Supporting Information

Preparation of Extremely Active Ethylene Tetramerization Catalyst $[iPrN(PAr_2)_2–CrCl_2]^+[B(C_6F_5)_4]^-$ (Ar = $–C_6H_4$-*p*-SiR_3)

Jung Hyun Lee [1], Jun Won Baek [1], Dong Geun Lee [1], Ji Hyeong Ko [1], Dong Geun Lee [2], Kye Sung Cho [2], Jin Woo Lee [2] and Bun Yeoul Lee [1,*]

[1]Department of Molecular Science and Technology, Ajou University, 206 Worldcup-ro, Yeongtong-gu, Suwon 16499, Korea

[2]Department of Base Chemical, Hanwha Total, 103 Dokgot 2-ro, Daesan-eup, Seosan-si 31900, Korea

(2-Ethylhexyl)$_3$SiH. 2-Ethylhexyl bromide (12.3 g, 58.3 mmol, purchased from Aldrich) dissolved in diethyl ether (28 mL) was added dropwise at room temperature for 30 min to a flask containing Mg powder (1.56 g, 64.2 mmol, purchased from Aldrich) in diethyl ether (30 mL). After the resulting solution was refluxed for 3 h, Mg metal added in excess was removed by Celite-aided filtration. The thus-prepared 2-ethyhexyl-MgBr was added dropwise to a solution of $HSiCl_3$ (1.44 g, 10.6 mmol, purchased from Aldrich) in THF (58 mL). Upon addition, heat was gently generated. The solution was stirred at room temperature for 24 h. After the solvent was removed using a vacuum line. The residue was dissolved in hexane (40 mL) and insoluble fractions were removed by Celite-aided filtration. Silica gel (4 g) was added to the filtrate. After stirring for 2 h, filtration was performed. Removal of solvent afforded a colorless oil. ^{1}H NMR analysis indicated that the product was contaminated with $CH_3(CH_2)_3C(H)(Et)CH_2–CH_2C(H)(Et)(CH_2)_3CH_3$. Pure (2-ethylhexyl)$_3$SiH was isolated via vacuum distillation at 60 °C (2.44 g, 58%). ^{1}H NMR (600 MHz, C_6D_6): δ 4.26 (septet, J = 3.6 Hz ,1H, SiH), 1.59 (septet, J = 6.6 Hz, 3H, $SiCH_2CH$), 1.49-1.38 (12H, CH_2), 1.38-1.30 (12H, CH_2), 0.95 (t, J = 7.2 Hz, 18H, CH_3), 0.76 (ddd, J = 15, 6.6, 3.6 Hz, 3H, $SiCH_2$), 0.73 (ddd, J = 15, 6.6, 3.6 Hz, 3H, $SiCH_2$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 36.5, 36.1, 29.4, 23.5, 18.0, 14.5, 11.2 ppm.

(3,7-Dimethyloctyl)$_3$SiH. It was prepared by the same procedure and experimental conditions as those employed for (2-ethylhexyl)$_3$SiH, using 3,7-dimethyloctyl-MgBr (65 mL, 1.05 M in diethyl ether, 68.2 mmol, purchased from Aldrich). Light yellow oil was obtained (7.27 g, 94 %). ^{1}H NMR (600 MHz, C_6D_6): δ 4.13 (septet, J = 3.6 Hz, 1H, SiH), 1.54 (m, 6H), 1.49-1.26 (15H, CH_2), 1.26-1.11 (9H), 0.97 (d, J = 6.6 Hz, 9H), 0.92 (dd, J = 7.2, 1.8 Hz, 18H) , 0.83-0.74 (m, 3H), 0.74-0.66 (m, 3H) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 39.8, 37.2, 36.0, 32.2, 28.4, 25.4, 23.0, 22.9, 19.6, 8.6 ppm.

(2-Ethylhexyl)$_3$SiCl. It was prepared by the same procedure and experimental conditions as those employed for (1-octyl)$_3$SiCl, using (2-ethylhexyl)$_3$SiH (1.40 g, 3.80 mmol). A yellow oil was obtained (1.40 g, 92 %). ^{1}H NMR (600 MHz, C_6D_6): δ 1.75 (septet, J = 6.6 Hz, 3H, $SiCH_2CH$), 1.44 (quintet, J = 6.6 Hz, 6H, CH_2), 1.40 (q, J = 6.6 Hz, 6H, CH_2), 1.36-1.26 (12H, CH_2), 0.96 (dd, J = 15, 6.6 Hz,

3H, $SiCH_2$), 0.95 (dd, J = 15, 6.6 Hz, 3H, $SiCH_2$), 0.94 (t, J = 6.6 Hz, 9H, CH_3), 0.91 (t, J = 7.8 Hz, 9H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 36.0, 35.3, 29.2, 29.0, 23.5, 23.1, 14.4, 10.9 ppm.

(3,7-Dimethyloctyl)$_3$SiCl. It was prepared by the same procedure and experimental conditions as those employed for (1-octyl)$_3$SiCl, using (3,7-dimethyloctyl)$_3$SiH (3.00 g, 6.63 mmol). A yellow oil is obtained. (3.00 g, 93 %). ^1H NMR (600 MHz, C_6D_6): δ 1.59-1.48 (m, 6H), 1.43-1.23 (15H, CH_2), 1.22-1.08 (9H), 0.917 (d, J = 6 Hz, 30H), 0.87-0.78 (br, 3H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 39.9, 39.8, 37.5, 37.0, 36.3, 35.7, 31.0, 30.4, 28.5, 25.5, 25.3, 23.0, 23.0, 22.9, 22.9, 19.7, 19.5, 13.4, 13.1 ppm.

BrC_6H_4-*p*-Si(1-hexyl)$_3$. It was prepared by the same procedure and experimental conditions as those employed for BrC_6H_4-*p*-Si(1-octyl)$_3$, using (1-hexyl)$_3$SiCl (0.218 g, 0.682 mmol, purchased from TCI), A colorless oil was obtained (0.280 g, 94%). ^1H NMR (600 MHz, C_6D_6): δ 7.41 (d, J = 7.8 Hz, 2H, C_6H_4), 7.21 (d, J = 8.4 Hz, 2H, C_6H_4), 1.40-1.32 (12H, CH_2), 1.32-1.23 (12H, CH_2), 0.91 (t, J= 7.2 Hz, 9H, CH_3), 0.81-0.76 (br, 6H, $SiCH_2$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 137.0, 136.1, 131.3, 124.1, 33.9, 31.9, 24.2, 23.1, 14.6, 12.7 ppm.

BrC_6H_4-*p*-Si(2-ethylhexyl)$_3$. It was prepared by the same procedure and experimental conditions as those employed for BrC_6H_4-*p*-Si(1-octyl)$_3$, using (2-ethylhexyl)$_3$SiCl (0.700 g, 1.74 mmol). The product was purified via column chromatography on silica gel eluting with hexane. A colorless oil was obtained (0.543 g, 60 %). ^1H NMR (600 MHz, C_6D_6): δ 7.40 (d, J = 8.4 Hz, 2H, C_6H_4), 7.30 (d, J = 8.4 Hz, 2H, C_6H_4), 1.63-1.58 (br, 3H, $SiCH_2CH$), 1.34 (m, CH_2, 6H), 1.31-1.17 (18H, CH_2), 0.95-0.84 (24H, $SiCH_2$, CH_3) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 138.8, 136.2, 131.1, 123.9, 36.0 (m), 36.0, 36.7, 29.2, 23.5, 19.1, 14.4, 10.9 ppm.

BrC_6H_4-*p*-Si(3,7-dimethyloctyl)$_3$. It was prepared by the same procedure and experimental conditions as those employed for BrC_6H_4-*p*-Si(1-octyl)$_3$, using (3,7-dimethyloctyl)$_3$SiCl (1.50 g, 3.08 mmol). A colorless oil was obtained (1.10 g, 61 %). ^1H NMR (600 MHz, C_6D_6): δ 7.43 (d, J = 8.4 Hz, 2H, C_6H_4), 7.26 (d, J = 8.4 Hz, 2H, C_6H_4), 1.53 (septet, J = 6.6 Hz, 3H), 1.49-1.21 (18H), 1.21-1.10

(m, 9H), 0.96 (d, J = 6 Hz, 9H), 0.92 (d, J = 6.6 Hz, 18H), 0.90 (td, J = 13.2, 4.2 Hz, 3H), 0.82 (td, J = 13.2, 4.2 Hz, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 136.9, 136.1, 131.5, 124.2, 39.8, 37.0, 36.1, 31.1, 28.4, 25.4, 23.0, 22.9, 19.6, 9.3 ppm.

$Et_2NP[C_6H_4$-*p*-Si(1-hexyl)$_3]_2$. It was prepared by the same procedure and experimental conditions as those employed for $Et_2NP[C_6H_4$-*p*-Si(1-octyl)$_3]_2$, using BrC_6H_4-*p*-Si(1-hexyl)$_3$ (0.197 g, 0.447 mmol). A light yellow oil was obtained (0.146 g, 79 %). ^{1}H NMR (600 MHz, C_6D_6): δ 7.64 (t, $^{3}J_{P\text{-}H}$ = 7.8 Hz, 4H, C_6H_4), 7.57 (d, J = 6.6 Hz, 4H, C_6H_4), 3.09 (q, J = 6.6 Hz, 2H, NCH_2CH_3), 3.07 (q, J = 6.6 Hz, 2H, NCH_2CH_3), 1.45 (m, 12H, CH_2), 1.37 (quintet, J = 7.8 Hz, 12H, CH_2), 1.28 (m, 24H, CH_2), 0.91-0.88 (br, 12H, $SiCH_2$), 0.90 (t, J =7.2 Hz, 18H, CH_3), 0.89 (t, J = 7.8 Hz, 6H, NCH_2CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 141.9 (d, $^{1}J_{P\text{-}C}$ = 15.8 Hz), 138.4, 134.3 (d, $^{3}J_{P\text{-}C}$ = 5.7 Hz), 131.8 (d, $^{2}J_{P\text{-}C}$ = 18.6 Hz), 44.9 (d, $^{2}J_{P\text{-}C}$ = 15.9 Hz), 34.0, 31.9, 24.4, 23.1, 14.7 (d, $^{3}J_{P\text{-}C}$= 2.85 Hz) 14.4, 13.0 ppm. ^{31}P (243 MHz, C_6D_6): δ 62.0 ppm.

$Et_2NP[C_6H_4$-*p*-Si(2-ethylhexyl)$_3]_2$. It was prepared by the same procedure and experimental conditions as those employed for $Et_2NP[C_6H_4$-*p*-Si(1-octyl)$_3]_2$, using BrC_6H_4-*p*-Si(2-ethylhexyl)$_3$ (0.457 g, 0.872 mmol). Light yellow oil was obtained (0.327 g, 72 %). ^{1}H NMR (600 MHz, C_6D_6): δ 7.67 (d, J = 7.2 Hz, 4H, C_6H_4), 7.63 (t, $^{3}J_{P\text{-}H}$ = 7.2 Hz, 4H, C_6H_4), 3.13 (q, J = 6.6 Hz, 2H, NCH_2CH_3), 3.12 (q, J = 6.6 Hz, 2H, NCH_2CH_3), 1.75-1.62 (br, 6H, $SiCH_2CH$), 1.52-1.19 (br, 48H, CH_2), 1.04 (m, 12H, $SiCH_2$), 0.92 (m, 42H, CH_3, NCH_2CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 141.7 (d, $^{1}J_{P\text{-}C}$ = 15.8 Hz), 140.0, 134.4 (d, $^{3}J_{P\text{-}C}$ = 5.9 Hz), 131.6 (d, $^{2}J_{P\text{-}C}$ = 18.8 Hz), 44.9 (d, $^{2}J_{P\text{-}C}$ = 14.4 Hz), 36.1 (br) 35.8, 29.2, 23.5, 19.2 (t, J = 12.9 Hz), 14.7 (d, $^{3}J_{P\text{-}C}$ = 2.9 Hz), 14.8, 11.0 ppm. ^{31}P NMR (243 MHz, C_6D_6): δ 61.5 ppm.

$Et_2NP[C_6H_4$-*p*-Si(3,7-dimethyloctyl)$_3]_2$. It was prepared by the same procedure and experimental conditions as those employed for $Et_2NP[C_6H_4$-*p*-Si(1-octyl)$_3]_2$, using BrC_6H_4-*p*-Si(3,7-dimethyloctyl)$_3$ (0.960 g, 1.58 mmol). Light yellow oil was obtained (0.705 g, 77 %). ^{1}H NMR (600 MHz, C_6D_6): δ 7.63 (t, $^{3}J_{P\text{-}H}$ = 7.2 Hz, 4H, C_6H_4), 7.61 (d, J = 6 Hz, 4H, C_6H_4), 3.09 (q, J = 7.2 Hz,

2H, NCH_2CH$_3$), 3.07 (q, J= 7.2 Hz, 2H, NCH_2CH$_3$), 1.55 (m, 12H), 1.49-1.24 (30H), 1.23-1.12 (18H), 1.07-0.95 (br, 6H), 0.97 (d, J = 6.0 Hz, 18H), 0.94-0.90 (6H), 0.92 (d, J = 6.6 Hz, 36H), 0.88 (t, J = 6.6 Hz, 6H, NCH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 141.9 (d, $^1J_{P\text{-}C}$ = 15.9 Hz), 138.2, 134.3 (d, $^3J_{P\text{-}C}$ = 5.7 Hz), 131.9 (d, $^2J_{P\text{-}C}$ = 18.8 Hz), 44.9 (d, $^2J_{P\text{-}C}$ = 15.8 Hz), 39.8, 37.0, 36.2, 31.2, 28.4, 25.4, 23.0, 22.9, 19.6, 14.8 (d, $^3J_{P\text{-}C}$ = 2.9 Hz), 9.5 ppm. ^{31}P (243 MHz, C_6D_6): δ 62.0 ppm.

ClP[C$_6$H$_4$-*p*-Si(1-hexyl)$_3$]$_2$. It was prepared by the same procedure and experimental conditions as those employed for ClP[C$_6$H$_4$-*p*-Si(1-octyl)$_3$]$_2$, using Et$_2$NP[C$_6$H$_4$-*p*-Si(1-hexyl)$_3$]$_2$ (0.146 g, 0.177 mmol). Light yellow oil was obtained quantitatively. ^{1}H NMR (600 MHz, C_6D_6): δ 7.67 (t, $^3J_{P\text{-}H}$ = 7.2 Hz, 4H, C$_6$H$_4$), 7.47 (d, J = 7.8 Hz, 4H, C$_6$H$_4$), 1.43-1.31 (24H, CH$_2$), 1.31-1.20 (24H, CH$_2$), 0.91 (t, J = 7.2 Hz, 18H), 0.85-0.79 (br, 12H, SiCH$_2$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 141.5, 139.9 (d, $^1J_{P\text{-}C}$= 33.0 Hz), 134.7 (d, $^3J_{P\text{-}C}$= 7.1 Hz), 131.5 (d, $^2J_{P\text{-}C}$= 24.5 Hz), 33.9, 31.9, 24.2, 23.1, 14.4, 12.8 ppm. ^{31}P (243 MHz, C_6D_6): δ 82.6 ppm.

ClP[C$_6$H$_4$-*p*-Si(2-ethylhexyl)$_3$]$_2$. It was prepared by the same procedure and experimental conditions as those employed for ClP[C$_6$H$_4$-*p*-Si(1-octyl)$_3$]$_2$, using Et$_2$NP[C$_6$H$_4$-*p*-Si(2-ethylhexyl)$_3$]$_2$ (0.327 g, 0.330 mmol). Light yellow oil was obtained quantitatively. ^{1}H NMR (600 MHz, C_6D_6): δ 7.64 (t, $^3J_{P\text{-}H}$ = 7.8 Hz, 4H, C$_6$H$_4$), 7.59 (d, J = 7.2 Hz, 4H, C$_6$H$_4$), 1.68-1.60 (br, 6H, SiCH$_2$CH), 1.36 (sextet, J = 7.2 Hz, 12H, CH$_2$), 1.33-1.20 (36H, CH$_2$), 0.99 (m, 12H, SiCH$_2$), 0.95-0.85 (36H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 143.2, 139.9 (d, $^1J_{P\text{-}C}$ = 31.5 Hz), 134.7 (d, $^3J_{P\text{-}C}$ = 5.7 Hz), 131.2 (d, $^2J_{P\text{-}C}$ = 23.0 Hz), 36.1 (m), 35.7, 29.2, 23.5, 19.1 (m), 14.5, 11.0 ppm. ^{31}P(243 MHz, C_6D_6): δ 82.3 ppm.

