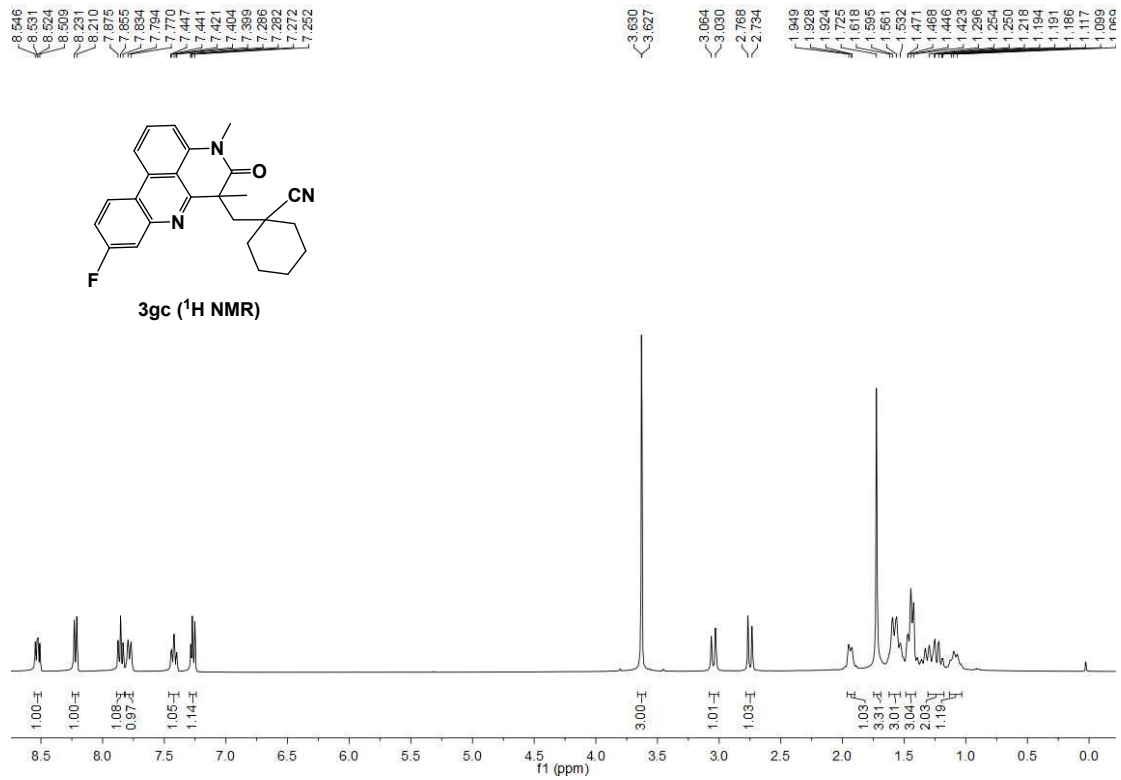
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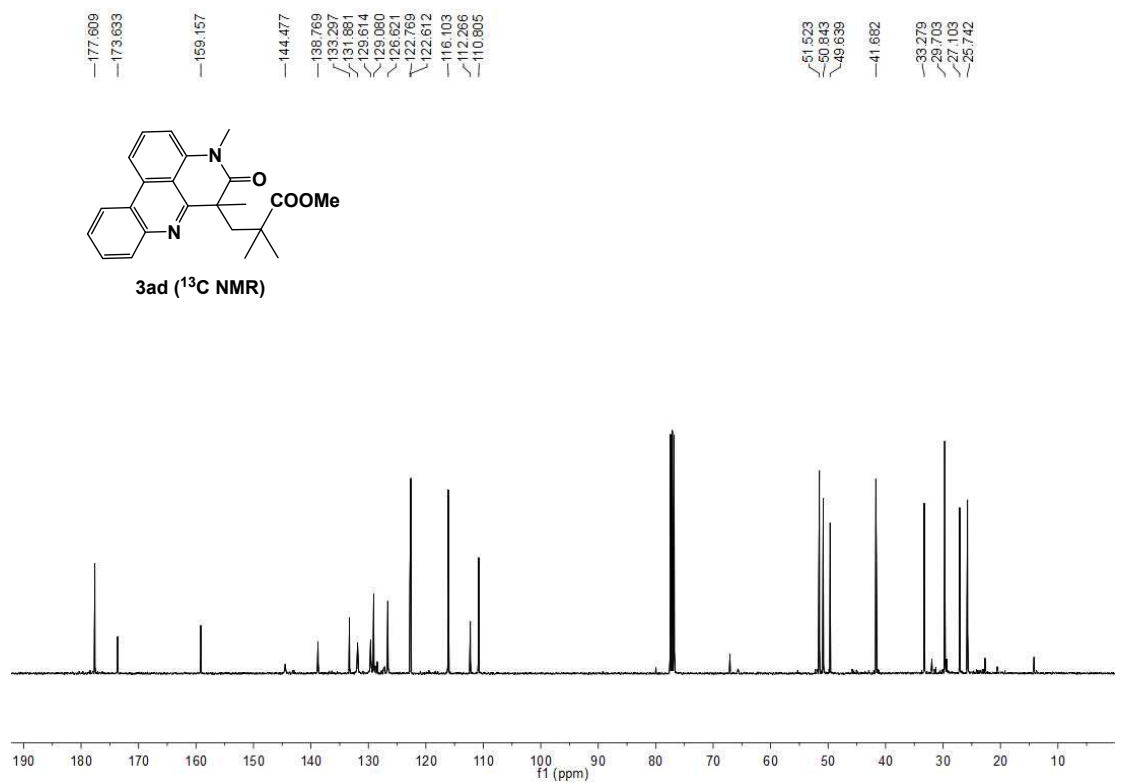
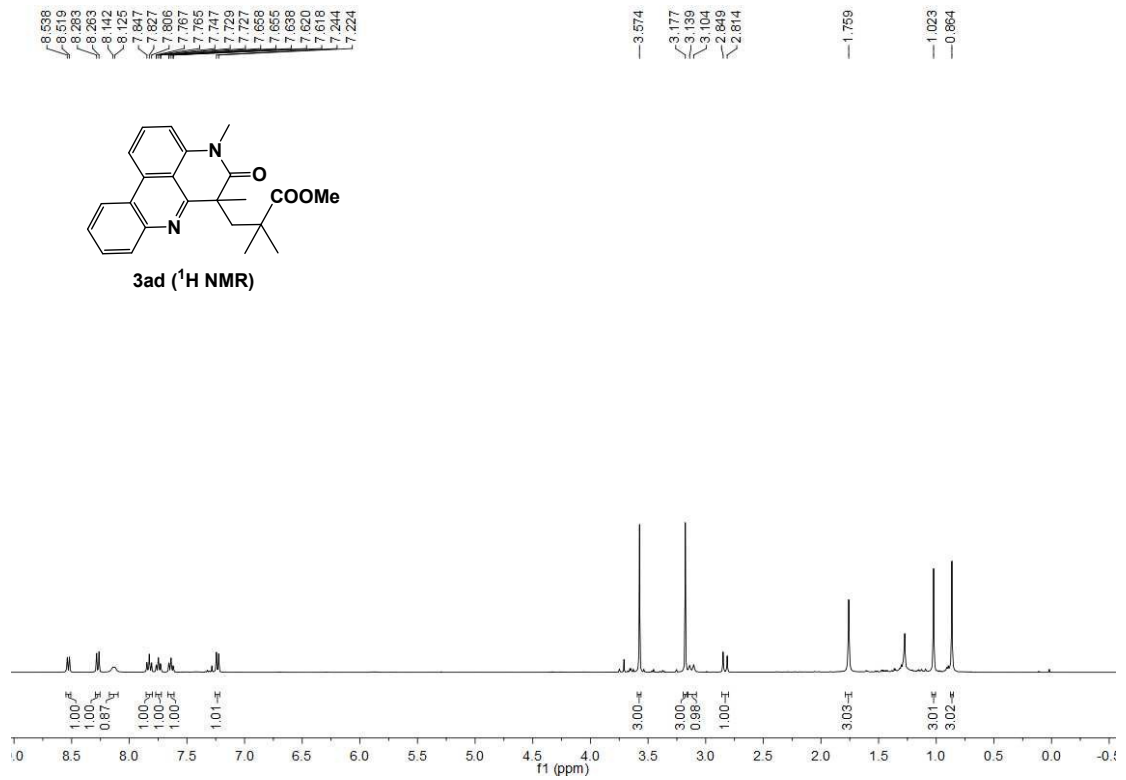






