Supporting Information

Povarov-Reductive Amination Cascade to Access to 6-Aminoquinolines and Anthrazolines

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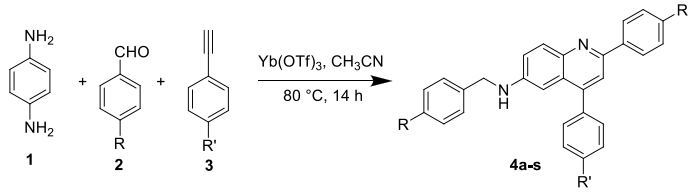
Contents

General information

All chemicals were obtained from commercial suppliers and were used without further purification. The melting points were determined using Mel-Temp melting point apparatus and were not corrected. All products were characterized by their ^{1}H, ^{13}C NMR on a Bruker AV-300 Spectrometer and their HRMS on a Bruker microTOF Focus Mass Spectrometer in positive ion mode. For ^{1}H NMR, chemical shifts (δ) are quoted in parts per million (ppm) using deuterated solvent as internal standard ($CDCl_3$: 7.26 ppm) and coupling constants are reported as values in hertz (Hz). Thin layer chromatography (TLC) was performed on pre-coated fluorescent silica gel on aluminum sheets and compound spots were detected under UV light. Silica gel 230-400 mesh was used for column chromatography.

General procedure for the synthesis of *N*-arylmethyl-2,4-diphenylquinolin-6-amine derivatives (4a-4s):



A mixture of 1,4-phenylenediamine **1** (1.0 mmol), arylaldehyde **2** (2.0 mmol), arylacetylene **3** (1.5 mmol), ytterbium triflate (0.05 mmol) in acetonitrile (3.0 ml) was stirred at 80°C for 14 h. The volatiles were evaporated and the residue was diluted with water (10 mL), extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated under vacuum and crude compound obtained was purified by column chromatography (EtOAc/hexanes) to afford tandem products **4a-s**.

N-Benzyl-2,4-diphenylquinolin-6-amine (**4a**): Yield 49%; Yellow solid; mp 148-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 – 8.04 (m, 3H), 7.71 (s, 1H), 7.58 – 7.40 (m, 8H), 7.40 – 7.27 (m, 5H), 7.20 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.84 (s, 1H), 4.48 (s, 1H), 4.33 (d, *J* = 3.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.27, 147.05, 146.32, 144.18, 140.47, 139.59, 139.23, 131.54, 129.71, 128.97, 128.86, 128.24, 127.85, 127.59, 127.51, 121.22, 119.80, 102.86, 48.66. HRMS calcd for $C_{28}H_{23}N_2$ 387.1856 $[M + H]^+$, found 387.1859.

N-(4-Methylbenzyl)-4-phenyl-2-p-tolylquinolin-6-amine (**4b**): Yield 38%; Yellow solid; mp 170-172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 2H), 7.69 (s, 1H), 7.60 – 7.41 (m, 5H), 7.38 – 7.26 (m, 3H), 7.25 – 7.05 (m, 5H), 6.82 (d, *J* = 2.3 Hz, 1H), 4.45 (s, 1H), 4.28 (s, 2H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.18, 147.05, 146.30, 144.00, 139.65, 138.81, 137.55, 137.22, 136.18, 131.32, 129.69, 129.62, 128.76, 128.19, 127.86, 127.63, 127.39, 121.14, 119.64, 102.86, 48.47, 21.42, 21.24. HRMS calcd for $C_{30}H_{27}N_2$ 415.2169 $[M + H]^+$, found 415.2159.

N-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-4-phenylquinolin-6-amine(**4c**): Yield 26%; Yellow solid; mp 147-149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 – 8.05 (m, 3H), 7.66 (s, 1H), 7.58 – 7.38 (m, 5H), 7.26 (dd, *J* = 11.8, 4.6 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.92 – 6.84 (m, 2H), 6.82 (s, 1H), 4.37 (s, 1H), 4.24 (s, 2H), 3.89

(s, 3H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 160.90, 159.45, 152.72, 147.29, 146.21, 143.64, 139.53, 131.21, 130.94, 129.66, 129.11, 128.80, 128.27, 127.43, 121.28, 119.45, 114.57, 102.81, 55.65, 48.14. HRMS calcd for $C_{30}H_{27}N_2O_2$ 447.2067 $[M + H]^+$, found 447.2048.

4-Phenyl-*N*-(3,4,5-trimethoxybenzyl)-2-(3,4,5-trimethoxy-phenyl)quinolin-6-amine (**4d**): Yield 57%; Yellow solid; mp 117-120 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (d, J = 9.0 Hz, 1H), 7.82 (s, 1H), 7.54 – 7.40(m, 6H), 7.32 (d, J = 9.1 Hz, 1H), 6.88 (s, 1H), 6.59 (s, 3H), 4.16 (s, 2H), 3.89 (s, 6H), 3.72 (s, 3H), 3.68 (s, 6H), 3.63 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 154.06, 153.84, 151.40, 148.57, 147.60, 146.22, 143.30, 141.02, 139.74, 139.39, 137.71, 135.84, 135.71, 131.16, 130.00, 129.25, 128.74, 127.57, 122.29, 119.42, 105.78, 105.58, 101.39, 60.95, 60.80, 60.47, 57.13, 56.86, 47.88. HRMS calcd for $C_{34}H_{35}N_2O_6$ 567.2490 $[M + H]^+$, found 567.2489.

N-(4-Chlorobenzyl)-2-(4-chlorophenyl)-4-phenylquinolin-6-amine (**4e**): Yield 28%; Yellow solid; mp 173-175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 3H), 7.65 (s, 1H), 7.53 – 7.44 (m, 5H), 7.44 – 7.35 (m, 2H), 7.35 – 7.13 (m, 5H), 6.72 (s, 1H), 4.56 (s, 1H), 4.29 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.87, 147.54, 146.16, 143.78, 139.19, 138.47, 137.58, 135.30, 133.47, 131.28, 129.53, 129.14, 129.00, 128.83, 128.76, 128.40, 127.78, 121.48, 119.43, 102.98, 47.99. HRMS calcd for $C_{28}H_{21}Cl_2N_2$ 455.1076 $[M + H]^+$, found 455.1070.

N-(4-Fluorobenzyl)-2-(4-fluorophenyl)-4-phenylquinolin-6-amine (**4f**): Yield 27%; Yellow solid; mp 172-174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.4, 5.6 Hz, 2H), 8.08 (d, J = 9.1 Hz, 1H), 7.65 (s, 1H), 7.53 – 7.36 (m, 5H), 7.27 (dd, J = 8.2, 5.4 Hz, 2H), 7.24 – 7.12 (m, 3H), 7.03 (t, J = 8.6 Hz, 2H), 6.77 (d, J = 2.1 Hz, 1H), 4.46 (s, 1H), 4.29 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.20, 147.40, 146.13, 143.89, 139.33, 136.33, 134.78, 131.30, 129.58, 129.27, 128.82, 128.35, 127.61, 121.36, 119.48, 115.92, 115.63, 102.91, 47.97. HRMS calcd for $C_{28}H_{21}F_2N_2$ 423.1667 $[M + H]^+$, found 423.1653.

N-(3-Nitrobenzyl)-2-(3-nitrophenyl)-4-phenylquinolin-6-amine (**4g**): Yield 48%; Yellow solid; mp 188-190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.61 (s, 1H), 8.32 (d, J = 8.2 Hz, 1H), 8.17 (s, 2H), 7.81 – 7.62 (m, 4H), 7.61 – 7.40 (m, 5H), 7.38 – 7.31 (m, 2H), 6.66 (s, 1H), 4.48 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.39, 149.20, 146.34, 141.39, 138.52, 133.34, 131.00, 129.95, 129.90, 129.66, 129.36, 128.91, 128.29, 123.80, 122.67, 122.43, 122.28, 119.43, 102.92, 47.91. HRMS calcd for $C_{28}H_{21}N_4O_4$ 477.1557 $[M + H]^+$, found 477.1575.

N-(4-Nitrobenzyl)-2-(4-nitrophenyl)-4-phenylquinolin-6-amine (**4h**): Yield 38%; Purple solid; mp 159-162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 – 8.24 (m, 5H), 8.18 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.71 (s, 1H), 7.53 – 7.37 (m, 4H), 7.33 (d, J = 7.0 Hz, 2H), 7.26 (dd, J = 9.7, 3.0 Hz, 2H), 6.64 (d, J = 2.2 Hz, 1H), 4.84 (s, 1H), 4.47 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.49, 148.44, 147.81, 146.62, 146.25, 145.75, 144.01, 138.71, 131.77, 129.41, 128.93, 128.68, 128.17, 128.08, 124.20, 121.84, 119.70, 102.95, 48.02. HRMS calcd for $C_{28}H_{21}N_4O_4$ 477.1557 $[M + H]^+$, found 477.1534.

N-Benzyl-4-(4-butylphenyl)-2-phenylquinolin-6-amine (**4i**): Yield 57%; Yellow solid; mp 129-131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 3H), 7.70 (s, 1H), 7.52 (t, J = 7.2 Hz, 2H), 7.45 (d, J = 7.2 Hz, 1H), 7.42 – 7.14

(m, 10H), 6.87 (d, *J* = 2.3 Hz, 1H), 4.51 (s, 1H), 4.35 (s, 2H), 2.78 – 2.71 (m, 2H), 1.80 – 1.64 (m, 2H), 1.56 – 1.37 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.23, 147.27, 146.25, 143.12, 140.39, 139.26, 136.74, 131.41, 129.55, 128.92, 128.84, 127.84, 127.52, 121.11, 119.79, 103.06, 48.70, 35.75, 33.78, 22.68, 14.11. HRMS calcd for $C_{32}H_{31}N_2$ 443.2482 $[M + H]^+$, found 443.2473.

4-(4-Butylphenyl)-*N*-(3-nitrobenzyl)-2-(3-nitrophenyl)quinolin-6-amine (**4j**): Yield 39%; Orange solid; mp 189-190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.60 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.19 (s, 1H), 8.17 (s, 1H), 7.77 – 7.61 (m, 3H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.40 – 7.20 (m, 6H), 6.74 (d, *J* = 2.2 Hz, 1H), 4.50 (s, 2H), 2.77 – 2.70 (m, 2H), 1.82 – 1.62 (m, 2H), 1.55 – 1.40 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.54, 149.46, 149.28, 148.03, 146.00, 144.10, 143.73, 141.85, 141.59, 136.01, 133.28, 133.04, 131.71, 129.78, 129.34, 128.88, 128.22, 123.43, 122.59, 122.43, 122.24, 121.64, 119.25, 103.28, 47.94, 35.65, 33.70, 22.66, 14.06. HRMS calcd for $C_{32}H_{29}N_4O_4$ 533.2183 $[M + H]^+$, found 533.2169.

N-Benzyl-4-(4-pentylphenyl)-2-phenylquinolin-6-amine (**4k**): Yield 32%; Brown solid; mp 120-122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.00 (m, 3H), 7.71 (s, 1H), 7.52 (t, *J* = 6.7 Hz, 2H), 7.47 – 7.41 (m, 1H), 7.42 – 7.26 (m, 8H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.88 (s, 1H), 4.46 (s, 1H), 4.34 (s, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 1.75 (br, 2H), 1.44 (br, 4H), 0.99 (br, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.20, 147.30, 146.25, 143.96, 143.18, 140.32, 139.24, 136.70, 131.35, 129.55, 128.93, 128.85, 127.84, 127.53, 121.15, 119.82, 103.02, 48.68, 36.06, 31.90, 31.29, 22.81, 14.20. HRMS calcd for $C_{33}H_{33}N_2$ 457.2638 $[M + H]^+$, found 457.2634.

N-(4-Methylbenzyl)-4-(4-pentylphenyl)-2-p-tolylquinolin-6-amine (**4l**): Yield 32%; Yellow solid; mp 171-173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 – 8.02 (m, 3H), 7.70 (s, 1H), 7.39 – 7.24 (m, 8H), 7.18 (d, *J* = 5.0 Hz, 2H), 7.10 (d, *J* = 3.1 Hz, 1H), 6.84 (s, 1H), 4.89 (s, 1H), 4.30 (s, 2H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H), 1.83 – 1.68 (m, 2H), 1.53 – 1.31 (m, 4H), 0.96 (t, *J* = 5.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.11, 146.23, 143.20, 138.93, 137.23, 136.70, 136.13, 131.12, 129.72, 129.61, 128.83, 127.89, 127.72, 127.44, 121.18, 119.74, 102.93, 48.43, 36.09, 31.92, 31.34, 22.85, 21.51, 21.33, 14.26. HRMS calcd for $C_{35}H_{37}N_2$ 485.2951 $[M + H]^+$, found 485.2957.

N-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-4-(4-pentylphenyl)-quinolin-6-amine(**4m**): Yield 42%; Yellow solid; mp 149-150 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.69 (s, 1H), 7.38 – 7.23 (m, 5H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 3H), 6.63 (s, 1H), 4.15 (s, 2H), 3.81 (s, 3H), 3.73 (s, 3H), 2.69 (t, *J* = 7.1 Hz, 2H), 1.76 – 1.58 (m, 2H), 1.47 – 1.27 (m, 4H), 1.00 – 0.83 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.77, 159.12, 151.28, 147.30, 146.14, 143.39, 143.05, 136.72, 132.81, 132.20, 130.93, 129.86, 129.21, 128.70, 127.39, 122.06, 118.78, 114.94, 114.63, 101.64, 56.10, 55.98, 47.06, 35.71, 31.72, 31.23, 22.71, 14.59. HRMS calcd for $C_{35}H_{37}N_2O_2$ 517.2850 $[M + H]^+$, found 517.2831.

N-(4-Chlorobenzyl)-2-(4-chlorophenyl)-4-(4-pentylphenyl)-quinolin-6-amine (**4n**): Yield 34%; Orange solid; mp 163-165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 3H), 7.65 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.14 (m, 9H), 6.76 (s, 1H), 4.56 (s, 1H), 4.31 (d, *J* = 3.0 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 1.82 – 1.65 (m, 2H), 1.52 – 1.34 (m, 4H), 0.97 (t, *J* = 5.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.83, 146.09, 143.42, 137.62, 136.32, 135.26,

133.41, 131.13, 129.43, 129.12, 129.00, 128.88, 128.79, 127.86, 121.47, 119.49, 103.13, 47.99, 36.06, 31.90, 31.32, 22.83, 14.24. HRMS calcd for $C_{33}H_{31}Cl_2N_2$ 525.1859 $[M + H]^+$, found 525.1839.

N-(4-Fluorobenzyl)-2-(4-fluorophenyl)-4-(4-pentylphenyl)-quinolin-6-amine (**4o**): Yield 37%; Yellow solid; mp 146-148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 – 8.09 (m, 2H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.65 (s, *J* = 1.4 Hz, 1H), 7.40 – 7.23 (m, 6H), 7.23 – 7.13 (m, 3H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.82 (s, 1H), 4.46 (s, 1H), 4.30 (s, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 1.85 – 1.70 (m, 2H), 1.55 – 1.33 (m, 4H), 0.98 (t, *J* = 5.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.29, 147.39, 146.01, 144.01, 143.31, 136.54, 134.85, 131.35, 129.50, 129.40, 129.29, 129.18, 128.86, 127.68, 121.23, 119.51, 115.90, 115.68, 103.08, 47.98, 36.06, 31.91, 31.35, 22.84, 14.24. HRMS calcd for $C_{33}H_{31}F_2N_2$ 493.2450 $[M + H]^+$, found 493.2460.

N-(3-Nitrobenzyl)-2-(3-nitrophenyl)-4-(4-pentylphenyl)quinolin-6-amine (**4p**): Yield 48%; Orange solid; mp 169-170 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.03 (s, 1H), 8.65 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 6.5 Hz, 1H), 8.19 – 8.09 (m, 2H), 7.95 (d, *J* = 9.1 Hz, 1H), 7.90 (s, 1H), 7.81 – 7.68 (m, 2H), 7.63 (t, *J* = 8.1 Hz, 1H), 7.39 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.28 – 7.07 (m, 4H), 6.52 (d, *J* = 1.9 Hz, 1H), 4.43 (d, *J* = 3.1 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.55 (m, 2H), 1.46 – 1.23 (m, 4H), 0.91 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.46, 149.36, 149.18, 148.09, 146.01, 143.92, 143.82, 141.70, 141.56, 135.93, 133.37, 133.14, 131.58, 129.85, 129.35, 128.90, 128.20, 123.52, 122.63, 122.45, 122.28, 121.76, 119.33, 103.16, 47.87, 35.98, 31.89, 31.27, 22.81, 14.23. HRMS calcd for $C_{33}H_{31}N_4O_4$ 547.2340 $[M + H]^+$, found 547.2362.

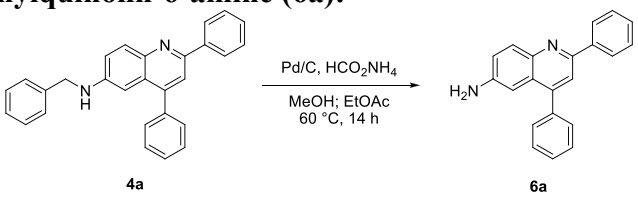
N-Benzyl-4-(4-methoxyphenyl)-2-phenylquinolin-6-amine (**4q**): Yield 61%; Orange solid; mp 135-137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.5 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.69 (s, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 6.3 Hz, 1H), 7.40 (s, *J* = 0.9 Hz, 1H), 7.39 – 7.27 (m, 6H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.87 (s, 1H), 4.46 (s, 1H), 4.34 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.01, 153.23, 146.89, 146.23, 143.98, 140.33, 139.21, 131.79, 131.37, 130.85, 128.96, 127.86, 127.52, 121.23, 119.81, 114.46, 102.87, 55.69, 48.65. HRMS calcd for $C_{29}H_{25}N_2O$ 417.1961 $[M + H]^+$, found 417.1973.

4-(4-Methoxyphenyl)-*N*-(4-methylbenzyl)-2-p-tolylquinolin-6-amine (**4r**): Yield 38%; Orange solid; mp 188-190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 3H), 7.66 (s, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.09 (m, 5H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 2.4 Hz, 1H), 4.41 (s, 1H), 4.29 (s, 2H), 3.93 (s, 3H), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.11, 152.84, 147.27, 146.36, 139.13, 137.26, 136.06, 131.70, 130.85, 129.75, 129.63, 127.86, 127.56, 121.41, 119.75, 114.47, 102.83, 55.68, 48.42, 21.48, 21.28. HRMS calcd for $C_{31}H_{29}N_2O$ 445.2274 $[M + H]^+$, found 445.2272.

4-(4-Methoxyphenyl)-*N*-(3-nitrobenzyl)-2-(3-nitrophenyl)-quinolin-6-amine (**4s**): Yield 52%; Yellow solid; mp 143-145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.54 (d, *J* = 7.6 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.23 – 8.09 (m, 3H), 7.80 – 7.62 (m, 3H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 3H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.73 (s, 1H), 4.92 (s, 1H), 4.49 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.44, 150.22, 149.38, 149.18, 148.16, 146.18, 143.45, 141.51, 133.40, 133.29, 131.20, 130.81, 130.66, 129.90, 128.38, 123.68, 122.64, 122.46, 122.37,

122.08, 119.37, 114.53, 103.02, 55.70, 47.88. HRMS calcd for $C_{29}H_{23}N_4O_5$ 507.1663 $[M + H]^+$, found 507.1658.

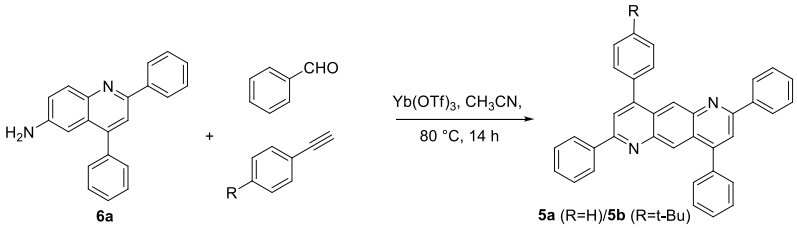
Synthesis of 2,4-diphenylquinolin-6-amine (6a):



To a slurry of compound **4a** (1 mmol), ammonium formate (5 mmol) in methanol (2 mL) and ethyl acetate (2 mL) was added Pd/C (10% wt). The reaction mass was allowed to stir at 60 °C for 14 h. After completion of reaction, the reaction mass was filtered off through celite pad and washed with ethyl acetate. The organic solvents were removed under vacuum on rotary evaporator and crude compound was purified by column chromatography over silica gel using EtOAc/hexanes to afford **6a**.

2,4-Diphenylquinolin-6-amine(**6a**): Yield 92%; Yellow solid; mp 140-142 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 – 8.03 (m, 3H), 7.73 (s, 1H), 7.63 – 7.35 (m, 8H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.00 (s, 1H), 3.99 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.63, 147.29, 145.12, 144.11, 140.14, 139.43, 131.59, 129.75, 128.98, 128.82, 128.40, 127.56, 121.82, 119.85, 106.05. HRMS calcd for $C_{21}H_{17}N_2$ 297.1386 $[M + H]^+$, found 297.1394.

