$B(C_6F_5)_3$-Catalyzed Redox-Neutral β-Alkylation of Tertiary Amines using *p*-Quinone Methides via Borrowing Hydrogen

Rui Li,[a] Yong Chen,[a] Kun Jiang,[b] Feiyi Wang,[a] Cuifen Lu,[a] Junqi Nie,[a] Zuxing Chen,[a] Guichun Yang,*[,a] Ying-Chun Chen,[b] Yu Zhao,*[,c] and Chao Ma*[,a]

[a]Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, College of Chemistry and Chemical Engineering, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University, Wuhan, 430062, China.

[b]College of Pharmacy, Third Military Medical University, Shapingba, Chongqing 400038, China.

[c]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543.

Email: machao@hubu.edu.cn; zhaoyu@nus.edu.sg; yangguichun@hubu.edu.cn

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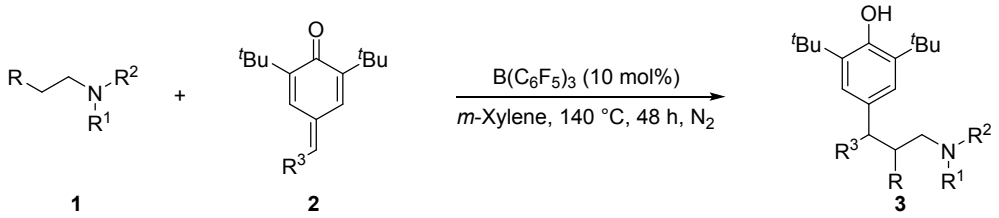
1. General Information

^{1}H and **^{13}C NMR** spectra were recorded on a Bruker (400 MHz) or Agilent (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra (**HRMS**) were obtained on Agilent 1260-6224 LC-MS TOF using ESI (electrospray ionization). For thin layer chromatography (**TLC**), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with phosphomolybdic acid solution followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

All reactions were carried out under nitrogen atmosphere. All commercially available reagents were used as received for the reactions without any purification. All solvents were dried on alumina columns using a solvent dispensing system. $B(C_6F_5)_3$ and tertiary amines were purchased from TCI or Alfa. *Para*-Quinone Methides[1] were synthesized following the reported procedure.

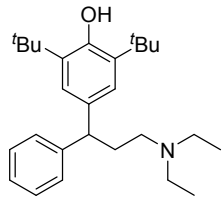
2. General Procedure for $B(C_6F_5)_3$ catalyzed β-alkylation of tertiary amines



1 **2** **3**

To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.01 mmol), tertiary amines **1** (0.5 mmol), *para*-quinone methides **2** (0.10 mmol) and anhydrous *m*-xylene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 140 °C for 48 hours. Upon cooling to room temperature, The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes:triethylamine = 2:100:1) to afford the desired tertiary amines.

3. Analytical data for 3



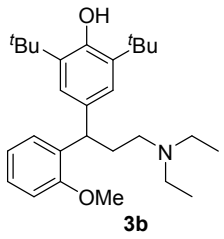
3a

Colorless gum, 30.5 mg, 77% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 4H), 7.18 – 7.14 (m, 1H), 7.04 (s, 2H), 5.02 (s, 1H), 3.82 (t, *J* = 7.7 Hz, 1H), 2.52 (q, *J* = 7.1 Hz, 4H), 2.41 – 2.34 (m, 2H), 2.21 – 2.15 (m, 2H), 1.40 (s, 18H), 0.96 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 151.93, 145.42, 135.51, 135.46, 128.33, 127.75, 125.88, 124.14, 51.09, 49.43, 46.96, 34.34, 33.16, 30.32, 11.57.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{42}NO, M+H]^+$: 396.32664; Found: 396.32609.



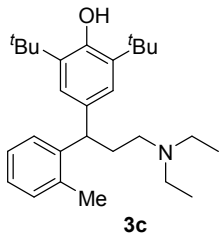
3b

Colorless oil, 25.0 mg, 59% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (d, *J* = 6.9 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.10 (s, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 4.98 (s, 1H), 4.27 (t, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 2.53 – 2.46 (m, 4H), 2.38 (dd, *J* = 15.2, 8.0 Hz, 2H), 2.20 – 2.10 (m, 2H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.92, 151.71, 135.20, 135.14, 134.09, 127.50, 126.66, 124.55, 120.54, 110.60, 55.36, 51.18, 47.05, 41.43, 34.32, 31.99, 30.38, 11.75.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{44}NO_2, M+H]^+$: 426.33720; Found: 426.33655.



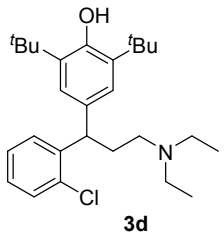
3c

Colorless oil, 27.2 mg, 66% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.05 (m, 2H), 7.01 (s, 2H), 4.99 (s, 1H), 4.04 (t, *J* = 7.6 Hz, 1H), 2.49 (q, *J* = 7.1 Hz, 4H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 2.18 – 2.11 (m, 2H), 1.39 (s, 18H), 0.94 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz,$CDCl_3$): δ 151.75, 143.42, 136.05, 135.38, 135.02, 130.33, 126.31, 125.99, 125.62, 124.50, 51.11, 46.94, 44.45, 34.31, 33.52, 30.33, 20.08, 11.73.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{44}NO, M+H]^+$: 410.34229; Found: 410.34134.



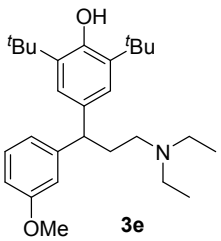
3d

Colorless oil, 29.5 mg, 69% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.06 (m, 3H), 5.03 (s, 1H), 4.40 (t, *J* = 7.7 Hz, 1H), 2.53 – 2.46 (m, 4H), 2.42 – 2.33 (m, 2H), 2.20 – 2.13 (m, 2H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.05, 143.02, 135.52, 134.02, 133.88, 129.56, 128.21, 126.94, 126.89, 124.51, 50.92, 47.07, 44.57, 34.34, 32.81, 30.34, 11.78.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{41}ClNO, M+H]^+$: 430.28767; Found: 430.28623.



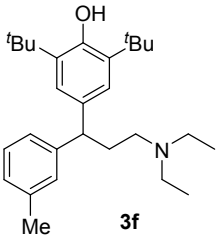
3e

Colorless oil, 25.3 mg, 59% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.9 Hz, 1H), 7.05 (s, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.71 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.02 (s, 1H), 3.83 – 3.77 (m, 4H), 2.50 (q, *J* = 7.1 Hz, 4H), 2.39 – 2.32 (m, 2H), 2.16 (dt, *J* = 14.7, 6.4 Hz, 2H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ159.52, 151.96, 147.26, 135.52, 135.35, 129.23, 124.13, 120.18, 113.72, 111.02, 55.09, 51.16, 49.51, 47.00, 34.34, 33.30, 30.34, 11.70.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{44}NO_2, M+H]^+$: 426.33720; Found: 426.33651.



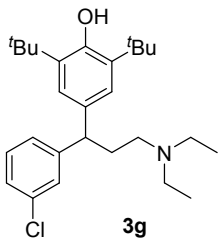
3f

Colorless oil, 30.1 mg, 73% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 – 7.07(m, 2H), 7.05 (s, 2H), 6.97 (d, *J* = 7.4 Hz, 1H), 5.02 (s, 1H), 3.77 (t, *J* = 7.7 Hz, 1H), 2.50 (q, *J* = 7.1 Hz, 4H), 2.38 – 2.33 (m, 2H), 2.32 (s, 3H), 2.19 – 2.12 (m, 2H), 1.41 (s, 18H), 0.97 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 151.88, 145.43, 137.73, 135.69, 135.47, 128.71, 128.18, 126.60, 124.60, 124.15, 51.19, 49.45, 46.99, 34.34, 33.40, 30.33, 21.52, 11.71.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{44}NO, M+H]^+$: 410.34229; Found: 410.34173.



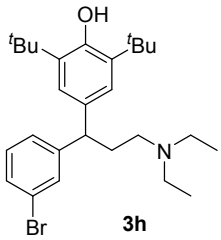
3g

Colorless oil, 27.5 mg, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.23 – 7.11 (m, 3H), 7.02 (s, 2H), 5.06 (s, 1H), 3.81 (t, *J* = 7.7 Hz, 1H), 2.50 (q, *J* = 7.1 Hz, 4H), 2.38 – 2.30 (m, 2H), 2.14 (dd, *J* = 14.8, 7.9 Hz, 2H), 1.41 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.14, 147.71, 135.75, 134.71, 134.04, 129.57, 128.08, 126.03, 125.88, 124.12, 50.94, 49.05, 46.95, 34.36, 33.17, 30.31, 11.64.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{41}ClNO, M+H]^+$: 430.28767; Found: 430.28746.



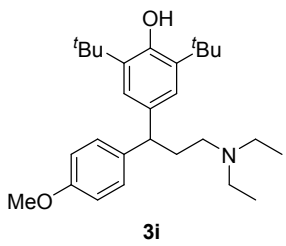
3h

Colorless oil, 32.9 mg, 70% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.01 (s, 2H), 5.06 (s, 1H), 3.80 (t, *J* = 7.7 Hz, 1H), 2.49 (q, *J* = 7.1 Hz, 4H), 2.37 – 2.30 (m, 2H), 2.17 – 2.10 (m, 2H), 1.41 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.13, 147.98, 135.69, 134.70, 131.00, 129.90, 128.97, 126.31, 124.11, 122.40, 50.92, 49.02, 46.93, 34.36, 33.24, 30.30, 11.67.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{41}BrNO, M+H]^+$: 474.23715; Found: 474.23663.



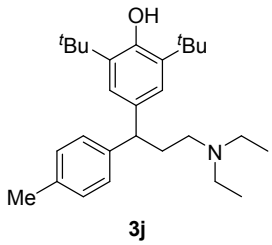
3i

Colorless oil, 23.3 mg, 54% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.6 Hz, 2H), 7.02 (s, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.00 (s, 1H), 3.79 – 3.75 (m, 4H), 2.49 (q, *J* = 7.1 Hz, 4H), 2.37 – 2.32 (m, 2H), 2.13 (dd, *J* = 15.4, 7.7 Hz, 2H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.68, 151.83, 137.72, 135.98, 135.49, 128.62, 124.05, 113.69, 55.19, 51.24, 48.59, 46.99, 34.33, 33.56, 30.34, 11.70.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{44}NO_2, M+H]^+$: 426.33720; Found: 426.33617.



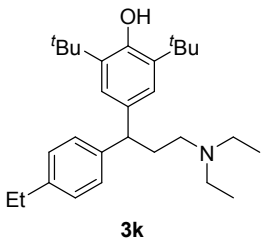
3j

Colorless oil, 25.0 mg, 61% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.04 (s, 2H), 5.00 (s, 1H), 3.77 (t, *J* = 7.7 Hz, 1H), 2.52 (q, *J* = 7.1 Hz, 4H), 2.37 (t, *J* = 6.9 Hz, 2H), 2.30 (s, 3H), 2.16 (ddd, *J* = 12.5, 9.3, 6.7 Hz, 2H), 1.40 (s, 18H), 0.96 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 151.88, 142.49, 135.71, 135.50, 135.26, 129.03, 127.54, 124.07, 51.11, 49.11, 46.91, 34.33, 33.16, 30.33, 20.97, 11.56.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{44}NO, M+H]^+$: 410.34229; Found: 410.34205.



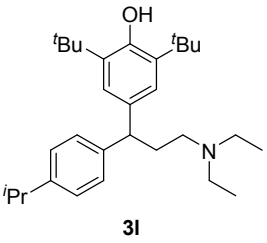
3k

Colorless oil, 28.2 mg, 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 2H), 5.01 (s, 1H), 3.78 (t, *J* = 7.7 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.50 (q, *J* = 7.1 Hz, 4H), 2.40 – 2.32 (m, 2H), 2.21 – 2.11 (m, 2H), 1.40 (s, 18H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 151.86, 142.81, 141.60, 135.75, 135.47, 127.77, 127.56, 124.12, 51.19, 49.16, 46.97, 34.33, 33.33, 30.34, 28.36, 15.49, 11.70.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{46}NO, M+H]^+$: 424.35794; Found: 424.35747.



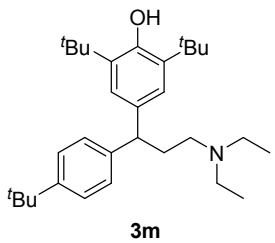
3l

Colorless oil, 29.0 mg, 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.05 (s, 2H), 5.01 (s, 1H), 3.77 (t, *J* = 7.7 Hz, 1H), 2.87 (dq, *J* = 13.8, 6.9 Hz, 1H), 2.50 (q, *J* = 7.1 Hz, 4H), 2.41 – 2.31 (m, 2H), 2.21 – 2.11 (m, 2H), 1.40 (s, 18H), 1.22 (d, *J* = 6.9 Hz, 6H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.89, 146.25, 142.91, 135.67, 135.51, 127.51, 126.33, 124.18, 51.11, 49.17, 46.97, 34.33, 33.59, 33.26, 30.34, 23.99, 11.64.

HRMS (ESI): m/z Calcd. for $[C_{30}H_{48}NO, M+H]^+$: 438.37359; Found: 438.37362.



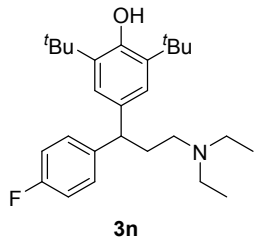
3m

Colorless oil, 23.2 mg, 51% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 2H), 7.05 (s, 2H), 5.01 (s, 1H), 3.77 (t, *J* = 7.7 Hz, 1H), 2.52 (q, *J* = 7.1 Hz, 4H), 2.40 – 2.35 (m, 2H), 2.16 (dt, *J* = 11.8, 6.8 Hz, 2H), 1.41 (s, 18H), 1.29 (s, 9H), 0.96 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 151.90, 148.50, 142.49, 135.54, 135.49, 127.21, 125.19, 124.20, 50.99, 49.08, 46.90, 34.34, 34.30, 33.13, 31.38, 30.34, 11.57.

HRMS (ESI): m/z Calcd. for $[C_{31}H_{50}NO, M+H]^+$: 452.38924; Found: 452.38870.



3n

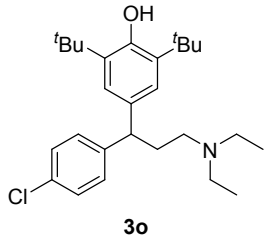
Colorless gum, 32.9 mg, 80% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.01 (s, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 5.04 (s, 1H), 3.82 (t, *J* = 7.7 Hz, 1H), 2.50 (q, *J* = 7.1 Hz, 4H), 2.38 – 2.30 (m, 2H), 2.17 – 2.11 (m, 2H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 161.17 (d, *J* = 241.5 Hz), 151.98, 141.16 (d, *J* = 3.0 Hz), 135.61, 135.40, 129.10 (d, *J* = 7.7 Hz), 124.05, 115.03 (d, *J* = 21.0 Hz), 51.05, 48.53, 46.95, 34.35, 33.49, 30.30, 11.63.

^{19}F NMR (600 MHz, $CDCl_3$): δ -117.74.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{41}FNO, M+H]^+$: 414.31722; Found: 414.31733.



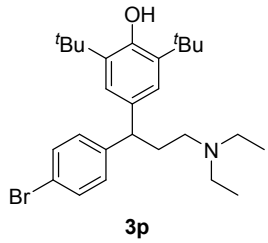
3o

Colorless oil, 33.5 mg, 78% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 2H), 5.04 (s, 1H), 3.82 (t, *J* = 7.7 Hz, 1H), 2.49 (q, *J* = 7.1 Hz, 4H), 2.37 – 2.30 (m, 2H), 2.18 – 2.10 (m, 2H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.04, 144.11, 135.67, 135.09, 131.46, 129.12, 128.41, 124.05, 51.08, 48.67, 46.98, 34.35, 33.39, 30.31, 11.71.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{41}ClNO, M+H]^+$: 430.28767; Found: 430.28796.



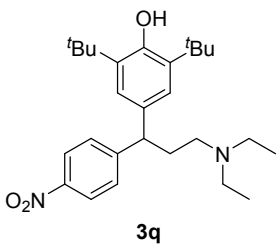
3p

Colorless oil, 34.2 mg, 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.00 (s, 2H), 5.05 (s, 1H), 3.80 (t, *J* = 7.7 Hz, 1H), 2.50 (q, *J* = 7.1 Hz, 4H), 2.37 – 2.31 (m, 2H), 2.14 (ddd, *J* = 14.2, 8.7, 4.5 Hz, 2H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.06, 144.61, 135.69, 134.93, 131.36, 129.53, 124.03, 119.56, 51.05, 48.74, 46.96, 34.35, 33.24, 30.30, 11.65.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{41}BrNO, M+H]^+$: 474.23715; Found: 474.23673.



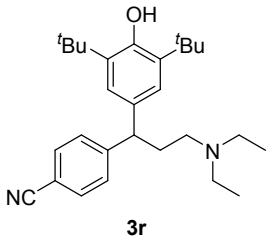
3q

Colorless oil, 25.0 mg, 57% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.00 (s, 2H), 5.11 (s, 1H), 3.98 (t, *J* = 7.7 Hz, 1H), 2.57 (q, *J* = 7.0 Hz, 4H), 2.43 – 2.38 (m, 2H), 2.26 – 2.19 (m, 2H), 1.40 (s, 18H), 0.98 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.36, 152.43, 146.25, 136.04, 133.58, 128.54, 124.09, 123.70, 50.70, 49.00, 46.84, 34.36, 32.85, 30.25, 11.40.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{41}N_2O_3, M+H]^+$: 441.31172; Found: 441.31126.



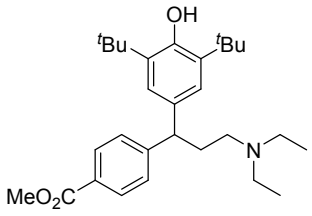
3r

Colorless oil, 30.5 mg, 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 6.99 (s, 2H), 5.10 (s, 1H), 3.91 (d, *J* = 7.4 Hz, 1H), 2.59 – 2.48 (m, 4H), 2.42 – 2.31 (m, 2H), 2.26 – 2.14 (m, 2H), 1.40 (s, 18H), 0.96 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.31, 151.25, 135.91, 133.86, 132.22, 128.55, 124.09, 119.08, 109.66, 50.75, 49.21, 46.88, 34.33, 32.96, 30.24, 11.55.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{41}N_2O, M+H]^+$: 421.32189; Found: 421.32188.



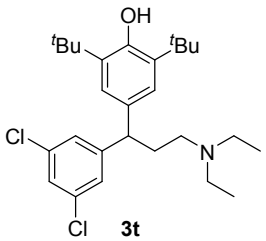
3s

Colorless oil, 28.1 mg, 62% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.01 (s, 2H), 5.07 (s, 1H), 3.92 – 3.87 (m, 4H), 2.54 (q, *J* = 7.1 Hz, 4H), 2.46 – 2.29 (m, 2H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.39 (s, 18H), 0.97 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.10, 152.16, 150.84, 135.75, 134.53, 129.76, 127.82, 124.12, 51.94, 50.90, 49.25, 46.92, 34.34, 30.27, 29.68, 11.46.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{44}NO_3, M+H]^+$: 454.33212; Found: 454.33043.



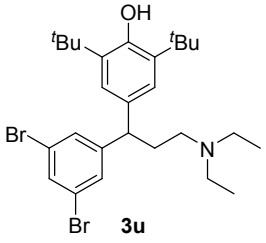
3t

Colorless oil, 37.0 mg, 80% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 – 7.13 (m, 3H), 6.99 (s, 2H), 5.09 (s, 1H), 3.81 (t, *J* = 7.7 Hz, 1H), 2.49 (q, *J* = 7.1 Hz, 4H), 2.35 – 2.29 (m, 2H), 2.11 (qd, *J* = 13.6, 6.1 Hz, 2H), 1.42 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.35, 149.17, 135.88, 134.64, 133.91, 126.39, 126.10, 124.09, 50.73, 48.74, 46.91, 34.38, 33.11, 30.29, 11.69.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{40}Cl_2NO, M+H]^+$: 464.24870; Found: 464.24821.



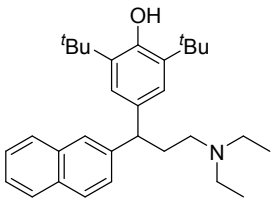
3u

Colorless oil, 42.2 mg, 76% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.34 (s, 2H), 6.99 (s, 2H), 5.09 (s, 1H), 3.80 (t, *J* = 7.7 Hz, 1H), 2.49 (q, *J* = 7.1 Hz, 4H), 2.34 – 2.29 (m, 2H), 2.10 (qd, *J* = 13.7, 6.6 Hz, 2H), 1.42 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.35, 149.74, 135.88, 133.86, 131.53, 129.73, 124.09, 122.76, 50.69, 48.68, 46.89, 34.38, 33.20, 30.28, 11.69.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{40}Br_2NO, M+H]^+$: 552.14767; Found: 552.14653.



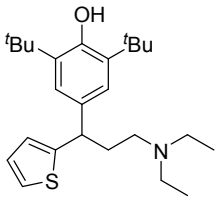
3v

Colorless oil, 35.8 mg, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.72 (m, 4H), 7.49 – 7.38 (m, 3H), 7.12 (s, 2H), 5.05 (s, 1H), 4.02 (t, *J* = 7.6 Hz, 1H), 2.53 (q, *J* = 7.1 Hz, 4H), 2.46 – 2.36 (m, 2H), 2.35 – 2.22 (m, 2H), 1.42 (s, 18H), 0.97 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.01, 142.89, 135.64, 135.37, 133.57, 132.10, 127.96, 127.68, 127.51, 126.55, 125.89, 125.76, 125.16, 124.24, 51.21, 49.45, 46.97, 34.35, 33.03, 30.32, 11.55.

HRMS (ESI): m/z Calcd. for $[C_{31}H_{44}NO, M+H]^+$: 446.34229; Found: 446.34198.



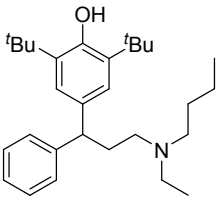
3w

Colorless oil, 26.0 mg, 65% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.08 (s, 2H), 6.90 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.83 (d, *J* = 3.5 Hz, 1H), 5.05 (s, 1H), 4.10 (t, *J* = 7.6 Hz, 1H), 2.54 – 2.47 (m, 4H), 2.39 (tdd, *J* = 16.4, 8.5, 4.7 Hz, 2H), 2.23 – 2.11 (m, 2H), 1.42 (s, 18H), 0.96 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.18, 150.33, 135.61, 135.11, 126.39, 124.07, 123.55, 123.08, 50.88, 47.00, 44.86, 35.31, 34.35, 30.33, 11.79.

HRMS (ESI): m/z Calcd. for $[C_{25}H_{40}NOS, M+H]^+$: 402.28306; Found: 402.28181.



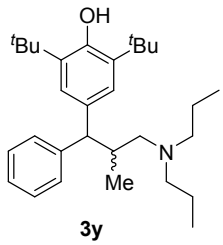
3x

Colorless oil, 30.1 mg, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 4H), 7.20 – 7.13 (m, 1H), 7.04 (s, 2H), 5.02 (s, 1H), 3.82 (t, *J* = 7.7 Hz, 1H), 2.49 (q, *J* = 7.1 Hz, 2H), 2.42 – 2.31 (m, 4H), 2.16 (dd, *J* = 14.9, 7.3 Hz, 2H), 1.40 (s, 18H), 1.31 – 1.23 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.92, 145.56, 135.55, 128.31, 127.80, 125.85, 124.19, 53.35, 51.73, 49.37, 47.54, 34.34, 33.28, 30.33, 29.11, 20.77, 14.06, 11.64.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{46}NO, M+H]^+$: 424.35794; Found: 424.35746.



3y

Colorless oil, mixture of diastereomers, 34.0 mg, 78% yield, 1.1:1 dr.

