Electronic Supporting Information

Tailor-made synthesis of fully alkylated/arylated nicotinates by $FeCl_3$-mediated condensation of enamino esters with enones

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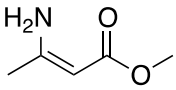
1. General information

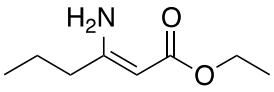
Unless otherwise noted, all reagents were commercially supplied and were used without further purification. α,β-Unsaturated ketones **2b**,[1] **2e–2g**,[2] **2h–2i**,[3] **2j**,[4] **2k-2m**,[5] **2s-2u**,[6] **13**,[7] and enamino esters **1b-1d**[8] were synthesized in from 72% to quantitative yields according to the method in the literature, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ using tetramethylsilane as an internal standard. ^{1}H NMR spectroscopic data are reported as follows: chemical shift (δ, ppm), chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, integration, coupling constant (Hz). ^{13}C NMR spectroscopic data are reported in terms of chemical shift (δ, ppm), and assignment was performed by DEPT experiment. Infrared spectra were recorded with a Shimadzu IR Affinity-1 spectrometer, and data are reported in frequency of absorption (wave numbers). Highresolution mass spectra were obtained with a AB SCIEX TripleTOF 4600 mass spectrometer. Melting points were recorded with a Stanford Research Systems MPA100 melting point apparatus. Microwave irradiation was used by Anton Paar Monowave 300.

2. Spectral data of enamino esters 1

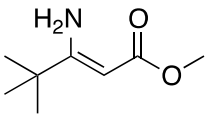
Methyl 3-amino-2-butenoate (1a) [9] White solid, mp 75–76 °C, R_f = 0.33 (silica gel, hexane/EtOAc = 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (s, 3H), 3.63 (s, 3H), 4.52 (s, 1H), 4.1–5.3 (br, 1H), 7.5–8.5 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 50.2 (CH_3), 84.0 (CH), 159.9 (C), 170.7 (C); IR (ATR/cm^{-1}): 3458, 1667, 1557.



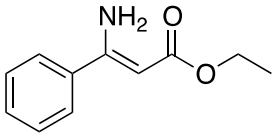
Ethyl 3-amino-2-hexenoate (1b)[10] Yellow oil, R_f = 0.32 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.55 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.09 (t, *J* = 7.2 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.2–5.7 (br, 1H), 4.53 (s, 1H), 7.3-8.4 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 14.7 (CH_3), 21.3 (CH_2), 38.5 (CH_2), 58.7 (CH_2), 83.7 (CH), 163.7 (C), 170.6 (C); IR (ATR/cm^{-1}): 3333, 1667, 1557.



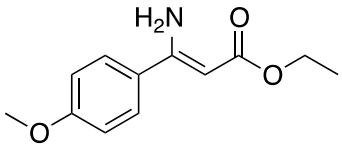
Methyl 3-amino-4,4-dimethyl-2-pentenoate (1c)[11] (1551.2 mg, 71% yield); Pale yellow oil, R_f = 0.55 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (s, 9H), 3.64 (s, 3H), 4.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9 (CH_3), 35.9 (C), 50.2 (CH_3), 80.0 (CH), 171.4 (C), 172.0 (C); IR (ATR/cm^{-1}): 3331, 1668, 1557.



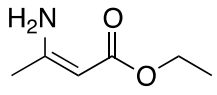
Ethyl 3-amino-4-phenyl-2-butenoate (1d)[10] Yellow oil, R_f = 0.38 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.96 (s, 1H), 7.40−7.43 (m, 3H), 7.53 (dd, *J* = 6.0, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7 (CH_3), 59.0 (CH_2), 84.8 (CH), 126.2 (CH), 128.9 (CH), 130.3 (CH), 137.8 (C), 160.6 (C), 170.5 (C); IR (ATR/cm^{-1}): 3326, 1661, 1557.



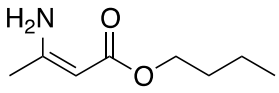
Ethyl 3-amino-4-(4-methoxyphenyl)-2-butenoate (1e)[10] Yellow oil, R_f = 0.21 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 3.83 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.93 (s, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8 (CH_3), 55.5 (CH_3), 59.0 (CH_2), 84.0 (CH), 114.3 (CH), 127.7 (CH), 130.1 (C), 160.3 (C), 161.4 (C), 170.7 (C); IR (ATR/cm^{-1}): 3323, 1645, 1557.



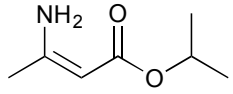
Ethyl 3-amino-2-butenoate (1f)[9] Colorless oil, R_f = 0.39 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 1.90 (s, 3H), 4.11 (q, *J* = 7.2 Hz, 2H), 4.4–5.4 (br, 1H), 4.53 (s, 1H), 7.5–8.5 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7 (CH_3), 22.5 (CH_3), 58.7 (CH_2), 84.5 (CH), 159.7 (C), 170.4 (C); IR (ATR/cm^{-1}): 3335, 1659, 1557.



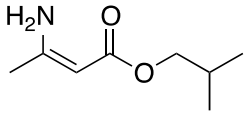
Butyl 3-amino-2-butenoate (1g)[12] Colorless oil, R_f = 0.31 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.39 (tq, *J* = 7.2, 7.2 Hz, 2H), 1.61 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.89 (s, 3H), 4.05 (t, *J* = 7.2 Hz, 2H), 4.3–5.2 (br, 1H), 4.53 (s, 1H), 7.4–8.5 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 19.4 (CH_2), 22.5 (CH_3), 31.3 (CH_2), 62.7 (CH_2), 84.5 (CH), 159.6 (C), 170.5 (C); IR (ATR/cm^{-1}): 3439, 1667, 1566.



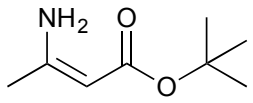
2-Propyl 3-amino-2-butenoate (1h)[9] Colorless oil, R_f = 0.31 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.4 Hz, 6H), 1.89 (s, 3H), 3.9-4.9 (br, 1H), 4.50 (s, 1H), 5.01 (septet, *J* = 6.4 Hz, 1H), 7.4–8.6 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3 (CH_3), 22.5 (CH_3), 65.5 (CH), 85.0 (CH), 159.5 (C), 170.0 (C); IR (ATR/cm^{-1}): 3439, 1667, 1566.



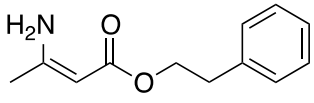
2-Methyl-1-propyl 3-amino-2-butenoate (1i)[13] Colorless oil, R_f = 0.32 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, *J* = 6.8 Hz, 6H), 1.90 (s, 3H), 1.91 (septet t, *J* = 6.8, 6.8 Hz, 1H), 3.84 (d, *J* = 6.8 Hz, 2H), 4.2–5.0 (br, 1H), 4.55 (s, 1H), 7.4–8.3 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4 (CH_3), 22.5 (CH_3), 28.1 (CH), 69.1 (CH_2), 84.5 (CH), 159.6 (C), 170.5 (C); IR (ATR/cm^{-1}): 3330, 1667, 1557.



2-Methyl-2-propyl 3-amino-2-butenoate (1j)[9] Colorless oil, R_f = 0.39 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H), 1.86 (s, 3H), 4.2–5.1 (br, 1H), 4.46 (s, 1H), 7.3–8.3 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 28.8 (CH_3), 78.3 (C), 86.2 (CH), 158.8 (C), 170.4 (C); IR (ATR/cm^{-1}): 3308, 1659, 1557, 1148.

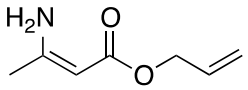


2-Phenylethyl 3-amino-2-butenoate (1k)[14] Colorless oil, R_f = 0.24 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 4.29 (t, *J* = 7.2 Hz, 2H), 4.3–5.0 (br, 1H), 4.54 (s, 1H), 7.2–7.4 (m, 5H), 7.5–8.6 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5

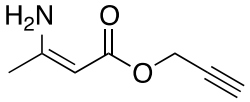


(CH_3), 35.7 (CH_2), 63.4 (CH_2), 84.3 (CH), 126.5 (CH), 128.5 (C), 129.1 (CH), 138.6 (C), 159.9 (C), 170.2 (C); IR (ATR/cm^{-1}): 3443, 1667, 1557.

3-Propenyl 3-amino-2-butenoate (1l)[9] Colorless oil, R_f = 0.29 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 4.2–4.9 (br, 1H), 4.5–4.6 (m, 3H), 5.19 (ddt, *J* = 10.4, 1.6, 1.6 Hz, 1H), 5.30 (ddt, *J* = 17.2, 1.6, 1.6 Hz, 1H), 5.95 (ddt, *J* = 17.2, 10.4, 1.6 Hz, 1H), 7.6–8.2 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 63.6 (CH_2), 84.1 (CH), 117.2 (CH_2), 133.6 (CH), 160.1 (C), 169.9 (C); IR (ATR/cm^{-1}): 3424, 1667, 1566.



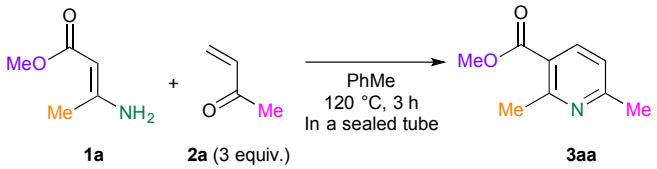
3-Propynyl 3-amino-2-butenoate (1m)[12] Colorless oil, R_f = 0.22 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 2.42 (t, *J* = 6.4 Hz, 1H), 4.2–5.5 (br, 1H), 4.56 (s, 1H), 4.66 (d, *J* = 6.4 Hz, 2H), 7.5–8.5 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5 (CH_3), 50.4 (CH_2), 74.0 (C), 79.2 (CH), 83.3 (CH), 161.0 (C), 169.1 (C); IR (ATR/cm^{-1}): 3474, 2126, 1667, 1557.



3. Synthesis of nicotinates 3 without using $FeCl_3$

To a solution of methyl 3-amino-2-butenoate (**1a**) (23.0 mg, 0.20 mmol) in toluene (0.5 mL), methyl vinyl ketone **2a** (48.7 μL, 0.60 mmol) was added, and the resultant solution was heated at 120 °C for 3 h in a sealed tube. After evaporation of the solvent under reduced pressure, the residue was treated by short silica gel column chromatography (hexane/EtOAc = 8/2) to give methyl 2,6-dimethylpyridine-3-carboxylate (**3a**) (26.9 mg, 0.16 mmol, 82%) as a pale yellow oil. Other nicotinates **3a**–**c** were also synthesized in a similar way.

Table S-1. Optimization of conditions of **1a** with **2a**

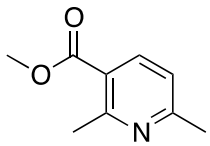


1a **2a** (3 equiv.) **3aa**

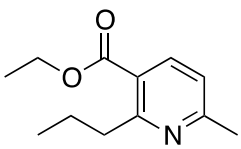
Entry	Solv.	Temp./°C	**2a**/equiv.	**3aa**/%[a]
1	MeOH	90	5	38
2	DMF	90	5	56
3	MeCN	90	5	53
4	EtOAc	90	5	54
5	THF	90	5	52
6	$CHCl_3$	90	5	58
7	Hexane	90	5	63
8	PhMe	90	5	72
9	PhMe	120	5	88
10	PhMe	120	3	87
11	PhMe	120	2	64

[a] NMR Yield.

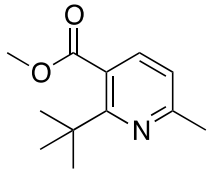
Methyl 2,6-dimethylpyridine-3-carboxylate (3aa)[15] (26.9 mg, 82% yield). Pale yellow oil, R_f = 0.37 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 2.80 (s, 3H), 3.89 (s, 3H), 7.04 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8 (CH_3), 24.9 (CH_3), 52.2 (CH_3), 120.6 (CH), 122.5 (C), 138.9 (CH), 159.7 (C), 161.5 (C), 167.3 (C); IR (ATR/cm^{-1}): 2951, 1722, 1275.



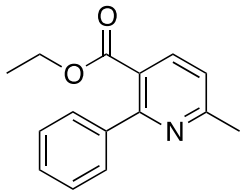
Ethyl 6-methyl-2-propylpyridine-3-carboxylate (3ba)[16] (32.9 mg, 80% yield); Yellow oil, R_f = 0.44 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.6 Hz, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.71 (tq, *J* = 7.6, 7.6 Hz, 2H), 2.55 (s, 3H), 3.09 (t, *J* = 7.6 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 14.4 (CH_3), 23.8 (CH_2), 24.9 (CH_3), 39.3 (CH_2), 61.2 (CH_2), 120.5 (CH), 122.9 (C), 138.9 (CH), 161.3 (C), 163.2 (C), 167.1 (C); IR (ATR/cm^{-1}): 1722, 1251.



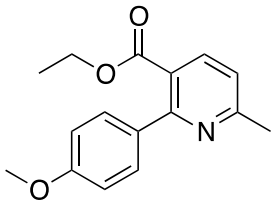
Ethyl 6-methyl-2-(2-methyl-1-propyl) pyridine-3-carboxylate (3ca) (17.2 mg, 42% yield). Yellow oil, R_f = 0.63 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.53 (s, 3H), 3.89 (s, 3H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8 (CH_3), 30.2 (CH_3), 39.3 (C), 52.5 (CH_3), 119.3 (CH), 125.0 (C), 136.9 (CH), 158.4 (C), 164.7 (C), 171.4 (C); IR (ATR/cm^{-1}): 1733, 1280, 1241, 1070; HRMS (ESI/TOF): *m/z calcd*. for $C_{12}H_{17}NO_2$ $[M + H]^+$ 208.1332, found 208.1323.



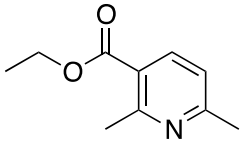
Ethyl 2-phenyl-6-methylpyridine-3-carboxylate (3da)[17] (40.7 mg, 85% yield). Yellow oil, R_f = 0.42 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, *J* = 7.2 Hz, 3H), 2.65 (s, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.4–7.5 (m, 3H), 7.5–7.6 (m, 2H), 8.02 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8 (CH_3), 25.0 (CH_3), 61.4 (CH_2), 121.3 (CH), 124.6 (C), 128.2 (CH), 128.5 (CH), 128.7 (CH), 138.4 (CH), 140.8 (C), 158.9 (C), 160.9 (C), 168.3 (C); IR (ATR/cm^{-1}): 1722, 1563, 1280.



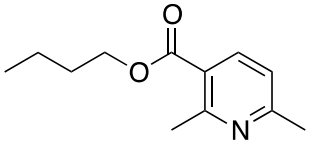
Ethyl 2-(4-methoxyphenyl)-6-methylpyridine-3-carboxylate (3ea) (46.3 mg, 86% yield). Yellow oil, R_f = 0.24 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, *J* = 7.2 Hz, 3H), 2.63 (s, 3H), 3.84 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (CH_3), 24.9 (CH_3), 55.5 (CH_3), 61.4 (CH_2), 113.7 (CH), 120.8 (CH), 124.3 (C), 130.2 (CH), 133.2 (C), 138.3 (CH), 158.3 (C), 160.2 (C), 160.8 (C), 168.6 (C); IR (ATR/cm^{-1}): 1714, 1516, 1250, HRMS (ESI/TOF): *m/z calcd*. for $C_{16}H_{17}NO_3$ $[M + H]^+$ 272.1281, found 272.1269.



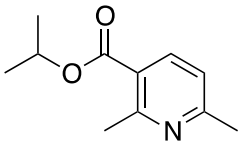
Ethyl 2,6-dimethylpyridine-3-carboxylate (3fa)[17] (30.2 mg, 85% yield). Pale yellow oil, R_f = 0.38 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, *J* = 7.2 Hz, 3H), 2.56 (s, 3H), 2.80 (s, 3H), 4.32 (q, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 24.8 (CH_3), 25.0 (CH_3), 61.2 (CH_2), 120.5 (CH), 122.9 (C), 138.9 (CH), 159.5 (C), 161.3 (C), 166.9 (C); IR (ATR/cm^{-1}): 2357, 1722, 1273.



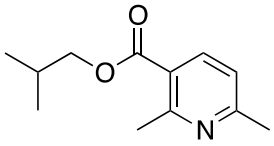
Butyl 2,6-dimethylpyridine-3-carboxylate (3ga) (37.9 mg, 92% yield). Pale yellow oil, R_f = 0.26 (silica gel, hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.6 Hz, 3H), 1.47 (tq, *J* = 7.6, 7.6 Hz, 2H), 1.74 (tt, *J* = 7.6, 7.6 Hz, 2H), 2.56 (s, 3H), 2.80 (s, 3H), 4.30 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3), 19.5 (CH_2), 24.8 (CH_3), 25.0 (CH_3), 30.9 (CH_2), 65.1 (CH_2), 120.6 (CH), 123.0 (C), 138.9 (CH), 159.5 (C), 161.3 (C), 167.0 (C); IR (ATR/cm^{-1}): 2963, 2359, 1722, 1275; HRMS (ESI/TOF): *m/z calcd.* for $C_{12}H_{17}NO_2$ $[M + H]^+$ 208.1332, found 208.1331.



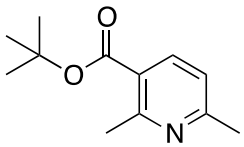
2-Propyl 2,6-dimethylpyridine-3-carboxylate (3ha) (35.9 mg, 81% yield). Yellow oil, R_f = 0.46 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, *J* = 6.0 Hz, 6H), 2.54 (s, 3H), 2.78 (s, 3H), 5.22 (septet, *J* = 6.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1 (CH_3), 24.8 (CH_3), 24.9 (CH_3), 68.7 (CH), 120.5 (CH), 123.4 (C), 138.8 (CH), 159.3 (C), 161.1 (C), 166.5 (C); IR (ATR/cm^{-1}): 2976, 2359, 1715, 1273; HRMS (ESI/TOF): *m/z calcd.* for $C_{11}H_{15}NO_2$ $[M + H]^+$ 194.1175, found 194.1173.



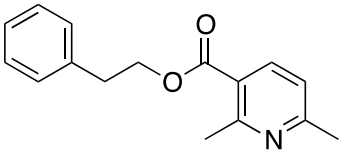
2-Methyl-1-propyl 2,6-dimethylpyridine-3-carboxylate (3ia) (29.4 mg, 79% yield). Yellow oil, R_f = 0.33 (silica gel, hexane/EtOAc = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (d, *J* = 6.8 Hz, 6H), 2.07 (triple septet, *J* = 6.8, 6.8 Hz, 1H), 2.56 (s, 3H), 2.81 (s, 3H), 4.09 (d, *J* = 6.8 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4 (CH_3), 24.8 (CH_3), 25.1 (CH_3), 28.0 (CH), 71.4 (CH_2), 120.6 (CH), 123.0 (C), 138.9 (CH), 159.6 (C), 161.4 (C), 167.0 (C); IR (ATR/cm^{-1}): 2961, 2357, 1721, 1257; HRMS (ESI/TOF): *m/z calcd.* for $C_{12}H_{17}NO_2$ $[M + H]^+$ 208.1332, found 208.1334.



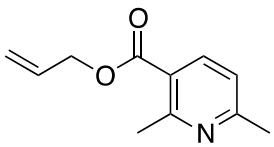
2-Methyl-2-propyl 2,6-dimethylpyridine-3-carboxylate (3ja)[17] (29.8 mg, 72% yield). Pale yellow oil, R_f = 0.37 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 9H), 2.55 (s, 3H), 2.77 (s, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8 (CH_3), 25.0 (CH_3), 28.4 (CH_3), 81.8 (C), 120.5 (CH), 124.6 (C), 138.8 (CH), 158.9 (C), 160.8 (C), 166.4 (C); IR (ATR/cm^{-1}): 2978, 1721, 1254.



2-Phenylethyl 2,6-dimethylpyridine-3-carboxylate (3ka) (41.6 mg, 82% yield). Yellow oil, R_f = 0.18 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 3H), 2.74 (s, 3H), 3.06 (t, *J* = 6.8 Hz, 2H), 4.52 (t, *J* = 6.8 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.2–7.4 (m, 5H), 8.00 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8 (CH_3), 24.9 (CH_3), 35.3 (CH_2), 65.6 (CH_2), 120.5 (CH), 122.7 (C), 126.8 (CH), 128.7 (CH), 129.0 (CH), 137.9 (C), 138.9 (CH), 159.6 (C), 161.4 (C), 166.7 (C); IR (ATR/cm^{-1}): 2968, 2359, 1726, 1271; HRMS (ESI/TOF): *m/z calcd.* for $C_{16}H_{18}NO_2$ $[M + H]^+$ 256.1332, found 256.1331.

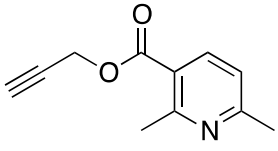


3-Propenyl 2,6-dimethylpyridine-3-carboxylate (3la) (28.9 mg, 76% yield). Pale yellow oil, R_f = 0.36 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 2.81 (s, 3H), 4.80 (ddd, *J* = 6.4, 1.2, 1.2 Hz, 2H), 5.29 (ddt, *J* = 10.4, 1.2, 1.2 Hz, 1H), 5.29 (ddt, *J* = 17.2, 1.2, 1.2 Hz, 1H), 6.03 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8 (CH_3), 25.0 (CH_3), 65.8 (CH_2), 118.7 (CH_2), 120.6 (CH), 122.6 (C), 132.2 (CH), 138.9 (CH), 159.8 (C), 161.6 (C), 166.5

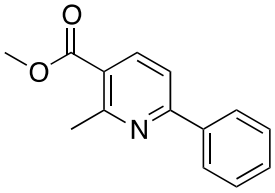


(C); IR (ATR/cm^{-1}): 2355, 1728, 1269; HRMS (ESI/TOF): *m/z calcd.* for $C_{11}H_{13}NO_2$ $[M + H]^+$ 192.1019, found 192.1019.

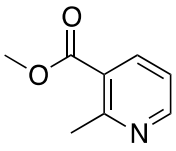
3-Propynyl 2,6-dimethylpyridine-3-carboxylate (3ma) (24.4 mg, 65% yield). Pale yellow oil, R_f = 0.29 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (t, *J* = 2.4 Hz, 1H), 2.57 (s, 3H), 2.82 (s, 3H), 4.90 (d, *J* = 2.4 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9 (CH_3), 25.0 (CH_3), 52.6 (CH_2), 75.2 (CH), 77.7 (C), 120.6 (CH), 121.8 (C), 139.1 (CH), 160.1 (C), 162.0 (C), 165.9 (C); IR (ATR/cm^{-1}): 3391, 2127, 1730; HRMS (ESI/TOF): *m/z calcd.* for $C_{11}H_{11}NO_2$ $[M + H]^+$ 190.0863, found 190.0862.



Methyl 2-methyl-6-phenylpyridine-3-carboxylate (3ab)[18] (40.2 mg, 89% yield). Yellow oil, R_f = 0.32 (silica gel, hexane/EtOAc = 95/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (s, 3H), 3.94 (s, 3H), 7.4–7.5 (m, 3H), 7.63 (d, *J* = 8.4 Hz, 1H), 8.0–8.1 (m, 2H), 8.26 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4 (CH_3), 52.3 (CH_3), 117.5 (CH), 123.5 (C), 127.5 (CH), 129.0 (CH), 129.8 (CH), 138.6 (C), 139.5 (CH), 159.3 (C), 160.2 (C), 167.2 (C); IR (ATR/cm^{-1}): 2951, 2355, 1728, 1267.



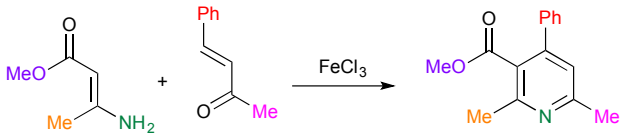
Methyl 2-methypyridine-3-carboxylate (3ac)[15] (27.5 mg, 91% yield). Yellow oil, R_f = 0.29 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (s, 3H), 3.91 (s, 3H), 7.19 (dd, *J* = 7.6, 4.8 Hz, 1H), 8.17 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.60 (dd, *J* = 4.8, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9 (CH_3), 52.3 (CH_3), 121.0 (CH), 125.5 (C), 138.5 (CH), 152.0 (CH), 160.0 (C), 167.1 (C); IR (ATR/cm^{-1}): 2949, 1726, 1277.



4. Synthesis of nicotinates 3 and 14 using $FeCl_3$

To a solution of methyl 3-amino-2-butenoate (**1a**) (46.0 mg, 0.40 mmol) in acetonitrile (0.5 mL), were added 4-phenyl-3-buten-2-one (**2d**) (29.2 mg, 0.20 mmol) and iron(III) chloride (32.4 mg, 0.20 mmol), and the resultant solution was heated at 150 °C for 1 h under microwave irradiation. After evaporation of the solvent under reduced pressure, the residue was washed with water (15 mL×3), and then extracted with chloroform (15 mL×3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by short silica gel column chromatography (hexane/EtOAc = 8/2) to afford methyl 2,6-dimethyl-4-phenylnicotinate (**3ad**) (35.5 mg, 0.16 mmol, 79%) as a yellow oil. Other nicotinates **3ae**–**3av**, and **14** were also synthesized in a similar way.

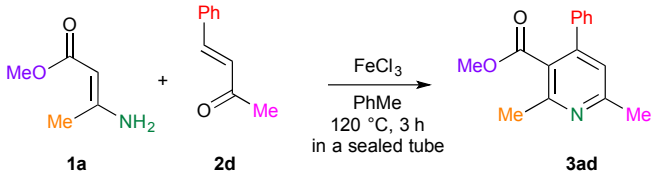
Table S-2. Study on the additives in the reaction of **1a** with **2d.**



1a **2d** **3ad**

Entry	Additive	Yield/%
1	*p*-TsOH · H_2O	0
2	NEt_3	0
3	BF_3 · Et_2O	20
4	$Cu(OAc)_2$	0
5	$Mn(OAc)_3$ · $2H_2O$	0
6	$Mg(OAc)_2$ · $4H_2O$	0
7	$CoSO_4$ · $7H_2O$	0
8	$AlCl_3$	23
9	$NiCl_2$	0
10	$SbCl_3$	0
11	$CuCl_2$ · $2H_2O$	0
12	$SnCl_2$ · $2H_2O$	26
13	$InCl_3$	30
14	$ZnCl_2$	34
15	$FeCl_3$	34
16	$FeCl_2$ · $4H_2O$	20
17	$FeCl_3$ · $6H_2O$	0
18	$Fe(OTs\text{-}p)_3$ · $6H_2O$	0
19	$Fe(NO_3)_3$ · $9H_2O$	0

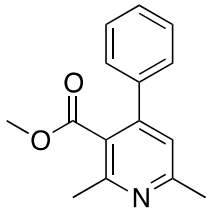
Table S-3. Optimization of reaction conditions for synthesizing **3ad**.



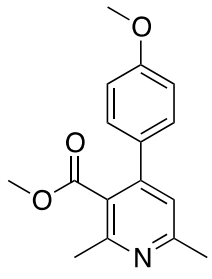
Entry	Solv.	Molar ratio			Temp./°C	Time/h	Yield/%[a]
		1a	**2d**	$FeCl_3$			
1	PhMe	1	1	1	120	3	40
2	$CHCl_3$	1	1	1	120	3	45
3	EtOAc	1	1	1	120	3	31
4	THF	1	1	1	120	3	29
5	MeCN	1	1	1	120	3	48
6	MeOH	1	1	1	120	3	46
7	H_2O	1	1	1	120	3	0
8	MeCN	1	1	2	120	3	16
9	MeCN	1	2	1	120	18	54
10	MeCN	2	1	1	120	3	73
11	MeCN	1	1	1	120	24	63
12[a]	MeCN	1	1	1	150	1	58
13	MeCN	2	1	1	150	1	72
14[b]	MeCN	2	1	1	150	1	87
15[b]	MeCN	2	1	0.2	150	1	74

[a]NMR yield. [b]Microwave heating was used.

Methyl 2,6-dimethyl-6-phenylpyridine-3-carboxylate (3ad) (35.5 mg, 79% yield). Yellow oil, R_f = 0.36 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 2.60 (s, 3H), 3.61 (s, 3H), 7.02 (s, 1H), 7.3–7.4 (m, 2H), 7.4–7.5 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 24.6 (CH_3), 52.3 (CH_3), 121.2 (CH), 125.7 (C), 127.9 (CH), 128.6 (CH), 128.7 (CH), 138.9 (C), 148.6 (C), 155.3 (C), 159.0 (C), 169.8 (C); IR (ATR/cm^{-1}): 2953, 1728, 1267; HRMS (ESI/TOF): *m/z calcd.* for $C_{15}H_{15}NO_2$ $[M + H]^+$ 242.1176, found 242.1172.

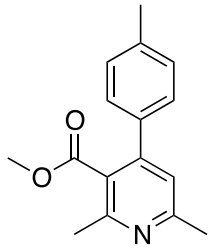


Methyl 2,6-dimethyl-4-(4-methoxyphenyl)pyridine-3-carboxylate (3ae) (35.1 mg, 65% yield). Yellow solid, mp 103–104 °C,



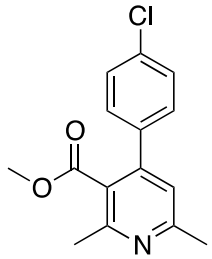
R_f = 0.20 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 2.58 (s, 3H), 3.66 (s, 3H), 3.85 (s, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.00 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 24.6 (CH_3), 52.3 (CH_3), 55.5 (CH_3), 114.3 (CH), 121.1 (CH), 125.6 (C), 129.2 (CH), 131.1 (C), 148.0 (C), 155.2 (C), 158.8 (C), 160.1 (C), 170.1 (C); IR (ATR/cm^{-1}): 2938, 1726, 1250; HRMS (ESI/TOF): *m/z calcd.* for $C_{16}H_{17}NO_3$ $[M + H]^+$ 272.1281, found 272.1294.

Methyl 2,6-dimethyl-4-(4-methylphenyl)pyridine-3-carboxylate (3af) (42.3 mg, 83% yield). Yellow oil, R_f = 0.28 (silica gel, hexane/EtOAc = 8/2).



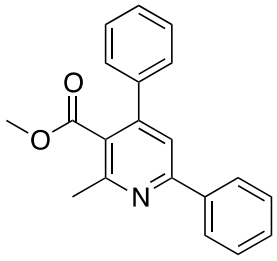
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.57 (s, 3H), 2.58 (s, 3H), 3.65 (s, 3H), 7.01 (s, 1H), 7.2–7.3 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 23.0 (CH_3), 24.6 (CH_3), 52.3 (CH_3), 121.2 (CH), 125.6 (C), 127.8 (CH), 129.5 (CH), 135.9 (C), 138.6 (C), 148.5 (C), 155.2 (C), 158.9 (C), 170.0 (C); IR (ATR/cm^{-1}): 2945, 1726, 1267; HRMS (ESI/TOF): *m/z calcd.* for $C_{16}H_{17}NO_2$ $[M + H]^+$ 256.1332, found 256.1342.

Methyl 4-(4-chlorophenyl)-2,6-dimethylpyridine-3-carboxylate (3ag)[19] (39.3 mg, 72% yield). Yellow oil, R_f = 0.26 (silica gel, hexane/EtOAc = 8/2).



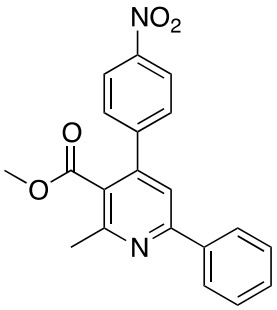
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (s, 3H), 2.59 (s, 3H), 3.65 (s, 3H), 6.98 (s, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1 (CH_3), 24.6 (CH_3), 52.4 (CH_3), 121.0 (CH), 125.5 (C), 129.0 (CH), 129.3 (CH), 134.9 (C), 137.3 (C), 147.3 (C), 155.6 (C), 159.2 (C), 169.5 (C); IR (ATR/cm^{-1}): 2951, 1726, 1261.

Methyl 4,6-diphenyl-2-methylpyridine-3-carboxylate (3ah)[20] (42.4 mg, 70% yield). White solid, mp 82–83 °C, R_f = 0.60 (silica gel, hexane/EtOAc = 8/2).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 3H), 3.65 (s, 3H), 7.4–7.5 (m, 8H), 7.58 (s, 1H), 8.04 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4 (CH_3), 52.3 (CH_3), 118.7 (CH), 126.7 (C), 127.4 (CH), 128.0 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 129.5 (CH), 138.9 (C), 139.0 (C), 149.1 (C), 156.0 (C), 157.7 (C), 169.7 (C); IR (ATR/cm^{-1}): 1726, 1271.

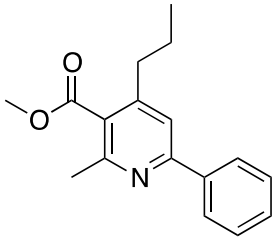
Methyl 2-methyl-4-(4-nitrophenyl)-6-phenylpyridine-3-carboxylate (3ai) (39.7 mg, 57% yield). Yellow solid, mp 141–142 °C,



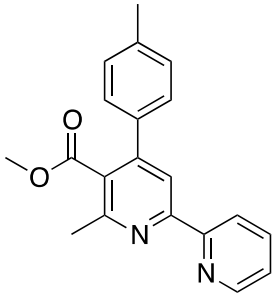
R_f = 0.41 (silica gel, hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (s, 3H), 3.67 (s, 3H), 7.4–7.5 (m, 3H), 7.55 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 8.05 (dd, *J* = 2.0, 8.4 Hz, 2H), 8.32 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5 (CH_3), 52.5 (CH_3), 118.1 (CH), 124.0 (CH), 126.1 (C), 127.4 (CH), 129.0 (CH), 129.1 (CH), 129.9 (CH), 138.4 (C), 145.6 (C), 148.1 (C), 156.7 (C), 158.1 (C), 168.9 (C); IR (ATR/cm^{-1}): 2951,

1728, 1518, 1271; HRMS (ESI/TOF): *m/z calcd.* for $C_{20}H_{16}N_2O_4$ $[M + H]^+$ 349.1183, found 349.1187.

