

Supporting Information

A Microwave-assisted, two-step synthesis of indolo[3,2-c]quinolines via Fisher Indolization and Oxidative Aromatization

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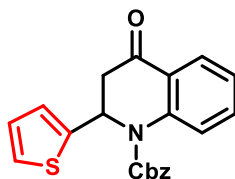
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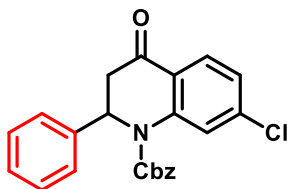
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CHARACTERIZATION

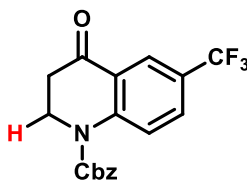
Data of known molecules are reported; **4a**¹, **4c**¹, **4e**², **4f**³, **4h**⁴, **5a**⁵, **5c**⁵, **5i**⁶, **5f**⁷, **5k**⁸, **6a**⁹, **6b**⁹, **7a**⁹



Benzyl 4-oxo-2-(thiophen-2-yl)-3,4-dihydroquinoline-1(2H)-carboxylate (4b): dark brown solid; **Yield:** 81%; **m.p.** 136-137 °C; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3068, 2964, 1712, 1689, 1596, 1479; **¹H NMR** (400 MHz, Chloroform-*d*) 7.96 (dd, *J*=7.86, 1.64 Hz, 1H), 7.81 (d, *J*=8.32 Hz, 1H), 7.51-7.36 (m, 6H), 7.16-7.12 (m, 2H), 6.83-6.80 (m, 2H), 6.41 (dd, *J*=5.64, 2.00 Hz, 1H), 5.41 (d, *J*=11.68 Hz, 1H), 5.36 (d, *J*=11.68 Hz, 1H), 3.34 (dd, *J*=5.66, 17.58 Hz, 1H), 3.24 (dd, *J*=17.58, 2.18 Hz, 1H); **¹³C NMR** (100 MHz, Chloroform-*d*₃) 192.16, 153.67, 142.23, 141.00, 135.48, 134.62, 128.73, 128.55, 128.23, 126.95, 126.70, 125.96, 125.55, 124.78, 124.44, 124.40, 68.66, 53.62, 43.43; **HRMS** (ESI) *m/z* calculated for C₂₁H₁₈NO₃S (M+H)⁺: 364.1007, found: 364.1021.

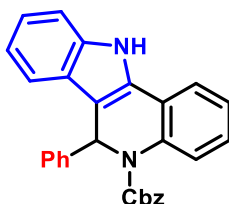


Benzyl 7-chloro-4-oxo-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (4d): white solid; **Yield:** 78%; **m.p.** 128-129 °C; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3062, 2960, 1702, 1683, 1594, 1563; **¹H NMR** (400 MHz, Chloroform-*d*) 7.93 (s, 1H), 7.85 (d, *J*= 8.54 Hz, 1H), 7.44-7.37 (m, 5H), 7.27-7.16 (m, 5H), 7.08 (dd, *J*=8.46, 1.92 Hz, 1H), 6.24 (dd, *J*=4.88, 2.68, 1H), 5.43 (d, *J*= 12.36 Hz, 1H), 5.35 (d, *J*= 12.36 Hz, 1H), 3.30 (m, 2H); **¹³C NMR** (100 MHz, Chloroform-*d*) 191.64, 153.97, 142.32, 140.89, 137.67, 135.28, 128.79, 128.65, 128.23, 127.82, 126, 49, 124.68, 124.22, 123.30, 68.84, 56.26, 42.07; **HRMS** (ESI) *m/z* calculated for C₂₃H₁₉ClNO₃ (M+H)⁺: 392.1053, found: 392.1066.

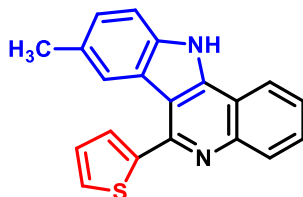


Benzyl 4-oxo-6-(trifluoromethyl)-3,4-dihydroquinoline-1(2H)-carboxylate (4g): slightly yellowish solid; **Yield:** 39%; **m.p.** 94-95 °C; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3037, 2960, 1713, 1683, 1621, 1576;

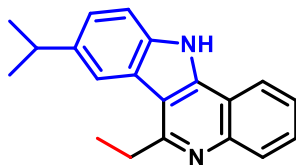
¹H NMR (400 MHz, Chloroform-*d*) 8.20 (d, *J*=2.40 Hz, 1H), 7.95 (d, *J*=8.74 Hz, 1H), 7.64 (dd, *J*=8.74, 2.40 Hz, 1H), 7.35-7.27 (m, 5H), 5.23 (s, 2H), 4.19 (t, *J*=6.40, 2H), 2.75 (t, *J*=6.40 Hz, 2H); **¹³C NMR** (100 MHz, Chloroform-*d*) 192.35, 153.40, 146.16, 135.25, 130.50, 128.80, 128.73, 128.41, 126.21, 125.03, 124.53, 123.86, 68.76, 44.44, 38.48 ; **HRMS** (ESI) *m/z* calculated for C₁₈H₁₅F₃NO₃ (M+H)⁺: 350.1004, found: 350.1001.



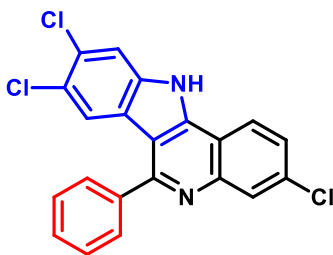
Benzyl 6-phenyl-6,11-dihydro-5H-indolo[3,2-*c*]quinoline-5-carboxylate (5b): white solid; **Yield**: 94%; **m.p.** 146-147 °C ; **IR** (ν_{max} /cm⁻¹) 3342, 3052, 2953, 1703, 1685, 1510; **¹H NMR** (400 MHz, DMSO-*d*₆) 11.83 (brs, 1H), 7.75-7.71 (m, 1H), 7.64-7.56 (m, 1H), 7.46 (d, *J*=8.00 Hz, 1H), 7.43-7.29 (m, 5H), 7.24-7.12 (m, 8H), 7.05 (m, 1H), 7.01 (s, 1H), 5.28 (s, 2H); **¹³C NMR** (100 MHz, DMSO-*d*₆) 154.59, 141.30, 137.65, 136.62, 134.30, 130.40, 128.93, 128.82, 128.55, 128.38, 127.82, 127.34, 126.84, 126.48, 125.62, 125.35, 122.88, 122.73, 121.99, 120.33, 118.84, 112.23, 112.10, 68.07, 54.96 ; **HRMS** (ESI) *m/z* calculated for C₂₉H₂₃N₂O₂ (M+H)⁺: 431.1760, found: 431.1772.



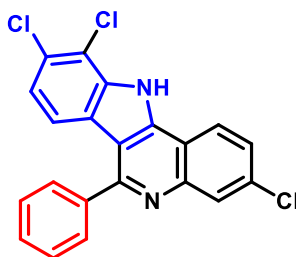
8-methyl-6-(thiophen-2-yl)-11H-indolo[3,2-*c*]quinoline (5d): yellow solid; **Yield**: 55%; **m.p.** 156-157 °C; **IR** (ν_{max} /cm⁻¹) 3405, 2970, 1751, 1662, 1558, 1458; **¹H NMR** (400 MHz, DMSO-*d*₆) 12.81 (s, 1H), 8.52 (m, 1H), 8.07 (m, 1H), 7.88-7.82 (m, 3H), 7.74 (m, 1H), 7.70-7.62 (m, 2H), 7.37-7.30 (m, 2H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, DMSO-*d*₆) 149.26, 145.00, 143.97, 141.89, 137.84, 129.56, 129.50, 129.09, 128.80, 128.80, 127.94, 127.47, 126.13, 122.36, 122.08, 121.36, 116.73, 112.19, 111.73, 21.97; **HRMS** (ESI) *m/z* calculated for C₂₀H₁₅N₂S (M+H)⁺: 315.0956, found: 315.09585.



6-ethyl-8-isopropyl-11H-indolo[3,2-c]quinoline (5e): white solid; **Yield:** 48%; **m.p.** 122-123 °C; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3420, 3053, 2958, 1625, 1590, 1563; **$^1\text{H NMR}$** (400 MHz, DMSO- d_6) 12.60 (s, 1H), 8.47 (dd, $J=8.40, 1.20$ Hz, 1H), 8.05 (d, $J=8.40$ Hz, 1H), 7.99 (s, 1H), 7.71-7.59 (m, 3H), 7.41 (dd, $J=8.40, 1.20$ Hz, 1H), 3.45 (q, $J=7.48$ Hz, 2H), 3.14 (septet, $J=6.84$ Hz, 1H), 1.49 (t, $J=7.48$ Hz, 3H), 1.34 (d, $J=6.84$ Hz, 6H); **$^{13}\text{C NMR}$** (100 MHz, DMSO- d_6) 159.35, 145.26, 141.37, 140.80, 137.80, 129.31, 128.32, 125.24, 124.16, 122.27, 122.21, 119.17, 116.82, 112.62, 112.10, 34.21, 30.77, 25.12, 12.59; **HRMS** (ESI) m/z calculated for $\text{C}_{20}\text{H}_{21}\text{N}_2$ ($\text{M}+\text{H}$) $^+$: 289.1705, found: 289.1706.

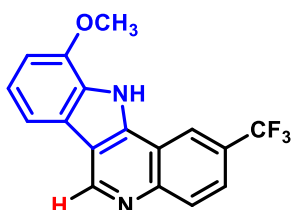


3,8,9-trichloro-6-phenyl-11H-indolo[3,2-c]quinoline (5g): slightly yellow solid; **Yield:** 44%; **m.p.** >300 °C; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3425, 3063, 2921, 1620, 1558, 1508; **$^1\text{H NMR}$** (400 MHz, DMSO- d_6) 13.1 (brs, 1H), 8.55 (d, $J=9.14$ Hz, 1H), 8.16 (d, $J=1.90$ Hz, 1H), 7.92 (s, 1H), 7.81-7.75 (m, 3H), 7.68-7.65 (m, 3H), 7.51 (s, 1H); **$^{13}\text{C NMR}$** (100 MHz, DMSO- d_6) 157.67, 145.36, 143.97, 142.80, 139.58, 134.23, 129.43, 128.76, 128.18, 127.52, 126.77, 125.40, 124.71, 124.41, 121.48, 114.45, 112.70, 112.35, 111.79; **HRMS** (ESI) m/z calculated for $\text{C}_{21}\text{H}_{12}\text{Cl}_3\text{N}_2$ ($\text{M}+\text{H}$) $^+$: 397.0066, found: 397.0073.

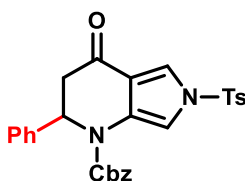


3,9,10-trichloro-6-phenyl-11H-indolo[3,2-c]quinoline (5h): slightly yellow solid; **Yield:** 25%; **m.p.** >300 °C; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3415, 3085, 2923, 1620, 1558, 1485; **$^1\text{H NMR}$** (400 MHz, DMSO-

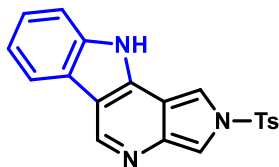
*d*₆) 13.44 (brs, 1H), 8.60 (d, *J*=8.86 Hz, 1H), 8.14 (d, *J*=2.22 Hz, 1H), 7.78 (dd, *J*=8.86, 2.14 Hz, 1H), 7.74 (d, *J*=8.68 Hz, 1H), 7.68 (d, *J*=8.68 Hz, 1H), 7.60-7.57 (m, 2H), 7.50-7.47 (m, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) 157.71, 145.42, 144.00, 142.89, 139.66, 134.26, 129.44, 129.18, 128.79, 128.21, 127.56, 126.84, 125.40, 124.73, 124.49, 121.54, 114.53, 112.42, 111.83; HRMS (ESI) *m/z* calculated for C₂₁H₁₂Cl₃N₂ (M+H)⁺: 397.0066, found: 397.0075.



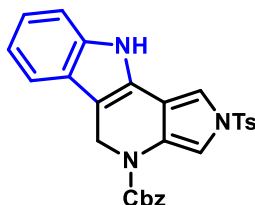
10-methoxy-2-(trifluoromethyl)-11*H*-indolo[3,2-*c*]quinoline (5j): slightly yellow solid; **Yield:** 51%; **m.p.** sublimizes at 255 °C; **IR** ($\nu_{\text{max}}/\text{cm}^{-1}$) 3576, 3015, 2921, 1674, 1635, 1596, 1104; **¹H NMR** (400 MHz, DMSO-*d*₆) 13.24 (s, 1H), 9.40 (s, 1H), 8.33 (d, *J*=8.2 Hz, 1H), 8.03 (dd, *J*=8.84, 2.00 Hz, 1H), 7.95 (dd, *J*=7.86, 0.62 Hz, 1H), 7.35 (t, *J*=7.88 Hz, 1H), 7.17 (d, *J*=7.64 Hz, 1H), 4.08 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) 146.85, 146.80, 140.55, 129.94, 129.60, 126.56, 126.25, 124.39, 123.54, 123.34, 121.99, 121.91, 116.94, 115.97, 113.17, 107.57, 56.14; **HRMS** (ESI) *m/z* calculated for C₁₇H₁₂F₃N₂O (M+H)⁺: 317.0902, found: 317.0903.