^{1}H NMR (400 MHz, $CDCl_3$): **major diastereomer** δ 7.31 – 7.23 (m, 4H), 7.18 – 7.11 (m, 1H), 7.07 (s, 2H), 4.98 (s, 1H), 3.36 (d, J = 10.6 Hz, 1H), 2.45 – 2.32 (m, 3H), 2.27 – 2.15 (m, 3H), 2.05 – 1.93 (m, 1H), 1.42 (s, 18H), 1.40 – 1.31 (m, 4H), 0.91 – 0.82 (m, 9H). **minor diastereomer** δ 7.31 – 7.23 (m, 4H), 7.18 – 7.11 (m, 1H), 7.04 (s, 2H), 4.98 (s, 1H), 3.45 (d, J = 9.9 Hz, 1H), 2.45 – 2.32 (m, 3H), 2.27 – 2.15 (m, 3H), 2.05 – 1.93 (m, 1H), 1.42 (s, 18H), 1.40 – 1.31 (m, 4H), 0.91 – 0.82 (m, 9H).

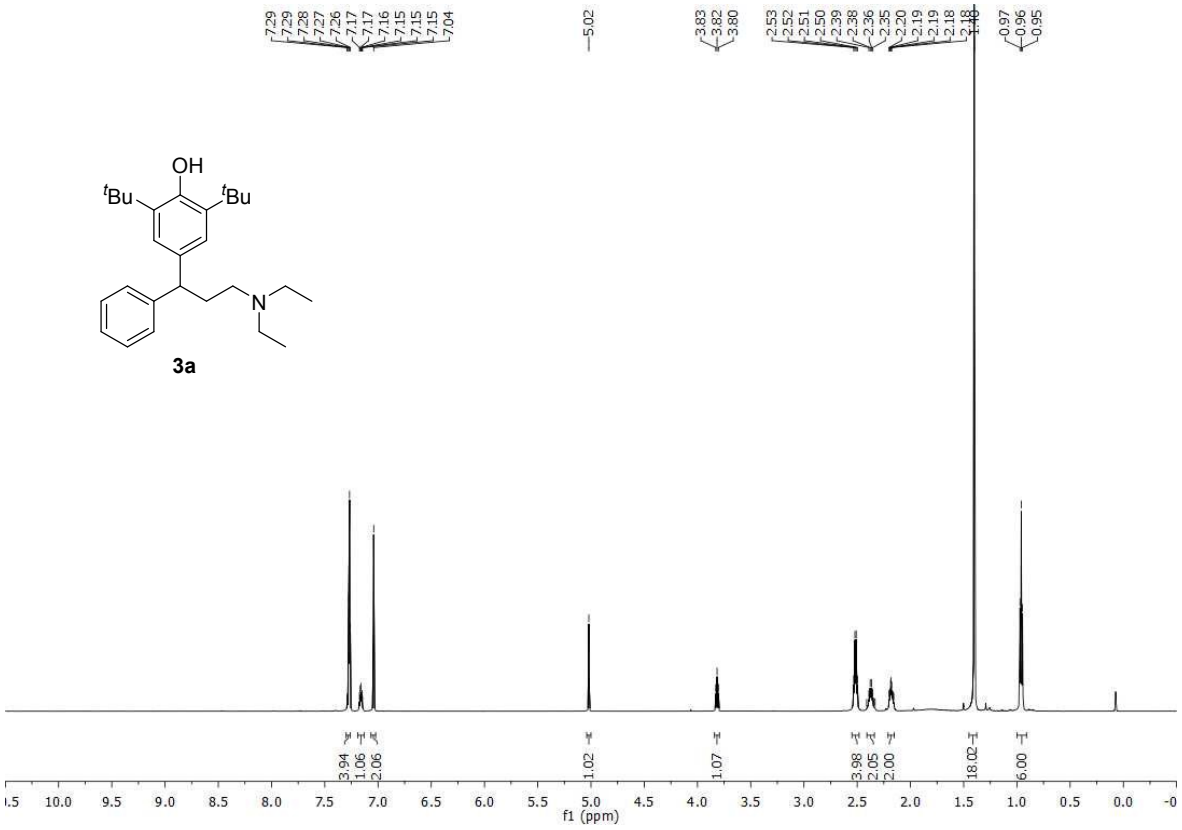
^{13}C NMR (100 MHz, $CDCl_3$): **major diastereomer** δ 151.82, 145.39, 135.49, 134.98, 128.26, 128.18, 125.64, 124.80, 59.85, 57.57, 56.92, 36.36, 34.30, 30.40, 20.22, 17.93, 11.97. **minor diastereomer** δ 151.79, 145.29, 135.33, 134.57, 128.24, 127.98, 125.64, 124.22, 59.85, 57.18, 56.66, 36.31, 34.29, 30.37, 20.06, 17.74, 11.94.

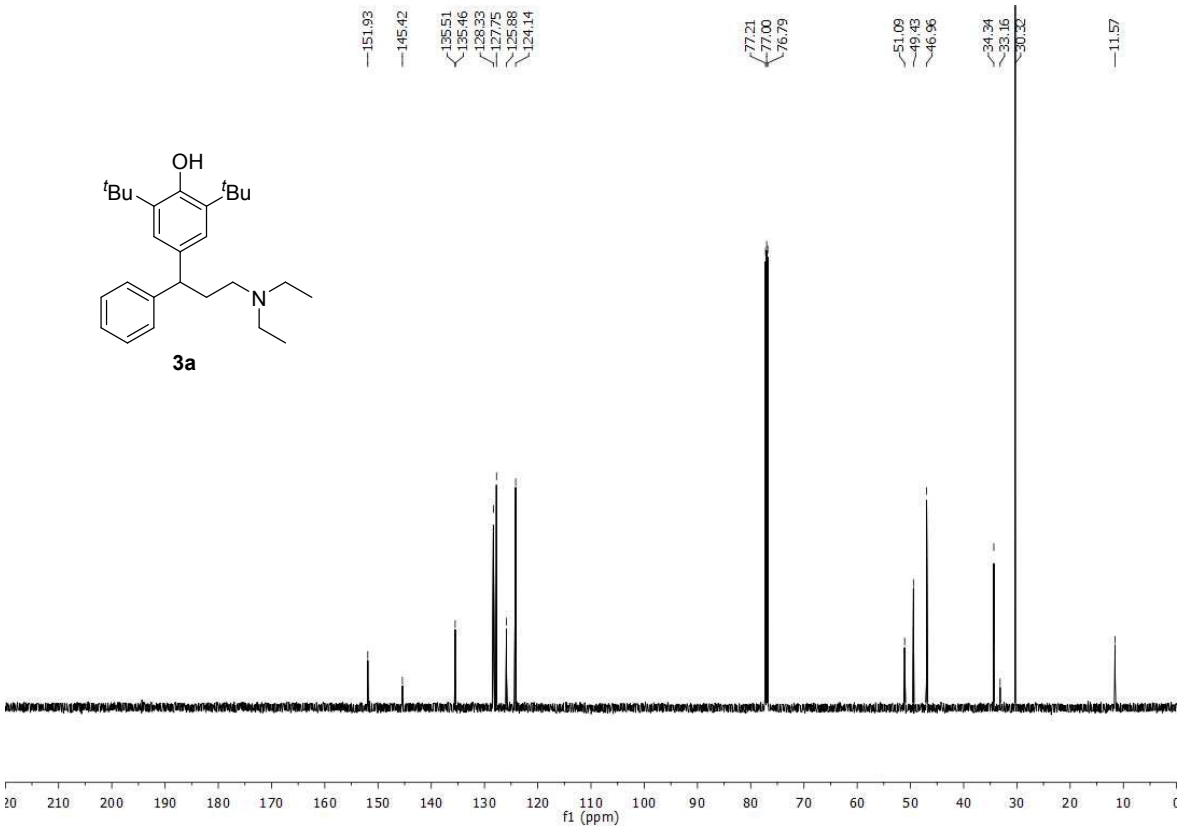
HRMS (ESI): m/z Calcd. for $[C_{30}H_{48}NO, M+H]^+$: 438.37359; Found: 438.37318.

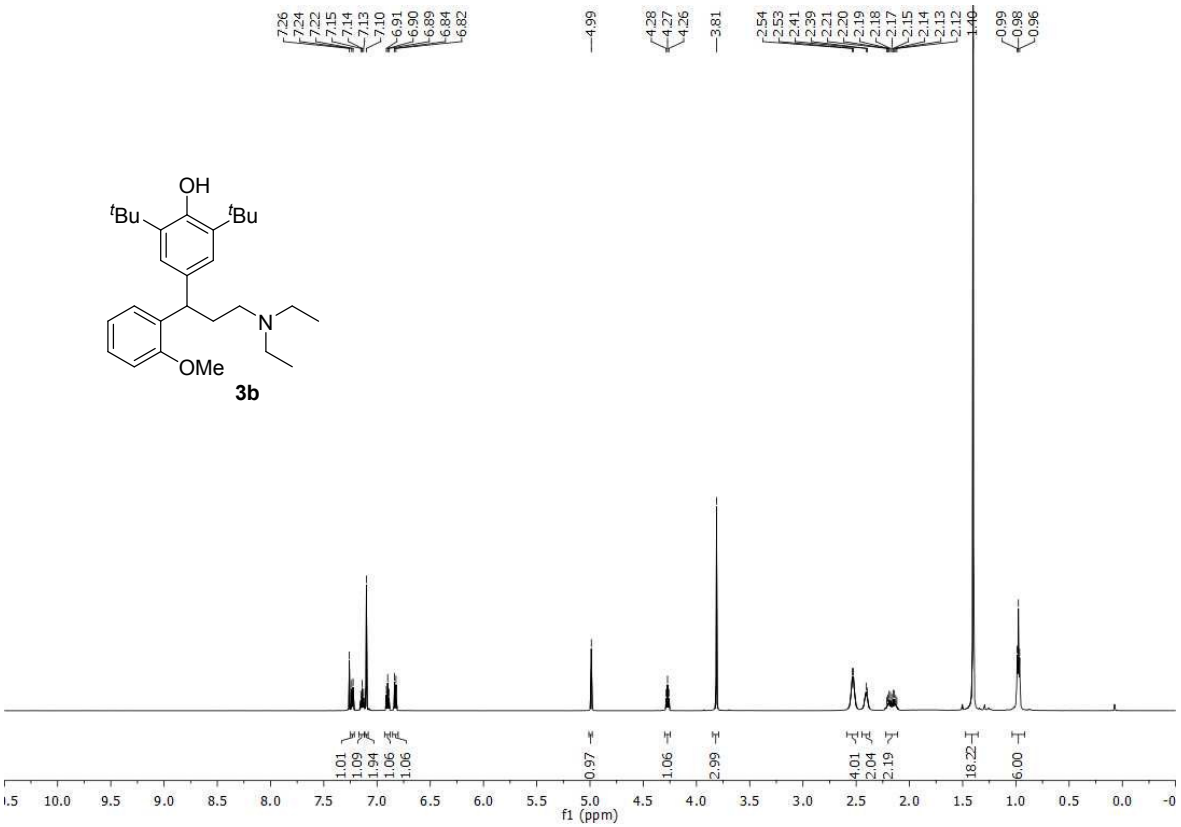
4. References

(1) (a) W.-D. Chu, L.-F. Zhang, X. Bao, X.-H. Zhao, C. Zeng, J- Y. Du, G.-B. Zhang, F.-X. Wang, X.-Y. Ma and C.-A. Fan, *Angew. Chem., Int. Ed.,* 2013, **52**, 9229-9233; (b) L. Caruana, F. Kniep, T. K. Johansen, P. H. Poulsen and K. A. Jørgensen, *J. Am. Chem. Soc.* 2014, **136**, 15929-15932.

