

Engineered N-GQDs/CoFe₂O₄ Spherical Composites as A Robust and Retrievable Catalyst: Fabrication, Characterization, and Investigation Catalytic Performance in Microwave-assisted synthesis of quinoline-3-carbonitrile derivatives

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General procedure for the Synthesis of quinoline-3-carbonitrile derivatives

A 25 ml round bottom flask was charged with the same molar ratio of various aryl aldehydes (**1**), methyl cyanoacetate (**2**), different substituted aniline (**3**), N-GQDs/CoFe₂O₄ (20 mg), and ethanol. The whole mixture was stirred for 1 minute at ambient temperature. After well mixing, the prepared mixture was exposed to microwave irradiation at 400 W. Upon completion of the time reaction (monitored by TLC), the crude product was filtered and washed with cold dry ethanol to get pure product.

Physical and Spectral data

6-bromo-2-methoxy-4-(4-nitrophenyl)quinoline-3-carbonitrile (4a): White solid, m.p. 129-132 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3010, 2951, 2213, 1730, 1585, 1090; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 3.98 (3H, s, OMe), 7.26 (1H, s, CH Ar.), 8.11- 8.15 (2H, d, *J*= 16 Hz, CH Ar.), 8.31 (2H, bs, CH Ar), 8.33- 8.37 (2H, d, *J*= 16 Hz, CH Ar).

6-bromo-2-methoxy-4-(3-nitrophenyl)quinoline-3-carbonitrile (4b): White solid, m.p. 129-131 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3012, 2945, 2218, 1738, 1589, 1081; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 3.97 (3H, s, OMe), 7.26 (1H, s, CH Ar), 7.71-7.77 (1H, t, *J*= 12 Hz, CH Ar), 8.32 (2H, bs, CH Ar), 8.39- 8.42 (2H, d, *J*= 12 Hz, CH Ar), 8.70 (1H, s, CH Ar).

6-bromo-2-methoxy-4-(4-chlorophenyl)quinoline-3-carbonitrile (4c): White solid, m.p. 134-132 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3022, 2951, 2220, 1731, 1581, 1078; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.94 (3H, s, OMe), 7.26 (2H, s, CH Ar), 7.47- 7.50 (2H, CH Ar, d, $J=12$ Hz), 7.92- 7.95 (2H, CH Ar, d, $J=12$ Hz), 8.21 (1H, s, CH Ar).

6-bromo-2-methoxy-4-(2-chlorophenyl)quinoline-3-carbonitrile (4d): White solid, m.p. 128-130 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3019, 2954, 2218, 1728, 1580, 1065; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.96 (3H, s, OMe), 7.26- 7.50 (3H, m, CH Ar), 7.78- 8.17 (1H, s CH Ar), 8.22- 8.25 (2H, d, $J=12$ Hz, CH Ar), 8.70 (1H, s, CH Ar).

6-bromo-2-methoxy-4-(4-bromophenyl)quinoline-3-carbonitrile (4e): White solid, m.p. 125-126 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3028, 2933, 2228, 1718, 1585, 1068; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.94 (3H, s, OMe), 7.26 (2H, bs, CH Ar), 7.47- 7.50 (2H, d, $J=12$ Hz, CH Ar), 7.92- 7.95 (2H, d, $J=12$ Hz, CH Ar), 8.21 (1H, s, CH Ar).

6-bromo-2-methoxy-4-(4-methylphenyl)quinoline-3-carbonitrile (4f): White solid, m.p. 133-135 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3018, 2918, 2231, 1728, 1575, 1070; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 2.43 (3H, s, CH_3), 3.93 (3H, s, OMe), 7.26 (1H, s, CH Ar), 7.29- 7.32 (2H, d, $J=12$ Hz, CH Ar), 7.62 (1H, s, CH Ar), 7.89- 7.92 (2H, d, $J=12$ Hz, CH Ar), 8.23 (1H, s, CH Ar).

6-bromo-2-methoxy-4-(4-(methylthio)phenyl)quinoline-3-carbonitrile (4g): Light yellow solid, m.p. 130-132 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3018, 2947, 2218, 1728, 1589, 1088; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 2.53 (3H, s, SMe), 3.92 (3H, s, OMe), 7.28- 7.31 (2H, d, $J=12$ Hz, CH Ar), 7.63 (2H, s, CH Ar), 7.90- 7.93 (2H, d, $J=12$ Hz, CH Ar), 8.18 (1H, s, CH Ar); ^{13}C NMR (100 MHz, DMSO- d_6): δ (ppm) 14.61, 53.28, 99.83, 100.44, 115.86, 119.89, 125.43, 126.60, 127.05, 127.15, 127.31, 127.53, 131.46, 138.30, 143.31, 149.80, 154.46, 60.22.

6-bromo-2-methoxy-4-(4-methoxyphenyl)quinoline-3-carbonitrile (4h): White solid, m.p. 128-131 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3010, 2957, 2214, 1720, 1585, 1092; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.89 (3H, s, OMe), 3.91 (3H, s, OMe), 6.67- 7.01 (2H, d, $J=$ 12 Hz, CH Ar), 7.62 (2H, s, CH Ar), 7.98- 8.02 (2H, d, $J=$ 12 Hz, CH Ar), 8.18 (1H, s, CH Ar).

6-bromo-4-(5-bromo-2-hydroxyphenyl)-2-methoxyquinoline-3-carbonitrile (4i): Yellow solid, m.p. 134-136 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3010, 2957, 2214, 1720, 1585, 1092; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.81 (3H, s, OMe), 6.69 (1H, bs, OH), 7.40- 7.51 (3H, m, CH Ar), 7.55- 7.62 (3H, m, CH Ar).

2,6-dimethoxy-4-(4-nitrophenyl)quinoline-3-carbonitrile (4j): White solid, m.p. 133-135 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3010, 2957, 2214, 1720, 1585, 1092; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.89 (3H, s, CH OMe), 3.98 (3H, s, CH OMe), 7.98 (1H, m, CH Ar), 8.11- 8.15 (2H, d, $J=$ 16 Hz, CH Ar), 8.31 (1H, CH Ar), 8.33- 8.37 (2H, d, $J=$ 16 Hz, CH Ar).

2,6-dimethoxy-4-(3-nitrophenyl)quinoline-3-carbonitrile (4k): White solid, m.p. 133-135 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3012, 2958, 2218, 1718, 1580, 1099; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.97 (6H, s, OMe), 7.70- 7.76 (2H, t, $J=$ 12 Hz, CH Ar), 8.31 (2H, bs, CH Ar), 8.39- 8.42 (3H, d, $J=$ 12 Hz, CH Ar), 8.70 (1H, s, CH Ar).

2,6-dimethoxy-4-(4-chlorophenyl)quinoline-3-carbonitrile (4l): White solid, m.p. 130-132 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3018, 2968, 2228, 1719, 1580, 1091; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.93 (6H, s, OMe), 7.25 (1H, s, CH Ar), 7.46- 7.49 (2H, d, $J=$ 12 Hz, CH Ar), 7.92- 7.95 (2H, d, $J=$ 12.4 Hz, CH Ar), 8.20 (2H, bs, CH Ar).

2,6-dimethoxy-4-(4-bromophenyl)quinoline-3-carbonitrile (4m): White solid, m.p. 130-132 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3020, 2966, 2235, 1721, 1576, 1085; ^1H NMR (400 MHz, DMSO- d_6): δ

(ppm) 3.89 (3H, s, OMe), 3.91 (3H, s, OMe), 6.98- 7.01 (2H, d, $J=12$ Hz, CH Ar), 7.26 (2H, bs, CH Ar), 7.99- 7.02 (2H, d, $J=12$ Hz, CH Ar), 8.18 (1H, s, CH Ar).

2,6-dimethoxy-4-(4-methylphenyl)quinoline-3-carbonitrile (4n): White solid, m.p. 130-132 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3033, 2981, 2215, 1720, 1567, 1095; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 1.55 (3H, s, Me), 3.94 (3H, s, OMe), 4.37 (3H, s, OMe), 7.20- 7.26 (3H, m, CH Ar), 8.01- 8.06 (2H, m, CH Ar), 8.22 (2H, bs, CH Ar).

2,6-dimethoxy-4-(4-(methylthiophenyl)quinoline-3-carbonitrile (4o): light Yellow solid, m.p. 133-135 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3033, 2986, 2230, 1712, 1575, 1089; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 2.53 (3H, s, CH SMe), 3.89 (3H, s, OMe), 3.92 (3H, s, OMe), 7.10 (2H, bs, CH Ar), 7.27- 7.30 (2H, d, $J=12$ Hz, CH Ar), 7.89- 7.92 (2H, d, $J=12$ Hz, CH Ar), 8.17 (1H, s, CH Ar); ^{13}C NMR (100 MHz, DMSO- d_6): δ (ppm) 14.61, 53.28, 53.49, 91.39, 100.45, 112.94, 113.58, 115.89, 116.06, 125.42, 127.52, 128.76, 128.98, 131.46, 147.44, 154.46, 155.81, 161.63, 179.79.

2,6-dimethoxy-4-(4-methoxyphenyl)quinoline-3-carbonitrile (4p): White solid, m.p. 132-133 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3034, 2988, 2231, 1715, 1579, 1092; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 3.89 (6H, s, OMe), 3.91 (3H, s, OMe), 6.98- 7.01 (2H, d, $J=12$ Hz, CH Ar), 7.26 (1H, s, CH Ar), 7.99- 8.02 (2H, d, $J=12$ Hz, CH Ar), 8.18 (2H, bs, CH Ar).

