Supporting Information

Rare-Earth-Catalyzed C-H Bond Addition of Pyridines to Olefins

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General Information

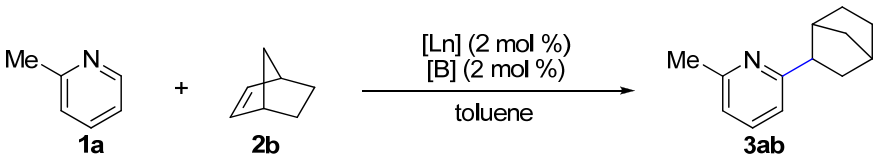
All manipulations of air- and moisture-sensitive compounds were performed under an argon atmosphere by use of standard Schlenk techniques or a nitrogen atmosphere in an mBRAUN Labmaster 130 glovebox. Argon, nitrogen and ethylene (Takachiho Chemical Industrial Co., Ltd.) were purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Toluene and THF were obtained from Kanato Kagaku Co., purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in a glovebox. Most pyridines and olefins were purchased from TCI, dried over CaH_2, vacuum-transferred, degassed by two freeze-pump-thaw cycles and kept in a glovebox. Pyridine-d_5 (**1k**-d_5) (Isotec Inc.) and pyridine-2-d_1 (**1k**-d) (CDN Isotopes Inc.) were dried over CaH_2, vacuum-transferred, degassed by two freeze-pump-thaw cycles and kept in a glovebox. 2-isopropylyridine (**1c**) and 2-tert-butylpyridine **(1d**) were prepared according to the procedures described in the literature.[1] $[Ph_3C][B(C_6F_5)_4]$ purchased from Tosoh Finechem Corporation and $B(C_6F_5)_3$ purchased from Strem Chemicals, Inc. were used without purification. $Cp'Sc(CH_2SiMe_3)_2(THF)$ (Cp' = $C_5Me_4SiMe_3$, C_5Me_5), $Cp'Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (Cp' = C_5H_5, C_5Me_4H, C_5Me_5) and $C_5Me_5Ln(CH_2C_6H_4NMe_2\text{-}o)_2$ (Ln = Sc, Y, Lu, La) were synthesized as described previously.[2-4] Silica gel column chromatography was performed with Merck Silica Gel 60 (0.040-0.063 mm). All ^1H NMR and ^{13}C NMR spectra of organic products were recorded on a JEOL AL-400 (400 MHz for ^1H, 100 MHz for ^{13}C) instrument in $CDCl_3$ with tetramethylsilane as an internal standard, unless otherwise mentioned. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), integration. Mass spectra (MS) were obtained on a JEOL JMS-700V (EI) and high-resolution MS were obtained on a Waters Synapt G2 (ESI+). GC/MS was obtained on a GCMS-QP2010 Ultra (Shimadzu Co.).

Condition Optimization

Table S1 summarizes the experimental results of catalyst screening on the reaction of α-picoline (**1a**) with norbornene (**2b**) under various conditions. In the presence of an equiv of $[Ph_3C][B(C_6F_5)]_4$ as an activator, the half-sandwich scandium dialkyl complexes with different Cp ligands all showed high activity for t*he ortho*-C-H addition of α-picoline to norbornene to give the corresponding alkylated product **3ab** at 70 °C in toluene (Table S1, entries 3-7). The neutral dialkyl complexes or the borate compound alone did not show any catalytic activity under the same conditions (Table S1, entries 1 and 2). The Cp-free tris(benzyl) complex is much less efficient than its Cp-coordinated bis(benzyl) analogues (Table S1, entry 8). The reaction could also take place at a lower temperature (50 °C), though a longer reaction time was needed for completion (Table S1, entry 9). THF is not a

suitable solvent for this reaction, probably because of its strong (non-liable) coordination to the active catalyst species (Table S1, entry 10). Besides $[Ph_3C][B(C_6F_5)]_4$, $B(C_6F_5)_3$ is also effective as an activator for $(C_5Me_5)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$, but BPh_3 did not work under the same conditions (Table S1, entries 11 vs. 12), suggesting that the formation of a weakly coordinated ion pair is critically important. However, $B(C_6F_5)_3$ did not work effectively with the THF-containing dialkyl complex $(C_5Me_5)Sc(CH_2SiMe_3)_2(THF)$ (Table S1, entry 13), although it worked well with the THF-free benzyl analogue $(C_5Me_5)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$. The yttrium half-sandwich bis(benzyl) complex is also effective for this reaction, although a longer reaction time is required to complete the reaction (Table S1, entries 11 vs. 14). The analogous lutetium and lanthanum complexes showed much lower activity under the same conditions (Table S1, entries 15 and 16).

Table S1. C-H Bond Addition of α-Picoline to Norbornene Catalyzed by Various Rare Earth Alkyl Complexes[a]



1a **2b** **3ab**

Entry	[Ln][b]	[B]	temp (°C)	time (h)	yield (%)[c]
1	$C_5Me_4SiMe_3ScR_2(THF)$	--	70	12	0
2	--	$[Ph_3C][B(C_6F_5)_4]$	70	12	0
3	$C_5Me_4SiMe_3ScR_2(THF)$	$[Ph_3C][B(C_6F_5)_4]$	70	4	98[d]
4	$C_5Me_5ScR_2(THF)$	$[Ph_3C][B(C_6F_5)_4]$	70	4	99
5	$C_5Me_5ScBz_2$	$[Ph_3C][B(C_6F_5)_4]$	70	4	99
6	$C_5Me_4HScBz_2$	$[Ph_3C][B(C_6F_5)_4]$	70	4	99
7	$CpScBz_2$	$[Ph_3C][B(C_6F_5)_4]$	70	4	91
8	$ScBz_3$	$[Ph_3C][B(C_6F_5)_4]$	70	12	10(12)
9	$C_5Me_5ScBz_2$	$[Ph_3C][B(C_6F_5)_4]$	50	15	97
10[e]	$C_5Me_5ScBz_2$	$[Ph_3C][B(C_6F_5)_4]$	70	24	< 5
11	$C_5Me_5ScBz_2$	$B(C_6F_5)_3$	70	4	99
12	$C_5Me_5ScBz_2$	BPh_3	70	12	0
13	$C_5Me_5ScR_2(THF)$	$B(C_6F_5)_3$	70	12	< 5
14	$C_5Me_5YBz_2$	$B(C_6F_5)_3$	70	12	96
15	$C_5Me_5LuBz_2$	$B(C_6F_5)_3$	70	24	34(34)
16	$C_5Me_5LaBz_2$	$B(C_6F_5)_3$	70	24	10(13)

[a] Reactions were carried out with 1 mmol of α-picoline and 1.5 mmol of norbornene in 3 mL of toluene, unless otherwise noted. [b] [Ln] = Half-sandwich rare earth dialkyl complex: R = CH_2SiMe_3, Bz = $CH_2C_6H_4NMe_2\text{-}o$. [c] GC yield of **3ab** and conversion of **1a** (in parenthesis) determined by use of tridecane as an internal standard. [d] Isolated yield. [e] THF as solvent.

General Procedure and Analytical Data for Compounds 3

A typical procedure for the catalytic ethylation of pyridines with ethylene

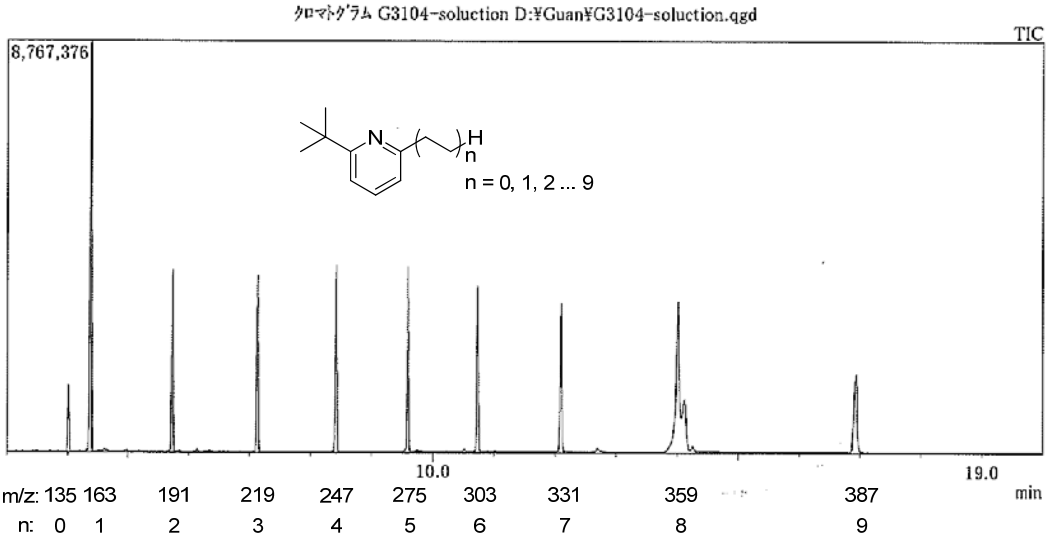
In a glovebox, a toluene solution (1.0 mL) of $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) was slowly added to a stirred toluene solution (1.0 mL) of $C_5Me_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (9.0 mg, 0.02 mmol) in a 30-mL Schlenk tube. After 1 min, α-picoline **1a** (93 mg, 1.0 mmol) in 1.0 mL of toluene was added. The Schlenk tube was taken out of the glovebox and was charged with ethylene (3 atm). The mixture was heated at 70 °C until obvious formation of white solid (polyethylene) was observed, which indicates the complete consumption of α-picoline **1a** and the start of ethylene polymerization. Then the mixture was cooled to room temperature and purified directly by silica gel column chromatography (hexane/ether=10/1) to afford compound **3aa**. To avoid possible loss on solvent evaporation under reduce pressure, 1.0 mL HCl/Et_2O (1 mol/L) was added to convert **3aa** to its hydrochloride salt **3aa·HCl** (156 mg, 98%, Table 1, entry 1).

A typical procedure for the catalytic alkylation of pyridines with other olefins

In a glovebox, a toluene solution (1.0 mL) of $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) was slowly added to a stirred toluene solution (1.0 mL) of $C_5Me_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (9.0 mg, 0.02 mmol) in a 10-mL Schlenk tube. After 1 min, 2-ethylpyridine **1b** (107 mg, 1.0 mmol), norbornene **2b** (141mg, 1.5 mmol) and 1.0 mL of toluene were added. The Schlenk tube was taken out of the glovebox and heated at 70 °C. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and purified directly by silica gel column chromatography (hexane/ether=10/1) to afford compound **3bb** (194 mg, 98%, Table 2, entry 1).

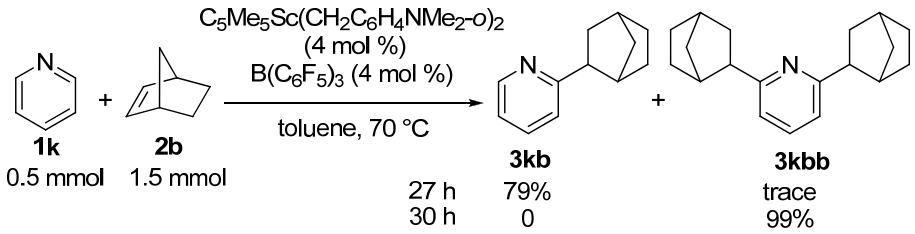
The reaction of 2-*tert*-butylpyridine with ethylene catalyzed by the scandium complex

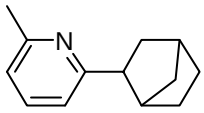
In a glovebox, a toluene solution (1.0 mL) of $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) was slowly added to a stirred toluene solution (1.0 mL) of $C_5Me_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (9.0 mg, 0.02 mmol) in a 30-mL Schlenk tube. After 1 min, 2-tert-butylpyridine **1d** (135 mg, 1.0 mmol) in 1.0 mL of toluene was added. The Schlenk tube was taken out of the glovebox and was charged with ethylene (3 atm). The mixture was heated at 70 °C and white solid was formed after 30 minutes. The GC/MS analysis of the solution showed a mixture of oligomers (See below).



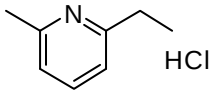
The reaction of pyridine with norbornene

In a glovebox, a toluene solution (1.0 mL) of $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) was slowly added to a stirred toluene solution (1.0 mL) of $C_5Me_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (9.0 mg, 0.02 mmol) in a 10-mL Schlenk tube. After 1 min, α-picoline **1a** (47 mg, 0.5 mmol), norbornene **2b** (141mg, 1.5 mmol) and 1.0 mL of toluene were added. The Schlenk tube was taken out of the glovebox and heated at 70 °C. The reaction was monitored with TLC. The mono-alkylation of pyridine took place rather slowly and no dialkylation product was observed at the early stage. After most pyridine was consumed, further alkylation of the mono-alkylation product took place rapidly and completed in ca. 3 hours to afford the dialkylation product **3kbb** in isolated 99% yield. If the reaction was quenched after the first 27 hours, the mono-alkylation product **3kb** could be isolated in 79% yield.

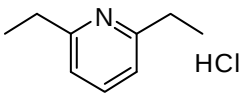




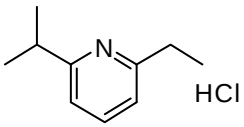
3ab: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 2.85 (dd, *J* = 8.9, 5.6 Hz, 1H), 2.51 (s, 3H), 2.44 (br, 1H), 2.36 (br, 1H), 1.91-1.85 (m, 1H), 1.77-1.71 (m, 1H), 1.62-1.51 (m, 3H), 1.43-1.38 (m, 1H), 1.30-1.25 (m, 1H), 1.18-1.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 157.4, 136.2, 120.0, 117.8, 49.6, 42.8, 37.4, 36.7, 36.0, 30.4, 29.0, 24.7. HR MS (ESI+): Found 188.1440 $[M+H]^+$, calcd. for $C_{13}H_{18}N^+$: 188.1434.



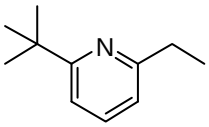
3aa·HCl: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (t, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 3.3 Hz, 1H), 7.70 (d, *J* = 3.4 Hz, 1H), 5.79 (br, 1H), 3.35 (q, *J* = 7.6 Hz, 2H), 3.02 (s, 3H), 1.47 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 152.8, 145.0, 124.5, 122.6, 25.5, 18.7, 12.9. HR MS (ESI+): Found 122.0969 $[M+H]^+$, calcd. for $C_8H_{12}N^+$: 122.0964.



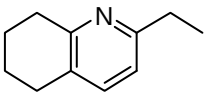
3ba·HCl: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (t, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 5.32 (br, 1H), 3.38 (q, *J* = 7.6 Hz, 4H), 1.47 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 145.3, 122.9, 25.8, 13.2. HR MS (ESI+): Found 136.1122 $[M+H]^+$, calcd. for $C_9H_{14}N^+$: 136.1121.



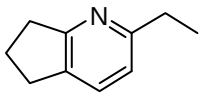
3ca·HCl: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (t, *J* = 7.9 Hz, 1H), 7.58-7.53 (m, 2H), 4.16-4.06 (m, 1H), 3.42 (q, *J* = 7.6 Hz, 2H), 1.50-1.40 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 159.1, 145.2, 122.9, 120.6, 31.4, 26.1, 22.2, 13.4. HR MS (ESI+): Found 150.1282 $[M+H]^+$, calcd. for $C_{10}H_{16}N^+$: 150.1277.



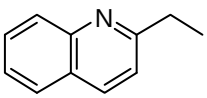
3da: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.35 (s, 9H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 162.0, 136.1, 118.5, 115.7, 37.3, 31.5, 30.2, 13.8. HR MS (ESI+): Found 164.1440 $[M+H]^+$, calcd. for $C_{11}H_{18}N^+$: 164.1434.



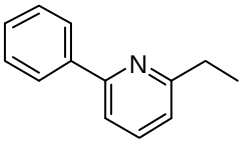
3ea: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.91-2.71 (m, 4H), 1.89-1.76 (m, 4H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 156.4, 137.3, 129.2, 119.0, 32.5, 31.1, 28.3, 23.1, 22.7, 14.3. HR MS (ESI+): Found 162.1285 $[M+H]^+$, calcd. for $C_{11}H_{16}N^+$: 162.1277.



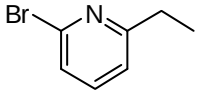
3fa: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 2.15 -2.07 (m, 2H), 1.29 (q, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 161.5, 133.8, 132.3, 119.0, 34.3, 31.2, 30.4, 23.2, 14.5. HR MS (ESI+): Found 148.1125 $[M+H]^+$, calcd. for $C_{10}H_{14}N^+$: 148.1121.



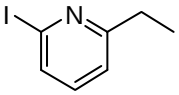
3ga: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.71-7.66 (m, 1H), 7.51-7.47 (m, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.40 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 147.8, 136.3, 129.3, 128.8, 127.4, 126.7, 125.6, 120.8, 32.3, 14.0. HR MS (ESI+): Found 158.0969 $[M+H]^+$, calcd. for $C_{11}H_{12}N^+$: 158.0964.



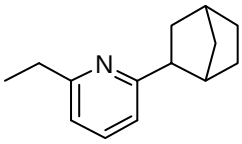
3ha: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.99 (m, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.54-7.37 (m, 4H), 7.10 (d, *J* = 7.6 Hz, 1H), 2.90 (q, *J* = 7.6 Hz, 2H), 1.37 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 156.8, 139.9, 137.0, 128.7, 127.0, 120.4, 117.7, 31.5, 13.8. HR MS (ESI+): Found 184.1131 $[M+H]^+$, calcd. for $C_{13}H_{14}N^+$: 184.1121.



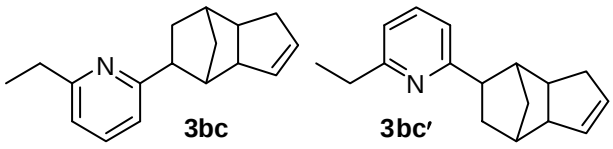
3ia: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 141.5, 138.8, 125.2, 120.8, 31.0, 13.7. HR MS (ESI+): Found 185.9917 $[M+H]^+$, calcd. for $C_7H_9BrN^+$: 185.9913.



3ja: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 137.8, 132.1, 121.1, 117.7, 31.1, 13.8. HR MS (ESI+): Found 233.9781 $[M+H]^+$, calcd. for $C_7H_9IN^+$: 233.9774.

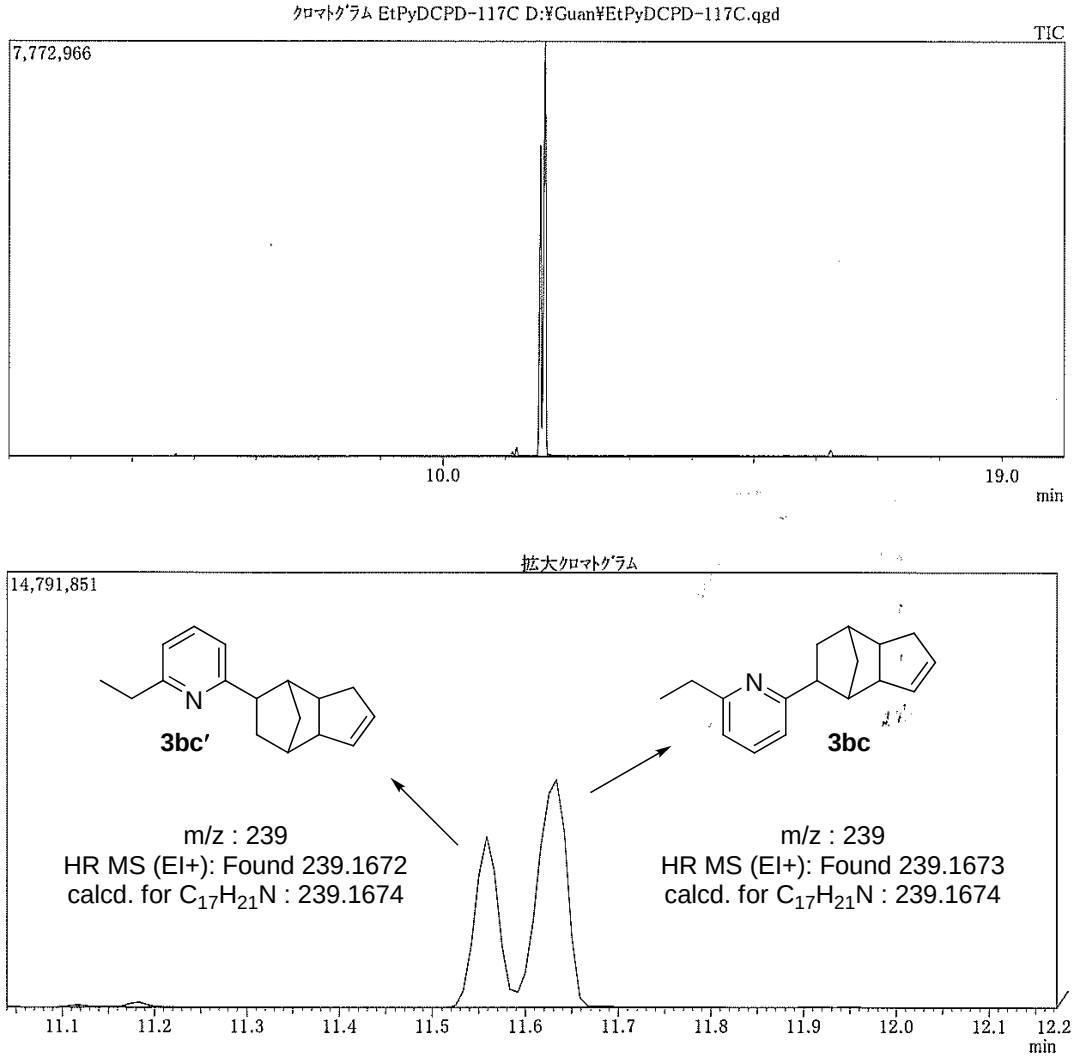


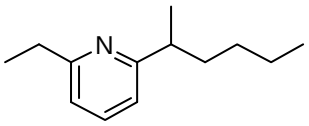
3bb: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 2.85 (dd, *J* = 8.9, 5.5 Hz, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 2.42 (br, 1H), 2.35 (br, 1H), 2.01-1.88 (m, 1H), 1.78-1.50 (m, 4H), 1.46-1.37 (m, 1H), 1.30-1.26 (m, 4H), 1.16-1.14 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 162.6, 136.3, 118.6, 118.2, 49.5, 42.9, 37.2, 36.7, 35.9, 31.5, 30.3, 29.0, 14.0. HR MS (ESI+): Found 202.1593 $[M+H]^+$, calcd. for $C_{14}H_{20}N^+$: 202.1590.



