Single-Electron Transmetalation: An Enabling Technology for Secondary Alkylboron Cross-Coupling

David N. Primer, Idris Karakaya, John C. Tellis, and Gary A. Molander*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

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General considerations

All reactions were carried out under an inert atmosphere of nitrogen or argon unless otherwise noted. Dioxane (99.9%, extra dry) was used as received. Cs_2CO_3 was used as received. $IrCl_3 \cdot xH_2O$, and $NiCl_2$-dme were purchased from commercial sources. All other reagents were purchased commercially and used as received. Photoredox reactions were irradiated with two or three standard 26 W compact fluorescent light bulbs. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500 or 400 MHz spectrometer. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration.

Synthesis of Secondary Alkyltrifluoroborates:

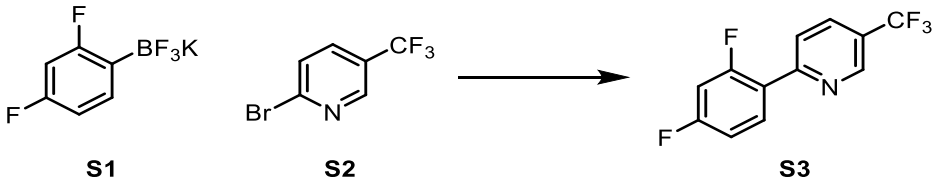
Most potassium organotrifluoroborates were purchased commercially. In cases where the desired potassium organotrifluoroborate was unavailable, the corresponding boronic acid derivative was converted to the trifluoroborate by the following procedure.

General Procedure for conversion of boronic acid to trifluoroborate:

To a solution of boronic acid derivative in acetone or MeOH (0.1 M) at 0 °C was added saturated aq KHF_2 (4.5 M) dropwise over 30 min. The resulting suspension was concentrated under reduced pressure. H_2O was azeotropically removed by suspension in toluene (100-150 mL) followed by rotary evaporation. The remaining solid was dried under high vacuum and then suspended in hot acetone (3 x 100 mL) and filtered. The filtrate was concentrated to a minimal volume (5 – 20 mL) and hexane or Et_2O (~200 mL) were added to yield a white precipitate. The precipitate was isolated by filtration, washing with hexanes (~30 mL) and CH_2Cl_2 (~30 mL), to afford the desired secondary alkyltrifluoroborate.

Synthesis of photocatalyst 4

The synthesis of photocatalyst **4** has been documented in literature reports and fully included in our previous report on benzylic cross-couplings, but to aid the practicing chemist, all details are included here as well.[1] The procedures below have proven the most reliable in our experience.

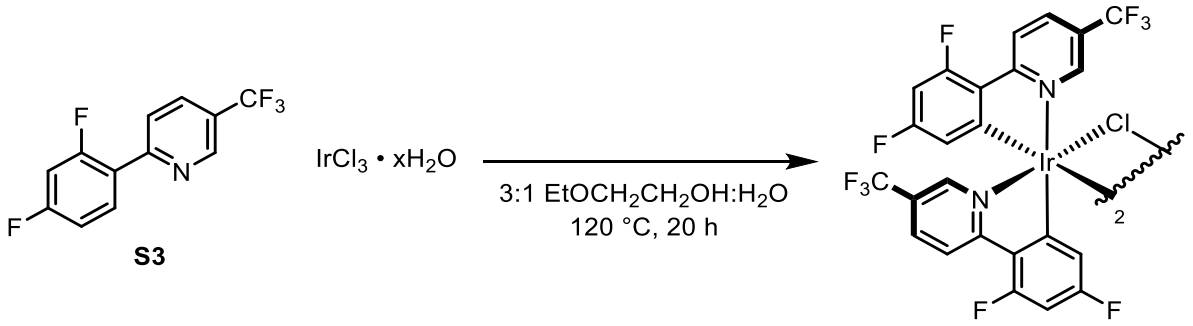


S1 **S2** **S3**

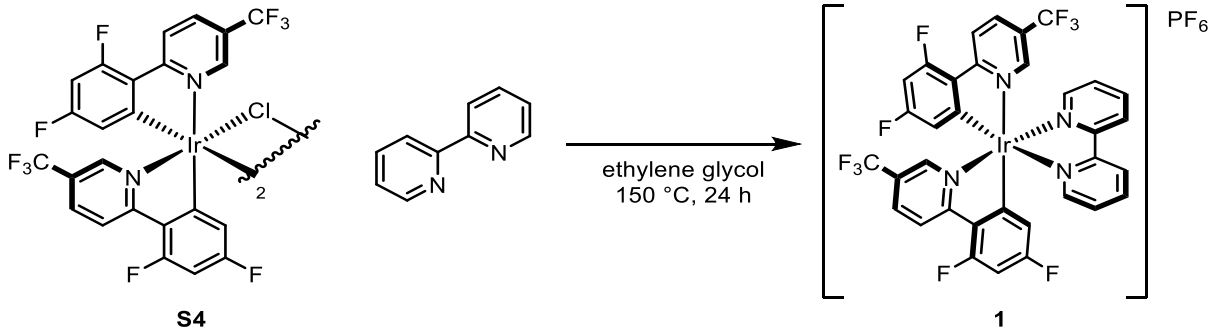
To a large vial equipped with a magnetic stir bar was added **S1** (3.3 g, 15 mmol) [Note: the boronic acid of **S1** serves equally well under these conditions], **S2** (2.26 g, 10 mmol), anhyd K_2CO_3 (6.9 g, 50 mmol), and $Pd(PPh_3)_4$ (1.16 g, 1 mmol). The vial was sealed tightly with a Teflon-coated septum cap and evacuated and purged with N_2 three times. The contents were dissolved in THF

[1] Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science*, **2014**, *345*, 433.

(32 mL) and degassed H_2O (16 mL), then stirred at 80 °C for 24 h. After cooling to rt, the reaction mixture was diluted with H_2O and extracted three times with CH_2Cl_2 (3 x 60 mL). The combined organic layers were dried ($MgSO_4$), filtered, concentrated under reduced pressure, and purified by silica gel column chromatography, eluting with 5% EtOAc in hexanes to afford ligand **S3** as a white solid (2.54 g, 98%). mp = 55-58 °C.
A small amount of PPh_3 was usually observed after column chromatography (<5 mol %), which did not interfere with subsequent reactions.



To a 20 mL round-bottom flask equipped with a magnetic stir bar was added ligand **S3** (428 mg, 1.65 mmol) and $IrCl_3$ hydrate (224 mg, 0.75 mmol). The flask was equipped with a cold water condenser and evacuated and purged with N_2 five times. The contents were suspended in rigorously degassed ethoxyethanol (9 mL) and H_2O (3 mL) and then heated with stirring to 120 °C for 20 h, during which time a yellow precipitate was observed to form. After cooling to rt, the precipitate was collected by vacuum filtration. The filter cake was washed copiously with H_2O (~75 mL) and hexanes (~30 mL) to afford iridium μ-Cl-dimer **S4** as a fine yellow powder (84%). mp >250 °C. Characterization data for this compound matched that reported in the literature.[2]

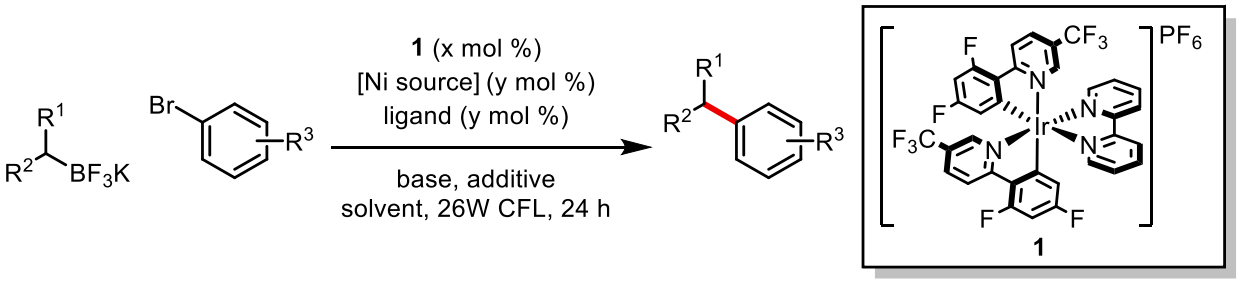


To a 15 mL round-bottom flask equipped with a magnetic stir bar was added iridium dimer **S4** (130 mg, 0.087 mmol) and 2,2'-bipyridine (32 mg, 0.21 mmol). The flask was attached to a reflux condenser and the contents were placed under an inert atmosphere by three evacuation/purge cycles. The reaction components were dissolved in degassed ethylene glycol (6 mL) and heated with stirring at 150 °C for 24 h. Upon cooling to rt, the reaction mixture was diluted with deionized H_2O and transferred to a separatory funnel. The aqueous phase was washed three times with hexanes, then drained into an Erlenmeyer flask and heated to ~85 °C for 5-15 min to remove

[2] Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem*. *Mater*. **2005**, *17*, 5712.

residual hexanes. Upon cooling to rt, an aq soln of NH_4PF_6 (10 mL, 0.1 g/mL) was added, resulting in the formation of a fine yellow precipitate that was isolated by vacuum filtration and then washing with H_2O (20 mL) and hexanes (15 mL). The solid was dried under high vacuum to remove residual H_2O and then dissolved in acetone and recrystallized by vapor diffusion with hexane to yield **1** as large yellow crystals (172 mg, 88%). mp = 199-202 °C. Characterization data for this compound matched that reported in the literature.[3]

Selected reaction optimization studies



Procedure for reaction screening at 0.10 or 0.05 mmol scale: To a reaction vial equipped with a Teflon coated magnetic stir bar in a glovebox was added a soln of nickel source and ligand (1:1) dissolved in THF. The solvent was removed *in vacuo* under an inert atmosphere. Additives were weighed into the vials (liquid additives were added after the stock solution). A stock solution of aryl bromide, secondary alkyltrifluoroborate, Ir catalyst **1**, and internal standard were then added by syringe and stirred for 16-24 h in front of a single 26 W CFL. Aliquots were then taken, diluted, and analyzed by HPLC or GC/MS. Reactions were compared within sets by crude product to internal standard (P/IS) ratios.

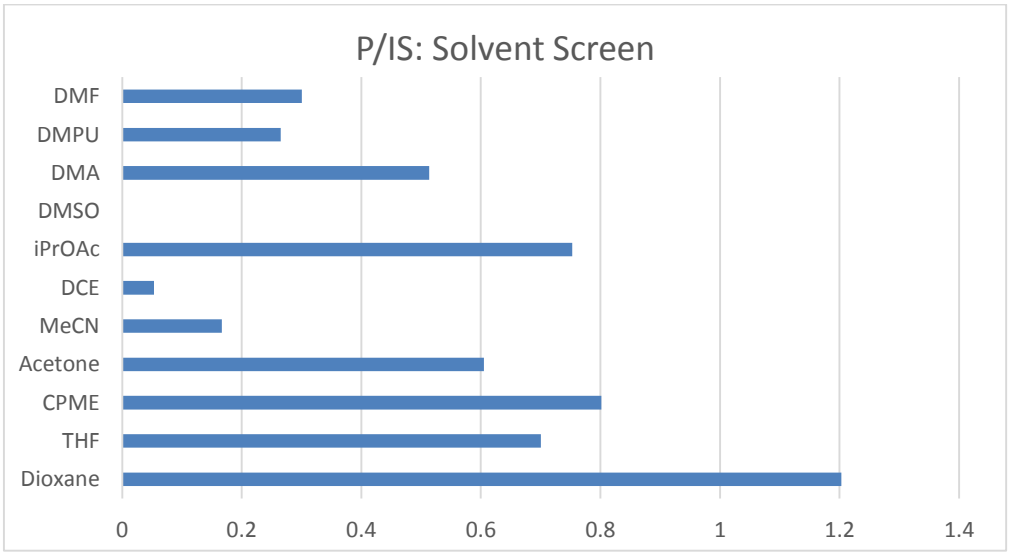


Figure S1: Comparison of Solvents
Conditions: 0.1 mmol Ar-Br, 1.5 equiv RBF_3K, 2.0 % $Ir(dFCF_3ppy)_2bpy\ PF_6$, 10.0 % Ni/dtbbpy, K_2CO_3 (1.0 equiv), 0.05 M in solvent

[3] Hanss, D.; Freys, J. C.; Bernardinelli, G.; Wenger, O. S. *Eur. J. Inorg. Chem.* **2009**, *2009*, 4850.

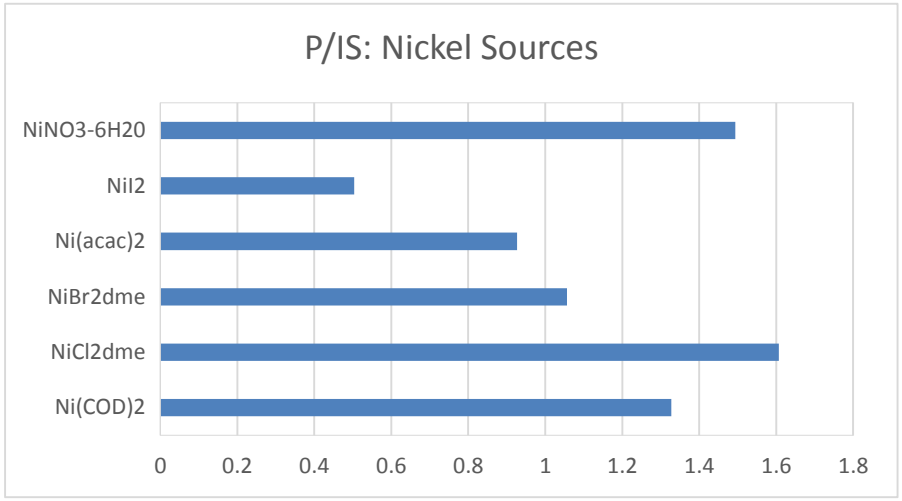


Figure S2: Nickel Sources
Conditions: 0.1 mmol Ar-Br, 1.5 equiv RBF_3K, 2.0% $Ir(dFCF_3ppy)_2bpy\ PF_6$, 10.0 % Ni source/dtbbpy, K_2CO_3 (1.0 equiv), 0.05 M in dioxane

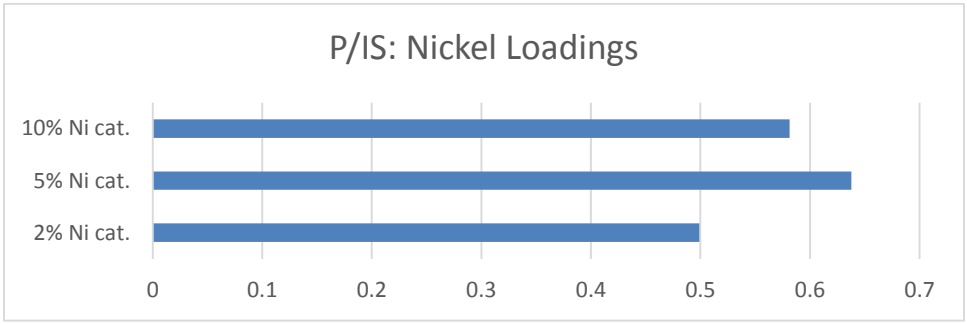


Fig. S3: Nickel Loadings
Conditions: 0.1 mmol Ar-Br, 1.5 equiv RBF_3K, 2.0% $Ir(dFCF_3ppy)_2bpy\ PF_6$, 1.5 equiv K_2CO_3 0.05 M in dioxane

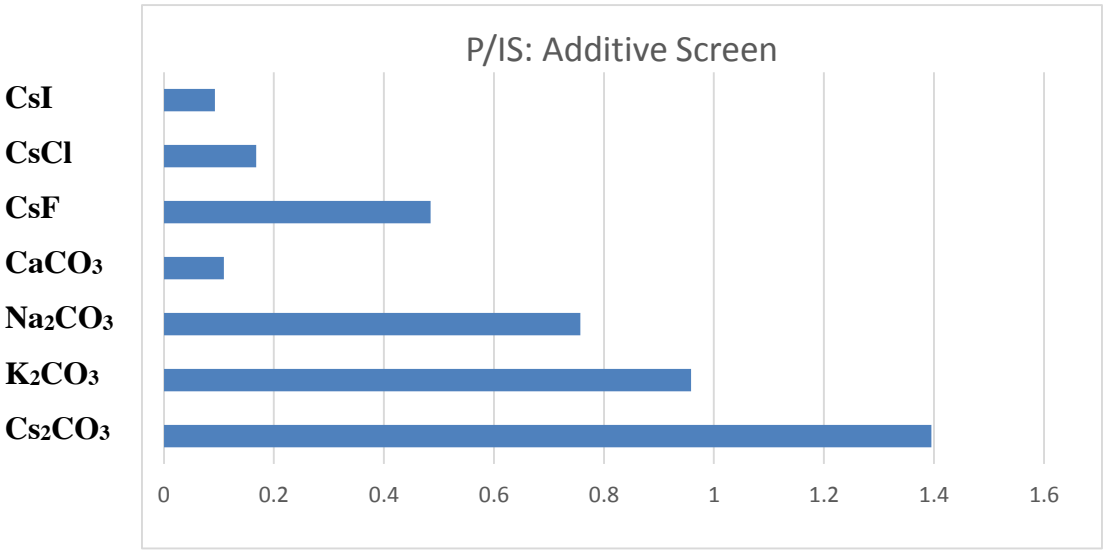
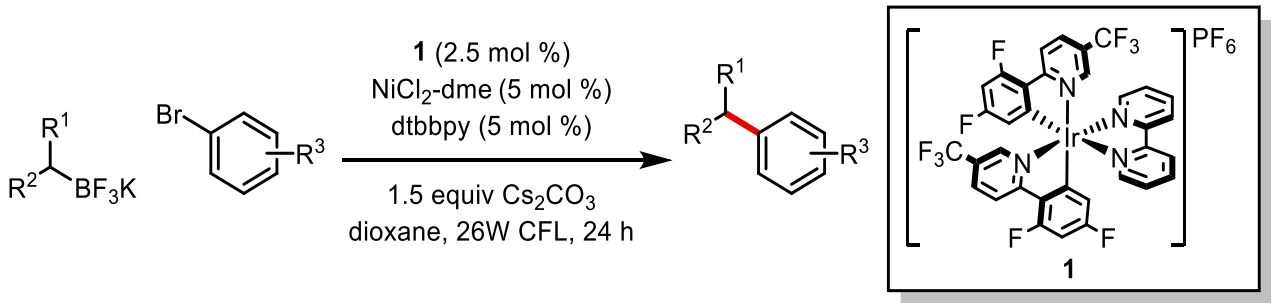


Figure S4: Comparison of Carbonate Bases and Cesium Salts
Conditions: 0.1 mmol Ar-Br, 1.5 equiv RBF_3K, 2.5% $Ir(dFCF_3ppy)_2bpy\ PF_6$, 5.0% Ni/dtbbpy, 1.5 equiv additive, 0.05 M in dioxane

General procedure for photoredox cross-coupling reactions



To a long, thin (~20 mL) borosilicate glass vial equipped with a Teflon-coated magnetic stir bar was added 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.7 mg, 0.025 mmol) and $NiCl_2$•dme (5.5 mg, 0.025 mmol) and 1.0 mL THF. The vial was capped and the resulting suspension was heated briefly with a heat gun until the nickel and ligand were fully solubilized, yielding a pale green solution. The solvent was then removed under vacuum to give a fine coating of the ligated nickel complex (pale evergreen in color). Once dry, aryl bromide (0.5 mmol, 1 equiv) (liquid aryl bromides were added with solvent), secondary alkyltrifluoroborate (0.75 mmol, 1.5 equiv), $Ir[dFCF_3ppy]_2(bpy)PF_6$ **1** (12.8 mg, 0.025 mmol) and Cs_2CO_3 (243 mg, 0.75 mmol) were added in succession. The vial was then capped and purged and evacuated four times. Under inert atmosphere, dioxane (10 mL) was introduced. The vial containing all the reagents was further sealed with parafilm and stirred for 24 hours approximately 4 cm away from two 26 W fluorescent light bulbs. A fan was blown across the reaction setup to maintain an ambient temperature around 24 °C. After 16-24 h, an aliquot was taken and analyzed on a GC/MS to monitor reaction completion and confirm formation of a single regioisomer (when applicable). Then, the crude reaction mixture was filtered through an approximately 2 cm x 2 cm cylindrical plug of Celite, washing with EtOAc (10–20 mL). The resulting solution was concentrated and the residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain products in pure form.

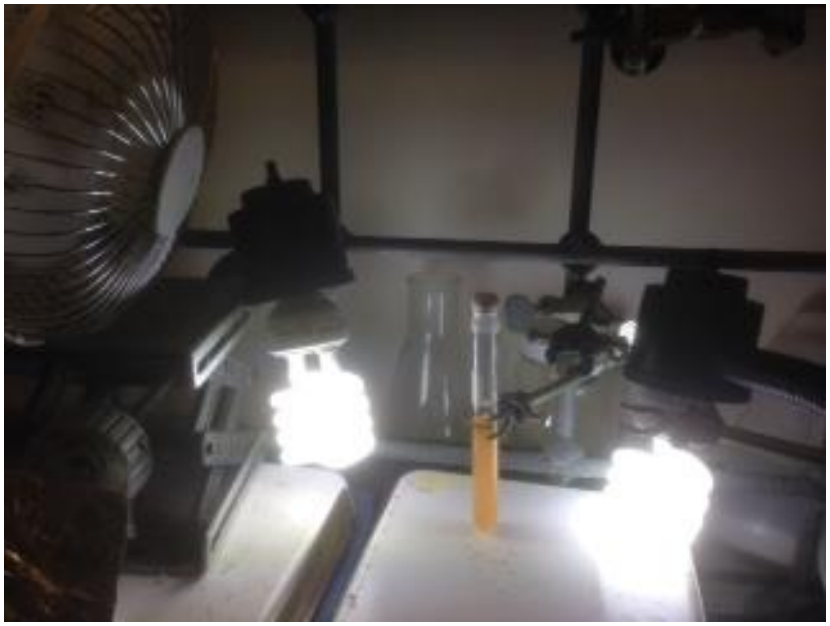


Fig S5: Photoredox cross-coupling reaction set-up (0.5 mmol scale)

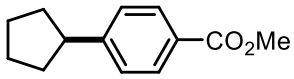
Gram scale reaction: To a ~125 mL long thin-walled vacuum flask equipped with a Teflon-coated magnetic stir bar was added $NiCl_2$•dme (20 mg, 0.093 mmol, 0.02 equiv) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (25 mg, 0.093, 0.02 equiv) and 5.0 mL of THF. The vial was capped and the resulting suspension was heated briefly with a heat gun until the nickel and ligand were fully solubilized, yielding a pale green solution. The solvent was then removed under vacuum to give a fine coating of the ligated nickel complex (pale evergreen in color). Once dry, methyl 4-bromobenzoate (1.000 g, 4.65 mmol, 1.00 equiv), potassium cyclohexyltrifluoroborate (1.325 g, 6.98 mmol, 1.50 equiv), $Ir[dFCF_3ppy]_2(bpy)PF_6$ **1** (47.0 mg, 0.047 mmol, 0.01 equiv), and Cs_2CO_3 (2.267 g, 6.98 mmol, 1.50 equiv) was added. The vial was then capped with a rubber septum and purged and evacuated four times. Under inert atmosphere, dioxane (95 mL, 0.05 M) was introduced. The vial containing all the reagents was further sealed with parafilm and stirred vigorously (a small vortex should be observed toward the top of the reaction mixture) for 36 h approximately 4 cm away from three 26 W fluorescent light bulbs. A fan was blown across the reaction setup to maintain an ambient temperature around 24 ^oC. After completion, the crude reaction mixture was filtered through an approximately 4 cm x 2 cm cylindrical plug of Celite, washing with EtOAc (60 mL). The resulting solution was concentrated and the residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain product in pure form.

Fig S6: Gram scale photoredox cross-coupling reaction set-up (4.65 mmol)

Compound Characterization Data

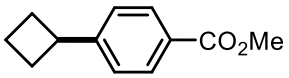
13

Methyl 4-cyclohexylbenzoate (**13**): obtained as a white crystalline solid (76 mg, 70%), on gram (4.65 mmol) scale (740 mg, 73%), mp = 38-40 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.58-2.54 (m, 1H), 1.87 (m, 4H), 1.77 (d, *J* = 12.5 Hz, 1 H), 1.48-1.31 (m, 4H), 1.29-1.25 (m, 1H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.1, 153.4, 129.6, 127.7, 126.8, 51.8, 44.6, 34.0, 26.7, 26.0
IR: ν = 2926, 2852, 1720, 1436, 1276, 1180, 1112, 1101, 1019, 762, 706 cm^{-1}
HRMS (ESI) m/z calc. for $C_{14}H_{18}O_2Na$ (M+Na) 241.1204, found 241.1214



14

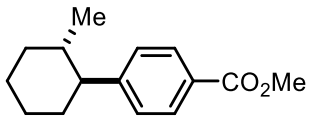
Methyl 4-cyclopentylbenzoate (**14**): obtained as a white amorphous solid (94 mg, 92%), mp = 32-33 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 3.04 (q, *J* = 8.5 H, 1H), 2.08 (m, 2H), 1.82-1.59 (m, 6H) – a small amount of methyl 4-bromobenzoate (<5%) was inseparable from the starting material after column chromatography.
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.1, 152.1, 129.5, 127.6, 127.0, 51.8, 45.9, 34.4, 25.5
Characterization data matched that reported in the literature.[4]



15

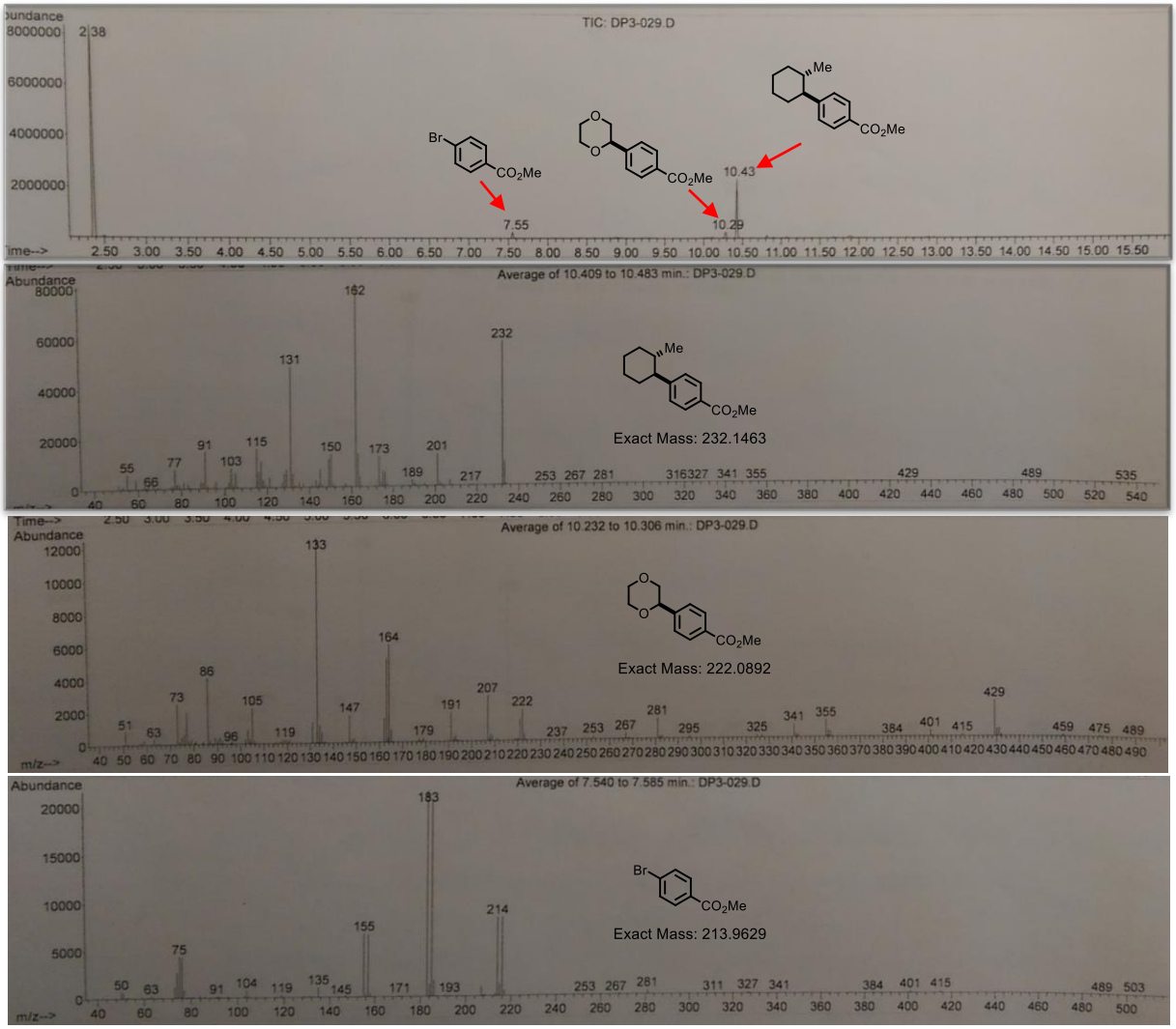
Methyl 4-cyclobutylbenzoate (**15**): obtained as a pale yellow oil (57 mg, 60%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (d, *J* = 8.5, 2H), 7.26 (d, *J* = 8.5, 2H) 3.90 (s, 3H), 3.59 (m, 1H), 2.39-2.34 (m, 2H), 2.20-2.00 (m, 3H), 1.90-1.84 (m, 1H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.3, 151.8, 129.7, 127.8, 126.4, 52.1, 40.4, 29.7, 18.4
IR: ν = 2951, 1721, 1609, 1435, 1276, 1108, 1020, 768, 646 cm^{-1}
HRMS (ESI) m/z calc. for $C_{12}H_{15}O_2$ (M+H) 191.1072, found 191.1065

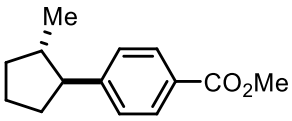
[4] Liu, Z.; Dong, N.; Xu, M.; Sun, Z.; Tu, T. *J*. *Org*. *Chem*. **2013**, *78*, 7436.



17

Methyl *trans*-4-(2-methylcyclohexyl)benzoate (17): obtained as a colorless oil (110 mg, 95%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, *J* = 8.0, 2H), 7.22 (d, *J* = 8.0, 2H), 3.89 (s, 3H), 2.16-2.11 (m, 1H), 1.84-1.76 (m, 4H), 1.64-1.58 (m, 1H), 1.46-1.32 (m, 3H), 1.12-1.10 (m, 1H), 0.64 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.1, 152.4, 129.6, 127.7, 127.5, 52.5, 51.8, 37.4, 35.5, 35.2, 26.7, 26.5, 20.6
IR: ν = 2924, 2853, 1722, 1609, 1435, 1276, 1180, 1112, 1102, 772, 708 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{21}O_2$ (M+H) 233.1542, found 233.1539
GCMS analysis of the reaction mixture after 16 hours confirms formation of a single regioisomer.





