Supporting Information

Silver-Promoted Benzannulations of Siloxy Alkynes with Pyridinium and Isoquinolinium Salts

Jaime R. Cabrera-Pardo, David I. Chai, and Sergey A. Kozmin*

Department of Chemistry, University of Chicago, Chicago, IL 60637, USA

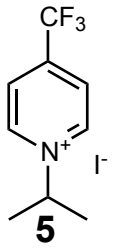
email: skozmin@uchicago.edu

General Information. Hexanes (ACS grade) and triethylamine (ACS grade) were purchased from Fisher Scientific and used without further purification. Dichloromethane was distilled over calcium hydride under a positive pressure of nitrogen. Unless otherwise noted, all reactions were performed under an inert atmosphere of nitrogen in flame-dried vials equipped with a stirbar and a cap with PTFE insert. Other commercially available reagents were obtained from Sigma-Aldrich and TCI America and were used without further purification unless otherwise noted. Solution-phase reactions were monitored by thin layer chromatography (TLC) using Whatman precoated silica gel plates. Column chromatography was performed by either CombiFlash® using Silcycle silica gel column (24g, 230-400 mesh) or flash column chromatography using Siliaflash® F60. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX-500 instrument and chemical shifts are reported in ppm using residual solvent peaks as internal standards. High-resolution mass spectra were recorded with a Waters Q-TOF Ultima tandem quandrupole/time-of-flight instrument.

General Procedure for the formation of *N*-Alkyl-pyridinium or *N*-Alkyl-isoquinolinium salts.

A 100 mL round-bottomed flame-dried flask containing *N*-Alkyl-pyridine or *N*-Alkyl-isoquinoline (5 mmol) in dichloromethane (0.2 mL) was treated with alkyl iodide (2 eq.). The mixture was stirred at reflux temperature for 12 h. The solvent was removed under reduced pressure and dried under vacuum until solid formed. The mixture was re-dissolved in ethanol (5 - 10 mL), and then diethyl ether (10 – 20 mL) was added. The mixture was cool down to 0 °C and the resulting precipitate collected by filtration.

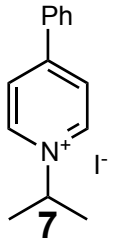
Pyridinium iodide 5 was obtained according to general procedure above (316 mg, 20% yield).



5

^{1}H NMR (CD_3CN): δ 9.35 (2H, d, J = 5.0 Hz), 8.43 (2H, br m), 5.25 (1H, septet, J = 6.5 Hz), 1.74 (6H,d, J = 6.5 Hz). ^{13}C NMR (CD_3CN): δ 144.9(t), 125.0 (q), 122.0, 119.8, 66.1(t), 21.7. HRMS-ESI calculated for $C_9H_{11}NF_3$ [M-I+] 190.0844, found 190.0843.

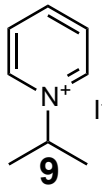
Pyridinium iodide 7 was obtained according to general procedure above (1.5 g, 92% yield).



7

^{1}H NMR (CD_3CN): δ 9.00 (2H, d, J = 7.0 Hz), 8.35 (2H, d, J = 7.0 Hz), 7.90 (2H, m), 7.67 (3H, m), 5.08 (1H, septet, J = 6.5 Hz), 1.71 (6H, d, J = 6.5 Hz). ^{13}C NMR (CD_3CN): δ 155.9, 142.3, 133.4, 131.7, 129.3, 127.7, 124.8, 63.7, 21.7. HRMS-ESI calculated for $C_{14}H_{16}N$ [M-I+] 198.1283, found 198.1282.

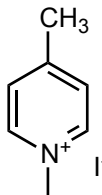
Pyridinium iodide 9 was obtained according to general procedure above (0.9 g, 72% yield).



9

^{1}H NMR (CD_3CN) δ 9.06 (2H, d, J = 6.0 Hz), 8.58 (1H, tt, J = 8.0, 1.5 Hz), 8.12 (2H, t, J = 7.0 Hz), 5.11 (1H, septet, J = 7.0 Hz), 1.70 (6H, d, J = 7.0 Hz). ^{13}C NMR (CD_3CN) δ 145.3, 142.4 (t), 127.9, 64.5, 21.7. HRMS-ESI calculated for $C_8H_{12}N$ [M-I+] 122.0964, found 122.0959.

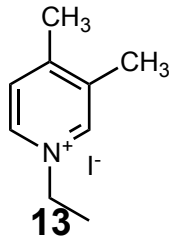
Pyridinium iodide 11 was obtained according to general procedure above (0.85 g, 65% yield).



11

^{1}H NMR (CD_3CN) δ 8.88 (2H, d, J = 5.5 Hz), 7.92 (2H, d, J = 5.0 Hz), 5.03 (1H, septet, J = 7.0 Hz), 2.66 (3H, s), 1.66 (6H, d, J = 6.0 Hz). ^{13}C NMR (CD_3CN) δ 159.7, 142.0, 117.5, 63.9, 22.4, 21.4. HRMS-ESI calculated for $C_9H_{14}N$ [M-I$^+$] 136.1126, found 136.1126.

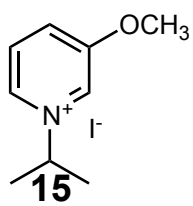
Pyridinium iodide 13 was obtained according to general procedure above (0.38 g, 30% yield).



13

^{1}H NMR ($CDCl_3$) δ 9.29 (1H, s), 9.05 (1H, d, J = 6.0 Hz), 7.79 (1H, d, J = 6.5 Hz), 4.85 (2H, q, J = 7.5 Hz), 2.51 (3H,s), 2.49 (3H, s), 1.65 (3H, t, J = 7.5 Hz).^{13}C NMR ($CDCl_3$) δ 157.6, 142.8, 141.2, 138.3, 128.5, 56.1, 20.3, 17.1, 16.9. HRMS-ES$^+$ calculated for $C_9H_{14}N$ [M-I]$^+$ 136.1126, found [M-I]$^+$ 136.1126.

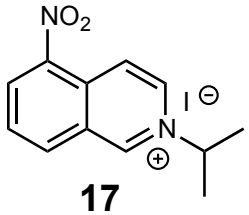
Pyridinium iodide 15 was obtained according to general procedure above (1.2 g, 86% yield).



15

^{1}H NMR ($CDCl_3$) δ 9.11 (1H, d, J = 1.0 Hz), 8.96 (1H, d, J = 6.0 Hz) 8.08 (1H, dd, J = 8.5, 6.0 Hz), 8.02 (1H, ddd, J = 9.0, 2.5, 1.0 Hz), 5.60 (1H, m, J = 7.0 Hz), 4.14 (3H, s), 1.74 (6H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$) δ 158.5, 134.8, 131.3, 129.9, 129.1, 65.2, 58.9, 23.3. HRMS-ES$^+$ calculated for $C_9H_{14}NO$ $[M\text{-}I]^+$ 152.1075, found $[M\text{-}I]^+$ 152.1076.

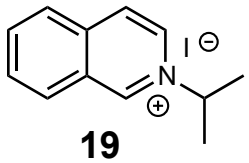
Isoquinolinium iodide 17 was obtained according to general procedure above (1.05 g, 62% yield).



17

^{1}H NMR (CD_3CN) δ 10.32 (1H, s), 9.05 (1H, d, J = 7.0 Hz), 8.98 (2H, t, J = 9.0 Hz), 8.82 (1H, dd, J = 7.0, 1.5 Hz), 8.19 (1H, t, J = 8.0 Hz), 5.23 (1H, m, J = 7.0 Hz), 1.79 (6H, d, J = 7.0 Hz). ^{13}C NMR (CD_3CN) δ 149.7, 138.4, 136.5, 135.4, 131.5, 131.1, 129.8, 123.5, 118.9, 66.3, 22.9. HRMS-ES$^+$ calculated for $C_{12}H_{13}N_2O_2$ $[M\text{-}I]^+$ 217.0977, found $[M\text{-}I]^+$ 217.0981.

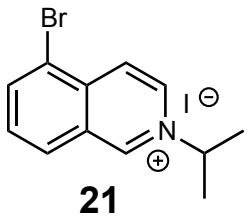
Isoquinolinium iodide 19 was obtained according to general procedure above (0.793 g, 53% yield).



19

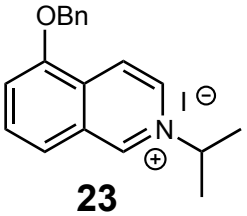
^{1}H NMR (CD_3CN) δ 10.00 (1H, s), 8.65 (1H, d, J = 7.0 Hz), 8.58 (1H, d, J = 8.5 Hz), 8.49 (1H, d, J = 7.0 Hz), 5.18 (1H, septet, J = 6.5 Hz), 1.79 (6H, d, J = 7.0 Hz). ^{13}C NMR (CD_3CN) δ 147.8, 137.8, 137.0, 132.7 (br m), 131.4, 130.4, 128.0, 127.2, 126.5, 64.8, 22.2. HRMS-ESI calculated for $C_{12}H_{14}N$ $[M\text{-}I^+]$ 172.1126, found 172.1123.

Isoquinolinium iodide 21 was obtained according to general procedure above (1.3 g, 69% yield). ^{1}H NMR (CD_3CN) δ 10.19 (1H, s), 8.78 (1H, dd, J = 7.0, 1.5 Hz), 8.67 – 8.62 (2H, m), 8.50 (1H, dd, J = 8.0, 1.0 Hz), 7.95 (1H, t, J = 8.0 Hz), 5.26 (1H, septet, J = 6.5 Hz), 1.80 (6H, d, J = 7.0 Hz). ^{13}C NMR (CD_3CN) δ 148.4, 140.5, 136.8, 134.4, 132.1, 130.6, 129.3, 125.6, 121.1, 65.2, 22.2. HRMS-ESI calculated for $C_{12}H_{13}NBr$ [M-I^{+}] 250.0231, found 250.0233.



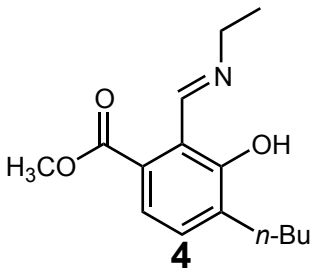
21

Isoquinolinium iodide 23 was obtained according to general procedure above (1.32 g, 65% yield). ^{1}H NMR (CD_3CN) δ 10.00 (1H, br s), 8.63 (2H, s), 8.13 (1H, d, J = 8.0 Hz), 7.97 (1H, t, J = 8.0 Hz), 7.70 (1H, d, J = 7.5 Hz), 7.97 (1H, t, J = 8.0 Hz), 7.70 (1H, d, J = 7.5 Hz), 7.61 (2H, d, J = 8.0 Hz), 7.48 (2H, t, J = 7.5 Hz), 7.43 (1H, m), 6.44 (2H, s), 5.19 (1H, m), 1.79 (6H, d, J = 7.0 Hz). ^{13}C NMR (CD_3CN) δ 153.3, 147.2, 136.0, 132.4, 132.3, 130.1, 129.0, 128.7, 128.4, 127.9, 121.7, 121.3, 115.9, 70.9, 64.9, 22.2. HRMS-ESI calculated for $C_{19}H_{20}NO$ [M-I^{+}] 278.1545 found 278.1548.



23

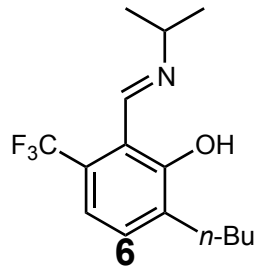
Phenol 4 was obtained according to general benzannulation procedure (27.6 mg, 70% yield).



4

^{1}H NMR ($CDCl_3$) δ 9.27 (1H, s), 7.24 (1H, d, J = 8.0 Hz), 7.12 (1H, d, J = 8.0 Hz), 3.82 (3H, s), 3.60 (2H, q, J = 7.0 Hz), 2.62 (2H, t, J = 7.5 Hz), 1.55 (2H, quintet, J = 7.5 Hz), 1.32 (2H, sextet, J = 7.5 Hz), 1.28 (3H, t, J = 7.5 Hz), 0.87 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 167.5, 164.0, 137.2, 131.3, 128.3, 120.1, 115.2, 52.3, 52.1, 31.2, 29.9, 22.7, 16.1, 14.0. HRMS-EI calculated for $C_{15}H_{21}NO_3$ [M^+] 263.1521 found 263.1528.

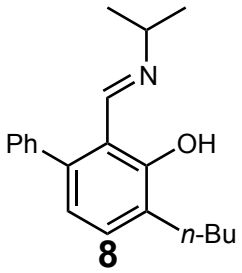
Phenol 6 was obtained according to general benzannulation procedure (36 mg, 85% yield).



6

^{1}H NMR ($CDCl_3$) δ 8.62 (1H, s), 7.14 (1H, d, J = 8.0 Hz), 7.00 (1H, d, J = 7.5 Hz), 3.57 (2H, septet, J = 6.0 Hz), 2.63 (2H, t, J = 8.0 Hz), 1.55 (2H, quintet, J = 7.5 Hz), 1.33 (2H, sextet, J = 8.0 Hz), 1.27 (6H,d, J = 6.0 Hz), 0.88 (3H, t, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$) δ 162.9, 159.6, 136.5, 135.5, 131.1, 130.4, 127.2, 127.0, 125.3, 123.1, 115.2, 113.0, 59.6, 31.2, 29.7, 24.1, 22.7, 14.0. HRMS-EI calculated for $C_{15}H_{20}F_3NO$ [M^+] 287.1497 found 287.1488.

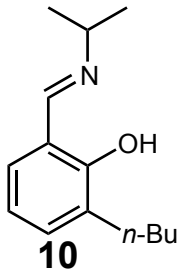
Phenol 8 was obtained according to general benzannulation procedure (37.7 mg, 85% yield).



8

^{1}H NMR ($CDCl_3$) δ 8.27 (1H, s), 7.36 – 7.28 (3H, m), 7.24 (2H, m), 7.12 (1H, d, J = 7.5 Hz), 6.60 (1H, d, J = 7.5 Hz), 3.30 (1H, septet, J = 6.5 Hz), 2.63 (2H, t, J = 8.0 Hz), 1.59 (2H, quintet, J = 8.0 Hz), 1.37 (2H, sextet, J = 7.5 Hz), 1.16 (6H, d, J = 6.0 Hz), 0.90 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 161.6, 142.1, 139.8, 131.9, 130.2, 129.9, 128.1, 127.2, 119.3, 115.0, 59.5, 31.7, 29.5, 24.2, 22.8, 14.0. HRMS-EI calculated for $C_{20}H_{25}NO$ [M^+] 295.1936 found 295.1939.

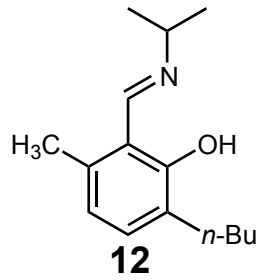
Phenol 10 was obtained according to general benzannulation procedure (23 mg, 70% yield).



10

^{1}H NMR ($CDCl_3$) δ 8.28 (1H, s), 7.11 (1H, d, J = 7.5 Hz), 7.04 (1H, d, J = 8.0 Hz), 6.74 (1H, t, J = 7.5 Hz), 3.50 (1H, septet, J = 6.5 Hz), 2.61 (2H, t, J = 8.0 Hz), 1.55 (2H, quintet, J = 8.0 Hz), 1.33 (2H, sextet, J = 7.5 Hz), 1.23 (6H, d, J = 6.0 Hz), 0.88 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 162.4, 162.3, 132.5, 130.7, 128.9, 118.1, 110.0, 59.7, 31.8, 29.4, 24.1, 22.7, 14.0. HRMS-EI calculated for $C_{14}H_{21}NO$ [M^+] 219.1623 found 219.1620.

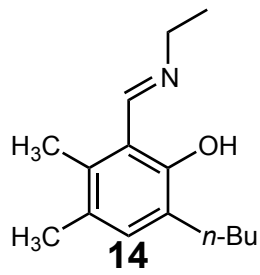
Phenol 12 was obtained according to general benzannulation procedure (23.1 mg, 66% yield).



12

^{1}H NMR ($CDCl_3$) δ 8.61 (1H, s), 6.97 (1H, d, J = 7.5 Hz), 6.47 (1H, d, J = 7.5 Hz), 3.47 (1H, septet, J = 6.5 Hz), 2.55 (2H, t, J = 8.5 Hz), 2.34 (3H, s), 1.53 (2H, quintet, J = 7.5 Hz), 1.33 (2H, sextet, J = 8.0 Hz), 1.23 (6H, d, J = 6.5 Hz), 0.87 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 160.8, 159.9, 135.8, 132.3, 129.0, 119.5, 115.8, 60.1, 31.8, 29.3, 24.3, 22.7, 18.7, 14.0. HRMS-EI calculated for $C_{15}H_{23}NO$ [M^+] 233.1780 found 233.1772.

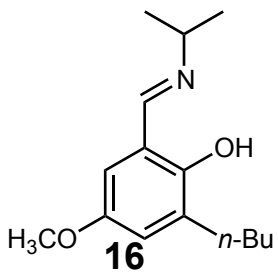
Phenol 14 was obtained according to general benzannulation procedure (19.1 mg, 55% yield).



14

^{1}H NMR ($CDCl_3$) δ 8.78 (1H,s), 6.97 (1H, s), 3.63 (2H, q, J = 7.5 Hz), 2.59 (2H, t, J = 8.0 Hz), 2.32 (3H, s), 2.20 (3H, s), 1.59 (2H, tt, J = 9.5, 7.5 Hz), 1.38 (2H, m), 1.32 (3H, t, J = 7.0 Hz), 0.93 (3H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 162.5, 158.9, 139.7, 134.7, 127.9, 125.0, 115.8, 53.9, 32.0, 29.3, 22.8, 19.7, 16.4, 14.3, 14.0. HRMS-ES$^+$ calculated for $C_{15}H_{25}NO$ [M+H]$^+$ 234.1858, found [M+H]$^+$ 234.1861.

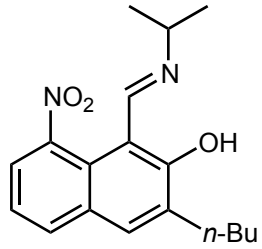
Phenol 16 was obtained according to general benzannulation procedure (22.8 mg, 61% yield).



16

^{1}H NMR ($CDCl_3$) δ 8.27 (1H, s), 6.78 (1H, d, J = 3.0 Hz), 6.57 (1H, d, J = 3.0 Hz), 3.74 (3H, s), 3.51 (1H, m, J = 6.5 Hz), 2.62 (2H, t, J = 7.5 Hz), 1.59 (2H, tt, J = 8.0, 2.0 Hz). 1.38 (2H, m, J = 7.5 Hz), 1.26 (6H, d, J = 6.5 Hz), 0.92 (3H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 162.0, 153.5, 151.4, 131.8, 119.6, 117.7, 111.7, 60.0, 55.8, 31.6, 29.5, 24.2, 22.7, 14.0. HRMS-ES$^+$ calculated for $C_{15}H_{24}NO_2$ $[M+H]^+$ 250.1807, found $[M+H]^+$ 250.1803.

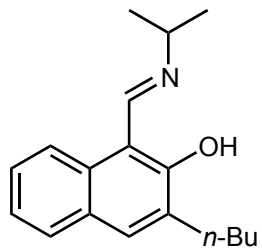
Naphthol 18 was obtained according to general benzannulation procedure (34.1 mg, 70% yield).



18

^{1}H NMR ($CDCl_3$) δ 7.93 (1H, s), 7.66 (2H, d, J = 7.5 Hz), 7.48 (1H, s), 7.16 (1H, dd, J = 8.0 Hz), 3.71 (1H, m, J = 6.5 Hz), 2.68 (2H, t, J = 7.0 Hz), 1.64 (2H, tt, J = 8.0 Hz), 1.44 (2H, m, J = 7.5 Hz), 1.38 (6H, d, J = 6.5 Hz), 0.96 (3H, t, J = 7,5 Hz). ^{13}C NMR ($CDCl_3$) δ 179.3, 156.5, 144.4, 140.3, 133.5, 132.5, 128.3, 125.8, 123.7, 121.0, 101.7, 52.6, 30.9, 29.8, 23.3, 22.7, 14.0. HRMS-ES$^+$ calculated for $C_{18}H_{23}N_2O_3$ $[M+H]^+$ 315.1709, found $[M+H]^+$ 315.1711.

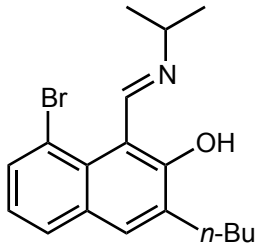
Naphthol 20 was obtained according to general benzannulation procedure (35.6 mg, 88% yield).



20

^{1}H NMR ($CDCl_3$) δ 8.61 (1H, s), 7.71 (1H, d, J = 8.0 Hz), 7.46 (2H, m), 7.28 (1H, t, J = 7.0 Hz), 7.12 (1H, t, J = 7.0 Hz), 3.70 (1H, septet, J = 6.5 Hz), 2.63 (2H, t, J = 8.0 Hz), 1.59 (2H, quintet, J = 7.5 Hz), 1.37 (2H, sextet, J = 7.5 Hz), 1.35 (6H, d, J = 6.5 Hz), 0.89 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 176.3, 154.0, 136.4, 133.7, 132.1, 127.5, 125.8, 125.0, 121.4, 116.1, 104.4, 52.6, 30.2, 28.9, 22.8, 21.8, 13.0. HRMS-EI calculated for $C_{18}H_{23}NO$ $[M^+]$ 269.1780 found 269.1783.

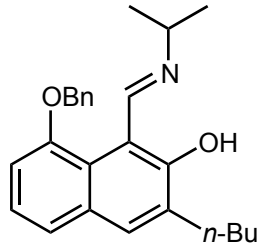
Naphthol 22 was obtained according to general benzannulation procedure (47 mg, 90% yield).