5. NMR spectra of the products



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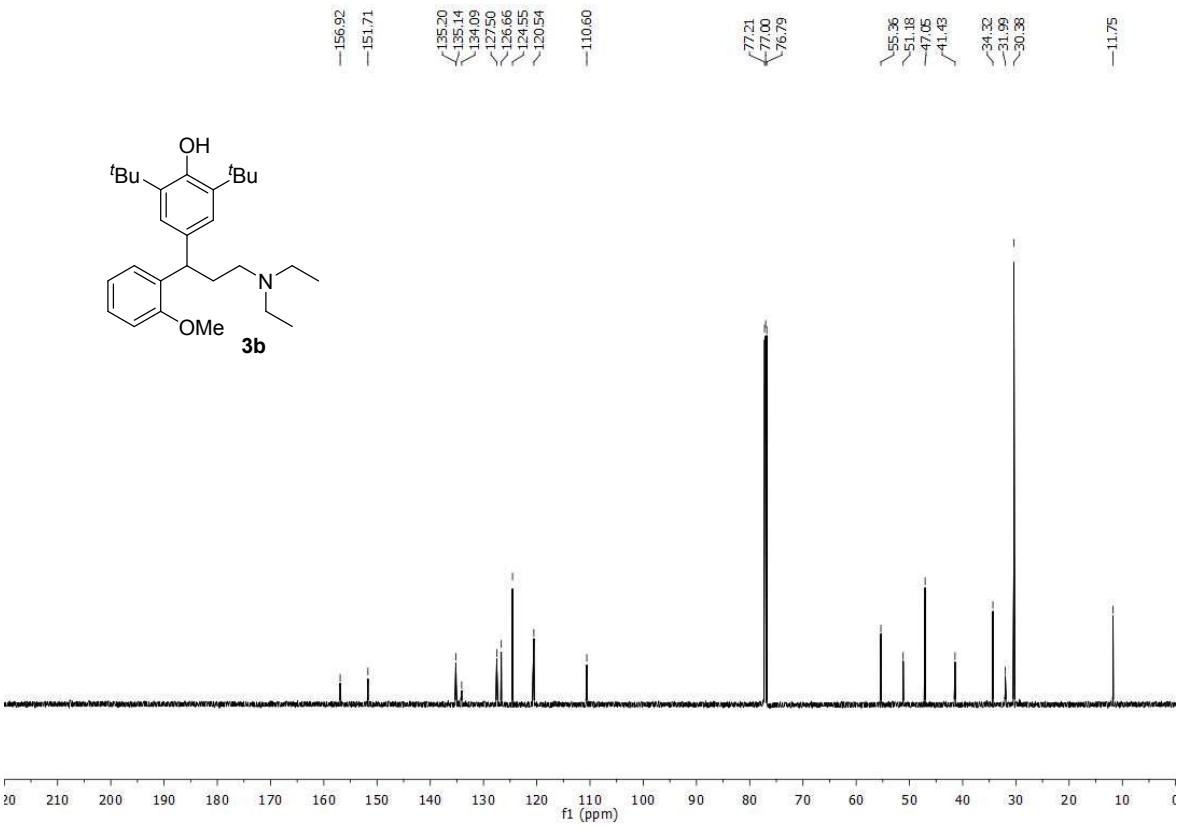
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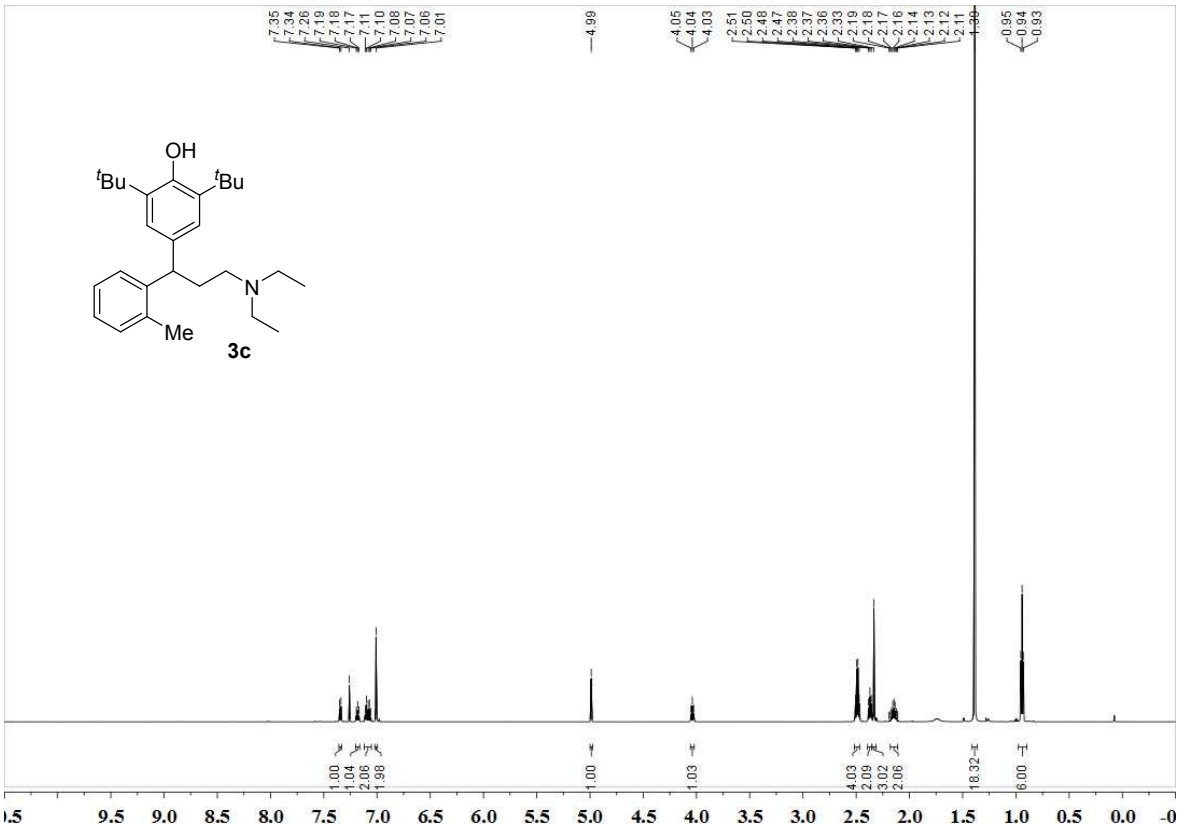
3b
f1 (ppm)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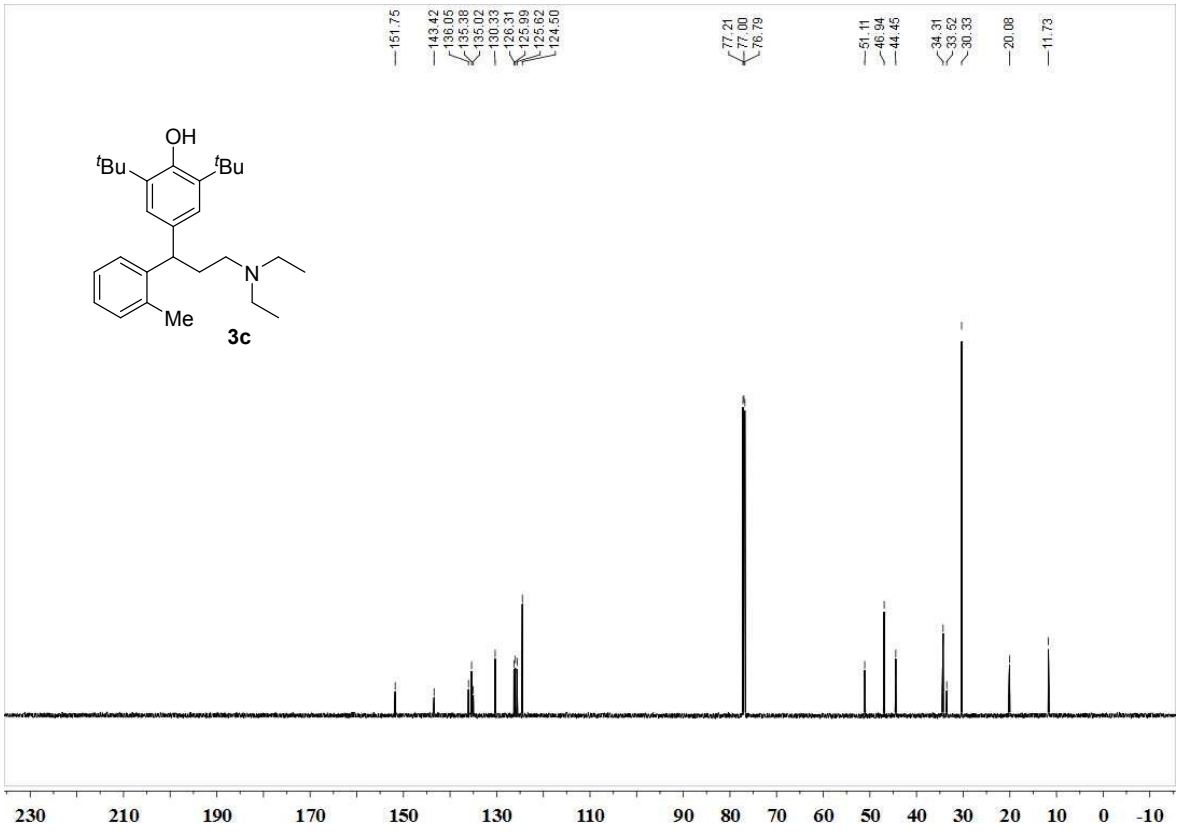
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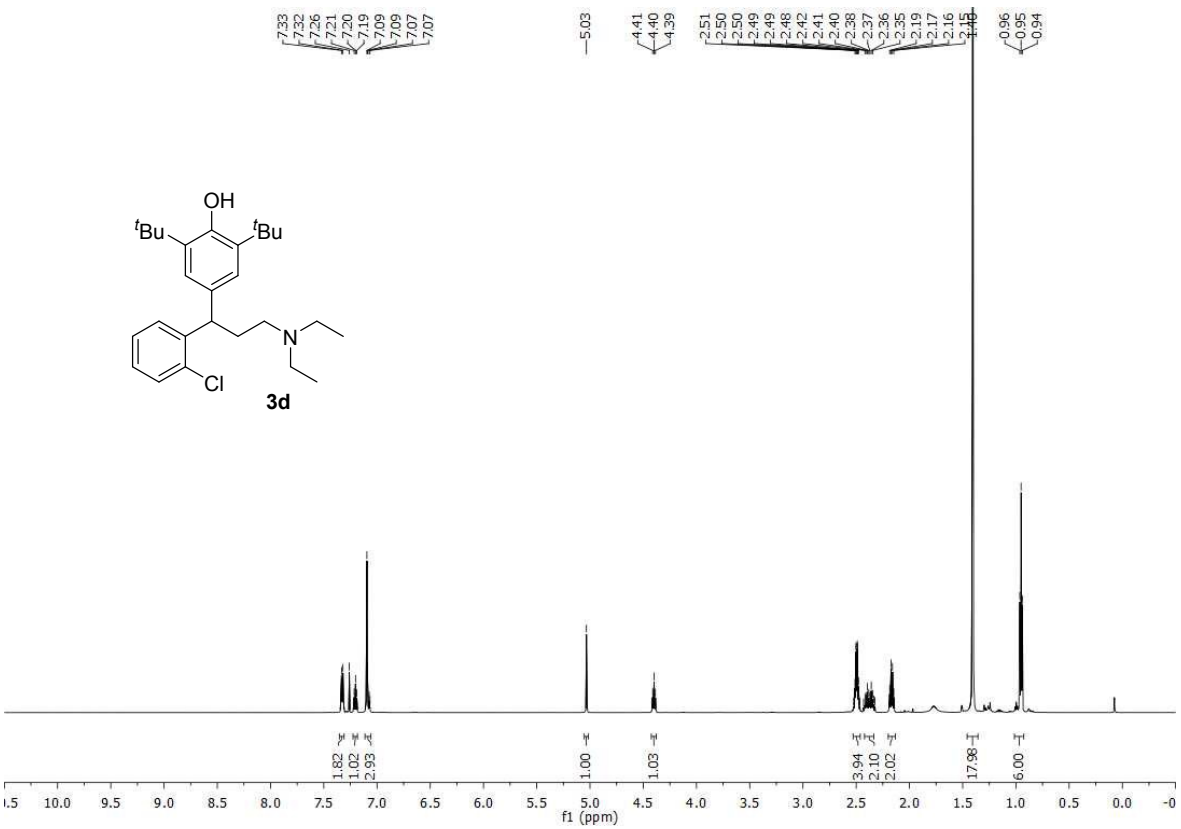
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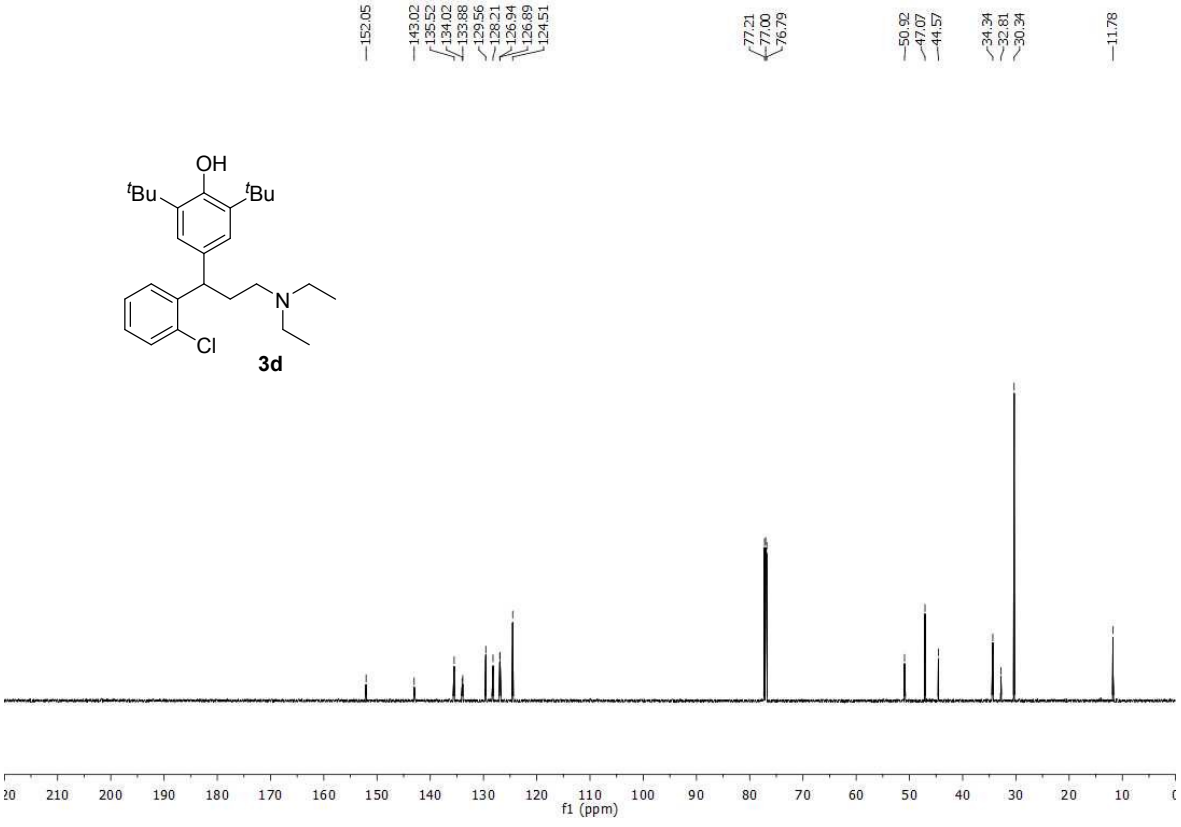
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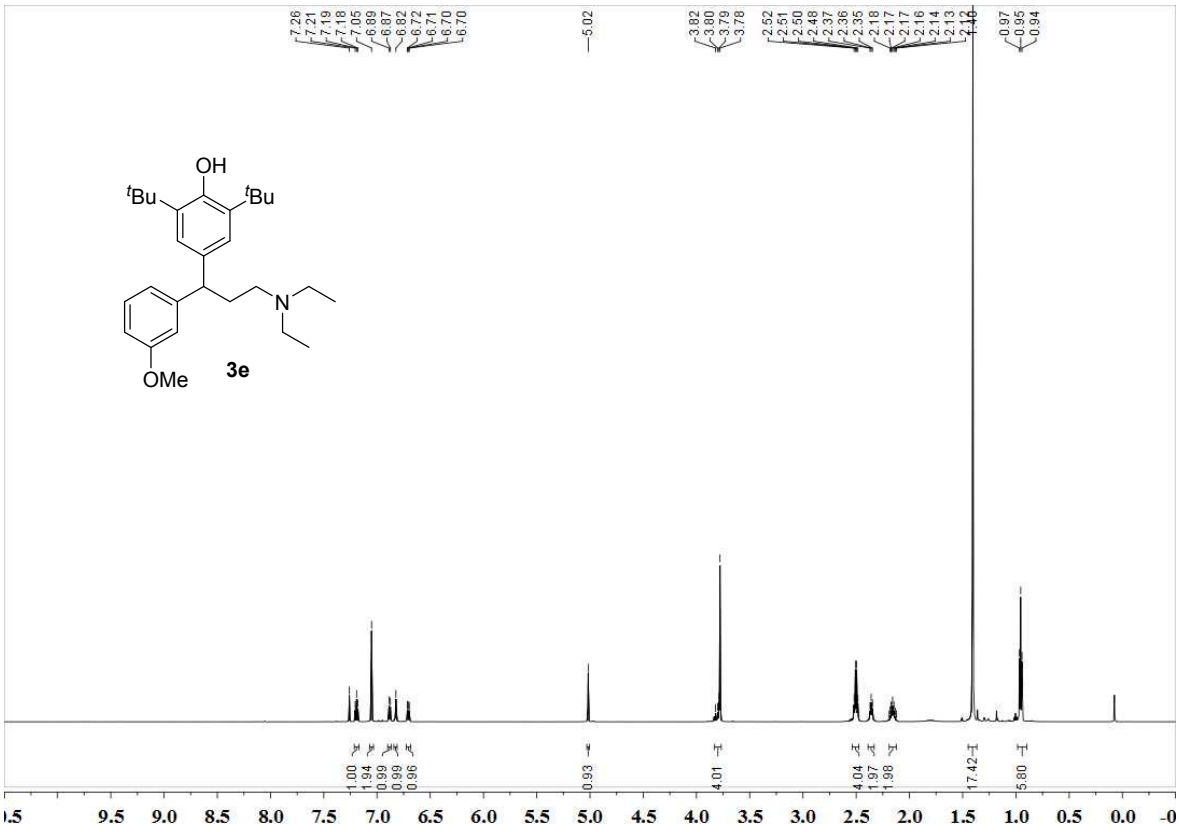
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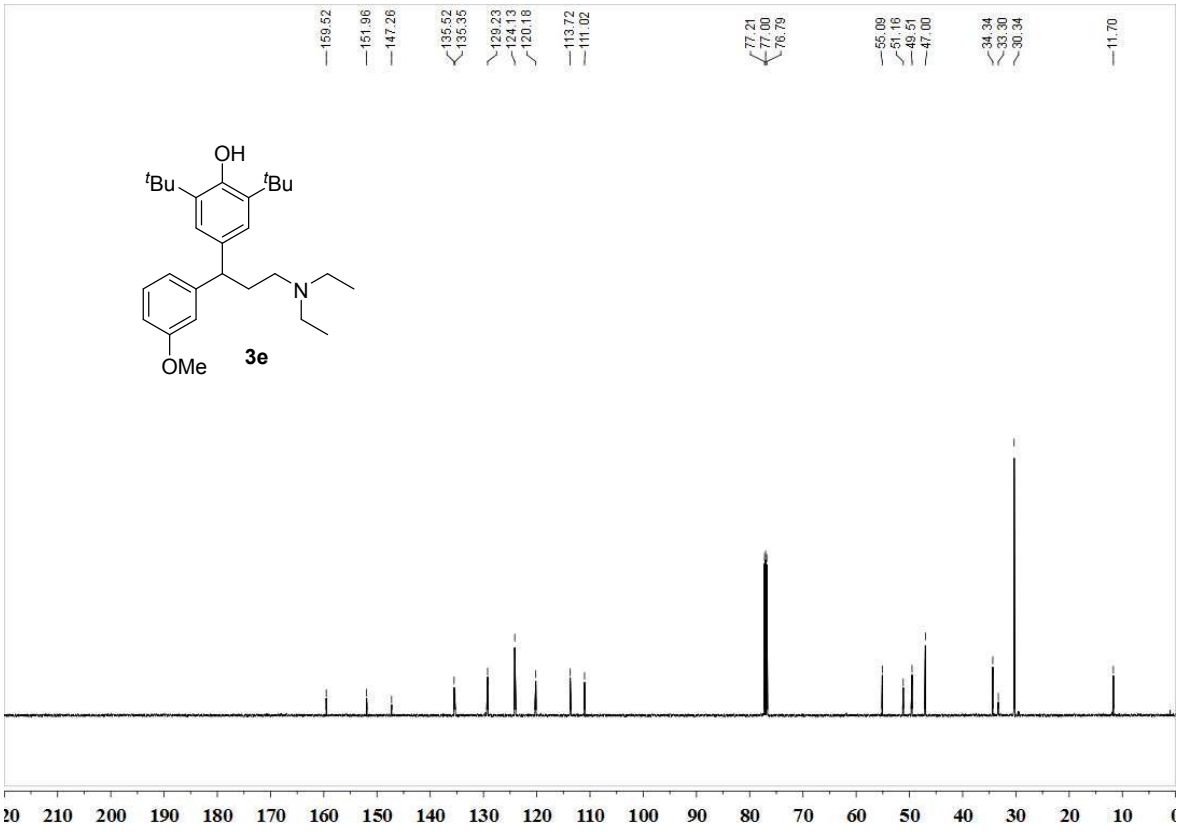
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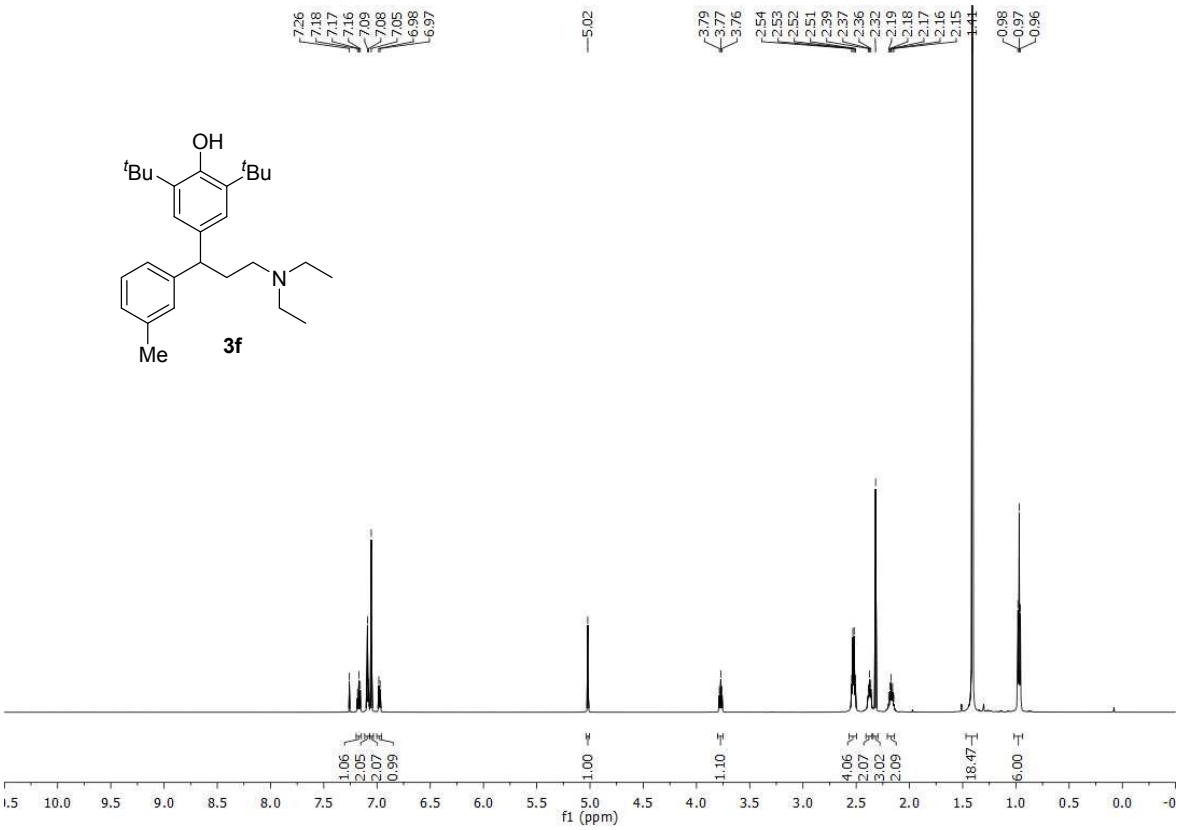
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Me
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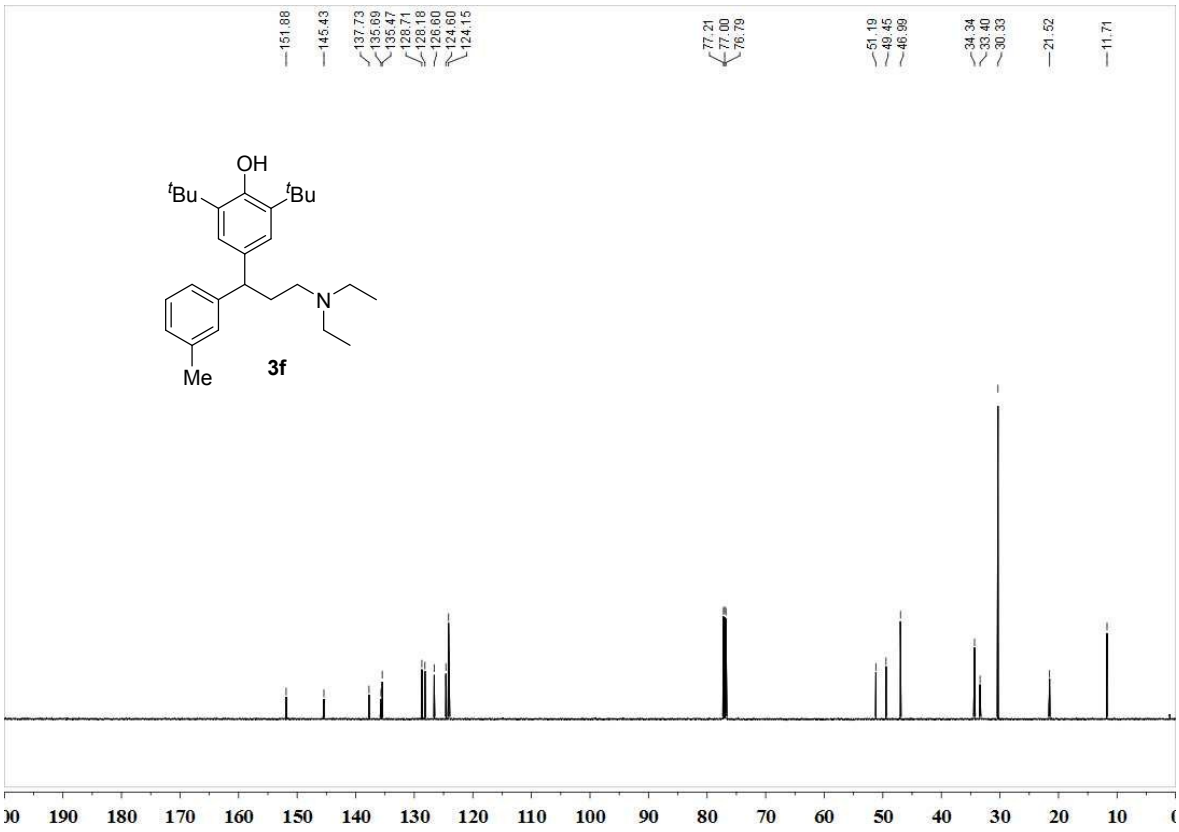
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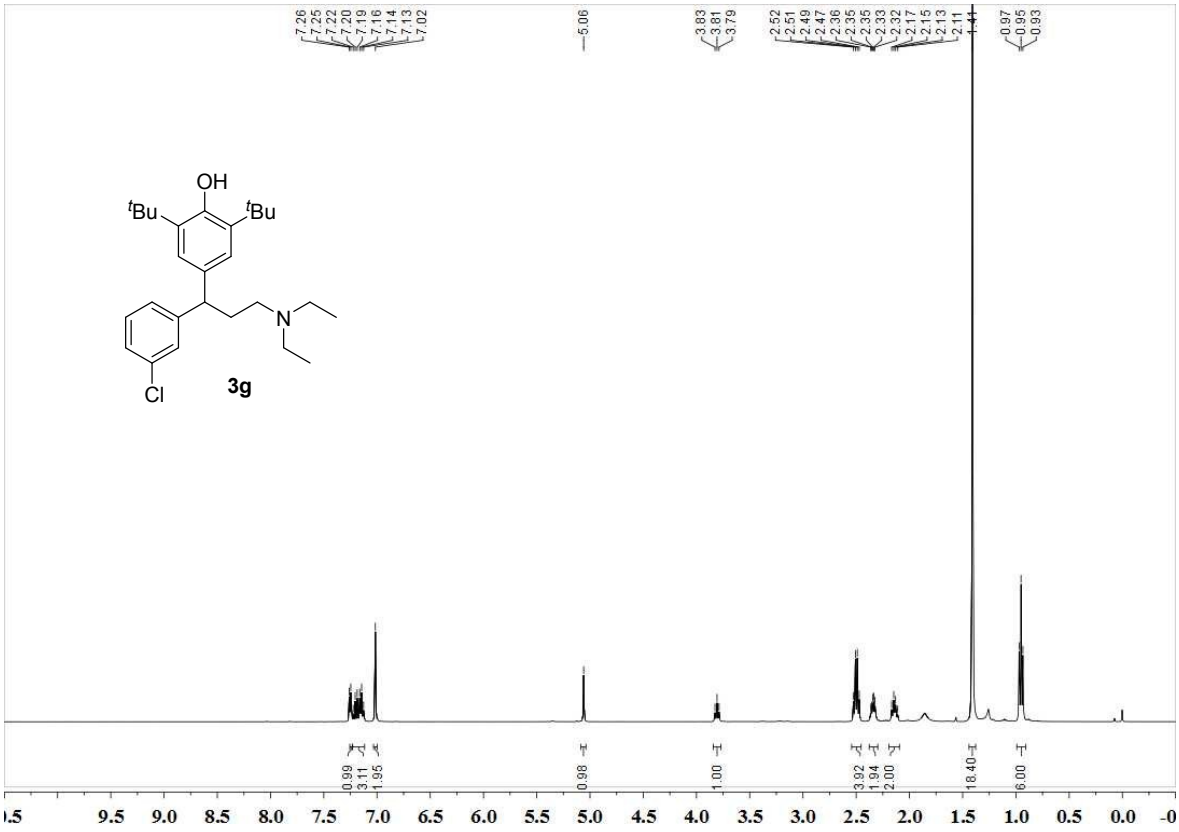
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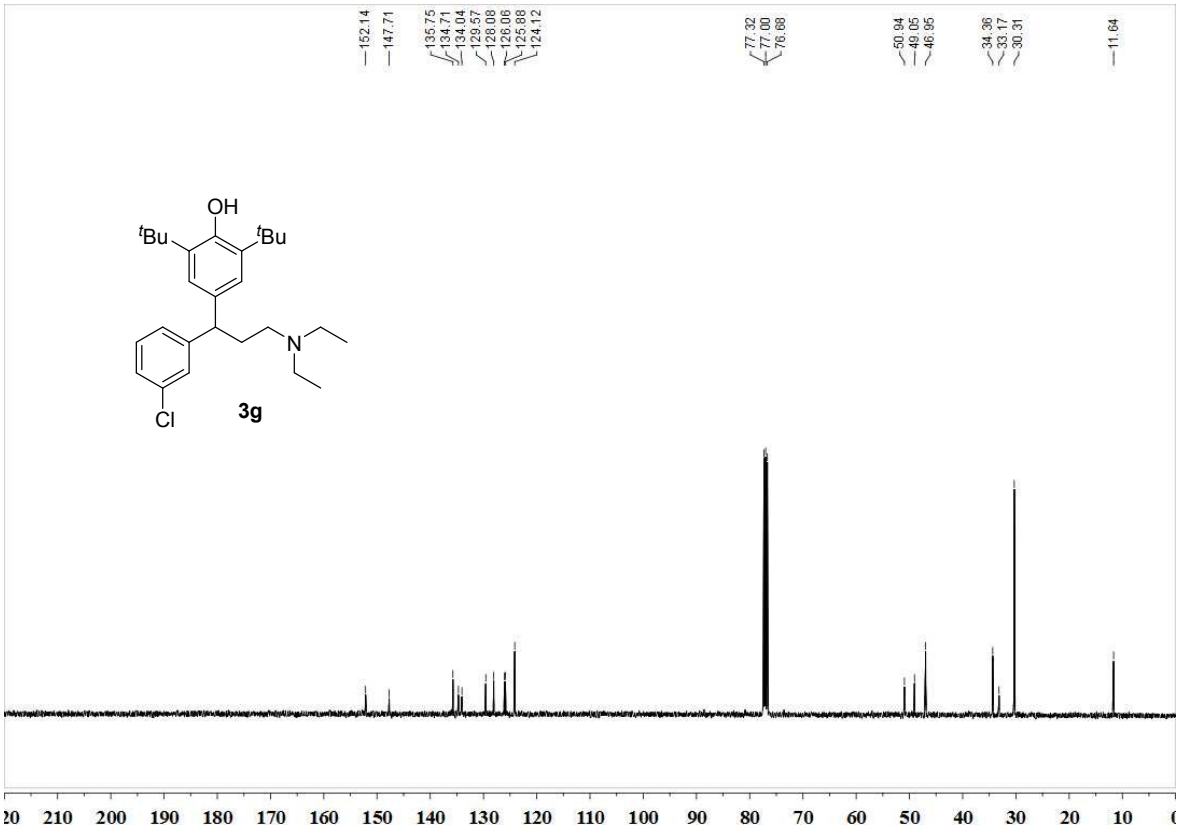