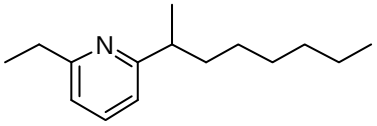
3bc **3bc′**

The ratio of **3bc** to **3bc'** (ca. 2 : 1) in the product mixture was determined by ^{1}H NMR. Selected NMR signals: ^{1}H NMR (400 MHz, $CDCl_3$): δ **3bc:** 7.45 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.76-5.74 (m, 1H), 5.67-5.65 (m, 1H), 3.20-3.15 (m, 1H), 2.95 (dd, *J* = 8.5, 5.2 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). δ **3bc':** 7.45 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.72-5.70 (m, 1H), 5.63-5.60 (m, 1H), 3.09-3.04 (m, 1H), 2.84 (dd, *J* = 8.1, 6.9 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ **3bc:** 165.62, 162.47, 136.07, 132.43, 131.73, 118.54, 118.39, 53.66, 45.63, 44.04, 42.03, 41.20, 38.67, 32.46, 31.45, 28.76, 13.93. δ **3bc':** 165.79, 162.53, 136.14, 132.72, 130.73, 118.43, 52.51, 47.29, 42.67, 41.22, 40.11, 38.96, 32.76, 32.19, 13.87. The GC/MS analysis of the mixture is shown below.

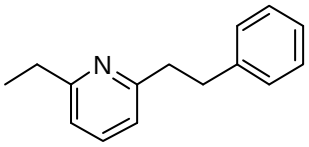




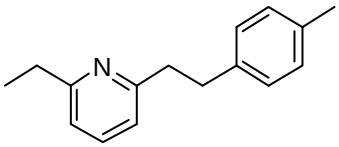
3bd: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 7.7 Hz, 1H), 6.95-6.92 (m, 2H), 2.89-2.74 (m, 3H), 1.74-1.68 (m, 1H), 1.60-1.51 (m, 1H), 1.30-1.13 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 162.6, 136.4, 118.9, 117.8, 42.1, 36.9, 31.5, 29.8, 22.8, 20.9, 14.1, 14.0. HR MS (ESI+): Found 192.1750 $[M+H]^+$, calcd. for $C_{13}H_{22}N^+$: 192.1747.



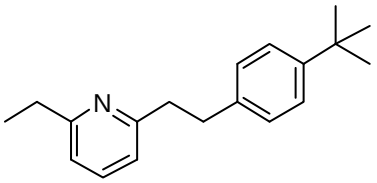
3be: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (t, *J* = 7.7 Hz, 1H), 6.96-6.92 (m, 2H), 2.87-2.76 (m, 3H), 1.75-1.67 (m, 1H), 1.59-1.50 (m, 1H), 1.31-1.14 (m, 14H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 162.7, 136.5, 118.9, 117.9, 42.1, 37.2, 31.8, 31.5, 29.4, 27.5, 22.6, 20.9, 14.2, 14.1. HR MS (ESI+): Found 220.2065 $[M+H]^+$, calcd. for $C_{15}H_{26}N^+$: 220.2060.



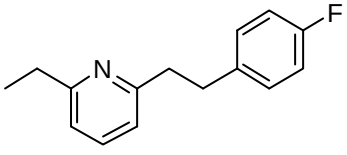
3bf: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.7 Hz, 1H), 7.29-7.16 (m, 5H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 3.10-3.01 (m, 4H), 2.82 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 160.6, 141.7, 136.6, 128.5, 128.3, 125.8, 120.0, 119.2, 40.2, 36.2, 31.5, 14.2. HR MS (ESI+): Found 212.1443 $[M+H]^+$, calcd. for $C_{15}H_{18}N^+$: 212.1434.



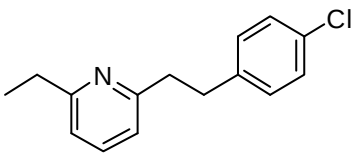
3bg: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.7 Hz, 1H), 7.11-7.06 (m, 4H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 3.08-2.97 (m, 4H), 2.82 (q, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 160.7, 138.7, 136.5, 135.2, 128.9, 128.3, 119.9, 119.1, 40.3, 35.7, 31.5, 21.0, 14.2. HR MS (ESI+): Found 226.1603 $[M+H]^+$, calcd. for $C_{16}H_{20}N^+$: 226.1590.



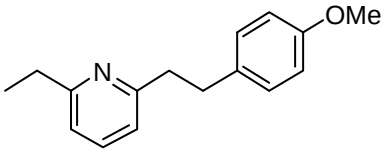
3bh: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 3.09-2.98 (m, 4H), 2.82 (q, *J* = 7.6 Hz, 2H), 1.35-1.27 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 160.9, 148.7, 138.8, 136.6, 128.2, 125.2, 119.9, 119.2, 40.1, 35.6, 34.3, 31.5, 31.4, 14.1. HR MS (ESI+): Found 268.2068 $[M+H]^+$, calcd. for $C_{19}H_{26}N^+$: 268.2060.



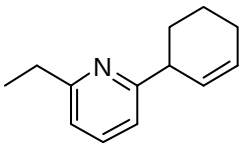
3bi: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.7 Hz, 1H), 7.14-7.11 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.96-6.91 (m, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.07- 2.98 (m, 4H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 161.2 (d, *J* = 242.7 Hz), 160.2, 137.3 (d, *J* = 2.6 Hz), 136.6, 129.8 (d, *J* = 7.4 Hz), 120.0, 119.3, 115.0 (d, *J* = 21.1 Hz), 40.2, 35.2, 31.5, 14.2. HR MS (ESI+): Found 230.1348 $[M+H]^+$, calcd. for $C_{15}H_{17}FN^+$: 230.1340.



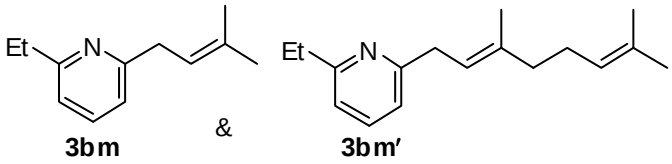
3bj: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.07-2.99 (m, 4H), 2.81 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 160.0, 140.1, 136.6, 131.5, 129.8, 128.3, 120.0, 119.3, 39.9, 35.4, 31.5, 14.2. HR MS (ESI+): Found 246.1055 $[M+H]^+$, calcd. for $C_{15}H_{17}ClN^+$: 246.1044.



3bk: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.06-2.95 (m, 4H), 2.82 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 160.6, 157.7, 136.5, 133.8, 129.4, 120.0, 119.1, 113.6, 55.2, 40.4, 35.3, 31.5, 14.2. HR MS (ESI+): Found 242.1551 $[M+H]^+$, calcd. for $C_{16}H_{20}NO^+$: 242.1539.

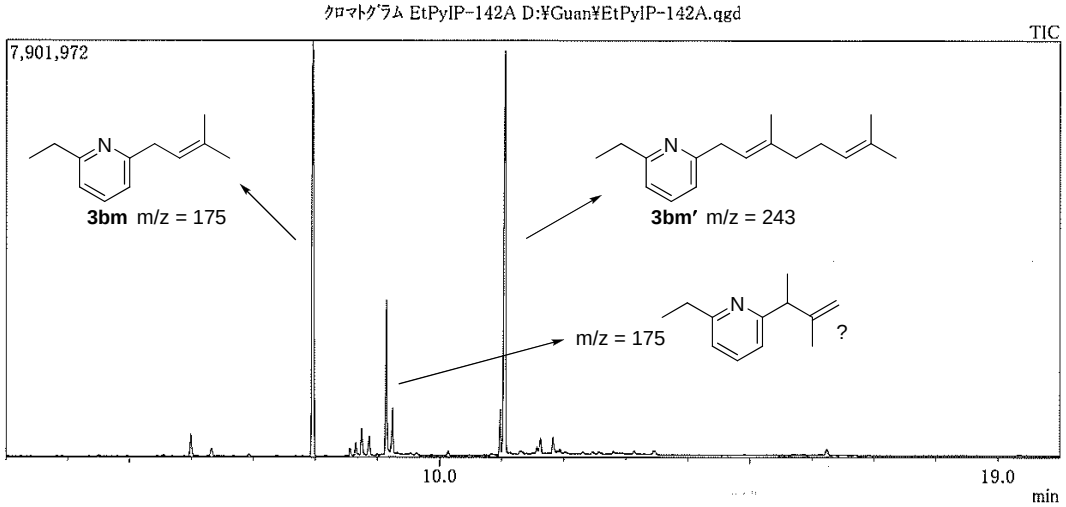


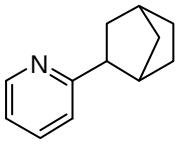
3bl: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, *J* = 7.7 Hz, 1H), 7.02-6.97 (m, 2H), 5.94-5.89 (m, 1H), 5.83-5.79 (m, 1H), 3.61-3.54 (m, 1H), 2.81 (q, *J* = 7.6 Hz, 2H), 2.13-2.05 (m, 3H), 1.73-1.56 (m, 3H), 1.29 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 163.0, 136.6, 129.1, 128.7, 119.2, 118.5, 44.1, 31.5, 30.6, 25.0, 20.9, 14.1. HR MS (ESI+): Found 188.1443 $[M+H]^+$, calcd. for $C_{13}H_{18}N^+$: 188.1434.



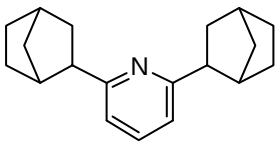
3bm **3bm′**

The ratio of **3bm** to **3bm'** (ca. 1.2 : 1) in the product mixture was determined by ^{1}H NMR. Selected NMR signals: ^{1}H NMR (400 MHz, $CDCl_3$): δ **3bm**: 7.51 (t, *J* = 7.7 Hz, 1H), 5.46-5.41 (m, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 1.76 (s, 3H), 1.68 (s, 3H), 1.30 (t, *J* = 7.7 Hz, 3H). δ **3bm'**: δ 7.51 (t, *J* = 7.7 Hz, 1H), 5.11 (t, *J* = 6.3 Hz, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 2.13-2.05 (m, 4H), 1.72 (s, 3H), 1.71 (s, 3H), 1.68 (s, 3H), 1.30 (t, *J* = 7.7 Hz, 3H). The GC/MS analysis is shown below.



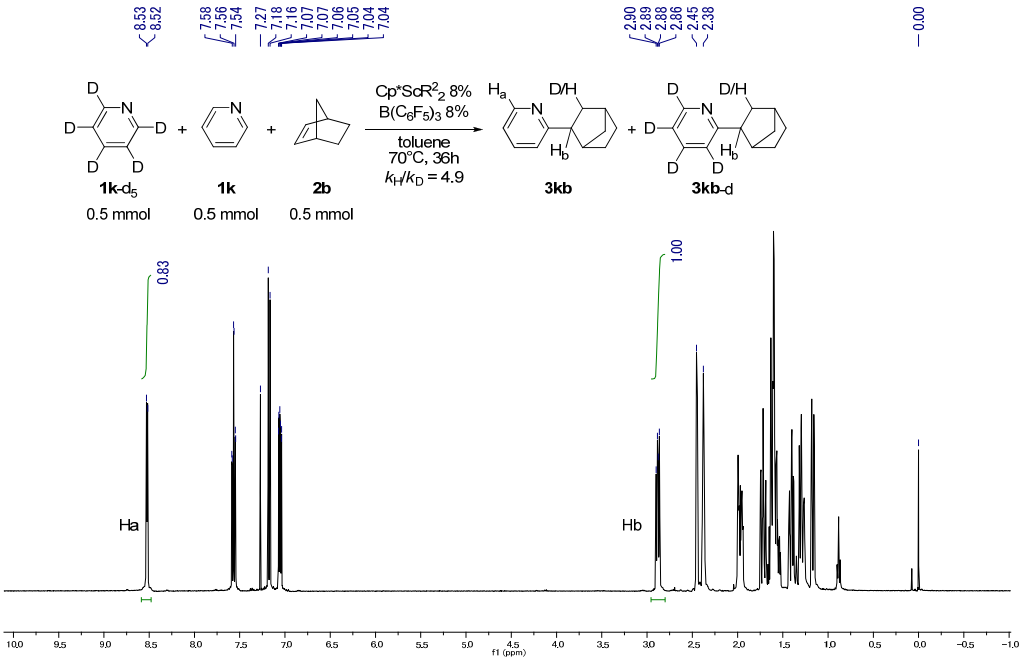


3kb: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.659-7.54 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.05 (ddd, *J* = 7.2, 4.8, 1.0 Hz, 1H), 2.88 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.45 (br, 1H), 2.38 (br, 1H), 1.98-1.94 (mc, 1H), 1.74-1.68 (m, 1H), 1.64-1.53 (m, 3H), 1.43-1.38 (m, 1H), 1.32-1.25 (m, 1H), 1.19-1.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 148.9, 136.0, 121.7, 120.6, 49.5, 42.9, 36.9, 36.7, 35.9, 30.3, 29.1. HR MS (ESI+): Found 174.1282 $[M+H]^+$, calcd. for $C_{12}H_{16}N^+$: 174.1277.



3kbb: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 2H), 2.80 (dd, *J* = 8.9, 5.4 Hz, 2H), 2.37 (br, 2H), 2.35 (br, 2H),2.06-2.01 (m, 2H), 1.77-1.72 (m, 2H), 1.63-1.51 (m, 6H), 1.40-1.24 (m, 4H), 1.13-1.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.73, 135.74, 118.62, 118.57, 49.48, 43.37, 43.27, 36.96, 36.90, 36.70, 35.87, 35.81, 30.41, 29.16. HR MS (ESI+): Found 268.2061 $[M+H]^+$, calcd. for $C_{19}H_{26}N^+$: 268.2060.

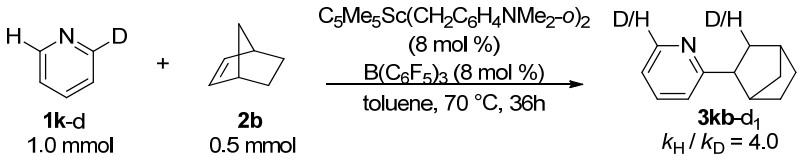
Kinetic Isotope Effect Experiment



In a glovebox, a toluene solution (1.0 mL) of $B(C_6F_5)_3$ (20.4mg, 0.04 mmol) was slowly added to a stirred toluene solution (1.0 mL) of $C_5Me_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (18.0 mg, 0.04 mmol) in a 10-mL Schlenk tube. After 1 min, a mixture of pyridine **1k** (39.5 mg, 0.5 mmol), **1k**-d_5 (42.0 mg, 0.5 mmol) and norbornene **2b** (47 mg, 0.5 mmol) in 1.0 mL of toluene was added. The Schlenk tube was taken out of the glovebox and heated at 70 °C for 36 h. The mixture then was cooled to room temperature and purified directly by silica gel column chromatography (hexane/ether=10/1) to afford **3kb** and **3kb**-*d*. The product mixture was analyzed by ^{1}H NMR. The conversion of **1k** ($\boldsymbol{C}_{1k}$) was determined by integration of the H_a signal of **3kb** (ddd, 8.53 ppm). The total conversion of **1k** and **1k**-d_5 ($\boldsymbol{C}_{total}$) was determined by integration of the H_b signals of **3kb** and **3kb**-*d* (dd, 2.88 ppm). The conversion of **1k**-d_5 could be calculated by $\boldsymbol{C}_{1k\text{-}d5} = \boldsymbol{C}_{total}\text{-}\boldsymbol{C}_{1k}$.

$$K_H / K_D = \frac{C_{1k}}{C_{1k\text{-}d5}} = \frac{C_{1k}}{C_{total} - C_{1k}} = \frac{0.83}{1 - 0.83} = 4.9$$

The kinetic isotope effect experiments were repeated twice, which gave the same k_H/k_D. Blank experiments were carried out and no H-D exchange was found between pyridine and pyridine-d5 (or toluene solvent). The reaction of pyridine-2-d_1 (**1k**-d) with norbornene (**2b**) was carried out similarly, which gave k_H/k_D = 4.0.



References

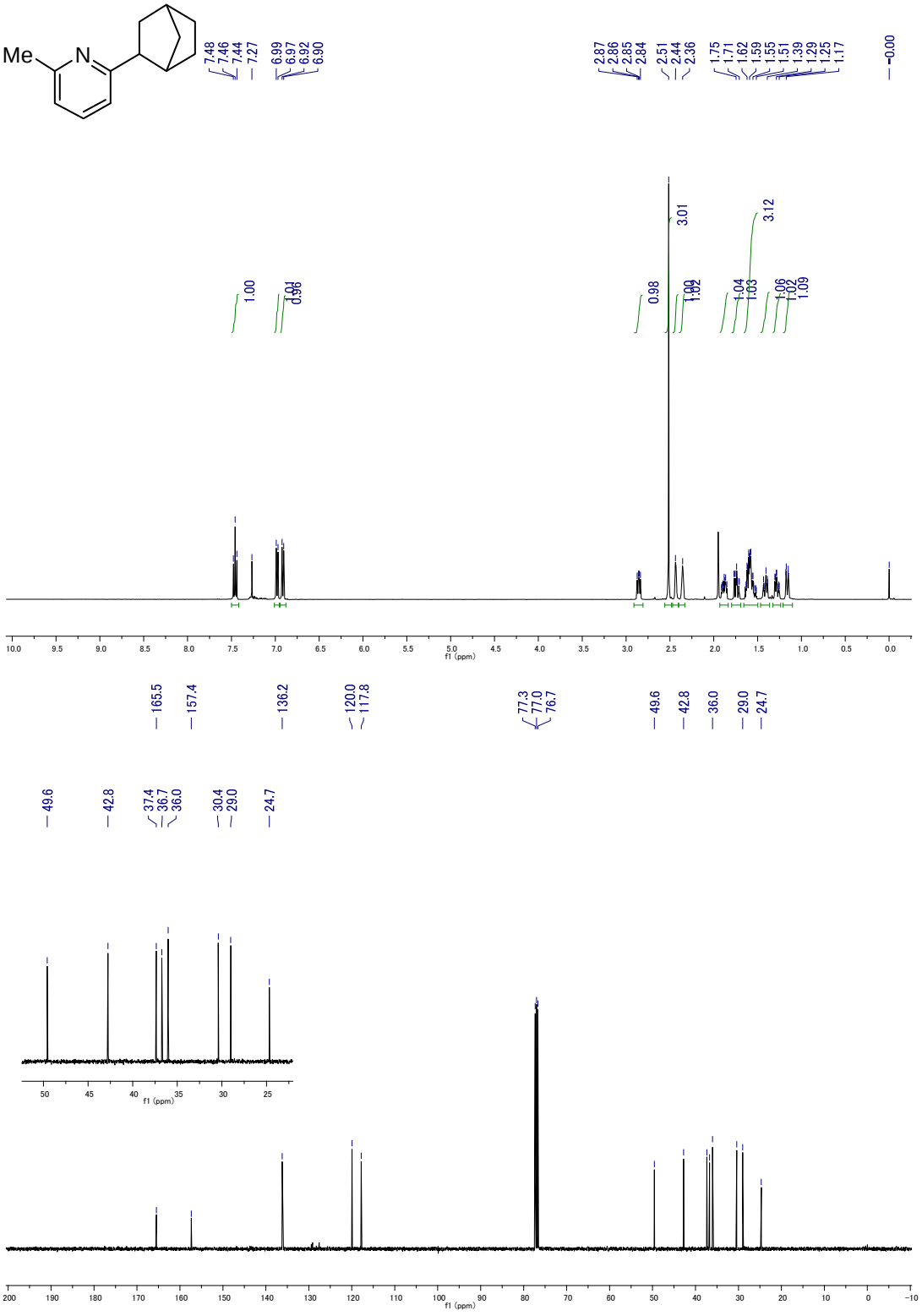
(1) Nienkemper, K.; Kotov, V. V.; Kehr, G.; Erker, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2006**, 366-379.

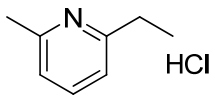
(2) Li, X.; Nishiura, M.; Hu, L.; Mori, K.; Hou, Z. *J. Am. Chem. Soc.* **2009**, *131*, 13870-13882.