18

Methyl *trans*-4-(2-methylcyclopentyl)benzoate (18): obtained as a pale yellow oil (99 mg, 91%)

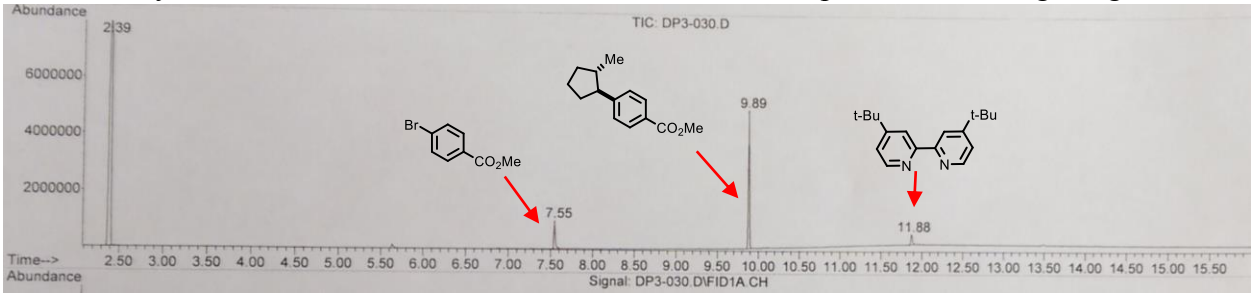
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (d, *J* = 8.0, 2H), 7.27 (d, *J* = 8.0, 2H), 3.90 (s, 3H), 2.50-2.44 (m, 1H) 2.10-2.08 (m, 1H), 2.00-1.92 (m, 2H), 1.78-1.71 (m, 3H), 1.34-1.30 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H)

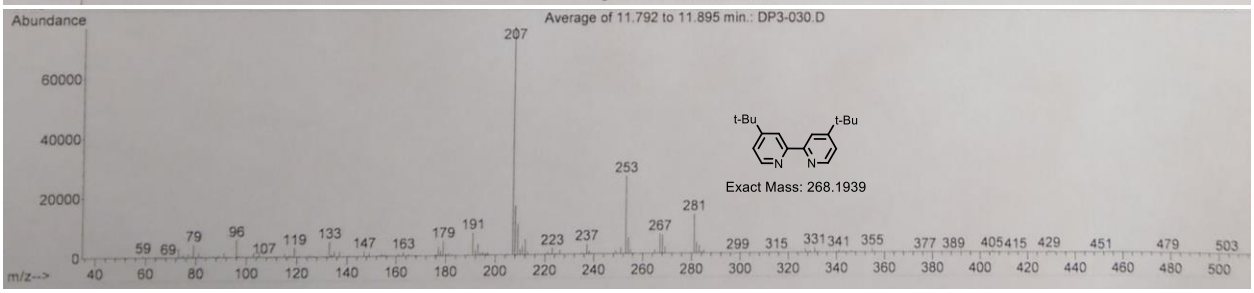
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.3, 151.4, 129.8, 128.0, 127.7, 54.7, 52.1, 43.4, 35.4, 34.9, 24.1, 18.6

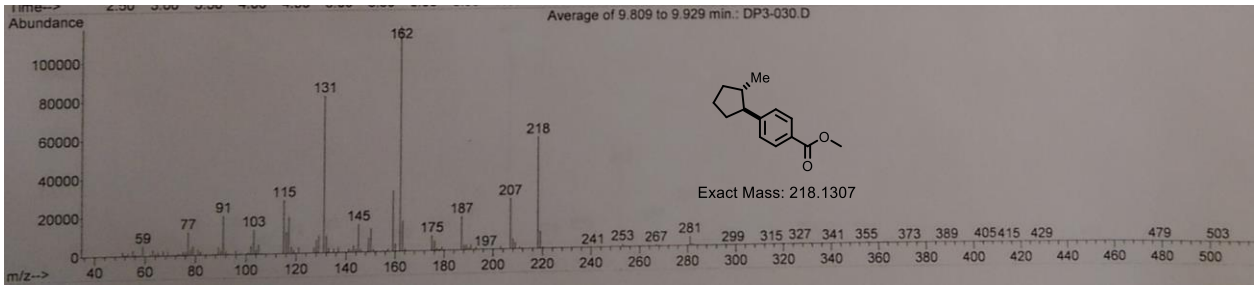
IR: ν = 2951, 2868, 1723, 1610, 1435, 1278, 1179, 1112, 770 cm^{-1}

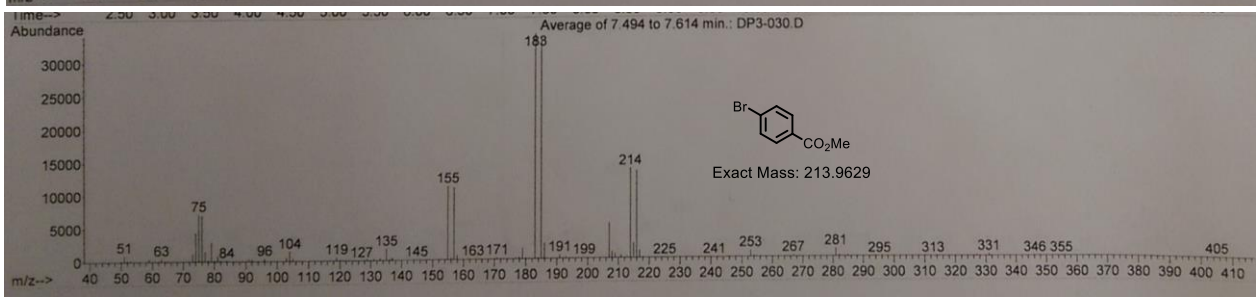
HRMS (ESI) m/z calc. for $C_{14}H_{19}O_2$ (M+H) 219.1385, found 219.1394

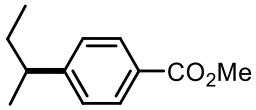
GCMS analysis of the reaction mixture after 16 hours confirms presence of a single regioisomer





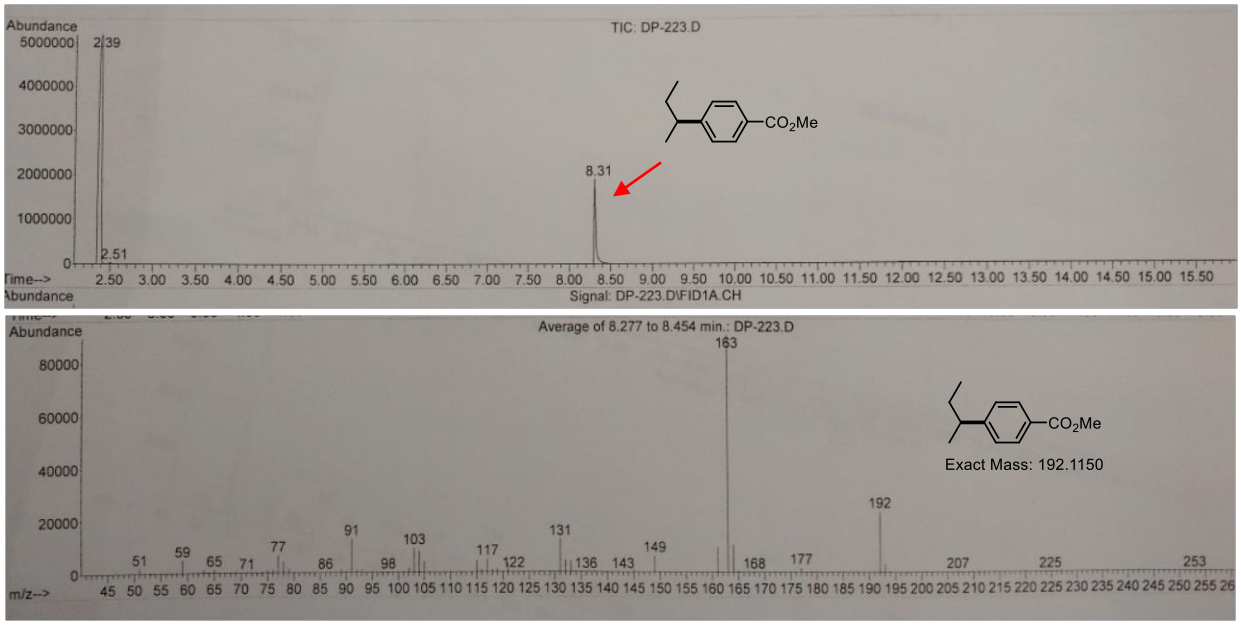




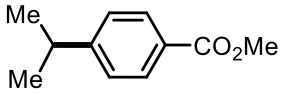


19

Methyl 4-(sec-butyl)benzoate (19): obtained as a colorless oil (73 mg, 76%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (m, 2H), 7.25 (m, 2H), 3.89 (s, 3H), 2.65 (m, 1H), 1.61 (m, 2H), 1.24 (m, 3H), 0.81 (m, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.3, 153.3, 129.8, 127.9, 127.2, 52.1, 41.9, 31.1, 21.7, 12.3
GCMS analysis of the reaction mixture after 24 hours confirms presence of a single regioisomer.



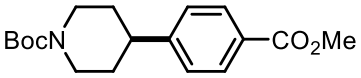
Characterization data matched that reported in the literature.[5]



20

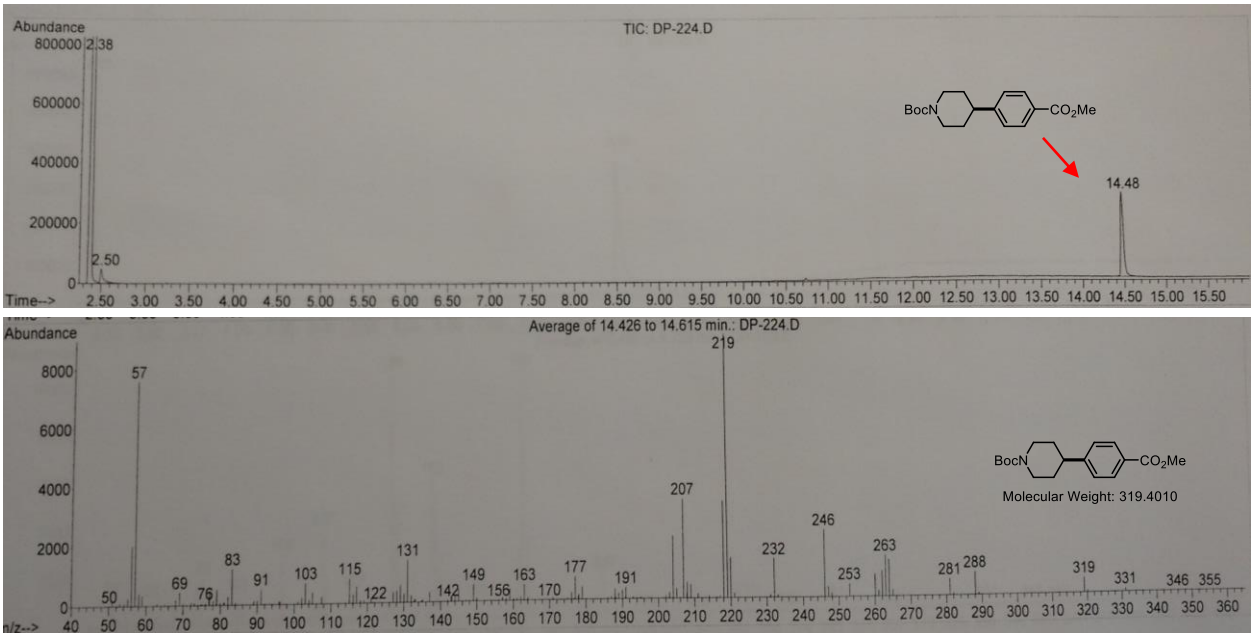
Methyl 4-isopropylbenzoate (20): obtained as a colorless oil (68 mg, 76%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H), 2.96 (sept, J = 7.0 Hz, 1H), 1.26 (d, J = 7.0 Hz, 6H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.3, 153.3, 129.8, 127.9, 127.2, 52.1, 41.9, 31.1, 21.7, 12.3p
Characterization data matched that reported in the literature.[6]

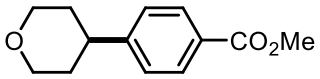
[5]Phapale, V. B.; Guisán-Ceinos, M.; Buñuel, E.; Cárdenas, D. J. *Chem. A Eur. J.* **2009**, *15*, 12681.
[6] Zhu, Y.; Yan, H.; Lu, L.; Liu, D.; Rong, G.; Mao, J. *J. Org. Chem.* **2013**, *78*, 9898.



21

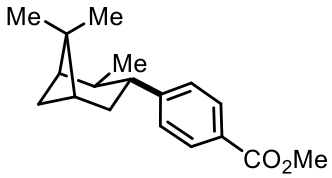
***tert*-Butyl 4-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (21)**: obtained as a white amorphous solid (147 mg, 92%), mp = 118-120 ºC
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.23 (bs, 2H), 3.87 (s, 3H), 2.80-2.65 (m, 3H), 1.81-1.78 (m, 2H), 1.62-1.58 (m, 2H), 1.46 (s, 9H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.1, 154.9, 151.2, 130.0, 128.4, 127.0, 79.7, 52.1, 44.3 (br), 42.9, 33.0, 28.6, 24.9
IR: ν = 2845, 1701, 1421, 1365, 1268, 1229, 1155, 1126, 1012, 770 cm^{-1}
HRMS (ESI) m/z calc. for $C_{18}H_{25}NO_4Na$ (M+Na) 342.1681, found 342.1685
GC analysis of the crude mixture after 24h confirms the formation of a single regioisomer.





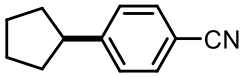
22

Methyl 4-(tetrahydro-2H-pyran-4-yl)benzoate (22): obtained as a white crystalline solid (91 mg, 83%), mp = 74-75 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.08 (d, *J* = 10.5 Hz, 2H), 3.89 (s, 3H), 3.52 (t, *J* = 11.5 Hz, 2H), 2.82-2.78 (m, 1H), 1.83-1.74 (m, 4H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.2, 151.2, 130.0, 128.4, 126.9, 68.3, 52.2, 41.8, 33.7
IR: ν = 2964, 2932, 2862, 1718, 1609, 1440, 1275, 1109, 1098, 1017, 764 cm^{-1}
HRMS (ESI) m/z calc. for $C_{13}H_{17}O_3$ (M+H) 221.1178, found 221.1179



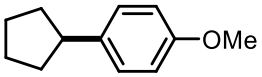
(±)-23

Methyl 4-((1R*,2R*,3R*,5R*)-3,6,6-trimethylbicyclo[3.1.1]heptan-2-yl)benzoate (23): obtained as a yellow oil (80 mg, 59%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H), 3.10-3.06 (m, 1H), 2.53-2.51 (m, 1H), 2.45-2.42 (m, 1H), 2.09-2.04 (m, 2H), 1.92-1.87 (m, 2H), 1.29 (s, 3H), 1.17-1.15 (m, 4H), 1.00 (d, *J* = 7.0 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.1, 154.8, 129.6, 128.3, 127.5, 51.8, 47.9, 45.6, 44.9, 41.7, 39.1, 37.2, 34.8, 28.4, 22.9, 20.8
IR: ν = 2950, 2904, 1723, 1610, 1434, 1278, 1112, 1019, 770, 707 cm^{-1}
HRMS (ESI) m/z calc. for $C_{18}H_{25}O_2$ (M+H) 273.1855, found 273.1850



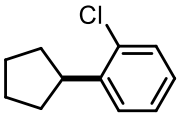
24

4-Cyclopentylbenzonitrile (24): obtained as a colorless oil (81 mg, 95%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.04 (q, *J* = 8.0 Hz, 1H), 2.10-2.08 (m, 2H), 1.84-1.81 (m, 2H), 1.73-1.70 (m, 2H), 1.60-1.57 (m, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 152.5, 132.2, 128.1, 119.4, 109.6, 46.1, 34.6, 25.7
IR: ν = 2955, 2869, 2227, 1607, 1504, 1451, 1416, 1178, 830, 657 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{12}H_{13}N$ (M+) 171.1048, found 171.1044



25

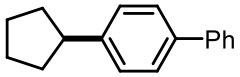
1-Cyclopentyl-4-methoxybenzene (25): obtained as a colorless oil (63 mg, 72%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.19 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 3.00-2.93 (m, 1H), 2.10-2.04 (m, 2H), 1.83-1.55 (m, 6H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 157.8, 138.7, 128.1, 113.8, 55.4, 45.3, 34.9, 25.6
IR: ν = 2950, 2866, 1612, 1513, 1463, 1245, 1178, 1033, 826 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{12}H_{16}O$ (M+) 176.1201, found 176.1199



26

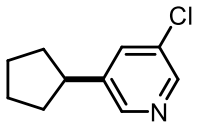
1-Chloro-2-cyclopentylbenzene (26): obtained as a yellow oil (80 mg, 89%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36-7.22 (m, 2H), 7.13-7.10 (m, 2H), 3.46 (q, *J* = 9 Hz, 1H), 2.16-2.07 (m, 2H), 1.83-1.72 (m, 4H), 1.59-1.57 (m, 2H)

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 143.8, 134.3, 129.5, 127.2, 127.0, 126.9, 42.3, 33.3, 25.6
IR: ν = 2951, 2868, 1475, 1442, 1355, 1035, 744 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{11}H_{13}Cl$ (M+) 180.0706, found 180.0711



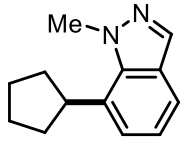
27

4-Cyclopentyl-1,1'-biphenyl (27): obtained as a pale yellow semi-solid (98 mg, 88%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67-7.65 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.51-7.48 (m, 2H), 7.41-7.38 (m, 3H) 3.11 (q, *J* = 7.5 Hz, 1H), 2.19-2.17 (m, 2H), 2.00-1.90 (m, 2H) 1.80-1.70 (m, 4H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 145.9, 141.4, 138.9, 129.0, 127.8, 127.23, 127.22, 127.17 45.9, 34.9, 25.8
IR: ν = 2952, 2869, 1598, 1486, 831, 764, 735, 698 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{17}H_{18}$ (M+) 222.1409, found 222.1406



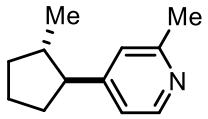
28

3-Chloro-5-cyclopentylpyridine (28): obtained as a pale yellow oil (80 mg, 88%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.39 (d, *J* = 2.5 Hz, 1H), 8.37 (d, *J* = 1.5 Hz, 1H), 7.53-7.52 (dd, *J* = 2.5, 1.5 Hz, 1H), 3.00 (m, 1H), 2.13-2.10 (m, 2H), 1.85-1.83 (m, 2H), 1.75-1.69 (m, 2H), 1.59-1.52 (m, 2H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 146.9, 146.0, 143.0, 134.0, 131.7, 42.8, 34.2, 25.3
IR: ν = 2954, 2868, 2361, 1580, 1440, 1420, 1295, 1233, 1107, 1022, 935, 879, 709 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{10}H_{13}NCl$ (M+H) 182.0737, found 182.0740



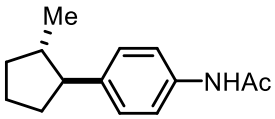
29

7-Cyclopentyl-1-methyl-1H-indazole (28): obtained as a dark yellow oil (80 mg, 80%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (s, 1H), 7.35-7.32 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 4.07 (s, 3H), 3.46 (m, 1H), 2.22-2.18 (m, 2H), 1.90-1.78 (m, 6H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 140.2, 140.0, 131.7, 126.3, 123.5, 116.8, 106.4, 43.6, 35.5, 33.6, 25.6
IR: ν = 2950, 2868, 1606, 1508, 1447, 1272, 1237, 982, 783, 740 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{13}H_{17}N_2$ (M+H) 201.1392, found 201.1390



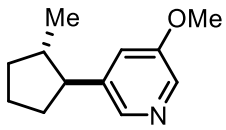
30

***trans*-2-Methyl-4-(2-methylcyclopentyl)pyridine (30)**: obtained as a yellow oil (62 mg, 71%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36 (d, *J* = 5.0 Hz, 1H), 6.97 (s, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 2.51 (s, 3H), 2.35 (m, 1H), 2.07-1.90 (m, 3H), 1.77-1.67 (m, 3H), 1.33-1.28 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 158.3, 155.1, 149.1, 122.6, 120.2, 53.9, 42.9, 34.9, 24.6, 24.1, 18.6
IR: ν = 2934, 2837, 1698, 1611, 1512, 1247, 1173, 1096, 1034, 818 cm^{-1}
HRMS (ESI) m/z calc. for $C_{12}H_{18}N$ (M+H) 176.1439, found 176.1439



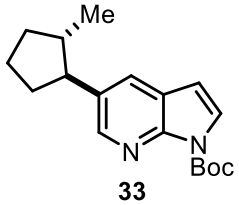
31

***trans*-*N*-(4-(2-Methylcyclopentyl)phenyl)acetamide (31)**: obtained as a white crystalline solid (90 mg, 83%), mp = 118-124 °C
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (br s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.37 (q, *J* = 9.0 Hz, 1H), 2.15 (s, 3H), 2.05-1.72 (m, 6H), 1.31-1.27 (m, 1H), 0.90 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 168.6, 141.7, 135.8, 128.0, 120.3, 54.2, 43.2, 35.5, 34.8, 24.6, 23.9, 18.7
IR: ν = 3246, 3123, 2946, 2865, 1661, 1610, 1557, 1512, 1413, 1369, 1327, 826 cm^{-1}
HRMS (ESI) m/z calc. for $C_{14}H_{20}NO$ (M+H) 218.1545, found 218.1545



32

***trans*-3-Methoxy-5-(2-methylcyclopentyl)pyridine (32)**: obtained as a yellow oil (61 mg, 64%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12 (d, *J* = 2.5 Hz, 1H), 8.07 (m, 1H), 7.02-7.01 (m, 1H), 3.84 (s, 3H), 2.43-2.38 (m, 1H), 2.09-2.07 (m, 1H), 2.00-1.98 (m, 1H), 1.94-1.89 (m, 1H), 1.76-1.69 (m, 3H), 1.31-1.29 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 155.8, 142.2, 141.6, 134.8, 119.6, 55.6, 51.7, 43.2, 35.3, 34.8, 24.0, 18.5
IR: ν = 2953, 2868, 1587, 1454, 1427, 1318, 1296, 1176, 1164, 1049, 867, 714 cm^{-1}
HRMS: (ESI) m/z calc. for $C_{12}H_{18}NO$ (M+H) 192.1388, found 192.1386



33

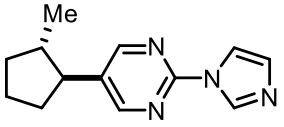
***tert*-Butyl *trans*-5-(2-methylcyclopentyl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate (33)**: obtained as a yellow oil (115 mg, 77%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.34 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 4.0 Hz, 1H), 6.43 (d, *J* = 4.0Hz, 1H), 2.53-2.47 (m, 1H), 2.12-2.10 (m, 1H), 2.02-1.90 (m, 2H), 1.81-1.72 (m, 3H), 1.65 (s, 9H), 0.90 (d, *J* = 6.5 Hz, 3H)

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 148.2, 147.4, 145.5, 135.4, 127.4, 126.7, 123.1, 104.5, 83.9, 52.0, 43.6, 35.7, 34.8, 28.3, 23.9, 18.4

IR: ν = 2951, 2868, 1757, 1728, 1532, 1472, 1398, 1356, 1318, 1253, 1145, 1092, 730 cm^{-1}

HRMS (ESI) m/z calc. for $C_{19}H_{25}N_2O_2$ (M+H) 301.1916, found 301.1905



34

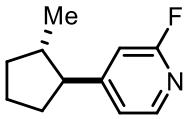
***trans*-2-(1H-Imidazol-1-yl)-5-(2-methylcyclopentyl)pyrimidine (34)**: obtained as a dark yellow oil (79 mg, 69%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.63 (s, 1H), 8.52 (s, 2H), 7.88 (s, 1H), 7.17 (s, 1H), 2.48-2.42 (m, 1H), 2.20-2.13 (s, 1H), 2.10-2.03 (m, 1H), 1.98-1.92 (m, 1H), 1.87-1.71 (m, 3H), 1.42-1.34 (m, 1H), 0.98 (d, *J* = 6.5 Hz, 3H)

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 159.4, 157.6, 136.0, 135.6, 130.3, 116.4, 48.9, 43.0, 34.7, 34.4, 23.6, 18.2

IR: ν = 3127, 2947, 2866, 1568, 1477, 1450, 1314, 1097, 931, 795, 754, 651 cm^{-1}

HRMS (ESI) m/z calc. for $C_{13}H_{17}N_4$ (M+H) 229.1453, found 229.1453



35

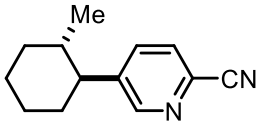
***trans*-2-Fluoro-4-(2-methylcyclopentyl)pyridine (35)**: obtained as a pale yellow oil (70 mg, 78%)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (d, *J* = 5.0 Hz, 1H), 7.01-6.99 (m, 1H), 6.75 (s, 1H), 2.49-2.43 (m, 1H), 2.15-2.08 (m, 1H), 2.04-1.89 (m, 2H), 1.83-1.65 (m, 3H), 1.37-1.29 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H)

^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 164.1 (d, *J* = 237.7 Hz), 160.9 (d, *J* = 7.4 Hz), 147.2 (d, *J* = 15.4 Hz), 120.6 (d, *J* = 3.6 Hz), 108.0 (d, *J* =36.6 Hz), 53.6 (d, *J* = 2.6 Hz), 42.9, 34.7, 34.6, 23.9, 18.3

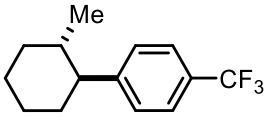
IR: ν = 2953, 2869, 1610, 1563, 1482, 1414, 1273, 996, 974, 832 cm^{-1}

HRMS (ESI) m/z calc. for $C_{11}H_{15}NF$ (M+H) 180.1189, found 180.1189



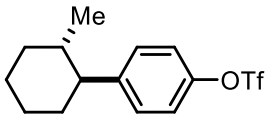
36

***trans*-5-(2-Methylcyclohexyl)picolinonitrile (36)**: Reaction was run on 0.40 mmol scale; obtained as a pale yellow oil (68 mg, 85%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.52 (s, 1H), 7.63-7.59 (m, 2H), 2.22-2.17 (m, 1H), 1.87-1.77 (m, 4H), 1.62-1.58 (m, 1H), 1.44-1.33 (m, 3H), 1.15-1.10 (m, 1H), 0.65 (d, J = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 151.3, 146.5, 135.6, 131.6, 128.5, 117.6, 50.1, 37.5, 35.5, 35.2, 26.6, 26.4, 20.7
IR: ν = 2925, 2854, 2234, 1566, 1470, 1024, 845, 652, 632 cm^{-1}
HRMS (ESI) m/z calc. for $C_{13}H_{17}N_2$ (M+H) 201.1392, found 201.1385



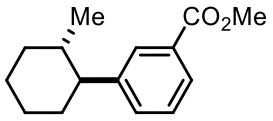
37

***trans*-1-(2-Methylcyclohexyl)-4-(trifluoromethyl)benzene (37)**: obtained as a colorless oil (90 mg, 74%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.17-2.12 (m, 1H), 1.82-177 (m, 4H), 1.61-1.57 (m, 1H), 1.45-1.35 (m, 3H), 1.13-1.10 (m, 1H), 0.65 (d, J = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 151.1, 128.2 (q, J = 32.1 Hz), 128.0, 125.3 (q, J = 3.9 Hz), 124.6 (q, J = 271.6 Hz), 52.6, 37.7, 35.7, 35.6, 26.9, 26.7, 20.8
^{19}F NMR ($CDCl_3$, 470 MHz): δ -62.2
IR: ν = 2928, 2858, 1618, 1325, 1163, 1124, 1069, 1020, 830 cm^{-1}
HRMS (ESI) m/z calc. for $C_{14}H_{17}F_3$ (M+) 242.1282, found 242.1283



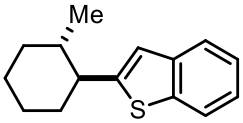
38

***trans*-4-(2-Methylcyclohexyl)phenyl trifluoromethanesulfonate (38)**: obtained as a colorless oil (120 mg, 75%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.22 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 2.14-2.09 (m, 1H), 1.85-1.78 (m, 4H), 1.60-1.53 (m, 1H), 1.44-1.35 (m, 3H), 1.13-1.06 (m, 1H), 0.65 (d, J = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 147.5, 147.3, 129.0, 120.9, 118.7 (q, J = 320.7 Hz), 51.8, 37.6, 35.5, 35.4, 26.7, 26.4, 20.5
^{19}F NMR ($CDCl_3$, 470 MHz): δ -72.9
IR: ν = 3339, 2970, 2929, 1426, 1379, 1213, 1142, 1131, 952, 883, 817 cm^{-1}
HRMS (ESI) m/z calc. for $C_{14}H_{16}O_3F_3S$ (M-H) 321.0772, found 321.0787



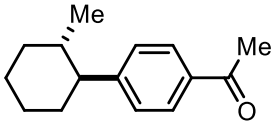
39

***trans*-Methyl 3-(2-methylcyclohexyl)benzoate (39)**: obtained as a colorless oil (100 mg, 86%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87-7.86 (m, 2H), 7.36-7.34 (m, 2H), 3.92 (s, 3H), 2.17-2.15 (m, 1H), 2.13-1.80 (m, 4H), 1.64-1.62 (m, 1H), 1.51-1.28 (m, 3H), 1.14-1.06 (m, 1H), 0.66 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 167.3, 147.1, 132.2, 130.0, 128.5, 128.2, 127.0, 52.3, 51.9, 37.5, 35.6, 35.5, 26.8, 26.5, 20.6
IR: ν = 2923, 2852, 1723, 1445, 1432, 1285, 1196, 1107, 1086, 752, 698 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{21}O_2$ (M+H) 233.1542, found 233.1553



40

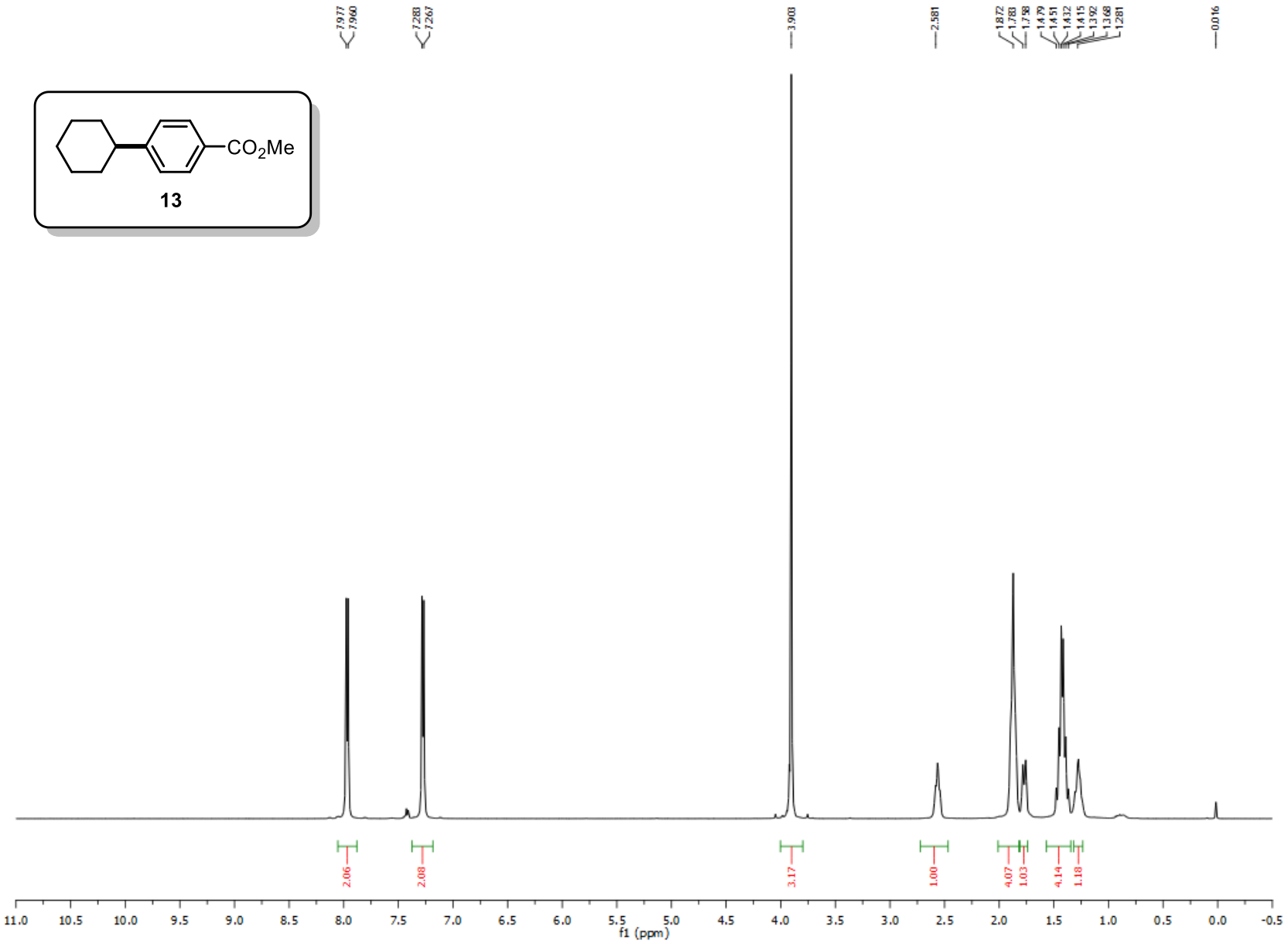
***trans*-2-(2-Methylcyclohexyl)benzo[b]thiophene (40)**: obtained as a colorless crystal (73 mg, 63%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.33-7.24 (m, 2H), 7.01 (s, 1H), 2.52-2.47 (m, 1H), 2.02 (dd, *J* = 3.0, 1.0 Hz, 1H), 1.85-1.78 (m, 3H), 1.60-1.36 (m, 4H), 1.15-1.13 (m, 1H), 0.83 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 152.1, 140.1, 139.0, 124.1, 123.4, 122.8, 122.4, 119.8, 48.4, 39.3, 36.8, 35.7, 26.9, 26.5, 21.0
IR: ν = 2923, 2851, 1445, 1443, 1309, 1128, 819, 744, 655, 636 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{19}S$ (M+H) 231.1207, found 231.1208