22

^{1}H NMR ($CDCl_3$) δ 9.56 (1H, s), 7.57 (1H, dd, J = 7.5, 1.0 Hz), 7.38 (1H, dd, J = 8.0, 1.0 Hz), 7.34 (1H, s), 6.94 (1H, t, J = 7.5 Hz), 3.69 (1H, septet, J = 6.5 Hz), 2.58 (2H, t, J = 7.5 Hz), 1.56 (2H, quintet, J = 8.0 Hz), 1.36 (8H, m), 0.88 (3H, t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 180.8, 156.4, 139.2, 135.0, 133.8, 132.2, 128.9, 128.4, 122.8, 114.5, 105.0, 51.7, 31.0, 29.8, 23.4, 22.8, 14.0. HRMS-EI calculated for $C_{18}H_{22}BrNO$ [M^+] 347.0885 found 347.0879.

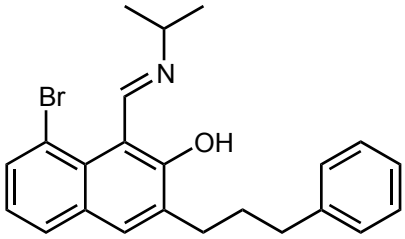
Naphthol 24 was obtained according to general benzannulation procedure (45.1 mg, 80% yield).



24

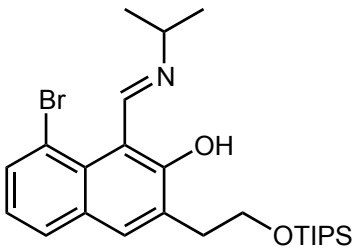
^{1}H NMR ($CDCl_3$) δ 9.59 (1H, s), 7.42 (3H, m), 7.37 – 7.29 (3H, m), 7.15 (1H, d, J = 7.5 Hz), 7.05 (1H, t, J = 7.5 Hz), 6.95 (1H, d, J = 7.5 Hz), 3.21 (1H, septet, J = 6.5 Hz), 2.61 (2H, t, J = 7.5 Hz), 1.58 (2H, quintet, J = 8.0 Hz), 1.38 (2H, sextet, J = 7.5 Hz), 1.05 (6H, d, J = 7.0 Hz), 0.88 (3H, t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 179.3, 159.5, 152.7, 137.5, 135.7, 134.0, 127.7, 127.6, 127.4, 127.0, 122.1, 121.3, 120.7, 108.8, 104.5, 70.4, 50.6, 30.1, 28.8, 22.1, 21.8, 13.1. HRMS-EI calculated for $C_{25}H_{29}NO_2$ [M^+] 375.2198 found 375.2194.

Naphthol 25 was obtained according to general benzannulation procedure (58.8 mg, 96% yield). ^{1}H NMR ($CDCl_3$) δ 9.64 (1H, s), 7.65 (1H, dd, J = 7.5, 1.0 Hz), 7.44 (1H, d, J = 7.5 Hz), 7.41 (1H, s), 7.27 (2H, dd, J = 15, 7.5 Hz), 7.23 (2H, d, J = 7.0 Hz), 7.17 (1H, dd, J = 7.5 Hz), 6.97 (1H, t, J = 8.0 Hz), 3.77 (1H, m, J = 6.5 Hz), 2.74 (2H, t, J = 8.0 Hz), 2.73 (2H, t, J = 7.0 Hz), 2.01 (2H, tt, J = 8.0, 7.0 Hz), 1.43 (6H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$) δ 180.8, 156.3, 142.4, 138.6, 135.1, 133.8, 132.1, 128.7, 128.4, 128.3, 128.2, 125.5, 122.8, 114.5, 104.9, 51.6, 35.8, 30.4, 29.7, 23.3. HRMS-ES^{+} calculated for $C_{23}H_{25}NOBr$ $[M+H]^{+}$ 410.1120, found $[M+H]^{+}$ 410.1102.



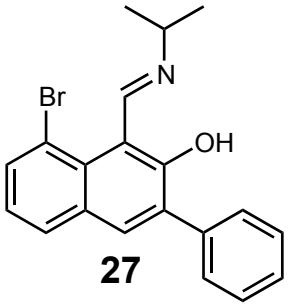
25

Naphthol 26 was obtained according to general benzannulation procedure (70.9 mg, 96% yield). ^{1}H NMR ($CDCl_3$) δ 9.54 (1H, s), 7.56 (1H, dd, J = 8.0, 1.0 Hz), 7.46 (1H, s), 7.36 (1H, dd, J = 7.5, 1.0 Hz), 6.89 (1H, t, J = 8.0 Hz), 3.90 (2H, t, J = 6.5 Hz), 3.70 (1H, septet, J = 6.5 Hz), 2.83 (2H, t, J = 6.5 Hz), 1.33 (6H, d, J = 7.0 Hz), 0.97 (3H, m), 0.93 (18H, d, J = 5.5 Hz). ^{13}C NMR ($CDCl_3$) δ 180.9, 156.3, 137.0, 135.7, 133.9, 132.4, 128.8, 128.5, 122.8, 114.5, 105.0, 62.3, 51.6, 33.6, 23.4, 18.0, 12.0. HRMS-EI calculated for $C_{25}H_{38}BrNO_2Si$ $[M^{+}]$ 491.1855 found 491.1862.



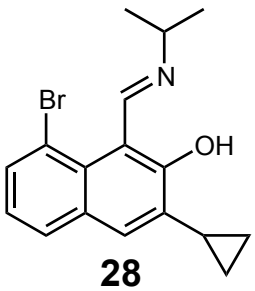
26

Naphthol 27 was obtained according to general benzannulation procedure (45.7 mg, 90% yield). ^{1}H NMR ($CDCl_3$) δ 9.56 (1H, s), 7.62 (1H, d, J = 7.5 Hz), 7.57 (3H, m), 7.45 (1H, d, J = 7.5 Hz), 7.37 (2H, t, J = 7.5 Hz), 7.28 (1H, t, J = 7.5 Hz), 6.93 (1H, t, J = 7.5 Hz), 3.69 (1H, septet, J = 6.5 Hz), 1.33 (6H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$) δ 179.6, 156.5, 138.0, 137.5, 136.9, 134.7, 132.9, 129.2, 129.2, 128.6, 128.1, 127.5, 123.1, 114.6, 105.7, 51.9, 23.4. HRMS-EI calculated for $C_{20}H_{18}BrNO$ [M^+] 367.0572 found 367.0577.



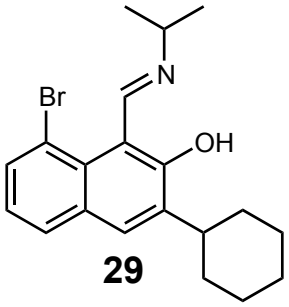
27

Naphthol 28 was obtained according to general benzannulation procedure (46.1 mg, 93% yield). ^{1}H NMR ($CDCl_3$) δ 9.65 (1H, s), 7.61 (1H, d, J = 7.5 Hz), 7.40 (1H, d, 7.5 Hz), 7.08 (1H, s), 6.94 (1H, dd, J = 8.0, 7.5 Hz), 3.77 (1H, m, J = 6.5 Hz), 2.29 (1H, tt, J = 8.5, 5.5 Hz), 1,43 (6H, d, J = 6.5 Hz), 0.99 (2H, td, J = 6.0, 4.5 Hz), 0.66 (2H, dd, J = 6.0, 4.0 Hz). ^{13}C NMR ($CDCl_3$) δ 181.2, 156.5, 140.1, 133.7, 131.7, 130.8, 128.7, 128.3, 122.8, 114.4, 104.7, 51.6, 23.3, 9.8, 7.3. HRMS-ES$^+$ calculated for $C_{17}H_{19}NOBr$ [M+H]$^+$ 332.0650, found [M+H]$^+$ 332.0646.



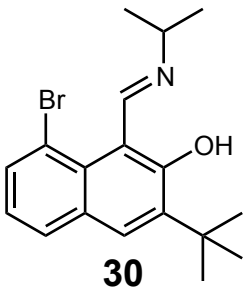
28

Naphthol 29 was obtained according to general benzannulation procedure (54.8 mg, 98% yield). ^{1}H NMR ($CDCl_3$) δ 9.61 (1H, s), 7.63 (1H, d, J = 8.0 Hz), 7.47 (1H, d, J = 7.5 Hz), 7.37 (1H, s), 6.97 (1H, dd, J = 8.0, 7.5 Hz), 3.75 (1H, m, J = 6.5 Hz), 3.08 (1H, tt, J = 12, 11.5 Hz), 1.92 (2H, d, J = 12.5 Hz), 1.84 (2H, d, J = 13 Hz), 1.51 (2H, m), 1.41 (6H, d, J = 6.5 Hz), 1.29 (4H, m). ^{13}C NMR ($CDCl_3$) δ 180.3, 156.3, 143.9, 133.8, 132.8, 131.9, 128.9, 128.5, 122.8, 114.4, 104.9, 51.6, 36.1, 32.9, 26.9, 26.5, 23.4. HRMS-ES$^+$ calculated for $C_{20}H_{25}NOBr$ $[M+H]^+$ 374.1120, found $[M+H]^+$ 374.1113.



29

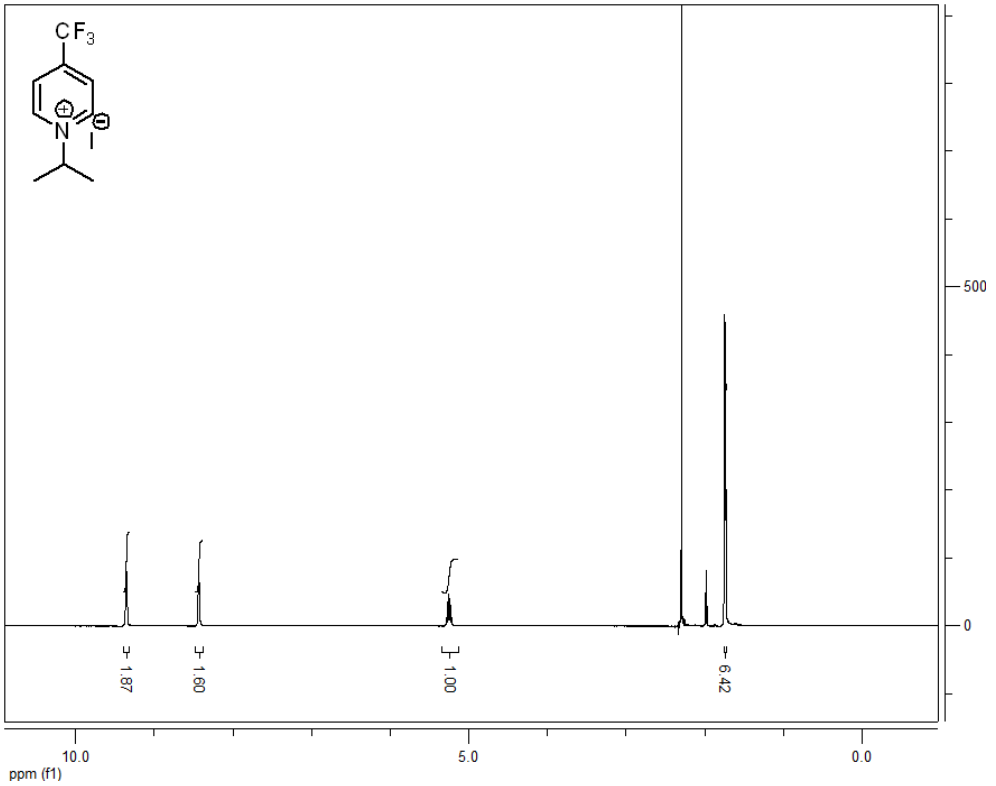
Naphthol 30 was obtained according to general benzannulation procedure (48.4 mg, 93% yield). ^{1}H NMR ($CDCl_3$) δ 9.53 (1H, s), 7.62 (1H, dd, J = 8.0, 1.0 Hz), 7.47 (1H, d, J = 1.5 Hz), 7.46 (1H, s), 6.96 (1H, dd, J = 7.5 Hz), 3.74 (1H, m, J = 6.5 Hz), 1.45 (9H, s), 1.42 (6H, d, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$) δ 181.5, 155.9, 145.4, 133.8, 133.3, 132.5, 128.8, 128.7, 122.7, 114.0, 105.8, 51.5, 35.0, 29.3, 23.4. HRMS-ES$^+$ calculated for $C_{18}H_{23}NOBr$ $[M+H]^+$ 348.0963, found $[M+H]^+$ 348.0965.

