Supporting Information

Regioselective addition of C(sp^3)–H bonds of alkyl pyridines to olefins catalysed by cationic zirconium complexes

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General considerations

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk or glovebox techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 400 MHz spectrometer. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. X-ray crystallographic data were collected using a Bruker AXS D8 X-ray diffractometer. HR-MS data were recorded by Bruker ESI-TOF. Toluene and hexane were freshly distilled by refluxing over sodium/benzophenone ketyl and distilled prior to use. C_6H_5Cl, C_6D_6 and C_6D_5Cl were degassed and distilled over CaH_2. $[Ph_3C][B(C_6F_5)_4]$ purchased from Strem Chemicals, Inc. was used without purification. $ZrBn_4$, ligand precursors, and complexes **2** and **3** were prepared according to reported procedures.[1] Alkyl pyridines and alkenes were distilled over CaH_2, flushed with argon and stored over molecular sieves (4 Å). Suitable single crystals of complex **1** were sealed in a thin-walled glass capillary for determination the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo-Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections.

Synthesis and characterization of complex 1

To a solution of $ZrBn_4$ (1.37 g, 3 mmol) in toluene (5 mL) was added dropwise aniline-bridged bis(phenol) (1.59 g, 3 mmol) in toluene (5 mL) at room temperature over 15 min. After stirring for 2 hours, toluene was removed under reduced pressure and hexane (5 mL) was added to extract the residue. Complex **1** was obtained as colorless solid after the hexane solution was cooled to -30 °C (2.16 g, 90%). Crystals suitable for X-ray diffraction analyses were grown from hexane solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 7.90 (m, 2H, Ar); 7.41 (m, 2H, Ar); 7.36 (m, 2H, Ar); 7.22 (m, 1H, Ar); 6.93 (m, 2H, Ar); 6.79 (m, 2H, Ar); 6.74 (m, 4H, Ar); 6.66 (m, 2H, Ar); 6.58 (m, 1H, Ar); 6.41 (m, 2H, Ar); 3.84 (br d, *J* = 13.52 Hz, 2H, ArCH_2); 3.87 (br d, *J* = 13.52 Hz, 2H, ArCH_2); 3.30 (s, 2H, PhCH_2); 1.91 (s, 2H, PhCH_2); 1.77 (s, 18H, C(CH_3)$_3$); 1.23 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 157.0, 149.3, 142.7, 140.3, 135.0, 134.6, 130.7, 130.2, 128.0, 127.9, 126.6, 125.3, 124.5, 124.3, 123.2, 122.0, 120.9 (Ar-C), 64.0 (ArCH_2N), 59.8 (PhCH_2), 59.6 (PhCH_2), 34.4 (*C*(CH$_3$)$_3$), 33.4 (*C*(CH$_3$)$_3$), 30.9 (C(*C*H$_3$)$_3$), 29.5 (C(*C*H$_3$)$_3$). Anal. Calcd for $C_{50}H_{63}NO_2Zr$: C, 74.90; H, 7.95; N, 1.74. Found: C, 74.95; H, 7.93; N, 1.75.

General procedure for alkylation reactions

In a glovebox filled with nitrogen, PhCl solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.01 mmol) was added to PhCl solution (1 mL) of **1** (80 mg, 0.01 mmol). A color change from orange to colorless was observed immediately. After 5 min, **4** (1 mmol) and **5** (4 mmol) were added to the mixture. The resulting solution was heated at 100 °C for desired time. After reaction, solvent was removed, and the product was purified by column chromatography (petroleum ether, silica gel, 0.5% NEt_3) and obtained as viscous colorless oil.

Characterizations of alkylation products

2-methyl-6-(2-phenylpropyl)pyridine (**6a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 1H, Ar-H), 7.25-7.24 (m, 2H, Ar-H), 7.21-7.14 (m, 3H, Ar-H), 6.92 (d, 1H, J = 6.92 Hz, Ar-H), 6.71 (d, 2H, J = 6.71 Hz, Ar-H), 3.31-3.22 (m, 1H, CH), 3.08-2.94 (m, 2H, CH_2), 2.53 (s, 3H, CH_3), 1.27 (d, 2H, J = 6.92Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 160.0, 157.7, 146.8, 136.2, 128.3, 127.1, 126.0, 120.5, 119.4, 47.1, 40.5, 24.6, 21.6. HR MS (ESI+): Found 212.1432 $[M+H]^+$, calcd. for $C_{15}H_{18}N^+$: 212.1439.

2-methyl-6-(3-phenylpropyl)pyridine (**6a'**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.49 (m, 1H, Ar-H), 7.33-7.27 (m, 2H, Ar-H), 7.24-7.19 (m, 3H, Ar-H), 7.00-6.96 (m, 2H, Ar-H), 2.83 (t, 2H, J = 7.76 Hz, CH_2), 2.72 (t, 2H, J = 7.68 Hz, CH_2), 2.56 (s, 3H, CH_3), 2.07 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 160.9, 157.3, 141.8, 136.0, 128.0, 127.8, 125.2, 120.0, 119.4, 37.6, 35.2, 31.3, 24.0. HR MS (ESI+): Found 212.1433 $[M+H]^+$, calcd. for $C_{15}H_{18}N^+$: 212.1439.

2-methyl-6-(2-(p-tolyl)propyl)pyridine (**6b**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.34 (m, 1H, Ar-H), 7.09-7.04 (m, 4H, Ar-H), 6.91 (d, 1H, J = 7.6 Hz, Ar-H), 6.71 (d, 1H, J = 7.6 Hz, Ar-H), 3.25-3.16 (m, 1H, CH), 3.01-2.89 (m, 2H, CH_2), 2.52 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 1.22 (d, 2H, J = 6.90 Hz, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): 160.1, 157.7, 143.8, 136.2, 135.4, 129.0, 126.9, 120.5, 47.1, 40.7, 24.6, 21.7, 21.0. HR MS (ESI+): Found 226.1599 $[M+H]^+$, calcd. for $C_{16}H_{20}N^+$: 226.1596.

2-(2-(4-(tert-butyl)phenyl)propyl)-6-methylpyridine (**6c**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 1H, Ar-H), 7.29-7.26 (m, 2H, Ar-H), 7.14-7.10 (m, 2H, Ar-H).

6.92 (d, 1H, J = 7.6 Hz, Ar-H), 6.75 (d, 1H, J = 7.6 Hz, Ar-H), 3.24-3.15 (m, 1H, CH), 3.07-2.87 (m, 2H, CH_2), 2.52 (s, 3H, CH_3), 1.28 (s, 3H, $C(CH_3)_3$), 1.21 (d, 2H, J = 6.90 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 160.2, 157.6, 148.7, 136.2, 128.1, 126.6, 125.1, 120.5, 47.1, 39.8, 34.3, 31.4, 24.6, 21.3. HR MS (ESI+): Found 268.2066 $[M+H]^+$, calcd. for $C_{19}H_{26}N^+$: 268.2065.

2-(2-(4-fluorophenyl)propyl)-6-methylpyridine (**6e**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 1H, Ar-H), 7.13-7.07 (m, 2H, Ar-H), 6.93-6.88 (m, 3H, Ar-H), 6.65 (d, 1H, J = 7.6 Hz, Ar-H), 3.27-3.18 (m, 1H, CH), 2.98-2.89 (m, 2H, CH_2), 2.50 (s, 3H, CH_3), 1.21 (d, 2H, J = 6.92 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 159.6, 157.7, 142.3, 136.2, 128.3, 120.6, 120.4, 115.0, 114.8, 47.2, 39.7, 24.6, 21.7. HR MS (ESI+): Found 230.1344 $[M+H]^+$, calcd. for $C_{15}H_{17}FN^+$: 230.1345.

2-(2-(4-chlorophenyl)propyl)-6-methylpyridine (**6f**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (m, 1H, Ar-H), 7.19-7.17 (m, 2H, Ar-H), 7.09-7.06 (m, 2H, Ar-H), 6.90 (d, 1H, J = 7.6 Hz, Ar-H), 6.65 (d, 1H, J = 7.6 Hz, Ar-H), 3.27-3.18 (m, 1H, CH), 2.99-2.90 (m, 2H, CH_2), 2.51 (s, 3H, CH_3), 1.23 (d, 2H, J = 6.92 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 159.5, 157.8, 145.2, 136.2, 128.5, 128.3, 120.7, 120.5, 46.9, 39.9, 24.5, 21.6. HR MS (ESI+): Found 246.1055 $[M+H]^+$, calcd. for $C_{15}H_{17}ClN^+$: 246.1050.

2-methyl-6-(2-(m-tolyl)propyl)pyridine (6g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, 1H, *J* = 7.6 Hz, Ar-*H*), 7.17-7.13 (m, 1H, Ar-*H*), 7.01-6.97 (m, 3H, Ar-*H*), 6.94-6.92 (m, 1H, Ar-*H*), 6.74 (d, 1H, *J* = 7.6 Hz, Ar-*H*), 3.08-3.02 (m, 1H, C*H*$_2$), 2.96-2.91 (m, 1H, C*H*$_2$), 2.54 (s, 3H, C*H*$_3$), 2.51 (s, 3H, C*H*$_3$), 2.07-1.99 (m, 2H, C*H*).

1.24 (d, 3H, *J* = 6.92Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 159.6, 157.2, 146.4, 137.2, 135.7, 127.6, 127.4, 126.2, 123.6, 120.0, 46.6, 39.8, 24.1, 21.0.

2-methyl-6-(2-(m-tolyl)propyl)pyridine (6h). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, 1H, *J* = 7.6 Hz, Ar-*H*), 7.18-7.12 (m, 3H, Ar-*H*), 7.07-7.04 (m, 1H, Ar-*H*), 6.95-6.92 (m, 1H, Ar-*H*), 6.71 (d, 1H, *J* = 7.6 Hz, Ar-*H*), 3.02-2.91 (m, 2H, C*H*$_2$), 2.53 (s, 3H, C*H*$_3$), 2.51 (s, 3H, C*H*$_3$), 2.09-1.99 (m, 2H, C*H*). 1.25 (d, 3H, *J* = 6.92Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):160.5, 158.9, 157.3, 148.4, 135.8, 129.0, 126.8, 125.7, 124.9, 120.2, 49.3, 39.7, 24.0, 20.9.

2-(2-(3-fluorophenyl)propyl)-6-methylpyridine (6i). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.8 (t, 1H, *J* = 7.7 Hz, Ar-*H*), 7.25-7.21 (m, 1H, Ar-*H*), 7.16-7.11 (m, 1H, Ar-*H*), 7.06-7.02 (m, 1H, Ar-*H*), 6.97-6.92 (m, 2H, Ar-*H*), 6.79-6.77 (d, 1H, *J* = 7.6 Hz, Ar-*H*), 3.13-2.97 (m, 2H, C*H*$_2$), 2.52 (s, 3H, C*H*$_3$), 2.07-1.99 (m, 1H, C*H*$_3$), 1.27 (d, 2H, *J* = 6.92Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 158.2, 157.2, 136.1, 135.8, 127.9, 127.8, 126.9, 126.8, 123.5, 120.1, 120.0, 119.7, 119.0, 114.9, 114.7, 44.8, 37.6, 33.5, 24.0, 19.8.

2-methyl-6-(2-methyloctyl)pyridine (**6j**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.40 (m, 1H, Ar-H), δ 6.92-6.86 (m, 2H, Ar-H), 2.75-2.70 (m, 1H, CH), 2.52-2.46 (m, 4H, alkyl-H), 1.93-1.86 (m, 1H, CH), 1.29-1.13 (m, 14H, alkyl-H), 0.86-0.82 (m, 6H, alkyl-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.0, 157.6, 136.1, 120.4, 120.3, 46.2, 36.8, 33.9, 31.9, 29.6, 26.9, 24.6, 22.7, 19.3, 14.1. HR MS (ESI+): Found 206.1910 $[M+H]^+$, calcd. for $C_{14}H_{24}N^+$: 206.1909.

2-methyl-6-(2-methylhexyl)pyridine (**6k**). ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.52-7.48 (m, 1H, Ar-H), δ 7.00-6.93 (m, 2H, Ar-H), 2.82-2.77 (m, 1H, CH), 2.59-2.53 (m, 4H, alkyl-H), 2.02-1.91 (m, 1H, CH), 1.40-1.18 (m, 6H, alkyl-H), 0.93-0.89 (m, 5H, alkyl-H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 160.5, 157.1, 135.6, 119.9, 119.8, 45.7, 36.0, 33.4, 28.7, 24.1, 22.4, 18.8, 13.6. HR MS (ESI+): Found 192.1751 $[M+H]^+$, calcd. for $C_{13}H_{22}N^+$: 192.1752.

2-(bicyclo[2.2.1]heptan-2-ylmethyl)-6-methylpyridine (**6l**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.38 (m, 1H, Ar-H), 6.90-6.85 (m, 2H, Ar-H), 2.69-2.64 (m, 1H, CH), 2.53-2.47 (m, 4H, alkyl-H), 2.17 (s, 1H, CH), 1.95 (s, 1H, CH), 1.90-1.82 (m, 1H, CH), 1.90-1.82 (m, 1H, CH), 1.46-1.21 (m, 6H, alkyl-H), 1.13-1.04 (m, 4H, alkyl-H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 160.8, 157.6, 136.2, 120.3, 120.0, 45.2, 42.4, 40.7, 37.7, 36.8, 35.3, 29.9, 28.8, 24.6. HR MS (ESI+): Found 202.1596 $[M+H]^+$, calcd. for $C_{14}H_{20}N^+$: 202.1596.

2,6-bis(bicyclo[2.2.1]heptan-2-ylmethyl)pyridine (**6m**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 1H, Ar-H), 6.89 (d, 2H, J = 7.6 Hz Ar-H), 2.72-2.67 (m, 2H, CH), 2.58-2.53 (m, 2H, CH_2), 2.19 (s, 2H, CH), 1.97 (s, 2H, CH), 1.93-1.86 (m, 2H, CH_2), 1.46-1.32 (m, 9H, alkyl-H), 1.16-1.07 (m, 7H, alkyl-H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 160.4, 135.6, 119.8, 44.6, 42.0, 40.2, 40.1, 37.2, 36.4, 34.8, 29.5, 28.4. HR MS (ESI+): Found 296.2377 $[M+H]^+$, calcd. for $C_{21}H_{30}N^+$: 296.2378.

2-((3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-6-yl)methyl)-6-methylpyridine (6n) + **2-((3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-5-yl)methyl)-6-methylpyridine** (**6n'**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.38 (m, 1H, Ar-H), 6.91-6.85 (m, 2H,

Ar-H), 5.61-5.58 (m, 1H, CH=CH), 5.47-5.46 (m, 1H, CH=CH), 3.03-2.93 (m, 1H, CH), 2.66-2.41 (m, 6H, alkyl-H), 2.19-1.84 (m, 5H, alkyl-H), 1.68-1.21 (m, 4H, alkyl-H), 0.97-0.85 (m, 1H, CH). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):δ 161.0, 157.6, 136.2, 132.4, 131.1, 130.6, 120.3, 119.9, 53.6, 52.3, 45.2, 44.8, 43.9, 42.4, 41.8, 41.4, 40.3, 38.3, 37.0, 34.0, 33.4, 32.3, 31.9, 29.9, 24.6. HR MS (ESI+): Found 240.1751$[M+H]^+$, calcd. for $C_{17}H_{22}N^+$: 240.1752.

2-(cyclohex-2-en-1-ylmethyl)-6-methylpyridine (**6o**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 1H, Ar-H), δ 6.95-6.89 (m, 2H, Ar-H), 5.69-5.53 (m, 2H CH=CH), 2.74-2.68 (m, 2H, CH), 2.52 (s, 3H, CH_3), 2.11-1.94 (m, 3H, alkyl-H), 1.78-1.68 (m, 2H, CH_2), 1.35-1.25 (m, 1H, CH). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):δ 160.3, 157.7, 136.1, 126.9, 126.3, 120.4, 45.3, 44.9, 34.4, 31.5, 28.5, 25.0, 25.6, 21.2. HR MS (ESI+): Found 188.1436 $[M+H]^+$, calcd. for $C_{13}H_{18}N^+$: 188.1439.

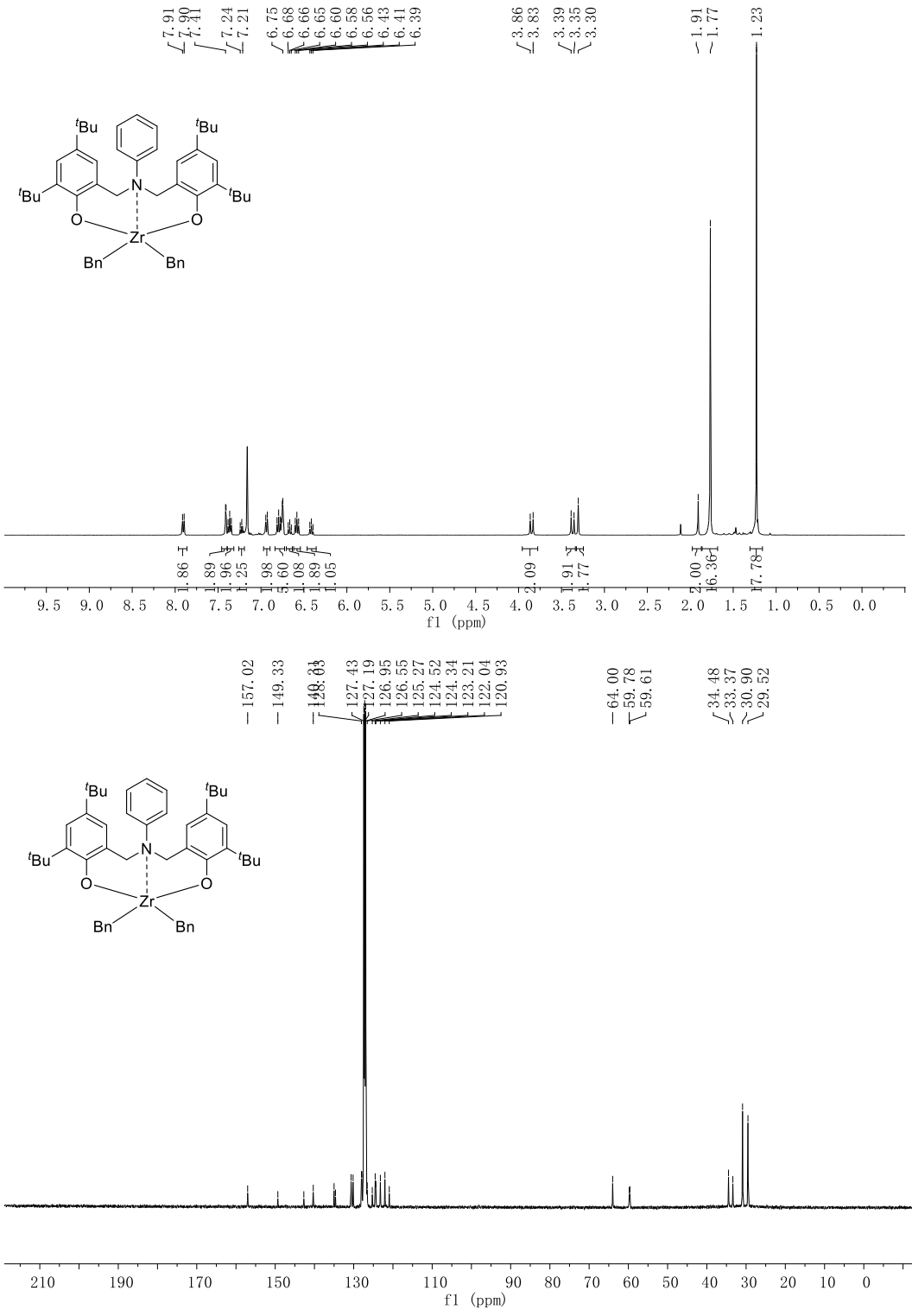
2,4-dimethyl-6-(2-methylhexyl)pyridine (**7b**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, 2H, J = 19.8 Hz, Ar-H), 2.71-2.66 (m, 1H, CH), 2.47-2.41 (m, 4H, alkyl-H), 2.24 (s, 3H, CH_3), 1.93-1.85 (m, 1H, CH), 1.34-1.10 (m, 6H, alkyl-H), 0.86-0.81 (m, 6H, alkyl-H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 156.8, 146.5, 120.9, 45.5, 36.1, 33.4, 28.8, 23.9, 22.5, 20.4, 18.8, 13.6. HR MS (ESI+): Found 206.1908 $[M+H]^+$, calcd. for $C_{14}H_{24}N^+$: 206.1909.

