Supporting Online Material for

A Meta-Selective Copper-Catalyzed C–H Bond Arylation

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Published 20 March 2009, *Science* **323**, 1593 (2009)
DOI: 10.1126/science.1169975

This PDF file includes:

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Supporting Information

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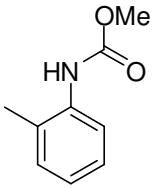
A. General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DPX 400 MHz operating at 400 and 100 MHz or a Bruker DPX 500 MHz operating at 500 and 125 MHz respectively. Chemical shifts (δ) are quoted relative to residual solvent and coupling constants (*J*) are corrected and quoted to the nearest 0.1 Hz. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum One-FT-IR spectrometer as solids or as neat films deposited in $CHCl_3$ or CH_2Cl_2. HRMS were measured either on a Micromass Q-TOF spectrometer using electrospray ionisation (ESI) or on a Bruker Apex IV Fourier transform ion cyclotron mass spectrometer (also ESI). Compounds with Br or Cl isotopes were quoted as *M* 78.9183 and *M* 34.9689 respectively. Melting points (m.p.) were recorded using a Reichert hot stage apparatus and are reported uncorrected. All solvents used were dried and distilled using standard methods. Dichloromethane and 1,2-dichloroethane were distilled from calcium hydride. All reagents were purchased at the highest commercial quality. All mixed solvent systems are reported as v/v solutions. All reactions were monitored by TLC carried out on glass precoated (0.25 mm) with Merck silica gel 60 PF_{254} or from ^{1}H NMR spectra taken from reaction samples. Flash column chromatography was performed with Merck 9383 Kieselgel 60 silica gel (230-400 mesh) or on a Flashmaster SOLO automated purification system using 50g silica cartridges. Reactions were carried out under an atmosphere of nitrogen unless otherwise stated. Commercially available $Cu(OTf)_2$ was dried under high vacuum at 100 ˚C and stored under nitrogen. $[Ph_2I]BF_4$ and $[PH_2I]OTf$ were prepared from $[Ph_2I]Br$ via oxidative anion metathesis using tetrafluoroboric acid and trifluoromethanesulfonic acid respectively.(S*1, 2*)

B. Synthesis and Analytical Data for Anilides

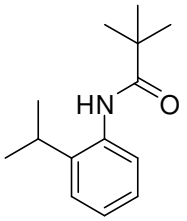
If not commercially available, pivanilides, acetanilides and benzanilides were prepared according to the general procedure of Daugulis (S*3*) with the modification that the crude anilide was taken up in CH_2Cl_2 and washed with water to remove traces of triethylamine hydrochloride, prior to recrystallisation from CH_2Cl_2/Hexane. Analytical data obtained for pivanilide (S*4*), 4-methylpivalanilide (S*3*), 2-fluoropivalanilide (S*5*), 2-methylpivalanilide (S*6*), 2-methoxypivalanilide,(S*7*) 3-methoxypivanilide (S*8*), 2-phenylpivalanlilide (S*4*), 2-bromo-4-methylpivalanilide(S*9*), 3-methylpivalanilide (S*6*), 3-fluoropivalanilide (S*6*), pivoylindoline (S*10*) and *N*-o-tolylbenzamide (S*11*) matched previously reported data. The known compound 1,1-diethyl-3-o-tolylurea (S*12*) was prepared by treatment of *ortho*-toluidine with diethylcarbamoyl chloride. Analytical data for the remaining anilides has not been previously reported and is as follows:

Methyl *o*-tolylcarbamate



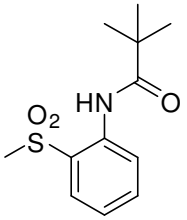
Prepared according to general procedure of Daugulis (S*3*) from methyl chloroformate and *ortho*-toluidine with the exception that pyridine was used in place of triethylamine. White solid (9.10 mmol, 46%). M.p. 52-53 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (br s, 1H), 7.21 (t, 1H, *J* = 7.7 Hz), 7.16 (d, 1H, *J* = 7.3 Hz), 7.04 (t, 1H, *J* = 7.4 Hz), 6.54 (br s, 1H), 3.78 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 135.7, 130.2, 127.9, 126.6, 124.1, 121.4, 52.2, 17.4; ν_{max}/cm^{-1} (solid): 3250; 1689, 1523, 1503, 1491, 1451; m/z HRMS (EI) found $[M]^+$ 165.0785, $C_9H_{11}NO_2$ requires 165.0784.

***N*-(2-isopropylphenyl)pivalamide**



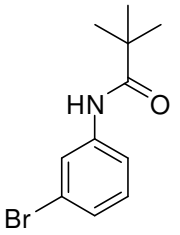
Prepared according to general procedure of Daugulis (S*3*) from pivaloyl chloride and 2-isopropylaniline. White solid (6.89 mmol, 69%). M.p. 125-127 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, 1H, *J* = 7.9 and 1.2 Hz), 7.32 (br s, 1H), 7.29 (d, 1H, *J* = 7.5 Hz), 7.21 (dt, 1H, *J* = 7.6 and 1.8 Hz), 7.16 (dt, 1H, J = 7.4 and 1.4 Hz), 2.99 (sept., 1H, *J* = 6.9 Hz), 1.36 (s, 9H), 1.28 (d, 6H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 139.5, 134.3, 126.3, 125.5, 125.3, 124.2, 39.6, 28.1, 27.6, 22.7; ν_{max}/cm^{-1} (solid): 3316, 2961, 1642, 1504, 1482, 1450; m/z HRMS (ESI) found $[M+H]^+$ 220.1698, $C_{14}H_{22}NO$ requires 220.1696.

_N_-(2-(methylsulfonyl)phenyl)pivalamide



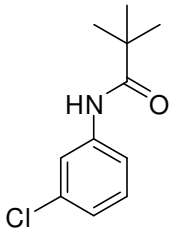
2-(Methylthio)aniline was pivalated according to the general procedure of Daugulis (S*3*) and the crude product was immediately subjected to oxidation with sodium perborate according to the procedure of McKillop (S*13*) to give the title product as a white solid (7.14 mmol, 71%). M.p. 119-120 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (s, 1H), 8.49 (dd, 1H, *J* = 0.9 and 8.4 Hz), 7.91 (dd, 1H, *J* = 1.6 and 8.0 Hz), 7.62 (dd, 1H, *J* = 1.5 and 7.8 Hz), 7.24 (t, 1H, *J* 8.0 Hz), 3.04 (s, 3H) 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 137.4, 135.2, 129.2, 127.0, 123.8, 122.8, 43.9, 40.0, 27.3; ν_{max}/cm^{-1} (film): 3352, 2966, 1695, 1586, 1533, 1463, 1431, 1305, 1168, 1137, 1120; m/z HRMS (ESI) found $[M+Na]^+$ 278.0830, $C_{12}H_{17}NO_3SNa$ requires 278.0827.

_N_-(3-bromophenyl)pivalamide



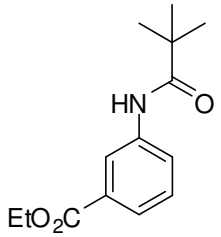
Prepared according to general procedure of Daugulis (S*3*) from pivaloyl chloride and 3-bromoaniline. White solid (7.92 mmol, 79%). M.p. 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (t, 1H, *J* = 1.9 Hz), 7.41 (d, 1H, *J* = 8.0 Hz), 7.38 (br s, 1H), 7.21 (d, 1H, *J* = 8.0 Hz), 7.15 (t, 1H, *J* = 8.0 Hz), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 139.2, 134.6, 129.8, 124.2, 120.1, 117.9, 39.7, 27.5; ν_{max}/cm^{-1} (solid): 3284, 2967, 1656, 1588, 1517, 1472, 1408; m/z HRMS (ESI) found $[M+H]^+$ 256.0333, $C_{11}H_{15}BrNO$ requires 256.0332.

_N_-(3-chlorophenyl)pivalamide



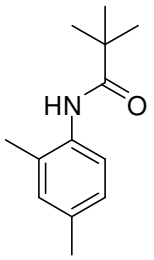
Prepared according to general procedure of Daugulis (S*3*) from pivaloyl chloride and 3-chloroaniline. White solid (7.67 mmol, 77%). M.p. 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (t, 1H, *J* = 1.9 Hz), 7.37 (br s, 1H), 7.35 (ddd, 1H, *J* = 0.8, 1.8 and 8.2 Hz), 7.22 (t, 1H, *J* = 8.1 Hz), 7.06 (ddd, 1H, *J* = 0.9, 1.9 and 8.0 Hz), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 139.2, 134.6, 129.8, 124.2, 120.1, 117.9, 39.7, 27.5; ν_{max}/cm^{-1} (solid): 3290, 2968, 1656, 1589, 1520, 1473, 1412; m/z HRMS (ESI) found $[M+H]^+$ 212.0839, $C_{11}H_{15}ClNO$ requires 212.0837.

Ethyl 3-pivalamidobenzoate



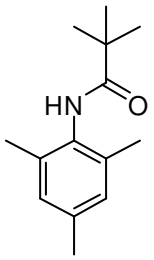
Prepared according to general procedure of Daugulis (S*3*) from pivaloyl chloride and ethyl 3-aminobenzoate. Off-white solid (8.35 mmol, 84%). M.p. 59-60 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (t, 1H, *J* = 1.9 Hz), 7.81 (ddd, 1H, *J* = 1.0, 2.2 and 8.1 Hz), 7.77 (br s, 1H), 7.66 (ddd, 1H, J = 1.1, 1.5 and 7.8 Hz), 7.25 (t, 1H, *J* = 7.9 Hz), 4.26 (q, 2H, *J* = 7.1 Hz), 1.27 (t, 3H, *J* = 7.1 Hz), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 166.1, 138.2, 130.8, 128.6, 124.9, 124.6, 121.0, 60.8, 39.4, 27.3, 14.1; ν_{max}/cm^{-1} (solid): 3301, 2958, 1719, 1658, 1589, 1537, 1425; m/z HRMS (ESI) found $[M+H]^+$ 250.1449, $C_{14}H_{20}NO_3$ requires 250.1443.

_N_-(2,4-dimethylphenyl)pivalamide



Prepared according to general procedure of Daugulis (S*3*) from pivaloyl chloride and 2,4-dimethylaniline. White solid (8.39 mmol, 84%). M.p. 107-108 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, 1H, *J* = 7.9 Hz), 7.18 (br s, 1H), 6.98 – 7.03 (m, 2H), 2.29 (s, 3H), 2.20 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 134.5, 133.1, 130.9, 129.1, 127.1, 123.2, 39.5, 27.6, 20.7, 17.4; ν_{max}/cm^{-1} (solid): 3272, 2955, 1647, 1500; m/z HRMS (ESI) found $[M+H]^+$ 206.1543, $C_{13}H_{20}NO$ requires 206.1539.

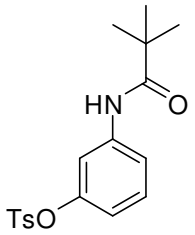
_N_-mesitylpivalamide



Prepared according to general procedure of Daugulis (S*3*) from pivaloyl chloride and 2,4,6-trimethylaniline. White solid (8.44 mmol, 84%). M.p. 179-180 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 2H), 6.82 (br s, 1H), 2.26 (s, 3H), 2.15 (s, 6H), 1.34 (s, 9H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 176.5, 136.5, 135.0, 131.2, 128.8, 39.2, 27.8, 20.8, 18.1; ν_{max}/cm^{-1} (solid): 3280, 2957, 1646, 1507, 1239, 1185; m/z HRMS (ESI) found $[M+H]^+$ 220.1698, $C_{14}H_{22}NO$ requires 220.1696.

3-Pivalamidophenyl 4-methylbenzenesulfonate



To a stirred solution of *N*-(3-hydroxyphenyl)pivalamide (S*14*) (1.93g, 10 mmol) and triethylamine (1.66 ml, 12 mmol) in CH_2Cl_2 (30 ml) was added tosyl chloride (2.28g, 12 mmol) and the reaction stirred at room temperature for 20h. After this time, the reaction was diluted with further CH_2Cl_2 and washed twice with satd. sodium bicarbonate solution. The organic layer was dried over magnesium sulphate and evaporated *in vacuo*. Trituration with Et_2O gave a white solid (8.01 mmol, 80%). M.p. 107-108 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, 2H, *J* = 8.3 Hz), 7.51 (d, 1H, *J* = 8.2 Hz), 7.38 (br s, 1H), 7.27-7.32 (m, 3H), 7.17 (t, 1H, *J* = 8.2 Hz), 6.62 (ddd, 1H, *J* = 0.8, 2.3 and 8.2 Hz), 2.43 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 149.6, 145.3, 139.3, 132.2, 129.7, 129.6, 128.4, 118.4, 117.4, 114.0, 39.6, 27.4, 21.6; ν_{max}/cm^{-1} (solid): 3304, 2967, 1663, 1594, 1522, 1484, 1426, 1369; m/z HRMS (ESI) found $[M+H]^+$ 348.1265, $C_{18}H_{22}NO_4S$ requires 348.1264.

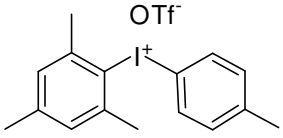
C. Synthesis and Analytical Data for Iodonium Salts

Aryl-mesityliodonium triflates were in general able to be synthesised in a one-pot procedure from the appropriate iodoarene and mesitylene according to the general procedure of Olofsson (S*15, 16*). The 4-iodophenyl substituted iodonium salt was unsuitable for synthesis by the one-pot method and was instead synthesised from reaction between the 4-iodophenylboronic acid and iodomesitylene diacetate followed by anion exchange (S*17, 18*).

General Procedure for one-pot preparation of diaryliodonium triflates (S*15, 16*)

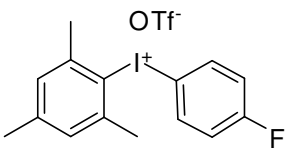
Mesitylene (1.40 ml, 10.0 mmol) was added to a solution of the appropriate iodoarene (9 mmol) and *m*CPBA ((dried under vacuum at rt for 1h, assume 65%) 2.64g, 10 mmol) in CH_2Cl_2 (40 ml) and the solution cooled to 0 ^oC. Trifluoromethanesulfonic acid (1.31 mL, 15.0 mmol) was added dropwise over 5 mins and the reaction allowed to slowly warm to rt over the course of 2h. The solvent was removed *in vacuo* and Et_2O added. The solvent was again removed *in vacuo* and this procedure was repeated several times until crystals started to form. At this point, the solution was stored at – 20 ^oC for 2h and the resulting crystals were filtered and washed on the filter with Et_2O to give the iodonium triflate as a solid which was dried at 100 ^oC under vacuum.

4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate



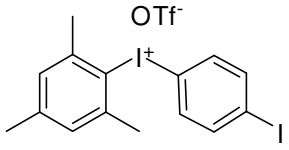
Prepared according to the general procedure from 4-iodotoluene. Product obtained as a white solid (2.99 g, 68%). M.p. 181-182 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, 2H, *J* = 8.5 Hz), 7.19 (d, 2H, *J* = 8.4 Hz), 7.07 (s, 2H), 2.60 (s, 6H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 142.7, 142.2, 133.1, 132.9, 130.2, 120.4, 107.7, 26.9, 21.1, 20.9; ν_{max}/cm^{-1} (solid): 1451, 1246, 1157; m/z HRMS (ESI) found $[M - OTf]^+$ 337.0464, $C_{16}H_{18}I$ requires 337.0453.

4-Fluorophenyl(mesityl)iodonium trifluoromethanesulfonate



Prepared according to the general procedure from 3-fluoroiodobenzene. Product obtained as an off-white solid (2.89 g, 66%). M.p. 177-178 °C; ^{1}H NMR (400 MHz, MeOD): δ 7.98 (dd, 2H, *J* = 4.8 and 9.1 Hz), 7.29 (t, 2H, *J* = 8.8 Hz), 7.25 (s, 2H), 2.68 (s, 6H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, MeOD): δ 166.2 (d, *J* = 253 Hz), 145.9, 143.4, 138.1 (d, *J* = 9.0 Hz), 131.3, 122.7, 120.6 (d, *J* = 23.4 Hz), 107.8 (d, *J* = 3.3 Hz), 27.0, 21.0; ν_{max}/cm^{-1} (solid): 1575, 1482, 1224, 1167; m/z HRMS (ESI) found $[M - OTf]^+$ 341.0193, $C_{15}H_{15}FI$ requires 341.0197.

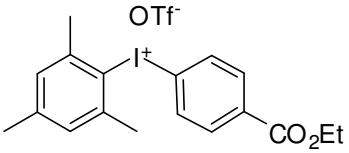
4-Iodophenyl(mesityl)iodonium trifluoromethanesulfonate



$BF_3.OEt_2$ (415 μL, 3.3 mmol) was added to a stirred solution of 4-iodophenylboronic acid (456 mg, 3.0 mmol) in CH_2Cl_2 (50 ml) at 0 °C and the solution was stirred for 10 mins before addition of a solution of iodomesitylene diacetate (1.20 g, 3.3 mmol) in CH_2Cl_2 (20 ml) dropwise over 10 mins. The reaction was allowed to warm to rt over the course of 2h and then 100 ml saturated aq. $NaBF_4$ solution was added with rapid stirring and the stirring continued for 30 mins. After this time the phases were separated, the aqueous layer extracted twice with CH_2Cl_2 and the combined organics dried ($MgSO_4$) and evaporated. The iodonium tetrafluoroborate was precipitated from a hot CH_2Cl_2 solution of the crude residue by addition of Et_2O. The solid was filtered, washed with Et_2O and dried under vacuum. The iodonium tetrafluoroborate was immediately taken up in MeCN (20 ml) and TMSOTf (0.90 ml, 5.0 mmol) was added at 0 °C and the solution allowed to warm to rt. After stirring for 15h, the solvent was removed *in vacuo* and the resulting residue taken up in Et_2O and stirred for 15 mins. The resulting precipitate were filtered, washed with Et_2O and dried under vacuum at 100 °C to give the title compound as a

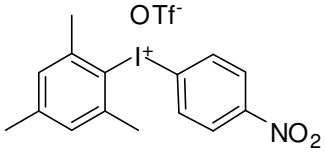
white solid (1.39 g, 78%). M.p. 188-189 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, 2H, *J* = 8.6 Hz), 7.41 (d, 2H, *J* = 8.6 Hz), 7.09 (s, 2H), 2.61 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 142.4, 141.0, 134.3, 130.3, 120.7, 111.1, 98.5, 27.0, 21.1; ν_{max}/cm^{-1} (solid): 1466, 1378, 1224, 1162; m/z HRMS (ESI) found $[M - OTf]^+$ 448.9252, $C_{15}H_{15}I_2$ requires 448.9258.

(4-(Ethoxycarbonyl)phenyl)(mesityl)iodonium trifluoromethanesulfonate



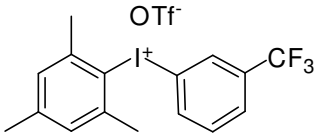
Prepared according to the general procedure from ethyl 4-iodobenzoate. Product obtained as a white solid (2.08 g, 42%). M.p. 178-179 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, 2H, *J* = 8.7 Hz), 7.76 (d, 2H, *J* = 8.7 Hz), 7.10 (s, 2H), 4.36 (q, 2H, *J* = 7.1 Hz), 2.61 (s, 6H), 2.35 (s, 3H), 1.36 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 144.5, 142.5, 133.4, 132.7, 132.6, 130.3, 120.6, 116.3, 61.7, 27.0, 21.1, 14.1; ν_{max}/cm^{-1} (solid): 2987, 1722, 1272, 1224; m/z HRMS (ESI) found $[M - OTf]^+$ 395.0498, $C_{18}H_{20}IO_2$ requires 395.0503.

4-Nitrophenyl(mesityl)iodonium trifluoromethanesulfonate



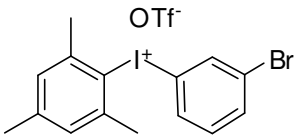
Prepared according to the general procedure from 4-iodonitrobenzene with the exception that the all the reagents apart from the trifluoromethanesulfonic acid were stirred together at room temperature for 20h before the addition of the latter reagent. Product obtained as a light yellow solid (2.79 g, 60%). M.p. 208 ˚C; ^{1}H NMR (400 MHz, MeOD): δ 8.30 (d, 2H, *J* = 9.1 Hz), 8.12 (d, 2H, *J* = 9.1 Hz), 7.28 (s, 2H), 2.67 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, MeOD): δ 151.3, 146.4, 143.7, 136.2, 131.6, 127.5, 122.4, 119.8, 27.1, 21.1; ν_{max}/cm^{-1} (solid): 1534, 1355, 1236, 1224; m/z HRMS (ESI) found $[M - OTf]^+$ 368.0138, $C_{15}H_{15}INO_2$ requires 368.0142.

3-trifluoromethylphenyl(mesityl)iodonium trifluoromethanesulfonate



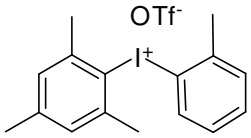
Prepared according to the general procedure from 3-iodobenzotrifluoride. Product obtained as an off-white solid (1.23 g, 25%). M.p. 181-183 ˚C; ^{1}H NMR (400 MHz, MeOD): δ 8.30 (s, 1H), 8.09 (d, 1H, *J* = 8.1 Hz), 7.98 (d, 1H, *J* = 7.8 Hz), 7.73 (t, 1H, *J* = 8.0 Hz), 7.30 (s, 2H), 2.70 (s, 6H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, MeOD): δ 146.3, 143.6, 138.4, 134.57 (q, 1H, *J* = 33.6Hz) 134.1, 131.73 (q, *J* = 3.7 Hz), 131.5, 129.97 (q, *J* = 3.2 Hz), 124.15 (q, *J* = 273 Hz), 122.4, 114.0, 27.0, 21.0; ν_{max}/cm^{-1} (solid): 1242, 1133; m/z HRMS (ESI) found [M - OTf]$^{+}$ 391.0159, $C_{16}H_{15}F_3I$ requires 391.0165.

3-Bromophenyl(mesityl)iodonium trifluoromethanesulfonate



Prepared according to the general procedure from 3-bromoiodobenzene. Product obtained as a white solid (1.98 g, 40%). M.p. 174-175 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (t, 1H, *J* = 1.6 Hz), 7.69 (d, 1H, *J* = 8.2 Hz), 7.63 (d, 1H, *J* = 8.1 Hz), 7.27 (t, 1H, *J* = 8.1 Hz), 7.11 (s, 2H), 2.62 (s, 6H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 142.4, 134.9, 134.8, 132.9, 131.6, 130.3, 124.9, 120.7, 111.8, 27.0, 21.1; ν_{max}/cm^{-1} (solid): 1454, 1223, 1165; m/z HRMS (ESI) found [M - OTf]$^{+}$ 400.9393, $C_{15}H_{15}BrI$ requires 400.9396.

2-methylphenyl(mesityl)iodonium trifluoromethanesulfonate



Prepared according to the general procedure from 2-iodotoluene. Product obtained as a white solid (3.73 g, 85%). M.p. 167-168 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.48 (m, 3H), 7.16 (dt, 1H, *J* = 1.8 and 7.7Hz), 7.09 (s, 2H), 2.57 (s, 9H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 142.3, 140.1, 133.7, 132.4, 132.4, 130.6, 129.7, 119.4,

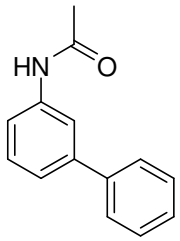
115.6, 26.8, 24.7, 20.9; ν_{max}/cm^{-1} (solid): 1468, 1244, 1154; m/z HRMS (ESI) found $[M - OTf]^+$ 337.0444, $C_{16}H_{18}I$ requires 337.0447.

D. Synthesis and Analytical Data for Aryl Anilides

General procedure for the meta-arylation of anilides

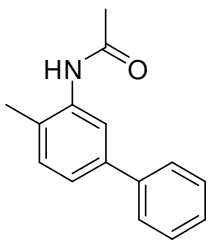
To a solution of the appropriate anilide (0.50 mmol) in 1,2-dichloroethane (2.5 ml) was added the appropriate iodonium salt (0.75 – 3.00 mmol) and $Cu(OTf)_2$ (18 mg, 0.050 mmol). The reaction was stirred for the specified time at the specified temperature before dilution with CH_2Cl_2 (25 ml) and washing with satd. sodium bicarbonate solution (25 ml). The aqueous phase was extracted with further CH_2Cl_2 (25 ml) and the combined organics were dried over magnesium sulphate and evaporated in vacuo. The crude residue was purified by flash column chromatography to yield the pure 3-arylanilide.

***N*-(biphenyl-3-yl)acetamide (2a)**



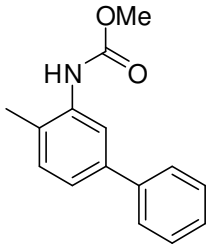
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 24h at 70 °C. Purified by flash chromatography with 1/20 Et_2O/CH_2Cl_2 on silica to give a white solid (15 mg, 14%). M.p. 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.58 (d, 2H, *J* = 8.1 Hz), 7.50 (d, 1H, *J* = 7.7 Hz), 7.31-7.46 (m, 5H), 7.23 (br s, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 142.1, 140.6, 138.2, 129.3, 128.7, 127.4, 127.1, 123.1, 118.7, 118.6, 24.6; ν_{max}/cm^{-1} (film): 3300, 3066, 1665, 1593, 1554, 1480, 1420, 1370, 1312; m/z HRMS (ESI) found $[M+H]^+$ 212.1082, $C_{14}H_{14}NO$ requires 212.1075.

***N*-(4-methylbiphenyl-3-yl)acetamide (2b)**



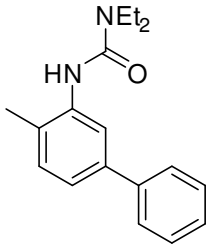
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 22h at 70 ^oC. Purified by flash chromatography with CH_2Cl_2 on silica to give a white solid (49 mg, 43%). M.p. 140-141 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.58 (d, 2H, *J* = 7.5 Hz), 7.41 (t, 2H, *J* = 7.5 Hz), 7.30-7.35 (m, 2H), 7.25 (d, 1H, *J* = 8.3 Hz), 7.06 (br s, 1H), 2.29 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 140.5, 139.7, 135.9, 130.8, 128.6, 127.1, 126.9, 123.9, 122.3, 24.1, 17.4; ν_{max}/cm^{-1} (solid): 3301, 1655, 1530, 1500, 1481, 1365; m/z HRMS (ESI) found $[M+H]^+$ 226.1227, $C_{15}H_{16}NO$ requires 226.1226.

Methyl 4-methylbiphenyl-3-ylcarbamate (2c)



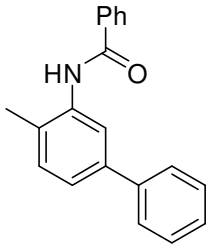
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 22h at 70 ^oC. Purified by flash chromatography with 3/7 Hexane/CH_2Cl_2 on silica to give a colourless oil (54 mg, 45%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (br s, 1H), 7.62 (d, 2H, *J* = 7.1 Hz), 7.43 (t, 2H, *J* = 7.5 Hz), 7.33 (t, 1H, *J* = 7.3 Hz), 7.29 (dd, 1H, *J* = 7.8 and 1.8 Hz), 7.23 (d, 1H, *J* = 7.8 Hz), 6.49 (br s, 1H), 3.81 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ 155.8, 140.2, 138.8, 137.2, 131.6, 131.3, 129.6, 127.9, 126.9, 123.7, 123.0, 52.4, 17.8; ν_{max}/cm^{-1} (solid): 3318, 1709, 1569, 1534, 1497, 1456, 1217; m/z HRMS (ESI) found $[M+H]^+$ 242.1180, $C_{15}H_{16}NO_2$ requires 242.1176.

1,1-Diethyl-3-(4-methylbiphenyl-3-yl)urea (2d)



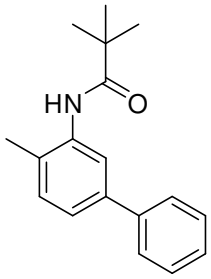
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 24h at 70 ^oC. Purified by flash chromatography with 1/40 Et_2O/CH_2Cl_2 on silica to give a white solid (45 mg, 32%). M.p. 114-115 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, 1H, *J* = 1.7 Hz), 7.63 (dd, 2H, *J* = 1.2 and 8.3 Hz), 7.40 (t, 2H, *J* = 7.5 Hz), 7.30 (t, 1H, *J* = 7.3 Hz), 7.24 (dd, 1H, *J* = 1.8 and 7.8Hz), 7.21 (d, 1H, *J* = 7.8 Hz), 6.22 (br s, 1H), 3.41 (q, 4H, *J* = 7.2 Hz), 2.28 (s, 3H), 1.26 (t, 6H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 140.9, 139.7, 137.6, 130.4, 128.4, 127.0, 126.9, 126.6, 121.9, 120.7, 41.7, 17.4, 13.8; ν_{max}/cm^{-1} (solid) 3240, 2975, 1631, 1530, 1505, 1485, 1453, 1442, 1413; m/z HRMS (ESI) found $[M+H]^+$ 283.1801, $C_{18}H_{23}N_2O$ requires 283.1805.

_N_-(4-methylbiphenyl-3-yl)benzamide (2e)



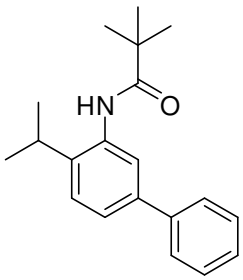
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 20h at 70 ^oC. Purified by flash chromatography with 1/5 Hexanes/CH_2Cl_2 on silica to give a white solid (105 mg, 73%). M.p. 139-140 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.91 (d, 2H, *J* = 7.1Hz), 7.87 (br s, 1H), 7.62 (d, 2H, *J* = 7.1Hz), 7.56 (tt, 1H, *J* = 7.4 and 2.2 Hz), 7.48 (t, 2H, *J* = 7.4 Hz), 7.43 (t, 2H, *J* = 7.5 Hz), 7.32-7.39 (m, 2H), 7.28 (d, 1H, *J* = 7.9Hz), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 140.4, 139.8, 136.0, 134.7, 131.8, 130.8, 128.7, 128.6, 128.5, 127.1, 127.0, 126.9, 123.9, 121.9; ν_{max}/cm^{-1} (solid): 3291, 3031, 1650, 1530, 1500, 1477, 1404, 1306; m/z HRMS (ESI) found $[M+H]^+$ 288.1384, $C_{20}H_{18}NO$ requires 288.1383.

_N_-(4-methylbiphenyl-3-yl)pivalamide (2f)



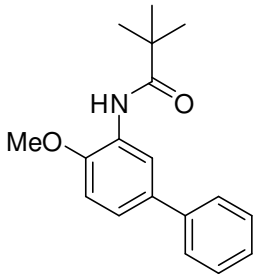
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 20h at 70 ^oC. Purified by flash chromatography with 1/9 Hexanes/CH_2Cl_2 on silica to give a white solid (105 mg, 79%). M.p. 109-110 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, 1H, *J* = 1.8 Hz), 7.63 (dd, 2H, *J* = 8.2 and 1.2 Hz), 7.42 (t, 2H, *J* = 7.5Hz), 7.30-7.35 (m, 3H), 7.24 (d, 1H, *J* = 7.9 Hz), 2.29 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 140.6, 139.8, 136.1, 130.6, 128.5, 127.5, 127.0, 127.0, 123.3, 121.4, 39.7, 27.6, 17.2; ν_{max}/cm^{-1} (film): 3301, 2963, 1651, 1525, 1485, 1454; m/z HRMS (ESI) found $[M+H]^+$ 268.1696, $C_{18}H_{22}NO$ requires 268.1696.

_N_-(4-isopropylbiphenyl-3-yl)pivalamide (2g)



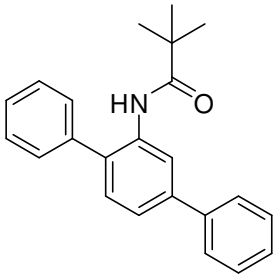
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 24h at 70 ^oC. Purified using Flashmaster SOLO purification system eluting with a Cyclohexane/$CHCl_3$ gradient to give a white solid (127 mg, 86%). M.p. 156-158 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, 1H, *J* = 1.9 Hz), 7.62 (d, 2H, *J* = 8.1 Hz), 7.38-7.43 (m, 4H), 7.34 (d, 1H, *J* = 8.1 Hz), 7.28 - 7.33 (m, 1H), 3.01 (sept., 1H, *J* = 6.8 Hz), 1.37 (s, 9H), 1.31 (d, 6H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 140.5, 139.3, 138.5, 134.7, 128.5, 127.1, 127.0, 125.7, 124.0, 122.8, 39.6, 27.9, 27.6, 22.7; ν_{max}/cm^{-1} (film): 3333, 2961, 1647, 1524, 1497, 1476, 1404; m/z HRMS (ESI) found $[M+H]^+$ 296.2009, $C_{20}H_{26}NO$ requires 296.2009.

_N_-(4-methoxybiphenyl-3-yl)pivalamide (2h)



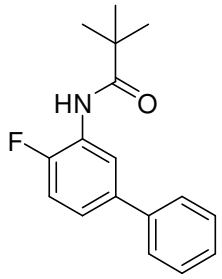
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 20h at 70 ^oC. Purified by flash chromatography with 2/8 Hexane/CH_2Cl_2 on silica to give a colourless oil (132 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.81 (d, 1H, *J* = 2.3 Hz), 8.19 (br s, 1H), 7.64 (d, 2H, *J* = 8.4 Hz), 7.40 (t, 2H, *J* = 7.6 Hz), 7.27-7.32 (m, 2H), 6.93 (d, 1H, *J* = 8.5 Hz), 3.92 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 147.4, 140.6, 134.1, 128.4, 128.0, 126.8, 126.6, 121.6, 118.3, 109.9, 55.8, 39.9, 27.5; ν_{max}/cm^{-1} (film): 3441, 2961, 1679, 1594, 1534, 1480, 1417; m/z HRMS (ESI) found $[M+H]^+$ 284.1644, $C_{18}H_{22}NO_2$ requires 284.1645.

_N_-(6-phenylbiphenyl-3-yl)pivalamide (2i)



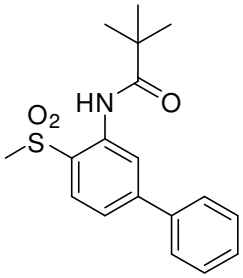
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 20h at 70 ^oC. Purified by flash chromatography with 4/6 Hexane/CH_2Cl_2 on silica to give a white solid (129 mg, 78%). M.p. 108-109 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, 1H, *J* = 1.8 Hz), 7.72 (d, 2H, *J* = 8.0 Hz), 7.57 (br s, 1H), 7.53 (t, 2H, *J* = 7.2 Hz), 7.41-7.46 (m, 6H), 7.34-7.37 (m, 1H), 7.33 (d, 1H, *J* = 7.8 Hz), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 141.3, 140.4, 137.7, 135.4, 130.9, 130.0, 129.2, 129.0, 128.6, 128.0, 127.3, 127.1, 122.4, 119.5, 39.8, 27.3; ν_{max}/cm^{-1} (solid): 3284, 2957, 1644, 1492; m/z HRMS (ESI) found $[M+H]^+$ 330.1852, $C_{23}H_{24}NO$ requires 330.1852.

_N_-(4-fluorobiphenyl-3-yl)pivalamide (2j)



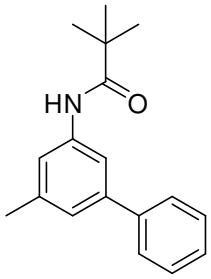
Following the general procedure using Ph_2IBF_4 (736 mg, 2.00 mmol) for 48h at 70 ^oC. Purified by flash chromatography with 40/60 CH_2Cl_2/Toluene on silica to give a colourless oil (74 mg, 55%).^1H NMR (400 MHz, $CDCl_3$): δ 8.67 (dd, 1H, *J* = 7.6 and 2.3 Hz), 7.67 (br s, 1H), 7.59 (d, 2H, *J* = 8.0Hz), 7.41 (t, 2H, *J* = 7.4 Hz), 7.32 (t, 1H, *J* = 7.3Hz), 7.26 (ddd, 1H, *J*= 8.8, 5.0 and 2.3 Hz), 7.15 (dd, 1H, *J* = 10.7 and 8.5 Hz) and 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 152.1 (d, *J* = 243 Hz), 140.0, 137.9 (d, *J* = 3.2 Hz), 128.6, 127.3, 127.1, 126.7 (d, *J* = 10.0 Hz), 122.5 (d, *J* = 7.6 Hz), 120.3, 114.8 (d, *J* = 19.6 Hz), 40.0, 27.5; ν_{max}/cm^{-1} (film): 3243, 2964, 1649, 1504, 1489; m/z HRMS (ESI) found $[M+H]^+$ 272.1459, $C_{17}H_{19}NOF$ requires 272.1451.

***N*-(4-(methylsulfonyl)biphenyl-3-yl)pivalamide (2k)**



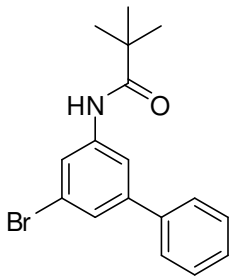
Following the general procedure using Ph_2IBF_4 (768 mg, 2.00 mmol) for 24h at 70 ^oC. Purified by flash chromatography with CH_2Cl_2 on silica to give a colourless oil (19 mg, 11%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.82 (d, 1H, *J* = 1.7 Hz), 7.97 (d, 1H, *J* = 8.3 Hz), 7.65 (d, 2H, *J* = 8.0 Hz), 7.40-7.48 (m, 4H), 3.08 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.5, 148.2, 138.9, 137.7, 129.8, 128.9, 128.7, 127.4, 125.3, 122.3, 121.3, 44.2, 40.2, 27.4; ν_{max}/cm^{-1} (film): 3361, 2966, 1695, 1605, 1566, 1404, 1310, 1150, 1128; m/z HRMS (ESI) found $[M+H]^+$ 332.1315, $C_{18}H_{22}NO_3S$ requires 332.1320.

***N*-(5-methylbiphenyl-3-yl)pivalamide (2l)**



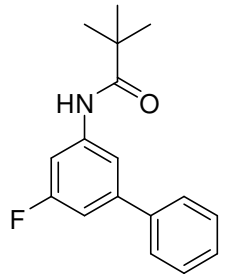
Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 15h at 60 ^oC. Purified by flash chromatography with 1/40 – 1/10 CH_2Cl_2/Toluene on silica to give a white solid (90 mg, 67%). M.p. 136-138 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.60 (m, 3H), 7.37-7.44 (m, 4H), 7.33 (t, 1H, *J* = 7.3 Hz), 7.16 (s, 1H), 2.40 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 176.6, 141.9, 140.8, 139.1, 138.3, 128.6, 127.3, 127.1, 123.8, 119.4, 115.9, 39.6, 27.6, 21.5; ν_{max}/cm^{-1} (solid): 3317, 2972, 1656, 1547, 1423; m/z HRMS (ESI) found $[M+H]^+$ 268.1699, $C_{18}H_{22}NO$ requires 268.1696.

***N*-(5-bromobiphenyl-3-yl)pivalamide (2m)**



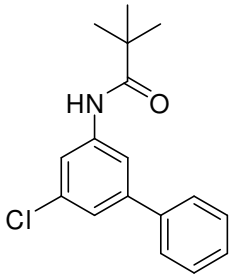
Following the general procedure using Ph_2IBF_4 (736 mg, 2.00 mmol) for 48h at 70 ^oC. Purified using Flashmaster SOLO, eluting with a cyclohexane/chloroform gradient to give a white solid (106 mg, 64%). M.p. 142-143 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (t, 1H, *J* = 1.8 Hz), 7.70 (t, 1H, *J* = 1.7 Hz), 7.54 (d, 2H, *J* = 8.0 Hz), 7.46 (t, 1H, *J* = 1.6 Hz), 7.40-7.44 (m, 3H), 7.36 (t, 1H, *J* = 7.2 Hz), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 143.6, 139.4, 139.2, 128.7, 127.9, 127.0, 125.7, 122.7, 121.5, 117.3, 39.6, 27.5; ν_{max}/cm^{-1} (film): 3300, 2967, 1655, 1565, 1520, 1418, 1400; m/z HRMS (ESI) found $[M+H]^+$ 332.0646, $C_{17}H_{19}BrNO$ requires 332.0645.

***N*-(5-fluorobiphenyl-3-yl)pivalamide (2n)**



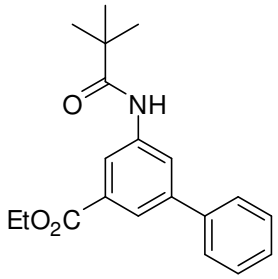
Following the general procedure using Ph_2IBF_4 (736 mg, 2.00 mmol) for 48h at 70 ^oC. Purified by flash chromatography with 1/1 toluene/CH_2Cl_2 on silica to give a colourless oil (84 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, 2H, *J* = 7.0 Hz), 7.45-7.52 (m, 2H), 7.39-7.45 (m, 3H), 7.36 (t, 1H, *J* = 7.3 Hz), 7.03 (ddd, 1H, J = 1.6, 2.3 and 9.6 Hz), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 163.23 (d, *J* = 244 Hz), 143.59 (d, *J* = 9.1 Hz), 139.69 (d, *J* = 11.6 Hz), 139.5, 128.7, 127.9, 127.0, 113.9, 109.56 (d, *J* = 22.4 Hz), 106.10 (d, *J* = 26.6 Hz), 39.7, 27.5; ν_{max}/cm^{-1} (film): 3340, 2967, 1662, 1616, 1600, 1537, 1468, 1447, 1407; m/z HRMS (ESI) found $[M+H]^+$ 272.1459, $C_{17}H_{19}NOF$ requires 272.1451.

