

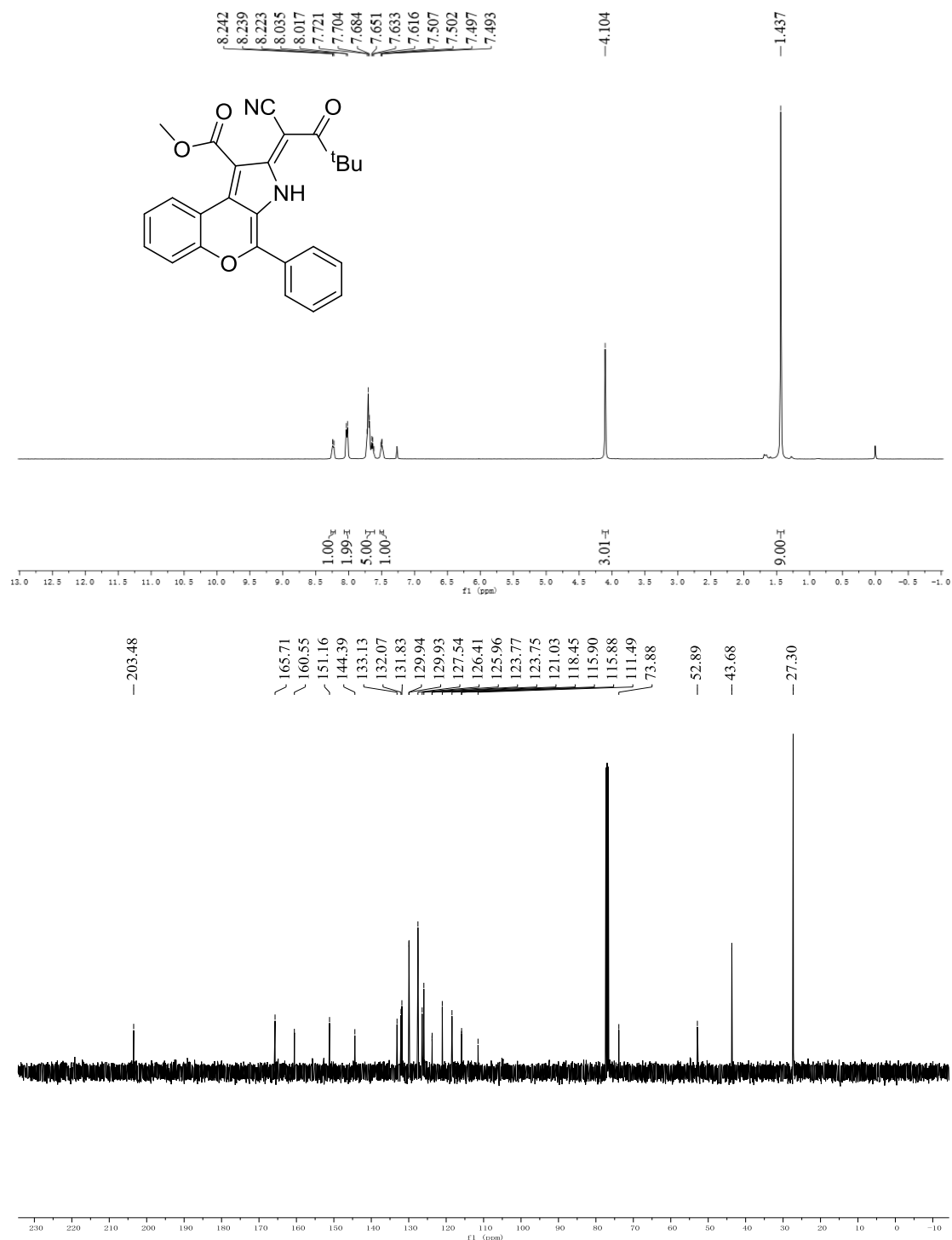
**Selective construction of functionalized chromeno[3,4-*b*]pyrroles and
benzo[*c*]chromenes via K₃PO₄ promoted three-component reaction**

Wang Jiang, Jing Sun, and Chao-Guo Yan*

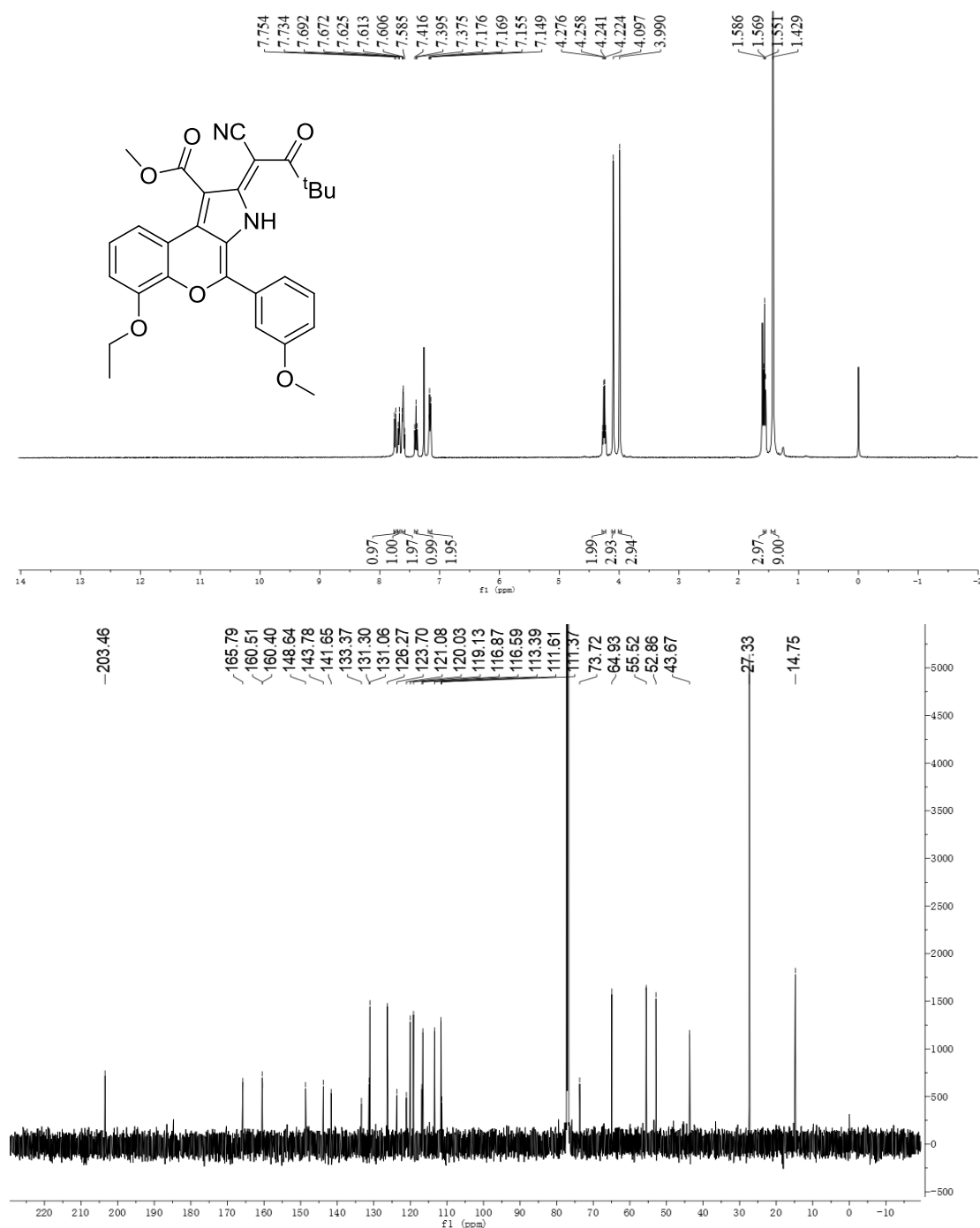
Supporting Information

Characterization data, ¹H NMR and ¹³C NMR spectra of the compounds 2-38

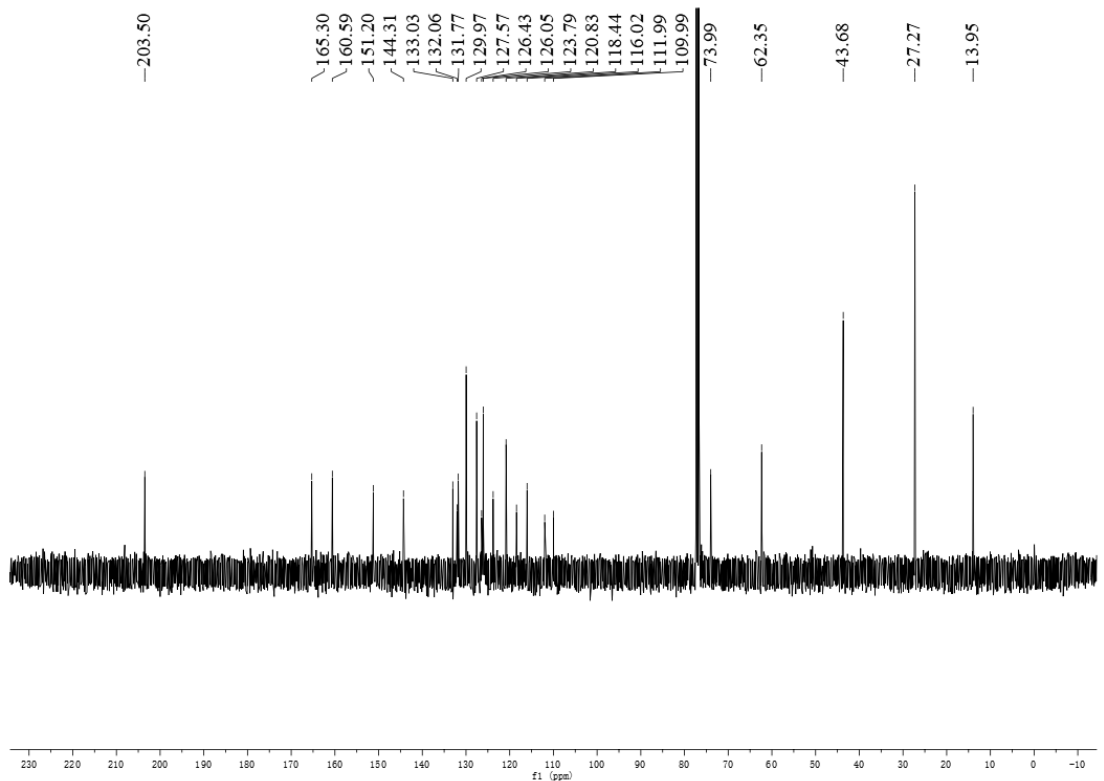
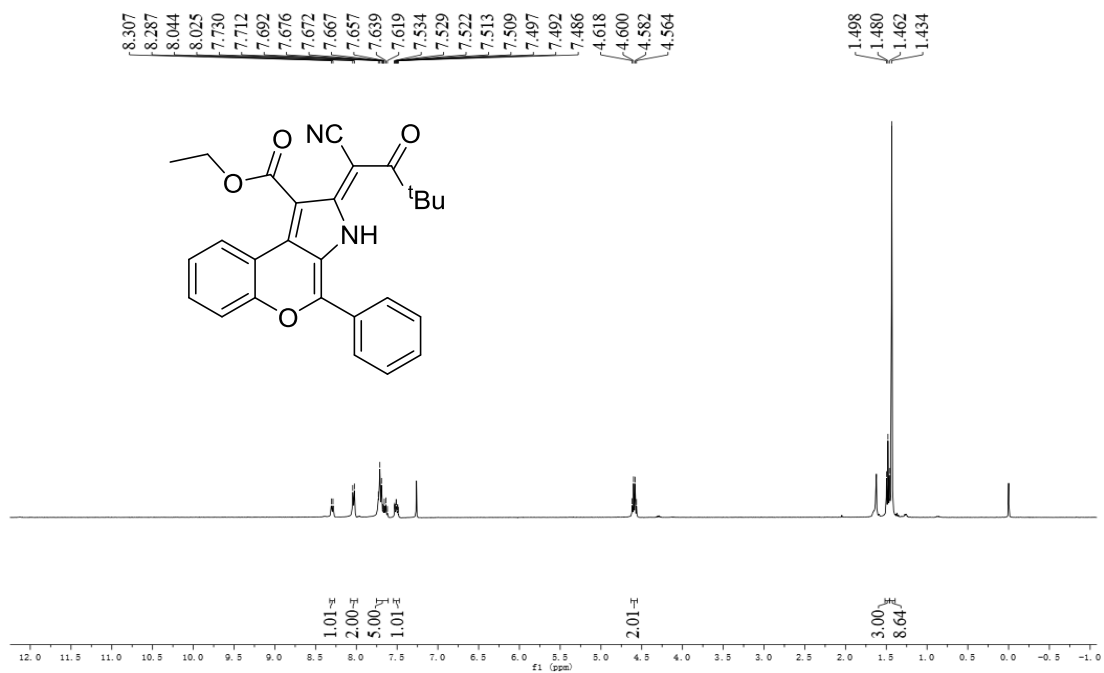
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-phenyl-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4a): red solid, 0.160g, 75%, m.p. 193~194 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.24~8.22 (m, 1H, ArH), 8.04~8.02 (m, 2H, ArH), 7.72~7.62 (m, 5H, ArH), 7.51-7.49 (m, 1H, ArH), 4.10 (s, 3H, OCH₃), 1.44 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.4, 165.7, 160.5, 151.1, 144.3, 133.1, 132.0, 131.8, 129.9, 129.9, 127.5, 126.4, 125.9, 123.7, 123.7, 121.0, 118.4, 115.9, 115.8, 111.4, 73.8, 52.8, 43.6, 27.3 (3C); IR (KBr) ν: 3430, 3120, 2970, 2196, 1708, 1400, 806 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₂N₂O₄Na ([M+Na]⁺): 449.1472. Found: 449.1468.



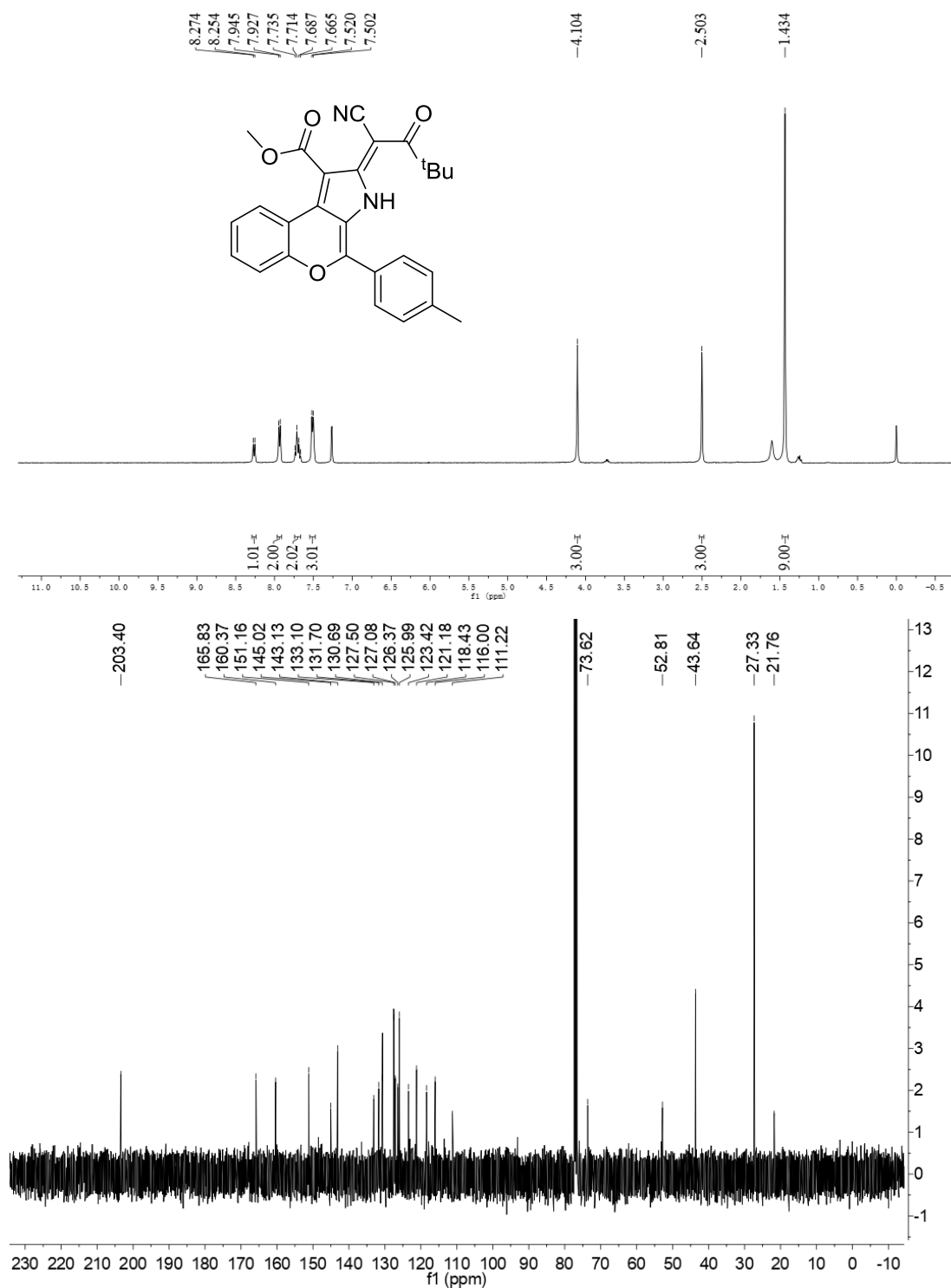
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-6-ethoxy-4-(3-methoxyphenyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4b): red solid, 0.137g, 55%, m.p. 223~224 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.75~7.73 (m, 1H, ArH), 7.69~7.67 (m, 1H, ArH), 7.62~7.58 (m, 2H, ArH), 7.42~7.38 (m, 1H, ArH), 7.18~7.15 (m, 2H, ArH), 4.25 (q, *J* = 6.8 Hz, 2H, OCH₂), 4.10 (s, 3H, OCH₃), 3.99 (s, 3H, OCH₃), 1.57 (t, *J* = 6.8 Hz, 3H, CH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.4, 165.8, 160.5, 160.4, 148.6, 143.8, 141.6, 133.3, 131.3, 131.0, 126.2, 123.7, 121.1, 120.0, 119.1, 116.8, 116.6, 113.4, 111.6, 111.3, 73.7, 64.9, 55.5, 52.8, 43.6, 27.3 (3C), 14.7; IR (KBr) ν: 3424, 2983, 2201, 1753, 1433, 842 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₉H₂₉N₂O₆ ([M+H]⁺): 501.2020. Found: 501.2012.



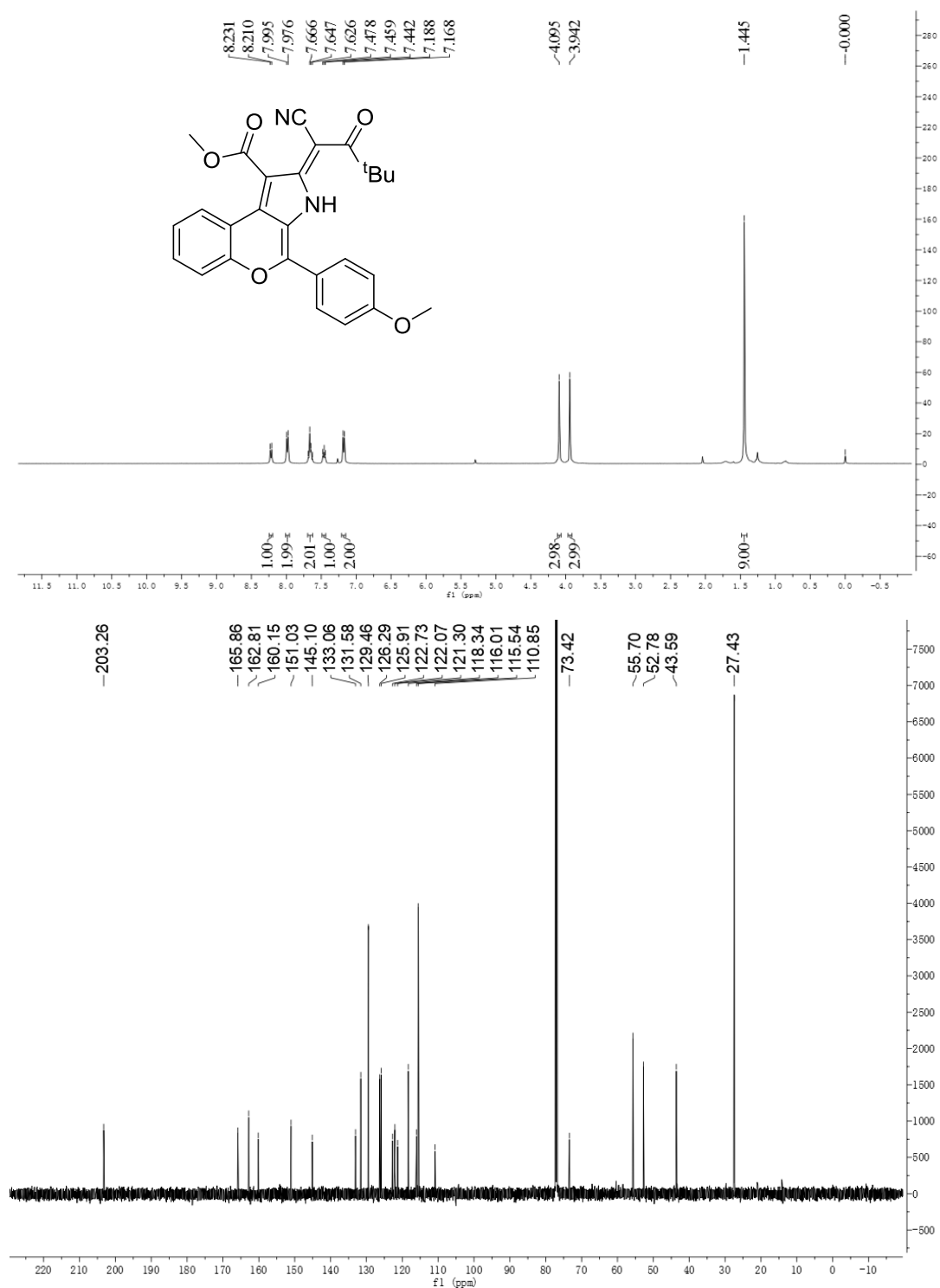
Ethyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-phenyl-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4c): red solid, 0.158g, 72%, m.p. 196~198 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.31~8.29 (m, 1H, ArH), 8.04~8.02 (m, 2H, ArH), 7.73~7.62 (m, 5H, ArH), 7.53~7.49 (m, 1H, ArH), 4.59 (q, *J* = 7.2 Hz, 2H, OCH₂), 1.48 (t, *J* = 7.2 Hz, 3H, CH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.5, 165.2, 160.5, 151.2, 144.3, 133.0, 132.0, 131.7, 129.9, 127.5, 126.4, 126.0, 123.7, 120.8, 118.4, 116.0, 111.9, 109.9, 73.9, 62.3, 43.6, 27.2 (3C), 13.9; IR (KBr) ν: 3429, 2876, 2195, 1763, 1409, 937 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₇H₂₄N₂O₄Na ([M+Na]⁺): 463.1628. Found: 463.1624.



