

Chitin and Silk Fibroin Biopolymers Modified by Oxone: Efficient Heterogeneous Catalysts for Knoevenagel reaction

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2-benzylidenemalononitrile (2a)

$C_{10}H_6N_2$, 154.17 g.mol⁻¹; (99 % yield); White crystal, m.p. = 82–84 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3032, 2223, 1591, 1566, 1541, 1450, 1217, 956, 756, 678, 617; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.90 (m, 2H), 7.76 (s, 1H), 7.64 (m, 1H), 7.54 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 159.9, 134.6, 130.7, 129.6, 113.7, 112.5, 82.9; MS (70 eV) m/z = 154 (M⁺, 100%), 127 (88%), 103 (60%).

2-(4-methyl-benzylidene)malononitrile (2b)

$C_{11}H_8N_2$, 168.20 g.mol⁻¹; (98% yield); Brown crystal, m.p. = 134–136 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3115, 3039, 2231, 1604, 1579, 1521, 1490, 1371, 1354, 1344, 1321, 1303, 1213, 935, 850, 833, 746, 682, 619.; ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.82–7.80 (d, J = 8.0 Hz, 2H), 7.72 (s, 1H), 7.35–7.33 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H).; ¹³C NMR (126 MHz, CDCl₃) δ (ppm) = 159.8, 146.4, 130.9, 130.9, 130.4, 128.5, 114.0, 112.8, 81.2, 22.0.; MS (70 eV), m/z = 168 (M⁺, 100%).

2-(4-(dimethylaminobenzylidene)malononitrile (2c)

$C_{11}H_{15}N_3$, 197.24 g.mol⁻¹; (91% yield); Orange crystal, m.p = 176–179 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3084, 3047, 2225, 1612, 1595, 1527, 1479, 1382, 1355, 1340, 1313, 1215, 1153, 1111, 1097, 952, 929, 827, 817, 738, 673, 619.; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.80–7.77 (d, J = 8.0 Hz, 2H), 7.43 (s, 1H), 6.68–6.66 (d, J = 8.0 Hz, 2H), 3.12 (s, 6H).; ¹³C NMR (100 MHz, CDCl₃) δ (ppm) = 190.3, 158.0, 154.2, 133.7, 119.3, 115.9, 114.9, 111.6, 71.19, 40.0.; MS (70 eV), m/z = 197 (M⁺, absent), 188 (52%), 153 (100%).

2-(3,4,5-trimethoxybenzylidene)malononitrile (2d)

$C_{13}H_{12}N_2O_3$, 244.25 g.mol⁻¹; (92% yield); Yellow crystal; m.p = 142–145 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3091, 3021, 2225, 1577, 1552, 1489, 1408, 1288, 1213, 1072, 1006, 937, 823, 615, 518; ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.63 (s, 2H), 7.17 (s, 1H), 3.96 (s, 3H), 3.89 (s, 6H).; ¹³C NMR (126 MHz, CDCl₃) δ (ppm) = 159.32, 153.35, 144.03, 125.89, 113.94, 113.15, 108.31, 80.59, 61.21, 56.34, 29.66; MS (70 eV), m/z = 244 (M⁺, 100).

2-(4-hydroxy-3-methoxybenzylidene)malononitrile (2e)

$C_{11}H_8N_2O_2$, 200.20 g.mol⁻¹; (94% yield); Yellow solid, m.p. = 134–135 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3394, 2227, 1618, 1564, 1514, 1282, 1138; ¹H NMR (400 MHz, MeOD) δ (ppm) = 7.94 (s, 1H), 7.57–7.56 (d, J = 2.5 Hz, 1H), 7.44–7.42 (m, 1H), 7.08–7.06 (d, J = 8.5 Hz, 1H), 3.95 (s, 3H); ¹³C NMR (100 MHz, MeOD) δ (ppm) = 159.83, 153.67, 146.02, 126.14, 124.72,

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115.25, 114.34, 111.14, 77.12, 55.22; MS (70 eV) m/z = 200 (M^+ , absent), 170 (100%), 142 (47%), 119 (42%).

2-(4-fluorobenzylidene)malononitrile (2f)

$C_{10}H_5N_2F$, 172.16 g.mol⁻¹; (98 % yield); White crystal, m.p. = 121–123 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3078, 3035, 2939, 2229, 1597, 1575, 1506, 1415, 1379, 1305, 1244, 1163, 1107, 943, 839, 804, 617, 563, 530, 410; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.98–7.96 (m, 2H), 7.75 (s, H), 7.27–7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.11 (d, $^1J_{C-F}$ = 207 Hz), 158.24, 133.44, 133.37, 127.36, 117.18, 113.53, 112.46, 82.49; MS (70 eV), m/z = 172 (M^+ , 100%), 145 (89%), 121 (54%).

2-(4-chlorobenzylidene)malononitrile (2g)

$C_{10}H_5N_2Cl$, 188.61 g.mol⁻¹; (98% yield); White crystal, m.p. = 161–163 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3084, 3047, 2225, 1612, 1595, 1527, 1479, 1382, 1355, 1340, 1215, 1153, 1111, 1097, 952, 929, 827, 817, 738, 673, 619; 1H NMR (500 MHz, $CDCl_3$) δ (ppm) = δ 7.78–7.76 (d, J = 8.5 Hz, 2H), 7.72 (s, 1H), 7.70–7.69 (d, J = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 158.5, 133.2, 131.9, 130.1, 129.8, 113.6, 112.5, 83.5; MS (70 eV) m/z = 188 (M^+ , 57%), 161 (25%), 153 (100%).

2-(4-bromobenzylidene)malononitrile (2h)

$C_{10}H_5N_2Br$, 232.07 g.mol⁻¹; (97% yield); White crystal, m.p. = 165–166 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3091, 3032, 2225, 1577, 1552, 1489, 1408, 1288, 1213, 1072, 1006, 937, 823, 615, 516; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.76–7.74 (d, J = 8.0 Hz, 2H), 7.69–7.65 (d, J = 8.0 Hz, 2H), 7.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 158.4, 133, 131.8, 129.9, 129.6, 83.5; MS (70 eV) m/z = 232 (M^+ , 31%), 234 (M^+ , 30%), 153 (100%).

2-(4-hydroxybenzylidene)malononitrile (2i)

$C_{10}H_6N_2O$, 170.17 g.mol⁻¹; (90 % yield); Yellow solid, m.p. = 187–190 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3352, 2225, 1610, 1579, 1566, 1519, 1444, 1436, 1300, 1220, 1174, 939, 839, 636, 607, 524; 1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.89–7.88 (d, J = 9.0 Hz, 2H), 7.87 (s, 1H), 6.92 (d, J = 9.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 164.0, 159.8, 133.7, 123.1, 116.3, 114.6, 113.6, 76.0; MS (70 eV) m/z = 170 (M^+ , 100%), 142 (44%), 142 (21%), 119 (38%).

2-(4-nitrobenzylidene)malononitrile (2j)

$C_{10}H_5N_3O_2$, 199.17 g.mol⁻¹; (99 % yield); Orange crystal, m.p. = 155–157 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3021, 2227, 1597, 1589, 1579, 1411, 1263, 1234, 1024, 974, 802, 692, 619; 1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.38–8.36 (d, J = 8.8 Hz, 2H), 8.07–8.04 (d, J = 8.8 Hz, 2H), 7.87 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 156.82, 150.33, 135.76, 131.27, 124.60, 112.58, 111.55, 87.52; MS (70 eV) m/z = 199 (M^+ , 84%), 169 (51%), 141 (68%), 126 (100%).

2-(4-cyanobenzylidene)malononitrile (2k)

$C_{11}H_5N_3$, 179.18 g.mol⁻¹; (92% yield); White crystal; m.p. = 151–154 °C; FTIR (pure) $\nu_{max}(cm^{-1})$ = 2920, 2850, 2222, 1604, 1571, 1512, 1369, 1319, 1278, 1236, 1184, 1153, 1022, 833, 609, 570, 528.; 1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.81–7.79 (d, J = 8.0 Hz, 2H), 7.79 (s, 1H), 6.68–6.66 (d, J = 8.0, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$); 190.3, 158.1, 154.2, 133.7, 119.3, 115.9, 114.8, 111.6, 110.9, 77.3, 76.9, 76.6.; MS (70 eV), m/z = 179 (M^+ , 100%).

2-(2-methyl-3-phenylallylidene)malononitrile (2l)

$C_{13}H_{10}N_2$, 194.24 g.mol⁻¹; (95 % yield); Orange crystal; m.p. = 128–130 °C; FTIR $\nu_{max}(cm^{-1})$ (pure) = 3338, 3198, 2957, 2203, 1681, 1595, 1522, 1372.; 1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.48–7.42 (m, 6H), 7.16–7.15 (m, 1H), 2.43 (d, J = 1.2 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) = 164.4, 149.6, 134.5, 133.4, 130.3, 130.2, 128.8, 114.5, 112.8, 81.0, 14.9.; MS (70 eV), m/z : 194 (M^+ , 75%), 193 (100%).



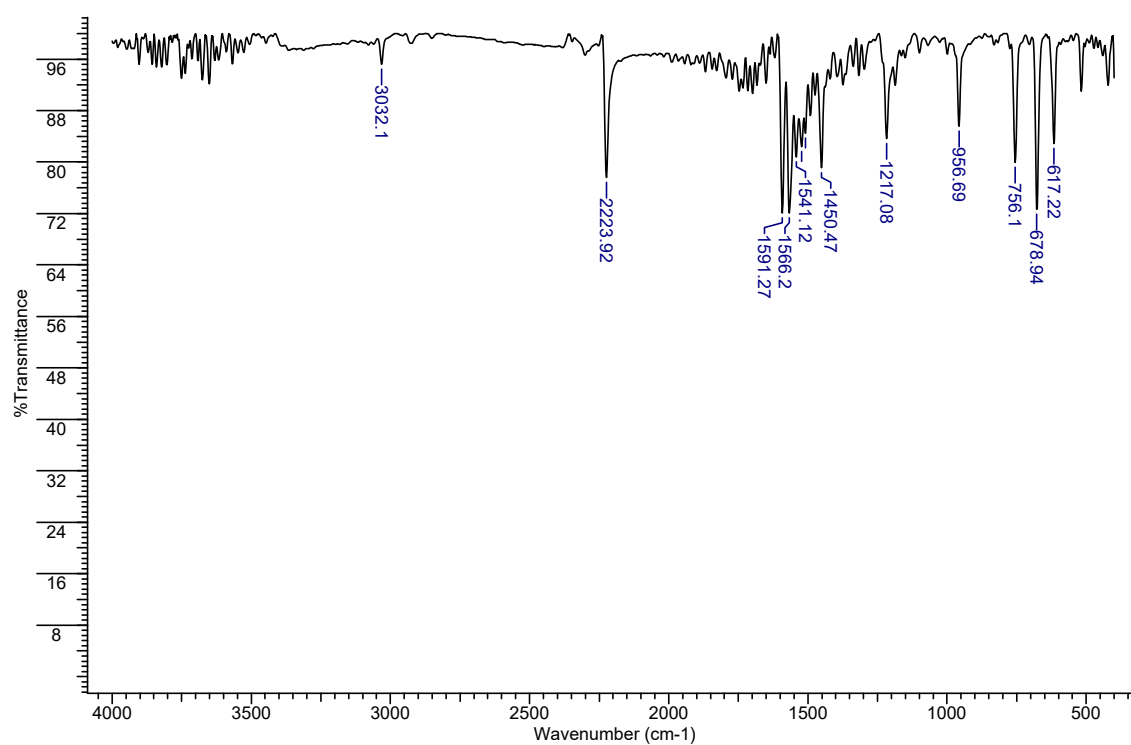


Figure S3. FT-IR of 2-benzylidenemalononitrile 2a.

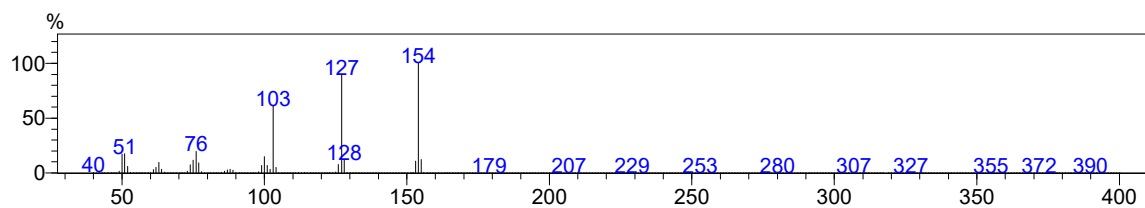


Figure S4. MS (70 eV) of 2-benzylidenemalononitrile 2a.

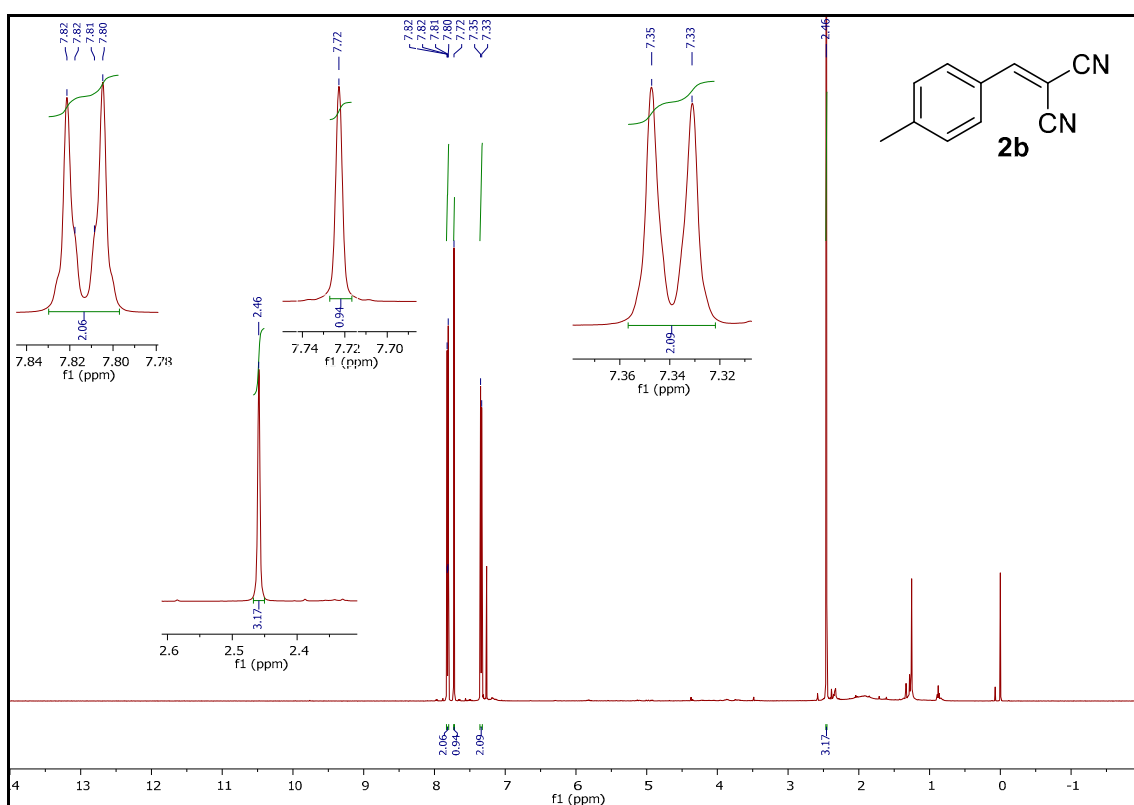


Figure S5. ¹H NMR (500 MHz, CDCl₃) of 2-(4-methylbenzylidene)malononitrile **2b**.

