Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.




# Supporting Information

## Synthesis of Substituted Quinolines via Allylic Amination and Intramolecular Heck-Coupling

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**General information:**

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous magnesium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 $F_{254}$ (0.25mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard for $^{1}$H NMR (400 MHz) and for $^{13}$C NMR (100 MHz). IR spectra were recorded on JASCO 480-plus instrument. GC-MS analysis carried out on an Agilent GC-MS (7890A – 5975C VL MSD) system.

**General Procedure for the Preparation of Aza Baylis-Hillman Adducts and Allyl Amines:** To the solution of $FeCl_2.4H_2O$ (10 mg, 0.05 mmol), Olefin (1.50 mmol) in dioxane (5 mL), was added the phenylhydroxylamine (0.5 mmol) solution slowly in dioxane (5 mL) via syringe pump over 4 hours at 40 $^oC$ (70 $^oC$ for styrenes). Reactions were allowed to continue for two more hours to get complete consumption of phenylhydroxylamine. After that the mixture was filtered through celite and the filtrate was concentrated to dryness. The crude product was purified over a short column of silica gel (hexane/ethylacetate eluents) to give the corresponding ABH adduct/Allylamine which was then directly analyzed by GC-MS, NMR and IR analysis.

**General Procedure for the Intramolecular Heck-coupling of Aza Baylis-Hillman Adducts and Allyl Amines:** ABH adduct/Allylamine (0.25 mmol), tetrabutyl ammoniumiodide (TBAI) (0.25 mmol) and $Pd(OAc)_2$ (0.025 mmol) were combined in a round-bottom flask. DMF (4 mL) was added to the same flask and kept for heating on a sand bath at 90 $^oC$ for 6-12 hours while stirring. Once the reaction is completed (monitored by TLC and GC-MS), the mixture was filtered through celite and the filtrate was concentrated to dryness. The crude product was purified over a short column of silica gel (hexane/ethylacetate eluents) to isolate substituted quinolines which were then directly analyzed by GC-MS, NMR and IR analysis.

## Spectral data:

**TABLE 1:**

**Methyl 2-((2-iodophenylamino)methyl)acrylate (1a):** $^1H$ NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H), 4.09 (d, 2H, *J* = 6.4 Hz), 4.58 (brs, 1H), 5.72 (s, 1H), 6.28 (s, 1H), 6.41-6.47 (m, 2H), 7.15 (t, 1H, *J* = 7.6 Hz), 7.68 (d, 1H, *J* = 7.6 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 44.9, 52.2, 85.7, 111.2, 119.2, 126.1, 129.6, 136.7, 139.3, 146.6, 166.8; IR (KBr): 3399, 3065, 2996, 2949, 1716, 1636, 1590, 1507, 1453, 1321, 1267, 1154, 1084, 1004, 949, 816, 744 $cm^{-1}$.

**Ethyl 3-(2-iodophenylamino)-2-methylenebutanoate (1b):** Confirmed the products by comparing our previous data (Reported in our previous publication: S. Murru, A. A. Gallo, R. S. Srivastava, *J. Org. Chem.* 2012, **77**, 7119)

**Benzyl 3-(2-iodophenylamino)-2-methylenebutanoate (1c):** $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.47 (d, 3H, *J* = 6.4 Hz), 4.45 (brs, 1H), 4.49 (t, 1H, J = 6.4 Hz), 5.25 (s, 2H), 5.73 (s, 1H), 6.24 (s, 1H), 6.37-6.44 (m, 2H), 7.12 (t, 1H, *J* = 7.6 Hz), 7.33-7.38 (m, 5H), 7.64 (d,

1H, *J* = 8.0 Hz; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$22.2, 50.3, 66.8, 85.7, 112.0, 119.1, 125.1, 128.3, 128.4, 128.8, 129.5, 135.9, 139.1, 141.9, 145.7, 166.3; IR (KBr): 3394, 3065, 2932, 1726, 1634, 1589, 1505, 1318, 1176, 1081, 819, 744 $cm^{-1}$.

**Methyl 3-(2-iodophenylamino)-2-methylenepentanoate (1d):** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.03 (t, 3H, *J* = 7.2 Hz), 1.65-1.71 (m, 1H), 1.86-1.91 (m, 1H), 3.80 (s, 3H), 4.29 (t, 1H, *J* = 7.2 Hz), 4.50 (d, 1H, *J* = 7.2 Hz), 5.68 (s, 1H), 6.22 (s, 1H), 6.37 – 6.43 (m, 2H), 7.13 (t, 1H, *J* = 8.0 Hz), 7.64 (d, 1H, *J* = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$10.8, 28.7, 52.1, 56.2, 85.8, 111.8, 118.9, 125.6, 129.5, 139.1, 140.5, 146.0, 167.1; IR (KBr): 3398, 3063, 2992, 1718, 1635, 1592, 1437, 1370, 1266, 1004, 951, 849, 744 $cm^{-1}$.

**4-(2-iodophenylamino)-3-methylenepentan-2-one (1e):** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.03 (d, 3H, *J* = 7.2 Hz), 2.34 (s, 3H), 4.02 (s, 2H), 4.35 (brs, 1H), 6.43 (t, 1H, *J* = 8.0 Hz), 6.94 (t, 1H, *J* = 7.6 Hz), 7.20 (t, 1H, *J* = 8.8 Hz), 7.64 (d, 1H, *J* = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$15.1, 25.6, 38.8, 85.8, 111.0, 118.9, 129.3, 139.1, 139.7, 142.3, 147.2, 199.0; IR (KBr): 3403, 3068, 2992, 1692, 1632, 1588, 1456, 1267, 1152, 1089, 952, 817, 742 $cm^{-1}$.

**2-Iodo-N-(2-phenylallyl)benzenamine (1f):** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.21 (d, 2H, *J* = 4.8 Hz), 4.51 (brs, 1H), 5.30 (s, 1H), 5.48 (s, 1H), 6.45 (t, 1H, *J* = 7.6 Hz), 6.57 (d, 1H, *J* = 8.0 Hz), 7.19 (t, 1H, *J* = 7.2 Hz), 7.31-7.38 (m, 3H), 7.44 (d, 2H, *J* = 8.0 Hz), 7.66 (d, 1H, *J* = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$48.2, 85.5, 111.1, 113.6, 119.0, 126.3, 128.1, 128.7, 129.6, 139.1, 139.4, 144.1, 147.1; IR (KBr): 3400, 3055, 1590, 1506, 1453, 1321, 1004, 905, 778, 742, 705 $cm^{-1}$.

**2-Iodo-N-(2-p-tolylallyl)benzenamine (1g):** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.36 (s, 3H), 4.18 (d, 2H, *J* = 5.6 Hz), 4.50 (brs, 1H), 5.24 (s, 1H), 5.45 (s, 1H), 6.44 (t, 1H, *J* = 8.0 Hz), 6.55 (d, 1H, *J* = 8.0 Hz), 7.17 (m, 3H), 7.34 (d, 2H, *J* = 8.0 Hz), 7.65 (d, 1H, *J* = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$21.3, 48.2, 85.5, 111.1, 112.8, 118.9, 126.1, 129.4, 129.6, 136.5, 138.0, 139.1, 143.8, 147.1; IR (KBr): 3399, 2918, 1590, 1506, 1453, 1321, 1073, 1004, 901, 822, 741 $cm^{-1}$.

**N-(2-(4-chlorophenyl)allyl)-2-iodobenzenamine (1h):** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.16 (d, 2H, *J* = 6.0 Hz), 4.45 (brs, 1H), 5.31 (s, 1H), 5.46 (s, 1H), 6.45 (t, 1H, *J* = 7.6 Hz), 6.54 (d, 1H, *J* 8.4 Hz), 7.18 (t, 1H, *J* = 6.8 Hz), 7.31 (d, 2H, *J* = 8.8 Hz), 7.35 (d, 2H, *J* = 8.8

Hz), 7.64 (d, 1H, *J* = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$48.2, 85.6, 111.1, 114.3, 119.2, 127.6, 128.9, 129.6, 134.0, 137.8, 139.2, 143.1, 146.9; IR (KBr): 3400, 3065, 2917, 1632, 1590, 1492, 1321, 1093, 1005, 833, 741 $cm^{-1}$.

**N-(2-(4-fluorophenyl)allyl)-2-iodobenzenamine (1i):** $^1$H NMR (400 MHz, $CDCl_3$): δ 4.15 (d, 2H, *J* = 5.6 Hz), 4.46 (brs, 1H), 5.28 (s, 1H), 5.42 (s, 1H), 6.45 (t, 1H, *J* = 8.0 Hz), 6.55 (d, 1H, *J* = 8.0 Hz), 7.01-7.05 (m, 2H), 7.18 (t, 1H, *J* = 8.0 Hz), 7.37 – 7.41 (m, 2H), 7.64 (d, 1H, *J* = 8.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$48.4, 85.6, 111.1, 113.7, 115.5, 115.7, 119.1, 127.9, 128.0, 129.6, 135.3, 135.4, 139.2, 143.1, 146.9, 161.5, 163.9; IR (KBr): 3401, 3065, 2921, 2856, 1631, 1590, 1507, 1453, 1321, 1233, 1161, 1005, 906, 837, 742, 647 $cm^{-1}$.

**2-Iodo-N-(4-methyl-2-methylenepent-3-enyl)benzenamine (1j):** $^1$H NMR (400 MHz, $CDCl_3$): δ 1.78 (s, 3H), 1.81 (s, 3H), 3.76 (d, 2H, *J* = 5.6 Hz), 4.40 (brs, 1H), 4.94 (s, 1H), 5.19 (s, 1H), 5.63 (s, 1H), 6.42 (t, 1H, *J* = 7.6 Hz), 6.50 (d, 1H, *J* = 8.4 Hz), 7.17 (t, 1H, *J* = 7.2 Hz), 7.64 (d, 1H, *J* = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$19.8, 26.9, 49.9, 85.5, 111.2, 113.8, 118.8, 123.6, 129.5, 137.7, 139.1, 142.4, 147.3; IR (KBr): 3399, 3066, 2967, 2926, 1590, 1505, 1453, 1318, 1004, 900, 741 $cm^{-1}$.

**2-iodo-N-((E)-7-methyl-3-methyleneocta-4,6-dien-2-yl)benzenamine (1k):** $^1$H NMR (400 MHz, $CDCl_3$): δ 1.49 (d, 3H, *J* = 6.8 Hz), 1.80 (s, 3H), 1.83 (s, 3H), 4.21 (brs, 1H), 4.35 (brs, 1H), 5.03 (s, 1H), 5.09 (s, 1H), 5.88 (d, 1H, *J* = 10.8 Hz), 6.15 (d, 1H, *J* = 15.6 Hz), 6.34 – 6.41 (m, 2H), 6.59 (dd, 1H, *J*1 = 15.6 Hz, *J*2 = 10.8 Hz), 7.10 (t, 1H, *J* = 7.2 Hz), 7.62 (d, 1H, *J* = 7.6 Hz).; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$18.8, 22.6, 26.4, 50.9, 85.4, 111.9, 113.1, 118.7, 125.3, 125.7, 129.4, 129.9, 137.0, 139.0, 146.3, 147.6; IR (KBr): 2988, 2956, 2931, 1586, 1507, 1460, 1343, 1011 $cm^{-1}$.

**TABLE 2:**

**Ethyl 3-(2-bromophenylamino)-2-methylenebutanoate (2b):** Confirmed the products by comparing our previous data **(**Reported in our previous publication: S. Murru, A. A. Gallo, R. S. Srivastava, *J. Org. Chem.* 2012, **77**, 7119)

**Ethyl 3-(2,5-dibromophenylamino)-2-methylenebutanoate (3b):** $^1$H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, 3H, *J* = 7.6 Hz), 1.46 (d, 3H, *J* = 6.8 Hz), 4.27 (q, 2H, *J* = 7.6 Hz), 4.41 (t, 1H, *J* = 6.8 Hz), 4.66 (d, 1H, *J* = 7.2 hz), 5.69 (s, 1H), 6.22 (s, 1H), 6.56 (s, 1H), 6.67 (d,

1H, *J* = 8.4 Hz), 7.17 (d, 1H, *J* = 8.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.4, 22.1, 50.2, 61.2, 108.4, 115.2, 120.9, 122.4, 124.8, 133.5, 141.6, 144.7, 166.3; IR (KBr): 3415, 3073, 2982, 1712, 1598, 1505, 1285, 1106, 743 $cm^{-1}$.

**Ethyl 3-(2-bromo-5-(trifluoromethyl)phenylamino)-2-methylenebutanoate (4b):** $^1$H NMR (400 MHz, $CDCl_3$): δ 1.12 (t, 3H, *J* = 7.2 Hz), 1.40 (d, 3H, *J* = 6.8 Hz), 3.94 (q, 2H, *J* = 7.2 Hz), 4.20 (t, 1H, *J* = 6.4 Hz), 4.75 (q, 1H, *J* = 7.2 Hz), 5.77 (s, 1H), 6.40 (s, 1H), 7.16 (d, 1H, *J* = 8.4 Hz), 7.59 (d, 1H, *J* = 8.4 Hz), 7.65 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.1, 23.3, 59.3, 61.1, 119.7, 122.5, 128.6, 129.0, 131.1, 133.7, 138.5, 150.5, 167.1; IR (KBr): 3408, 3070, 2981, 2933, 1715, 1594, 1323, 1282, 1107, 741 $cm^{-1}$.

**Ethyl 3-(2-iodo-4-methylphenylamino)-2-methylenebutanoate (5b):** $^1$H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, 3H, *J* = 6.8 Hz), 1.43 (d, 3H, *J* = 6.8 Hz), 2.16 (s, 3H), 4.24 (q, 2H, *J* = 7.2 Hz), 4.29 (brs, 1H), 4.42 (t, 1H, *J* = 6.8 Hz), 5.66 (s, 1H), 6.16 (s, 1H), 6.28 (d, 1H, *J* = 8.8 Hz), 6.93 (dd, 1H, *J*1 = 8.4 Hz, *J*2 = 1.6 Hz), 7.47 (t, 1H, *J* = 1.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.4, 19.9, 22.2, 50.5, 61.0, 85.7, 111.9, 124.4, 128.4, 130.1, 139.4, 142.3, 143.7, 166.7; IR (KBr): 3389, 3062, 2968, 1715, 1589, 1506, 1266, 1099, 1003, 742 $cm^{-1}$.

**Ethyl 3-(2-iodo-3,5-dimethylphenylamino)-2-methylenebutanoate (6b):** $^1$H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, 3H, *J* = 7.2 Hz), 1.44 (d, 3H, *J* = 6.4 Hz), 2.17 (s, 3H), 2.36 (s, 3H), 4.25 (q, 2H, *J* = 7.2 Hz), 4.44 (t, 1H, *J* = 6.0 Hz), 4.56 (d, 1H, *J* = 6.8 Hz), 5.67 (s, 1H), 6.01 (s, 1H), 6.17 (s, 1H), 6.45 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.4, 21.4, 22.3, 29.6, 50.5, 60.9, 89.1, 110.0, 120.2, 124.3, 138.6, 141.9, 142.3, 145.8, 166.6; IR (KBr): 3386, 3060, 2968, 1715, 1586, 1265, 1098, 743 $cm^{-1}$.

**Ethyl 3-(2-bromopyridin-3-ylamino)-2-methylenebutanoate (7b):** $^1$H NMR (400 MHz, $CDCl_3$): δ 1.32 (m, 3H), 1.50 (d, 3H, *J* = 6.4 Hz), 4.27 (q, 2H, *J* = 7.2 Hz), 4.42 (t, 1H, *J* = 6.8 Hz), 4.71 (d, 1H, *J* = 6.4 Hz), 5.70 (s, 1H), 6.22 (s, 1H), 6.67 (d, 1H, *J* = 8.0 Hz), 7.05 (dd, 1H, $J^1$ = 8.0 Hz, $J^2$ = 4.4 Hz), 7.68 (d, 1H, *J* = 4.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.2, 21.9, 49.7, 61.0, 118.5, 123.6, 124.5, 130.3, 137.4, 140.7, 141.2, 166.0; IR (KBr): 3408, 3061, 2980, 2934, 1713, 1579, 1487, 1378, 1284, 1264, 1181, 1133, 1106, 1042, 956, 789 $cm^{-1}$.

**TABLE 3:**

**Methyl quinoline-3-carboxylate (1a'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 4.02 (s, 3H), 7.63 (t, 1H, *J* = 7.2 Hz), 7.83 (t, 1H, *J* = 7.2 Hz), 7.94 9d, 1H, *J* = 8.0 Hz), 8.16 (d, 1H, *J* = 8.0 Hz), 8.86 (s, 1H), 9.45 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$52.5, 123.0, 126.8, 127.5, 129.1, 129.5, 131.9, 138.8, 149.8, 150.0, 165.9; IR (KBr): 2954, 2915, 1726, 1621, 1564, 1440, 1272, 1128, 1054, 805, 762 $cm^{-1}$.

**Ethyl 2-methylquinoline-3-carboxylate (1b', 2b'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, 3H, *J* = 7.2 Hz), 3.00 (s, 3H), 4.44 (q, 2H, *J* = 7.2 Hz), 7.26 (s, 1H), 7.54 (t, 1H, *J* = 6.8 Hz), 7.76 – 7.80 (m, 1H), 7.87 (d, 1H, *J* = 8.0 Hz), 8.04 (d, 1H, *J* = 8.0 Hz), 8.74 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.3, 25.7, 61.4, 123.9, 125.7, 126.5, 128.4, 128.5, 131.7, 139.9, 148.6, 158.5, 166.5; IR (KBr): 3062, 2963, 2926, 2852, 1725, 1620, 1562, 1423, 1258, 1199, 1062 $cm^{-1}$.

**Benzyl 2-methylquinoline-3-carboxylate (1c'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 3H), 5.40 (s, 2H), 7.38 – 7.45 (m, 3H), 7.49 – 7.55 (m, 3H), 7.78 (t, 1H, *J*1 = 7.6 Hz, *J*2 = 1.6 Hz), 7.85 (d, 1H, *J* = 8.4 Hz), 8.04 (1H, d, *J* = 8.4 Hz), 8.77 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$26.0, 67.4, 123.7, 125.9, 126.7, 128.6, 128.7, 128.75, 128.9, 131.2, 132.0, 135.9, 140.3, 148.9, 158.8, 166.5; IR (KBr): 3062, 2972, 2928, 1724, 1619, 1563, 1455, 1422, 1240, 1126, 1055, 788, 750 $cm^{-1}$.

**Methyl 2-ethylquinoline-3-carboxylate (1d'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, 3H, *J* = 7.2 Hz), 3.34 (q, 2H, *J* = 7.2 Hz), 3.97 (s, 3H), 7.52 9t, 1H, *J* = 7.6 Hz), 7.77 (t, 1H, *J* = 7.6 Hz), 7.82 (d, 1H, *J* = 7.6 Hz), 8.00 (d, 1H, *J* = 8.4 Hz), 8.70 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.1, 31.2, 52.6, 123.5, 125.8, 126.7, 128.6, 128.9, 131.8, 140.2, 148.9, 163.2, 167.2; IR (KBr): 2951, 2919, 2874, 1725, 1620, 1563, 1437, 1273, 1252, 1201, 1127, 1069, 803, 754 $cm^{-1}$.

**1-(2-Methylquinolin-3-yl)ethanone (1e'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 2.69 (s, 3H), 2.88 (s, 3H), 7.52 (t, 1H, *J* = 7.6 Hz), 7.73 – 7.78 (m, 1H), 7.82 (d, 1H, *J* = 8.0 Hz), 8.00 (d, 1H, *J* = 8.4 Hz), 8.44 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$25.9, 29.4, 125.8, 126.9, 128.5, 128.8, 131.3, 131.9, 138.4, 148.5, 157.8, 200.1; IR (KBr): 2965, 2920, 1680, 1618, 1561, 1418, 1253, 1196, 1029, 926, 862, 781, 750, 691 $cm^{-1}$.

**3-Phenylquinoline (1f'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.44 (t, 1H, *J* = 7.2 Hz), 7.51 – 7.61 (m, 3H), 7.71 – 7.74 (m, 3H), 7.89 (d, 1H, *J* = 8.0 Hz), 8.15 (d, 1H, *J* = 8.8 Hz), 8.31 (d, 1H, *J* = 2.0 Hz), 9.19 (d, 1H, *J* = 2.0 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 126.4, 127.2, 127.7, 128.2, 128.3, 129.0, 129.4, 129.45, 129.6, 131.1, 133.5, 138.1, 150.2; IR (KBr): 2963, 2926, 1725, 1493, 1459, 1262, 1074, 1025, 902, 787, 761, 697 $cm^{-1}$.

**3-p-Tolylquinoline (1g'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.04 (d, 1H, *J* = 8.0 Hz), 7.08 (d, 1H, *J* = 8.0 Hz), 7.25 (s, 1H), 7.32 (d, 2H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* = 7.6 Hz), 7.61 (d, 2H, *J* = 7.6 Hz), 7.70 (t, 1H, *J* = 7.6 Hz), 7.87 (d, 1H, *J* = 8.4 Hz), 8.11 (d, 1H, *J* = 6.8 Hz), 8.28 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.4, 121.6, 122.8, 126.3, 126.8, 127.1, 127.5, 128.1, 129.4, 129.7, 130.1, 133.0, 138.3, 150.2; IR (KBr): 3015, 2969, 2921, 1667, 1540, 1456, 1261, 815, 751 $cm^{-1}$.

**3-(4-Chlorophenyl)quinoline (1h'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, 2H, *J* = 8.8 Hz), 7.58 (t, 1H, *J* = 7.6 Hz), 7.62 (d, 2H, *J* = 8.8 Hz), 7.70 – 7.75 (m, 1H), 7.87 (d, 1H, *J* = 8.4 Hz), 8.13 (d, 1H, *J* = 8.4 Hz), 8.27 (s, 1H), 9.12 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 127.5, 128.1, 128.2, 128.9, 129.4, 129.6, 129.9, 132.9, 133.5, 134.6, 136.5, 147.5, 149.6; IR (KBr): 3052, 2925, 1604, 1512, 1231, 1161, 833, 752 $cm^{-1}$.

**3-(4-Fluorophenyl)quinoline (1i'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.20 – 7.26 (m, 2H), 7.59 (t, 1H, *J* = 7.6 Hz), 7.66 – 7.69 (m, 2H), 7.33 (t, 1H, *J* = 7.6 Hz), 7.88 (d, 1H, *J* = 8.0 Hz), 8.14 (d, 1H, *J* = 8.0 Hz), 8.27 (s, 1H), 9.14 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 116.3, 116.5, 127.3, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 134.3, 147.5, 149.9, 161.9, 164.4; IR (KBr): 3048, 2925, 1604, 1512, 1341, 1231, 1161, 954, 910, 833, 785, 752 $cm^{-1}$.

**1,2-dihydro-3-(2-methylprop-1-enyl)quinoline (1J'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.75 (s, 3H), 1.77 (s, 3H), 3.46 (d, 2H, *J* = 7.2 Hz), 5.46 (t, 1H, *J* = 2.0 Hz), 6.96 (s, 1H), 7.12 (t, 1H, *J* = 6.8 Hz), 7.18 (t, 1H, *J* = 6.8 Hz), 7.35 (d, 1H, *J* = 8.0 Hz), 7.59 (d, 1H, *J* = 8.0 Hz), 7.92 (brs, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 24.1, 25.7, 68.1, 111.0, 116.2, 119.0, 119.1, 121.1, 121.9, 123.0, 128.8, 131.9, 136.5; IR (KBr): 3414, 2962, 2925, 1716, 1455, 1262, 1079, 789, 740 $cm^{-1}$.

**2-methyl-3-((E)-4-methylpenta-1,3-dienyl)quinoline (1k'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.89 (s, 3H), 1.92 (s, 3H), 2.76 (s, 3H), 6.15 (d, 1H, *J* = 8.4 Hz), 6.68 (d, 1H, *J* = 15.2 Hz), 7.02 (d, 1H, *J*1 = 15.2 Hz, *J*2 = 11.2 Hz), 7.46 (t, 1H, *J* = 7.6 Hz), 7.61 (t, 1H, *J* = 7.6 Hz), 7.77 (d, 1H, *J* = 7.6 Hz), 7.97 (d, 1H, *J* = 8.4 Hz), 8.15 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 24.1, 26.5, 29.9, 125.5, 125.7, 126.1, 127.6, 127.65, 128.5, 129.0, 129.4, 130.9, 131.5, 138.5, 146.9, 157.6; IR (KBr): 2961, 2924, 2854, 1725, 1685, 1617, 1490, 1461, 1377, 1261, 1101, 799, 752 $cm^{-1}$.

**Ethyl 7-bromo-2-methylquinoline-3-carboxylate (3b'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.46 (t, 3H, *J* = 7.2 Hz), 2.98 (s, 3H), 4.45 (q, 2H, *J* = 7.2 Hz), 7.64 (d, 1H, *J* = 8.8 Hz), 7.73 (d, 1H, *J* = 8.8 Hz), 8.24 (s, 1H), 8.70 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.5, 25.9, 61.7, 124.5, 124.6, 126.3, 129.8, 130.4, 131.3, 139.8, 149.3, 159.9, 166.5; IR (KBr): 2963, 2916, 1727, 1614, 1477, 1262, 1177, 1062, 803 $cm^{-1}$.

**Ethyl 7-(trifluoromethyl)-2-methylquinoline-3-carboxylate (4b'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, 3H, *J* = 7.2 Hz), 2.98 (s, 3H), 4.44 (q, 2H, *J* = 7.2 hz), 7.67 (d, 1H, *J* = 8.4 Hz), 7.95 (d, 1H, *J* = 8.4 Hz), 8.32 (s, 1H), 8.72 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.4, 25.8, 61.9, 122.2, 122.3, 122.35, 126.0, 126.6, 126.65, 127.4, 129.7, 139.5, 147.7, 160.1, 166.2; IR (KBr): 2982, 2934, 2875, 1730, 1603, 1563, 1447, 1431, 1347, 1324, 1283, 1191, 1130, 1058, 934, 819 $cm^{-1}$.

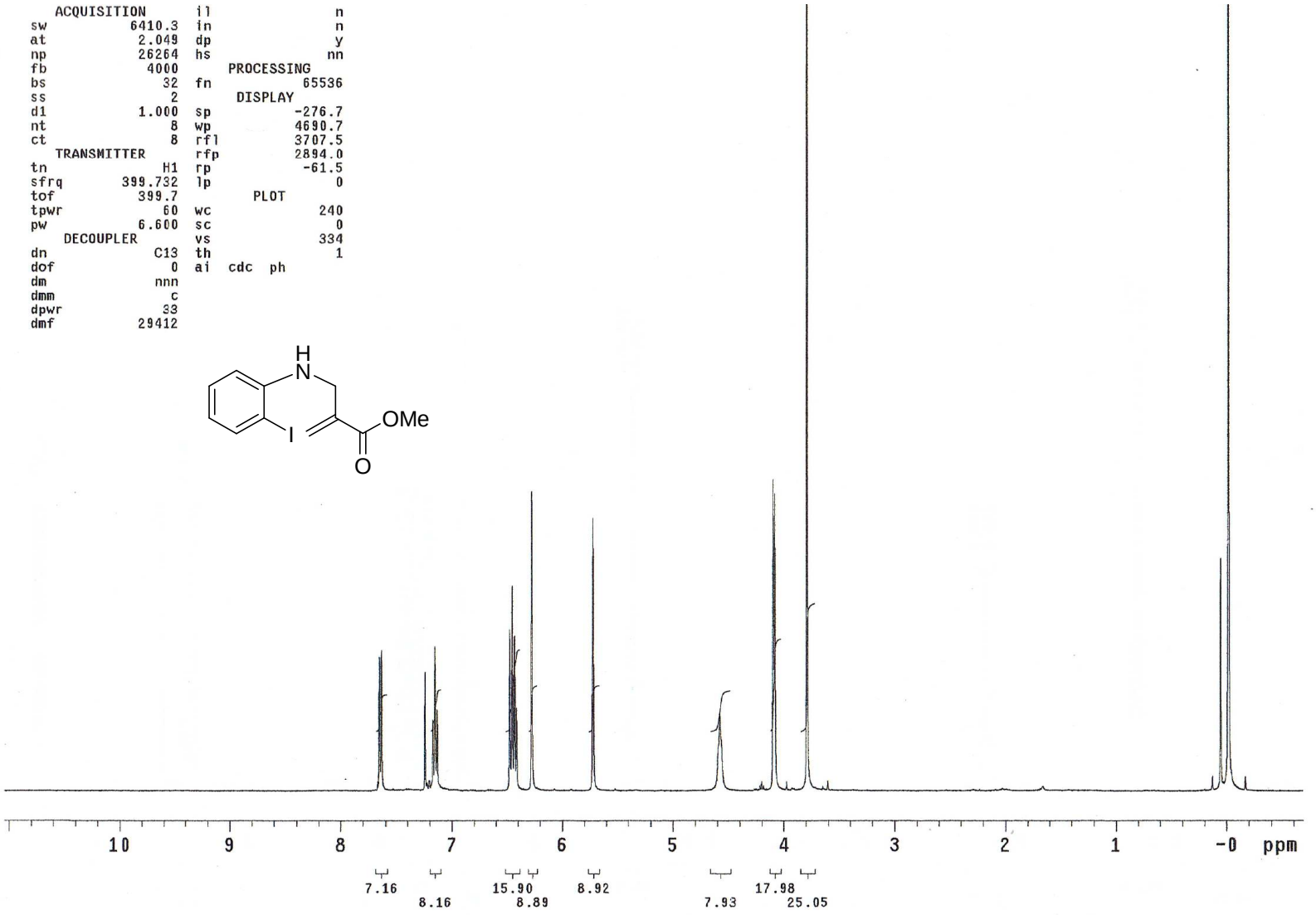
**Ethyl 2,6-dimethylquinoline-3-carboxylate (5b'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, *J* = 7.2 Hz), 2.51 (s, 3H), 2.94 (s, 3H), 4.41 (q, 2H, *J* = 7.2 Hz), 7.58 (d, 1H, *J* = 8.0 Hz), 7.59 (s, 1H), 7.90 (d, 1H, *J* = 8.4 hz), 8.62 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.5, 21.7, 25.8, 61.5, 126.0, 127.4, 128.3, 129.5, 134.1, 136.6, 139.5, 147.4, 157.7, 166.9; IR (KBr): 2977, 2915, 1720, 1594, 1566, 1277, 1239, 1215, 1069, 828, 778 $cm^{-1}$.

**Ethyl 2,5,7-trimethylquinoline-3-carboxylate (6b'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.45 (t, 3H, *J* = 7.2 Hz), 2.50 (s, 3H), 2.67 (s, 3H), 2.96 (s, 3H), 4.43 (q, 2H, *J* = 7.2 Hz), 7.18 (s, 1H), 7.65 (s, 1H), 8.82 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.6, 18.6, 22.2, 25.9, 61.5, 122.7, 123.5, 126.0, 129.5, 135.4, 136.4, 142.2, 149.5, 158.1, 167.2; IR (KBr): 2978, 2927, 1720, 1620, 1600, 1566, 1444, 1380, 1269, 1226, 1086, 1056, 857, 778 $cm^{-1}$.