2-(2-methylhexyl)quinoline (**7c**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.01 (m, 2H, Ar-H), 7.75 (d, 2H, J = 8.1 Hz Ar-H), 7.67-7.63 (m, 1H, Ar-H), 7.47-7.43 (m, 1H, Ar-H), 7.25-7.23 (m, 1H, Ar-H), 3.00-2.95 (m, 1H, CH_2), 2.76-2.71 (m, 1H, CH_2), 2.09-2.02 (m, 1H, CH), 1.41-1.22 (m, 6H, alkyl-H), 0.90-0.84 (m, 6H, alkyl-H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 161.9, 147.5, 135.4, 128.8, 128.4, 127.0, 126.2, 125.1, 121.6, 46.4, 36.20, 33.6, 28.8, 22.4, 19.0, 13.6. HR MS (ESI+): Found 228.1755 $[M+H]^+$, calcd. for $C_{16}H_{22}N^+$: 228.1752.

^{1}H and ^{13}C NMR spectra. Minor set of signals in spectra of compounds 6b, c, e, and f correspond to linear alkylation products.

Complex 1



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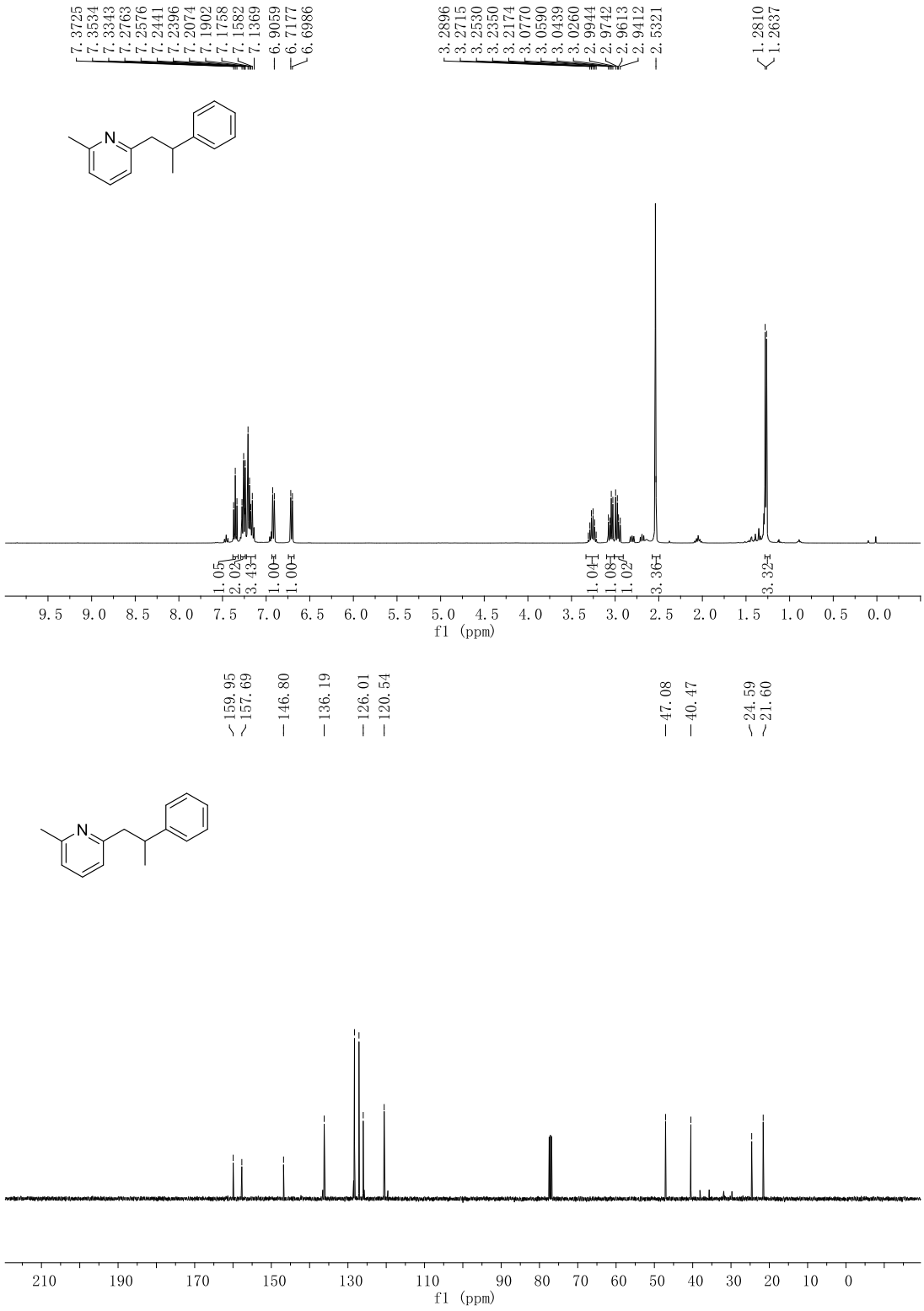
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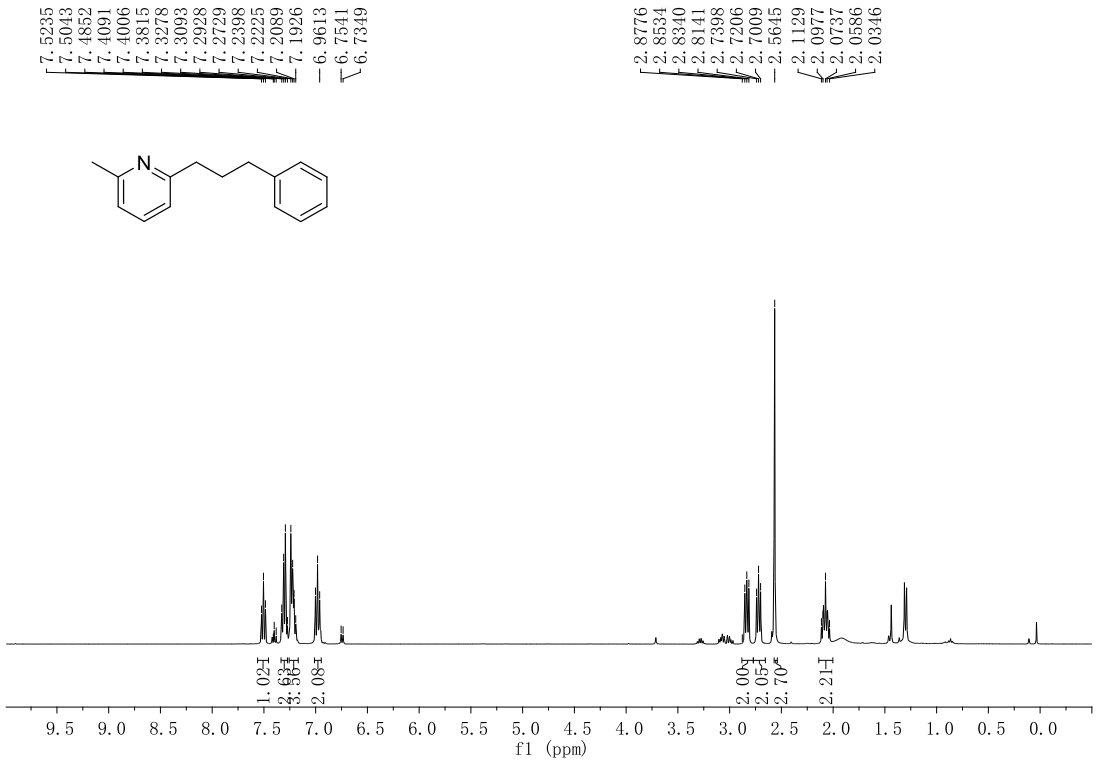
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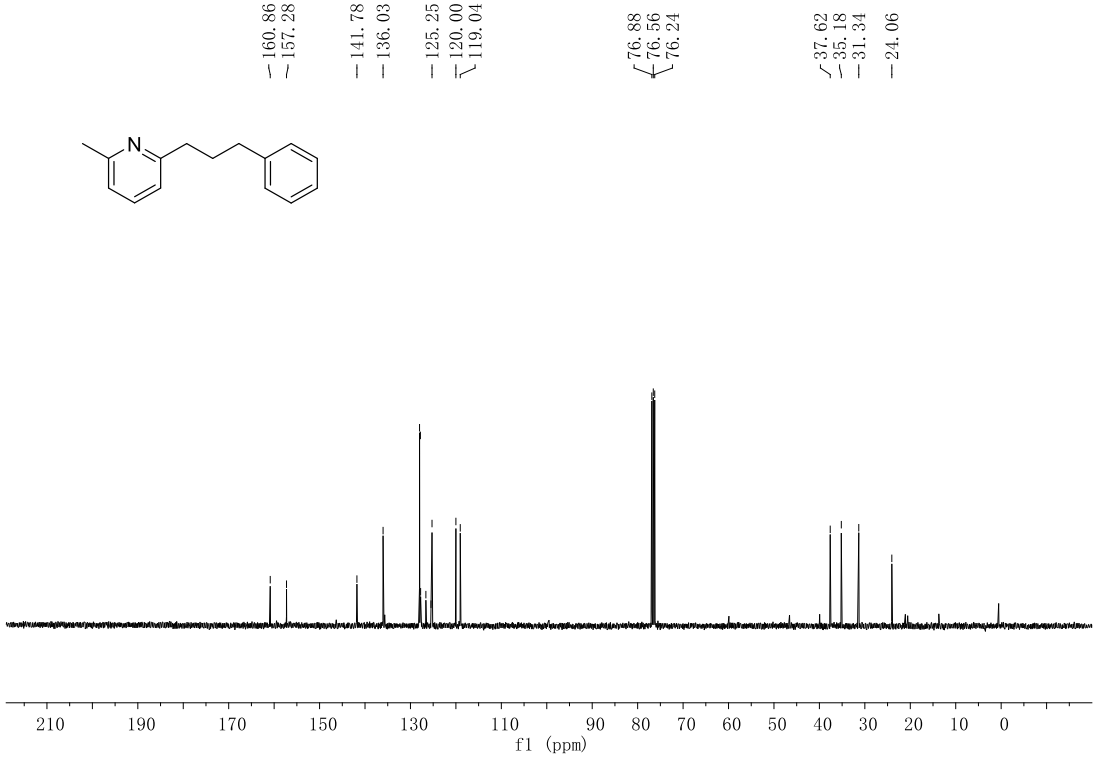
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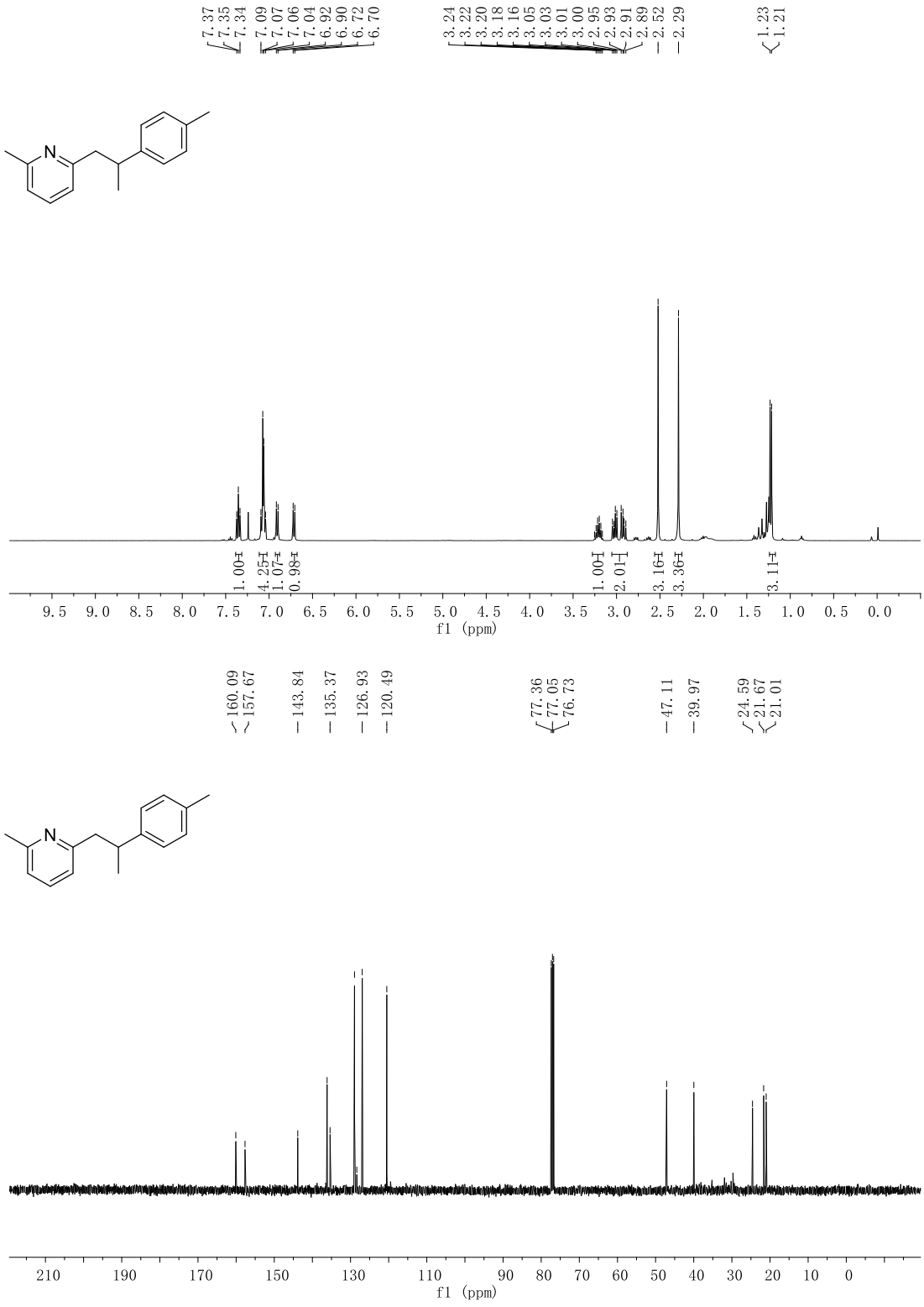
6b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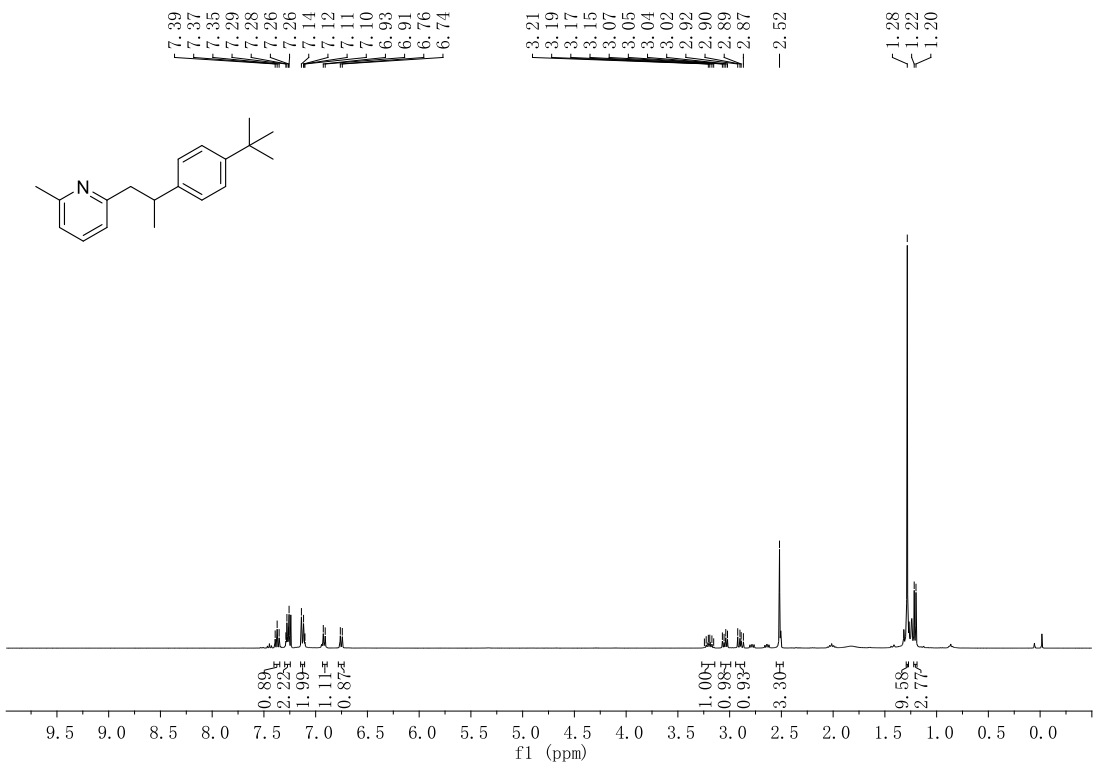
2.91
2.89
2.52
2.29
1.23
1.21
1.00
4.25
1.07
0.98
1.00
2.01
3.16
3.36
3.11
f1 (ppm)
160.09
157.67
143.84
135.37
126.93
120.49
77.36
77.05
76.73
47.11
39.97
24.59
21.67
21.01
f1 (ppm)

6c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7.14
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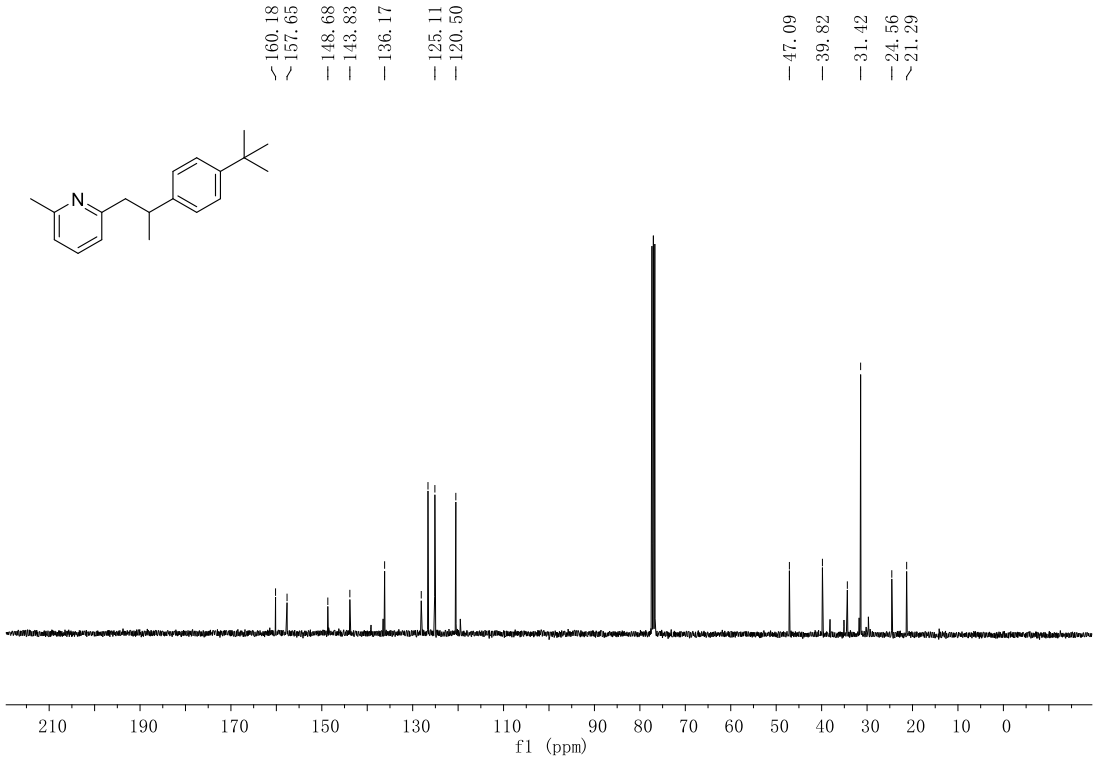
7.11
7.10
6.93
6.91
6.76
6.74
3.21
3.19
3.17
3.15
3.07
3.05
3.04
3.02
2.92
2.90
2.89
2.87
2.52
1.28
1.22
1.20
N
0.89
2.22
1.99
1.11
0.87
1.00
0.98
0.93
3.30
9.58
2.77
f1 (ppm)