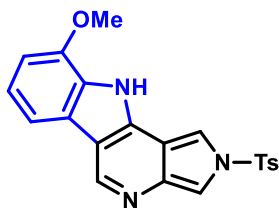
Benzyl 4-oxo-2-phenyl-6-tosyl-2,3,4,6-tetrahydro-1*H*-pyrrolo[3,4-*b*]pyridine-1-carboxylate (7b): white solid; **Yield:** 47% (over two steps); **m.p.** 208-209 °C; **IR** ($\nu_{\text{max}}/\text{cm}^{-1}$) 3065, 2953, 1710, 1694, 1585, 1512; **¹H NMR** (400 MHz, Chloroform-*d*₃) 7.88-7.61 (m, 3H), 7.50-7.28 (m, 7H), 7.27-7.19 (m, 4H), 7.08 (brs, 2H), 5.91 (brs, 1H), 5.27 (s, 2H), 3.14 (dd, *J*= 16.66, 6.06 Hz, 1H), 2.98 (d, *J*=16.66 Hz, 1H), 2.48 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*₃) 189.32, 153.31, 146.02, 138.99, 135.44, 134.75, 130.30, 128.85, 128.66, 128.50, 128.17, 127.80, 127.45, 125.95, 119.90, 117.56, 109.37, 57.04, 44.01, 21.73; **HRMS** (ESI) *m/z* calculated for C₂₈H₂₅N₂O₅S (M+H)⁺: 501.1484, found: 501.14815.



2-tosyl-2,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-*b*]indole (8a): yellow solid; **Yield:** 54%; **m.p.** decomposed; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3338, 3059, 2952, 1731, 1645, 1602, 1595; **$^1\text{H NMR}$** (400 MHz, DMSO- d_6) 12.37 (s, 1H), 9.16 (s, 1H), 8.11(m, 2H), 8.02 (d, $J=8.50$ Hz, 2H), 7.94 (d, $J=2.42$ Hz, 1H), 7.62 (d, $J=8.20$ Hz, 1H), 7.47 (d, $J=8.20$ Hz, 2H), 7.36 (m, 1H), 7.26 (m, 1H), 2.35 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, DMSO- d_6) 147.15, 146.79, 139.88, 137.78, 135.44, 134.88, 131.01, 127.89, 127.75, 124.70, 123.31, 121.27, 119.59, 112.86, 112.45, 111.14, 108.26, 21.57; **HRMS** (ESI) m/z calculated for $\text{C}_{20}\text{H}_{16}\text{N}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$: 362.0963, found: 362.0965.

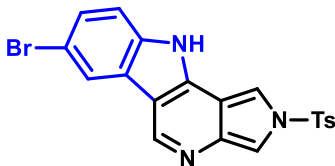


Benzyl 2-tosyl-5,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-*b*]indole-4(2*H*)-carboxylate (8aa): light brown solid; **Yield:** 91%; **m.p.** decomposed; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3345, 3059, 2985, 1683, 1661, 1595, 1553; **$^1\text{H NMR}$** (400 MHz, DMSO- d_6) 11.39 (s, 1H), 7.80 (brs, 1H), 7.53-7.31 (m, 12H), 7.12 (m, 1H), 7.00 (t, $J=7.28$ Hz, 1H), 5.30 (s, 2H), 5.11-5.30 (m, 2H), 2.36 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, DMSO- d_6) 145.94, 137.37, 135.12, 130.87, 129.03, 128.75, 128.57, 128.23, 127.04, 125.12, 124.88, 122.77, 119.92, 118.61, 111.86, 111.78, 55.37, 44.23, 21.54; **HRMS** (ESI) m/z calculated for $\text{C}_{28}\text{H}_{24}\text{N}_3\text{O}_4\text{S}$ ($\text{M}+\text{H}$) $^+$: 498.1488, found: 498.1505.

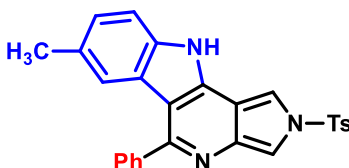


9-methoxy-2-tosyl-2,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-*b*]indole (8b): slightly yellow solid; **Yield:** 37%; **m.p.** decomposed; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3645, 3065, 2930, 1728, 1654, 1622, 1580, 1544; **$^1\text{H NMR}$** (400 MHz, DMSO- d_6) 12.43 (s, 1H), 9.12 (s, 1H), 8.10 (d, $J=2.44$ Hz, 1H), 8.01-7.98 (m, 3H), 7.69 (d, $J=7.96$ Hz, 1H), 7.48 (d, $J=7.96$ Hz, 2H), 7.17 (d, $J=7.82$ Hz, 1H), 6.95 (d, $J=7.62$ Hz, 1H), 4.01 (s, 3H), 2.36 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, DMSO- d_6) 146.17, 145.65, 134.04, 133.89, 129.95, 129.48, 126.78, 126.65, 126.60, 123.59, 120.90, 111.65, 111.02, 110.38,

110.16, 107.67, 104.38, 54.82, 20.50; **HRMS** (ESI) m/z calculated for $C_{21}H_{18}N_3O_3S$ (M+H)⁺: 392.1069, found: 392.1074.

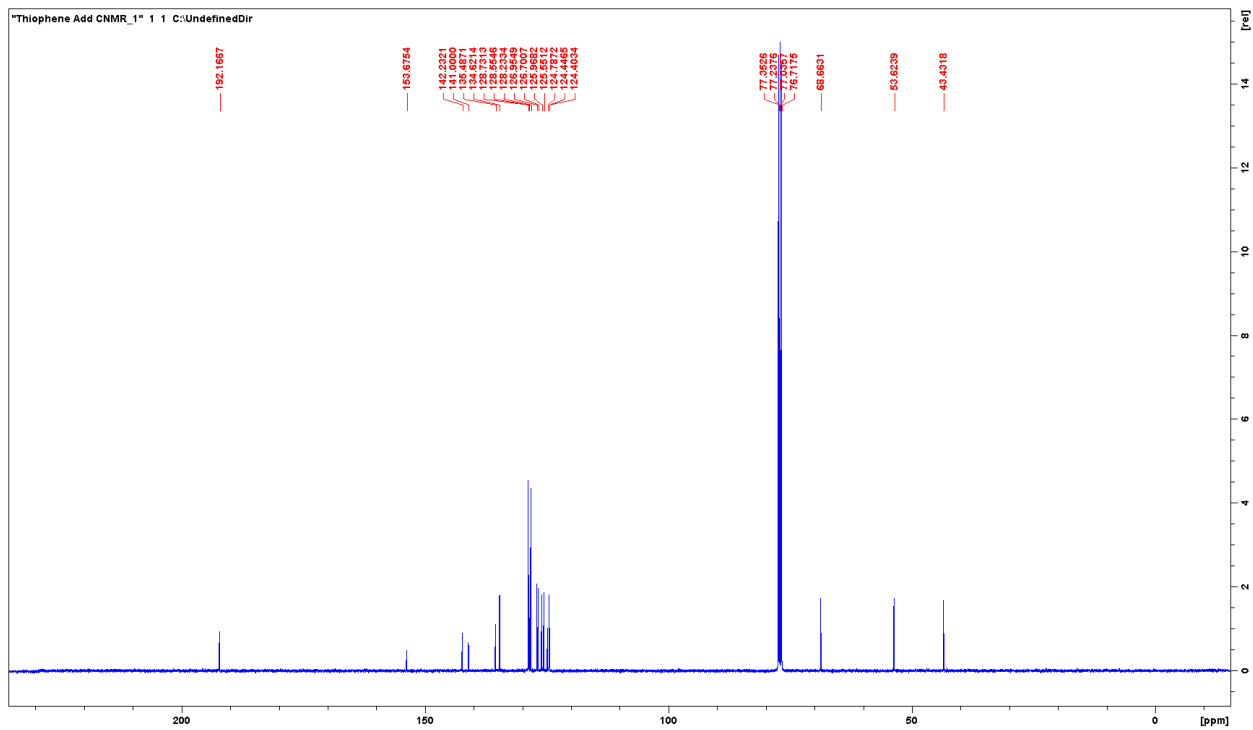
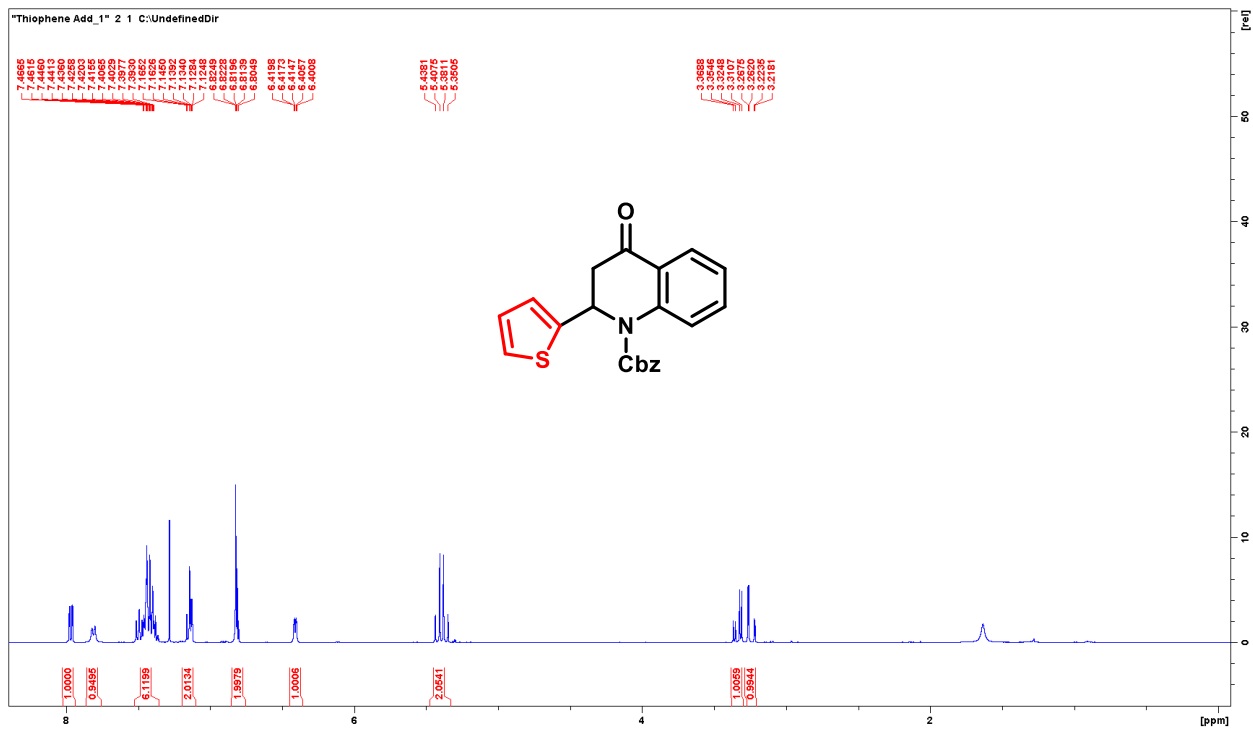


7-bromo-2-tosyl-2,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-b]indole (8c): slightly brown solid; **Yield**: 46%; **m.p.** decomposed; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3351, 3068, 2921, 1719, 1643, 1594, 1541; **¹H NMR** (400 MHz, DMSO- d_6) 12.51 (s, 1H), 9.19 (s, 1H), 8.39 (d, $J=1.86$ Hz, 1H), 8.14 (d, $J=2.38$ Hz, 1H), 8.03 (d, $J=8.76$ Hz, 2H), 7.94 (d, $J=1.90$ Hz, 1H), 7.61 (d, $J=8.20$ Hz, 1H), 7.49-7.46 (m, 3H), 2.36 (s, 3H); **¹³C NMR** (100 MHz, DMSO- d_6) 146.02, 145.76, 135.51, 135.41, 133.75, 129.96, 129.50, 126.76, 126.04, 124.23, 121.19, 113.40, 112.70, 111.92, 109.64, 109.39, 107.73, 20.51; **HRMS** (ESI) m/z calculated for $C_{20}H_{15}BrN_3O_2S$ (M+H)⁺: 440.0068, found: 440.00795.