_N_-(5-chlorobiphenyl-3-yl)pivalamide (2o)



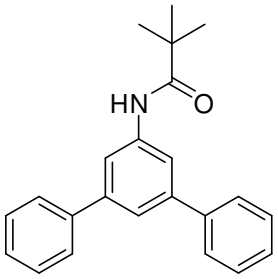
Following the general procedure using Ph_2IBF_4 (736 mg, 2.00 mmol) for 48h at 70 ^oC. Purified using Flashmaster SOLO, eluting with a cyclohexane/chloroform gradient to give a white solid (87 mg, 61%). M.p. 131-133 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (t, 1H, *J* = 1.7 Hz), 7.61 (t, 1H, *J* = 1.9 Hz), 7.57 (br s, 1H), 7.52 (d, 2H, *J* = 8.0 Hz), 7.41 (t, 2H, *J* = 7.5 Hz), 7.35 (t, 1H, *J* = 7.2 Hz), 7.29 (t, 1H, *J* = 1.7 Hz), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 143.2, 139.3, 139.3, 134.7, 128.7, 127.9, 126.9, 122.7, 118.7, 116.9, 39.6, 27.4; ν_{max}/cm^{-1} (film): 3332, 2967, 1660, 1599, 1588, 1525, 1436, 1399; m/z HRMS (ESI) found $[M+H]^+$ 288.1149, $C_{17}H_{19}ClNO$ requires 288.1150.

Ethyl 5-pivalamidobiphenyl-3-carboxylate (2p)



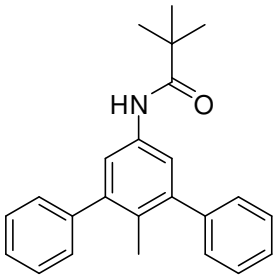
Following the general procedure using Ph_2IBF_4 (736 mg, 2.00 mmol) for 48h at 70 ^oC. Purified by flash chromatography with 1/20 Et_2O/Toluene on silica to give a white solid (51 mg, 31%). M.p. 128-129 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (t, 1H, *J* = 1.9 Hz), 8.01 (t, 1H, *J* = 1.6 Hz), 7.95 (dd, 1H, *J* = 1.5 and 2.0 Hz), 7.62 (d, 2H, *J* = 7.0 Hz), 7.57 (br s, 1H), 7.43 (t, 2H, *J* = 7.4 Hz), 7.35 (t, 1H, *J* = 7.3 Hz), 4.40 (q, 2H, *J* = 7.1 Hz), 1.40 (t, 3H, *J* = 7.1 Hz), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 166.1, 142.3, 139.7, 138.6, 131.5, 128.7, 127.8, 127.1, 123.8, 123.1, 119.4, 61.2, 39.7, 27.5, 14.3; ν_{max}/cm^{-1} (solid): 3297, 2974, 1715, 1656, 1547, 1416; m/z HRMS (ESI) found $[M+H]^+$ 326.1752, $C_{20}H_{24}NO_3$ requires 326.1756.

2,2-Dimethyl-N-[1,1';3',1'']terphenyl-5'-yl-propionamide (2q)



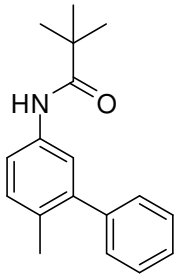
Following the general procedure using Ph_2IOTf (860 mg, 2.00 mmol) and pivanilide (0.50 mmol) for 48h at 70 ^oC. Purified by flash chromatography with 3/7 Hexane/CH_2Cl_2 on silica to give a white solid (108 mg, 66%). m.p. 162-163 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2H, *J* = 1.6 Hz), 7.66 (dd, 4H, *J* = 8.3 and 1.2 Hz), 7.57 (t, 1H, *J* = 1.6 Hz), 7.56 (br s, 1H), 7.45 (t, 4H, *J* = 7.5 Hz), 7.37 (tt, 2H, *J* = 7.3 and 1.2 Hz), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 142.5, 140.6, 138.8, 128.6, 127.5, 127.2, 121.9, 117.7, 39.6, 27.6; ν_{max}/cm^{-1} (solid): 3344, 2962, 1655, 1597, 1545, 1422; m/z HRMS (ESI) found $[M+H]^+$ 330.1854, $C_{23}H_{24}NO$ requires 330.1852.

2,2-Dimethyl-*N*-(2'-methyl-[1,1';3',1'']terphenyl-5'-yl)-propionamide (2r)



Following the general procedure using 4-methylpivanilide (0.50 mmol) and Ph_2IOTf (860 mg, 2.00 mmol) for 20h at 70 ^oC. Purified by flash chromatography with 3/7 Hexane/CH_2Cl_2 on silica to give a white solid (143 mg, 83%). M.p. 208-209 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 2H), 7.32-7.43 (m, 11H), 2.08 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 143.4, 141.9, 135.0, 129.2, 128.8, 127.9, 126.8, 120.7, 39.5, 27.5, 18.0; ν_{max}/cm^{-1} (solid): 3349, 2960, 1651, 1590, 1523, 1402; m/z HRMS (ESI) found $[M+H]^+$ 344.2010, $C_{24}H_{26}NO$ requires 344.2009.

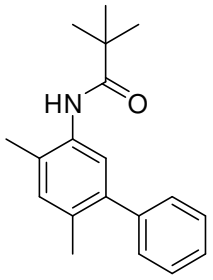
***N*-(6-methylbiphenyl-3-yl)pivalamide (2s)**



In this example, the stoichiometry was reversed to favour monoarylation. To a solution of the 4-methylpivanilide (191mg, 1.00 mmol) in 1,2-dichloroethane (2.5 ml) was added Ph_2IOTf (0.50 mmol) and $Cu(OTf)_2$ (18 mg, 0.050 mmol). The reaction was stirred for 17h at 60 ˚C before dilution with CH_2Cl_2 (25 ml) and washing with satd. sodium bicarbonate solution (25 ml). The aqueous phase was extracted with further CH_2Cl_2 (25 ml) and the combined organics were dried over magnesium sulphate and evaporated in vacuo. The crude residue was purified by flash column chromatography with 1/3 Hexane/CH_2Cl_2 to give a white solid (68mg, 51%). M.p. 138-139 ˚C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, 1H, *J* = 2.4 and 8.2 Hz), 7.30-7.41 (m, 7H), 7.21 (d, 1H, *J* =

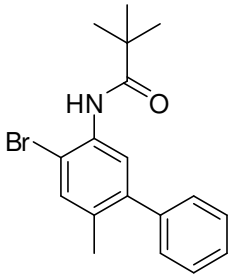
8.2 Hz), 2.23 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 142.3, 141.4, 135.6, 131.2, 130.6, 129.0, 128.0, 126.8, 121.4, 119.0, 39.5, 27.6, 19.7; ν_{max}/cm^{-1} (film): 3329, 2964, 1654, 1588, 1505, 1487, 1401, 1215; m/z HRMS (ESI) found $[M+H]^+$ 268.1712, $C_{18}H_{22}NO$ requires 268.1701.

***N*-(4,6-dimethylbiphenyl-3-yl)pivalamide (2t)**



Following the general procedure using Ph_2IOTf (430 mg, 1.00 mmol) for 29h at 70 °C. Purified by flash chromatography with 15/85 Hexane/CH_2Cl_2 on silica to give a white solid (118 mg, 84%). M.p. 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.35-7.40 (m, 2H), 7.28-7.34 (m, 3H), 7.21 (br s, 1H), 7.09 (s, 1H), 2.26 (s, 3H), 2.23 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 141.4, 140.2, 133.3, 132.2, 132.0, 129.2, 128.3, 127.9, 126.6, 124.7, 39.5, 27.6, 19.8, 17.2; ν_{max}/cm^{-1} (solid): 3335, 2959, 1651, 1518, 1489, 1397; m/z HRMS (ESI) found $[M]^+$ 282.1852, $C_{19}H_{24}NO$ requires 282.1852.

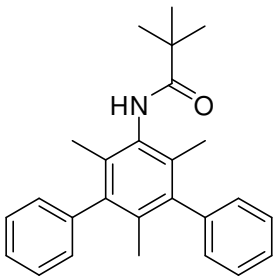
***N*-(4-bromo-6-methylbiphenyl-3-yl)pivalamide (2u)**



Following the general procedure using Ph_2IBF_4 (736 mg, 2.00 mmol) for 48h at 70 °C. Purified by flash chromatography with 1/1 Hexane/CH_2Cl_2 on silica to give a white solid (115 mg, 67%). M.p. 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.94 (br s, 1H), 7.44 (s, 1H), 7.36-7.41 (m, 2H), 7.30-7.35 (m, 3H), 2.22 (s, 3H), 1.35 (s, 9H); ^{13}C

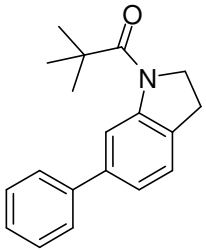
NMR (100 MHz, $CDCl_3$): δ 176.5, 142.1, 140.5, 133.3, 133.1, 132.4, 129.0, 128.0, 127.0, 123.0, 112.2, 40.0, 27.5, 19.7; ν_{max}/cm^{-1} (solid): 3332, 2959, 1658, 1509, 1490, 1383; m/z HRMS (ESI) found $[M+H]^+$ 346.0803, $C_{18}H_{21}BrNO$ requires 346.0801.

2,2-Dimethyl-*N*-(2',4',6'-trimethyl-[1,1';3',1'']terphenyl-5'-yl)-propionamide (2v)



Following the general procedure using *N*-mesitylpivalamide (0.50 mmol) and Ph_2IOTf (1290 mg, 3.00 mmol) for 48h at 70 °C. Purified by flash chromatography with CH_2Cl_2 on silica to give a white solid (81mg, 44%). M.p. >275 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (t, 4H, *J* = 7.9 Hz), 7.32 (t, 2H, *J* = 7.4 Hz), 7.17 (d, 4H, *J* = 7.1Hz), 6.99 (br s, 1H), 1.92 (s, 6H), 1.65 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 141.6, 140.3, 133.2, 132.5, 131.6, 129.3, 128.3, 126.5, 39.2, 27.7, 19.3, 16.4; ν_{max}/cm^{-1} (solid): 3289, 2964, 1646, 1508, 1440; m/z HRMS (ESI) found $[M+H]^+$ 372.2323, $C_{26}H_{30}NO$ requires 372.2322.

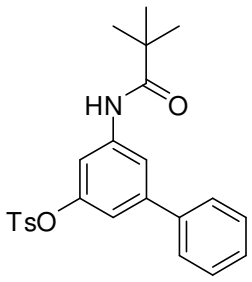
2,2-Dimethyl-1-(6-phenylindolin-1-yl)propan-1-one (2w)



Following the general procedure using Ph_2IBF_4 (276 mg, 0.75 mmol) for 22h at 50 °C. Purified by flash chromatography with 4/6 Hexane/CH_2Cl_2 on silica to give a colourless oil (108 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, 1H, *J* = 0.9 Hz), 7.60 (d, 2H, *J* = 7.1 Hz), 7.37 (t, 2H, *J* = 7.5 Hz), 7.28 (t, 1H, *J* = 7.3 Hz), 7.22-7.25 (m, 2H), 4.27 (t, 2H, *J* = 8.1 Hz), 3.16 (t, 2H, *J* = 8.1 Hz), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 145.3, 141.2, 140.7, 129.9, 128.4, 127.2, 126.9, 124.3, 122.5, 117.2, 49.7, 40.2,

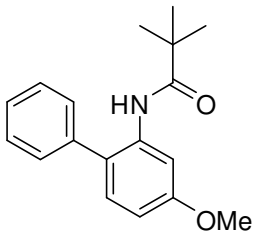
28.9, 27.6; ν_{max}/cm^{-1} (film): 2959, 1644, 1478, 1416, 1401, 1361; m/z HRMS (ESI) found $[M+H]^+$ 280.1697, $C_{19}H_{22}NO$ requires 280.1696.

5-Pivalamidobiphenyl-3-yl 4-methylbenzenesulfonate (2x)



Following the general procedure using Ph_2IBF_4 (736 mg, 2.00 mmol) for 48h at 70 °C. Purified by flash chromatography with CH_2Cl_2 on silica to give a colourless oil which solidified on standing (136 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, 1H, *J* = 1.7 Hz), 7.77 (d, 2H, *J* = 8.4 Hz), 7.44 (br s, 1H), 7.32-7.42 (m, 7H), 7.25 (t, 1H, *J* = 2.1 Hz), 6.82 (dd, 1H, *J* = 1.6 and 2.1 Hz), 2.45 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 149.9, 145.4, 143.1, 139.5, 139.2, 132.2, 129.7, 128.7, 128.5, 127.9, 126.9, 117.1, 116.1, 112.6, 39.6, 27.4, 21.6; ν_{max}/cm^{-1} (solid): 3313, 2966, 1658, 1593, 1533, 1463, 1417, 1371; m/z HRMS (ESI) found $[M + H]^+$ 424.1576, $C_{24}H_{26}NO_4S$ requires 424.1577.

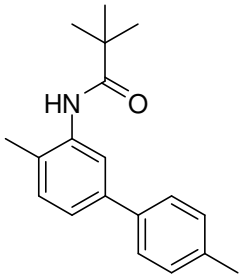
***N*-(4-methoxybiphenyl-2-yl)pivalamide (2y)**



Following the general procedure using Ph_2IOTf (323 mg, 0.75 mmol) for 22h at 50 °C. Purified by flash chromatography with CH_2Cl_2 on silica to give a white solid (108 mg, 76%). M.p. 81-82 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, 1H, *J* = 2.6 Hz), 7.54 (br s, 1H), 7.48 (t, 2H, *J* = 7.3 Hz), 7.39 (t, 1H, *J* = 7.4 Hz), 7.34 (dd, 2H, *J* = 1.4 and 8.2 Hz), 7.14 (d, 1H, *J* = 8.4 Hz), 6.72 (dd, 1H, *J* = 2.7 and 8.5 Hz), 3.86 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 159.6, 137.8, 136.1, 130.3, 129.5, 129.0, 127.7, 124.1,

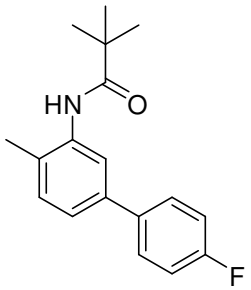
110.5, 105.0, 55.4, 39.8, 27.3; ν_{max}/cm^{-1} (solid): 3269, 2955, 1648, 1611, 1506, 1480; m/z HRMS (ESI) found $[M+H]^+$ 284.1642, $C_{18}H_{22}NO_2$ requires 284.1645.

***N*-(4',4-dimethylbiphenyl-3-yl)pivalamide (3a)**



Following the general procedure using 4-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (486 mg, 1.00 mmol) for 24h at 70 °C. Purified by flash chromatography with 3/17 Hexane/CH_2Cl_2 on silica to give a white solid (115 mg, 82%). M.p. 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, 1H, *J* = 1.8 Hz), 7.52 (d, 2H, *J* = 8.1 Hz), 7.28-7.33 (m, 2H), 7.20-7.24 (m, 3H), 2.38 (s, 3H), 2.28 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 139.8, 137.7, 136.8, 136.1, 130.6, 129.3, 127.2, 126.8, 123.1, 121.1, 39.7, 27.7, 21.0, 17.2; ν_{max}/cm^{-1} (film): 3309, 2965, 1650, 1495; m/z HRMS (ESI) found $[M+H]^+$ 282.1859, $C_{19}H_{24}NO$ requires 282.1858.

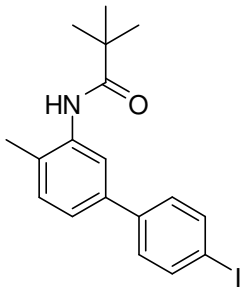
***N*-(4'-fluoro-4-methylbiphenyl-3-yl)pivalamide (3b)**



Following the general procedure using 4-fluorophenyl(mesityl)iodonium trifluoromethanesulfonate (490 mg, 1.00 mmol) for 24h at 70 °C. Purified by flash chromatography with 3/7 Hexane/CH_2Cl_2 on silica to give a white solid (111 mg, 78%). M.p. 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, 1H, *J* = 1.4 Hz), 7.56 (dd, 2H, J = 8.8 and 5.4 Hz), 7.34 (br s, 1H), 7.20-7.26 (m, 2H), 7.08 (t, 2H, *J* = 8.7 Hz), 2.28 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 162.3 (d, *J* = 246 Hz), 138.8,

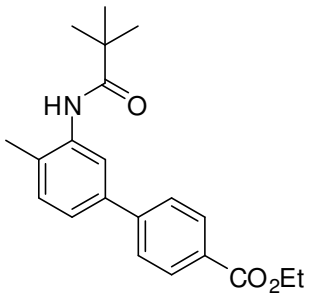
136.7 (d, J = 2.8 Hz), 136.2, 130.6, 128.5 (d, J = 8.0 Hz), 127.3, 123.0, 121.1, 115.4 (d, J = 21.4 Hz), 39.7, 27.6, 17.1; ν_{max}/cm^{-1} (solid): 3301, 2964, 1650, 1512, 1495, 1456; m/z HRMS (ESI) found $[M+H]^+$ 286.1601, $C_{18}H_{21}FNO$ requires 286.1602.

_N_-(4'-iodo-4-methylbiphenyl-3-yl)pivalamide (3c)



Following the general procedure using 4-iodophenyl(mesityl)iodonium trifluoromethanesulfonate (600 mg, 1.00 mmol) for 24h at 70 ^oC. Purified using Flashmaster SOLO, eluting with a cyclohexane/chloroform gradient to give a white solid (96 mg, 49%). M.p. 144-146 $^\circ C$; ^1H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, 1H, J = 1.4 Hz), 7.75 (d, 2H, J = 8.4 Hz), 7.36-7.40 (m, 3H), 7.24-7.31 (m, 2H), 2.31 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 140.0, 138.5, 137.5, 136.3, 130.7, 128.8, 127.8, 122.9, 120.8, 92.8, 39.7, 27.6, 17.2; ν_{max}/cm^{-1} (film): 3301, 2961, 1651, 1526, 1478, 1445, 1384; m/z HRMS (ESI) found $[M+H]^+$ 394.0659, $C_{18}H_{21}INO$ requires 394.0662.

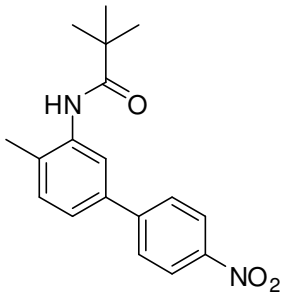
Ethyl 4'-methyl-3'-pivalamidobiphenyl-4-carboxylate (3d)



Following the general procedure using (4-(ethoxycarbonyl)phenyl) (mesityl)iodonium trifluoromethanesulfonate (544 mg, 1.00 mmol) for 24h at 70 ^oC, the only difference being a wash with 10% NaOH solution during the workup, to remove an impurity most likely arising from decomposition of the excess iodonium salt. Purified by flash chromatography with 1/50 Et_2O/CH_2Cl_2 on silica to give a white solid (139 mg, 82%).

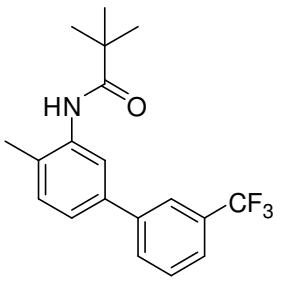
M.p. 111-112 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, 1H, *J* = 1.8 Hz), 8.06 (d, 2H, *J* = 8.5 Hz), 7.65 (d, 2H, *J* = 8.6 Hz), 7.37 (br s, 1H), 7.31 (dd, 1H, *J* = 7.9 and 1.9 Hz), 7.24 (d, 1H, *J* = 7.9 Hz), 4.38 (q, 2H, *J* = 7.1 Hz), 2.28 (s, 3H), 1.40 (t, 3H, *J* = 7.1 Hz), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 166.4, 144.9, 138.5, 136.3, 130.8, 129.8, 129.0, 128.5, 126.7, 123.4, 121.4, 60.8, 39.7, 27.6, 17.2, 14.2; ν_{max}/cm^{-1} (solid): 3301, 2961, 1709, 1648, 1608, 1491; m/z HRMS (ESI) found $[M+H]^+$ 340.1906, $C_{21}H_{26}NO_3$ requires 340.1907.

_N_-(4-methyl-4'-nitrobiphenyl-3-yl)pivalamide (3e)



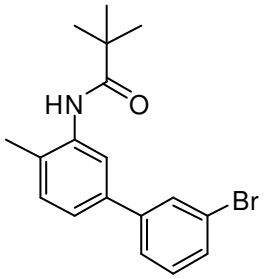
Following the general procedure using 4-nitrophenyl(mesityl)iodonium trifluoromethanesulfonate (517 mg, 1.00 mmol) for 24h at 70 ^{o}C. Purified by flash chromatography with 1/100 Et_2O/CH_2Cl_2 on silica to give a yellow oil (94 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, 1H, *J* = 1.6 Hz), 8.23 (d, 2H, *J* = 8.9Hz), 7.74 (d, 1H, *J* = 8.9 Hz), 7.40 (br s, 1H), 7.32 (dd, 1H, *J* = 1.8 and 7.9 Hz), 7.29 (d, 1H, *J* = 7.3 Hz), 2.33 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 147.0, 146.8, 137.1, 136.6, 131.0, 128.9, 127.5, 123.8, 123.2, 121.1, 39.8, 27.6, 17.2; ν_{max}/cm^{-1} (solid): 3323, 2965, 1662, 1596, 1572, 1513, 1480, 1445, 1340; m/z HRMS (ESI) found $[M+H]^+$ 313.1538, $C_{18}H_{21}N_2O_3$ requires 313.1552.

_N_-(4-methyl-3'-(trifluoromethyl)biphenyl-3-yl)pivalamide (3f)



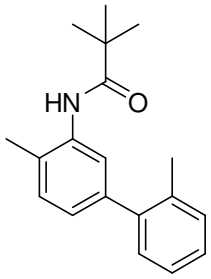
Following the general procedure using 3-trifluoromethylphenyl(mesityl)iodonium trifluoromethanesulfonate (540 mg, 1.00 mmol) for 24h at 70 ^{o}C, the only difference being a wash with 10% NaOH solution during the workup, to remove an impurity most likely arising from decomposition of the excess iodonium salt. Purified by flash chromatography with 3/7 Hexane/CH_2Cl_2 on silica to give a white solid (117 mg, 70%). M.p. 60-62 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, 1H, *J* = 1.6 Hz), 7.82 (s, 1H), 7.78 (d, 1H, *J* = 7.7 Hz), 7.57 (d, 1H, *J* = 7.8 Hz), 7.51 (t, 1H, *J* = 7.7 Hz), 7.35 (br s, 1H), 7.30 (dd, 1H, *J* =7.9 and 1.8 Hz), 7.26 (d, 1H, *J* = 7.9 Hz), 2.30 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 141.4, 138.4, 136.4, 131.0 (q, *J* = 31.9 Hz), 130.9, 130.4 (d, *J* = 0.9 Hz), 129.0, 128.2, 124.2 (q, *J* = 272 Hz), 123.8 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 3.8 Hz), 123.3, 121.2, 39.8, 27.6, 17.3; ν_{max}/cm^{-1} (solid): 3319, 2969, 1650, 1506, 1485, 1338; m/z HRMS (ESI) found $[M+H]^+$ 336.1569, $C_{19}H_{21}F_3NO$ requires 336.1570.

***N*-(3'-bromo-4-methylbiphenyl-3-yl)pivalamide (3g)**



Following the general procedure using 3-bromophenyl(mesityl)iodonium trifluoromethanesulfonate (551 mg, 1.00 mmol) for 24h at 70 ^{o}C. Purified by flash chromatography with 3/7 to 1/9 Hexane/CH_2Cl_2 on silica to give a colourless oil which solidified on standing (125 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, 1H, *J* = 1.4 Hz), 7.72 (t, 1H, *J* = 1.8 Hz), 7.50 (d, 1H, *J* = 7.7 Hz), 7.42 (d, 1H, *J* = 8.0 Hz), 7.34 (br s, 1H), 7.19-7.26 (m, 3H), 2.26 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 142.7, 138.3, 136.3, 130.7, 130.0, 130.0, 129.8, 128.1, 125.7, 123.2, 122.7, 121.1, 39.7, 27.6, 17.2; ν_{max}/cm^{-1} (solid): 3308, 2974, 1650, 1527, 1494, 1470, 1455, 1386; m/z HRMS (ESI) found $[M+H]^+$ 346.0801, $C_{18}H_{21}BrNO$ requires 346.0801.

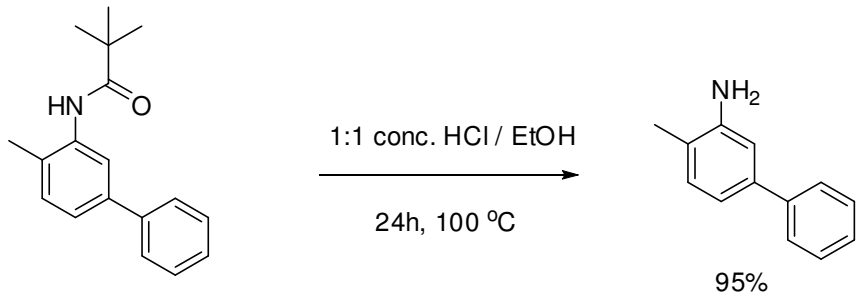
***N*-(2',4-dimethylbiphenyl-3-yl)pivalamide (3h)**



Following the general procedure using 2-methylphenyl(mesityl)iodonium trifluoromethanesulfonate (486 mg, 1.00 mmol) for 24h at 70 ^{o}C. Purified by flash chromatography with CH_2Cl_2 on silica to give a white solid (62 mg, 44%). M.p. 115-116 $^{\circ}$C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 1H, *J* = 1.7 Hz), 7.20 (br s, 1H), 7.11-7.16 (m, 5H), 6.95 (dd, 1H, *J* = 7.7 and 1.8 Hz), 2.22 (s, 3H), 2.20 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 141.3, 140.5, 135.4, 135.3, 130.1, 129.9, 129.7, 127.1, 127.0, 125.5, 125.5, 123.8, 39.6, 27.6, 20.5, 17.3; ν_{max}/cm^{-1} (solid): 3293, 2971, 1645, 1521, 1502, 1483; m/z HRMS (ESI) found $[M+H]^+$ 282.1854, $C_{19}H_{24}NO$ requires 282.1852.

E. Procedure for Cleavage of Pivanilide Group

The following procedure allows for cleavage of the pivanilide amide of a representative substrate, *N*-(4-methylbiphenyl-3-yl)pivalamide (**2f**):

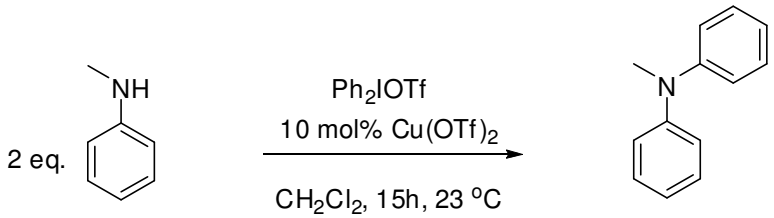


To a stirred solution of *N*-(4-methylbiphenyl-3-yl)pivalamide (**2f**) (29 mg, 0.109 mmol) in ethanol (0.5 ml) was added conc. HCl (0.5 ml) and the reaction was heated to 100 ˚C in a sealed tube for 24h. After this time, the reaction tube was cooled and 10% NaOH solution added until the pH was alkaline. The alkaline solution was diluted with water (30 ml) and extracted with CH_2Cl_2 (3 x 30 ml). The combined organics were washed with satd. NaCl solution, dried over $MgSO_4$ and the solvent evaporated *in vacuo* to give 4-methylbiphenyl-3-amine as a colourless oil (19 mg, 0.104 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, 2H, *J* = 8.0 Hz), 7.42 (t, 2H, *J* = 7.6 Hz), 7.32 (t, 1H, *J* = 7.3 Hz), 7.13 (d, 1H, *J* = 7.7 Hz), 6.97 (dd, 1H, *J* = 1.7 and 7.7 Hz), 6.93 (d, 1H, *J* = 1.7 Hz), 3.80 (br s, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 141.3, 140.1, 130.8, 128.5, 126.9, 126.9, 121.6, 117.6, 113.7, 17.0; ν_{max}/cm^{-1} (film): 3462, 3377, 3028, 1621, 1566, 1485, 1415, 1314; m/z HRMS (ESI) found $[M+H]^+$ 184.1128, $C_{13}H_{14}N$ requires 184.1126.

F. Arylation Experiments on Anilines

The treatment of aniline with diaryliodonium salts and catalytic copper is known to give *N*-arylation in good yield (S*19*).

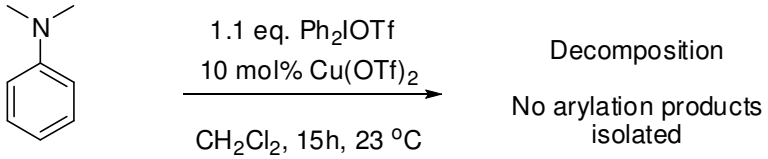
The treatment of *N*-methylaniline with PH_2IOTf and catalytic $Cu(OTf)_2$ resulted in *N*-phenylation of the starting material, as well as some apparent decomposition of the starting material under the reaction conditions.



63%

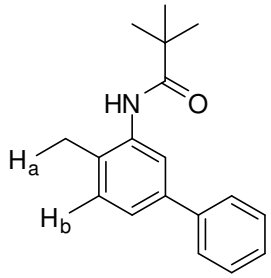
To a solution of the *N*-methylaniline (107 mg, 1.00 mmol) in dichloromethane (2.5 ml) was added Ph_2IOTf (230 mg, 0.50 mmol) and $Cu(OTf)_2$ (18 mg, 0.050 mmol). The reaction was stirred for 15h at 23 ˚C before dilution with CH_2Cl_2 (25 ml) and washing with satd. sodium bicarbonate solution (25 ml). The aqueous phase was extracted with further CH_2Cl_2 (25 ml) and the combined organics were dried over magnesium sulphate and evaporated *in vacuo*. The crude residue was purified by flash column chromatography with 9/1 Hexane/CH_2Cl_2 to give *N*-methyl-*N*-phenylaniline as a colourless oil (57 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, 4H, *J* = 7.3 and 8.6 Hz), 7.07 (d, 4H, *J* = 8.6 Hz), 7.00 (t, 2H, *J* = 7.3 Hz), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 129.1, 121.2, 120.4, 40.2. This analytical data matches previously reported data (S*20*).

The treatment of *N,N*-dimethylaniline with PH_2IOTf and catalytic $Cu(OTf)_2$ resulted in rapid decomposition of the starting material and no arylation products were able to be isolated .

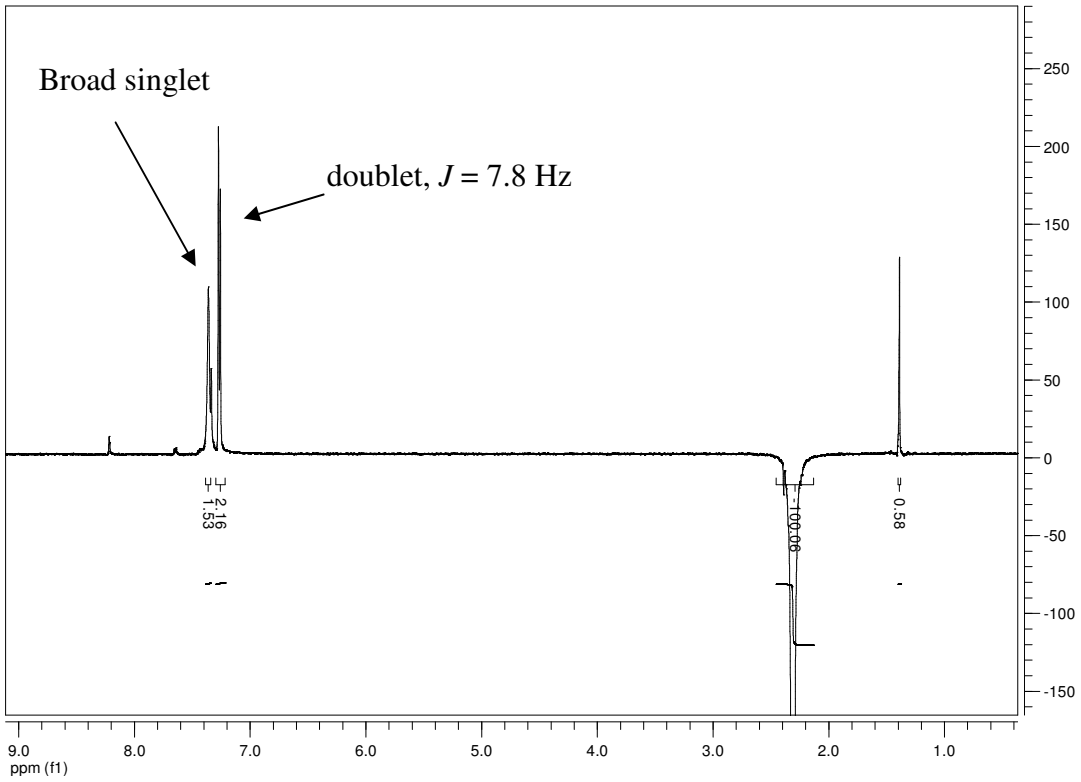


G. Representative Proof of Regioselectivity (nOe)

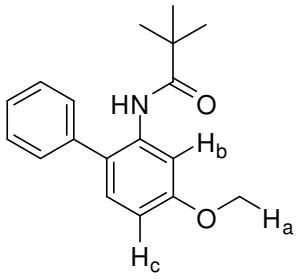
Example 1: **2f**



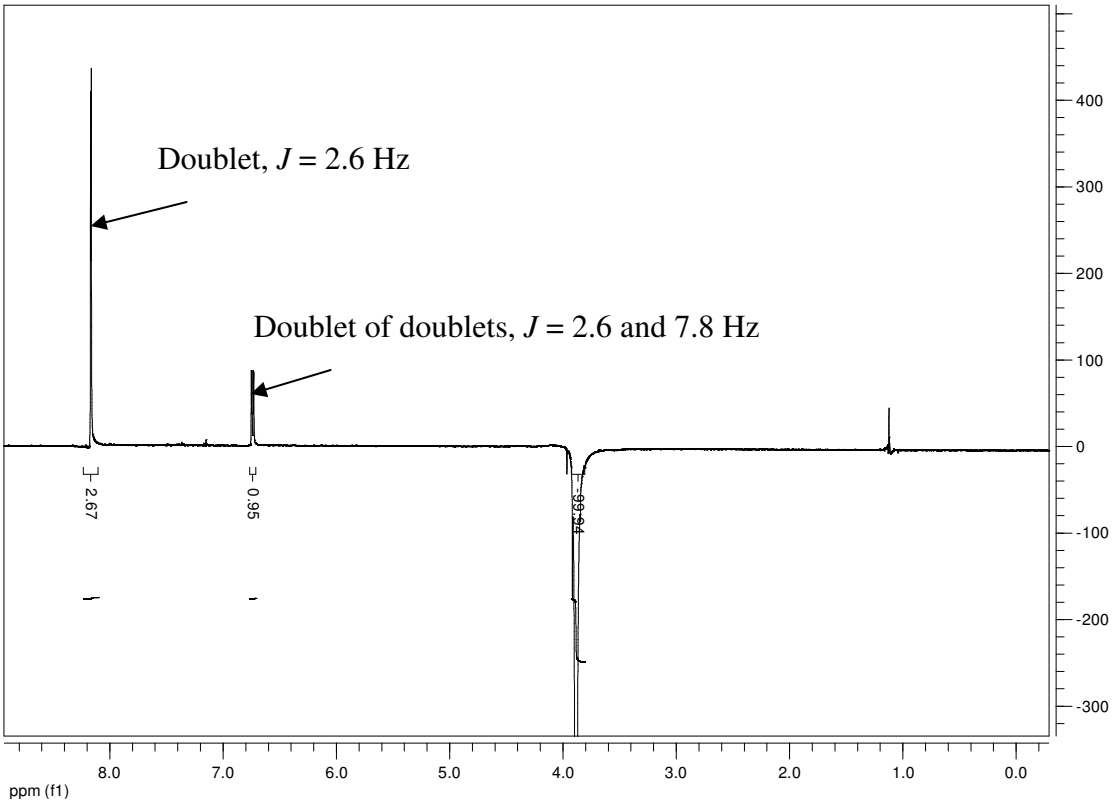
Irradiation of methyl protons (H_a) results in nOe interaction with a doublet (H_b, J = 7.8 Hz) and a broad singlet (NH), thereby confirming the structure given above.



Example 2: **2y**



Irradiation of methyl protons (H_a) of methoxy group results in nOe interaction with a doublet (H_b, J = 2.6 Hz) and a doublet of doublets (H_c, J = 2.6 and 8.4 Hz, thereby confirming the structure given above.



H. References

S1. P. Kazmierczak, L. Skulski, *Synthesis*, 1027 (1995).

S2. P. Kazmierczak, L. Skulski, *Bull. Chem. Soc. Jpn.* **70**, 219 (1997).

S3. O. Daugulis, V. G. Zaitsev, *Angew. Chem. Int. Ed.* **44**, 4046 (2005).

S4. W. M. Seganish, P. DeShong, *J. Org. Chem.* **69**, 6790 (2004).

S5. O. Lerman, Y. Tor, D. Hebel, S. Rozen, *J. Org. Chem.* **49**, 806 (1984).

S6. G. Brasche, J. Garcia-Fortanet, S. L. Buchwald, *Org. Lett.* **10**, 2207 (2008).

S7. F. Bruyneel, E. Enaud, L. Billottet, S. Vanhulle, J. Marchand-Brynaert, *Eur. J. Org. Chem.* **2008**, 72 (2008).

S8. H. P. Thomas Jensen, Benny Bang-Andersen, Robert Madsen, Morten Jørgensen,, *Angew. Chem. Int. Ed.* **47**, 888 (2008).

S9. J. Heinicke *et al.*, *Tetrahedron* **57**, 9963 (2001).

S10. J. P. Wolfe, R. A. Rennels, S. L. Buchwald, *Tetrahedron* **52**, 7525 (1996).

S11. T. Miura, Y. Takahashi, M. Murakami, *Chem. Commun.*, 3577 (2007).

S12. S. Sueyoshi, M. Tanoo, *Chem. Pharm. Bull.* **33**, 488 (1985).

S13. A. McKillop, J. A. Tarbin, *Tetrahedron* **43**, 1753 (1987).

S14. L. R. Hillis, S. J. Gould, *J. Org. Chem.* **50**, 718 (1985).

S15. M. Bielawski, B. Olofsson, *Chem. Commun.*, 2521 (2007).

S16. M. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Cat.* **349**, 2610 (2007).

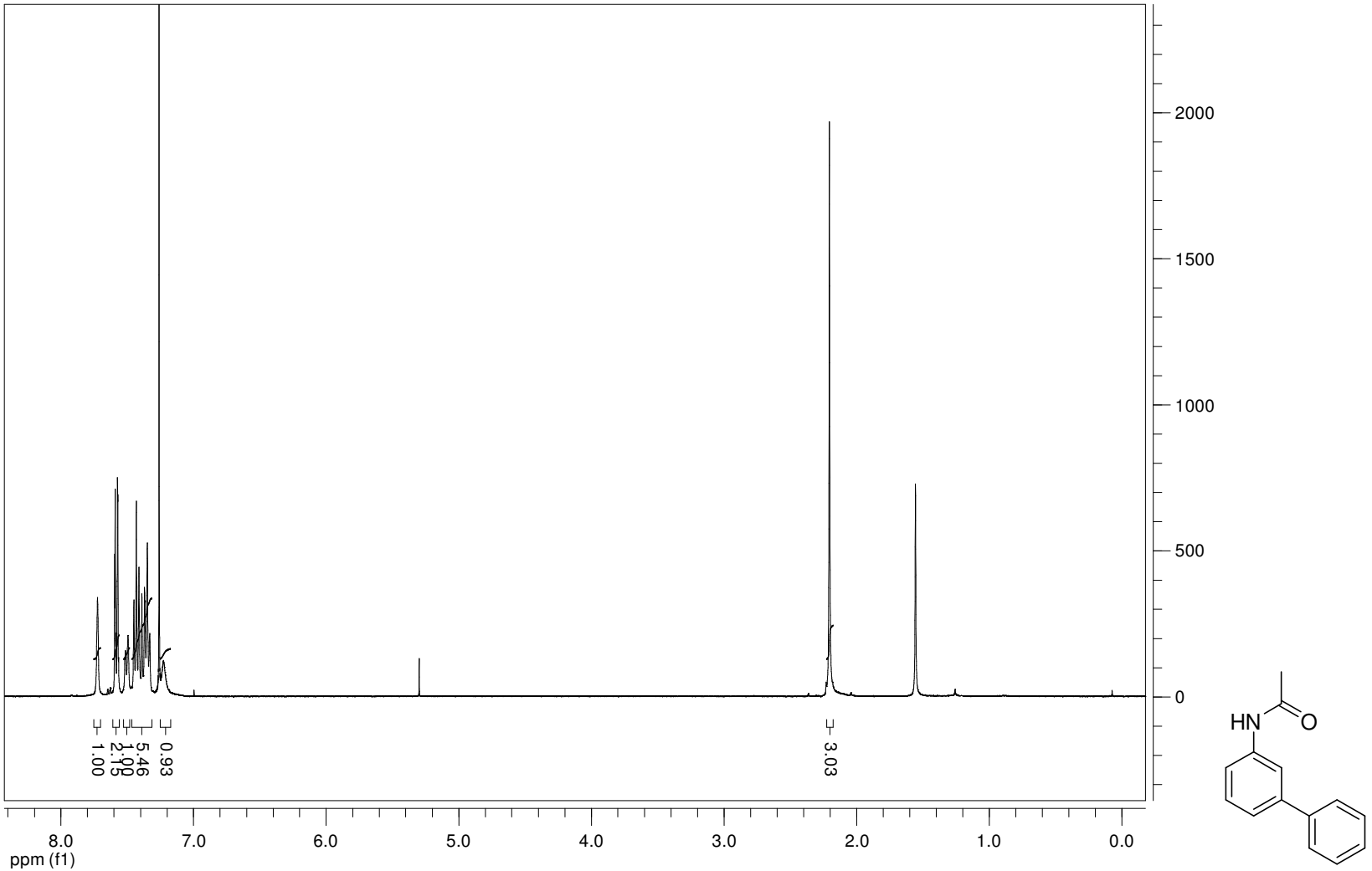
S17. M. Ochiai, M. Toyonari, T. Nagaoka, D.-W. Chen, M. Kida, *Tetrahedron Lett.* **38**, 6709 (1997).