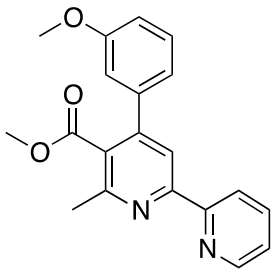
Methyl 2-methyl-6-phenyl-4-propylpyridine-3-carboxylate (3aj) (38.4 mg, 72% yield). Yellow oil, R_f = 0.61 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.68 (tq, *J* = 7.2, 7.2 Hz, 2H), 2.61 (s, 3H), 2.64 (t, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 7.41 (s, 1H), 7.4–7.5 (m, 3H), 7.98 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 23.5 (CH_3), 23.8 (CH_2), 35.7 (CH_2), 52.3 (CH_3), 118.6 (CH), 127.3 (CH), 127.6 (C), 128.9 (CH), 129.3 (CH), 139.3 (C), 150.0 (C), 155.5 (C), 157.5 (C), 169.8 (C); IR (ATR/cm^{-1}): 2955, 1726, 1269; HRMS (ESI/TOF): *m/z calcd.* for $C_{17}H_{19}NO_2$ $[M + H]^+$ 270.1489, found 270.1490.



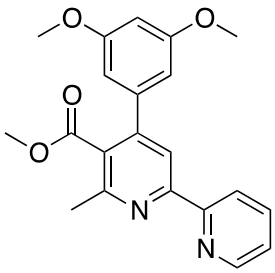
Methyl 2-methyl-4-(4-methylphenyl)-6-(2-pyridinyl)pyridine-3-carboxylate (3ak) (226.8 mg, 72% yield). Brown oil, R_f = 0.23 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.69 (s, 3H), 3.68 (s, 3H), 7.23 (br d, *J* = 8.0 Hz, 2H), 7.31 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 7.35 (br d, *J* = 8.0 Hz, 2H), 7.82 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 8.28 (s, 1H), 8.47 (ddd, *J* = 7.6, 0.8, 0.8 Hz, 1H), 8.67 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2 (CH_3), 23.1 (CH_3), 52.2 (CH_3), 118.9 (CH), 121.6 (CH), 123.9 (CH), 127.8 (CH), 127.9 (C), 129.3 (C), 135.7 (C), 136.9 (CH), 138.4 (C), 148.9 (C), 149.2 (CH), 155.2 (C), 155.6 (C), 155.9 (C), 169.7 (C); IR (ATR/cm^{-1}): 1730, 1557, 1267; HRMS (ESI/TOF): *m/z calcd.* for $C_{20}H_{18}N_2O_2$ $[M + H]^+$ 319.1441, found 319.1441.



Methyl 2-methyl-4-(3-methoxyphenyl)-6-(2-pyridinyl)pyrinine-3-carboxylate (3al) (37.6 mg, 57% yield). Yellow oil, R_f = 0.19 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (s, 3H), 3.68 (s, 3H), 3.83 (s, 3H), 6.9−7.0 (m, 3H), 7.3−7.4 (m, 2H), 7.82 (dd, *J* = 7.6, 7.6 Hz, 1H), 8.30 (s, 1H), 8.48 (d, *J* = 7.6 Hz, 1H), 8.67 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1 (CH_3), 52.2 (CH_3), 55.3 (CH_3), 113.2 (CH), 114.4 (CH), 118.8 (CH), 120.3 (CH), 121.6 (CH), 124.0 (CH), 127.9 (C), 129.6 (CH), 136.8 (CH), 140.0 (C), 148.9 (C), 149.2 (CH), 155.3 (C), 155.5 (C), 155.9 (C), 159.7 (C), 169.5 (C); IR (ATR/cm^{-1}): 1729, 1549, 1271; HRMS (ESI/TOF): *m/z calcd*. for $C_{20}H_{18}N_2O_3$ $[M + H]^+$ 335.1390, found 335.1375.

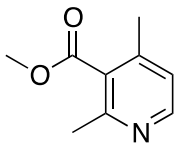


Methyl 2-methyl-4-(3,5-dimethoxyphenyl)-6-(2-pyridinyl) pyridine-3-carboxylate (3am) (186.6 mg, 52% yield). Yellow oil, R_f = 0.15 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H), 3.70 (s, 3H), 3.79 (s, 6H), 6.50 (t, *J* = 2.0 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 2H), 7.28 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.78 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 8.31 (s, 1H), 8.46 (ddd, *J* = 7.6, 1.2, 0.8 Hz, 1H), 8.65 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H); ^{13}C



NMR (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 52.2 (CH_3), 55.3 (CH_3), 100.8 (CH), 105.9 (CH), 118.6 (CH), 121.5 (CH), 123.9 (CH), 127.8 (C), 136.8 (CH), 140.6 (C), 148.8 (CH), 149.1 (C), 155.1 (C), 155.4 (C), 155.9 (C), 160.8 (C), 169.5 (C); IR(ATR/cm^{-1}): 1730, 1580, 1268; HRMS (ESI/TOF): *m/z calcd*. for $C_{21}H_{20}N_2O_4$ $[M + H]^+$ 365.1496, found 365.1484.

Methyl 2,4-dimethylpyridine-3-carboxylate (3an) (26.5 mg, 81% yield). Yellow oil, R_f = 0.21 (silica gel, hexane/EtOAc = 8/2).



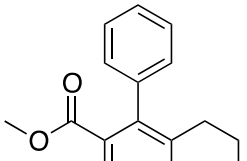
^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.54 (s, 3H), 3.94 (s, 3H), 6.99 (d, *J* = 4.8 Hz, 1H), 8.38 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6 (CH_3), 23.1 (CH_3), 52.4 (CH_3), 122.8 (CH), 129.5 (C), 145.0 (C), 149.7 (CH), 155.4 (C), 169.3 (C); IR (ATR/cm^{-1}): 1732, 1287; HRMS (ESI/TOF): *m/z calcd.* for $C_9H_{11}NO_2$ $[M + H]^+$ 166.0863, found 166.0865.

Methyl 2-methyl-4-phenylpyridine-3-carboxylate (3ao) (17.7 mg, 39% yield). Yellow oil, R_f = 0.26 (silica gel, hexane/EtOAc = 8/2). ^1H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 3.64 (s, 3H), 7.17 (d, *J* = 5.2 Hz, 1H), 7.3–7.4 (m, 2H), 7.4–7.5 (m, 3H), 8.57 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (CH_3), 52.4 (CH_3), 121.8 (CH), 127.9 (CH), 128.5 (C), 128.8 (CH), 129.0 (CH), 138.5 (C), 148.2 (C), 149.8 (CH), 155.8 (C), 169.4 (C); IR (ATR/cm^{-1}): 2955, 1728, 1267; HRMS (ESI/TOF): *m/z calcd.* for $C_{14}H_{13}NO_2$ $[M + H]^+$ 228.1019, found 228.1027.

Methyl 2,5,6-trimethylpyridine-3-carboxylate (3ap) (29.7 mg, 83% yield). Pale yellow oil, R_f = 0.38 (silica gel, hexane/EtOAc = 8/2). ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.50 (s, 3H), 2.76 (s, 3H), 3.89 (s, 3H), 7.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6 (CH_3), 22.8 (CH_3), 24.4 (CH_3), 52.1 (CH_3), 122.8 (C), 128.7 (C), 139.5 (CH), 156.7 (C), 160.3 (C), 167.5 (C); IR (ATR/cm^{-1}): 2951, 1728, 1281. HRMS (ESI/TOF): *m/z calcd.* for $C_{10}H_{13}NO_2$ $[M + H]^+$ 180.1019, found 180.1020.

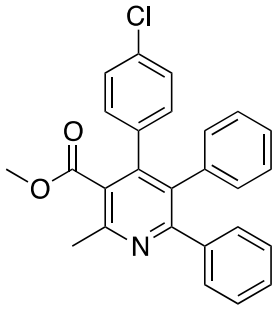
Methyl 2,4,5,6-tetramethylpyridine-3-carboxylate (3aq)[21] (31.3 mg, 82% yield). White solid, mp 55–56 °C, R_f = 0.21 (silica gel, hexane/EtOAc = 8/2). ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.20 (s, 3H), 2.44 (s, 3H), 2.50 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8 (CH_3), 17.1 (CH_3), 22.7 (CH_3), 23.5 (CH_3), 52.3 (CH_3), 127.5 (C), 127.9 (C), 142.5 (C), 150.8 (C), 156.9 (C), 170.3 (C); IR (ATR/cm^{-1}): 2947, 1726, 1267.

Methyl 2-methyl-5,6,7,8-tetrahydroquinoline-3-carboxylate (3ar) (43.8 mg, 78% yield). Orange solid, mp 68–69 °C, R_f = 0.28 (s ilica gel, hexane/EtOAc = 8/2). ^1H NMR (400 MHz, $CDCl_3$) δ 1.70 (tt, *J* = 6.0, 6.8 Hz,



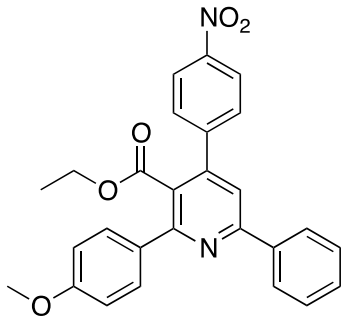
2H), 1.86 (tt, J = 6.0, 6.8 Hz, 2H), 2.40 (t, J = 6.0 Hz, 2H), 2.97 (t, J = 6.8 Hz, 2H), 2.53 (s, 3H), 3.46 (s, 3H), 7.1–7.2 (m, 2H), 7.3–7.4 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_3), 22.9 (CH_2), 23.0 (CH_2), 27.1 (CH_2), 33.3 (CH_2), 52.0 (CH_3), 127.1 (C), 127.6 (C), 128.0 (CH), 128.3 (CH), 128.6 (CH), 137.3 (C), 147.8 (C), 151.5 (C), 158.2 (C), 169.3 (C); IR (ATR/cm^{-1}): 2938, 1730, 1271; HRMS (ESI/TOF): *m/z calcd.* for $C_{18}H_{19}NO_2$ $[M + H]^+$ 282.1489, found 282.1484.

Methyl-4-(4-chlorophenyl)-5,6-diphenyl-2-methylpyridiney-3-carboxylate (3as) (20.2 mg, 24% yield). White solid,



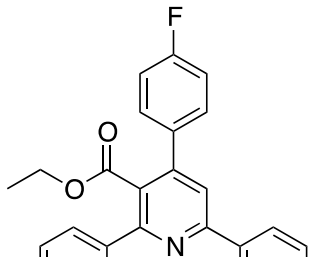
mp 133–134 °C, R_f = 0.55 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 3H), 3.59 (s, 3H), 6.7–6.8 (m, 2H), 6.9–7.0 (m, 2H), 7.0–7.1 (m, 3H), 7.1–7.2 (m, 5H), 7.2–7.3 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1 (CH_3), 52.4 (CH_3), 126.9 (CH), 127.9 (CH), 127.9 (CH), 128.1 (CH), 128.4 (C), 130.0 (CH), 130.6 (CH), 131.3 (CH), 132.5 (C), 133.8 (C), 135.9 (C), 137.0 (C), 140.3 (C), 146.7 (C), 153.8 (C), 158.5 (C), 169.1 (C), one signal of a tertiary carbon was not observed presumably due to overlapping with another signal; IR (ATR/cm^{-1}): 3055, 1730, 1549, 1227; HRMS (ESI/TOF): *m/z calcd.* for $C_{26}H_{20}ClNO_2$ $[M + H]^+$ 414.1255, found 414.1254.

Ethyl 2-(4-methoxyphenyl)-4-(4-nitrophenyl)-6-phenylpyridine-3-carboxylate (3ei) (67.4 mg, 74% yield); White



solid, mp 67−68 °C, R_f = 0.30 (silica gel, hexane/EtOAc = 8/2), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H), 3.87 (s, 3H), 4.01 (q, J = 7.2 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 7.4−7.5 (m, 3H), 7.63 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 8.12 (dd, J = 8.8, 1.6 Hz, 2H), 8.32 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 55.4 (CH_3), 61.7 (CH_2), 113.9 (CH), 118.1 (CH), 123.7 (CH), 125.9 (C), 127.2 (CH), 128.9 (CH), 129.3 (CH), 129.8 (CH), 130.0 (CH), 132.2 (C), 138.1(C), 145.2 (C), 147.3 (C), 148.0 (C), 156.6 (C), 157.5 (C), 160.5 (C), 168.4 (C); IR(ATR/cm^{-1}):1723, 1516, 1349, 1251; HRMS (ESI/TOF): *m/z calcd*. for $C_{27}H_{22}N_2O_5$ $[M + H]^+$ 455.1602, found 455.1607.

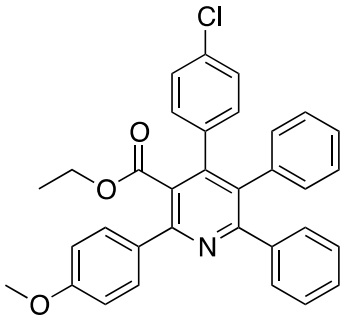
Ethyl 4-(4-fluorophenyl)-2-(4-methoxyphenyl)-6-(4-methylphenyl)pyridine-3-carboxylate (3et) (62.7 mg, 71%



yield); Pale yellow oil, R_f = 0.40 (silica gel, hexane/EtOAc = 8/2), ^{1}H NMR

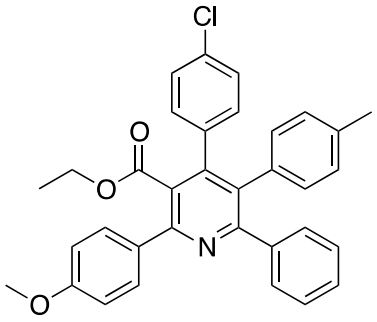
(400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 3.85 (s, 3H), 4.00 (q, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.14 (dd, *J* = 8.8, 8.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.4−7.5 (m, 2H), 7.60 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.3 (CH_3), 55.3 (CH_3), 61.4 (CH_2), 113.8 (CH), 115.5 (CH, *J* = 21.6 Hz), 118.4 (CH), 126.2 (C), 127.1 (CH), 129.5 (CH), 130.0 (CH, *J* = 8.2 Hz), 130.0 (CH), 132.6 (C), 134.8 (C, *J* = 3.5 Hz), 135.7 (C), 139.7 (C), 148.4 (C), 156.1 (C), 157.1 (C), 160.3 (C), 163.0 (C, *J* = 248 Hz), 168.9 (C); IR(ATR/cm^{-1}): 1723, 1506, 1252, HRMS (ESI/TOF): *m/z calcd*. for $C_{28}H_{24}FNO_3$ $[M + H]^+$ 442.1813; found 442.1810.

Ethyl 4-(4-chlorophenyl)-2-(4-methoxyphenyl)-5,6-diphenylpyridine-3-carboxylate (3es) (38.5 mg, 37% yield);



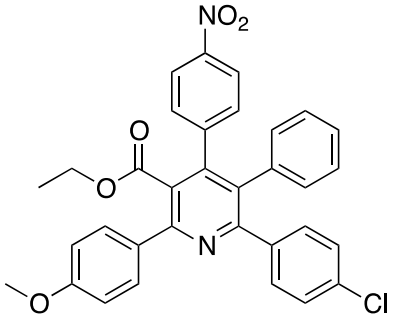
White solid, mp 235−237 °C. R_f = 0.48 (silica gel, hexane/EtOAc = 8/2), ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 3.85 (s, 3H), 3.93 (q, *J* =7.2 Hz, 2H), 6.85 (dd, *J* = 1.6, 8.0 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.0−7.1 (m, 5H), 7.1−7.2 (m, 5H), 7.34 (dd, *J* = 1.6, 8.0 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7 (CH_3), 55.5 (CH_3), 61.6 (CH_2), 114.0 (CH), 127.0 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 128.0 (CH), 130.2 (CH), 130.2 (CH), 130.9 (CH), 131.3 (CH), 132.3 (C), 133.0 (C), 133.8 (C), 135.7 (C), 137.2 (C), 140.3 (C), 147.4 (C), 154.2 (C), 158.3 (C), 160.5 (C), 168.6 (C) one quaternary carbon is lacked because of overlapping; IR(ATR/cm^{-1}): 1729, 1514, 1251; HRMS (ESI/TOF): *m/z calcd*. for $C_{33}H_{26}ClNO_3$ $[M + H]^+$ 520.1674, found 520.1661.

Ethyl 4-(4-chlorophenyl)-2-(4-methoxyphenyl)-5-(4-methylphenyl)-6-phenylpyridine-3-carboxylate (3eu) (44.8 mg, 42% yield);

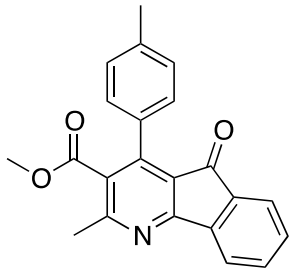


White solid, mp 229−230 °C. R_f = 0.43 (silica gel, hexane/EtOAc = 8/2), ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 2.21 (s, 3H), 3.85 (s, 3H), 3.91 (q, t = 7.2 Hz, 2H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 7.1−7.2 (m, 5H), 7.3−7.4 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.1 (CH_3), 55.3 (CH_3), 61.4 (CH_2), 113.8 (CH), 127.6 (CH), 127.7 (CH), 127.8 (CH), 128.5 (CH), 130.0 (CH), 130.1 (CH), 130.8 (CH), 130.9 (CH), 132.2 (C), 132.8 (C), 133.5 (C), 133.8 (C), 135.7 (C), 136.4 (C), 140.3 (C), 147.3 (C), 153.8 (C), 158.2 (C), 160.3 (C), 168.5 (C) one quaternary carbon is lacked because of overlapping; IR(ATR/cm^{-1}): 1730, 1533, 1250; HRMS (ESI/TOF): *m/z calcd*. for $C_{34}H_{28}ClNO_3$ $[M + H]^+$ 534.1831, found 534.1833.

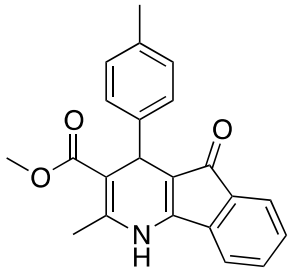
Ethyl 6-(4-chlorophenyl)-2-(4-methoxyphenyl)-4-(4-nitrophenyl)-5-phenylpyridine-3-carboxylate (3ev) (56.5 mg, 50% yield); White solid, mp 211−212 °C, R_f = 0.40 (silica gel, hexane/EtOAc = 8/2), ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H), 3.86 (s, 3H), 3.90 (q, t = 7.2 Hz, 2H), 6.8−6.9 (m, 2H), 6.98 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.0−7.1 (m, 3H), 7.15 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.27 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.30 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.72 (dd, *J* = 6.8, 2.0 Hz, 2H), 8.04 (dd, *J* = 6.8, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (CH_3), 55.3 (CH_3), 61.6 (CH_2), 113.9 (CH), 122.7 (CH), 127.1 (C), 127.4 (CH), 127.9 (CH), 128.2 (CH), 130.0 (CH), 130.4 (CH), 130.8 (CH), 131.4 (CH), 131.6 (C), 132.2 (C), 134.2 (C), 136.3 (C), 138.1 (C), 143.9 (C), 146.5 (C), 147.1 (C), 154.5 (C), 156.9 (C), 160.5(C), 168.0 (C); IR(ATR/cm^{-1}): 1728, 1516, 1348, HRMS (ESI/TOF): *m/z calcd*. for $C_{33}H_{25}ClN_2O_5$ $[M + H]^+$ 565.1525; found 565.1536.



Methyl 2-methyl-4-(4-methylphenyl)-5-oxo-indeno[1,2-*b*]pyridine-3-carboxylate (14)[22] (66.7 mg, 71% yield). Yellow solid, mp 179–181 °C, R_f = 0.28 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.63 (s, 3H), 3.57 (s, 3H), 7.24 (br s, 4H), 7.38 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.55 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.59 (br d, *J* = 7.6 Hz, 1H), 7.86 (br d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 23.5 (CH_3), 52.2 (CH_3), 121.1 (C), 122.1 (C), 123.8 (CH), 128.2 (CH), 128.7 (CH), 129.5 (C), 130.3 (C), 131.2 (CH), 134.4 (CH), 135.4 (C), 139.1 (C), 142.3 (C), 146.8 (C), 160.7 (C), 165.6 (C), 168.5 (C), 190.2 (C); IR (ATR/cm^{-1}): 2920, 1730, 1712, 1557, 1236.



Methyl 4,5-dihydro-2-methyl-4-(4-methylphenyl)-5-oxo-*1H*-Indeno[1,2-b]pyridine-3-carboxylate (15)[23] (45.7 mg, 14% yield). Red solid, mp 255–260 °C, R_f = 0.05 (silica gel, hexane/EtOAc = 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.50 (s, 3H), 3.59 (s, 3H), 4.96 (s, 1H), 6.48 (br s, 1H), 7.01–7.04 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.24–7.28 (m, 2H), 7.34–7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9 (CH_3), 21.0 (CH_3), 36.7 (CH_3), 51.1 (CH), 107.9 (C), 111.1 (C), 116.6 (CH), 121.4 (CH), 127.6 (CH), 129.0 (CH), 130.0 (CH), 131.1 (CH), 133.9 (C), 135.8 (C), 136.1 (C), 142.7 (C), 143.3 (C), 152.5 (C), 167.8 (C), 192.0 (C); IR (ATR/cm^{-1}): 3269, 1697, 1634, 1504, 1173.

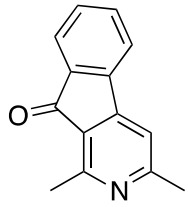


5. Synthesis of 4-azafluorenone 12

Azafluorenones **12** were synthesized according to the method in the literature.[24] An excess amount of polyphosphoric acid (PPA, 0.5mL) and nicotinate **3ad** (44.3 mg, 0.18 mmol) was heated 210 °C for 2 h under microwave irradiation.

To the reaction mixture, saturated $NaHCO_3$ aqueous solutionwas added, and the reaction mixture was extracted with chloroform (10 mL × 3). The organic layer was washed with water, and was dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (hexane/EtOAc = 8/2) to afford 2-azafluorenone **12** (34.2 mg, 0.16 mmol, 91%) as a white solid.

1,3-Dimethyl-3-azafluorenone **12**[25] (34.2 mg, 91%). White solid, mp 155–157 °C, R_f = 0.13 (silica gel, hexane/EtOAc, 8/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 2.79 (s, 3H), 7.20 (s, 1H), 7.43 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.54 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (CH_3), 25.7 (CH_3), 113.0 (CH), 121.5 (CH), 123.2 (C), 124.4 (CH), 131.3 (CH), 134.5 (C), 135.0 (CH), 141.5 (C), 153.1 (C), 157.4 (C), 164.9 (C), 193.6 (C); IR (ATR/cm^{-1}): 1703, 1593, 1186.



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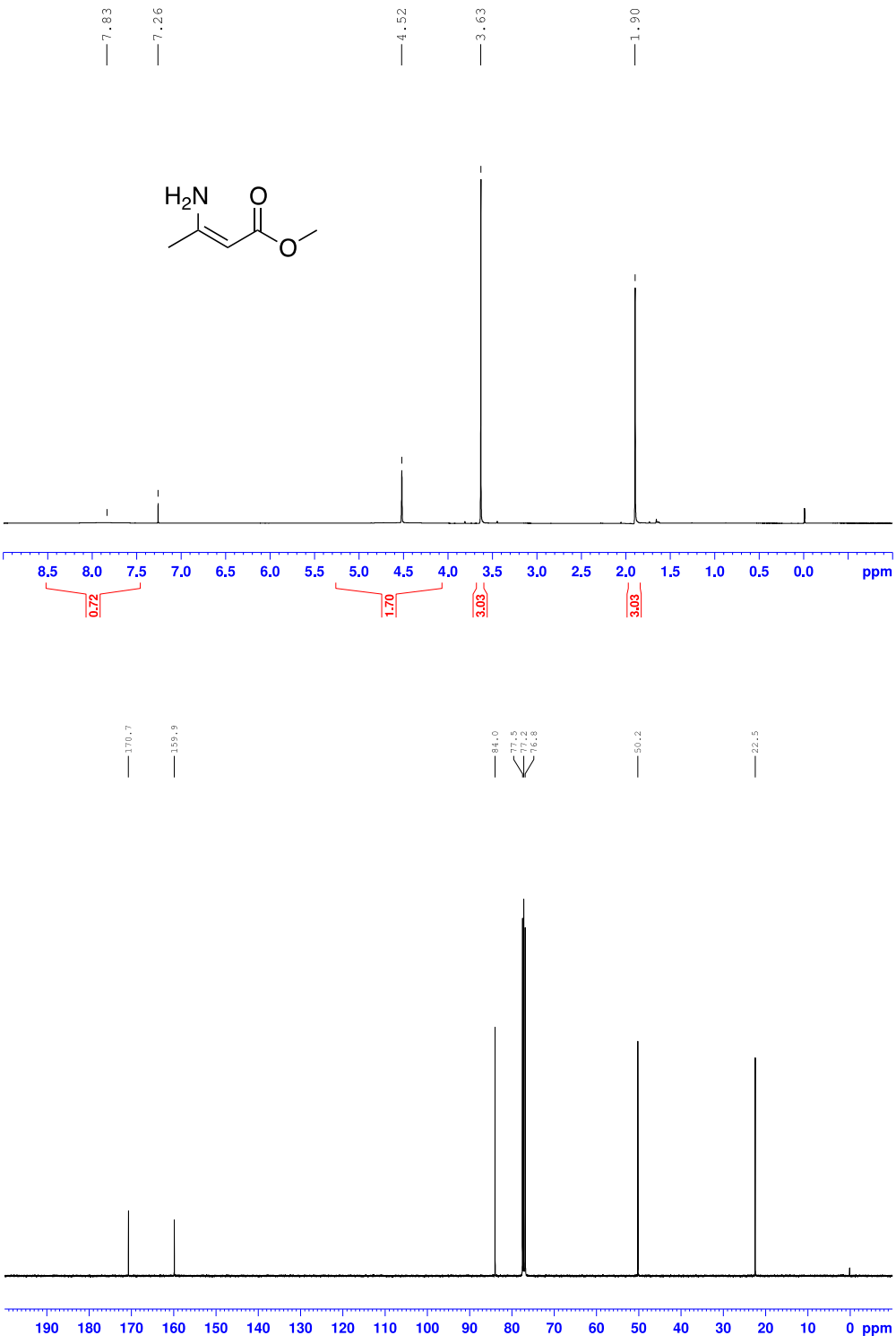
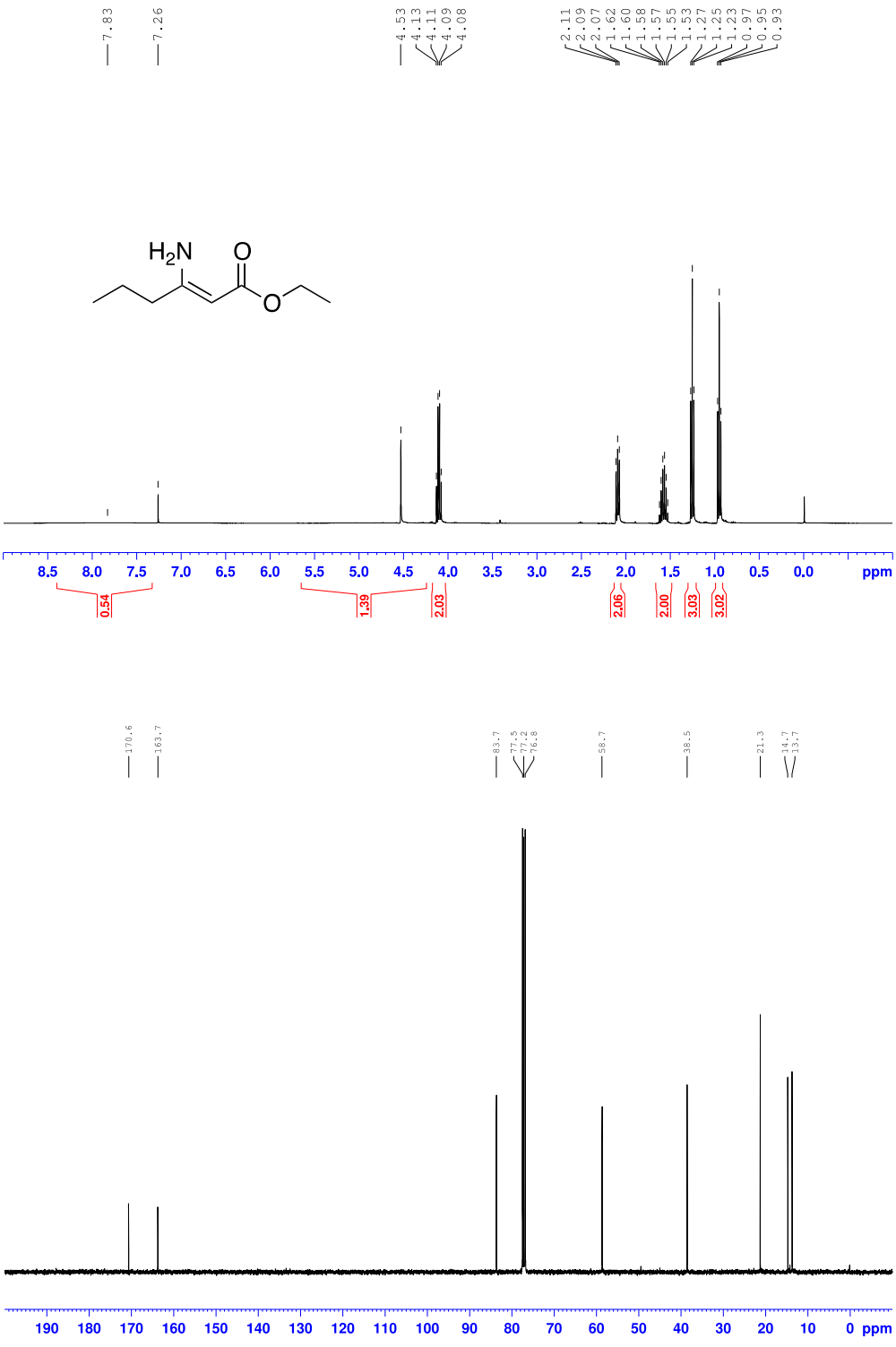
7. Copies of ^{1}H NMR and ^{13}C NMR spectra of enamino esters 1

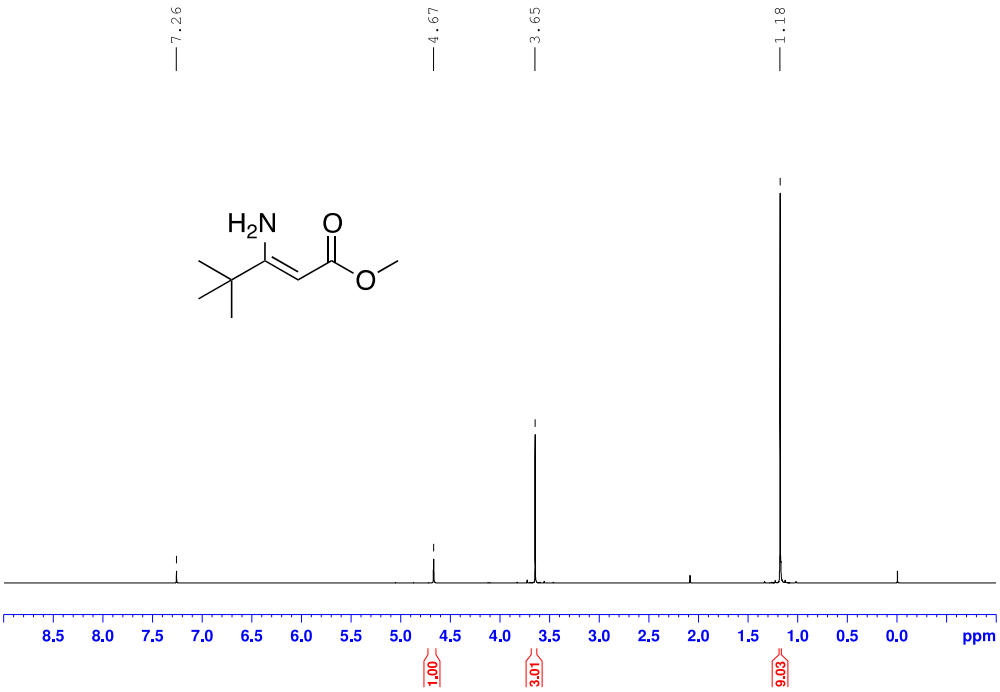
Methyl 3-amino-2-butenoate (1a)

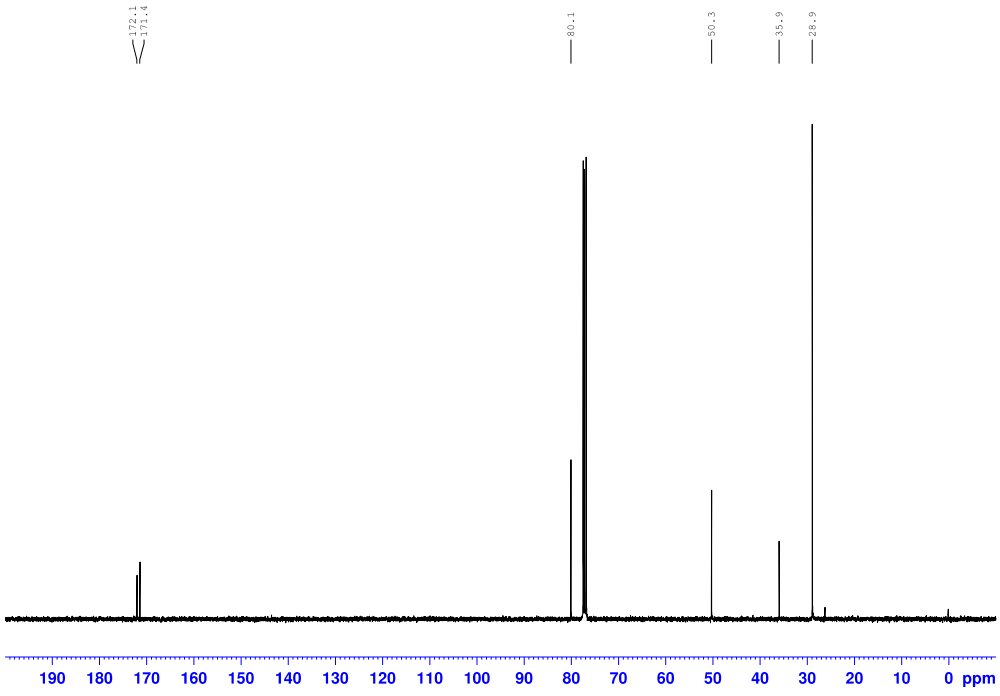


Ethyl 3-amino-2-hexenoate (1b)