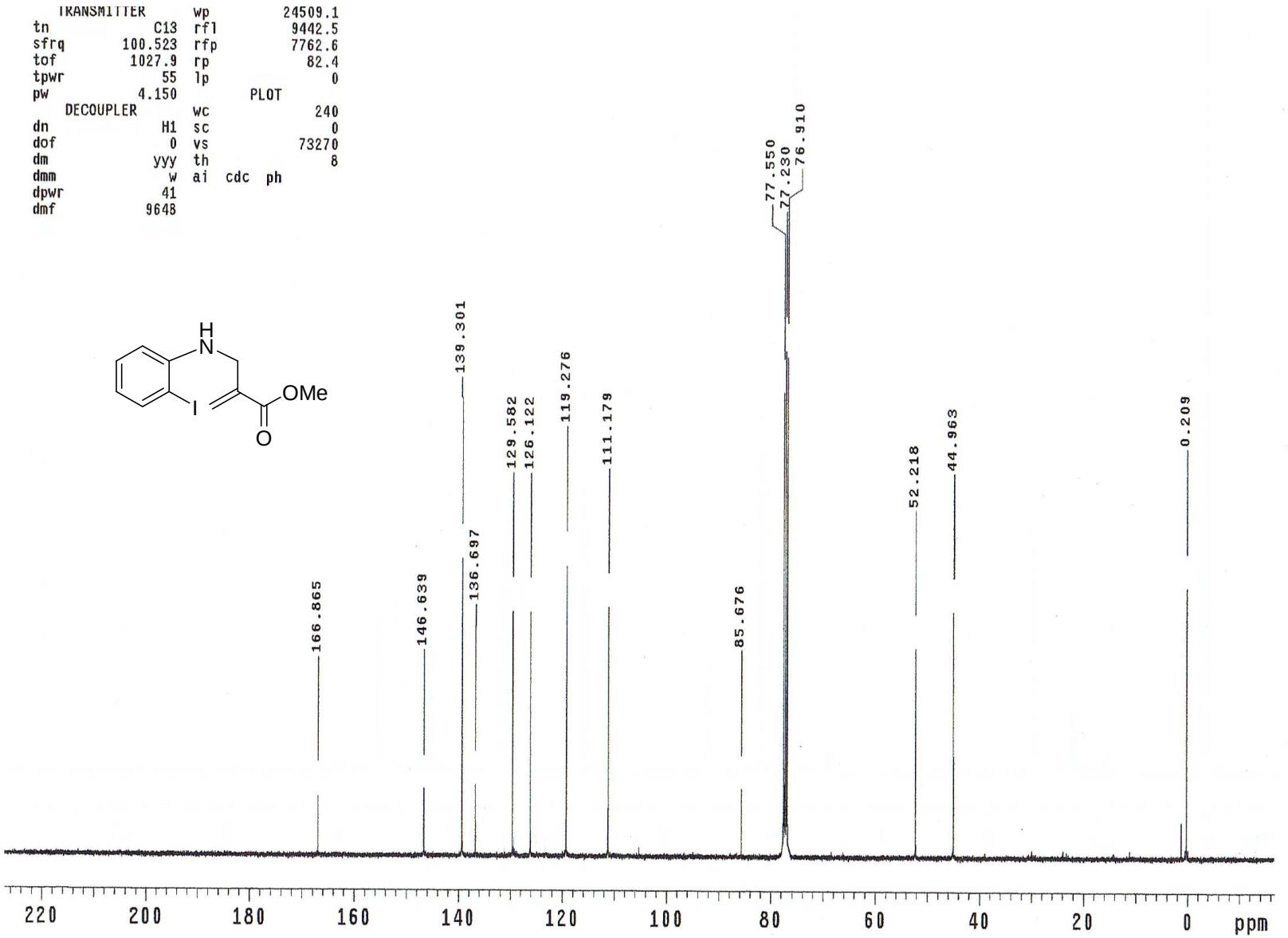
**Ethyl 2-methyl-1,5-naphthyridine-3-carboxylate (7b'):** $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.41 (t, 3H, *J* = 7.2 Hz), 2.98 (s, 3H), 4.42 (q, 2H, *J* = 7.2 Hz), 7.64 (dd, 1H, $J^1$ = 8.4 Hz, $J^2$ = 4.0 Hz), 8.29 (d, 1H, *J* = 8.4 Hz), 8.89 (s, 1H), 8.95 (d, 1H, *J* = 3.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$14.4, 25.6, 61.9, 126.1, 127.4, 136.5, 140.6, 142.1, 144.6, 151.5, 159.7, 166.2; IR (KBr): 2982, 2928, 1725, 1588, 1472, 1263, 1204, 1125, 1065, 934, 832, 784 $cm^{-1}$.

# Spectra

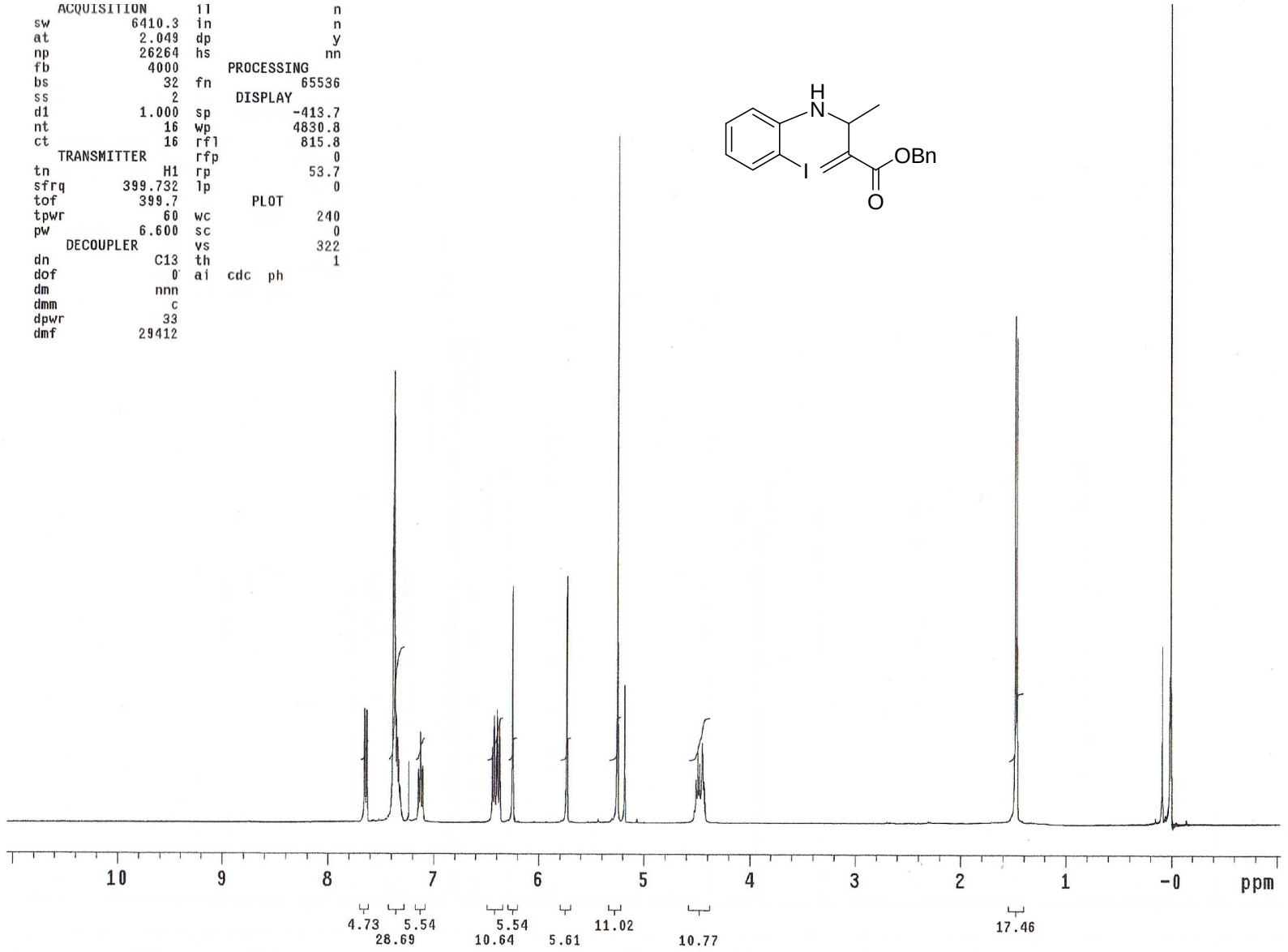
**Methyl 2-((2-iodophenylamino)methyl)acrylate (1a):** $^{1}$H NMR (400 MHz, $CDCl_3$)



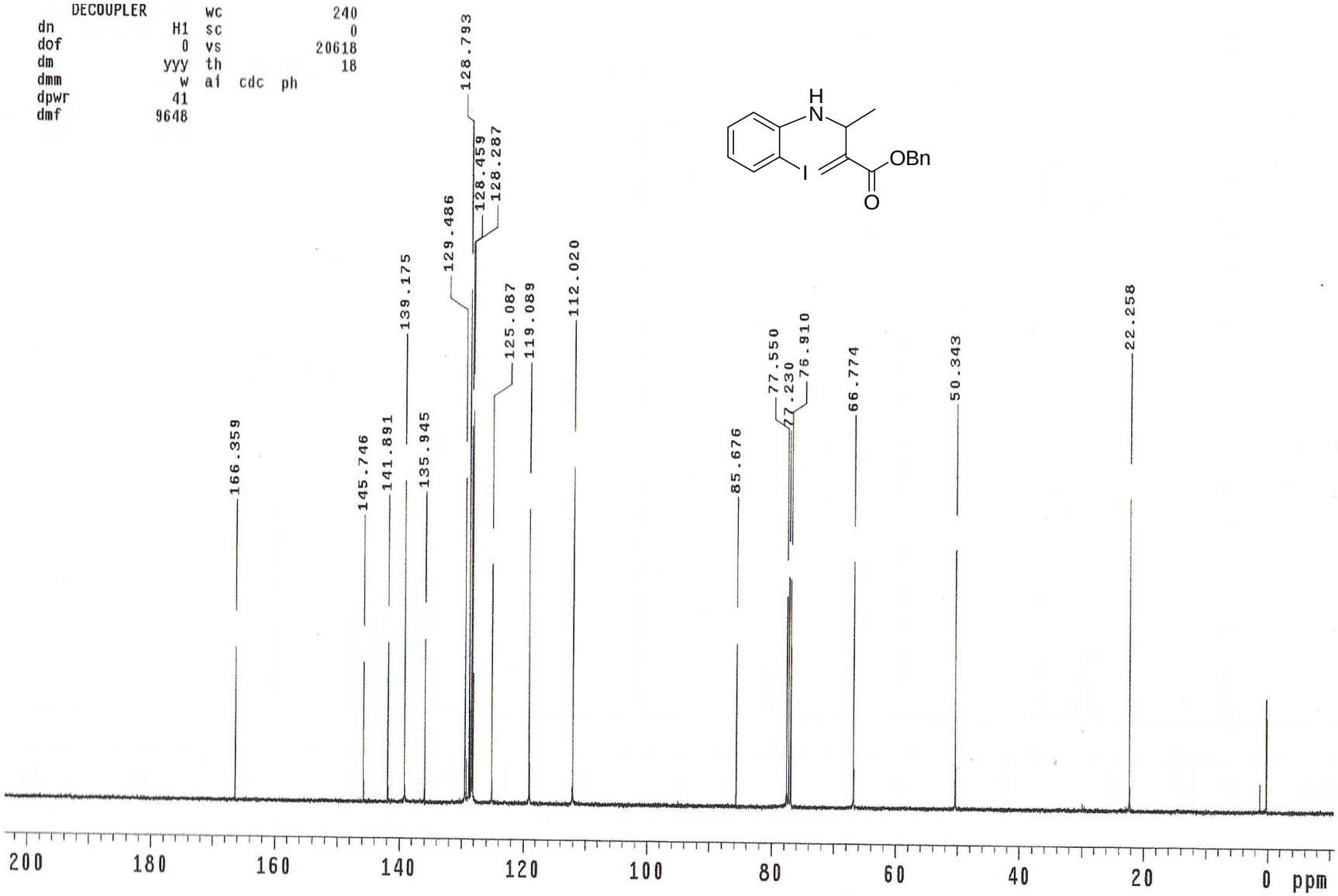
**Methyl 2-((2-iodophenylamino)methyl)acrylate (1a):** $^{1}$H NMR (400 MHz, $CDCl_3$)



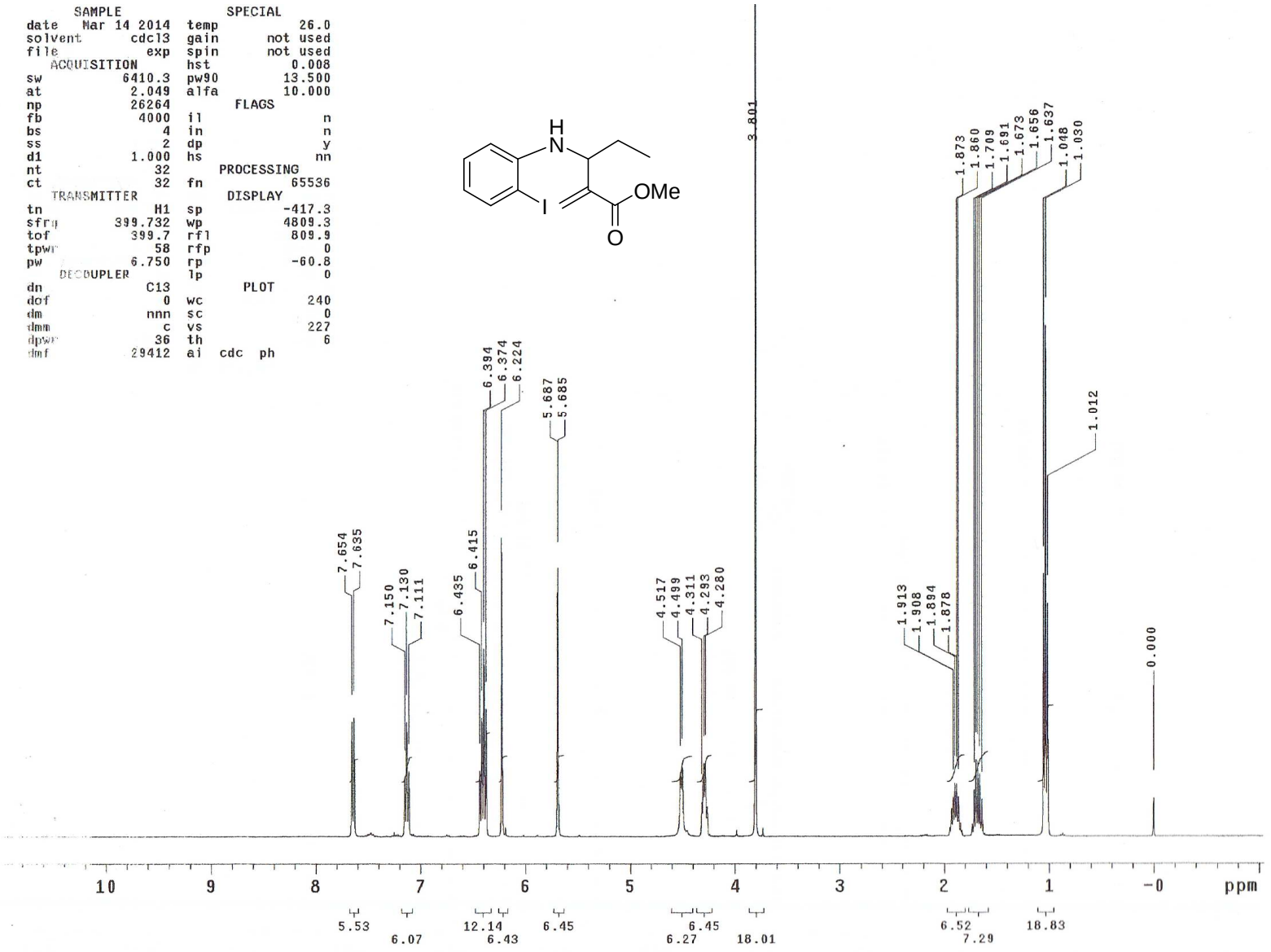
**Benzyl 3-(2-iodophenylamino)-2-methylenebutanoate (1c):** $^{1}$H NMR (400 MHz, $CDCl_3$)



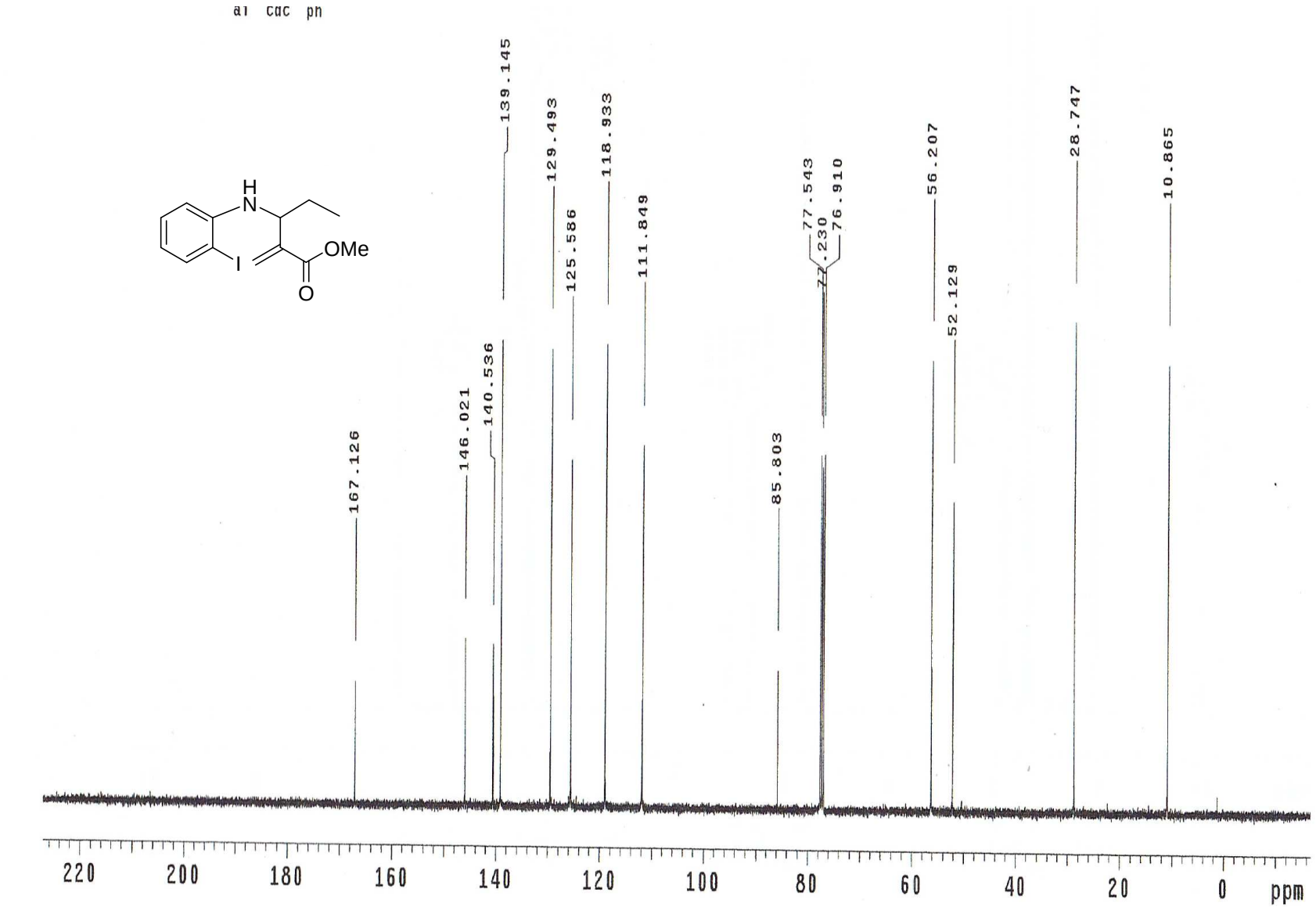
**Benzyl 3-(2-iodophenylamino)-2-methylenebutanoate (1c):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



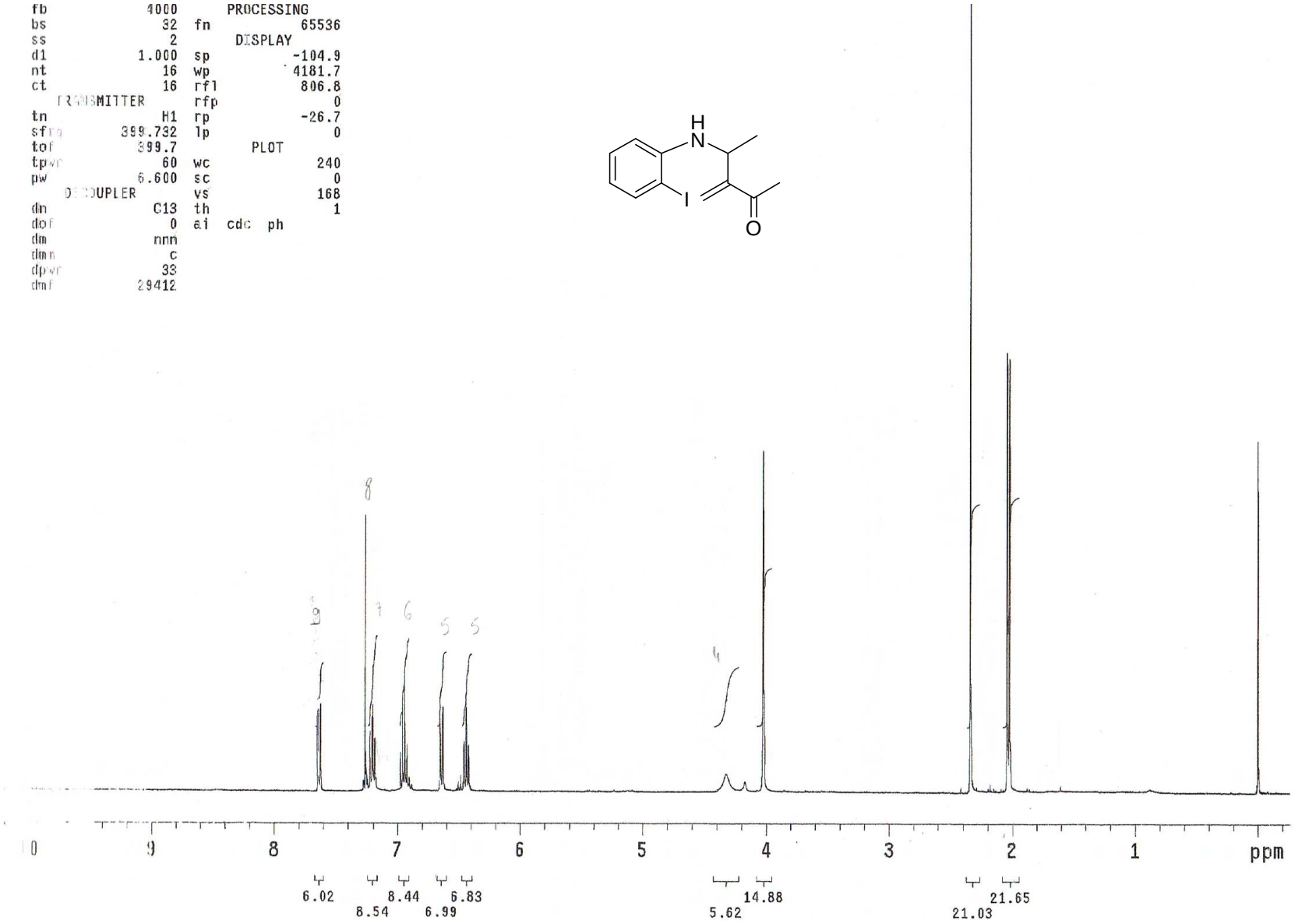
**Methyl 3-(2-iodophenylamino)-2-methylenepentanoate (1d):** $^{1}$H NMR (400 MHz, $CDCl_3$)



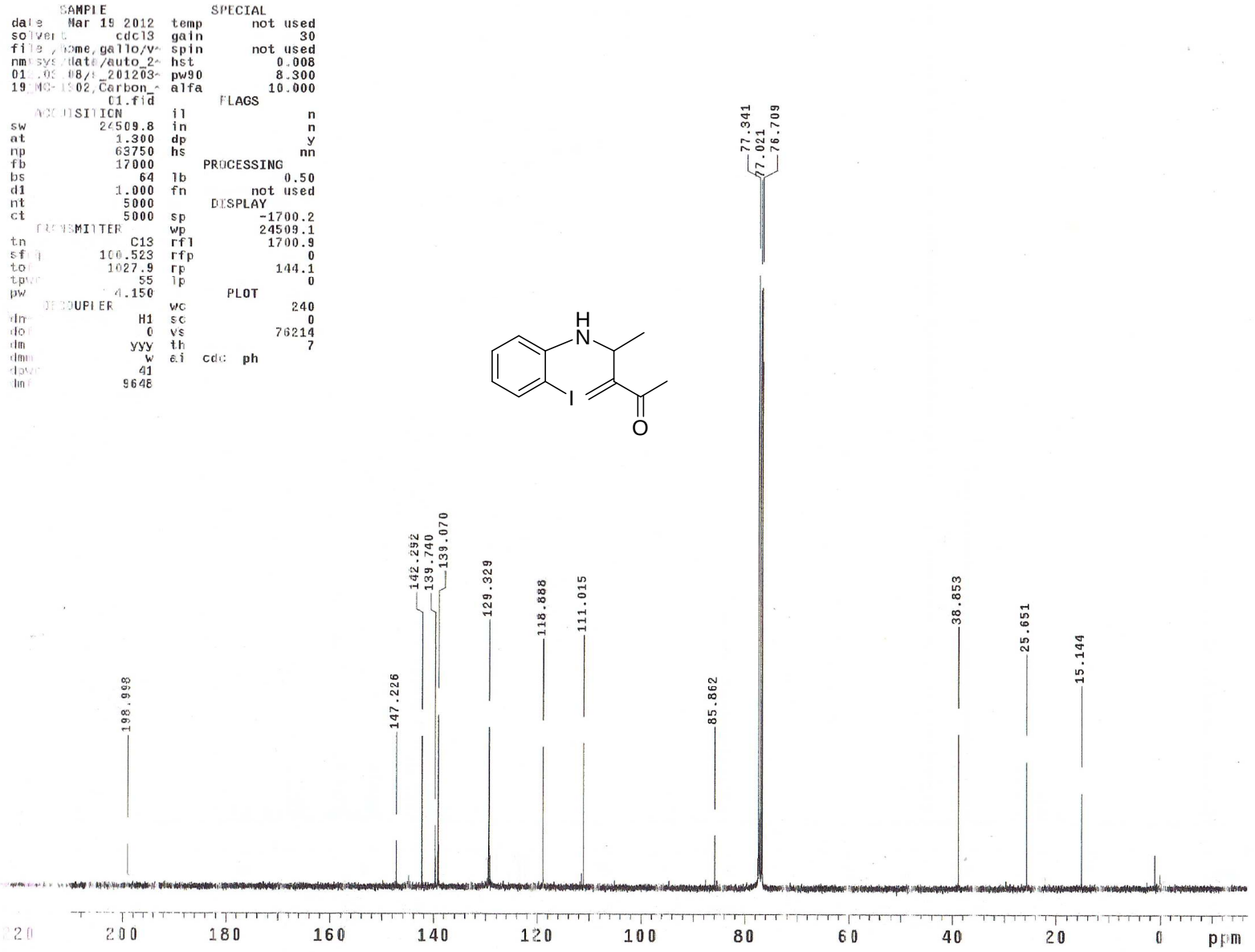
**Methyl 3-(2-iodophenylamino)-2-methylenepentanoate (1d):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



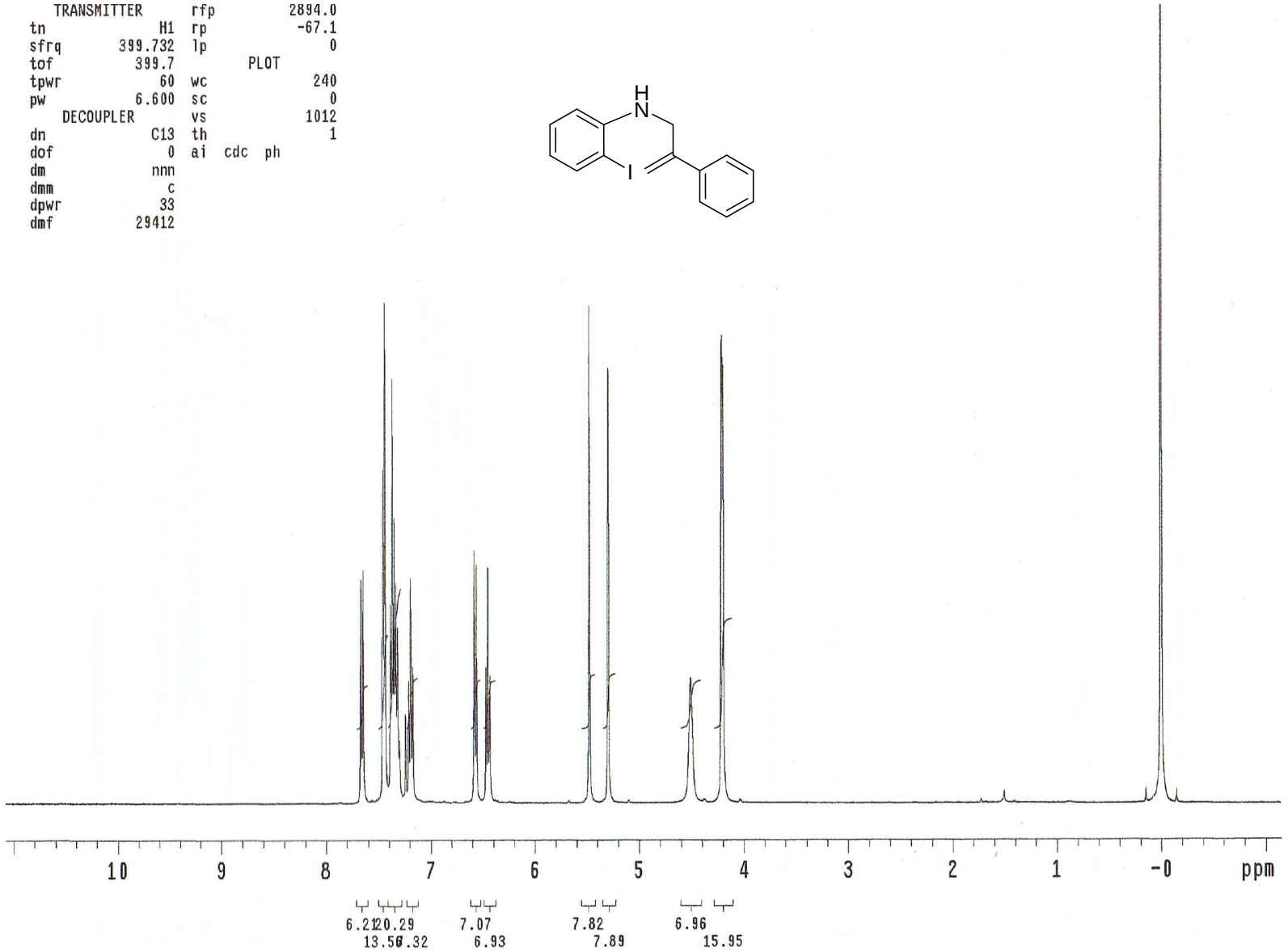
**4-(2-iodophenylamino)-3-methylenepentan-2-one (1e):** $^{1}$H NMR (400 MHz, $CDCl_3$)



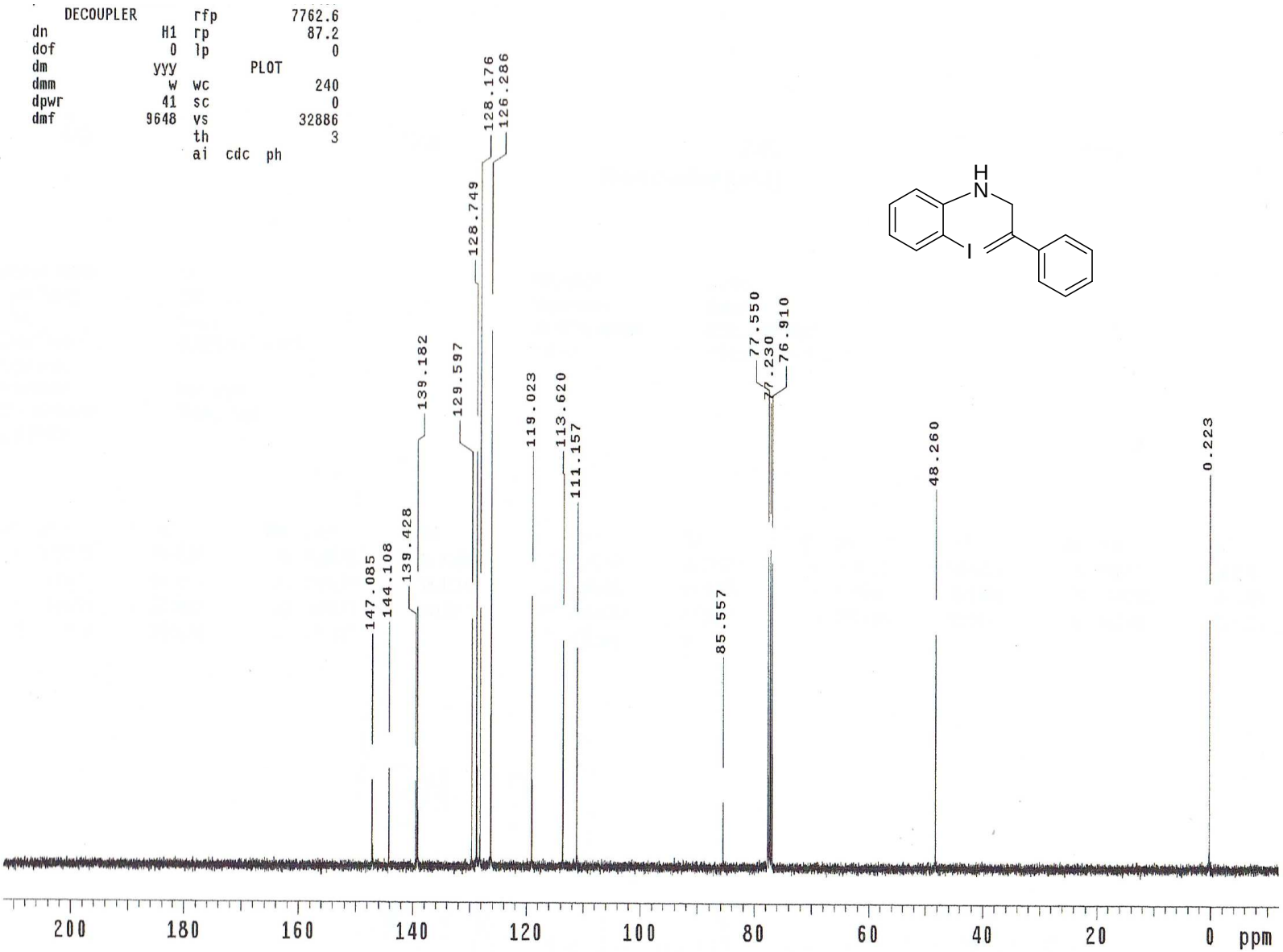
**4-(2-iodophenylamino)-3-methylenepentan-2-one (1e):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