ClP[C$_6$H$_4$-*p*-Si(3,7-dimethyloctyl)$_3$]$_2$. It was prepared by the same procedure and experimental conditions as those employed for ClP[C$_6$H$_4$-*p*-Si(1-octyl)$_3$]$_2$, using Et$_2$NP[C$_6$H$_4$-*p*-Si(3,7-dimethyloctyl)$_3$]$_2$ (0.705 g, 0.608 mmol). Light yellow oil was obtained quantitatively. ^{1}H NMR (600 MHz, C_6D_6): δ 7.68 (t, $^3J_{P\text{-}H}$ = 7.8 Hz, 4H, C$_6$H$_4$), 7.52 (d, J = 6.6 Hz, 4H, C$_6$H$_4$), 1.54 (septet, J = 6.6 Hz, 6H), 1.50-1.22 (36H), 1.22- 1.10 (18H), 0.95 (d, J = 6 Hz, 18H), 0.93 (td, J = 13.2, 3 Hz, 6H),

0.92 (d, J = 6.6 Hz, 36H), 0.85 (td, J = 13.2, 3.0 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 141.3, 139.9 (d, $^1J_{P\text{-}C}$ = 33.2 Hz), 134.7 (d, $^3J_{P\text{-}C}$ = 5.7 Hz), 131.5 (d, $^2J_{P\text{-}C}$ = 23.0 Hz), 39.8, 37.0, 36.1, 31.1, 28.4, 25.4, 23.0, 22.9, 19.6, 9.3 (m) ppm. ^{31}P (243 MHz, C_6D_6): δ 82.5 ppm.

iPrN(PAr$_2$)$_2$ (Ar = –C$_6$H$_4$-*p*-Si(1-hexyl)$_3$). It was prepared by the same procedure and experimental conditions as those employed for iPrN(PAr$_2$)$_2$ (Ar = –C$_6$H$_4$-*p*-Si(1-octyl)$_3$), using ClP[C$_6$H$_4$-*p*-Si(1-hexyl)$_3$]$_2$ (0.139 g, 0.177 mmol). A light yellow viscous oil was obtained (0.132 g, 76 %). ^1H NMR (600 MHz, C_6D_6): δ 8.08-7.29 (br, 8H, C_6H_4), 7.52 (d, J = 7.2 Hz, 8H, C_6H_4), 3.87 (m, 1H, NC*H*CH$_3$) 1.45 (m, 24H, CH_2), 1.38 (m, 24H, CH_2), 1.30 (m, 48H, CH_2), 1.24 (d, J = 6 Hz, 6H, NCHC*H*$_3$), 0.93 (t, J = 6.6 Hz, 36H, CH_3), 0.91-0.86 (br, 24H, $SiCH_2$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 141.89-140.81 (br), 138.9, 134.2 (d, $^3J_{P\text{-}C}$ = 4.2 Hz), 133.2-132.3 (br), 52.5 (t, $^2J_{P\text{-}C}$ = 10.2 Hz), 34.0, 32.0, 24.5 (t, $^3J_{P\text{-}C}$ = 7.1 Hz), 24.3, 23.1, 14.4, 12.9 ppm. ^{31}P (243 MHz, C_6D_6): δ 55.1, 41.9 ppm.

iPrN(PAr$_2$)$_2$ (Ar = –C$_6$H$_4$-*p*-Si(2-ethylhexyl)$_3$). It was prepared by the same procedure and experimental conditions as those employed for iPrN(PAr$_2$)$_2$ (Ar = –C$_6$H$_4$-*p*-Si(1-octyl)$_3$), using ClP[C$_6$H$_4$-*p*-Si(2-ethylhexyl)$_3$]$_2$ (0.266 g, 0.279 mmol). A colorless viscous oil was obtained (0.220 g, 92 %). ^1H NMR (600 MHz, C_6D_6): δ 8.01-7.34 (br, 8H, C_6H_4), 7.68 (d, J = 4.8 Hz, 8H, C_6H_4), 3.97 (m, 1H, NC*H*CH$_3$), 1.77-1.66 (br, 12H, SiCH$_2$C*H*), 1.46-1.26 (96H, CH_2), 1.27 (d, J = 7.8 Hz, 6H, NCHC*H*$_3$), 1.13-1.03 (br, 24H, $SiCH_2$), 1.01-0.91 (72H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 141.9-140.8 (br), 140.7, 134.3 (d, $^3J_{P\text{-}C}$ = 4.4 Hz), 133.2-132.1 (br), 52.6 (t, $^2J_{P\text{-}C}$ = 10.1 Hz), 36.2 (d, J = 5.7 Hz), 35.8, 29.3 (m), 24.8-24.5 (br), 23.6, 19.2, 14.5, 11.0 ppm. ^{31}P (243 MHz, C_6D_6): δ 55.0, 43.1 ppm.

iPrN(PAr$_2$)$_2$ (Ar = –C$_6$H$_4$-*p*-Si(3,7-dimethyloctyl)$_3$). It was prepared by the same procedure and experimental conditions as those employed for iPrN(PAr$_2$)$_2$ (Ar = –C$_6$H$_4$-*p*-Si(1-octyl)$_3$), using ClP[C$_6$H$_4$-*p*-Si(3,7-dimethyloctyl)$_3$]$_2$ (0.400 g, 0.356 mmol). A light yellow viscous oil was obtained (0.355 g, 98 %). ^1H NMR (600 MHz, C_6D_6): δ 8.11- 7.30 (br, 8H, C_6H_4), 7.58 (d, J = 7.2 Hz, 8H, C_6H_4), 3.87 (m, 1H, NC*H*CH$_3$), 1.60-1.51 (m, 24H), 1.51-1.27 (54H), 1.27-1.11 (48H), 1.10-0.89 (br,

24H), 1.01 (d, J = 7.2 Hz, 36H), 0.94 (d, J = 6.6 Hz, 72H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 141.7-141.0 (br), 138.7, 134.2 ($^3J_{P\text{-}C}$ = 4.2 Hz), 133.4-132.4 (br), 52.5 (t, $^2J_{P\text{-}C}$ = 10.5 Hz), 39.8, 37.1, 36.2 (d, J = 3.0 Hz), 31.3, 28.4, 25.5, 24.6 (t, $^3J_{P\text{-}C}$ = 7.2 Hz), 23.0, 22.9, 19.7, 9.46 (d, J = 4.2 Hz)ppm. ^{31}P (243 MHz, C_6D_6): δ 56.5, 42.0 ppm.

$C_6H_{11}N(PAr_2)_2$ (Ar = –C_6H_4-*p*-Si(1-octyl)$_3$). It was prepared by the same procedure and experimental conditions as those employed for iPrN(PAr_2)$_2$ (Ar = –C_6H_4-*p*-Si(1-octyl)$_3$), using cyclohexylamine (0.0141 g, 0.143 mmol, purchased from Aldrich) instead of $iPrNH_2$ and ClP[C_6H_4-*p*-Si(1-octyl)$_3$]$_2$ (0.300 g, 0.314 mmol). A light yellow viscous oil was obtained (0.258 g, 93 %). ^1H NMR (600 MHz, C_6D_6): δ 8.03-7.29 (br, 8H, C_6H_4), 7.56 (s, 8H, C_6H_4), 3.48 (m, 1H, NCH), 2.22-2.10 (br, 2H, NCH_2), 1.61 (br, 3H, NCH_2), 1.55-1.46 (br, 24H, CH_2), 1.46-1.39 (quintet, J = 6.6 Hz, 24H, CH_2), 1.39-1.24 (96H, CH_2), 1.12-1.03 (br, 3H, NCH_2), 0.94 (t, J = 6.6 Hz, 36H, CH_3), 0.97-0.88 (br, 24H, $SiCH_2$), 0.82 (m, 2H, NCH_2) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 142.3-140.7 (br), 138.9, 134.2, 133.4-132.1 (br), 61.2 (m), 35.5 (t, $^3J_{P\text{-}C}$ = 7.2 Hz), 34.4, 32.4, 29.8, 29.8, 26.6, 26.1, 24.4, 23.2, 14.4, 13.0 ppm. ^{31}P (243 MHz, C_6D_6): δ 54.7, 46.3 ppm.

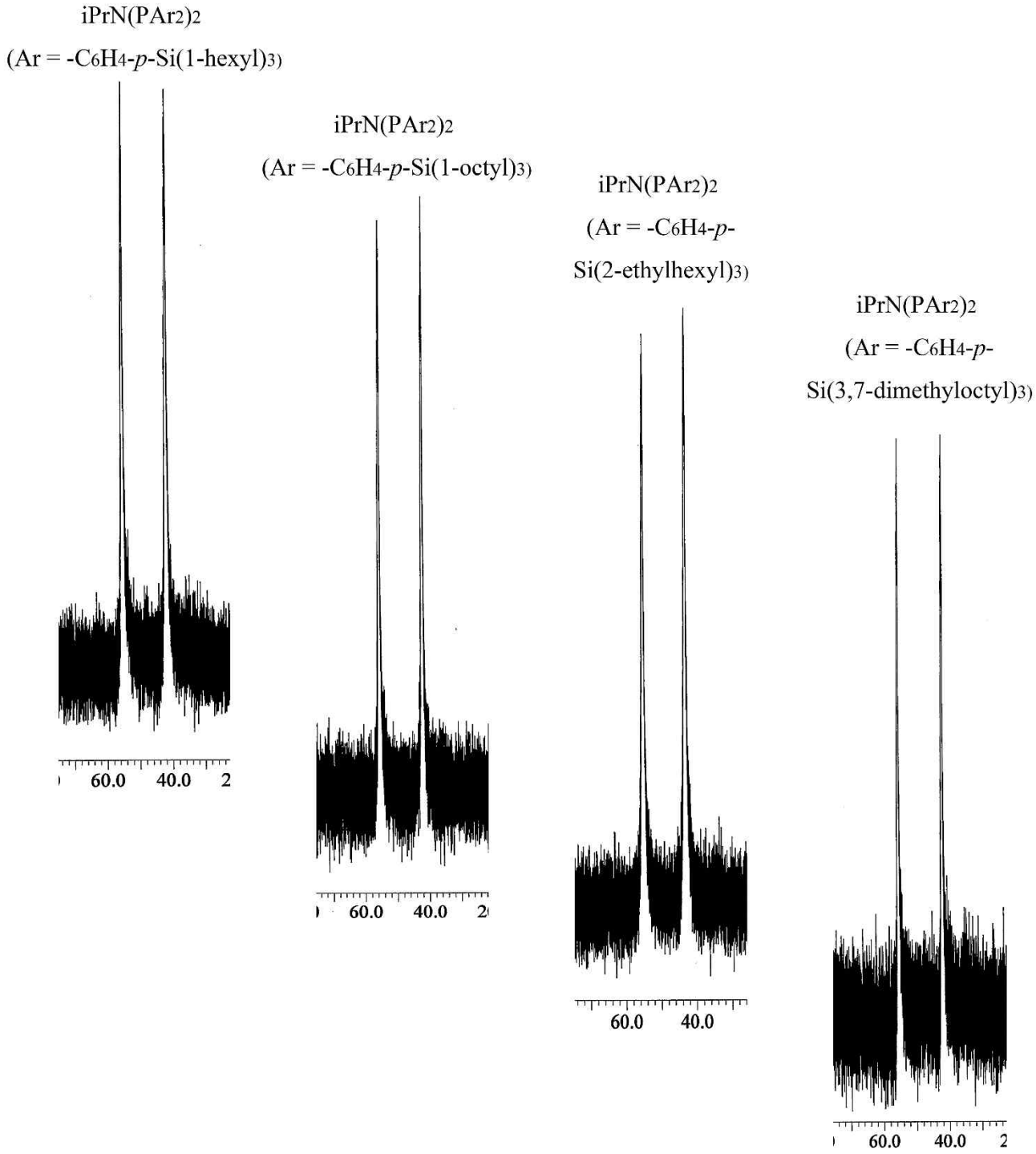
2-Et-6-Me-$C_6H_3N(PAr_2)_2$ (Ar = –C_6H_4-*p*-Si(nBu)$_3$). It was prepared by the same procedure and experimental conditions as those employed for iPrN(P[C_6H_4-*p*-Si(1-octyl)$_3$]$_2$)$_2$, using 2-methyl-6-ethylaniline (0.0520 g, 0.385 mmol, purchased from TCI) instead of $iPrNH_2$ and ClP[C_6H_4-*p*-Si(n-Bu)$_3$]$_2$ (0.524 g, 0.848 mmol). Light yellow oil was obtained (0.470 g, 94 %). ^1H NMR (600 MHz, C_6D_6): δ 7.82 (t, $^3J_{P\text{-}H}$ = 7.2 Hz, 4H, C_6H_4), 7.79 (t, , $^3J_{P\text{-}H}$ = 7.8 Hz, 4H, C_6H_4), 7.49 (d, J = 7.2 Hz, 4H, C_6H_4), 7.46 (d, J = 6.6Hz, 4H, C_6H_4), 7.10-7.07 (br, 2H), 6.97 (t, J = 5.4 Hz, 1H), 2.20 (q, J = 7.8 Hz, 2H, CH_2CH_3), 1.89 (s, 3H, CH_3), 1.41-1.31 (48H, CH_2), 0.91 (t, J = 6.6Hz, 36H, CH_3), 0.86 (t, J = 7.2Hz, 3H, CH_2CH_3), 0.84-0.78 (br, 24H, SiH_2) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 145.9 (t, $^3J_{P\text{-}C}$ = 5.85 Hz), 144.8, 140.6 (d, $^2J_{P\text{-}C}$ = 21.6 Hz), 140.0, 139.7, 139.1, 136.1, 134.6, 134.3 (dd, J = 24.5, 4.4 Hz), 134.1 (t, $^3J_{P\text{-}C}$ = 7.2 Hz), 131.3, 129.2, 127.1, 126.9, 27.2, 26.5, 25.6, 21.3, 15.3, 14.0, 12.5 ppm. ^{31}P (243 MHz, C_6D_6): 57.0 ppm.

iPrN(PPh$_2$)(PAr$_2$) (Ar = –C$_6$H$_4$-*p*-Si(1-decyl)$_3$). A solution of iPrNH$_2$ (0.0620 g, 1.05 mmol) in CH_2Cl_2 (0.25 mL) was added dropwise to a solution of ClP[C$_6$H$_4$-*p*-Si(1-decyl)$_3$]$_2$ (0.118 g, 0.105 mmol) in CH_2Cl_2 (0.50 mL) and the resulting solution was stirred overnight at room temperature. After the solvent was removed using a vacuum line, the residue was dissolved in hexane (2 mL). Insoluble fractions were removed by Celite-aided filtration. Volatiles in the filtrate were removed using a vacuum line to afford iPrN(H)P[C$_6$H$_4$-*p*-Si(1-decyl)$_3$]$_2$ as a colorless oil (0.0972 g, 81%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.60 (t, *J* = 7.2 Hz, 4H, C$_6$H$_4$), 7.57 (d, *J* = 6 Hz, 4H, C$_6$H$_4$), 3.26 (m, 1H, NC*H*CH$_3$), 1.63 (t, *J* = 6.6 Hz, 1H, NH), 1.47 (quintet, *J* = 7.8 Hz, 24H, CH_2), 1.39 (quintet, *J* = 7.2 Hz, 24H, CH_2), 1.34-1.21 (br, 48H, CH_2), 1.00 (d, *J* = 6 Hz, 6H, NCHC*H*$_3$), 0.92 (t, *J* = 7.2 Hz, 18H, CH_3), 0.95-0.89 (br, 12H, CH_2) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): 144.3 (d, $^1J_{P\text{-}C}$ = 12.9 Hz), 138.3, 134.4 (d, $^3J_{P\text{-}C}$ = 5.7 Hz), 131.0 (d, $^2J_{P\text{-}C}$ = 20.1 Hz), 48.9 (d, $^2J_{P\text{-}C}$ = 22.9 Hz), 34.3, 32.4, 29.8, 26.2 (d, $^3J_{P\text{-}C}$ = 7.2 Hz), 24.4, 23.1, 14.4, 13.0 ppm. ^{31}P (243 MHz, C_6D_6): 35.3 ppm. The resulting compound iPrN(H)P[C$_6$H$_4$-*p*-Si(1-decyl)$_3$]$_2$ (0.0891 g, 0.0778 mmol) was dissolved in CH_2Cl_2 (0.30 mL) and then Et_3N (0.0787 g, 0.778 mmol) and a solution of Ph_2PCl (0.0189 g, 0.0856 mmol) in CH_2Cl_2 (0.50 mL) were successively added. After stirring overnight at room temperature, all volatiles were removed using a vacuum line. Hexane (1.2 mL) was added to the residue and insoluble fractions were removed by Celite-aided filtration. Silica gel (~0.155 g) which had been treated beforehand with hexane/Et_3N (v/v, 50:1) was added to the filtrate. After stirring for 30 min, filtration was performed. Removal of solvent afforded a light yellow oil (0.0750 g, 73 %), which was used for the next step without further purification. NMR (600 MHz, C_6D_6): δ 7.98-7.28 (br, 4H), 7.53 (d, *J* = 6.6 Hz, 4H), 7.19-7.08 (br, 10H), 3.75 (m, 1H, NC*H*CH$_3$), 1.40 (m, 24H, CH_2), 1.33(quintet, *J* = 6.6 Hz, 24H, CH_2), 1.28-1.18 (48H, CH_2), 1.17 (d, *J* = 6.6 Hz, 6H, NCHC*H*$_3$), 0.96 (t, *J* = 6.6 Hz, 18H, CH_3), 0.95-0.91 (br, 12H, $SiCH_2$) ppm. ^{13}C{^{1}H}NMR (150 MHz, C_6D_6): δ 141.4 (d, $^1J_{P\text{-}C}$ = 18.6 Hz), 140.8 (d, $^1J_{P\text{-}C}$ = 13.1 Hz), 138.9, 134.3 (d, $^3J_{P\text{-}C}$ = 5.9 Hz), 133.4 (d, $^2J_{P\text{-}C}$ = 20.1 Hz), 132.8 (d, $^2J_{P\text{-}C}$ = 20.1 Hz), 128.8,

128.4 (d, $^{3}J_{P\text{-}C}$ = 7.2 Hz), 52.5 (t, $^{2}J_{P\text{-}C}$ = 14.4 Hz), 34.3, 32.4, 29.8, 29.7, 24.6 (t, $^{3}J_{P\text{-}C}$ = 5.7 Hz), 24.4, 23.2, 14.4, 12.9 ppm. ^{31}P (243 MHz, C_6D_6): 55.0, 43.3 ppm.

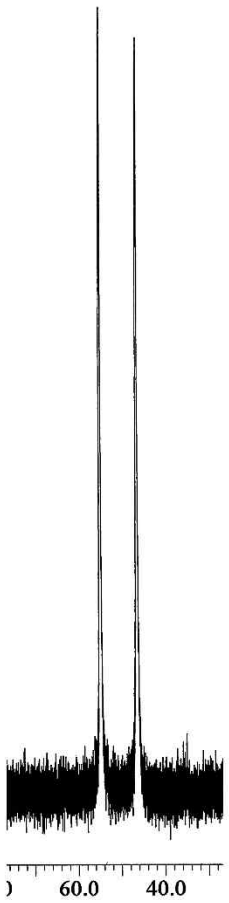
***Ortho*-$C_6H_4(PPh_2)(PAr_2)$ (Ar = –C_6H_4-*p*-Si(nBu)$_3$).** $BrC_6H_4P(C_6H_5)_2$ (0.339 g, 0.992 mmol, purchased from TCI) was dissolved in THF (5.6 mL) and cooled to −78 °C. nBuLi (0.40 mL, 2.48 M in hexane, 0.992 mmol) was added dropwise and the resulting solution was stirred for 1 h at −78 °C. $(nBu)_3SiCl$ (0.612 g, 0.992 mmol) dissolved in THF (3.0 mL) was added dropwise and the solution was allowed to warm to room temperature. After stirring for 2 h, the solvent was removed using a vacuum line. The residue was dissolved in hexane (15 mL) and insoluble fractions were removed by Celite-aided filtration. The product was purified by column chromatography on silica gel eluting with hexane/toluene (v/v, 10:1) (colorless oil, 0.524 g, 63 %). ^{1}H NMR (600 MHz, C_6D_6): 7.43 (t, *J* = 6.6 Hz, 4H), 7.37 (dd, *J* = 7.2, 1.2 Hz, 4H), 7.35 (m, 5H), 7.25 (dtd, *J* = 7.8, 3.6, 1.2 Hz, 1H), 7.04 (m, 6H), 6.93 (dtd, *J* = 17.4, 7.2, 1.2 Hz, 2H) , 1.35 (24H, CH_2), 0.89 (t, *J* = 7.8 Hz, 18H, CH_3), 0.83-0.75 (br, 12H, $SiCH_2$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 145.0 (d, $J_{P\text{-}C}$ = 5.9 Hz), 144.9 (d, $J_{P\text{-}C}$ = 5.7 Hz), 144.5 (d, $J_{P\text{-}C}$ = 5.7 Hz), 144.4 (d, $J_{P\text{-}C}$ = 5.9 Hz), 138.8 (d, $J_{P\text{-}C}$ = 11.1 Hz), 138.5, 138.3 (d, $J_{P\text{-}C}$ = 11.1 Hz), 135.0 (d, $J_{P\text{-}C}$ = 5.7 Hz), 134.5 (m), 133.7 (d, $J_{P\text{-}C}$ = 2.9 Hz), 133.6 (d, $J_{P\text{-}C}$ = 4.4 Hz) 129.5 (d, $J_{P\text{-}C}$ = 14.3 Hz), 128.7 (d, $J_{P\text{-}C}$ = 5.7 Hz), 128.6, 27.2, 26.5, 14.0, 12.6 ppm. ^{31}P (243 MHz, C_6D_6): −12.0 (d, *J* = 157 Hz), −12.9 (d, *J* = 157 Hz) ppm.

Figure S1. ^{31}P NMR spectra of bis(phosphine) ligands in C_6D_6.