General procedure for the synthesis of anthrazolines (5a & 5b):



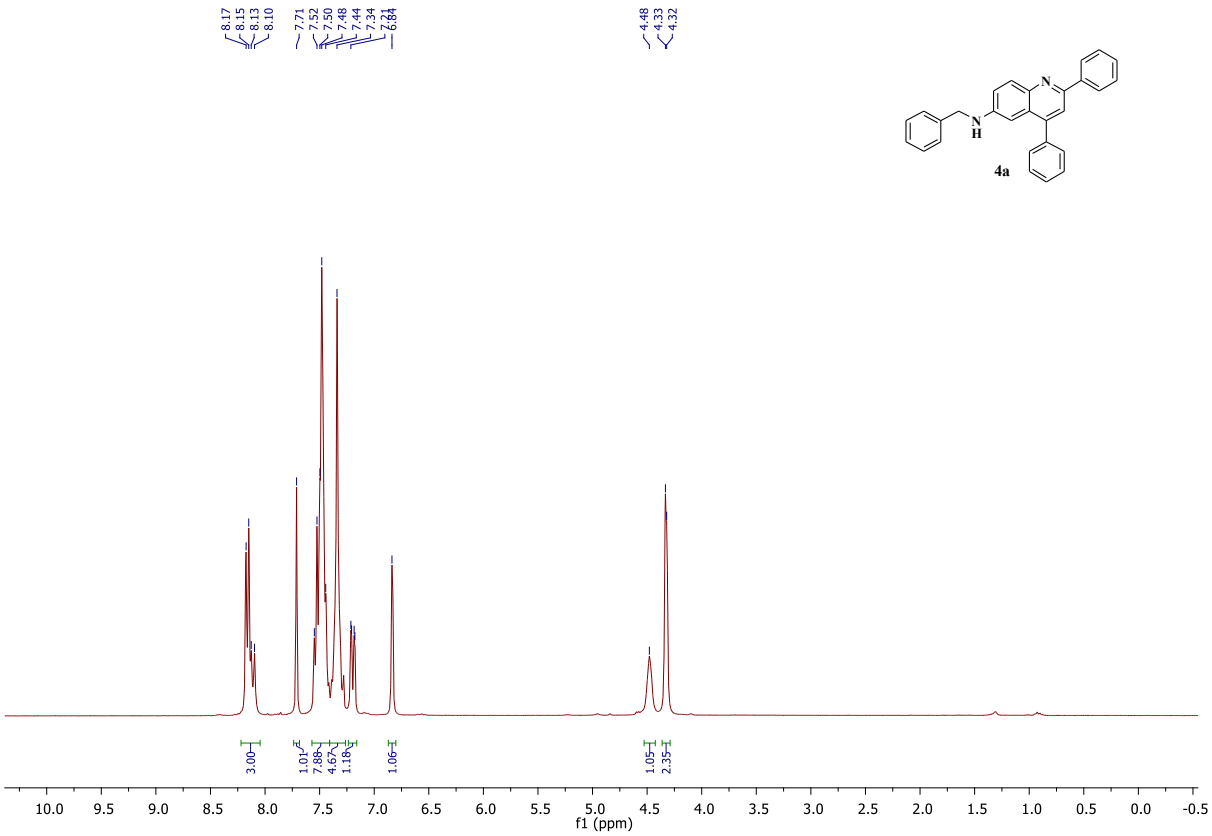
A mixture of **6a** (1.0 mmol), benzaldehyde/4-tolualdehyde (1.1 mmol), phenylacetylene/4-*t*-butylphenylacetylene (1.1 mmol) and ytterbium triflate (0.05 mmol) in acetonitrile (3 ml) was stirred at 80°C for 14 h. The volatiles were evaporated and the residue was diluted with water (10 mL), extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated *in vacuo* and the crude compound obtained was purified by column chromatography (EtOAc/hexanes) to afford **5a**/**5b**.

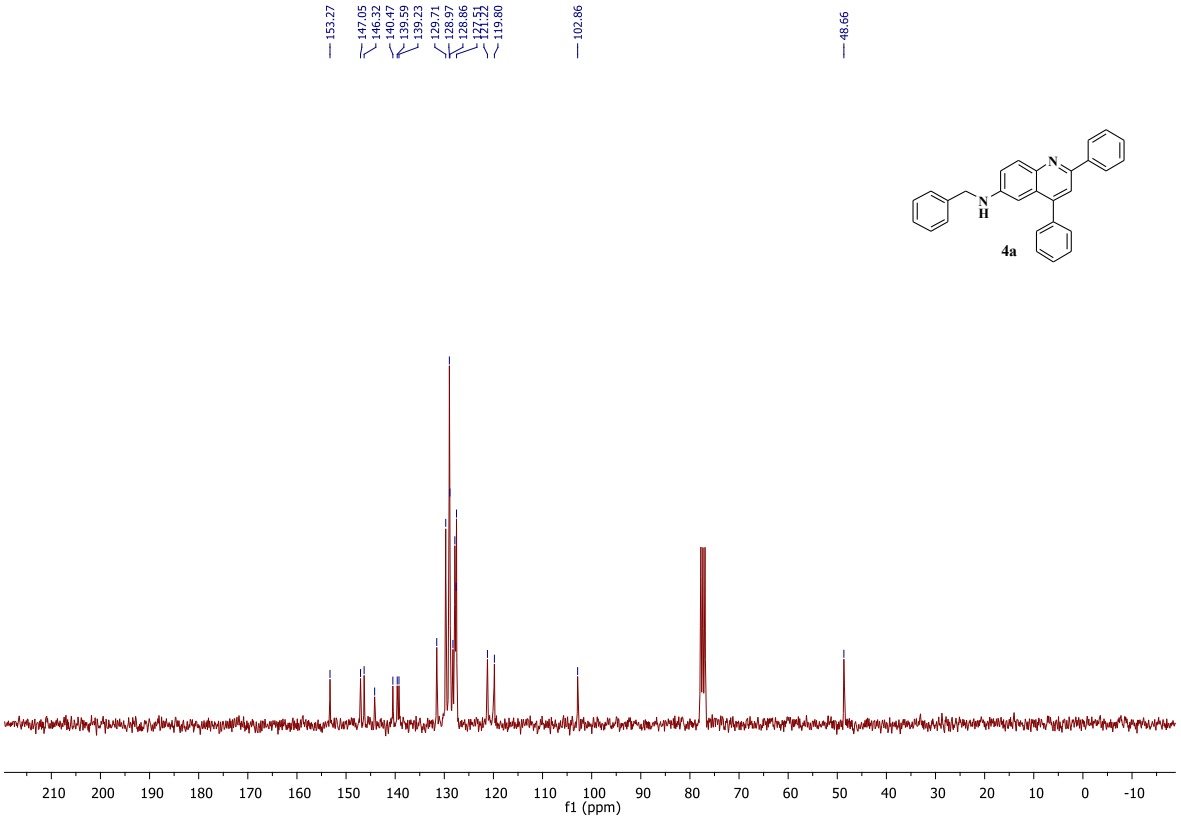
2,4,7,9-Tetraphenylpyrido[2,3-g]quinoline (**5a**): Yield 62%; Yellow solid; mp 259-261 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 2H), 8.27 (d, *J* = 7.2 Hz, 4H), 7.63 – 7.43 (m, 8H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.08 (s, 4H), 6.71 (br, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.85, 150.77, 150.43, 141.91, 139.18, 132.98, 129.81, 129.12, 127.72, 127.42, 122.25, 120.13. HRMS calcd for $C_{36}H_{25}N_2$ 485.2012 $[M + H]^+$, found 485.2029.

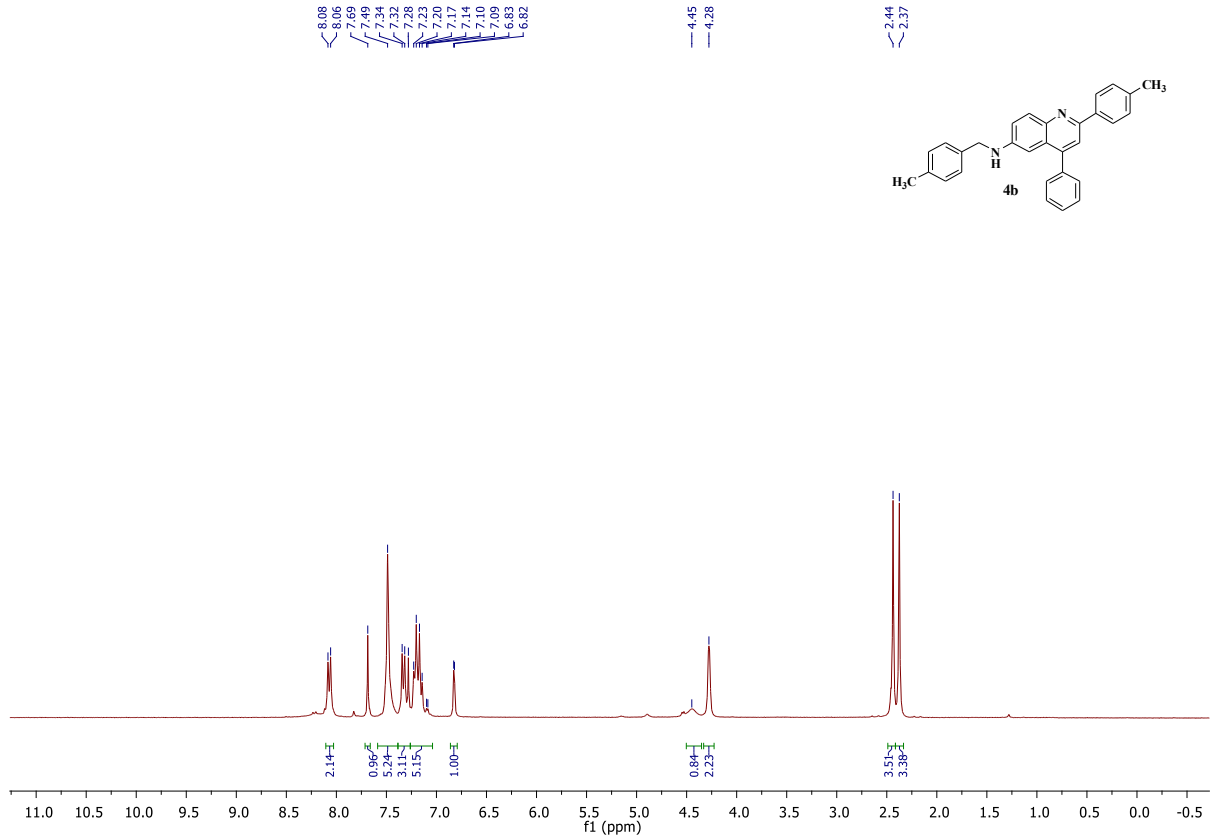
4-(4-*tert*-Butylphenyl)-7,9-diphenyl-2-p-tolylpyrido[2,3-g]quinoline (**5b**): Yield 48%; White solid; mp 254-255 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 – 8.22 (m, 4H), 8.17 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.41 (m, 5H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.08 (dd, *J* = 15.6, 7.8 Hz, 4H), 6.77 (d, *J* = 6.0 Hz, 1H), 6.68 (s, 1H), 6.60 (s, 2H), 2.47 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.74, 156.63, 150.72, 150.52, 150.28, 142.06, 139.89, 139.27, 139.06, 136.41, 132.86, 129.85, 129.75, 129.11, 127.70, 127.60, 127.31, 122.40, 122.17, 120.11, 119.79,

34.85, 31.64, 21.60. HRMS calcd for $C_{41}H_{35}N_2$ 555.2795 $[M + H]^+$, found 555.2770.

