

Supporting Information

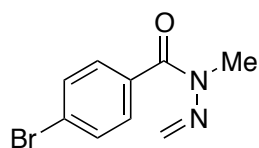
Synthesis of phthalazinones via palladium(II)-catalysed intramolecular oxidative C–H/C–H cross-coupling of *N'*-methylenebenzohydrazides

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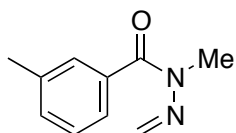
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General. All reactions were carried out with standard Schlenk techniques under an argon or nitrogen atmosphere. Column chromatography was carried out on Wakogel C-200 (75–150 μm). Preparative thin-layer chromatography was performed on silica gel 60 PF₂₅₄ (Merck). Proton chemical shifts were referenced to the residual CHCl₃ signal at 7.26 ppm. Carbon chemical shifts were referenced to the central peak of CDCl₃ at 77.0 ppm.

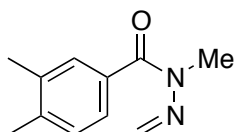
Materials. Benzohydrazides **1** were prepared by the literature methods.¹ Benzoquinone was sublimed prior to use. All other commercially available chemical resources were used as received without further purification.



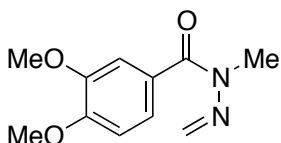
4-Bromo-*N*-methyl-*N'*-methylenebenzohydrazide (1e): white solid; mp. 70–72 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.38 (s, 3H), 6.45 (d, J = 10.5 Hz, 1H), 6.73 (d, J = 11.0 Hz, 1H), 7.48–7.54 (m, 4H); ¹³C NMR (125.7 MHz, CDCl₃) δ 27.6, 124.9, 129.5, 130.8, 131.1, 133.8, 170.4; IR (ν/cm^{-1}): 1655, 1601, 1412, 1049; HRMS (EI) calcd for C₉H₉BrN₂O [M]⁺ 239.9893, found 239.9895.



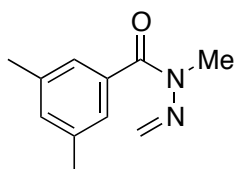
N,3-Dimethyl-N'-methylenebenzohydrazide (1f): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.36 (s, 3H), 3.37 (s, 3H), 6.42 (d, $J = 11.0$ Hz, 1H), 6.70 (d, $J = 11.0$ Hz, 1H), 7.21–7.28 (m, 2H), 7.35–7.41 (m, 2H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 21.3, 27.6, 126.3, 127.4, 129.1, 129.7, 131.0, 135.0, 137.3, 171.7; IR (ν/cm^{-1}): 1662, 1600, 1370, 1177, 1046, 740, 637; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}]^+$ 176.0944, found 176.0950.



N,3,4-Trimethyl-N'-methylenebenzohydrazide (1g): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.28 (s, 3H + 3H), 3.38 (s, 3H), 6.44 (d, $J = 11.0$ Hz, 1H), 6.71 (d, $J = 9.5$ Hz, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.33–7.37 (m, 1H), 7.40 (s, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 19.7, 19.8, 27.7, 127.0, 128.8, 128.9, 130.4, 132.5, 135.9, 139.3, 171.7; IR (ν/cm^{-1}): 1655, 1593, 1377, 1049; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}]^+$ 190.1101, found 190.1106.

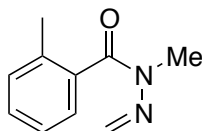


3,4-Dimethoxy-N-methyl-N'-methylenebenzohydrazide (1h): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 3.38 (s, 3H), 3.89 (s, 3H), 3.90 (s, 3H), 6.45 (d, $J = 10.5$ Hz, 1H), 6.72 (d, $J = 11.0$ Hz, 1H), 6.86 (d, $J = 9.0$ Hz, 1H), 7.26 (d, $J = 2.5$ Hz, 1H), 7.31 (dd, $J = 8.5, 2.5$ Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 27.9, 55.88, 55.92, 109.8, 113.2, 123.7, 126.9, 128.8, 148.0, 151.0, 170.7; IR (ν/cm^{-1}): 1655, 1593, 1377, 1049; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_3$ $[\text{M}]^+$ 222.0999, found 222.1003.

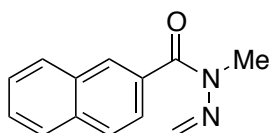


N,3,5-Trimethyl-N'-methylenebenzohydrazide (1i): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.34 (s, 6H), 3.38 (s, 3H), 6.44 (d, $J = 11.0$ Hz, 1H), 6.72 (d, $J = 11.0$ Hz, 1H), 7.07

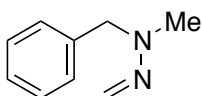
(s, 1H), 7.18 (s, 2H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 21.2, 27.6, 126.7, 129.1, 131.9, 135.1, 137.1, 172.0; IR (ν/cm^{-1}): 1666, 1593, 1369, 1176, 1072, 652; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}]^+$ 190.1101, found 190.1106.



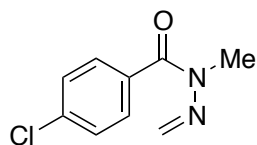
N,2-Dimethyl-N'-methylenebenzohydrazide (1j): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.28 (s, 3H), 3.44 (s, 3H), 6.44 (d, $J = 11.0$ Hz, 1H), 6.76 (d, $J = 11.0$ Hz, 1H), 7.22–7.27 (m, 3H), 7.30–7.36 (m, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 19.3, 27.0, 125.3, 126.6, 128.9, 129.8 [overlapping], 134.5, 136.6, 172.6; IR (ν/cm^{-1}): 1666, 1600, 1377, 1030, 633; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}]^+$ 176.0944, found 176.0950.



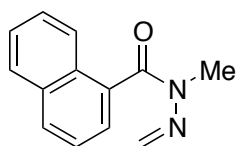
N-Methyl-N'-methylene-2-naphthohydrazide (1k): white solid; mp. 80–82 °C; ^1H NMR (500 MHz, CDCl_3) δ 3.44 (s, 3H), 6.45 (d, $J = 10.5$ Hz, 1H), 6.75 (d, $J = 10.0$ Hz, 1H), 7.47–7.50 (m, 2H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.81–7.86 (m, 2H), 7.88 (d, $J = 7.5$ Hz, 1H), 8.16 (s, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 27.7, 126.2, 126.3, 126.9, 127.2, 127.6, 128.8, 129.2, 129.8, 132.38, 132.45, 134.09, 171.50; IR (ν/cm^{-1}): 1651, 1601, 1477, 1373, 1184, 1038, 960, 818; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}]^+$ 212.0944, found 212.0953.



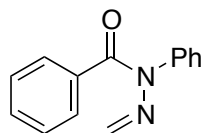
1-Benzyl-1-methyl-2-methylenehydrazine (1l): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.63 (s, 3H), 4.39 (s, 2H), 6.07 (d, $J = 11.0$ Hz, 1H), 6.14 (d, $J = 11.0$ Hz, 1H), 7.22–7.33 (m, 5H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 36.1, 62.0, 121.1, 127.3, 128.2, 128.4, 137.8; IR (ν/cm^{-1}): 1573, 1016, 737, 699; HRMS (ESI) calcd for $\text{C}_9\text{H}_{13}\text{N}_2$ $[\text{M} + \text{H}]^+$ 149.1073, found 149.1066.



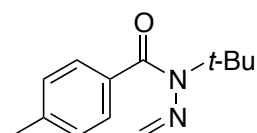
4-Chloro-N-methyl-N'-methylenebenzohydrazide: white solid; mp. 81–83 °C; ^1H NMR (500 MHz, CDCl_3) δ 3.38 (s, 3H), 6.44 (d, $J = 9.5$ Hz, 1H), 6.72 (d, $J = 10.0$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 27.6, 127.8, 129.5, 131.0, 133.3, 136.4, 170.3; IR (ν/cm^{-1}): 1655, 1601, 1415, 1207, 1049, 829, 744; HRMS (EI) calcd for $\text{C}_9\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}]^+$ 196.0398, found 196.0403.



N-Methyl-N'-methylene-1-naphthohydrazide: pale yellow crystal; mp. 113–134 °C; ^1H NMR (500 MHz, CDCl_3) δ 3.52 (s, 3H), 6.29 (d, $J = 9.5$ Hz, 1H), 6.72 (d, $J = 11.0$ Hz, 1H), 7.42–7.54 (m, 4H), 7.67–7.73 (m, 1H), 7.83–7.92 (m, 2H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 27.2, 124.75, 124.85, 125.1, 126.0, 126.6, 128.3, 129.3, 129.9, 133.2, 134.5, 172.1; IR (ν/cm^{-1}): 1658, 1601, 1369, 1173, 783; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}]^+$ 212.0944, found 212.0950.

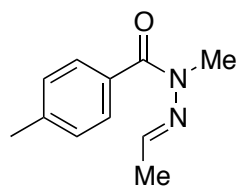


N'-Methylene-N-phenylbenzohydrazide: yellow crystal; mp. 135–136 °C; ^1H NMR (500 MHz, CDCl_3) δ 6.30–6.45 (m, 2H), 7.22–7.25 (m, 2H), 7.40–7.50 (m, 4H), 7.53–7.58 (m, 2H), 7.74–7.79 (m, 2H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 127.7, 129.3, 129.4, 129.5, 130.3, 130.6, 132.6, 135.1, 135.4, 170.9; IR (ν/cm^{-1}): 1666, 1597, 1369, 717, 702, 652; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}]^+$ 224.0944, found 224.0949.

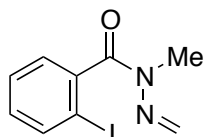


N-(tert-Butyl)-4-methyl-N'-methylenebenzohydrazide: pale yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.53 (s, 9H), 2.33 (s, 3H), 6.74 (d, $J = 12.0$ Hz, 1H), 6.83 (d, $J = 11.0$ Hz, 1H), 7.12 (d, $J = 7.5$ Hz, 2H), 7.35 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 21.3,

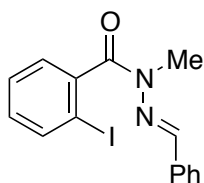
28.1, 60.2, 128.8, 129.2, 133.3, 140.4, 152.6, 169.5; IR (ν/cm^{-1}): 1647, 1362, 1342, 829; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}$ $[\text{M}]^+$ 218.1414, found 218.1421.



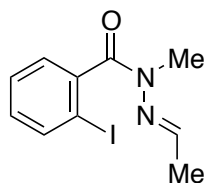
***N'*-Ethyldene-*N*,4-dimethylbenzohydrazide**: colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.95 (d, $J = 5.0$ Hz, 3H), 2.38 (s, 3H), 3.38 (s, 3H), 7.14 (q, $J = 5.2$ Hz, 1H), 7.18 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 18.9, 21.4, 28.6, 128.0, 129.9, 132.3, 138.8, 140.2, 170.6; IR (ν/cm^{-1}): 1657, 1410, 1365, 1331, 1049; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}]^+$ 190.1101, found 190.1104.



2-Iodo-*N*-methyl-*N'*-methylenebenzohydrazide (3a): white solid; mp. 111–112 °C; ^1H NMR (500 MHz, CDCl_3) δ 3.39 (s, 3H), 6.43 (d, $J = 11.0$ Hz, 1H), 6.74 (d, $J = 11.0$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.80 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 27.3, 92.8, 127.5, 127.8, 130.0, 130.6, 138.6, 143.1, 171.7; IR (ν/cm^{-1}): 1658, 1601, 1477, 1381, 1207, 1061, 775, 625; HRMS (ESI) calcd for $\text{C}_9\text{H}_9\text{IN}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$ 310.9652, found 310.9662.

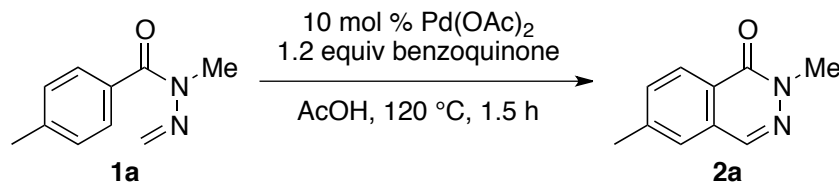


***N'*-Benzylidene-2-iodo-*N*-methylbenzohydrazide (3m)**: yellow solid; mp. 68–69 °C; ^1H NMR (500 MHz, CDCl_3) δ 3.56 (s, 3H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.25–7.36 (m, 6H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.75 (s, 1H), 7.85 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 28.2, 93.1, 127.0, 127.5, 127.7, 128.5, 129.6, 129.7, 134.3, 138.2, 139.7, 143.1, 171.5; IR (ν/cm^{-1}): 1674, 1604, 1473, 1392, 1338, 1061, 760, 737, 698; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{13}\text{IN}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$ 386.9965, found 386.9992.

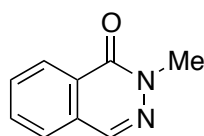


***N'*-Ethylidene-2-iodo-*N*-methylbenzohydrazide (3n)**: white solid; mp. 68–69 °C; ^1H NMR (500 MHz, CDCl_3) δ 1.91 (d, $J = 4.5$ Hz, 3H), 3.43 (s, 3H), 7.09 (t, $J = 6.0$ Hz, 1H), 7.2 (q, $J = 5.0$ Hz, 1H), 7.25 (d, $J = 7.0$ Hz, 1H), 7.41 (t, $J = 8.5$ Hz, 1H), 7.82 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 18.8, 28.0, 93.1, 127.5, 127.6, 129.5, 138.4, 140.1, 143.4, 171.1; IR (ν/cm^{-1}): 1655, 1620, 1412, 1365, 1331, 1061, 1030; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{11}\text{IN}_2\text{NaO}$ [$\text{M} + \text{Na}$] $^+$ 324.9808, found 324.9793.

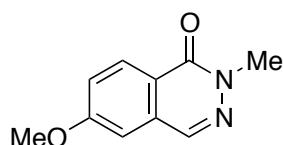
General Procedure for Palladium(II)-Catalysed Oxidative C–H/C–H Cross-Coupling of *N*-Methyl-*N'*-methylenebenzohydrazides **1**



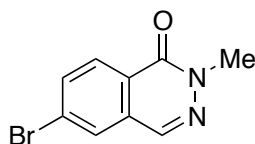
2,6-Dimethylphthalazin-1(2H)-one (2a). A Schlenk tube was charged with $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.020 mmol) and benzophenone (26.1 mg, 0.241 mmol), and then the tube was evacuated and backfilled with nitrogen. Substrate **1a** (35.2 mg, 0.200 mmol) and acetic acid (1.0 mL) were added via syringe through the septum. After heating at 120 °C for 1.5 h, the reaction mixture was diluted with AcOEt (10 mL) and quenched with saturated K_2CO_3 aqueous solution. The mixture was washed with water and brine, dried over Na_2SO_4 , and concentrated. The residue was subjected to preparative thin-layer chromatography on silica gel ($\text{CHCl}_3:\text{MeOH} = 40:1$) to afford the title compound (27.4 mg, 79%) as a pale yellow crystal: mp. 144–146 °C; ^1H NMR (500 MHz, CDCl_3) δ 2.52 (s, 3H), 3.83 (s, 3H), 7.45 (s, 1H), 7.56 (d, $J = 8.5$ Hz, 1H), 8.06 (s, 1H), 8.29 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 21.8, 39.3, 125.6 [overlapping], 126.4, 130.0, 133.1, 137.5, 143.7, 159.7; IR (ν/cm^{-1}): 1643, 1585, 1358, 1038, 841, 690; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ [M] $^+$ 174.0793, found 174.0793.



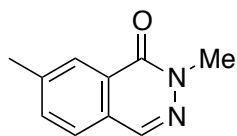
2-Methylphthalazin-1(2H)-one (2b). According to the general procedure, **1b** (32.0 mg, 0.197 mmol), Pd(OAc)₂ (4.5 mg, 0.020 mmol), and benzoquinone (26.0 mg, 0.241 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 2 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (23.0 mg, 73%) as a white crystal: mp. 113–114 °C (lit.² 112–114 °C). ¹H and ¹³C NMR spectra were identical to those in the literature. Error! Bookmark not defined.



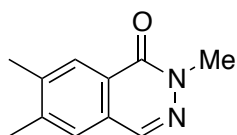
6-Methoxy-2-methylphthalazin-1(2H)-one (2c). According to the general procedure, **1c** (38.2 mg, 0.199 mmol), Pd(OAc)₂ (4.6 mg, 0.020 mmol), and benzoquinone (43.5 mg, 0.402 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 5 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (22.6 mg, 60%) as a pale yellow crystal: mp. 117–118 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.83 (s, 3H), 3.94 (s, 3H), 6.99–7.01 (m, 1H), 7.28–7.32 (m, 1H), 8.06 (s, 1H), 8.33 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 39.2, 55.7, 106.5, 121.0, 121.6, 128.6, 131.9, 137.1, 159.5, 163.2; IR (ν/cm⁻¹): 1639, 1616, 1589, 1362, 1265, 1041, 845; HRMS (EI) calcd for C₁₀H₁₀N₂O₂ [M]⁺ 190.0737, found 190.0744.



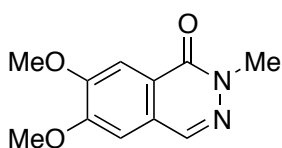
6-Bromo-2-methylphthalazin-1(2H)-one (2e). According to the general procedure, **1e** (48.4 mg, 0.201 mmol), Pd(OAc)₂ (4.6 mg, 0.020 mmol), and benzoquinone (43.8 mg, 0.405 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 24 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (12.6 mg, 26%) as a white crystal: mp. 235–236 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.84 (s, 3H), 7.83–7.87 (m, 2H), 8.06 (s, 1H), 8.27–8.30 (m, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 39.5, 126.4, 128.0, 128.4, 128.5, 131.1, 134.9, 136.1, 159.2; IR (ν/cm⁻¹): 1639, 1585, 1362, 1038, 795, 679; HRMS (EI) calcd for C₉H₇BrN₂O [M]⁺ 237.9736, found 237.9739.



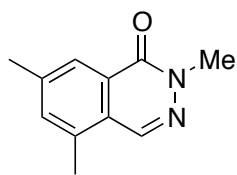
2,7-Dimethylphthalazin-1(2H)-one (2f). According to the general procedure, **1f** (34.7 mg, 0.197 mmol), Pd(OAc)₂ (4.6 mg, 0.020 mmol), and benzoquinone (25.8 mg, 0.239 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 1.5 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (29.3 mg, 85%) as a pale yellow crystal: mp. 54–57 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.54 (s, 3H), 3.83 (s, 3H), 7.53–7.62 (m, 2H), 8.08 (s, 1H), 8.21 (s, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 21.9, 39.3, 125.9, 126.1, 127.6, 127.7, 134.3, 137.5, 142.5, 159.7; IR (ν/cm⁻¹): 1643, 1593, 1346, 594; HRMS (EI) calcd for C₁₀H₁₀N₂O [M]⁺ 174.0788, found 174.0793.



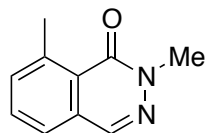
2,6,7-Trimethylphthalazin-1(2H)-one (2g). According to the general procedure, **1g** (37.6 mg, 0.198 mmol), Pd(OAc)₂ (4.5 mg, 0.020 mmol), and benzoquinone (43.2 mg, 0.400 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 2 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (23.3 mg, 63%) as a pale yellow crystal: mp. 139–140 °C (lit.³ 139–140 °C). ¹H and ¹³C NMR spectra were identical to those in the literature.^{Error! Bookmark not defined.}



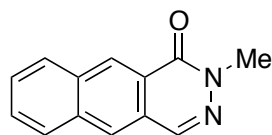
6,7-Dimethoxy-2-methylphthalazin-1(2H)-one (2h). According to the general procedure, **1h** (38.2 mg, 0.196 mmol), Pd(OAc)₂ (4.5 mg, 0.020 mmol), and benzoquinone (43.5 mg, 0.402 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 2 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (25.4 mg, 59%) as a pale yellow crystal: mp. 179–182 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.84 (s, 3H), 4.01 (s, 3H), 4.04 (s, 3H), 6.99 (s, 1H), 7.76 (s, 1H), 8.02 (s, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 39.5, 56.3, 56.5, 105.6, 106.3, 122.8, 125.2, 136.6, 152.9, 153.7, 159.3; IR (ν/cm⁻¹): 1639, 1597, 1504, 1281, 1138, 1045; HRMS (EI) calcd for C₁₁H₁₂N₂O₃ [M]⁺ 220.0842, found 220.0848.



2,5,7-Trimethylphthalazin-1(2H)-one (2i). According to the general procedure, **1i** (37.9 mg, 0.199 mmol), Pd(OAc)₂ (4.5 mg, 0.020 mmol), and benzoquinone (43.3 mg, 0.401 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 7 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (12.1 mg, 32%) as a pale yellow crystal: mp. 128–129 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.50 (s, 3H), 2.61 (s, 3H), 3.85 (s, 3H), 7.40 (s, 1H), 8.08 (s, 1H), 8.27 (s, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 18.0, 21.8, 39.4, 124.1, 126.4, 128.2, 134.6, 134.9, 135.5, 142.1, 159.9; IR (ν/cm⁻¹): 1639, 1585, 1362, 1335, 1038, 795, 679, 486; HRMS (EI) calcd for C₁₁H₁₂N₂O [M]⁺ 188.0944, found 188.0949.