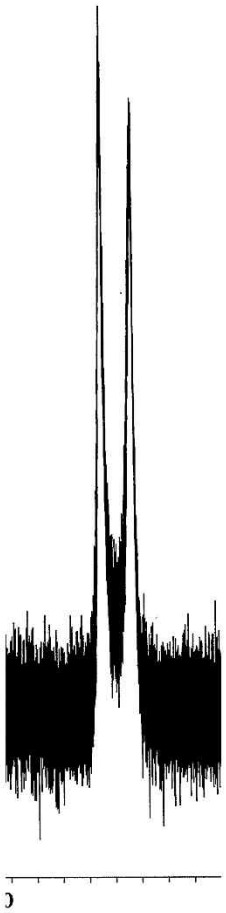
$C_6H_{11}(PAr_2)_2$

(Ar = -C_6H_4-*p*-Si(1-octyl)$_3$)



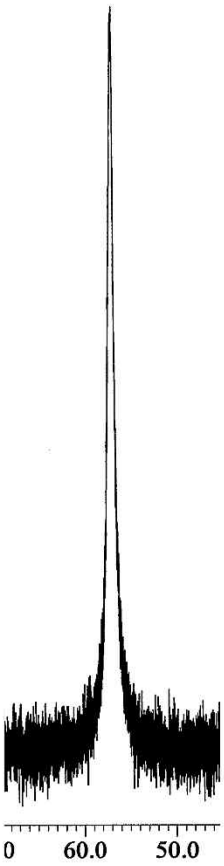
iPrN(PPh_2)(PAr_2)

(Ar = -C_6H_4-*p*-Si(1-decyl)$_3$).



2-Et-6-Me-$C_6H_3N(PAr_2)_2$

(Ar = -C_6H_4-*p*-Si(nBu)$_3$))



Ortho-$C_6H_4(PPh_2)(PAr_2)$

(Ar = -C_6H_4-*p*-Si(nBu)$_3$)

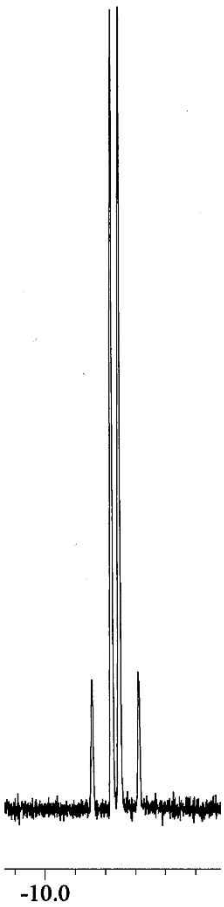


Figure S2. ^{31}P NMR spectra of $Et_2NP(C_6H_4\text{-}p\text{-}SiR_3)_2$ in C_6D_6.

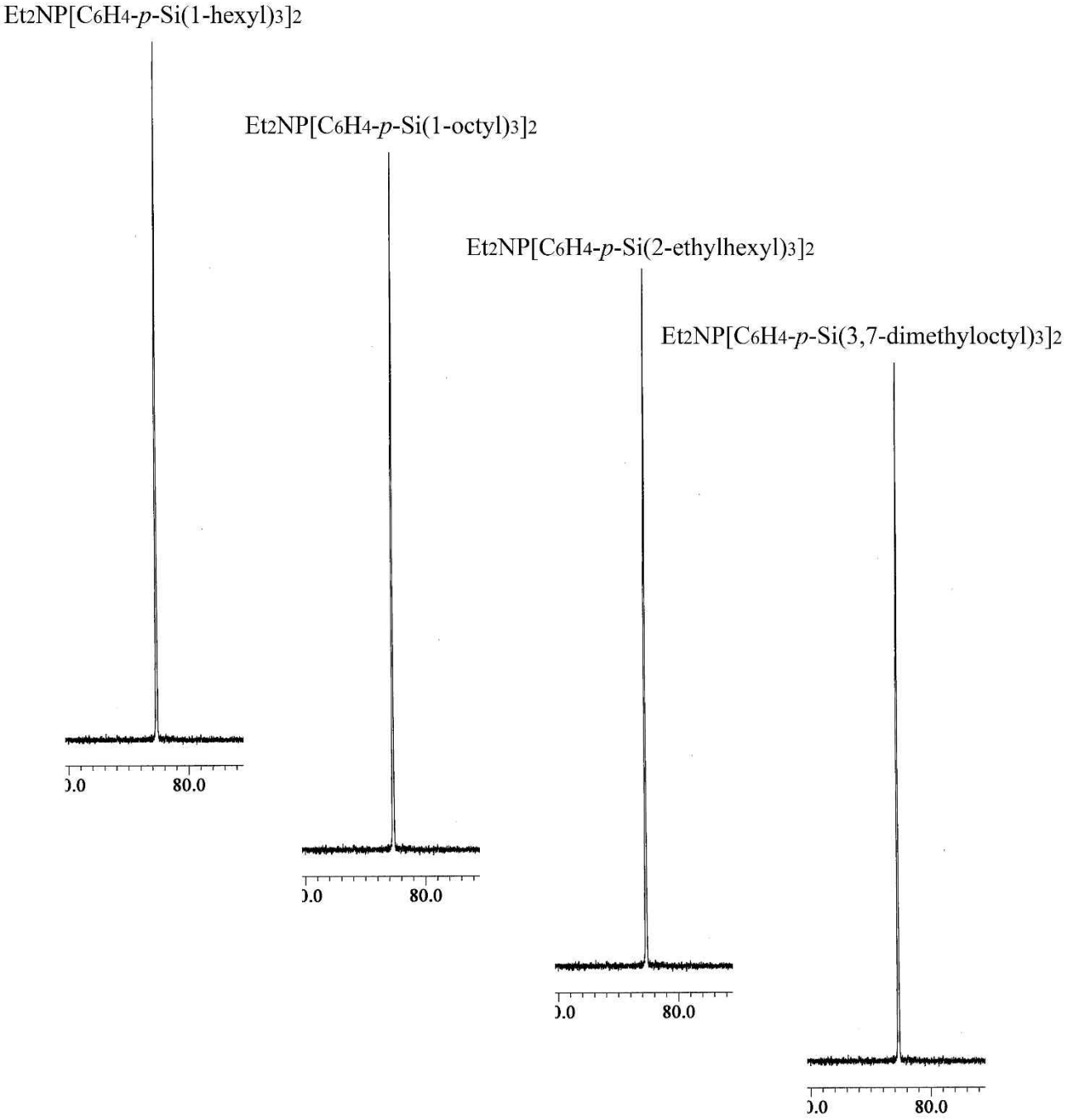


Figure S3. ^{31}P NMR spectra of $ClP(C_6H_4\text{-}p\text{-}SiR_3)_2$ in C_6D_6.

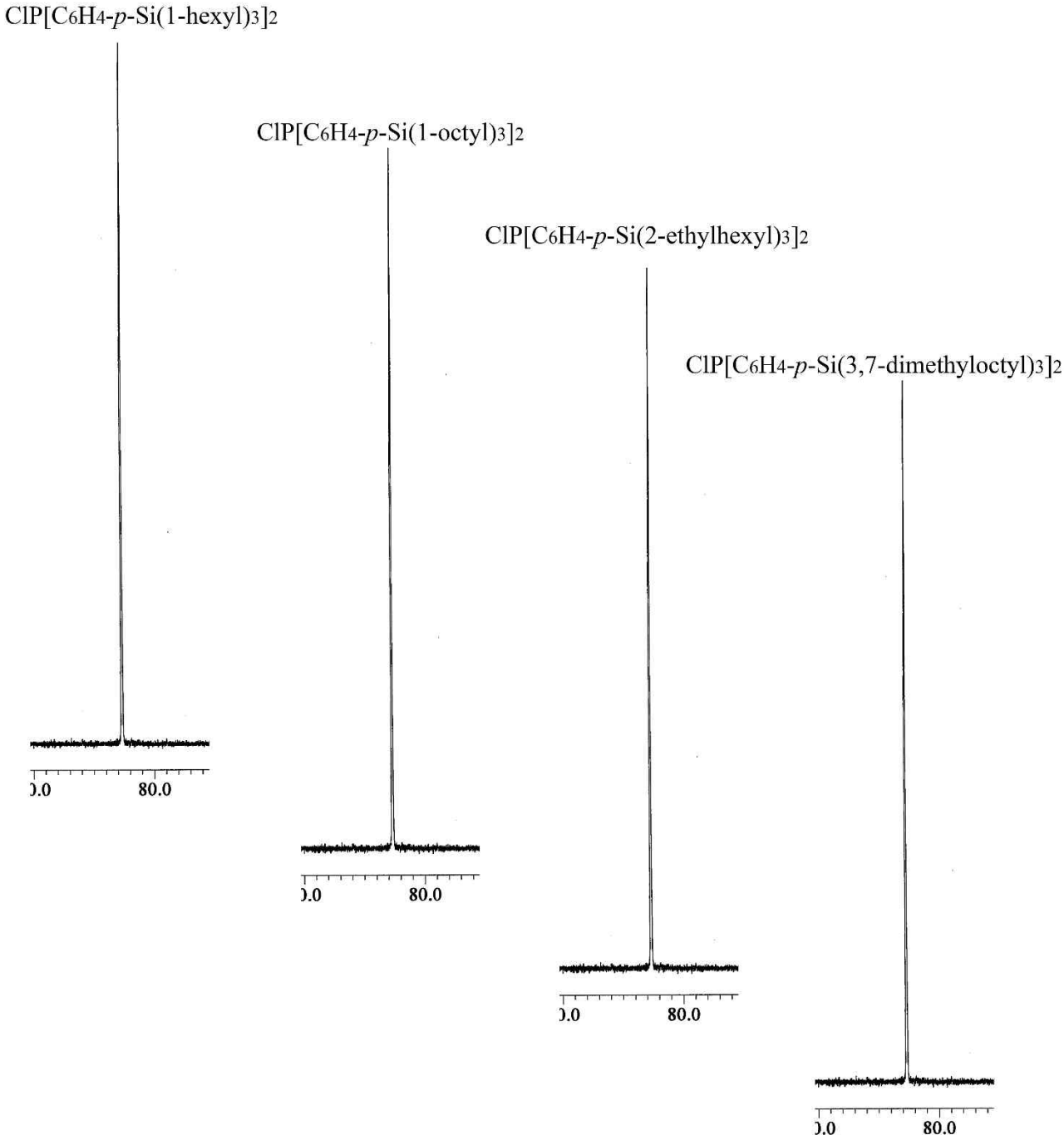


Figure S4. ^{1}H and ^{13}C NMR spectra of HSi(2-ethylhexyl)$_3$ in C_6D_6.

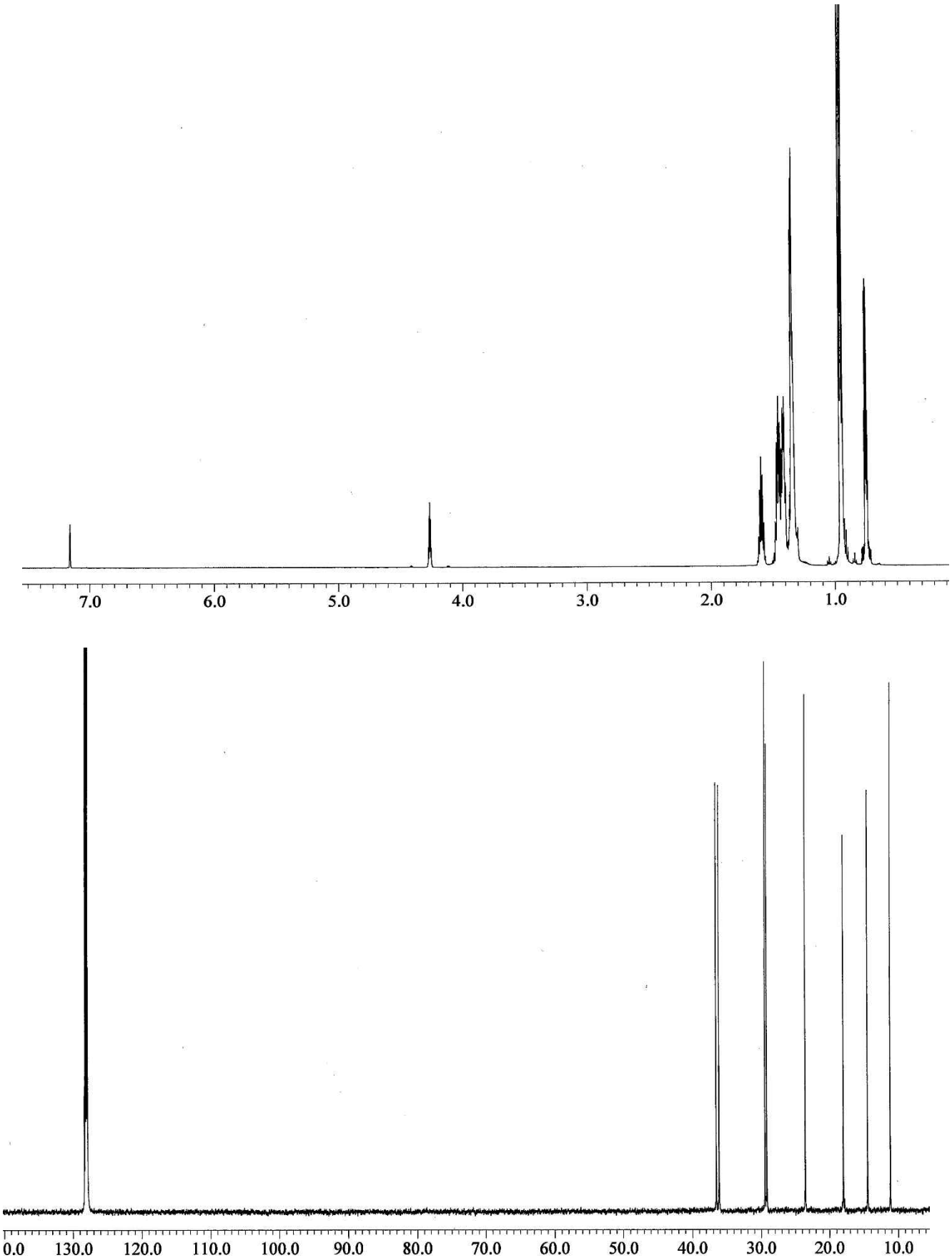


Figure S5. ^{1}H and ^{13}C NMR spectra of HSi(3,7-dimethyloctyl)$_3$ in C_6D_6.

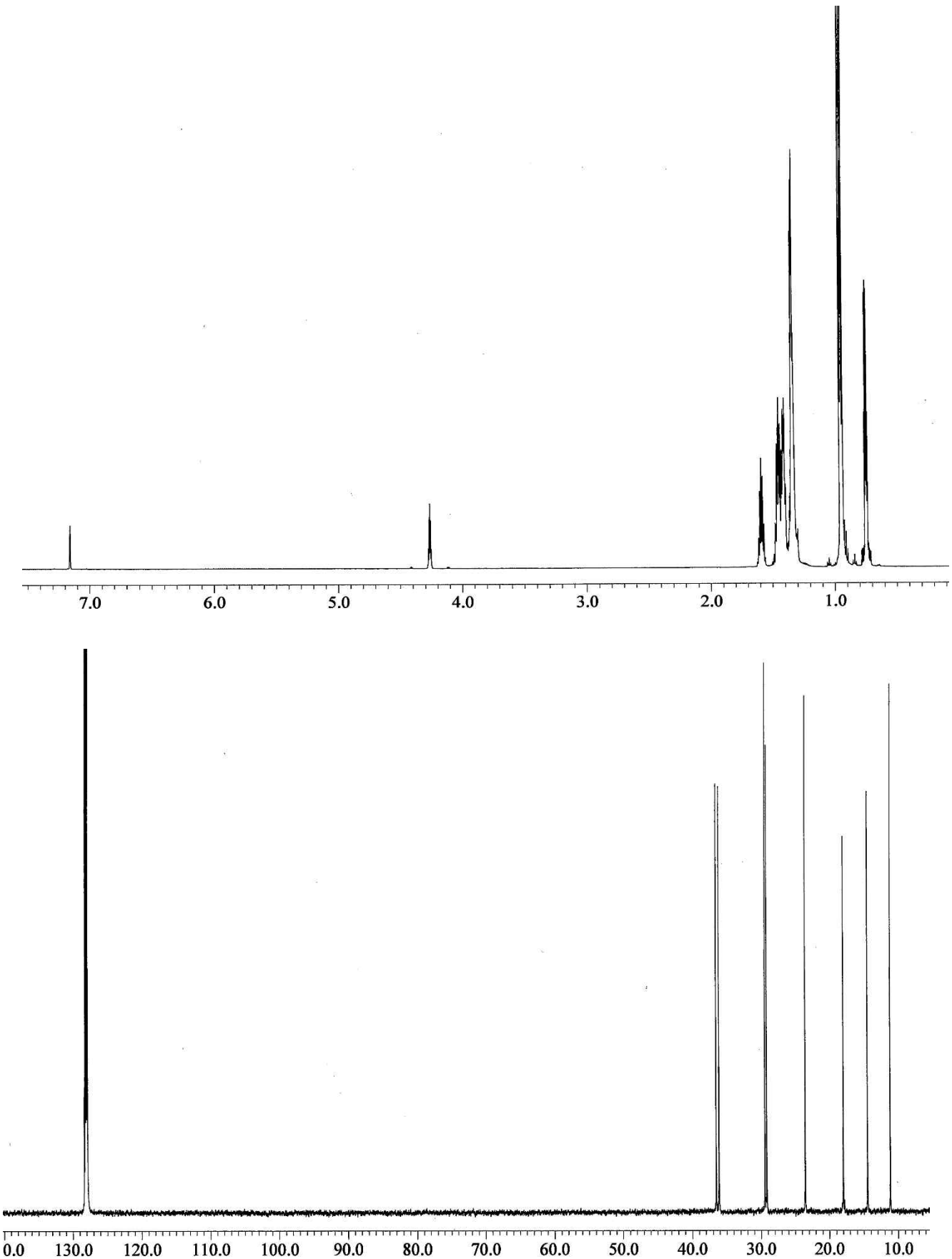


Figure S6. ^{1}H and ^{13}C NMR spectra of $ClSi(1\text{-octyl})_3$ in C_6D_6.

