Supporting Information

Experimental section

General. Anhydrous solvents were transferred by an oven dried syringe. Dichloromethane was distilled from calcium hydride. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Mercury plus (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spetra were recorded with a Varian Mercury plus (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform.

Representative procedure for the reaction: TEMPO (156.3 mg, 1.0 mmol) and 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (19.4 mg, 0.05 mmol) was added to a solution of cinnamaldehyde (66.1 mg, 0.5 mmol) and phenol (47.1 mg, 0.5 mmol) in toluene (0.5 M, 1 ml) under nitrogen atmosphere. The reaction mixture was stirred at 100^{o}C for 4h until consumption of starting aldehyde. Then, benzylamine (109.2 mg, 1.0 mmol) was added to the reaction vessel and the reaction mixture was stirred at 40^{o}C for 18h. The solvent was removed under vacuum, the residue was purifiedby flash silica gel column chromatography by using 20% ethyl acetate/hexane as an eluent to obtain *N*-benzylcinnamamide **1c** (71.1 mg, 60 %).

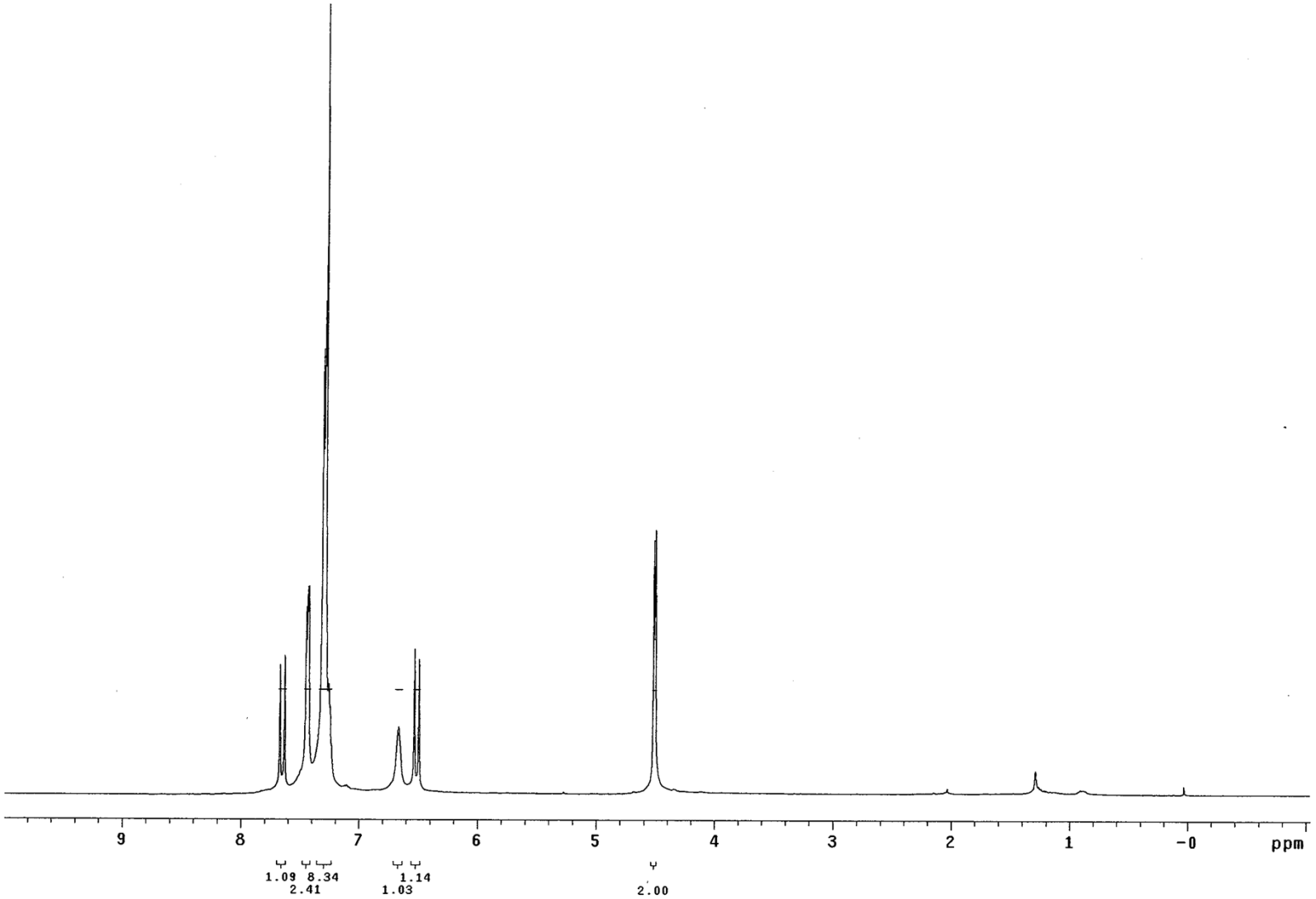
***N*-benzylcinnamamide (1b):** The representative experimental procedure was applied to cinnamaldehyde **1a** (66.1 mg, 0.5 mmol) and benzylamine (107.2 mg, 1.0 mmol) to yield **1b** (71.1 mg, 60 %).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.65 (d, 1H, J = 15.2Hz), 7.44 (m, 2H), 7.28 (m, 8H), 6.67 (s, 1H), 6.52 (d, 1H, J = 15.6 Hz), 4.52 (d, 2H, J = 5.2 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 165.9, 140.9, 138.2, 134.7, 129.5, 128.7, 128.5, 127.7(2C), 127.3, 120.7, 43.8 ppm

IR (neat, cm^{-1}): 3054, 2987, 1670, 1628, 1514, 1265

HRMS: $C_{16}H_{15}NO$ Cacld : 237.1154, $[M]^+$ Found : 237.1154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2.41
1.14
1.03
2.00

ppm
200
180
160
140
120
100
80
60
40
20

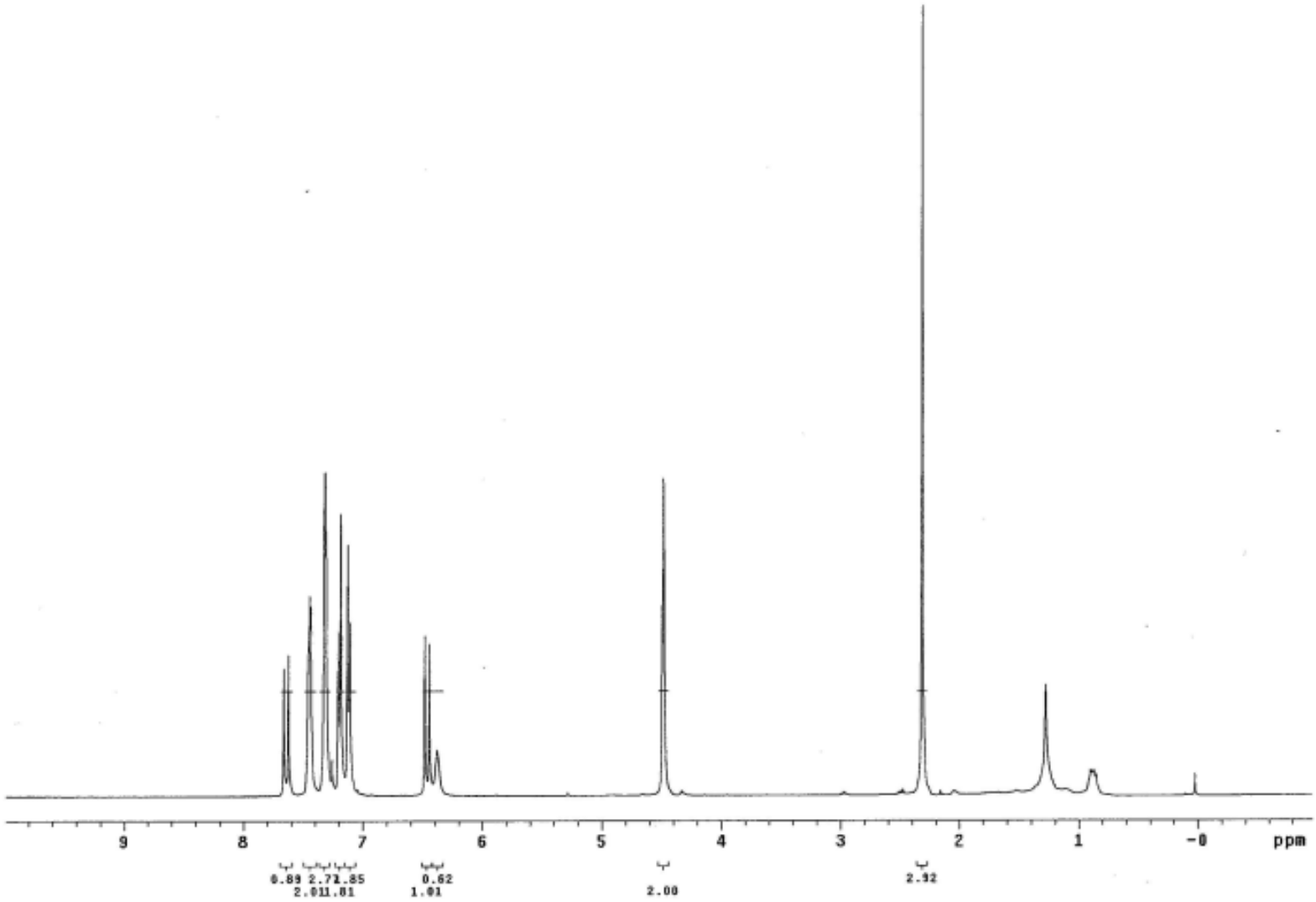
***N*-(4-methylbenzyl)cinnamamide (2b):** The representative experimental procedure was applied to cinnamaldehyde **1a** (66.1 mg, 0.5 mmol) and 4-Methylbenzylamine (121.2 mg, 1.0 mmol) to yield **2b** (68.8 mg, 55 %).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.65 (d, 1H, J = 15.6 Hz), 7.45 (dd, 2H, J =4.0, 2.4 Hz), 7.32 (m, 3H), 7.20 (d, 2H, J = 7.6 Hz), 7.12 (d, 2H, J =8.0 Hz), 6.47 (d, 1H, J = 15.6 Hz), 6.38 (s, 1H), 4.49 (d, 2H, J = 4.4 Hz), 2.32 (s, 3H) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 165.7, 141.0, 137.1, 135.2, 134.8, 129.6, 129.3, 128.7, 127.8(2C), 120.7, 43.7, 43.6, 21.3 ppm

IR (neat, cm^{-1}): 3259, 3060, 2924, 1617, 1515

HRMS: $C_{17}H_{17}NO$ Cacld : 251.1310, $[M]^+$ Found : 251.1312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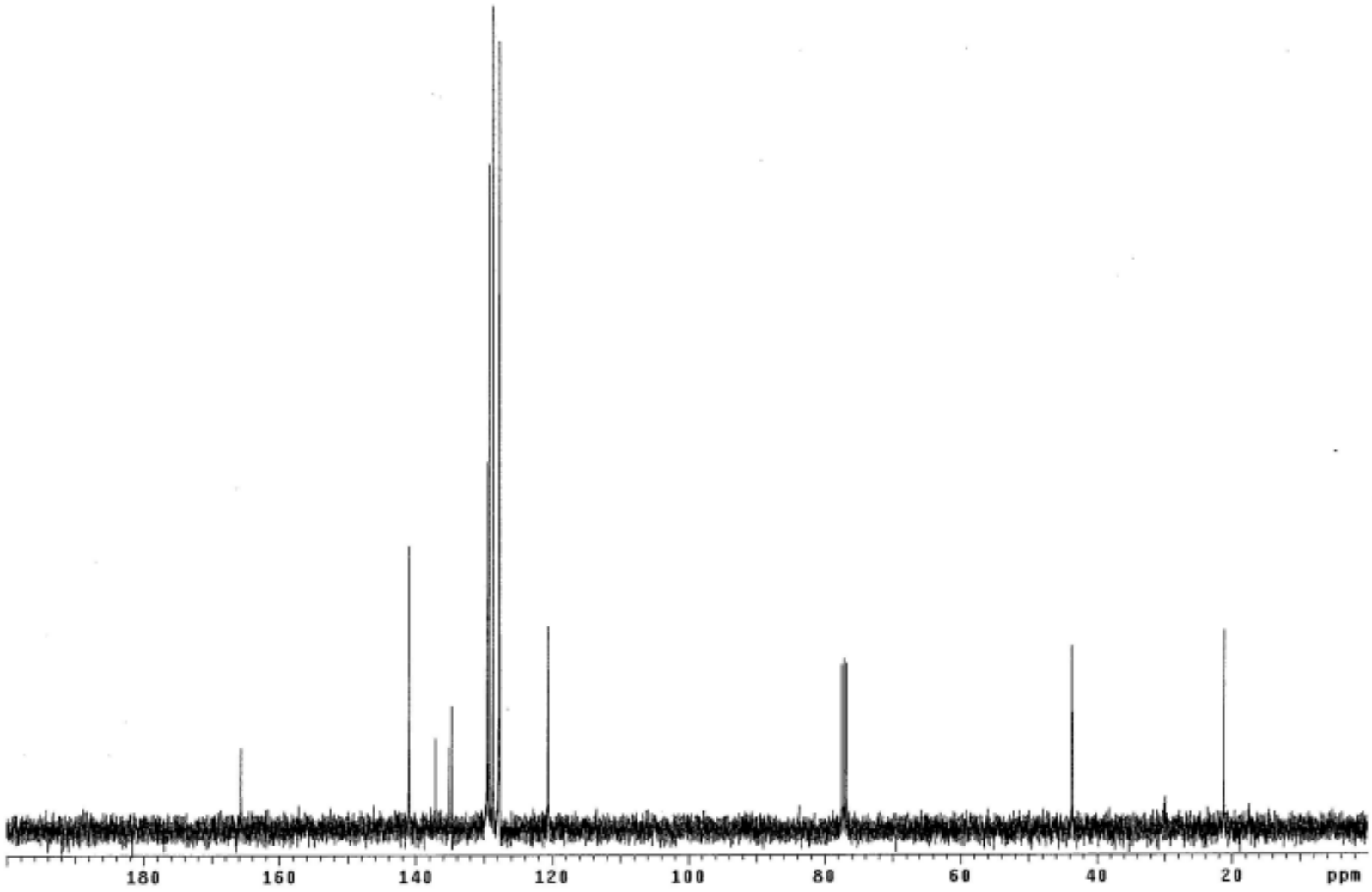
2.00
2.92