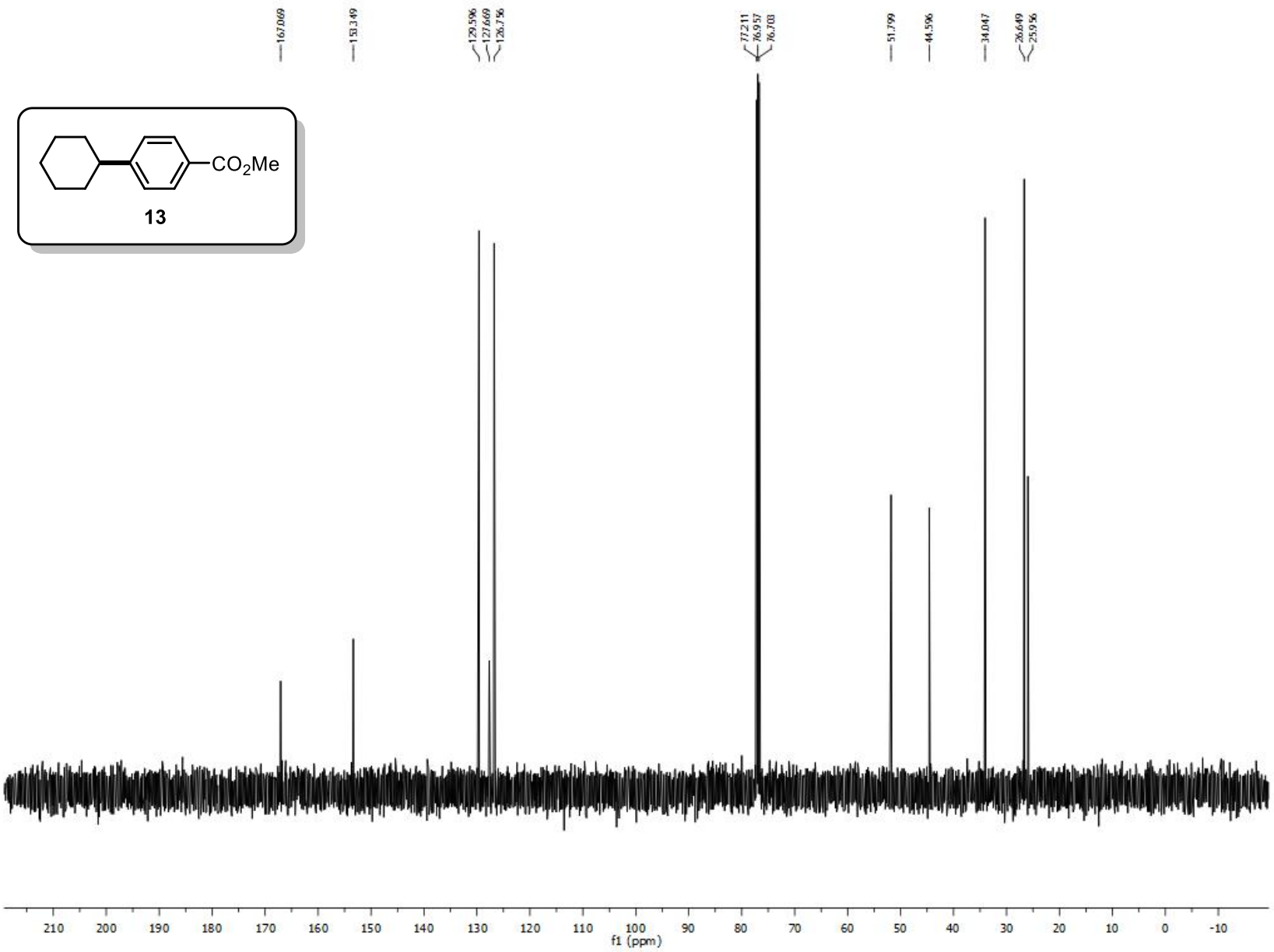
41

***trans*-1-(4-(2-Methylcyclohexyl)phenyl)ethan-1-one (41)**: obtained as a colorless oil (89 mg, 82%)
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78-7.77 (m, 2H), 7.38-7.37 (m, 2H), 2.61 (s, 3H), 2.19-2.14 (m, 1H), 1.86-1.78 (m, 4H), 1.65-1.62 (m, 1H), 1.49-1.27 (m, 3H), 1.14-1.08 (m, 1H), 0.66 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 198.4, 147.4, 137.1, 132.4, 128.4, 127.1, 126.0, 52.3, 37.5, 35.6, 35.5, 26.8, 26.6, 26.5, 20.6
IR: ν = 2922, 2853, 1685, 1600, 1444, 1359, 1266, 1229, 1186, 799, 698 cm^{-1}
HRMS (ESI) m/z calc. for $C_{15}H_{21}O$ (M+H) 217.1592, found 217.1586

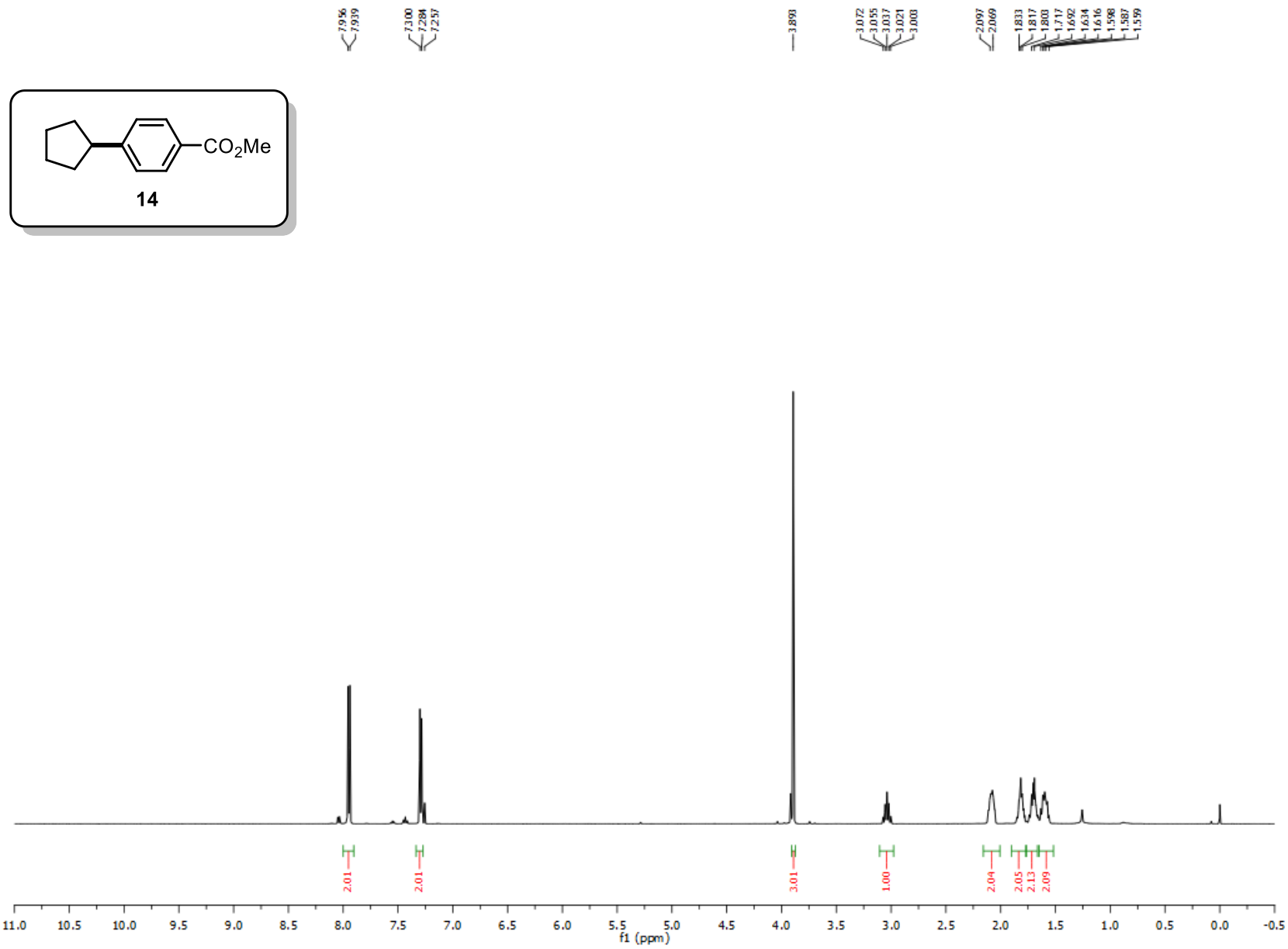
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-cyclohexylbenzoate (**13**)



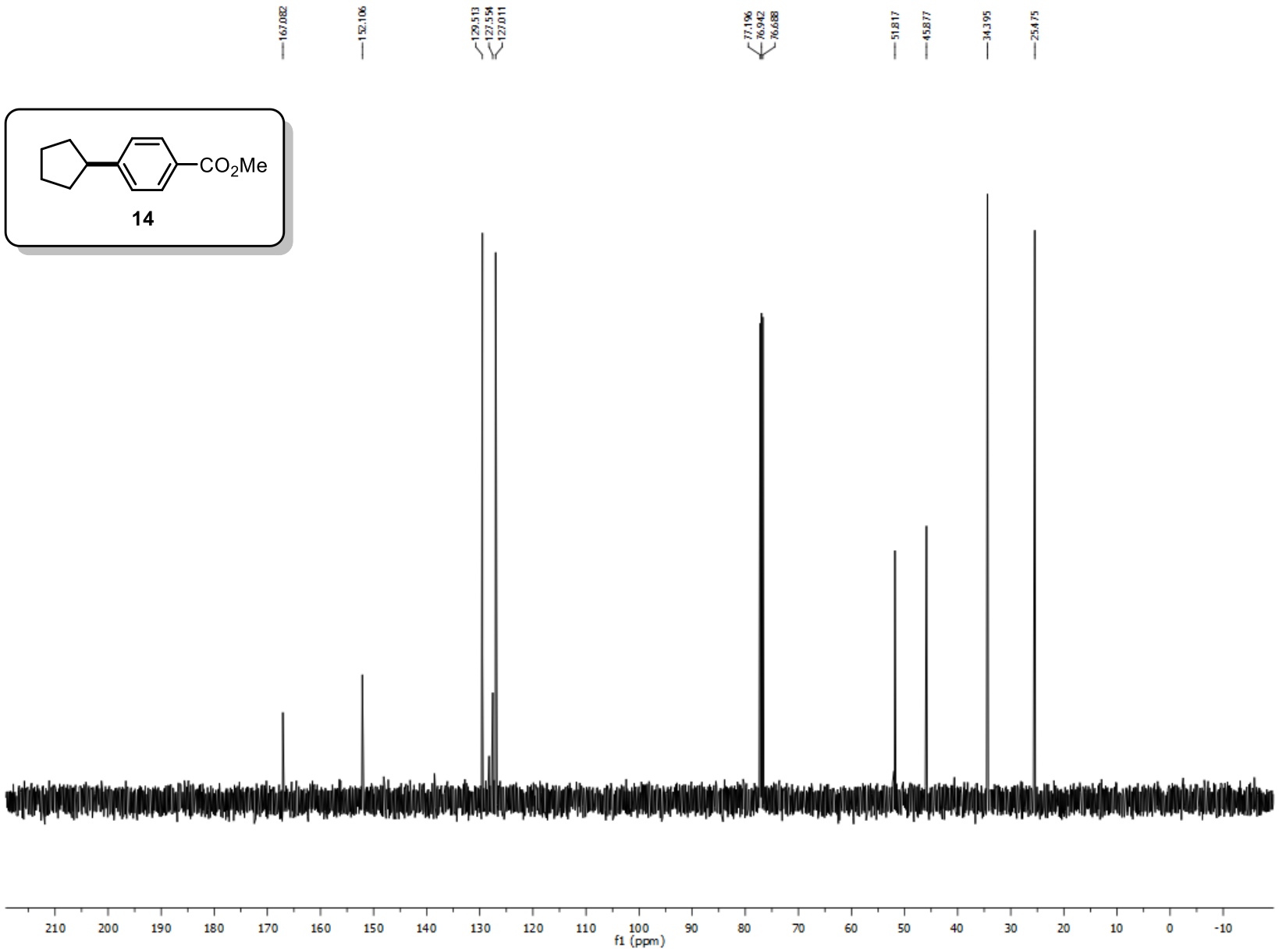
^{13}C NMR ($CDCl_3$, 125.8 MHz) methyl 4-cyclohexylbenzoate (**13**)



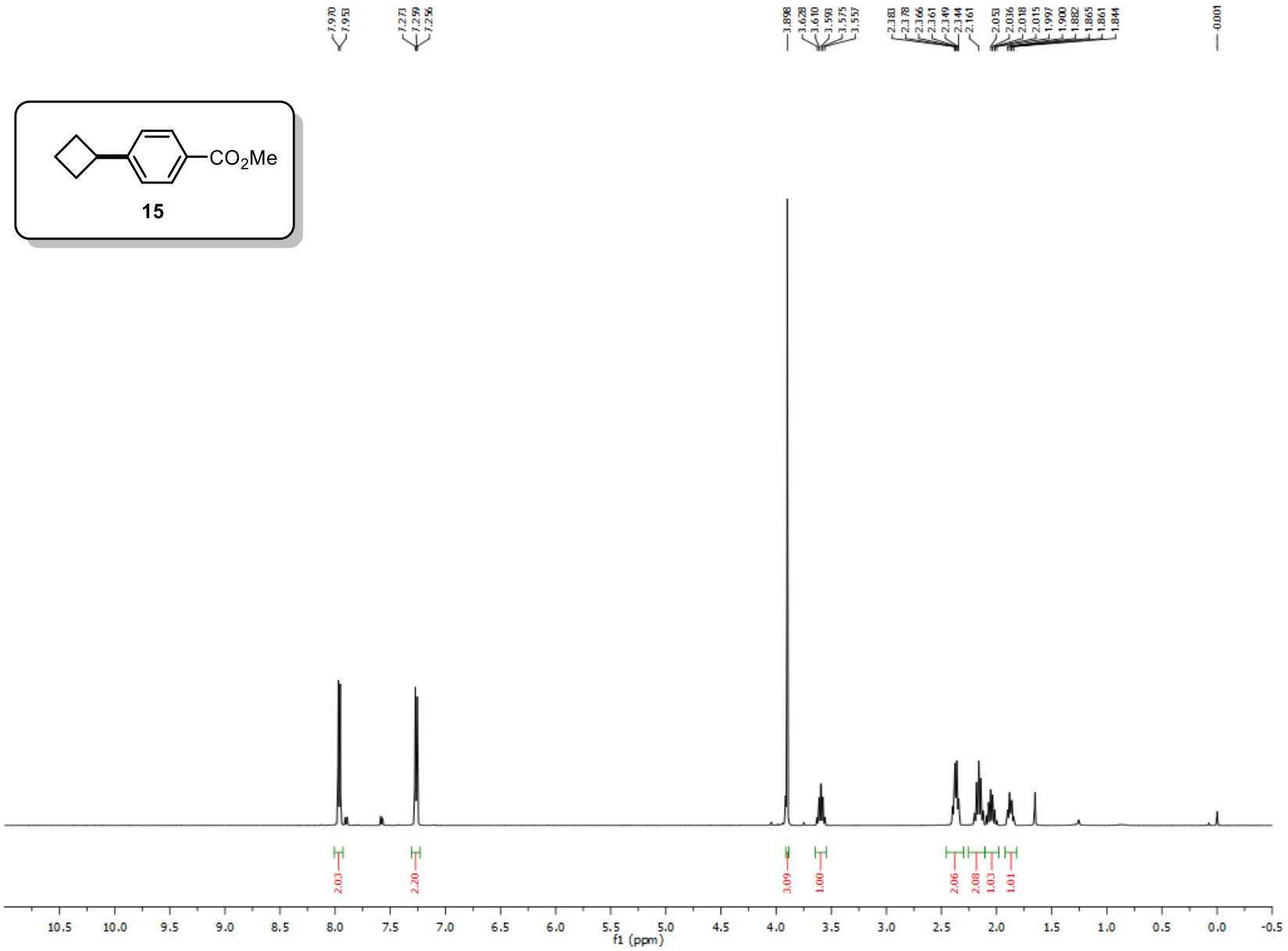
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-cyclopentylbenzoate (**14**)



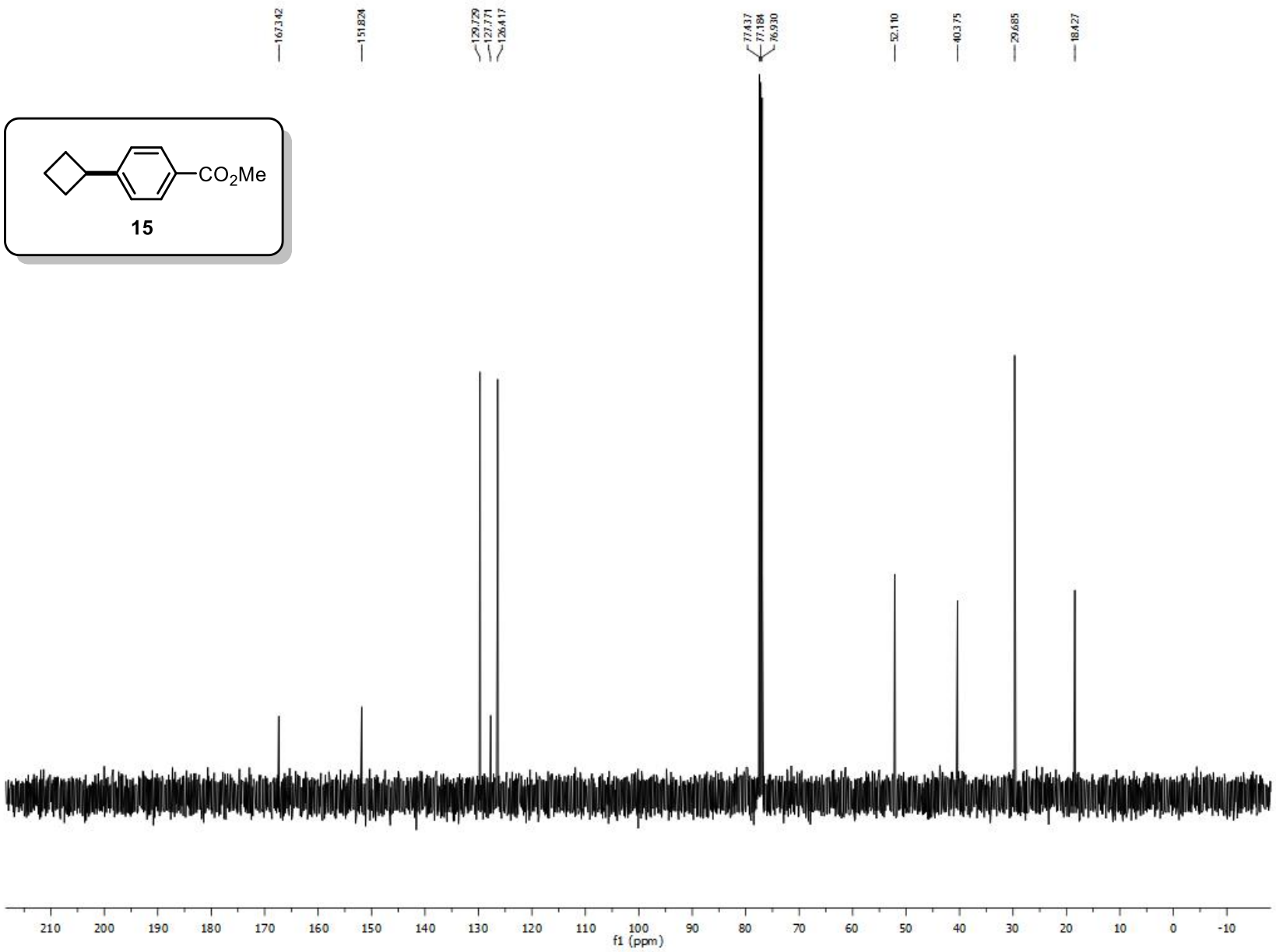
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-cyclopentylbenzoate (**14**)



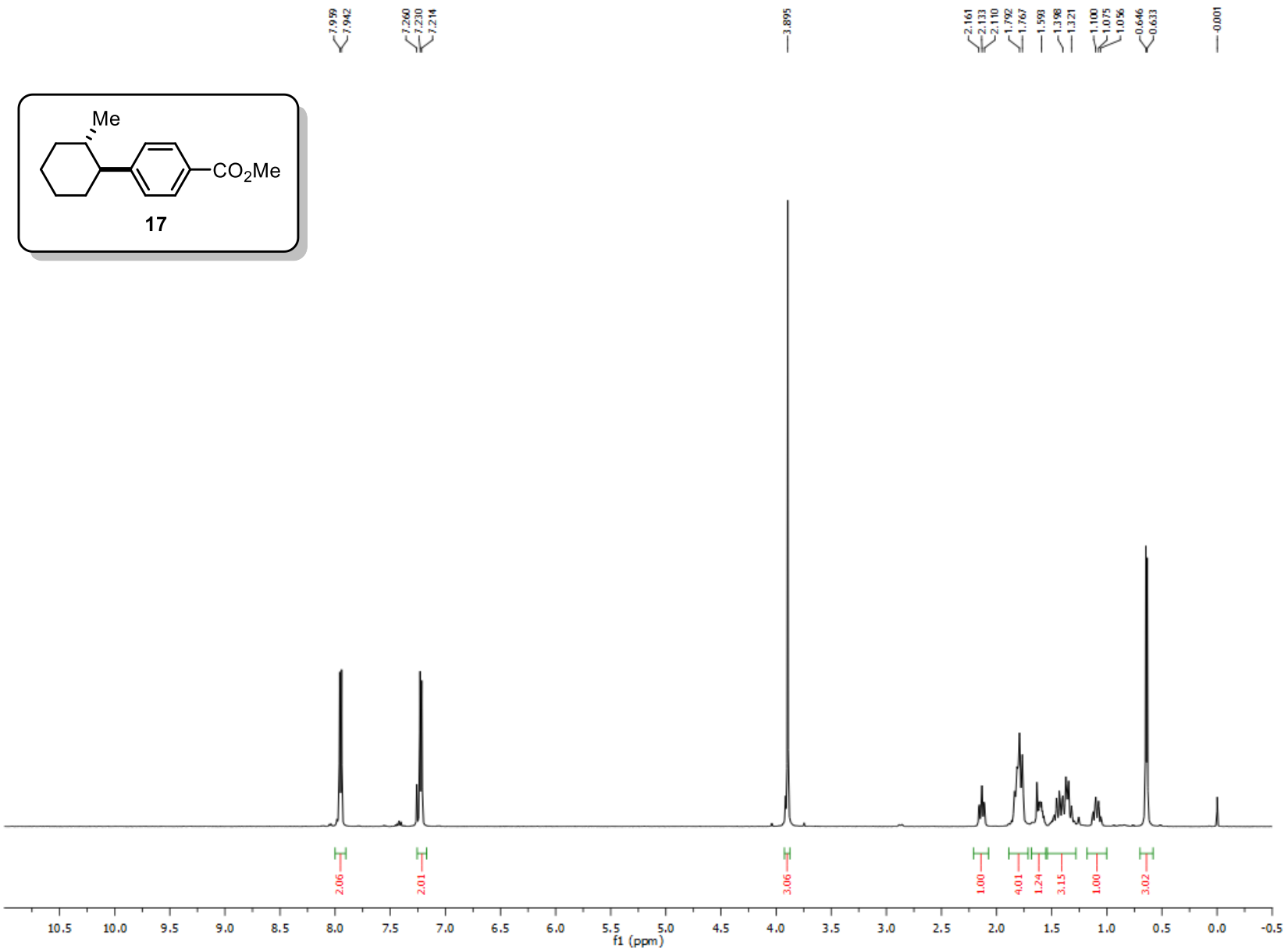
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-cyclobutybenzoate (**15**)



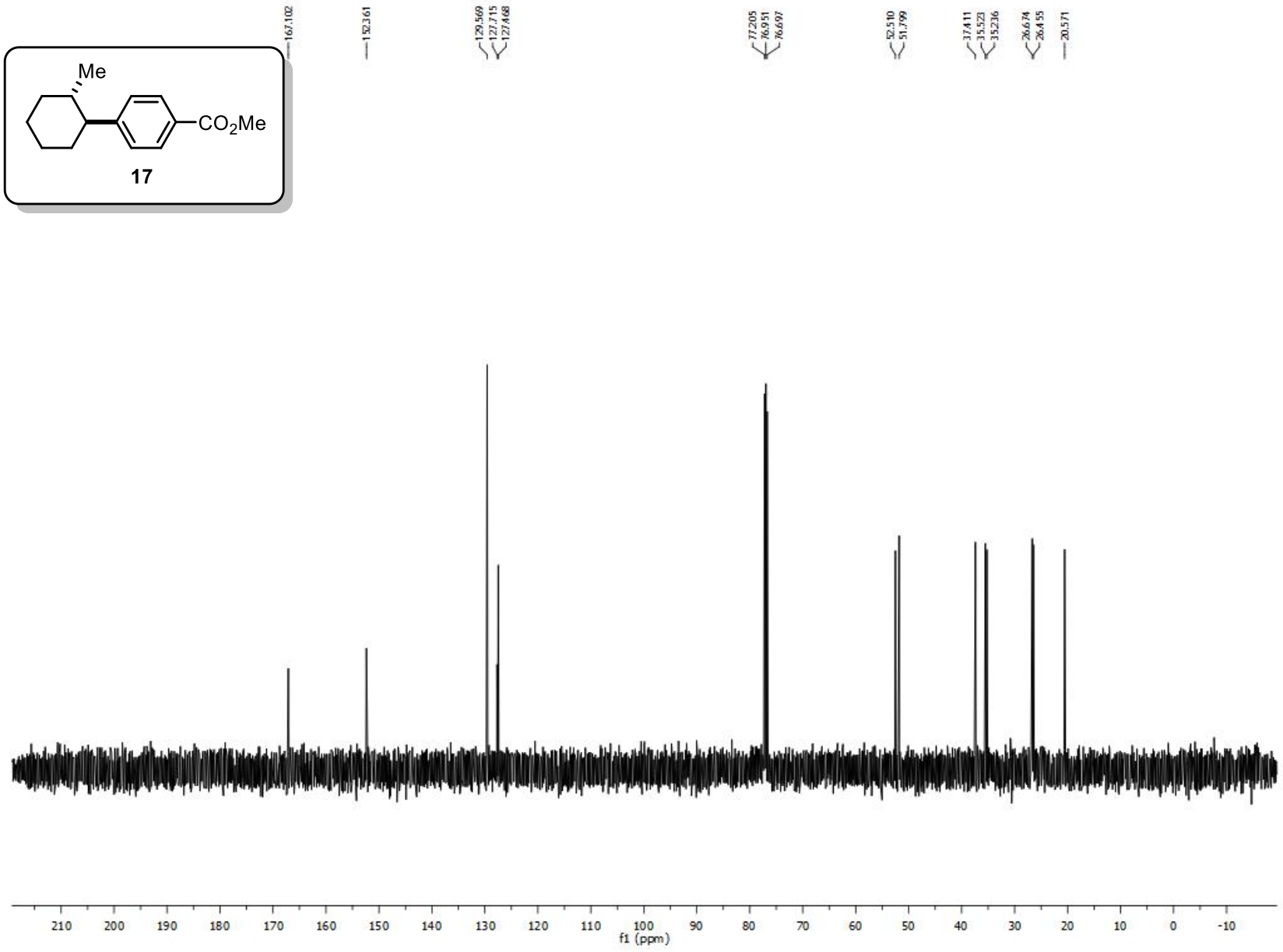
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-cyclobutylbenzoate (**15**)



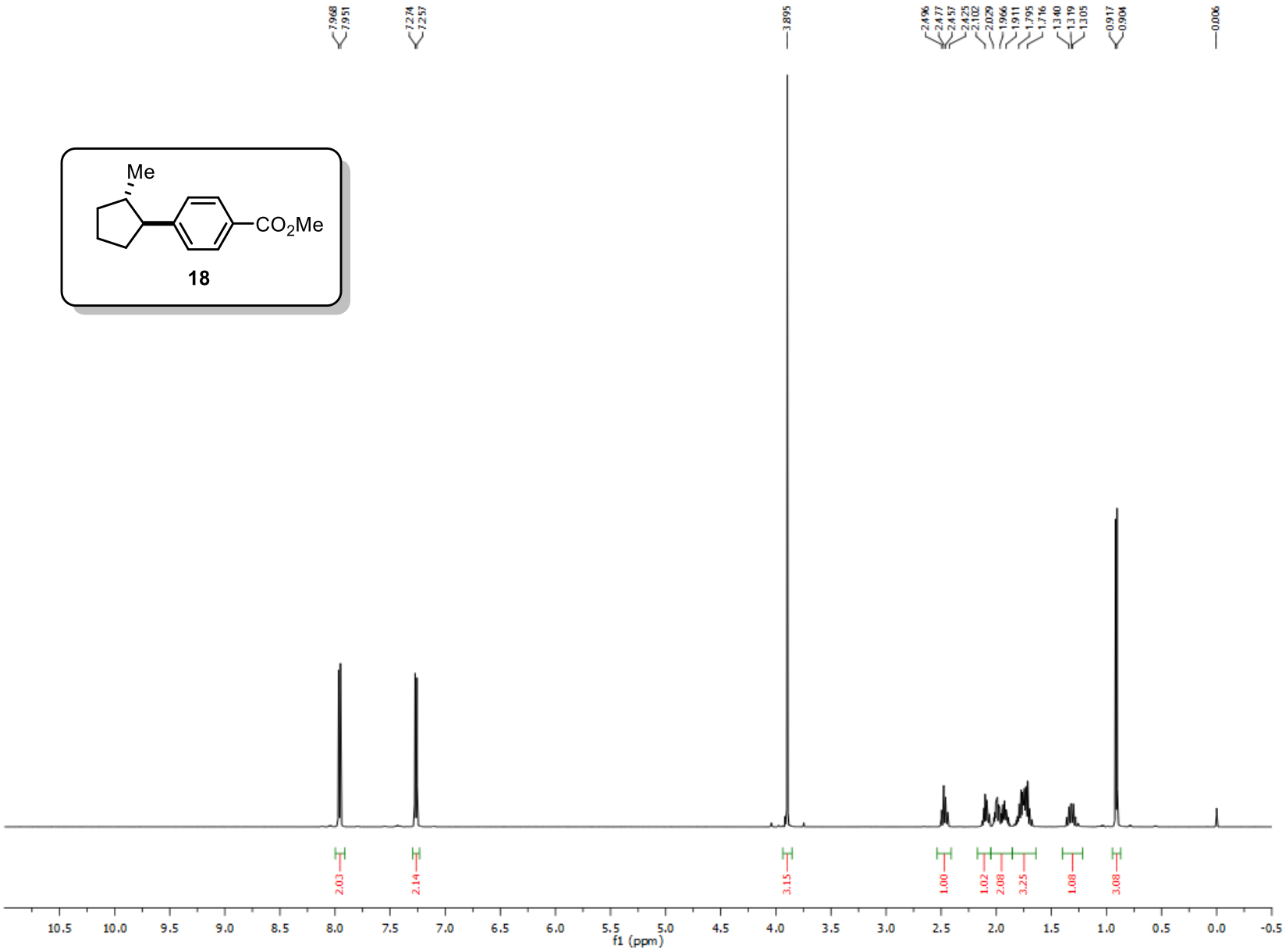
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-(2-methylcyclohexyl)benzoate (**17**)



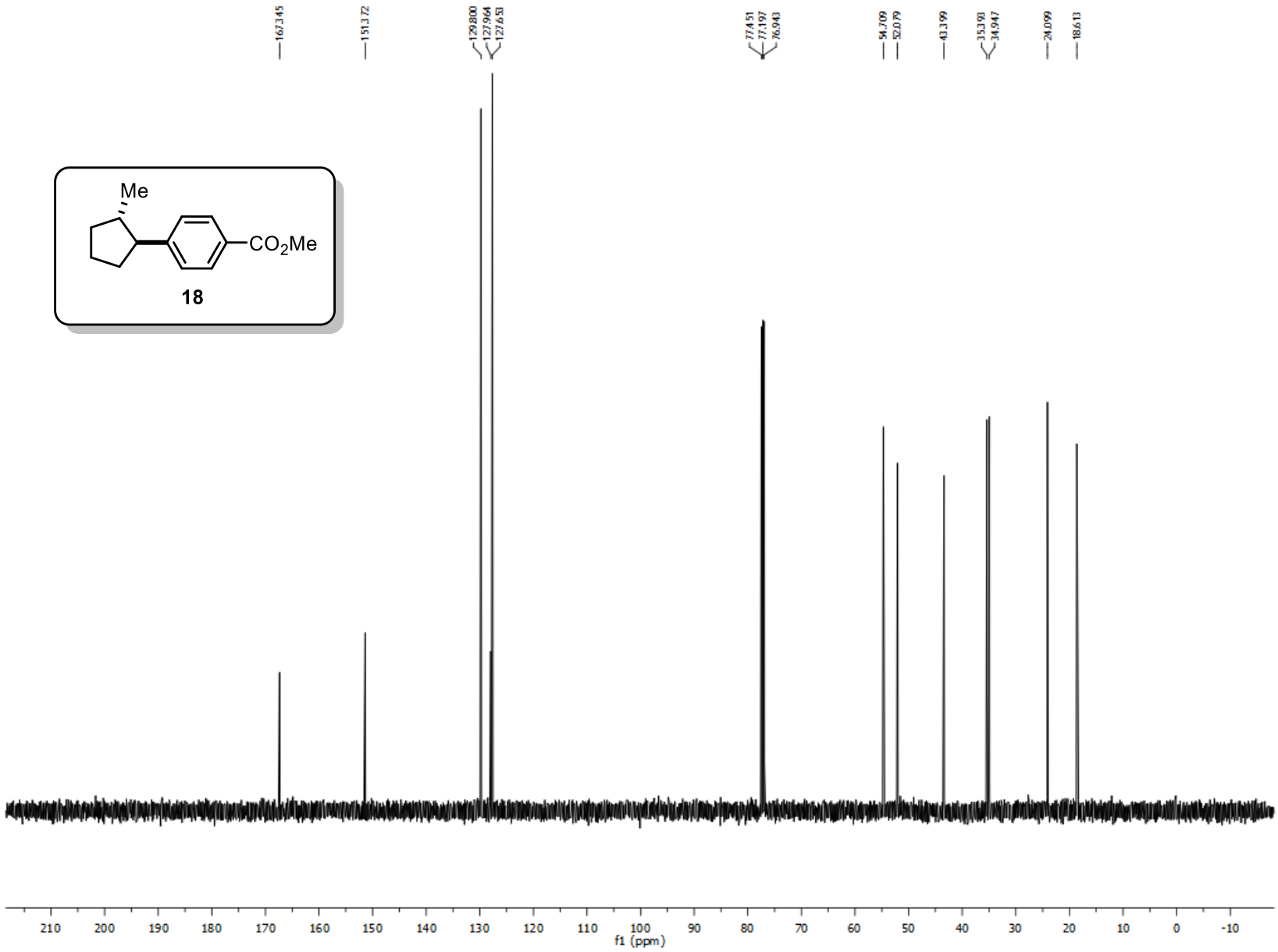
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-(2-methylcyclohexyl)benzoate (**17**)



