Supplementary Information for Rh(I)-Catalyzed Alkylation of Quinolines and Pyridines via C-H Bond Activation.

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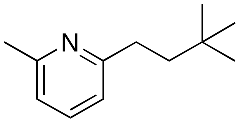
General Procedures. All reagents were degassed and handled under an inert nitrogen atmosphere using syringe and cannula techniques. Unless otherwise noted, all organic preparations were carried out in flame- or oven-dried glassware under a nitrogen atmosphere and all catalytic alkylation reactions were assembled in a nitrogen-filled Vacuum Atmospheres inert atmosphere box. Flash column chromatography was carried out using a Biotage SP Flash Purification System (Biotage No. SP1-B1A) with Flash+ cartridges (Biotage No. FPK0-1107-16046, or FPL0-1118-15045) using hexanes/ethyl acetate gradients calculated using the TLC data recorded for each compound (vide infra). NMR spectroscopy (^{1}H and ^{13}C) was conducted using a Bruker AMX-400 or AVB-400 spectrometer at room temperature. Chemical shifts are reported in ppm relative to residual protonated solvent ($CHCl_3$, 7.26 ppm), and coupling constants are reported in Hz. IR spectroscopy was conducted using a Nicolet Avatar 360 FTIR spectrometer equipped with a single-bounce ZnSe attenuated total reflectance plate, and only partial data are listed. Mass spectrometry was performed by the University of California, Berkeley mass spectrometry facility using a VG ProSpec (EBE geometry) spectrometer equipped with an electron impact source (EI ionization).

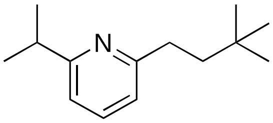
Materials. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $[RhCl(coe)_2]_2$ (also available from Strem Chemical)[1] and PCy_3•1HCl[2] were prepared as previously reported. All liquid reagents (including olefins and heterocycles) were thoroughly degassed using three freeze-pump-thaw cycles prior to introduction to the glove box. THF and ether were obtained from a Seca Solvent System by GlassContour (solvent dried over alumina under a nitrogen atmosphere).

General Procedure for Catalytic Alkylation Reactions.

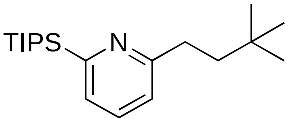
To a 2 mL sealable glass vessel containing a stir bar was added $[RhCl(coe)_2]_2$ (0.0286 g, 0.0400 mmol), PCy_3•HCl (0.0380 g, 0.120 mmol), heterocycle (0.800 mmol), olefin (4.00 mmol), and THF (reaction diluted to a total concentration of 0.8 M). Solid reagents were rinsed into the vessel using the added THF. The volumes of the heterocycle and olefin are not negligible at the concentrations used and must therefore be included in the concentration calculation. The vessel was sealed and heated at 165 °C with stirring for the time specified for each compound and then cooled to room temperature. The mixture was transferred to a scintillation vial using 3x0.5 mL of CH_2Cl_2 and 0.5 mL of MeOH, and the reaction was quenched with excess triethylamine (0.5 mL). The mixture was then concentrated on a rotary evaporator. The crude mixture was loaded onto a Biotage samplet using a minimal amount of CH_2Cl_2 (ca. 0.5 mL). This solvent was removed by briefly placing the samplet under vacuum in a vacuum desicator, and the samplet was loaded into a Biotage SP1 system. Eluting with an ethyl acetate/hexanes gradient calculated by the biotage from the rf of the product in a specificied ethyl acetate/hexanes mixture provided the desired product.



2-(3,3-Dimethylbutyl)-6-methylpyridine (3): The reaction was conducted at 165 °C for 14 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.3 in 10% ethyl acetate/hexanes) to provide 0.841 g, 59% of **3** as a light yellow oil. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.45 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 2.72 (m, 2H), 2.52 (s, 3H), 1.57 (m, 2H), 0.96 (s, 9H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 162.64, 157.59, 136.54, 120.28, 119.25, 44.37, 33.98, 30.58, 29.40, 24.60. HRMS-EI (*m/z*): calculated for $C_{12}H_{19}N$: 177.151750; observed: 177.151252. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3064, 2953, 2902, 2866, 1590, 1578, 1455, 1364.

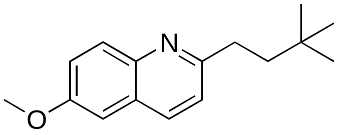


2-(3,3-Dimethylbutyl)-6-isopropylpyridine (4): The reaction was conducted at 165 °C for 14 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf$_{prod}$ = 0.6 in 10% ethyl acetate/hexanes) to provide 0.137 g, 83% of **4** as a light yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.50 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.1 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 1H), 3.03 (sept, *J* = 6.8 Hz, 1H), 7.43 (m, 2H), 1.60 (m, 2H), 1.28 (d, *J* = 6.8 Hz, 6H), 0.97 (s, 9H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 166.77, 162.26, 136.56, 119.46, 116.84, 44.12, 36.53, 33.99, 30.58 29.44, 22.82. HRMS-EI (*m/z*): calculated for $C_{14}H_{23}N$: 205.183050; observed: 205.181679. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3059, 2955, 2905, 2867, 1589, 1576, 1469, 1449, 1363.

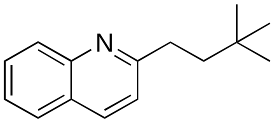


2-(3,3-Dimethylbutyl)-6-(triisopropylsilyl)pyridine (5): The reaction was conducted at 165 °C for 24 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf$_{prod}$ = 0.31 in hexanes) to provide 0.164 g, 64% of **5** as a light yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.8 Hz, 1H), 7.24 (dd, J_1 = 7.6

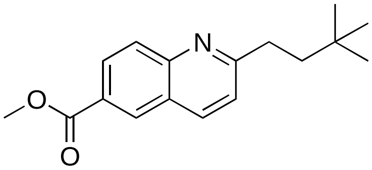
Hz, J_2 = 1.0 Hz, 1H), 6.99 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H), 2.75 (m, 2H), 1.63 (m, 2H), 1.44 (sept, J = 7.6 Hz, 3H), 1.11 (d, J = 7.3 Hz, 18H), 0.96 (s, 9H). $^{13}C\ \{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 162.47, 133.23, 127.63, 120.90, 99.99, 44.03, 34.19, 30.55, 29.45, 18.73, 11.03. HRMS-EI (*m/z*): calculated for $C_{20}H_{37}NSi$: 319.269529; observed: 319.269257. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3049, 2953, 2864, 1574, 1562, 1464, 1441, 1389, 1364.



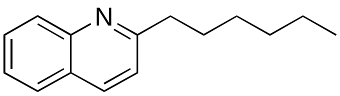
2-(3,3-Dimethylbutyl)-6-methoxyquinoline (6): The reaction was conducted at 165 °C for 14 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.27 in 10% ethyl acetate/hexanes) to provide 0.186 g, 96% of **6** as a yellow oil. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.94 (m, 2H), 7.31 (dd, J_1 = 9.5 Hz, J_2 = 2.7 Hz, 1H), 7.24 (d, J = 8.6 Hz, 1H), 7.02 (d, J = 2.9 Hz, 1H), 3.89 (s, 3H), 2.90 (m, 2H), 1.67 (m, 2H), 1.00 (s, 9H). $^{13}C\ \{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 161.15, 157.12, 143.90, 135.13, 130.19, 127.50, 121.76, 121.57, 105.21, 55.49, 44.32, 34.58, 30.68, 29.42. HRMS-EI (*m/z*): calculated for $C_{16}H_{21}NO$: 243.162314; observed: 243.162712. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2953, 2864, 1624, 1601, 1567, 1498, 1482, 1463, 1228.



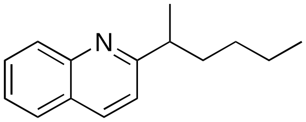
2-(3,3-Dimethylbutyl)quinoline (7): The reaction was conducted at 165 °C for 9.5 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.37 in 10% ethyl acetate/hexanes) to provide 0.174 g, 98% of **7** as a light yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, J_1 = 8.1 Hz, J_2 = 1.0 Hz, 1H), 7.66 (m, 1H), 7.46 (m, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 2.95 (m, 2H), 1.69 (m, 2H), 1.01 (s, 9H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 163.73, 147.90, 136.27, 129.34, 128.80, 127.50, 126.69, 125.64, 121.36, 44.25, 34.92, 30.72, 29.42. HRMS-EI (*m/z*): calculated for $C_{15}H_{19}N$: 213.151750; observed: 213.151402. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3056, 2953, 2864, 1619, 1600, 1562, 1503.



Methyl 2-(3,3-dimethylbutyl)quinoline-6-carboxylate (8): The reaction was conducted at 165 °C for 7 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.20 in 10% ethyl acetate/hexanes) to provide 0.210 g, 96% of **8** as a beige solid (mp = 86-90 ºC). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.53 (d, *J* = 1.7 Hz, 1H), 8.25 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 2.96 (m, 2H), 1.70 (m, 2H), 1.01 (s, 9H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 166.81, 166.32, 149.88, 137.35, 130.71, 129.11, 128.91, 127.20, 125.81, 122.21, 52.34, 44.01, 35.09, 30.71, 29.38. HRMS-EI (*m/z*): calculated for $C_{17}H_{21}NO_2$: 271.157229, observed: 271.156650. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2945, 2900, 2863, 1951, 1714, 1621, 1600, 1479, 1433.

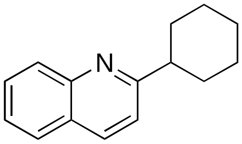


2-Hexylquinoline (9): The reaction was conducted at 165 °C for 9.5 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.39 in 10% ethyl acetate/hexanes) to provide 0.141 g, 80% of **9** as a light yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, J_1 = 8.6 Hz, J_2 = 1.2 Hz, 1H), 7.66 (td, J_1 = 6.8 Hz, J_2 = 1.5 Hz, 1H), 7.46 (td, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 2.96 (m, 2H), 1.80 (m, 2H), 1.41 (m, 2H), 1.32 (m, 4H), 0.88 (m, 3H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 163.17, 147.92, 136.21, 129.34, 128.84, 127.50, 126.73, 125.65, 121.40, 39.44, 31.78, 30.12, 29.29, 22.62, 14.13. HRMS-EI (*m/z*): calculated for $C_{15}H_{19}N$: 213.151750, observed: 213.151522. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3055, 2953, 2925, 2855, 1618, 1600, 1503.

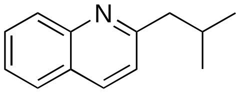


2-(Hexan-2-yl)quinoline (10): The reaction was conducted at 165 °C for 9.5 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.50 in 10% ethyl acetate/hexanes) to provide 0.0241 g, 14% of **10** as a light yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.07 (m, 2H), 7.77 (dd, J_1 = 8.1 Hz, J_2 = 1.2 Hz, 1H), 7.68 (td, J_1 = 7.1 Hz, J_2 = 1.5 Hz, 1H), 7.48 (td, J_1 = 7.1 Hz, J_2 = 1.2 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 2.96 (sext, *J* = 7.3 Hz, 1H), 1.81 (m, 1H), 1.68 (m, 1H), 1.36 (d, *J* = 7.1 Hz, 3H), 1.30 (m, 3H), 1.17 (m, 1H), 0.85 (m, 3H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 167.31, 147.81, 136.32, 129.22, 129.06, 127.48, 126.98, 125.64, 119.58, 40.07, 36.87, 29.96, 22.86, 20.88, 14.07. HRMS-EI (*m/z*): calculated for

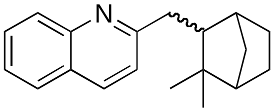
$C_{15}H_{19}N$: 213.151750, observed: 213.151180. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3057, 2957, 2926, 2856, 1618, 1600, 1502.



2-Cyclohexylquinoline (11): The reaction was conducted at 165 °C for 9.5 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.50 in 10% ethyl acetate/hexanes) to provide 0.169 g, 96% of **11** as a light yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.11 (d, J = 7.8 Hz, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.76 (dd, J_1 = 8.1 Hz, J_2 = 1.2 Hz, 1H), 7.67 (td, J_1 = 6.8 Hz, J_2 = 1.5 Hz, 1H), 7.47 (td, J_1 = 7.1 Hz, J_2 = 1.2 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 2.92 (tt, J_1 = 12.2 Hz, J_2 = 3.4 Hz, 1H), 2.03 (m, 1H), 1.90 (m, 2H), 1.79 (m, 1H), 1.63 (qd, J_1 = 12.7 Hz, J_2 = 3.2 Hz, 2H), 1.47, (qt, J_1 = 12.7 Hz, J_2 = 3.2 Hz, 2H), 1.35 (tt, J_1 = 12.0 Hz, J_2 = 2.7 Hz, 1H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 166.88, 147.84, 136.34, 129.26, 129.01, 127.47, 127.00, 125.63, 119.61, 47.70, 32.88, 26.58, 26.13. HRMS-EI (*m/z*): calculated for $C_{15}H_{17}N$: 211.136100, observed: 211.136130. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3056, 2923, 2850, 1618, 1600, 1561, 1501, 1448, 1426.

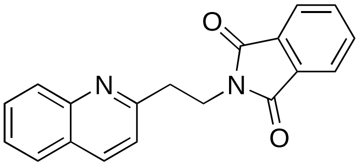


2-Isobutylquinoline (12): To a 20 mL thick-walled pressure tube containing a stir bar was added $[RhCl(coe)_2]_2$ (0.0574 g, 0.0800 mmol), PCy_3•HCl (0.0761 g, 0.240 mmol), quinoline (0.19 mL, 1.6 mmol), and THF (1 mL). The tube was sealed with a septum, removed from the glove box, placed under nitrogen, and cooled to -78 °C. 2-Methylpropene was then bubble into the reaction mixture to give a total volume of approximately 2 mL. The septum was quickly exchanged for a threaded Teflon stopper, the tube was sealed, and the reaction mixture was allowed to warm to room temperature. The reaction was conducted at 165 °C for 19 h. The tube was carefully removed from the oil bath cooled to room temperature before the Teflon stopper was slowly removed (excess 2-methypropene boils away). The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.43 in 10% ethyl acetate/hexanes) to provide 0.270 g, 91% of **12** as a colorless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.08 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 2.88 (d, *J* = 7.6 Hz, 2H), 2.25 (sept, *J* = 6.8 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 6H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 162.26, 147.96, 135.95, 129.31, 128.90, 127.51, 126.73, 125.66, 122.06, 43.36, 29.50, 22.59. HRMS-EI (*m/z*): calculated for $C_{13}H_{15}N$: 185.120450, observed: 185.119475. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3057, 2955, 2868, 1618, 1599, 1561, 1503.