180
160
140
120
100
80
60
40
20
ppm

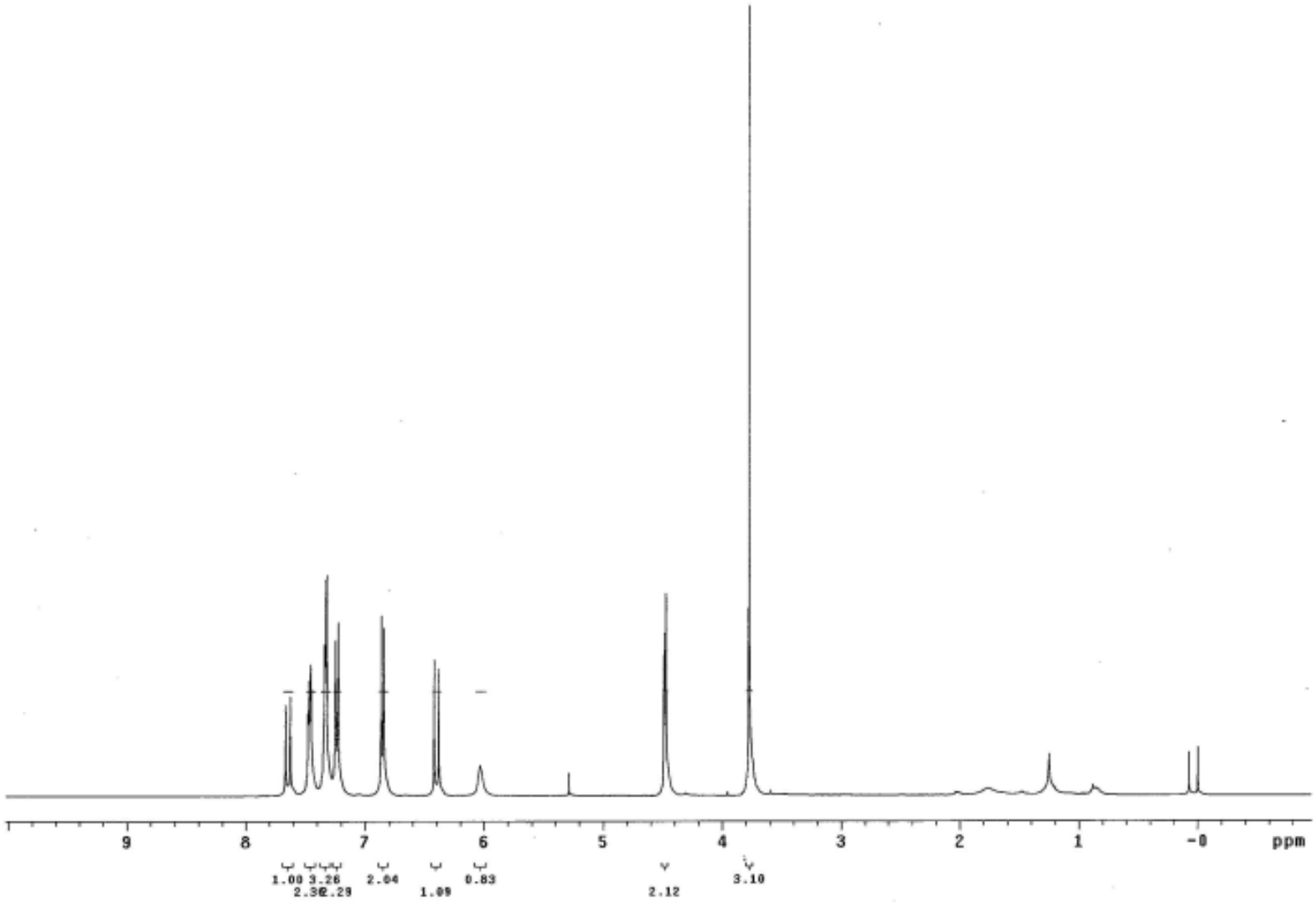
***N*-(4-methoxybenzyl)cinnamamide (3b):** The representative experimental procedure was applied to cinnamaldehyde **1a** (66.1 mg, 0.5 mmol) and 4-methoxylbenzylamine (137.2 mg, 1.0 mmol) to yield **3b** (79.3 mg, 59 %).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.65 (d, 1H, J = 16.0 Hz), 7.47 (dd, 2H, J = 8.0, 4.4Hz), 7.33 (m, 3H), 7.24 (d, 2H, J = 8.4 Hz), 6.86 (d, 2H, J = 8.8 Hz), 6.41 (d, 1H, J = 15.6 Hz), 6.04 (s, 1H), 4.49 (d, 2H, J = 5.6 Hz), 3.78 (s, 3H) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 165.6, 158.9, 141.0, 134.8, 130.3, 129.6, 129.2, 128.7, 127.7, 120.6, 114.1, 55.4, 43.4, 43.3 ppm

IR (neat, cm^{-1}): 3298, 2927, 1653, 1614, 1512, 1248

HRMS: $C_{17}H_{17}NO_2$ Cacld : 267.1259, $[M]^+$ Found : 267.1259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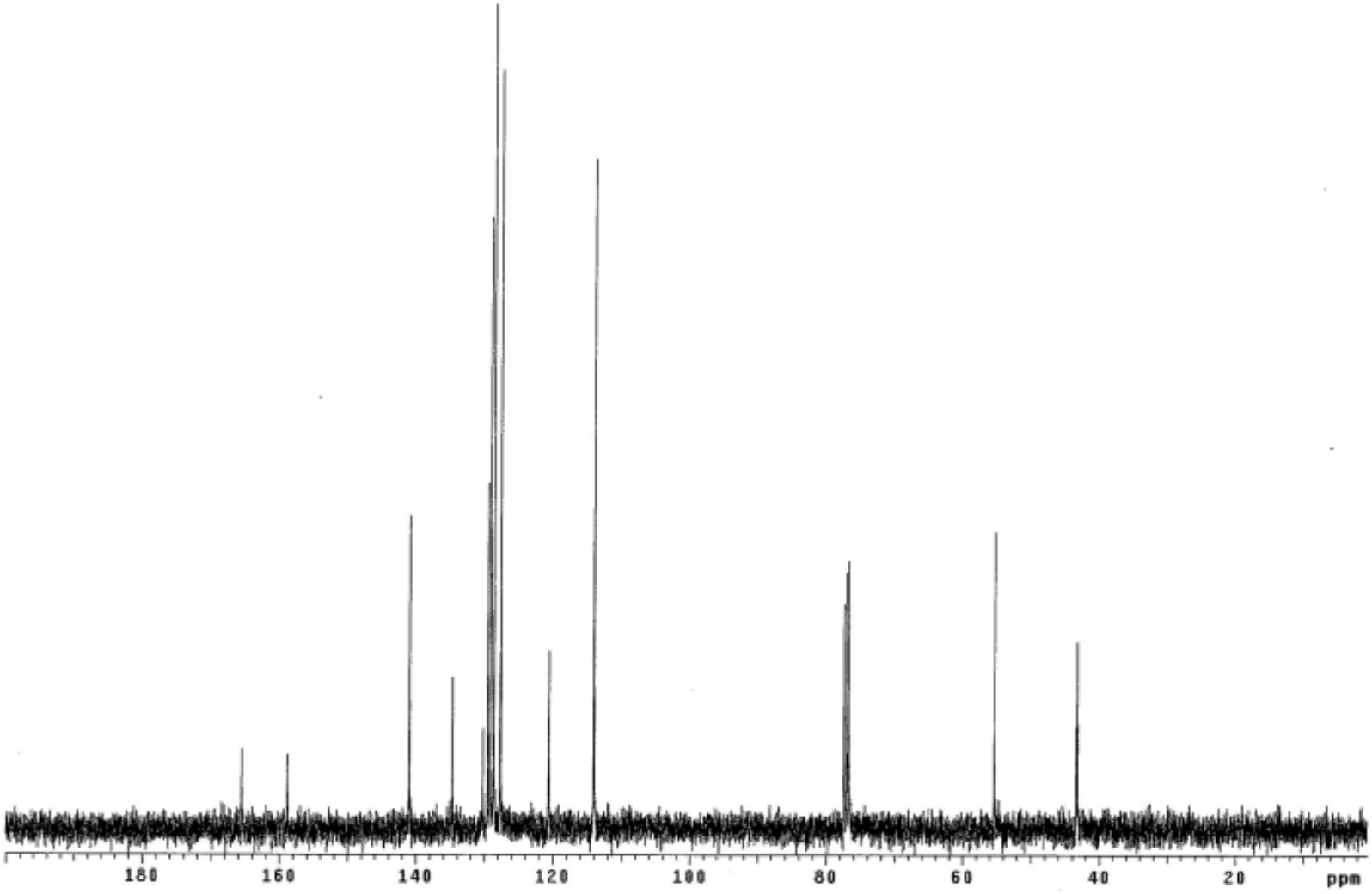
3.10


180
160
140
120
100
80
60
40
20
ppm

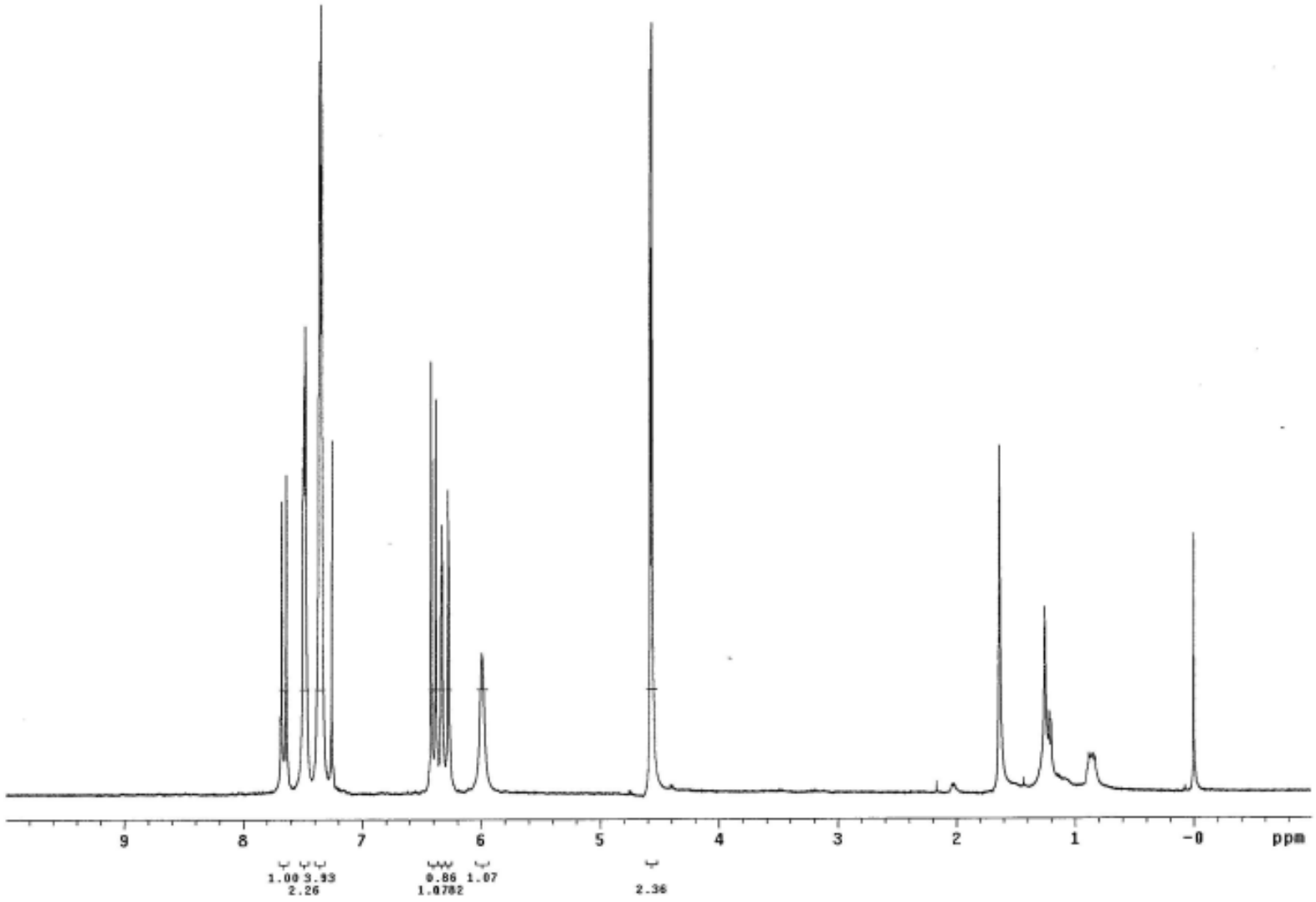
***N*-(furan-2-ylmethyl)cinnamamide (4b):** The representative experimental procedure was applied to cinnamaldehyde **1a** (66.1 mg, 0.5 mmol) and furfurylamine (97.1 mg, 1.0 mmol) to yield **4b** (46.6 mg, 41 %).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.66 (d, 1H, J = 16.0 Hz), 7.49 (m, 2H), 7.36 (m, 4H), 6.40 (d, 1H, J = 16.0 Hz), 6.33 (m, 1H), 6.28 (m, 1H), 6.00 (s, 1H), 4.58 (d, 2H, J = 5.6 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 165.6, 151.2, 142.2, 141.5, 134.7, 129.8, 128.8, 127.8, 120.3, 110.6, 107.7, 36.9 ppm