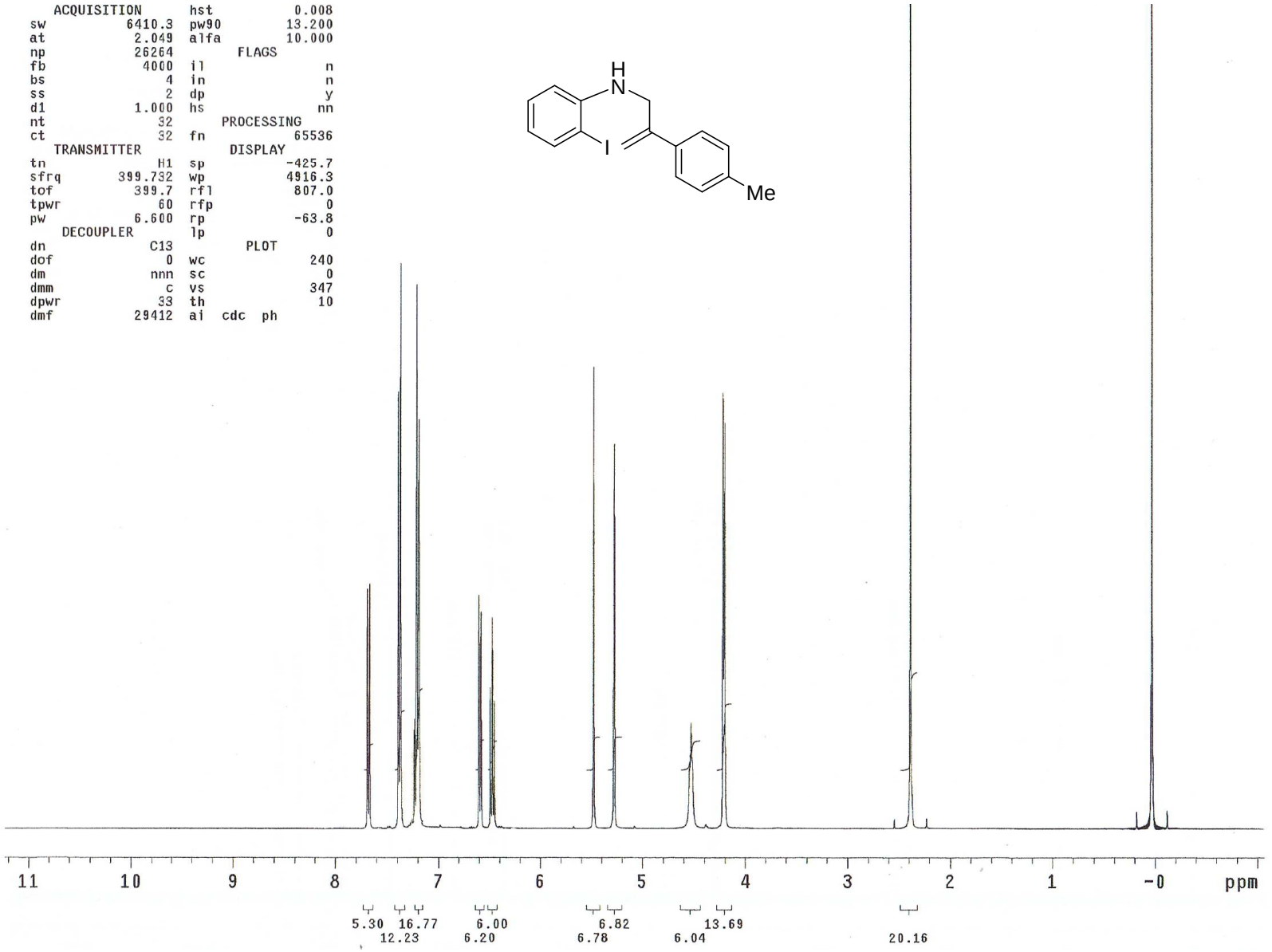
**2-Iodo-N-(2-phenylallyl)benzenamine (1f):** $^{1}$H NMR (400 MHz, $CDCl_3$)



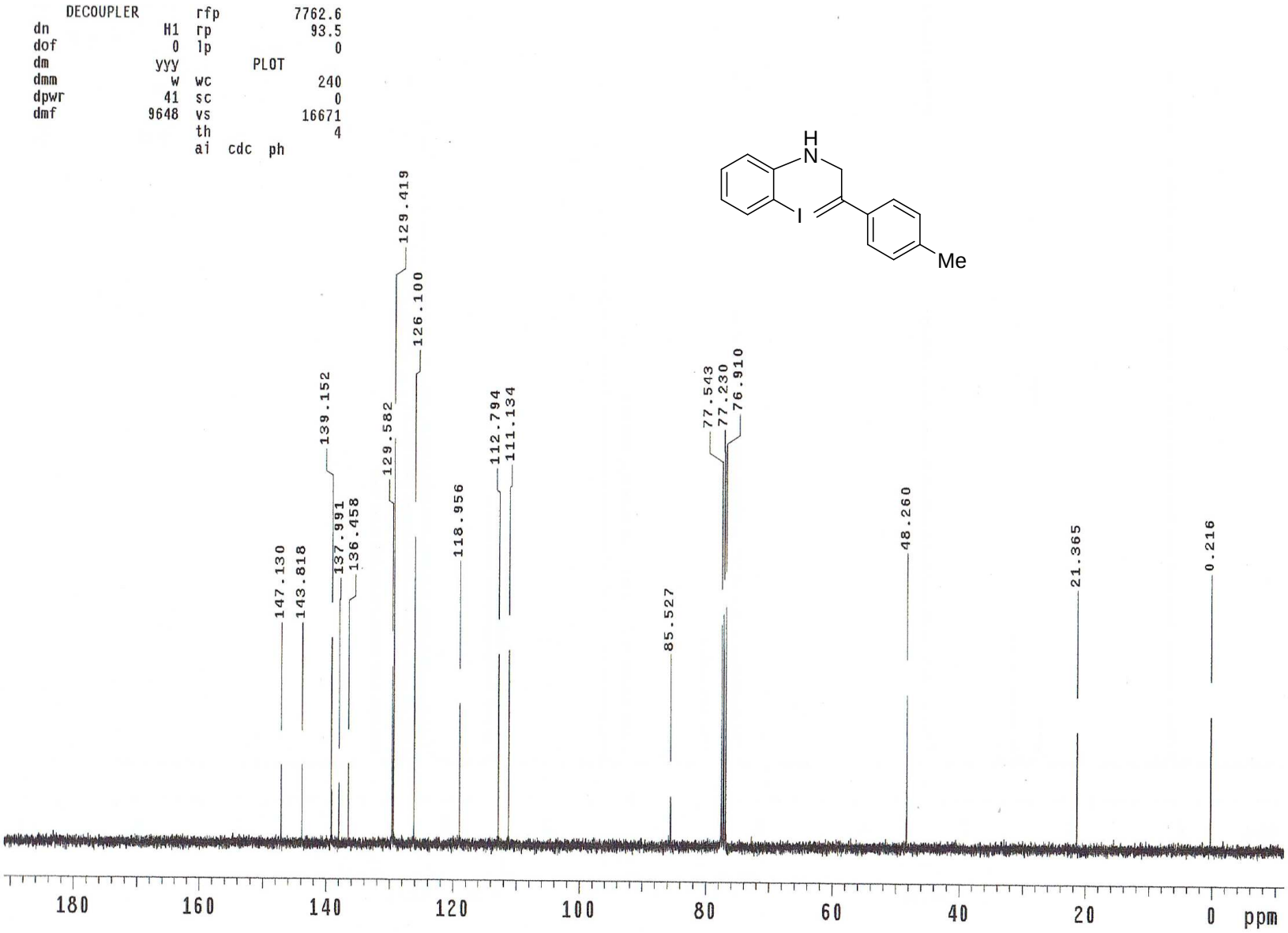
**2-Iodo-N-(2-phenylallyl)benzenamine (1f):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



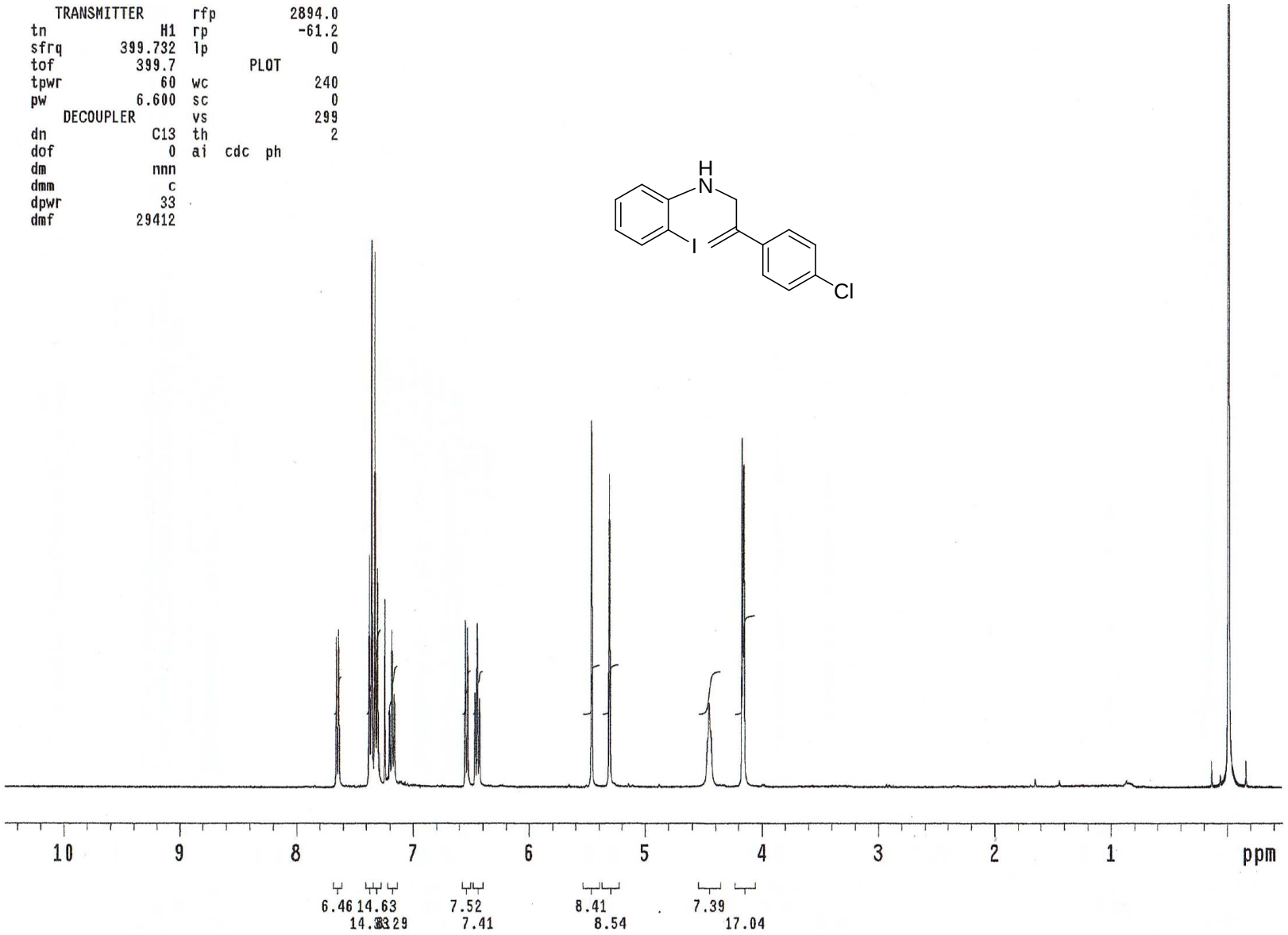
**2-Iodo-N-(2-p-tolylallyl)benzenamine (1g):** $^{1}$H NMR (400 MHz, $CDCl_3$)



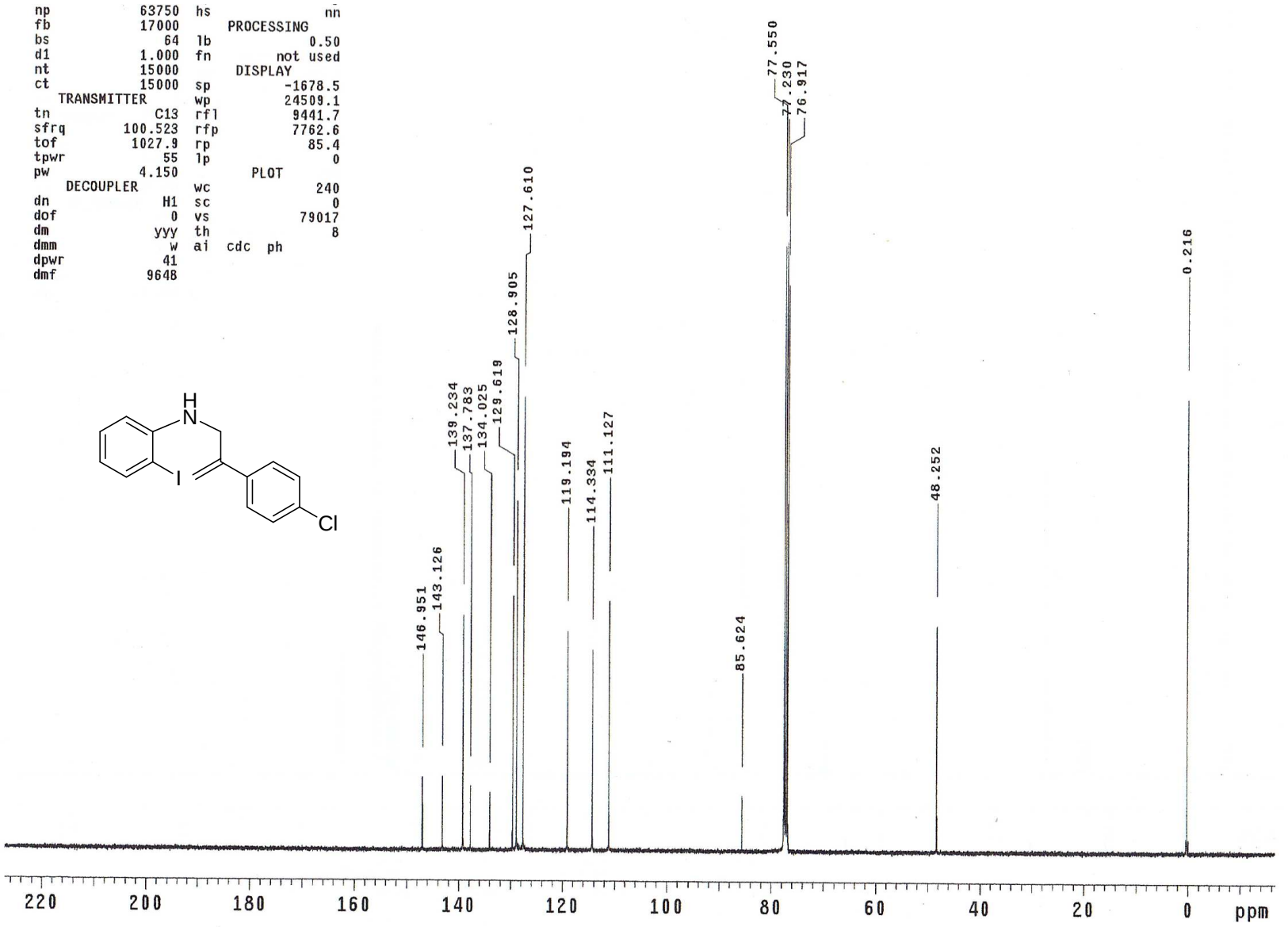
**2-Iodo-N-(2-p-tolylallyl)benzenamine (1g):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



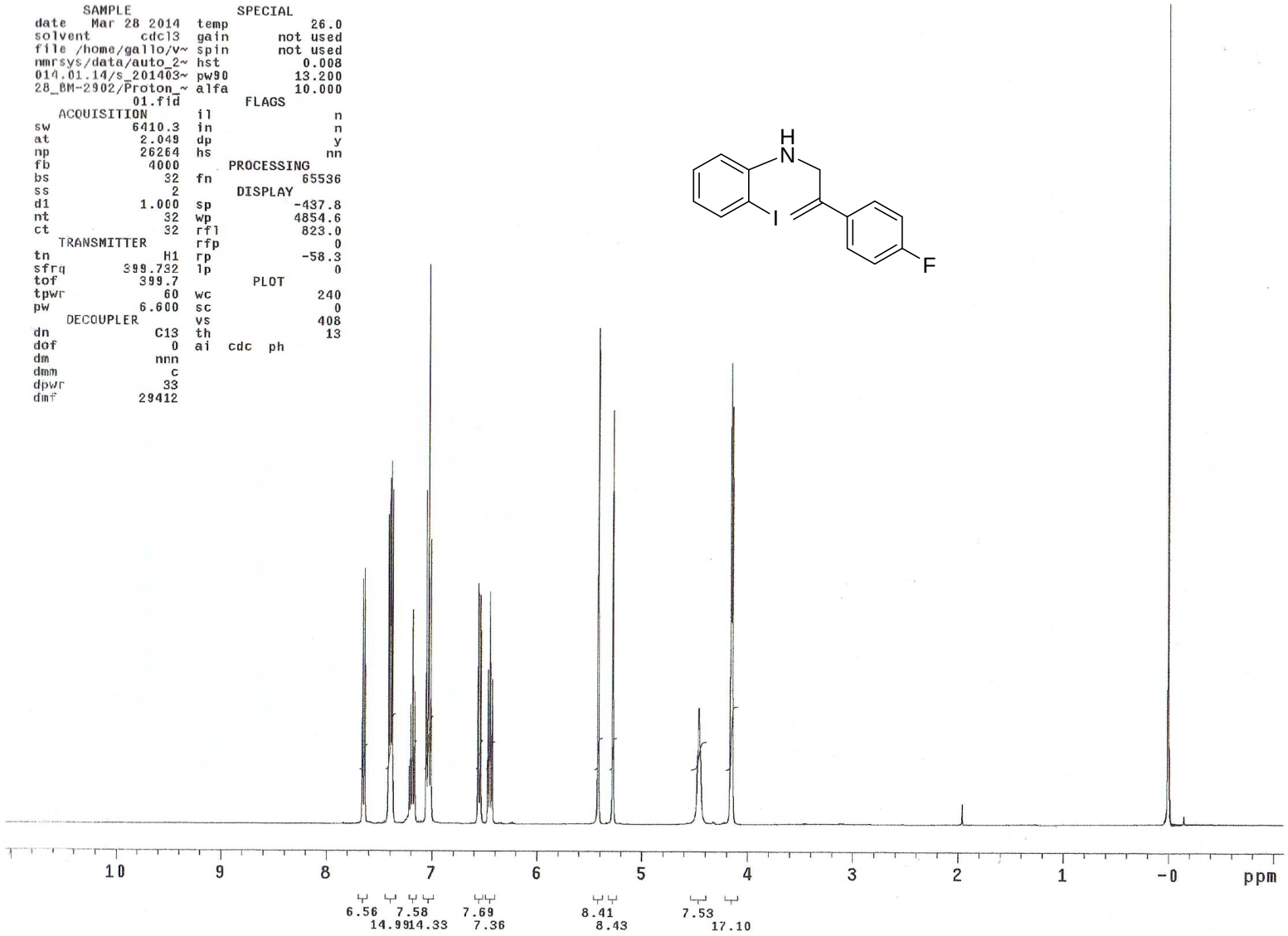
**N-(2-(4-chlorophenyl)allyl)-2-iodobenzenamine (1h):** $^{1}$H NMR (400 MHz, $CDCl_3$)



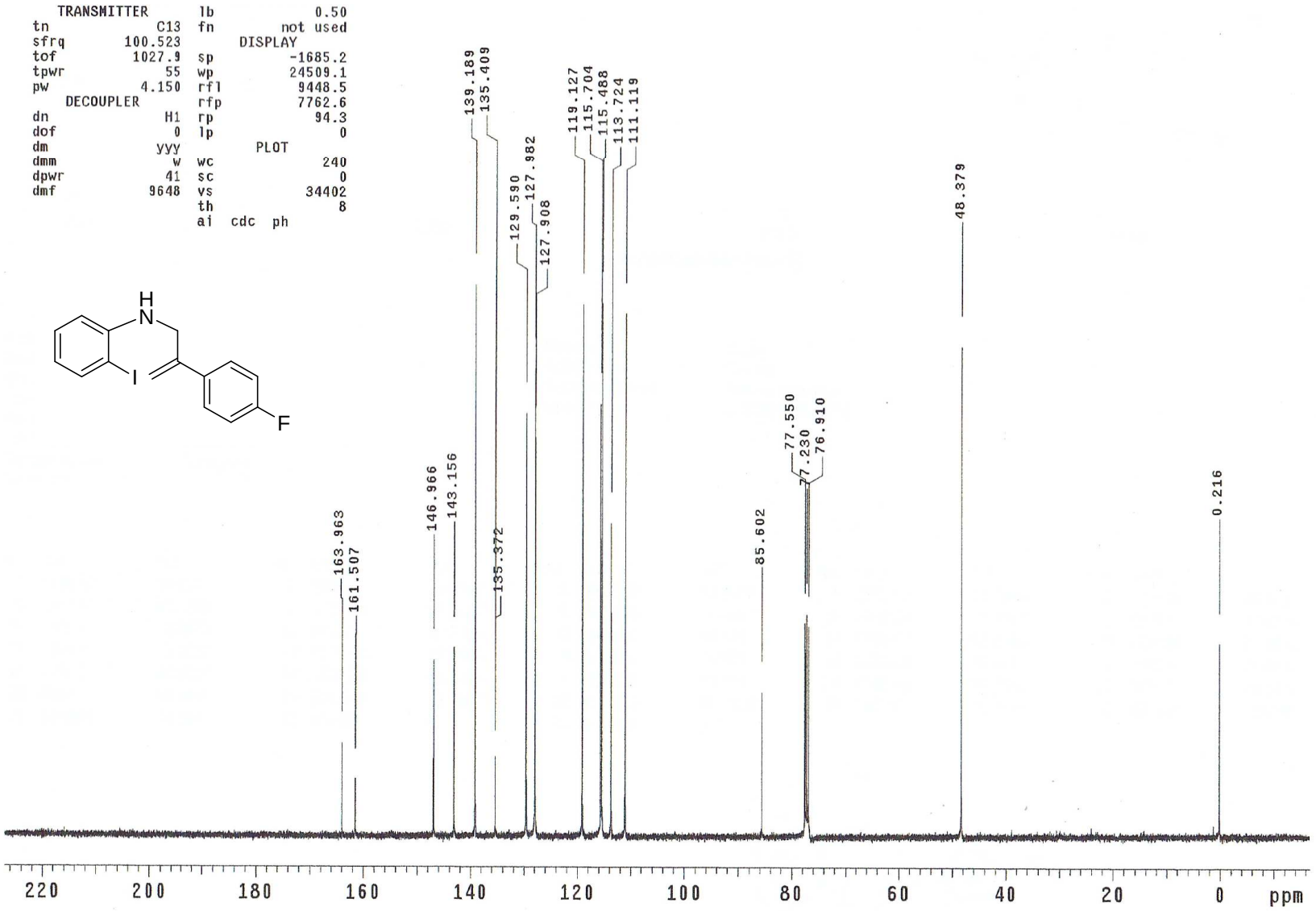
**N-(2-(4-chlorophenyl)allyl)-2-iodobenzenamine (1h):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



**N-(2-(4-fluorophenyl)allyl)-2-iodobenzenamine (1i):** $^{1}$H NMR (400 MHz, $CDCl_3$)

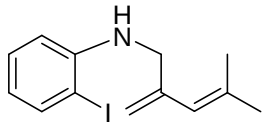


**N-(2-(4-fluorophenyl)allyl)-2-iodobenzenamine (1i):** $^{13}C$ NMR (100 MHz, $CDCl_3$)

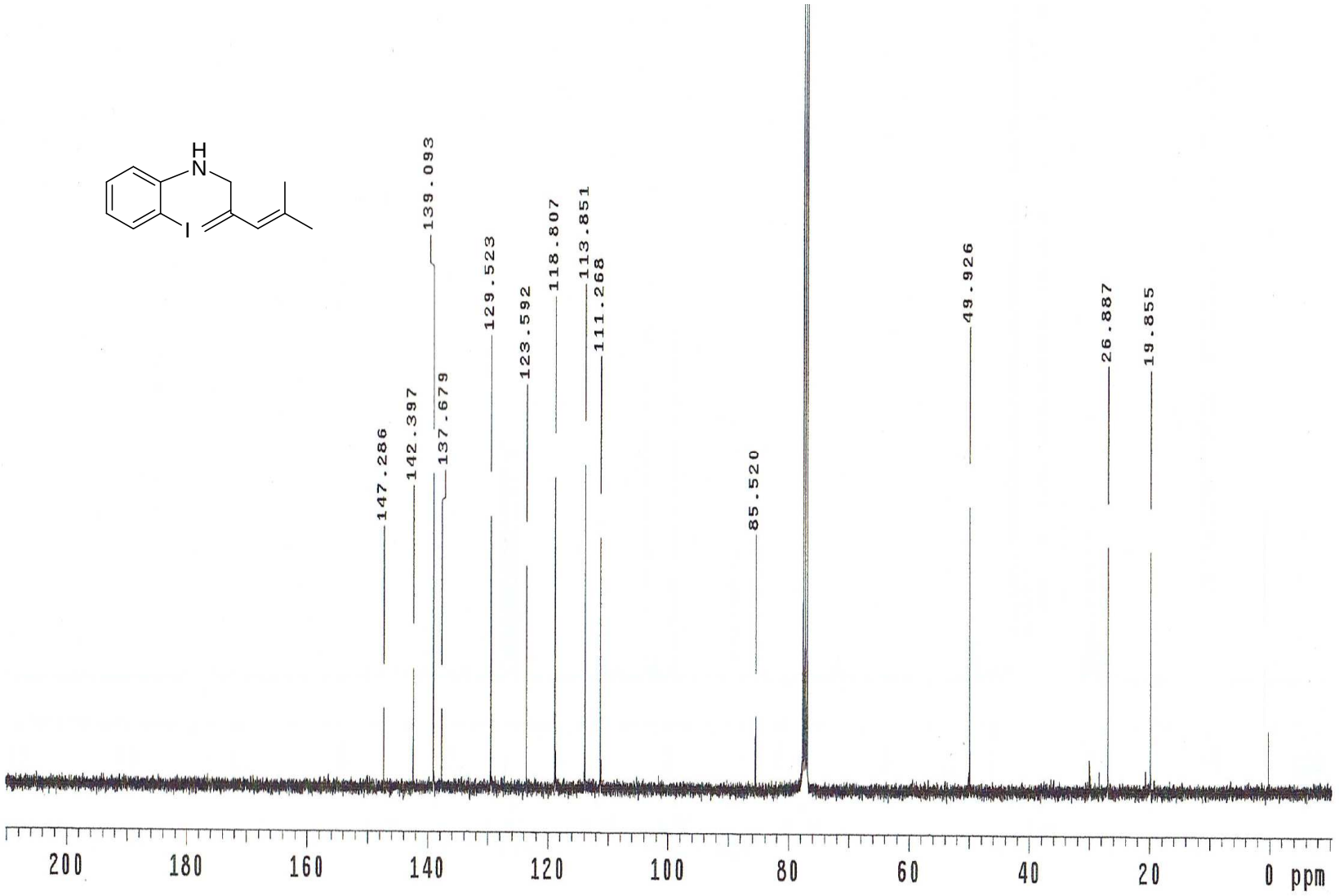


**2-Iodo-N-(4-methyl-2-methylenepent-3-enyl)benzenamine (1j):** $^{1}$H NMR (400 MHz, $CDCl_3$)

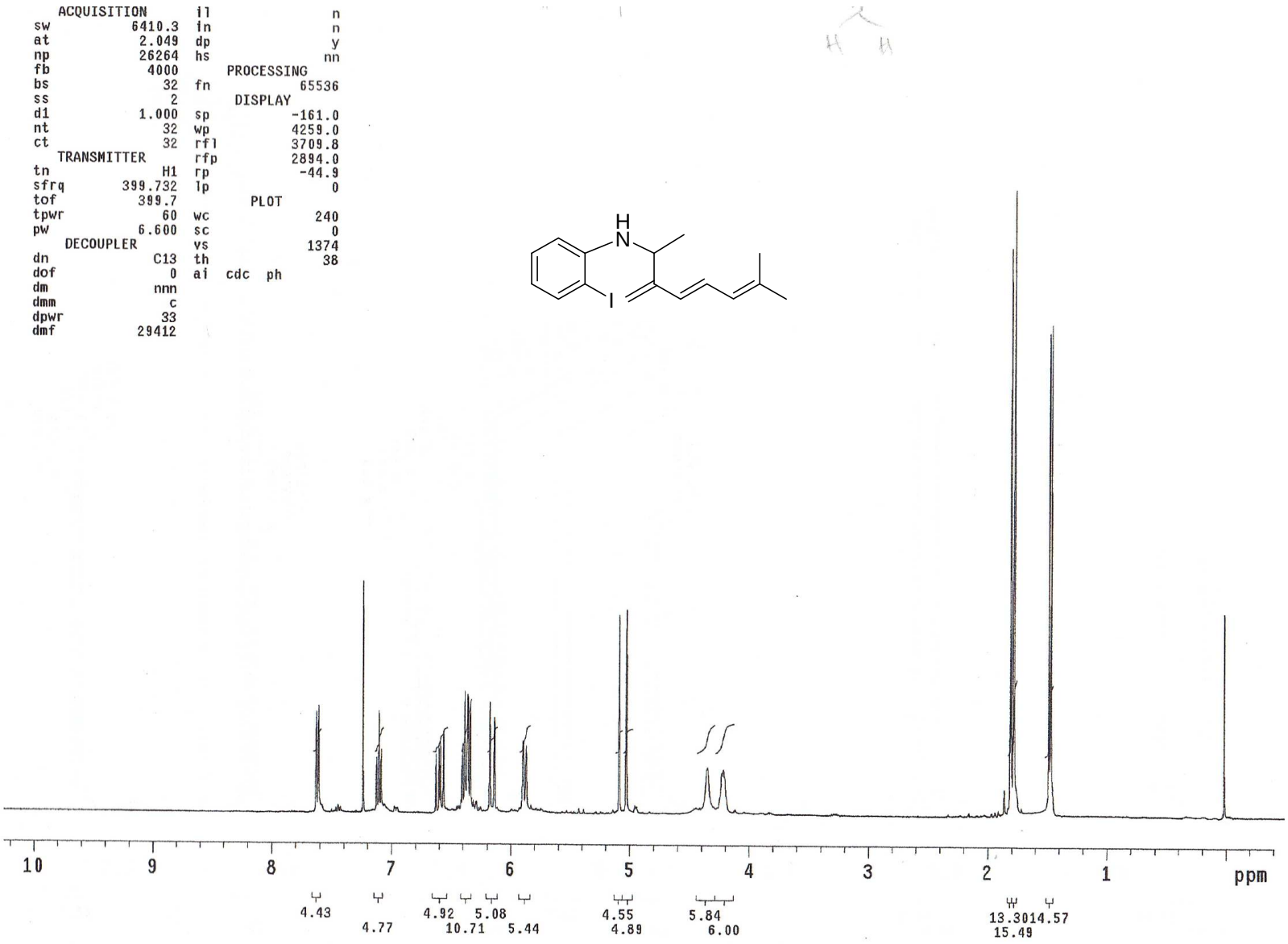
| ACQUISITION | | | |
|---|---|---|---|
| sw | 6410.3 | hst | 0.008 |
| at | 2.049 | pw90 | 13.500 |
| np | 26264 | alfa | 10.000 |
| fb | 4000 | FLAGS | |
| bs | 4 | il | n |
| ss | 2 | in | n |
| d1 | 1.000 | dp | y |
| nt | 32 | hs | nn |
| ct | 32 | PROCESSING | |
| TRANSMITTER | | fn | 65536 |
| tn | H1 | DISPLAY | |
| sfrq | 399.732 | sp | -455.0 |
| tof | 399.7 | wp | 4900.0 |
| tpwr | 58 | rfl | 809.9 |
| pw | 6.750 | rfp | 0 |
| DECOUPLER | | rp | -61.6 |
| dn | C13 | lp | 0 |
| dof | 0 | PLOT | |
| dm | nnn | wc | 240 |
| dmm | c | sc | 0 |
| dpwr | 36 | vs | 369 |
| dmf | 29412 | th | 9 |
| | | ai cdc ph | |



