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Supporting Information

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Supporting Information

A General and Selective Copper-Catalyzed Cross-Coupling of Tertiary Grignard Reagents with Azacyclic Electrophiles

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Contents

1. General

Abbreviations

*t*Am	*tert*-amyl (1,1-dimethylpropyl)
Arl	aryl
CC	(flash) column chromatography (on SiO_2, unless otherwise mentioned)
hexanes	*n*-hexane (variable grades) or petroleum ether fraction (40–60 °C)
A aq	aqueous solution of *A*
A sat	saturated aqueous solution of *A*

Analytical Data

All data were obtained from the service units of the Institut für Organische Chemie, RWTH Aachen University, Germany. **NMR**: Chemichal shifts are given in ppm relative to (internal) tetramethylsilane (TMS), coupling constants *J* are given in Hz. **Melting points** (M.p.): measured on a heated metal-block using digital thermometers; thus "corrected values".[1]

Chemicals

Commercially available materials were used as received. Grignard reagents were prepared from *tert*-alkyl chlorides and high purity magnesium (99.98%) in THF and were titrated against salicylaldehyde phenylhydrazone[2] prior to use. *tert*-Alkyl chlorides were obtained commercially or prepared according to literature methods. Chloro-heterocycles were obtained from commercial sources. All reactions were carried out with dry, degassed solvents in Schlenk vessels under argon.

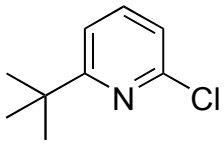
[1] G. V. D. Tiers, *J. Chem. Educ.* **1990**, *67*, 258–259.
[2] B. E. Love, E. G. Jones, *J. Org. Chem.* **1999**, *64*, 3755–3756.

General Procedure

General procedure for copper-catalyzed cross-coupling of tertiary-alkyl Grignard reagents with chloro-aza-cycles (GP)

In a dried round-bottom Schlenk flask under argon, anhydrous THF (1 mL) is added to the aza-aryl chloride (1.0 mmol) and CuI (5 mol-%). The mixture was cooled to 0 °C (or –10 °C) with stirring. A solution of the Grignard reagent (1.0–2.5 mmol) in THF was added slowly, and the reaction mixture stirred from 0 °C to r.t. (or at 0 °C), until a GC/MS analysis (quench a small sample with NH_4Cl aq/*t*BuOMe) or TLC indicated completion of the reaction. The reaction was quenched by careful addition of NH_4Cl sat. (3 mL) and *t*BuOMe (5 mL) and the organic phase collected. The aqueous phase was extracted with *t*BuOMe (3 mL). The combined organic phase was washed with NH_4Cl sat. (3×3 mL) and H_2O (3 mL) and dried over $MgSO_4$. Filtration and evaporation afforded crude products, which were purified by crystallization, distillation or column chromatography (CC).

2. Pyridines



2-*tert*-Butyl-6-chloropyridine (1a). A) In a Schlenk flask under argon, 2,6-dichloropyridine (5.0 g, 33 mmol, 97% purity) and CuI (191 mg, 1.0 mmol, 3 mol-%) were stirred in THF (20 mL) at 0 °C. A solution of *t*BuMgCl (33 mL, 1.5 M in THF, 50 mmol) was added and the reaction mixture stirred for 19 h with warming from 0 °C to r.t. (ice/water-bath). The reaction was quenched by addition of NH_4Cl aq, water and *t*BuOMe. The aqueous phase was extracted with *t*BuOMe (1×) and the combined organic phases washed with NH_4Cl/NH_3 aq (2 x). After drying ($MgSO_4$) and evaporation of the organic phase, the residue was purified by CC (*t*BuOMe/hexanes = 1:60) to give 4.78 g (84.5%) of a colorless liquid of characteristic odor.

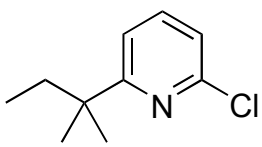
B) An analogous reaction with a higher catalyst loading (CuI = 312 mg, 1.64 mmol, 5%) gave similar results (≥85% yield).

C) A reaction with 2,6-dichloropyridine (0.10 mol, 14.80 g, 98% purity), CuI (5 mol-%) and *t*BuMgCl (0.20 mol, 1.0 M in THF) in which the crude was purified by distillation in vacuum (ca. 15 mbar/90 °C) afforded 11.10 g (65%) of the product.

D) In a reaction at larger scale with lower excess of Grignard reagent (dichloropyridine: 38.6 g, 0.261 mol; CuI = 1.47 g, 3 mol-%; *t*BuMgCl [1.1 M] = 340 mL, 0.339 mol, 1.3 equiv; THF = 160 mL; overnight), some un-reacted dichloropyridine remained. CC gave a pure fraction and a mixed fraction which was separated by another CC. Total yield = 34.6 g (78%).

Notes: The catalytic reaction displays a slow exotherm at room temperature, especially at large scale and high reactant concentrations, but is slow at 0 °C. Use of a large room temperature water bath will dissipate the heat of reaction, preventing a thermal overrun.

Known compound; **CAS-Nr.**: 97691-23-1. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, CH_3), 7.10 (d, J = 7.9, 1 H, Arl-H), 7.23 (d, J = 7.6, 1 H, Arl-H), 7.39 (dd, J = 7.9, 7.6, 1 H, Arl-H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 29.9, 37.5, 117.4, 121.1, 138.7, 150.2, 170.6 ppm. Analytical data agree with those reported in the literature.[3]



2-Chloro-6-*tert*-amylpyridine (6a). Prepared according to the **GP** from 2,6-dichloropyridine (33.8 mmol, 5.00 g, 98% purity), CuI (323 mg, 5 mol-%) and *t*AmMgCl (67.6 mmol, 0.7 M in THF). Purification by CC (*n*-pentane/CH_2Cl_2 = 5:1) gave 4.56 g (74%) of a colorless liquid.

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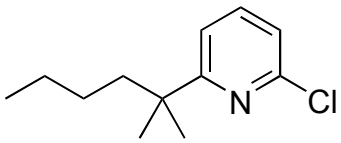
[3] a) J. Baur, H. Jacobsen, P. Burger, G. Artus, H. Berke, L. Dahlenburg, *Eur. J. Inorg. Chem.* **2000**, 1411–1422. b) D. B. Grotjahn, D. A. Lev, *J. Am. Chem. Soc.* **2004**, *126*, 12232–12233, with Supporting Information.

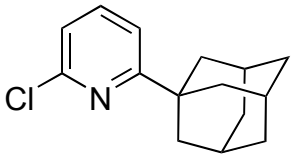
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.69 (t, J = 7.5, 3 H, CH_3), 1.30 (s, 6 H, CH_3), 1.73 (q, J = 7.4, 2 H, CH_2), 7.09 (d, J = 7.7, 1 H, Arl-H), 7.18 (d, J = 7.7, 1 H, Arl-H), 7.54 (t, J = 7.8, 1 H, Arl-H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 9.1, 27.2, 35.6, 40.8, 118.4, 120.9, 138.4, 150.2, 169.5 ppm. **IR** (neat): ν = 2965m, 2878s, 1562s, 1433s, 1401s, 1131s, 795s cm^{-1}. **MS** (EI): m/z (%) = 184 (1) M^+, 168 (77), 155 (100), 139 (16), 127 (15), 117 (16). **EA** calcd. for $C_{10}H_{14}ClN$ (183.08): C 65.39, H 7.68, N 7.63; found: C 65.59, H 7.95, N 7.68.

2-Chloro-6-(1,1-dimethylpentyl)pyridine (8a). Prepared according to the **GP** (0 °C to r.t., overnight) from 2,6-dichloropyridine (534 mg, 97% purity, 3.50 mmol), CuI (33 mg, 5 mol-%) and (1,1-dimethylpentyl-magnesium chloride (5.25 mmol, 0.5 M in THF). Purification by CC (*n*-pentane/DCM 5:1) afforded 597 mg (81%) of a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, J = 7.4, 3 H, CH_3), 0.99–1.08 (m, 2 H, CH_2), 1.18–1.28 (m, 2 H, CH_2), 1.32 (s, 6 H, CH_3), 1.66–1.71 (m, 2 H, CH_2), 7.10 (d, J = 7.7, 1 H, Arl-H), 7.18 (d, J = 7.7, 1 H, Arl-H), 7.54 (t, J = 7.9, 1 H, Arl-H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.1, 23.4, 27.0, 27.7, 40.6, 42.9, 118.2, 120.9, 138.4, 150.2, 169.8 ppm. **IR** (neat): ν = 2959 (s), 2864 (s), 1581 (s), 1559 (s), 1469 (s), 1431 (s), 1400 (s), 798 (s), 743 (s) cm^{-1}. **MS** (EI): m/z (%) = 212 (100) M^+, 194 (13), 176 (71), 155 (16), 99 (5). **EA** calcd. for $C_{12}H_{18}ClN$ (211.73): C 68.07; H 8.57; N 6.62; found: C 68.49; H 8.96; N 6.93.

2-Adamantyl-6-chloropyridine (13a). A solution of adamantylmagnesium-chloride[4] (0.52 M in Et_2O; 11 mL, 5.72 mmol, 1.6 equiv) was added to 2,6-di-chloropyridine (530 mg, 3.575 mmol) and CuI (60 mg, 0.35 mmol, 10 mol-%) in THF (8 mL) at 0 °C. After warming to r.t., the reaction mixture was freed from most of the Et_2O under reduced pressure and stirred for 24 h at r.t. After quenching with *t*BuOMe/NH_4Cl aq and wash-ing with NH_4Cl/NH_3 aq, the organic phase was evaporated and separated by CC (EtOAc/hexanes = 1:100–1:50) to give 547 mg (62%) of a colorless solid.



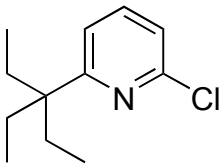
Notes: Adamantyl Grignard reagents are prepared in Et_2O (THF is not suitable),[4] but Et_2O is not a good solvent for the present cross-coupling reaction. Thus, the majority of Et_2O was removed from the reaction mixture by vacuum evaporation.

Known compound; **CAS-Nr.:** 151068-93-8. **M.p.**: 124–125 °C (Lit.: 109–112 °C).[5] **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.74–1.81 (m, 6 H), 1.93–2.02 (m, 6 H), 2.05–2.15 (m, 3 H), 7.10 (dd, J = 7.8, 0.8, 1 H), 7.15 (d, J = 7.7, 0.8, 1 H), 7.56 (t, J = 7.8, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 28.8 (CH),

[4] G. Molle, P. Bauer, J. E. Dubois, *J. Org. Chem.* **1982**, *47*, 4120–4128.
[5] N. Kanomata, M. Igarashi, M. Tada, *Heterocycles* **1993**, *36*, 1127–1138.

36.8 (CH_2), 39.1 (C), 41.8 (CH_2), 117.2 (CH), 121.1 (CH), 138.7 (CH), 150.4 (C), 170.3 (C) ppm. **IR** (KBr): ν = 2904s, 1558s, 1434s, 1131m cm^{-1}. **MS** (GC/MS, EI): m/z (%) = 247/249 (100) M^+, 190 (25). **EA** calcd. for $C_{15}H_{18}ClN$ (247.76): C 72.71, H 7.32, N 5.65; found: C 72.92, H 7.57, N 5.44.

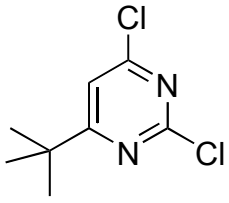
This compound has previously been obtained by a radical substitution of 2,6-dichloropyridine in very low (3%) yield.[5]



2-Chloro-6-(1,1-diethylpropyl)-pyridine (11a). In a Schlenk vessel, LiCl (750 mg, 17.7 mmol) was heated in high vacuum. After cooling, CuI (95 mg, 0.50 mmol, 9.5 mol-%), 2,6-dichloropyridine (775 mg, 5.42 mmol) and THF (5 mL) were added and the mixture stirred at 0 °C. A solution of triethylcarbinylmagnesiumchloride (29.5 mL, 0.43 M in THF, 12.7 mmol, 2.4 equiv.) was added and the reaction mixture then reduced in vacuum to a total volume of ca 20 mL. After stirring for 6 days, the reaction was worked up the usual way and the raw product purified by CC (*t*BuOMe/hexanes = 1:30) to give 164 mg (15%) of colorless oil. *Note*: The initial addition of LiCl may be omitted.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (t, J = 7.4, 9 H), 1.75 (q, J = 7.4, 6 H), 7.09 (dd, J = 7.8, 0.8, 1 H), 7.16 (dd, J = 7.8, 0.7, 1 H), 7.54 (t, J = 7.8, 1 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 8.1 (CH_3), 27.9 (CH_2), 47.09 (C), 119.9 (CH), 120.7 (CH), 138.0 (CH), 150.3 (C), 168.2 (C) ppm. **IR** (film): ν = 2965s, 1563m, 1433m, 1132m, 792m cm^{-1}. **MS** (GC/MS, EI): m/z (%) = 211/213 (5) M^+, 196/198 (90), 183 (95), 182 (100), 168/170 (97), 140/142 (60). **EA** calcd. for $C_{12}H_{18}ClN$ (211.73): C 68.07, H 8.57, N 6.62; found: C 67.86, H 8.20, N 6.91.

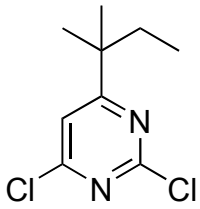
3. Diazines (Pyrimidines)



4-*tert*-Butyl-2,6-dichloropyrimidine (3b): Prepared according to the **GP** from 2,4,6-trichloropyrimidine (2.69 mmol, 500 mg, 99% purity), CuI (5 mol-%) and *t*BuMgCl (2.69 mmol, 1.0 M in THF). Purification by CC (*n*-pentane/CH_2Cl_2 2:1) gave 540 mg (98%) of a slightly yellow solid.

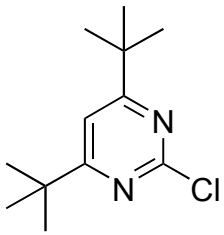
M.p.: 61–62 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.35 (s, 9 H), 7.28 (s, 1 H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 29.0, 38.2, 115.6, 160.2, 162.5, 183.0 ppm. **IR** (KBr): ν = 2966s, 2870w, 1559s, 1520s, 1479m, 1455m, 1364m, 1303s, 1260s, 1101s, 1023s, 882s, 824s cm^{-1}. **MS** (EI): m/z (%) = 205/207 (10) M^+, 204/206 (10), 189/191 (100), 161/163 (9), 153 (5), 126/128 (4), 118 (17), 90/92 (3), 65/67 (4). **EA** calcd. for $C_8H_{10}Cl_2N_2$ (205.08): C 46.85, H 4.91, N 13.66; found: C 46.91, H 4.98, N 13.43.

4-*tert*-Amyl-2,6-dichloro-pyrimidine (7b): Prepared according to the **GP** from 2,4,6-trichloropyrimidine (556 mg, 0.35 mL, 3.0 mmol; purity 99%), CuI (17.1 mg, 0.09 mmol) and *t*AmylMgCl (2.7 mL, 1.11 M in THF, 3.0 mmol) in THF (3 mL). Reaction temperature: –10→0 °C, time: 20 min. Purification by CC (*t*BuOMe/hexanes = 1:60) gave 624 mg (95%) of a colorless liquid.



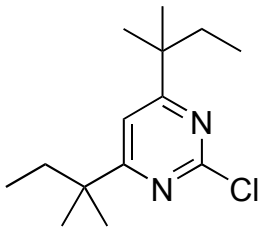
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74 (t, J = 7.6, 3 H, CH_3), 1.31 (s, 6 H, CH_3), 1.75 (q, J = 7.6, 2 H, CH_2), 7.26 (s, 1 H, CH) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 8.93 (CH_3), 26.31 (CH_3), 34.91 (CH_2), 41.63 (C), 116.61 (CH), 160.25 (C), 162.51 (C), 182.50 (C) ppm. **IR** (film): ν = 2968m, 1556s, 1517s, 1388s, 1286s, 824m cm^{-1}. **MS** (GC/MS, EI): m/z (%) = 218/220/220 (2) M^+, 203/205 (100), 190/192 (85), 175/177 (24). **EA** calcd. for $C_9H_{12}Cl_2N_2$ (219.11): C 49.33, H 5.52, N 12.79; found: C 49.96, H 5.30, N 12.52.

4,6-Di-*tert*-butyl-2-chloropyrimidine (1b): Prepared according to the **GP** from 2,4,6-trichloropyrimidine (556 mg/0.35 mL, 3.0 mmol; purity 99%), CuI (57.2 mg, 0.3 mmol) and *t*BuMgCl (6.15 mL, 1.22 M in THF, 7.5 mmol) in THF (3 mL). Reaction temperature: –10→0 °C, reaction time: 2 h. Purification by CC (*t*BuOMe/hexanes = 1:60 or *n*-pentane/CH_2Cl_2 = 3:1) gave 565 mg (83%) of a white crystalline solid.



M.p.: 82–83 °C. **^{1}H NMR** (400 MHz, $CHCl_3$): δ = 1.34 (s, 18 H), 7.22 (s, 1 H) ppm. **^{13}C NMR** (100 MHz, $CHCl_3$): δ = 29.5 (CH_3), 38.0 (C), 110.1 (CH), 160.1 (C), 181.3 (C) ppm. **IR** (KBr): ν = 2970s, 1569m, 1263s, 1165m, 1101s, 1061m cm^{-1}. **MS** (EI): m/z (%) = 226/228 (15, M+), 225/227 (16), 211 (100), 196 (15), 184 (43), 169 (6). **EA** calcd. for $C_{12}H_{19}ClN_2$ (226.75): C 63.56, H 8.45, N 12.35; found: C 63.85, H 8.53, N 12.38.

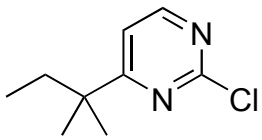
4,6-Di-*tert*-amyl-2-chloro-pyrimidine (6b). Prepared according to the **GP** from 2,4,6-trichloropyrimidine (556 mg, 0.35 mL, 3.0 mmol; purity 99%), CuI (57.2 mg, 0.3 mmol) and *t*AmMgCl (6.67 mL, 1.11 M in THF, 7.5 mmol) in THF (3 mL). Reaction temperature: –10 °C→0 °C, reaction time: 2 h. Purification by CC (*t*BuOMe/hexanes = 1:60) gave 486 mg (64%) of a colorless liquid and 185 mg (33%) of the side-product 4-*tert*-amyl-2-chloro-primidine as yellow liquid.



B) Prepared according to the **GP** from 2,4,6-trichloro-pyrimidine (2.6 mmol, 500 mg, 99% purity), CuI (5 mol-%) and *t*AmMgCl (5.9 mmol, 0.5 M in THF). Purification by CC (*n*-pentane/CH_2Cl_2 2:1) afforded 410 mg (60%) of yellow liquid.

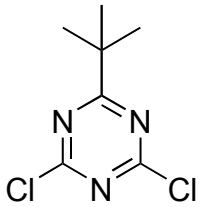
*Data for 4,6-di-tert-amyl-2-chloro-pyrimidine (**6b**):* **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.71 (t, J =7.7, 6 H, CH_3), 1.30 (s, 12 H, CH_3), 1.73 (q, J = 7.4, 4 H, CH_2), 7.13 (s, 1 H, CH) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 9.0, 26.6, 35.1, 41.2, 112.1, 160.5, 180.2 ppm. **IR** (neat): ν = 2967s, 2878s, 1568s, 1514s, 1463m, 1288m, 1255s, 868m, 794m cm^{-1}. **MS** (CI, CH_4, 70 eV): m/z (%) = 255/257 (100)$[M+H]^+$, 239/241 (7), 226 (21), 219 (71), 211 (1), 198 (1). **EA** calcd. for $C_{14}H_{23}ClN_2$ (254.80): C 65.99, H 9.10, N 10.99; found: C 65.24, H 8.79, N 11.40.

Data for *4-tert-amyl-2-chloro-pyrimidine*: **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 0.73 (t, J = 7.4, 3 H, CH_3), 1.32 (s, 6 H, CH_3), 1.75 (q, J = 7.4, 2 H, CH_2), 7.25 (d, J = 5.2, 1 H, CH), 8.53 (d, J = 5.2, 1 H, CH) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 8.92 (CH_3), 26.41 (CH_3), 35.00 (CH_2), 41.29 (C), 116.28 (CH), 159.18 (CH), 161.06 (C), 181.11 (C) ppm. **MS** (GC/MS, EI): m/z (%) = 183/185 (2) M^+, 169/171 (76), 156/158 (100). **IR** (film): ν = 2968s, 1570s, 1533s, 1342s, 1182s, 858m cm^{-1}. **EA** calcd. for $C_9H_{13}ClN_2$ (268.40): C 58.54, H 7.10, N 15.17; found: C 58.61, H 6.76, N 14.96.



4. Triazines

4-*tert*-Butyl-2,6-dichloro-1,3,5-triazine (3c). Prepared according to the **GP** from cyanuric chloride (purity 99%; 558.8 mg, 3.0 mmol), CuI (28.6 mg, 0.15 mmol) and *t*BuMgCl (2.63 mL, 1.22 M in THF, 3.15 mmol) in THF (3 mL). Temperature –10→0 °C, reaction time: 30 min. Purification by CC (*t*BuOMe/hexanes = 1:60) gave 395 mg (64%) of a colorless liquid.



Note: The product is partly hydrolyzed during aqueous work-up and on the SiO_2 column, which reduces the yield. According to the GC/MS analysis of the reaction mixture, the alkylation reaction is essentially quantitative and no notable side-products are formed. A non-aqueous, distillative work-up is recommended in order to secure higher yields; see also the derivatization reaction below.

Known compound;[6] **CAS-Nr.**: 705-23-7. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, CH_3) ppm. **^{13}C** NMR (75 MHz, $CDCl_3$): δ = 28.58 (CH_3), 40.23 (C), 171.68 (C), 190.45 (C) ppm. **MS** (GC/MS, EI): m/z (%) = 190/192/194 (100) M^+.

This compound has earlier been obtained by the non-catalyzed substitution reaction of *t*BuMgCl with cyanuric chloride in refluxing toluene (112 °C, 3.5 h, 24% yield).[6] The 32% yield reported in Ref.[6b] is apparently based on recovered starting material.

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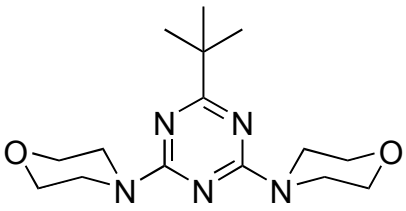
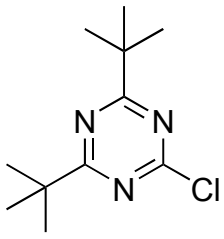
[6] a) Brit. Petroleum Co. Ltd., GB 1102013, **1964**. b) A. D. Forbes, P. Gould, I. R. Hills, *J. Chem. Soc.* **1965**, 1113–1117. c) Q. Wang, D. Wang, Q. Zheng, M. Wang, *Org. Lett.* **2007**, *9*, 2847–2850.

Given the sensitivity of 4-*tert*-butyl-2,6-dichloro-1,3,5-triazine towards hydrolysis, a mono-*tert*-butylation reaction mixture of cyanuric chloride was also submitted to an in situ derivatization with morpholine[7] in order to assess the yield of the alkylation step:



2-*tert*-Butyl-4,6-dimorpholino-1,3,5-triazine (4c). The initial alkylation was performed according to the **GP** with cyanuric chloride (purity 99%; 558.8 mg, 3.0 mmol), CuI (28.6 mg, 0.15 mmol) and *t*BuMgCl (3.13 mL, 0.99 M in THF, 3.10 mmol) in THF (3 mL). Reaction temperature: –10 °C→0 °C. After 30 min of stirring, morpholine (2.61 g/2.64 mL, 30 mmol) was added at 0 °C and the reaction mixture stirred for another 30 min at r.t. Work up: quenching with NH_4Cl aq, extraction with CH_2Cl_2, drying over $MgSO_4$. Purification by CC (EtOAc/hexanes = 1:6) gave 833 mg (90%) of a white crystalline solid.

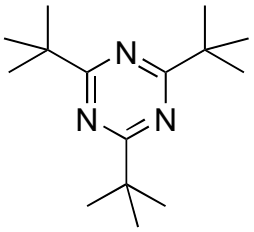
M.p.: 161–162 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.25 (s, 9 H, CH_3), 3.71 (t, J = 4.7, 8 H, CH_2), 3.80 (br s, 8 H, CH_2) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 28.9, 39.0, 43.5, 66.8, 165.1, 184.1 ppm. **IR** (KBr): ν = 3462w, 2967s, 2896m, 2855m, 1540s, 1478s, 1441s, 1260s, 1223s, 1116m, 996m, 704m cm^{-1}. **MS** (EI): m/z (%) = 307 (100) M^+, 292 (26), 277 (88), 262 (36), 250 (58), 232 (14), 220 (14), 207 (6), 193 (4), 176 (4), 164 (3), 138 (6), 113 (13), 94 (5), 81 (5), 69 (11). **EA** calcd. for $C_{15}H_{25}N_5O_2$ (307.39): C 58.61, H 8.20, N 22.78; found: C 58.89, H 8.33, N 22.53.



2-Chloro-4,6-di-*tert*-butyl-1,3,5-triazine (1c). Cyanuric chloride (5.35 g, 29.0 mmol) and CuI (190 mg, 1 mmol, 3.4 mol-%) in THF (20 mL) were stirred at 0 °C. Over 20 min, *t*BuMgCl (40 mL, 1.75 M in THF, 70 mmol, 2.4 equiv) was added and the reaction mixture stirred for 2 h at 0 °C. The reaction was diluted with *t*BuOMe (100 mL) and quenched with HCl 2.4 M and water (caution: HCN smell). The organic phase was washed with NH_4Cl aq, $NaHCO_3$ aq and water, then dried ($MgSO_4$), filtered and evaporated to dryness. The residue was dissolved in hexanes and filtered over a column of SiO_2. Product fractions (TLC) were combined and evaporated. The product was shortly dried in HV (1 h; may sublime) and then by standing in air for several hours to give 5.996 g (90%) of colorless crystals.

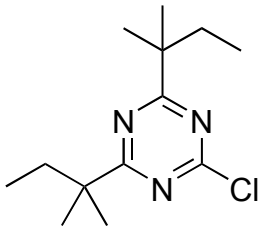
M.p.: 65–66 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.39 (s, 18 H, CH_3) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 29.7, 39.7, 171.8, 187.6 ppm. **IR** (KBr): ν = 2969s, 2932s, 2871s, 1547s, 1497s, 1365s, 1271s, 1234s, 1208s, 904s, 871s, 841m, 800s cm^{-1}. **MS** (CI, CH_4, 70 eV): m/z (%) = 228 (100) $[M+H]^+$, 225/227 (12), 210/212 (20), 207/209 (44), 192 (45), 187 (7), 83/85 (35). **EA** calcd. for $C_{11}H_{18}ClN_3$ (227.73): C 58.01, H 7.97, N 18.45; found: C 58.04, H 7.85, N 18.33.

[7] Bis-morpholino-triazines: R. Menicagli, S. Samaritani, V. Zucchelli, *Tetrahedron* **2000**, *56*, 9705–9711.



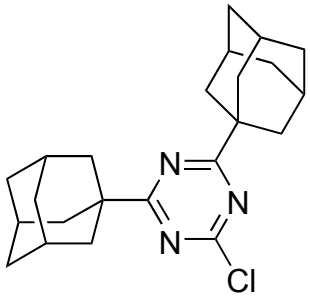
2,4,6-Tri-*tert*-butyl-1,3,5-triazine (5c). To cyanuric chloride (purity: 99%; 559 mg, 3 mmol) and CuI (28.6 mg, 0.15 mmol) in THF (3 mL) at 0 °C, *t*BuMgCl (5.0 mL, 1.5 M in THF, 7.5 mmol) was added and the mixture stirred for 1 h at 0 °C; then, another addition of CuI (17.1 mg, 0.09 mmol) and *t*BuMgCl (4.0 mL, 1.5 M in THF, 6.0 mmol) was followed by stirring for 1 h at 0 °C and 48 h at r.t. The reaction mixture was quenched by addition of NH_4Cl aq and extracted with *t*BuOMe. The organic phase was dried over $MgSO_4$, filtered and evaporated. The residue was separated by CC (hexanes) to give 384 mg (51%) of a white crystalline solid.

Known compound;[8] **CAS-Nr.**: 56382-55-9. **M.p.**: 88–90 °C (Lit.: 91–93 °C).[8] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.36 (s, 27 H, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 29.06 (CH_3), 39.50 (C), 183.84 (C) ppm. **IR** (KBr): ν = 2974s, 1534s, 1363s, 1242s, 912s cm^{-1}. **MS** (GC/MS): m/z (%) = 249 (14) M^+, 234 (100), 207 (23). **EA** calcd. for $C_{15}H_{27}N_3$ (249.39): C 72.24, H 10.91, N 16.85; found: C 72.29, H 10.90, N 16.67.



2-Chloro-4,6-di-*tert*-amyl-1,3,5-triazine (6c). Prepared according to the GP from cyanuric chloride (558.8 mg, purity 99%, 3.0 mmol), CuI (28.6 mg, 0.15 mmol, 5 mol-%) and *t*AmMgCl (5.6 mL, 1.13 M in THF, 6.3 mmol) in THF (3 mL), reaction temperature: 0 °C, reaction time: 1 h. Purification by CC (*t*BuOMe/hexanes = 1:60→1:30, or *n*-pentane/CH_2Cl_2 = 5:1) gave 692 mg (90%) of a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (t, J =7.6, 6 H, CH_3), 1.56 (s, 12 H, CH_3), 1.80 (q, J = 7.4, 4 H, CH_2) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 9.0, 25.9, 34.6, 43.1, 171.0, 186.9 ppm. **IR** (neat): ν = 2969s, 2879m, 1540s, 1499s, 1371m, 1274s, 1204w, 868m, 797w cm^{-1}. **MS** (CI, CH_4, 70 eV): m/z (%) = 256/258 (100) $[M+H]^+$, 240 (11), 227 (22), 220 (37), 192 (5), 123 (10), 98 (2), 83/85 (6). **EA** calcd. for $C_{13}H_{22}ClN_3$ (255.79): C 61.04, H 8.67, N 16.43; found: C 60.89, H 8.37, N 16.53.

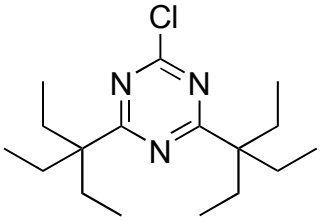


4,6-Diadamantyl-2-chloro-1,3,5-triazine (13c). A solution of adamantylmagnesium chloride (0.52 M in Et_2O; 10.5 mL, 5.46 mmol, 2.5) was added to cyanuric chloride (400 mg, 2.17 mmol) and CuI (21 mg, 0.11 mmol, 5 mol-%) in THF (5 mL) at 0 °C. After stirring for 1 h at 0 °C and for 3 h at r.t., the reaction was quenched with NH_4Cl aq and *t*BuOMe. The organic phase was washed with NH_4Cl aq (2 M, 2 ×), NH_3 aq (3 M, 2 ×) and H_2O. Purification by CC (EtOAc/hexanes 1:100–1:50) gave 560 mg (67%) of a colorless solid.

[8] W. Jarre, D. Bieniek, F. Korte, *Tetrahedron* **1975**, *31*, 619–623.

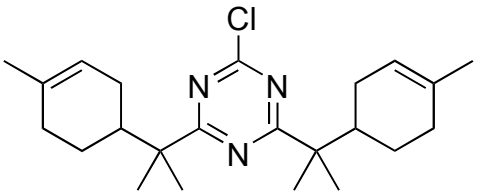
M.p.: 200–201 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.72–1.83 (m, 12 H), 2.00–2.06 (m, 12 H), 2.07–2.14 (m, 6 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 28.4 (CH), 36.6 (CH_2), 40.5 (CH_2), 41.5 (C), 171.2 (C), 186.5 (C) ppm. **IR** (KBr): ν = 2902s, 1540s, 1495s, 1258s, 1099m cm^{-1}. **MS** (GC/MS, EI): *m*/*z* (%) = 383/385 (100) M^+, 326 (10), 135 (22). **EA** calcd. for $C_{23}H_{30}ClN_3$ (383.96): C 71.95, H 7.88, N 10.94; found: C 71.99, H 7.76, N 10.88.

2-Chloro-4,6-bis(1,1-diethylpropyl)-1,3,5-triazine (11c). Prepared according to the **GP** from cyanuric chloride (461 mg, 2.5 mmol), CuI (24 mg, 0.125 mmol, 5 mol-%) and triethylmethylmagnesiumchloride (10 mL, 0.55 M, 5.5 mmol, 2.2 equiv). After stirring for 1 h at 0 °C and 1 h at r.t., the reaction was quenched. Purification by CC (hexanes→*t*BuOMe/hexanes = 1:60) gave 531 mg (68%) of colorless liquid.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.67 (t, *J* = 7.4, 18 H, CH_3), 1.83 (q, *J* = 7.4, 12 H, CH_2) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 8.05 (CH_3), 27.34 (CH_2), 49.58 (C), 170.86 (C), 185.92 (C) ppm. **IR** (film): ν = 2966s, 1540s, 1495s, 1265s, 816m cm^{-1}. **MS** (GC/MS, EI): *m*/*z* (%) = 311/313 (8) M^+, 282/284 (100), 268/270 (37). **EA** calcd. for $C_{17}H_{30}ClN_3$ (311.89): C 65.47, H 9.70, N 13.47; found: C 65.48, H 9.90, N 13.87.

Di-4,6-α-terpinyl-2-chloro-1,3,5-triazine (12c).



A) *Limonene hydrochloride (terpinyl chloride)*: Prepared from (+)-limonene.[9] The tertiary chloride is partially racemized under these conditions.

B) *α-Terpinylmagnesiumchloride*: Magnesium turnings (99.98% purity; 4.0 g, 165 mmol) were stirred with a crystal of iodine (30 mg) and α-terpinyl chloride (1.0 g of a total of 10.0 g, 57.9 mmol) in THF (5 mL). Ethylene bromide (0.2 mL) was added and the mixture warmed. After the reaction set in, the mixture was stirred in a r.t. water bath and the remaining terpinyl chloride (9.0 g) addded as solution in THF (25 mL) in portions of ca 5 mL over 1.5 h. After completion of the addition, the mixture was stirred for 2 h at r.t. Titration (1 mL Grignard + H_2O, HCl 0.1 M, methyl orange) indicated a concentration of the final solution of 0.37 M (yield ca 30%).

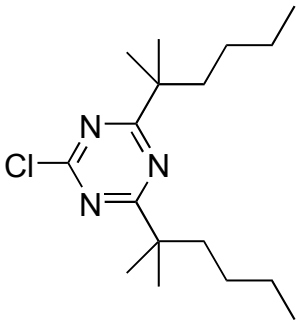
C) *Di-4,6-α-terpinyl-2-chloro-1,3,5-triazine (12c):* A solution of α-terpinylmagnesiumchloride (0.37 M in THF; 12.7 mL, 4.7 mmol, 2.2. equiv) was added to cyanuric chloride (400 mg, 2.17 mmol) and CuI (21 mg, 0.11 mmol, 5 mol-%) in THF (3 mL) at 0 °C. After stirring for 6 h at 0 °C, NH_4Cl aq was added to quench the reaction. CC (*t*BuOMe/hexanes = 1:60) gave the product as colorless oil (703

[9] M. C. S. de Mattos, A. M. Sanseverino, *Synth. Commun.* **2000**, *30*, 1975–1983.

mg, 83%). According to the NMR and GC/MS analysis, the product is a mixture of *meso* and chiral diasteroemers. Ca 5% of the limonenyl groups are isomers with an exocyclic double bond.

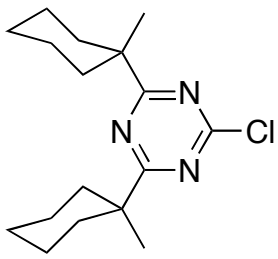
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13–1.26 (m, 2 H), 1.29 (s, 6 H, 2 Me), 1.33 (s, 6 H, 2 Me), 1.43–1.55 (m, 2 H), 1.62 (br. s, 6 H, 2 Me), 1.66–2.03 (m, 8 H), 2.07–2.17 (m, 2 H), 5.29–5.35 (m, 2 H alkene) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 22.7, 23.4, 23.7, 24.7, 26.8, 31.3, 42.8, 45.5, 120.5, 133.8, 170.8, 186.9 ppm. **IR** (film): ν = 2968s, 1539s, 1496s, 1269m, 849w cm^{-1}. **MS** (GC/MS, EI): *m*/*z* (%) = 387/389 (1) M^+, 293 (11), 199/201 (100). **EA** calcd. for $C_{23}H_{34}ClN_3$ (387.99): C 71.20, H 8.83, N 10.83; found: C 70.95, H 9.05, N 10.84.