160.18
157.65
148.68
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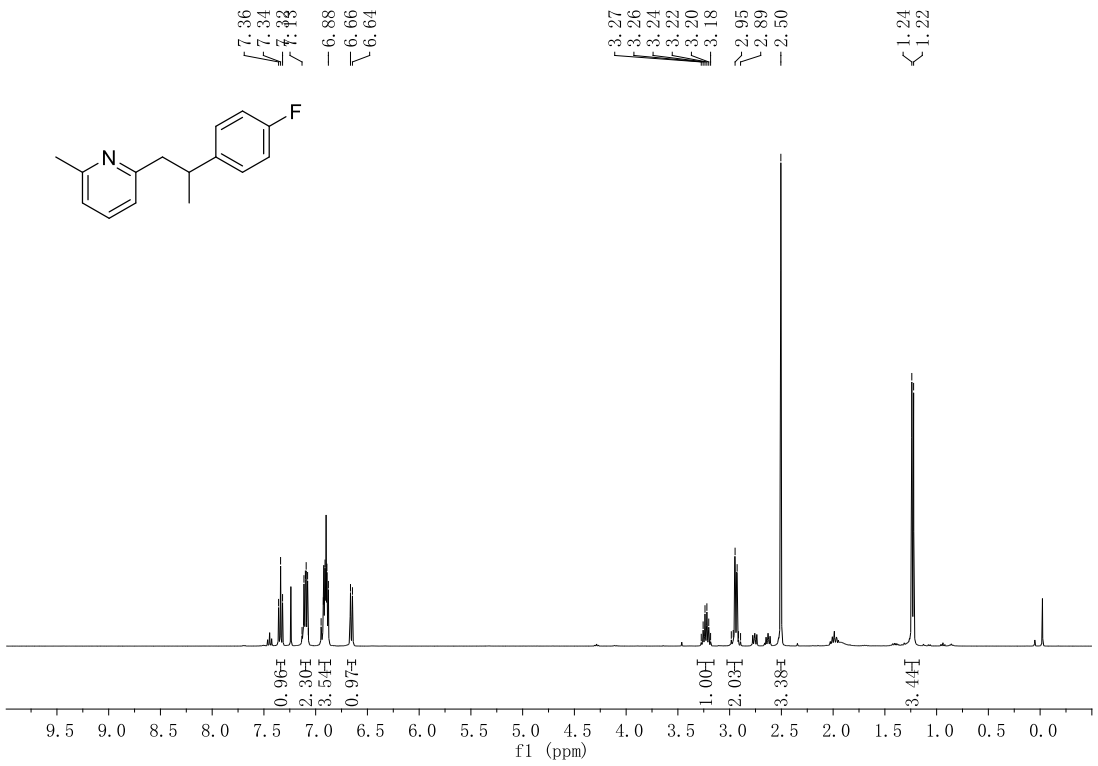
136.17
125.11
120.50
47.09
39.82
31.42
24.56
21.29
N
f1 (ppm)

6e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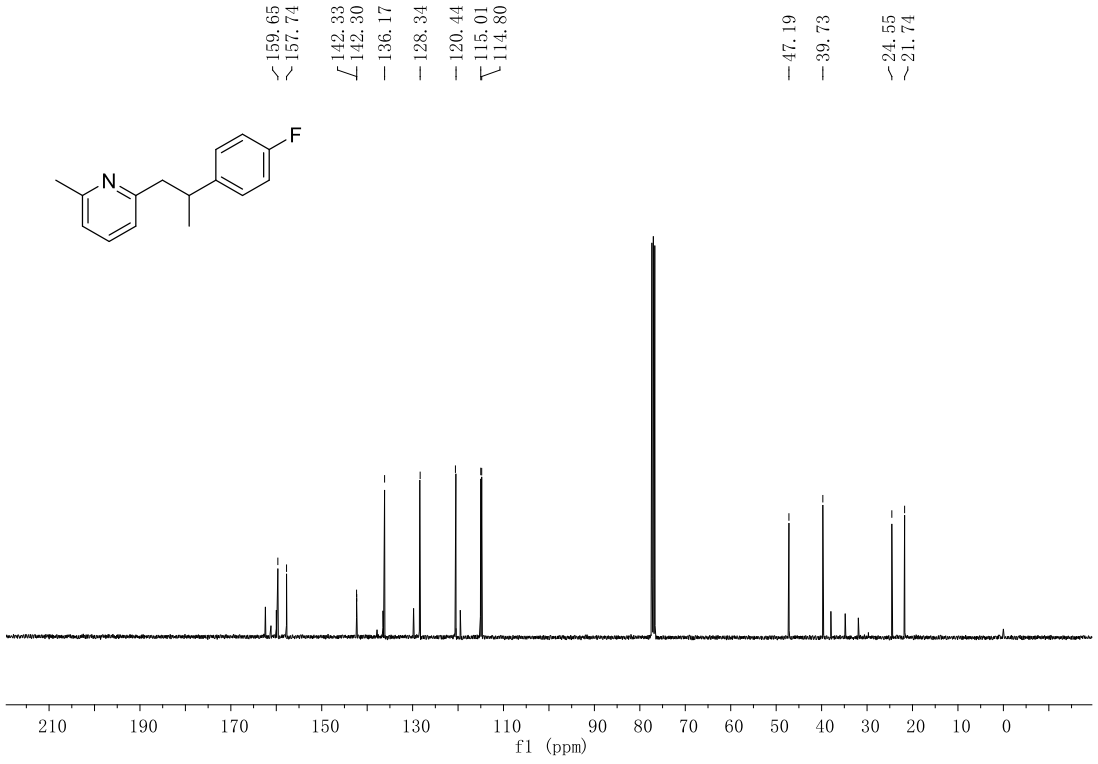
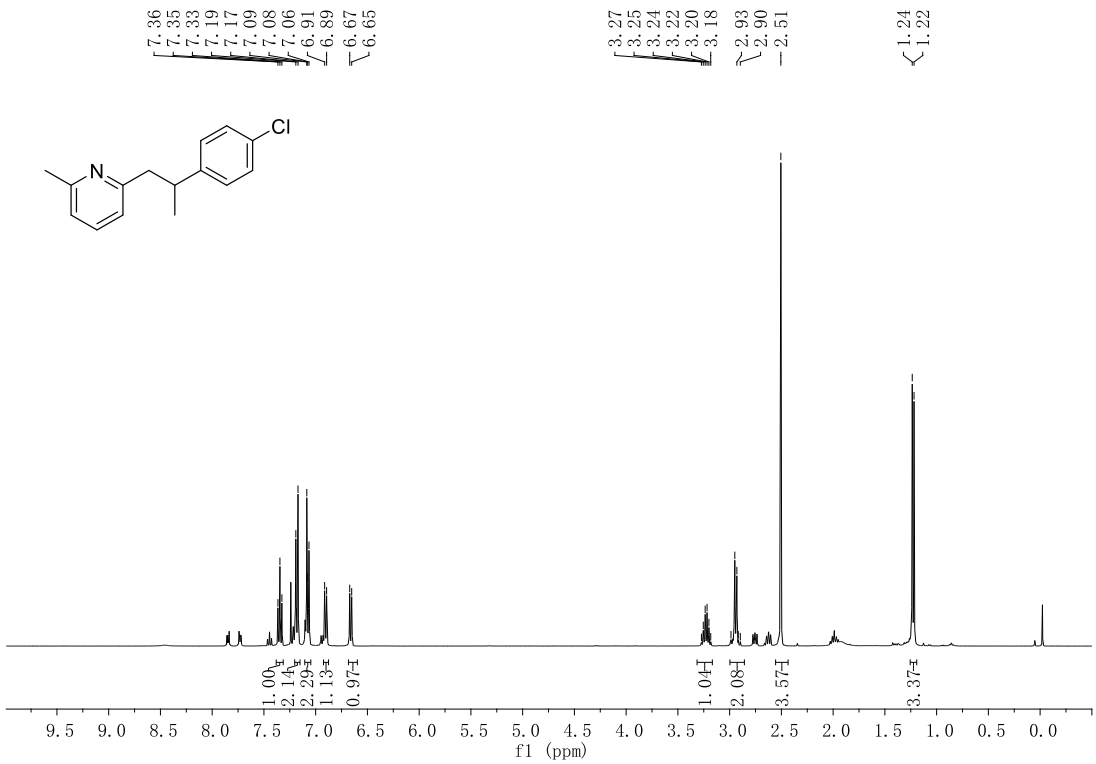
7.13
6.88
6.66
6.64
3.27
3.26
3.24
3.22
3.20
3.18
2.95
2.89
2.50
1.24
1.22
F
N
0.96
2.30
3.54
0.97
1.00
2.03
3.38
3.44
f1 (ppm)


159.65
157.74
142.33
142.30
136.17
128.34
120.44
115.01
114.80
47.19
39.73
24.55
21.74
F
N
f1 (ppm)

6f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7.17
7.09
7.08
7.06
6.91
6.89
6.67
6.65
3.27
3.25
3.24
3.22
3.20
3.18
2.93
2.90
2.51
1.24
1.22
Cl
N
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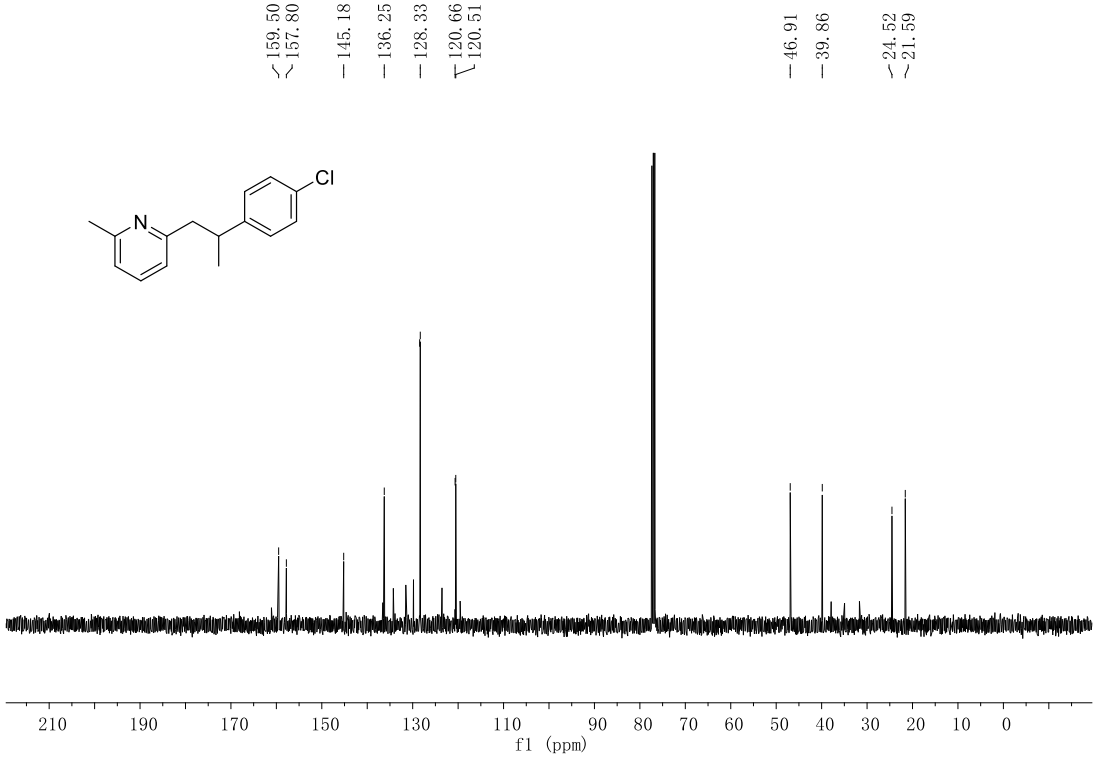
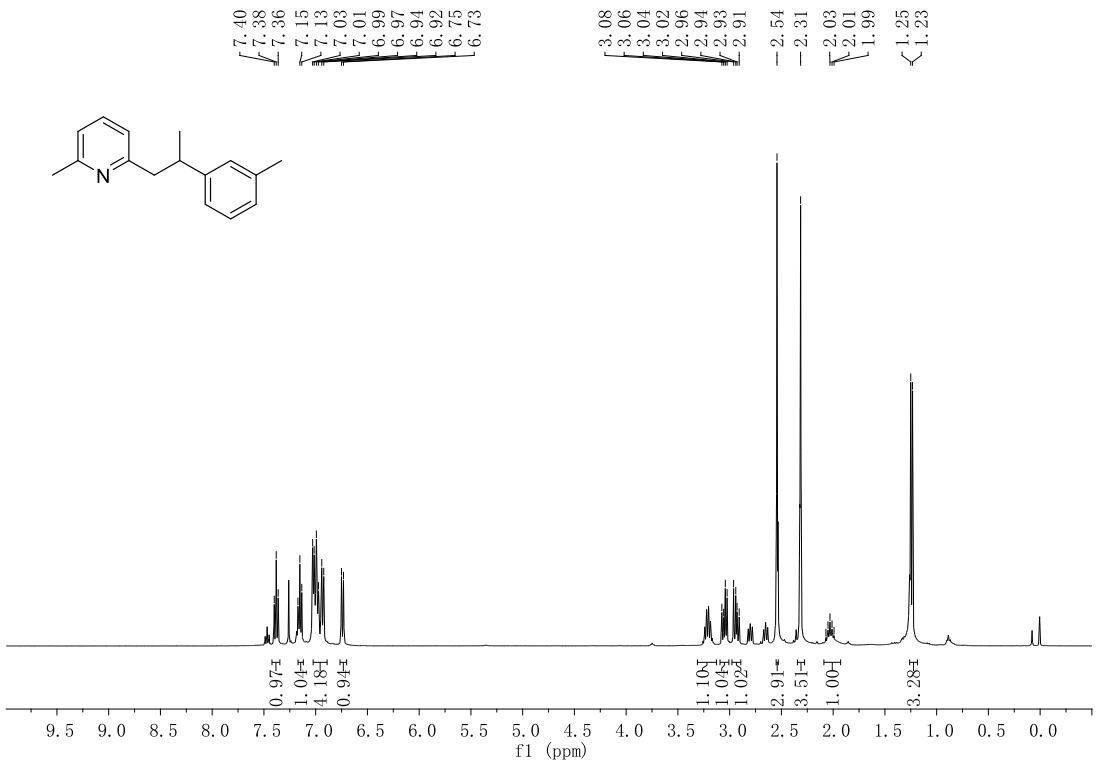
2.14
2.29
1.13
0.97
1.04
2.08
3.57
3.37
f1 (ppm)


159.50
157.80
145.18
136.25
128.33
120.66
120.51
46.91
39.86
24.52
21.59
Cl
N
f1 (ppm)

6g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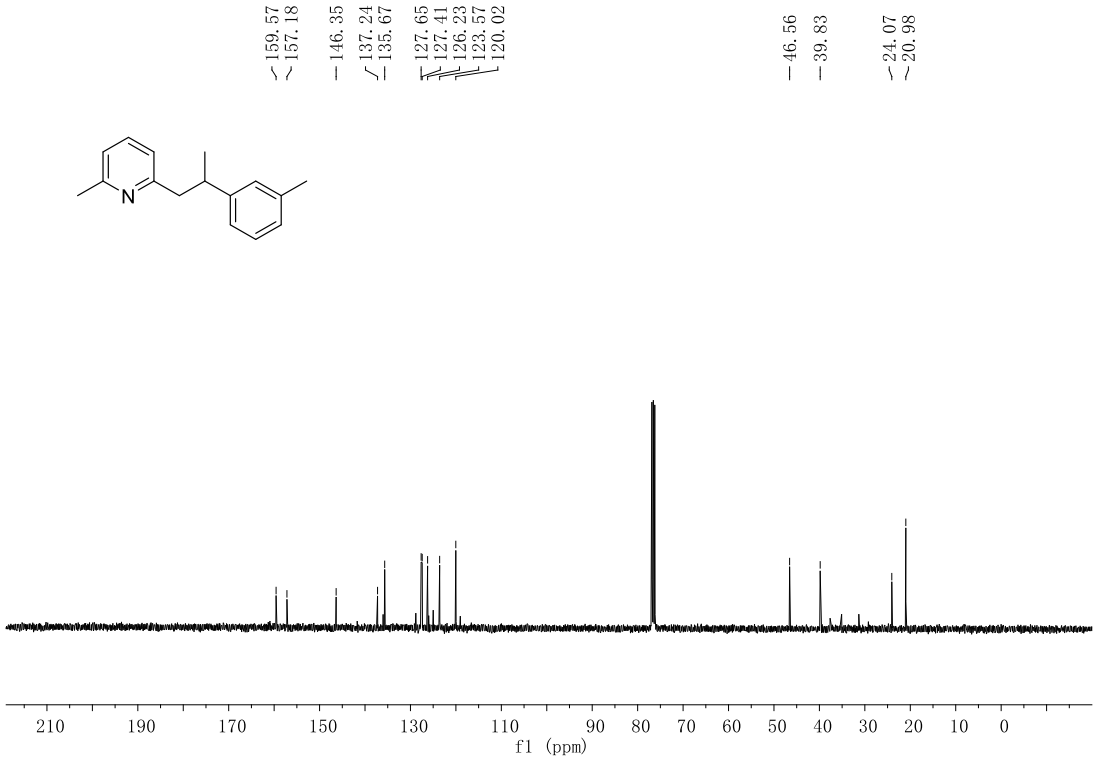
7.03
7.01
6.99
6.97
6.94
6.92
6.75
6.73
3.08
3.06
3.04
3.02
2.96
2.94
2.93
2.91
2.54
2.31
2.03
2.01
1.99
1.25
1.23
0.97
1.04
4.18
0.94
1.10
1.04
1.02
2.91
3.51
1.00
3.28
f1 (ppm)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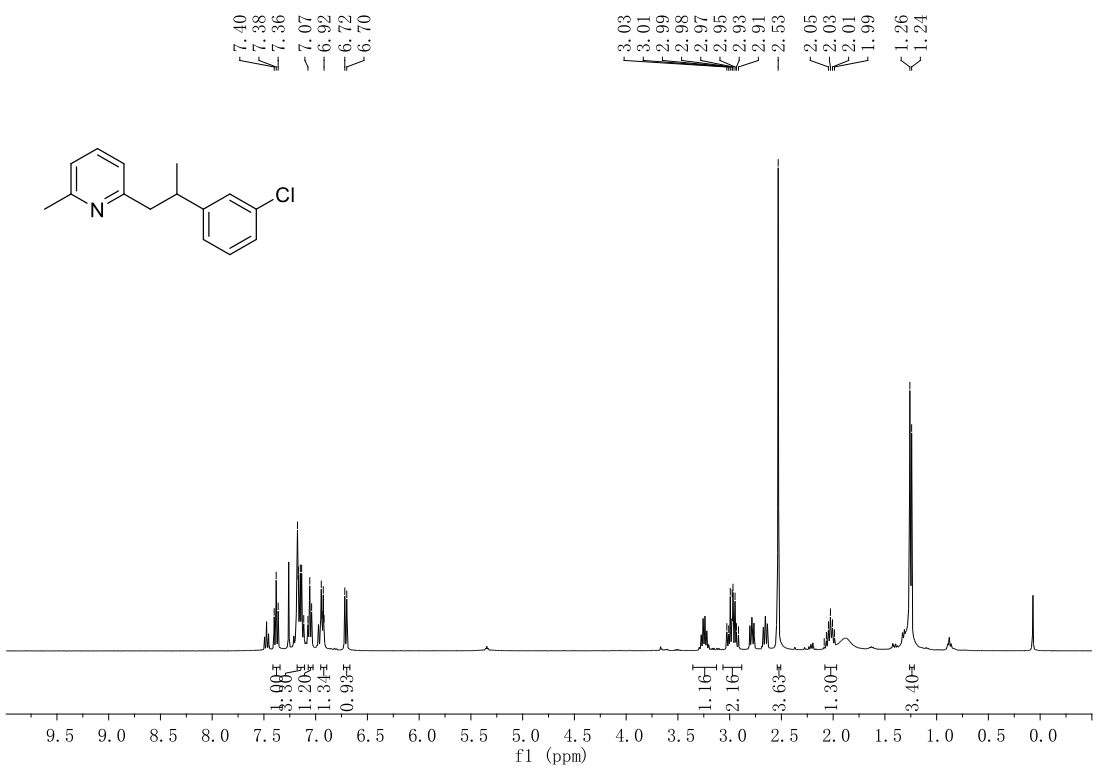
157.18
146.35
137.24
135.67
127.65
127.41
126.23
123.57
120.02
46.56
39.83
24.07
20.98
f1 (ppm)