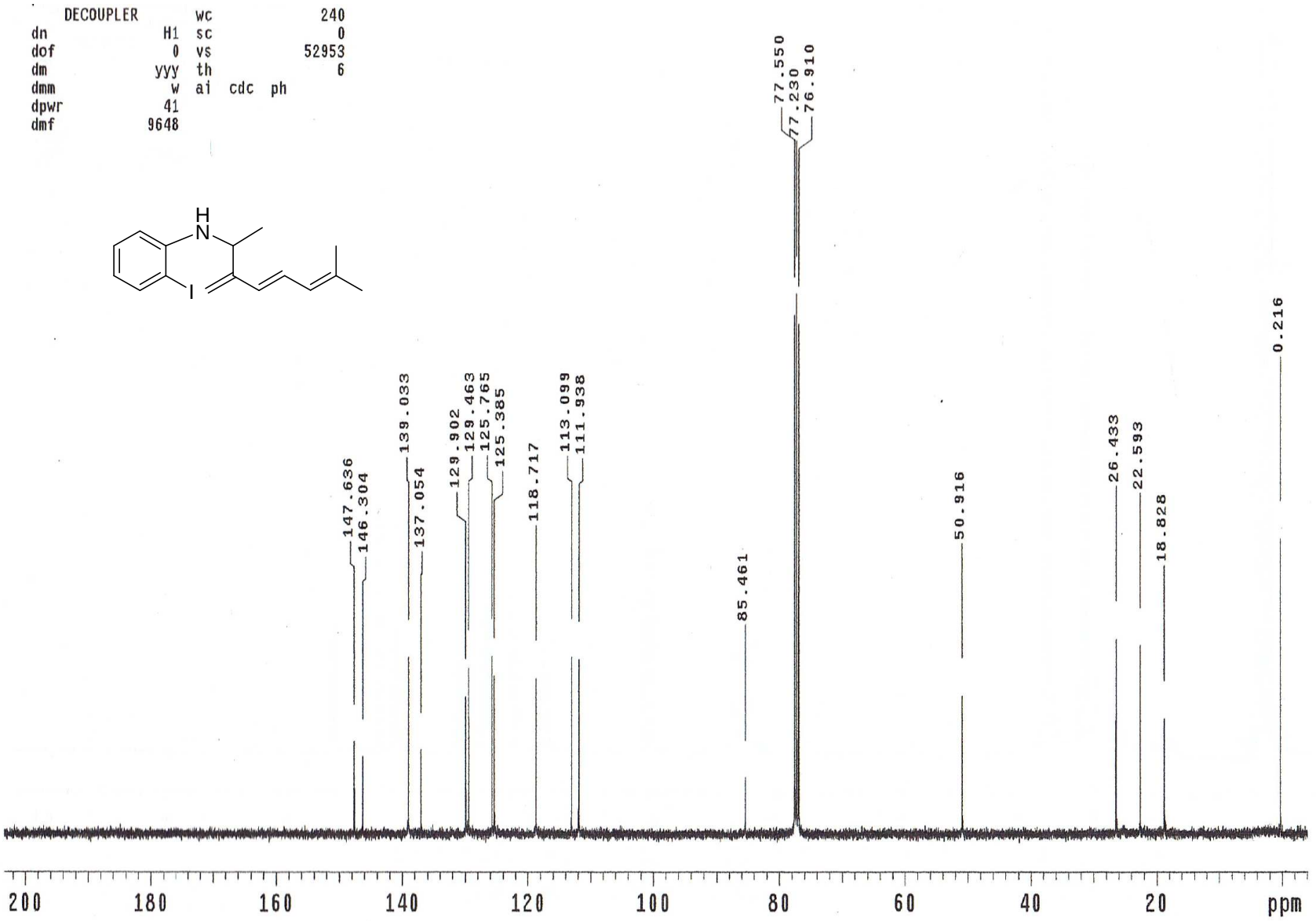
**2-Iodo-N-(4-methyl-2-methylenepent-3-enyl)benzenamine (1j):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



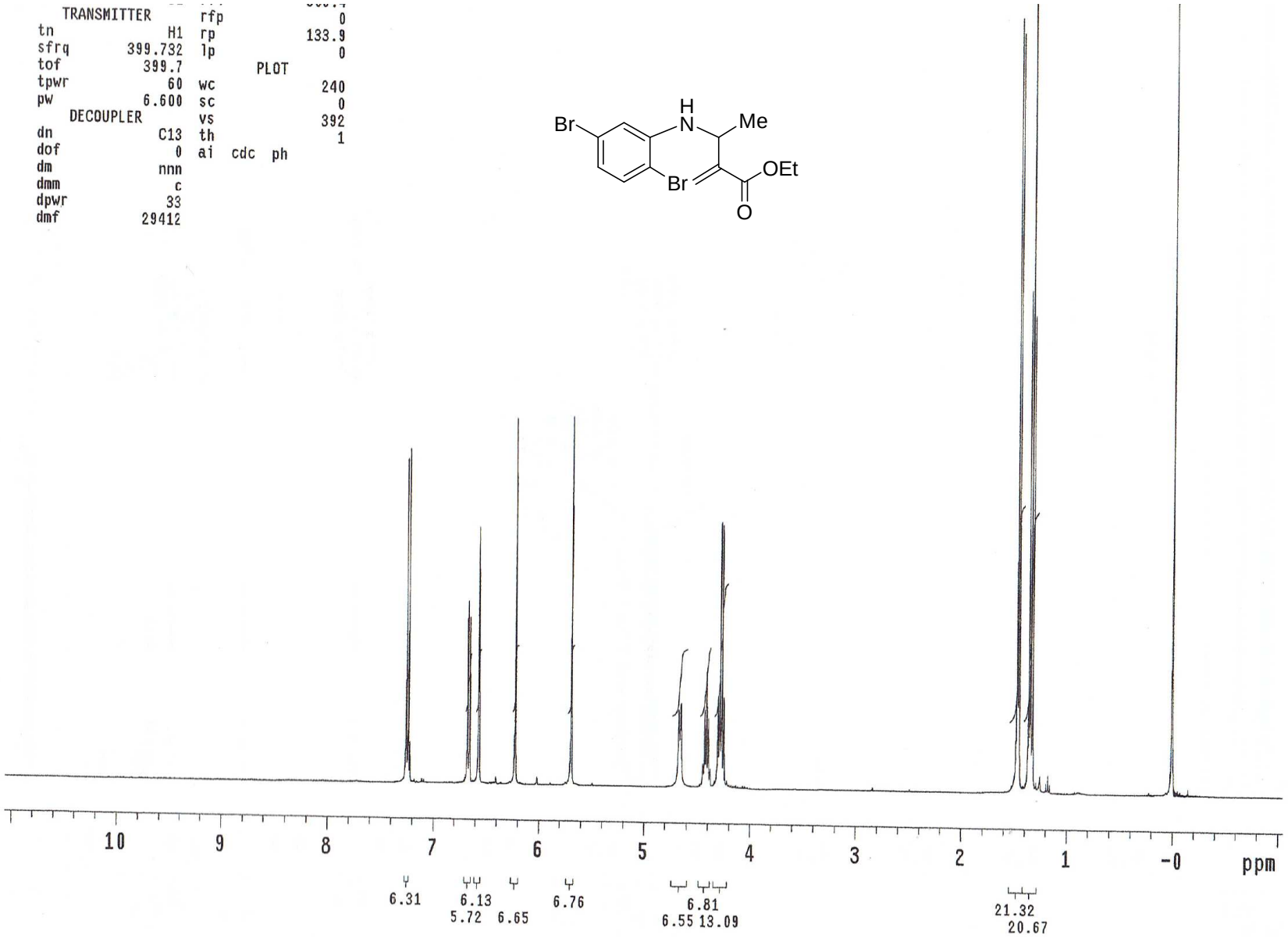
**2-Iodo-N-((E)-7-methyl-3-methyleneocta-4,6-dien-2-yl)benzenamine (1k):** $^{1}$H NMR (400 MHz, $CDCl_3$)



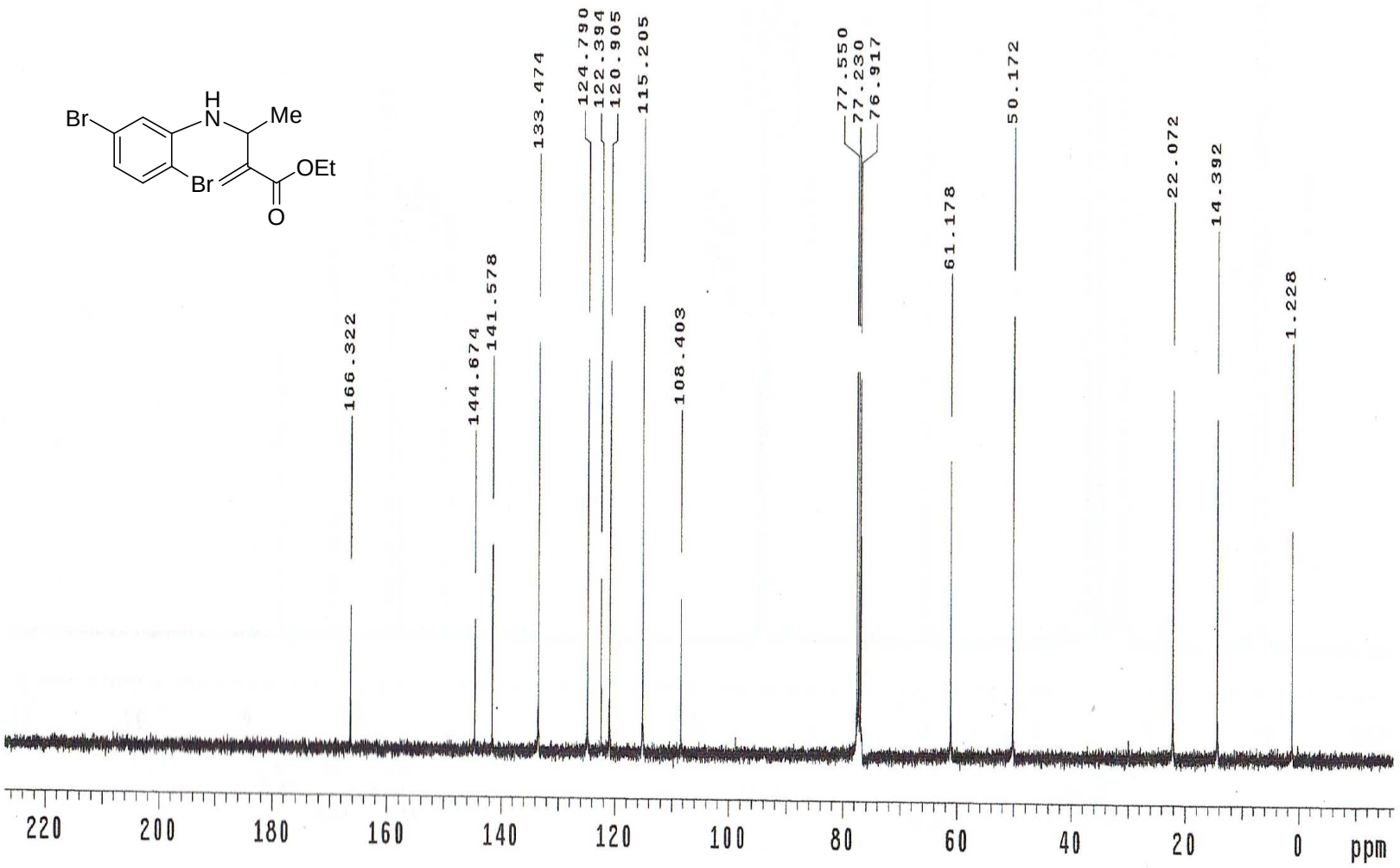
**2-Iodo-N-((E)-7-methyl-3-methyleneocta-4,6-dien-2-yl)benzenamine (1k):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



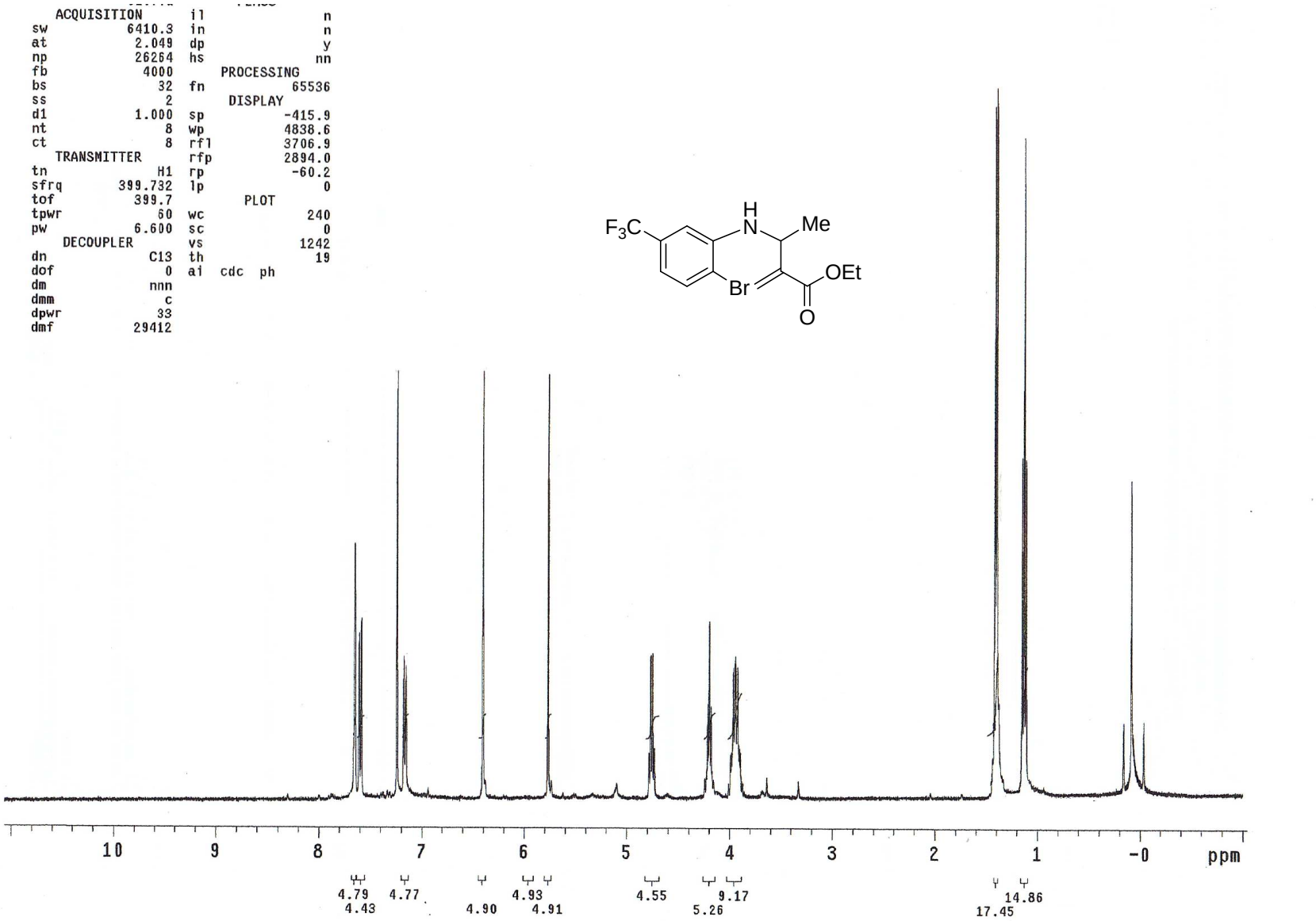
**Ethyl 3-(2,5-dibromophenylamino)-2-methylenebutanoate (3b):** $^{1}H$ NMR (400 MHz, $CDCl_3$)



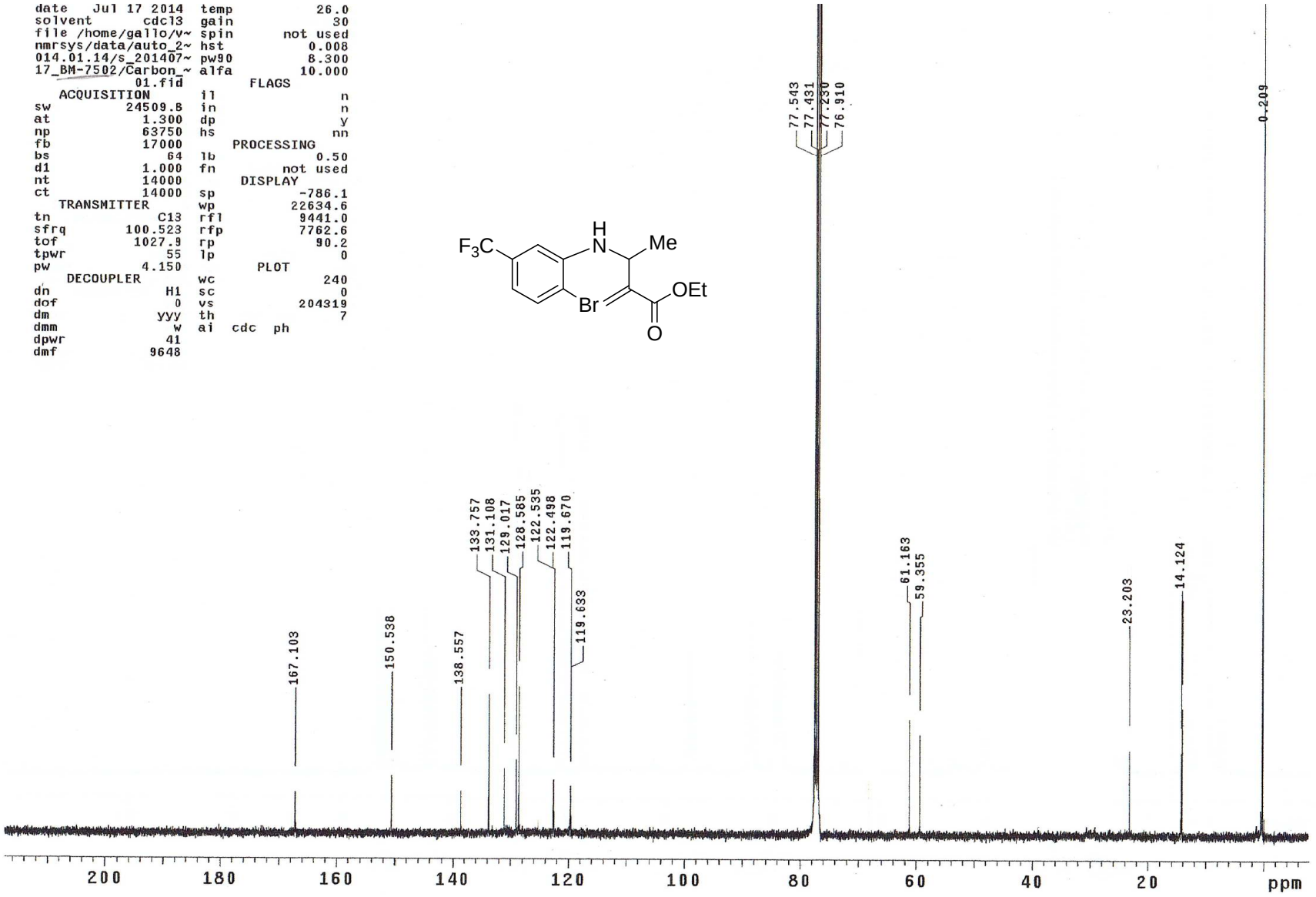
**Ethyl 3-(2,5-dibromophenylamino)-2-methylenebutanoate (3b):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



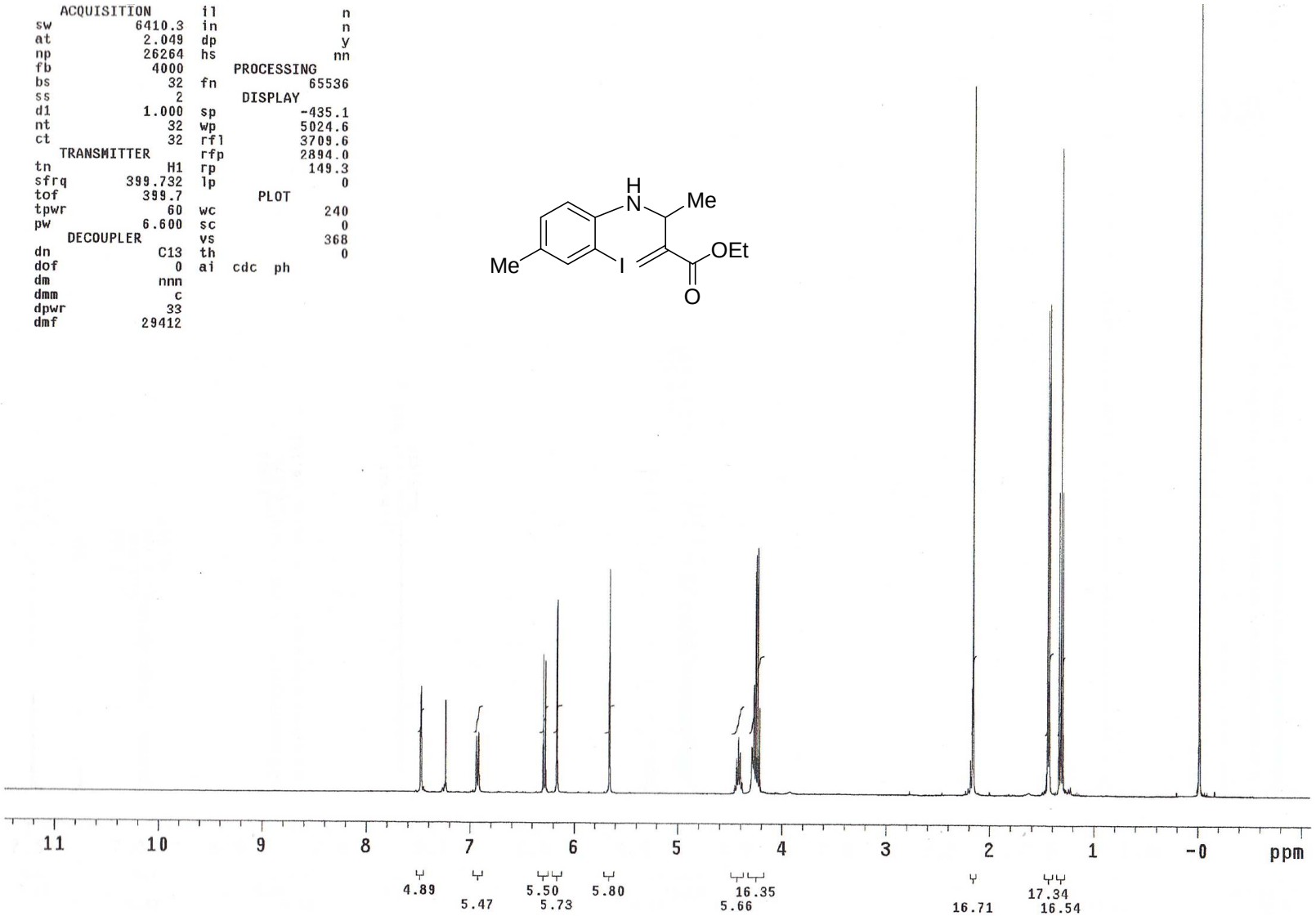
**Ethyl 3-(2-bromo-5-(trifluoromethyl)phenylamino)-2-methylenebutanoate (4b):** $^{1}$H NMR (400 MHz, $CDCl_3$)



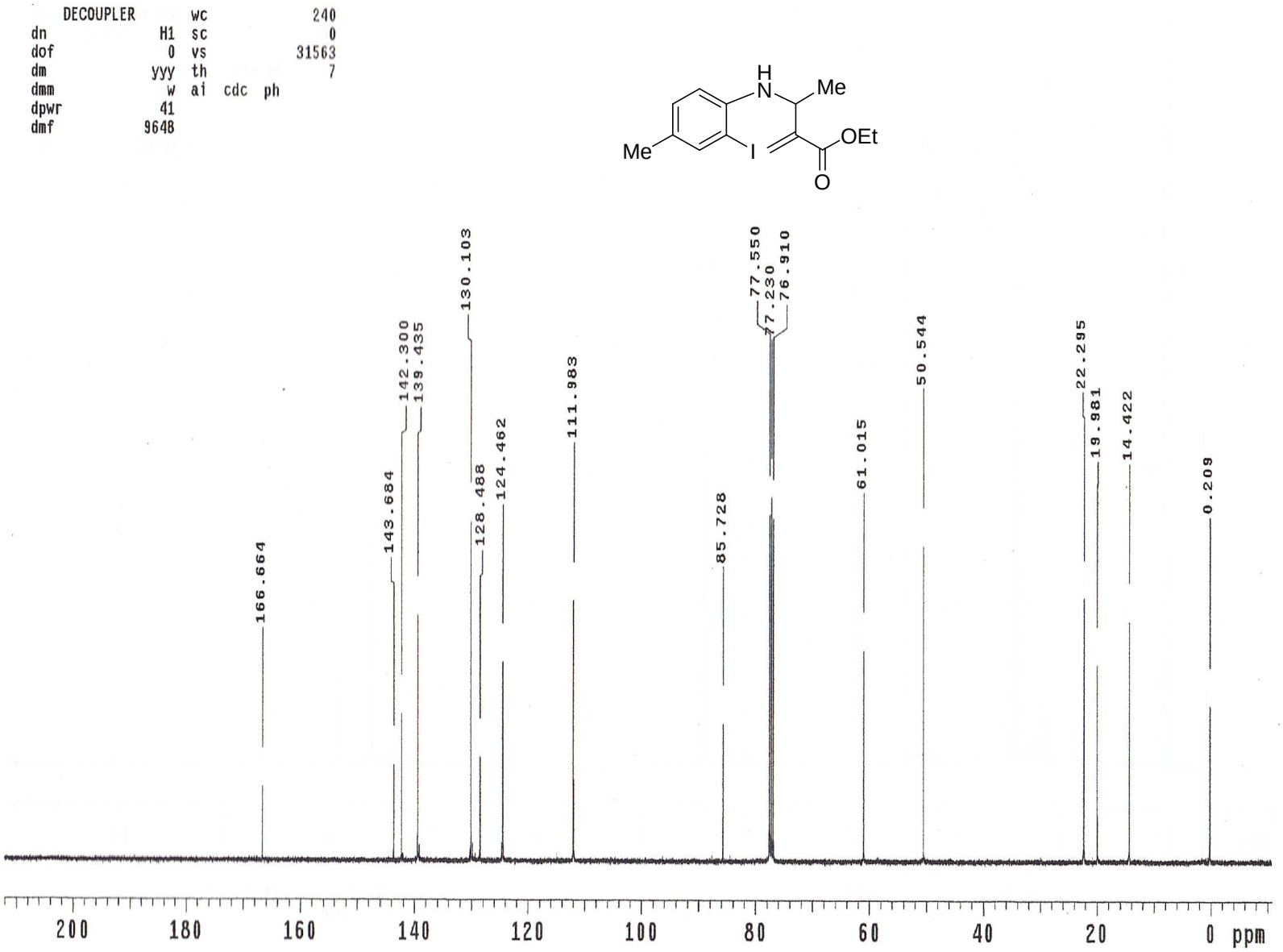
**Ethyl 3-(2-bromo-5-(trifluoromethyl)phenylamino)-2-methylenebutanoate (4b):** $^{13}$C NMR (100 MHz, $CDCl_3$)



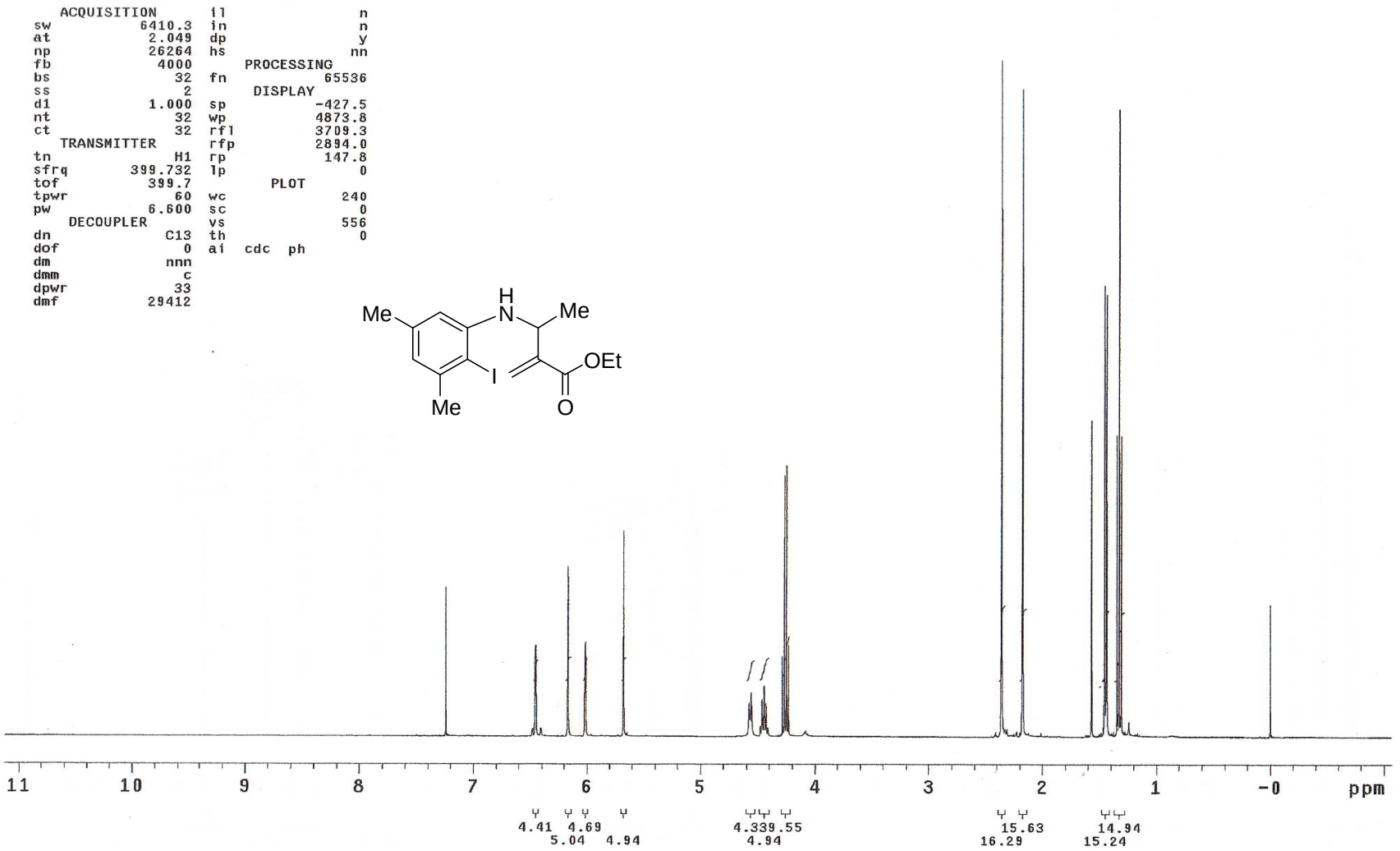
**Ethyl 3-(2-iodo-4-methylphenylamino)-2-methylenebutanoate (5b):** $^{1}$H NMR (400 MHz, $CDCl_3$)