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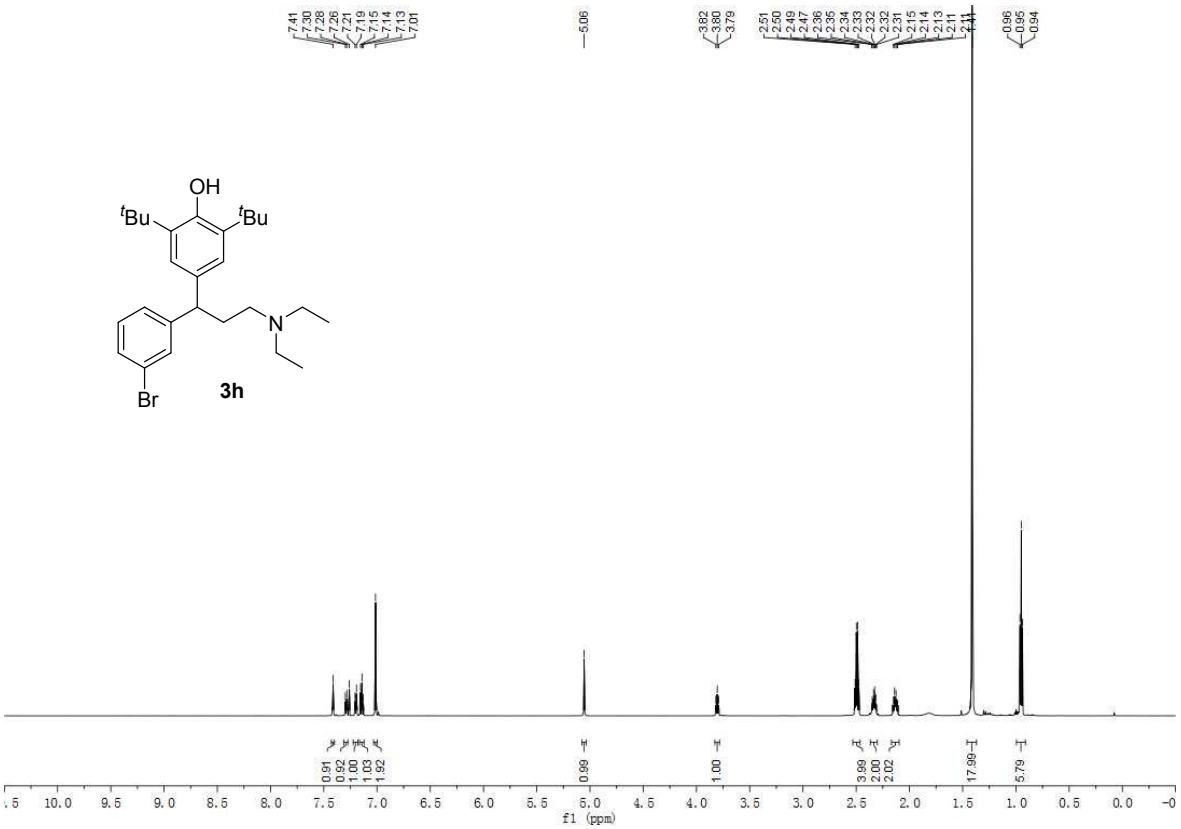
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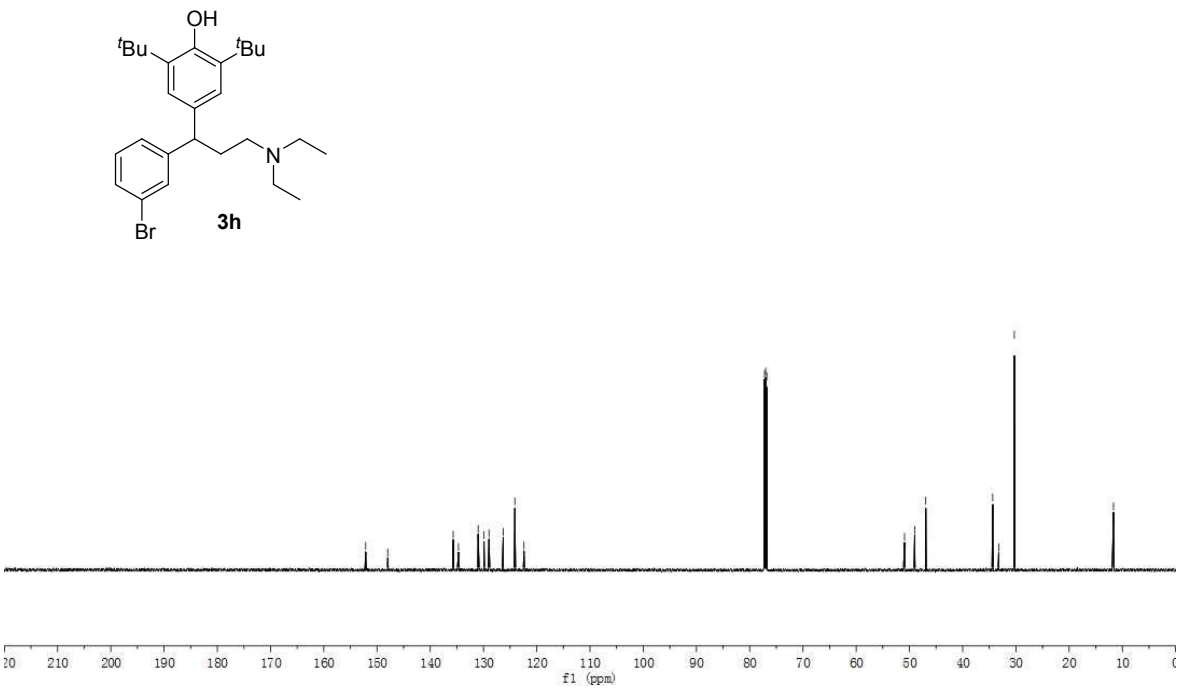
f1 (ppm)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tBu
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Br
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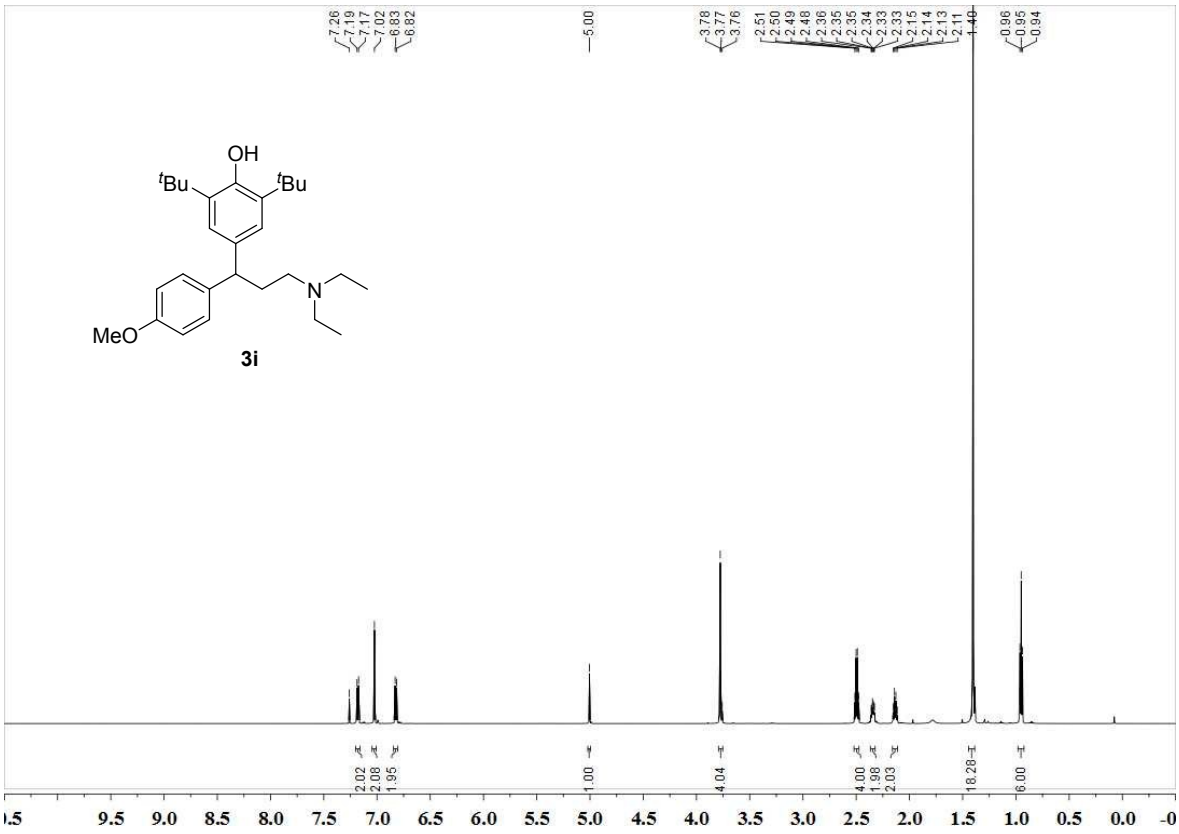
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5.00
3.78
3.77
3.76
2.51
2.50
2.49
2.48
2.36
2.35
2.35
2.34
2.33
2.33
2.15
2.14
2.13
2.11
1.40
0.96
0.95
0.94
OH
tBu
tBu
N
MeO
3i
2.02
2.08
1.95
1.00
4.04
4.00
1.98
2.03
18.28
6.00
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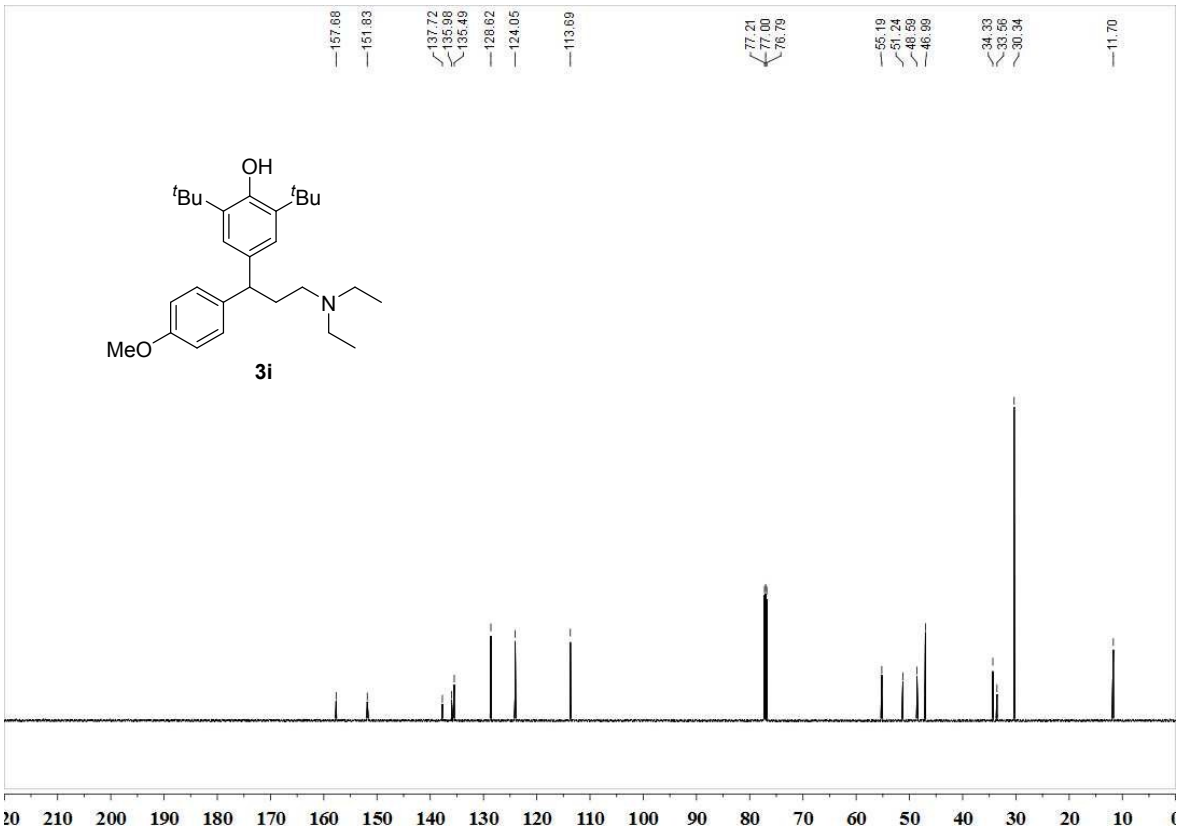
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135.49
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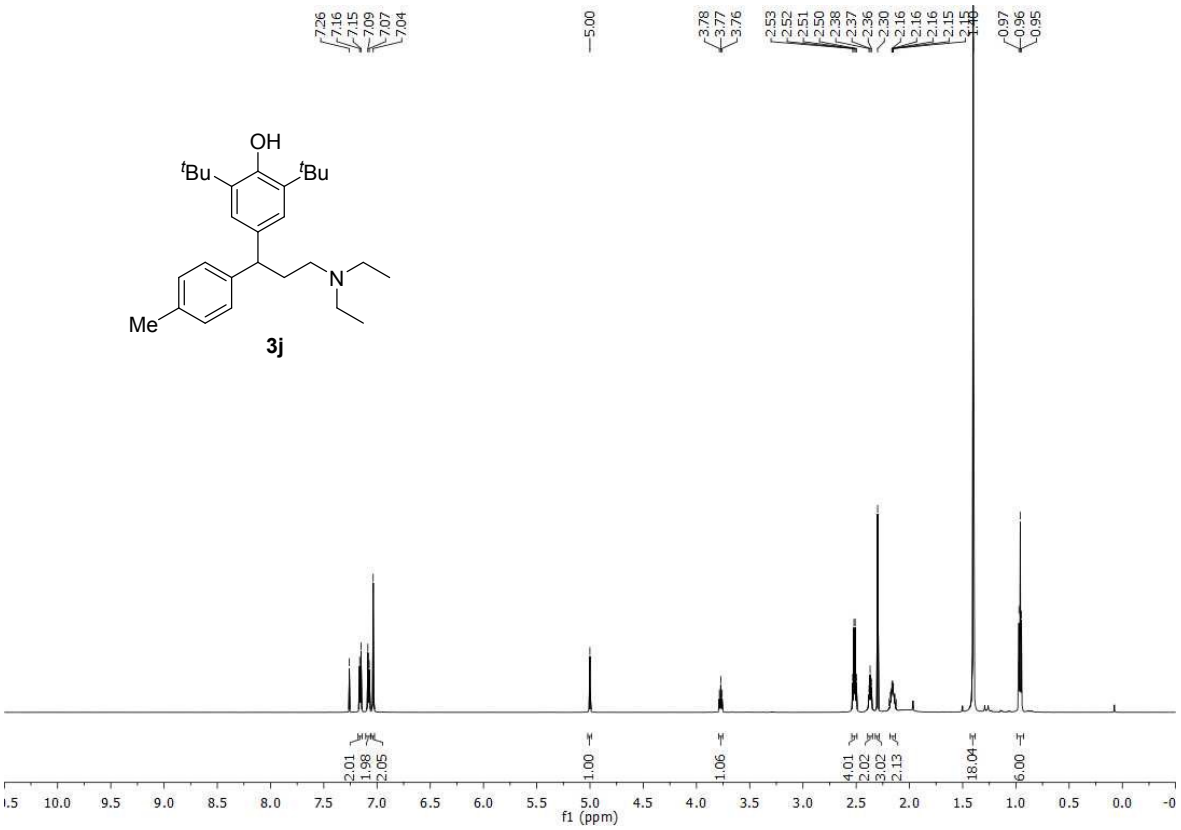
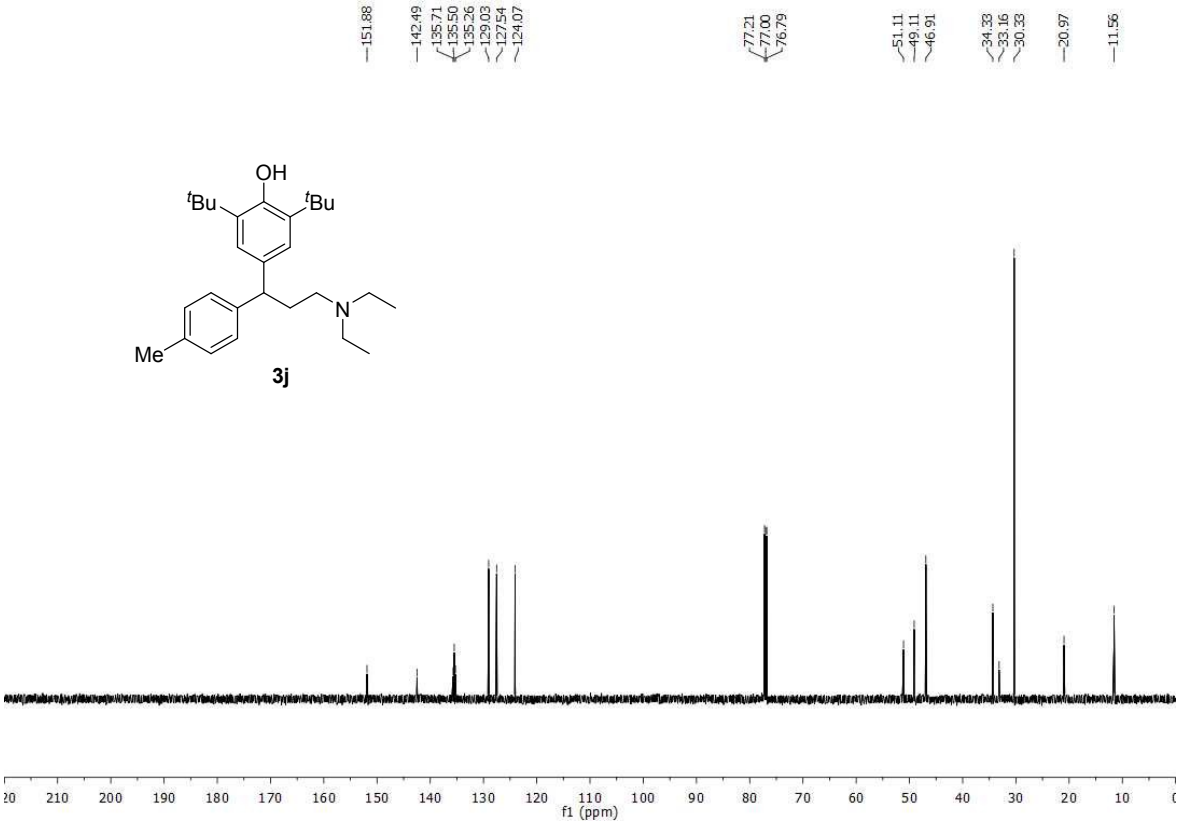
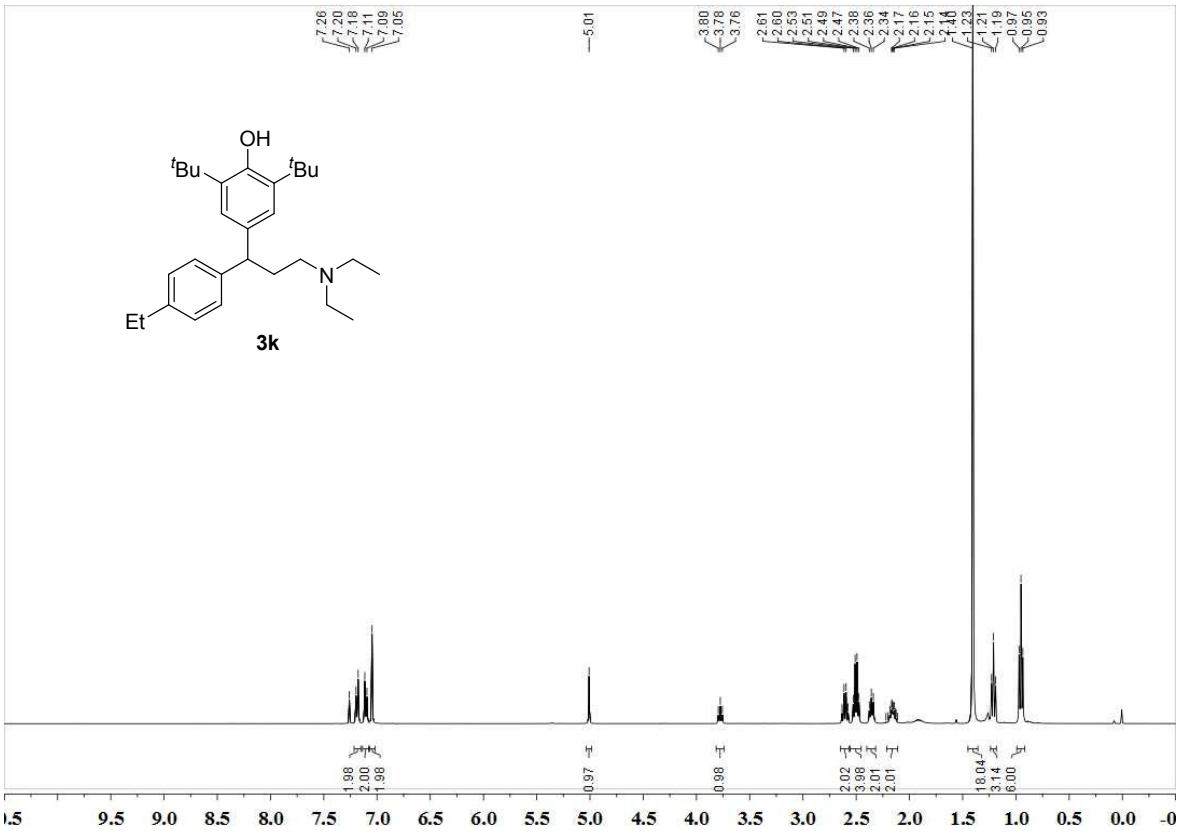
124.05
113.69
77.21
77.00
76.79
55.19
51.24
48.59
46.99
34.33
33.56
30.34
11.70
OH
tBu
tBu
N
MeO
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