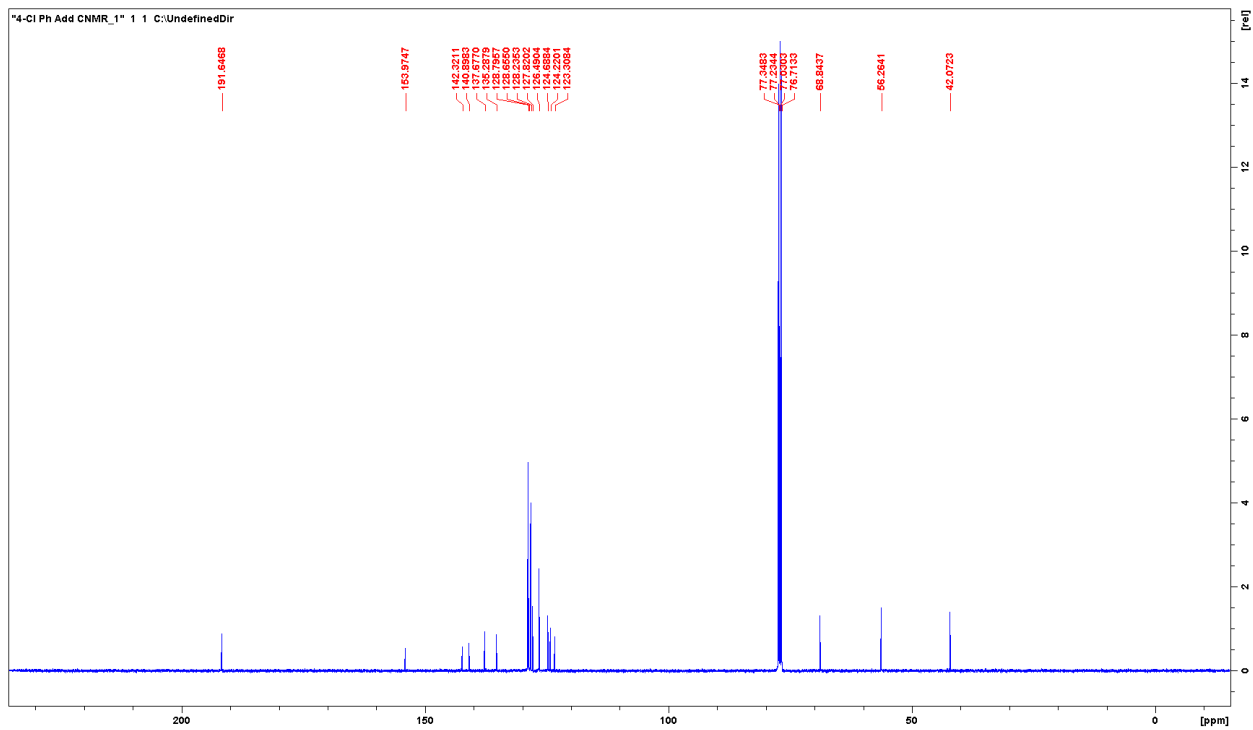
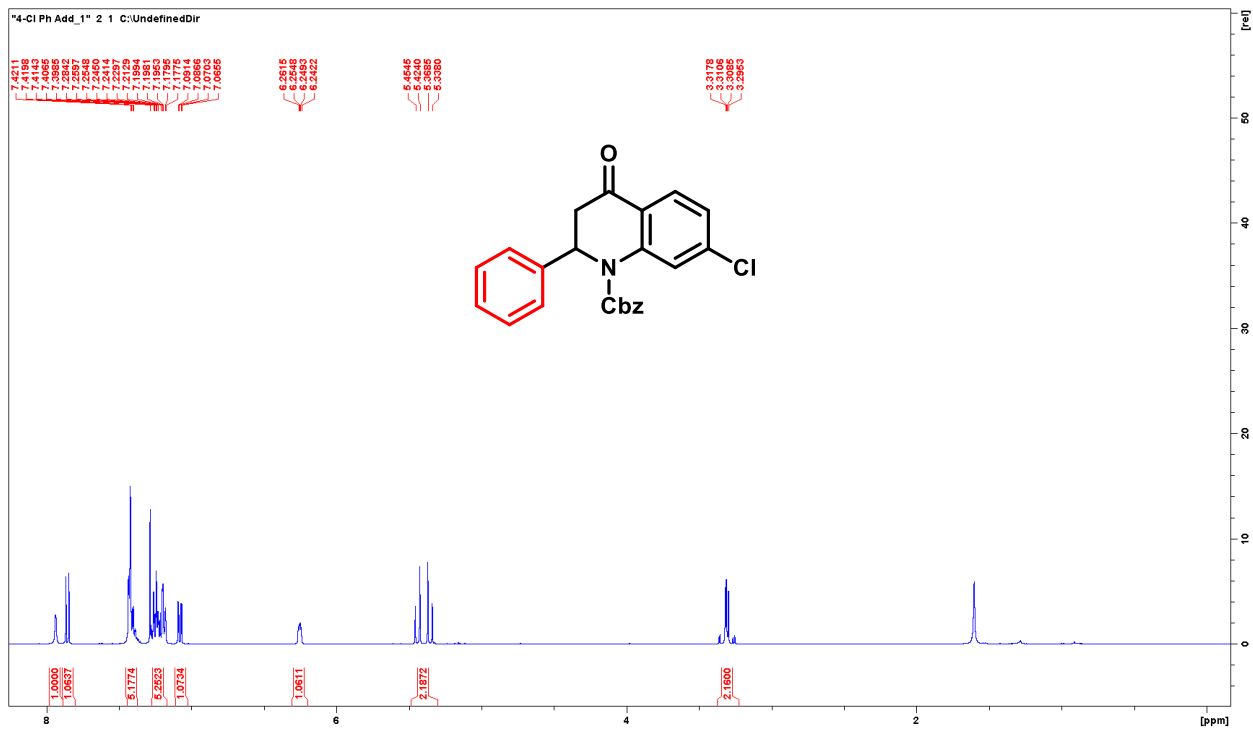


7-methyl-5-phenyl-2-tosyl-2,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-b]indole (8d): slightly brown solid; **Yield**: 39%; **m.p.** decomposed; **IR** ($\nu_{\max}/\text{cm}^{-1}$) 3313, 3064, 2922, 1732, 1645, 1615, 1595; **¹H NMR** (400 MHz, DMSO- d_6) 12.41 (s, 1H), 8.10 (d, $J=2.00$ Hz, 1H), 8.02 (d, $J=8.54$ Hz, 2H), 7.94 (d, $J=2.70$ Hz, 1H), 7.67-7.64 (m, 2H), 7.58-7.56 (m, 2H), 7.52-7.47 (m, 4H), 7.12 (dd, $J=8.20, 1.10$ Hz, 1H), 6.96 (s, 1H), 2.36 (s, 3H), 2.23 (s, 3H); **¹³C NMR** (100 MHz, DMSO- d_6) 145.65, 140.43, 133.92, 129.92, 128.68, 128.38, 128.21, 127.90, 127.58, 126.63, 125.01, 124.71, 122.24, 119.65, 114.48, 111.82, 111.13, 109.62, 108.29, 107.90, 107.39, 20.80, 20.50; **HRMS** (ESI) m/z calculated for $C_{27}H_{22}N_3O_2S$ (M+H)⁺: 452.1433, found: 452.1448.

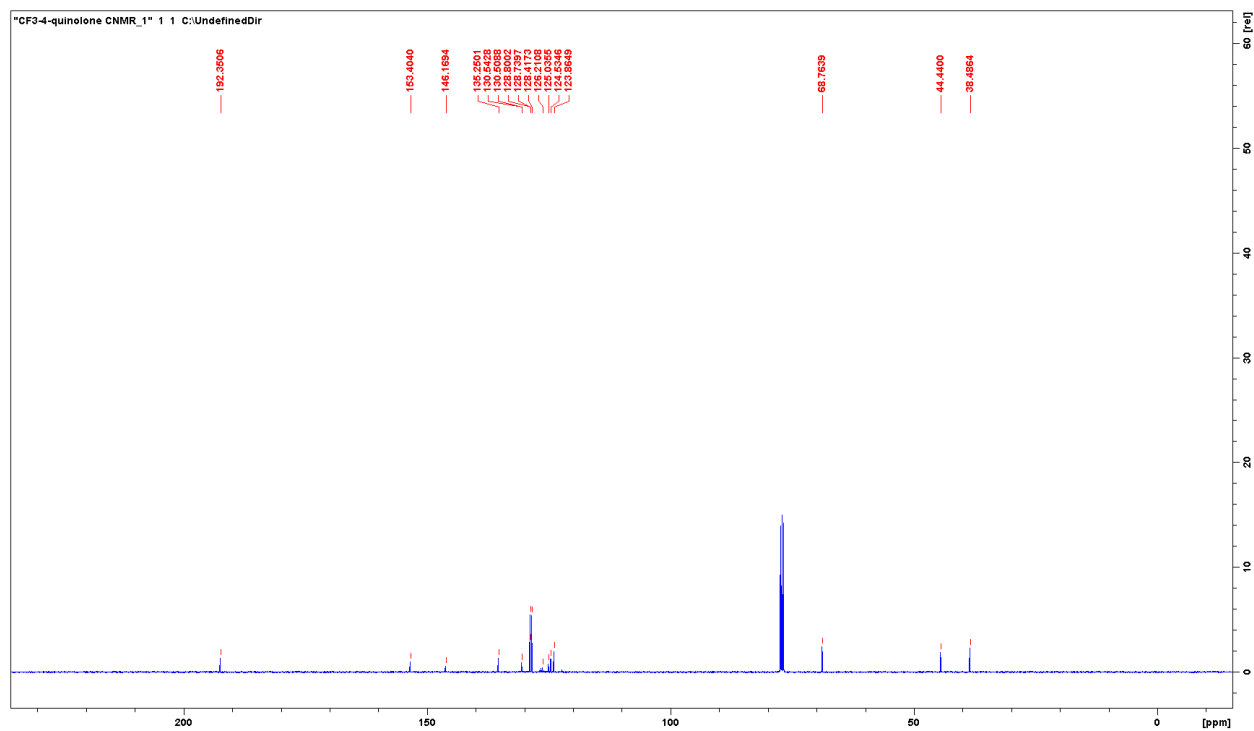
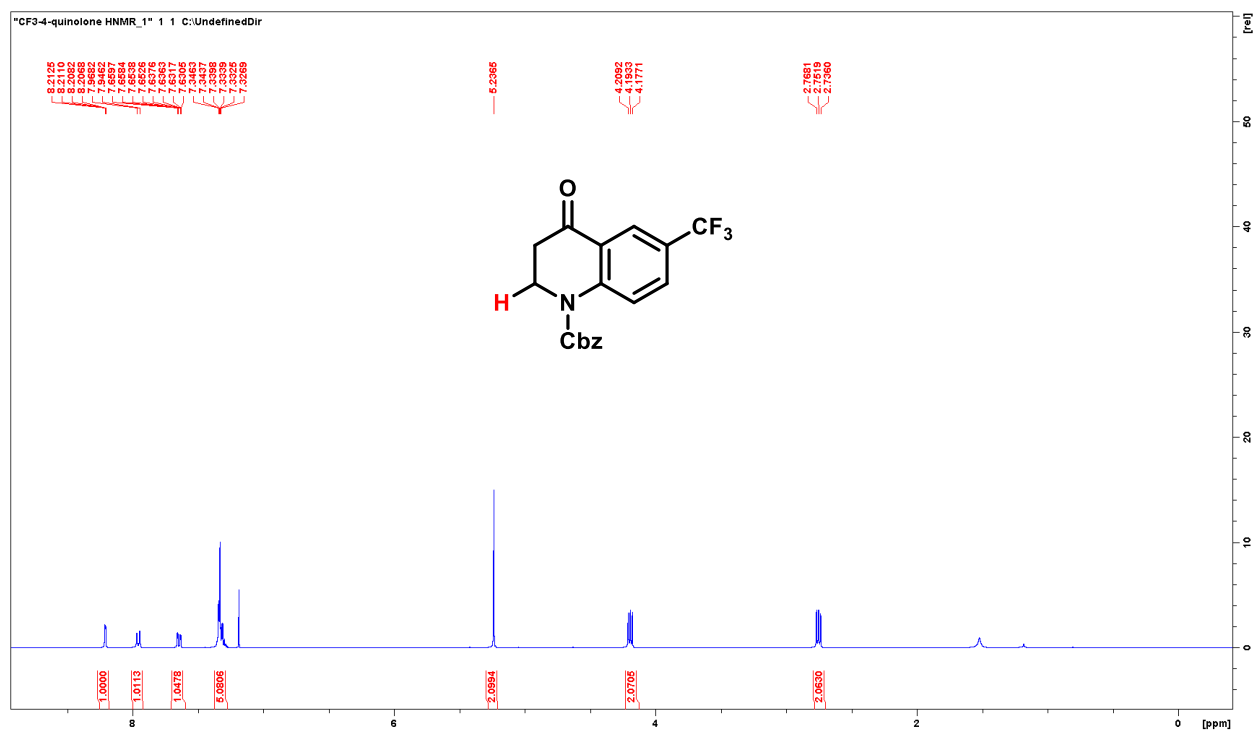
Benzyl 4-oxo-2-(thiophen-2-yl)-3,4-dihydroquinoline-1(2H)-carboxylate (4b)