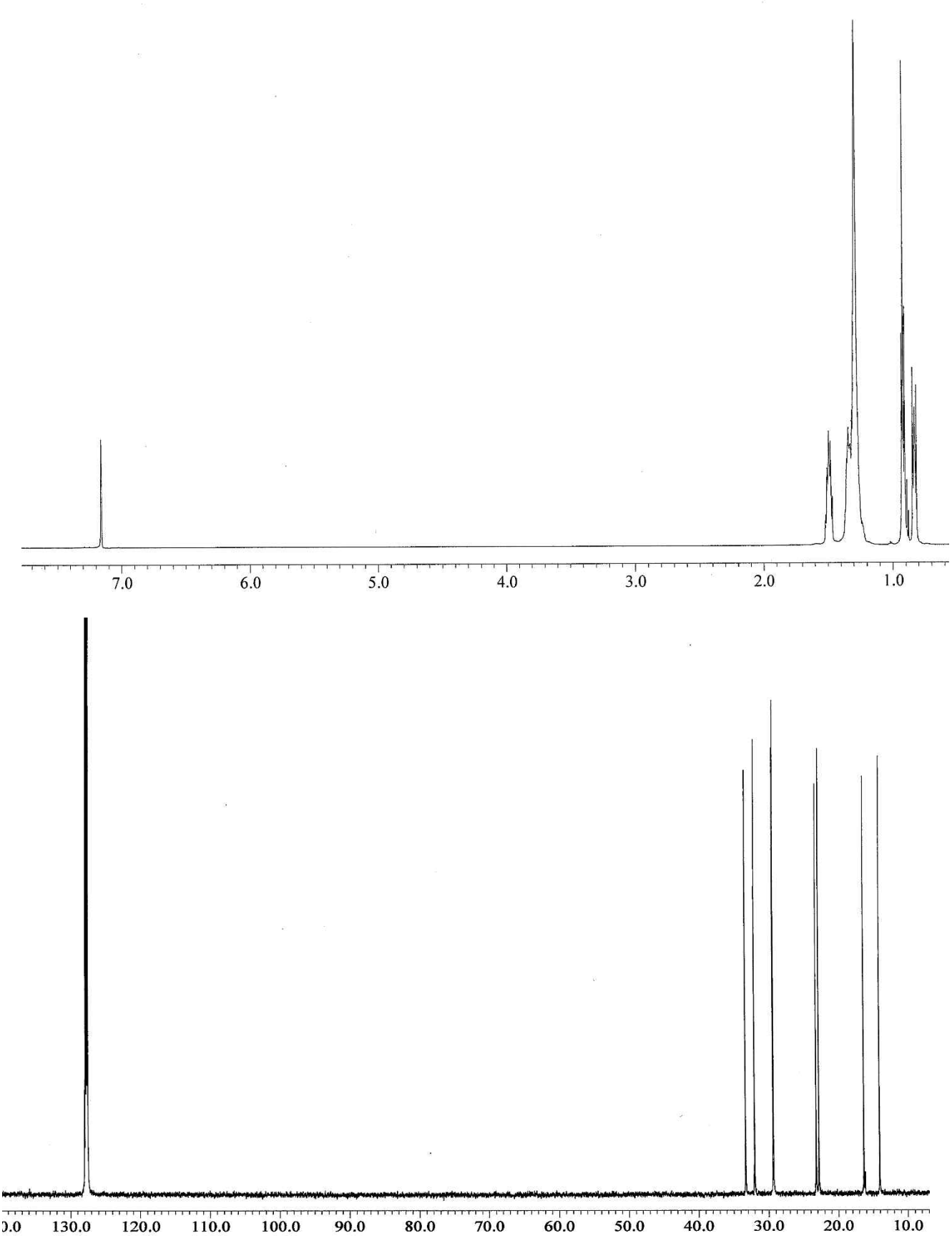
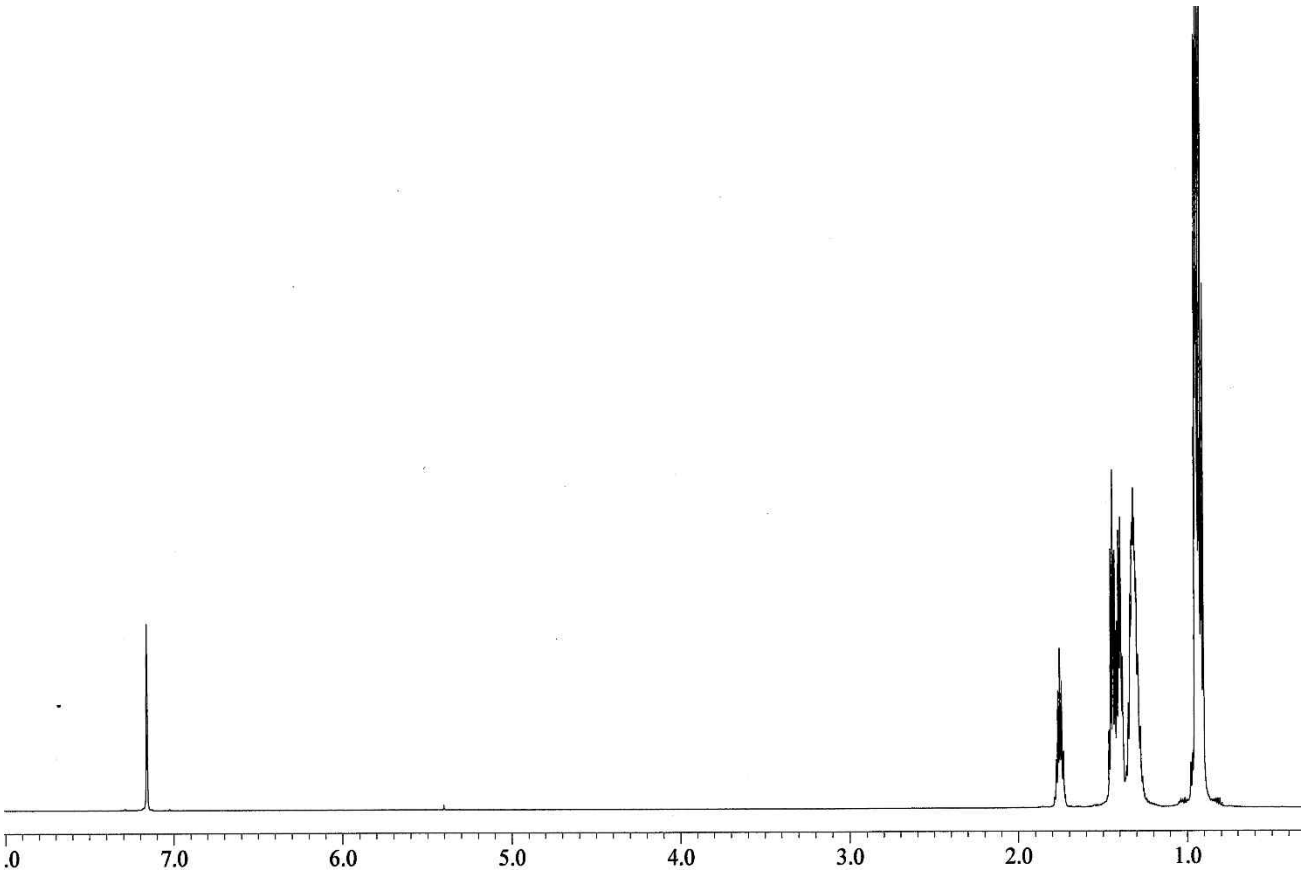


Figure S7. ^{1}H and ^{13}C NMR spectra of $ClSi(2\text{-ethylhexyl})_3$ in C_6D_6.



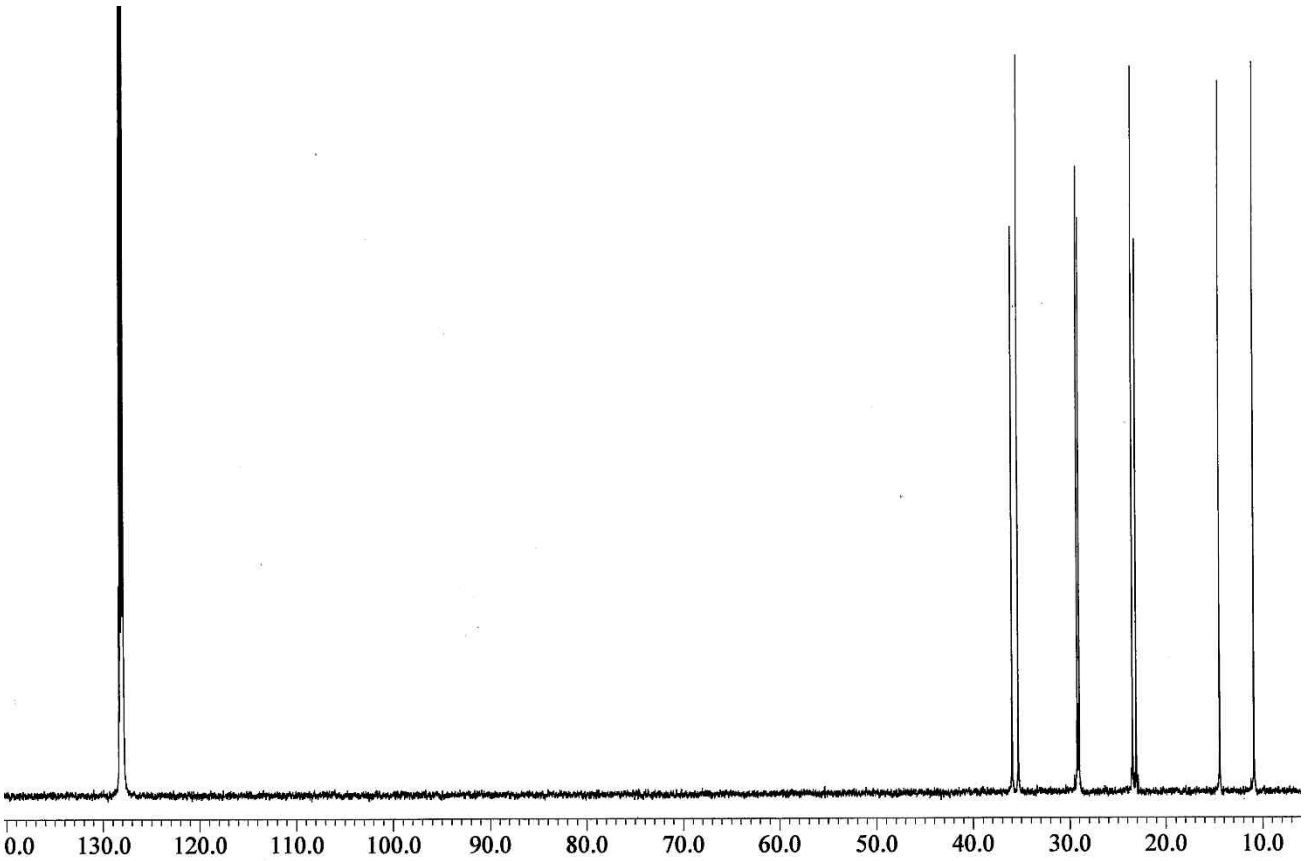


Figure S8. ^{1}H and ^{13}C NMR spectra of ClSi(3,7-dimethyloctyl)$_3$ in C_6D_6.

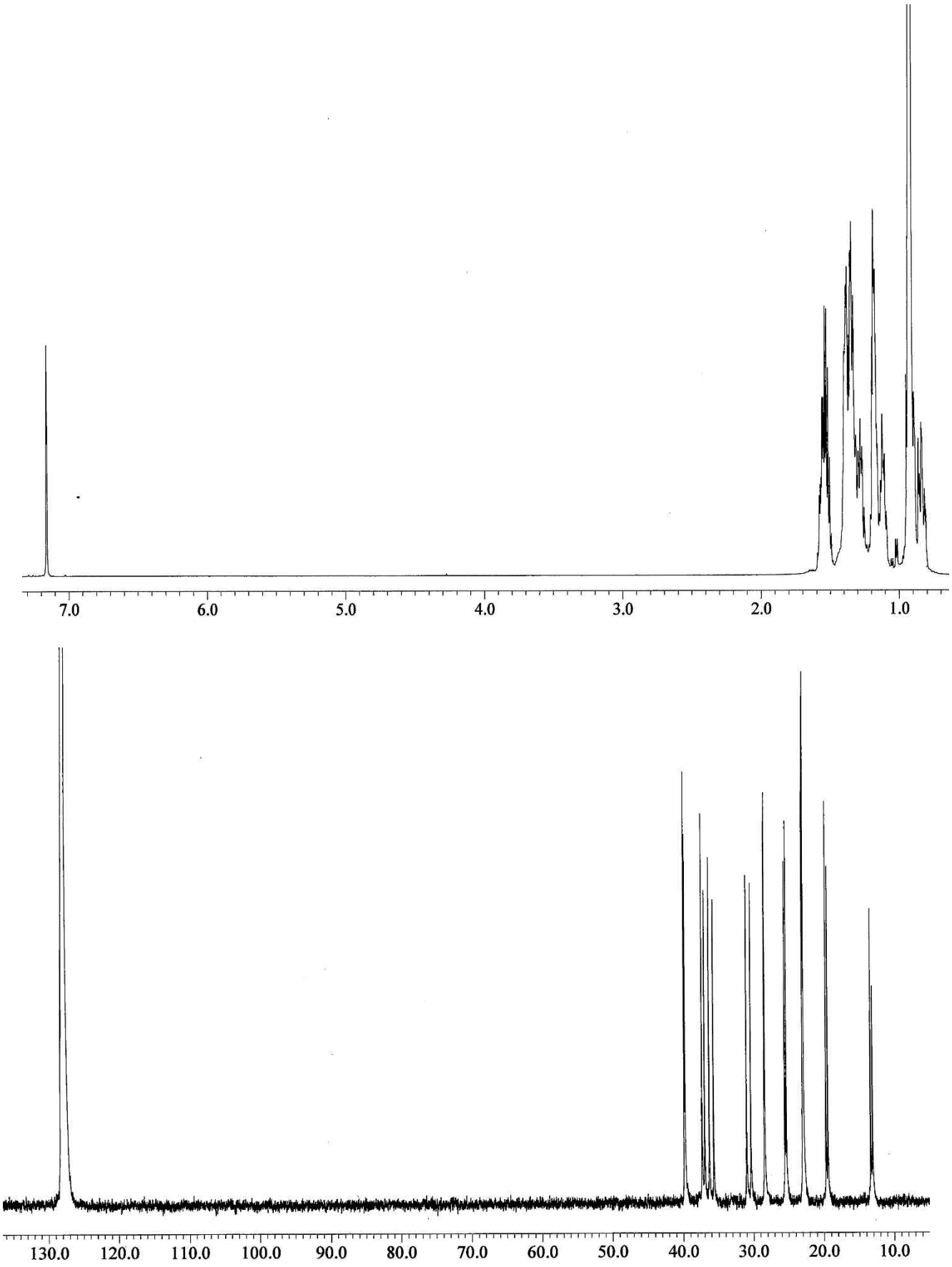


Figure S9. ^{1}H and ^{13}C NMR spectra of BrC_6H_4-*p*-Si(1-hexyl)$_3$ in C_6D_6.

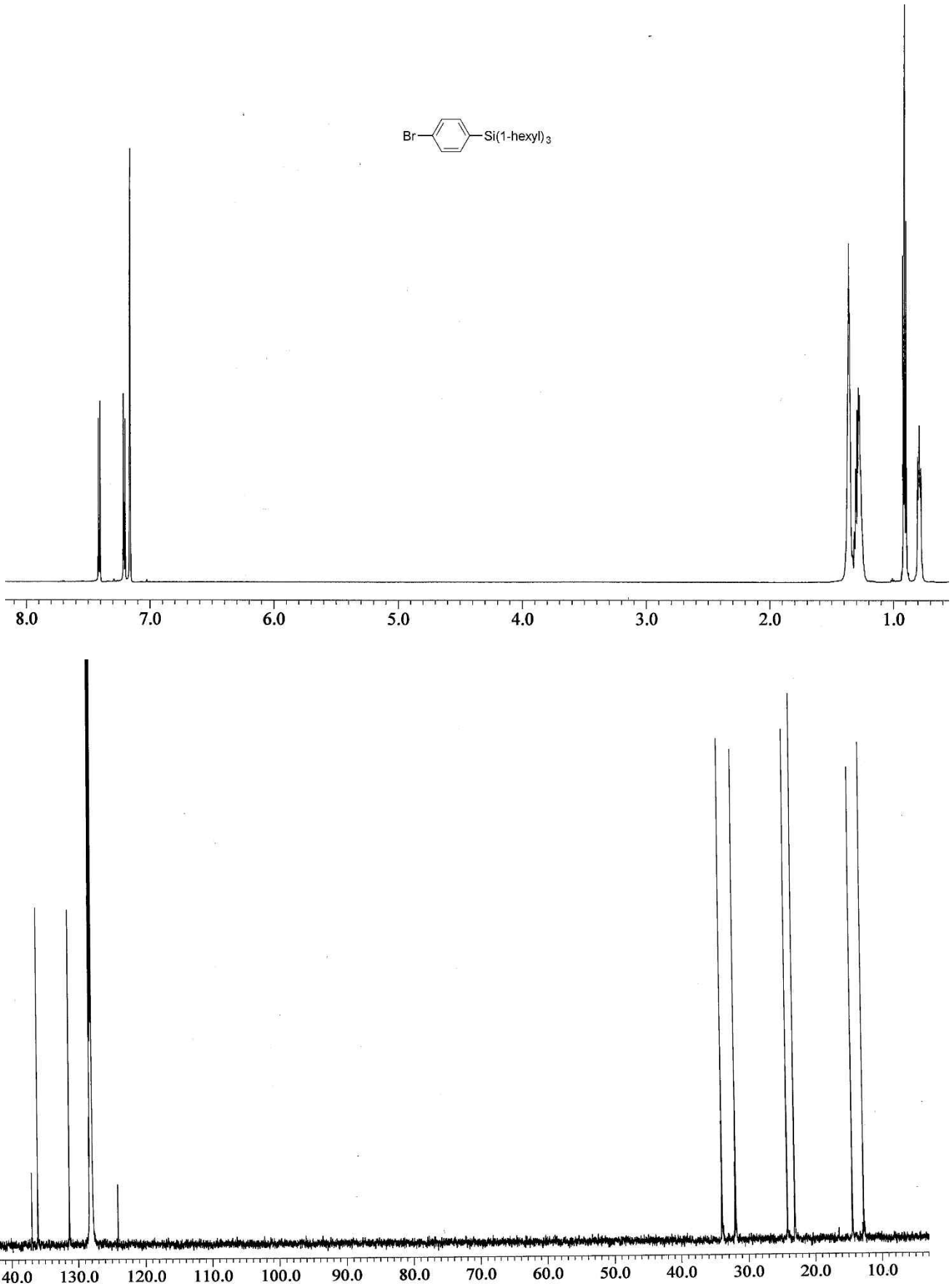


Figure S10. ^{1}H and ^{13}C NMR spectra of BrC_6H_4-*p*-Si(1-octyl)$_3$ in C_6D_6.