2-Chloro-4,6-bis-(1,1-dimethylpentyl)-1,3,5-triazine (9c). Prepared according to the **GP** from 2,4,6-trichloro-triazine (3.47 mmol, 635 mg, 99% purity), CuI (5 mol-%) and (1,1-dimethylpentyl)magnesiumchloride (7.55 mmol, 0.5 M, THF). Reaction time (not optimized): 12 h. CC (*n*-pentane/CH_2Cl_2 = 5:1) afforded colorless liquid (968 mg, 93%).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* =7.4, 6 H, CH_3), 1.01–1.10 (m, 4 H, CH_2), 1.18–1.30 (m, 4 H, CH_2), 1.34 (s, 12 H, CH_3), 1.71–1.77 (m, 4 H, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.0, 23.3, 26.6, 27.0, 42.0, 42.9, 170.9, 186.9 ppm. **IR** (KBr): ν = 2960 (s), 2932 (s), 2864 (s), 1540 (s), 1498 (s), 1369 (w), 1275 (s), 903 (w), 877 (m), 817 (w) cm^{-1}. **MS** (EI, 70 eV): *m*/*z* (%) = 311/313 (5) M^+, 296/298 (6), 268/270 (60), 255/257 (100), 240/242 (4), 199/201 (34), 126 (7), 99 (7), 57 (19). **EA** calcd. for $C_{17}H_{30}ClN_3$ (311.89): C 65.47; H 9.70; N 13.47; found: C 65.38; H 9.50; N 13.71.

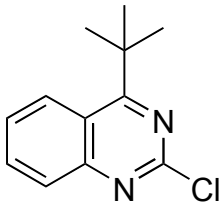
2-Chloro-4,6-bis(1-methylcyclohexyl)-1,3,5-triazine (10c). Prepared according to the **GP**, starting from 2,4,6-trichloro-triazine (3.0 mmol, 558 mg, 99% purity), CuI (5 mol-%) and 1-methylcyclohexylmagnesium chloride (7.2 mmol, 0.75 M in THF). Reaction time: 2.5 h. Purification by CC (*n*-pentane/CH_2Cl_2 = 7:1) afforded 821 mg (88%) of a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 6 H, CH_3), 1.26–1.65 (m, 16 H, CH_2), 2.22–2.29 (m, 4 H, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 23.0, 25.9, 28.5, 36.1, 43.5, 171.3, 187.1 ppm. **IR** (neat): ν = 2930 (s), 2856 (s), 1540 (s), 1496 (s), 1449 (s), 1269 (s), 1222 (m), 915 (w), 890 (m), 838 (m), 776 (w) cm^{-1}. **MS** (EI, 70 eV): *m*/*z* (%) = 307/309 (100) M^+, 292/294 (84), 252/254 (56), 238/240 (14), 225/227 (15), 124 (11), 97 (27), 55 (33). **EA** calcd. for $C_{17}H_{26}ClN_3$ (307.86): C 66.32; H 8.51; N 13.65; found: C 66.58; H 8.32; N 13.83.

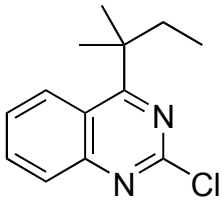
5. Other Heterocycles

4-*tert*-Butyl-2-chloroquinazoline (1d). Prepared according to the **GP** from 2,4-dichloroquinazoline (398 mg, 2.0 mmol), CuI (19.1 mg, 0.1 mmol) and *t*BuMgCl (2.1 mL, 1.0 M in THF, 2.1 mmol) in THF (8 mL), temperature 0 °C, reaction time 20 min. CC (hexanes/EtOAc = 20:1) gave 442 mg (90%) white solid.



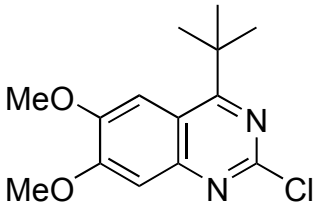
M.p.: 89–90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.57 (s, 9 H, CH_3), 7.52 (ddd, *J* = 8.5, 6.9, 1.4, 1 H-Arl), 7.77 (ddd, *J* = 8.4, 7.0, 1.4, 1 H-Arl), 7.92 (d, *J* = 8.5, 1 H-Arl), 8.38 (d, *J* = 8.8, 1 H-Arl) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 29.4, 39.3, 120.3, 125.3, 125.5, 127.9, 132.3, 151.6, 155.1, 179.5 ppm. **IR** (KBr): ν = 2972m, 1529m, 1365s, 1275s, 1103s, 895s, 763s cm^{-1}. **MS** (EI): *m*/*z* (%) = 220 (30) M^+, 205 (100), 178 (43), 129 (32), 102 (23). **EA** calcd. for $C_{12}H_{13}ClN_2$ (220.70): C 65.31, H 5.94, N 12.69; found: C 65.16, H 5.95, N 12.49.

4-*tert*-Amyl-2-chloroquinazoline (6d). Prepared according to the **GP** from 2,4-dichloroquinazoline (398 mg, 2.0 mmol), CuI (19.1 mg, 0.1 mmol) and *t*AmMgCl (2.19 mL, 0.96 M in THF, 2.1 mmol) in THF (8 mL). Temperature 0 °C, reaction time 20 min. CC (hexanes/EtOAc = 20:1) gave 413 mg (88%) of colorless solid.



M.p.: 94 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 0.63 (t, *J* =7.6, 3 H, CH_3), 1.50 (s, 6 H, CH_3), 2.03 (q, *J* = 7.4, 2 H, CH_2), 7.49 (ddd, *J* = 8.7, 6.8, 1.4, 1 H-Arl), 7.76 (ddd, *J* = 8.3, 6.9, 1.4, 1 H-Arl), 7.90 (dd, *J* = 8.5, 0.6, 1 H-Arl), 8.36 (dd, *J* = 8.7, 0.6, 1 H-Arl) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 9.4, 28.5, 35.6, 44.4, 121.9, 126.2, 126.6, 129.1, 133.5, 152.7, 156.2, 180.1 ppm. **MS** (GC/MS, EI): *m*/*z* (%) = 233/235 (22) M^+, 219/221 (100), 206 (42), 178 (18). **IR** ($CHCl_3$): ν = 2972s, 1531s, 1277s, 1164s, 763s cm^{-1}. **EA** calcd. for $C_{13}H_{15}ClN_2$:(234.72): C 66.52, H 6.44, N 11.93; found: C 66.56, H 6.28, N 12.26.

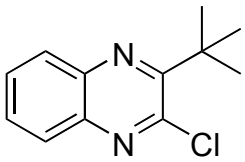
4-*tert*-Butyl-2-chloro-6,7-dimethoxyquinazoline (1e). Prepared according to the **GP** (–10 to 0 ° C, 15 min) from 2,4-dichloro-6,7-dimethoxyquinazoline (1.50 mmol, 400 mg, 97% purity), CuI (5 mol-%) and *t*BuMgCl (3.70 mmol, 1.25 M in THF). Purification by CC (*n*-pentane/EtOAc = 5:4) afforded 362 mg (63%) of a light orange solid.



M.p.: 103–105 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.64 (s, 9 H, CH_3), 4.04 (s, 6 H, CH_3O), 7.29 (s, 1 H-Arl), 7.62 (s, 1 H-Arl) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 30.2, 39.8, 56.1, 56.3, 102.7, 104.5, 107.2, 116.8, 148.8, 151.2, 155.3, 177.1 ppm. **IR** (KBr): ν = 2973s, 2932s, 2870m, 1620s, 1571m, 1504s, 1466s, 1415s, 1239s, 1202s, 1159s, 1138s, 1029m, 1010m, 987m, 900s, 845s cm^{-1}. **MS** (EI): *m*/*z* (%) =

218 (3) M^+, 206 (6), 189 (21), 132 (4), 117 (3). **EA** calcd. for $C_{12}H_{11}ClN_2$ (218.68): C 59.89, H 6.10, N 9.98; found: C 59.49, H 6.17, N 9.71.

3-*tert*-Butyl-2-chloro-quinoxaline (1f). Prepared according to the **GP** from 2,3-dichloroquinoxaline (purity 97%; 615 mg, 3.0 mmol), CuI (28.6 mg, 0.15 mmol) and *t*BuMgCl (3 mL, 1.5 M in THF, 4.5 mmol) in THF (3 mL). Reaction temperature: –10 °C, time: 20 min. CC on Al_2O_3 (neutral; *t*BuOMe/hexanes = 1:60) gave 442 mg (67%) bright yellow solid. An analytical sample was recrystallized from pentane at –18 °C.

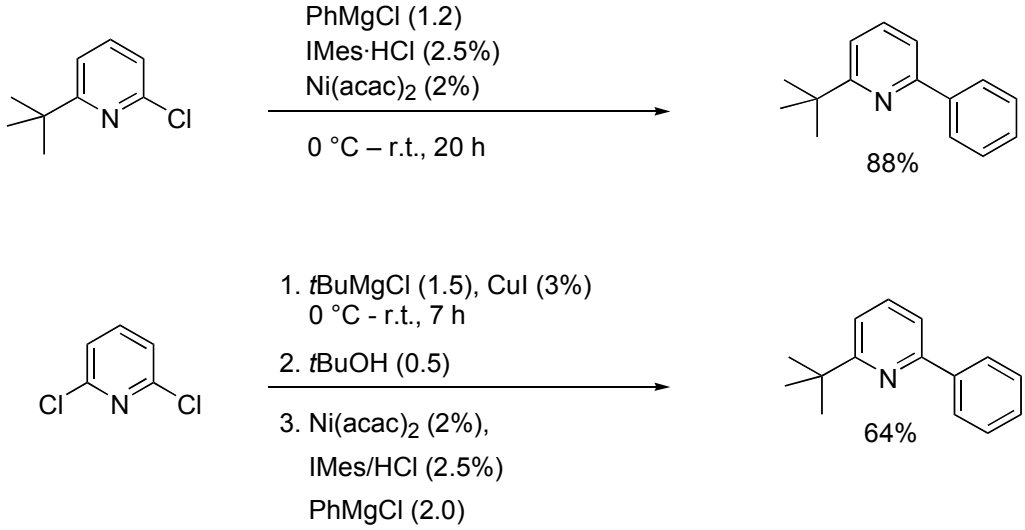


Notes: The product decomposed on a SiO_2 column; CC should be performed quickly, on Al_2O_3.

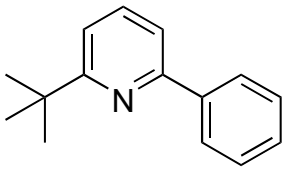
Known compound;[10] **CAS-Nr.**: 33870-78-9. **M.p.**: 36–37 °C. (Lit.: 37 °C). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.62 (s, 9 H, CH_3), 7.68–7.75 (m, 2 H, Arl-H), 7.95–7.98 (m, 1 H, Arl-H), 8.03–8.06 (m, 1 H, Arl-H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 28.74 (CH_3), 39.18 (CH), 127.63 (CH), 128.99 (CH), 129.80 (CH), 130.04 (CH), 139.79 (C), 140.23 (C), 146.29 (C), 160.24 (C) ppm. **MS** (GC/MS, EI): *m*/*z* (%) = 220/222 (27) M^+, 205/207 (100), 178 (35), 129 (33). **IR** (KBr): ν = 2965s, 1622w, 1556m, 1469m, 1368m, 1260m, 1143s, 1084s, 760s cm^{-1}. **EA** calcd. for $C_{12}H_{13}ClN_2$ (220.70): C 65.31, H 5.94, N 12.69; found: C 65.34, H 6.08, N 12.58.

6. Sequential (One-Pot) Couplings

Pyridines



[10] C. Iijima, E. Hayashi, *Yakugaku Zasshi* **1971**, *91*, 721–726; *Chem. Abstr.* **1971**, *75*, 129758. b) C. Iijima, T. Morikawa, E. Hayashi, *Yakugaku Zasshi* **1975**, *95*, 784–792; *Chem. Abstr.* **1976**, *84*, 4901.



2-*tert*-Butyl-6-phenylpyridine (17). A) *Stepwise synthesis*:[11] To a solution of 2-*tert*-butyl-6-chloropyridine (509 mg, 3.00 mmol), nickel(II)acetylacetonate (96% purity; 16.1 mg, 0.060 mmol, 2 mol-%) and IMes·HCl[12] (25.6 mg, 0.075 mmol) in THF (5 mL) under argon, PhMgCl (2.25 mL, 1.6 M in THF, 3.6 mmol) was added dropwise at 0 °C. The ice-bath was removed and the reaction mixture stirred for 23 h at r.t. The reaction was quenched by addition of NH_4Cl aq and extracted with *t*BuOMe (3 × 20 mL). The combined organic phase was dried (Na_2SO_4) and evaporated. Purification by CC (*t*BuOMe/hexanes = 1:100) gave a colorless liquid (556 mg, 88%).

B) One-pot synthesis: To 2,6-dichloropyridine (98% purity; 1.51 g, 10 mmol) and CuI (57.2 mg, 0.3 mmol) in THF (10 mL), *t*BuMgCl (10 mL, 1.5 M in THF, 15 mmol) was added at 0 °C. The ice-bath was removed and the reaction mixture stirred in a water bath at r.t. for 8 h. After cooling to 0 °C, *tert*-butanol (370.5 mg, 5.0 mmol) was added dropwise and the mixture stirred for 30 min at 0 °C. To the mixture, $Ni(acac)_2$ (96% purity; 51mg, 0.20 mmol) and IMes·HCl (85 mg, 0.25 mmol) were added, followed by dropwise addition of PhMgCl (12.5 mL, 1.6 M in THF, 20 mmol) at 0 °C. After stirring for 18 h at r.t. and for another 6 h at 50 °C, the reaction mixture (solidified) was worked up as above to give 1.36 g (64%) of colorless liquid.

Known compound; **CAS-Nr.**: 59321-55-0. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.42 (s, 9 H, CH_3), 7.24 (d, J = 7.8, 1 H), 7.34–7.40 (m, 1 H), 7.42–7.47 (m, 2 H), 7.52 (d, J = 7.8, 1 H), 7.63 (t, J = 8.1, 1 H), 8.07–8.11 (m, 2 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 30.42 (CH_3), 37.88 (C), 116.87 (CH), 117.35 (CH), 126.84 (CH), 128.58 (CH), 128.64 (CH), 136.74 (CH), 139.90 (C), 155.31 (C), 168.88 (C). ppm. **MS** (GC/MS): m/z (%) = 211 (40) M^+, 210 (42), 196 (100), 169 (50). **EA** calcd. for $C_{15}H_{17}N$ (211.30): C 85.26, H 8.11, N 6.63; found: C 85.34, H 8.17, N 7.03.

This compound has previously been prepared from pinacolone either in 5 linear steps (<30% overall yield)[13] or by a convergent synthesis (>8 steps from commercial starting materials, low overall yield).[14]

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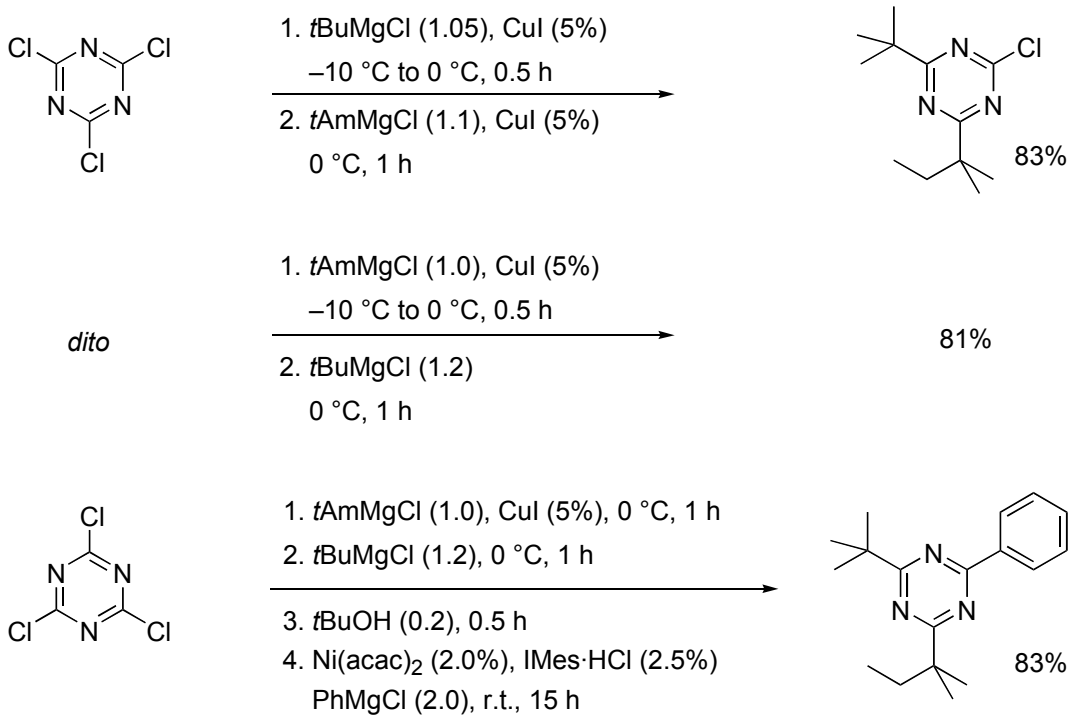
[11] The Herrmann protocol of Ni/N-heterocyclic carbene-catalyzed cross-coupling was applied: V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr, W. A. Herrmann, *Angew. Chem.* **2000**, *112*, 1672–1674; *Angew. Chem. Int. Ed.* **2000**, *39*, 1602–1604.

[12] Prepared according to: L. Hintermann, *Beilstein J. Org. Chem.* **2007**, *3*, 22.

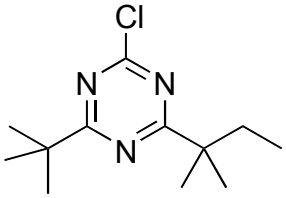
[13] W. M. Owton, P. T. Gallagher, M. Brunavs, *Synth. Commun.* **1992**, *22*, 351–357.

[14] J. Boivin, F. Carpentier, R. Jrad, *Synthesis* **2006**, 1664–1672.

Triazines

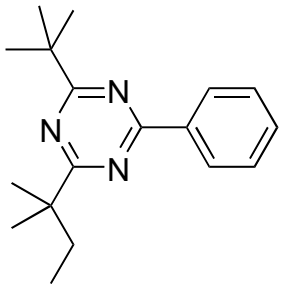


4-*tert*-Amyl-6-*tert*-Butyl-2-chloro-1,3,5-triazine (18). A) To cyanuric chloride (99% purity; 3.73 g, 20 mmol) and CuI (190.5 mg, 1 mmol) in THF (20 mL), *t*AmMgCl (20 mL, 1.0 M in THF, 20 mmol) was added at –10 °C. After stirring for 1 h at 0 °C, *t*BuMgCl (16 mL, 1.5 M in THF, 24 mmol) was added and the reaction stirred for 1 h at 0 °C. Usual workup (cf. **GP**) and CC (*t*BuOMe/hexanes = 1:100) gave 3.93 g (81%) of a colorless liquid.



B) Analogously, a reaction on a 3 mmol scale was performed with initial addition of *t*BuMgCl (1.05 equiv.), followed by addition of *t*AmMgCl (1.1 equiv) and a new portion of CuI catalyst (5 mol-%; this second addition is probably not necessary); the yield in this inverted addition sequence was 83%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.75 (t, J = 7.4, 3 H, CH_3), 1.34 (s, 6 H, CH_3), 1.38 (s, 9 H, CH_3), 1.79 (q, J = 7.4, 2 H, CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 9.12 (CH_3), 26.10 (CH_3), 28.79 (CH_3), 34.69 (CH_2), 39.80 (C), 43.24 (C), 170.97 (C), 186.96 (C), 187.28 (C) ppm. **IR** (film): ν = 2969s, 1542s, 1500s, 1275s, 870m cm^{-1}. **MS** (GC/MS): m/z (%) = 241/243 (2) M^+, 226/228 (100), 213/215 (68), 198 (14). **EA** calcd. for $C_{12}H_{20}ClN_3$ (241.76): C 59.62, H 8.34, N 17.38; found: C 59.63, H 8.38, N 17.54.

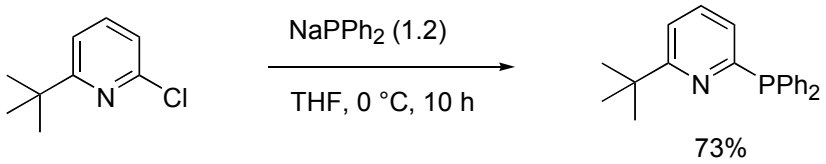


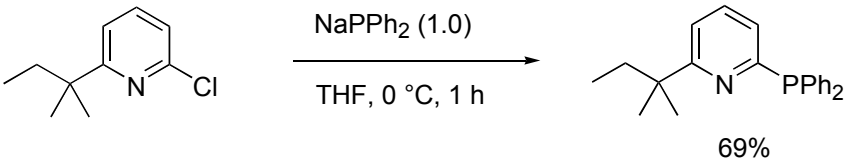
6-*tert*-Butyl-4-*tert*-amyl- 2-phenyl-1,3,5-triazine (19). To cyanuric chloride (99% purity; 931 mg, 5.00 mmol) and CuI (47.6 mg, 0.25 mmol) in THF (5 mL) at 0 °C, *t*AmMgCl (5.0 mL, 1.0 M in THF, 5.0 mmol) was added and the mixture stirred for 1 h at 0 °C. Then, *t*BuMgCl (4.0 mL, 1.5 M in THF, 6.0 mmol) was added and the reaction mixture stirred for 1 h at 0 °C. Subsequently, *tert*-butanol (74.1 mg, 1.0 mmol) was added and the reaction mixture stirred for 30 min at 0 °C. Eventually, $Ni(acac)_2$ (96% purity; 26 mg, 0.10 mmol) and IMes·HCl (43 mg, 0.13 mmol) were added to the reaction mixture at 0 °C, followed by dropwise addition of PhMgCl (6.3 mL, 1.6 M in THF, 10 mmol) at 0 °C and warming to r.t. with stirring. The reaction was finally heated to 50 °C for 6 h. Following the usual work-up, CC (hexanes) gave 1.18 g (83%) of colorless liquid. According to the ^{1}H NMR and GC/MS analysis, the product contained traces of 4,6-di-*tert*-amyl-2-phenyl-1,3,5-triazine (4%) and 4,6-di-*tert*-butyl-2-phenyl-1,3,5-triazine (3%).

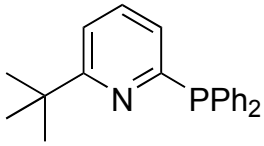
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (t, J = 7.4, 3 H, CH_3), 1.40 (s, 6 H, CH_3), 1.44 (s, 9 H, CH_3), 1.85 (q, J = 7.4, 2 H, CH_2), 7.46–7.53 (m, 3 H), 8.58–8.61 (m, 2 H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 9.17 (CH_3), 26.28 (CH_3), 28.96 (CH_3), 34.78 (CH_2), 39.56 (C), 42.92 (C), 128.48 (CH), 128.78 (CH), 131.93 (CH), 136.87 (C), 170.09 (C), 184.40 (C), 184.89 (C) ppm. **IR** (film): 2967m, 2361w, 1529s, 1379m cm^{-1}. **MS** (GC/MS): m/z (%) = 283 (11) M^+, 268 (78%), 255 (100). **EA** calcd. for $C_{18}H_{25}N_3$ (283.41): C 76.28, H 8.89, N 14.83; found: C 76.29, H 8.79, N 15.19.

7. Synthetic Applications

Synthesis of ALPYPHOS ligands

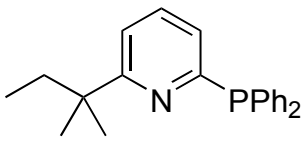






6-*tert*-Butyl-6-diphenylphosphinopyridine (14). To a solution of $NaPPh_2$ (50 mL, 0.5 M in THF, 25 mmol; prepared from PPh_3 and sodium in liquid ammonia)[15] at 0 °C, 6-*tert*-butyl-2-chloropyridine (3.526 g, 20.8 mmol) was added dropwise with stirring. The reaction mixture was stirred over night at r.t. and quenched by addition of EtOH (5 mL). The solvents were removed in vacuum and the residue taken up in CH_2Cl_2/hexanes (1:1, 50 mL). The solution was filtered through a short column of Al_2O_3 (under argon; elute with additional degassed solvent mixture) and the filtrate evaporated to a small volume with cooling (induces product crystallization; seeding recommended); the crystalline slurry of product was cooled to –10 °C, filtered and the solids washed with little hexanes to give colorless crystalline solid (4.85 g, 73%).

CAS-Nr.: 290333-90-3. **^{31}P NMR** (121 MHz, C_6D_6): δ = –3.6 (s) ppm. Analytical data corresponded to the literature values.[3]

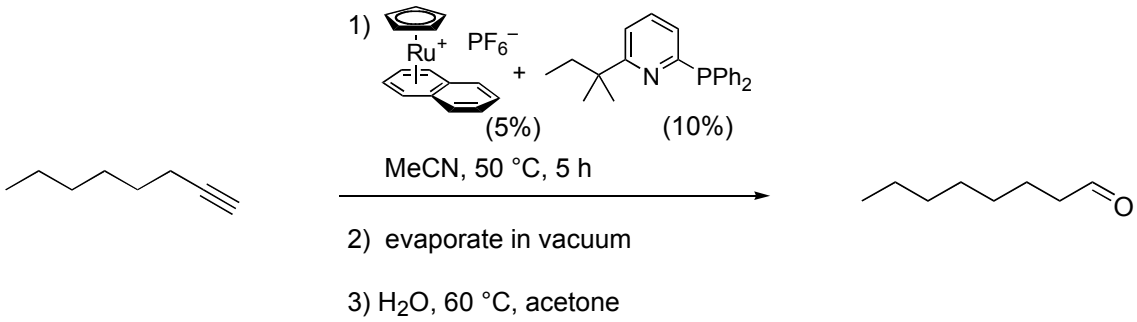


6-*tert*-Amyl-2-diphenylphosphinopyridine *or* (6-*tert*-amyl-2-pyridyl)-diphenylphosphane (TAMPYPHOS) (15). In a dried round-bottom Schlenk flask under argon, 2-chloro-6-*tert*-amylpyridine (12.0 mmol, 2.197 g) in anhydrous THF (15 mL) was cooled to 0 °C. A solution of $NaPPh_2$ (12.0 mmol, 1.0 M in THF)[15] was added dropwise with stirring. The orange reaction mixture was stirred at 0 °C for 1.0 h. The reaction was allowed to warm to r.t. and quenched with NH_4Cl sat (100 mL), then extracted with *t*BuOMe (2×100 mL). The combined organic phases were washed with H_2O (100 mL) and dried over Na_2SO_4. Evaporation followed by CC under argon (*n*-pentane/CH_2Cl_2 = 3:1) gave 2.746 g (69%) of white solid.

[15] W. Hewertson, H. R. Watson, *J. Chem. Soc.* **1962**, 1490–1494.

CAS-Nr.: 947315-18-6. **M.p.**: 75–76 °C. **^{1}H NMR** (300 MHz, C_6D_6): δ = 0.64 (t, J = 7.4, 3 H, CH_3), 1.24 (s, 6 H, CH_3), 1.69 (q, J = 7.4, 2 H, CH_2), 6.82 (dt, J = 7.3, 1.2, 1 H, Arl-H), 6.95 (dt, J = 7.9, 1.6, 1 H, Arl-H), 6.99 (dd, J = 7.3, 2.5, 1 H, Arl-H), 7.02–7.13 (m, 6 H, Arl-H), 7.48–7.55 (m, 4 H, Arl-H) ppm; **^{13}C NMR** (75 MHz, C_6D_6): δ = 9.3, 27.4, 35.8, 41.1, 118.3, 125.2 (d, J_{PC} =22.6), 128.5 (d, J_{PC} = 6.8), 128.8, 134.6 (d, J_{PC} = 19.6), 135.5 (d, J_{PC} = 3.7), 137.9 (d, J_{PC} = 12.0), 162.7 (d, J_{PC} = 3.0), 168.3 (d, J_{PC} = 9.8) ppm. **^{31}P NMR** (121 MHz, C_6D_6): δ = –3.7 (s) ppm. **IR** (KBr): ν = 3449w, 3062m, 2957s, 2869s, 1556s, 1431s, 1380s, 806s, 744s, 695s cm^{-1}. **MS** (EI): m/z (%) = 333 (74) M^+, 318 (41), 305 (100). **EA** calcd. for $C_{22}H_{24}NP$ (333.41): C 79.25, H 7.26, N 4.20; found: C 79.17, H 7.41, N 4.14.

Catalytic hydration of a terminal alkyne with in situ generated [CpRu(TAMPYPHOS)$_2$]PF$_6$

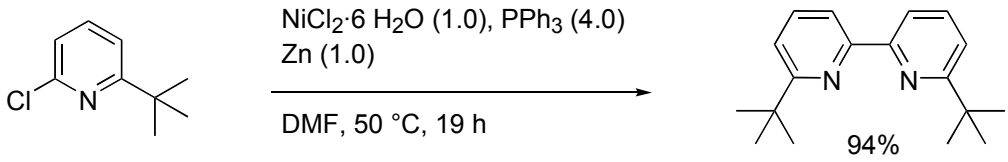


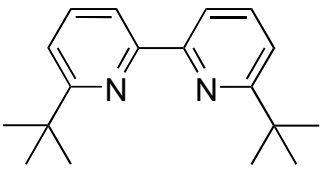
Catalytic anti-Markovnikov hydration of 1-octyne to octanal:[16] A Schlenk flask charged with [CpRu(η^6-naphthalene)]PF$_6$ (22 mg, 0.05 mmol, 5 mol-%),[17] 2-(diphenylphosphino)-6-*tert*-amylpyridine (34 mg, 0.1 mmol, 10 mol %) and degassed CH_3CN (2 mL) was heated to 60 °C for 5 h. After removal of the solvent, the residual yellow resin was dried for 1 h in a high vacuum. A solution of 1-octyne (110 mg, 1 mmol, 1 equiv), H_2O (90 µL, 5 mmol, 5 equiv) and tetradecane (80 mg) in acetone (4 mL) was added to the residue and the yellow reaction mixture kept at 45 °C (60 °C). Aliquots (approximately 100 µL) were removed at certain intervals and diluted with 1.5 mL of dry acetone; of this, 1 µL portions were injected into a GC apparatus equipped with a FID detector. Yields were calculated from peak areas relative to the internal standard tetradecane by applying response factors obtained with pure product samples.

Comparison of the initial reaction rates indicated a relative catalytic activity (*RCA*; rate with ligand **15**/rate with ligand **14**)[16] of *RCA* = 1.2.

[16] Method: A. Labonne, T. Kribber, L. Hintermann, *Org. Lett.* **2006**, *8*, 5853–5856.
[17] E. P. Kündig, F. R. Monnier, *Adv. Synth. Cat.* **2004**, *346*, 901–904.

Synthesis of a bulky bipyridine ligand: 6,6´-di-*tert*-butyl-2,2´-bipyridine (16)





6,6'-Di-*tert*-butyl-2,2'-bipyridine (16). The coupling procedure of Tiecco et al was used.[18] Zinc powder (654 mg, 10 mmol) was added to a stirred blue solution of $NiCl_2 \cdot 6\ H_2O$ (2.38 g, 10 mmol) and triphenylphosphine (10.5 g, 40 mmol) in DMF (30 mL) under argon at 50 °C. After 1 h, the color had changed to red-brown. 6-*tert*-Butyl-2-chloro-pyridine (1.70 g, 10 mmol) was added and the reaction stirred for 15 h at 50 °C. The reaction mixture was poured into NH_3 aq (25%, 500 mL) and extracted with *t*BuOMe (3×250 mL). The combined organic layers were evaporated and the residue dissolved in ethanol (50 mL). Solid I_2 (total ca. 9.5 g) was added in portions with stirring until the brown color of iodine persisted. A solution of Na_2SO_3 (3 g) in water (50 mL) was added to quench excess iodine. The mixture was extracted with *t*BuOMe (3 × 100 mL) and the combined organic phases dried (Na_2SO_4) and evaporated. The residue was purified by CC (*t*BuOMe/hexanes = 1:100) to give a white crystalline solid (1.26 g, 94%).

Notes: The I_2-oxidation step (not part of the literature procedure) converts PPh_3 to PPh_3O for easier chromatographic separation of the (apolar) bipyridine reaction product. We recommend to remove most of the PPh_3O by a crystallization (use seeding) from the crude *t*BuOMe extract, prior to chromatography, because large amounts of PPh_3O will easily block the SiO_2-column.

Known compound; **CAS-Nr.**: 6859-28-5. **M.p.**: 122–123 °C. (Lit.: 122.5–123 °C).[19] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.42 (s, 18 H, CH_3), 7.31 (dd, J = 8.0, 0.8, 2 H), 7.71 (t, J = 7.7, 2 H), 8.32 (dd, J = 7.7, 0.8, 2 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 30.22 (CH_3), 37.54 (C), 117.53 (CH), 118.42 (CH), 136.56 (CH), 154.99 (C), 167.98 (C) ppm. **MS** (GC/MS): m/z (%) = 268 (57) M^+, 267 (58), 253 (100), 237 (30), 212 (37). **IR** (KBr): ν = 2956s, 1571s, 1435m, 1260m, 1143m, 805s cm^{-1}. **EA** calcd. for $C_{18}H_{24}N_2$ (268.40): C 80.55, H 9.01, N 10.44; found: C 80.49, H 9.05, N 10.31.

This compound has previously been obtained as a minor side-product from the reaction of excess *t*BuLi with pyridine.[19]

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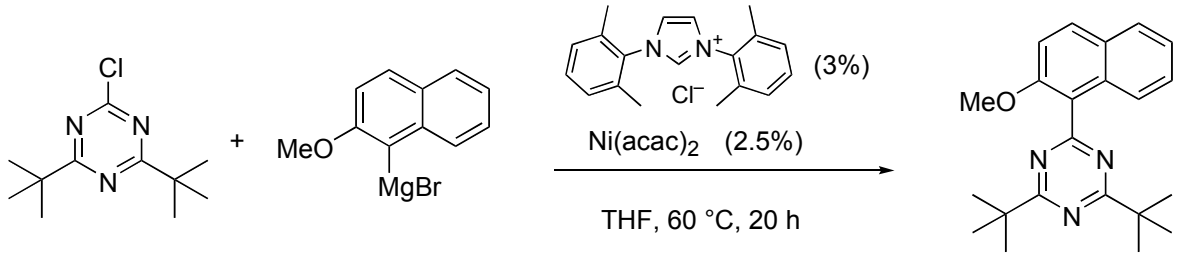
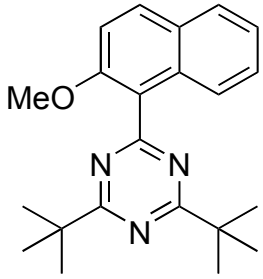
[18] a) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, M. Montanucci, *Synthesis*, **1984**, 736–738. For related procedures, see: b) J. Nasielski, A. Standaert, R. Nasielski-Hinkens, *Synth. Commun.* **1991**, *21*, 901–906. c) M. Iyoda, H. Otsuka, K. Sato, N. Nisato, M. Oda, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80–87.

[19] F. V. Scalzi, N. F. Golob, *J. Org. Chem.* **1971**, *36*, 2541–2542.

Cross-coupling of a triazine building block





4,6-Di-*tert*-butyl-2-(2-methoxy-naphth-1-yl)-1,3,5-triazine (20).[11] A mixture of 1-bromo-2-methoxynaphthalene (500 mg, 2.10 mmol), magnesium turnings (68 mg, 2.8 mmol) and iodine (ca 20 mg) in THF (10 mL) was stirred overnight at 50 °C to give the Grignard reagent, which was transferred (by syringe) into a Schlenk vessel containing 2-chloro-4,6-di-*tert*-butyl-1,3,5-triazine (410 mg, 1.80 mmol), $Ni(acac)_2$ (12 mg, 0.047 mmol, 2.5 mol-%) and IXy·HCl[12] (17 mg, 0.054 mmol, 3 mol-%). The reaction mixture was stirred for 20 h at 60 °C, then quenched by addition of NH_4Cl aq (6 mL), water (6 mL), *t*BuOMe (15 mL) and HCl (2.4 M, 1.5 mL). The aqueous phase was extracted with 2×15 mL *t*BuOMe. The combined organic phases were dried ($MgSO_4$), filtered and evaporated. Purification by CC (*t*BuOMe/hexanes = 1:30→1:20) and crystallization of the product fractions from hexanes gave large transparent crystals (223 mg). The mother liquors were chromatographed (EtOAc/hexanes = 1:60) to give a second product fraction (173 mg), total 396 mg (63%) of colorless crystalline material.