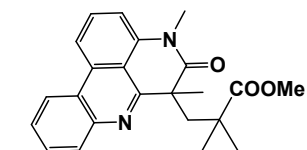




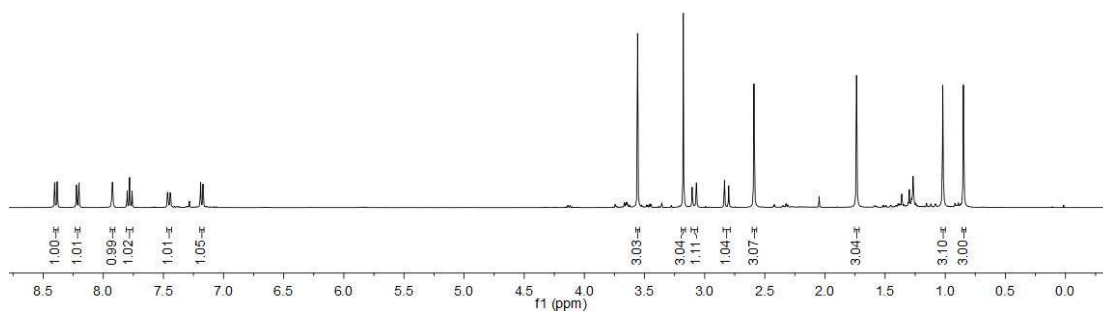


8.404
8.383
8.223
8.203
7.925
7.801
7.781
7.761
7.466
7.445
7.441
7.191
7.171

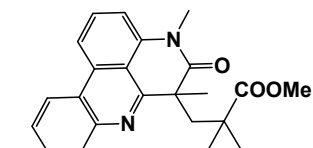
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2.835
2.800
2.590
1.737
1.020
0.849