S18. D. Naumann, R. Gnann, V. Padelidakis, W. Tyrra, *Journal of Fluorine Chemistry* **72**, 79 (1995).

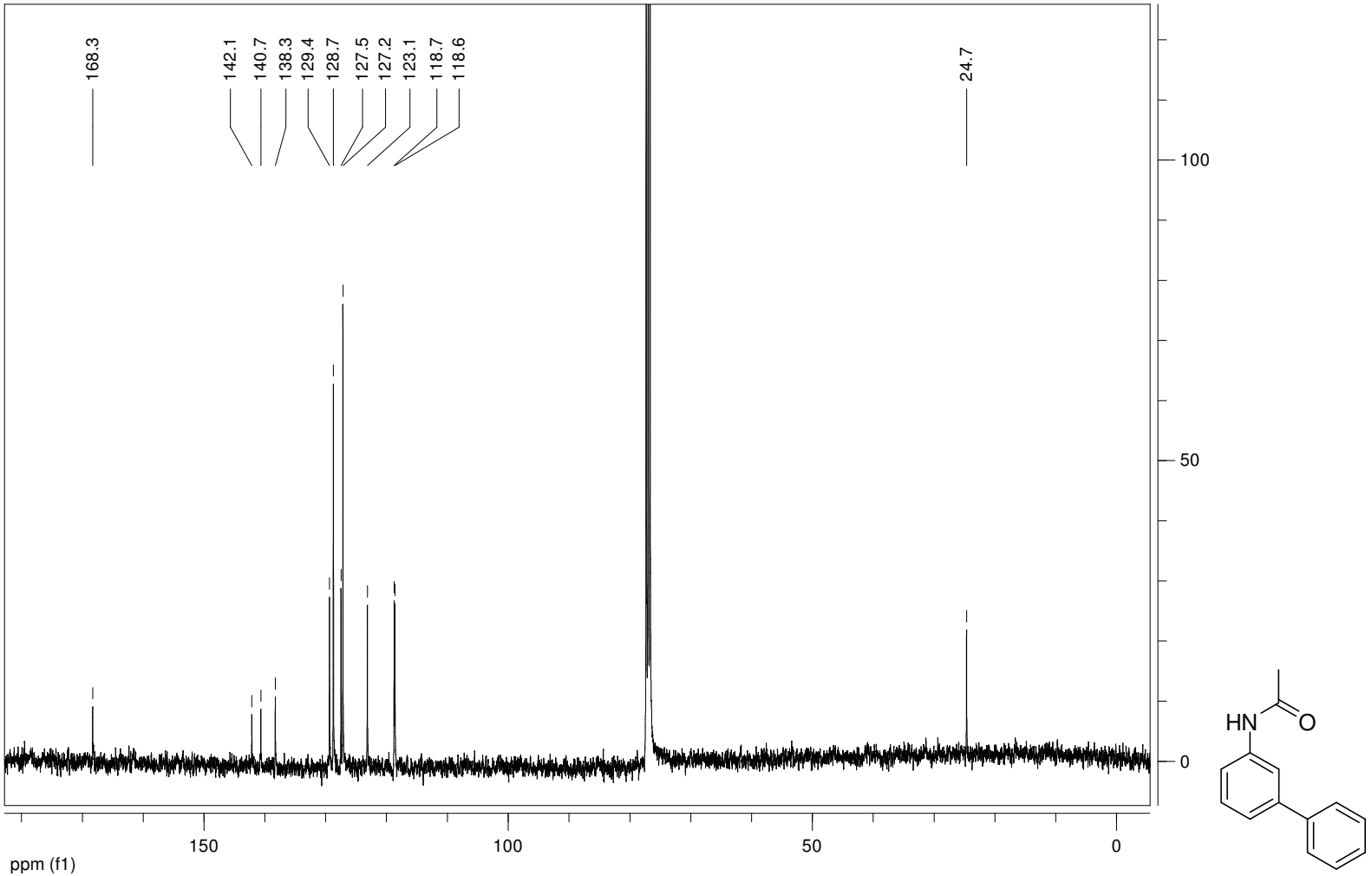
S19. S.-K. Kang, S.-H. Lee, D. Lee, *Synlett* **2000**, 1022 (2000).

S20. L. Ackermann, J. H. Spatz, C. J. Gschrei, R. Born, A. Althammer, *Angew. Chem. Int. Ed.* **45**, 7627 (2006).

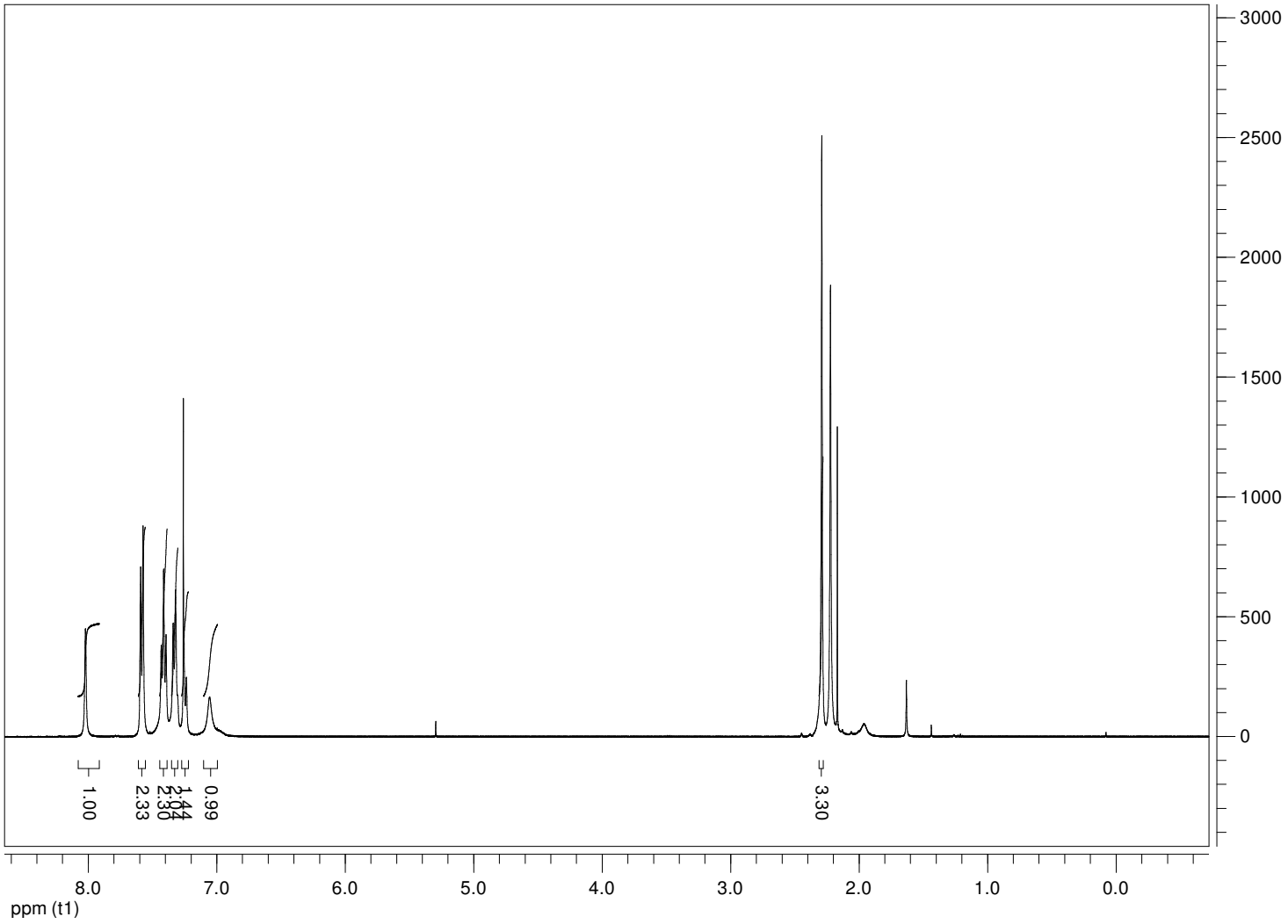
***N*-(biphenyl-3-yl)acetamide (2a)**

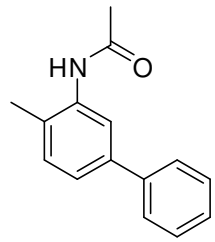


***N*-(biphenyl-3-yl)acetamide (2a)**

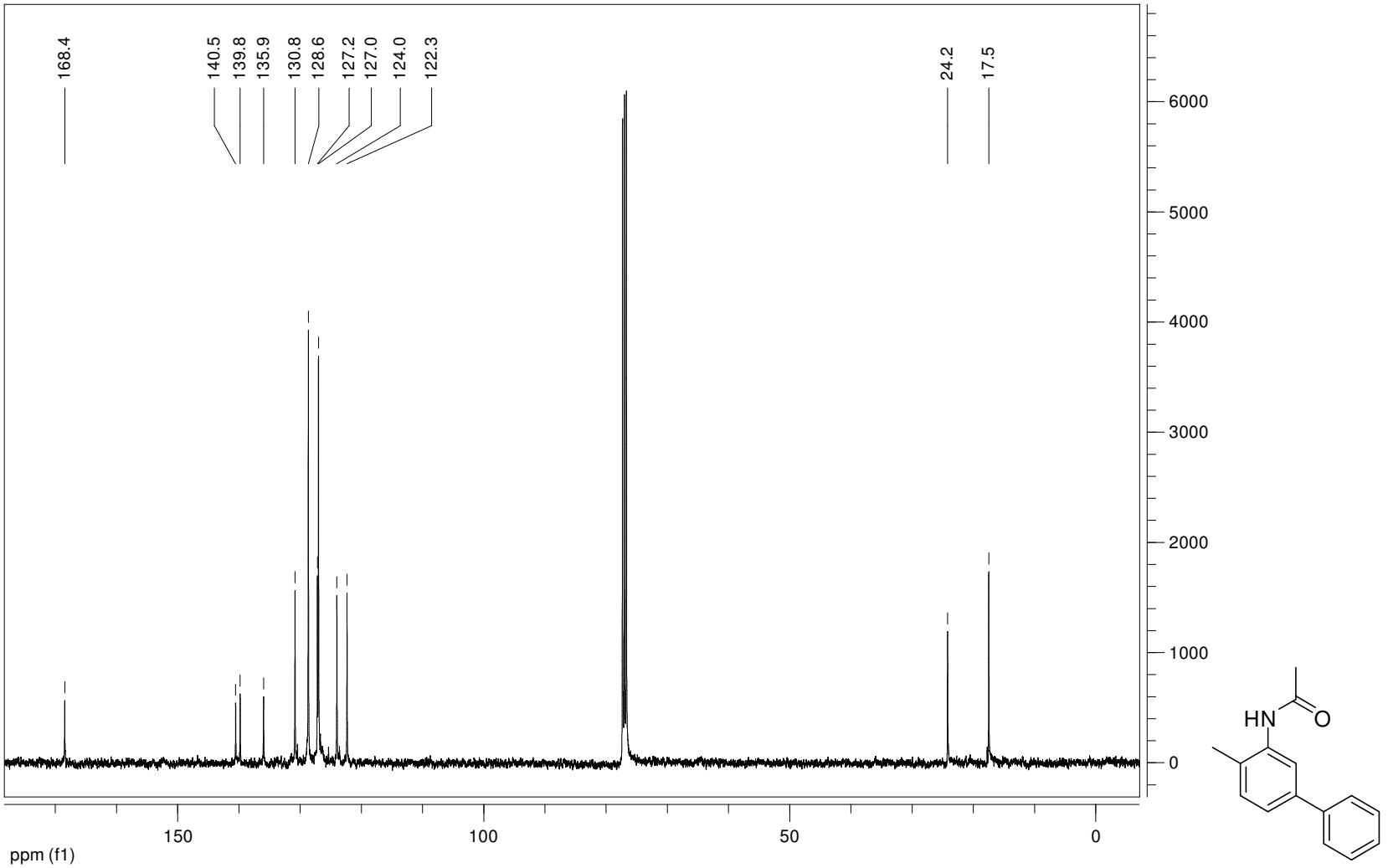


***N*-(4-methylbiphenyl-3-yl)acetamide (2b)**

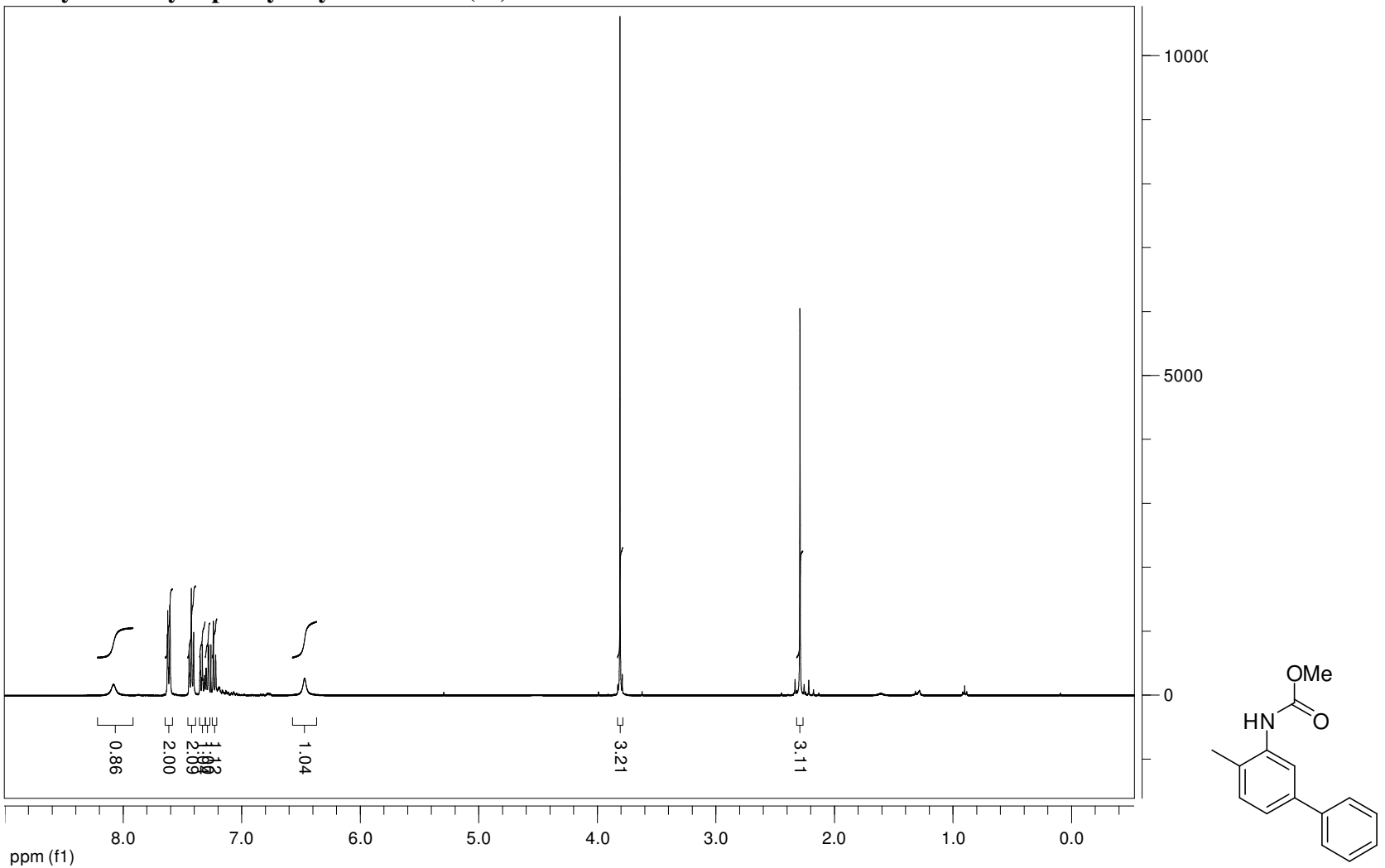




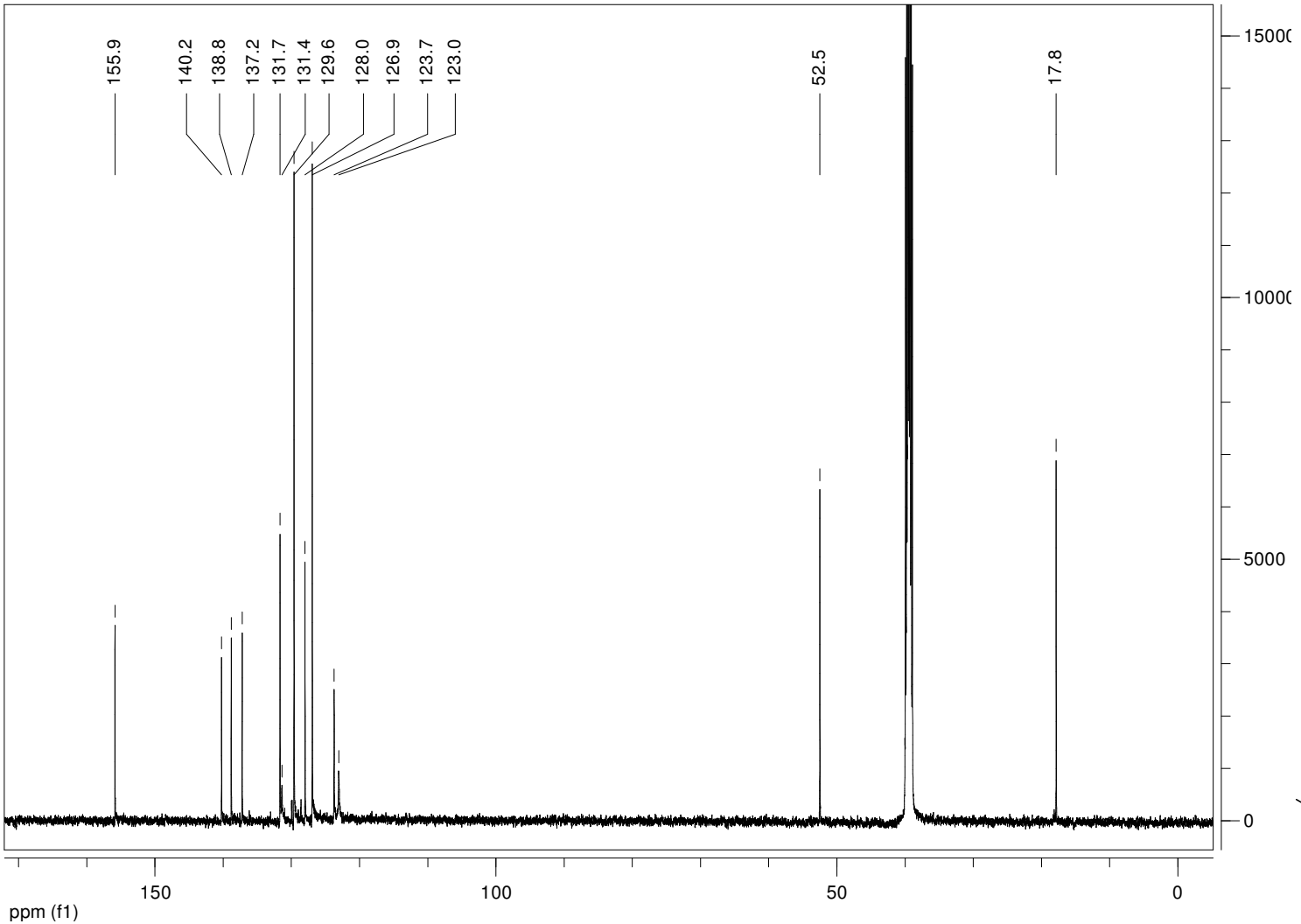
***N*-(4-methylbiphenyl-3-yl)acetamide (2b)**



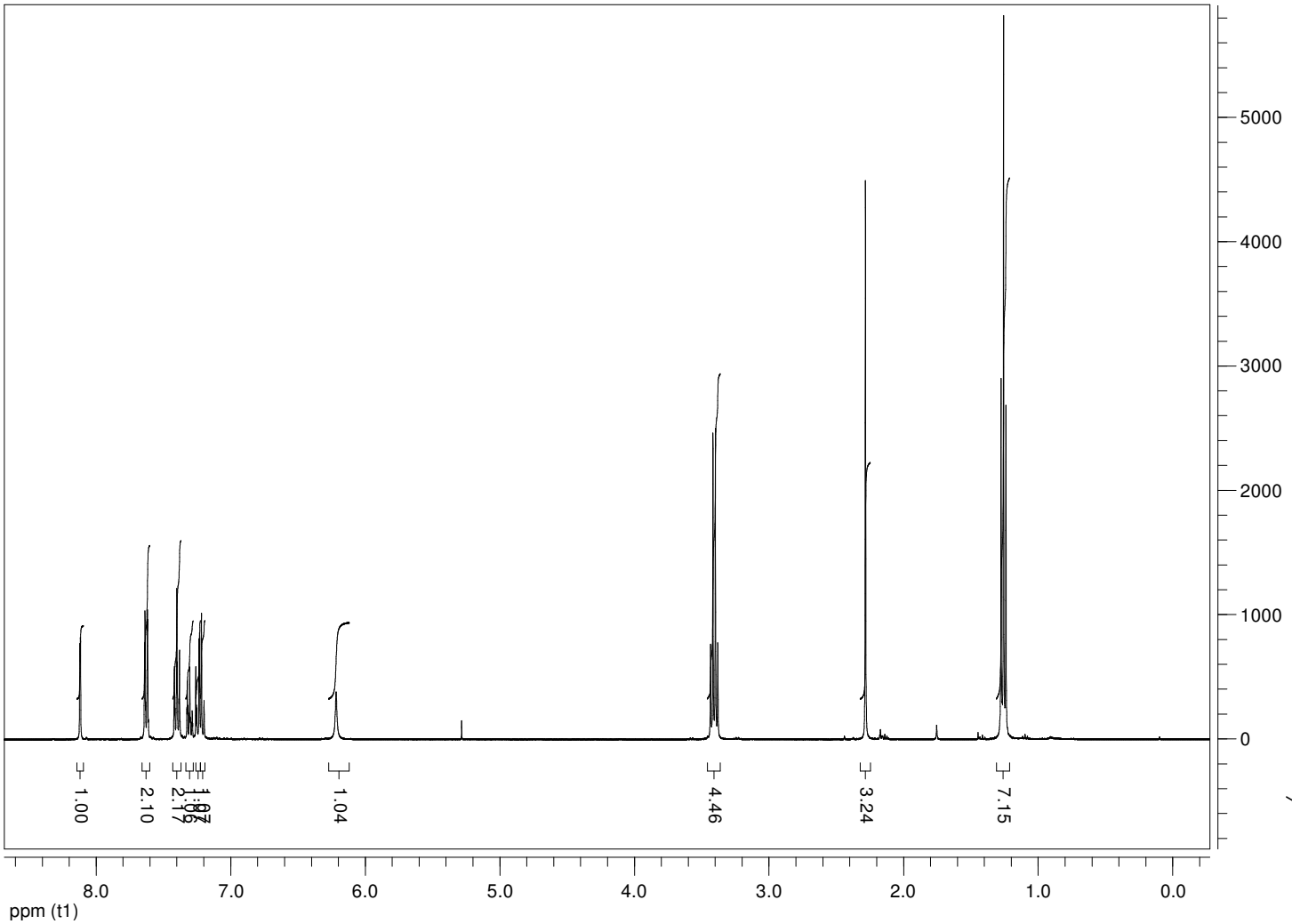
Methyl 4-methylbiphenyl-3-ylcarbamate (2c)



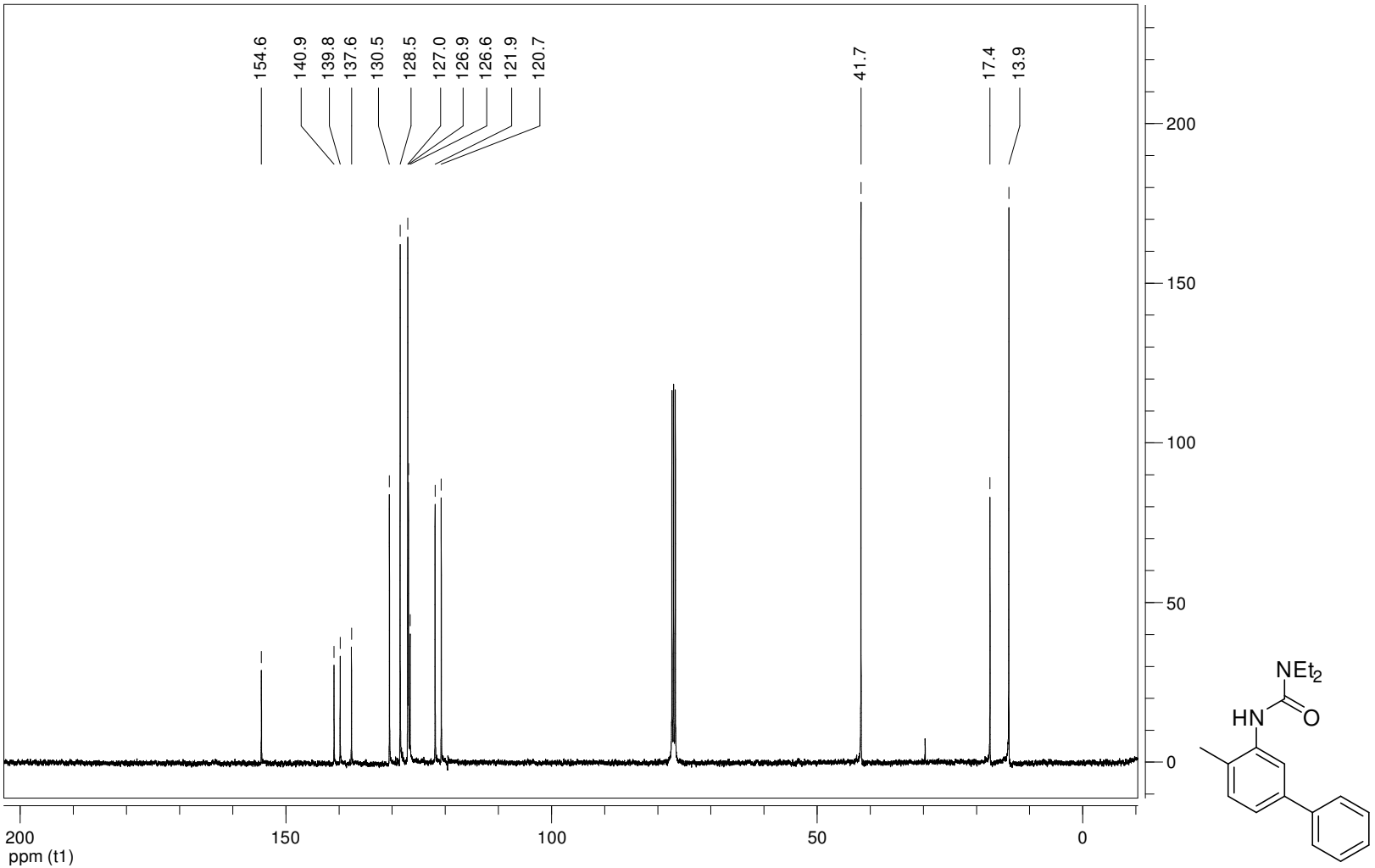
2,2-Dimethyl-N-[1,1';3',1'']terphenyl-5'-yl-propionamide (2c)



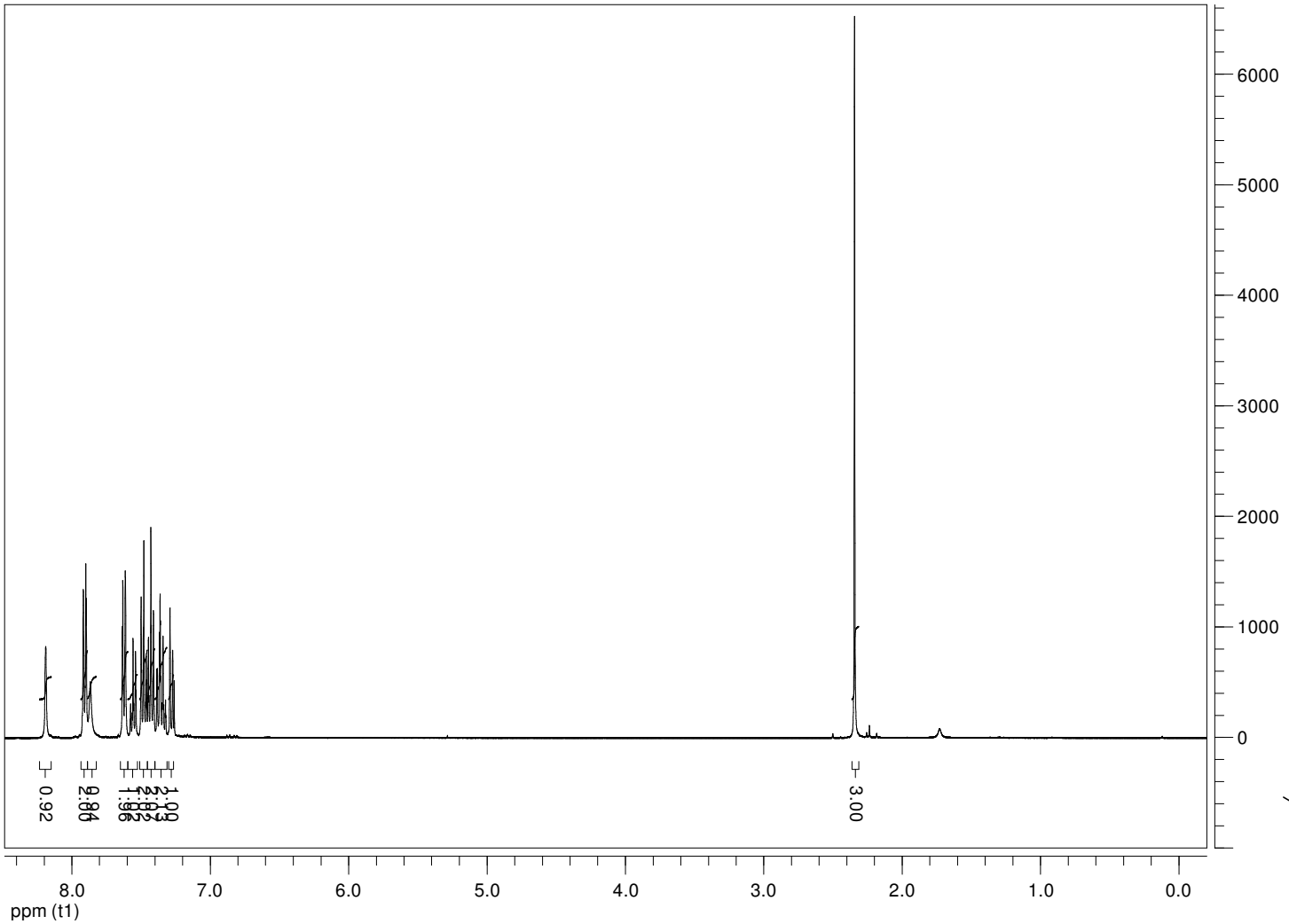
1,1-Diethyl-3-(4-methylbiphenyl-3-yl)urea (2d)

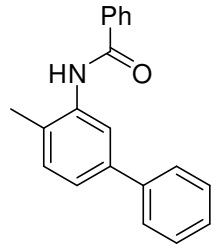


1,1-Diethyl-3-(4-methylbiphenyl-3-yl)urea (2d)

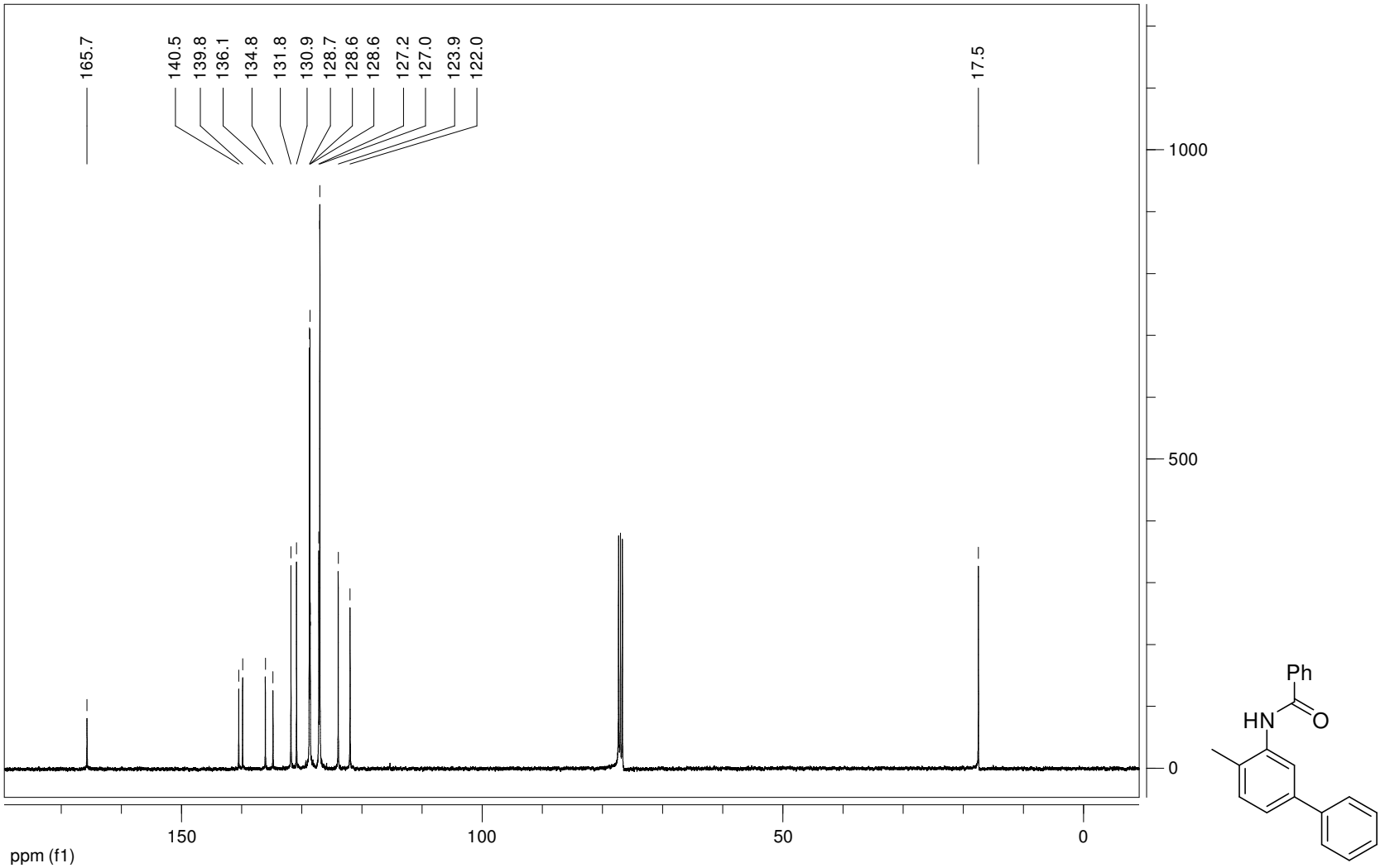


_N_-(4-methylbiphenyl-3-yl)benzamide (2e)

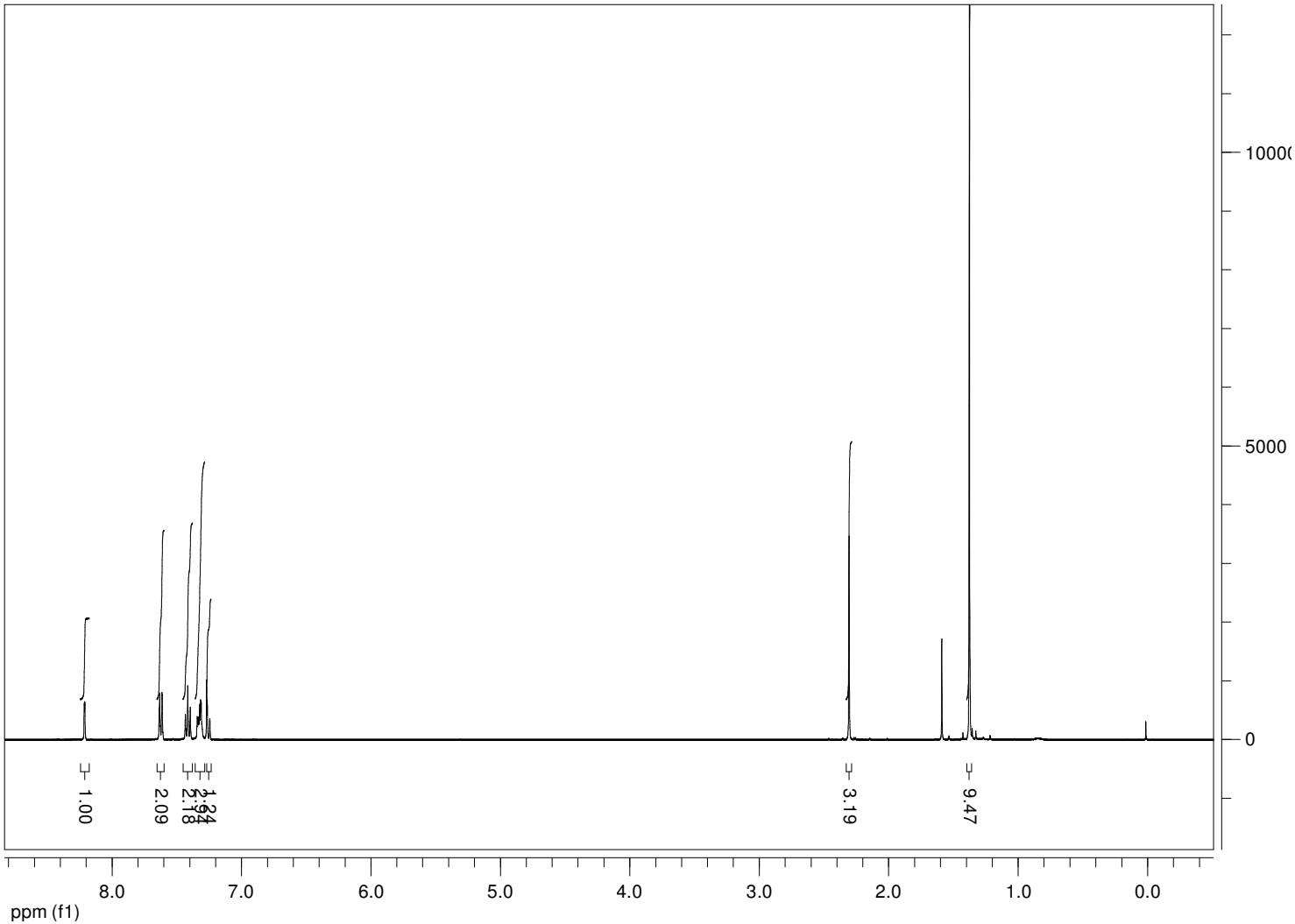




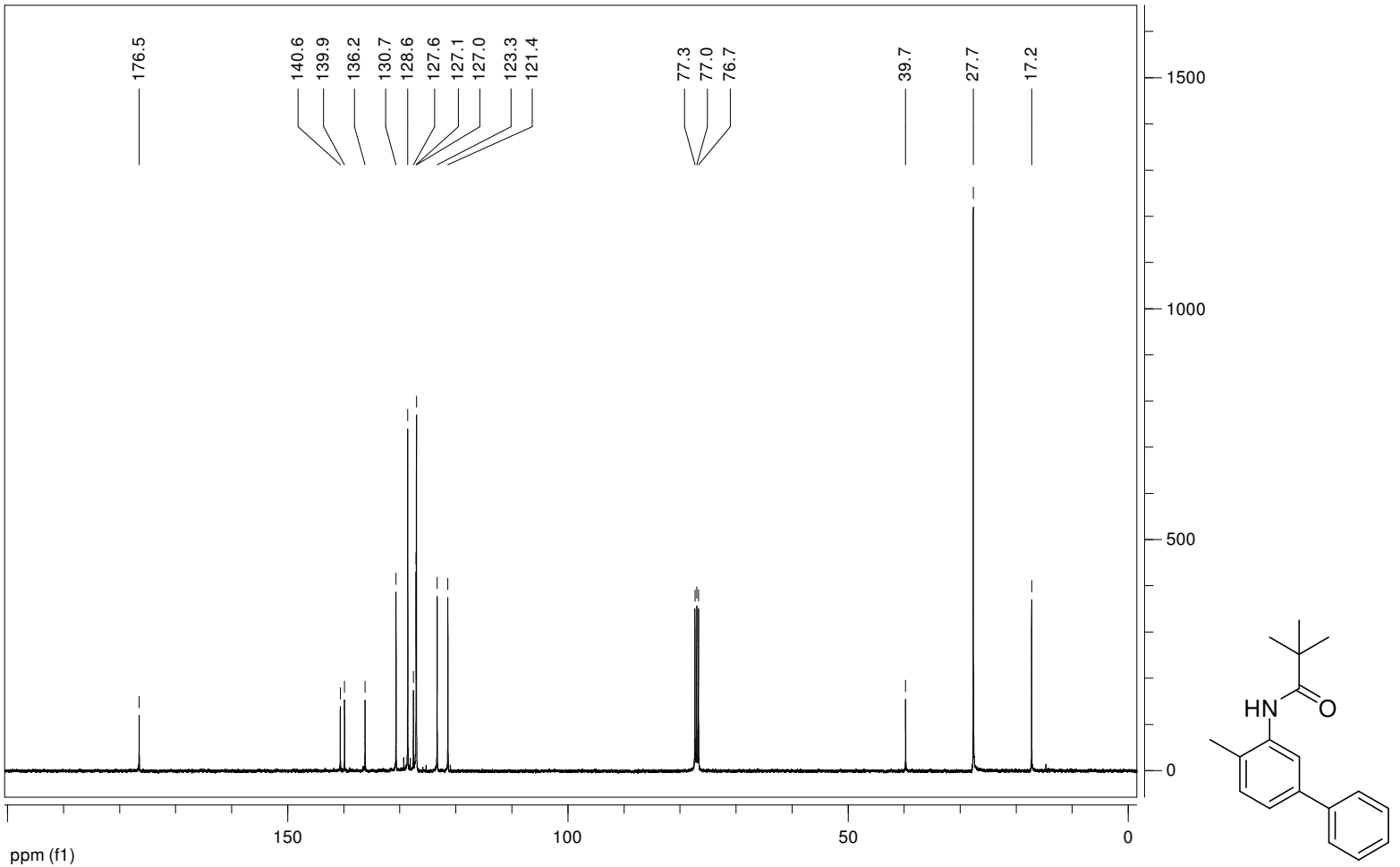
***N*-(4-methylbiphenyl-3-yl)benzamide (2e)**