OH
tBu
tBu
N
Me
3j
f1 (ppm)


OH
tBu
tBu
N
Me
3j
f1 (ppm)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7.05
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3.80
3.78
3.76
2.61
2.60
2.53
2.51
2.49
2.47
2.38
2.36
2.34
2.17
2.16
2.15
2.14
1.23
1.21
1.19
0.97
0.95
0.93
OH
tBu
tBu
N
Et
3k
1.98
2.00
1.98
0.97
0.98
2.02
3.98
2.01
2.01
18.04
3.14
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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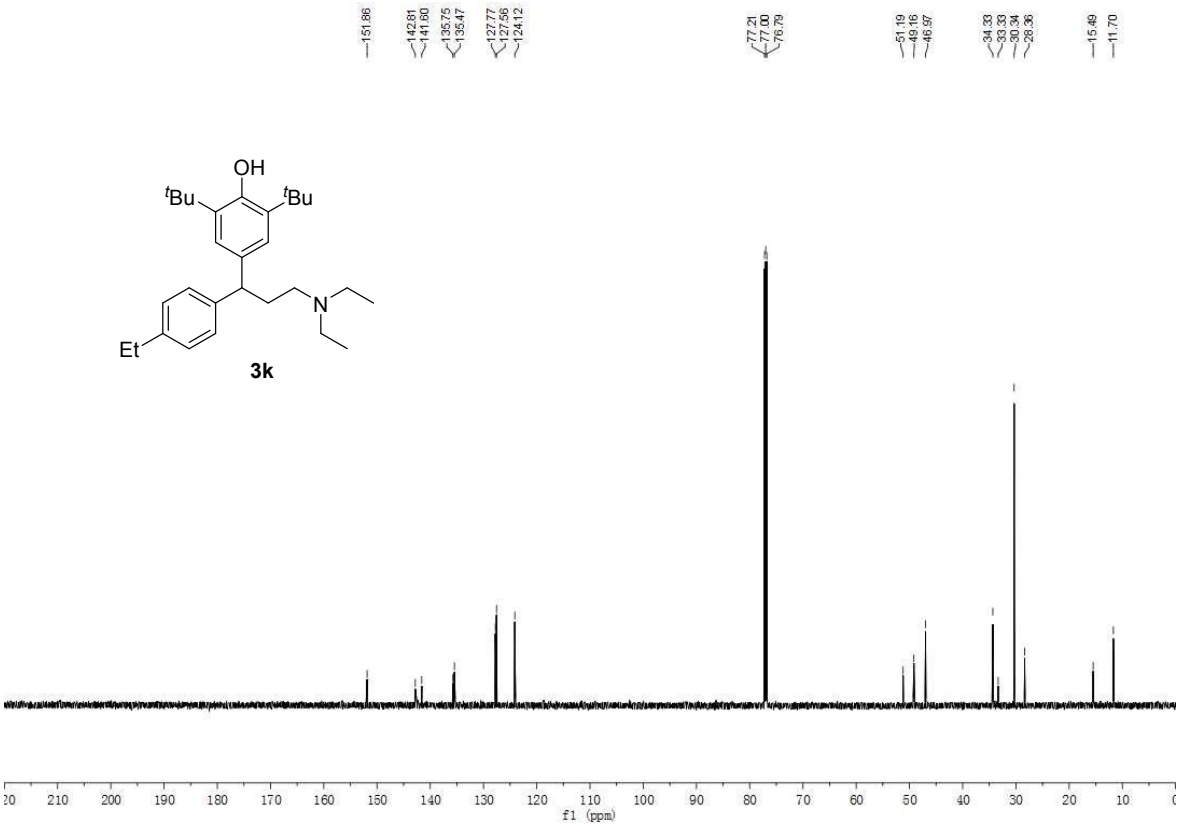
0.0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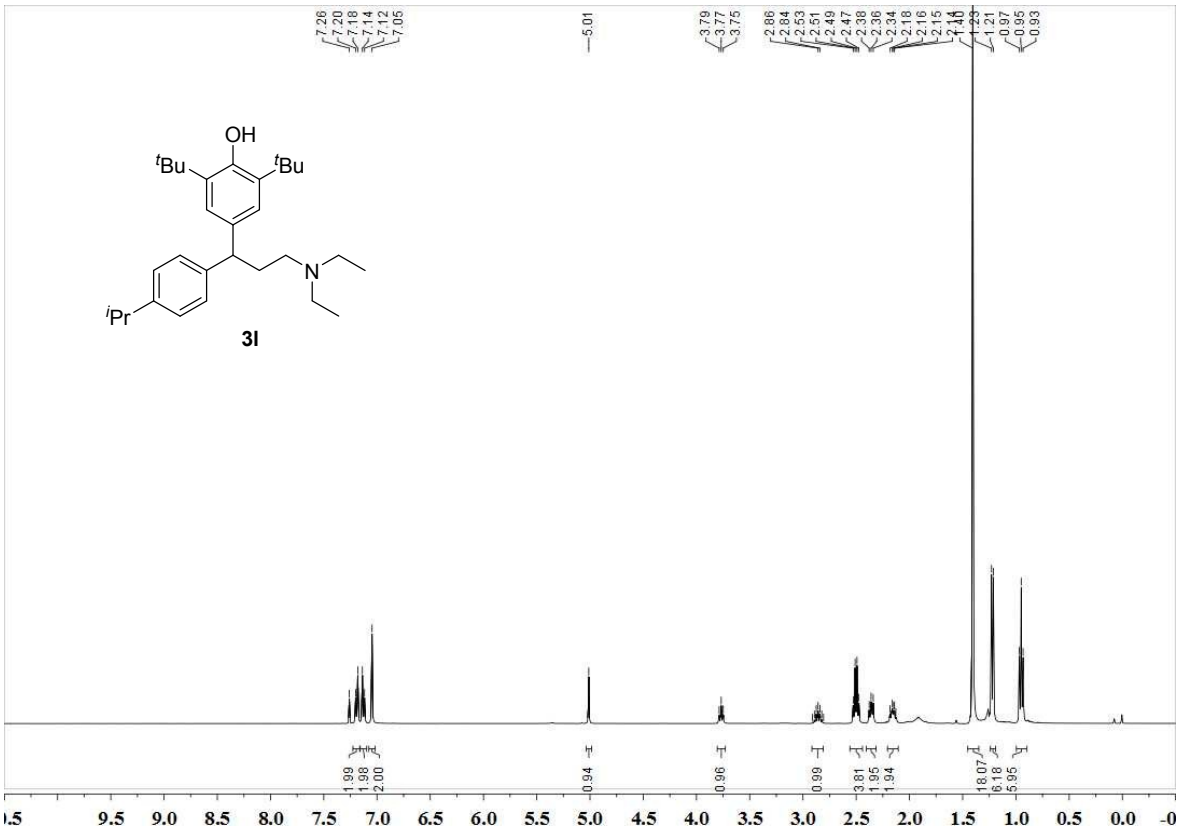
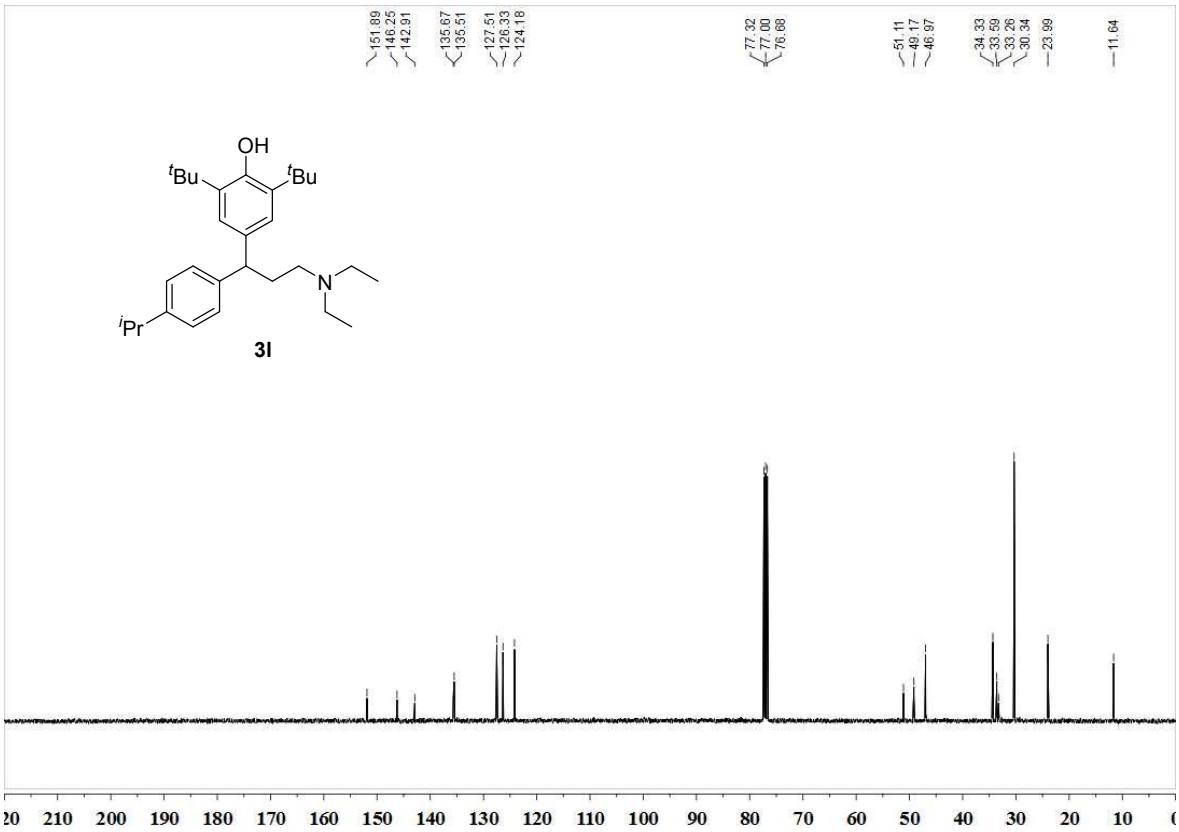
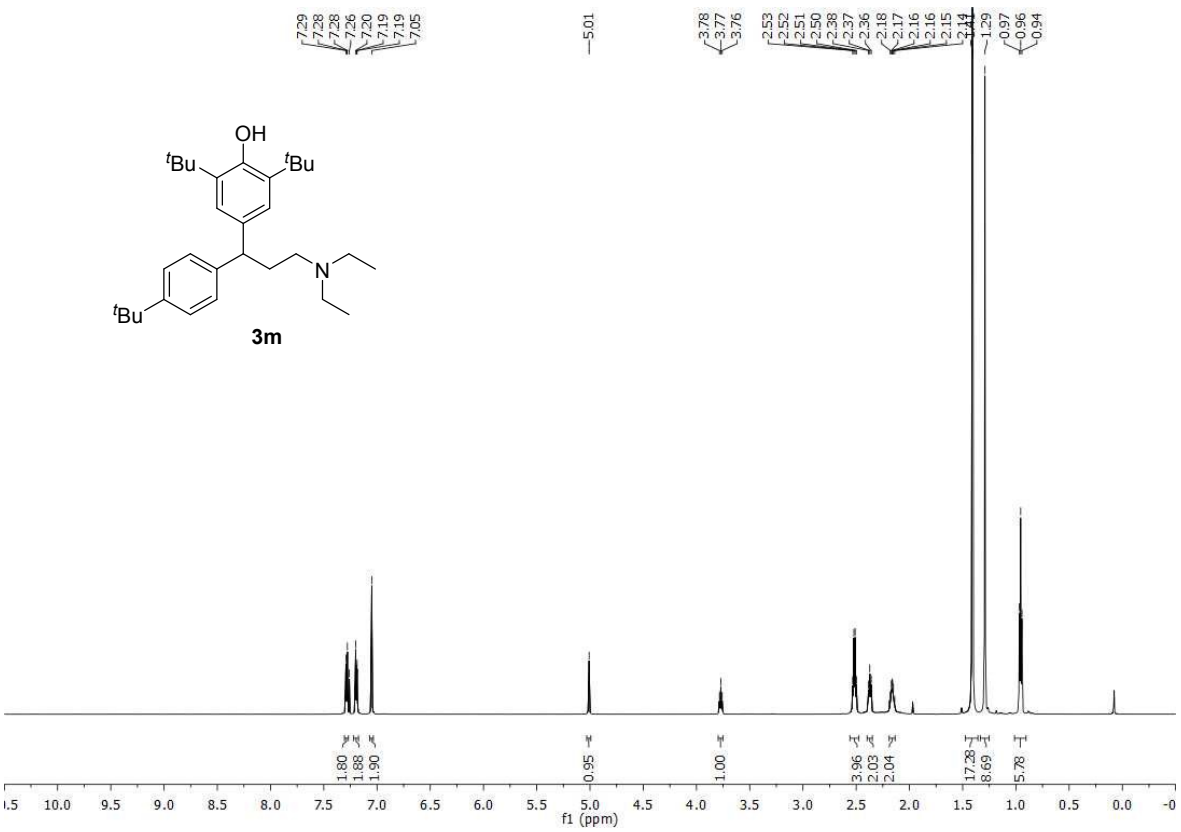
127.56
124.12
77.21
77.00
76.79
51.19
49.16
46.97
34.33
33.33
30.34
28.36
15.49
11.70
OH
tBu
tBu
N
Et
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OH
tBu
tBu
N
iPr
3l


OH
tBu
tBu
N
iPr
3l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7.28
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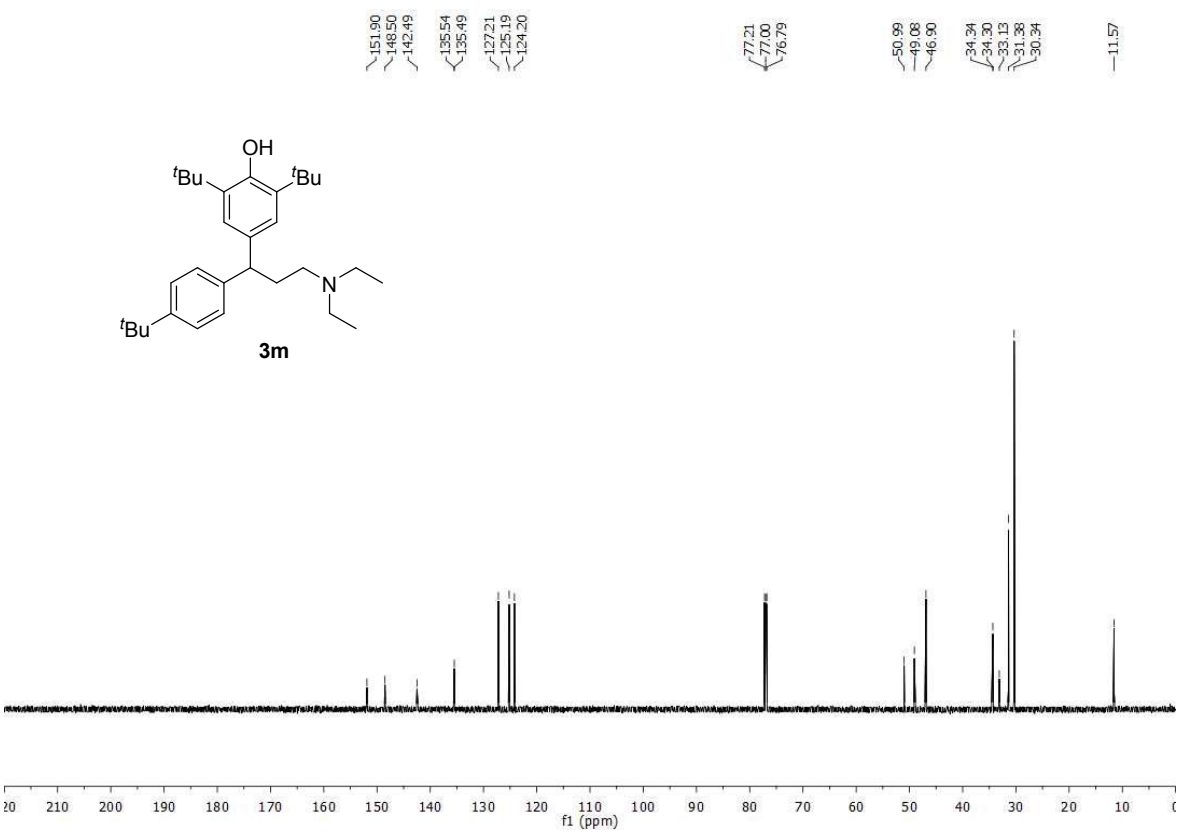
7.26
7.20
7.19
7.19
7.05
5.01
3.78
3.77
3.76
2.53
2.52
2.51
2.50
2.38
2.37
2.36
2.18
2.17
2.16
2.16
2.15
2.14
1.29
0.97
0.96
0.94
OH
tBu
tBu
tBu
N
3m
1.80
1.88
1.90
0.95
1.00
3.96
2.03
2.04
17.28
8.69
5.78
f1 (ppm)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135.49
127.21
125.19
124.20
77.21
77.00
76.79
50.99
49.08
46.90
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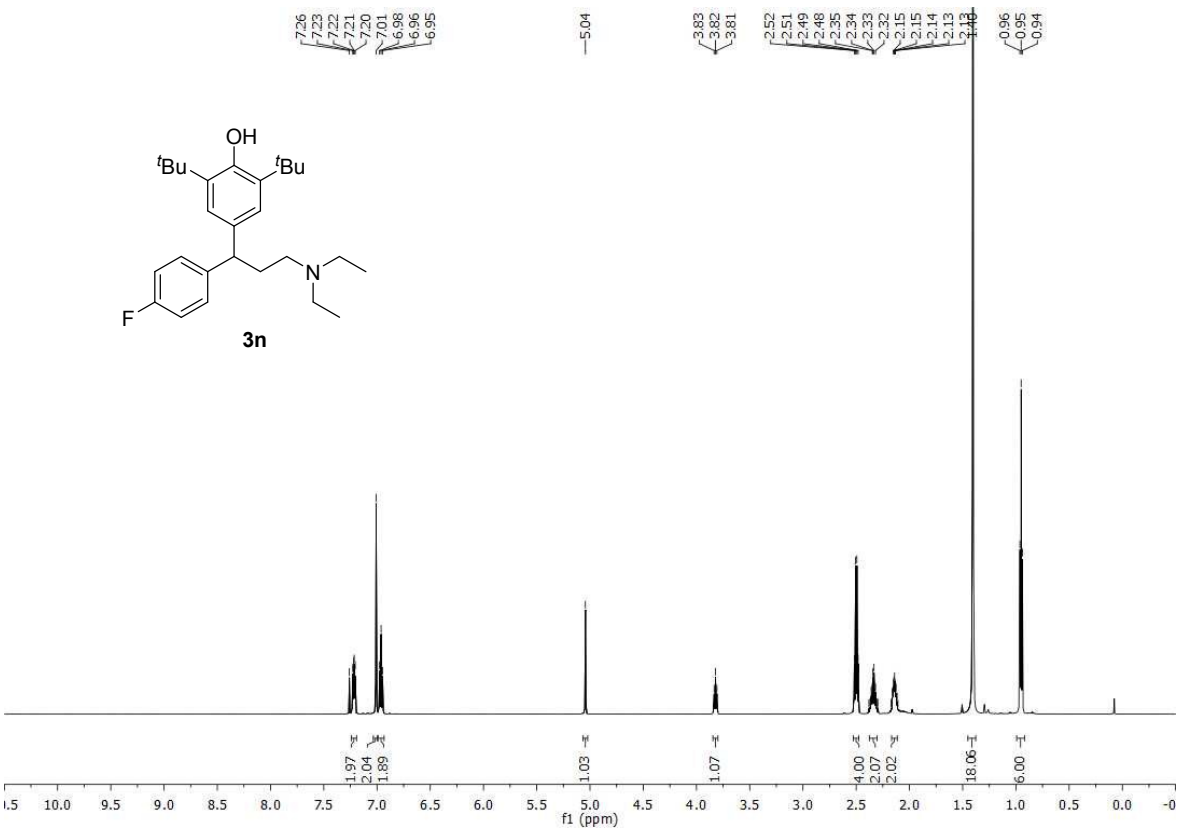
34.30
33.13
31.38
30.34
11.57
OH
tBu
tBu
tBu
N
3m
f1 (ppm)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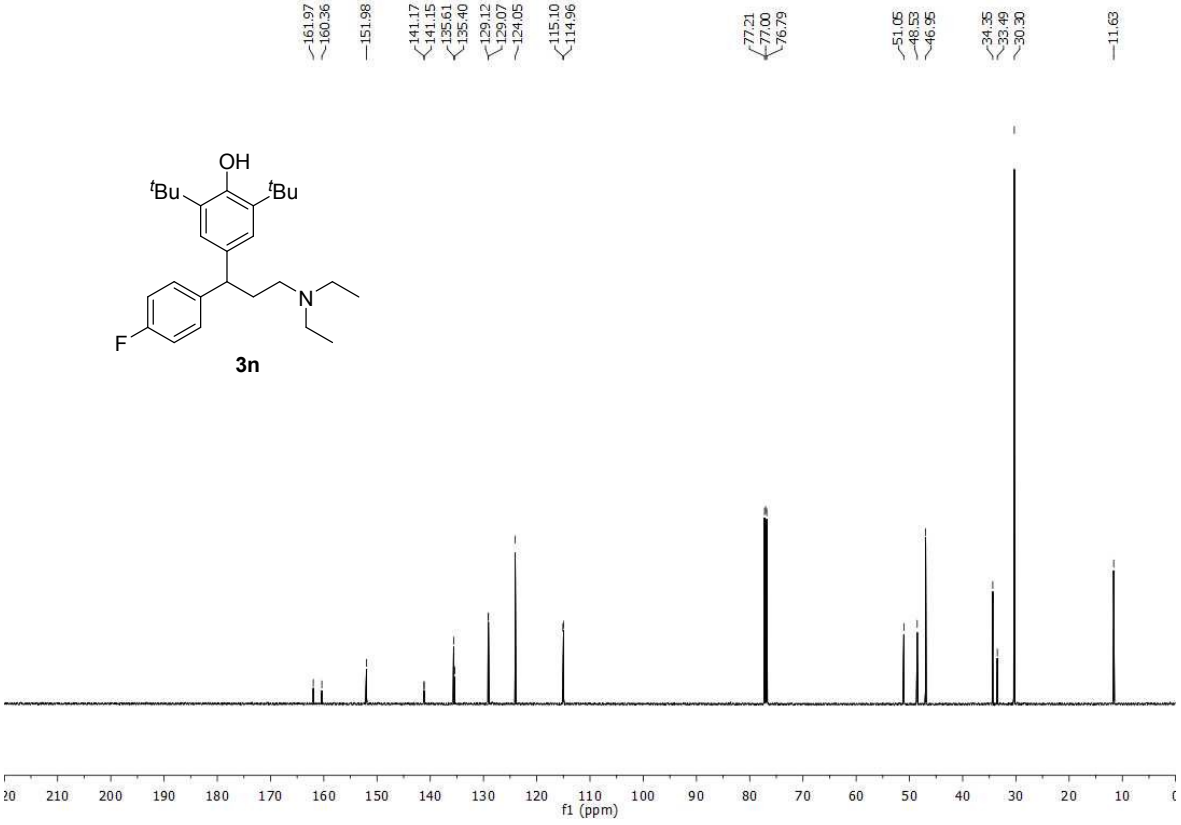
7.23
7.22
7.21
7.20
7.01
6.98
6.96
6.95
5.04
3.83
3.82
3.81
2.52
2.51
2.49
2.48
2.35
2.34
2.33
2.32
2.15
2.14
2.13
1.43
0.96
0.95
0.94
OH
tBu
tBu
N
F
3n
1.97
2.04
1.89
1.03
1.07
4.00
2.07
2.02
18.06
6.00
f1 (ppm)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160.36
151.98
141.17
141.15
135.61
135.40
129.12
129.07
124.05
115.10
114.96
77.21
77.00
76.79
51.05
48.53
46.95
34.35
33.49
30.30
11.63
OH
tBu
tBu
N
F
3n
f1 (ppm)