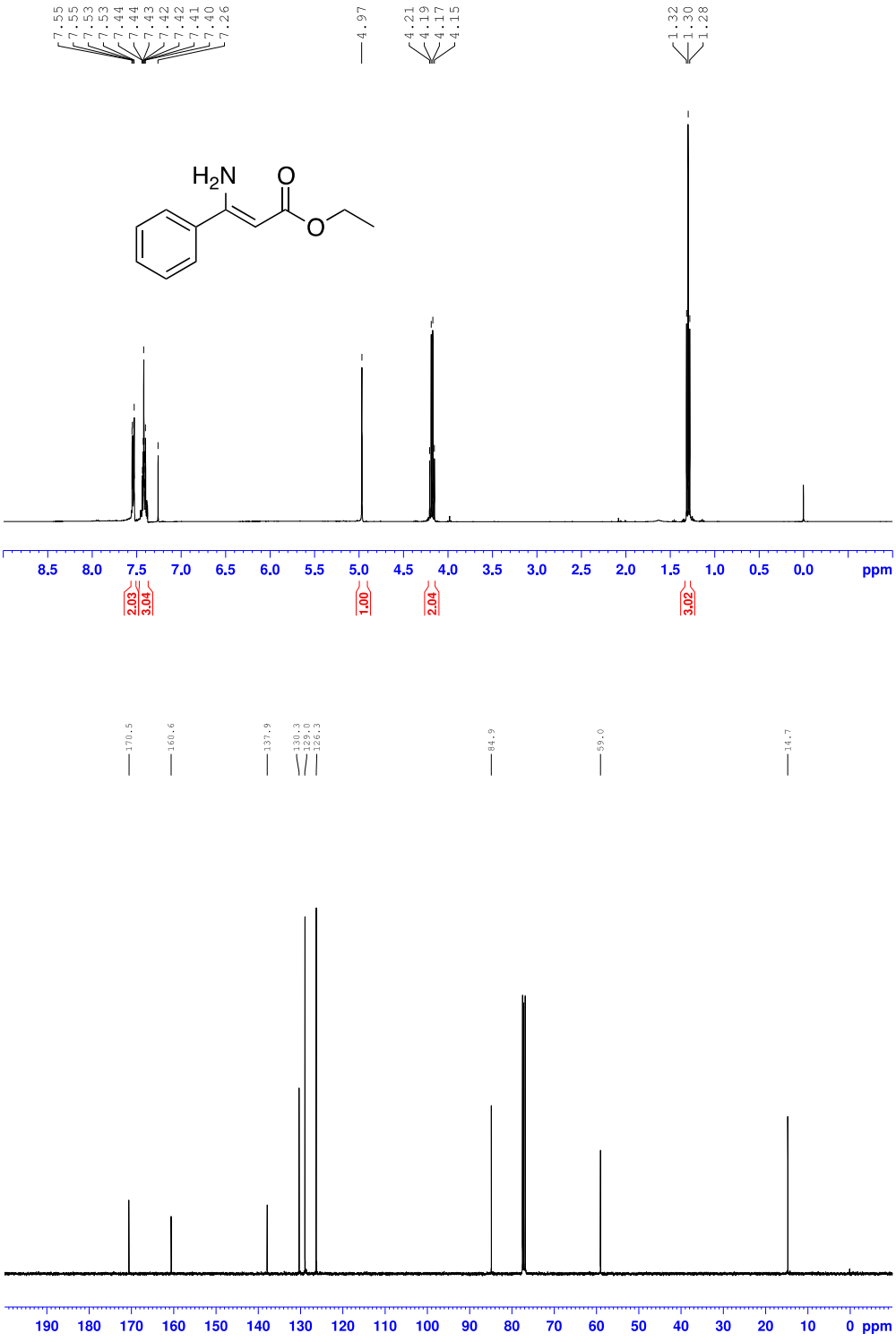


Methyl 3-amino-4,4-dimethyl-2-pentenoate (1c)

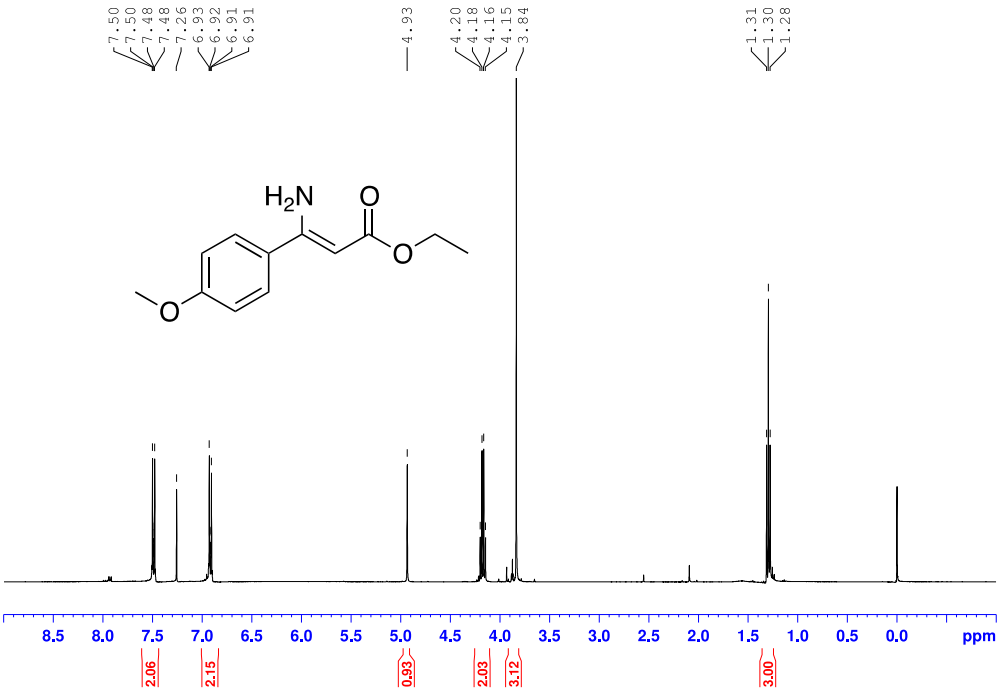


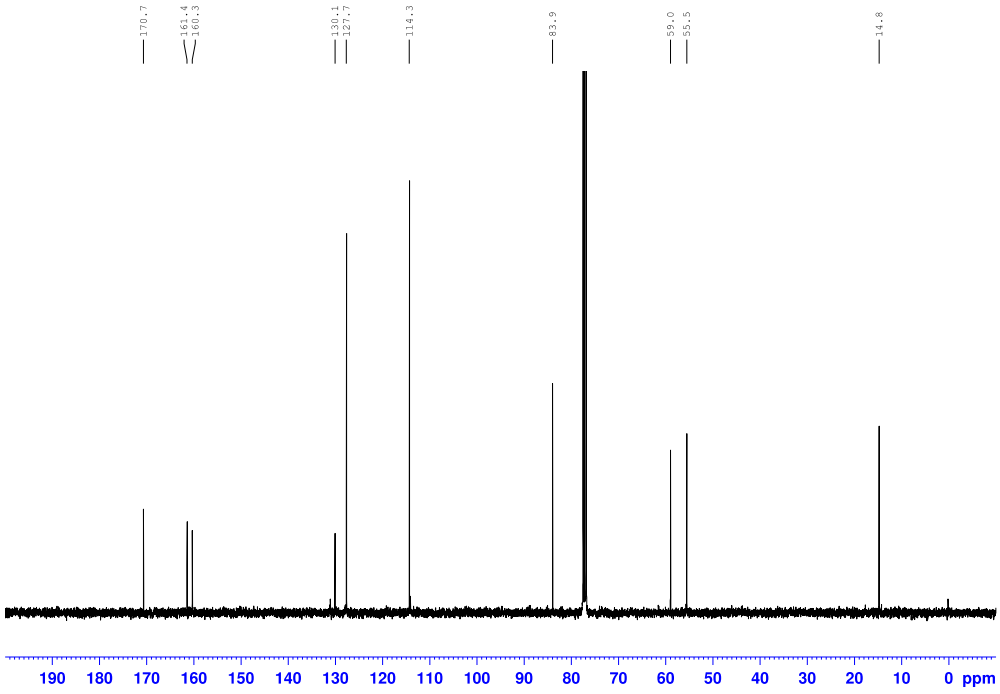


Ethyl 3-amino-4-phenyl-2-butenoate (1d)

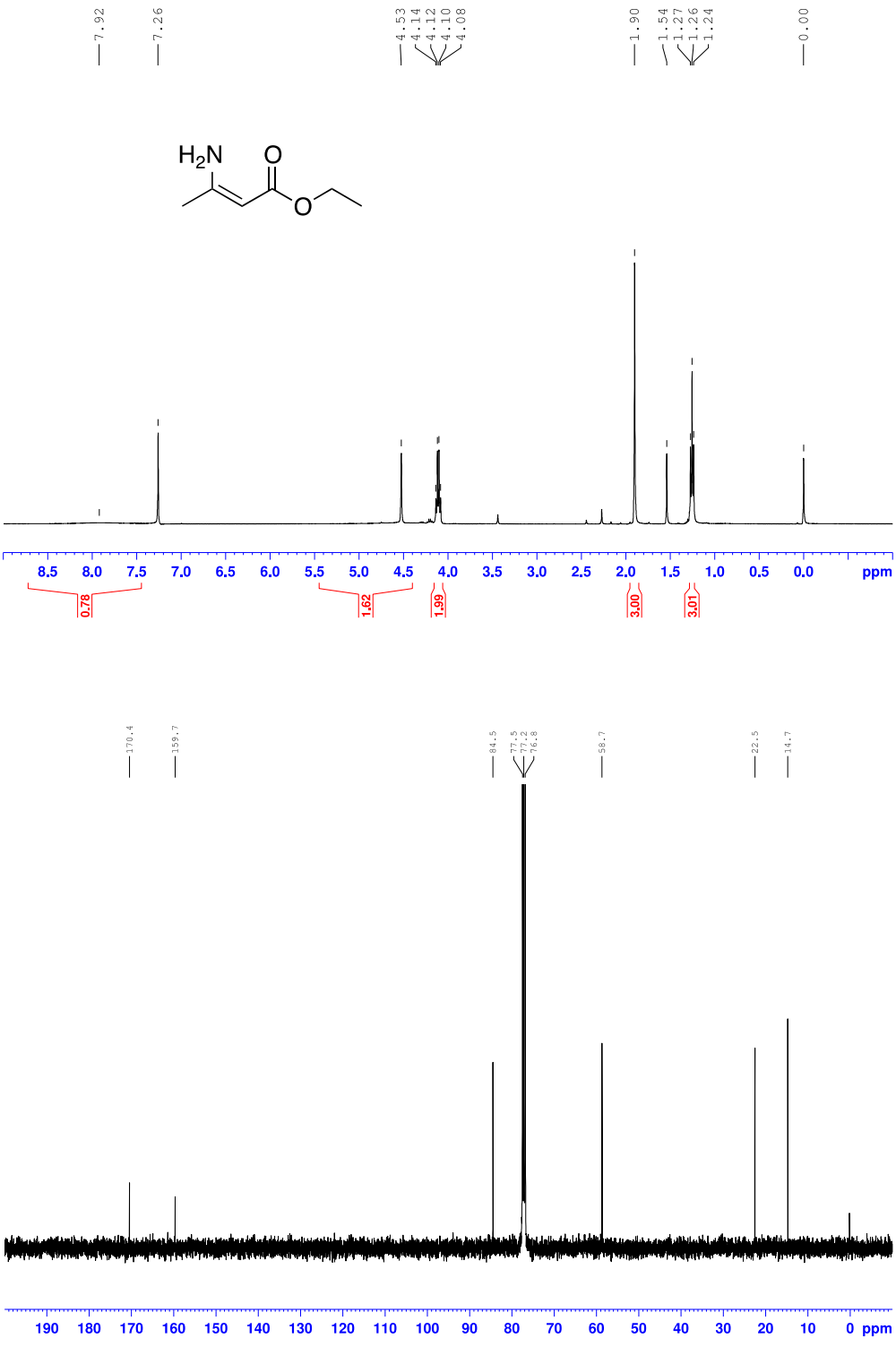


Ethyl 3-amino-4-(4-methoxyphenyl)-2-butenoate (1e)

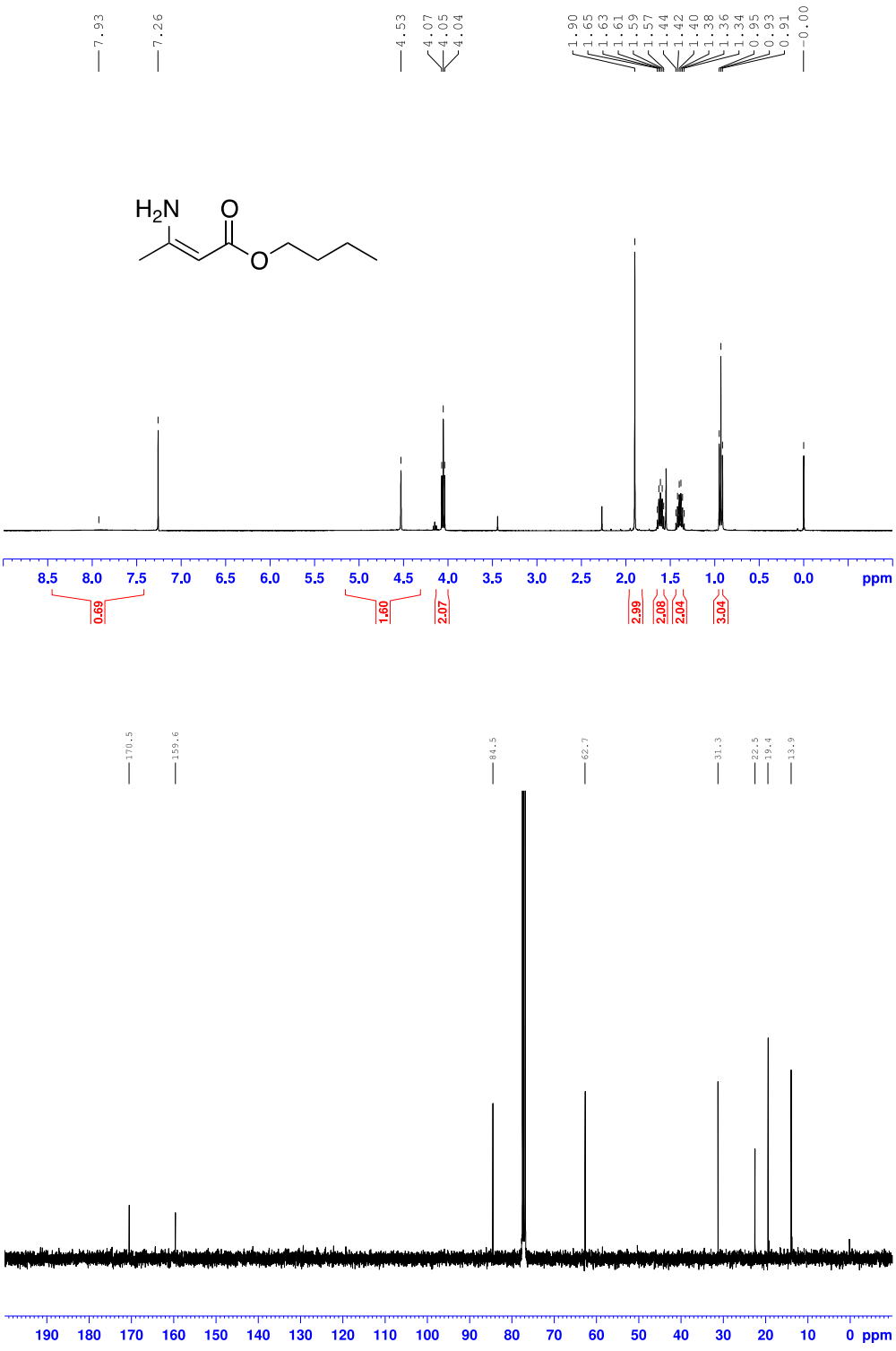




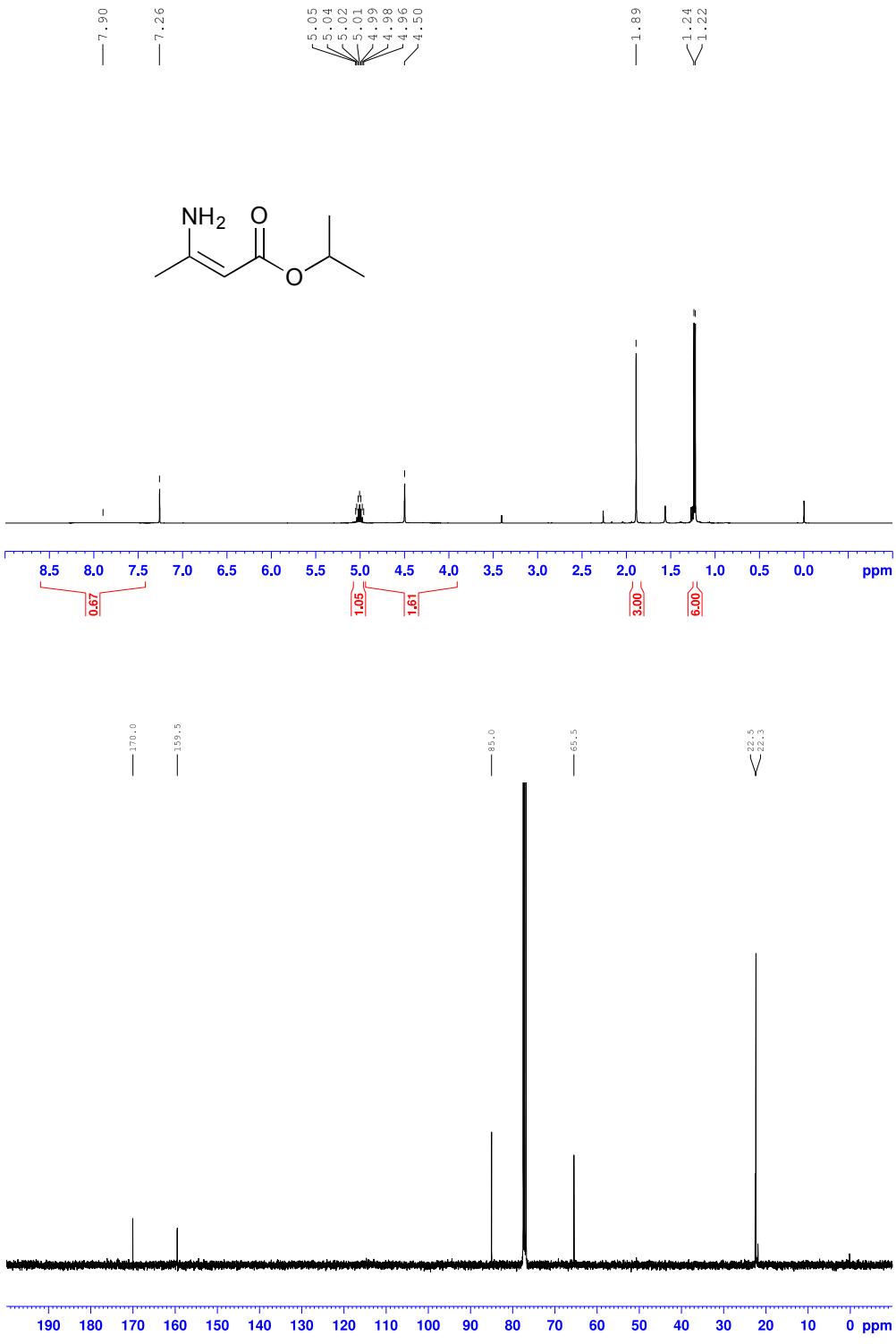
Ethyl 3-amino-2-butenoate (1f)



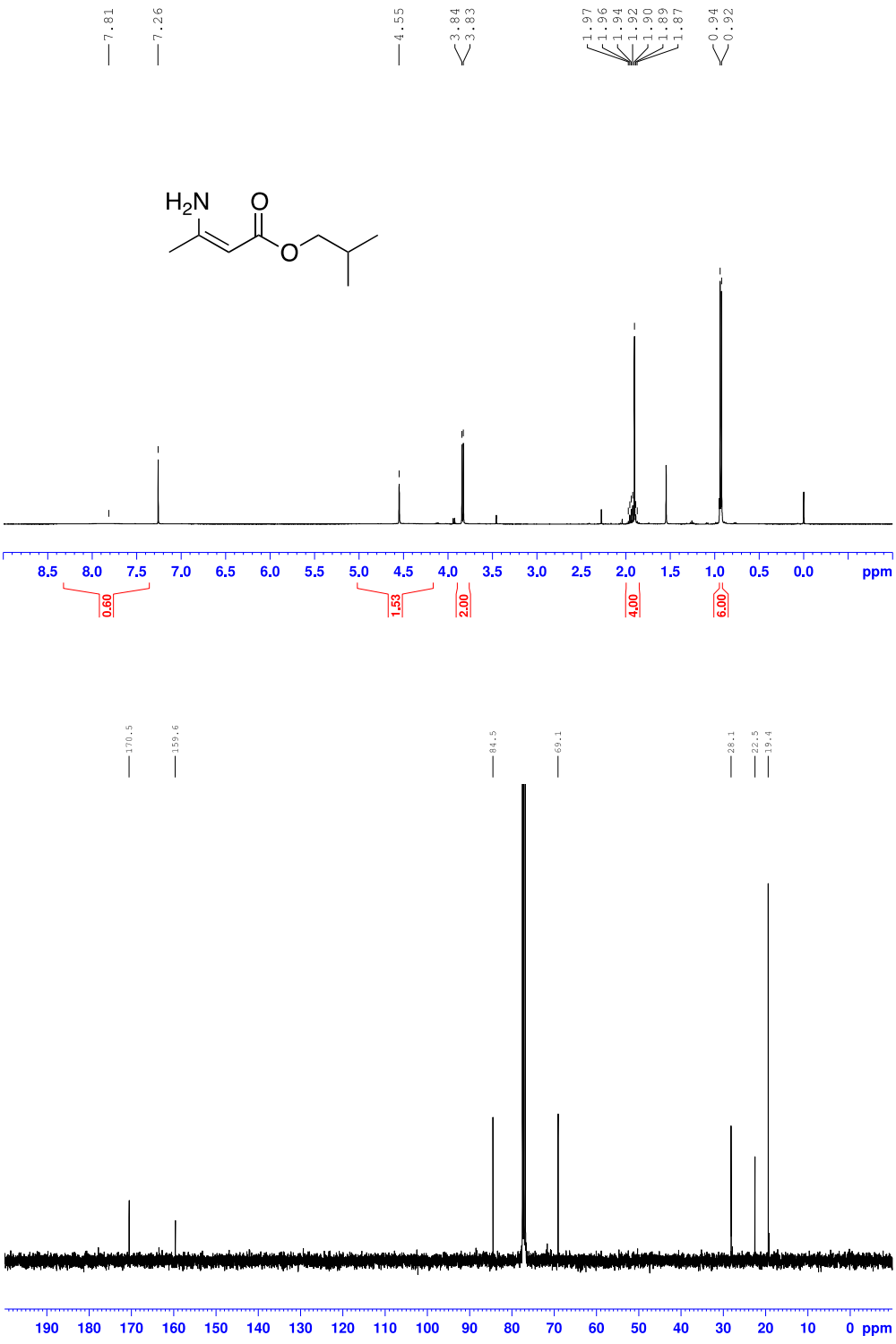
Butyl 3-amino-2-butenoate (1g)



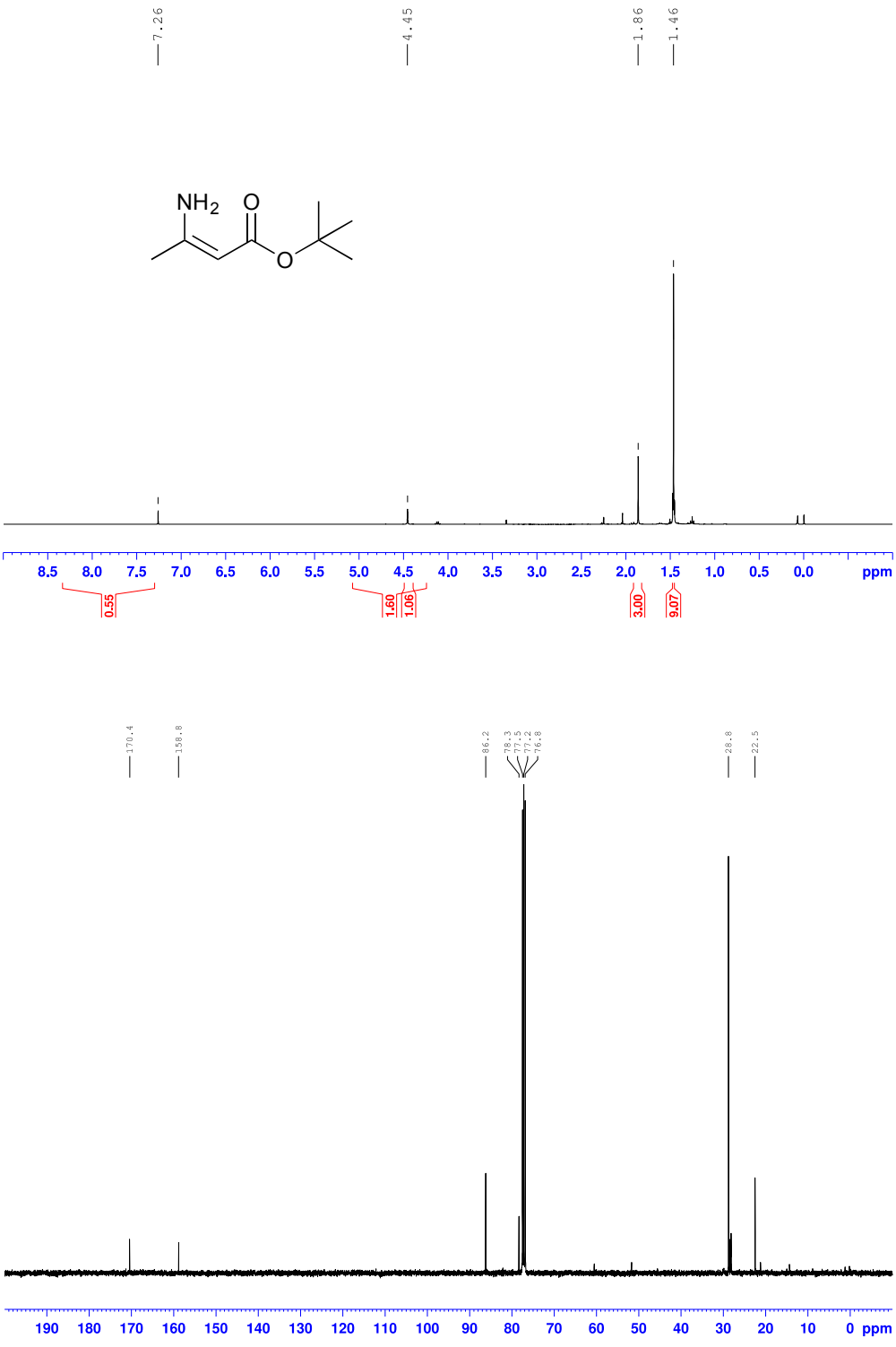
2-Propyl 3-amino-2-butenoate (1h)



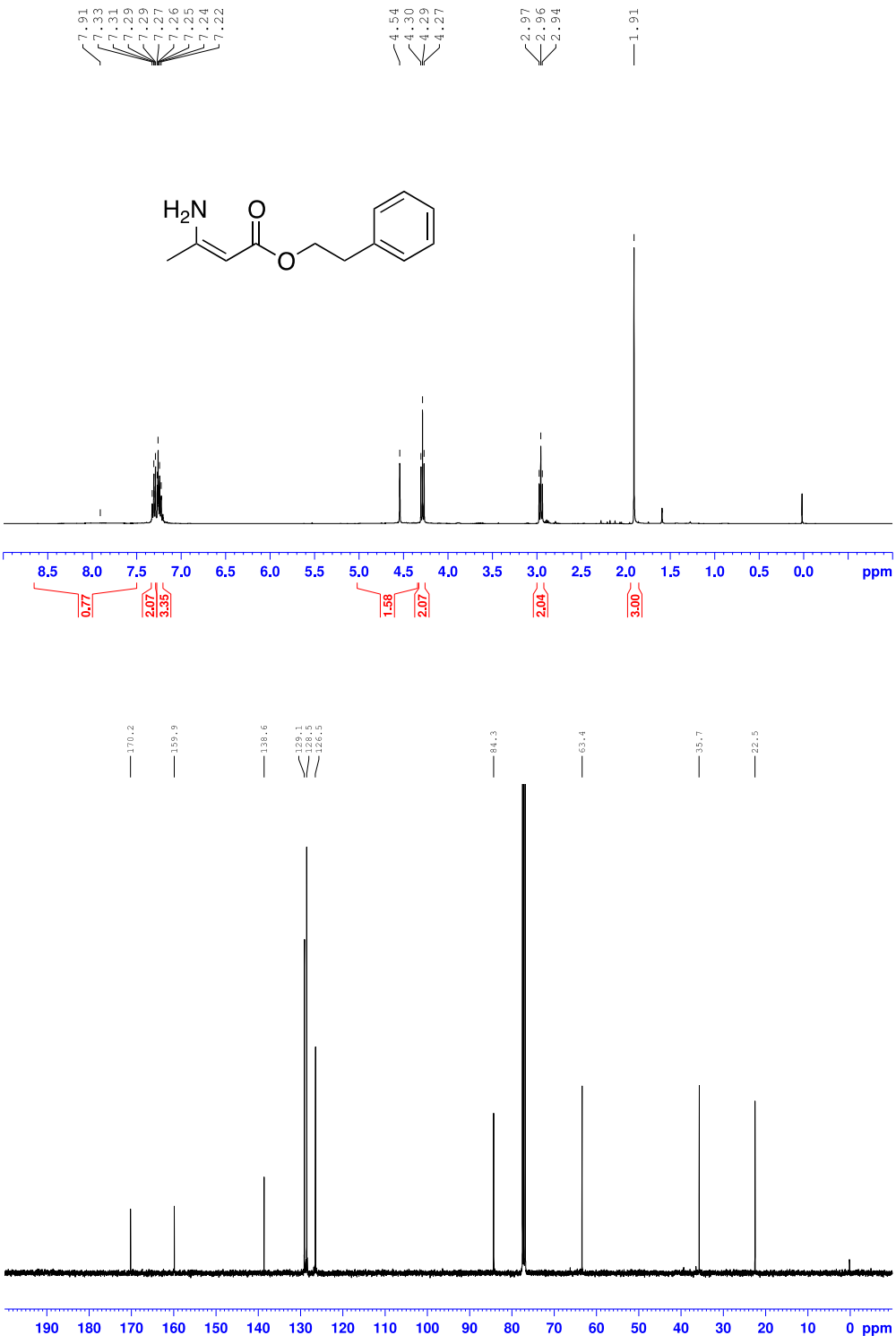
2-Methyl-1-propyl 3-amino-2-butenoate (1i)



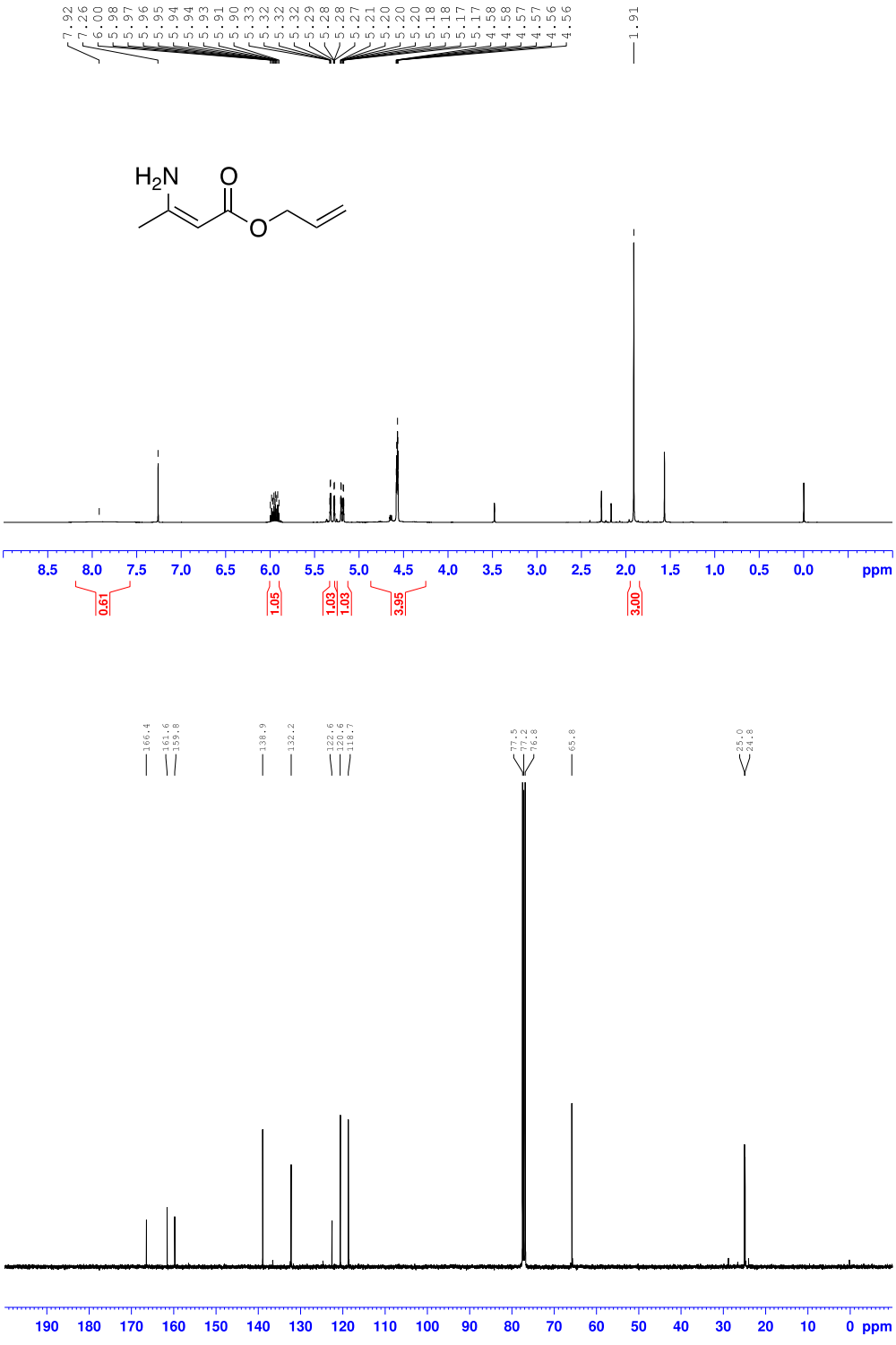
2-Methyl-2-propyl 3-amino-2-butenoate (1j)