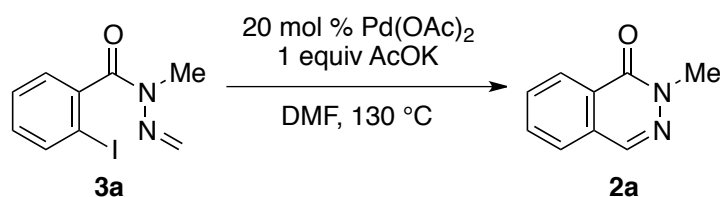
2,8-Dimethylphthalazin-1(2H)-one (2j). According to the general procedure, **1j** (34.7 mg, 0.197 mmol), Pd(OAc)₂ (4.6 mg, 0.020 mmol), and benzoquinone (43.6 mg, 0.403 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 24 h. Purification by preparative thin-layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (8.4 mg, 24%) as a pale yellow crystal: mp. 102–104 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.95 (s, 3H), 3.80 (s, 3H), 7.47–7.51 (m, 2H), 7.60–7.65 (m, 1H), 8.04 (s, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 22.9, 39.6, 124.3, 125.9, 131.4, 132.4, 134.3, 137.9, 141.0, 160.7; IR (ν/cm⁻¹): 1639, 1597, 1504, 1281, 1138, 1045; HRMS (EI) calcd for C₁₀H₁₀N₂O [M]⁺ 174.0788, found 174.0793.



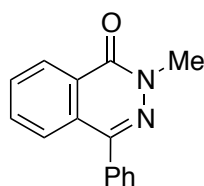
2-Methylbenzo[g]phthalazin-1(2H)-one (2k). According to the general procedure, **1k** (42.0 mg, 0.198 mmol), Pd(OAc)₂ (4.6 mg, 0.020 mmol), and benzoquinone (43.4 mg, 0.402 mmol) were reacted in AcOH (2.0 mL) at 120 °C for 1.5 h. Purification by preparative thin-

layer chromatography on silica gel (CHCl₃:MeOH = 40:1) afforded the title compound (30.0 mg, 72%) as a pale yellow crystal: mp. 158–161 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.86 (s, 3H), 7.62–7.69 (m, 2H), 8.00–8.06 (m, 1H), 8.08–8.13 (m, 1H), 8.18 (s, 1H), 8.25 (s, 1H), 8.97 (s, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 39.0, 124.2, 126.2, 126.4, 127.7, 128.1, 128.5, 128.6, 129.5, 134.3, 135.0, 138.3, 159.8; IR (ν/cm⁻¹): 1643, 1350, 1030, 953, 729, 471; HRMS (EI) calcd for C₁₃H₁₀N₂O [M]⁺ 210.0788, found 210.0793.

General Procedure for Palladium-Catalysed Heck-Type Cyclisation of 2-Iodo-*N*-methyl-*N'*-methylenbenzohydrazides **3**

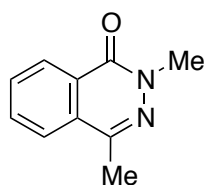


2,6-Dimethylphthalazin-1(2H)-one (2a). A Schlenk tube was charged with **3a** (42.5 mg, 0.148 mmol), Pd(OAc)₂ (6.7 mg, 0.030 mmol) and AcOK (14.7 mg, 0.150 mmol), and then the tube was evacuated and backfilled with nitrogen. DMF (1.5 mL) were added via syringe through the septum. After heating at 130 °C for 0.5 h, the reaction mixture was filtered through a plug of Florisil® eluting with AcOEt. The eluent was washed with water and brine, and concentrated under reduced pressure. The residue was subjected to preparative thin-layer chromatography on silica gel (hexane:AcOEt = 3:1) to afford the title compound (14.3 mg, 61%).



2-Methyl-4-phenylphthalazin-1(2H)-one (2m). According to the general procedure, **3m** (54.5 mg, 0.150 mmol), Pd(OAc)₂ (6.8 mg, 0.030 mmol), and AcOK (14.9 mg, 0.152 mmol) were reacted in DMF (1.5 mL) at 130 °C for 1 h. Purification by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 3:1) afforded the title compound (16.1 mg, 46%) as a pale yellow solid: mp. 163–164 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.90 (s, 3H), 7.45–7.58 (m, 5H), 7.65–7.77 (m, 3H), 8.51 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (125.7 MHz, CDCl₃) δ 39.8, 126.9, 127.2, 128.4, 128.9, 129.3, 129.5, 129.6, 131.6, 132.9, 135.3, 147.2,

159.6; IR (ν/cm^{-1}): 1655, 1581, 1350, 1335, 787, 690; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}]^+$ 236.0944, found 236.0950.

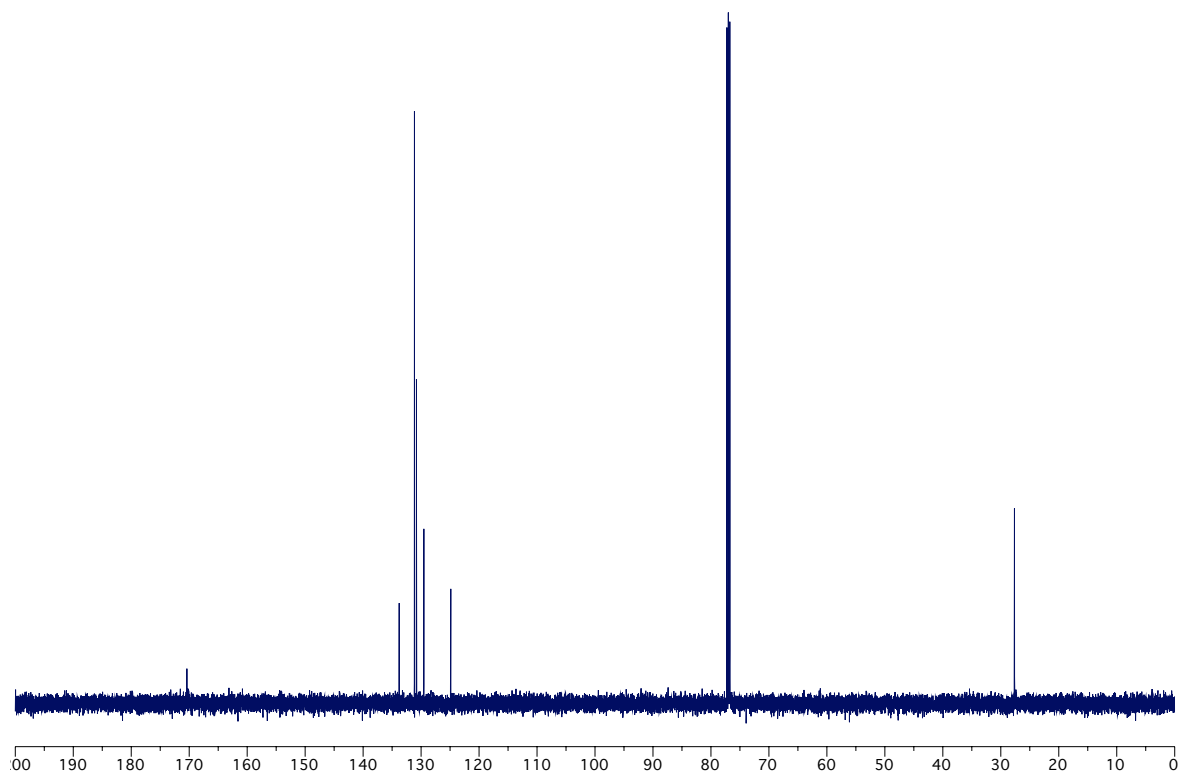
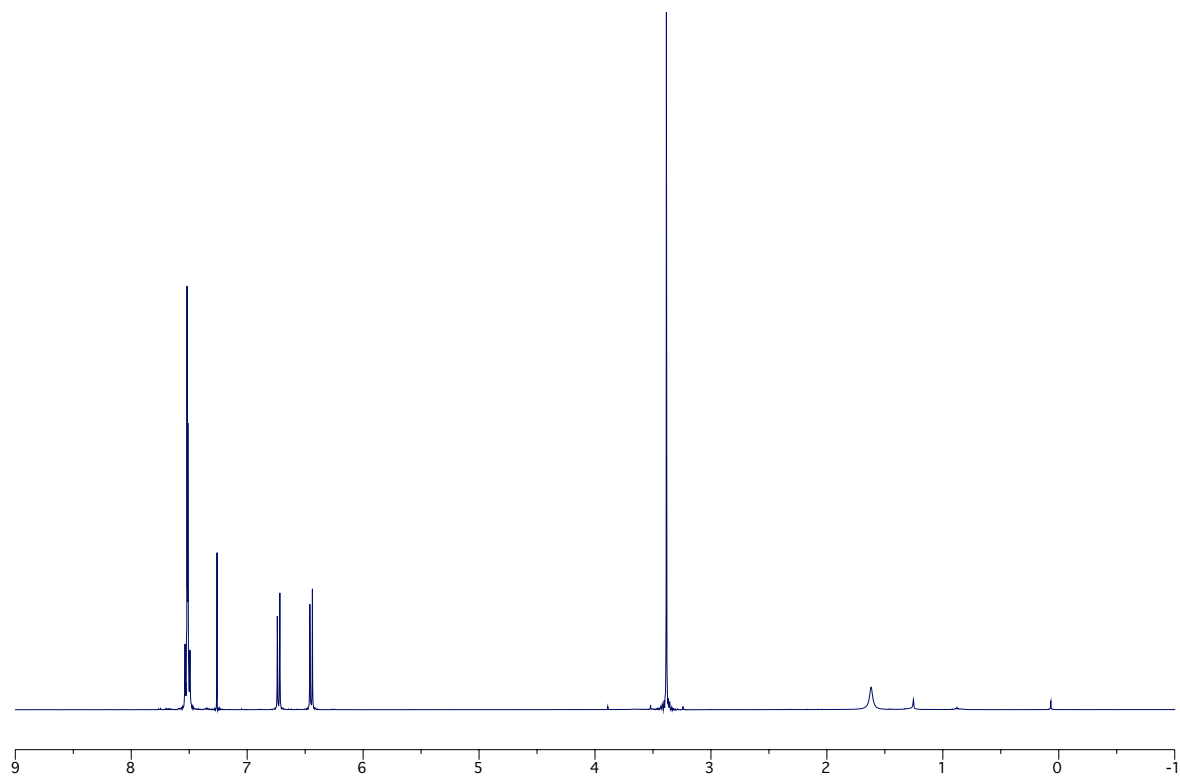
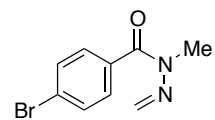


2,4-Dimethylphthalazin-1(2H)-one (2n). According to the general procedure, **3n** (45.1 mg, 0.149 mmol), $\text{Pd}(\text{OAc})_2$ (6.8 mg, 0.030 mmol), and AcOK (14.7 mg, 0.150 mmol) were reacted in DMF (1.5 mL) at 130 °C for 0.5 h. Purification by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 2:1) afforded the title compound (7.7 mg, 30%) as a white solid: mp. 111–112 °C (lit.⁴ 110–112 °C). ^1H and ^{13}C NMR spectra were identical to those in the literature.^{4,5}