2,6-dimethoxy-4-(methyl)quinoline-3-carbonitrile (4q): Light Yellow solid, m.p. 129-131 °C; FT-IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3028, 2980, 2218, 1710, 1573, 1078; ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 1.55 (3H, s, Me), 2.43 (3H, s, OMe), 3.92 (3H, s, OMe), 7.25 (1H, s, CH Ar), 7.29- 7.32 (3H, m, CH Ar), 7.88- 8.91 (2H, d, $J=12$ Hz, CH Ar), 8.22 (1H, s, CH Ar).

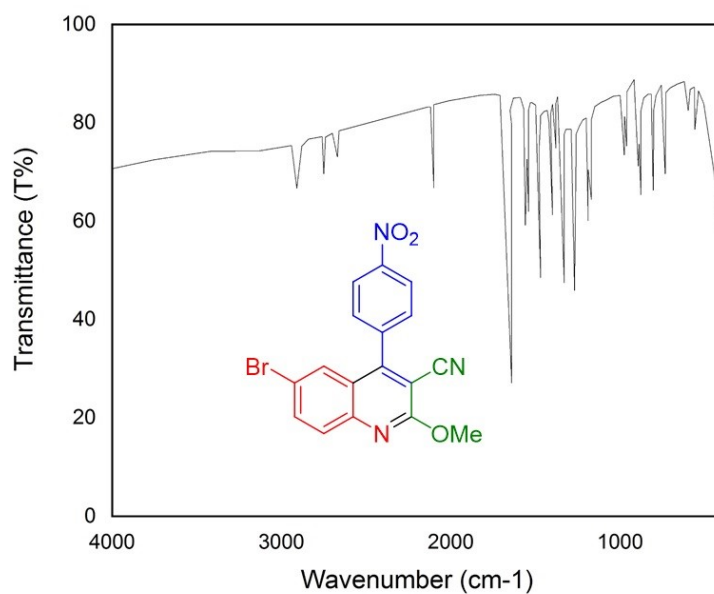


Figure S1. FT-IR spectrum of compound 4a

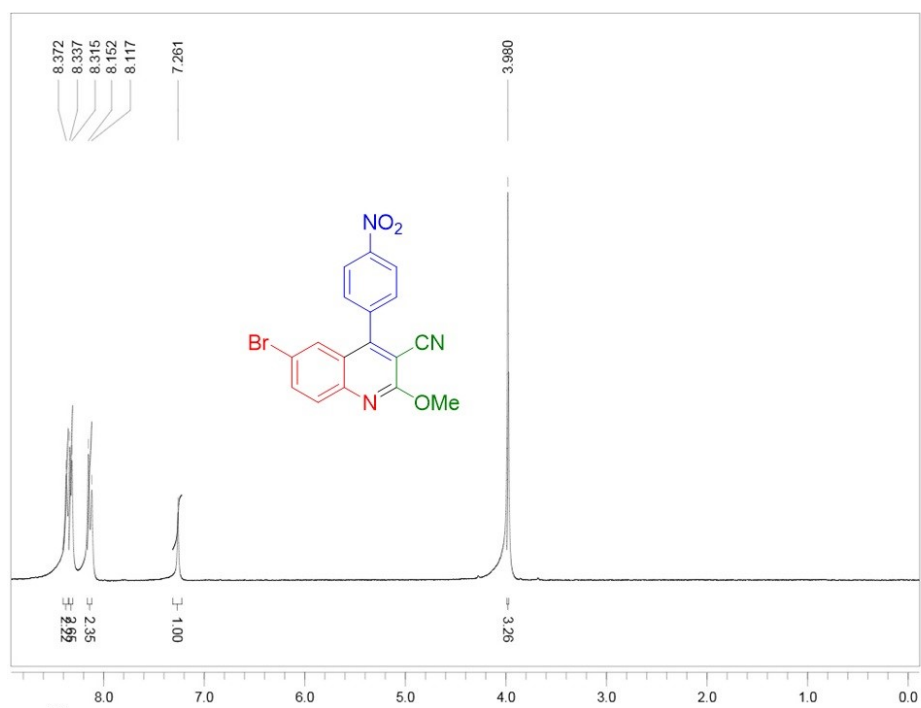