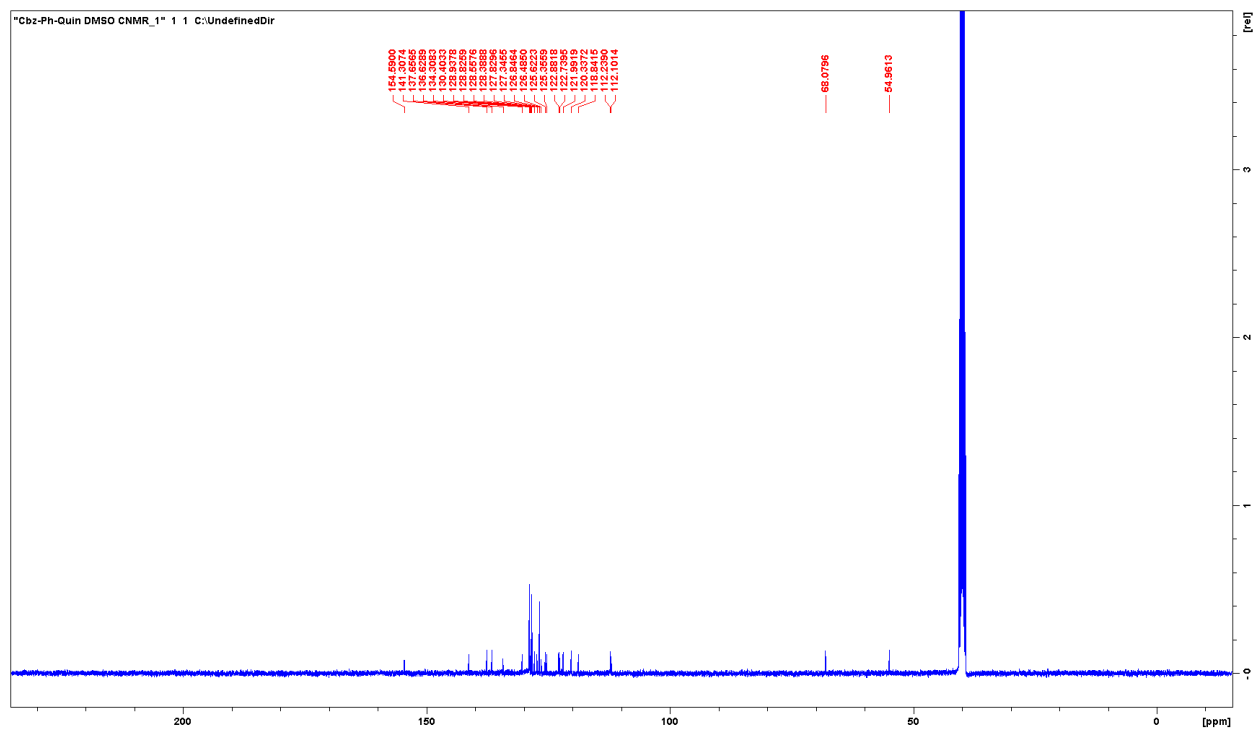
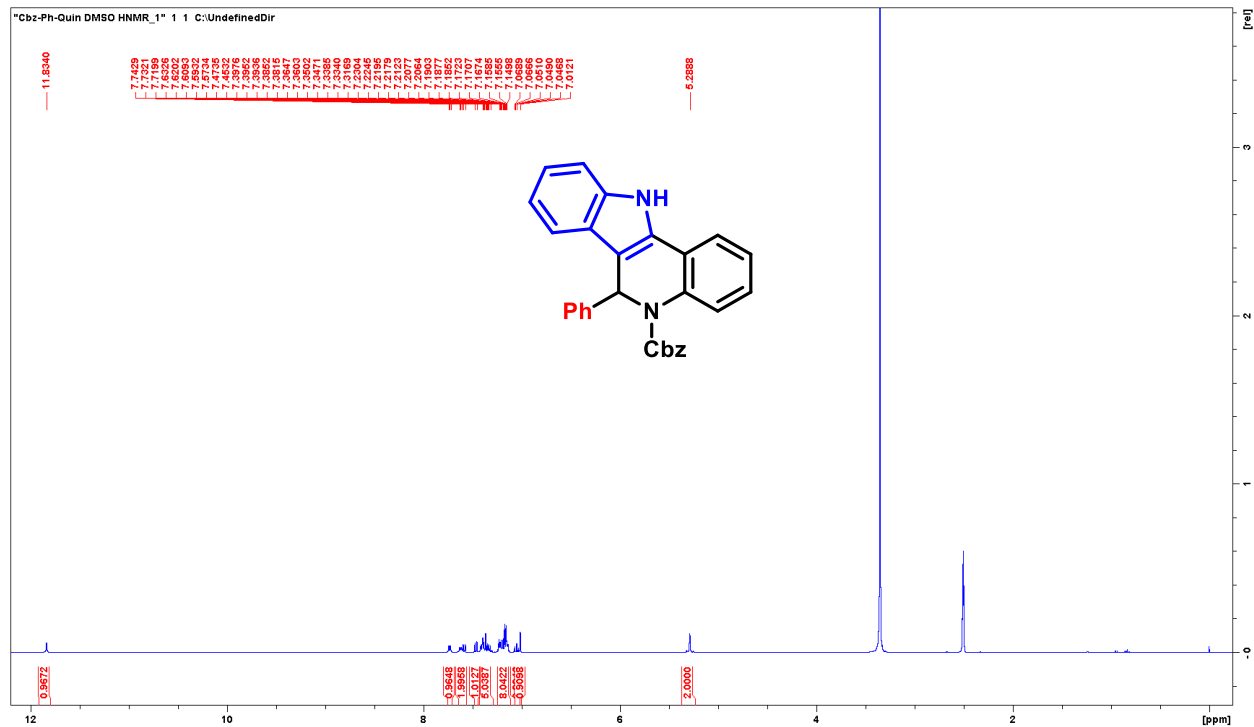
Benzyl 7-chloro-4-oxo-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (4d)



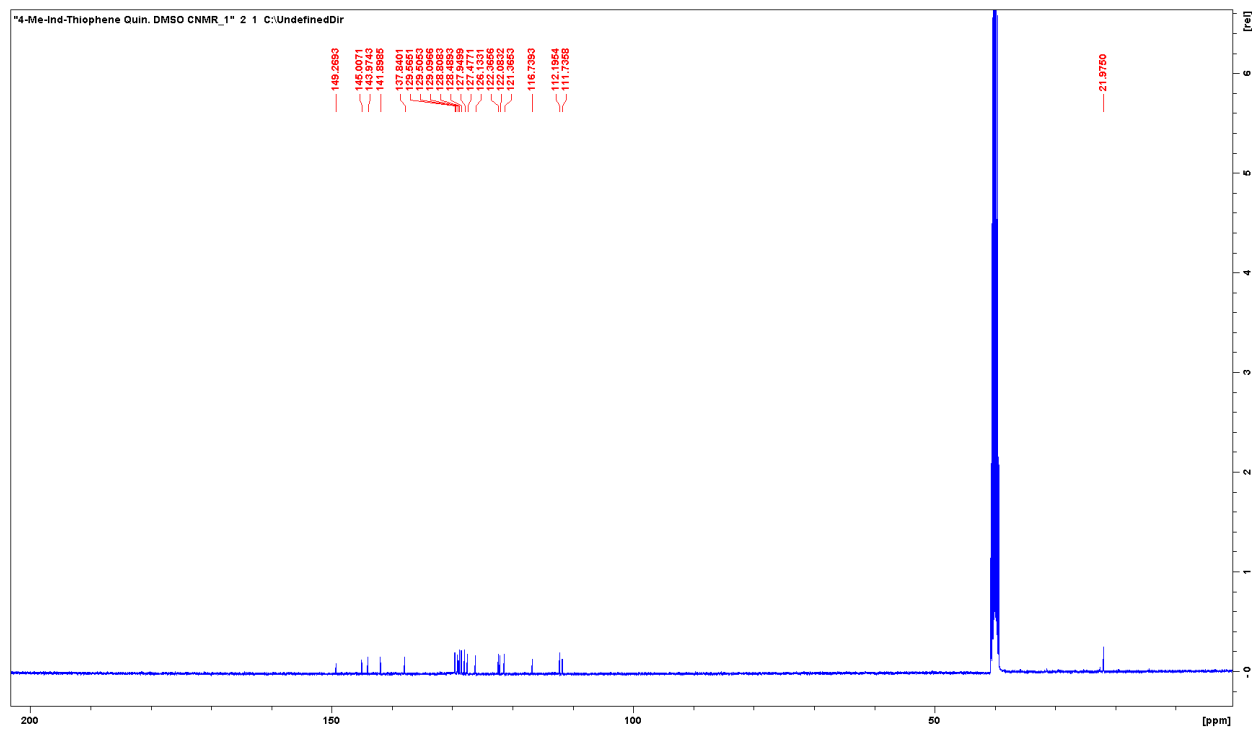
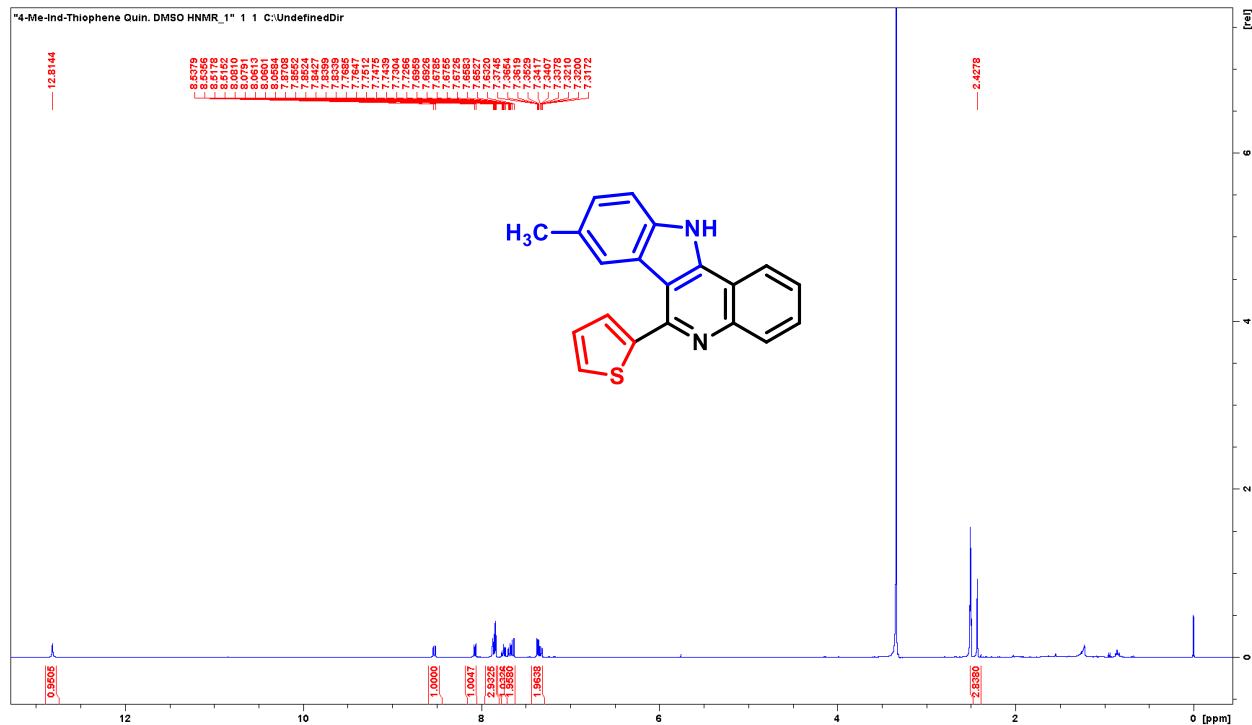
Benzyl 4-oxo-6-(trifluoromethyl)-3,4-dihydroquinoline-1(2H)-carboxylate (4g)