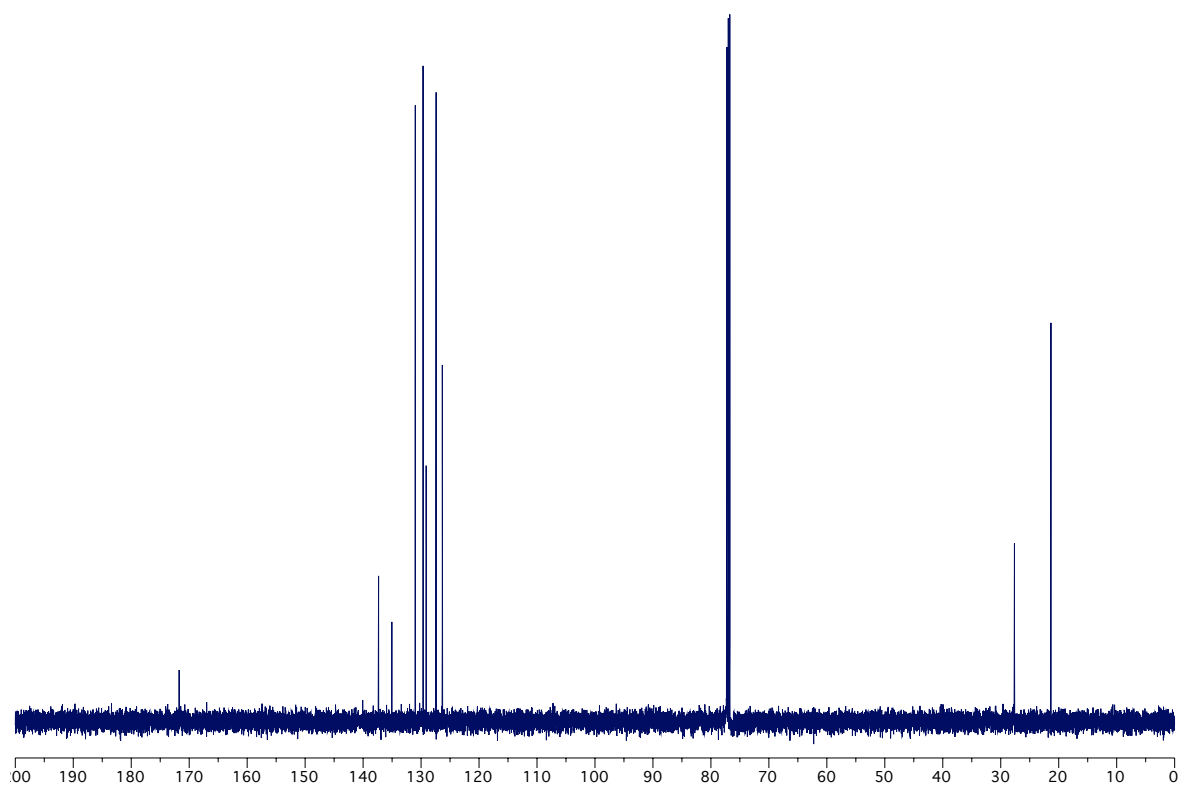
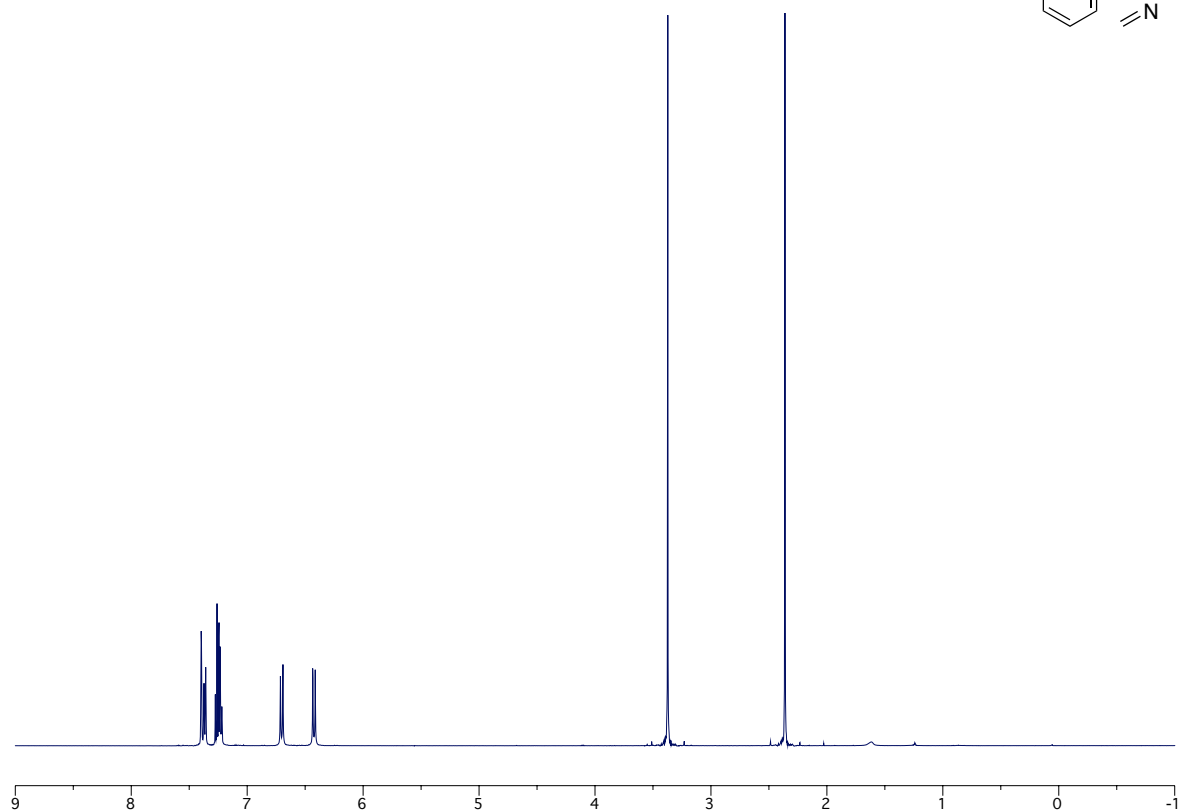
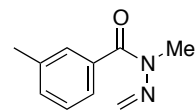
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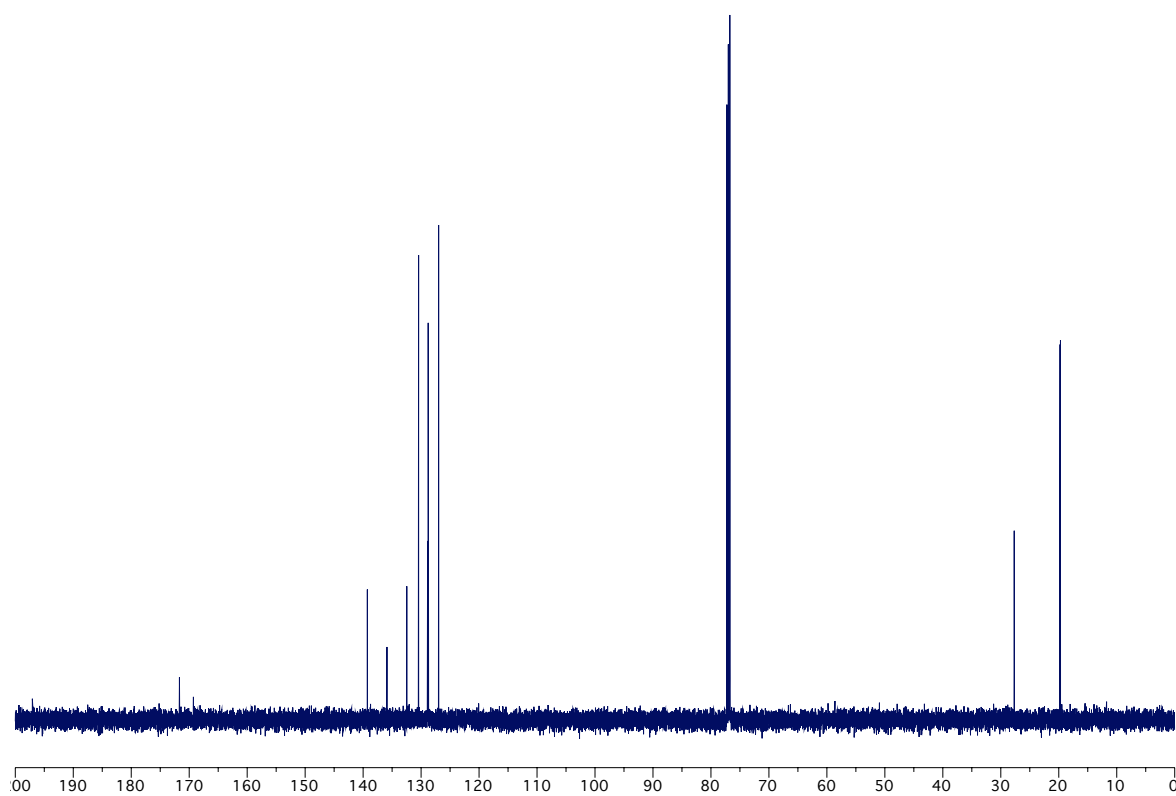
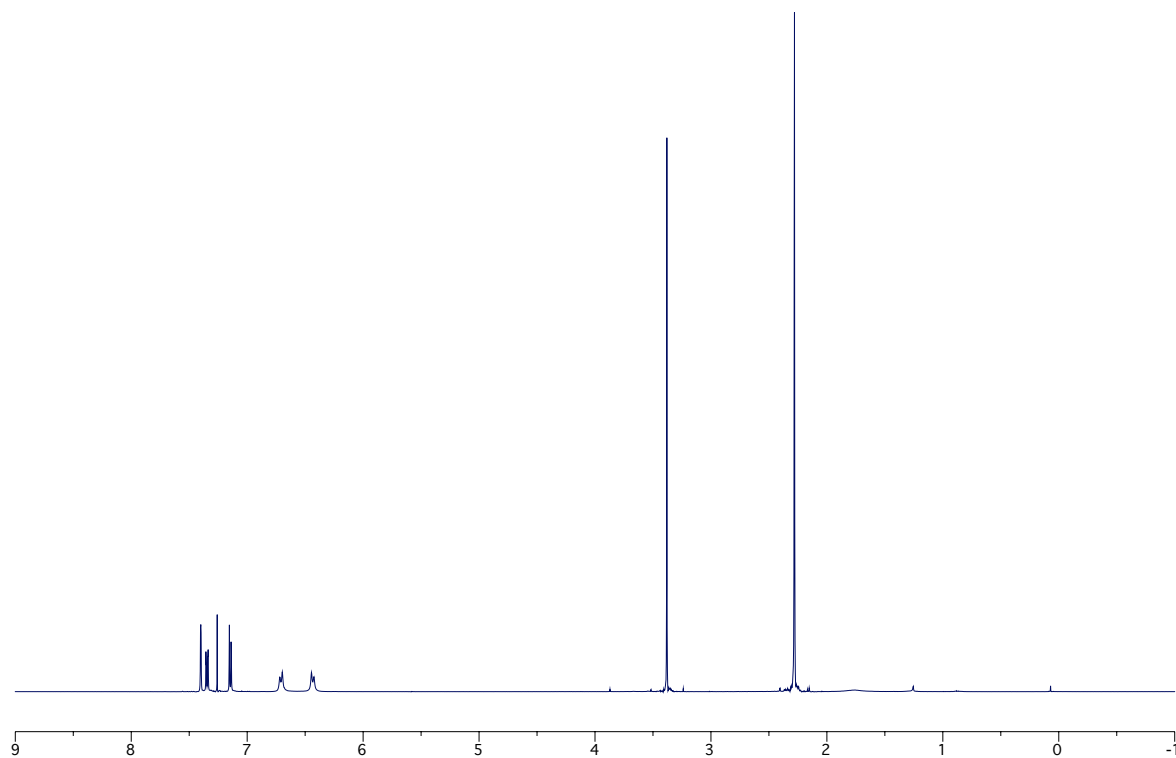
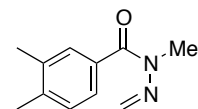
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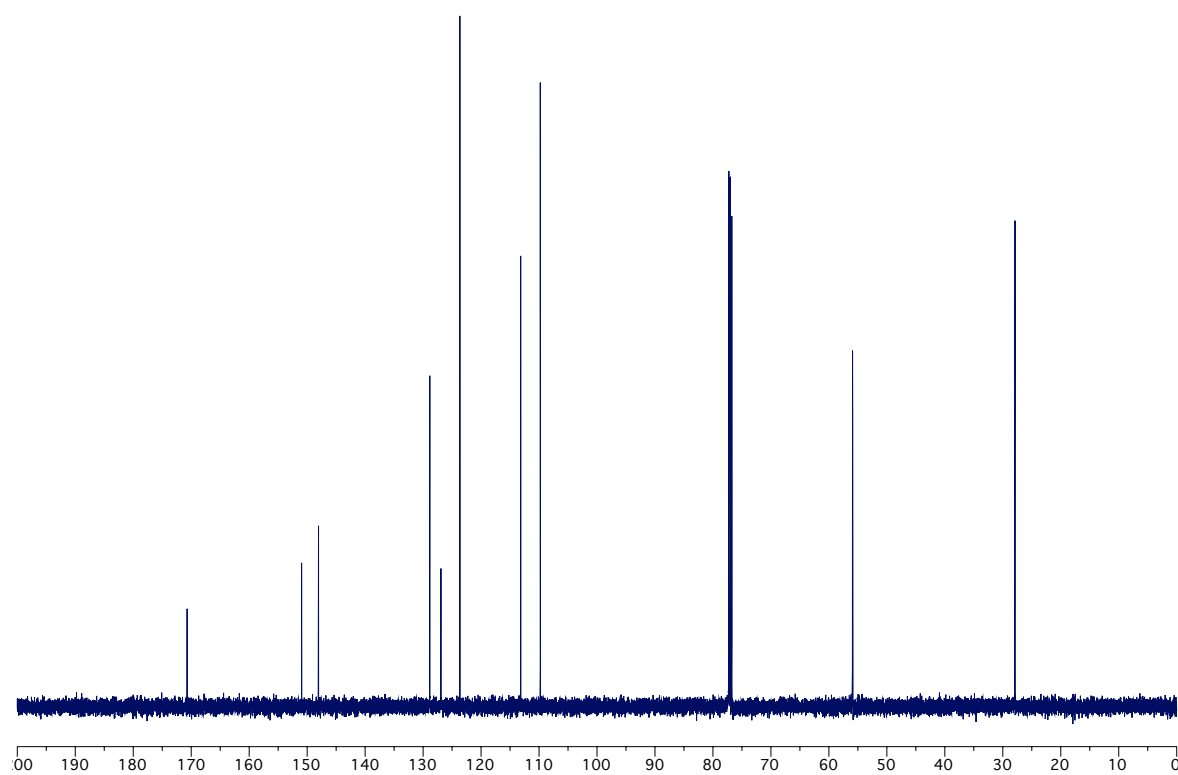
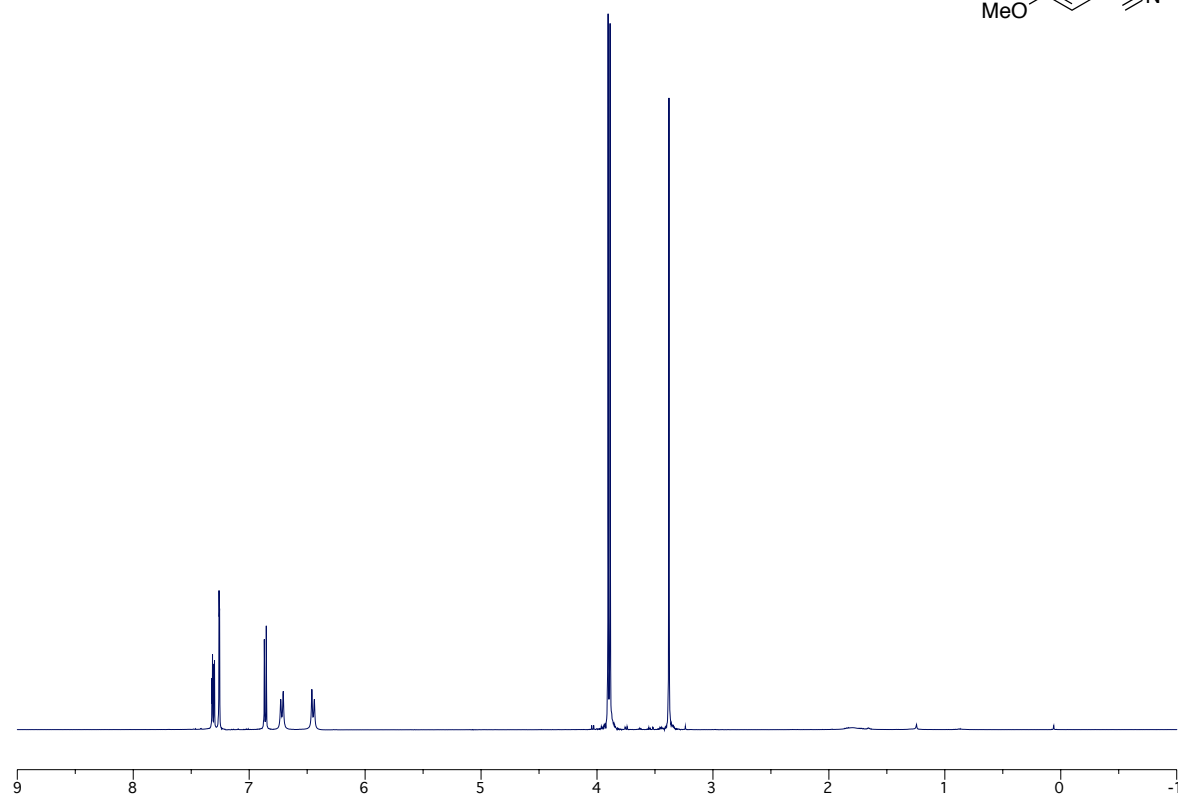
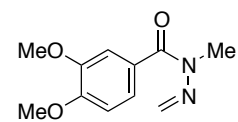
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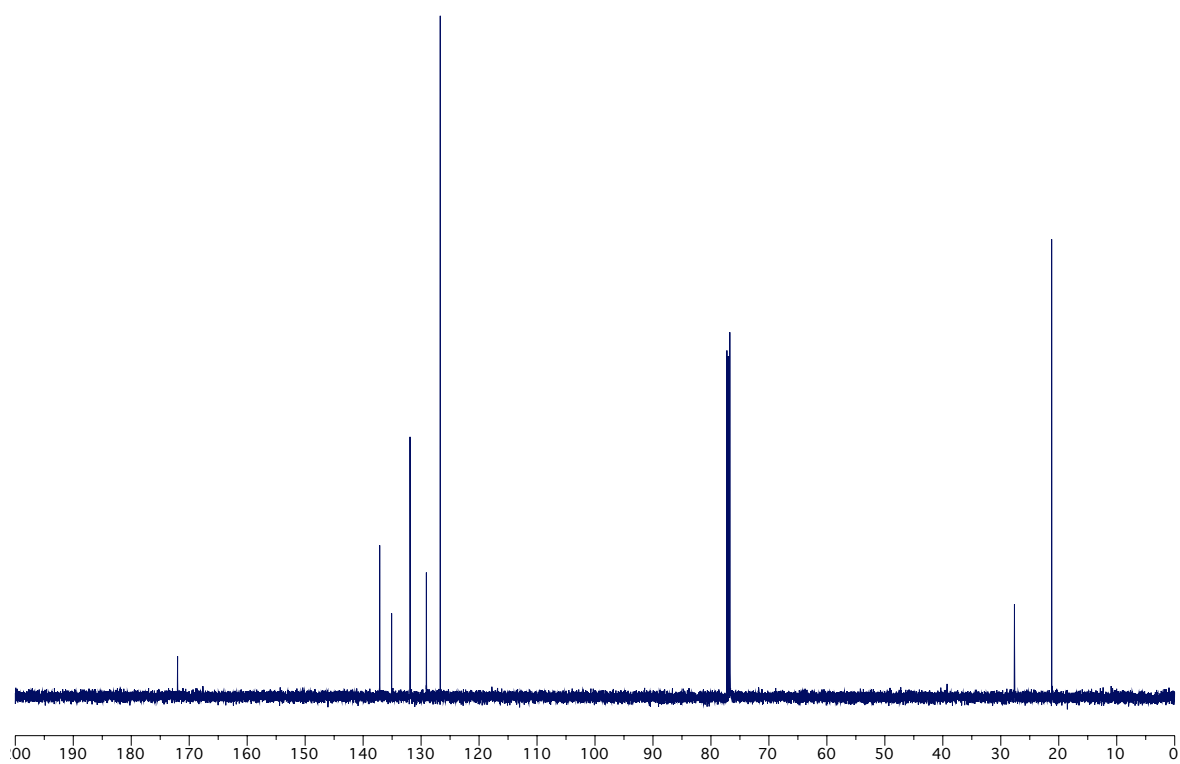
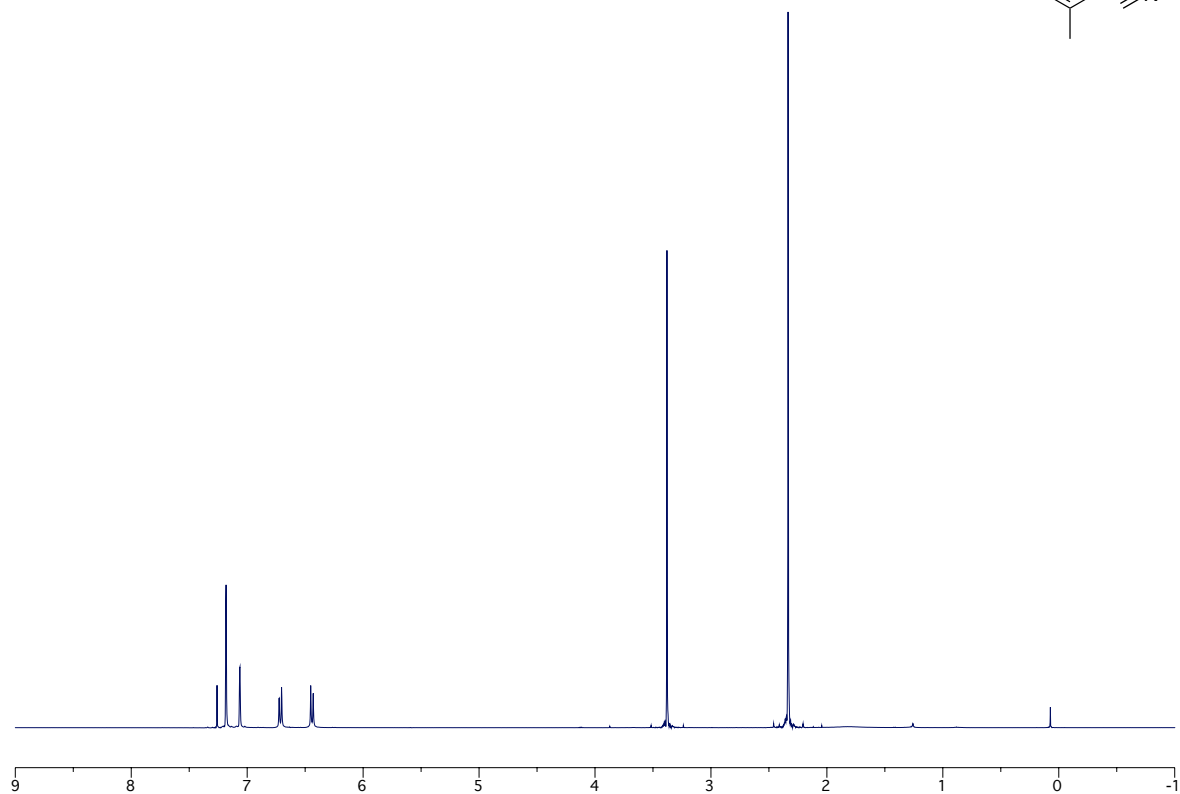
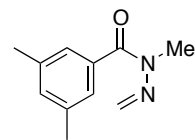
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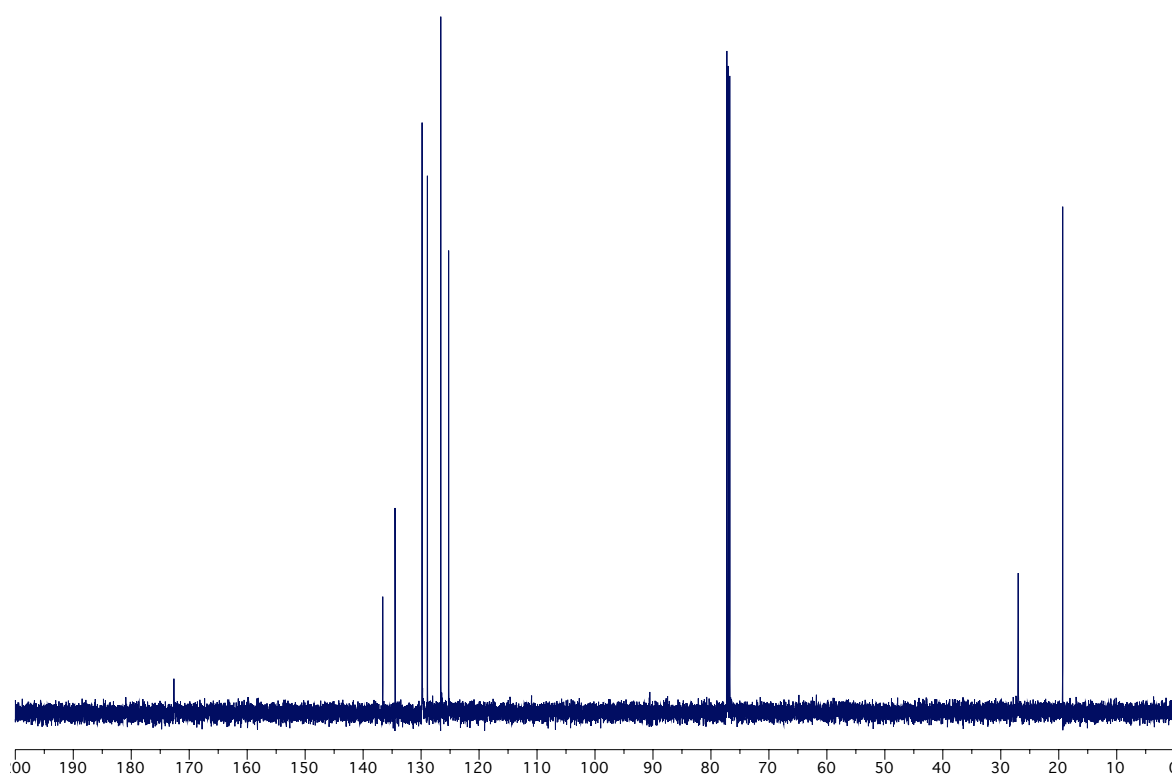
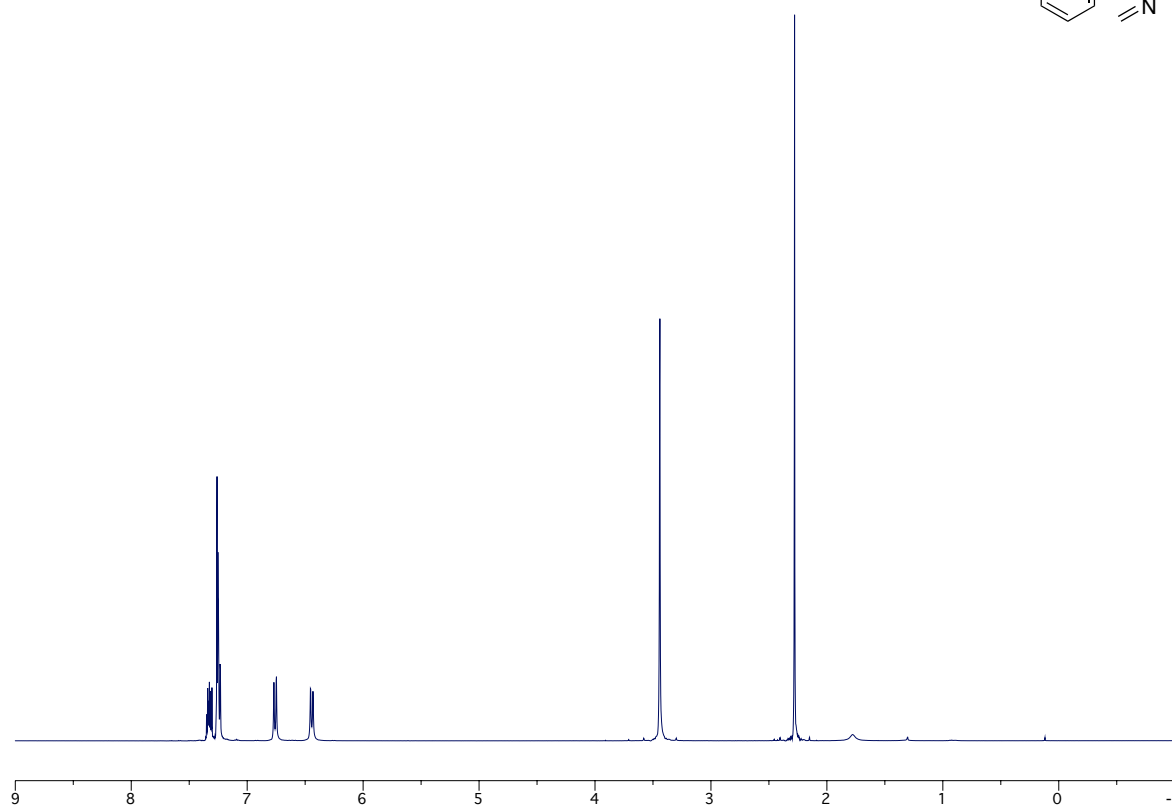
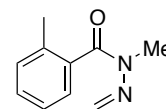
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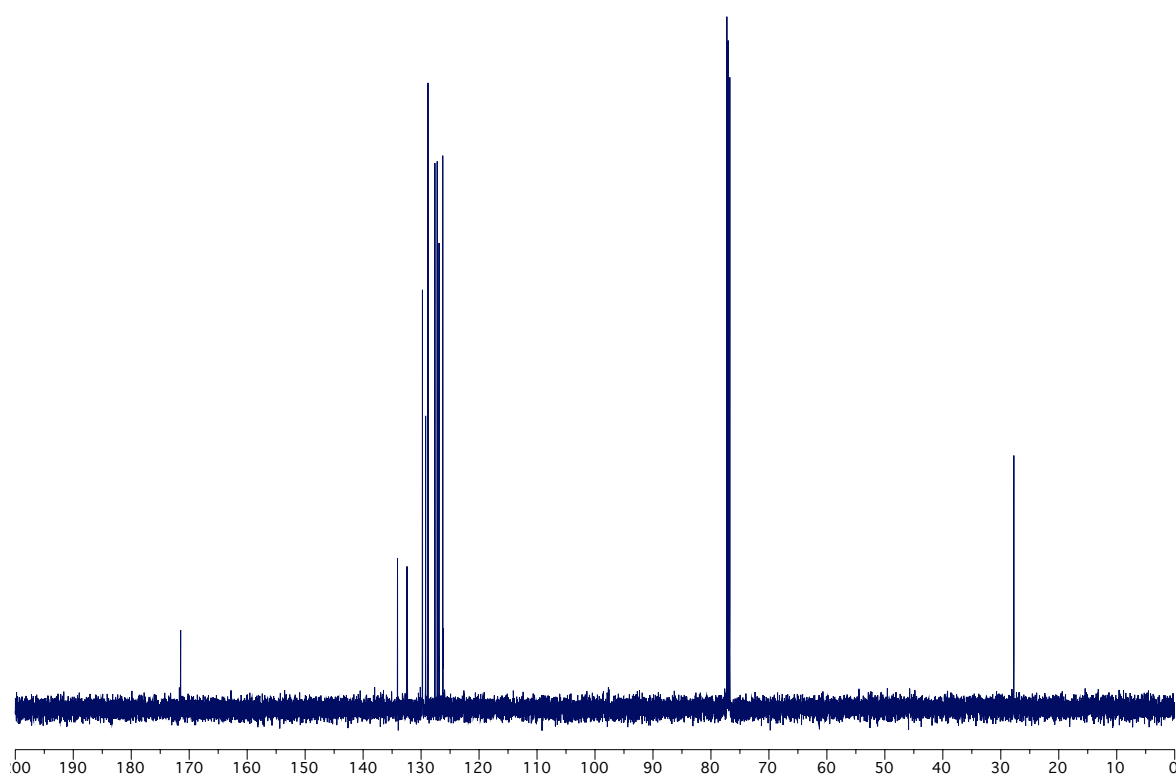
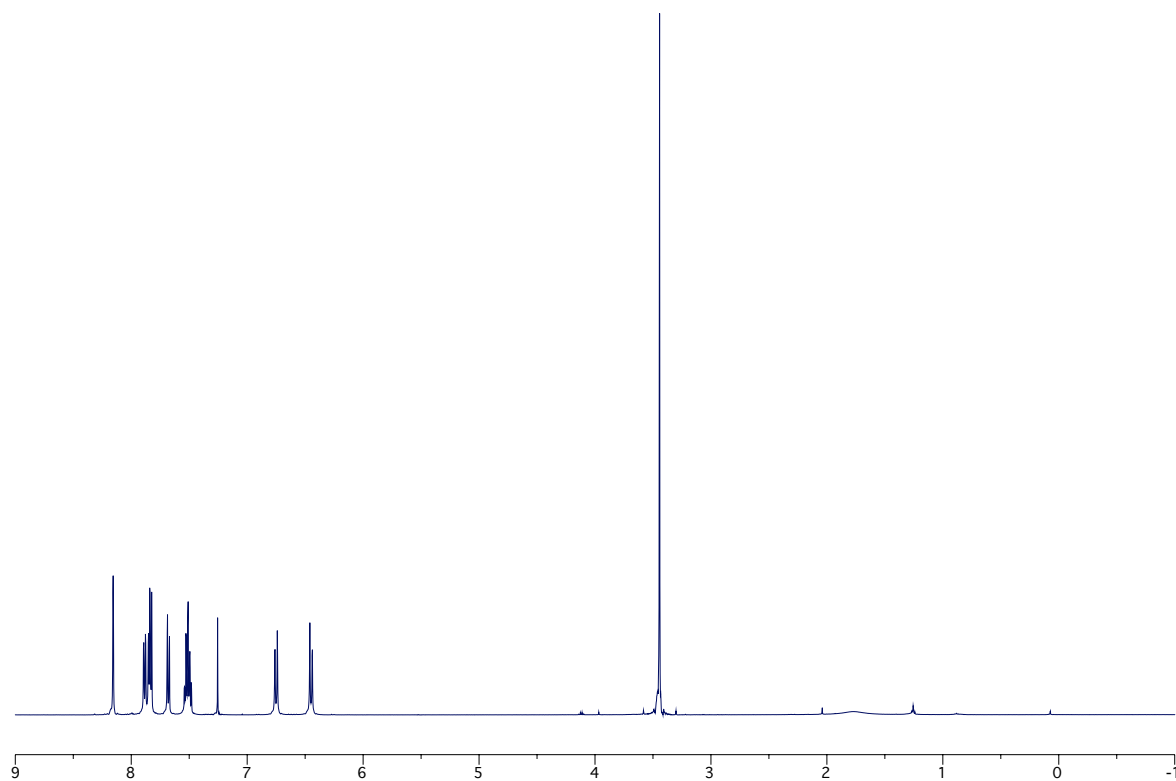
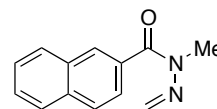
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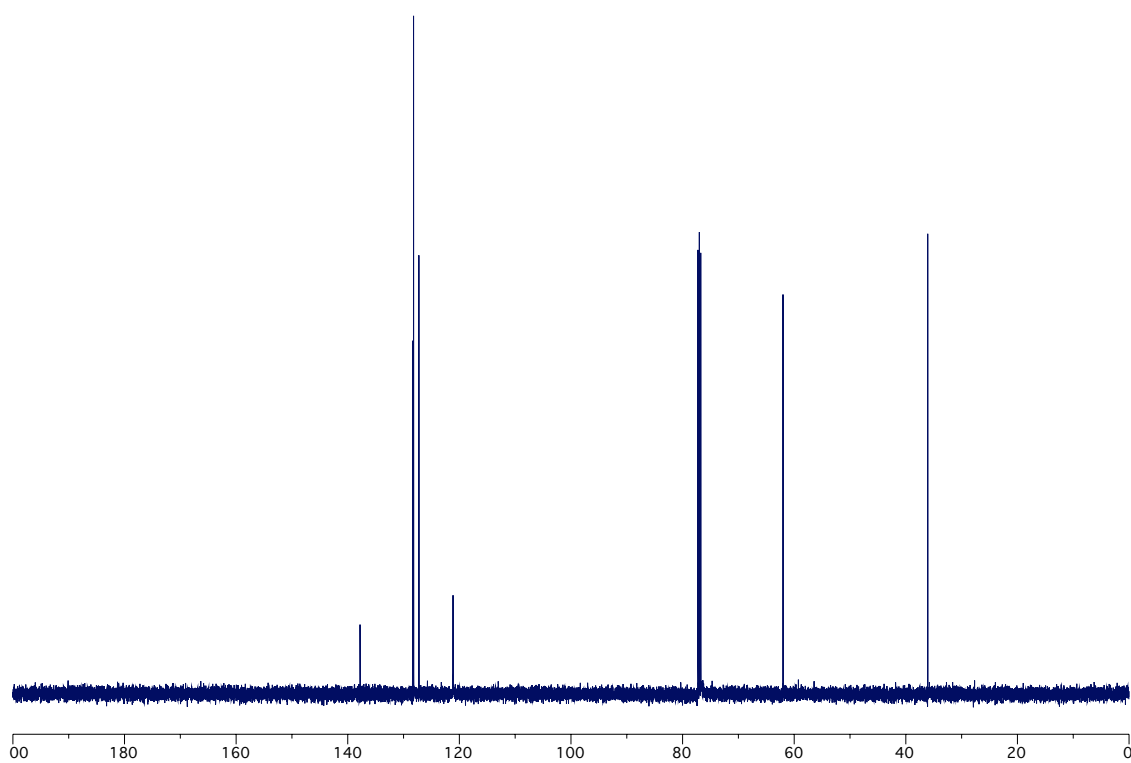
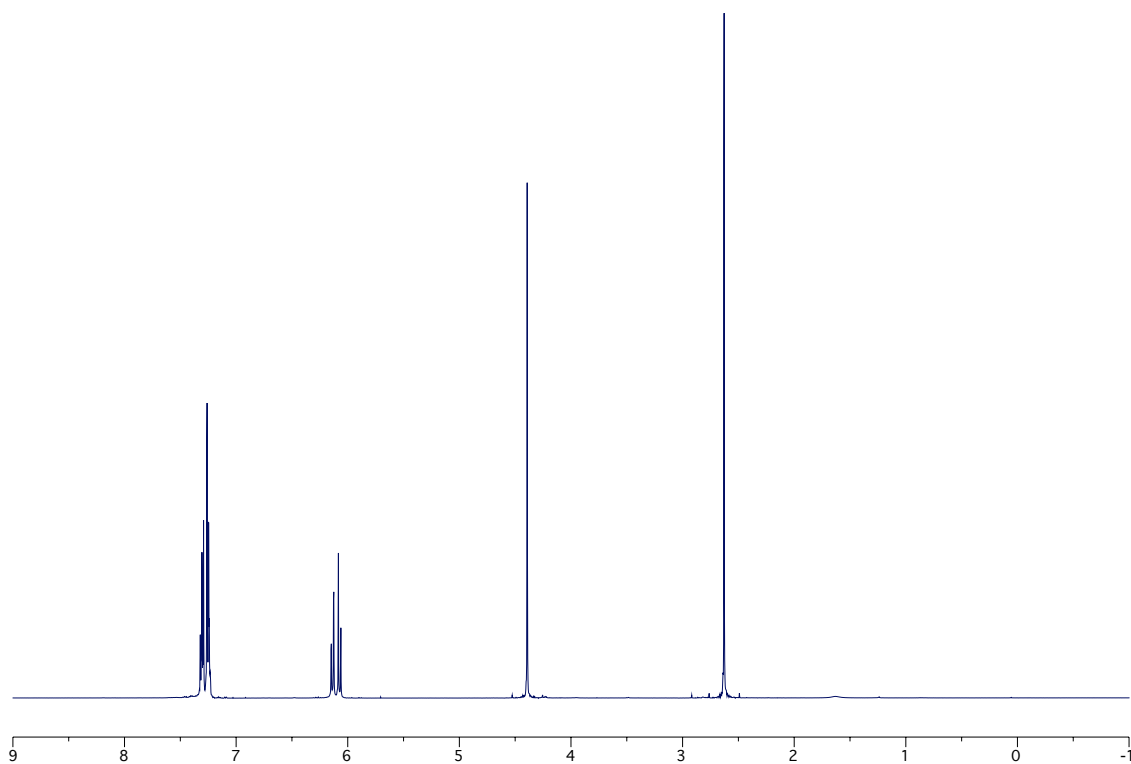
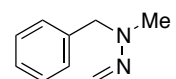
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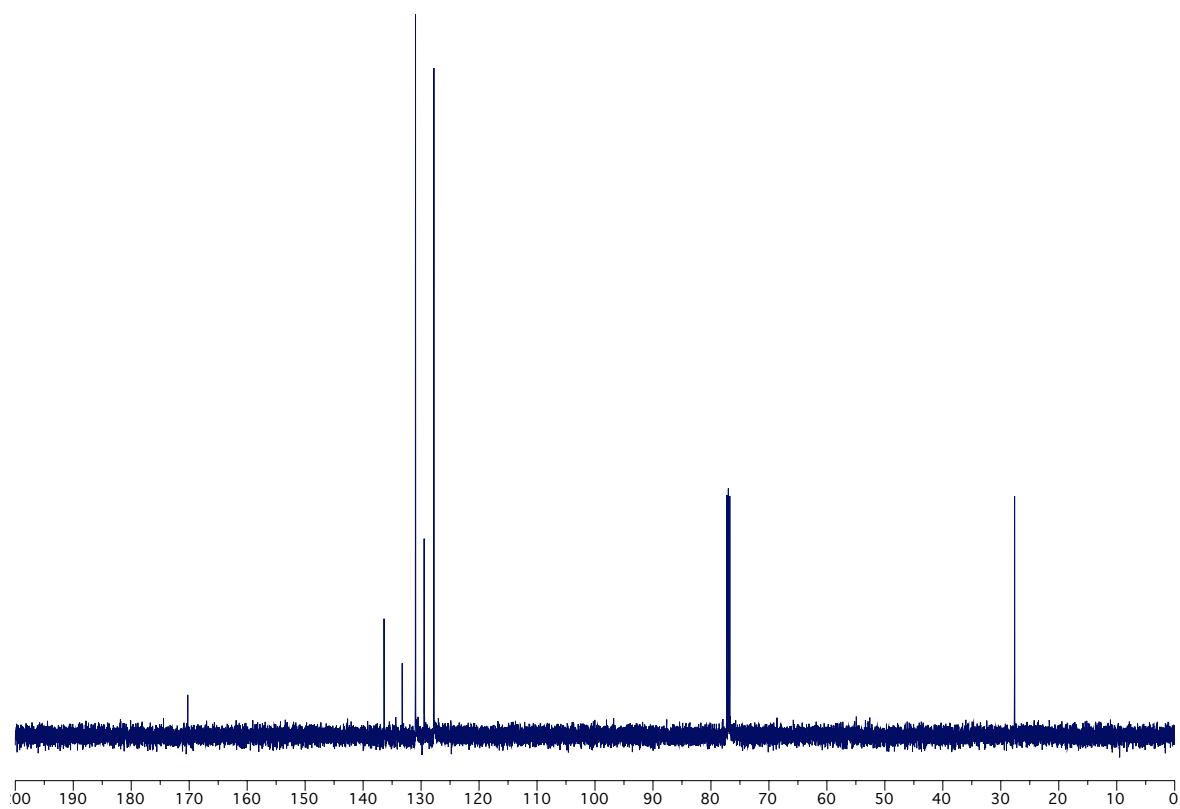
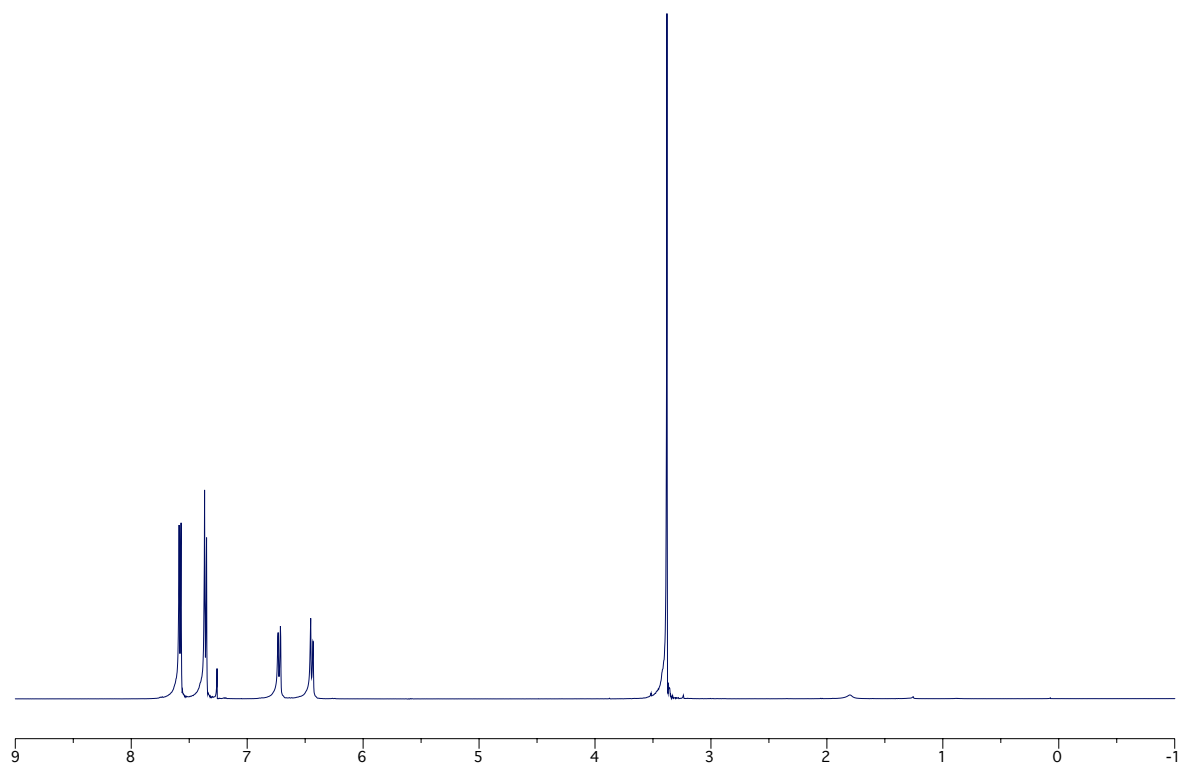
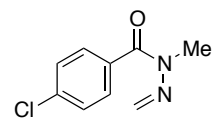