Figure S2. ¹H NMR spectrum of compound 4a

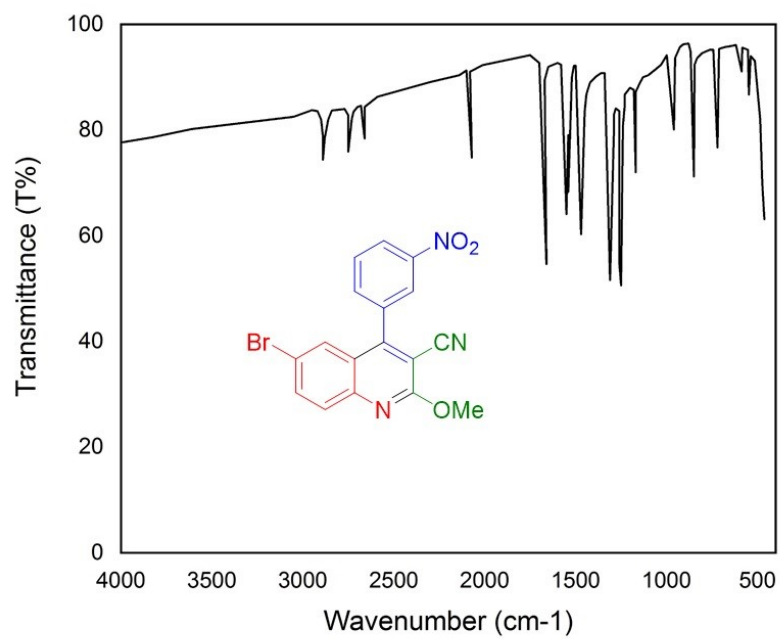


Figure S3. FT-IR spectrum of compound 4b

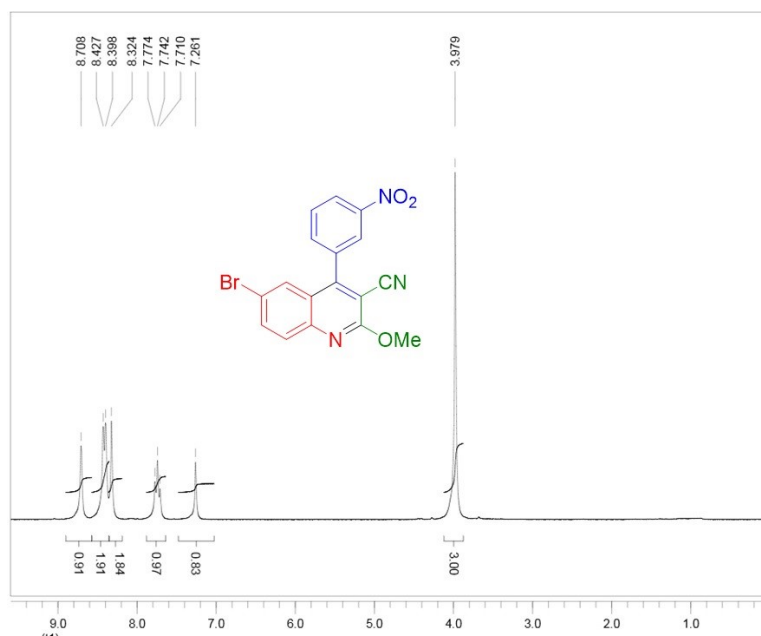


Figure S4. ¹H NMR spectrum of compound 4b

Figure S5. FT-IR spectrum of compound 4c

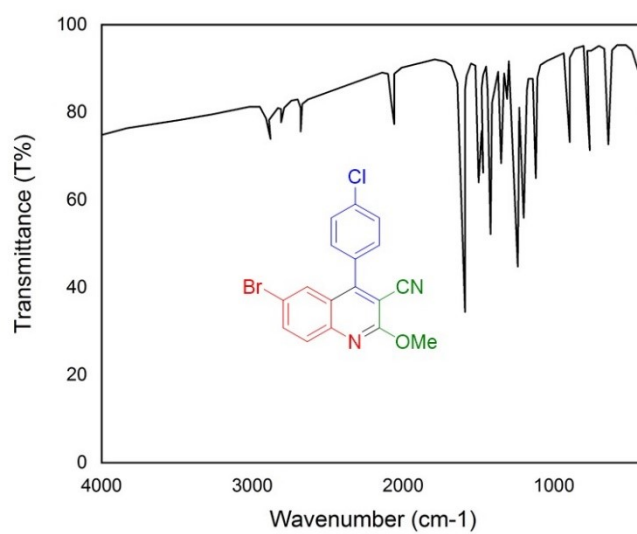


Figure S6. ¹H NMR spectrum of compound 4c

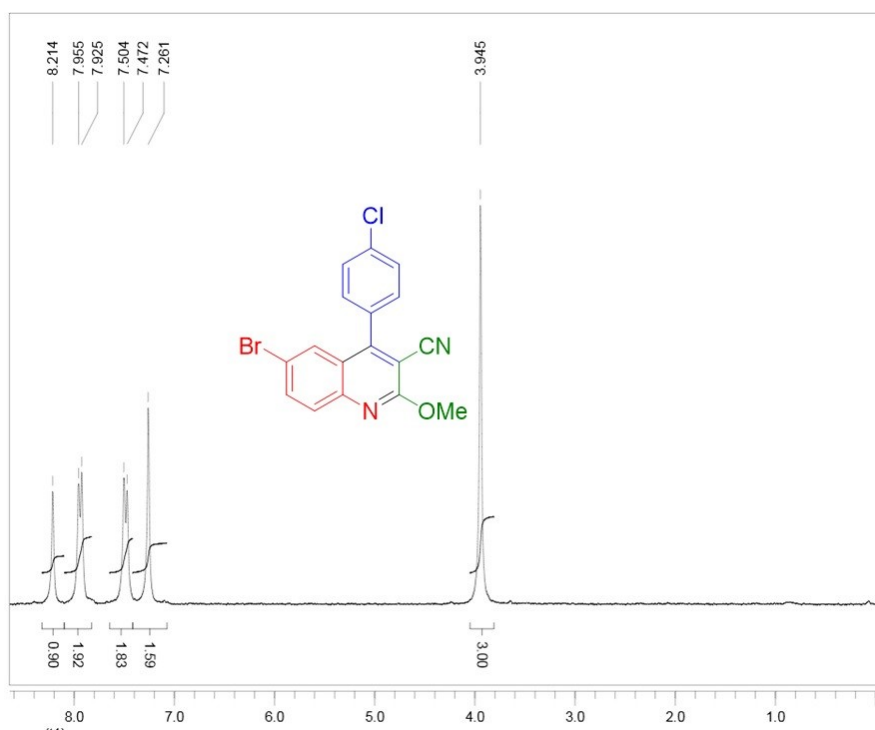


Figure S7. FT-IR spectrum of compound 4d

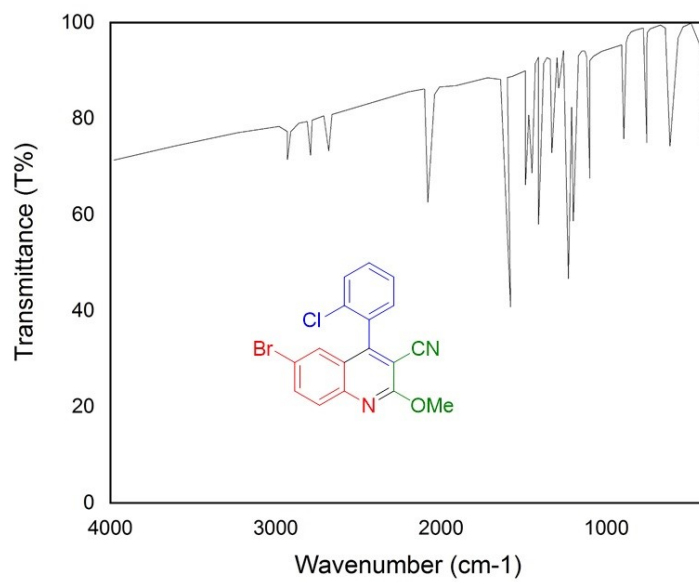


Figure S8. ¹H NMR spectrum of compound 4d