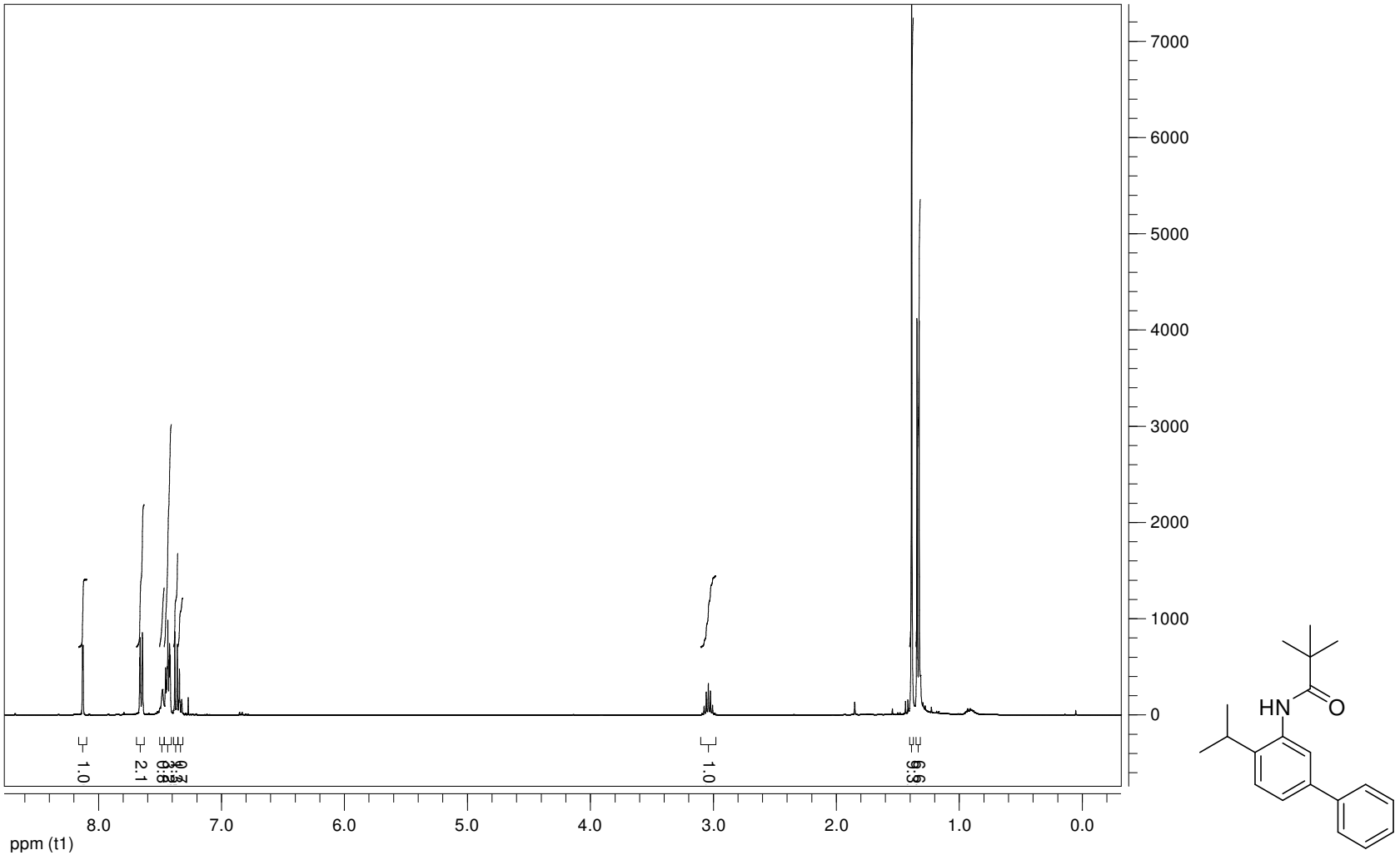
***N*-(4-methylbiphenyl-3-yl)pivalamide (2f)**



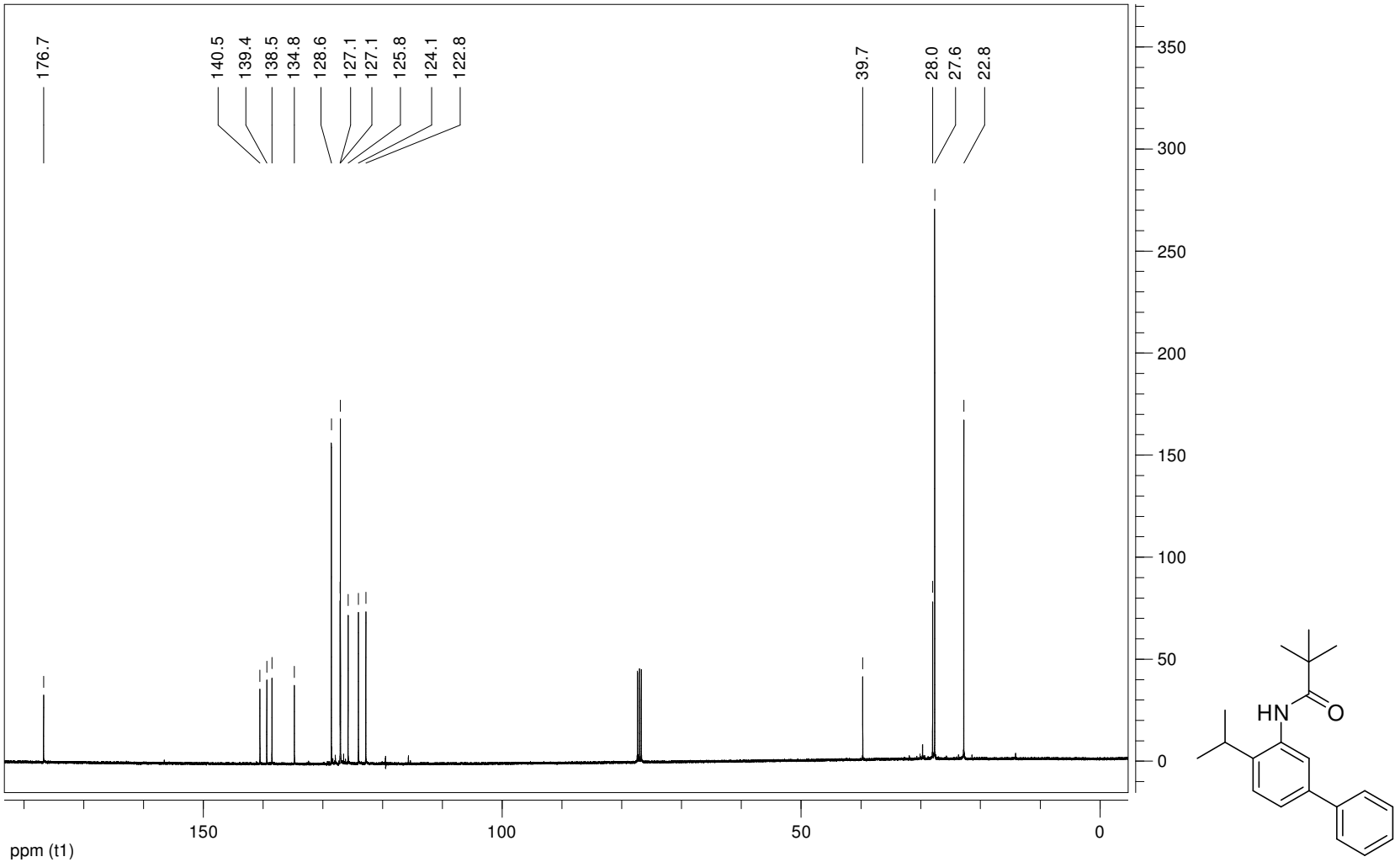
_N_-(4-methylbiphenyl-3-yl)pivalamide (2f)



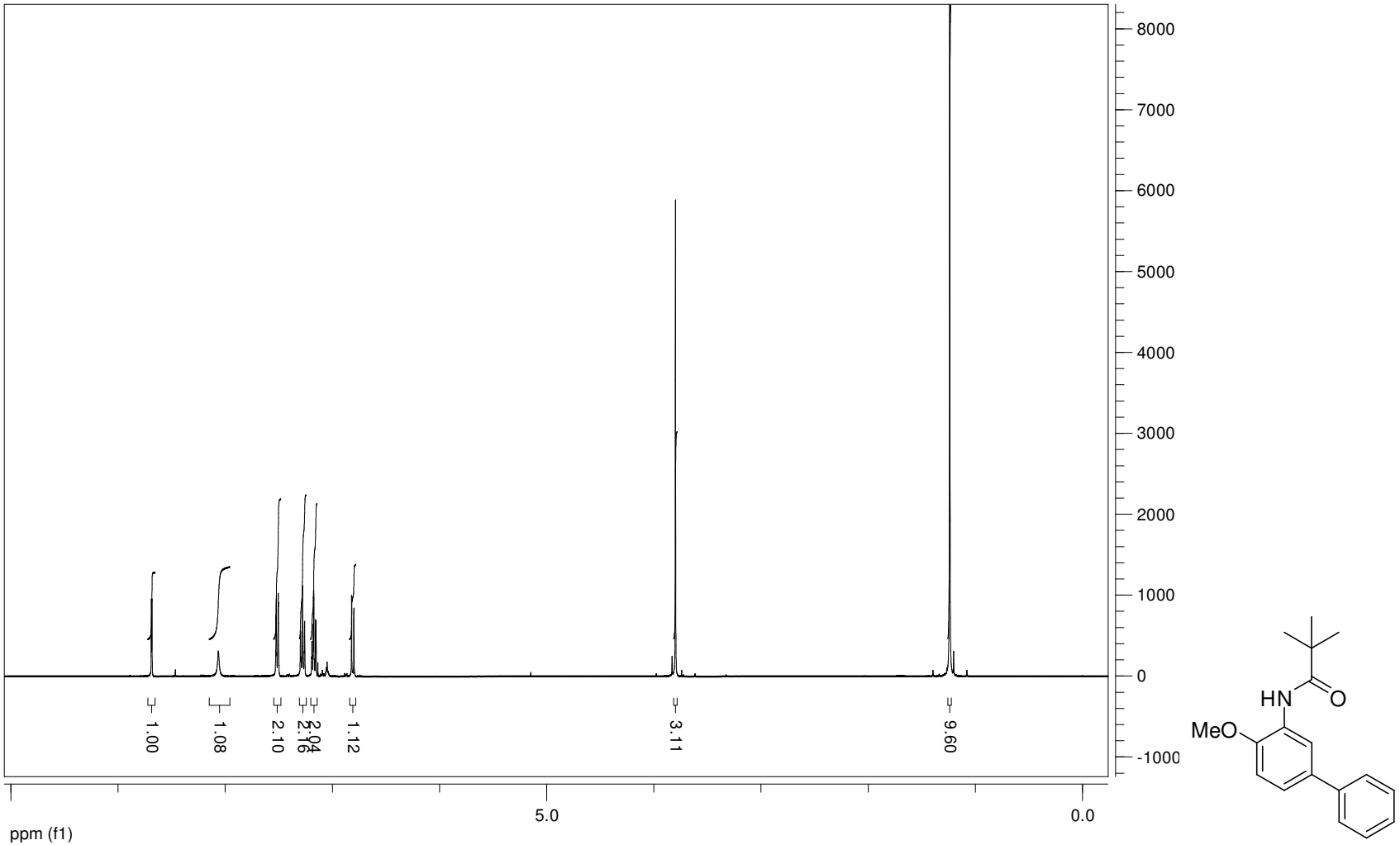
***N*-(4-isopropylbiphenyl-3-yl)pivalamide (2g)**



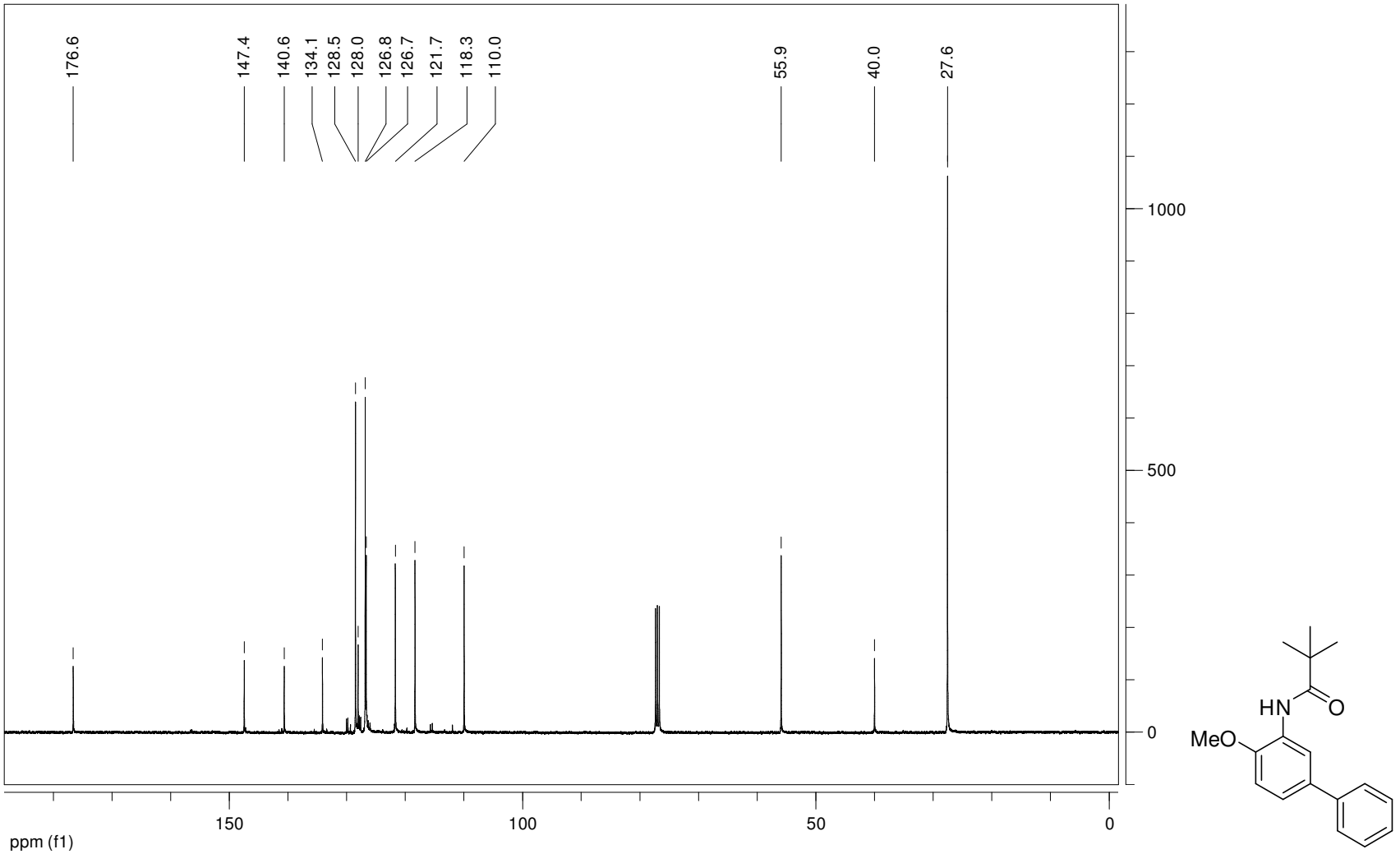
***N*-(4-isopropylbiphenyl-3-yl)pivalamide (2g)**



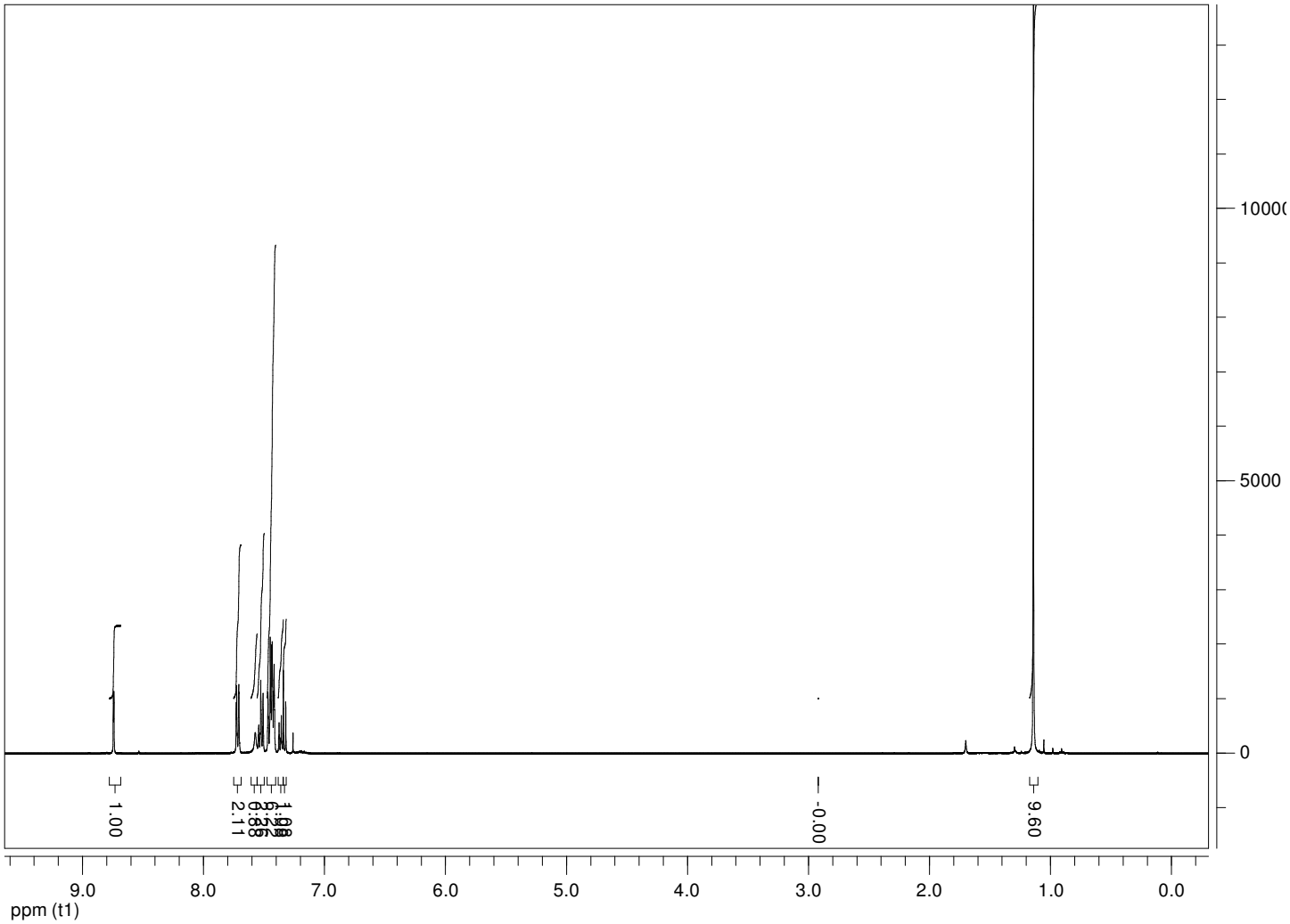
_N_-(4-methoxybiphenyl-3-yl)pivalamide (2h)



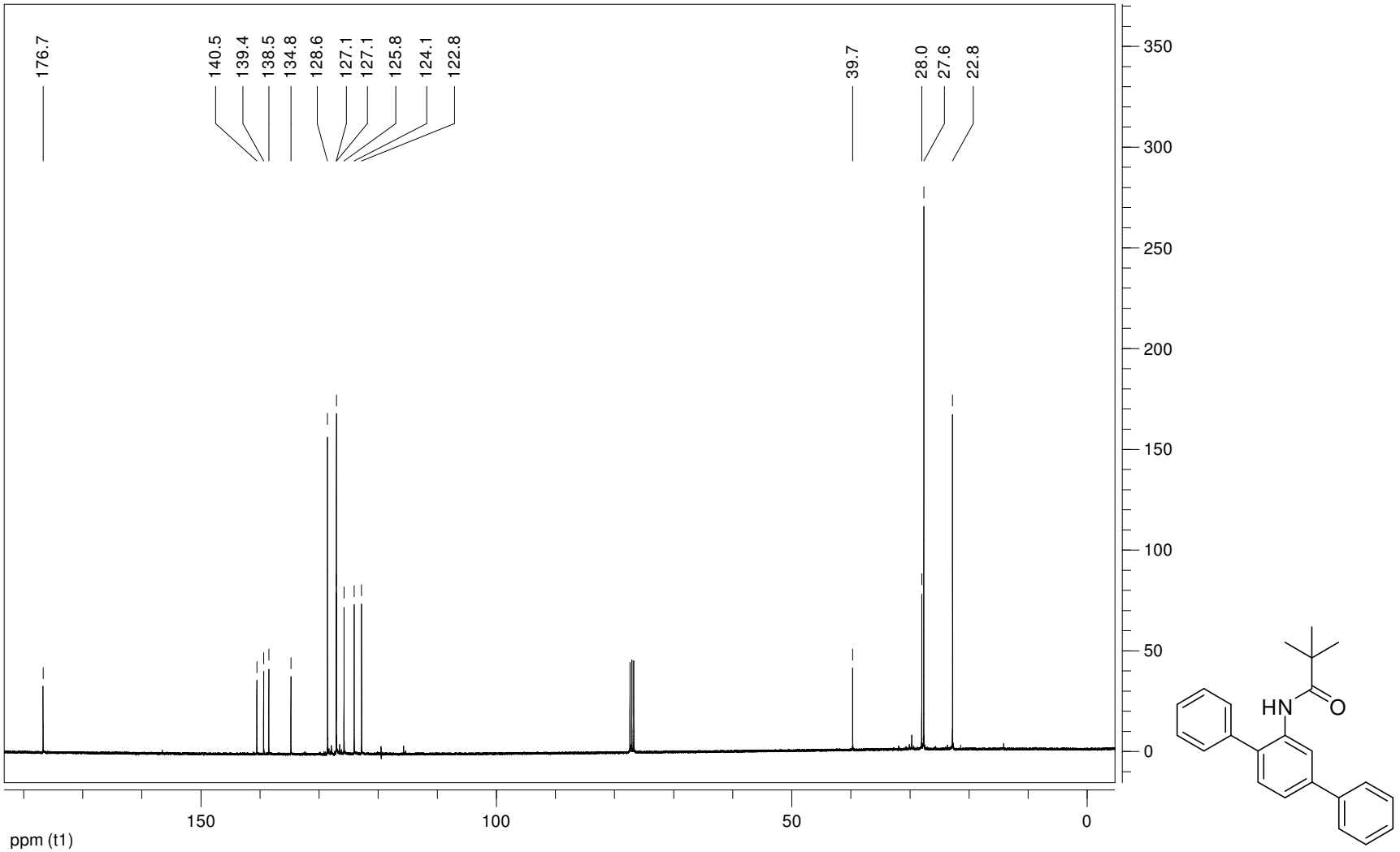
_N_-(4-methoxybiphenyl-3-yl)pivalamide (2h)



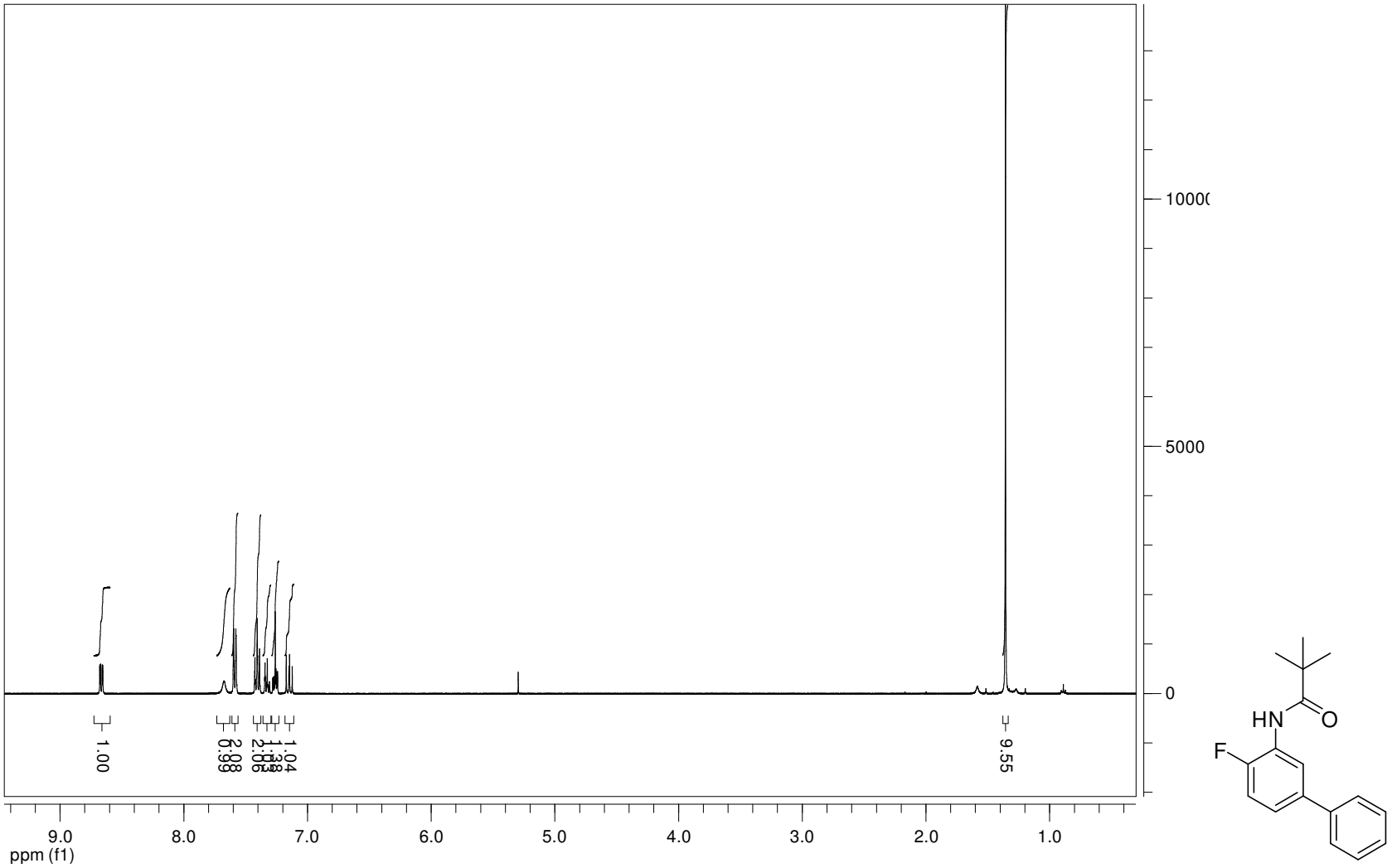
_N_-(6-phenylbiphenyl-3-yl)pivalamide (2i)



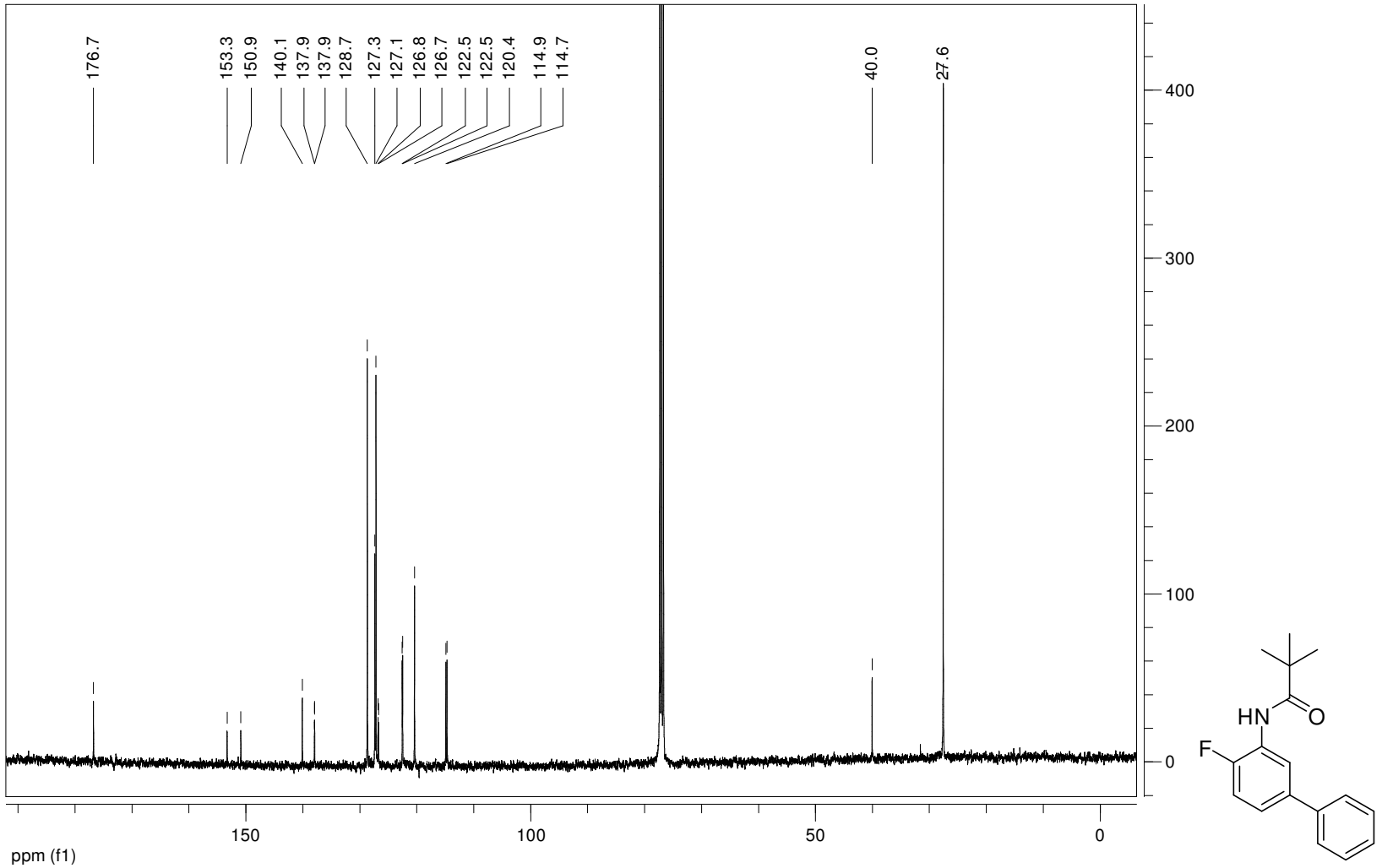
_N_-(6-phenylbiphenyl-3-yl)pivalamide (2i)



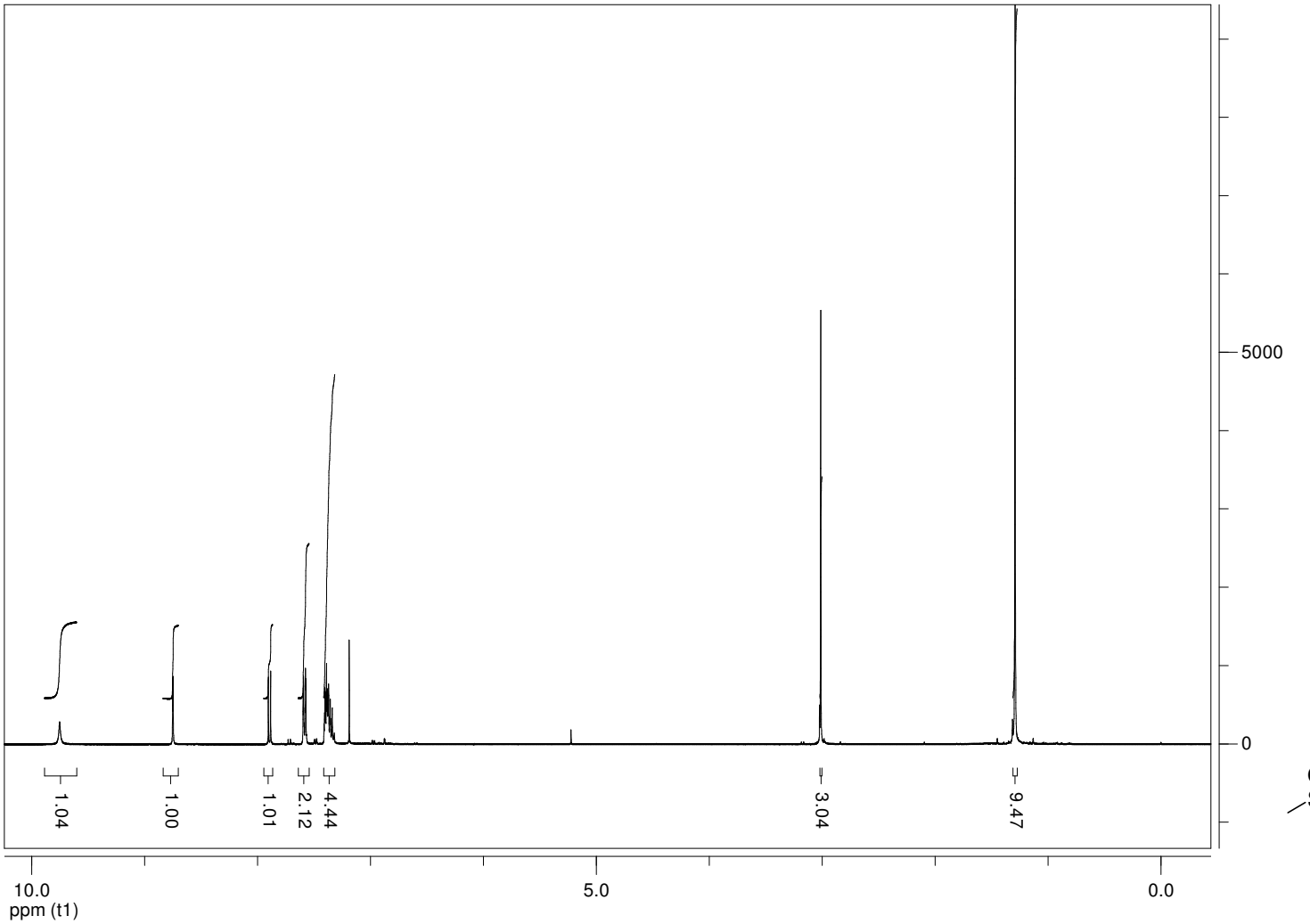
_N_-(4-fluorobiphenyl-3-yl)pivalamide (2j)



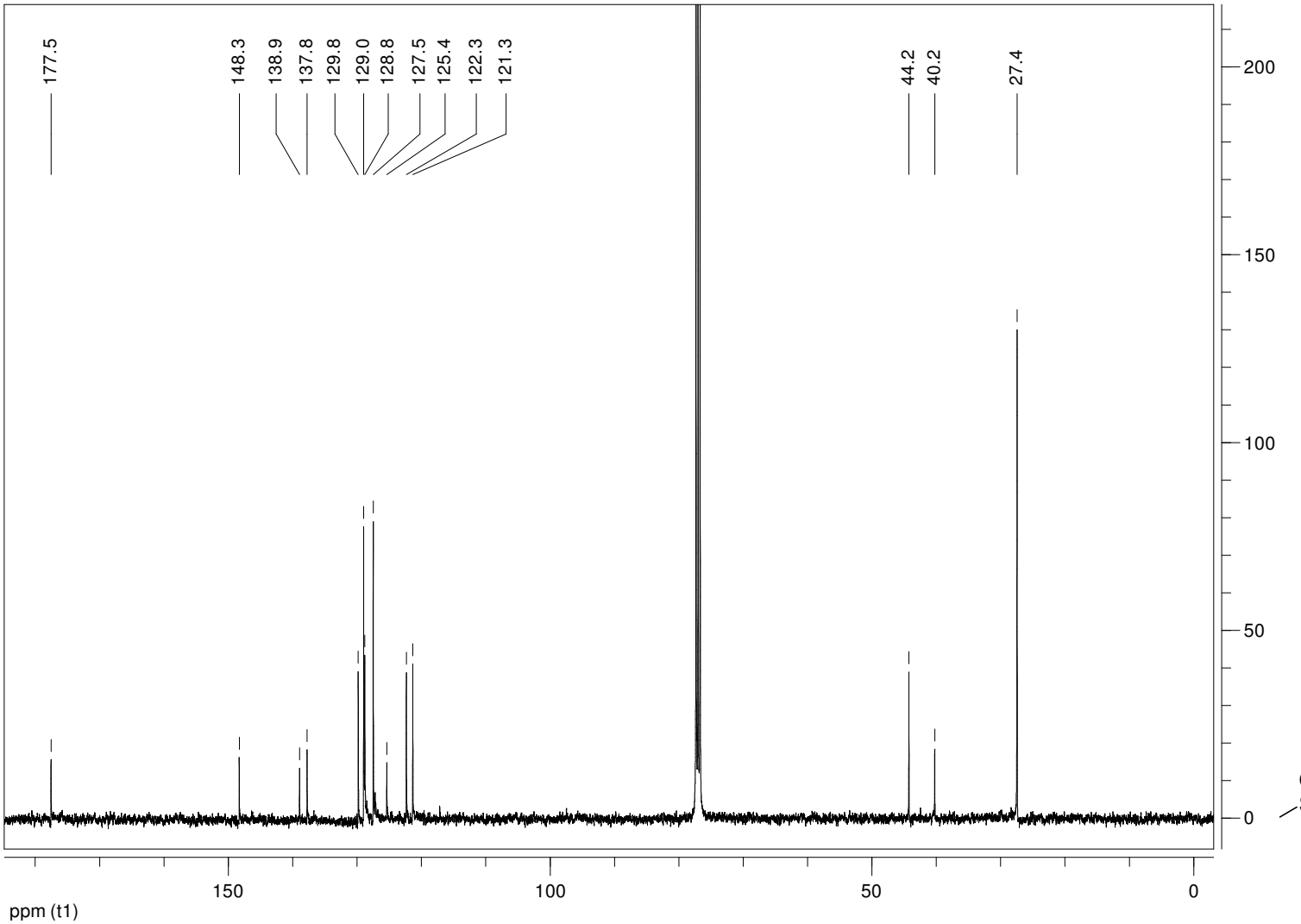
_N_-(4-fluorobiphenyl-3-yl)pivalamide **(2j)**