^{1}H NMR & ^{13}C NMR spectra of compounds **4a-s**, **5a** & **6a,b**



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6.82
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4.28
2.44
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N
H
H3C
4b
2.14
0.96
5.24
3.11
5.15
1.00
0.84
2.23
3.51
3.38
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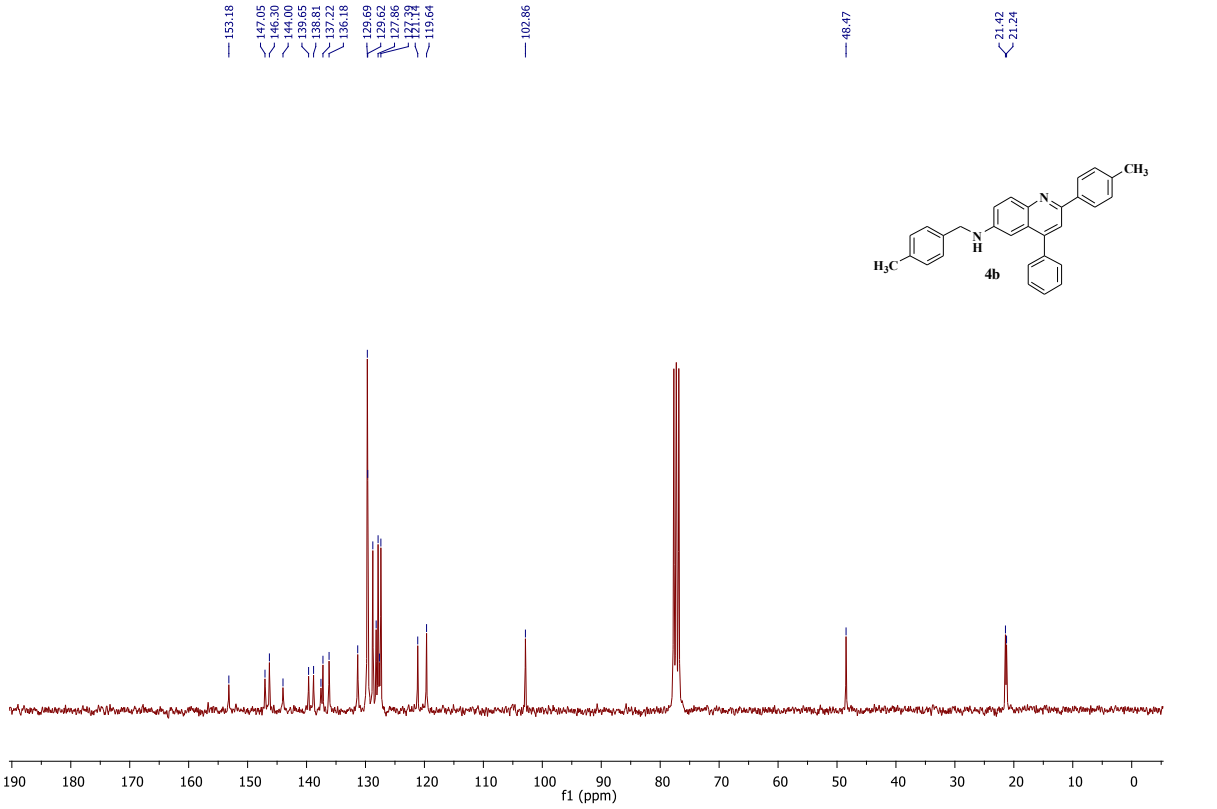
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H
H3C
4b
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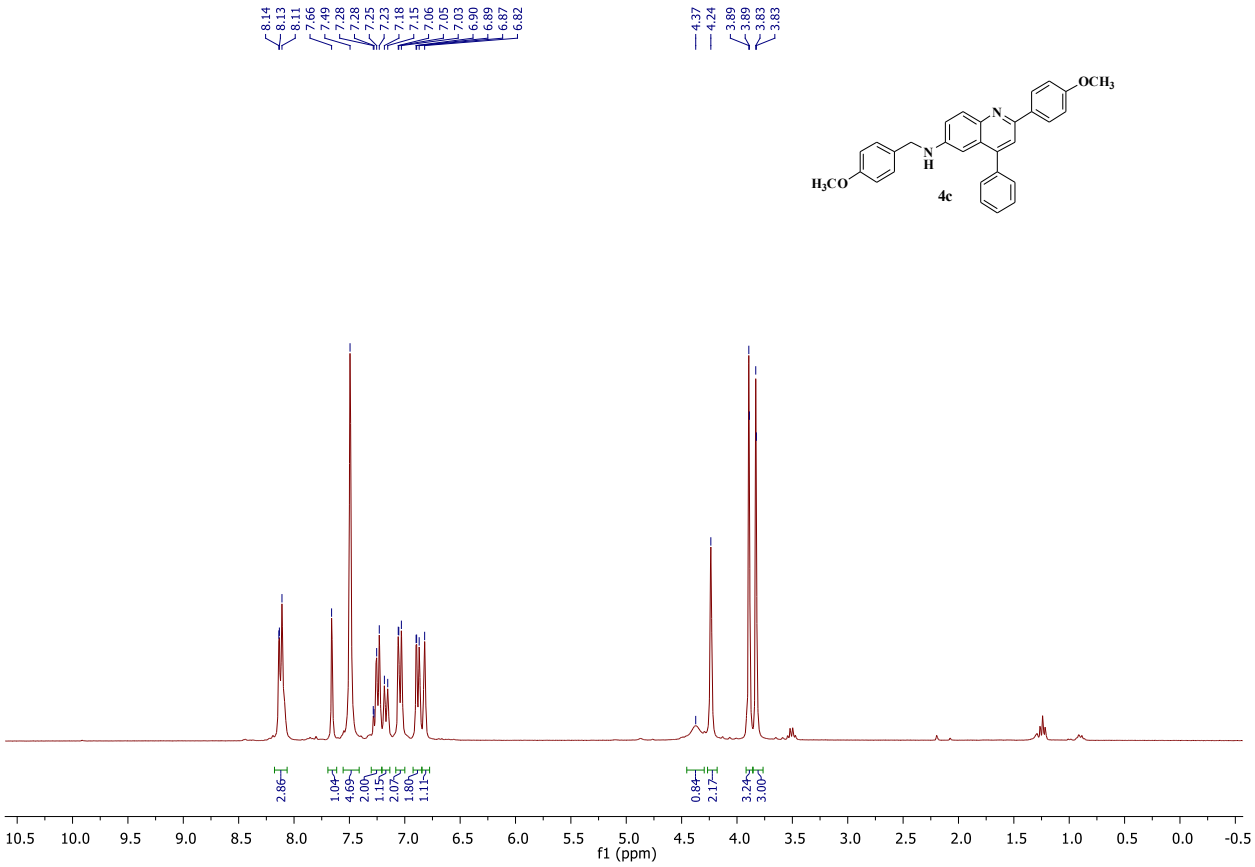
f1 (ppm)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H
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4c
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4.69
2.00
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2.07
1.80
1.11
0.84
2.17
3.24
3.00
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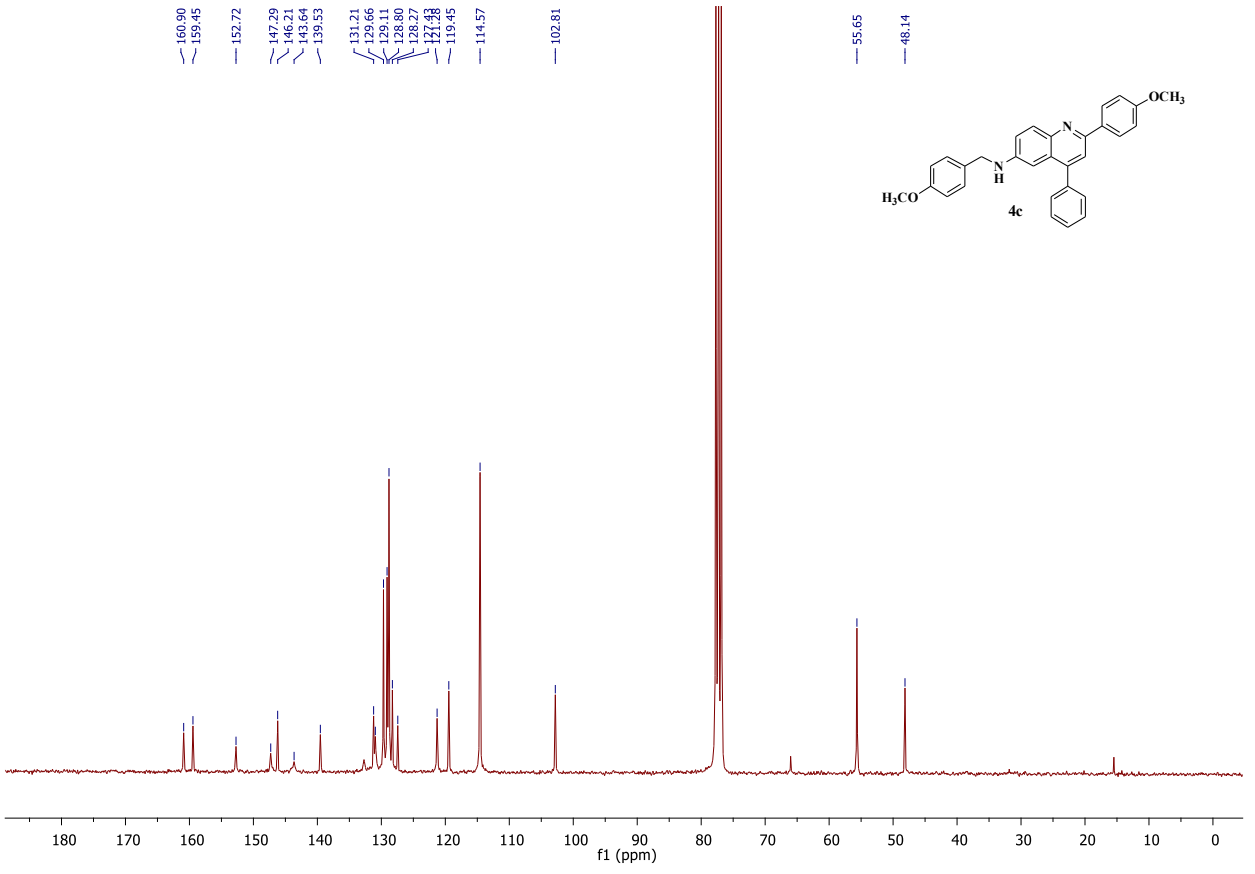
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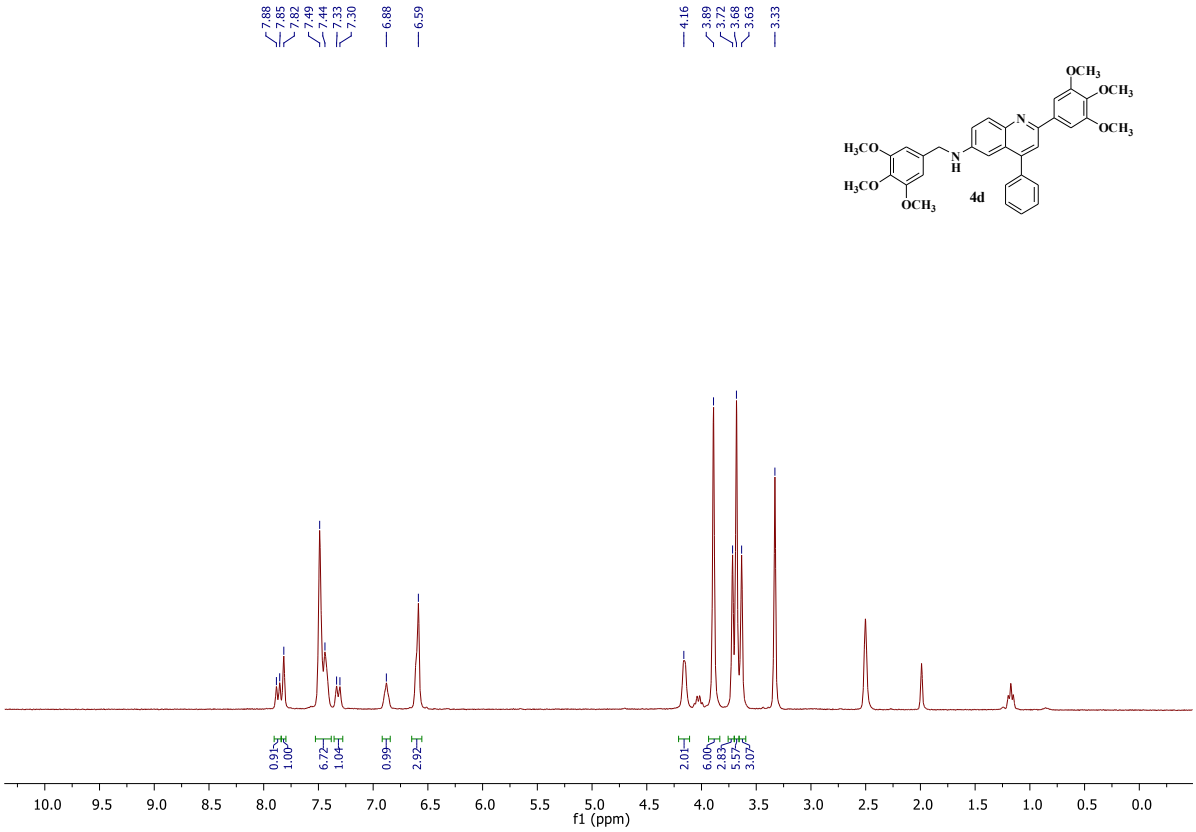
f1 (ppm)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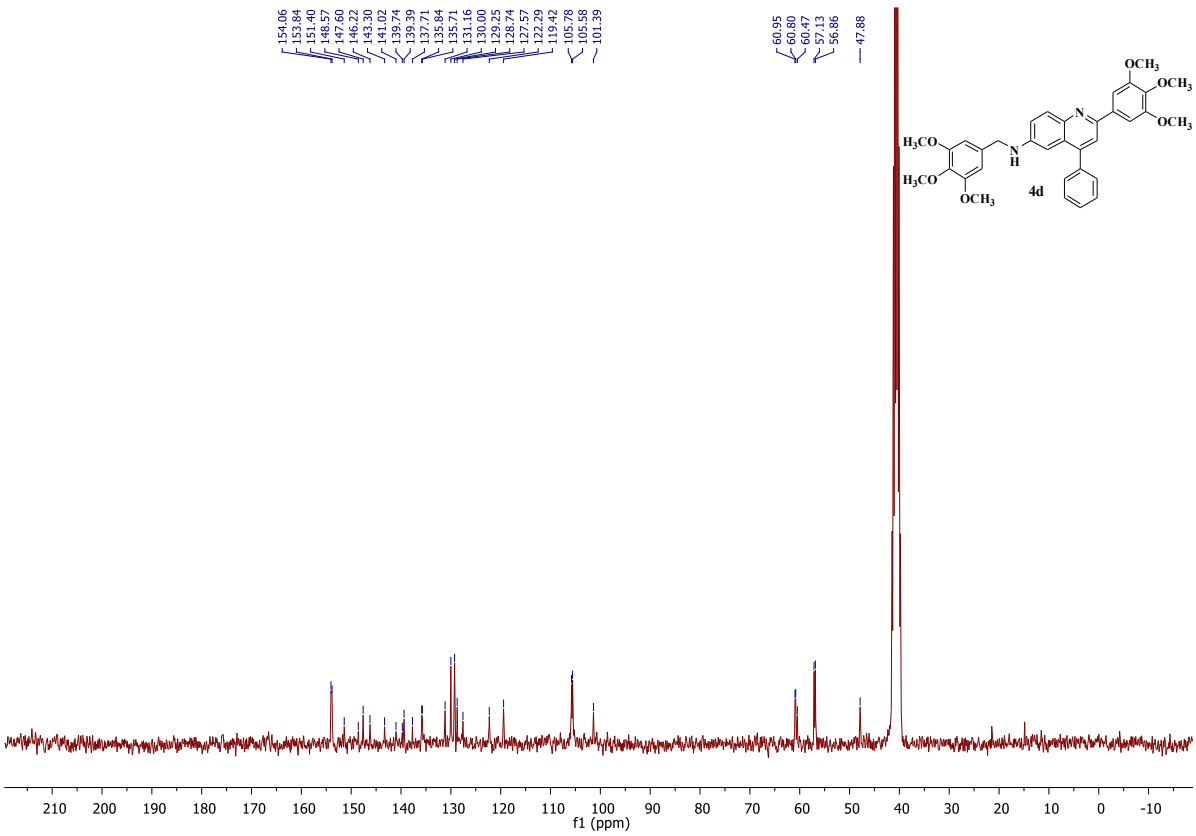
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129.25
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127.57
122.29
119.42
105.78
105.58
101.39
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60.47
57.13
56.86
47.88
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OCH3
OCH3
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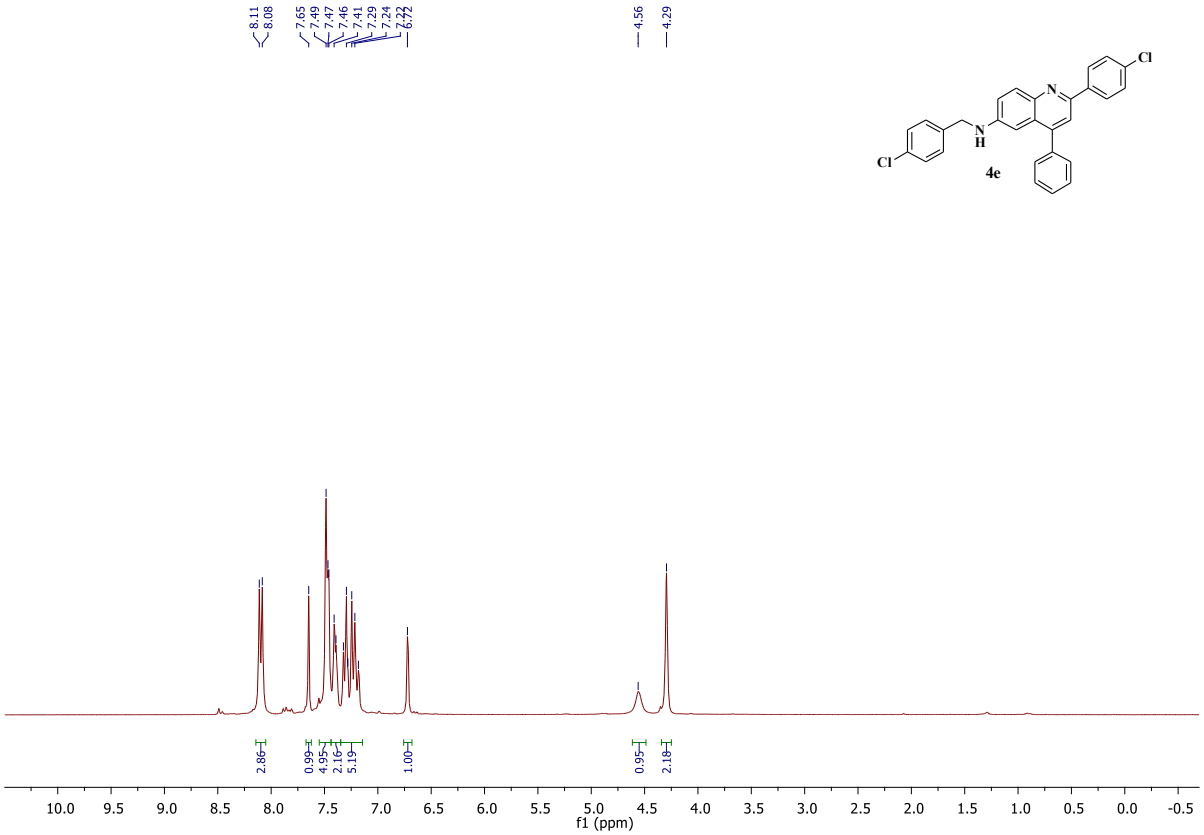