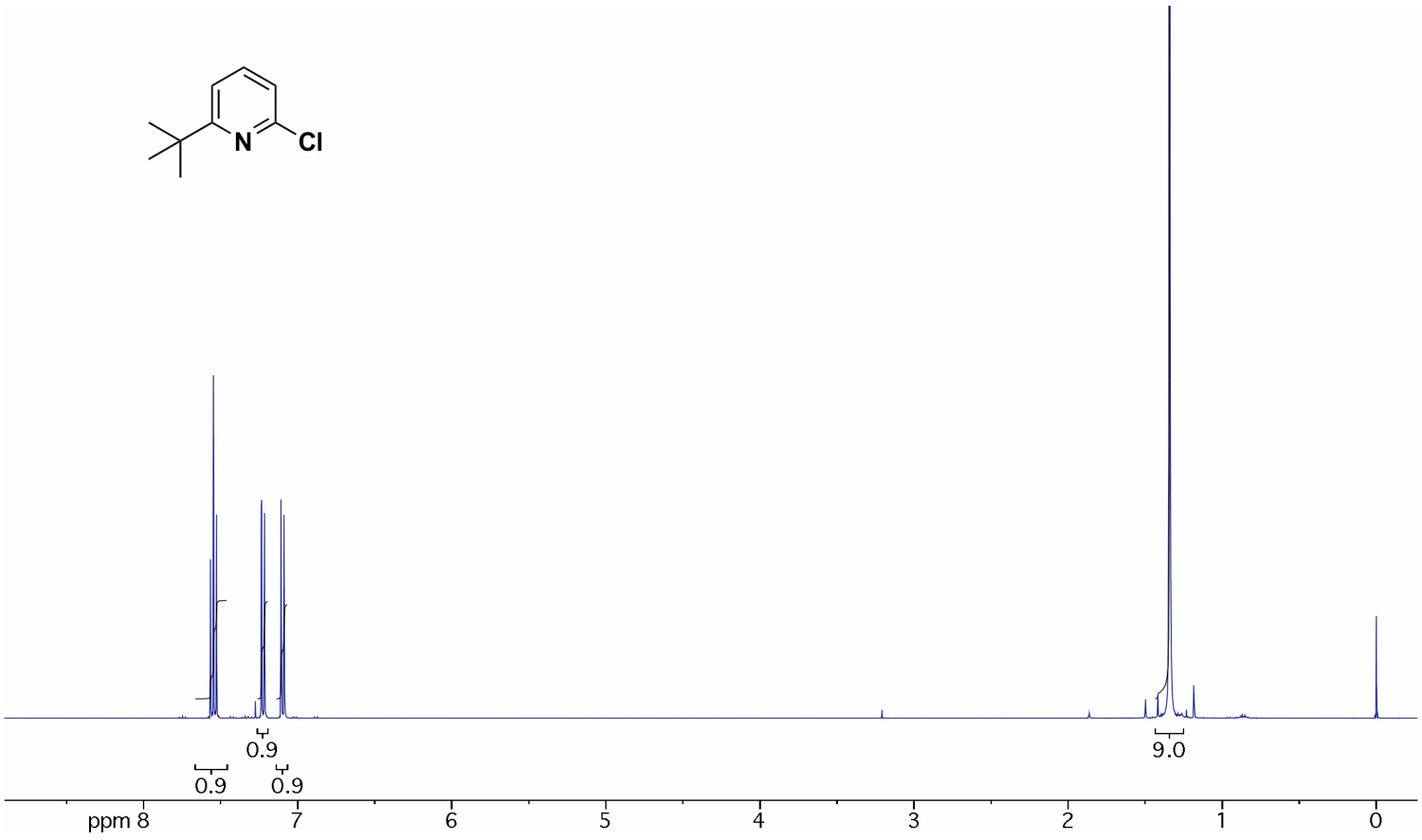
M.p.: 141–142 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.45 (s, 18 H, CH_3), 3.90 (s, 3 H, OCH_3), 7.31–7.42 (m, 3 H), 7.55–7.78 (m, 1 H), 7.80 (dd, J = 7.7, 1.7, 1 H), 7.92 (d, J = 9.2, 1 H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 29.06 (CH_3), 39.62 (C), 57.80 (CH_3), 115.23 (CH), 123.07 (CH), 123.94 (C), 124.37 (CH), 126.98 (CH), 128.12 (CH), 129.40 (C), 131.23 (CH), 132.38 (C), 155.46 (C), 172.22 (C), 184.86 (C) ppm. **IR** (KBr): ν = 2965s, 1521s, 1462m, 1258s, 1076m cm^{-1}. **MS** (GC/MS, EI): m/z (%) = 349 (100) M^+, 334 (80), 292 (44), 251 (42), 184 (62). **EA** calcd. for $C_{22}H_{27}N_3O$ (349.47): C 75.61, H 7.79, N 12.02; found: C 75.66, H 7.88, N 11.95.

8. Copies of NMR Spectra

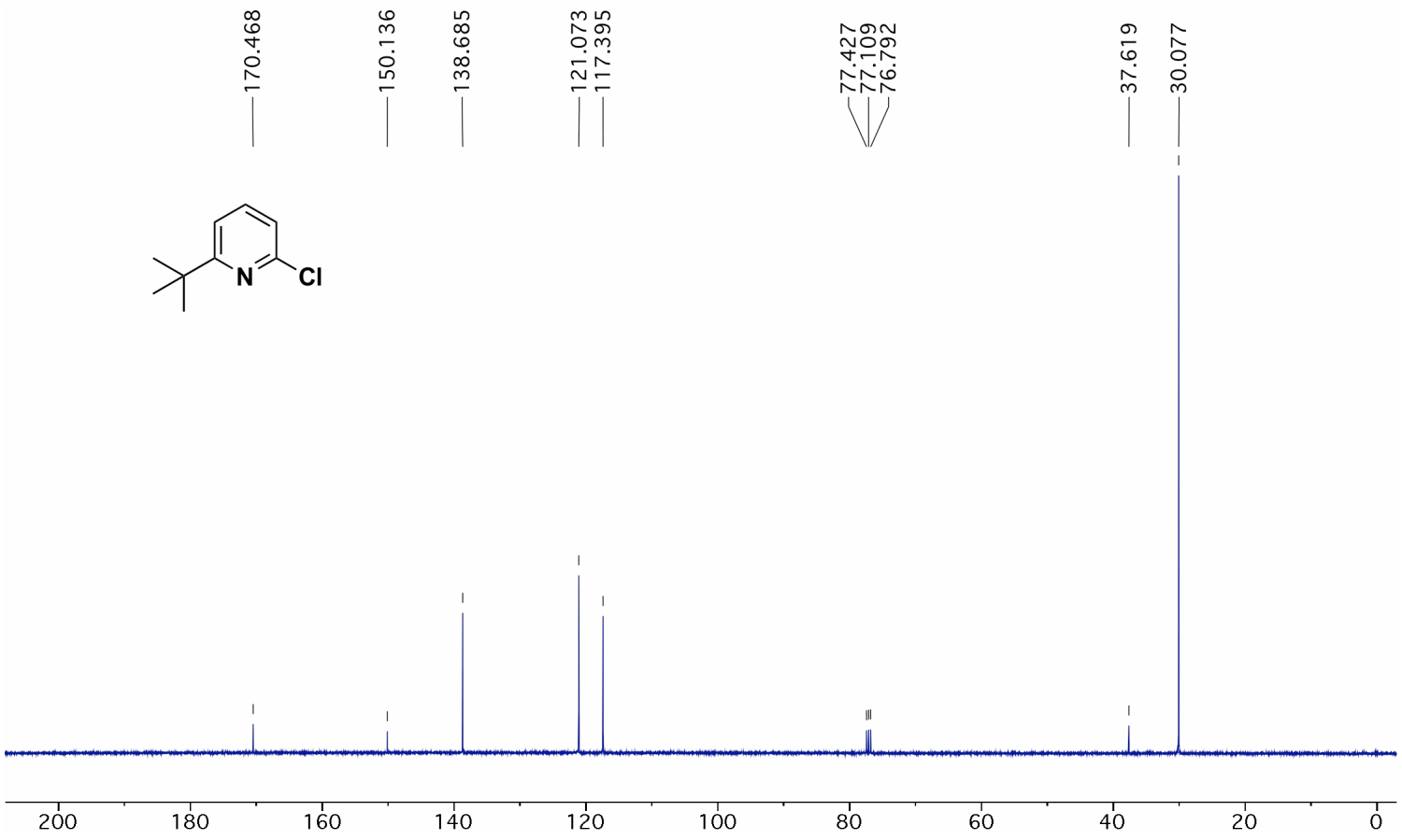
NMR spectra were handled using the iNMR 2.5.3 program of Giuseppe Balacco.

Spectra are presented in increasing order of the compound number.

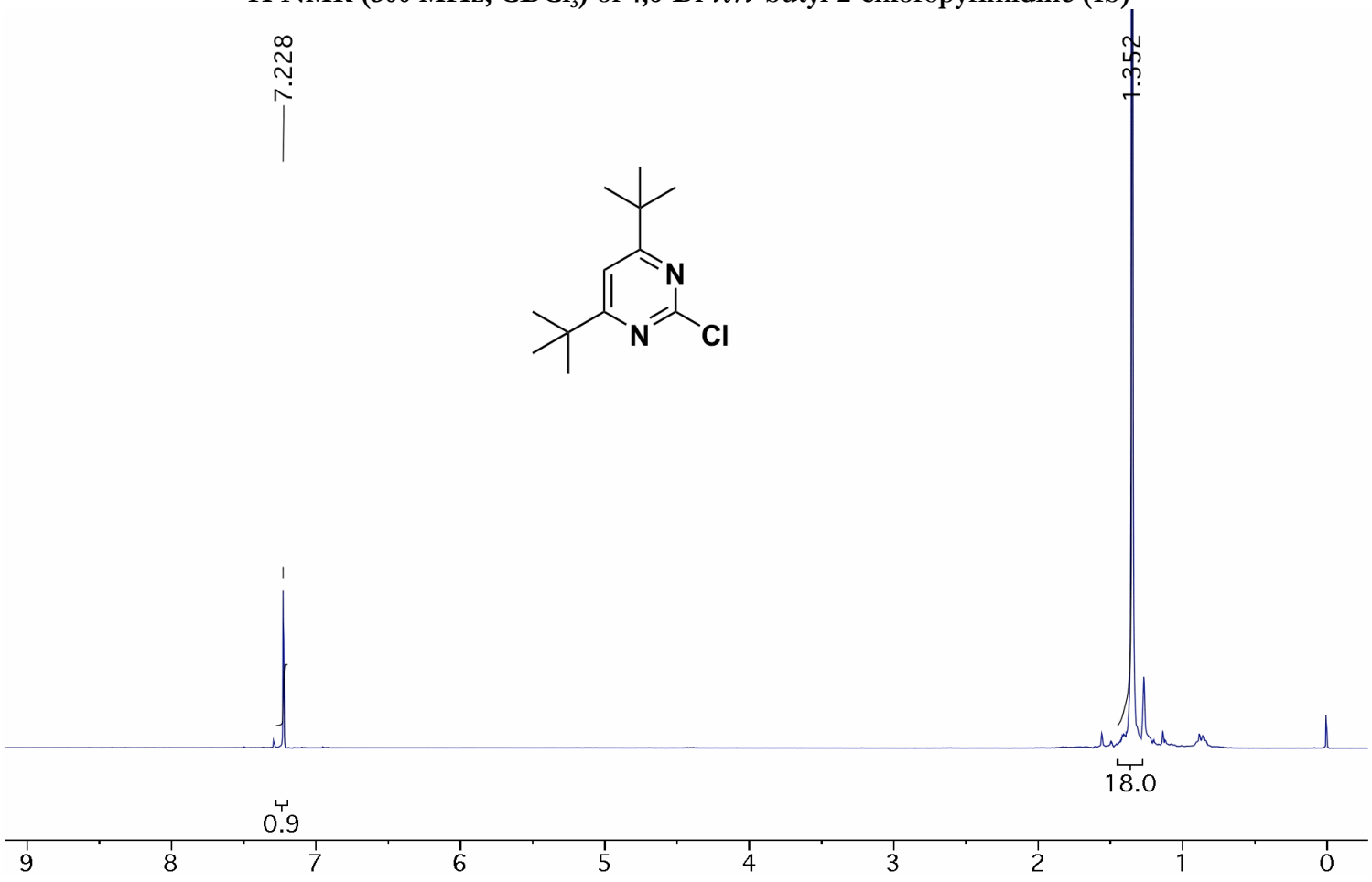
^{1}H NMR (400 MHz, $CDCl_3$) of 2-*tert*-Butyl-6-chloropyridine (1a)



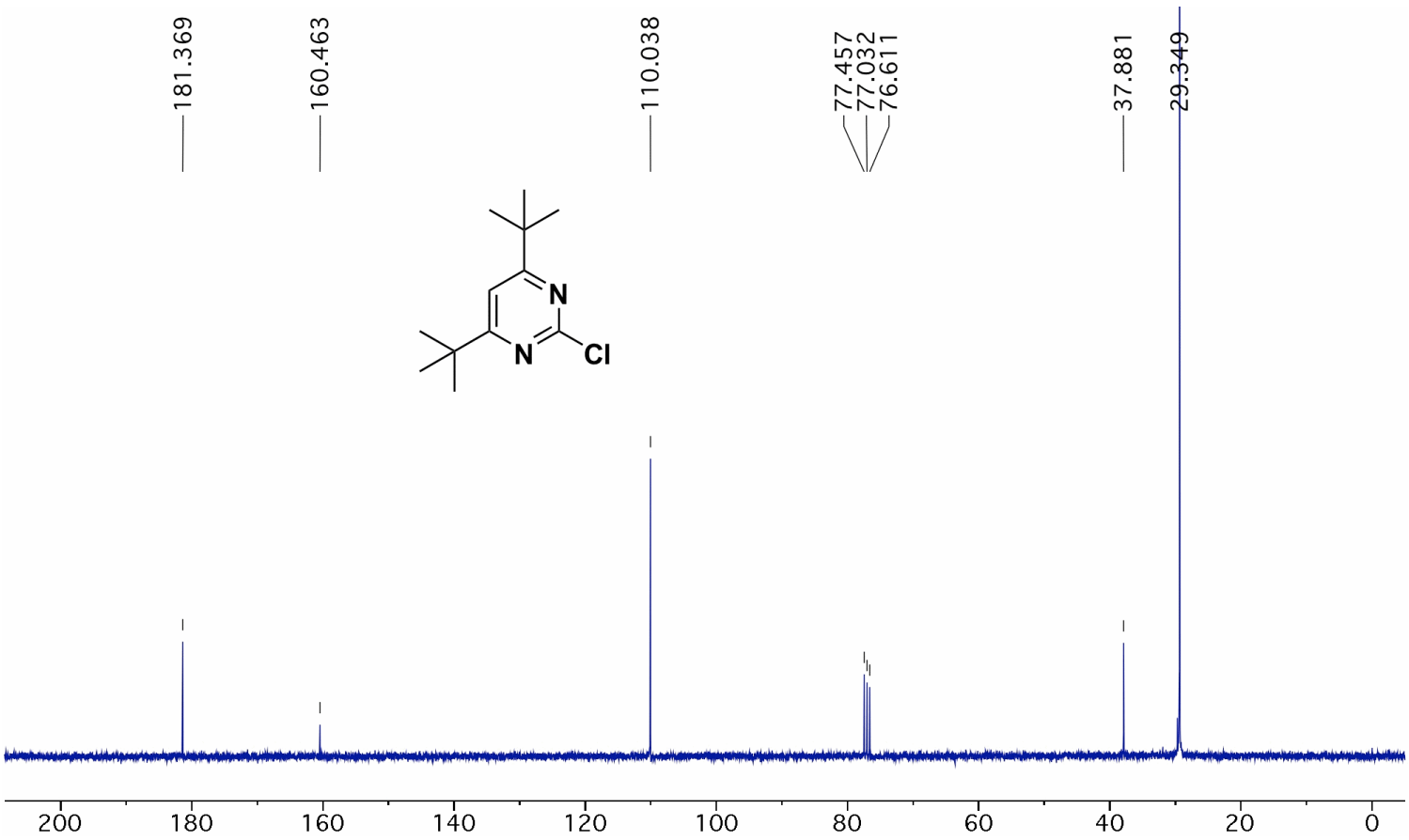
^{13}C NMR (100 MHz, $CDCl_3$) of 2-*tert*-Butyl-6-chloropyridine (1a)



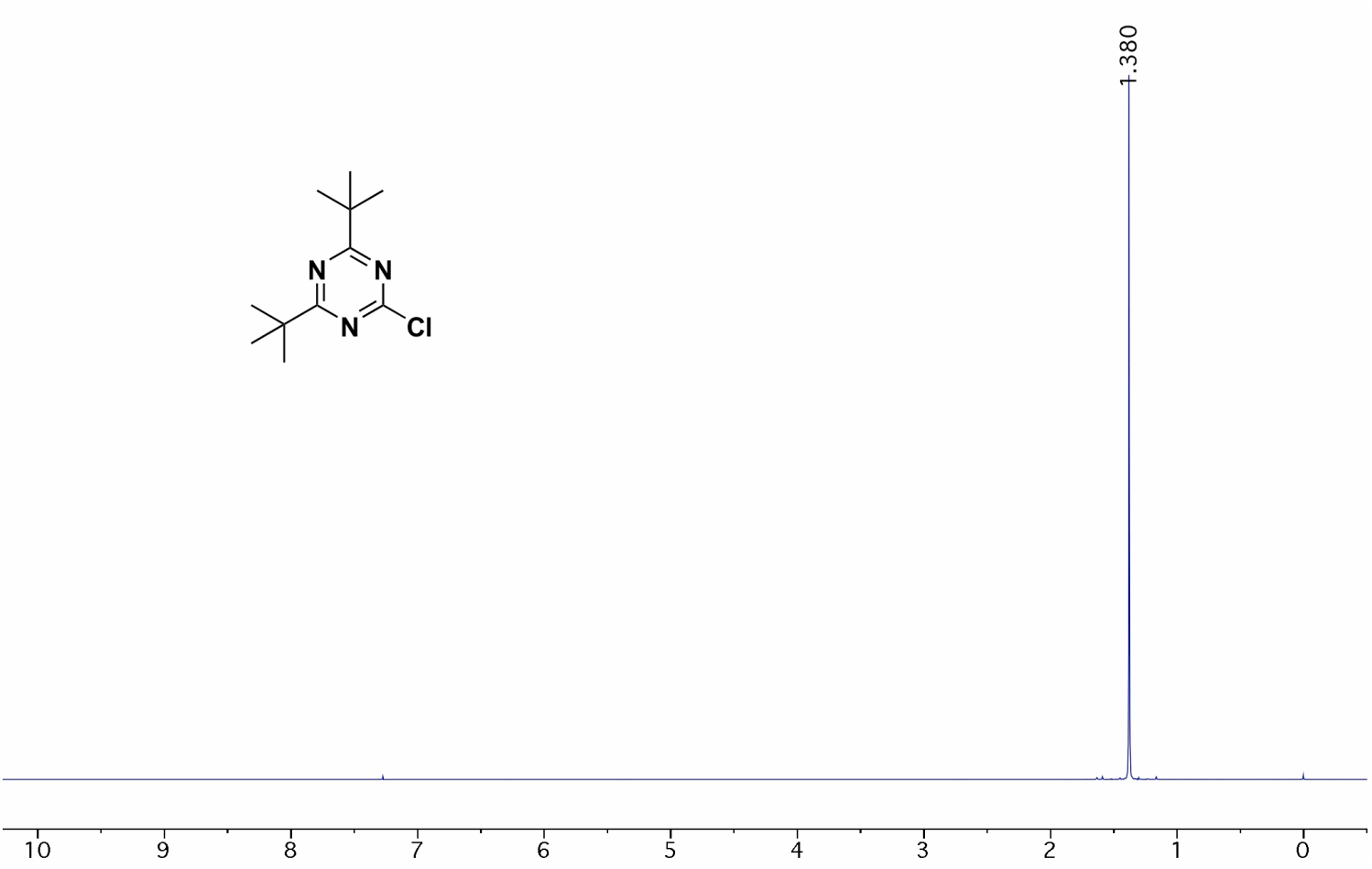
^{1}H NMR (300 MHz, $CDCl_3$) of 4,6-Di-*tert*-butyl-2-chloropyrimidine (1b)



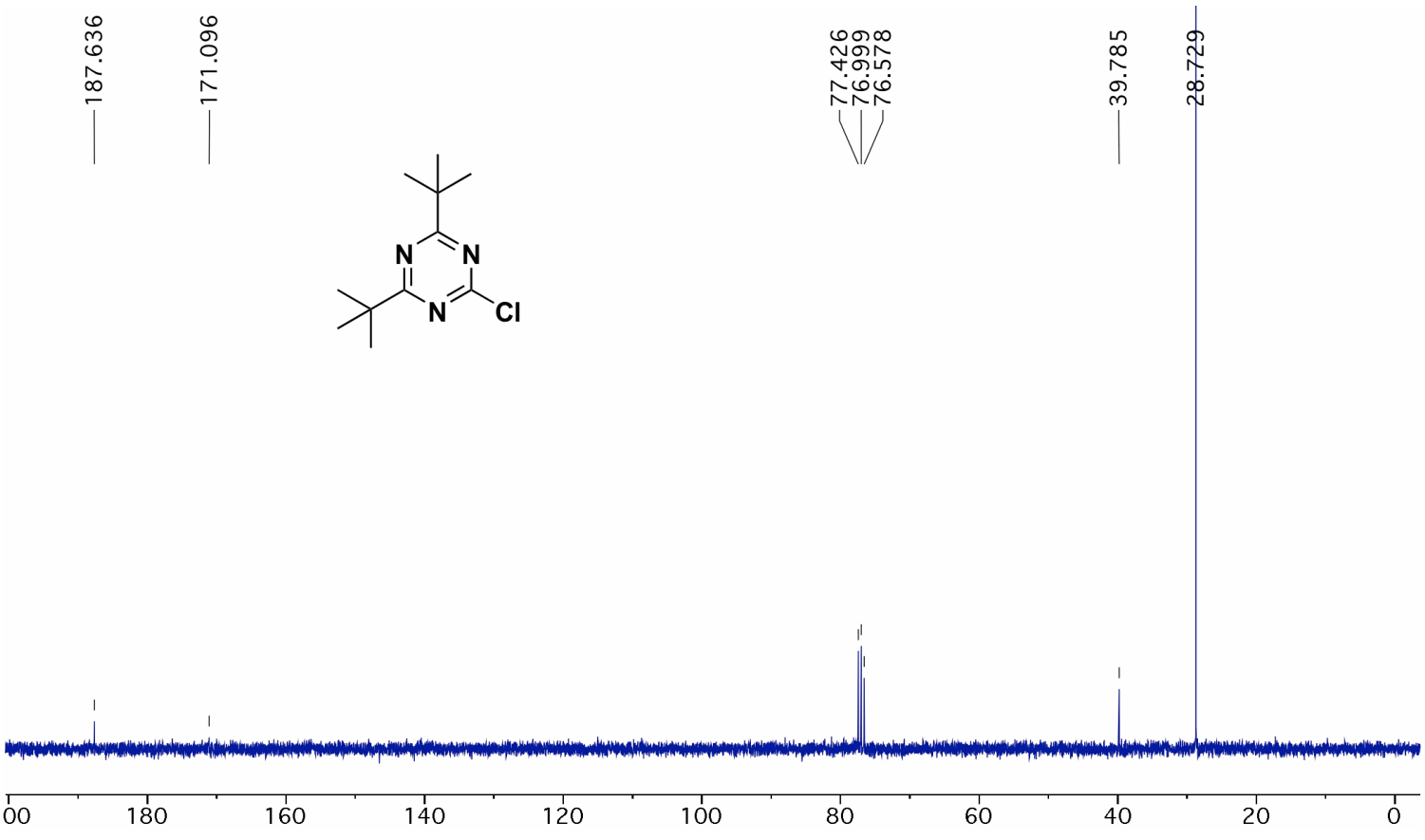
^{13}C NMR (76 MHz, $CDCl_3$) of 4,6-Di-*tert*-butyl-2-chloropyrimidine (1b)



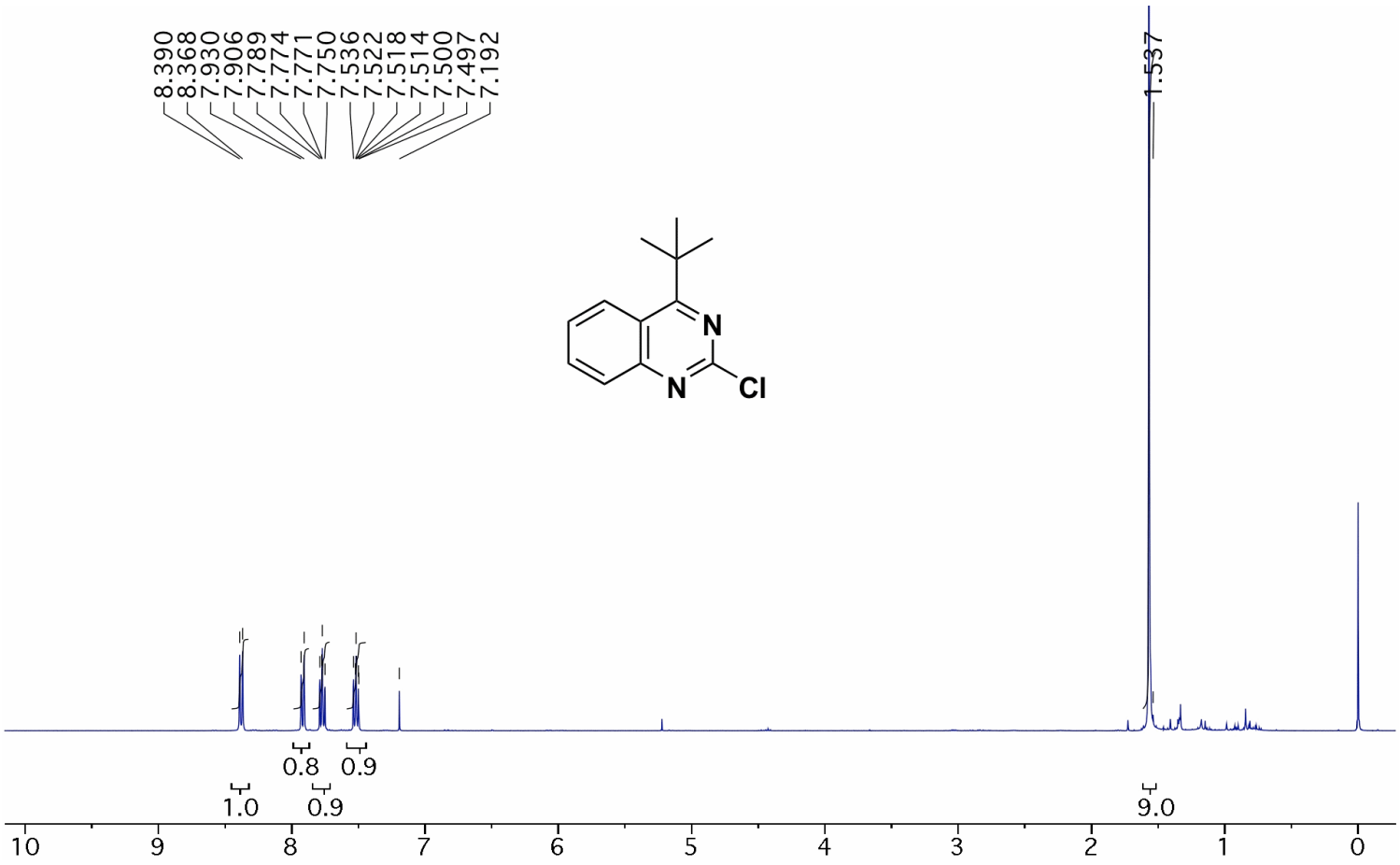
^{1}H NMR (300 MHz, $CDCl_3$) of 2-Chloro-4,6-di-*tert*-butyl-1,3,5-triazine (1c)



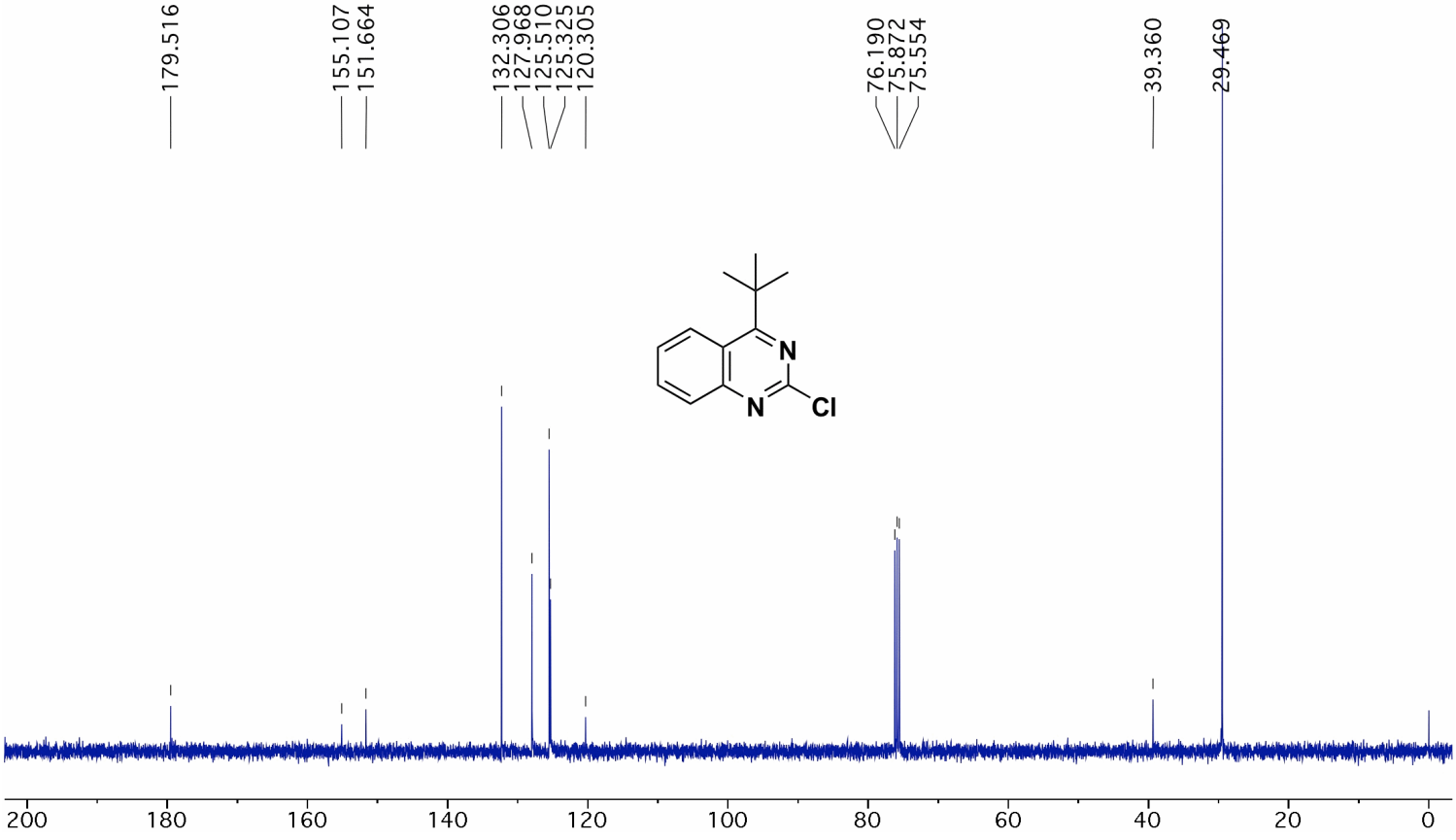
^{13}C NMR (76 MHz, $CDCl_3$) of 2-Chloro-4,6-di-*tert*-butyl-1,3,5-triazine (1c)



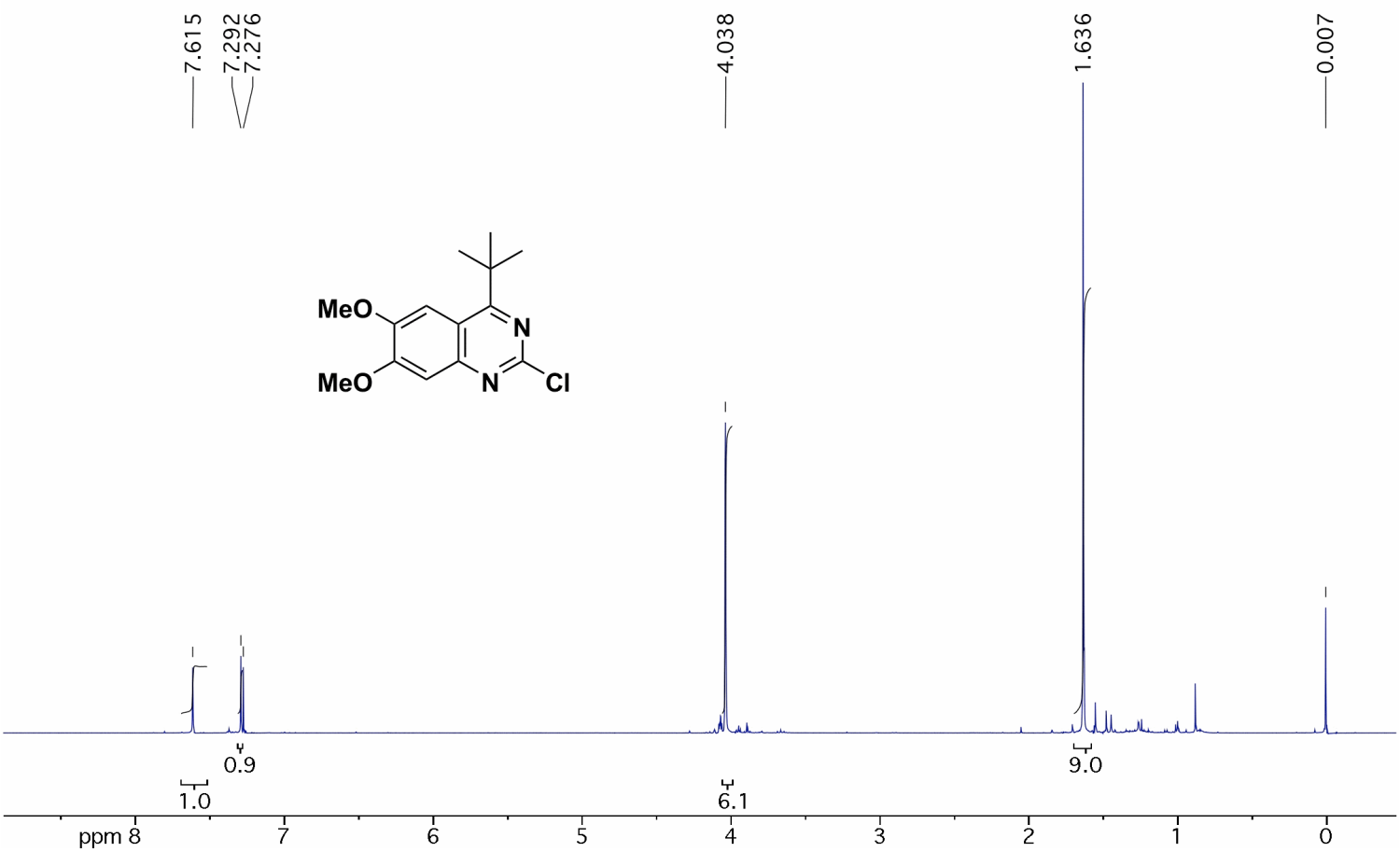
^{1}H NMR (400 MHz, $CDCl_3$) of 4-*tert*-Butyl-2-chloroquinazoline (1d)