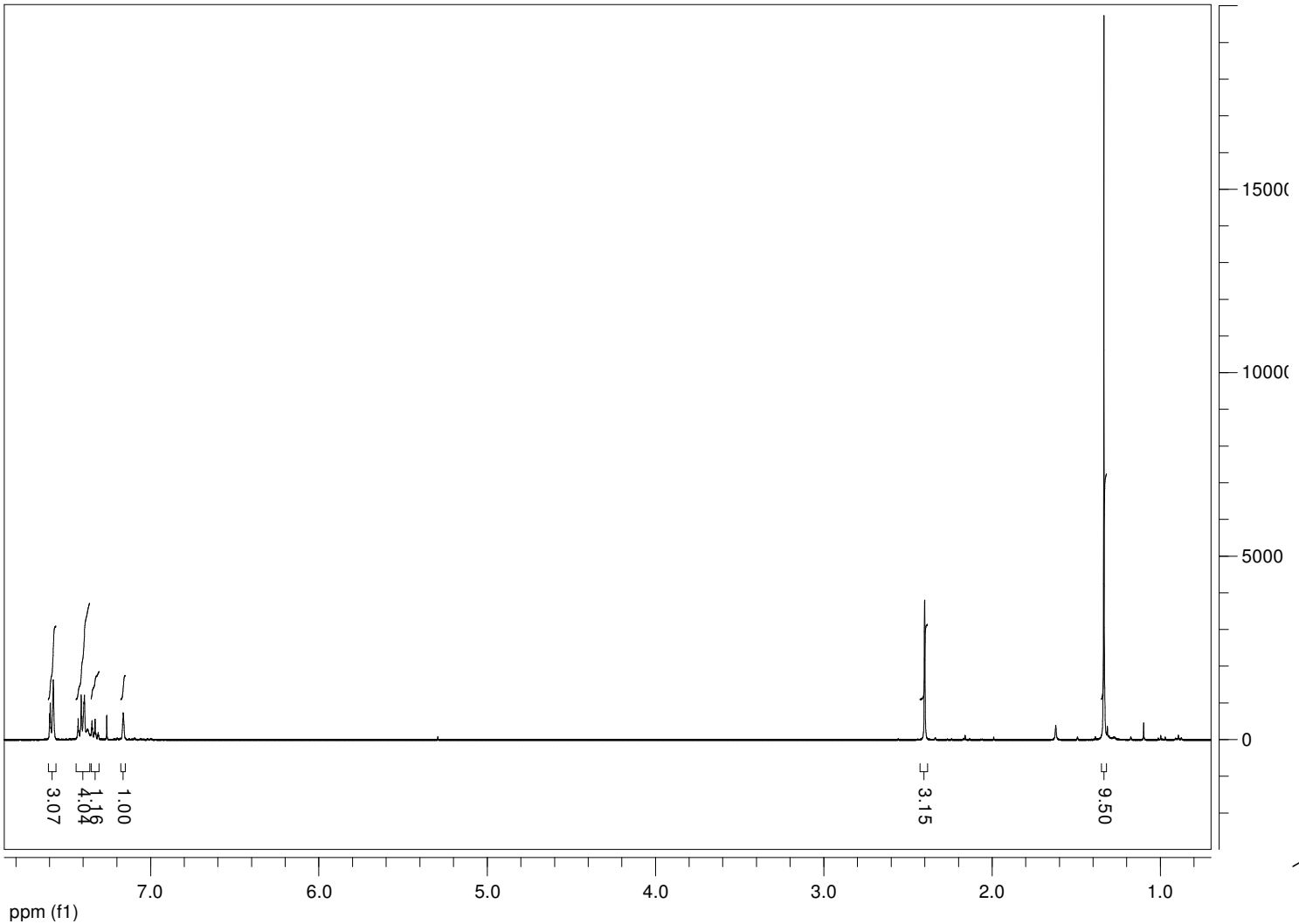
***N*-(4-(methylsulfonyl)biphenyl-3-yl)pivalamide (2k)**



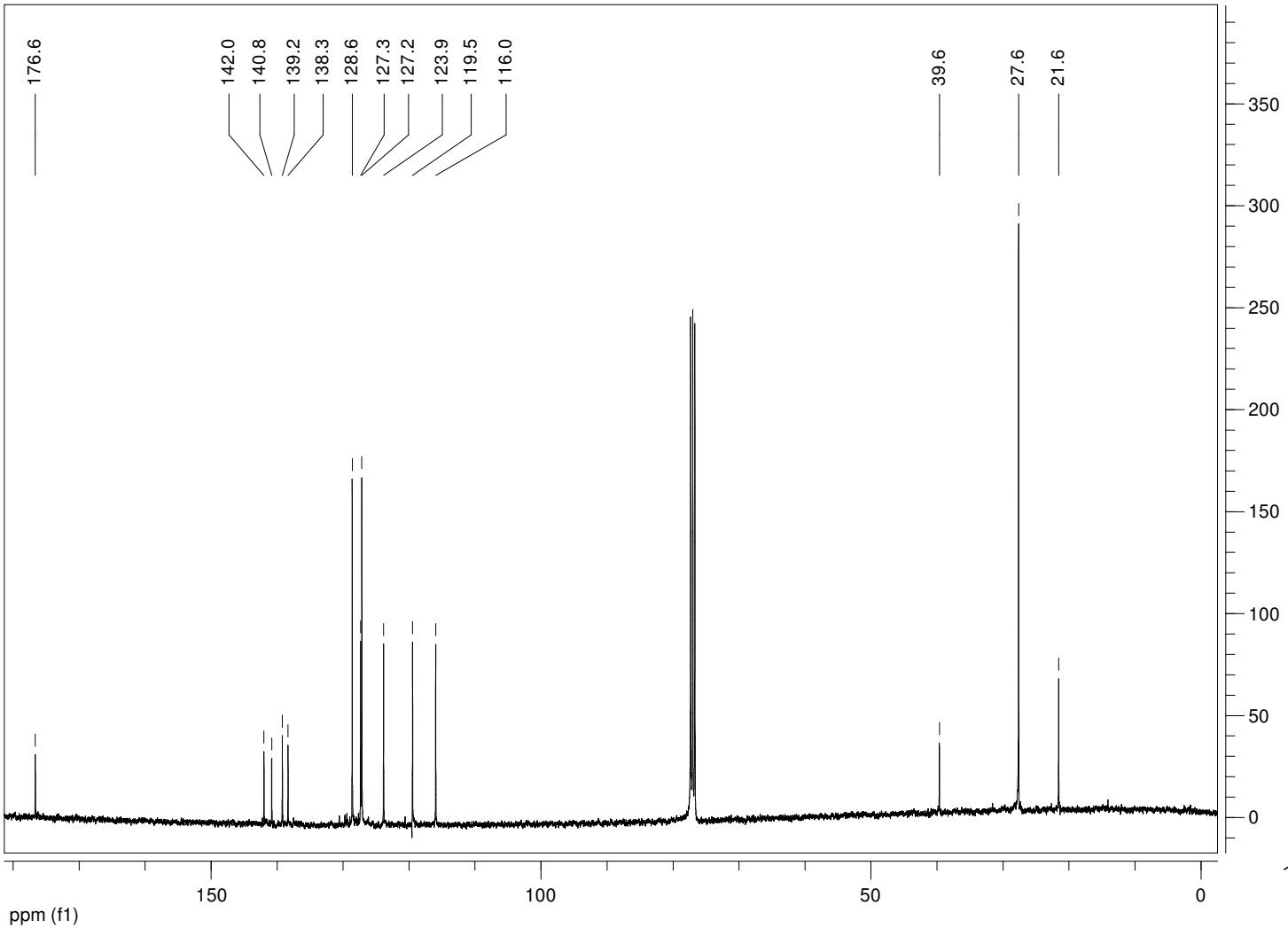
_N_-(4-(methylsulfonyl)biphenyl-3-yl)pivalamide (2k)



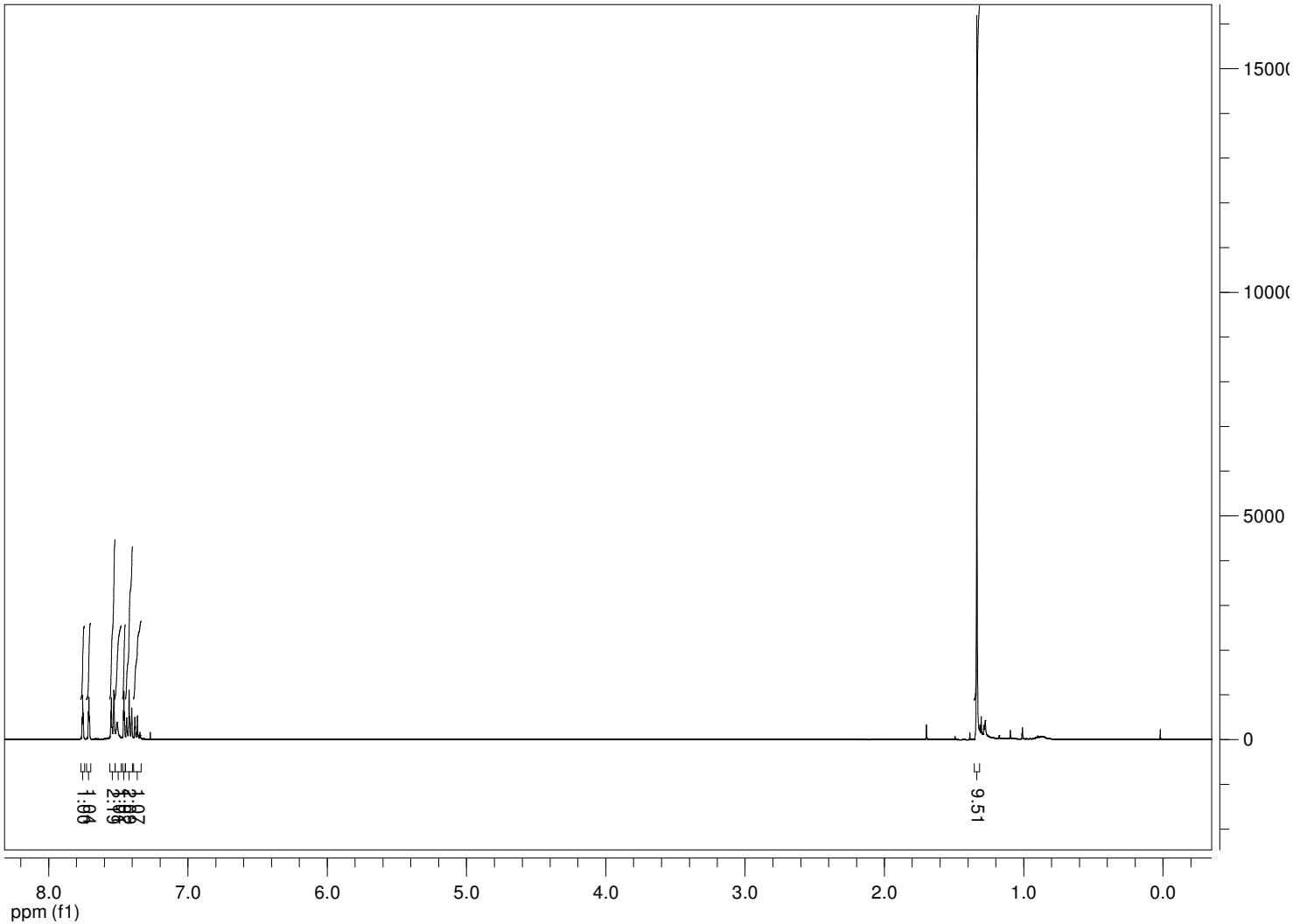
_N_-(5-methylbiphenyl-3-yl)pivalamide (2l)



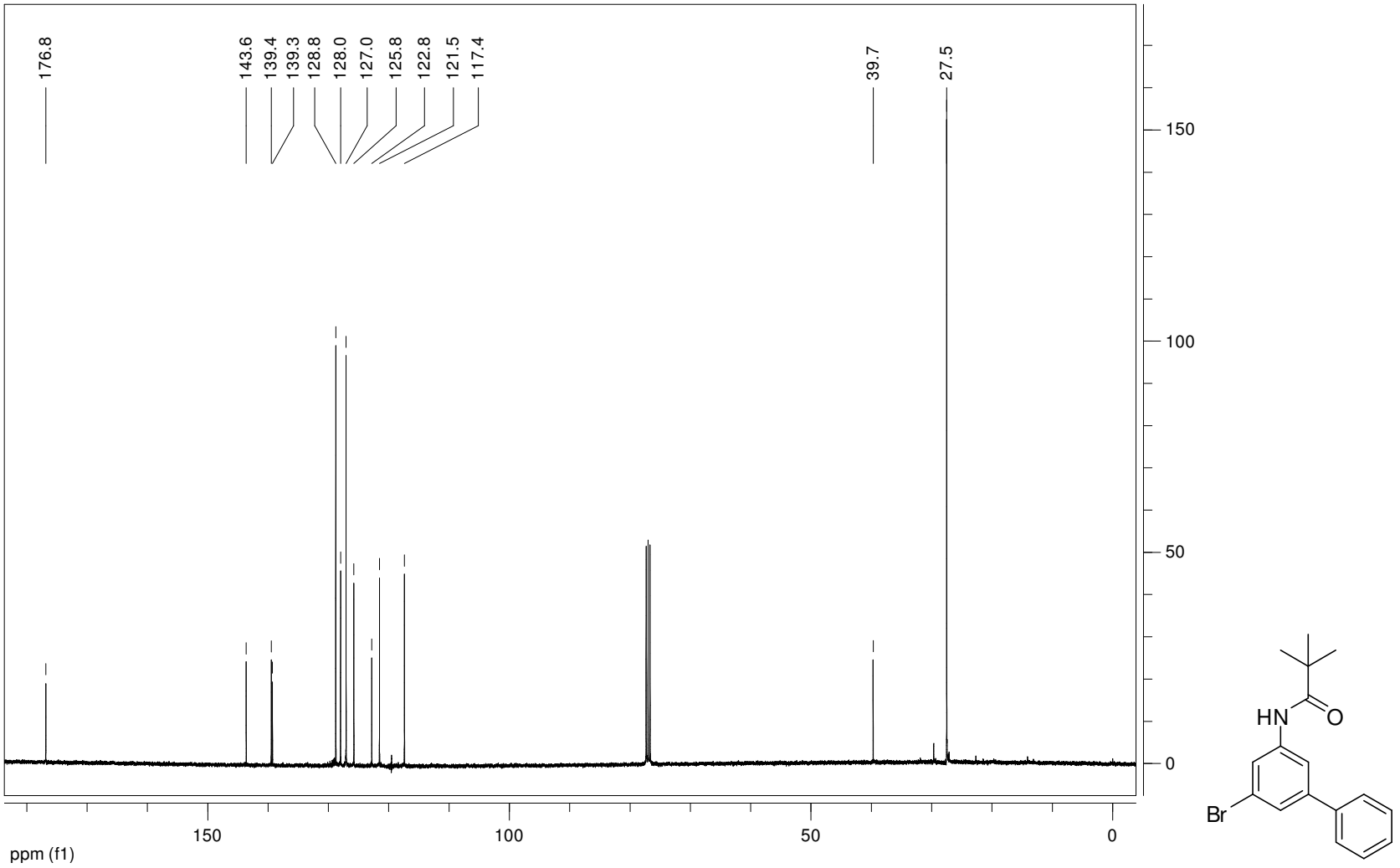
***N*-(5-methylbiphenyl-3-yl)pivalamide (2l)**



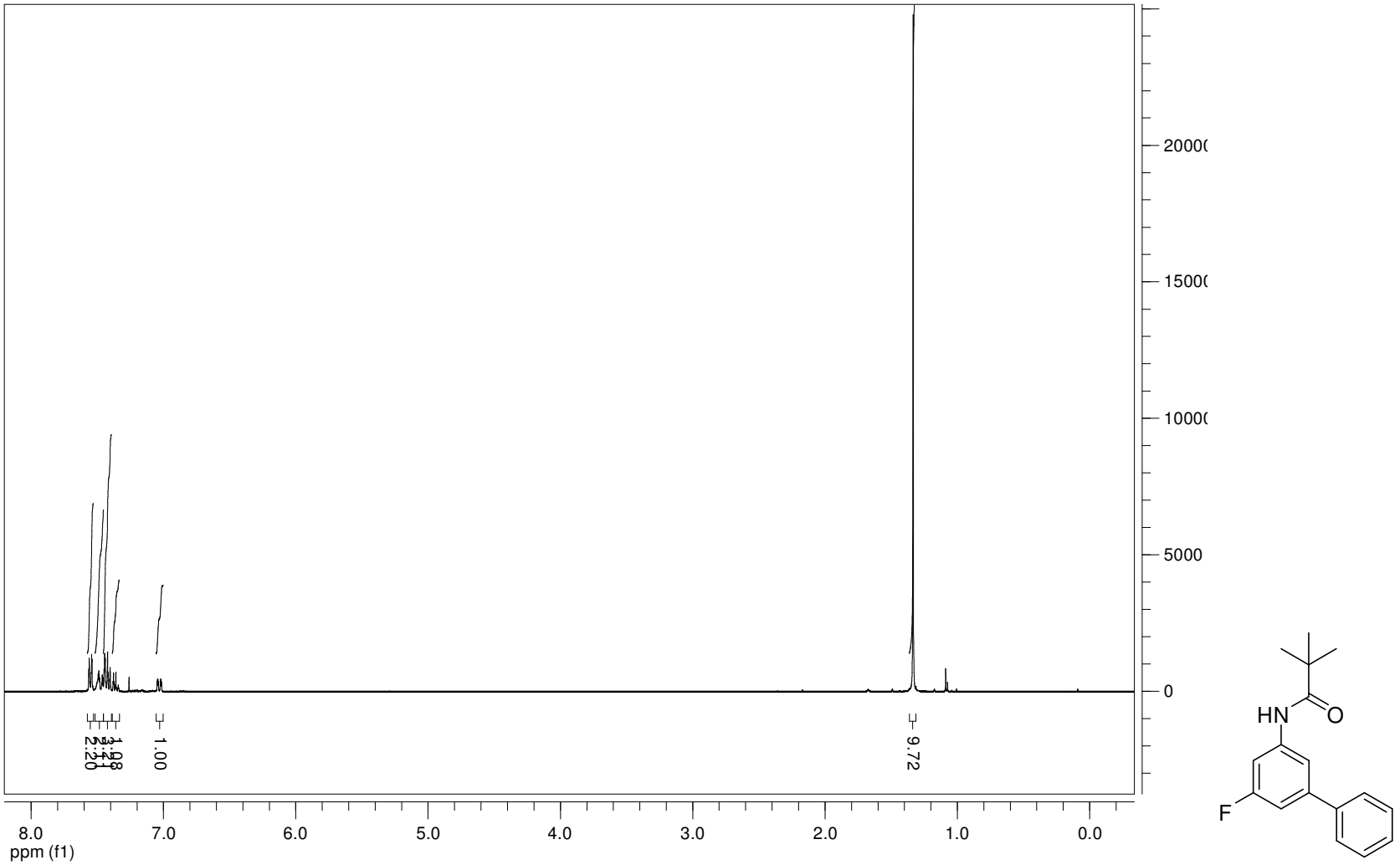
_N_-(5-bromobiphenyl-3-yl)pivalamide (2m)



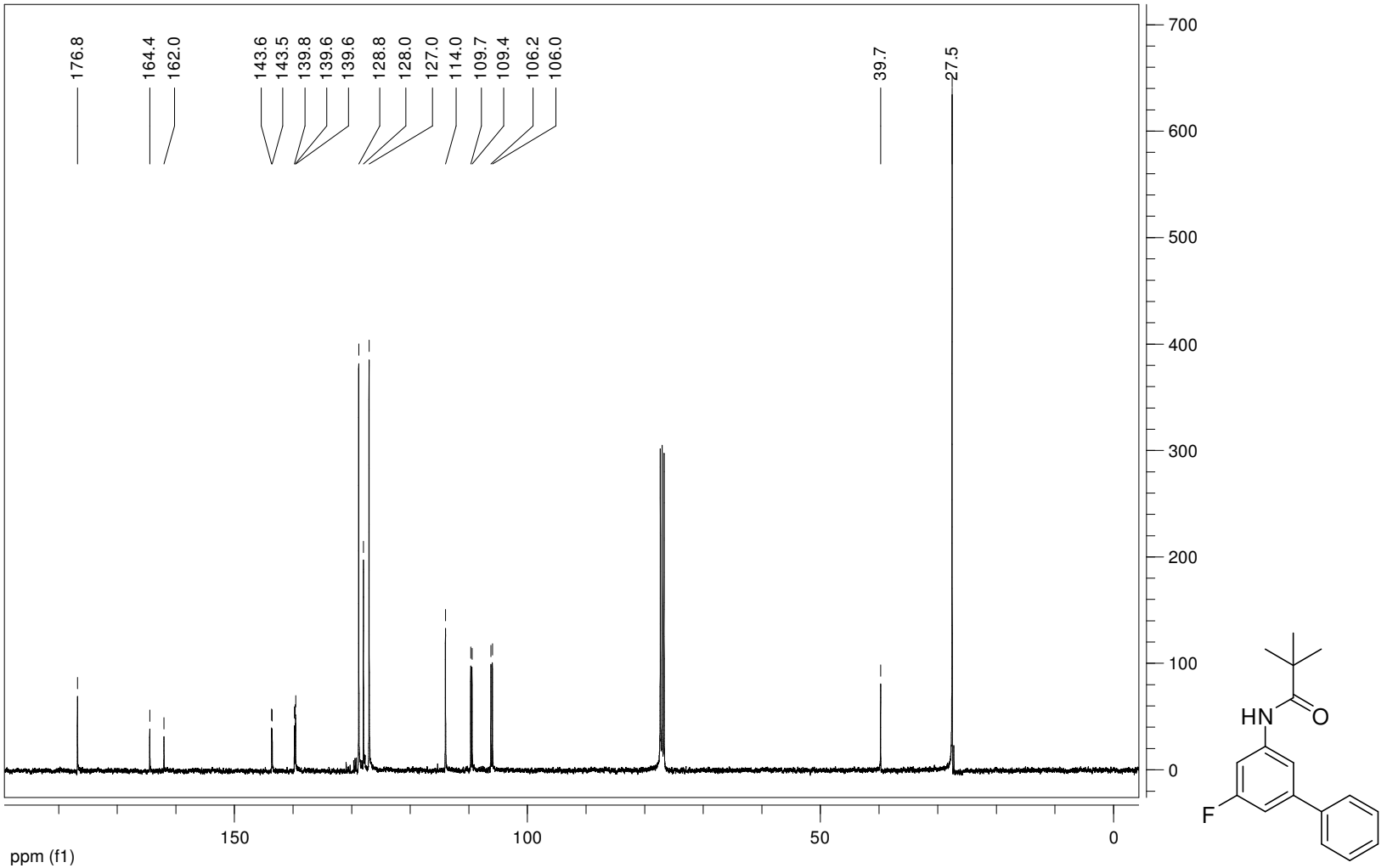
***N*-(5-bromobiphenyl-3-yl)pivalamide (2m)**



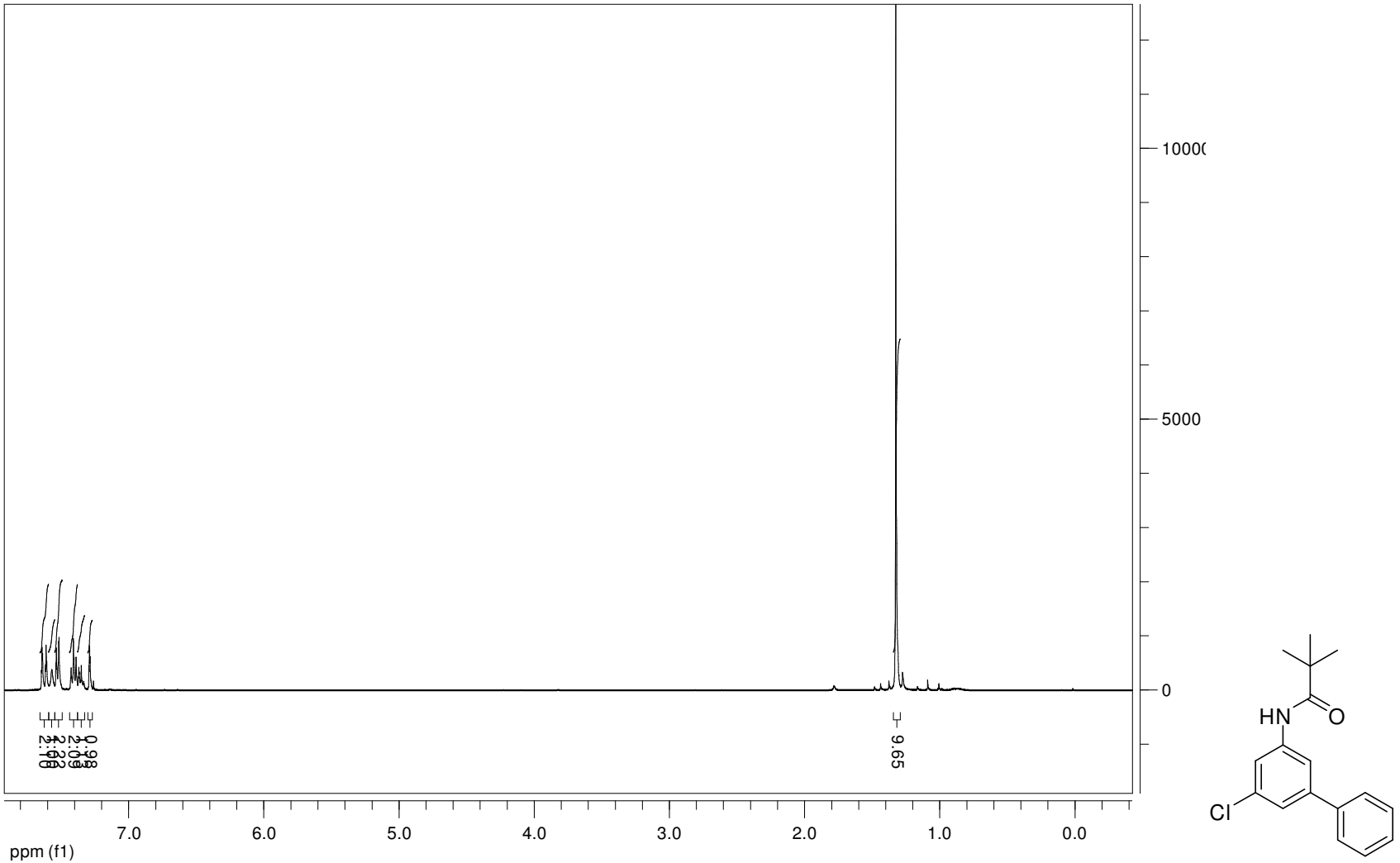
***N*-(5-fluorobiphenyl-3-yl)pivalamide (2n)**



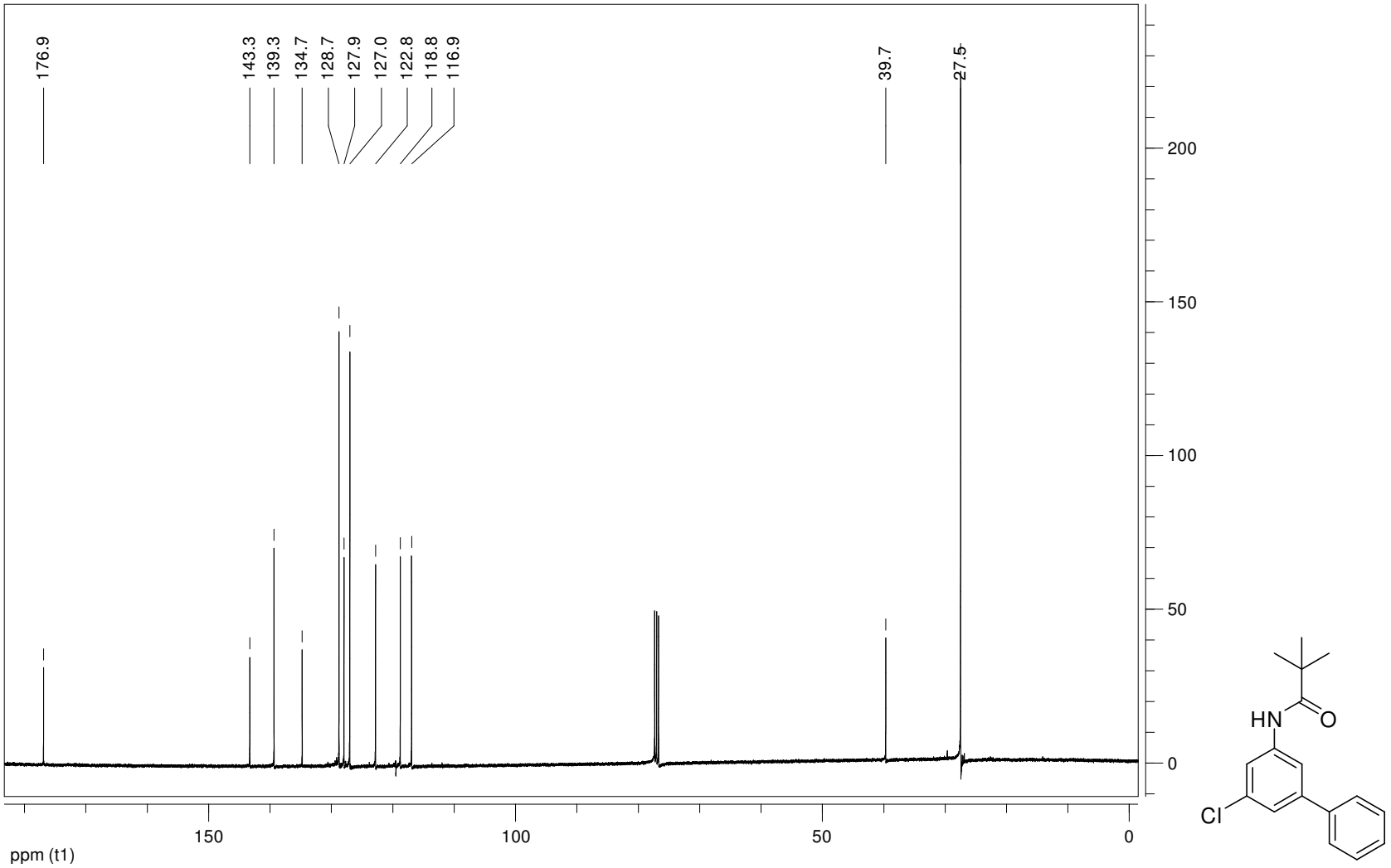
_N_-(5-fluorobiphenyl-3-yl)pivalamide (2n)



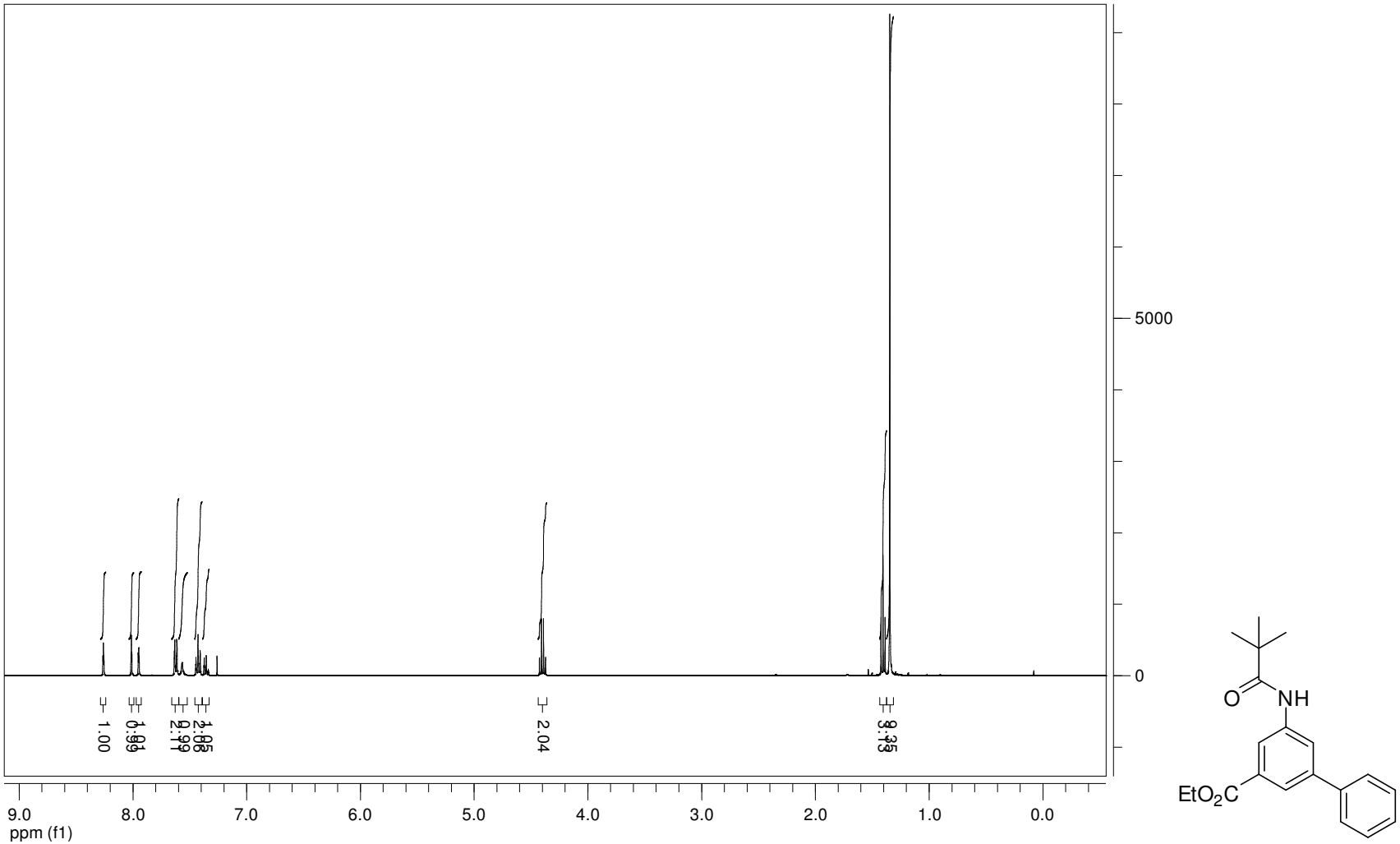
N-(5-chlorobiphenyl-3-yl)pivalamide (2o)



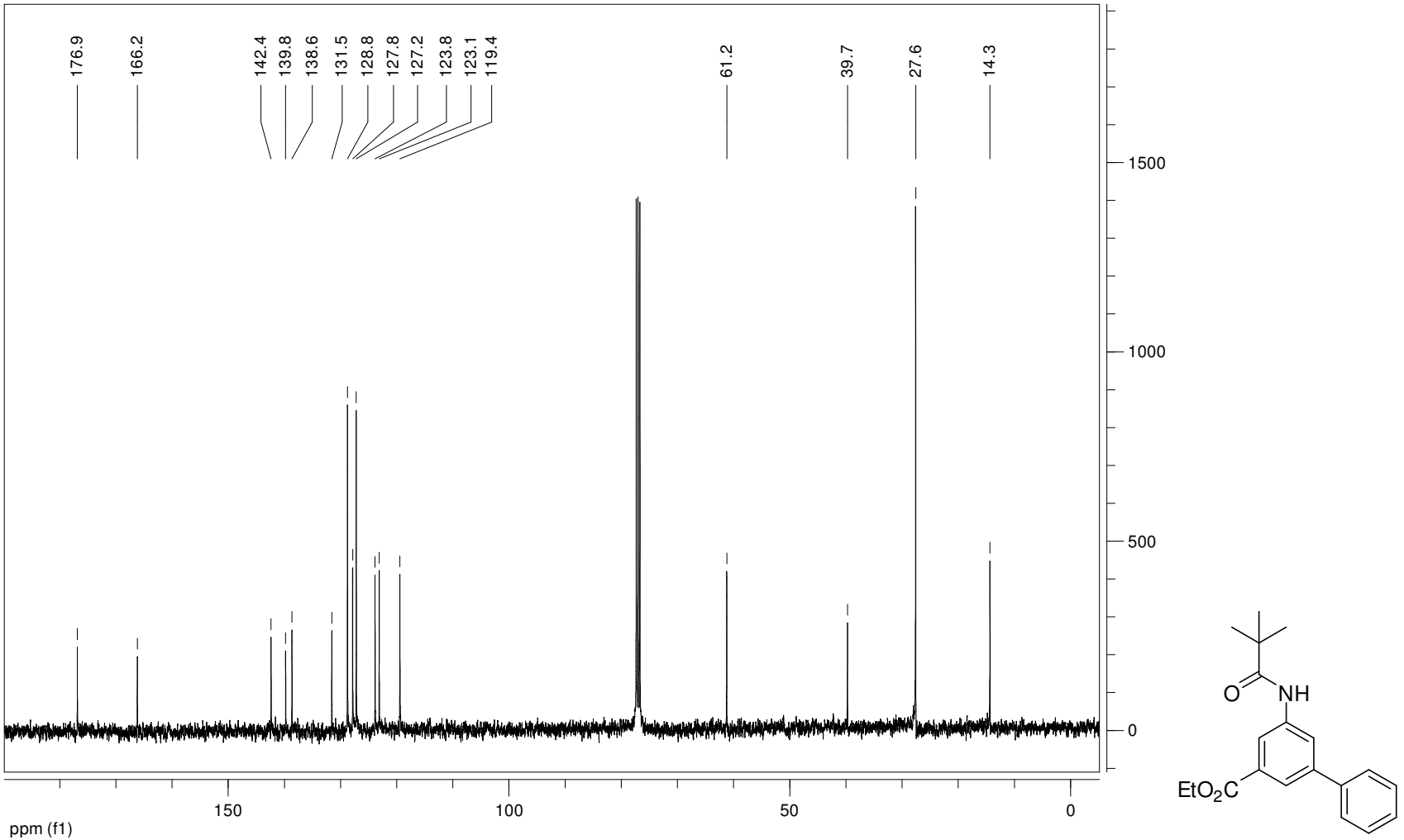
_N_-(5-chlorobiphenyl-3-yl)pivalamide (2o)



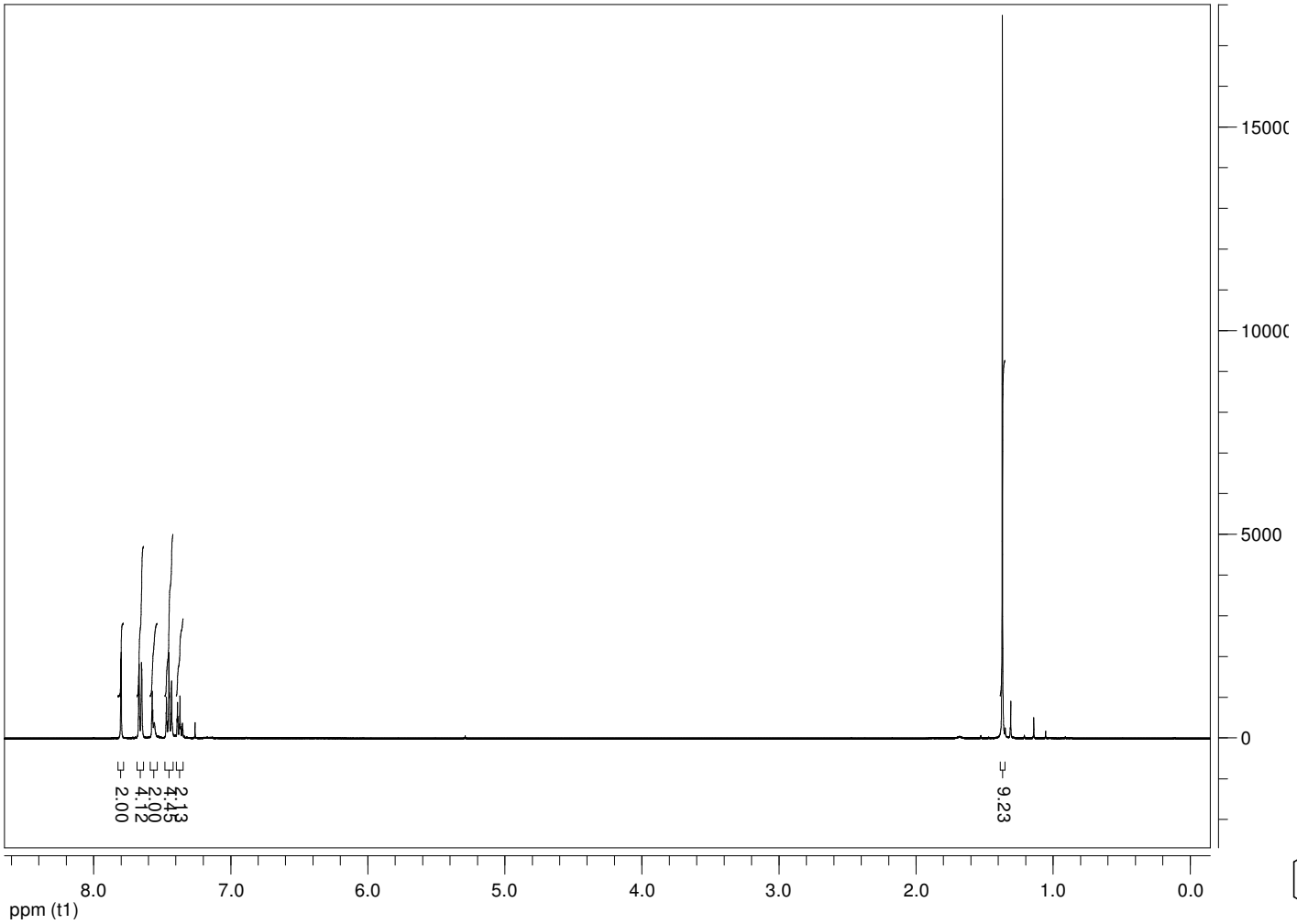
Ethyl 5-pivalamidobiphenyl-3-carboxylate (2p)