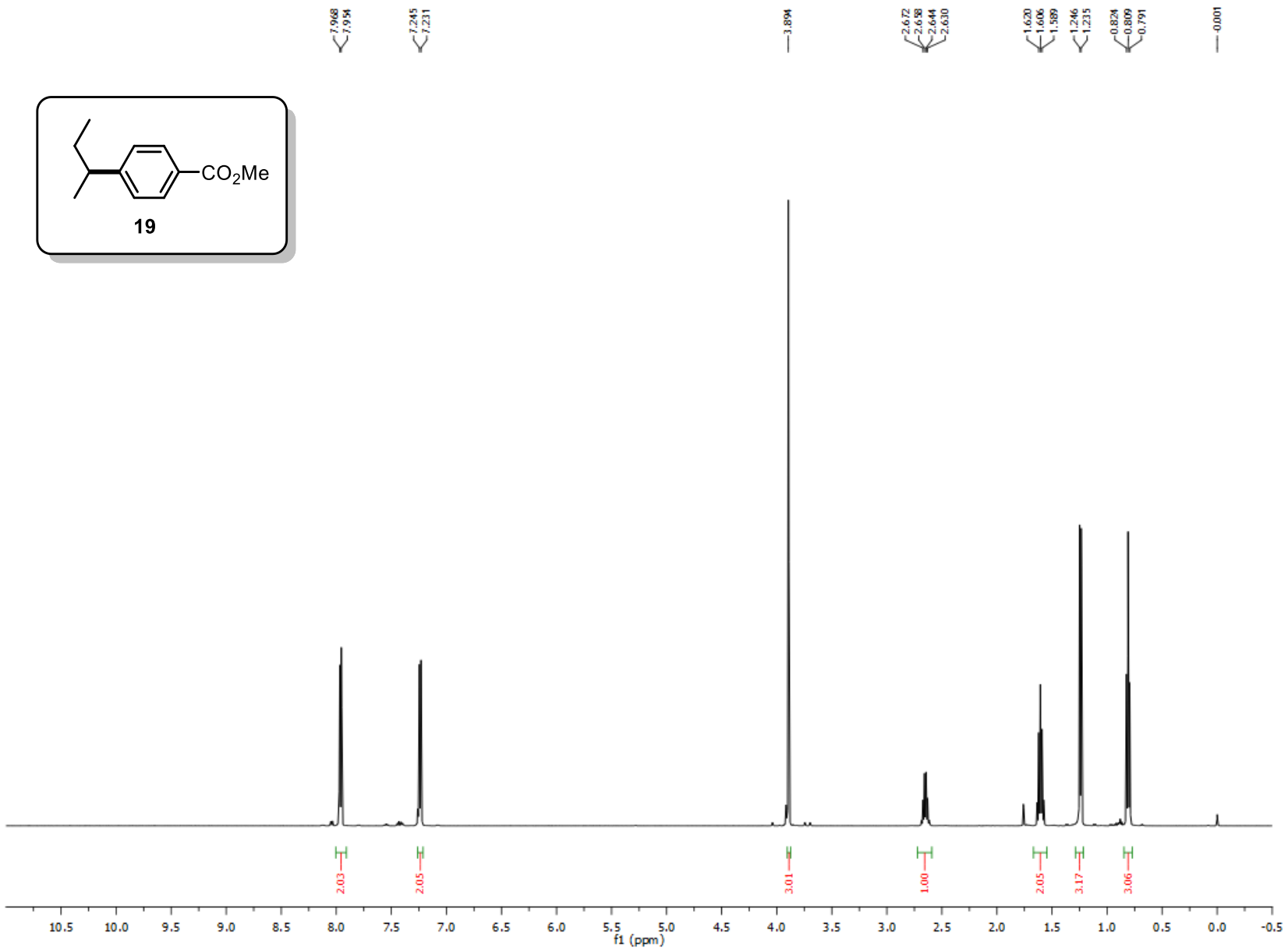
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-(2-methylcyclopentyl)benzoate (**18**)



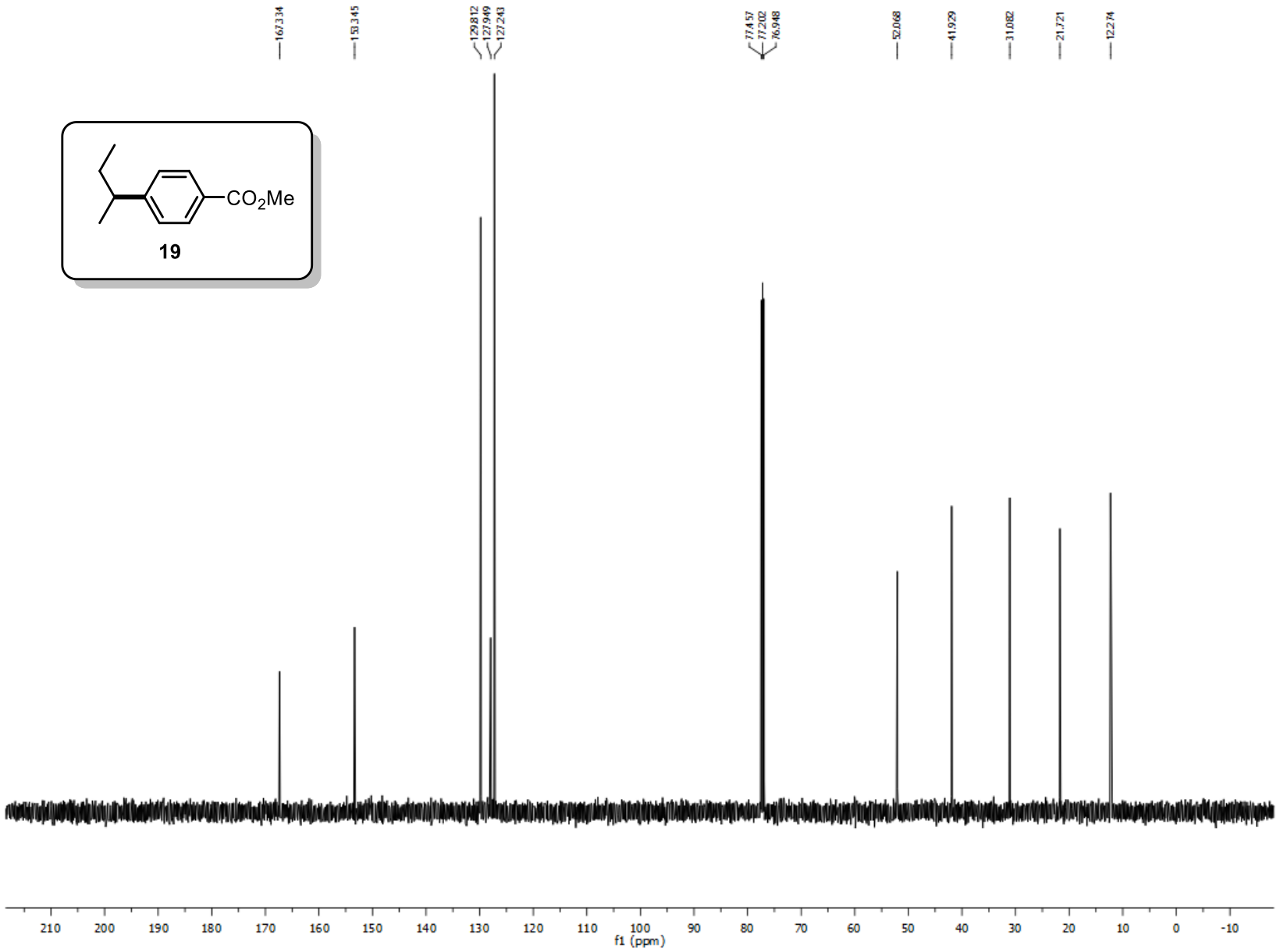
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-(2-methylcyclopentyl)benzoate (**18**)



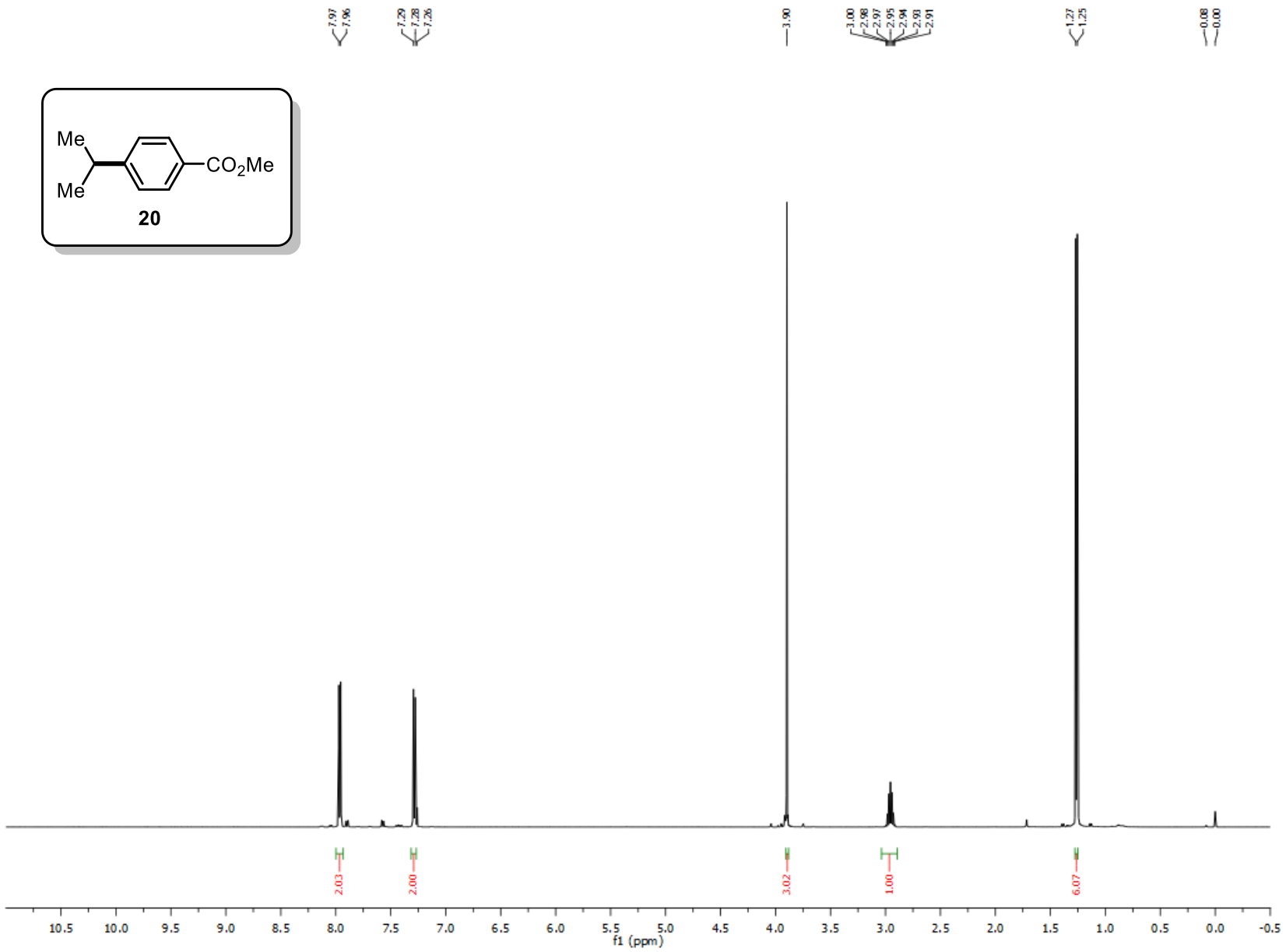
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-(sec-butyl)benzoate (**19**)



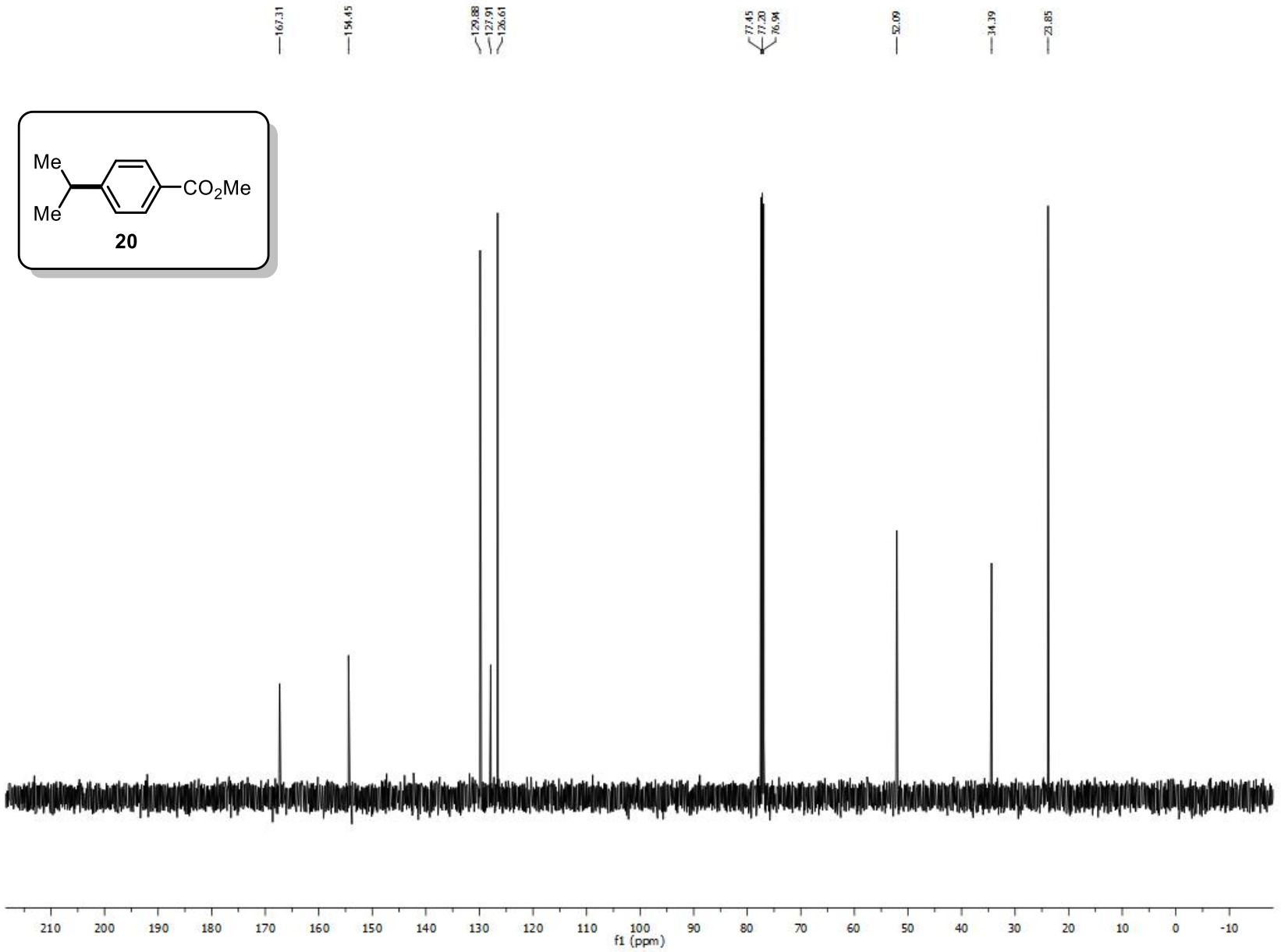
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-(sec-butyl)benzoate (**19**)



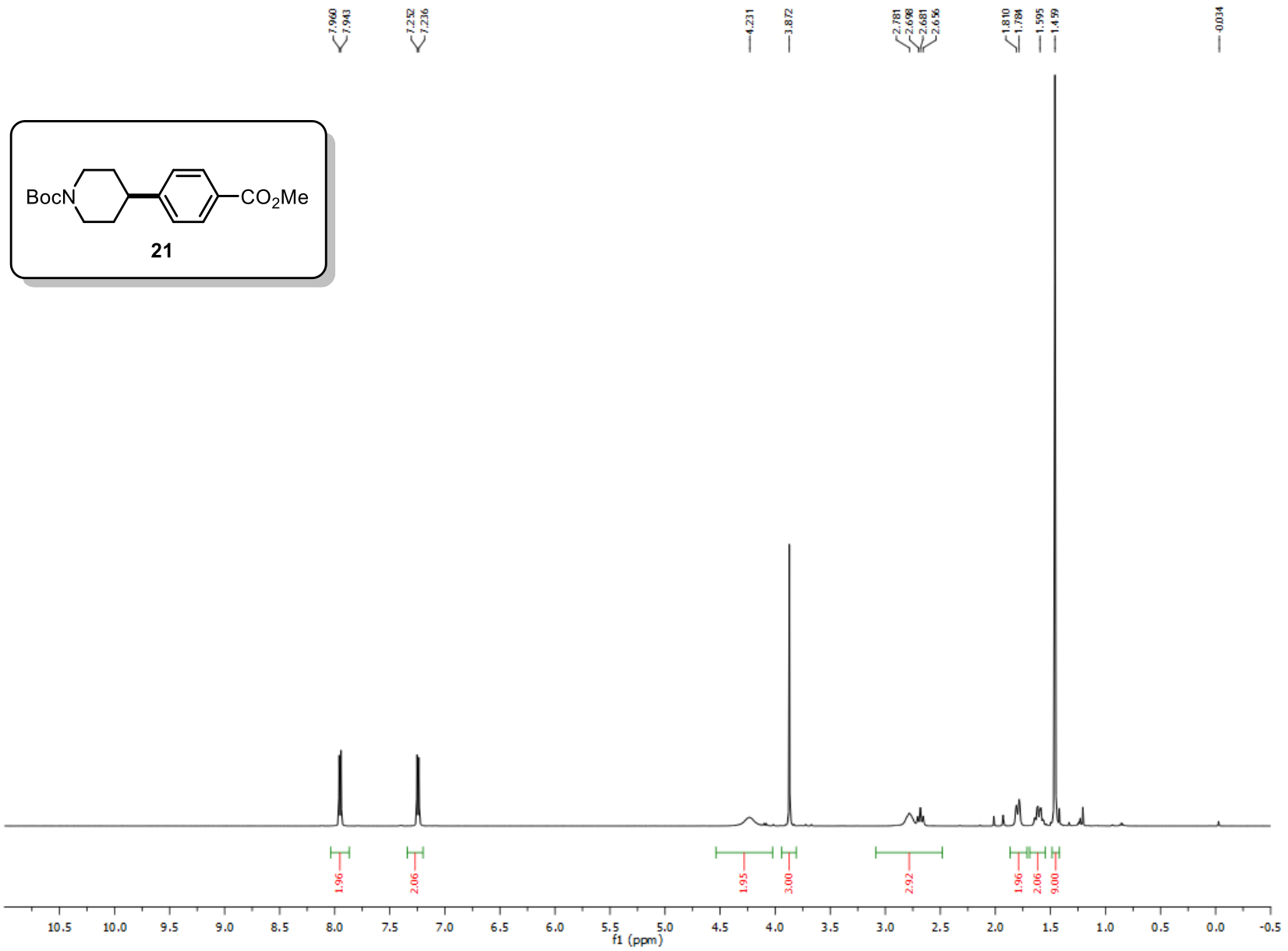
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-isopropylbenzoate **(20)**



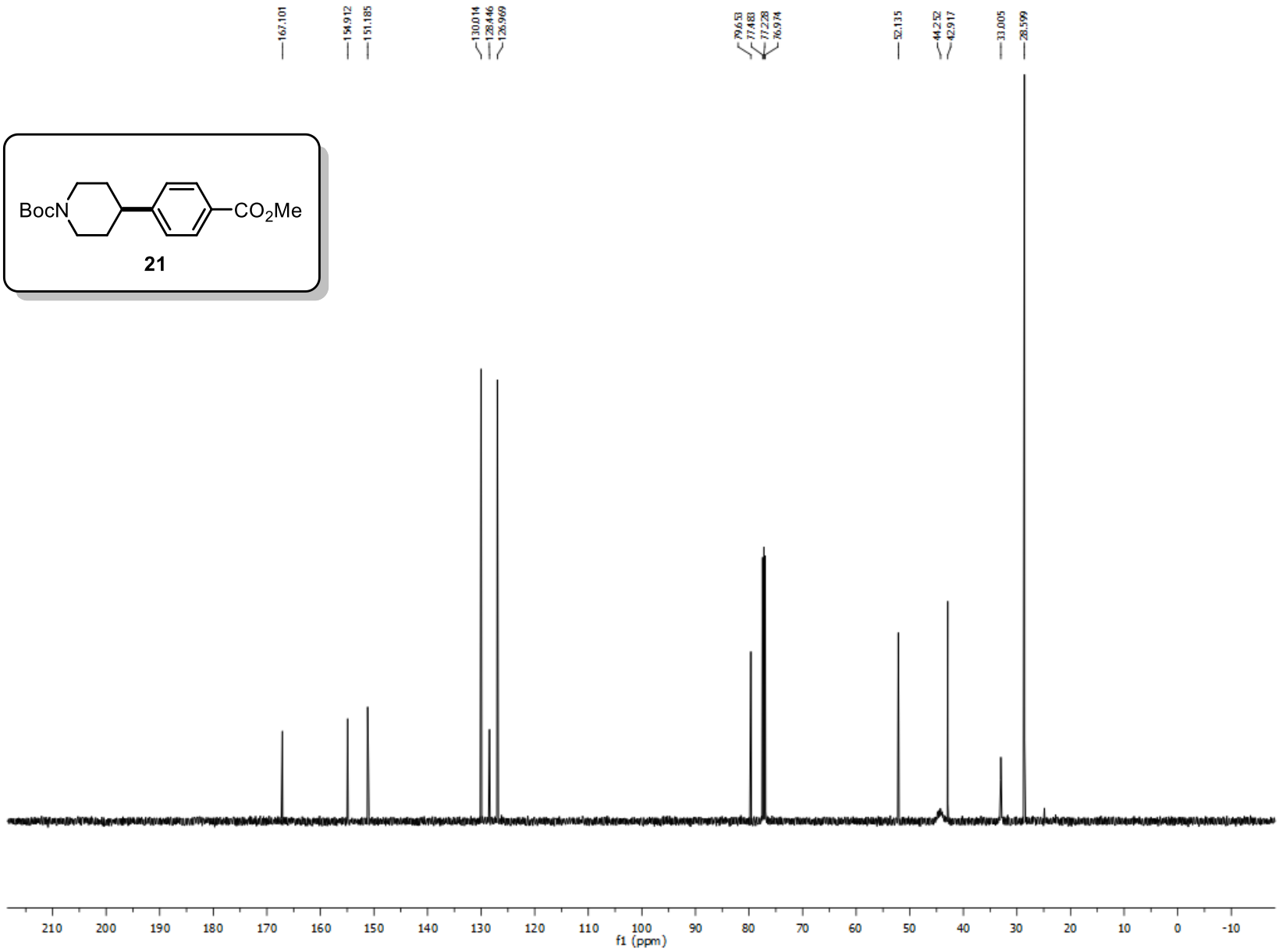
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-isopropylbenzoate **(20)**



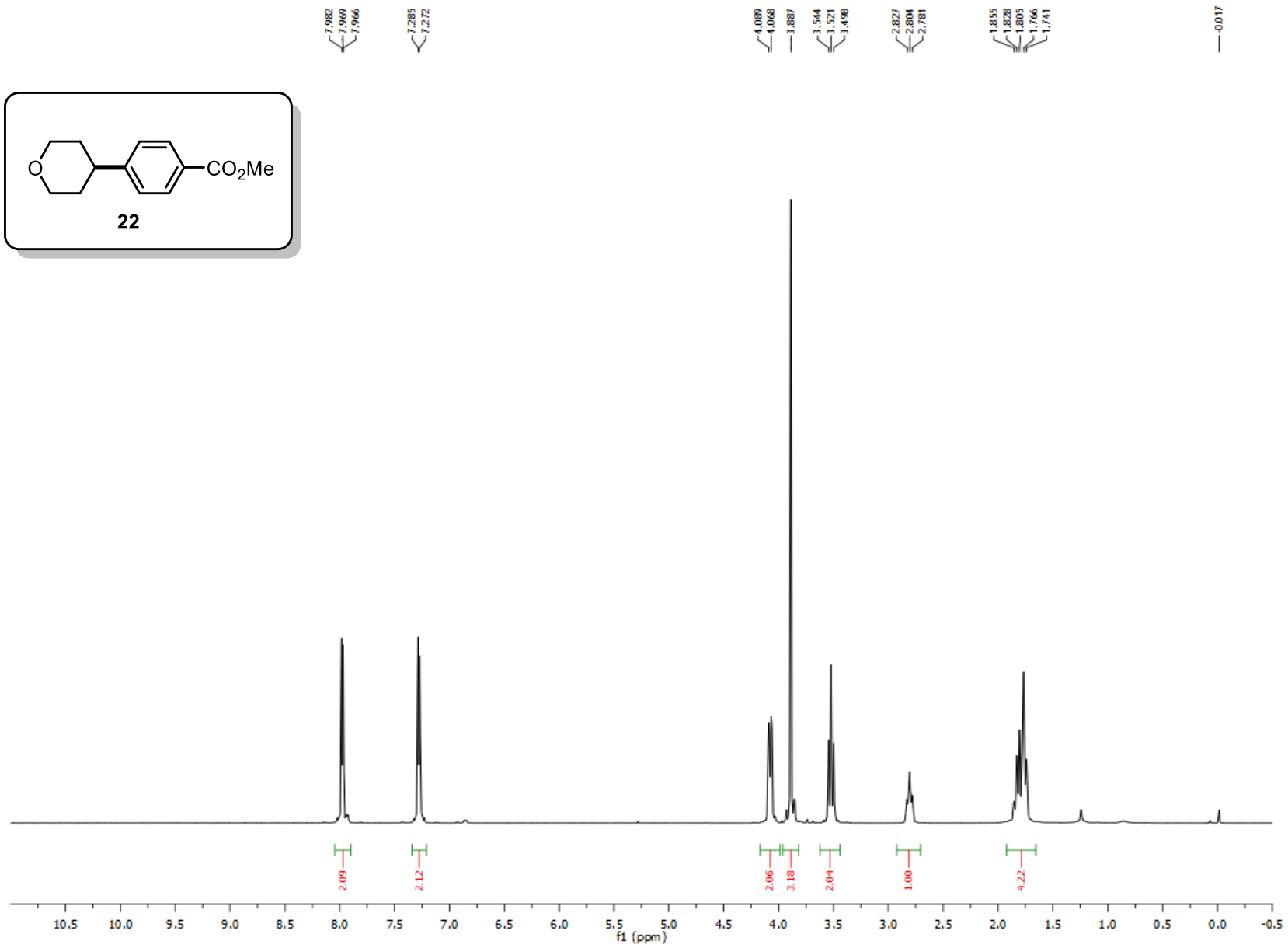
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of *tert*-butyl 4-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (**21**)



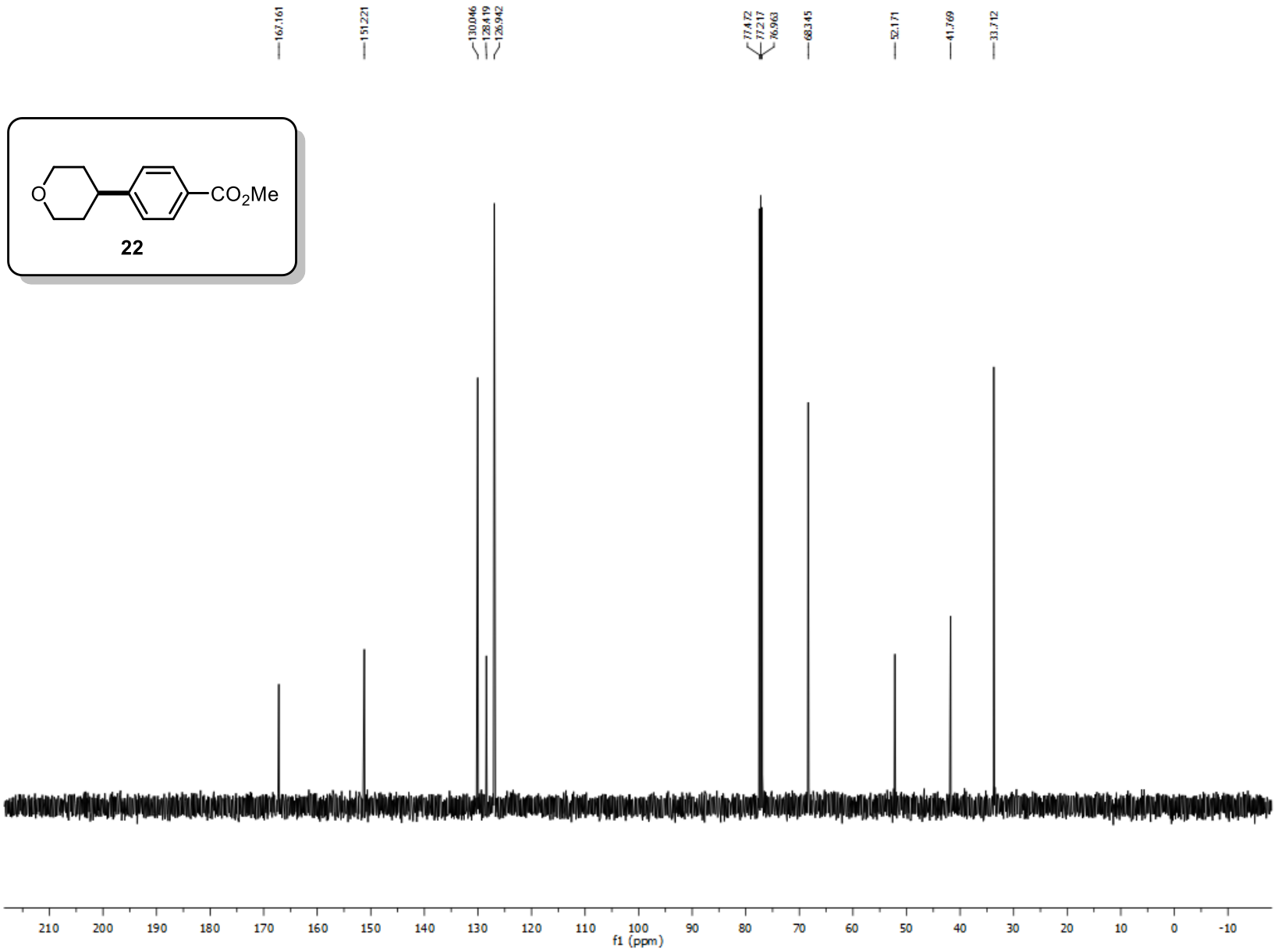
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of *tert*-butyl 4-(4-(methoxycarbonyl)phenyl)piperidine-1-carboxylate (**21**)



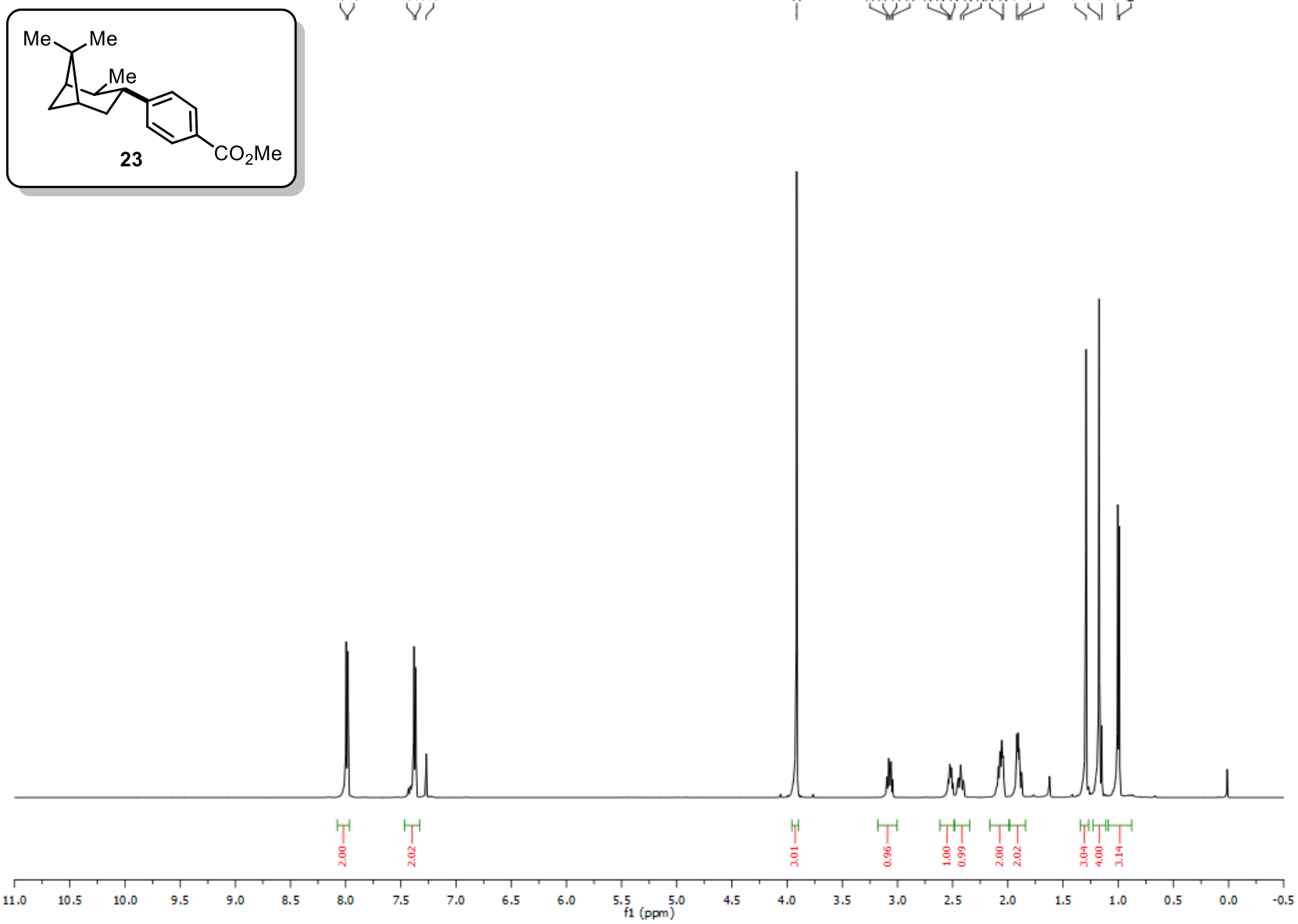
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-(tetrahydro-2H-pyran-4-yl)benzoate (**22**)