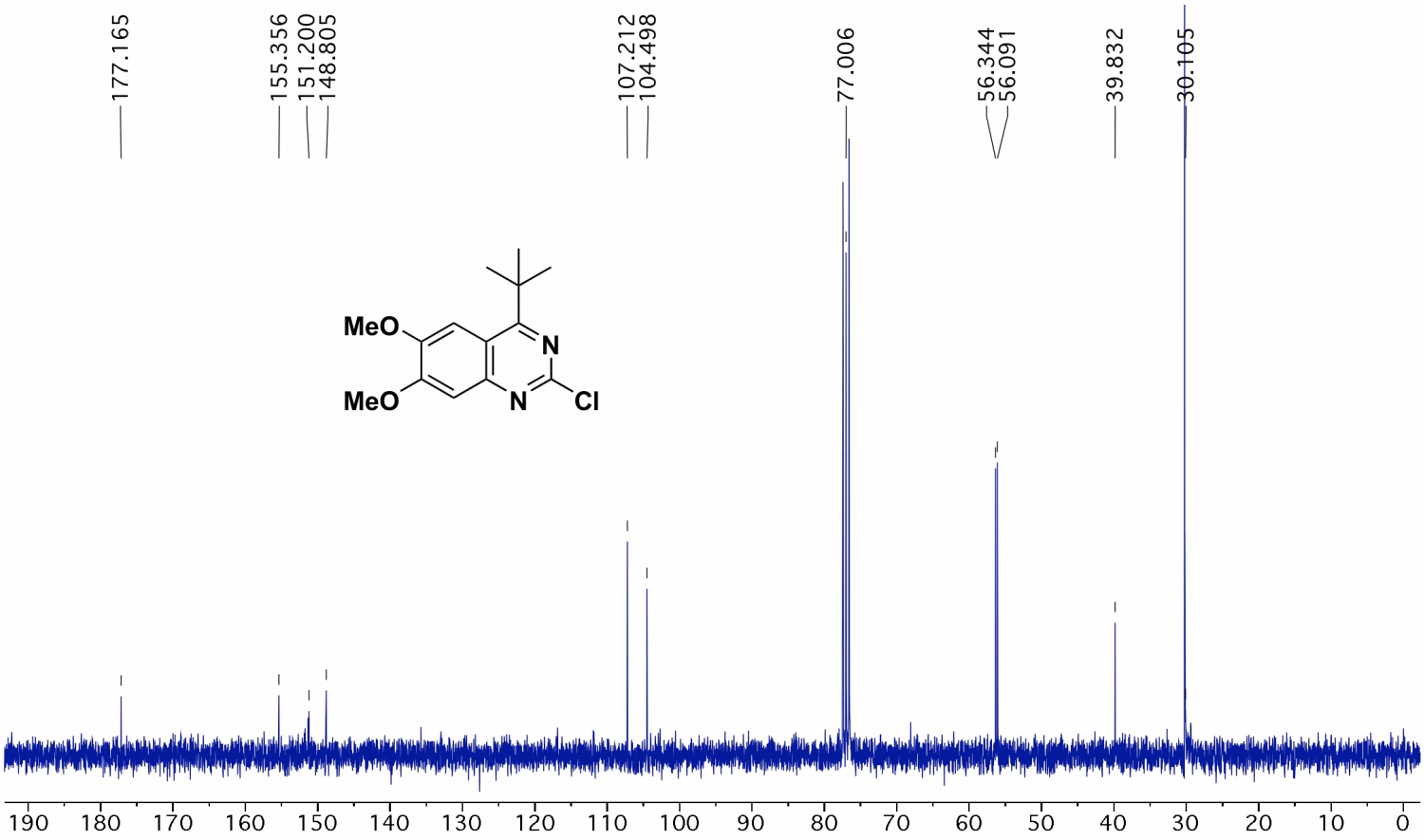
^{13}C NMR (100 MHz, $CDCl_3$) of 4-*tert*-Butyl-2-chloroquinazoline (1d)



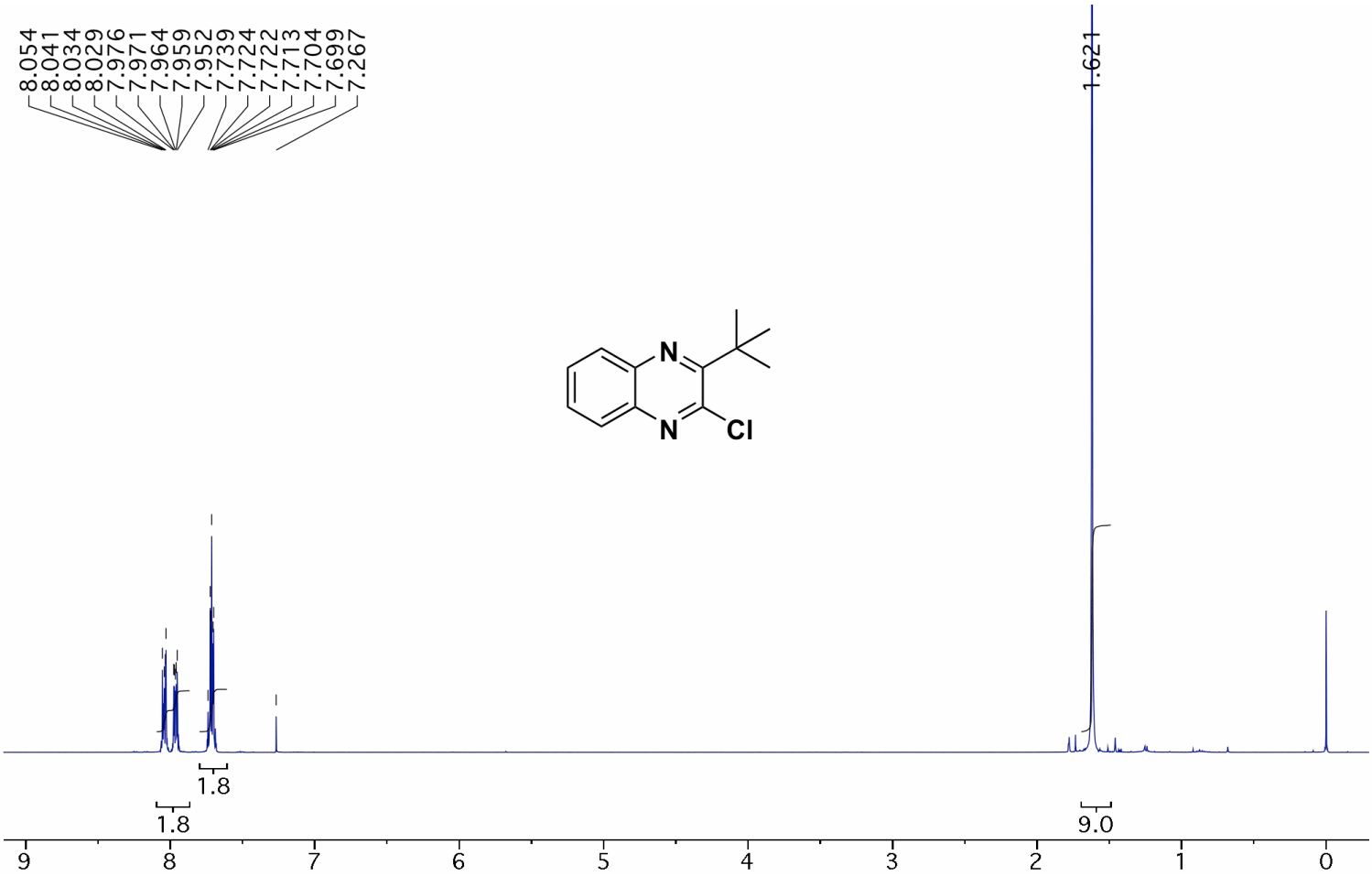
^{1}H NMR (300 MHz, $CDCl_3$) of 4-*tert*-Butyl-2-chloro-6,7-dimethoxyquinazoline (1e)



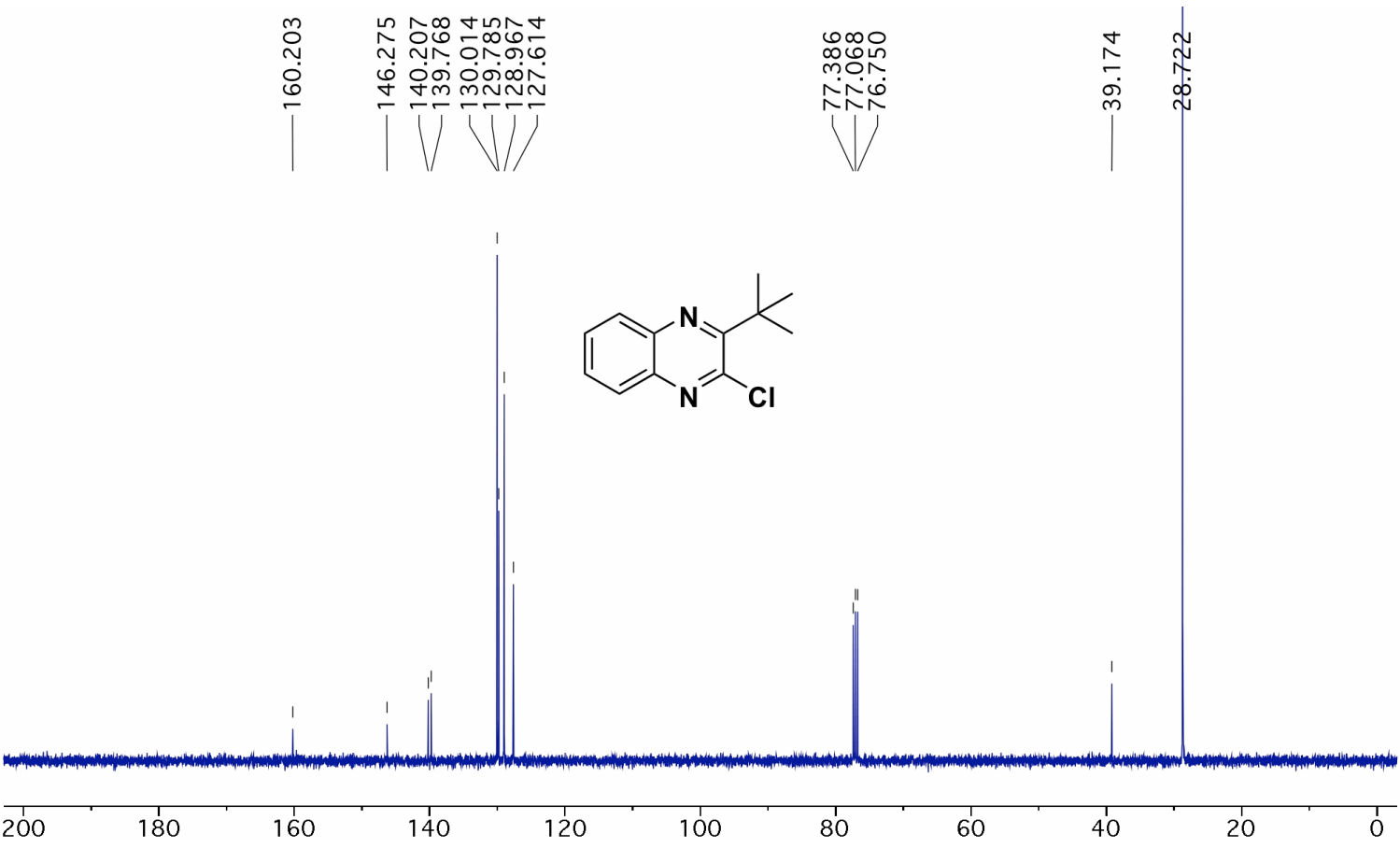
^{13}C NMR (76 MHz, $CDCl_3$) of 4-*tert*-Butyl-2-chloro-6,7-dimethoxyquinazoline (1e)



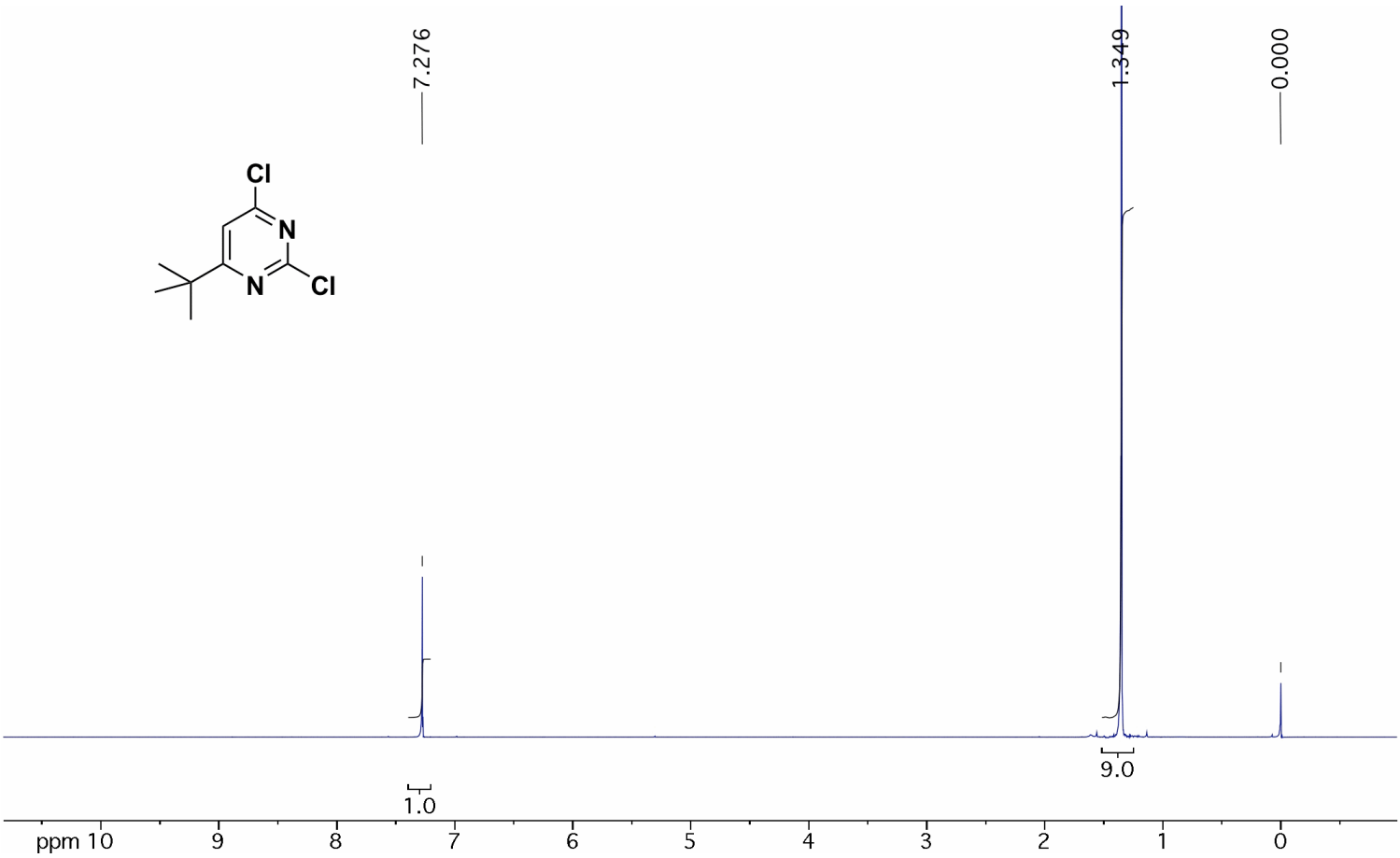
^{1}H NMR (400 MHz, $CDCl_3$) of 3-*tert*-Butyl-2-chloro-quinoxaline (1f)



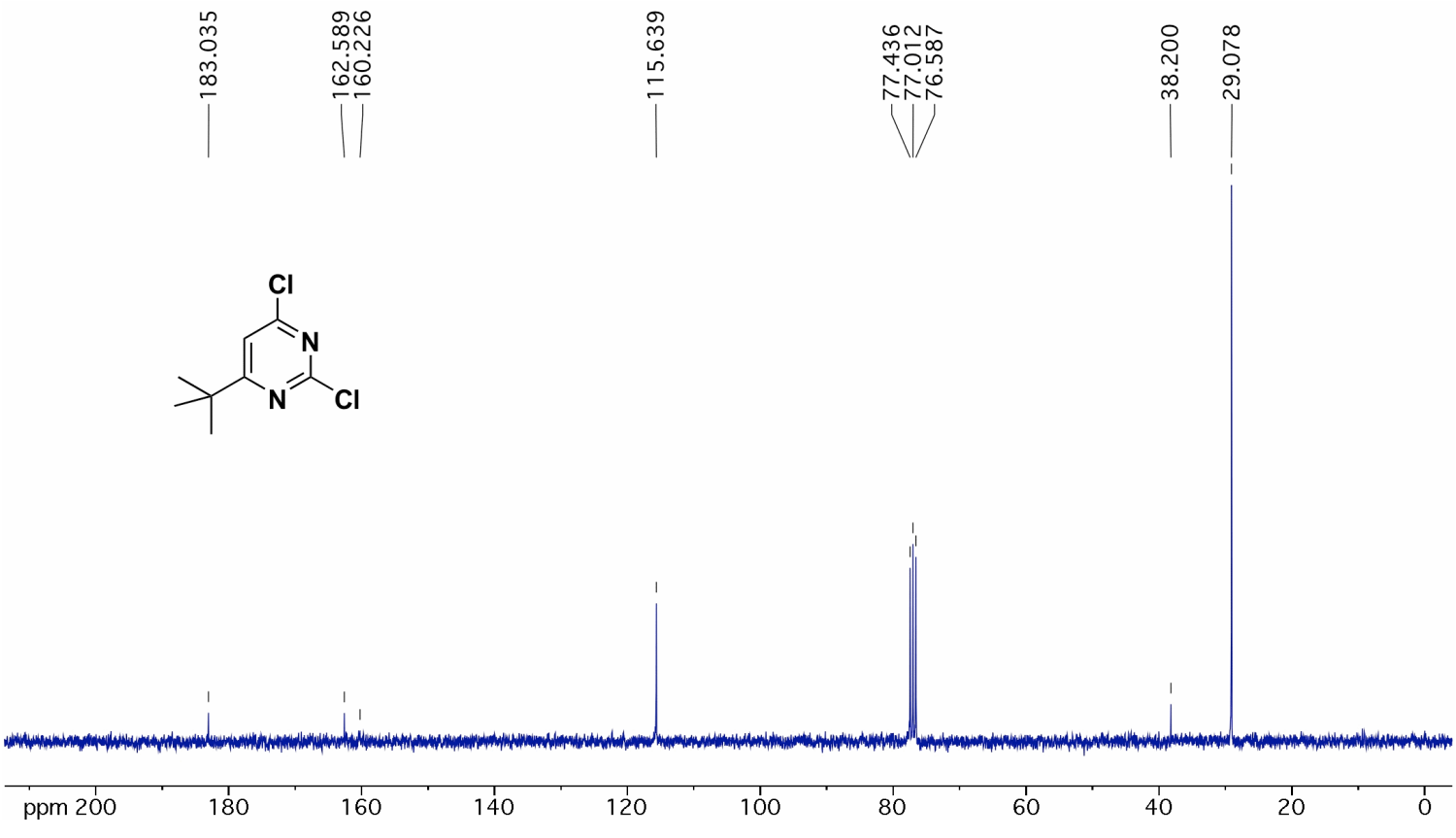
^{13}C NMR (100 MHz, $CDCl_3$) of 3-*tert*-Butyl-2-chloro-quinoxaline (1f)



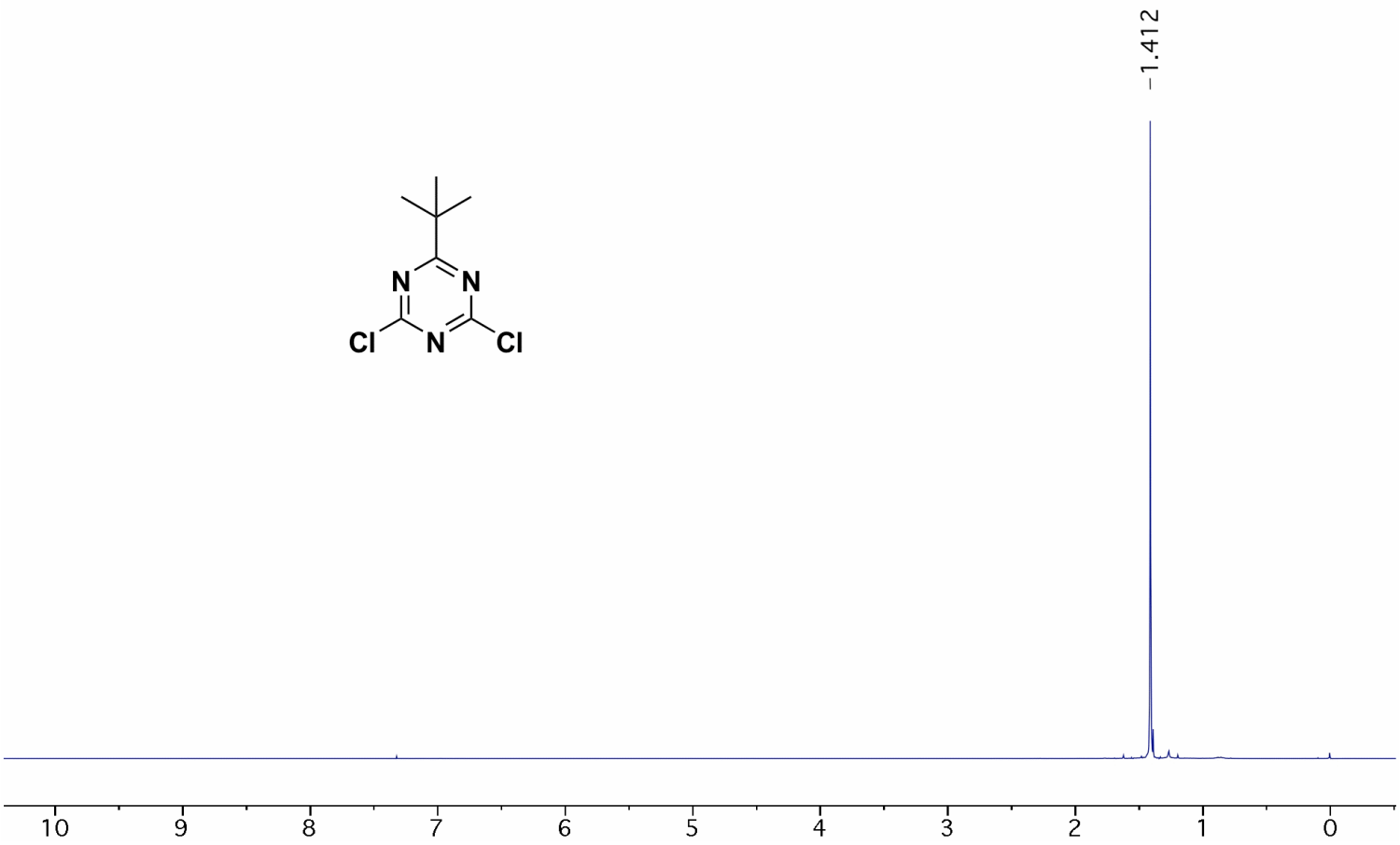
^{1}H NMR (300 MHz, $CDCl_3$) of 4-*tert*-Butyl-2,6-dichloropyrimidine (3b)



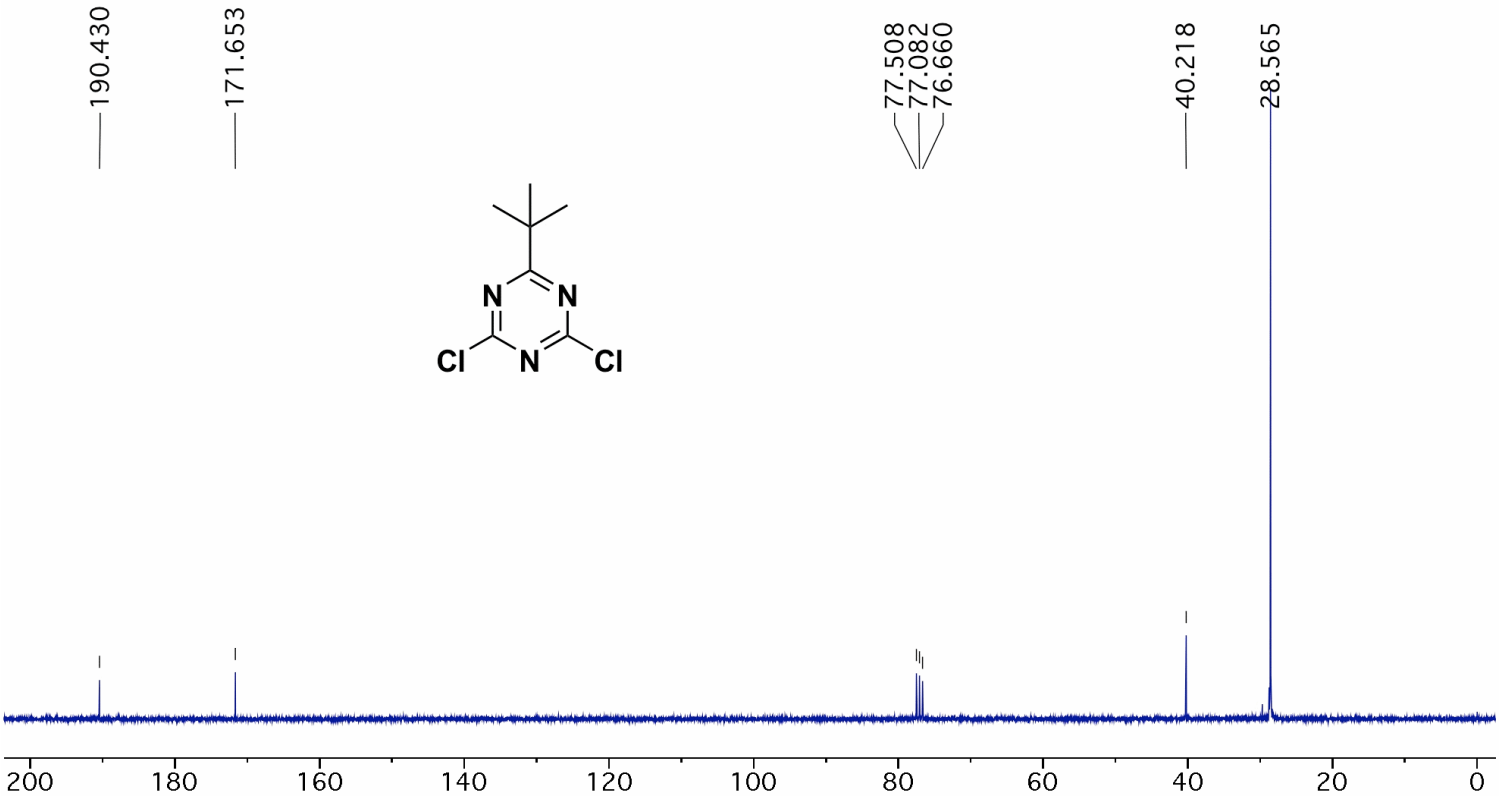
^{13}C NMR (76 MHz, $CDCl_3$) of 4-*tert*-Butyl-2,6-dichloropyrimidine (3b)



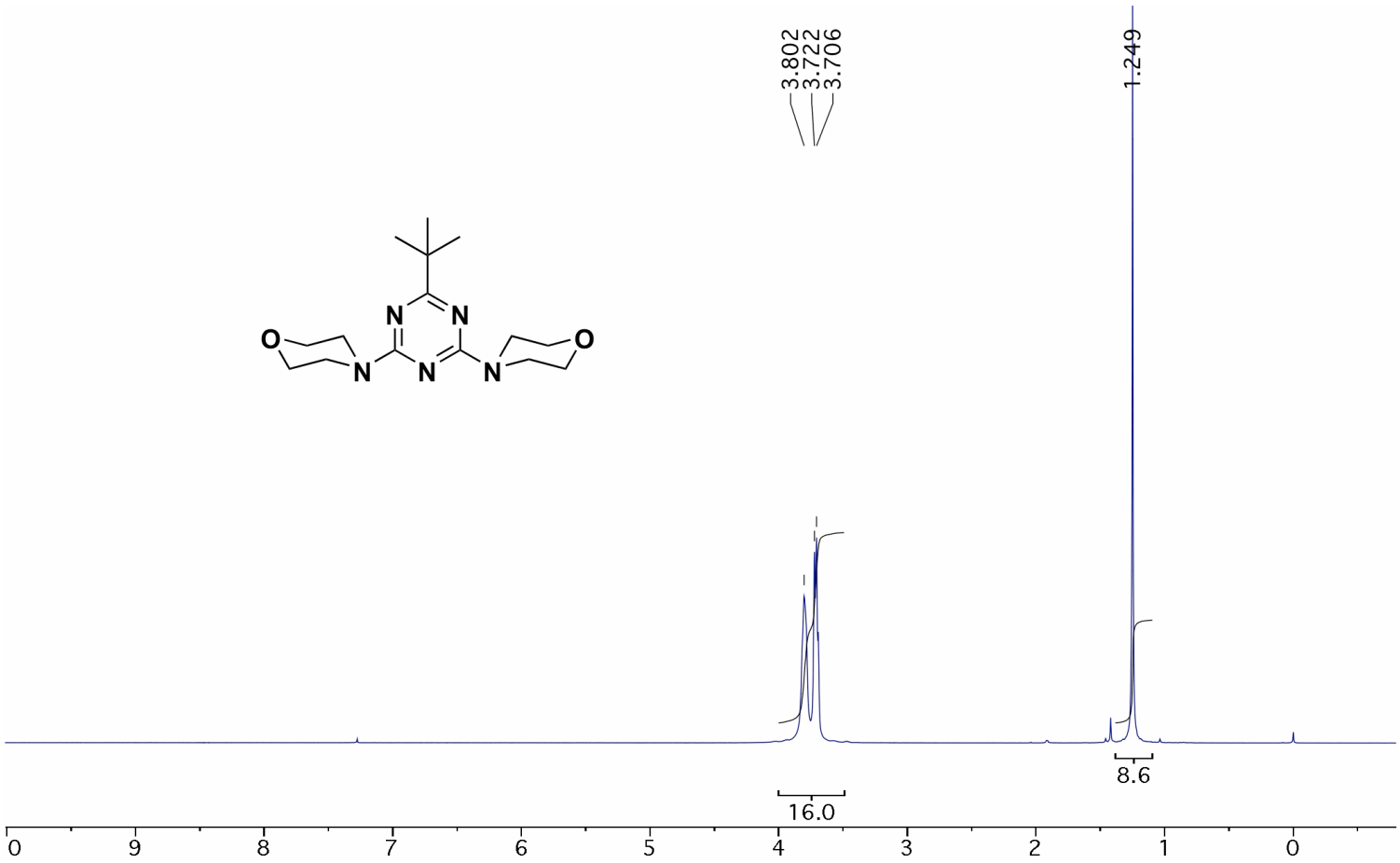
^{1}H NMR (300 MHz, $CDCl_3$) of 4-*tert*-Butyl-2,6-dichloro-1,3,5-triazine (3c)



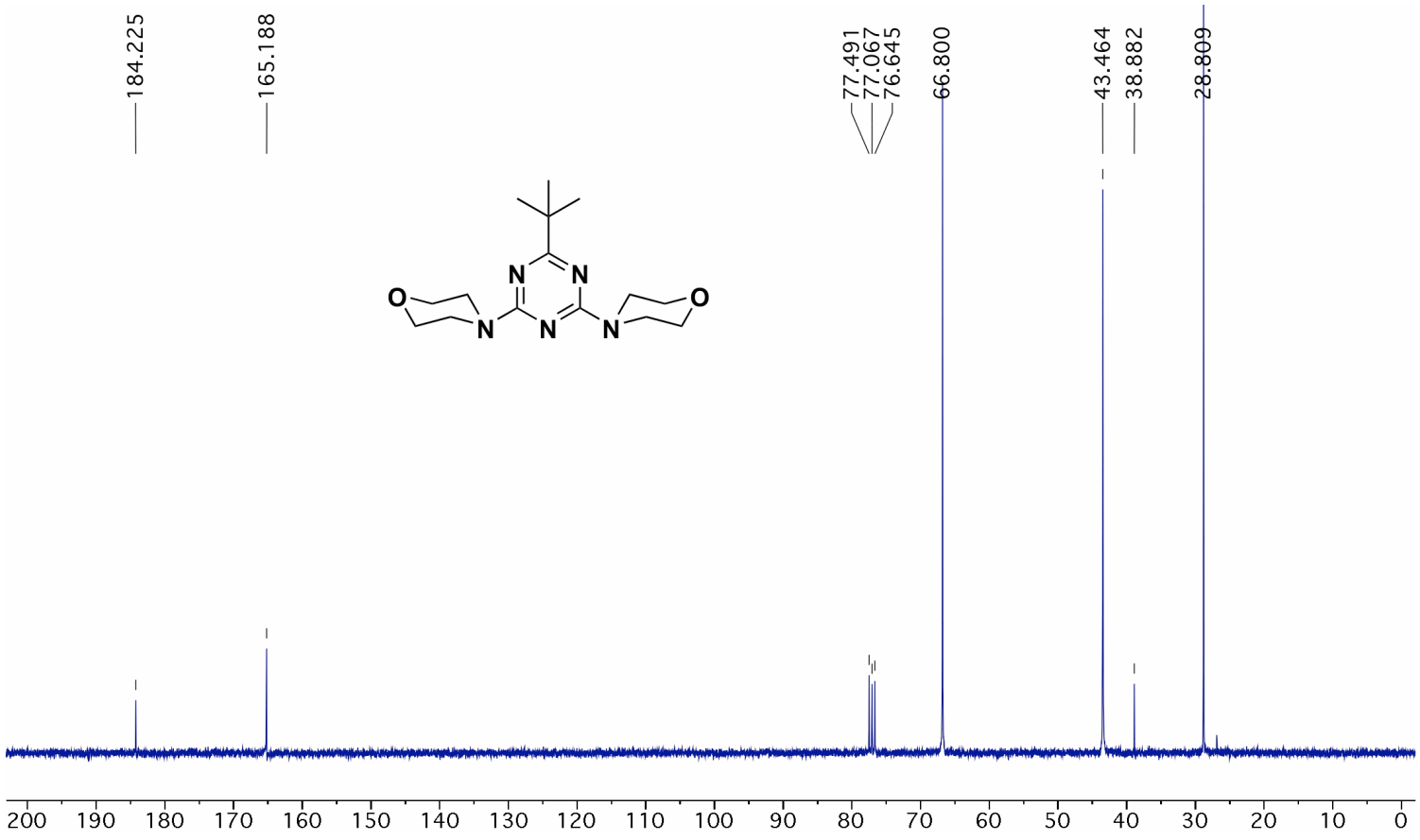
^{13}C NMR (76 MHz, $CDCl_3$) of 4-*tert*-Butyl-2,6-dichloro-1,3,5-triazine (3c)



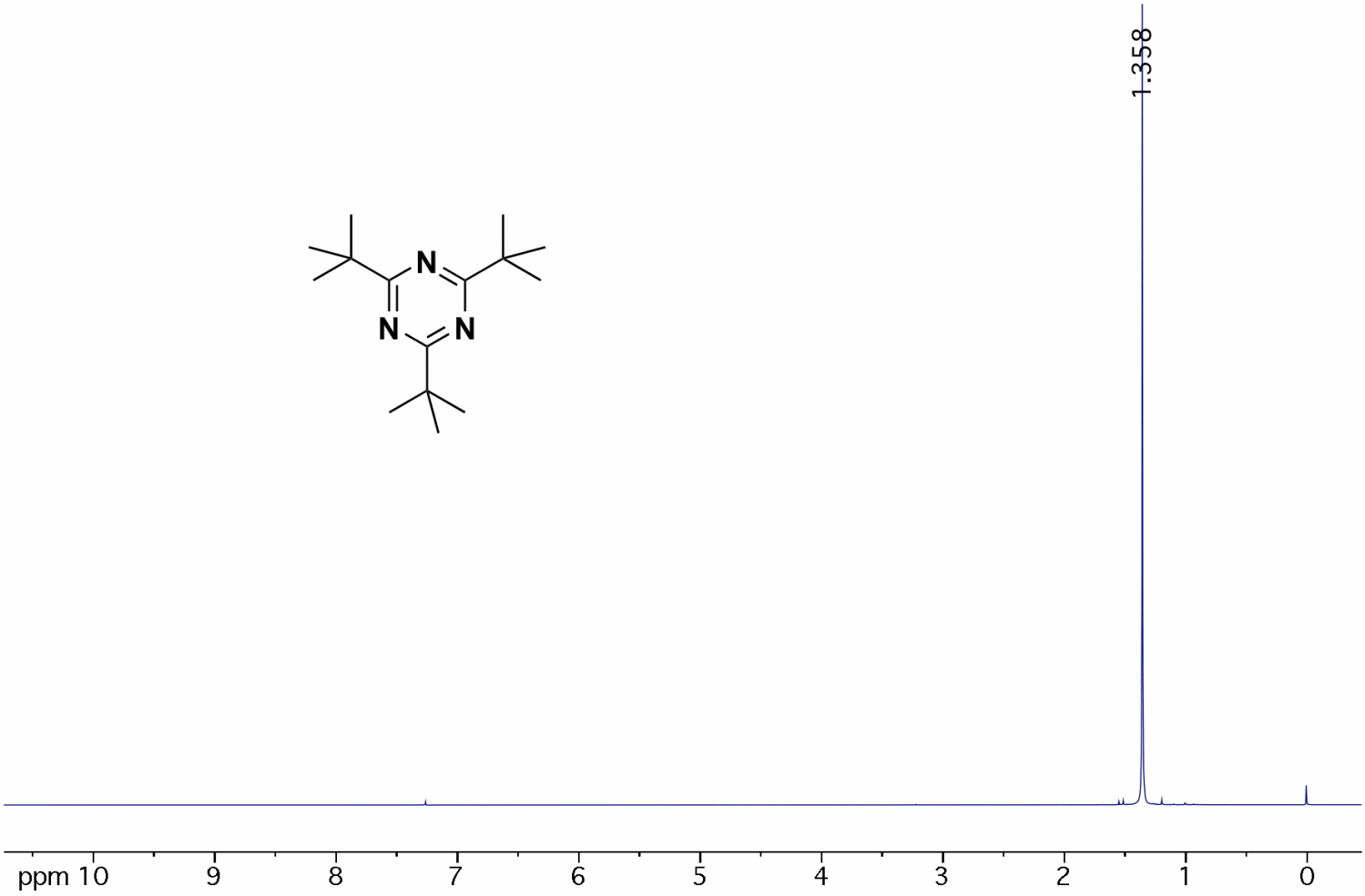
^{1}H NMR (300 MHz, $CDCl_3$) of 2-*tert*-Butyl-4,6-dimorpholino-1,3,5-triazine (4c)