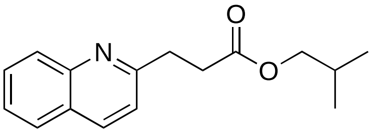


2-((3,3-Dimethylbicyclo[2.2.1]heptan-2-yl)methyl)quinoline (13): The reaction was conducted at 165 °C for 19 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.5 in 10% ethyl acetate/hexanes) to provide 0.173 g, 90% of **13** (2:1 mixture of diastereomers) as a colorless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.07 (m, 2H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.69 (t, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.30 (m, 1H), 2.70-3.12 (m, 2H), 1.90-2.13 (m, 2H), 1.60-1.90 (m, 4H), 1.32 (m, 2H), 1.00-1.20 (m, 5H), 0.97 (s, 2H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 163.30 (1C), 163.09 (1C), 148.00 (1C), 147.91 (1C), 135.95 (1C), 135.85

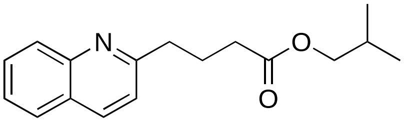
(1C), 129.26 (1C), 129.22 (1C), 128.91 (1C), 128.87 (1C), 127.50 (1C), 127.48 (1C), 126.66 (2C), 125.60 (1C), 125.59 (1C), 121.90 (1C), 121.84 (1C), 54.27 (1C), 50.91 (1C), 49.63 (1C), 49.22 (1C), 42.11 (1C), 41.16 (1C), 40.80 (1C), 40.49 (1C), 37.47 (1C), 37.04 (1C), 36.48 (1C), 35.76 (1C), 32.22 (1C), 29.76 (1C), 27.92 (1C), 25.26 (1C), 24.82 (1C), 24.22 (1C), 21.88 (1C), 20.51 (1C). HRMS-EI (*m/z*): calculated for $C_{19}H_{23}N$: 265.183050, observed: 265.182605. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3056, 2951, 2873, 1618, 1599, 1562, 1504.



2-(2-(Quinolin-2-yl)ethyl)isoindoline-1,3-dione (14): The reaction was conducted at 165 °C for 3.5 h (NOTE: only 2 equiv olefin used). The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.12 in 20% ethyl acetate/hexanes) to provide 0.128 g, 53% of **14** as a beige solid (mp = 127-129 ºC). ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.80 (m, 2H), 7.75 (m, 1H), 7.69 (m, 2H), 7.64 (m, 1H), 7.47 (td, J_1 = 6.8 Hz, J_2 = 1.0 Hz, 1H), 7.32 (d, *J* = 8.3, 1H), 4.22 (m, 2H), 3.37 (m, 2H). ^{13}C {^1H} NMR (100.61 MHz, $CDCl_3$): δ 168.26, 158.67, 147.99, 136.46, 133.87, 132.21, 129.42, 129.04, 127.55, 126.86, 126.00, 123.23, 121.46, 37.47, 37.19. HRMS-EI (*m/z*): calculated for $C_{19}H_{14}N_2O_2$: 302.105528, observed: 302.105464. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2920, 1764, 1699, 1616, 1601, 1397, 1363, 1329.

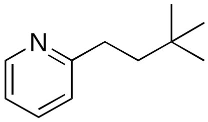


Isobutyl 3-(quinolin-2-yl)propanoate (15): The reaction was conducted at 165 °C for 16 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf$_{prod}$ = 0.25 in 10% ethyl acetate/hexanes) to provide 0.109 g, 53% of **15** as a yellow oil. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 8.09 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.71 (m, 1H), 7.52 (m, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 3.90 (d, *J* = 6.8 Hz, 2H), 3.45 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.3 Hz, 2H), 1.94 (sept, *J* = 6.8 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 6H). ^{13}C {^{1}H} NMR (100.61 MHz, CDCl$_3$): δ 173.24, 160.51, 147.92, 136.29, 129.40, 128.92, 127.53, 126.87, 125.88, 121.52, 70.65, 33.60, 33.21, 27.72, 19.09. HRMS-EI (*m/z*): calculated for $C_{16}H_{19}NO_2$: 257.141579; observed: 257.140984. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 2960, 2874, 1951, 1731, 1619, 1601, 1565, 1504.

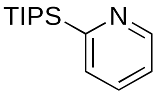


Isobutyl 4-(quinolin-2-yl)butanoate (16): The reaction was conducted at 165 °C for 14 h. The crude mixture was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf$_{prod}$ = 0.40 in 20% ethyl acetate/hexanes) to provide 0.126 g, 57% of **16** as a yellow oil. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 8.07 (m, 2H), 7.77 (m, 1H), 7.68 (m, 1H), 7.48 (m, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 3.88 (d, *J* = 6.6 Hz, 2H), 3.05 (t, *J* = 7.8 Hz, 2H), 2.47 (t, *J* = 7.8 Hz, 2H), 2.21 (pent, *J* = 7.6 Hz, 2H), 1.94 (sept, *J* = 7.1 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 6H). ^{13}C {^{1}H} NMR (100.61 MHz, CDCl$_3$): δ 173.50, 161.73, 136.41, 129.44, 128.90, 127.54, 126.80, 125.85, 121.39, 70.54, 38.36, 33.83, 27.72, 25.01, 19.14. HRMS-EI (*m/z*): calculated for $C_{17}H_{21}NO_2$: 271.157229; observed:

271.157546. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3055, 2960, 2873, 1730, 1618, 1600, 1503.

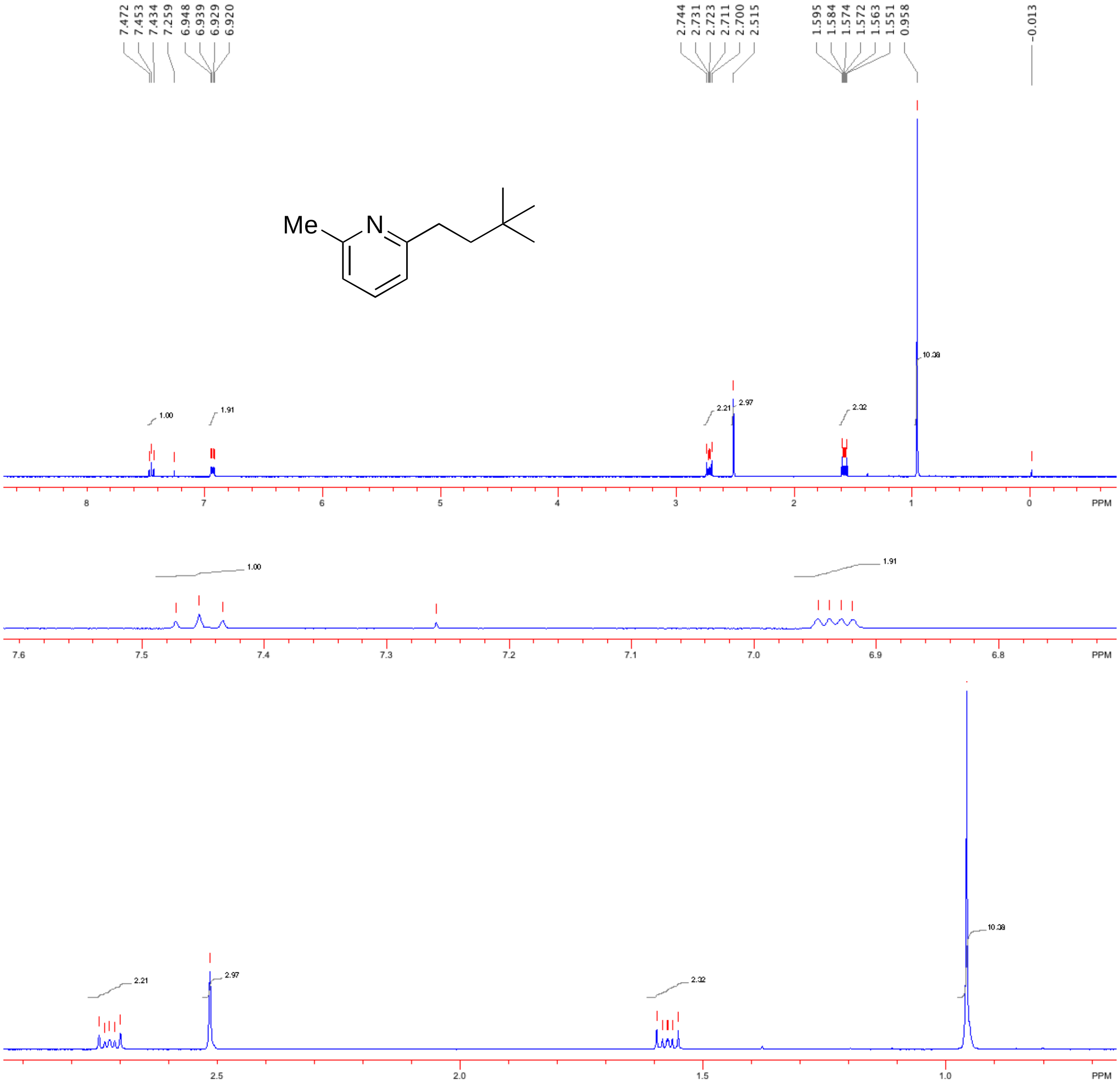


2-(3,3-dimethylbutyl)pyridine (17): To a THF (2.5 mL) solution of **5** (0.163 g, 0.51 mmol) in a round bottomed flask fitted with a reflux condenser under N_2 was added 48% aqueous HF (0.1 mL, 25 mmol). The resulting solution was heated at reflux for 15 h, an additional 0.1 mL of HF solution was added, and the solution was heated at reflux for 8 h. The reaction mixture was then cooled to room temperature, and the reaction was quenched with 30 mL of 1M NaOH, and extracted with 4x20 mL of ethyl ether. Small portions of MeOH (1-2 mL) were added to the mixture to break up emulsions that formed during the extraction. The combined organic phases were dried over $MgSO_4$, concentrated on a rotary evaporator, and purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.28 in 10% ethyl acetate/hexanes) to provide 0.0671 g (80%) of **17** as a colorless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.0 Hz, 1H), 7.57 (td, J_1 = 7.8 Hz, J_2 = 2.0 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (m, 1H), 2.76 (m, 2H), 1.61 (m, 2H), 0.97 (s, 9H). ^{13}C {^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 163.15, 149.11, 136.43, 122.68, 120.84, 44.38, 33.86, 30.55, 29.35. HRMS-EI (*m/z*): calculated for $C_{11}H_{17}N$: 163.136100; observed: 163.135739. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3008, 2953, 2865, 1586, 1569, 1474, 1433, 1364.



2-(triisopropylsilyl)pyridine (18): To an ethereal (21 mL) solution of 2-bromopyridine (2 mL, 21 mmol) under N_2 cooled to -78 °C was added *n*-BuLi (11.6 mL, 22 mmol) drop-wise using a syringe pump over ca. 0.5 h. The cold bath was then removed, and the reaction mixture was stirred for 1 h. Triisopropylsilyl trifluoromethanesulfonate (TipsOTf, 6.2 mL, 23 mmol) was then added dropwise via syringe, and the reaction mixture was stirred for 3 h. The reaction mixture was then quenched with water (ca. 50 mL) and extracted with 3x25 mL of ethyl ether. The combined organic phases were dried over Mg_2SO_4, concentrated, and the crude product was purified by flash chromatography using an ethyl acetate/hexanes gradient (rf_{prod} = 0.37 in 5% ethyl acetate/hexanes) to provide 1.78 g (36%) of **18** as a colorless oil. ^1H NMR (400.13 MHz, $CDCl_3$): δ 8.78 (m, 1H), 7.54 (td, J_1 = 7.6 Hz, J_2 = 1.8 Hz, 1H), 7.46 (dt, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 7.16 (ddd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, J_3 = 1.5 Hz, 1H), 1.48 (sept, J = 7.3 Hz, 3H), 1.08 (d, J = 7.6 Hz, 18H). ^{13}C {^1H} NMR (100.61 MHz, $CDCl_3$): δ 165.04, 150.03, 133.26, 130.85, 122.29, 18.56, 10.96. HRMS-EI (*m/z*): calculated for $C_{14}H_{25}NSi$: 235.175628; observed: 235.176302. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 3066, 2942, 2889, 2864, 1574, 1557, 1463, 1416.