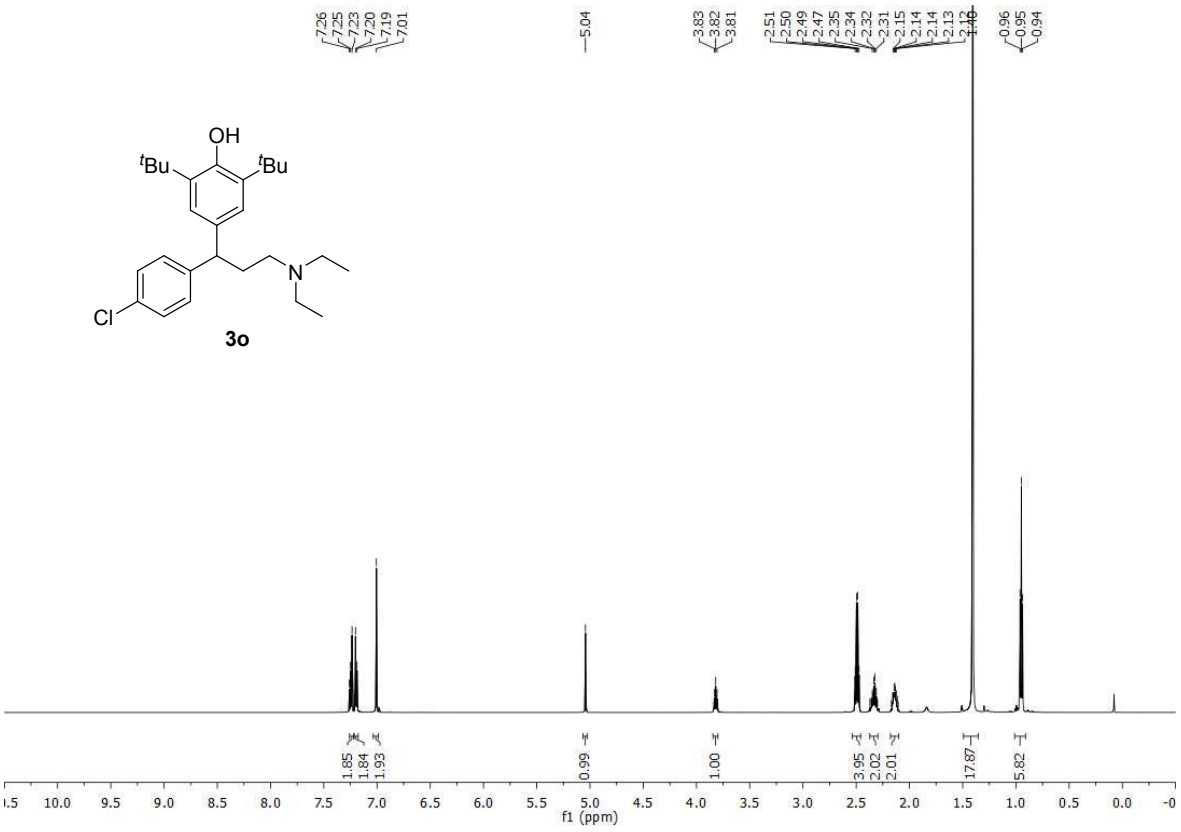
OH
tBu
tBu
N
F

3n


-117.74
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

OH
tBu
tBu
N
Cl

3o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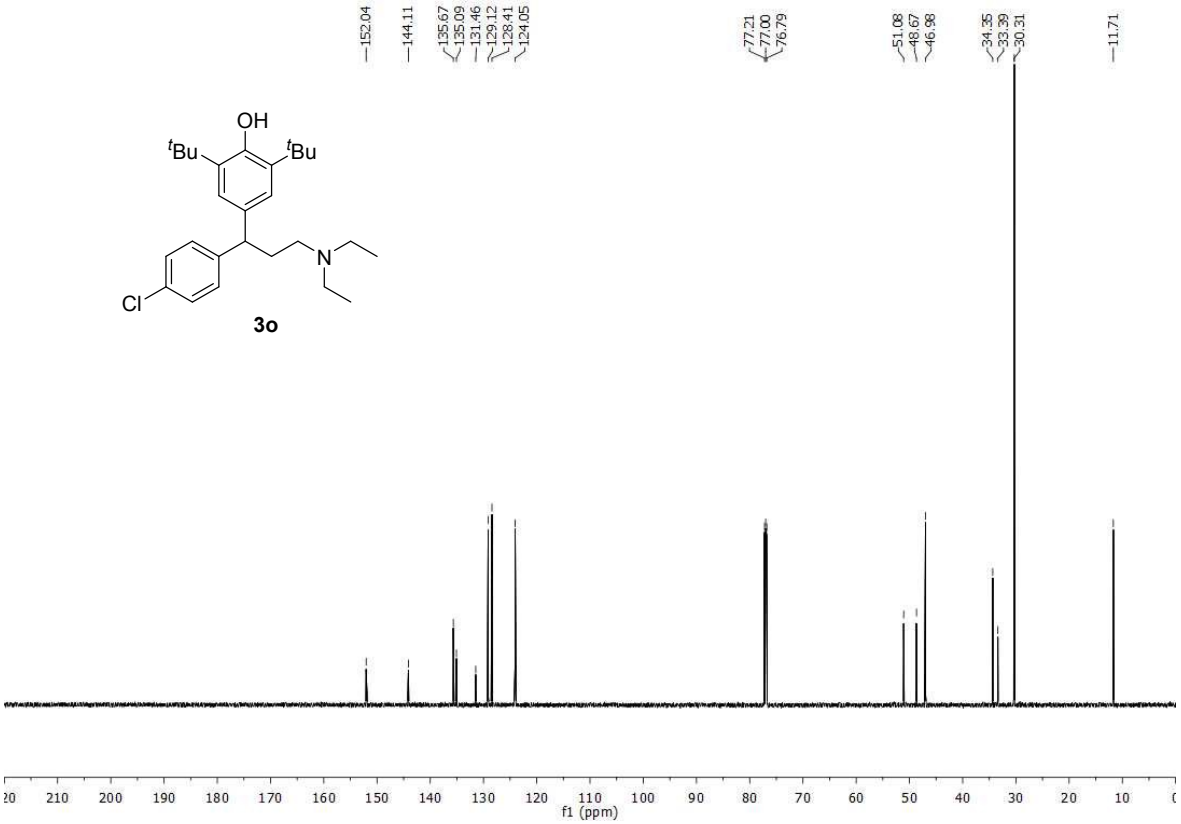
7.25
7.23
7.20
7.19
7.01
5.04
3.83
3.82
3.81
2.51
2.50
2.49
2.47
2.35
2.34
2.32
2.31
2.15
2.14
2.14
2.13
2.12
1.00
0.96
0.95
0.94
1.85
1.84
1.93
0.99
1.00
3.95
2.02
2.01
17.87
5.82
f1 (ppm)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144.11
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135.09
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129.12
128.41
124.05
77.21
77.00
76.79
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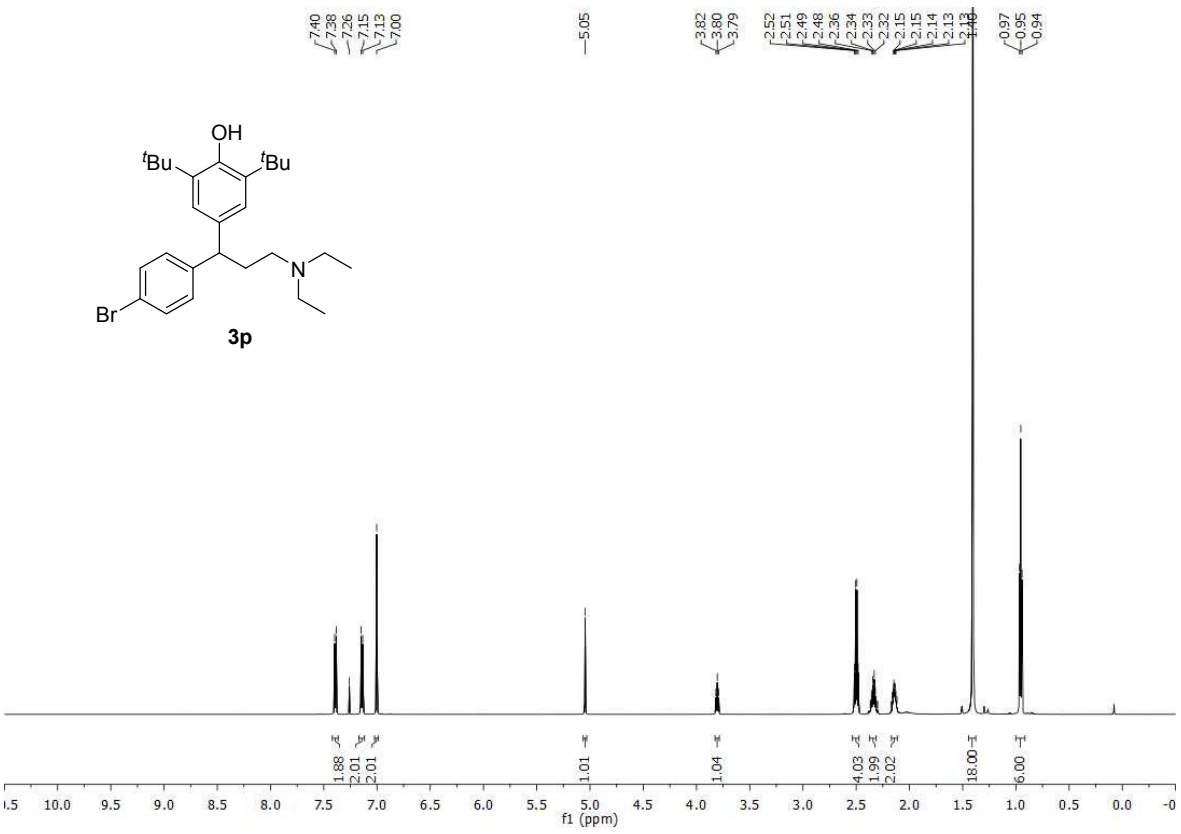
34.35
33.39
30.31
11.71
OH
tBu
tBu
N
Cl
f1 (ppm)

3o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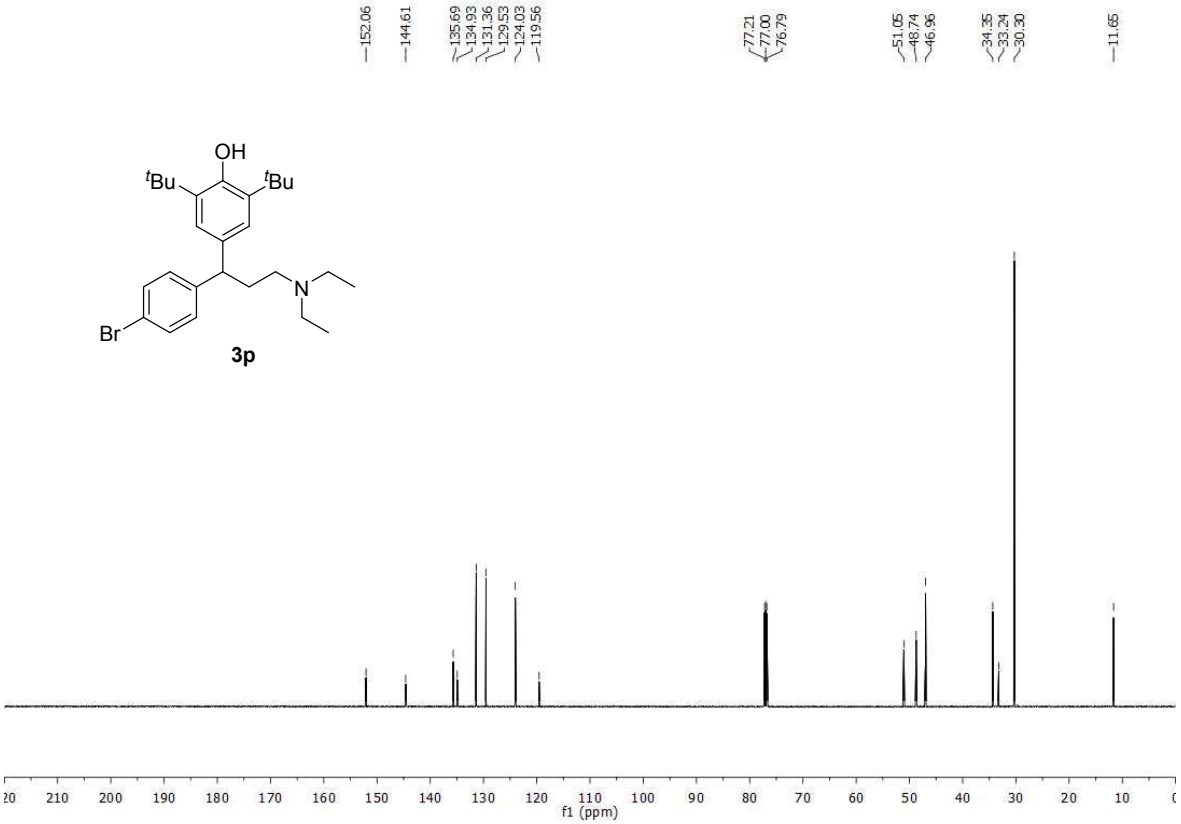
7.38
7.26
7.15
7.13
7.00
5.05
3.82
3.80
3.79
2.52
2.51
2.49
2.48
2.36
2.34
2.33
2.32
2.15
2.14
2.13
0.97
0.95
0.94
OH
tBu
tBu
N
Br
1.88
2.01
2.01
1.01
1.04
4.03
1.99
2.02
18.00
6.00
f1 (ppm)

3p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144.61
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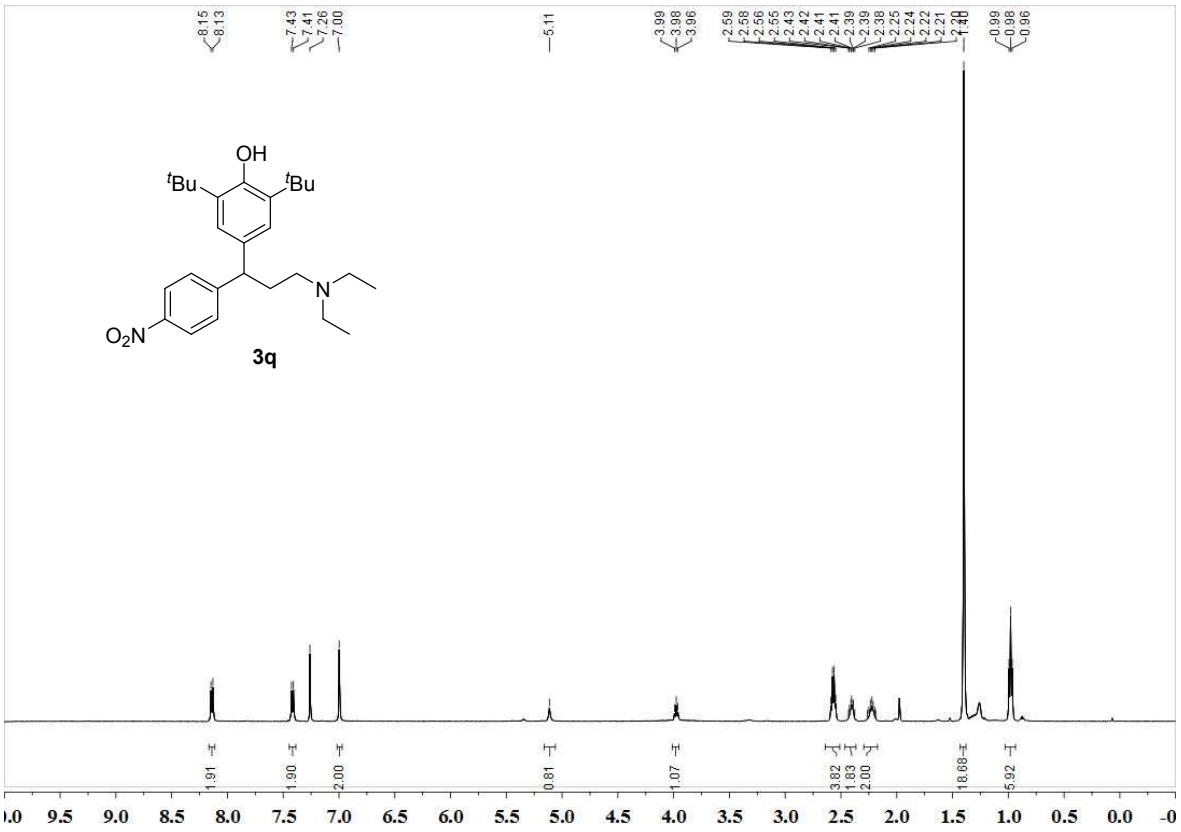
134.93
131.36
129.53
124.03
119.56
77.21
77.00
76.79
51.05
48.74
46.96
34.35
33.24
30.30
11.65
OH
tBu
tBu
N
Br
3p
f1 (ppm)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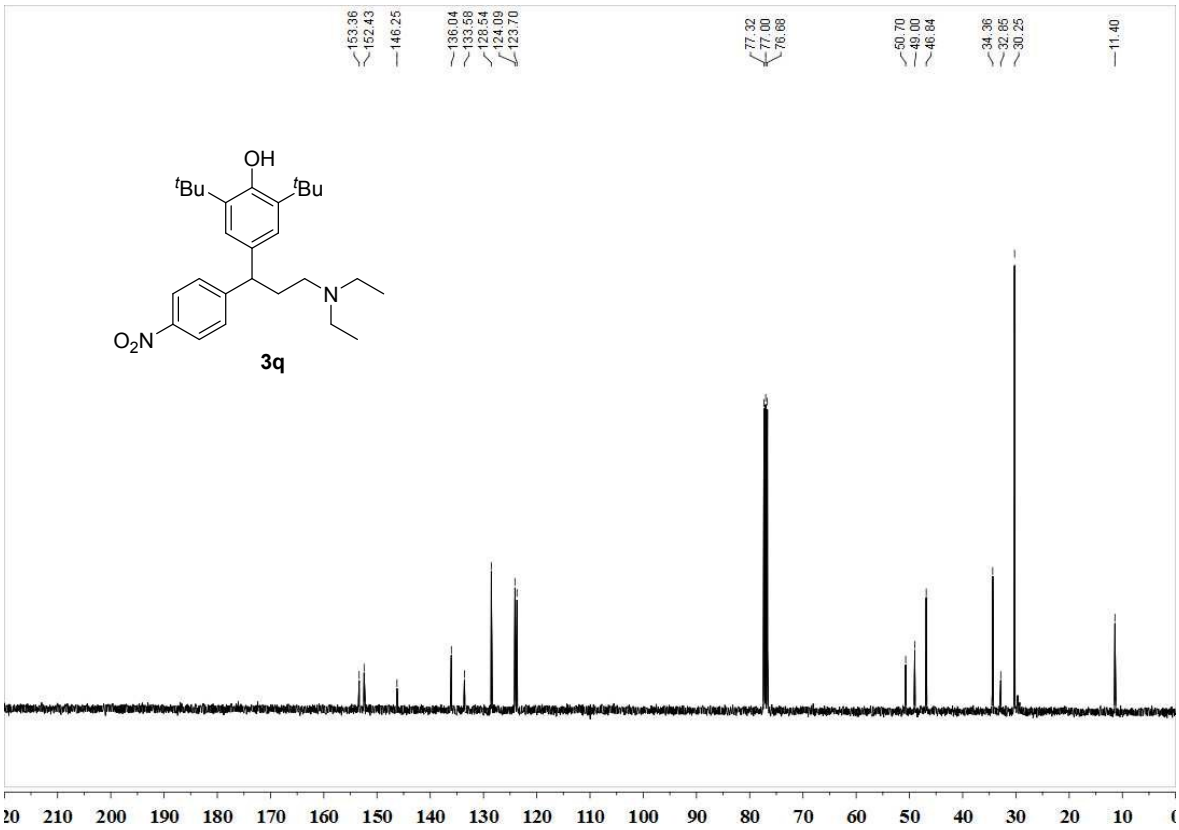
8.13
7.43
7.41
7.26
7.00
5.11
3.99
3.98
3.96
2.59
2.58
2.56
2.55
2.43
2.42
2.41
2.39
2.38
2.25
2.24
2.22
2.21
1.20
0.99
0.98
0.96
OH
tBu
tBu
N
O2N
3q
1.91
1.90
2.00
0.81
1.07
3.82
1.83
2.00
18.68
5.92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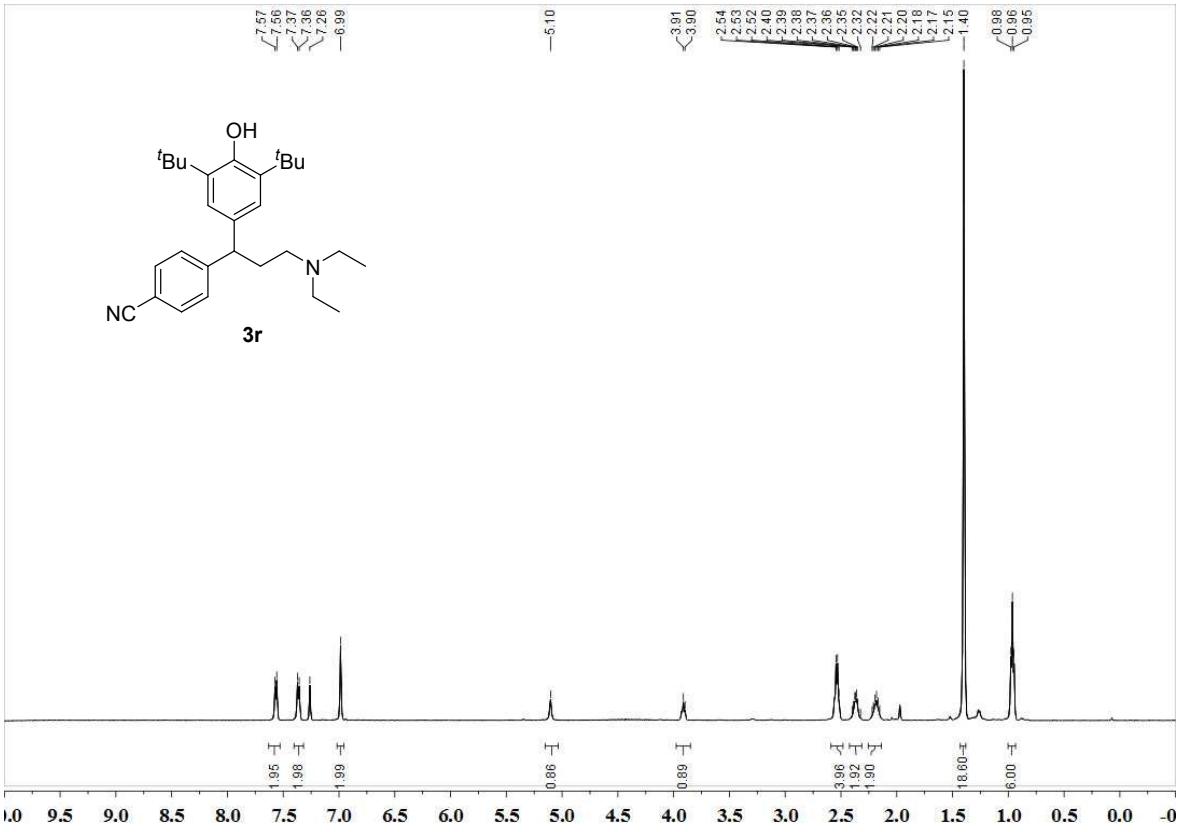
136.04
133.58
128.54
124.09
123.70
77.32
77.00
76.68
60.70
49.00
46.04
34.36
32.85
30.25
11.40
OH
tBu
tBu
N
O2N
3q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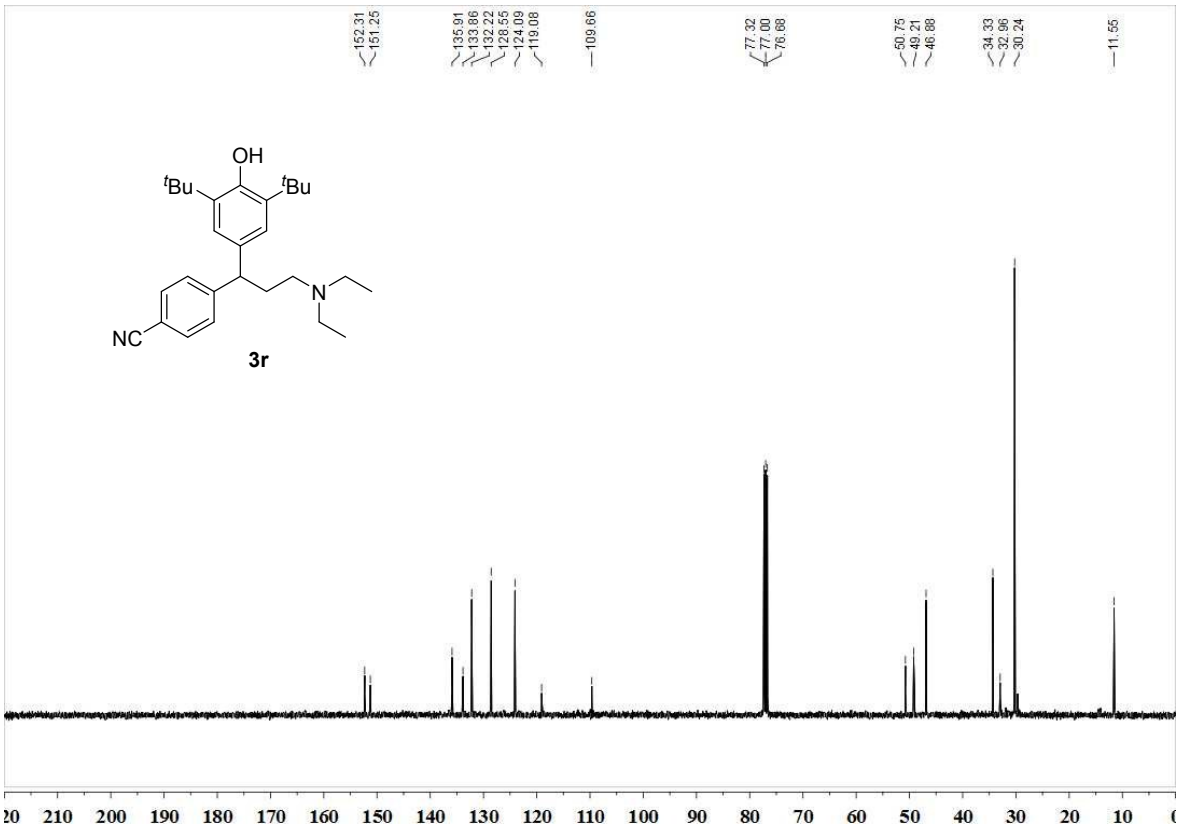
7.56
7.37
7.36
7.26
6.99
5.10
3.91
3.90
2.54
2.53
2.52
2.40
2.39
2.38
2.37
2.36
2.35
2.32
2.22
2.21
2.20
2.18
2.17
2.15
1.40
0.98
0.96
0.95
OH
tBu
tBu
N
NC
3r
1.95
1.98
1.99
0.86
0.89
3.96
1.92
1.90
18.60
6.00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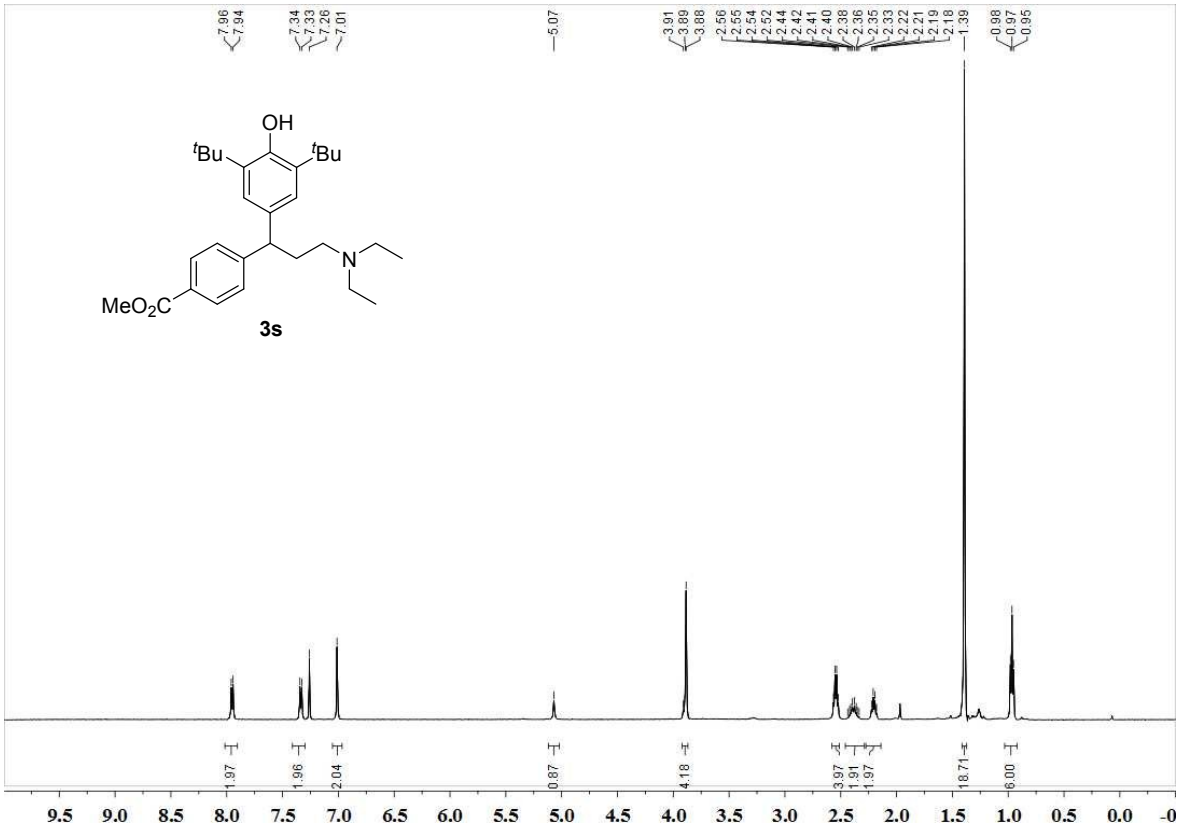
133.86
132.22
128.55
124.09
119.08
109.66
77.32
77.00
76.68
60.75
49.21
46.88
34.33
32.96
30.24
11.55
OH
tBu
tBu
N
NC
3r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7.94
7.34
7.33
7.26
7.01
5.07
3.91
3.89
3.88
2.56
2.55
2.54
2.52
2.44
2.42
2.41
2.40
2.38
2.36
2.35
2.33
2.22
2.21
2.19
2.18
1.39
0.98
0.97
0.95
OH
tBu
tBu
N
MeO2C
3s
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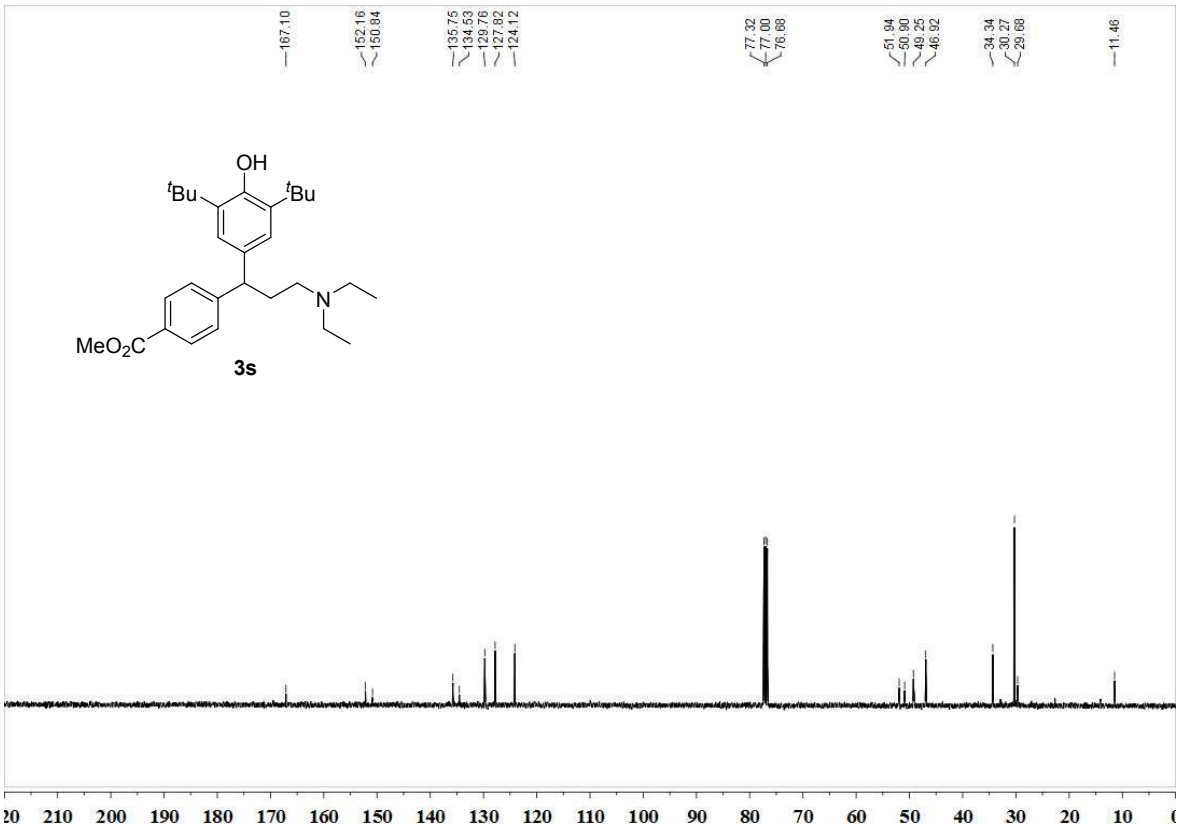
1.96
2.04
0.87
4.18
3.97
1.91
1.97
18.71
6.00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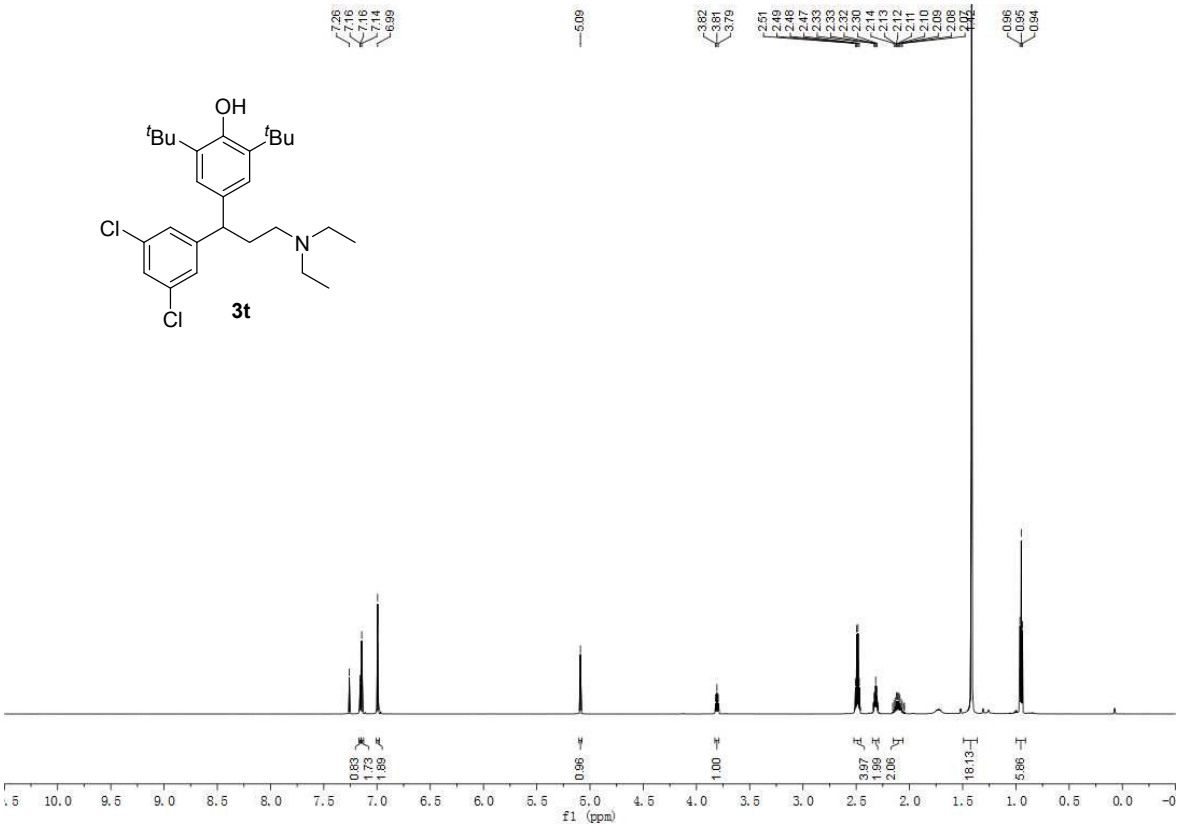
135.75
134.53
129.76
127.82
124.12
77.32
77.00
76.68
51.94
50.90
49.25
46.92
34.34
30.27
29.68
11.46
OH
tBu
tBu
N
MeO2C
3s