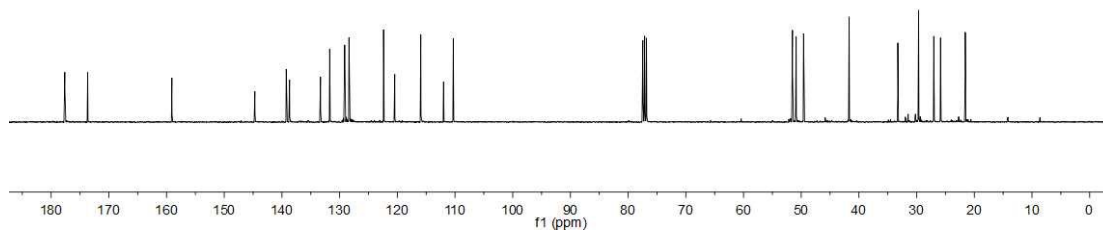
3a'd (¹H NMR)

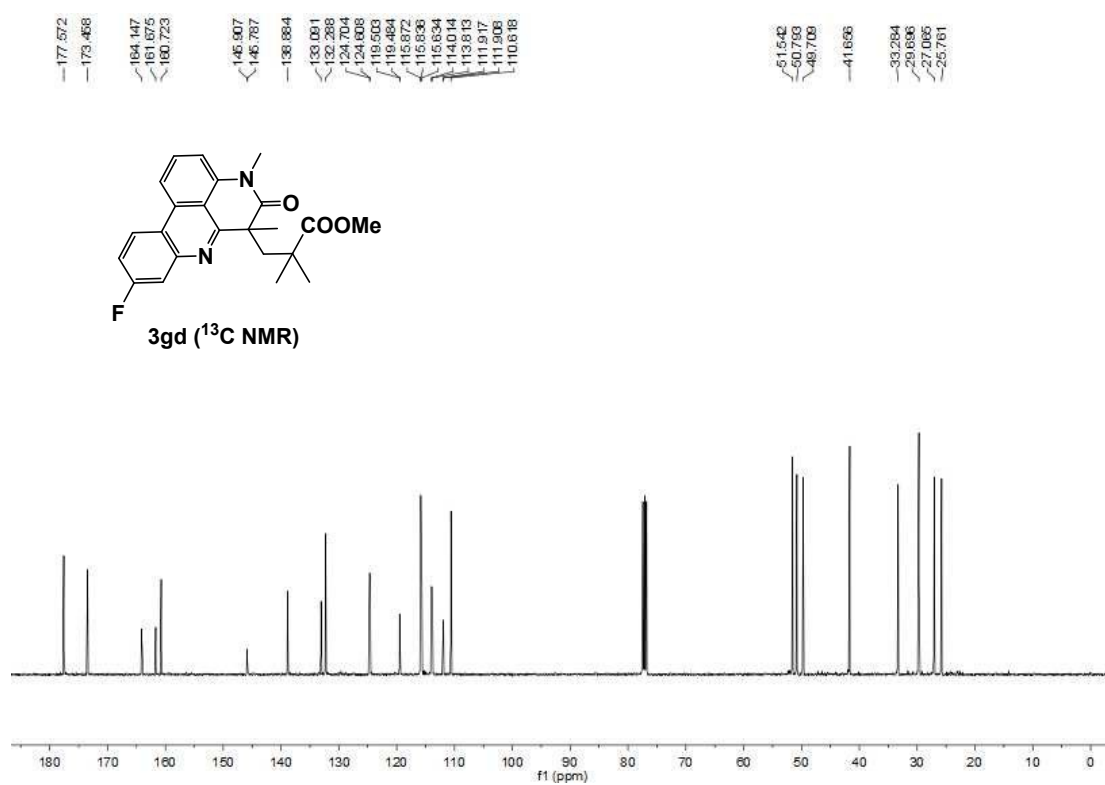
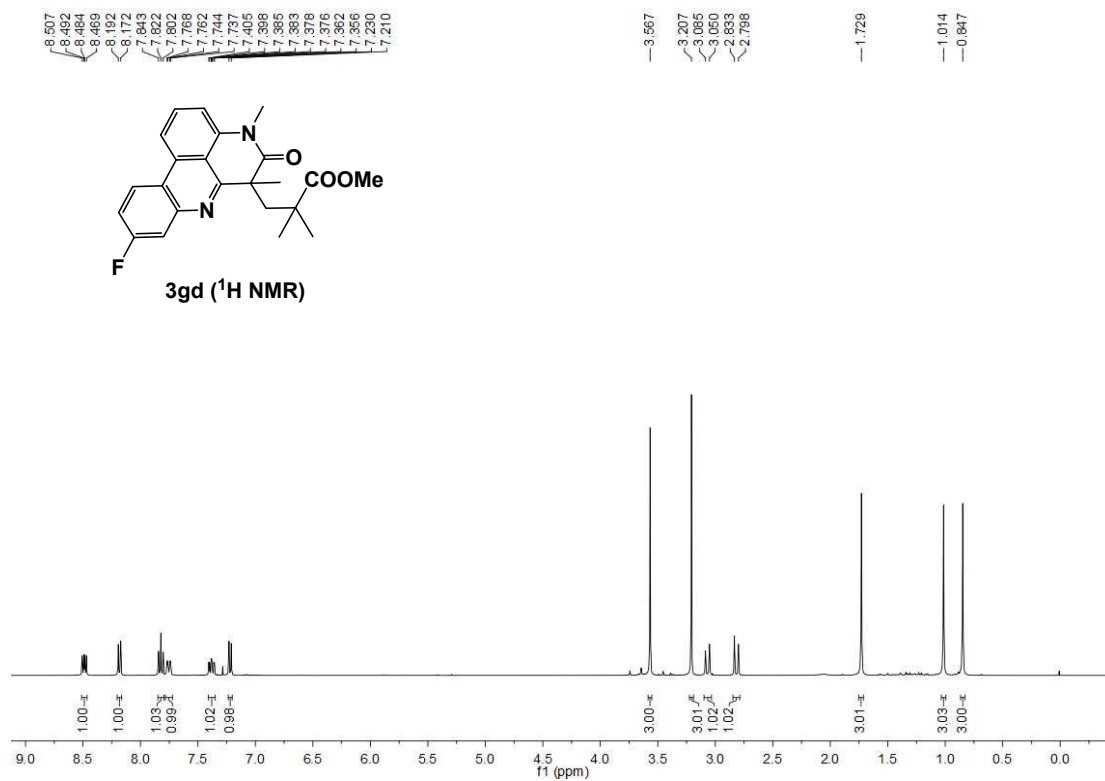