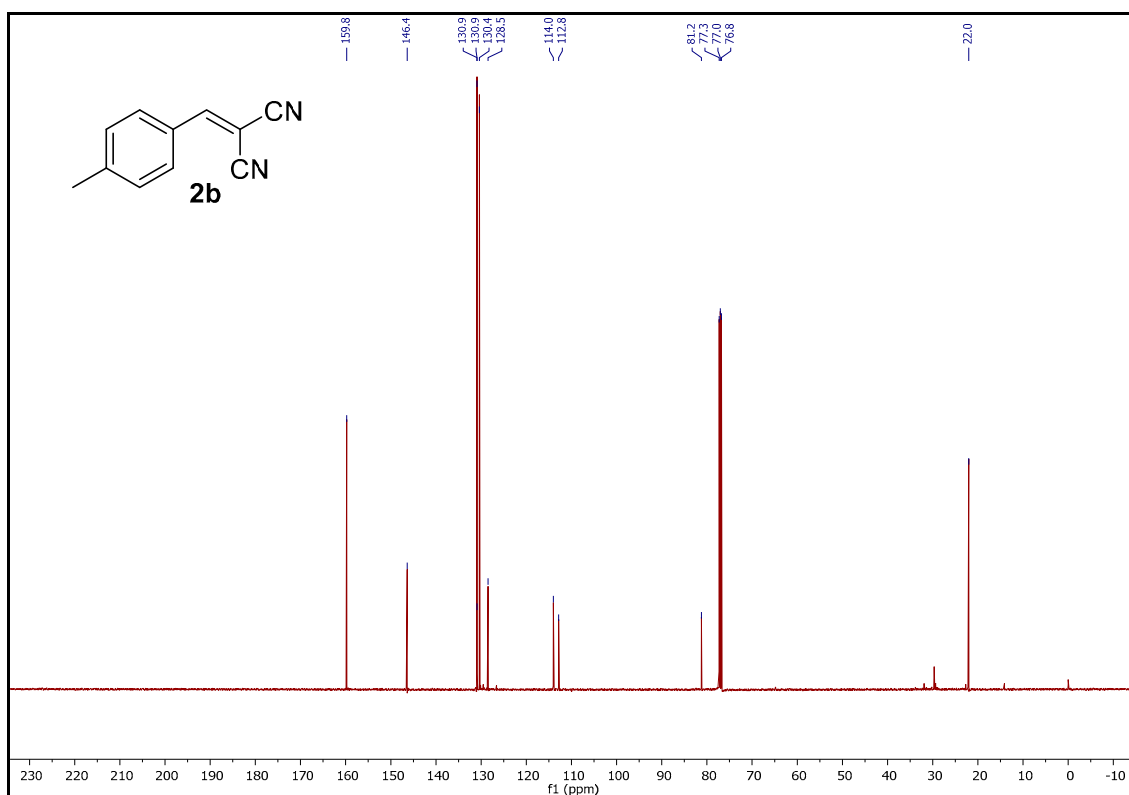


Figure S6. ¹³C NMR (125 MHz, CDCl₃) of 2-(4-methylbenzylidene)malononitrile **2b**.

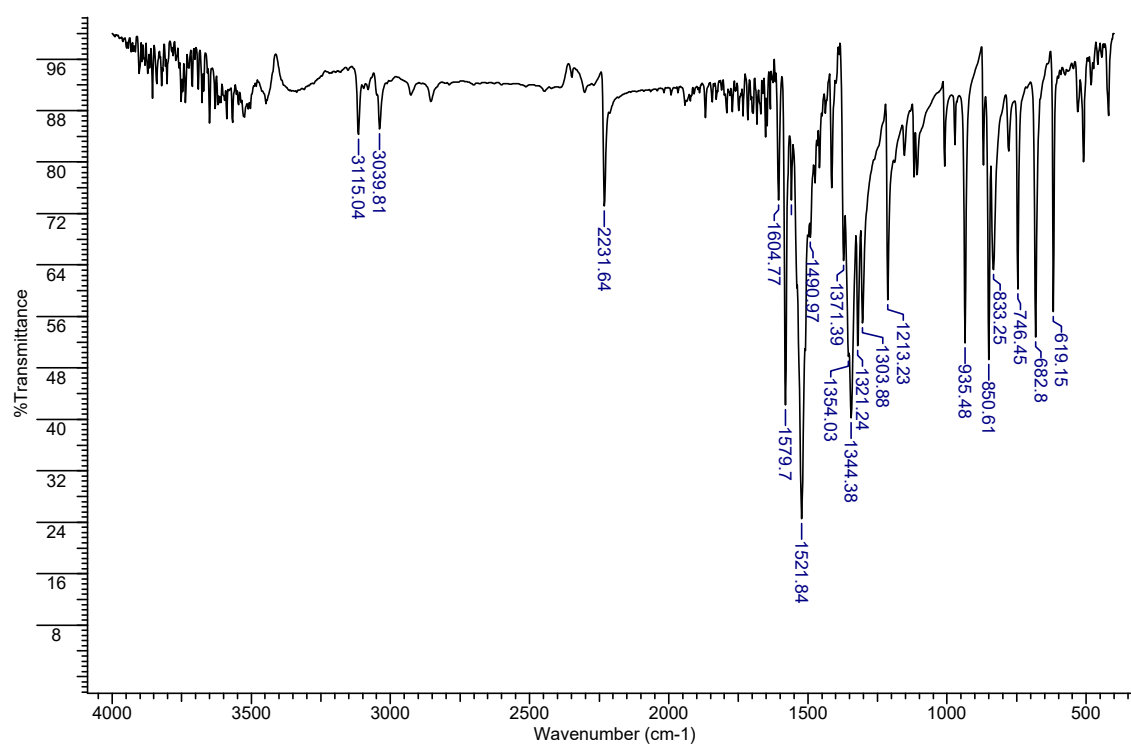


Figure S7. FT-IR of 2-(4-methylbenzylidene)malononitrile **2b**.

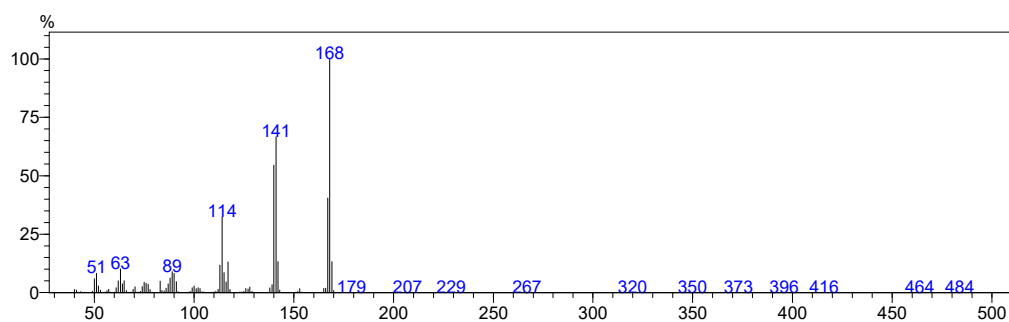


Figure S8. MS (70 eV) of 2-(4-methylbenzylidene)malononitrile **2b**.

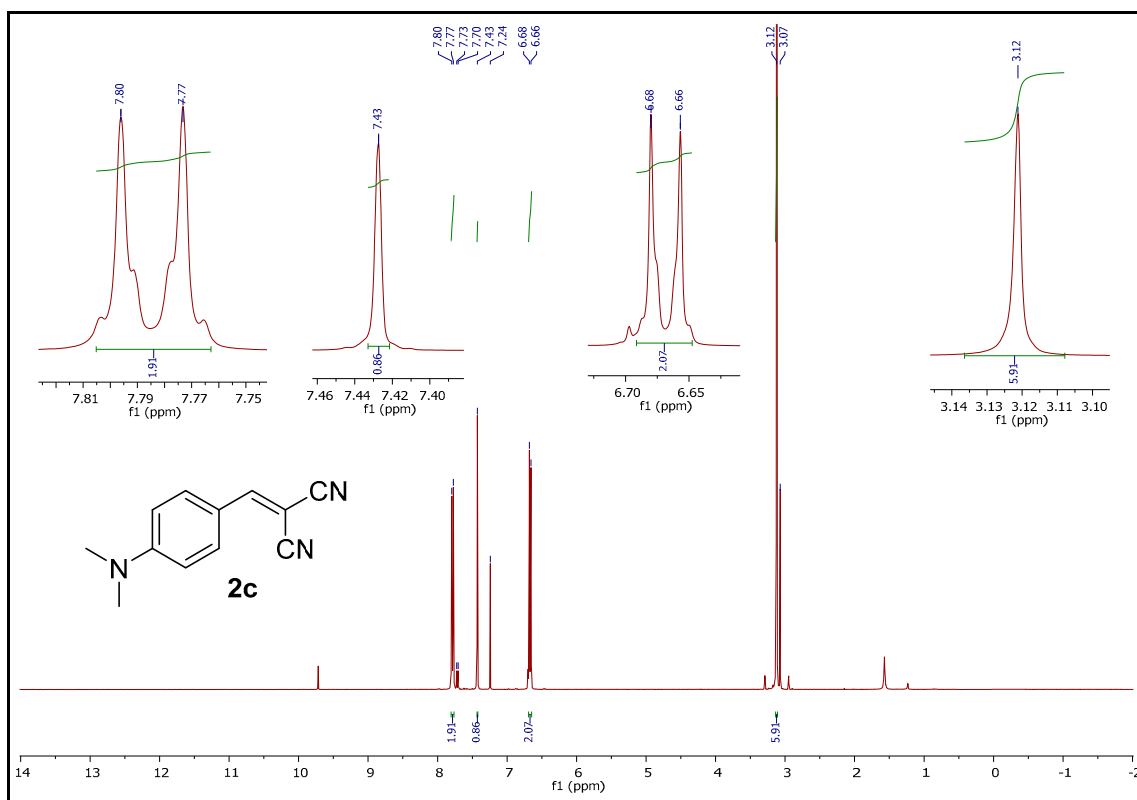


Figure S9. ¹H NMR (400 MHz, CDCl₃) of 2-(4-(dimethylamino)benzylidene) malononitrile 2c.

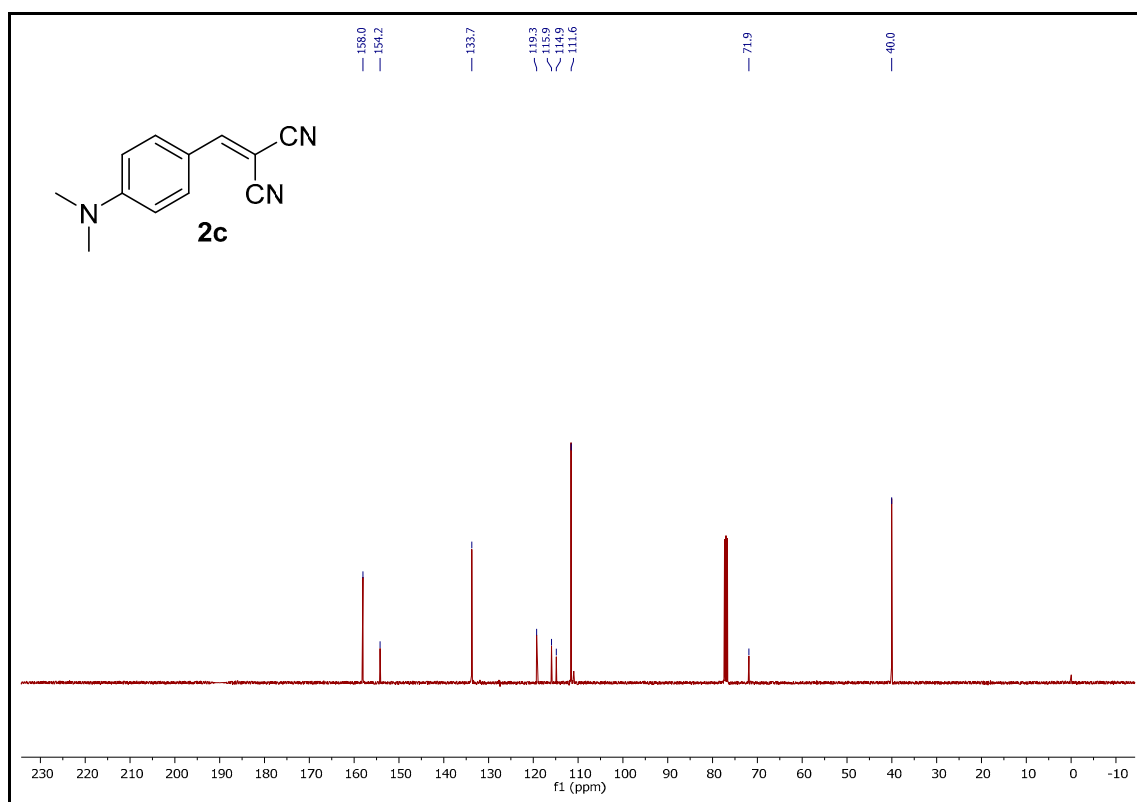


Figure S10. ¹³C NMR (100 MHz, CDCl₃) of 2-(4-(dimethylamino)benzylidene)malononitrile 2c.