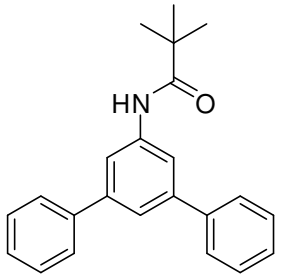


Ethyl 5-pivalamidobiphenyl-3-carboxylate (2p)

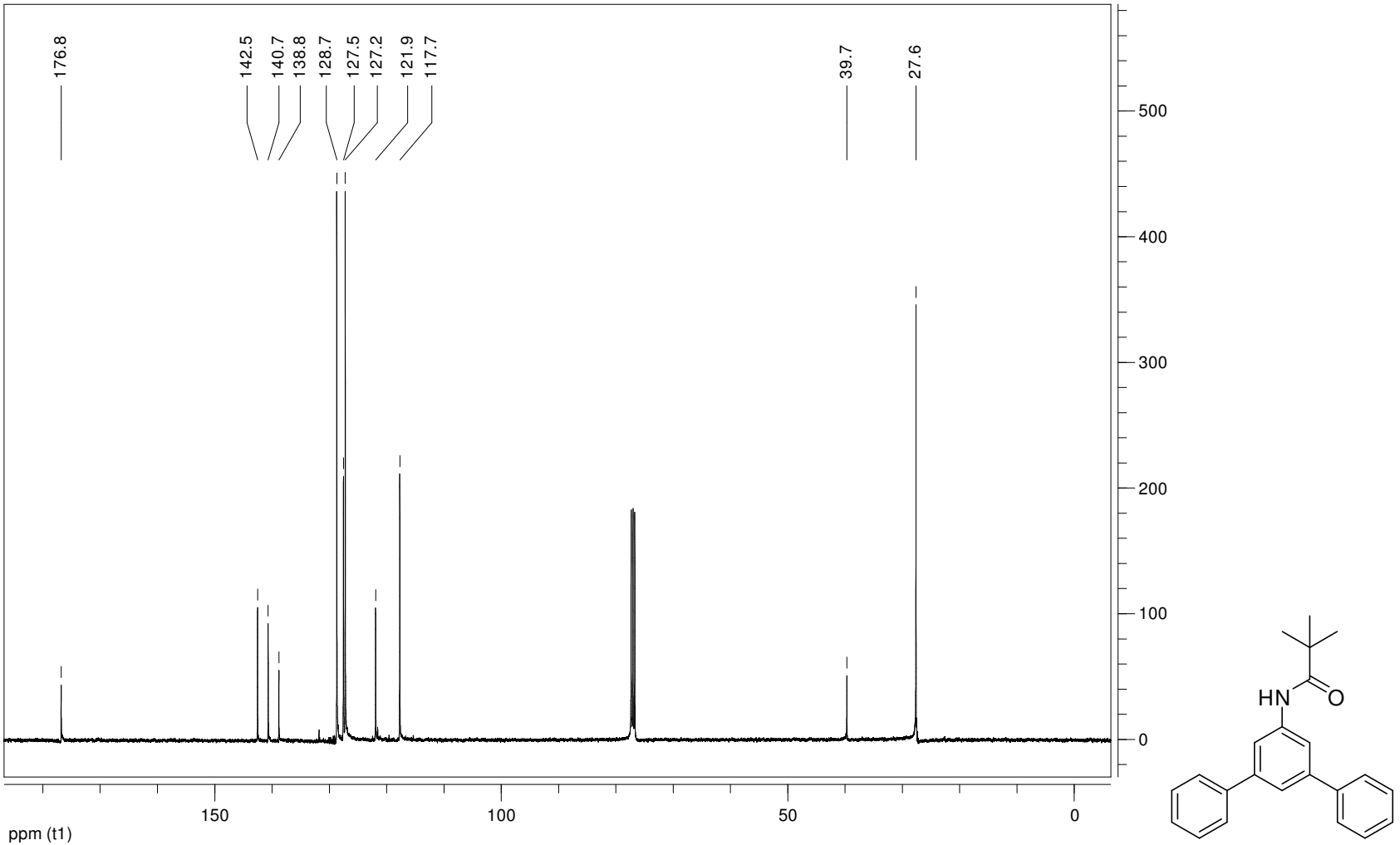


2,2-Dimethyl-N-[1,1';3',1'']terphenyl-5'-yl-propionamide (2q)

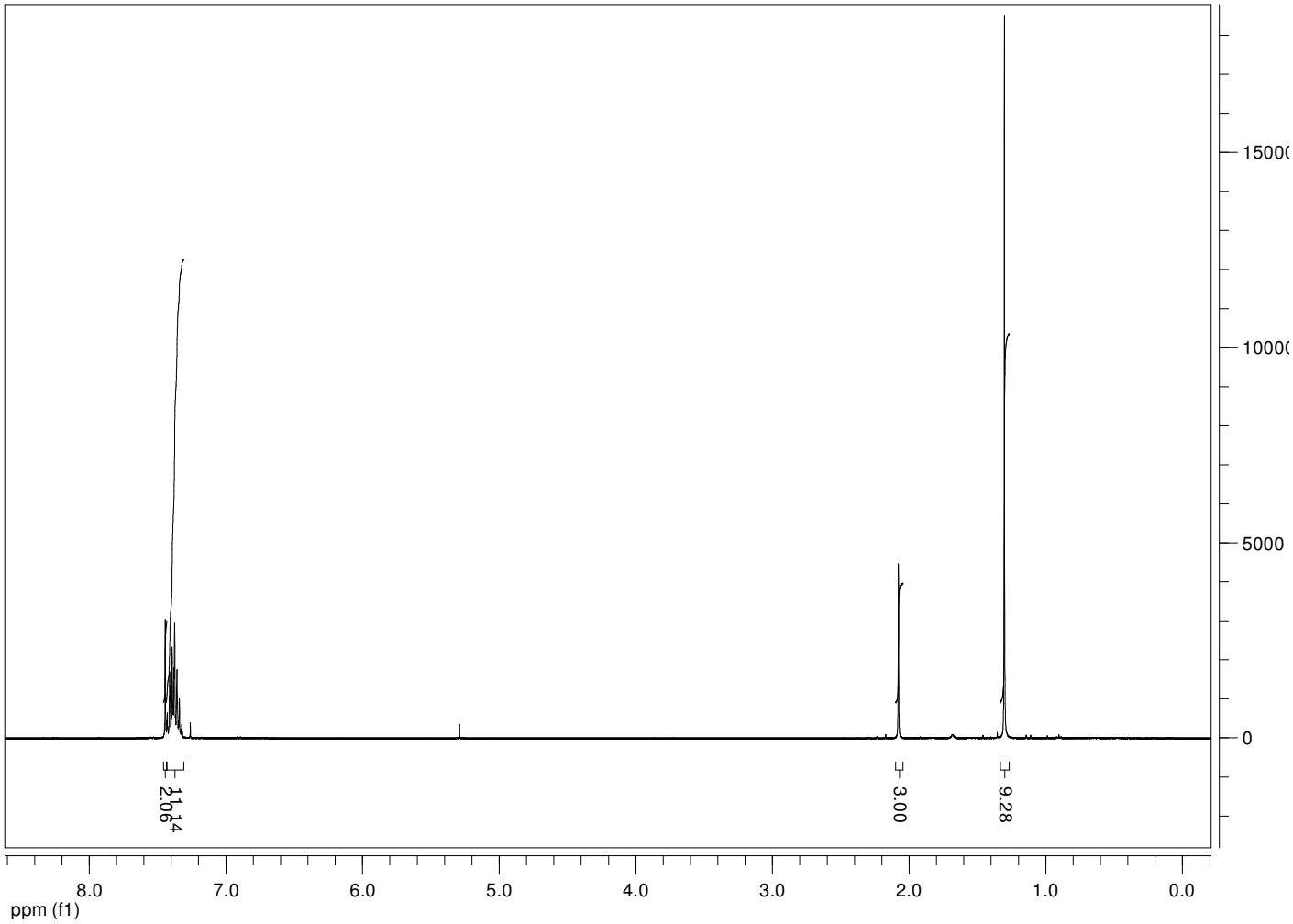


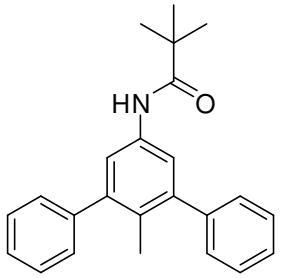


2,2-Dimethyl-N-[1,1';3',1'']terphenyl-5'-yl-propionamide (2q)

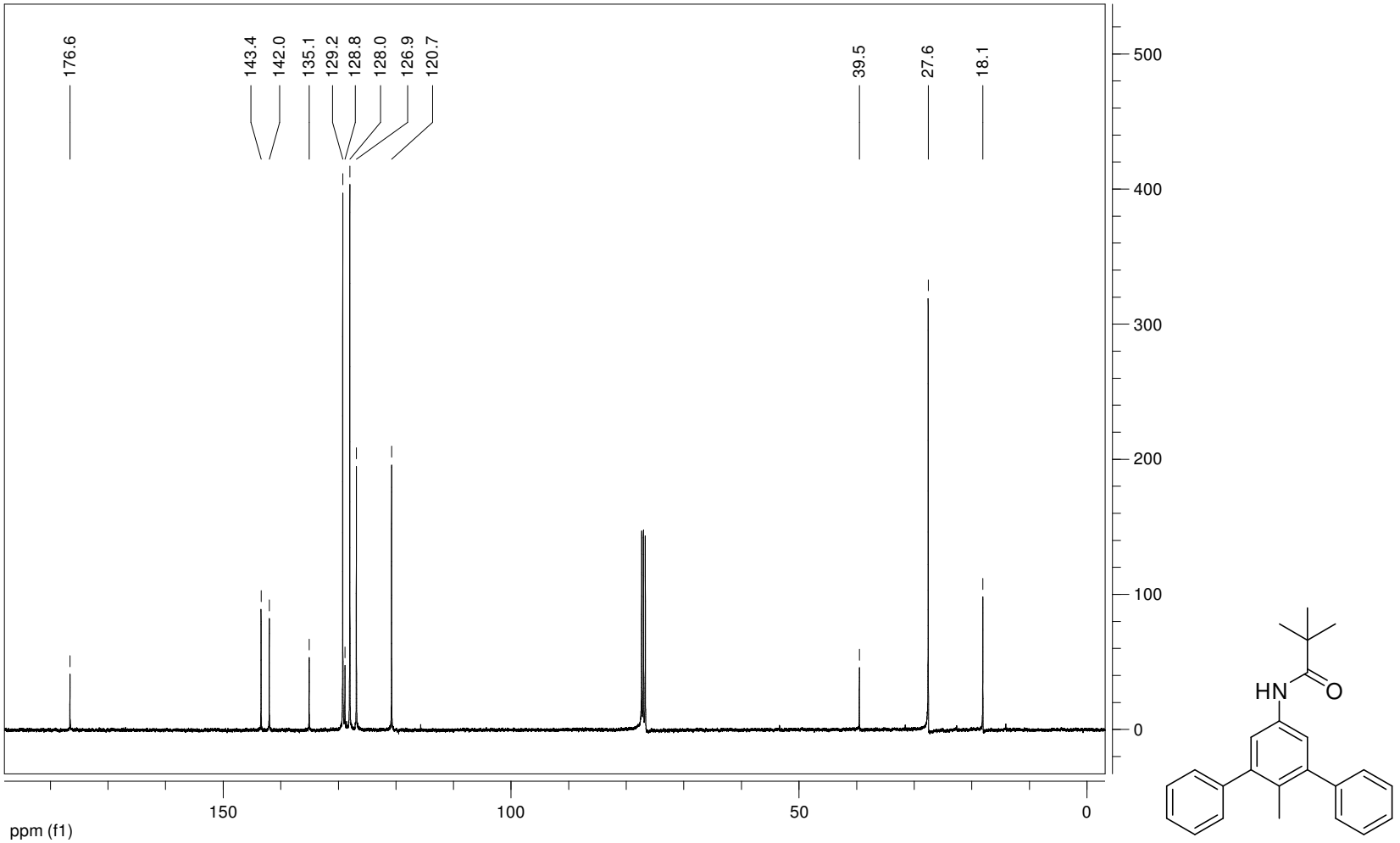


2,2-Dimethyl-N-(2'-methyl-[1,1';3',1'']terphenyl-5'-yl)-propionamide (2r)

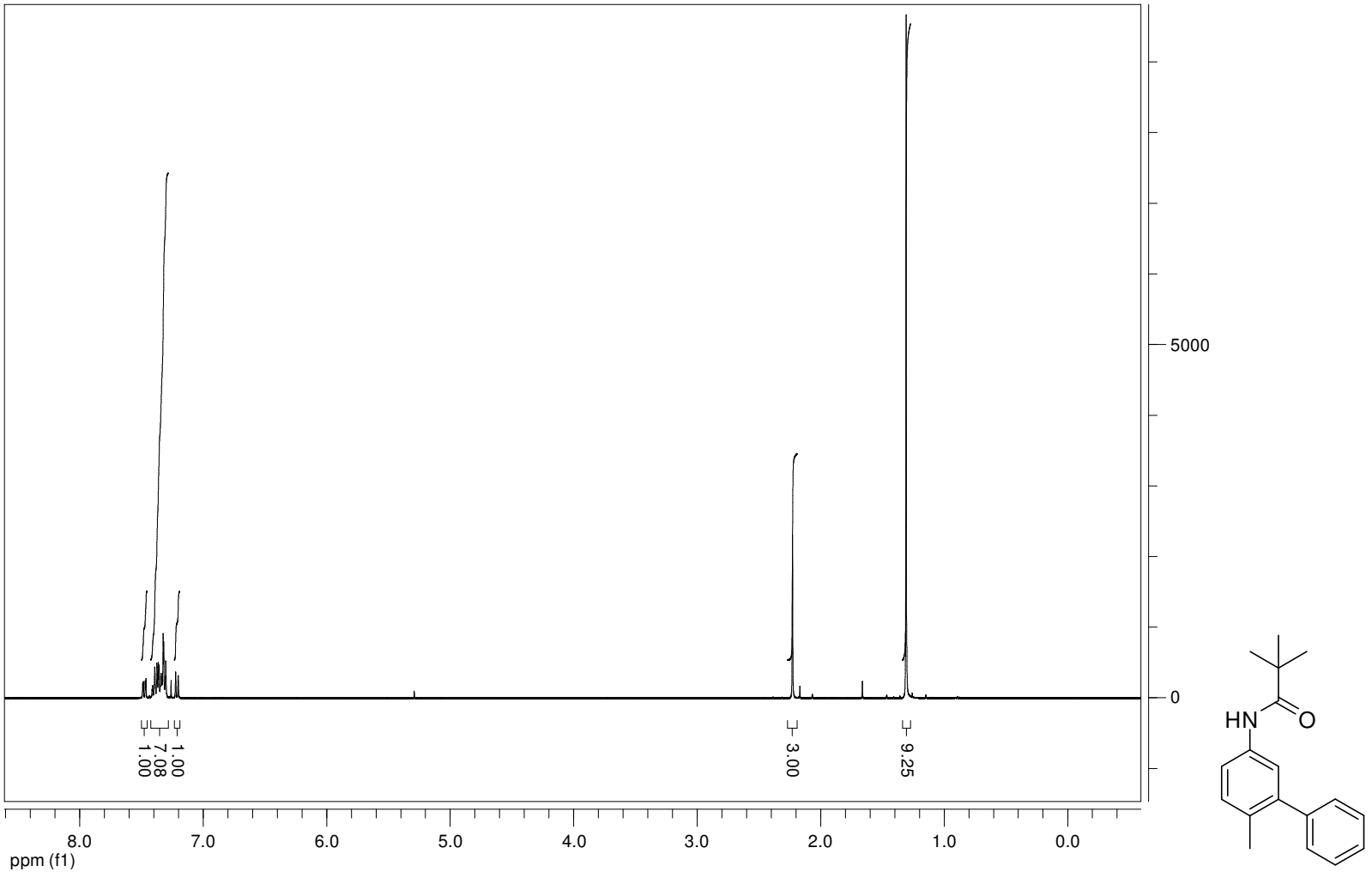




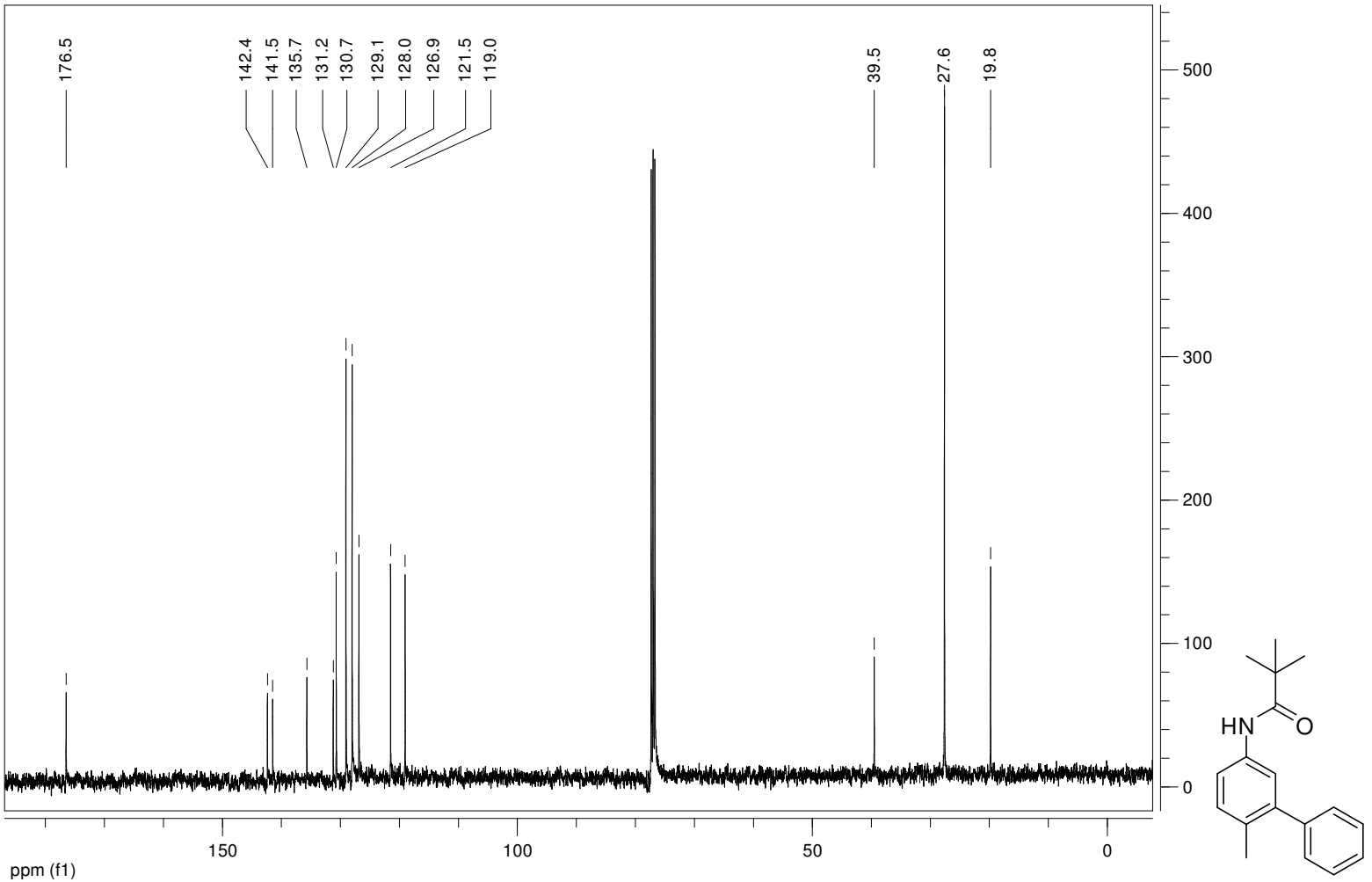
2,2-Dimethyl-N-(2'-methyl-[1,1';3',1'']terphenyl-5'-yl)-propionamide (2r)



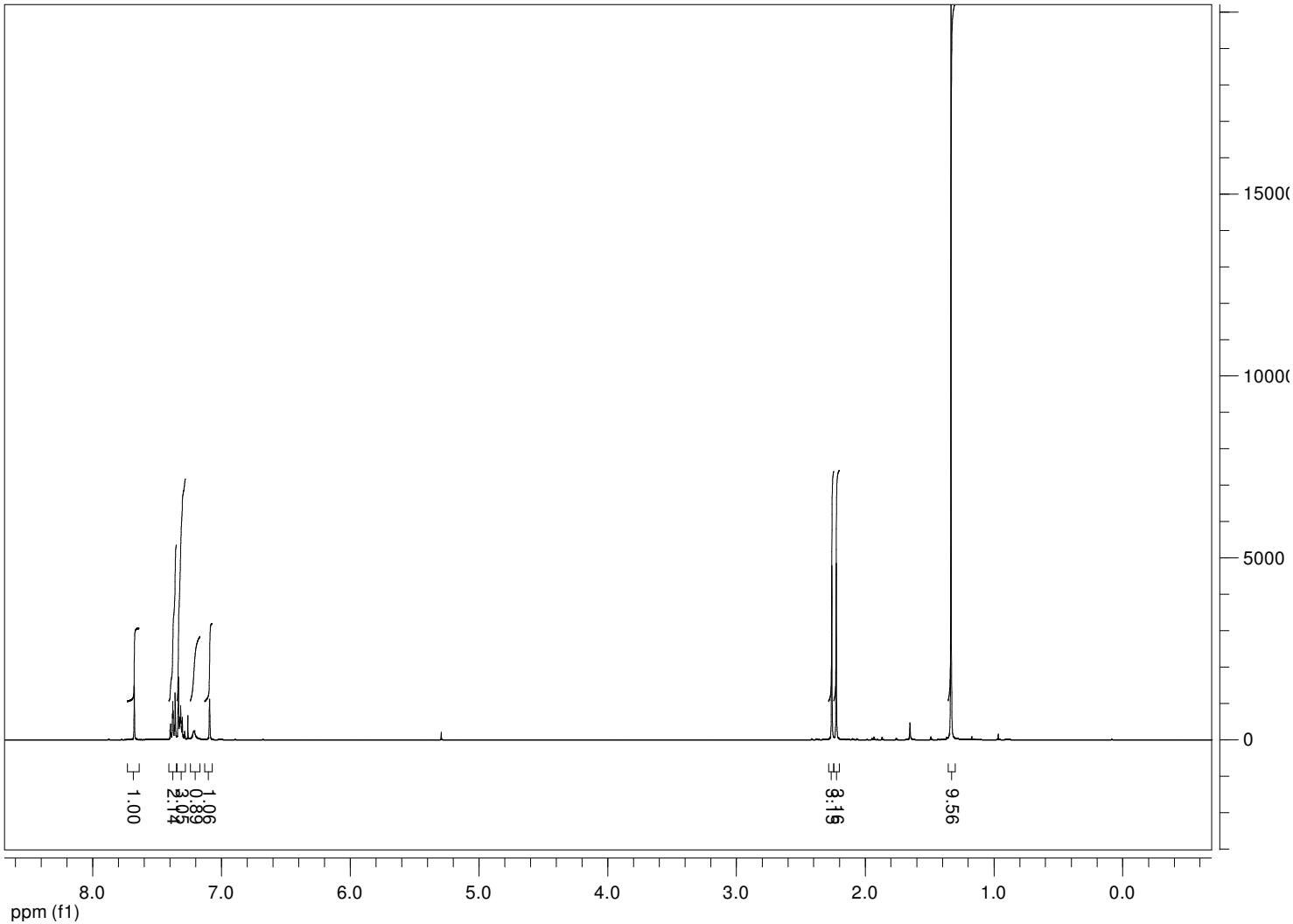
***N*-(6-methylbiphenyl-3-yl)pivalamide (2s)**



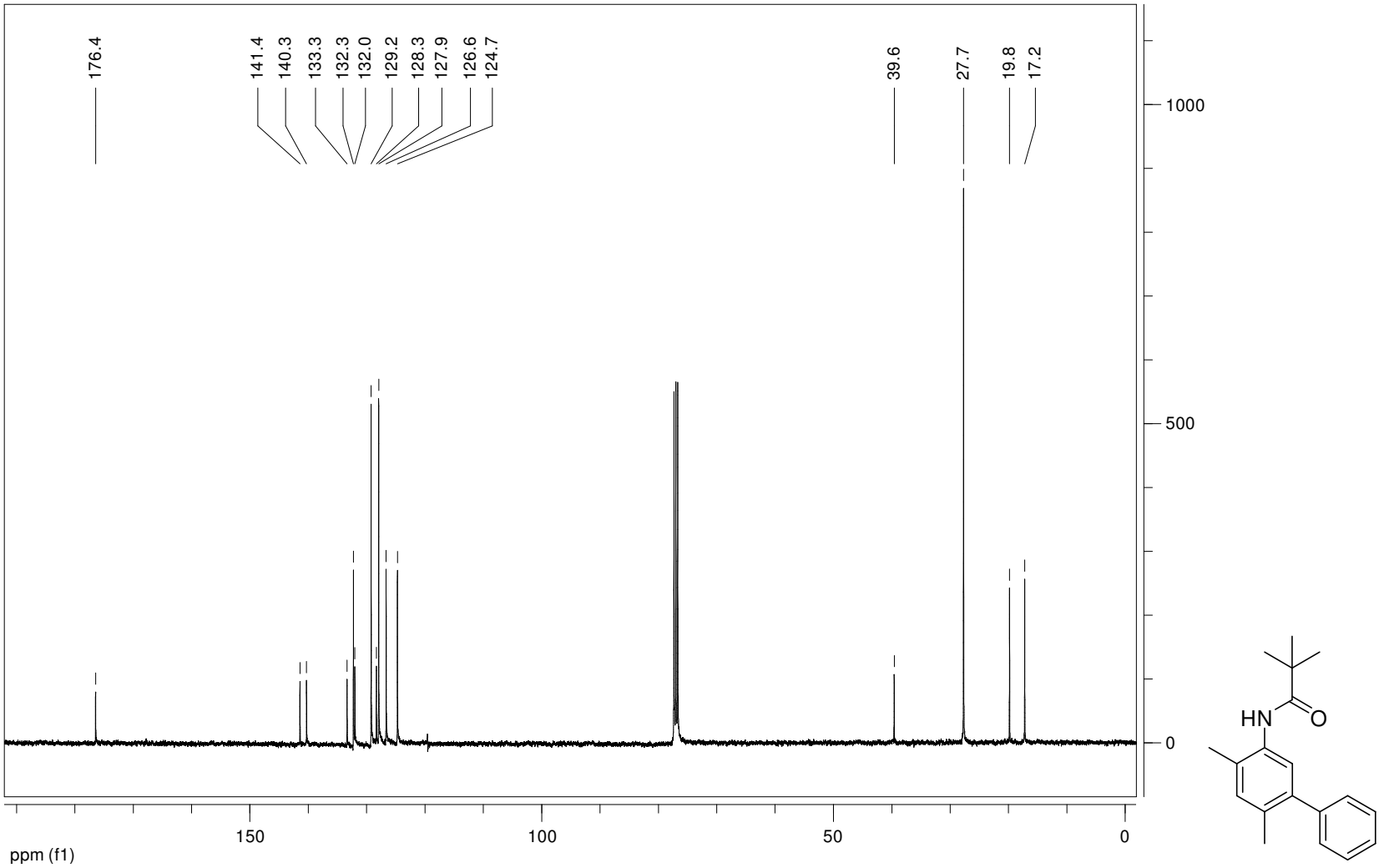
_N_-(6-methylbiphenyl-3-yl)pivalamide (2s)



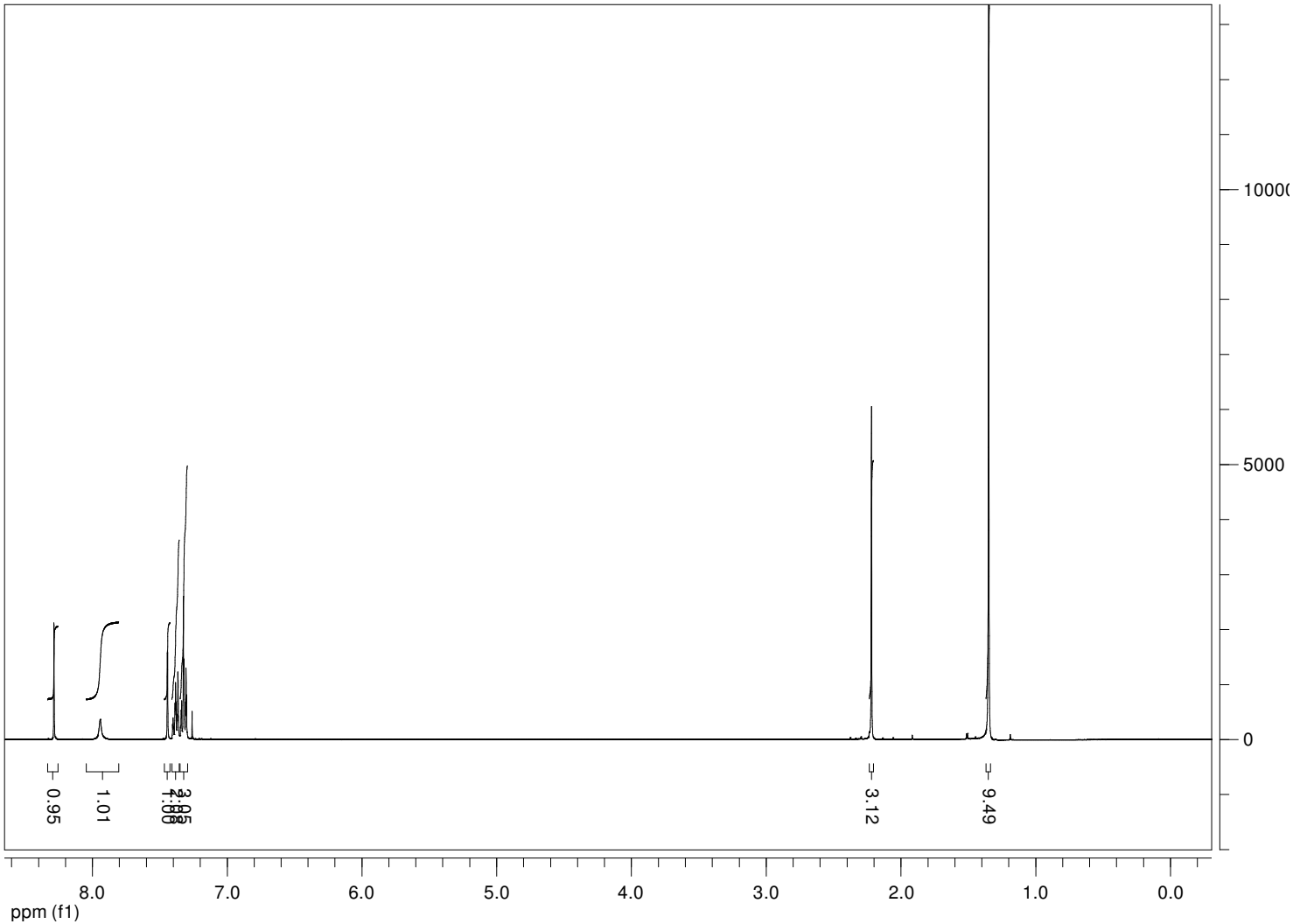
_N_-(4,6-dimethylbiphenyl-3-yl)pivalamide (2t)



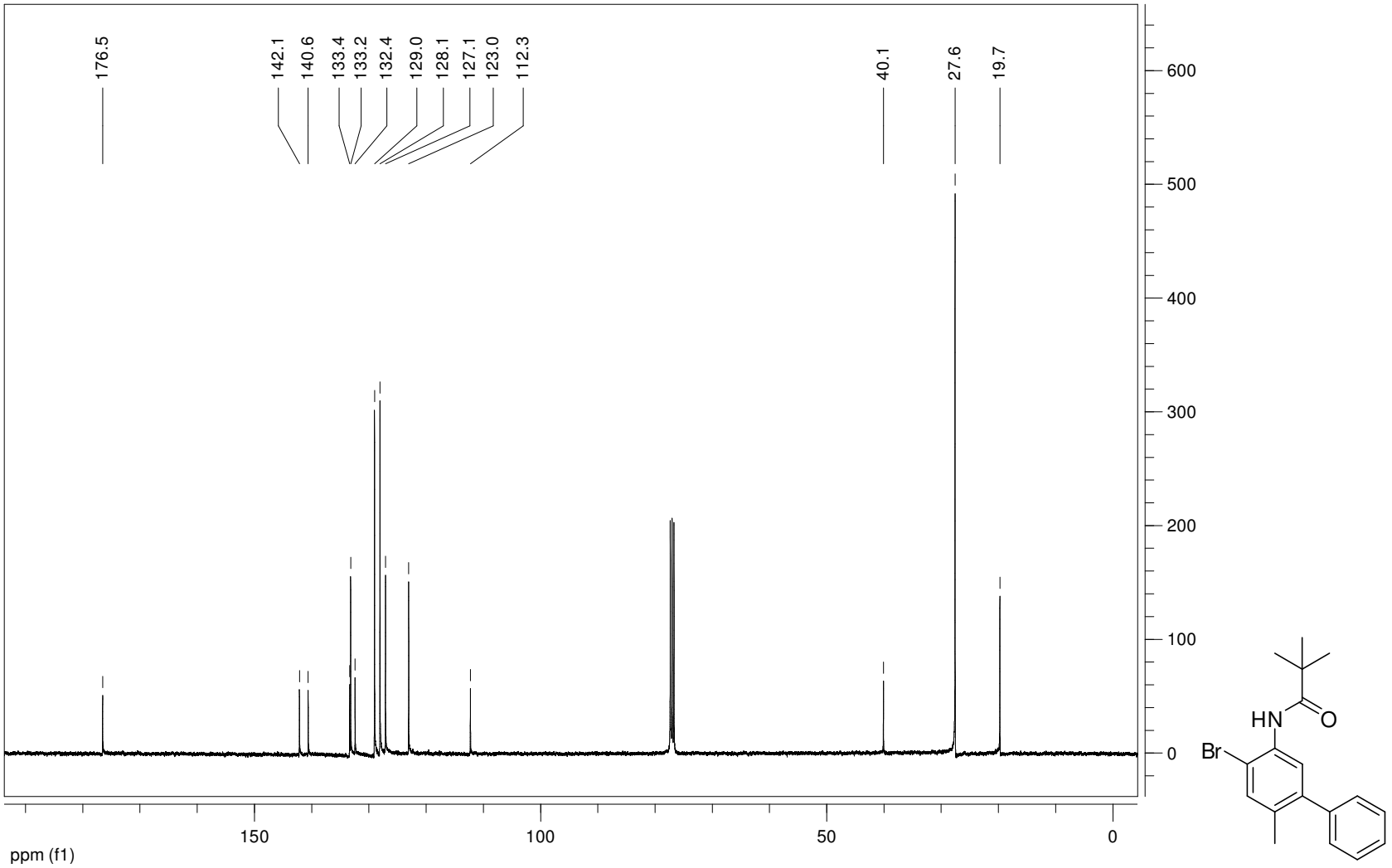
_N_-(4,6-dimethylbiphenyl-3-yl)pivalamide (2t)



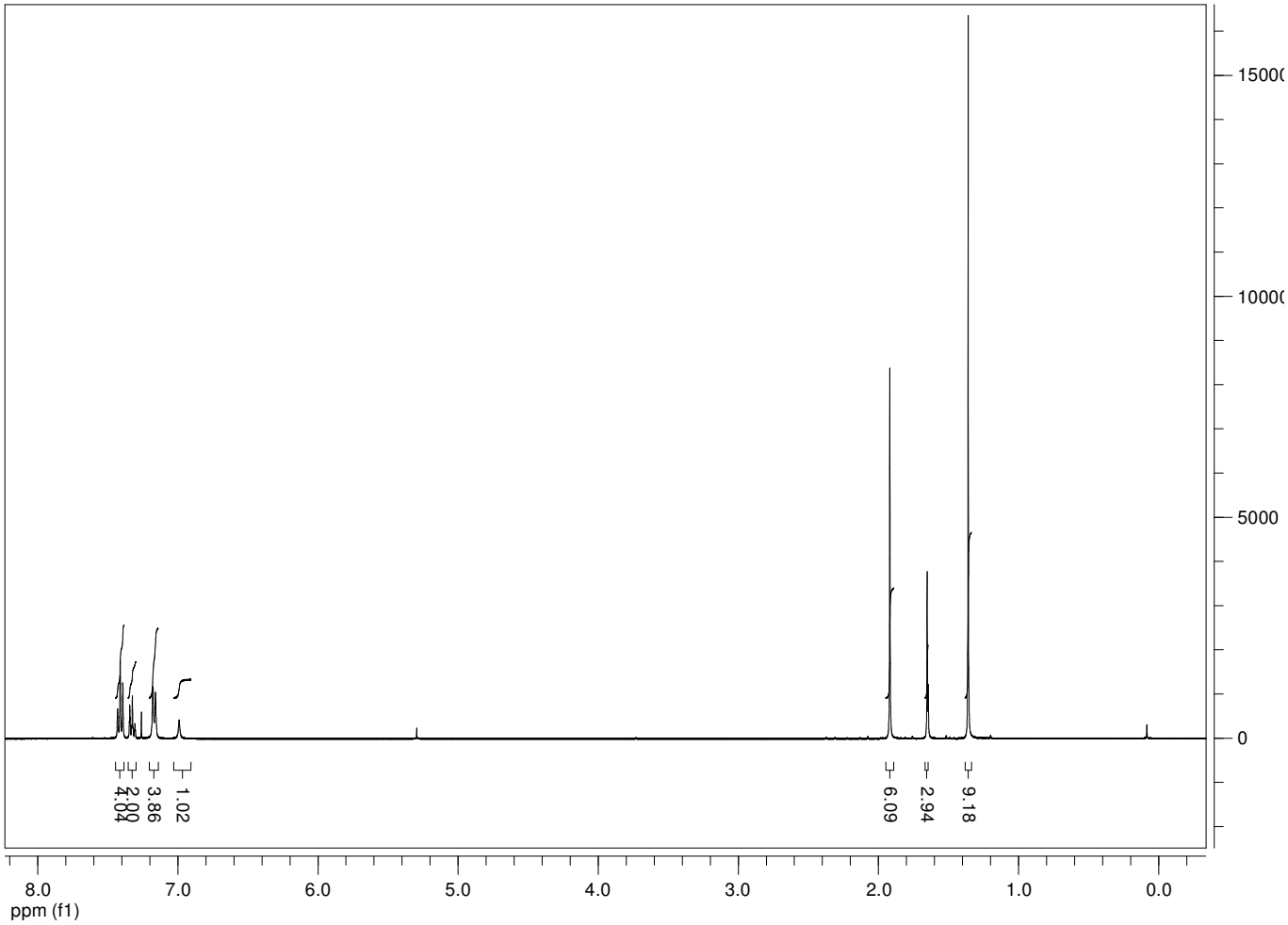
_N_-(4-bromo-6-methylbiphenyl-3-yl)pivalamide (2u)

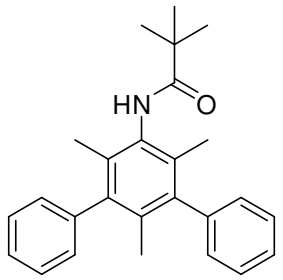


_N_-(4-bromo-6-methylbiphenyl-3-yl)pivalamide (2u)

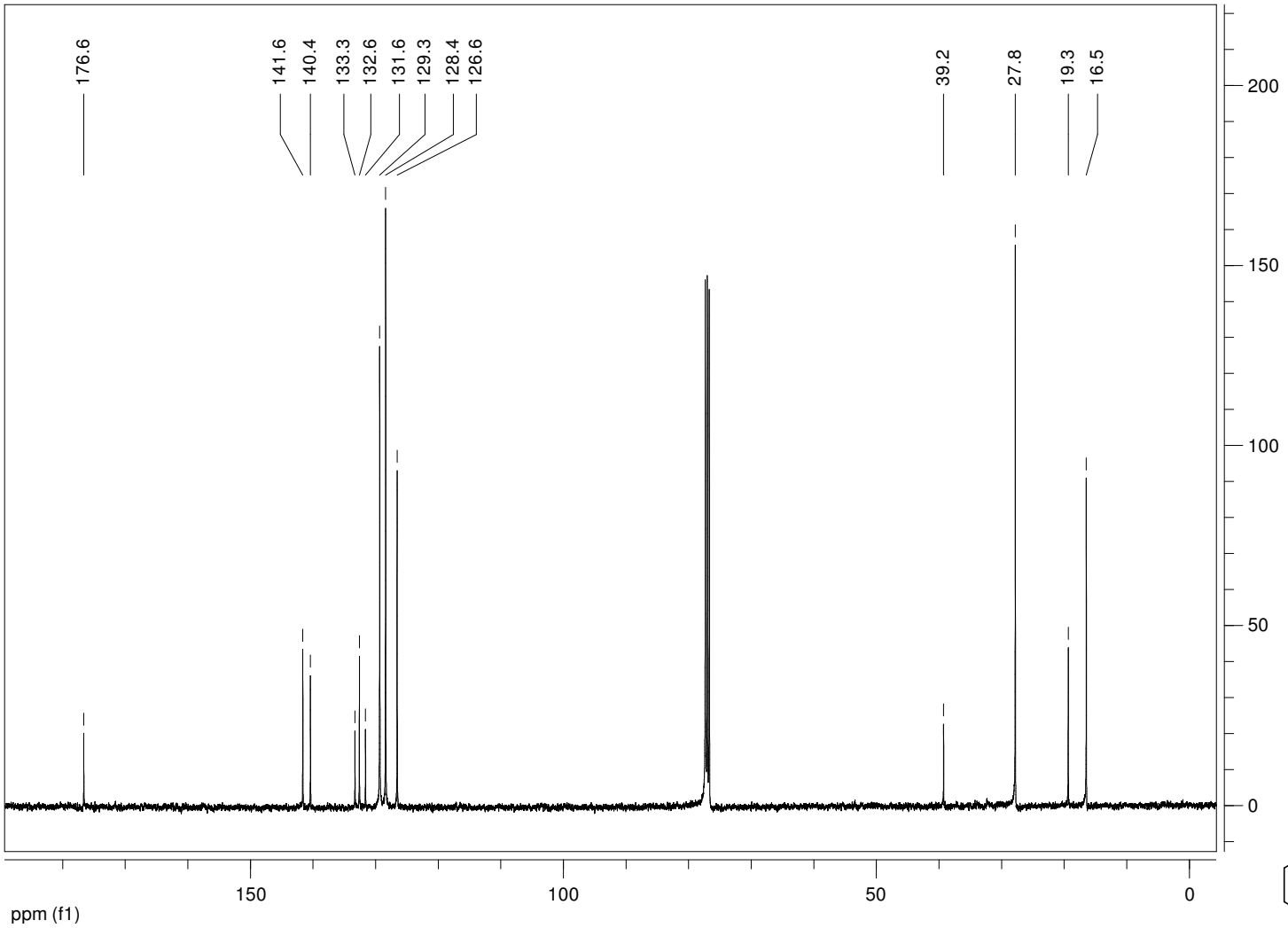


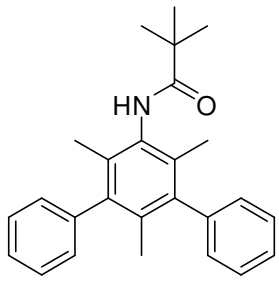
***N*-(6-2,2-Dimethyl-N-(2',4',6'-trimethyl-[1,1';3',1'']terphenyl-5'-yl)-propionamide (2v)**



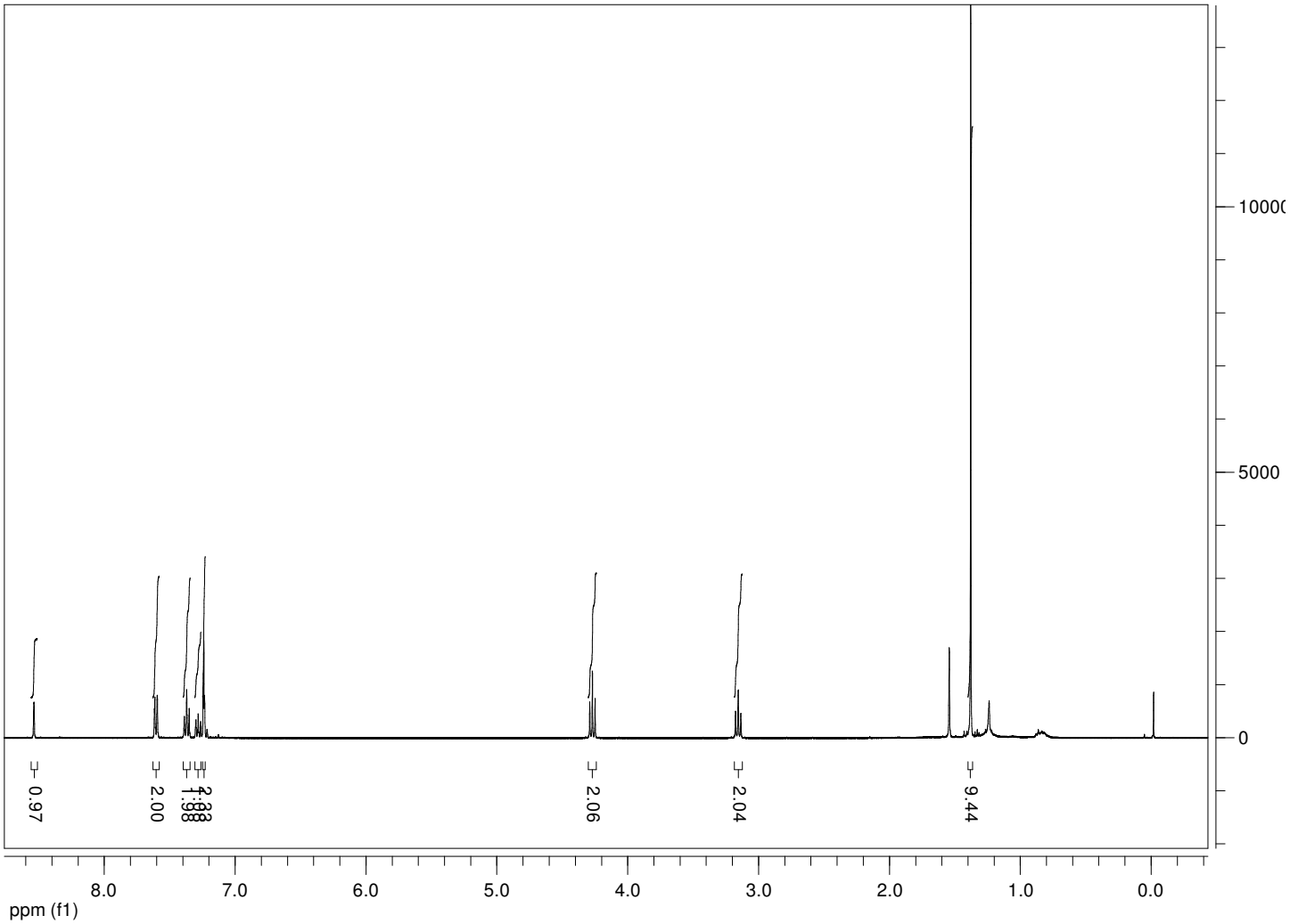


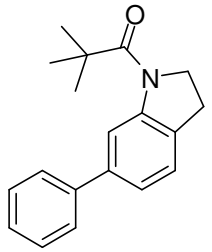
2,2-Dimethyl-N-(2',4',6'-trimethyl-[1,1';3',1'']terphenyl-5'-yl)-propionamide (2v)



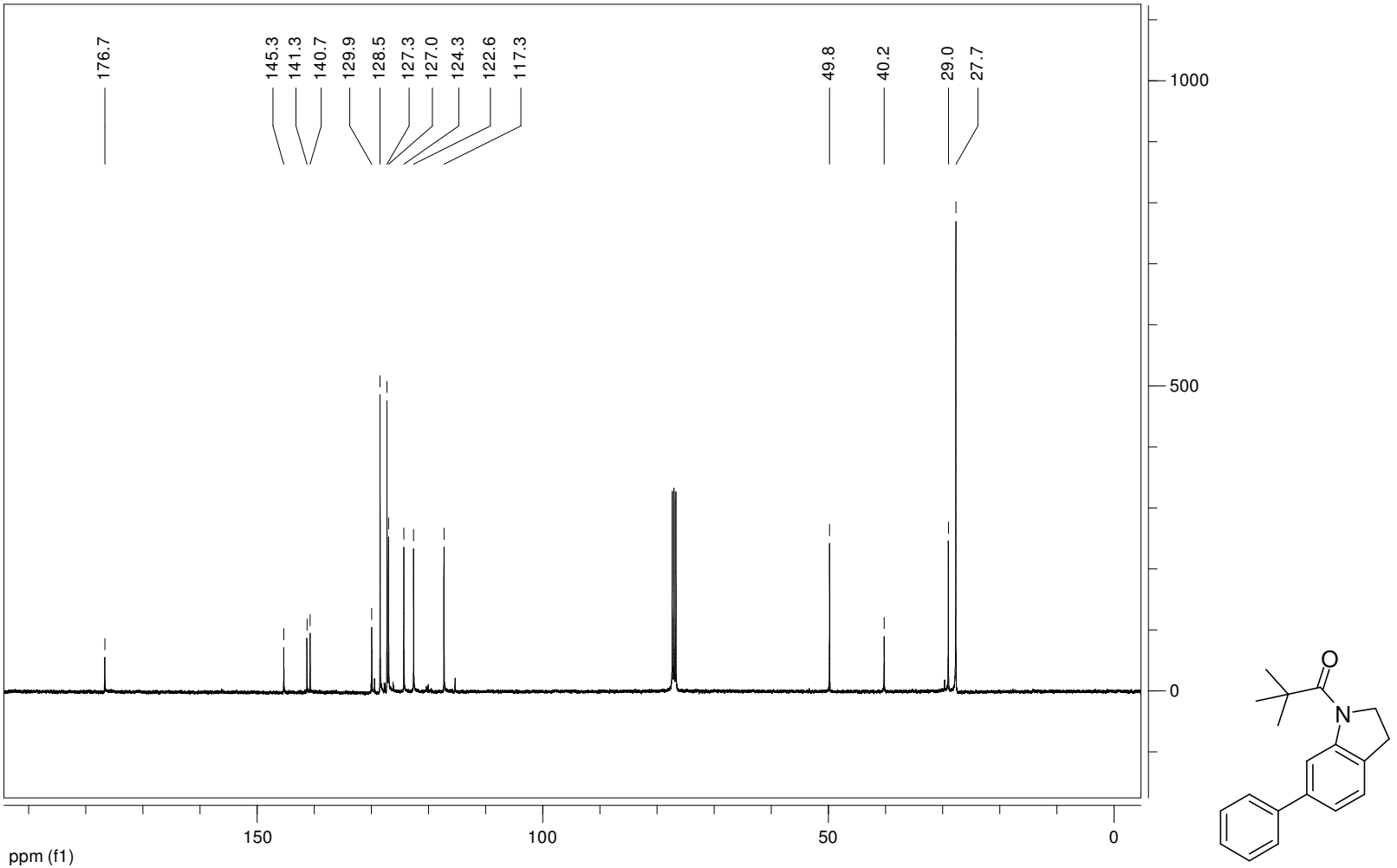


2,2-Dimethyl-1-(6-phenylindolin-1-yl)propan-1-one (2w)

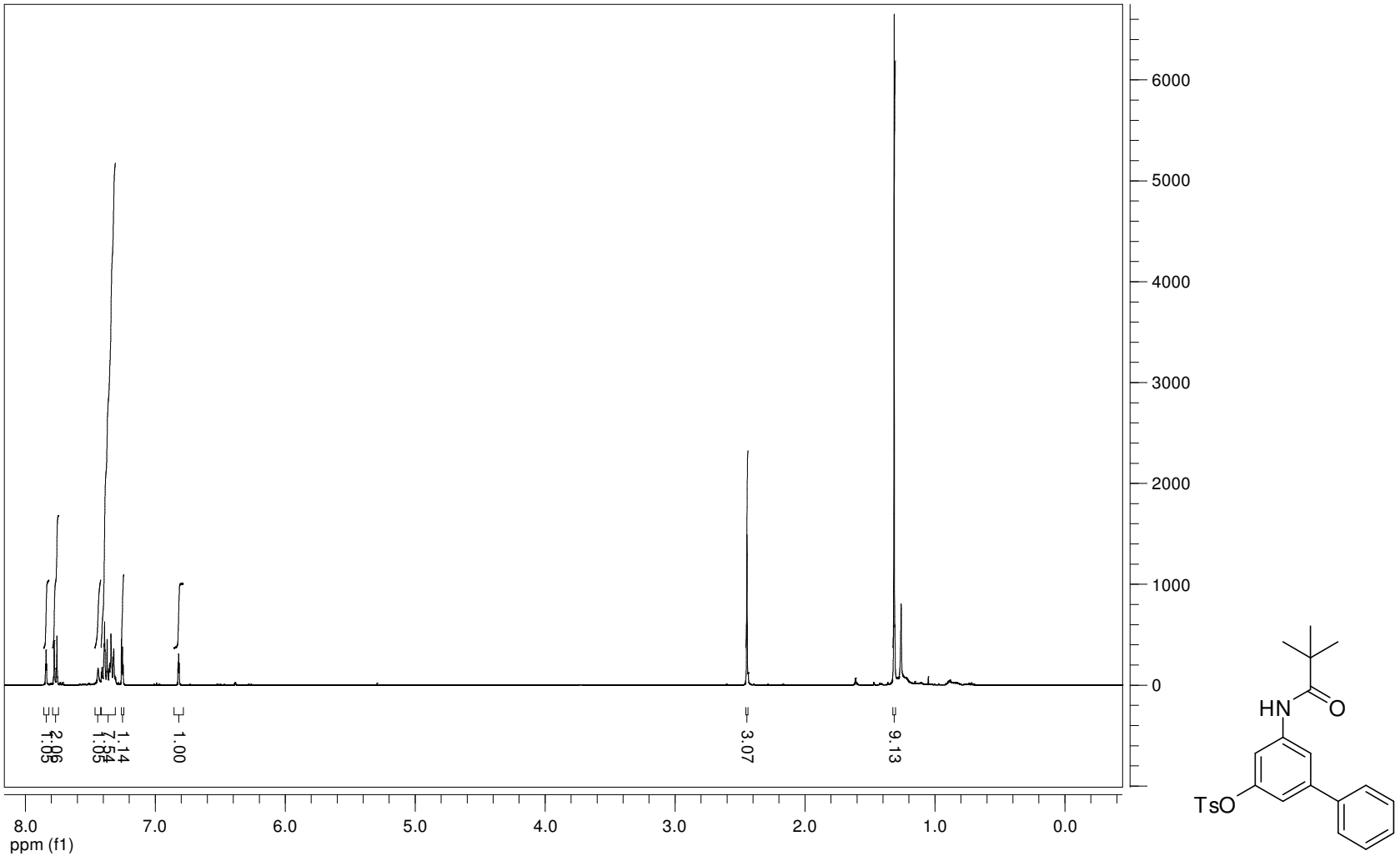




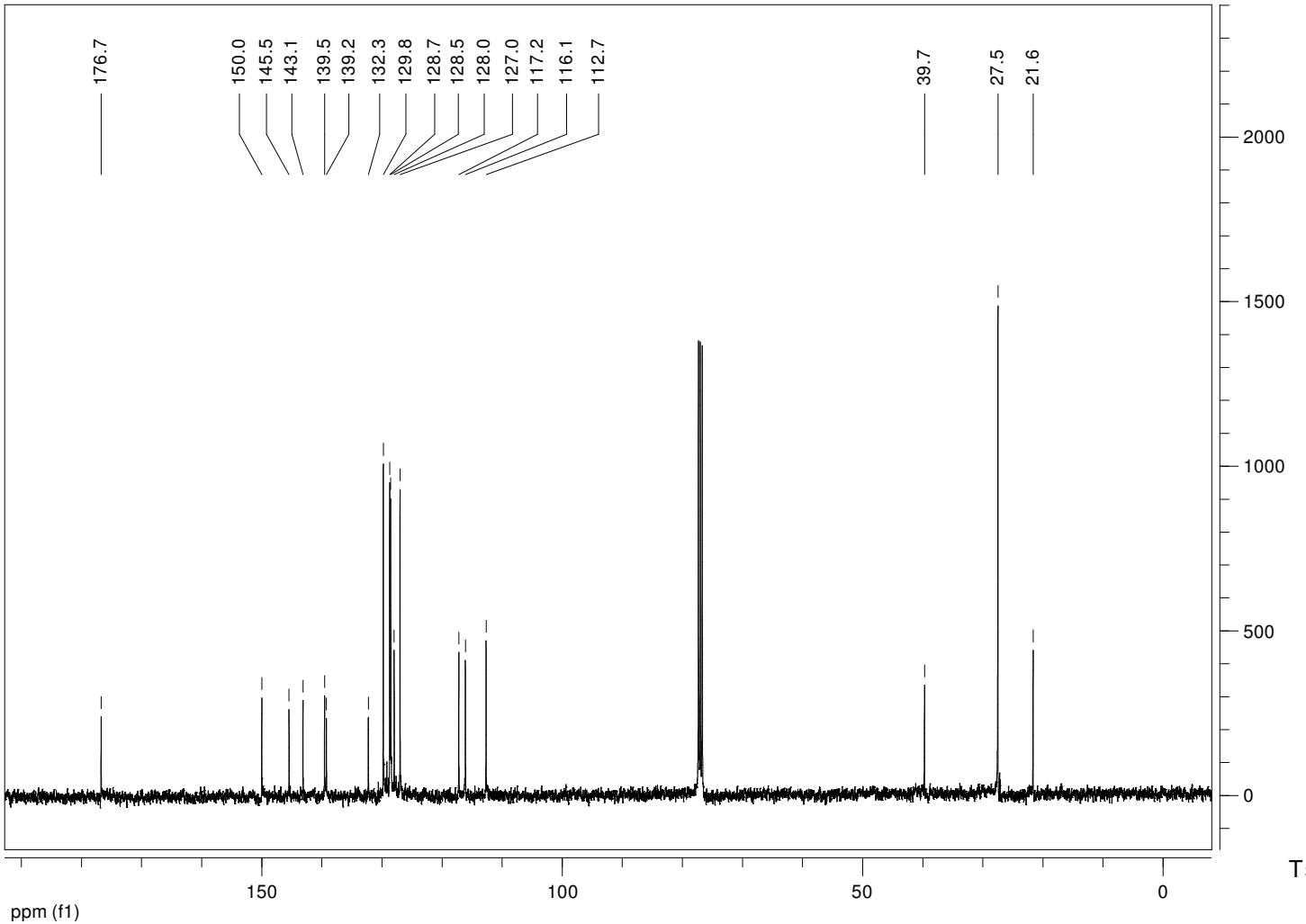
2,2-Dimethyl-1-(6-phenylindolin-1-yl)propan-1-one (2w)

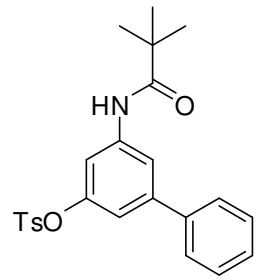


5-Pivalamidobiphenyl-3-yl 4-methylbenzenesulfonate (2x)

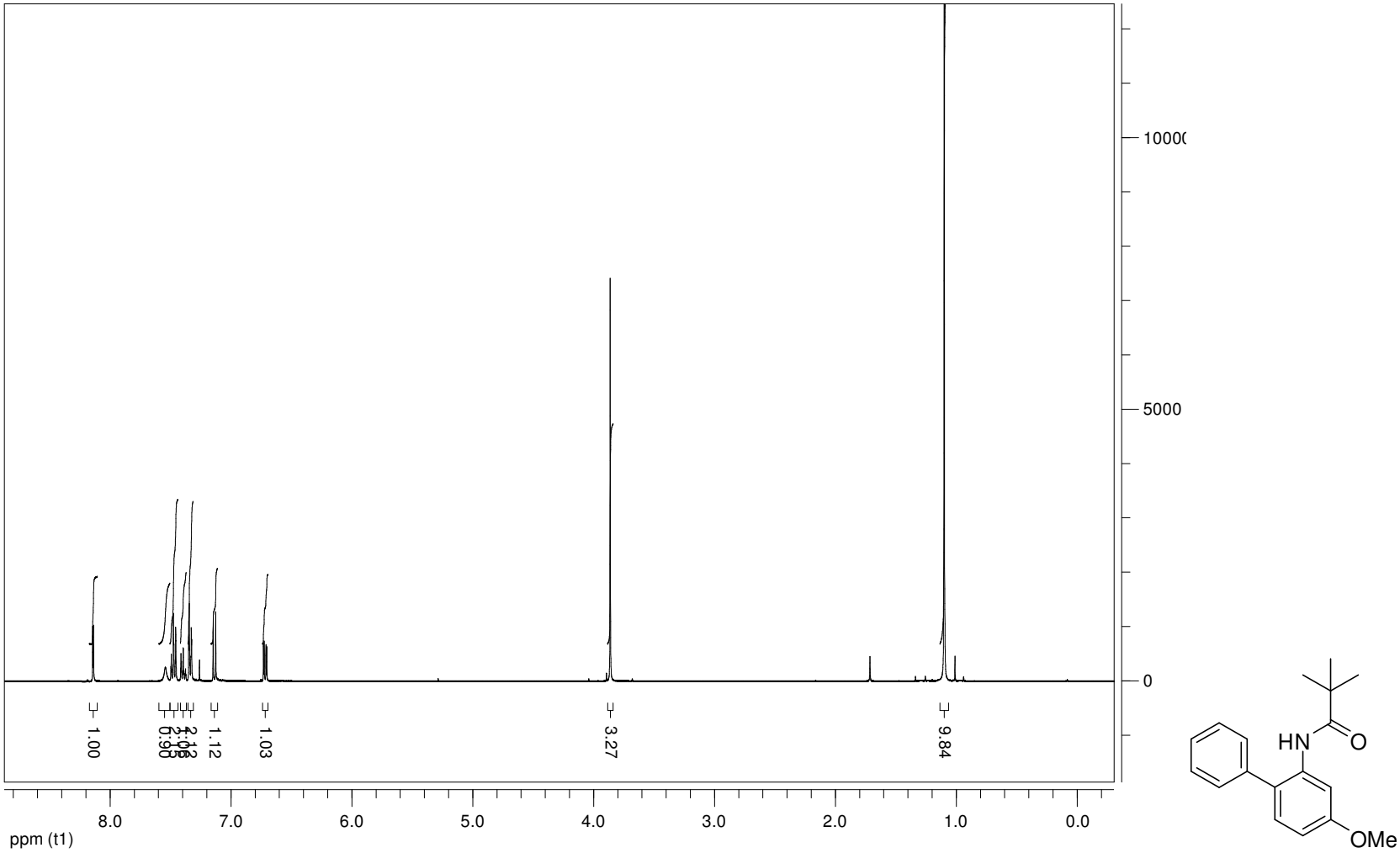


5-Pivalamidobiphenyl-3-yl 4-methylbenzenesulfonate (2x)

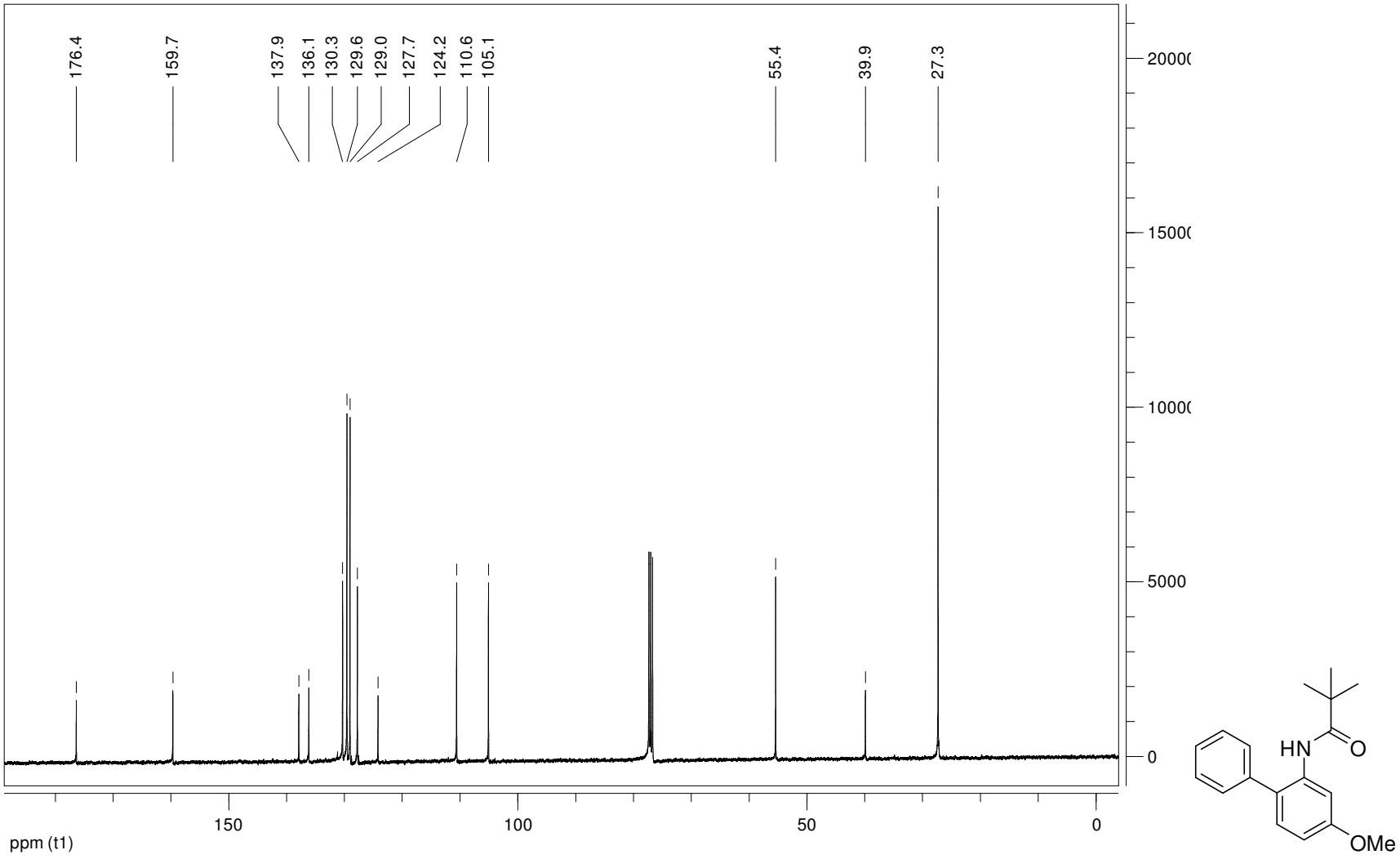




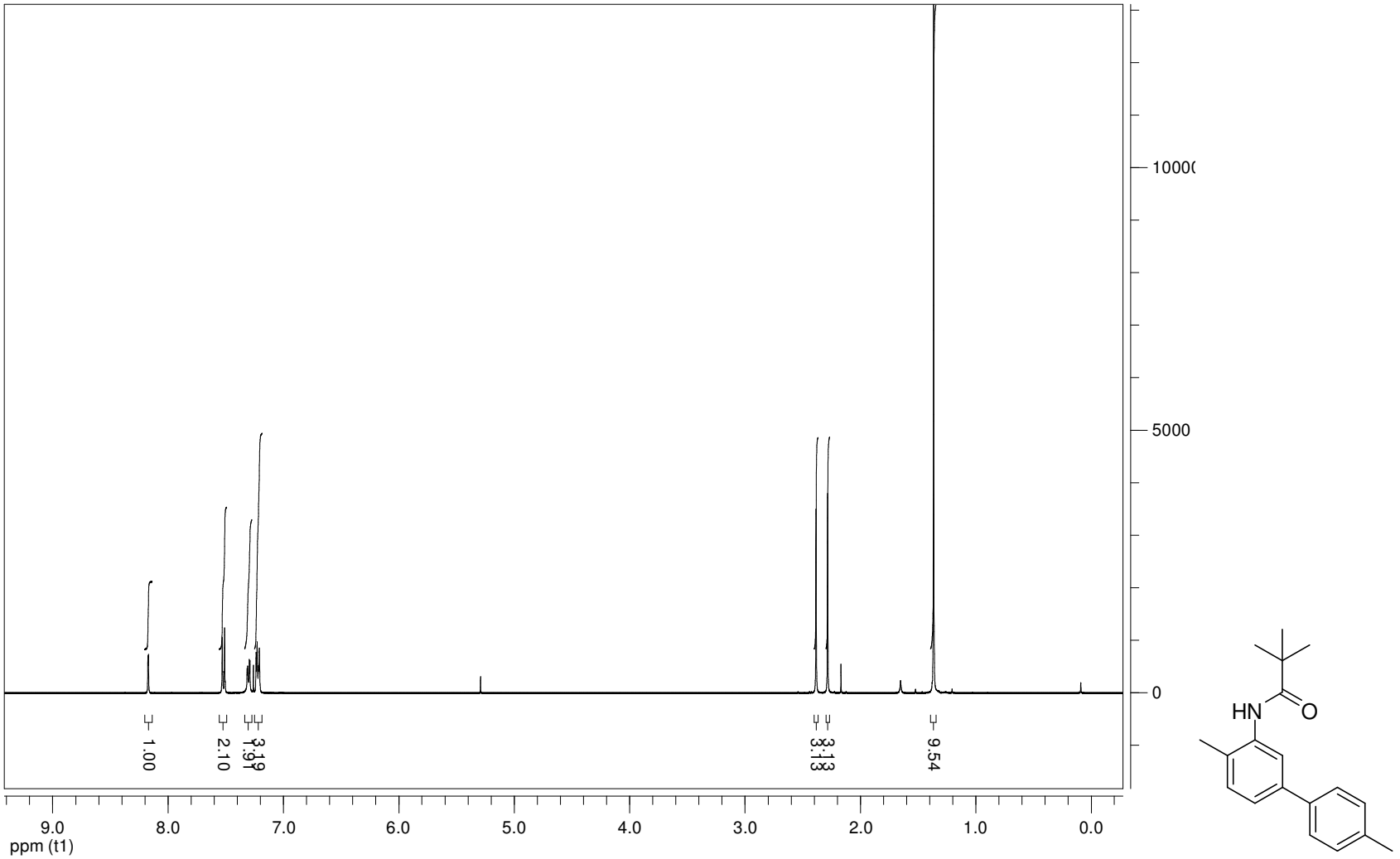
_N_-(4-methoxybiphenyl-2-yl)pivalamide (2y)



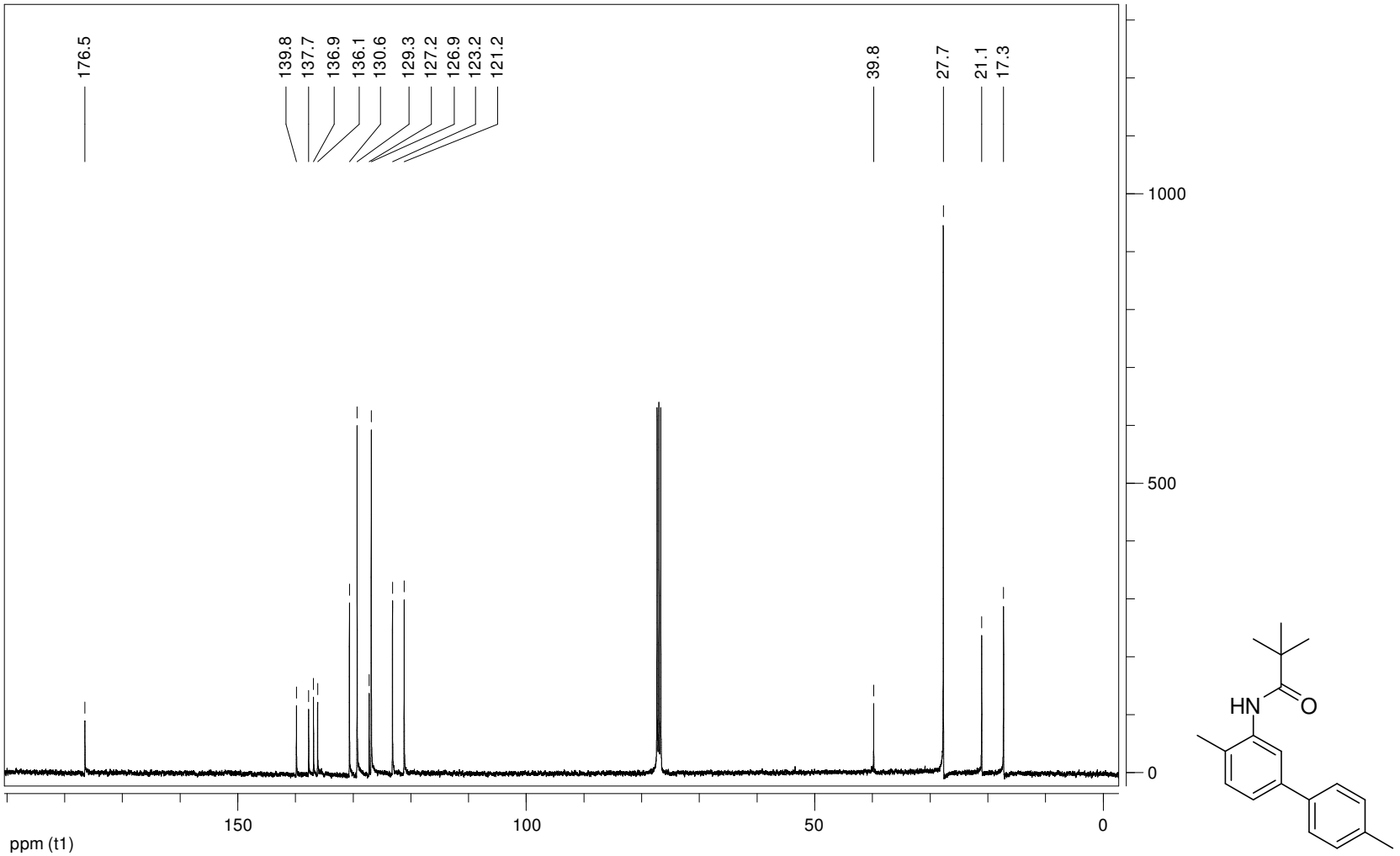
***N*-(4-methoxybiphenyl-2-yl)pivalamide (2y)**



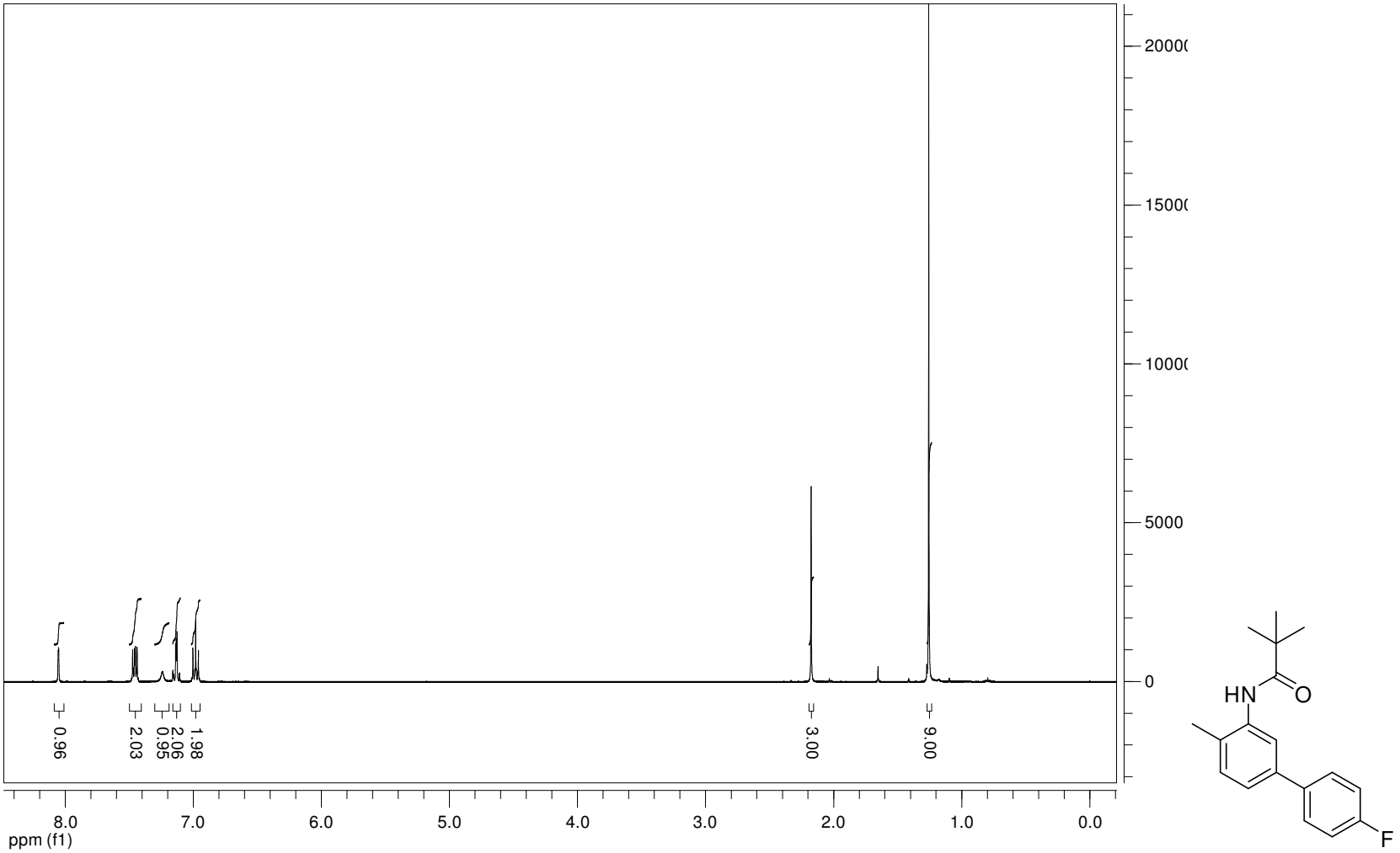
_N_-(4',4-dimethylbiphenyl-3-yl)pivalamide (3a)



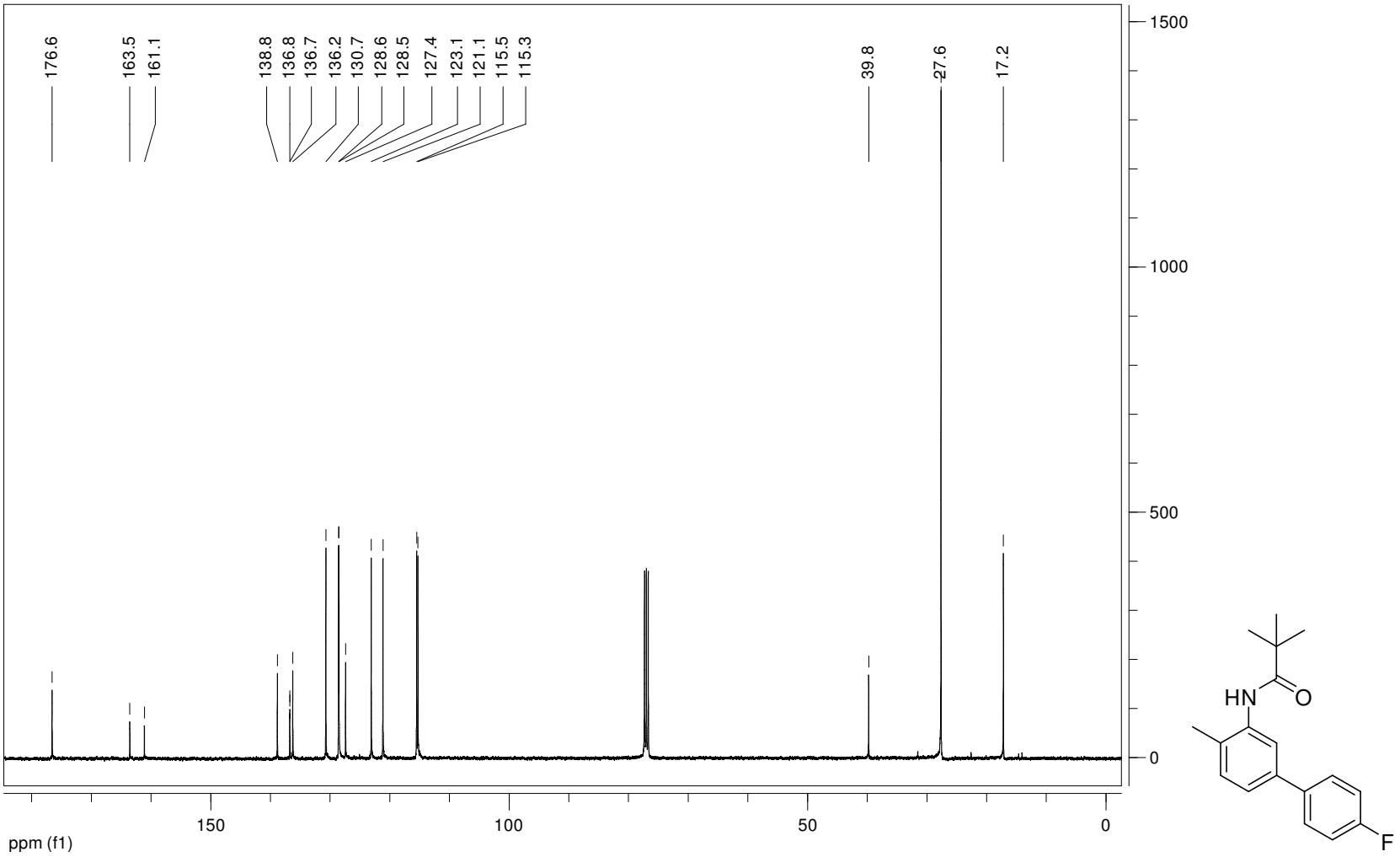
_N_-(4',4-dimethylbiphenyl-3-yl)pivalamide (3a)