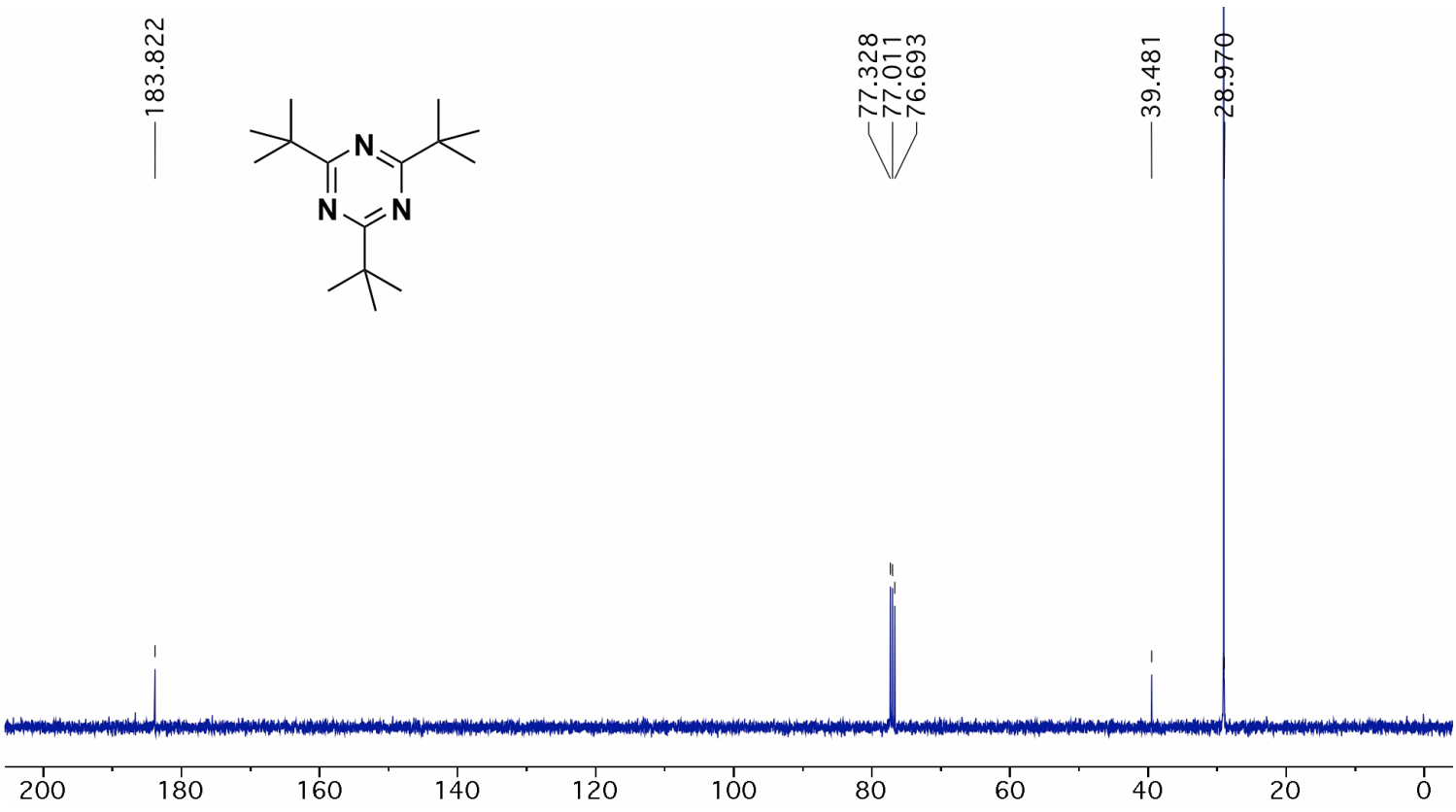
^{13}C NMR (76 MHz, $CDCl_3$) of 2-*tert*-Butyl-4,6-dimorpholino-1,3,5-triazine (4c)



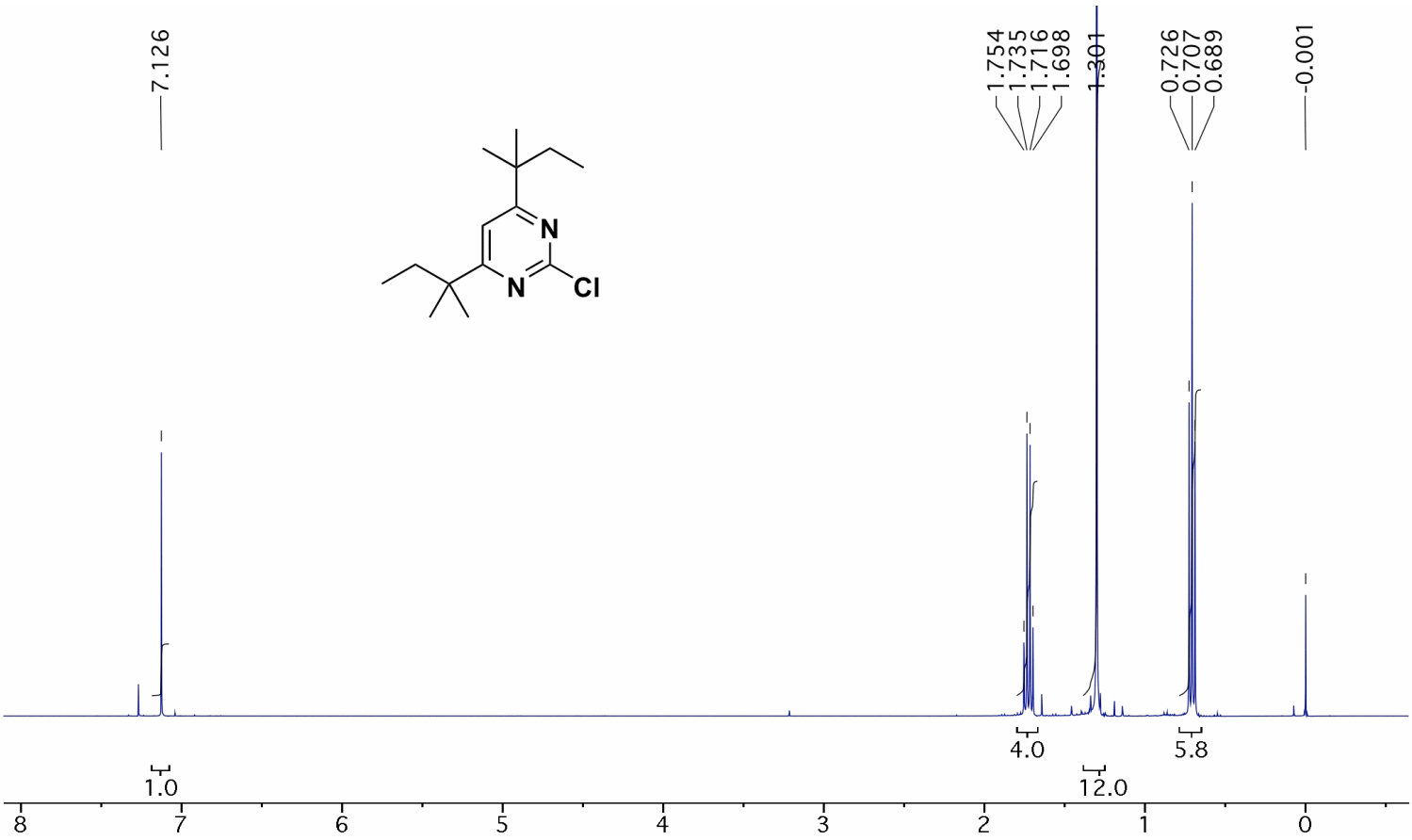
^{1}H NMR (400 MHz, $CDCl_3$) of 2,4,6-Tri-*tert*-butyl-1,3,5-triazine (5c)



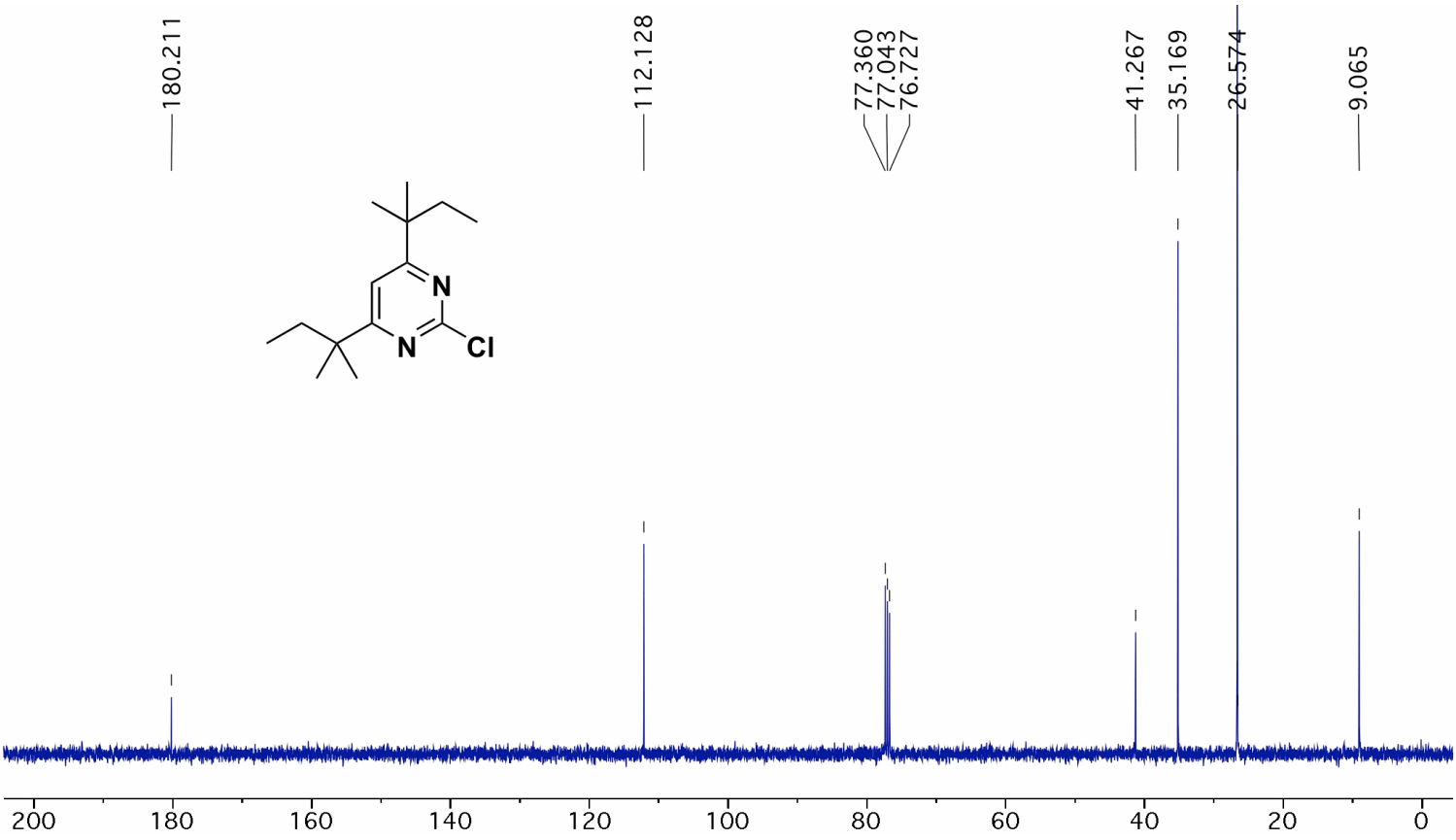
^{13}C NMR (100 MHz, $CDCl_3$) of 2,4,6-Tri-*tert*-butyl-1,3,5-triazine (5c)



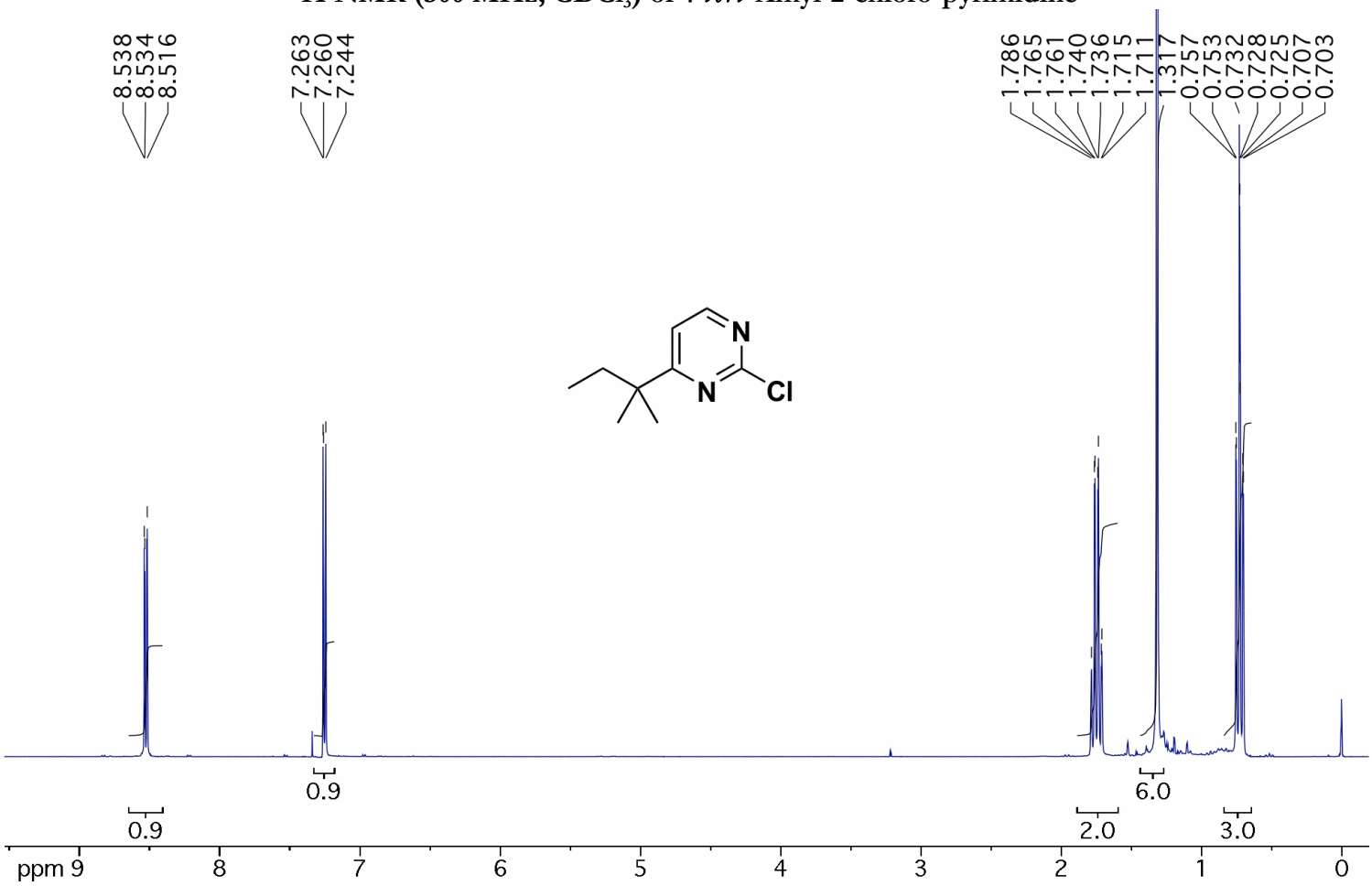
^{1}H NMR (400 MHz, $CDCl_3$) of 4,6-Di-*tert*-amyl-2-chloro-pyrimidine (6b)



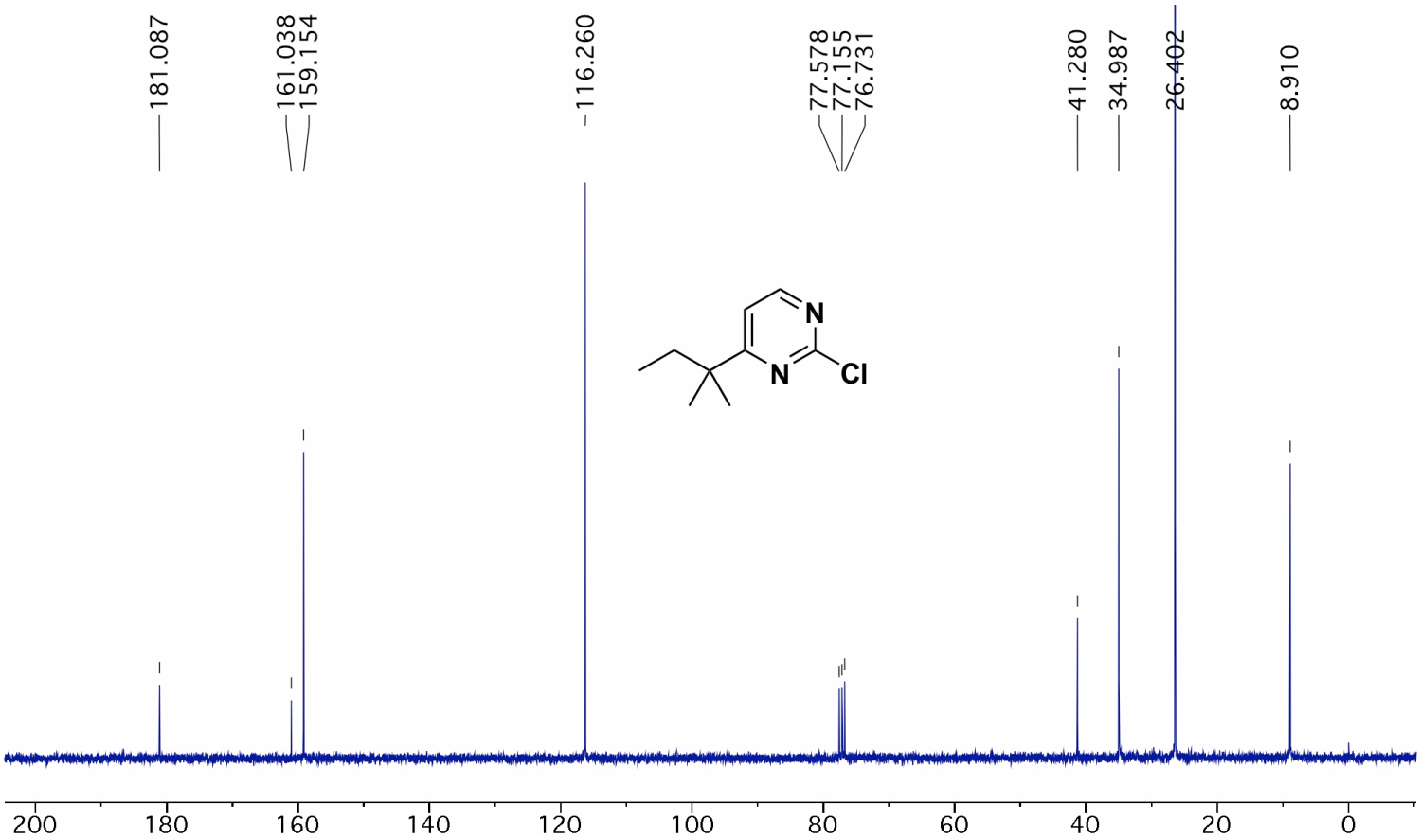
^{13}C NMR (100 MHz, $CDCl_3$) of 4,6-Di-*tert*-amyl-2-chloro-pyrimidine (6b)



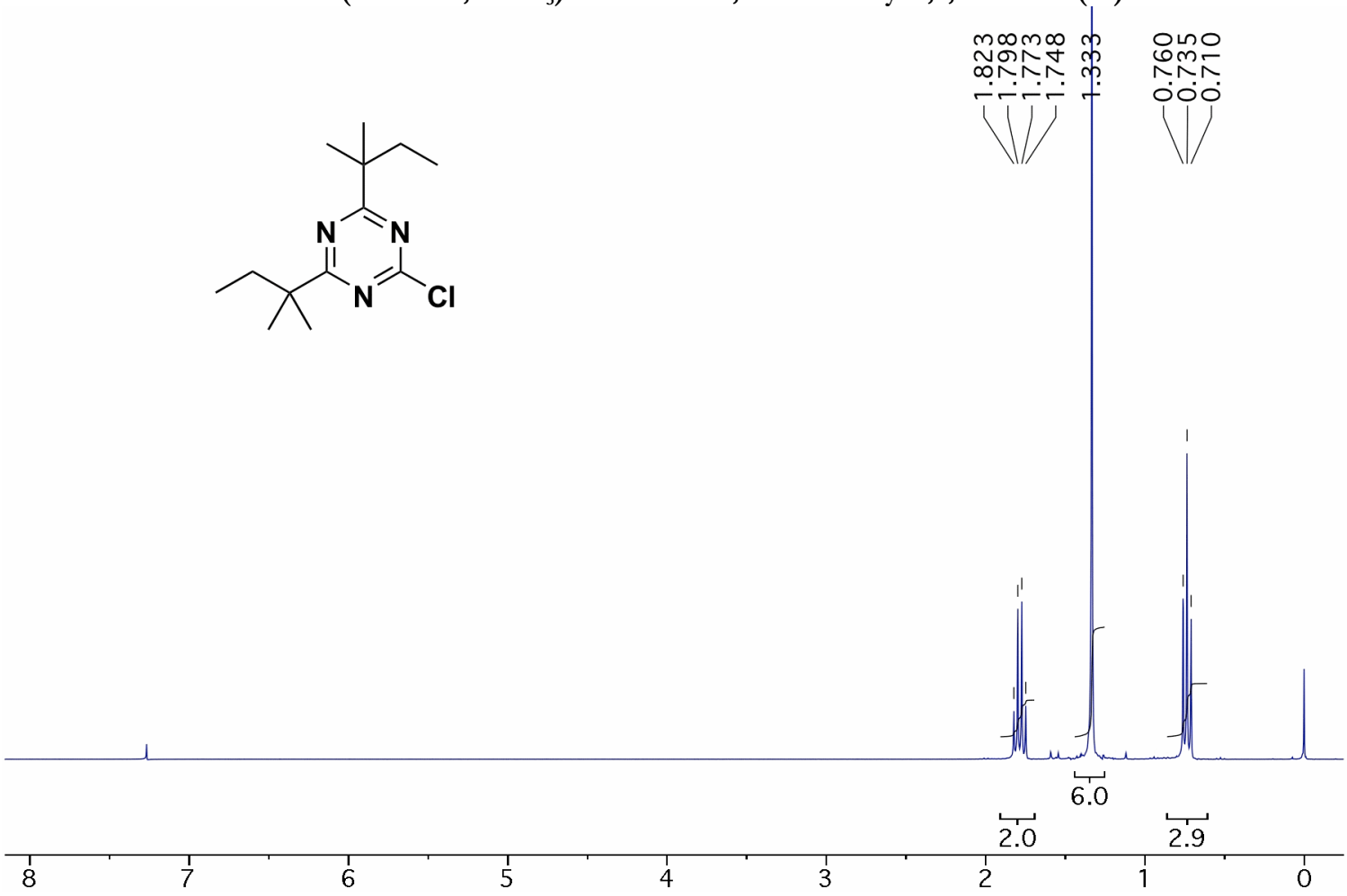
^{1}H NMR (300 MHz, $CDCl_3$) of 4-*tert*-Amyl-2-chloro-pyrimidine



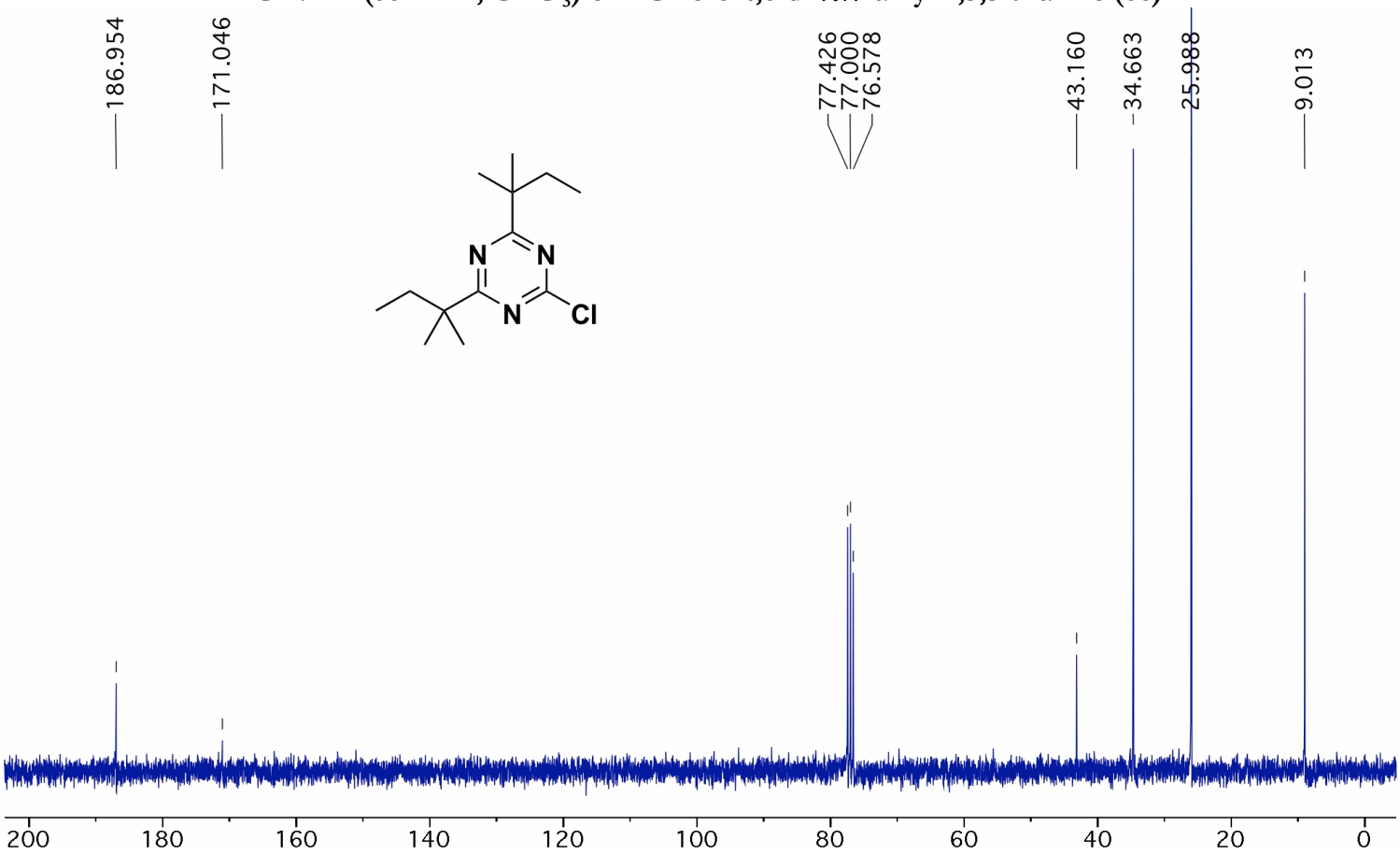
^{13}C NMR (76 MHz, $CDCl_3$) of 4-*tert*-Amyl-2-chloro-pyrimidine



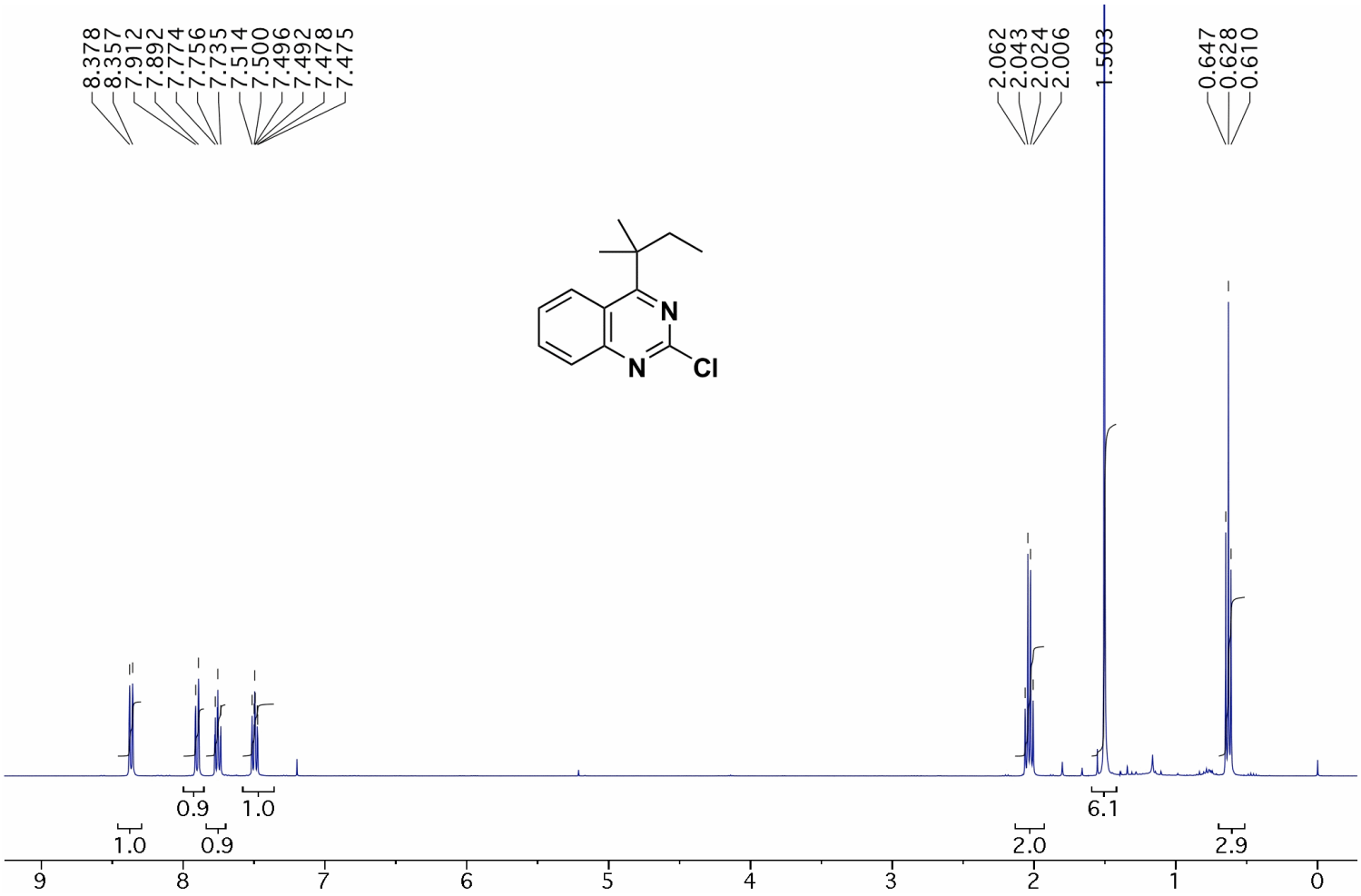
^{1}H NMR (300 MHz, $CDCl_3$) of 2-Chloro-4,6-di-*tert*-amyl-1,3,5-triazine (6c)



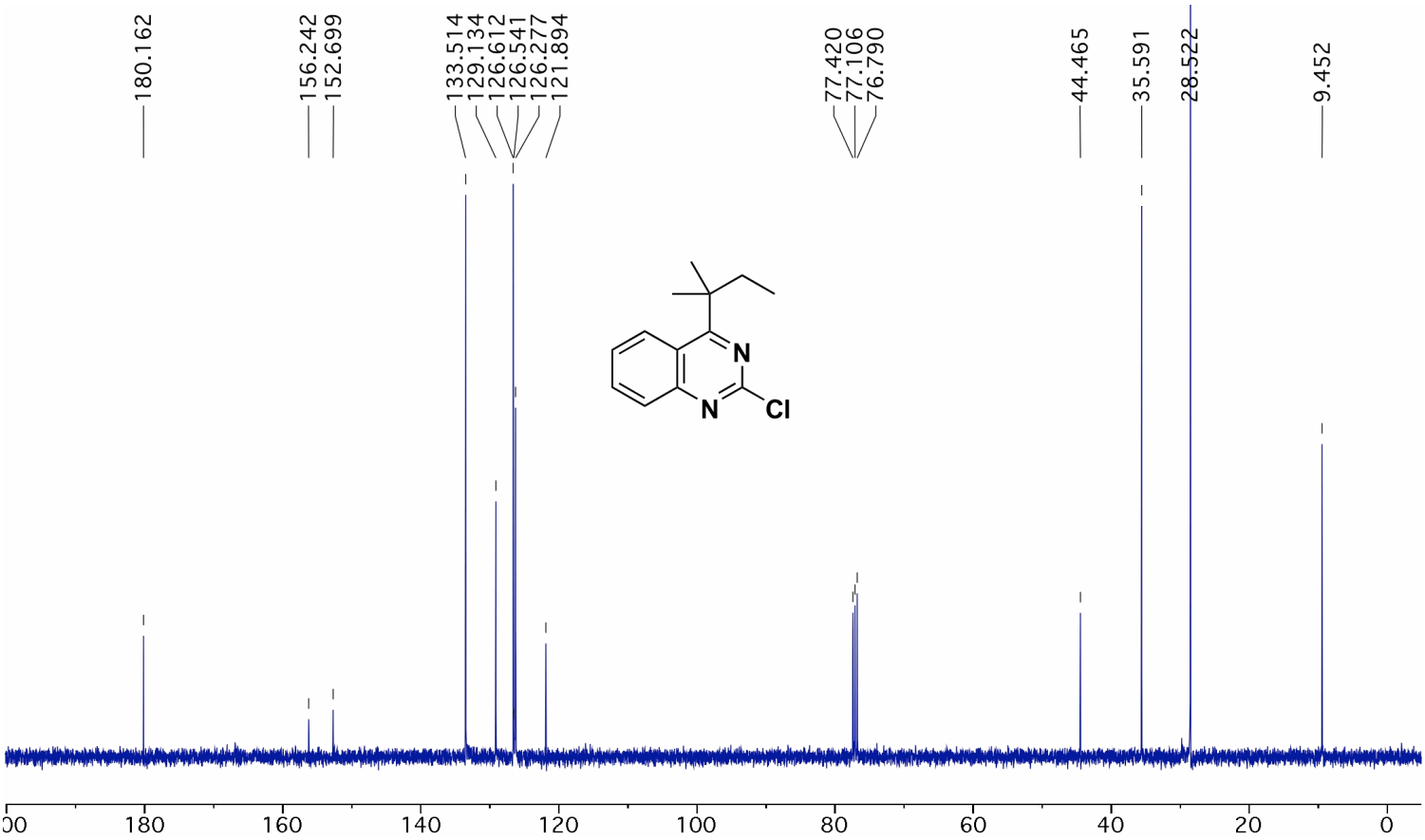
^{13}C NMR (76 MHz, $CDCl_3$) of 2-Chloro-4,6-di-*tert*-amyl-1,3,5-triazine (6c)



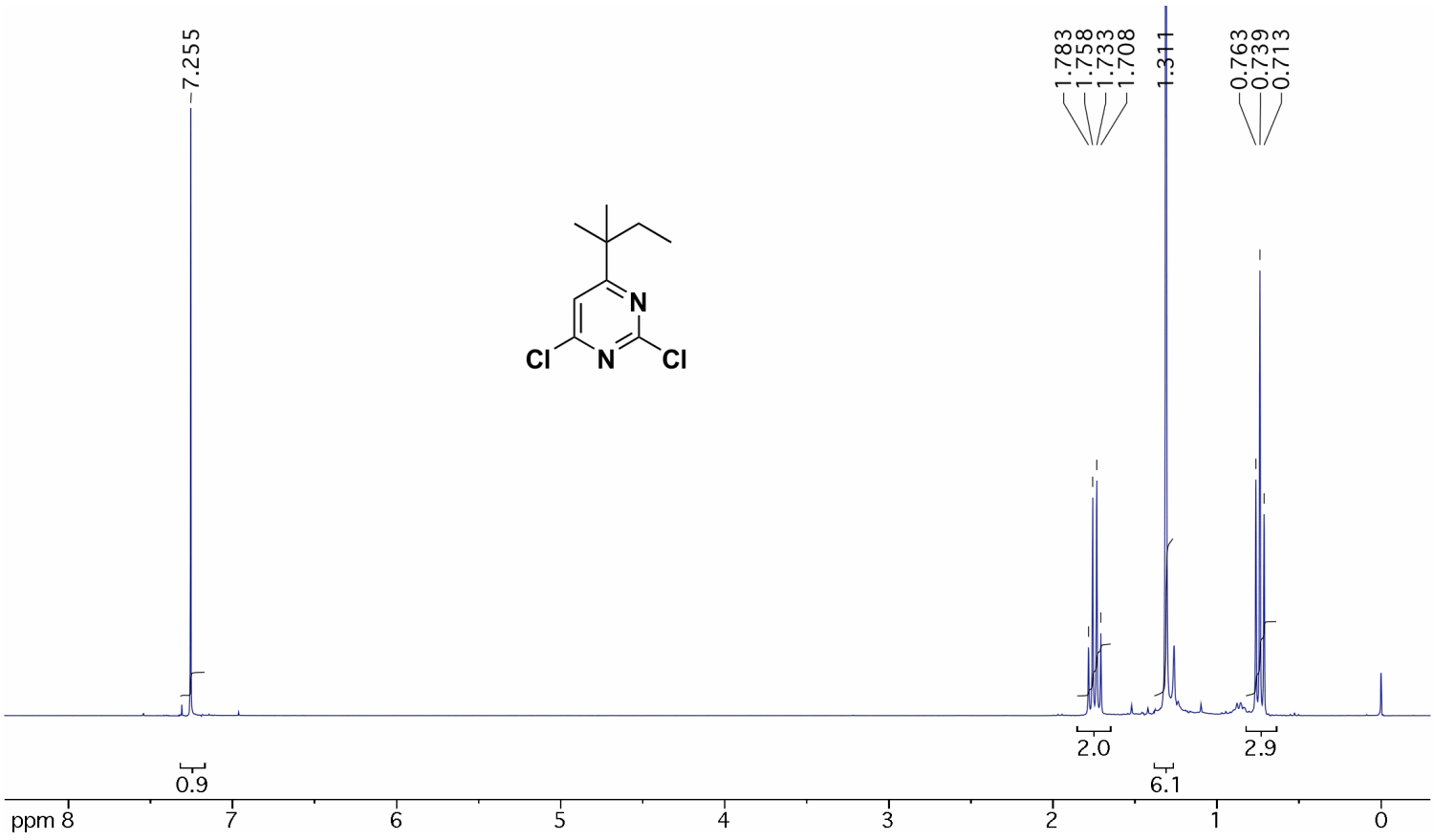
^{1}H NMR (400 MHz, $CDCl_3$) of 4-*tert*-Amyl-2-chloroquinazoline (6d)