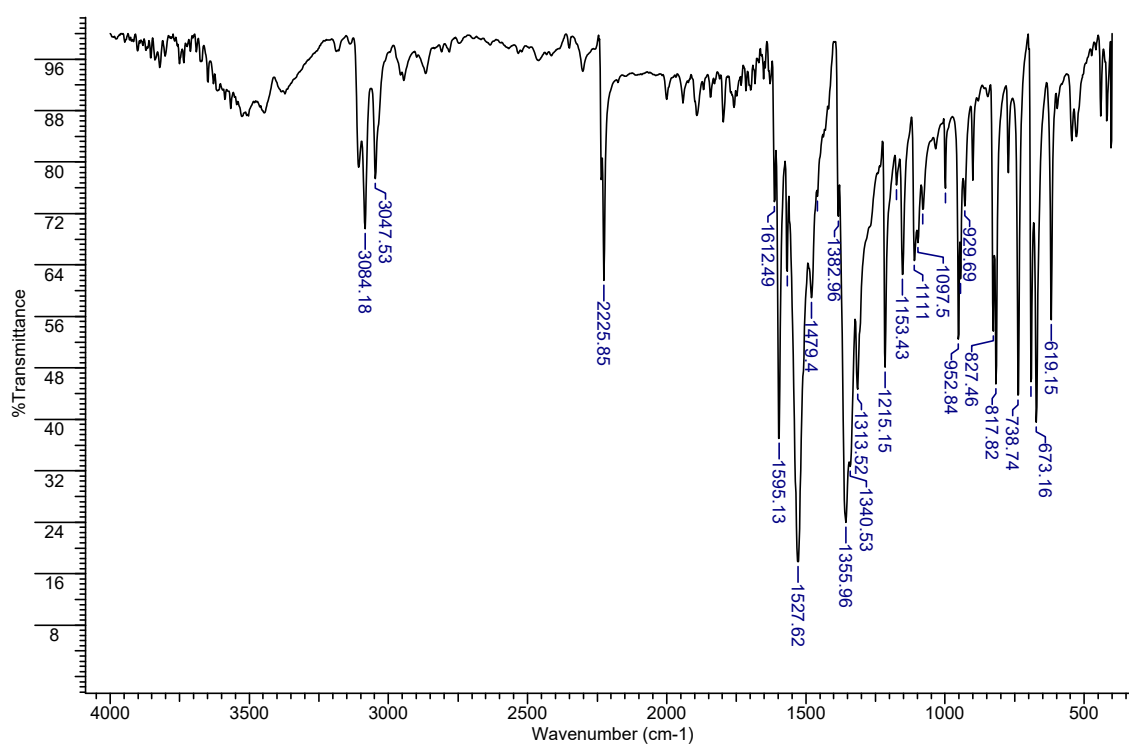


Figure S11. FT-IR of 2-(4-(dimethylamino)benzylidene)malononitrile 2c.

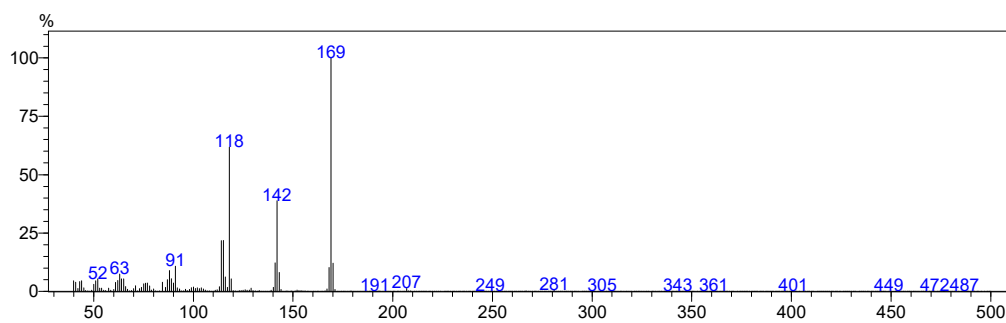


Figure S12. MS (70 eV) of 2-(4-(dimethylamino)benzylidene)malononitrile 2c.

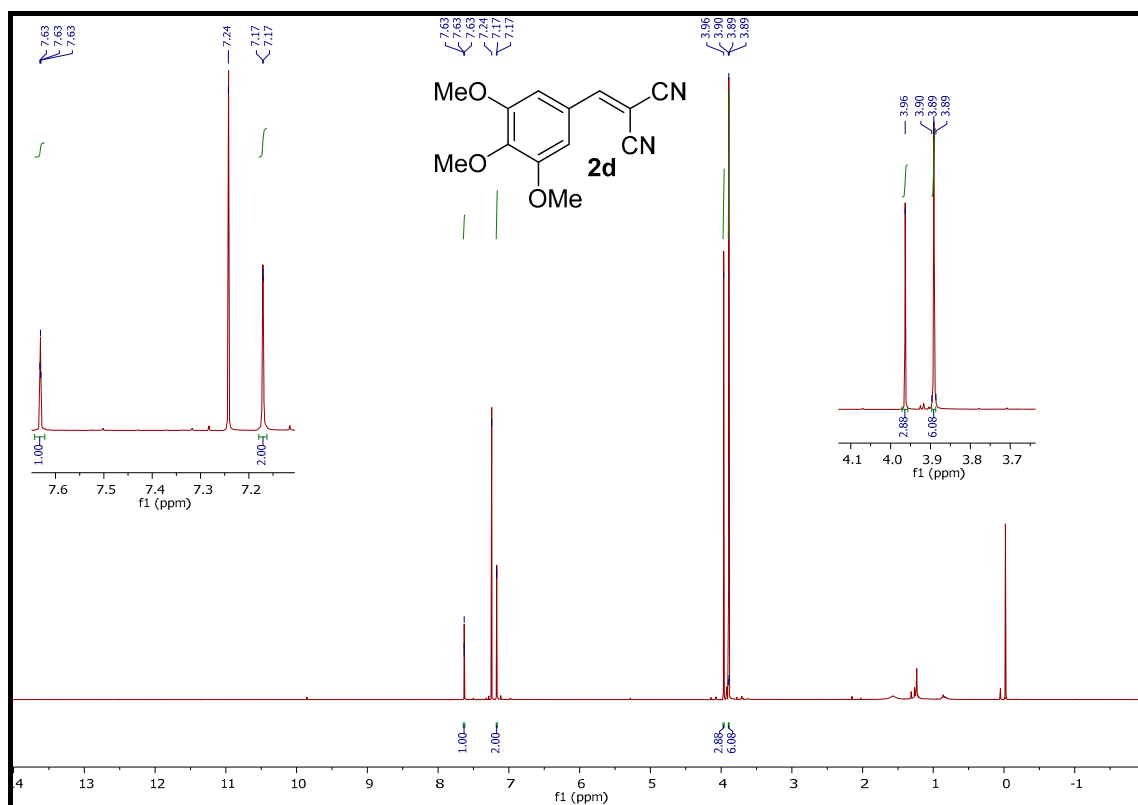


Figure S13. ¹H NMR (500 MHz, CDCl₃) of 2-(3,4,5-trimethoxybenzylidene)malononitrile **2d**.

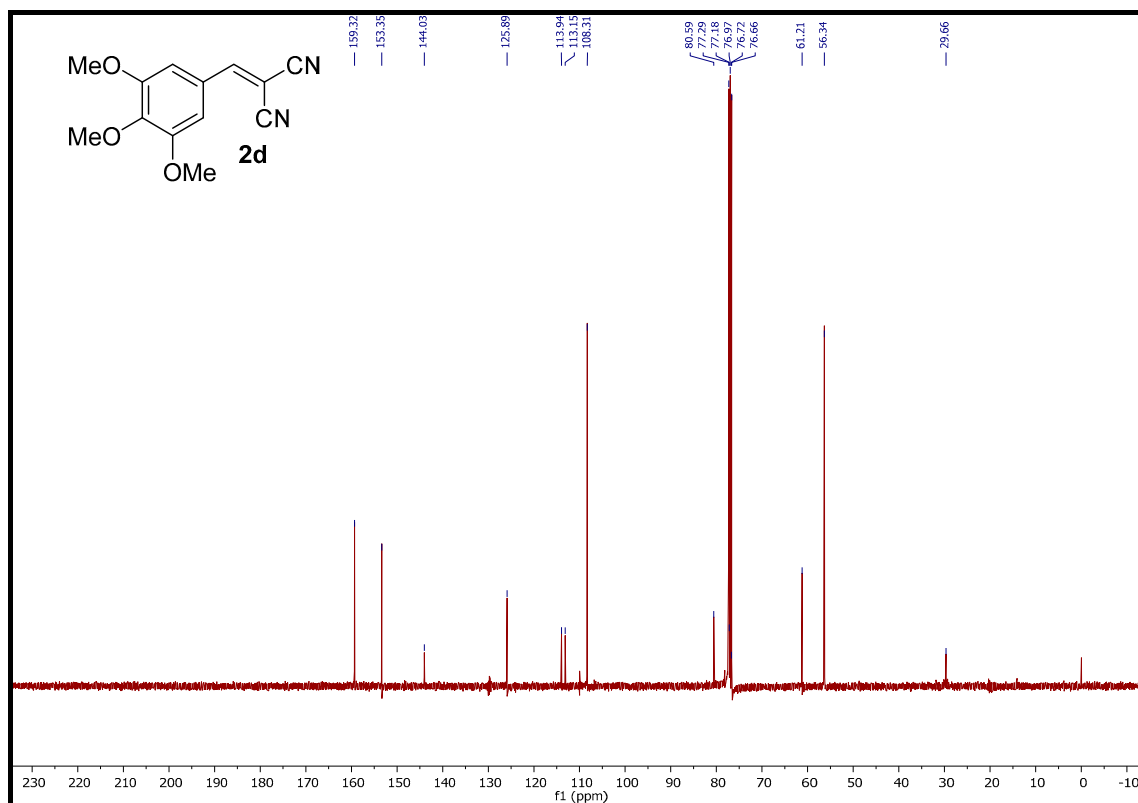


Figure S14. ¹³C NMR (125 MHz, CDCl₃) of 2-(3,4,5-trimethoxybenzylidene)malononitrile **2d**.

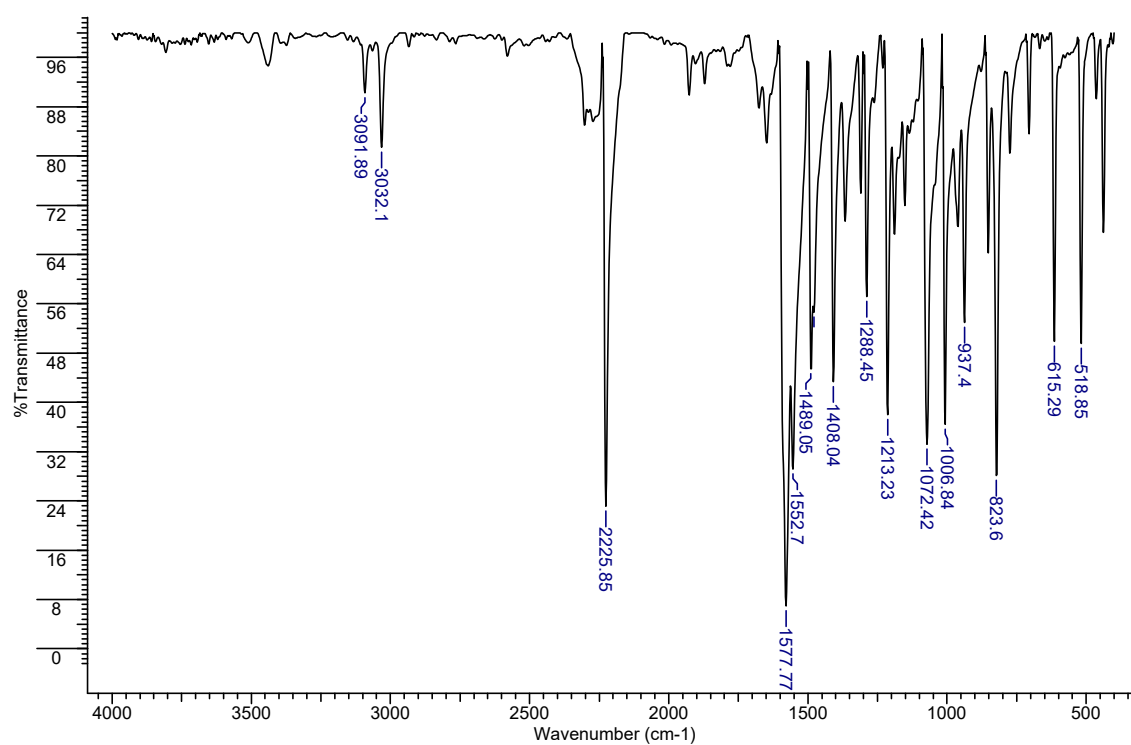


Figure S15. FT-IR of 2-(3,4,5-trimethoxybenzylidene)malononitrile **2d**.

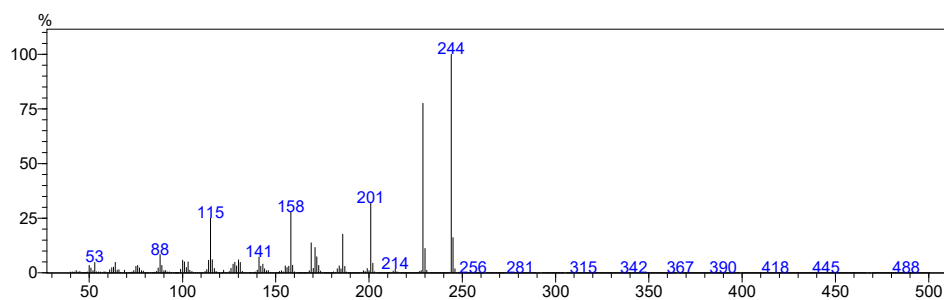


Figure S16. MS (70 eV) of 2-(3,4,5-trimethoxybenzylidene)malononitrile **2d**.