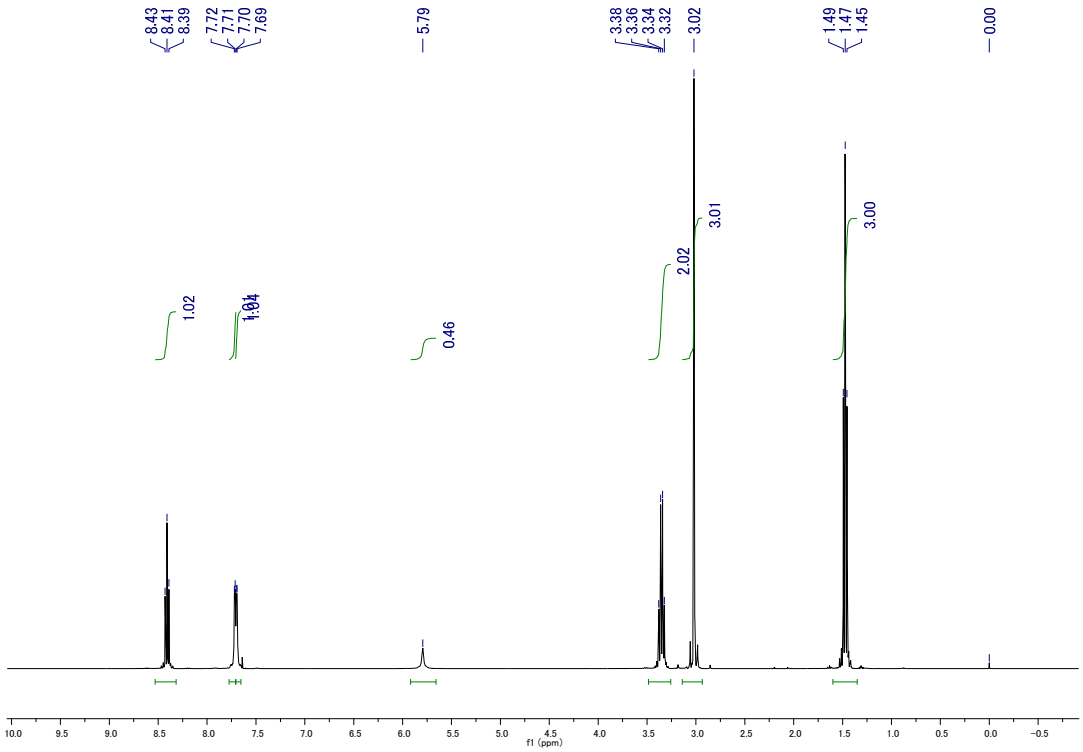
(3) Li, X.; Nishiura, M.; Mori, K.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2007**, 4137-4139.

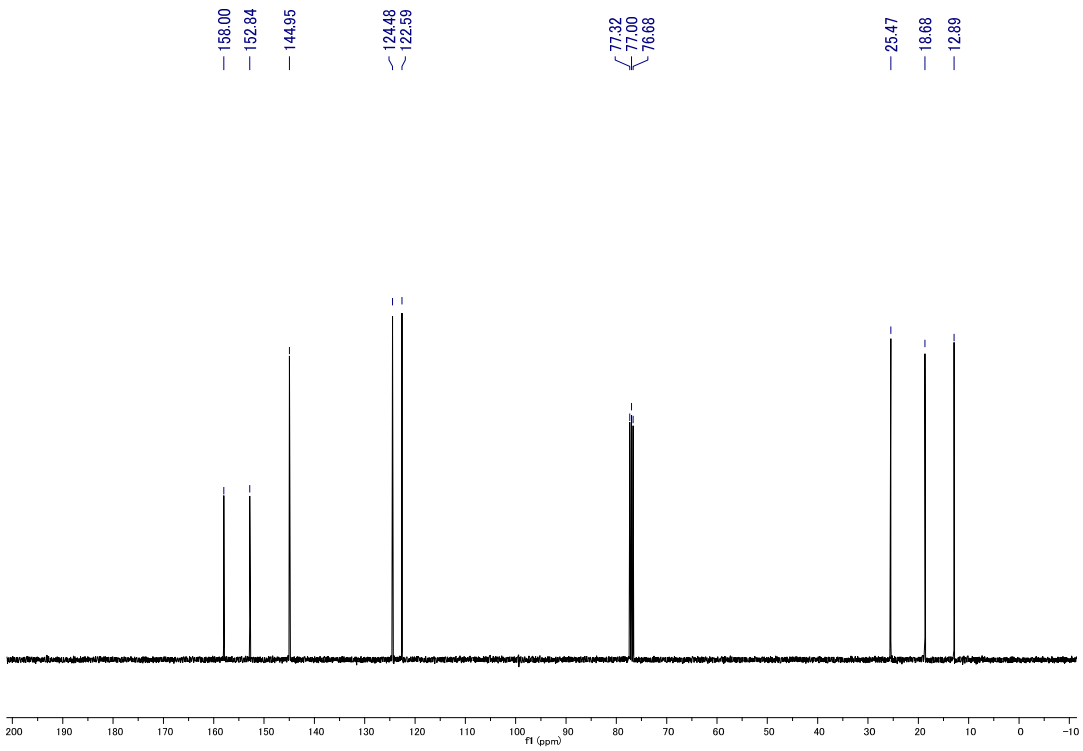
(4) Nishiura, M.; Baldamus, J.; Shima, T.; Mori, K.; Hou, Z. *Chem-Eur. J.* **2011**, *17*, 5033-5044.

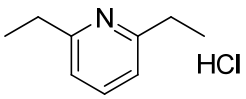
^{1}H and ^{13}C NMR Spectral Charts

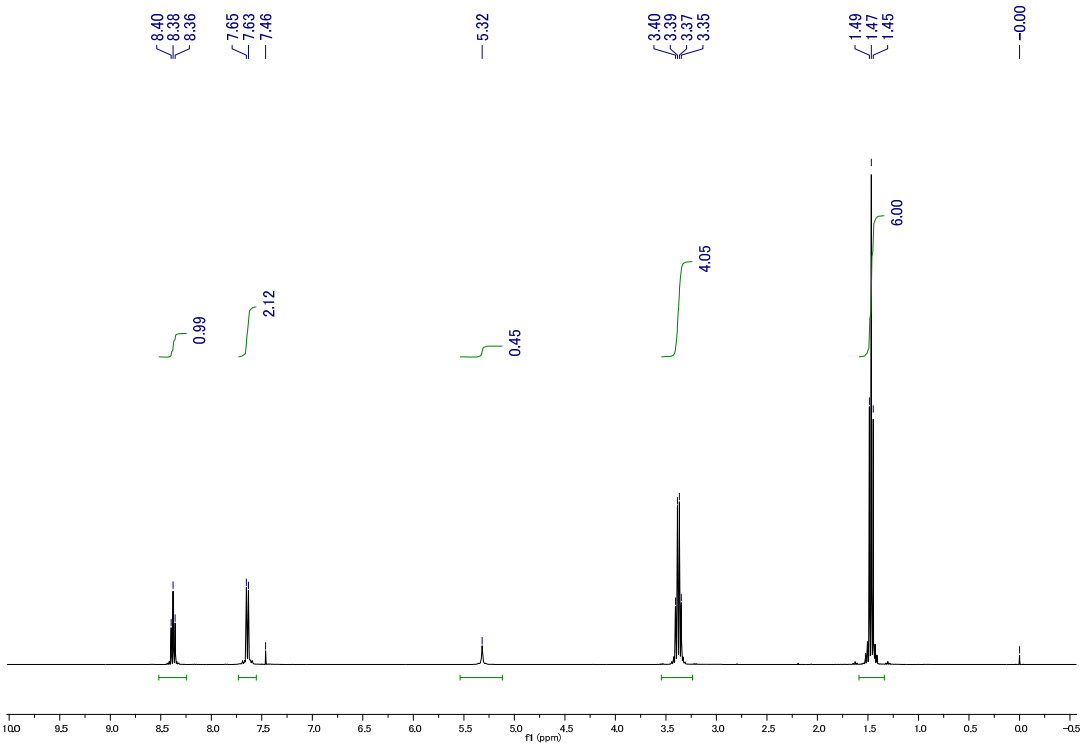


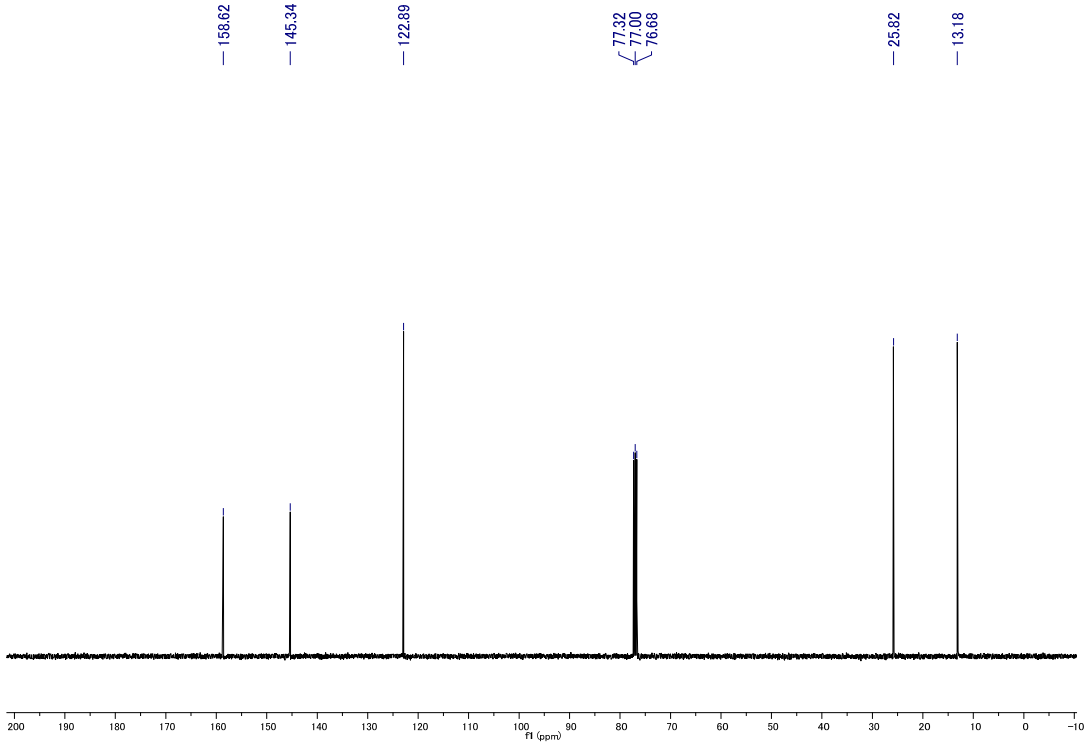

N
HCl

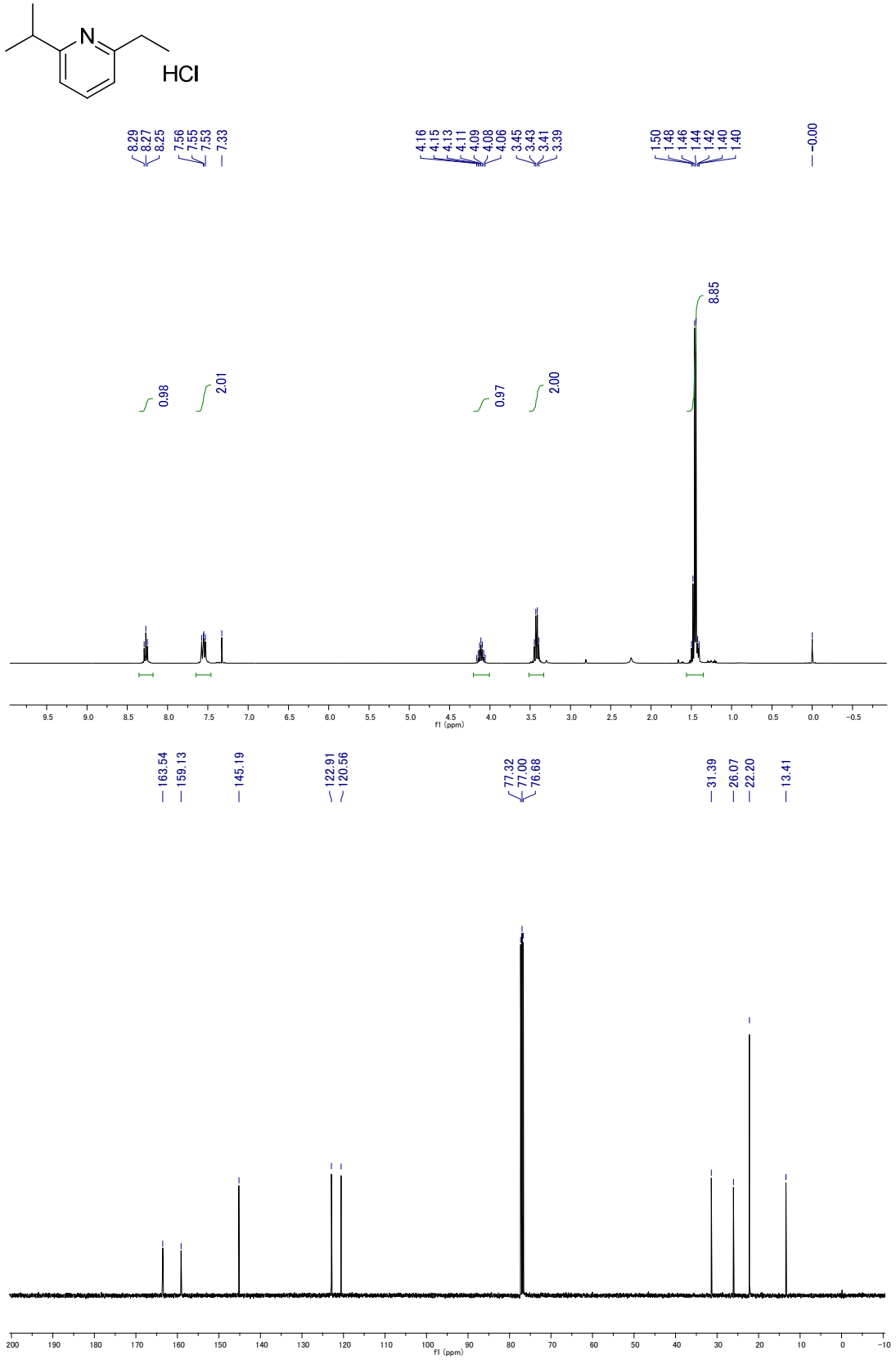

8.43
8.41
8.39
7.72
7.71
7.70
7.69
5.79
3.38
3.36
3.34
3.32
3.02
1.49
1.47
1.45
0.00
1.02
1.01
1.01
0.46
2.02
3.01
3.00
f1 (ppm)


158.00
152.84
144.95
124.48
122.59
77.32
77.00
76.68
25.47
18.68
12.89
f1 (ppm)


N
HCl


8.40
8.38
8.36
7.65
7.63
7.46
5.32
3.40
3.39
3.37
3.35
1.49
1.47
1.45
0.00
0.99
2.12
0.45
4.05
6.00
f1 (ppm)


158.62
145.34
122.89
77.32
77.00
76.68
25.82
13.18
f1 (ppm)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7.33
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4.15
4.13
4.11
4.09
4.08
4.06
3.45
3.43
3.41
3.39
1.50
1.48
1.46
1.44
1.42
1.40
1.40
0.00
0.98
2.01
0.97
2.00
8.85
f1 (ppm)
163.54
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76.68
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22.20
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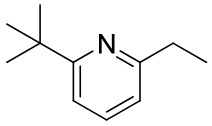
f1 (ppm)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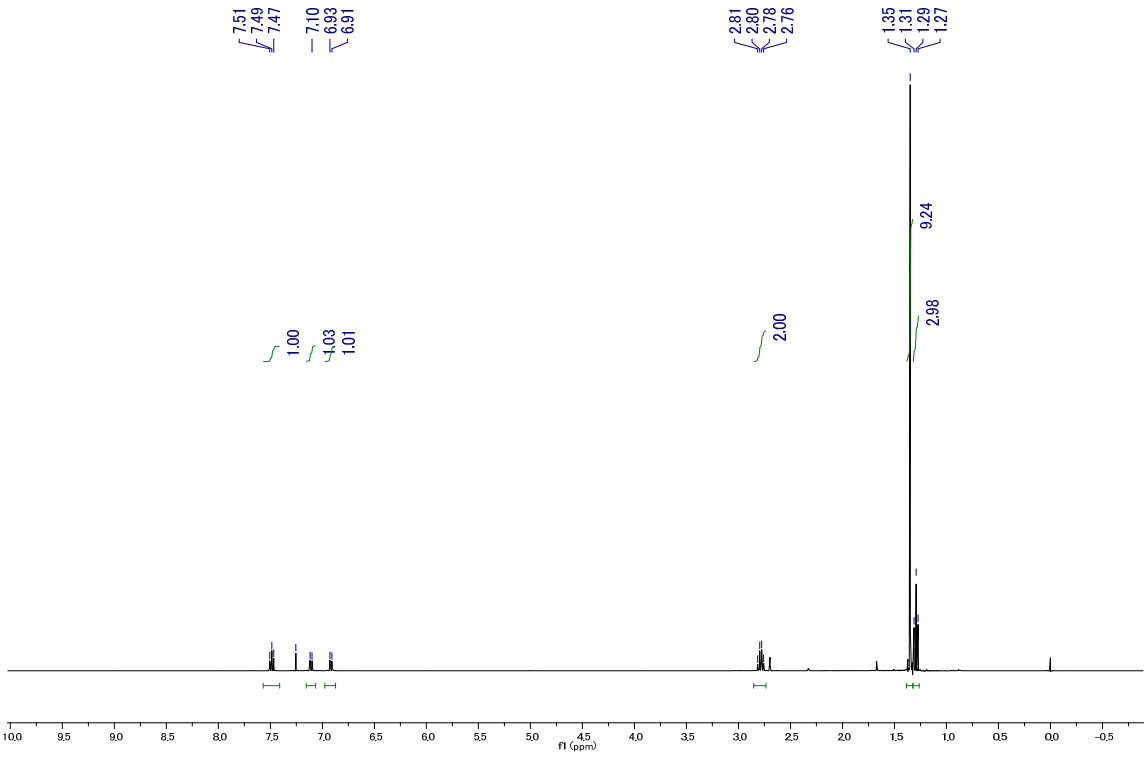
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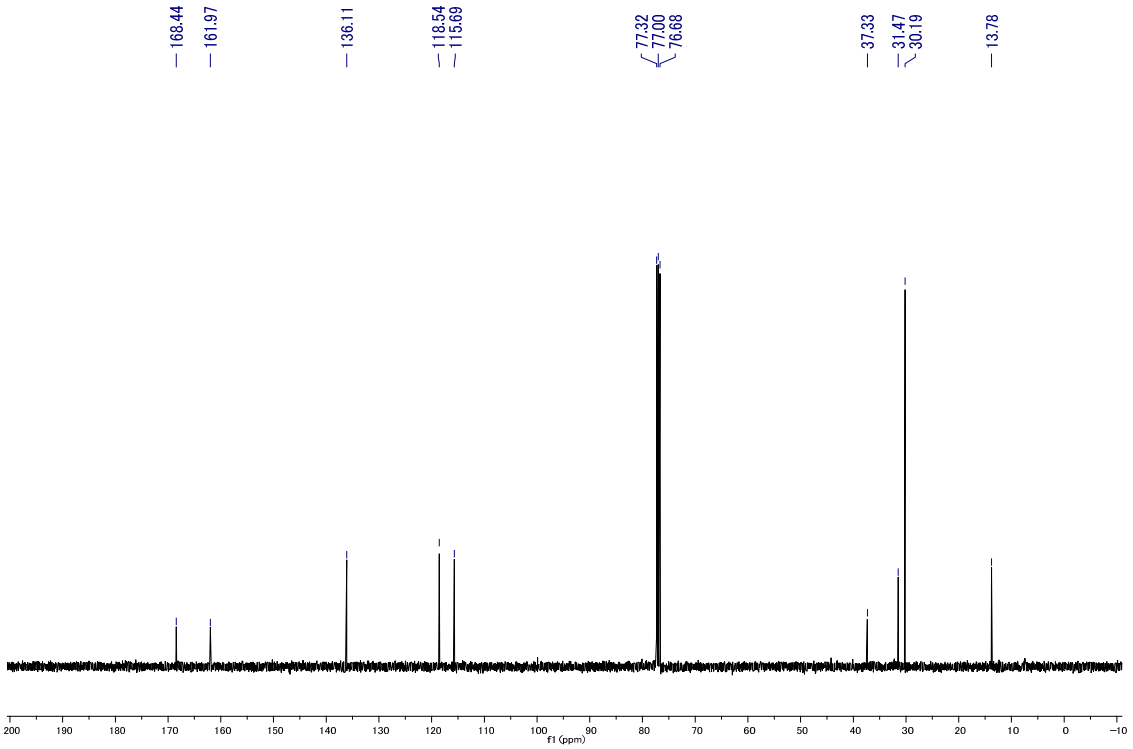
1.01
f1 (ppm)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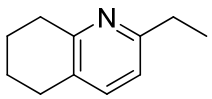
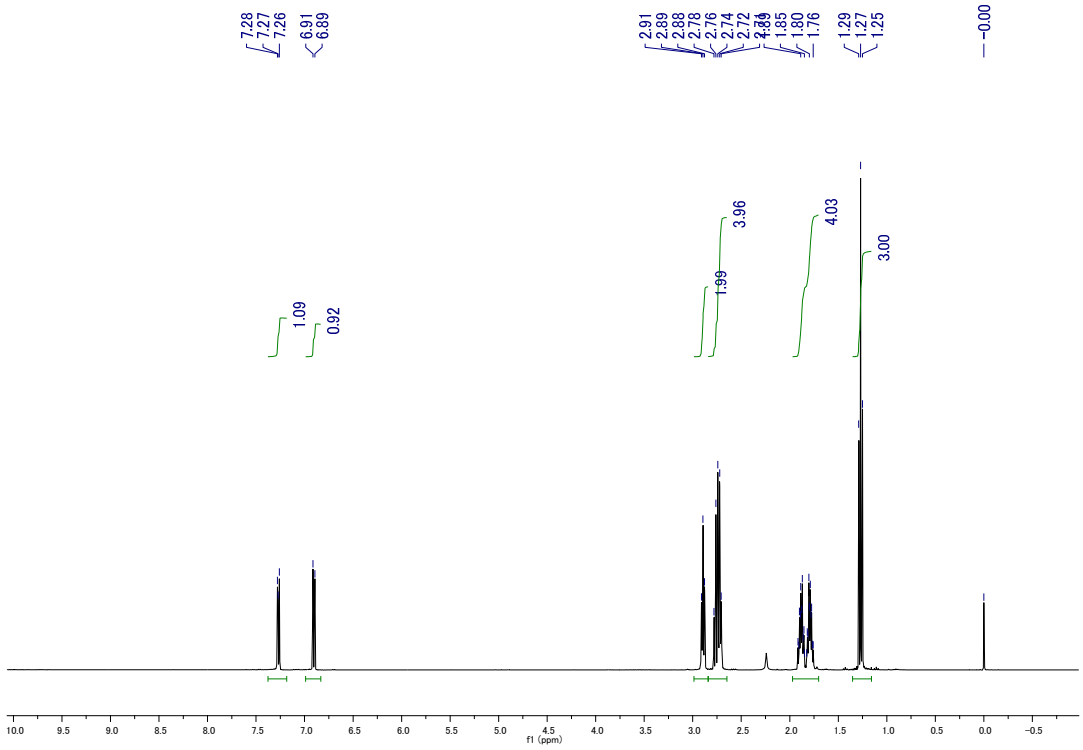
13.78
f1 (ppm)