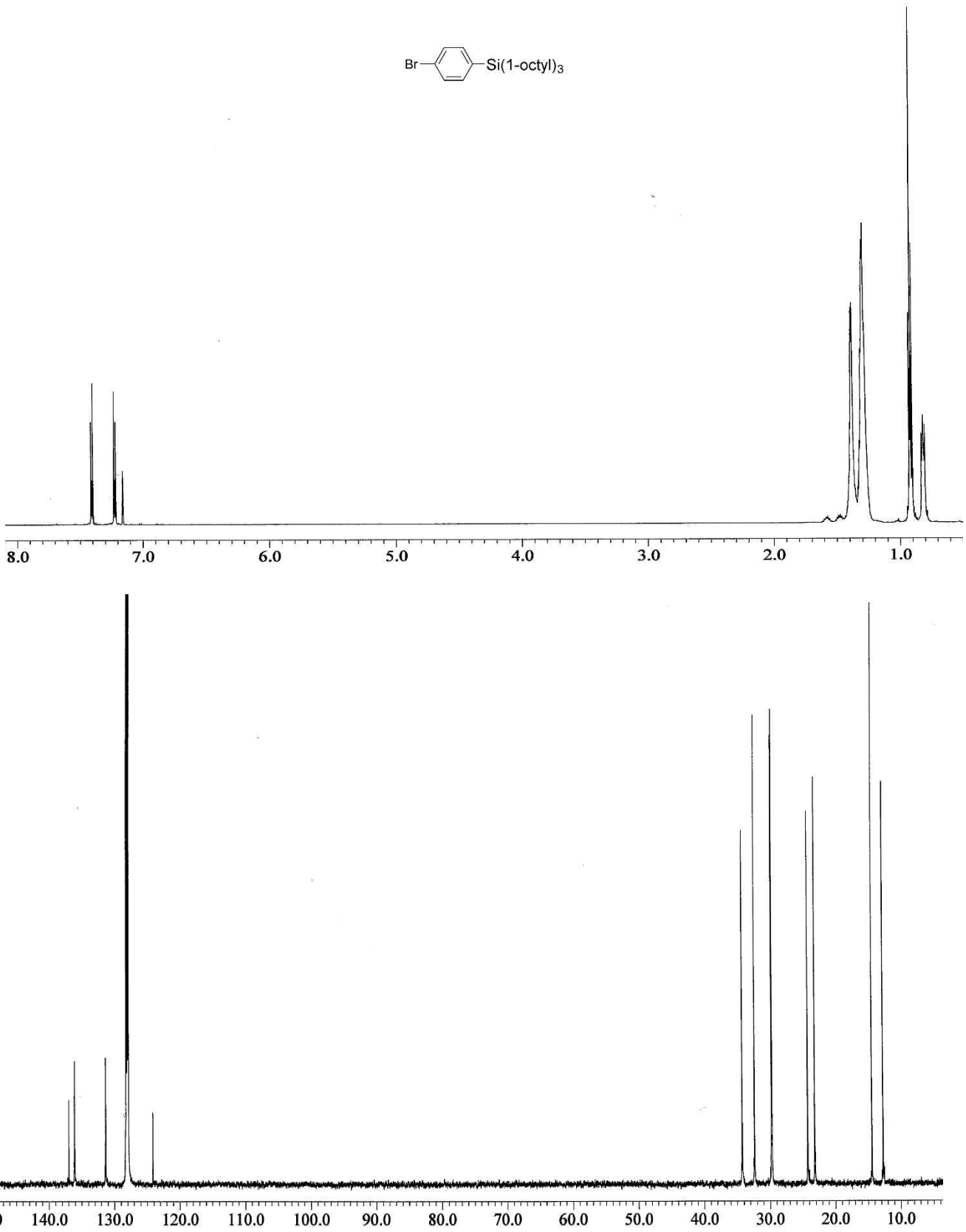


Figure S11. ^{1}H and ^{13}C NMR spectra of BrC_6H_4-*p*-Si(2-ethylhexyl)$_3$ in C_6D_6.

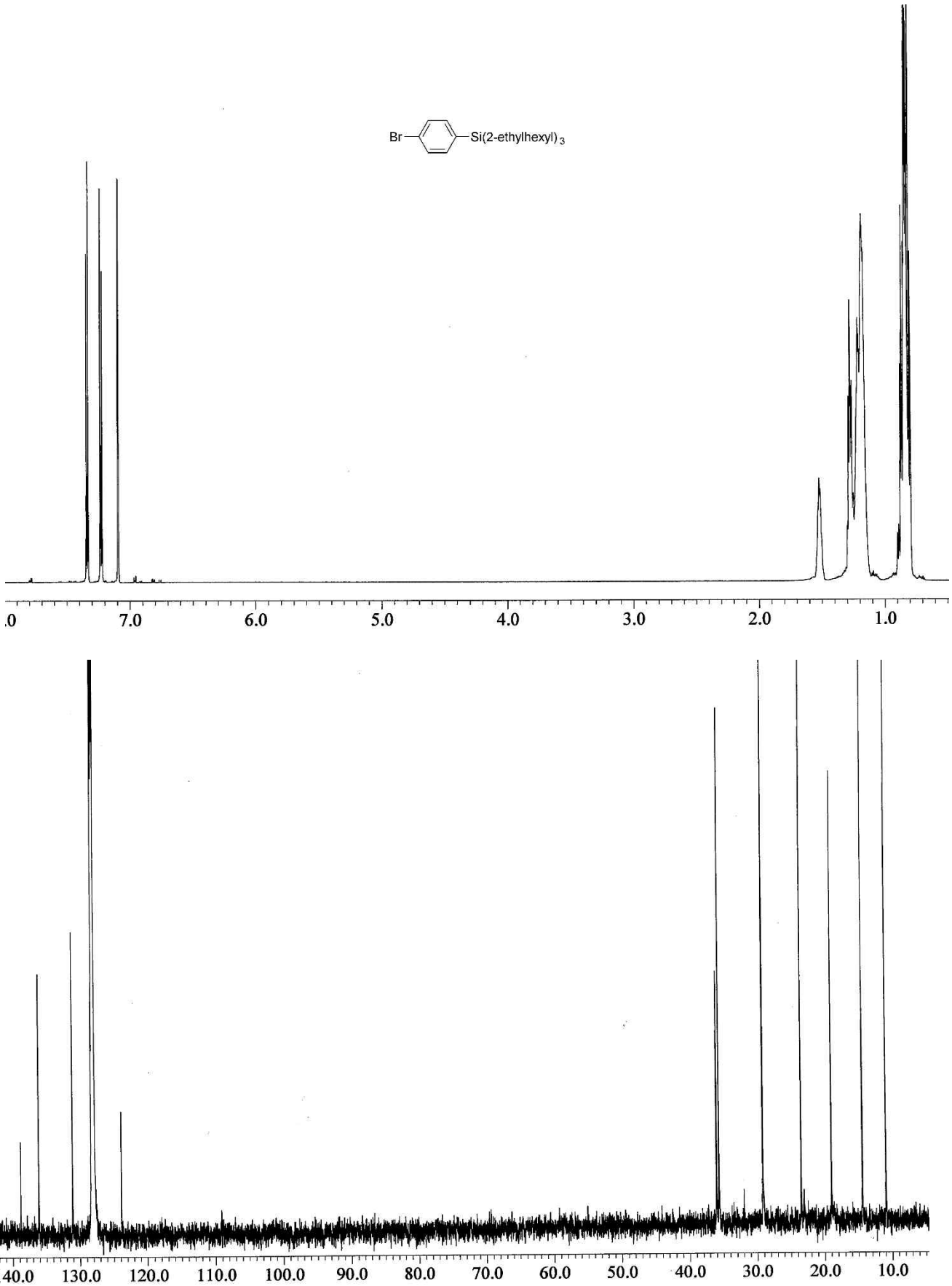


Figure S12. ^{1}H and ^{13}C NMR spectra of BrC_6H_4-*p*-Si(3,7-dimethyloctyl)$_3$ in C_6D_6.

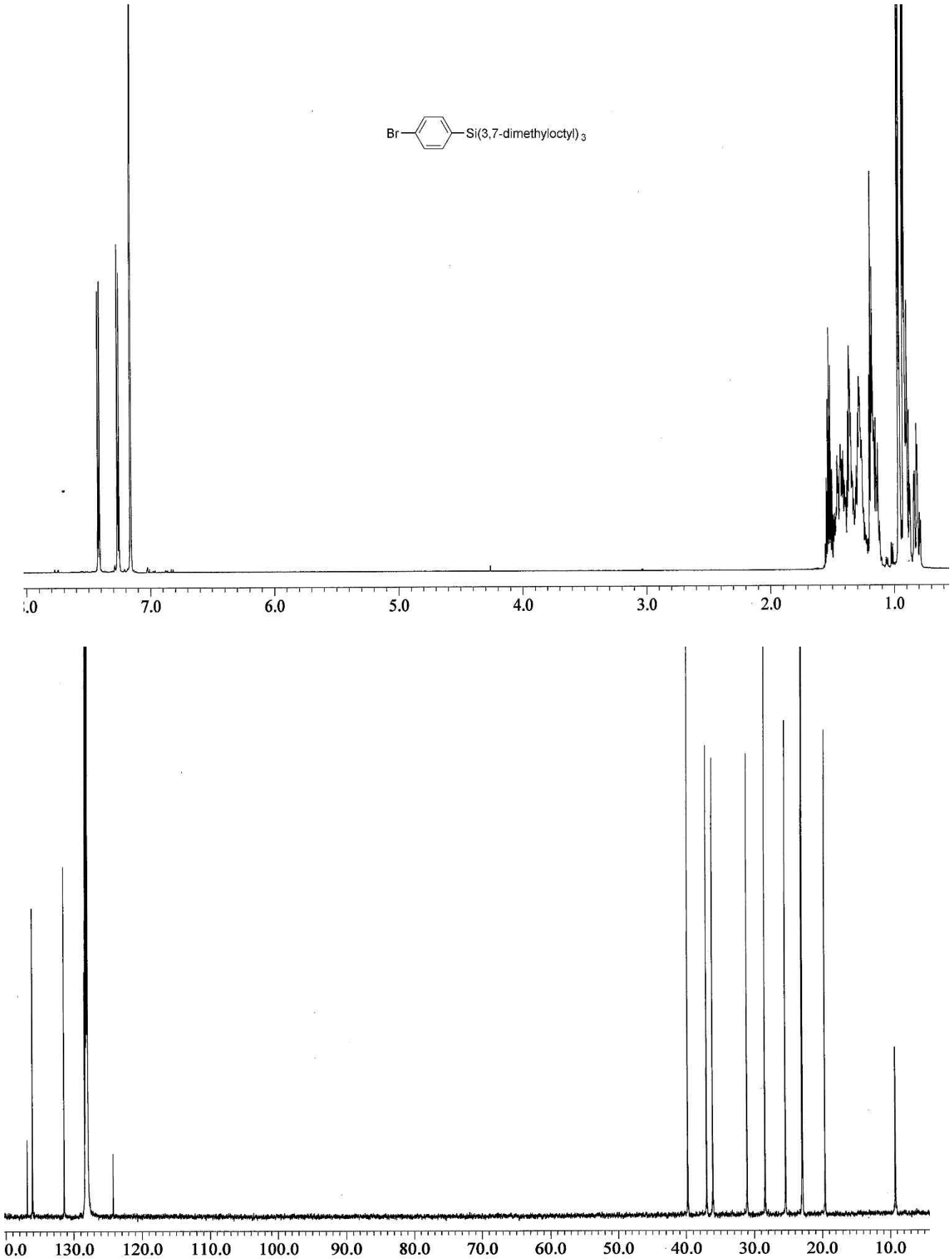


Figure S13. ^{1}H and ^{13}C NMR spectra of $Et_2NP(C_6H_4\text{-}p\text{-}Si(1\text{-hexyl})_3)_2$ in C_6D_6.

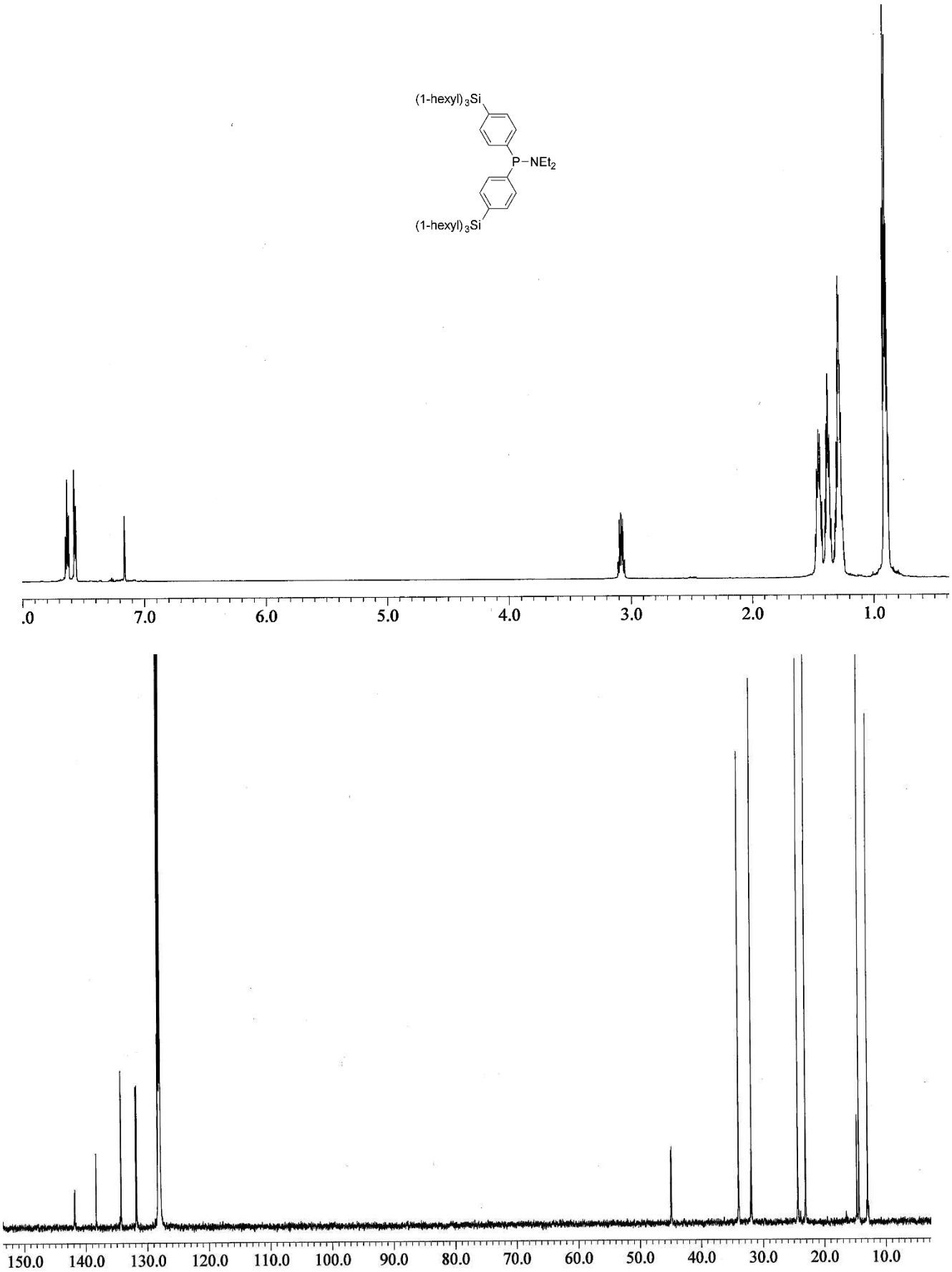


Figure S14. ^{1}H and ^{13}C NMR spectra of $Et_2NP(C_6H_4\text{-}p\text{-}Si(1\text{-octyl})_3)_2$ in C_6D_6.

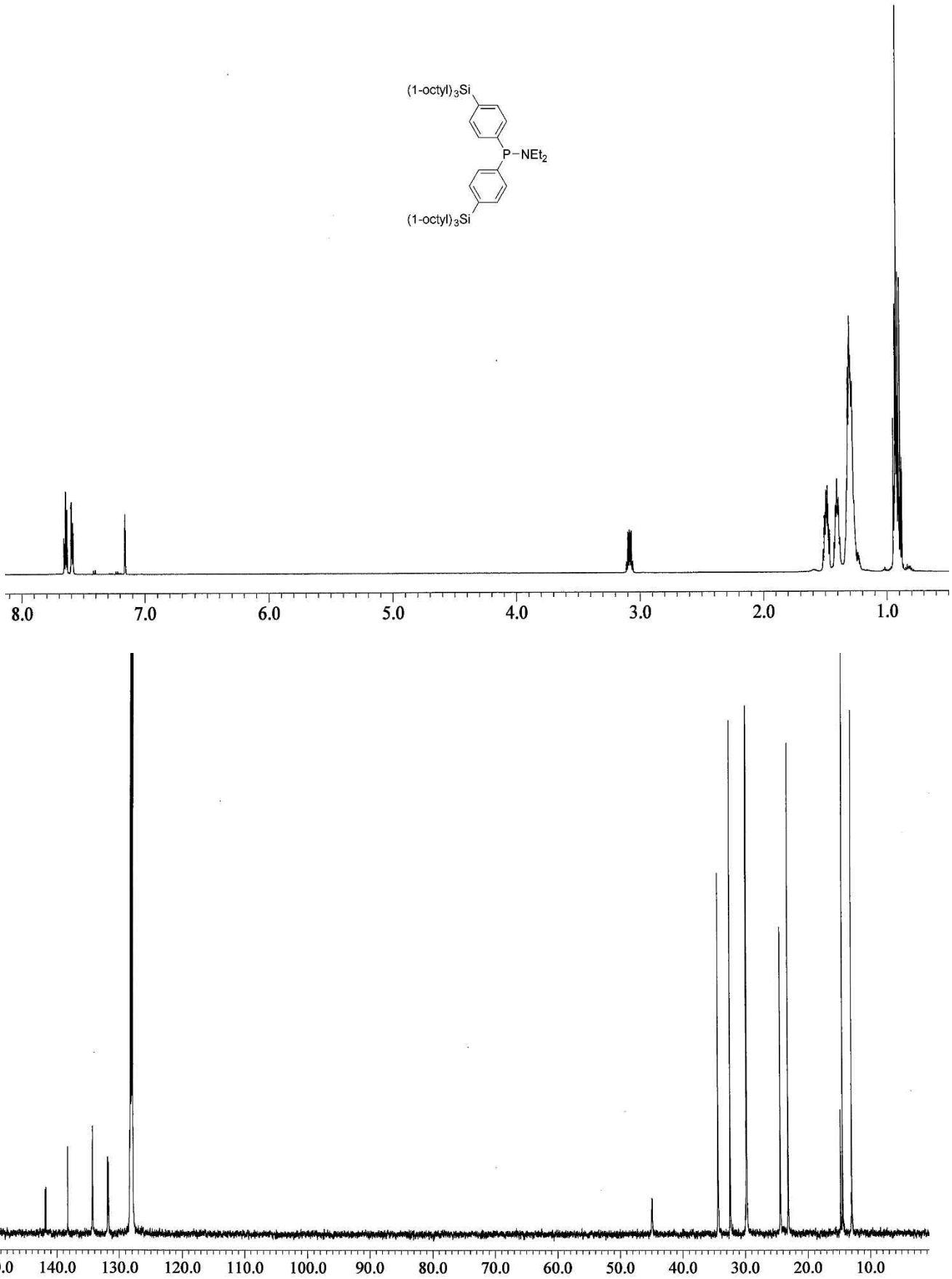


Figure S15. ^{1}H and ^{13}C NMR spectra of $Et_2NP(C_6H_4\text{-}p\text{-}Si(2\text{-ethylhexyl})_3)_2$ in C_6D_6.