IR (neat, cm^{-1}): 3271, 3063, 1657, 1620, 1449

HRMS: $C_{14}H_{13}NO_2$ Cacld : 227.0946, $[M]^+$ Found : 227.0944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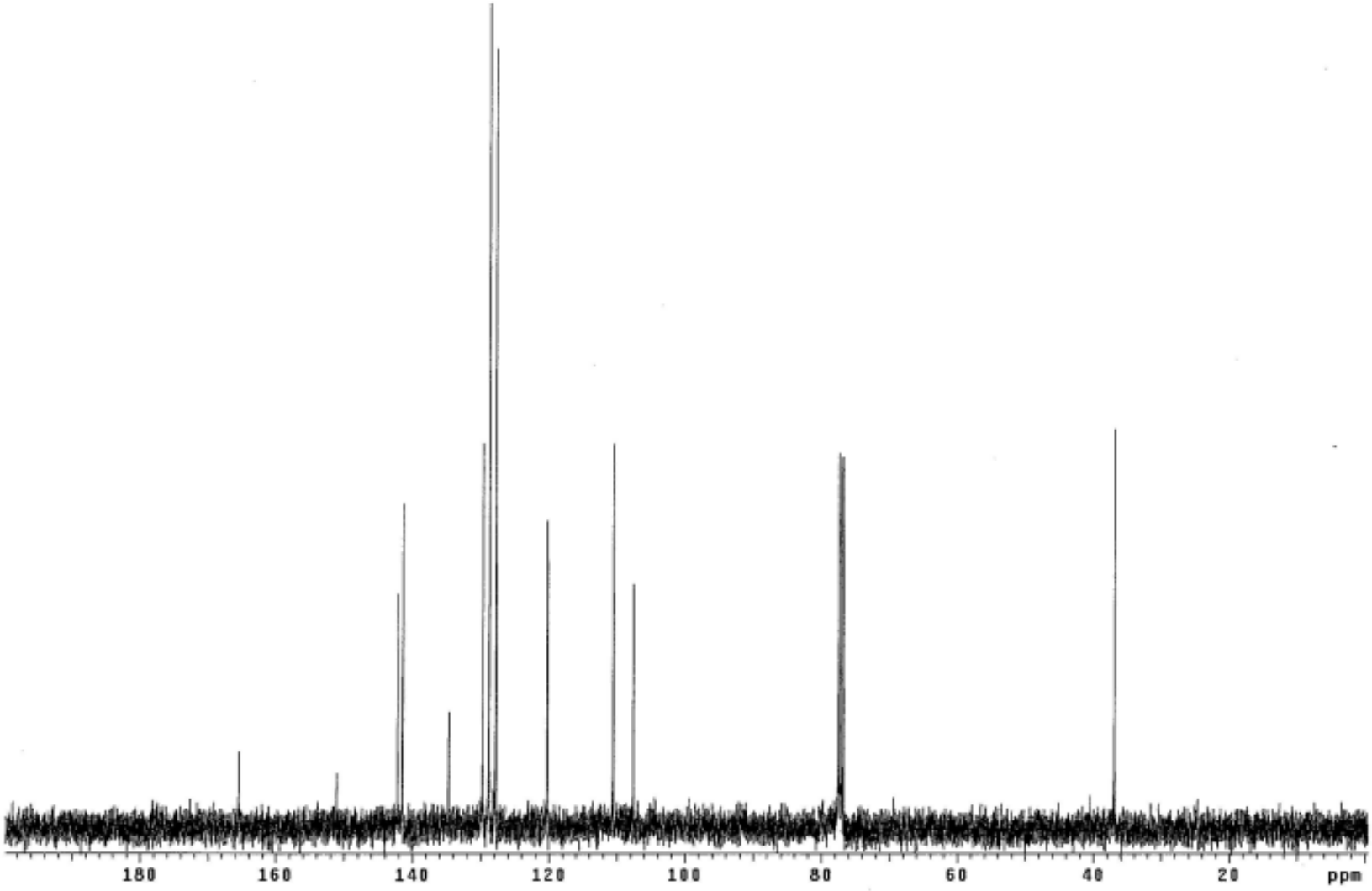
2.36


180
160
140
120
100
80
60
40
20
ppm

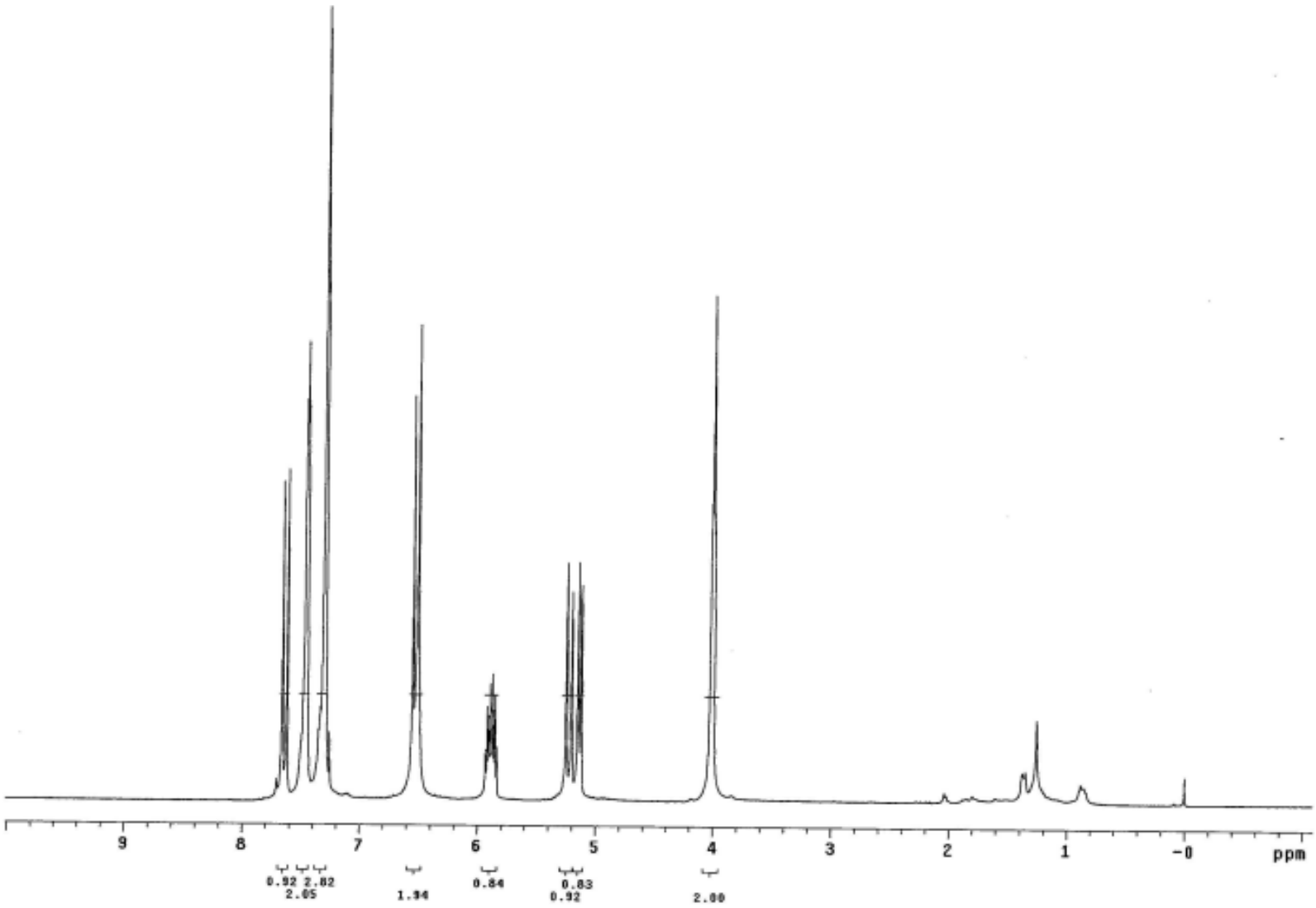
***N*-allylcinnamamide (5b):** The representative experimental procedure was applied to cinnamaldehyde **1a** (66.1 mg, 0.5 mmol) and allylamine (57.1 mg, 1.0 mmol) to yield **5b** (46.9 mg, 50 %).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.64 (d, 1H, J =15.6 Hz), 7.47 (m, 2H), 7.33 (m, 3H), 6.53 (d, 2H, J =15.6 Hz), 5.89 (m, 1H), 5.23 (dd, 1H, J = 16.0, 1.6 Hz), 5.14 (dd, 1H, J = 8.0, 1.6 Hz), 4.01 (t, 2H, J = 5.2 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 165.9, 140.9, 134.7, 134.0, 129.5, 128.7, 127.7, 120.7, 116.4, 42.3 ppm

IR (neat, cm^{-1}): 3285, 3084, 1658, 1618, 1450, 1223

HRMS: $C_{12}H_{13}NO$ Cacld : 187.0997, $[M]^+$ Found : 187.0995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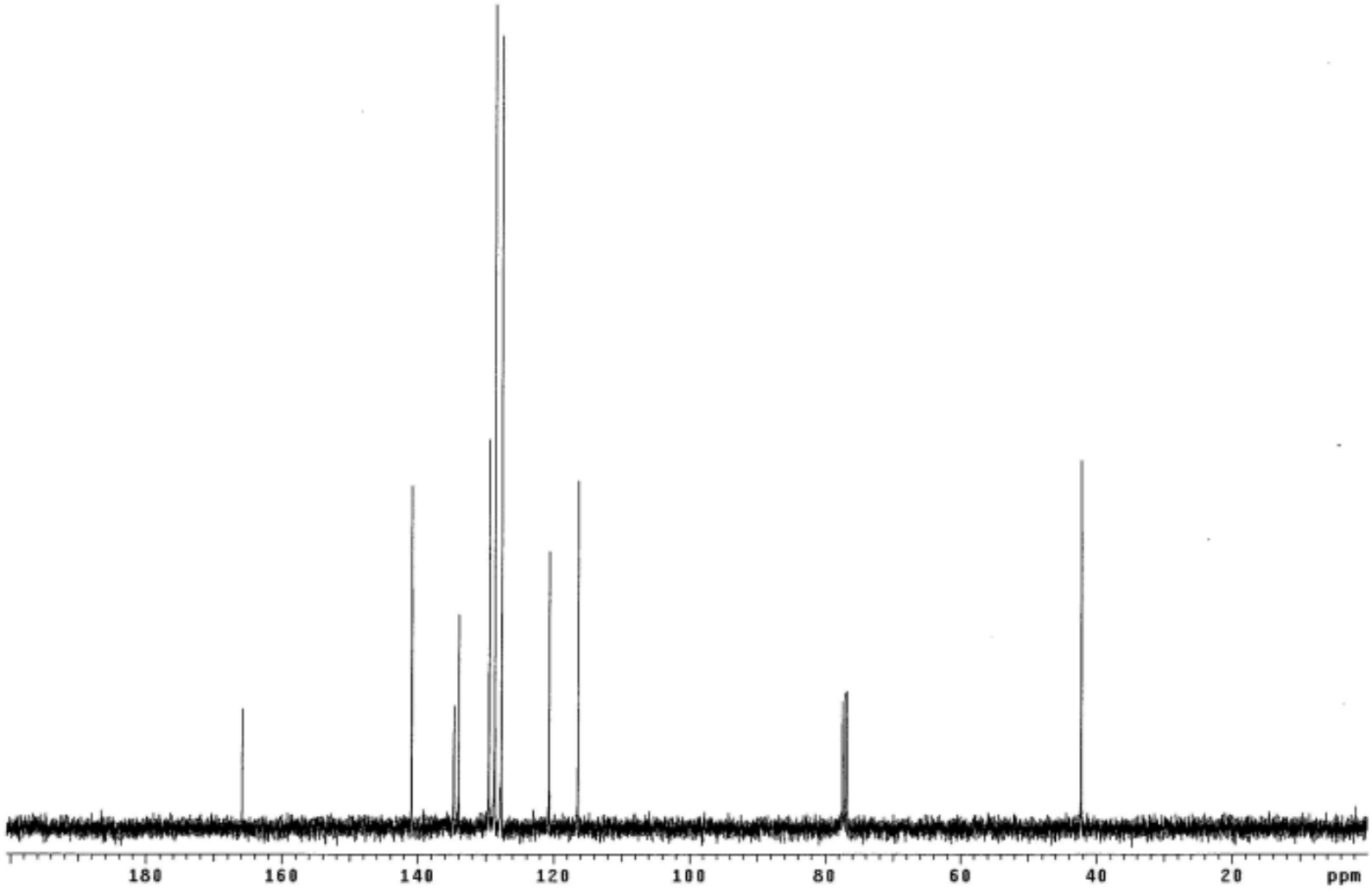
2.00


180
160
140
120
100
80
60
40
20
ppm

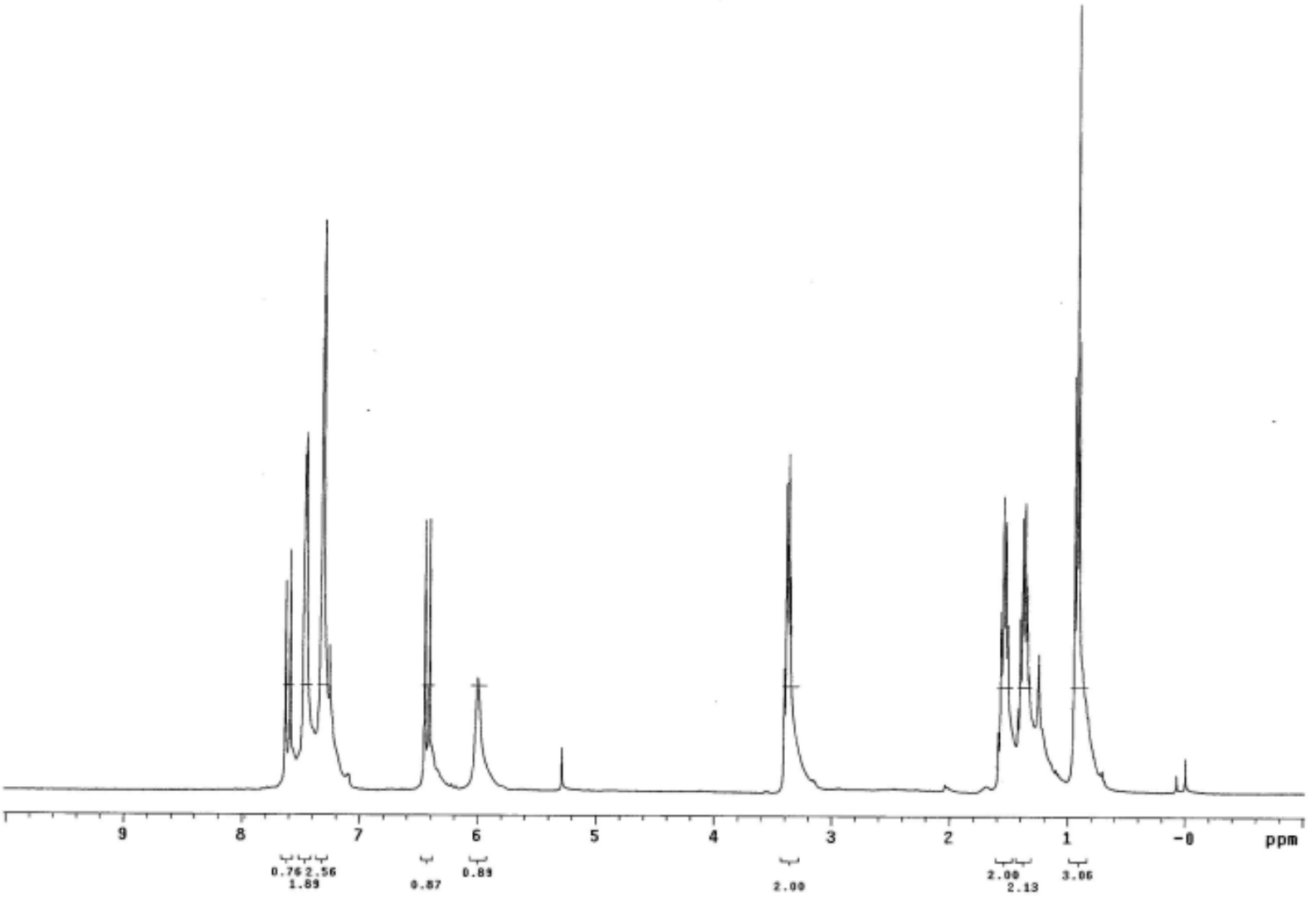
***N*-butylcinnamamide (6b):** The representative experimental procedure was applied to cinnamaldehyde **1a** (66.1 mg, 0.5 mmol) and *N*-butylamine (73.1 mg, 1.0 mmol) to yield **6b** (48.8 mg, 52 %).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.61 (d, 1H, J = 15.6 Hz), 7.47 (m, 2H), 7.32 (m, 3H), 6.43 (d, 1H, J = 16.0 Hz), 6.00 (s, 1H), 3.38 (m, 2H), 1.55 (m, 2H), 1.38 (m, 2H), 0.93 (t, 3H, J = 7.6 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 166.0, 140.5, 134.8, 129.4, 128.6, 127.6, 121.0, 39.7, 31.8, 20.3, 13.9 ppm