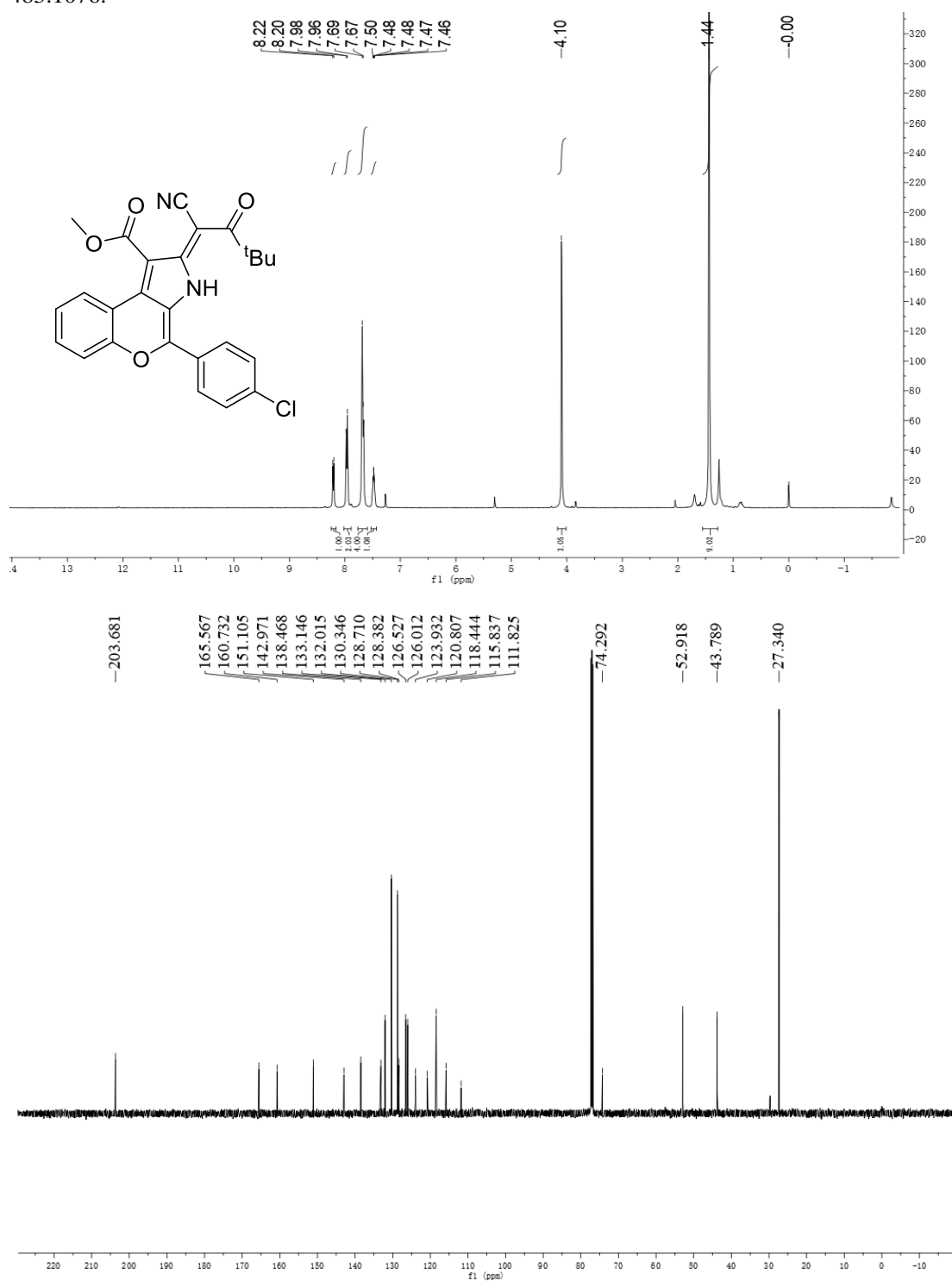
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4d): red solid, 0.170g, 77%, m.p. 194~196 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.27~8.25 (m, 1H, ArH), 7.94~7.93 (m, 2H, ArH), 7.74~7.67 (m, 2H, ArH), 7.52~7.50 (m, 3H, ArH), 4.10 (s, 3H, OCH₃), 2.50 (s, 3H, CH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, DMSO-*d*₆) δ: 203.4, 165.8, 160.3, 151.1, 145.0, 143.1, 133.0, 131.6, 130.7, 127.5, 127.0, 126.3, 125.9, 123.4, 121.1, 118.4, 116.0, 111.2, 73.6, 52.8, 43.6, 27.3, 21.7; IR (KBr) ν: 3426, 2956, 2210, 1786, 1480, 860 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₇H₂₄N₂O₄Na ([M+Na]⁺): 463.1628. Found: 463.1627.



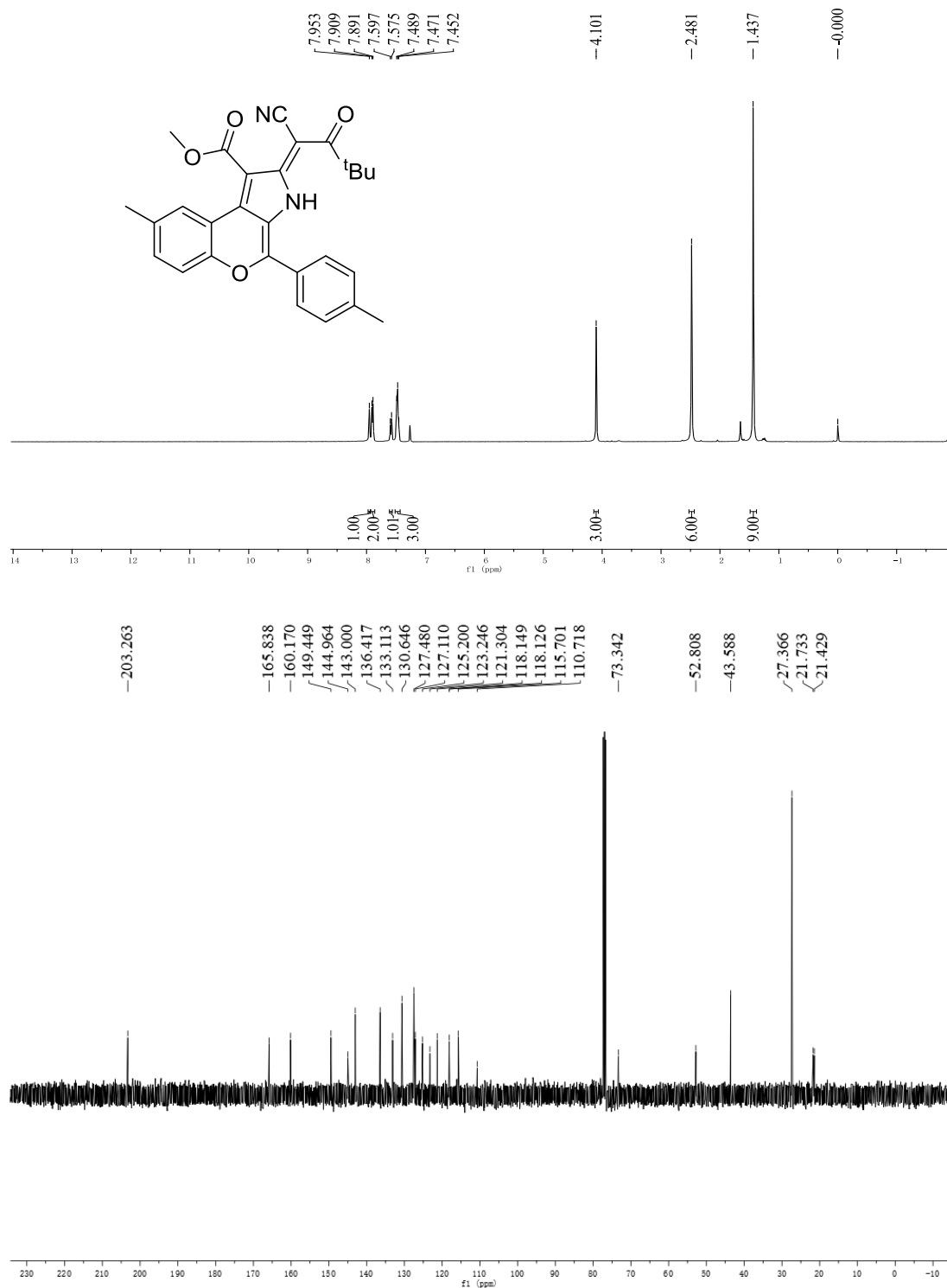
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-(4-methoxyphenyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4e): red solid, 0.148g, 65%, m.p. 195~197 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.23~8.21 (m, 1H, ArH), 7.99~7.97 (m, 2H, ArH), 7.67~7.63 (m, 2H, ArH), 7.48~7.44 (m, 1H, ArH), 7.19~7.17 (m, 2H, ArH), 4.10 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 1.45 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.2, 165.8, 162.8, 160.1, 151.0, 145.1, 133.0, 131.6, 129.4, 126.3, 125.9, 122.7, 122.0, 121.3, 118.3, 116.0, 115.5, 110.8, 73.4, 55.7, 52.8, 43.6, 27.4 (3C); IR (KBr) ν: 3429, 2960, 2198, 1756, 1463, 873 cm⁻¹. MS (m/z): HRMS (ESI) Calcd. for C₂₇H₂₅N₂O₅ ([M+H]⁺): 457.1758. Found: 457.1756.



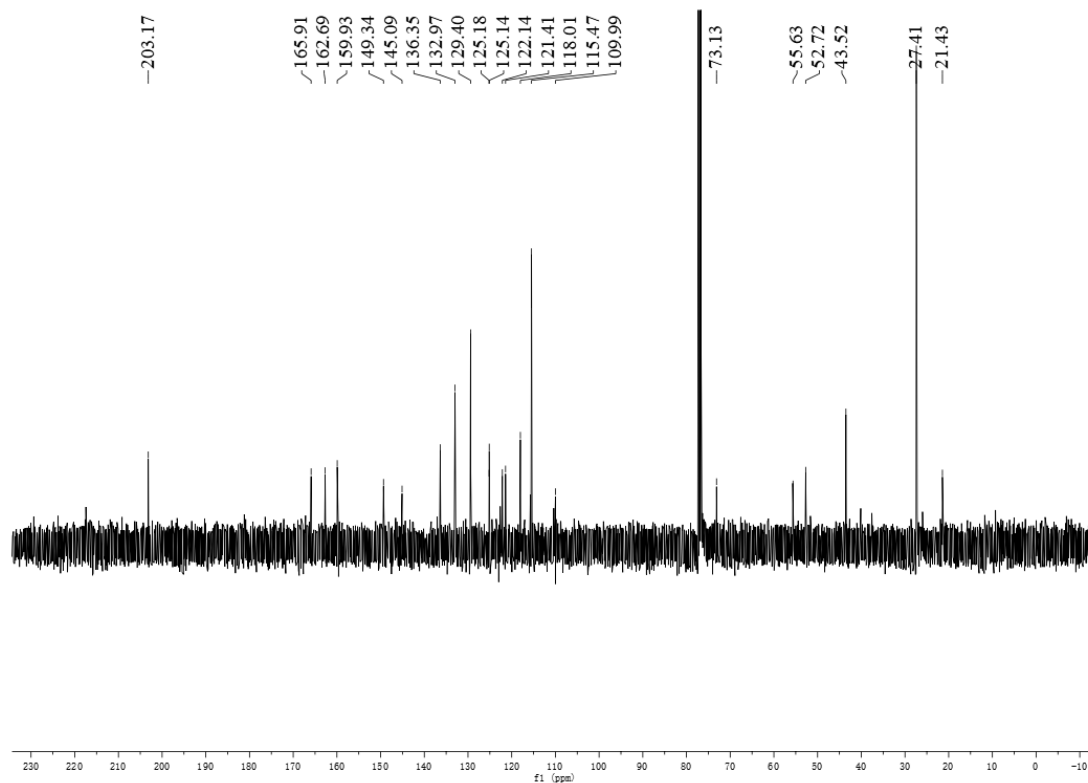
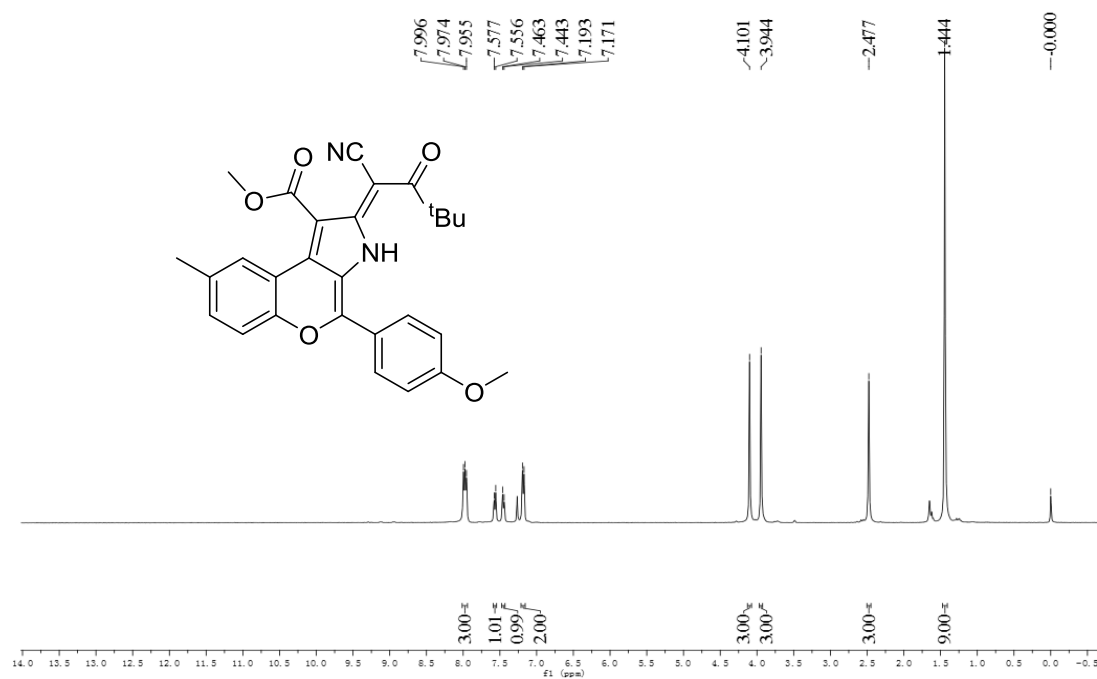
Methyl (Z)-4-(4-chlorophenyl)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4f): red solid, 0.153g, 67%, m.p. 196~198 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.22~8.20 (m, 1H, ArH), 7.98~7.96 (m, 2H, ArH), 7.69~7.67 (m, 4H, ArH), 7.50~7.46 (m, 1H, ArH), 4.10 (s, 3H, OCH₃), 1.44 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.6, 165.5, 160.7, 151.1, 142.9, 138.4, 133.1, 132.0, 130.3, 128.7, 128.3, 126.5, 126.0, 123.9, 120.8, 118.4, 115.8, 111.8, 74.2, 52.9, 43.7, 27.3 (3C); IR (KBr) ν: 3429, 2965, 2194, 1675, 1430, 828 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₁ClN₂O₄Na ([M+Na]⁺): 483.1082. Found: 483.1076.



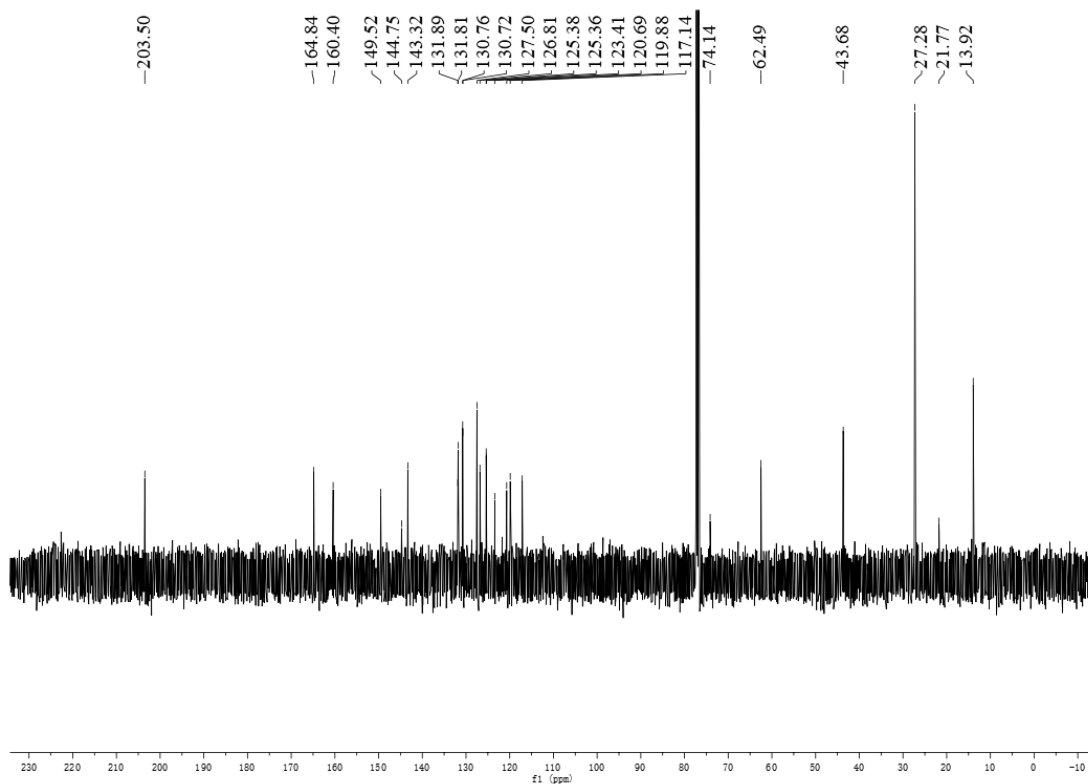
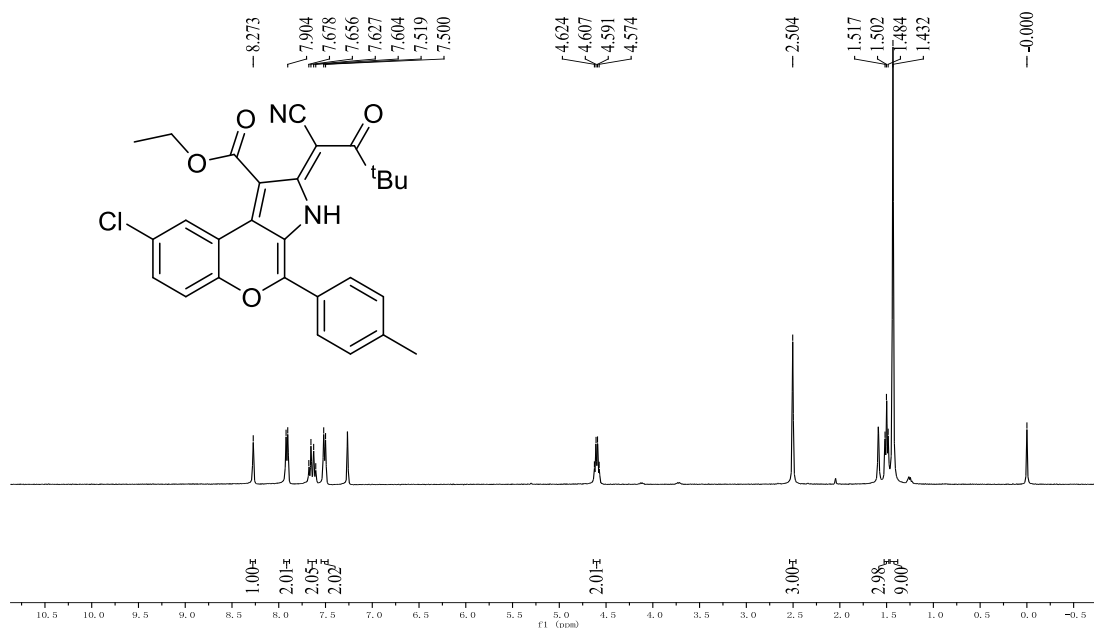
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-8-methyl-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4g): red solid, 0.195g, 88%, m.p. 238~239 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (s, 1H, ArH), 7.91~7.89 (m, 2H, ArH), 7.60~7.58 (m, 1H, ArH), 7.49~7.45 (m, 3H, ArH), 4.10 (s, 3H, OCH₃), 2.48 (s, 6H, CH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.2, 165.8, 160.1, 149.4, 144.9, 143.0, 136.4, 133.1, 130.6, 127.4, 127.1, 125.2, 123.2, 121.3, 118.1, 118.1, 115.7, 110.7, 73.3, 52.8, 43.5, 27.3 (3C), 21.7, 21.4; IR (KBr) ν: 3429, 2976, 2196, 1708, 1496, 796 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₈H₂₆N₂O₄Na ([M+Na]⁺): 477.1785. Found: 477.1780.



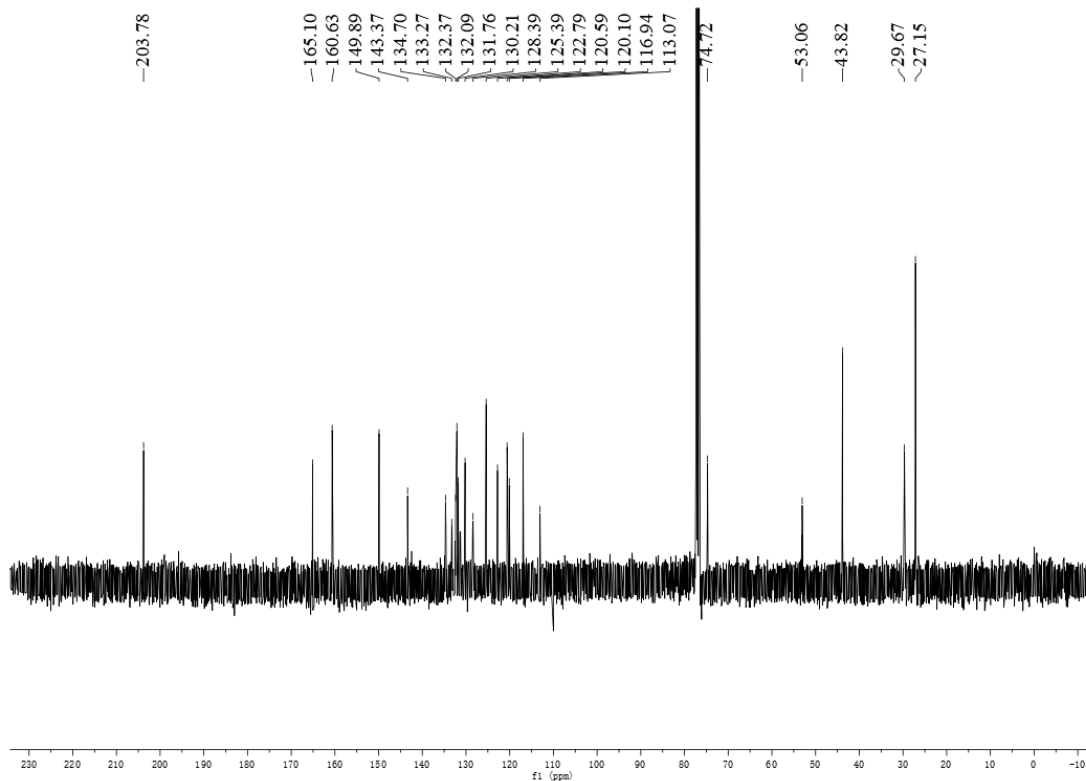
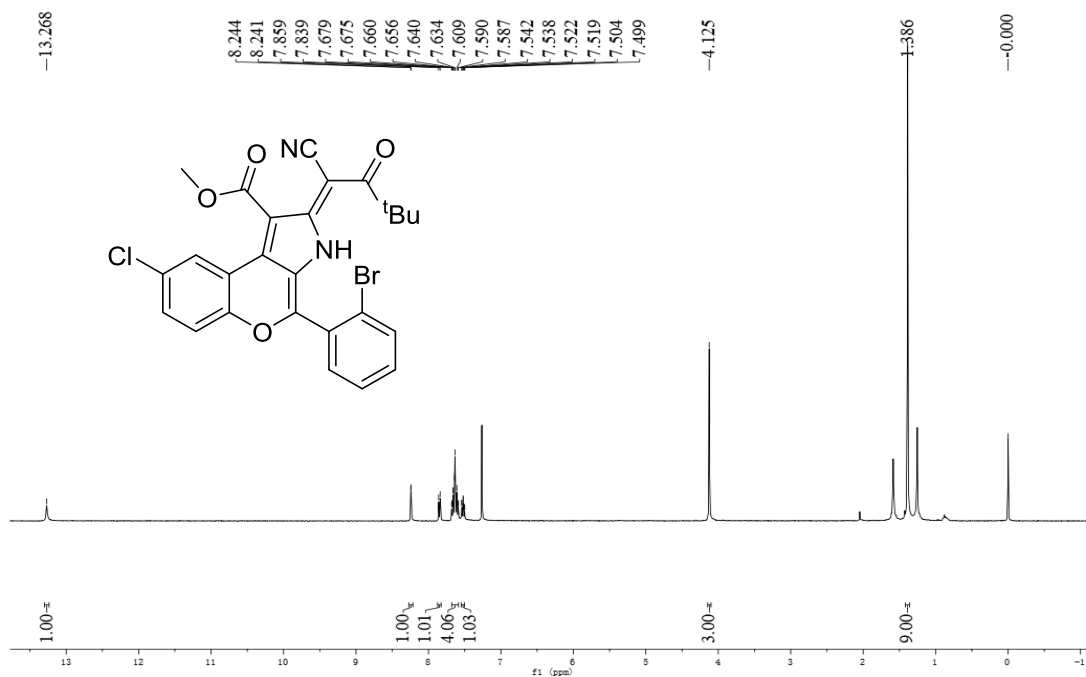
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-(4-methoxyphenyl)-8-methyl-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4h): red solid, 0.195g, 84%, m.p. 170~171 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.99~7.96 (m, 3H, ArH), 7.57 (d, *J* = 8.0 Hz, 1H, ArH), 7.45 (d, *J* = 8.0 Hz, 1H, ArH), 7.19~7.17 (m, 2H, ArH), 4.10 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 2.48 (s, 3H, CH₃), 1.44 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.1, 165.9, 162.6, 159.9, 149.3, 145.0, 136.3, 132.9, 129.4, 125.1, 125.1, 122.1, 121.4, 118.0, 115.4, 109.9, 73.1, 55.6, 52.7, 43.5, 27.4(3C), 21.4; IR (KBr) ν: 3430, 3185, 2198, 1706, 1483, 809 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₈H₂₆N₂O₅Na ([M+Na]⁺): 493.1734. Found: 493.1722.