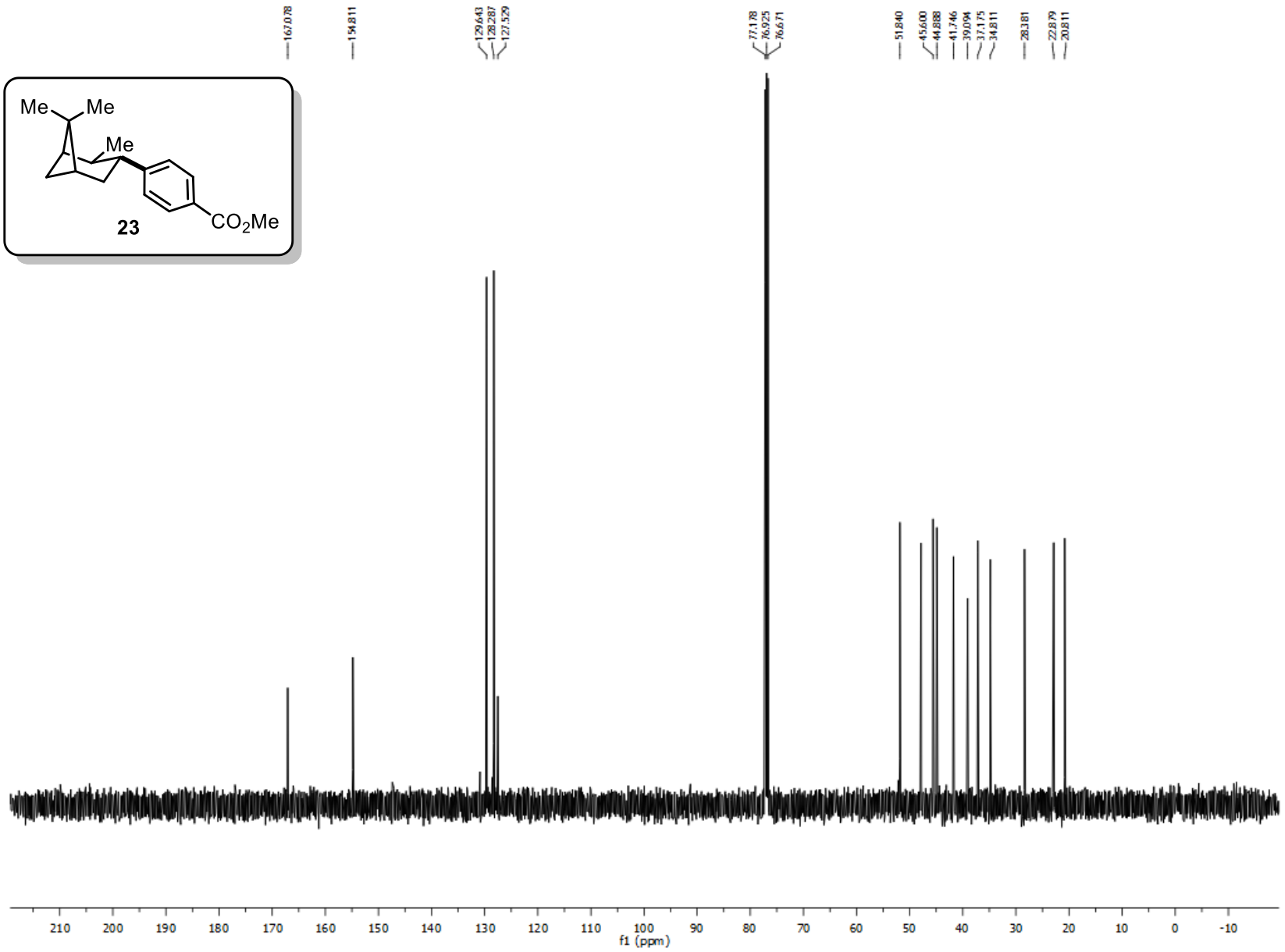
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-(tetrahydro-2H-pyran-4-yl)benzoate (**22**)



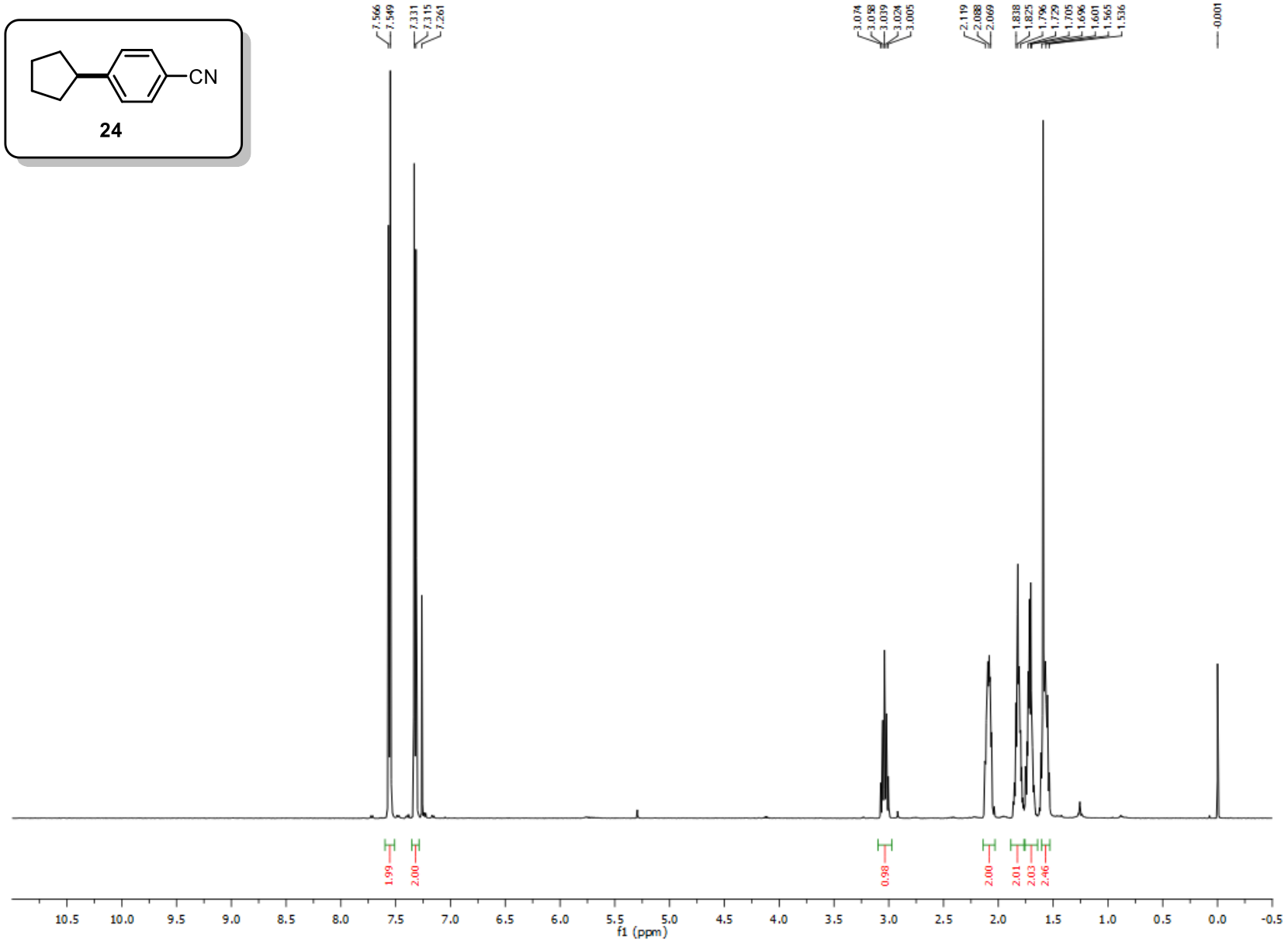
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of methyl 4-((3,6,6-trimethylbicyclo[3.1.1]heptan-2-yl)benzoate (**23**)



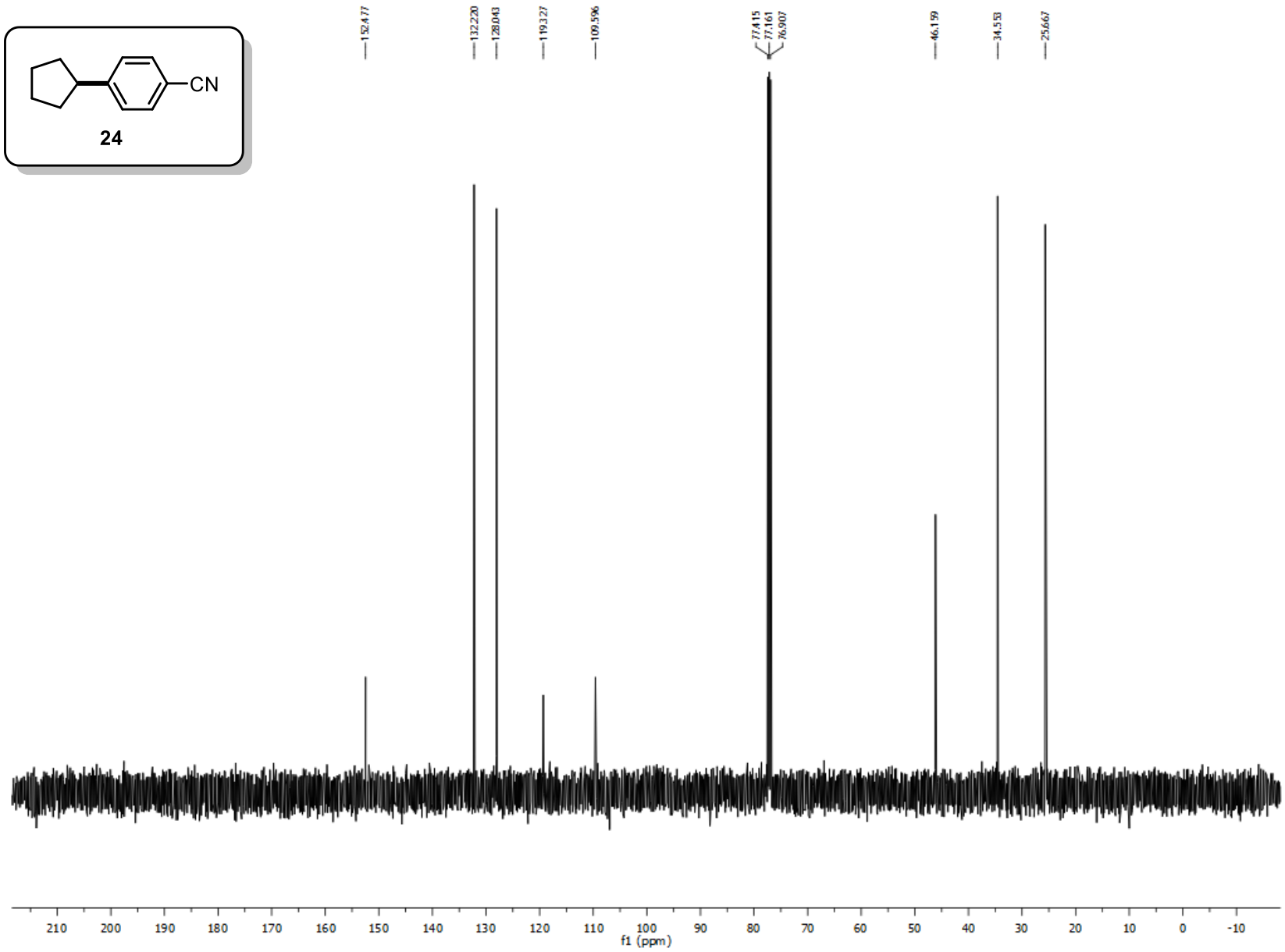
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of methyl 4-((3,6,6-trimethylbicyclo[3.1.1]heptan-2-yl)benzoate (**23**)



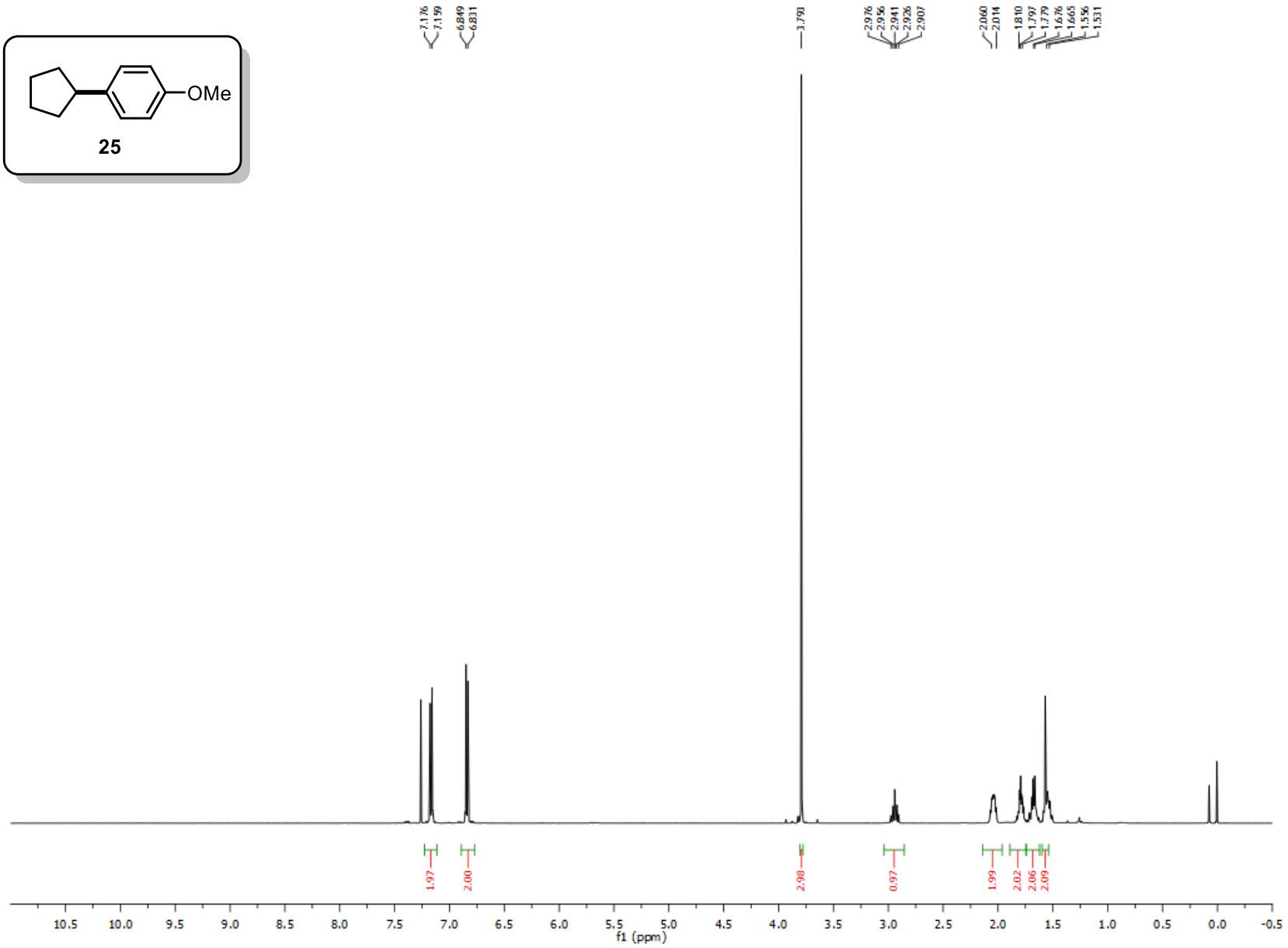
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-cyclopentylbenzonitrile (**24**)



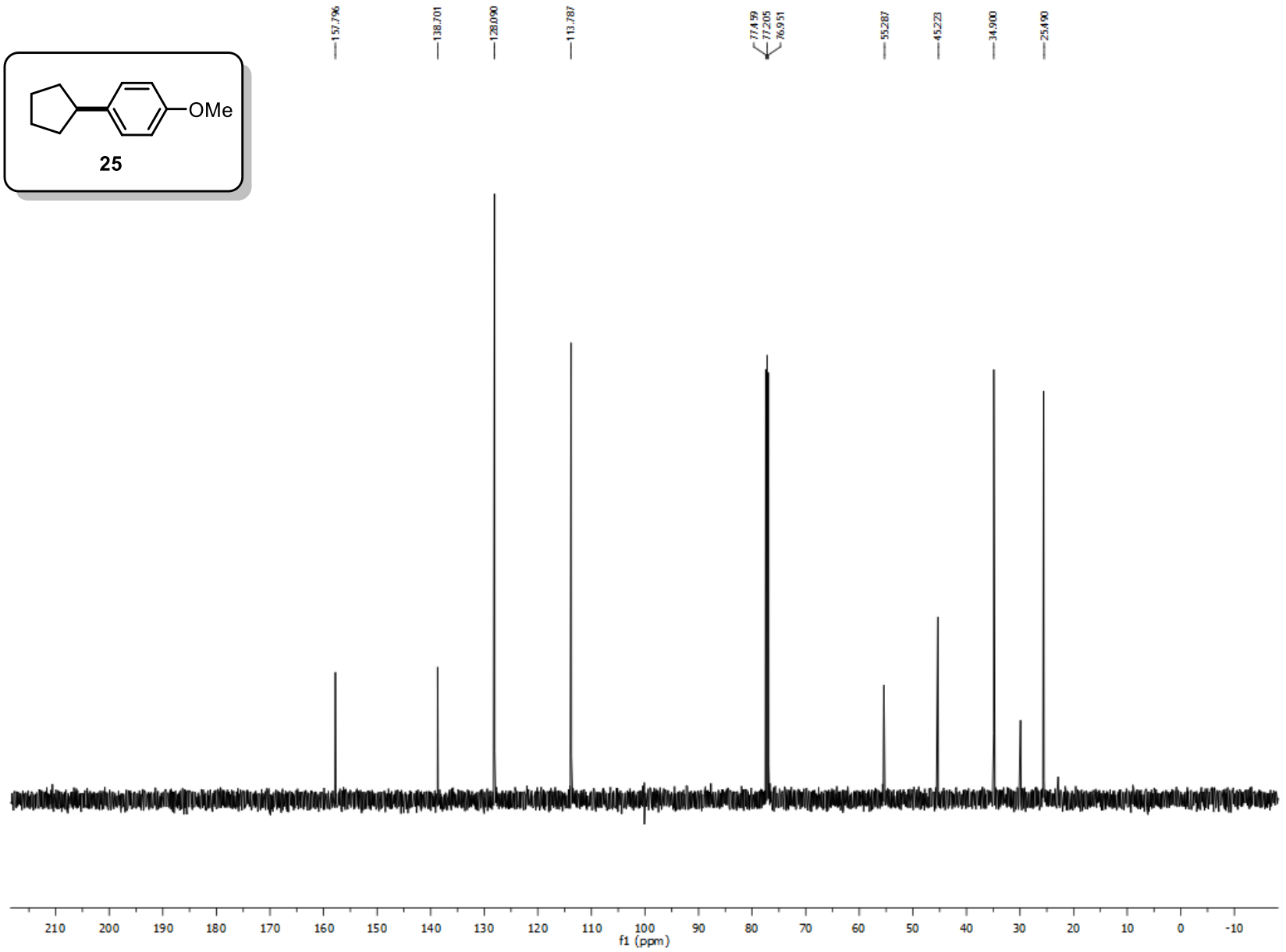
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-cyclopentylbenzonitrile (**24**)



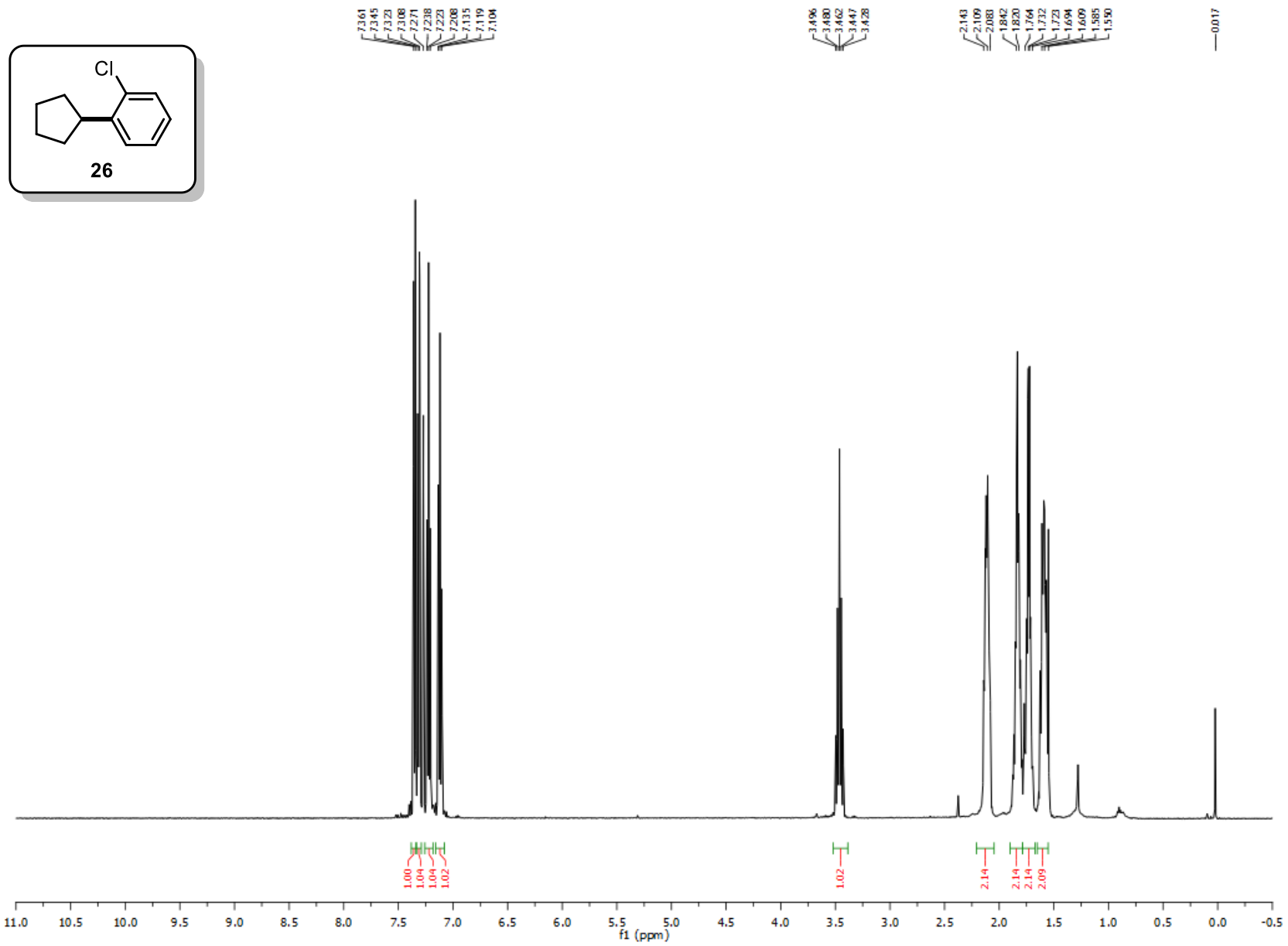
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-cyclopentyl-4-methoxybenzene (**25**)



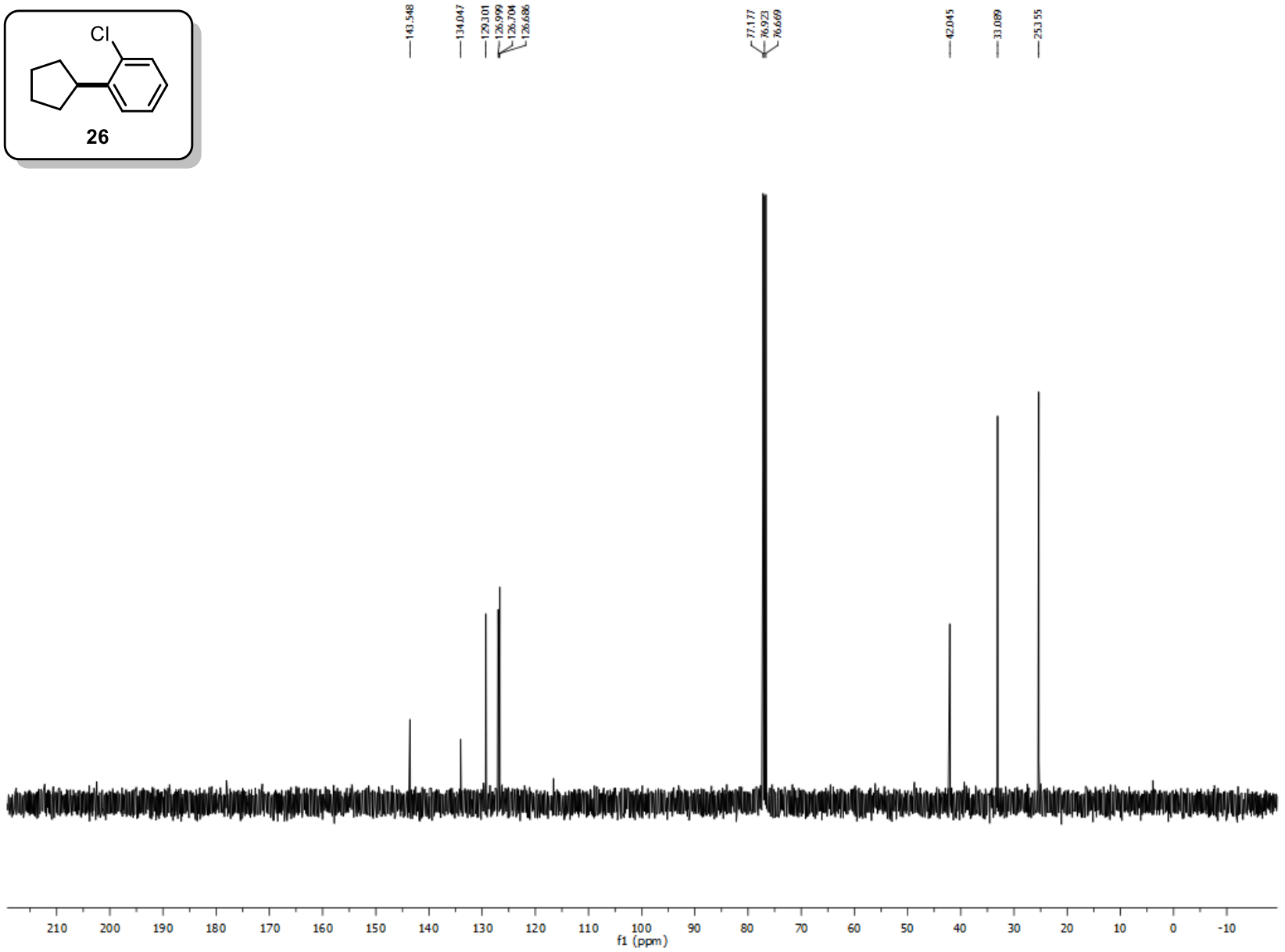
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 1-cyclopentyl-4-methoxybenzene (**25**)



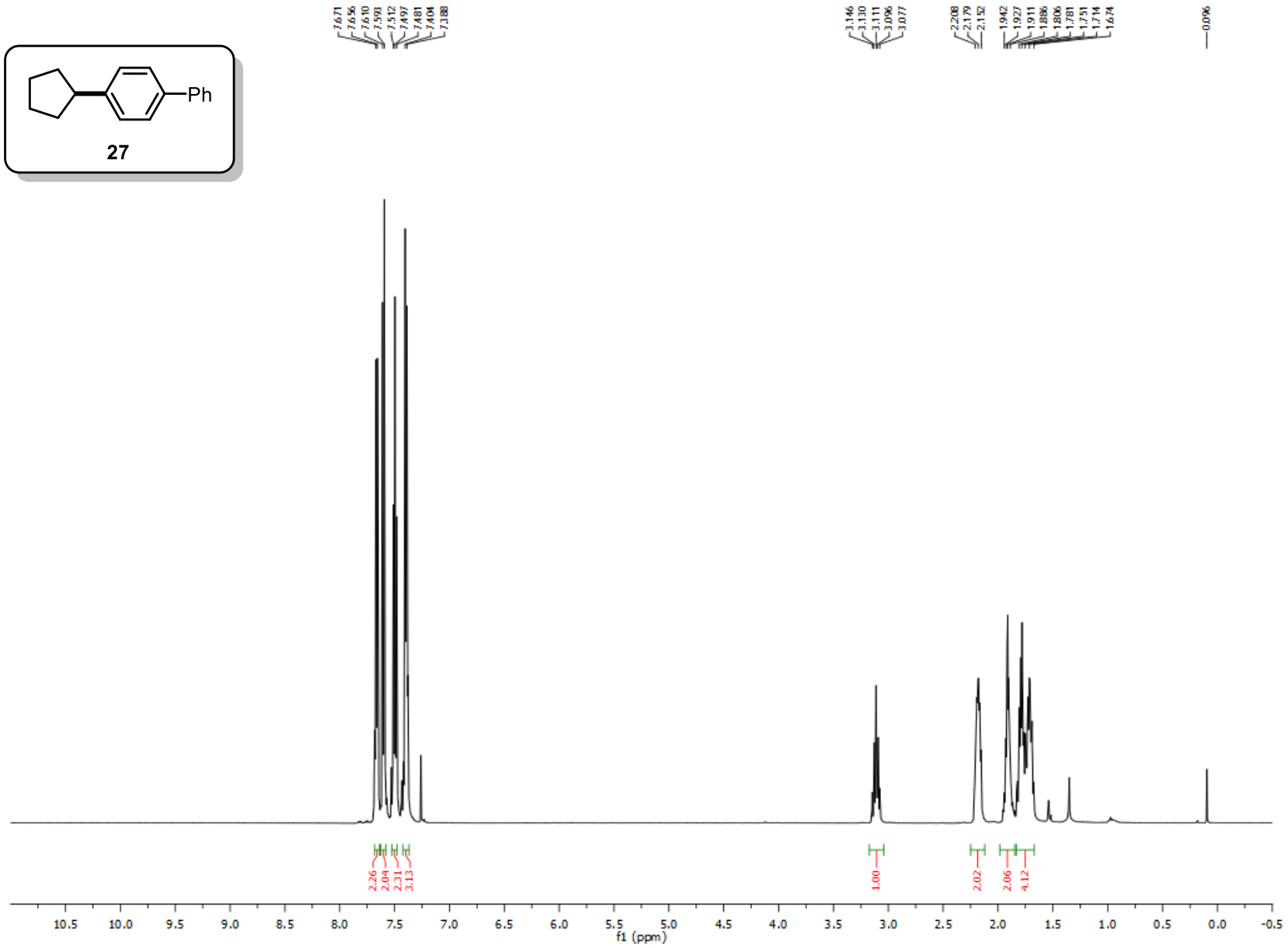
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 1-chloro-2-cyclopentylbenzene (**26**)