f1 (ppm)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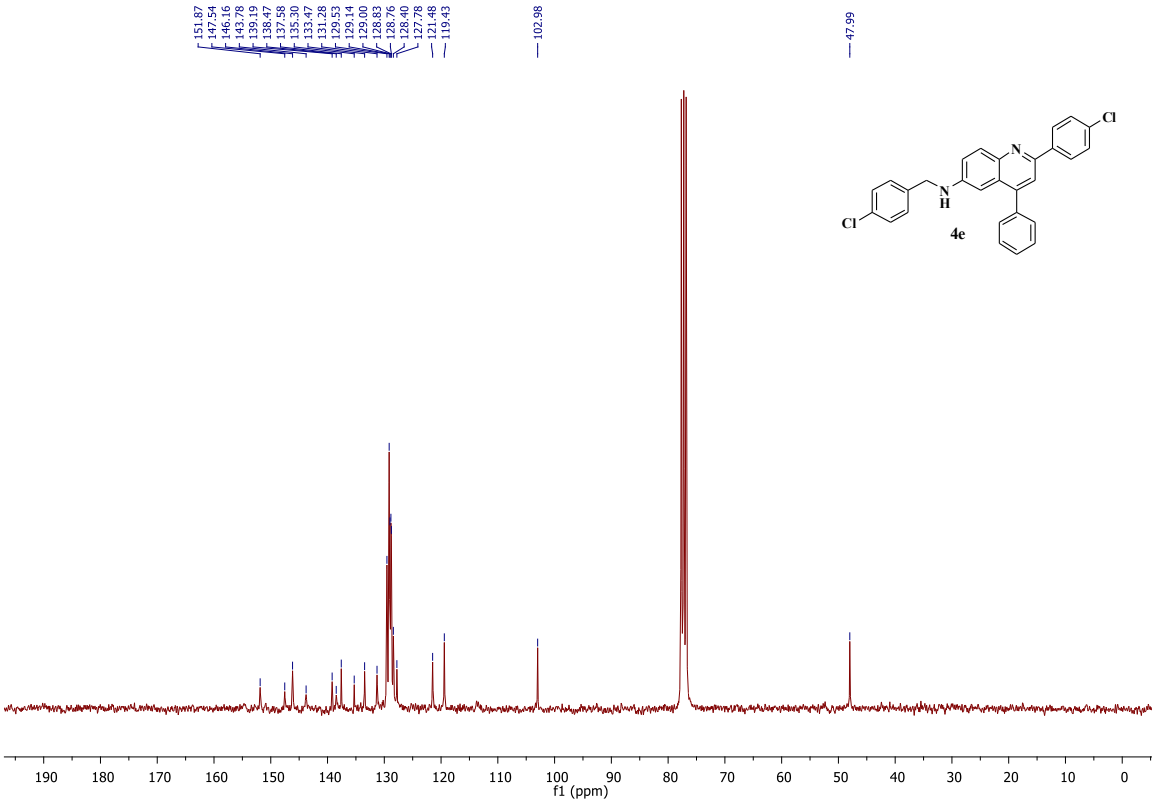
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Cl
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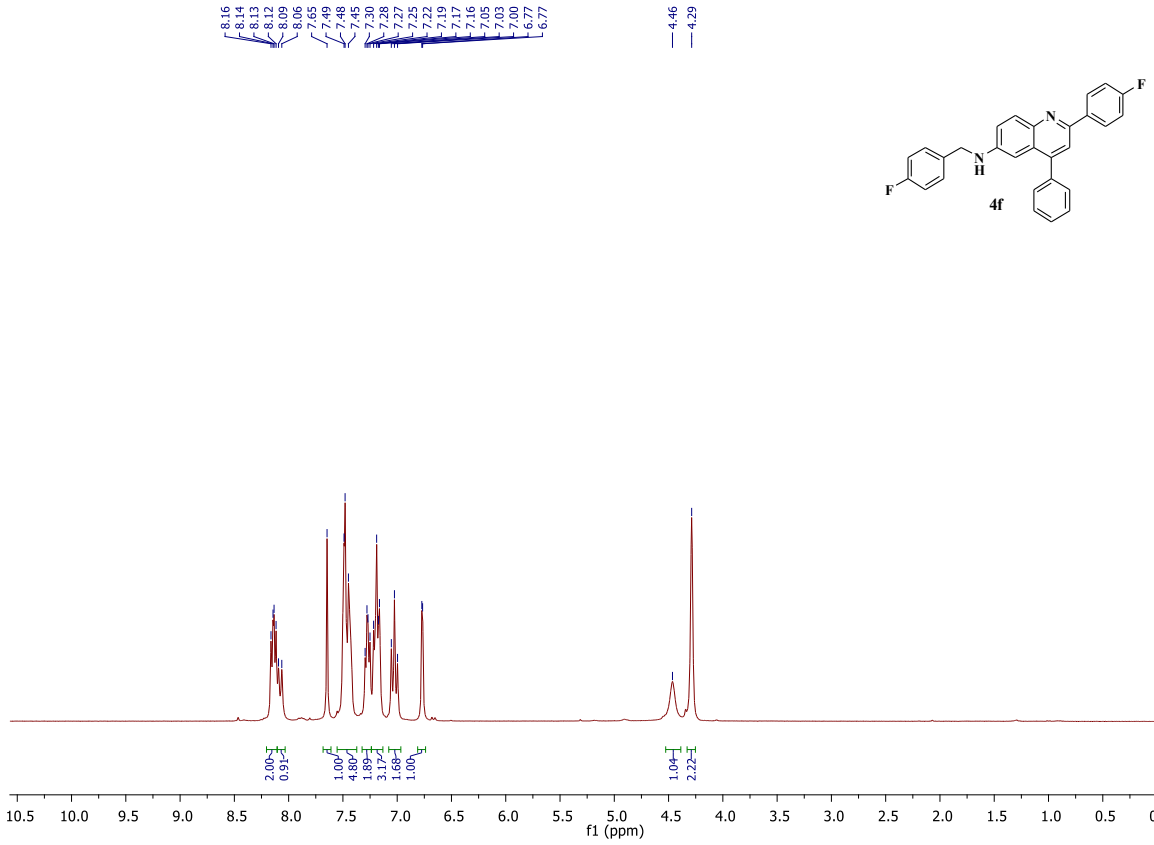
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1.00
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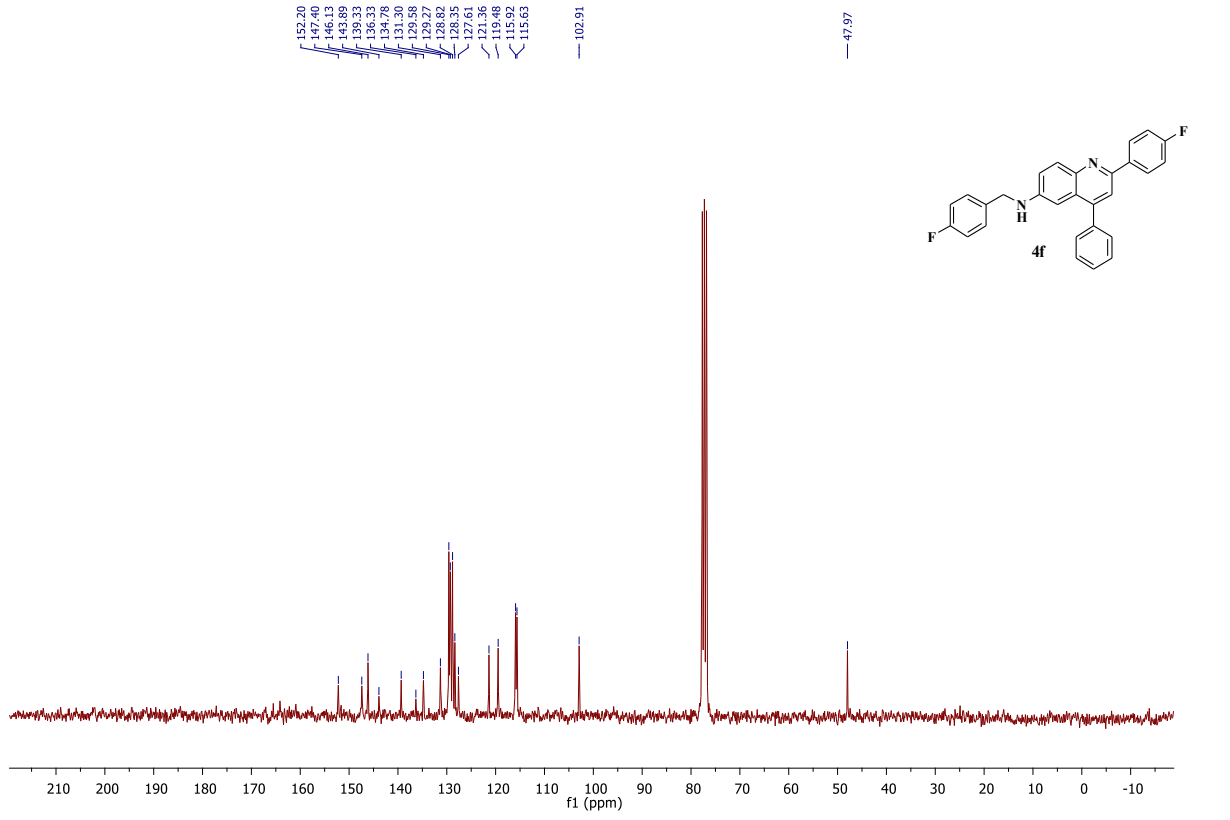
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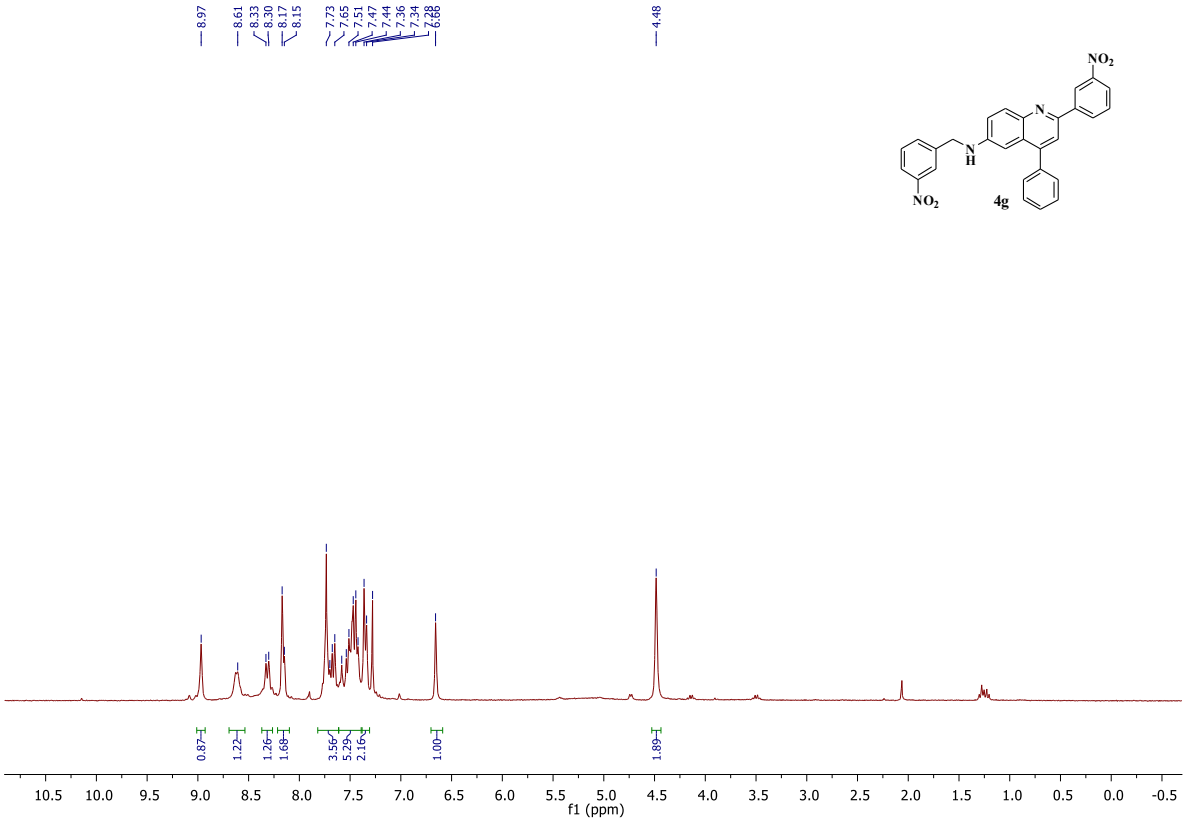
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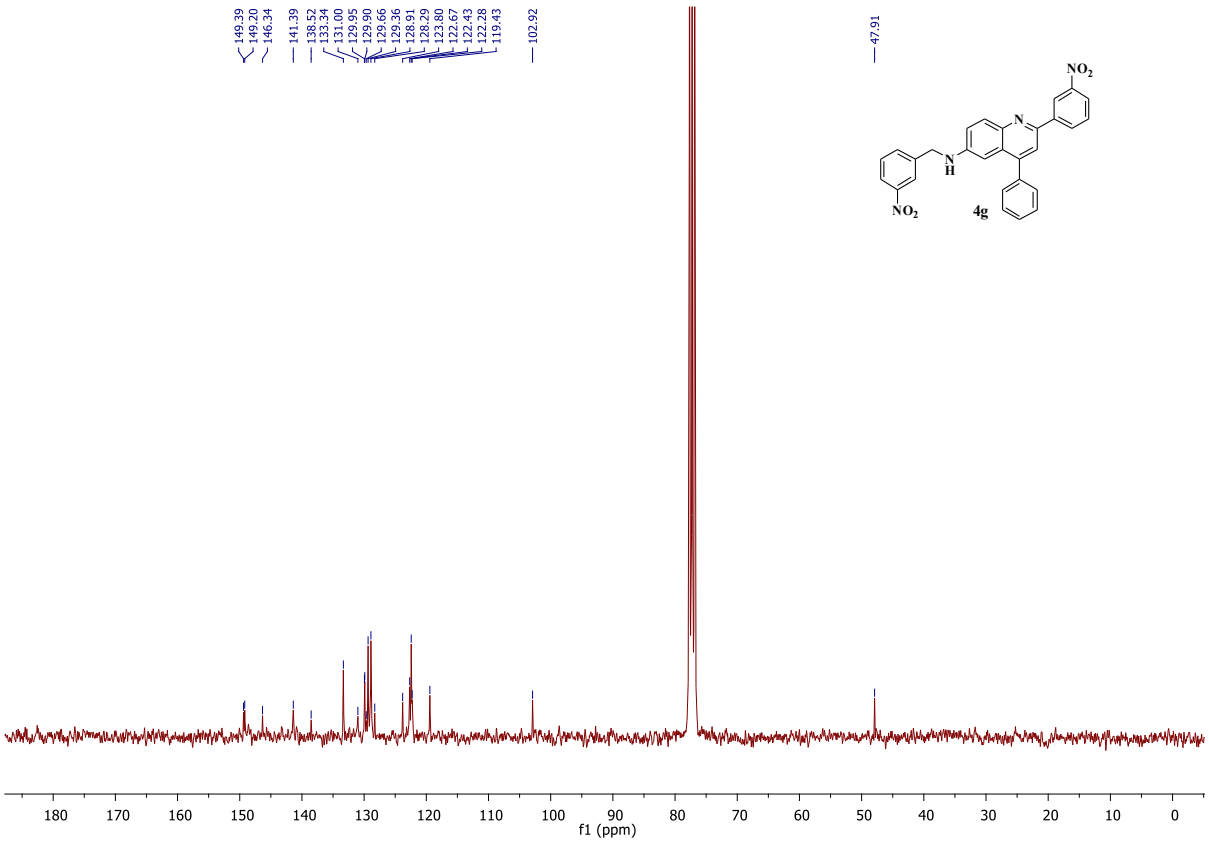
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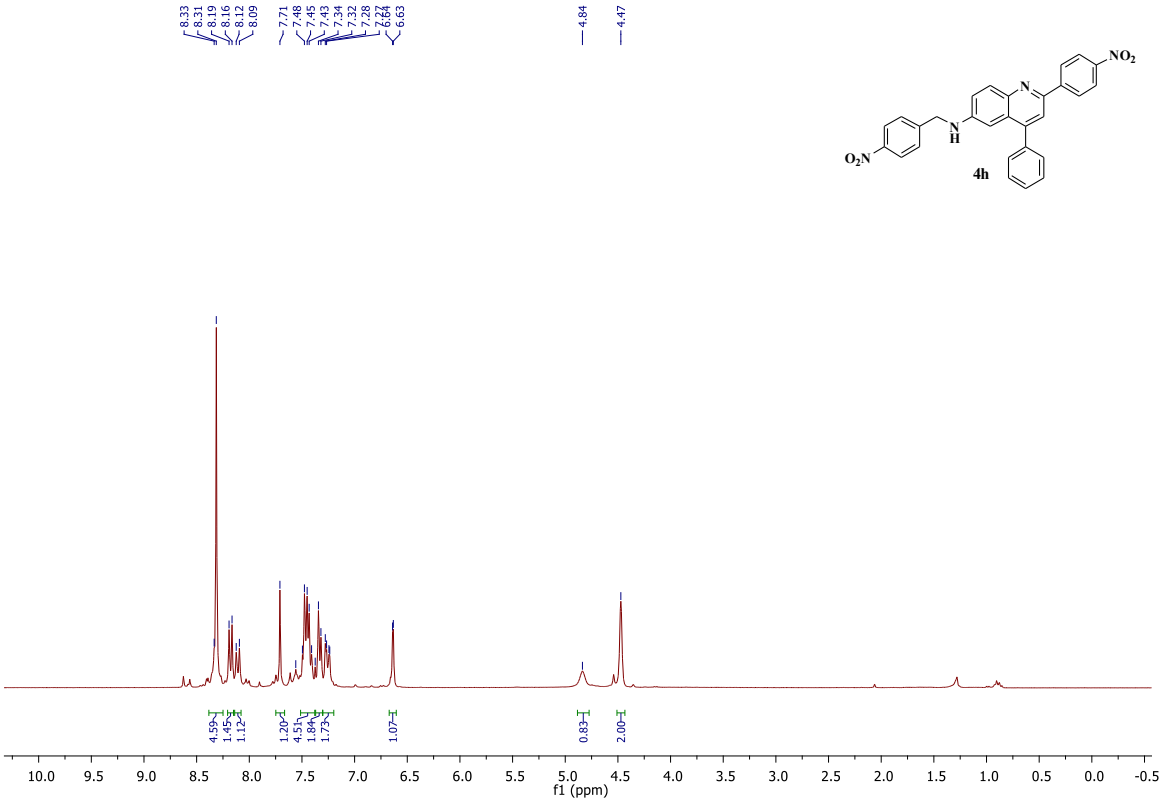
f1 (ppm)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O2N
4h
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1.12
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1.73
1.07
0.83
2.00
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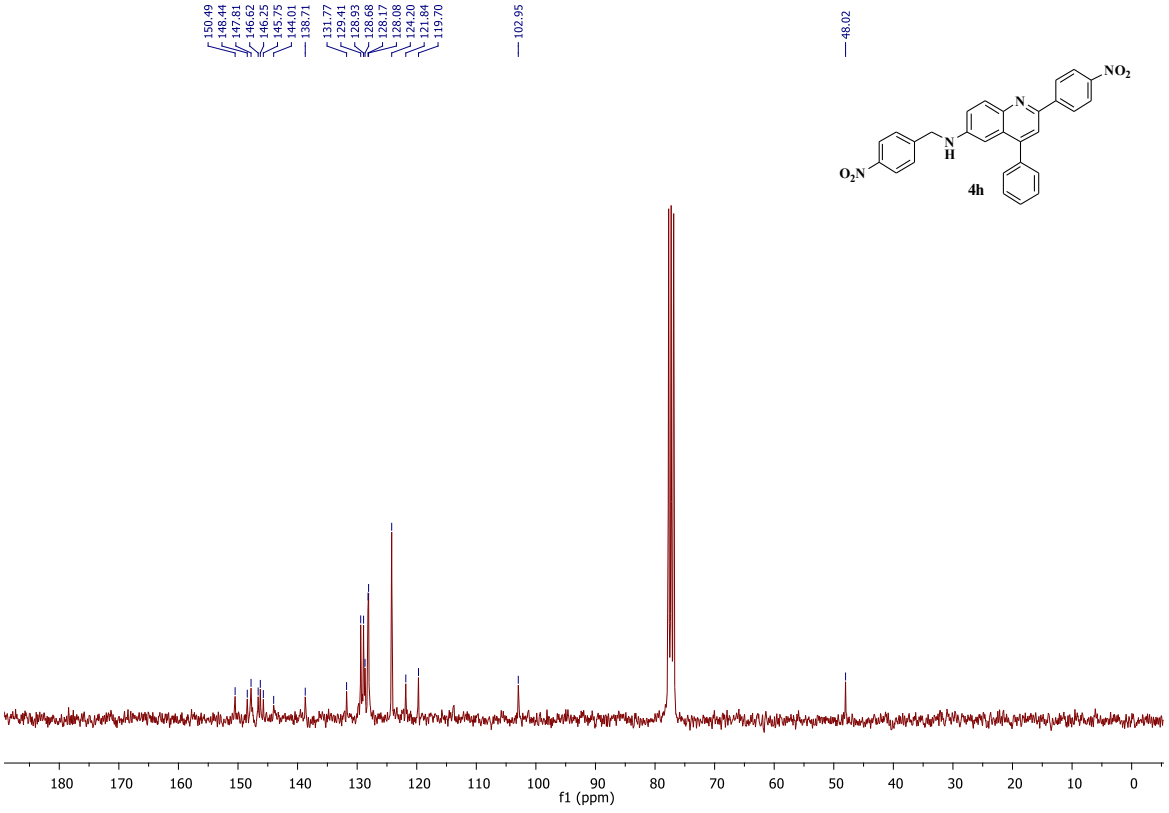
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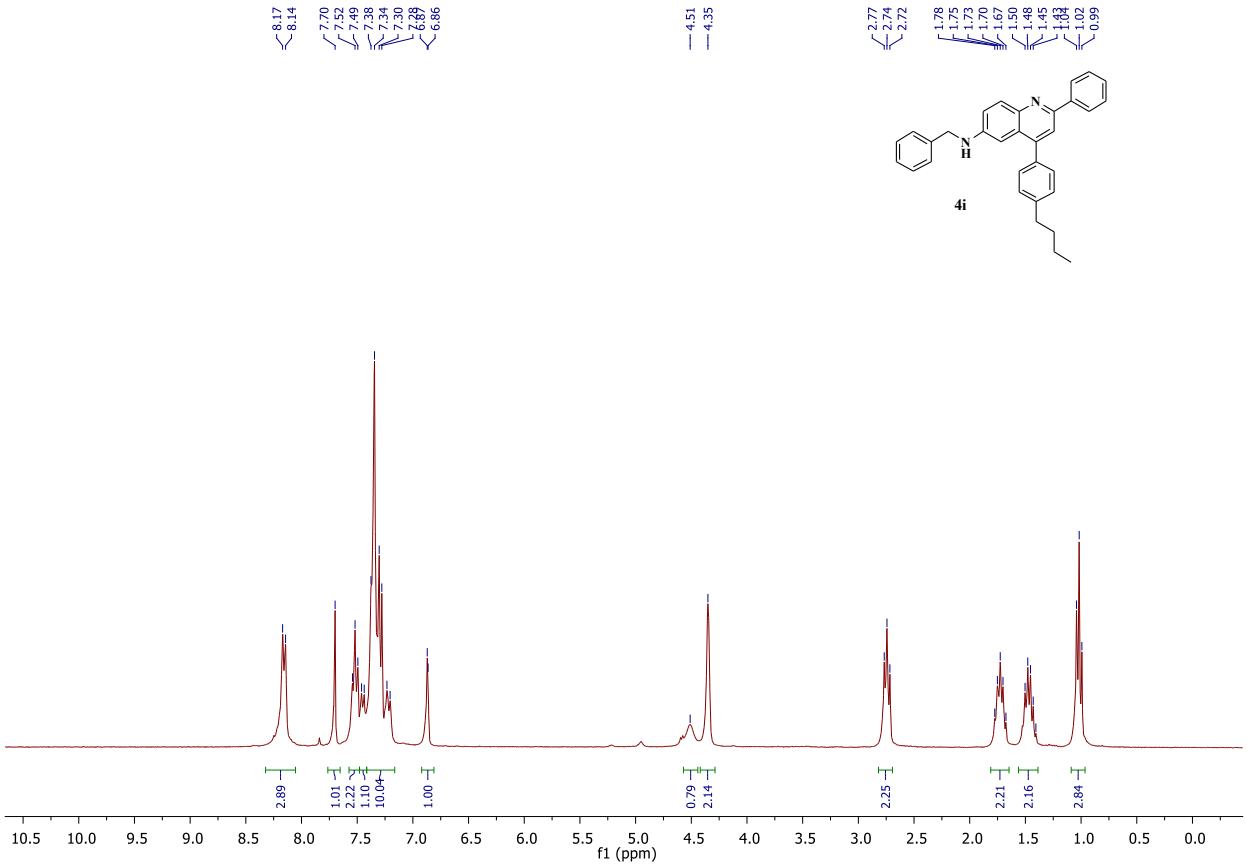
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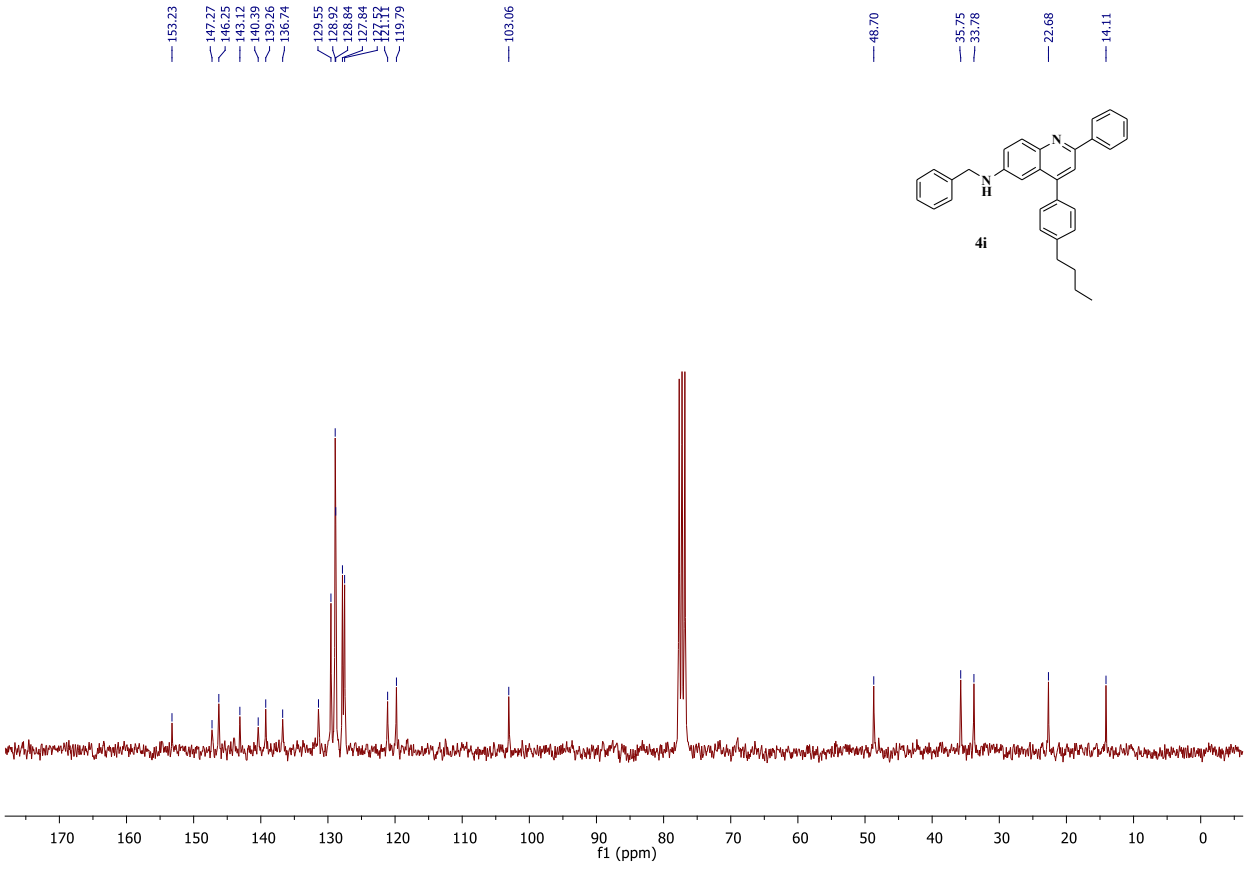
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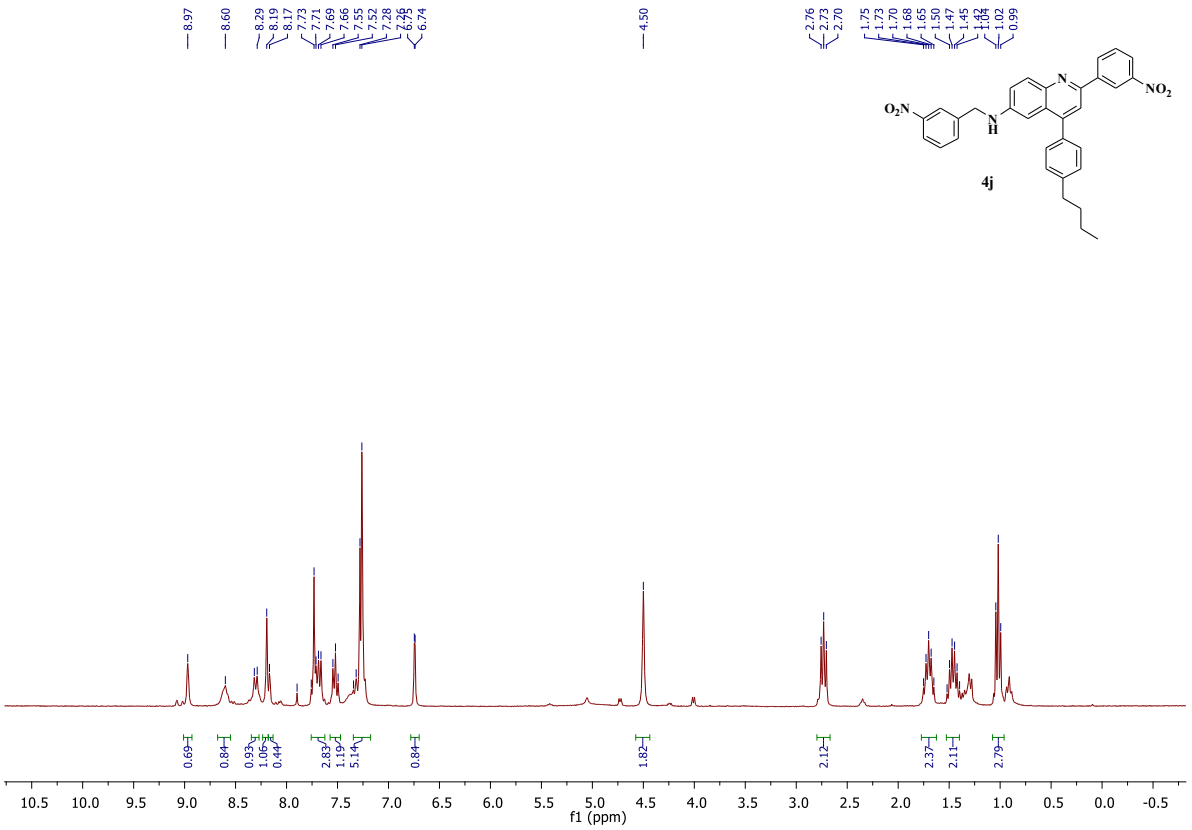
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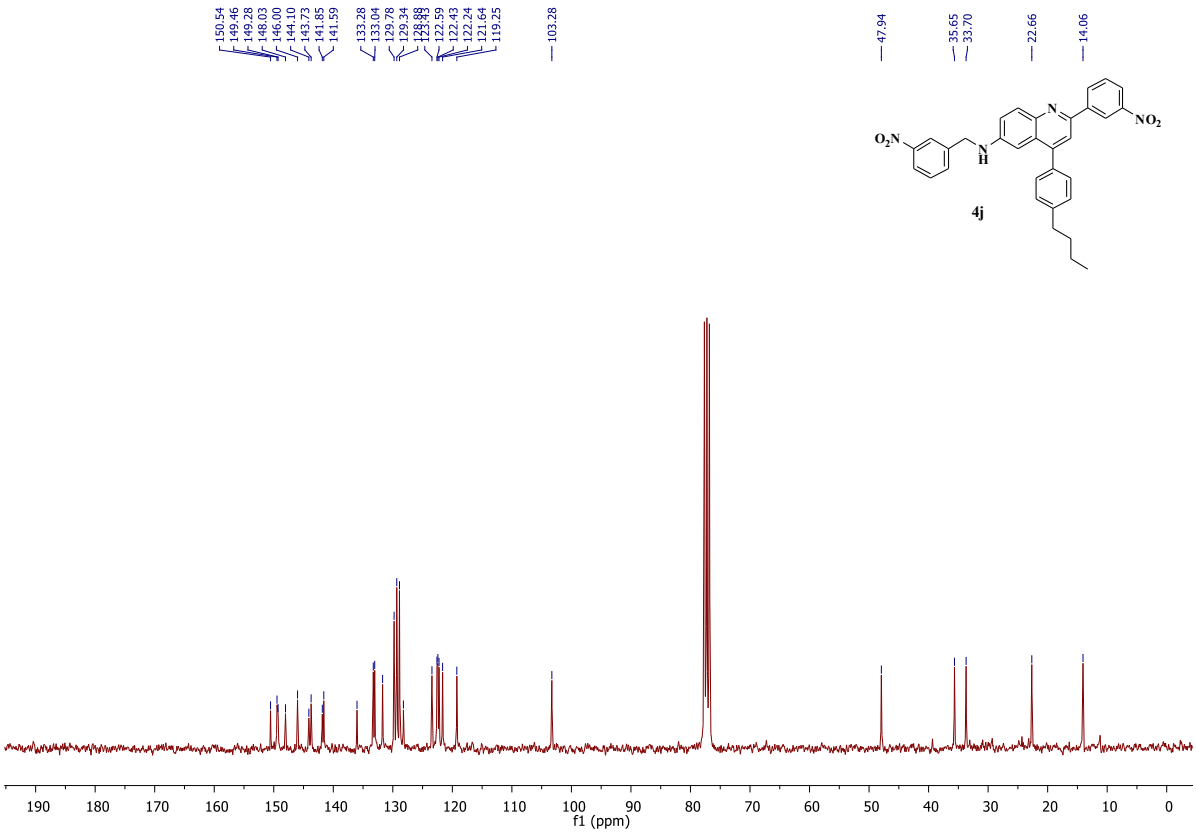
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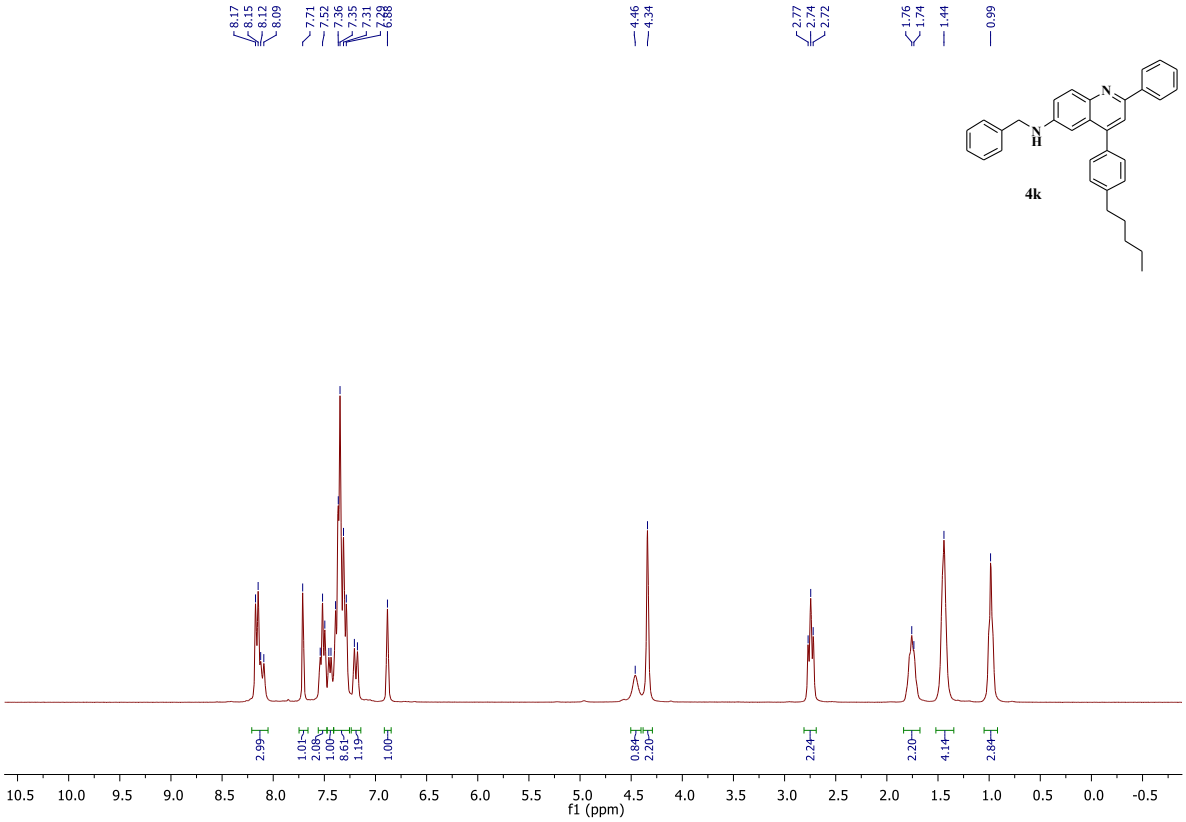
4j
f1 (ppm)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2.20