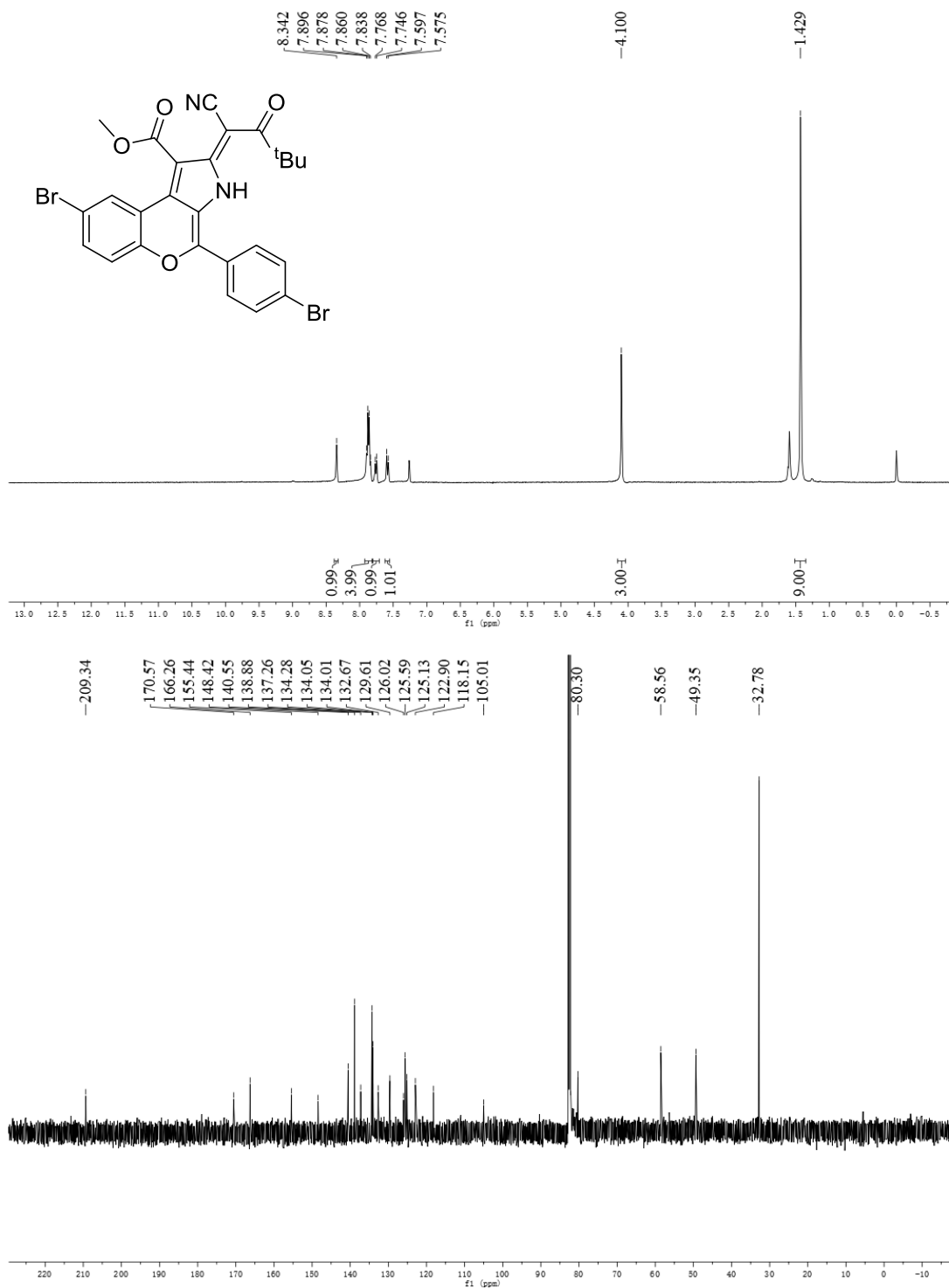
Ethyl (Z)-8-chloro-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4i): red solid, 0.196g, 80.3%, m.p. 185~186 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.27 (s, 1H, ArH), 7.91 (d, *J* = 7.6 Hz, 2H, ArH), 7.68~7.60 (m, 2H, ArH), 7.51 (d, *J* = 7.6 Hz, 2H, ArH), 4.60 (q, *J* = 6.8 Hz, 2H, OCH₂), 2.50 (s, 3H, CH₃), 1.50 (t, *J* = 6.8 Hz, 3H, CH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.5, 164.8, 160.4, 149.5, 144.7, 143.3, 131.8, 131.8, 130.7, 130.7, 127.4, 126.8, 125.3, 125.3, 123.4, 120.6, 119.8, 117.1, 74.1, 62.4, 43.6, 27.2(3C), 21.7, 13.9; IR (KBr) ν: 3437, 3111, 2950, 2194, 1709, 1399, 807 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₈H₂₅ClN₂O₄Na ([M+Na]⁺): 511.1395. Found: 511.1390.



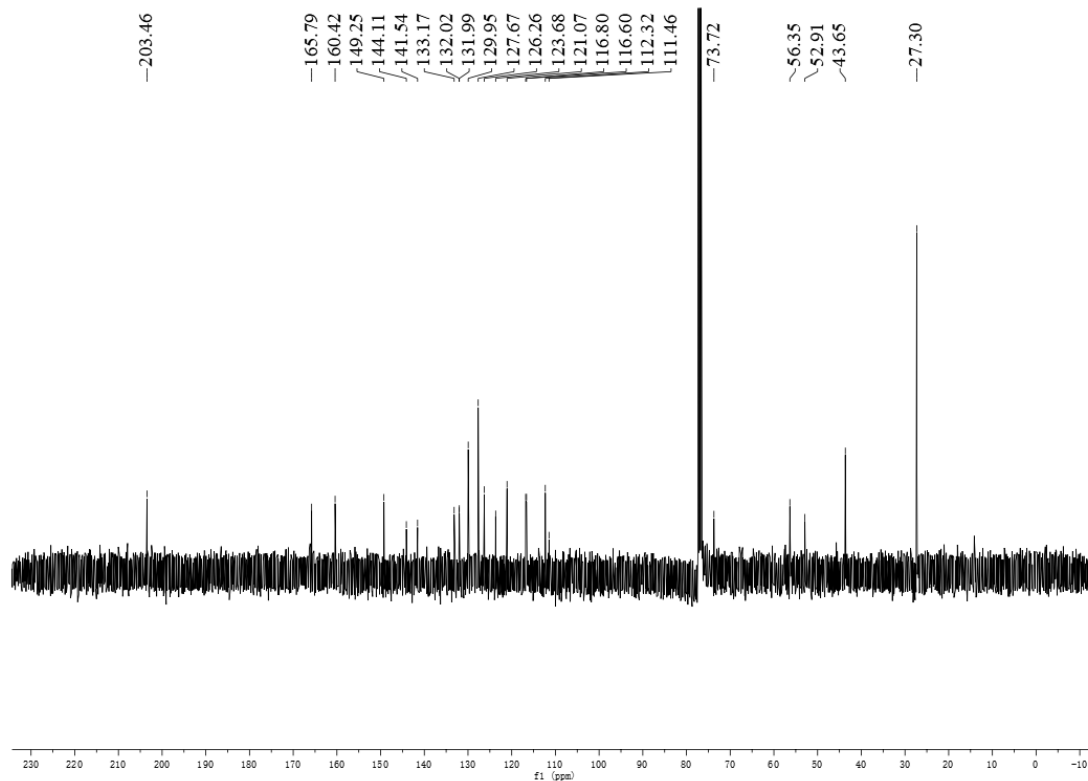
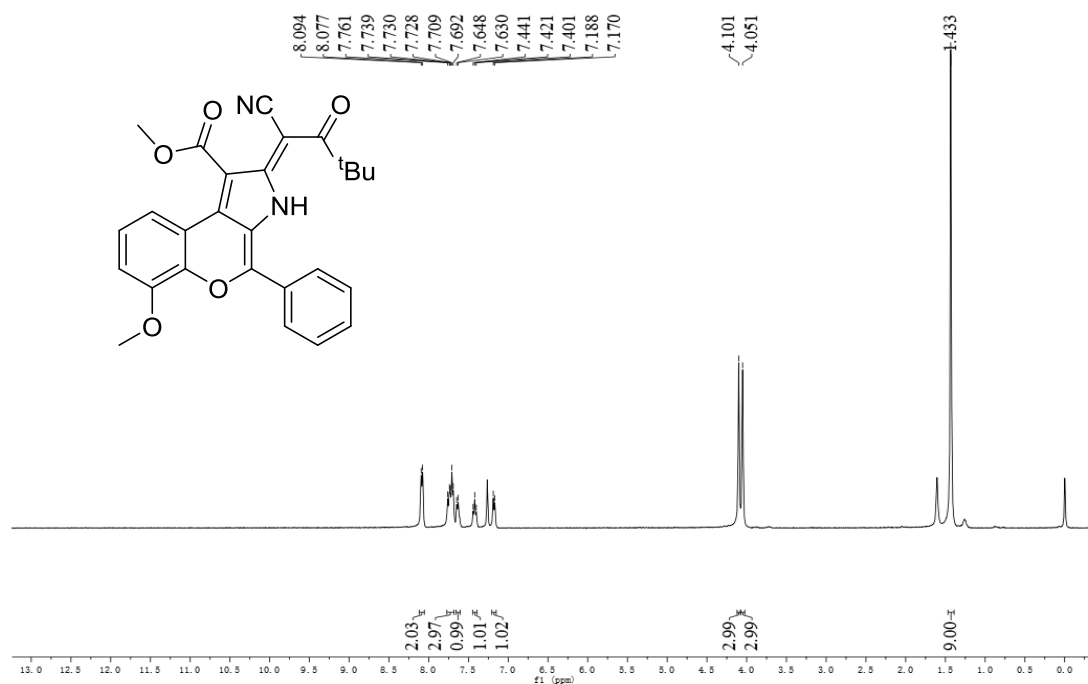
Methyl (Z)-4-(2-bromophenyl)-8-chloro-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4j): red solid, 0.178g, 33%, m.p. 161~162 °C; ¹H NMR (400 MHz, CDCl₃) δ: 13.27 (s, 1H, NH), 8.24~8.24 (m, 1H, ArH), 7.86~7.84 (m, 1H, ArH), 7.68~7.59 (m, 4H, ArH), 7.54~7.50 (m, 1H, ArH), 4.12 (s, 3H, OCH₃), 1.39 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.7, 165.1, 160.6, 149.8, 143.3, 134.6, 133.2, 132.3, 132.0, 131.7, 130.2, 128.3, 125.3, 122.7, 120.5, 120.1, 116.9, 113.0, 74.7, 53.0, 43.8, 29.6, 27.1 (3C); IR (KBr) ν: 3501, 2976, 2196, 1739, 896 cm⁻¹. MS (m/z): HRMS (ESI) Calcd. for C₂₆H₂₀BrClN₂O₄Na ([M+Na]⁺): 561.0187. Found: 561.0180.



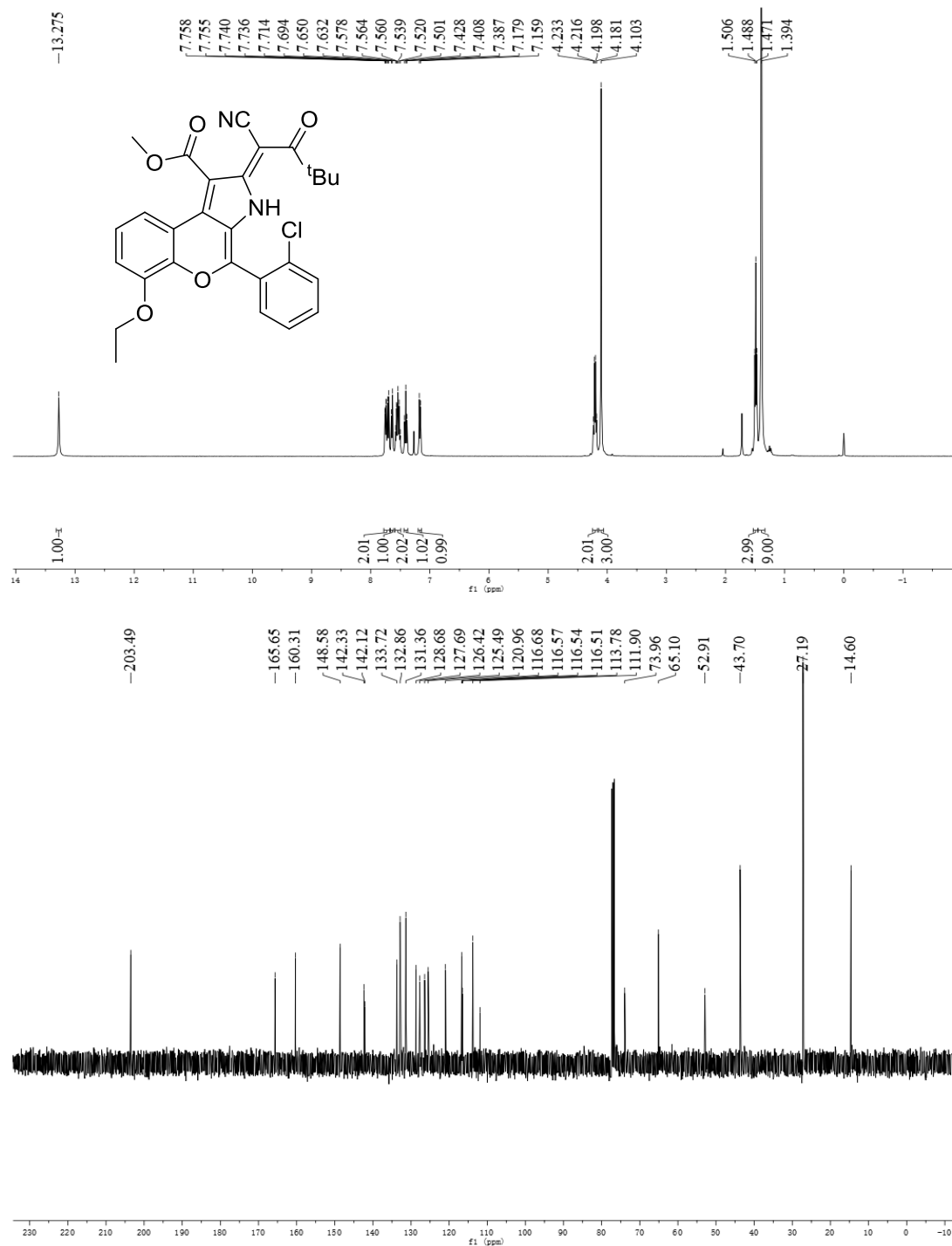
Methyl (Z)-8-bromo-4-(4-bromophenyl)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4k): red solid, 0.166g, 57%, m.p. 200~201 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.34 (s, 1H, ArH), 7.90~7.84 (m, 4H, ArH), 7.77~7.75 (m, 1H, ArH), 7.60~7.58 (m, 1H, ArH), 4.10 (s, 3H, OCH_3), 1.43 (s, 9H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ : 209.3, 170.5, 166.2, 155.4, 148.4, 140.5, 138.8, 137.2, 134.2, 134.0, 134.0, 132.6, 129.6, 126.0, 125.5, 125.1, 122.9, 118.1, 105.0, 80.2, 58.5, 49.3, 32.7 (3C); IR (KBr) ν : 3449, 2894, 2193, 1762, 1424, 853 cm^{-1} . MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{20}\text{Br}_2\text{N}_2\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 604.9682. Found: 604.9670.



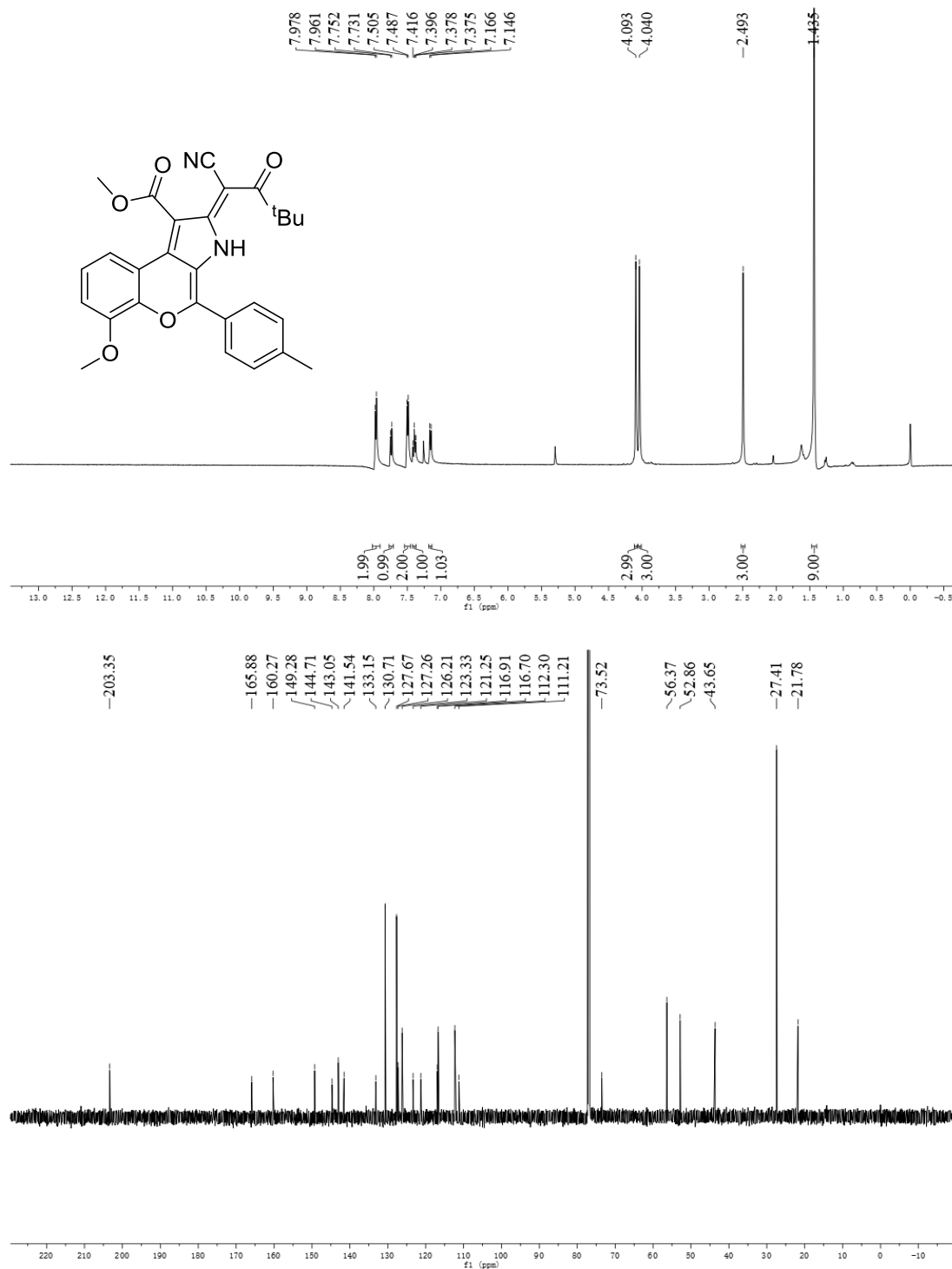
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-6-methoxy-4-phenyl-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4I): red solid, 0.176g, 77%, m.p. 220~221 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.09~8.08 (m, 2H, ArH), 7.76~7.69 (m, 3H, ArH), 7.65~7.63 (m, 1H, ArH), 7.44~7.40 (m, 1H, ArH), 7.19~7.17 (m, 1H, ArH), 4.10 (s, 3H, OCH₃), 4.05 (s, 3H, OCH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.4, 165.7, 160.4, 149.2, 144.1, 141.5, 133.1, 132.0, 131.9, 129.9, 127.6, 126.2, 123.6, 121.0, 116.8, 116.6, 112.3, 111.4, 73.7, 56.3, 52.9, 43.6, 27.3 (3C); IR (KBr) ν: 3429, 2990, 2205, 1728, 1430, 796 cm⁻¹. MS (m/z): HRMS (ESI) Calcd. for C₂₇H₂₄N₂O₅Na ([M+Na]⁺): 479.1577. Found: 479.1575.