7.26
7.16
7.16
7.14
6.99
5.09
3.82
3.81
3.79
2.51
2.49
2.48
2.47
2.33
2.33
2.32
2.30
2.14
2.13
2.12
2.11
2.10
2.09
2.08
2.07
1.42
0.96
0.95
0.94
OH
tBu
tBu
Cl
Cl
N
3t
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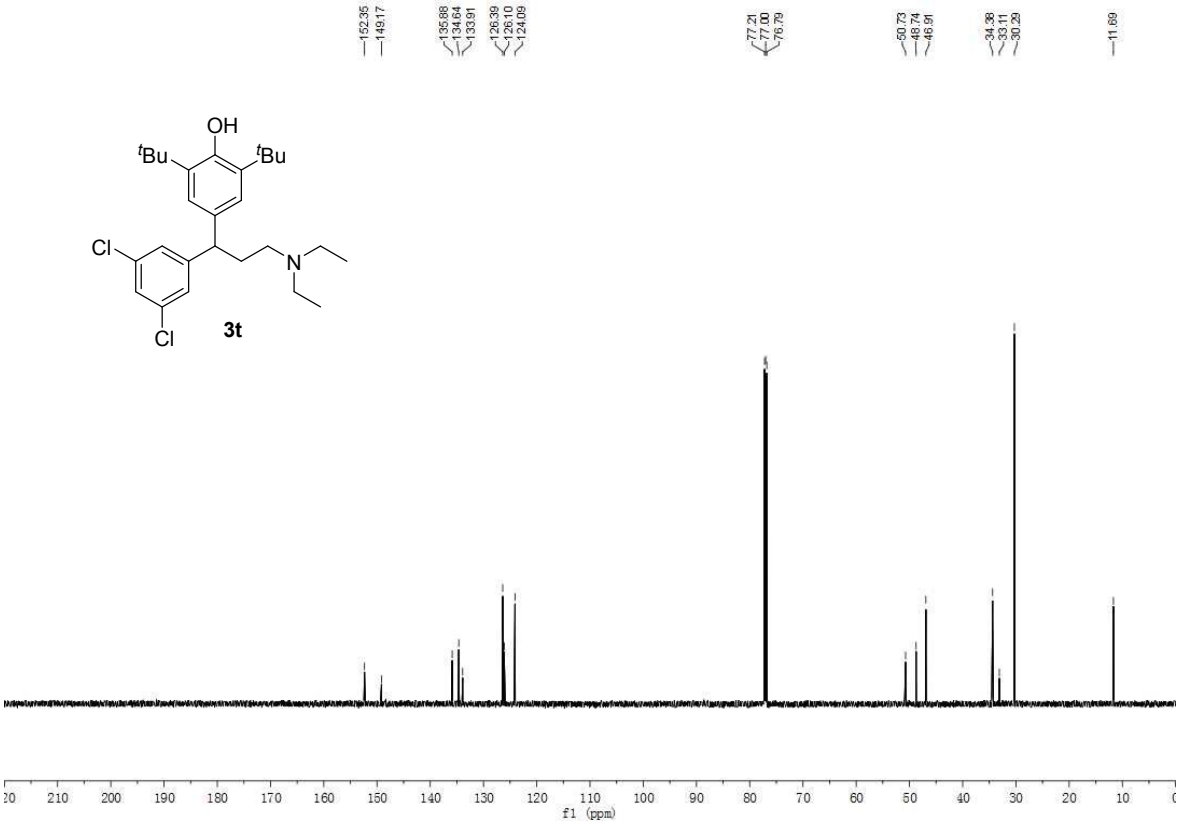
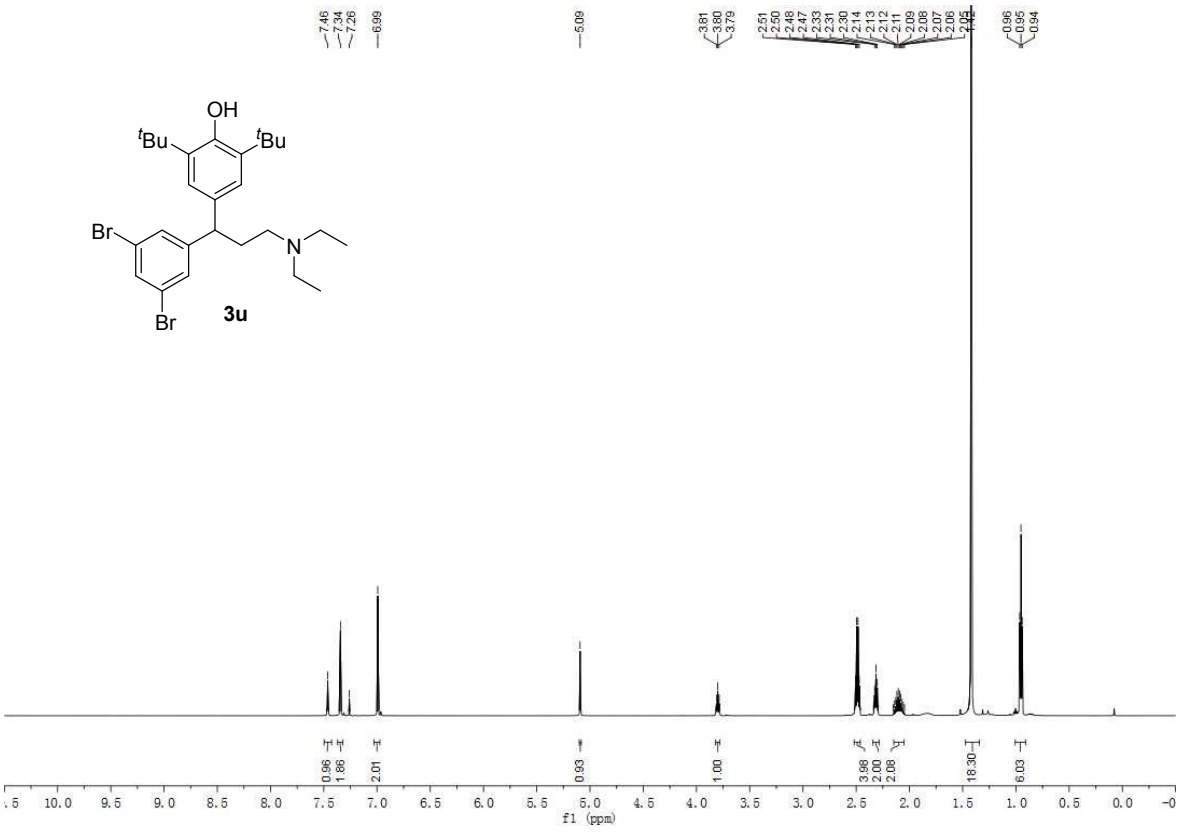
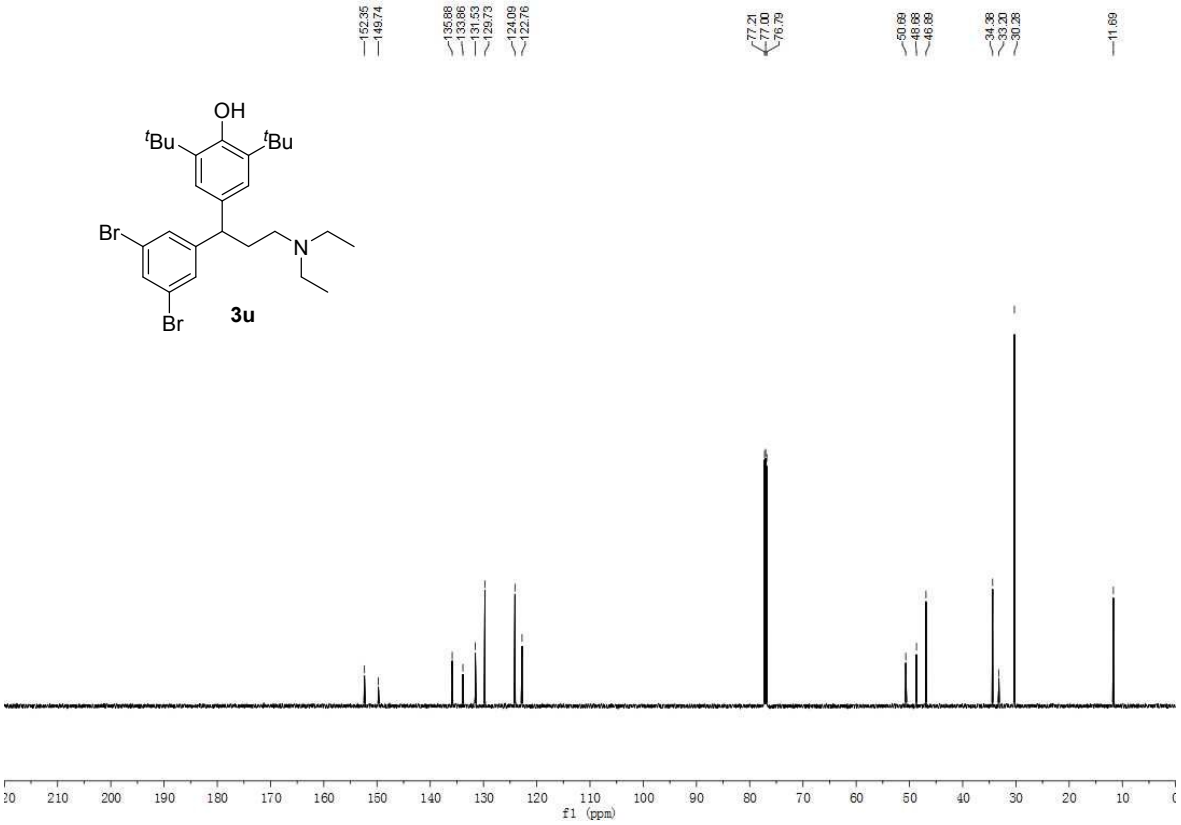
1.89
0.96
1.00
3.97
1.99
2.06
18.13
5.86
f1 (ppm)


OH
tBu
tBu
Cl
Cl
N
3t
152.35
149.17
135.88
134.64
133.91
126.39
126.10
124.09
77.21
77.00
76.79
60.73
48.74
46.91
34.38
33.11
30.29
11.69
f1 (ppm)


OH
tBu
tBu
Br
Br
N
3u
7.46
7.34
7.26
6.99
5.09
3.81
3.80
3.79
2.51
2.50
2.49
2.47
2.33
2.31
2.30
2.14
2.13
2.12
2.11
2.09
2.08
2.07
2.06
2.05
0.96
0.95
0.94
0.96
1.86
2.01
0.93
1.00
3.98
2.00
2.08
18.30
6.03
f1 (ppm)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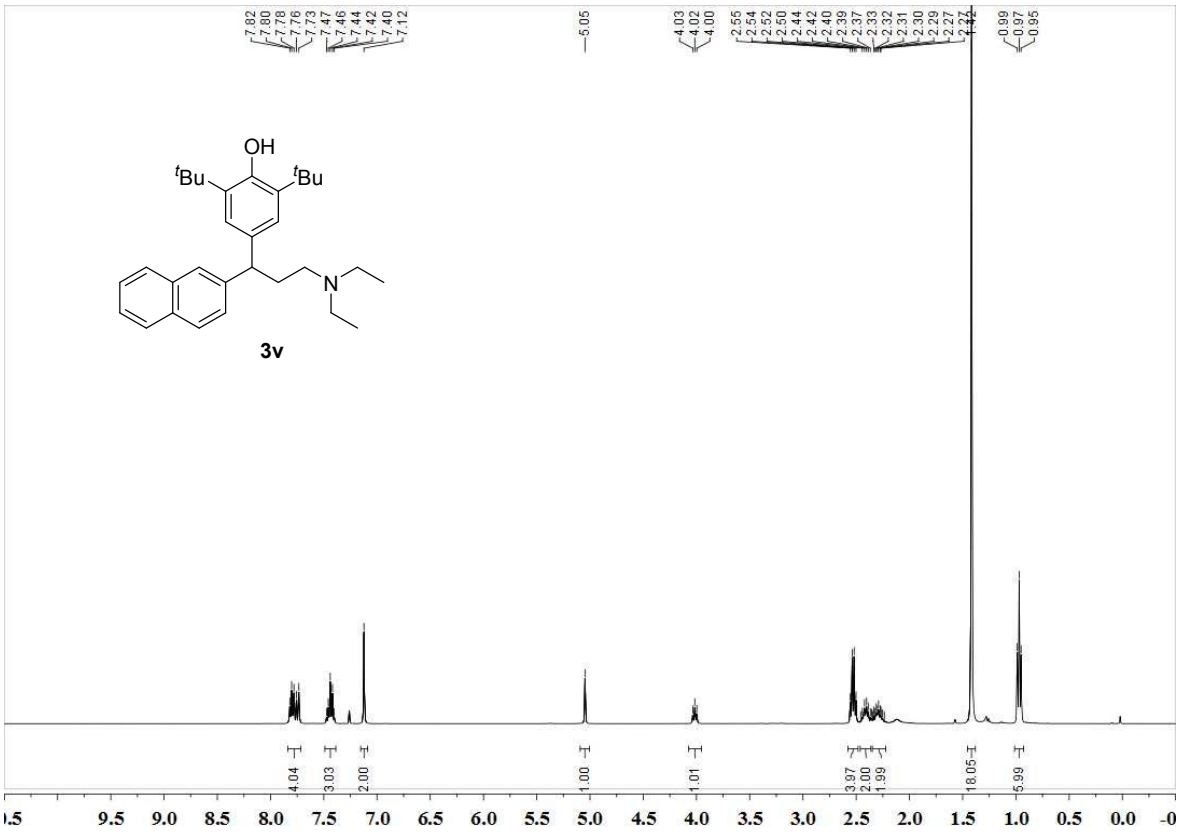
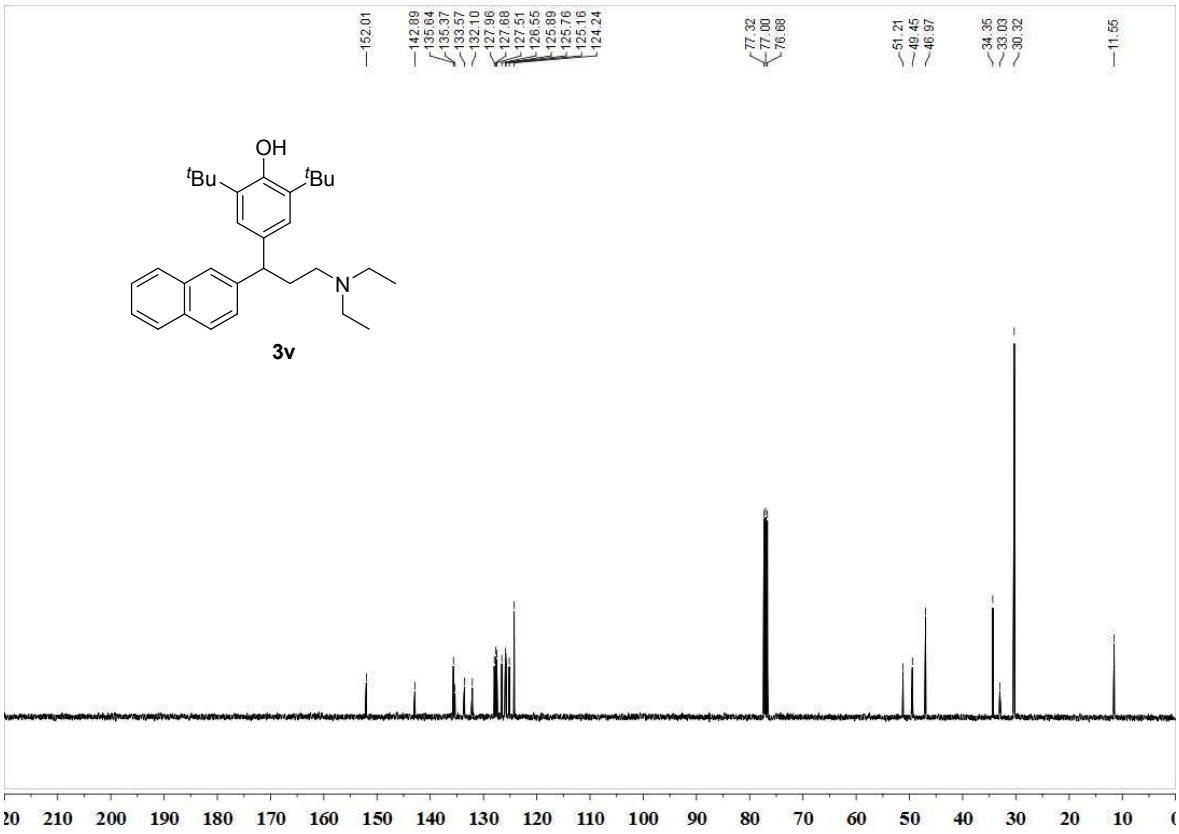
133.86
131.53
129.73
124.09
122.76
77.21
77.00
76.79
60.89
48.88
46.89
34.38
33.20
30.28
11.69
OH
tBu
tBu
Br
Br
N
3u
f1 (ppm)