177.626
173.667
159.072
144.689
138.257
136.675
133.310
130.124
128.165
126.384
122.385
120.445
115.932
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21.558

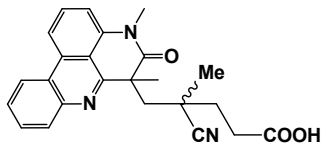


3a'd (¹³C NMR)

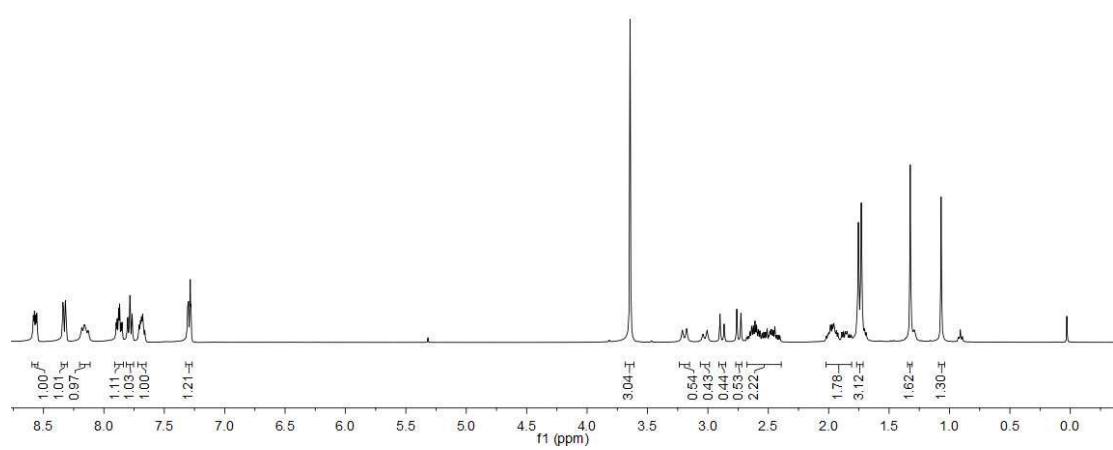




8.584, 8.575, 8.564, 8.564, 8.555, 8.339, 8.335, 8.319, 8.314, 8.182, 8.162, 8.130, 7.898, 7.890, 7.878, 7.870, 7.858, 7.850, 7.802, 7.785, 7.766, 7.707, 7.689, 7.679, 7.662, 7.506, 7.300, 7.285, 7.280, 3.644, 3.211, 3.176, 3.007, 2.900, 2.865, 2.761, 2.726, 2.651, 2.637, 2.624, 2.610, 2.597, 2.582, 2.569, 2.552, 2.538, 2.524, 2.510, 2.471, 2.471, 2.469, 2.448, 1.989, 1.986, 1.972, 1.964, 1.958, 1.953, 1.945, 1.936, 1.924, 1.891, 1.877, 1.862, 1.856, 1.849, 1.842, 1.754, 1.730, 1.325, 1.089