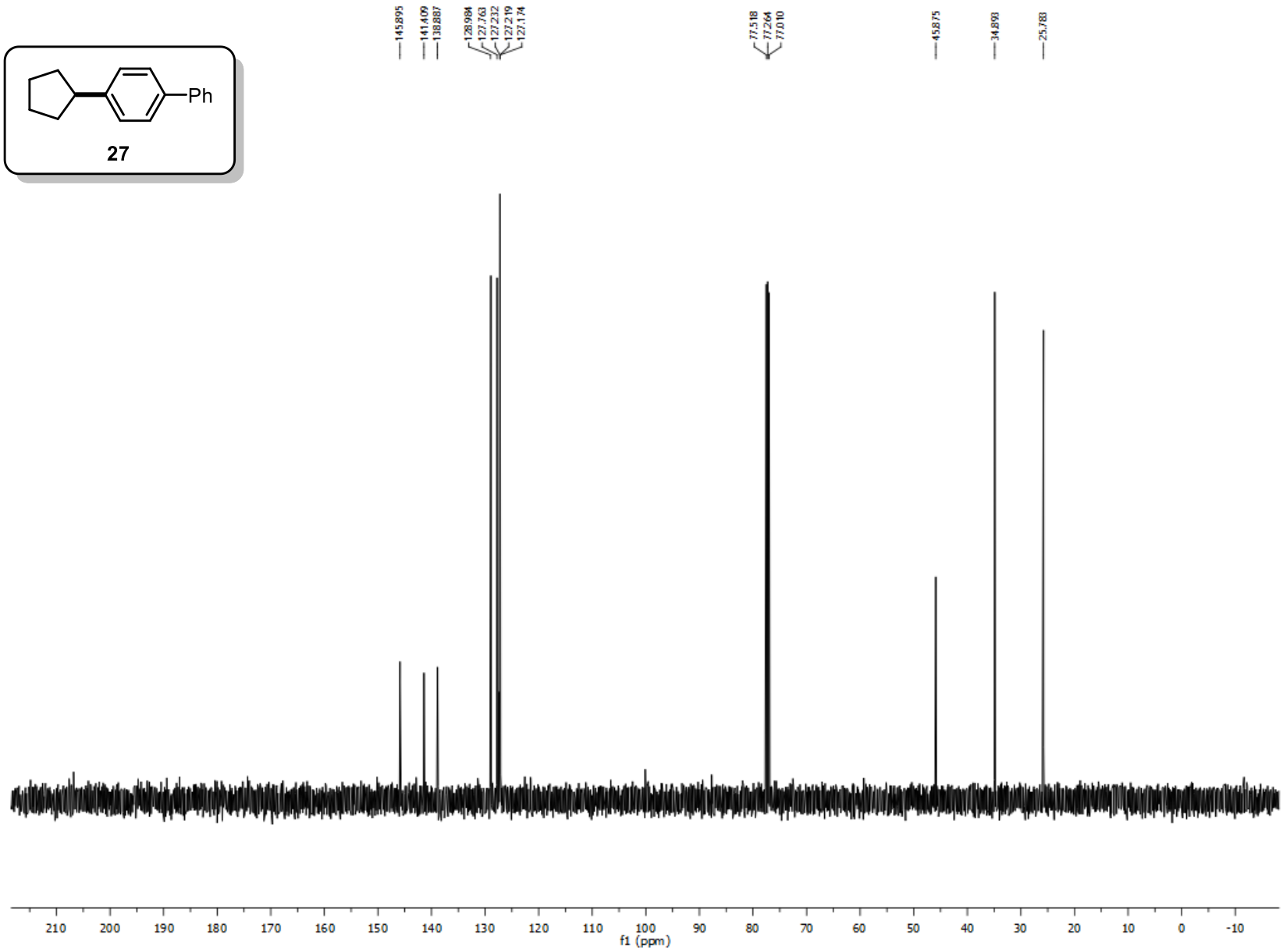
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 1-chloro-2-cyclopentylbenzene (**26**)



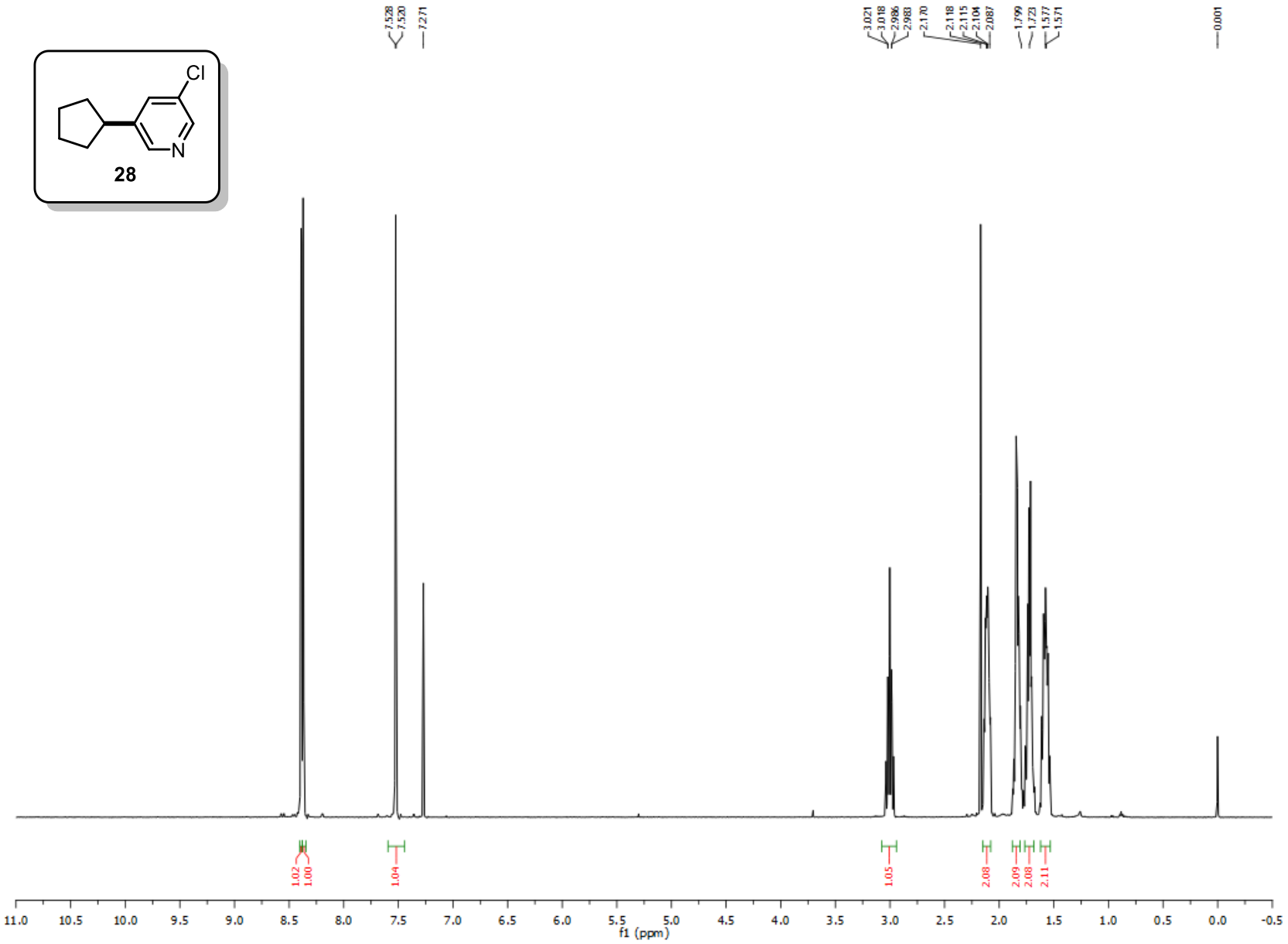
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 4-cyclopentyl-1,1'-biphenyl (**27**)



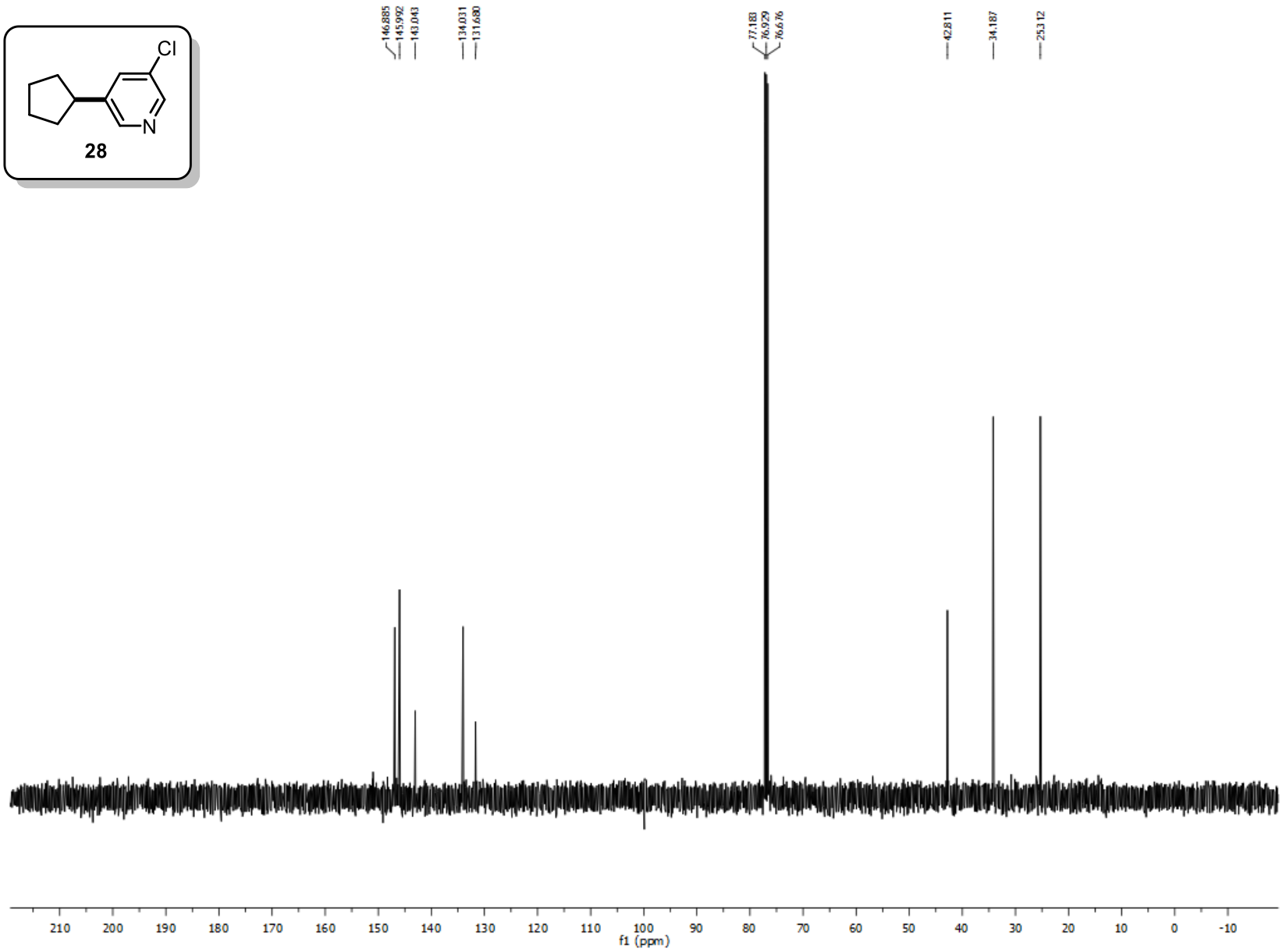
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 4-cyclopentyl-1,1'-biphenyl (**27**)



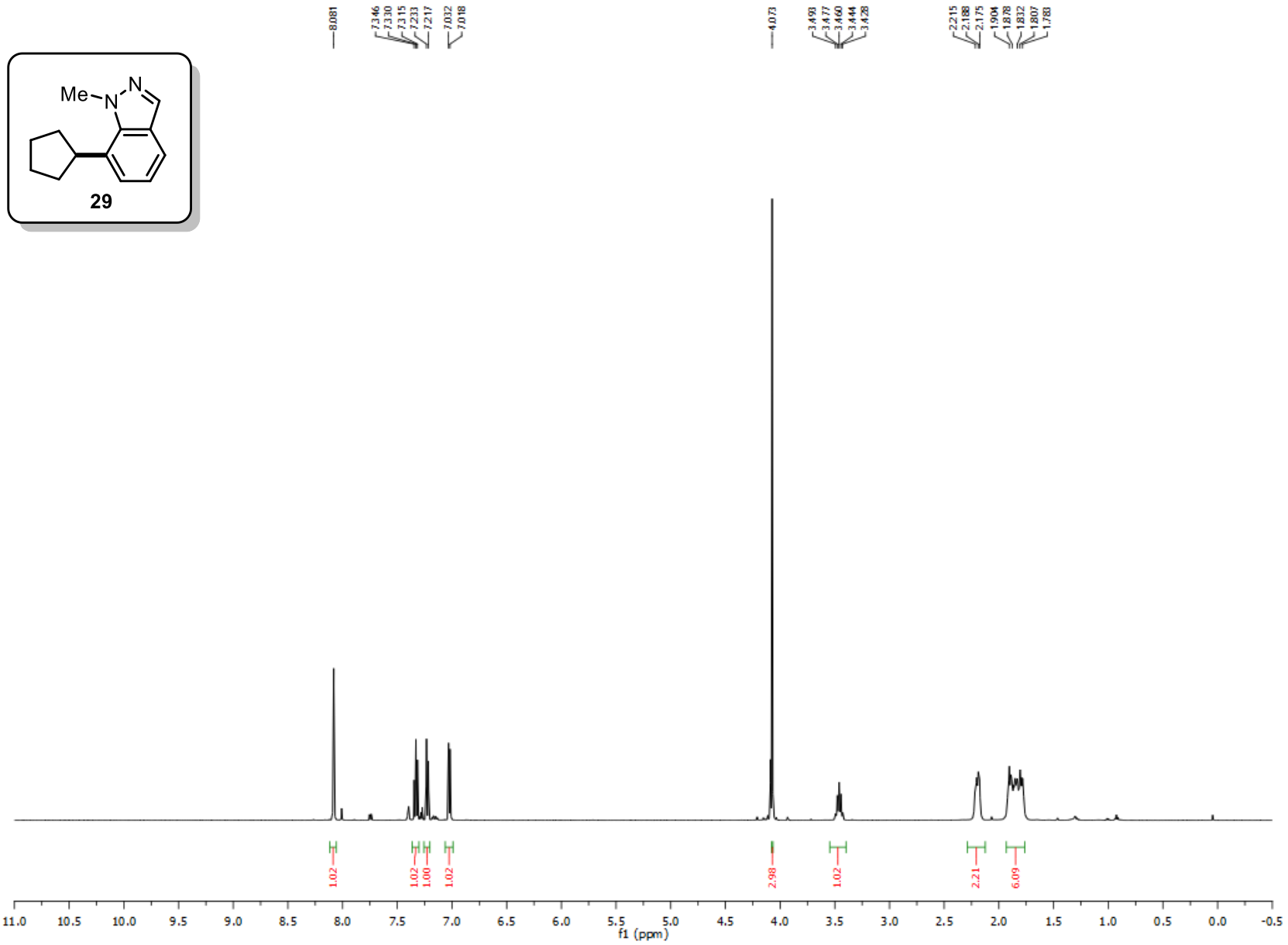
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 3-chloro-5-cyclopentylpyridine (**28**)



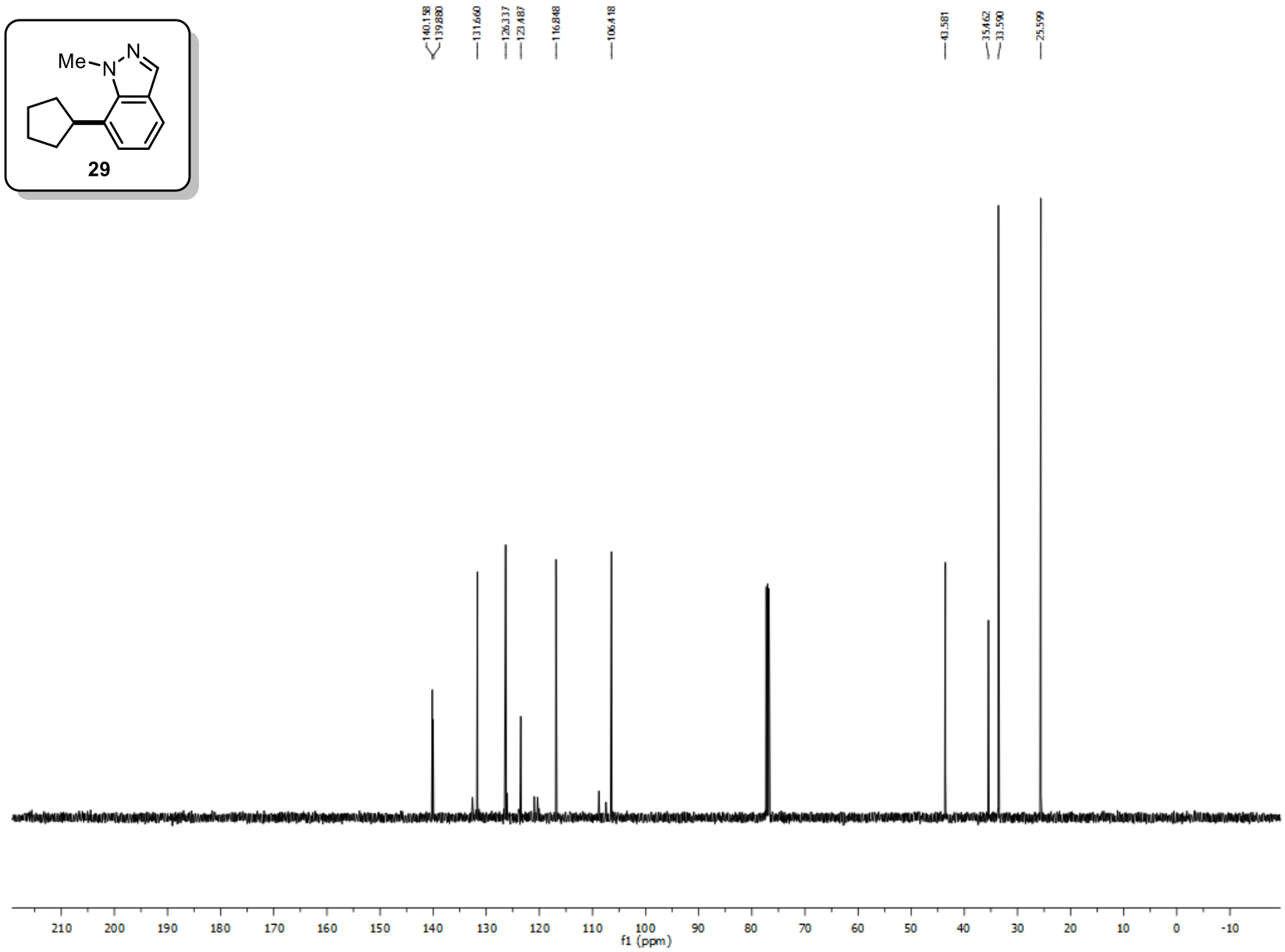
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 3-chloro-5-cyclopentylpyridine (**28**)



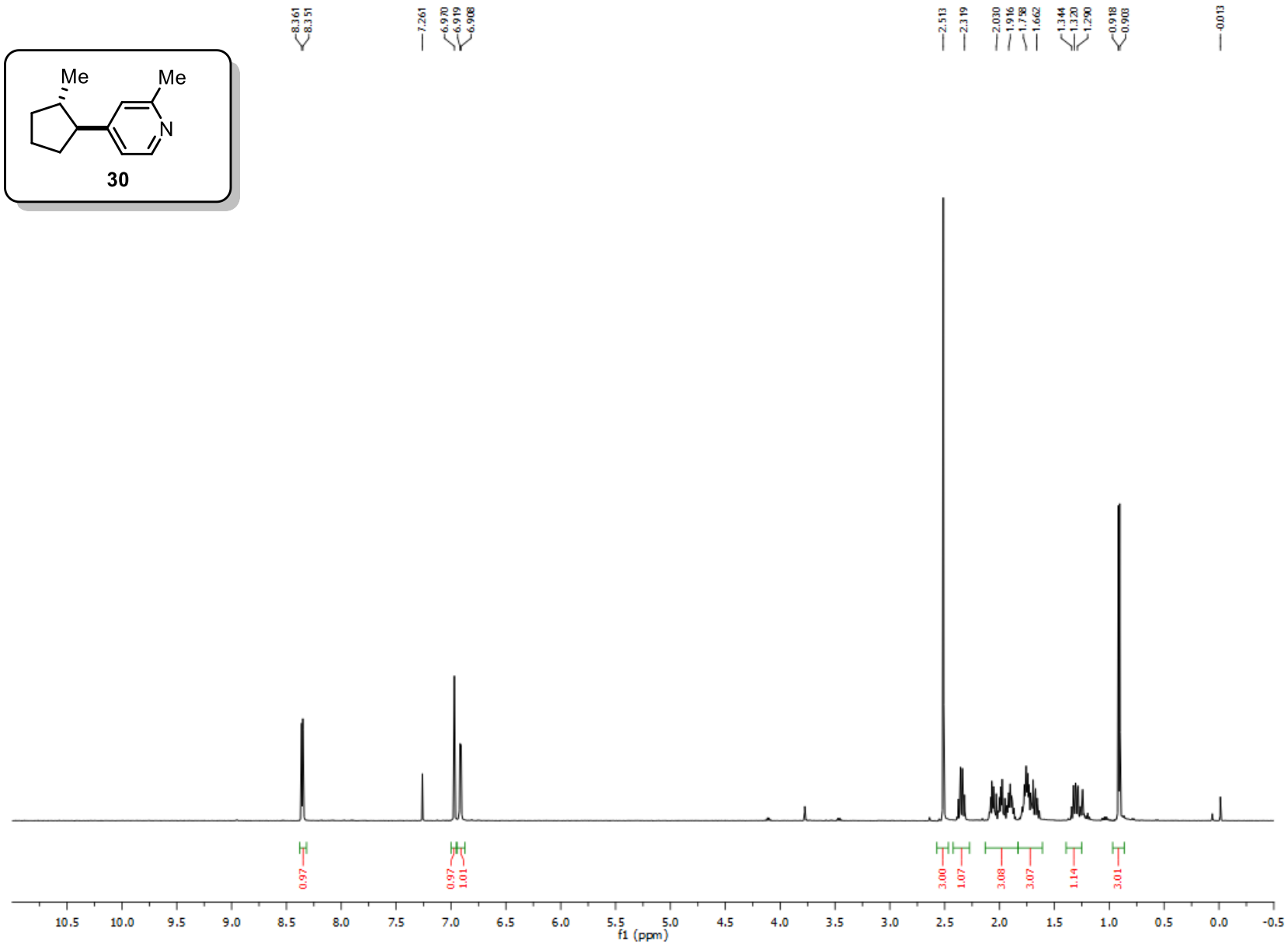
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 7-cyclopentyl-1-methyl-1H-indazole (**29**)



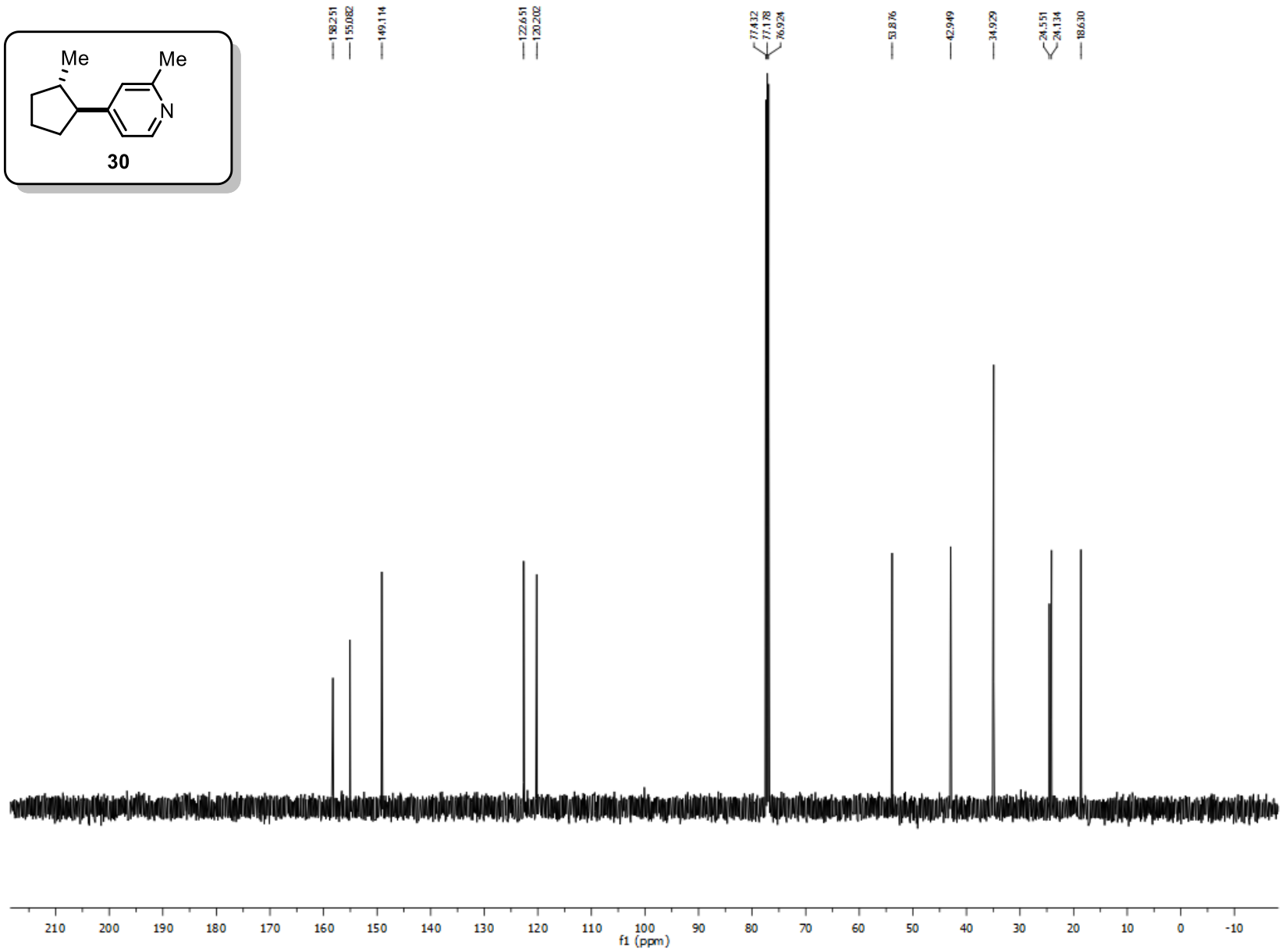
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of 7-cyclopentyl-1-methyl-1H-indazole **(29)**



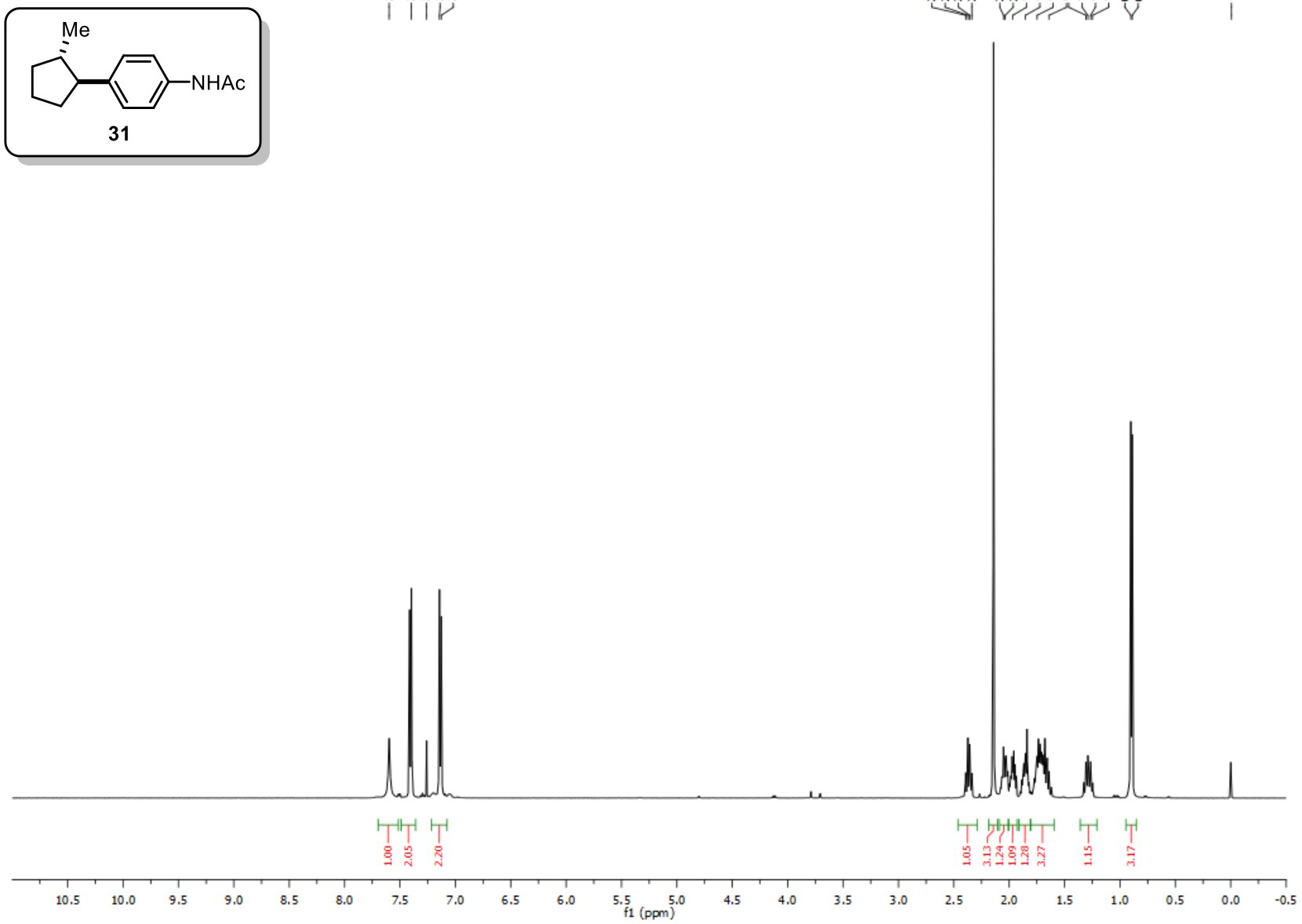
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-2-methyl-4-(2-methylcyclopentyl)pyridine **(30)**



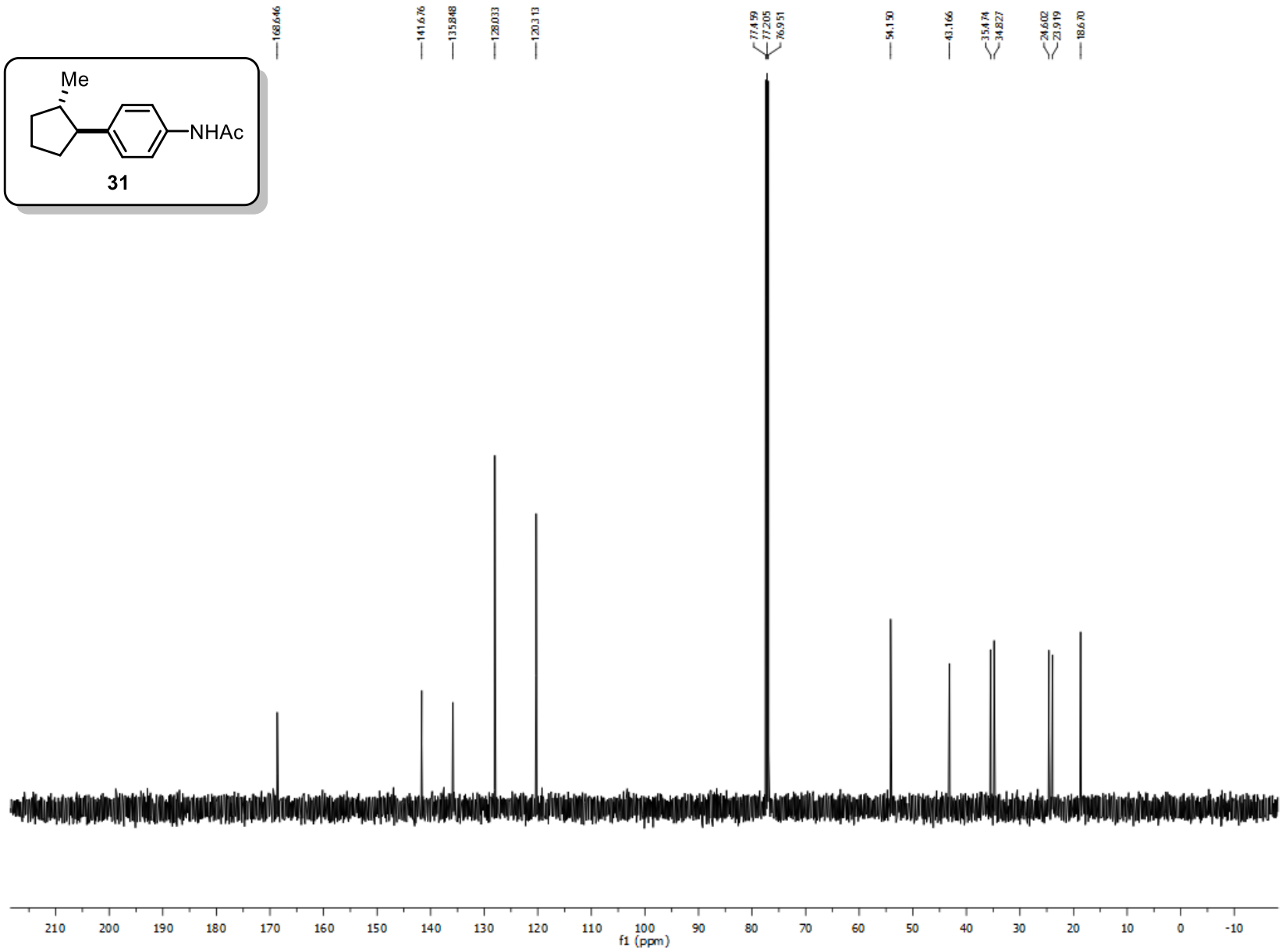
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans* -2-methyl-4-(2-methylcyclopentyl)pyridine **(30)**