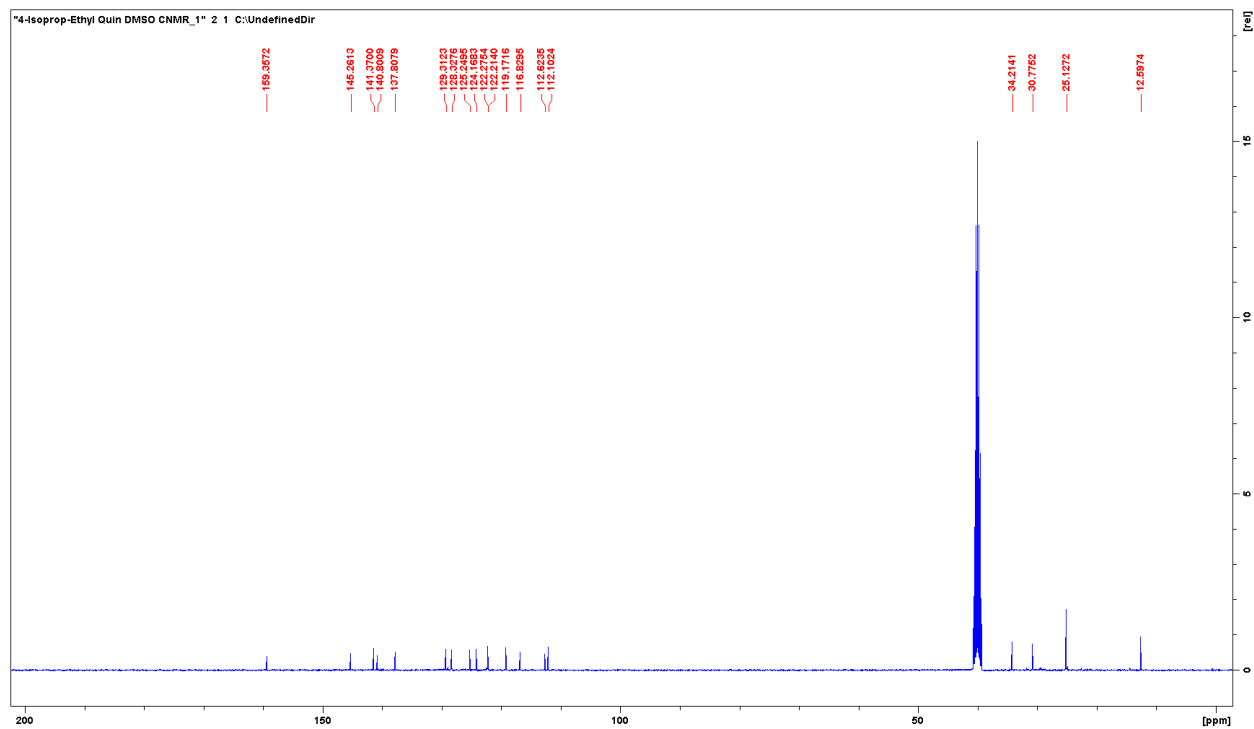
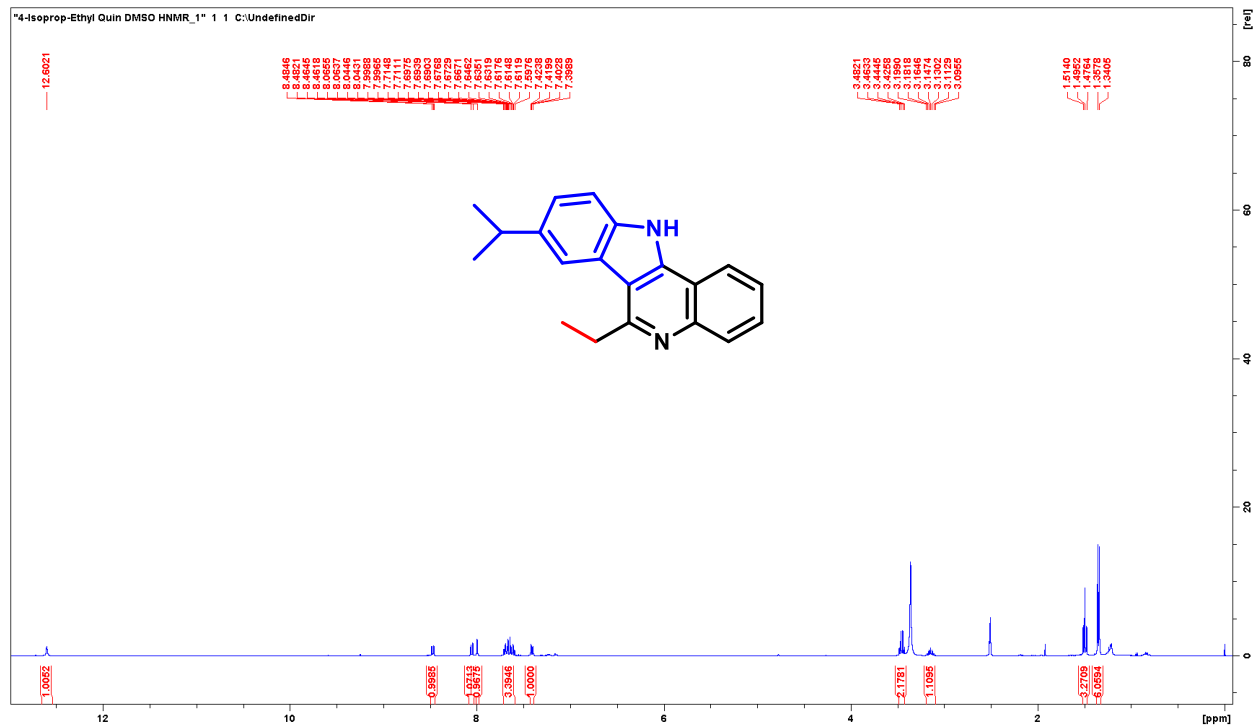
Benzyl 6-phenyl-6,11-dihydro-5H-indolo[3,2-c]quinoline-5-carboxylate (5b)



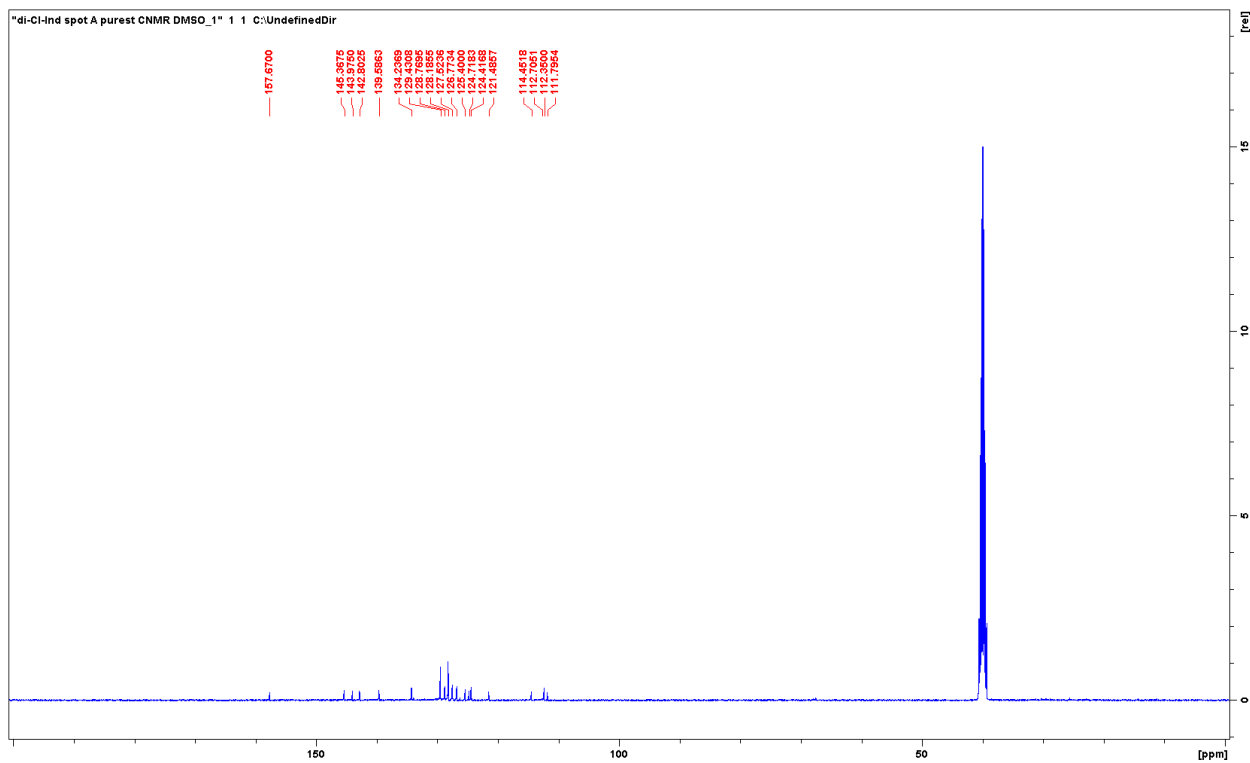
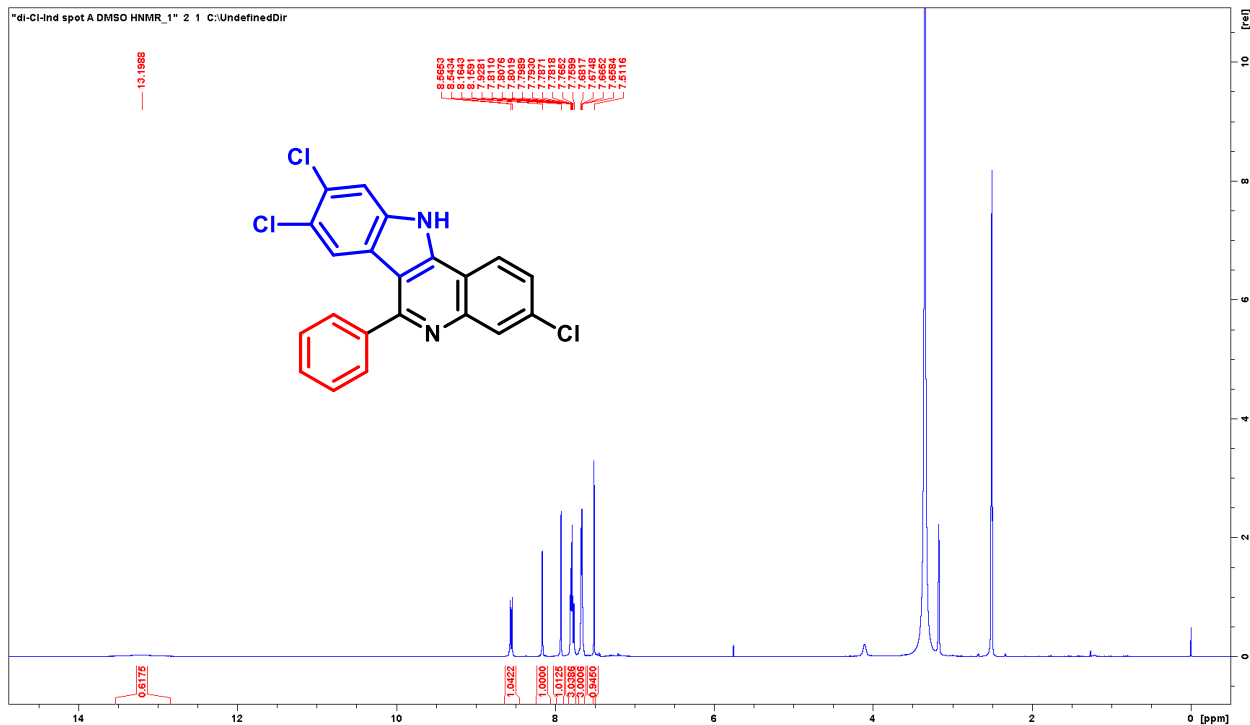
8-methyl-6-(thiophen-2-yl)-11H-indolo[3,2-c]quinoline (5d)