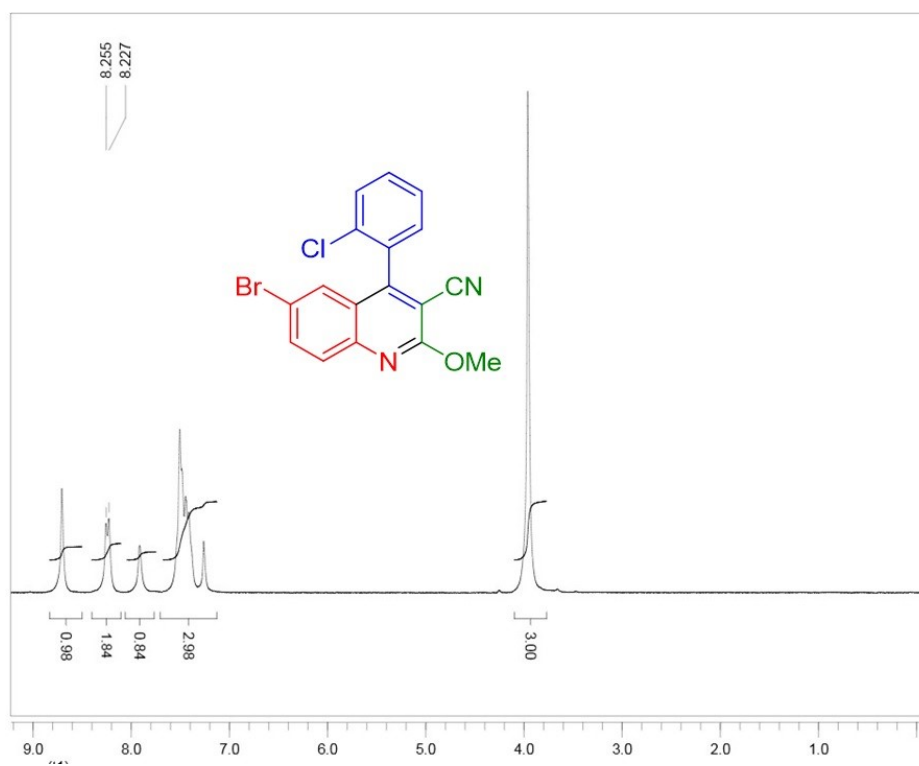


Figure S9. FT-IR spectrum of compound 4e

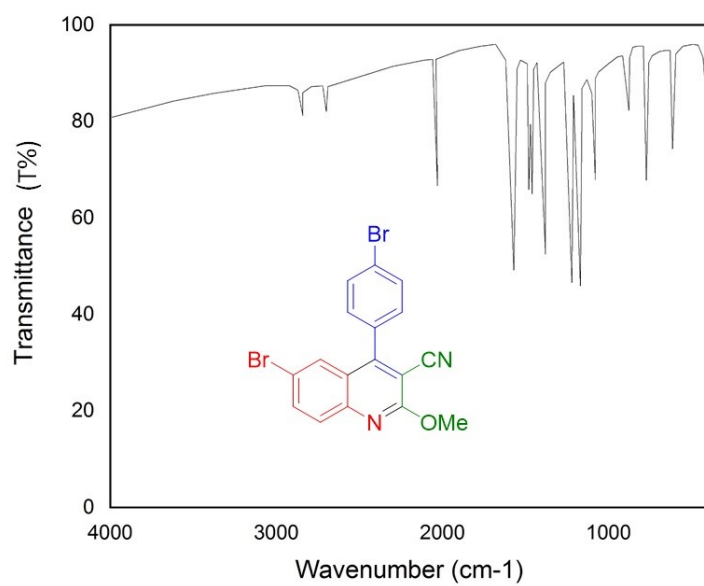


Figure S10. ¹H NMR spectrum of compound 4e

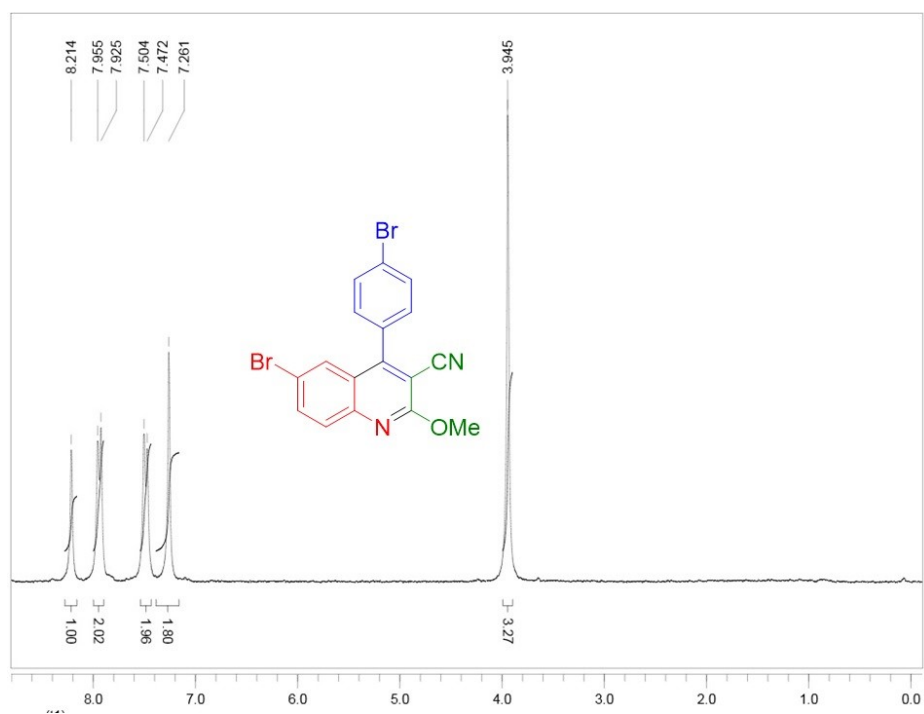


Figure S11. FT-IR spectrum of compound 4f

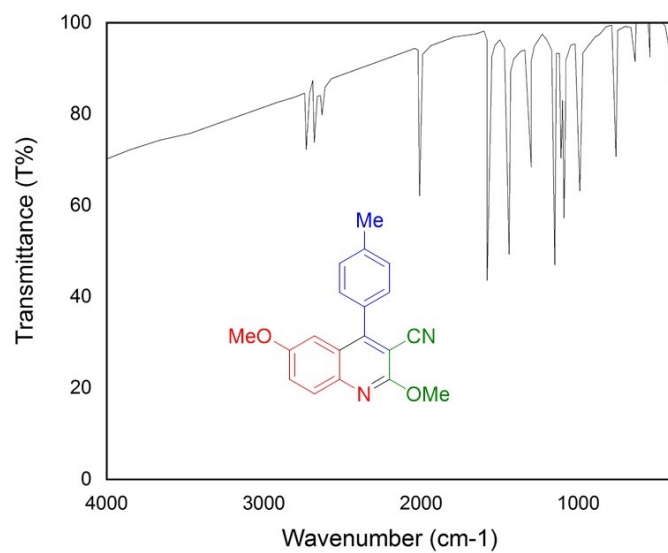


Figure S12. ^1H NMR spectrum of compound 4f

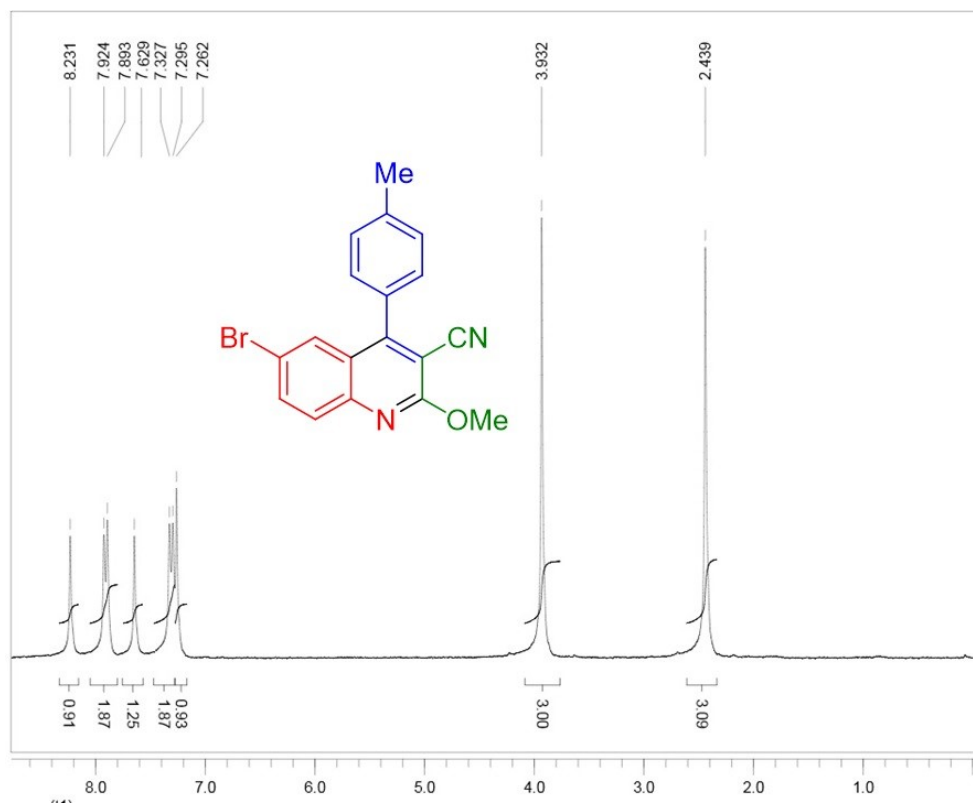


Figure S13. FT-IR spectrum of compound 4g

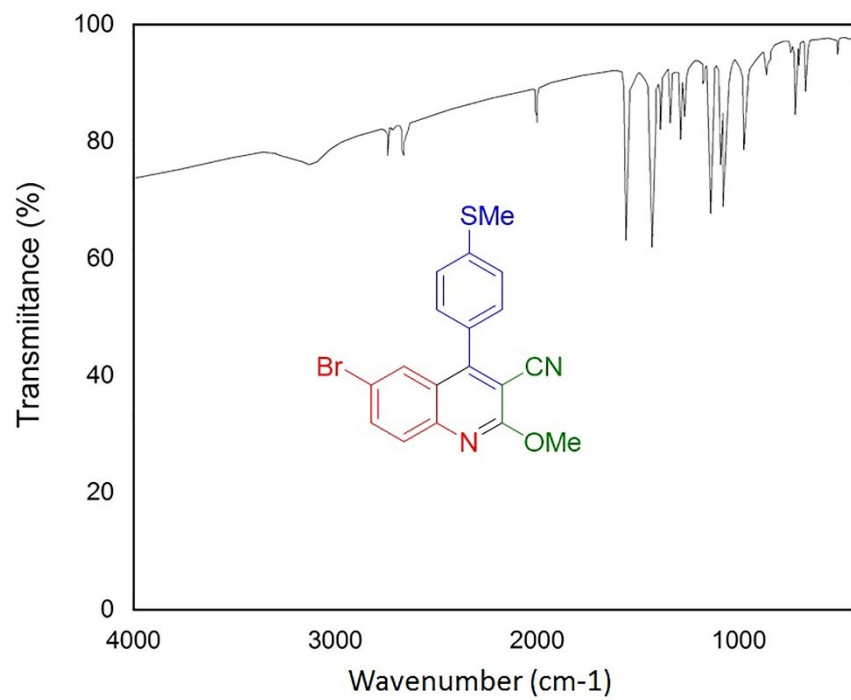
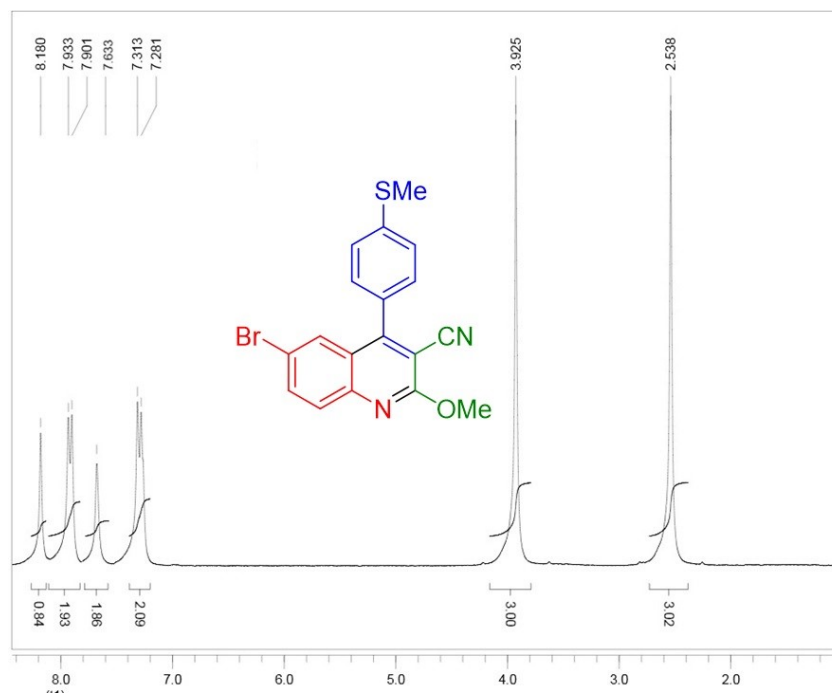