Compound **3**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2.700
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1.574
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Me
N
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2.21
2.97
2.32
10.38
8
7
6
5
4
3
2
1
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7.5
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6.9
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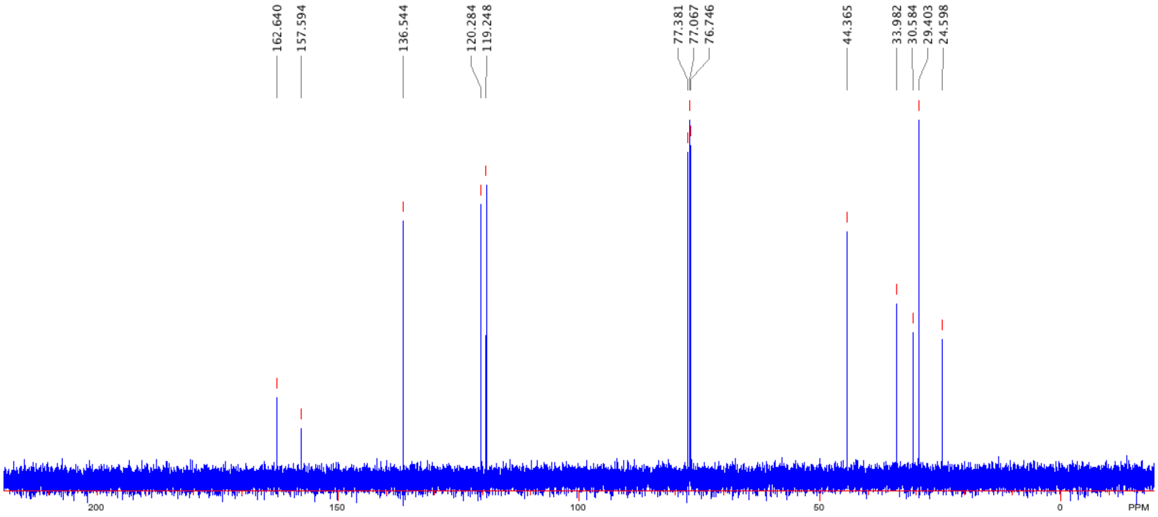
1.5
1.0
PPM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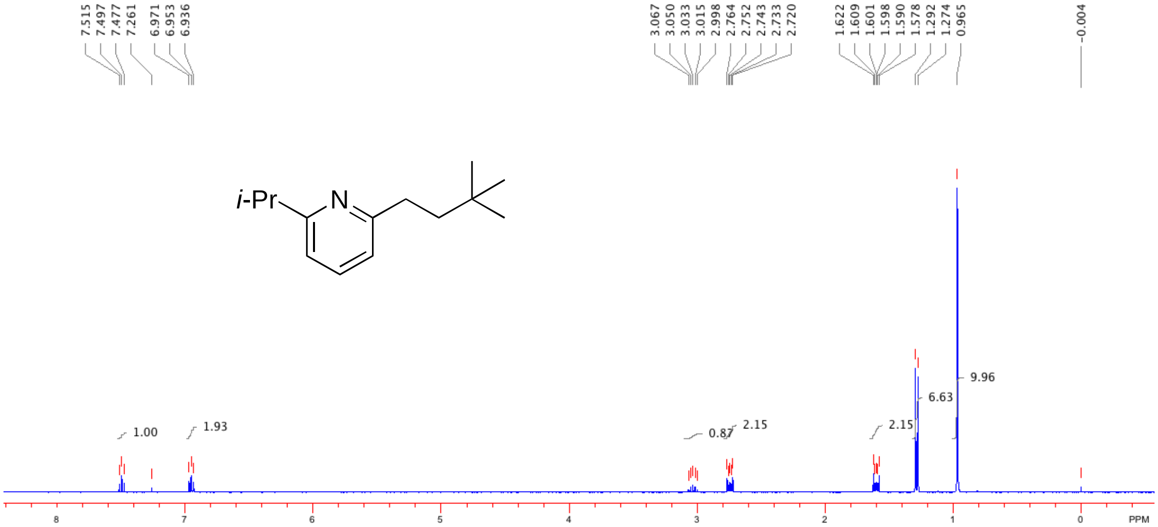
Compound **4**



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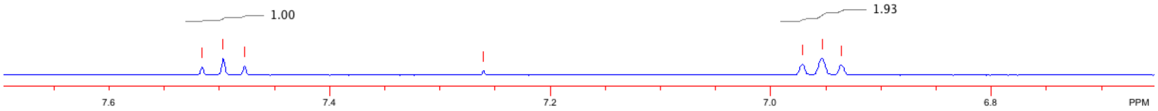

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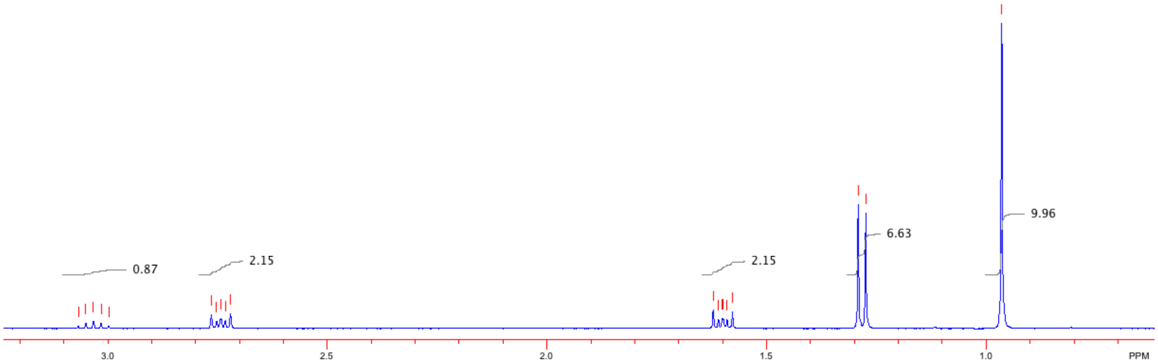

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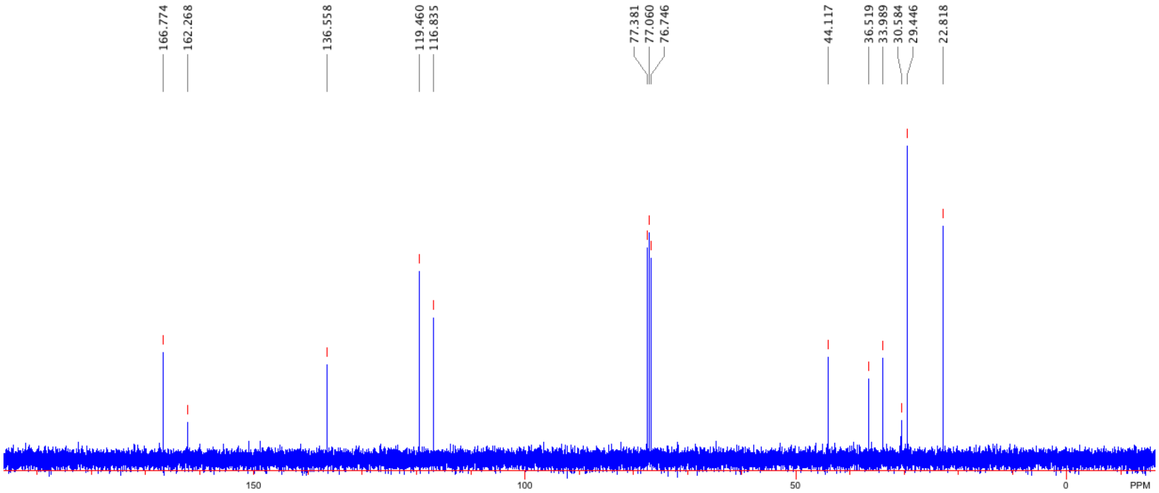