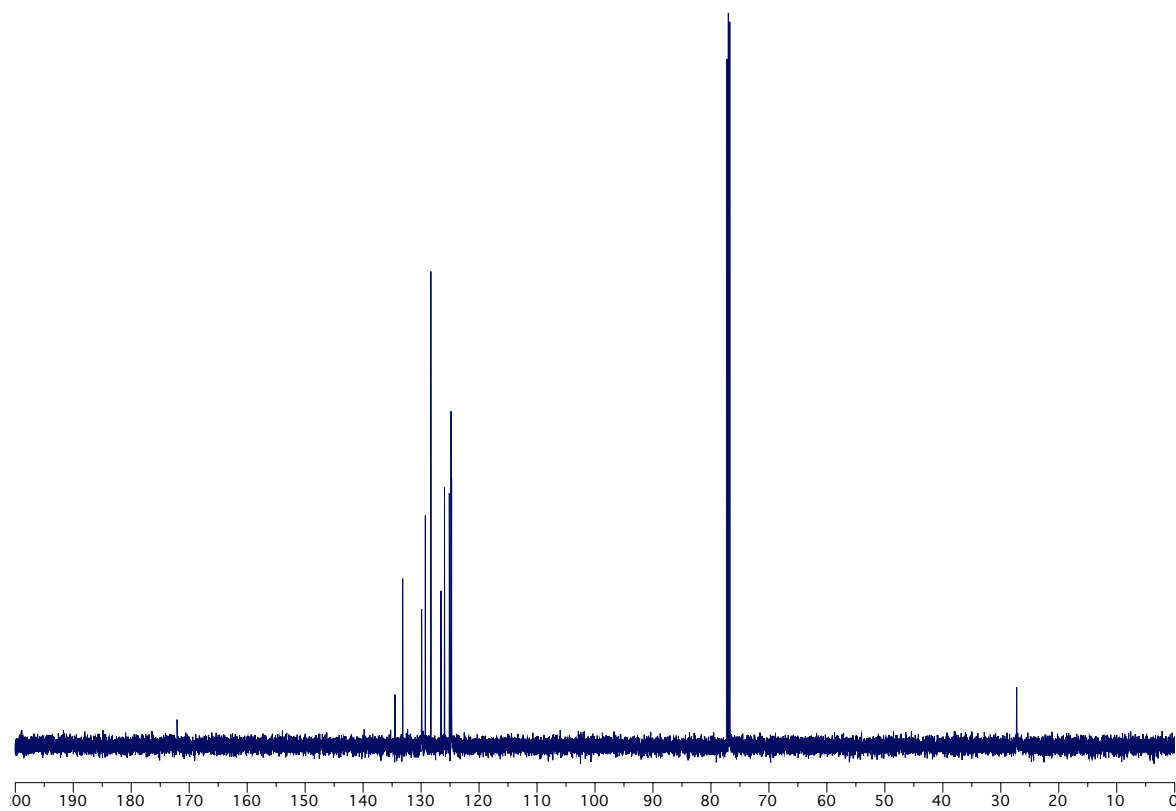
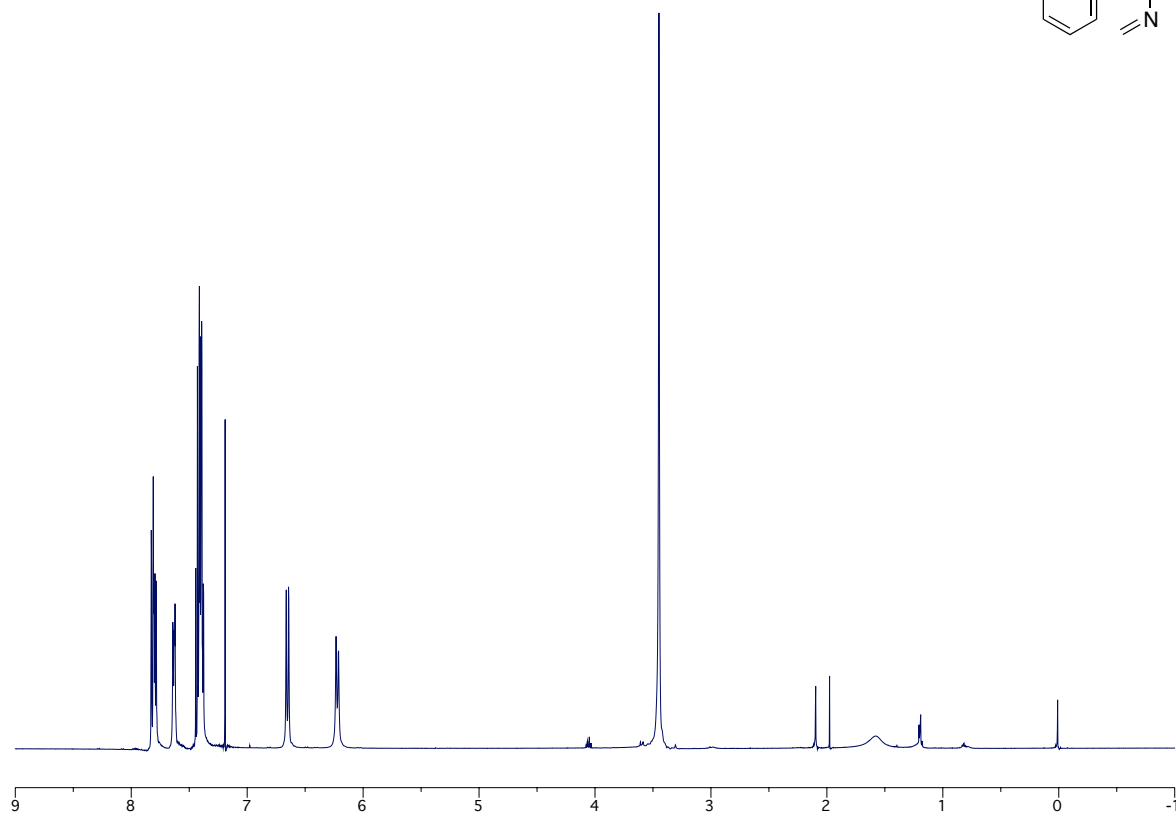
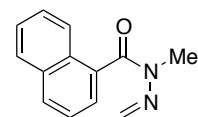
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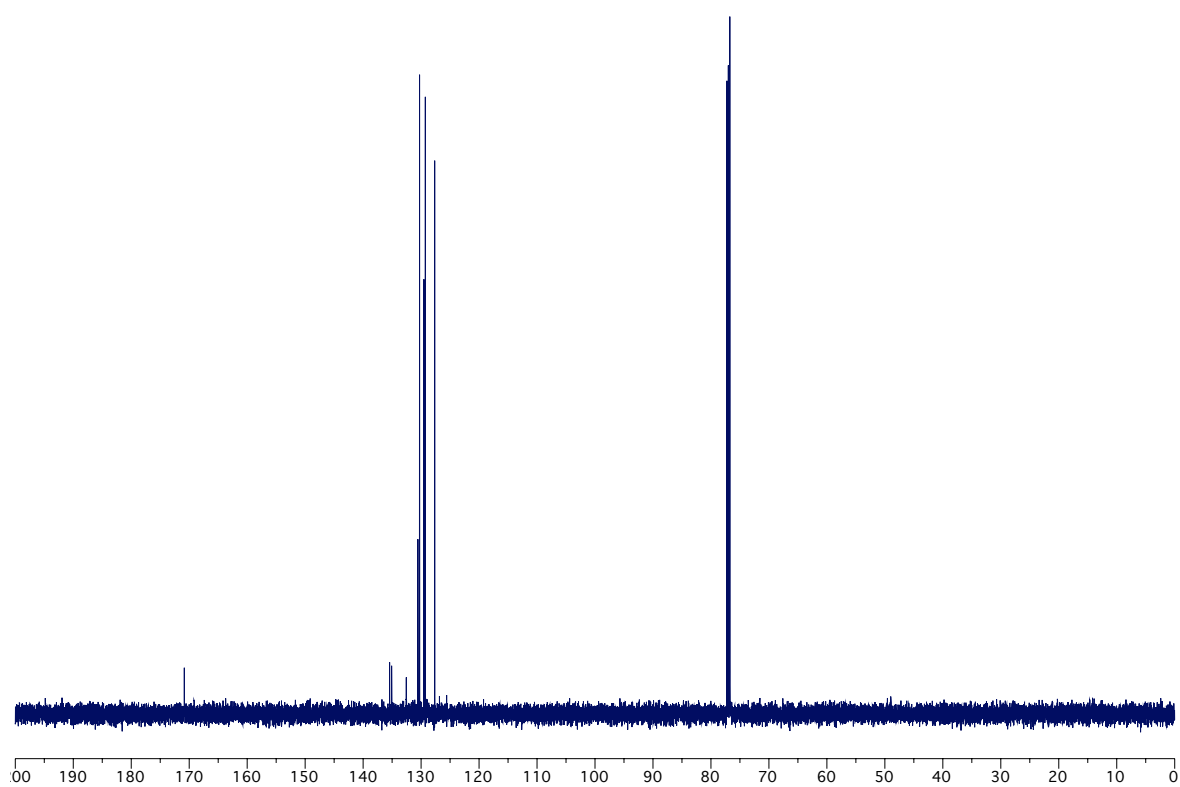
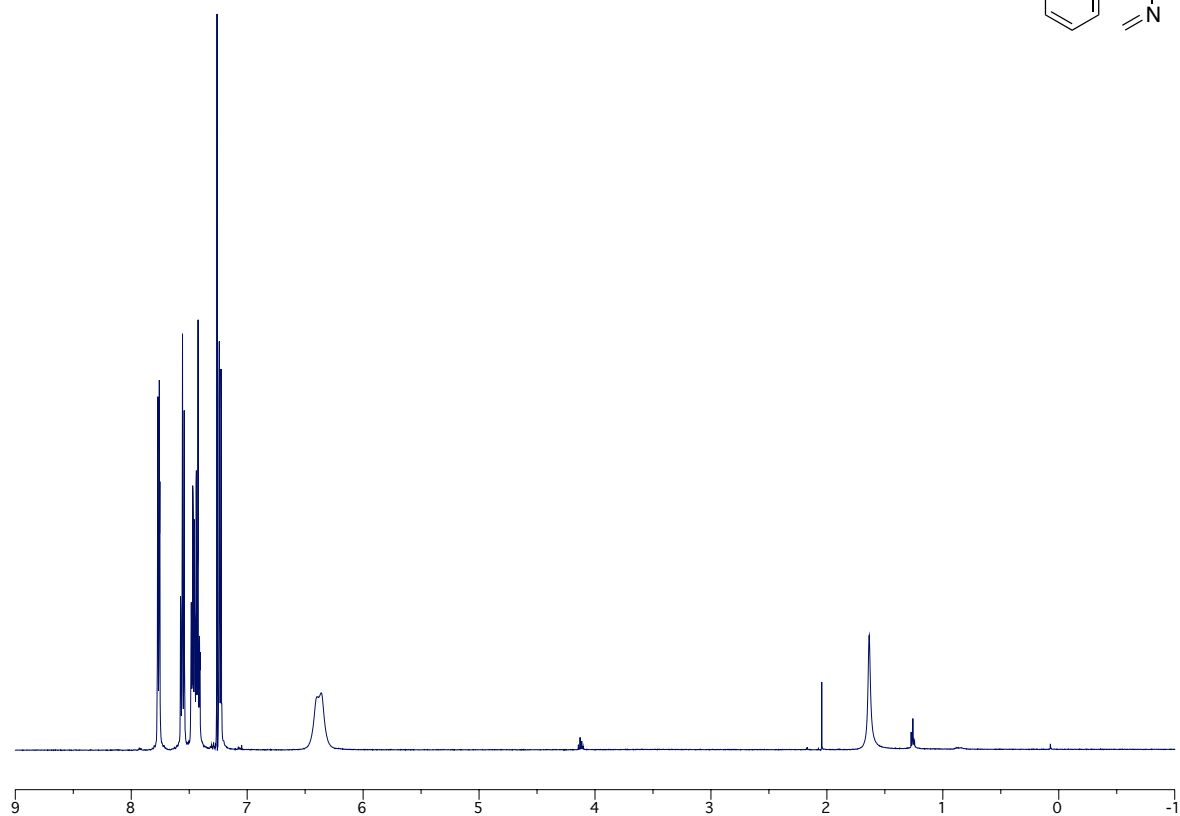
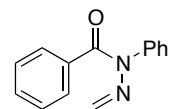