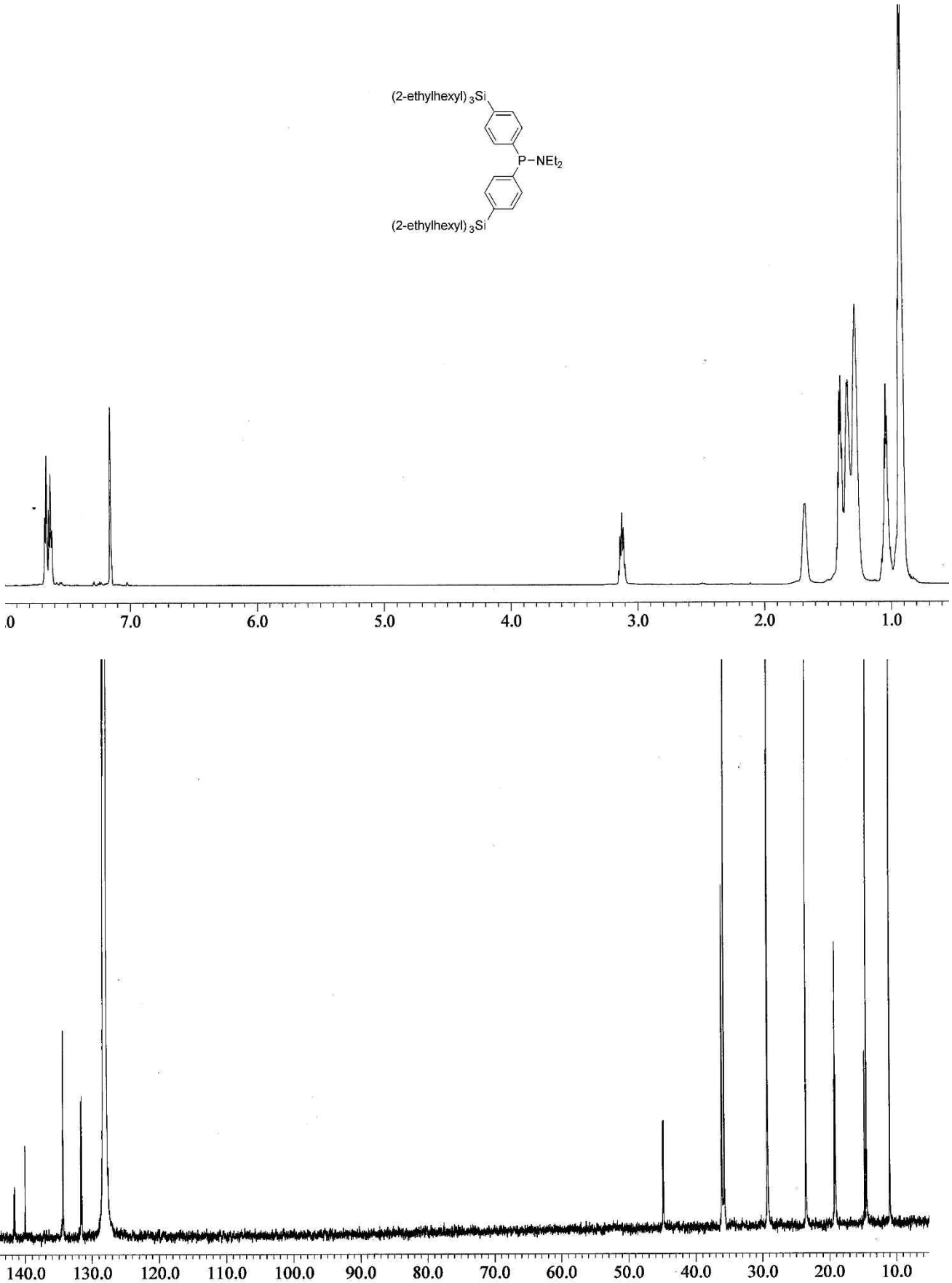


Figure S16. ^{1}H and ^{13}C NMR spectra of $Et_2NP(C_6H_4\text{-}p\text{-}Si(3,7\text{-dimethyloctyl})_3)_2$ in C_6D_6.

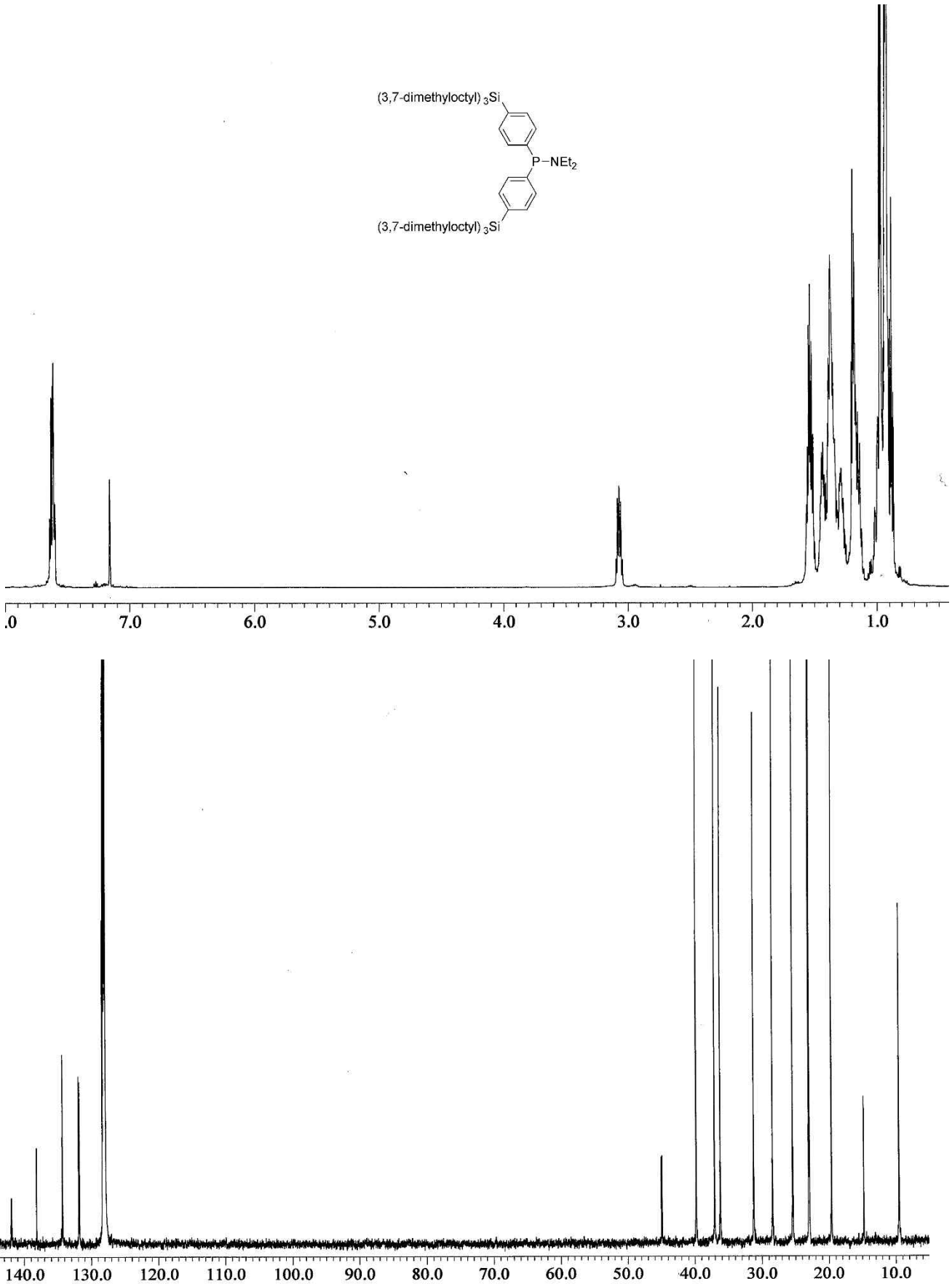


Figure S17. ^{1}H and ^{13}C NMR spectra of $ClP(C_6H_4\text{-}p\text{-}Si(1\text{-hexyl})_3)_2$ in C_6D_6.

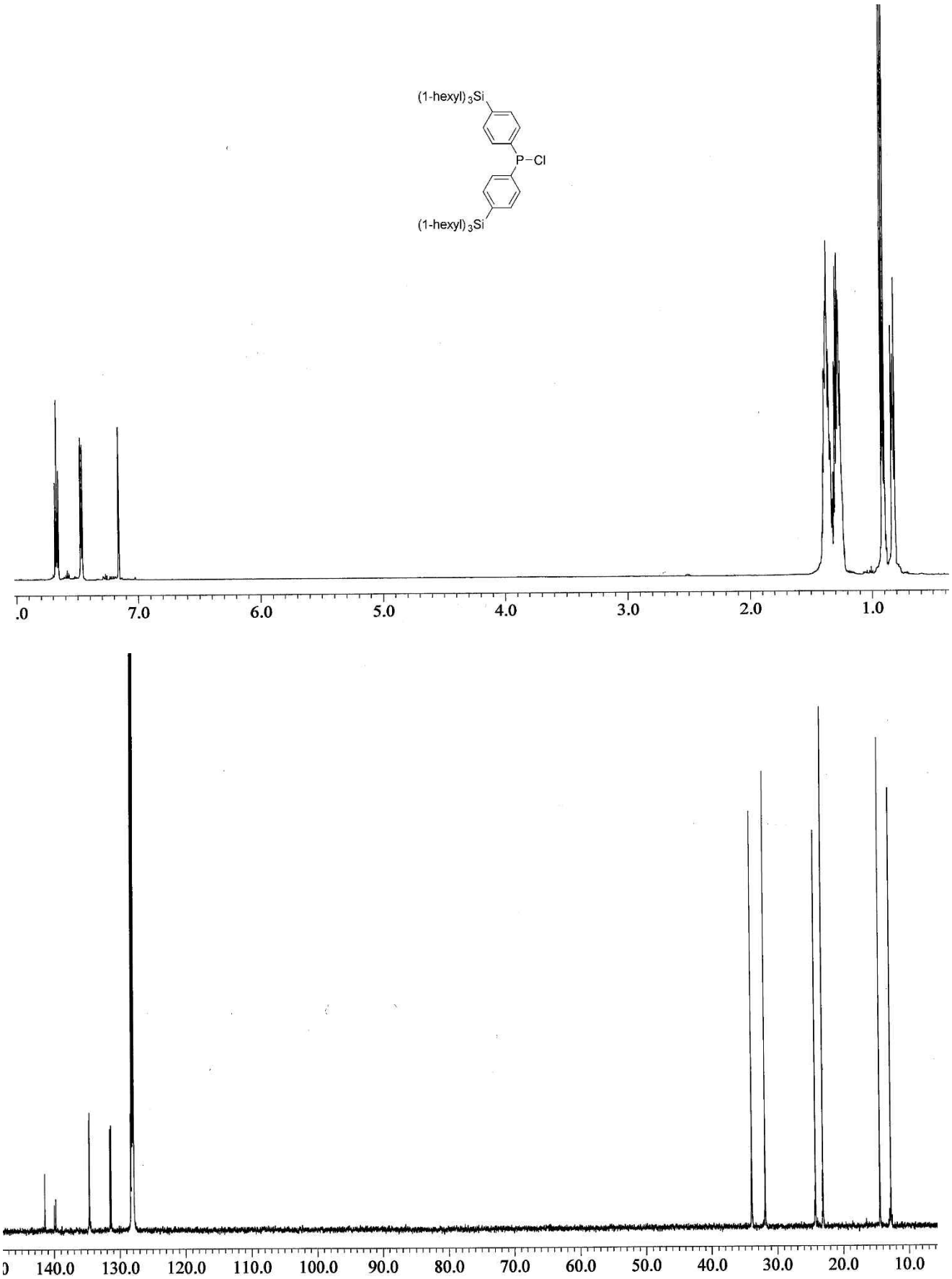


Figure S18. ^{1}H and ^{13}C NMR spectra of $ClP(C_6H_4\text{-}p\text{-}Si(1\text{-octyl})_3)_2$ in C_6D_6.

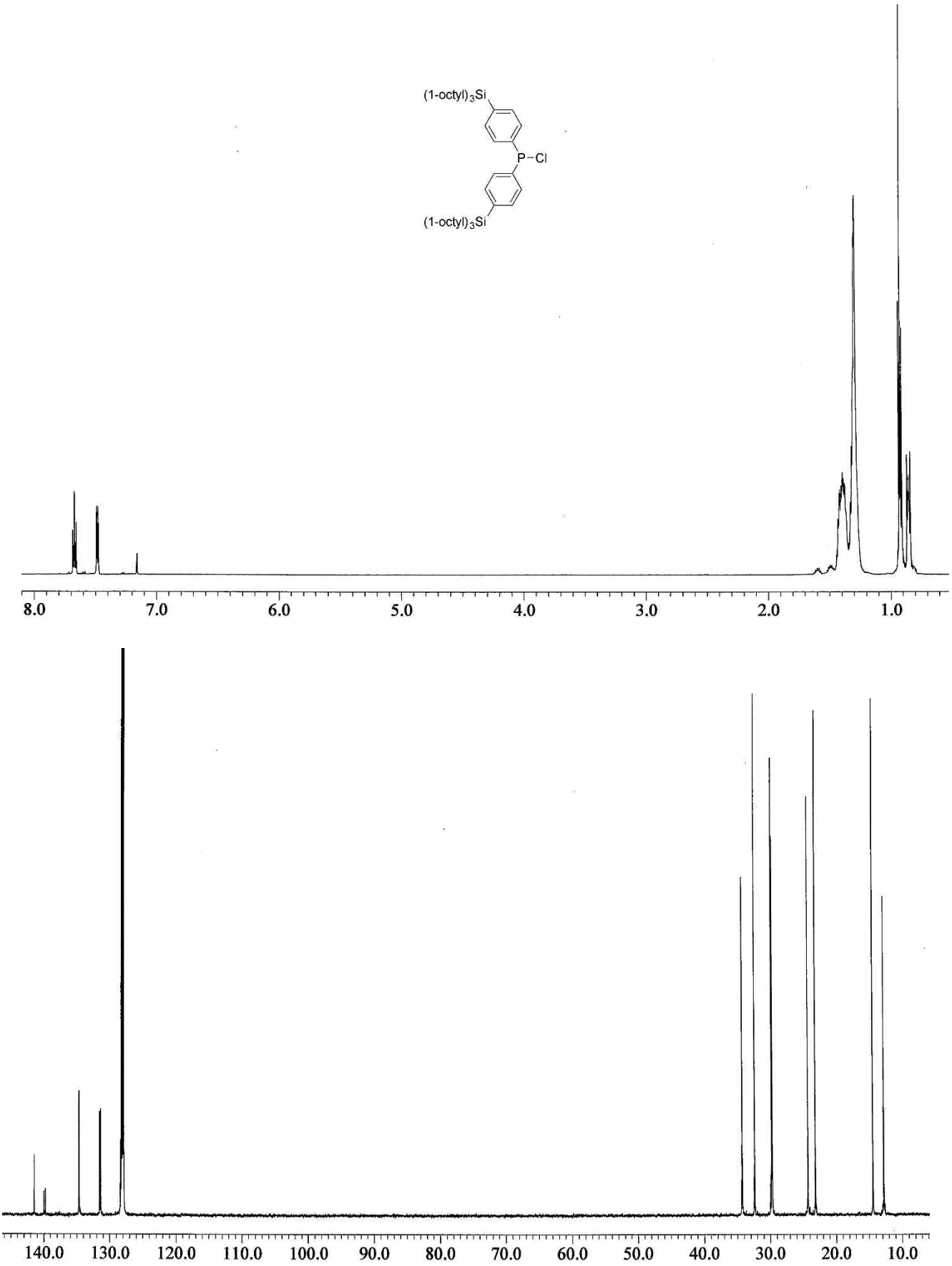


Figure S19. ^{1}H and ^{13}C NMR spectra of $ClP(C_6H_4\text{-}p\text{-}Si(2\text{-ethylhexyl})_3)_2$ in C_6D_6.

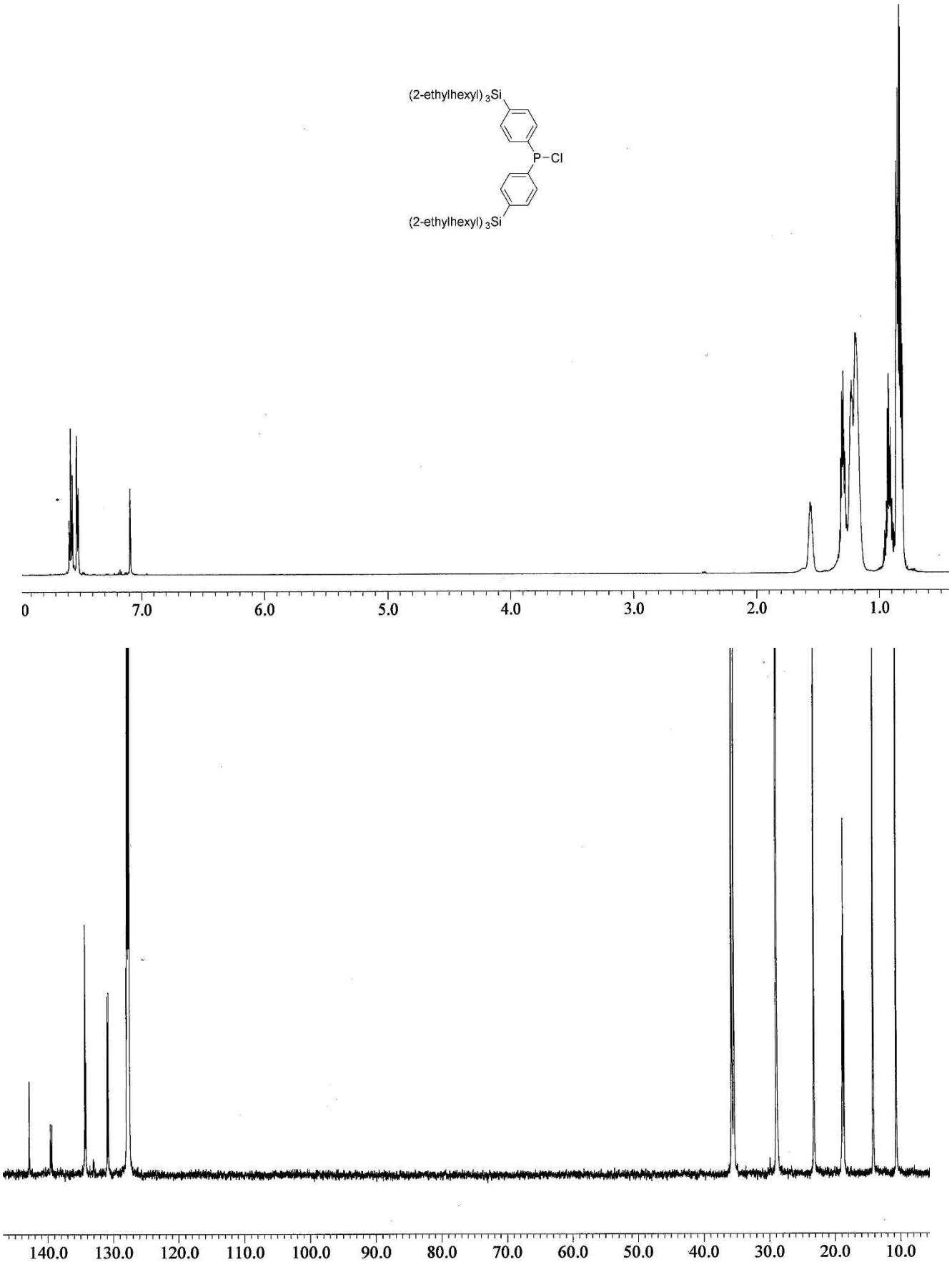


Figure S20. ^{1}H and ^{13}C NMR spectra of $ClP(C_6H_4\text{-}p\text{-}Si(3,7\text{-dimethyloctyl})_3)_2$ in C_6D_6.