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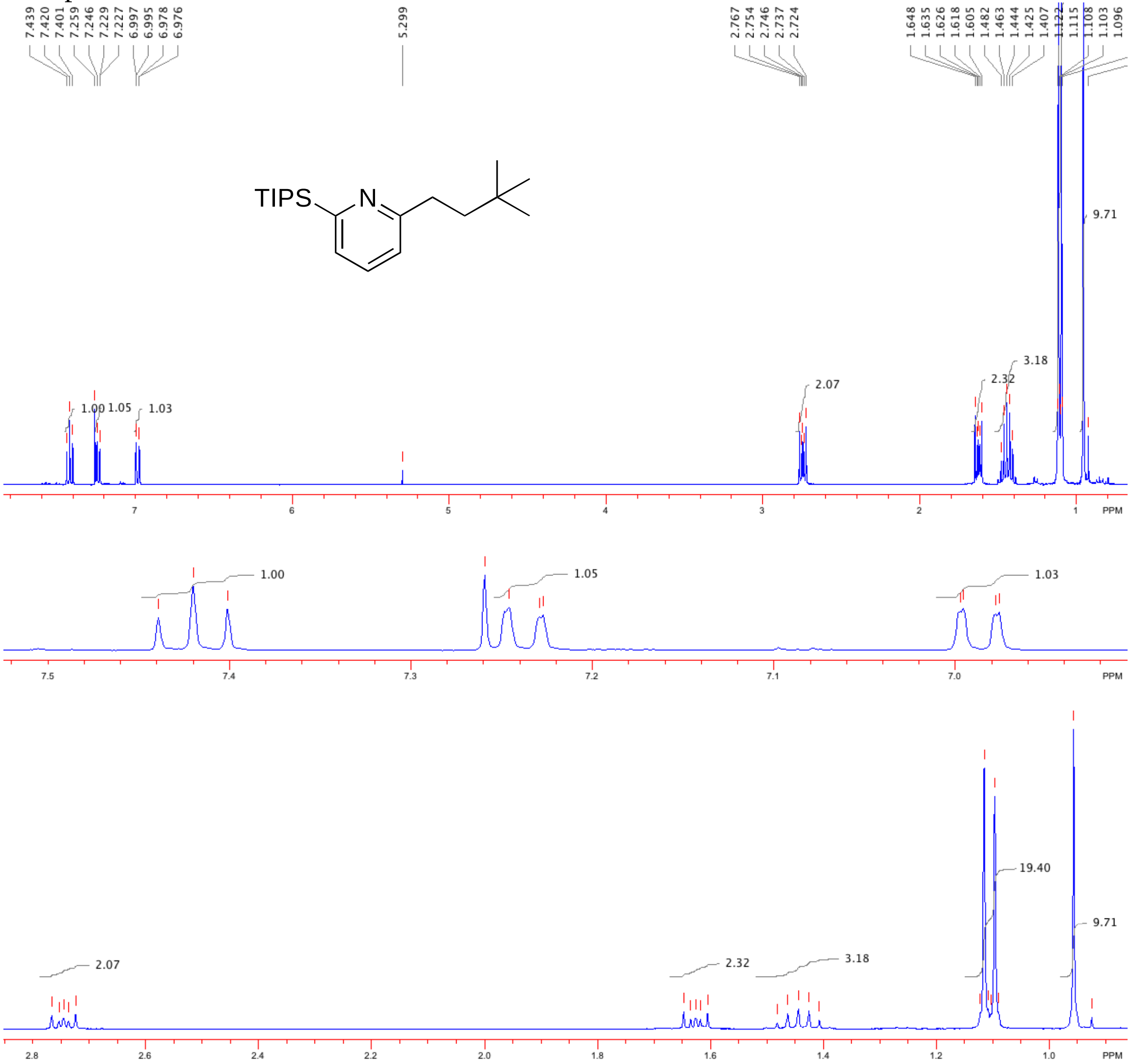
Compound **5**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2
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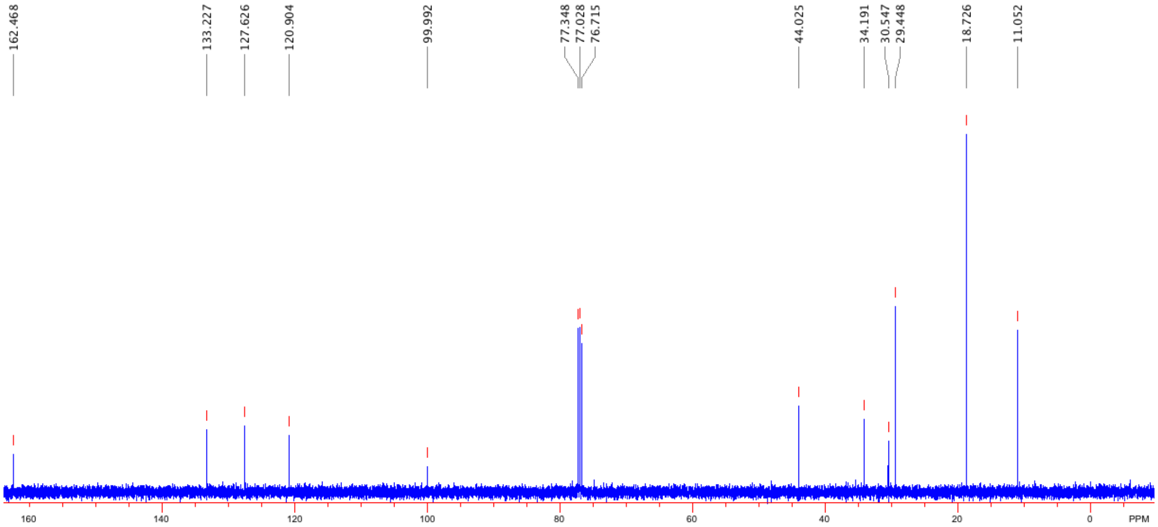
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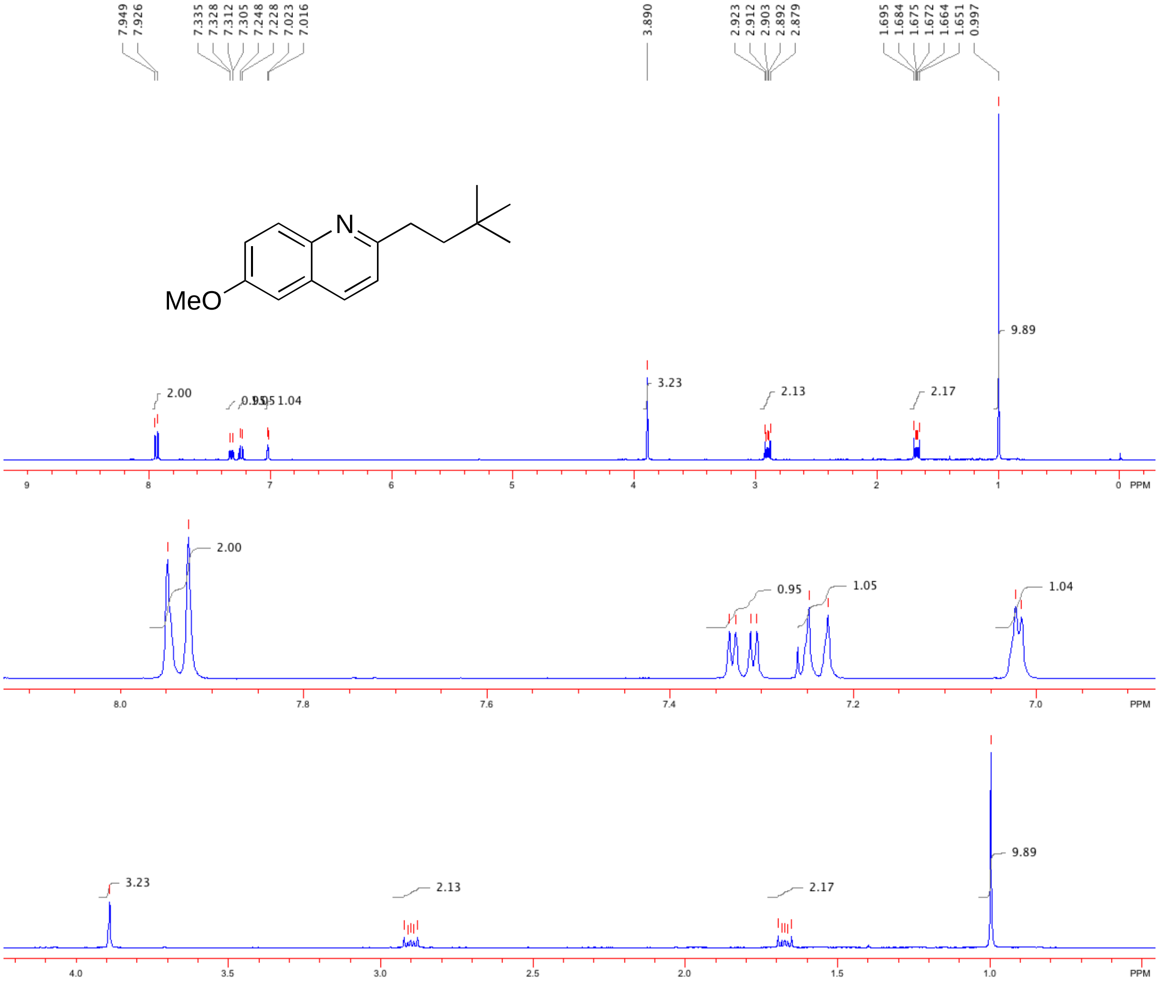
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1.05
1.04
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3
2
1
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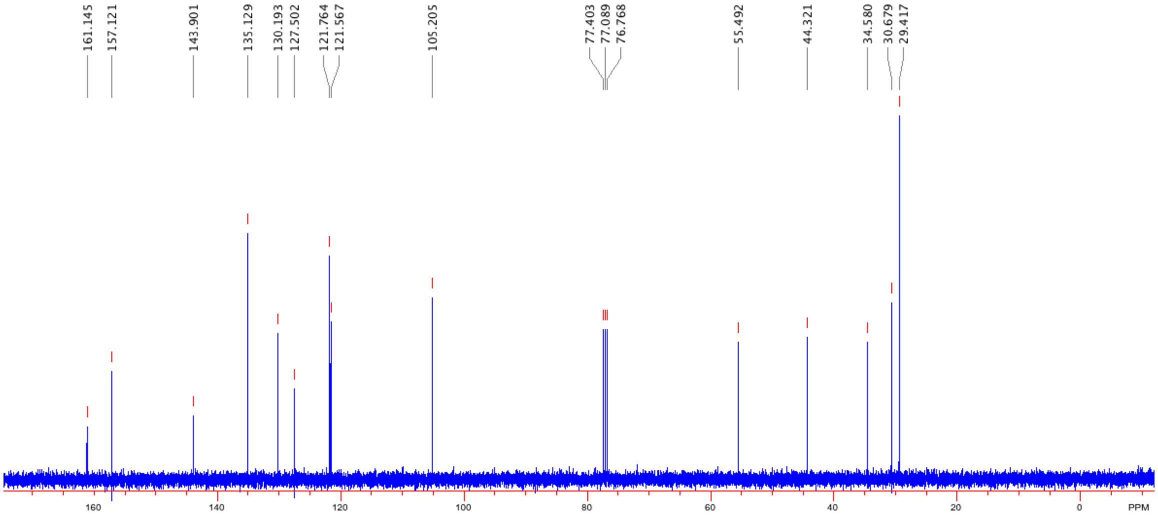
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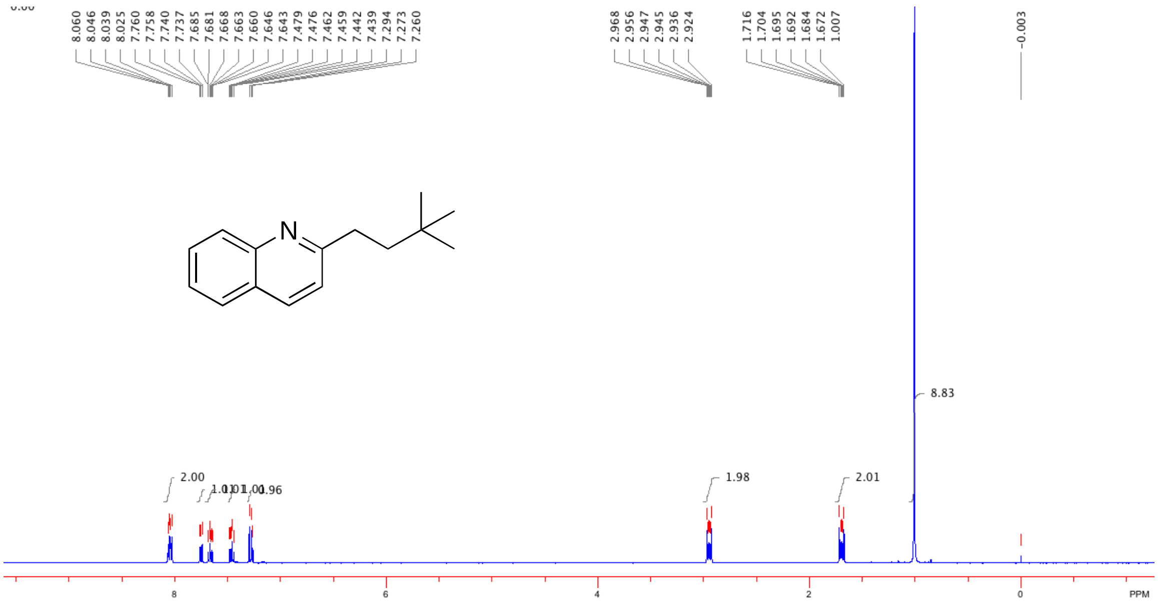
Compound **7**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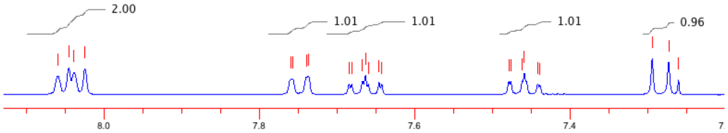
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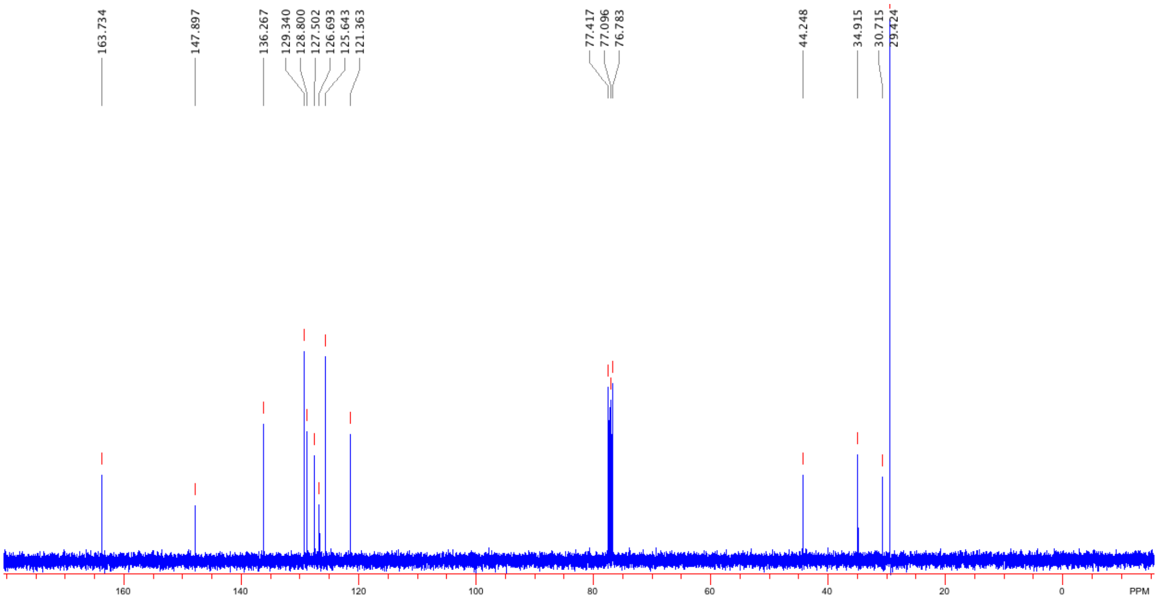
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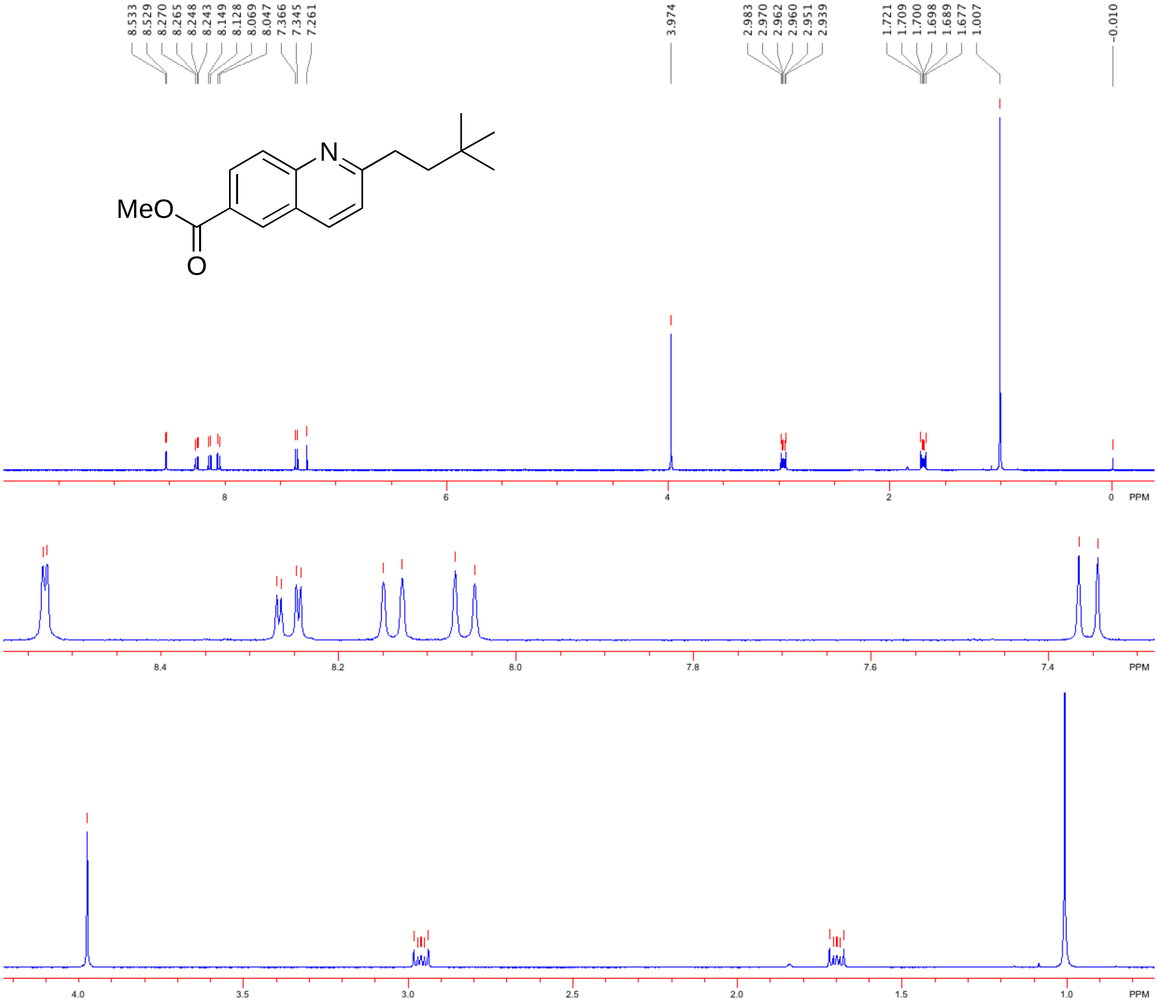
Compound **8**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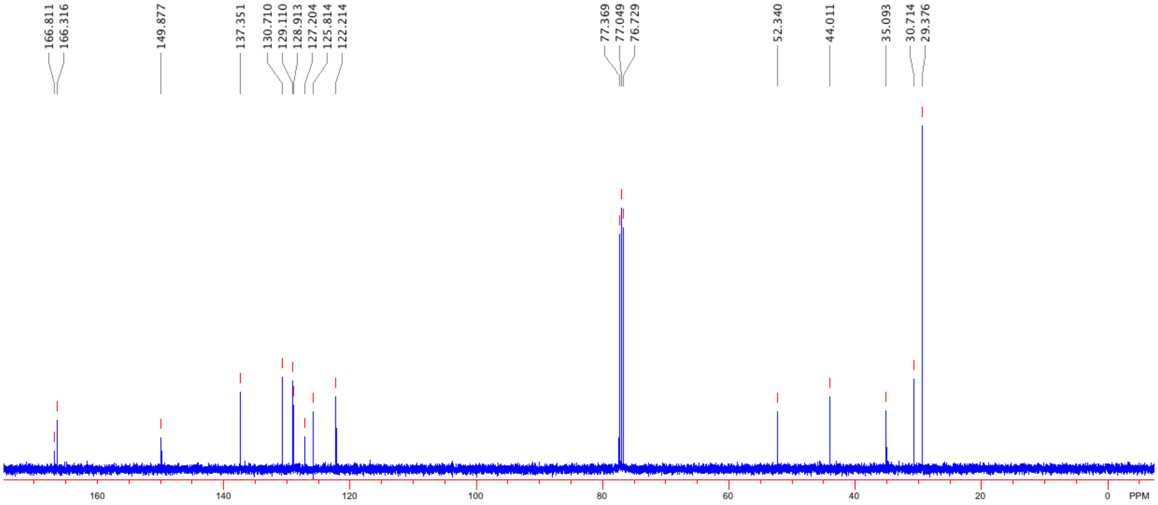
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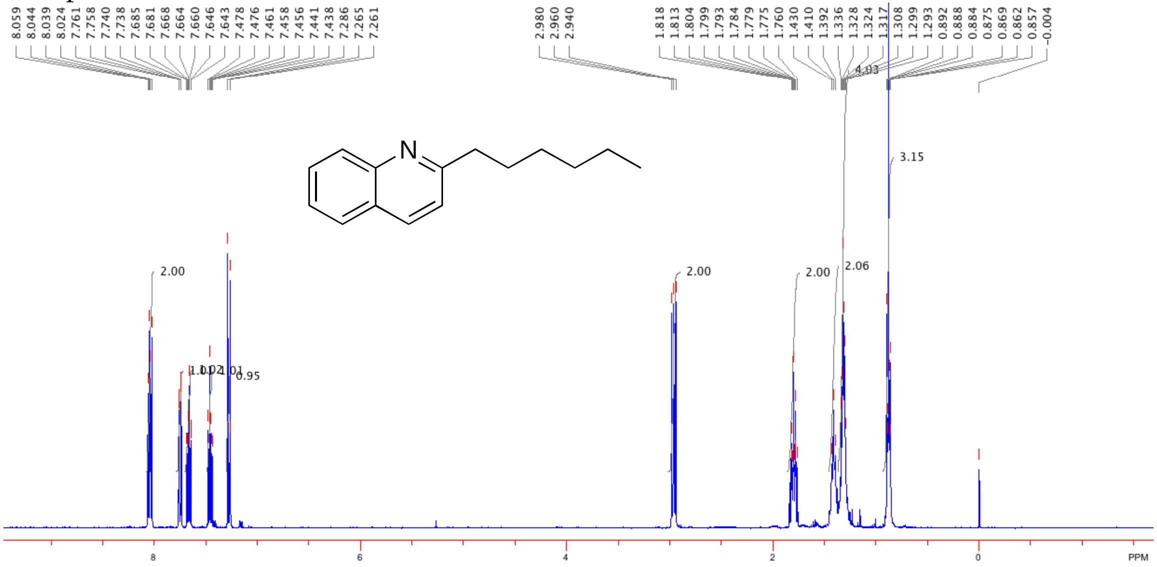
Compound **9**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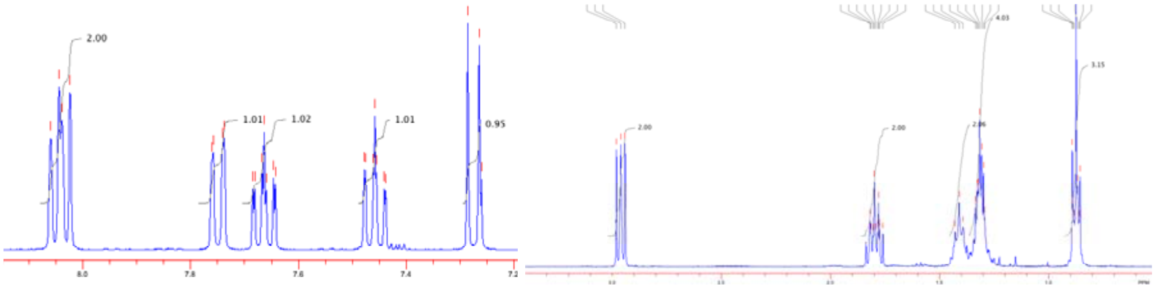
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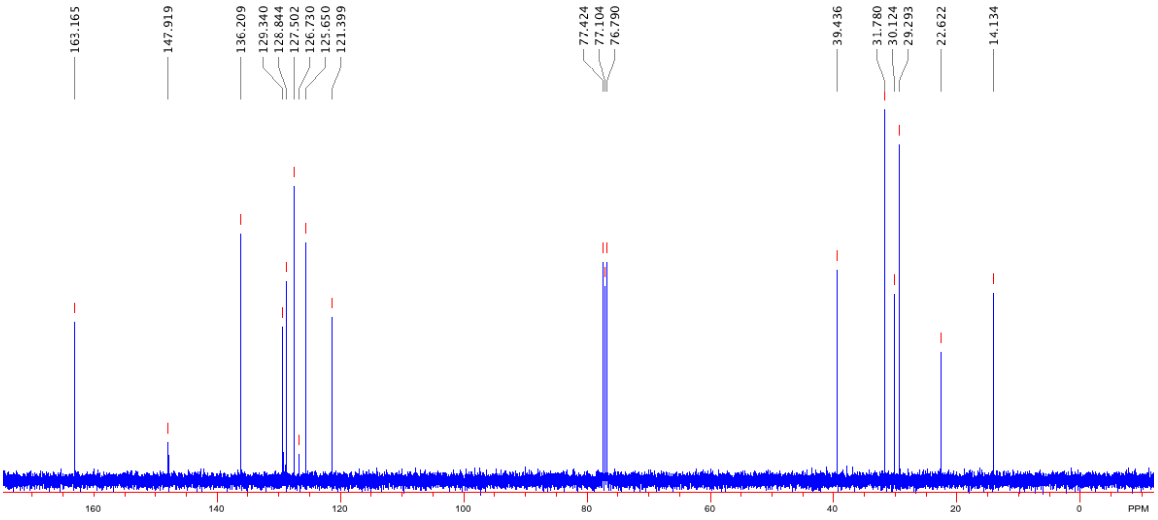
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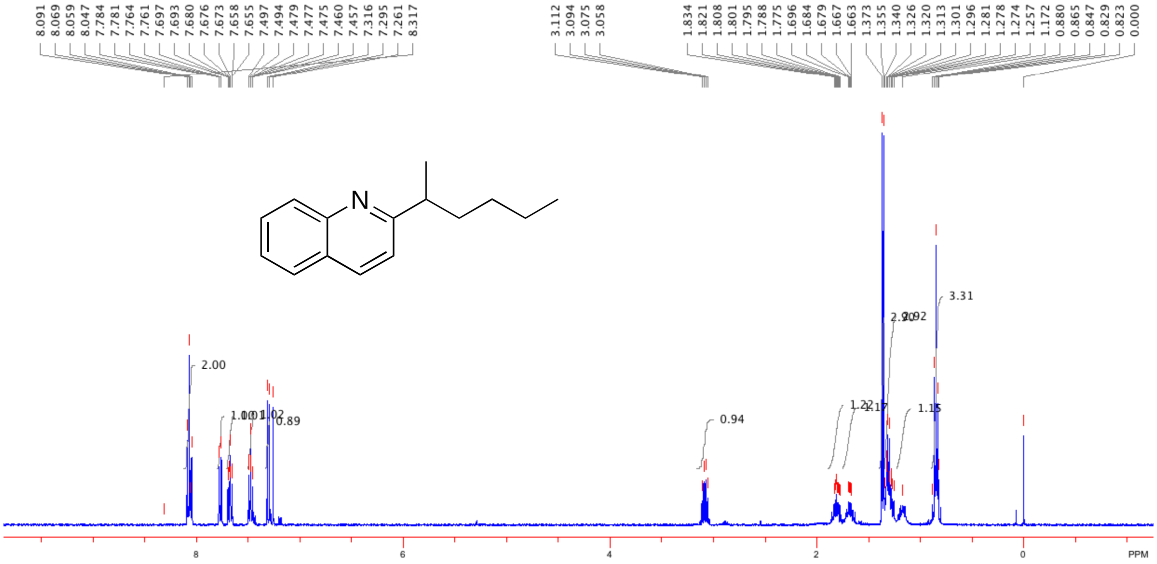
PPM