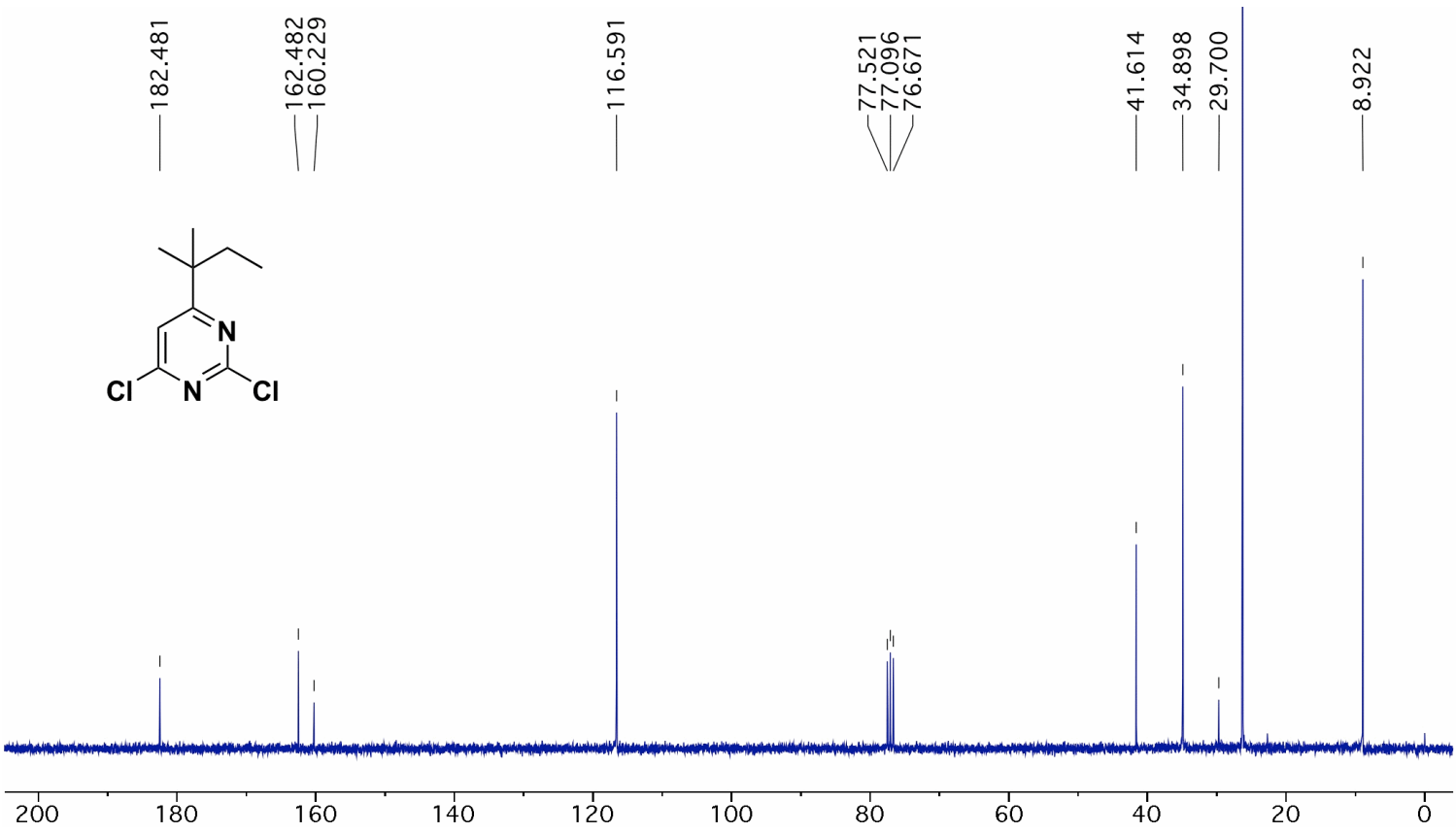
^{13}C NMR (100 MHz, $CDCl_3$) of 4-*tert*-Amyl-2-chloroquinazoline (6d)



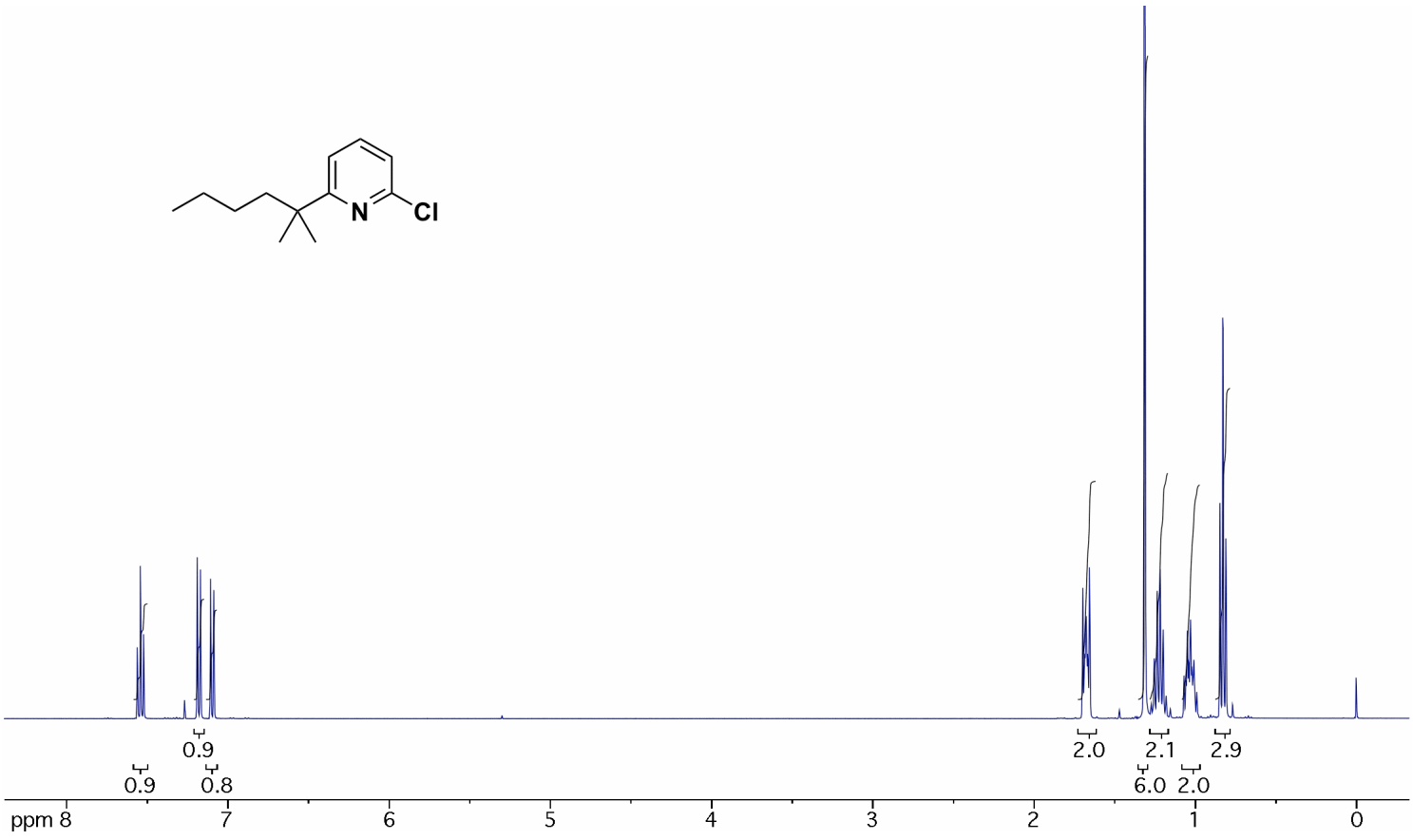
^{1}H NMR (300 MHz, $CDCl_3$) of 4-*tert*-Amyl-2,6-dichloro-pyrimidine (7b)



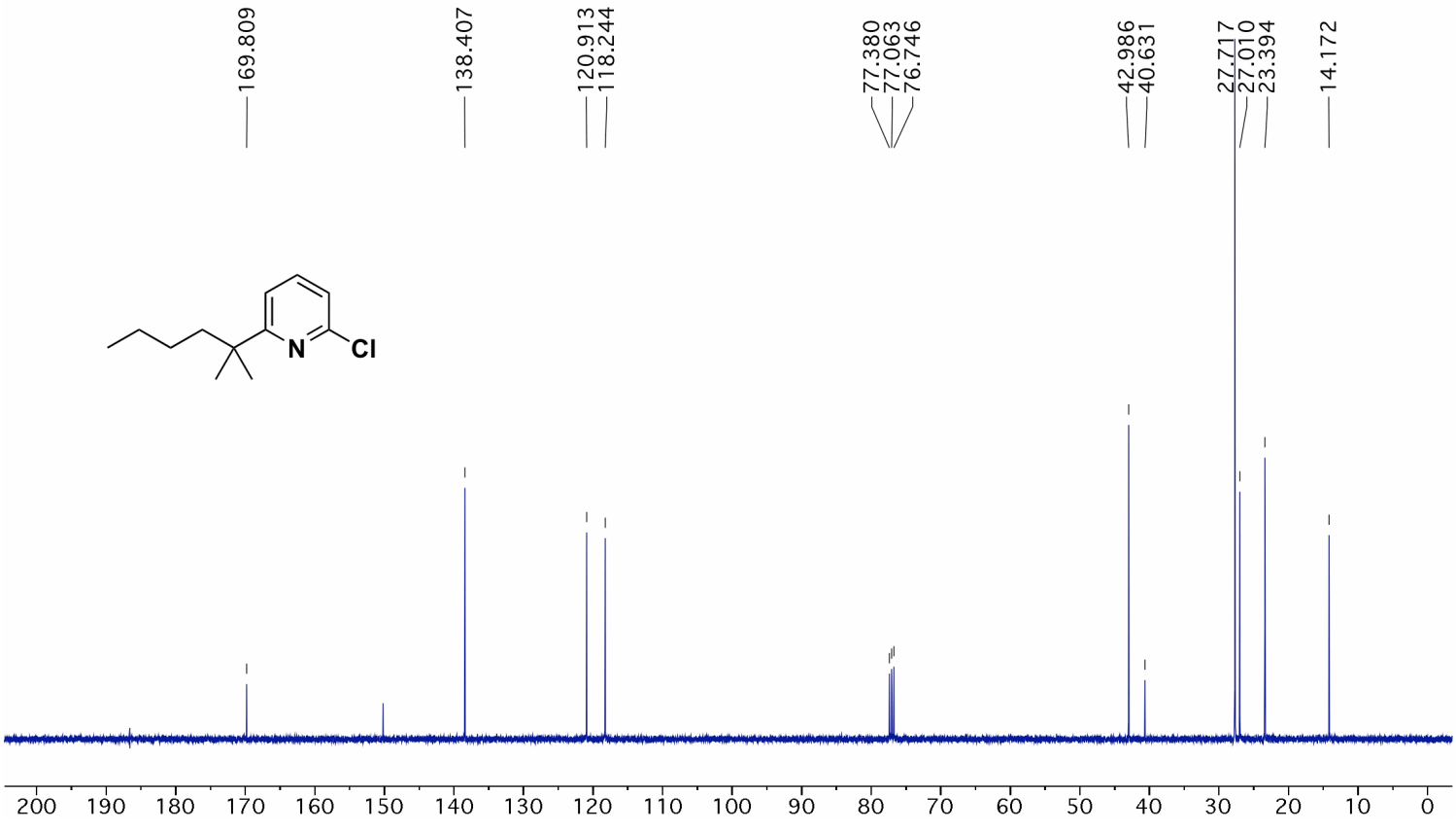
^{13}C NMR (76 MHz, $CDCl_3$) of 4-*tert*-Amyl-2,6-dichloro-pyrimidine (7b)



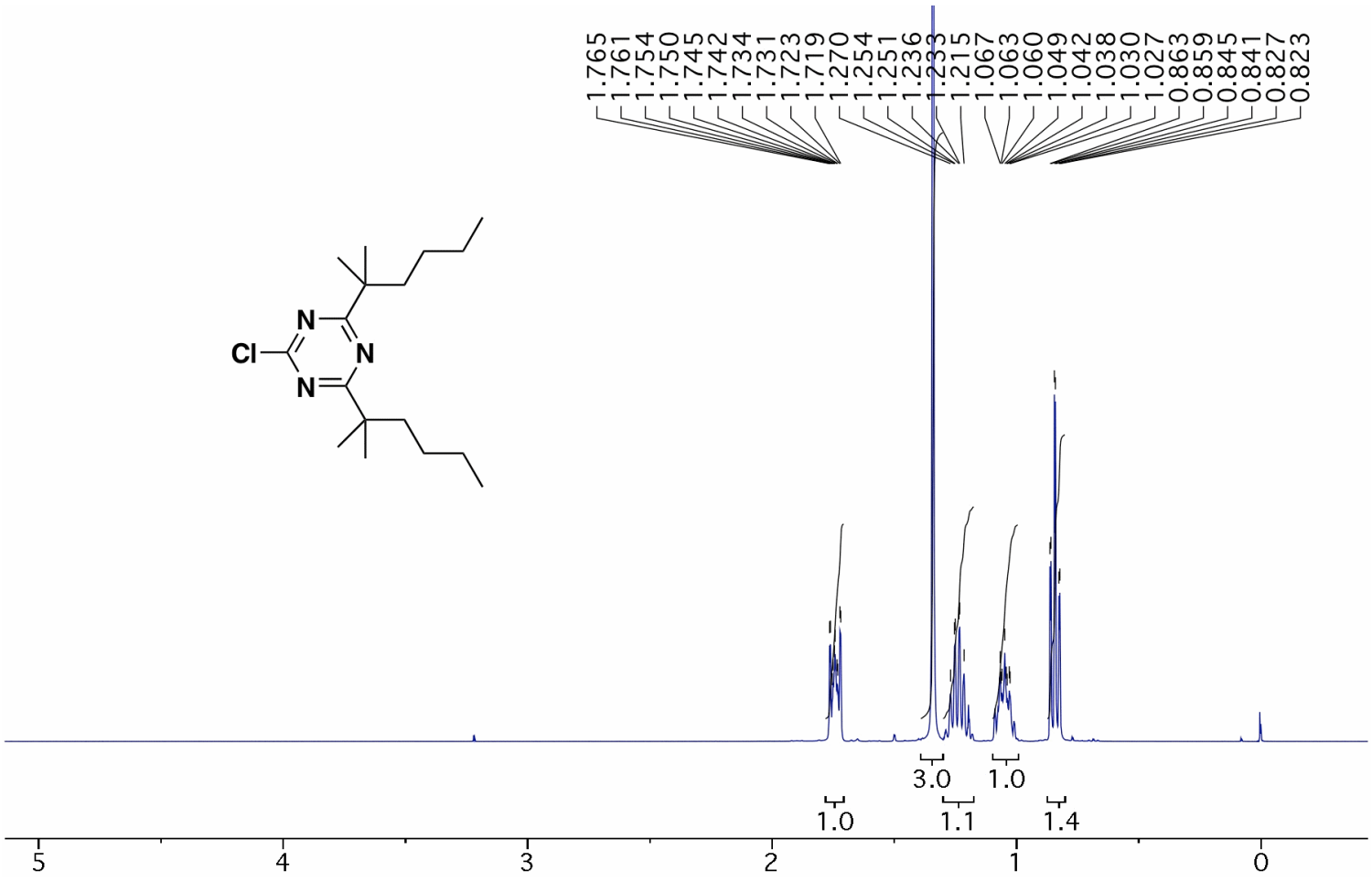
^{1}H NMR (400 MHz, $CDCl_3$) of 2-Chloro-6-(2-methylhexan-2-yl)pyridine (8a)



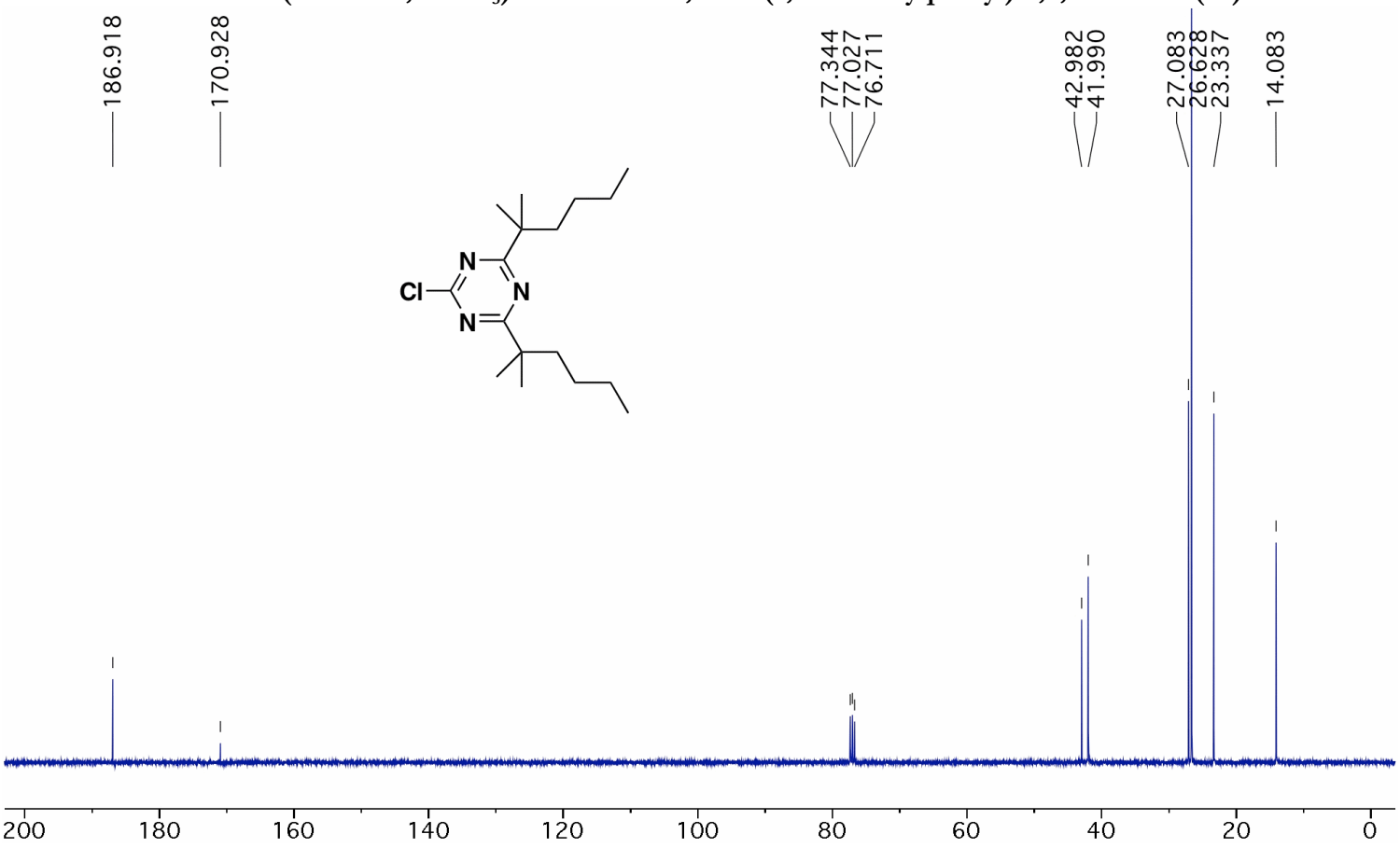
^{13}C NMR (400 MHz, $CDCl_3$) of 2-Chloro-6-(2-methylhexan-2-yl)pyridine (8a)



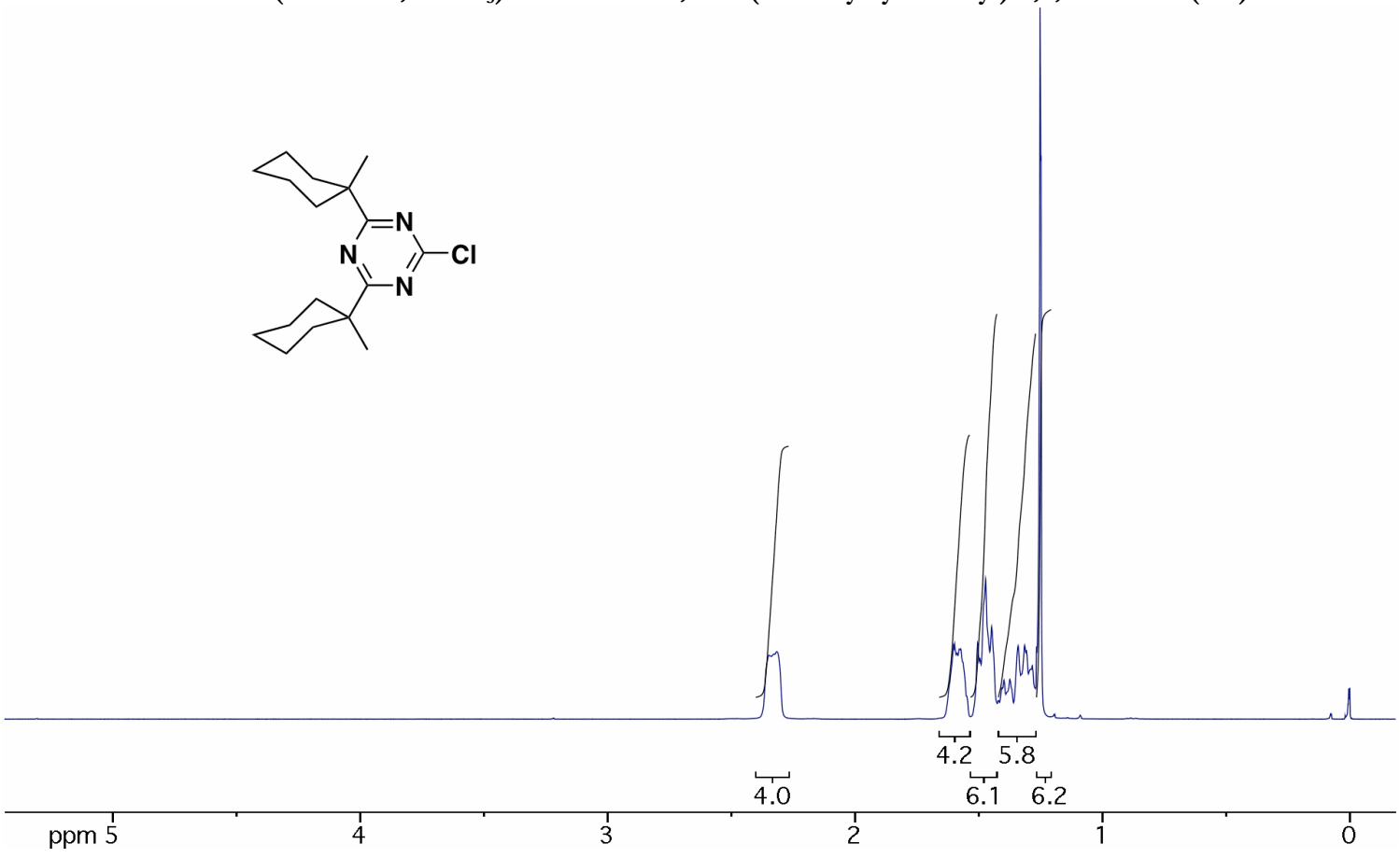
^{1}H NMR (400 MHz, $CDCl_3$) of 2-Chloro-4,6-bis-(1,1-dimethylpentyl)-1,3,5-triazine (9c)



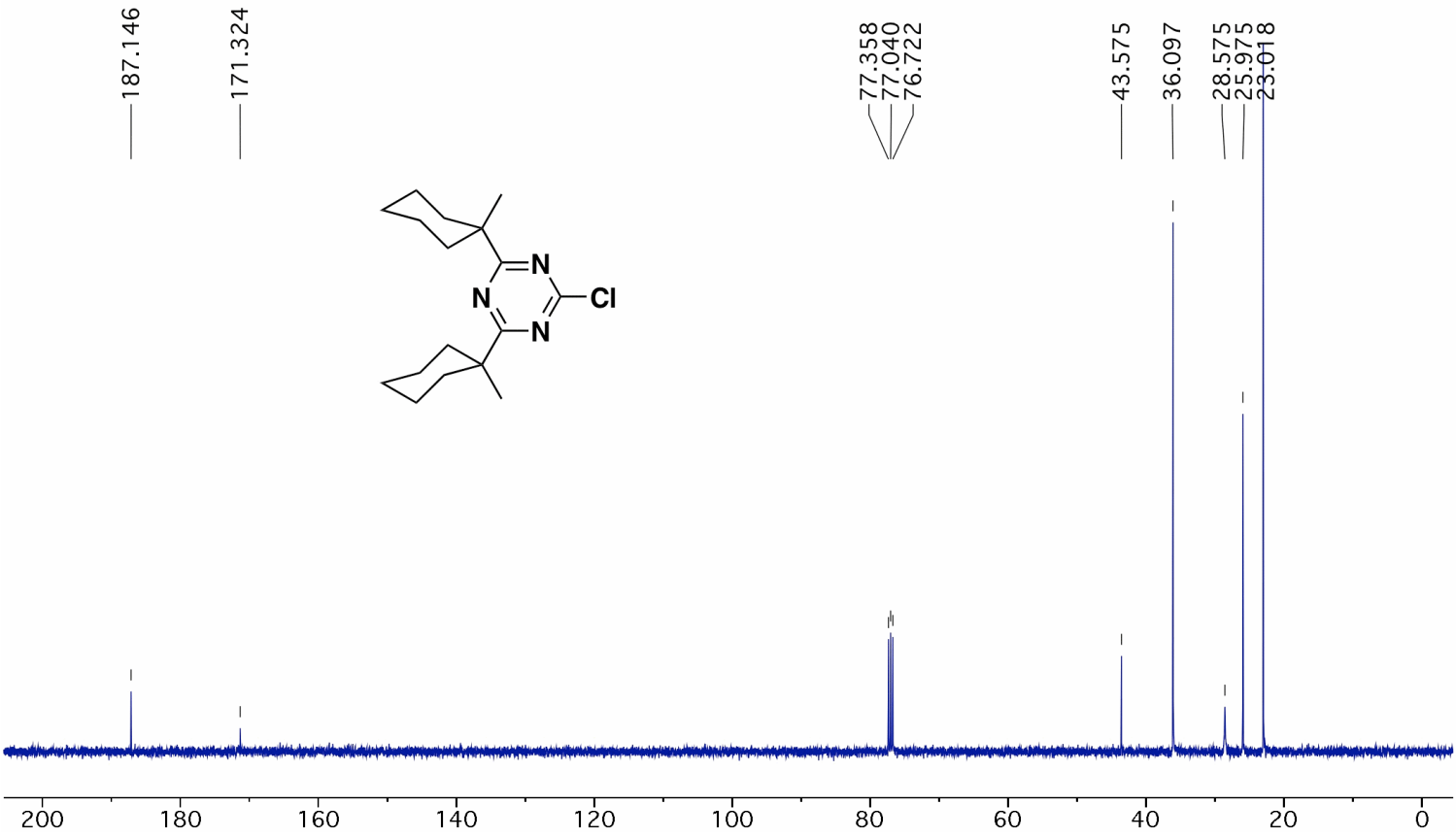
^{13}C NMR (100 MHz, $CDCl_3$) of 2-Chloro-4,6-bis-(1,1-dimethylpentyl)-1,3,5-triazine (9c)



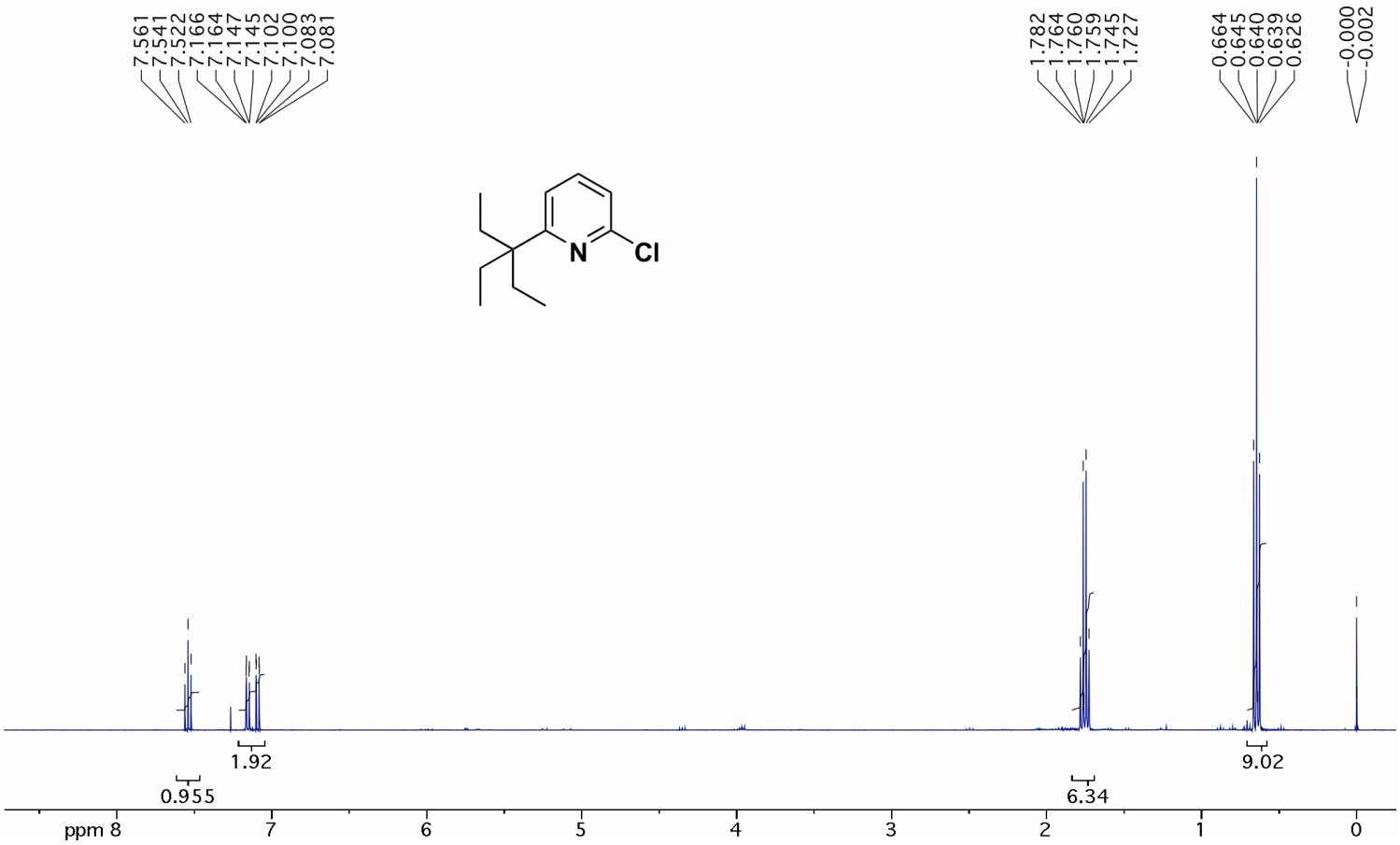
^{1}H NMR (400 MHz, $CDCl_3$) of 2-Chloro-4,6-bis(1-methylcyclohexyl)-1,3,5-triazine (10c)



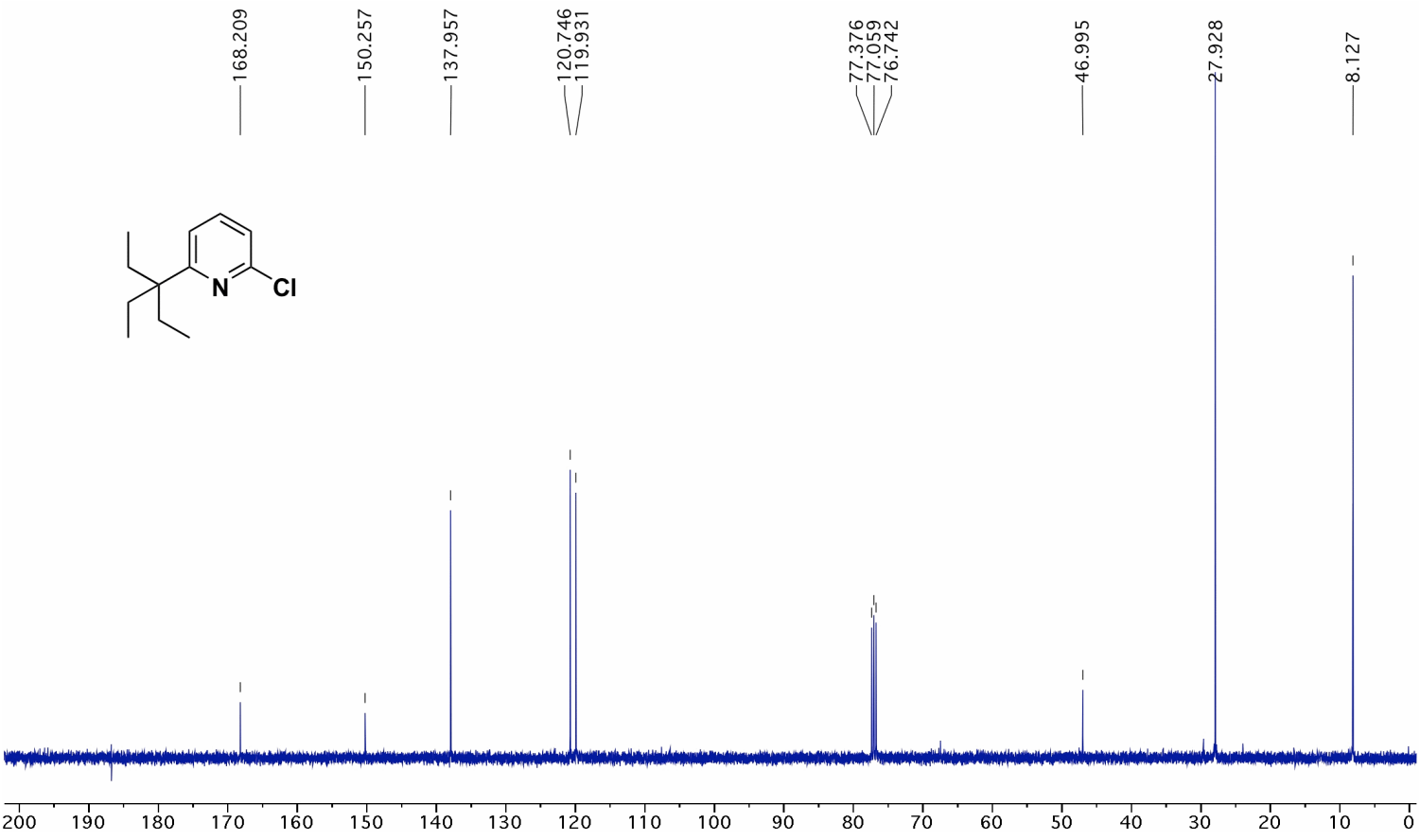
^{13}C NMR (100 MHz, $CDCl_3$) of 2-Chloro-4,6-bis(1-methylcyclohexyl)-1,3,5-triazine (10c)