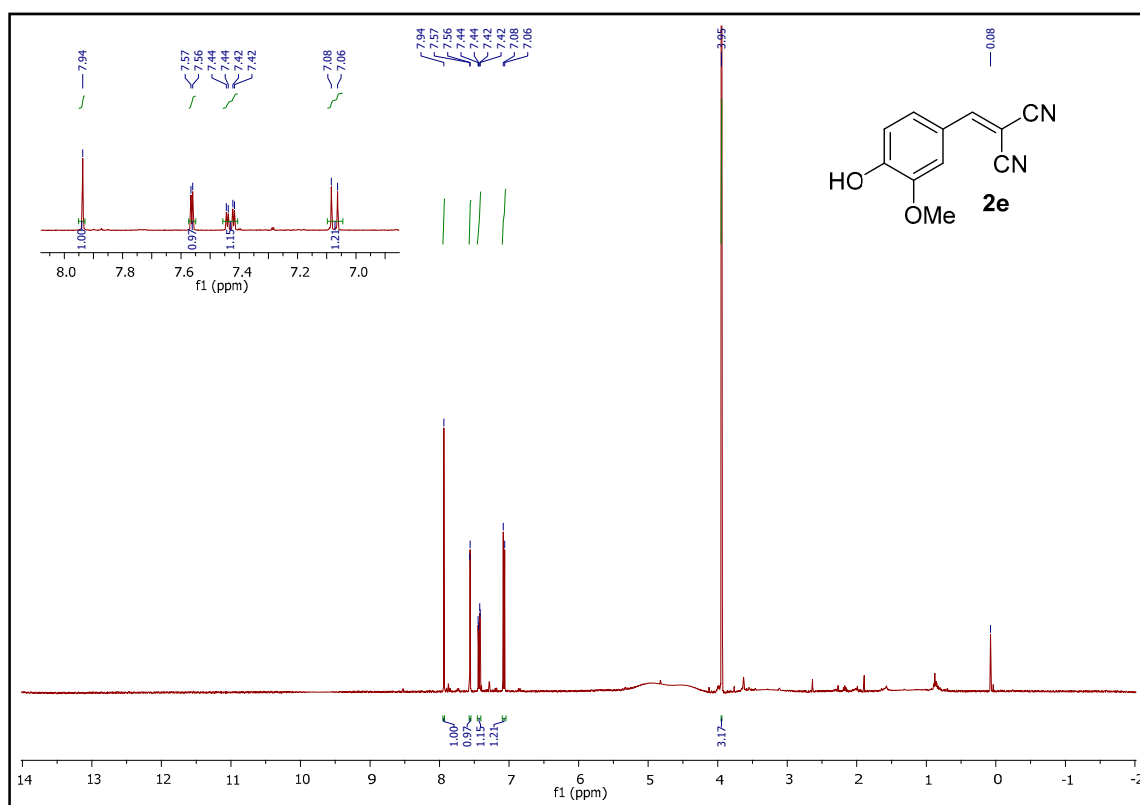


Figure S17. ¹H NMR (400 MHz, MeOD) of 2-(4-hydroxy-3-methoxybenzylidene)malononitrile **2e**.

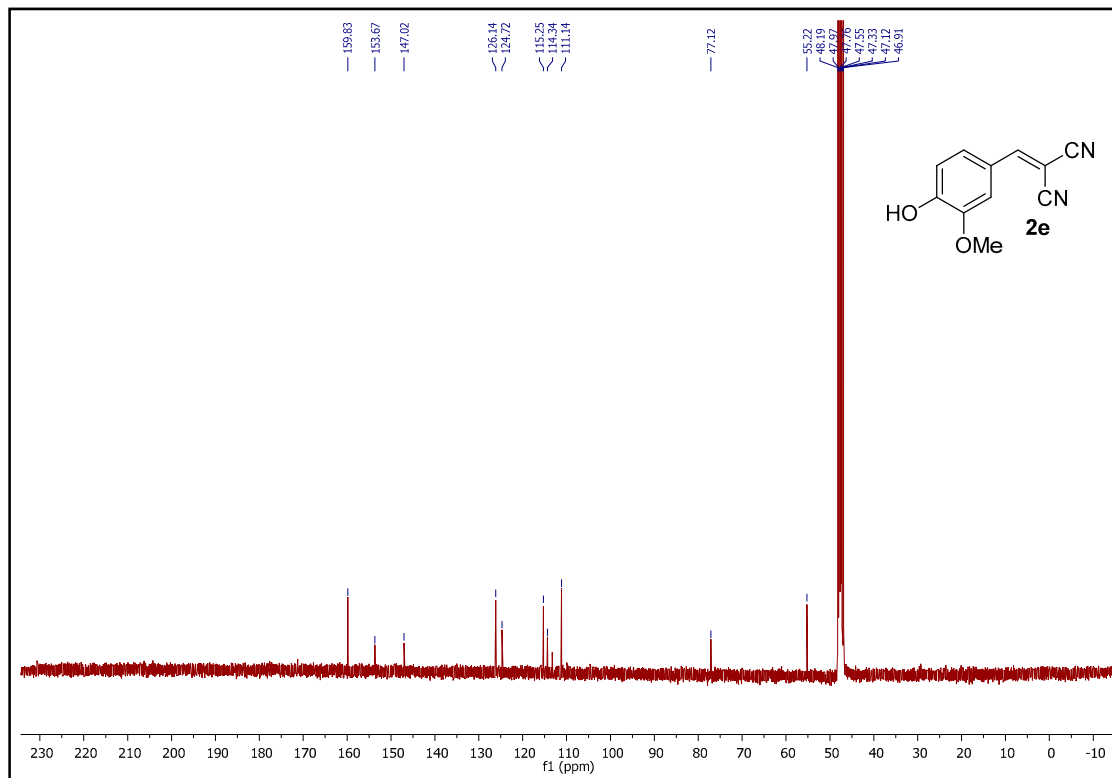


Figure S18. ¹³C NMR (100 MHz, MeOD) of 2-(4-hydroxy-3-methoxybenzylidene)malononitrile **2e**.

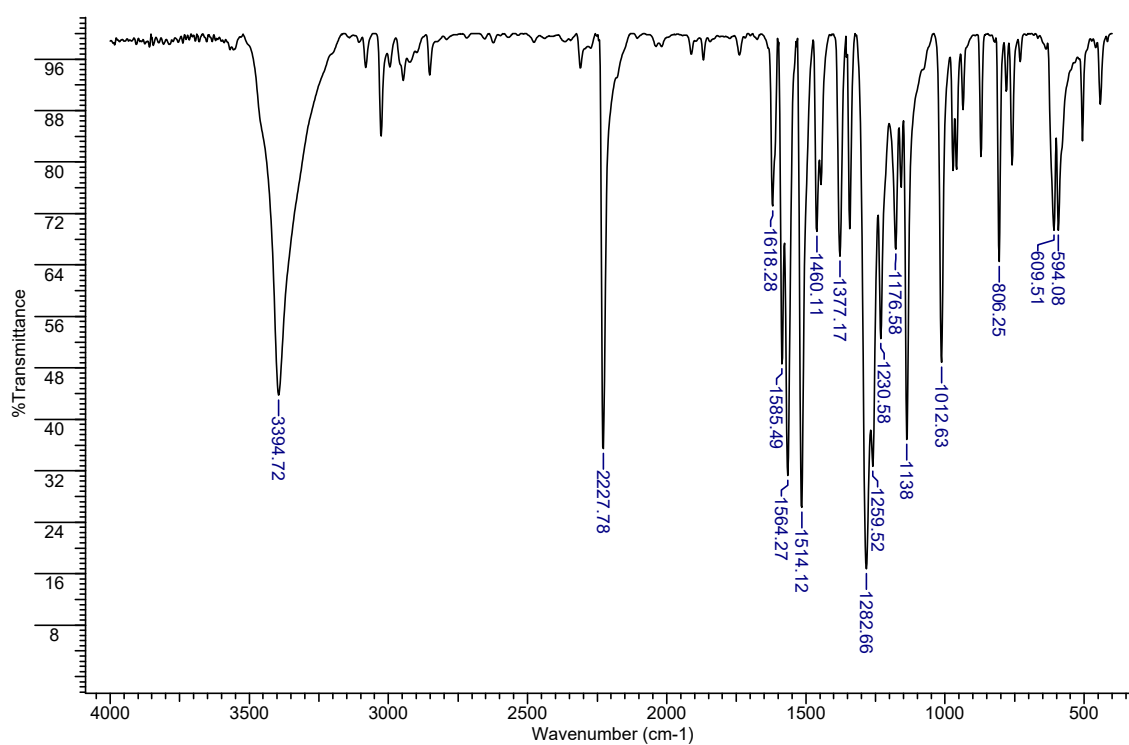


Figure S19. FT-IR of 2-(4-hydroxy-3-methoxybenzylidene)malononitrile **2e**.

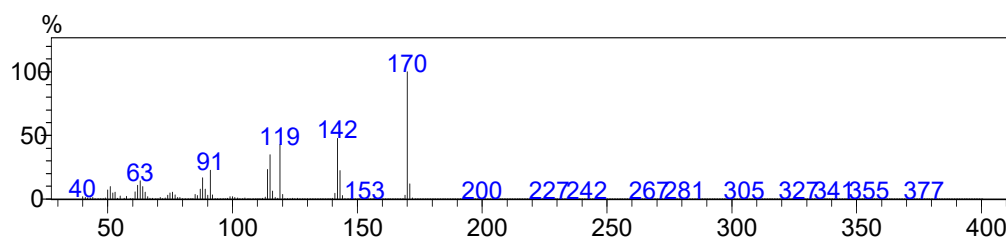


Figure S20. MS (70 eV) of 2-(4-hydroxy-3-methoxybenzylidene)malononitrile **2e**.

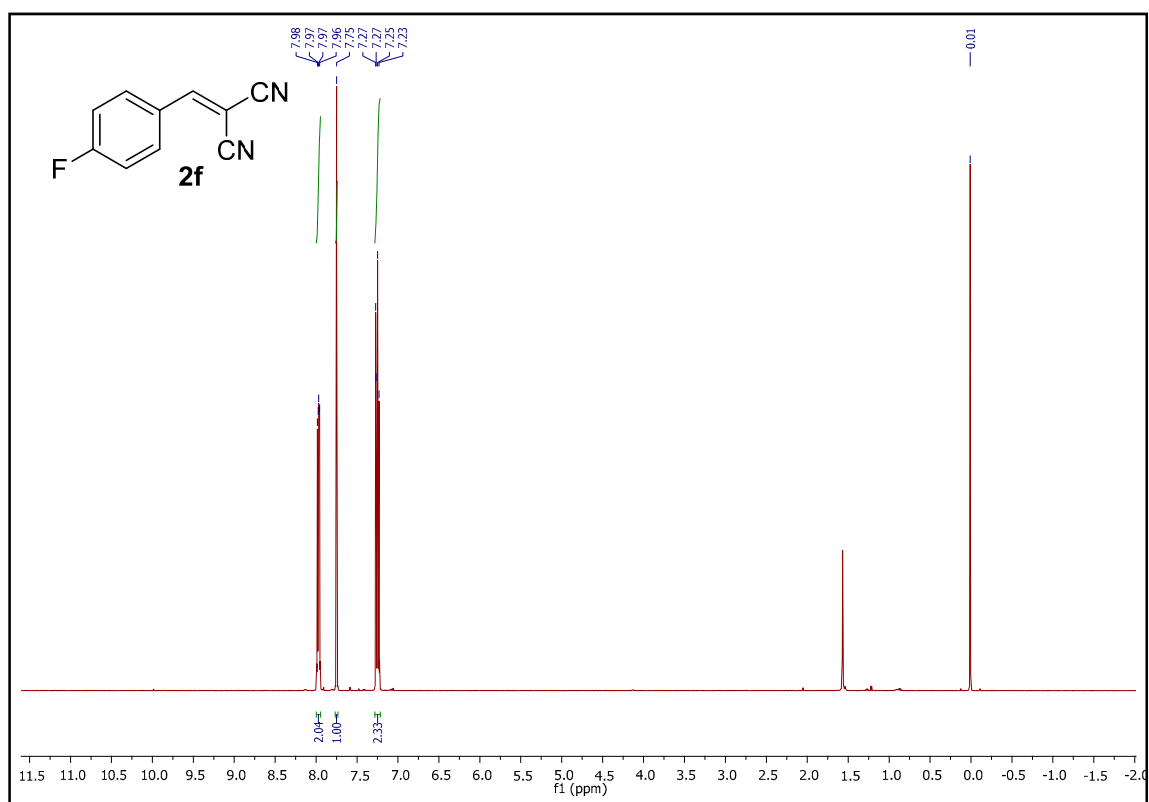


Figure S21. ¹H NMR (400 MHz, CDCl₃) of 2-(4-fluorobenzylidene)malononitrile **2f**.

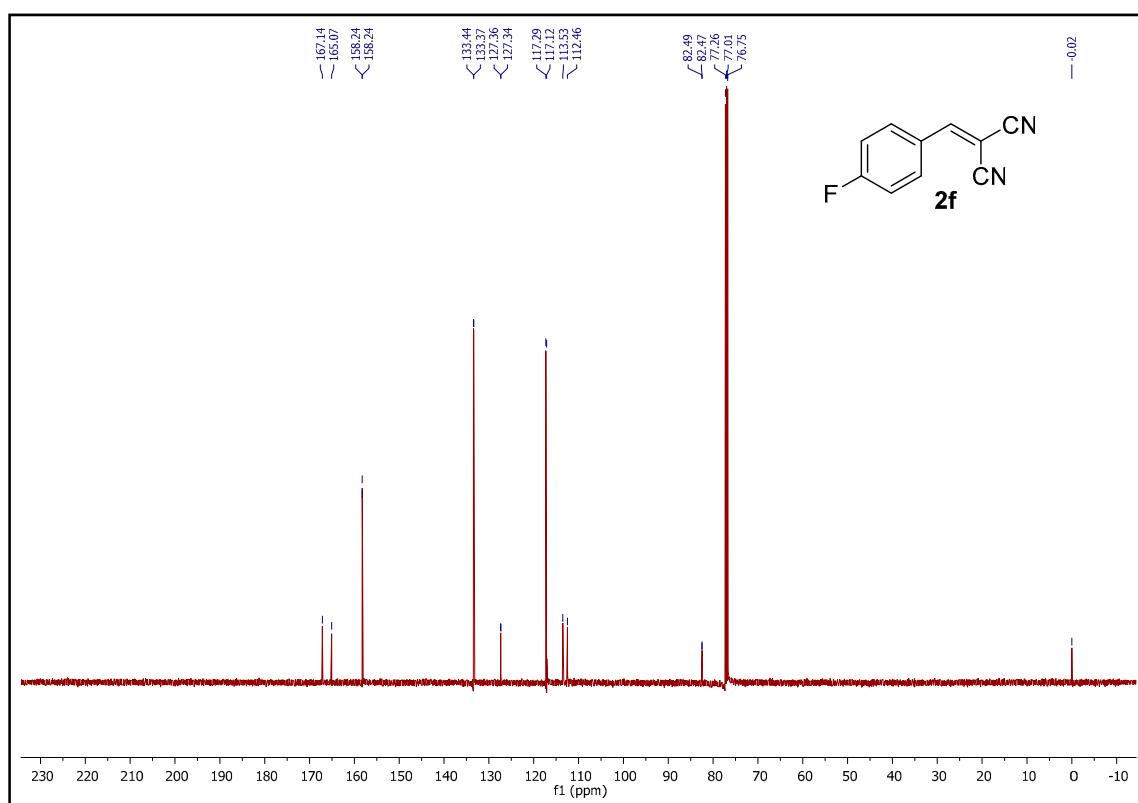


Figure S22. ¹³C NMR (100 MHz, CDCl₃) of 2-(4-fluorobenzylidene)malononitrile **2f**.