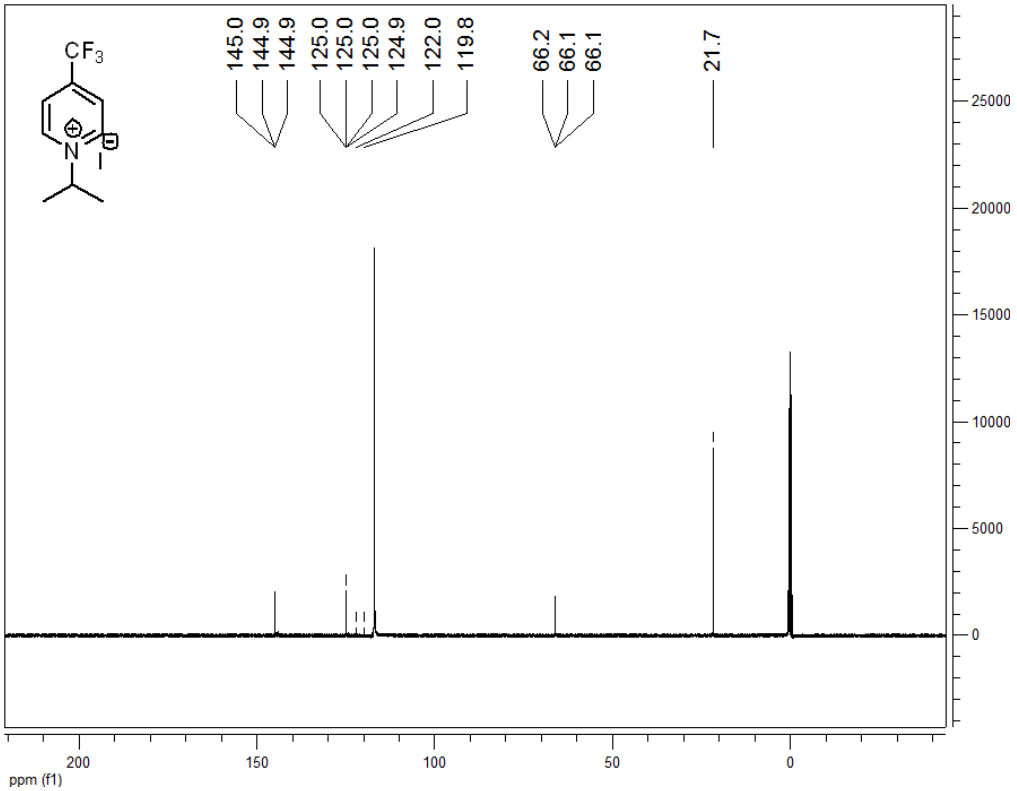


30

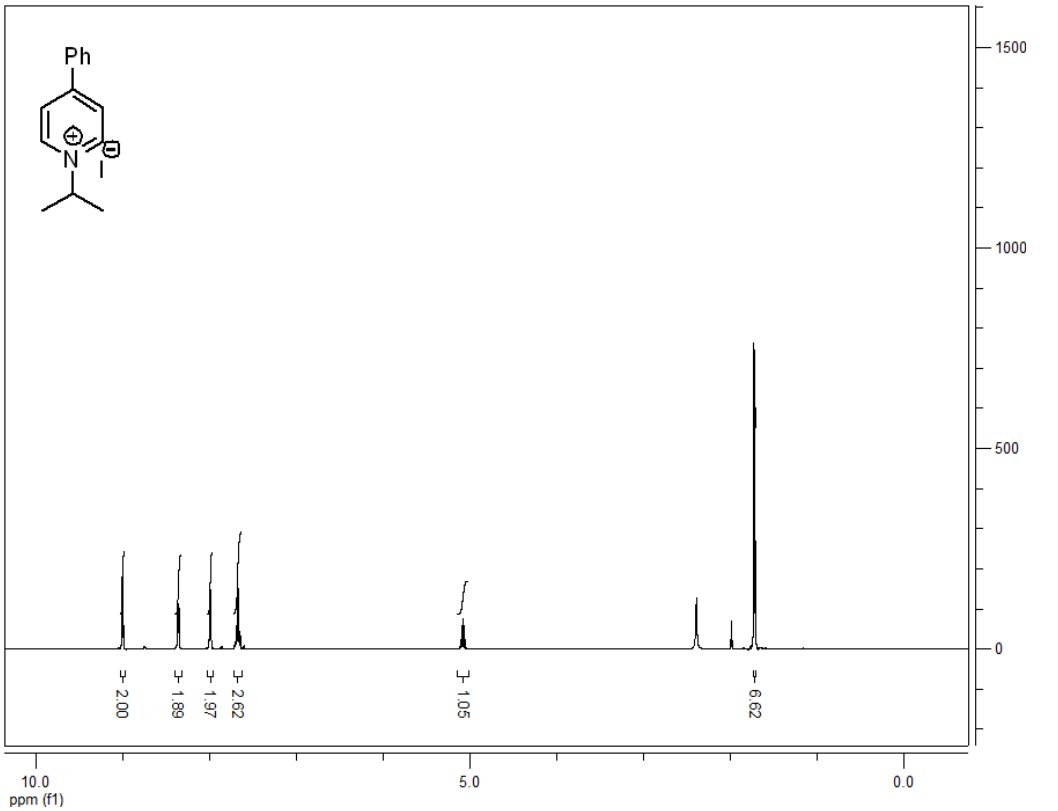
NMR DATA

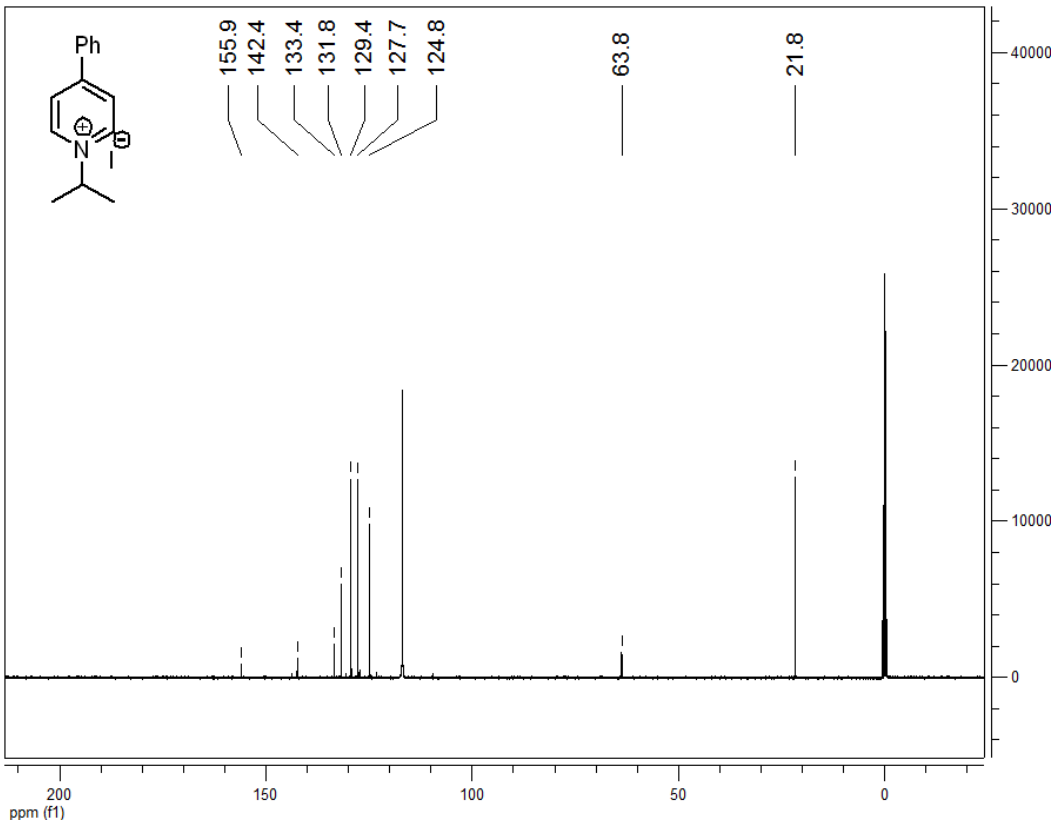
Pyridinium 5



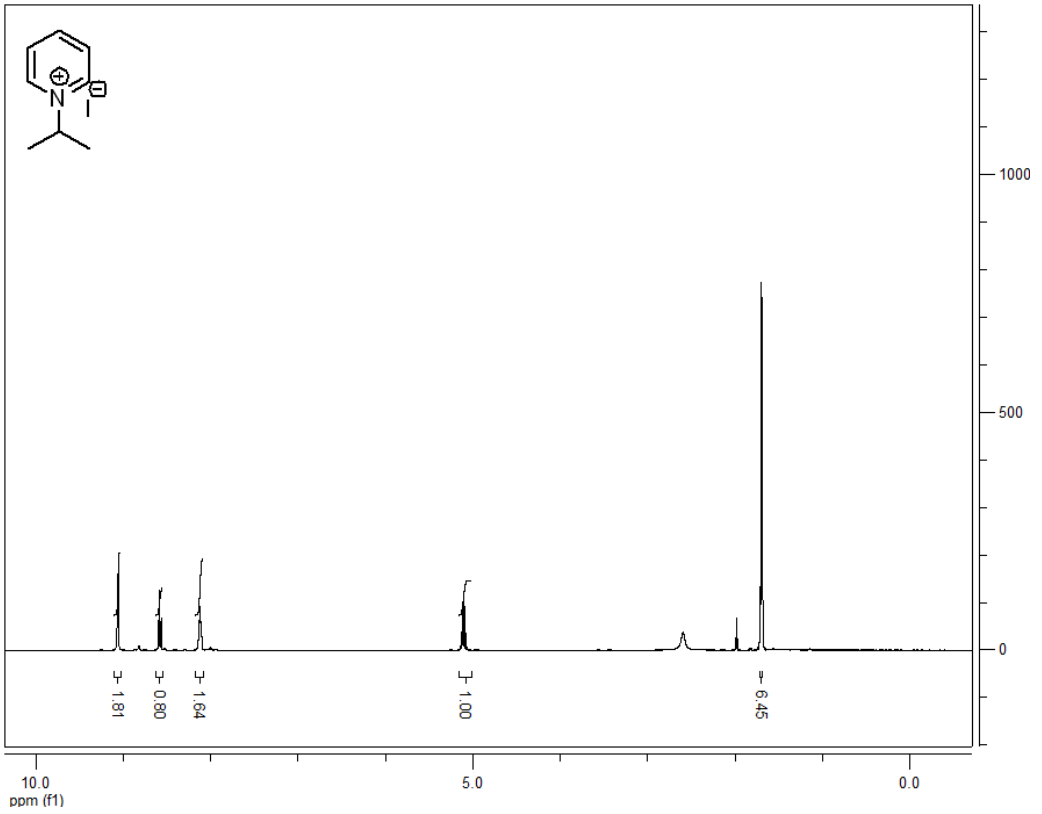


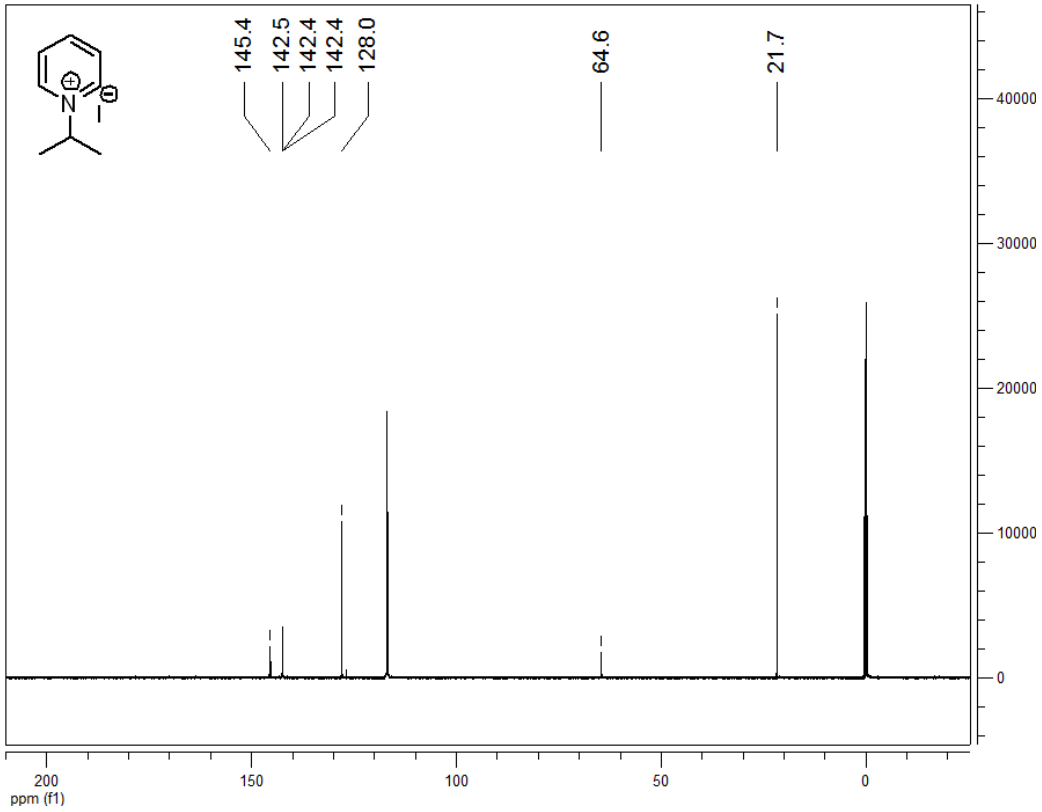
Pyridinium 7



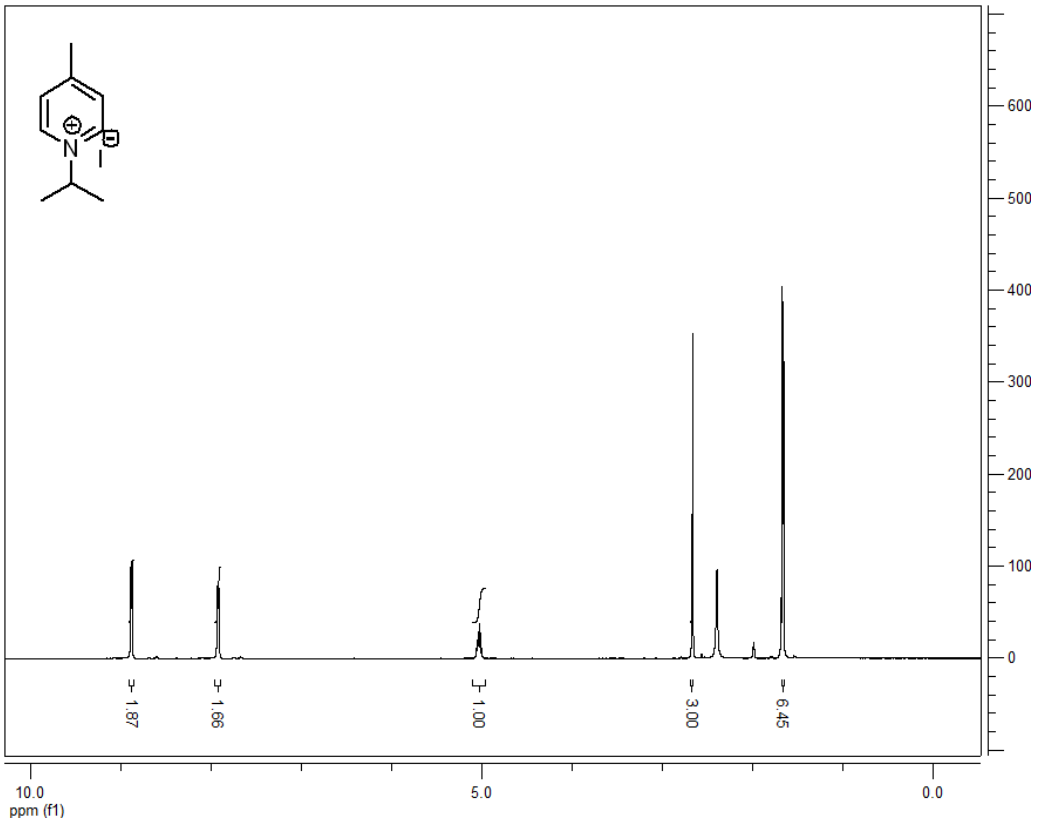


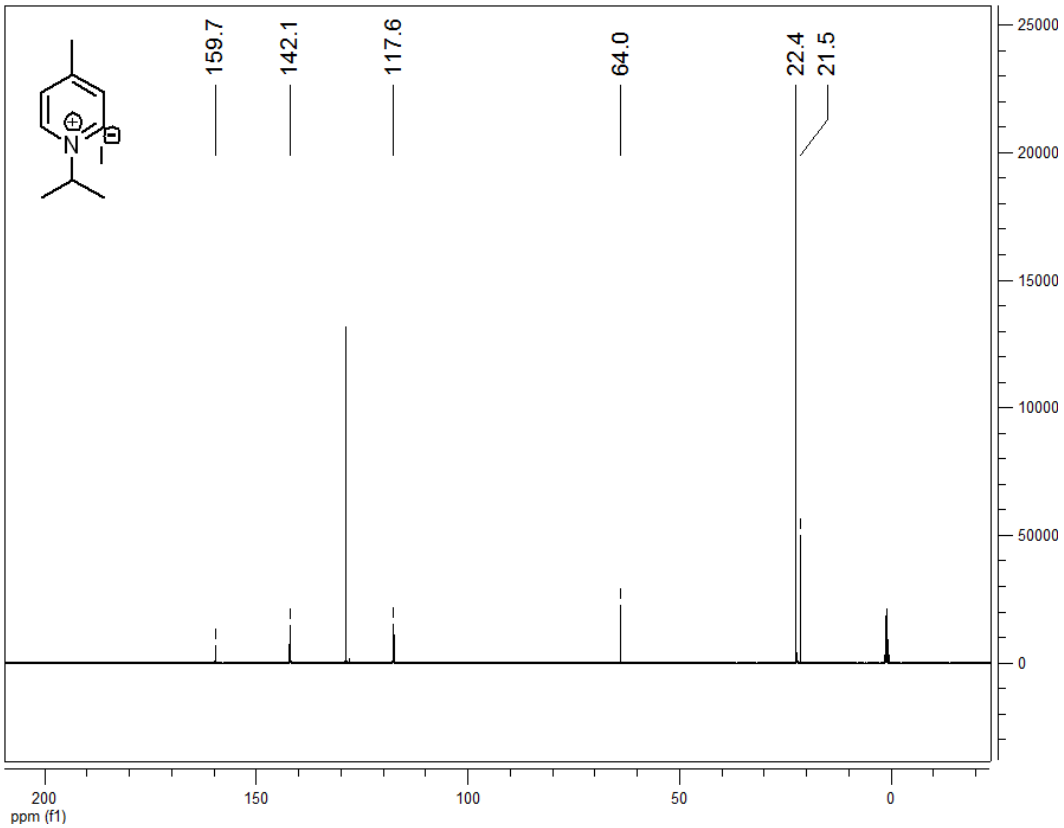
Pyridinium 9



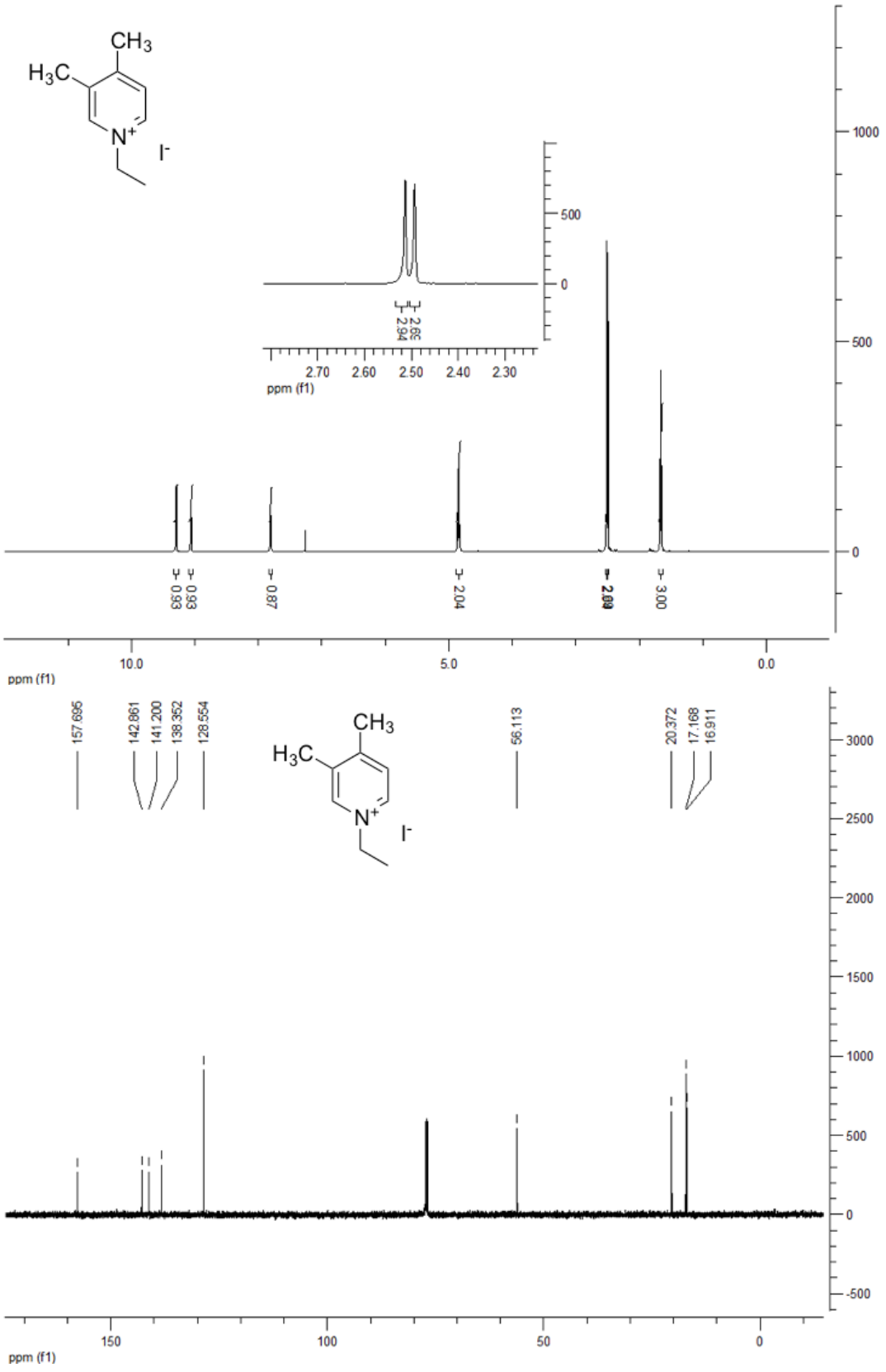


Pyridinium 11

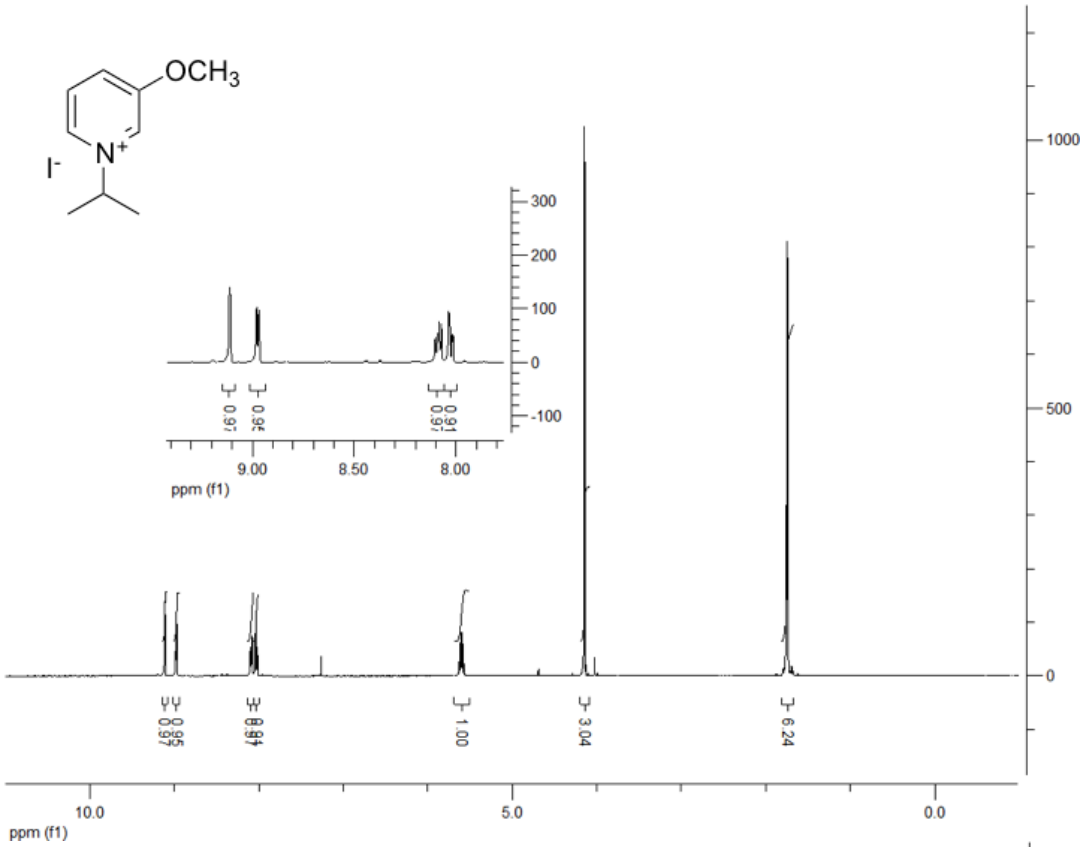


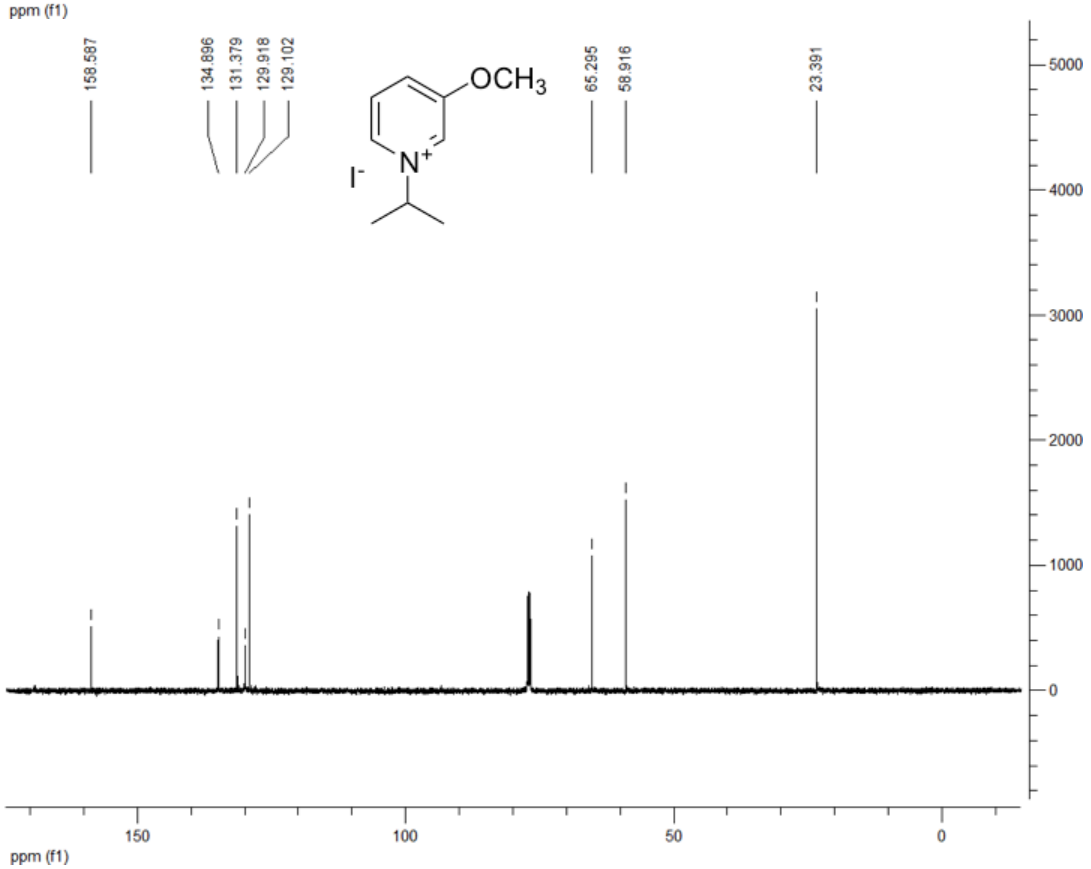


Pyridinium 13

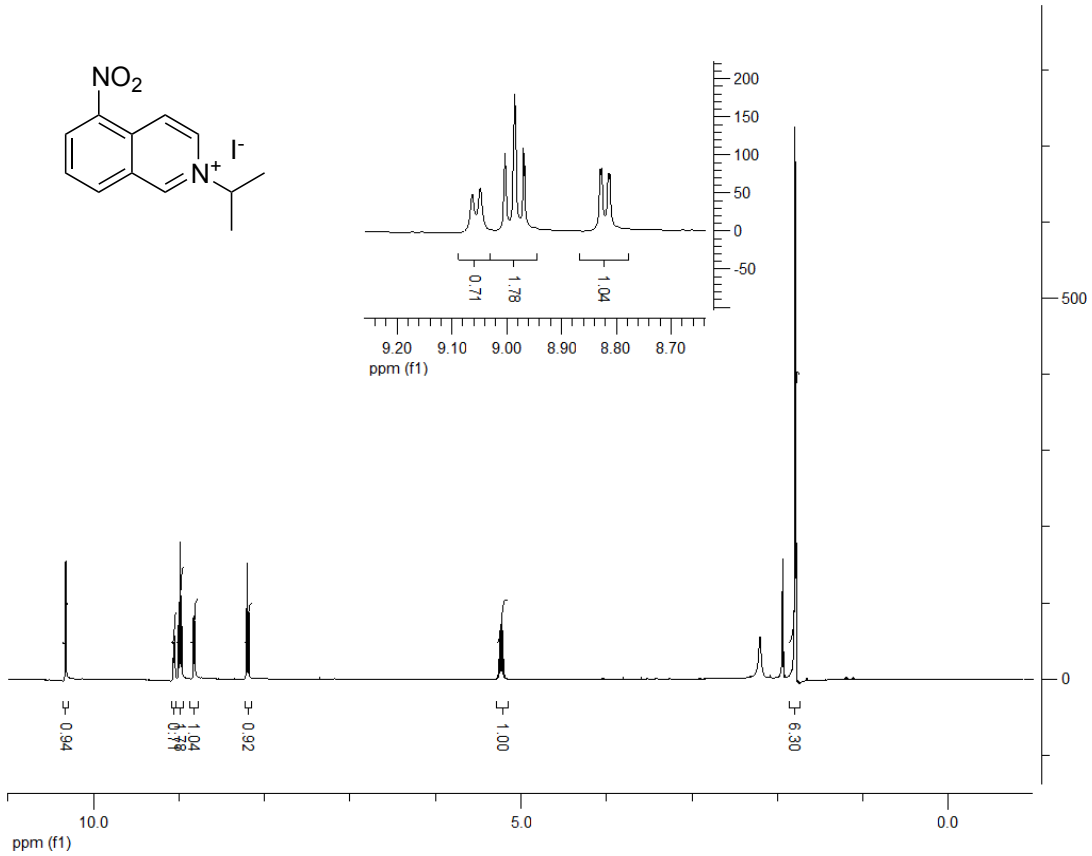


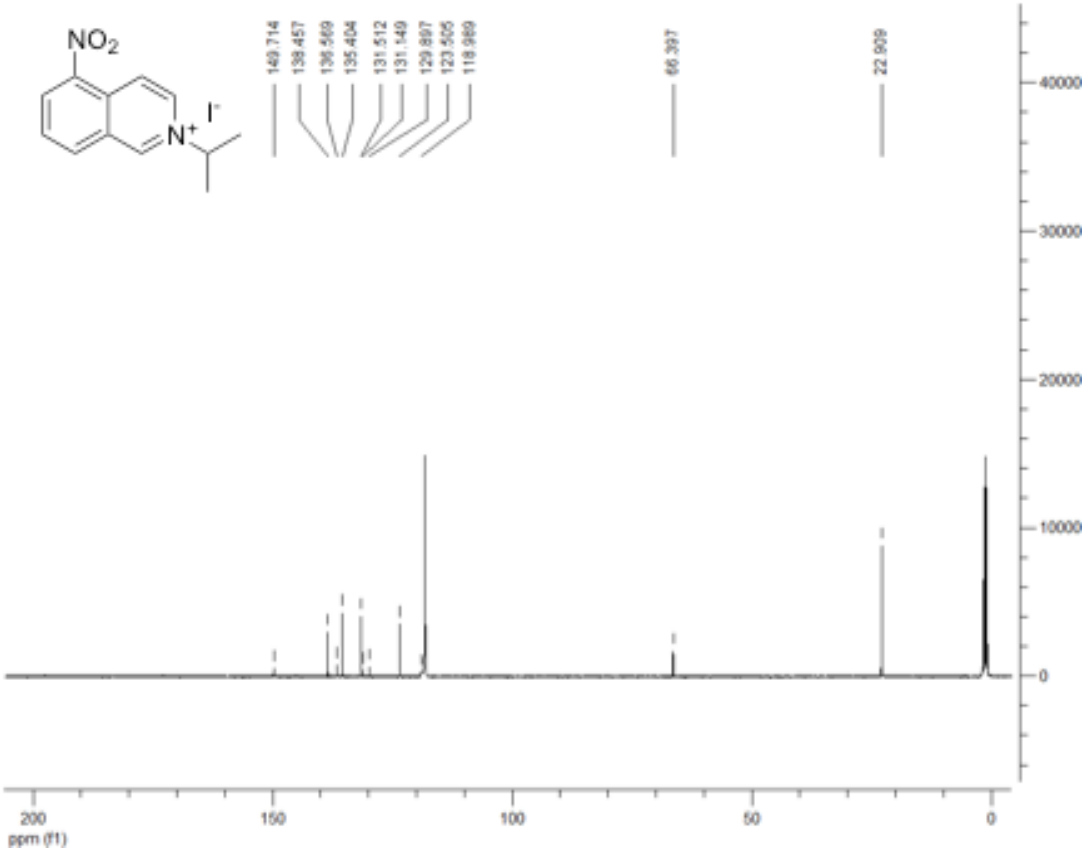
Pyridinium 15



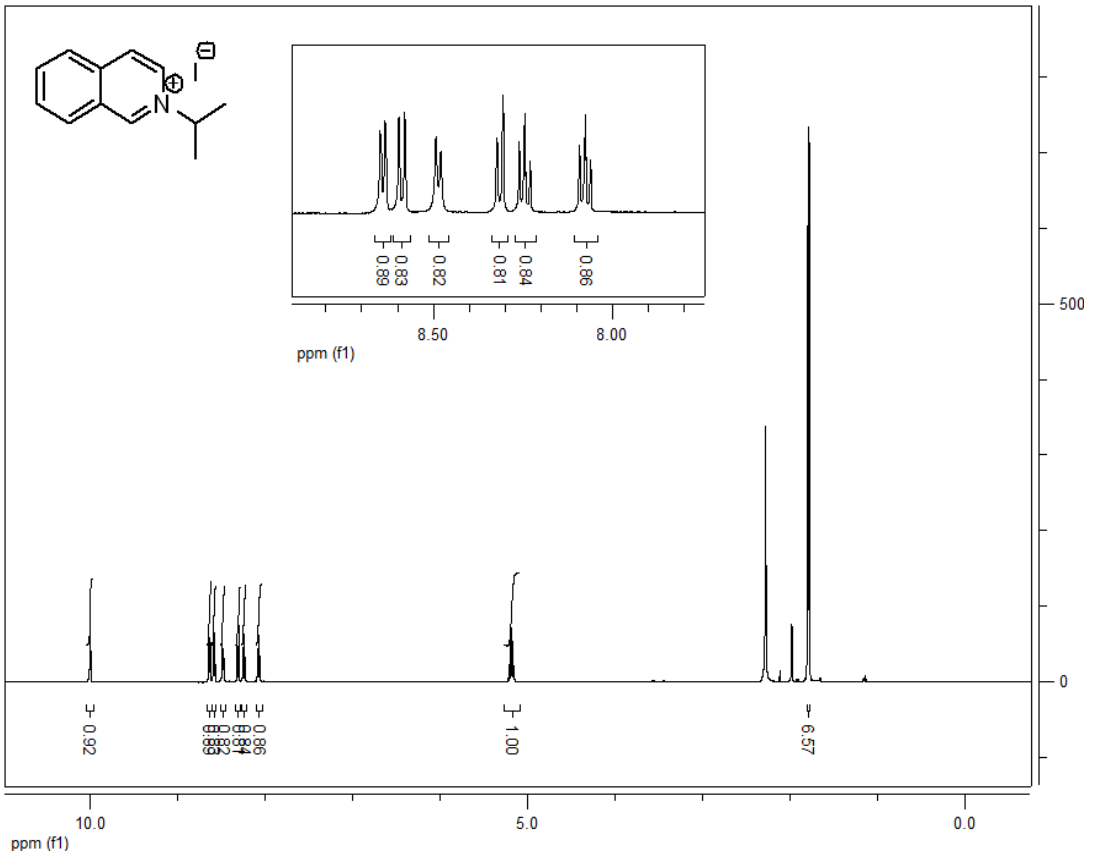


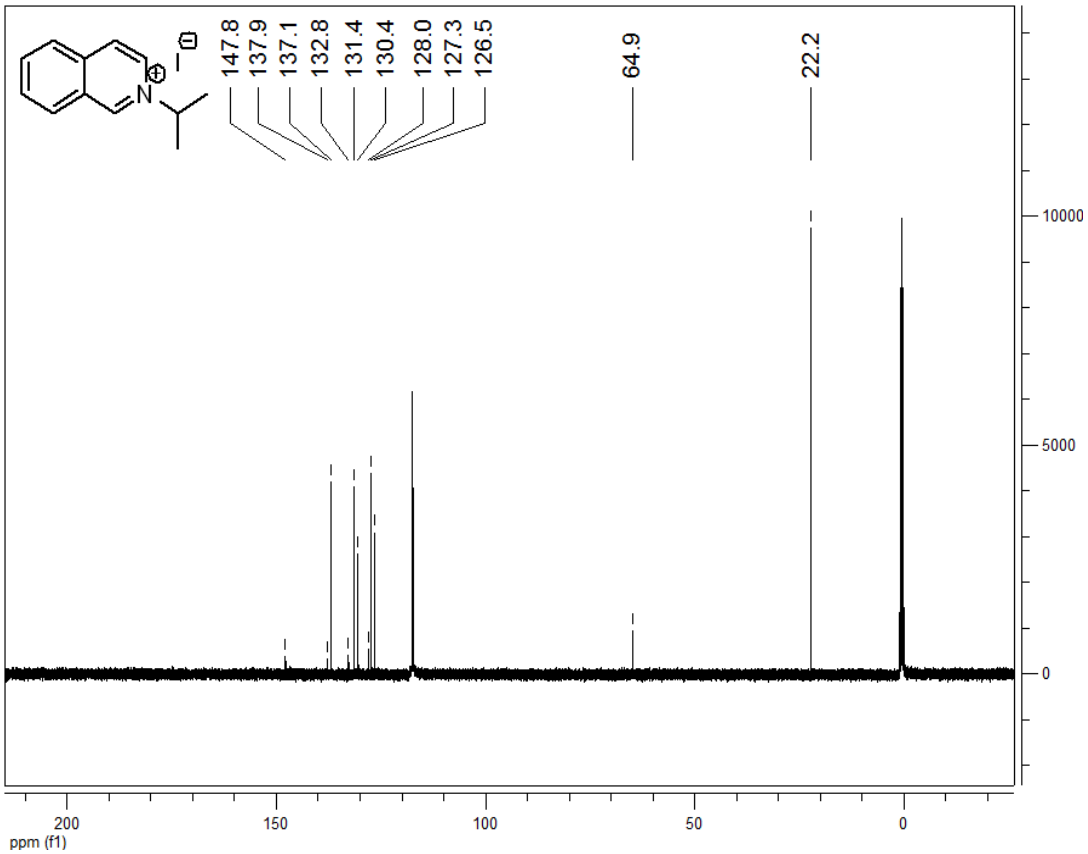
Isoquinolinium 17



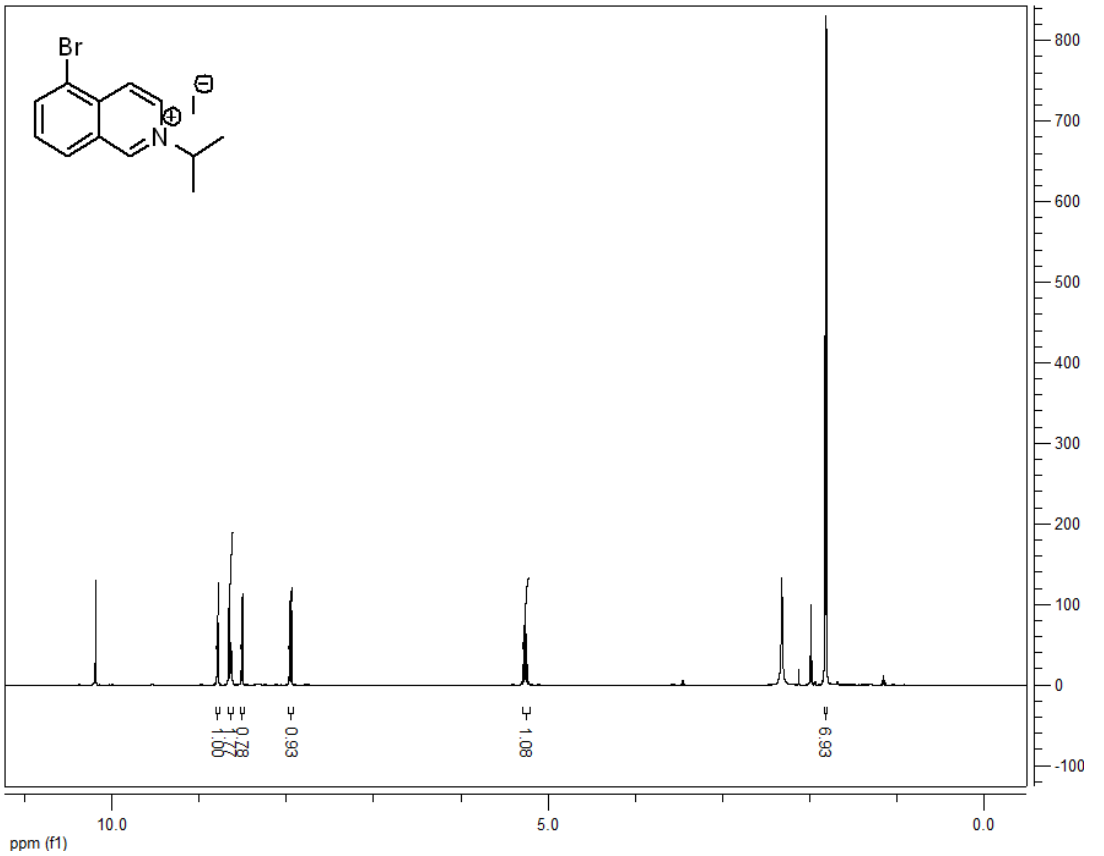


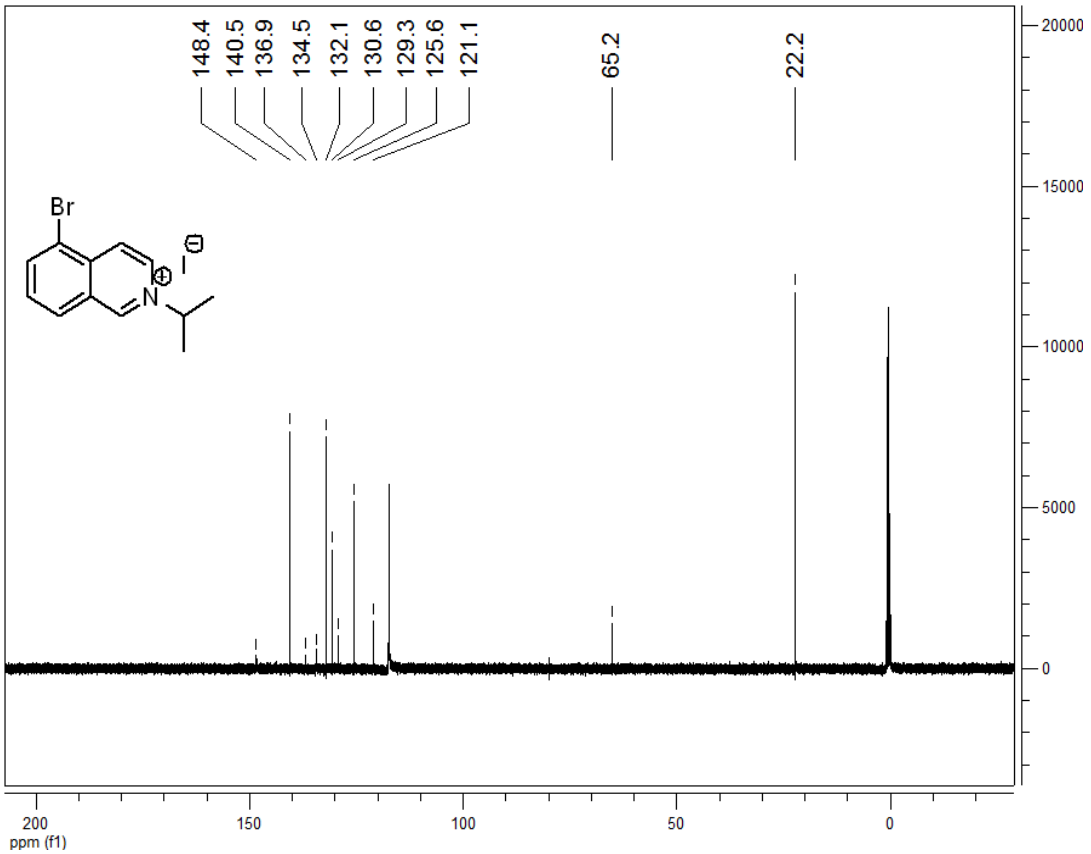
Isoquinolinium 19



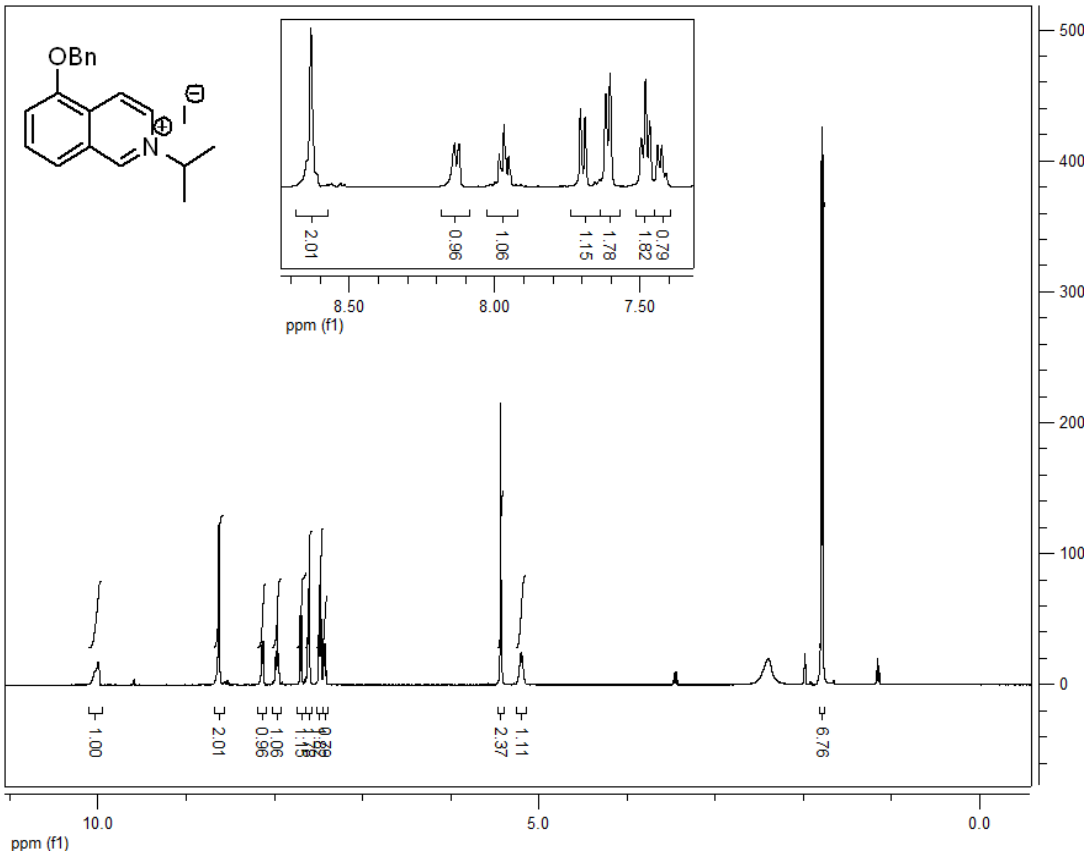


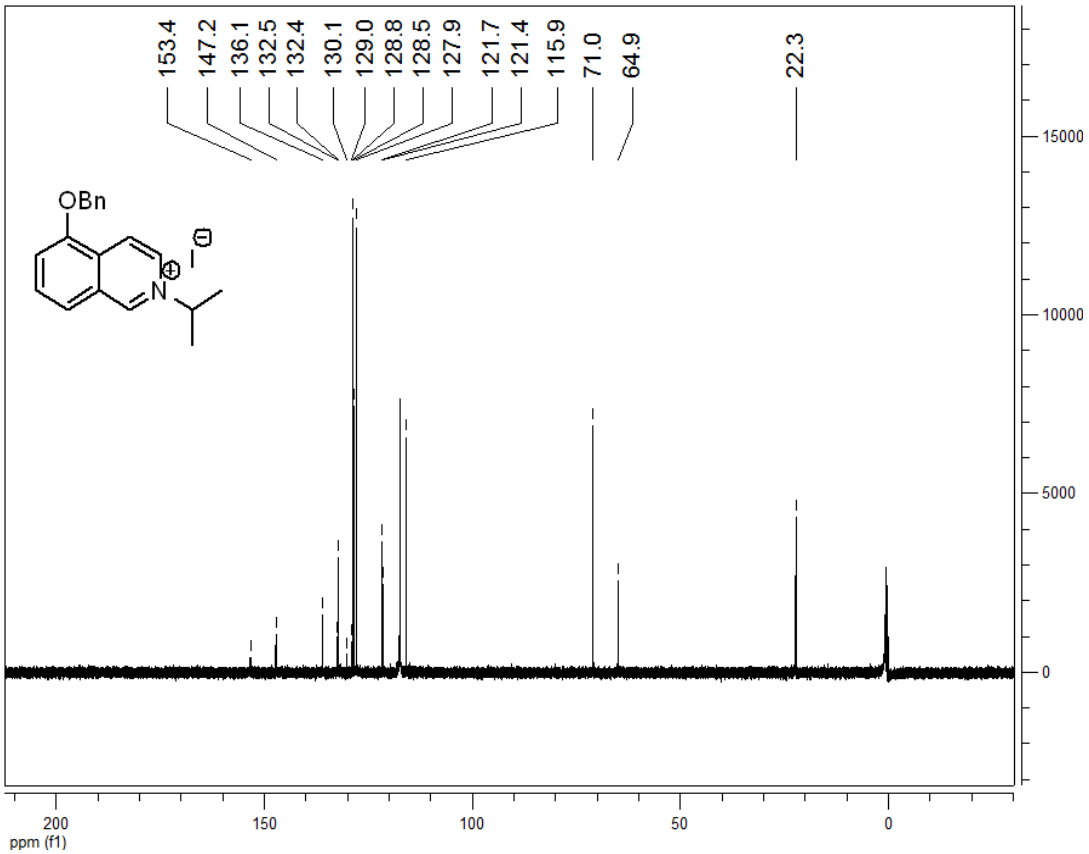
Isoquinolinium 21