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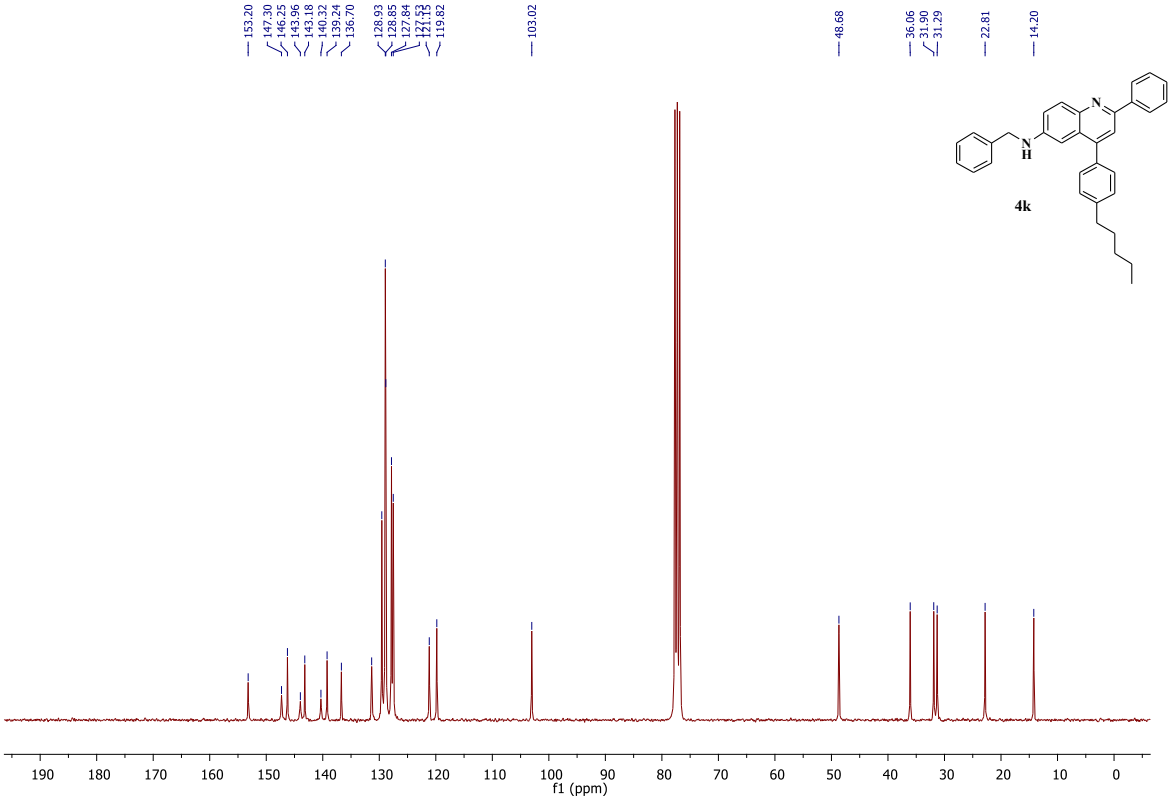
2.84
f1 (ppm)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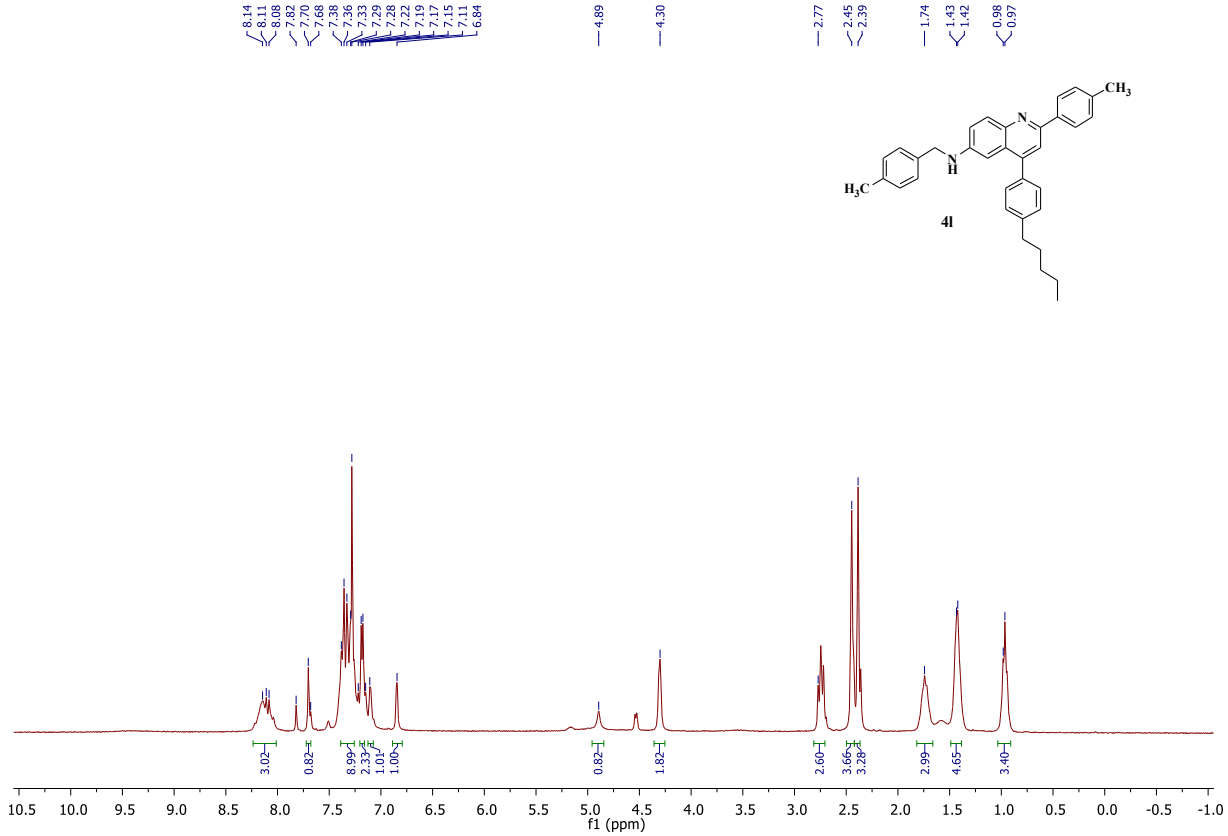
4k
f1 (ppm)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7.15
7.11
6.84
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H
H3C
4l
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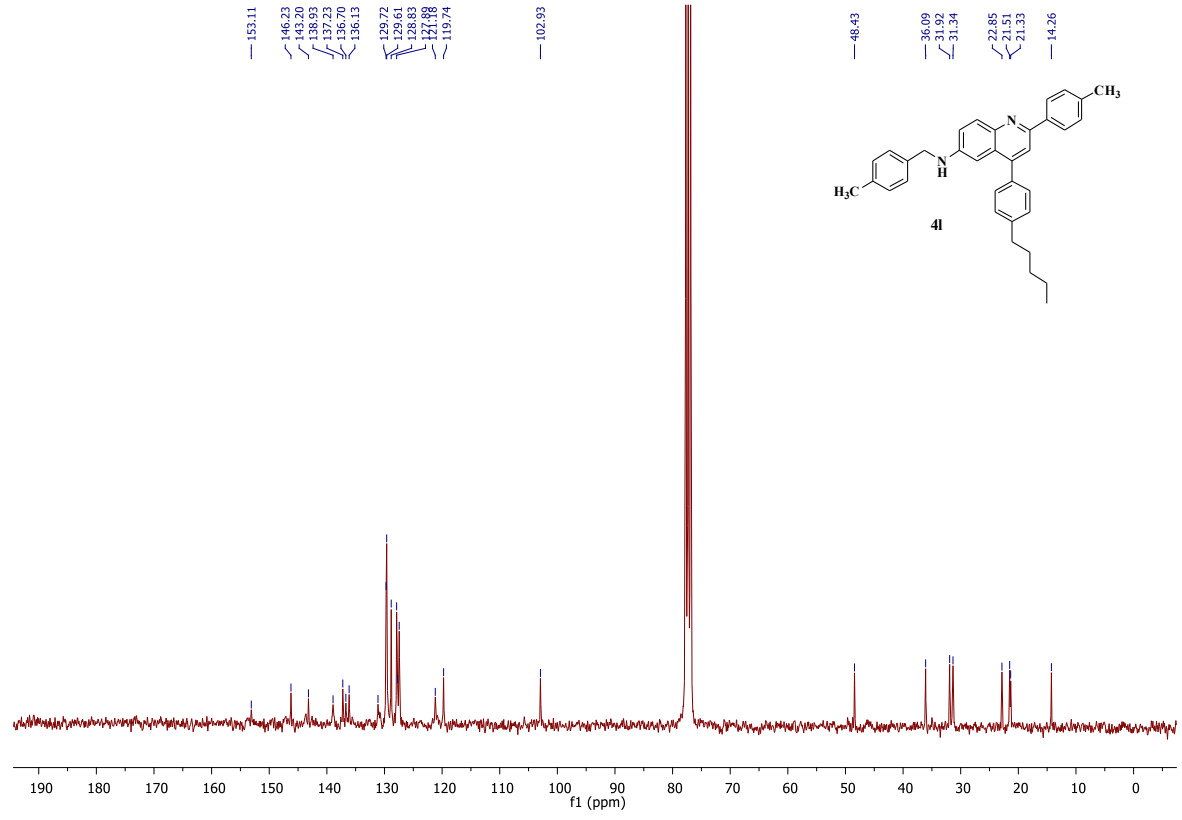
0.82
8.99
2.33
1.01
1.06
0.82
1.82
2.60
3.66
3.28
2.99
4.65
3.40
f1 (ppm)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136.13
129.72
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128.83
119.74
102.93
48.43
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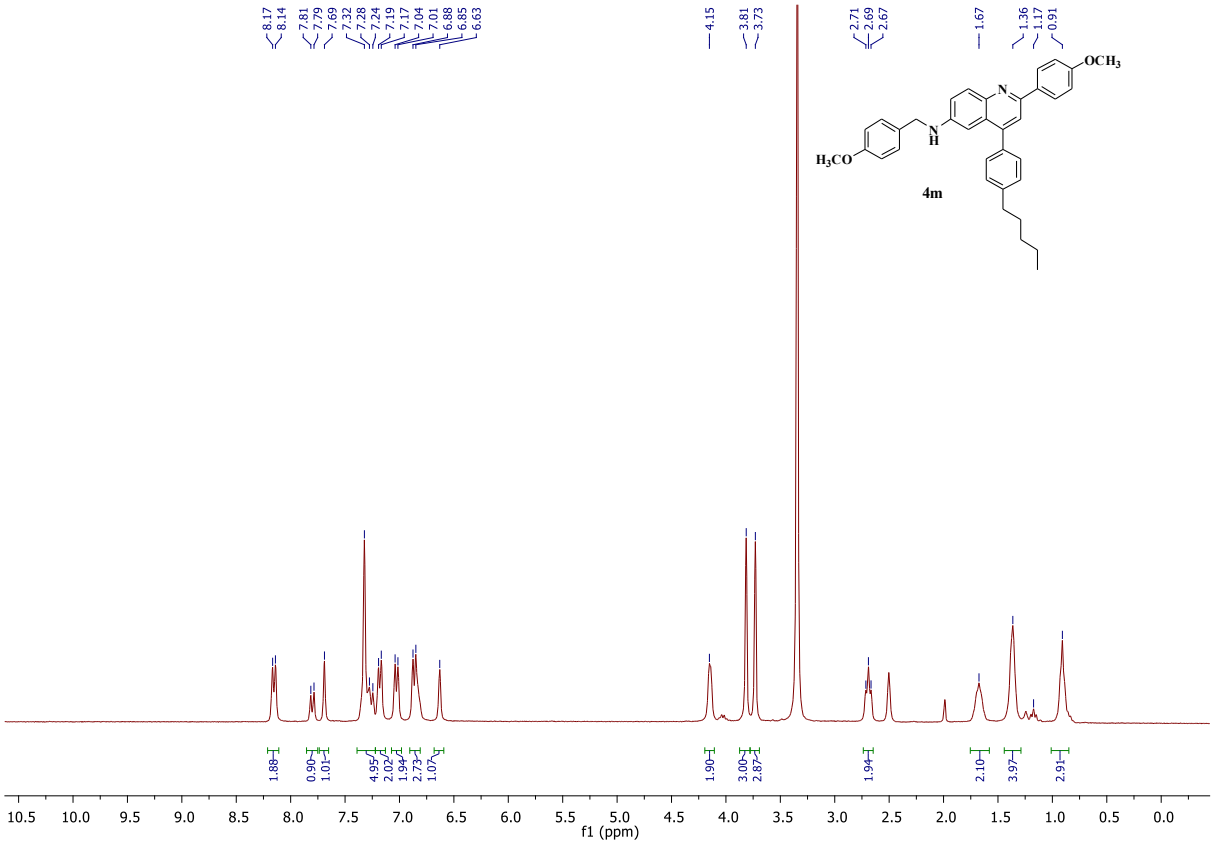
22.85
21.51
21.33
14.26
CH3
N
H
H3C
4l
f1 (ppm)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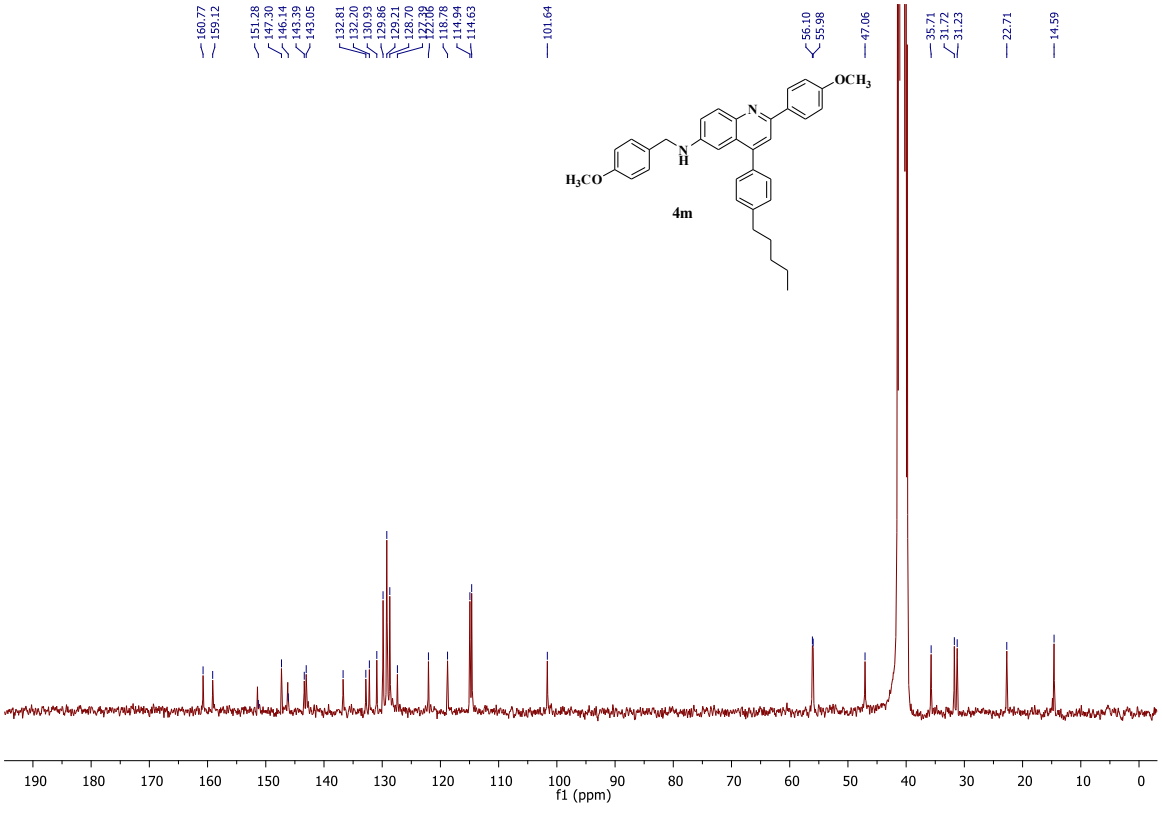
7.24
7.19
7.17
7.04
7.01
6.88
6.85
6.63
4.15
3.81
3.73
2.71
2.69
2.67
1.67
1.36
1.17
0.91
OCH3
N
H
H3CO
4m
1.88
0.90
1.01
4.95
2.02
1.94
2.73
1.07
1.90
3.00
2.87
1.94
2.10
3.97
2.91
f1 (ppm)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143.39
143.05
132.81
132.20
130.93
129.86
129.21
128.70
122.39
122.08
118.78
114.94
114.63
101.64
56.10
55.98
47.06
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31.72
31.23
22.71
14.59
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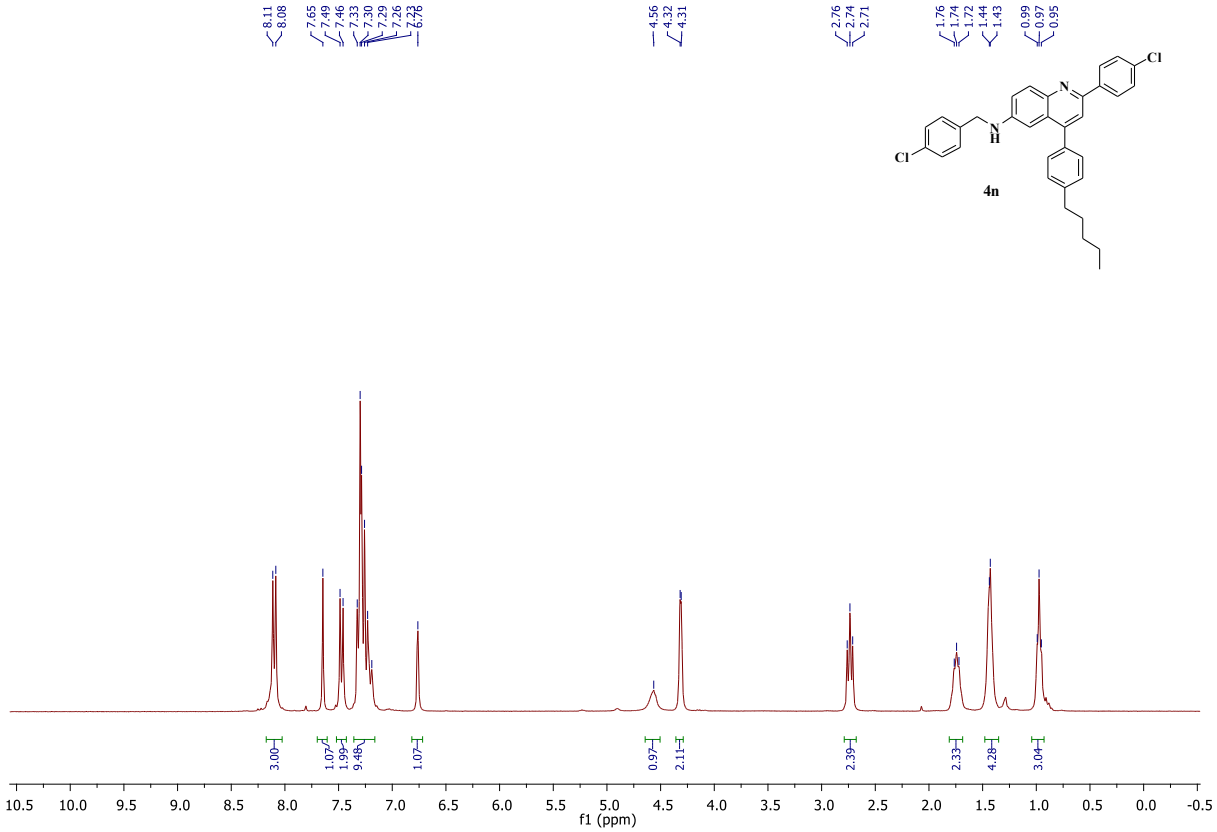
N
H
H3CO
4m
f1 (ppm)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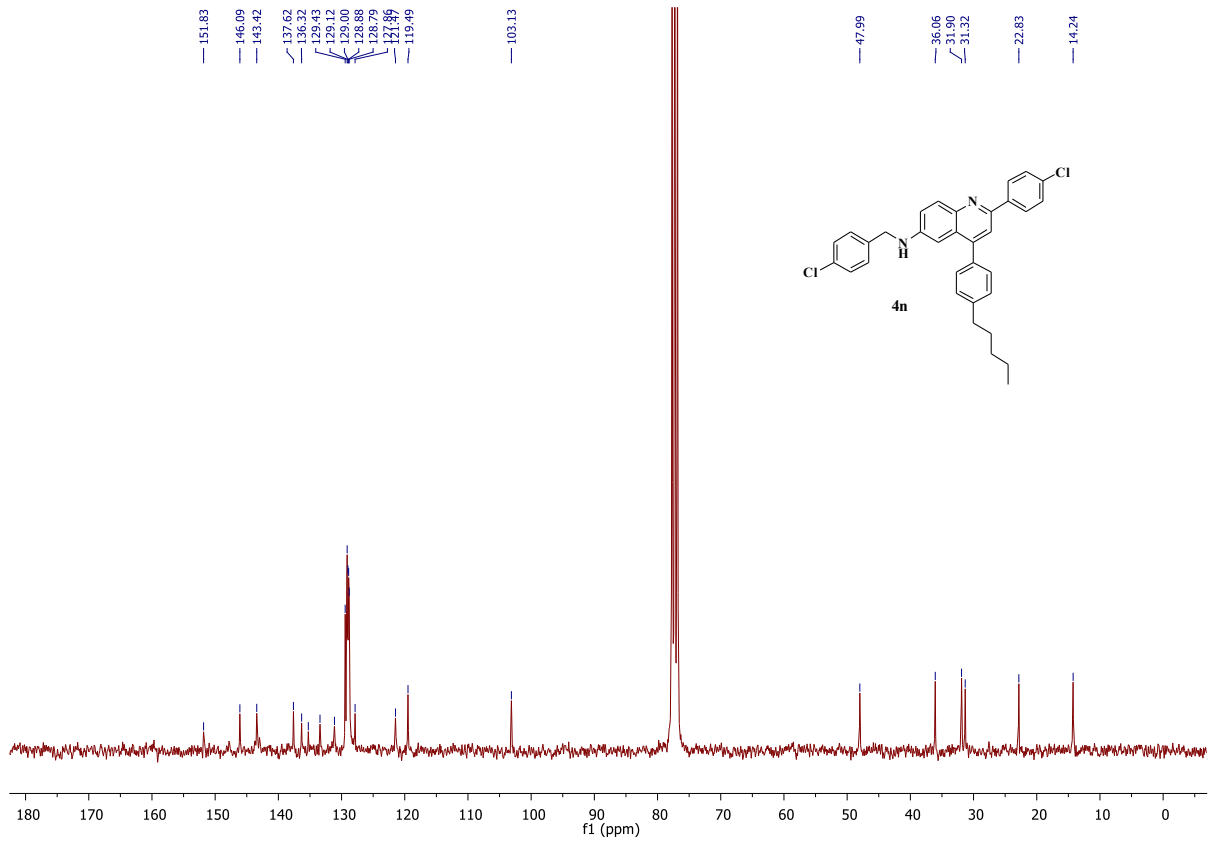