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2.72
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1.80
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1.09
0.92
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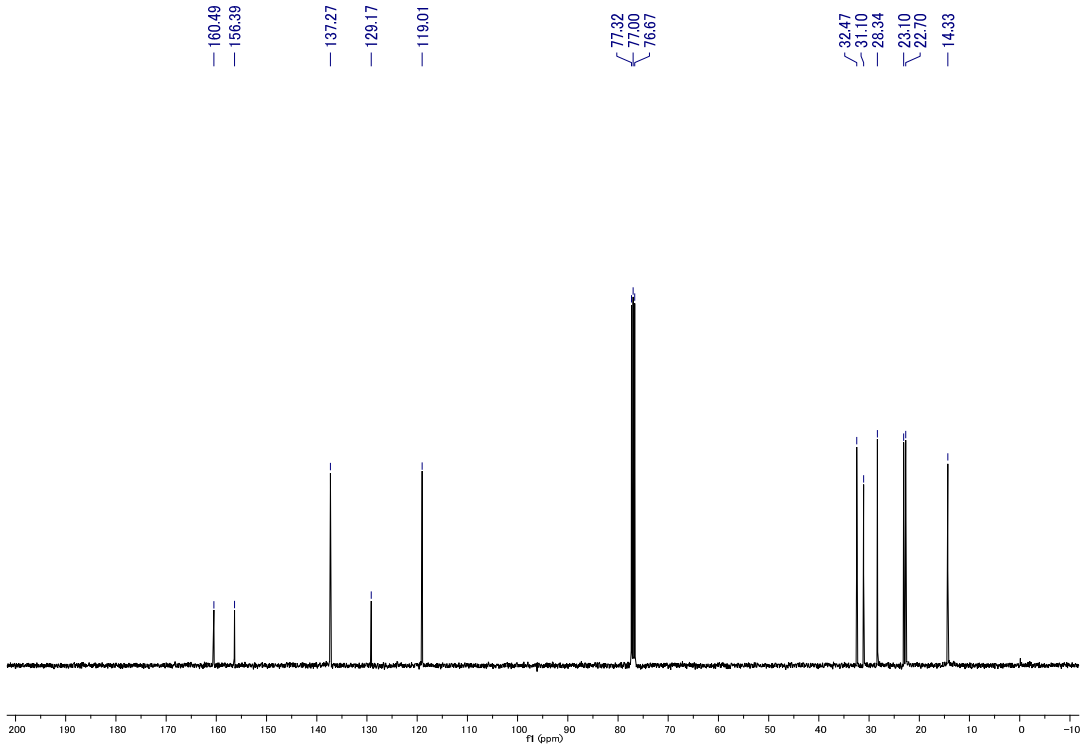
3.00
f1 (ppm)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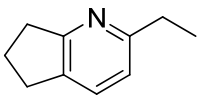
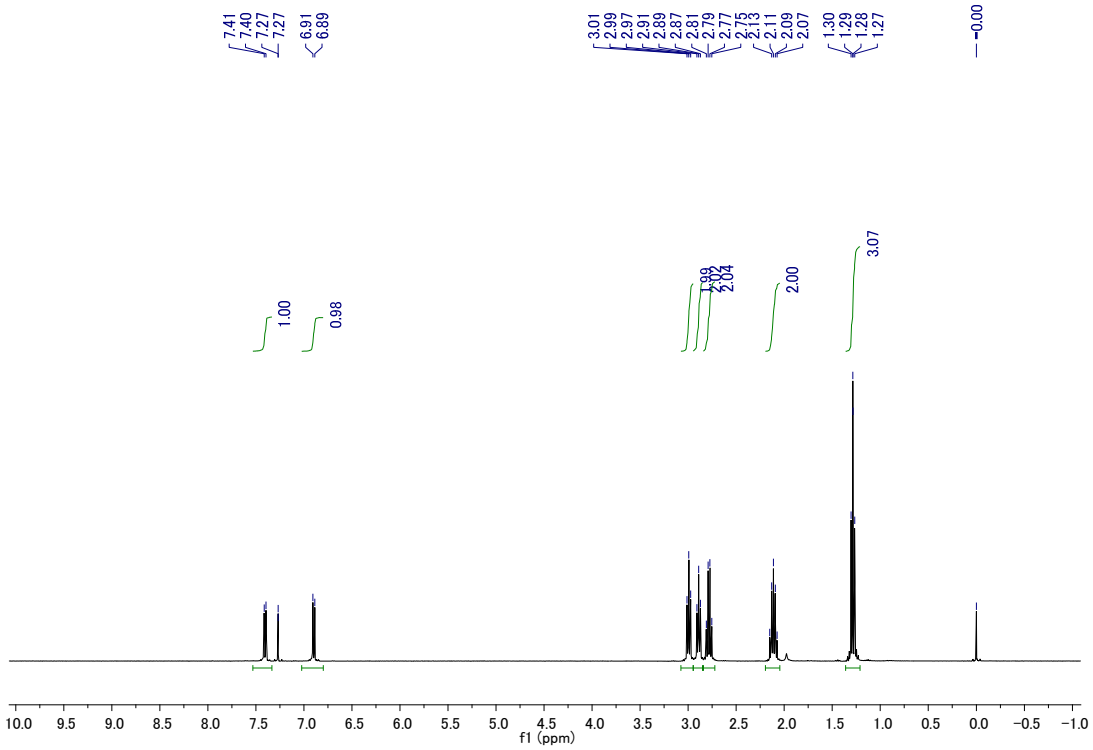
23.10
22.70
14.33
f1 (ppm)

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2.77
2.75
2.13
2.11
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1.27
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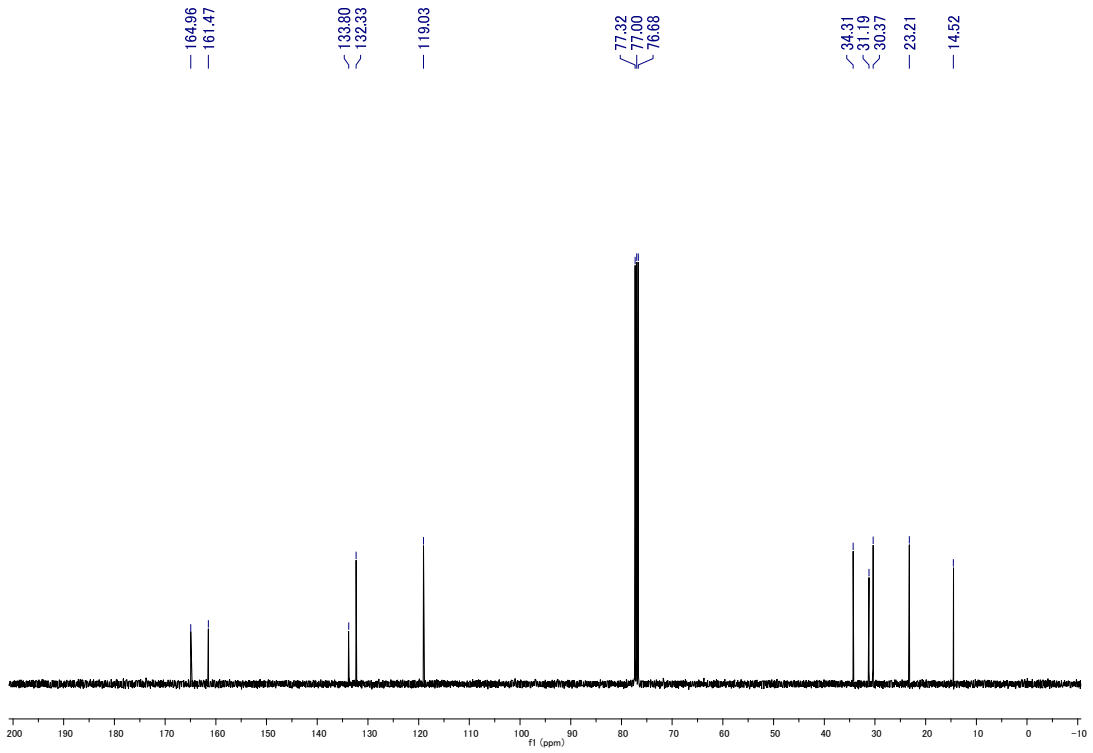
2.00
3.07
f1 (ppm)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76.68
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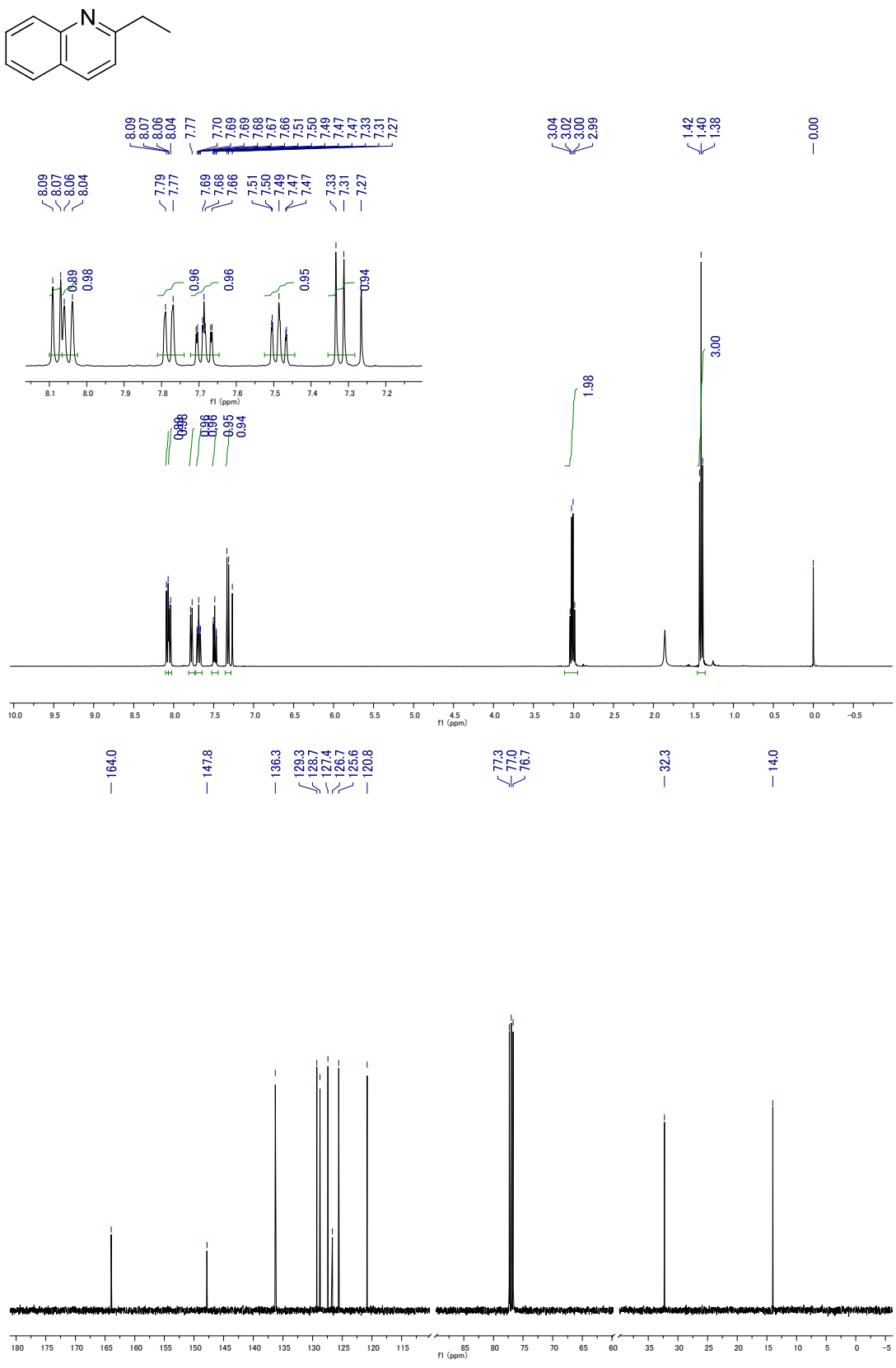
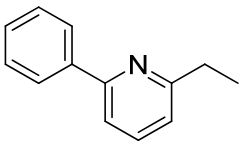
31.19
30.37
23.21
14.52
f1 (ppm)