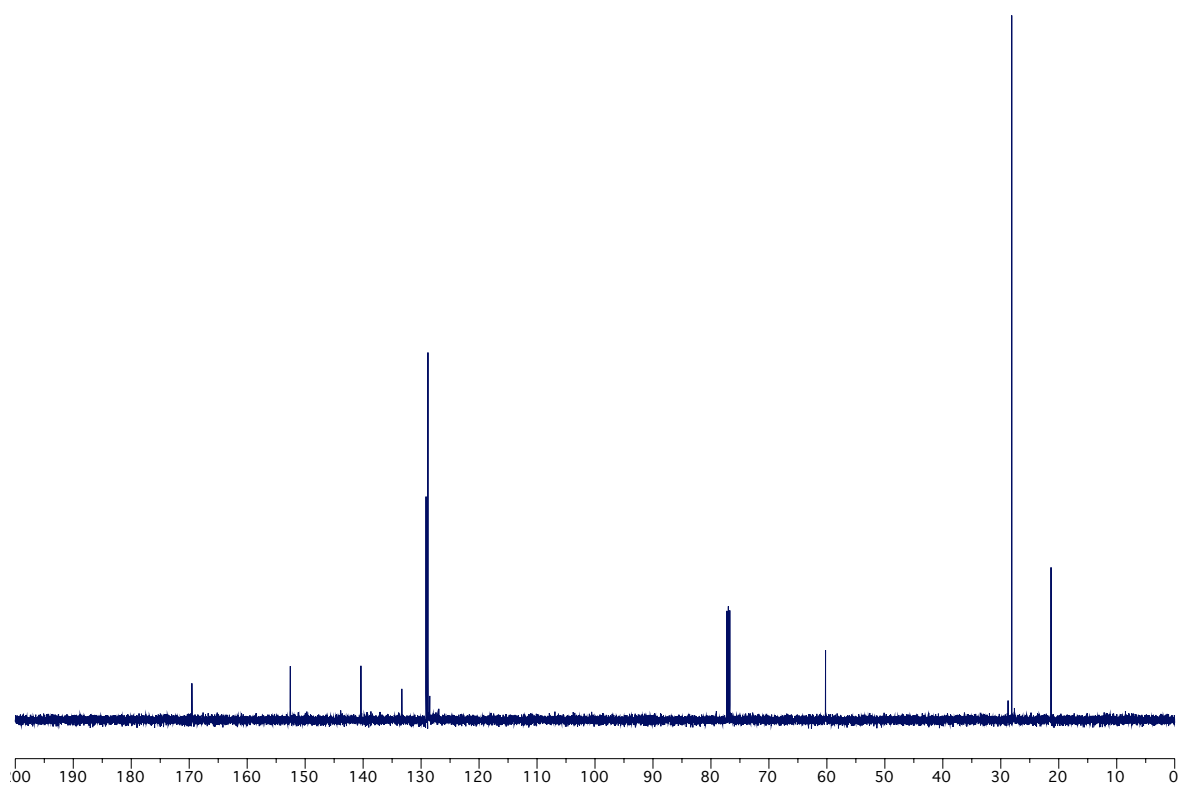
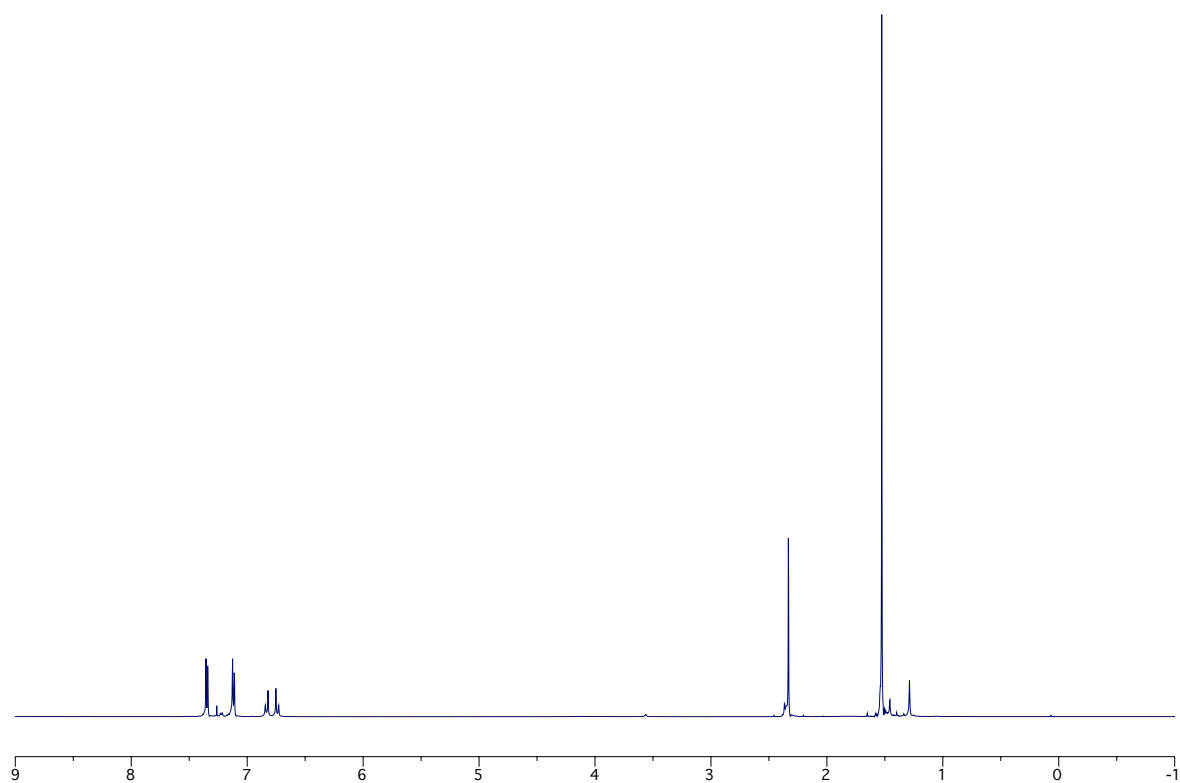
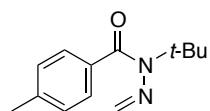
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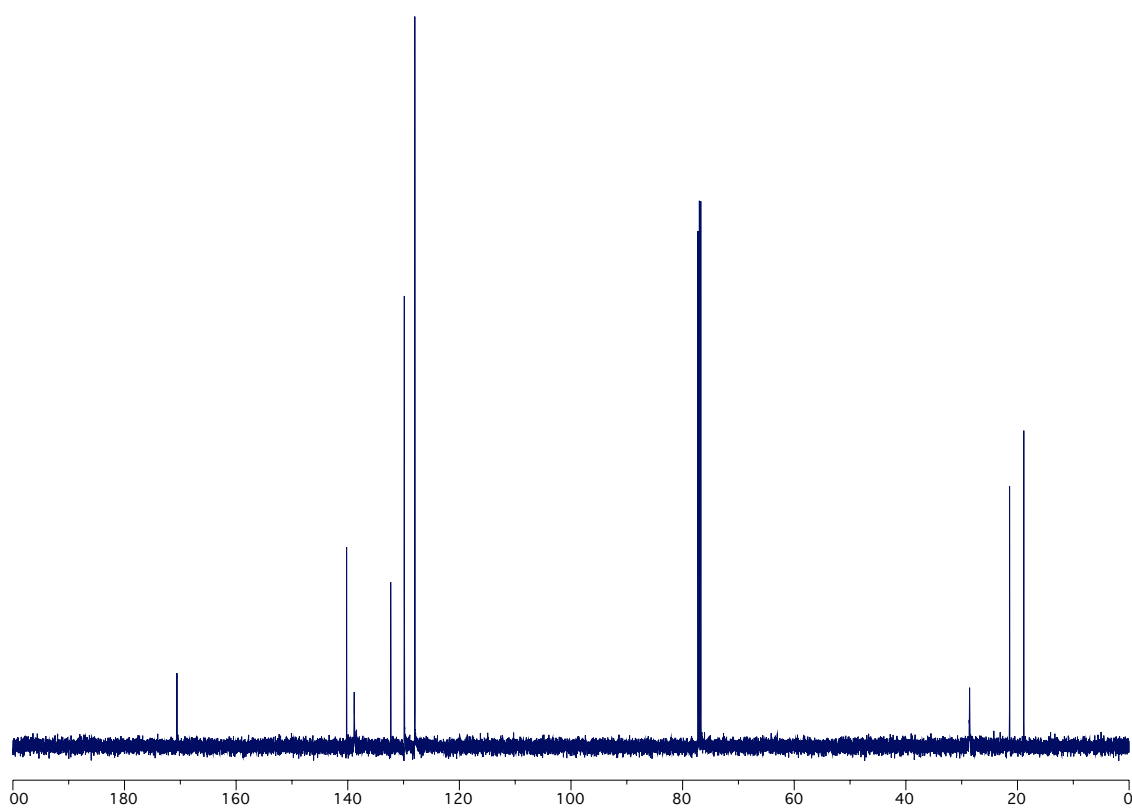
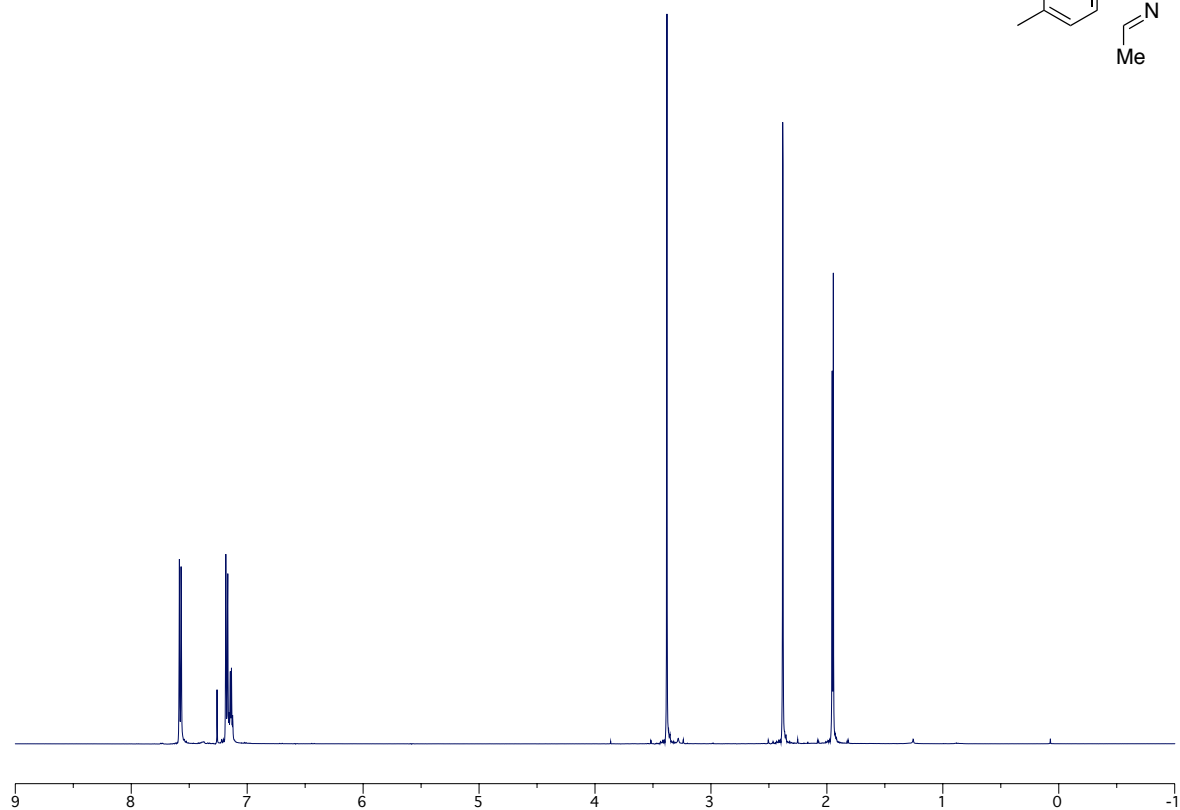
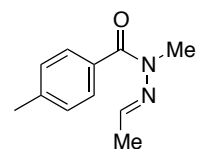