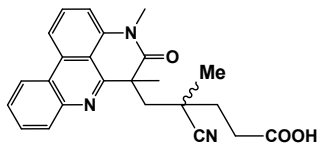


3ae (¹H NMR)

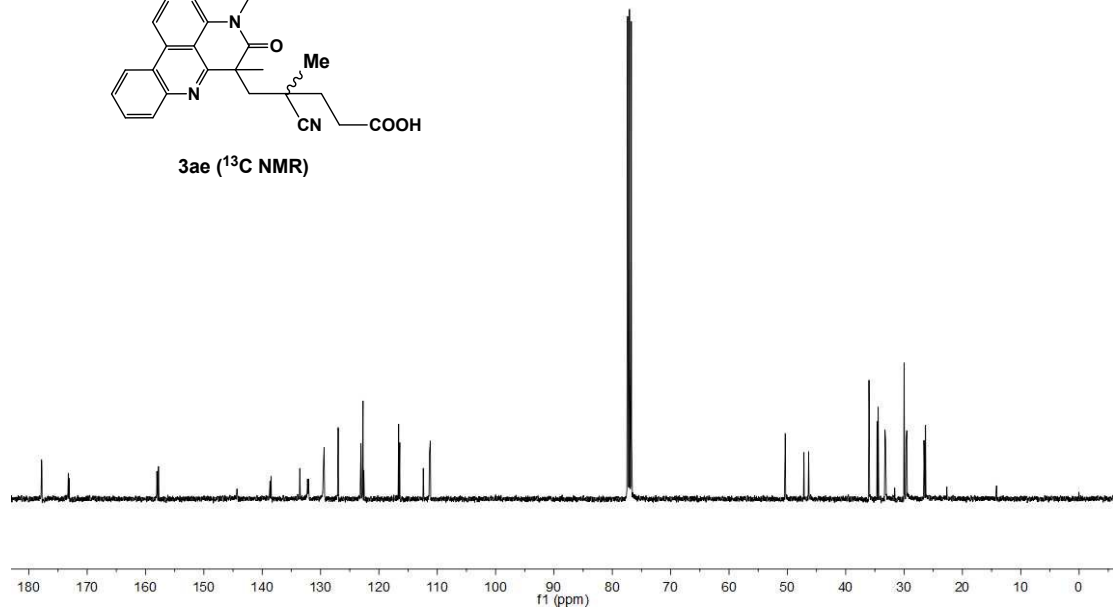


177.804, 177.751, 173.230, 173.076, 156.049, 157.779, 144.318, 136.088, 136.488, 133.560, 133.489, 132.246, 132.076, 129.528, 129.450, 129.393, 129.344, 126.982, 123.074, 122.761, 122.719, 122.594, 116.613, 116.418, 112.398, 112.329, 111.332, 111.183

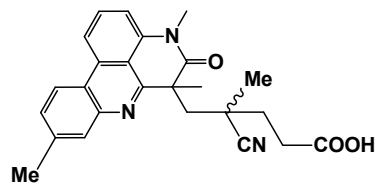
50.105, 49.169, 46.355, 46.355, 36.016, 34.630, 34.432, 33.268, 33.164, 29.997, 29.677, 29.537, 26.687, 26.322



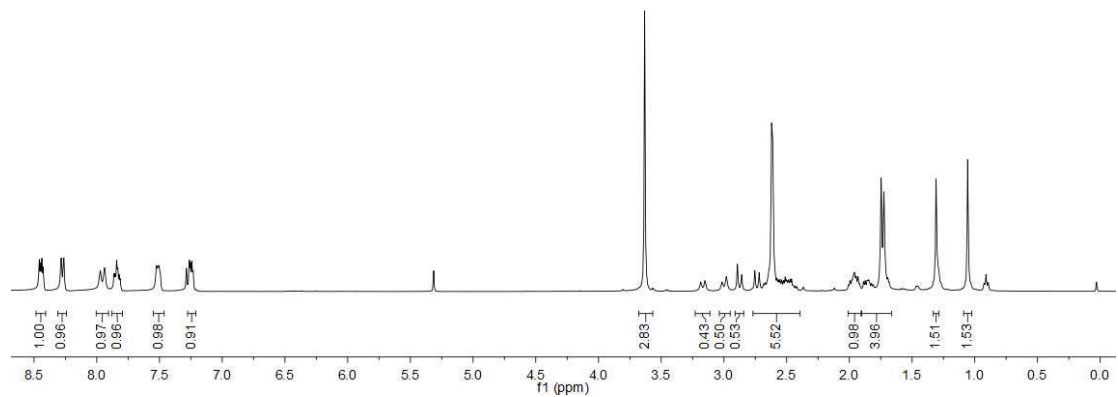
3ae (¹³C NMR)