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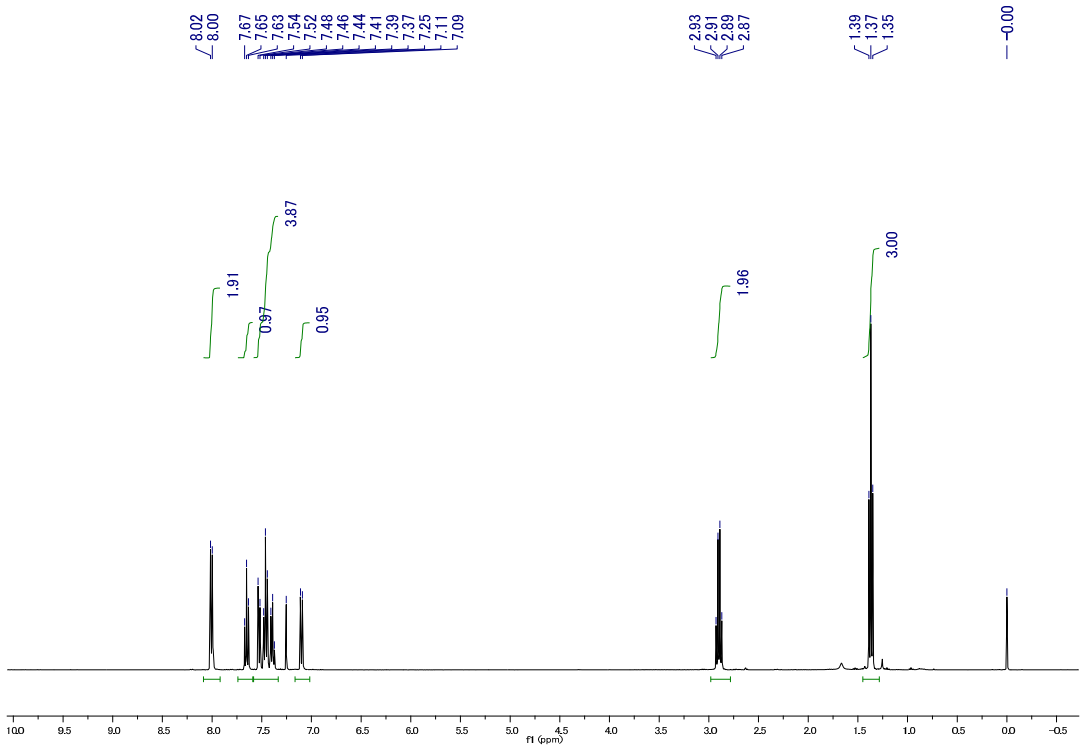
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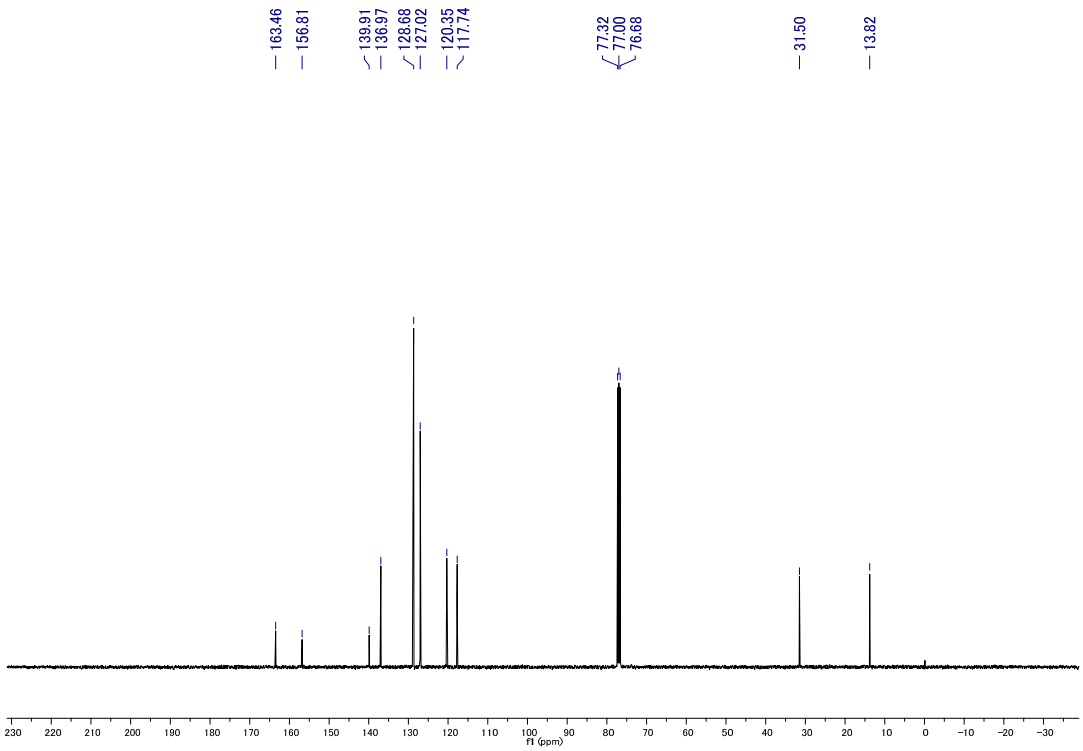
7.44
7.41
7.39
7.37
7.25
7.11
7.09
2.93
2.91
2.89
2.87
1.39
1.37
1.35
0.00
1.91
3.87
0.97
0.95
1.96
3.00
f1 (ppm)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77.00
76.68
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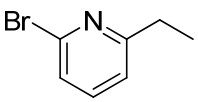
13.82
f1 (ppm)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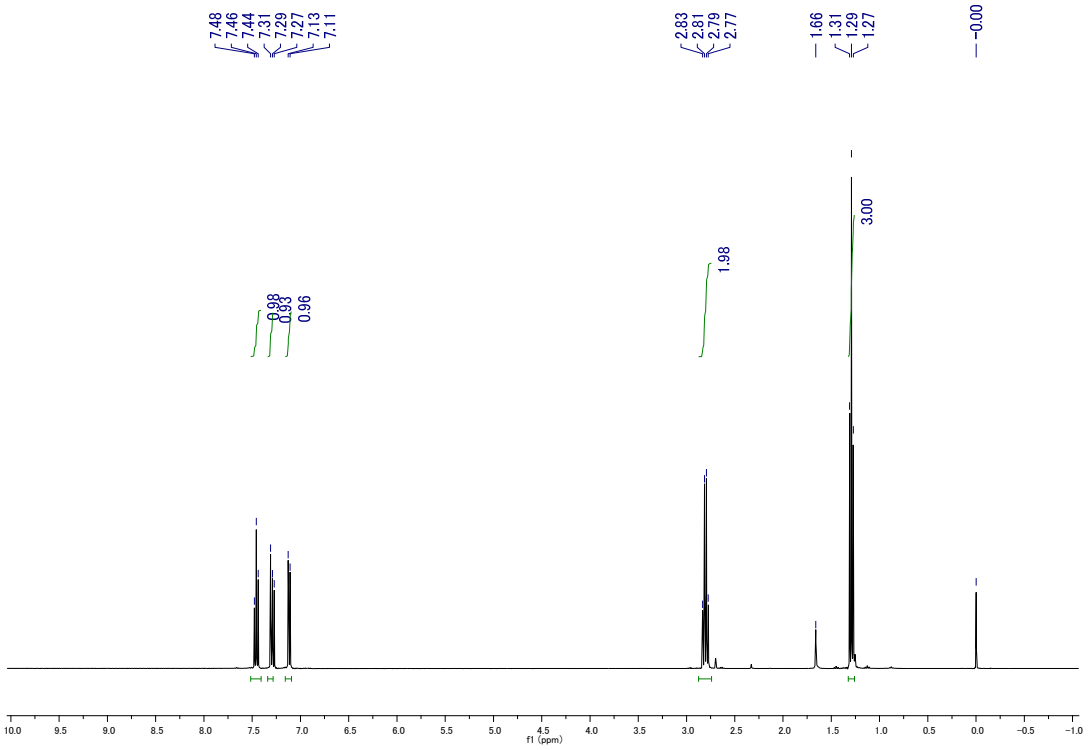
N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7.27
7.13
7.11
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2.81
2.79
2.77
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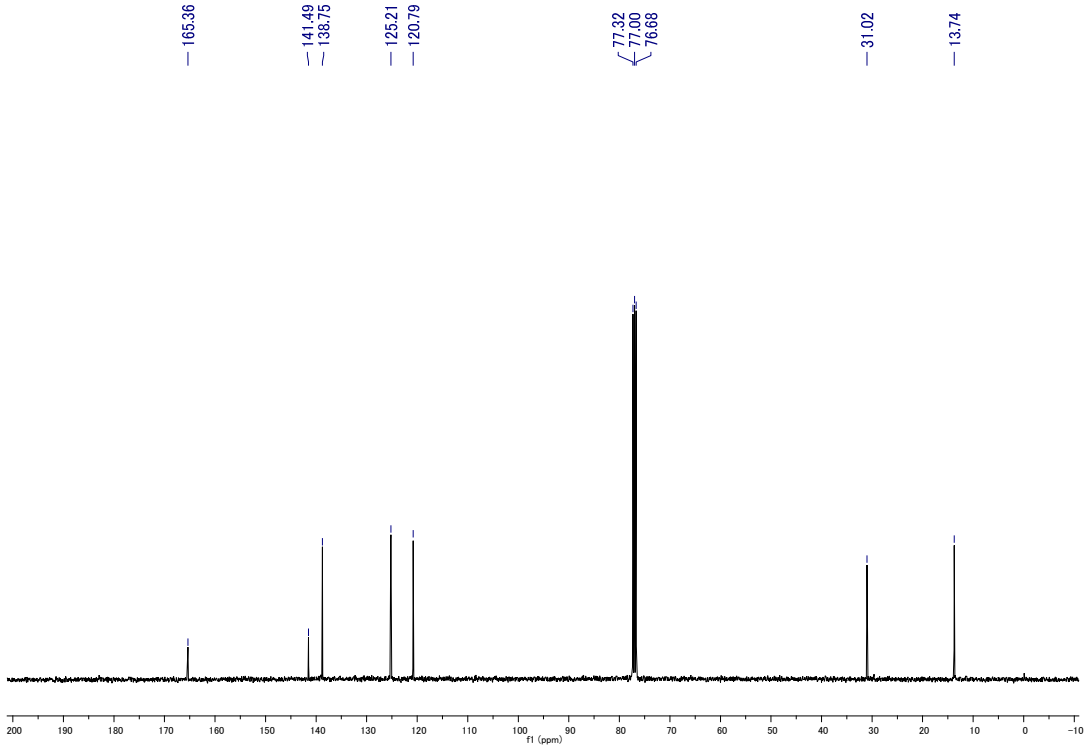
1.29
1.27
0.00
0.98
0.93
0.96
1.98
3.00
f1 (ppm)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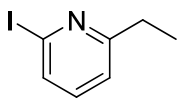
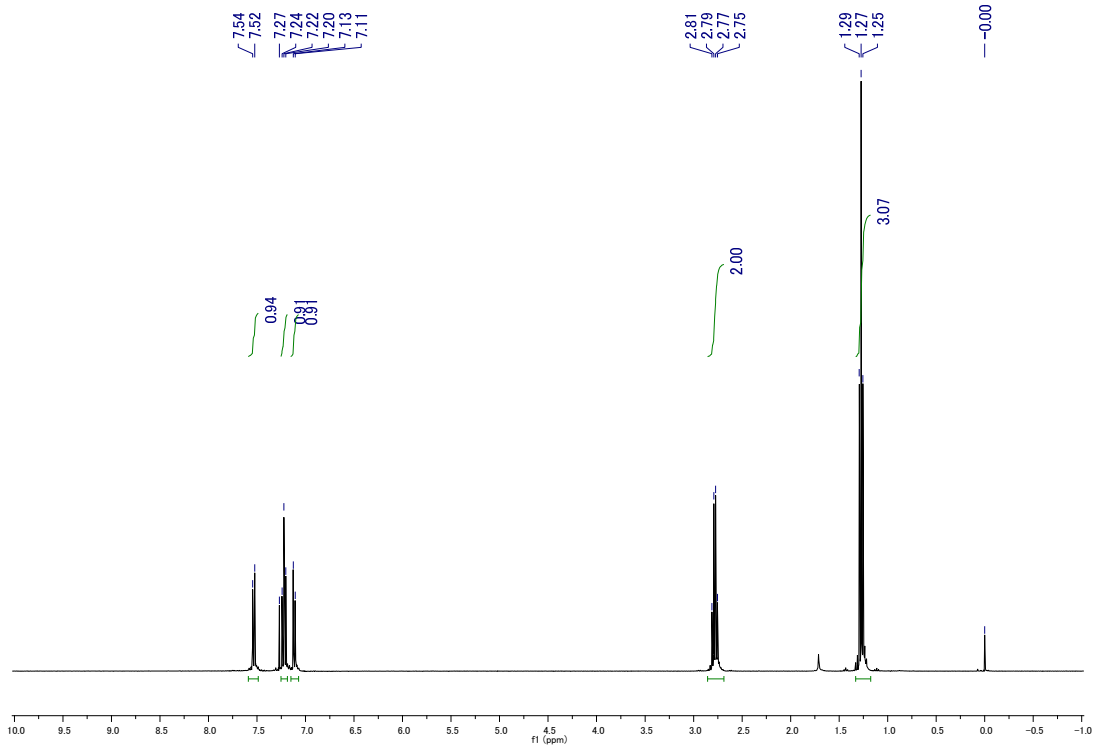
f1 (ppm)

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2.79
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1.27
1.25
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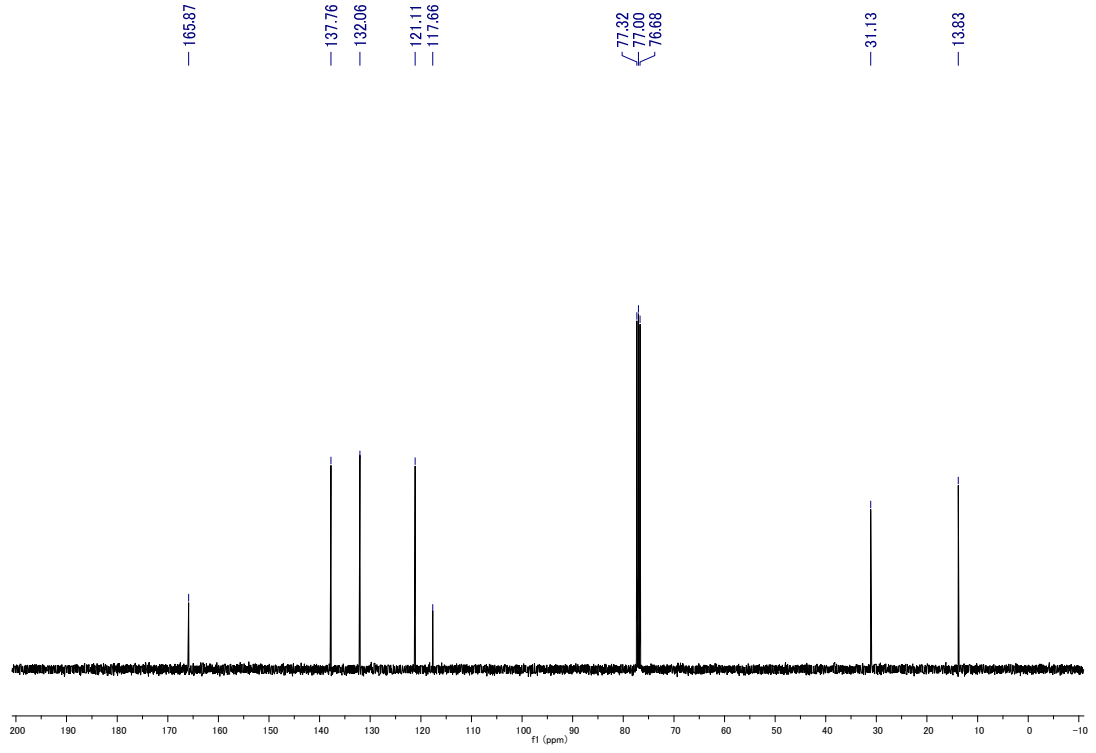
0.91
f1 (ppm)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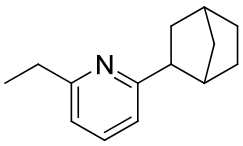
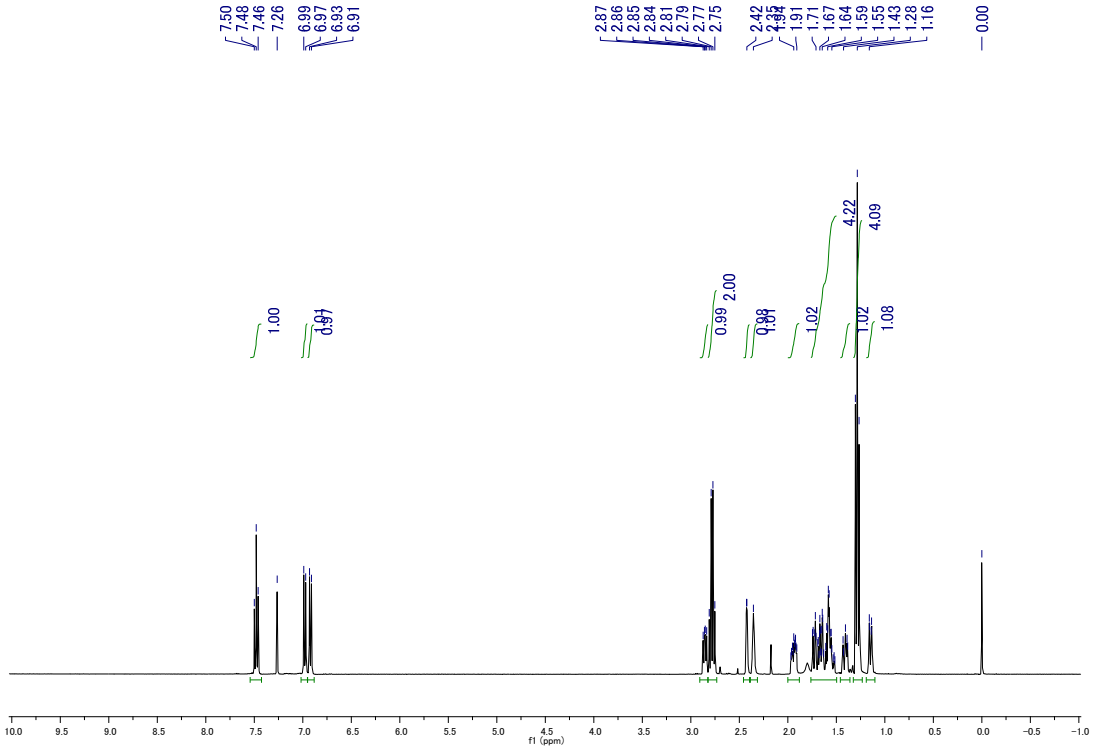
13.83
f1 (ppm)

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1.71
1.67
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1.01
1.02
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4.09
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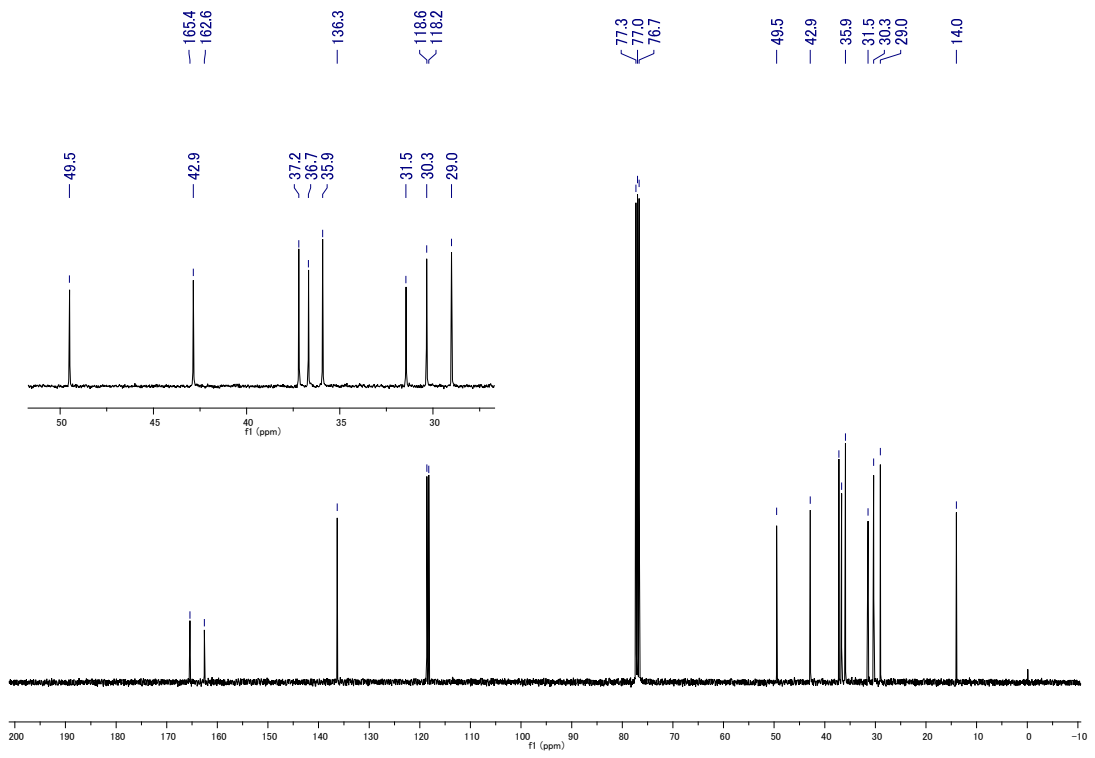
1.08
f1 (ppm)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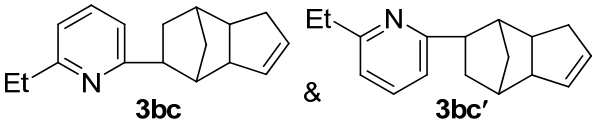
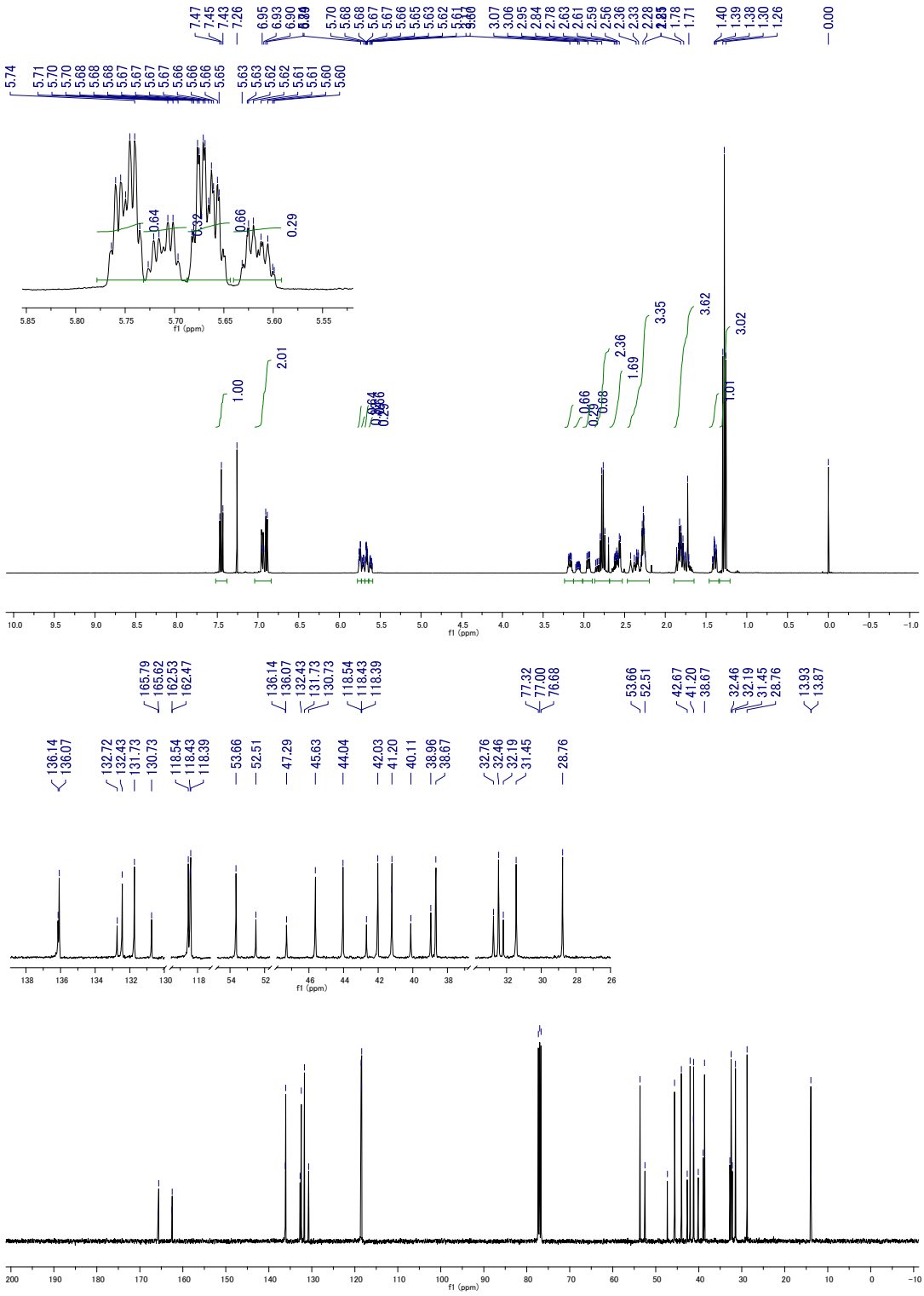
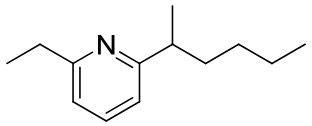
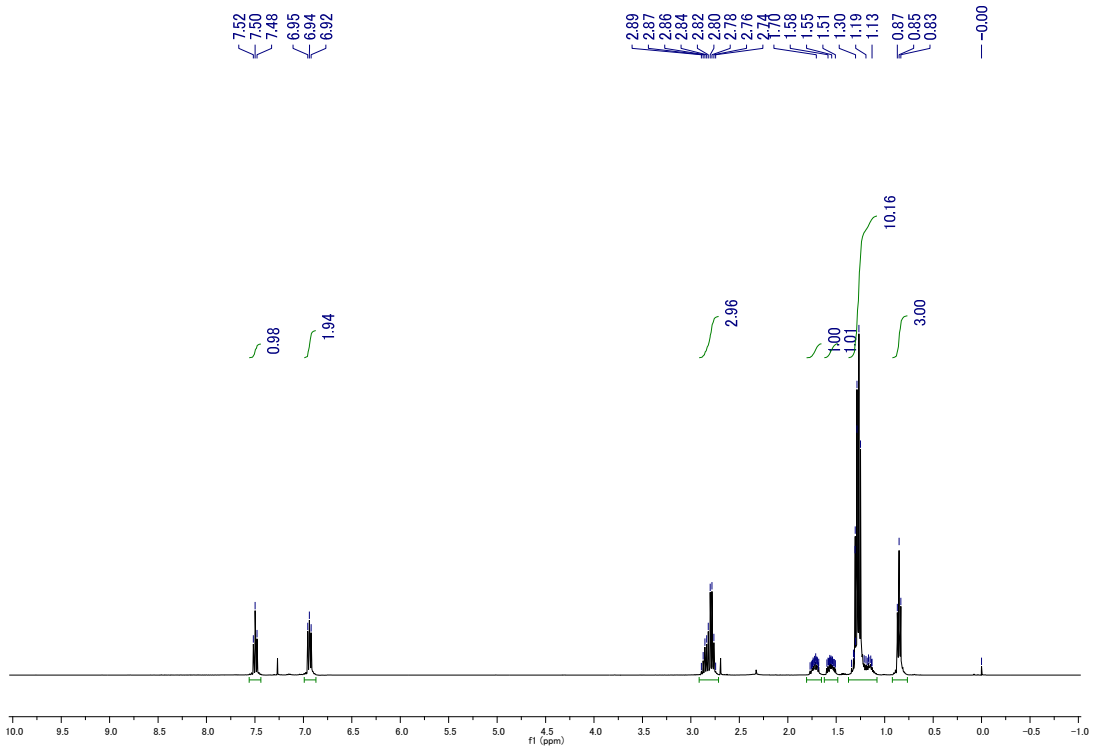
14.0
37.2
36.7
35.9
f1 (ppm)