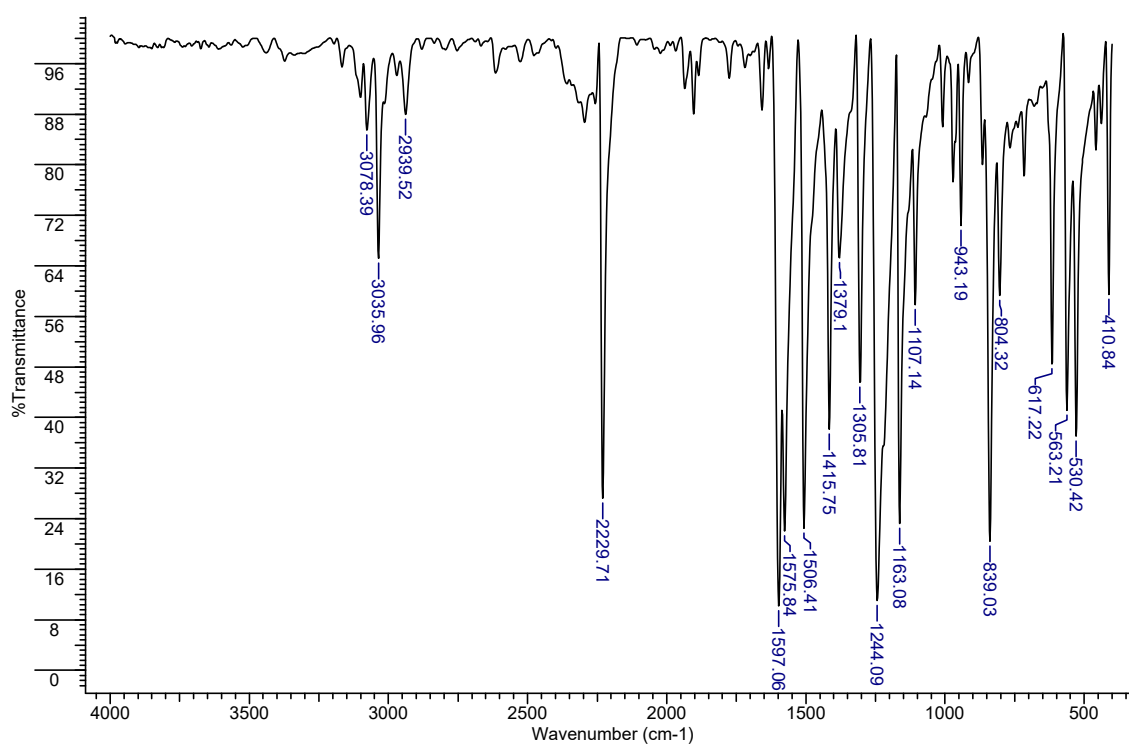


Figure S23. FT-IR of 2-(4-fluorobenzylidene)malononitrile **2f**.

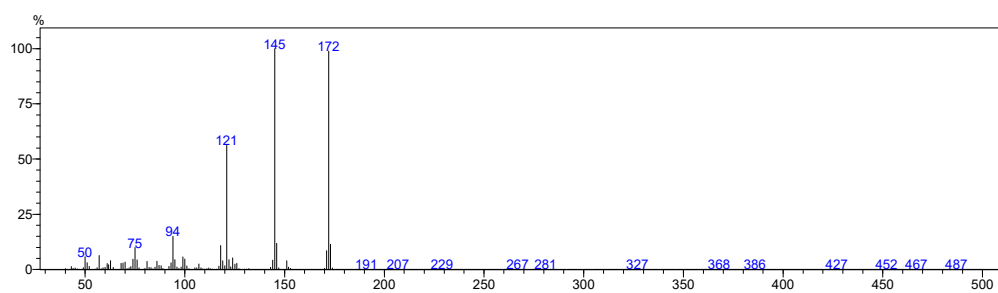


Figure S24. MS (70 eV) of 2-(4-fluorobenzylidene)malononitrile **2f**.

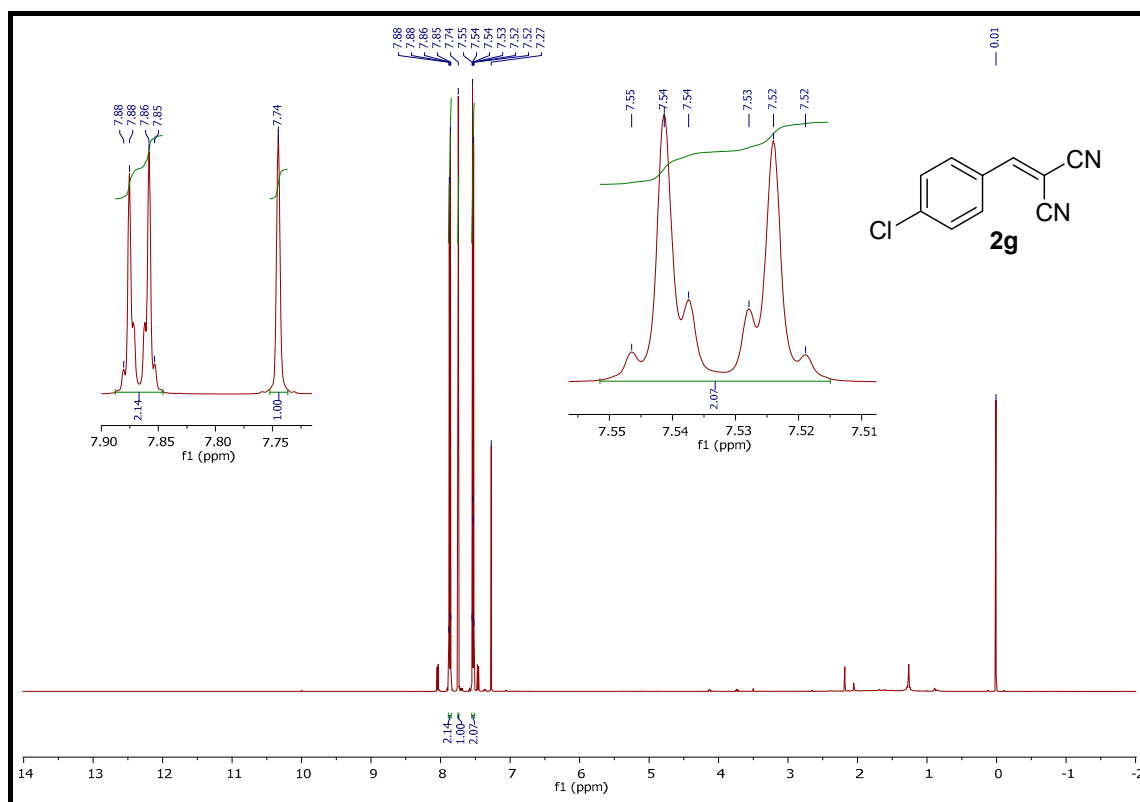


Figure S25. ¹H NMR (500 MHz, CDCl₃) of 2-(4-chlorobenzylidene)malononitrile **2g**.

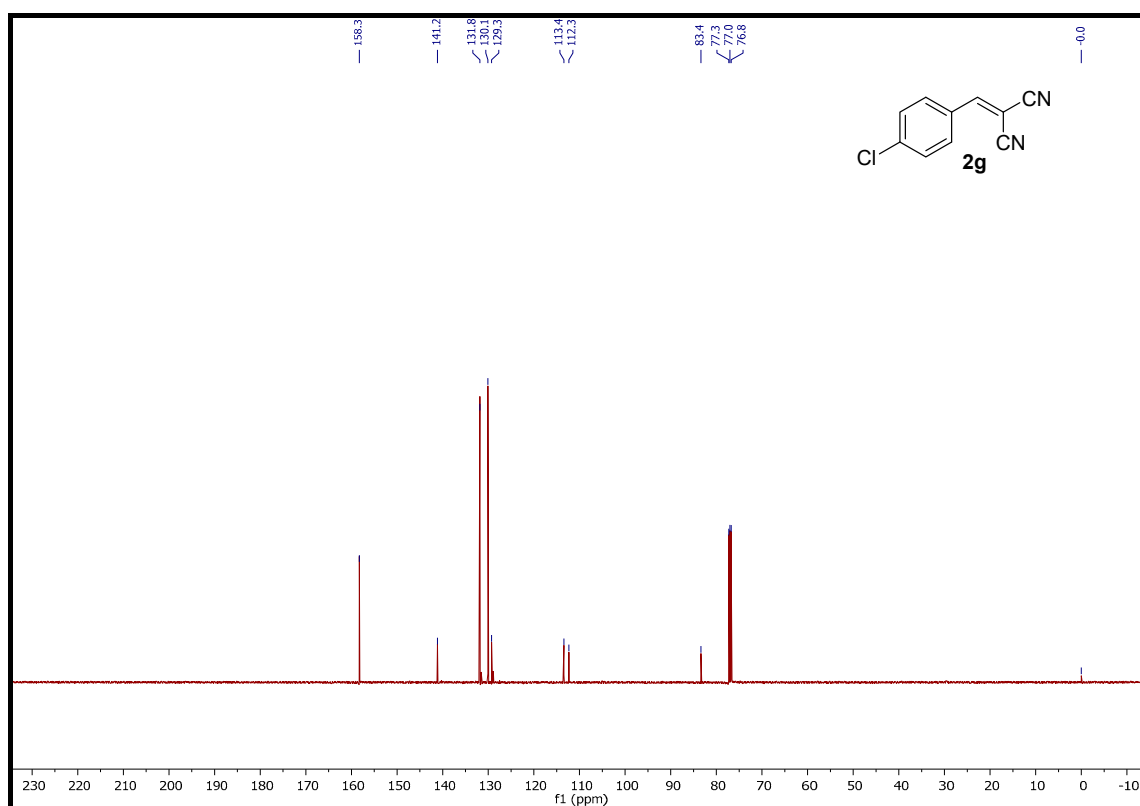


Figure S26. ¹³C NMR (125 MHz, CDCl₃) of 2-(4-chlorobenzylidene)malononitrile **2g**.

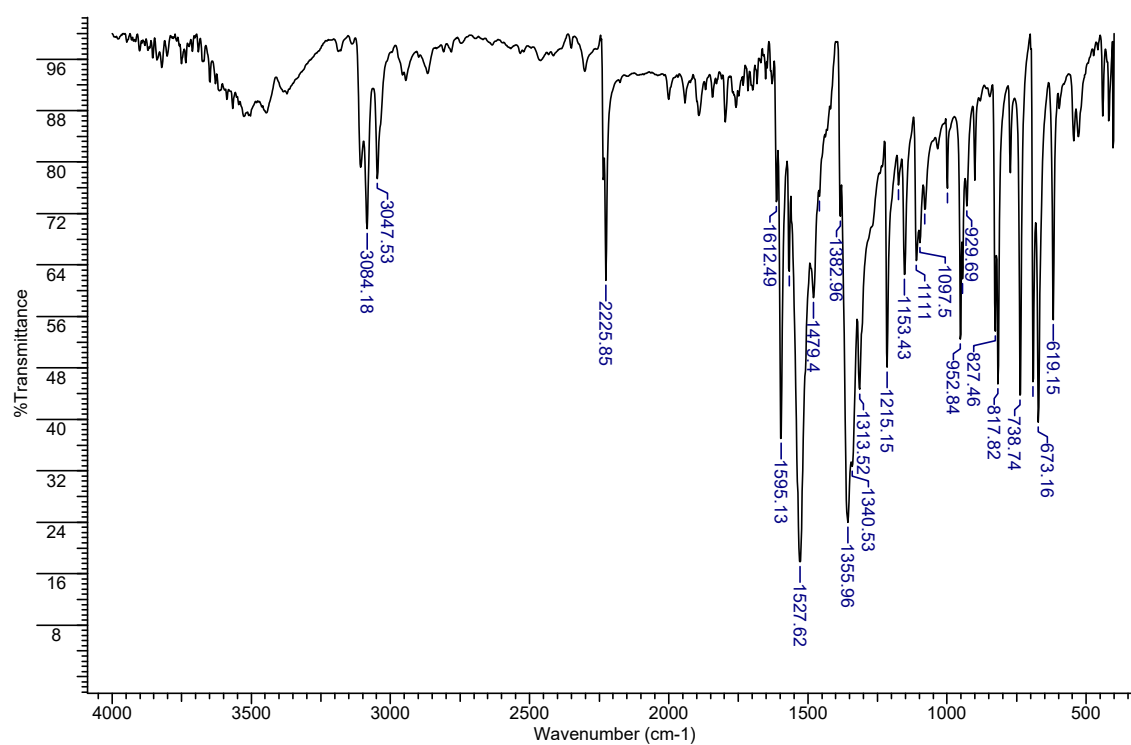


Figure S27. FT-IR of 2-(4-chlorobenzylidene)malononitrile **2g**.

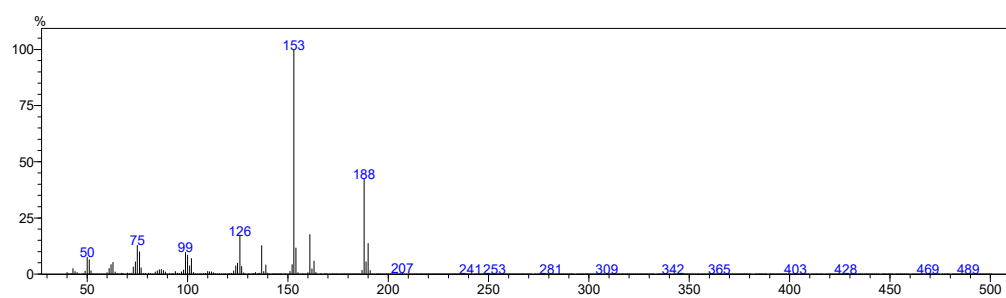


Figure S28. MS (70 eV) of 2-(4-chlorobenzylidene)malononitrile **2g**.