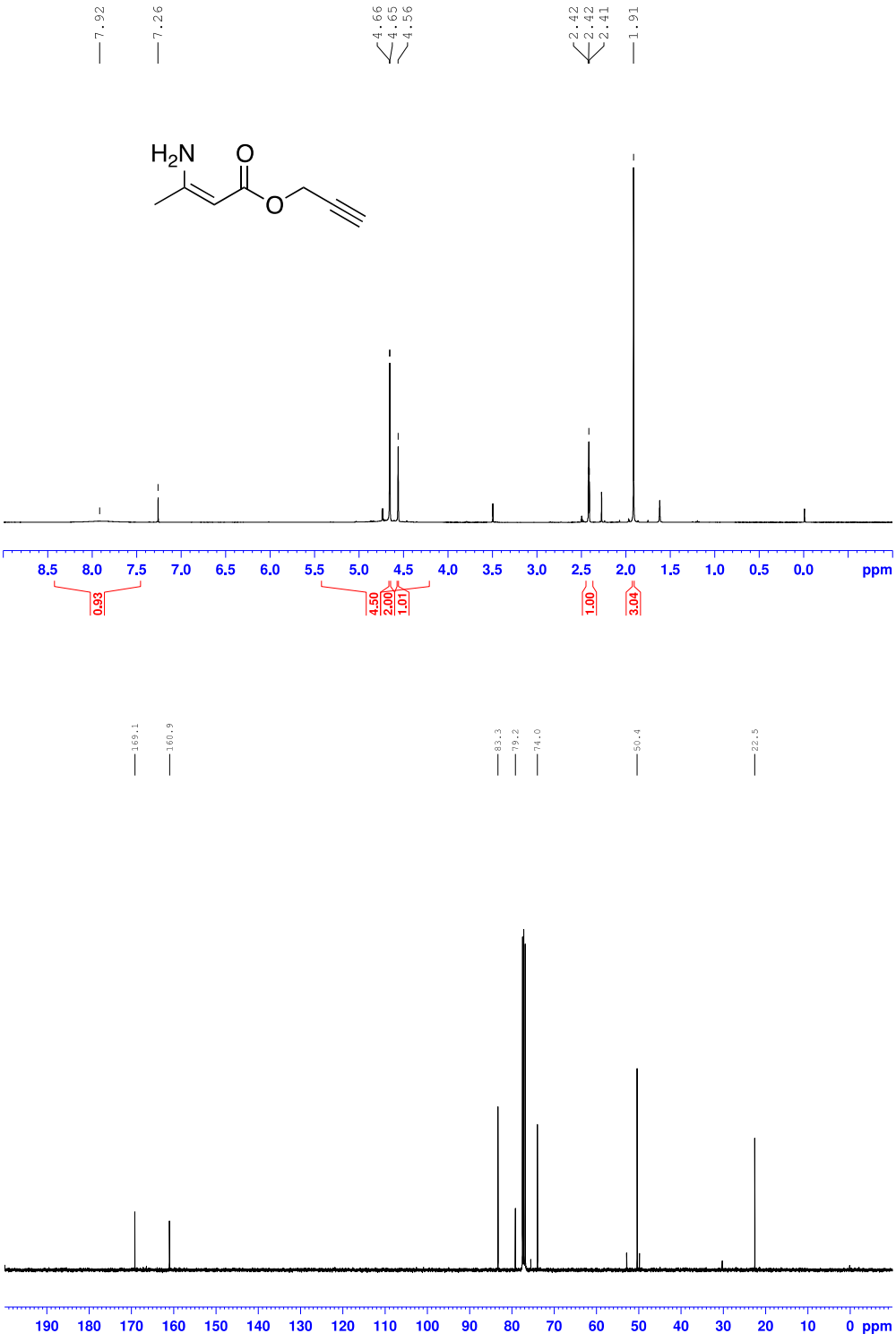
2-Phenylethyl 3-amino-2-butenoate (1k)



Propenyl 3-amino-2-butenoate (1l)

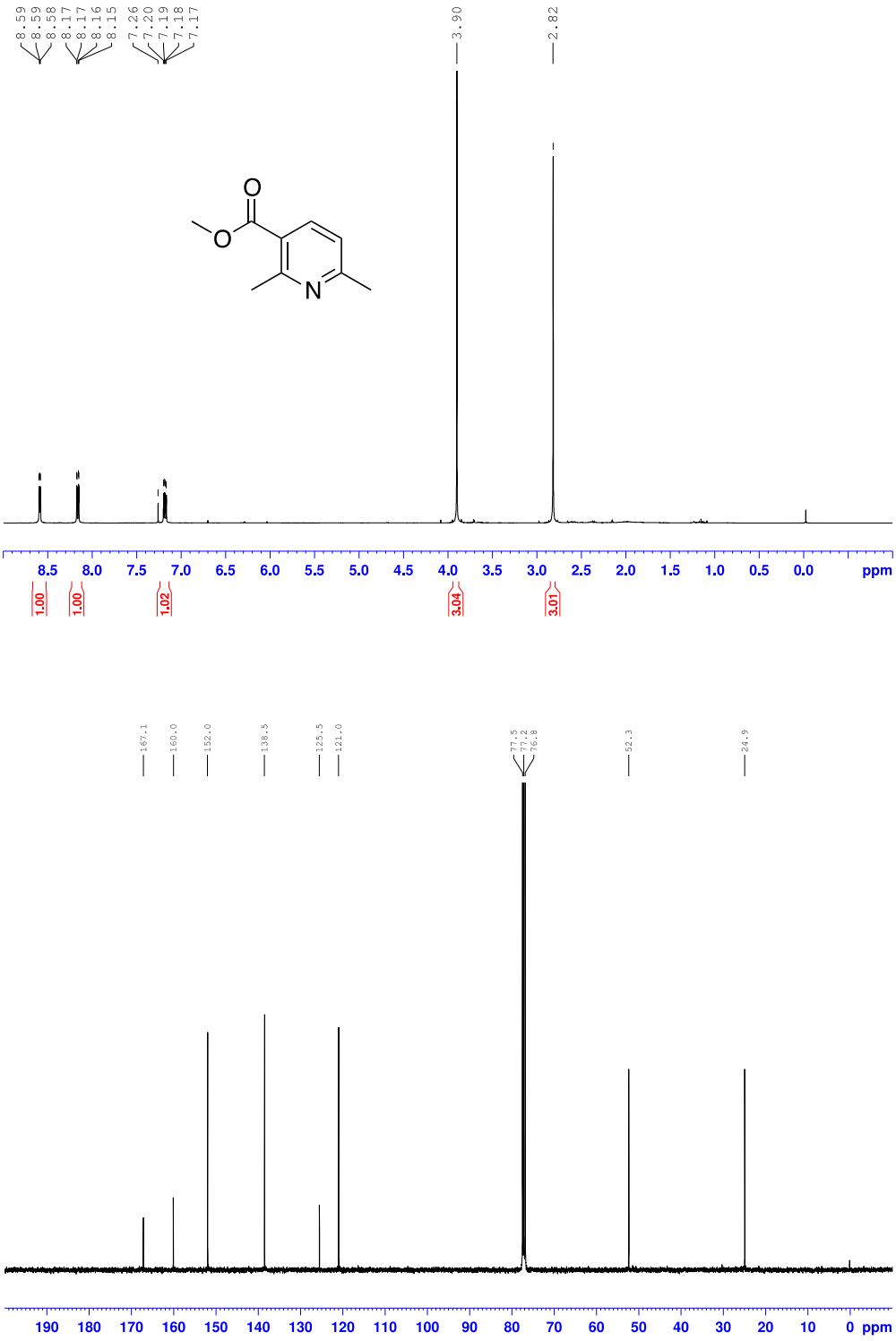


3-Propynyl 3-amino-2-butenoate (1m)

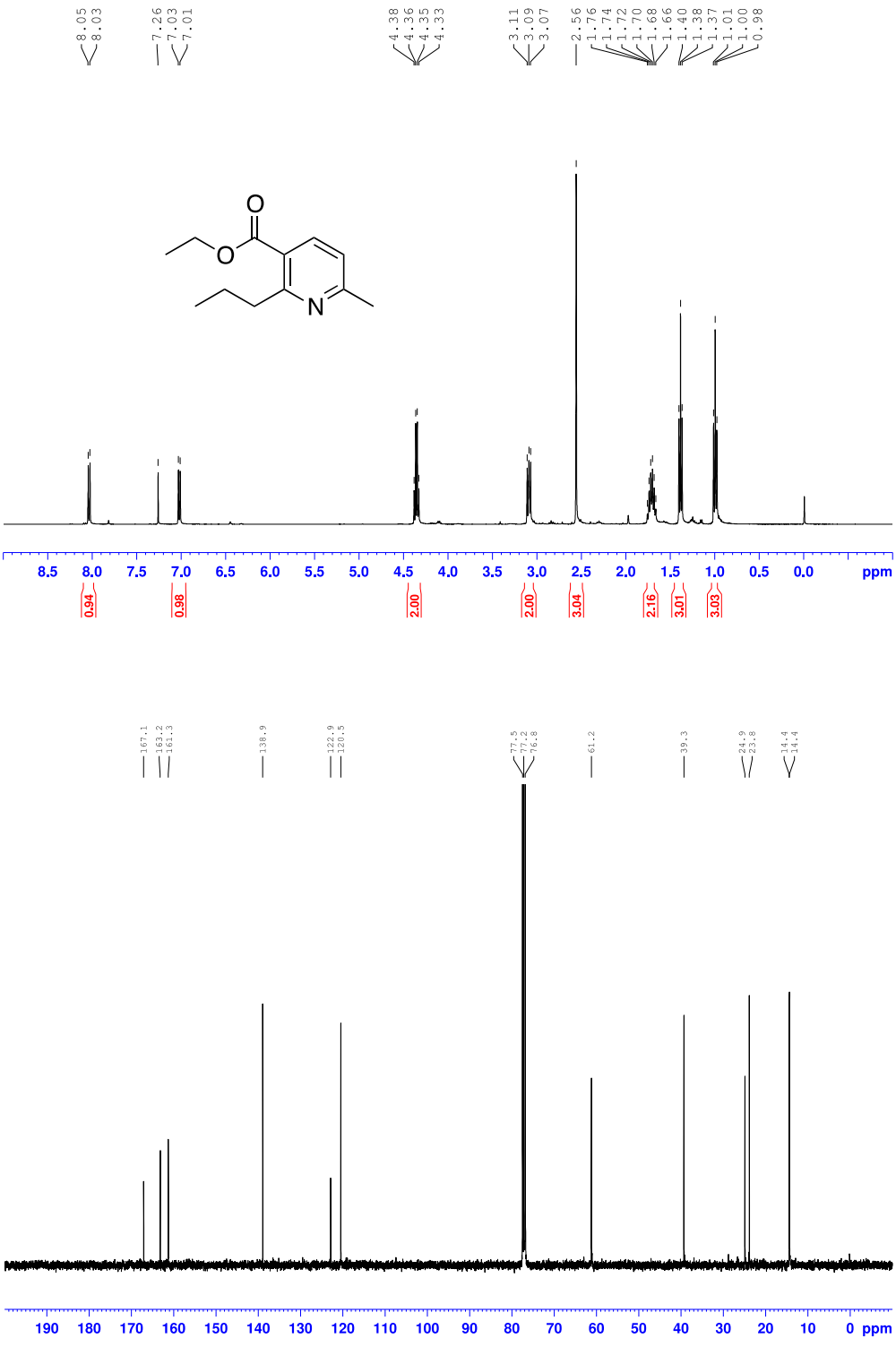


8. Copies of ^{1}H NMR and ^{13}C NMR spectra of nicotinates 3

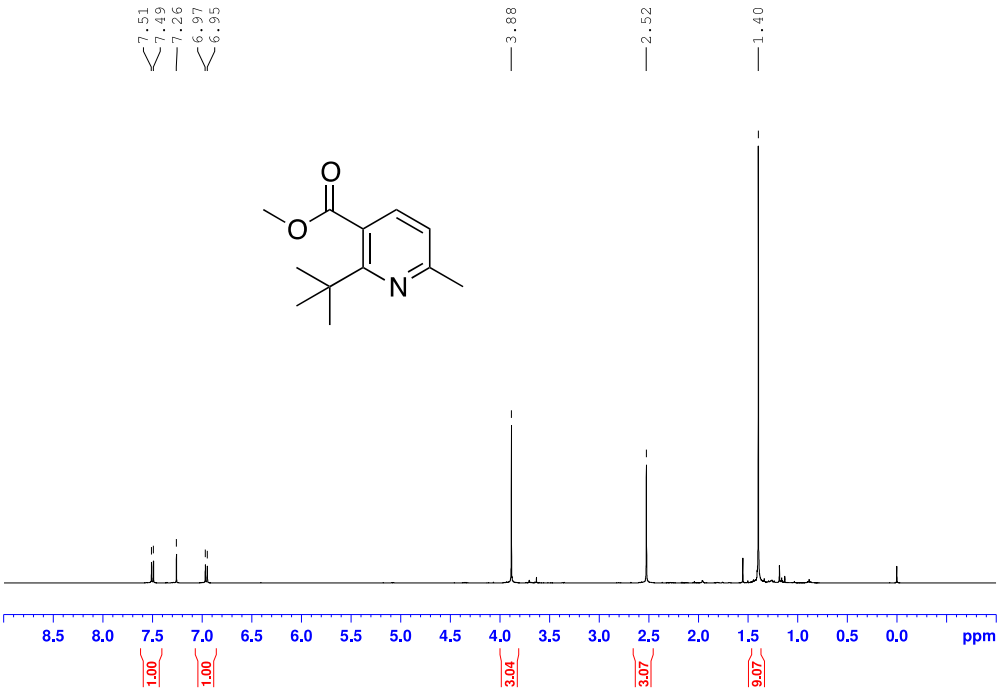
Methyl 2,6-dimethylpyridine-3-carboxylate (3aa)

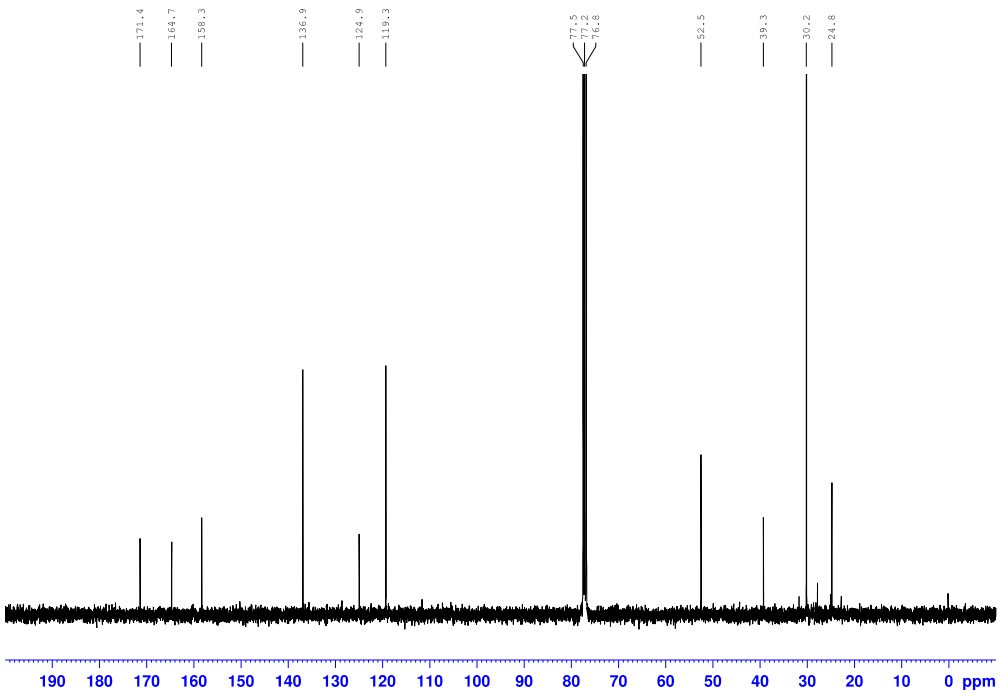


Ethyl 6-methyl-2-propylpyridine-3-carboxylate (3ba)



Methyl 6-methyl-2-(2-methyl-1-propyl) pyridine-3-carboxylate (3ca)





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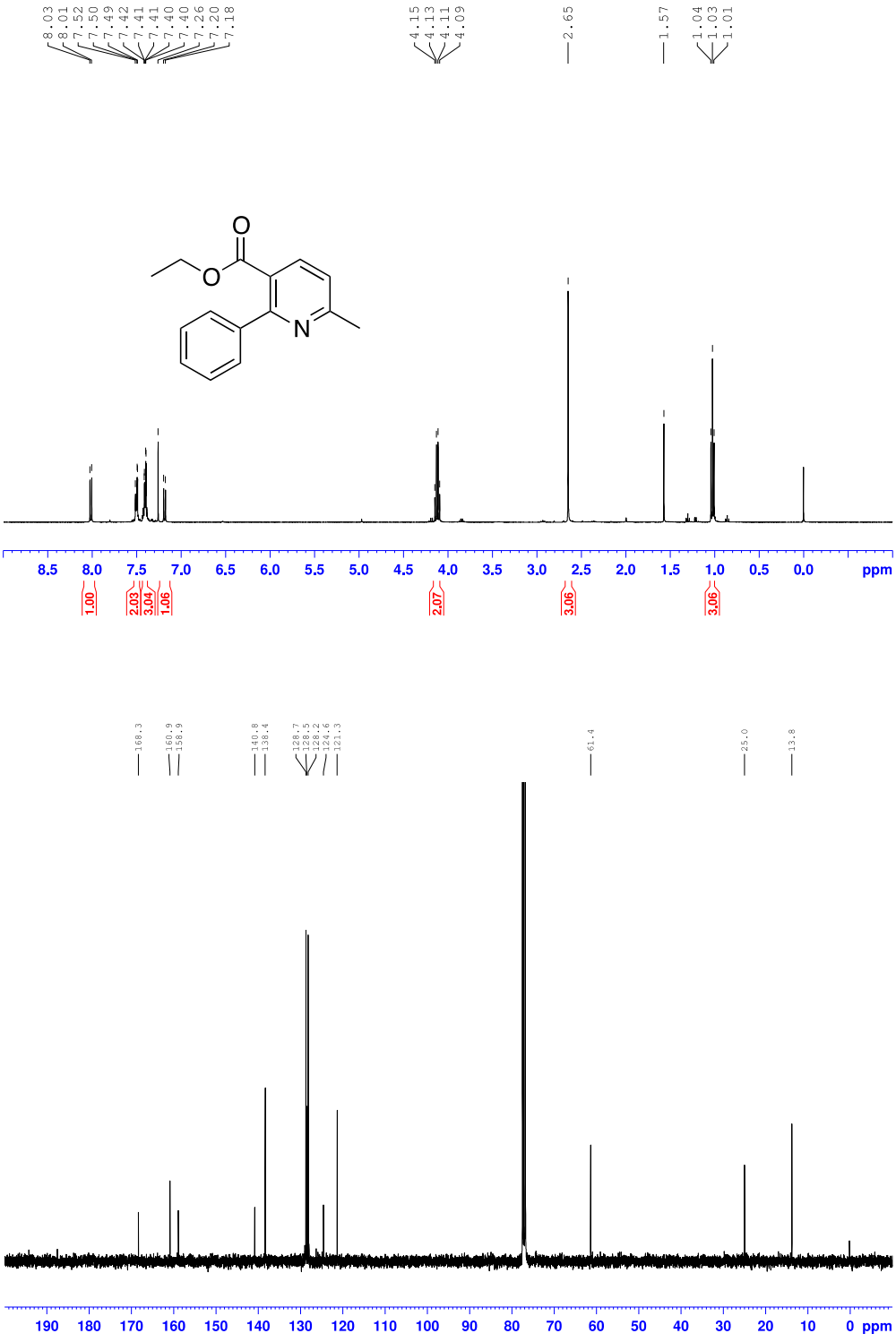
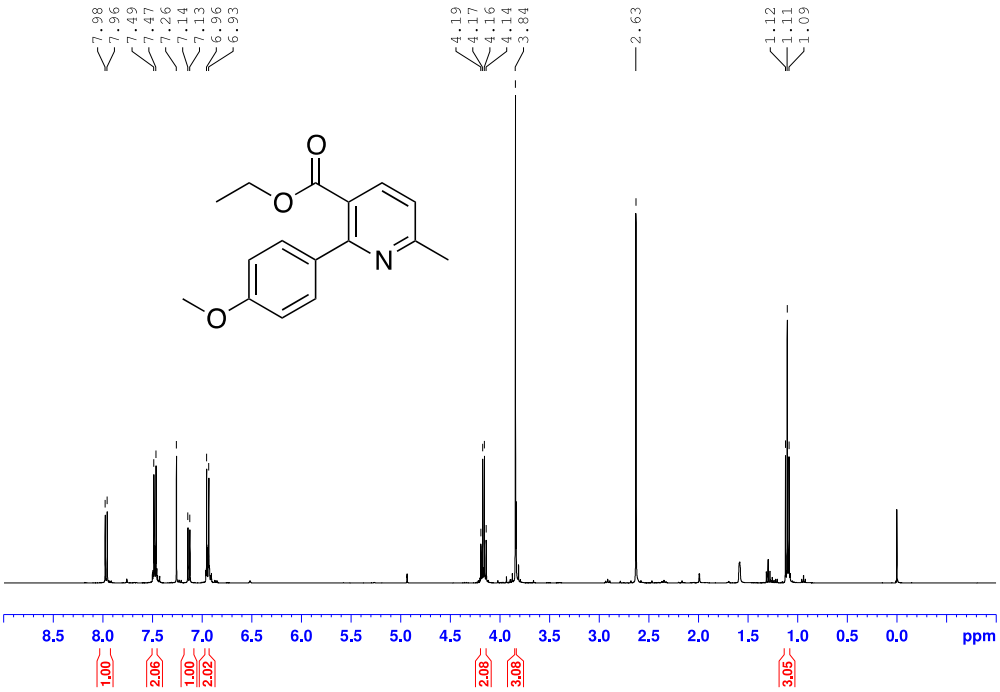
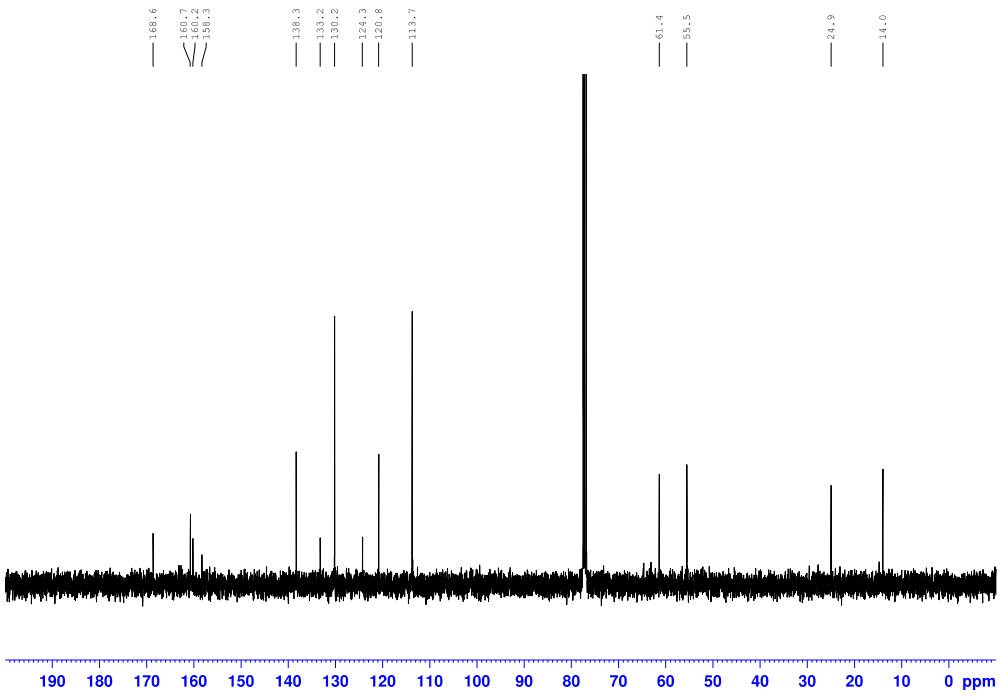
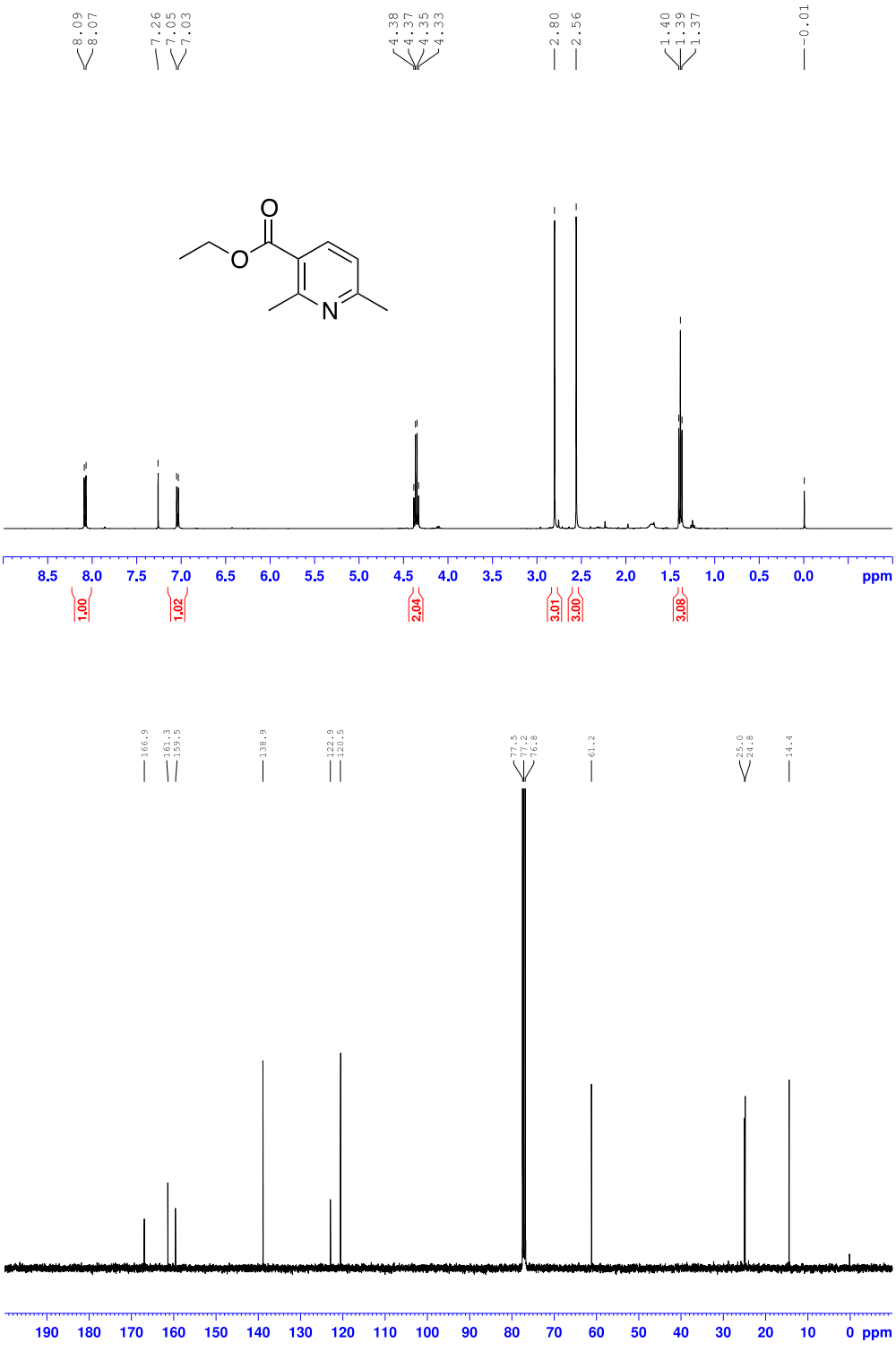


Ethyl 2-(4-methoxyphenyl)-6-methylpyridine-3-carboxylate (3ea)

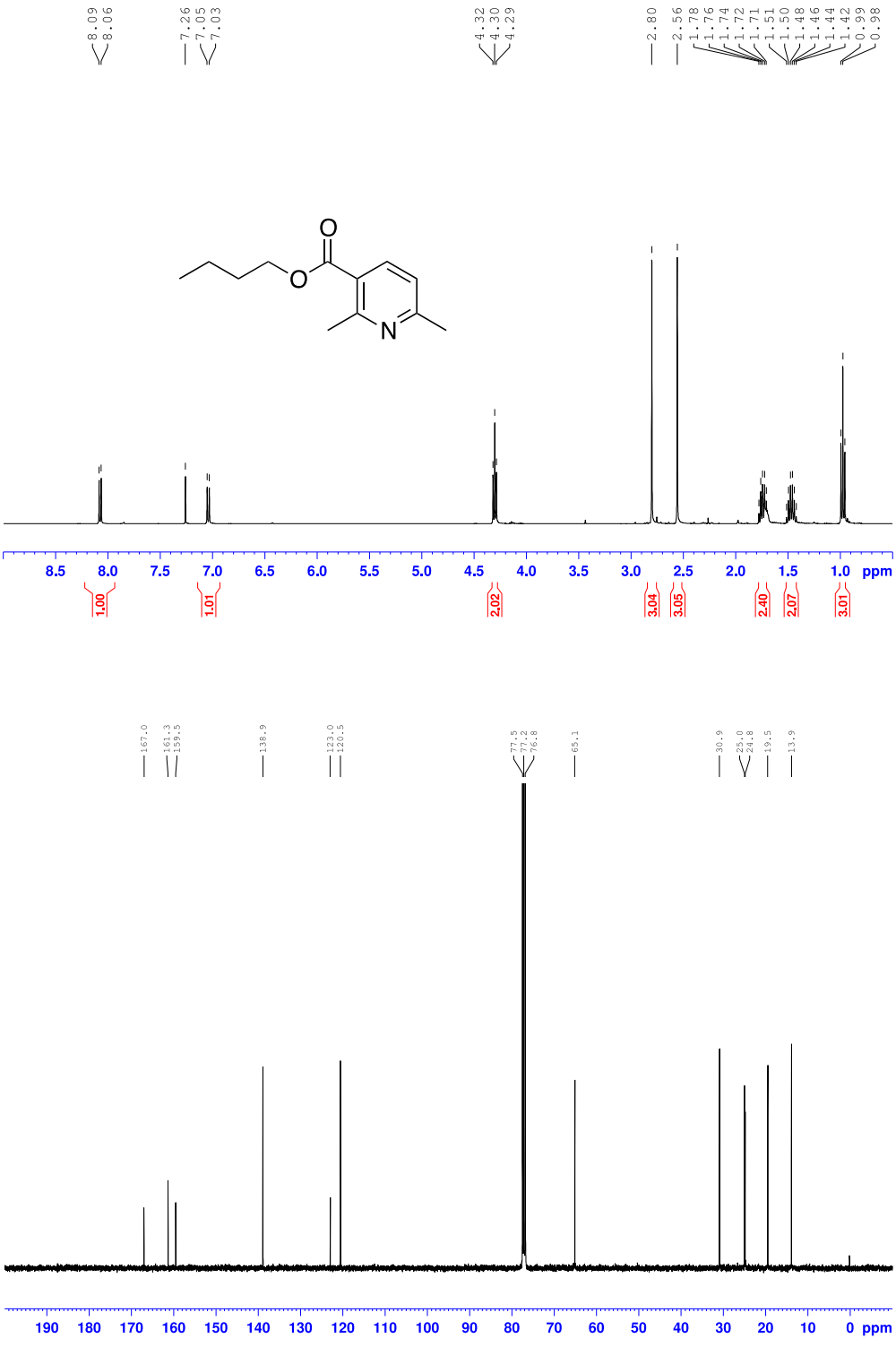




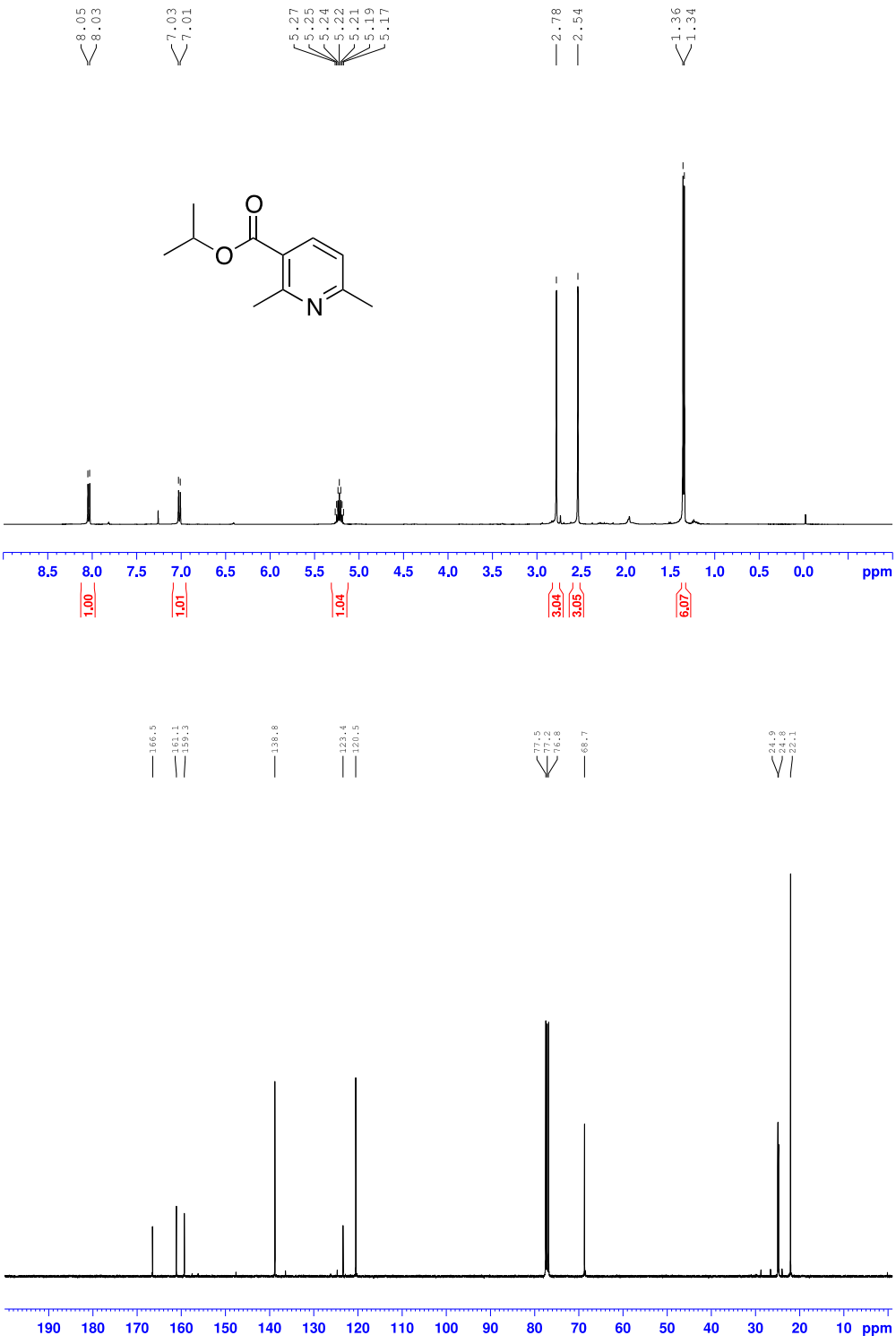
Ethyl 2,6-dimethylpyridine-3-carboxylate (3fa)