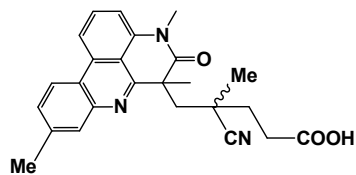
8.458, 8.448, 8.438, 8.427, 8.282, 8.262, 7.972, 7.938, 7.862, 7.853, 7.842, 7.654, 7.634, 7.612, 7.523, 7.514, 7.506, 7.487, 7.262, 7.253, 7.242, 7.233, 3.632, 3.185, 3.151, 3.015, 2.981, 2.893, 2.858, 2.754, 2.719, 2.683, 2.671, 2.641, 2.620, 2.611, 2.577, 2.564, 2.540, 2.520, 2.500, 2.512, 2.501, 2.488, 2.472, 2.460, 2.447, 2.432, 2.419, 1.984, 1.979, 1.966, 1.960, 1.945, 1.932, 1.920, 1.912, 1.872, 1.858, 1.852, 1.845, 1.824, 1.824, 1.747, 1.725, 1.695, 1.683, 1.309, 1.187



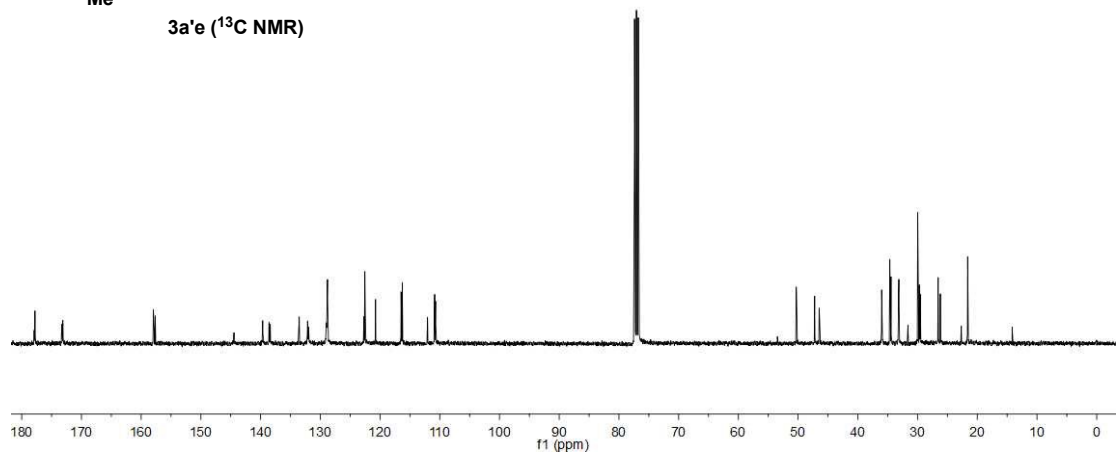
3a'e (¹H NMR)