7.30
7.29
7.26
7.23
6.76
4.56
4.32
4.31
2.76
2.74
2.71
1.76
1.74
1.72
1.44
1.43
0.99
0.97
0.95
Cl
N
H
Cl
4n
3.00
1.07
1.99
9.48
1.07
0.97
2.11
2.39
2.33
4.28
3.04
f1 (ppm)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129.43
129.12
129.00
128.88
128.79
127.86
121.47
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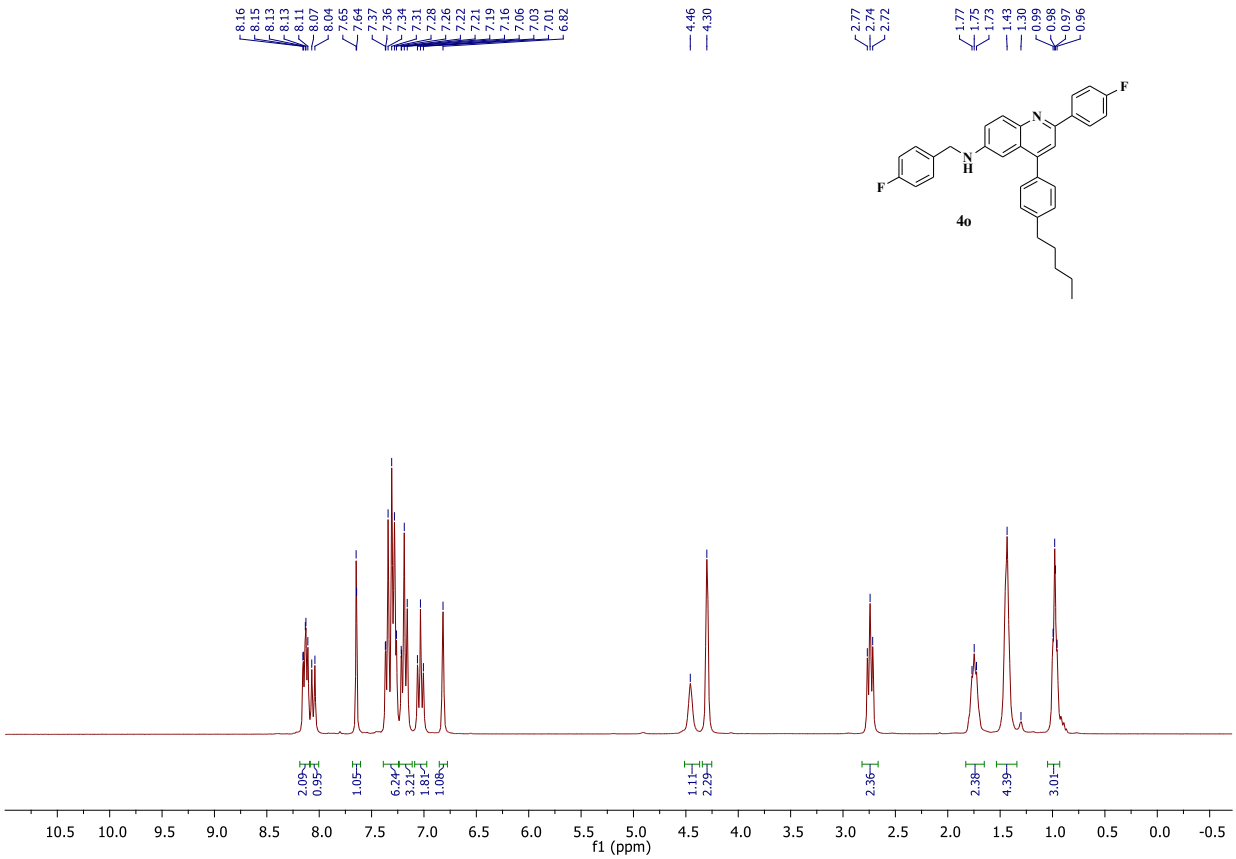
103.13
47.99
36.06
31.90
31.32
22.83
14.24
Cl
N
H
Cl
4n
f1 (ppm)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8.04
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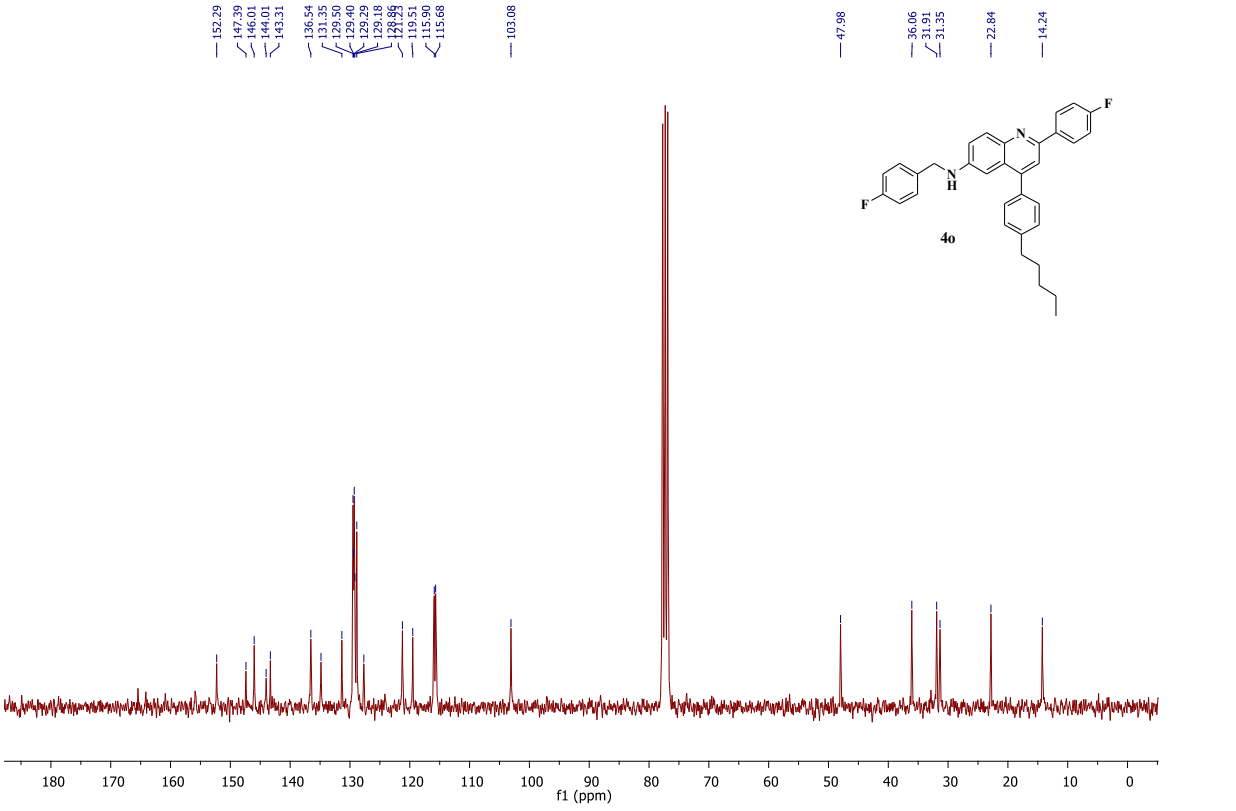
7.37
7.36
7.34
7.31
7.28
7.26
7.22
7.21
7.19
7.16
7.06
7.03
7.01
6.82
4.46
4.30
2.77
2.74
2.72
1.77
1.75
1.73
1.43
1.30
0.99
0.98
0.97
0.96
F
N
H
F
4o
2.09
0.95
1.05
6.24
3.21
1.81
1.08
1.11
2.29
2.36
2.38
4.39
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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144.01
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129.29
129.18
119.51
115.90
115.68
103.08
47.98
36.06
31.91
31.35
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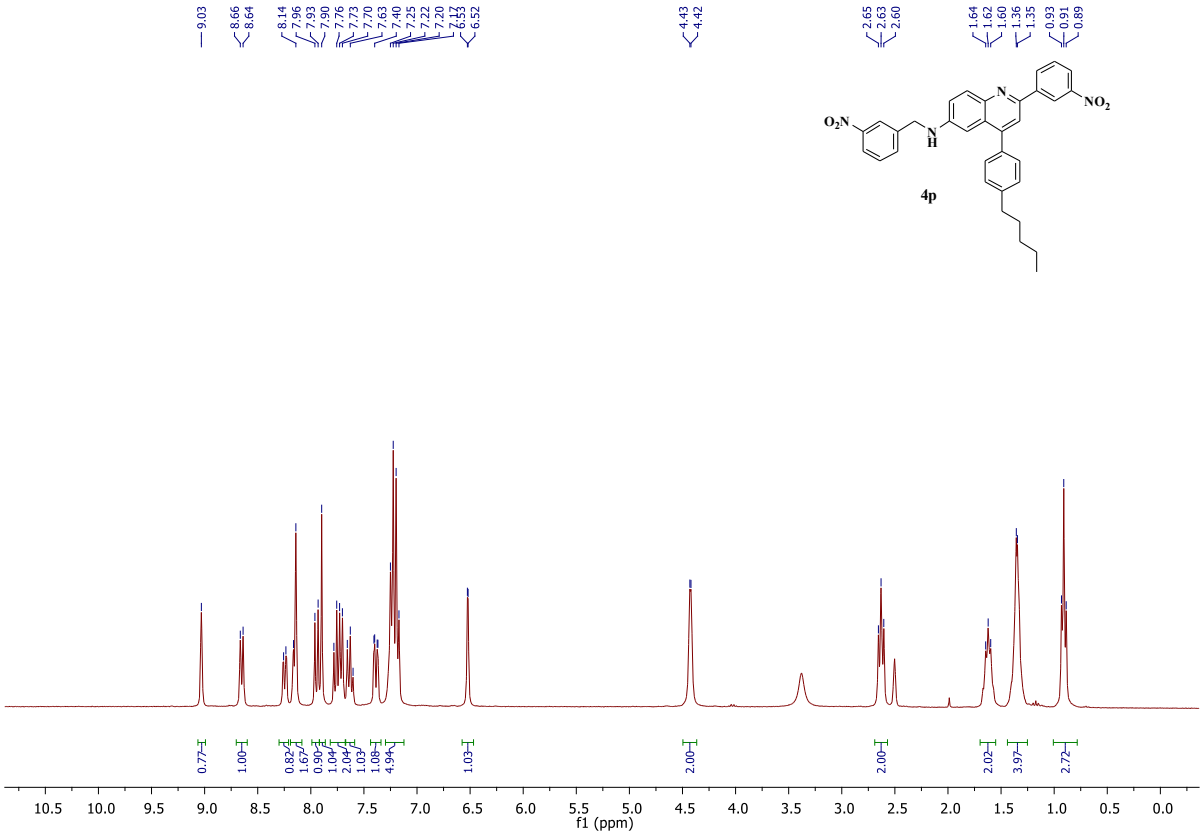
14.24
F
N
H
F
4o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.64
8.14
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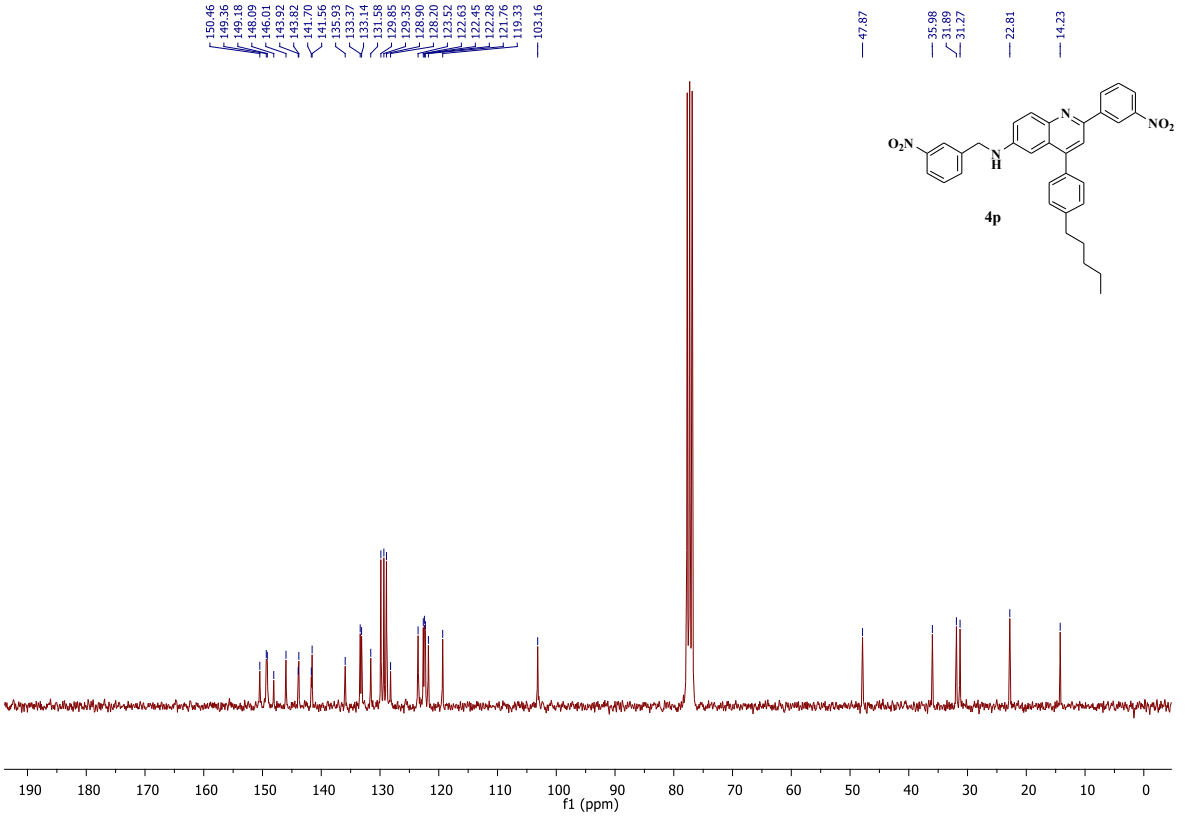
7.93
7.90
7.76
7.73
7.70
7.63
7.40
7.25
7.22
7.20
7.13
6.53
6.52
4.43
4.42
2.65
2.63
2.60
1.64
1.62
1.60
1.36
1.35
0.93
0.91
0.89
O2N
NO2
N
H
4p
0.77
1.00
0.82
1.67
0.90
1.04
2.04
1.03
1.08
4.94
1.03
2.00