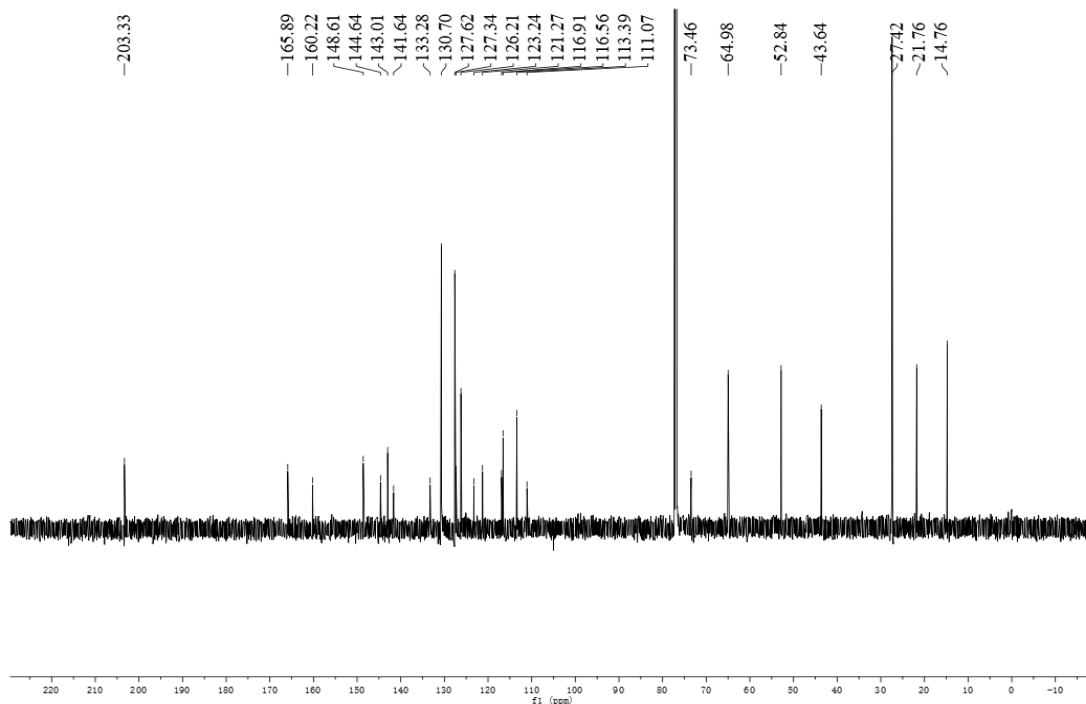
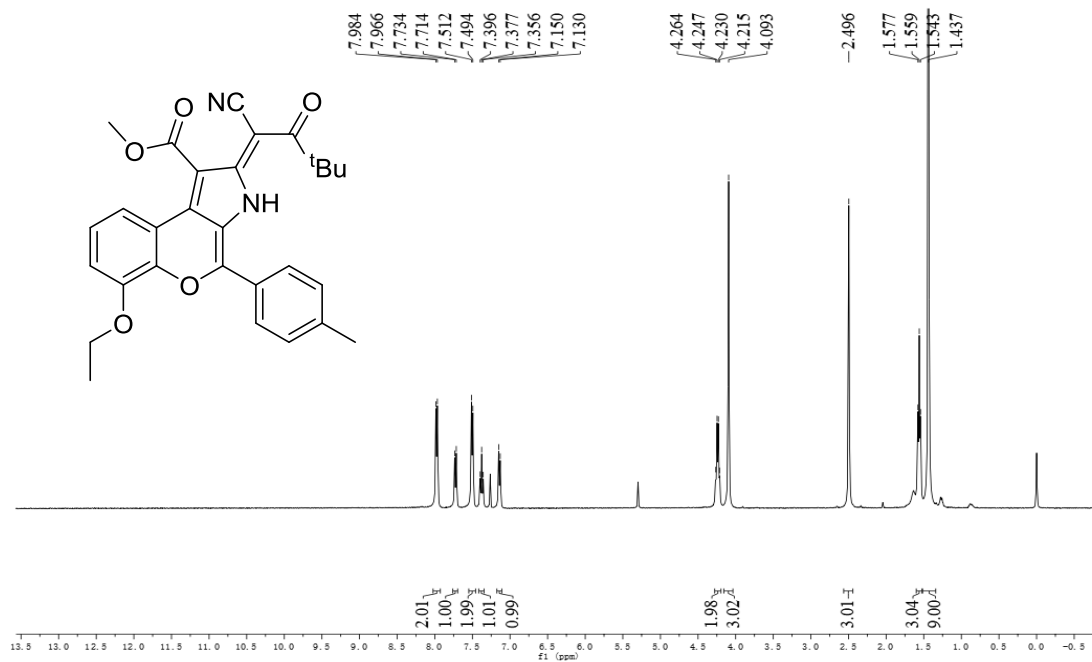
Methyl (Z)-4-(2-chlorophenyl)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-6-ethoxy-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4m): red solid, 0.243g, 48%, m.p. 236~237 °C; ¹H NMR (400 MHz, CDCl₃) δ: 13.28 (s, 1H, NH), 7.76~7.69 (m, 2H, ArH), 7.65~7.63 (m, 1H, ArH), 7.58~7.50 (m, 2H, ArH), 7.43~7.39 (m, 1H, ArH), 7.18~7.16 (m, 1H, ArH), 4.21 (q, *J* = 6.8 Hz, 2H, OCH₂), 4.10 (s, 3H, OCH₃), 1.49 (t, *J* = 6.8 Hz, 3H, CH₃), 1.39 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.4, 165.6, 160.3, 148.5, 142.3, 142.1, 133.7, 132.8, 131.3, 128.6, 127.6, 126.4, 125.4, 120.9, 116.6, 116.5, 116.5, 116.5, 113.7, 111.9, 73.9, 65.1, 52.9, 43.7, 27.1 (3C), 14.6; IR (KBr) ν: 3500, 2934, 2190, 1758, 1422, 815 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₈H₂₅ClN₂O₅Na ([M+Na]⁺): 527.1344. Found: 527.1338.



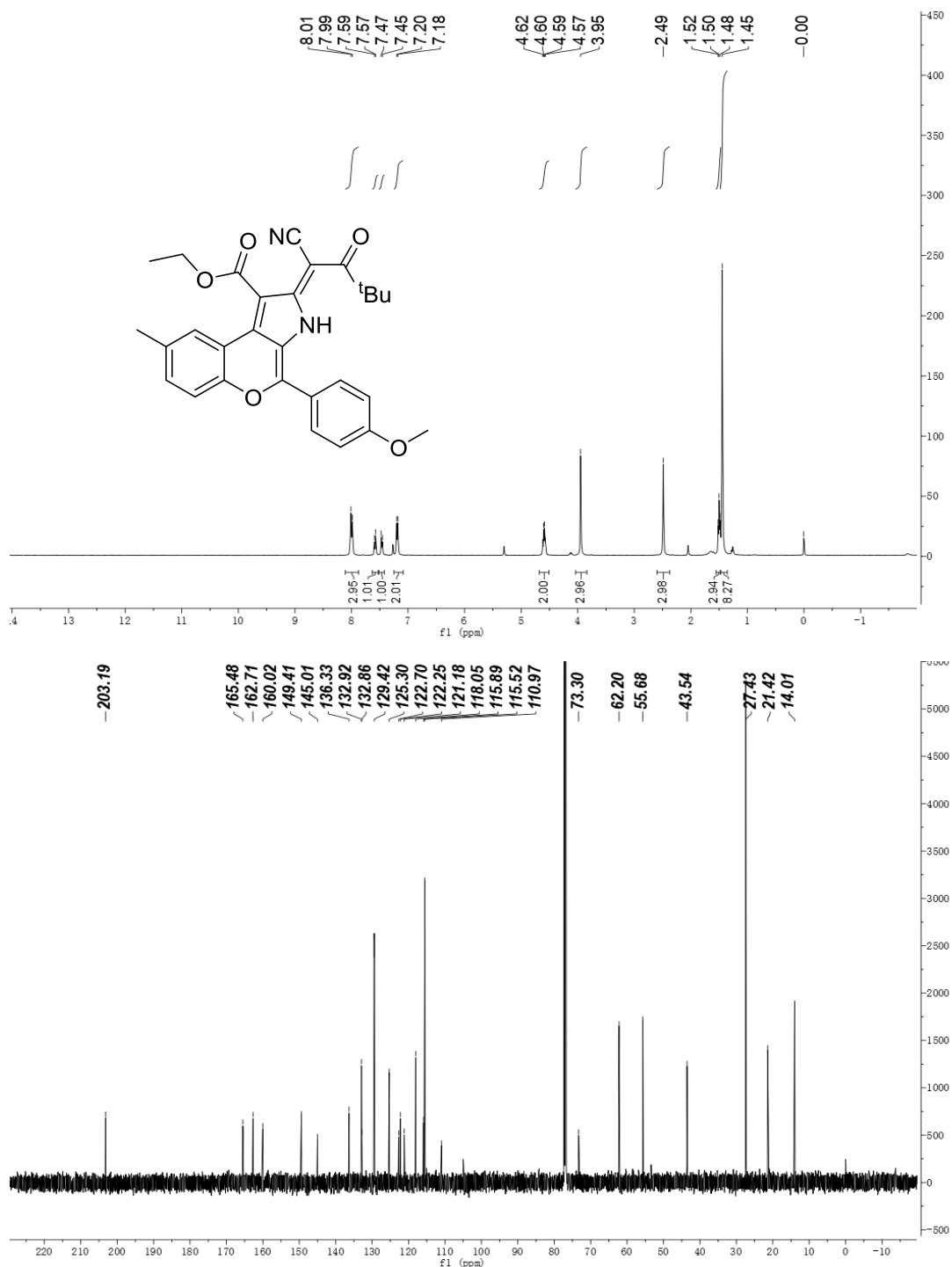
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-6-methoxy-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4n): red solid, 0.195g, 83%, m.p. 2776~279 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.98~7.96 (m, 2H, ArH), 7.75~7.73 (m, 1H, ArH), 7.50~7.48 (m, 2H, ArH), 7.42~7.38 (m, 1H, ArH), 7.17~7.15 (m, 1H, ArH), 4.09 (s, 3H, OCH₃), 4.04 (s, 3H, OCH₃), 2.49 (s, 3H, CH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.3, 165.8, 160.2, 149.2, 144.7, 143.0, 141.5, 133.1, 130.7, 127.6, 127.2, 126.2, 123.3, 121.2, 116.9, 116.7, 112.3, 111.2, 73.5, 56.3, 52.8, 43.6, 27.4 (3C), 21.7; IR (KBr) ν: 3426, 2953, 2190, 1756, 1429, 851 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₈H₂₆N₂O₅Na ([M+Na]⁺): 493.1734. Found: 493.1733.



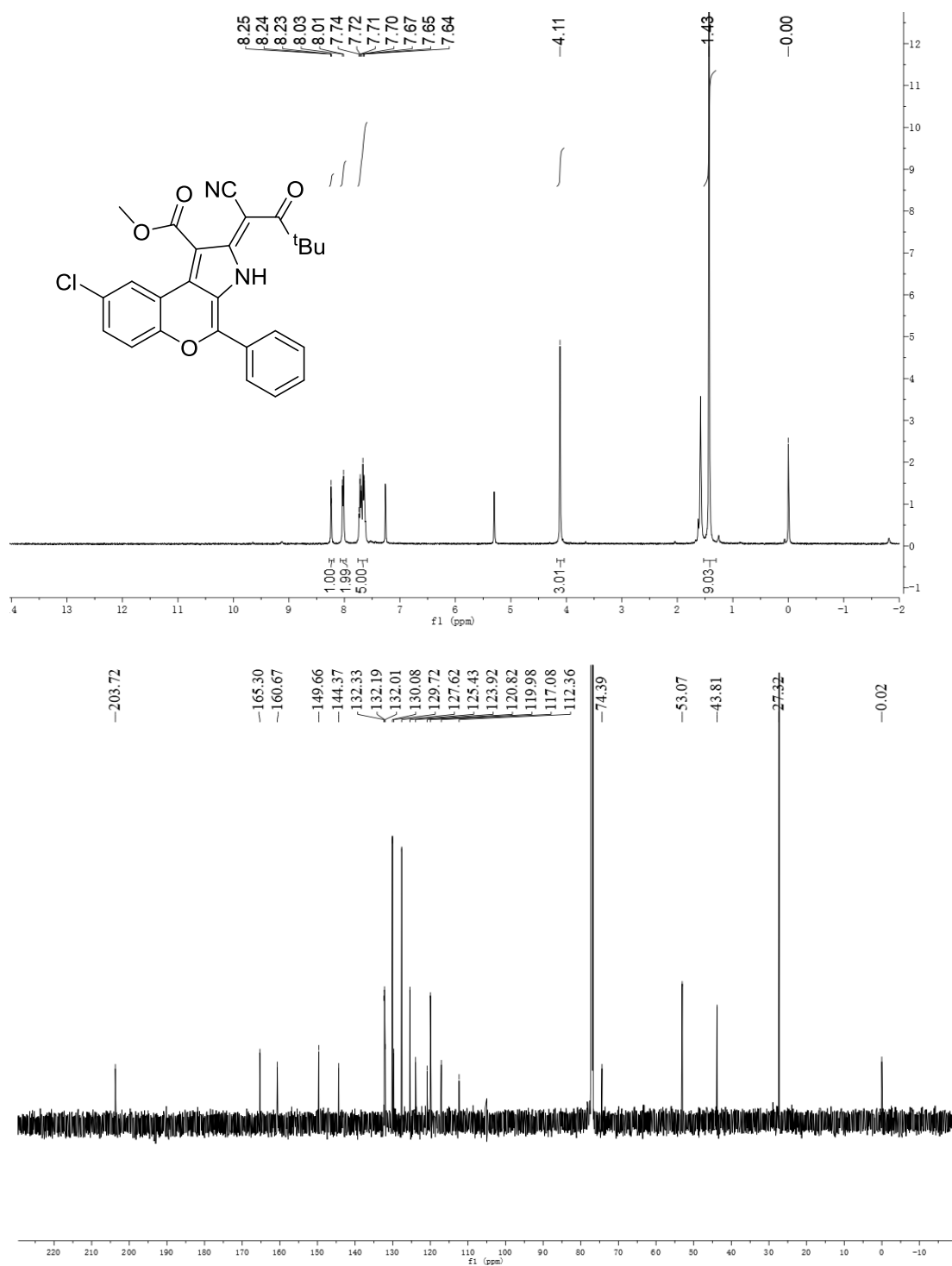
Methyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-6-ethoxy-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4o): red solid, 0.142g, 59%, m.p. 239~240 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.97 (d, *J* = 7.2 Hz, 2H, ArH), 7.73~7.71 (m, 1H, ArH), 7.50 (d, *J* = 7.2 Hz, 2H, ArH), 7.40~7.36 (m, 1H, ArH), 7.15~7.13 (m, 1H, ArH), 4.24 (q, *J* = 6.8 Hz, 2H, OCH₂), 4.09 (s, 3H, OCH₃), 2.50 (s, 3H, CH₃), 1.56 (t, *J* = 6.8 Hz, 3H, CH₃), 1.44 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.3, 165.8, 160.2, 148.6, 144.6, 143.0, 141.6, 133.2, 130.6, 127.6, 127.3, 126.2, 123.2, 121.2, 116.9, 116.5, 113.3, 111.0, 73.4, 64.9, 52.8, 43.6, 27.4 (3C), 21.7, 14.7; IR (KBr) ν: 3425, 2961, 2198, 1752, 1425, 808 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₉H₂₈N₂O₅Na ([M+Na]⁺): 507.1890. Found: 507.1889.



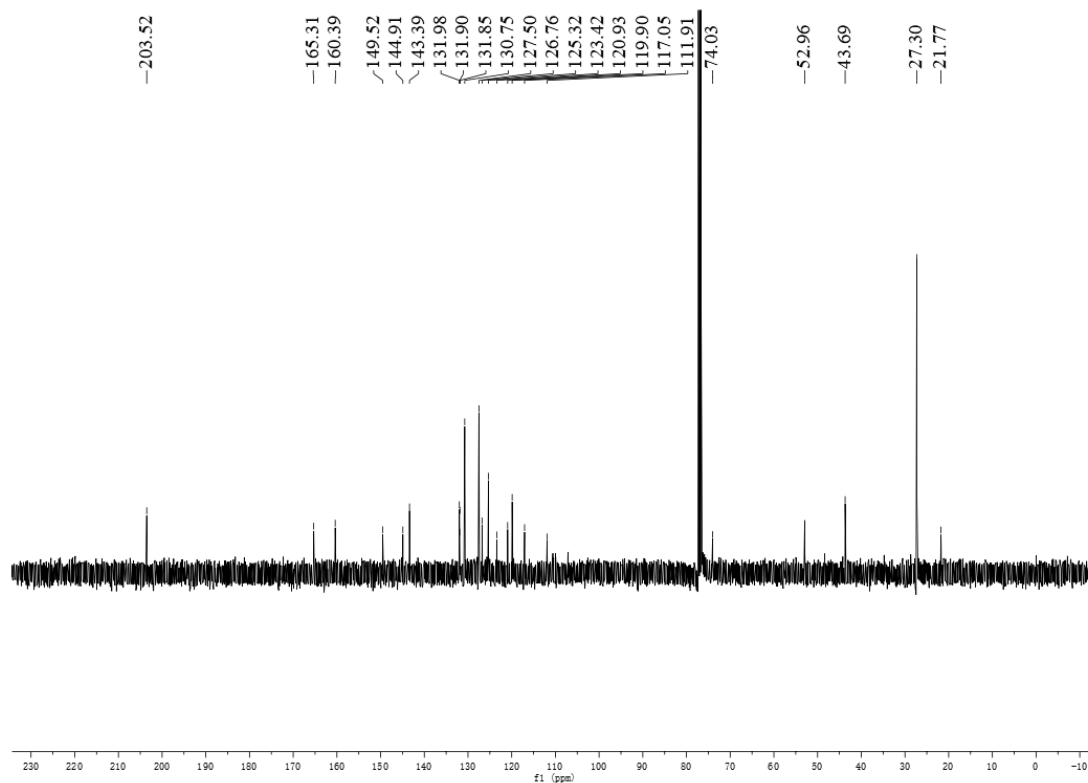
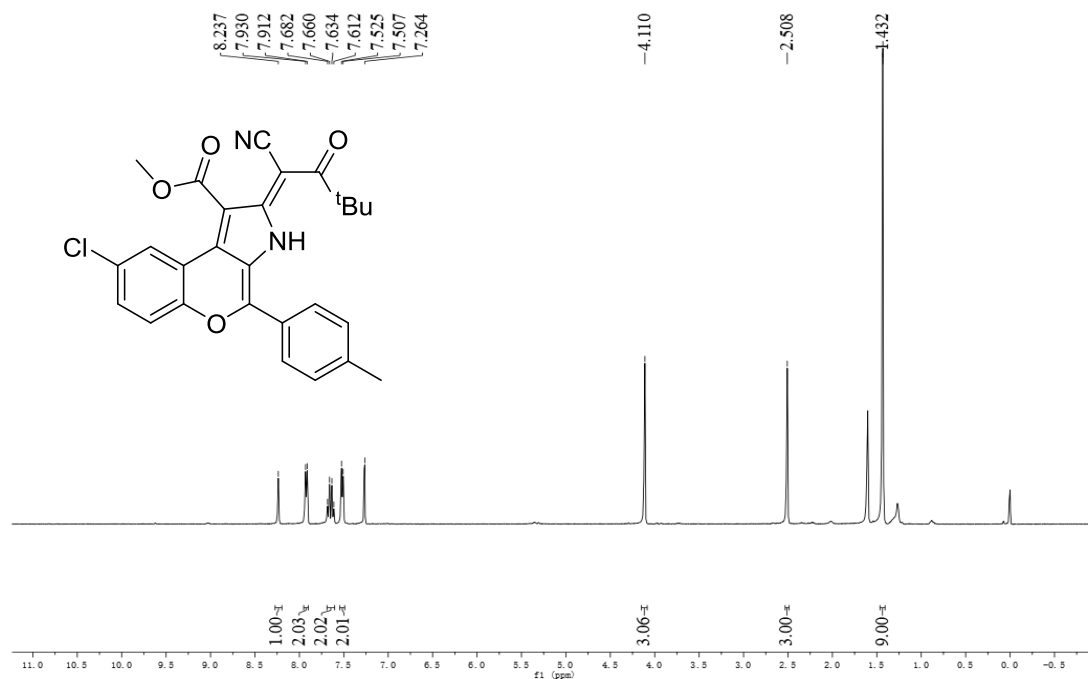
Ethyl (Z)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-(4-methoxyphenyl)-8-methyl-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4p): red solid, 0.185g, 76%, m.p. 170~172 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.01~7.98 (m, 3H, ArH), 8.01~7.98 (m, 3H, ArH), 7.59~7.57 (m, 1H, ArH), 7.47~7.45 (m, 1H, ArH), 7.20~7.18 (m, 2H, ArH), 4.59 (q, *J* = 6.4 Hz, 2H, OCH₂), 3.95 (s, 3H, OCH₃), 2.49 (s, 3H, CH₃), 1.49 (t, *J* = 6.4 Hz, 3H, CH₃), 1.44 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.2, 165.5, 162.7, 160.0, 149.4, 145.0, 136.3, 132.9, 132.8, 129.4, 125.3, 122.7, 122.2, 121.2, 118.0, 115.9, 115.5, 110.9, 73.3, 62.2, 55.7, 43.5, 27.4 (3C), 21.4, 14.0; IR (KBr) ν: 3431, 2956, 2197, 1752, 1430, 830 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₉H₂₈N₂O₅Na ([M+Na]⁺): 507.1890. Found: 507.1889.



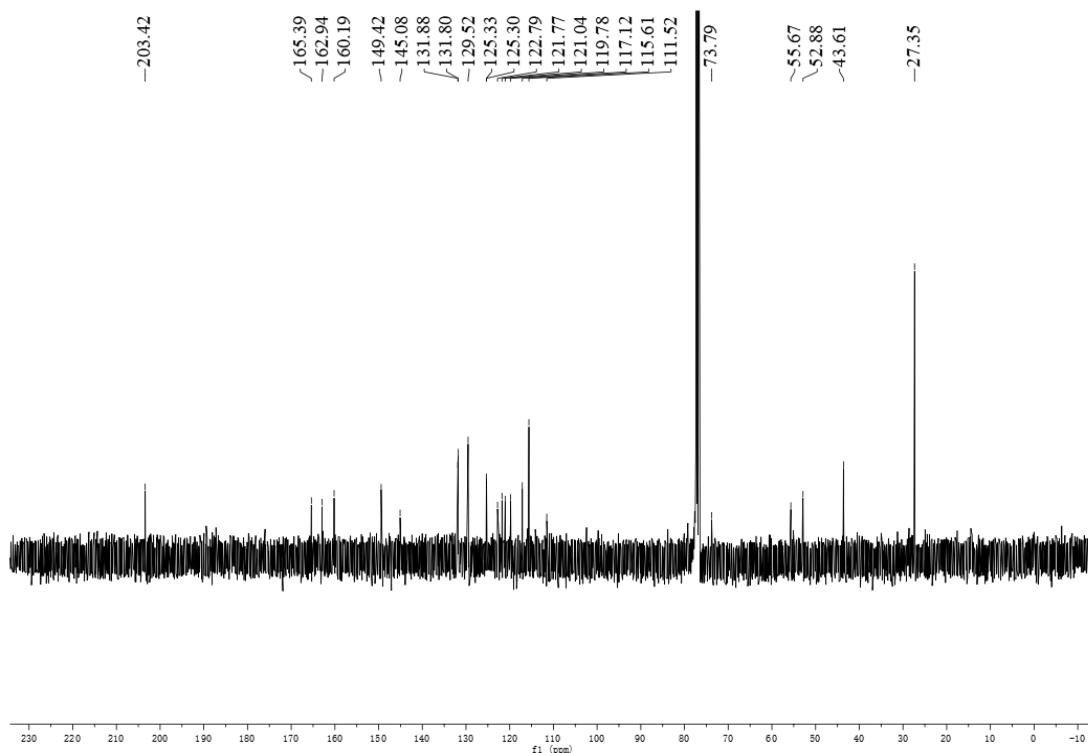
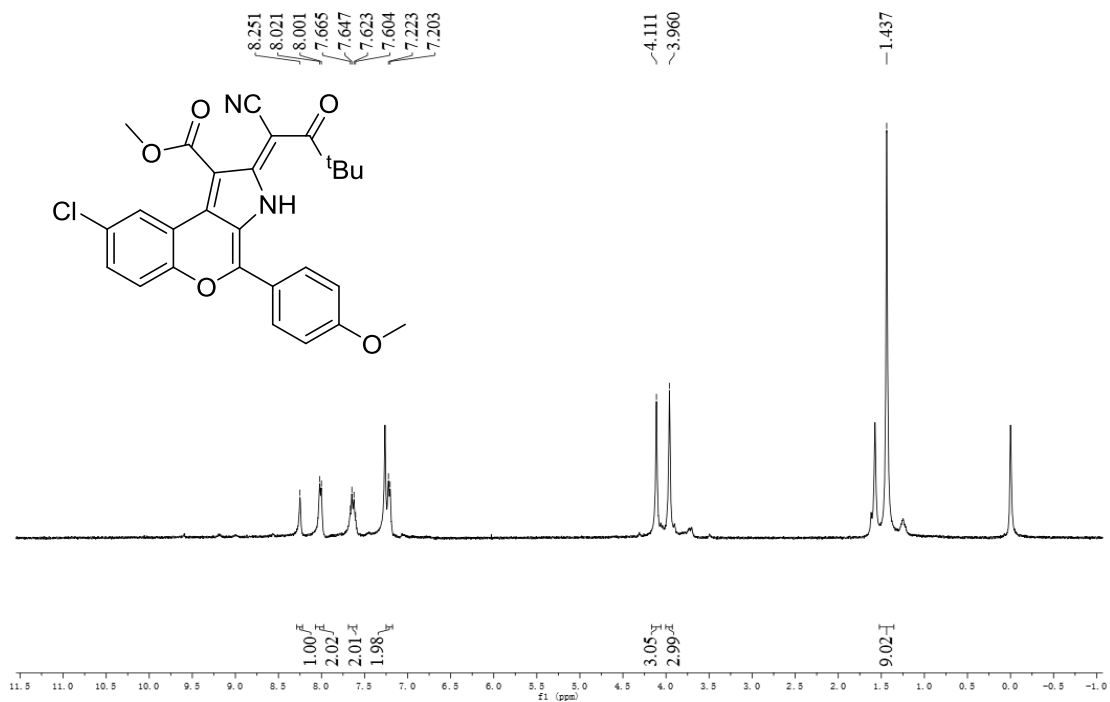
Methyl (Z)-8-chloro-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-phenyl-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4q): red solid, 0.112g, 49%, m.p. 180~181 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.25~8.24 (m, 1H, ArH), 8.03~8.02 (m, 2H, ArH), 7.73~7.62 (m, 5H, ArH), 4.12 (s, 3H, OCH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.7, 165.3, 160.6, 149.6, 144.3, 132.3, 132.1, 132.0, 130.0, 129.7, 127.6, 125.4, 123.9, 120.8, 119.9, 117.0, 112.3, 74.3, 53.0, 43.8, 27.3 (3C); IR (KBr) ν: 3430, 2964, 2192, 1679, 1425, 876 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₁N₂O₄Na ([M+Na]⁺): 483.1082. Found: 483.1080.