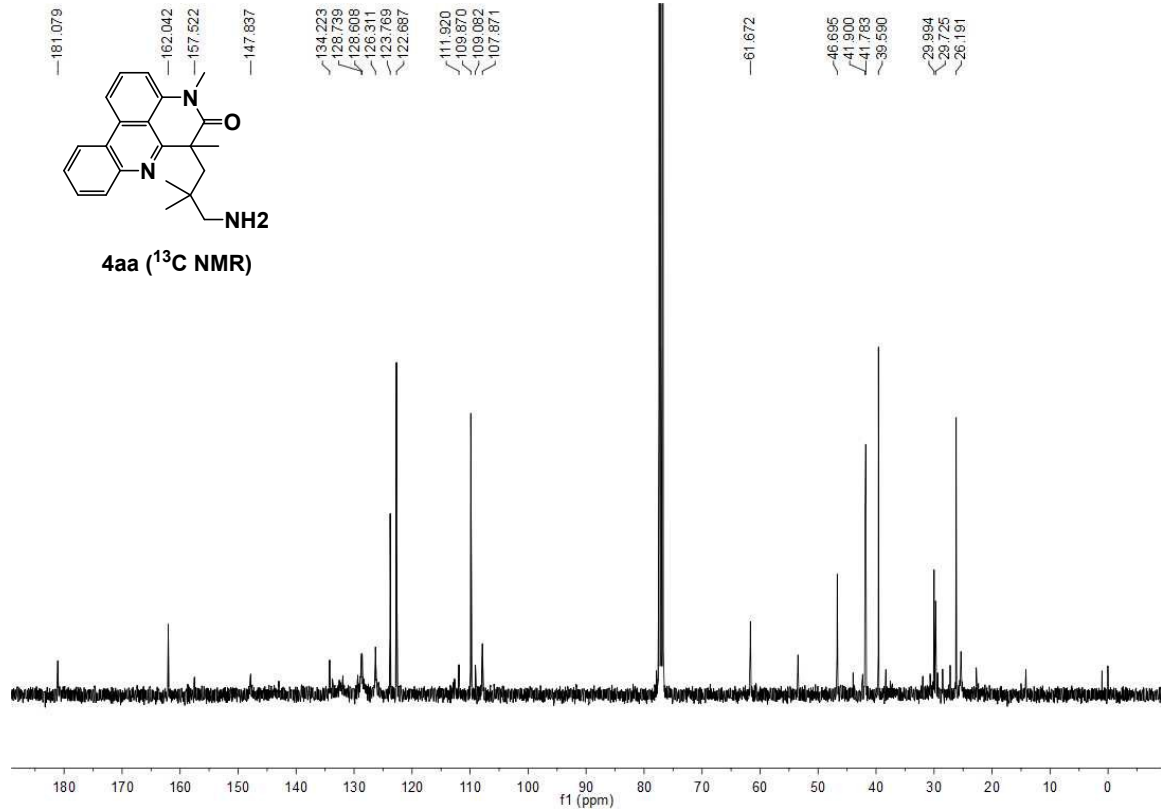
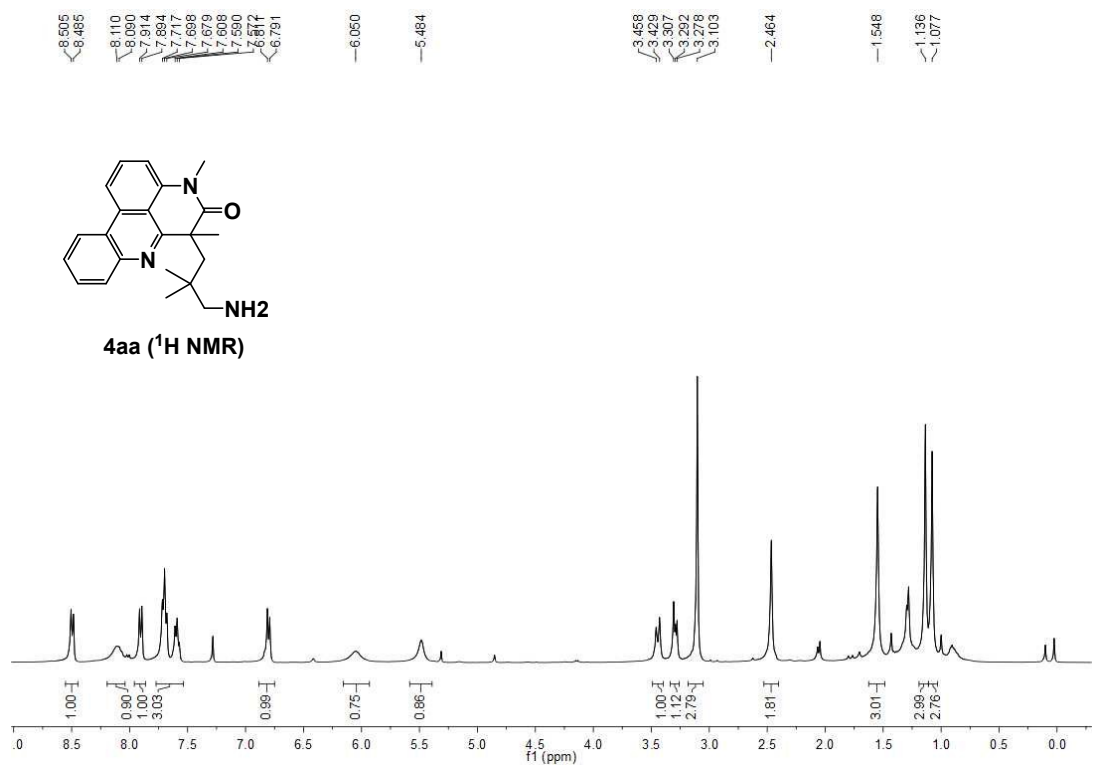


177.988, 177.780, 173.292, 173.114, 157.949, 157.636, 144.470, 138.643, 138.593, 138.386, 133.602, 133.529, 132.140, 131.962, 128.011, 128.910, 128.798, 122.707, 122.583, 122.543, 122.491, 120.755, 116.476, 116.272, 112.101, 112.044, 110.857, 110.700, 50.309, 50.253, 47.224, 46.470, 36.009, 35.947, 34.641, 34.441, 33.223, 33.129, 33.970, 29.696, 29.544, 26.549, 26.179, 21.608



3a'e (¹³C NMR)





6. Crystal structure and data of 3za

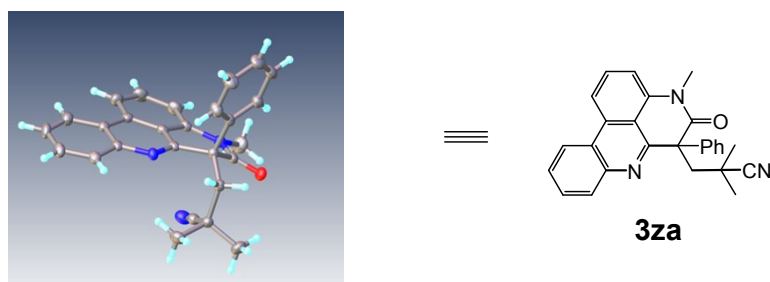


Figure S1 Crystal structures of **3za** (CCDC: 1572151).