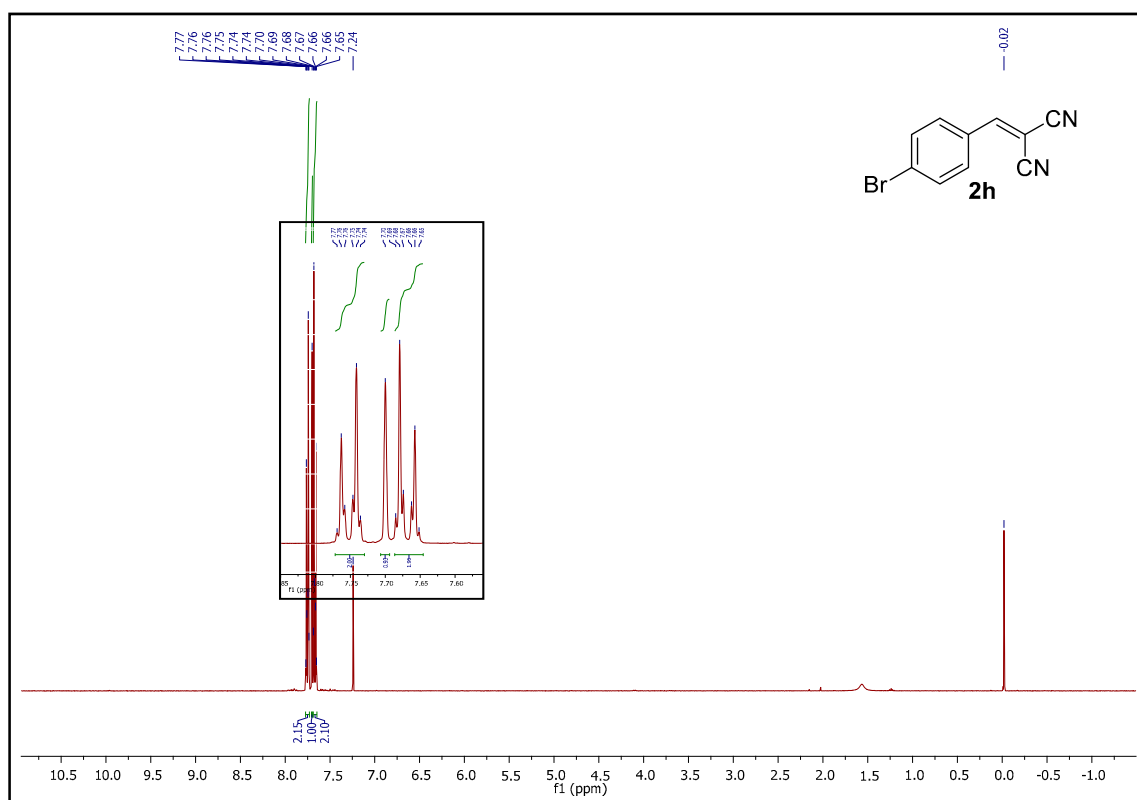


Figure S29. ¹H NMR (400 MHz, CDCl₃) of 2-(4-bromobenzylidene)malononitrile **2h**.

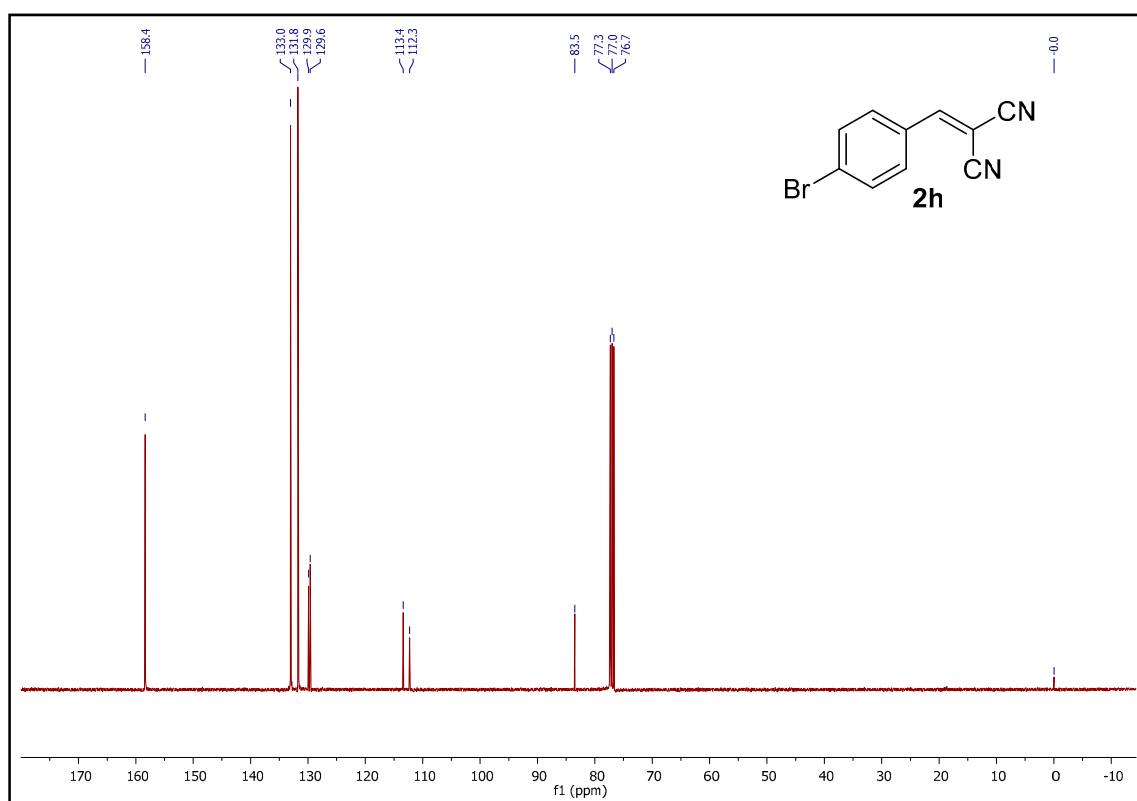


Figure S30. ¹³C NMR (100 MHz, CDCl₃) of 2-(4-bromobenzylidene)malononitrile **2h**.

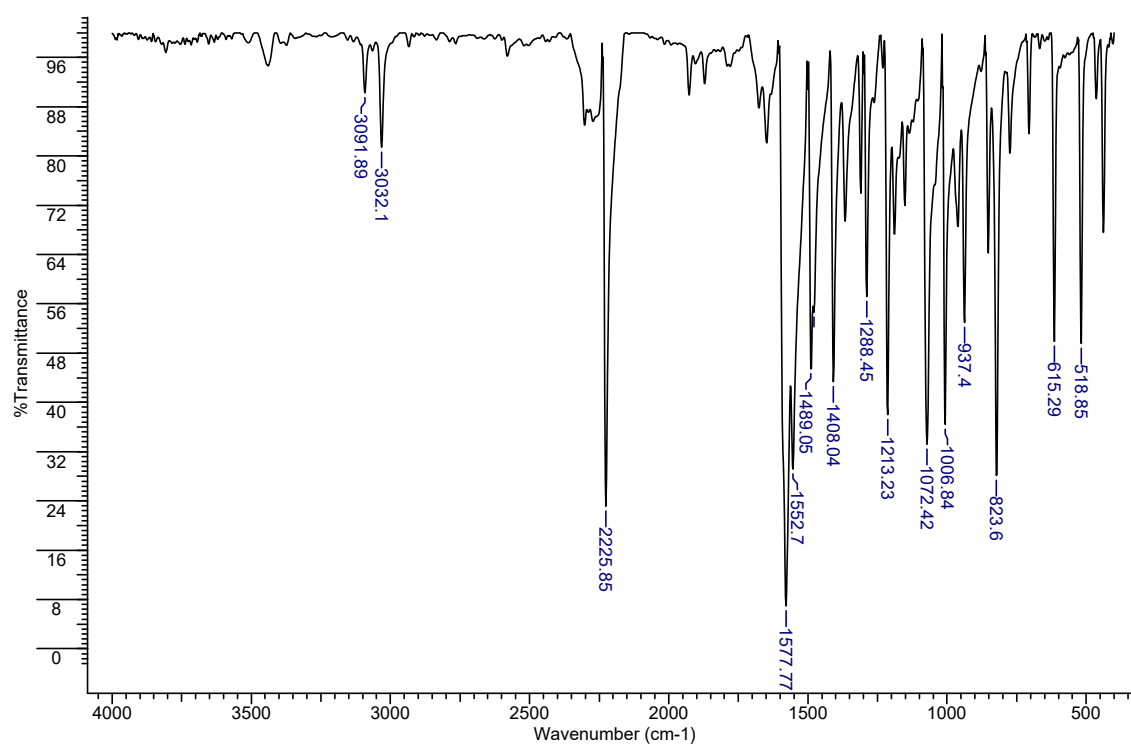


Figure S31. FT-IR of 2-(4-bromobenzylidene)malononitrile **2h**.

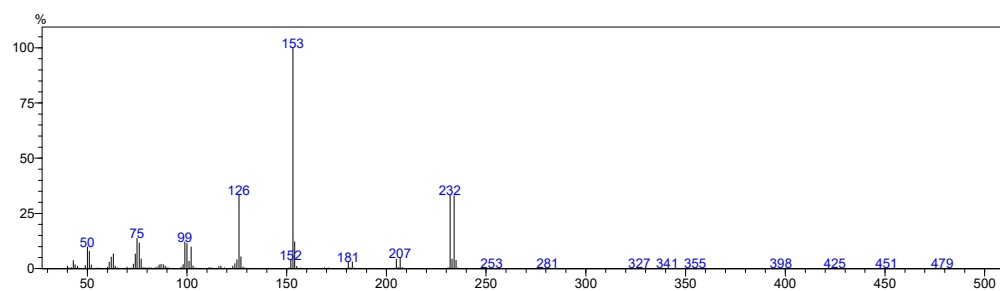
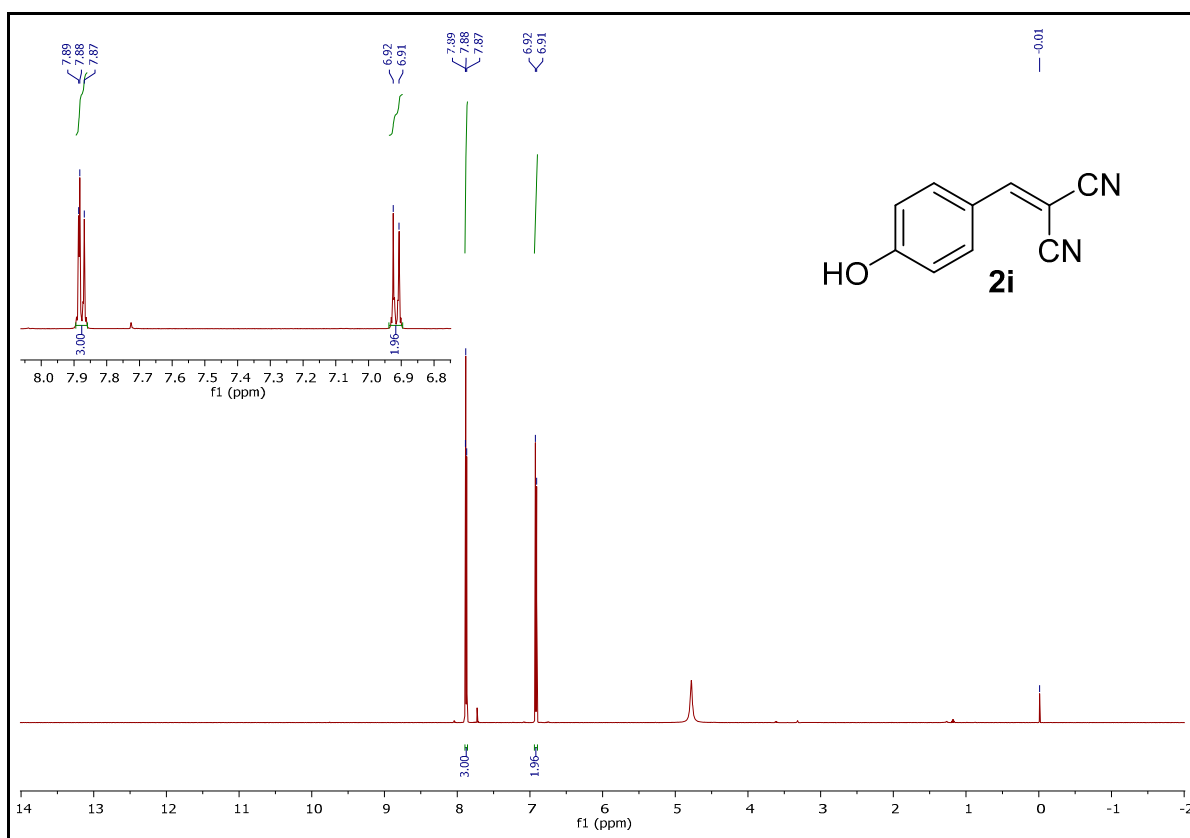
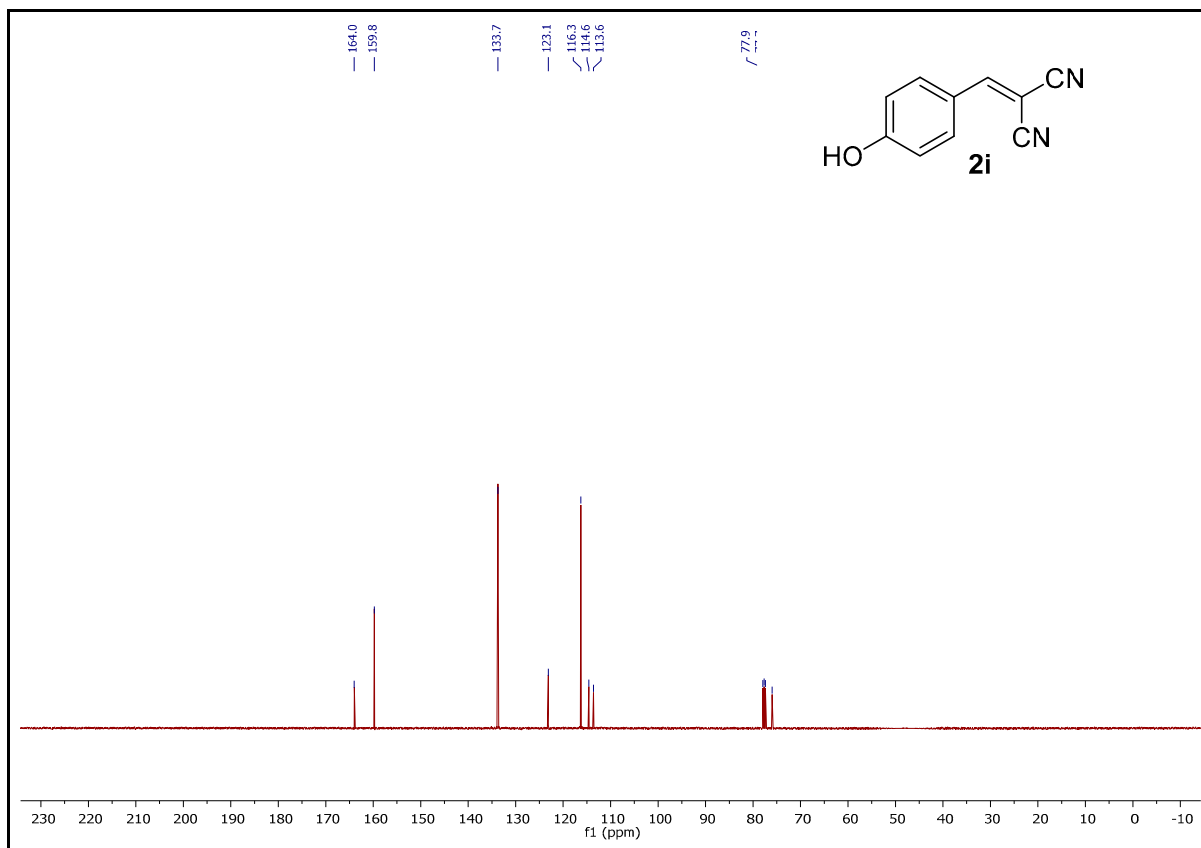


Figure S32. MS (70 eV) of 2-(4-bromobenzylidene)malononitrile **2h**.