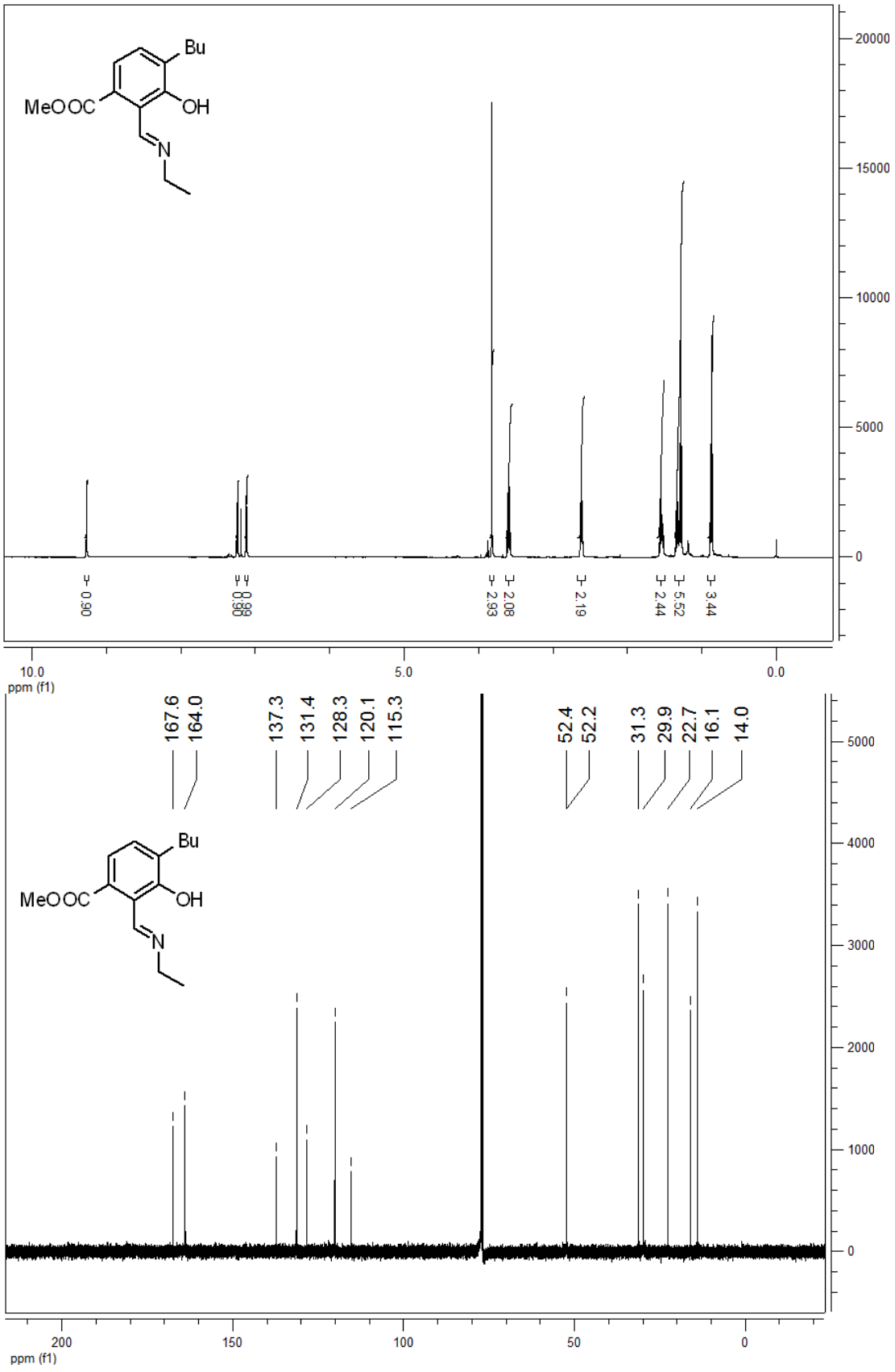


Isoquinolinium 23





Phenol 4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MeOOC
OH
N
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0.89
0.89
2.93
2.08
2.19
2.44
5.52
3.44
20000
15000
10000
5000
0
10.0
5.0
0.0
ppm (f1)
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164.0
137.3
131.4
128.3
120.1
115.3
52.4
52.2
31.3
29.9
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4000
3000
2000
1000
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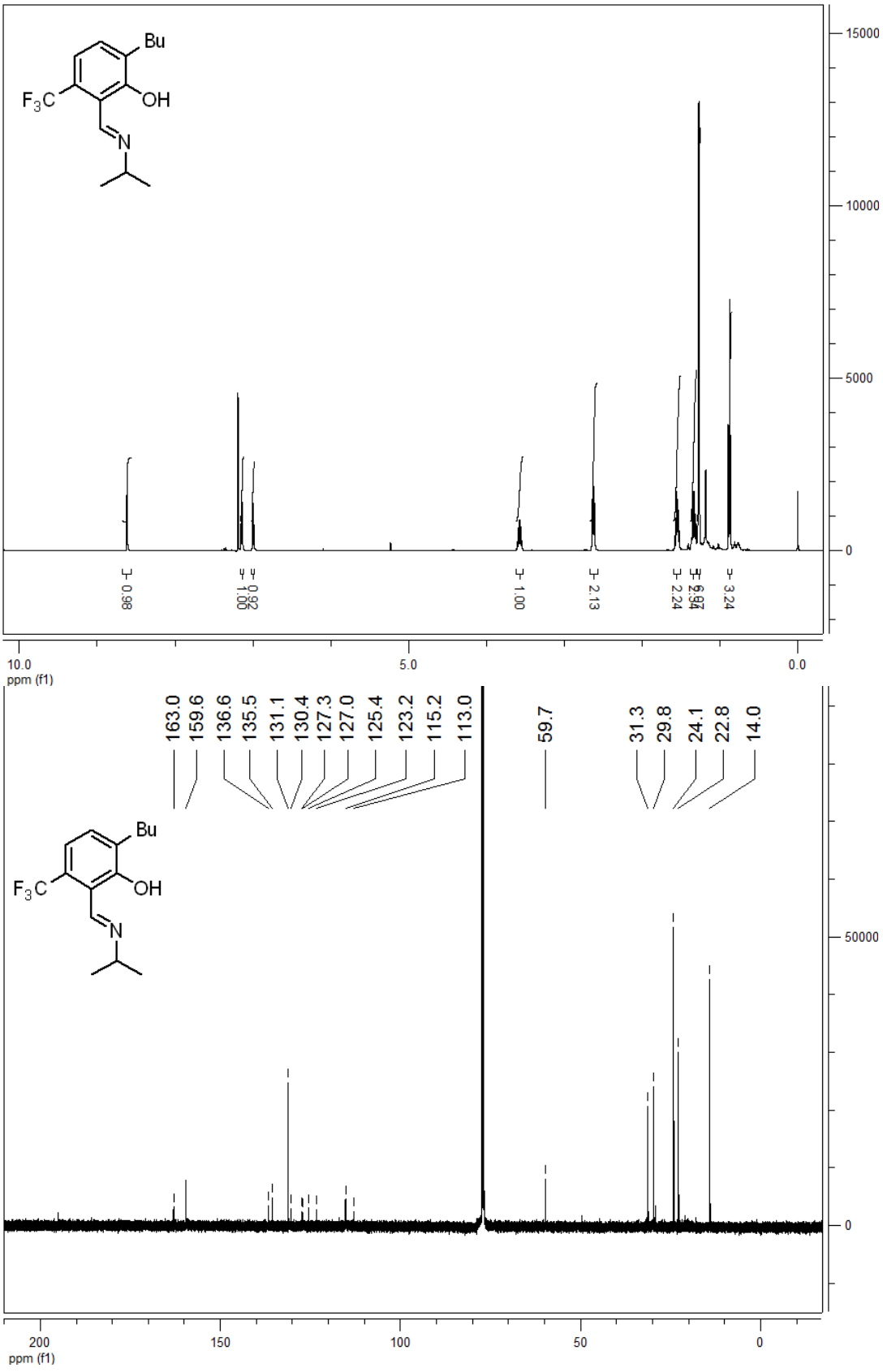
200
150
100
50
0
ppm (f1)

Phenol 6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F3C
OH
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1.00
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2.07
3.24
10.0
ppm (f1)
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159.6
136.6
135.5
131.1
130.4
127.3
127.0
125.4
123.2
115.2
113.0
59.7
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22.8