2.00
2.02
3.97
2.72
f1 (ppm)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141.56
135.93
133.37
133.14
131.58
129.85
129.35
128.90
128.20
123.52
122.63
122.45
122.28
121.76
119.33
103.16
47.87
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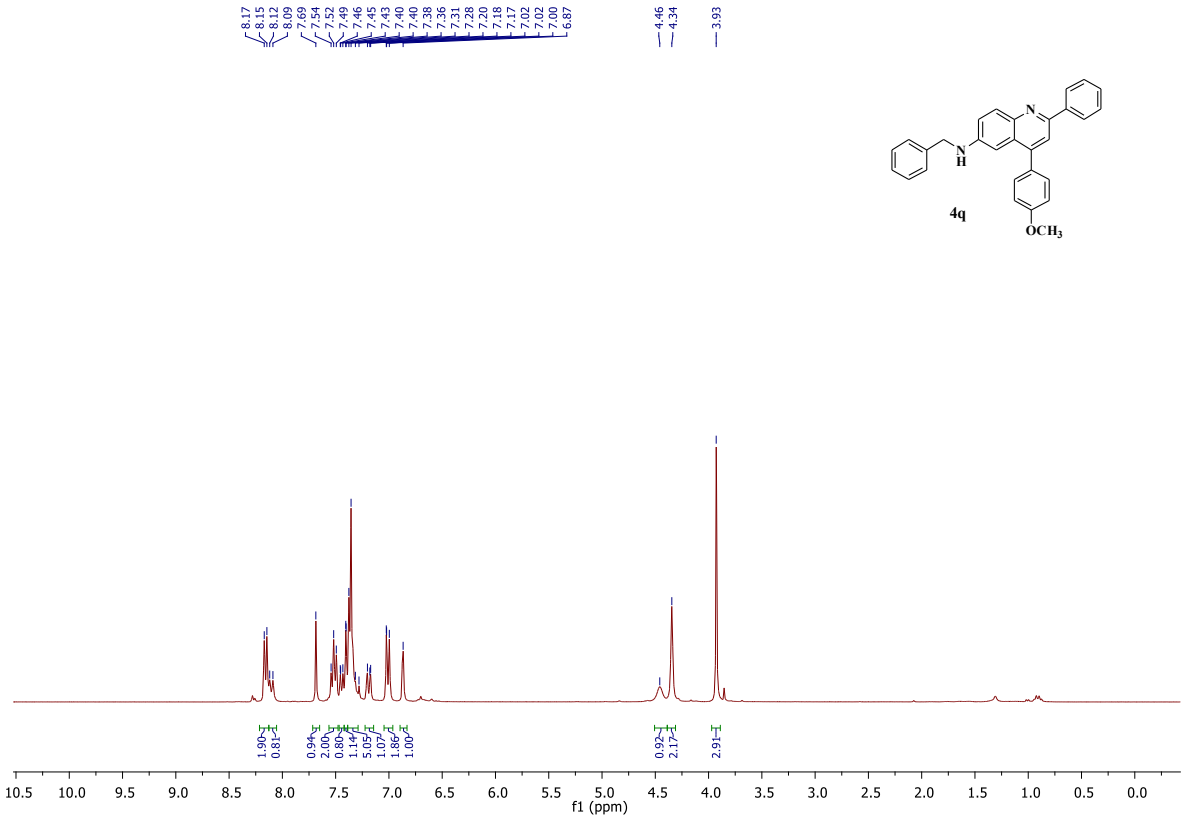
O2N
NO2
N
H
4p
f1 (ppm)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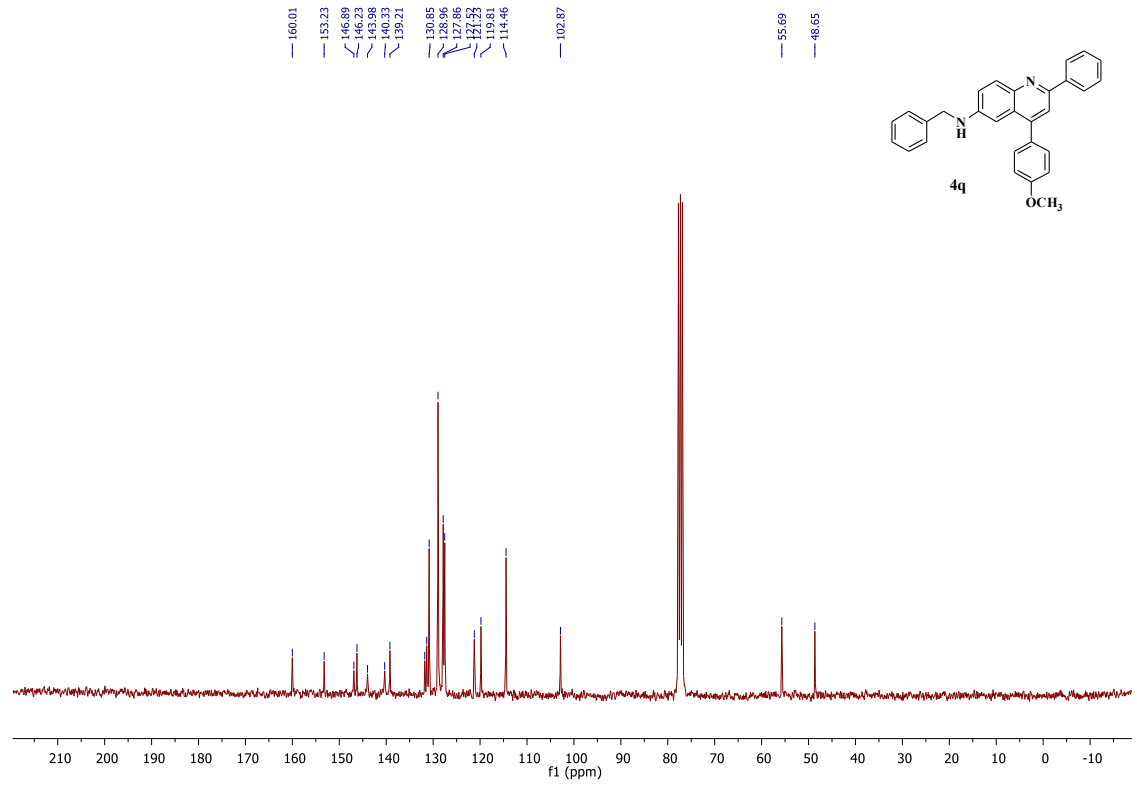
8.09
7.69
7.54
7.52
7.49
7.46
7.45
7.43
7.40
7.40
7.38
7.36
7.31
7.28
7.20
7.18
7.17
7.02
7.02
7.00
6.87
4.46
4.34
3.93
4q
OCH3
1.90
0.81
0.94
2.00
0.89
1.14
5.05
1.07
1.86
1.00
0.92
2.17
2.91
f1 (ppm)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140.33
139.21
130.85
128.96
127.86
121.53
121.23
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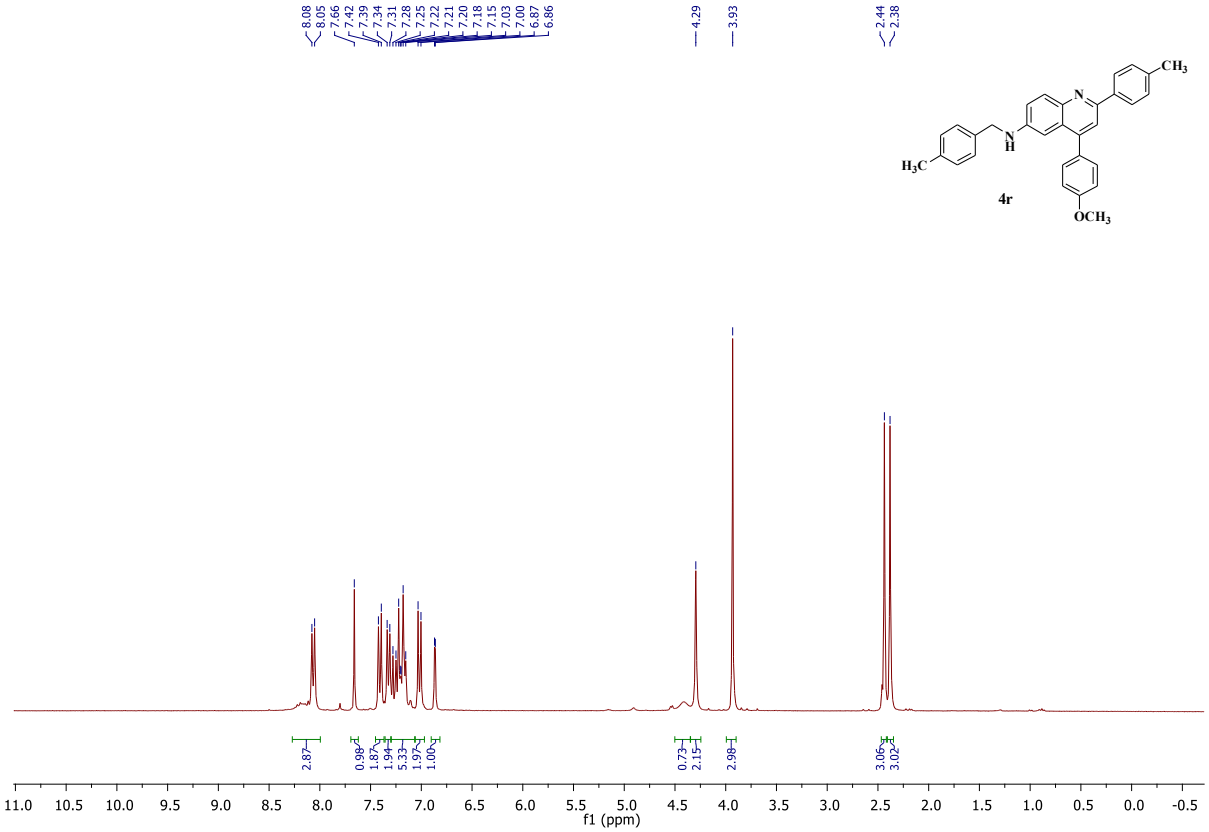
114.46
102.87
55.69
48.65
4q
OCH3
f1 (ppm)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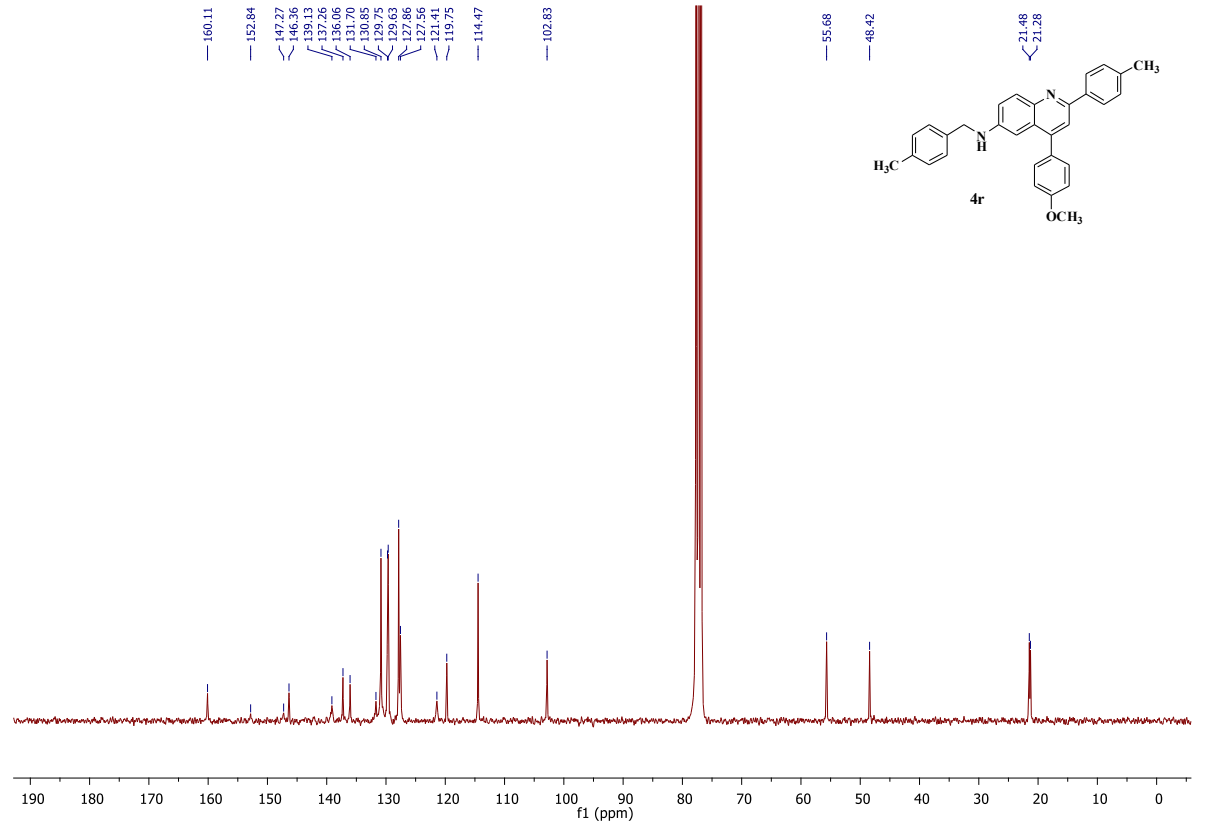
7.31
7.28
7.25
7.22
7.21
7.20
7.18
7.15
7.03
7.00
6.87
6.86
4.29
3.93
2.44
2.38
CH3
N
H
H3C
OCH3
4r
2.87
0.98
1.87
1.94
5.33
1.97
1.00
0.73
2.15
2.98
3.06
3.02
f1 (ppm)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129.63
127.86
127.56
121.41
119.75
114.47
102.83
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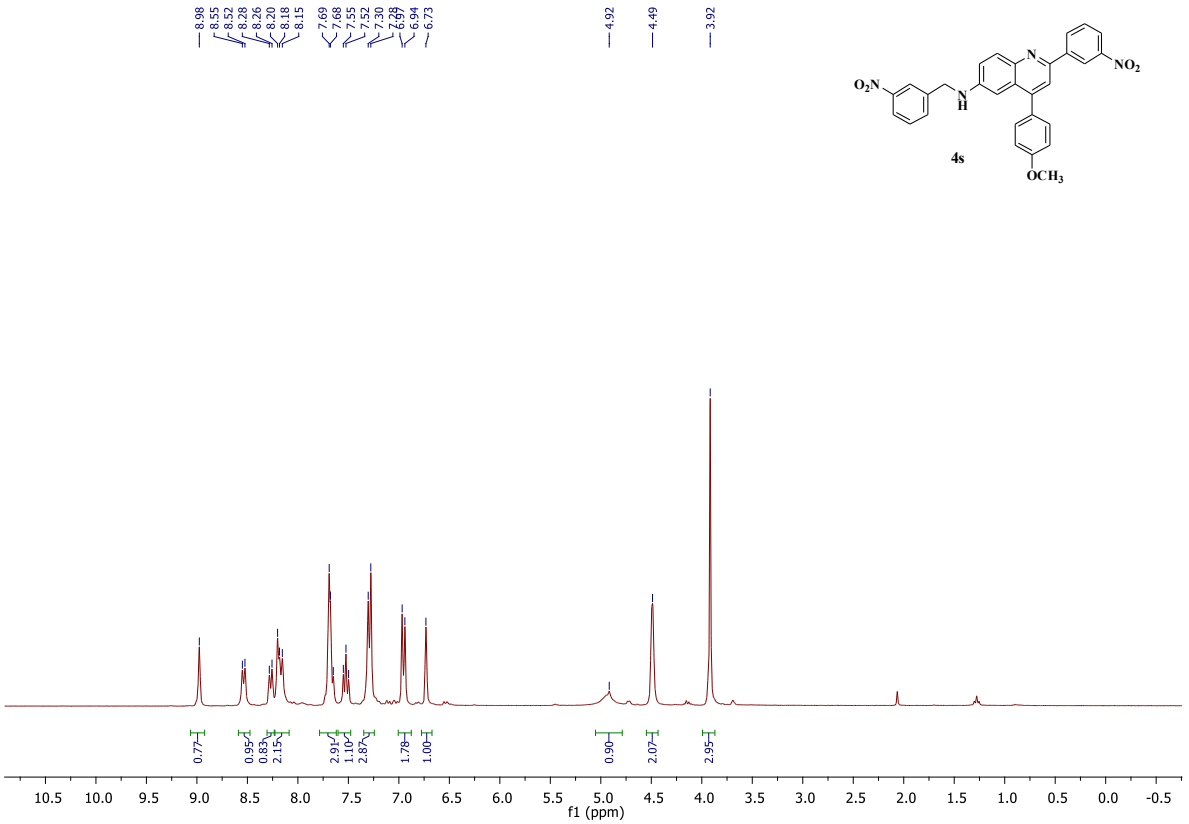
48.42
21.48
21.28
CH3
N
H
H3C
OCH3
4r
f1 (ppm)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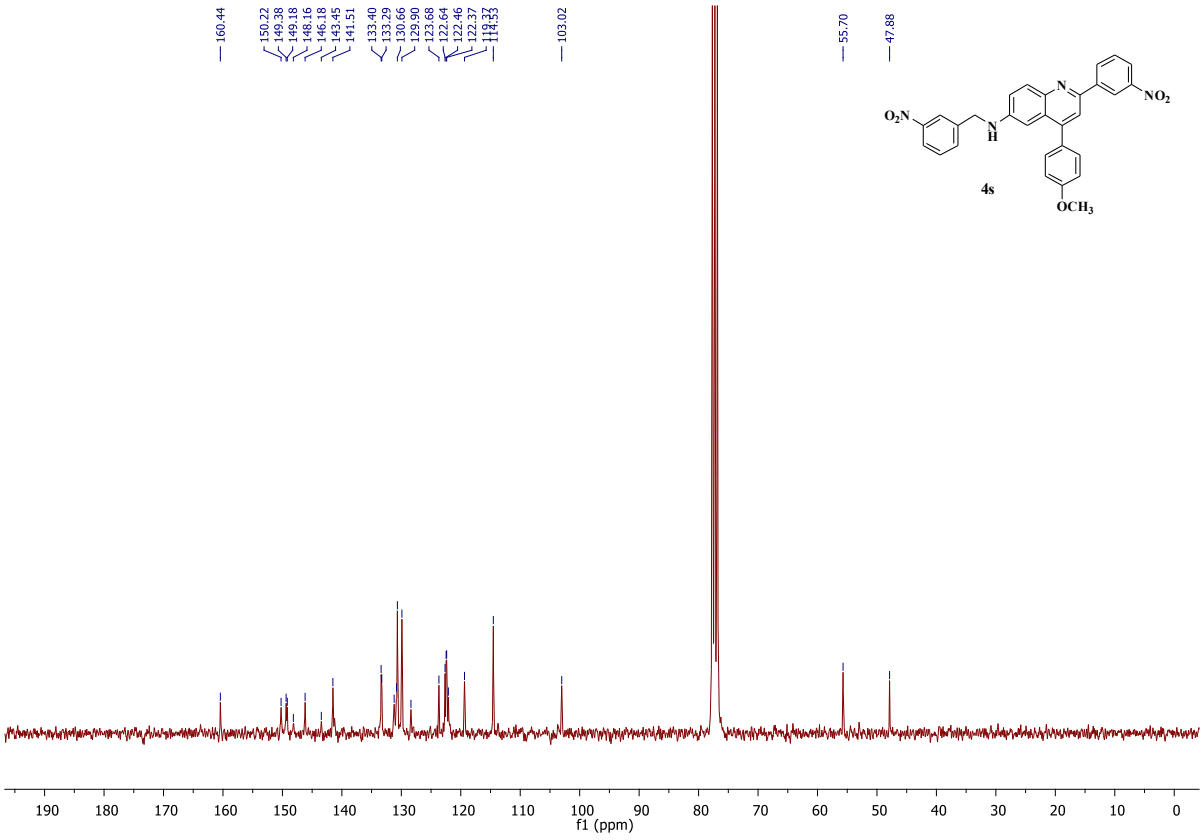
7.68
7.55
7.52
7.30
7.28
6.97
6.94
6.73
4.92
4.49
3.92
0.77
0.99
0.85