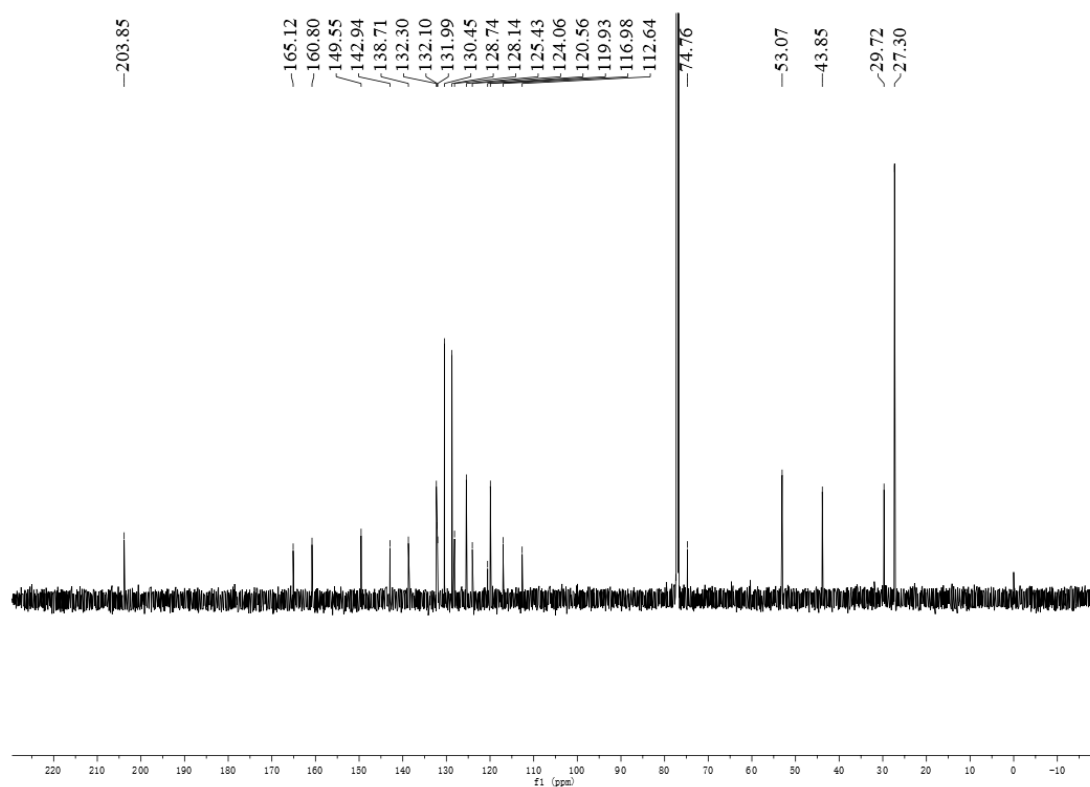
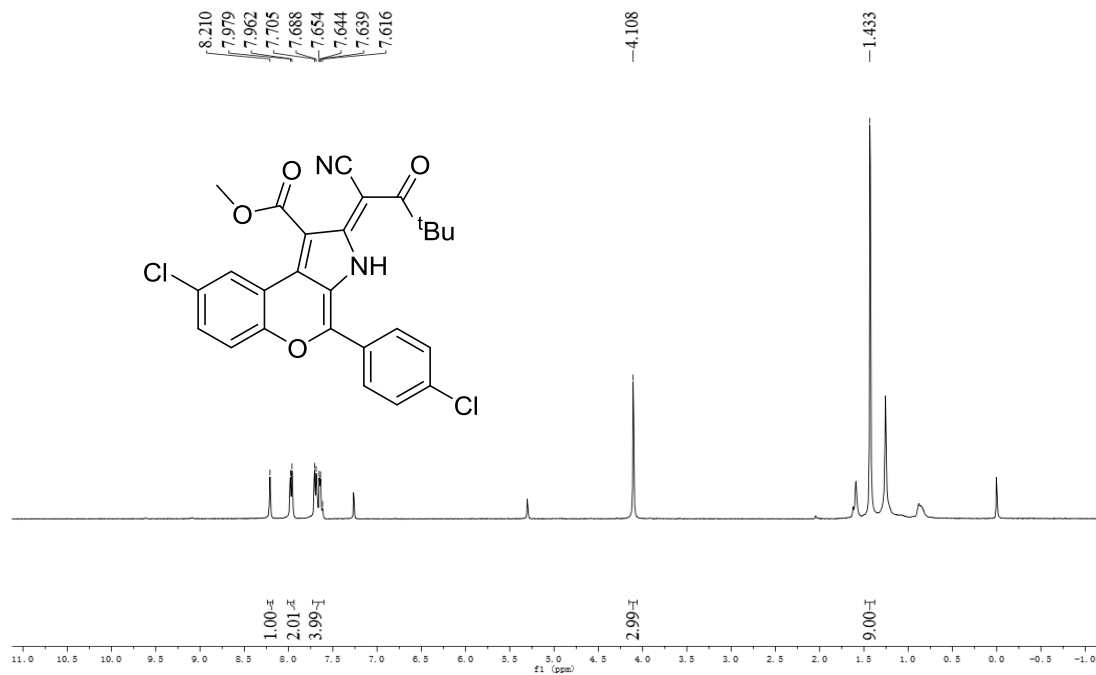
Methyl (Z)-8-chloro-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4r): red solid, 0.201g, 85%, m.p. 181~182 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.24 (s, 1H, ArH), 7.92 (d, *J* = 7.2 Hz, 2H, ArH), 7.68~7.61 (m, 2H, ArH), 7.51 (d, *J* = 7.2 Hz, 2H, ArH), 4.11 (s, 3H, OCH₃), 2.51 (s, 3H, CH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.5, 165.3, 160.3, 149.5, 144.9, 143.3, 131.9, 131.9, 131.8, 130.7, 127.5, 126.7, 125.3, 123.4, 120.9, 119.8, 117.0, 111.9, 74.0, 52.9, 43.6, 27.3 (3C), 21.7; IR (KBr) ν: 3428, 2970, 2180, 1760, 1473, 825 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₇H₂₄ClN₂O₄Na ([M+Na]⁺): 497.1239. Found: 497.1237.



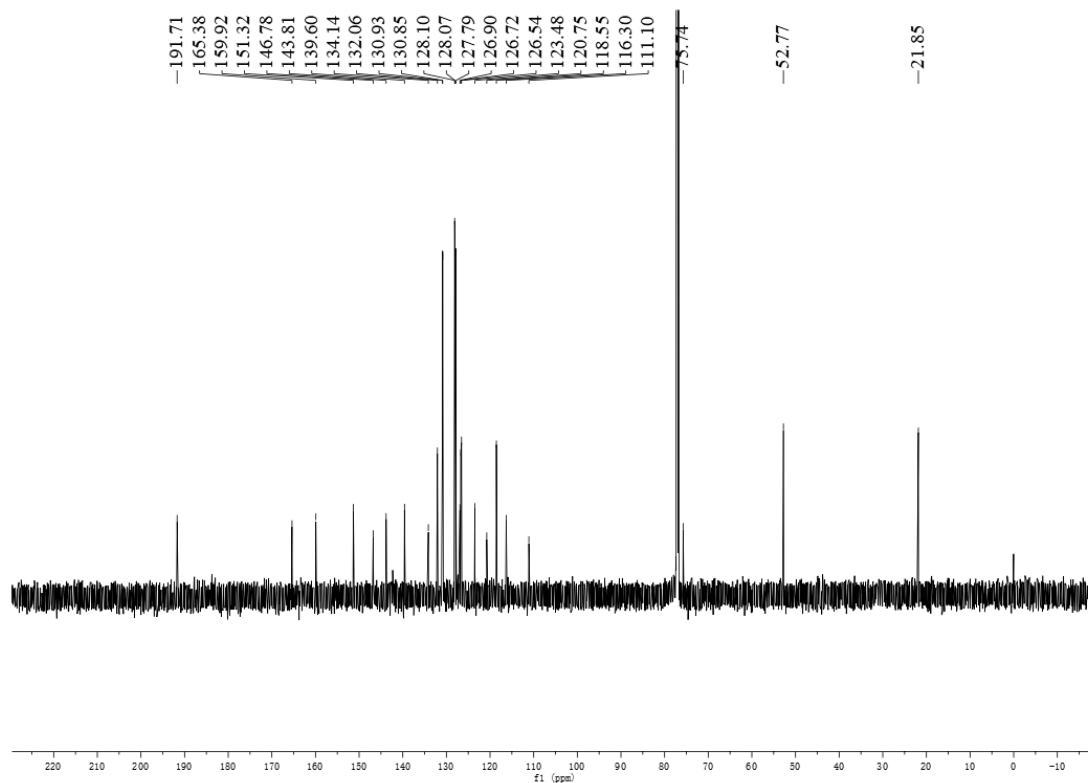
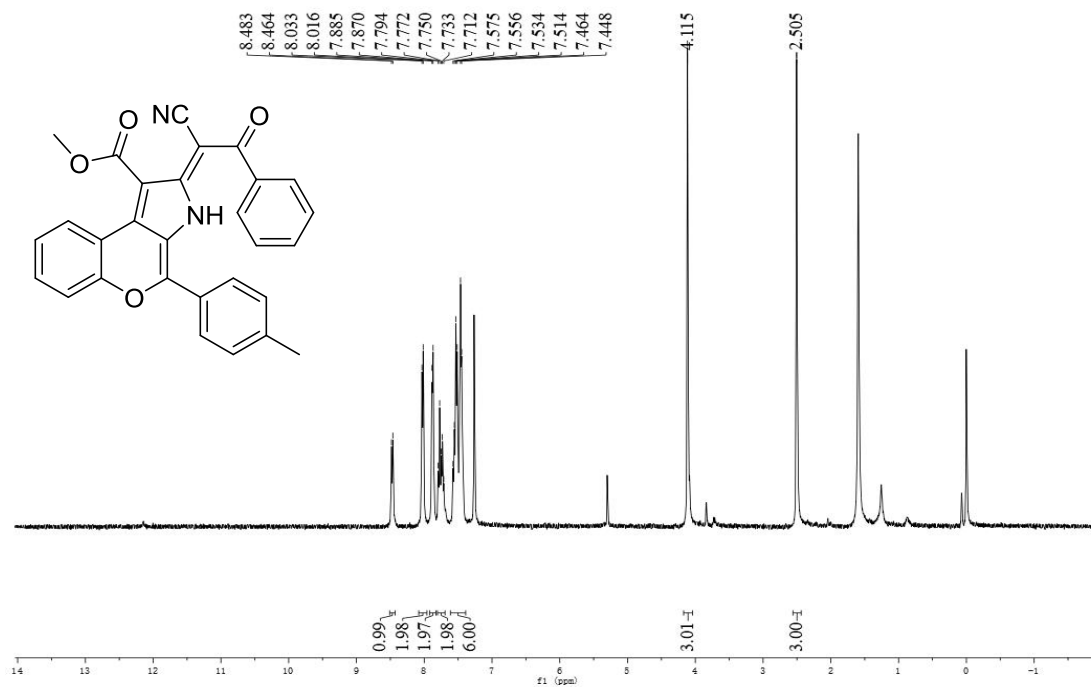
Methyl (Z)-8-chloro-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-4-(4-methoxyphenyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4s): red solid, 0.160g, 65%, m.p. 179~178 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.25 (s, 1H, ArH), 8.02~8.00 (m, 2H, ArH), 7.66~7.60 (m, 2H, ArH), 7.22~7.20 (m, 2H, ArH), 4.11 (s, 3H, OCH₃), 3.96 (s, 3H, OCH₃), 1.44 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ: 203.4, 165.3, 162.9, 160.1, 149.4, 145.0, 131.8, 131.8, 129.5, 125.3, 125.3, 122.7, 121.7, 121.0, 119.7, 117.1, 115.6, 111.5, 73.7, 55.6, 52.8, 43.6, 27.3 (3C); IR (KBr) ν: 3428, 2960, 2198, 1726, 1441, 764 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₇H₂₄ClN₂O₂ ([M+H]⁺): 491.1368. Found: 491.1365.



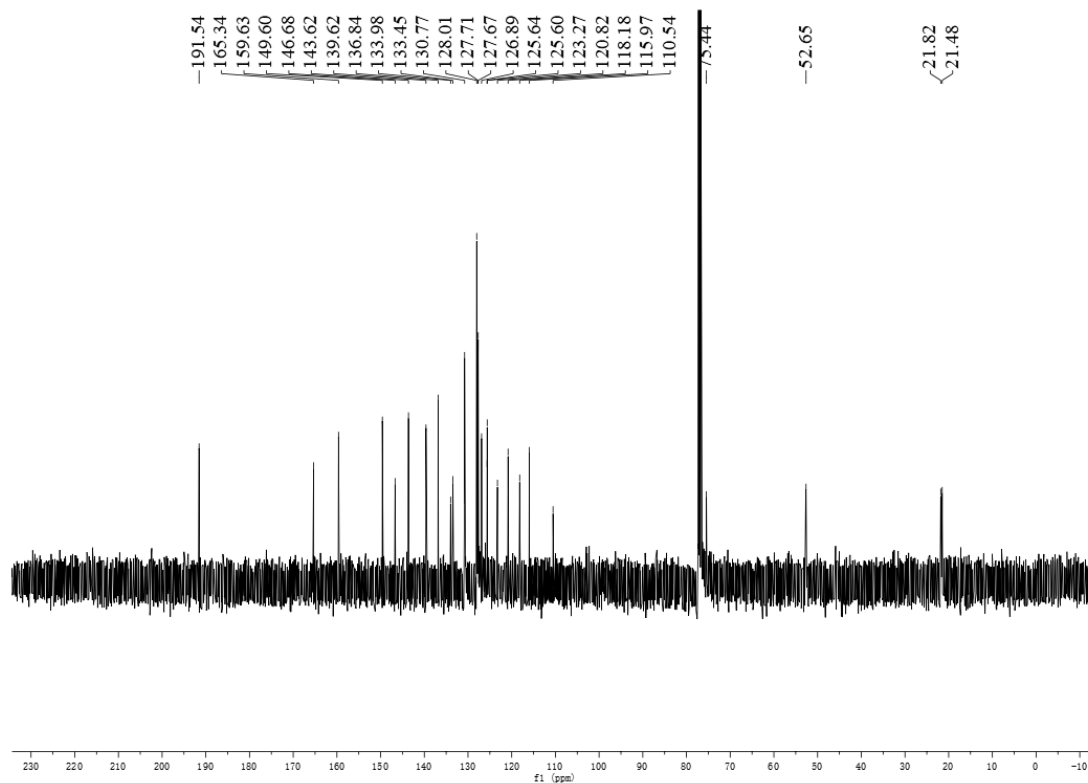
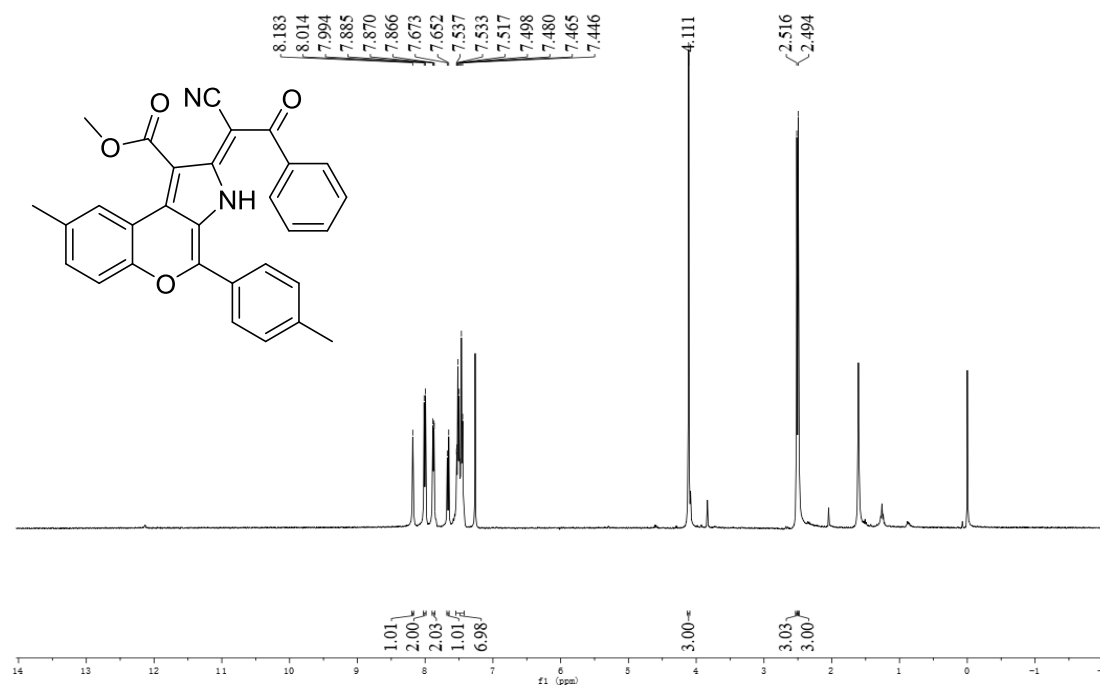
Methyl (Z)-8-chloro-4-(4-chlorophenyl)-2-(1-cyano-3,3-dimethyl-2-oxobutylidene)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (4t): red solid, 0.195g, 79%, m.p. 181~182 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.21 (s, 1H, ArH), 7.98~7.96 (m, 2H, ArH), 7.71~7.62 (m, 4H, ArH), 4.11 (s, 3H, OCH₃), 1.43 (s, 9H, C(CH₃)₃); ¹³C NMR (150 MHz, CDCl₃) δ: 203.8, 165.1, 160.7, 149.5, 142.9, 138.7, 132.3, 132.1, 131.9, 130.4, 128.7, 128.1, 125.4, 124.0, 120.5, 119.9, 116.9, 112.6, 74.7, 53.0, 43.8, 29.7, 27.3 (3C); IR (KBr) ν: 3447, 2903, 2196, 1752, 1428, 877 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₀Cl₂N₂O₄Na ([M+Na]⁺): 517.0692. Found: 517.0693.



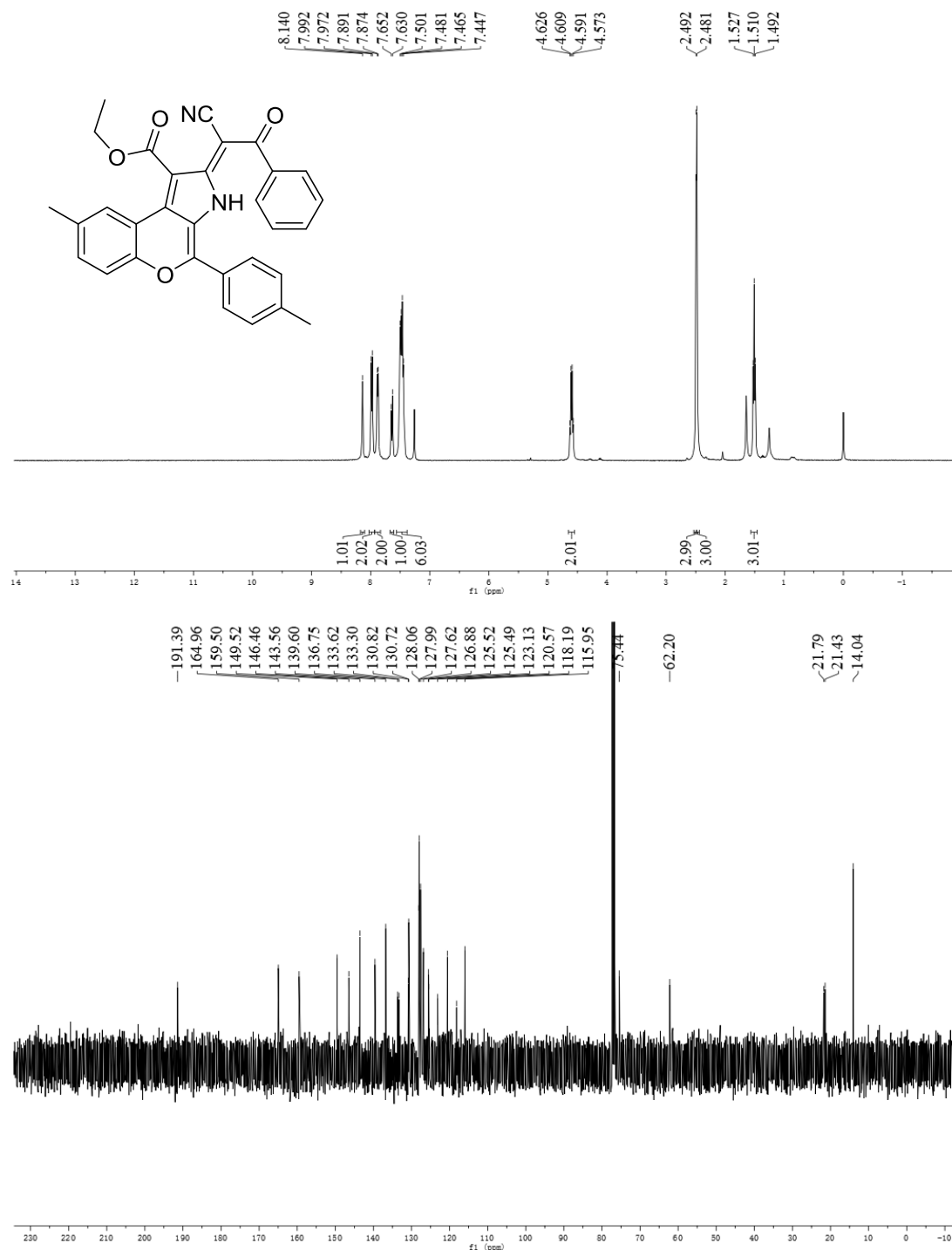
Methyl (Z)-2-(1-cyano-2-oxo-2-phenylethylidene)-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (5a): red solid, 0.139g, 61%, m.p. 209~210 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.48~8.46 (m, 1H, ArH), 8.03~8.02 (m, 2H, ArH), 7.89~7.87 (m, 2H, ArH), 7.79~7.71 (m, 2H, ArH), 7.58~7.45 (m, 6H, ArH), 4.12 (s, 3H, OCH₃), 2.51 (s, 3H, CH₃); ¹³C NMR (150 MHz, CDCl₃) δ: 191.7, 165.3, 159.9, 151.3, 146.7, 143.8, 139.6, 134.1, 132.0, 130.9, 130.8, 128.1, 128.0, 127.7, 126.9, 126.7, 126.5, 123.4, 120.7, 118.5, 116.3, 111.1, 75.7, 52.7, 21.8; IR (KBr) ν: 3429, 2977, 2194, 1740, 1460, 799 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₉H₂₀N₂O₄Na ([M+Na]⁺): 483.1315. Found: 483.1316.