Figure S33. ¹H NMR (500 MHz, CDCl₃) of 2-(4-hydroxybenzylidene)malononitrile **2i**.Figure S34. ¹³C NMR (125 MHz, CDCl₃) of 2-(4-hydroxybenzylidene)malononitrile **2i**.

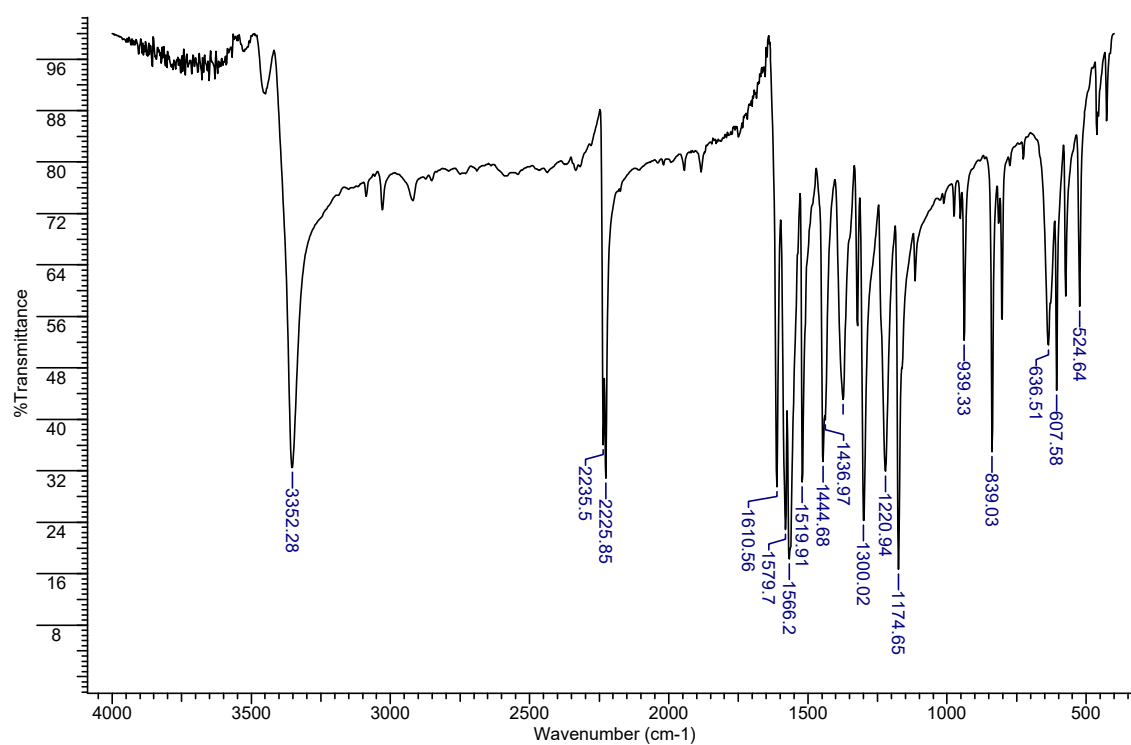


Figure S35. FT-IR of 2-(4-hydroxybenzylidene)malononitrile **2i**.

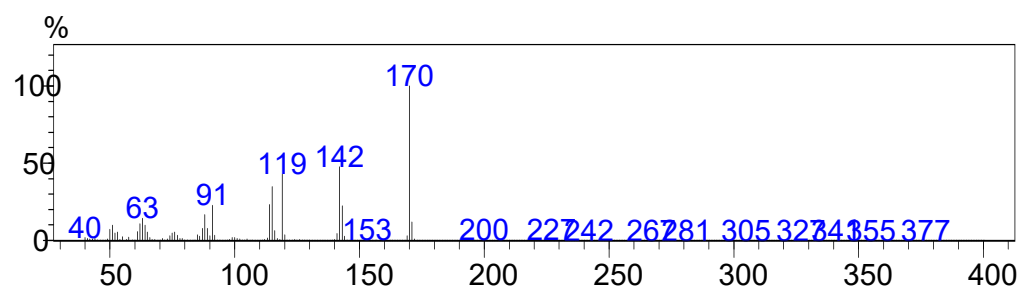


Figure S36. MS (70 eV) of 2-(4-hydroxybenzylidene)malononitrile **2i**.

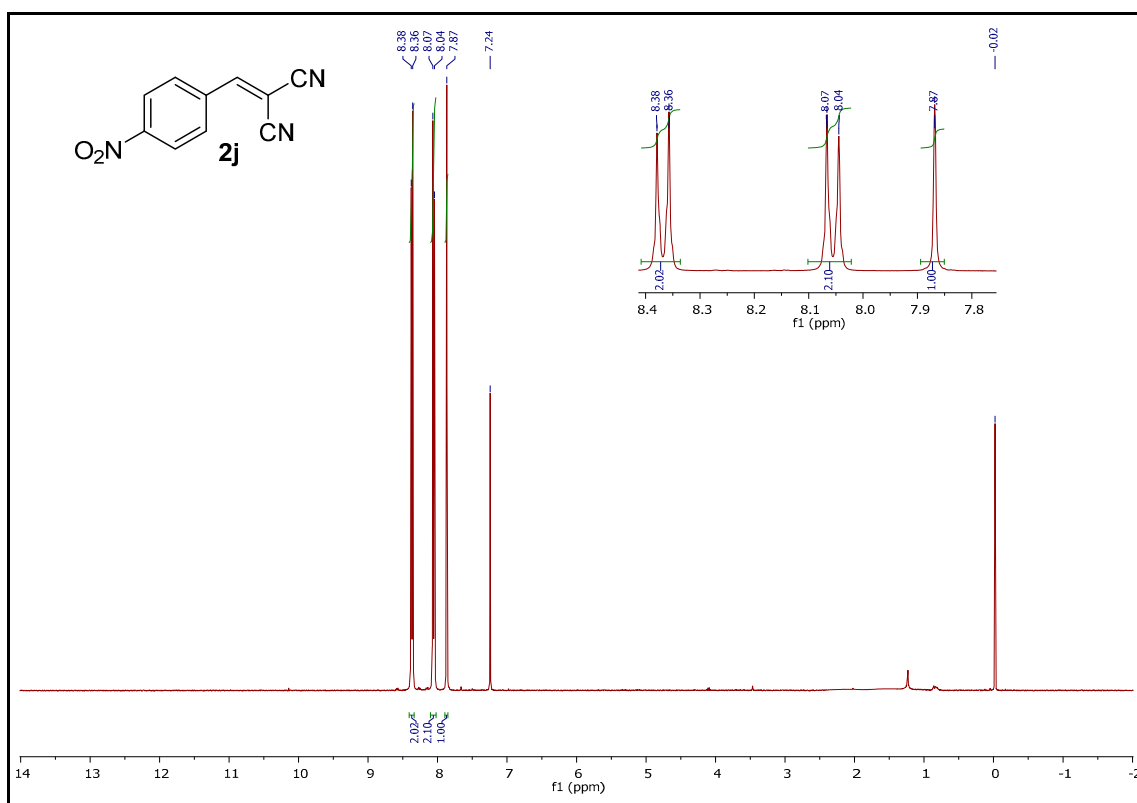


Figure S37. ¹H NMR (500 MHz, CDCl₃) of 2-(4-nitrobenzylidene)malononitrile **2j**.

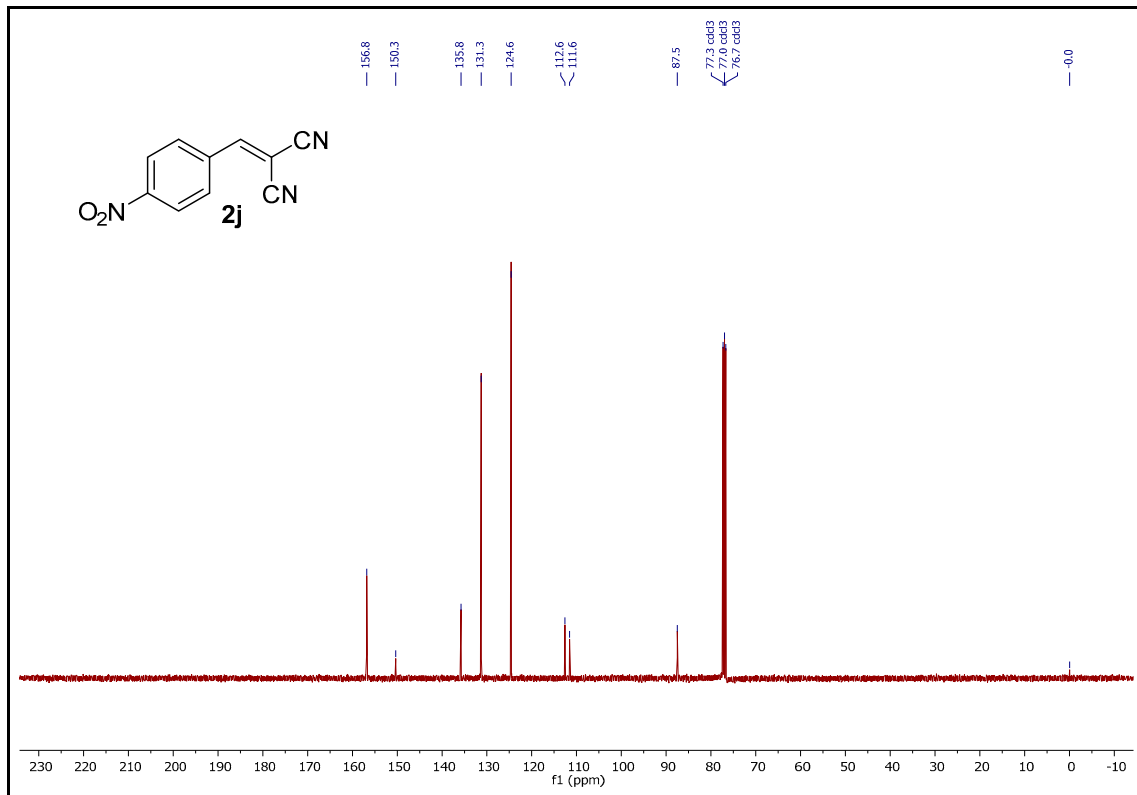


Figure S38. ¹³C NMR (125 MHz, CDCl₃) of 2-(4-nitrobenzylidene)malononitrile **2j**.

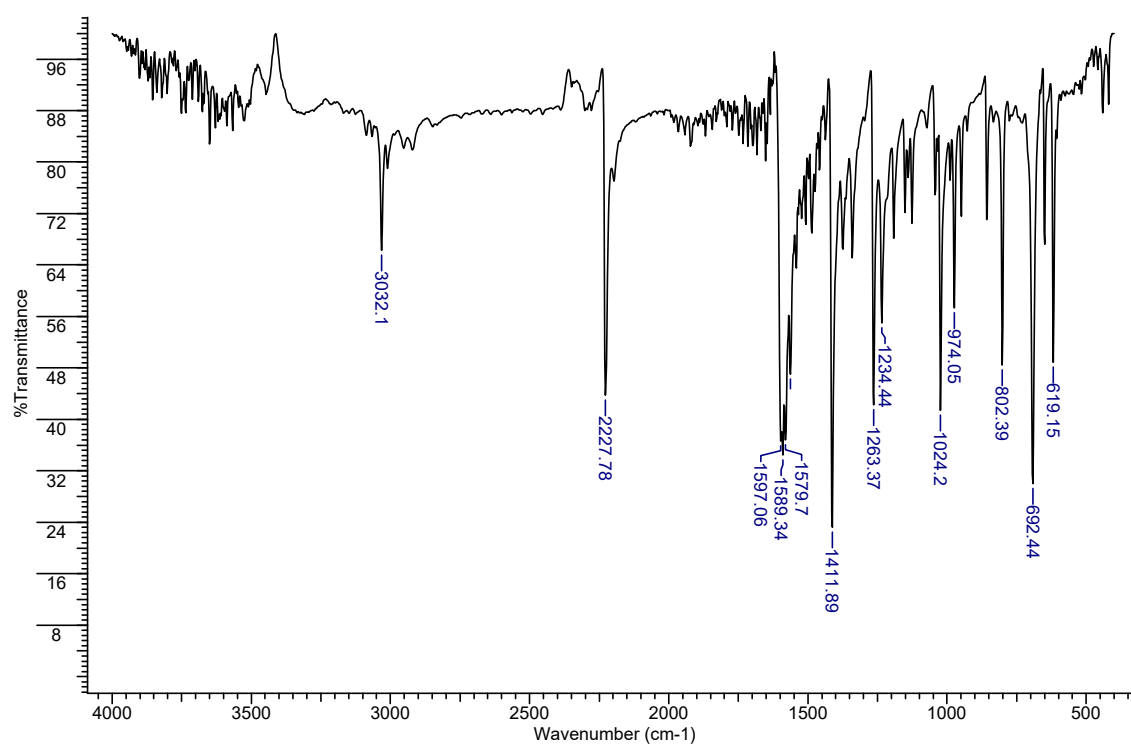


Figure S39. FT-IR of 2-(4-nitrobenzylidene)malononitrile **2j**.

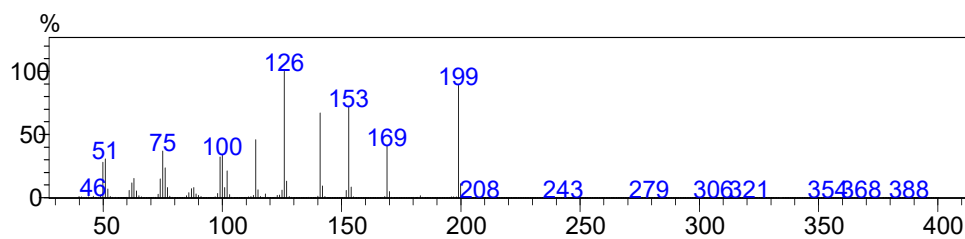


Figure S40. MS (70 eV) of 2-(4-nitrobenzylidene)malononitrile **2j**.