Figure S14. ¹H NMR spectrum of compound 4g



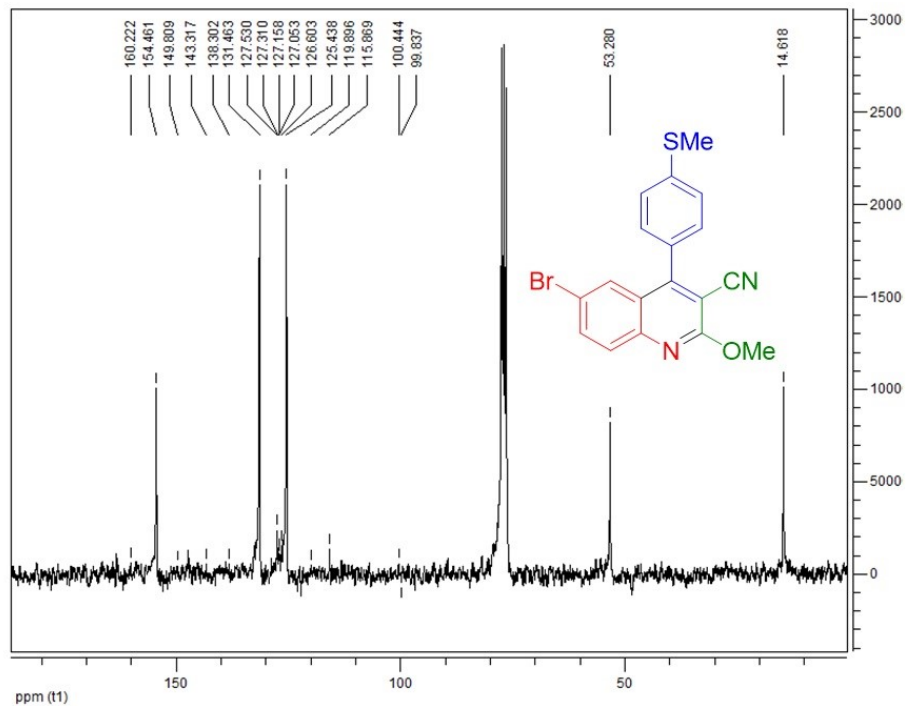


Figure S15. ^{13}C NMR spectrum of compound 4g

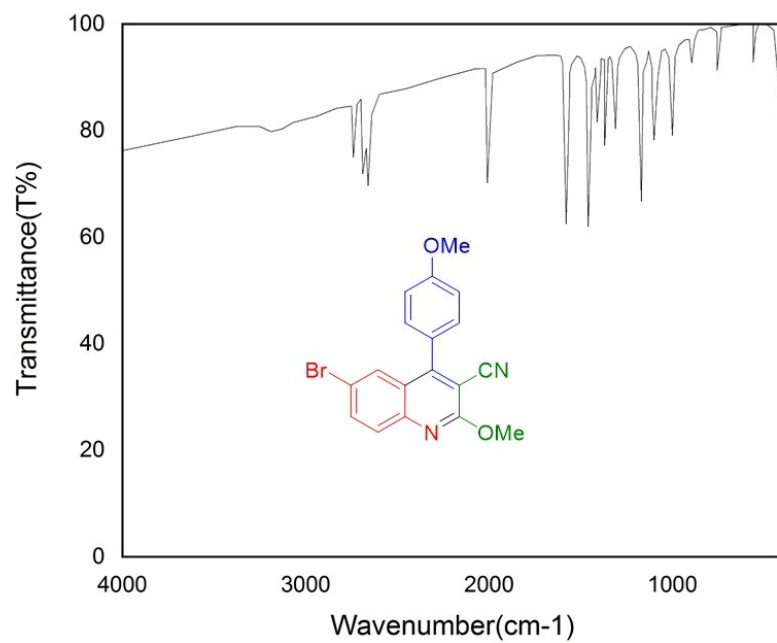


Figure S16. FT-IR spectrum of compound 4h

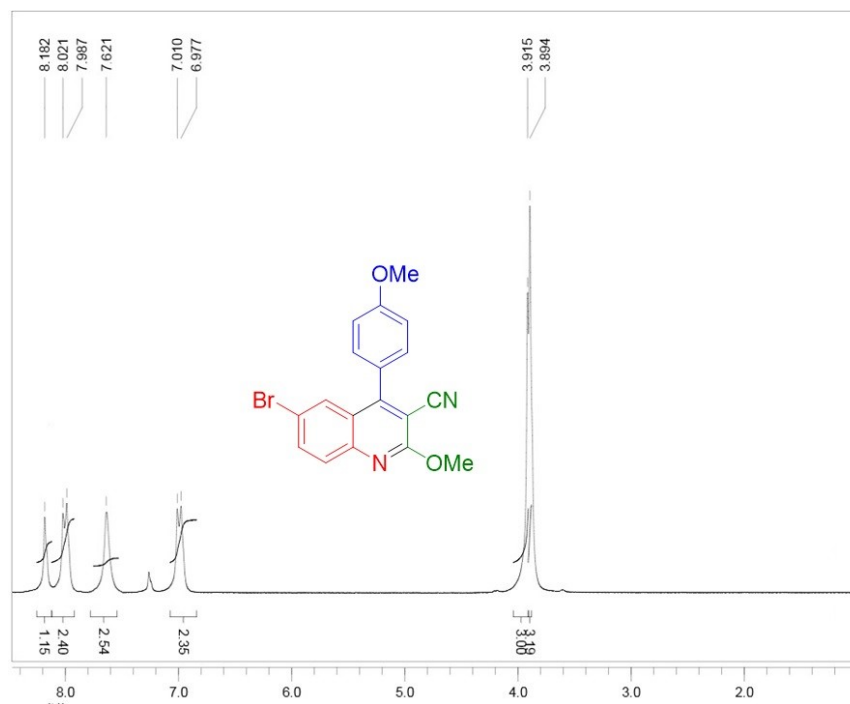


Figure S17. ¹H NMR spectrum of compound 4h

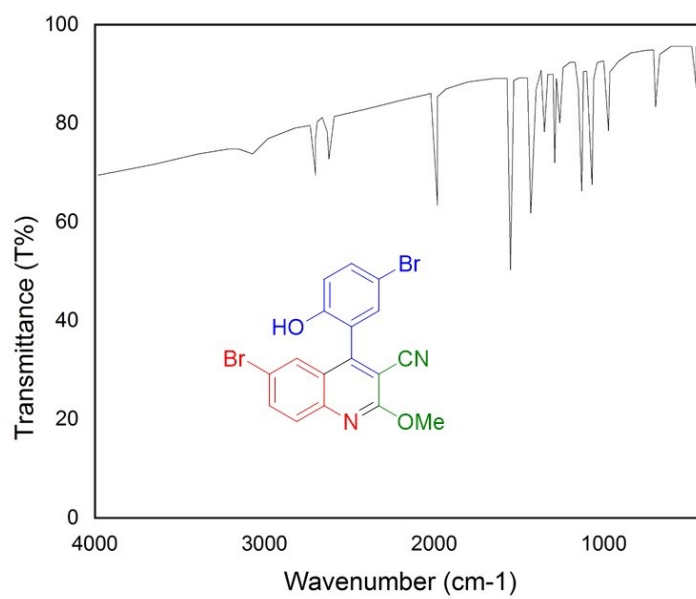


Figure S18. FT-IR spectrum of compound 4i

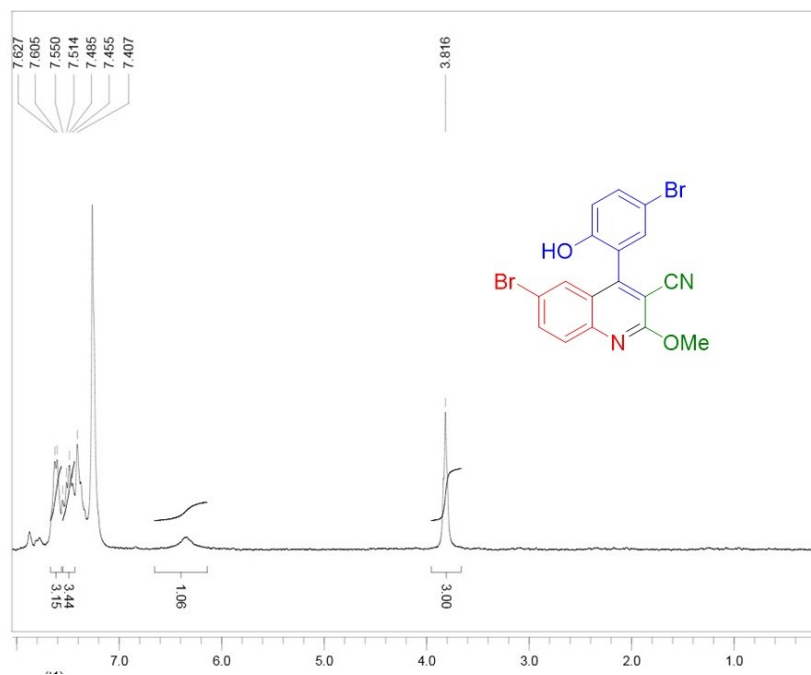


Figure S19. ¹H NMR spectrum of compound 4i