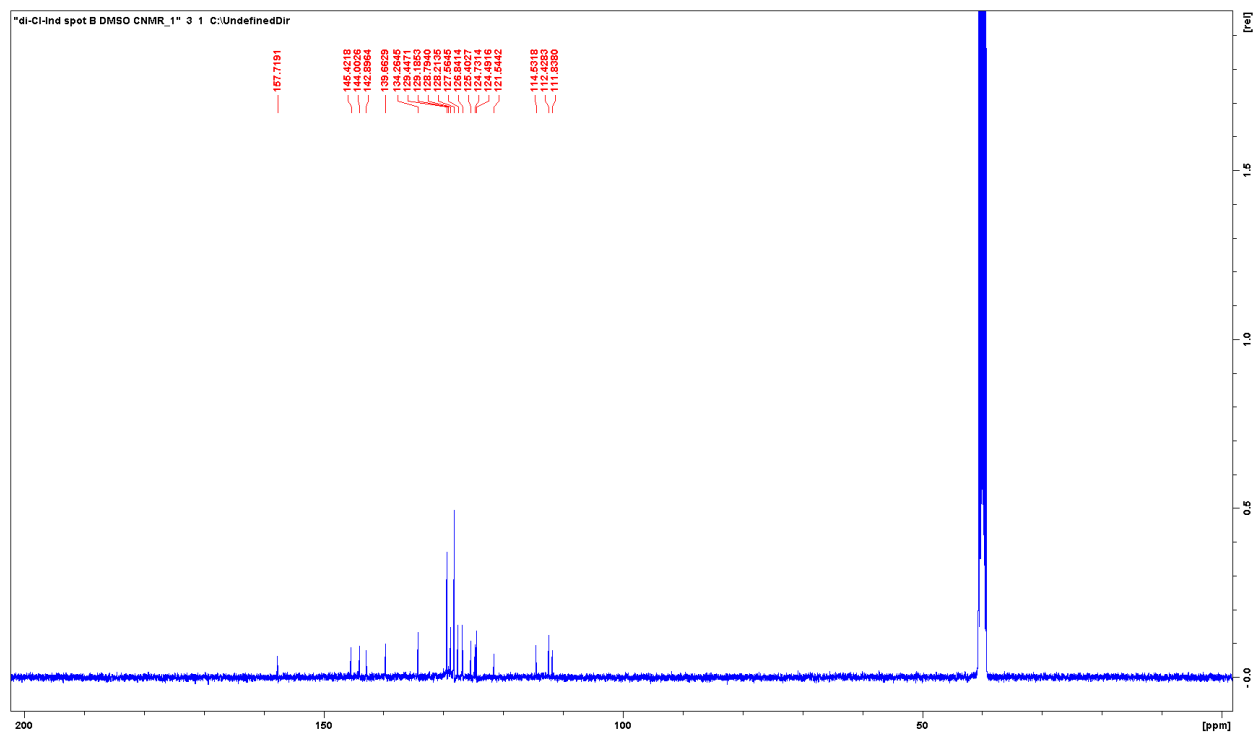
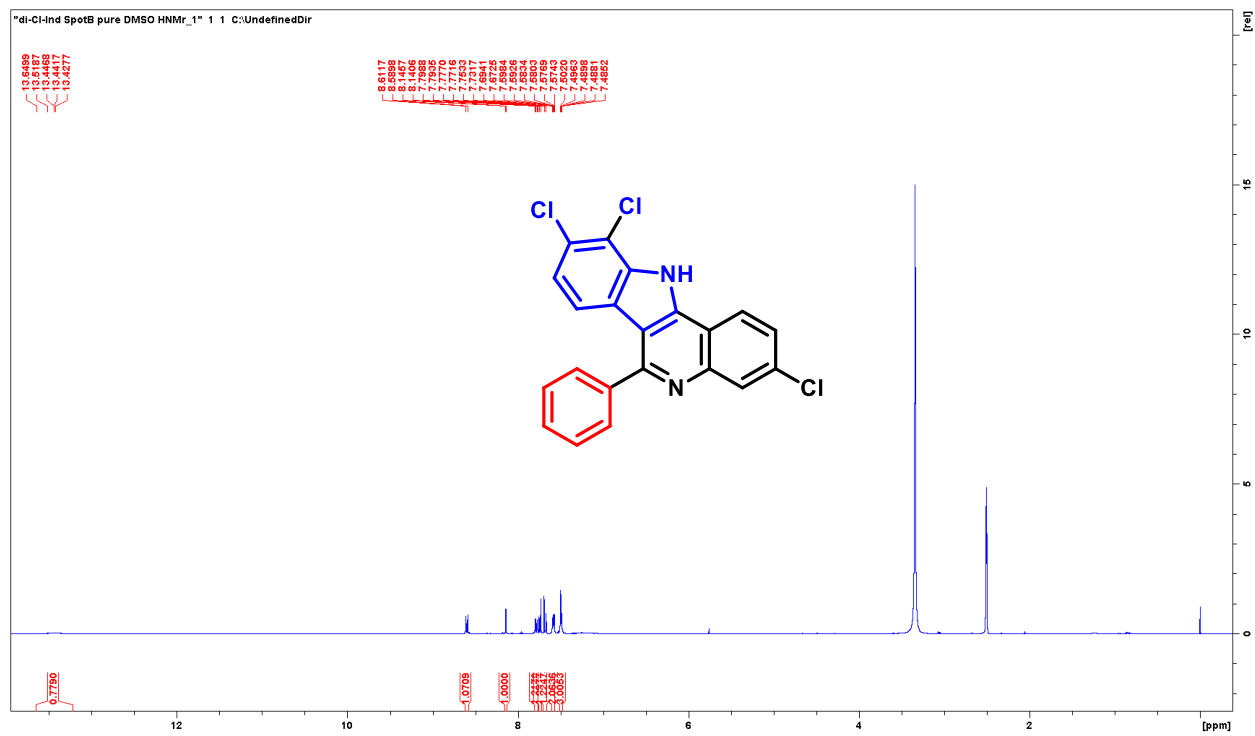
6-ethyl-8-isopropyl-11H-indolo[3,2-c]quinoline (5e)



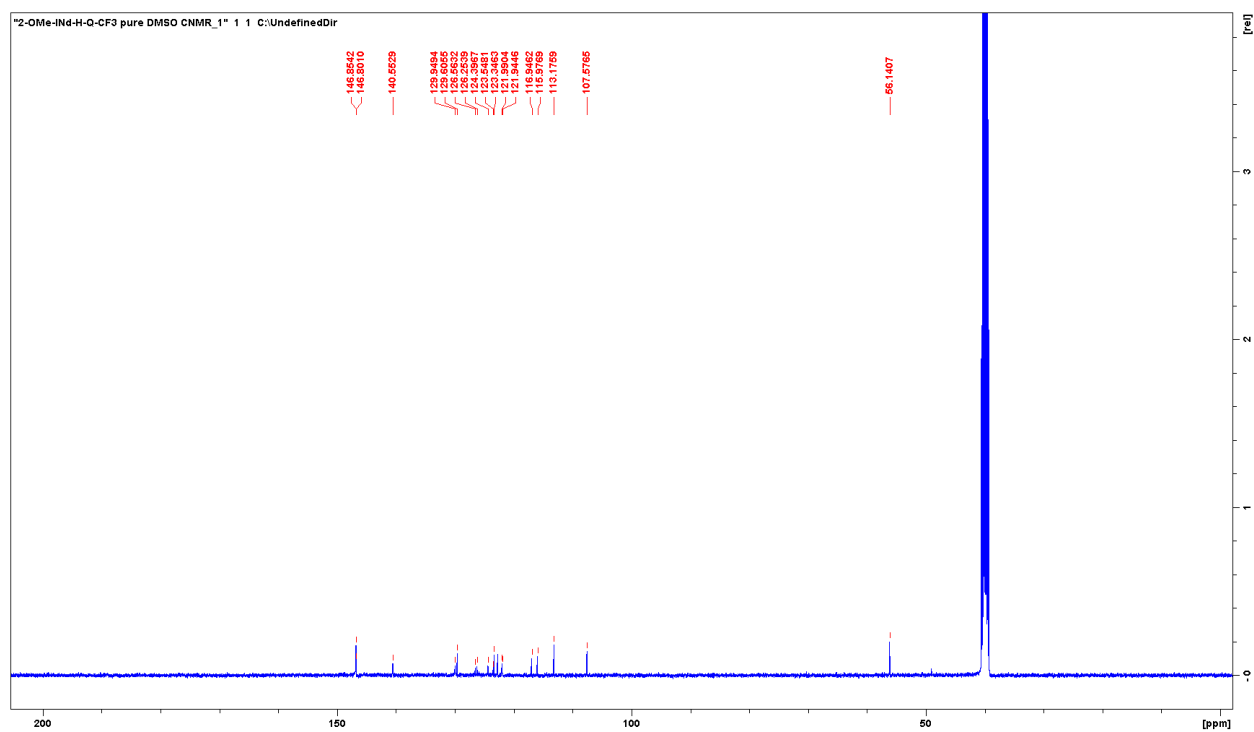
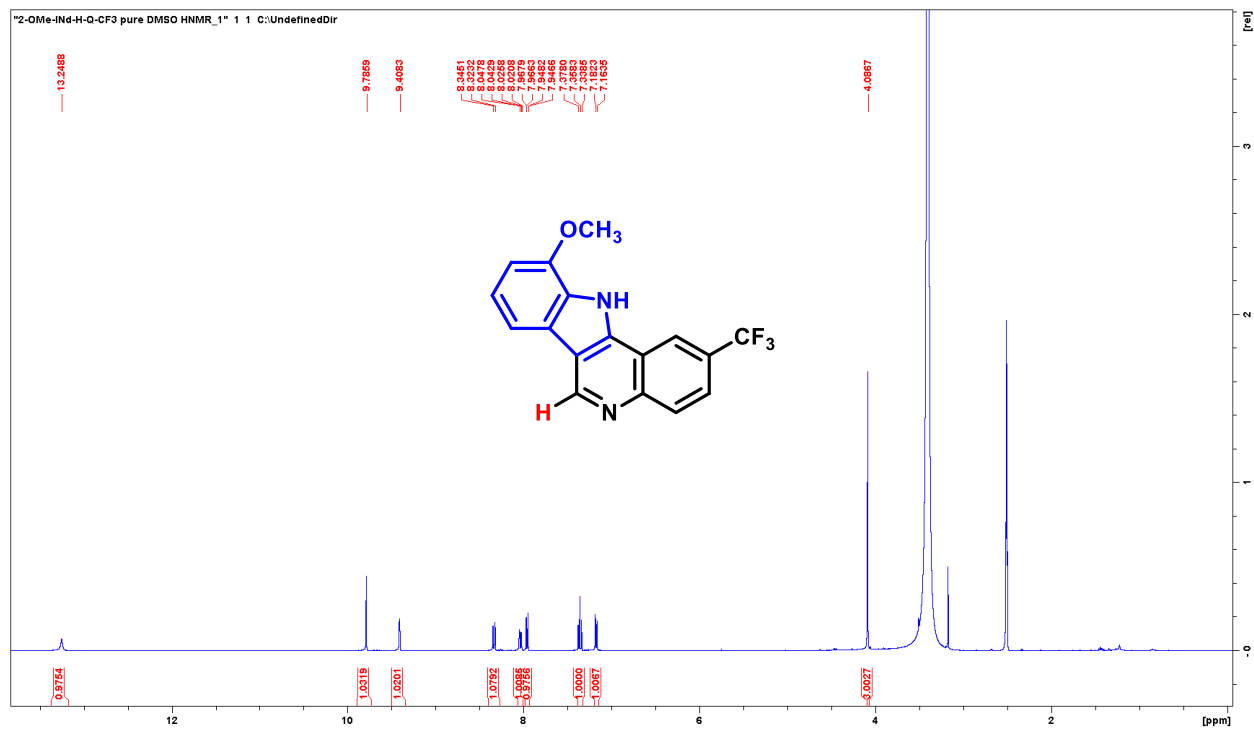
3,8,9-trichloro-6-phenyl-11H-indolo[3,2-c]quinoline (5g)



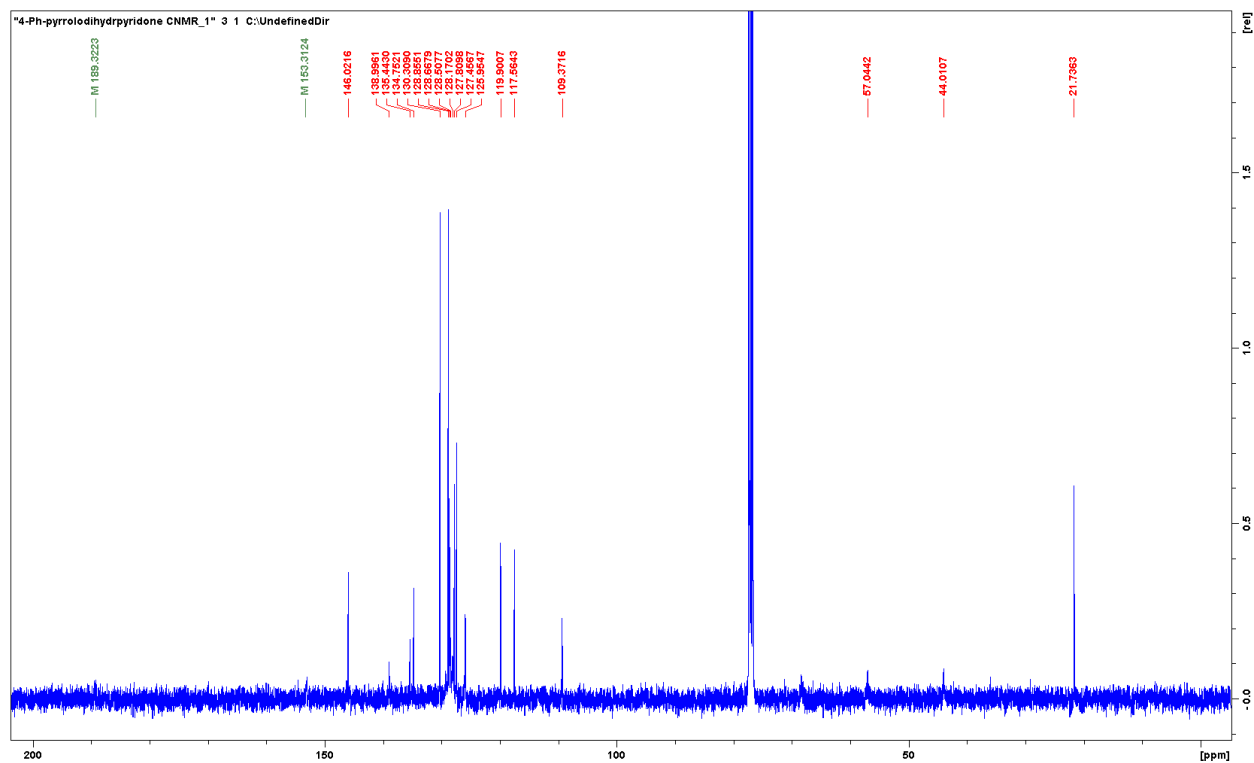
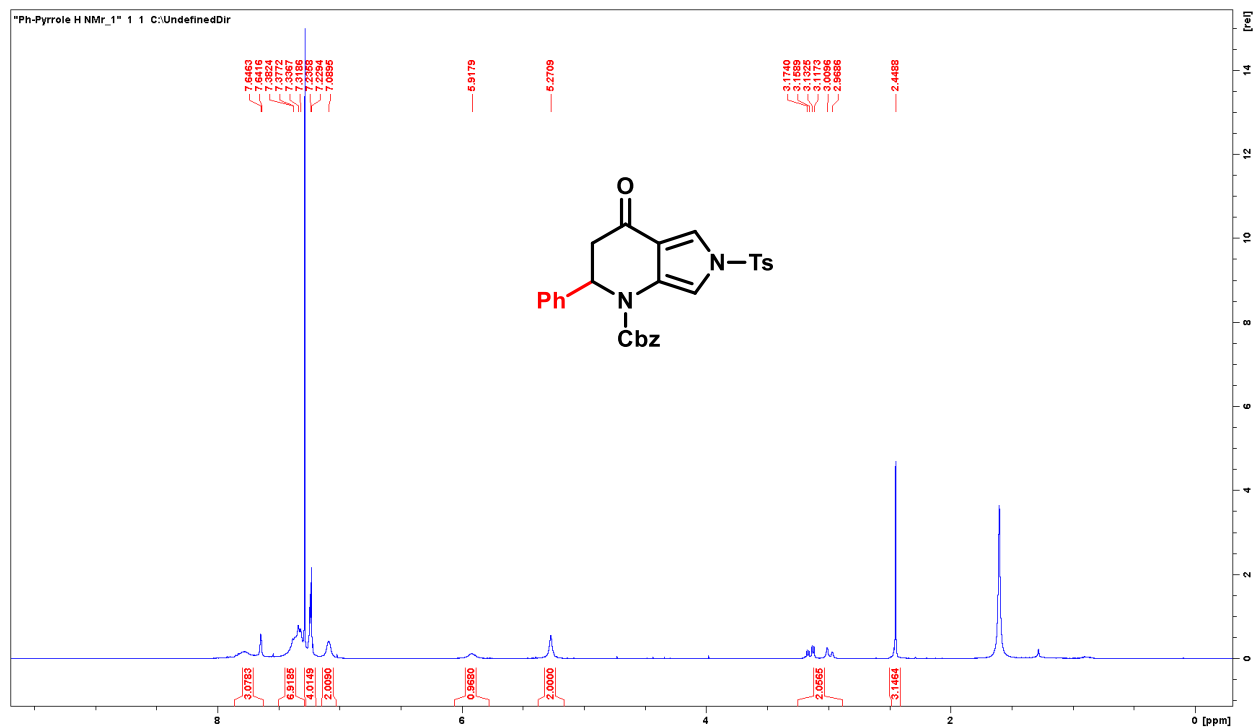
3,9,10-trichloro-6-phenyl-11H-indolo[3,2-c]quinoline (5h)