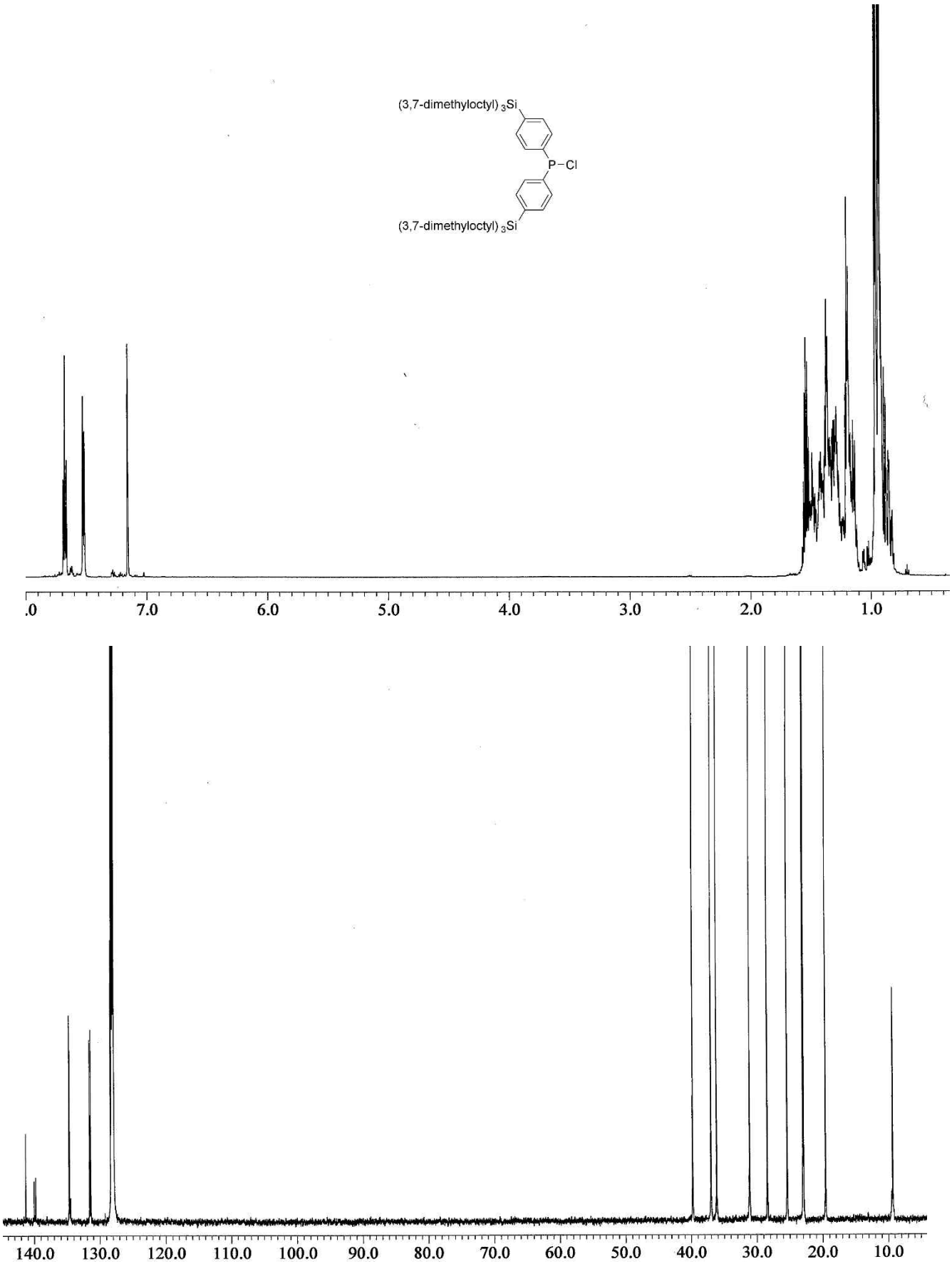


Figure S21. ^{1}H and ^{13}C NMR spectra of $iPrN(PAr_2)_2$ (Ar = $–C_6H_4$-*p*-Si(1-hexyl)$_3$) in C_6D_6.

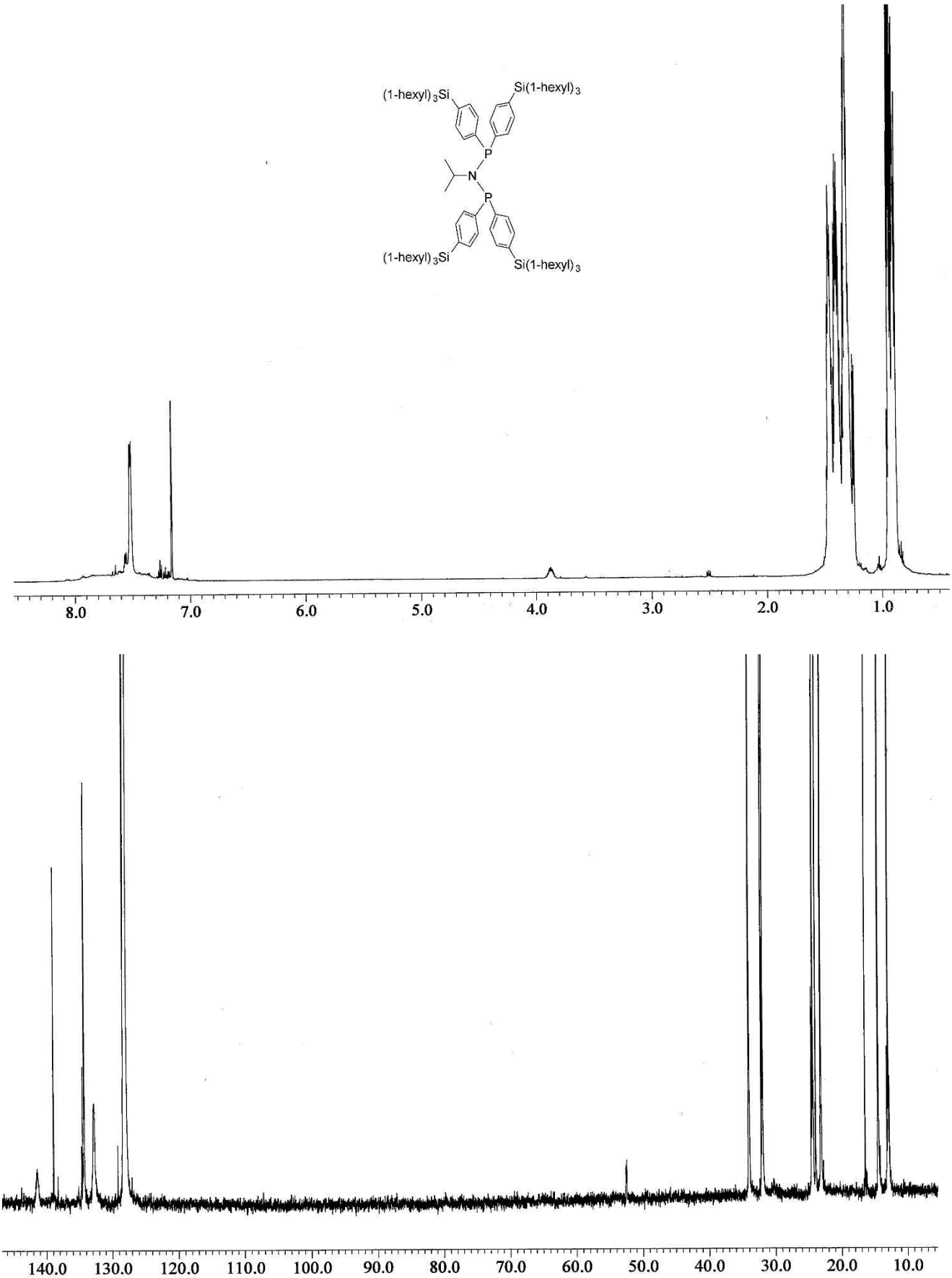
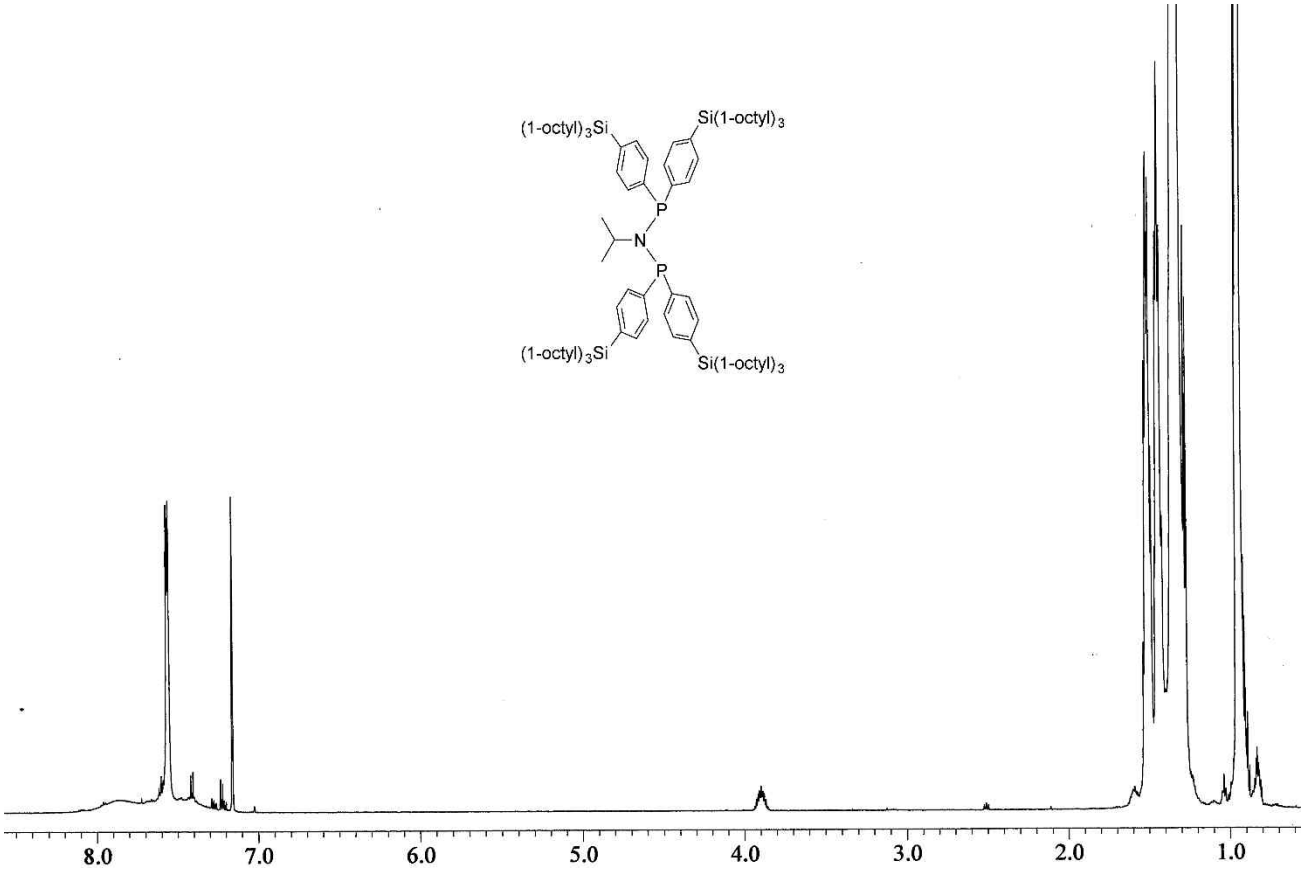


Figure S22. ^{1}H and ^{13}C NMR spectra of iPrN(PAr_2)$_2$ (Ar = –C_6H_4-*p*-Si(1-octyl)$_3$) in C_6D_6.



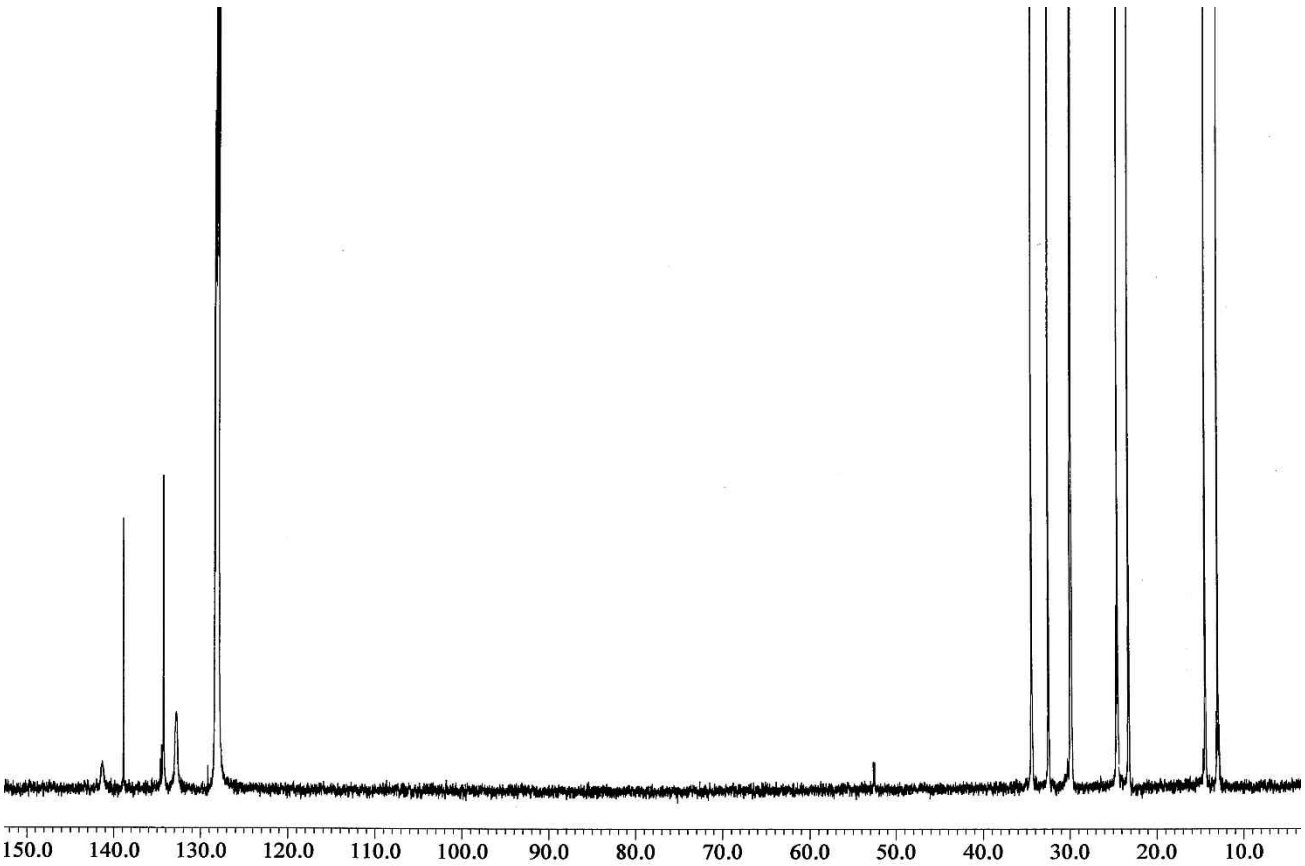


Figure S23. ^{1}H and ^{13}C NMR spectra of $iPrN(PAr_2)_2$ (Ar = $–C_6H_4$-*p*-Si(2-ethylhexyl)$_3$) in C_6D_6.

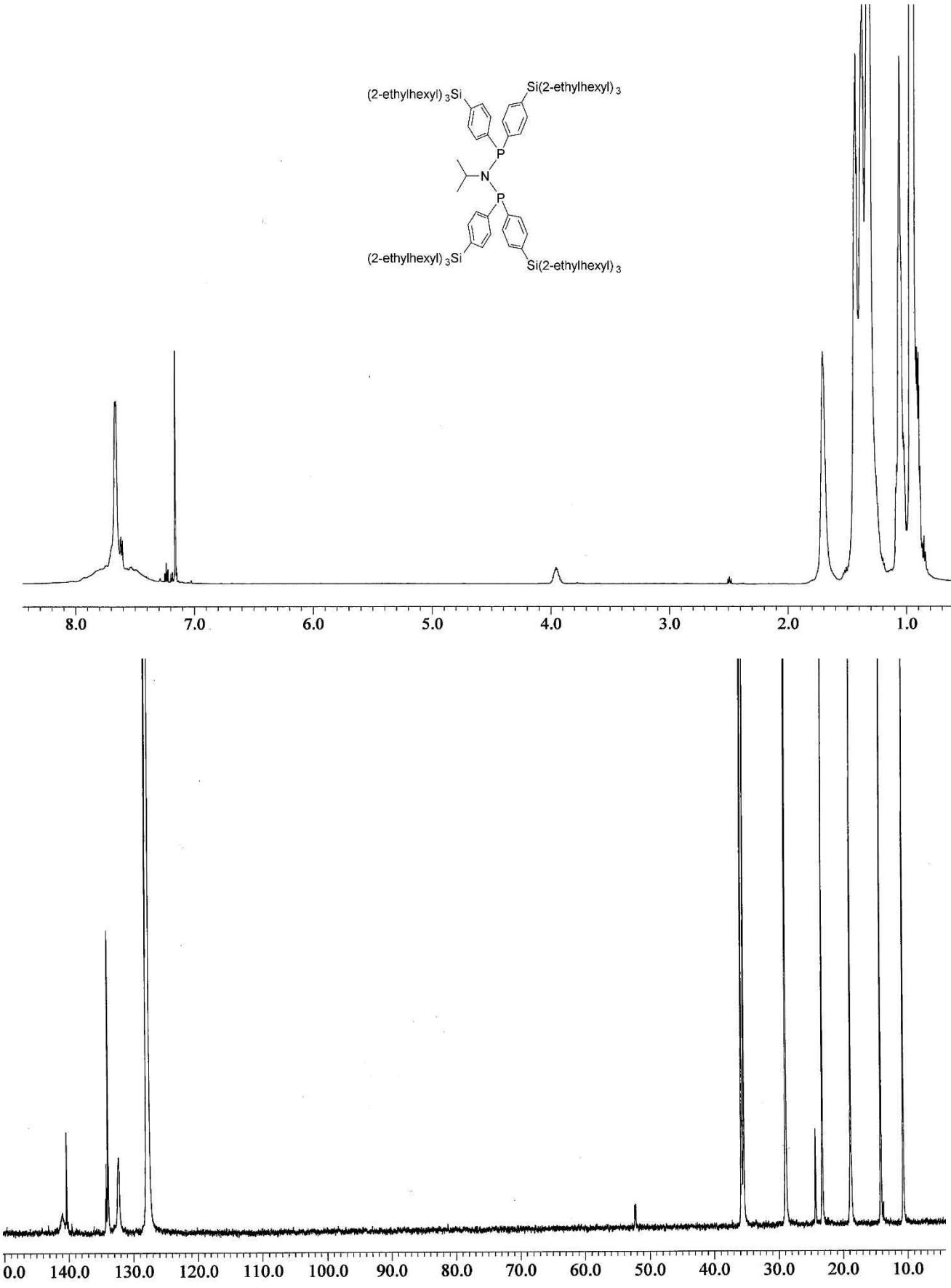


Figure S24. ^{1}H and ^{13}C NMR spectra of $iPrN(PAr_2)_2$ (Ar = $–C_6H_4$-*p*-Si(3,7-dimethyloctyl)$_3$) in C_6D_6.