6h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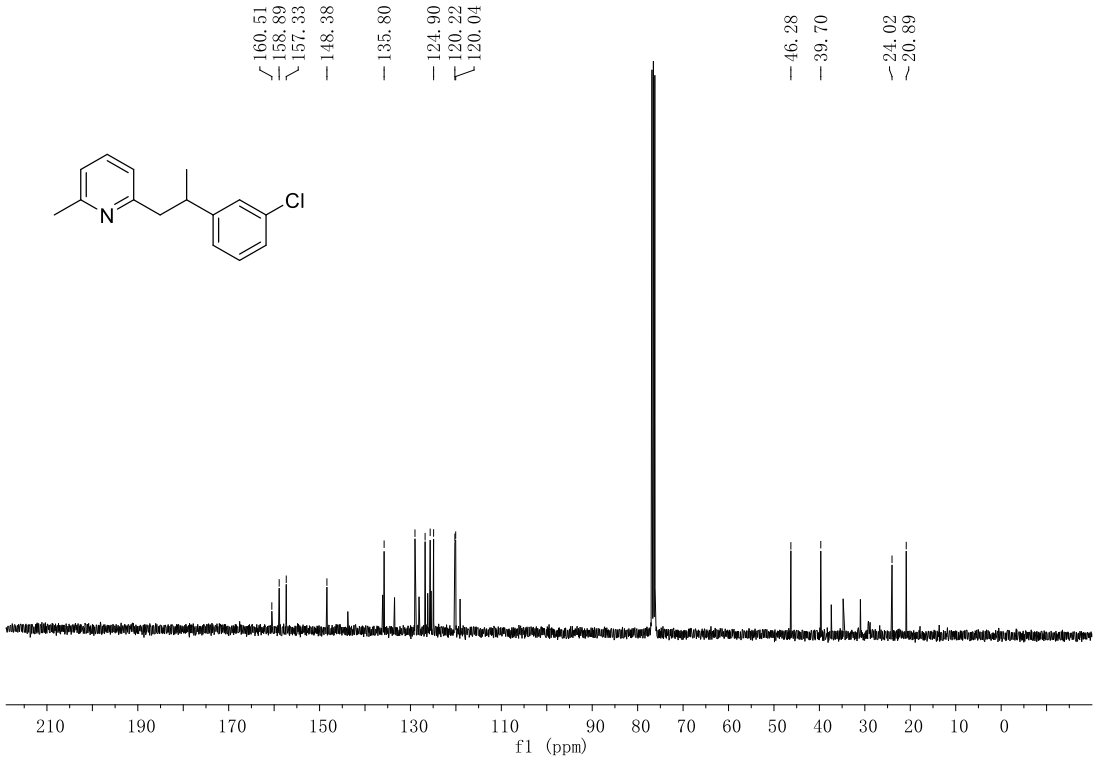
7.38
7.36
7.07
6.92
6.72
6.70
3.03
3.01
2.99
2.98
2.97
2.95
2.93
2.91
2.53
2.05
2.03
2.01
1.99
1.26
1.24
Cl
N
1.00
3.35
1.20
1.34
0.93
1.16
2.16
3.63
1.30
3.40
f1 (ppm)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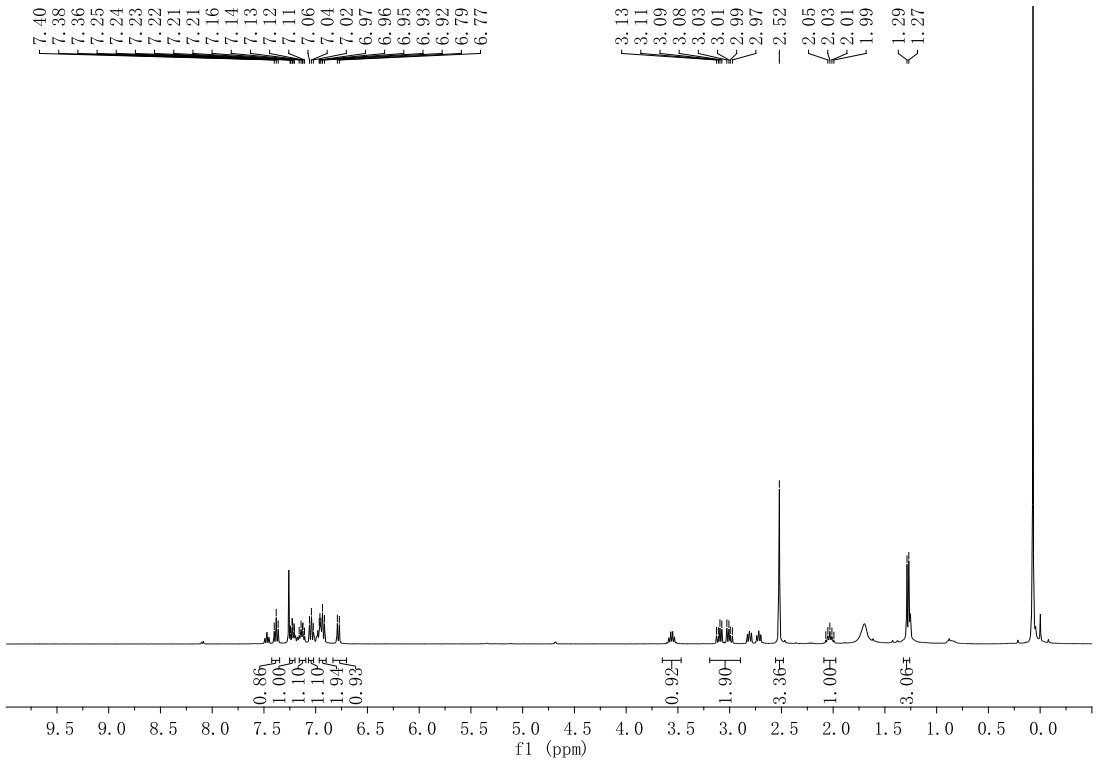
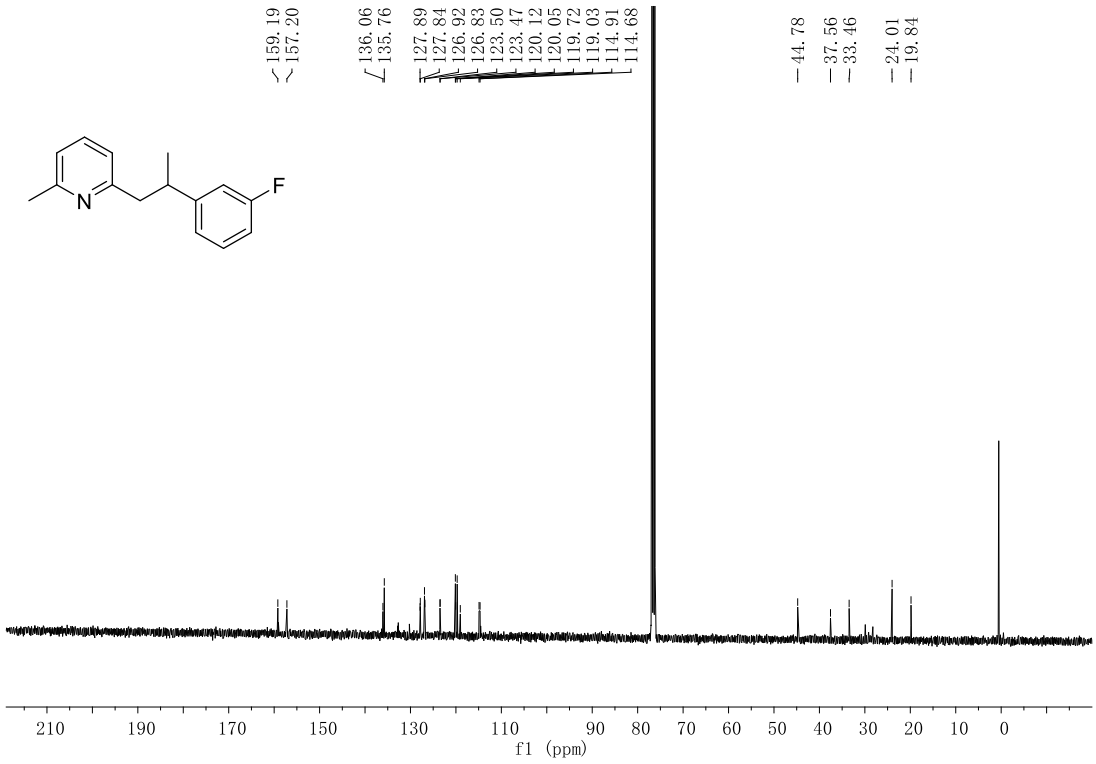
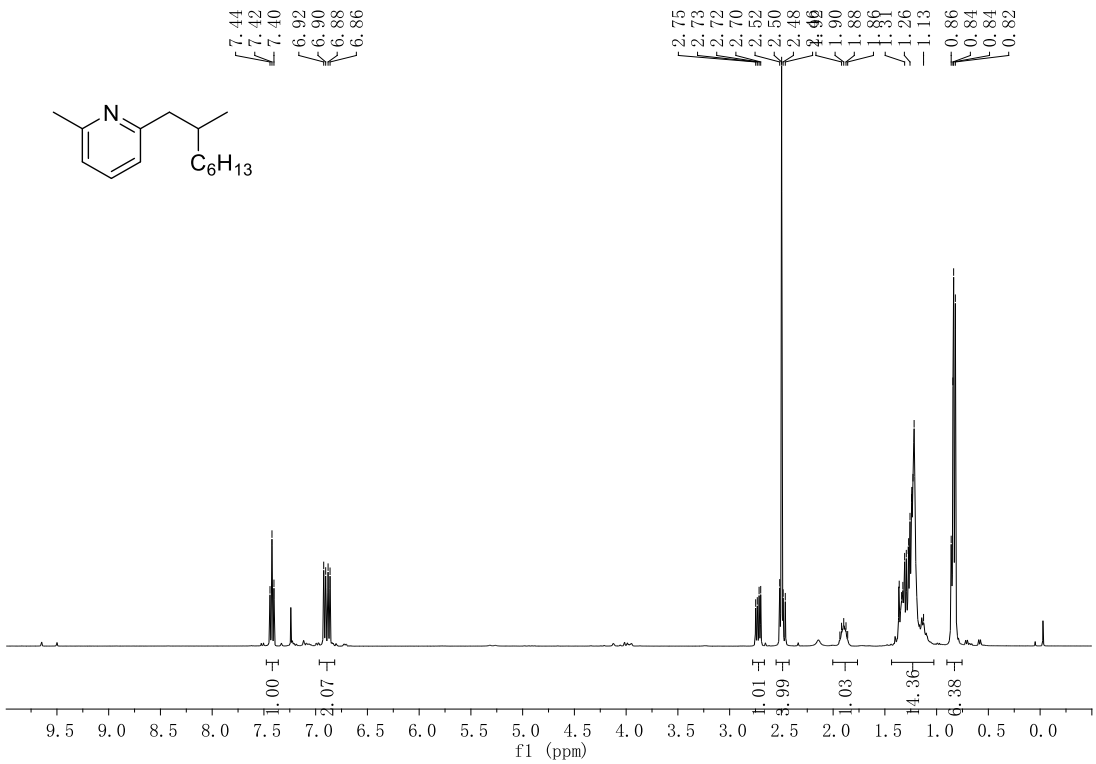
157.33
148.38
135.80
124.90
120.22
120.04
46.28
39.70
24.02
20.89
Cl
N
f1 (ppm)

6i


7.40
7.38
7.36
7.25
7.24
7.23
7.22
7.21
7.21
7.16
7.14
7.13
7.12
7.11
7.06
7.04
7.02
6.97
6.96
6.95
6.93
6.92
6.79
6.77
3.13
3.11
3.09
3.08
3.03
3.01
2.99
2.97
2.52
2.05
2.03
2.01
1.99
1.29
1.27
0.86
1.00
1.10
1.10
1.94
0.93
0.92
1.90
3.36
1.00
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.19
157.20
136.06
135.76
127.89
127.84
126.92
126.83
123.50
123.47
120.12
120.05
119.72
119.03
114.91
114.68
44.78
37.56
33.46
24.01
19.84
N
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6j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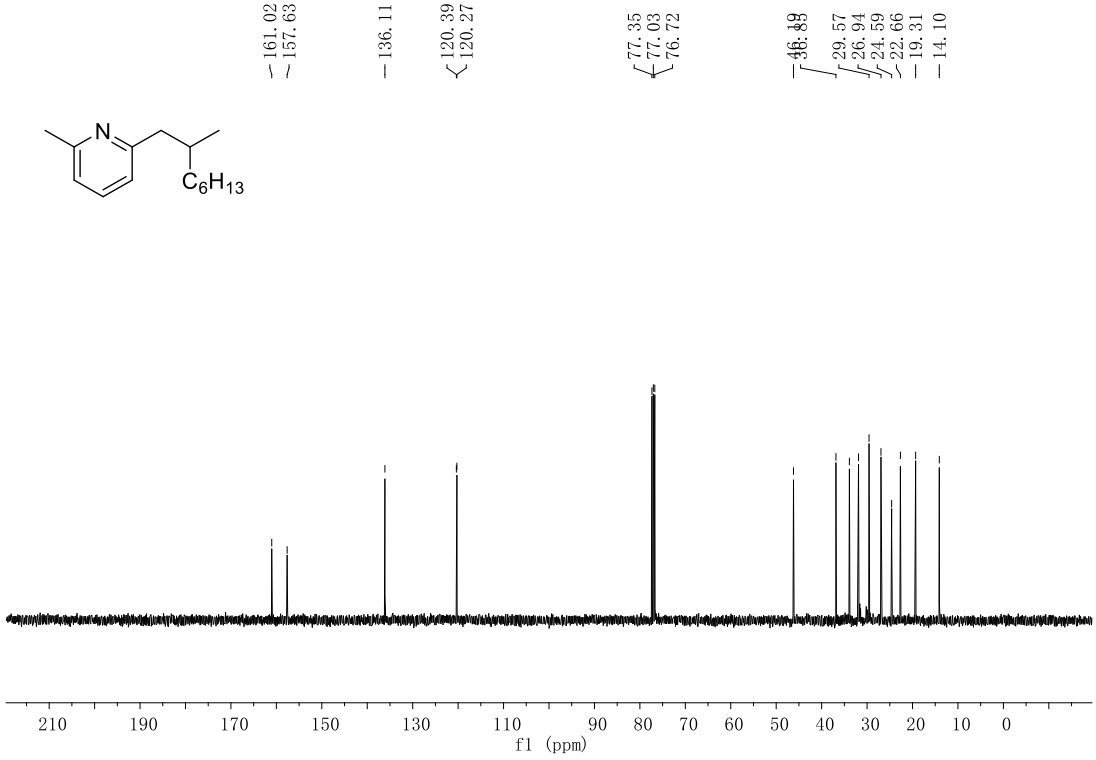
7.42
7.40
6.92
6.90
6.88
6.86
2.75
2.73
2.72
2.70
2.52
2.50
2.48
1.90
1.88
1.86
1.31
1.26
1.13
0.86
0.84
0.84
0.82
N
C6H13
1.00
2.07
1.01
3.99
1.03
4.36
6.38
f1 (ppm)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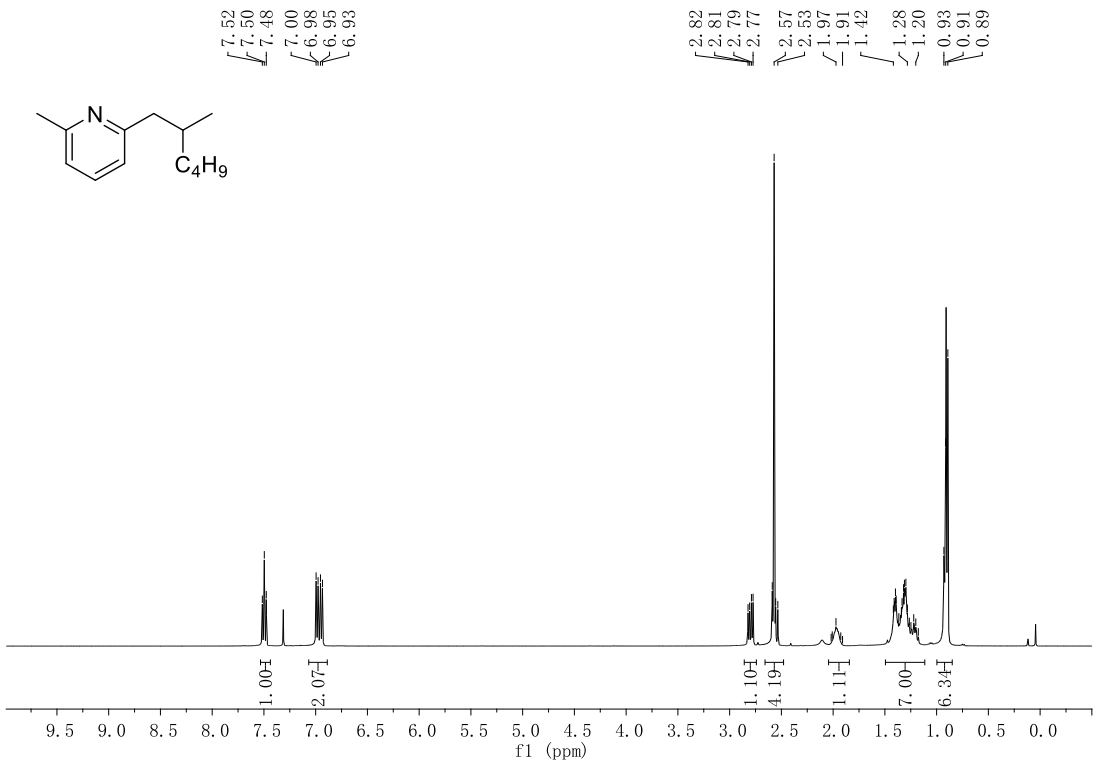
157.63
136.11
120.39
120.27
77.35
77.03
76.72
46.19
38.83
29.57
26.94
24.59
22.66
19.31
14.10
N
C6H13
f1 (ppm)