IR (neat, cm^{-1}): 3290, 2961, 1659, 1621, 1450, 1265

HRMS: $C_{13}H_{17}NO$ Cacld : 203.1310, $[M]^+$ Found : 203.1308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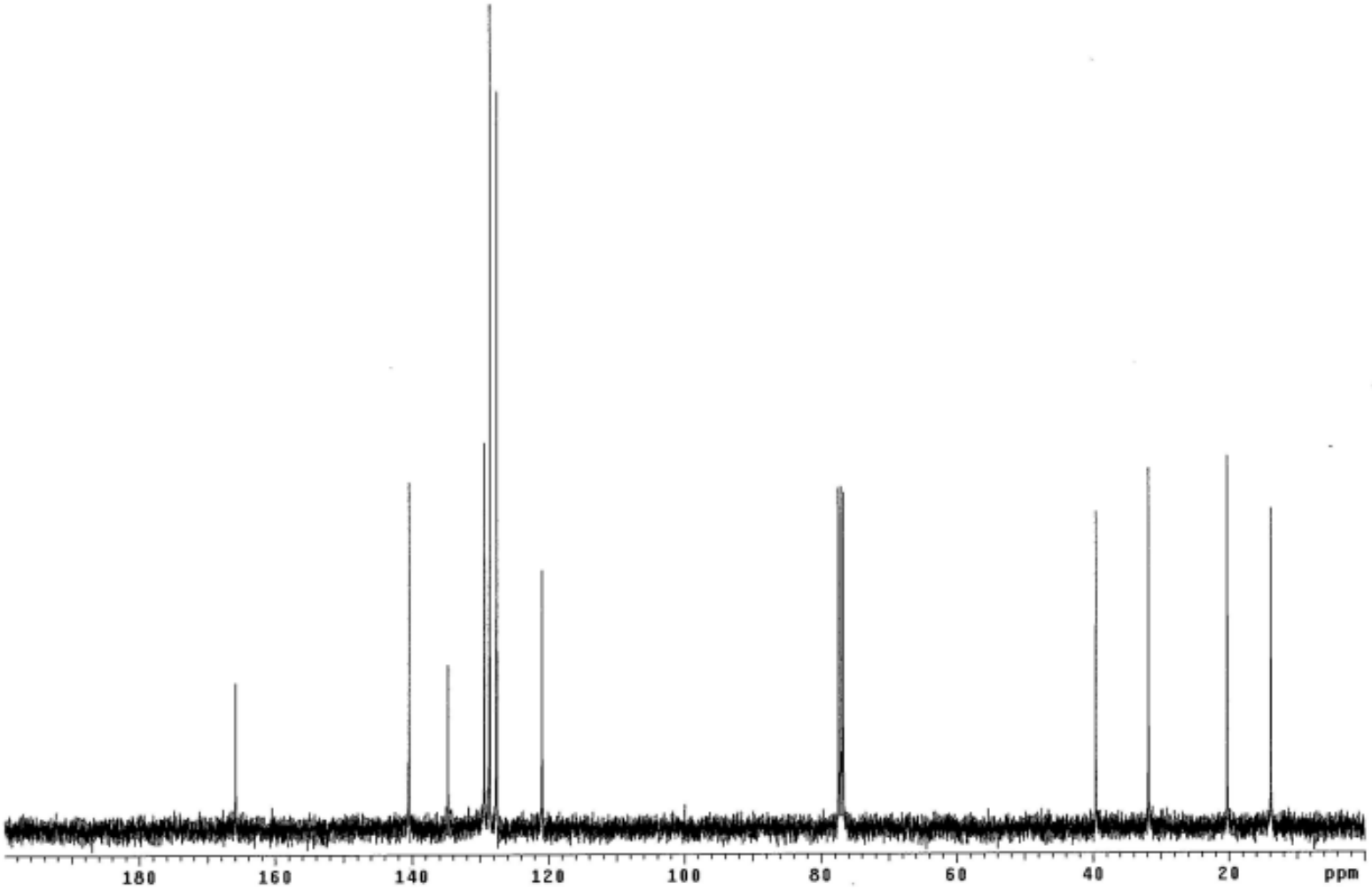

180
160
140
120
100
80
60
40
20
ppm

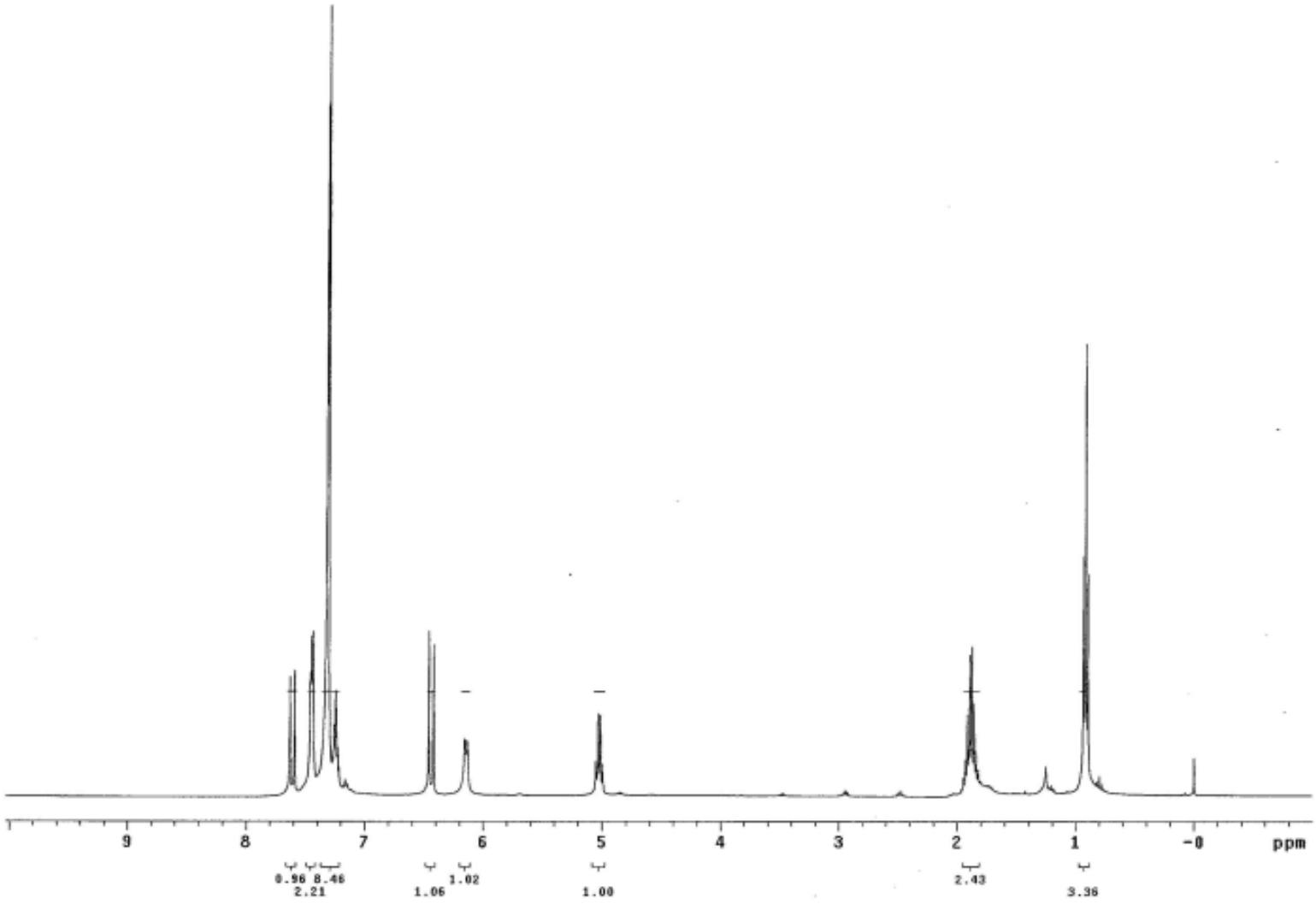
***N*-(1-phenylpropyl)cinnamamide (7b):** The representative experimental procedure was applied to cinnamaldehyde **1a** (66.1 mg, 0.5 mmol) and (*S*)-(−)-α-ethylbenzylamine (135.2 mg, 1.0 mmol) to yield **7b** (80.0 mg, 60 %).

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.61 (d, 1H, J = 16.0 Hz), 7.45 (dd, 2H, J = 8.0, 3.6 Hz), 7.27 (m, 8H), 6.44 (d, 1H, J = 16.0 Hz), 6.15 (d, 1H, J = 8.0 Hz), 5.03 (m, 1H), 1.89 (m, 2H), 0.92 (t, 3H, J = 7.2 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 165.2, 142.0, 140.9, 134.7, 129.4, 128.6, 128.4, 127.6, 127.1, 126.6, 120.9, 55.2, 29.3, 11.0 ppm

IR (neat, cm^{-1}): 3276, 3063, 2967, 1619, 1450, 1219

HRMS: $C_{18}H_{19}NO$ Cacld : 265.1467, $[M]^+$ Found : 265.1465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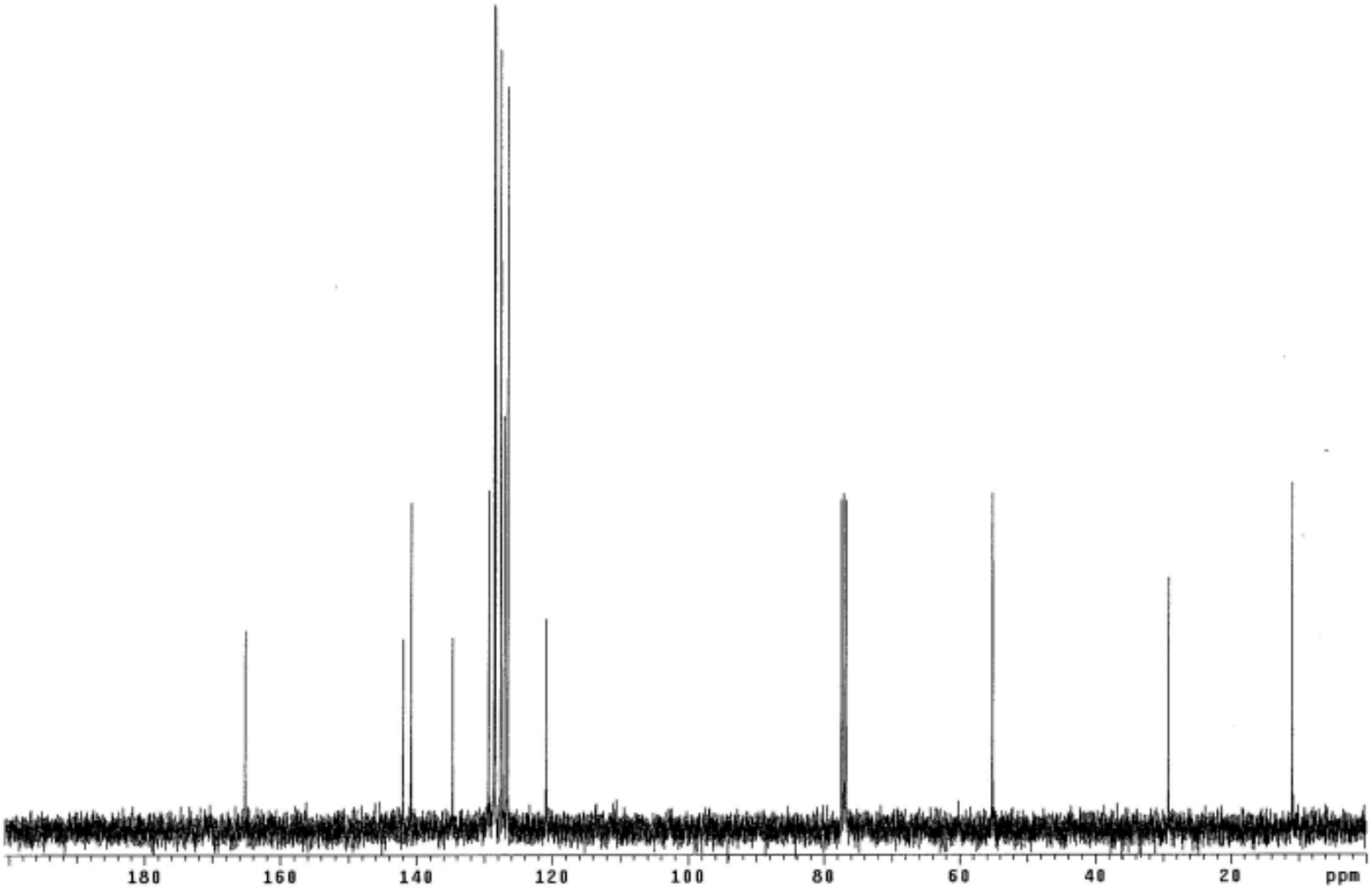
1.00
2.43
3.38