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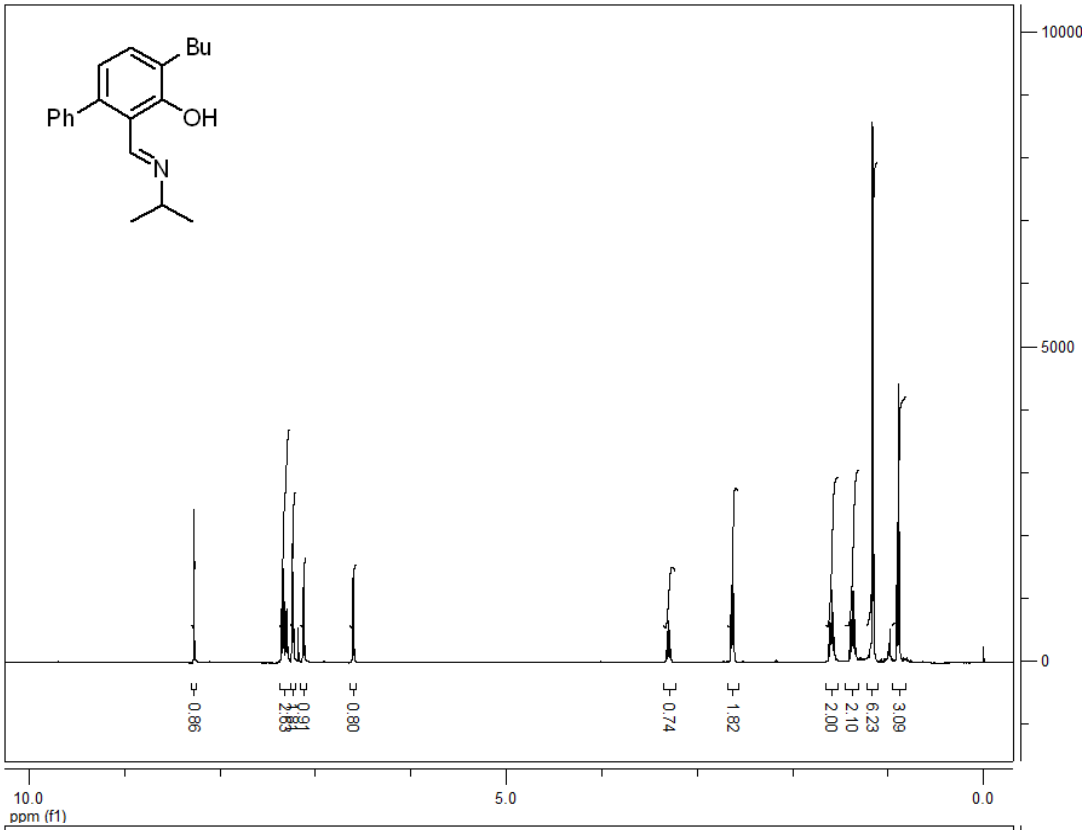
100
50
0

Phenol 8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Ph
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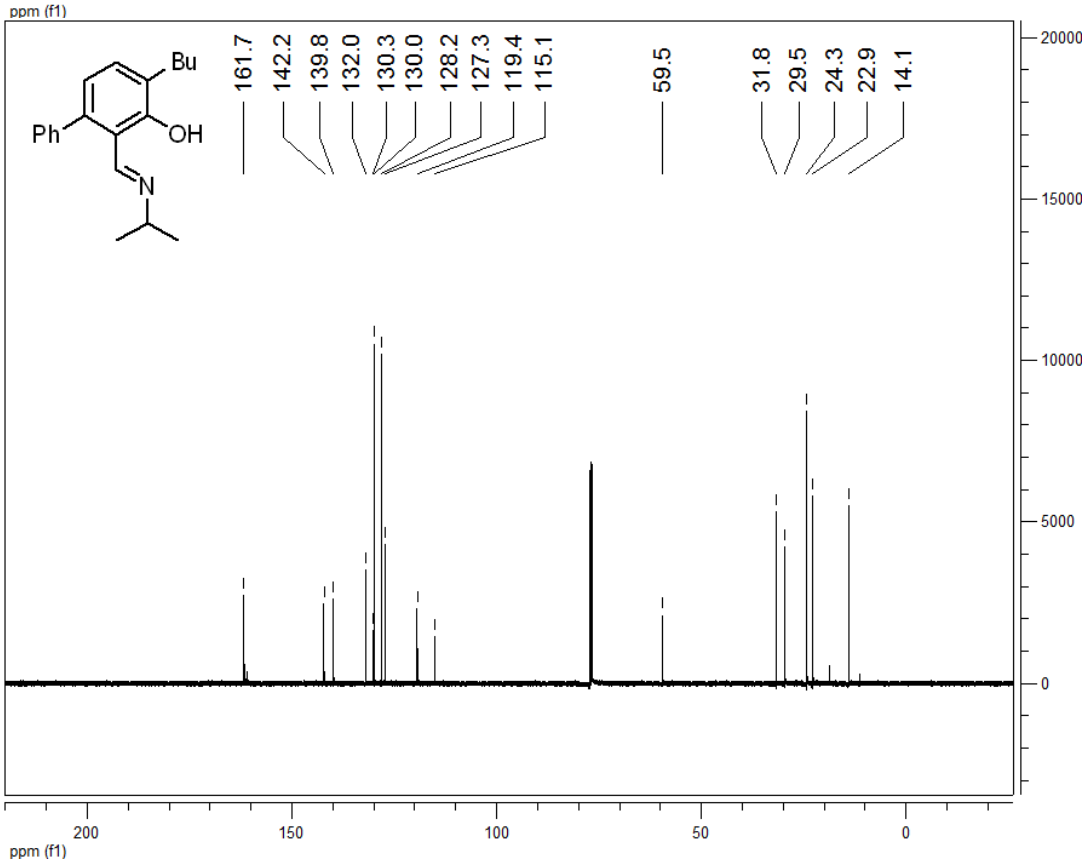
6.23
3.09
10.0
5.0
0.0
ppm (f1)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Ph
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130.3
130.0
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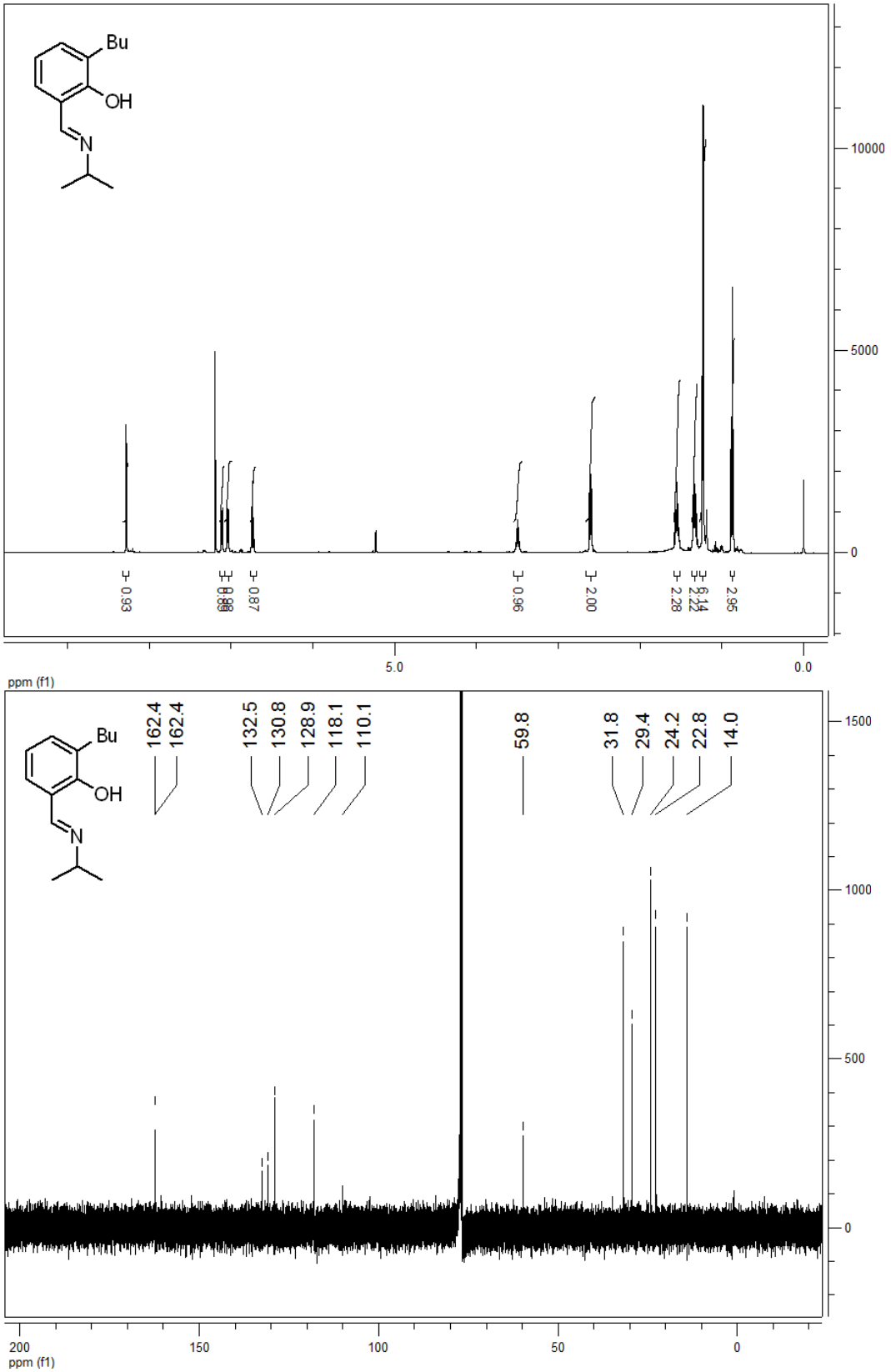
127.3
119.4
115.1
59.5
31.8
29.5
24.3
22.9
14.1
20000
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

Phenol 10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OH
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5.0
0.0
ppm (f1)
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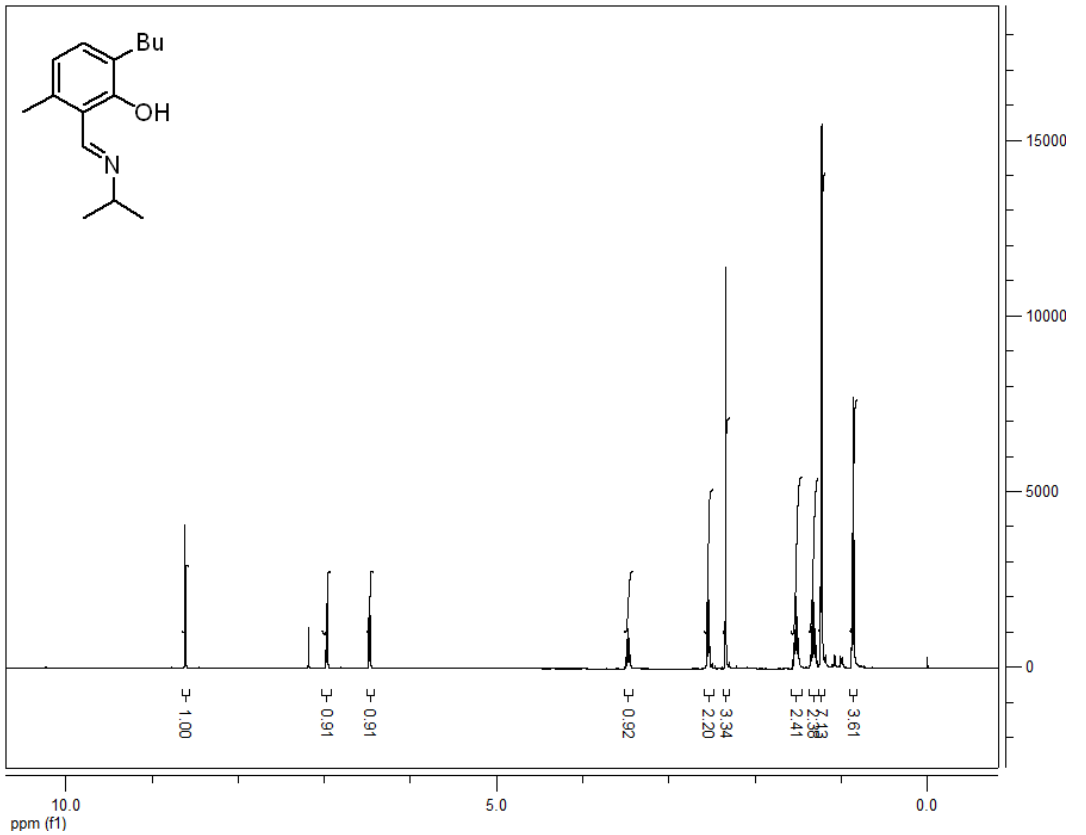
162.4
132.5
130.8
128.9
118.1
110.1
59.8
31.8
29.4
24.2
22.8
14.0
1500
1000
500
0
200
150
100
50
0
ppm (f1)