6k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7.50
7.48
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6.95
6.93
2.82
2.81
2.79
2.77
2.57
2.53
1.97
1.91
1.42
1.28
1.20
0.93
0.91
0.89
N
C4H9
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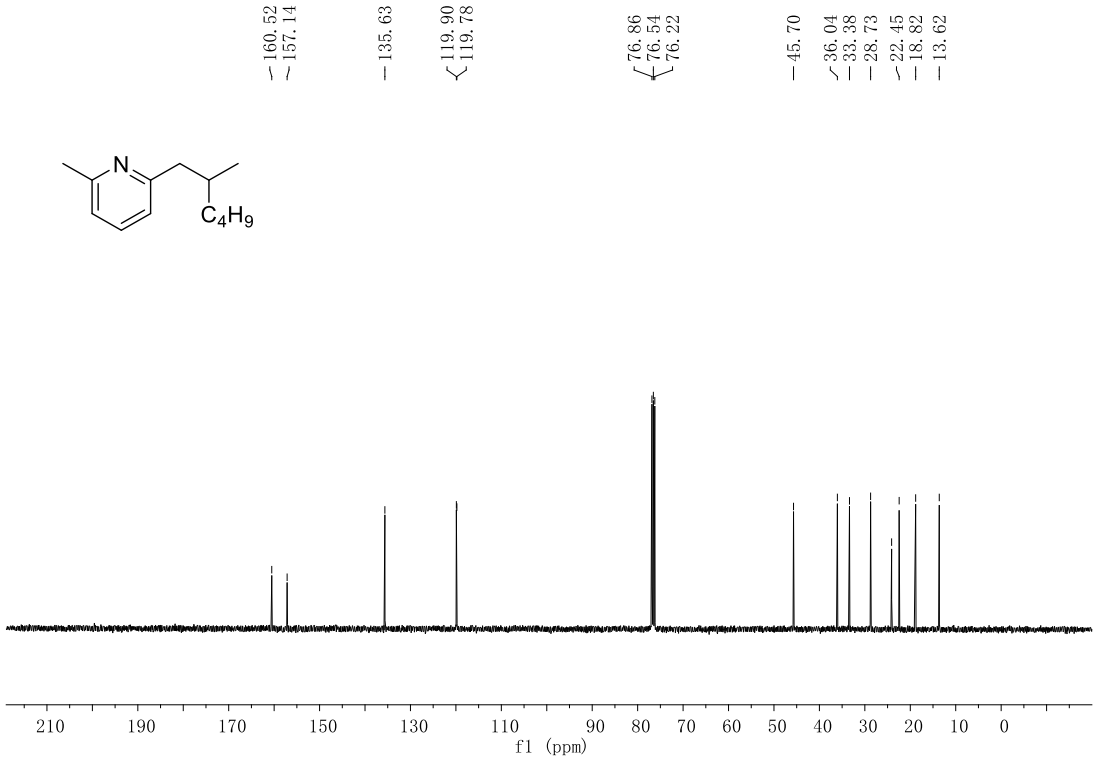
2.07
1.10
4.19
1.11
7.00
6.34
f1 (ppm)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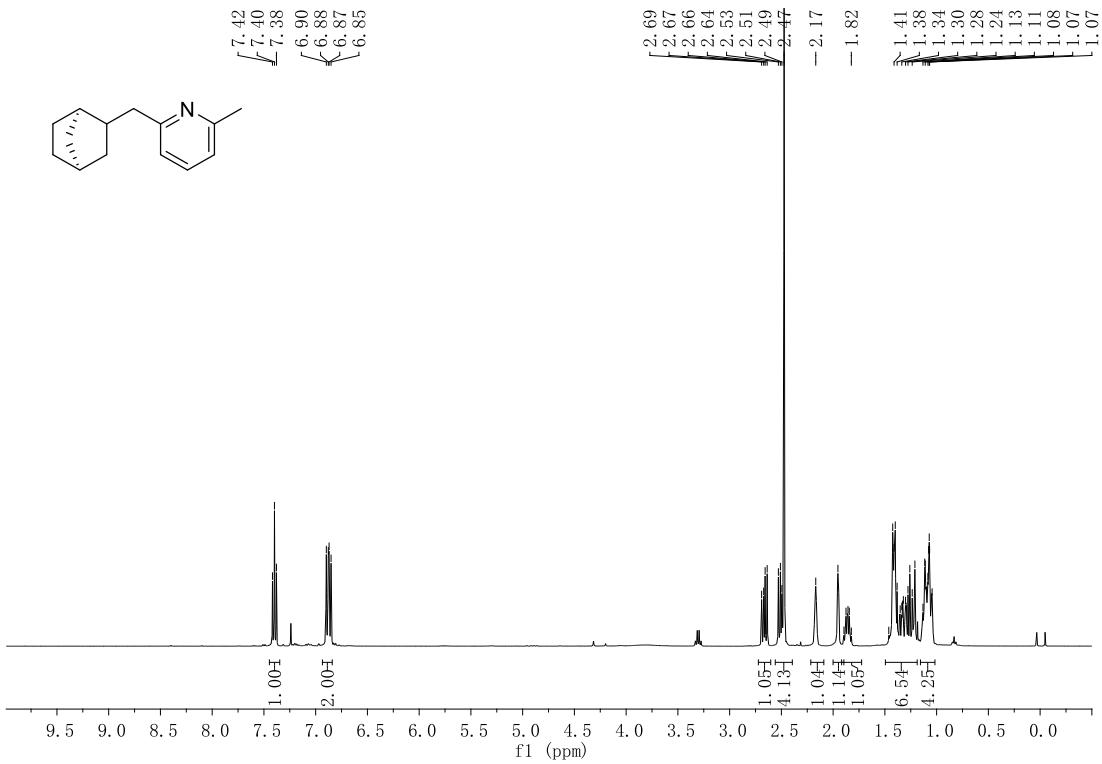
157.14
135.63
119.90
119.78
76.86
76.54
76.22
45.70
36.04
33.38
28.73
22.45
18.82
13.62
N
C4H9
f1 (ppm)

6l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7.40
7.38
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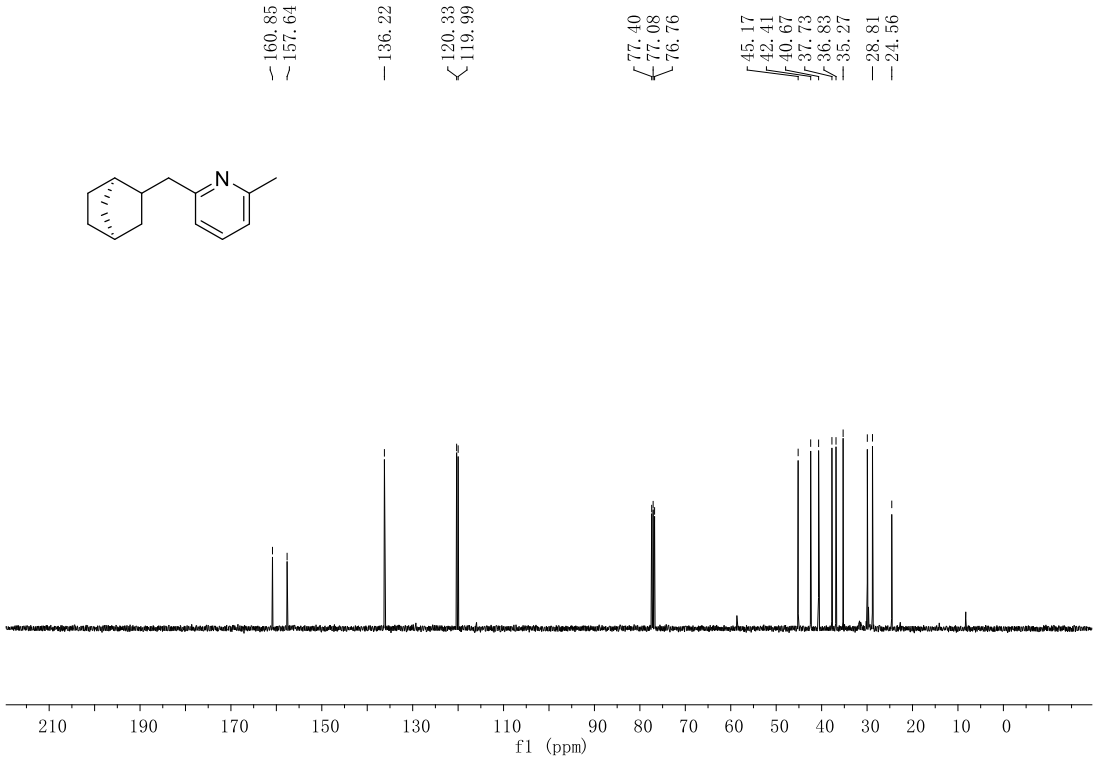
6.88
6.87
6.85
2.69
2.67
2.66
2.64
2.53
2.51
2.49
2.47
2.17
1.82
1.41
1.38
1.34
1.30
1.28
1.24
1.13
1.11
1.08
1.07
1.07
N
1.00
2.00
1.05
4.13
1.04
1.14
1.05
6.54
4.25
f1 (ppm)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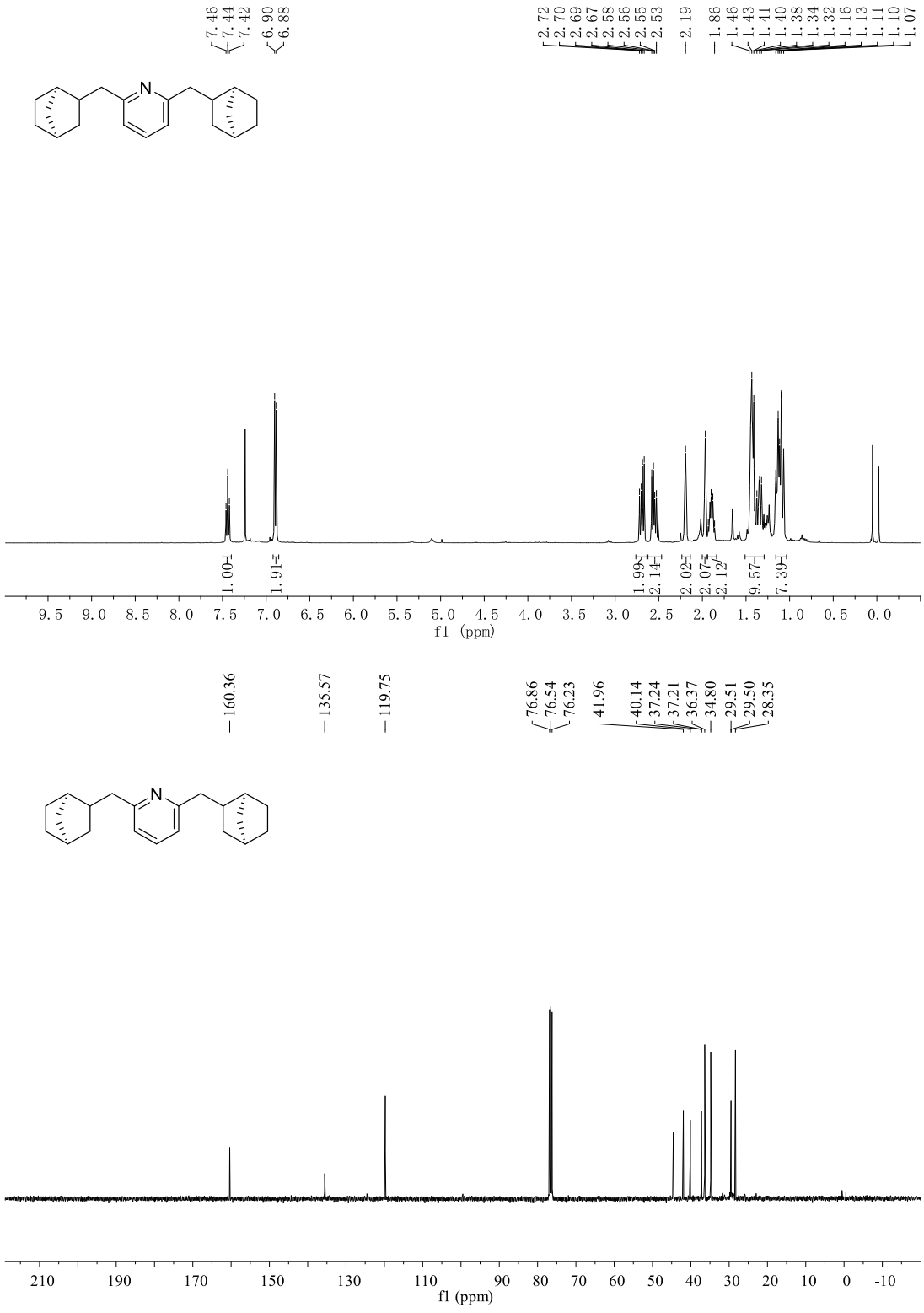
136.22
120.33
119.99
77.40
77.08
76.76
45.17
42.41
40.67
37.73
36.83
35.27
28.81
24.56
N
f1 (ppm)

6m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7.44
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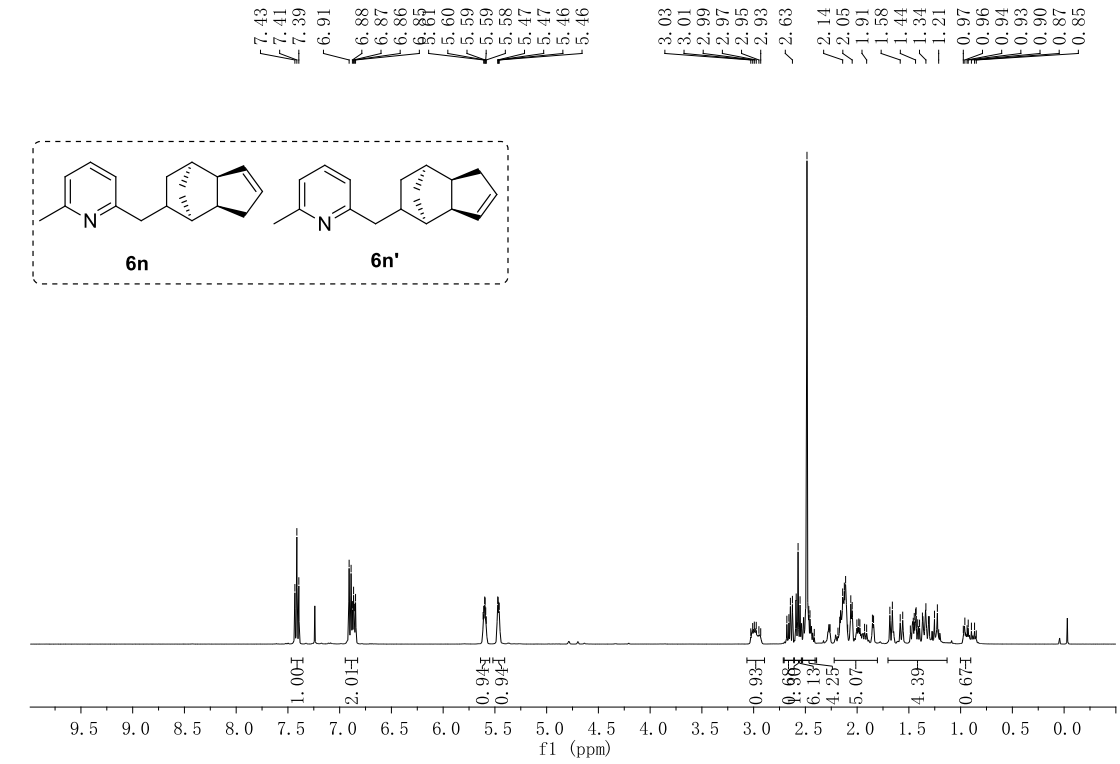
6.90
6.88
2.72
2.70
2.69
2.67
2.58
2.56
2.55
2.53
2.19
1.86
1.46
1.43
1.41
1.40
1.38
1.34
1.32
1.16
1.13
1.11
1.10
1.07
N
1.00
1.91
1.99
2.14
2.02
2.07
2.12
9.57
7.39
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
160.36
135.57
119.75
76.86
76.54
76.23
41.96
40.14
37.24
37.21
36.37
34.80
29.51
29.50
28.35
N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

6n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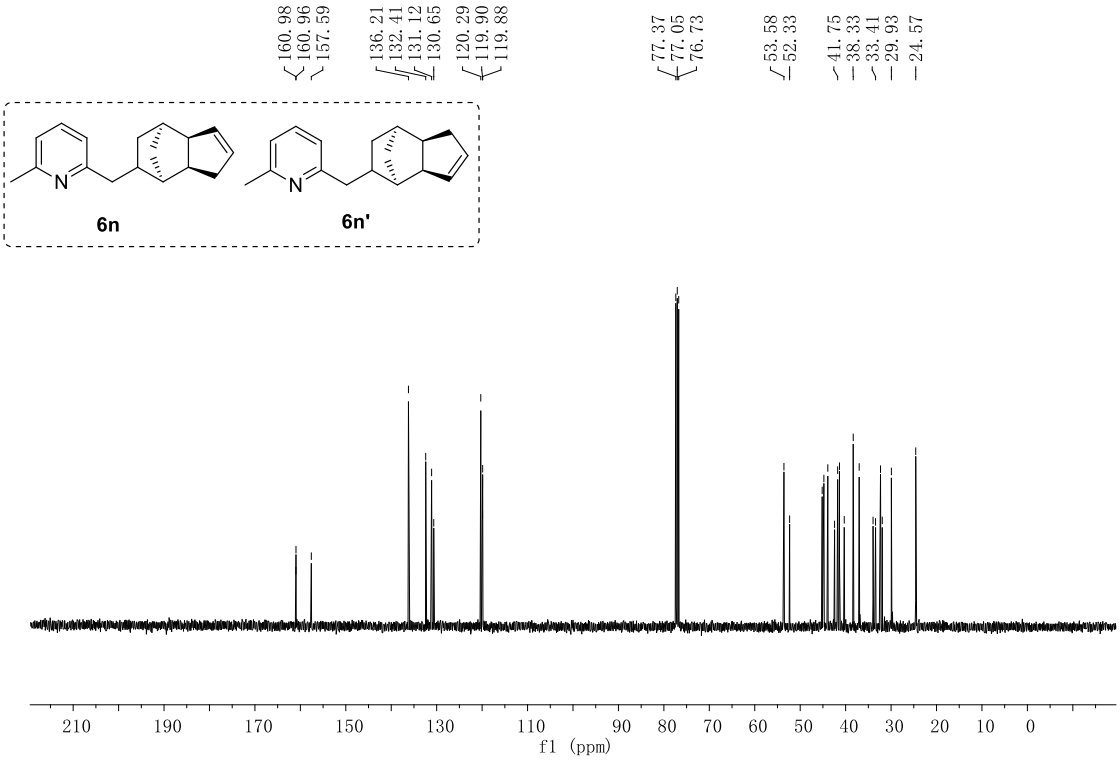
7.39
6.91
6.88
6.87
6.86
6.85
5.60
5.59
5.58
5.47
5.46
3.03
3.01
2.99
2.97
2.95
2.93
2.63
2.14
2.05
1.91
1.58
1.44
1.34
1.21
0.97
0.96
0.94
0.93
0.90
0.87
0.85
6n
6n'
1.00
2.01
0.94
0.94
0.93
4.25
5.07
4.39
0.67
f1 (ppm)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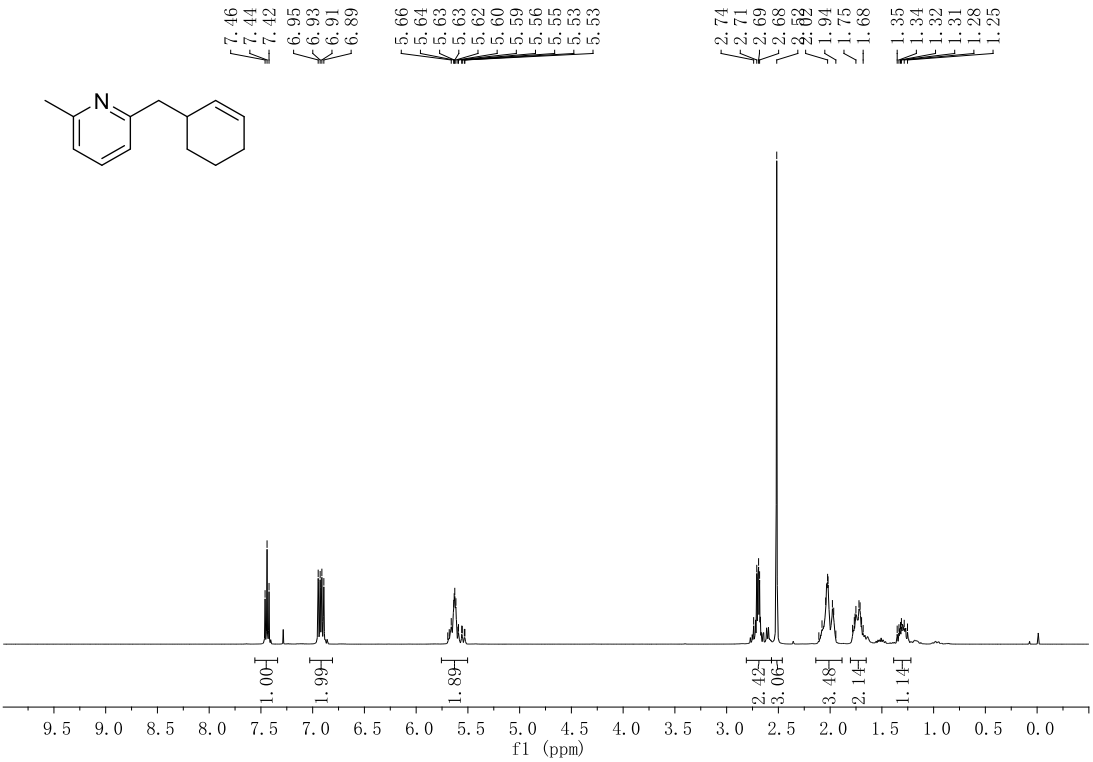
132.41
131.12
130.65
120.29
119.90
119.88
77.37
77.05
76.73
53.58
52.33
41.75
38.33
33.41
29.93
24.57
6n
6n'
f1 (ppm)