7.82
7.80
7.78
7.76
7.73
7.47
7.46
7.44
7.42
7.40
7.12
5.05
4.03
4.02
4.00
2.55
2.54
2.52
2.50
2.44
2.42
2.40
2.39
2.37
2.33
2.32
2.31
2.30
2.29
2.27
0.99
0.97
0.95
OH
tBu
tBu
N
3v
4.04
3.03
2.00
1.00
1.01
3.97
2.00
1.99
18.05
5.99


OH
tBu
tBu
N
3v
152.01
142.89
135.64
135.37
133.57
132.10
127.96
127.68
127.51
126.55
125.89
125.76
125.16
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77.00
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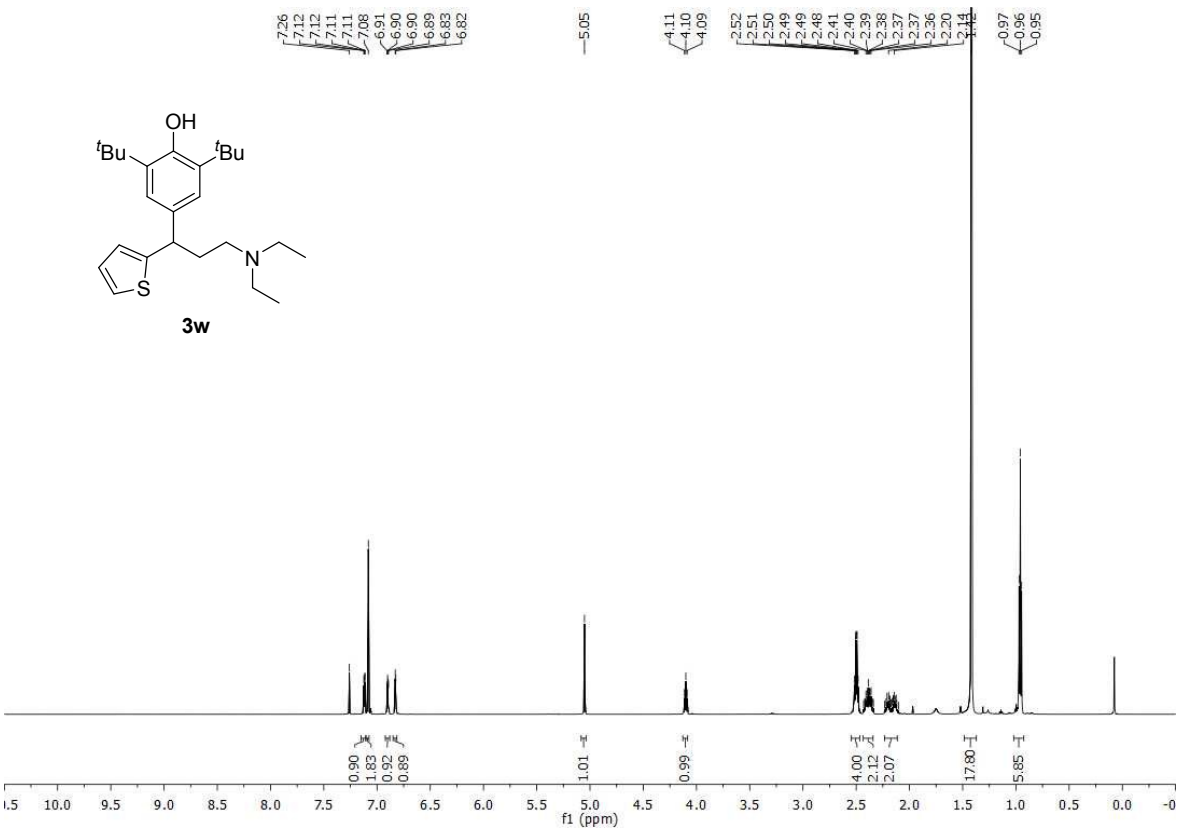
49.45
46.97
34.36
33.03
30.32
11.55


OH
tBu
tBu
N
S
3w
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7.12
7.12
7.11
7.11
7.08
6.91
6.90
6.90
6.89
6.83
6.82
5.05
4.11
4.10
4.09
2.52
2.51
2.50
2.49
2.49
2.48
2.41
2.40
2.39
2.38
2.37
2.37
2.26
2.20
2.14
0.97
0.96
0.95
0.90
1.83
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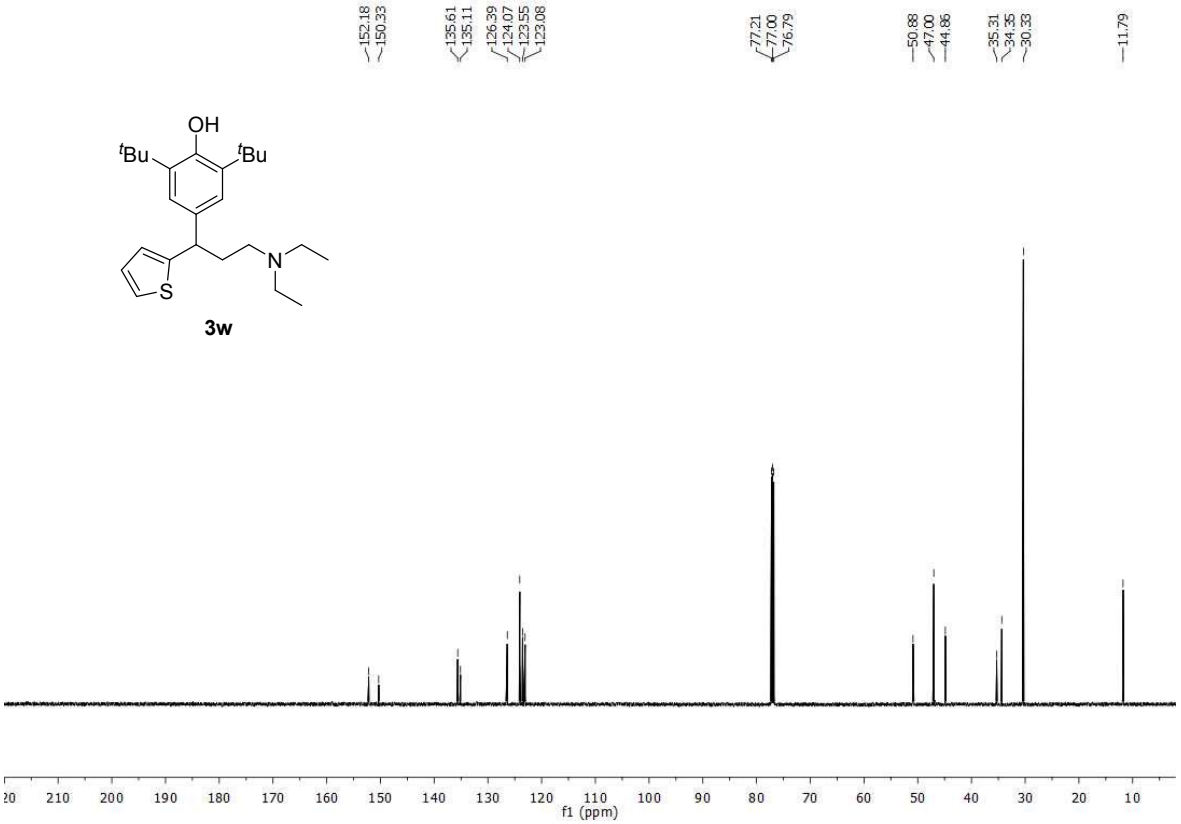
0.89
1.01
0.99
4.00
2.12
2.07
17.80
5.85
f1 (ppm)


152.18
150.33
135.61
135.11
126.39
124.07
123.55
123.08
77.21
77.00
76.79
50.88
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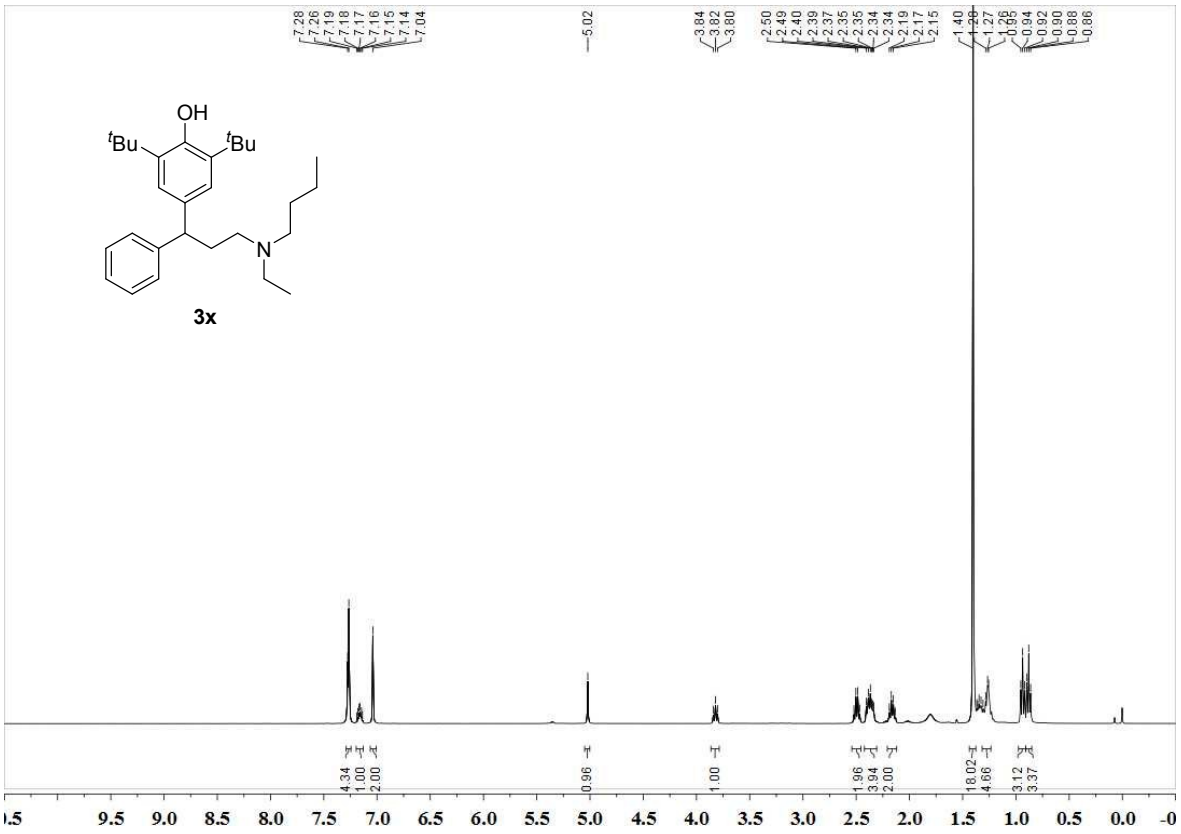
44.86
35.31
34.35
30.33
11.79
OH
tBu
tBu
N
S
3w
f1 (ppm)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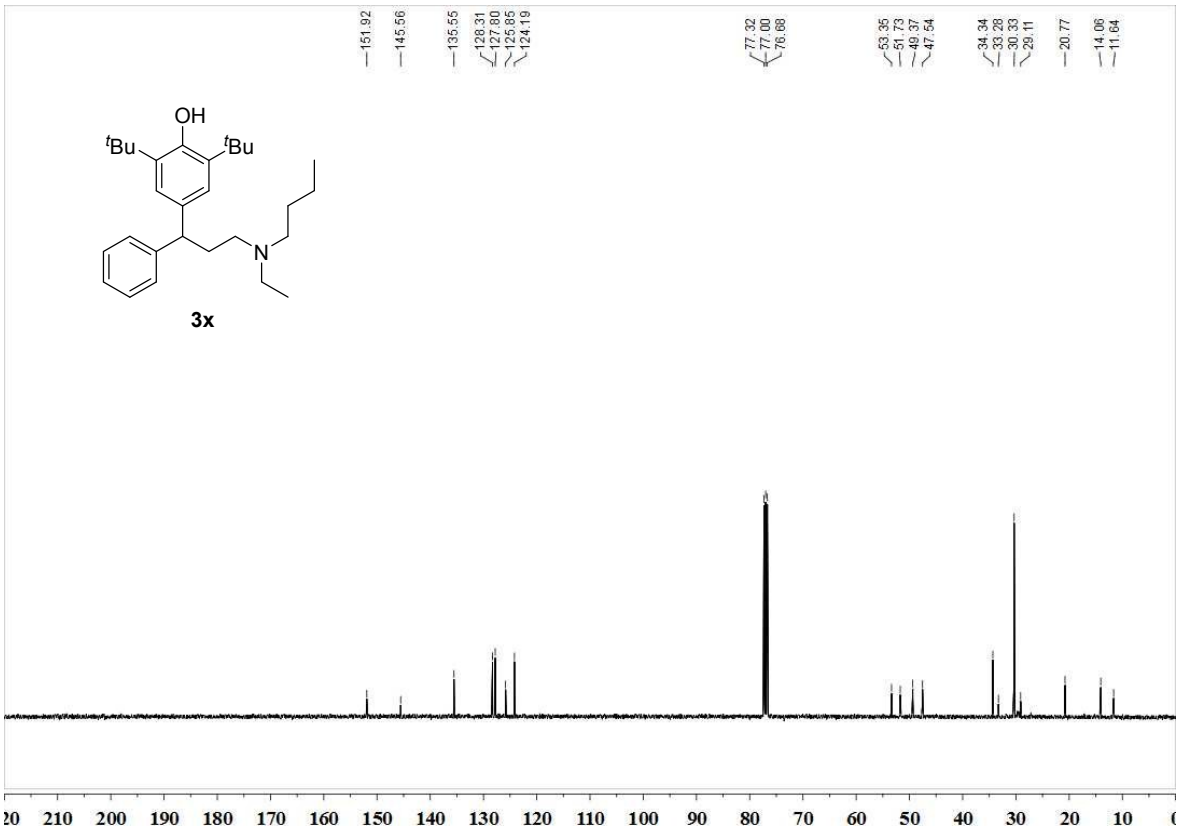
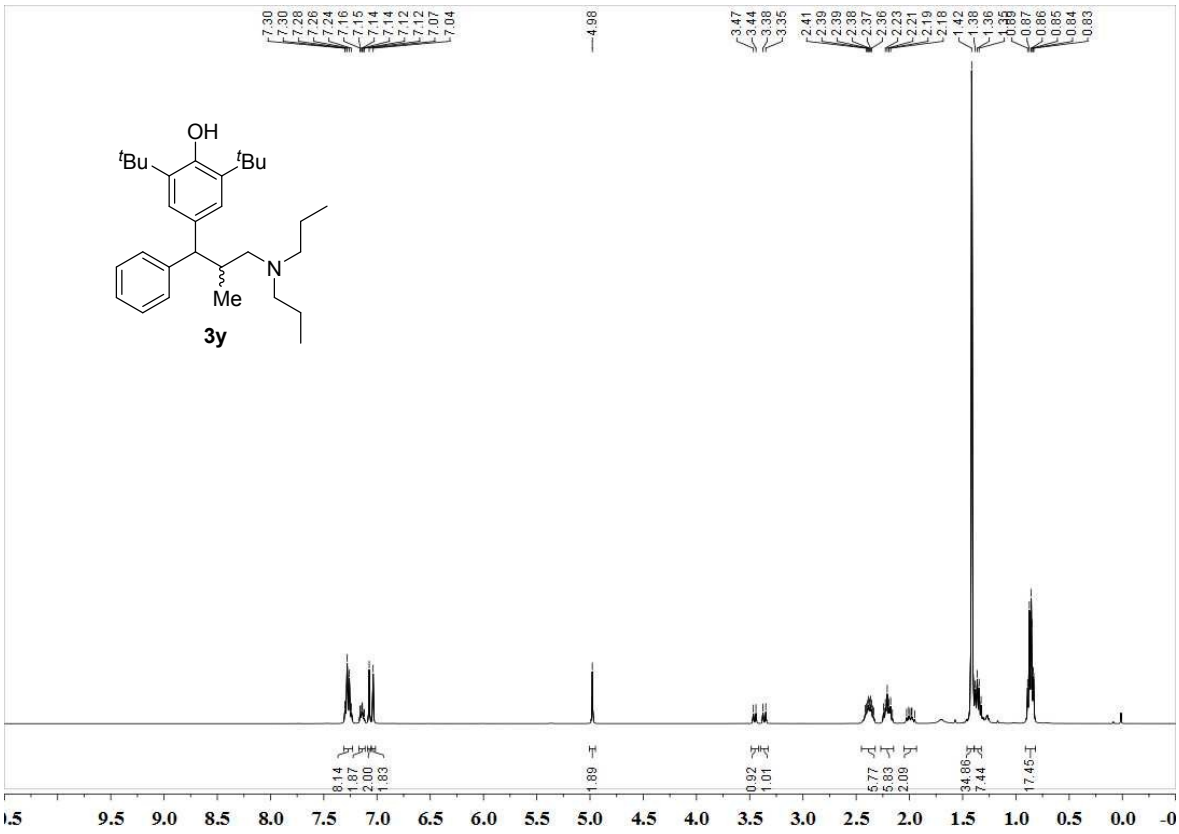
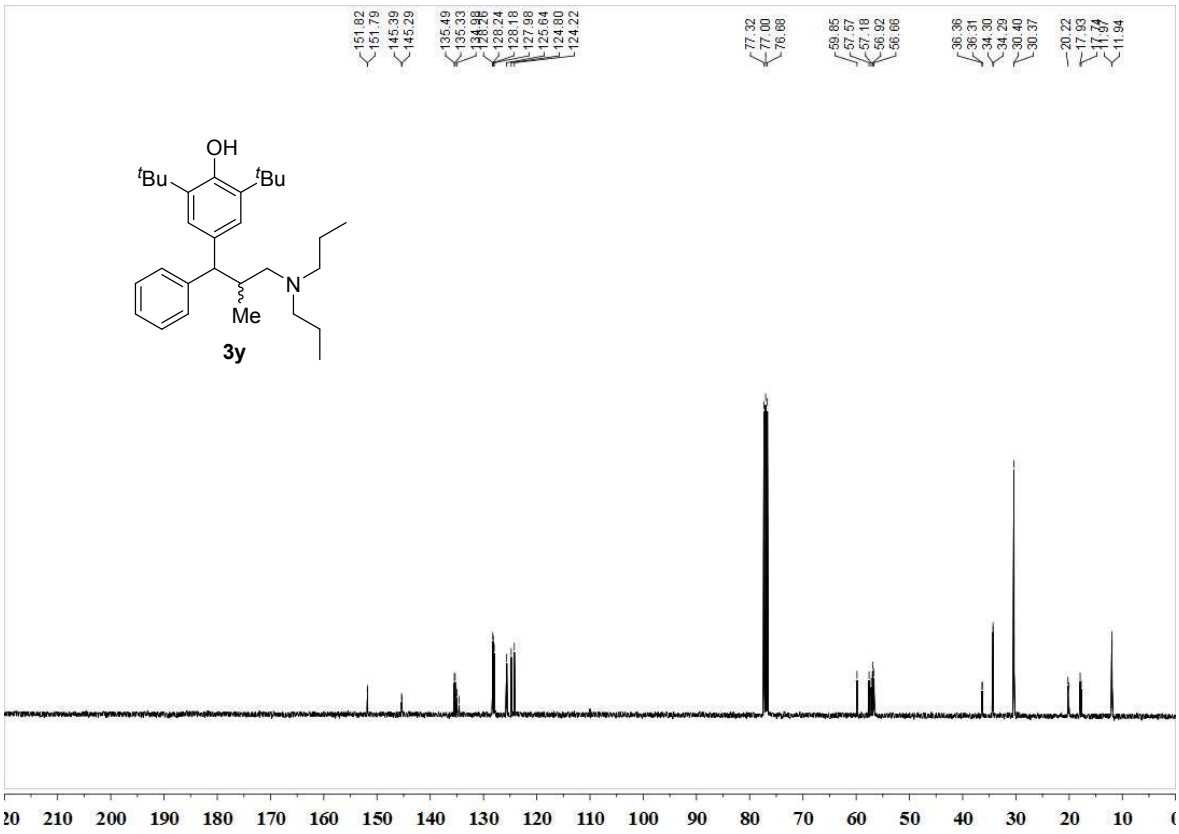
7.26
7.19
7.18
7.17
7.16
7.15
7.14
7.04
5.02
3.84
3.82
3.80
2.50
2.49
2.40
2.39
2.37
2.35
2.35
2.34
2.34
2.19
2.17
2.15
1.40
1.27
0.94
0.92
0.90
0.88
0.86
OH
tBu
tBu
N
3x
4.34
1.00
2.00
0.96
1.00
1.96
3.94
2.00
18.02
4.66
3.12
3.37


OH
tBu
tBu
N
3x
151.92
145.56
135.55
128.31
127.80
125.85
124.19
77.32
77.00
76.68
53.35
51.73
49.37
47.54
34.34
33.28
30.33
29.11
20.77
14.06
11.64


OH
tBu
tBu
N
Me
3y
7.30
7.30
7.28
7.26
7.24
7.16
7.15
7.14
7.14
7.12
7.12
7.07
7.04
4.98
3.47
3.44
3.38
3.35
2.41
2.39
2.39
2.38
2.37
2.36
2.23
2.21
2.19
2.18
1.42
1.38
1.36
0.87
0.86
0.85
0.84
0.83
8.14
1.87
2.00
1.83
1.89
0.92
1.01
5.77
5.63
2.09
34.86
7.44
17.45


151.82
151.79
145.39
145.29
135.49
135.33
128.24
128.18
127.98
125.64
124.80
124.22
77.32
77.00
76.68
59.85
57.57
57.18
56.92
56.66
36.36
36.31
34.30
34.29
30.40
30.37
20.22
17.93
11.94
OH
tBu
tBu
N
Me
3y
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10