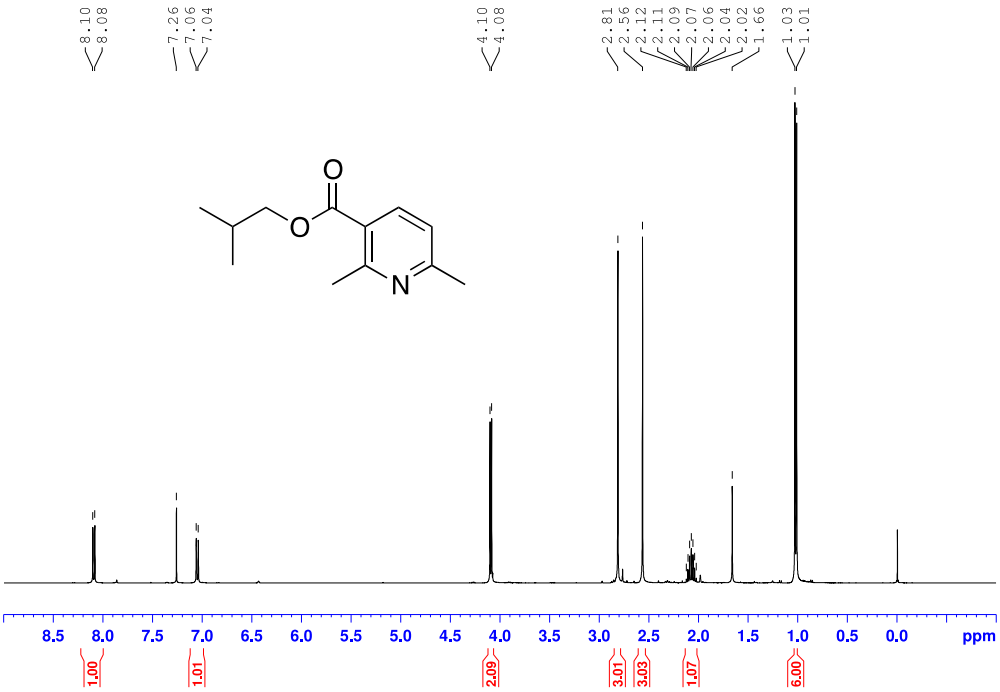
Butyl 2,6-dimethylpyridine-3-carboxylate (3ga)

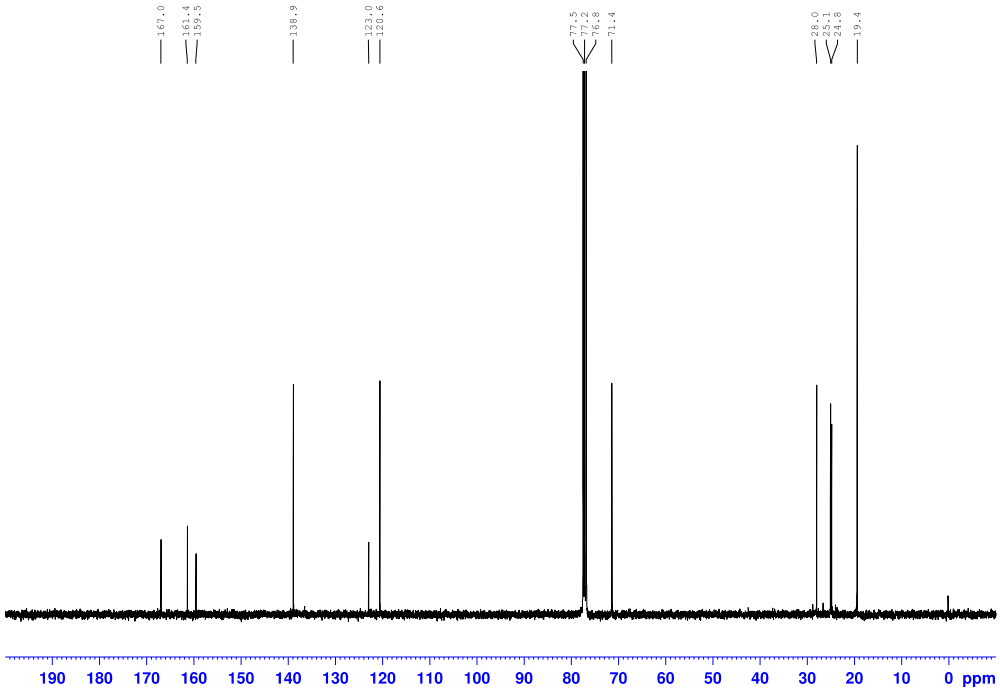


2-Propyl 2,6-dimethylpyridine-3-carboxylate (3ha)

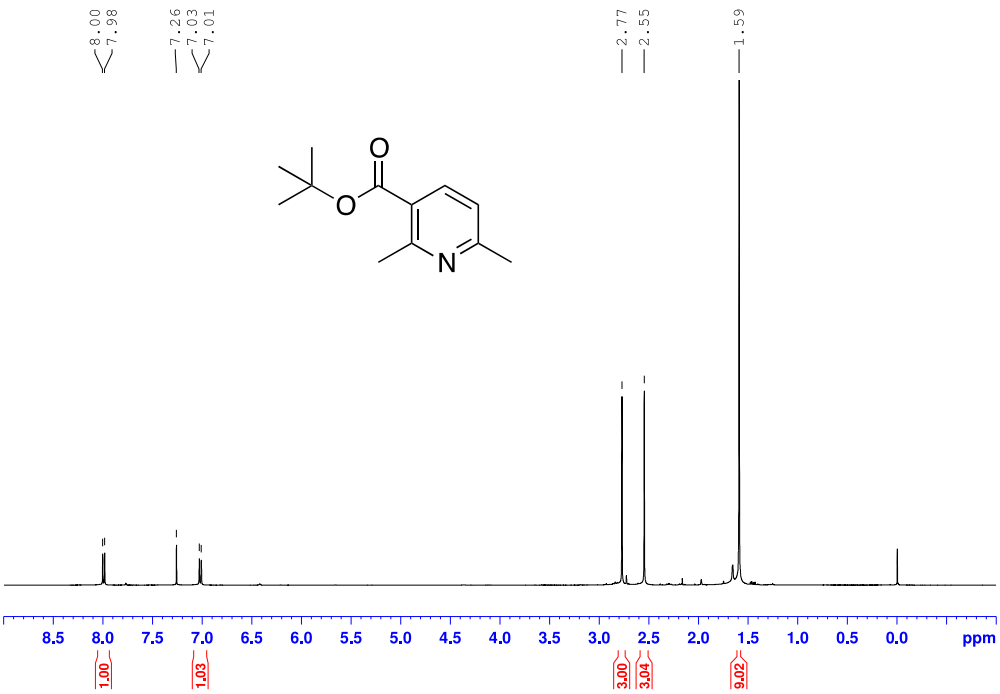


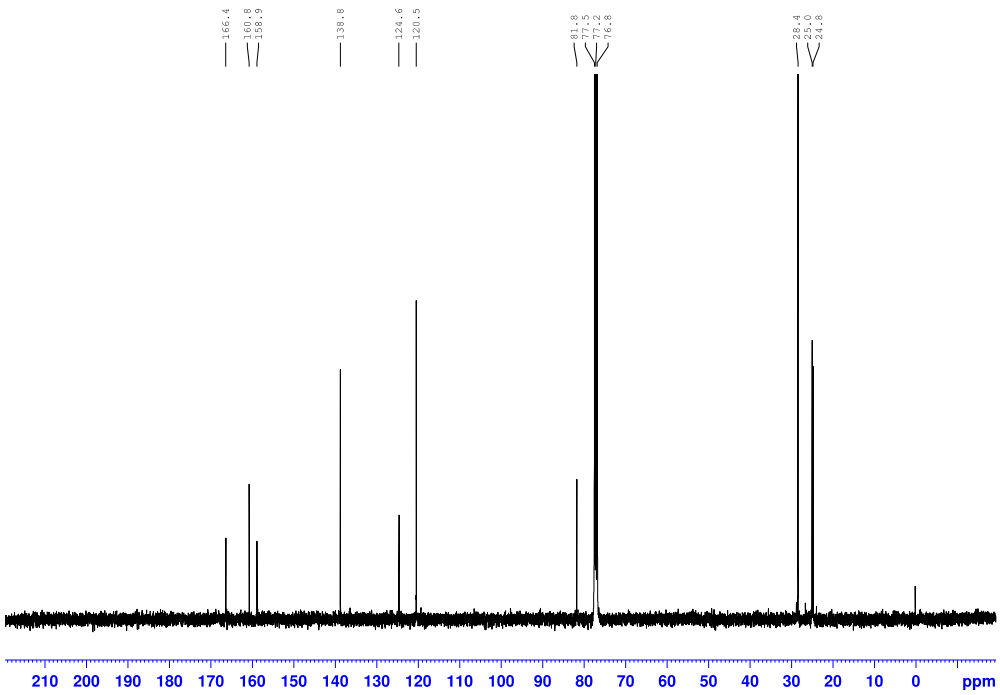
2-Methyl-1-propyl 2,6-dimethylpyridine-3-carboxylate (3ia)



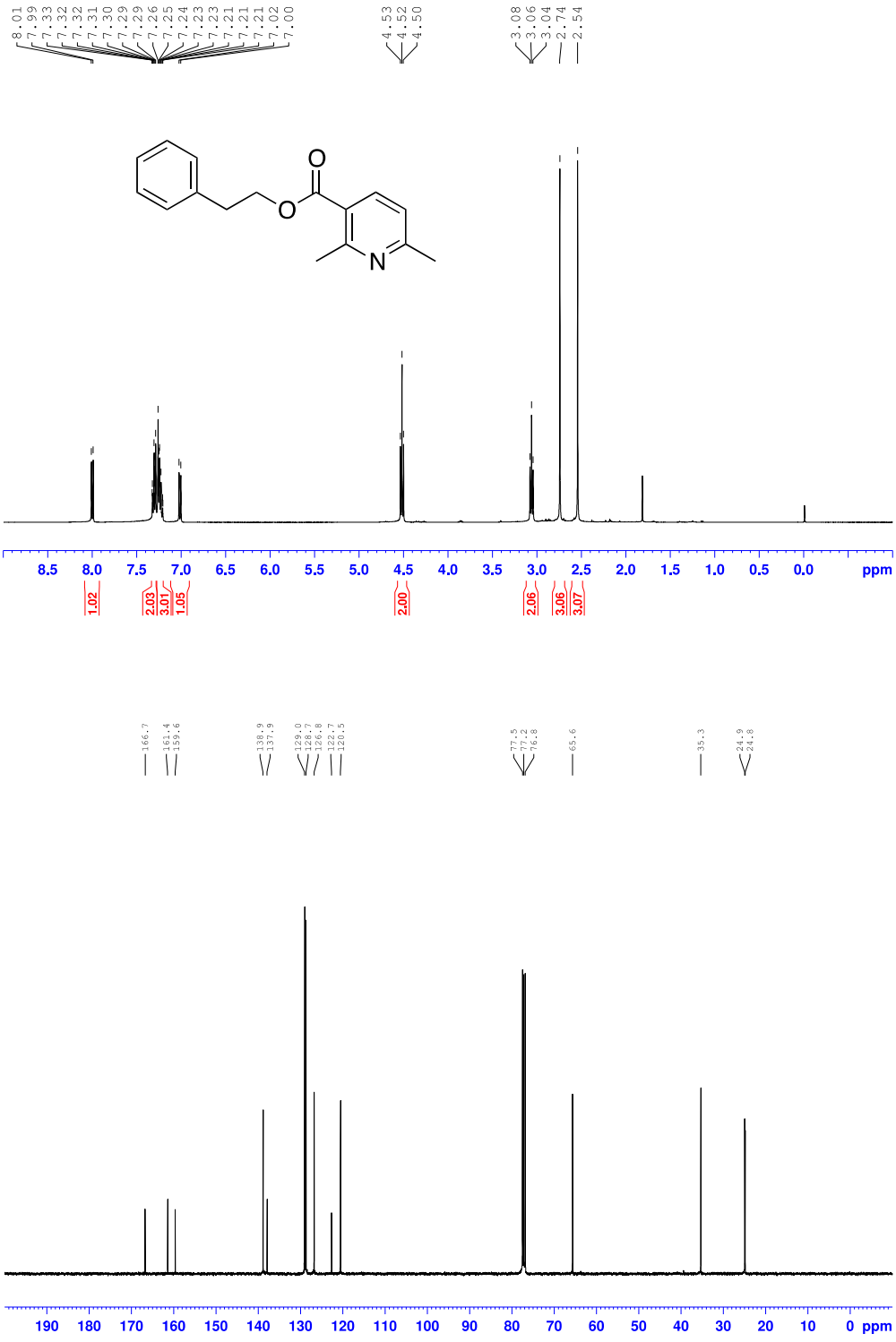


2-Methyl-2-propyl 2,6-dimethylpyridine-3-carboxylate (3ja)

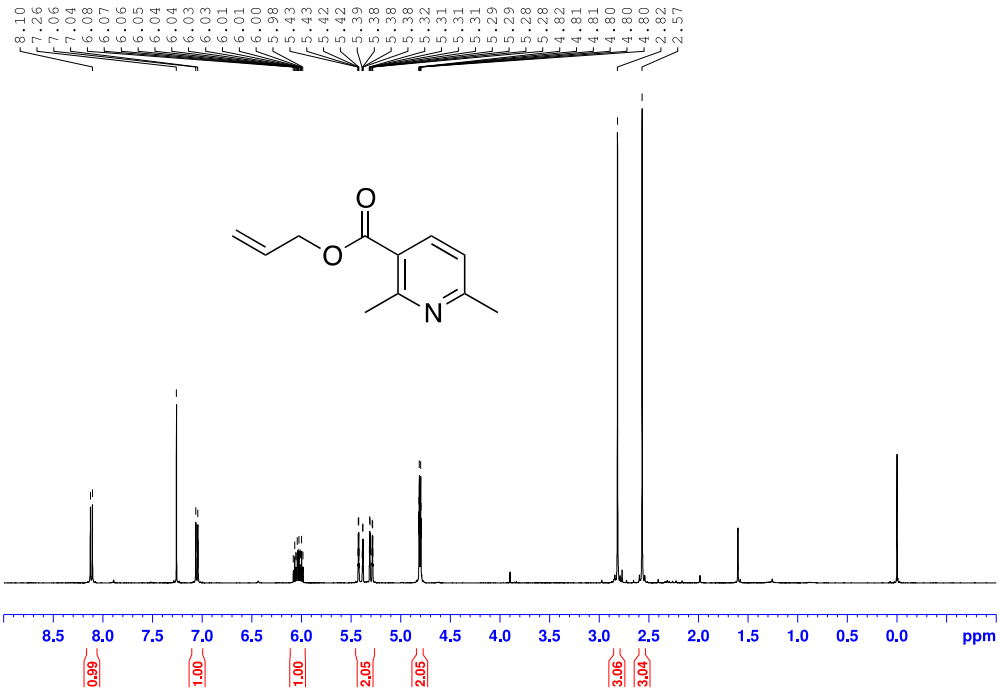


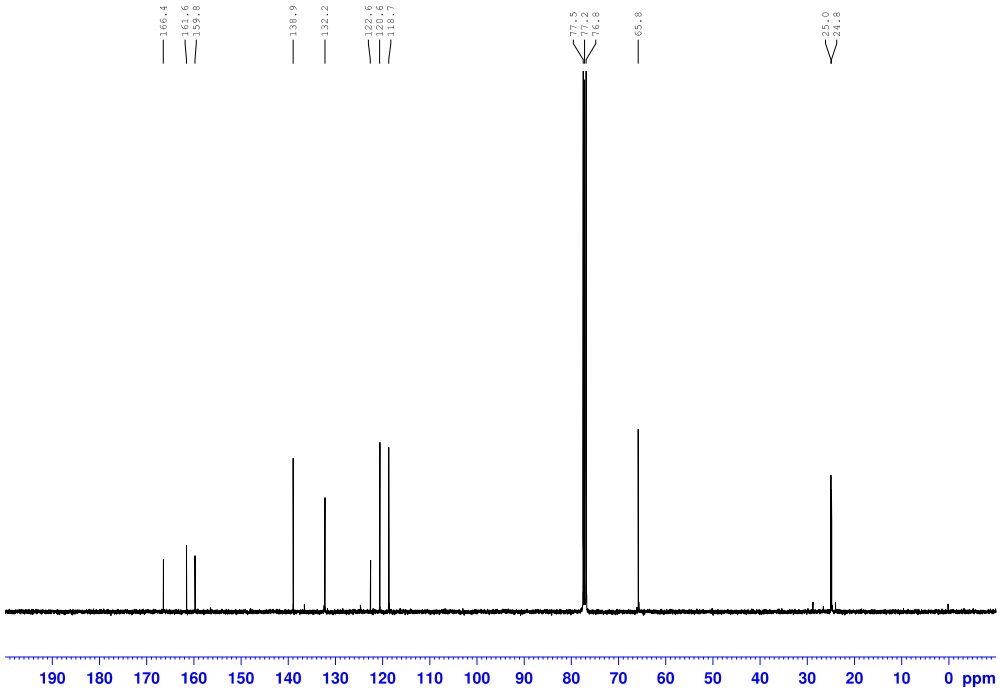


2-Phenylethyl 2,6-dimethylpyridine-3-carboxylate (3ka)

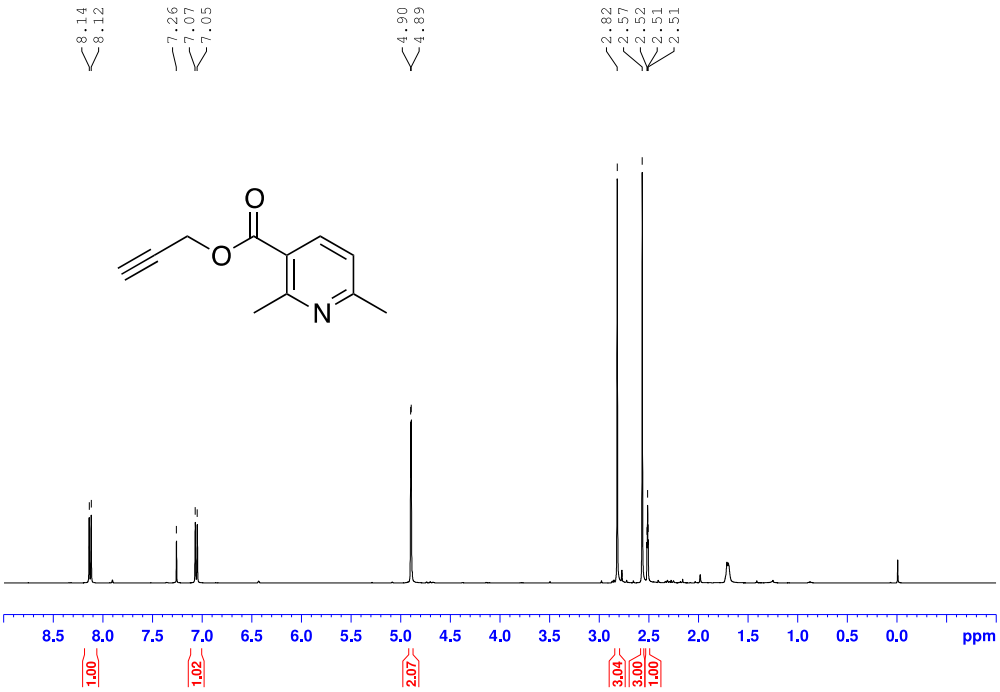


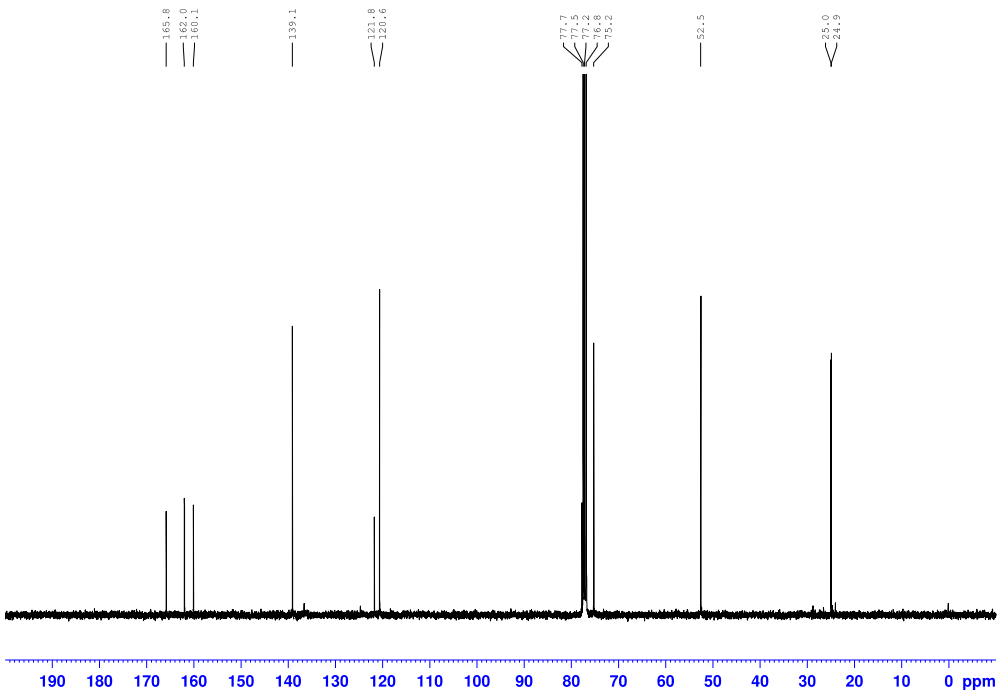
3-Propenyl 2,6-dimethylpyridine-3-carboxylate (3la)



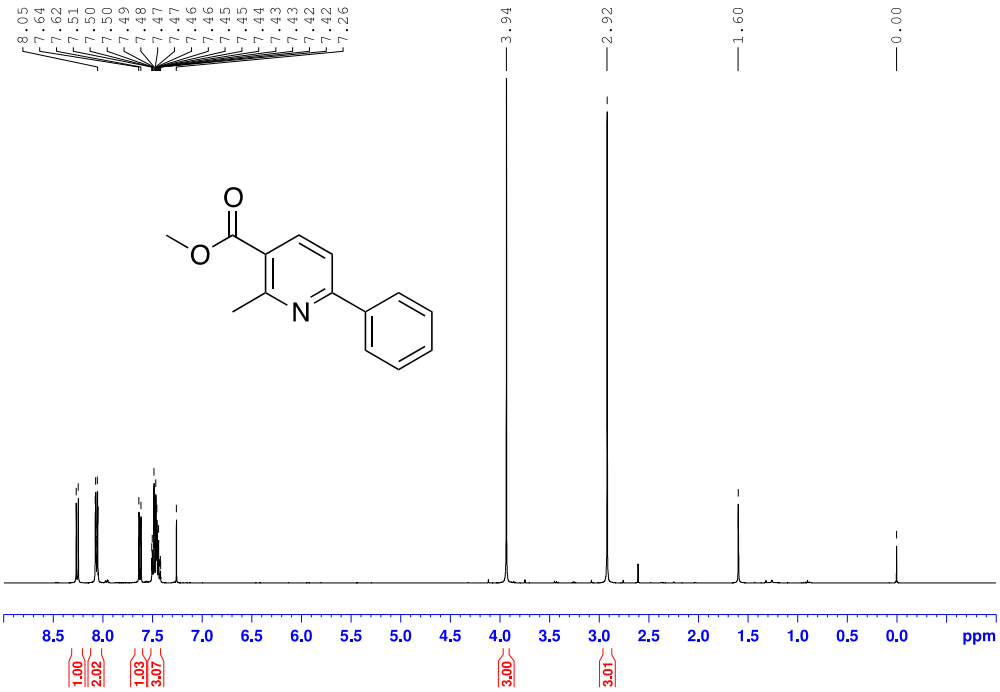


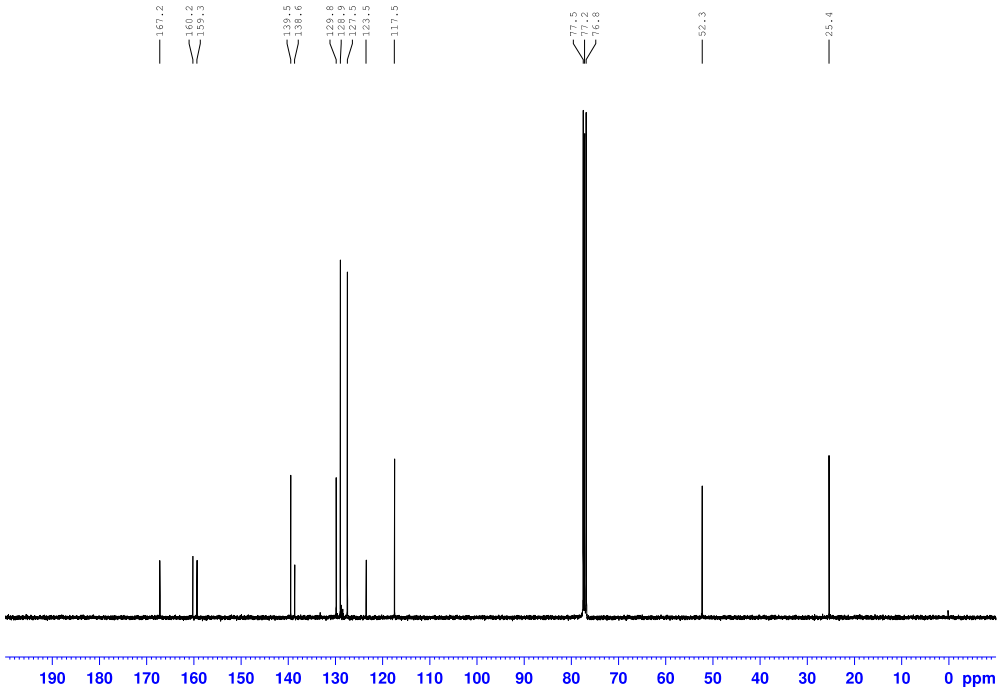
3-Propynyl 2,6-dimethylpyridine-3-carboxylate (3ma)



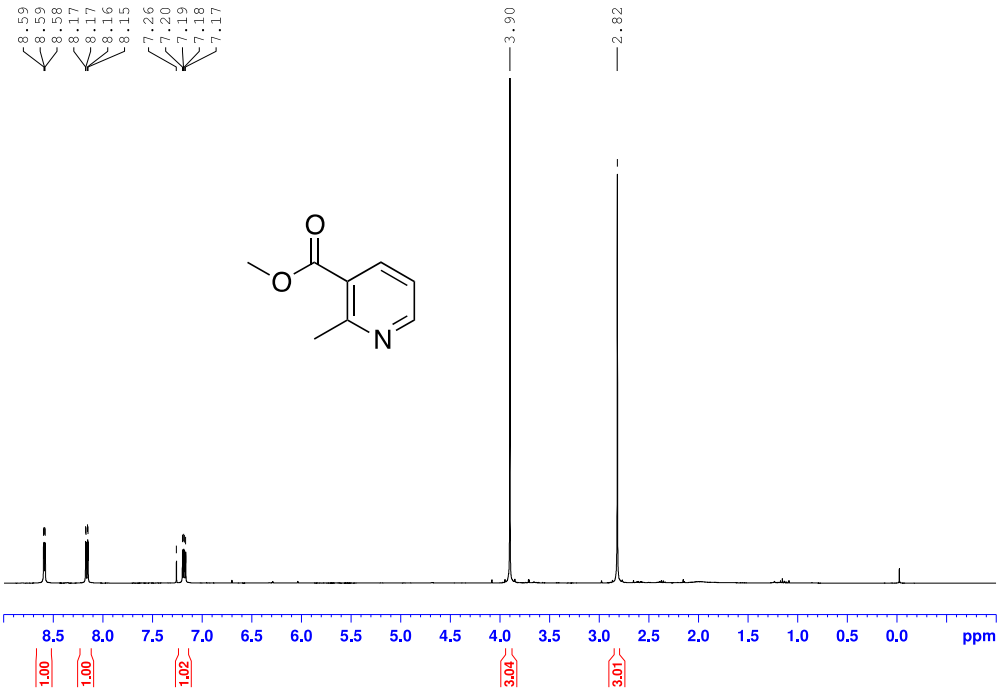


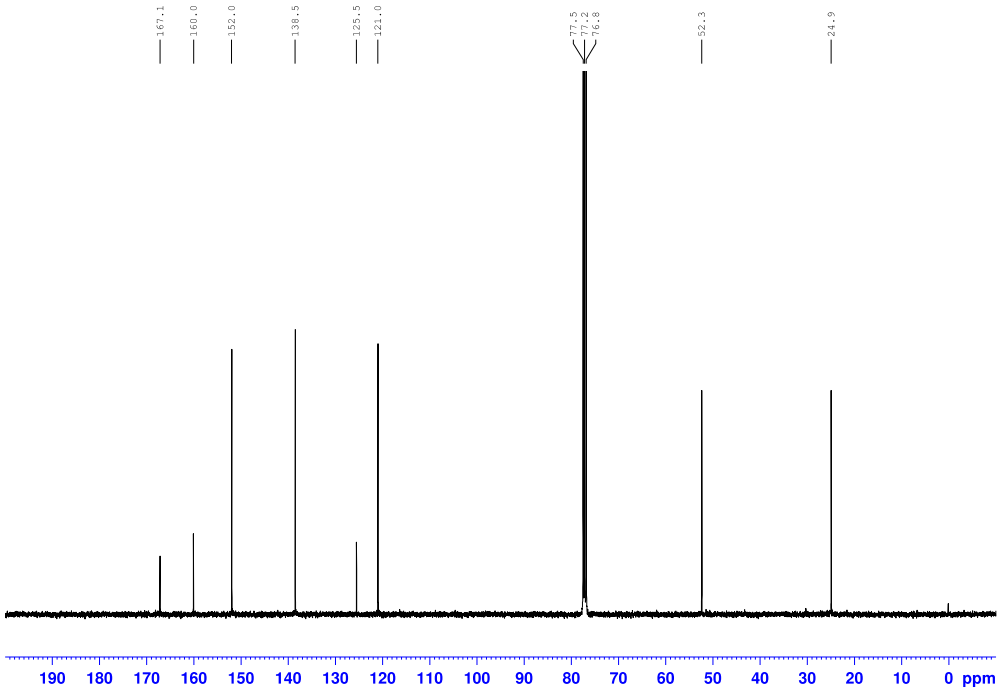
Methyl 2-methyl-6-phenylpyridine-3-carboxylate (3ab)