Et
N
3bc
&
Et
N
3bc′



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2.74
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1.58
1.55
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1.19
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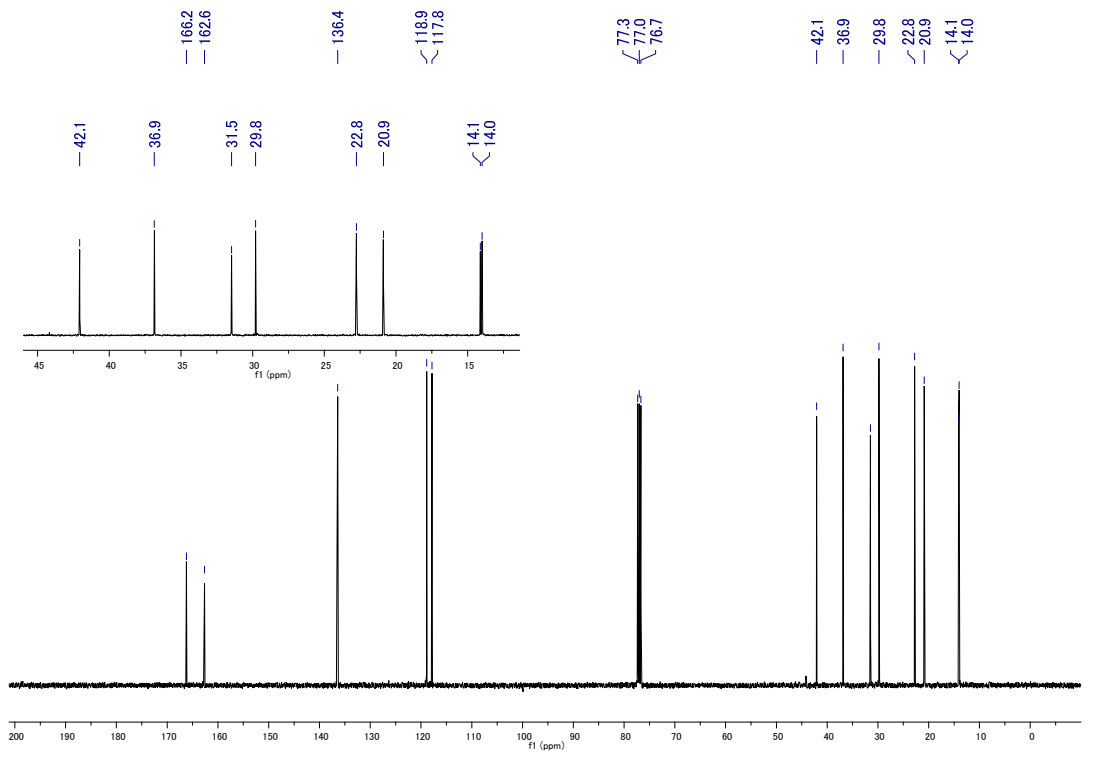
f1 (ppm)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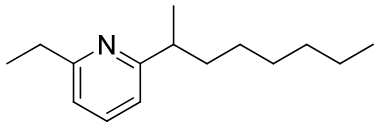
22.8
20.9
14.1
14.0
31.5
f1 (ppm)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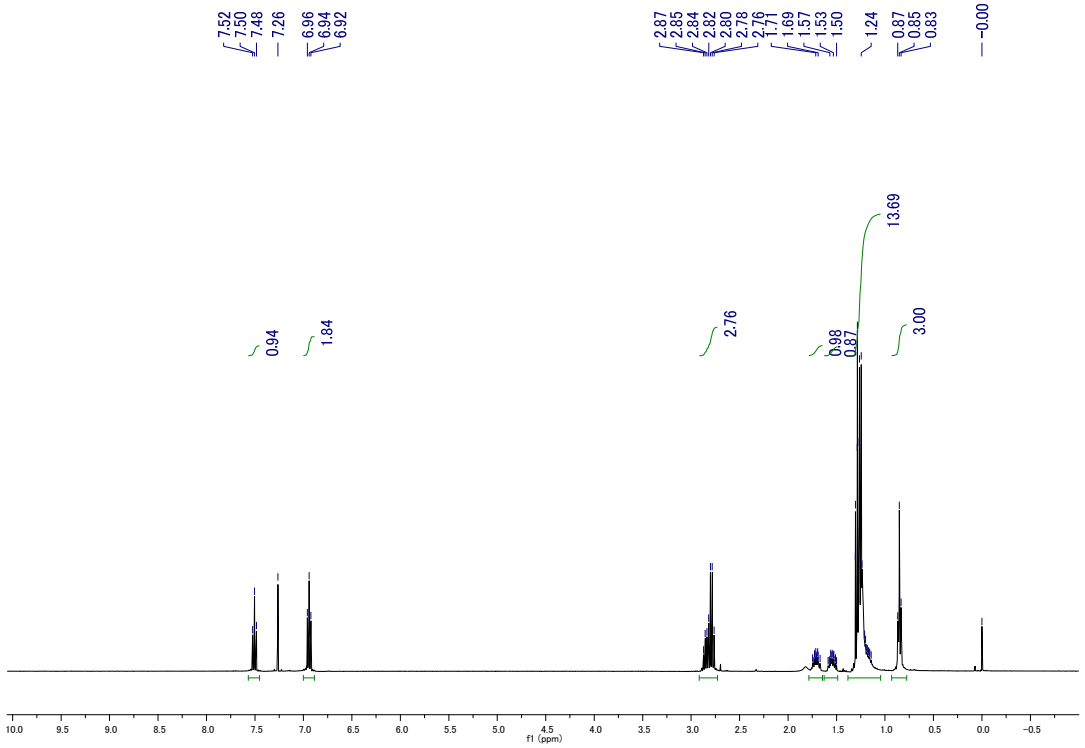
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1.50
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1.84
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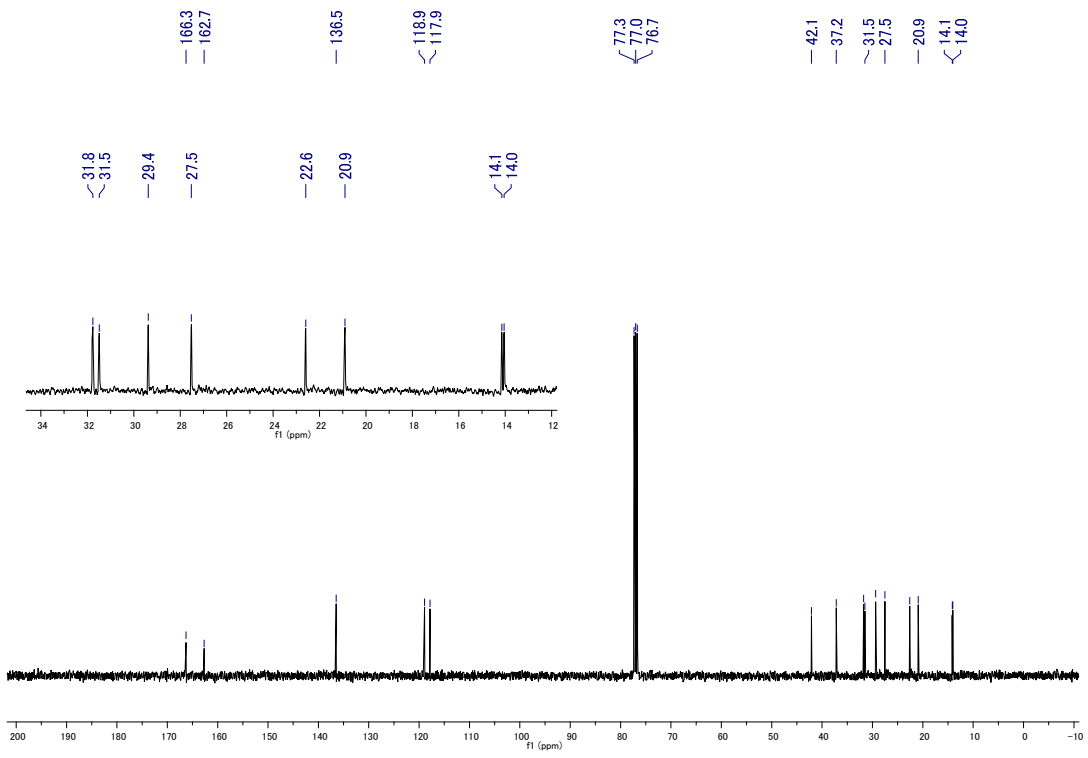
0.98
0.87
3.00
f1 (ppm)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20.9
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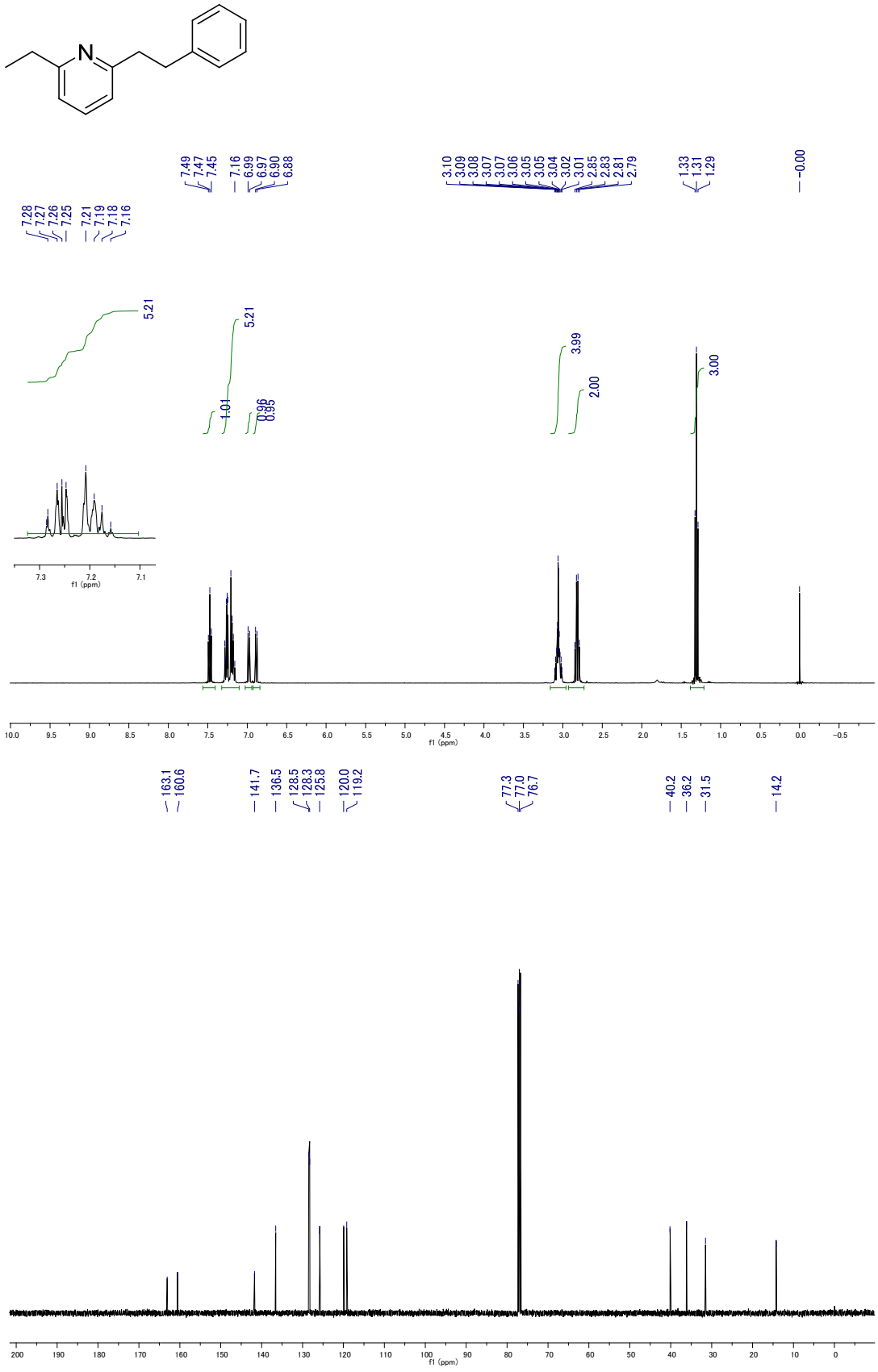
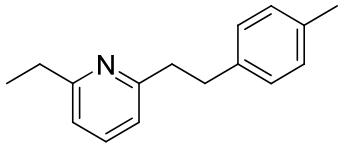
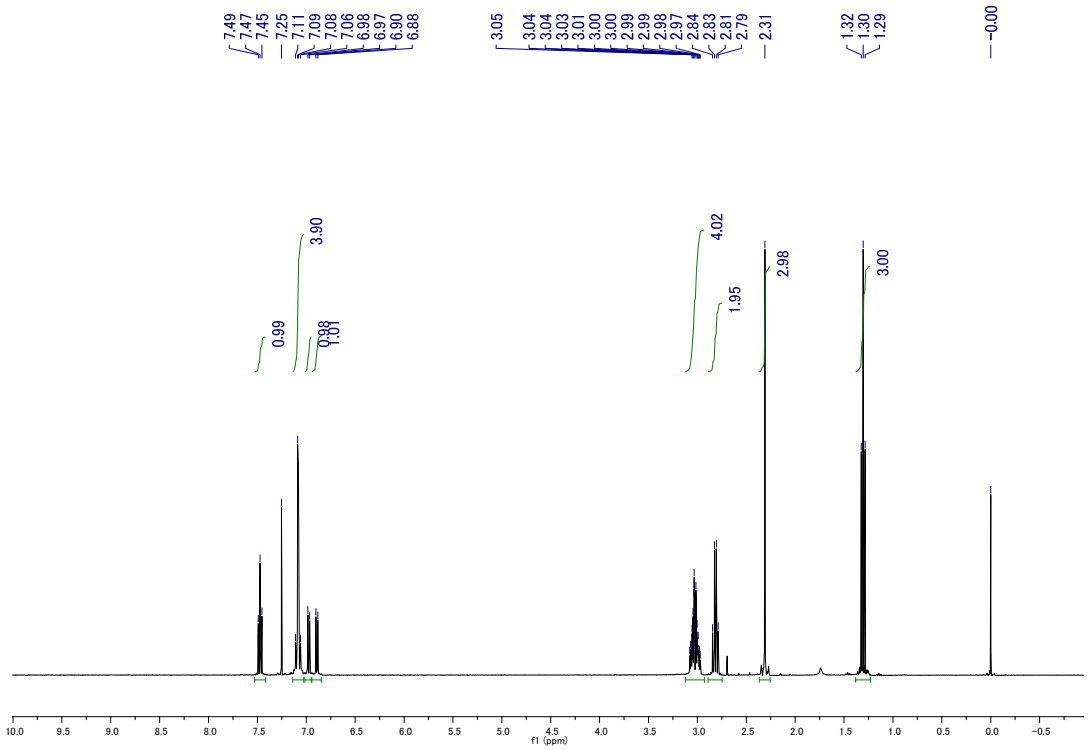
14.0
f1 (ppm)



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1.32
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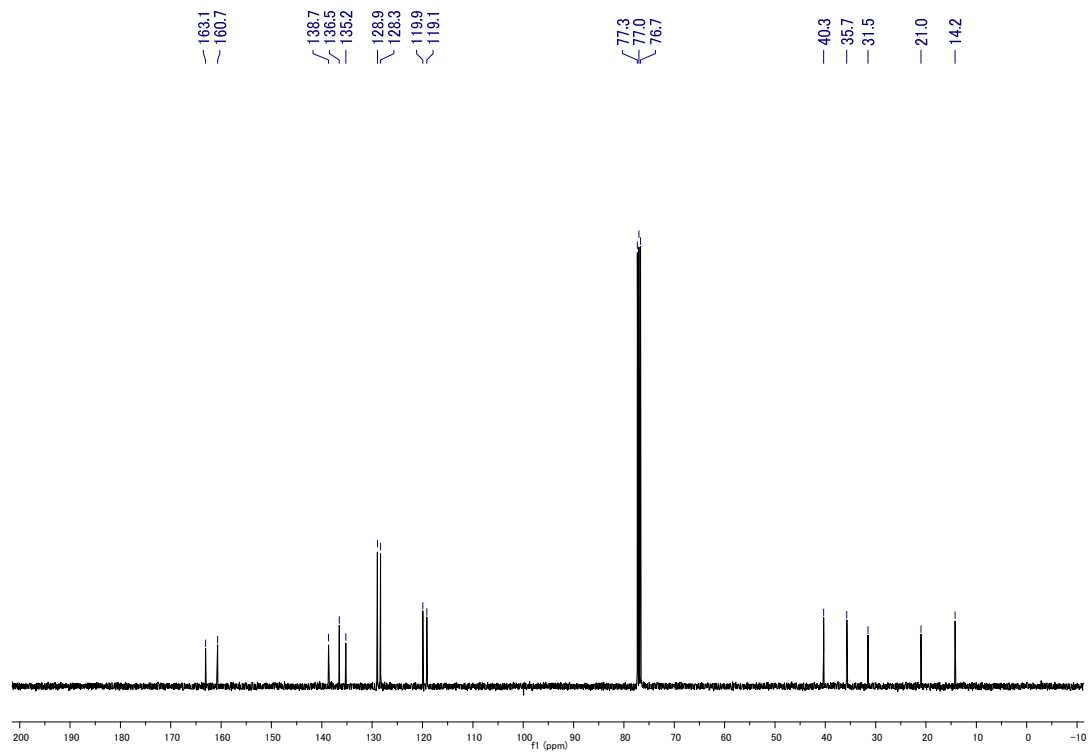
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31.5
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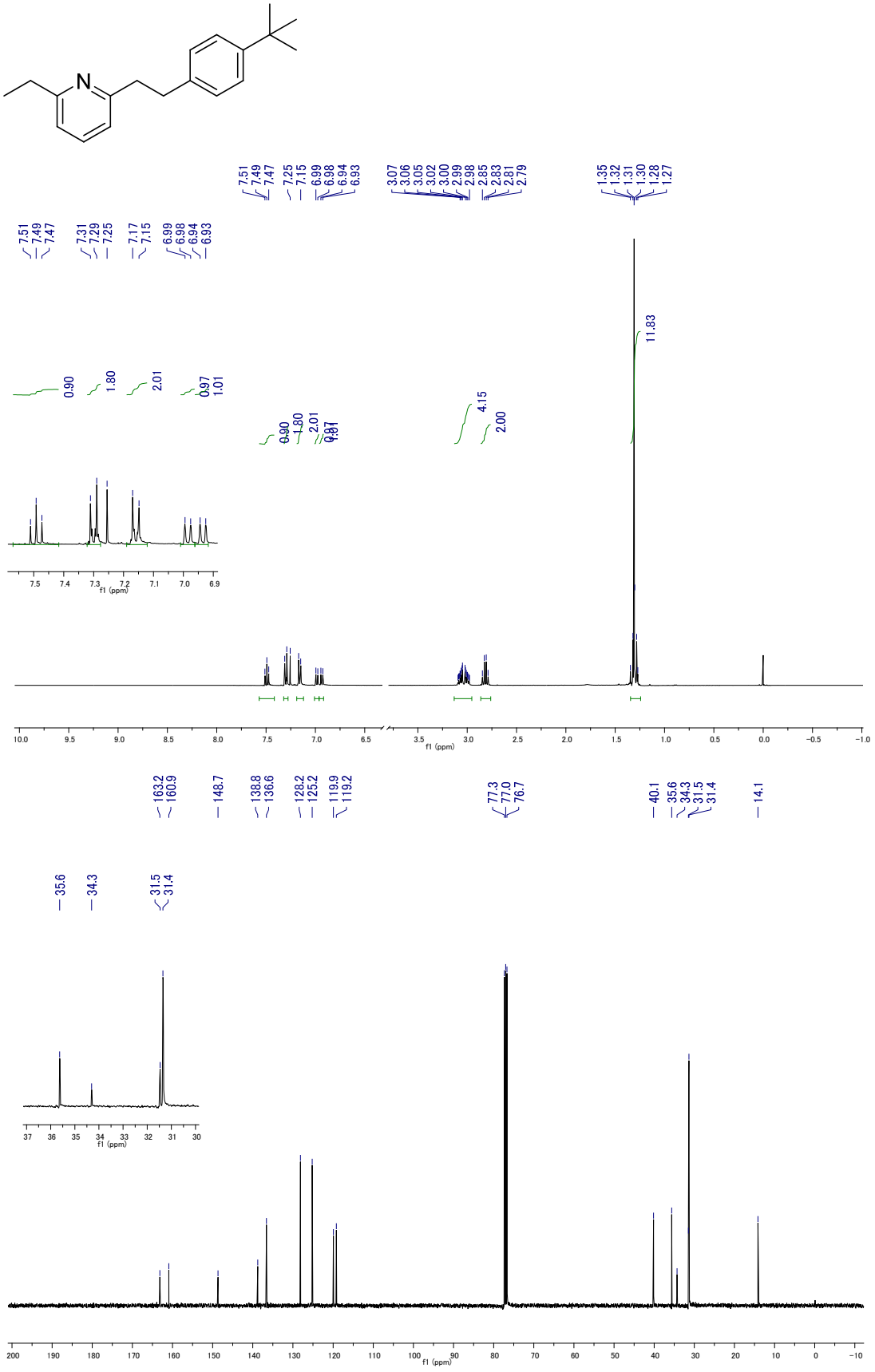
14.2
f1 (ppm)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6.93
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3.06
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3.02
3.00
2.99
2.98
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1.28
1.27
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1.01
4.15
2.00
11.83
f1 (ppm)
163.2
160.9
148.7
138.8
136.6
128.2
125.2
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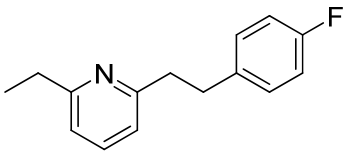
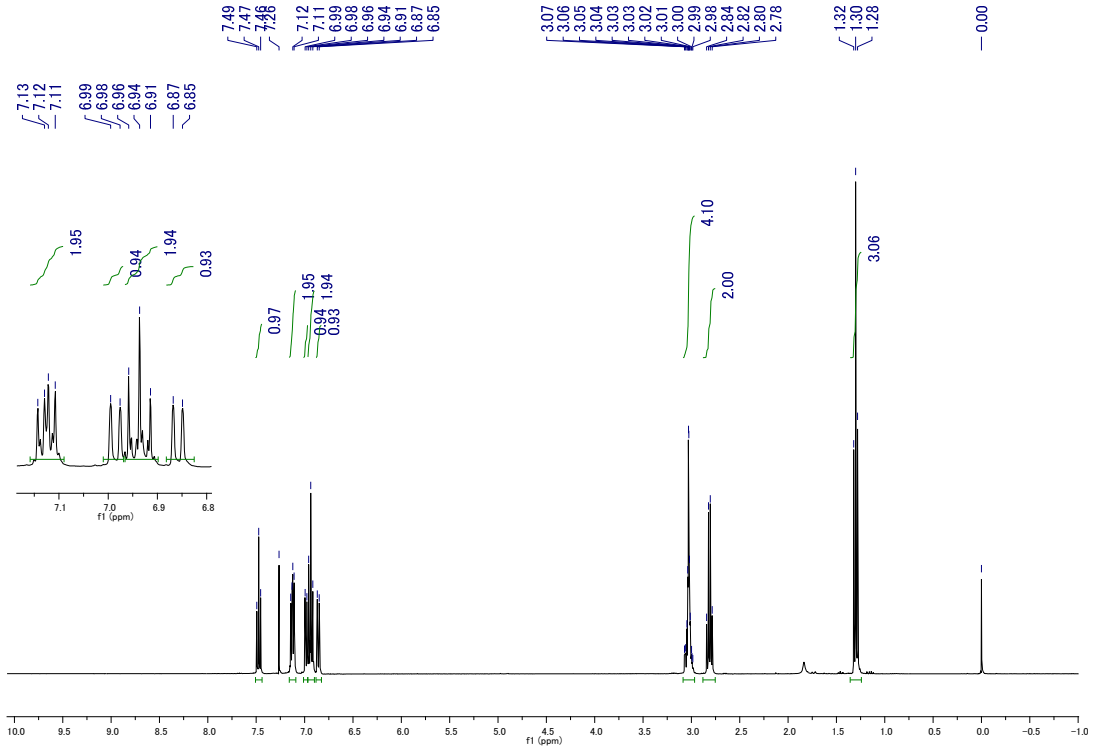
f1 (ppm)