180
160
140
120
100
80
60
40
20
ppm

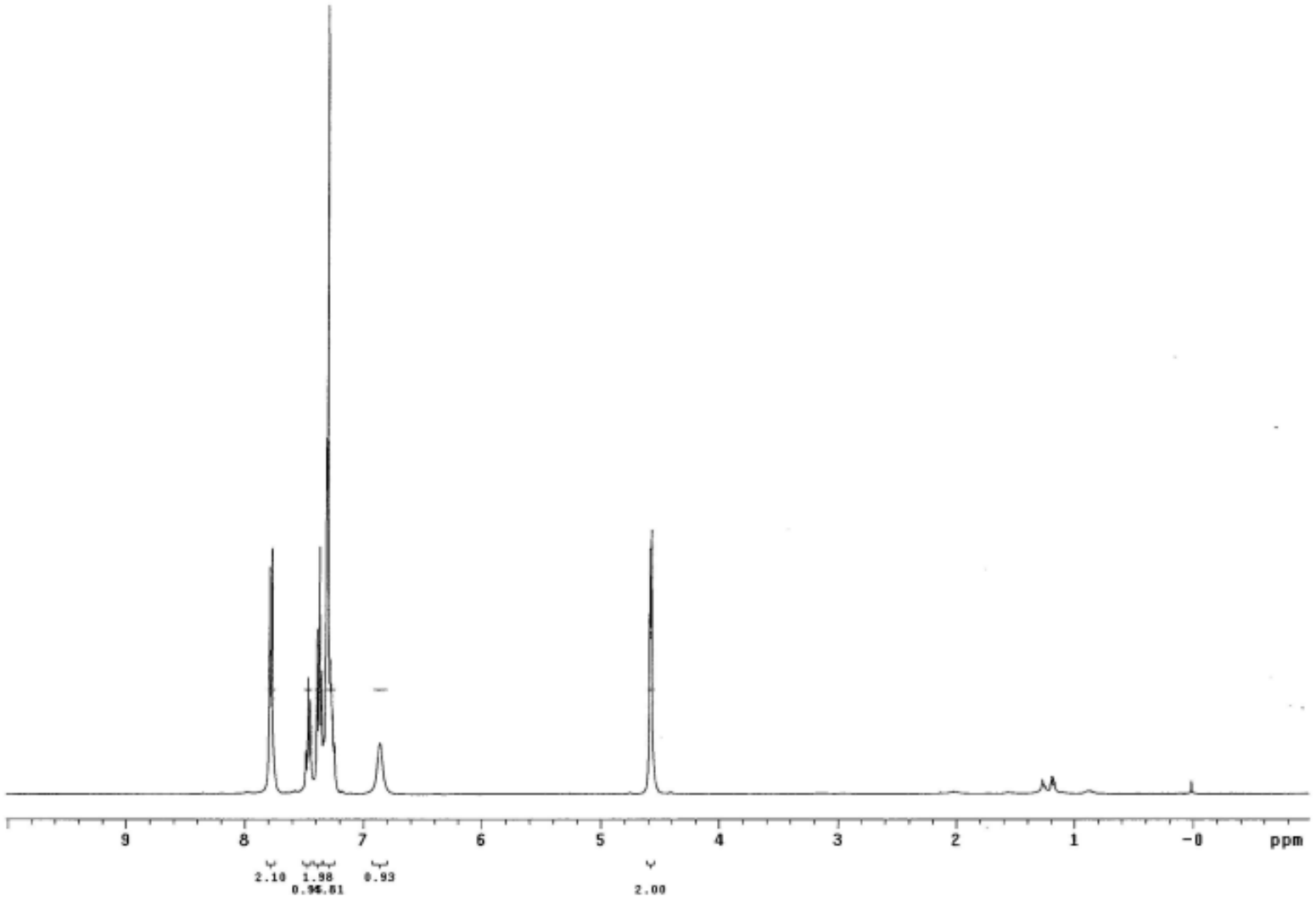
***N*-benzylbenzamide (8b):** The representative experimental procedure was applied to benzaldehyde (53.1 mg, 0.5 mmol) and benzylamine (109.2 mg, 1.0 mmol) to yield **8b** (58.4 mg, 55 %)

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.78 (d, 2H, J = 7.6 Hz), 7.47 (t, 1H, J = 6.8 Hz), 7.38 (t, 2H, J = 7.6 Hz), 7.28 (m, 5H), 6.86 (s, 1H), 4.59 (d, 2H, J = 5.2 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 167.3, 138.1, 134.2, 131.3, 128.6, 128.4, 127.7, 127.3, 126.9, 44.1 ppm

IR (neat, cm^{-1}): 3327, 3066, 1644, 1538, 1489

HRMS: $C_{14}H_{13}NO$ Cacld : 211.0997, $[M]^+$ Found : 211.0994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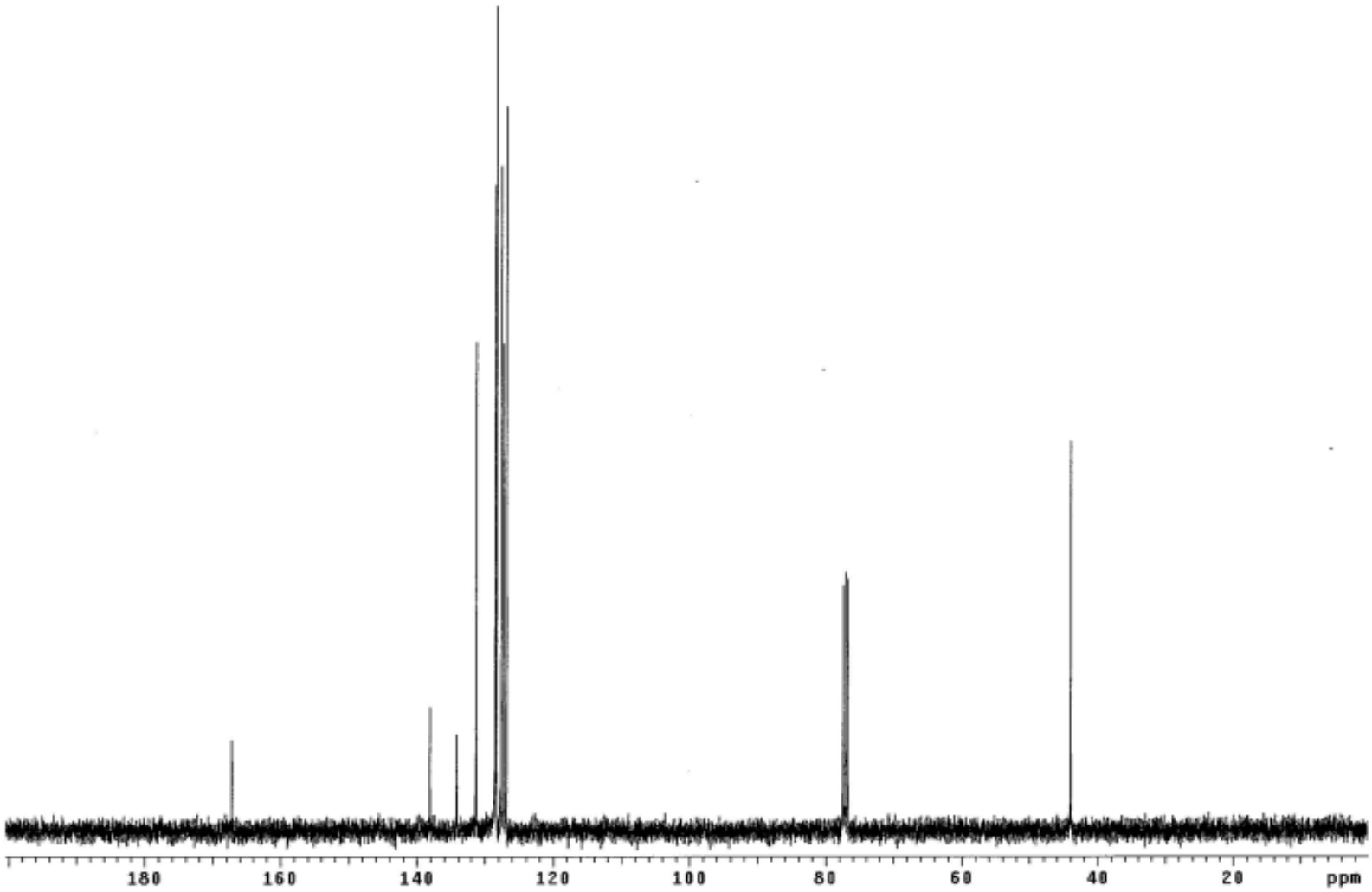
2.00


180
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140
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100
80
60
40
20
ppm

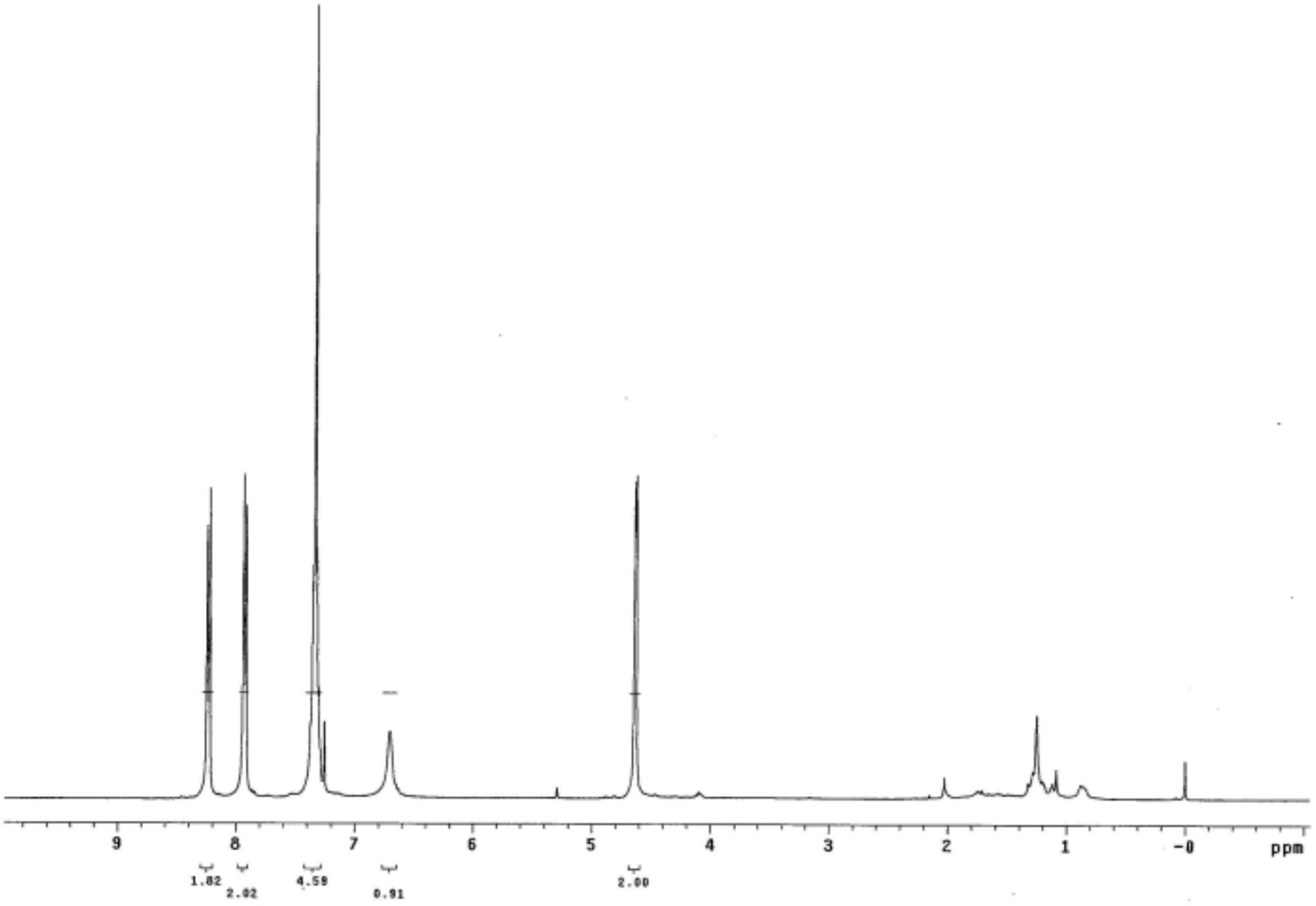
***N*-benzyl-4-nitrobenzamide (9b):** The representative experimental procedure was applied to 4-nitrobenzaldehyde (75.6 mg, 0.5 mmol) and benzylamine (109.2 mg, 1.0 mmol) to yield **9b** (71.0 mg, 55 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, 2H, J = 8.0 Hz), 7.93 (d, 2H, J = 8.4 Hz), 7.34 (m, 5H), 6.71 (s, 1H), 4.64 (d, 2H, J = 4.8 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 149.5, 139.9, 137.4, 128.9, 128.2, 127.9, 123.8, 44.6 ppm

IR (neat, cm^{-1}): 3279, 3053, 1665, 1601, 1486, 1265

HRMS: $C_{14}H_{12}N_2O_3$ Cacld : 256.0848, $[M]^+$ Found : 256.0848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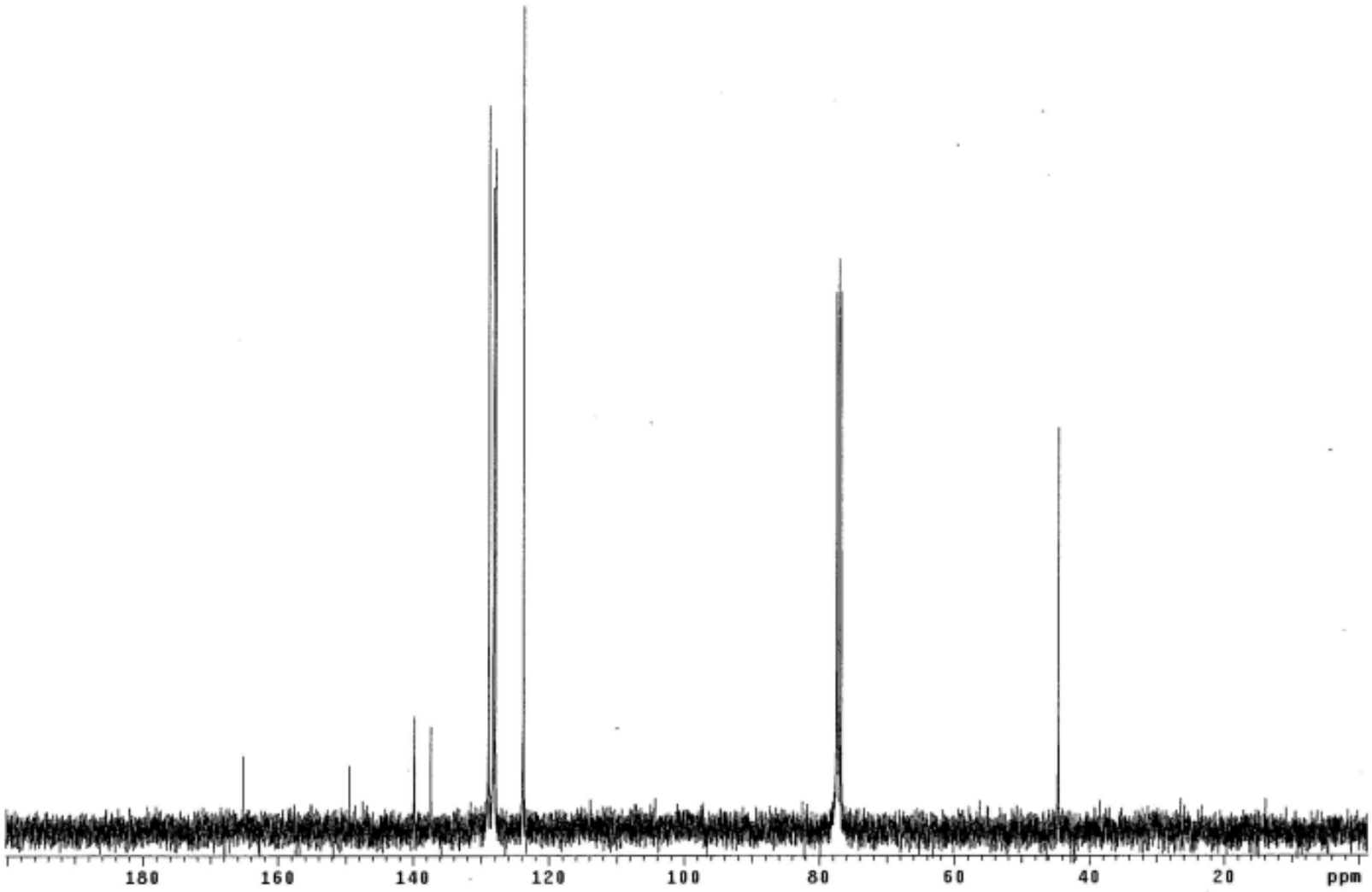