6o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7.44
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6.95
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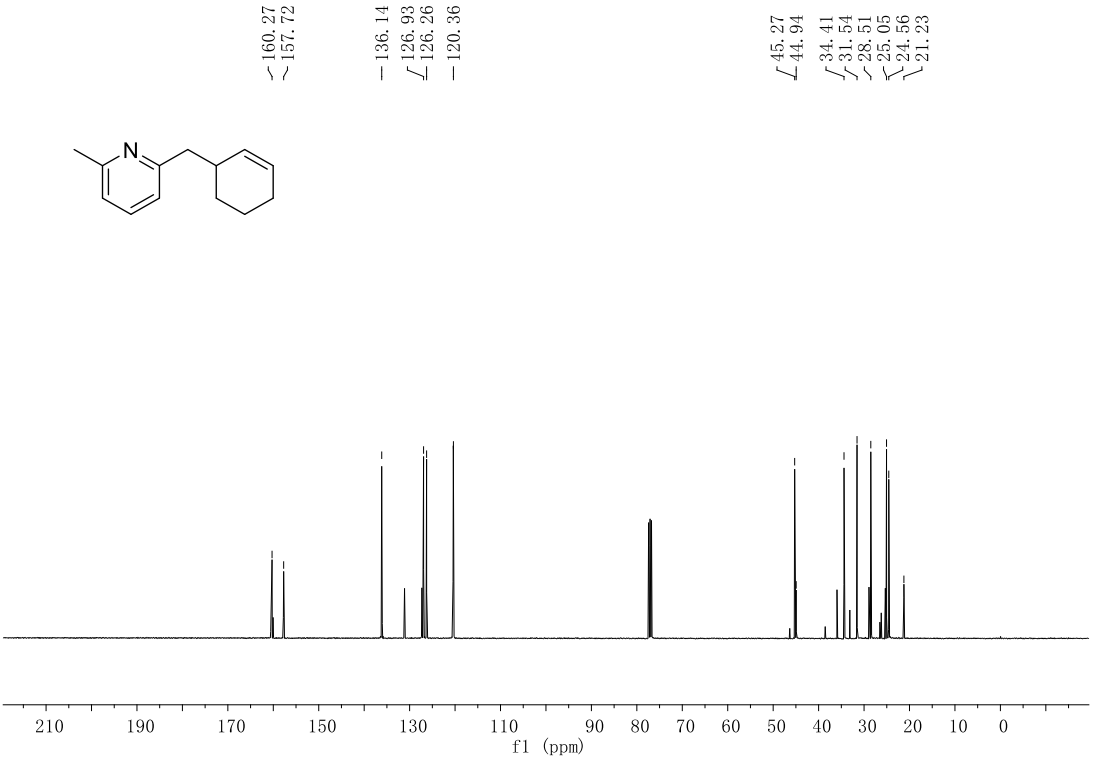
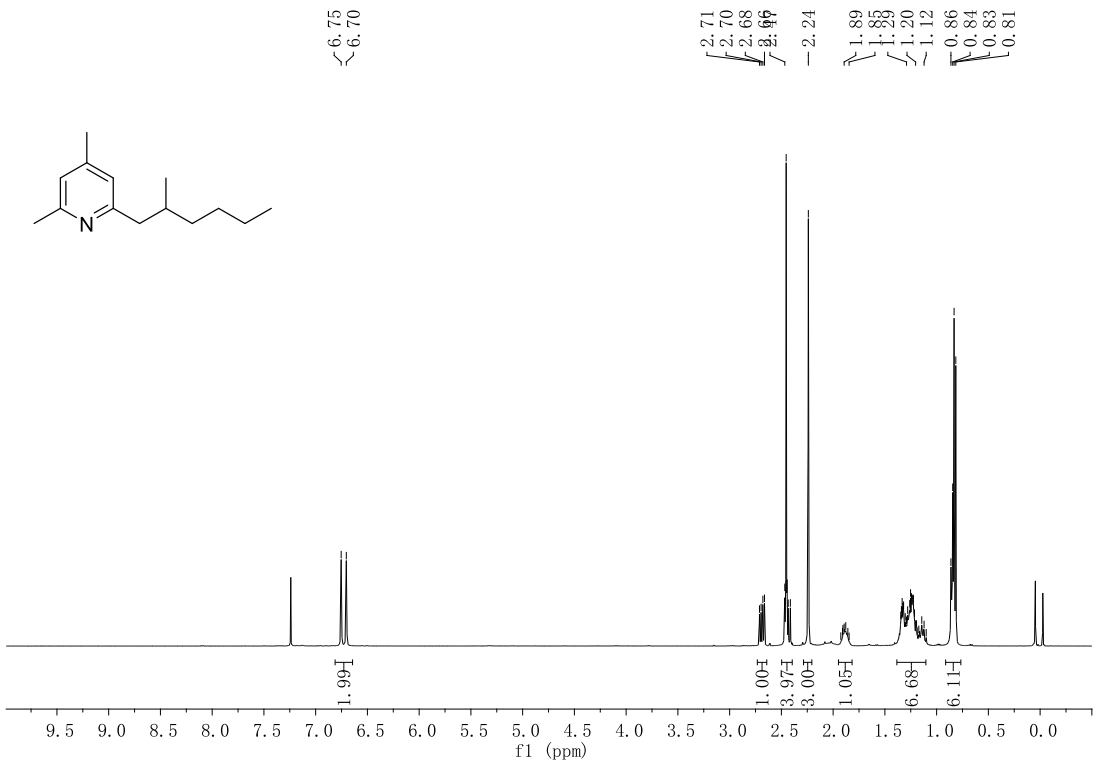
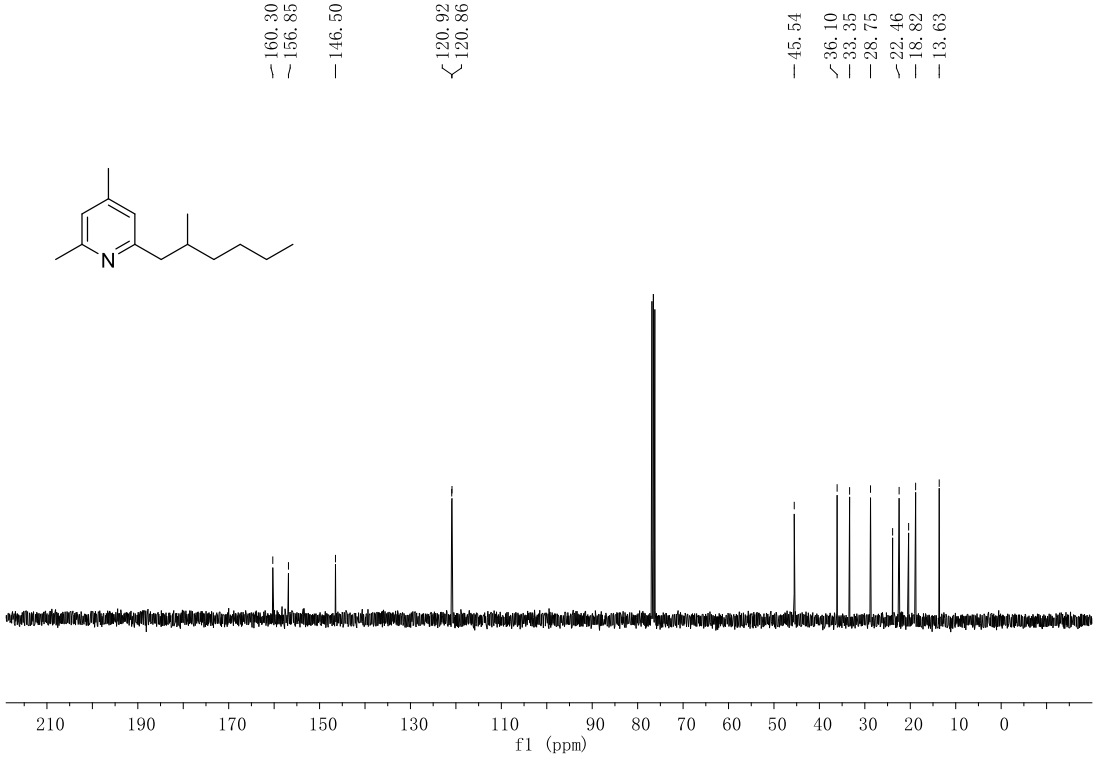
6.91
6.89
5.66
5.64
5.63
5.63
5.62
5.60
5.59
5.56
5.55
5.53
5.53
2.74
2.71
2.69
2.68
2.62
2.62
1.94
1.75
1.68
1.35
1.34
1.32
1.31
1.28
1.25
N
1.00
1.99
1.89
2.42
3.06
3.48
2.14
1.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

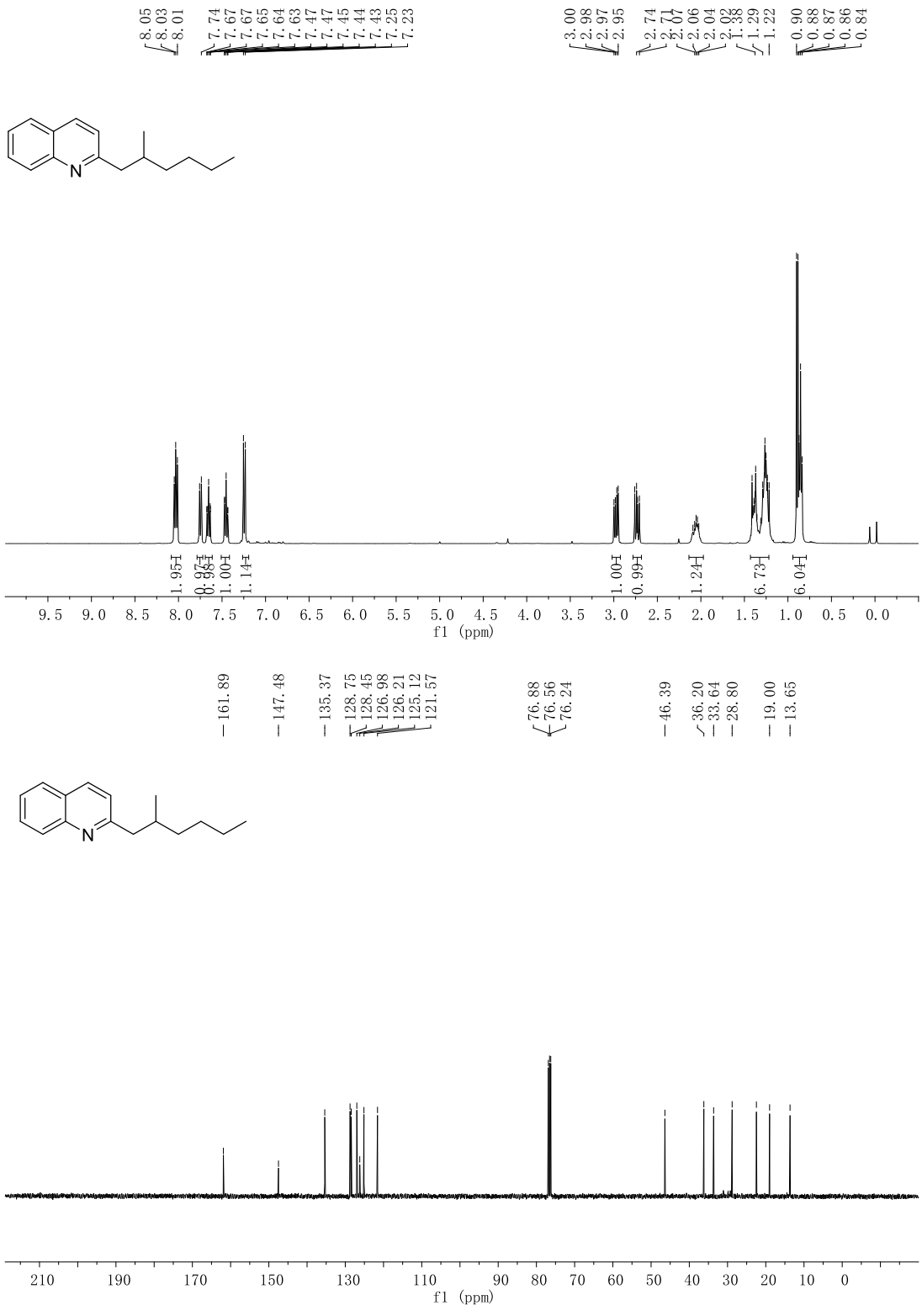

160.27
157.72
136.14
126.93
126.26
120.36
45.27
44.94
34.41
31.54
28.51
25.05
24.56
21.23
N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7b


6.75
6.70
2.71
2.70
2.68
2.24
1.89
1.85
1.20
1.12
0.86
0.84
0.83
0.81
1.99
1.00
3.97
3.00
1.05
6.68
6.11
f1 (ppm)


160.30
156.85
146.50
120.92
120.86
45.54
36.10
33.35
28.75
22.46
18.82
13.63
f1 (ppm)

7c


8.05
8.03
8.01
7.74
7.67
7.67
7.65
7.64
7.63
7.47
7.47
7.45
7.44
7.43
7.25
7.23
3.00
2.98
2.97
2.95
2.74
2.71
2.07
2.06
2.04
2.02
1.38
1.29
1.22
0.90
0.88
0.87
0.86
0.84
N
1.95
0.97
0.98
1.00
1.14
1.00
0.99
1.24
6.73
6.04
f1 (ppm)
161.89
147.48
135.37
128.75
128.45
126.98
126.21
125.12
121.57
76.88
76.56
76.24
46.39
36.20
33.64
28.80
19.00
13.65
N
f1 (ppm)

Crystallographic data for complex 1

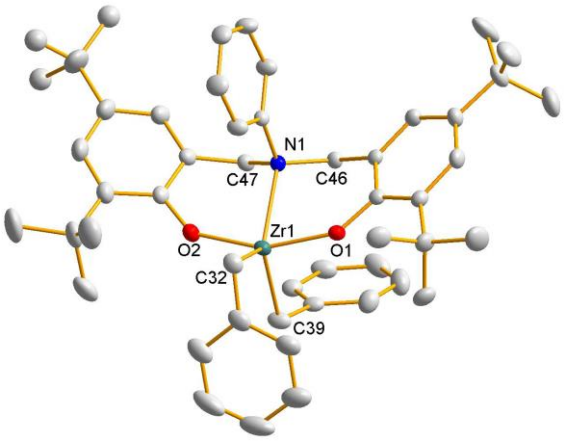


Figure S1 Molecular structure of **1** showing 30% probability ellipsoids; hydrogen atoms are omitted for clarity.

Table S1 Selected bond lengths (Å) and bond angles (deg) for complex **1**

Bond lengths	**1**	**Bond angles**	**1**	**Bond angles**	**1**
Zr1-O1	1.998(2)	O1-Zr1-O2	157.58(10)	C39-Zr1-C46	106.17(17)
Zr1-O2	1.997(2)	O1-Zr1-C39	98.61(14)	O1-Zr1-N1	80.52(9)
Zr1-N1	2.512(3)	O2-Zr1-C39	99.53(14)	O2-Zr1-N1	80.41(9)
Zr1-C39	2.250(4)	O1-Zr1-C46	95.16(13)	C39-Zr1-N1	112.66(13)
Zr1-C46	2.268(4)	O2-Zr1-C46	92.33(13)	C46-Zr1-N1	141.15(14)

Table S3. Crystallographic data for complex **1**

Compound	**1**
Formula	$C_{50}H_{63}NO_2Zr$
fw	801.23
T/K	223(2)
Crystal system	Orthorhombic
Crystal size/mm	0.50×0.30×0.20
Space group	*P*bca
a/Å	15.634(3)
b/Å	20.940(4)
c/Å	28.234(6)
α/deg	90
β/deg	90
γ/deg	90
V/Å^3	9243(3)
Z	36
D_{calcd}/g cm^{-3}	1.152
μ/mm^{-1}	0.274
F(000)	3408.0
θ_{max}/deg	3.17-25.00
Unique reflns	6348
max, min transm	0.9472, 0.8751
No. of variables	493
final R indices (I > 2σ(I))	R_1 = 0.0430, wR_2 = 0.1060
R indices (all data)	R_1 = 0.0606, wR_2 = 0.1122
goodness-of-fit on F^2	1.188
Largest diff. peak,hole/e Å^{-3}	0.696, –0.400

DFT Data

1. Computational details

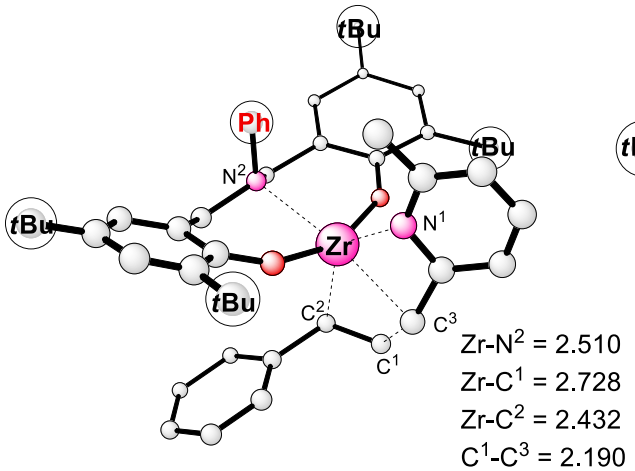
All calculations were carried out by using the Gaussian 09 suite of computational programs. All stationary points along the reaction coordinate were fully optimized at the DFT level using the B3LYP hybrid functional. The 6-31G(d) basis set was applied for all atoms except Zr, which was described by the LanL2DZ basis set and effective core potential implemented. Frequencies were analytically computed at the same level of theory to get the thermodynamic corrections and to confirm whether the structures are minima (no imaginary frequency) or transition states (only one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were carried out to confirm that all transition state structures connect the proposed reactants and products. The solvation effect was examined by performing single-point self-consistent reaction field (SCRF) calculations based on the SMD solvation model for gas-phase optimized structures. Chlorobenzene was used as the solvent, corresponding to the original experimental conditions. All SCRF calculations were done at the B3LYP level by using a larger basis set of SDD for Zr and 6-311+G(d,p) for the rest elements. The relative free energies (in kcal/mol) corrected by solvation effects are used for discussion.