F
N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2.80
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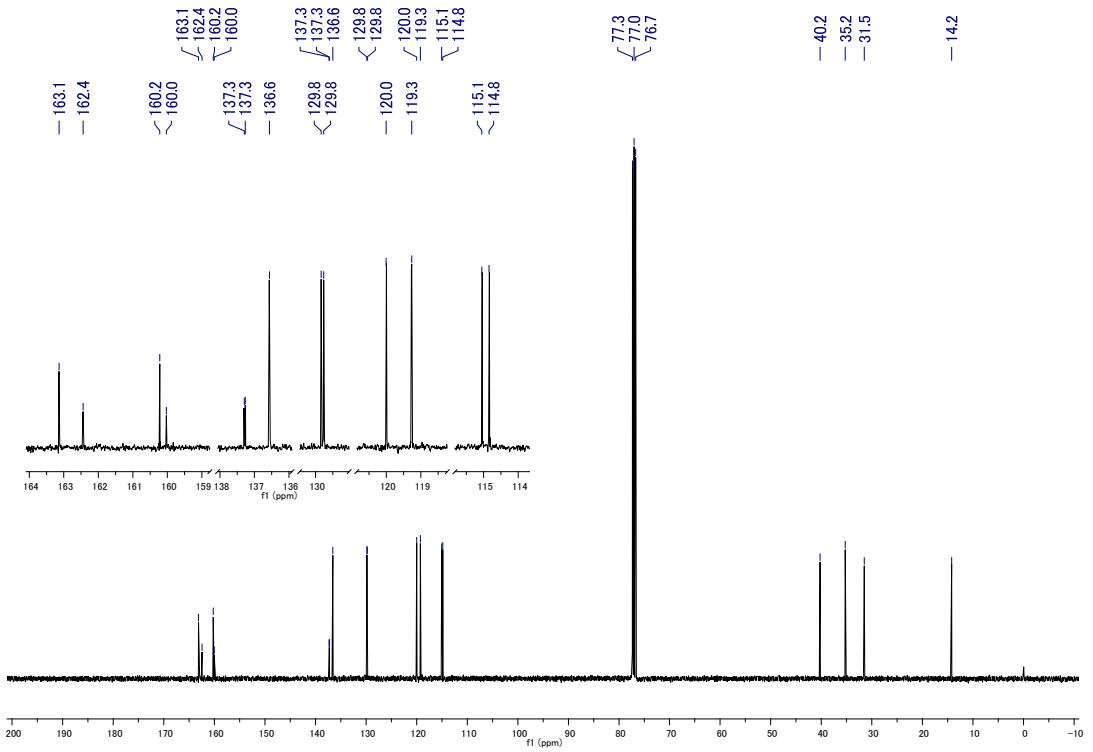
0.94
1.94
0.93
0.97
1.95
1.94
6.94
0.93
4.10
2.00
3.06
f1 (ppm)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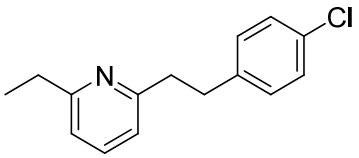
162.4
160.2
160.0
137.3
137.3
136.6
129.8
129.8
120.0
119.3
115.1
114.8
77.3
77.0
76.7
40.2
35.2
31.5
14.2
f1 (ppm)


Cl
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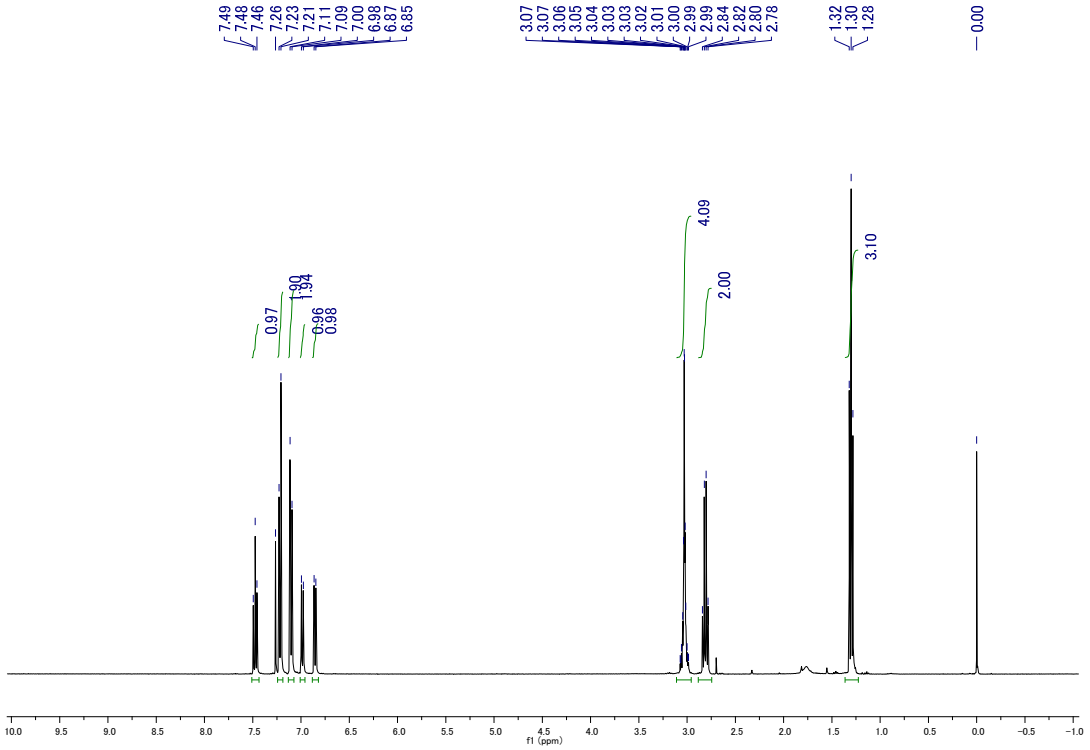
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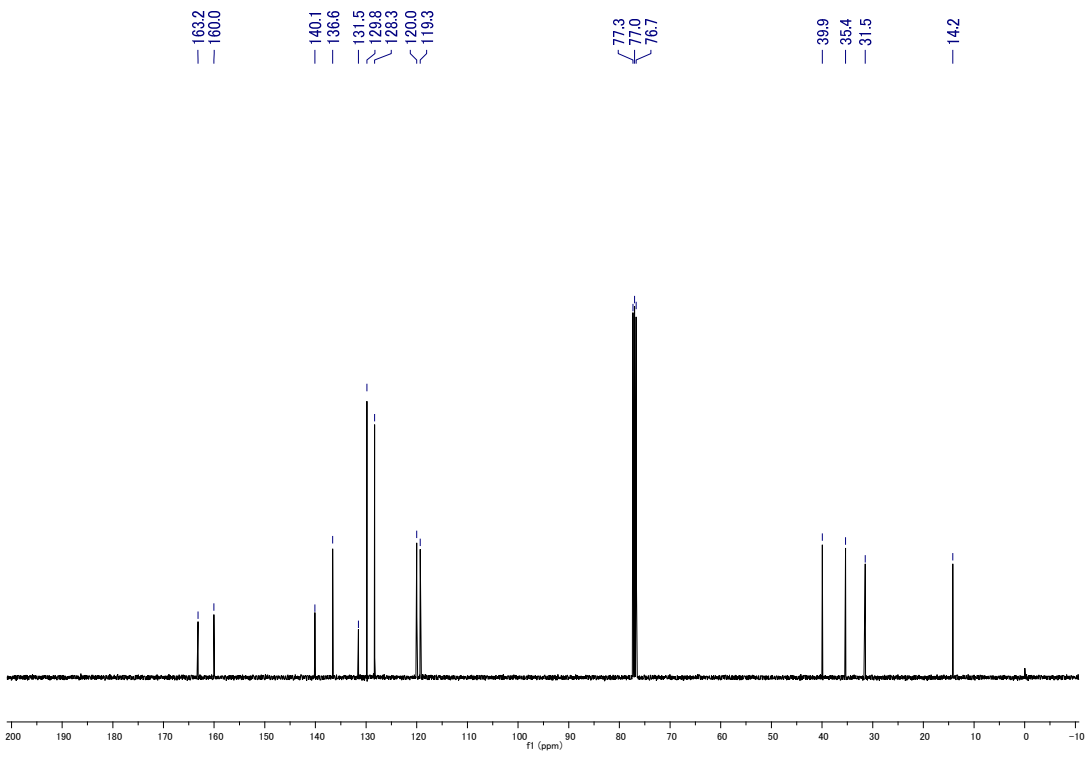
7.48
7.46
7.26
7.23
7.21
7.11
7.09
7.00
6.98
6.87
6.85
3.07
3.07
3.06
3.05
3.04
3.03
3.03
3.02
3.01
3.00
2.99
2.99
2.84
2.82
2.80
2.78
1.32
1.30
1.28
0.00
0.97
1.90
1.94
0.96
0.98
4.09
2.00
3.10
f1 (ppm)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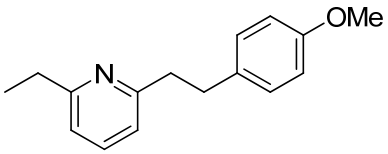
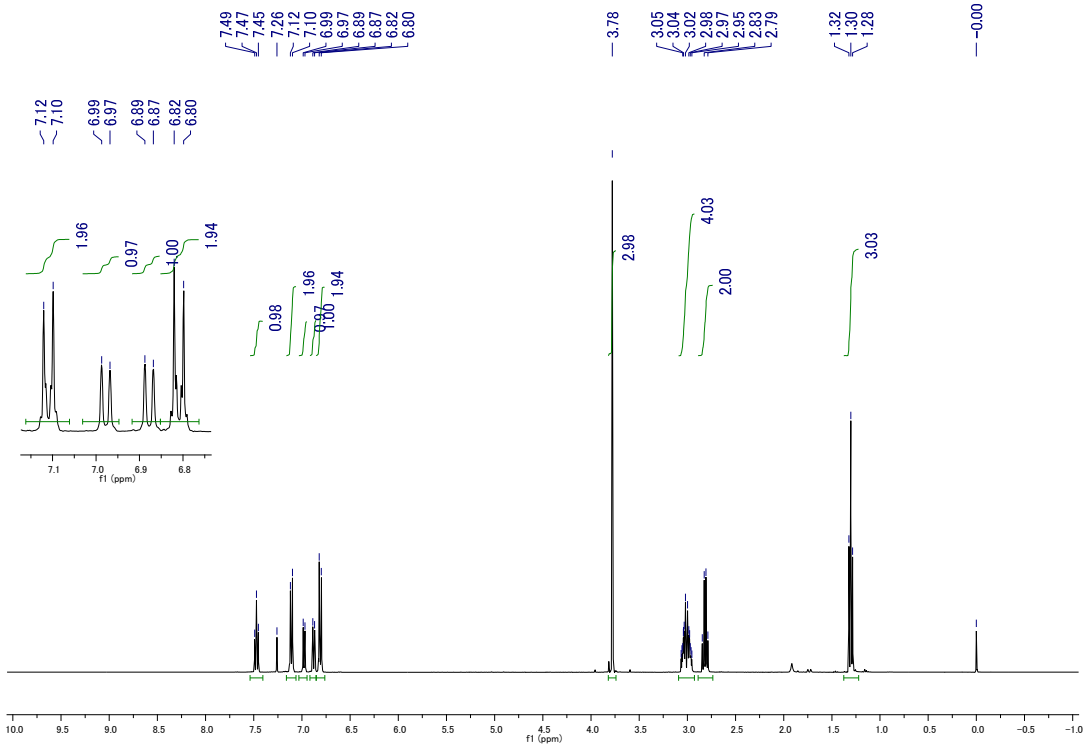
140.1
136.6
131.5
129.8
128.3
120.0
119.3
77.3
77.0
76.7
39.9
35.4
31.5
14.2
f1 (ppm)


OMe
N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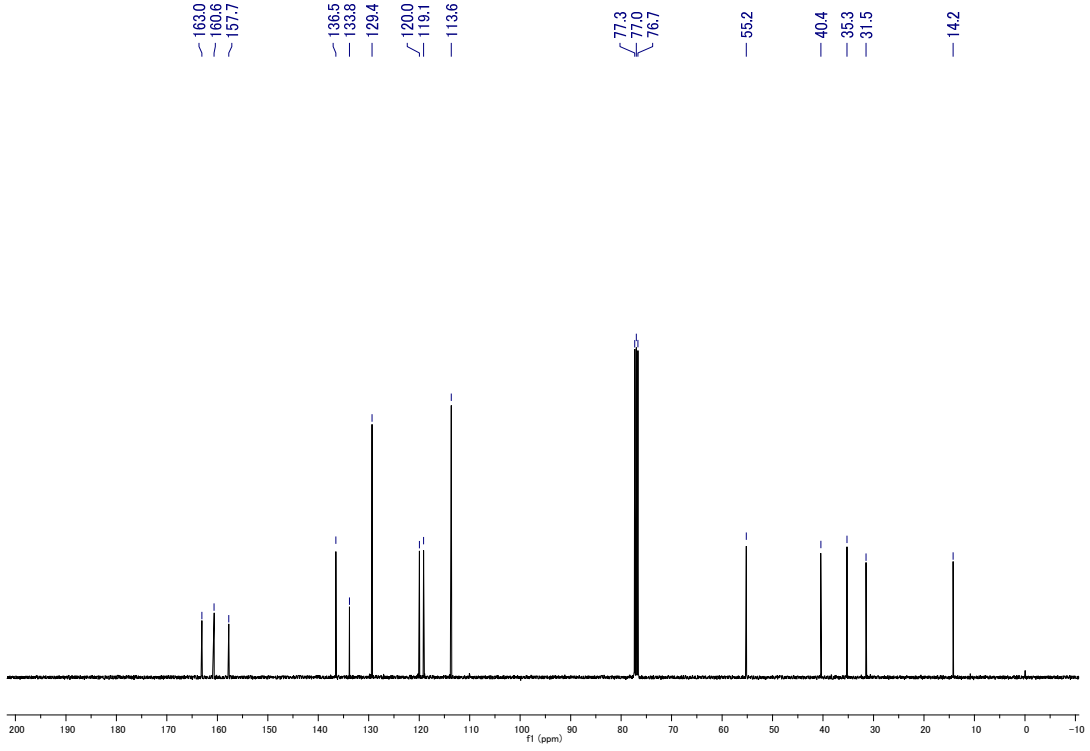
7.12
7.10
6.99
6.97
6.89
6.87
6.82
6.80
3.78
3.05
3.04
3.02
2.98
2.97
2.95
2.83
2.79
1.32
1.30
1.28
0.00
1.96
0.97
1.00
1.94
0.98
1.96
1.94
2.98
4.03
2.00
3.03
f1 (ppm)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160.6
157.7
136.5
133.8
129.4
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119.1
113.6
77.3
77.0
76.7
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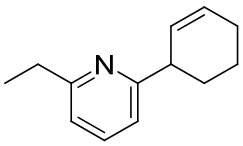
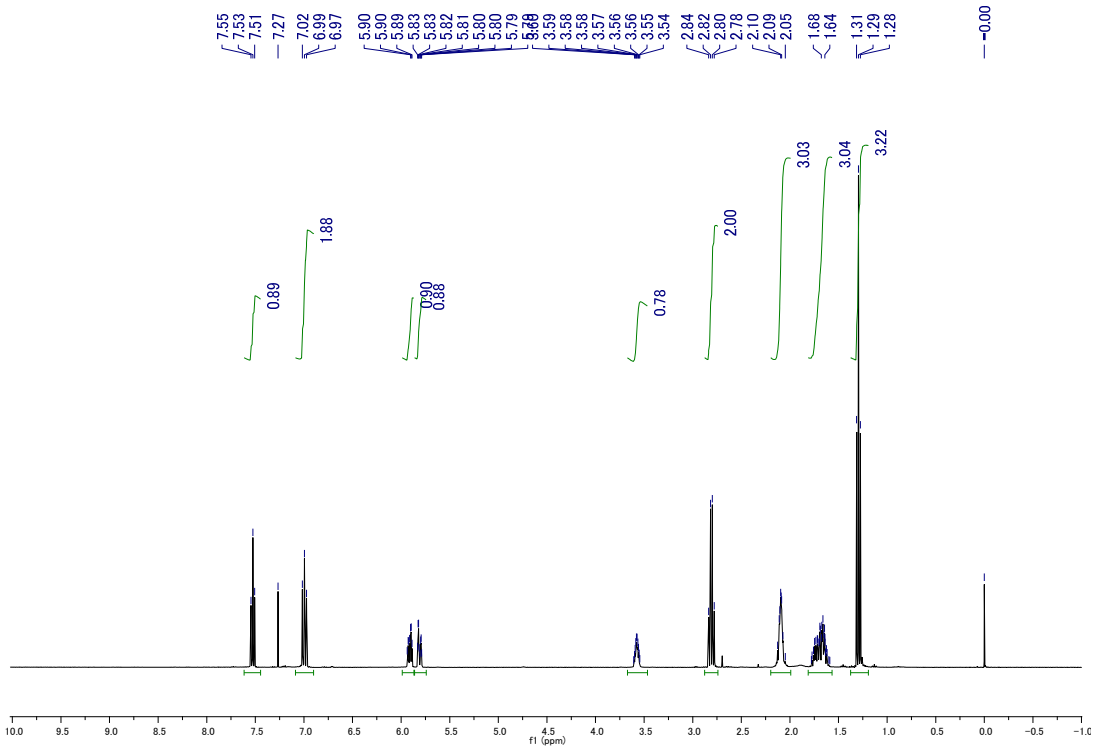
40.4
35.3
31.5
14.2
f1 (ppm)