180
160
140
120
100
80
60
40
20
ppm

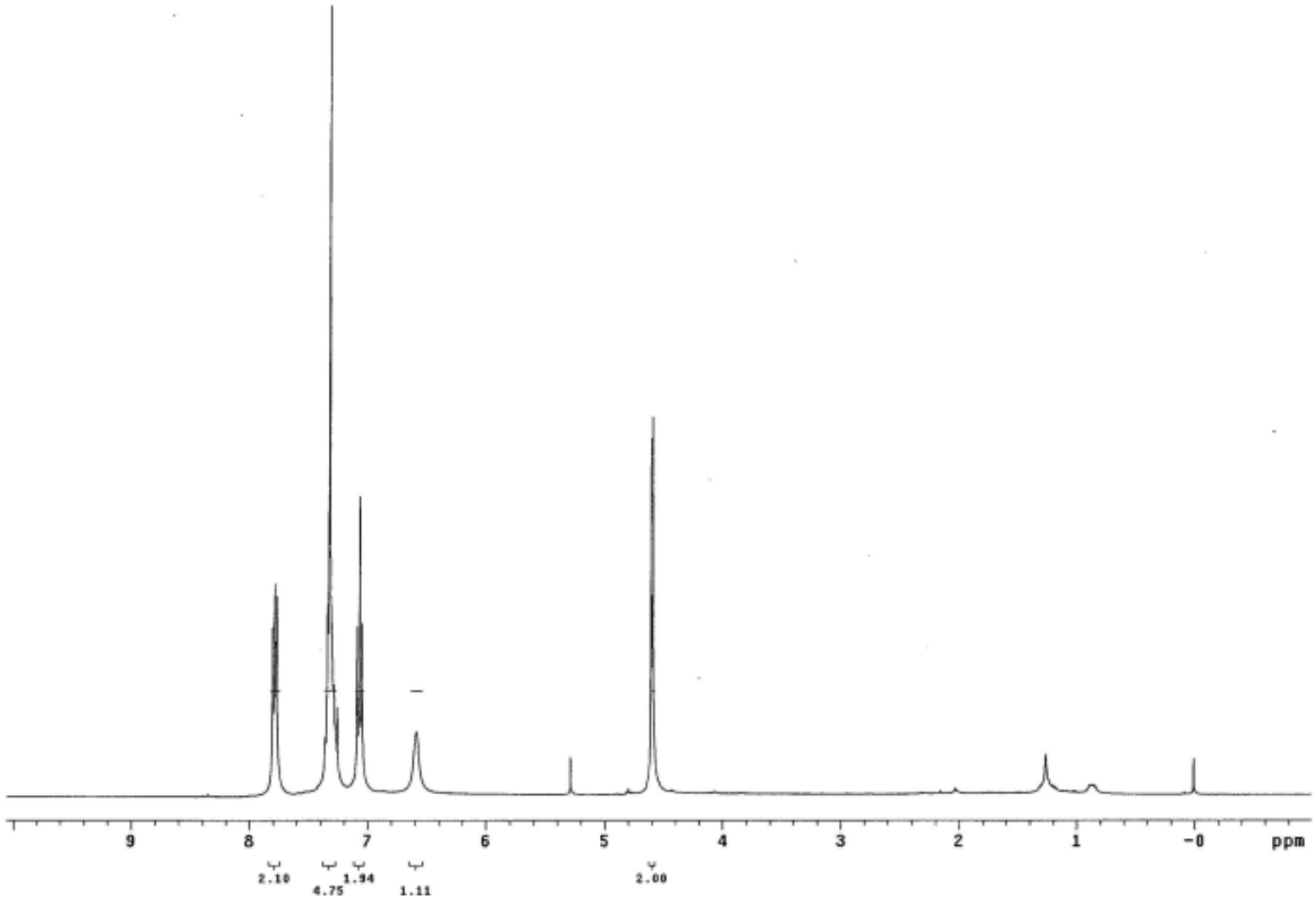
***N*-benzyl-4-fluorobenzamide (10b):** The representative experimental procedure was applied to 4-fluorobenzaldehyde (62.1 mg, 0.5 mmol) and benzylamine (109.2 mg, 1.0 mmol) to yield **10b** (64.2 mg, 56 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, 2H, J = 8.0, 5.2 Hz), 7.32 (m, 5H), 7.08 (m, 2H), 6.59 (s, 1H), 4.60 (d, 2H, J = 5.6 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 165.9, 163.4, 138.0, 129.4, 129.3, 128.8, 127.9, 127.6, 115.7, 115.5, 44.4 ppm

IR (neat, cm^{-1}): 3322, 3054, 1649, 1498, 1265

HRMS: $C_{14}H_{12}FNO$ Cacld : 229.0903, $[M]^+$ Found : 229.0904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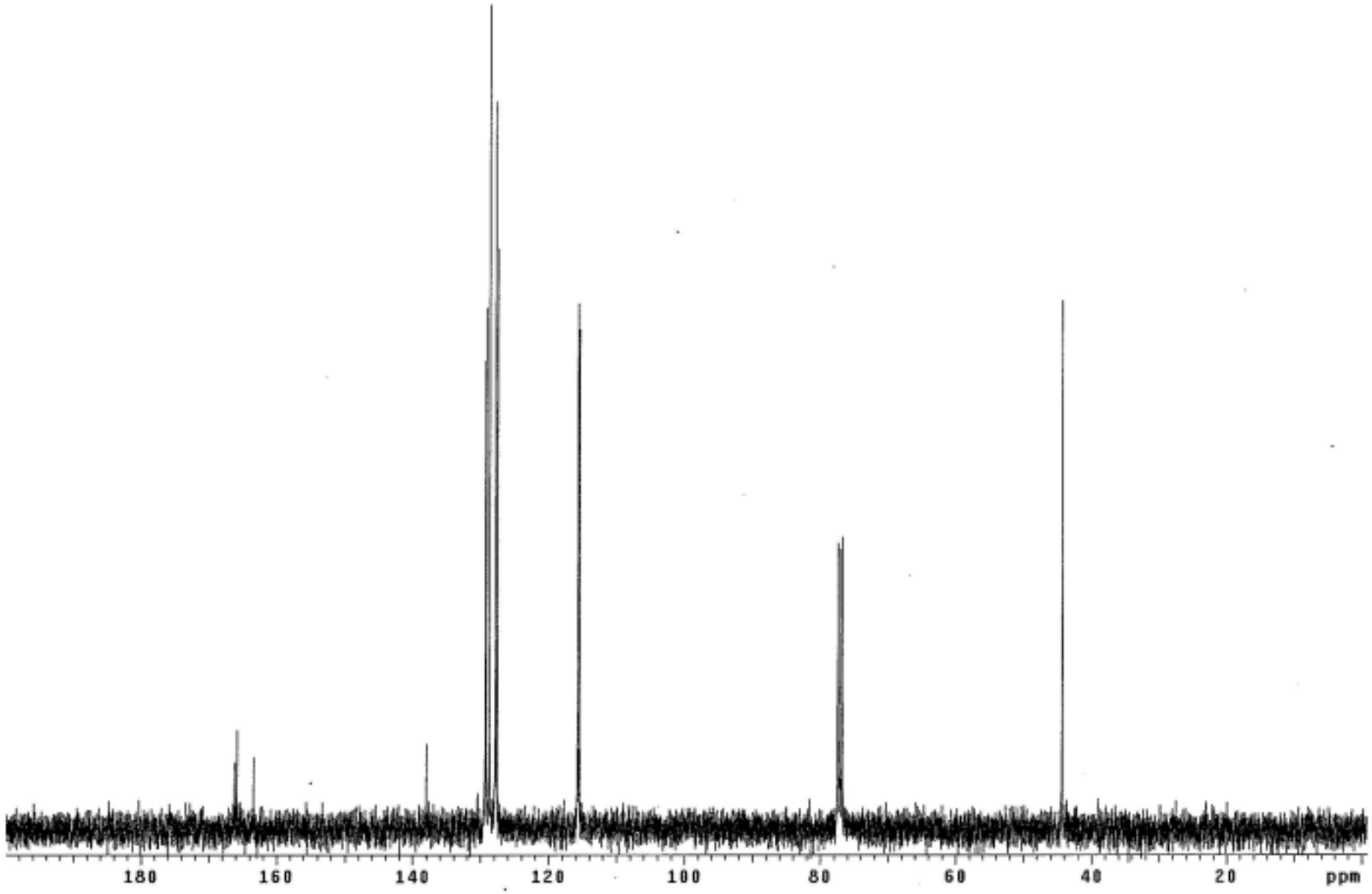
180
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140
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100
80
60
40
20
ppm

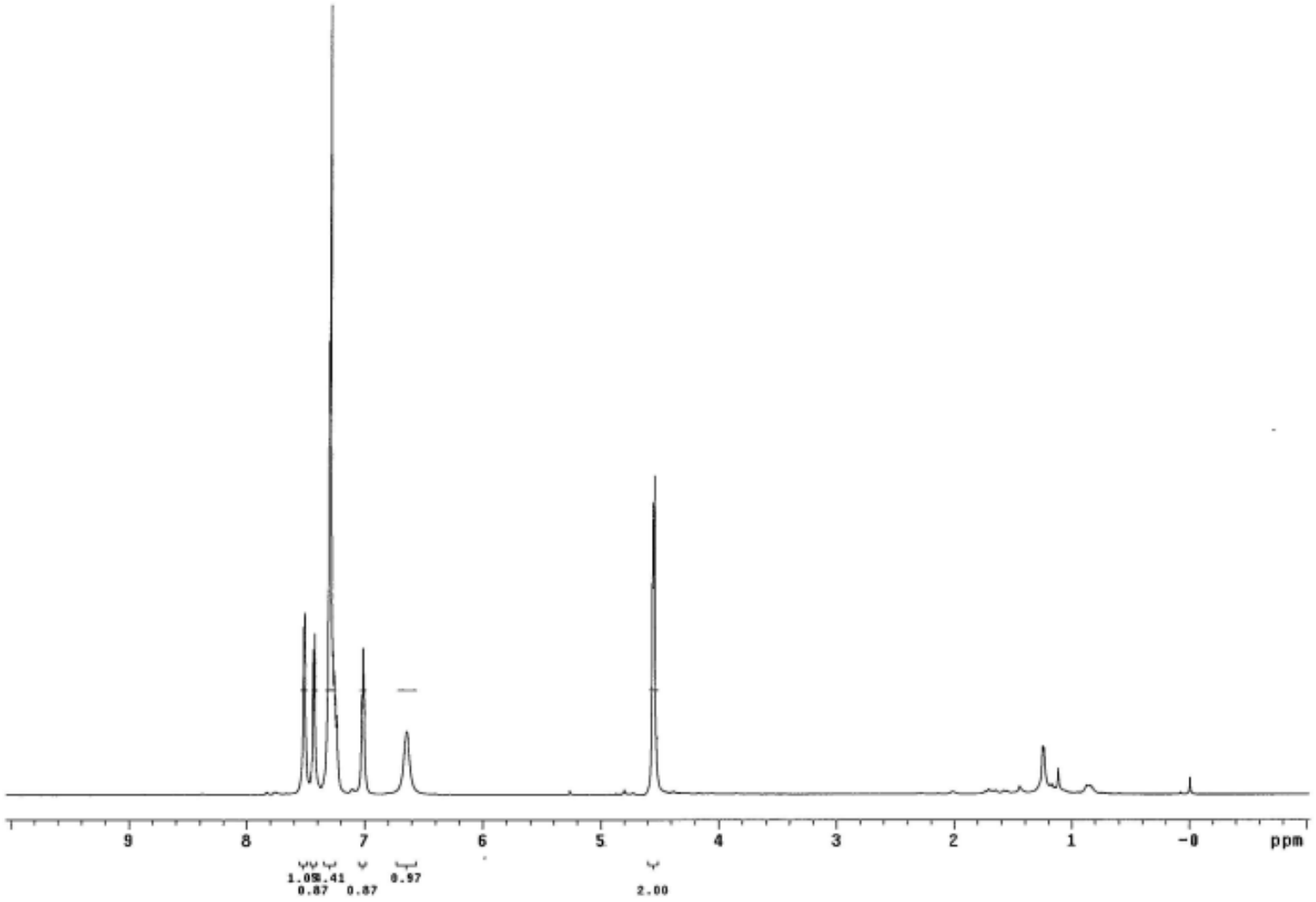
***N*-benzylthiophene-2-carboxamide (11b):** The representative experimental procedure was applied to 2-thiophenecarboxaldehyde (56.1 mg, 0.5 mmol) and benzylamine (109.2 mg, 1.0 mmol) to yield **11b** (58.7 mg, 54 %)

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.52 (d, 1H, J = 3.2 Hz), 7.44 (d, 1H, J = 4.8 Hz), 7.27 (m, 5H), 7.02 (t, 1H, J = 4.0 Hz), 6.65 (s, 1H), 4.56 (d, 2H, J = 5.2 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 161.8, 138.8, 138.1, 130.0, 128.7, 128.2, 127.9, 127.6 (2C), 44.1 ppm