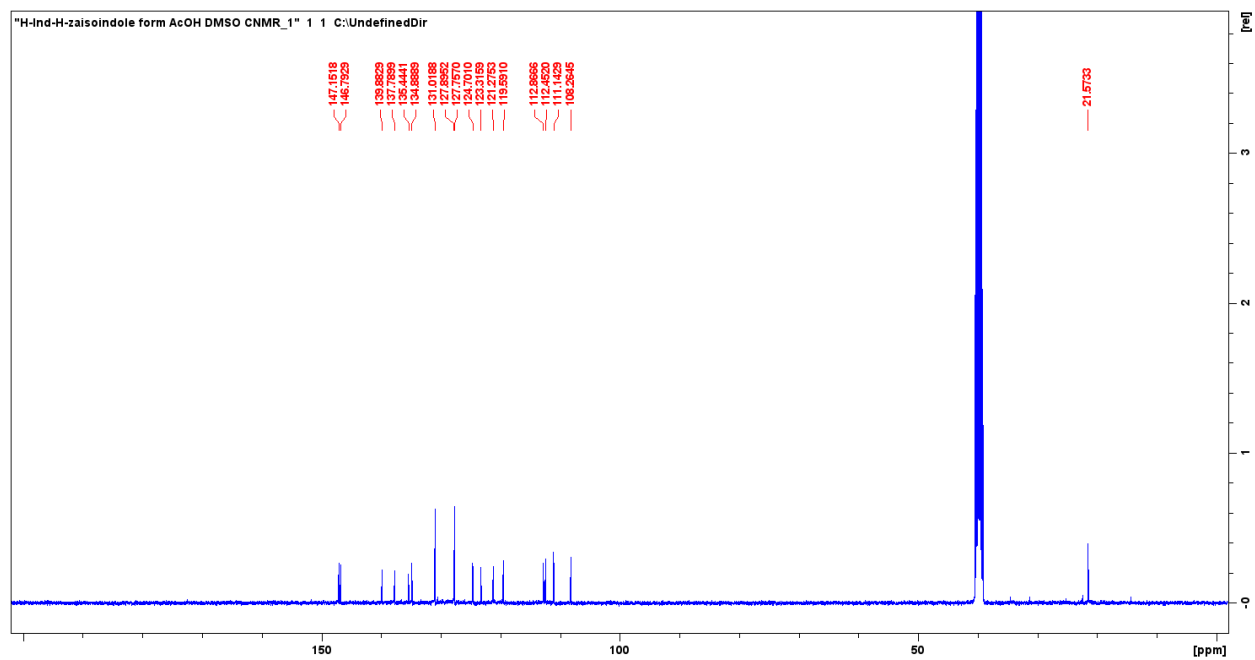
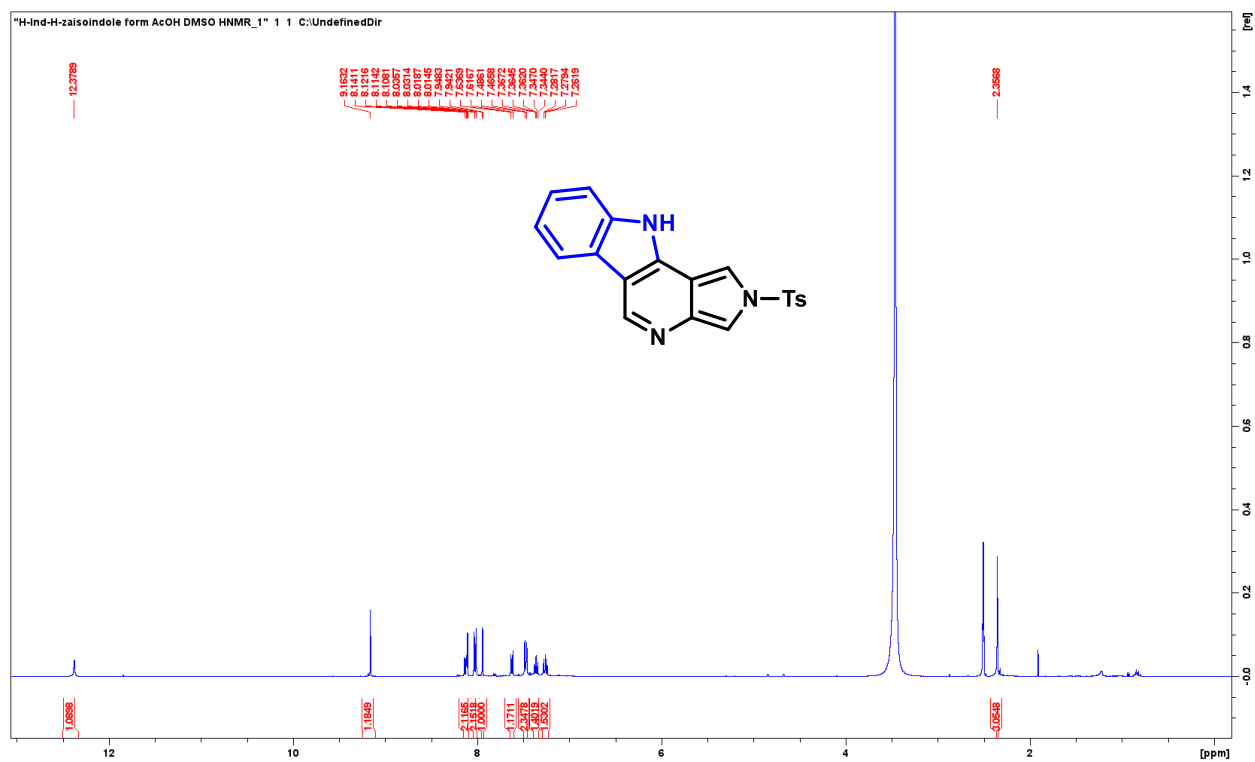
10-methoxy-2-(trifluoromethyl)-11H-indolo[3,2-c]quinoline (5j)



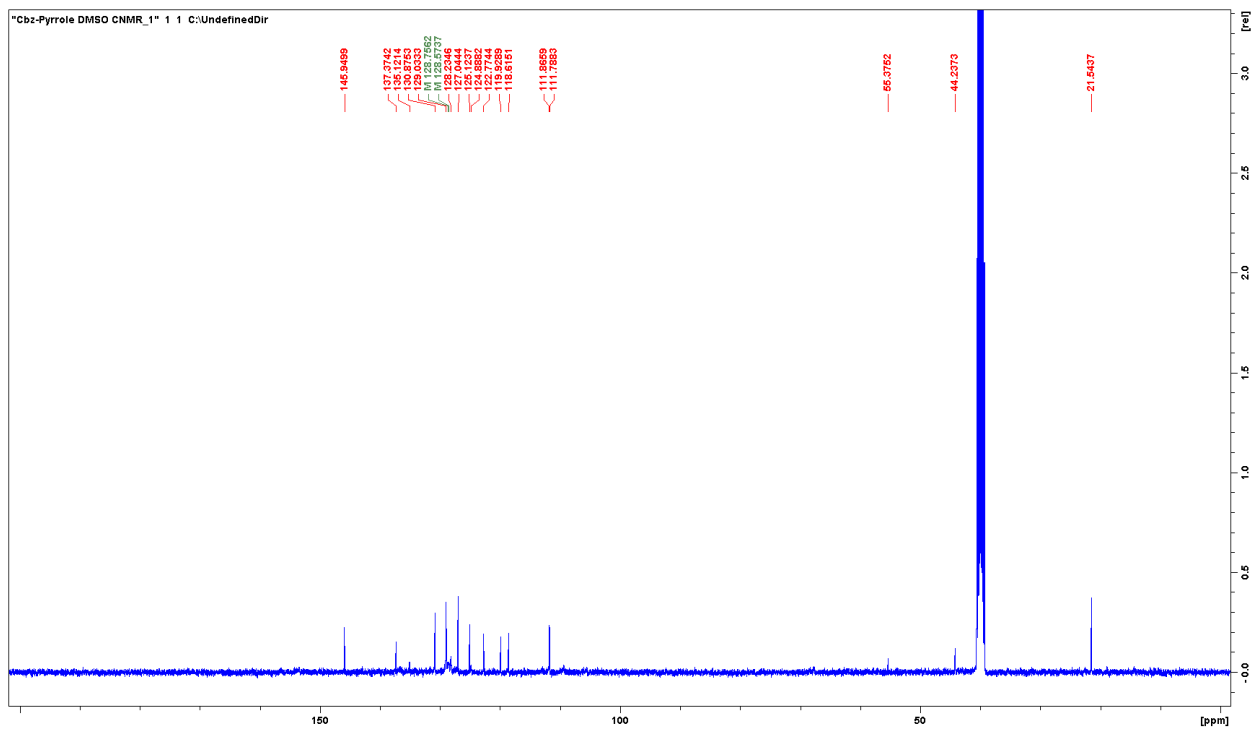
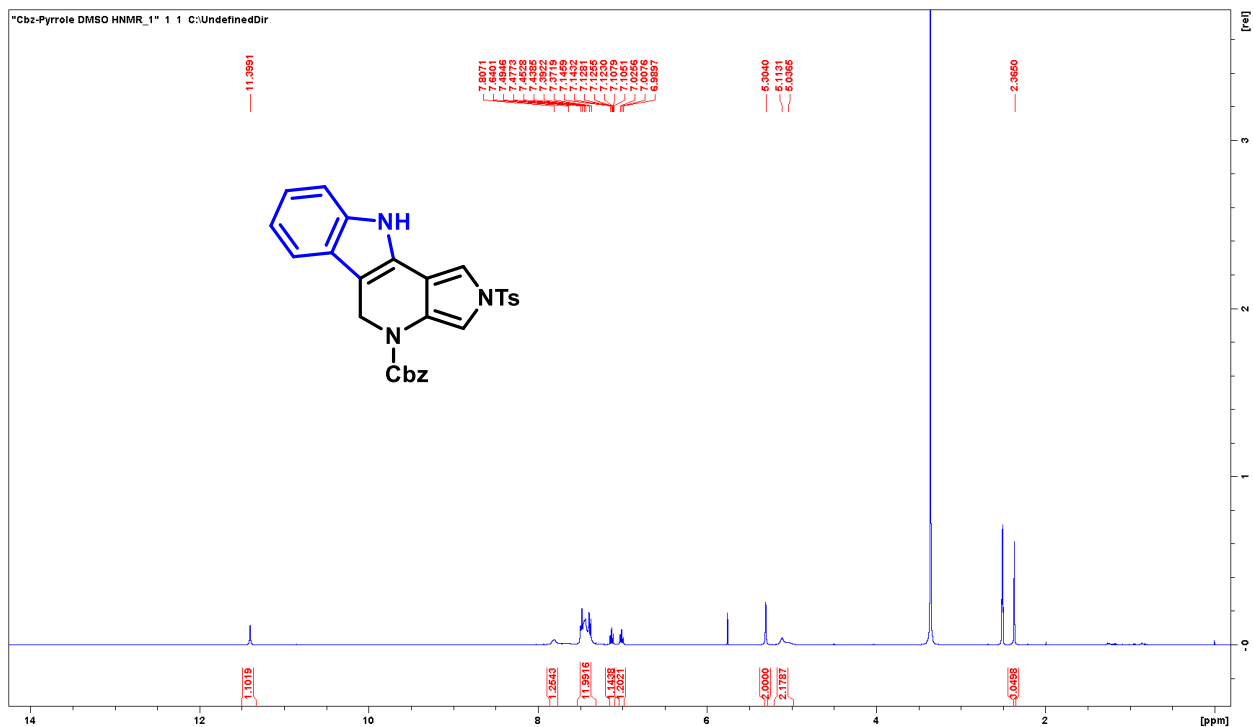
Benzyl 4-oxo-2-phenyl-6-tosyl-2,3,4,6-tetrahydro-1H-pyrrolo[3,4-b]pyridine-1-carboxylate (7b)