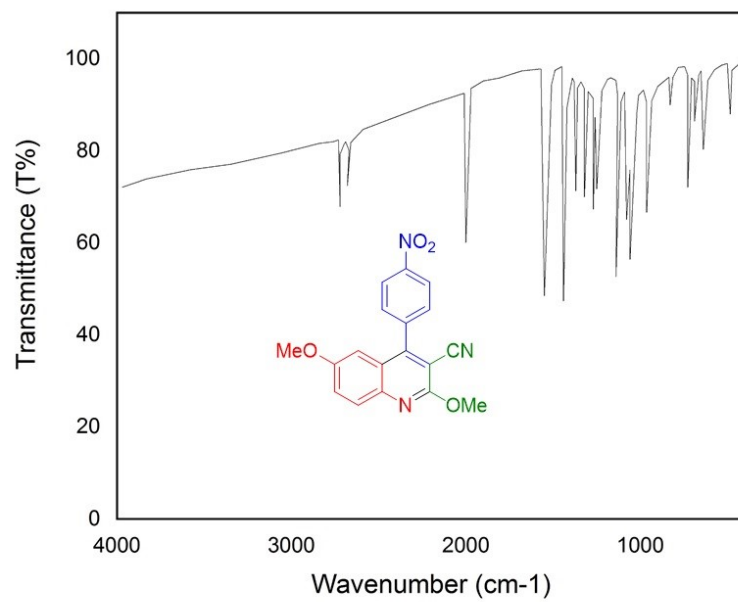


Figure S20. FT-IR spectrum of compound 4j

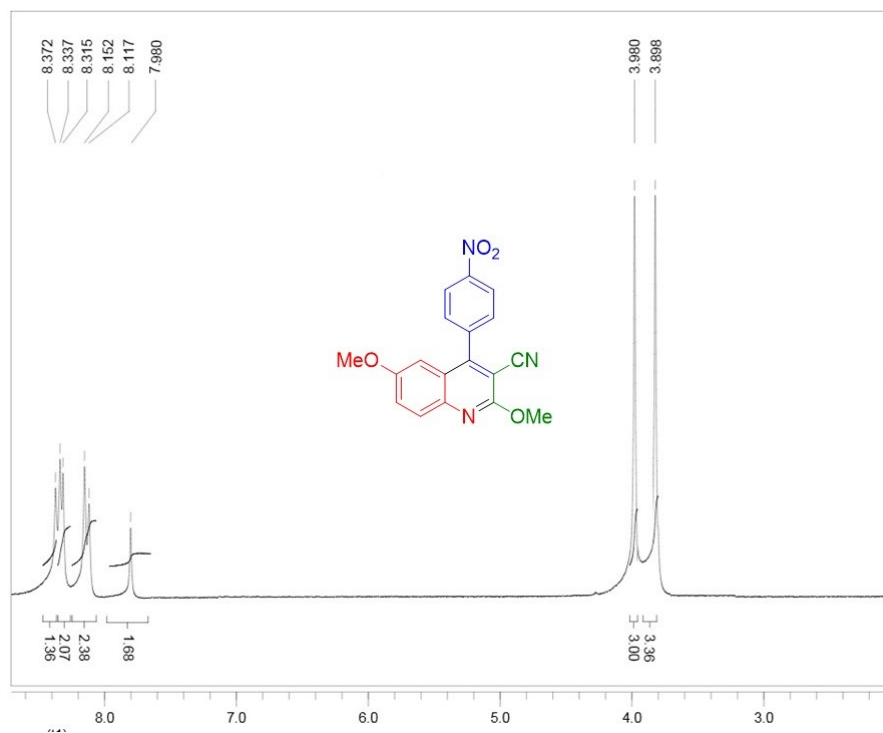


Figure S21. ¹H NMR spectrum of compound 4j

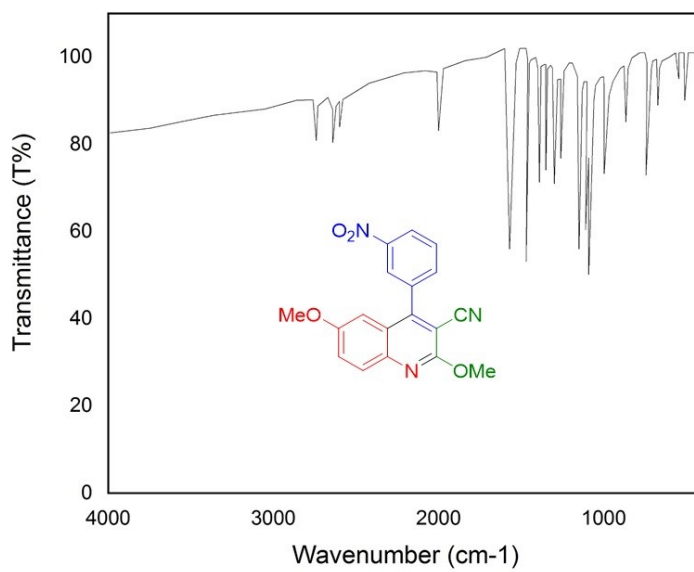


Figure S22. FT-IR spectrum of compound 4k

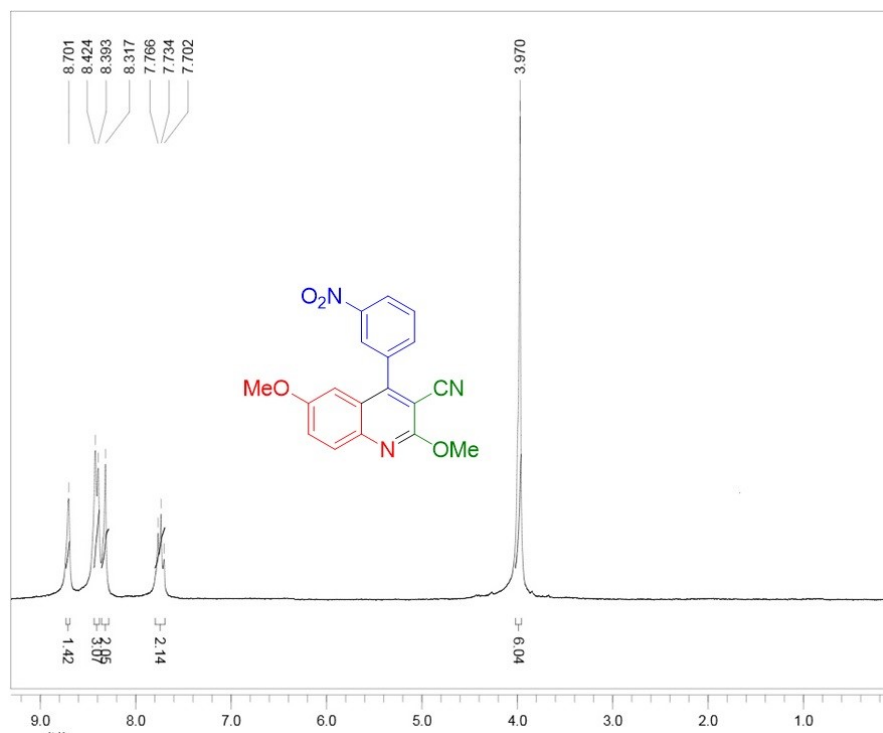


Figure S23. ¹H NMR spectrum of compound 4k

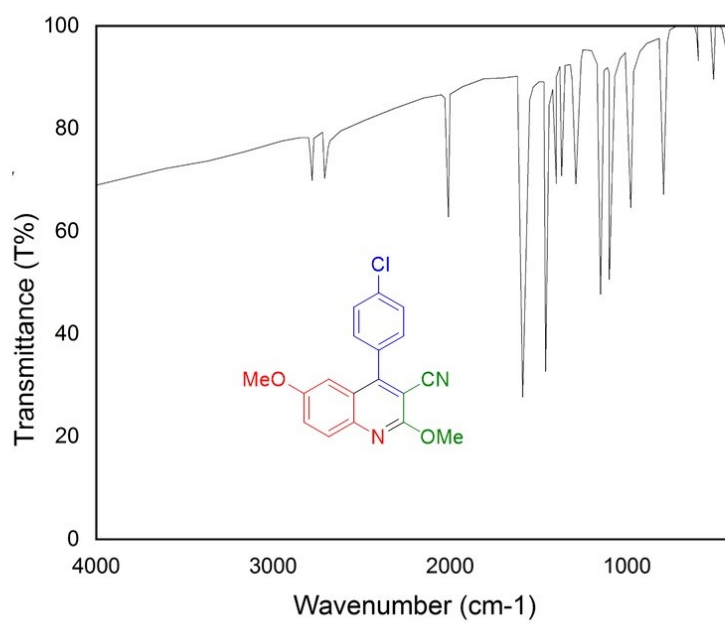


Figure S24. FT-IR spectrum of compound 4l

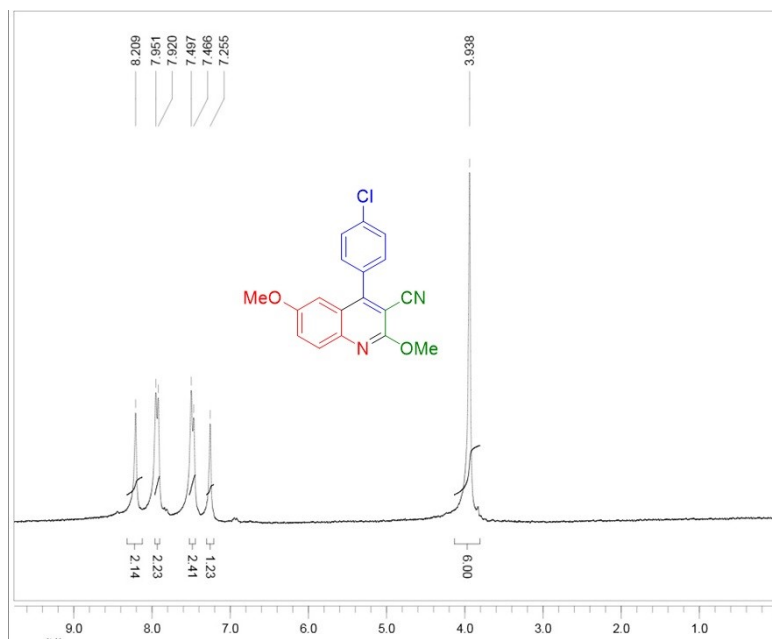