IR (neat, cm^{-1}): 3347, 3088, 1621, 1545, 1422

HRMS: $C_{12}H_{11}NOS$ Cacld : 217.0561, $[M]^+$ Found : 217.0564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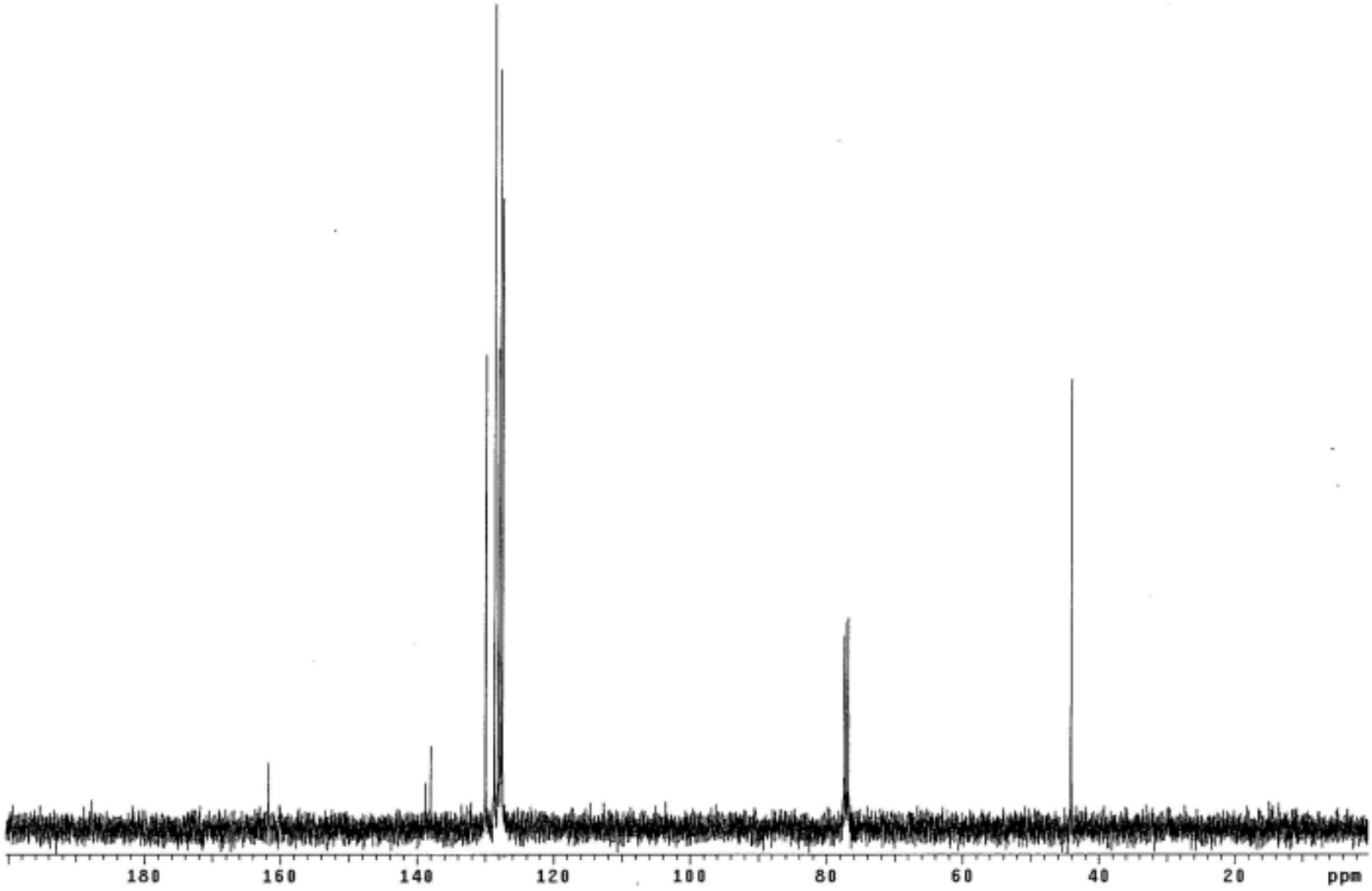
180
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100
80
60
40
20
ppm

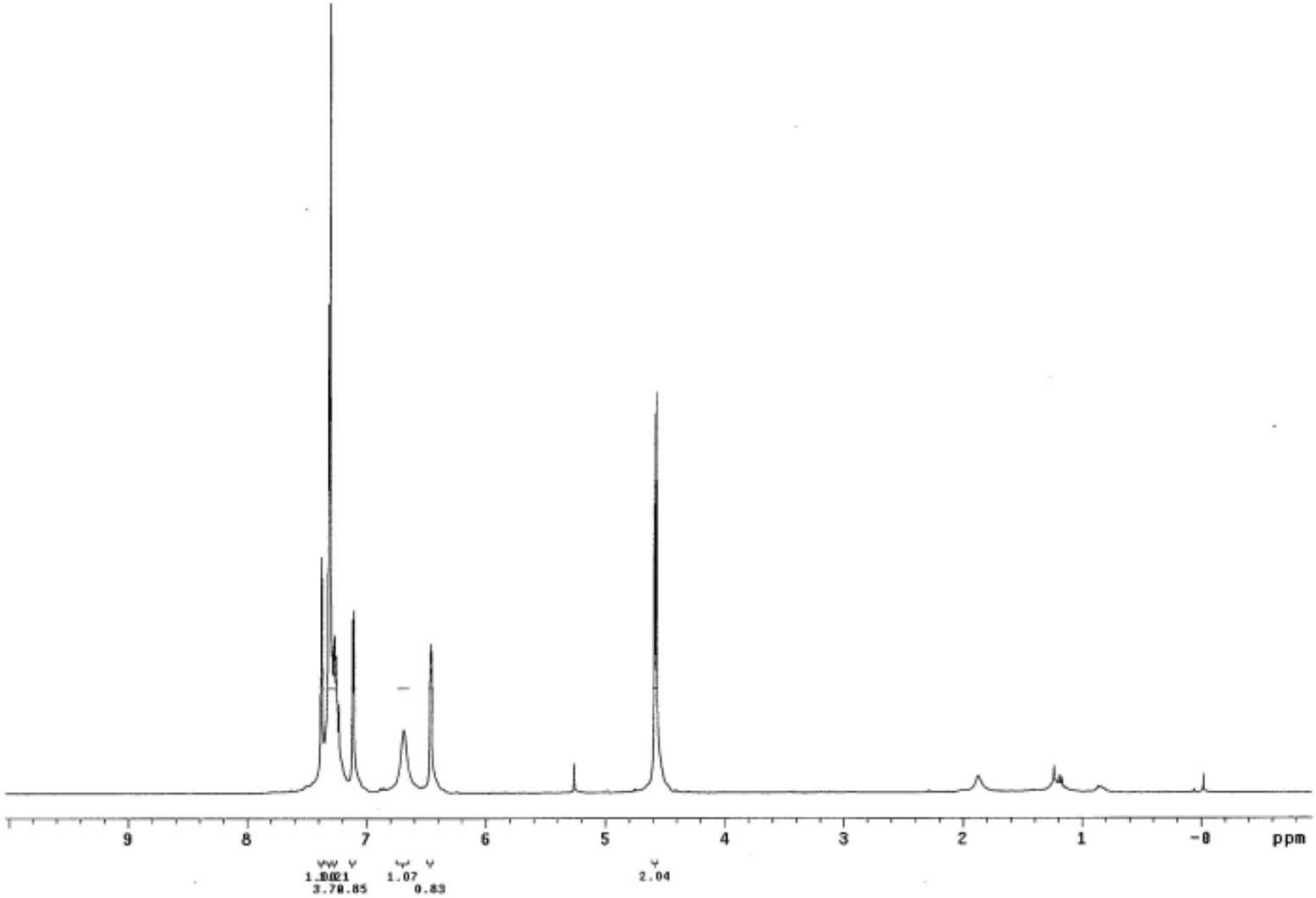
***N*-benzylfuran-2-carboxamide (12b):** The representative experimental procedure was applied to furfural (48.0 mg, 0.5 mmol) and benzylamine (109.2 mg, 1.0 mmol) to yield **12b** (71.9 mg, 72 %)

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.38 (s, 1H), 7.31 (m, 4H), 7.27 (m, 1H), 7.12 (d, 1H, J = 3.6 Hz), 6.70 (s, 1H), 6.47 (m, 1H), 4.58 (d, 2H, J = 6.0 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 158.0, 147.6, 143.7, 137.8, 128.5, 127.7, 127.4, 114.2, 112.0, 43.1 ppm

IR (neat, cm^{-1}): 3288, 3125, 3064, 1659, 1476

HRMS: $C_{12}H_{11}NO_2$ Cacld : 201.0790, $[M]^+$ Found : 201.0790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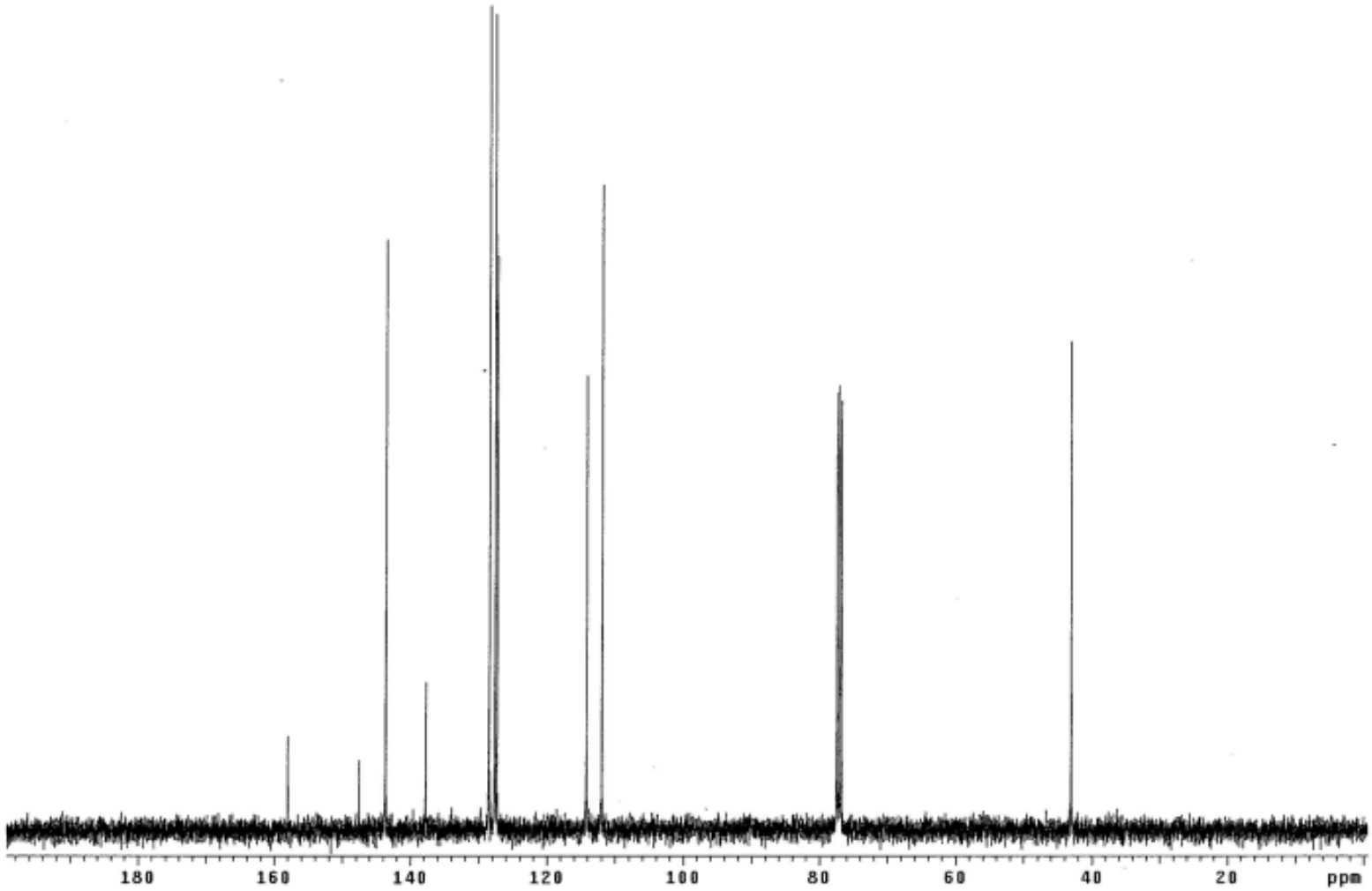
2.04


180
160
140
120
100
80
60
40
20
ppm

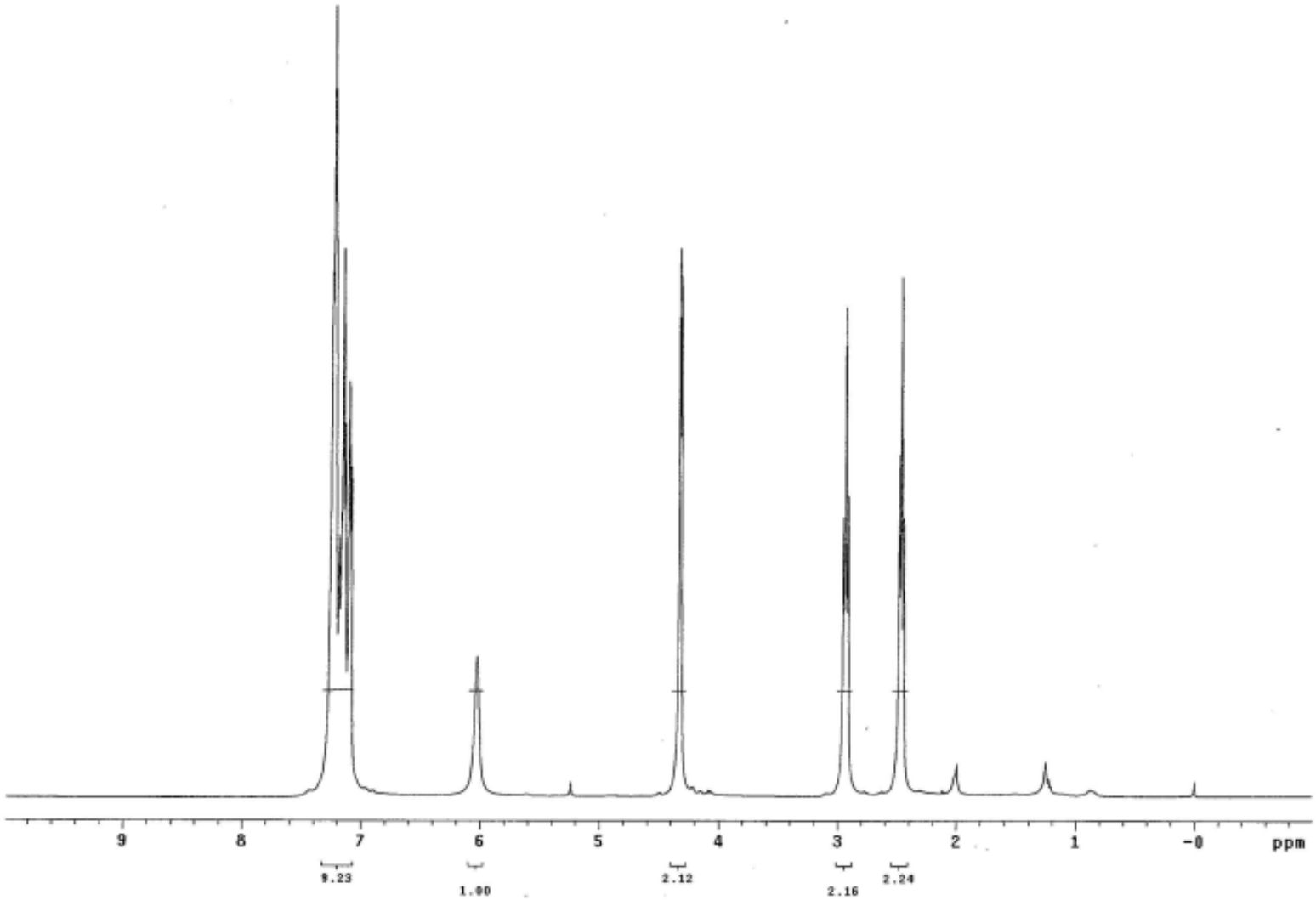
***N*-benzyl-3-phenylpropanamide (13b):** The representative experimental procedure was applied hydrocinnamaldehyde (67.1 mg, 0.5 mmol) and benzylamine (109.2 mg, 1.0 mmol) to yield **13b** (53.7 mg, 45 %)