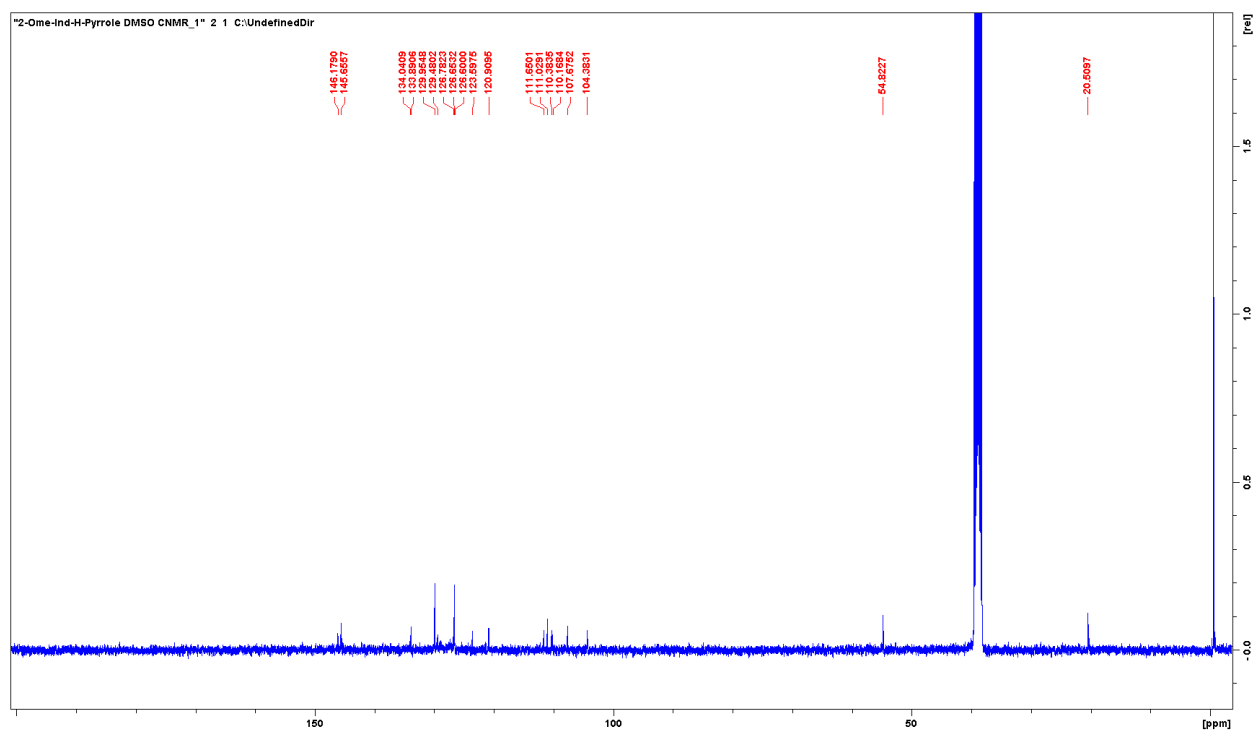
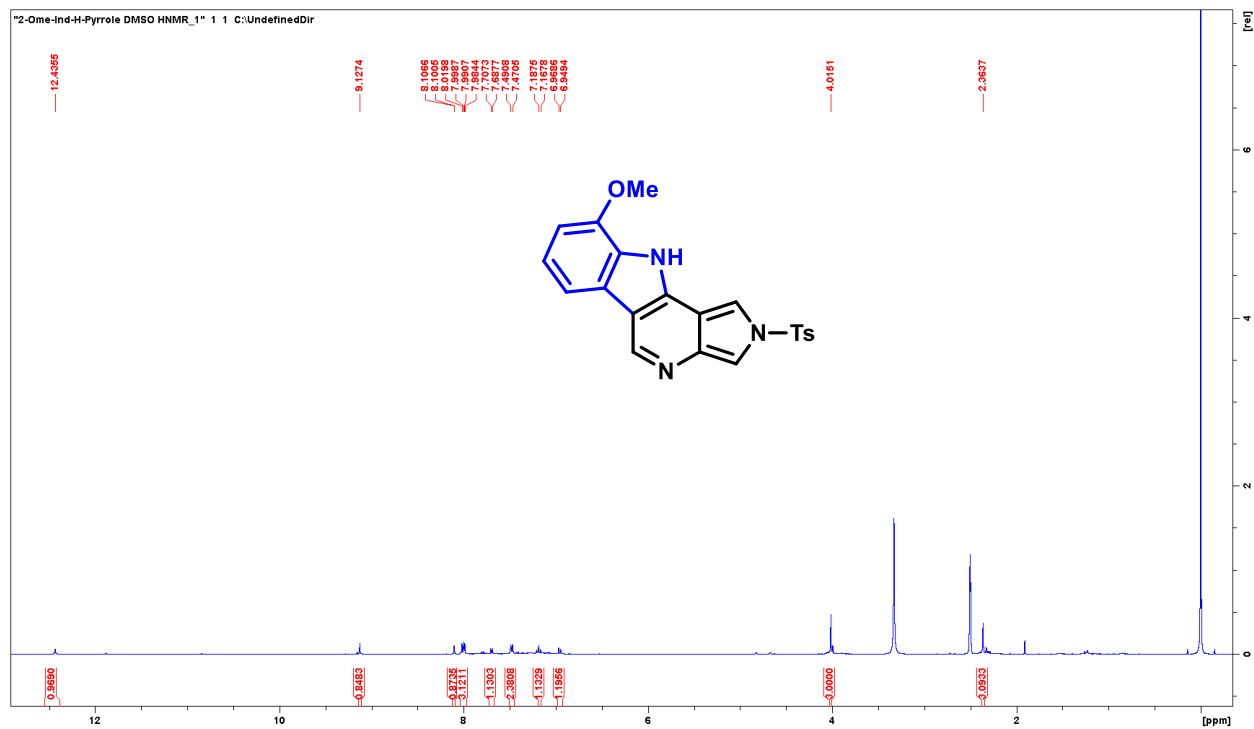
2-tosyl-2,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-b]indole (8a)



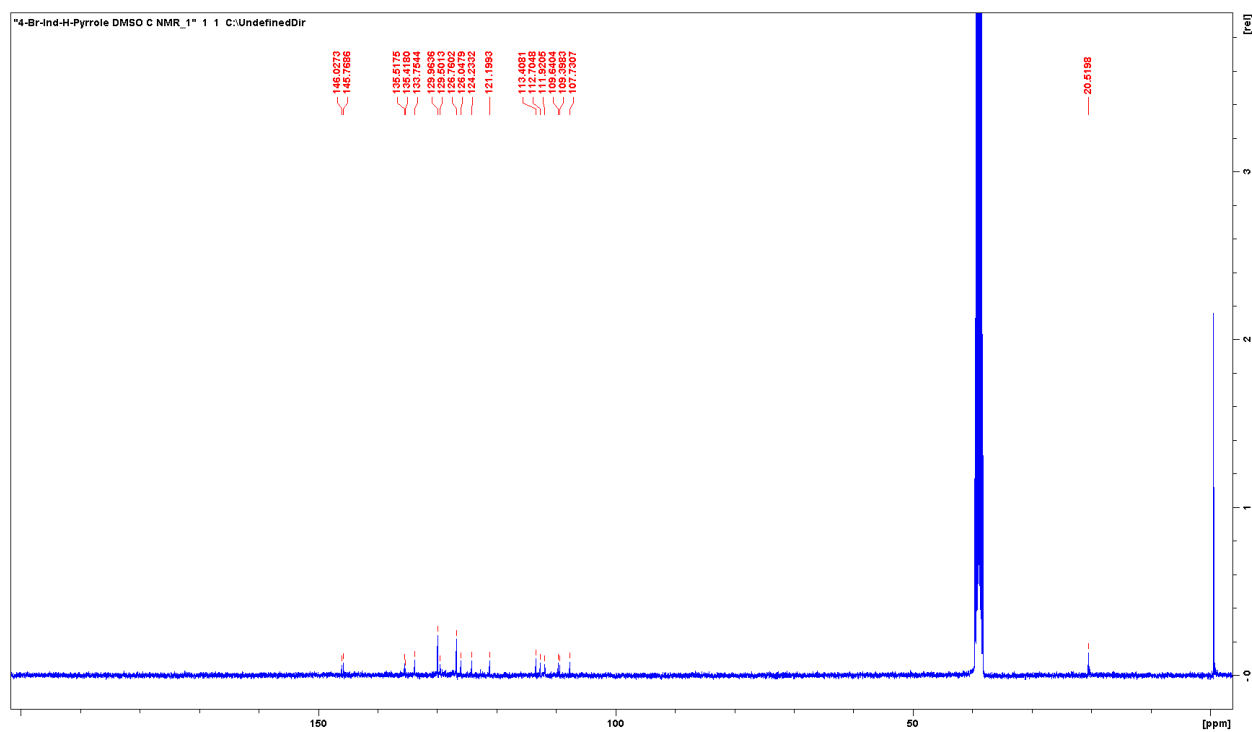
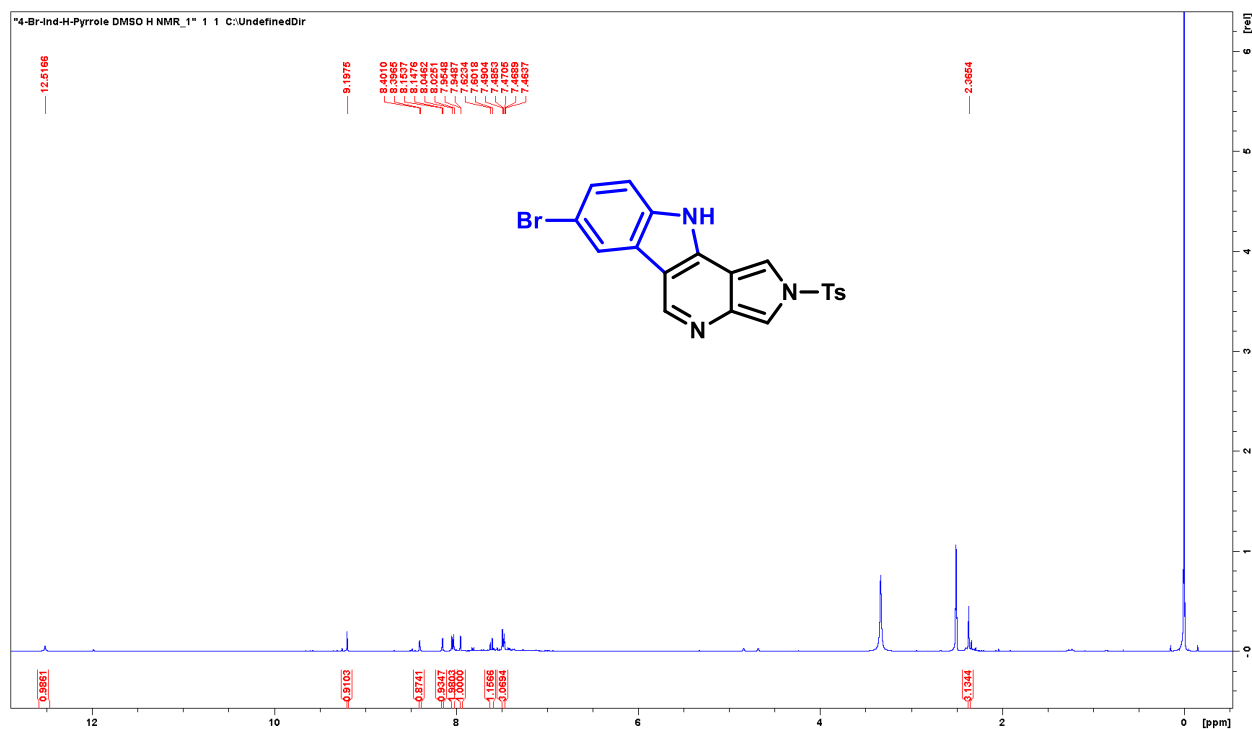
Benzyl 2-tosyl-5,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-b]indole-4(2H)-carboxylate (8aa)



9-methoxy-2-tosyl-2,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-b]indole (8b)



7-bromo-2-tosyl-2,10-dihydropyrrolo[3',4':5,6]pyrido[4,3-b]indole (8c)



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