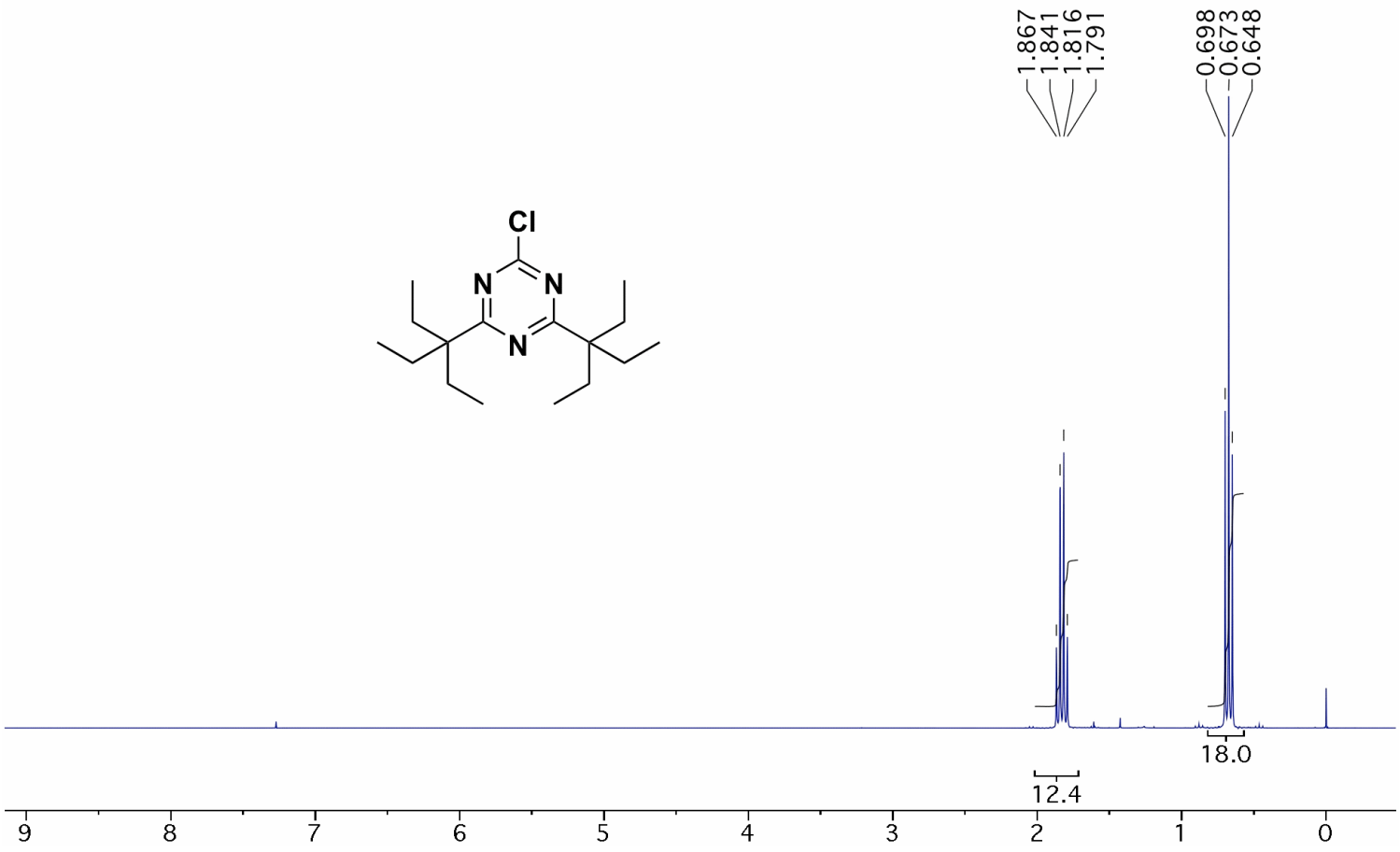
^{1}H NMR (400 MHz, $CDCl_3$) of 2-Chloro-6-(1,1-diethylpropyl)-pyridine (11a)



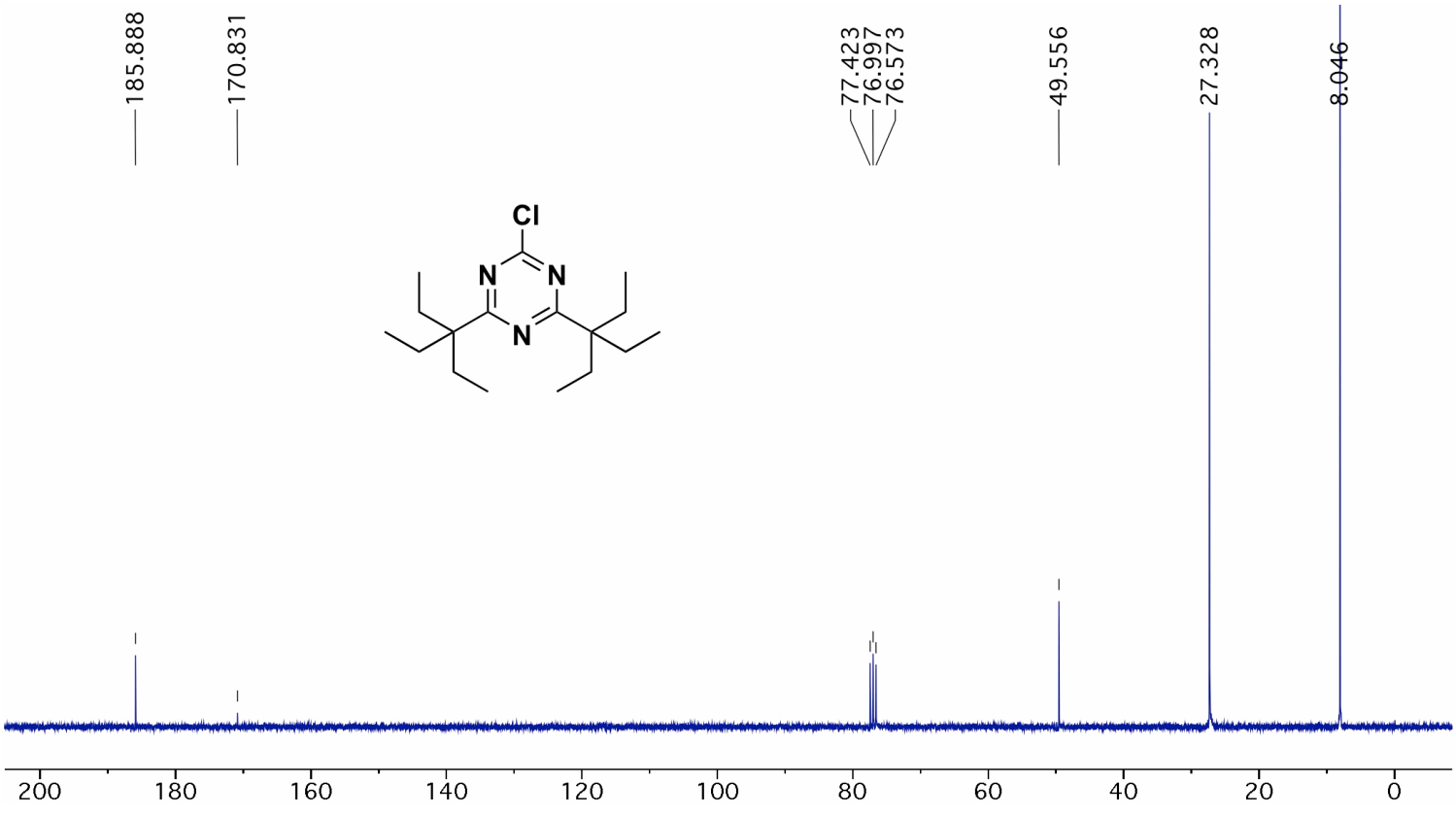
^{13}C NMR (100 MHz, $CDCl_3$) of 2-Chloro-6-(1,1-diethylpropyl)-pyridine (11a)



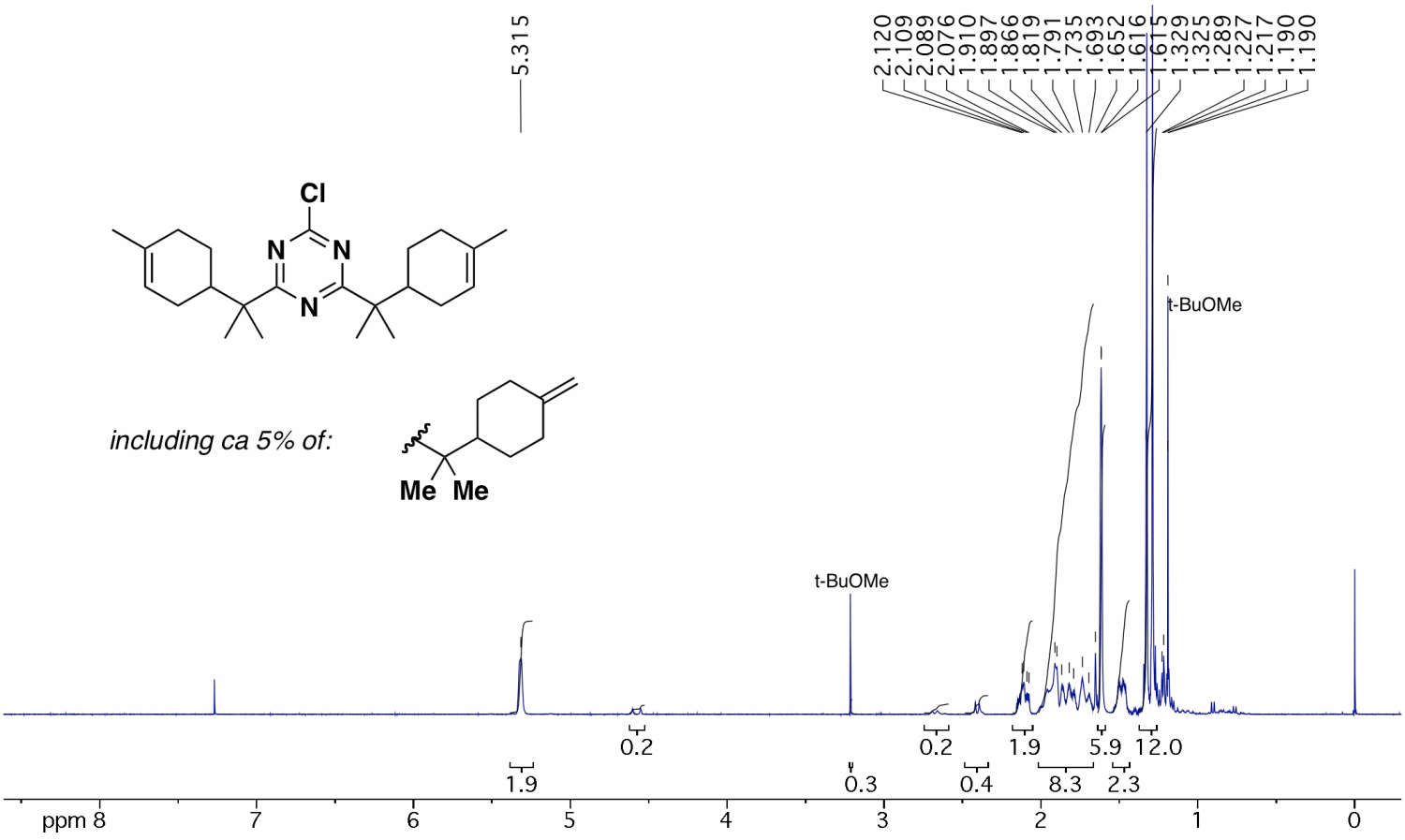
^{1}H NMR (300 MHz, $CDCl_3$) of 2-Chloro-4,6-bis(1,1-diethylpropyl)-1,3,5-triazine (11c)



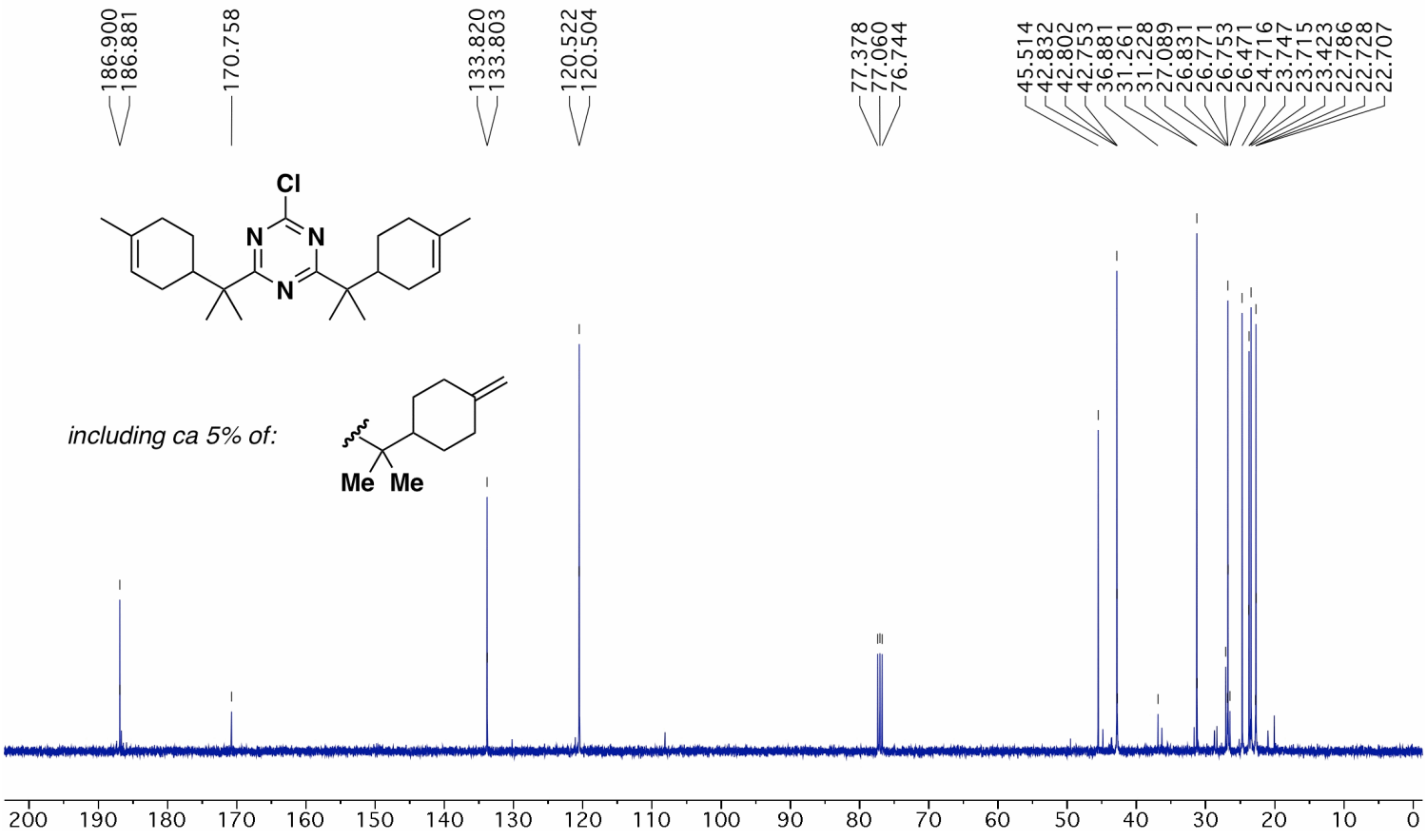
^{13}C NMR (76 MHz, $CDCl_3$) of 2-Chloro-4,6-bis(1,1-diethylpropyl)-1,3,5-triazine (11c)



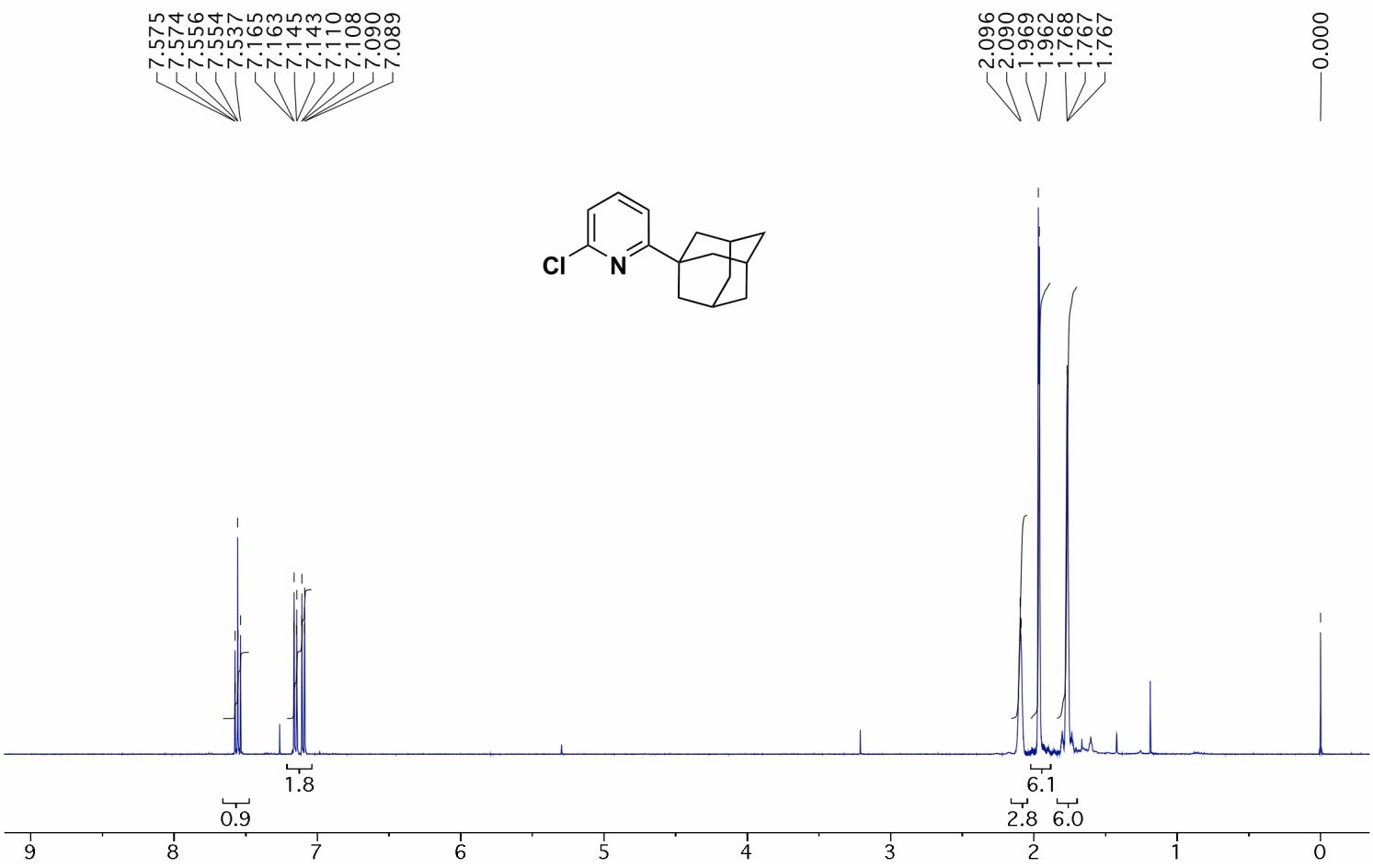
^{1}H NMR (400 MHz, $CDCl_3$) of Di-4,6-α-terpinyl-2-chloro-1,3,5-triazine (12c)



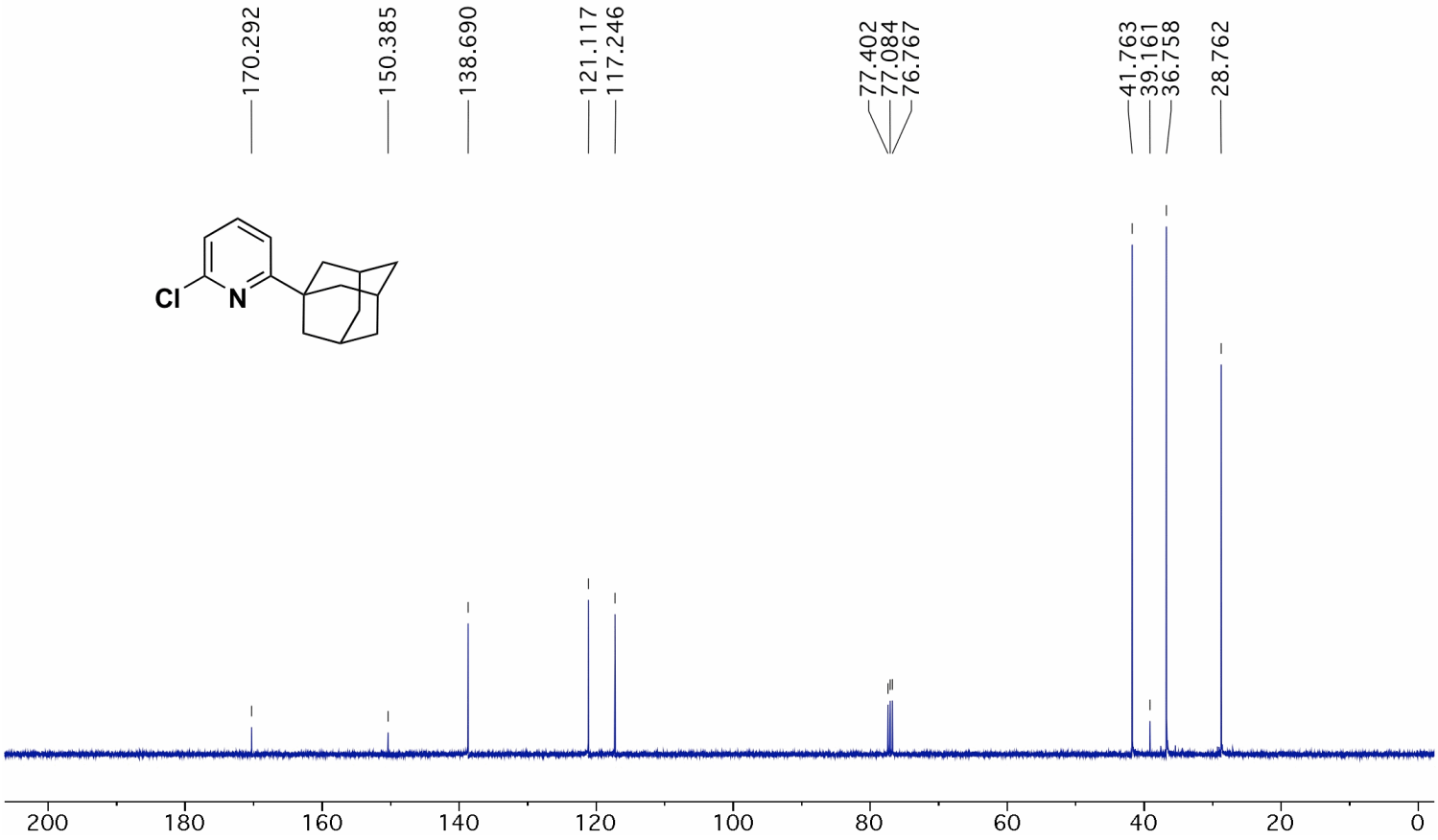
^{13}C NMR (100 MHz, $CDCl_3$) of Di-4,6-α-terpinyl-2-chloro-1,3,5-triazine (12c)



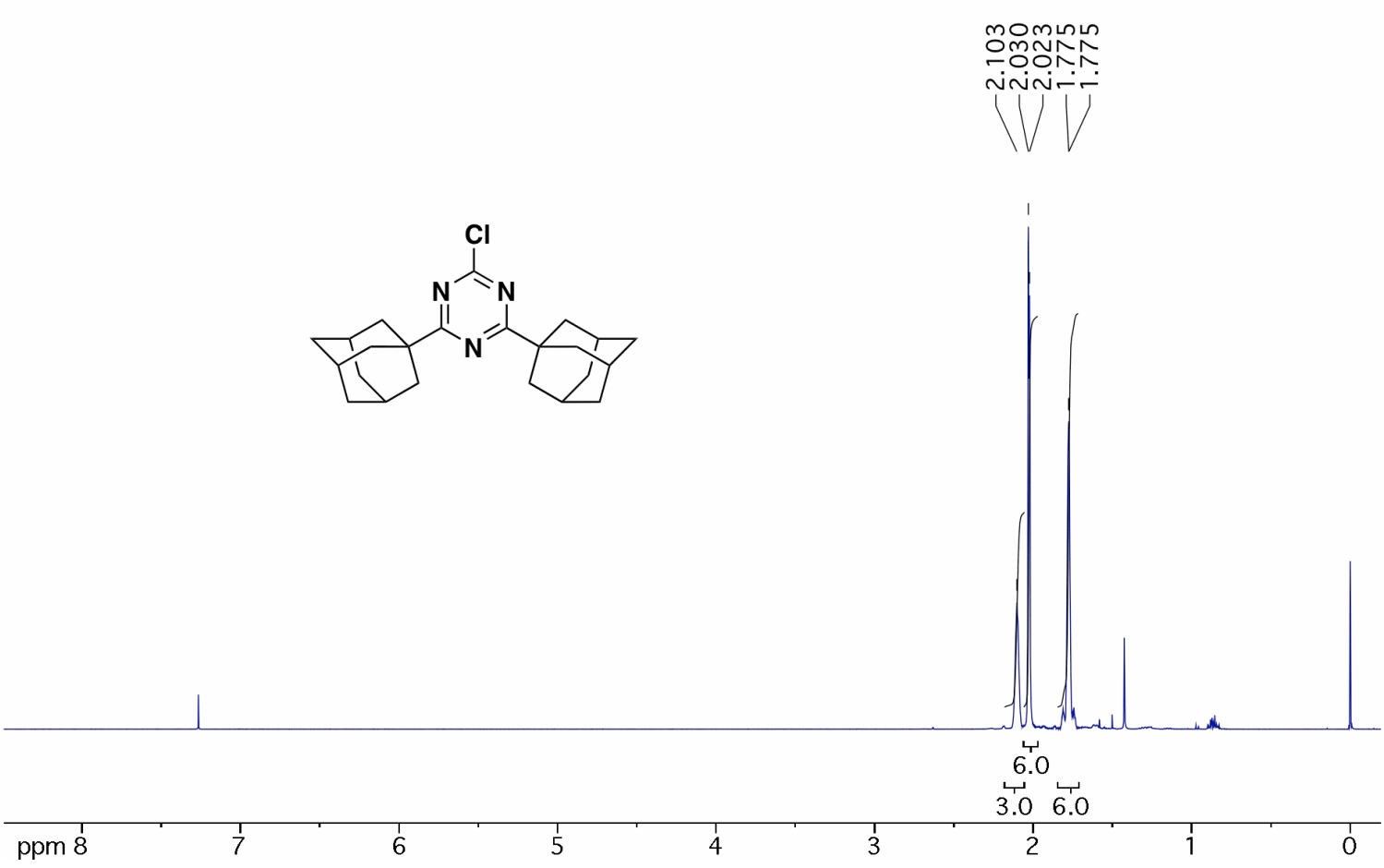
^{1}H NMR (300 MHz, $CDCl_3$) of 2-Adamantyl-6-chloropyridine (13a)



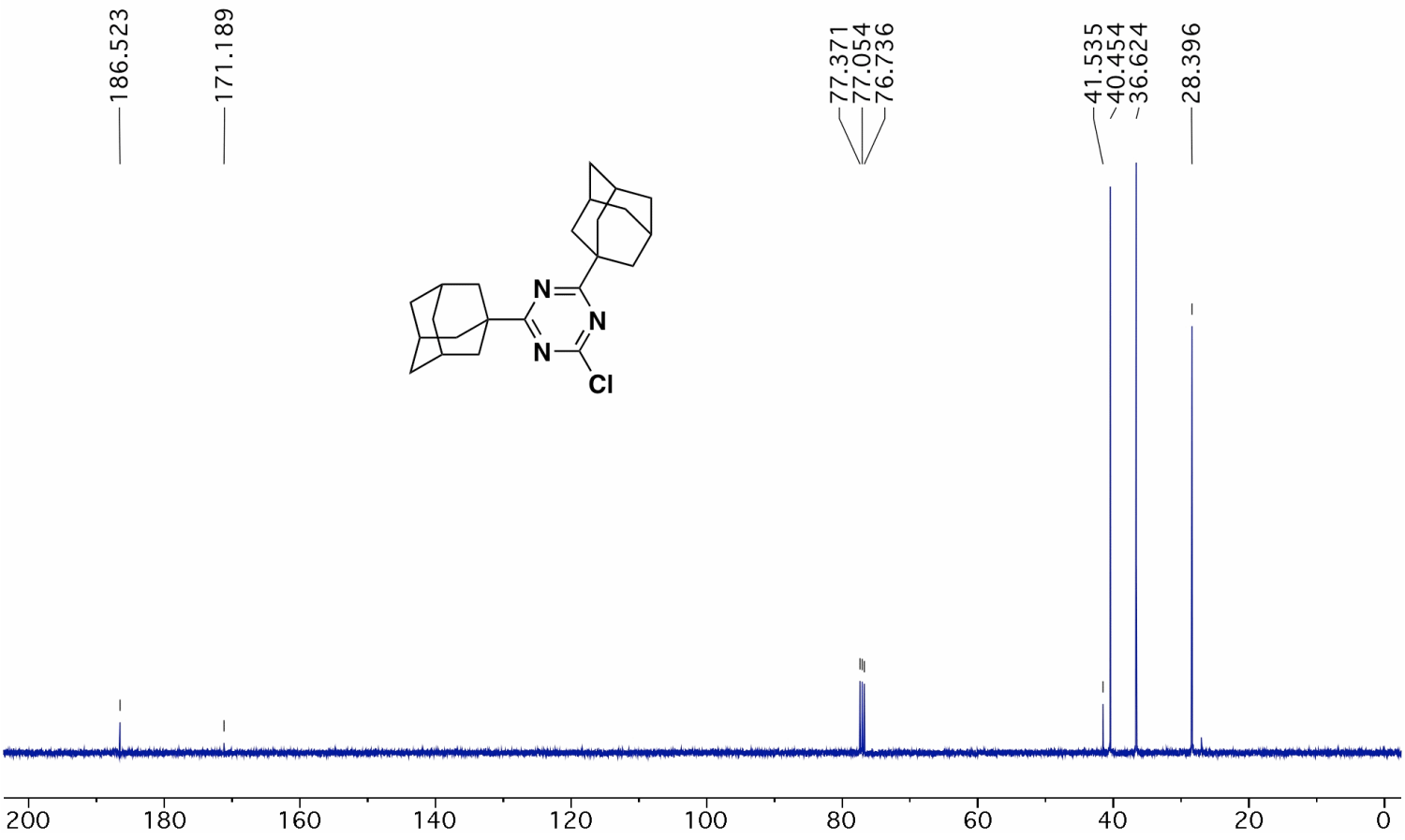
^{13}C NMR (100 MHz, $CDCl_3$) of 2-Adamantyl-6-chloropyridine (13a)



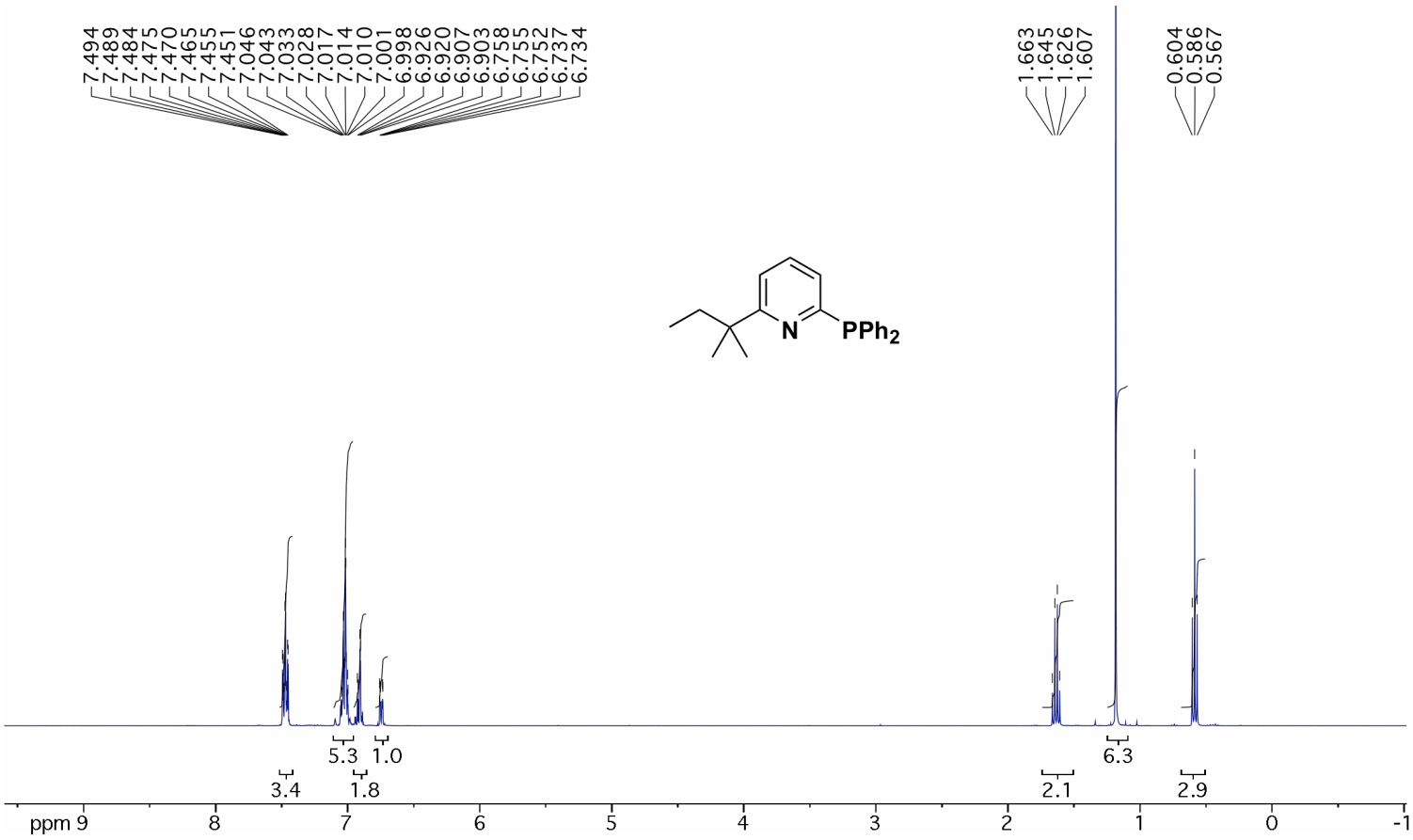
^{1}H NMR (400 MHz, $CDCl_3$) of 4,6-Diadamantyl-2-chloro-1,3,5-triazine (13c)



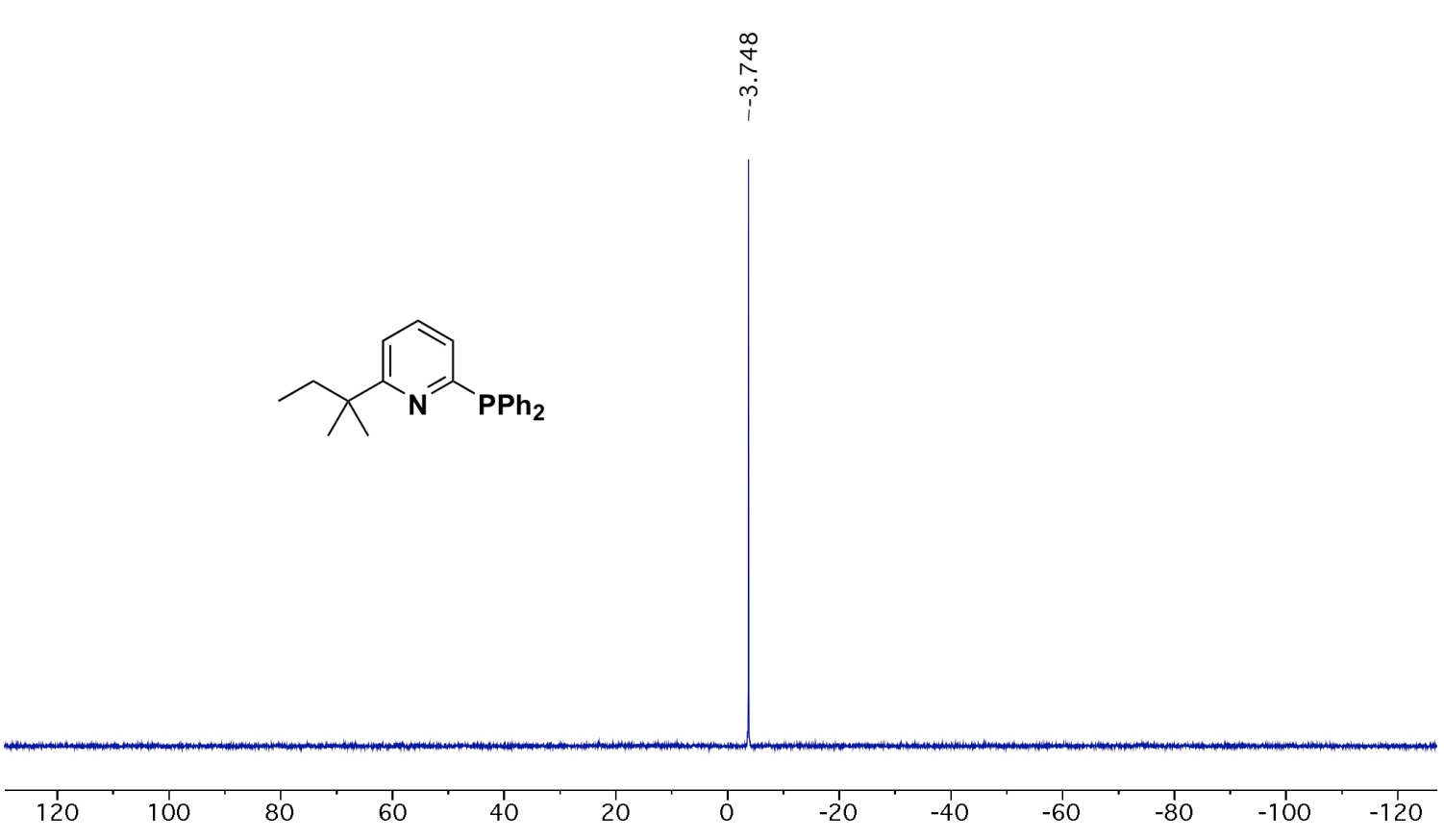
^{13}C NMR (100 MHz, $CDCl_3$) of 4,6-Diadamantyl-2-chloro-1,3,5-triazine (13c)