Table S1 Crystal data and structure refinement for **3za**.

Compound	3za
Formula	C ₂₇ H ₂₃ N ₃ O
Crystal system	Tetragonal
Formula weight	405.48
Space group	I4 ₁ cd
a/Å	31.825(9)
b/Å	31.825(9)
c/Å	8.303(2)
α/°	90
β/°	90
γ/°	90
V/Å ³	8409.0(5)
Z	16
D _c /g cm ⁻³	1.281
μ/mm ⁻¹	0.08
F(000)	3424
Observed reflection/unique	22708 / 3034
R _{int}	0.049
Goodness-of-fit on F ²	1.126
R ₁ ^a , wR ₂ ^b [I > 2σ(I)]	0.0329,0.0924
R ₁ , wR ₂ (all data)	0.0381,0.0969

Table S2 Bond lengths (Å) and angles (°) for compound **3za**.

C1—C2	1.412(3)	C14—O1	1.222(3)
C1—C6	1.408(4)	C15—C16	1.524(3)
C1—N2	1.392(3)	C15—C17	1.558(4)
C15—C23	1.535(4)	C17—C18	1.388(4)
C2—C3	1.371(4)	C16—N2	1.304(3)
C3—C4	1.390(4)	C17—C22	1.388(4)
C4—C5	1.369(4)	C18—C19	1.389(4)
C5—C6	1.411(4)	C19—C20	1.372(4)

C6—C7	1.448(4)	C21—C22	1.382(4)
C7—C8	1.406(4)	C20—C21	1.390(4)
C7—C12	1.411(4)	C23—C24	1.571(4)
C8—C9	1.371(4)	C9—C10	1.393(4)
C10—C11	1.378(4)	C24—C25	1.531(4)
C11—C12	1.418(3)	C24—C26	1.542(4)
C11—N1	1.415(4)	C24—C27	1.482(4)
C12—C16	1.426(4)	C27—N3	1.147(4)
C13—N1	1.470(3)	C12—C16—C15	118.3(2)
C14—C15	1.532(3)	N2—C16—C12	124.1(2)
C14—N1	1.363(3)	N2—C16—C15	117.6(2)
C6—C1—C2	120.1(2)	C18—C17—C15	122.5(2)
N2—C1—C2	117.0(2)	C22—C17—C15	119.2(2)
N2—C1—C6	122.9(2)	C22—C17—C18	118.3(3)
C3—C2—C1	119.9(3)	C17—C18—C19	120.8(2)
C5—C4—C3	120.8(3)	C2—C3—C4	120.3(2)
C4—C5—C6	120.7(3)	C20—C19—C18	120.4(3)
C1—C6—C5	118.1(2)	C19—C20—C21	119.4(3)
C1—C6—C7	118.2(2)	C15—C23—C24	117.8(2)
C5—C6—C7	123.6(2)	C22—C21—C20	120.2(3)
C8—C7—C6	123.6(2)	C21—C22—C17	120.9(3)
C8—C7—C12	119.1(2)	C7—C12—C11	120.0(2)
C12—C7—C6	117.2(2)	C7—C12—C16	119.1(2)
C9—C8—C7	119.7(3)	C11—C12—C16	120.9(2)
C11—C10—C9	120.4(2)	N1—C14—C15	118.4(2)
C8—C9—C10	121.5(3)	C25—C24—C23	110.4(2)
C10—C11—C12	119.2(2)	C25—C24—C26	109.7(3)
C10—C11—N1	121.4(2)	C26—C24—C23	110.9(2)
N1—C11—C12	119.4(2)	C27—C24—C23	111.3(2)
O1—C14—C15	119.5(2)	C27—C24—C25	107.1(2)
O1—C14—N1	121.9(2)	C27—C24—C26	107.3(2)
C14—C15—C17	106.6(2)	C23—C15—C17	108.96(19)
C14—C15—C23	109.0(2)	N3—C27—C24	178.6(3)
C16—C15—C14	112.86(19)	C11—N1—C13	118.2(2)
C16—C15—C17	107.8(2)	C14—N1—C11	123.57(19)
C16—C15—C23	111.4(2)	C14—N1—C13	117.6(2)
C16—N2—C1	118.0(2)		