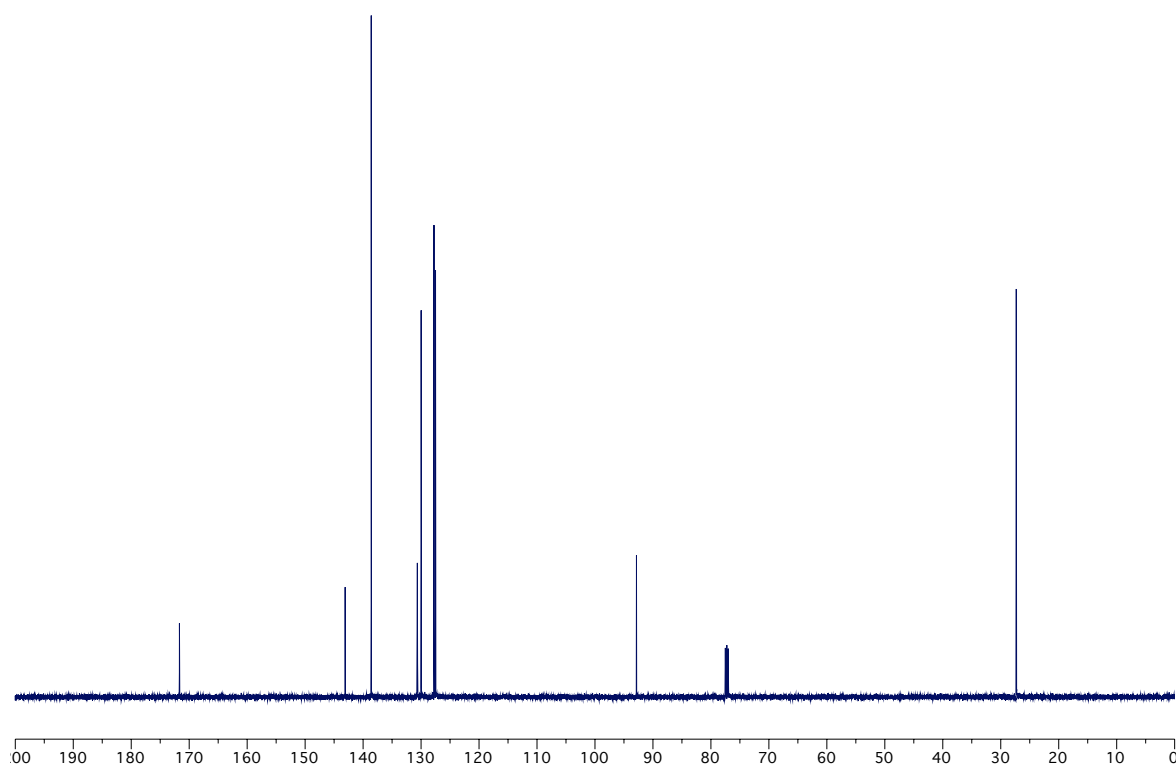
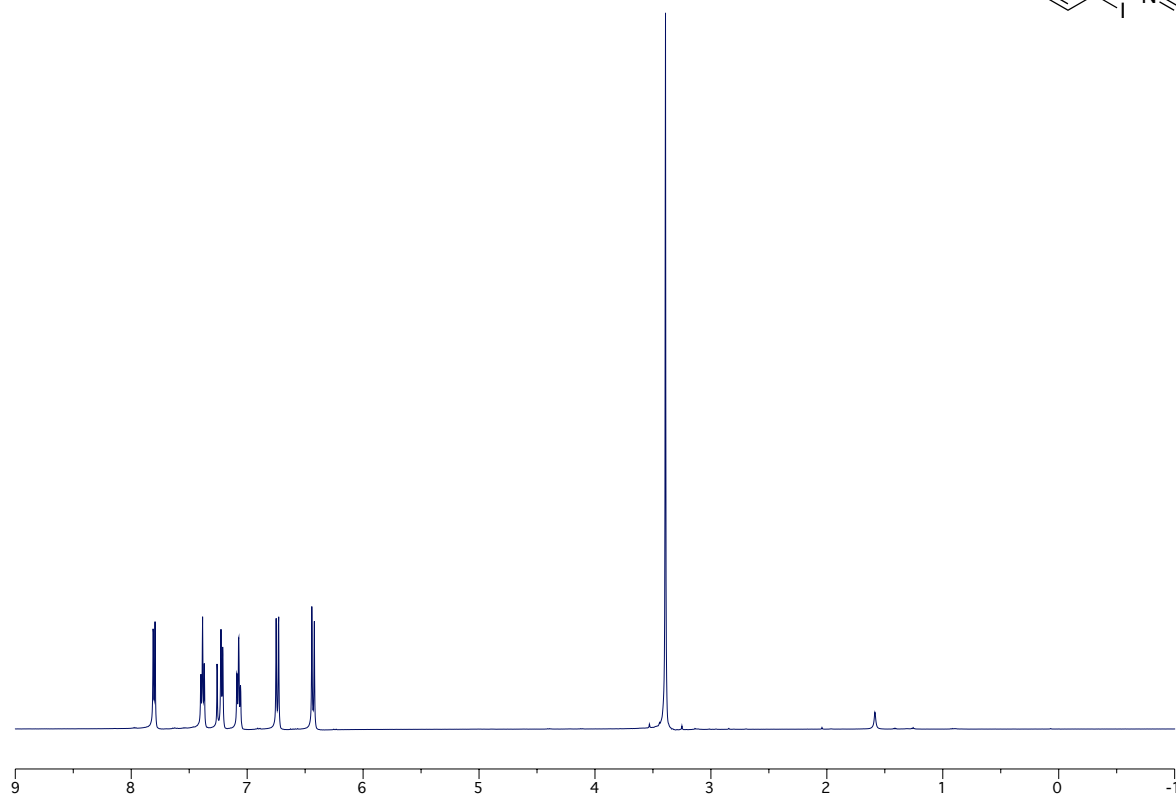
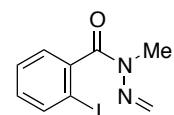




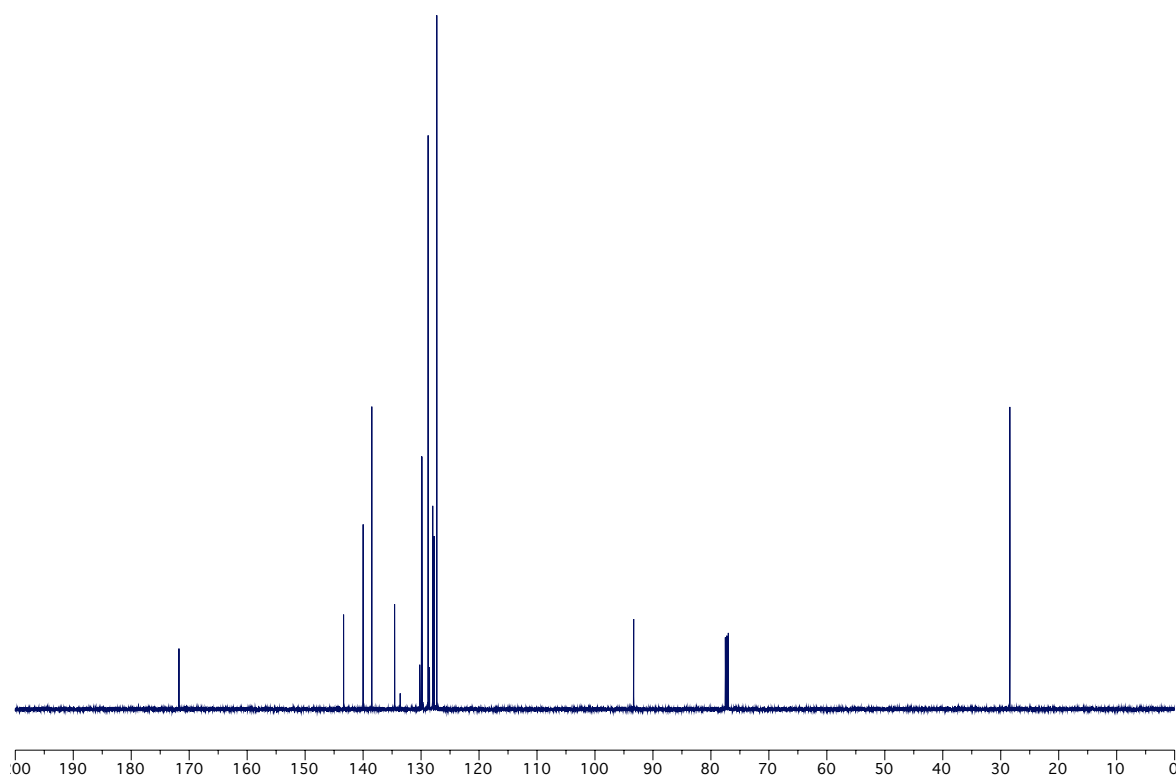
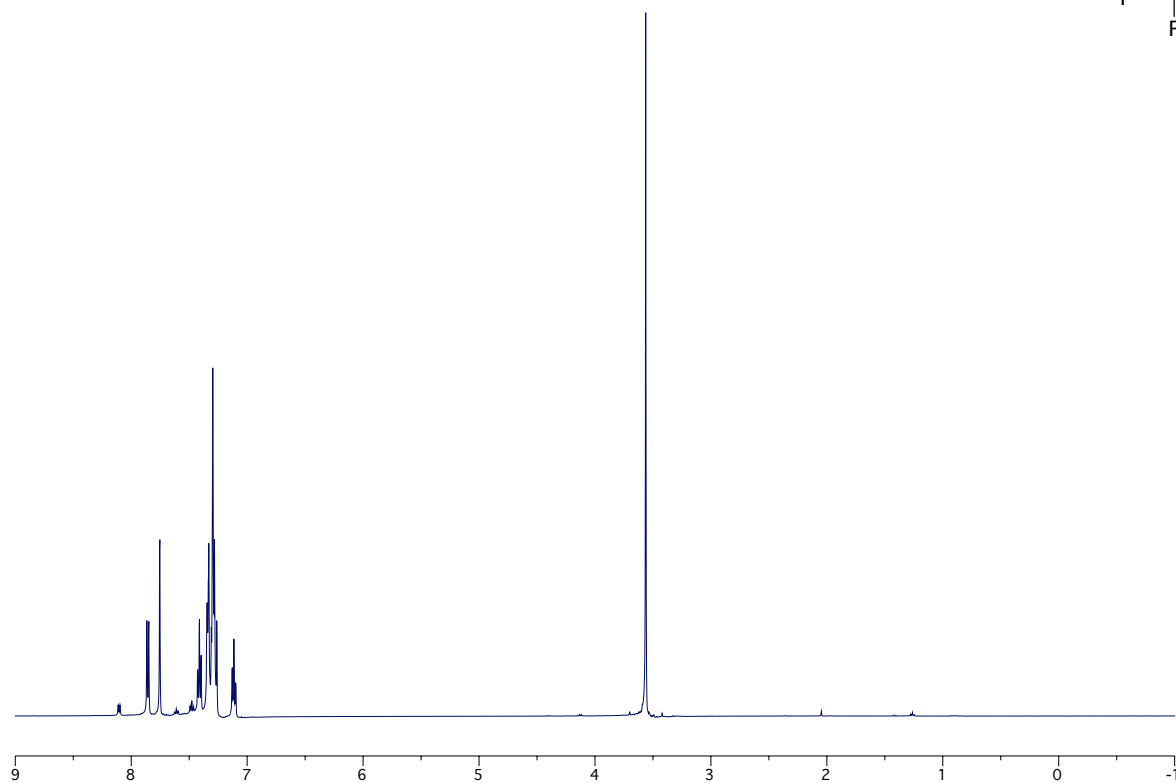
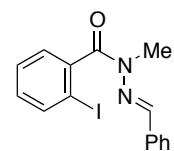




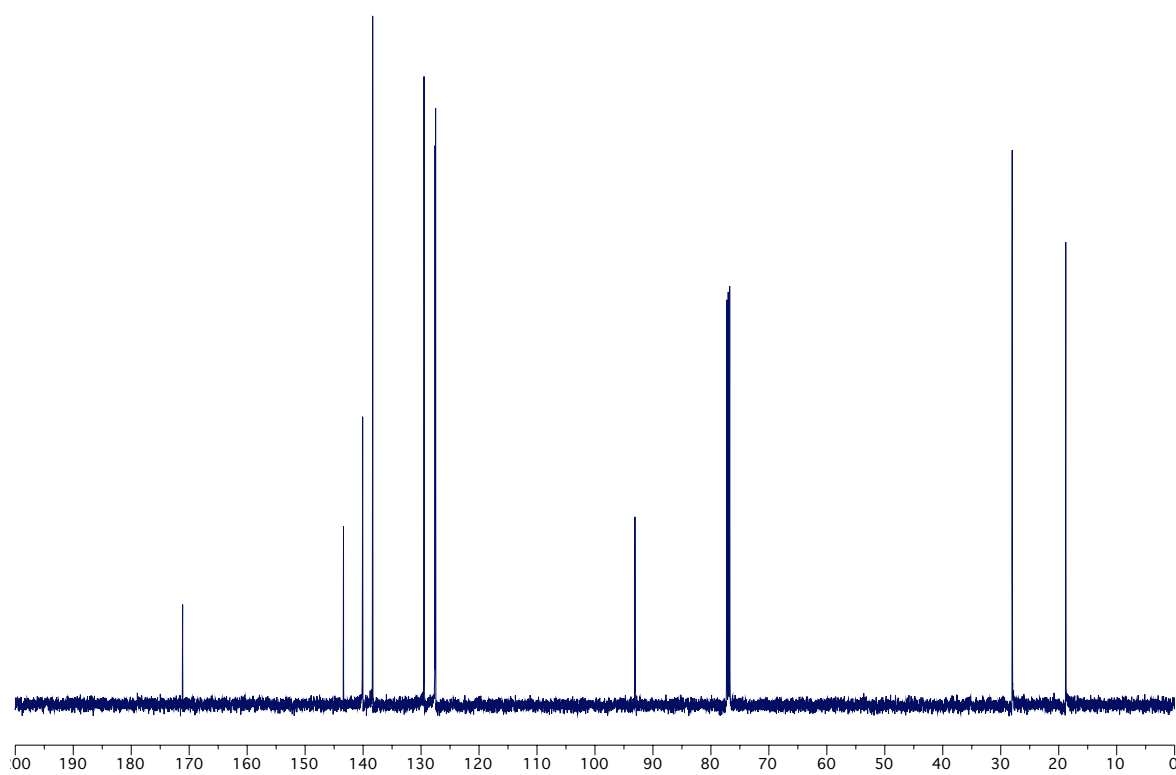
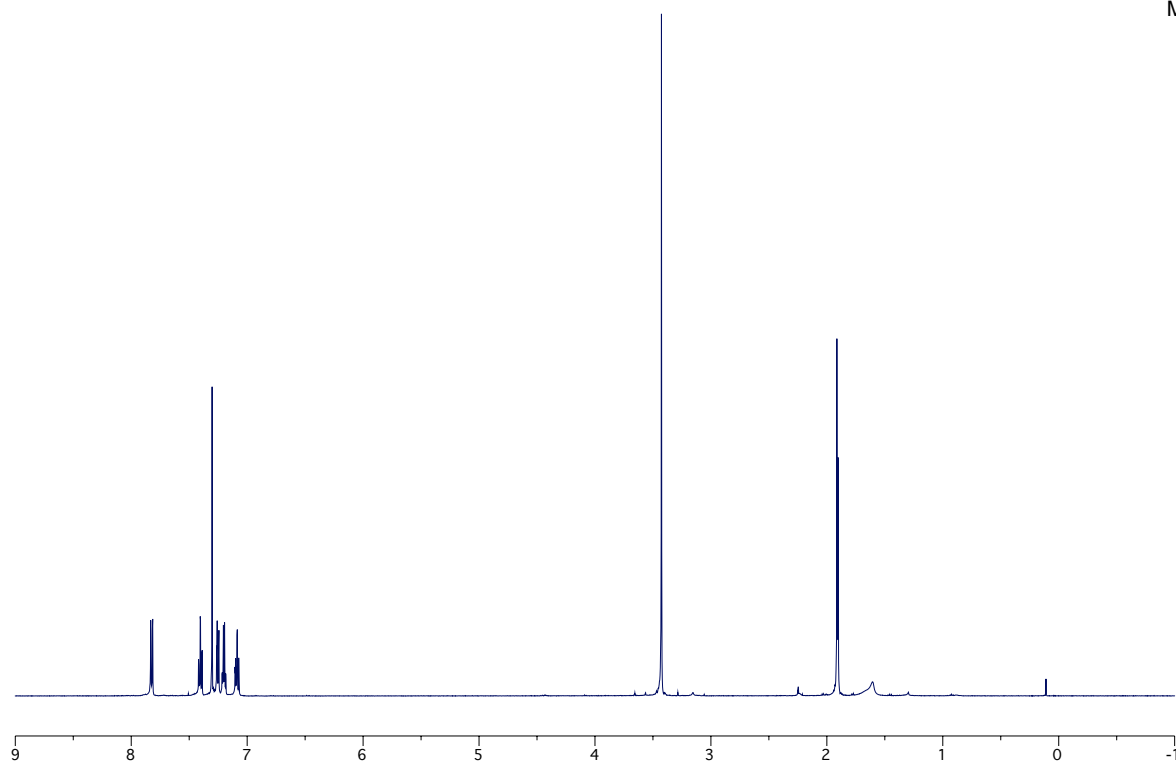
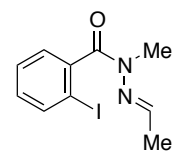
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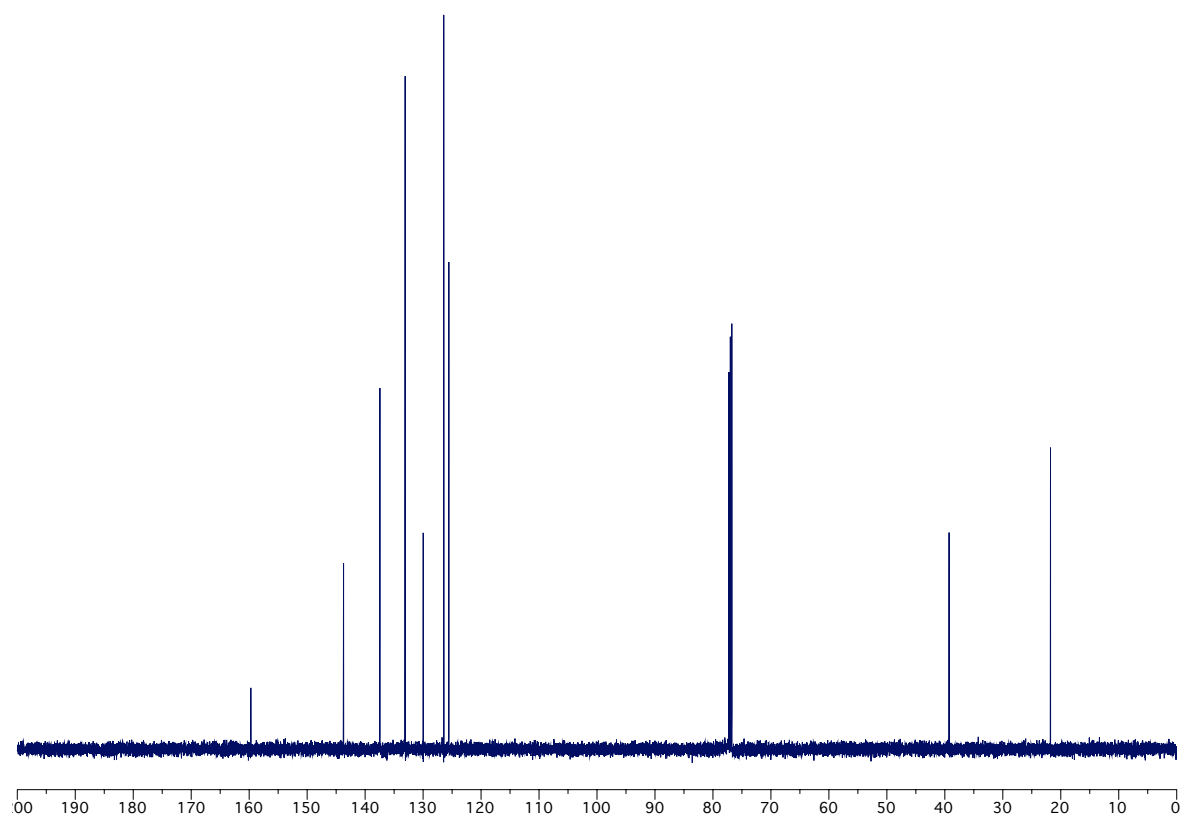
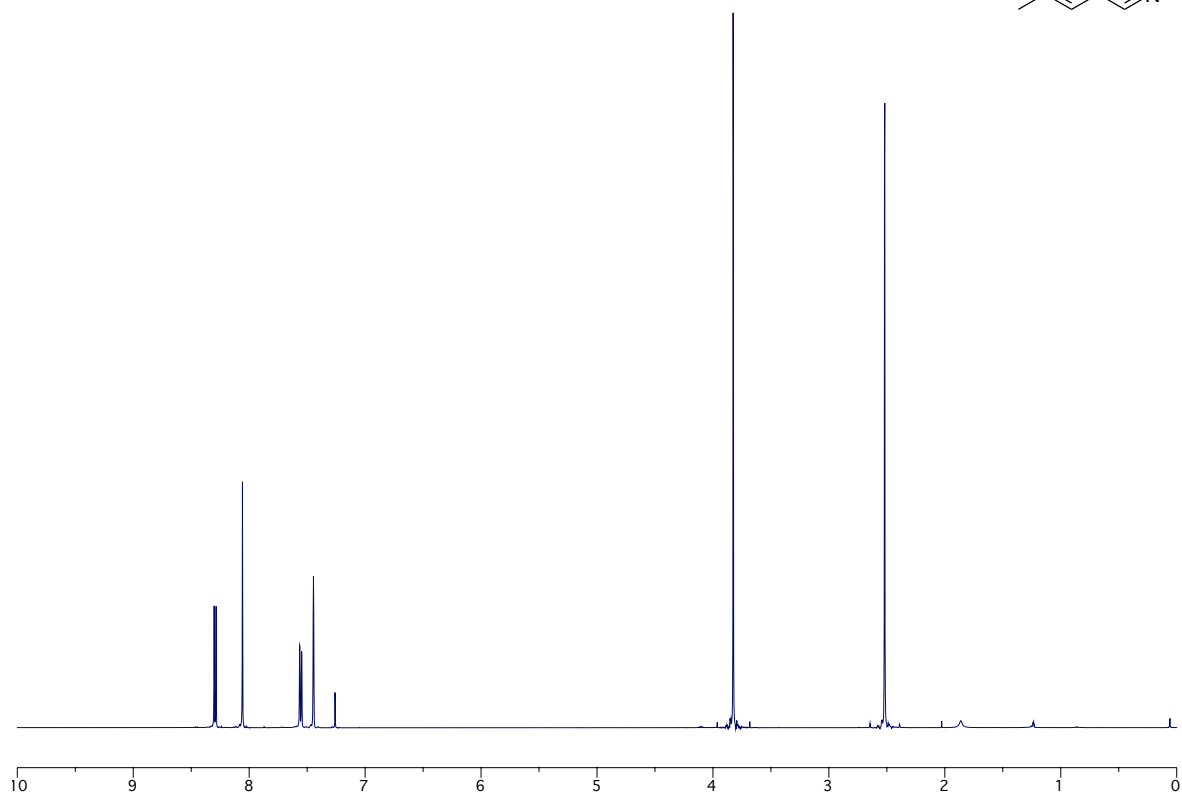
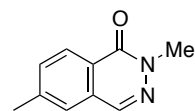
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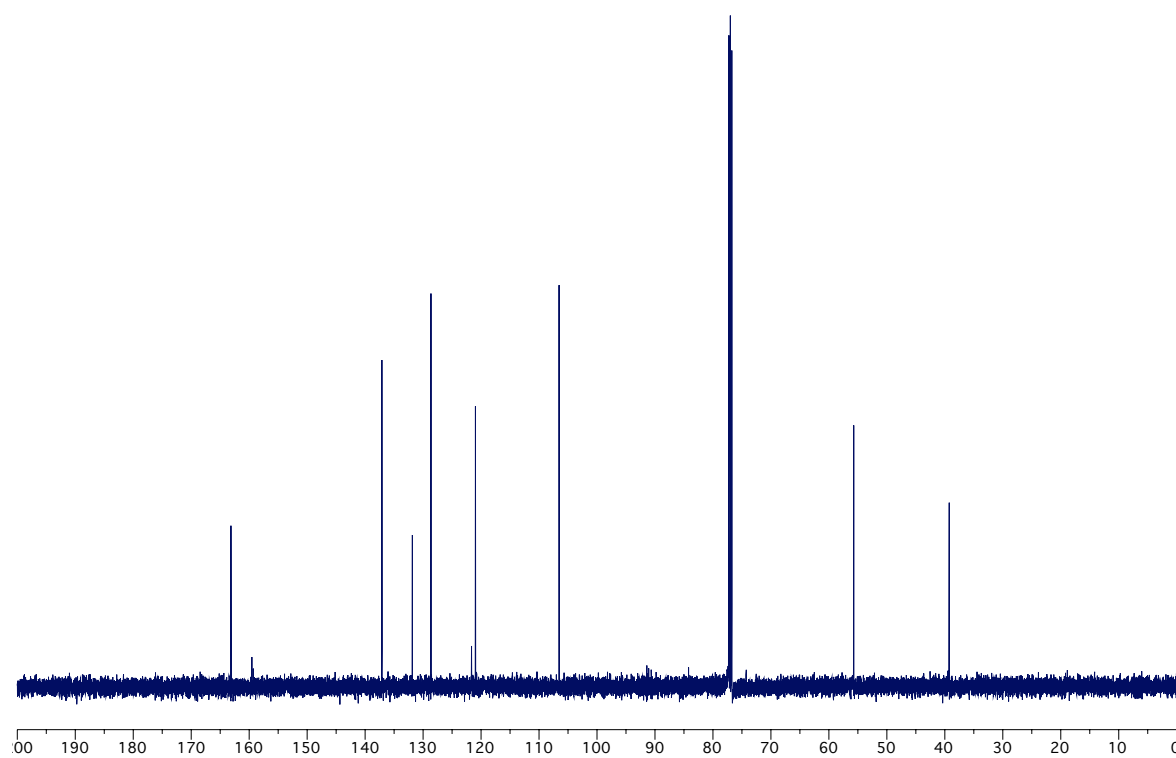
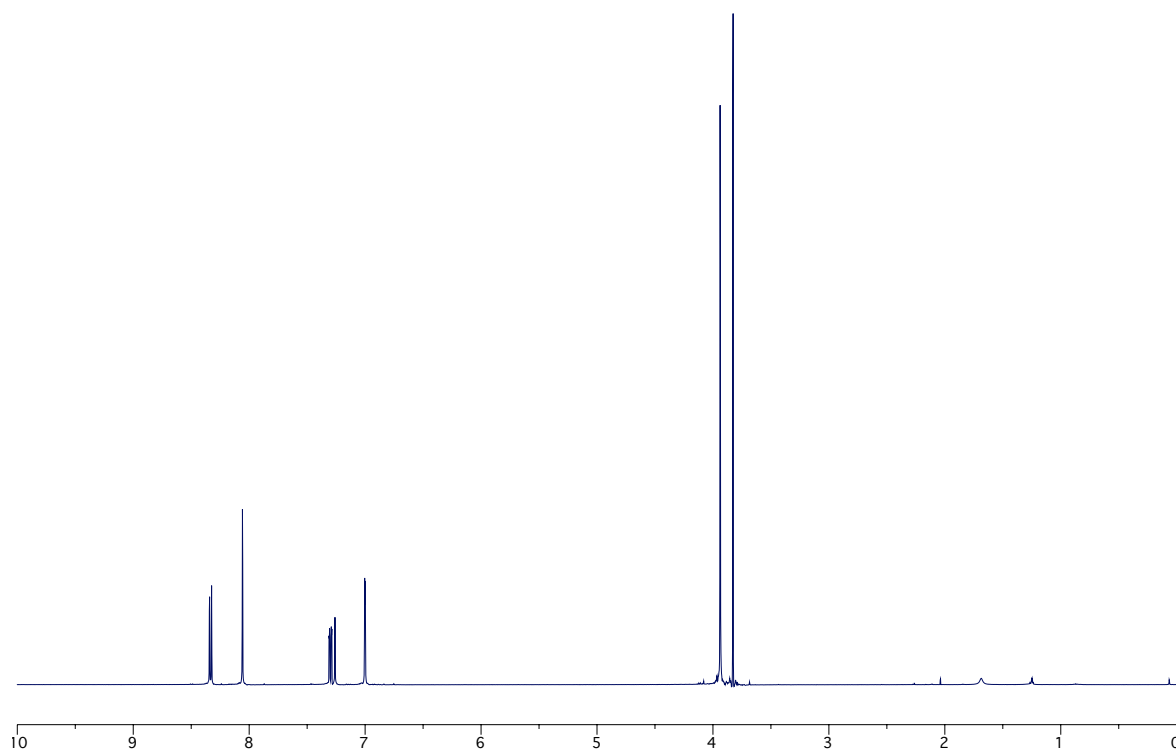
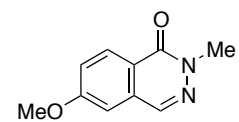
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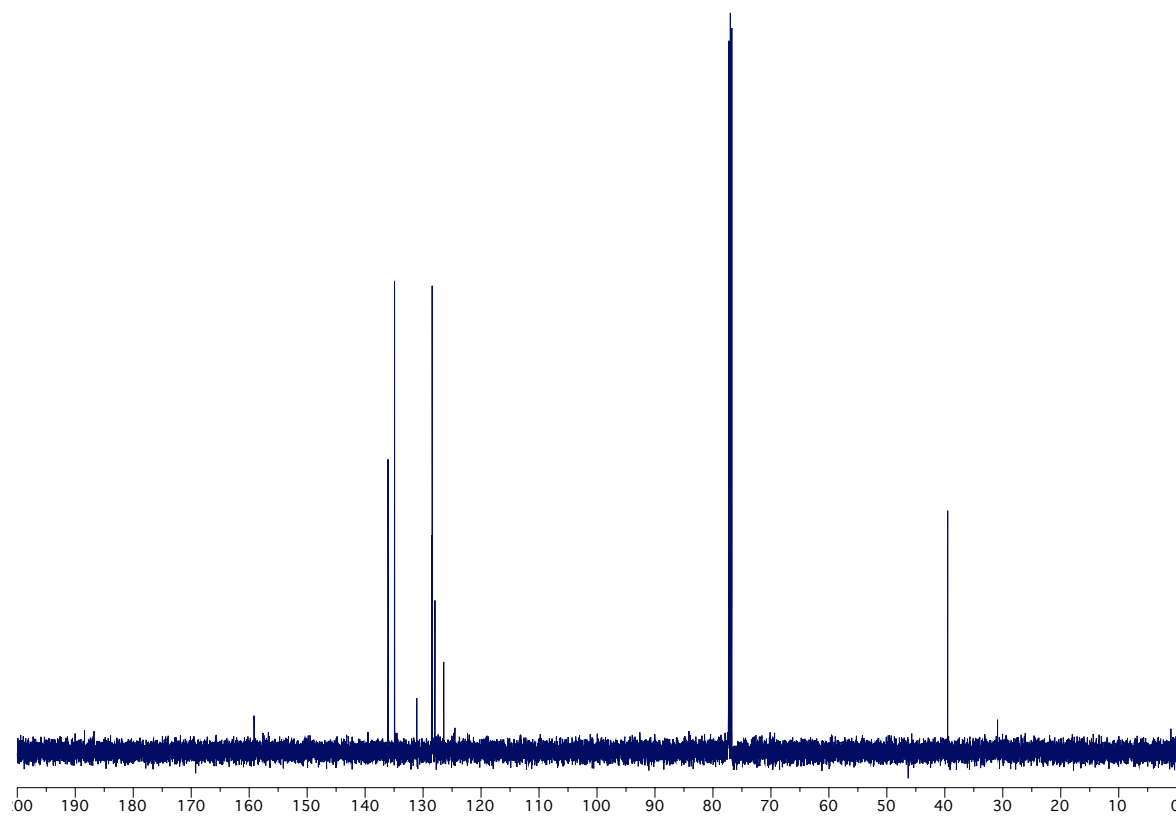
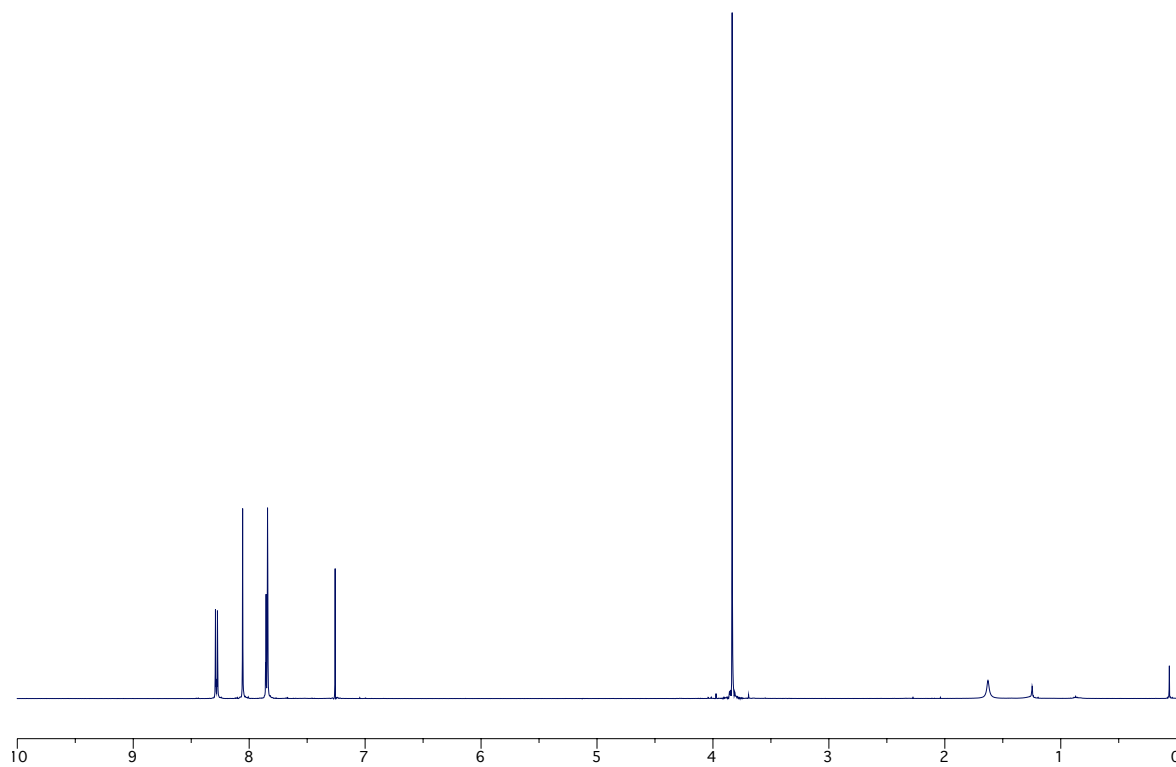
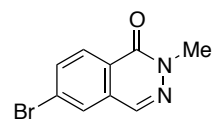
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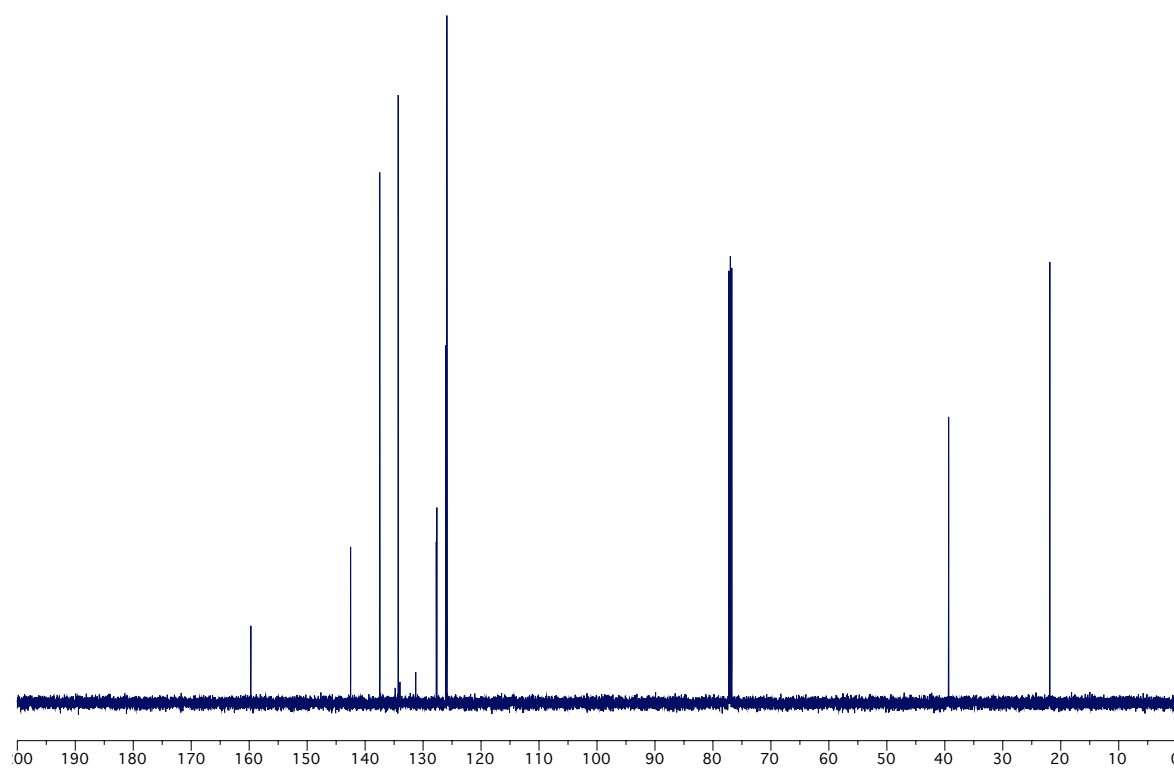
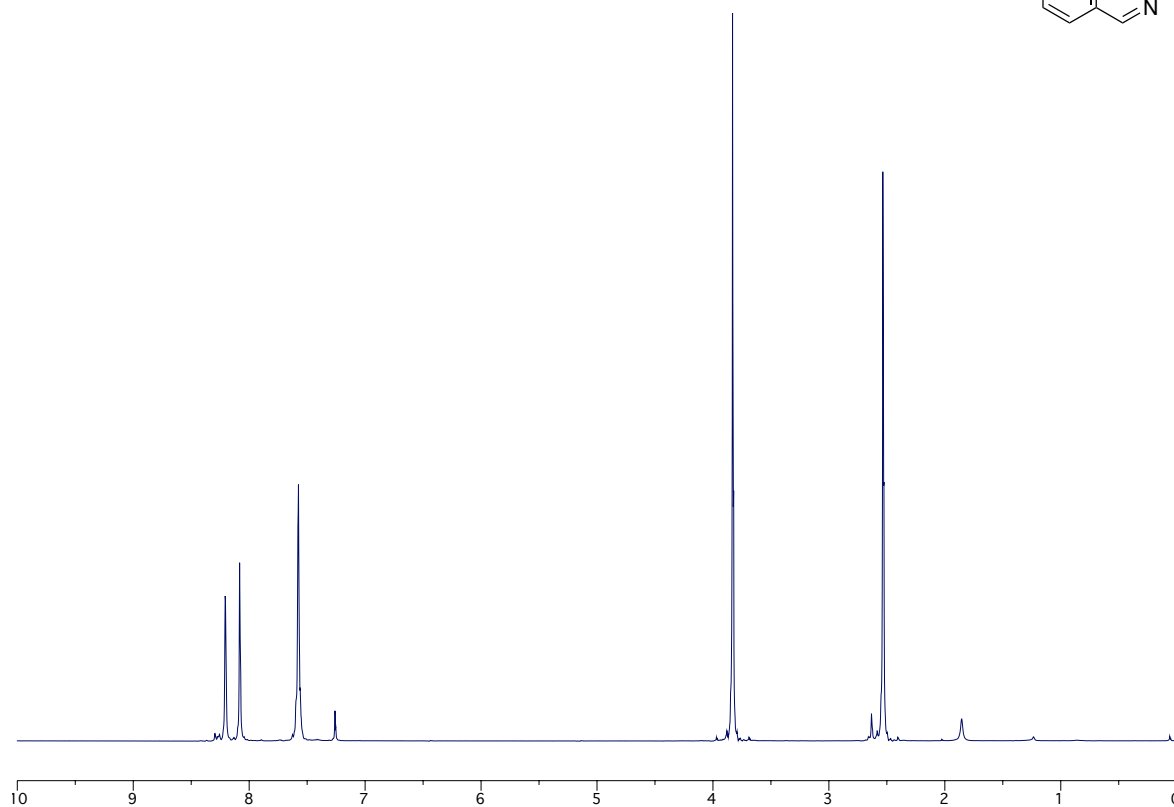
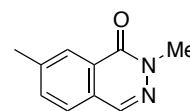
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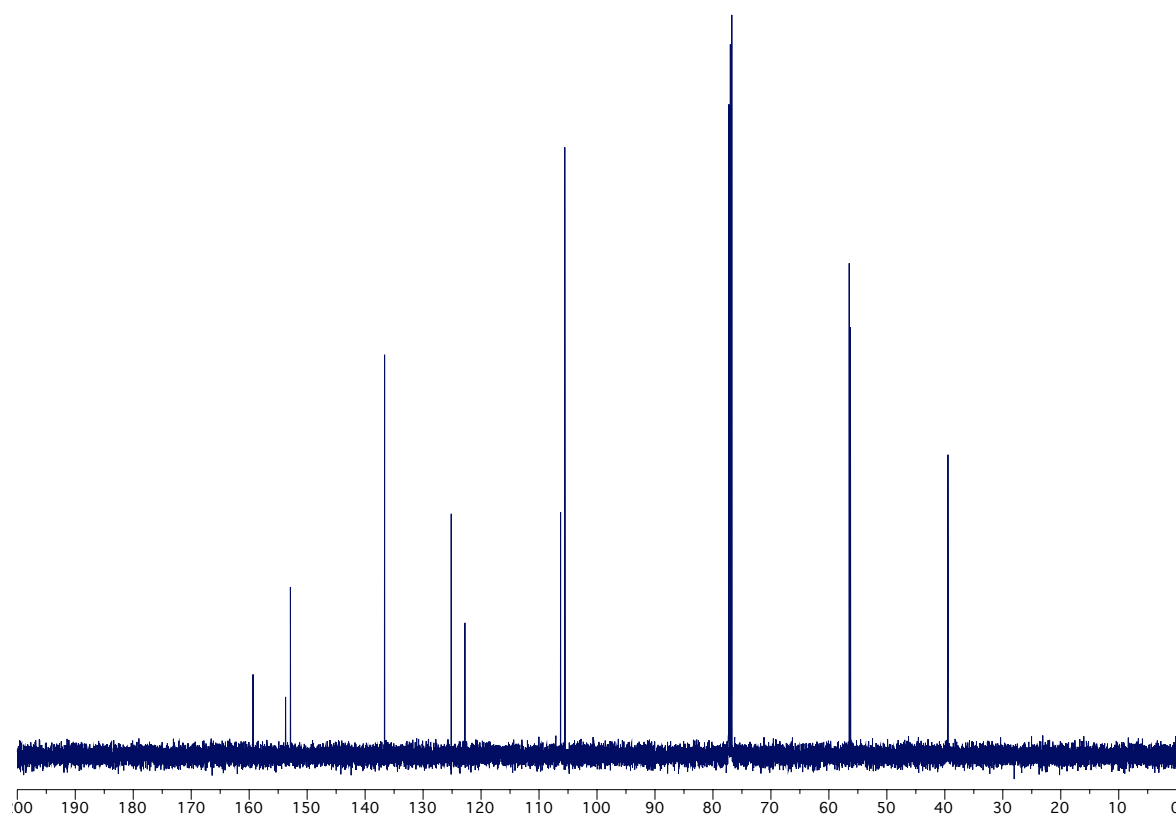
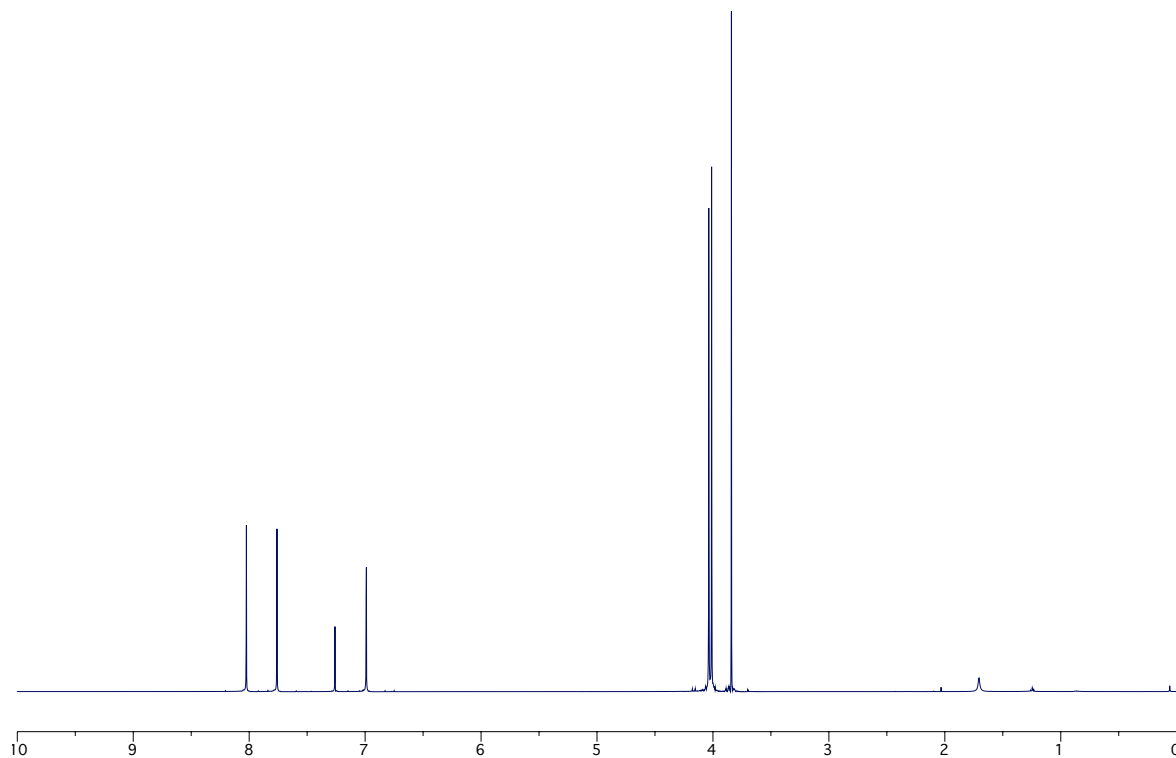
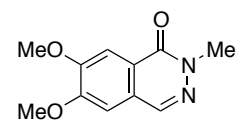
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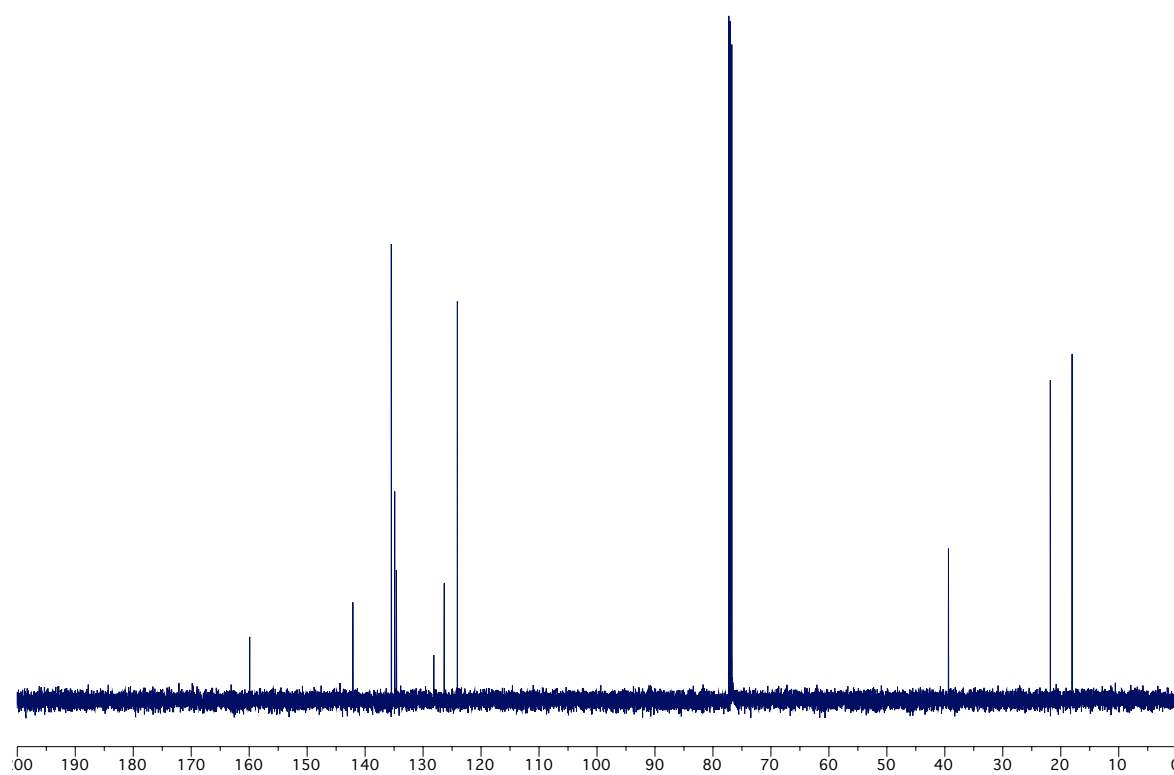
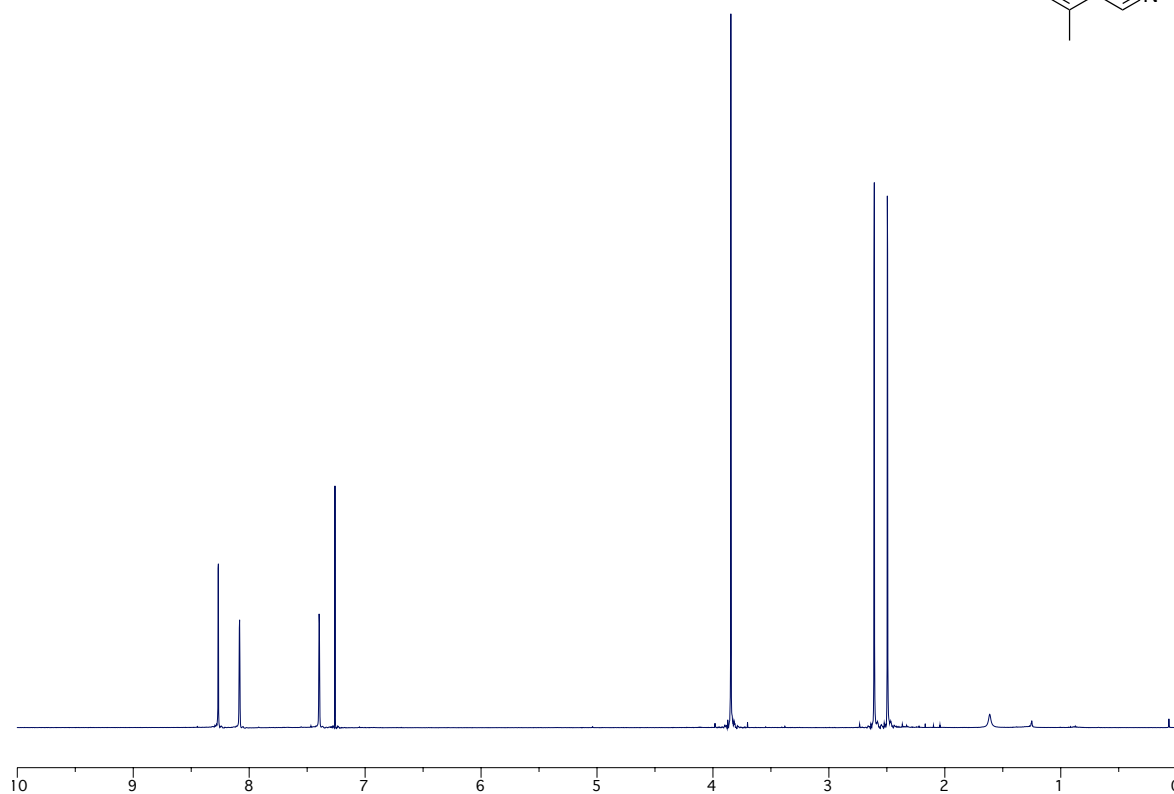
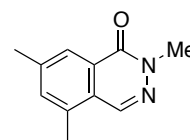
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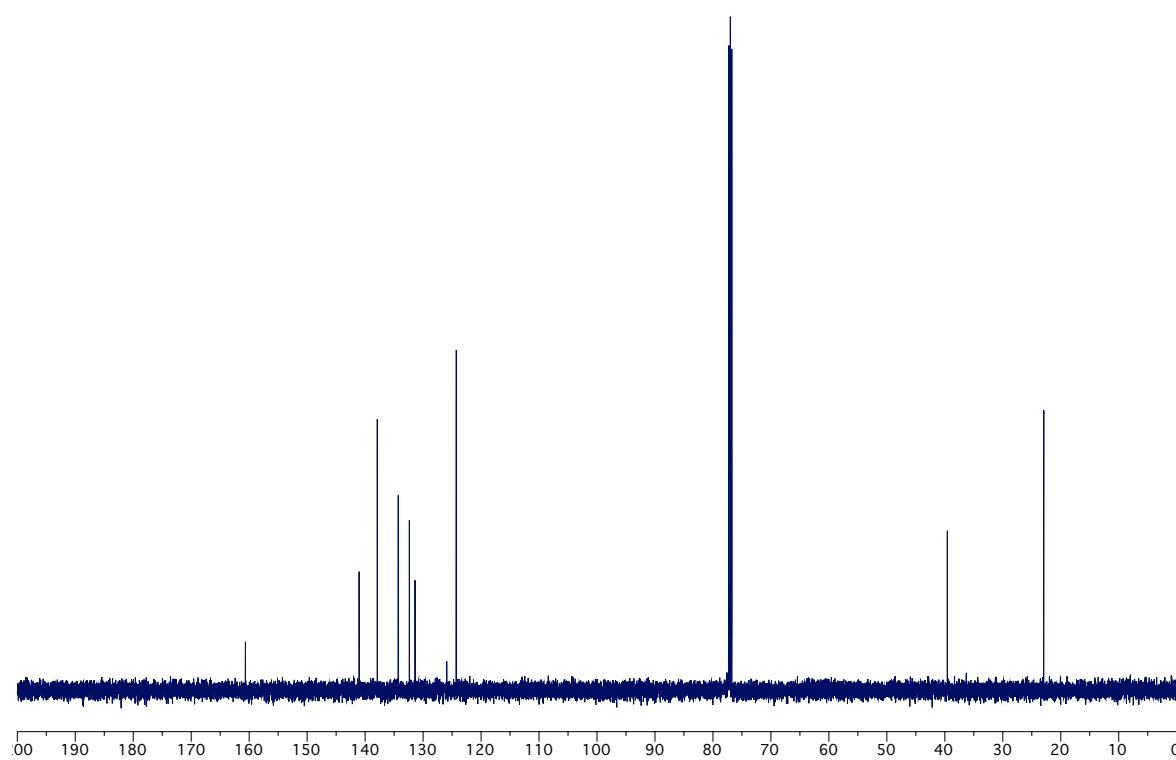
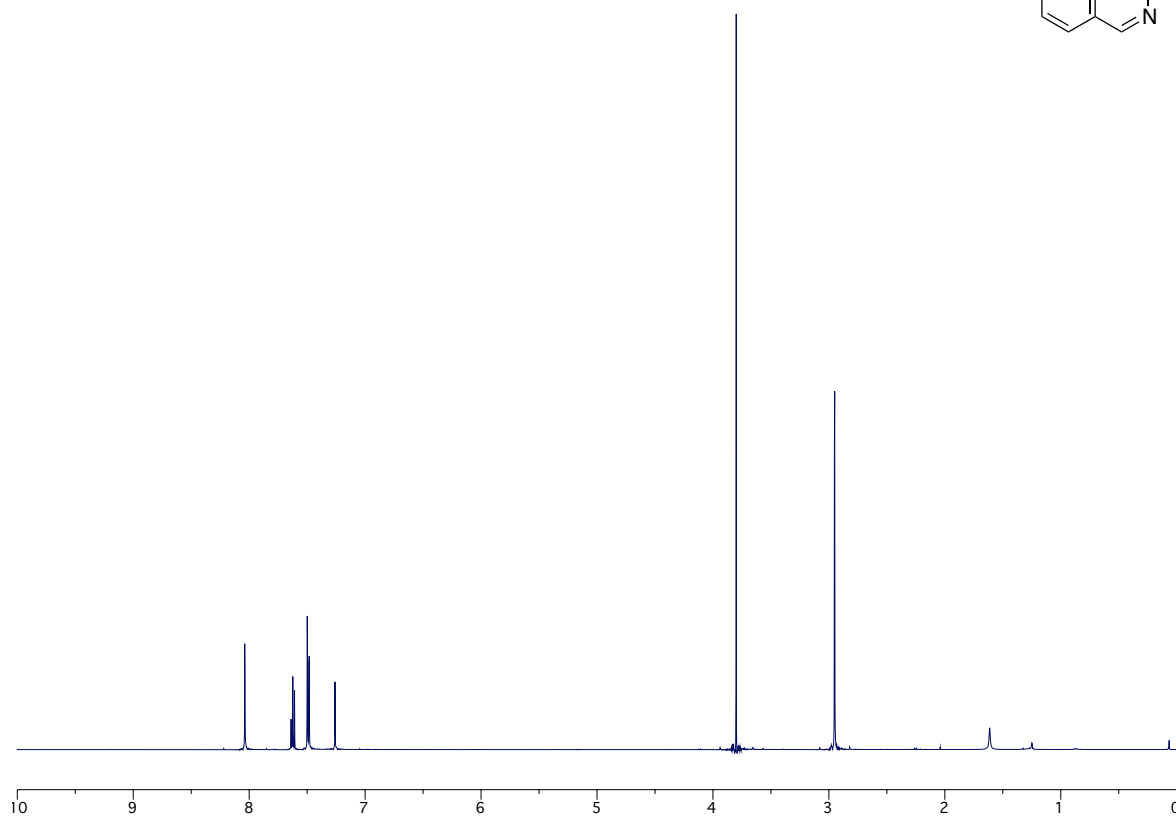
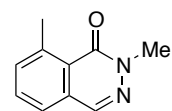
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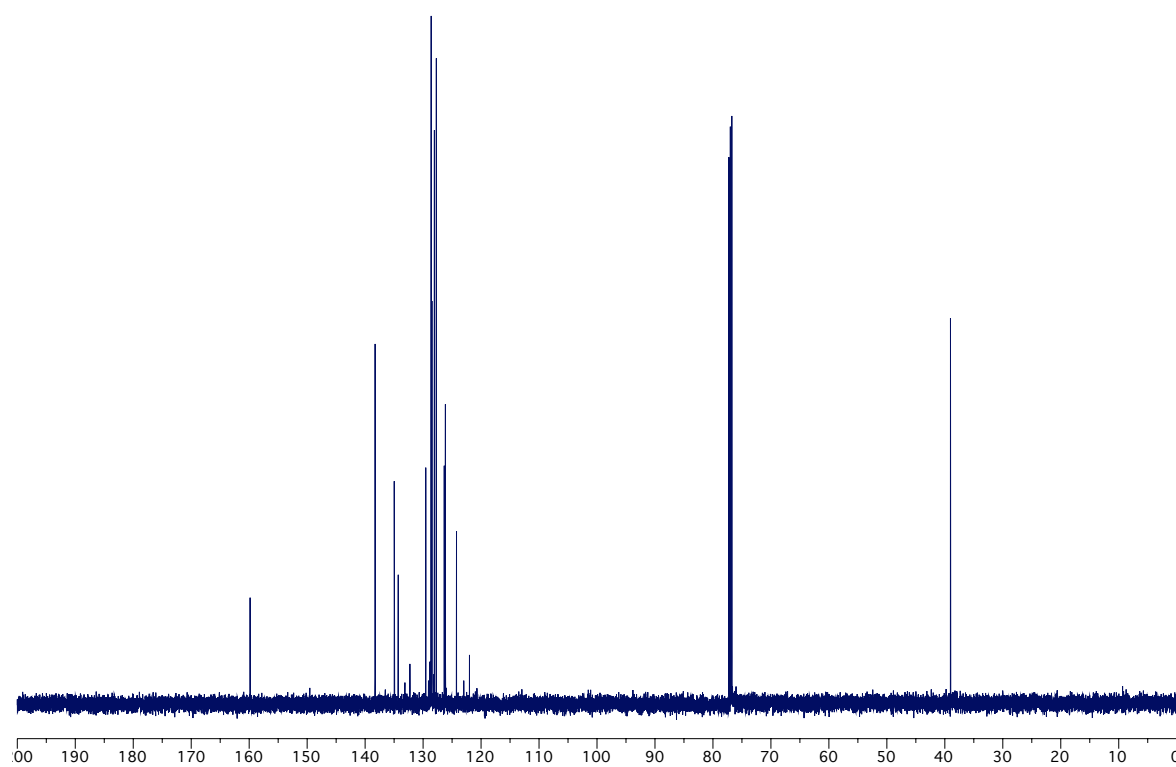
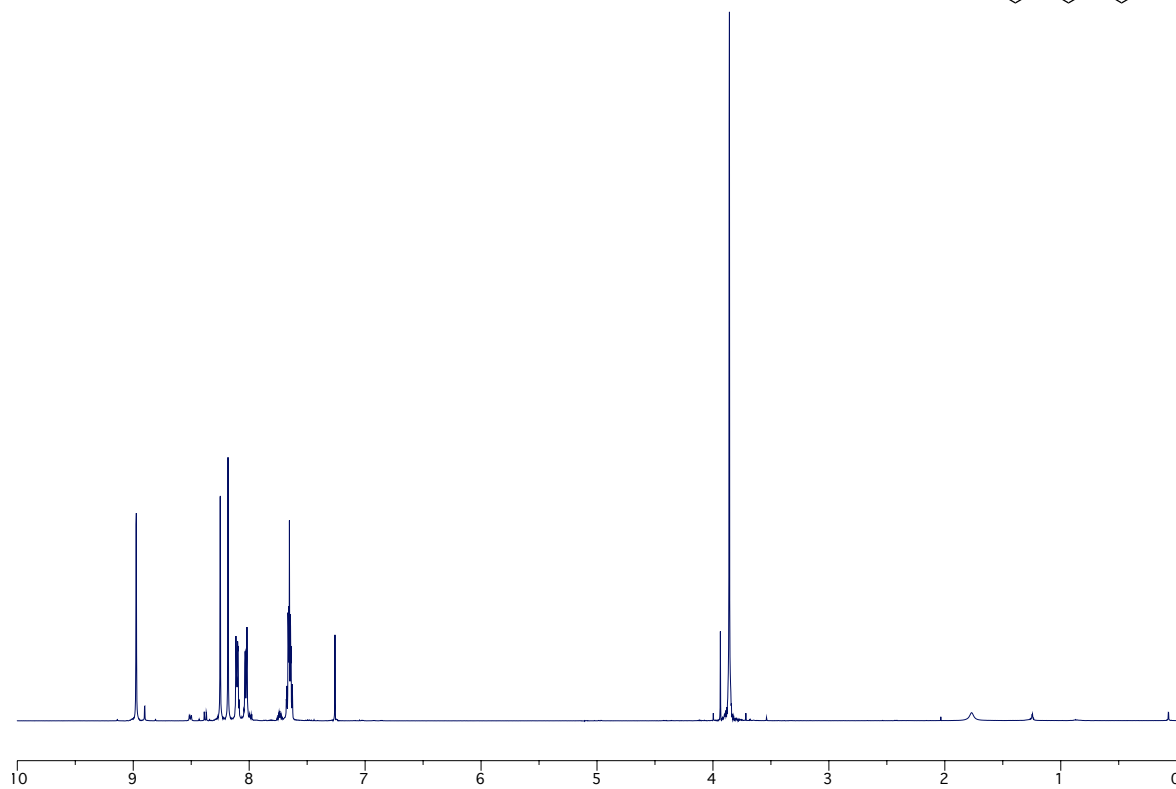
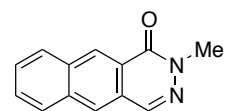
2i



2j



2k



2m