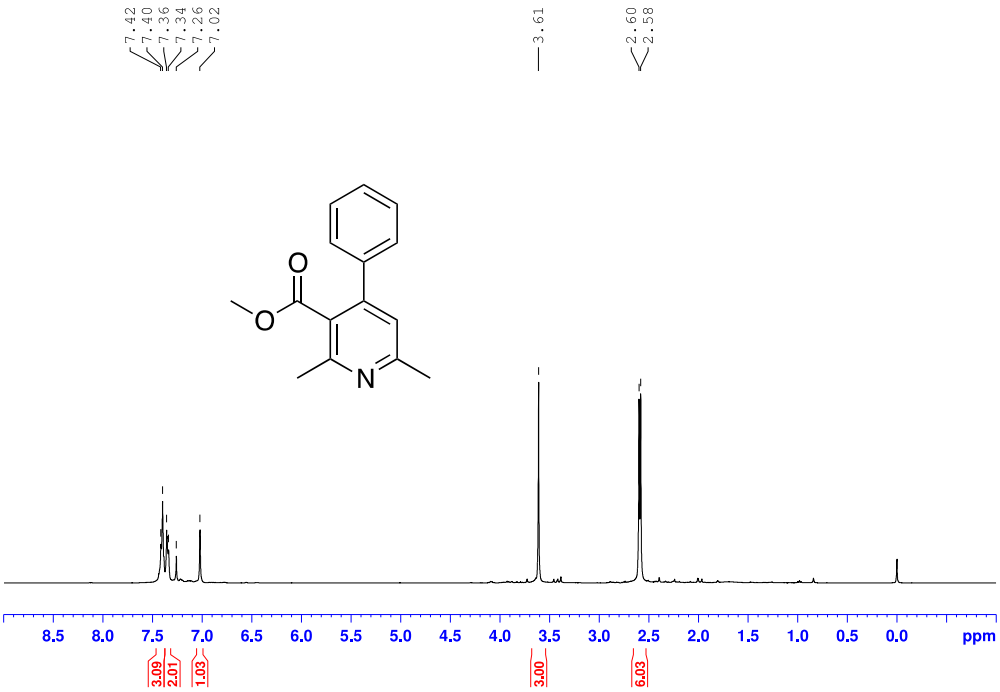


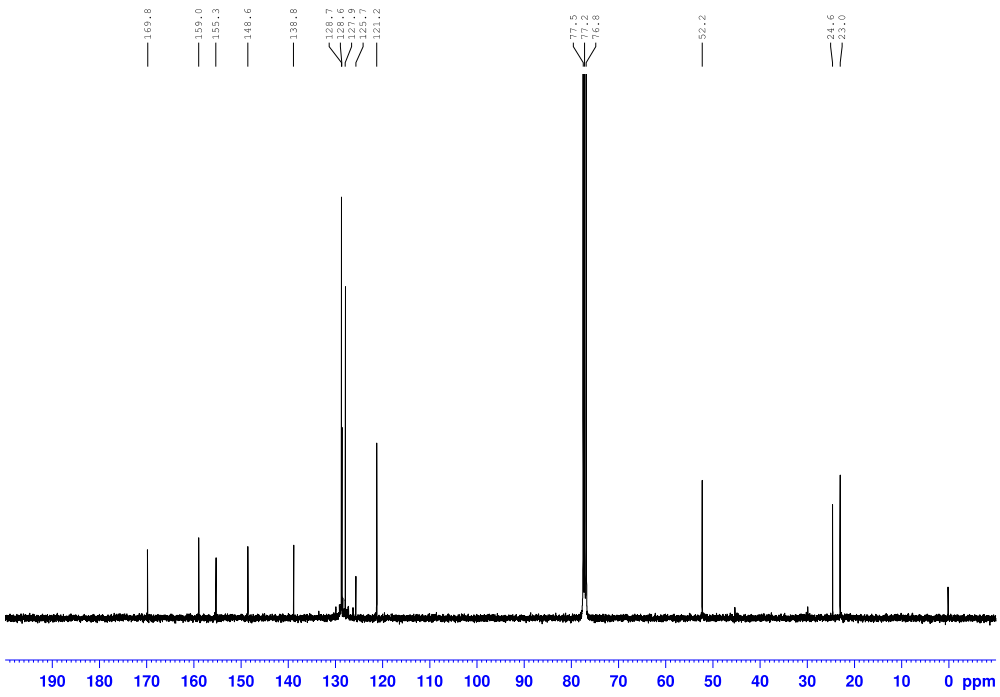
Methyl 2-methypyridine-3-carboxylate (3ac)



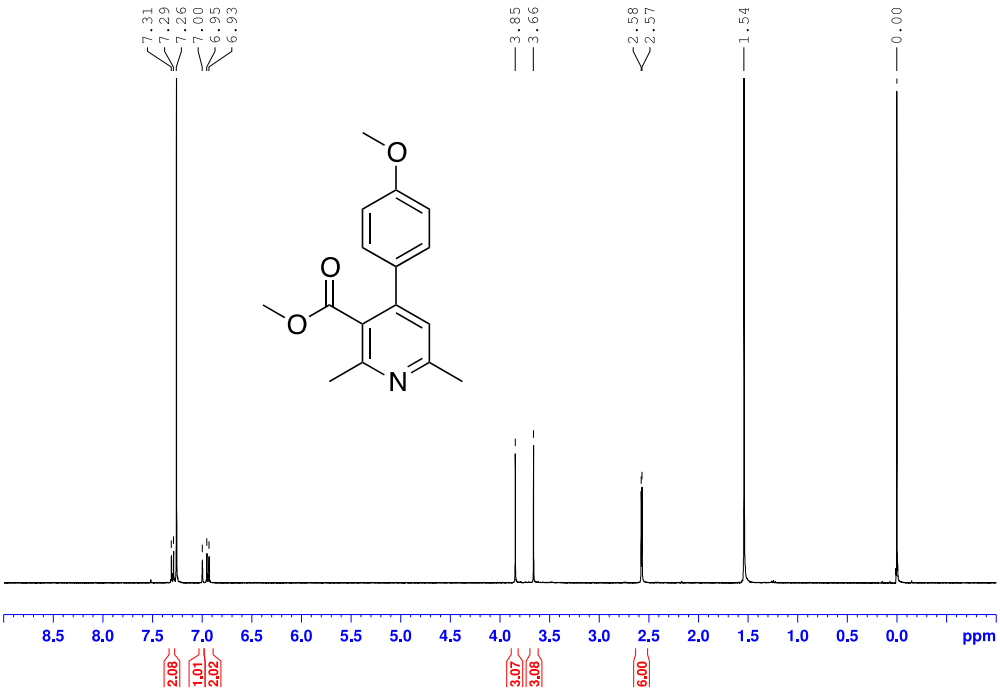


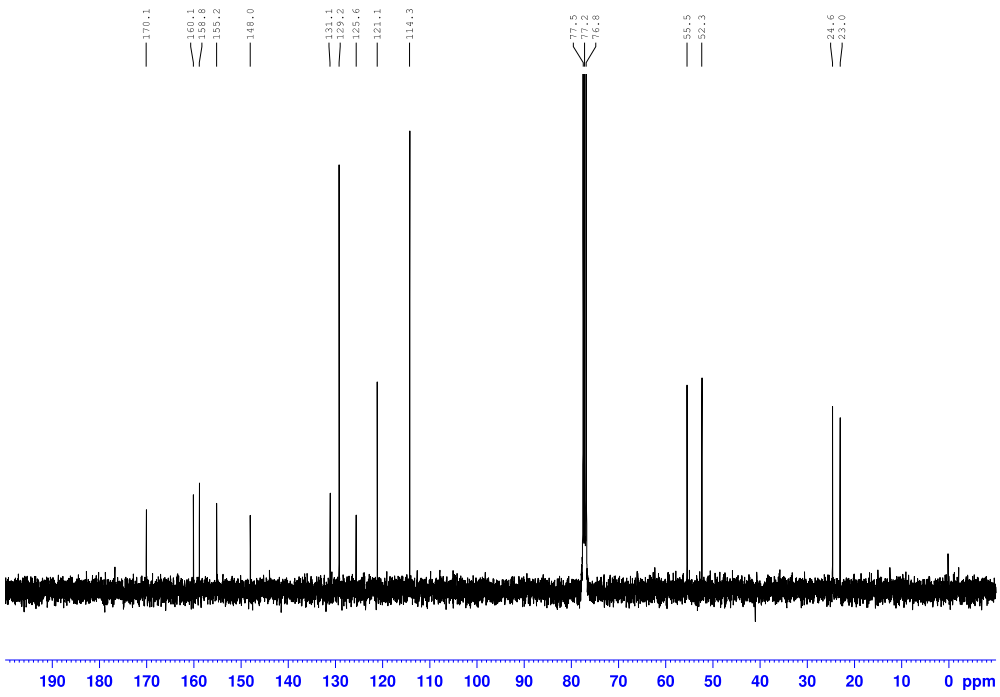
Methyl 2,6-dimethyl-4-phenylpyridine-3-carboxylate (3ad)



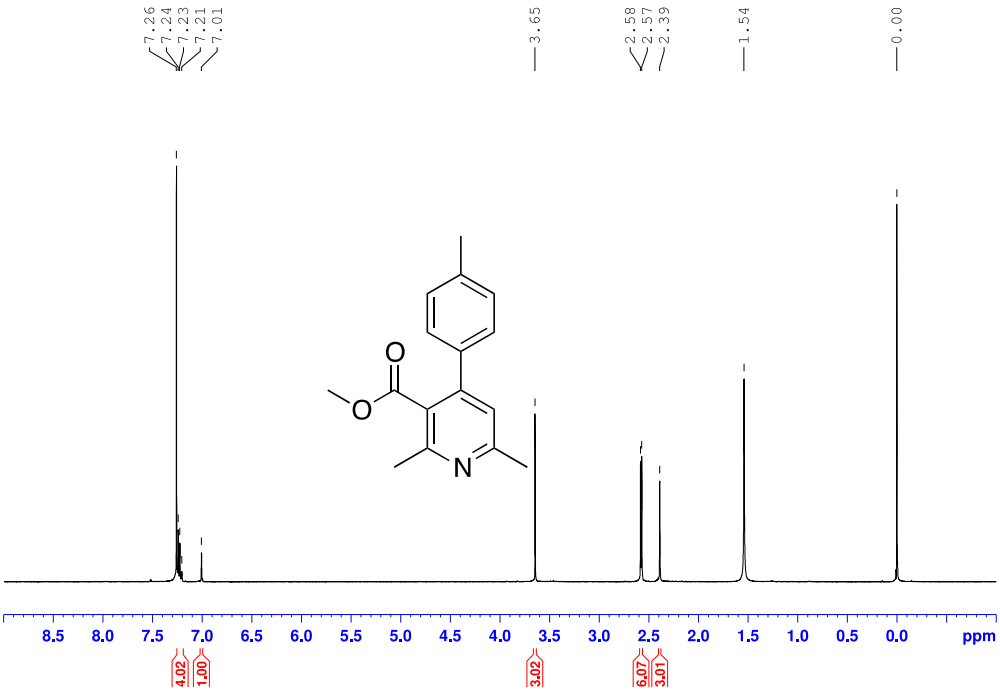


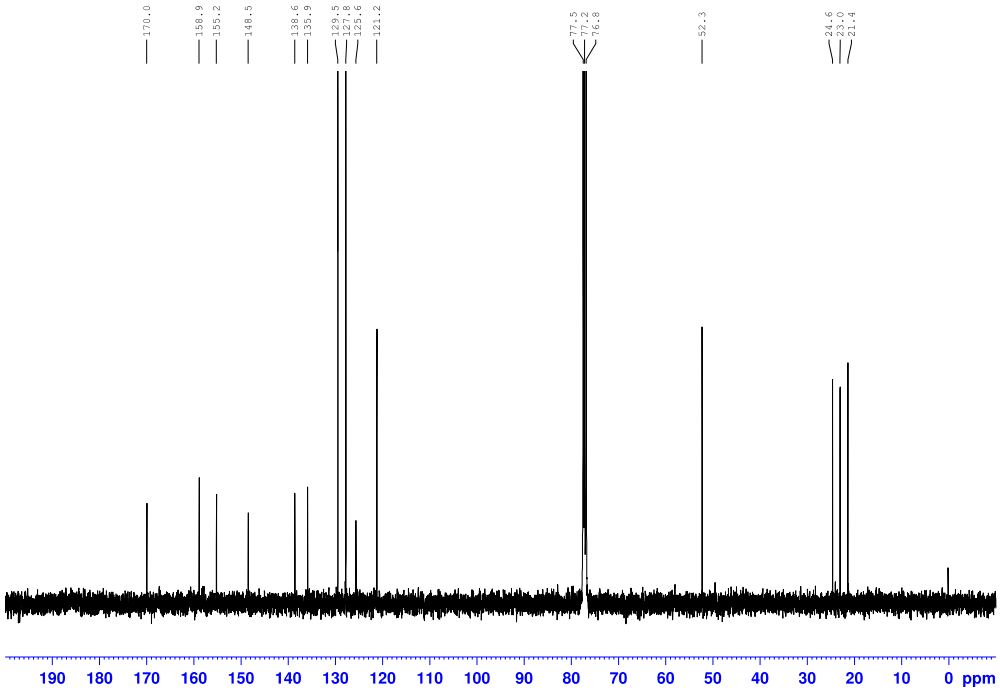
Methyl 2,6-dimethyl-4-(4-methoxyphenyl)pyridine-3-carboxylate (3ae)



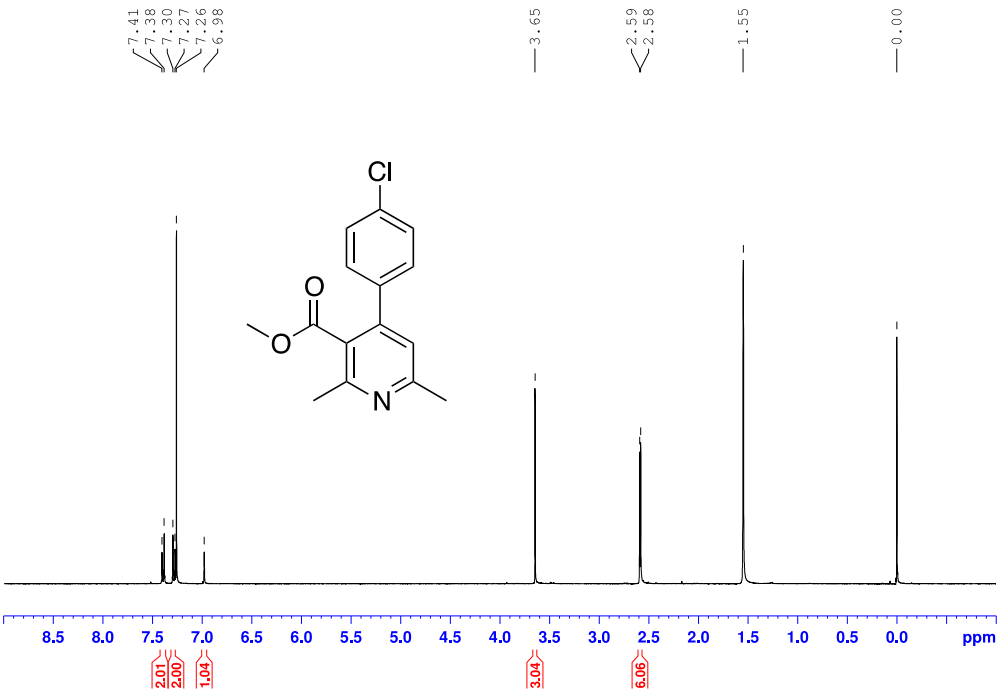


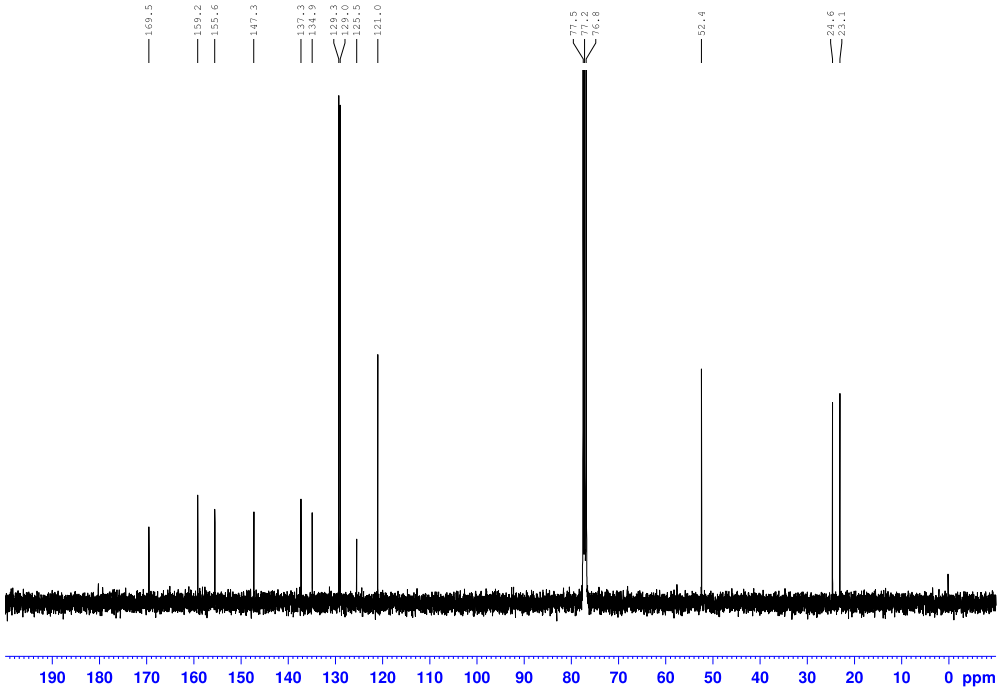
Methyl 2,6-dimethyl-4-(4-methylphenyl)pyridine-3-carboxylate (3af)



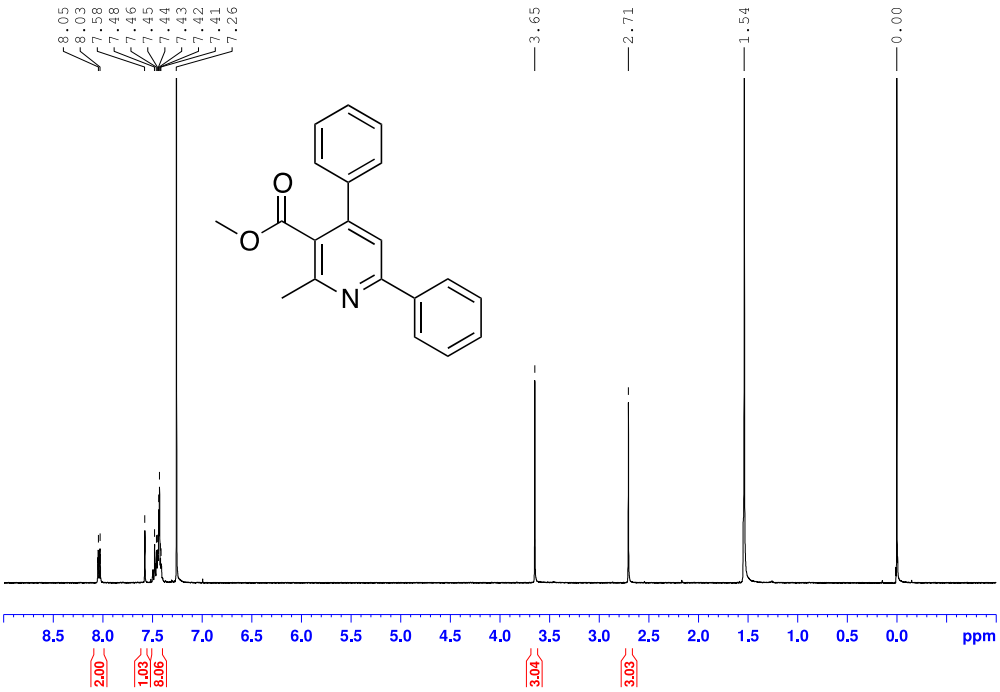


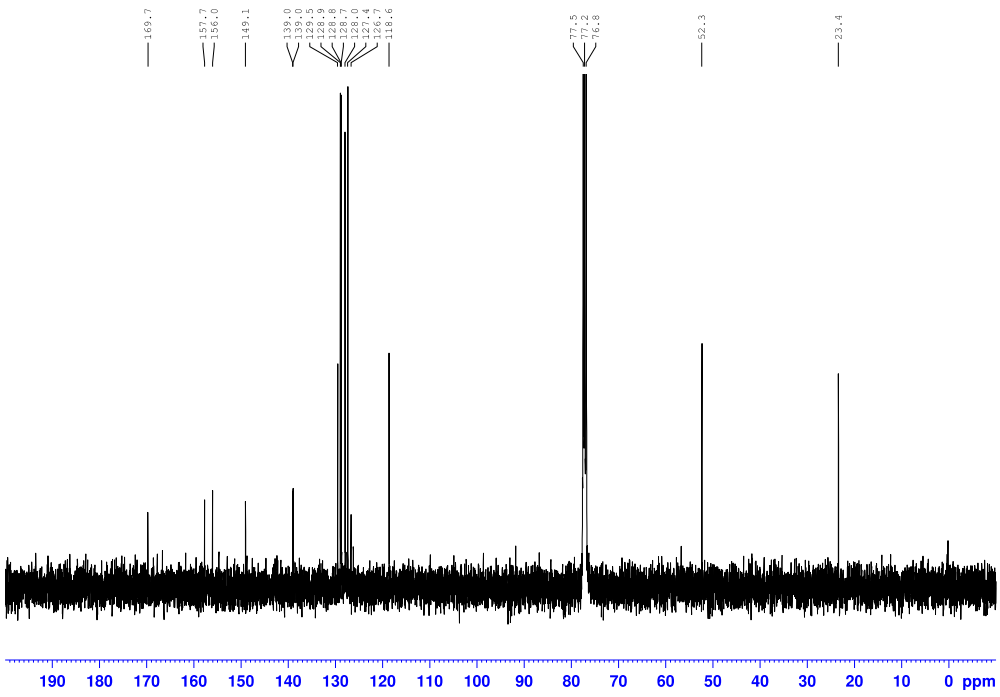
Methyl 4-(4-chlorophenyl)-2,6-dimethylpyridine-3-carboxylate (3ag)



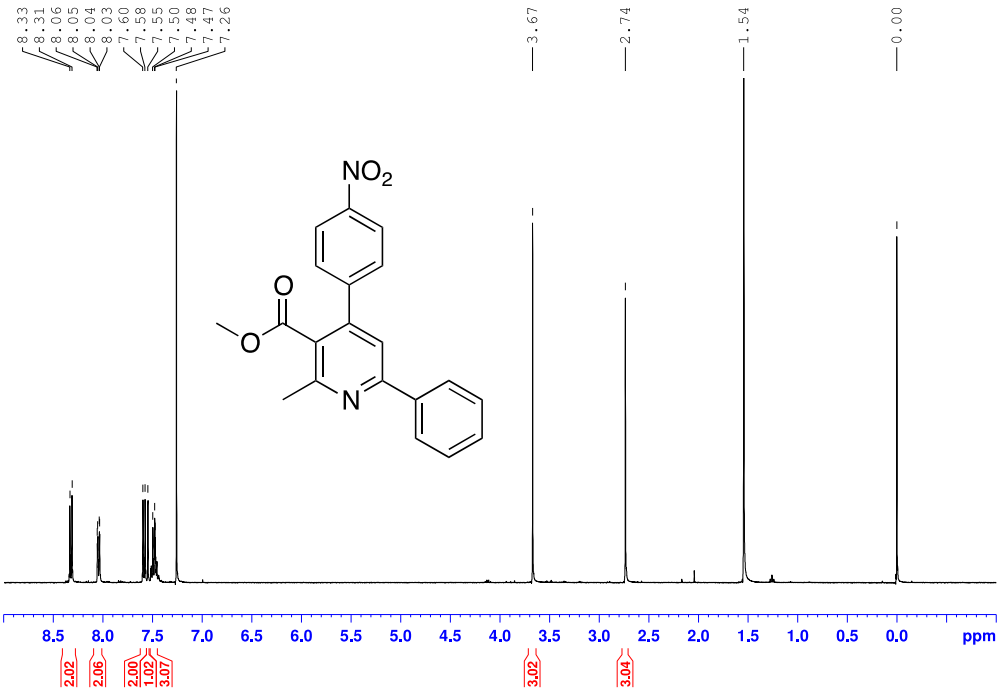


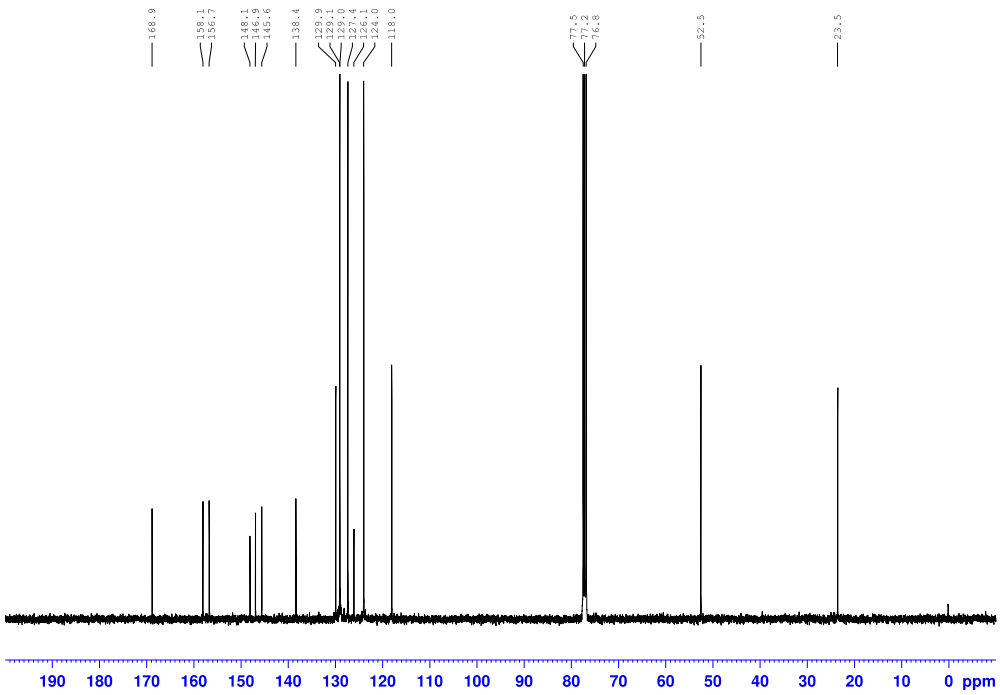
Methyl 4,6-diphenyl-2-methylpyridine-3-carboxylate (3ah)



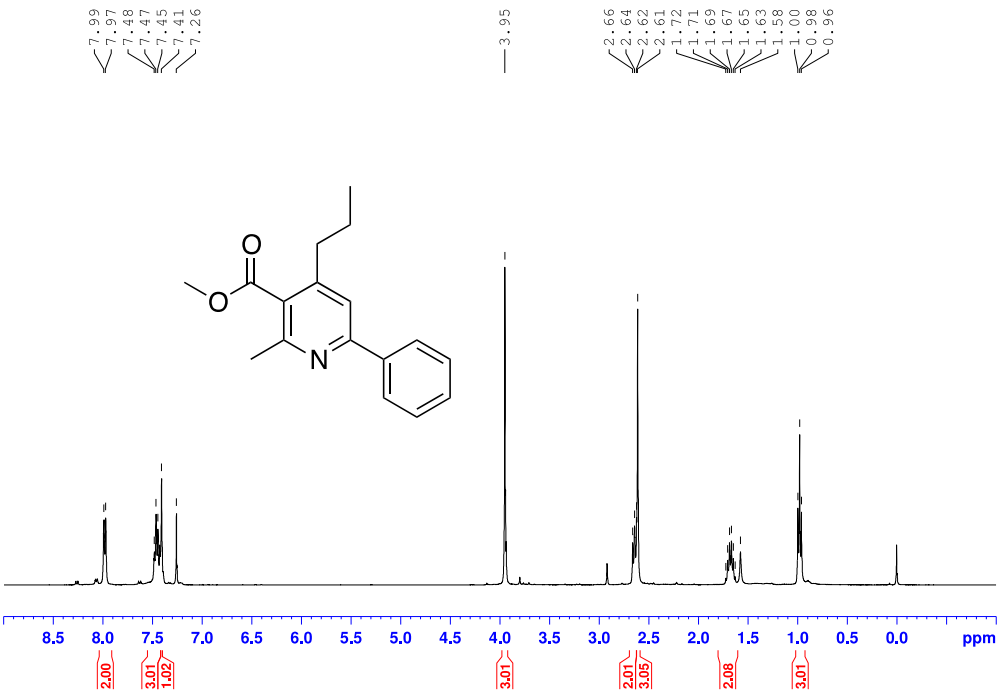


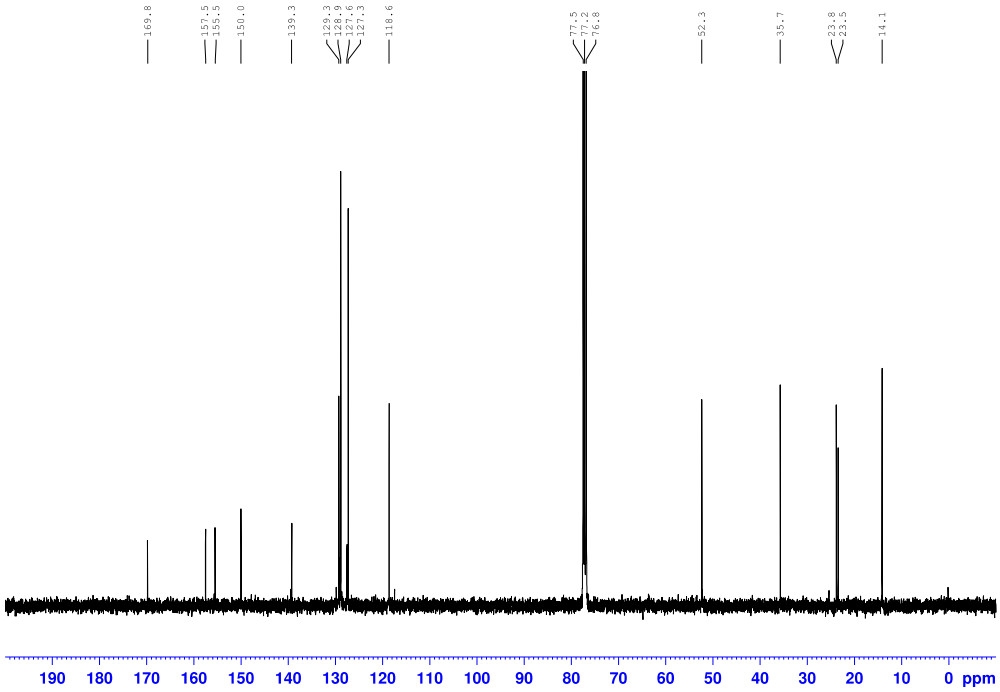
Methyl 2-methyl-4-(4-nitrophenyl)-6-phenylpyridine-3-carboxylate (3ai)



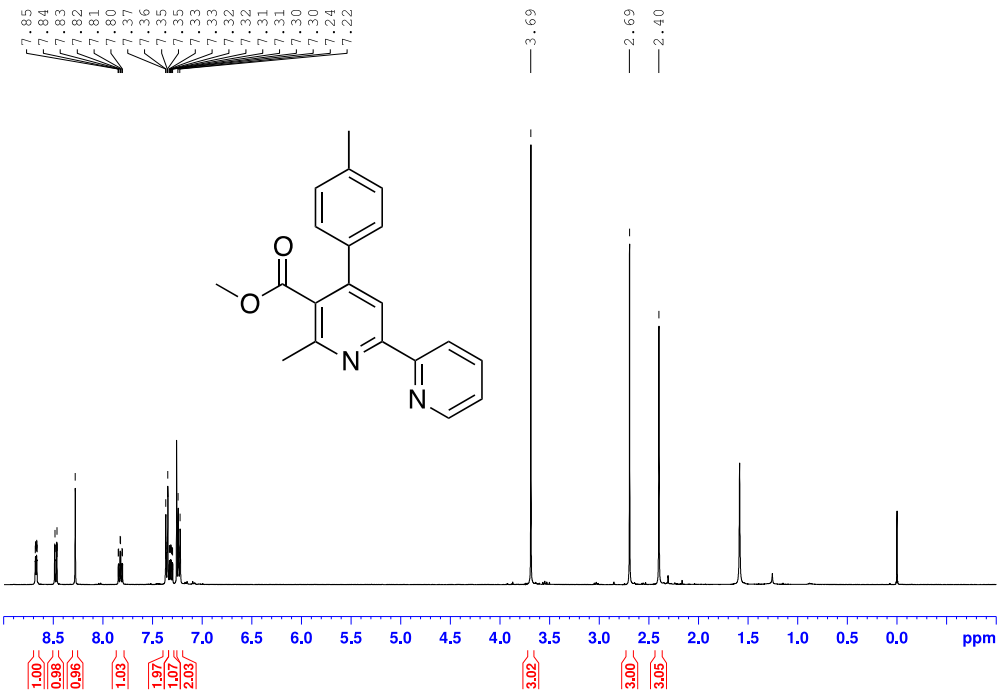


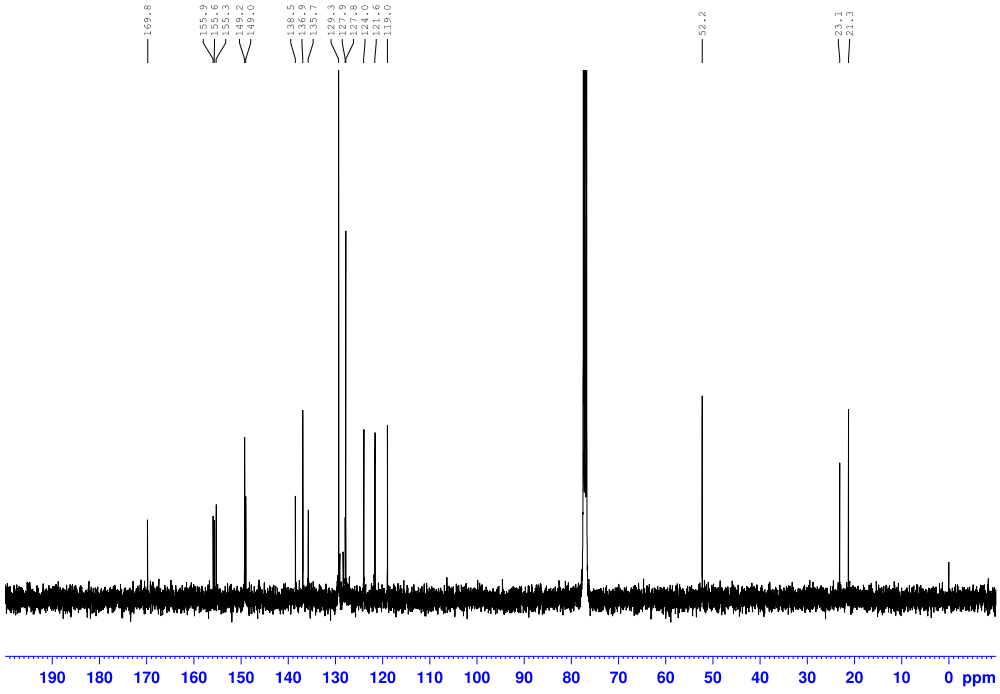
Methyl 2-methyl-6-phenyl-4-propylpyridine-3-carboxylate (3aj)