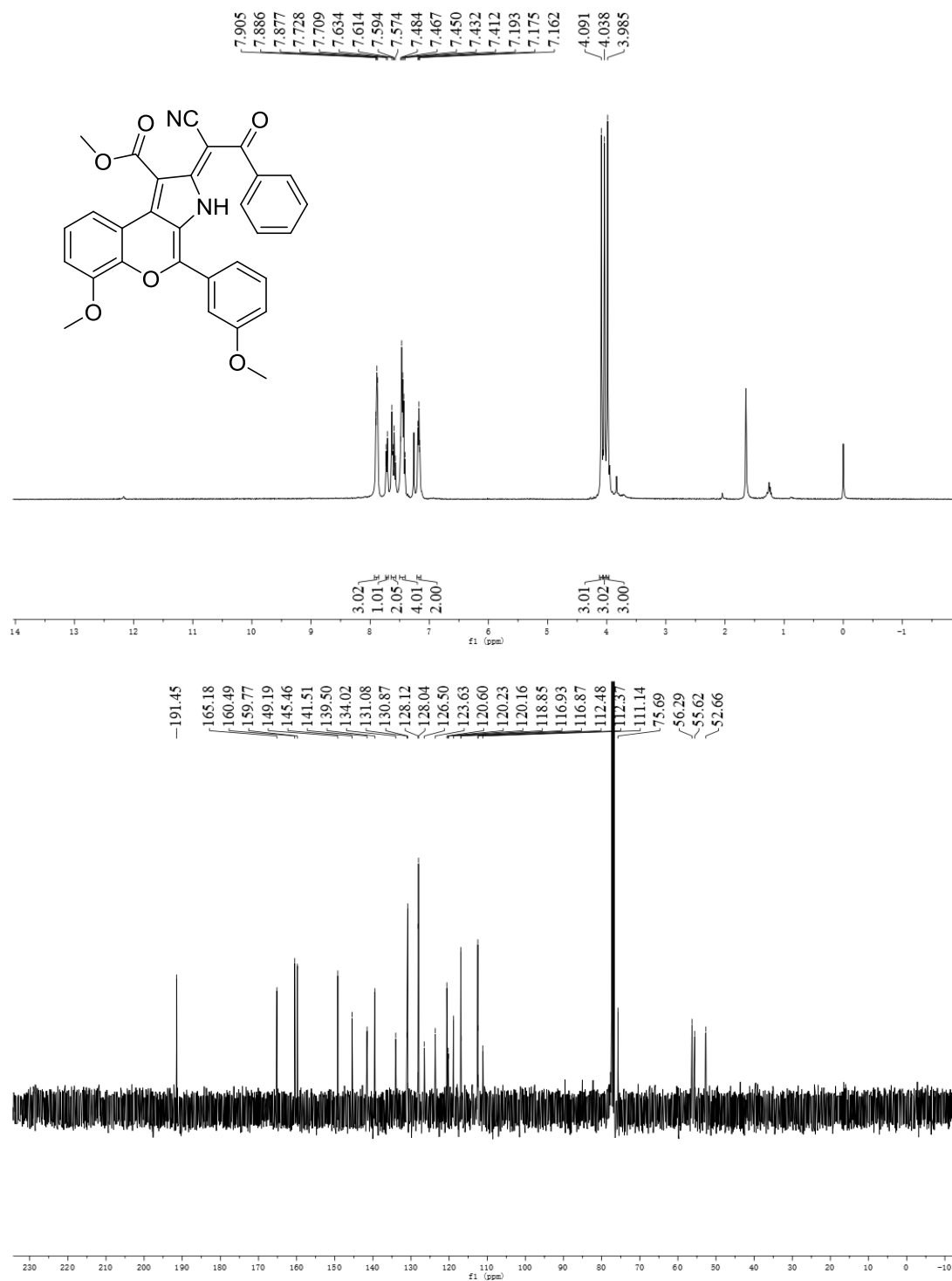
Methyl (Z)-2-(1-cyano-2-oxo-2-phenylethylidene)-8-methyl-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (5b): red solid, 0.144g 61%, m.p. 223~224 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.18 (s, 1H, ArH), 8.01~7.99 (m, 1H, ArH), 7.89~7.87 (m, 2H, ArH), 7.69~7.65 (m, 4H, ArH), 7.54~7.45 (m, 7H, ArH), 4.11 (s, 3H, OCH₃), 2.52 (s, 3H, CH₃), 2.50 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 191.5, 165.3, 159.6, 149.5, 146.6, 143.6, 139.6, 136.8, 133.9, 133.4, 130.7, 128.0, 127.7, 127.6, 126.8, 125.6, 125.6, 123.2, 120.8, 118.1, 115.9, 110.5, 75.4, 52.6, 21.8, 21.4; IR (KBr) ν: 3431, 2950, 2198, 1734, 1450, 850 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₂N₂O₄Na ([M+Na]⁺): 497.1472. Found: 497.1473.



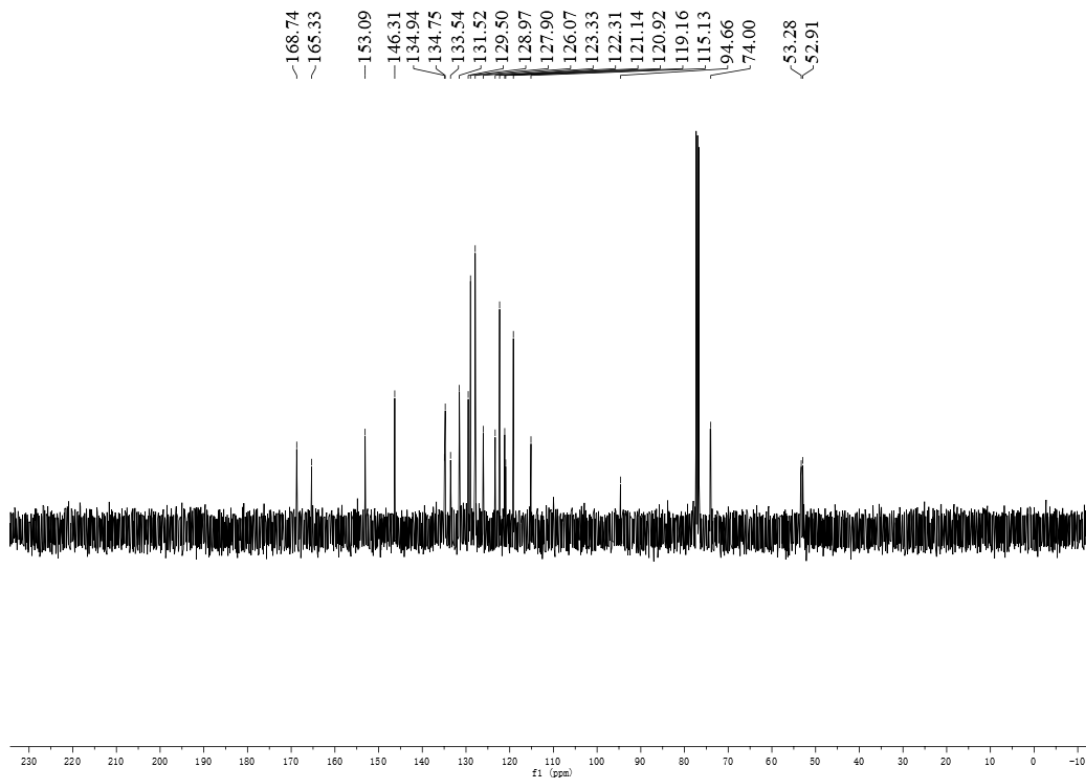
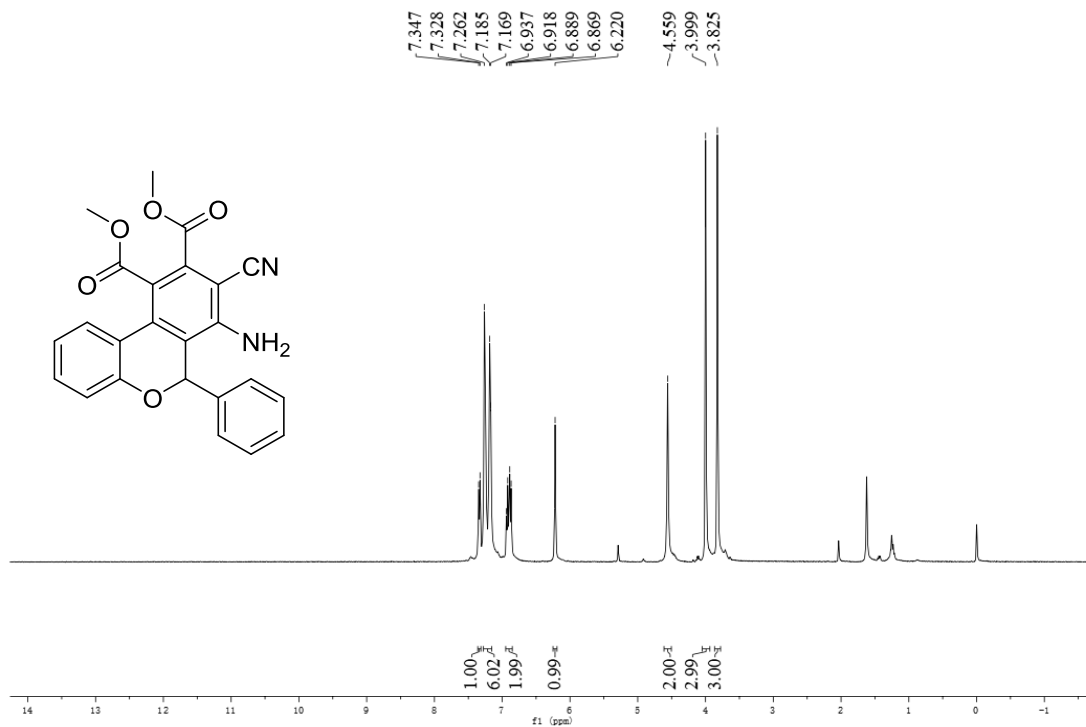
Ethyl (Z)-2-(1-cyano-2-oxo-2-phenylethylidene)-8-methyl-4-(p-tolyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (5c): red solid, 0.196g, 80%, m.p. 205~206 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.14 (s, 1H, ArH), 7.99~7.97 (m, 2H, ArH), 7.89~7.86 (m, 2H, ArH), 7.65~7.63 (m, 1H, ArH), 7.50~7.45 (m, 6H, ArH), 4.60 (q, $J = 7.2$ Hz, 2H, OCH_2), 2.49 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 1.51 (t, $J = 7.2$ Hz, 3H, CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 191.3, 164.9, 159.5, 149.5, 146.4, 143.5, 139.5, 136.7, 133.6, 133.3, 130.8, 130.7, 128.0, 127.9, 127.6, 126.8, 125.5, 125.4, 123.1, 120.5, 118.1, 115.9, 75.4, 62.2, 21.7, 21.4, 14.0; IR (KBr) ν : 3432, 2951, 2200, 1752, 1451, 860 cm^{-1} . MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{24}\text{N}_2\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 511.1628. Found: 511.1628.



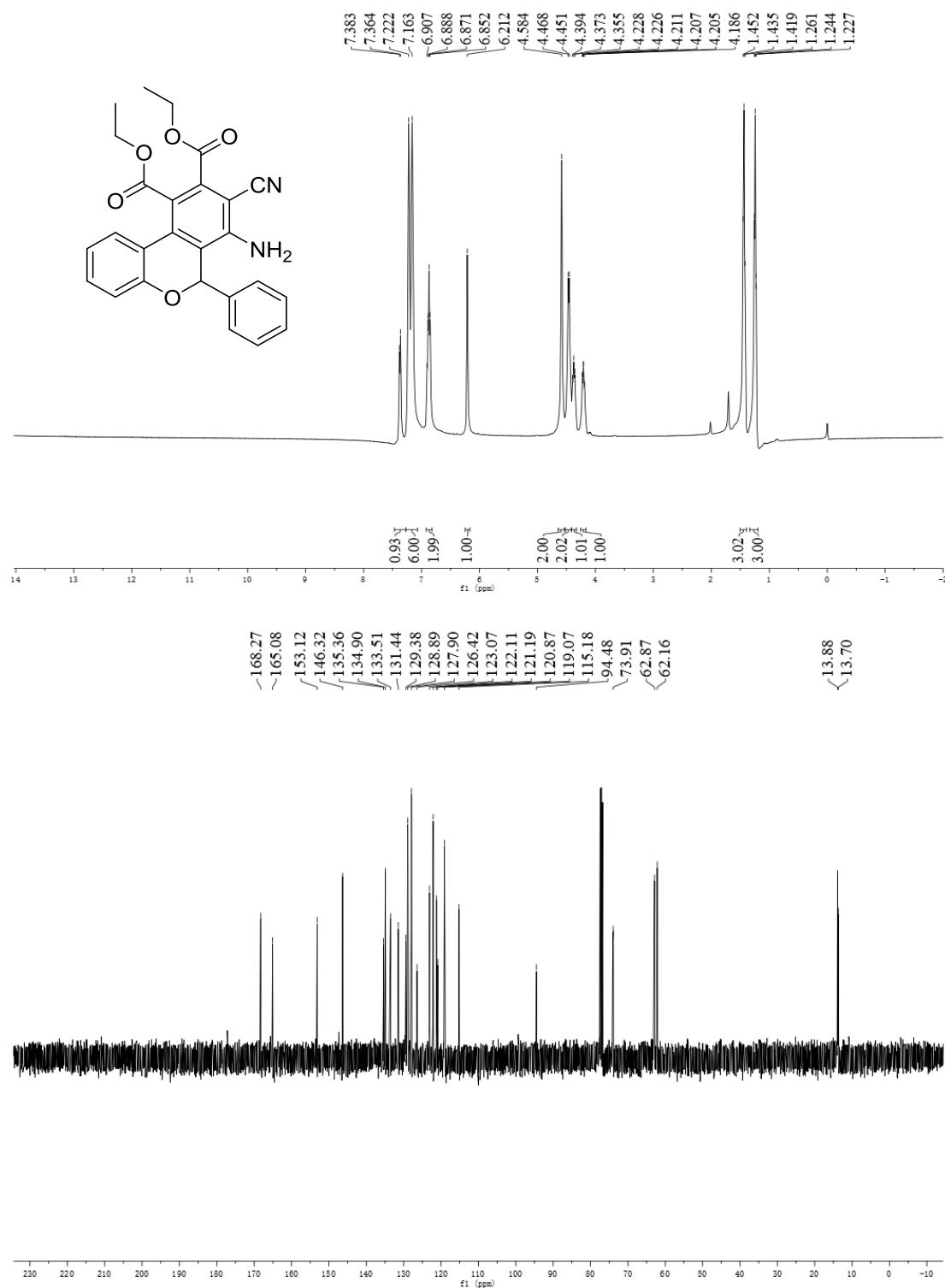
Methyl (Z)-2-(1-cyano-2-oxo-2-phenylethylidene)-6-methoxy-4-(3-methoxyphenyl)-2,3-dihydrochromeno[3,4-b]pyrrole-1-carboxylate (5d): red solid, 0.207g 82%, m.p. 217~218 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.90~7.88 (m, 3H, ArH), 7.73~7.71 (m, 1H, ArH), 7.63~7.57 (m, 2H, ArH), 7.48~7.41 (m, 4H, ArH), 7.19~7.16 (m, 2H, ArH), 4.09 (s, 3H, OCH₃), 4.04 (s, 3H, OCH₃), 3.98 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 191.4, 165.1, 160.4, 159.7, 149.1, 145.4, 141.5, 139.5, 134.0, 131.0, 130.8, 128.1, 128.0, 126.4, 123.6, 120.6, 120.2, 120.1, 118.8, 116.9, 116.8, 112.4, 112.3, 111.1, 75.6, 56.2, 55.6, 52.6; IR (KBr) ν: 3430, 2988, 2837, 2193, 1721, 1444, 888 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₂N₂O₆Na ([M+Na]⁺): 529.1370. Found: 529.1396.



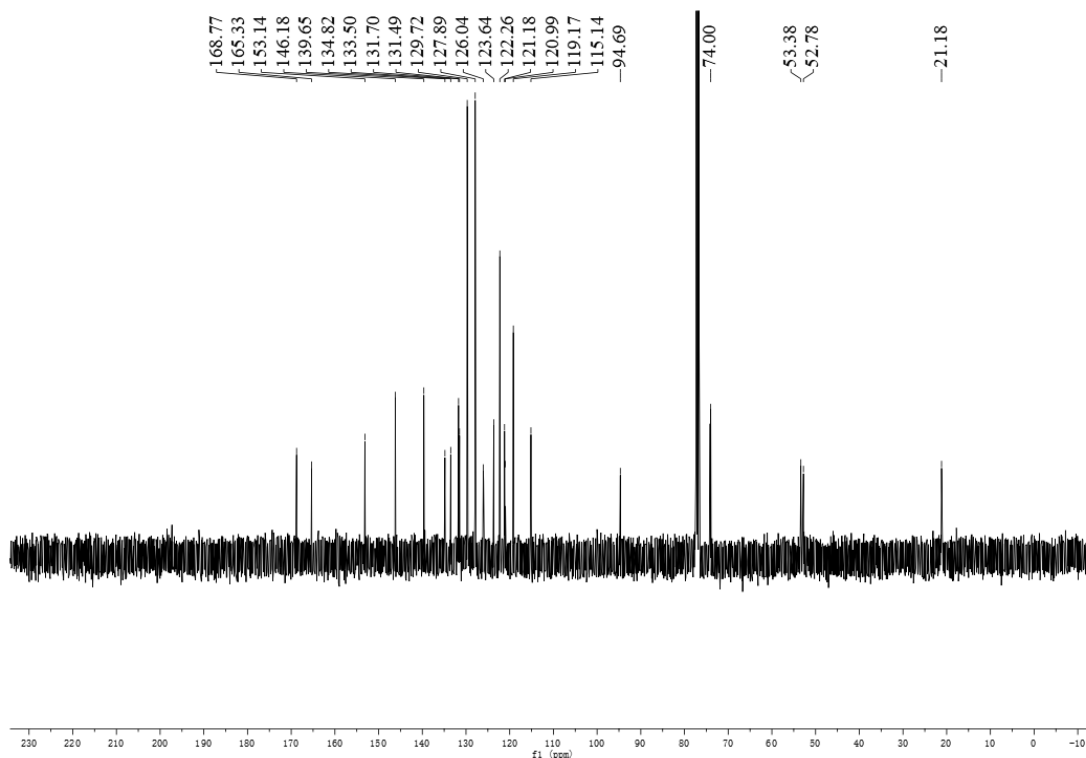
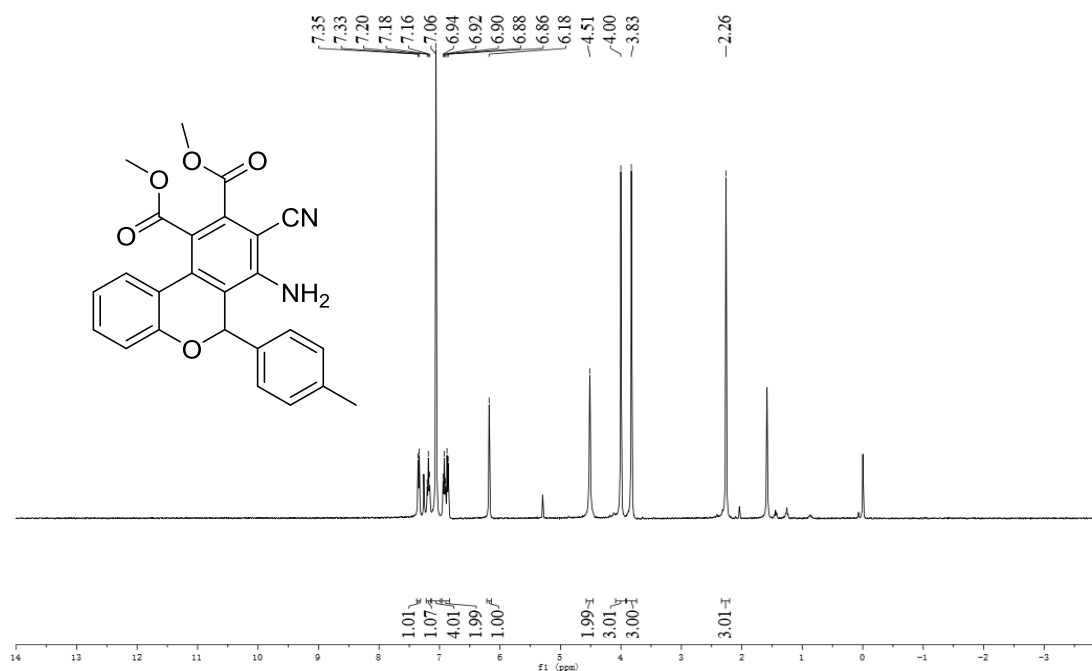
Dimethyl 7-amino-8-cyano-6-phenyl-6H-benzo[*c*]chromene-9,10-dicarboxylate (6a): light yellow solid, 0.168g, 81%, m.p. 207~208 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.35~7.33 (m, 1H, ArH), 7.26~7.17 (m, 6H, ArH), 6.94~6.87 (m, 2H, ArH), 6.22 (s, 1H, CH), 4.56 (s, 2H, NH₂), 4.00 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 168.7, 165.3, 153.0, 146.3, 134.9, 134.7, 133.5, 131.5, 129.5, 128.9, 127.8, 126.0, 123.3, 122.3, 121.1, 120.9, 119.1, 115.1, 94.6, 74.0, 53.2, 52.9; IR (KBr) ν: 3426, 3350, 2978, 2224, 1736, 1450, 881 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₄H₁₈N₂O₅Na ([M+Na]⁺): 437.1108. Found: 437.1113.