2. Calculated Energy Values

Table S2. Energies (in Hartree) calculated at SMD-B3LYP/BSII//B3LYP/BS1 level

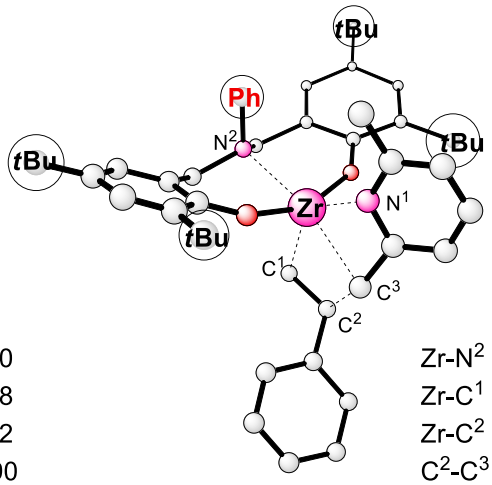
Species	E_0[a]	H_{298}[b]	G_{298}[c]	E[d]	G_{Sol}[e]
IN1	-2288.008615	-2287.949389	-2288.102505	-2289.0564243	-2290.244356
IN2	-2214.192699	-2214.132472	-2214.288583	-2215.2738305	-2216.444778
1-TS1	-2287.986780	-2287.928823	-2288.078390	-2289.0355643	-2290.223877
1-TS2	-2287.990063	-2287.932156	-2288.081757	-2289.0386208	-2290.225281
2-TS1	-2214.174139	-2214.115312	-2214.266511	-2215.256126	-2216.427558
2-TS2	-2214.175604	-2214.116810	-2214.268135	-2215.2574451	-2216.426053

[a] Sum of electronic and zero-point energies
[b] Sum of electronic and thermal enthalpies
[c] Sum of electronic and thermal free energies
[d] Electronic energies
[e] Single point energies in solution



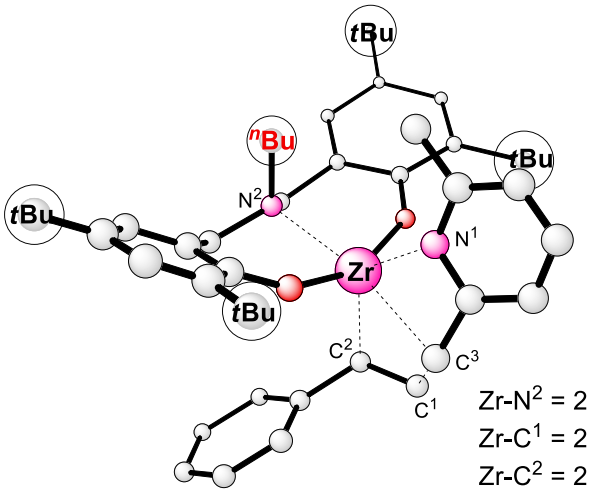
Zr-N^2 = 2.510
Zr-C^1 = 2.728
Zr-C^2 = 2.432
C^1-C^3 = 2.190

1-TS1 (R = Ph)



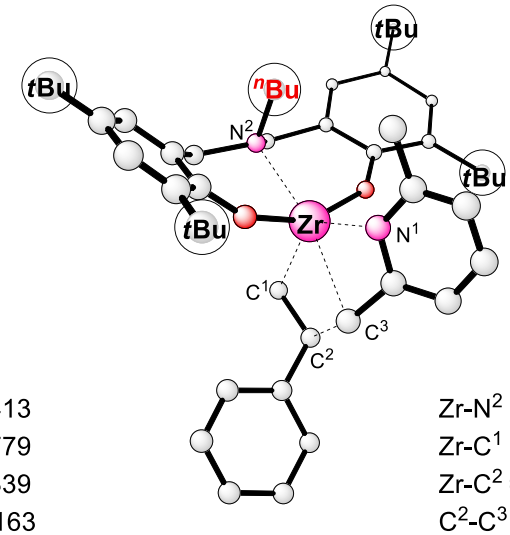
Zr-N^2 = 2.490
Zr-C^1 = 2.304
Zr-C^2 = 2.867
C^2-C^3 = 2.194

1-TS2 (R = Ph)



Zr-N^2 = 2.413
Zr-C^1 = 2.779
Zr-C^2 = 2.339
C^1-C^3 = 2.163

2-TS1 (R = ^{n}Bu)



Zr-N^2 = 2.416
Zr-C^1 = 2.296
Zr-C^2 = 2.888
C^2-C^3 = 2.182

2-TS2 (R = ^{n}Bu)

According to above geometric structures, the steric effect of the R group is greater in **1-TS1** and **1-TS2** than that in **2-TS1** and **2-TS2**, which could be concluded from longer Zr-N2 distances in the former two TS. Thus, the migratory insertion via **1-TS2** could avoid steric repulsion between olefin and the ligand, being lower in energy than **1-TS1**, and branched products formed predominantly when R = Ph. On the contrary, when R = ^{n}Bu, the **2-TS1** is more favorable than **2-TS2** should be attributed to electronic effect. The C1-C3 coupling becomes predominant could be attributed to the more electron deficient nature of C1 than C2.

Cartesian Coordinates for All Species

IN1

C	-10.01308	-0.86765	2.48988
C	-8.91705	-0.01676	2.19646
C	-9.10098	1.36929	2.04075
C	-10.38797	1.91035	2.13391
C	-11.5006	1.11454	2.40534
C	-11.26948	-0.25859	2.58616
H	-10.50193	2.98041	1.99693
H	-12.12237	-0.88624	2.8079
C	-7.94702	2.33844	1.91286
H	-7.46417	2.44778	2.8916
N	-6.82777	2.03934	0.94051
C	-5.77705	3.08274	1.19675
H	-6.23537	4.07783	1.11163
H	-5.51584	2.97376	2.25402
C	-4.51424	3.06241	0.36128
C	-4.01401	4.2875	-0.09727
C	-3.77923	1.88654	0.13829
C	-2.80038	4.37782	-0.77658
H	-4.59679	5.18219	0.09885
C	-2.53349	1.92437	-0.54251
C	-2.09599	3.1789	-0.97865
H	-1.15149	3.23409	-1.50368
O	-4.28854	0.71533	0.60713
O	-7.66241	-0.52202	2.0135
Zr	-5.79244	-0.31345	1.38247
C	-9.8529	-2.39104	2.68861
C	-12.93055	1.67461	2.50719
C	-1.67845	0.65925	-0.77612
C	-2.22213	5.70776	-1.29309
C	-4.81081	-2.24893	2.1932
H	-4.97466	-2.72568	3.15916
C	-5.34516	-3.00096	1.04534
C	-5.64497	-4.36697	0.96035
C	-6.00849	-2.65148	-1.20832
C	-6.10115	-4.87	-0.25008
H	-5.47664	-5.00793	1.81902
H	-6.31261	-5.93021	-0.35797
H	-3.73949	-2.04067	2.06885
C	-6.25784	-4.01375	-1.34712
N	-5.60118	-2.16294	-0.00567
H	-6.56816	-4.40252	-2.31099
C	-6.10945	-1.70468	-2.36979
H	-6.63592	-0.78427	-2.10572
H	-5.10571	-1.4191	-2.70737
H	-6.6296	-2.17172	-3.21003
C	-4.88788	-0.27811	4.53215
H	-5.7824	-0.74603	4.94326
C	-5.07276	0.80783	3.72953
H	-6.0572	1.26665	3.71668
C	-11.17613	-3.06732	3.10726
H	-11.56858	-2.66151	4.04635
H	-11.95216	-2.97572	2.33946
H	-10.9978	-4.13708	3.26114
C	-8.82462	-2.68361	3.80883
H	-7.83593	-2.28788	3.56812
H	-9.15253	-2.24171	4.75723
H	-8.73421	-3.7662	3.9594
C	-13.81983	1.00719	1.43034
H	-13.86904	-0.07961	1.55612
H	-14.84357	1.39481	1.48989
H	-13.43811	1.21197	0.42343
C	-12.97626	3.19937	2.28964
H	-12.38835	3.73831	3.04173
H	-12.60959	3.48264	1.29613
H	-14.0105	3.55053	2.36948
C	-13.50748	1.37073	3.91081
H	-12.90094	1.83747	4.69538
H	-14.52795	1.76268	3.99352
H	-13.54952	0.29551	4.11418
C	-3.13363	6.90661	-0.96732
H	-4.12119	6.81011	-1.43387
H	-3.27282	7.03484	0.11253
H	-2.68056	7.82735	-1.34987
C	-0.84327	5.95965	-0.63672
H	-0.12841	5.16213	-0.86521
H	-0.41641	6.9014	-1.00094
H	-0.93328	6.02769	0.45351
C	-2.05346	5.63382	-2.82982
H	-1.63573	6.57288	-3.2112
H	-1.37843	4.8253	-3.12937
H	-3.01751	5.4664	-3.3239
C	-1.2782	0.03717	0.5839
H	-0.66739	-0.85933	0.4223
H	-0.6825	0.74608	1.17152
H	-2.15283	-0.24787	1.17265
C	-9.40633	-3.04904	1.36113
H	-9.29774	-4.13217	1.49451
H	-10.15549	-2.88238	0.57822
H	-8.45005	-2.65666	1.00893
C	-0.37181	0.96971	-1.53638
H	-0.56221	1.38572	-2.5319
H	0.27247	1.66551	-0.98768
H	0.19248	0.04074	-1.67244
H	-8.35061	3.32845	1.66113
C	-7.33592	2.03983	-0.4337
C	-7.12357	3.10759	-1.31905
C	-8.11419	0.95426	-0.8678
C	-7.66981	3.08103	-2.60303
H	-6.53142	3.96382	-1.02934
C	-8.67065	0.94294	-2.14964
H	-8.33368	0.13251	-0.19769

C	-8.44844	2.00349	-3.02579
H	-7.48782	3.91788	-3.27097
H	-9.28471	0.09996	-2.45356
H	-8.88025	1.99466	-4.02192
C	-2.46337	-0.37182	-1.62175
H	-3.37548	-0.69619	-1.11793
H	-2.73556	0.05556	-2.59434
H	-1.84155	-1.2563	-1.80655
H	-4.23874	1.40576	3.37369
C	-3.63498	-0.88867	4.95344
C	-3.6914	-1.98717	5.83417
C	-2.37234	-0.41322	4.54229
C	-2.52497	-2.5937	6.29343
H	-4.65962	-2.35629	6.16393
C	-1.20967	-1.02342	4.99711
H	-2.30118	0.43513	3.86871
C	-1.28268	-2.11347	5.87371
H	-2.5834	-3.43525	6.9769
H	-0.2423	-0.64954	4.67555
H	-0.37051	-2.5829	6.2304

IN2

C	-10.12812	-0.82698	2.30799
C	-8.963920	-0.01926	2.23079
C	-9.059500	1.38414	2.22919
C	-10.3199	1.99226	2.26740
C	-11.49418	1.24287	2.32966
C	-11.35416	-0.15441	2.35461
H	-10.36302	3.07656	2.26124
H	-12.25697	-0.74783	2.41279
C	-7.84031	2.27964	2.28937
H	-7.41941	2.28199	3.30223
N	-6.71105	1.94574	1.37028
C	-5.66532	3.00502	1.52856
H	-6.13215	3.99308	1.42181
H	-5.32828	2.94337	2.5707
C	-4.48293	2.93067	0.58945
C	-4.06298	4.10161	-0.05135
C	-3.75576	1.73963	0.41571
C	-2.92216	4.1273	-0.85358
H	-4.64589	5.00394	0.10225
C	-2.57734	1.71677	-0.37429
C	-2.21076	2.92299	-0.98267
H	-1.31897	2.93073	-1.59515
O	-4.22676	0.61433	1.02468
O	-7.72058	-0.57737	2.1524
Zr	-5.78326	-0.36729	1.779
C	-10.06878	-2.36992	2.34611
C	-12.89612	1.87654	2.37474
C	-1.72031	0.44417	-0.55325
C	-2.43236	5.39428	-1.57807
C	-4.8102	-2.37682	2.45694
H	-4.95462	-2.94694	3.3752
C	-5.35461	-3.04321	1.25484
C	-5.59693	-4.40789	1.04704
C	-6.16117	-2.51527	-0.91723
C	-6.08075	-4.8158	-0.18859
H	-5.36423	-5.11995	1.83157
H	-6.24124	-5.87092	-0.3919
H	-3.73951	-2.16111	2.33733
C	-6.34405	-3.86769	-1.18553
N	-5.68455	-2.12959	0.29398
H	-6.69853	-4.17641	-2.163
C	-6.47749	-1.44602	-1.92567
H	-7.37275	-0.88345	-1.63367
H	-5.64682	-0.73816	-2.01576
H	-6.6686	-1.88153	-2.90949
C	-4.80025	-0.50948	4.82604
H	-5.48864	-1.26644	5.1992
C	-5.35445	0.59232	4.24314
H	-6.4245	0.74862	4.3489
C	-7.16611	1.81163	-0.04896
H	-6.28499	1.5352	-0.63914
H	-7.87576	0.97656	-0.07639
C	-11.46703	-3.00533	2.49832
H	-11.96391	-2.6935	3.42357
H	-12.12504	-2.76942	1.65471
H	-11.36249	-4.09512	2.53406
C	-9.22241	-2.84361	3.55355
H	-8.19248	-2.48547	3.49561
H	-9.65883	-2.48818	4.49429
H	-9.20227	-3.93956	3.58829
C	-13.71594	1.40054	1.15116
H	-13.83239	0.31178	1.13408
H	-14.71974	1.84058	1.17298
H	-13.23477	1.70146	0.21329
C	-12.84117	3.41611	2.34633
H	-12.29894	3.82242	3.20808
H	-12.36814	3.79264	1.43169
H	-13.85809	3.82129	2.37913
C	-13.61677	1.44432	3.67458
H	-13.06349	1.77577	4.56071
H	-14.61922	1.88583	3.71621
H	-13.73143	0.35714	3.73804
C	-3.33398	6.61148	-1.29609
H	-4.36315	6.44745	-1.63655
H	-3.35935	6.86383	-0.22957
H	-2.94848	7.48641	-1.83014
C	-0.9985	5.73876	-1.10777
H	-0.29133	4.93012	-1.32051
H	-0.63744	6.63735	-1.62141
H	-0.97395	5.93179	-0.0292
C	-2.42409	5.14265	-3.10526
H	-2.07063	6.035	-3.63499
H	-1.76513	4.31217	-3.37993
H	-3.43051	4.90823	-3.47122
C	-1.22403	-0.05397	0.82559

H	-0.61663	-0.95873	0.70169
H	-0.59706	0.70593	1.30689
H	-2.05267	-0.28782	1.49725
C	-9.46519	-2.90504	1.02621
H	-9.42641	-4.00082	1.04619
H	-10.08251	-2.60797	0.17004
H	-8.45188	-2.53391	0.86448
C	-0.47086	0.6985	-1.42255
H	-0.72967	1.00922	-2.44094
H	0.18989	1.4561	-0.98683
H	0.10501	-0.2299	-1.50215
C	-2.54337	-0.6637	-1.25261
H	-3.41082	-0.9615	-0.66087
H	-2.89069	-0.32391	-2.2361
H	-1.91974	-1.55225	-1.40953
H	-8.16242	3.3125	2.10152
C	-7.82855	3.03648	-0.69951
H	-7.14557	3.89386	-0.66858
H	-8.72973	3.31538	-0.14048
C	-8.21152	2.75247	-2.16027
H	-7.31024	2.47322	-2.72386
H	-8.88327	1.88304	-2.19739
C	-8.88871	3.94811	-2.83842
H	-9.14752	3.71729	-3.87704
H	-9.81269	4.22772	-2.31872
H	-8.23098	4.8253	-2.84579
C	-3.39236	-0.79956	5.06341
C	-3.06273	-1.99073	5.7397
C	-2.35191	0.0703	4.6762
C	-1.73638	-2.30646	6.02365
H	-3.85755	-2.66385	6.05184
C	-1.02874	-0.24848	4.95653
H	-2.57791	0.9961	4.15599
C	-0.71766	-1.43604	5.63096
H	-1.49801	-3.22495	6.55116
H	-0.23505	0.42841	4.65529
H	0.31799	-1.67744	5.85177
H	-4.7492	1.45346	3.97484

1-TS1

C	-10.17157	-0.80468	2.41989
C	-9.02181	0.0073	2.25136
C	-9.13581	1.40536	2.1507
C	-10.39912	2.00439	2.17599
C	-11.56191	1.24885	2.32681
C	-11.40342	-0.14043	2.45567
H	-10.455	3.0836	2.08218
H	-12.29701	-0.73623	2.58536
C	-7.92145	2.30055	2.12582
H	-7.43126	2.29386	3.10642
N	-6.82301	1.99402	1.12398
C	-5.72814	3.00096	1.4045
H	-6.1652	4.00723	1.39923
H	-5.41858	2.81091	2.43736
C	-4.51525	2.97868	0.50908
C	-4.04796	4.16951	-0.0555
C	-3.78151	1.79462	0.34552
C	-2.86516	4.20987	-0.79345
H	-4.62412	5.07523	0.10547
C	-2.57011	1.77889	-0.38974
C	-2.16395	3.00065	-0.93824
H	-1.24438	3.01953	-1.50818
O	-4.28193	0.67735	0.94291
O	-7.76947	-0.52861	2.15094
Zr	-5.84204	-0.23023	1.74916
C	-10.09663	-2.34149	2.55098
C	-12.97034	1.86882	2.35674
C	-1.71811	0.50352	-0.56678
C	-2.31876	5.49809	-1.4351
C	-4.61292	-2.35507	2.61195
H	-4.42549	-3.04983	3.42424
C	-5.32594	-2.99294	1.50553
C	-5.73653	-4.33386	1.46614
C	-6.06512	-2.62631	-0.7103
C	-6.27811	-4.82018	0.28497
H	-5.58096	-4.97402	2.32794
H	-6.57126	-5.86308	0.20608
H	-3.67239	-1.8986	2.28901
C	-6.41242	-3.9709	-0.81948
N	-5.5712	-2.14573	0.46174
H	-6.78228	-4.34971	-1.76628
C	-6.13472	-1.70176	-1.89267
H	-6.92208	-2.00767	-2.587
H	-6.31096	-0.66482	-1.60166
H	-5.18117	-1.72916	-2.43473
C	-5.26627	-1.08773	4.27412
H	-6.11491	-1.72451	4.50293
C	-5.48369	0.29666	4.0961
H	-6.51329	0.61781	4.26349
C	-11.47935	-2.97541	2.8136
H	-11.93526	-2.60309	3.73758
H	-12.1792	-2.80403	1.98846
H	-11.36223	-4.0594	2.91981
C	-9.18684	-2.73614	3.73948
H	-8.16522	-2.37613	3.60135
H	-9.57382	-2.32348	4.67824
H	-9.15482	-3.82747	3.8418
C	-13.81833	1.27586	1.20562
H	-13.92625	0.18948	1.29266
H	-14.82501	1.70968	1.21452
H	-13.36484	1.49185	0.23141
C	-12.93614	3.40008	2.18717
H	-12.37858	3.88987	2.99401
H	-12.49084	3.69631	1.23014
H	-13.95723	3.79525	2.2092
C	-13.64701	1.54727	3.7111
H	-13.07313	1.96346	4.5469
H	-14.65397	1.97915	3.74302

H	-13.74442	0.46886	3.8751
C	-3.21248	6.71884	-1.14344
H	-4.22494	6.59176	-1.54472
H	-3.28971	6.92235	-0.06896
H	-2.78404	7.60952	-1.61505
C	-0.90524	5.79429	-0.87868
H	-0.20205	4.98232	-1.09165
H	-0.5029	6.70774	-1.33211
H	-0.93274	5.93854	0.20747
C	-2.23848	5.31365	-2.9698
H	-1.84676	6.22225	-3.4419
H	-1.57888	4.48501	-3.24827
H	-3.22871	5.1111	-3.3941
C	-1.25499	-0.01563	0.81574
H	-0.64924	-0.92187	0.69429
H	-0.64065	0.7347	1.32629
H	-2.10431	-0.25147	1.46117
C	-9.55412	-2.94968	1.2367
H	-9.50864	-4.04263	1.31573
H	-10.21302	-2.70246	0.39603
H	-8.55096	-2.58629	1.00508
C	-0.44982	0.75915	-1.40732
H	-0.68783	1.09901	-2.42139
H	0.21415	1.49588	-0.94199
H	0.11406	-0.17544	-1.49965
H	-8.24945	3.33241	1.9473
C	-4.44566	1.30569	4.42689
C	-4.84305	2.54802	4.95593
C	-3.06912	1.05987	4.27754
C	-3.89998	3.50759	5.32416
H	-5.90087	2.75054	5.1115
C	-2.12759	2.01842	4.64728
H	-2.72541	0.11588	3.86358
C	-2.53711	3.24795	5.16952
H	-4.23167	4.45344	5.74319
H	-1.06963	1.80473	4.52437
H	-1.80135	3.9929	5.45709
H	-4.32595	-1.40097	4.71416
C	-7.36292	2.07784	-0.24258
C	-7.24992	3.23937	-1.01837
C	-8.08116	0.99067	-0.75755
C	-7.82506	3.29805	-2.28869
H	-6.71414	4.10445	-0.65377
C	-8.66178	1.05846	-2.02596
H	-8.22202	0.09671	-0.1618
C	-8.53276	2.21034	-2.80007
H	-7.7188	4.20541	-2.87592
H	-9.22213	0.2067	-2.40061
H	-8.98266	2.2629	-3.78684
C	-2.53682	-0.5892	-1.29385
H	-3.42131	-0.87858	-0.72319
H	-2.85966	-0.23567	-2.28045
H	-1.9191	-1.48331	-1.44359