Phenol 12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OH
N
15000
10000
5000
0
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0.91
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2.41
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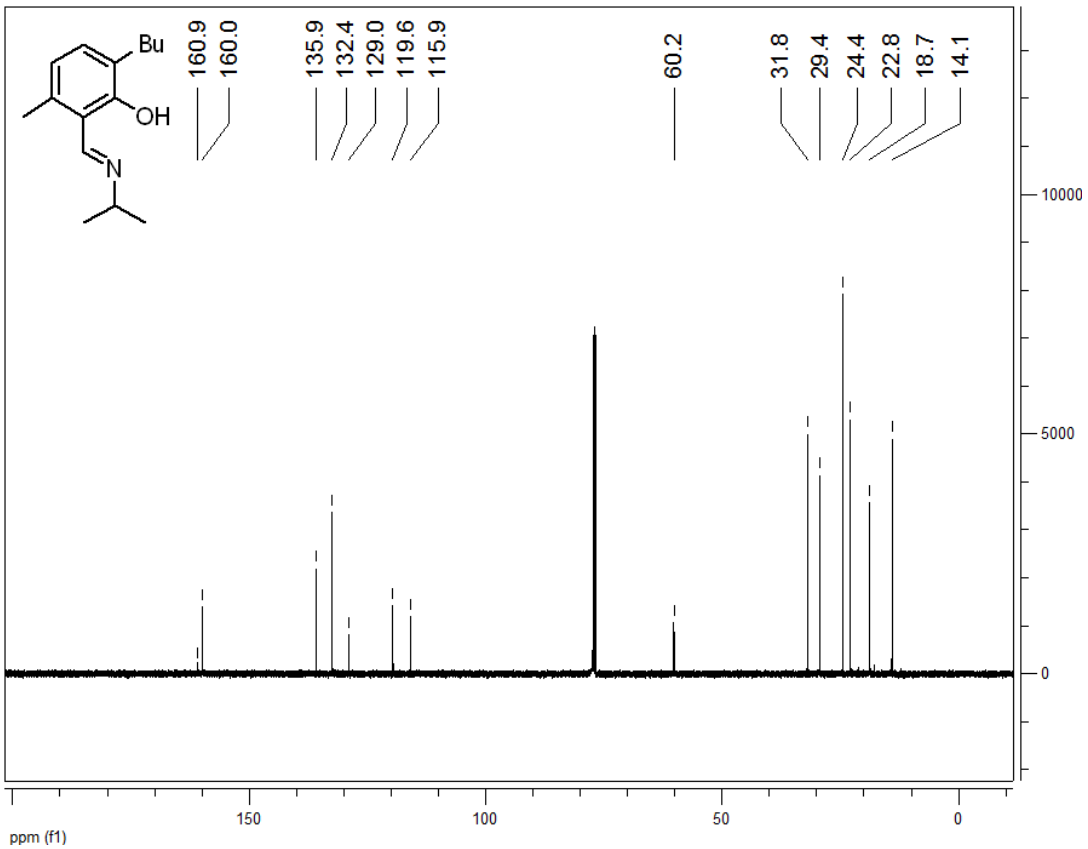
10.0
5.0
0.0
ppm (f1)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OH
N
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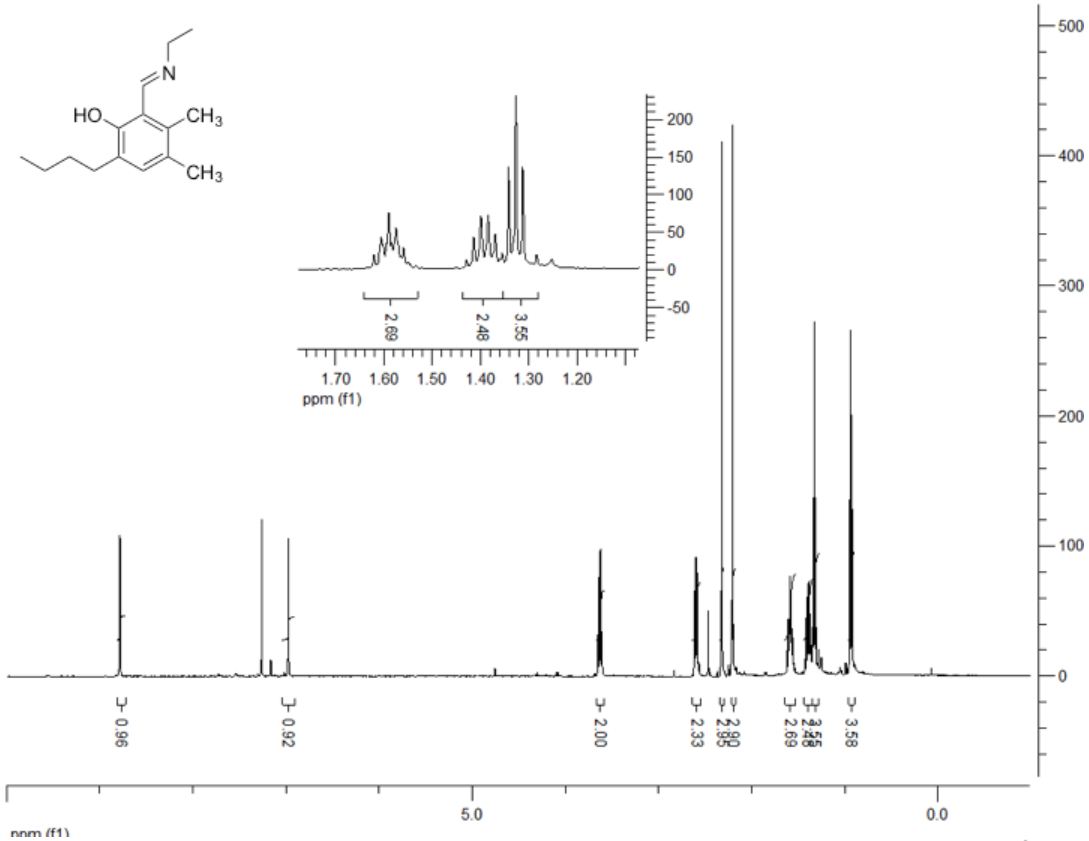
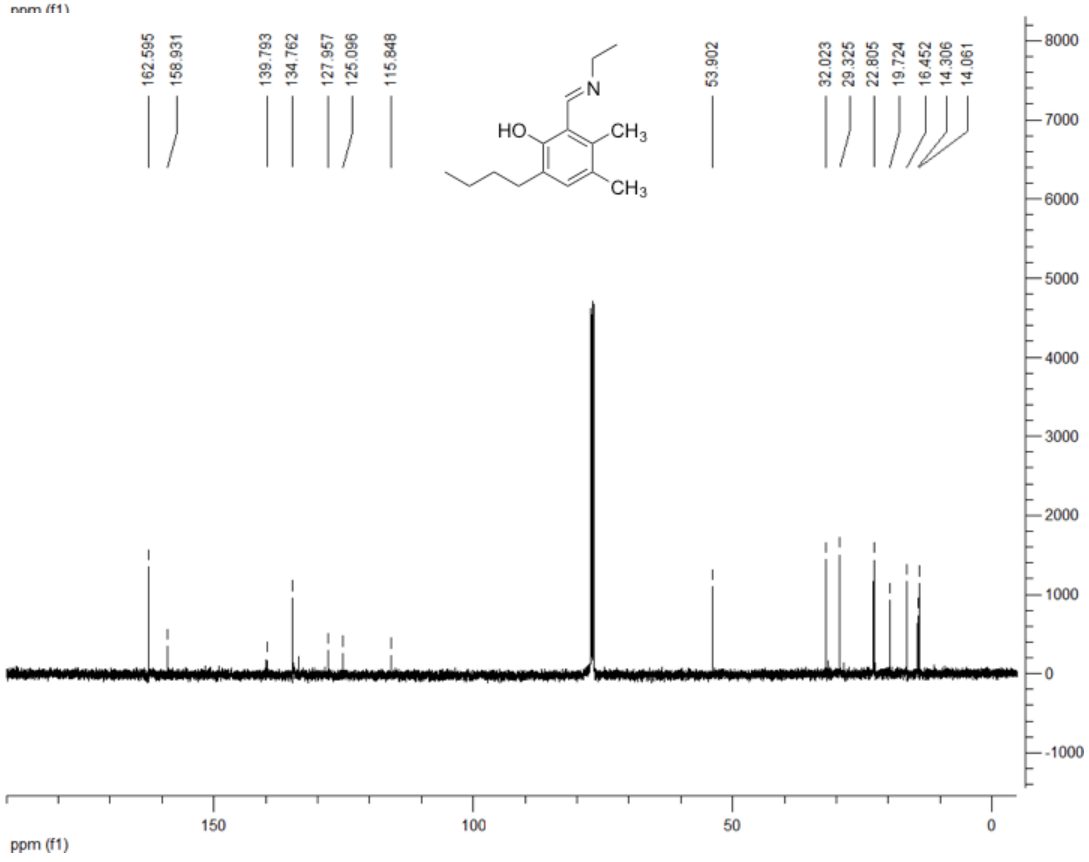
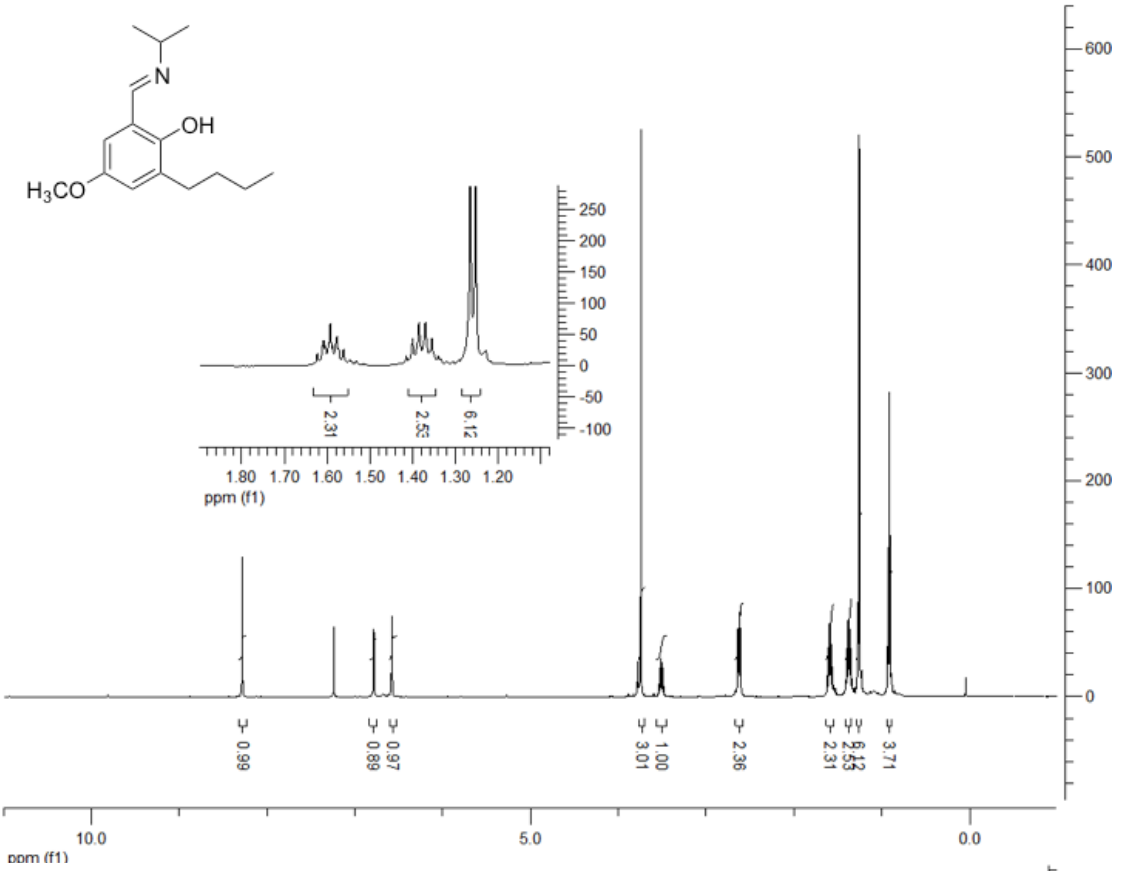
160.0
135.9
132.4
129.0
119.6
115.9
60.2
31.8
29.4
24.4
22.8
18.7
14.1
10000
5000
0
150
100
50
0
ppm (f1)

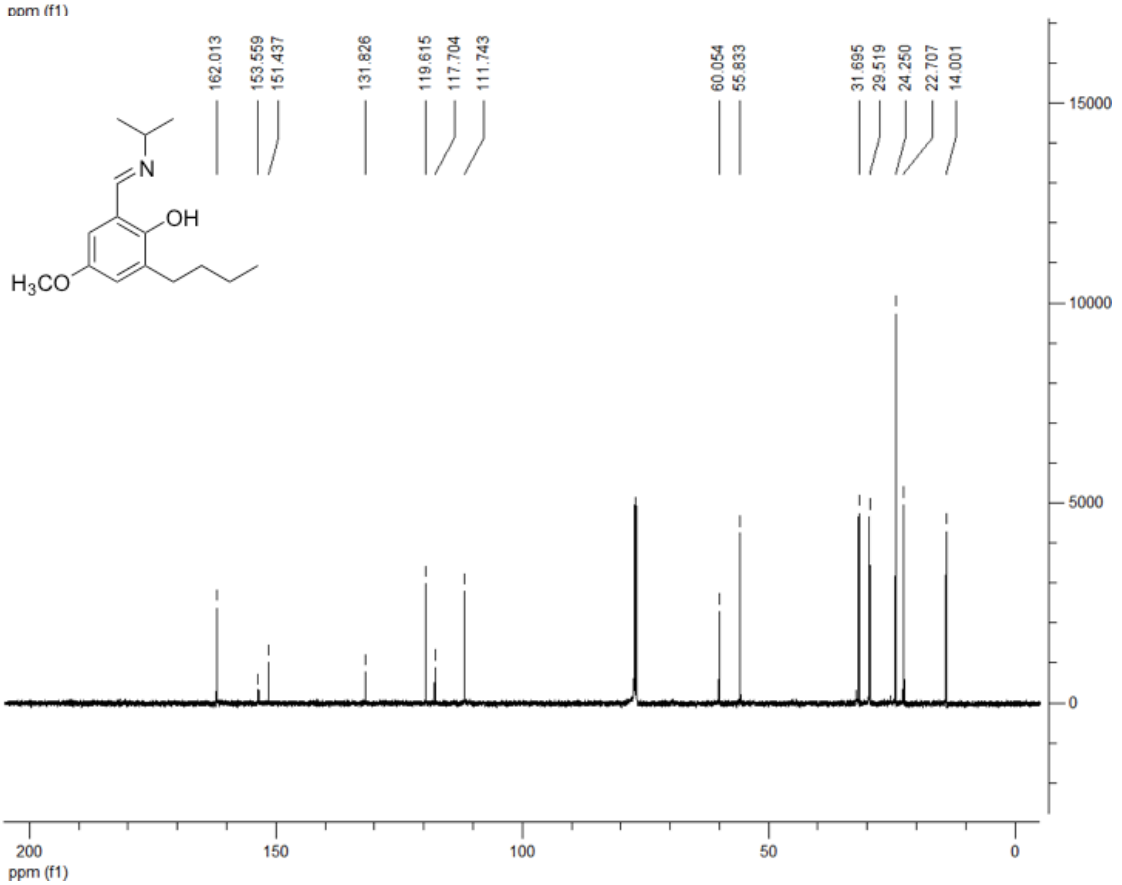
Phenol 14


HO
N
CH3
CH3
2.69
2.48
3.55
1.70 1.60 1.50 1.40 1.30 1.20
ppm (f1)
0.96
0.92
2.00
2.33
2.90
2.95
2.69
3.58
5.0
0.0

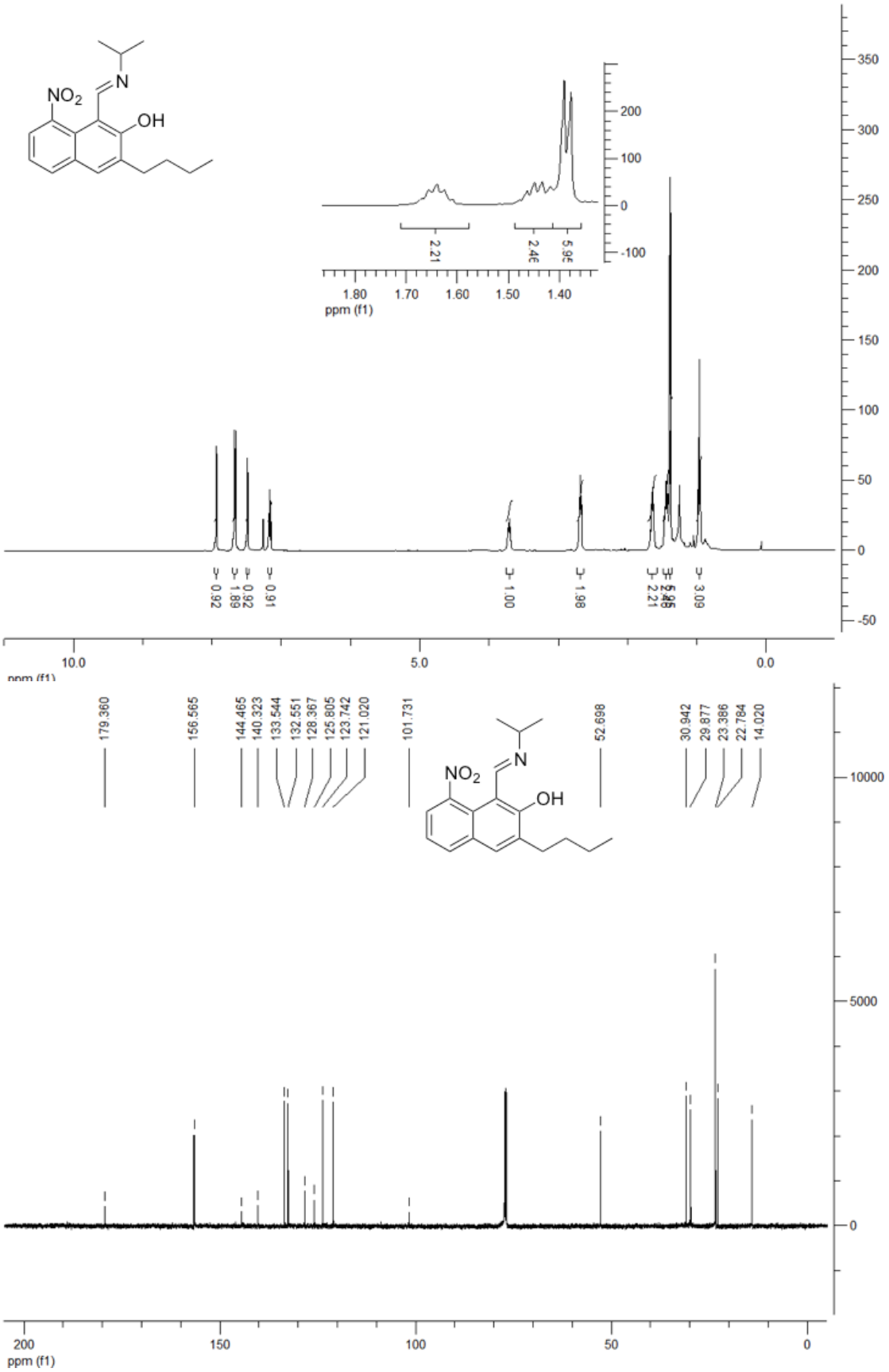

162.595
158.931
139.793
134.762
127.957
125.096
115.848
53.902
32.023
29.325
22.805
19.724
16.452
14.306
14.061
HO
N
CH3
CH3
150
100
50
0
ppm (f1)

Phenol 16

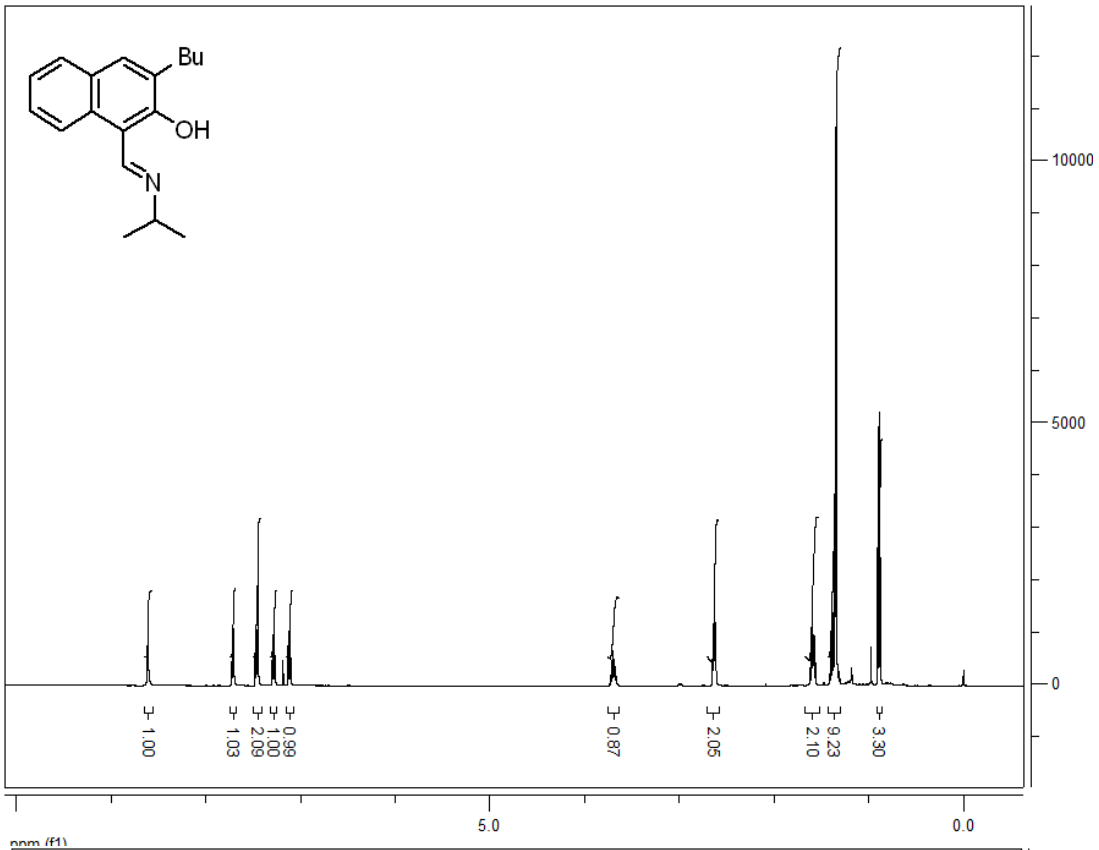

N
OH
H3CO
2.31
2.53
6.12
1.80 1.70 1.60 1.50 1.40 1.30 1.20
ppm (f1)
0.99
0.89
0.97
3.01
1.00
2.36
2.31
3.71
10.0
5.0
0.0

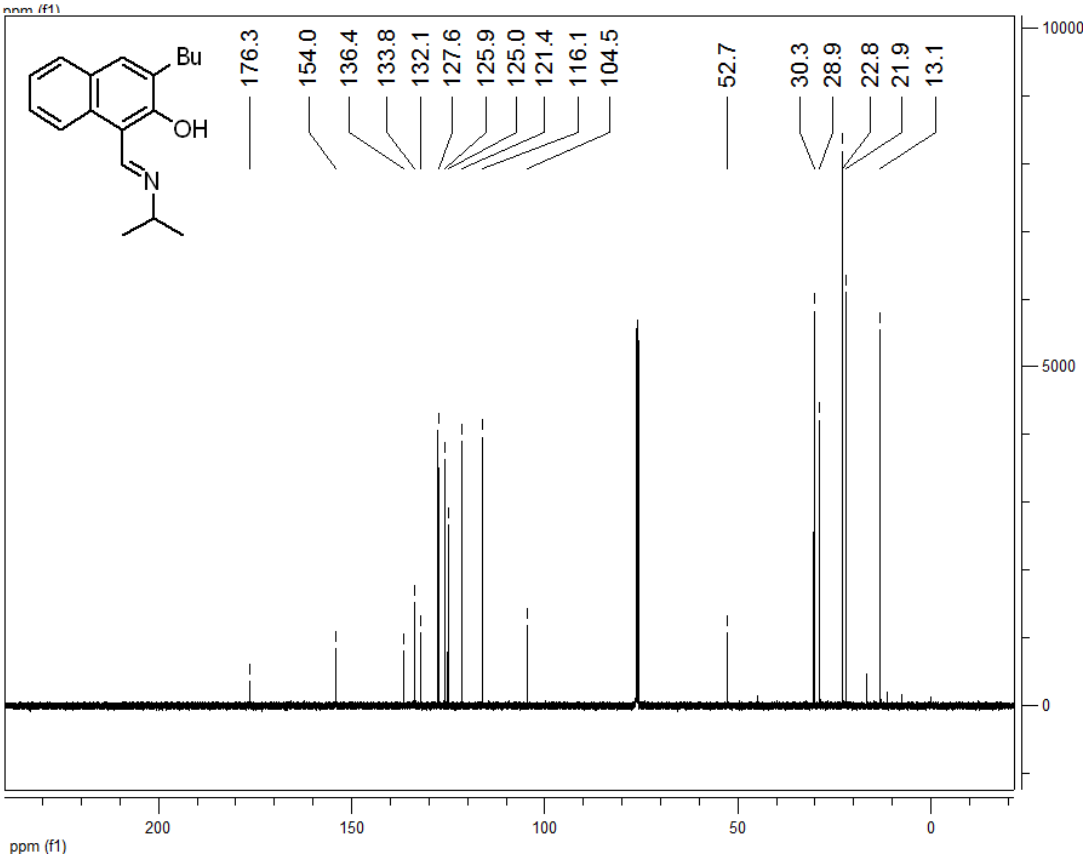

162.013
153.559
151.437
131.826
119.615
117.704
111.743
60.054
55.833
31.695
29.519
24.250
22.707
14.001
N
OH
H3CO
200
150
100
50
0
ppm (f1)