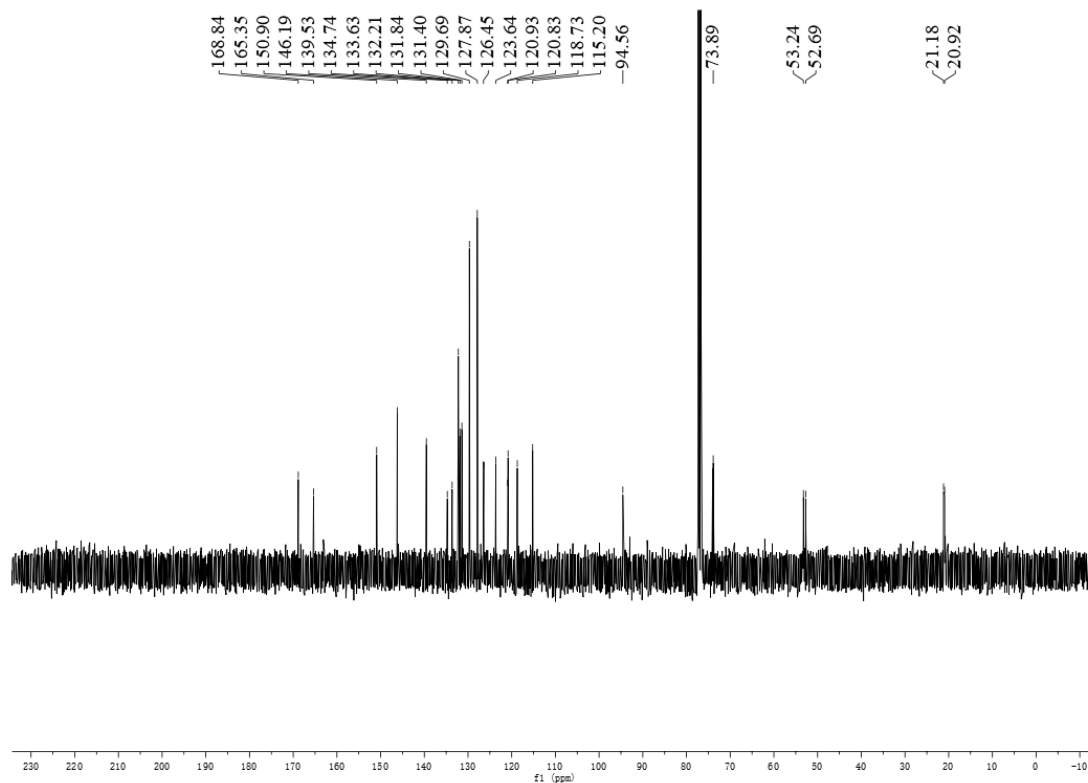
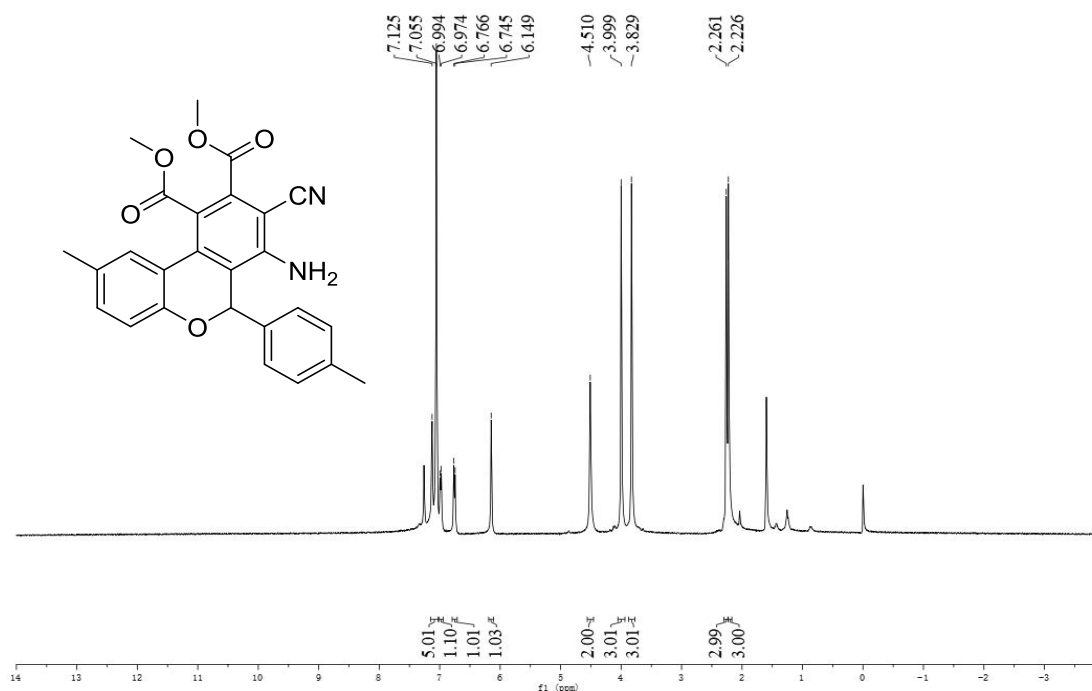
Diethyl 7-amino-8-cyano-6-phenyl-6H-benzo[c]chromene-9,10-dicarboxylate (6b): light yellow solid, 0.166g, 75%, m.p. 209~210 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.38~7.36 (m, 1H, ArH), 7.22~7.16 (m, 6H, ArH), 6.91~6.85 (m, 2H, ArH), 6.21 (s, 1H, CH), 4.58 (s, 2H, NH₂), 4.47~4.45 (m, 2H, OCH₂), 4.39~4.36 (m, 1H, OCH₂), 4.23~4.19 (m, 1H, OCH₂), 1.44 (t, *J* = 6.8 Hz, 3H, CH₃), 1.24 (t, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 168.2, 165.0, 153.1, 146.3, 135.3, 134.9, 133.5, 131.4, 129.3, 128.8, 127.9, 126.4, 123.0, 122.1, 121.1, 120.8, 119.0, 115.1, 94.4, 73.9, 62.8, 62.1, 13.8, 13.7; IR (KBr) ν: 3420, 2970, 2213, 1730, 1385, 794 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₂N₂O₅Na ([M+Na]⁺): 465.1421. Found: 465.1423.



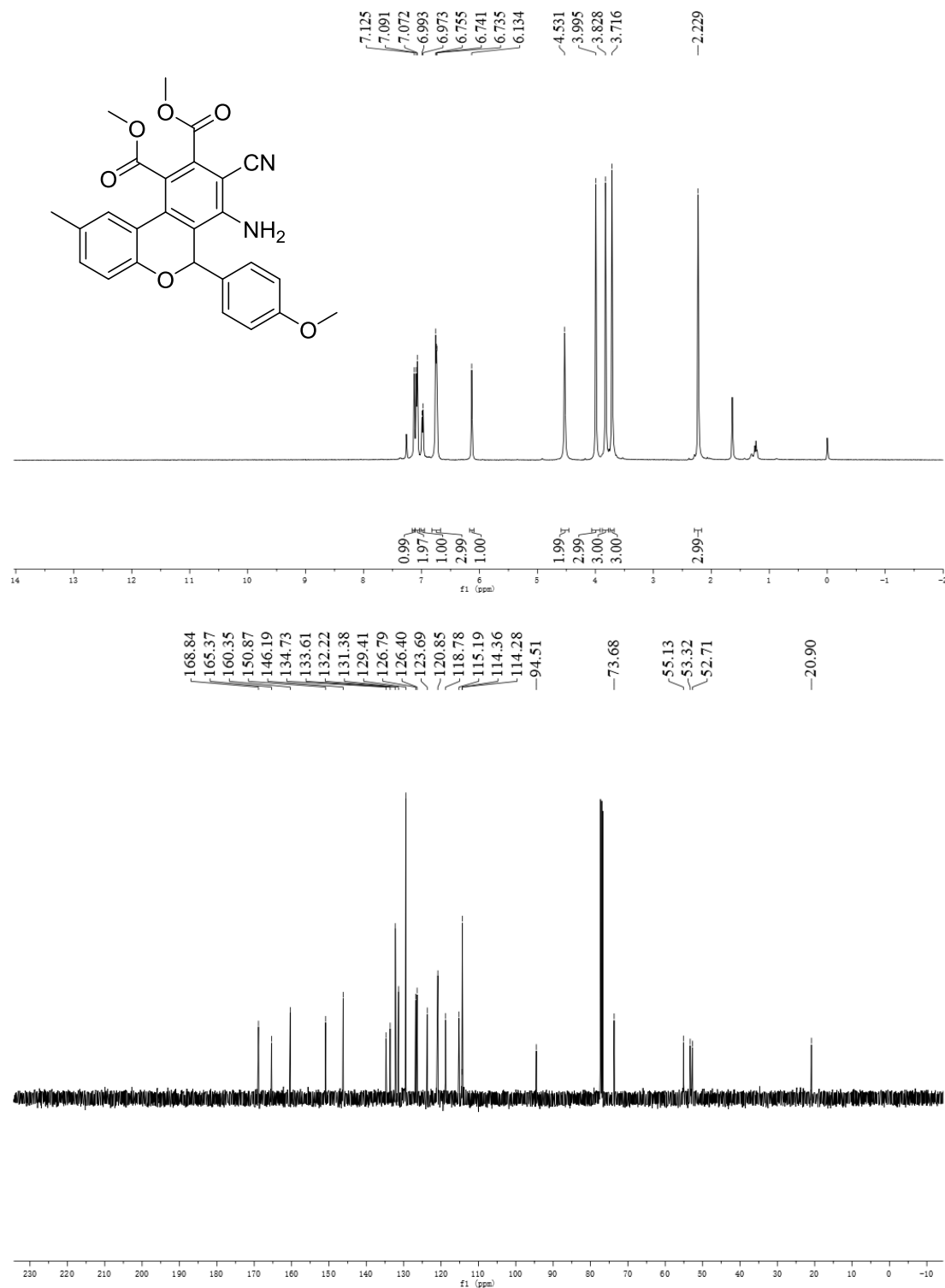
Dimethyl 7-amino-8-cyano-6-(p-tolyl)-6H-benzo[c]chromene-9,10-dicarboxylate (6c): light yellow solid, 0.178g, 83%, m.p. 215~216 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.35~7.33 (m, 1H, ArH), 7.20~7.16 (m, 1H, ArH), 7.06~7.06 (m, 4H, ArH), 6.94~6.86 (m, 2H, ArH), 6.18 (s, 1H, CH), 4.51 (s, 2H, NH_2), 4.00 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.7, 165.3, 153.1, 146.1, 139.6, 134.8, 133.5, 131.7, 131.4, 129.7, 127.8, 126.0, 123.6, 122.2, 121.1, 120.9, 119.1, 115.1, 94.6, 74.0, 53.3, 52.7, 21.1; IR (KBr) ν : 3425, 2970, 2216, 1733, 1397, 806 cm^{-1} . MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 451.1264. Found: 451.1265.



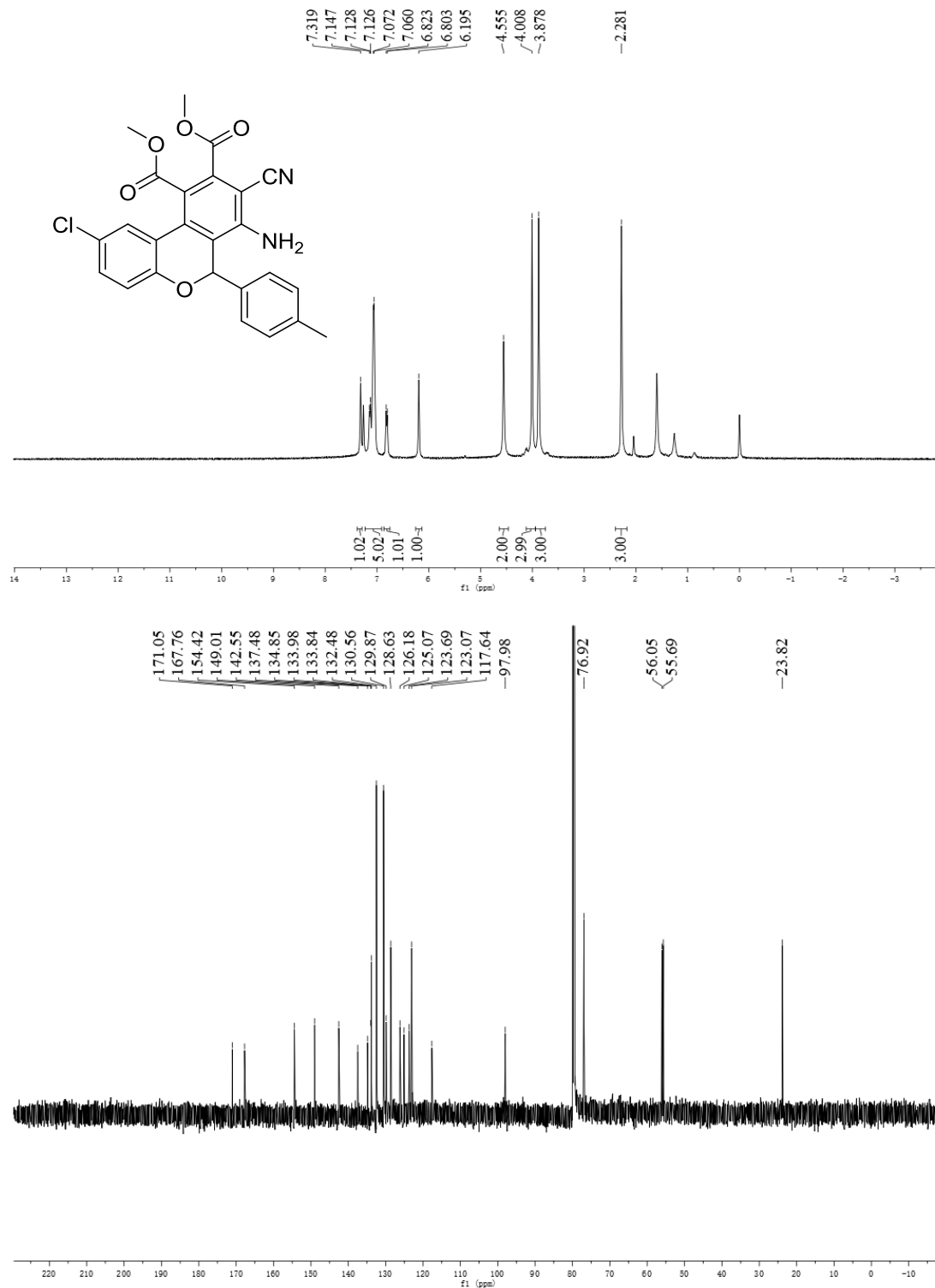
Dimethyl 7-amino-8-cyano-2-methyl-6-(p-tolyl)-6H-benzo[c]chromene-9,10-dicarboxylate (6d): light yellow solid, 0.188g, 85%, m.p. 228~229 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.12~7.06 (m, 5H, ArH), 6.99~6.97 (m, 1H, ArH), 6.77~6.74 (m, 4H, ArH), 6.15 (s, 1H, CH), 4.51 (s, 2H, NH₂), 4.00 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 2.26 (s, 3H, CH₃), 2.23 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 168.8, 165.3, 150.9, 146.1, 139.5, 134.7, 133.6, 132.2, 131.8, 131.4, 129.6, 127.8, 126.4, 123.6, 120.9, 120.8, 118.7, 115.1, 94.5, 73.8, 53.2, 52.6, 21.1, 20.9; IR (KBr) ν: 3429, 3342, 2963, 2220, 1653, 917 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₂N₂O₅Na ([M+Na]⁺): 465.1421. Found: 465.1423.



Dimethyl 7-amino-8-cyano-6-(4-methoxyphenyl)-2-methyl-6H-benzo[c]chromene-9,10-dicarboxylate (6e): light yellow solid, 0.185g, 81%, m.p. 225~226 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.12~7.07 (m, 5H, ArH), 6.99~6.97 (m, 1H, ArH), 6.76~6.74 (m, 4H, ArH), 6.13 (s, 1H, CH), 4.53 (s, 2H, NH_2), 4.00 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.23 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.8, 165.3, 160.3, 150.8, 146.1, 134.7, 133.6, 132.2, 131.3, 129.4, 126.7, 126.3, 123.6, 120.8, 118.7, 115.1, 114.3, 114.2, 94.5, 73.6, 55.1, 53.3, 52.7, 20.9; IR (KBr) ν : 3463, 2983, 2217, 1767, 1461, 896 cm^{-1} . MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_6\text{Na}$ ($[\text{M}+\text{Na}]^+$): 481.1370. Found: 481.1369.

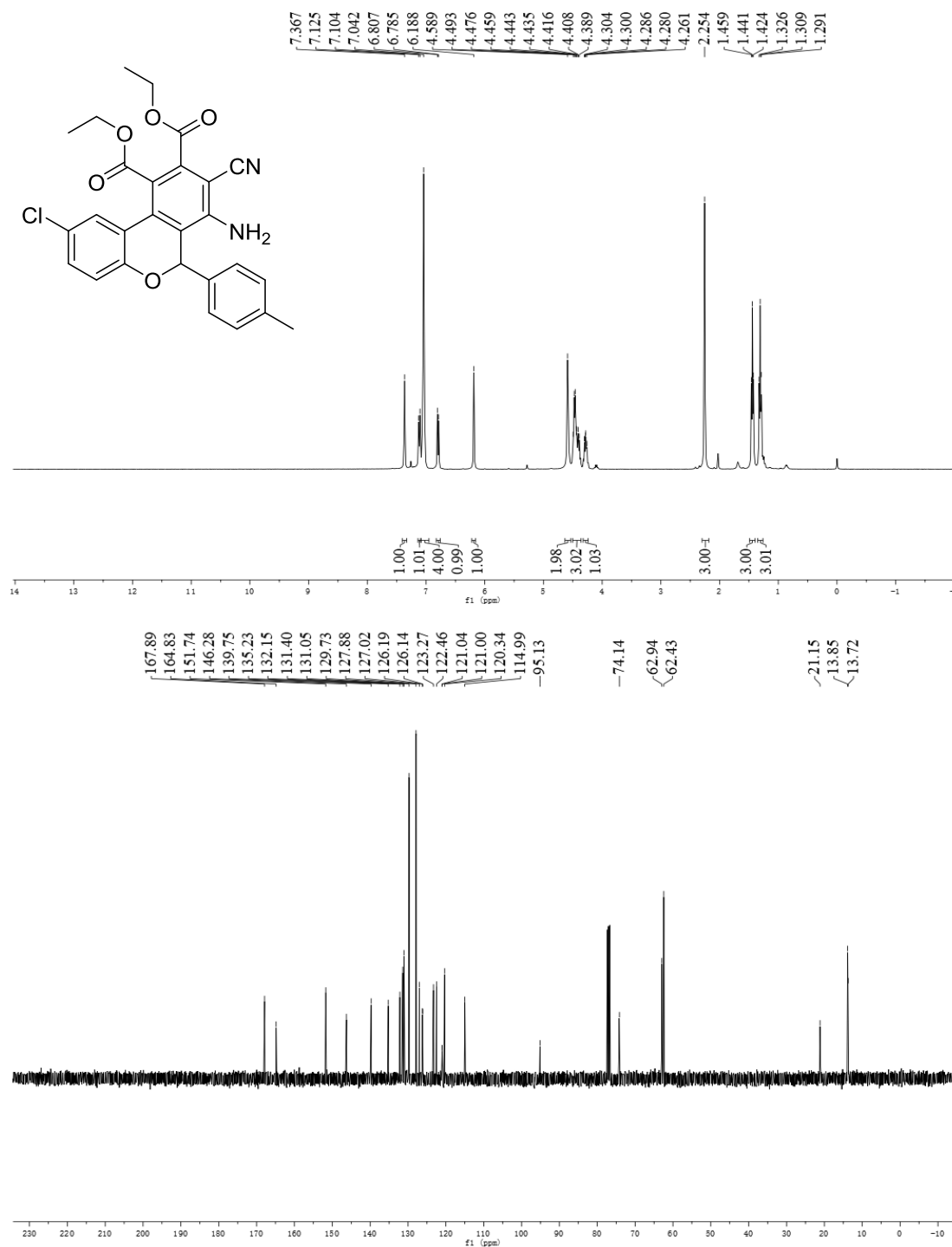


Dimethyl 7-amino-2-chloro-8-cyano-6-(p-tolyl)-6H-benzo[c]chromene-9,10-dicarboxylate (6f): light yellow solid, 0.203g, 88%, m.p. 227~228 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.32 (s, 1H, ArH), 7.15~7.06 (m, 5H, ArH), 6.82~6.80 (m, 1H, ArH), 6.19 (s, 1H, CH), 4.55 (s, 2H, NH₂), 4.00 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 2.28 (s, 3H, CH₃); ¹³C NMR (150 MHz, CDCl₃) δ: 171.0, 167.7, 154.4, 149.0, 142.5, 137.4, 134.8, 133.9, 133.8, 132.4, 130.5, 129.8, 128.6, 126.1, 125.0, 123.6, 123.0, 117.6, 97.9, 76.9, 56.0, 55.6, 23.8; IR (KBr) ν: 3451, 2999, 2216, 1676, 1308, 799 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₅H₁₉ClN₂O₅Na ([M+Na]⁺): 485.0875. Found: 485.0877.

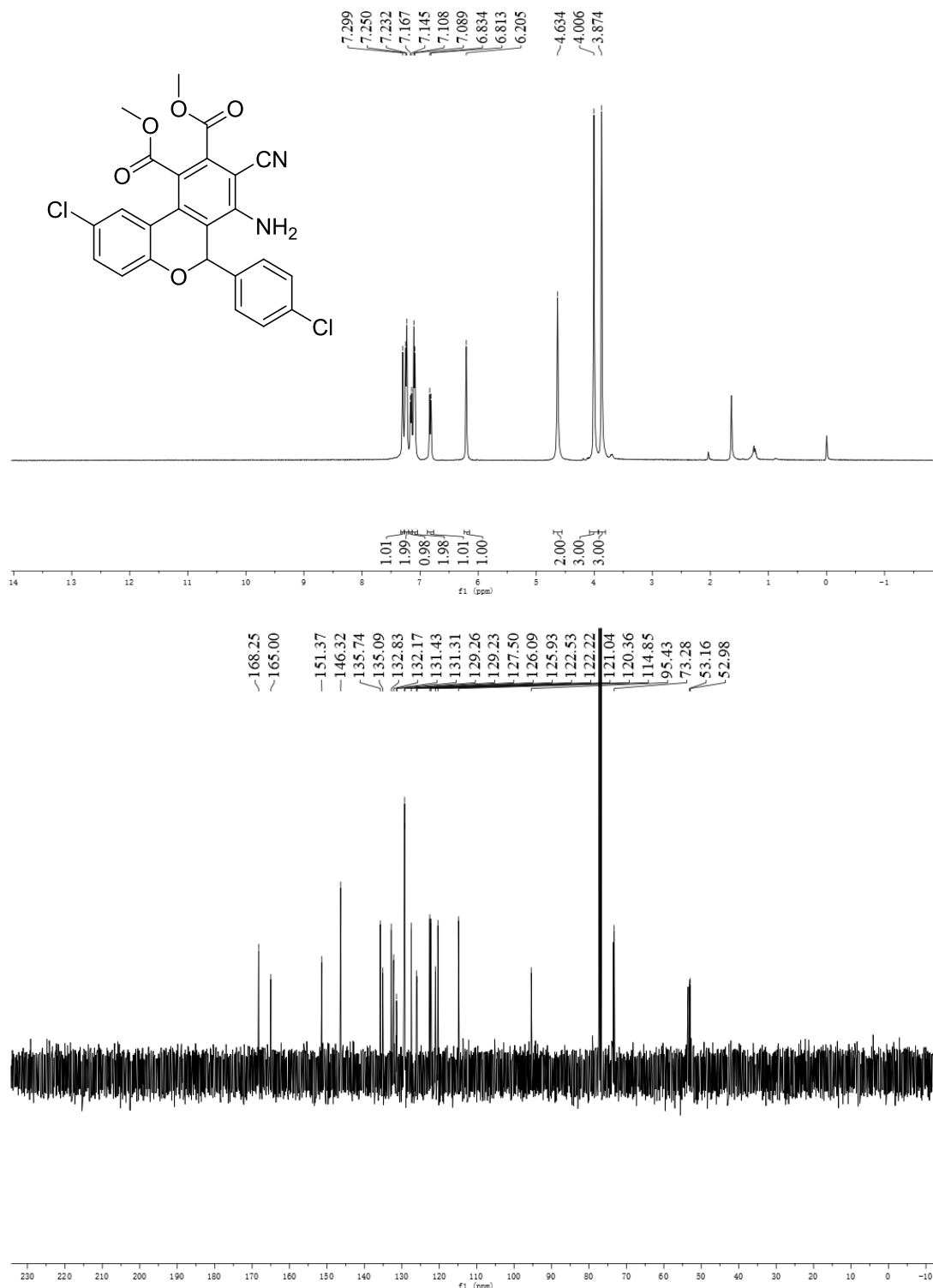


Diethyl 7-amino-2-chloro-8-cyano-6-(p-tolyl)-6H-benzo[c]chromene-9,10-dicarboxylate (6g):