2.15
2.91
1.10
2.87
1.78
1.00
0.90
2.07
2.95
f1 (ppm)
4s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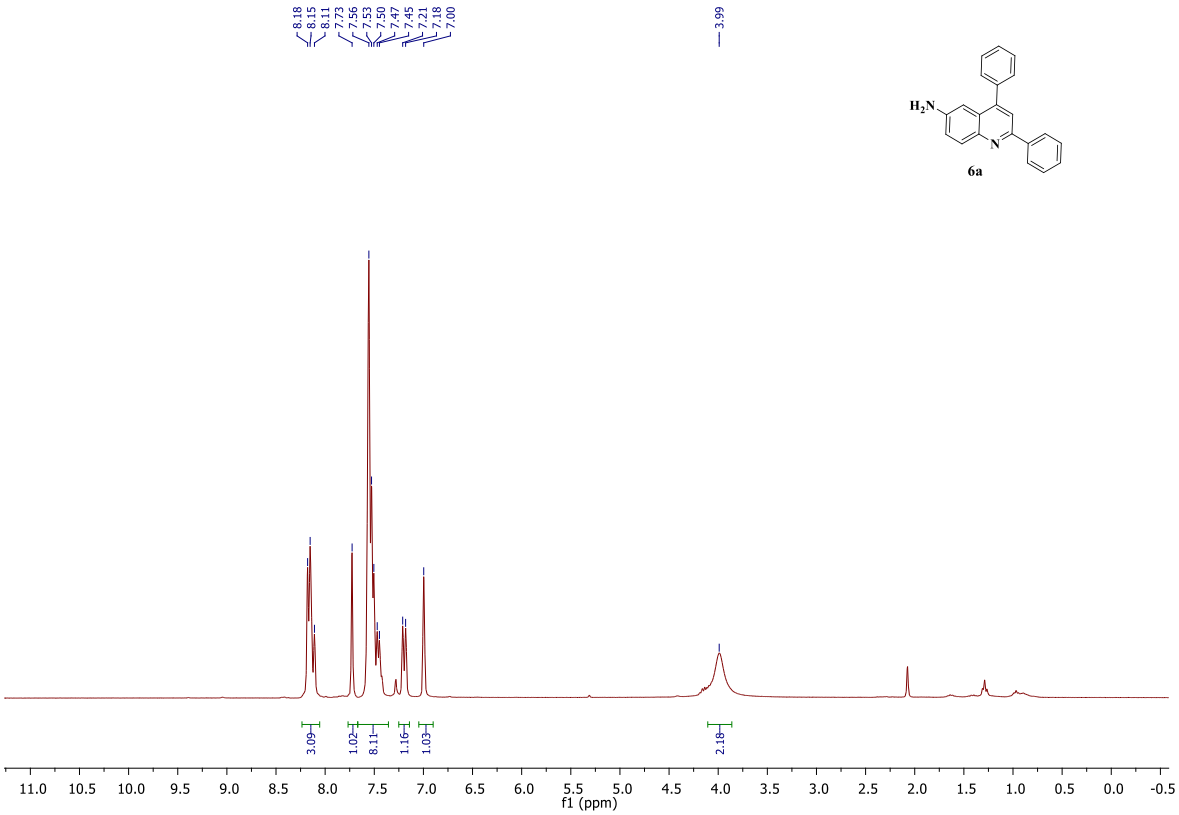
123.68
122.64
122.46
122.37
103.02
55.70
47.88
f1 (ppm)
4s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7.53
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7.47
7.45
7.21
7.18
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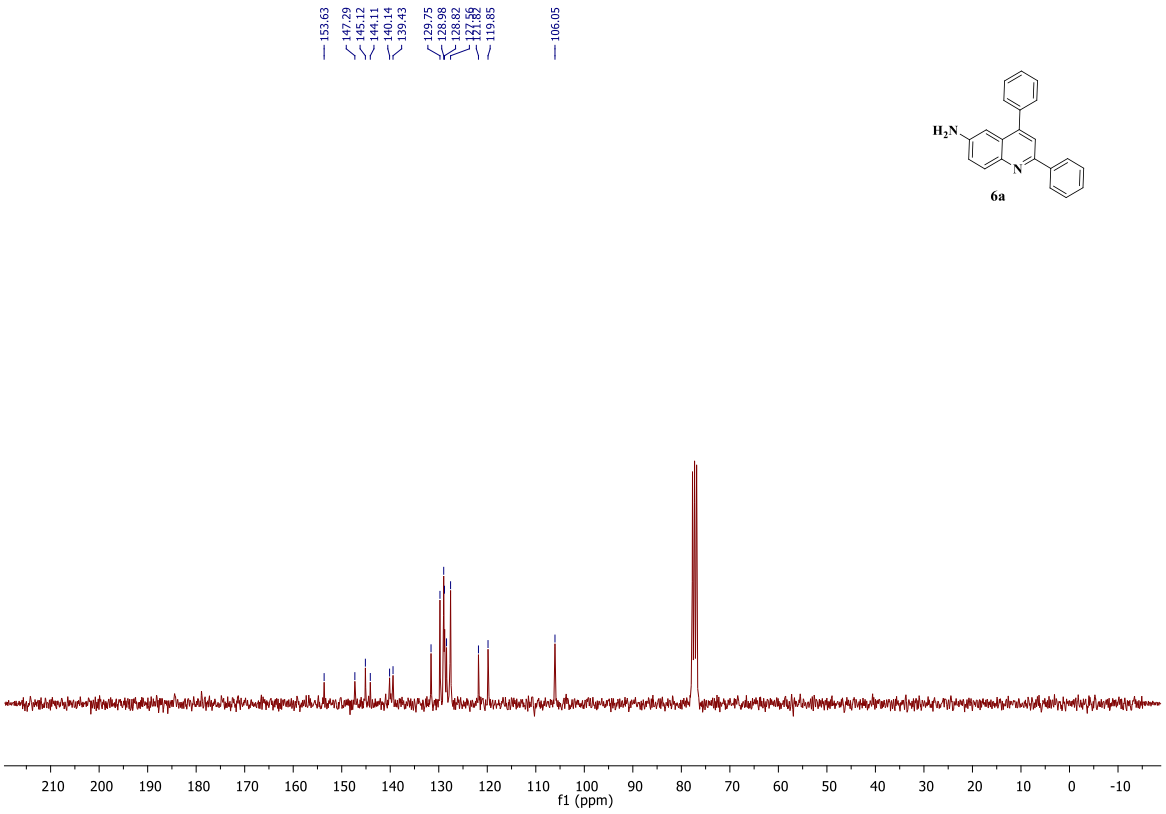
H2N
N
6a
3.09
1.02
8.11
1.16
1.03
2.18
f1 (ppm)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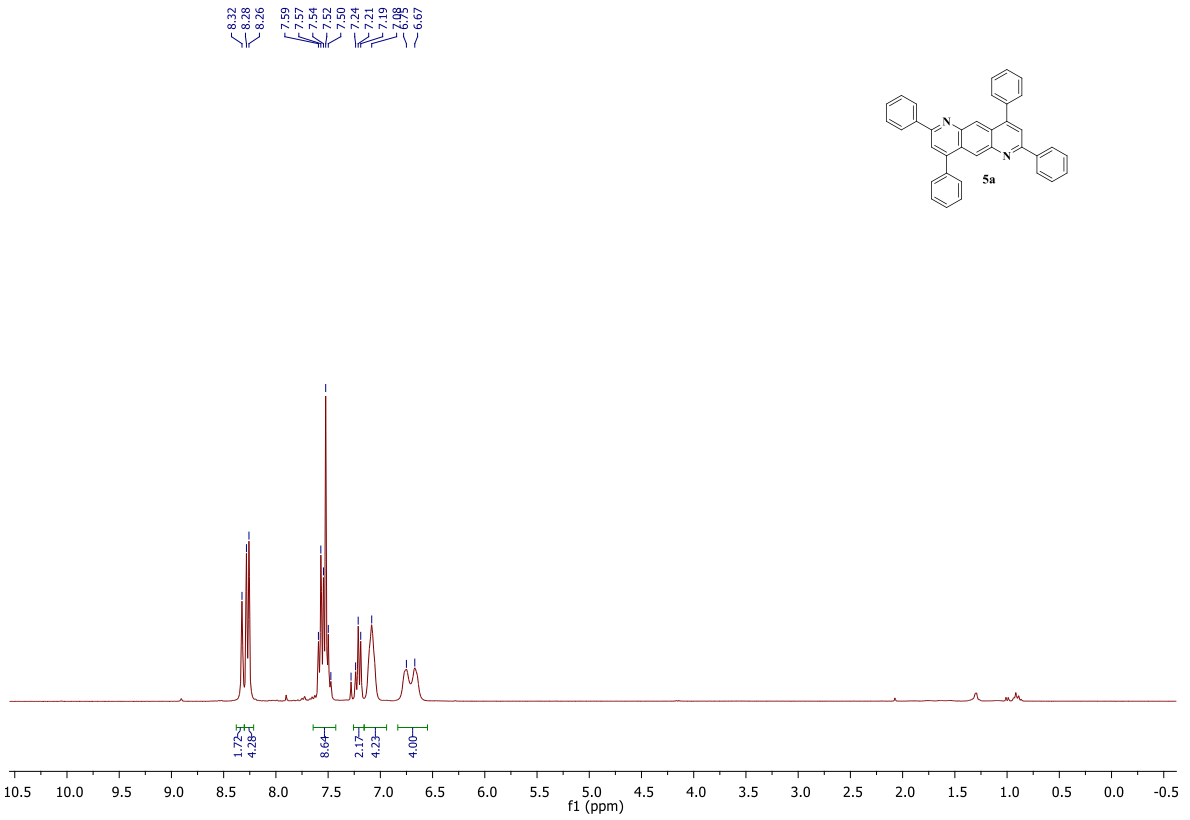
106.05
H2N
N
6a
f1 (ppm)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7.52
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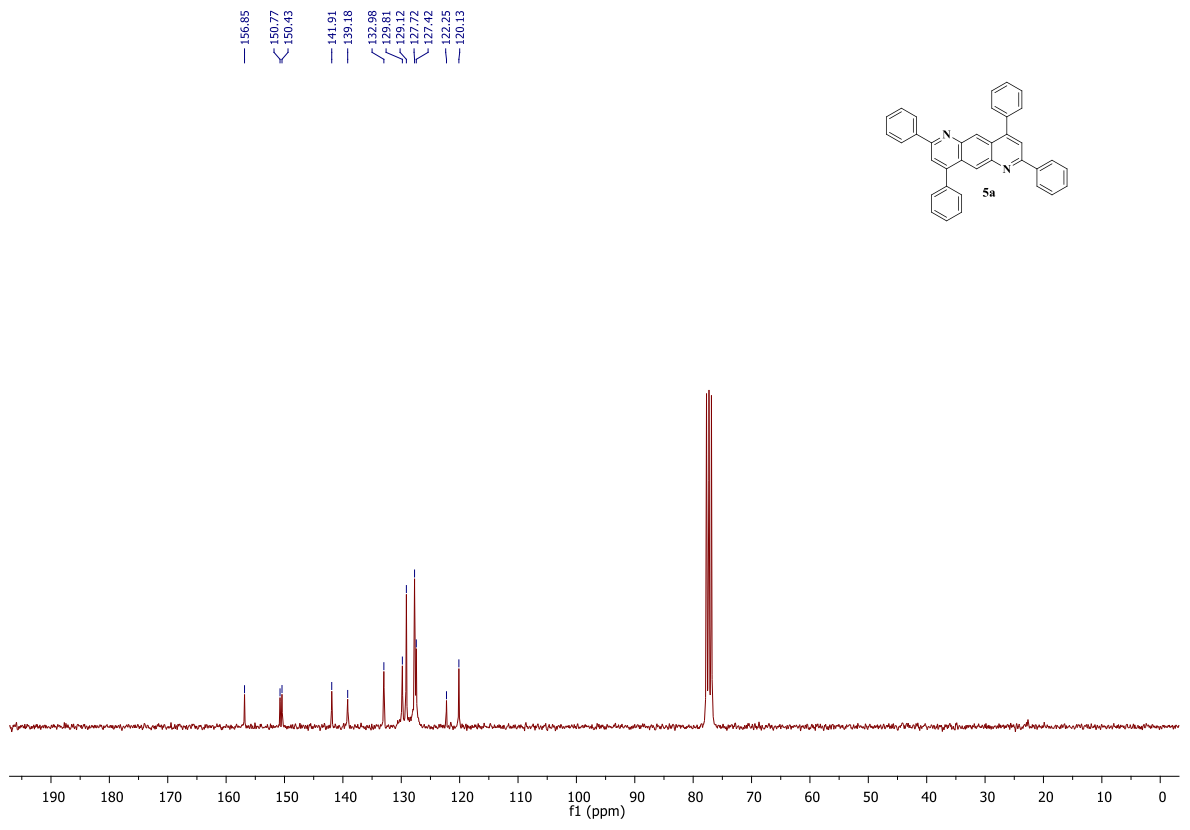
7.24
7.21
7.19
6.98
6.95
6.67
5a
1.72
4.28
8.64
2.17
4.23
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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132.98
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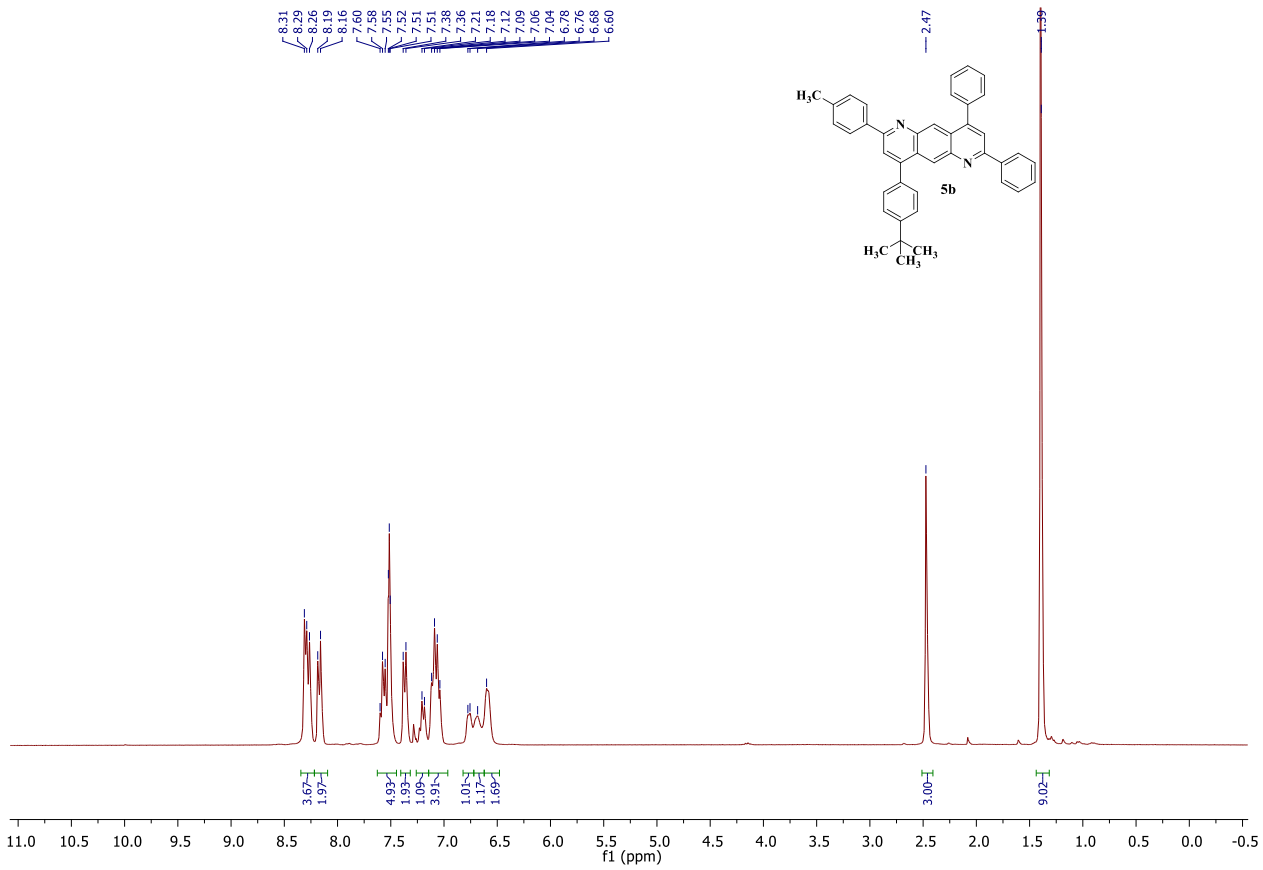
127.42
122.25
120.13
5a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.58
7.55
7.52
7.51
7.51
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7.36
7.21
7.18
7.12
7.09
7.06
7.04
6.78
6.76
6.68
6.60
2.47
1.39
5b
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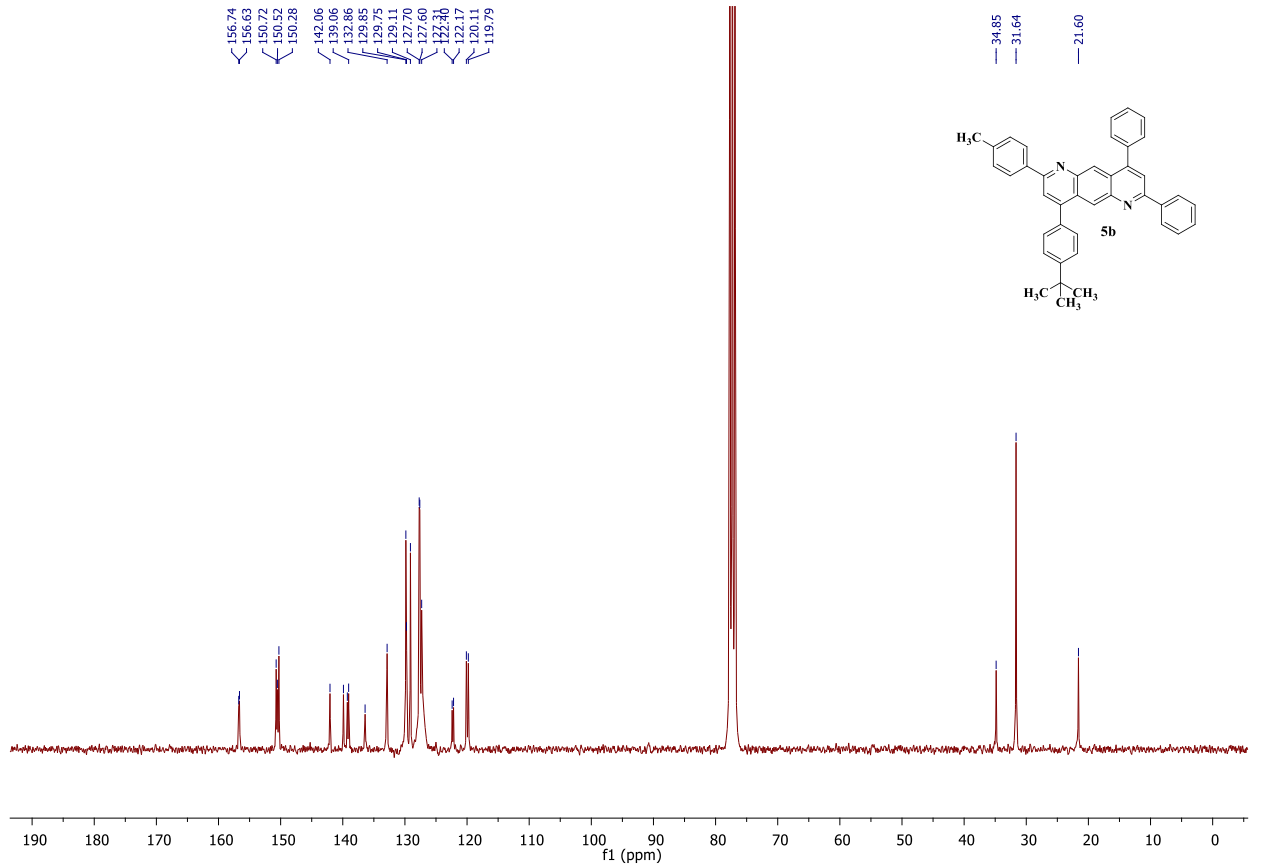
1.69
3.00
9.02
f1 (ppm)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127.70
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122.17
120.11
119.79
34.85
31.64
21.60
5b
f1 (ppm)