Naphthol 18

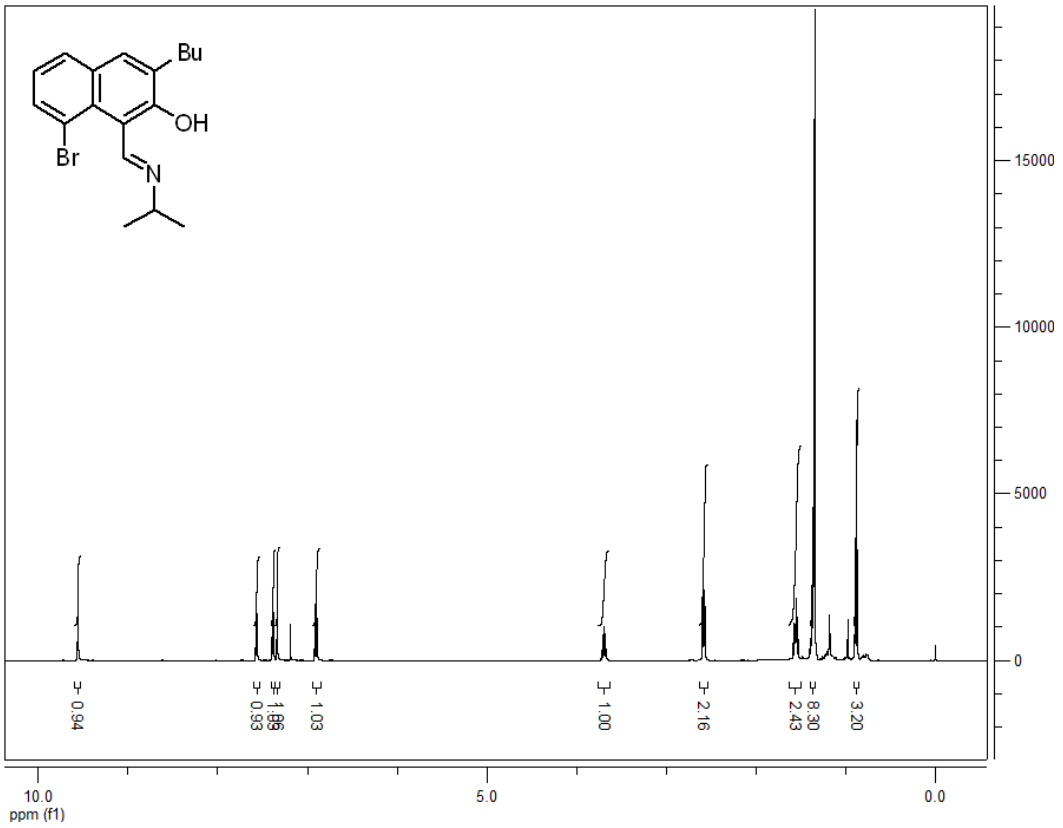

NO2
N
OH
2.21
2.46
5.95
1.80
1.70
1.60
1.50
1.40
ppm (f1)
0.92
1.68
2.02
0.91
1.00
1.98
2.21
3.09
10.0
5.0
0.0
179.360
156.565
144.465
140.323
133.544
132.551
128.367
125.805
123.742
121.020
101.731
52.698
30.942
29.877
23.386
22.784
14.020
200
150
100
50
0
ppm (f1)

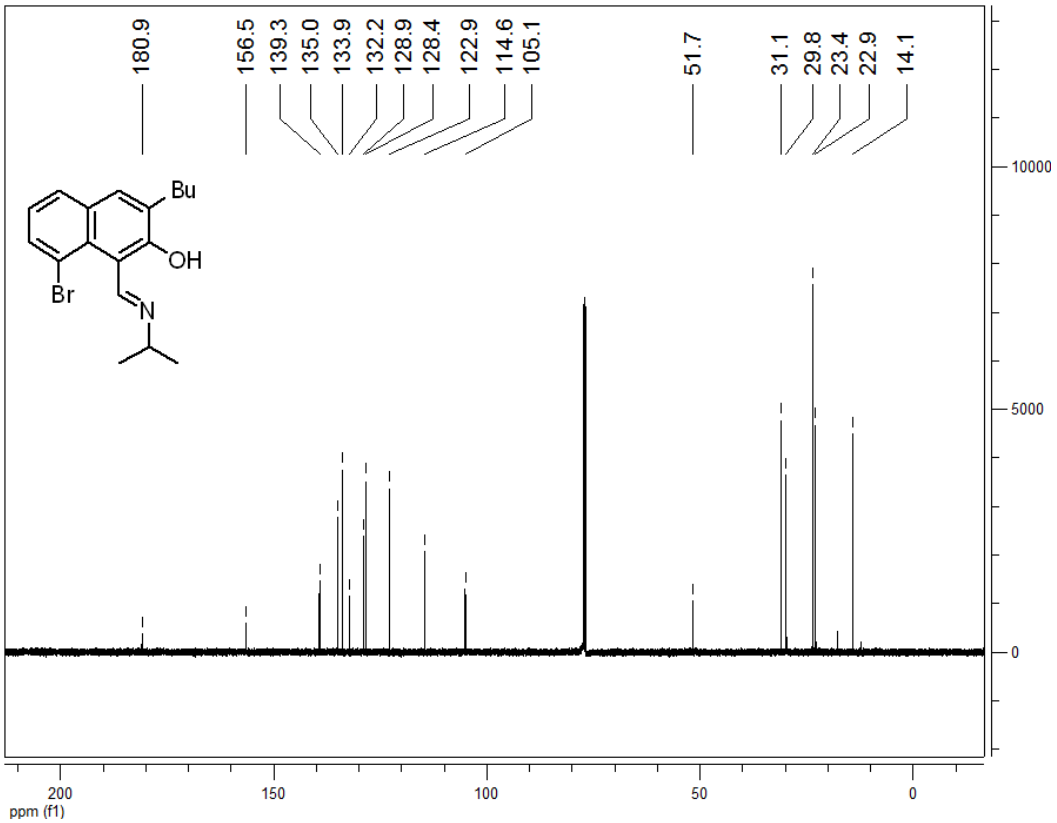
Naphthol 20


Bu
OH
N
10000
5000
0
1.00
1.03
2.09
1.00
0.99
0.87
2.05
9.23
2.10
3.30
5.0
0.0

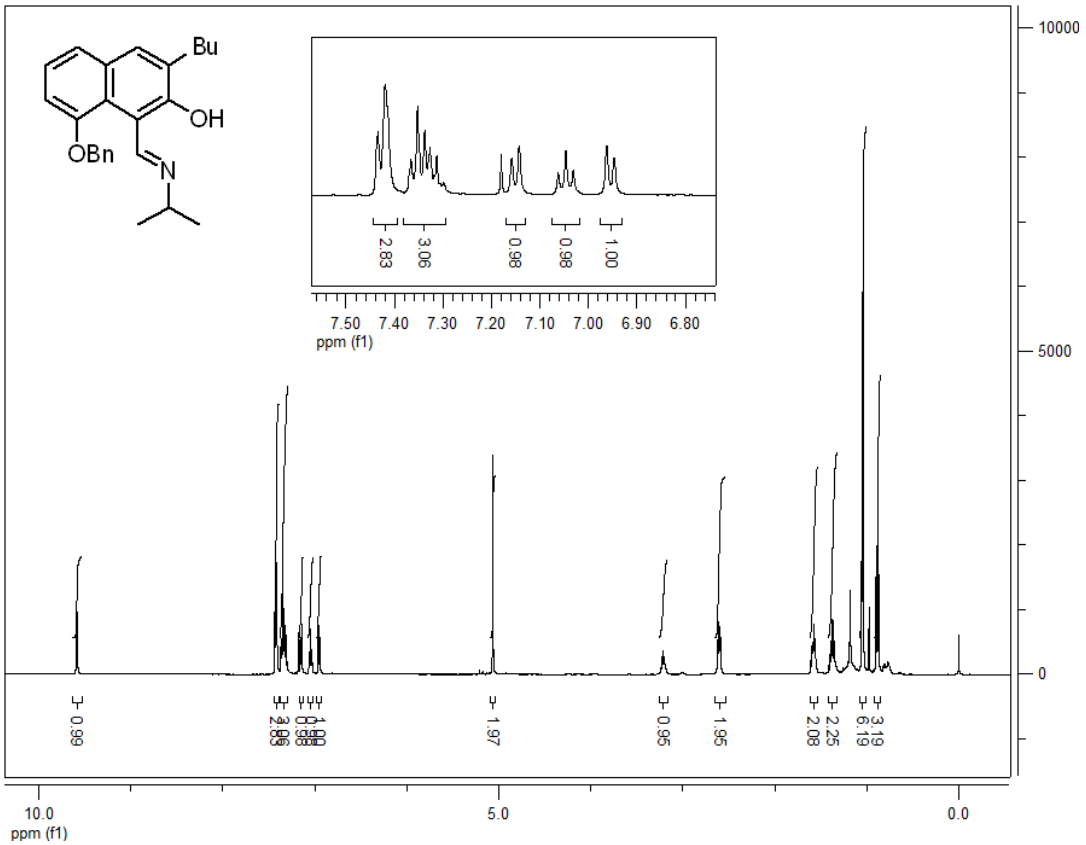

Bu
OH
N
176.3
154.0
136.4
133.8
132.1
127.6
125.9
125.0
121.4
116.1
104.5
52.7
30.3
28.9
22.8
21.9
13.1
10000
5000
0
200
150
100
50
0
ppm (f1)

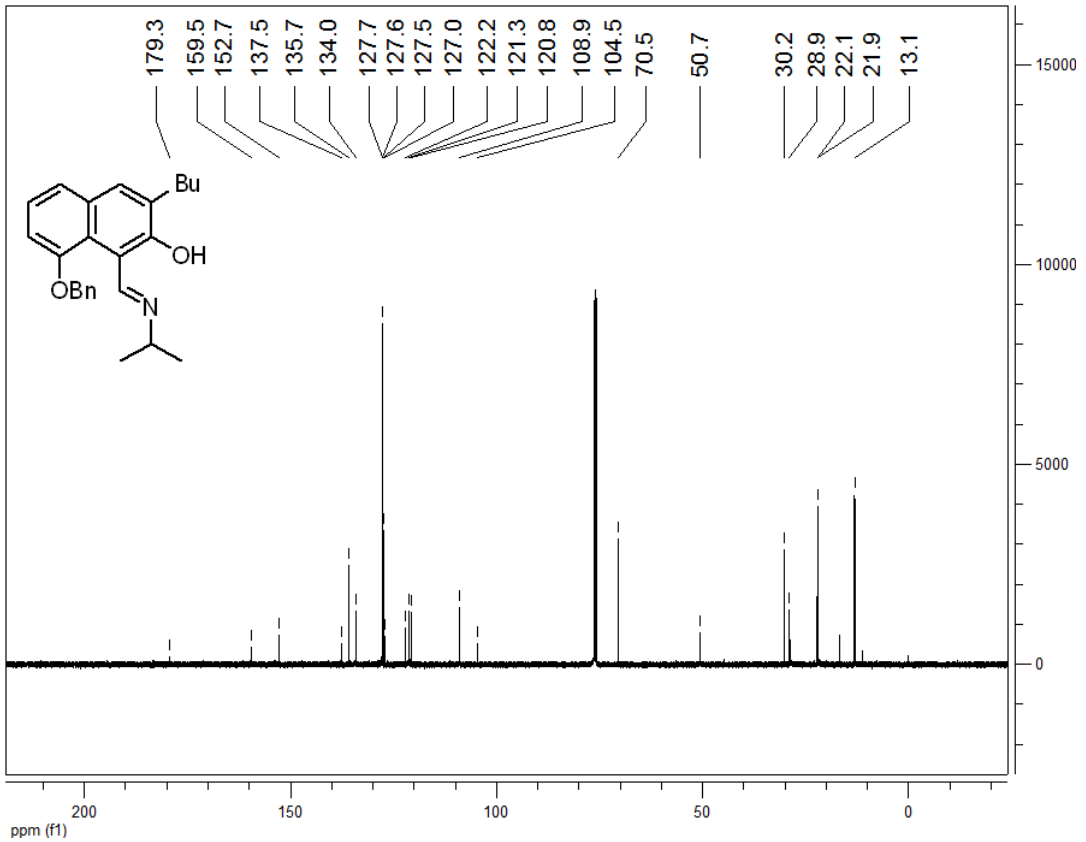
Naphthol 22


Bu
OH
Br
N
15000
10000
5000
0
0.94
0.93
1.03
1.00
2.16
2.43
8.30
3.20
10.0
ppm (f1)
5.0
0.0

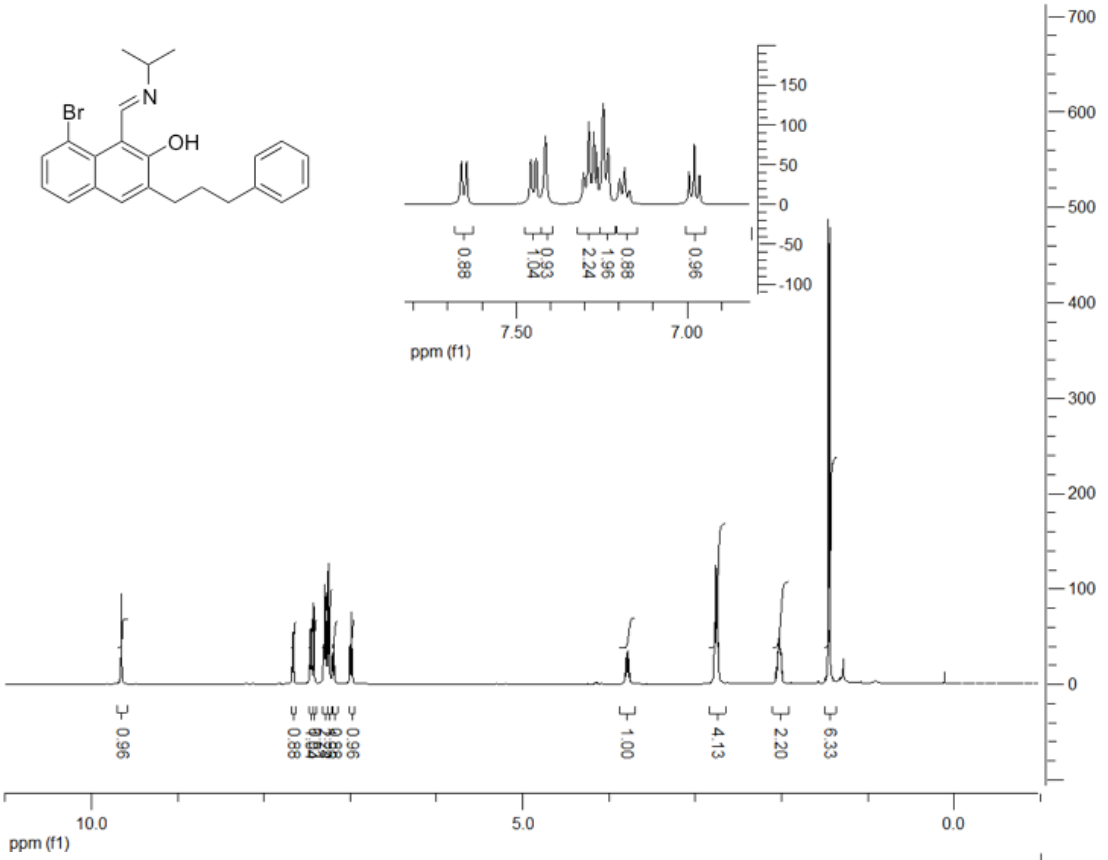

180.9
156.5
139.3
135.0
133.9
132.2
128.9
128.4
122.9
114.6
105.1
51.7
31.1
29.8
23.4
22.9
14.1
Bu
OH
Br
N
10000
5000
0
200
ppm (f1)
150
100
50
0

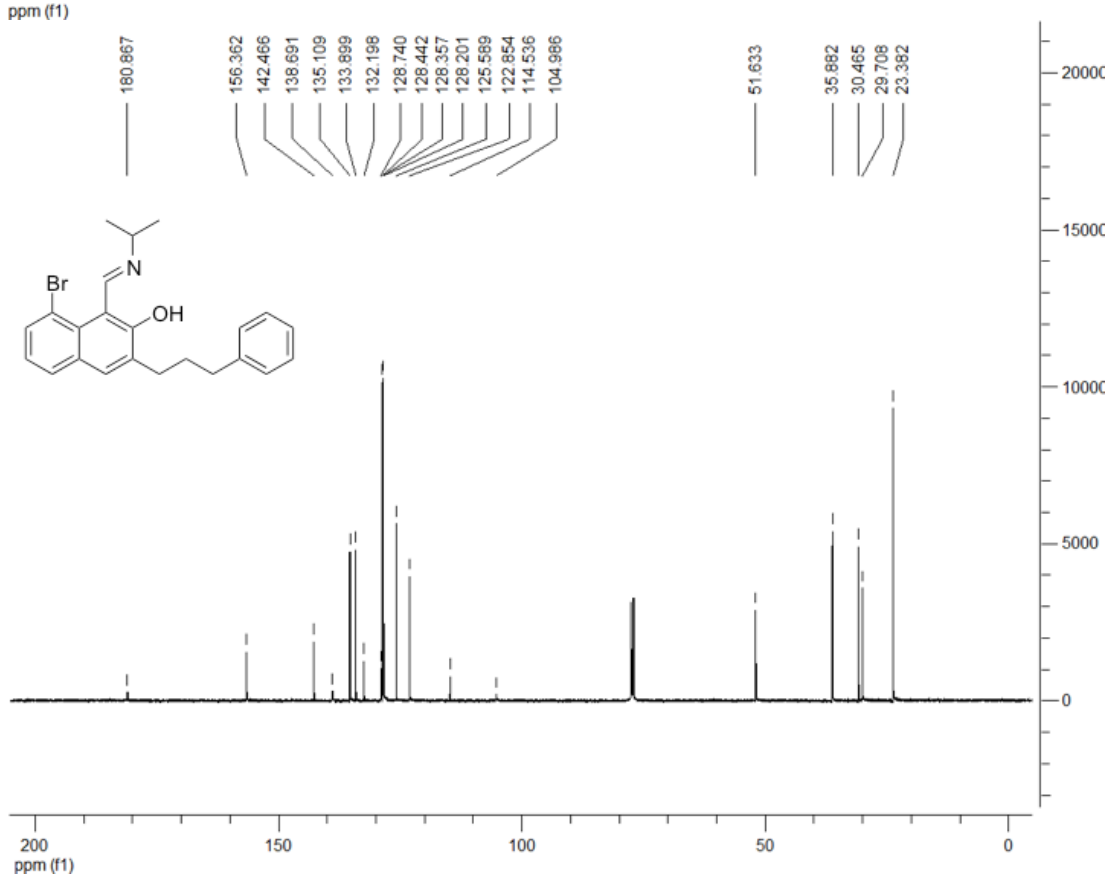
Naphthol 24


Bu
OH
OBn
N
2.83
3.09
0.98
0.98
1.00
7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80
ppm (f1)
0.99
1.97
0.95
1.95
2.08
2.25
6.19
3.19
10000
5000
0
10.0
5.0
0.0
ppm (f1)

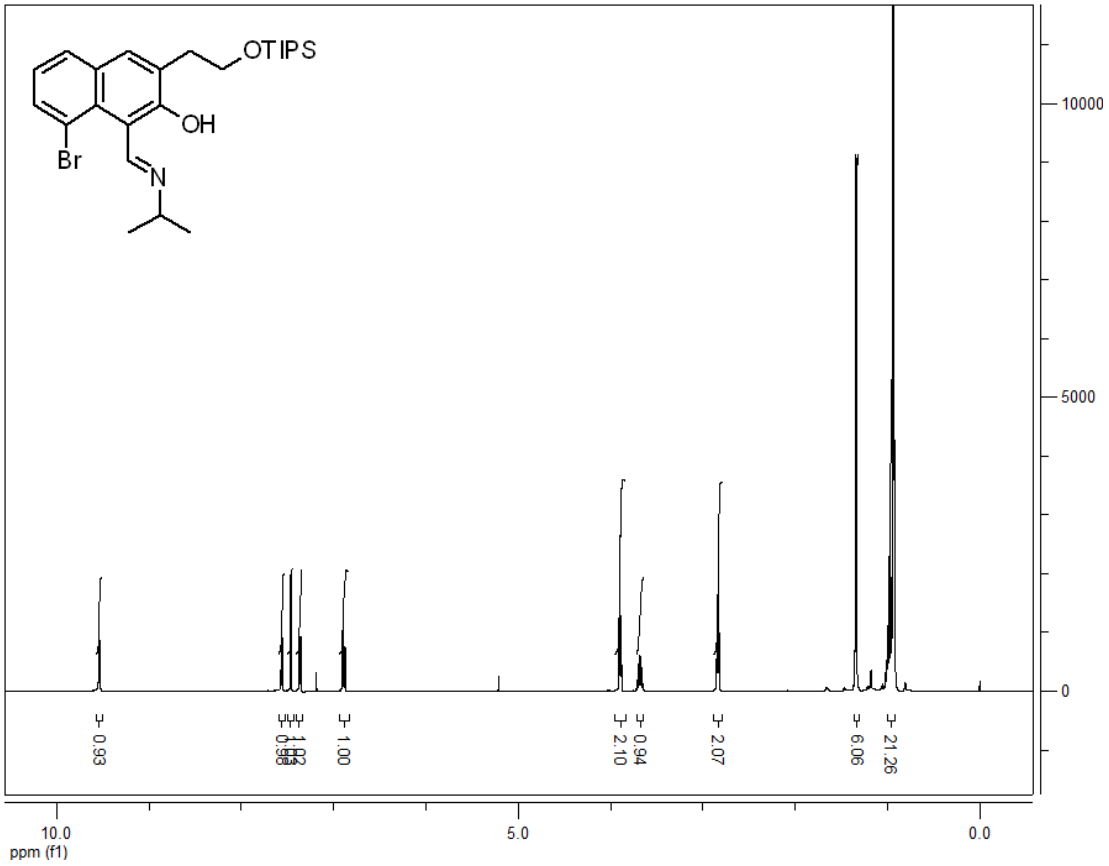

179.3
159.5
152.7
137.5
135.7
134.0
127.7
127.6
127.5
127.0
122.2
121.3
120.8
108.9
104.5
70.5
50.7
30.2
28.9
22.1
21.9
13.1
Bu
OH
OBn
N
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