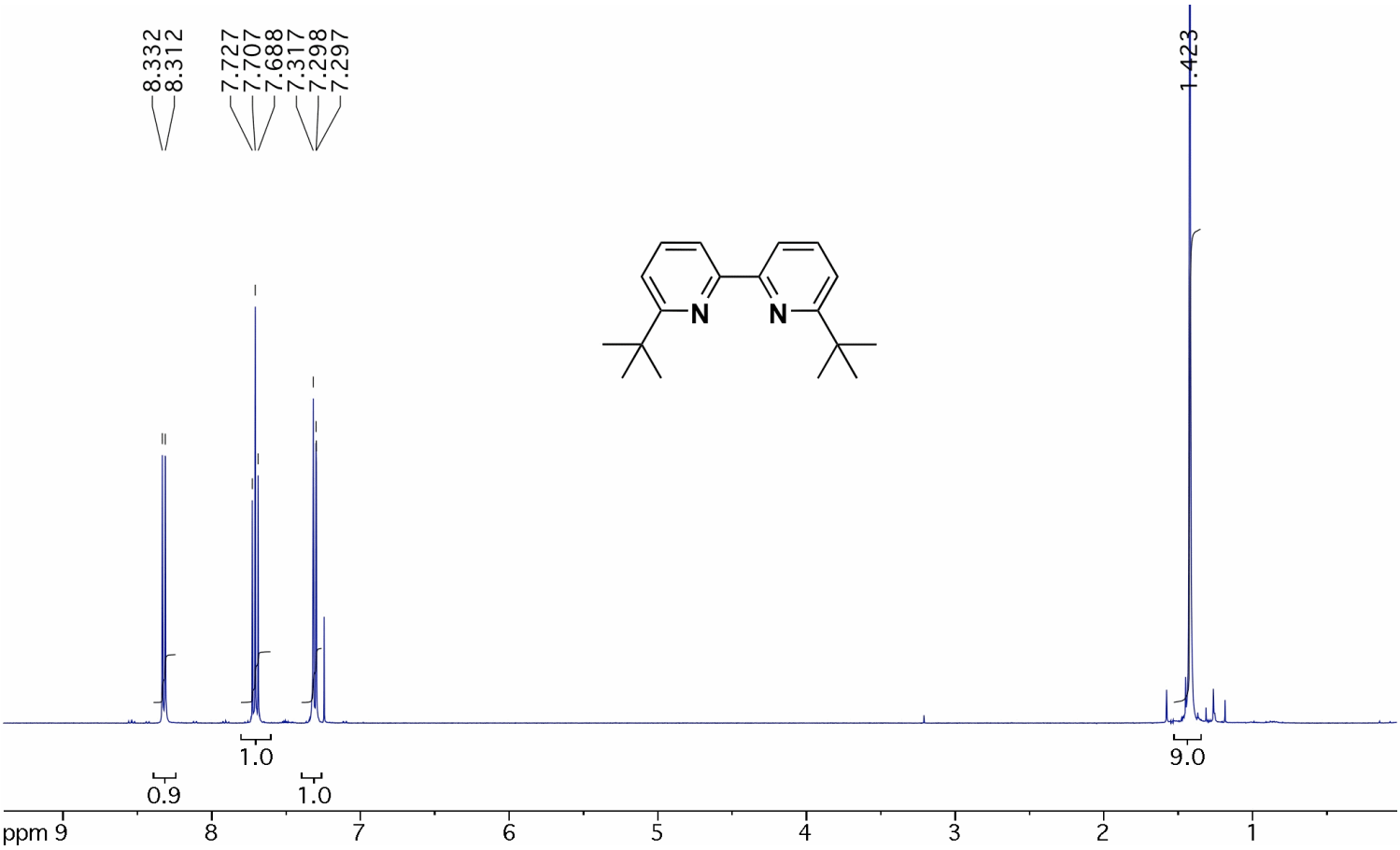
^{1}H NMR (400 MHz, C_6D_6) of 6-*tert*-Amyl-2-diphenylphosphinopyridine (TAMPYPHOS) (15)



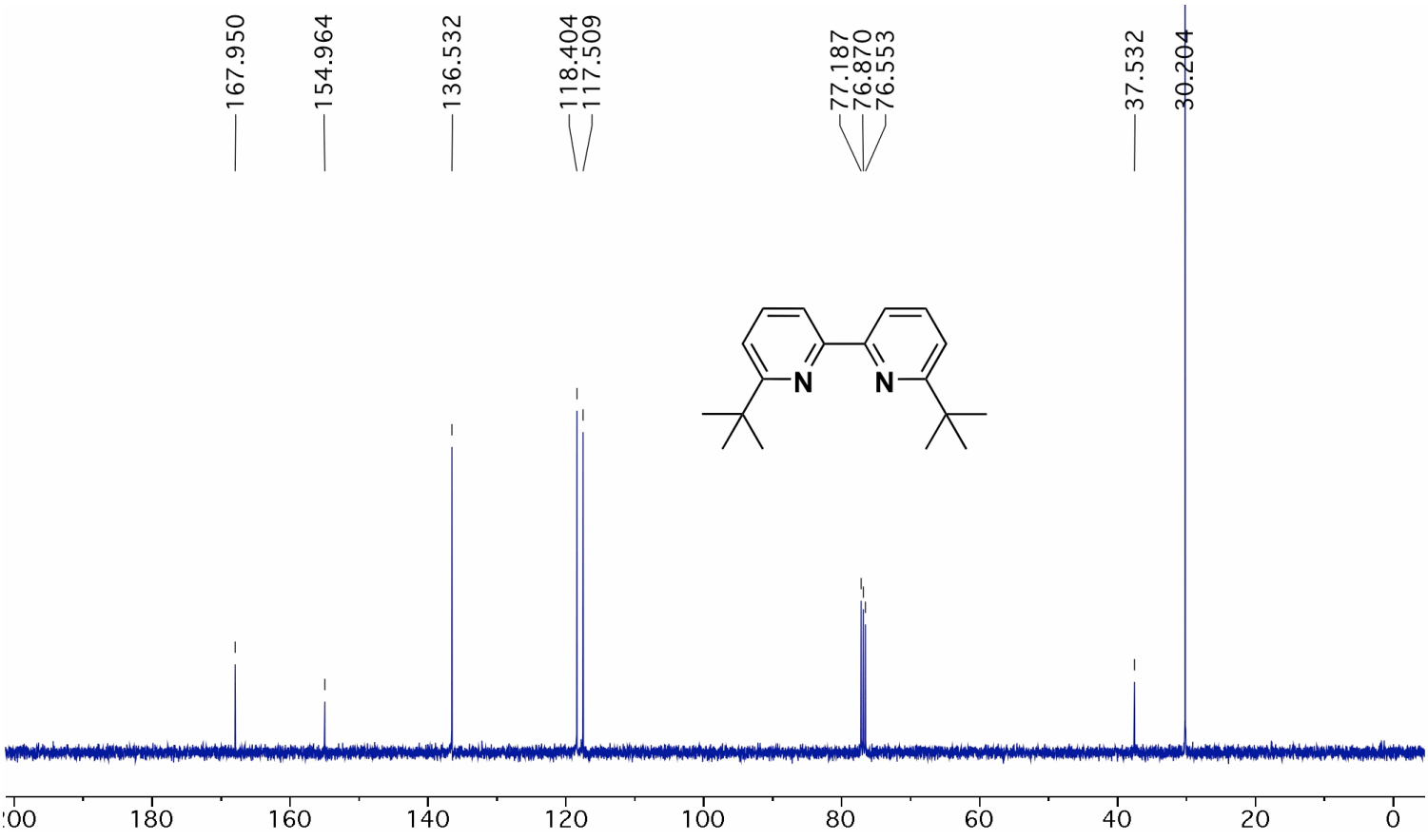
^{31}P NMR (121 MHz, C_6D_6) of 6-*tert*-Amyl-2-diphenylphosphinopyridine (TAMPYPHOS) (15)



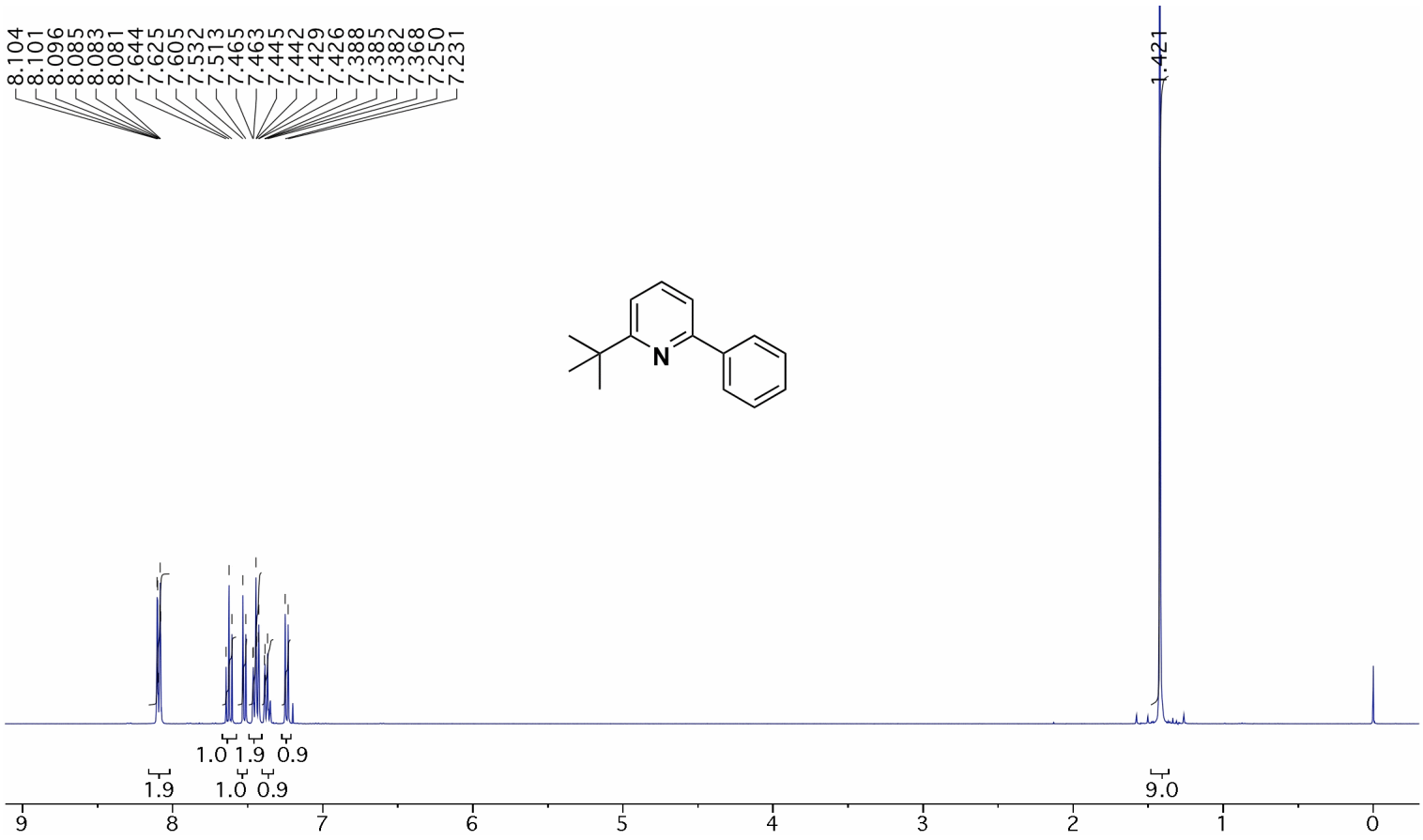
^{1}H NMR (400 MHz, $CDCl_3$) of 6,6'-Di-*tert*-butyl-2,2'-bipyridine (16)



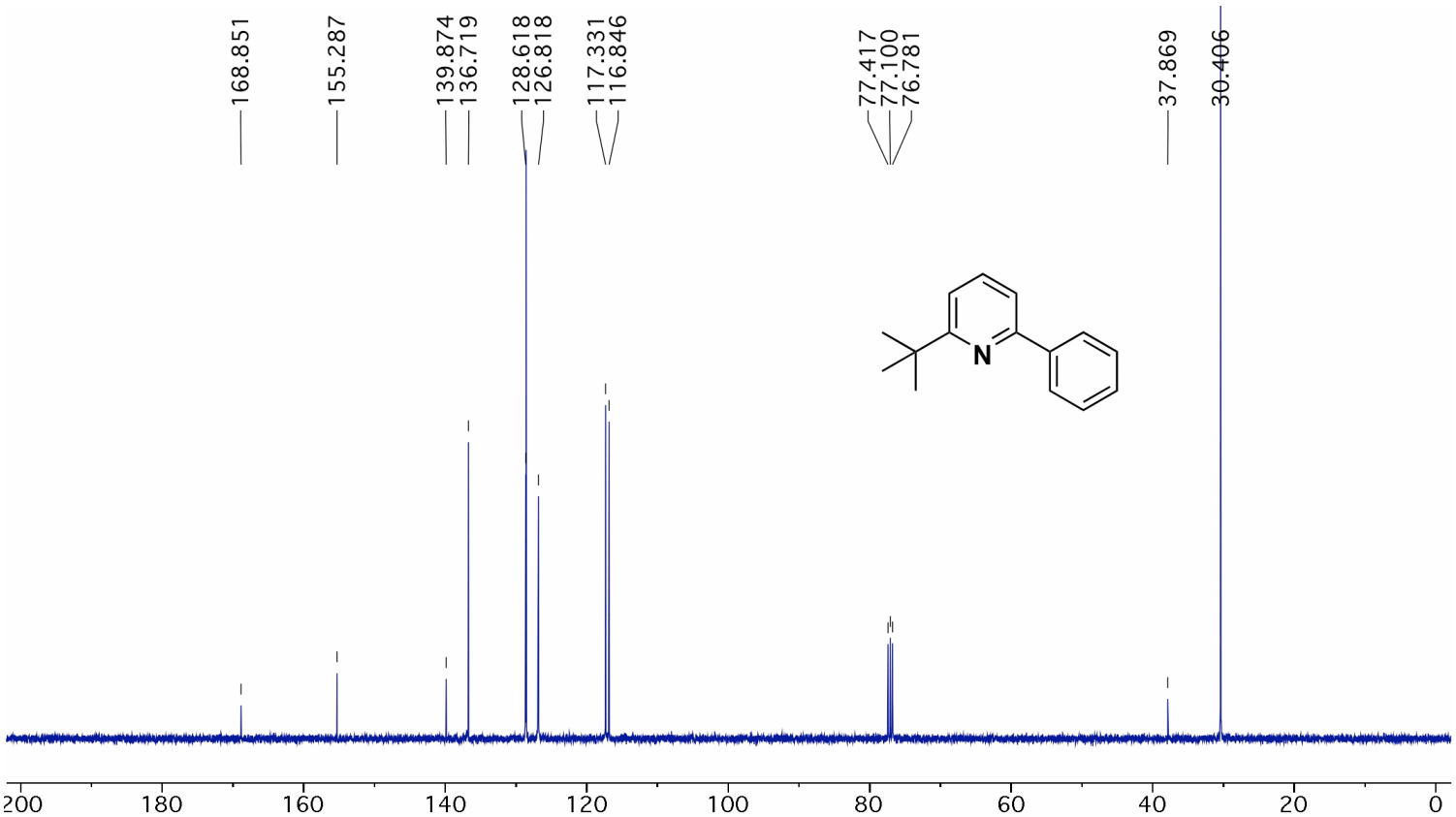
^{13}C NMR (100 MHz, $CDCl_3$) of 6,6'-Di-*tert*-butyl-2,2'-bipyridine (16)



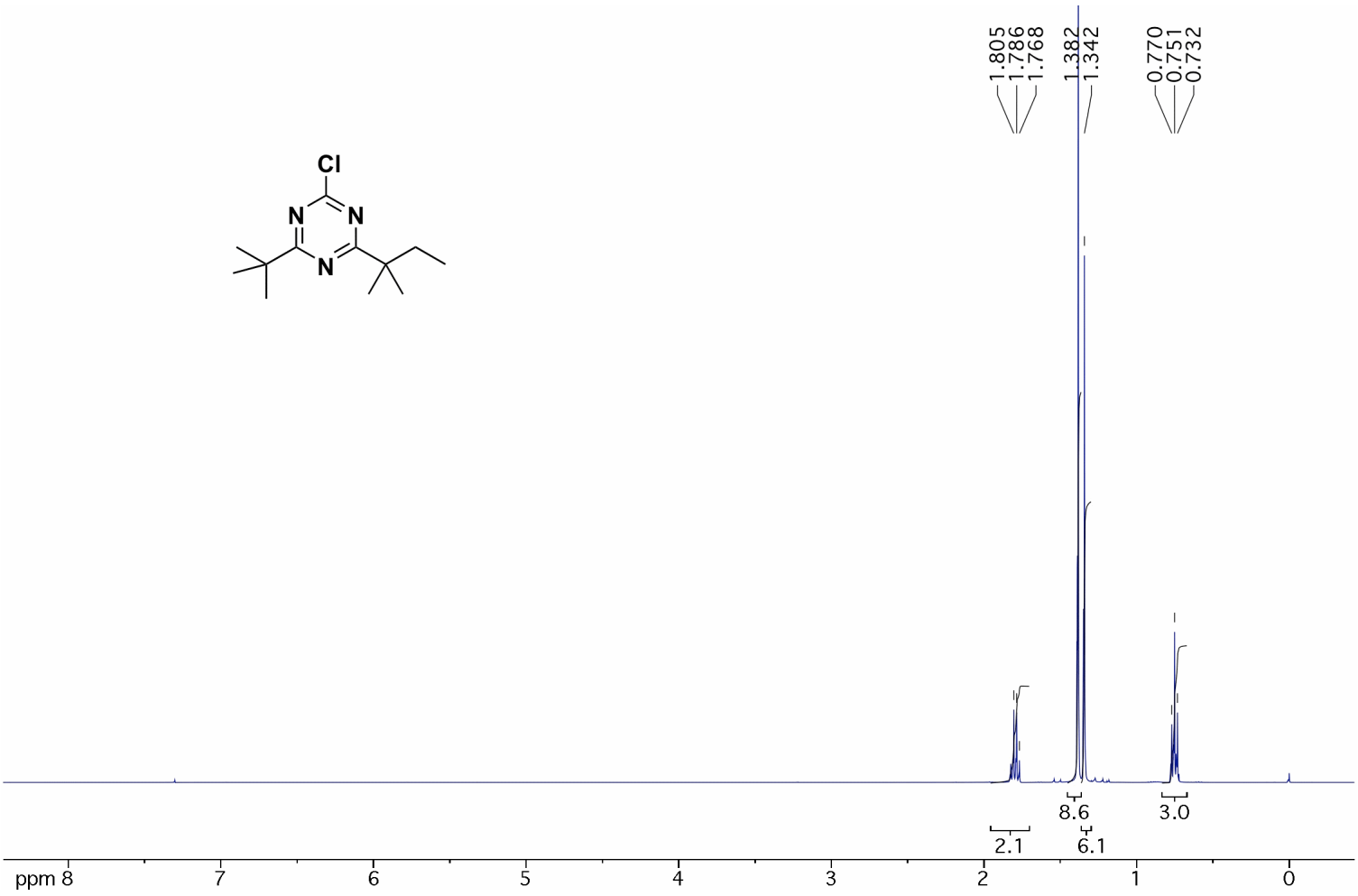
^{1}H NMR (400 MHz, $CDCl_3$) of 2-*tert*-Butyl-6-phenylpyridine (17)



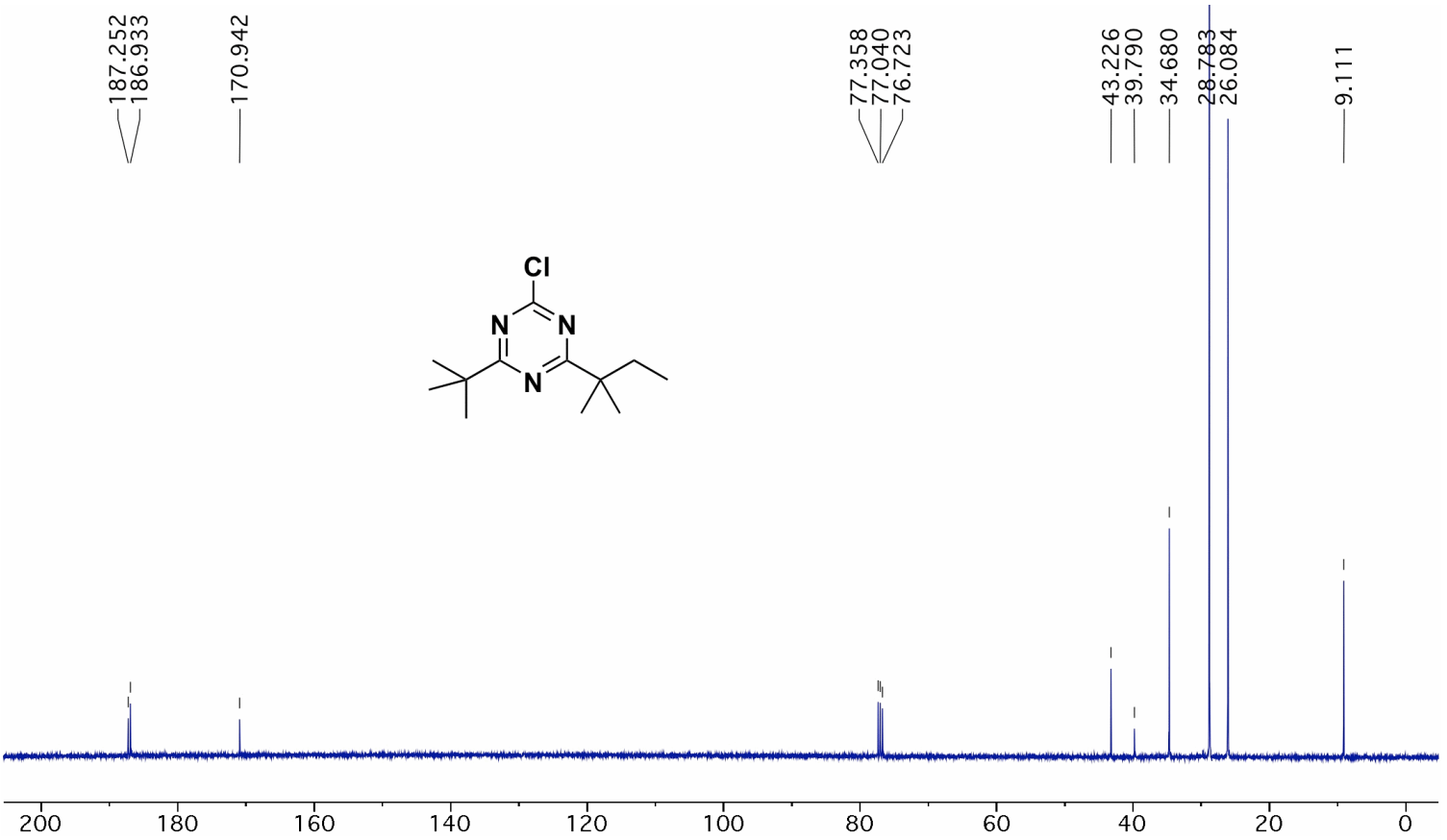
^{13}C NMR (100 MHz, $CDCl_3$) of 2-*tert*-Butyl-6-phenylpyridine (17)



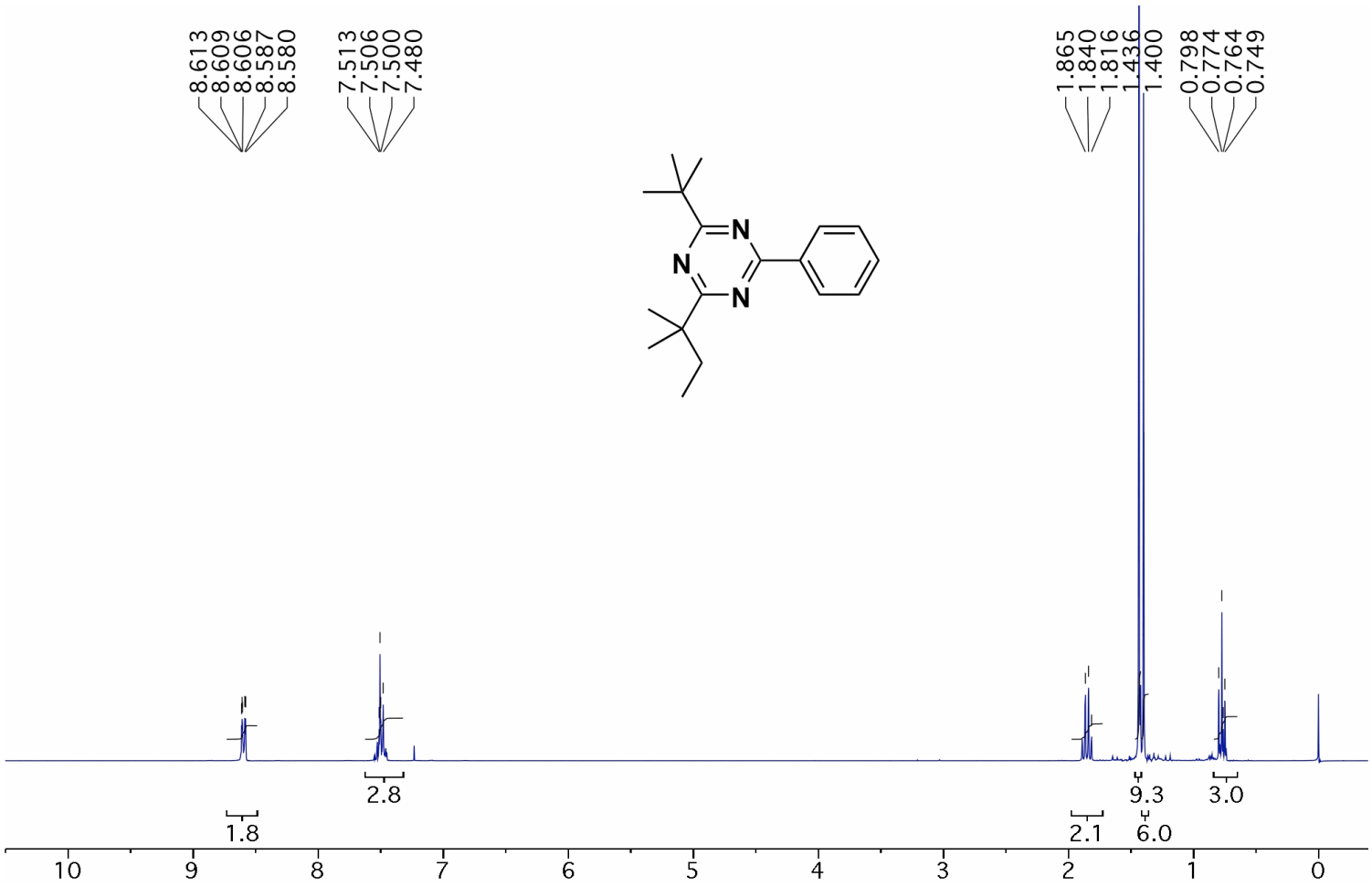
^{1}H NMR (400 MHz, $CDCl_3$) of 4-*tert*-Amyl-6-*tert*-Butyl-2-chloro-1,3,5-triazine (18)



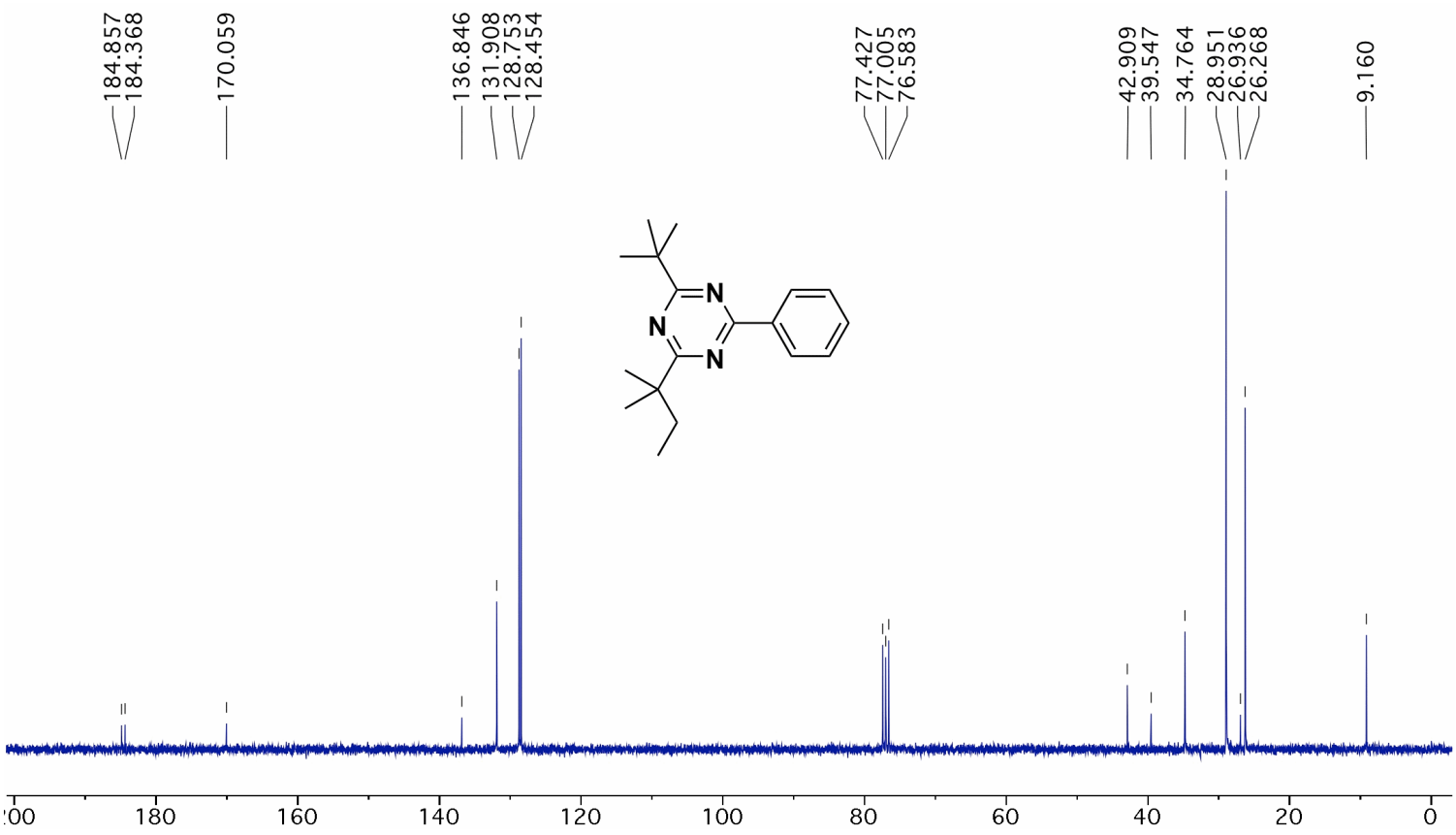
^{13}C NMR (100 MHz, $CDCl_3$) of 4-*tert*-Amyl-6-*tert*-Butyl-2-chloro-1,3,5-triazine (18)



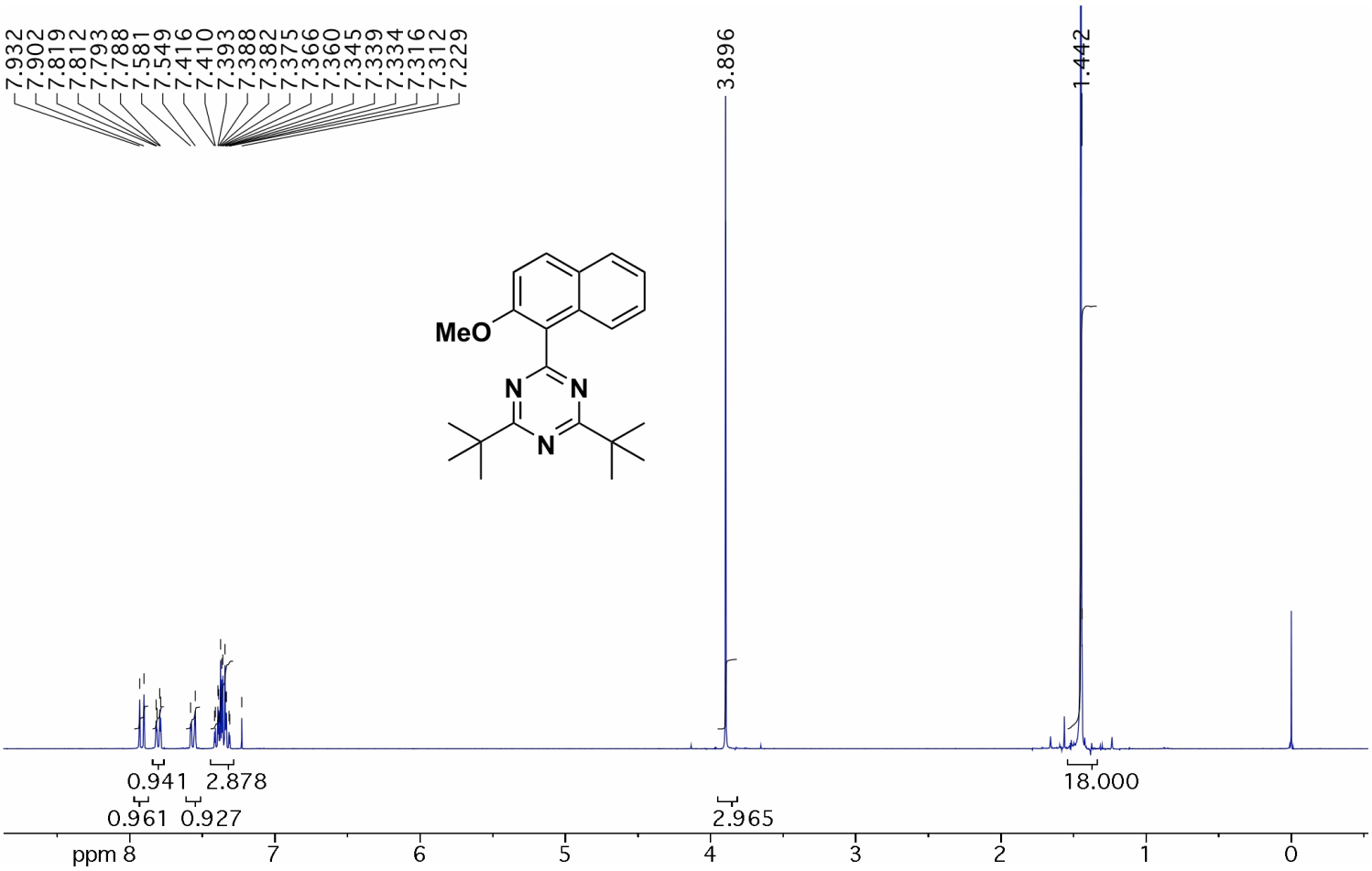
^{1}H NMR (300 MHz, $CDCl_3$) of 6-*tert*-Butyl-4-*tert*-amyl- 2-phenyl-1,3,5-triazine (19)



^{13}C NMR (76 MHz, $CDCl_3$) of 6-*tert*-Butyl-4-*tert*-amyl- 2-phenyl-1,3,5-triazine (19)



^{1}H NMR (400 MHz, $CDCl_3$) of 4,6-Di-*tert*-butyl-2-(2-methoxy-naphth-1-yl)-1,3,5-triazine (20)



^{13}C NMR (100 MHz, $CDCl_3$) of 4,6-Di-*tert*-butyl-2-(2-methoxy-naphth-1-yl)-1,3,5-triazine (20)