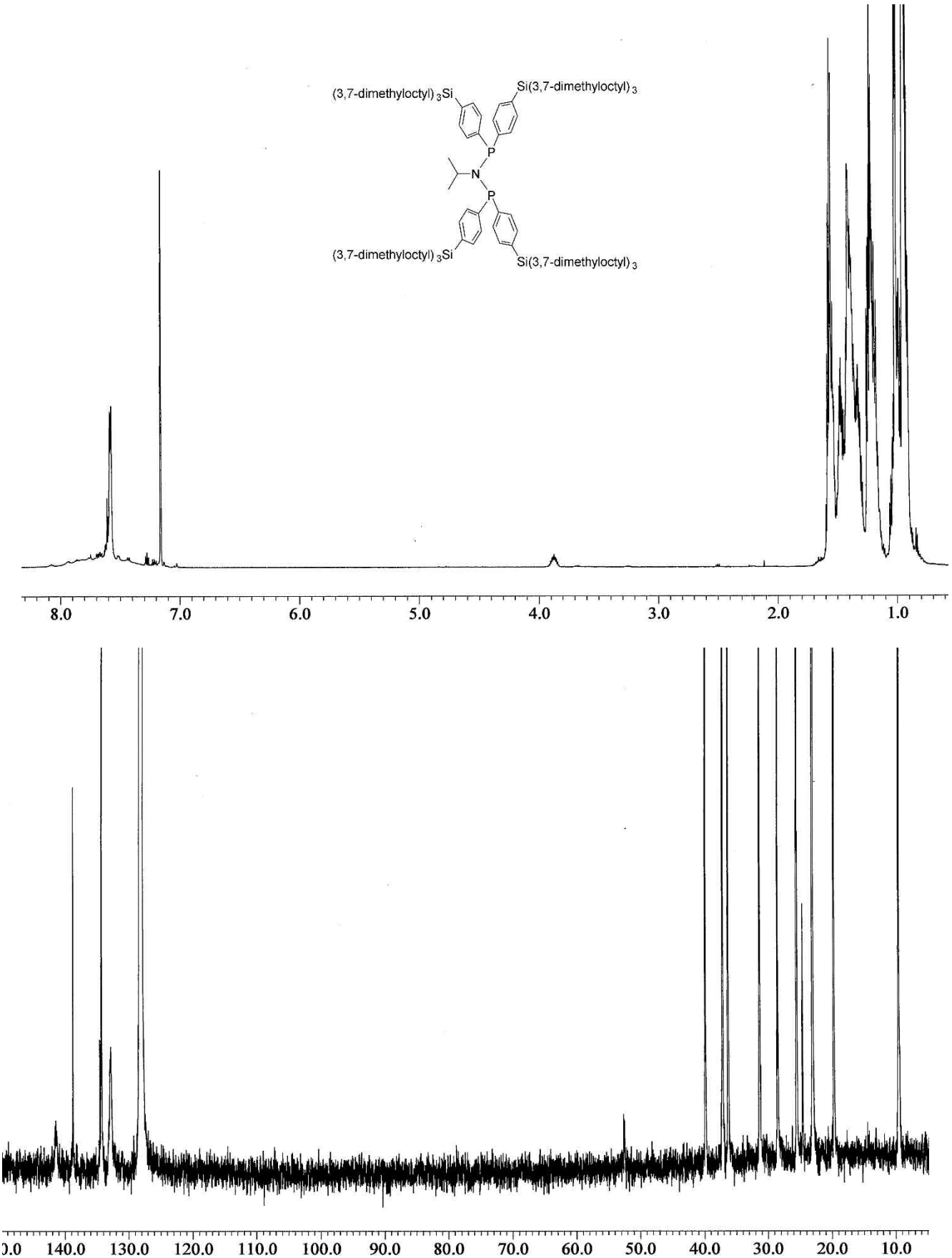


Figure S25. ^{1}H and ^{13}C NMR spectra $C_6H_{11}N(PAr_2)_2$ (Ar = $-C_6H_4$-*p*-Si(1-octyl)$_3$) in C_6D_6.

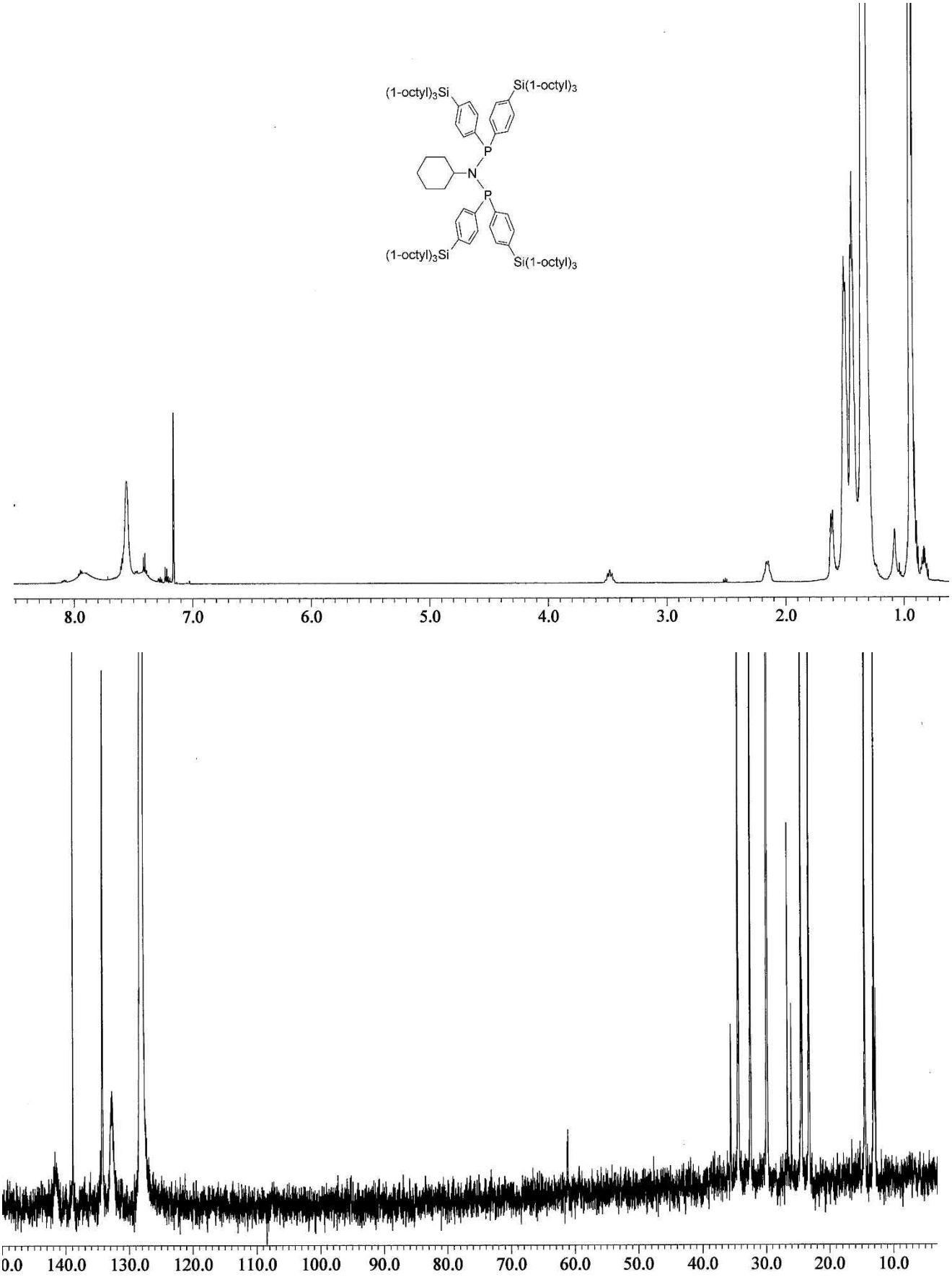


Figure S26. ^{1}H and ^{13}C NMR spectra of 2-Et-6-Me-$C_6H_3N(PAr_2)_2$ (Ar = –C_6H_4-*p*-Si(nBu)$_3$) in C_6D_6.

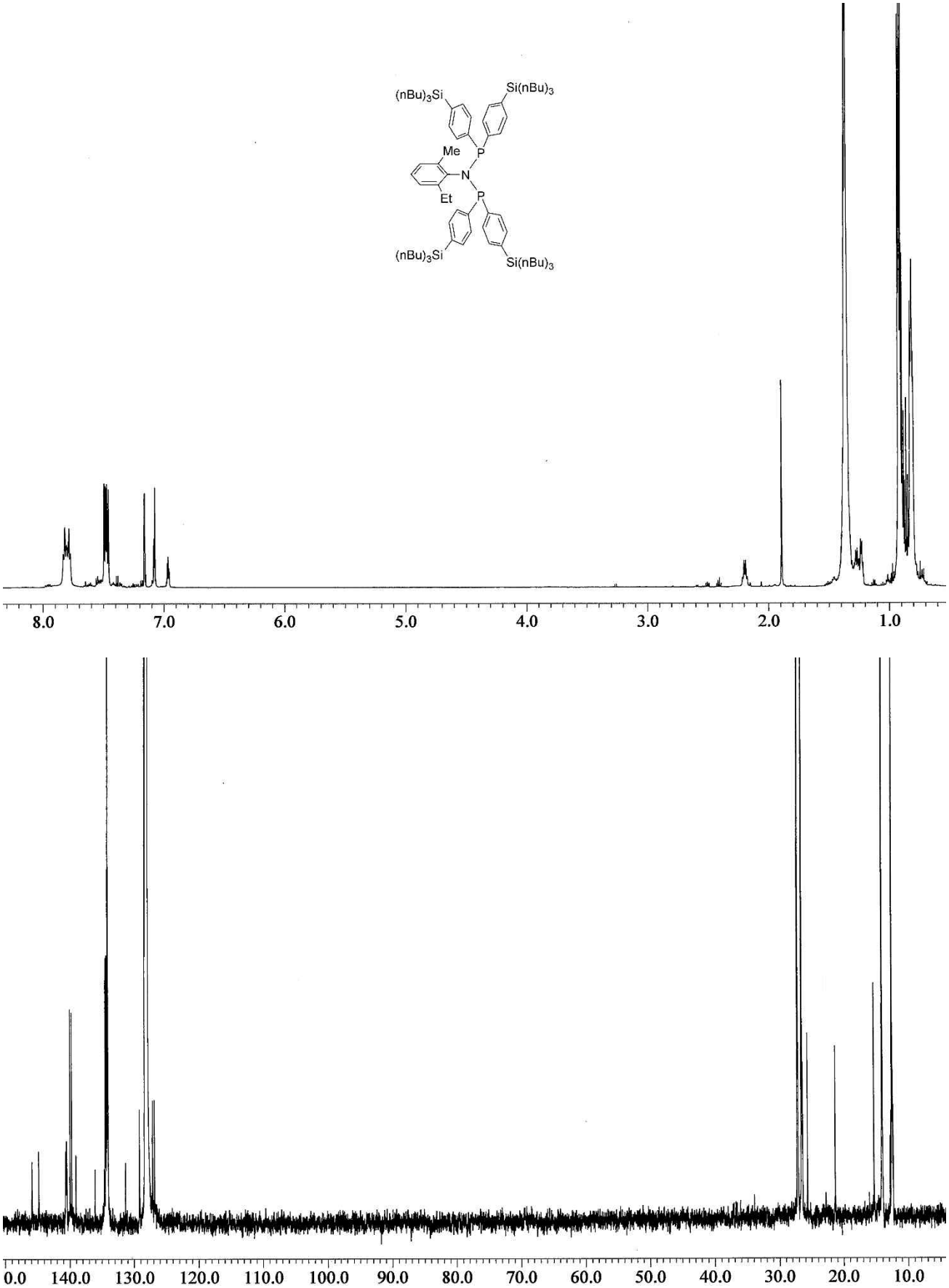


Figure S27. ^{1}H and ^{13}C NMR spectra of iPrN(H)PAr_2 (Ar = $-C_6H_4$-*p*-Si(1-decyl)$_3$) in C_6D_6.

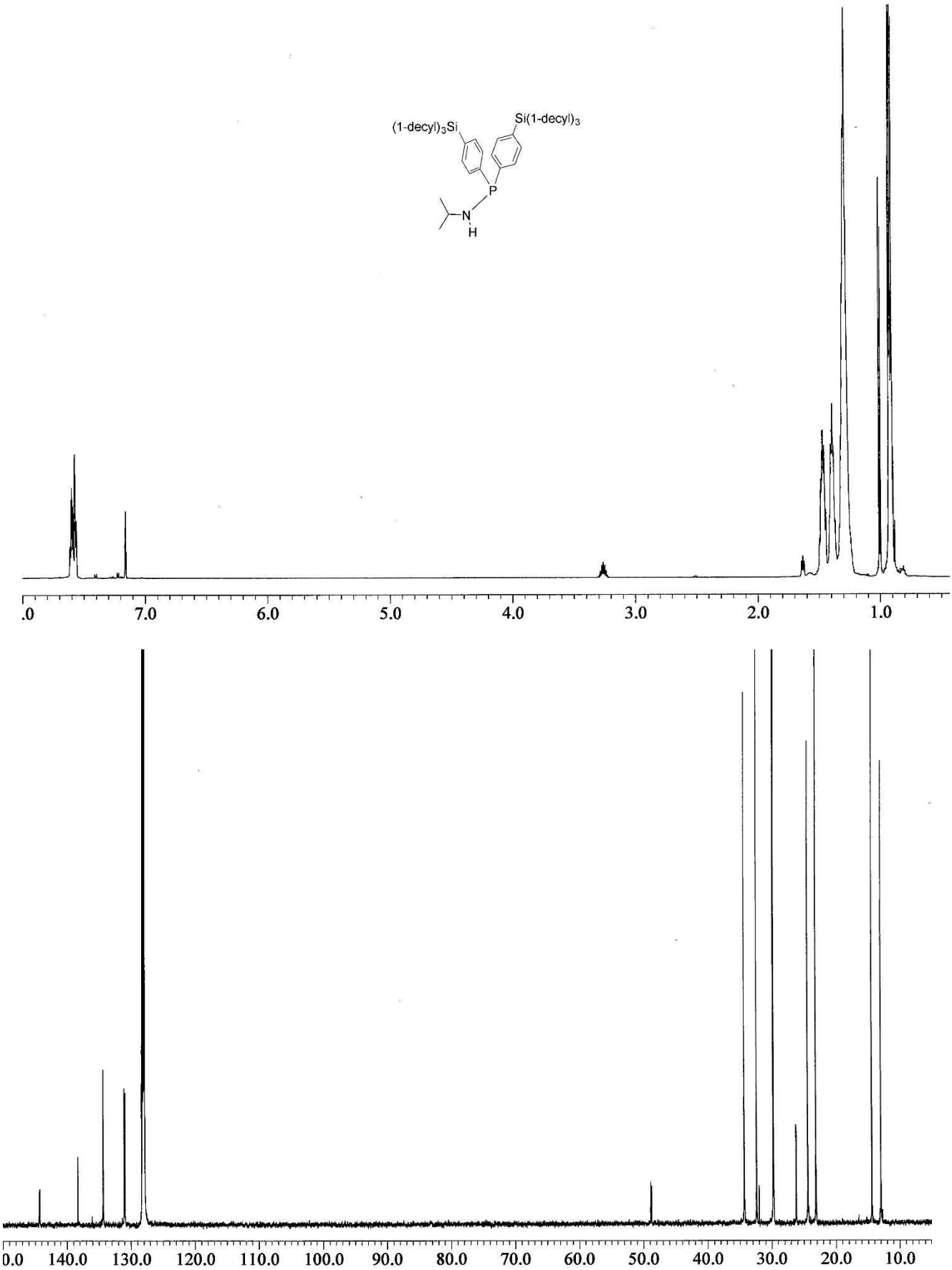


Figure S28. ^{1}H and ^{13}C NMR spectra of iPrN(PPh_2)(PAr_2) (Ar = –C_6H_4-*p*-Si(1-decyl)$_3$) in C_6D_6.

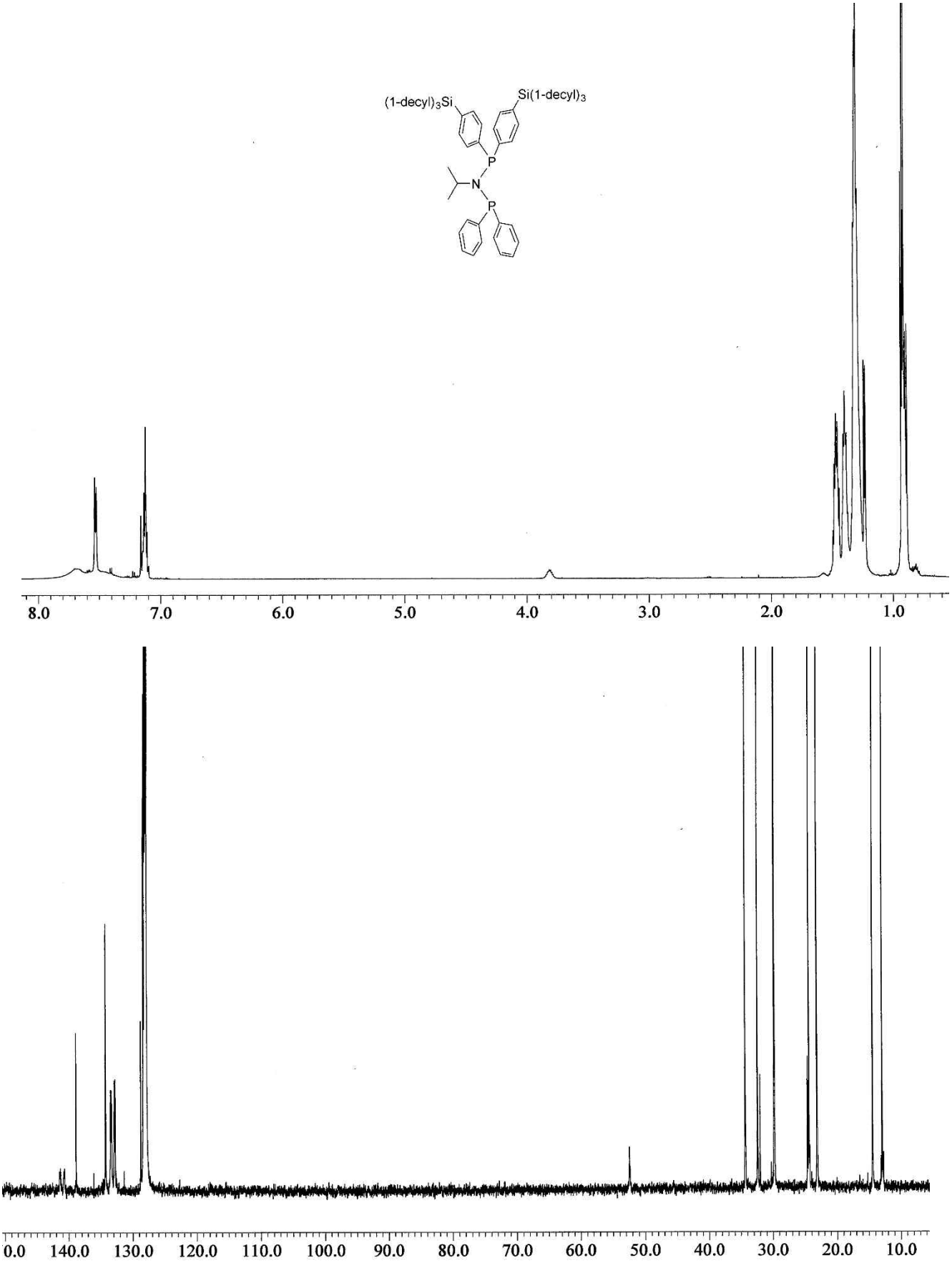


Figure S29. ^{1}H and ^{13}C NMR spectra of *ortho*-$C_6H_4N(PPh_2)(PAr_2)$ (Ar = –C_6H_4-*p*-Si(1-octyl)$_3$) in C_6D_6.