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7.51
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7.02
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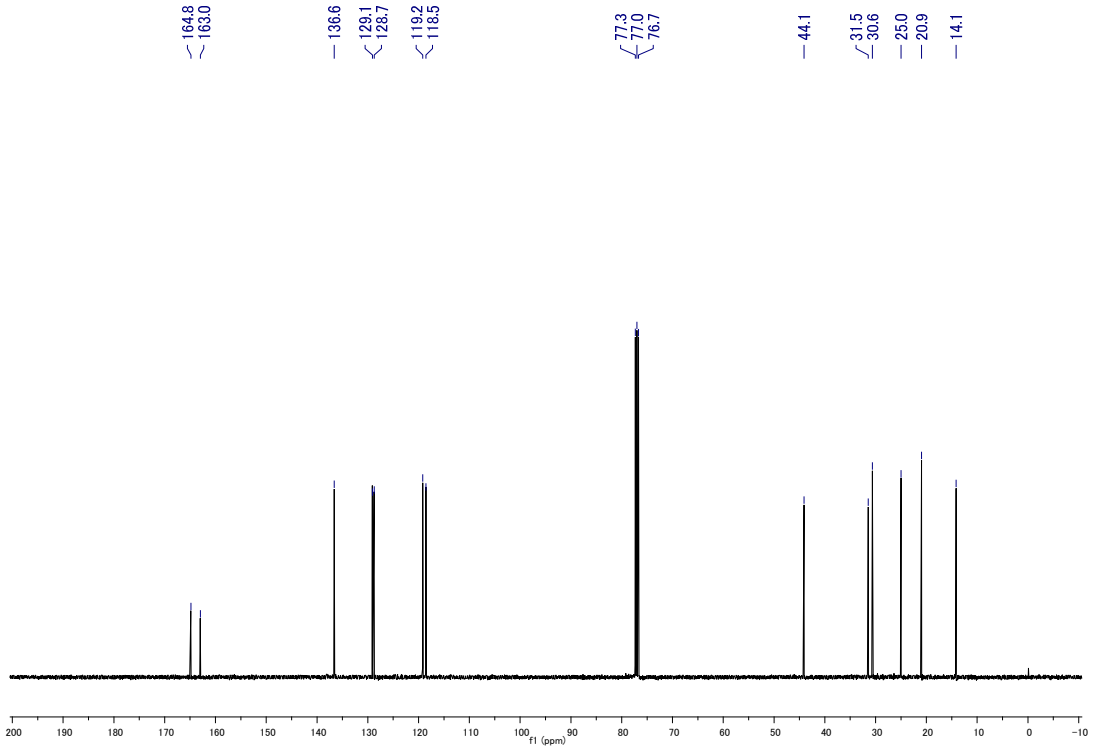
6.97
5.90
5.90
5.89
5.83
5.83
5.82
5.81
5.80
5.80
5.79
3.59
3.58
3.58
3.57
3.56
3.56
3.55
3.54
2.84
2.82
2.80
2.78
2.10
2.09
2.05
1.68
1.64
1.31
1.29
1.28
0.00
0.89
1.88
0.90
0.88
0.78
2.00
3.03
3.04
3.22
f1 (ppm)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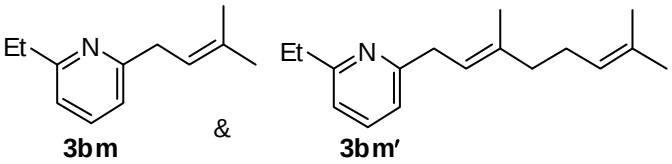
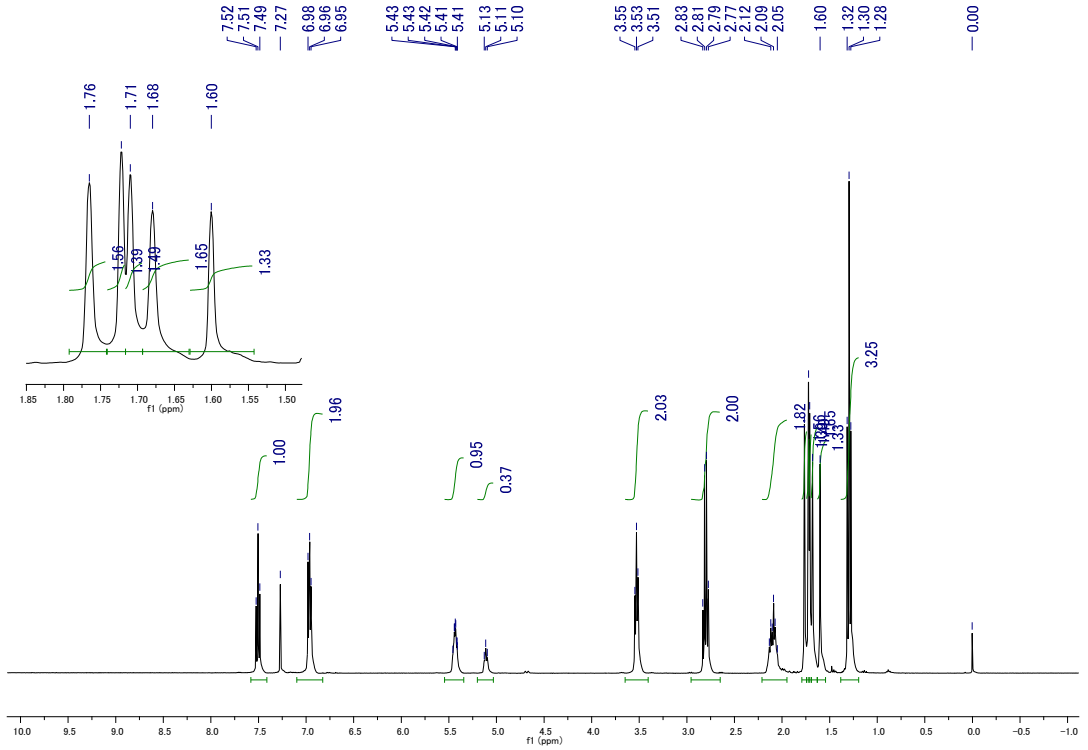
163.0
136.6
129.1
128.7
119.2
118.5
77.3
77.0
76.7
44.1
31.5
30.6
25.0
20.9
14.1
f1 (ppm)


Et
N
&
Et
N

3bm **3bm′**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6.96
6.95
5.43
5.43
5.42
5.41
5.41
5.13
5.11
5.10
3.55
3.53
3.51
2.83
2.81
2.79
2.77
2.12
2.09
2.05
1.60
1.32
1.30
1.28
0.00
1.76
1.71
1.68
1.60
1.56
1.39
1.49
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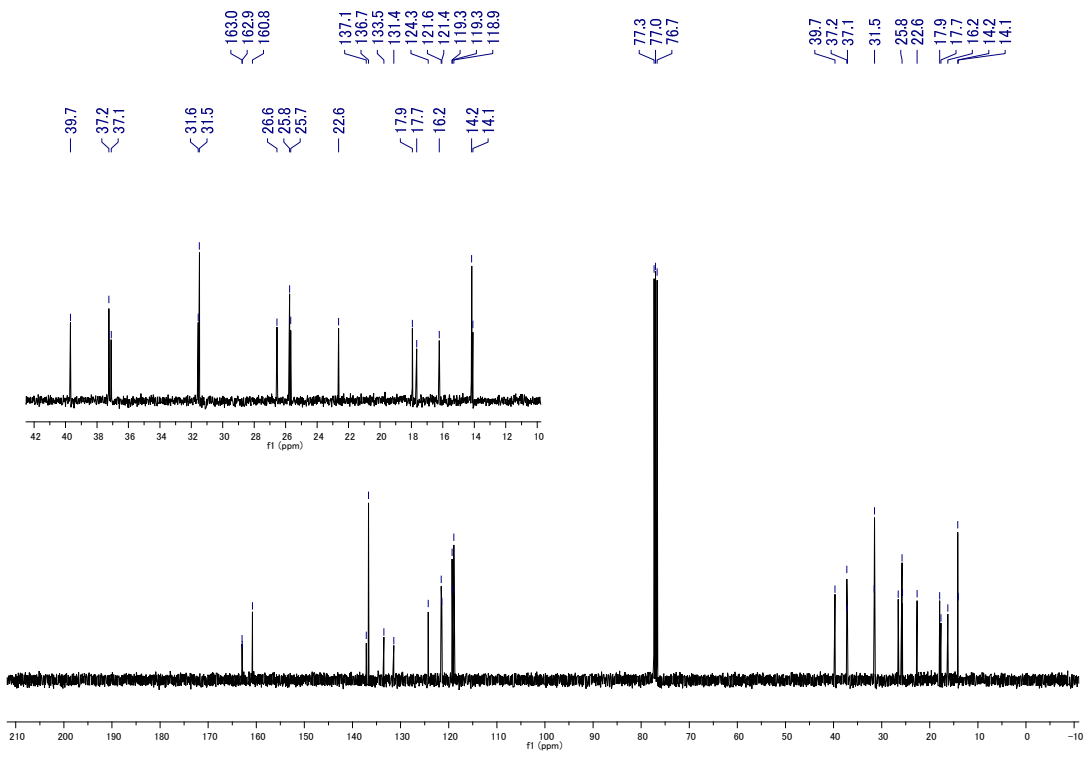
1.33
1.00
1.96
0.95
0.37
2.03
2.00
1.82
3.25
f1 (ppm)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162.9
160.8
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136.7
133.5
131.4
124.3
121.6
121.4
119.3
119.3
118.9
77.3
77.0
76.7
39.7
37.2
37.1
31.5
25.8
22.6
17.9
17.7
16.2
14.2
14.1
39.7
37.2
37.1
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31.5
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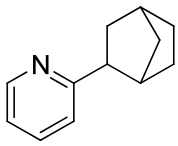
25.8
25.7
22.6
17.9
17.7
16.2
14.2
14.1
f1 (ppm)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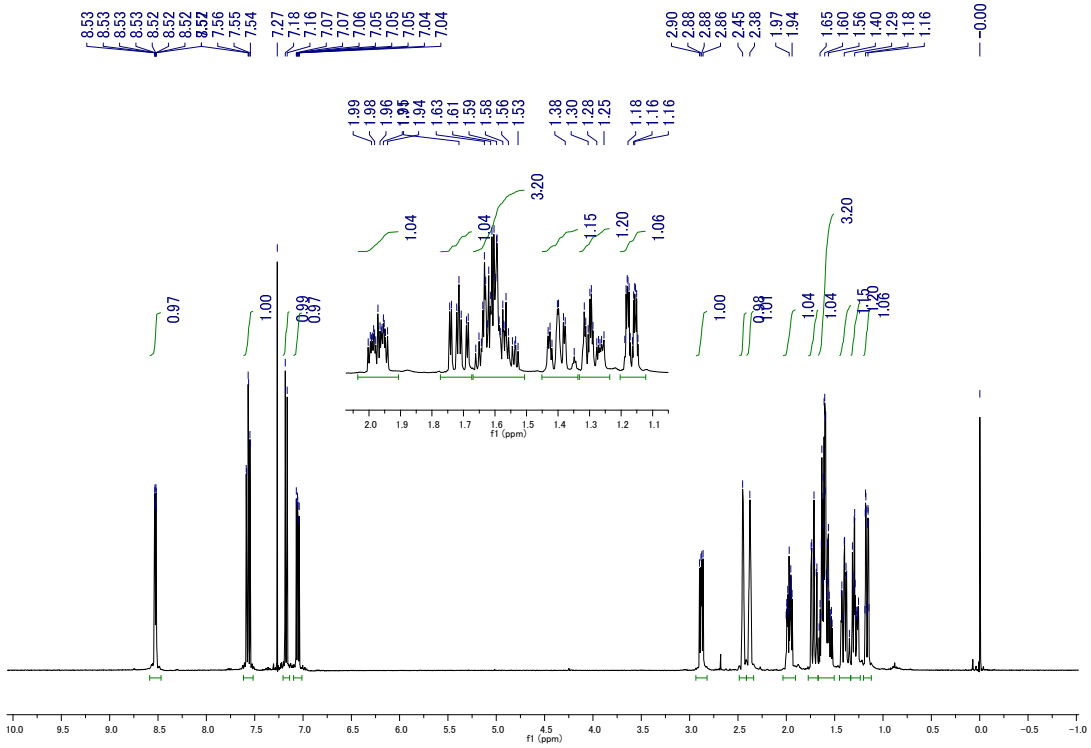
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8.52
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7.55
7.54
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7.18
7.16
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7.05
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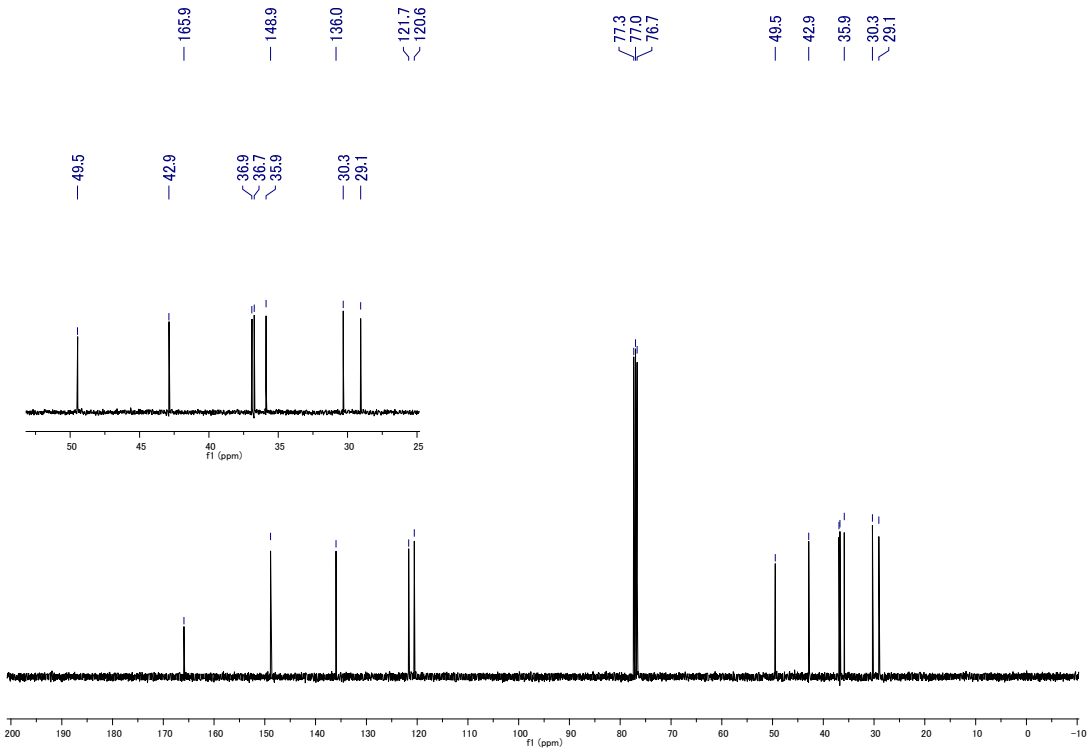
2.86
2.45
2.38
1.97
1.94
1.65
1.60
1.56
1.40
1.29
1.18
1.16
0.00
1.99
1.98
1.96
1.94
1.63
1.61
1.59
1.58
1.56
1.53
1.38
1.30
1.28
1.25
1.18
1.16
1.16
3.20
1.04
1.04
1.15
1.20
1.06
0.97
1.00
0.99
0.97
1.00
1.04
1.04
3.20
f1 (ppm)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76.7
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35.9
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29.1
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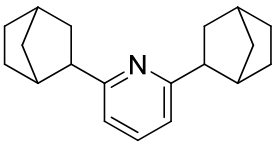
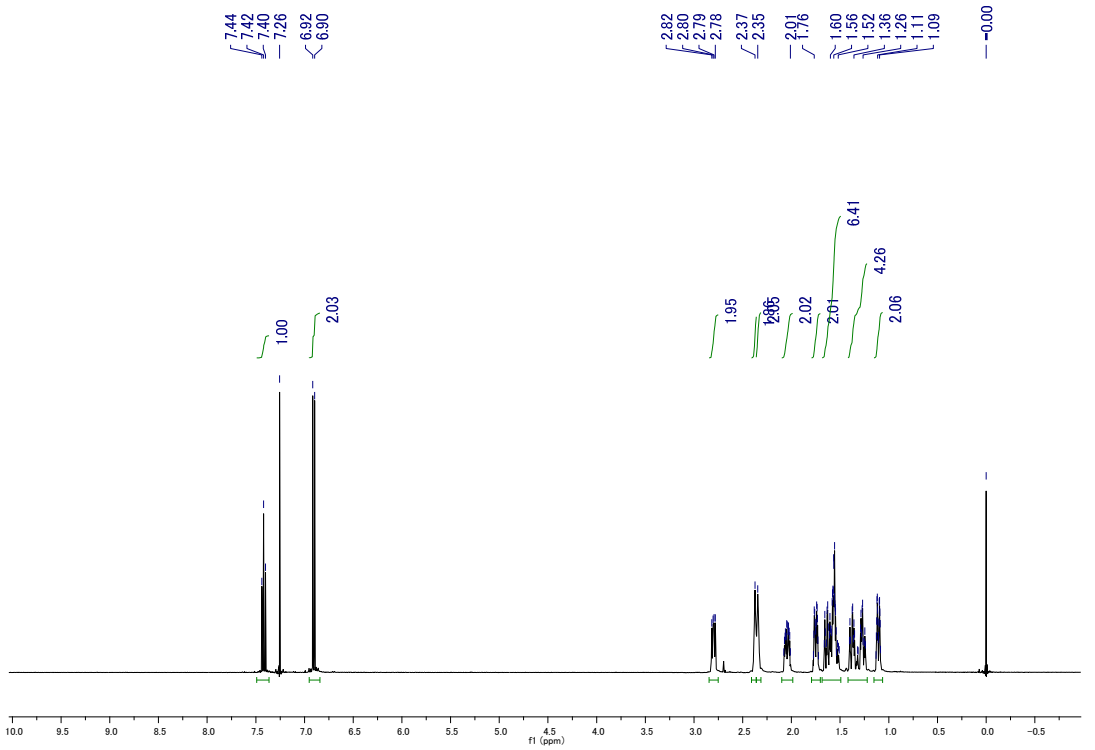
42.9
36.9
36.7
35.9
30.3
29.1
f1 (ppm)

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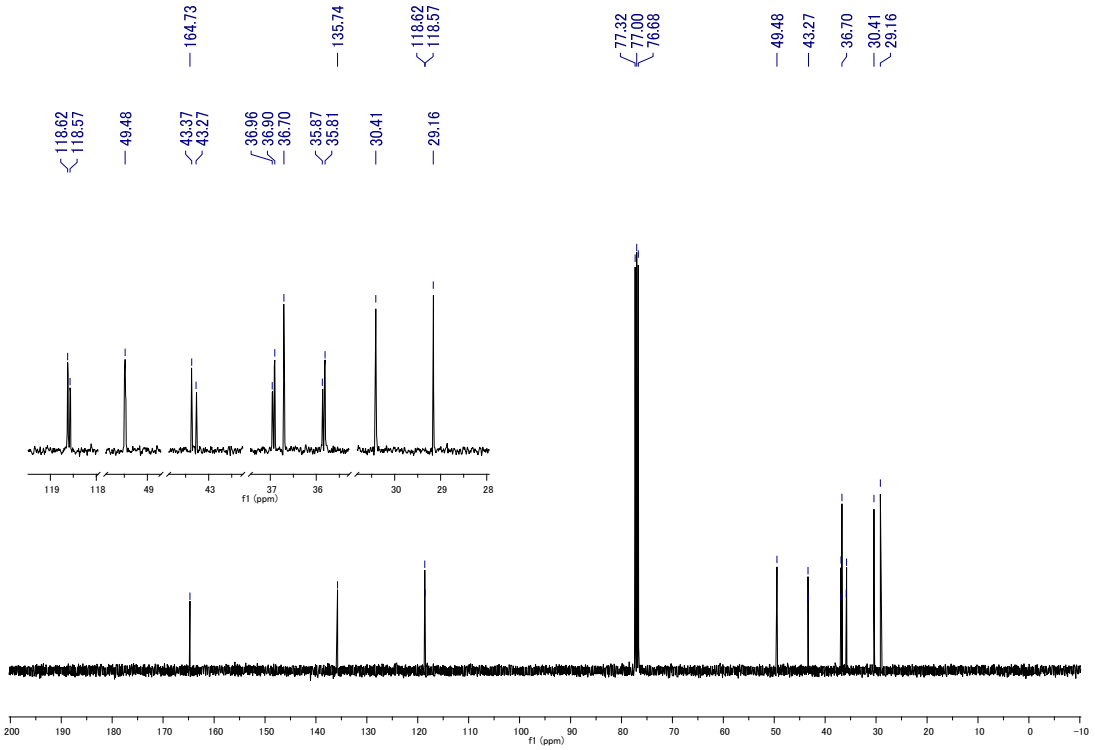
6.90
2.82
2.80
2.79
2.78
2.37
2.35
2.01
1.76
1.60
1.56
1.52
1.36
1.26
1.11
1.09
0.00
1.00
2.03
1.95
2.02
2.01
6.41
4.26
2.06
f1 (ppm)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77.00
76.68
49.48
43.27
36.70
30.41
29.16
f1 (ppm)