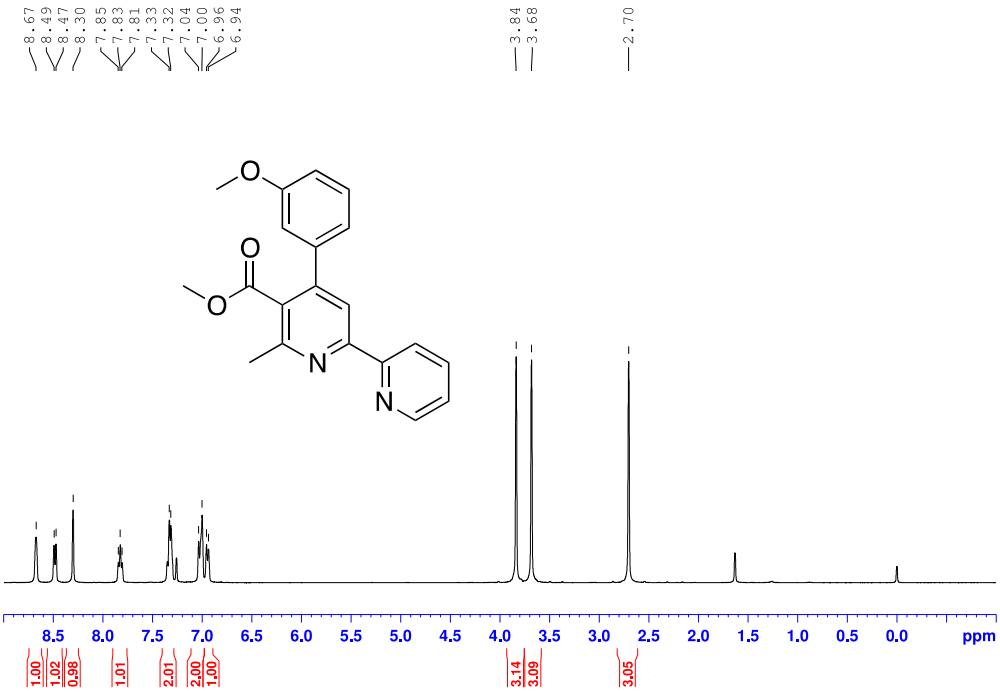


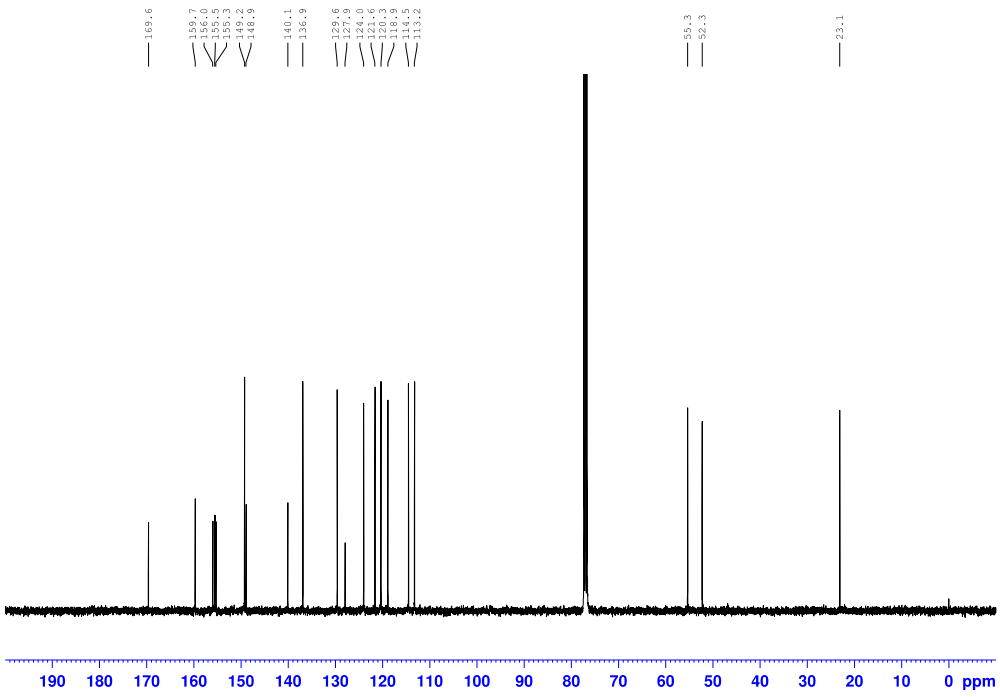
Methyl 2-methyl-4-(4-methylphenyl)-6-(2-pyridinyl)pyridine-3-carboxylate (3ak)



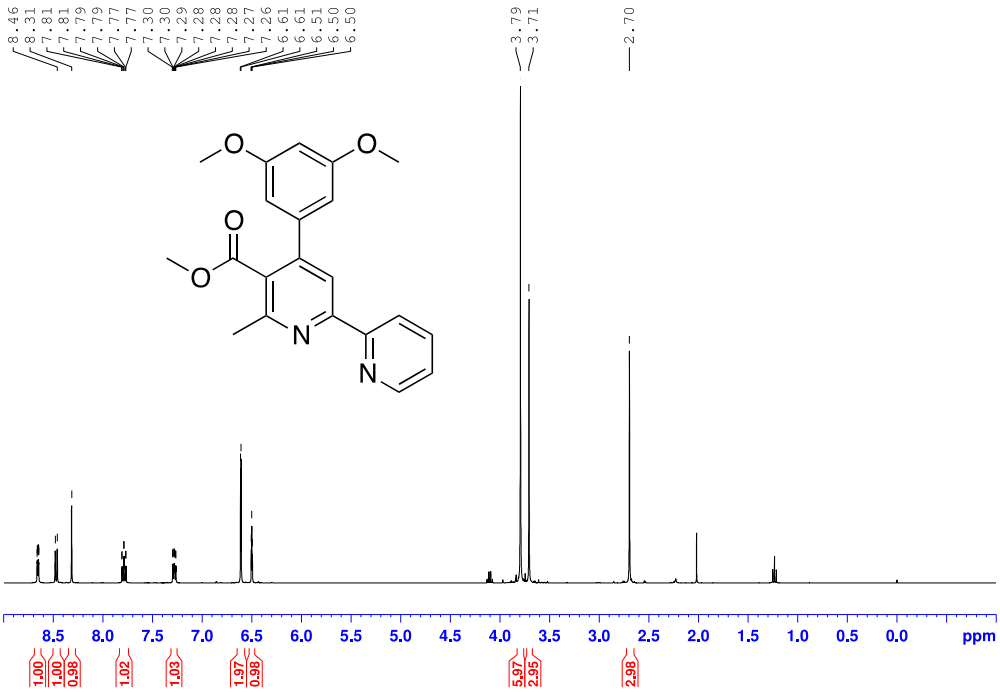


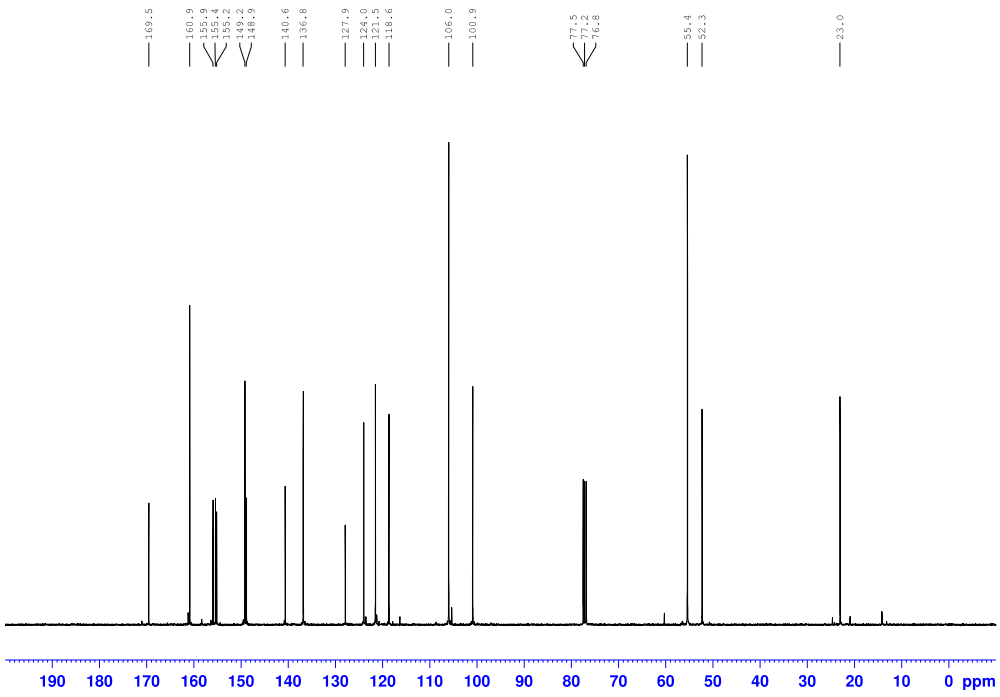
Methyl 2-methyl-4-(3-methoxyphenyl)-6-(2-pyridinyl) pyrinine-3-carboxylate (3al)



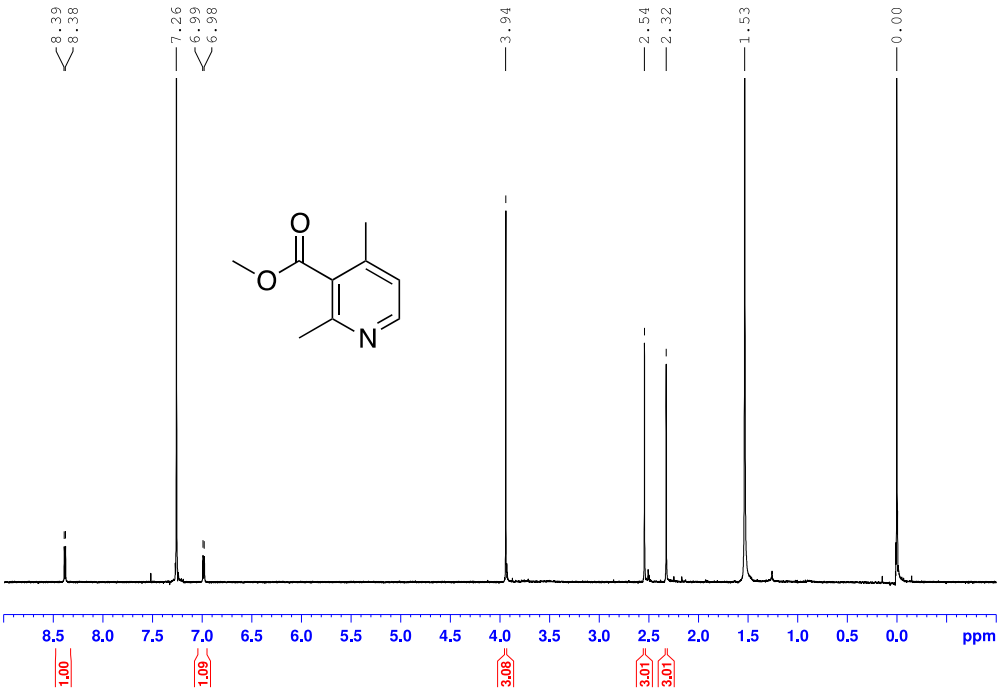


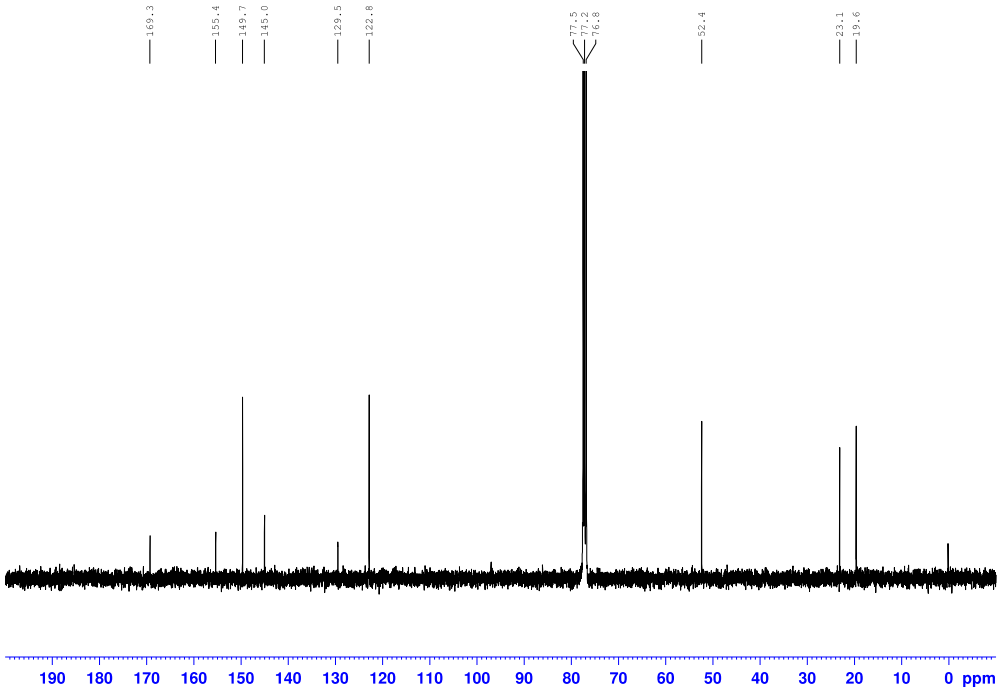
Methyl 2-methyl-4-(3,5-dimethoxyphenyl)-6-(2-pyridinyl) pyridine-3-carboxylate (3am)



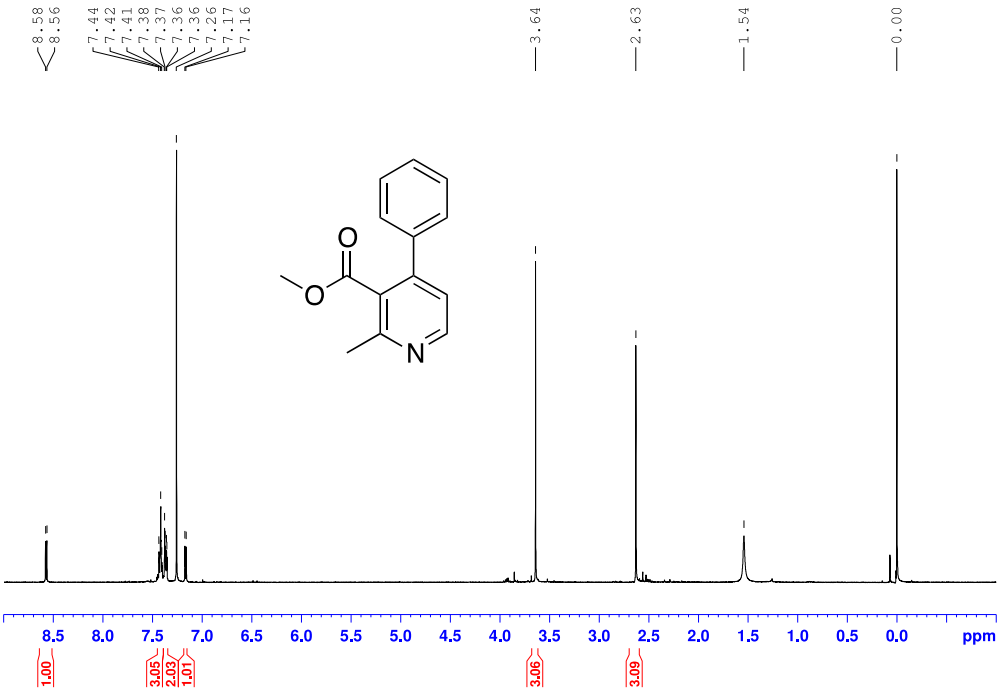


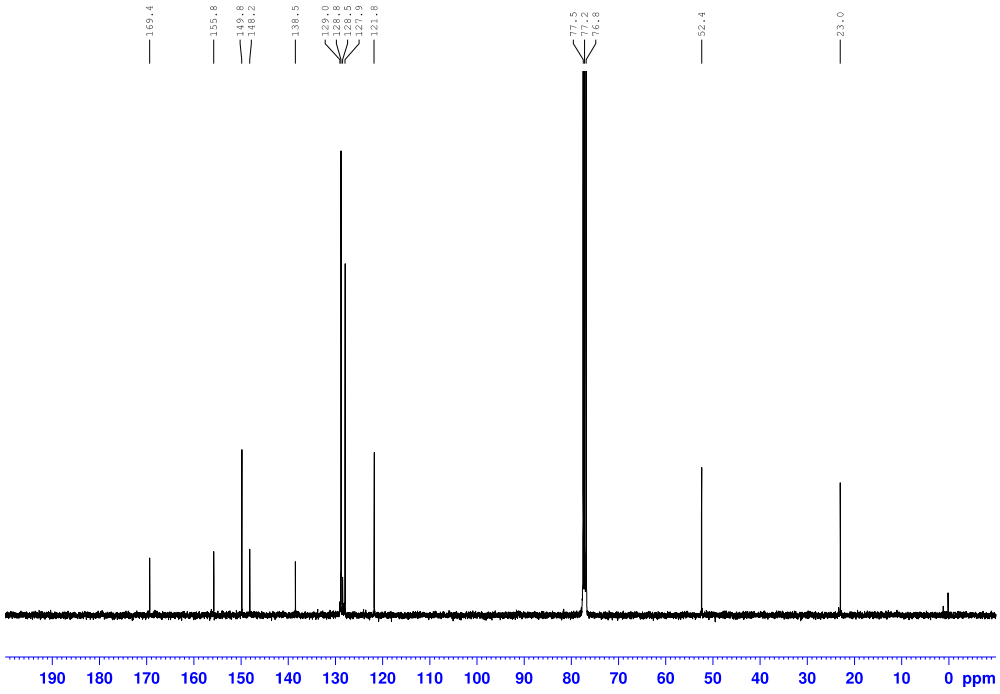
Methyl 2,4-dimethylpyridine-3-carboxylate (3an)



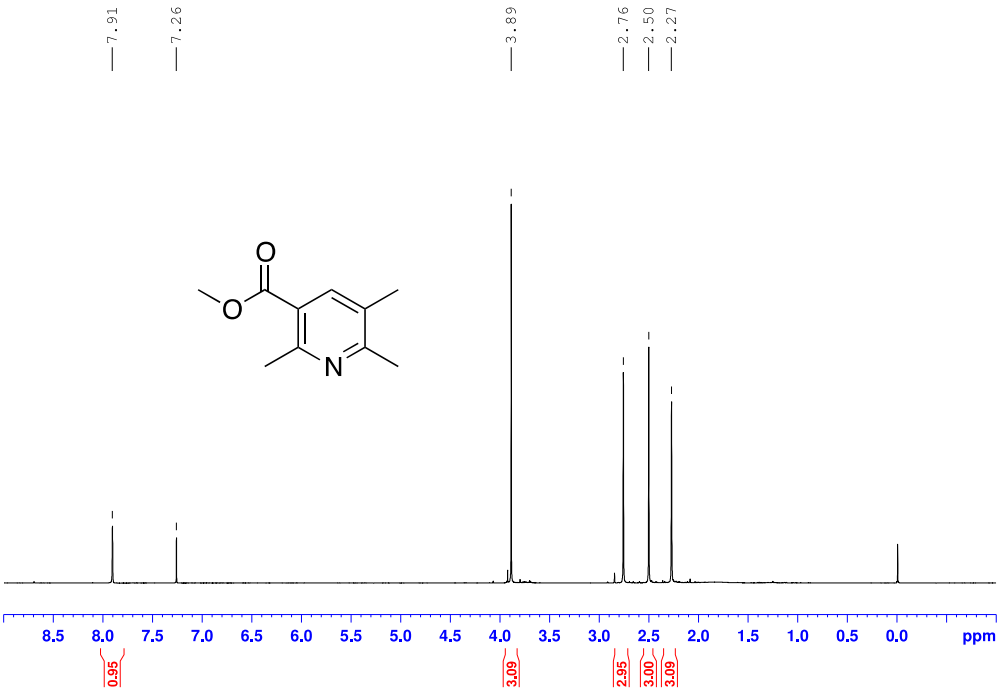


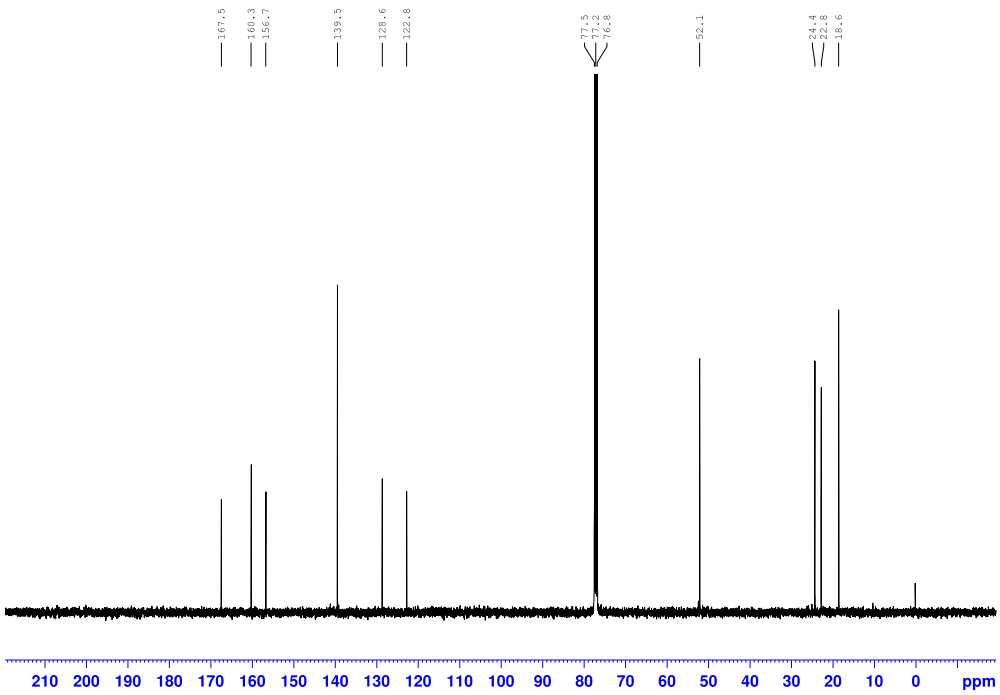
Methyl 2-methyl-4-phenylpyridine-3-carboxylate (3ao)



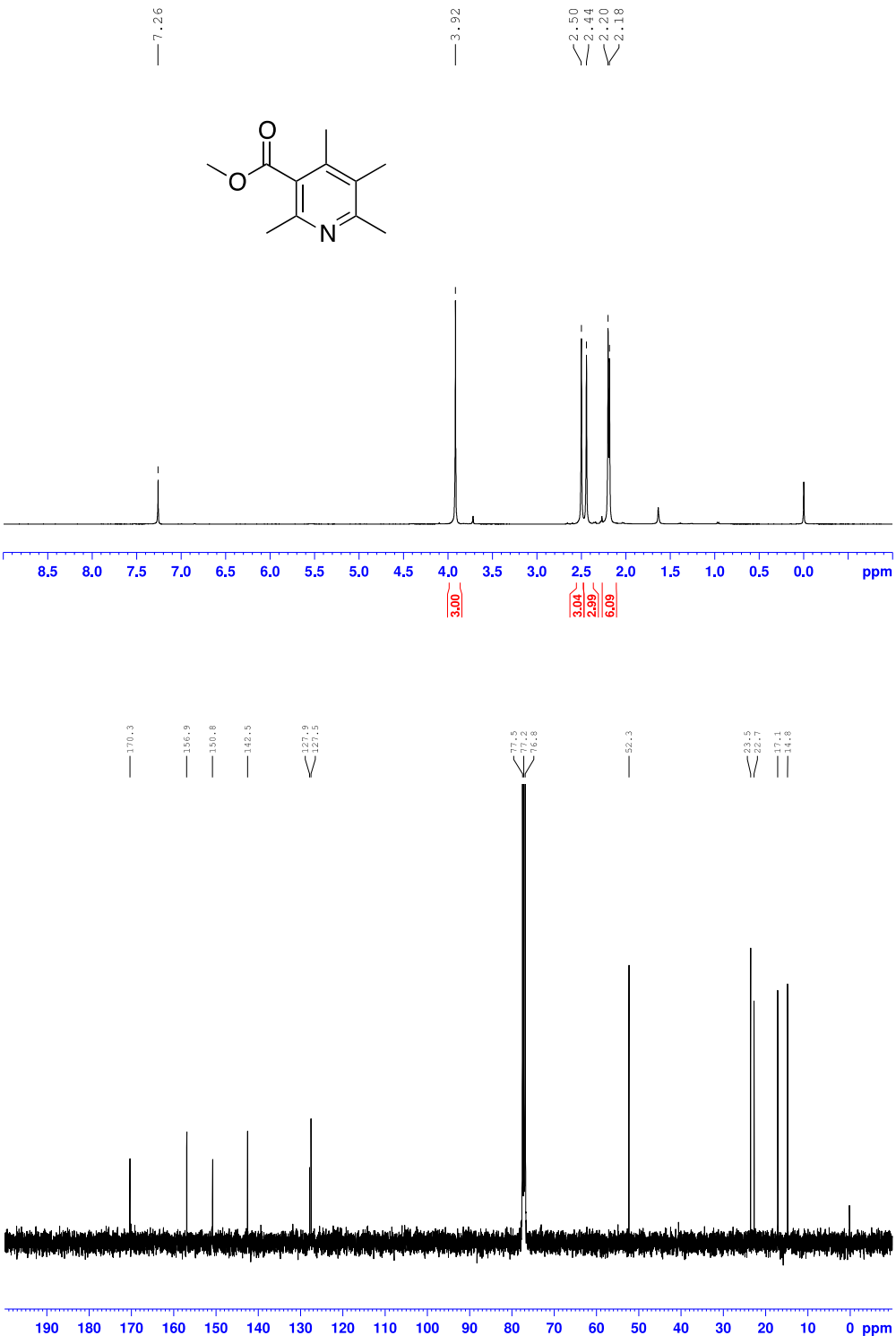


Methyl 2,5,6-trimethylpyridine-3-carboxylate (3ap)

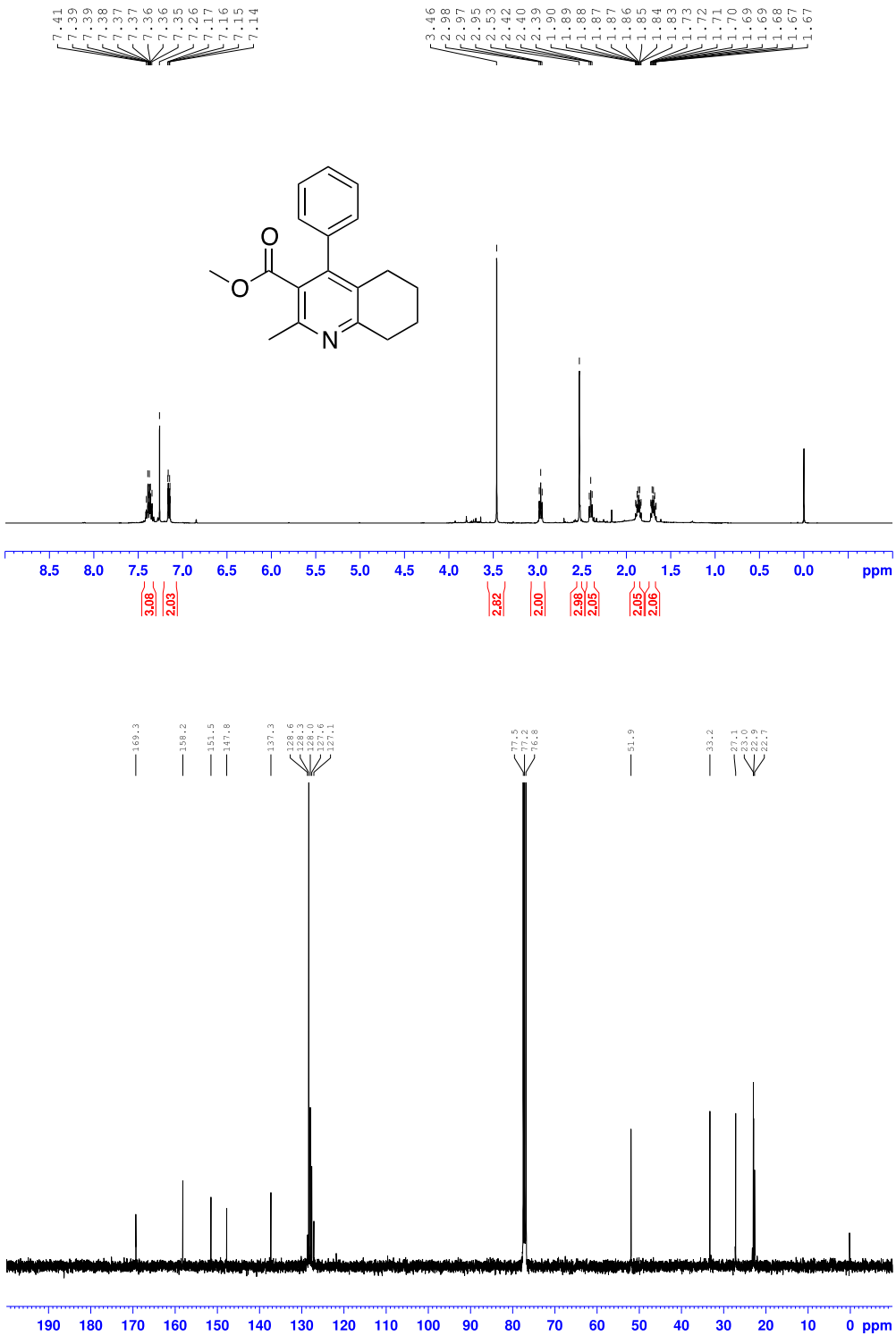




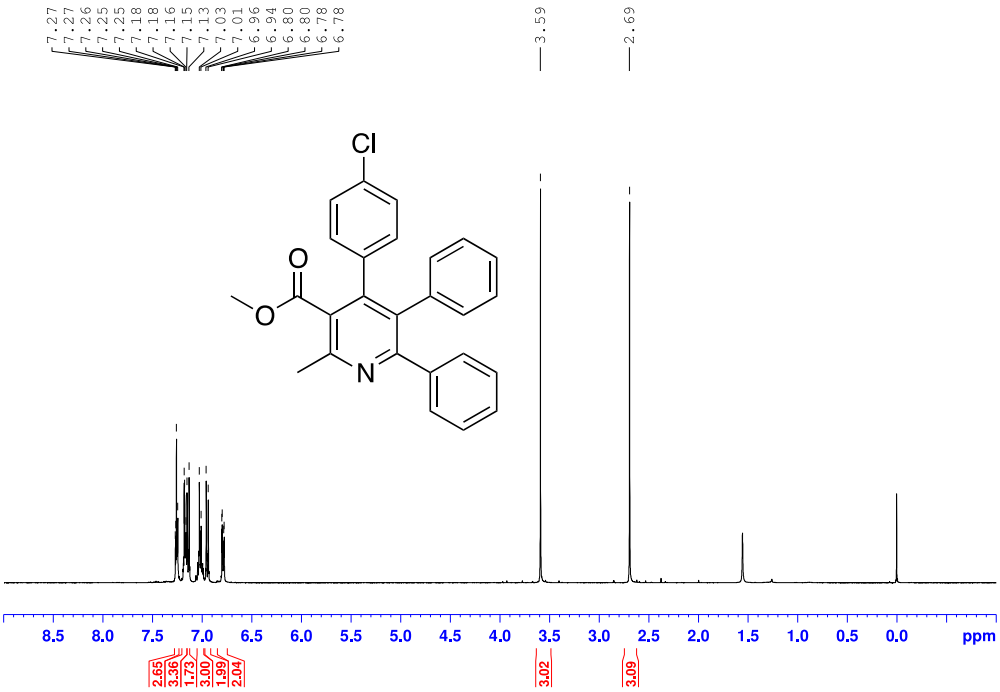
Methyl 2,4,5,6-tetramethylpyridine-3-carboxylate (3aq)

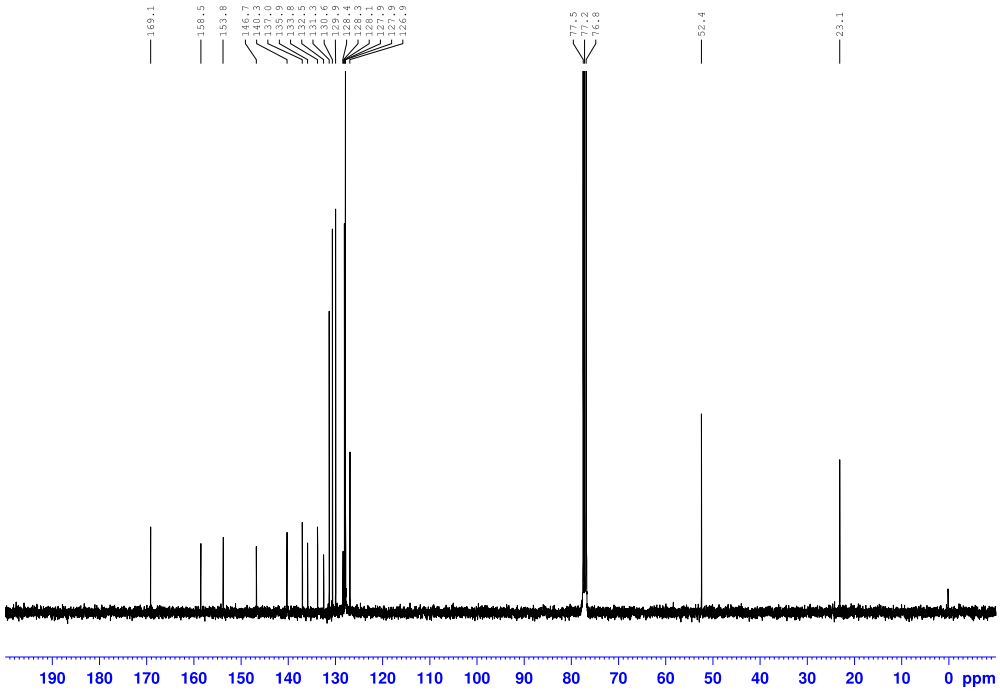


Methyl 2-methyl-5,6,7,8-tetrahydroquinoline-3-carboxylate (3ar)