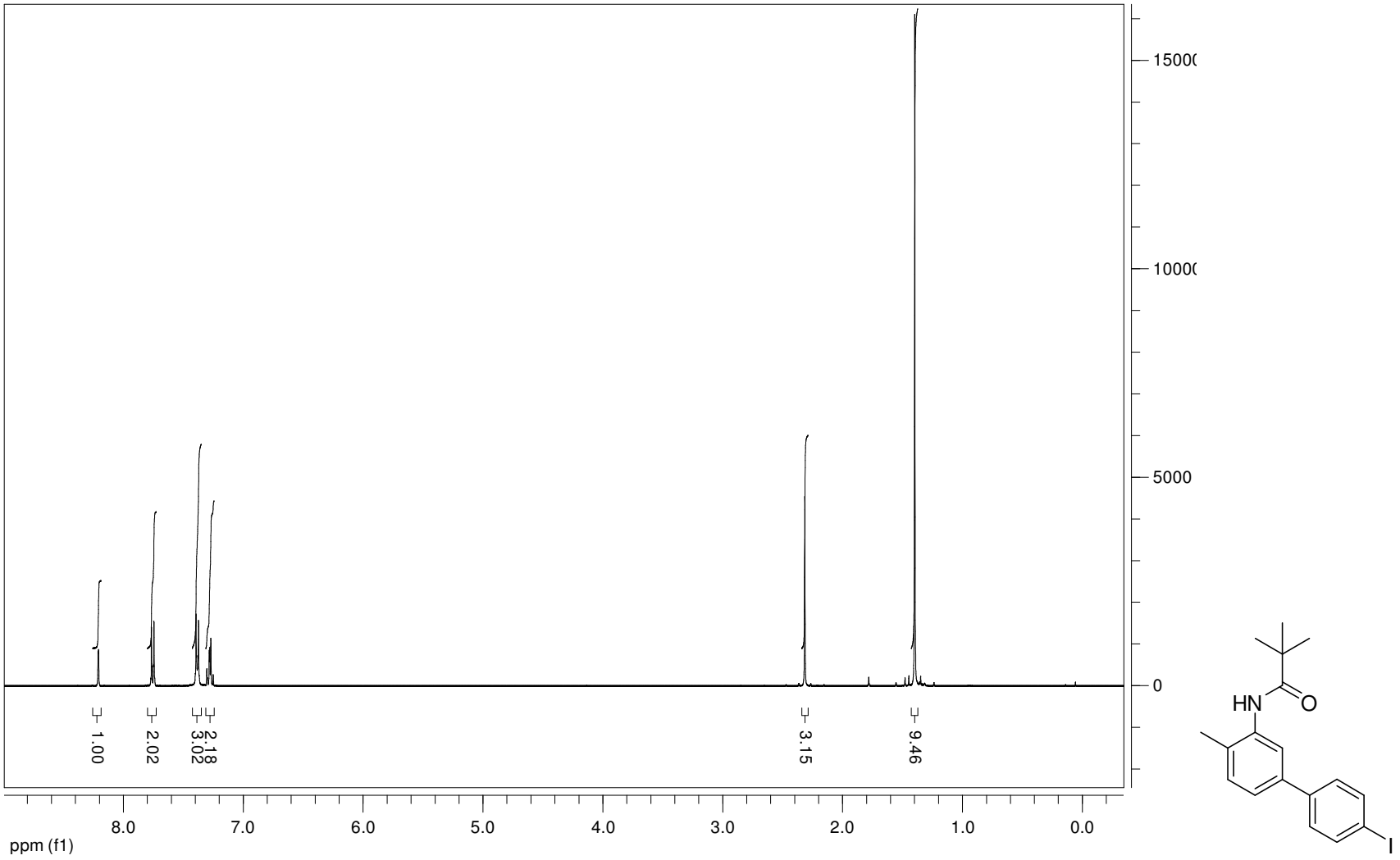
_N_-(4'-fluoro-4-methylbiphenyl-3-yl)pivalamide (3b)



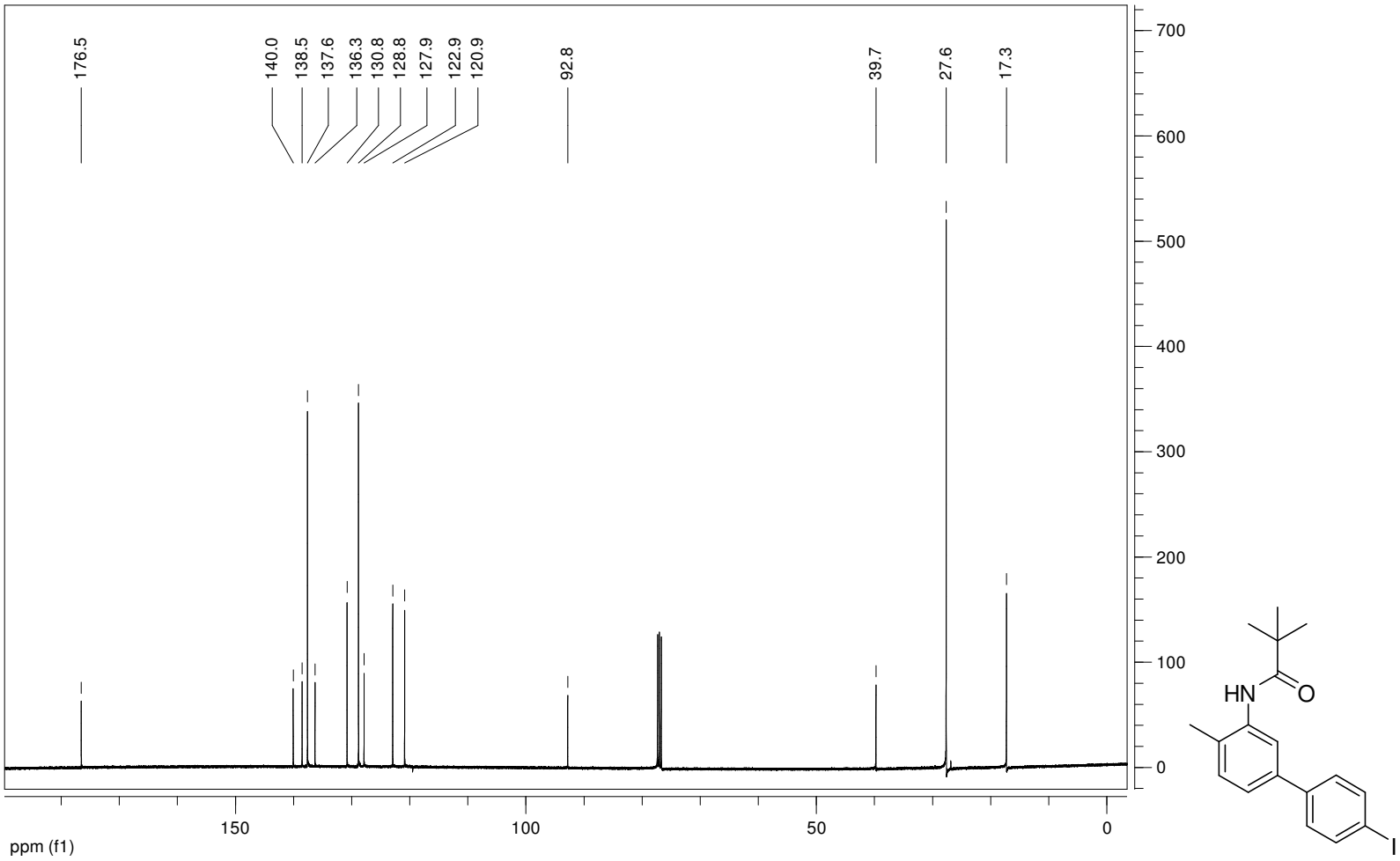
_N_-(4'-fluoro-4-methylbiphenyl-3-yl)pivalamide (3b)



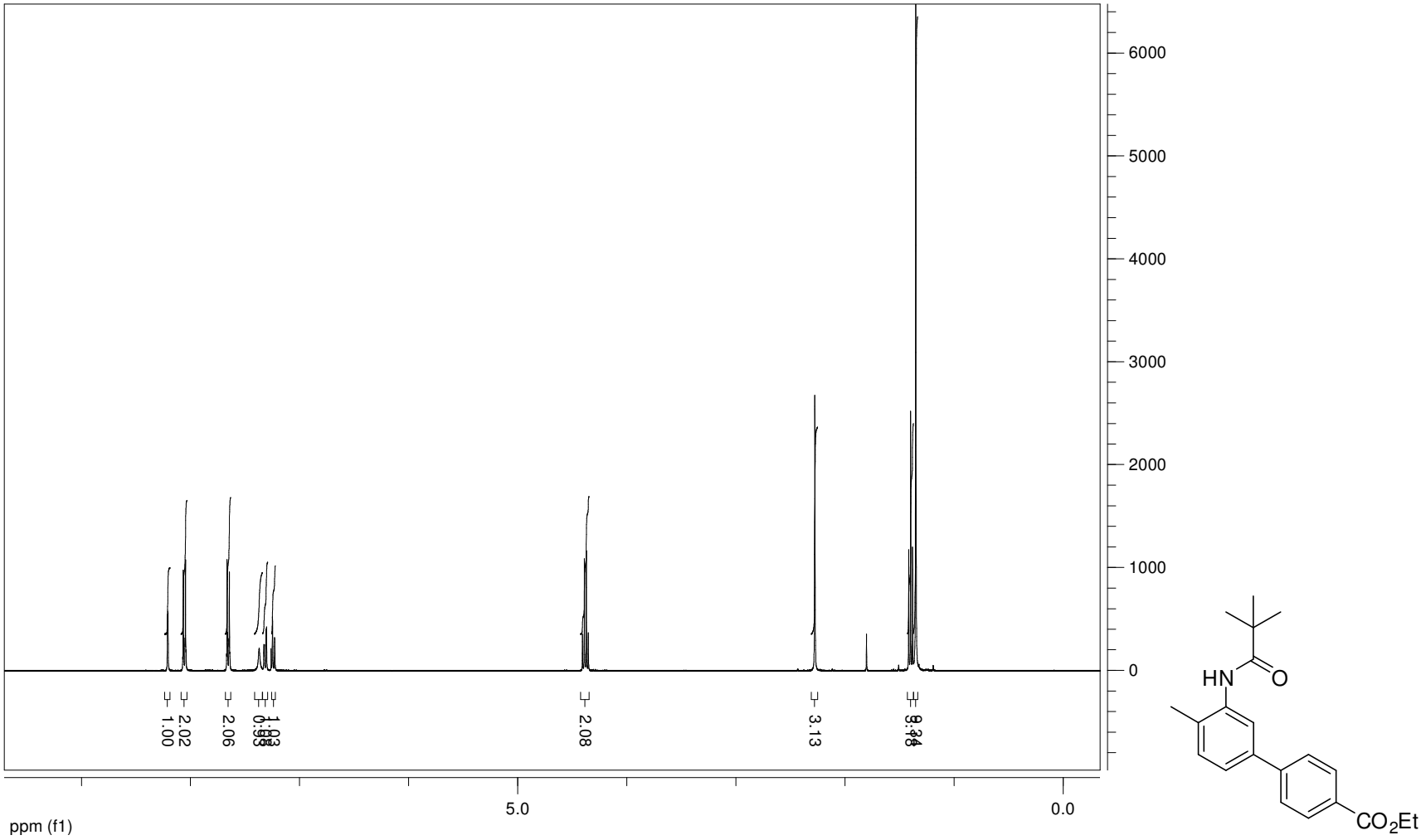
***N*-(4'-iodo-4-methylbiphenyl-3-yl)pivalamide (3c)**



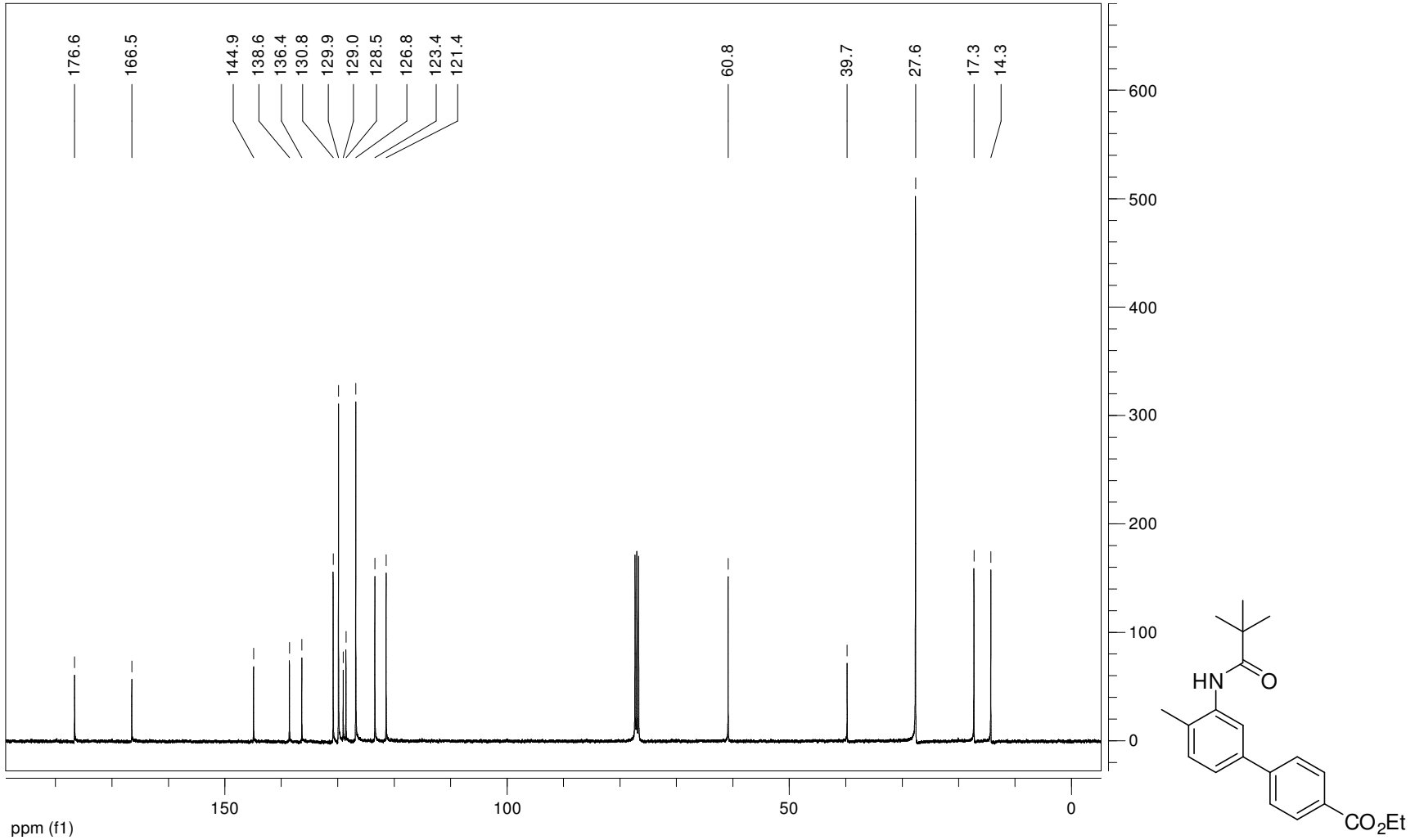
***N*-(4'-iodo-4-methylbiphenyl-3-yl)pivalamide (3c)**



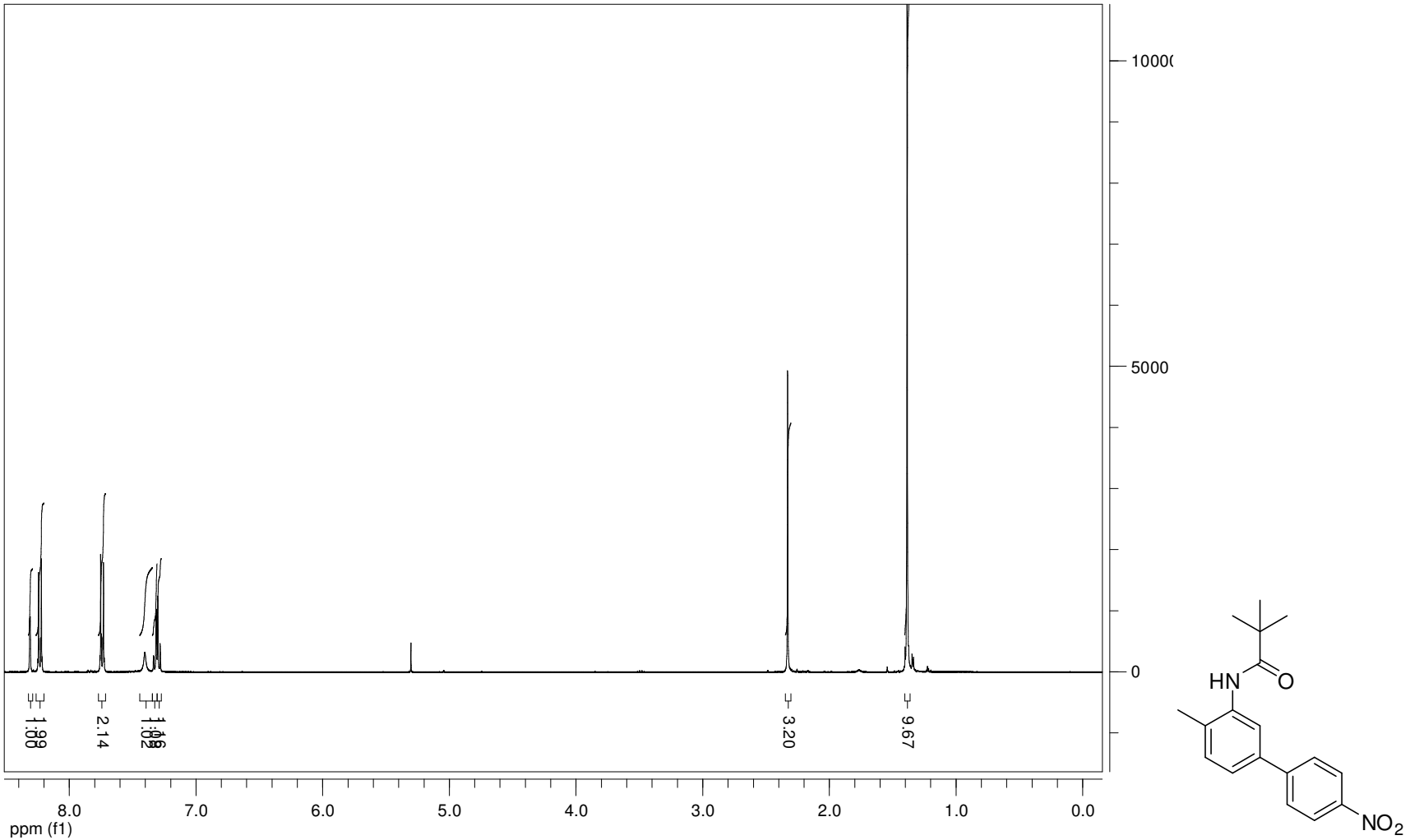
Ethyl 4'-methyl-3'-pivalamidobiphenyl-4-carboxylate (3d)



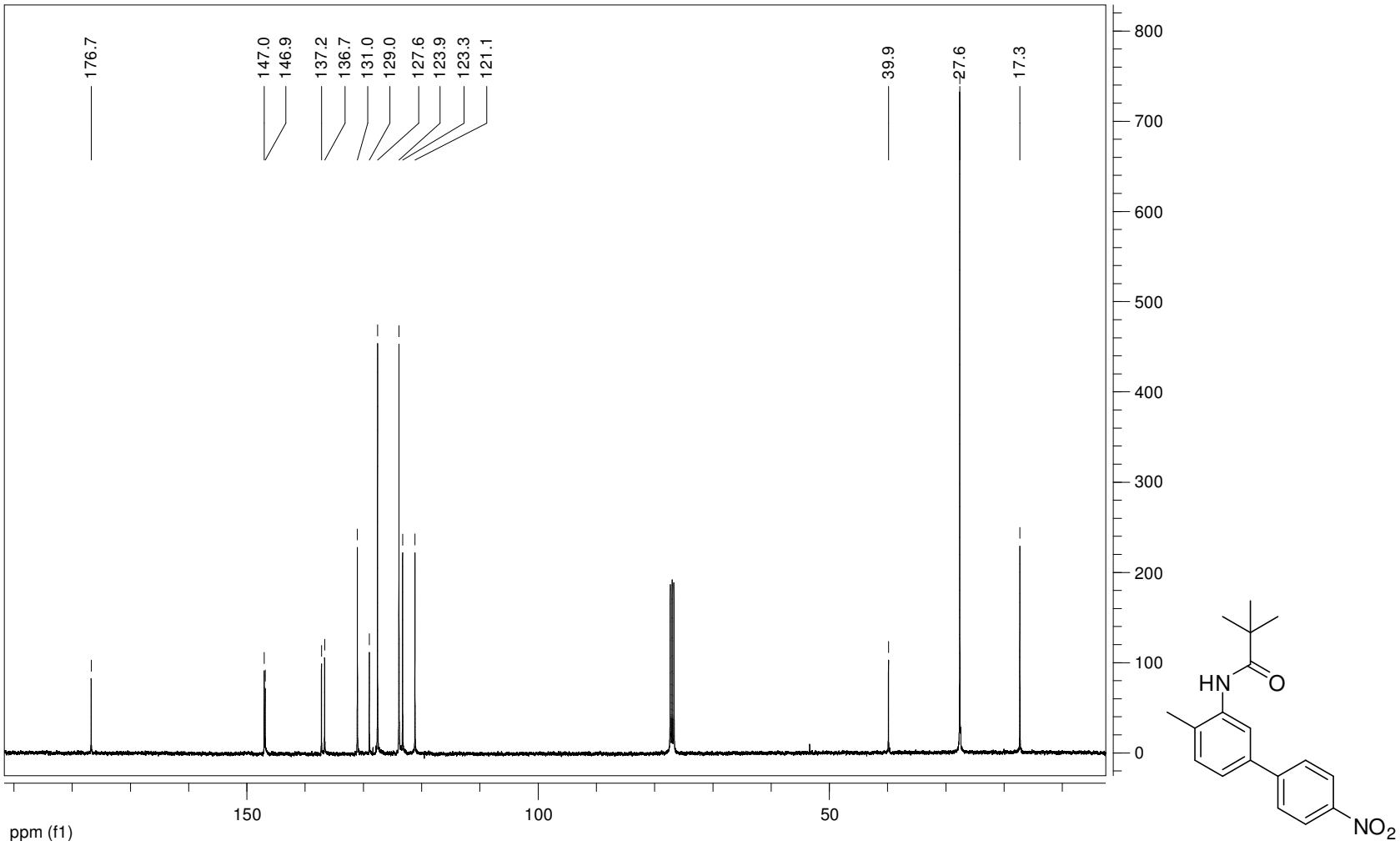
Ethyl 4'-methyl-3'-pivalamidobiphenyl-4-carboxylate (3d)



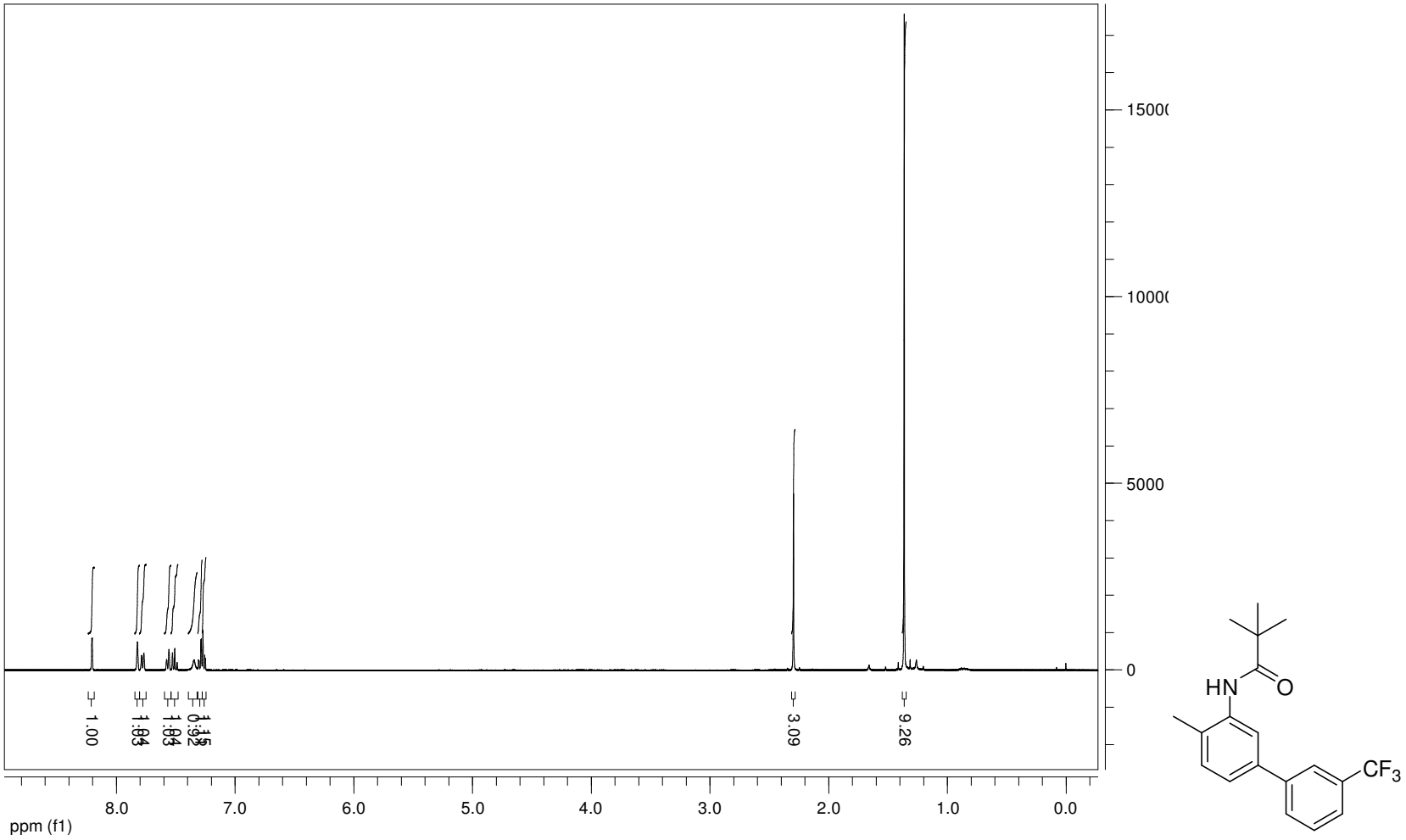
_N_-(4-methyl-4'-nitrobiphenyl-3-yl)pivalamide (3e)



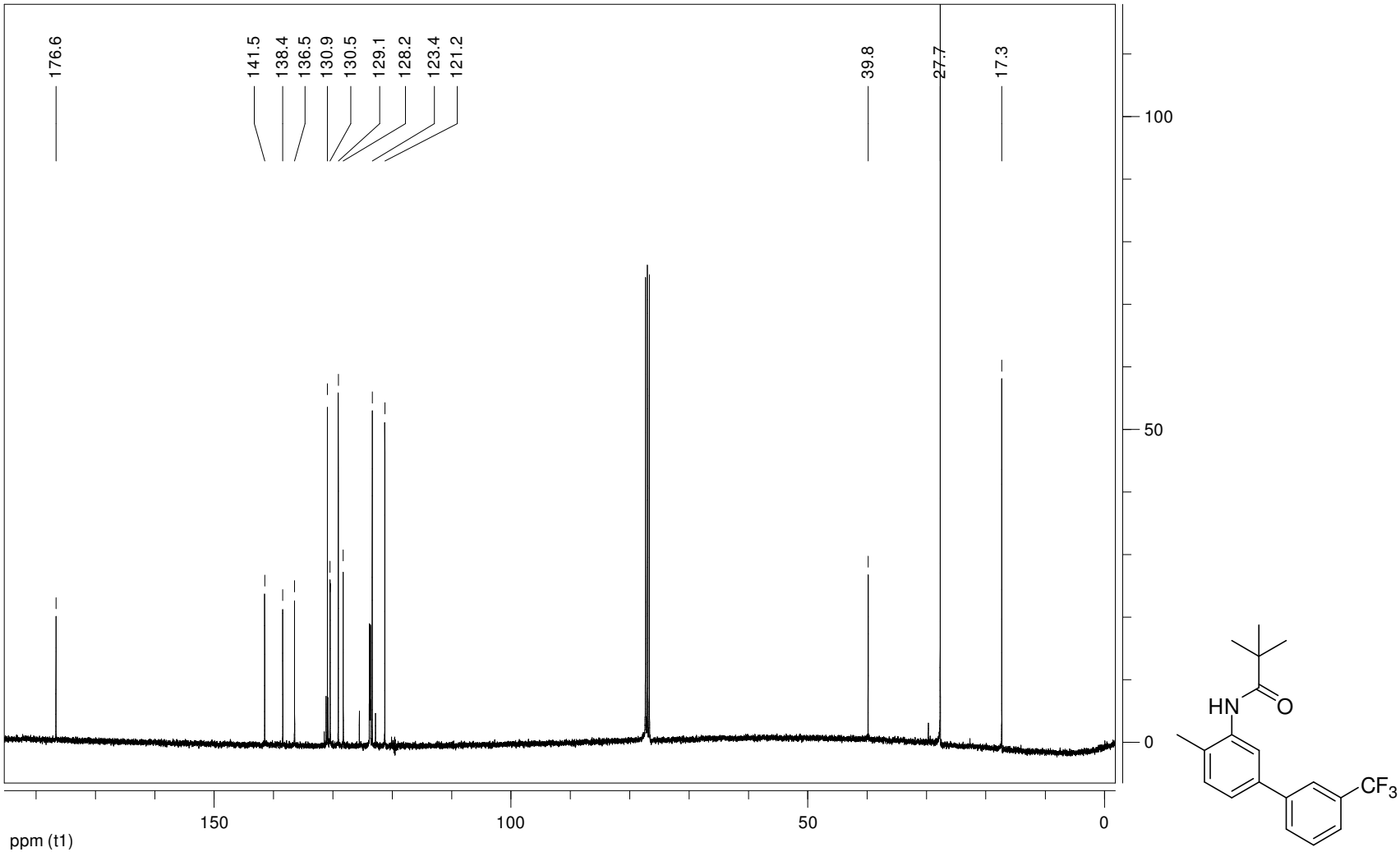
***N*-(4-methyl-4'-nitrobiphenyl-3-yl)pivalamide (3e)**



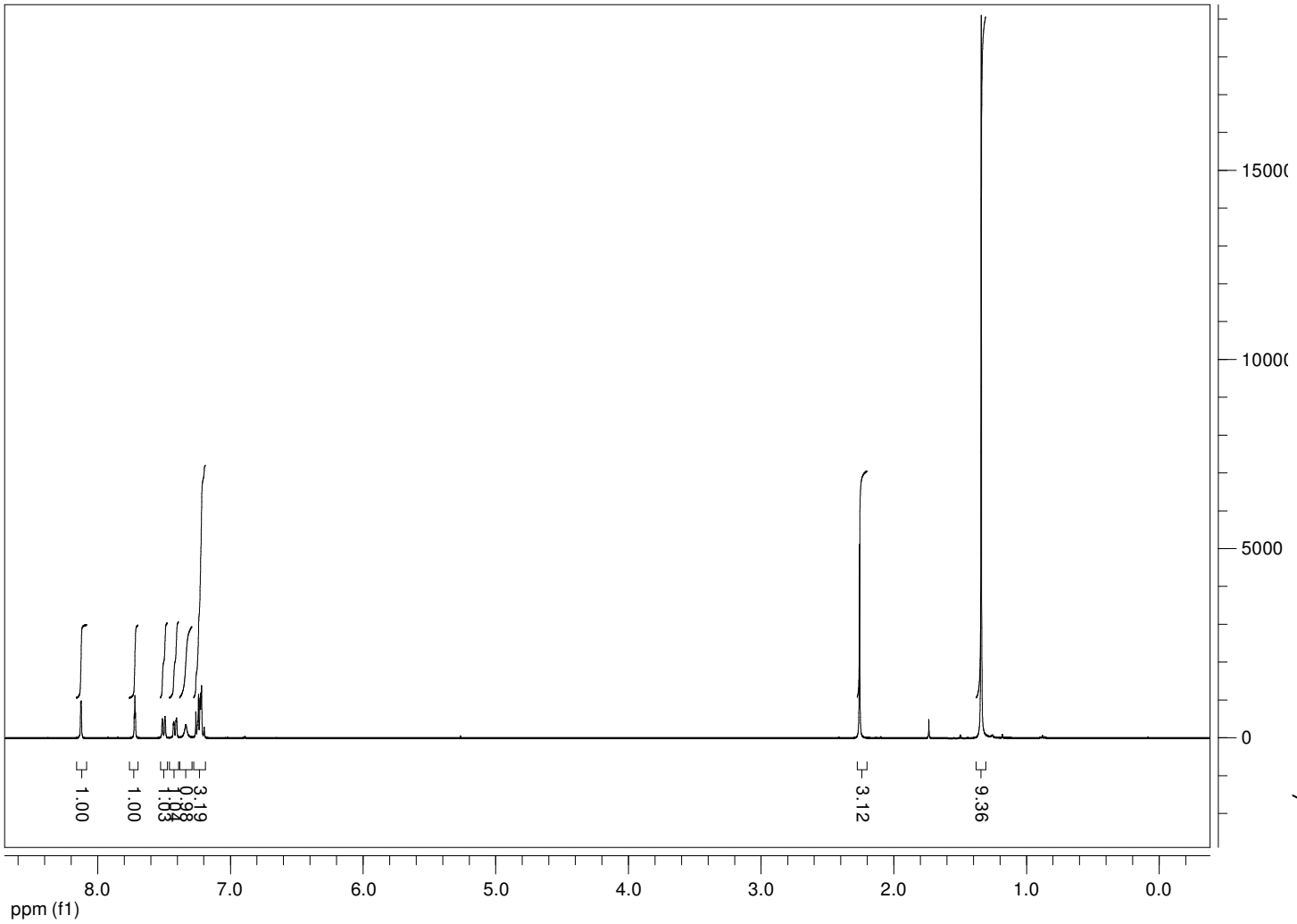
***N*-(4-methyl-3'-(trifluoromethyl)biphenyl-3-yl)pivalamide (3f)**



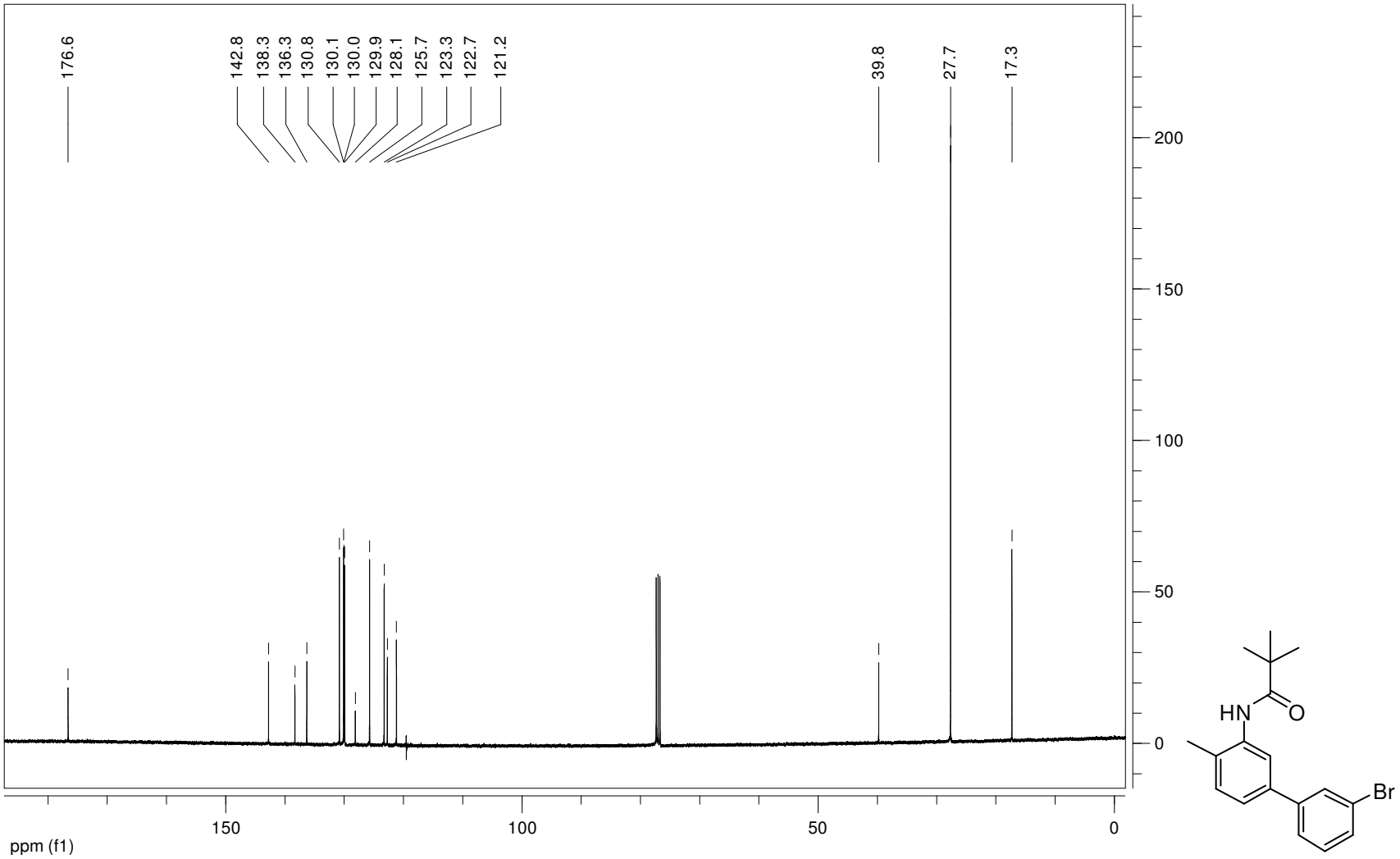
***N*-(4-methyl-3'-(trifluoromethyl)biphenyl-3-yl)pivalamide (3f)**



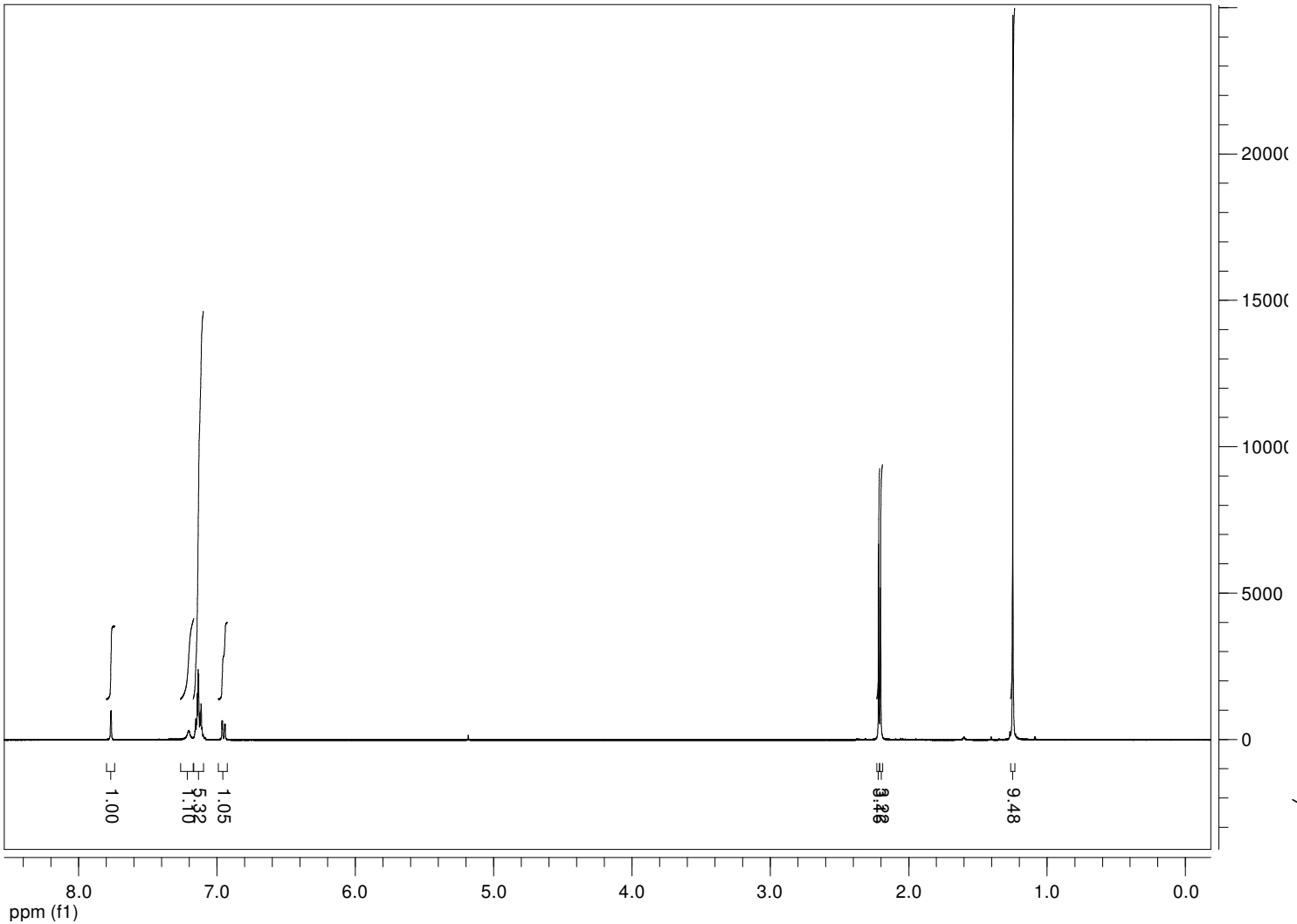
***N*-(3'-bromo-4-methylbiphenyl-3-yl)pivalamide (3g)**



_N_-(3'-bromo-4-methylbiphenyl-3-yl)pivalamide (3g)



_N_-(2',4-dimethylbiphenyl-3-yl)pivalamide (3h)



***N*-(2',4-dimethylbiphenyl-3-yl)pivalamide (3h)**