Figure S25. ¹H NMR spectrum of compound 4l

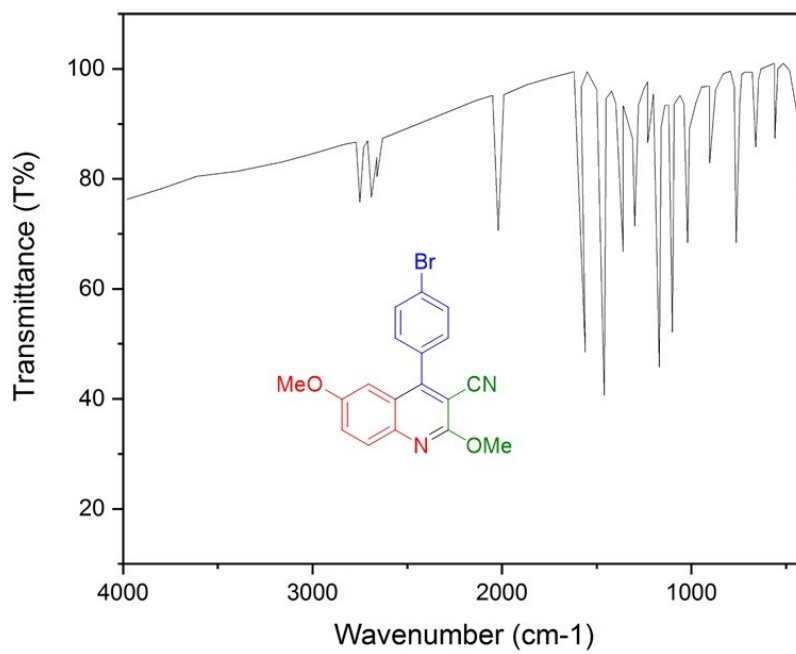


Figure S26. FT-IR spectrum of compound 4m

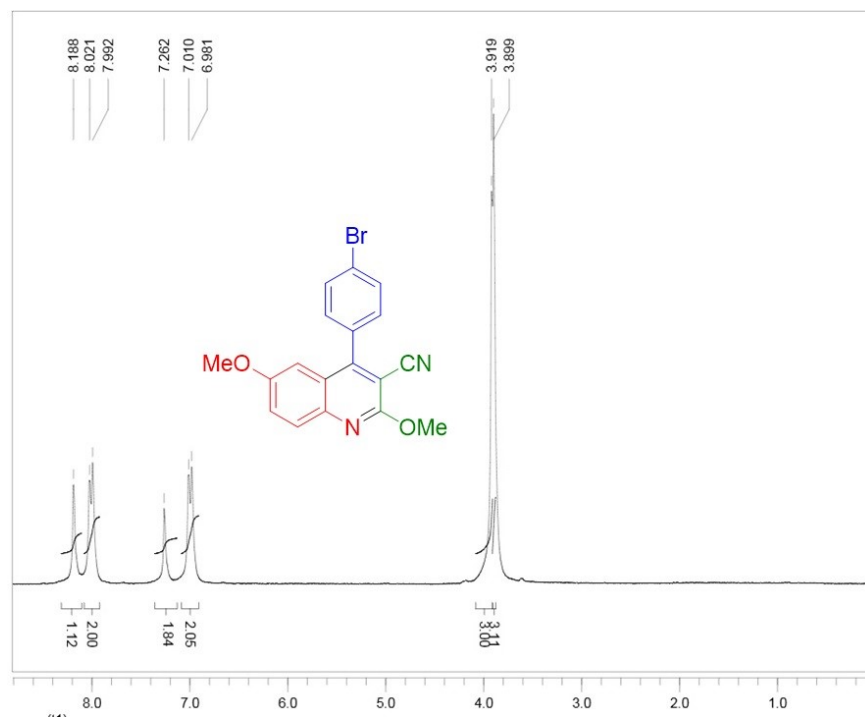


Figure S27. ¹H NMR spectrum of compound 4m

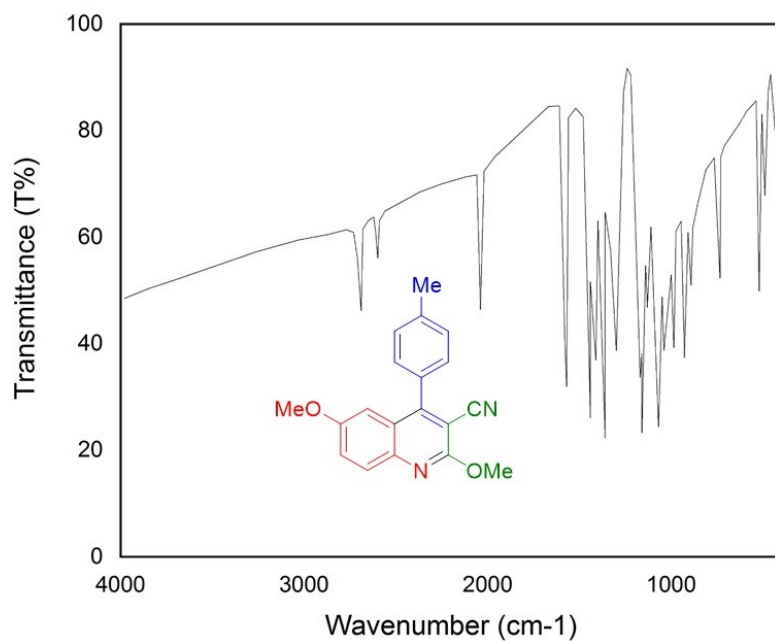


Figure S28. FT-IR spectrum of compound 4n

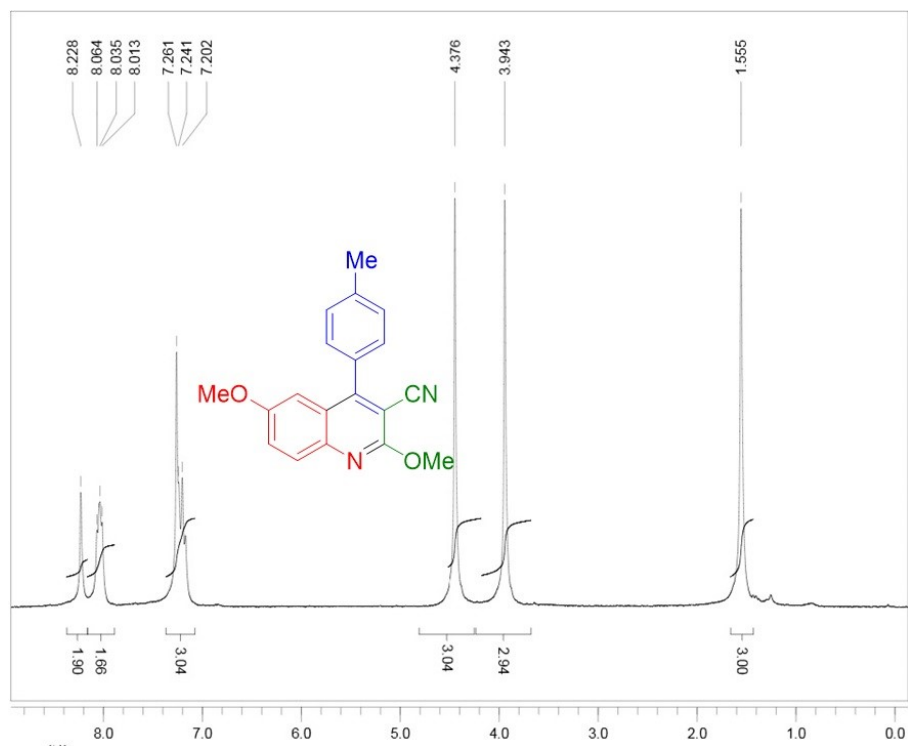


Figure S29. ¹H NMR spectrum of compound 4n

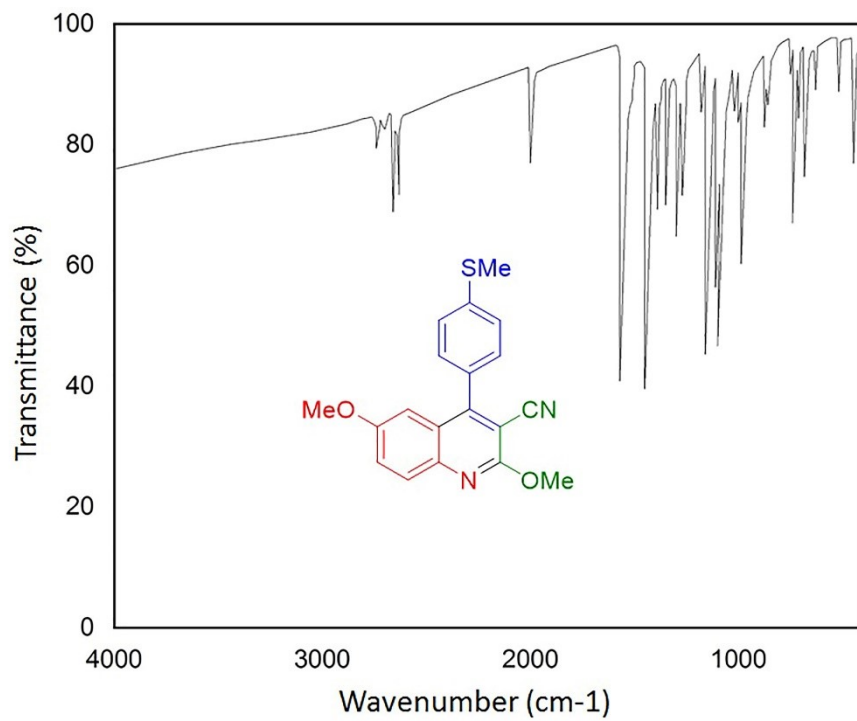


Figure S30. FT-IR spectrum of compound 4o

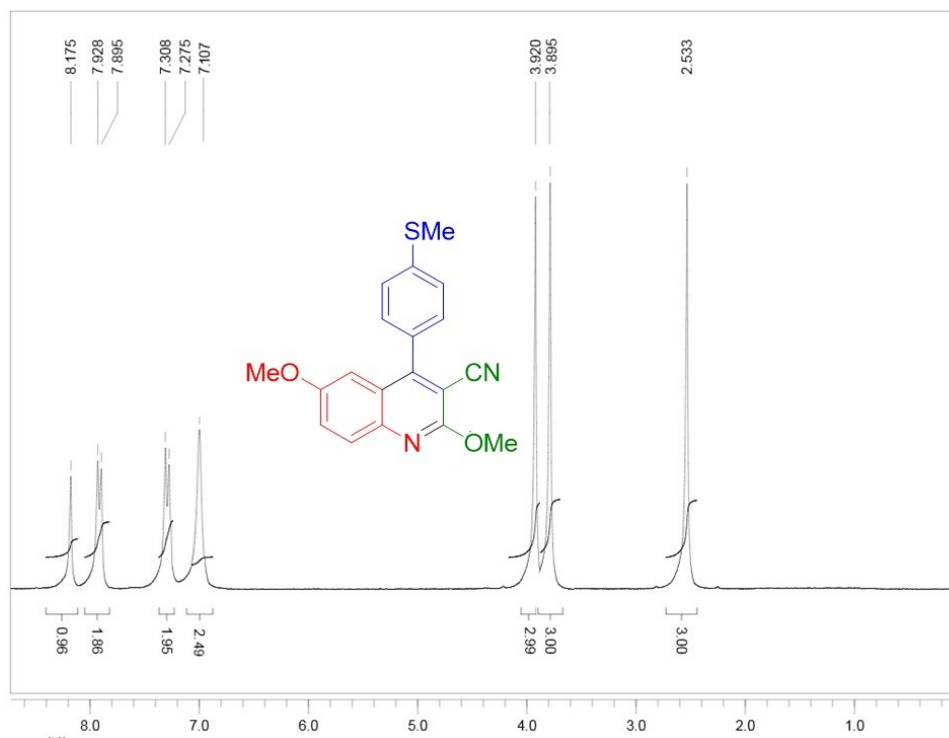