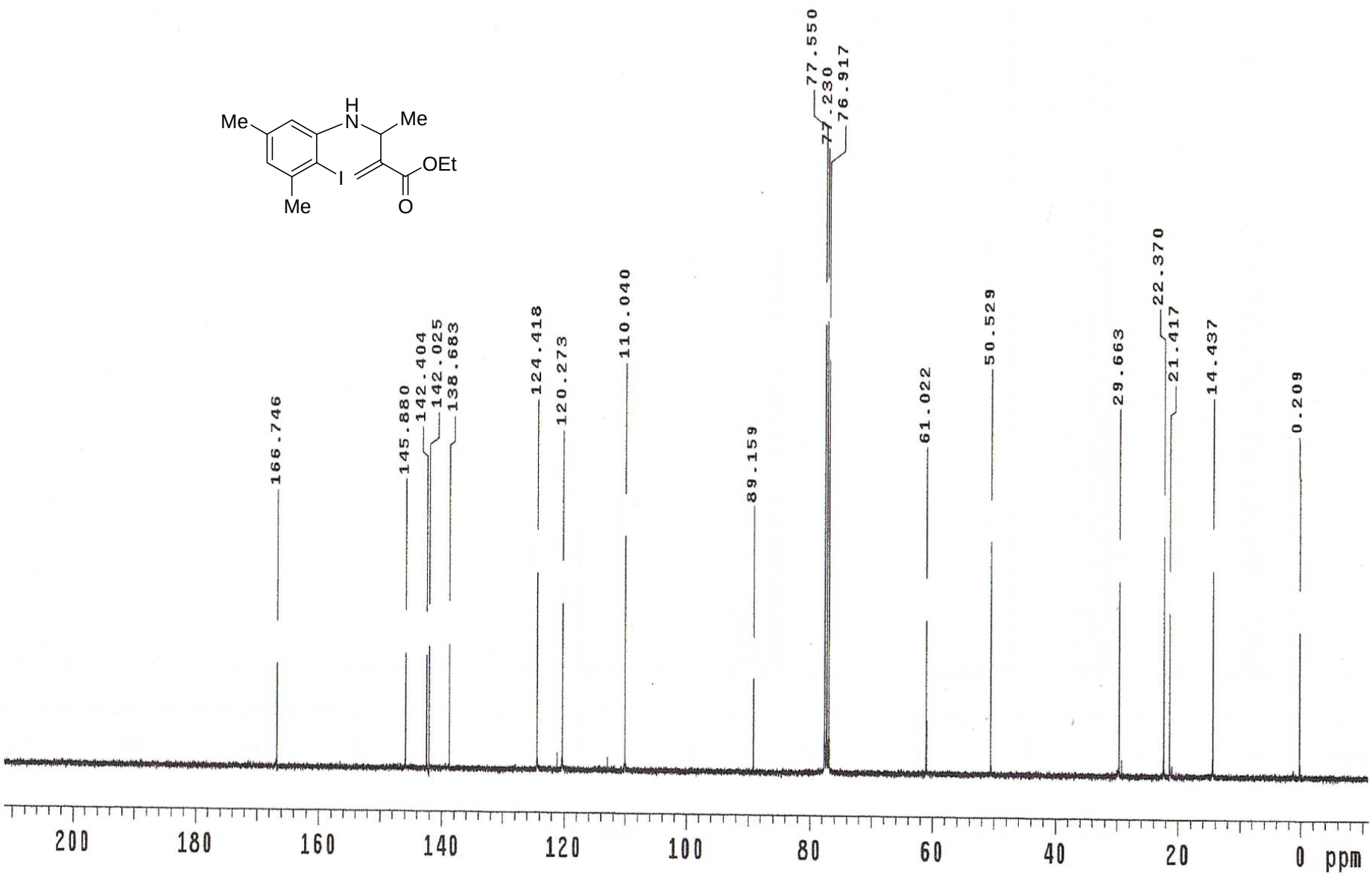
**Ethyl 3-(2-iodo-4-methylphenylamino)-2-methylenebutanoate (5b):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



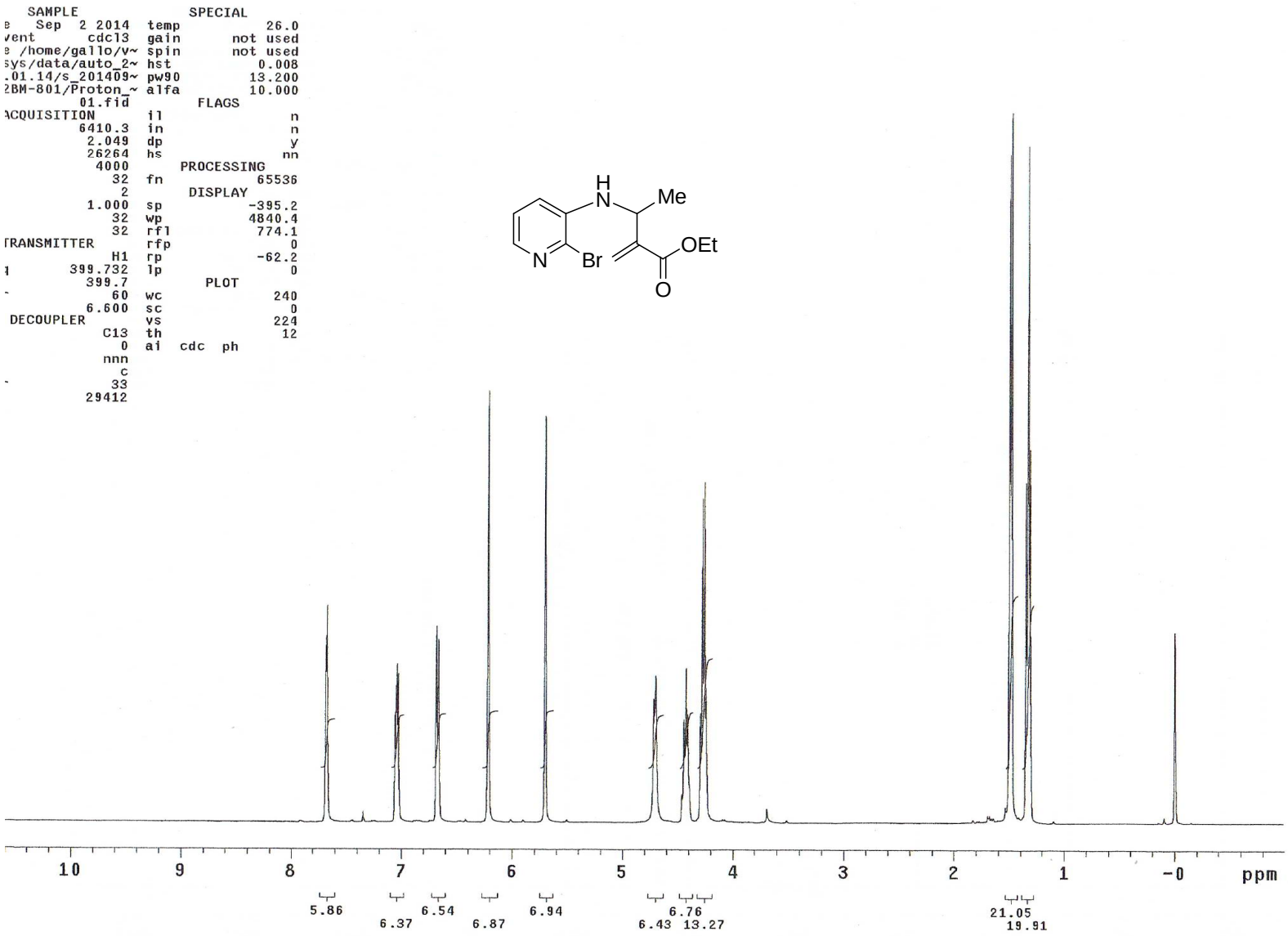
**Ethyl 3-(2-iodo-3,5-dimethylphenylamino)-2-methylenebutanoate (6b):** $^{1}$H NMR (400 MHz, $CDCl_3$)



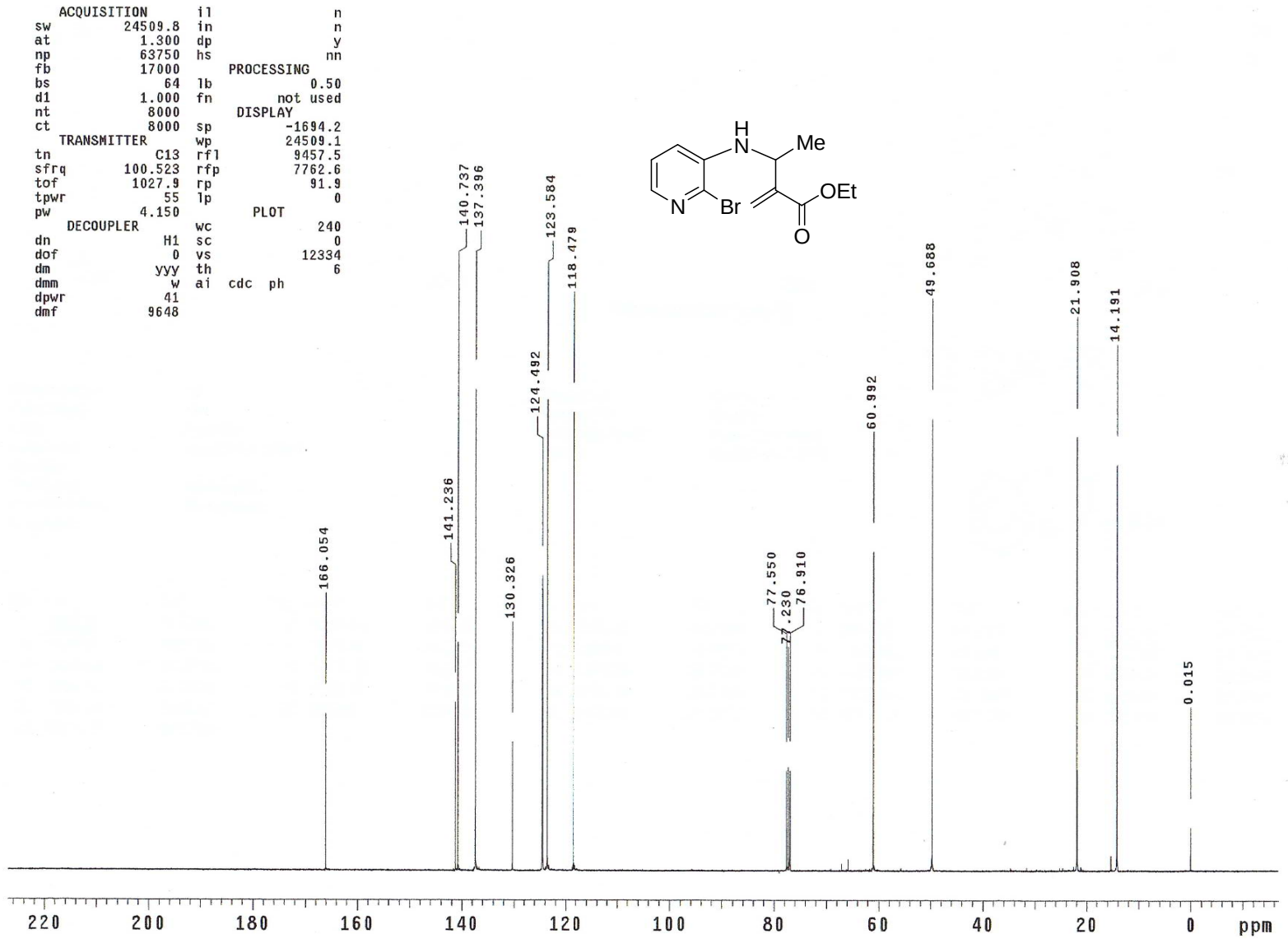
**Ethyl 3-(2-iodo-3,5-dimethylphenylamino)-2-methylenebutanoate (6b):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



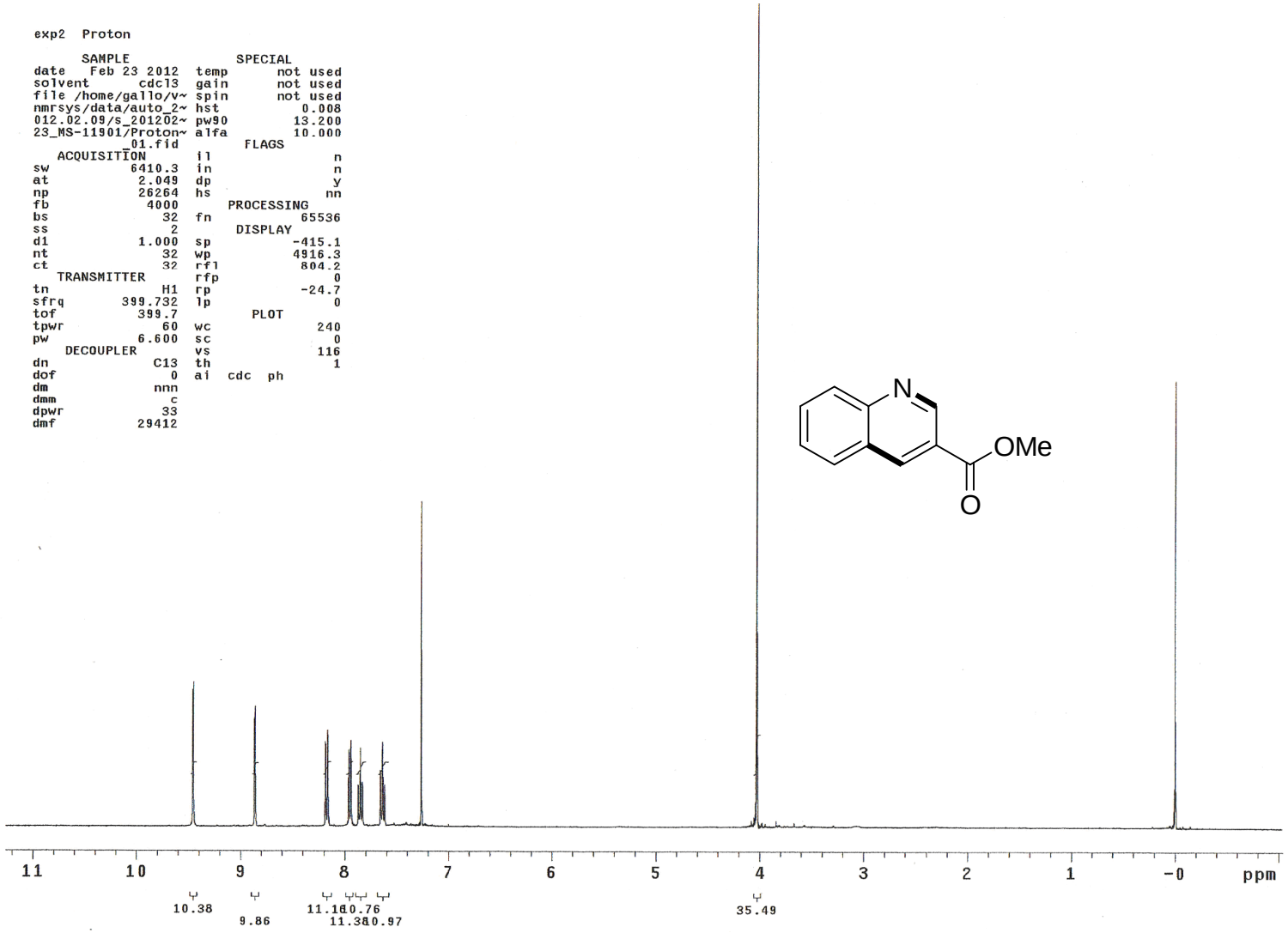
**Ethyl 3-(2-bromopyridin-3-ylamino)-2-methylenebutanoate (7b):** $^{1}$H NMR (400 MHz, $CDCl_3$)



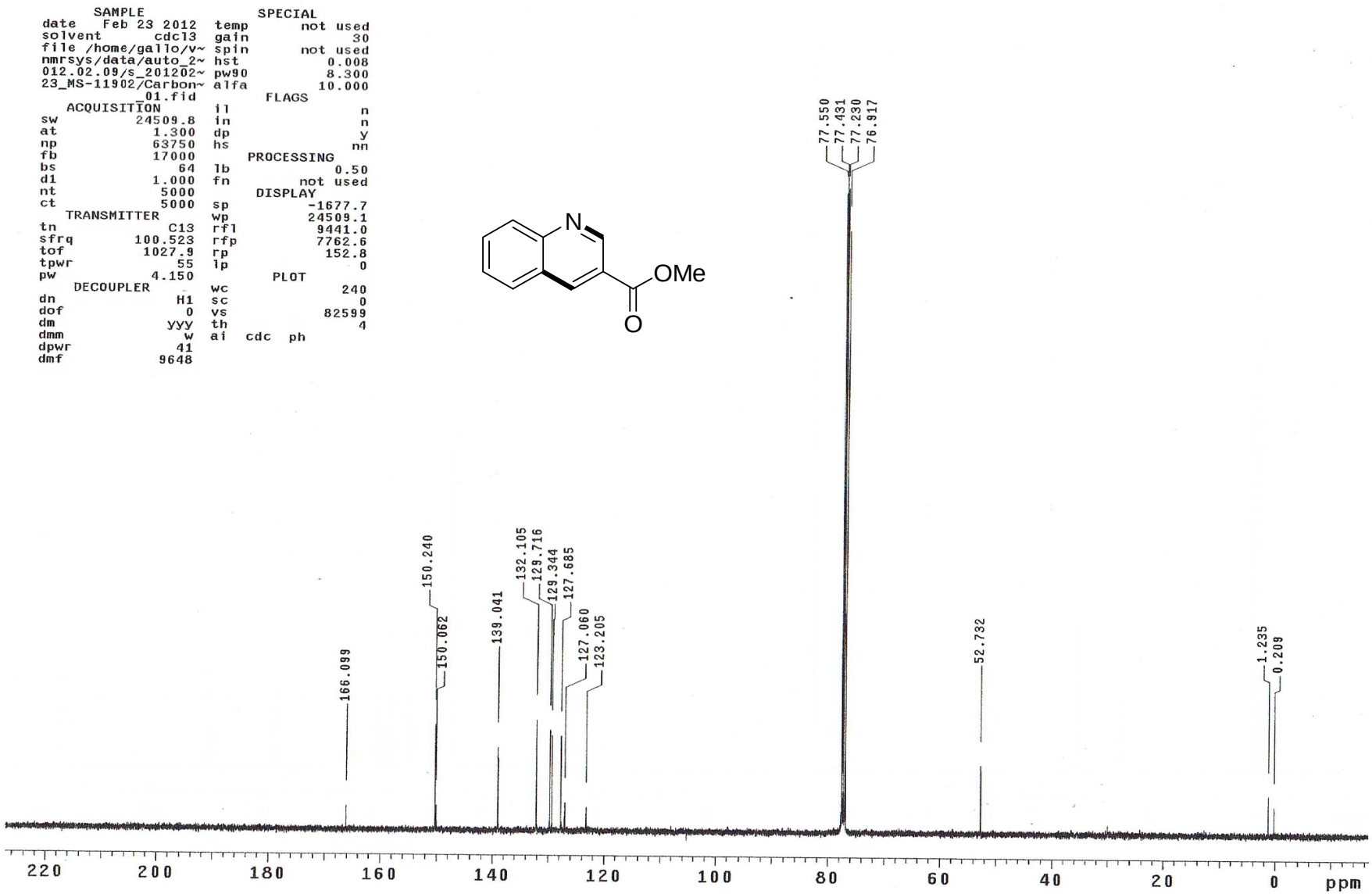
**Ethyl 3-(2-bromopyridin-3-ylamino)-2-methylenebutanoate (7b):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



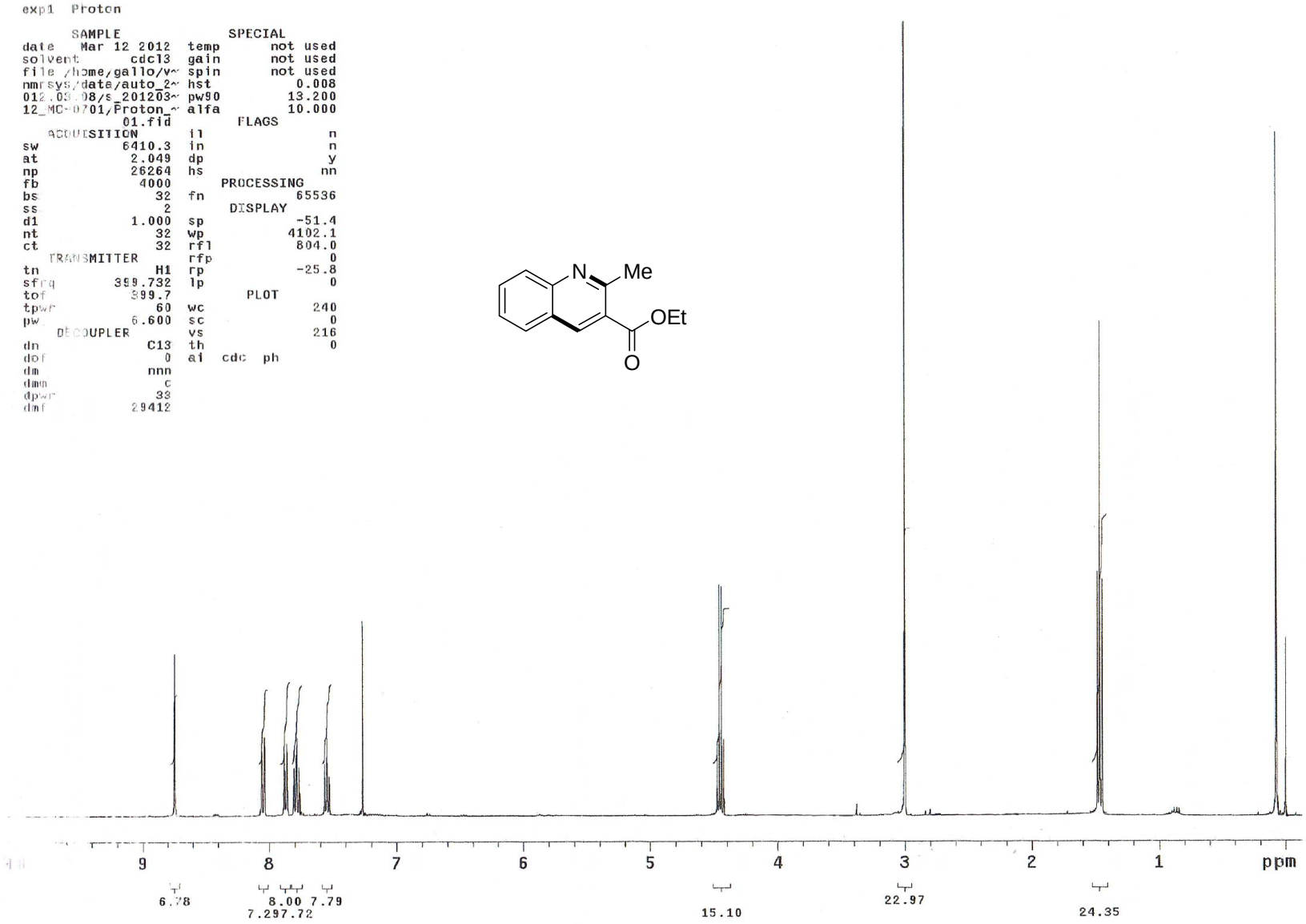
**Methyl quinoline-3-carboxylate (1a'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



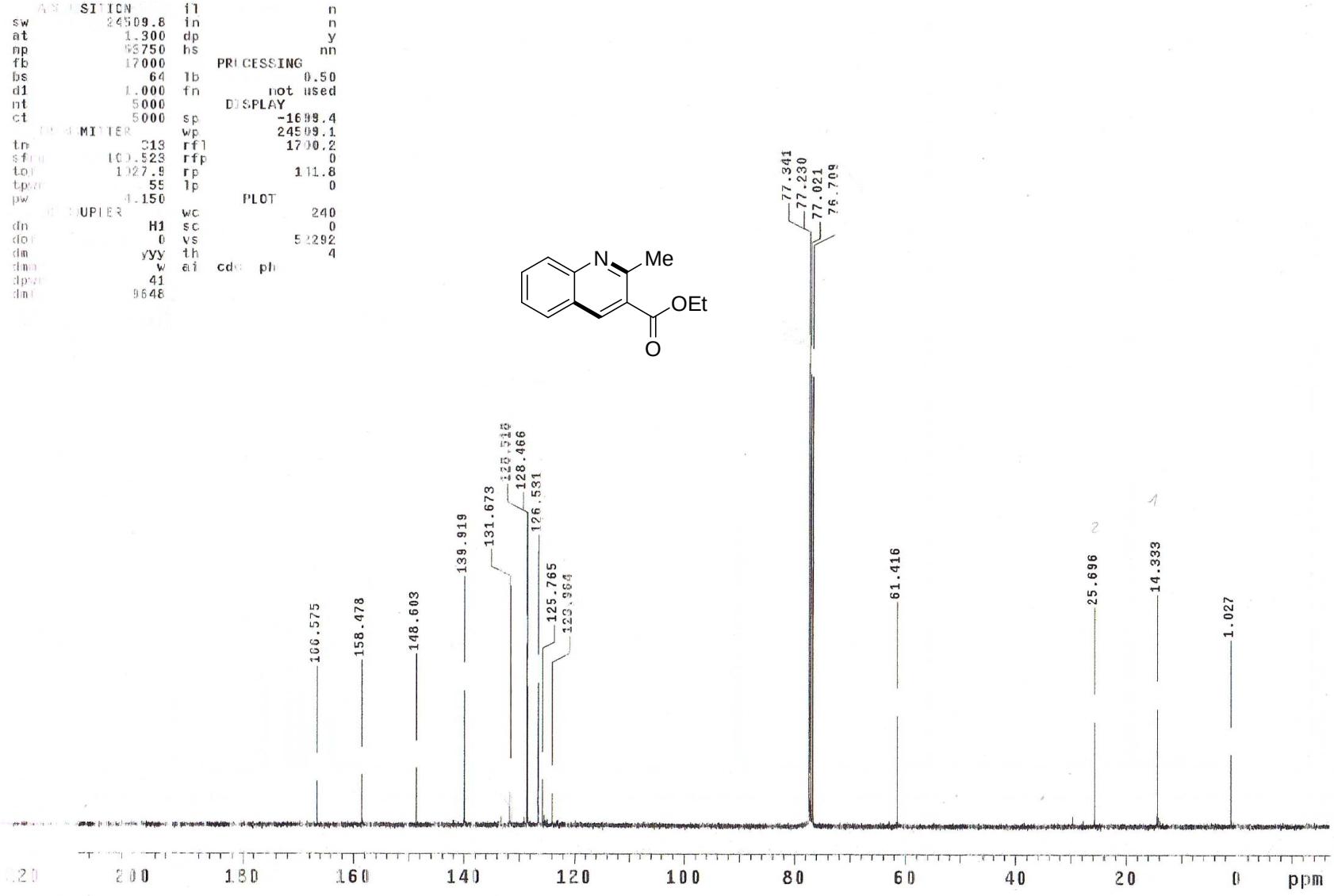
**Methyl quinoline-3-carboxylate (1a'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



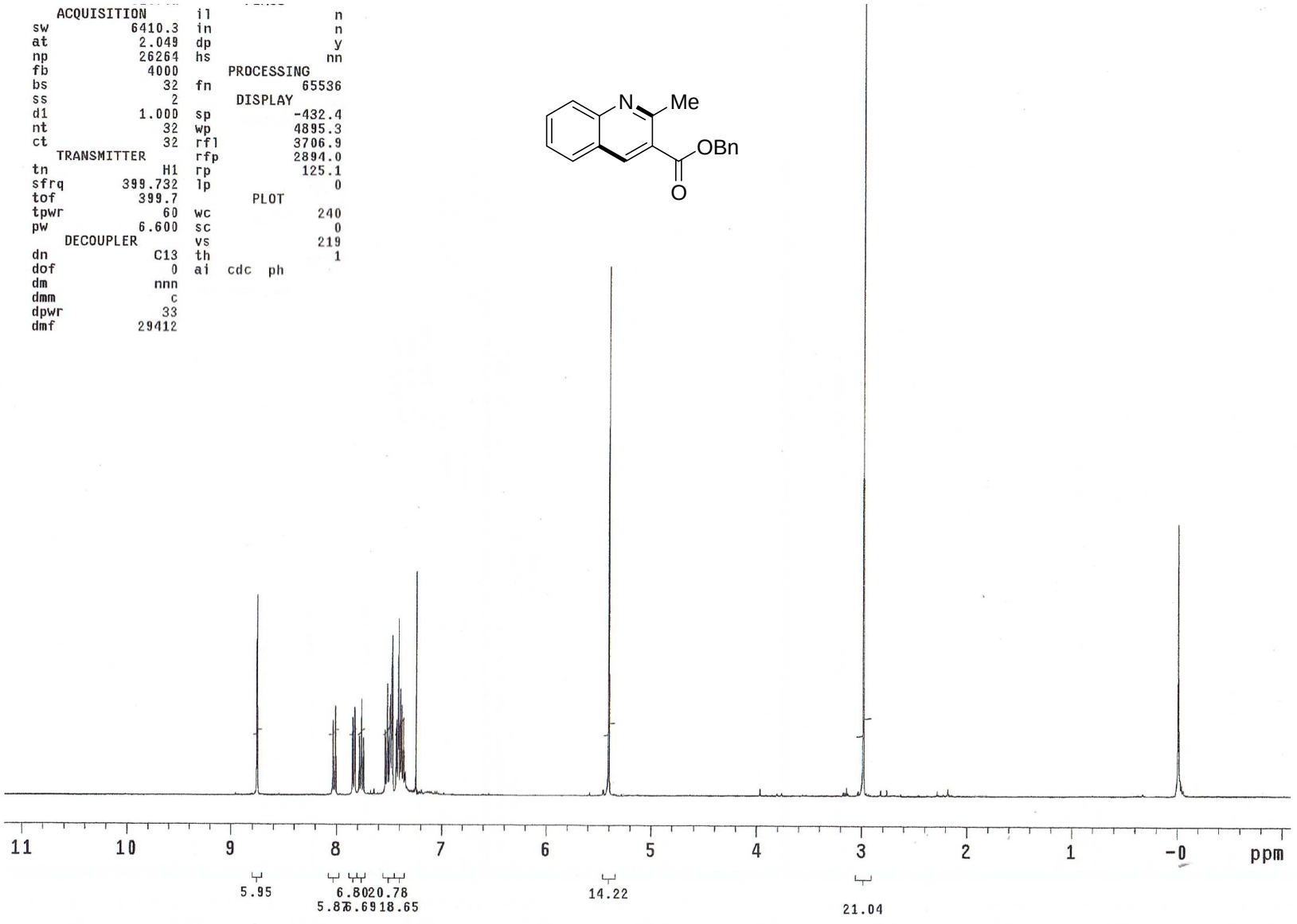
**Ethyl 2-methylquinoline-3-carboxylate (1b', 2b'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



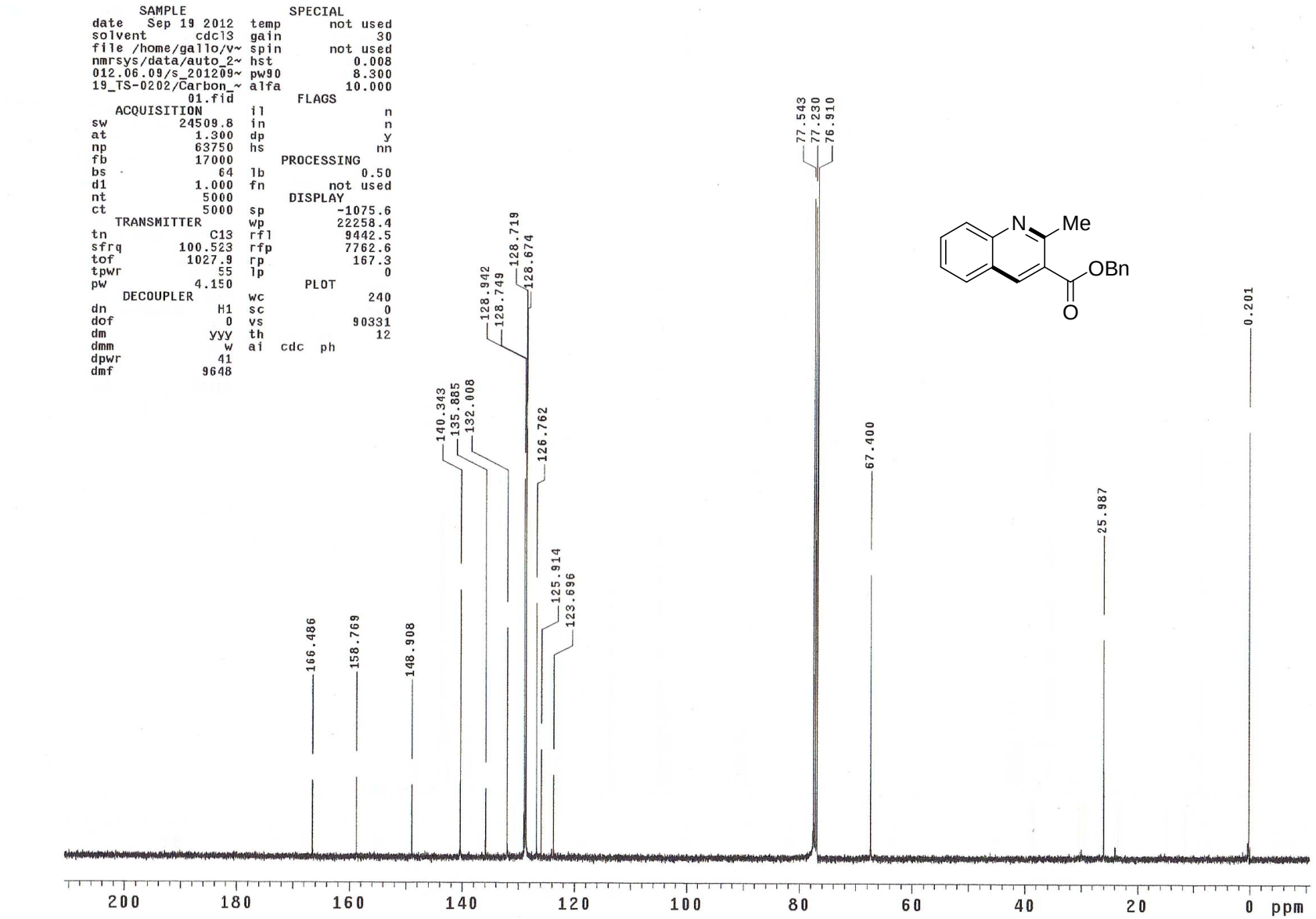
**Ethyl 2-methylquinoline-3-carboxylate (1b', 2b'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



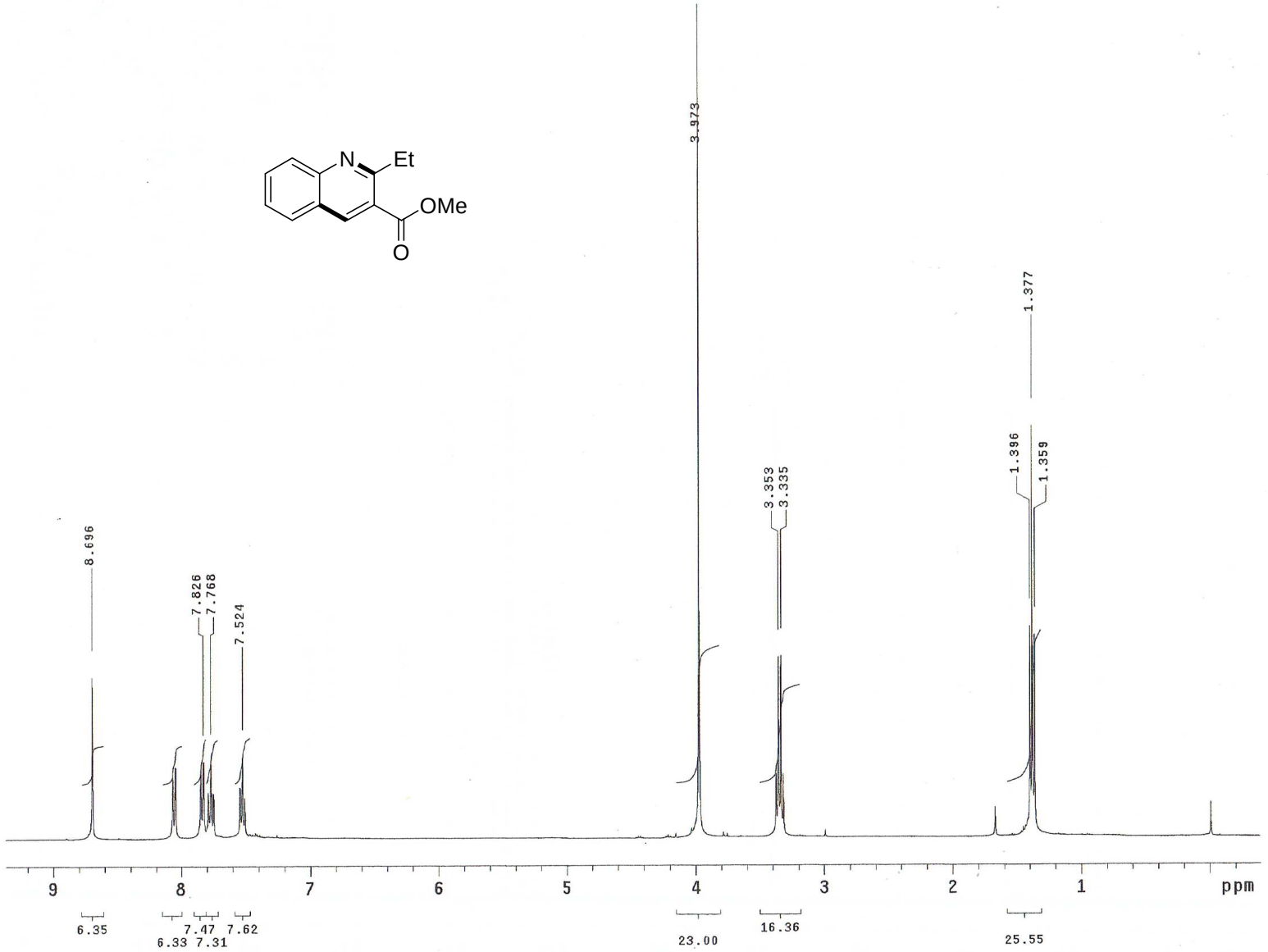
**Benzyl 2-methylquinoline-3-carboxylate (1c'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



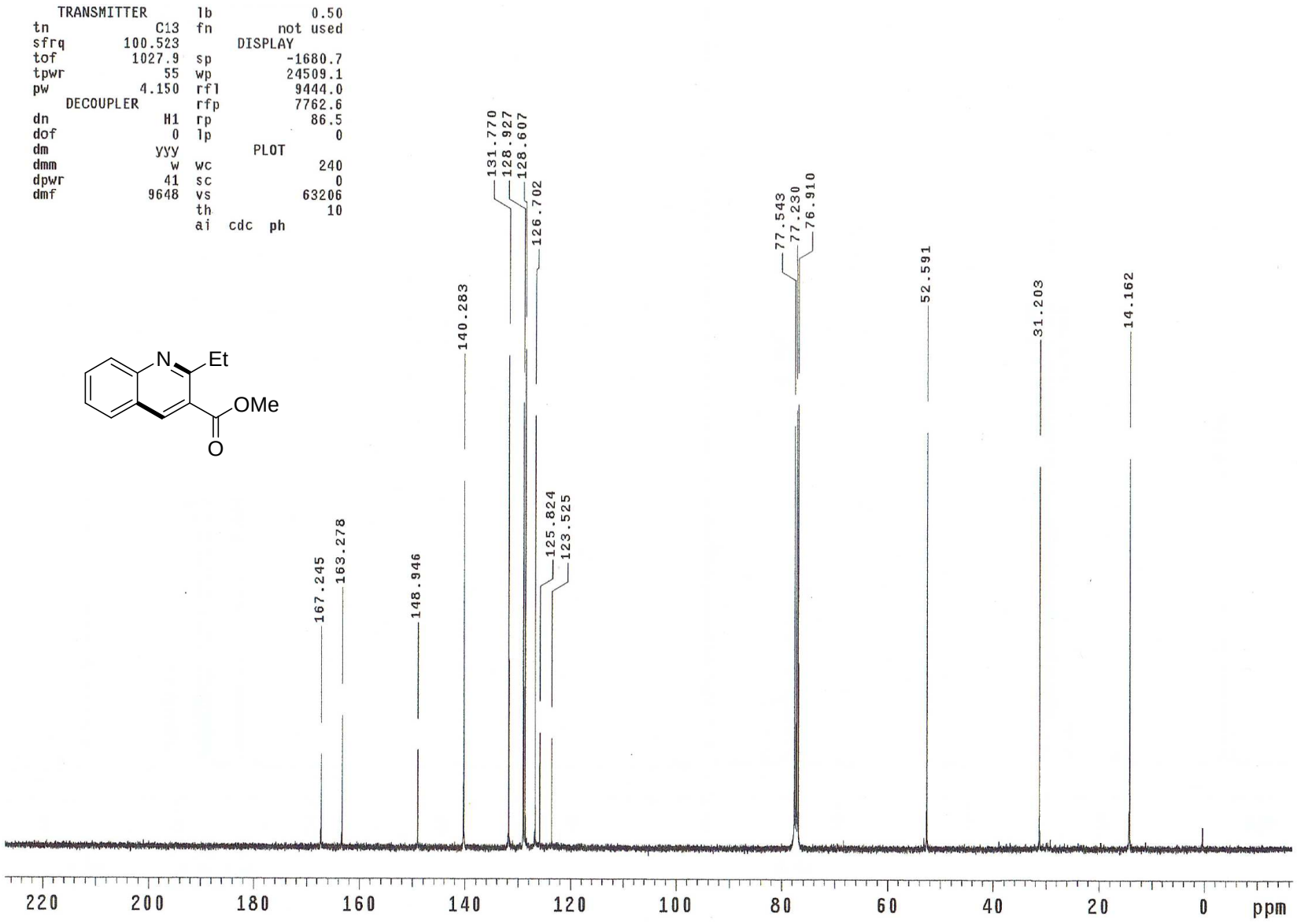
**Benzyl 2-methylquinoline-3-carboxylate (1c'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



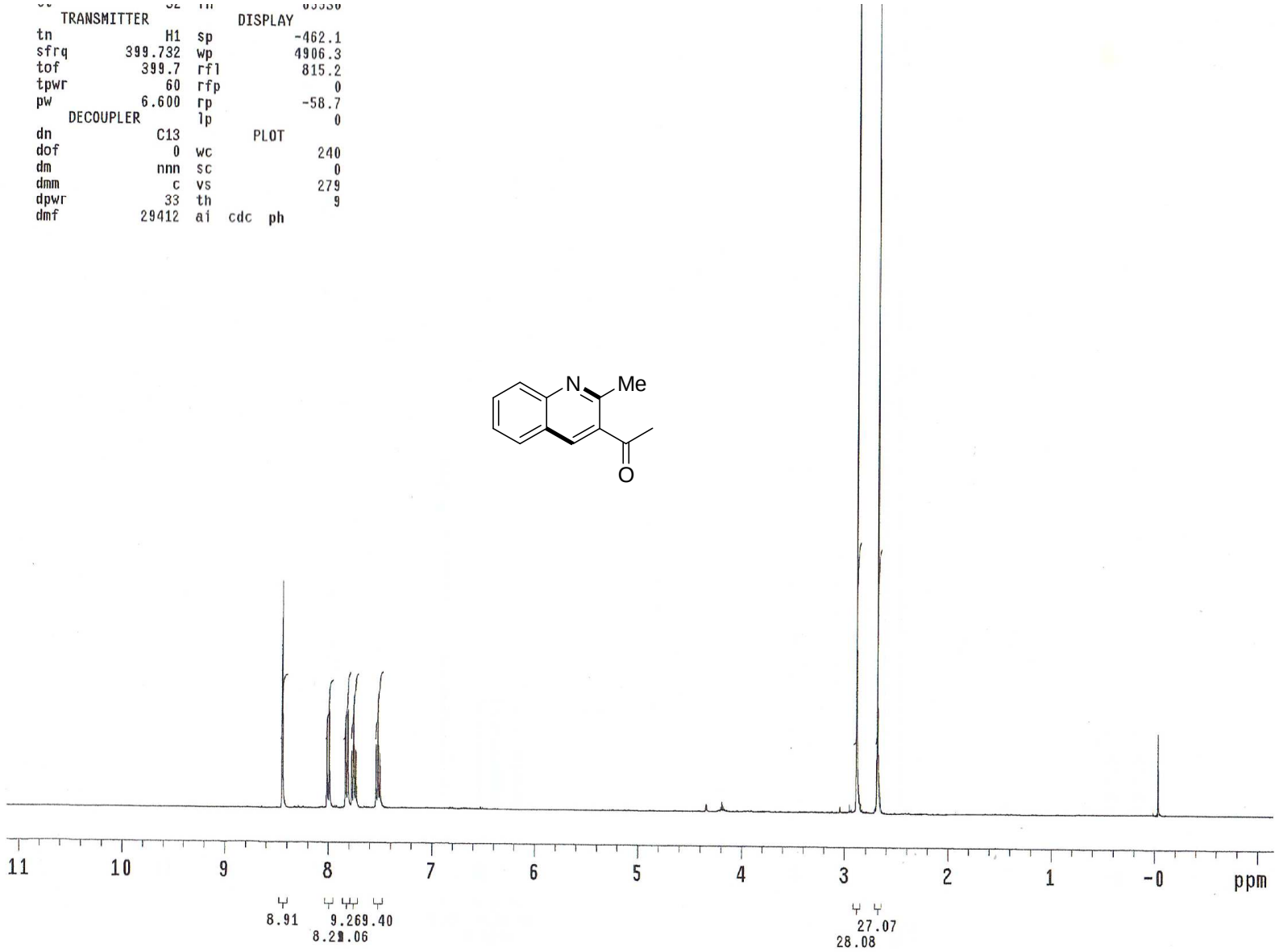
**Methyl 2-ethylquinoline-3-carboxylate (1d'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



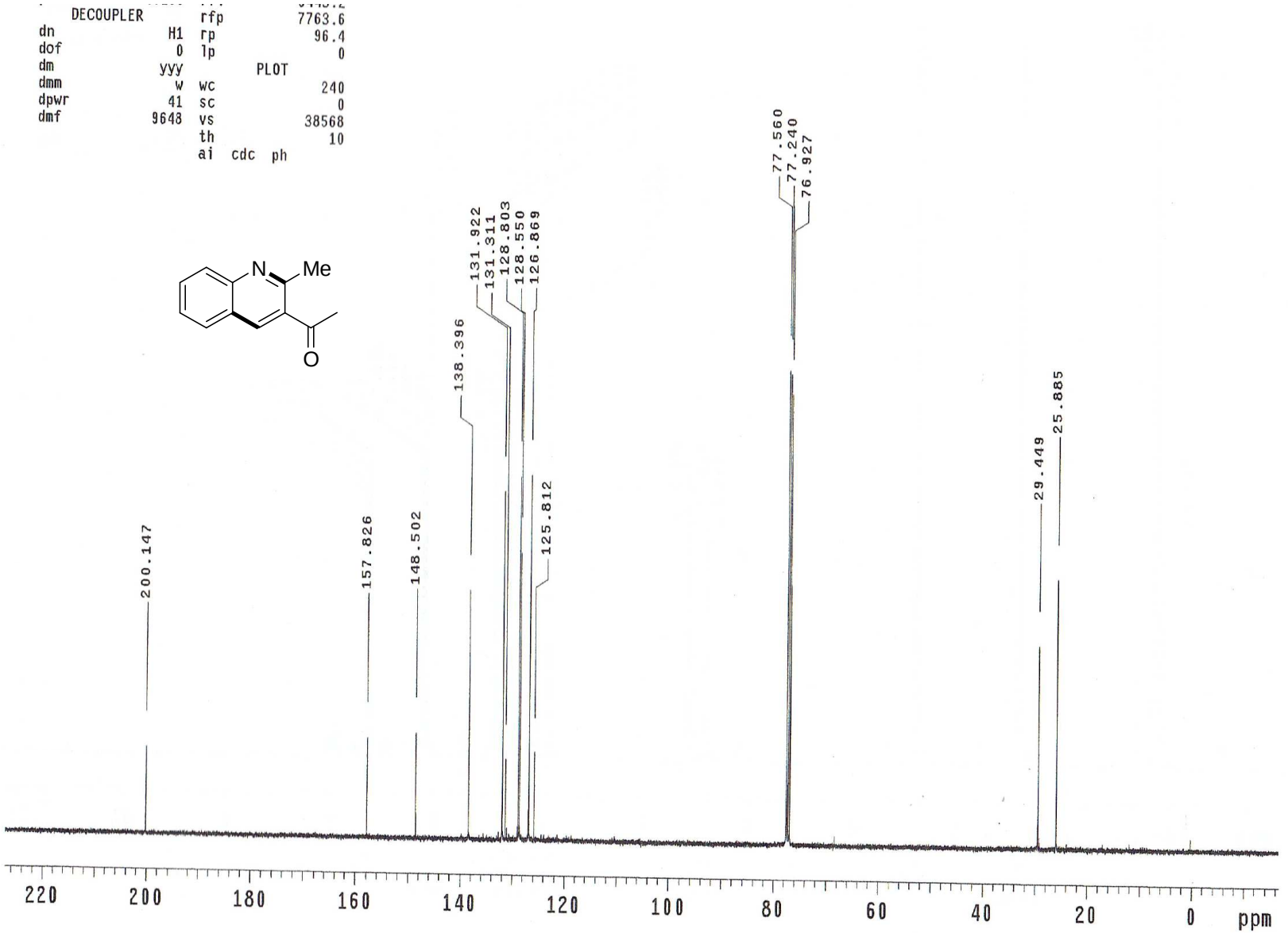
**Methyl 2-ethylquinoline-3-carboxylate (1d'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



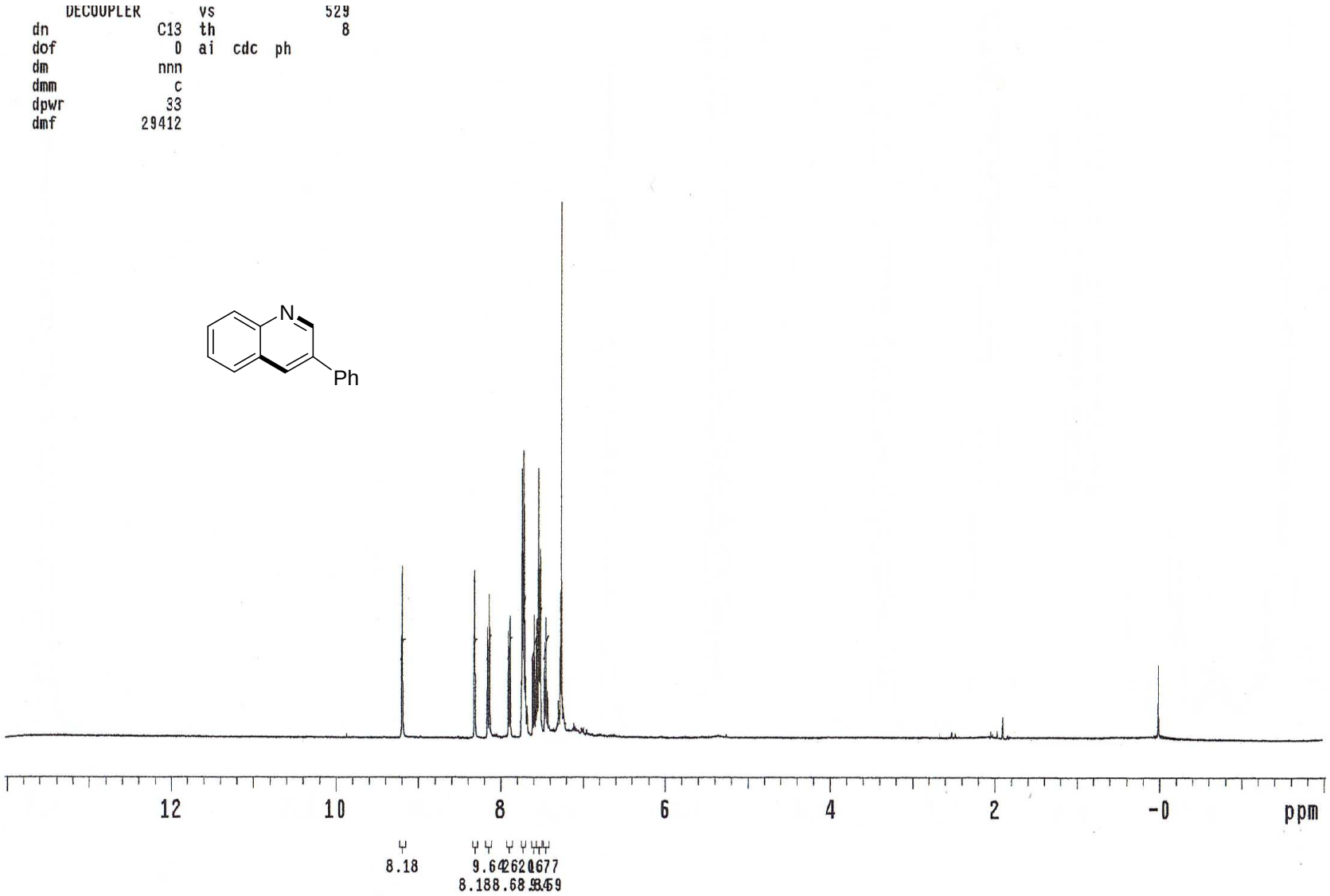
**1-(2-methylquinolin-3-yl)ethanone (1e'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



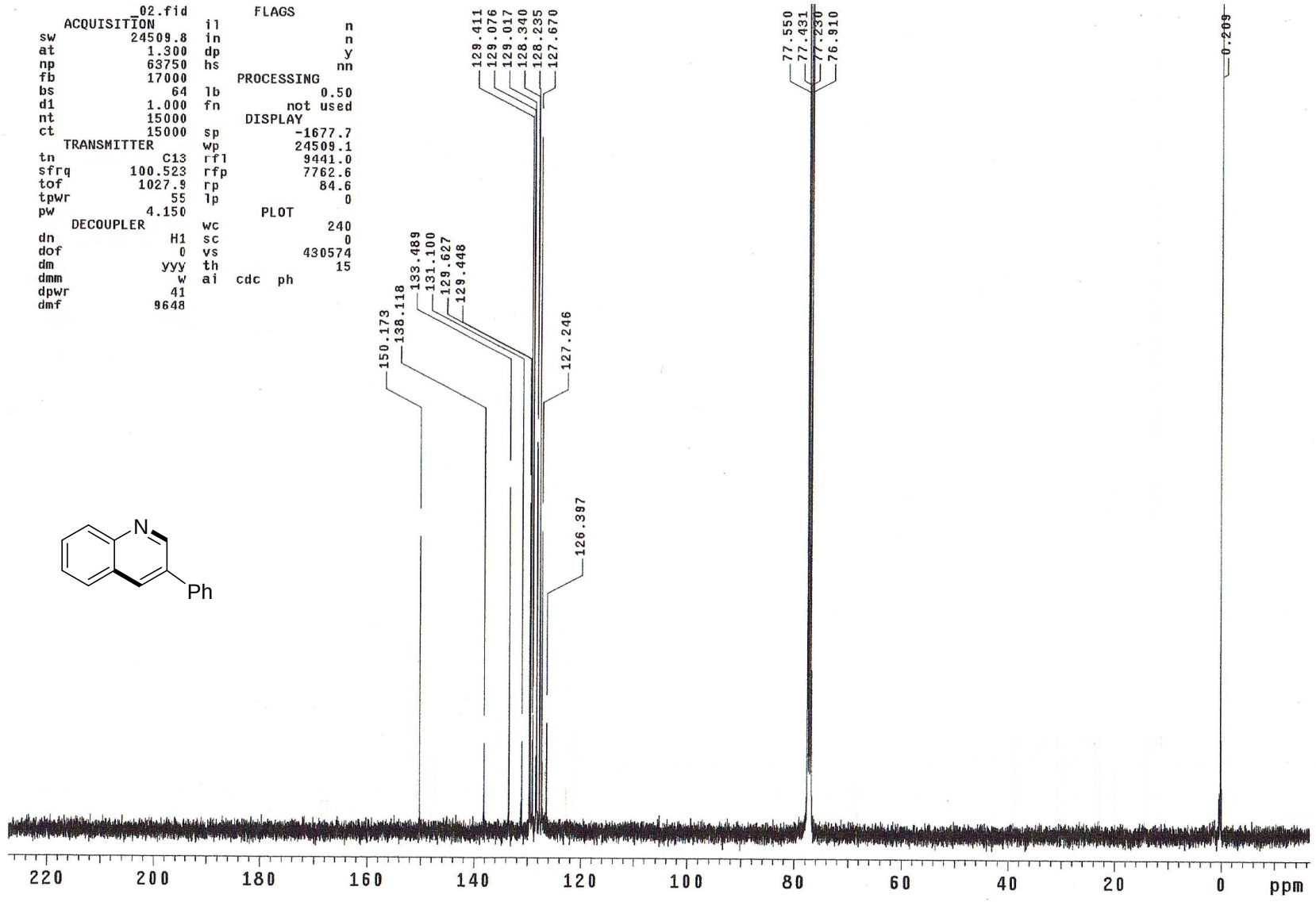
**1-(2-methylquinolin-3-yl)ethanone (1e'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



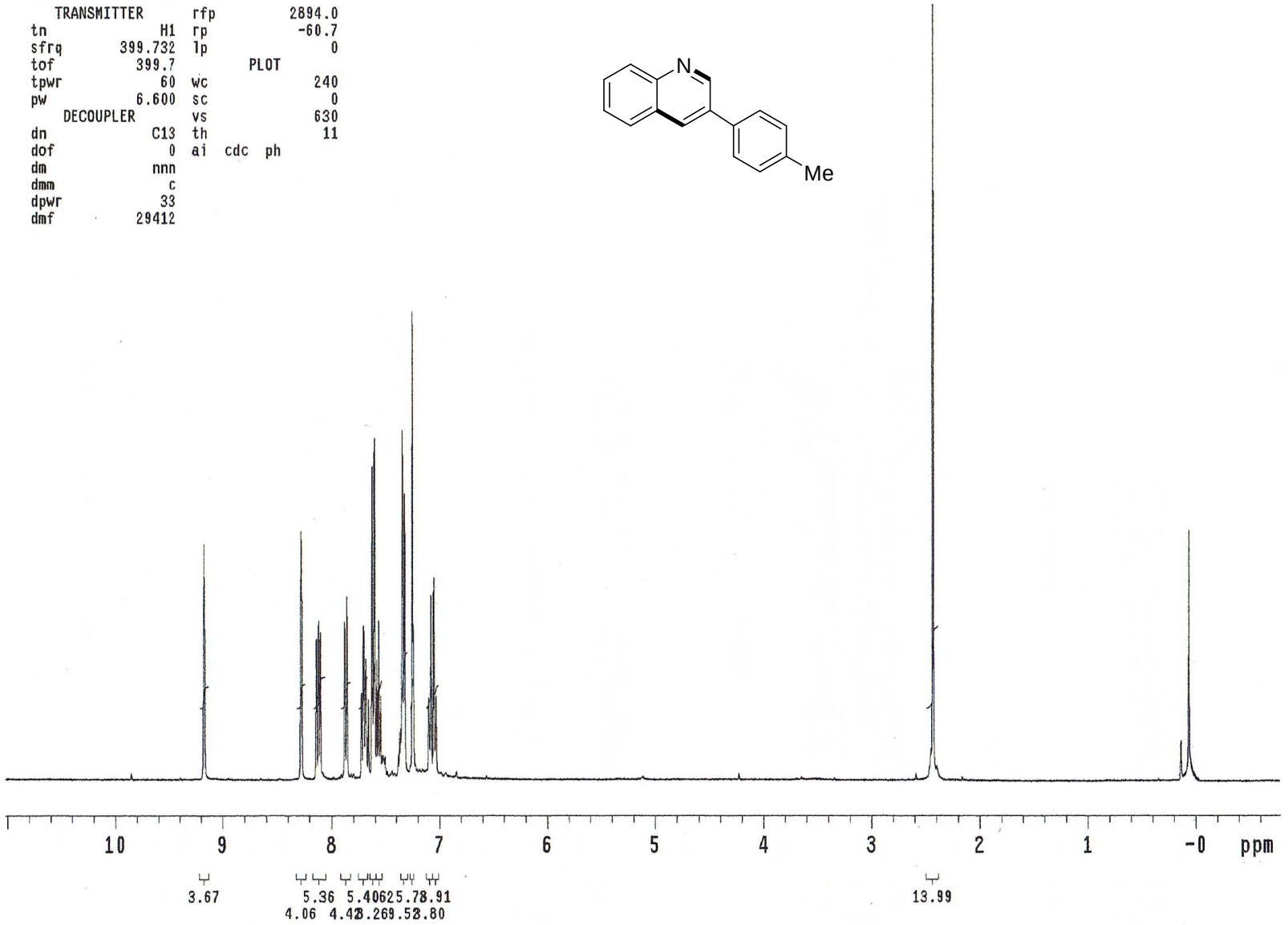
**3-Phenylquinoline (1f'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



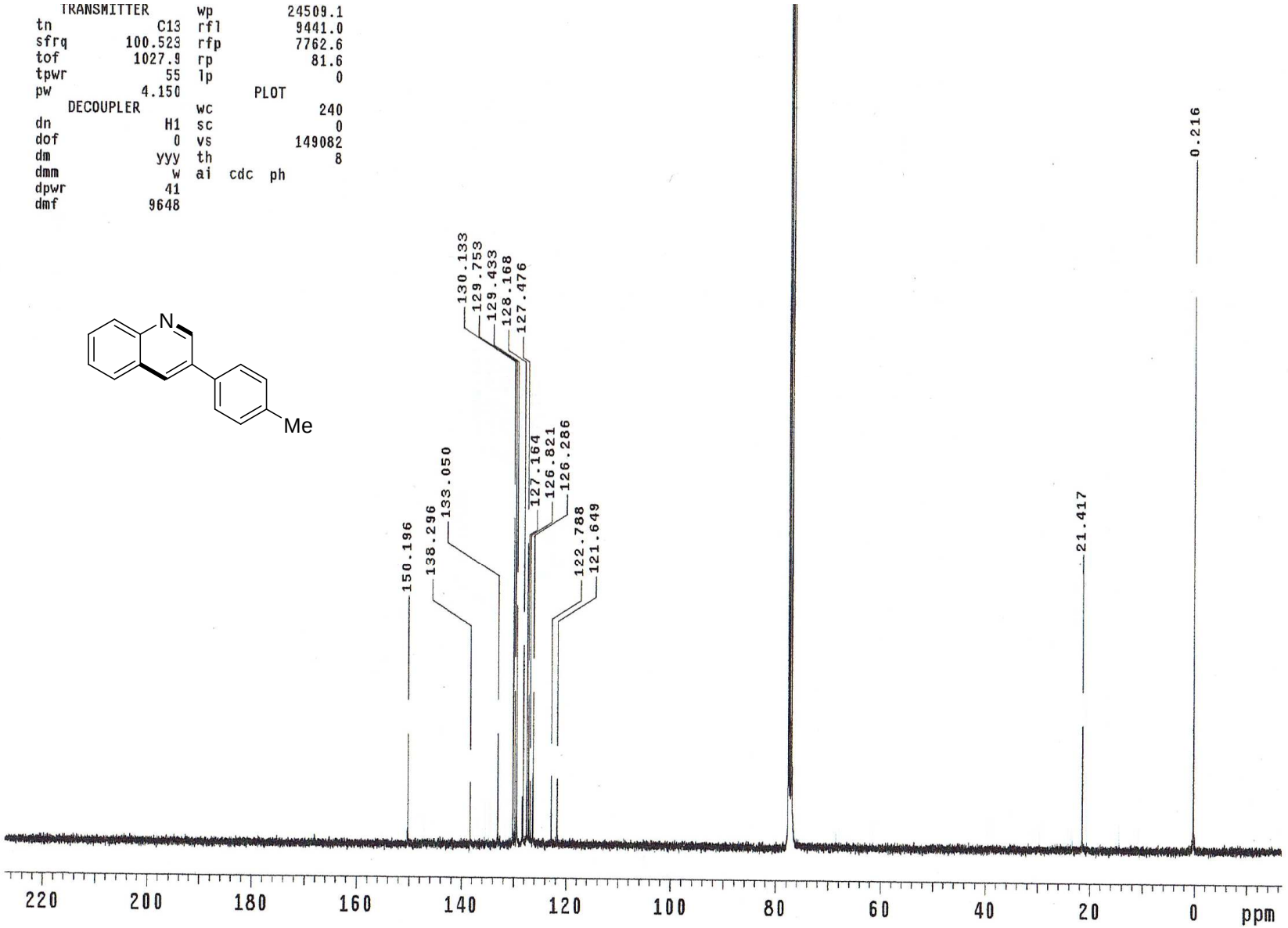
**3-Phenylquinoline (1f'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