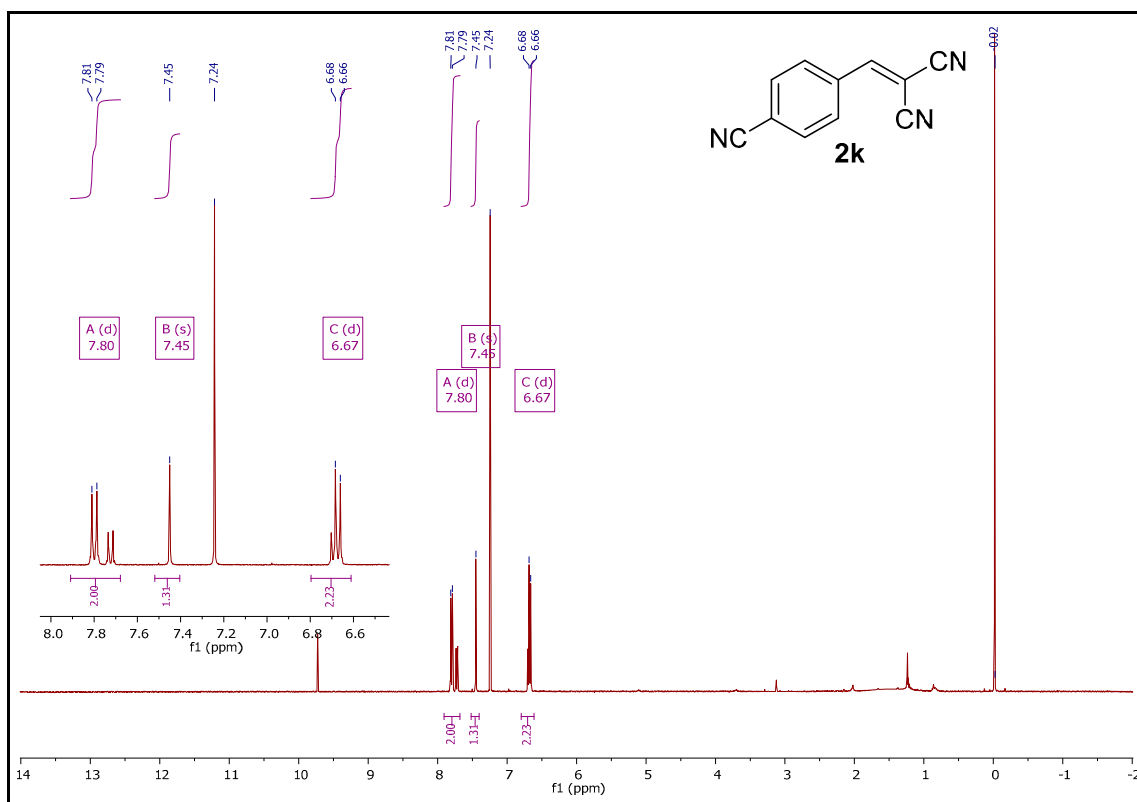


Figure S41. ¹H NMR (400 MHz, CDCl₃) of 2-(4-cyanobenzylidene)malononitrile **2k**.

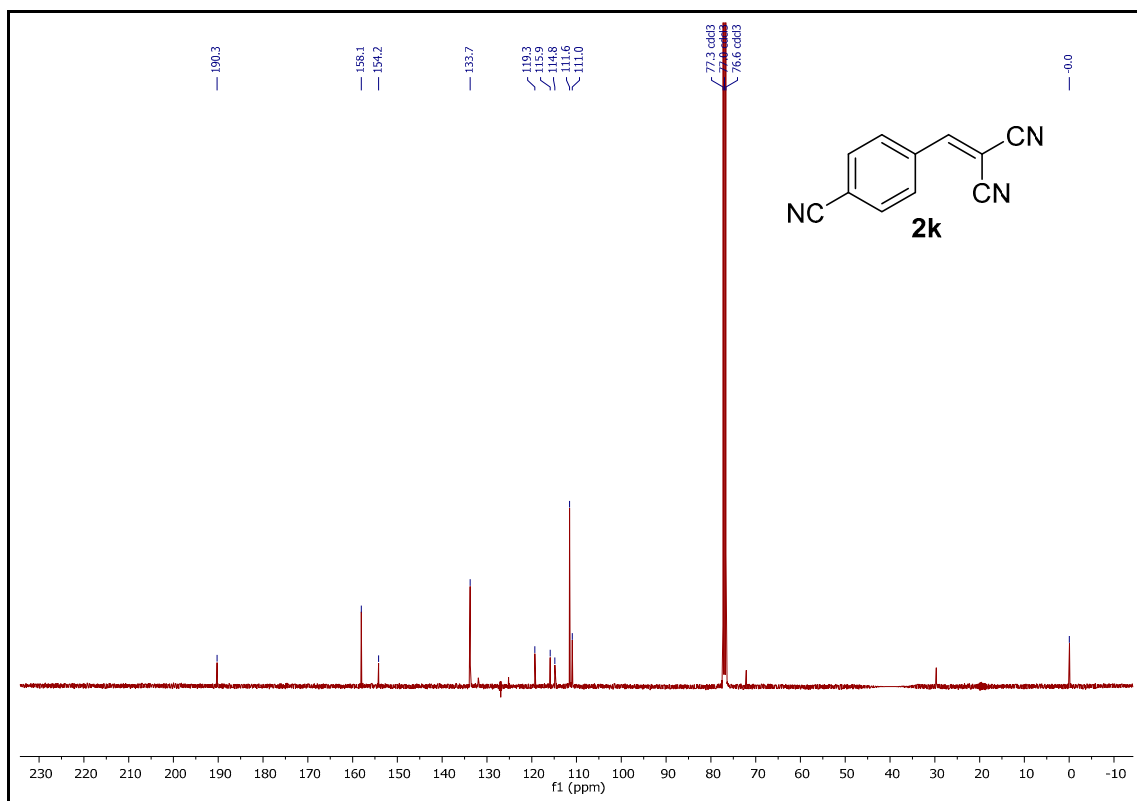


Figure S42. ¹³C NMR (100 MHz, CDCl₃) of 2-(4-cyanobenzylidene)malononitrile **2k**.

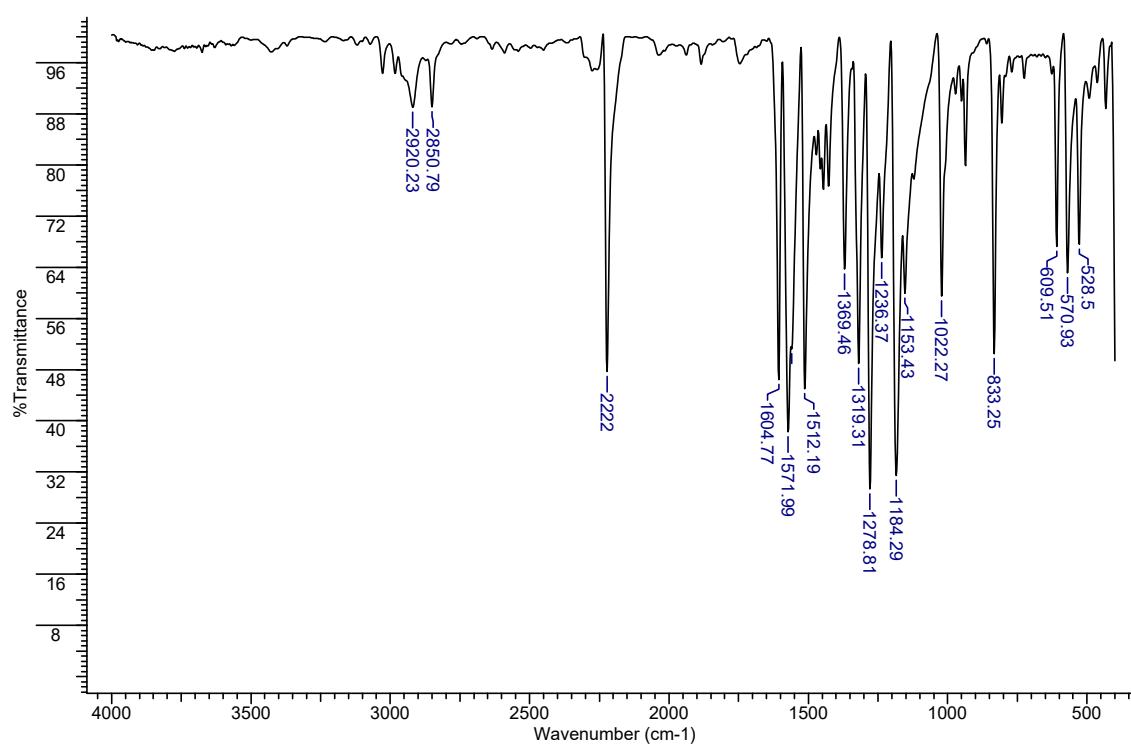


Figure S43. FT-IR of 2-(4-cyanobenzylidene)malononitrile **2k**.

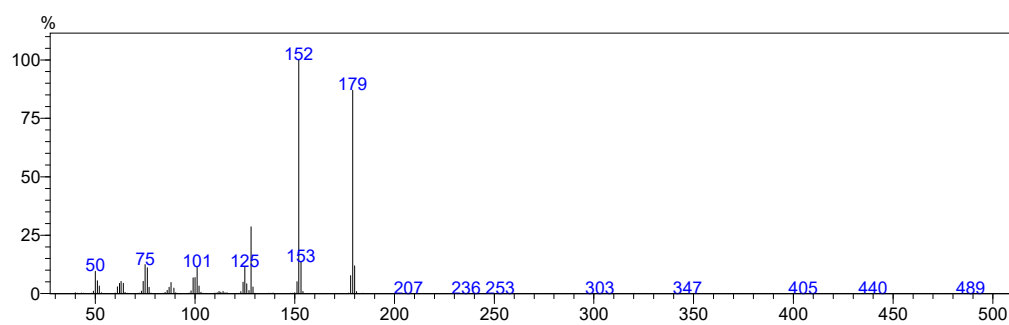
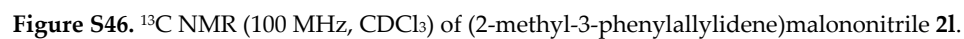
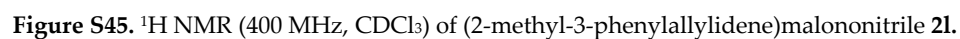


Figure S44. MS (70 eV) of 2-(4-cyanobenzylidene)malononitrile **2k**.



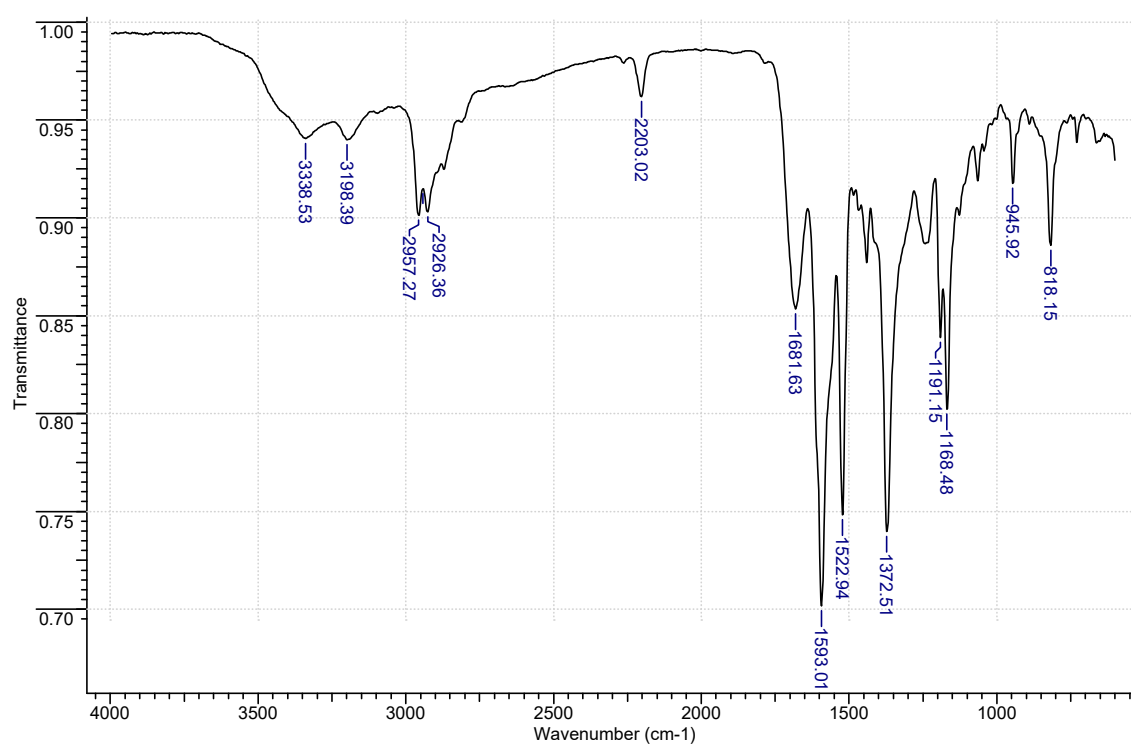


Figure S47. FT-IR of 2-(3-phenylallylidene)malononitrile 21.

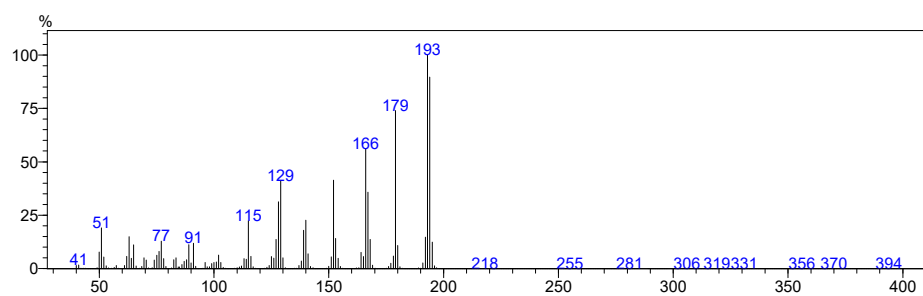


Figure S48. MS (70 eV) of 2-(3-phenylallylidene)malononitrile 21.