Compound **10**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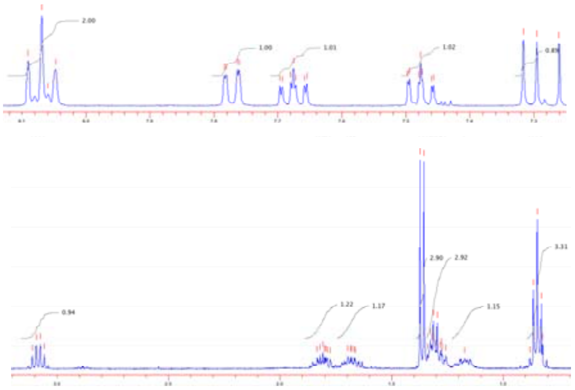
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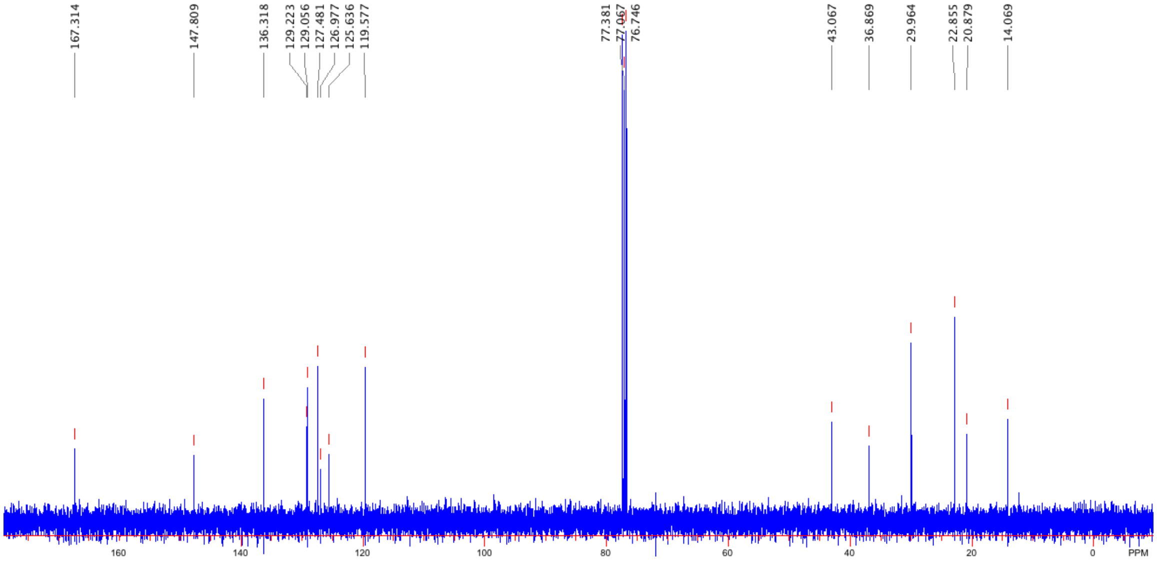
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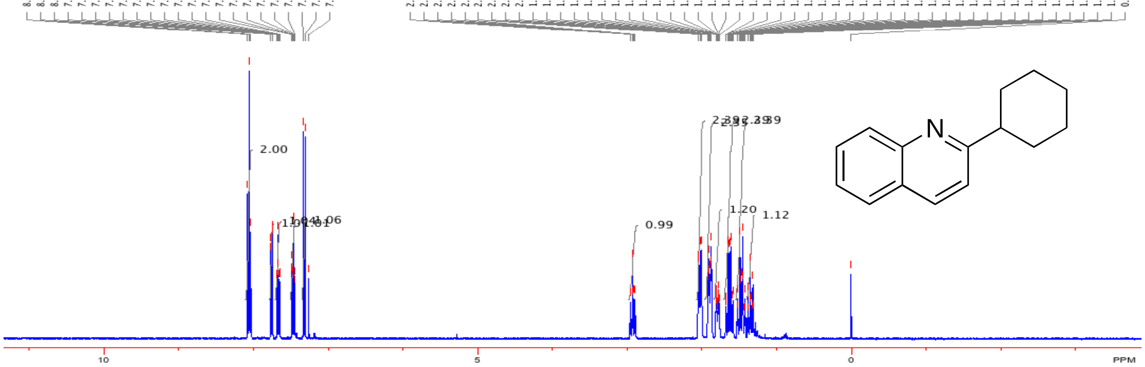
Compound **11**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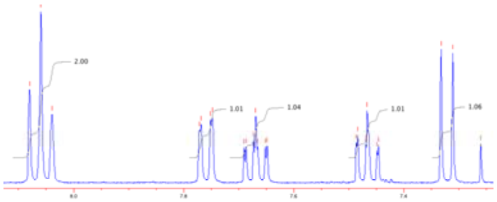
2.953
2.932
2.923
2.914
2.893
2.046
2.041
2.013
2.008
1.919
1.911
1.903
1.887
1.879
1.872
1.813
1.810
1.806
1.802
1.799
1.795
1.783
1.779
1.775
1.766
1.682
1.674
1.651
1.642
1.620
1.612
1.587
1.581
1.529
1.521
1.497
1.490
1.482
1.466
1.457
1.449
1.433
1.425
1.418
1.388
1.381
1.358
1.349
1.340
1.326
1.318
1.309
0.002
2.00
1.01
1.04
1.01
1.06
0.99
2.39
2.35
2.39
2.39
1.20
1.12
N
10
5
0
PPM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1.04
1.01
1.06
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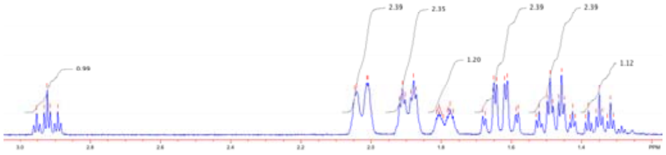
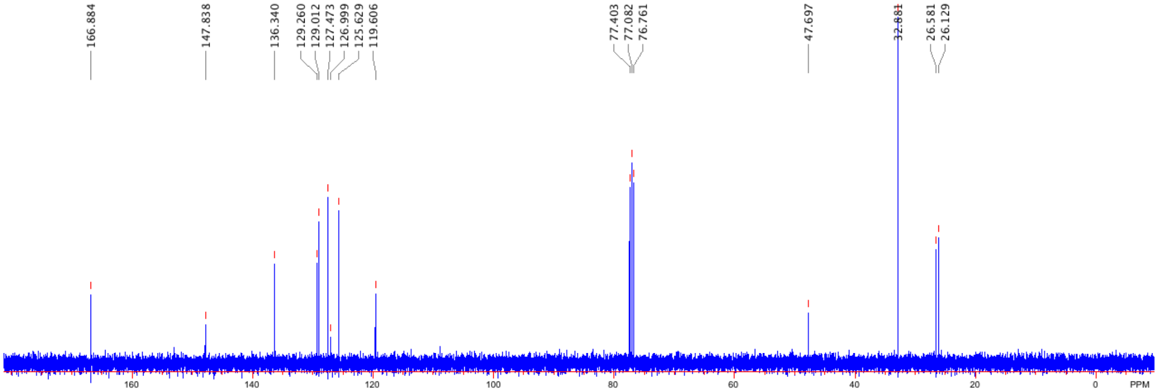
7.4


0.99
2.39
2.35
1.20
2.39
2.39
1.12
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
PPM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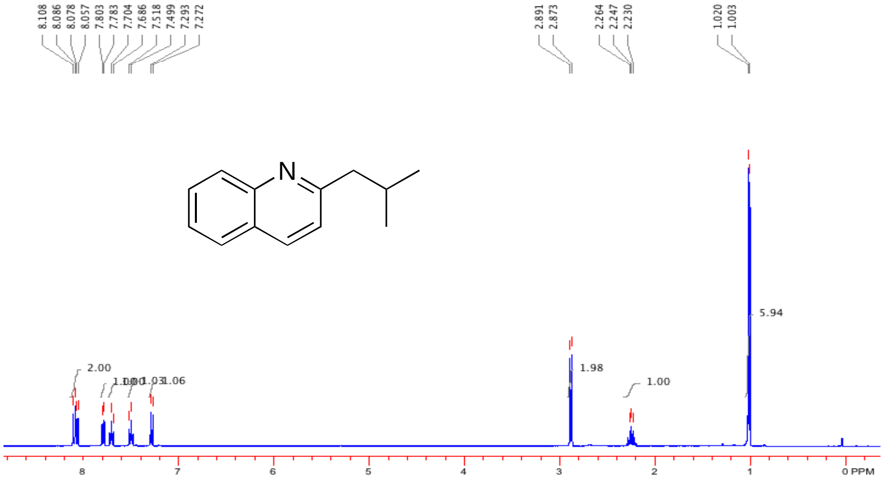
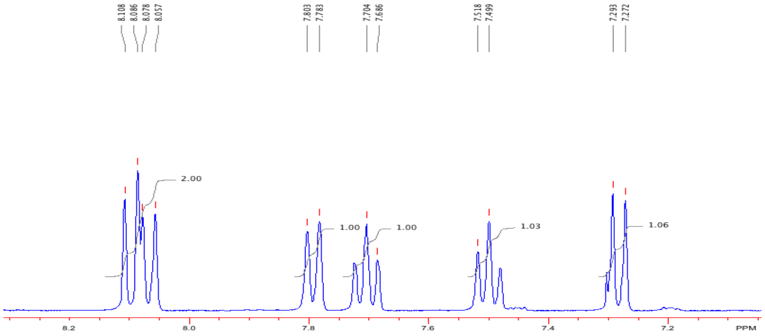
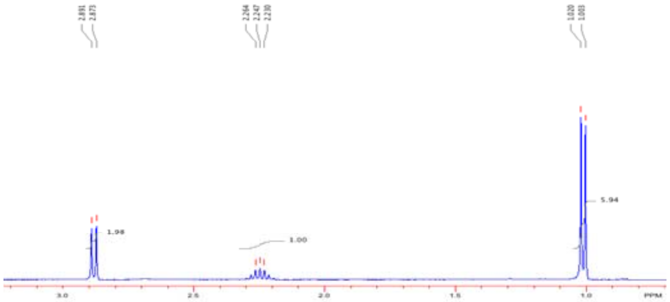
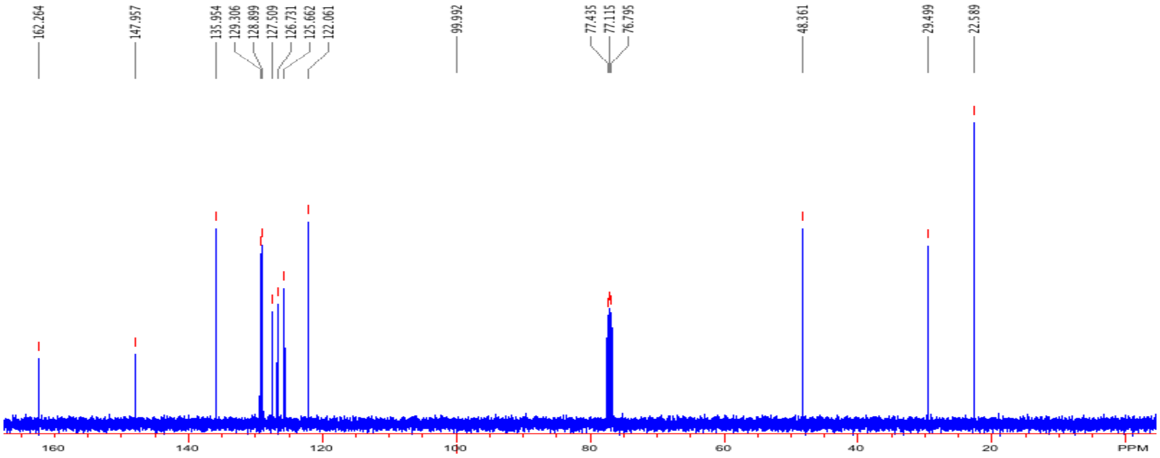
147.838
136.340
129.260
129.012
127.473
126.999
125.629
119.606
77.403
77.082
76.761
47.697
32.881
26.581
26.129
160
140
120
100
80
60
40
20
0
PPM

Compound **12**

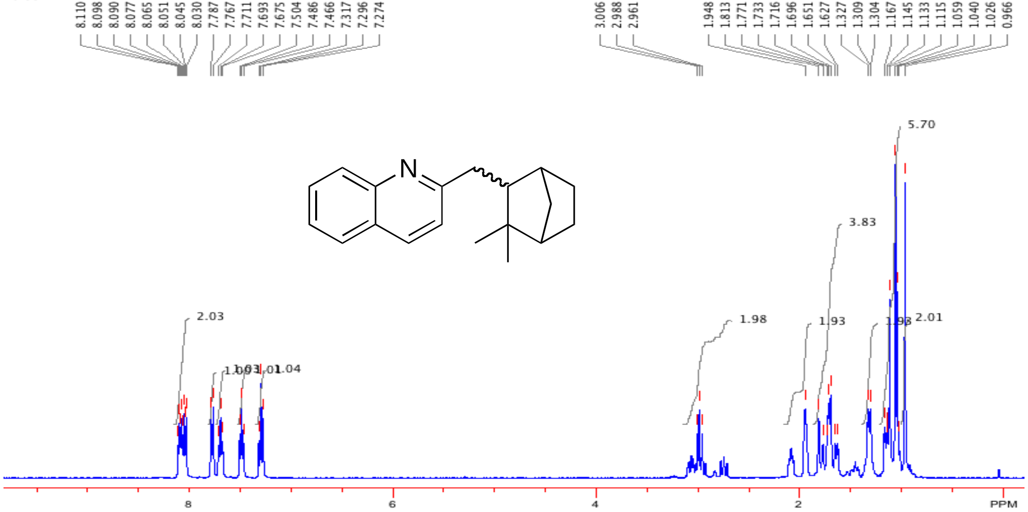

8.108
8.086
8.078
8.057
7.803
7.783
7.704
7.686
7.518
7.499
7.293
7.272
2.891
2.873
2.264
2.247
2.230
1.020
1.003
N
2.00
1.00
1.00
1.03
1.06
1.98
1.00
5.94
8
7
6
5
4
3
2
1
0 PPM

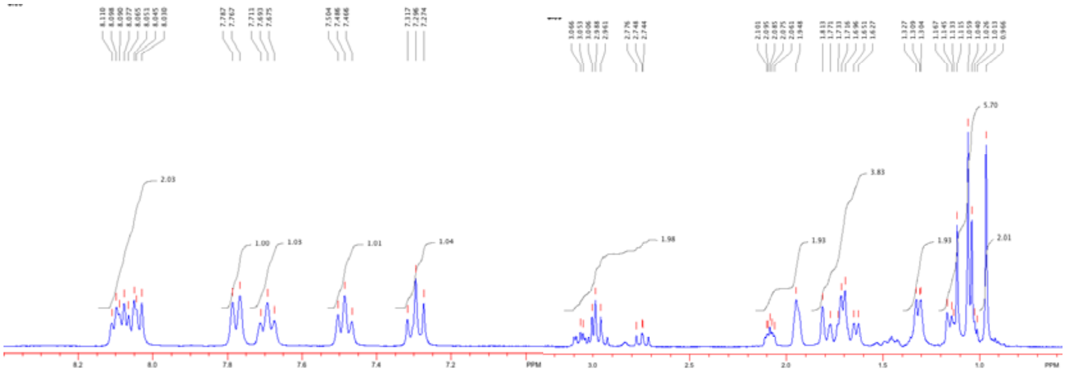

8.108
8.086
8.078
8.057
7.803
7.783
7.704
7.686
7.518
7.499
7.293
7.272
2.00
1.00
1.00
1.03
1.06
8.2
8.0
7.8
7.6
7.4
7.2
PPM

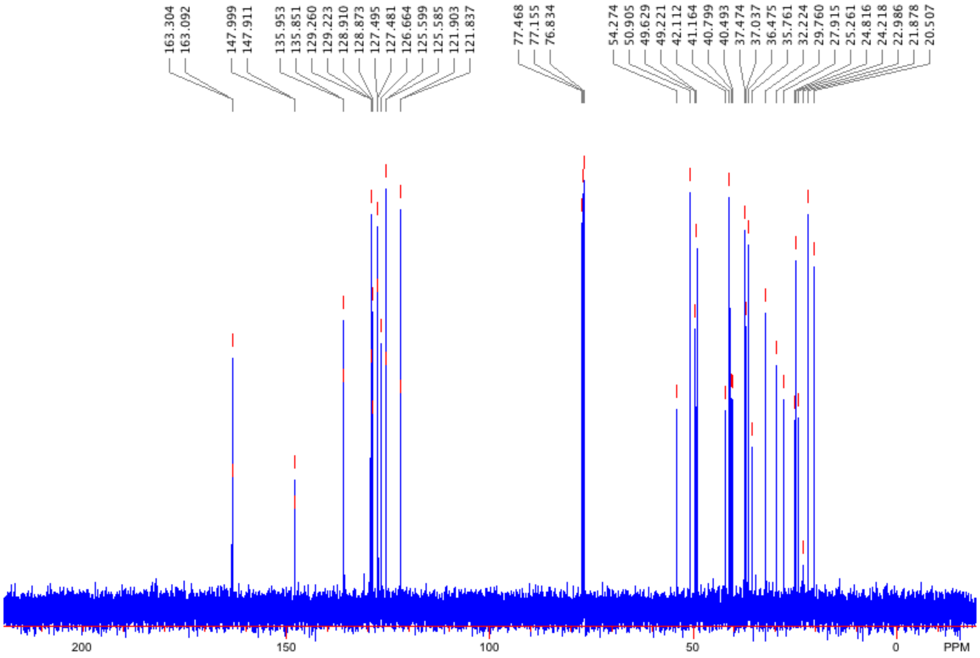

2.891
2.873
2.264
2.247
2.230
1.020
1.003
1.98
1.00
5.94
3.0
2.5
2.0
1.5
1.0
PPM


162.264
147.957
135.954
129.306
128.899
127.509
126.731
125.662
122.061
99.992
77.435
77.115
76.795
48.361
29.499
22.589
160
140
120
100
80
60
40
20
PPM

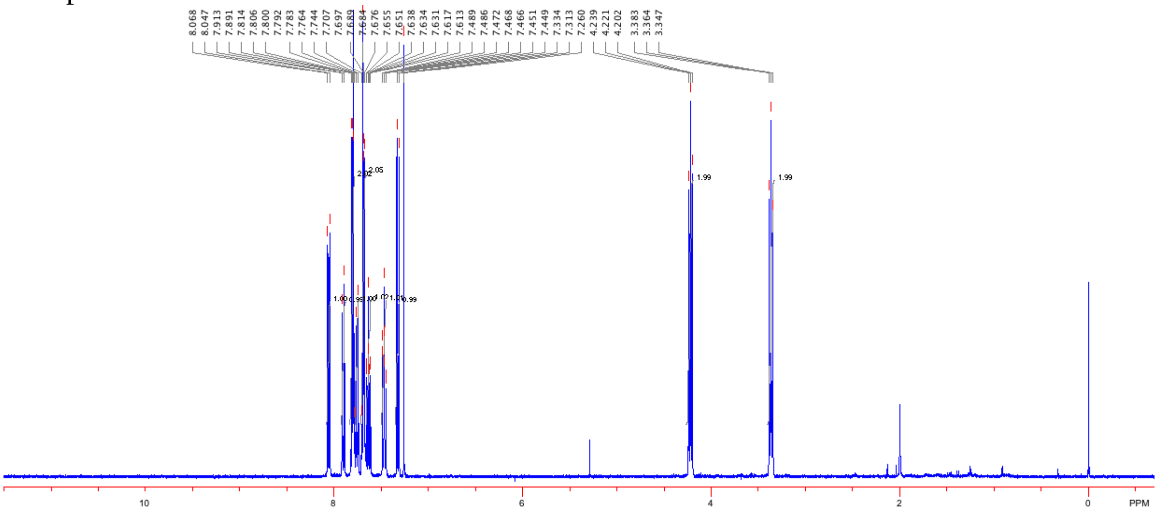
Compound **13**

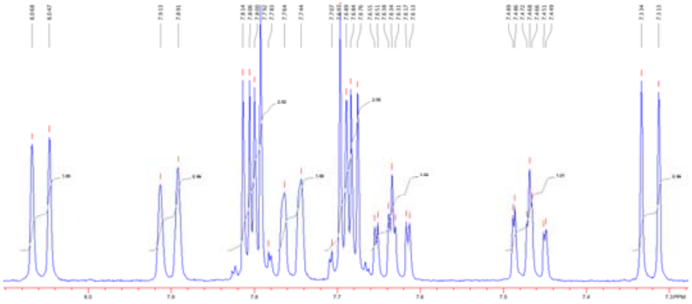

8.110
8.098
8.090
8.077
8.065
8.051
8.045
8.030
7.787
7.767
7.711
7.693
7.675
7.504
7.486
7.466
7.317
7.296
7.274
3.006
2.988
2.961
1.948
1.813
1.771
1.733
1.716
1.696
1.651
1.627
1.327
1.309
1.304
1.167
1.145
1.133
1.115
1.059
1.040
1.026
0.966
N
5.70
3.83
2.03
1.00
1.03
1.01
1.04
1.98
1.93
1.93
2.01
8
6
4
2
PPM

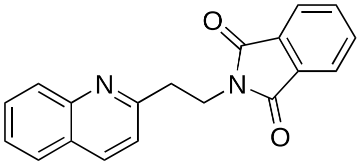

2.03
1.00
1.03
1.01
1.04
1.98
1.93
3.83
1.93
5.70
2.01
8.2
8.0
7.8
7.6
7.4
7.2
PPM
3.0
2.5
2.0
1.5
1.0
PPM

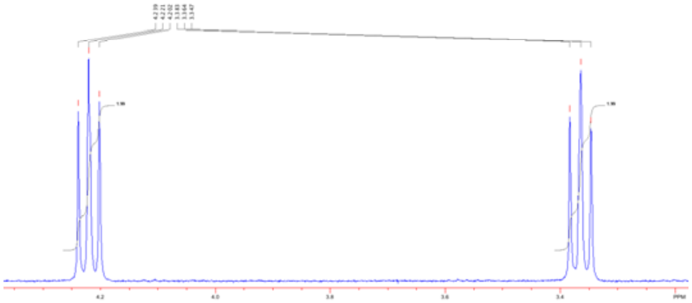

163.304
163.092
147.999
147.911
135.953
135.851
129.260
129.223
128.910
128.873
127.495
127.481
126.664
125.599
125.585
121.903
121.837
77.468
77.155
76.834
54.274
50.905
49.629
49.221
42.112
41.164
40.799
40.493
37.474
37.037
36.475
35.761
32.224
29.760
27.915
25.261
24.816
24.218
22.986
21.878
20.507
200
150
100
50
0
PPM

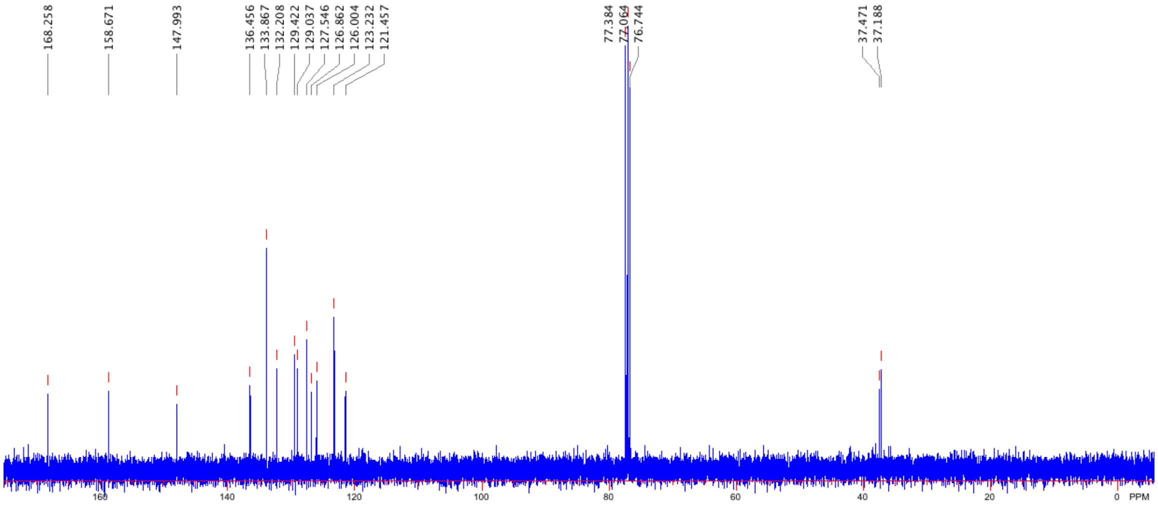
Compound **14**


8.068
8.047
7.913
7.891
7.814
7.806
7.800
7.792
7.783
7.764
7.744
7.707
7.697
7.689
7.684
7.676
7.655
7.651
7.638
7.634
7.631
7.617
7.613
7.489
7.486
7.472
7.468
7.466
7.451
7.449
7.334
7.313
7.260
4.239
4.221
4.202
3.383
3.364
3.347
1.00
0.99
1.00
1.02
1.01
0.99
2.02
2.05
1.99
1.99
10
8
6
4
2
0
PPM

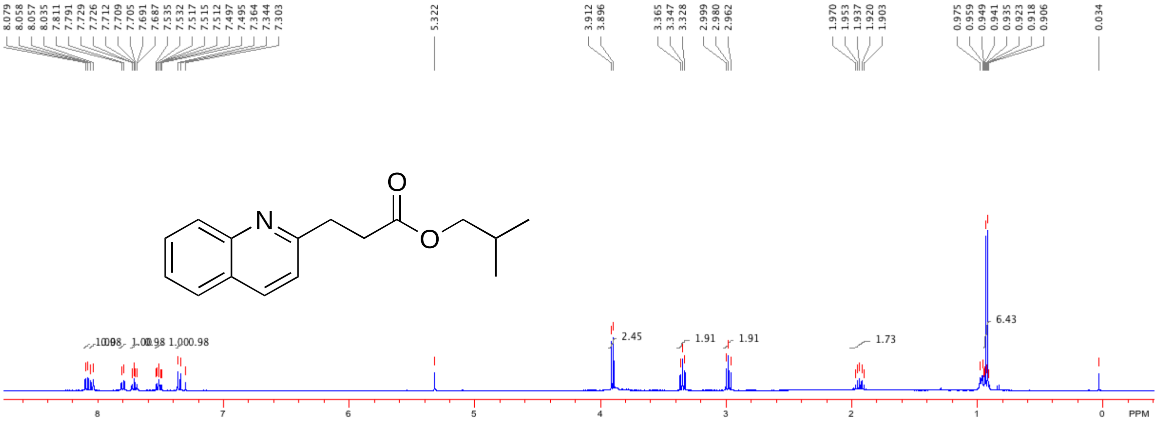

8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
PPM


N
N
O
O

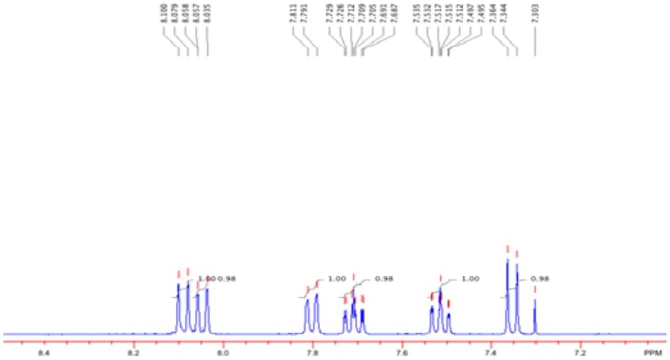

4.239
4.221
4.202
3.383
3.364
3.347
1.99
1.99
4.2
4.0
3.8
3.6
3.4
PPM


168.258
158.671
147.993
136.456
133.867
132.208
129.422
129.037
127.546
126.862
126.004
123.232
121.457
77.384
77.064
76.744
37.471
37.188
160
140
120
100
80
60
40
20
0
PPM

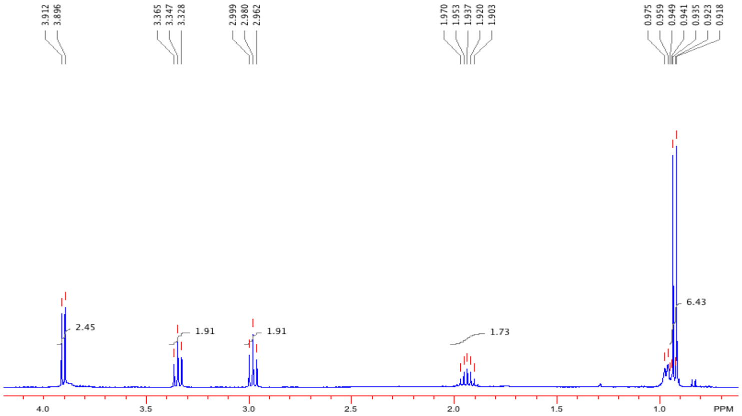
Compound **15**



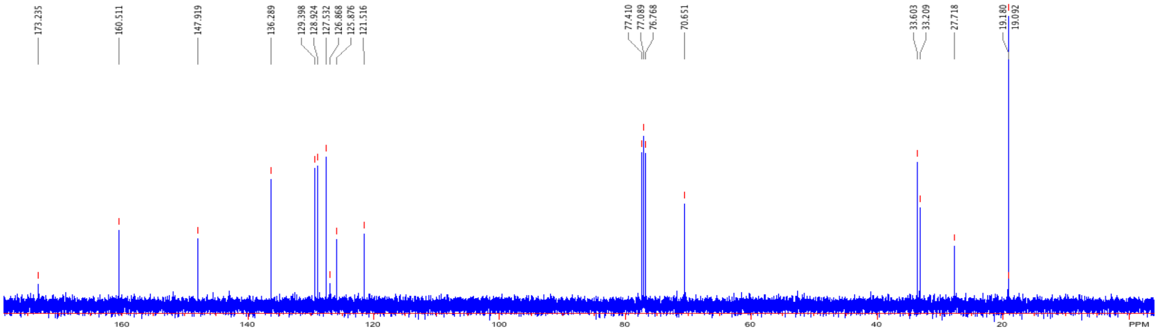
8.079
8.058
8.057
8.035
7.811
7.791
7.729
7.726
7.712
7.709
7.705
7.691
7.687
7.535
7.532
7.517
7.515
7.512
7.497
7.495
7.364
7.344
7.303
5.322
3.912
3.896
3.365
3.347
3.328
2.999
2.980
2.962
1.970
1.953
1.937
1.920
1.903
0.975
0.959
0.949
0.941
0.935
0.923
0.918
0.906
0.034
O
N
O
1.00
0.98
1.00
0.98
1.00
0.98
2.45
1.91
1.91
1.73
6.43
8
7
6
5
4
3
2
1
0
PPM



8.100
8.079
8.058
8.057
8.035
7.811
7.791
7.729
7.726
7.712
7.709
7.705
7.691
7.687
7.535
7.532
7.517
7.515
7.512
7.497
7.495
7.364
7.344
7.303
1.00
0.98
1.00
0.98
1.00
0.98
8.4
8.2
8.0
7.8
7.6
7.4
7.2
PPM



3.912
3.896
3.365
3.347
3.328
2.999
2.980
2.962
1.970
1.953
1.937
1.920
1.903
0.975
0.959
0.949
0.941
0.935
0.923
0.918
2.45
1.91
1.91
1.73
6.43
4.0
3.5
3.0
2.5
2.0
1.5
1.0
PPM