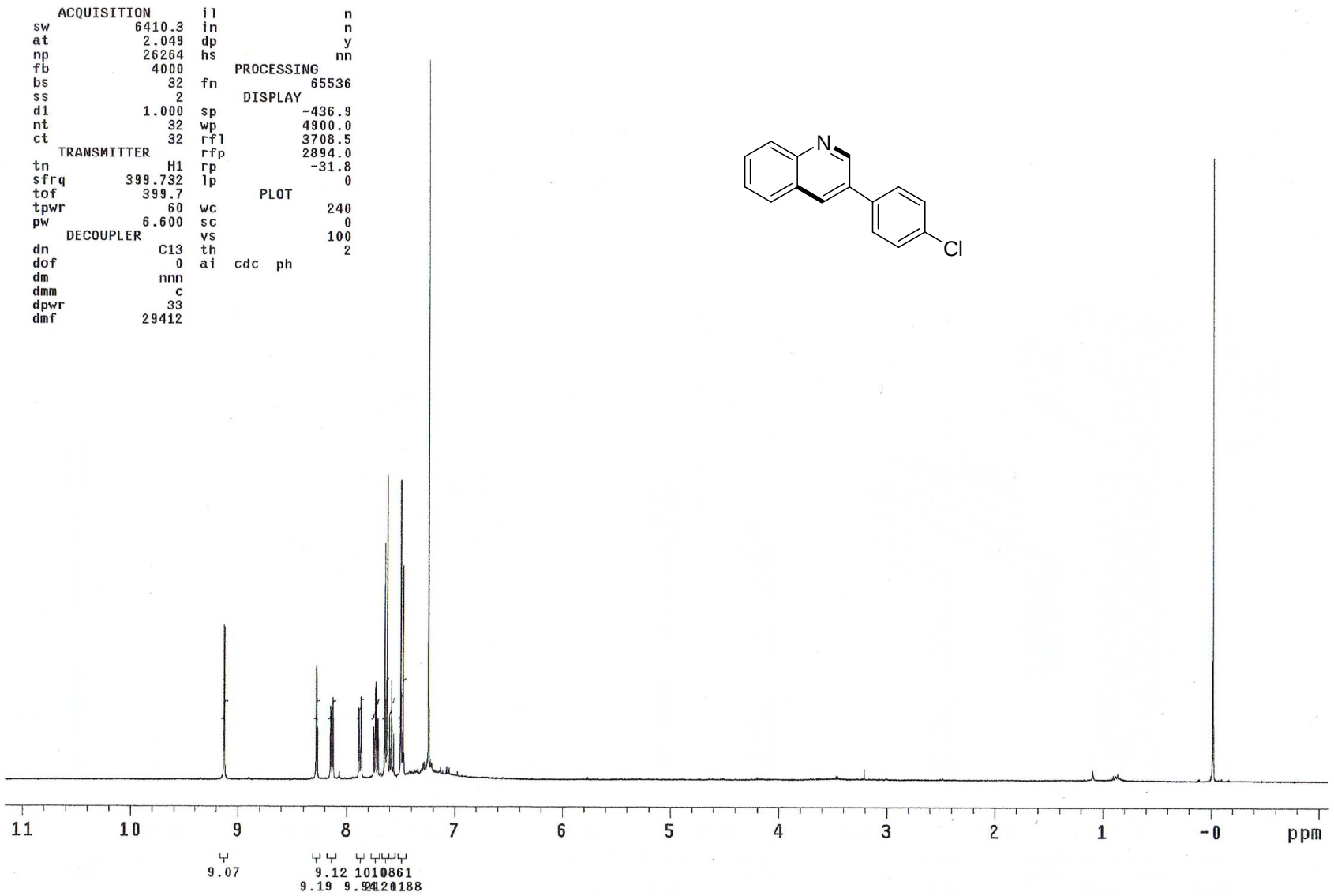
**3-p-Tolylquinoline (1g'):** $^{1}H$ NMR (400 MHz, $CDCl_3$)



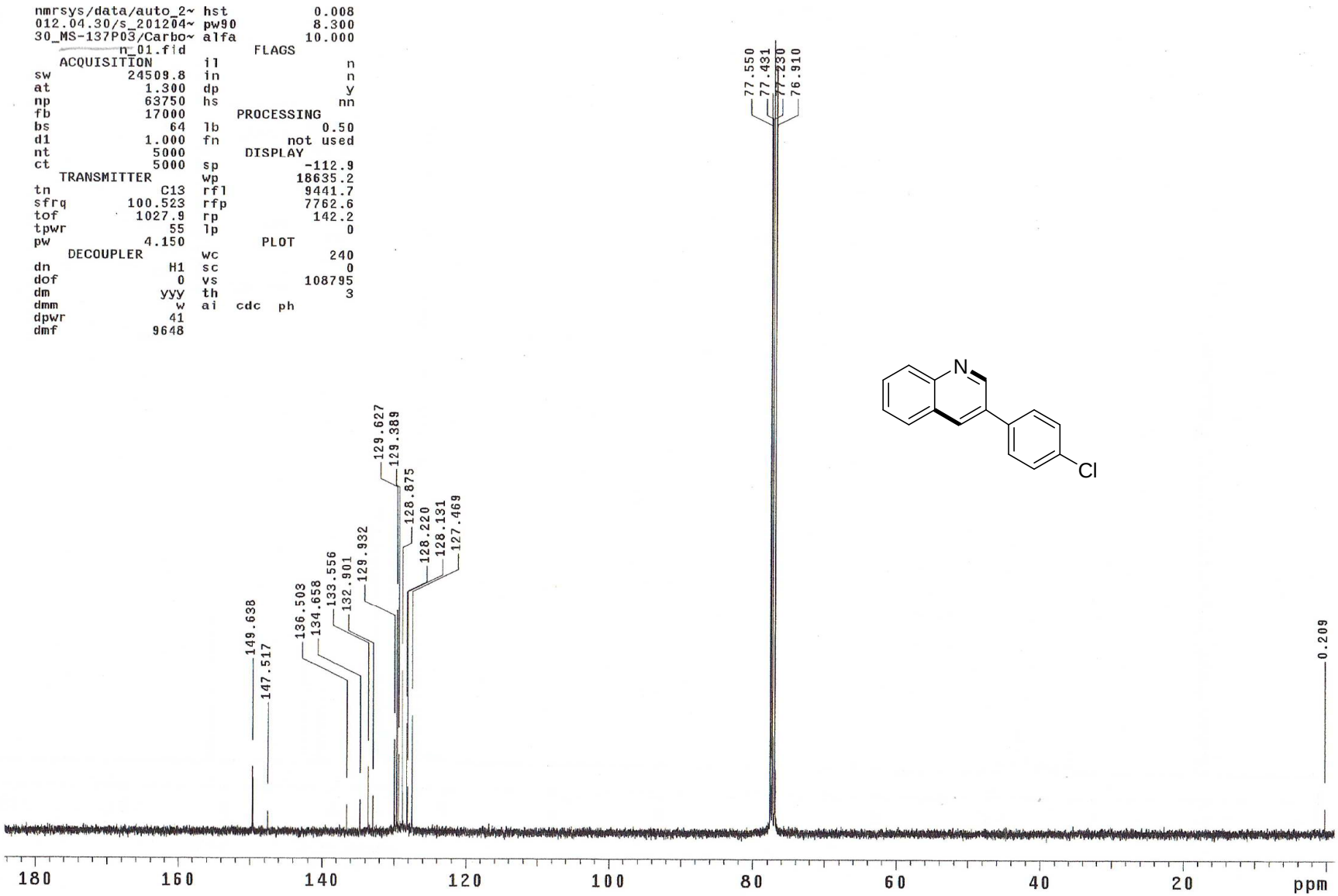
**3-p-Tolylquinoline (1g'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



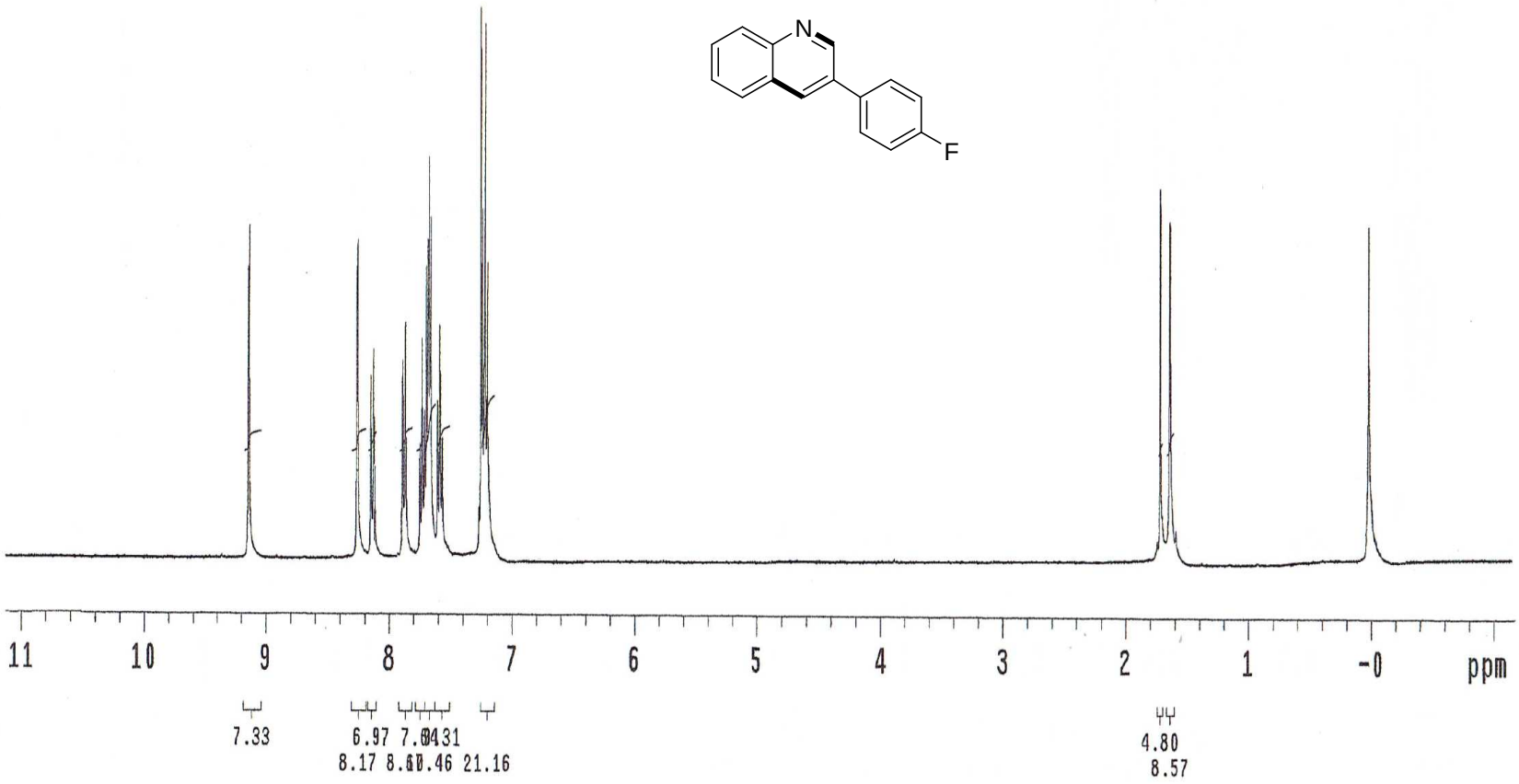
**3-(4-chlorophenyl)quinoline (1h'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



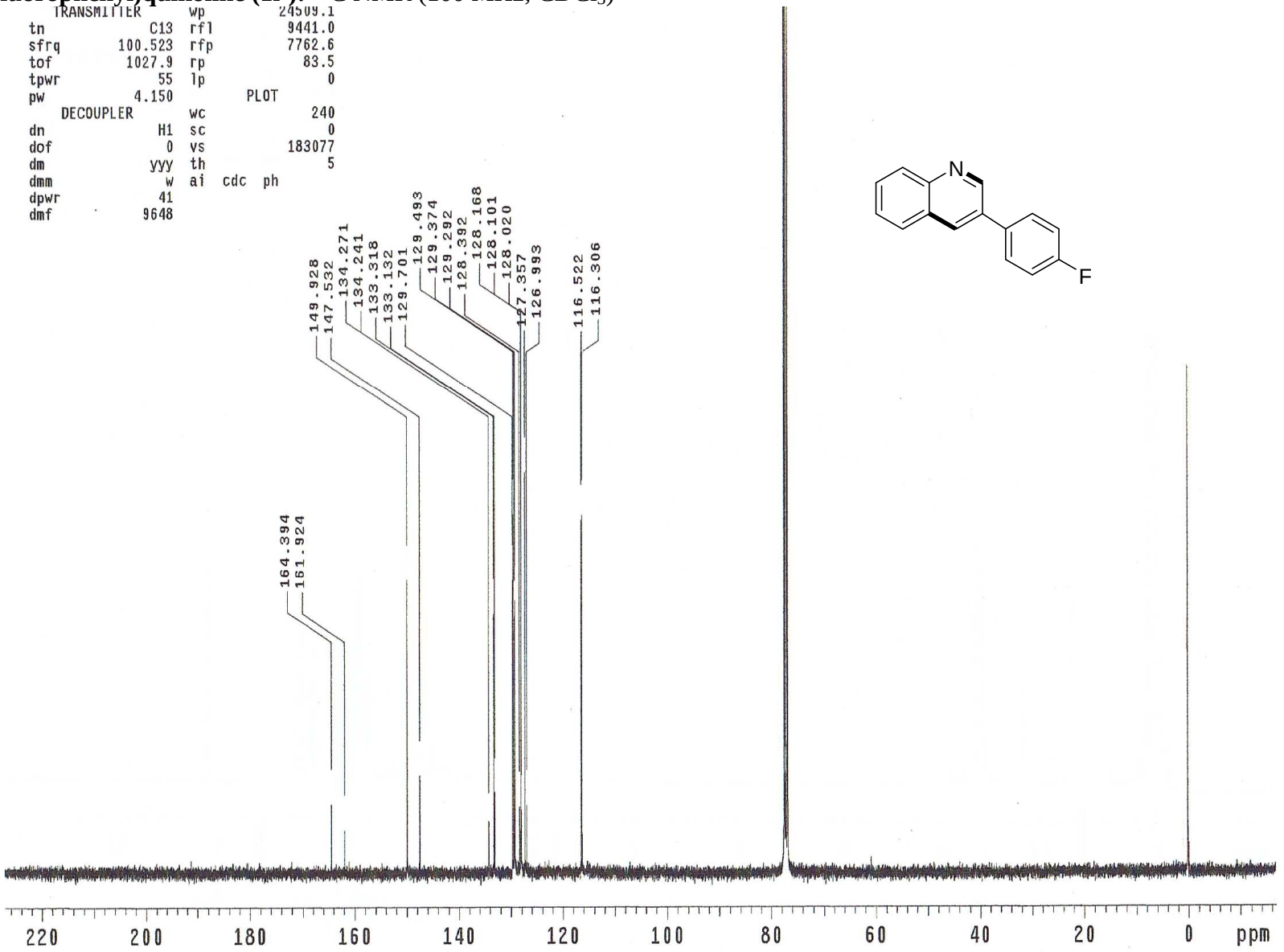
**3-(4-chlorophenyl)quinoline (1h'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



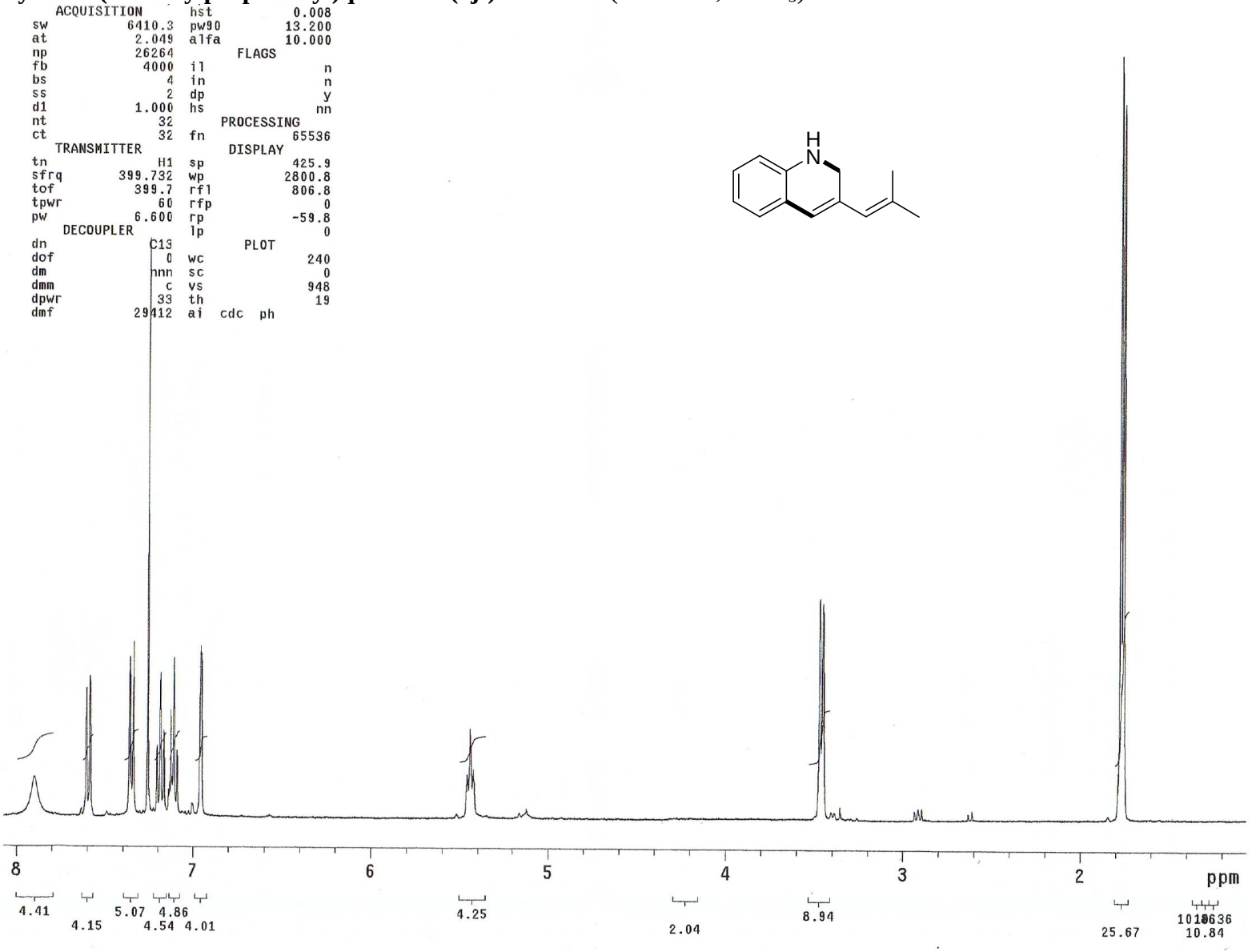
**3-(4-fluorophenyl)quinoline (1i'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



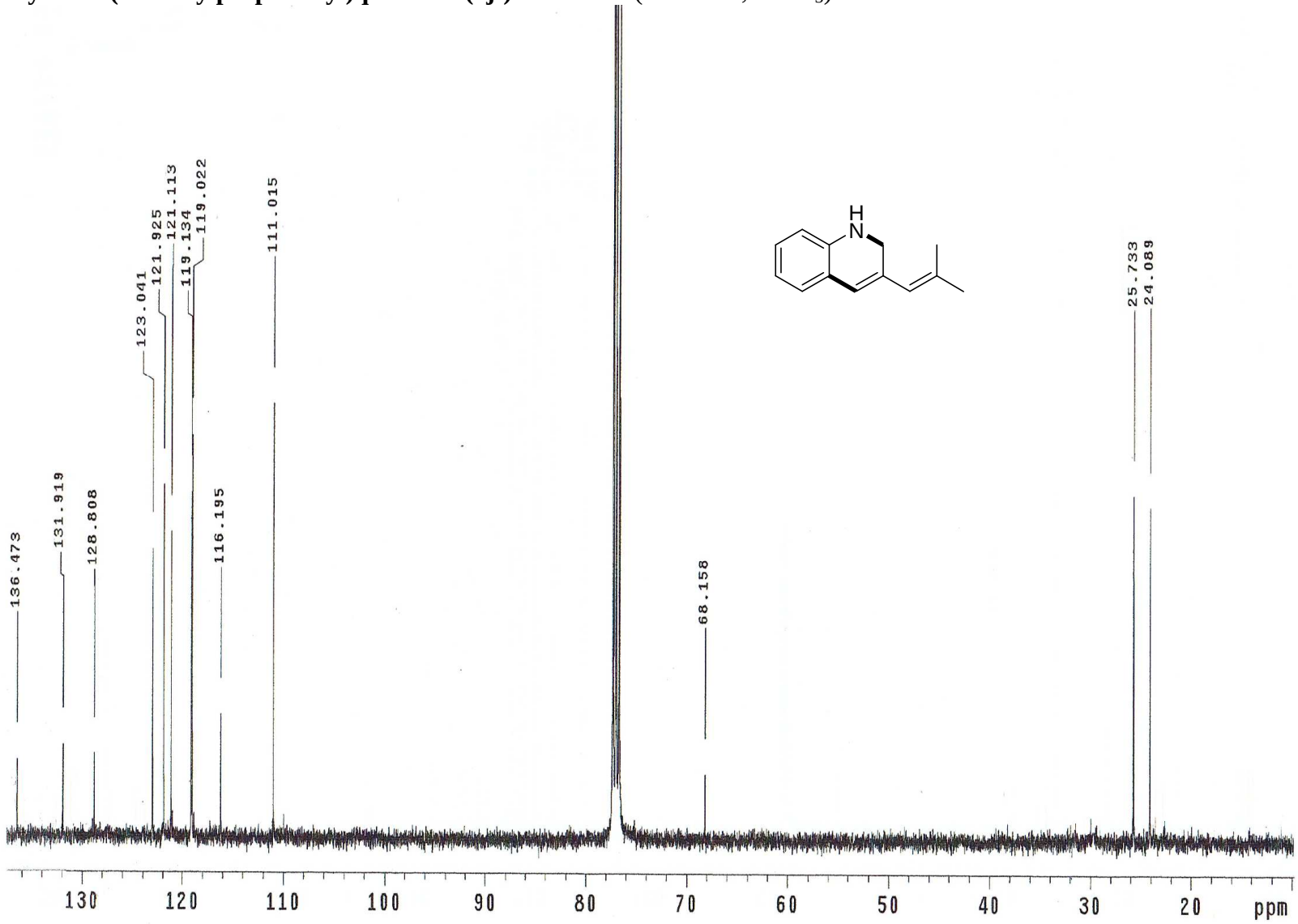
**3-(4-fluorophenyl)quinoline (1i'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



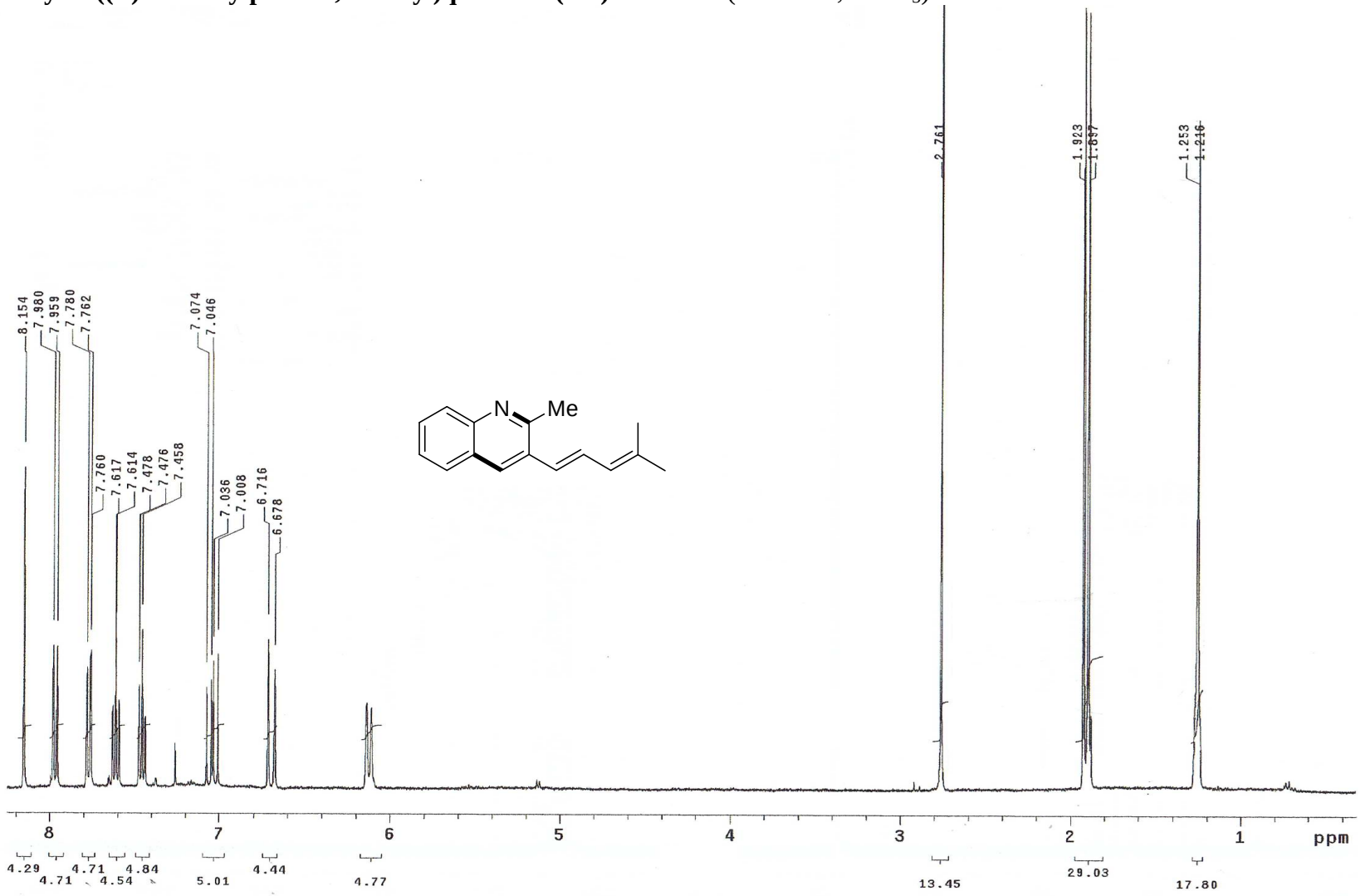
**1,2-dihydro-3-(2-methylprop-1-enyl)quinoline (1j'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



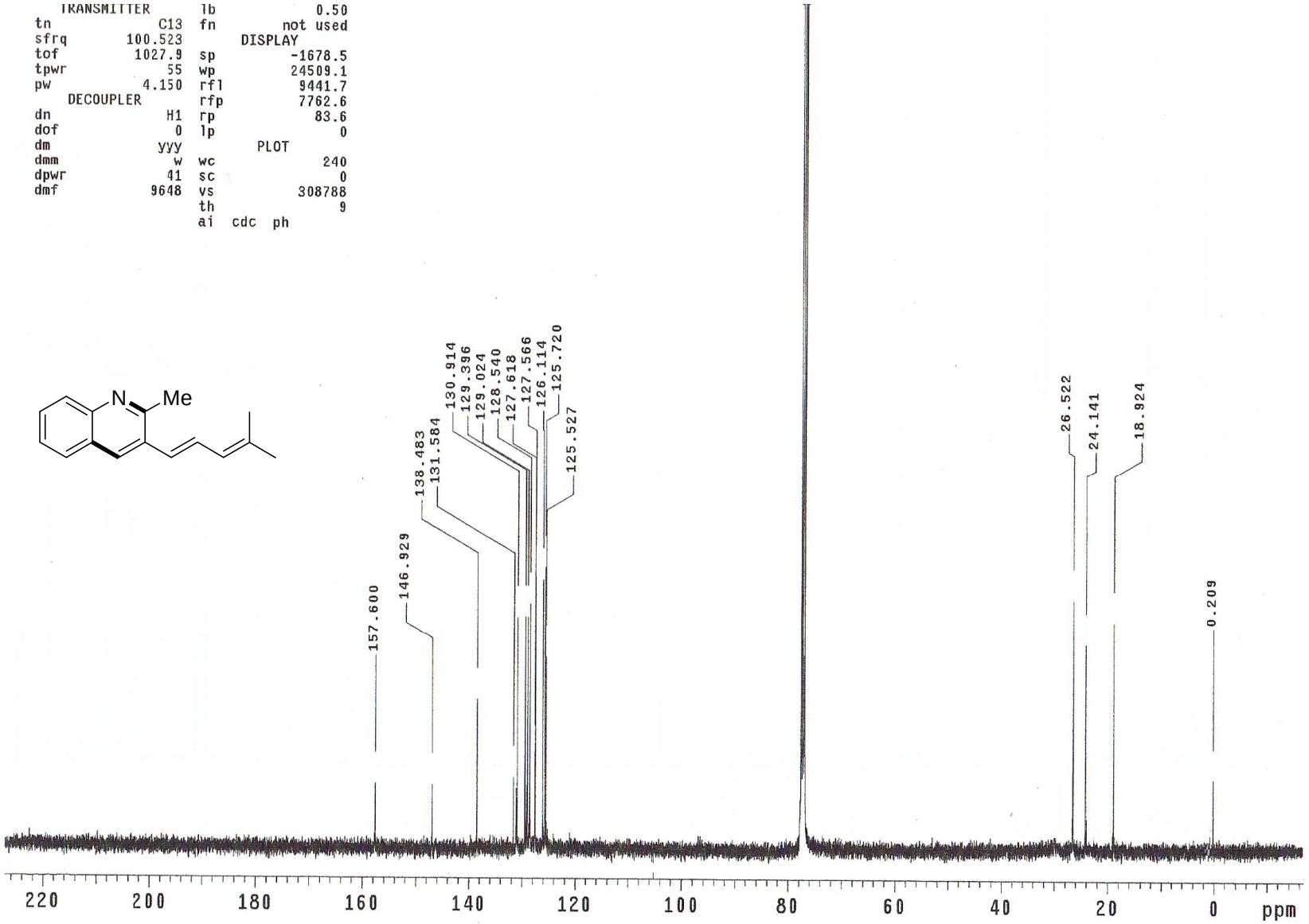
**1,2-dihydro-3-(2-methylprop-1-enyl)quinoline (1j'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



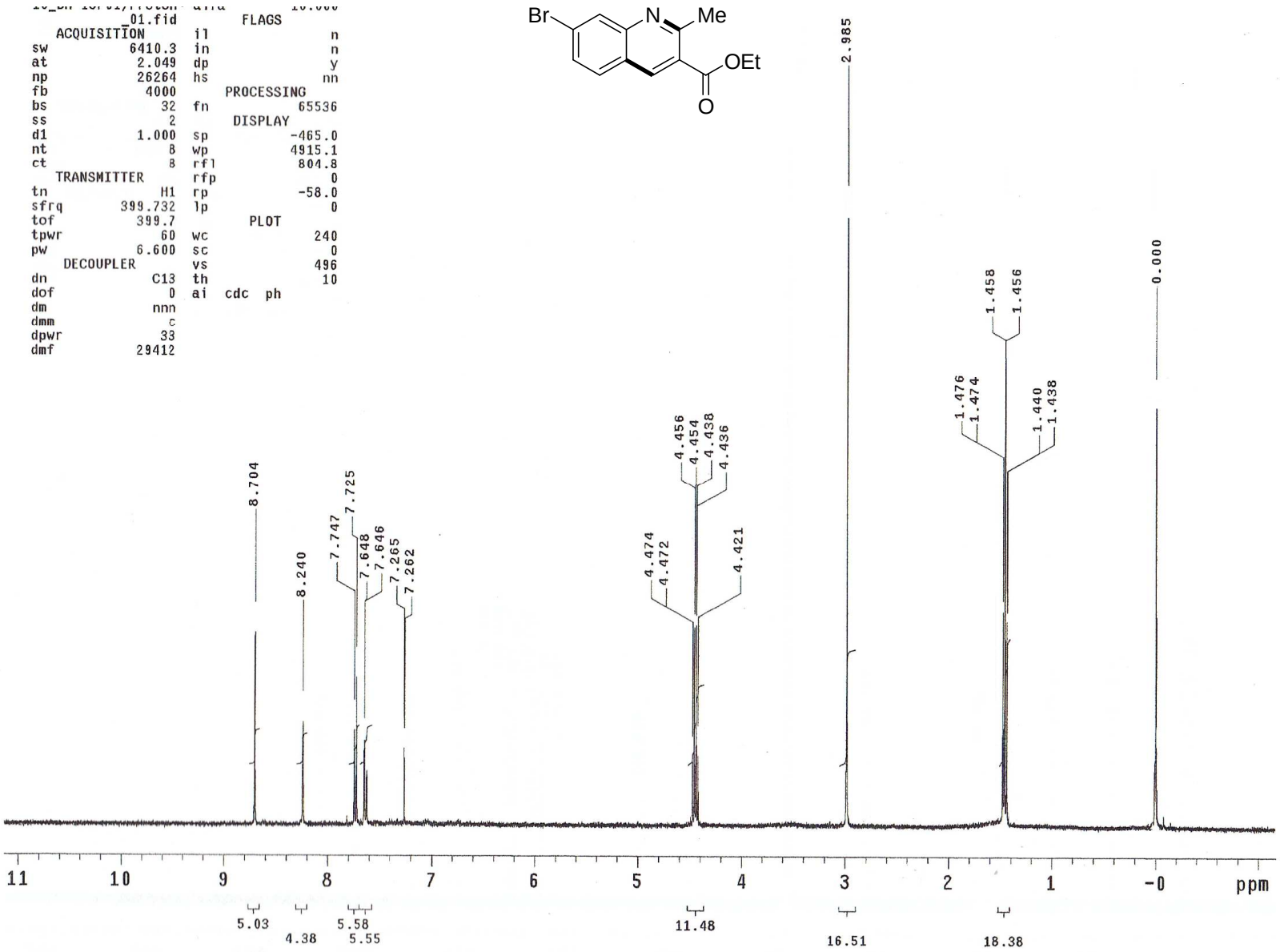
**2-Methyl-3-((E)-4-methylpenta-1,3-dienyl)quinoline (1k'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