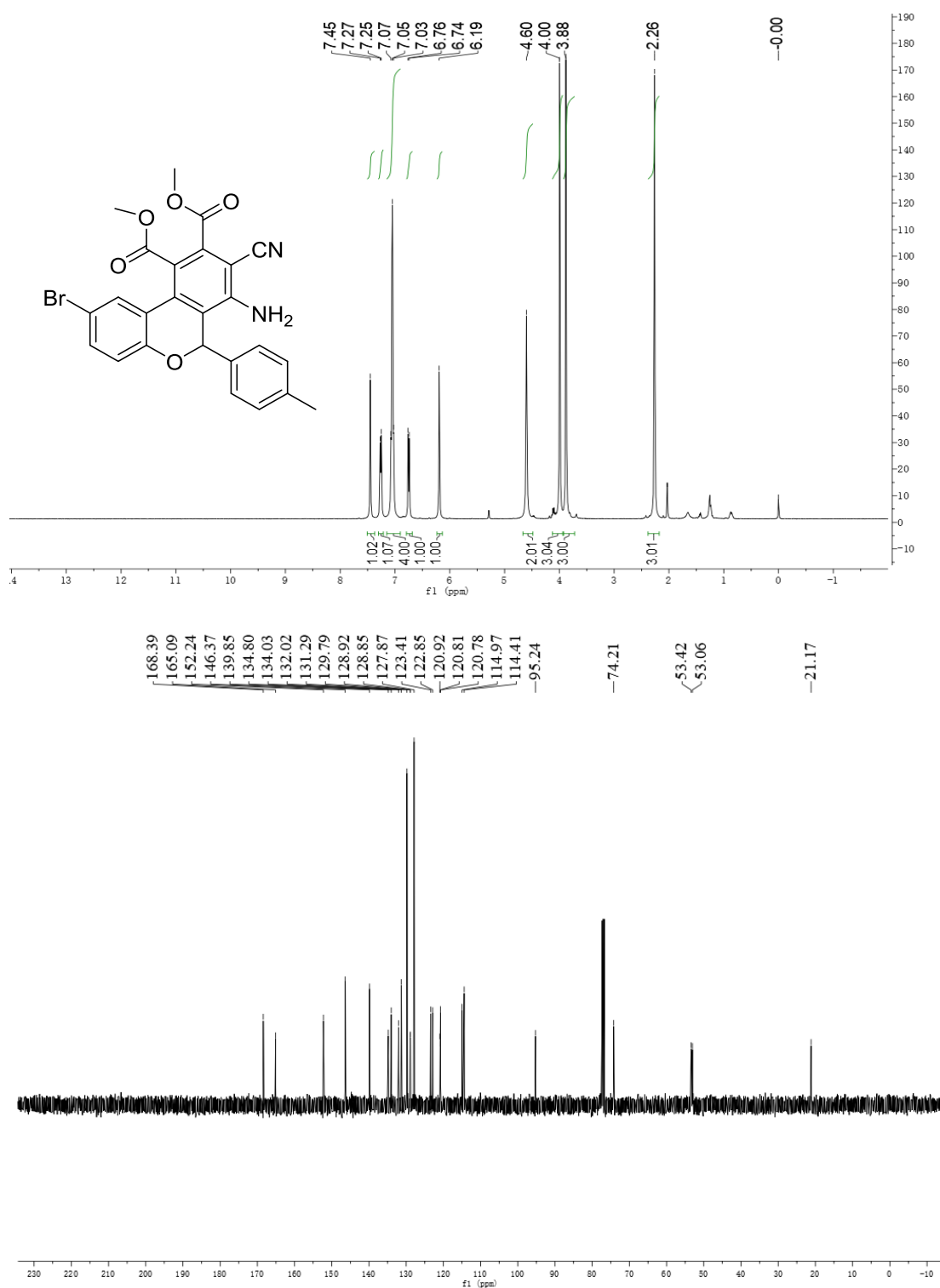
light yellow solid, 0.200g, 82%, m.p. 230~231 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.37 (s, 1H, ArH), 7.12~7.10 (m, 1H, ArH), 7.04~7.04 (m, 4H, ArH), 6.81~6.78 (m, 1H, ArH), 6.19 (s, 1H, CH), 4.59 (s, 2H, NH₂), 4.49~4.39 (m, 3H, OCH₂), 4.30~4.26 (m, 1H, OCH₂), 2.25 (s, 3H, CH₃), 1.44 (t, *J* = 7.2 Hz, 3H, CH₃), 1.31 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 167.8, 164.8, 151.7, 146.2, 139.7, 135.2, 132.1, 131.4, 131.0, 129.7, 127.8, 127.0, 126.1, 126.1, 123.2, 122.4, 121.0, 121.0, 120.3, 114.9, 95.1, 74.1, 62.9, 62.4, 21.1, 13.8, 13.7; IR (KBr) ν: 3436, 2963, 2217, 1750, 1400, 825 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₇H₂₃ClN₂O₅Na ([M+Na]⁺): 513.1188. Found: 513.1194



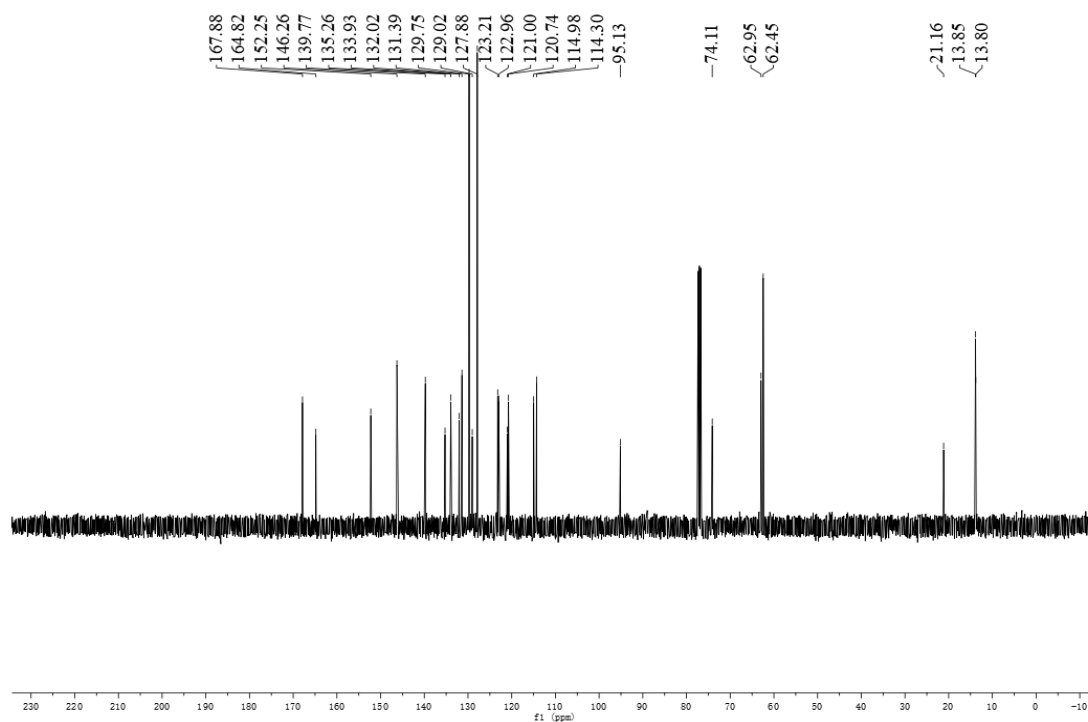
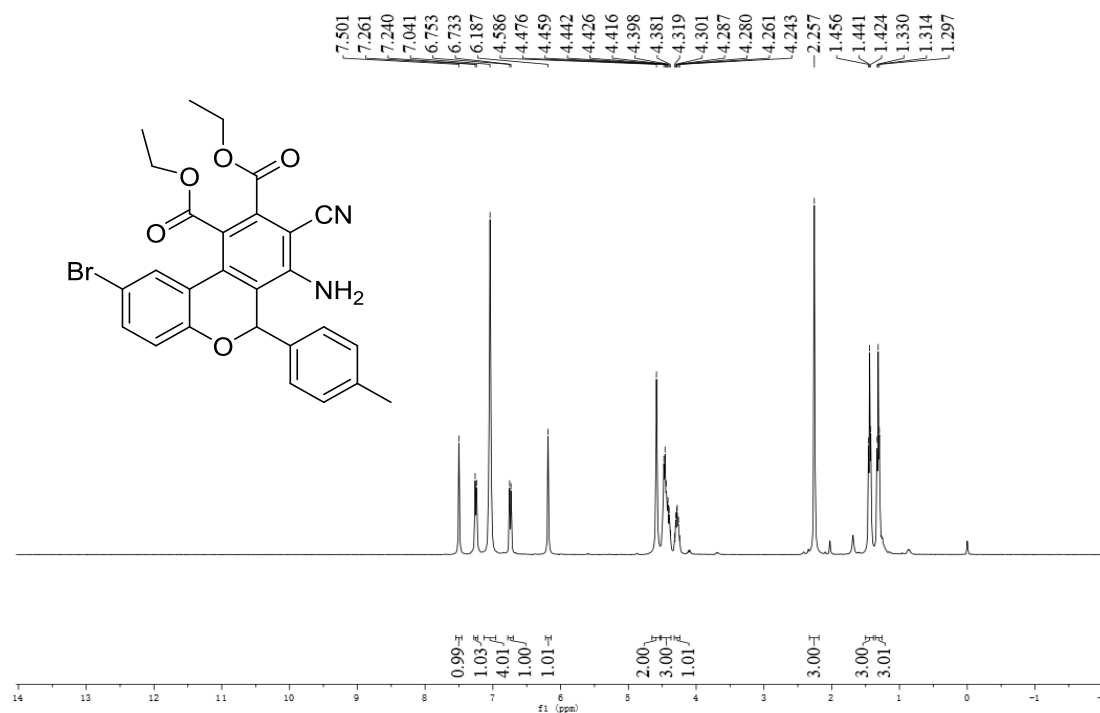
Dimethyl 7-amino-2-chloro-6-(4-chlorophenyl)-8-cyano-6H-benzo[c]chromene-9,10-dicarboxylate (6h): light yellow solid, 0.183g, 76%, m.p. 212~213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.30 (s, 1H, ArH), 7.25~7.23 (m, 2H, ArH), 7.17~7.14 (m, 1H, ArH), 7.11~7.09 (m, 2H, ArH), 6.83~6.81 (m, 1H, ArH), 6.20 (s, 1H, CH), 4.63 (s, 2H, NH₂), 4.00 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 168.2, 164.9, 151.3, 146.3, 135.7, 135.0, 132.8, 132.1, 131.4, 131.3, 129.2, 129.2, 127.4, 126.0, 125.9, 122.5, 122.2, 121.0, 120.3, 114.8, 95.4, 73.2, 53.1, 52.9; IR (KBr) ν: 3420, 3120, 2976, 2220, 1635, 809 cm⁻¹. MS (m/z): HRMS (ESI) Calcd. for C₂₄H₁₆Cl₂N₂O₅Na ([M+Na]⁺): 505.0328. Found: 505.0330



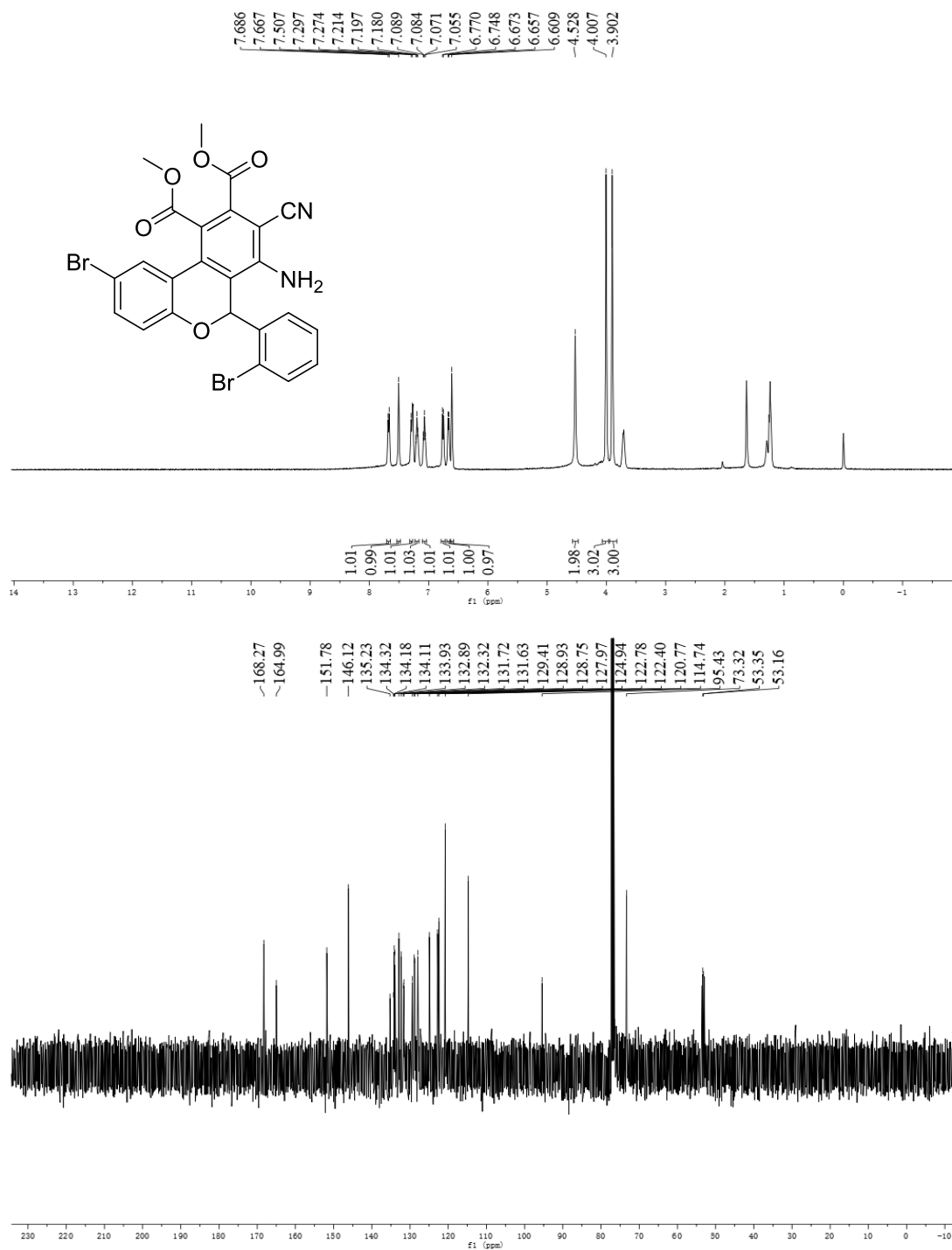
Dimethyl 7-amino-2-bromo-8-cyano-6-(p-tolyl)-6H-benzo[c]chromene-9,10-dicarboxylate (6i): light yellow solid, 0.229g, 90%, m.p. 235~236 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.45 (s, 1H, ArH), 7.27~7.25 (m, 1H, ArH), 7.07~7.03 (m, 4H, ArH), 6.76~6.74 (m, 1H, ArH), 6.19 (s, 1H, CH), 4.60 (s, 2H, NH₂), 4.00 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 2.26 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 168.3, 165.0, 152.2, 146.3, 139.8, 134.8, 134.0, 132.0, 131.2, 129.7, 128.9, 128.8, 127.8, 123.4, 122.8, 120.9, 120.8, 120.7, 114.9, 114.4, 95.2, 74.2, 53.4, 53.0, 21.1; IR (KBr) ν: 3431, 3325, 2988, 2216, 1708, 1495, 862 cm⁻¹. MS (m/z): HRMS (ESI) Calcd. for C₂₅H₁₉BrN₂O₅Na ([M+Na]⁺): 529.0370. Found: 529.0369



Diethyl 7-amino-2-bromo-8-cyano-6-(p-tolyl)-6H-benzo[c]chromene-9,10-dicarboxylate (6j): light yellow solid, 0.230g, 86%, m.p. 220~221 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.50 (s, 1H, ArH), 7.26~7.24 (m, 1H, ArH), 7.04~7.04 (m, 4H, ArH), 6.75~6.73 (m, 1H, ArH), 6.19 (s, 1H, CH), 4.59 (s, 2H, NH_2), 4.48~4.38 (m, 3H, OCH_2), 4.32~4.24 (m, 1H, OCH_2), 2.26 (s, 3H, CH_3), 1.44 (t, $J = 6.4$ Hz, 3H, CH_3), 1.31 (t, $J = 6.4$ Hz, 3H, CH_3); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 167.8, 164.8, 152.2, 146.2, 139.7, 135.2, 133.9, 132.0, 131.3, 129.7, 129.0, 127.8, 123.2, 122.9, 120.9, 120.7, 114.9, 114.3, 95.1, 74.1, 62.9, 62.4, 21.1, 13.8, 13.8; IR (KBr) ν : 3427, 2977, 2210, 1696, 1388, 796 cm^{-1} . MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{27}\text{H}_{23}\text{BrN}_2\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 557.0683. Found: 557.0676

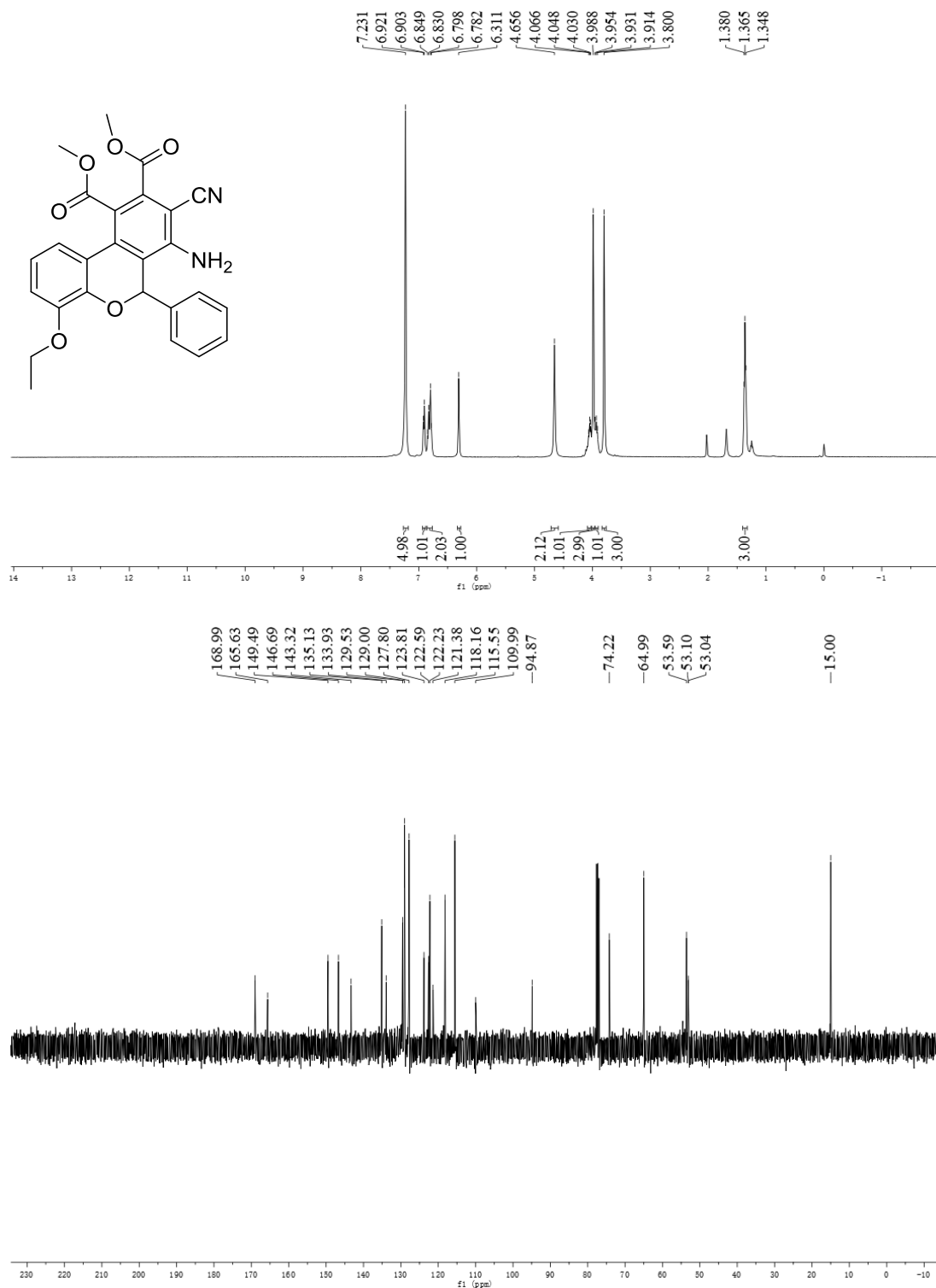


Dimethyl 7-amino-2-bromo-6-(2-bromophenyl)-8-cyano-6H-benzo[c]chromene-9,10-dicarboxylate (6k): light yellow solid, 0.214g, 75%, m.p. 165~166 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.69~7.67 (m, 1H, ArH), 7.51 (s, 1H, ArH), 7.30~7.27 (m, 1H, ArH), 7.21~7.18 (m, 1H, ArH), 7.09~7.06 (m, 1H, ArH), 6.77~6.75 (m, 1H, ArH), 6.67~6.66 (m, 1H, ArH), 6.61 (s, 1H, CH), 4.53 (s, 2H, NH_2), 4.01 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.2, 164.9, 151.7, 146.1, 135.2, 134.3, 134.1, 134.1, 133.9, 132.8, 132.3, 131.7, 131.6, 129.4, 128.9, 128.7, 127.9, 124.9, 122.7, 122.4, 120.7, 114.7, 95.4, 73.3, 53.3, 53.1; IR (KBr) ν : 3425, 3309, 2960, 2217, 1738, 1260, 870 cm^{-1} . MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 592.9318. Found: 592.9313.



Dimethyl 7-amino-8-cyano-4-ethoxy-6-phenyl-6H-benzo[c]chromene-9,10-dicarboxylate (6l):

light yellow solid, 0.165g, 72%, m.p. 180~182 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.23~7.23 (m, 5H, ArH), 6.92~6.90 (m, 1H, ArH), 6.85~6.78 (m, 2H, ArH), 6.31 (s, 1H, CH), 4.66 (s, 2H, NH_2), 4.07~4.03 (m, 1H, OCH_2), 3.99 (s, 3H, OCH_3), 3.96~3.91 (m, 1H, OCH_2), 3.80 (s, 3H, OCH_3), 1.32 (t, $J=6.4$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.9, 165.6, 149.4, 146.6, 143.3, 135.1, 133.9, 129.5, 128.9, 127.7, 123.8, 122.5, 122.2, 121.3, 118.1, 115.5, 109.9, 94.8, 74.2, 64.9, 53.5, 53.1, 53.0, 15.0; IR (KBr) ν : 3426, 3330, 2983, 2219, 1600, 1480, 876 cm^{-1} . MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_6\text{Na}$ ($[\text{M}+\text{Na}]^+$): 481.1370. Found: 481.1371.



Dimethyl 7-amino-8-cyano-4-ethoxy-6-(3-methoxyphenyl)-6H-benzo[c]chromene-9,10-dicarboxylate (6m): light yellow solid, 0.144g, 59%, m.p. 201~202 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.12 (t, *J*=8.0 Hz, 1H, ArH), 6.93~6.90 (m, 2H, ArH), 6.86~6.71 (m, 4H, ArH), 6.28 (s, 1H, CH), 4.66 (s, 2H, NH₂), 4.09~4.03 (m, 1H, OCH₂), 4.00 (s, 3H, OCH₃), 3.97~3.95 (m, 1H, OCH₂), 3.80 (s, 3H, OCH₃), 3.70 (s, 3H, OCH₃), 1.40 (t, *J*=6.8 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 168.6, 165.3, 159.8, 149.2, 146.4, 143.0, 136.4, 134.8, 133.5, 129.7, 123.6, 122.2, 122.0, 121.2, 119.4, 119.4, 117.9, 115.1, 115.0, 112.8, 94.7, 73.8, 64.6, 55.2, 53.3, 52.8, 14.7; IR (KBr) ν: 3428, 3342, 3248, 2980, 2226, 1653, 1254 cm⁻¹. MS (*m/z*): HRMS (ESI) Calcd. for C₂₇H₂₄N₂O₇Na ([M+Na]⁺): 511.1476. Found: 511.1478.