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147.919
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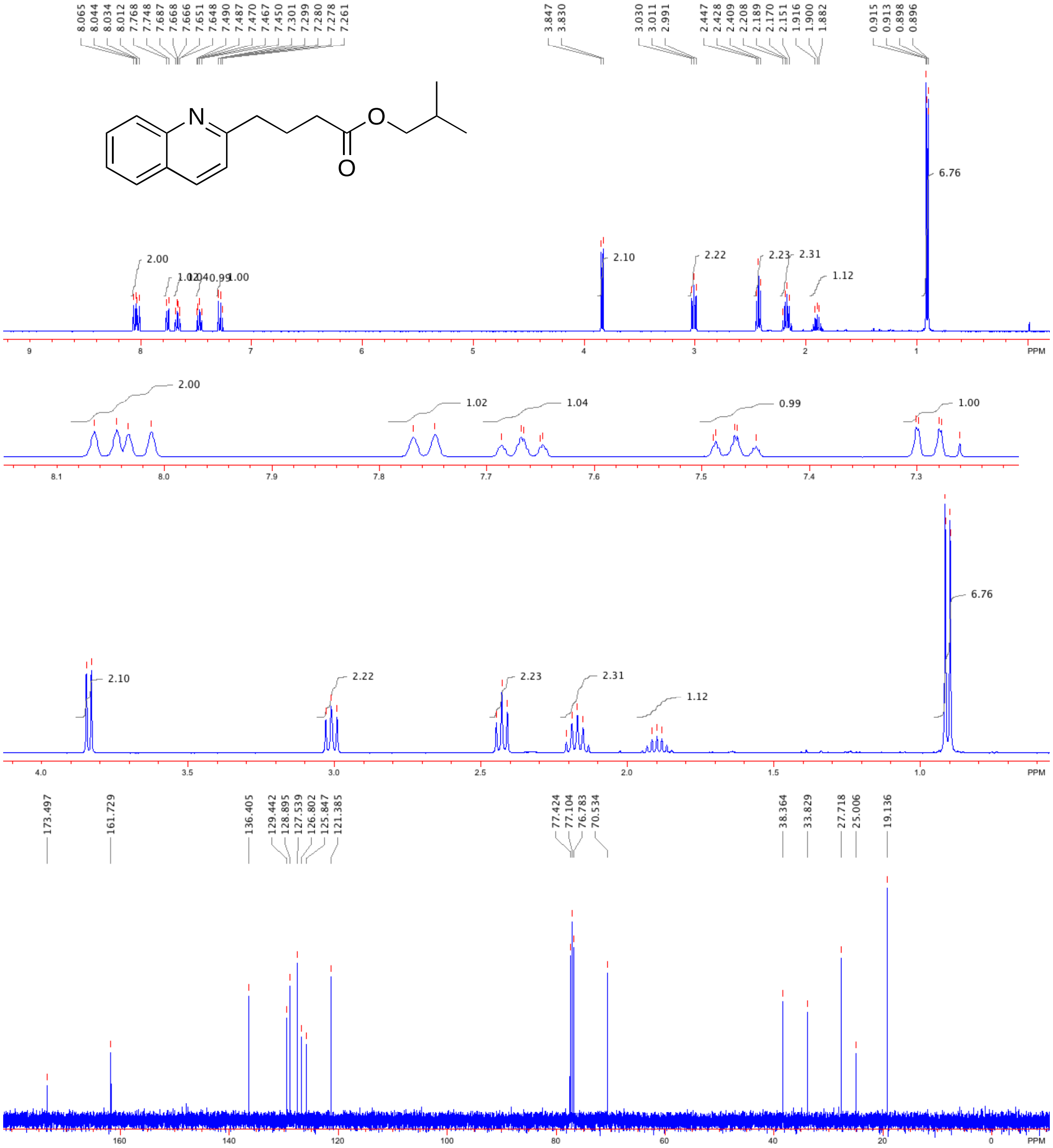
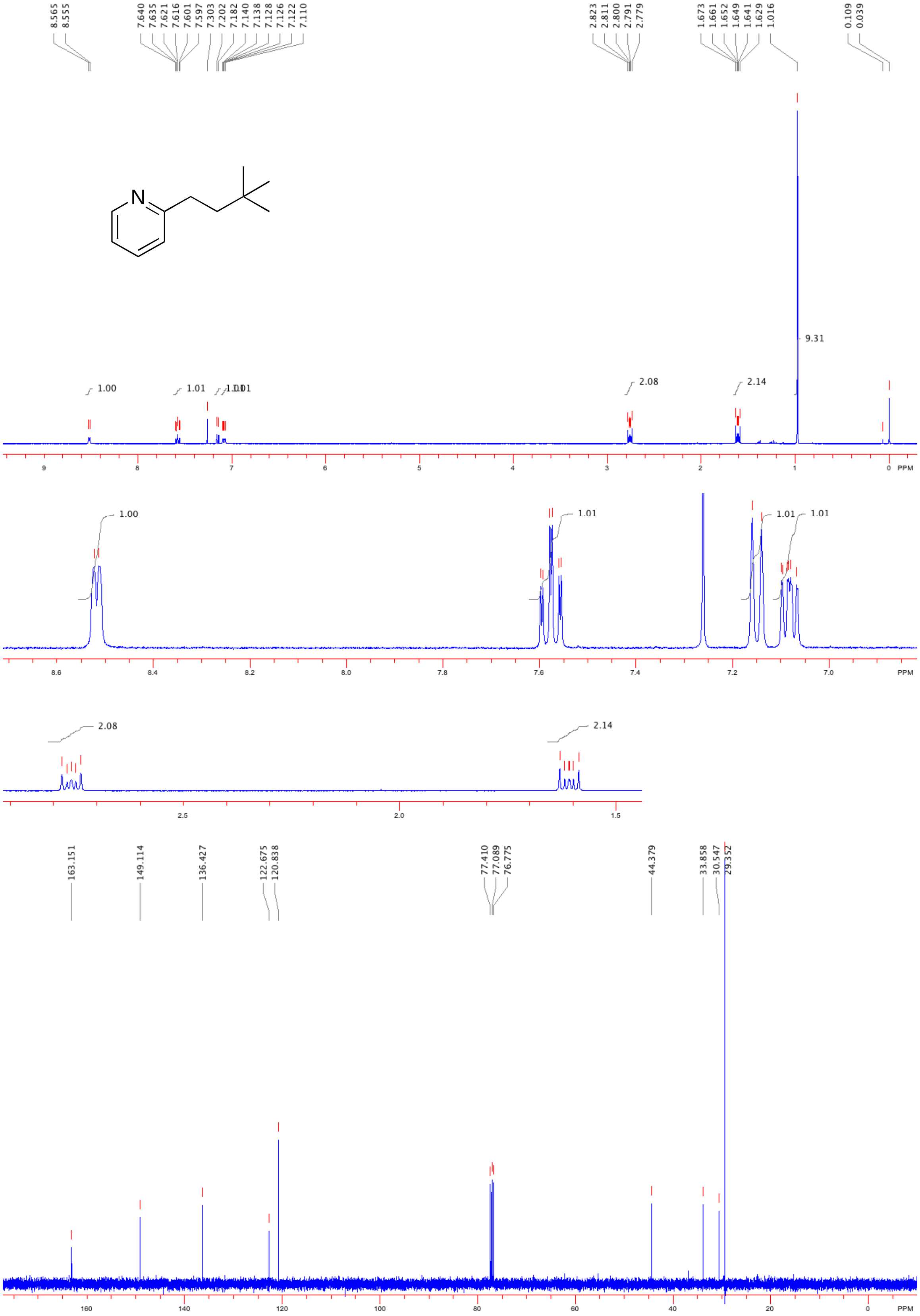
129.398
128.924
127.532
126.868
125.876
121.516
77.410
77.089
76.768
70.651
33.603
33.209
27.718
19.180
19.092
160
140
120
100
80
60
40
20
PPM

Compound **16**


8.065
8.044
8.034
8.012
7.768
7.748
7.687
7.668
7.666
7.651
7.648
7.490
7.487
7.470
7.467
7.450
7.301
7.299
7.280
7.278
7.261
3.847
3.830
3.030
3.011
2.991
2.447
2.428
2.409
2.208
2.189
2.170
2.151
1.916
1.900
1.882
0.915
0.913
0.898
0.896
N
O
O
2.00
1.02
1.04
0.99
1.00
2.10
2.22
2.23
2.31
1.12
6.76
PPM
173.497
161.729
136.405
129.442
128.895
127.539
126.802
125.847
121.385
77.424
77.104
76.783
70.534
38.364
33.829
27.718
25.006
19.136
PPM

Compound **17**



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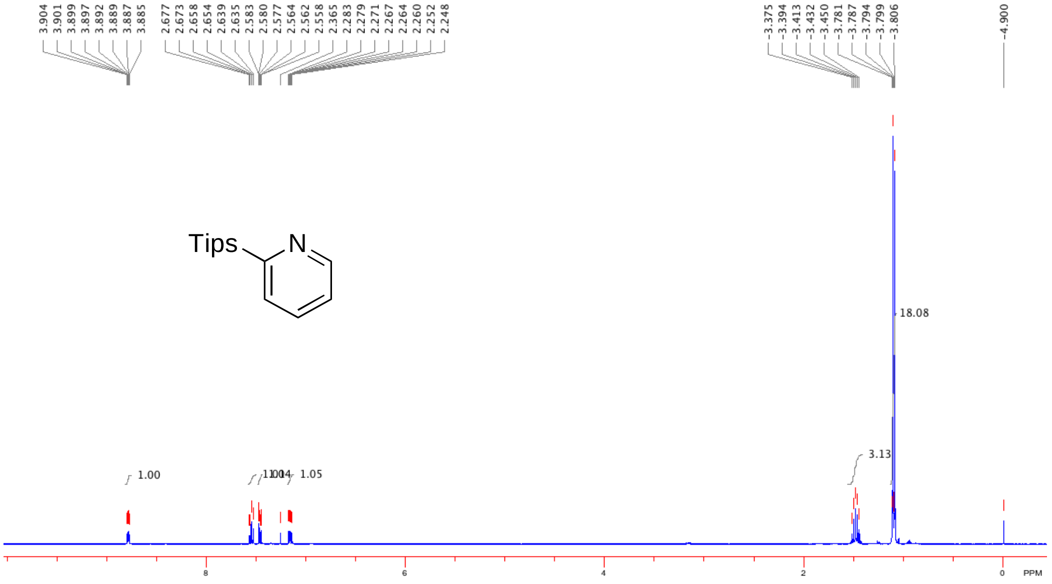
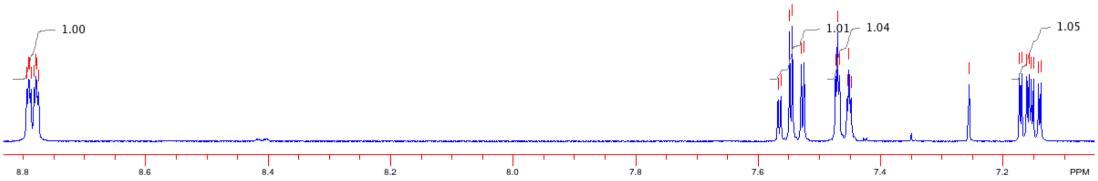
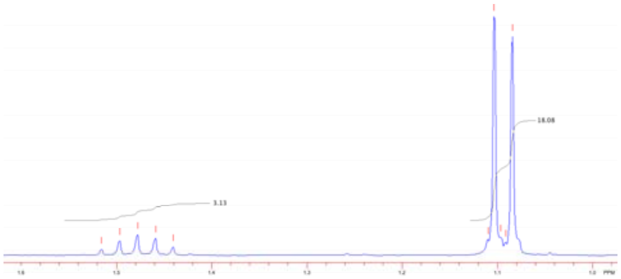
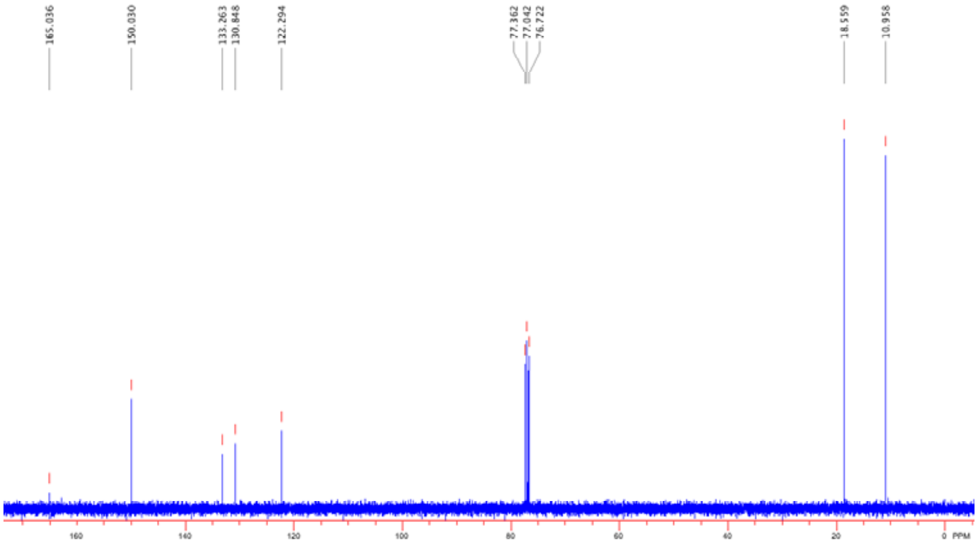
7.635
7.621
7.616
7.601
7.597
7.303
7.202
7.182
7.140
7.138
7.128
7.126
7.122
7.110
2.823
2.811
2.800
2.791
2.779
1.673
1.661
1.652
1.649
1.641
1.629
1.016
0.109
0.039
N
1.00
1.01
1.01
1.01
2.08
2.14
9.31
9
8
7
6
5
4
3
2
1
0
PPM
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
PPM
2.5
2.0
1.5
163.151
149.114
136.427
122.675
120.838
77.410
77.089
76.775
44.379
33.858
30.547
29.352
160
140
120
100
80
60
40
20
0
PPM

Compound **18**:


3.904
3.901
3.899
3.897
3.892
3.889
3.887
3.885
2.677
2.673
2.658
2.654
2.639
2.635
2.583
2.580
2.577
2.564
2.562
2.558
2.365
2.283
2.279
2.271
2.267
2.264
2.260
2.252
2.248
-3.375
-3.394
-3.413
-3.432
-3.450
-3.781
-3.787
-3.794
-3.799
-3.806
-4.900
Tips
N
1.00
1.01
1.04
1.05
3.13
18.08
8
6
4
2
0
PPM


1.00
1.01
1.04
1.05
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
PPM


18.08
3.13


165.036
150.030
133.263
130.848
122.294
77.362
77.042
76.722
18.559
10.958
160
140
120
100
80
60
40
20
0
PPM

(1) van der Ent, A.; Onderlinden, A. L. *Inorg. Synth.* **1973**, *14*, 92-93.

(2) Wiedemann, S. H.; Ellman, J. A.; Bergman, R. G. *J. Org. Chem.* **2006**, *71*, 1969.