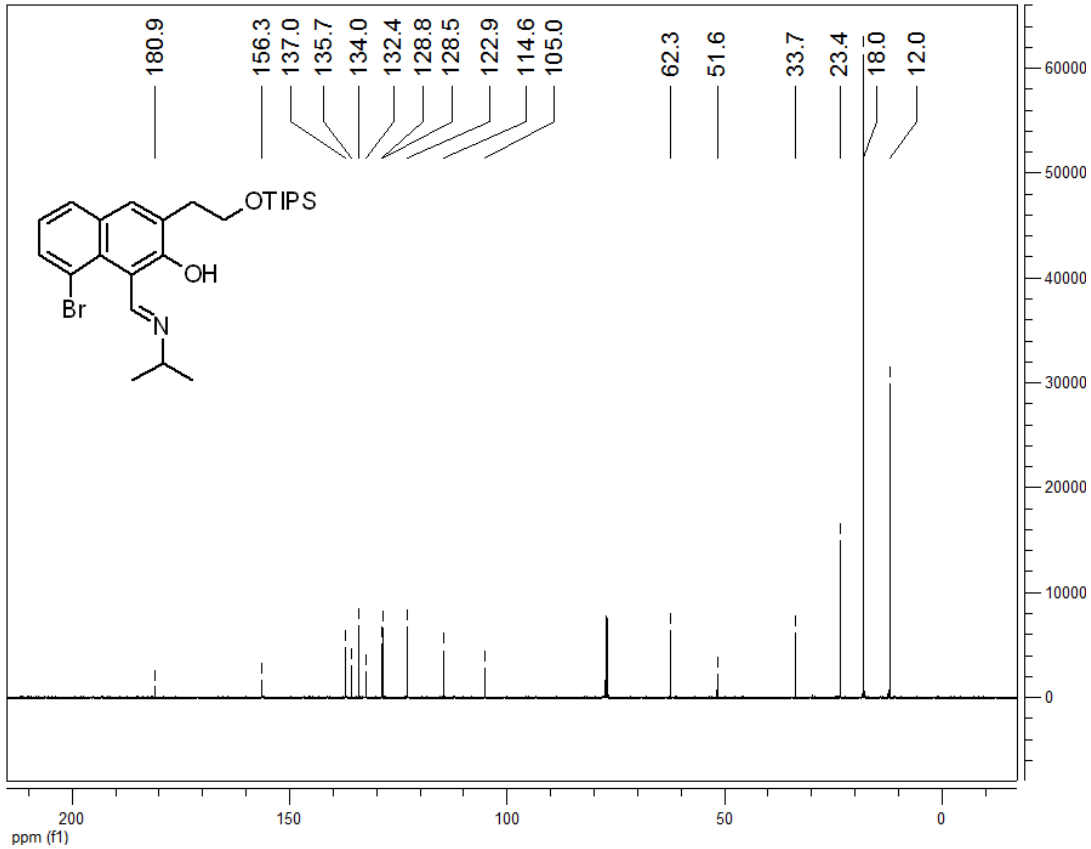
Naphthol 25


Br
N
OH
0.96
0.88
0.96
1.00
4.13
2.20
6.33
ppm (f1)

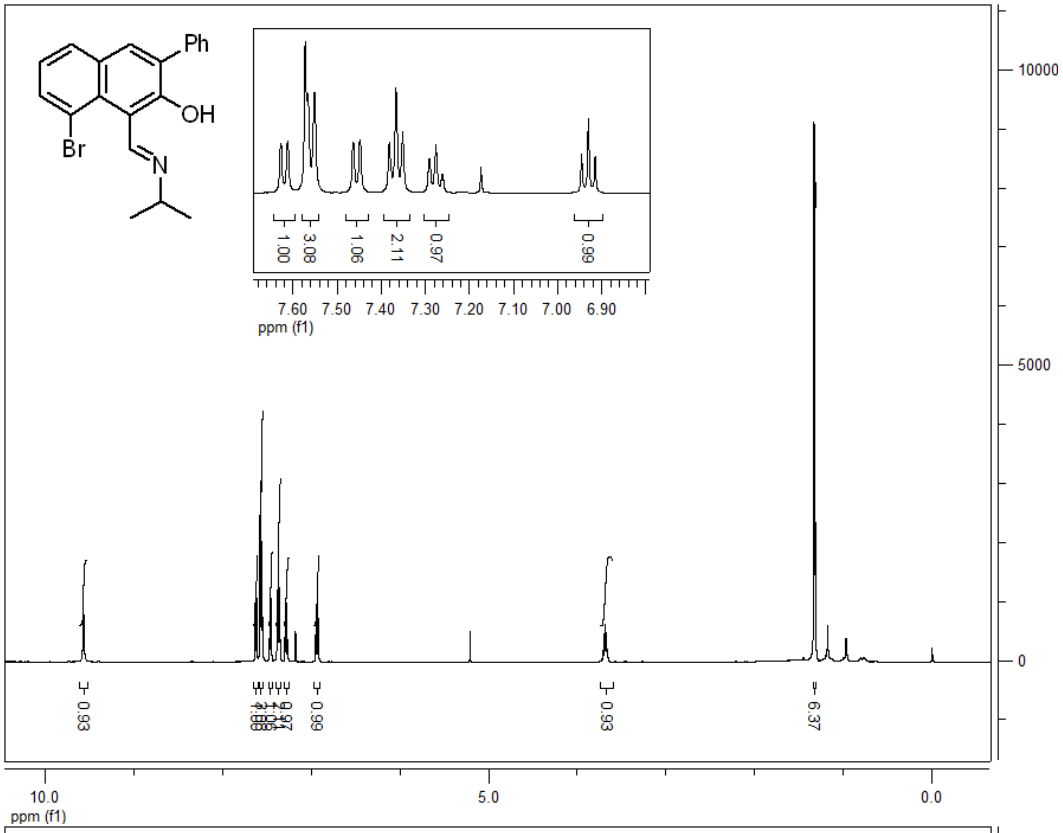

180.867
156.362
142.466
138.691
135.109
133.899
132.198
128.740
128.442
128.357
128.201
125.589
122.854
114.536
104.986
51.633
35.882
30.465
29.708
23.382
Br
N
OH
ppm (f1)

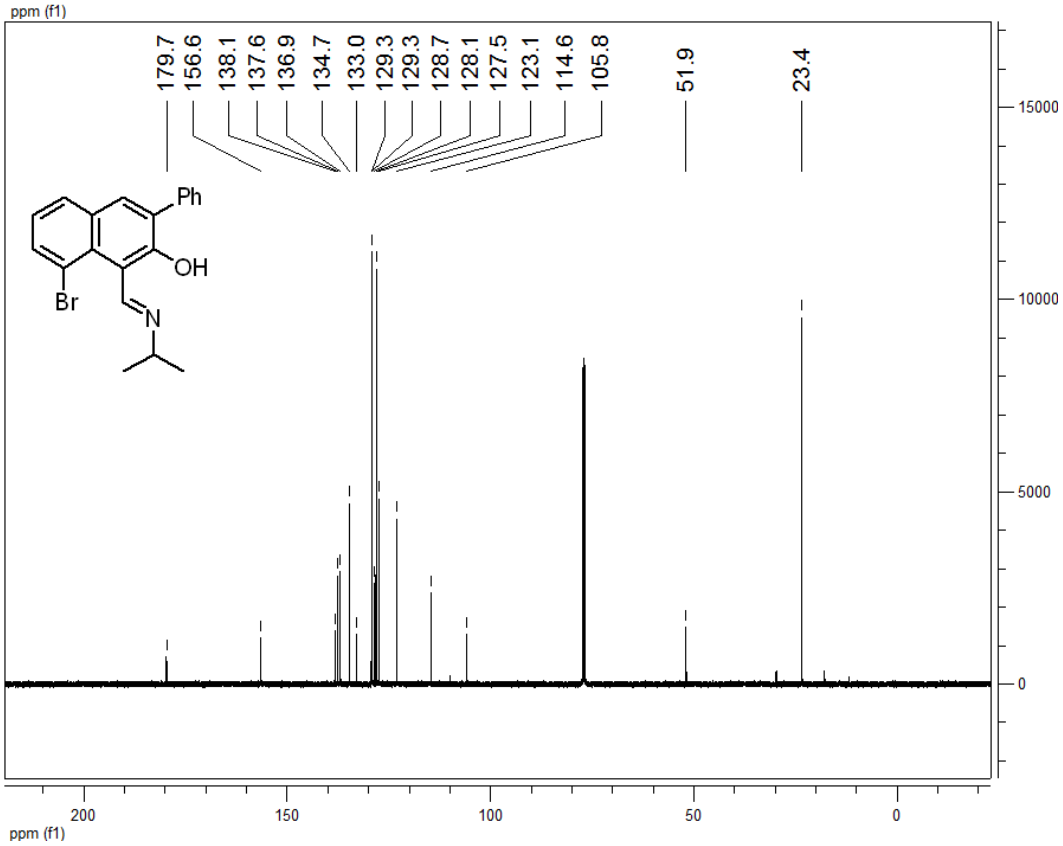
Naphthol 26


OTIPS
OH
Br
N
0.93
1.00
0.94
2.10
2.07
6.06
21.26
10000
5000
0
10.0
5.0
0.0
ppm (f1)

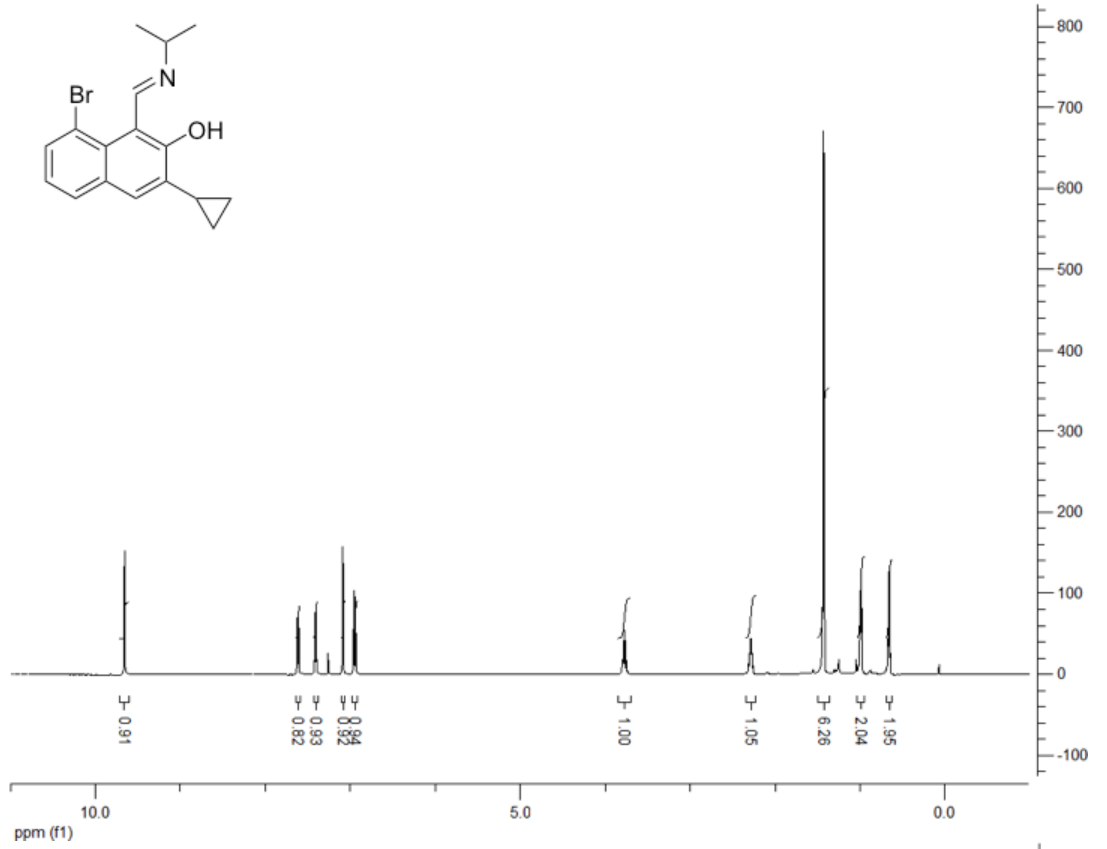

180.9
156.3
137.0
135.7
134.0
132.4
128.8
128.5
122.9
114.6
105.0
62.3
51.6
33.7
23.4
18.0
12.0
OTIPS
OH
Br
N
60000
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (f1)

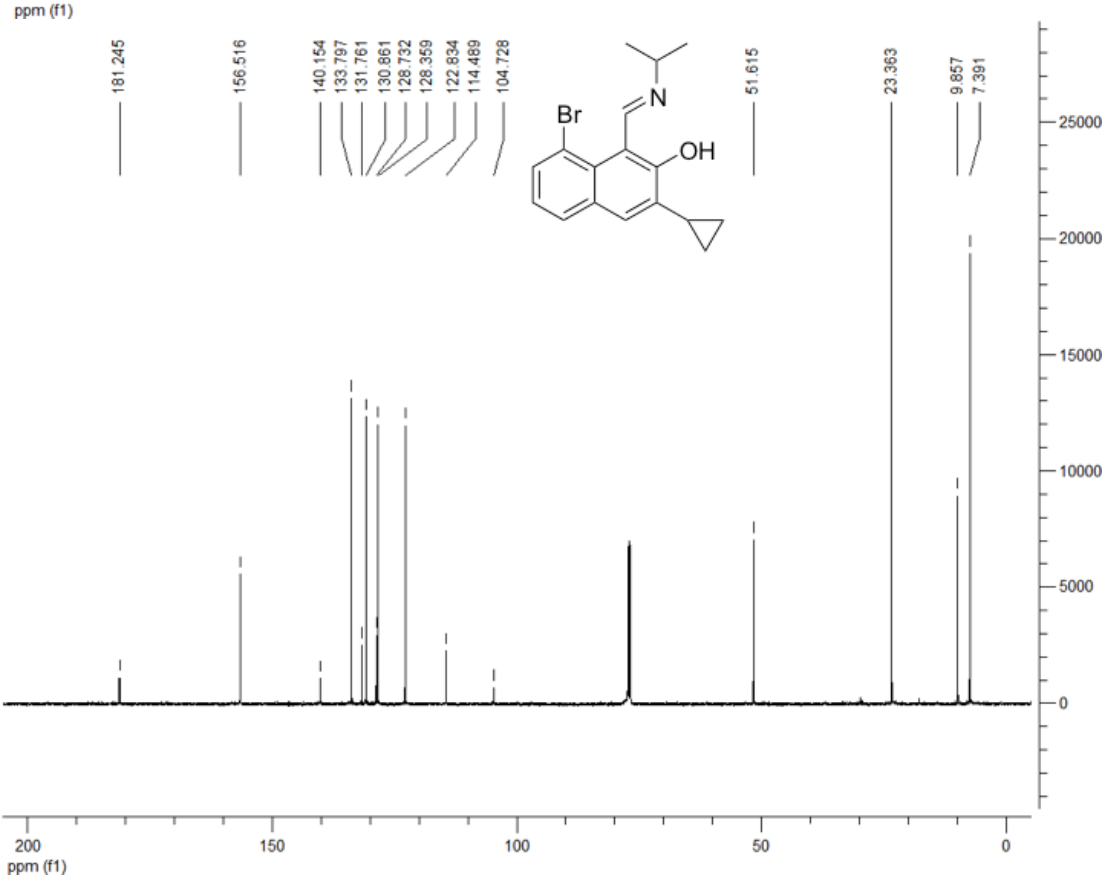
Naphthol 27


Ph
OH
Br
N
1.00
3.08
1.06
2.11
0.97
0.96
7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90
ppm (f1)
0.93
0.99
0.99
6.37
10000
5000
0
10.0
5.0
0.0
ppm (f1)

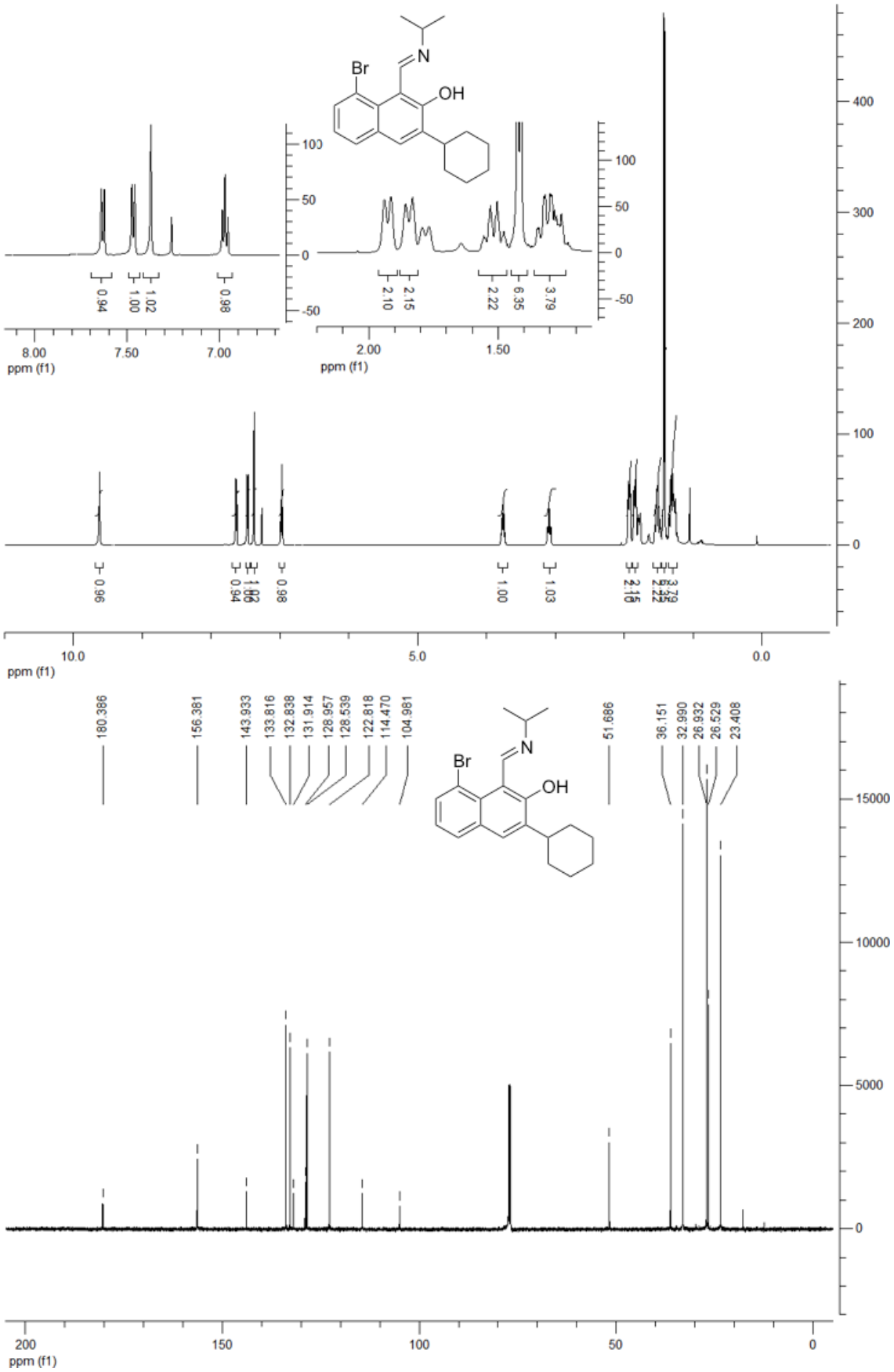

179.7
156.6
138.1
137.6
136.9
134.7
133.0
129.3
129.3
128.7
128.1
127.5
123.1
114.6
105.8
51.9
23.4
Ph
OH
Br
N
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

Naphthol 28


Br
N
OH
0.91
0.82
0.93
0.92
0.84
1.00
1.05
9.26
2.04
1.95
800
700
600
500
400
300
200
100
0
-100
10.0
5.0
0.0
ppm (f1)


181.245
156.516
140.154
133.797
131.761
130.861
128.732
128.359
122.834
114.489
104.728
51.615
23.363
9.857
7.391
Br
N
OH
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

Naphthol 29


Br
N
OH
0.94
1.00
1.02
0.98
2.10
2.15
2.22
6.35
3.79
ppm (f1)
0.96
0.64
0.98
1.00
1.03
10.0
5.0
0.0
180.386
156.381
143.933
133.816
132.838
131.914
128.957
128.539
122.818
114.470
104.981
51.686
36.151
32.990
26.932
26.529
23.408
200
150
100
50
0

Naphthol 30