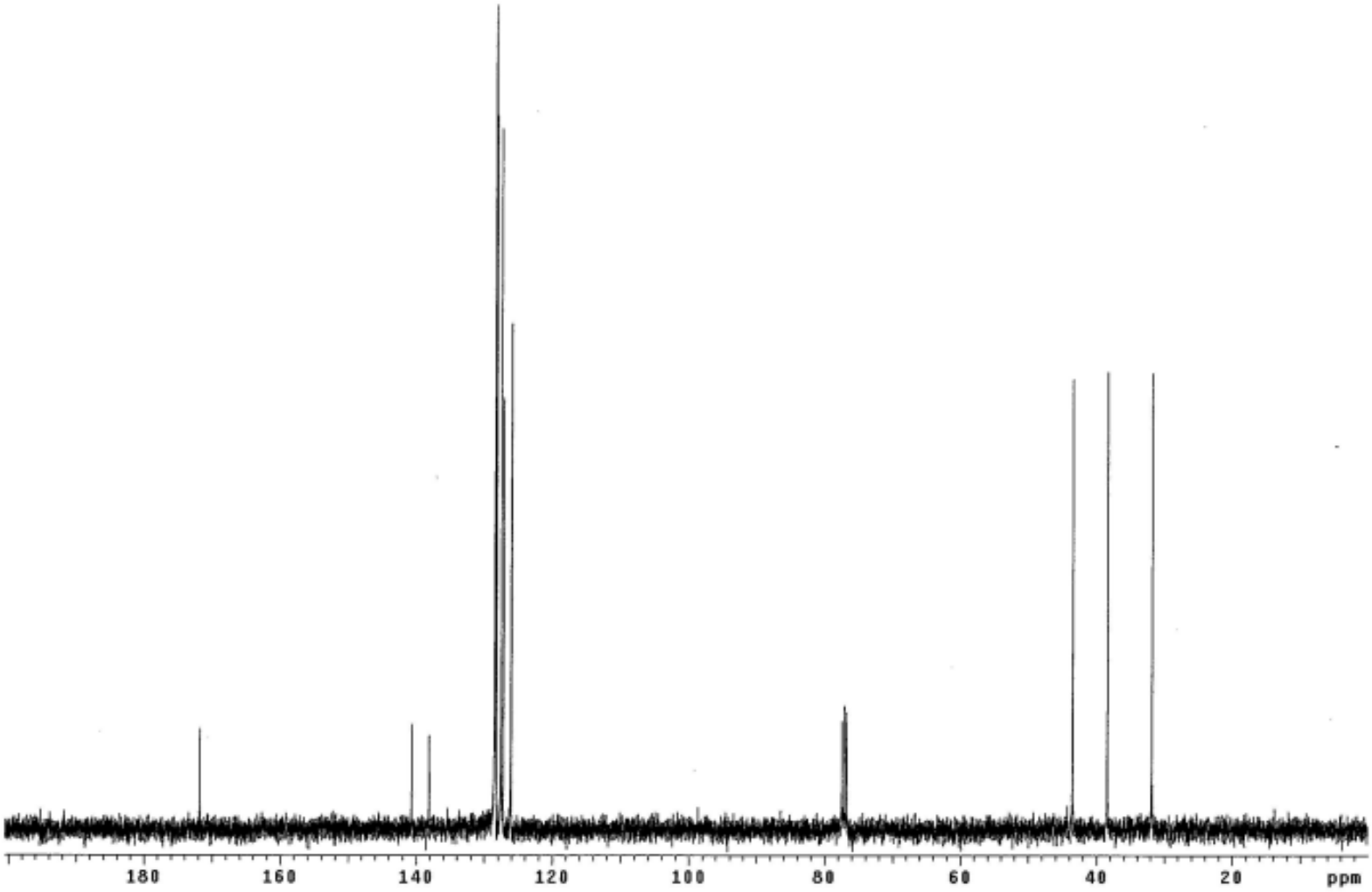
^{1}H NMR (400 MHz, $CDCl_3$):δ 7.17 (m, 10H), 6.03 (s, 1H), 4.33 (d, 2H, J = 5.2 Hz), 2.94 (t, 2H, J = 7.2 Hz), 2.47 (t, 2H, J = 7.6 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 171.8, 140.7, 138.1, 128.5, 128.4, 128.3, 127.6, 127.3, 126.1, 43.6, 38.5, 31.9 ppm

IR (neat, cm^{-1}): 3285, 3030, 2929, 1639, 1454

HRMS: $C_{16}H_{17}NO$ Cacld :239.1310, $[M]^+$ Found : 239.1309


9
8
7
6
5
4
3
2
1
-0
ppm
9.23
1.00
2.12
2.16
2.24


180
160
140
120
100
80
60
40
20
ppm

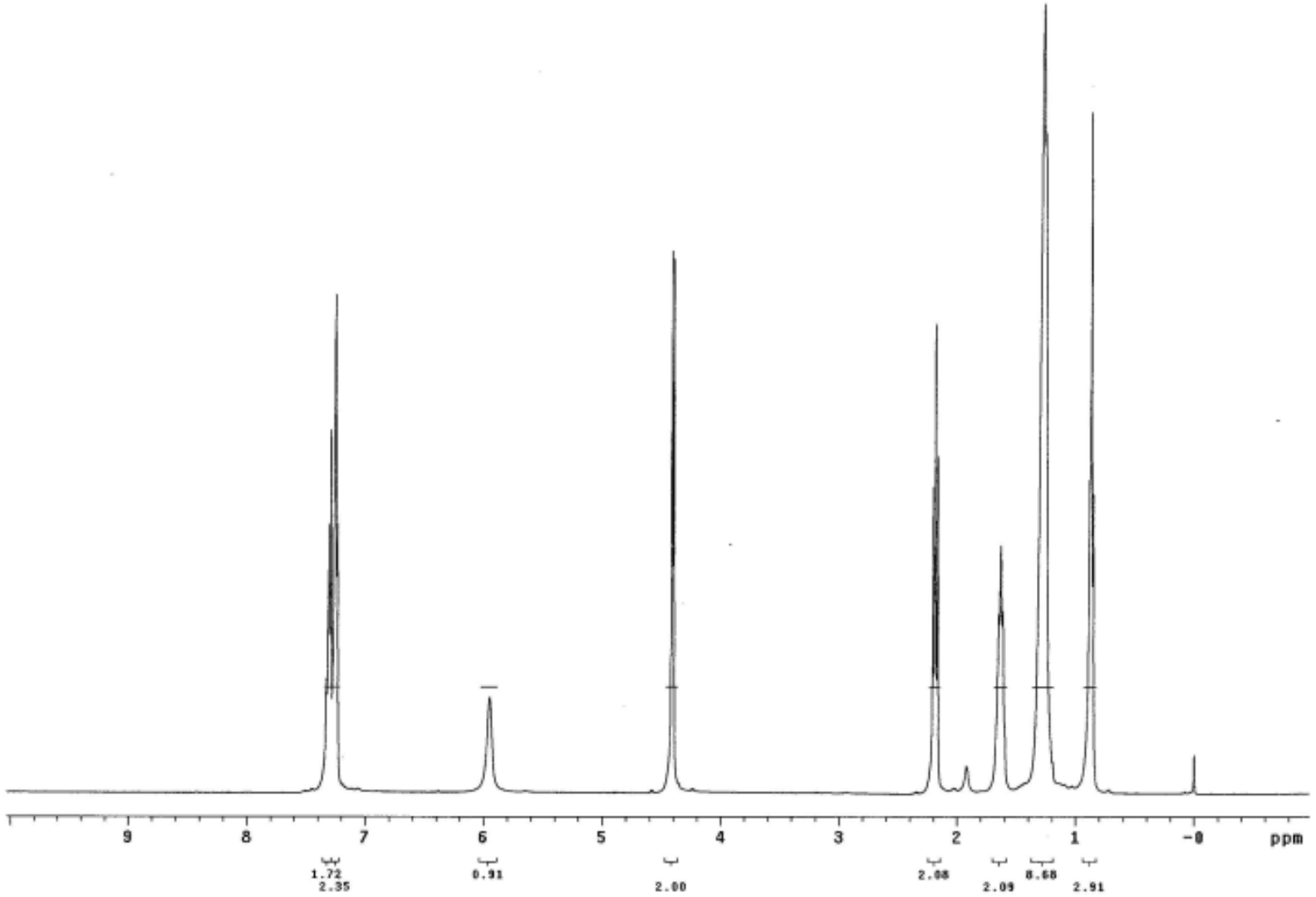
***N*-benzyloctanamide (14b):** The representative experimental procedure was applied to octanal (64.1mg, 0.5 mmol) and benzylamine (109.2 mg, 1.0 mmol) to yield **14b** (42.8 mg, 38 %)

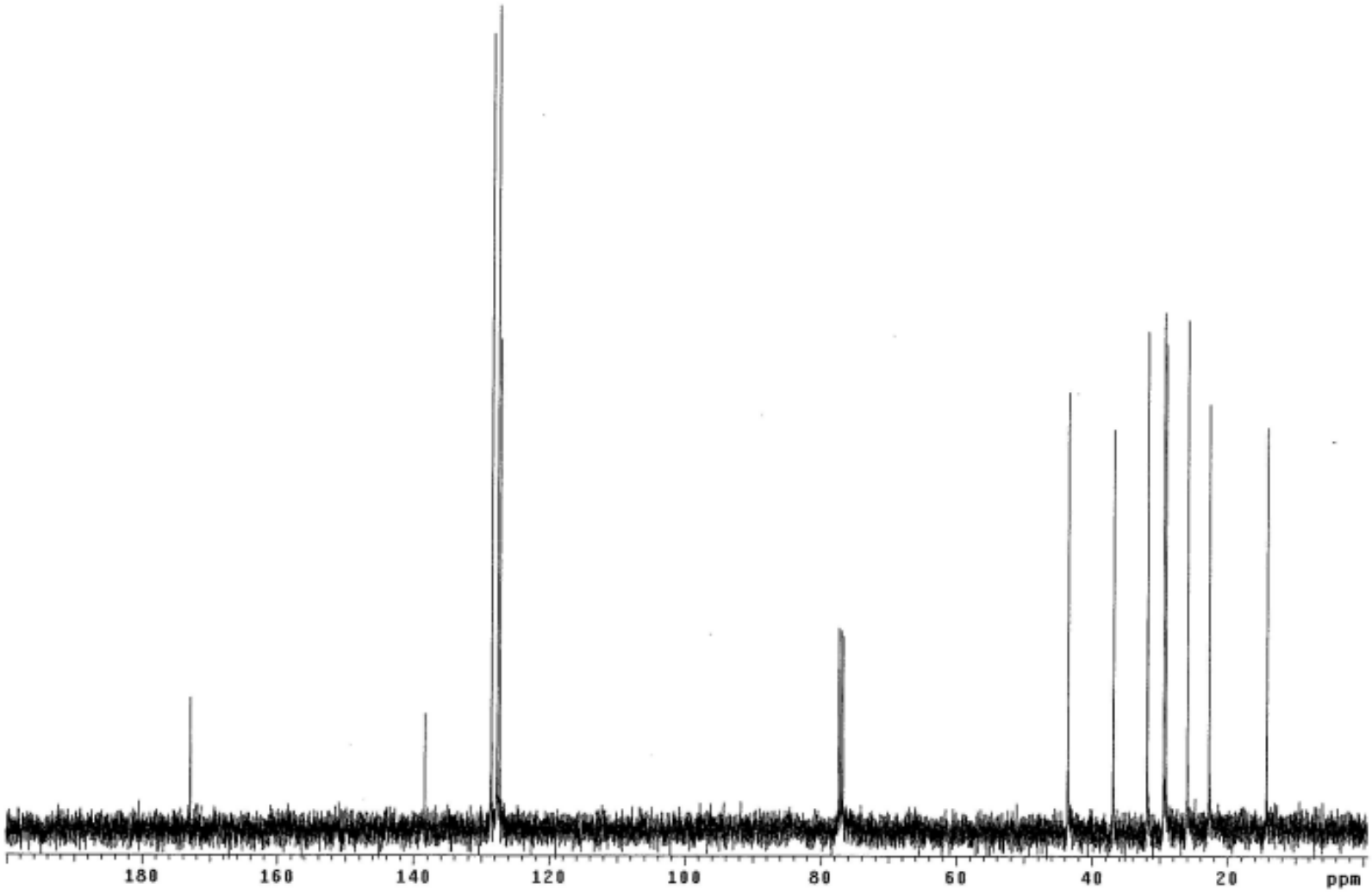
^{1}H NMR (400 MHz, $CDCl_3$):δ 7.32 (m, 2H), 7.26 (m, 2H), 5.95 (s, 1H), 4.41 (d, 2H, J = 5.6 Hz), 2.19 (t, 2H, J = 7.6 Hz), 1.63 (m, 2H), 1.27 (m, 8H), 0.87 (t, 3H, J = 6.4 Hz) ppm

^{13}C NMR (100 MHz, $CDCl_3$):δ 173.0, 138.4, 128.6, 127.7, 127.4, 43.7, 36.9, 31.9, 29.5, 29.2, 26.0, 22.8, 14.3 ppm

IR (neat, cm^{-1}): 3294, 2928, 1657, 1632, 1265

HRMS: $C_{15}H_{23}NO$ Cacld : 233.1780, $[M]^+$ Found : 233.1781


9
8
7
6
5
4
3
2
1
-0
ppm
1.72
2.35
0.91
2.00
2.08
2.09
6.68
2.91


180
160
140
120
100
80
60
40
20
ppm