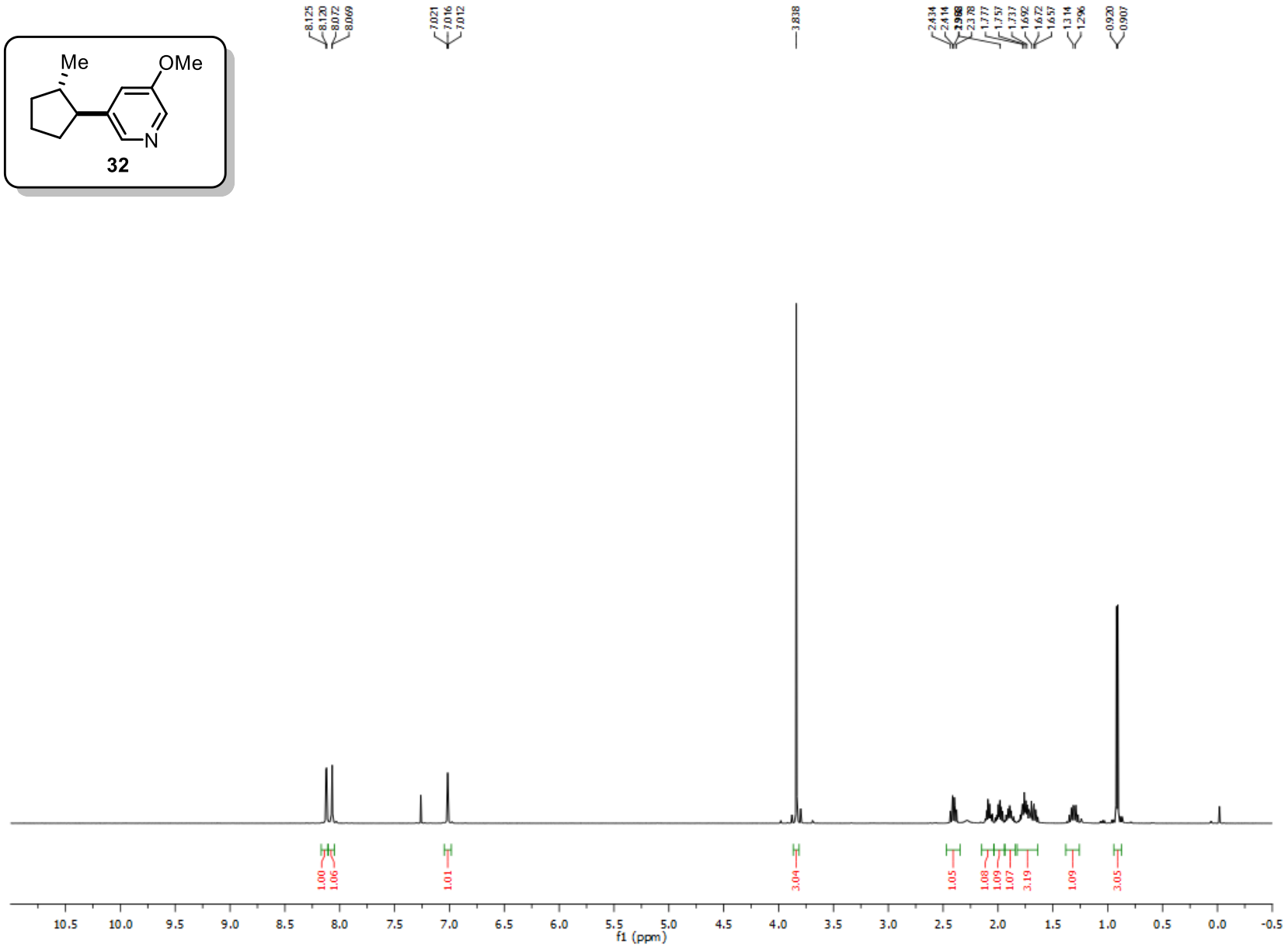
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans* -N-(4-(2-methylcyclopentyl)phenyl)acetamide **(31)**



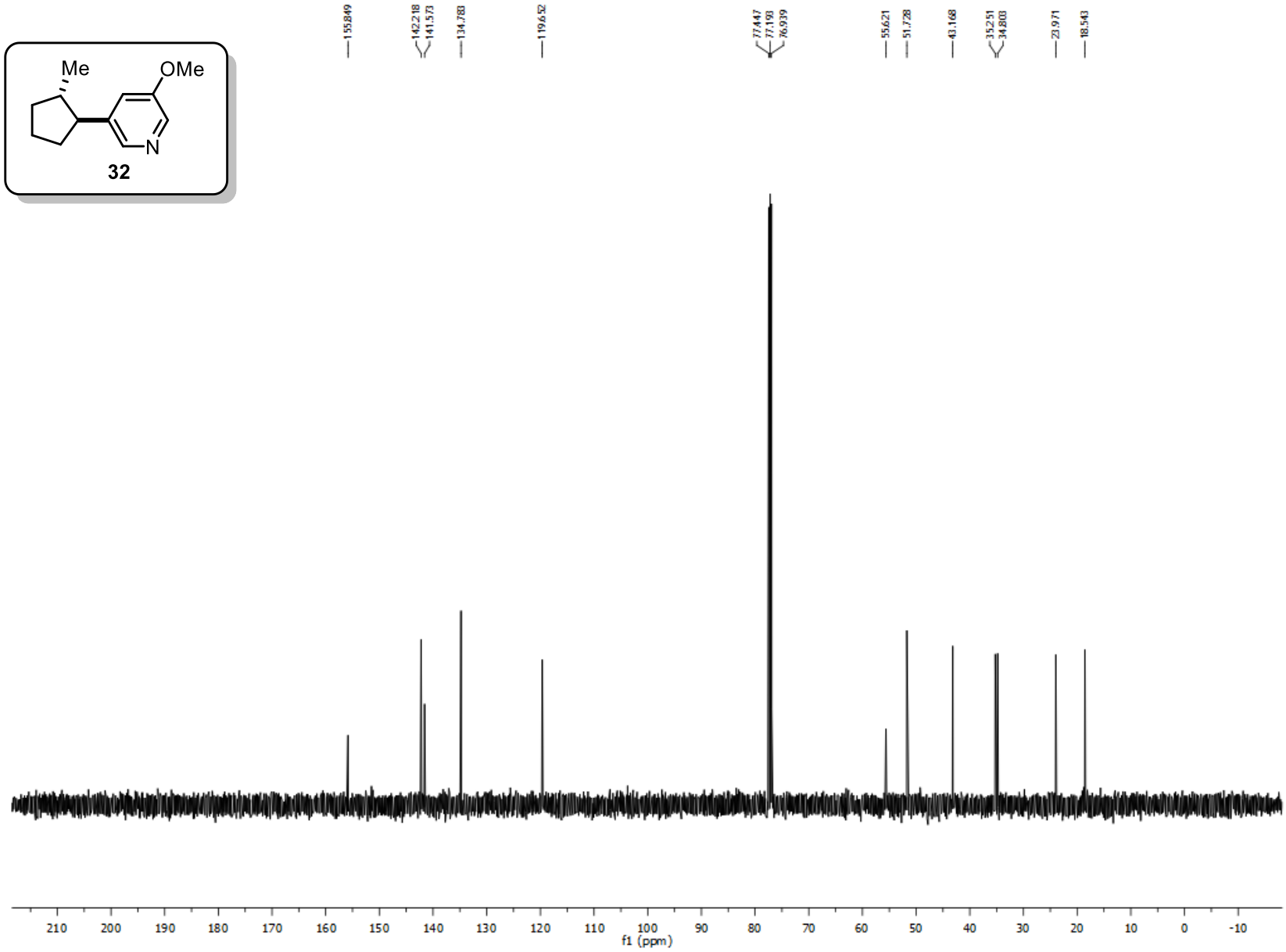
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans* -N-(4-(2-methylcyclopentyl)phenyl)acetamide **(31)**



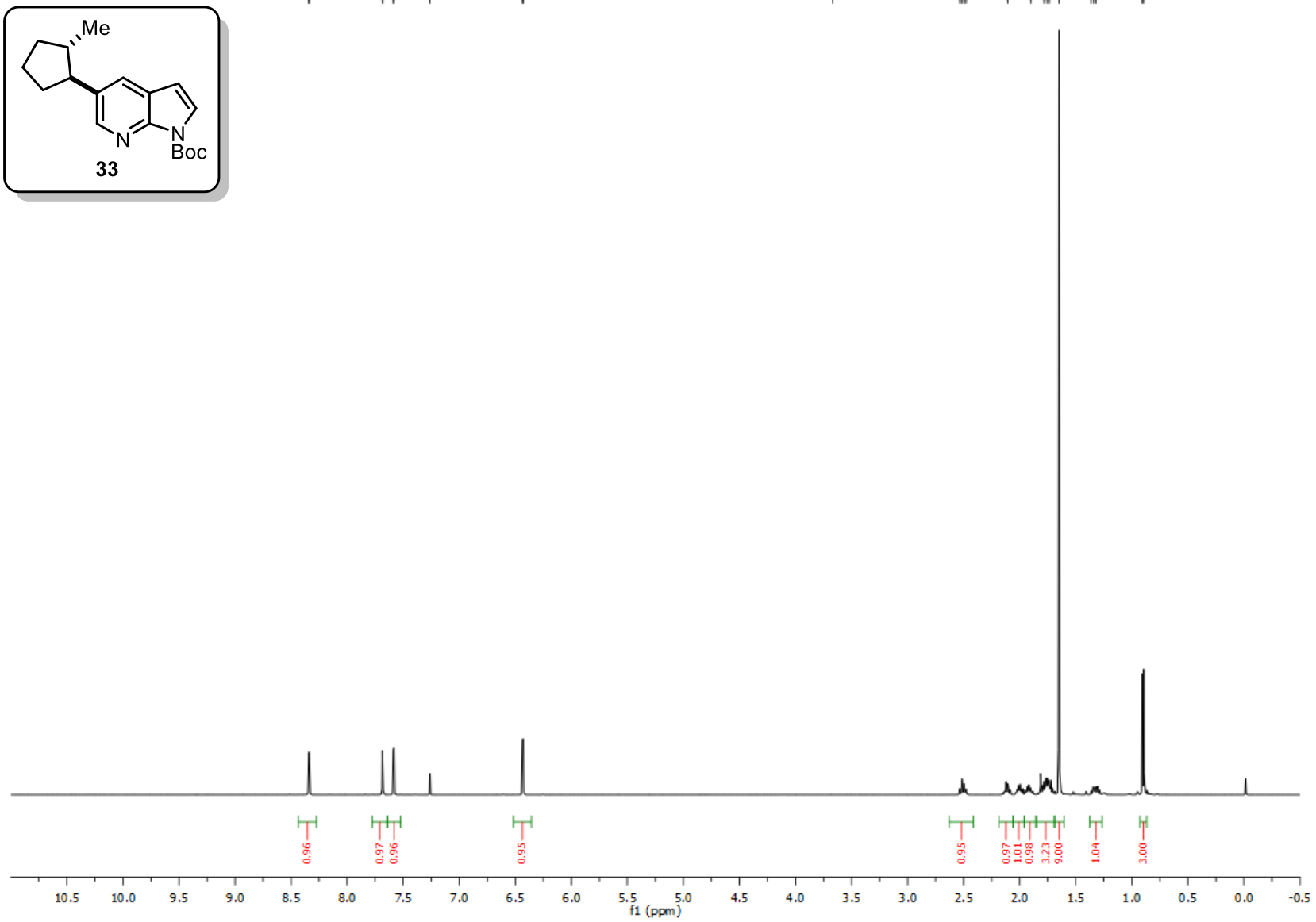
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-3-methoxy-5-(2-methylcyclopentyl)pyridine **(32)**



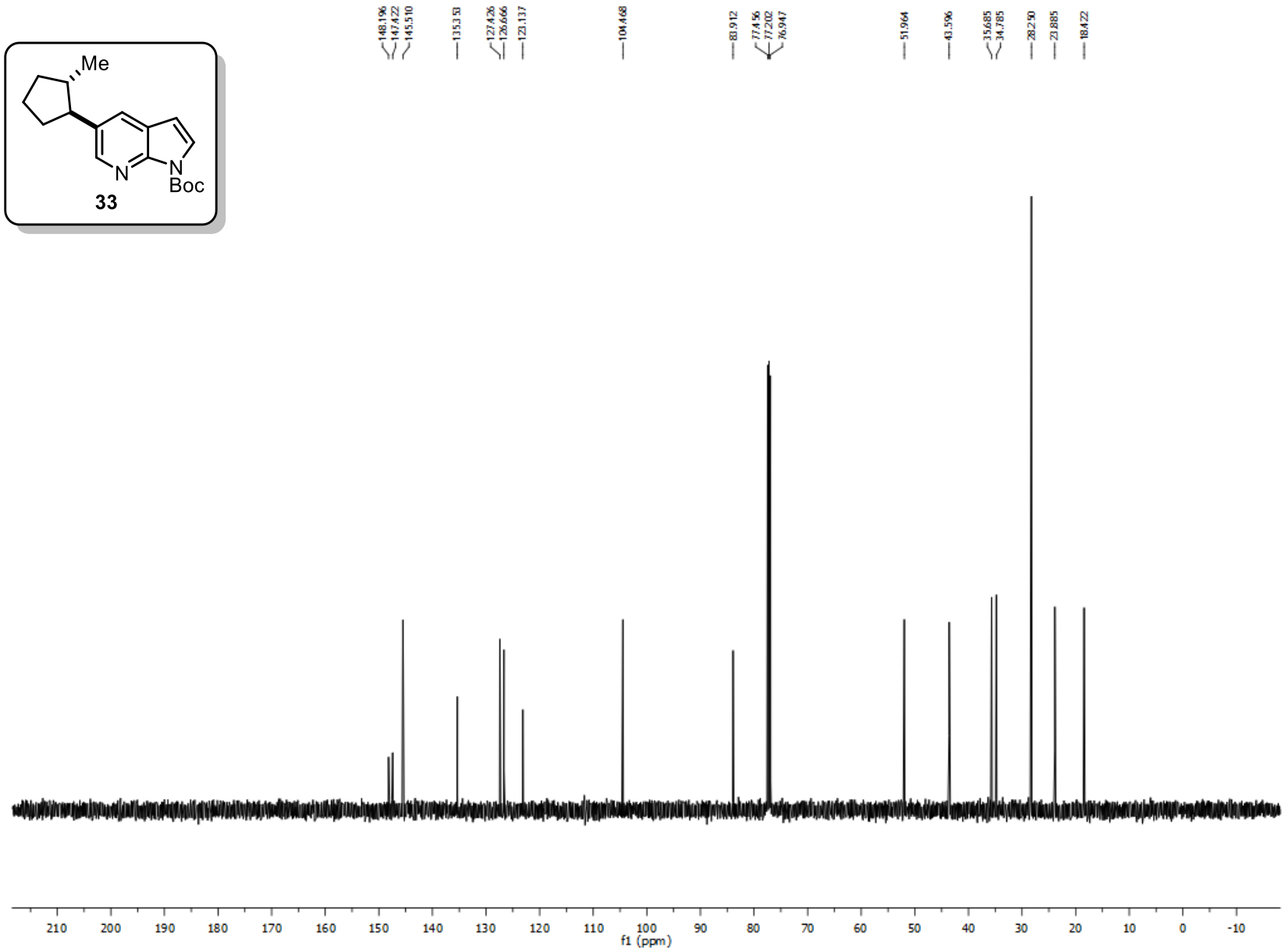
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-3-methoxy-5-(2-methylcyclopentyl)pyridine **(32)**



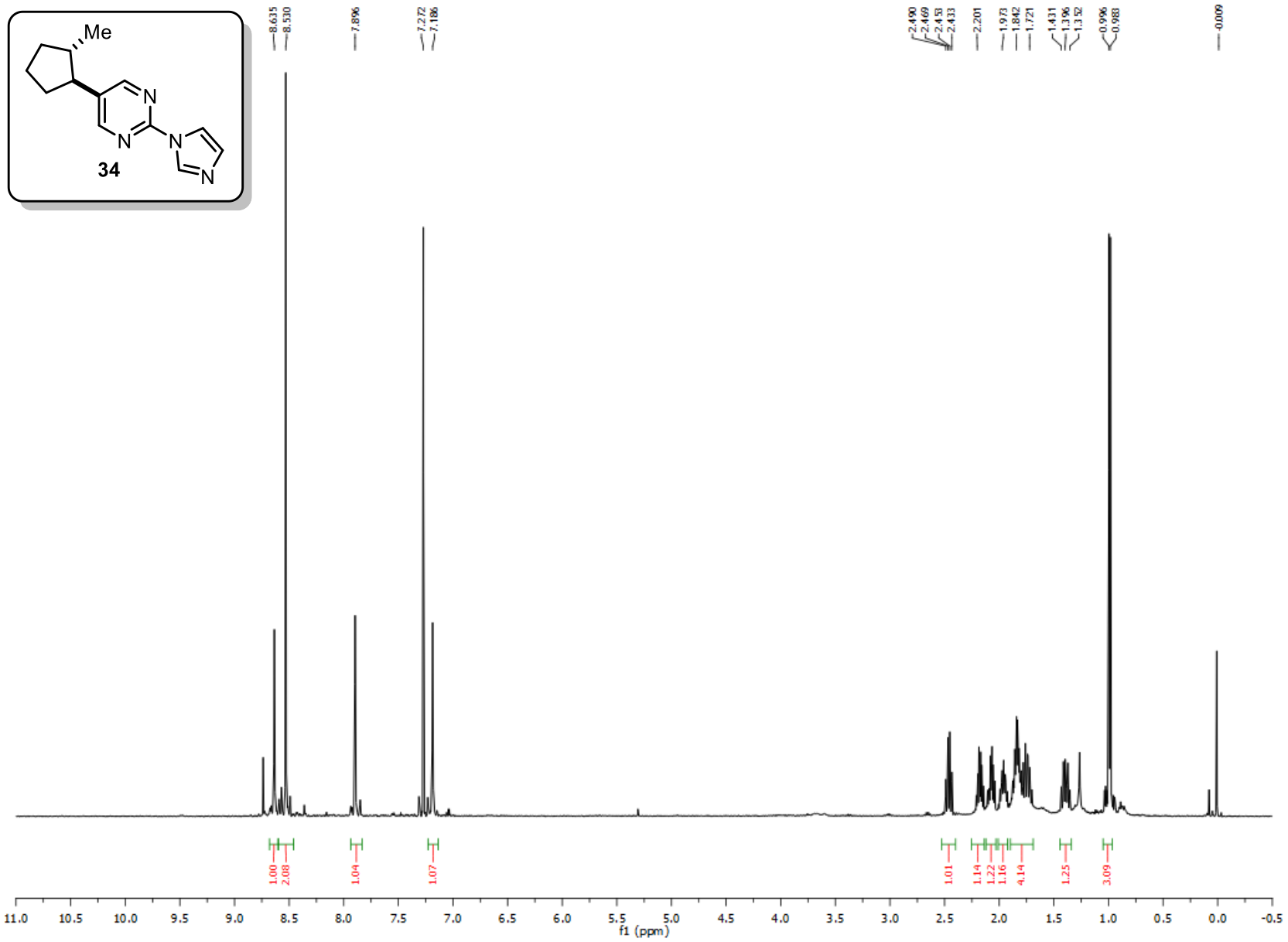
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*tert*-butyl *trans*-5-(2-methylcyclopentyl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate **(33)**



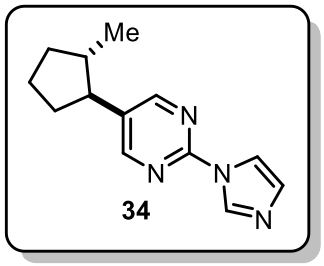
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*tert*-butyl *trans*-5-(2-methylcyclopentyl)-1H-pyrrolo[2,3-b]pyridine-1-carboxylate **(33)**



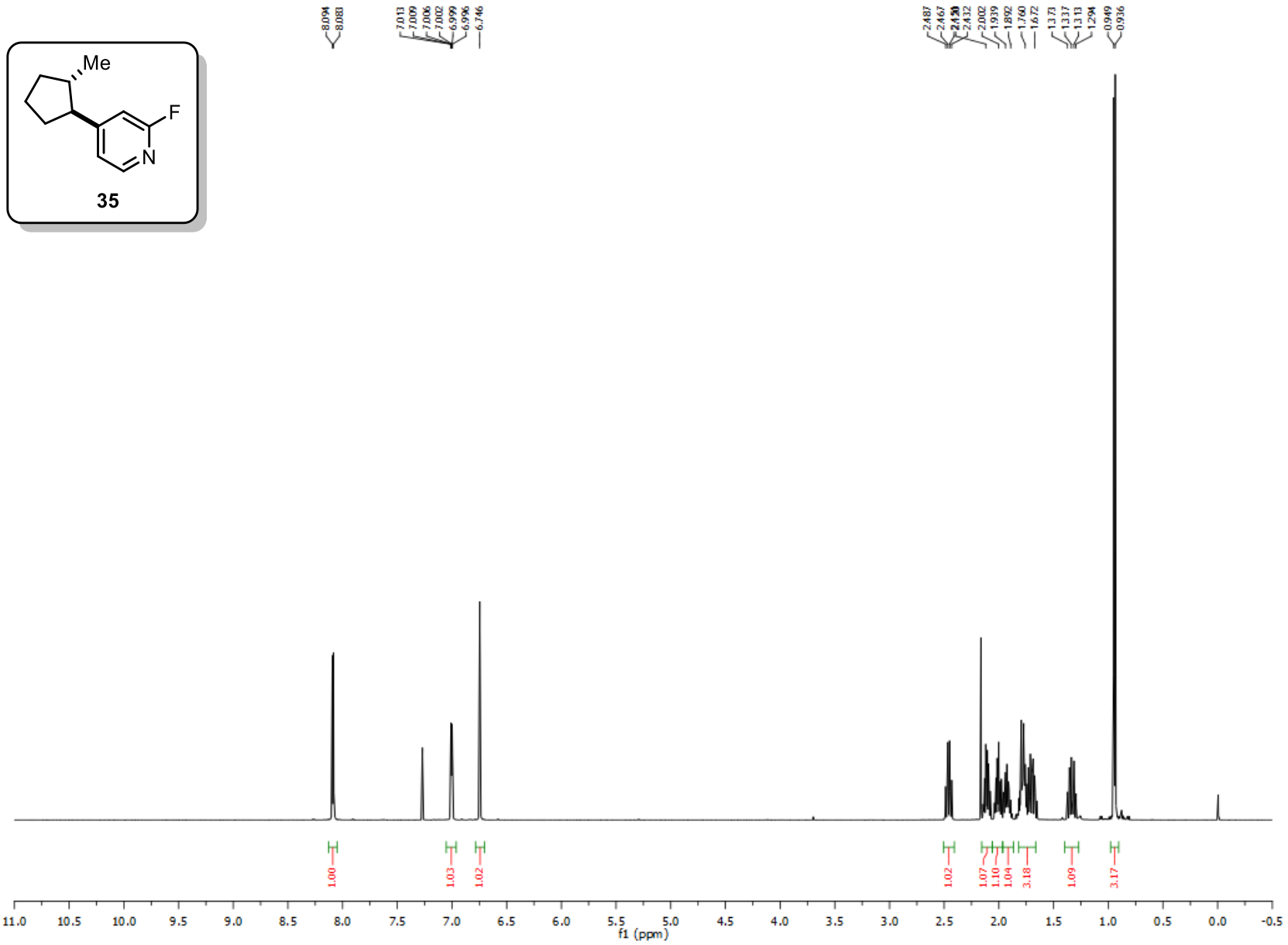
^{1}H NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-2-(1H-Imidazol-1-yl)-5-(2-methylcyclopentyl)pyrimidine **(34)**



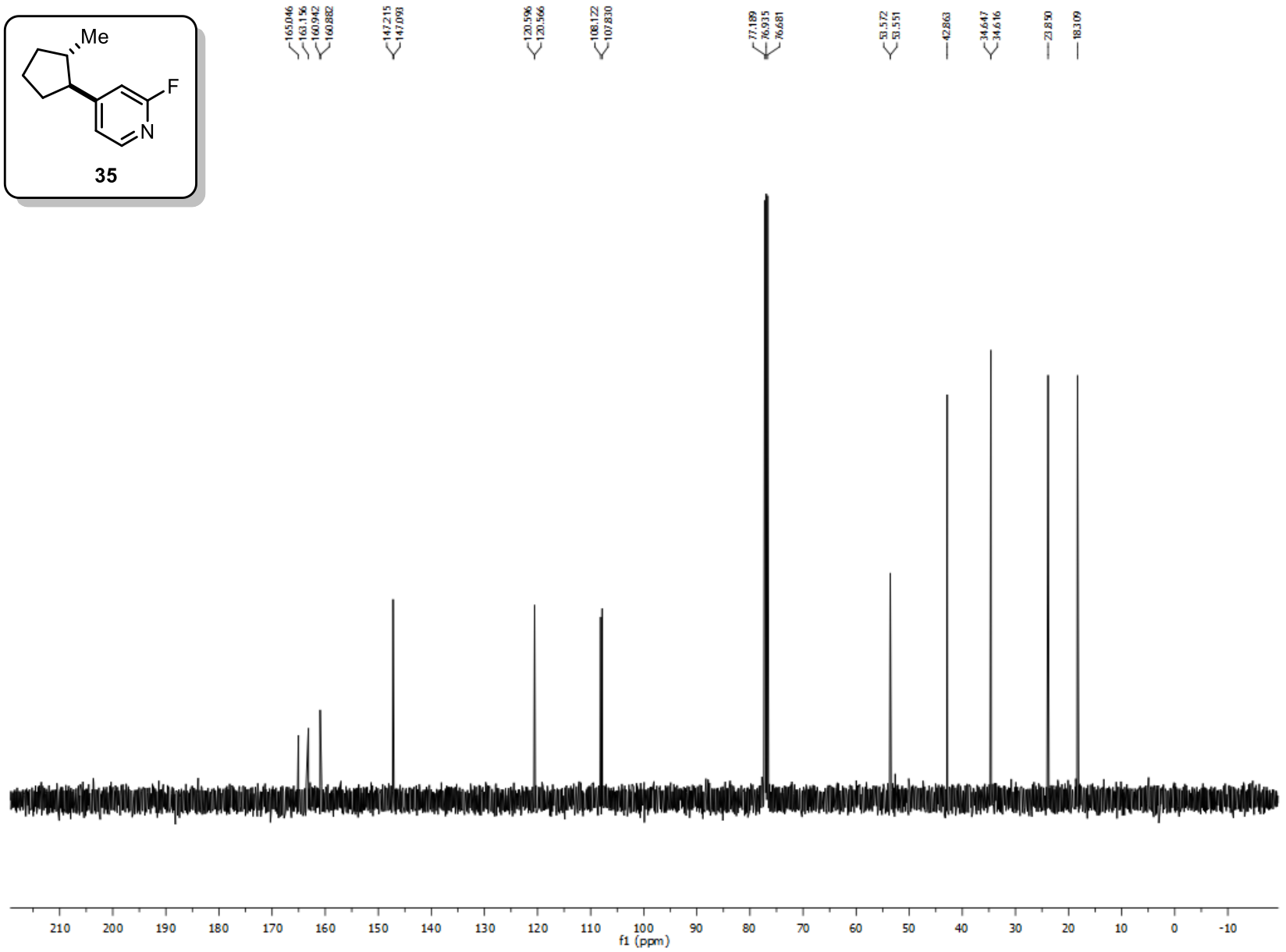
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-2-(1H-Imidazol-1-yl)-5-(2-methylcyclopentyl)pyrimidine **(34)**



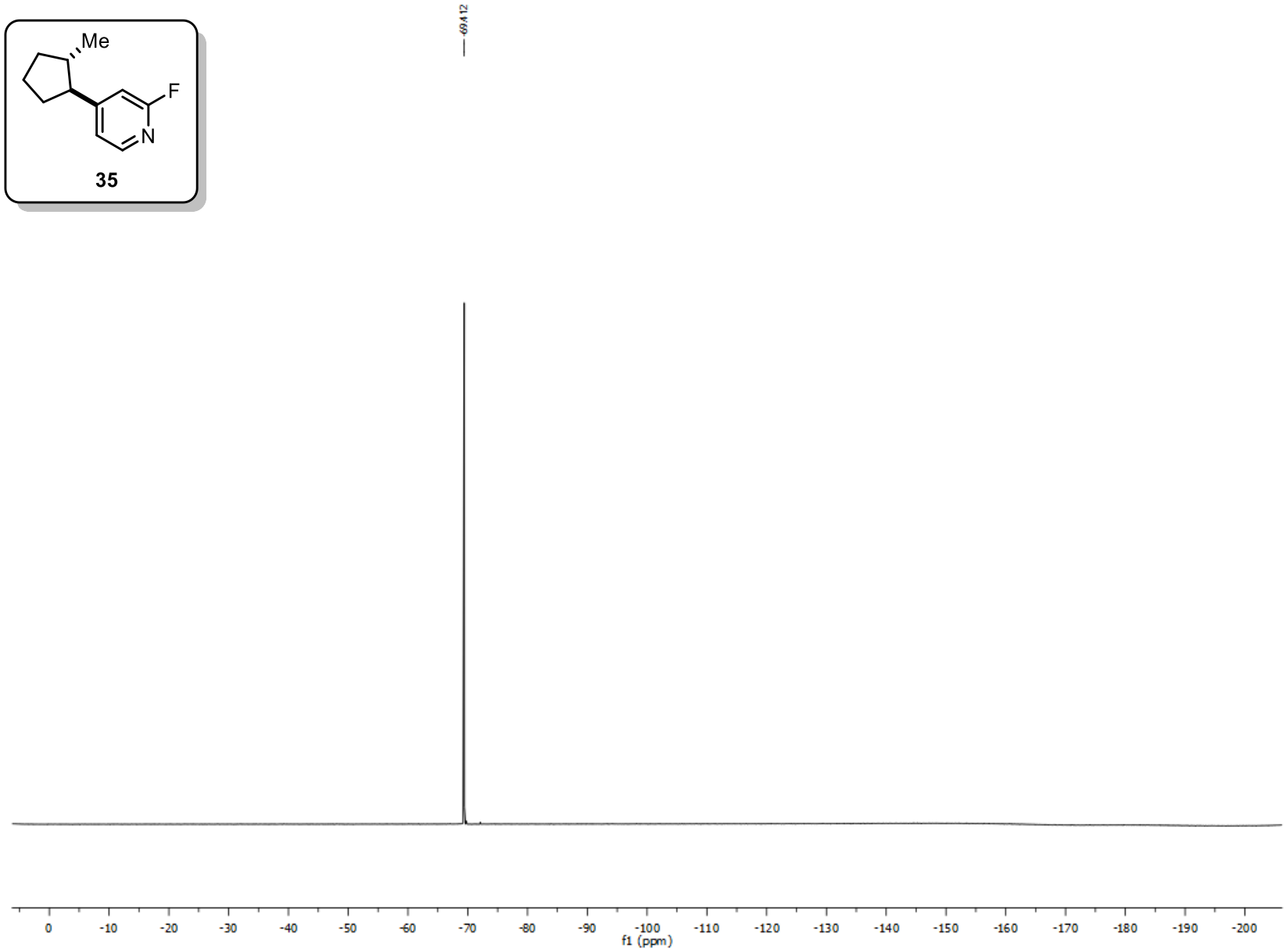
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-2-fluoro-4-(2-methylcyclopentyl)pyridine **(35)**



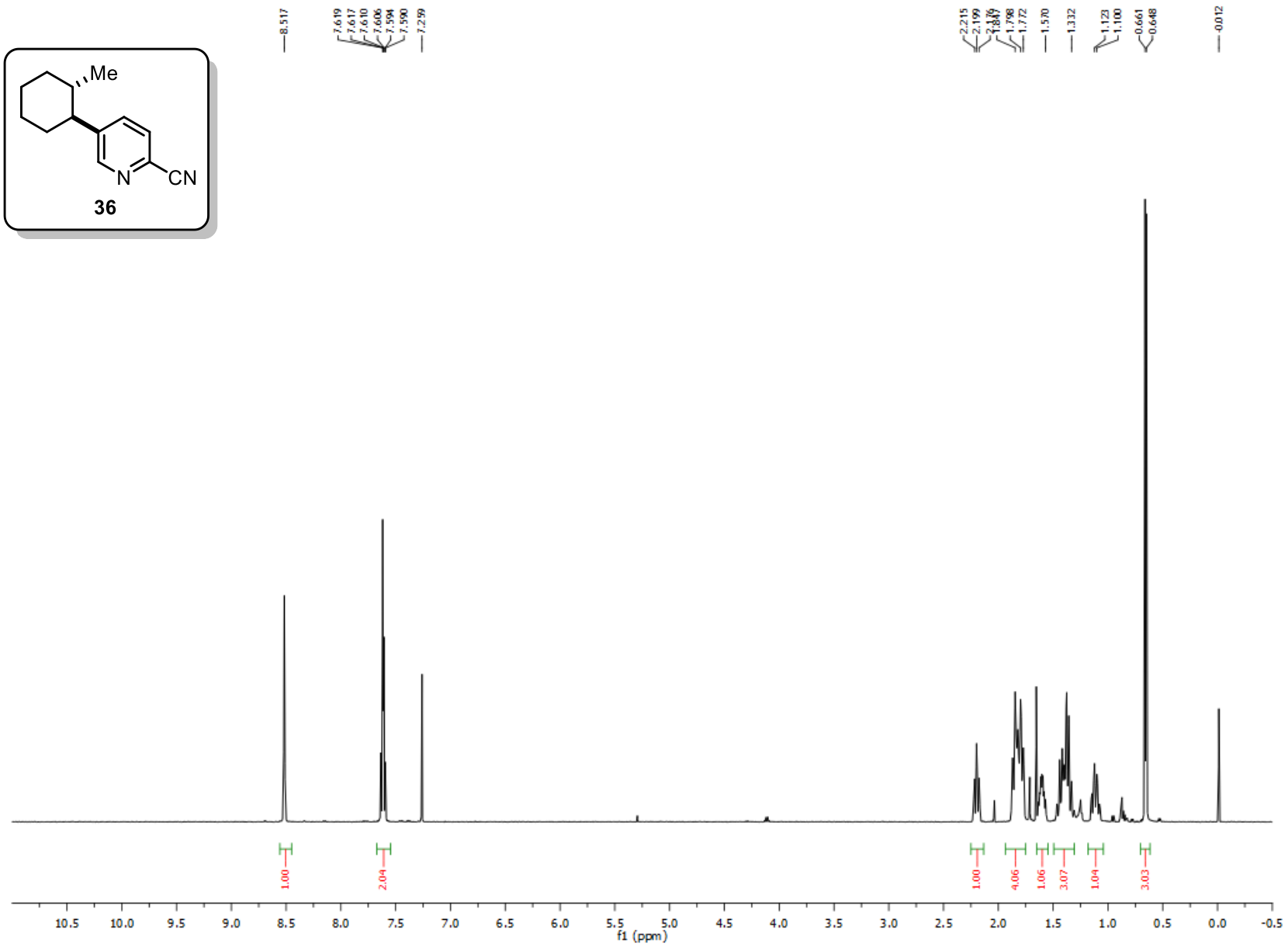
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of(±)-*trans*-2-fluoro-4-(2-methylcyclopentyl)pyridine **(35)**