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C	-10.07512	-0.87298	2.28764
C	-8.92857	-0.05415	2.13196
C	-9.04494	1.34677	2.09188
C	-10.30903	1.94218	2.15002
C	-11.46972	1.17923	2.27809
C	-11.30808	-0.21352	2.35621
H	-10.36695	3.0244	2.10324
H	-12.19948	-0.81528	2.474
C	-7.83154	2.24396	2.11357
H	-7.34148	2.18492	3.09243
N	-6.73521	1.98767	1.09657
C	-5.63492	2.97504	1.41753
H	-6.06978	3.97973	1.48804
H	-5.30847	2.71796	2.43106
C	-4.45068	3.0093	0.48341
C	-3.99319	4.23663	-0.00738
C	-3.74612	1.83257	0.18737
C	-2.8465	4.32218	-0.7967
H	-4.54934	5.13289	0.2485
C	-2.57368	1.86287	-0.60804
C	-2.17261	3.12031	-1.07306
H	-1.28132	3.17453	-1.6842
O	-4.23047	0.67408	0.71496
O	-7.67913	-0.58545	1.99569
Zr	-5.76097	-0.25417	1.57285
C	-9.99132	-2.41167	2.38844
C	-12.87886	1.79503	2.34136
C	-1.75733	0.59322	-0.93068
C	-2.30764	5.65162	-1.35585
C	-4.37745	-2.34318	2.48612
H	-4.08928	-3.01911	3.28276
C	-5.14156	-3.04159	1.44586
C	-5.46076	-4.40645	1.46436
C	-6.03853	-2.79311	-0.72525
C	-6.02633	-4.96762	0.3267
H	-5.21094	-5.00893	2.3311
H	-6.24306	-6.03142	0.29141
H	-3.48305	-1.85984	2.08234
C	-6.28228	-4.16468	-0.7882
N	-5.50131	-2.24903	0.39443
H	-6.67974	-4.59402	-1.7019
C	-6.35025	-1.89507	-1.89117
H	-7.43189	-1.75515	-1.99908
H	-5.88313	-0.91406	-1.78611
H	-5.98995	-2.34615	-2.82169
C	-4.81609	-1.01015	4.17227
H	-5.56283	-1.7012	4.5555
C	-5.31773	0.27811	3.77002
H	-6.31007	0.50469	4.16366
C	-11.37065	-3.05802	2.63773
H	-11.82865	-2.70651	3.56875
H	-12.07115	-2.87301	1.81596
H	-11.24816	-4.14335	2.72234

C	-9.08066	-2.81935	3.57281
H	-8.06257	-2.44234	3.45185
H	-9.48004	-2.43311	4.51765
H	-9.03447	-3.91229	3.65126
C	-13.73083	1.25136	1.16911
H	-13.83625	0.16199	1.20963
H	-14.73825	1.68253	1.20069
H	-13.28156	1.50991	0.20334
C	-12.8478	3.33239	2.23924
H	-12.28655	3.78646	3.06423
H	-12.40773	3.67158	1.29416
H	-13.8694	3.72442	2.28434
C	-13.55001	1.41435	3.68305
H	-12.97295	1.79421	4.53385
H	-14.5572	1.84357	3.73797
H	-13.64615	0.32978	3.80053
C	-3.1857	6.85199	-0.95312
H	-4.21005	6.75612	-1.33238
H	-3.23055	6.98053	0.1347
H	-2.76648	7.77223	-1.37362
C	-0.87911	5.89655	-0.81318
H	-0.18946	5.09603	-1.10091
H	-0.47839	6.83737	-1.20837
H	-0.87997	5.96159	0.28091
C	-2.26526	5.5825	-2.9015
H	-1.88301	6.52392	-3.31303
H	-1.61475	4.77739	-3.25905
H	-3.26591	5.41297	-3.31553
C	-1.22595	-0.03384	0.38101
H	-0.65071	-0.94112	0.16052
H	-0.5619	0.66518	0.90276
H	-2.03832	-0.30213	1.06065
C	-9.443	-2.99636	1.06619
H	-9.39506	-4.09039	1.12701
H	-10.09927	-2.73653	0.22706
H	-8.4398	-2.62647	0.84723
C	-0.53353	0.89523	-1.82051
H	-0.82158	1.31739	-2.78979
H	0.16999	1.5831	-1.3386
H	0.0061	-0.0374	-2.0172
H	-8.16052	3.2831	1.98681
C	-7.27185	2.13732	-0.26524
C	-7.21819	3.35411	-0.95727
C	-7.91997	1.04853	-0.85996
C	-7.78065	3.46546	-2.2294
H	-6.73686	4.2212	-0.52564
C	-8.48603	1.16704	-2.13099
H	-8.02255	0.11334	-0.3208
C	-8.41443	2.37415	-2.82404
H	-7.72227	4.41494	-2.75329
H	-8.99426	0.31409	-2.57156
H	-8.85352	2.46667	-3.81273
C	-2.63408	-0.42952	-1.69204
H	-3.49063	-0.75175	-1.09698
H	-3.00448	0.00065	-2.6301
H	-2.04131	-1.31783	-1.94243
H	-4.61827	1.10746	3.86832
C	-3.47543	-1.17645	4.77686
C	-3.29191	-2.17479	5.74972
C	-2.38729	-0.35314	4.43868
C	-2.06196	-2.33141	6.38642
H	-4.12587	-2.81791	6.02261
C	-1.1546	-0.52045	5.06533
H	-2.49816	0.415	3.67845
C	-0.98917	-1.5061	6.043
H	-1.94183	-3.09539	7.14878
H	-0.32123	0.12036	4.79277
H	-0.02836	-1.62938	6.53395

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C	-9.95345	-0.85164	2.29985
C	-8.78964	-0.04825	2.20219
C	-8.88088	1.35438	2.21997
C	-10.13403	1.97433	2.26025
C	-11.31186	1.22766	2.30808
C	-11.17614	-0.17027	2.34053
H	-10.17018	3.05887	2.26961
H	-12.08153	-0.75893	2.40672
C	-7.6365	2.20208	2.30876
H	-7.14446	2.05789	3.27999
N	-6.57361	1.95017	1.27325
C	-5.50053	2.99183	1.48138
H	-5.97545	3.97966	1.51072
H	-5.09197	2.80917	2.4836
C	-4.39644	3.00125	0.4574
C	-4.05656	4.18882	-0.19716
C	-3.66167	1.82932	0.21858
C	-2.98599	4.24148	-1.09039
H	-4.63964	5.07858	0.01574
C	-2.55602	1.8319	-0.66784
C	-2.26715	3.05127	-1.2932
H	-1.43009	3.08269	-1.97818
O	-4.06926	0.70921	0.88069
O	-7.53768	-0.58237	2.10339
Zr	-5.60746	-0.20885	1.75006
C	-9.89836	-2.39108	2.40389
C	-12.7124	1.86573	2.34297
C	-1.69273	0.57889	-0.92433
C	-2.57106	5.52529	-1.83179
C	-3.94654	-2.38723	2.19607
H	-3.43095	-3.12214	2.80721
C	-4.78775	-2.98786	1.15707
C	-4.89337	-4.36301	0.91678
C	-6.1424	-2.49218	-0.71223
C	-5.60416	-4.78876	-0.19879
H	-4.38801	-5.0659	1.57019
H	-5.67609	-5.84746	-0.43013
H	-3.23209	-1.65861	1.80753

C	-6.20696	-3.84687	-1.03682
N	-5.45764	-2.08725	0.38493
H	-6.74008	-4.15721	-1.92875
C	-6.8278	-1.44335	-1.5415
H	-6.14137	-0.62559	-1.78469
H	-7.19943	-1.86782	-2.47726
H	-7.68562	-1.02646	-1.00062
C	-4.71799	-1.5319	4.02683
H	-5.47827	-2.29061	4.19383
C	-5.13579	-0.14863	4.03992
H	-6.15699	-0.01968	4.41063
C	-7.12634	1.97144	-0.12072
H	-6.30021	1.71116	-0.79029
H	-7.87331	1.1739	-0.17104
C	-9.27266	-2.99268	1.12577
H	-9.85542	-2.71591	0.23887
H	-8.24598	-2.65158	0.98669
H	-9.26119	-4.08752	1.19
C	-11.29795	-3.01898	2.57017
H	-11.80412	-2.66659	3.47537
H	-11.9468	-2.81973	1.71003
H	-11.19521	-4.10622	2.65557
C	-13.52664	1.38585	1.1172
H	-13.64612	0.29732	1.10496
H	-14.52927	1.82875	1.13121
H	-13.03956	1.68078	0.1804
C	-12.65164	3.40498	2.30597
H	-12.11796	3.81495	3.17138
H	-12.16678	3.77393	1.39433
H	-13.66728	3.81414	2.32474
C	-13.44227	1.44333	3.64088
H	-12.89257	1.77677	4.52849
H	-14.44292	1.88946	3.67448
H	-13.56239	0.35698	3.70913
C	-3.48	6.71916	-1.48196
H	-4.5246	6.53435	-1.75917
H	-3.44411	6.96234	-0.4137
H	-3.14825	7.60702	-2.03054
C	-1.11872	5.89669	-1.44607
H	-0.40935	5.10477	-1.70898
H	-0.80819	6.80727	-1.97154
H	-1.03258	6.08023	-0.3691
C	-2.65116	5.28959	-3.35947
H	-2.35348	6.19629	-3.89896
H	-1.98976	4.47977	-3.68511
H	-3.67182	5.033	-3.66615
C	-1.05252	0.11102	0.40505
H	-0.46958	-0.80398	0.24426
H	-0.37366	0.8775	0.7958
H	-1.80559	-0.08701	1.1712
C	-9.06329	-2.79892	3.64281
H	-9.02425	-3.89163	3.72731
H	-8.03838	-2.4243	3.57997
H	-9.51461	-2.40768	4.56156
C	-0.53845	0.85149	-1.91168
H	-0.90123	1.15364	-2.90055
H	0.14773	1.62229	-1.54414
H	0.04391	-0.06676	-2.04435
C	-2.55634	-0.54945	-1.5366
H	-3.37662	-0.84189	-0.87807
H	-2.98217	-0.23014	-2.4956
H	-1.93826	-1.43554	-1.72599
H	-7.92268	3.25969	2.26823
C	-7.76316	3.28258	-0.60164
H	-7.02836	4.09505	-0.56814
H	-8.59442	3.56616	0.05514
C	-8.28784	3.14302	-2.04006
H	-7.46082	2.84578	-2.70001
H	-9.02506	2.32886	-2.08048
C	-8.92237	4.43395	-2.5674
H	-9.285	4.30383	-3.59235
H	-9.77444	4.7401	-1.94892
H	-8.19967	5.25846	-2.57174
H	-3.75142	-1.77108	4.45992
C	-4.20301	0.92732	4.47383
C	-4.71498	2.05216	5.14867
C	-2.81644	0.87275	4.24231
C	-3.87558	3.0823	5.5734
H	-5.77881	2.10202	5.37289
C	-1.97775	1.90088	4.67031
H	-2.38477	0.02425	3.71796
C	-2.50163	3.01281	5.33426
H	-4.29494	3.93242	6.10447
H	-0.90982	1.83336	4.48272
H	-1.84575	3.81155	5.66722

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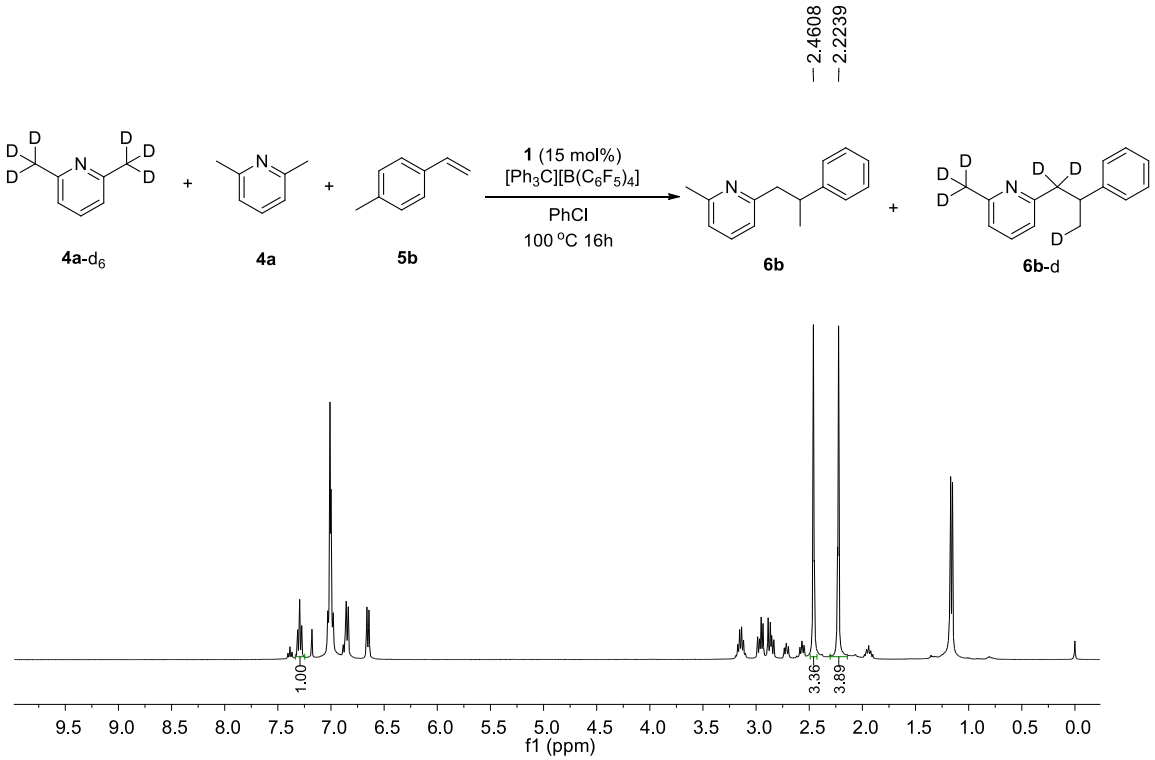
C	-10.15409	-0.79882	2.22278
C	-8.97443	-0.01468	2.15309
C	-9.04494	1.38922	2.18176
C	-10.28913	2.02729	2.2256
C	-11.47869	1.30034	2.26633
C	-11.36592	-0.09965	2.27304
H	-10.30808	3.11206	2.24418
H	-12.28077	-0.67528	2.32317
C	-7.79553	2.23033	2.27929
H	-7.33503	2.11444	3.26909
N	-6.70419	1.94167	1.28549
C	-5.63082	2.97799	1.49859
H	-6.09434	3.97179	1.48825
H	-5.26152	2.81581	2.52002
C	-4.4885	2.95628	0.51613
C	-4.10815	4.13311	-0.13635
C	-3.76053	1.7727	0.31519
C	-3.00302	4.16364	-0.98782
H	-4.68827	5.03188	0.04523
C	-2.62182	1.75272	-0.52749
C	-2.2926	2.96223	-1.15165

H	-1.42982	2.97636	-1.80442
O	-4.20645	0.66162	0.96739
O	-7.73287	-0.57421	2.06563
Zr	-5.78385	-0.23344	1.79634
C	-10.12742	-2.34168	2.2685
C	-12.86806	1.96126	2.31528
C	-1.76895	0.48432	-0.74109
C	-2.54697	5.43488	-1.72724
C	-4.30869	-2.38983	2.60665
H	-3.95347	-3.11115	3.33445
C	-5.08966	-3.03515	1.54191
C	-5.331	-4.41433	1.45046
C	-6.14615	-2.65494	-0.5406
C	-5.93774	-4.90585	0.30249
H	-4.99673	-5.07504	2.24316
H	-6.09899	-5.97353	0.18456
H	-3.45867	-1.82525	2.21369
C	-6.31962	-4.02533	-0.71606
N	-5.55212	-2.18474	0.58374
H	-6.76736	-4.39601	-1.63156
C	-6.61198	-1.65114	-1.55867
H	-7.50632	-1.12502	-1.20164
H	-5.83361	-0.90876	-1.76389
H	-6.87434	-2.14236	-2.4989
C	-4.82875	-1.18544	4.35021
H	-5.55161	-1.92293	4.69146
C	-5.38357	0.11722	4.02978
H	-6.37872	0.27864	4.45186
C	-7.21016	1.92302	-0.12653
H	-6.3612	1.64679	-0.76116
H	-7.95357	1.12134	-0.17982
C	-11.53782	-2.95024	2.41507
H	-12.03463	-2.62445	3.33544
H	-12.18587	-2.7063	1.56599
H	-11.4538	-4.04163	2.45718
C	-9.29626	-2.81952	3.48459
H	-8.2622	-2.47146	3.42973
H	-9.73304	-2.45294	4.42063
H	-9.28739	-3.91544	3.52573
C	-13.69326	1.51701	1.08348
H	-13.82861	0.4308	1.05103
H	-14.68926	1.97419	1.1092
H	-13.20466	1.82243	0.15089
C	-12.78133	3.4994	2.30587
H	-12.23534	3.88401	3.17515
H	-12.29568	3.87664	1.39812
H	-13.78959	3.92566	2.33855
C	-13.60151	1.52796	3.60757
H	-13.04451	1.83735	4.49929
H	-14.59505	1.98895	3.65165
H	-13.7382	0.4426	3.65735
C	-3.44683	6.6454	-1.4126
H	-4.48609	6.47436	-1.71742
H	-3.43688	6.89688	-0.34564
H	-3.08617	7.52348	-1.95866
C	-1.10043	5.78789	-1.30437
H	-0.39582	4.98392	-1.54207
H	-0.76239	6.68969	-1.82796
H	-1.04107	5.97887	-0.22686
C	-2.58827	5.18685	-3.25449
H	-2.25948	6.08326	-3.79309
H	-1.9326	4.36245	-3.55412
H	-3.60452	4.94567	-3.58743
C	-1.19719	0.00481	0.61505
H	-0.59781	-0.90243	0.47243
H	-0.54629	0.77083	1.05218
H	-1.98872	-0.21755	1.33454
C	-9.5206	-2.89652	0.96013
H	-9.50322	-3.99288	0.98569
H	-10.11907	-2.59097	0.09354
H	-8.49808	-2.54547	0.81543
C	-0.56872	0.73602	-1.67762
H	-0.88289	1.03849	-2.68287
H	0.11133	1.49906	-1.28328
H	0.00598	-0.19077	-1.78103
C	-2.62376	-0.63288	-1.38542
H	-3.46398	-0.92109	-0.75019
H	-3.01662	-0.30666	-2.35617
H	-2.00855	-1.52429	-1.55838
H	-8.07529	3.28733	2.19571
C	-7.8353	3.21781	-0.66333
H	-7.10702	4.03613	-0.62044
H	-8.69224	3.50929	-0.04419
C	-8.30459	3.04222	-2.11668
H	-7.45059	2.74091	-2.73931
H	-9.03107	2.21906	-2.16683
C	-8.9337	4.31459	-2.6935
H	-9.25624	4.1598	-3.72836
H	-9.81172	4.62209	-2.11324
H	-8.22098	5.14778	-2.68756
C	-3.49302	-1.32432	4.97609
C	-3.28059	-2.35894	5.90384
C	-2.43553	-0.44231	4.69362
C	-2.05296	-2.49531	6.55003
H	-4.09043	-3.0479	6.13415
C	-1.20482	-0.58822	5.32965
H	-2.56947	0.35578	3.96843
C	-1.01077	-1.61166	6.26199
H	-1.91109	-3.28928	7.27729
H	-0.39557	0.09864	5.09967
H	-0.05205	-1.719	6.76069
H	-4.71622	0.96211	4.20471

Kinetic isotope effect study



In a glovebox filled with nitrogen, PhCl solution (1.0 mL) of $[Ph_3C][B(C_6F_5)_4]$ (138 mg, 0.15 mmol) was slowly added to PhCl solution (1.0 mL) of **1** (120 mg, 0.15 mmol) under stirring in a 10 mL Schlenk tube. A color change from orange to colorless was observed immediately. After 5 min, a mixture of 2,6-lutidine **4a** (58 μL, 0.5 mmol), **4a**-*d*$_6$ (58 μL, 0.5 mmol) and **5b** (527 μL, 4 mmol) in 1.0 mL of PhCl was added. The Schlenk tube was taken out of the glovebox and heated at 100 ℃ for 16 h. After reaction, solvent was removed, and the product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, 0.5% NEt_3) to afford **6b** and **6b**-*d*. The product mixture was analyzed by ^{1}H NMR spectroscopy. K_H/K_D was determined as follows:

$$k_H / k_D = \frac{3.36}{3.89 - 3.36} = 6.3$$

References

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