Figure S31. ¹H NMR spectrum of compound 4o

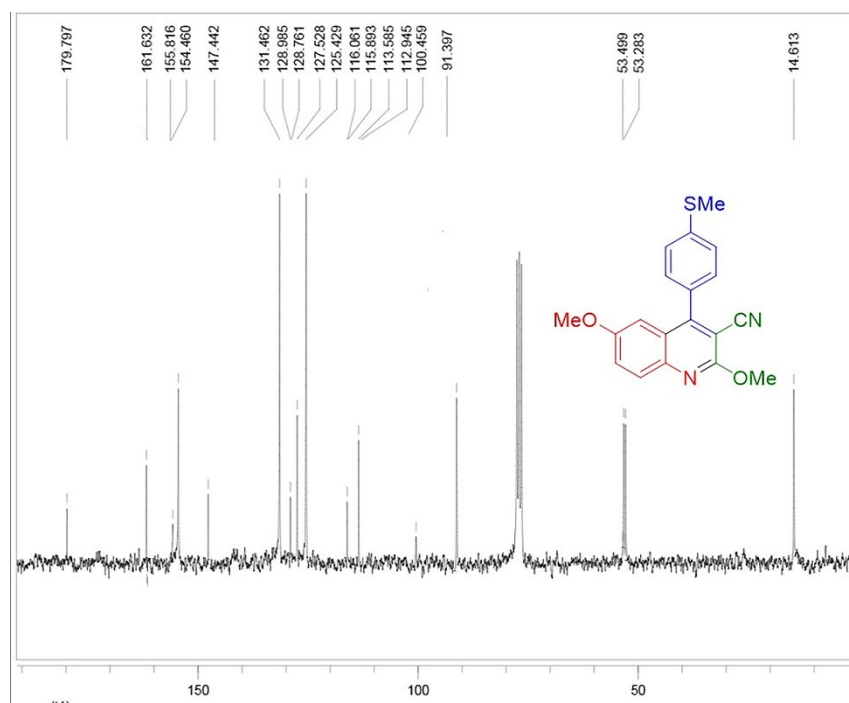


Figure S32. ^{13}C NMR spectrum of compound 4o

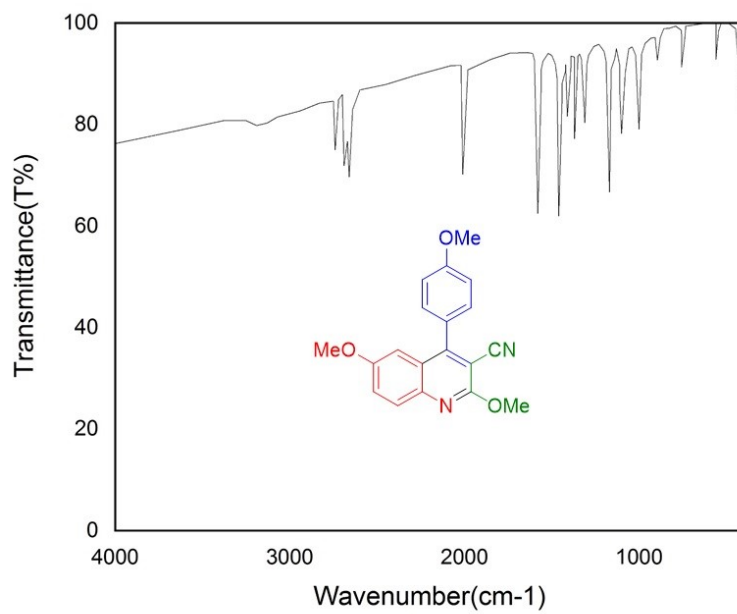


Figure S32. FT-IR spectrum of compound 4p

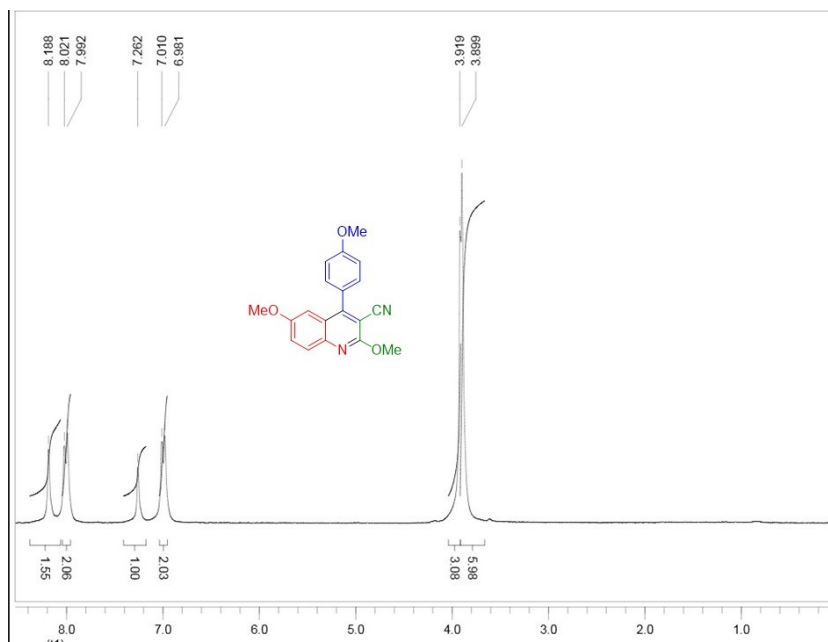


Figure S33. ^1H NMR spectrum of compound 4p

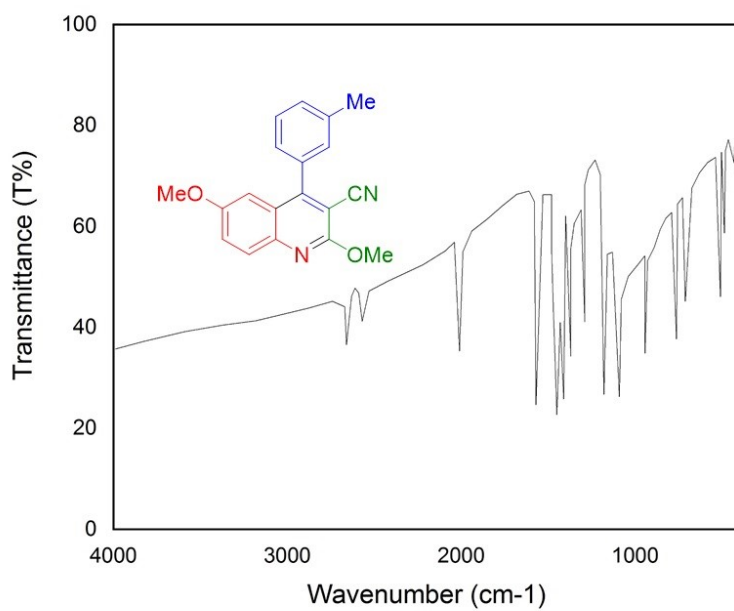


Figure S34. FT-IR spectrum of compound 4q

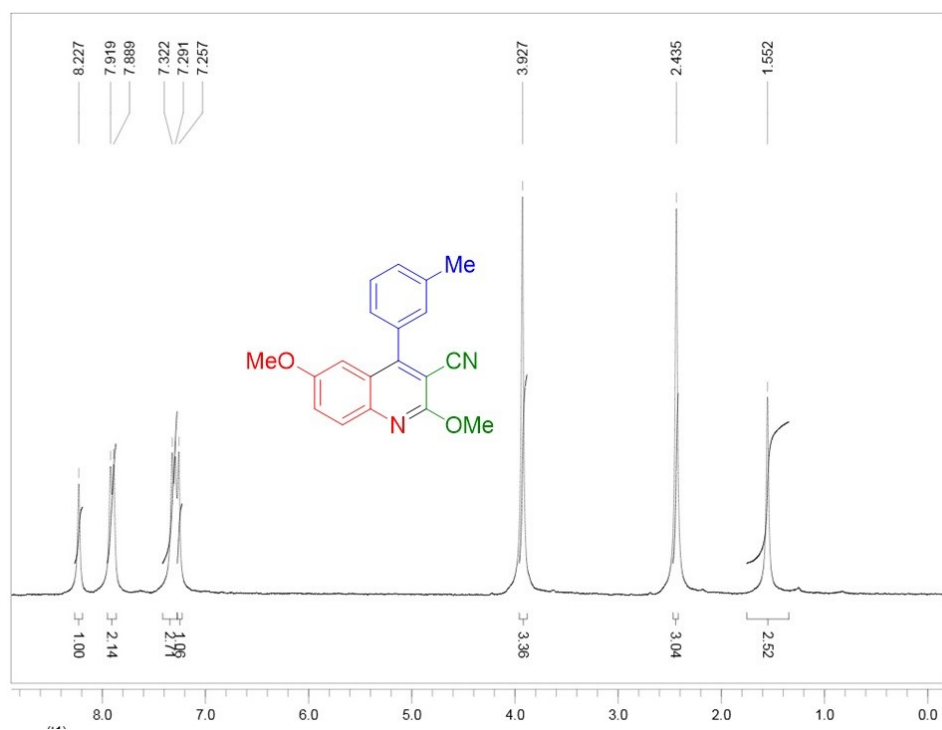


Figure S35. ¹H NMR spectrum of compound 4q