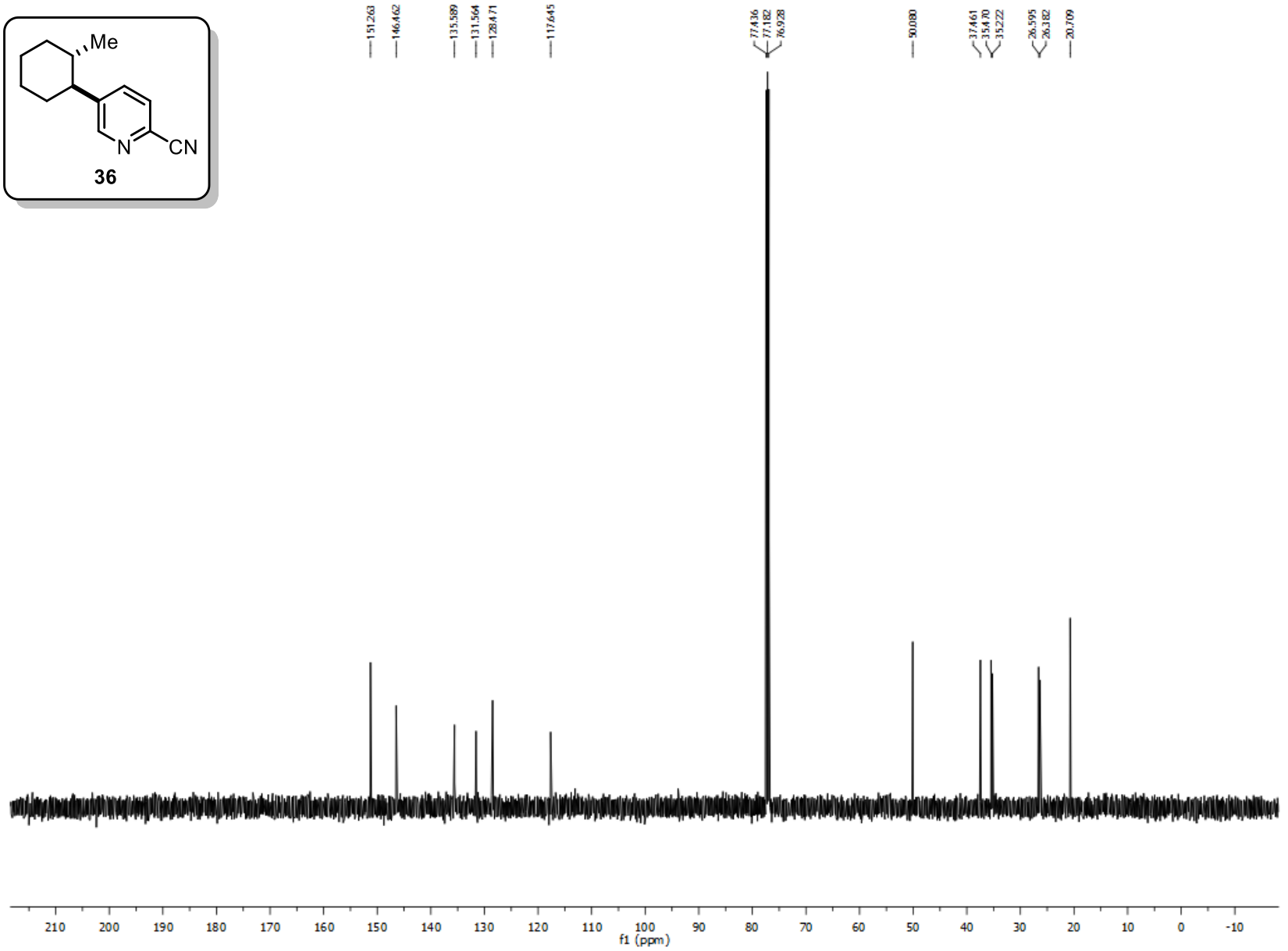
^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of (±)-*trans*-2-fluoro-4-(2-methylcyclopentyl)pyridine **(35)**



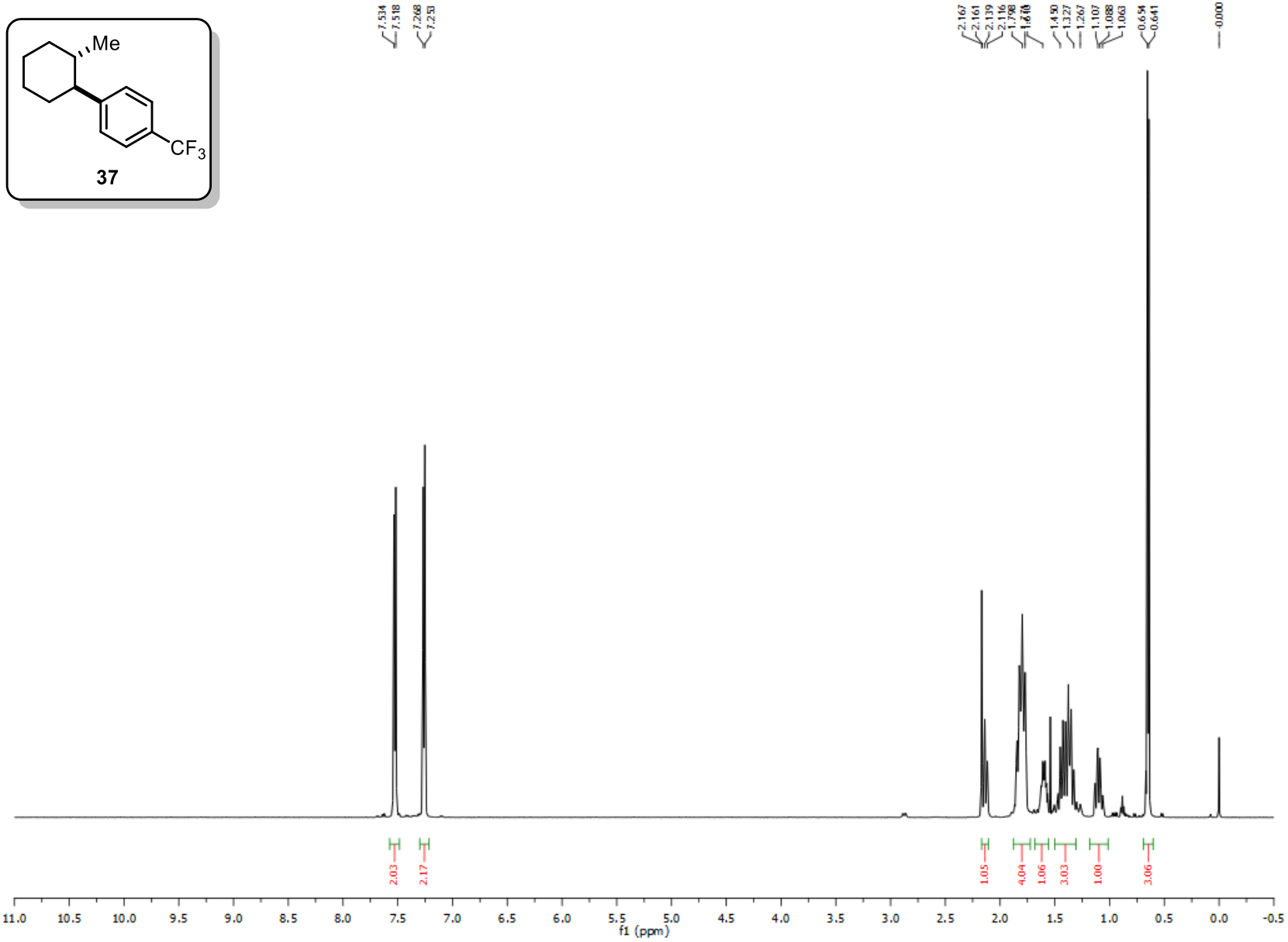
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-5-(2-methylcyclopentyl)picolinonitrile **(36)**



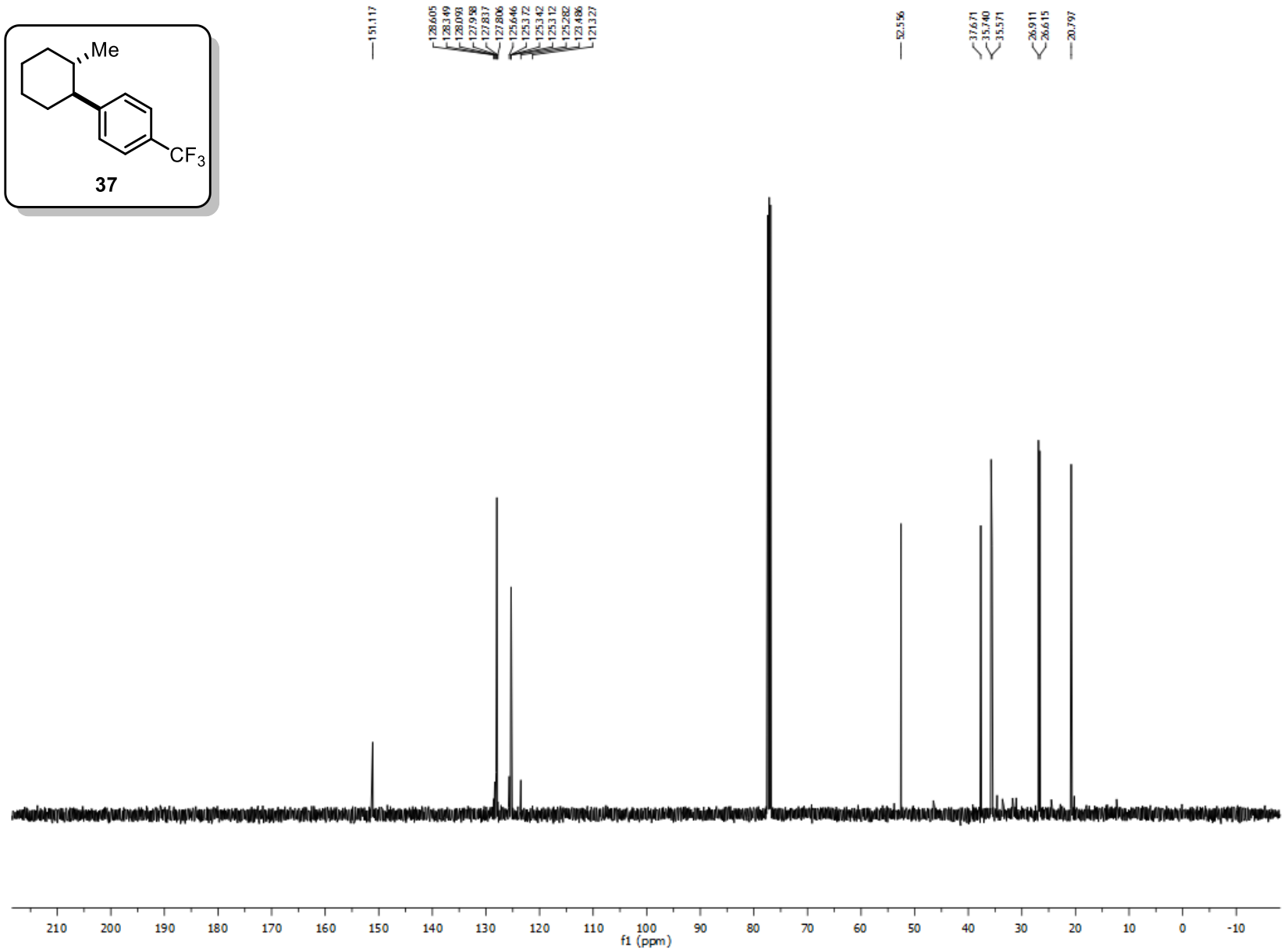
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-5-(2-methylcyclopentyl)picolinonitrile **(36)**



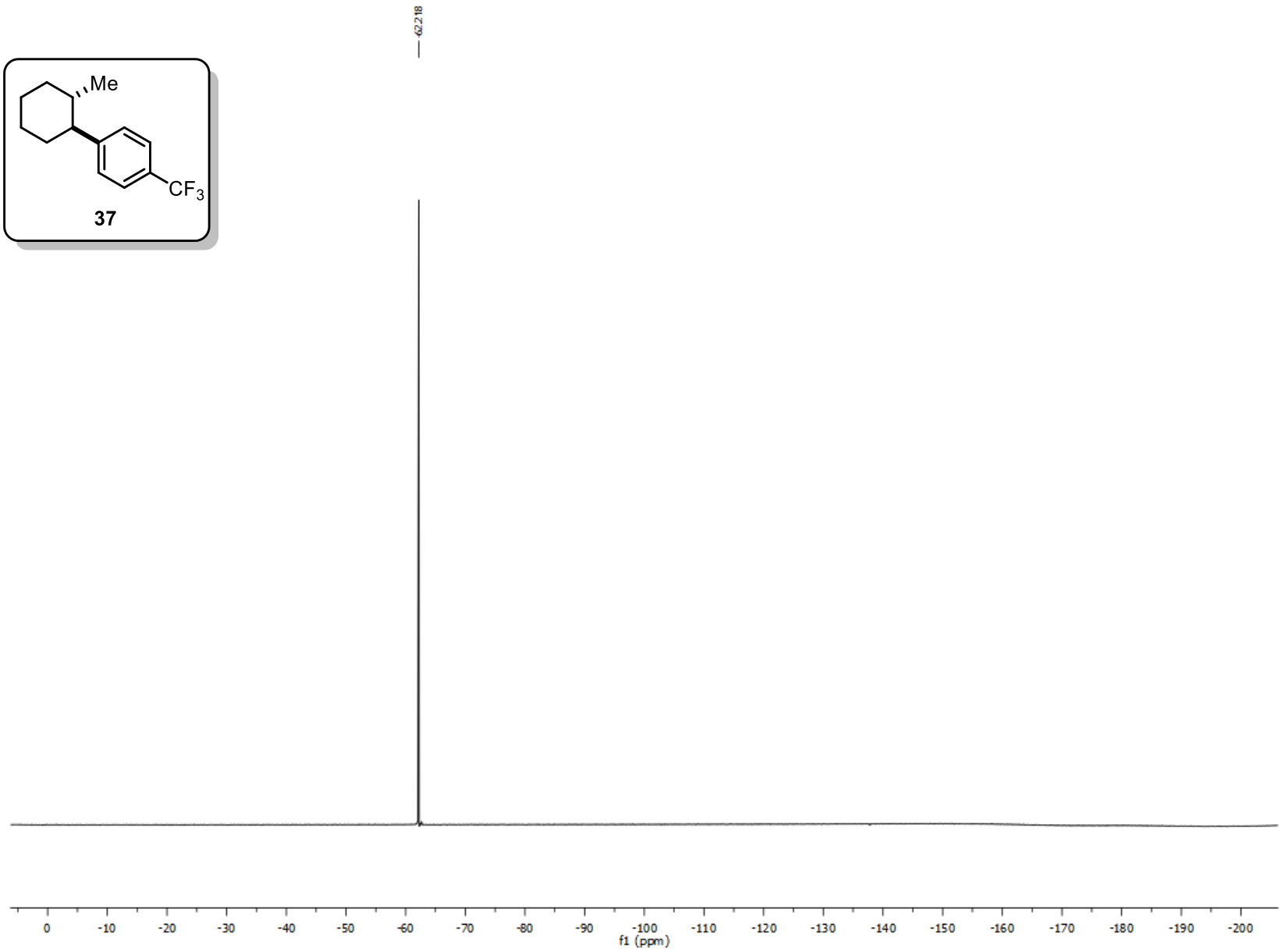
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-1-(2-methylcyclohexyl)-4-(trifluoromethyl)benzene **(37)**



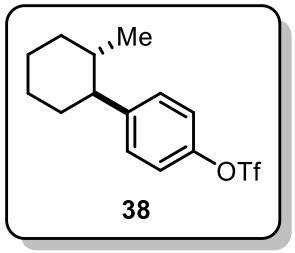
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-1-(2-methylcyclohexyl)-4-(trifluoromethyl)benzene (**37**)



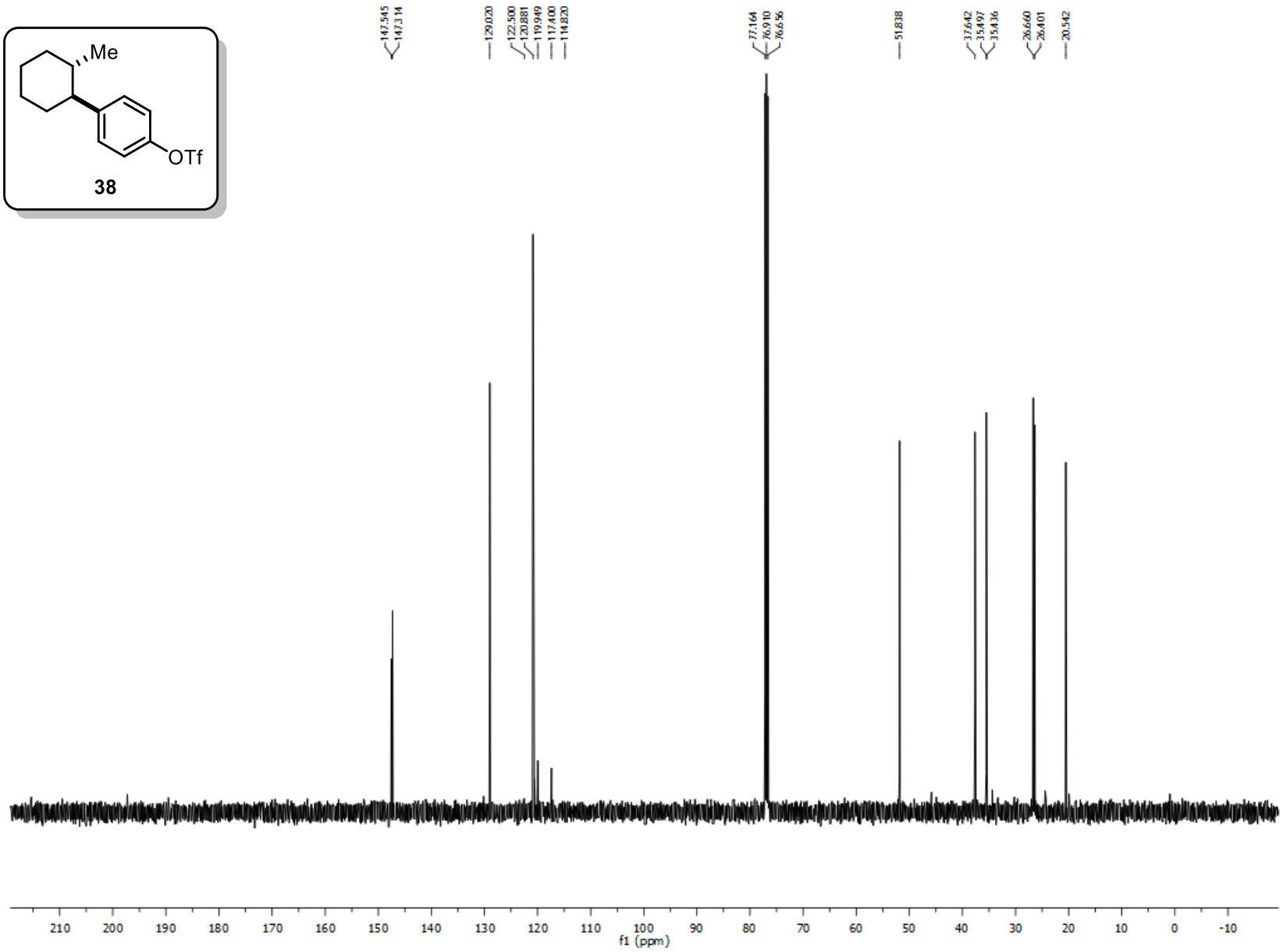
^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of (±)-*trans*-1-(2-methylcyclohexyl)-4-(trifluoromethyl)benzene (**37**)



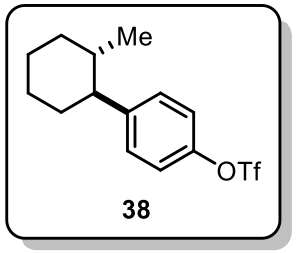
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-4-(2-methylcyclohexyl)phenyl trifluoromethanesulfonate (**38**)



^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-4-(2-methylcyclohexyl)phenyl trifluoromethanesulfonate (**38**)



^{19}F NMR ($CDCl_3$, 470.8 MHz) spectrum of (±)-*trans*-4-(2-methylcyclohexyl)phenyl trifluoromethanesulfonate (**38**)



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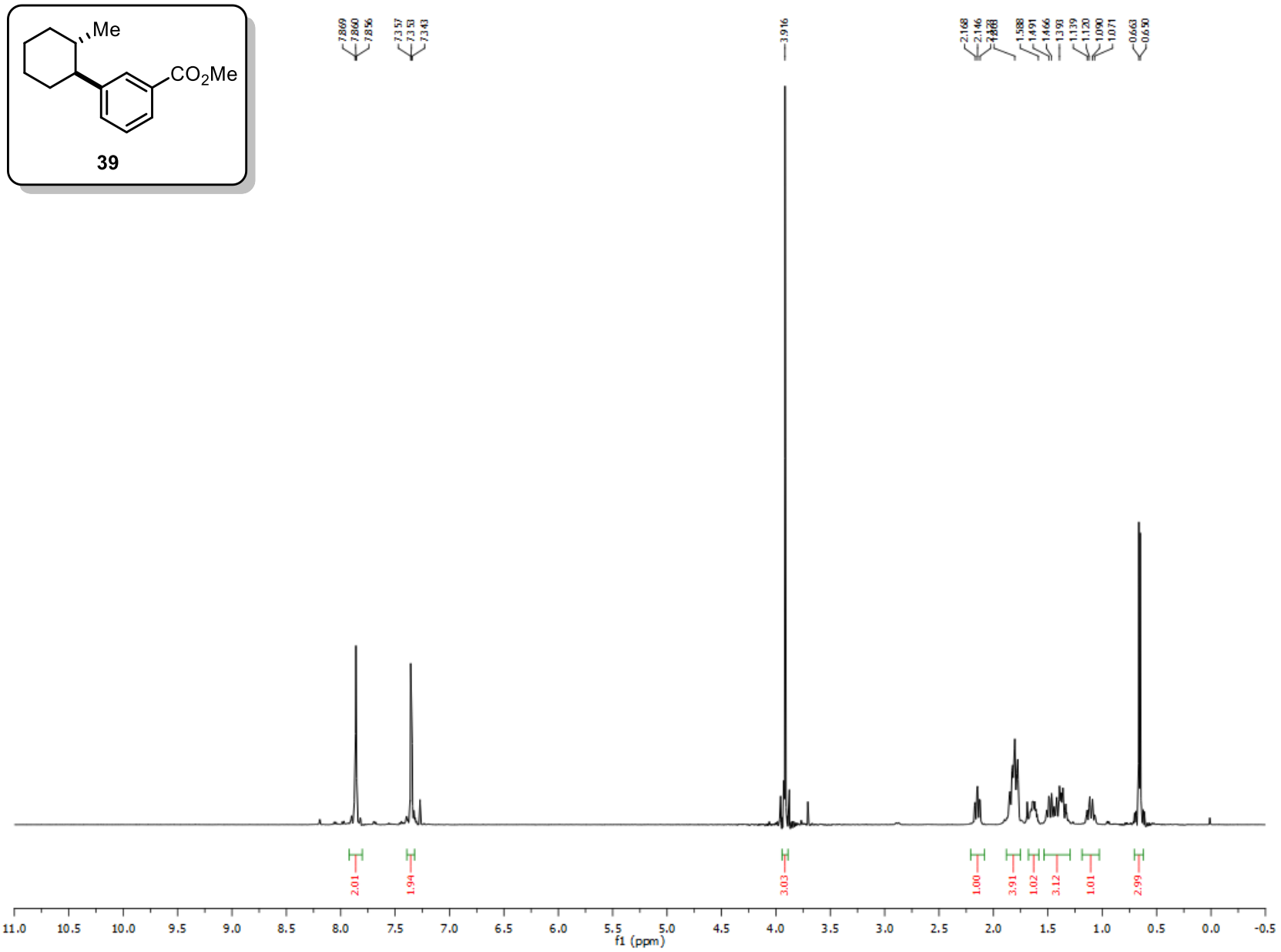
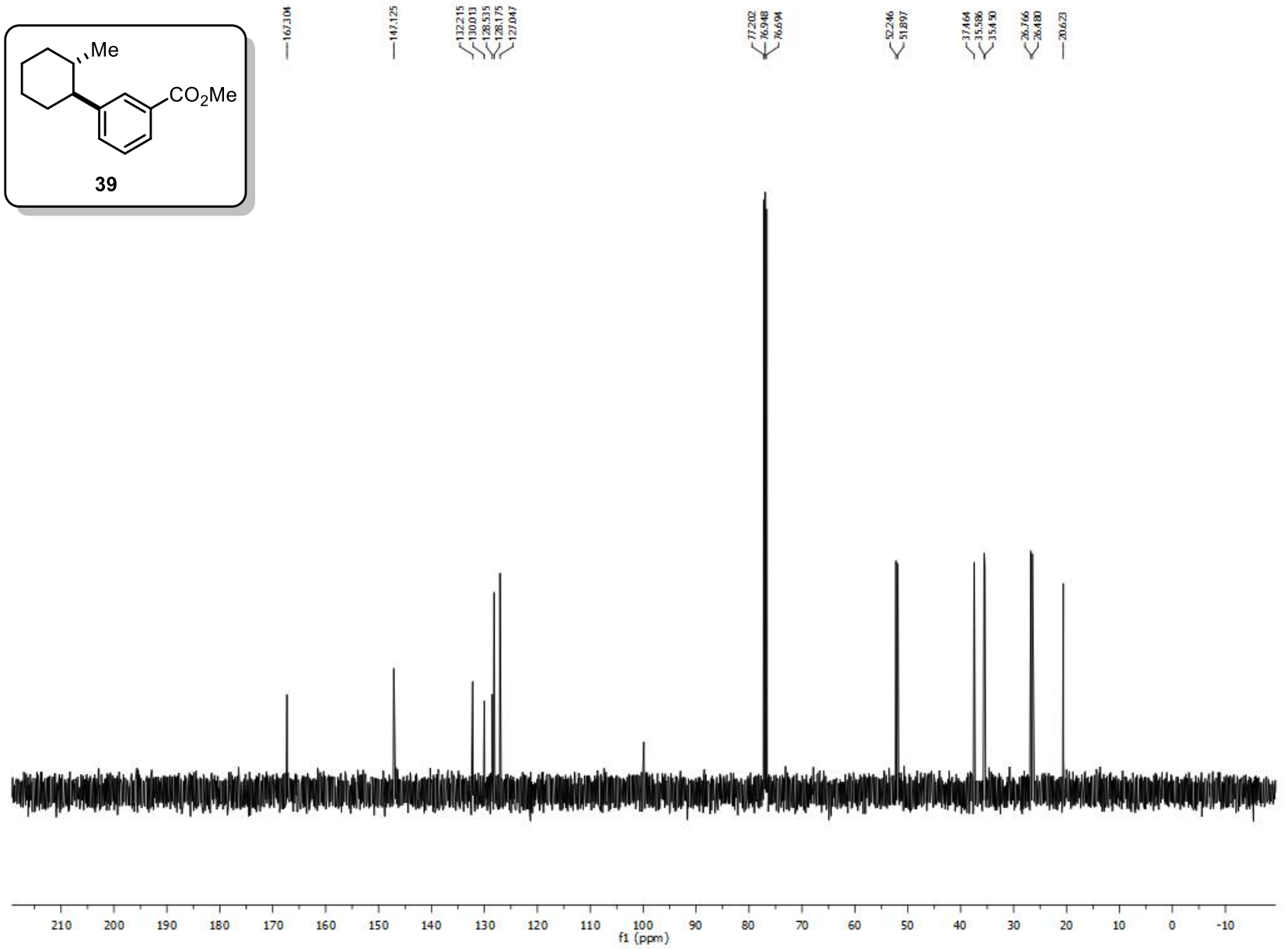
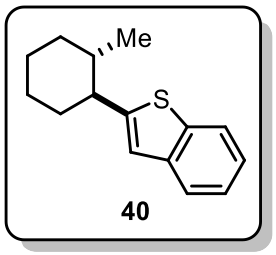
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-methyl 3-(2-methylcyclohexyl)benzoate **(39)**



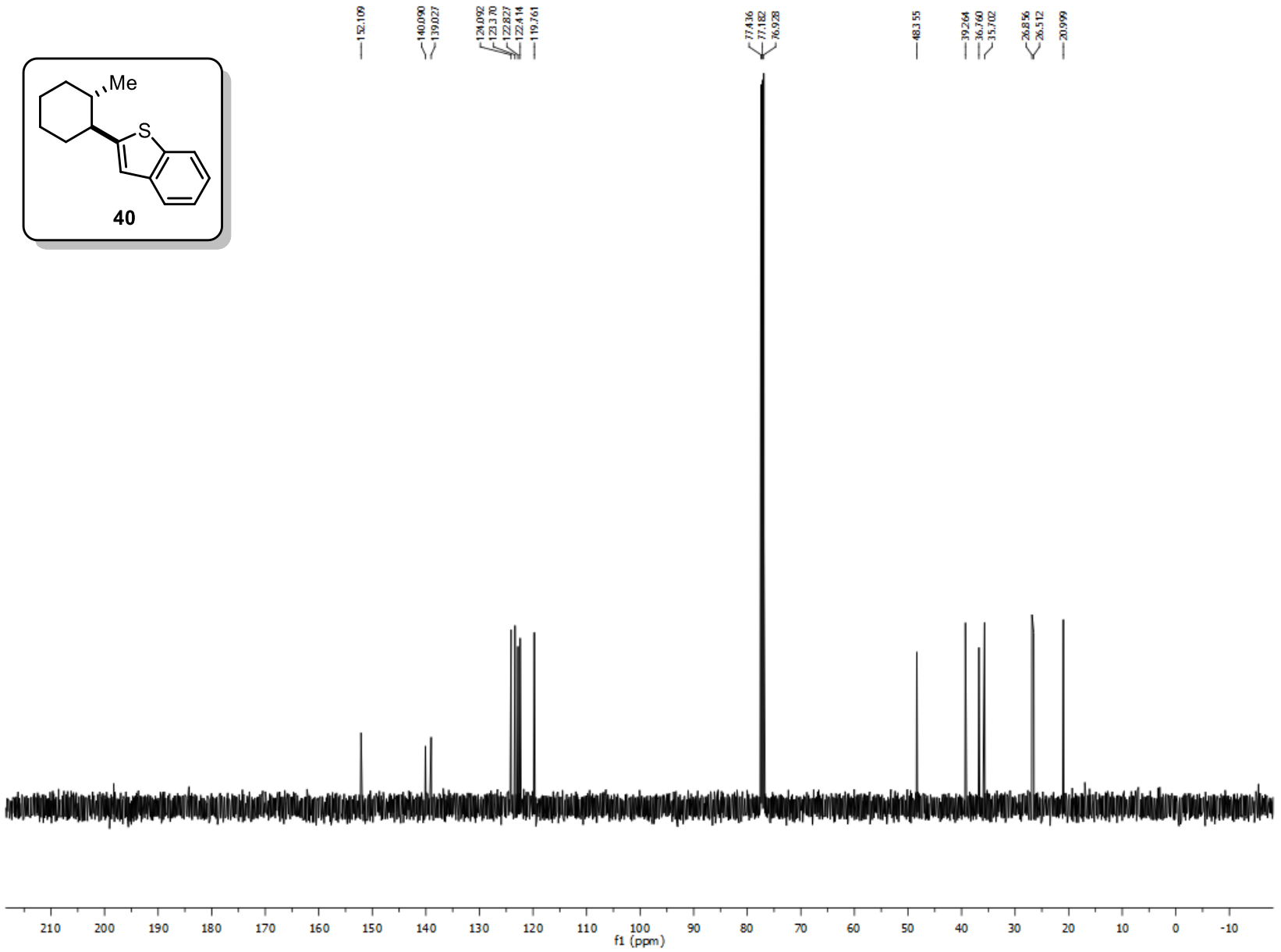
^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-methyl 3-(2-methylcyclohexyl)benzoate **(39)**



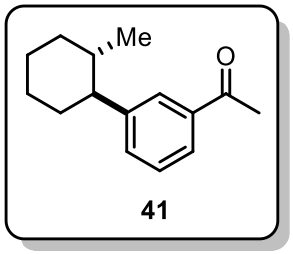
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-2-(2-Methylcyclohexyl)benzo[b]thiophene **(40)**



^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-2-(2-Methylcyclohexyl)benzo[b]thiophene **(40)**



^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of (±)-*trans*-1-(4-(2-Methylcyclohexyl)phenyl)ethan-1-one **(41)**



^{13}C NMR ($CDCl_3$, 125.8 MHz) spectrum of (±)-*trans*-1-(4-(2-Methylcyclohexyl)phenyl)ethan-1-one **(41)**