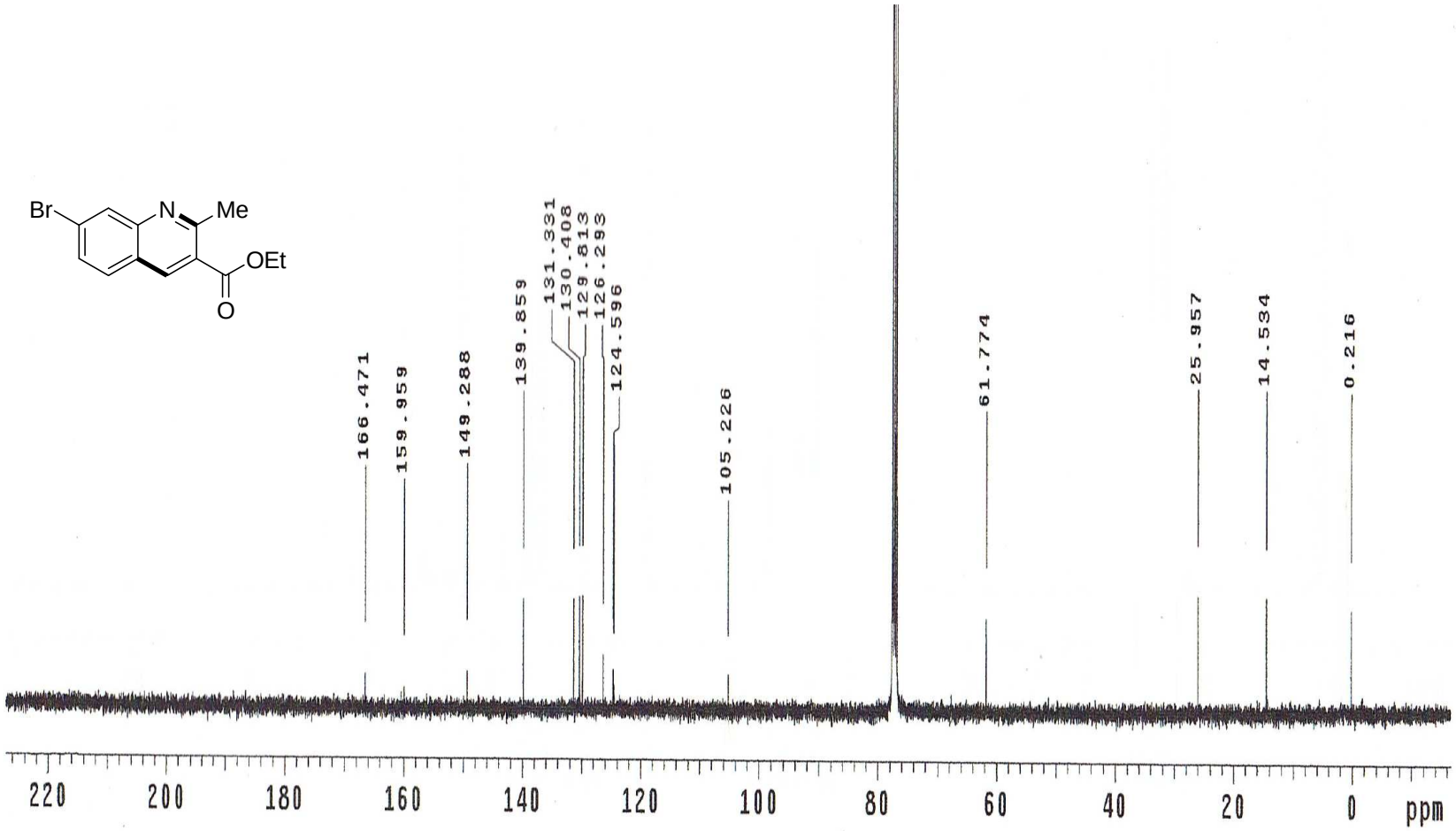
**2-Methyl-3-((E)-4-methylpenta-1,3-dienyl)quinoline (1k'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



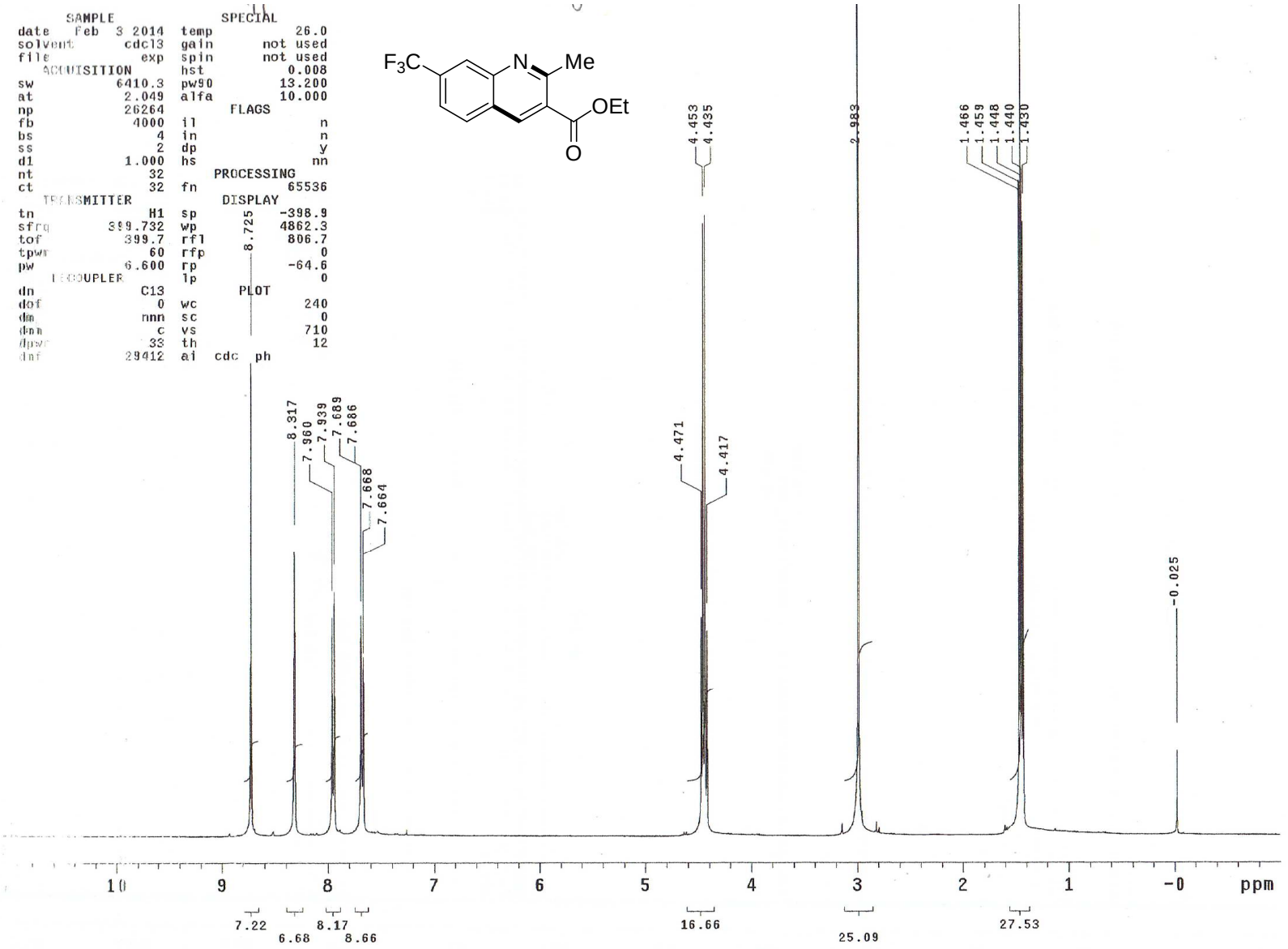
**Ethyl 7-bromo-2-methylquinoline-3-carboxylate (3b'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



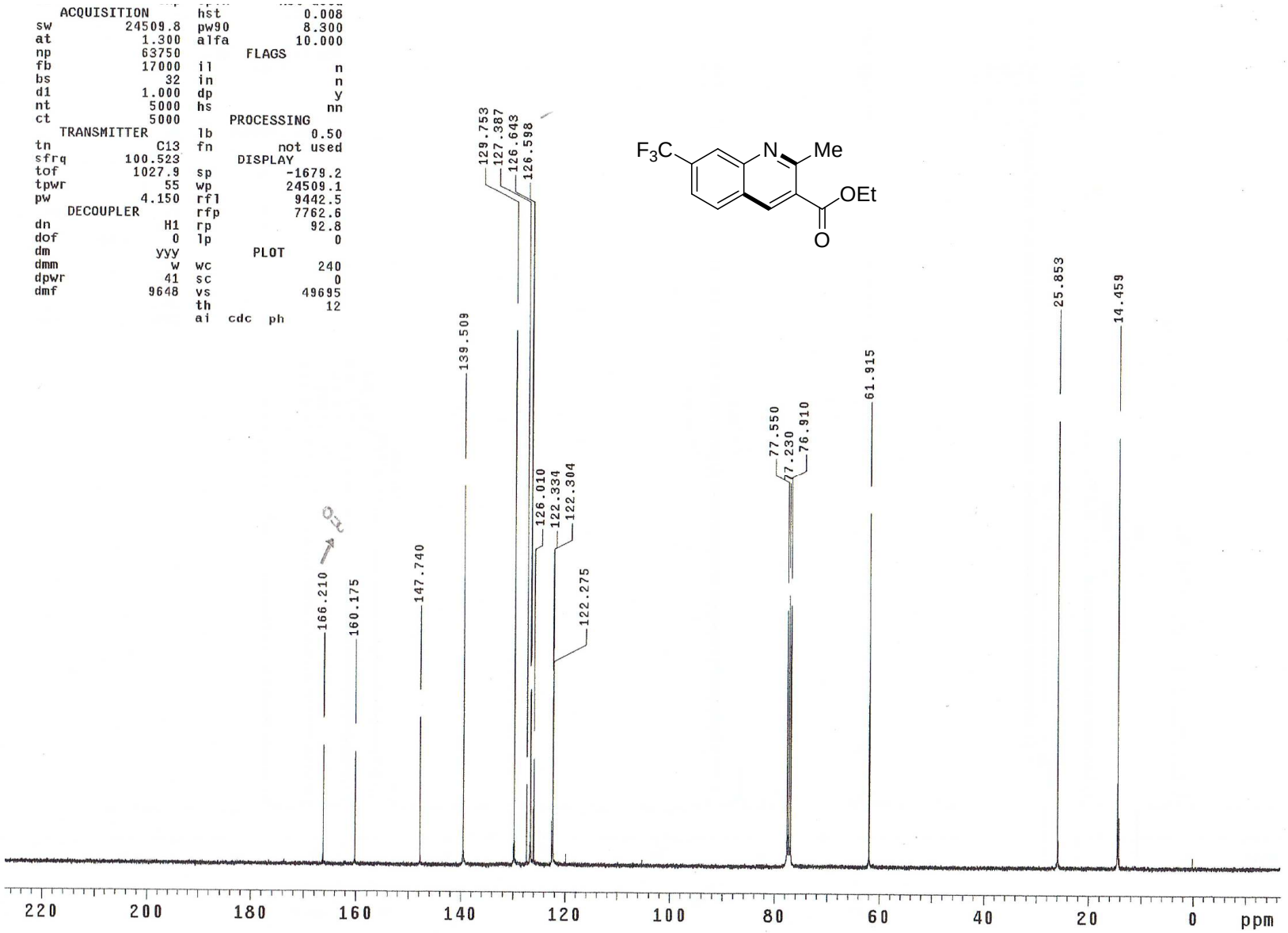
**Ethyl 7-bromo-2-methylquinoline-3-carboxylate (3b'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



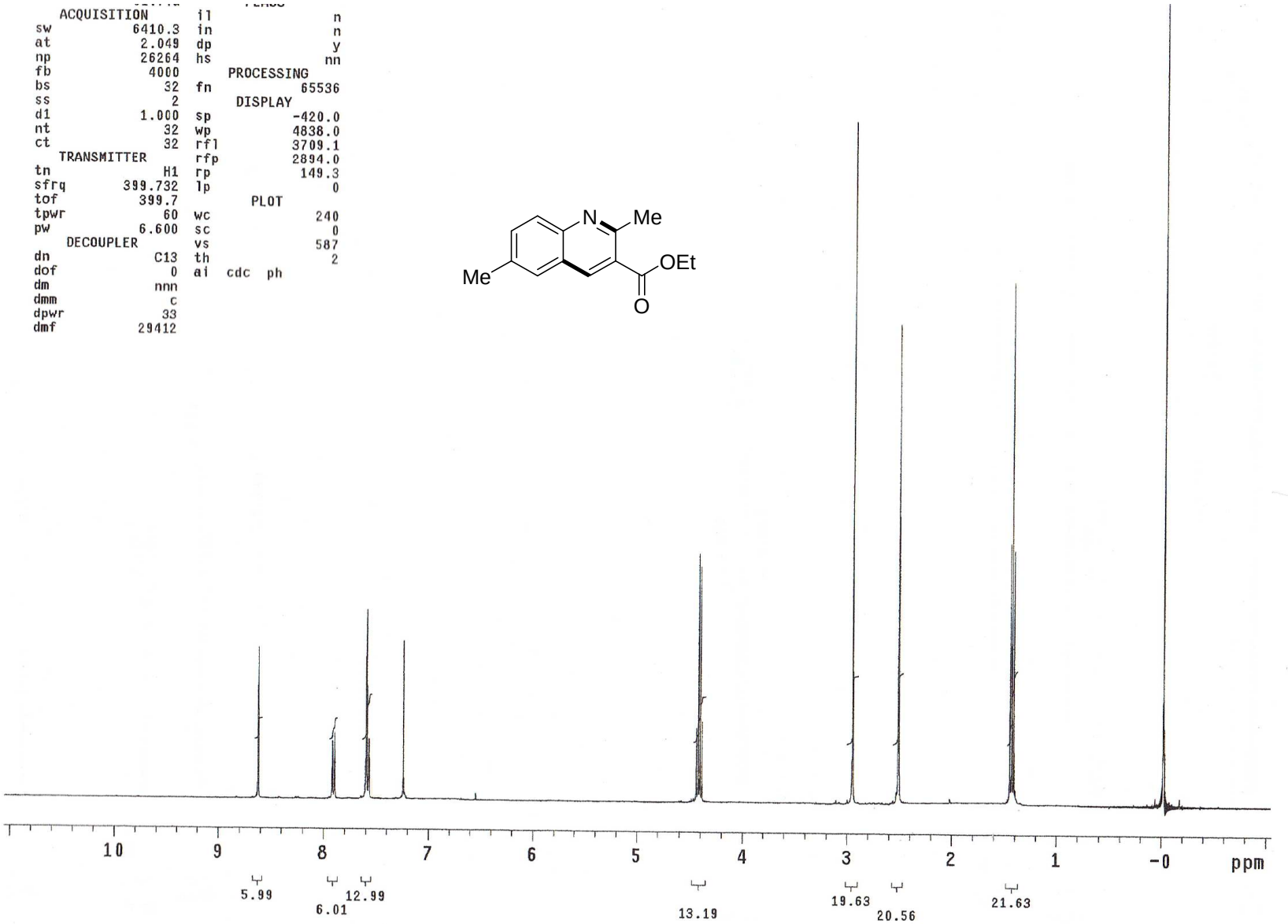
**Ethyl 7-(trifluoromethyl)-2-methylquinoline-3-carboxylate (4b'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



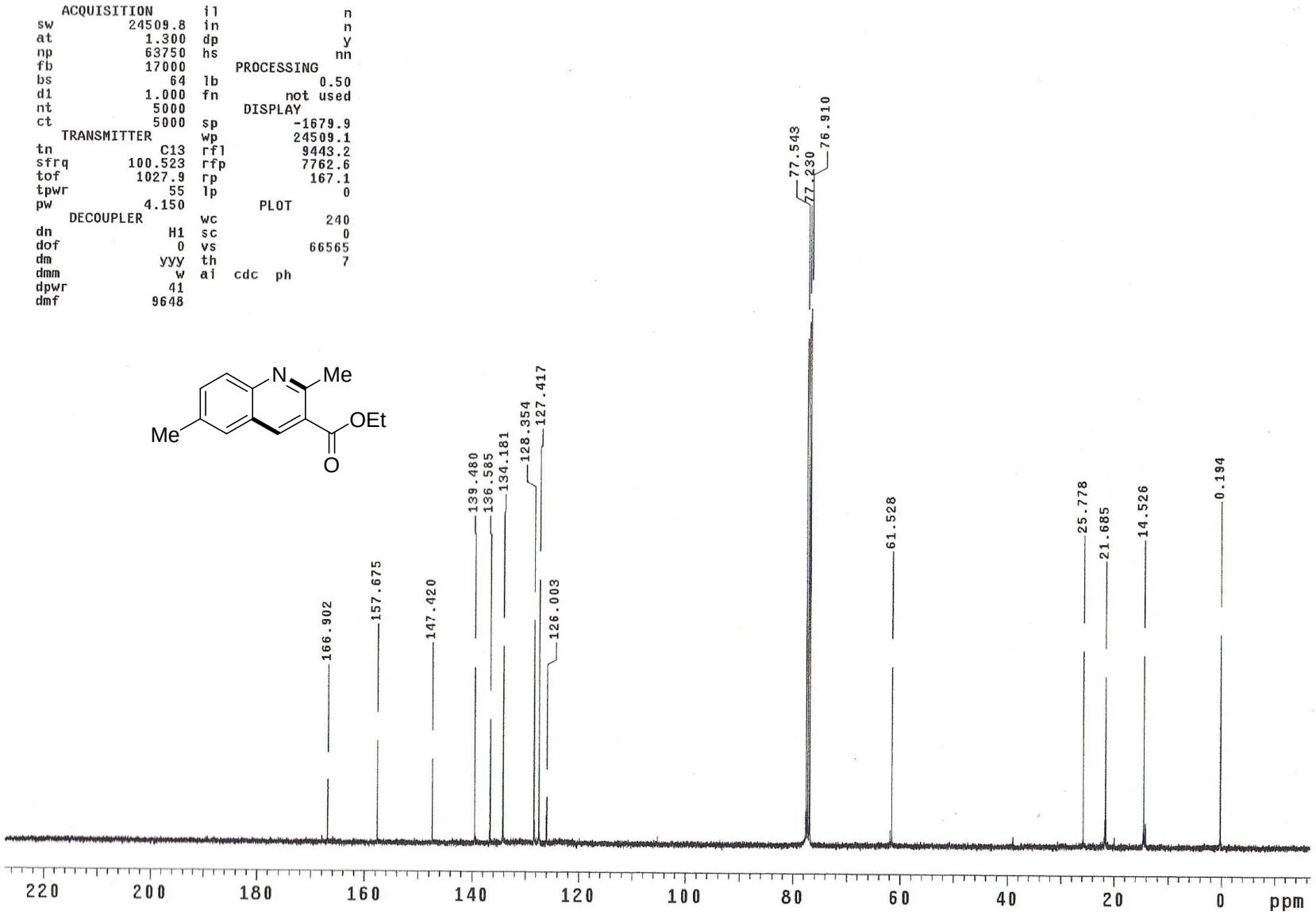
**Ethyl 7-(trifluoromethyl)-2-methylquinoline-3-carboxylate (4b'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



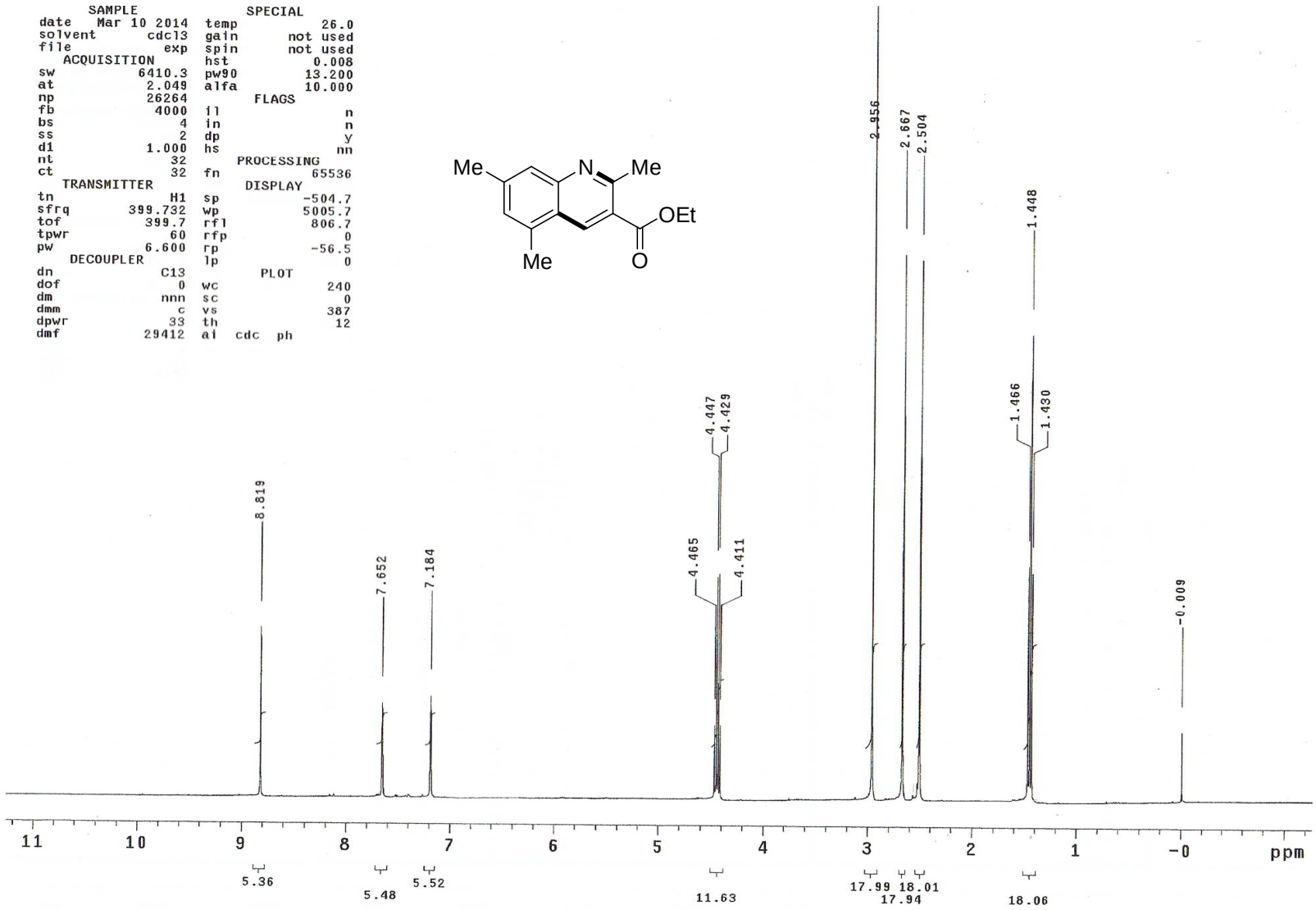
**Ethyl 2,6-dimethylquinoline-3-carboxylate (5b'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



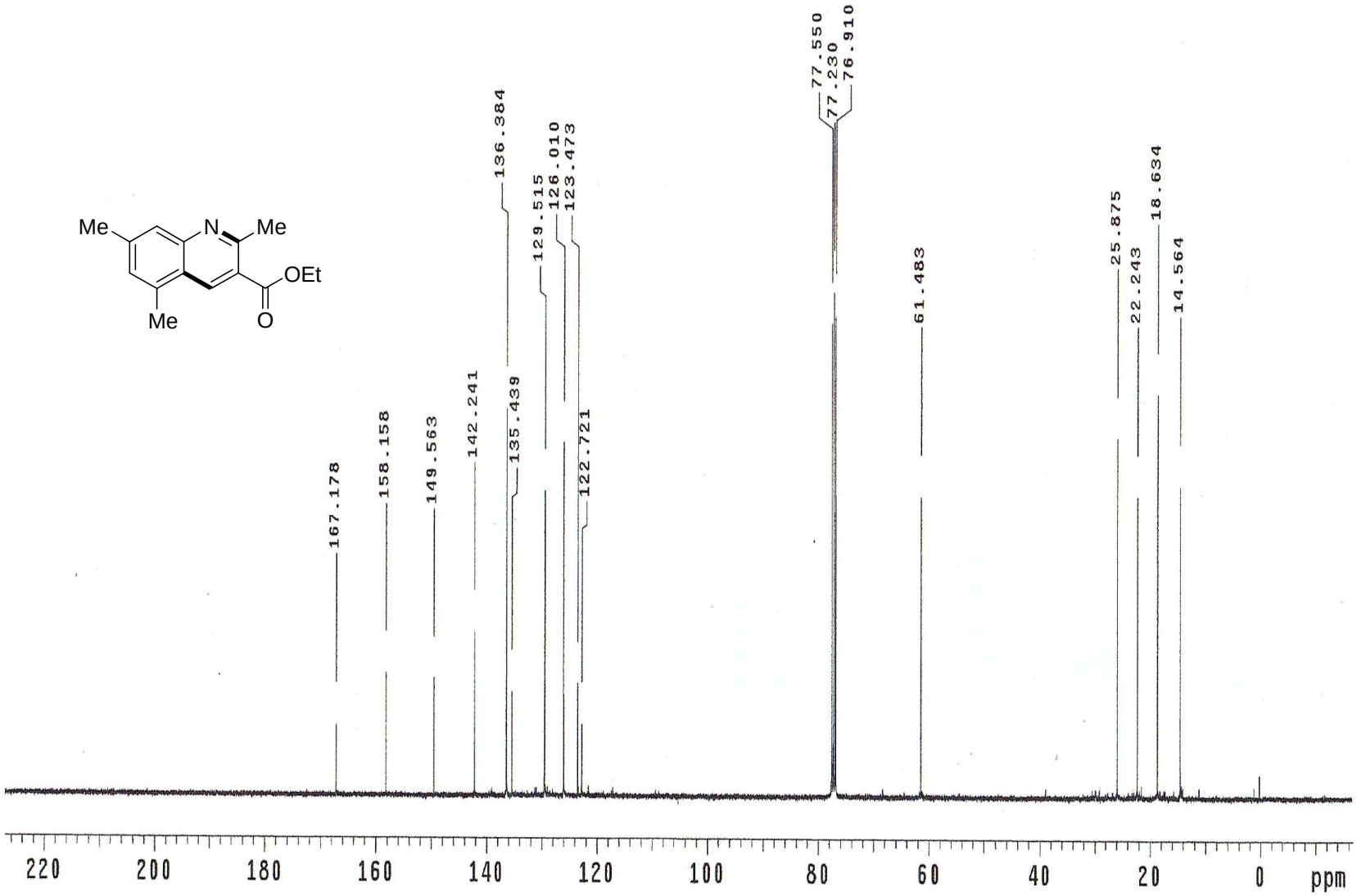
**Ethyl 2,6-dimethylquinoline-3-carboxylate (5b'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



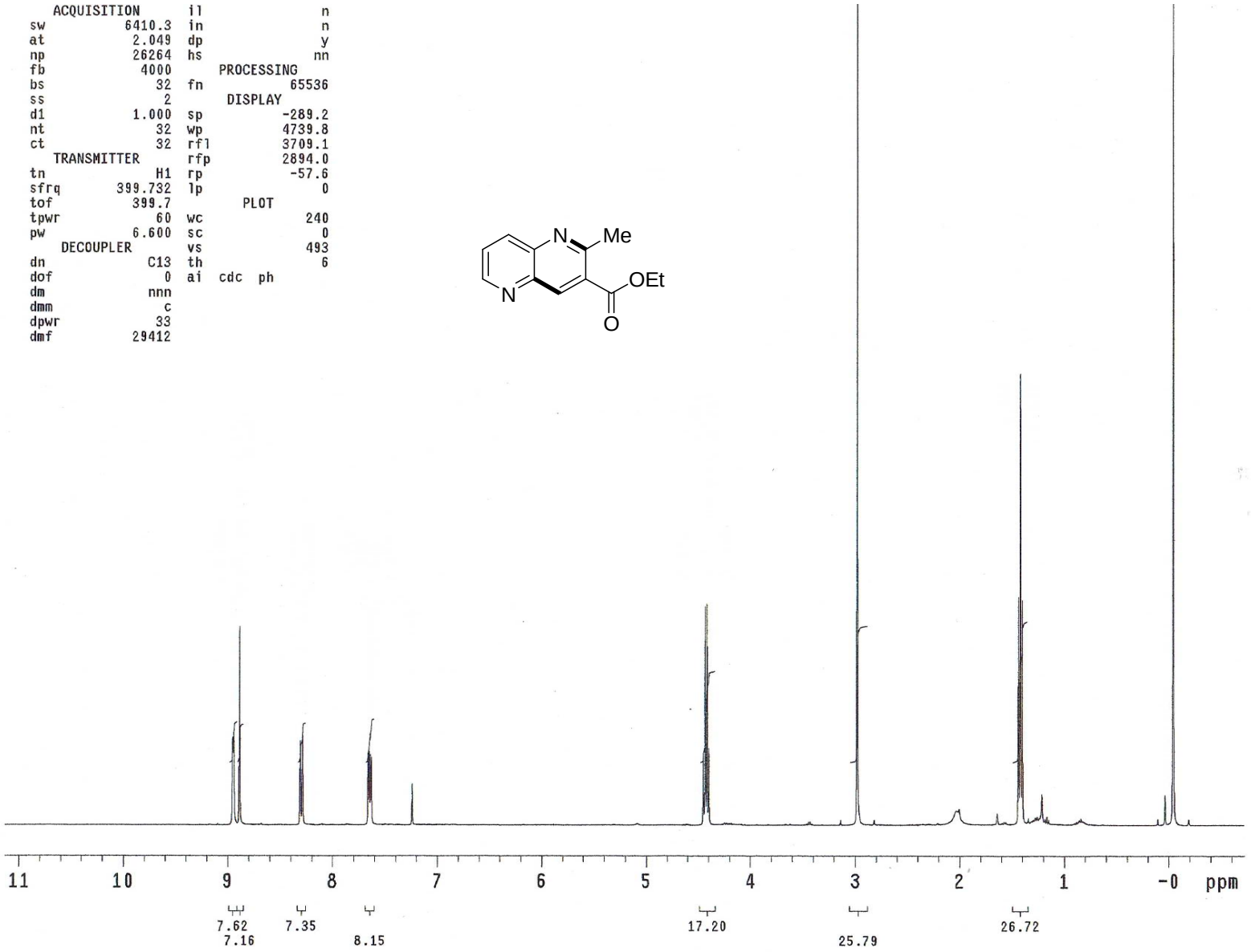
**Ethyl 2,5,7-trimethylquinoline-3-carboxylate (6b'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



**Ethyl 2,5,7-trimethylquinoline-3-carboxylate (6b'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)



**Ethyl 2-methyl-1,5-naphthyridine-3-carboxylate (7b'):** $^{1}$H NMR (400 MHz, $CDCl_3$)



**Ethyl 2-methyl-1,5-naphthyridine-3-carboxylate (7b'):** $^{13}C$ NMR (100 MHz, $CDCl_3$)