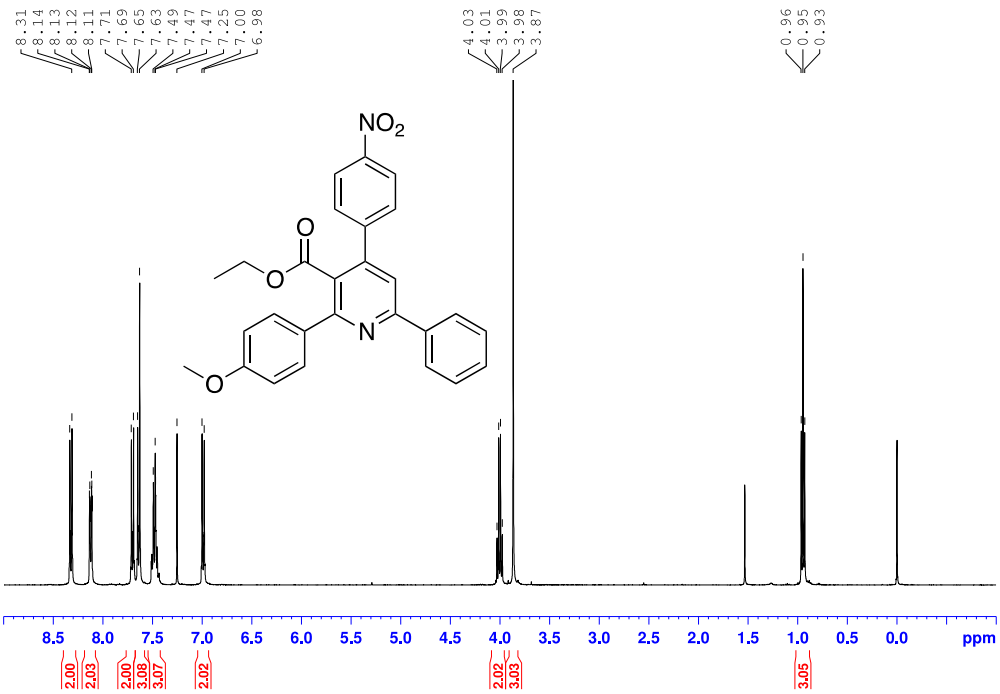


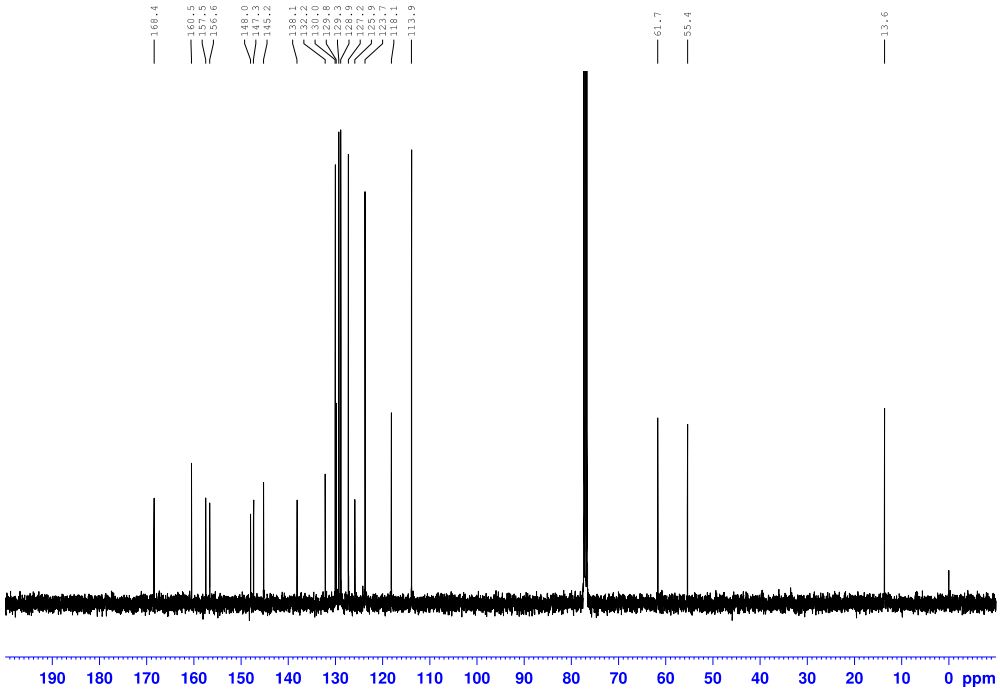
Methyl-4-(4-chlorophenyl)-5,6-diphenyl-2-methylpyridiney-3-carboxylate (3as)



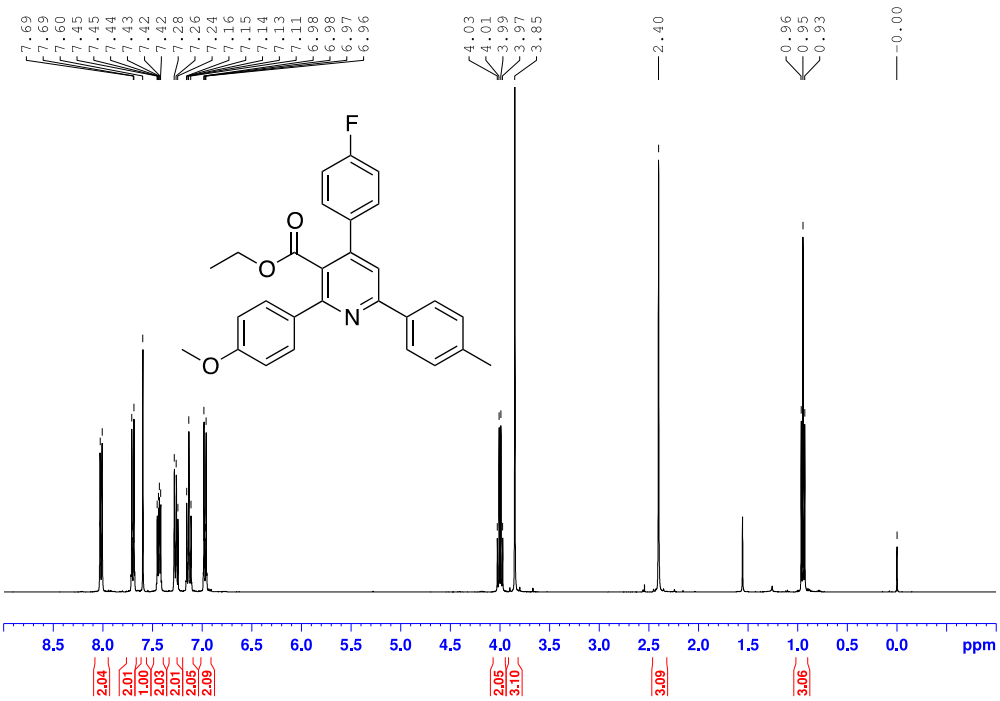


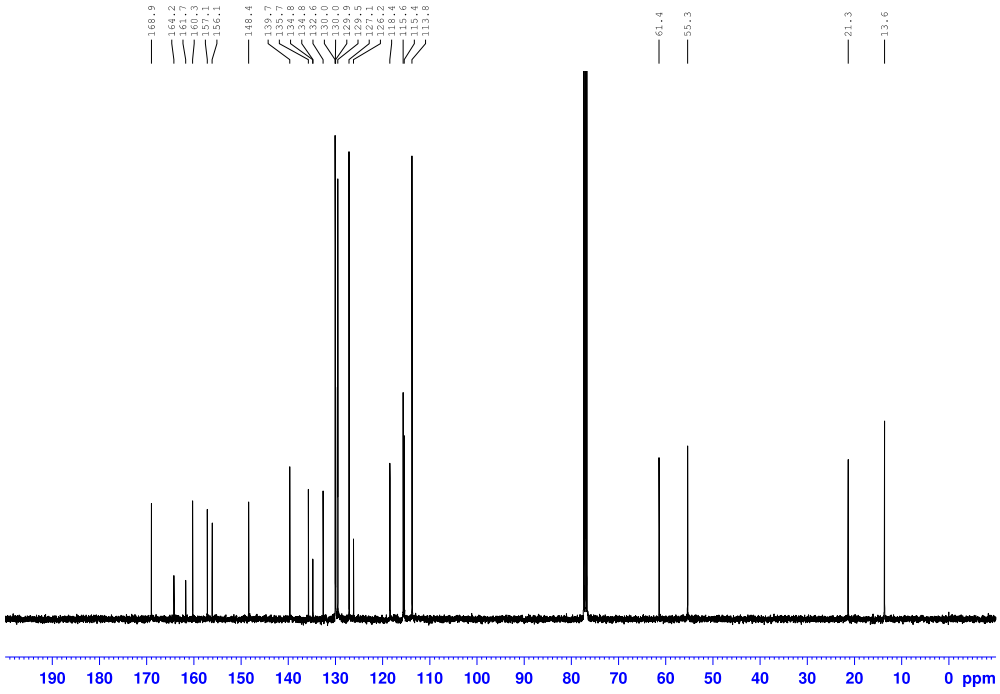
Ethyl 2-(4-methoxyphenyl)-4-(4-nitrophenyl)-6-phenylpyridine-3-carboxylate (3ei)



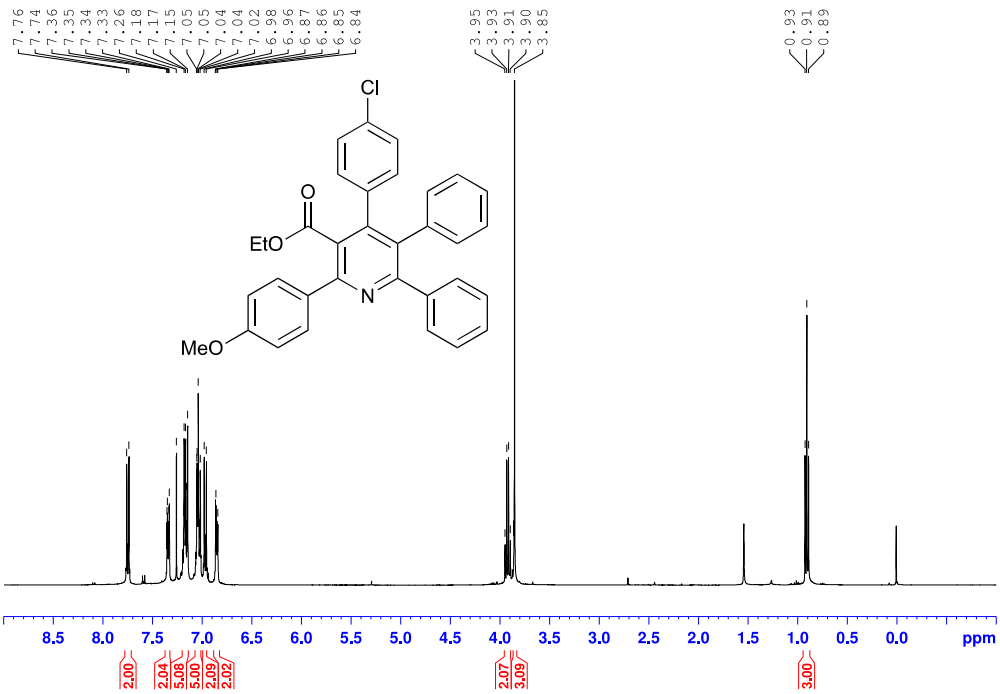


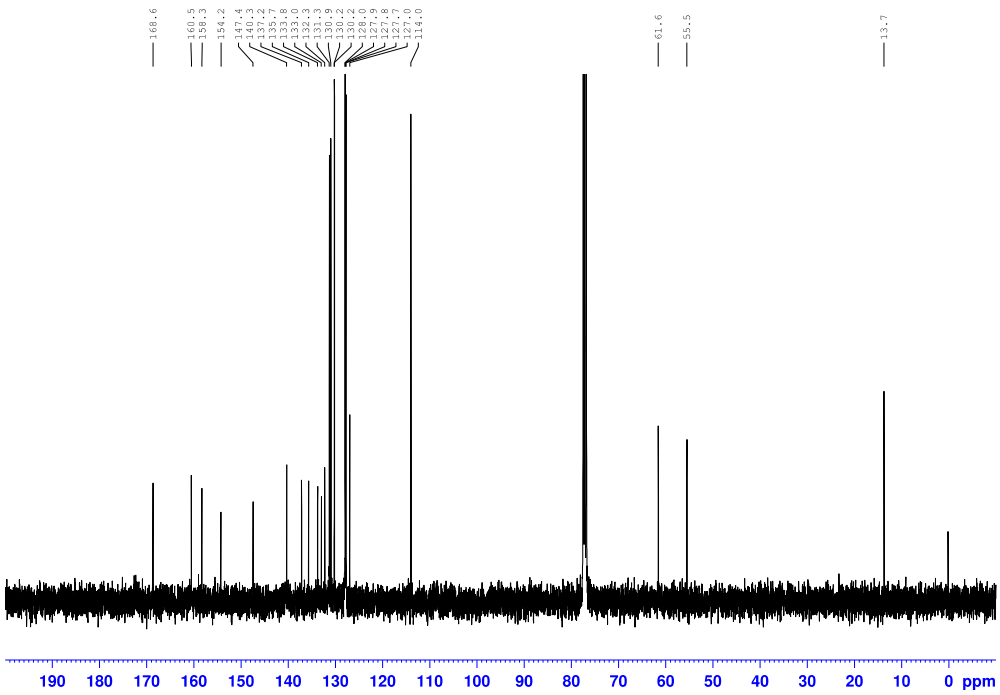
Ethyl 4-(4-fluorophenyl)-2-(4-methoxyphenyl)-6-(4-methylphenyl)pyridine-3-carboxylate (3et)



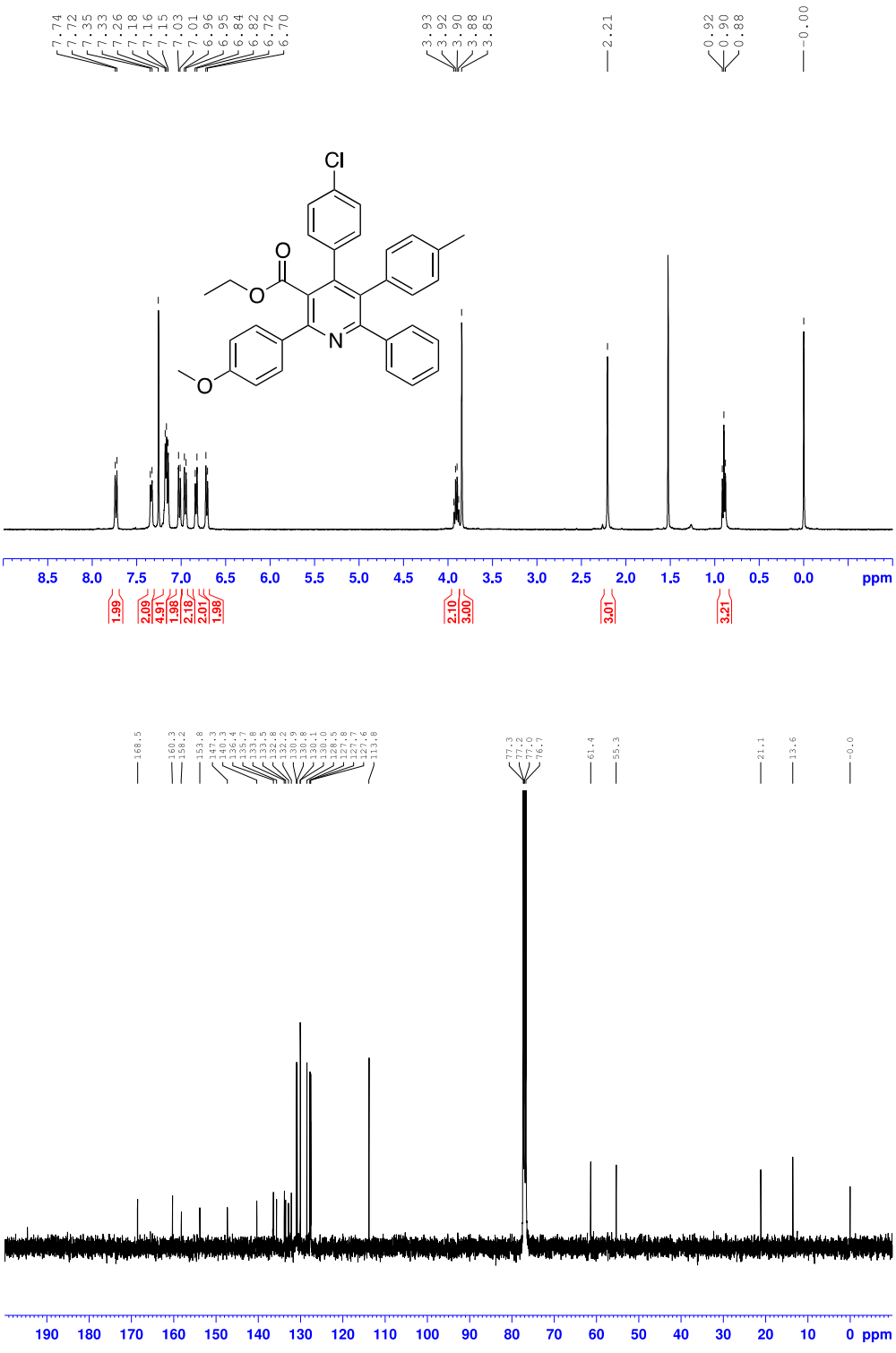


Ethyl 4-(4-chlorophenyl)-2-(4-methoxyphenyl)-5,6-diphenylpyridine-3-carboxylate (3es)

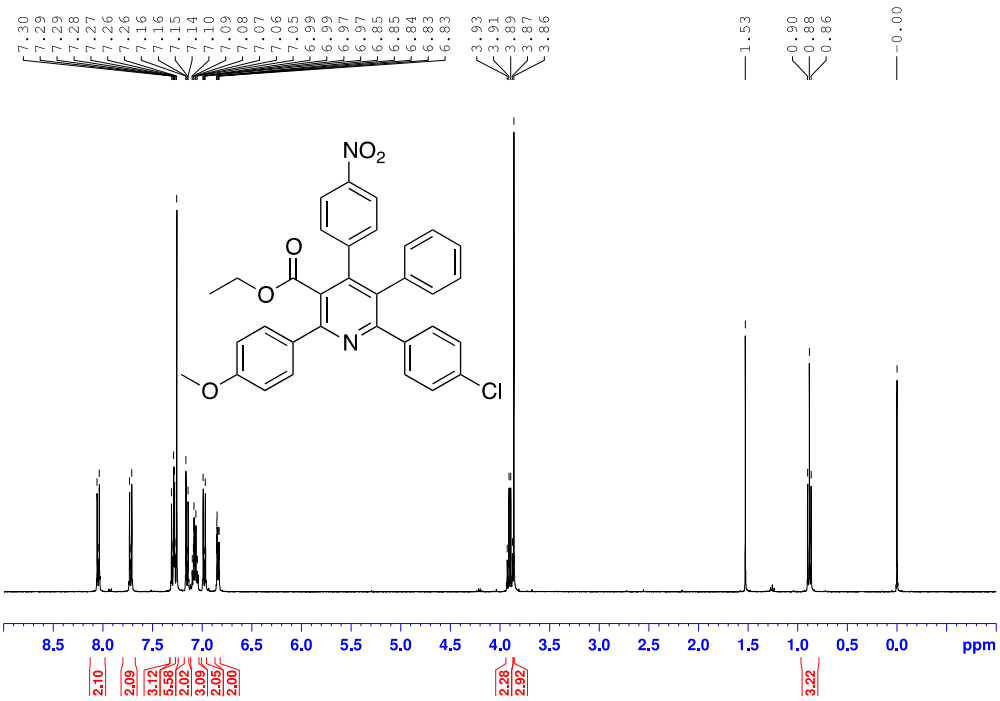


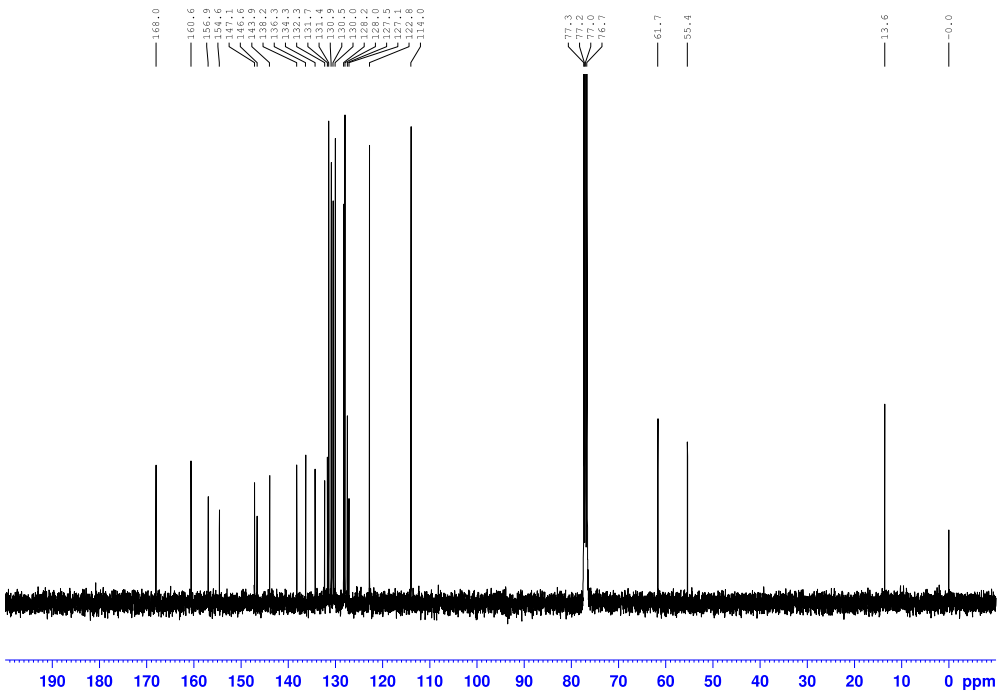


Ethyl 4-(4-chlorophenyl)-2-(4-methoxyphenyl)-5-(4-methylphenyl)-6-phenylpyridine-3-carboxylate (3eu)



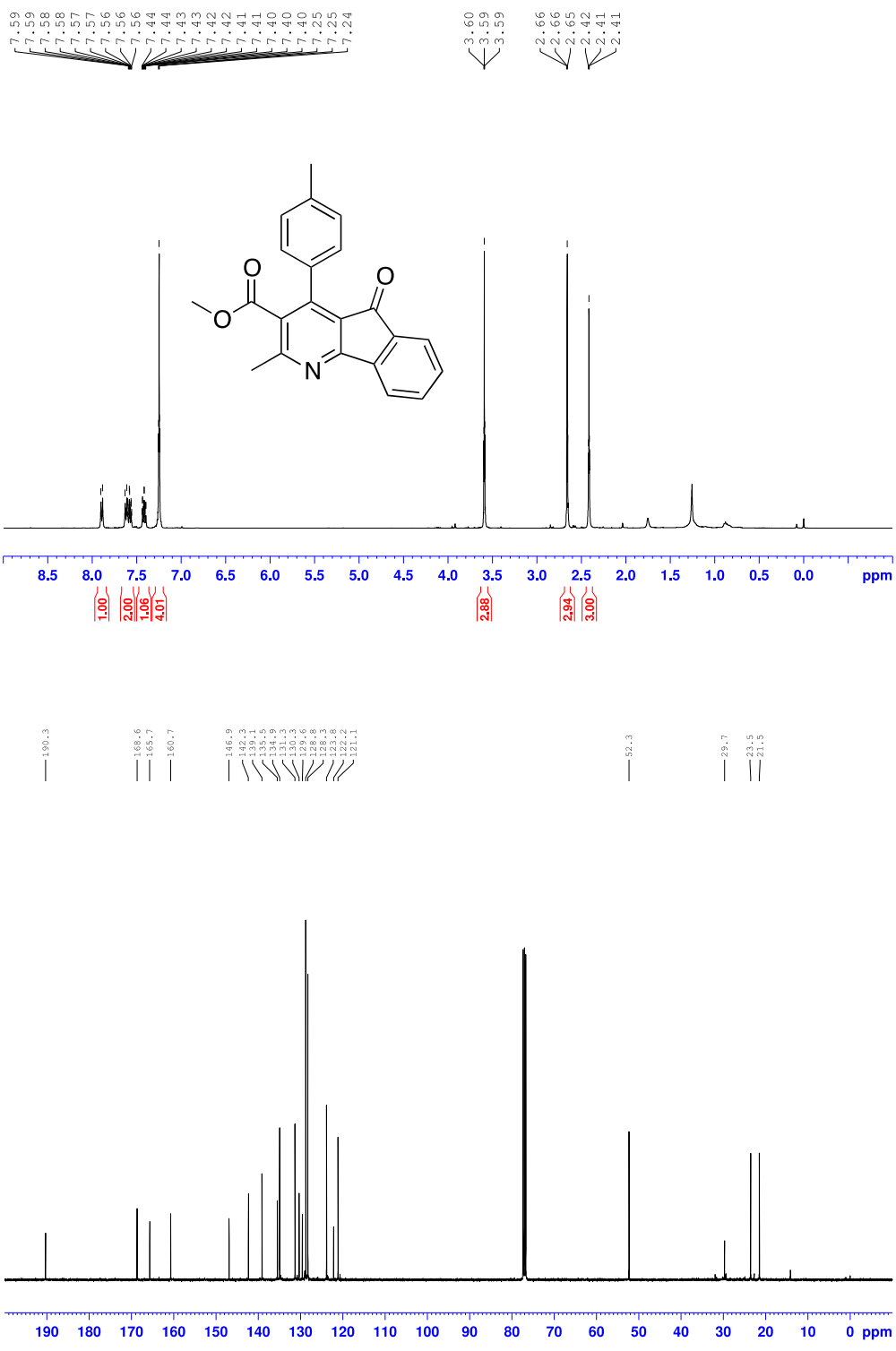
Ethyl 6-(4-chlorophenyl)-2-(4- methoxyphenyl)-4-(4-nitrophenyl)-5-phenyl-3-carboxylate (3ev)



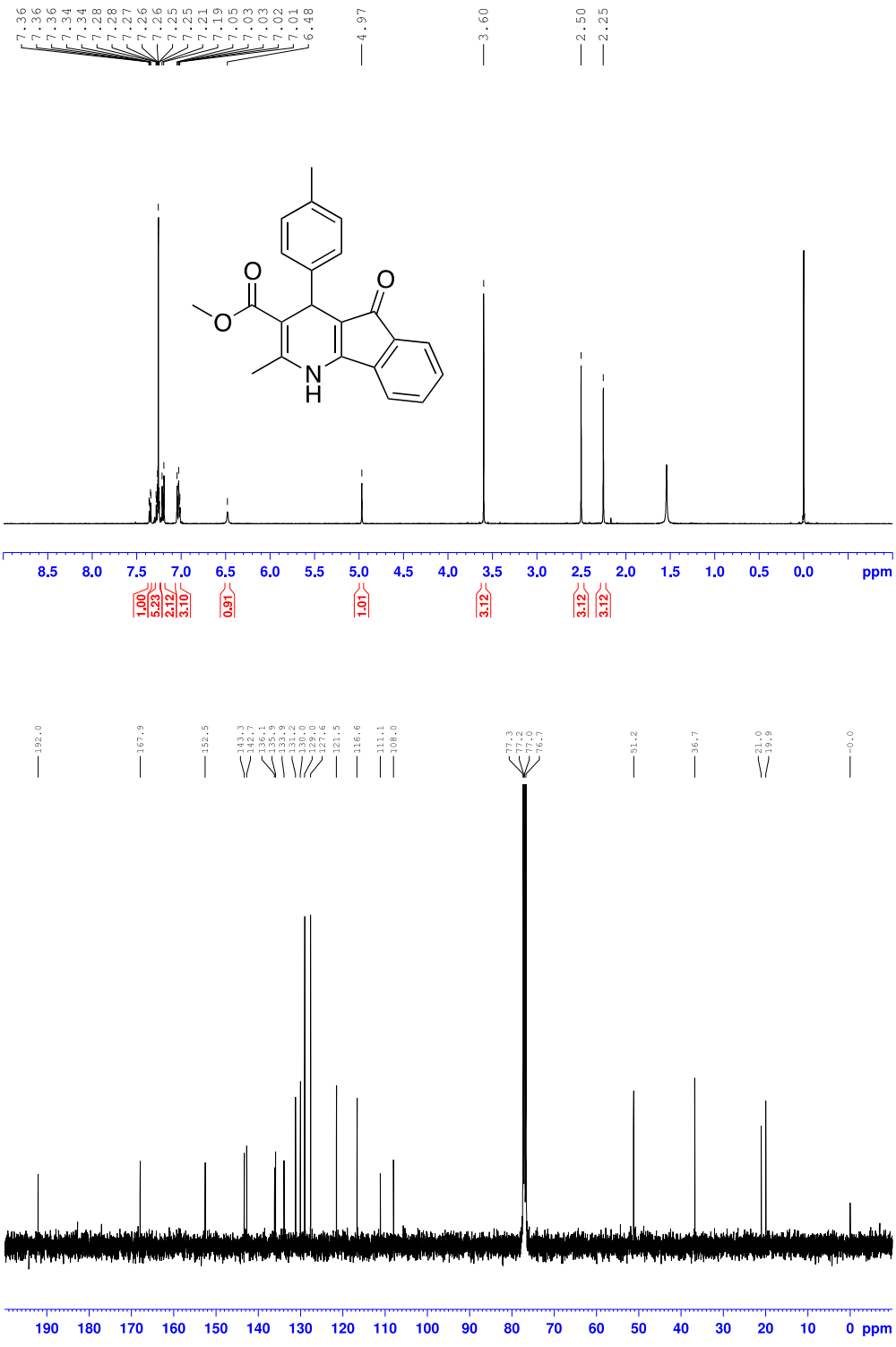


9. Copies of ^{1}H NMR and ^{13}C NMR spectra of azafluorenones

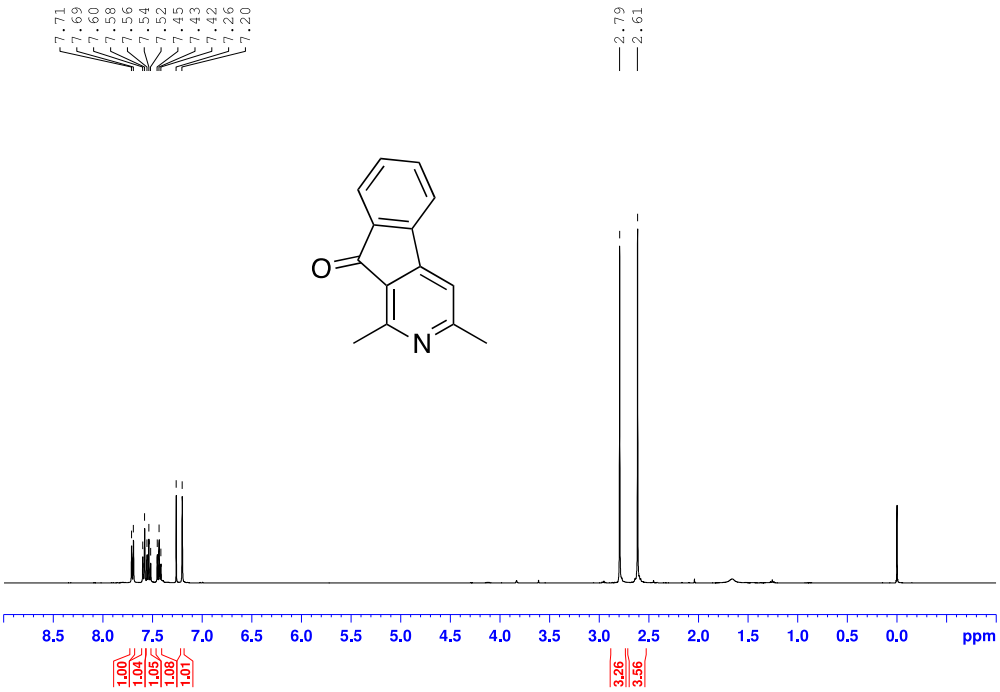
Methyl 2-methyl-4-(4-methylphenyl)-5-oxo-indeno[1,2-*b*]pyridine-3-carboxylate (14)

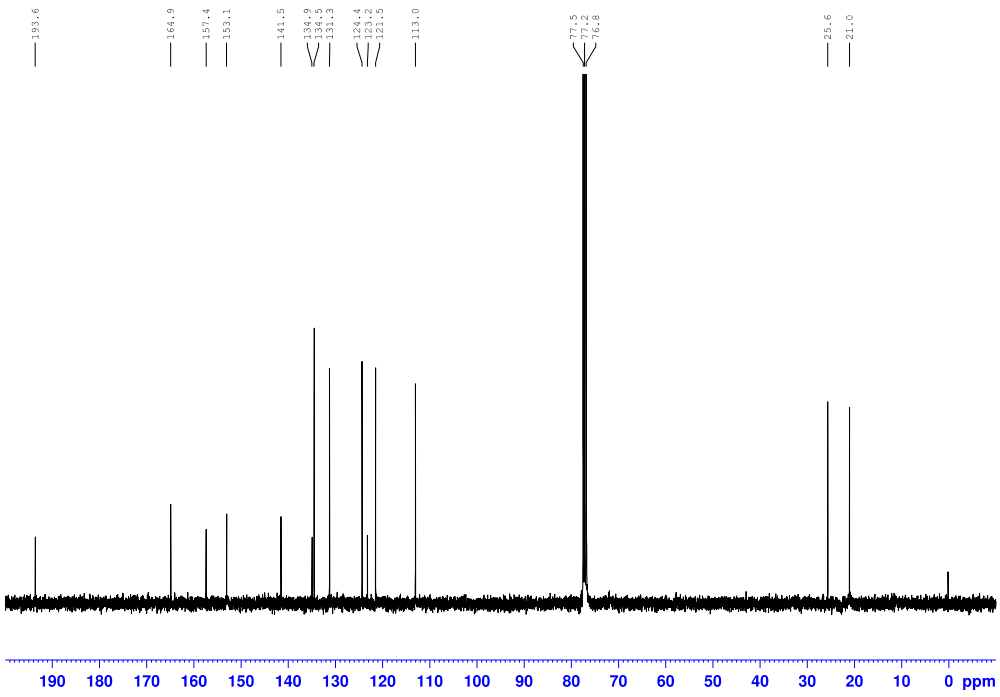


Methyl 4,5-dihydro-2-methyl-4-(4-methylphenyl)-5-oxo-*1H*-indeno[1,2-*b*]pyridine-3-carboxylate (15)



1,3-Dimethyl-3-azafluorenone 12


7.71
7.69
7.60
7.58
7.56
7.54
7.52
7.45
7.43
7.42
7.26
7.20
2.79
2.61
O
N
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.04
1.05
1.08
1.01
3.26
3.56


193.6
164.9
157.4
153.1
141.5
136.9
134.5
131.3
124.4
123.2
121.5
113.0
77.5
77.2
76.8
25.6
21.0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm