Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Metal-Free Nitrative Cyclization of *N*-Aryl Imines with *tert*-Butyl Nitrite: Dehydrogenative Access to 3-Nitroindoles

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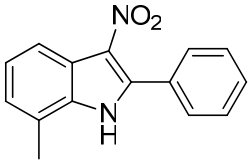
List of Contents

(A) Typical Experimental Procedure

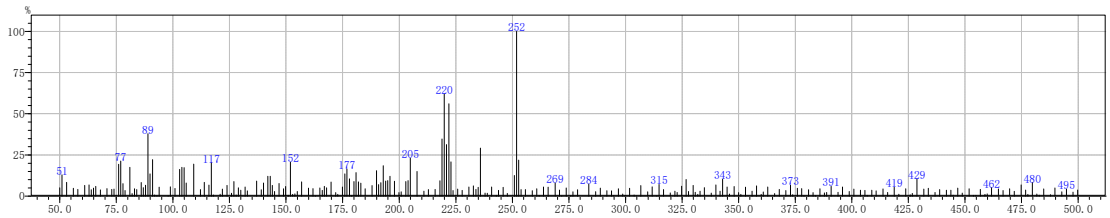
(a) Typical Experimental Procedure for the synthesis of 3-nitroindoles:

To a Schlenk tube were added imines **1** (0.2 mmol), *tert*-butyl nitrite (**2a**, TBN) (2.0 equiv), 1,4-dioxane (4 mL). Then the tube was stirred at 70 ^{o}C (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to afford the desired product **3**.

(b) Figure S1 The O-18 labelling experiment using $H_2{}^{18}O$



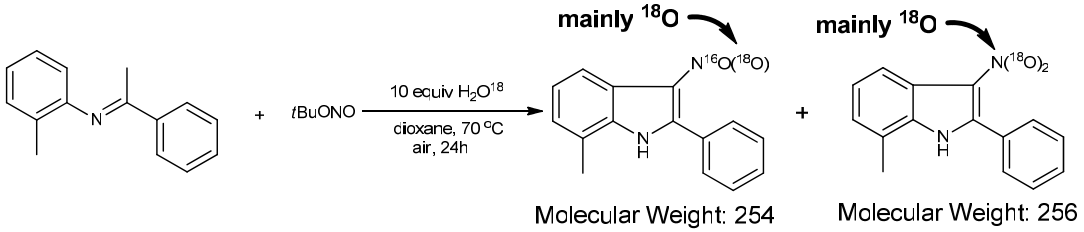
Exact Mass: 252

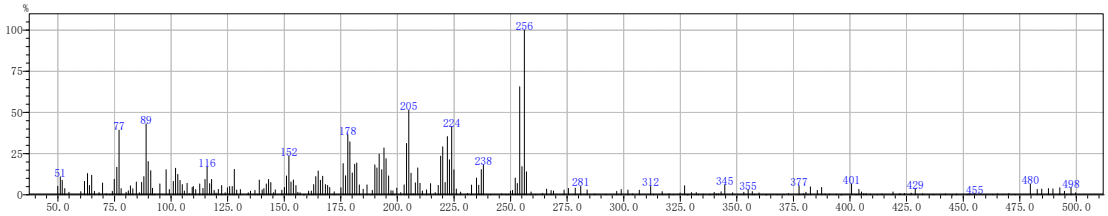


[MS Spectrum]
# of Peaks257
Raw Spectrum 18.545 (scan : 3010) Base Peakm/z 251.85 (Inten : 4,499)
Background 18.500 (scan : 3001)

m/z	Absolute Intensity	Relative Intensity						
50.00	232	5.16	56.00	217	4.82	62.95	310	6.89
51.00	581	12.91	58.00	188	4.18	63.90	178	3.96
53.00	380	8.45	61.00	291	6.47	64.90	223	4.96

65.90	268	5.96	140.00	360	8.00	197.90	408	9.07
67.90	174	3.87	142.00	545	12.11	202.90	397	8.82
70.90	206	4.58	142.95	545	12.11	203.95	426	9.47
73.00	186	4.13	143.90	294	6.53	204.90	1040	23.12
73.95	190	4.22	144.90	131	2.91	207.90	672	14.94
76.00	869	19.32	146.90	347	7.71	217.95	421	9.36
76.95	959	21.32	148.85	200	4.45	218.90	1565	34.79
77.95	341	7.58	149.80	266	5.91	219.90	2789	61.99
81.00	787	17.49	150.90	26	0.58	220.90	1411	31.36
86.00	377	8.38	151.90	930	20.67	221.95	2523	56.08
86.95	235	5.22	156.90	391	8.69	222.85	940	20.89
87.90	296	6.58	166.90	270	6.00	223.80	154	3.42
88.95	1706	37.92	167.90	232	5.16	225.80	193	4.29
89.90	609	13.54	169.90	386	8.58	227.80	160	3.56
90.95	1001	22.25	174.90	251	5.58	230.80	250	5.56
93.90	243	5.40	175.95	611	13.58	232.80	283	6.29
98.90	255	5.67	176.90	739	16.43	233.90	188	4.18
102.95	731	16.25	178.00	478	10.62	234.85	242	5.38
103.95	791	17.58	180.00	398	8.85	235.90	1314	29.21
104.95	779	17.31	180.95	644	14.31	240.90	251	5.58
105.90	360	8.00	181.95	388	8.62	243.90	159	3.53
109.20	874	19.43	183.00	355	7.89	245.90	240	5.33
112.20	184	4.09	188.00	288	6.40	250.85	568	12.63
113.90	379	8.42	189.95	699	15.54	**251.85**	**4499**	**100.00**
115.90	304	6.76	190.85	317	7.05	252.80	988	21.96
116.95	913	20.29	191.85	370	8.22	**253.80**	**181**	**4.02**
123.90	295	6.56	192.95	831	18.47	**255.80**	**182**	**4.05**
126.95	399	8.87	193.95	412	9.16	258.80	151	3.36
137.00	413	9.18	194.90	427	9.49			
139.00	179	3.98	195.95	545	12.11			





[MS Spectrum]

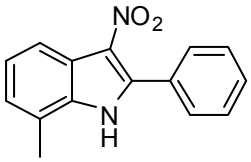
# of Peaks259

Raw Spectrum 18.945 (scan : 3090) Base Peak m/z 256.05 (Inten : 11,717)
Background 18.885 (scan : 3078)

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
49.95	617	5.27	179.05	3770	32.18
51.00	1281	10.93	180.10	1571	13.41
51.90	1043	8.90	181.10	2184	18.64
61.75	965	8.24	182.05	2261	19.30
63.05	1520	12.97	190.05	2127	18.15
63.95	668	5.70	191.00	1913	16.33
64.95	1386	11.83	192.00	2895	24.71
69.75	847	7.23	193.05	1797	15.34
74.95	1119	9.55	194.05	3346	28.56
76.05	1962	16.74	195.00	2582	22.04
77.00	4614	39.38	196.15	1347	11.50
87.95	1300	11.09	204.05	3658	31.22
89.00	5043	43.04	205.00	6008	51.28
89.95	2365	20.18	206.05	1544	13.18
91.00	1723	14.71	208.00	858	7.32
97.80	1793	15.30	209.00	1911	16.31
101.00	963	8.22	209.95	825	7.04
102.05	1886	16.10	214.65	797	6.80
102.95	1470	12.55	218.05	678	5.79
104.00	1022	8.72	219.10	2754	23.50
115.00	1104	9.42	220.05	3424	29.22
115.95	1985	16.94	221.05	874	7.46
117.05	807	6.89	222.10	4147	35.39
117.95	1096	9.35	223.05	2494	21.29
127.95	1815	15.49	224.05	4822	41.15
139.00	1051	8.97	224.95	1780	15.19
143.05	1104	9.42	232.80	704	6.01
144.05	882	7.53	234.95	1205	10.28
151.00	1353	11.55	236.00	689	5.88
152.05	2749	23.46	237.05	1801	15.37
153.05	915	7.81	238.00	2141	18.27
154.00	1066	9.10	**252.05**	**1198**	**10.22**
155.15	664	5.67	252.95	811	6.92
163.00	739	6.31	**254.05**	**7686**	**65.60**
163.95	1304	11.13	255.05	2008	17.14
165.05	1705	14.55	**256.05**	**11717**	**100.00**
166.00	1039	8.87	257.05	1642	14.01
167.00	1333	11.38	259.10	207	1.77
176.10	2228	19.02			
177.05	1368	11.68			
178.05	4300	36.70			

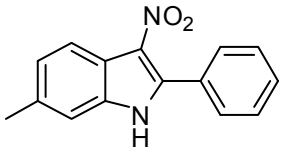
(B) Analytical data

7-Methyl-3-nitro-2-phenyl-1*H*-indole (3a):



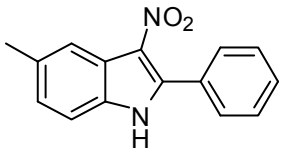
Yellow solid, mp 225.7-227.9 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.36 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 3.6 Hz, 2H), 7.54-7.52 (m, 3H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 142.0, 134.1, 131.1, 130.9, 130.6, 128.9, 125.9, 124.7, 123.0, 122.7, 118.9, 16.6; IR (KBr, cm-1): 3260, 1440, 1330; HRMS (EI) for $C_{15}H_{13}N_2O_2$ $(M^+ + H)^+$: calcd 253.0972, found 253.0958.

6-Methyl-3-nitro-2-phenyl-1*H*-indole (3b):



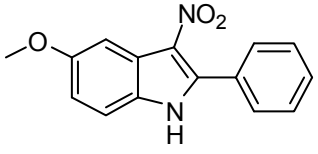
Yellow solid, mp 223.1-225.5 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.49 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.79-7.77 (m, 2H), 7.55-7.53 (m, 3H), 7.38 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 141.6, 135.5, 135.3, 131.4, 130.8, 129.2, 126.3, 121.3, 121.0, 113.1, 21.7; IR (KBr, cm-1): 3239, 1450, 1338; HRMS (EI) for $C_{15}H_{13}N_2O_2$ $(M^+ + H)^+$: calcd 253.0972, found 253.0960.

5-Methyl-3-nitro-2-phenyl-1*H*-indole (3c)[1]:



Yellow solid, mp 242.1-244.5 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.49 (s, 1H), 8.07 (s, 1H), 7.78-7.76 (m, 2H), 7.54-7.53 (m, 3H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 142.3, 134.5, 133.4, 131.5, 131.0, 130.9, 129.4, 127.1, 123.5, 121.3, 113.3, 22.1; IR (KBr, cm-1): 3236, 1447, 1348; HRMS (EI) for $C_{15}H_{13}N_2O_2$ $(M^+ + H)^+$: calcd 253.0972, found 253.0957.

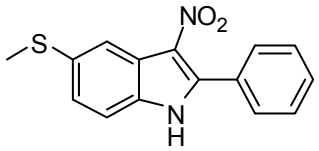
5-Methoxy-3-nitro-2-phenyl-1*H*-indole (3d):



Yellow solid, mp 248.3-250.8 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 7.77-7.75 (m, 3H), 7.54 (brs, 3H), 7.48 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ:

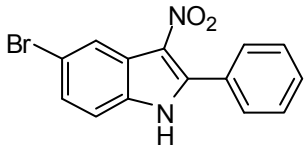
158.3, 142.1, 131.3, 130.7, 130.6, 129.7, 129.1, 123.9, 115.4, 114.3, 102.9, 55.9; IR (KBr, cm-1): 3171, 1342, 1205; HRMS (EI) for $C_{15}H_{13}N_2O_3$ $(M^+ + H)^+$: calcd 269.0921, found 269.0905.

5-(Methylthio)-3-nitro-2-phenyl-1*H*-indole (3e):



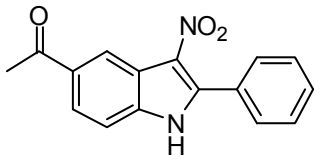
Yellow solid, mp 268.4-270.7 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.76 (s, 1H), 8.17 (d, *J* = 1.6 Hz, 1H), 7.80-7.78 (m, 2H), 7.56-7.53 (m, 4H), 7.35-7.32 (m, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 142.3, 134.7, 132.9, 130.9, 130.8, 130.5, 129.0, 125.3, 123.6, 119.2, 113.8, 16.9; IR (KBr, cm-1): 3265, 1446, 1305; HRMS (EI) for $C_{15}H_{13}N_2O_2S$ $(M^+ + H)^+$: calcd 285.0692, found 285.0677.

5-Bromo-3-nitro-2-phenyl-1*H*-indole (3f):



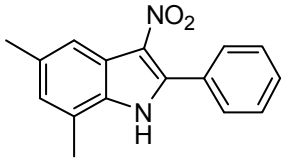
Yellow solid, mp 269.9-272.5 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.79 (s, 1H), 8.40 (d, *J* = 1.6 Hz, 1H), 7.81-7.79 (m, 2H), 7.57-7.49 (m, 5H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 143.2, 133.5, 131.2, 130.8, 130.6, 129.2, 128.2, 124.6, 123.8, 117.7, 115.3; IR (KBr, cm-1): 3171, 1344, 1205; HRMS (EI) for $C_{15}H_{10}BrN_2O_2$ $(M^+ + H)^+$: calcd 316.9920, found 316.9905.

1-(3-Nitro-2-phenyl-1*H*-indol-5-yl)ethanone (3g)



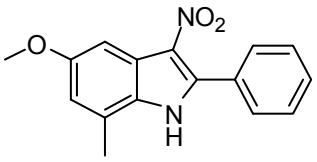
Yellow solid, mp 276.1-278.4 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.89 (s, 1H), 8.91 (d, *J* = 1.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.84-7.82 (m, 2H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.59-7.56 (m, 3H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.5, 143.6, 136.2, 132.7, 130.4, 129.9, 129.3, 128.3, 124.5, 121.5, 121.3, 112.9, 26.9; IR (KBr, cm-1): 3255, 1662, 1440, 1341; HRMS (EI) for $C_{16}H_{13}N_2O_2$ $(M^+ + H)^+$: calcd 281.0921, found 281.0910.

5,7-Dimethyl-3-nitro-2-phenyl-1*H*-indole (3h):



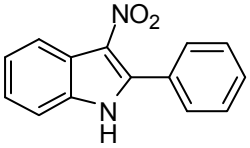
Yellow solid, mp 209.2-211.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (s, 1H), 7.98 (s, 1H), 7.64 (d, *J* = 3.6 Hz, 2H), 7.47-7.45 (m, 3H), 6.99 (s, 1H), 2.49 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 134.3, 131.1, 130.1, 130.0, 129.4, 128.5, 127.2, 121.9, 120.5, 118.6, 21.6, 16.1; IR (KBr, cm-1): 3257, 1321, 1275; HRMS (EI) for $C_{16}H_{15}N_2O_2$ $(M^+ + H)^+$: calcd 267.1128, found 267.1112.

5-Methoxy-7-methyl-3-nitro-2-phenyl-1*H*-indole (3i):



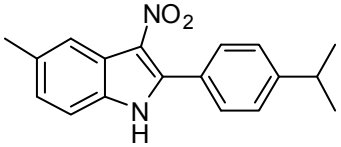
Yellow solid, mp 259.8-262.3 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.29 (s, 1H), 7.74-7.72 (m, 2H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.53-7.51 (m, 3H), 6.83 (d, *J* = 1.2 Hz, 1H), 3.89 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 158.4, 141.9, 131.3, 130.8, 130.5, 129.2, 128.9, 124.4, 123.4, 115.9, 100.4, 55.8, 16.6; IR (KBr, cm-1): 3257, 1321, 1275; HRMS (EI) for $C_{16}H_{15}N_2O_3$ $(M^+ + H)^+$: calcd 283.1077, found 283.1069.

3-Nitro-2-phenyl-1*H*-indole (3j)[2]:



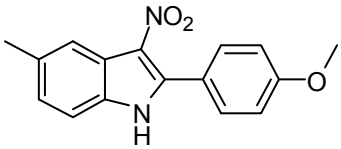
Yellow solid, mp 245.5-247.9 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.62 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.81-7.79 (m, 2H), 7.59-7.55 (m, 4H), 7.42-7.36 (m, 2H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 142.1, 134.9, 131.2, 130.9, 130.8, 129.2, 125.4, 124.6, 123.0, 121.5, 113.3; IR (KBr, cm-1): 3244, 1457, 1335.

2-(4-Isopropylphenyl)-5-methyl-3-nitro-1*H*-indole (3k):



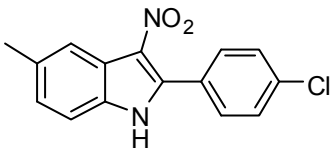
Yellow solid, mp 248.6-250.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.42 (s, 1H), 8.07 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.46-7.41 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 1H), 3.05-2.98 (m, 1H), 2.51 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 151.8, 142.3, 134.2, 133.2, 130.8, 128.7, 127.2, 126.8, 123.4, 121.1, 112.9, 34.9, 24.2, 21.9; IR (KBr, cm-1): 3278, 1368, 1290; HRMS (EI) for $C_{18}H_{19}N_2O_2$ $(M^+ + H)^+$: calcd 295.1441, found 295.1423.

2-(4-Methoxyphenyl)-5-methyl-3-nitro-1*H*-indole (3l):



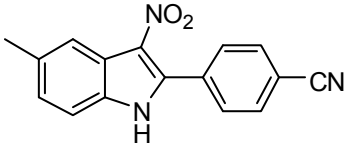
Yellow solid, mp 248.6-250.7 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.38 (s, 1H), 8.05 (s, 1H), 7.76-7.74 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.19-7.16 (m, 1H), 7.09-7.07 (m, 2H), 3.89 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 162.1, 142.2, 134.1, 133.0, 132.3, 126.6, 123.4, 123.1, 121.1, 114.5, 112.8, 103.6, 55.8, 21.8; IR (KBr, cm-1): 3276, 1388, 1301; HRMS (EI) for $C_{16}H_{15}N_2O_3$ $(M^+ + H)^+$: calcd 283.1077, found 283.1062.

2-(4-Chlorophenyl)-5-methyl-3-nitro-1*H*-indole (3m):



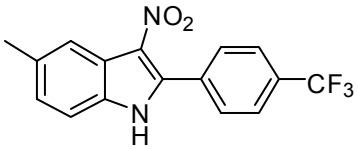
Yellow solid, mp 271.1-278.8 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.76 (s, 1H), 8.04 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 140.4, 136.1, 134.2, 133.1, 132.3, 129.8, 129.1, 126.8, 122.9, 120.8, 112.9, 21.6; IR (KBr, cm-1): 3226, 1421, 1377; HRMS (EI) for $C_{15}H_{12}ClN_2O_2$ $(M^+ + H)^+$: calcd 287.0582, found 287.0565.

4-(5-Methyl-3-nitro-1*H*-indol-2-yl)benzonitrile (3n):



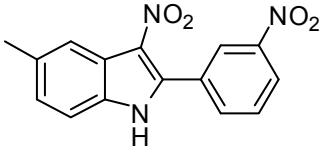
Yellow solid, mp 288.1-289.8 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.7 (s, 1H), 8.07 (s, 1H), 8.02-7.95 (m, 4H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 139.5, 135.8, 134.7, 133.5, 132.9, 131.8, 127.4, 123.0, 121.1, 119.0, 114.1, 113.3, 21.8; IR (KBr, cm-1): 3463, 1449, 1338; HRMS (EI) for $C_{16}H_{12}N_3O_2$ $(M^+ + H)^+$: calcd 278.0924, found 278.0912.

5-Methyl-3-nitro-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (3o):



Yellow solid, mp 298.1-299.5 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.7 (s, 1H), 8.07 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.25-7.23 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 139.9, 135.3, 134.7, 133.4, 131.9, 131.7, 127.3, 126.5 (d, *J* = 6.0 Hz, 1C), 126.1-125.9 (m, 1C), 123.8, 123.0, 121.1, 113.2, 21.8; ^{19}F NMR (282 MHz, C_3D_6O): δ: -63.3 (s, 3F); IR (KBr, cm-1): 3232, 1447, 1369; HRMS (EI) for $C_{15}H_{10}F_3N_2O_2$ $(M^+ + H)^+$: calcd 321.0845, found 321.0821.

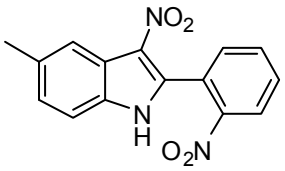
5-Methyl-3-nitro-2-(3-nitrophenyl)-1*H*-indole (3p):



Yellow solid, mp 283.4-285.8 °C (uncorrected); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.92 (s, 1H), 8.67 (s, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.08 (s, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0

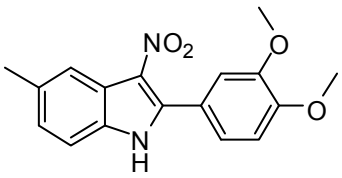
Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 147.5, 138.7, 136.8, 133.6, 132.3, 131.4, 129.8, 126.4, 124.8, 124.6, 121.6, 119.8, 112.8, 21.7; IR (KBr, cm-1): 3320, 1519, 1448, 1370; HRMS (EI) for $C_{15}H_{12}N_3O_4$ $(M^+ + H)^+$: calcd 298.0822, found 298.0818.

5-Methyl-3-nitro-2-(2-nitrophenyl)-1*H*-indole (3q):



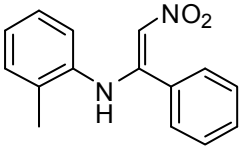
Yellow solid, mp 280.1-282.7 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.83 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.94 (t, J = 7.6 Hz, 1H), 7.89-7.83 (m, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.27-7.24 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 149.9, 138.5, 134.8, 134.6, 133.6, 133.3, 132.2, 127.2, 126.9, 125.6, 122.5, 120.9, 113.3, 21.8; IR (KBr, cm-1): 3313, 1523, 1445, 1366; HRMS (EI) for $C_{15}H_{12}N_3O_4$ $(M^+ + H)^+$: calcd 298.0822, found 298.0815.

2-(3,4-Dimethoxyphenyl)-5-methyl-3-nitro-1*H*-indole (3r):



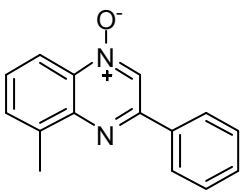
Yellow solid, mp 266.6-268.9 °C (uncorrected); ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.41 (s, 1H), 8.06 (s, 1H), 7.43-7.36 (m, 3H), 7.19 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 150.4, 148.1, 141.9, 132.9, 131.8, 125.8, 123.8, 123.0, 122.0, 121.8, 119.8, 113.6, 112.4, 111.2, 55.8, 55.7, 21.5; IR (KBr, cm-1): 3301, 1435, 1368; HRMS (EI) for $C_{17}H_{16}N_2O_4$ $(M^+ + H)^+$: calcd 312.1110, found 312.1101.

(*E*)-2-Methyl-*N*-(2-nitro-1-phenylvinyl)aniline (4a):



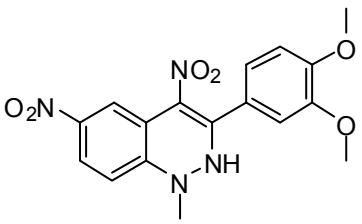
Yellow solid, mp 162.4-164.7 °C (uncorrected) (ref. 160 °C) [3]; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.47 (s, 1H), 7.42-7.37 (m, 1H), 7.33-7.29 (m, 2H), 7.25-7.23 (m, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.82 (s, 1H), 6.55 (d, J = 8.0 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 136.2, 132.1, 131.6, 130.9, 130.8, 128.8, 128.3, 126.5, 126.3, 125.7, 113.8, 18.1; LRMS (EI, 70 eV) m/z (%): 254 (M+, 21), 208 (100), 193 (67), 165 (13). HRMS (EI) for $C_{15}H_{15}N_2O_2$ $(M^+ + H)^+$: calcd 255.1128, found 255.1105.

5-Methyl-3-phenylquinoxaline 1-oxide (5a)[3]:



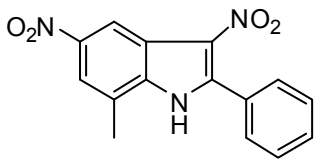
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.88 (s, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.15-8.13 (m, 2H), 7.66 (d, *J* = 6.8 Hz, 1H), 7.61-7.54 (m, 4H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.4, 144.4, 138.9, 135.8, 131.9, 130.7, 129.3, 129.2, 128.7, 127.1, 126.9, 116.5, 17.6. HRMS (EI) for $C_{15}H_{13}N_2O$ $(M^+ + H)^+$: calcd 237.1102, found 237.1089.

3-(3,4-Dimethoxyphenyl)-1-methyl-4,6-dinitro-1,2-dihydrocinnoline (6t):



Yellow solid, mp 310.5-312.9 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, 400 MHz, $CDCl_3$) δ: 9.28 (s, 1H), 8.51 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 7.54 (d, *J* = 9.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 4.24 (s, 3H), 3.98 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, 400 MHz, $CDCl_3$) δ: 169.8, 150.5, 148.6, 146.9, 143.6, 143.2, 127.5, 125.9, 123.9, 123.6, 121.9, 116.2, 111.5, 110.7, 55.9, 44.2; IR (KBr, cm-1): 3348, 1496, 1346; HRMS (EI) for $C_{17}H_{16}N_4O_6$ $(M^+ + H)^+$: calcd 372.1070, found 372.1056.

7-Methyl-3,5-dinitro-2-phenyl-1H-indole (7a):



Yellow solid, mp 298.1-300.8 ^{o}C (uncorrected), ^{1}H NMR (400 MHz, C_3D_6O) δ: 11.84 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.79-7.70 (m, 2H), 7.59-7.57 (m, 3H), 7.39 (d, *J* = 8.0 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, C_3D_6O) δ: 142.0, 141.3, 135.6, 131.5, 130.9, 130.4, 129.6, 129.5, 125.2, 120.6, 113.5, 17.2; IR (KBr, cm-1): 3328, 1529, 1411, 1359; HRMS (EI) for $C_{14}H_{10}N_3O_4$ $(M^+ + H)^+$: calcd 284.0666, found 284.0641.

(C) References

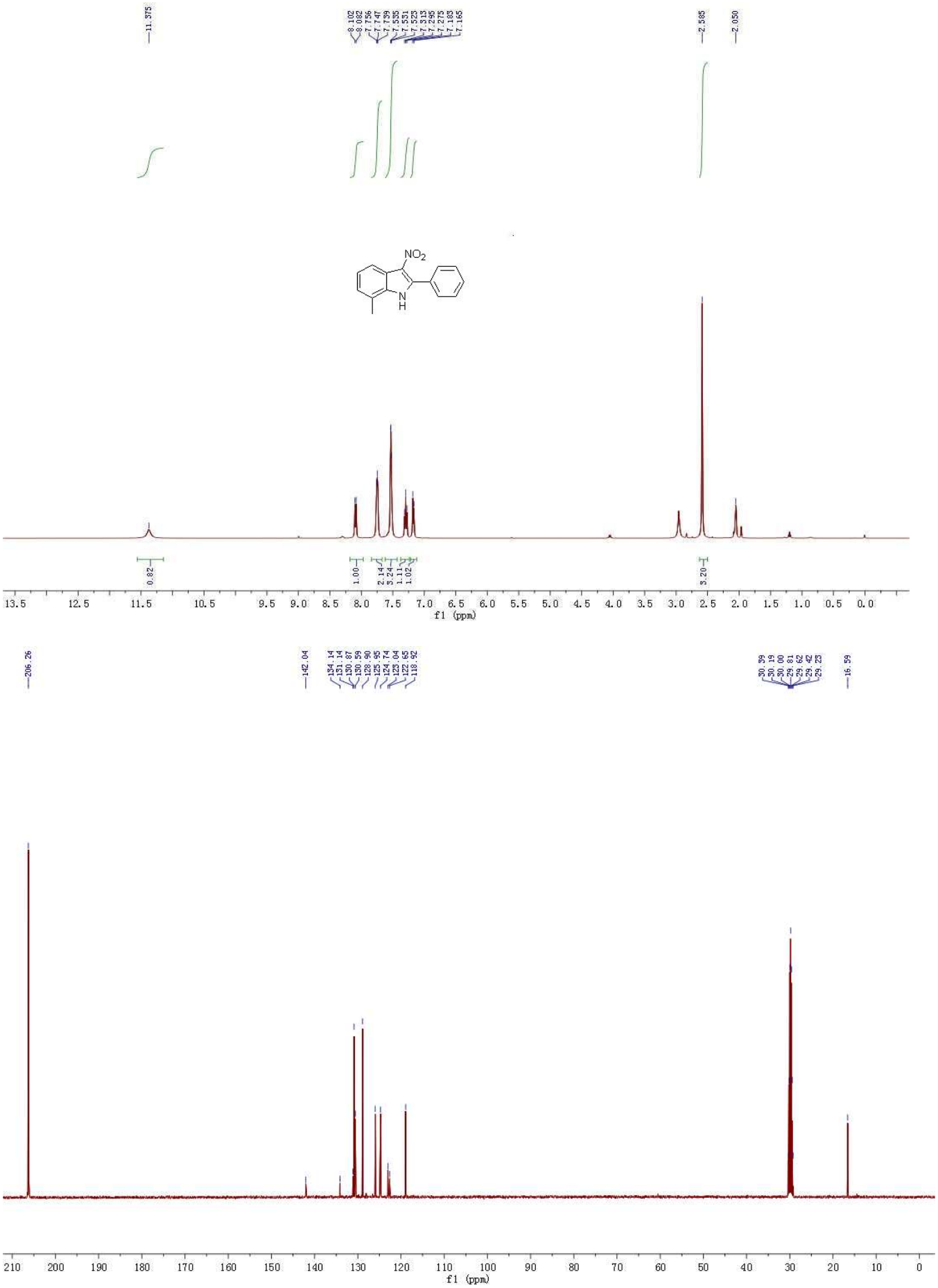
(1) H. H. Nguyen and M. J. Kurth, *Org.Lett.*, 2013, **15**, 362.

(2) W. Q. Yu, Y. F. Du and K. Zhao, *Org.Lett.,* 2009, **11**, 2417.

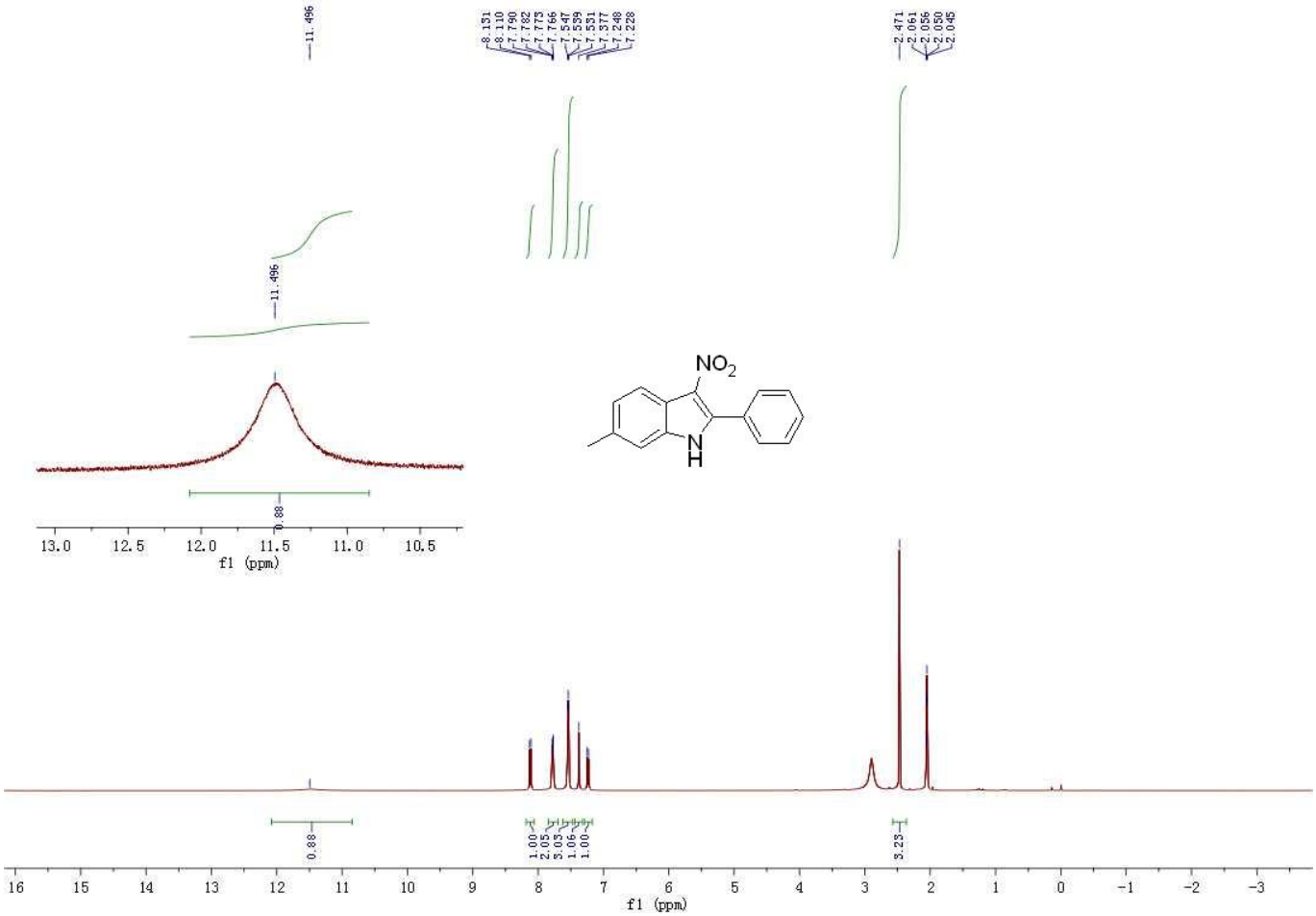
(3) A. Roychowdhury, V. V. Kumar and A. P. Bhaduri, *Synthetic Communications.,* 2006, **36**, 715.

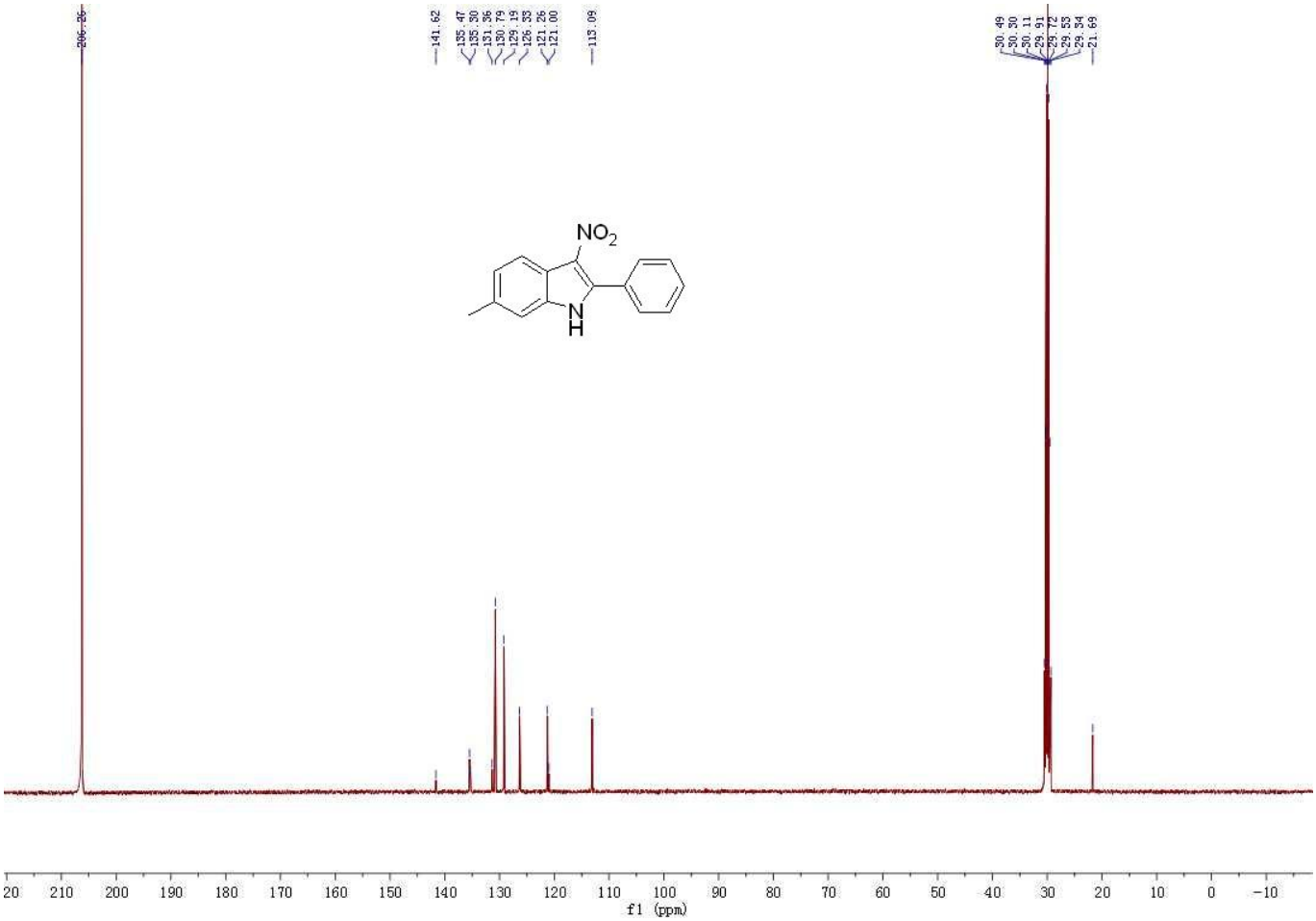
(D) Spectra

7-Methyl-3-nitro-2-phenyl-1*H*-indole (3a)

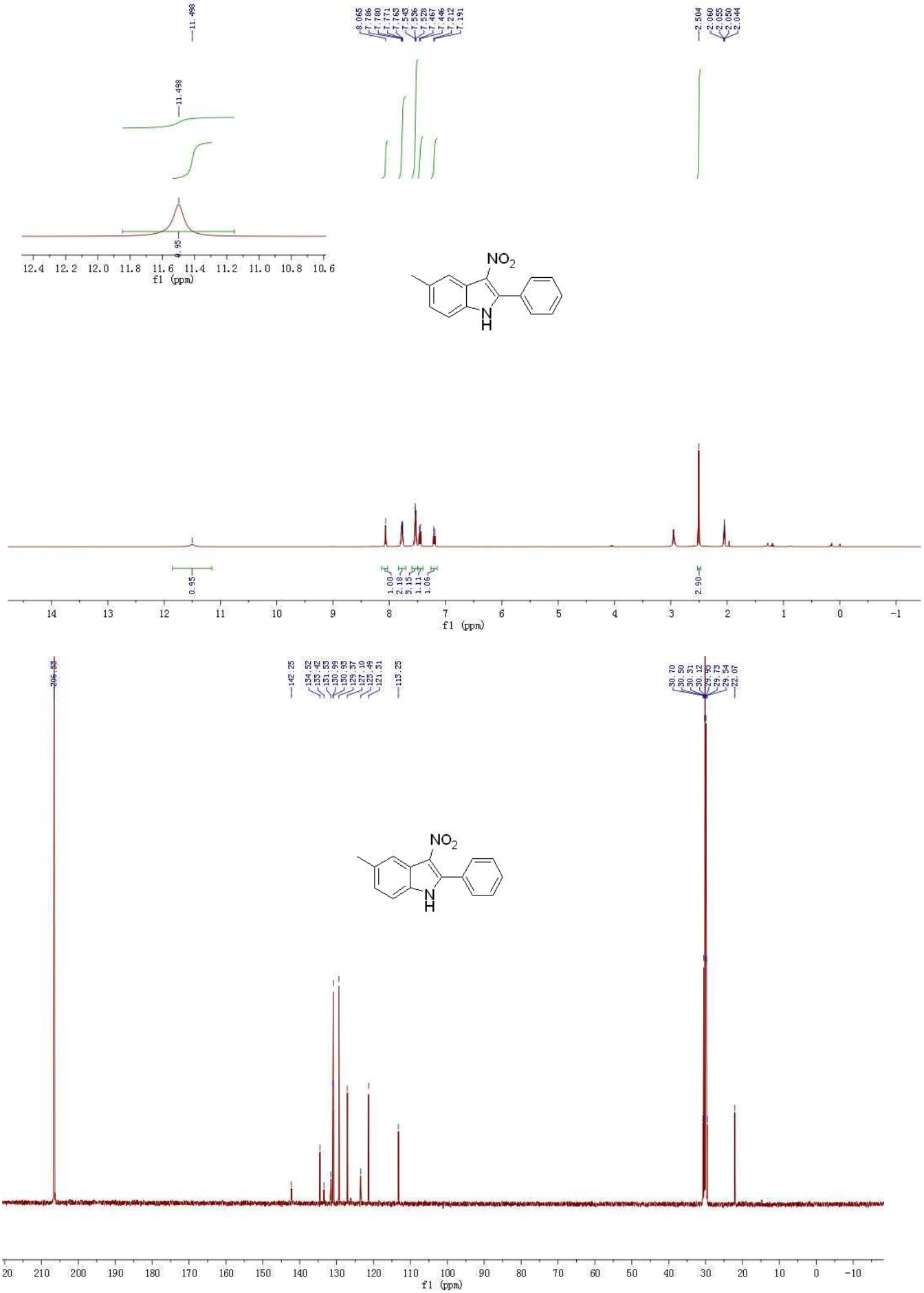


6-Methyl-3-nitro-2-phenyl-1*H*-indole (3b)

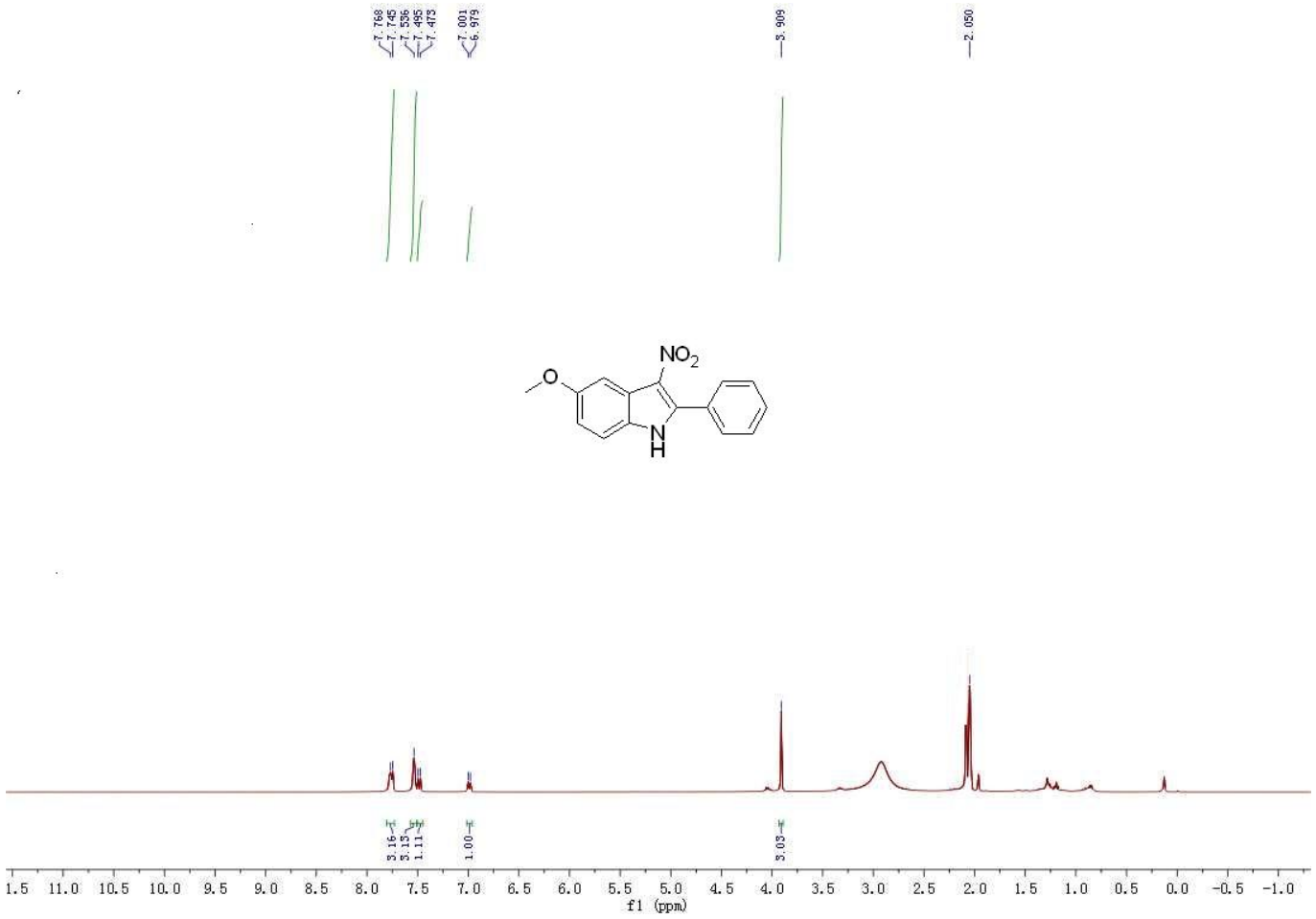


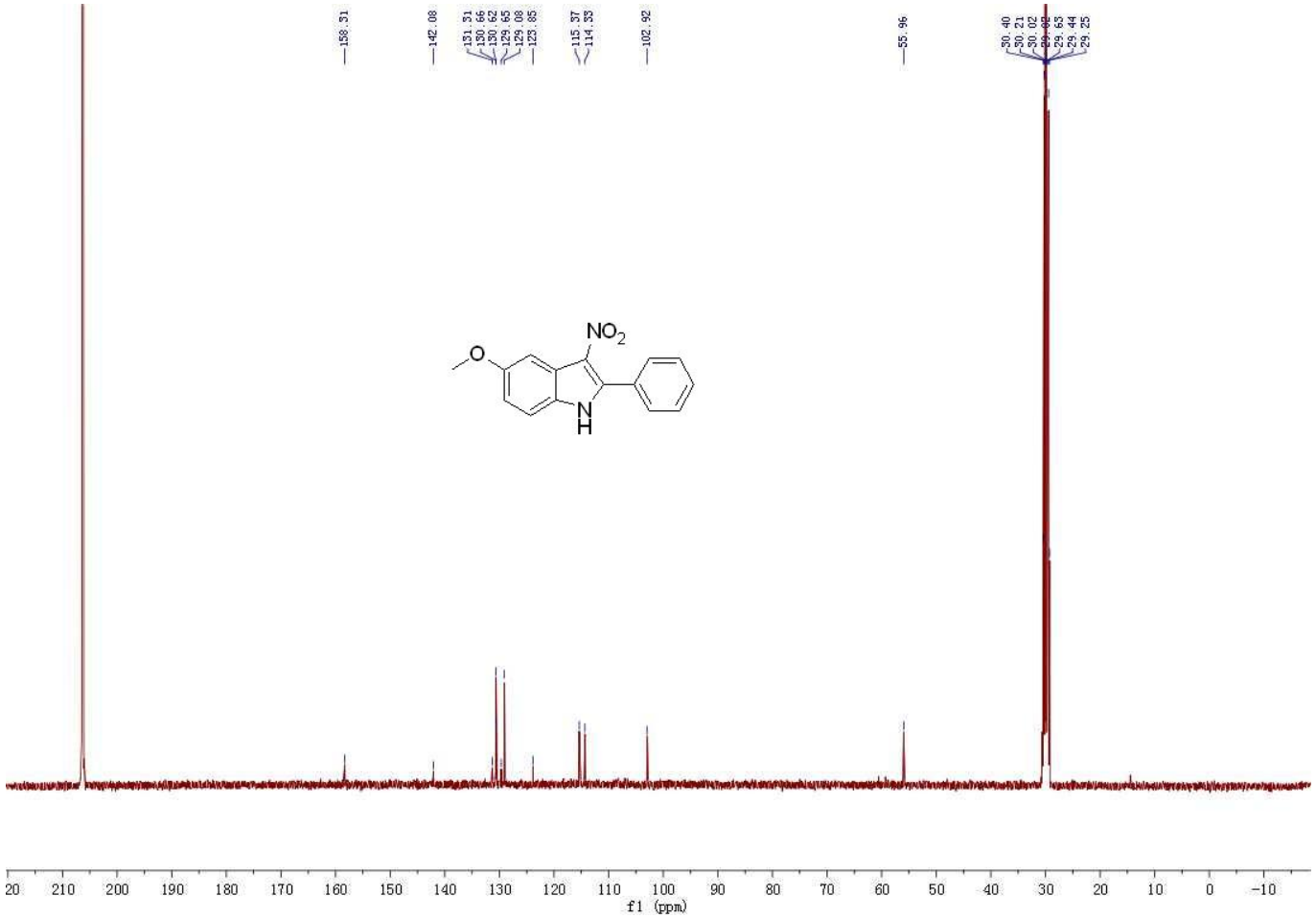


5-Methyl-3-nitro-2-phenyl-1*H*-indole (3c)

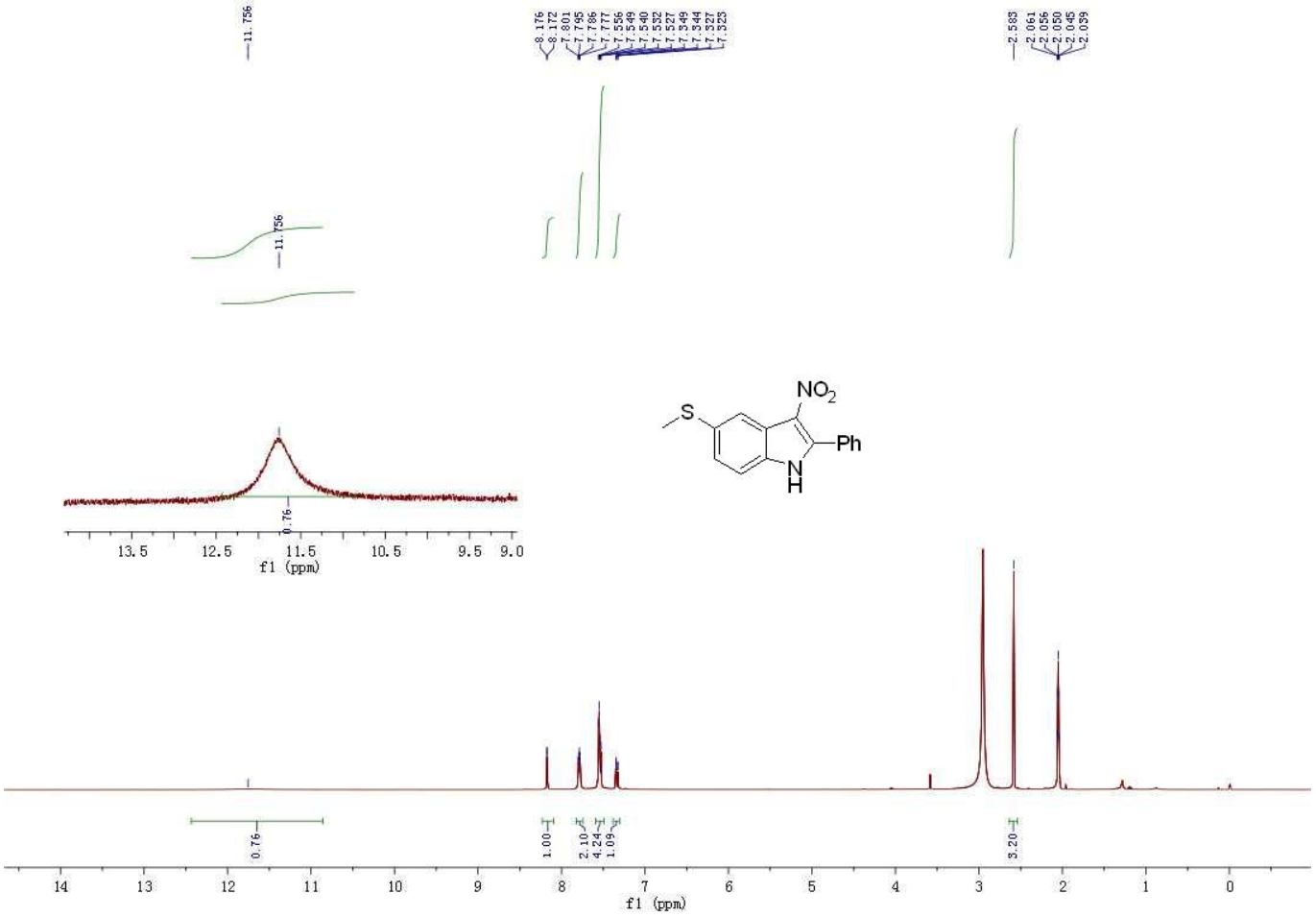


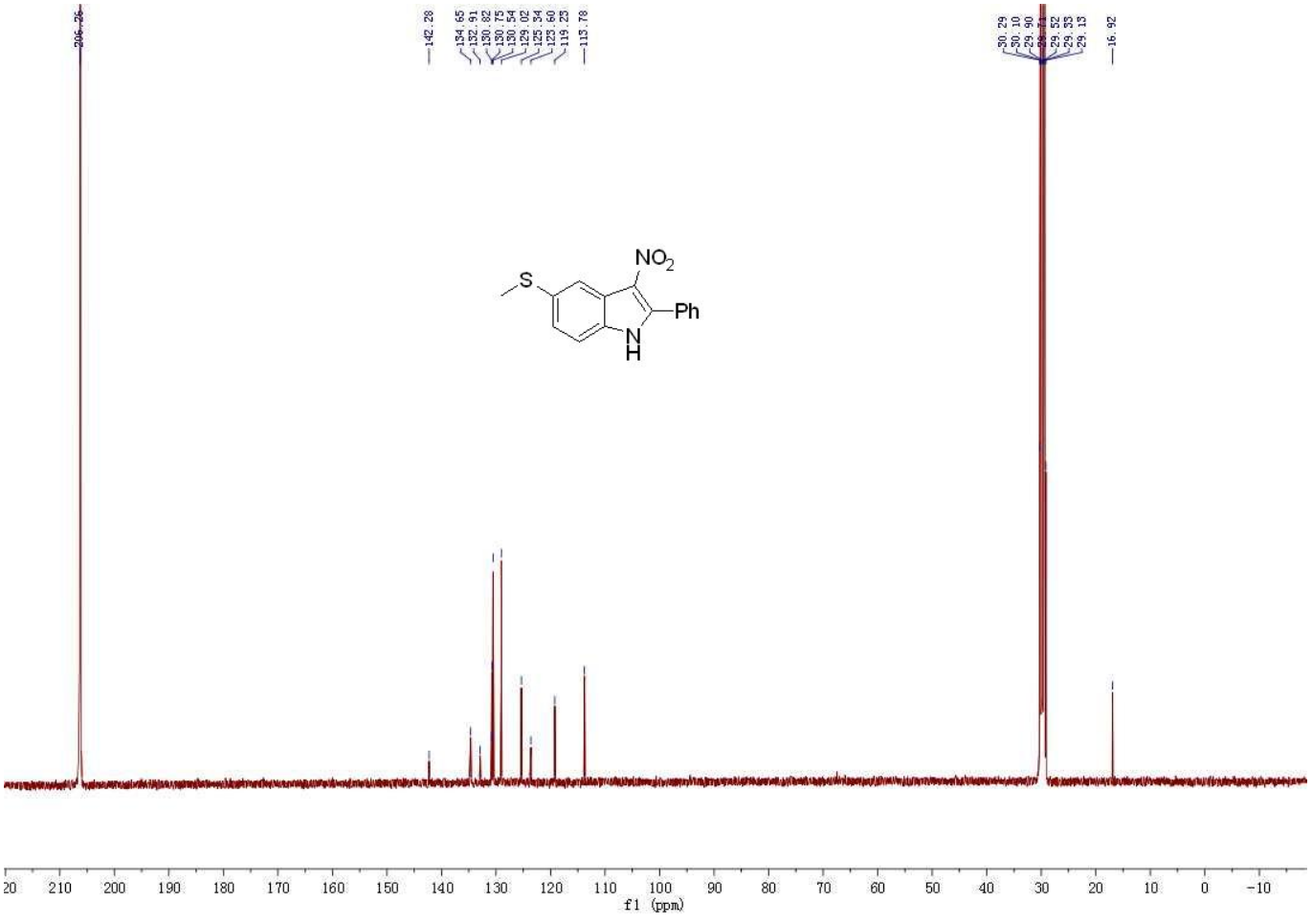
5-Methoxy-3-nitro-2-phenyl-1*H*-indole (3d)



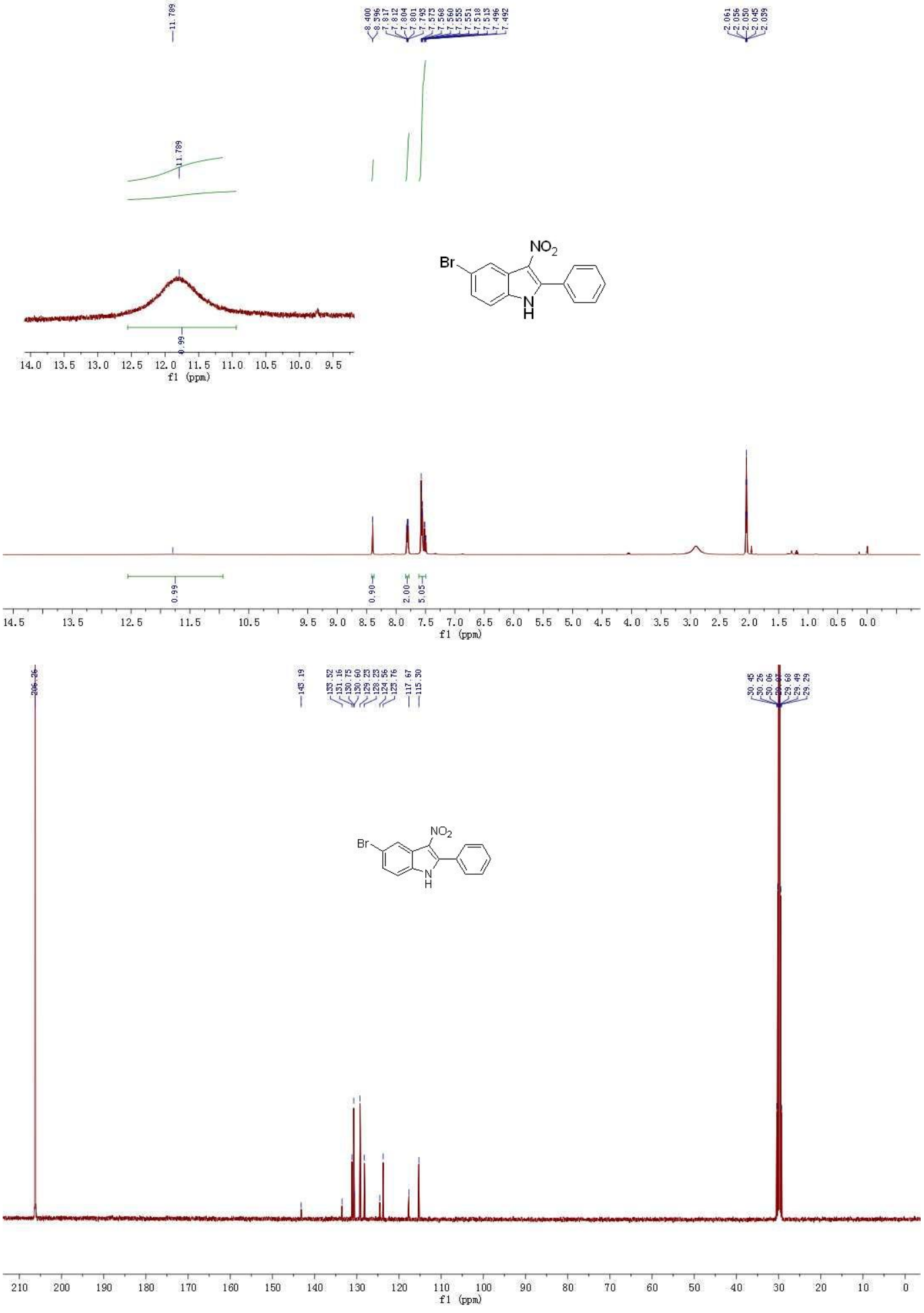


5-(Methylthio)-3-nitro-2-phenyl-1*H*-indole (3e)

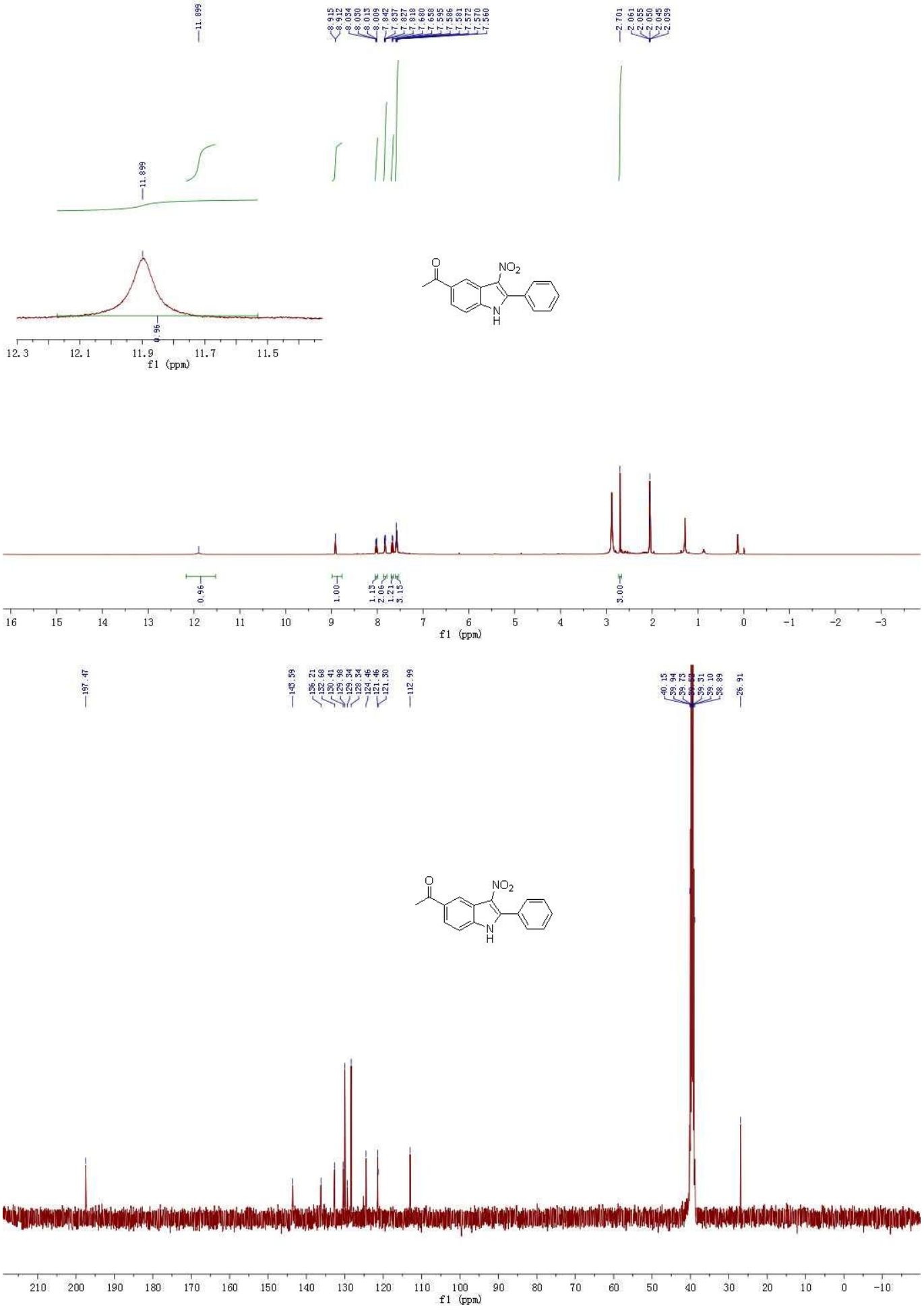




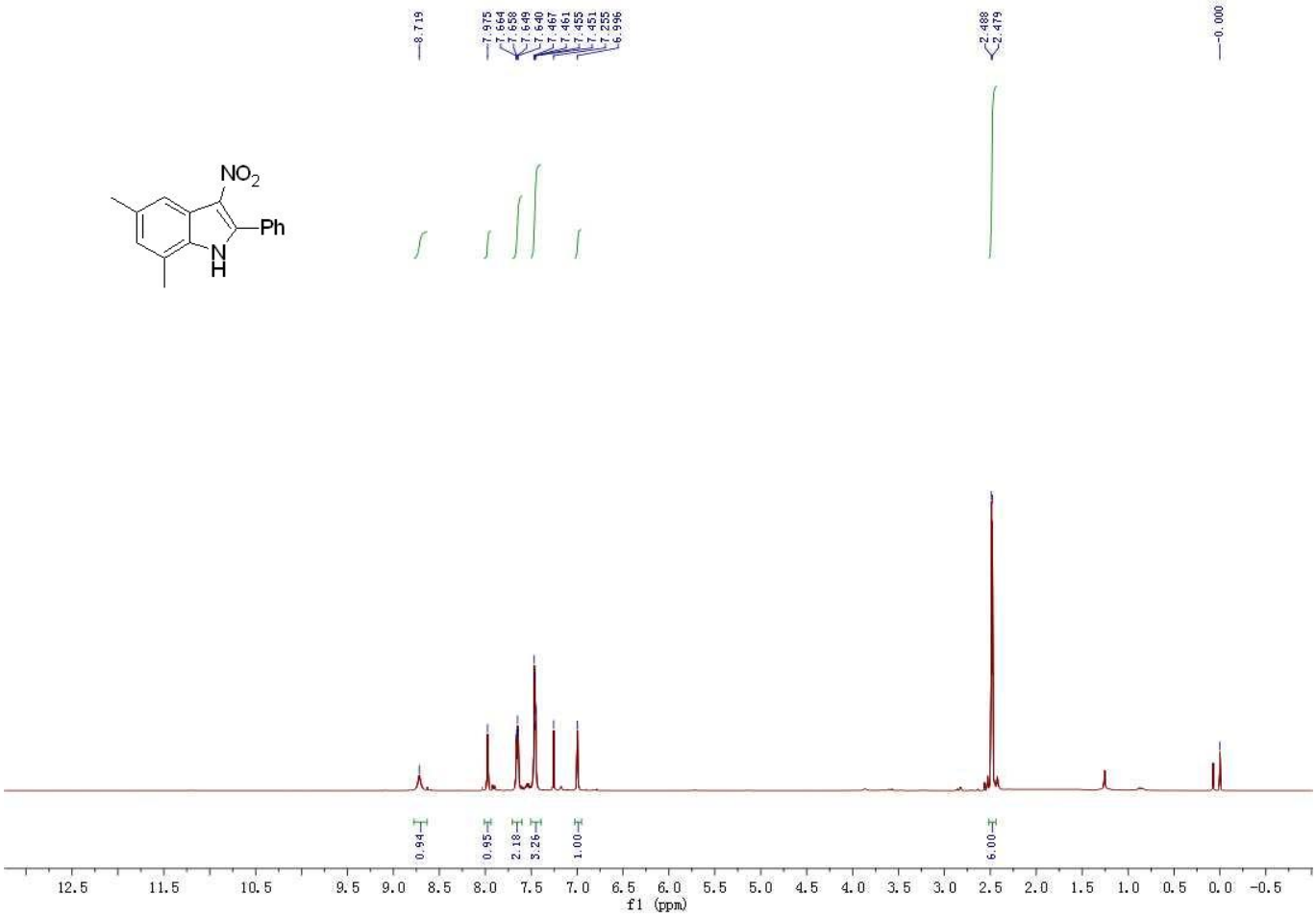
5-Bromo-3-nitro-2-phenyl-1*H*-indole (3f)

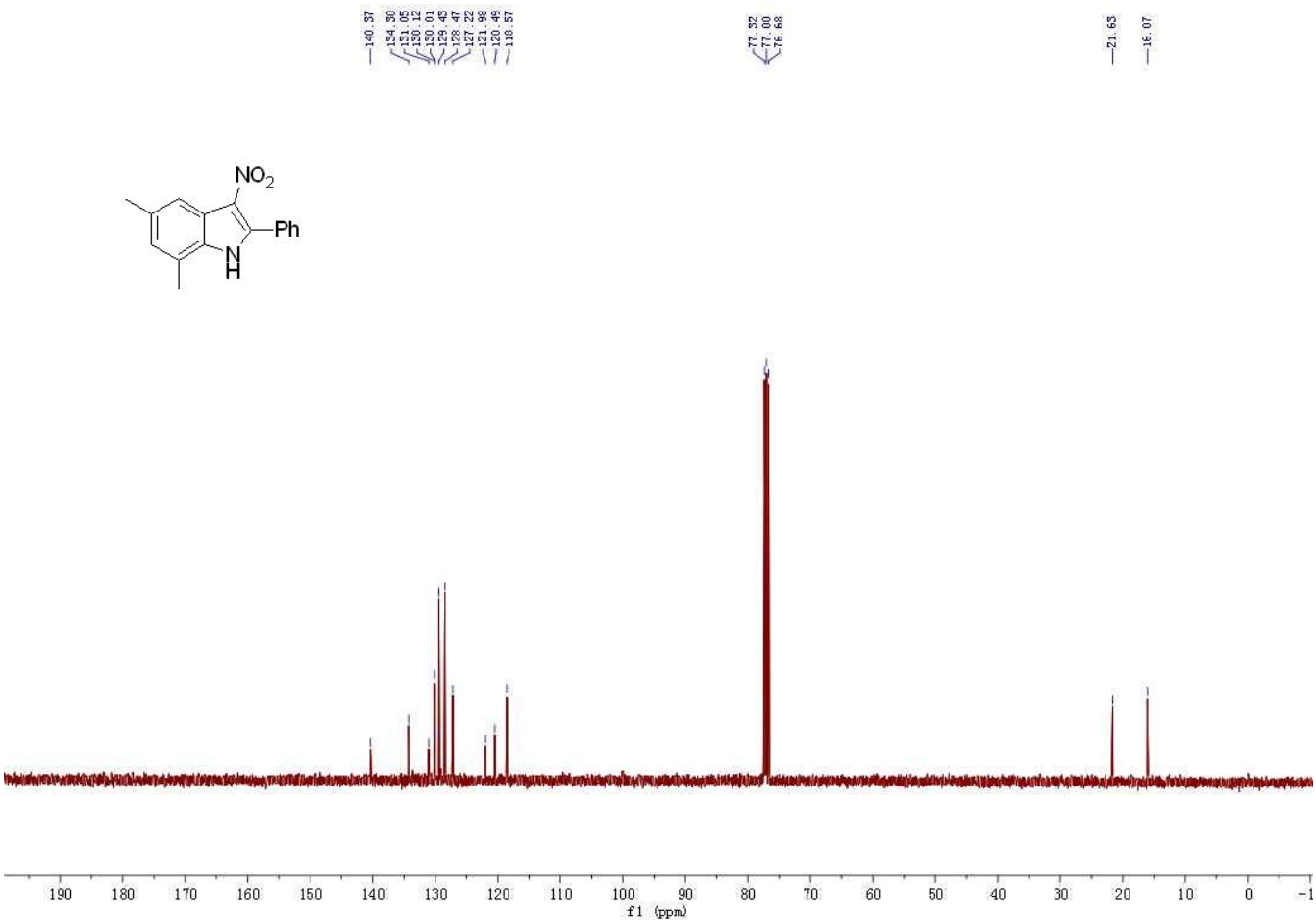


1-(3-Nitro-2-phenyl-1*H*-indol-5-yl)ethanone (3g)

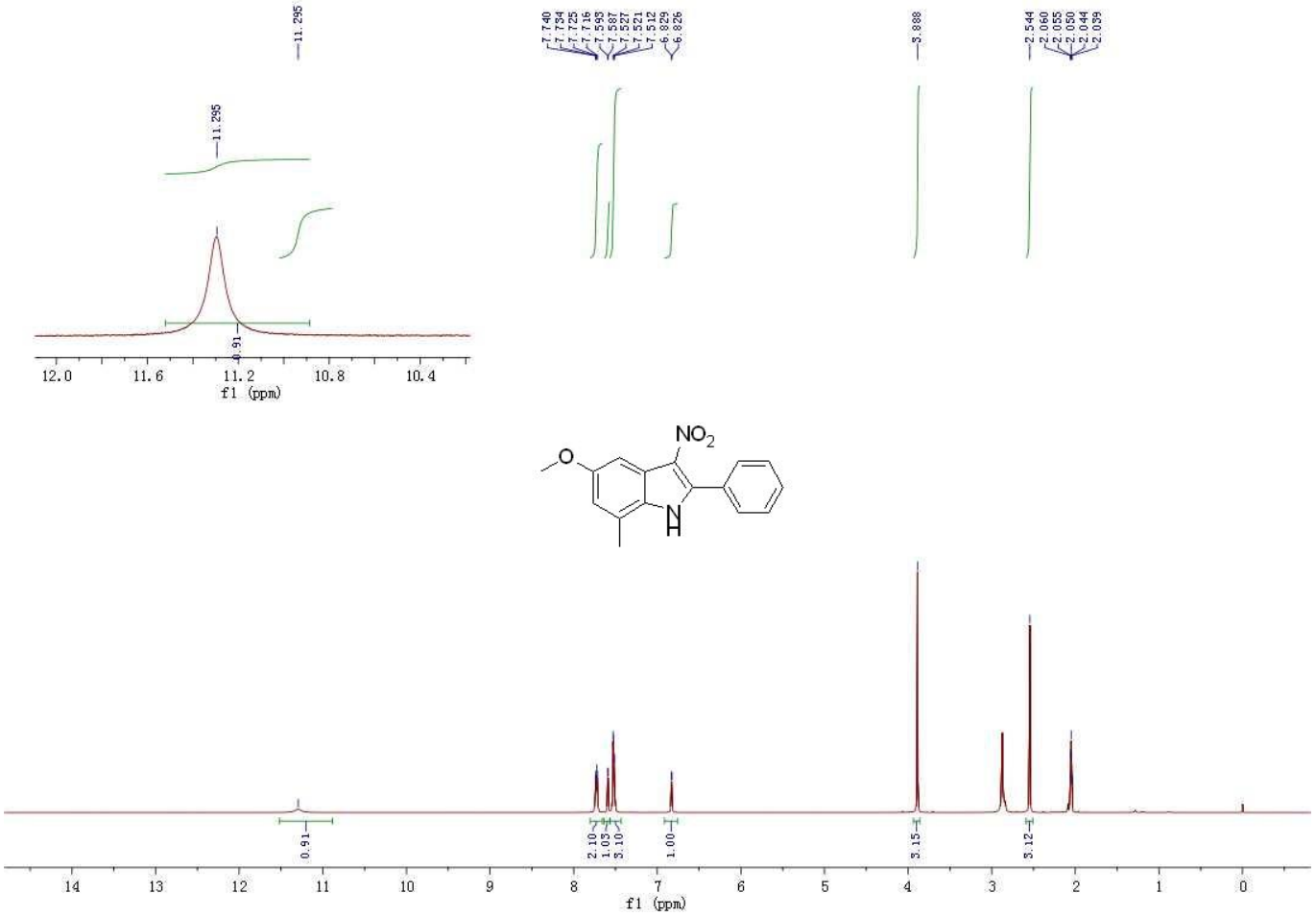


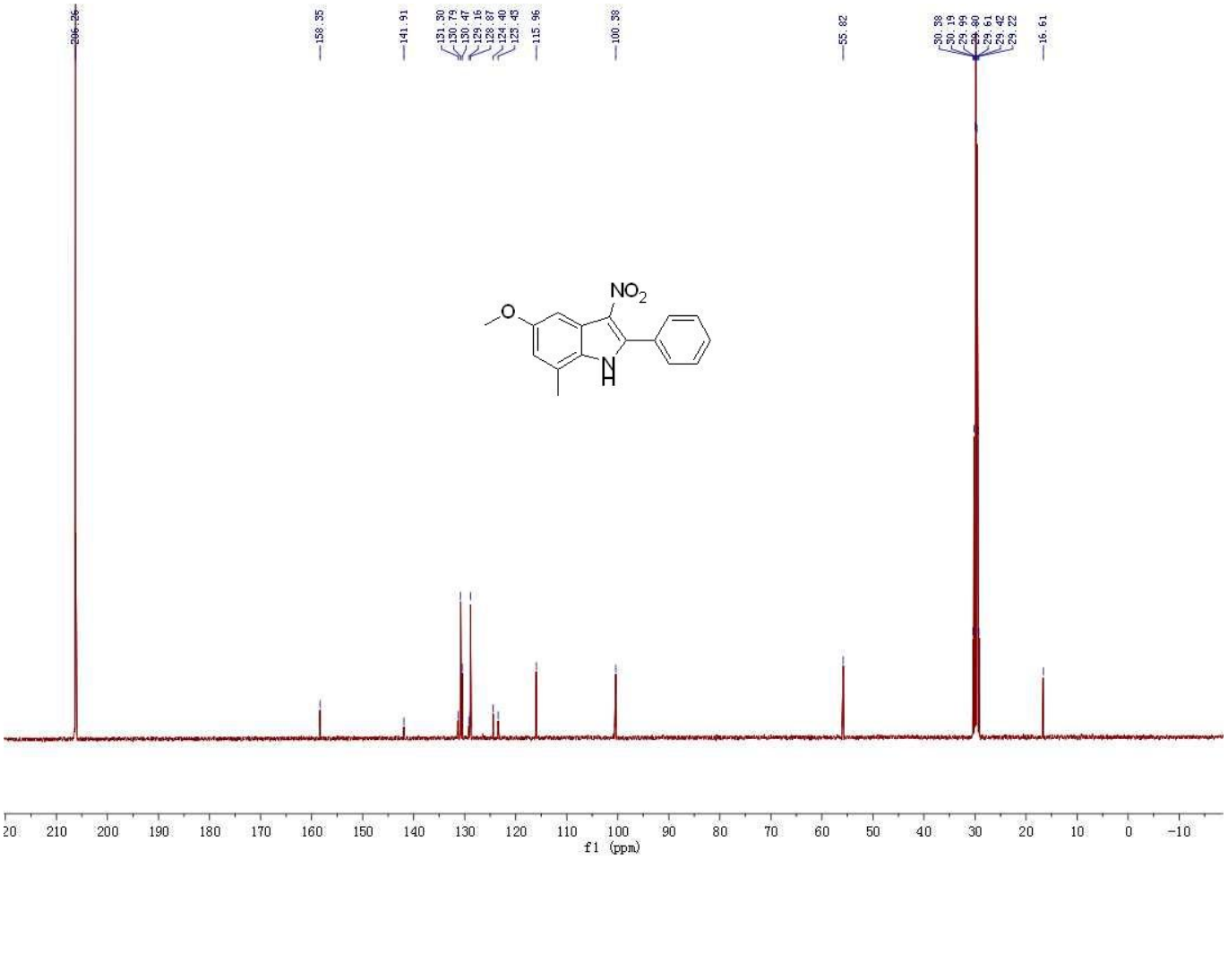
5,7-Dimethyl-3-nitro-2-phenyl-1*H*-indole (3h)



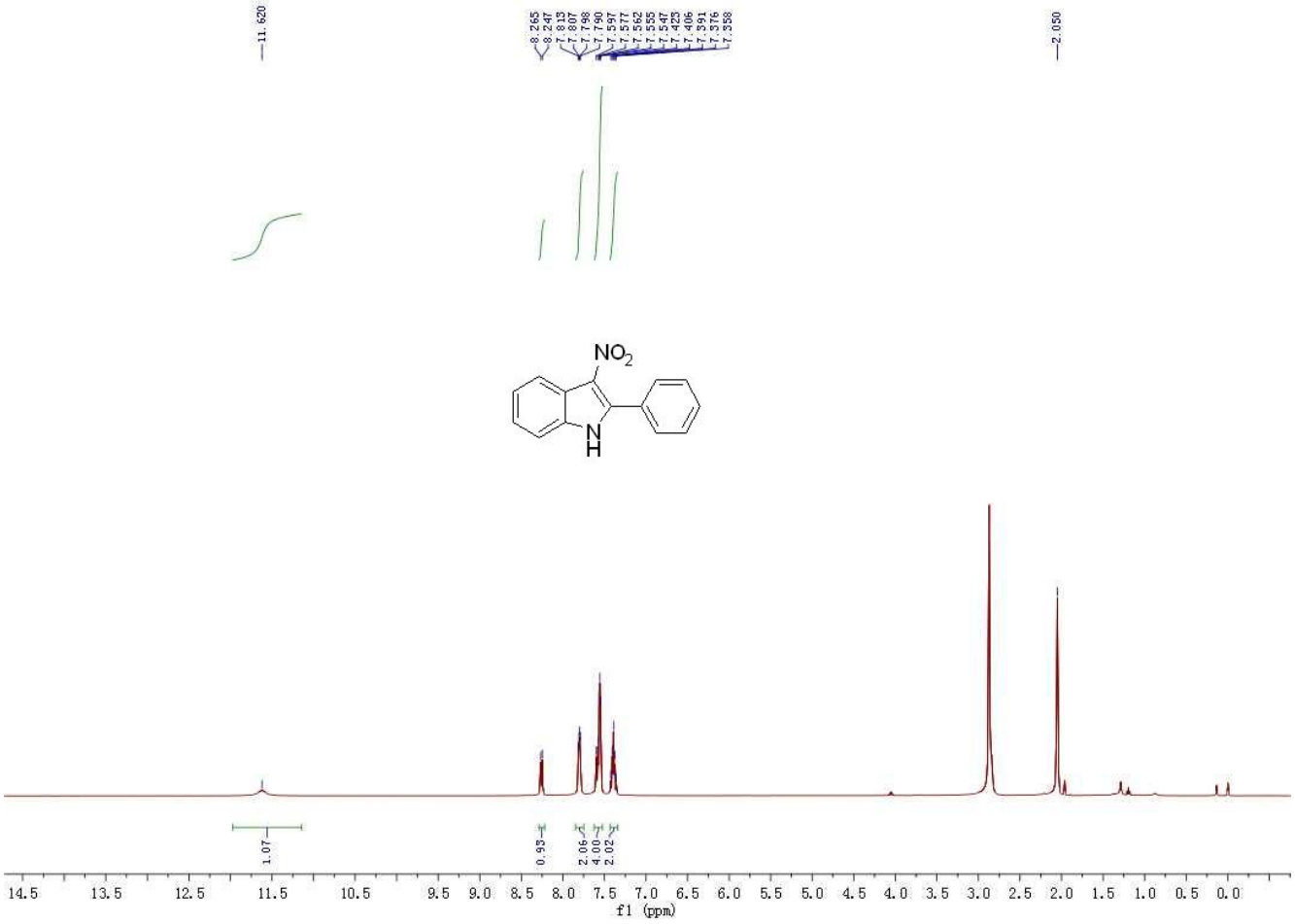


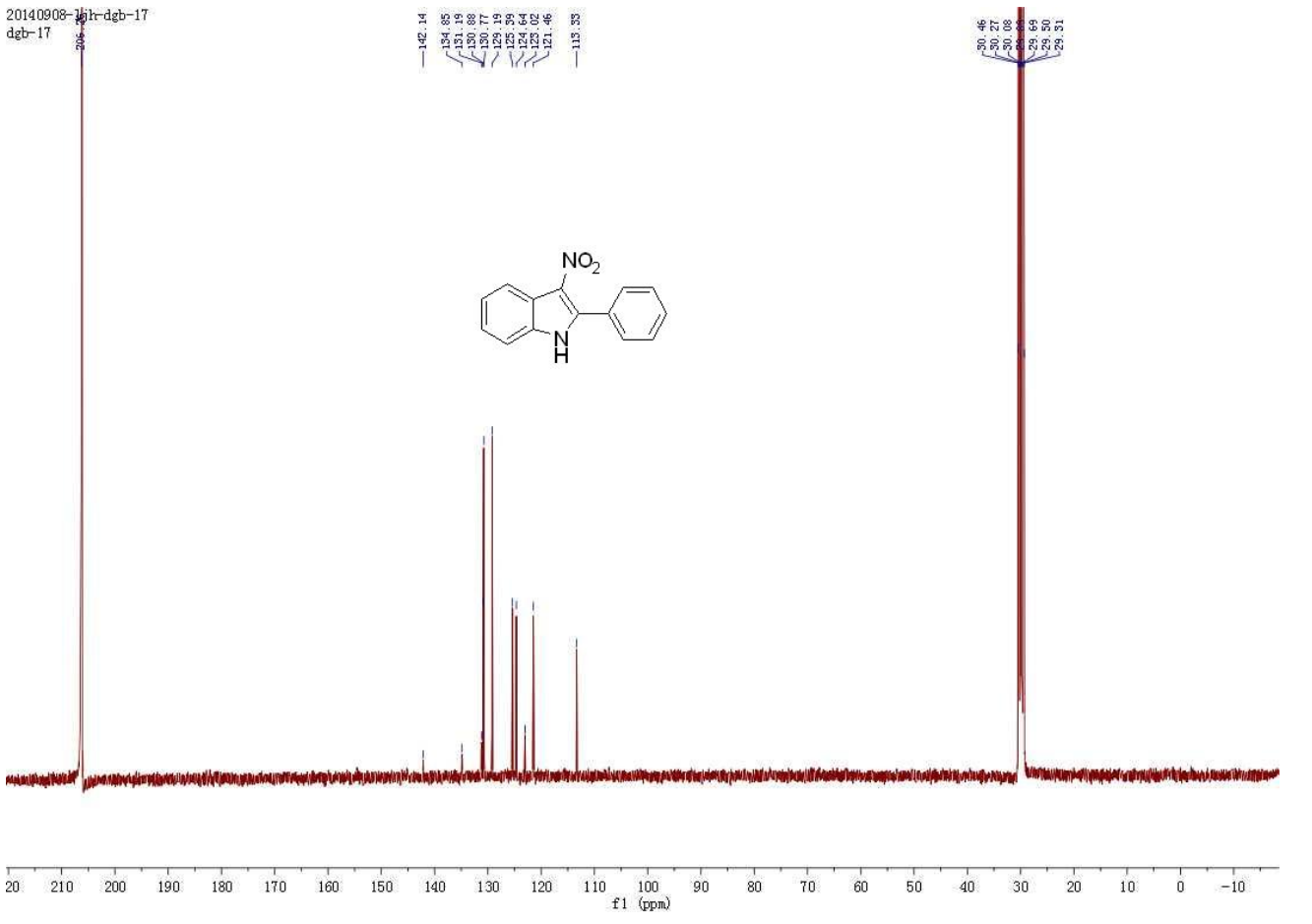
5-Methoxy-7-methyl-3-nitro-2-phenyl-1*H*-indole (3i)



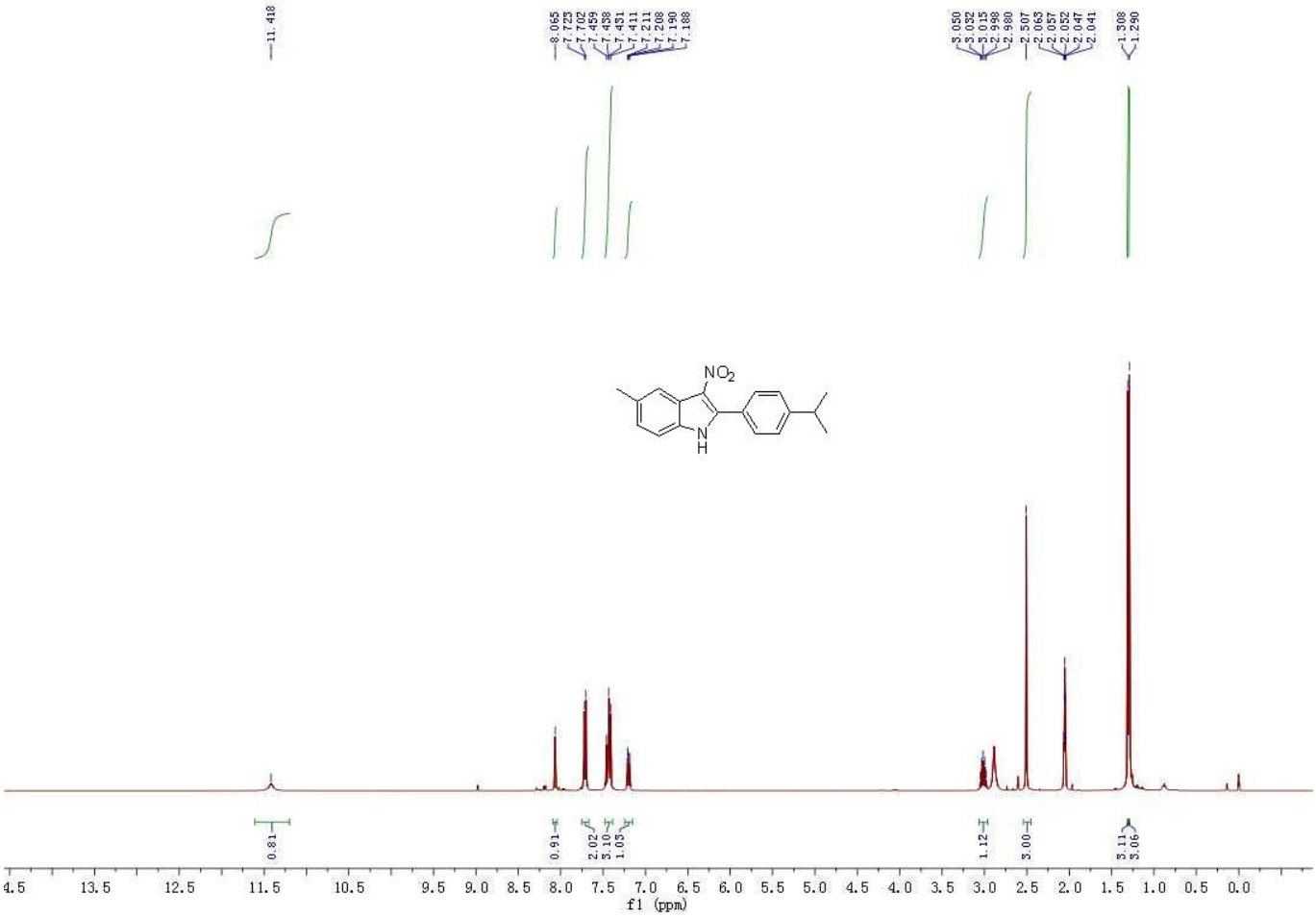


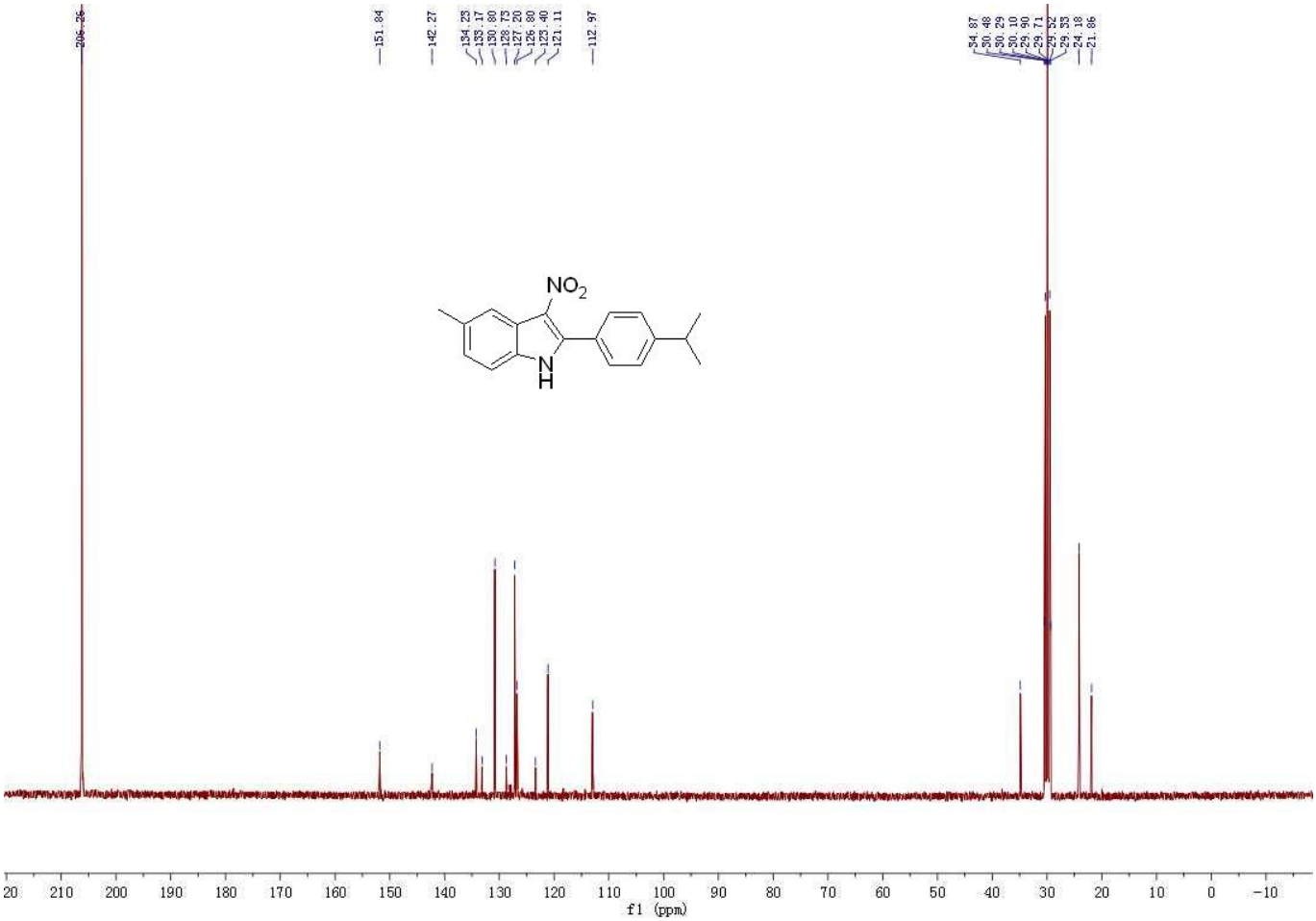
3-Nitro-2-phenyl-1*H*-indole (3j)



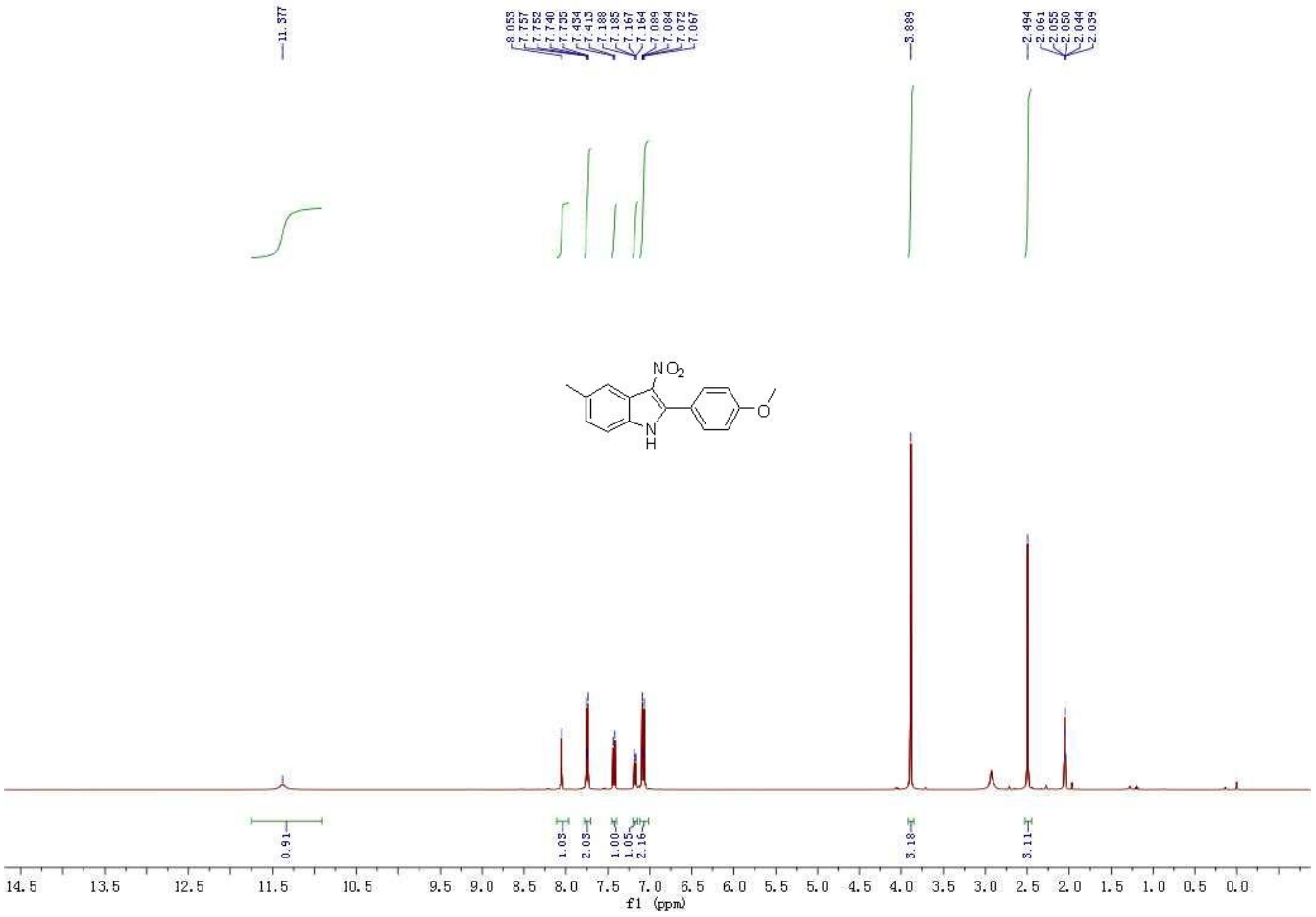


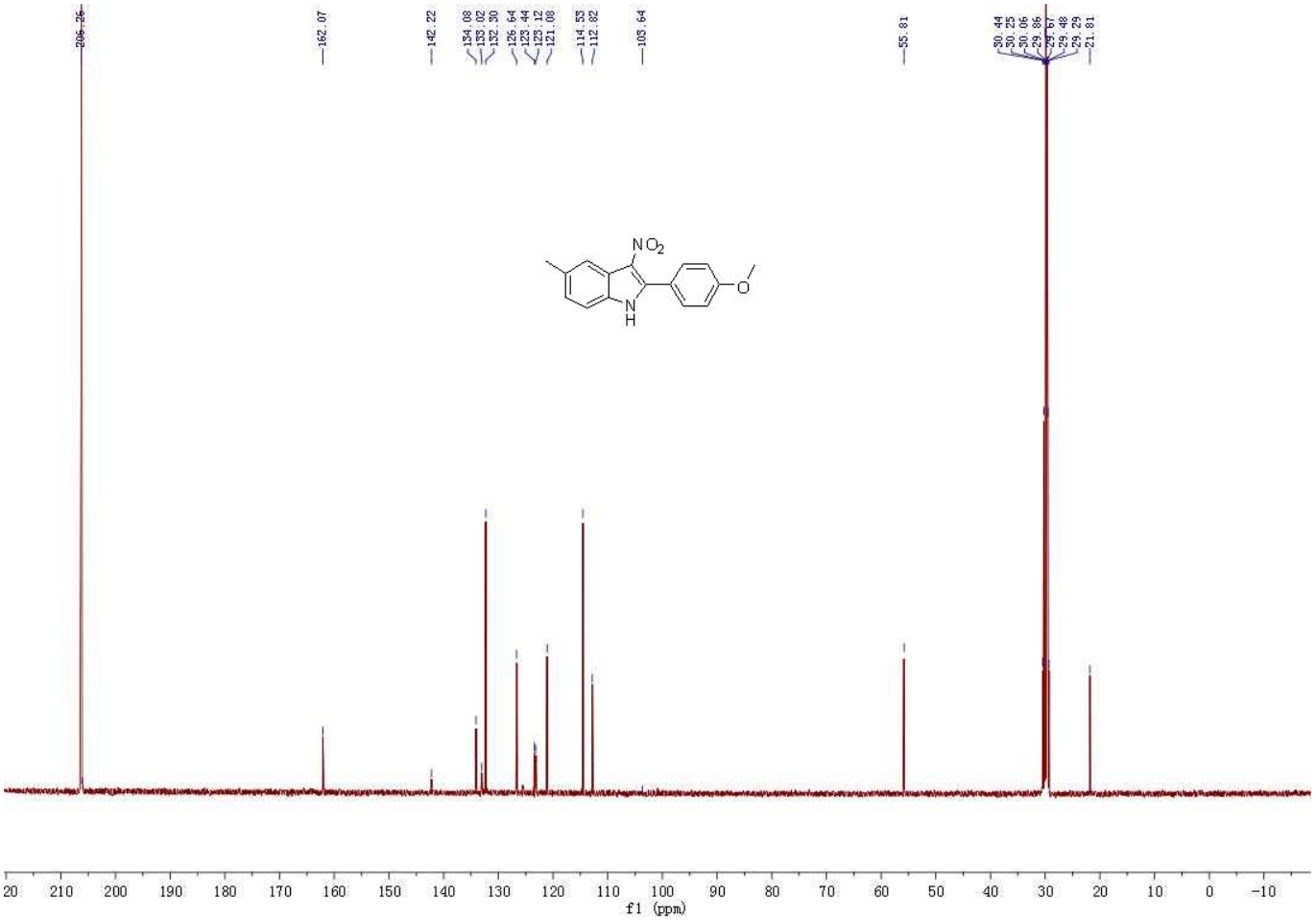
2-(4-Isopropylphenyl)-5-methyl-3-nitro-1*H*-indole (3k):



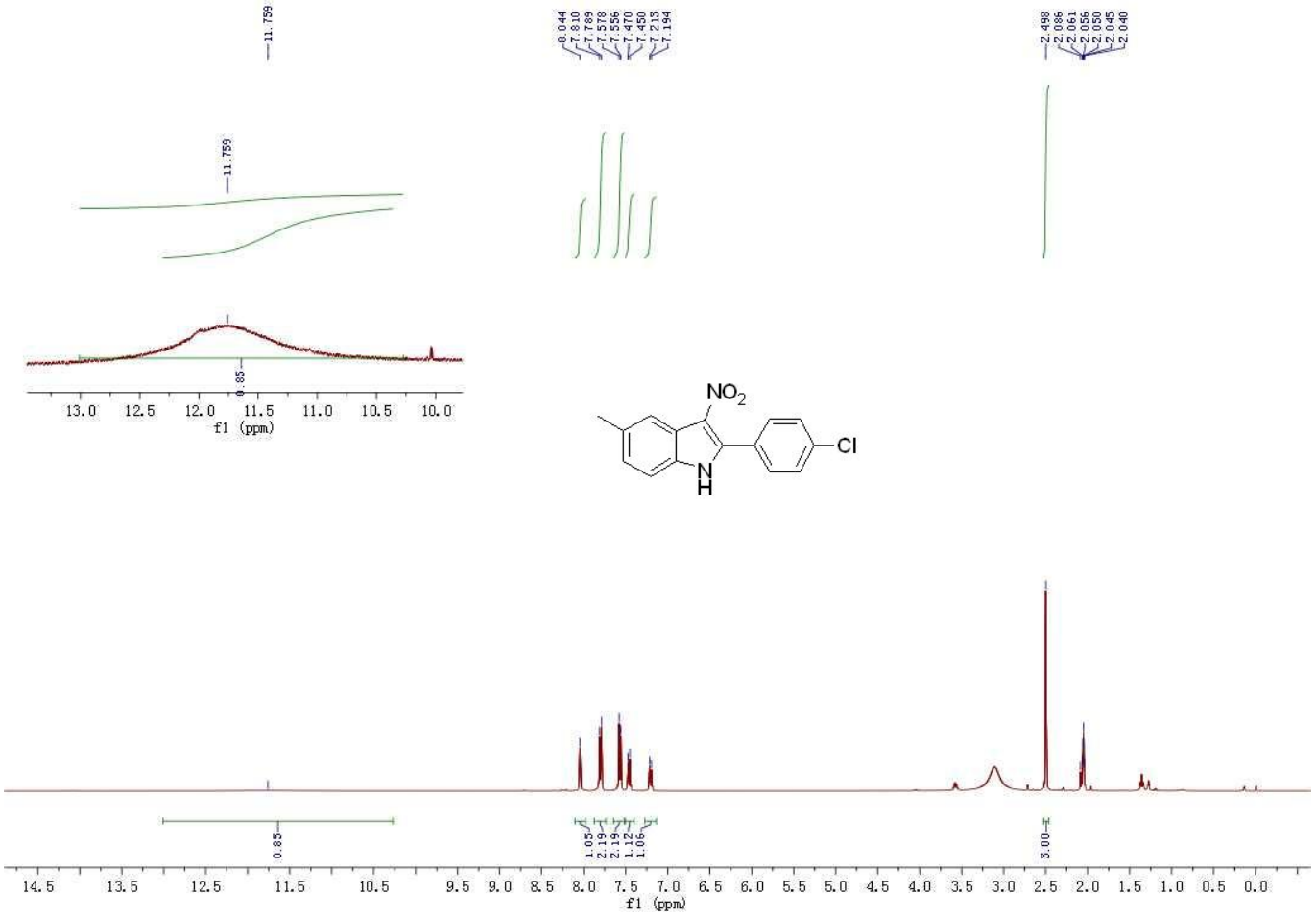


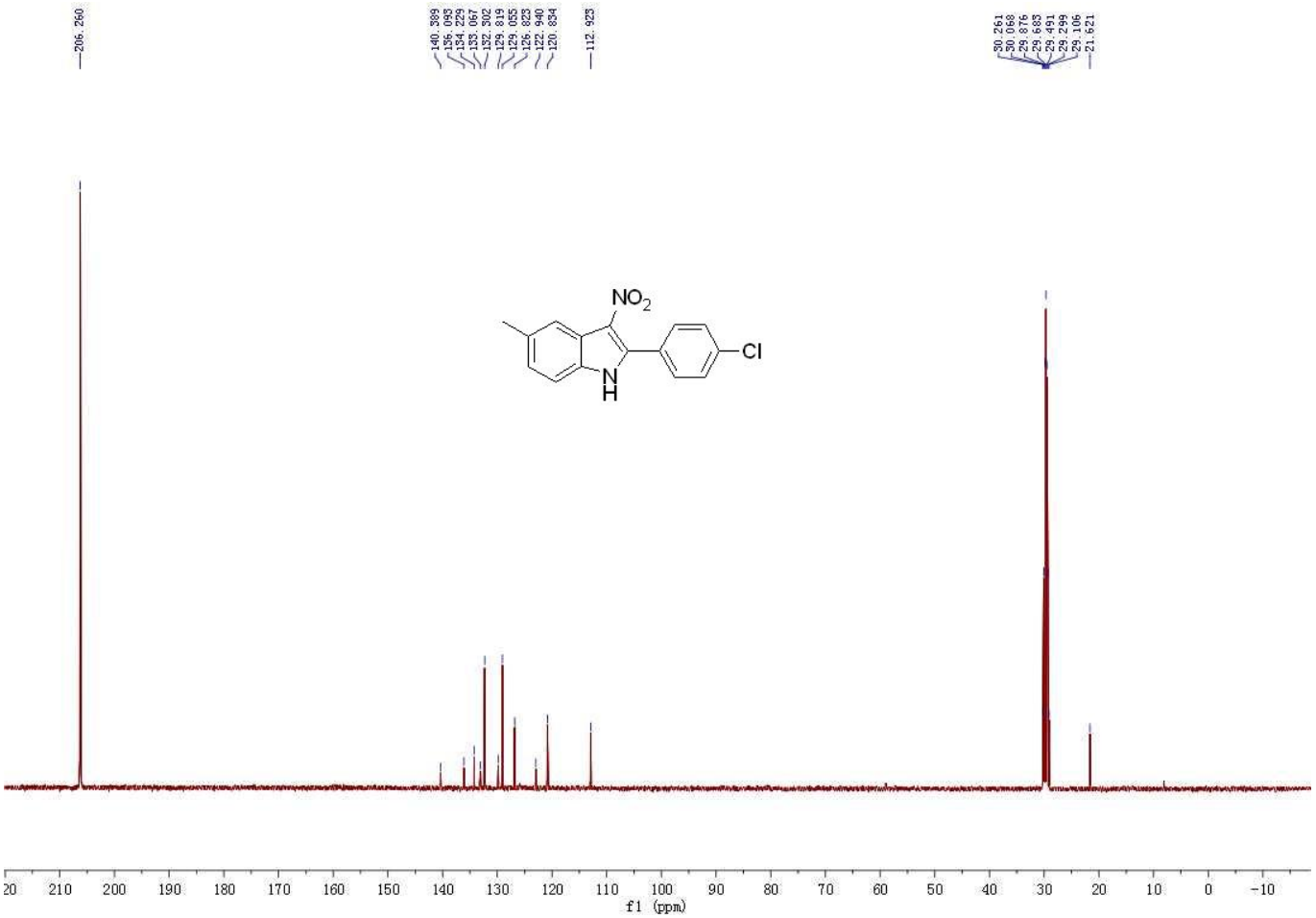
2-(4-Methoxyphenyl)-5-methyl-3-nitro-1*H*-indole (3l):



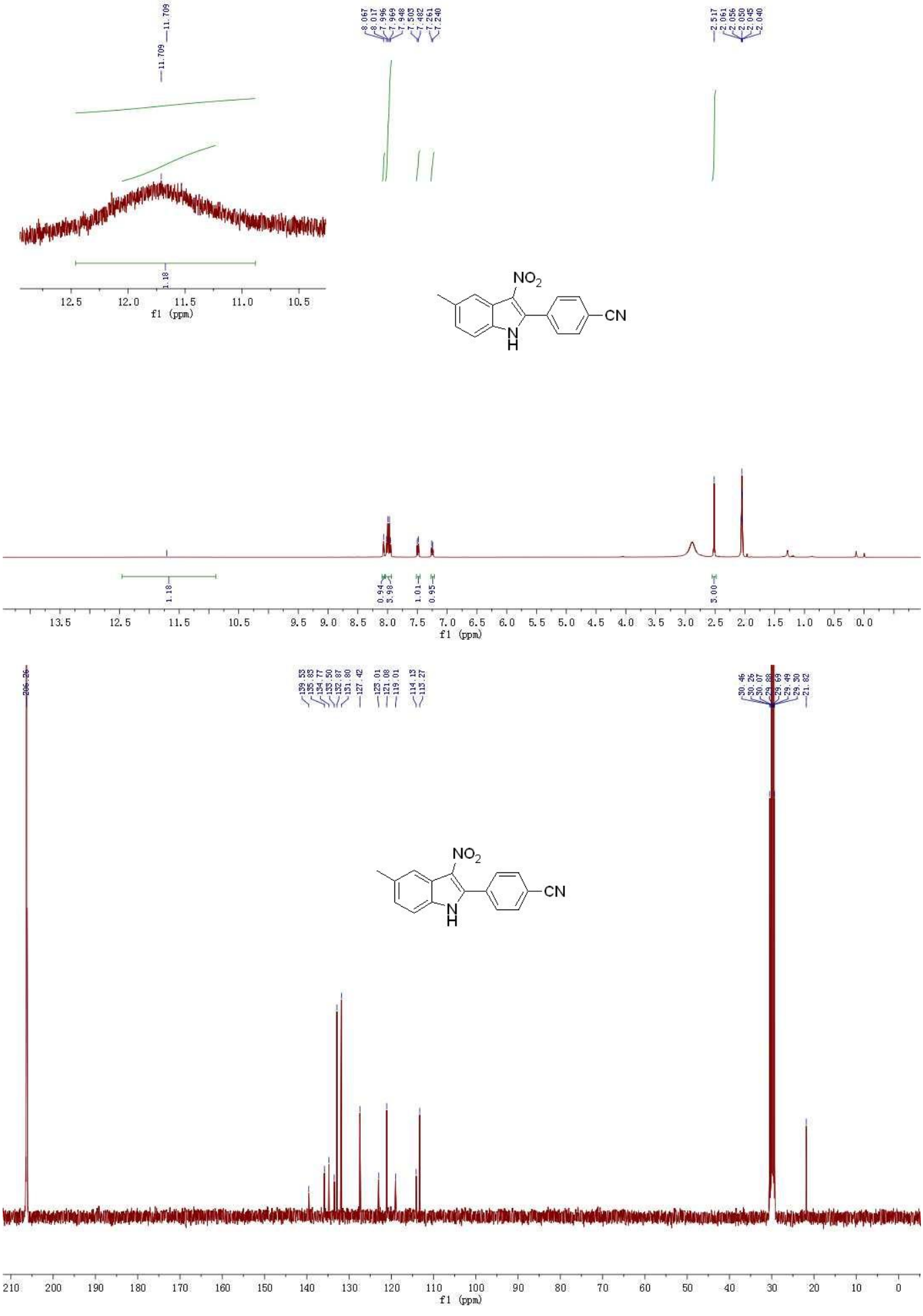


2-(4-Chlorophenyl)-5-methyl-3-nitro-1*H*-indole (3m):

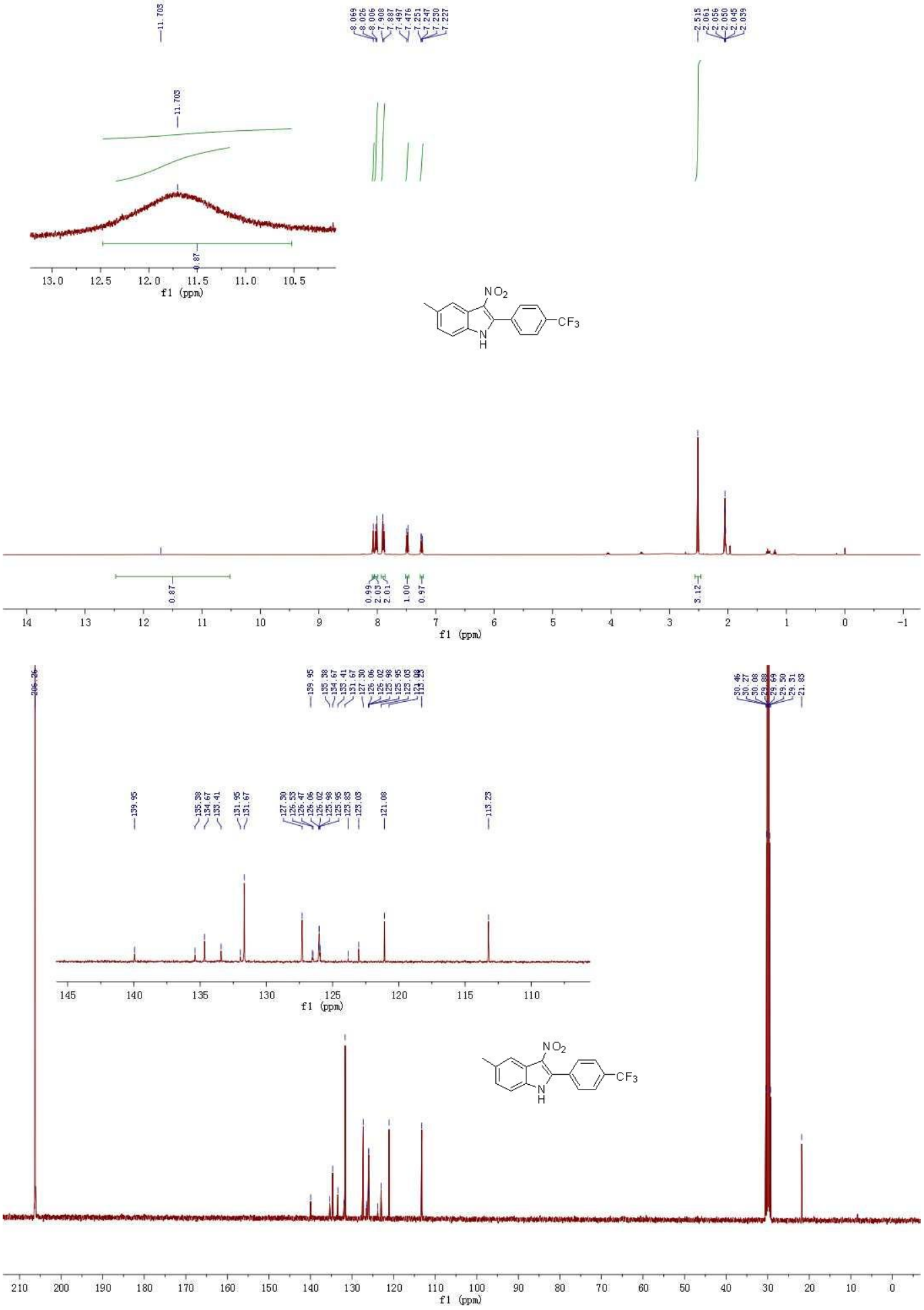


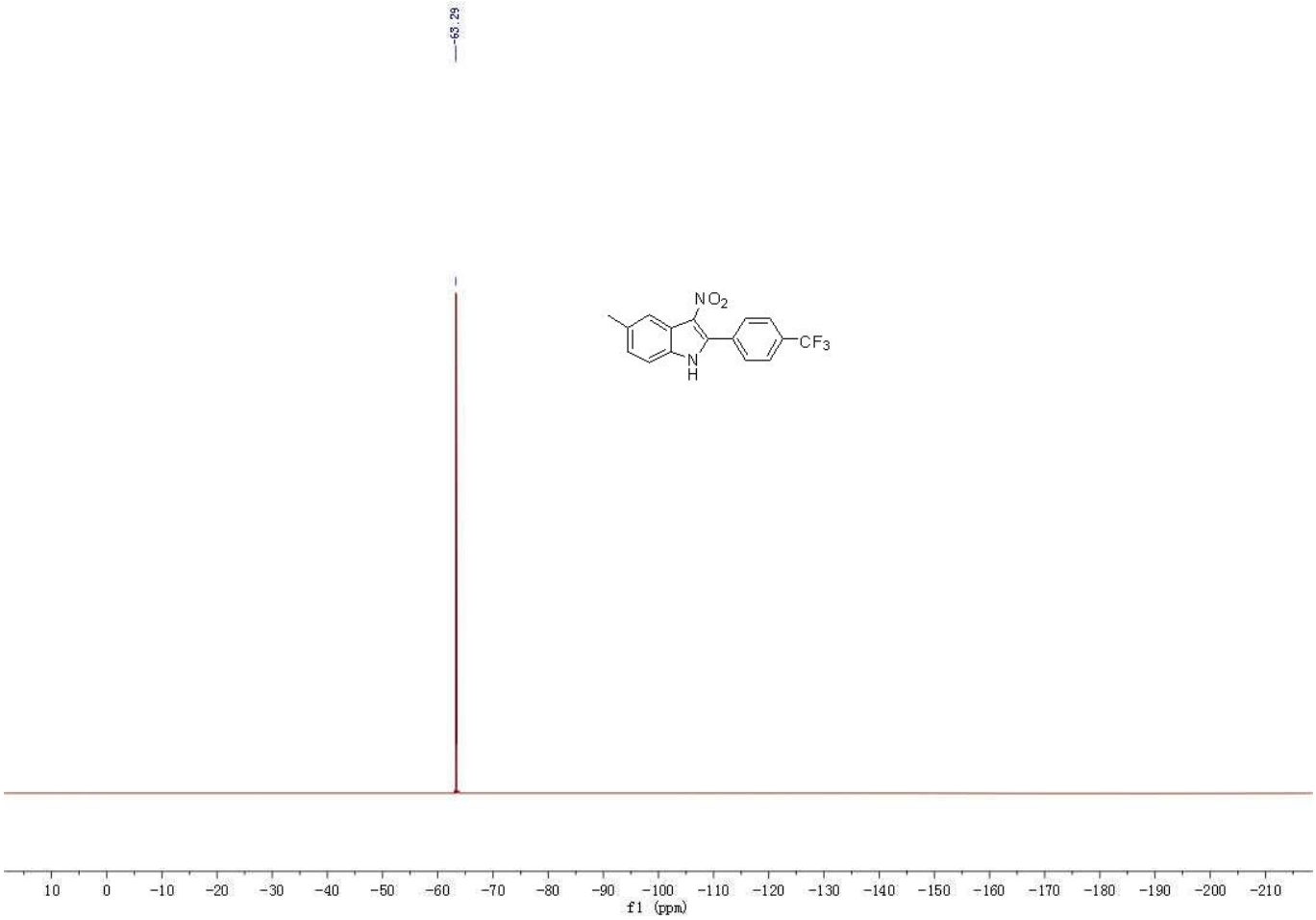


4-(5-Methyl-3-nitro-1*H*-indol-2-yl)benzonitrile (3n)

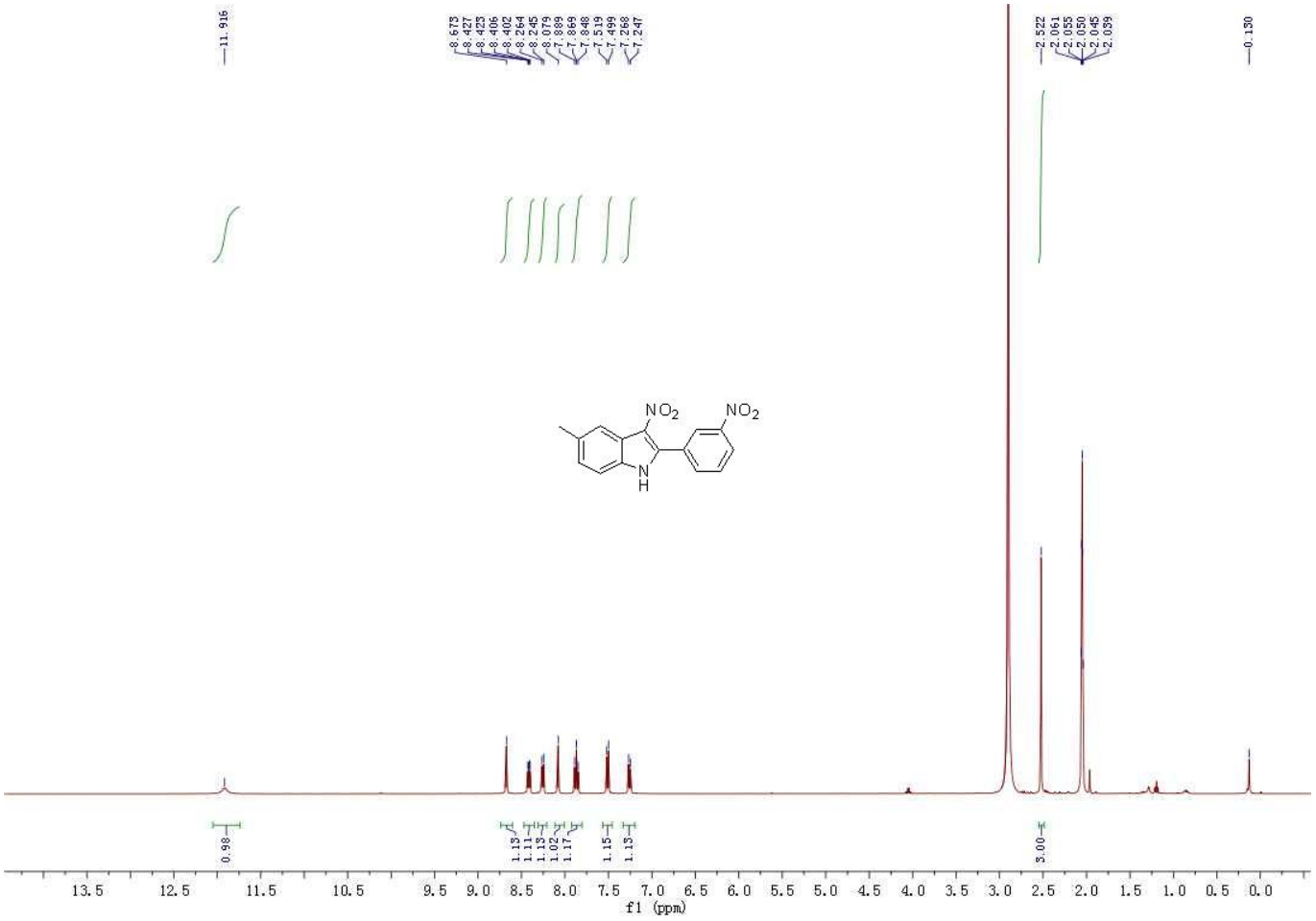


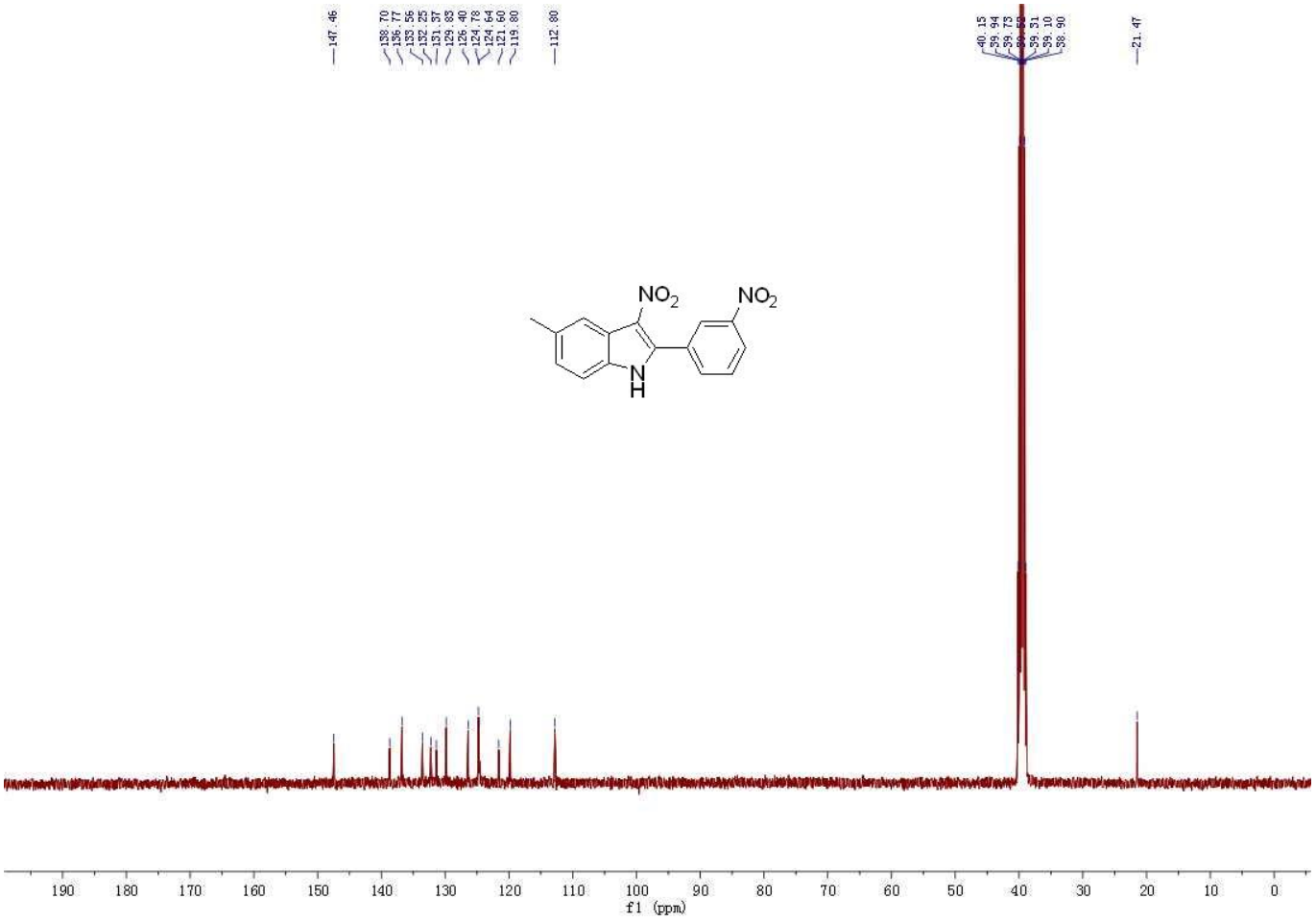
5-Methyl-3-nitro-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (3o)



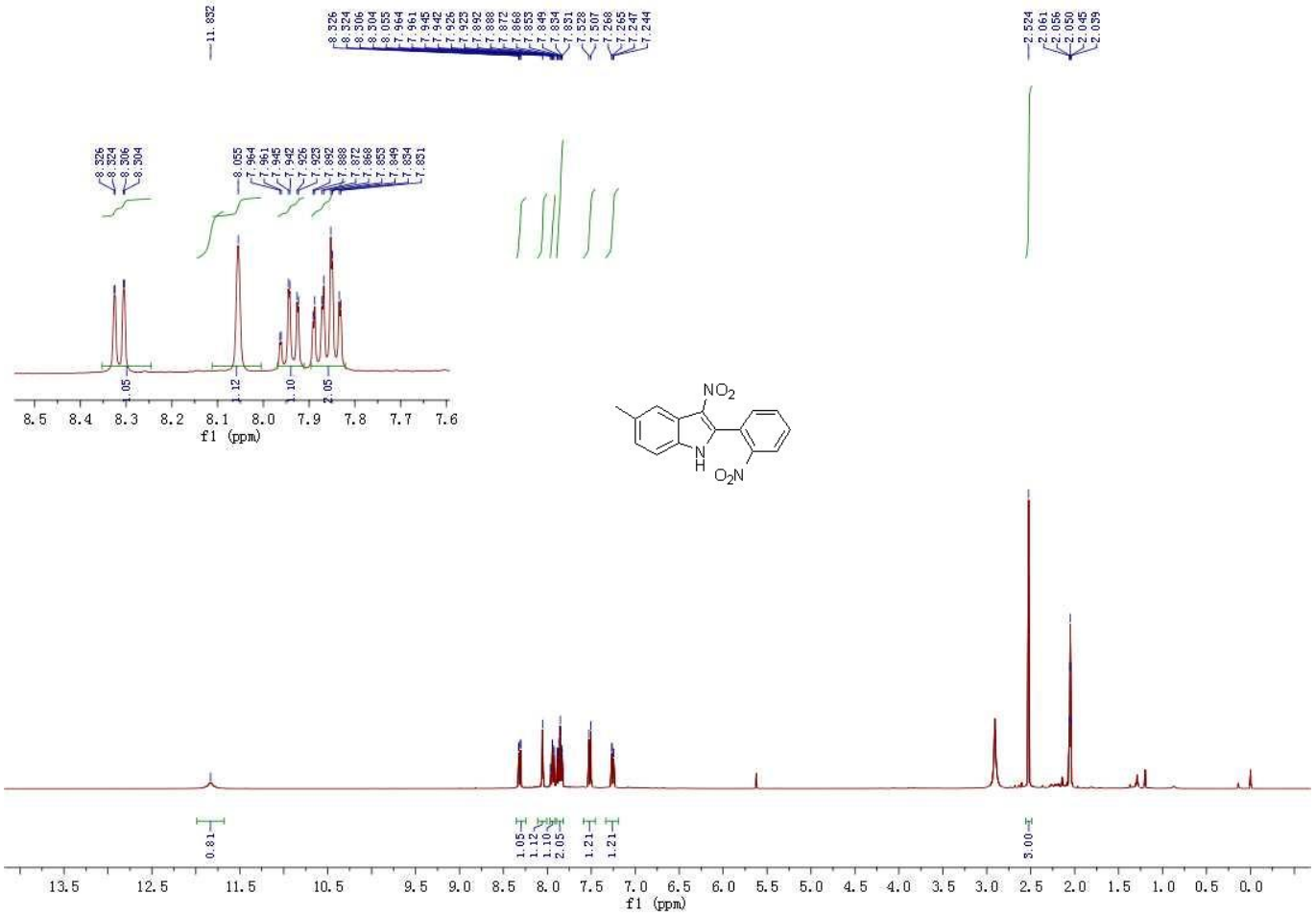

-63.29
NO2
CF3
N
H
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

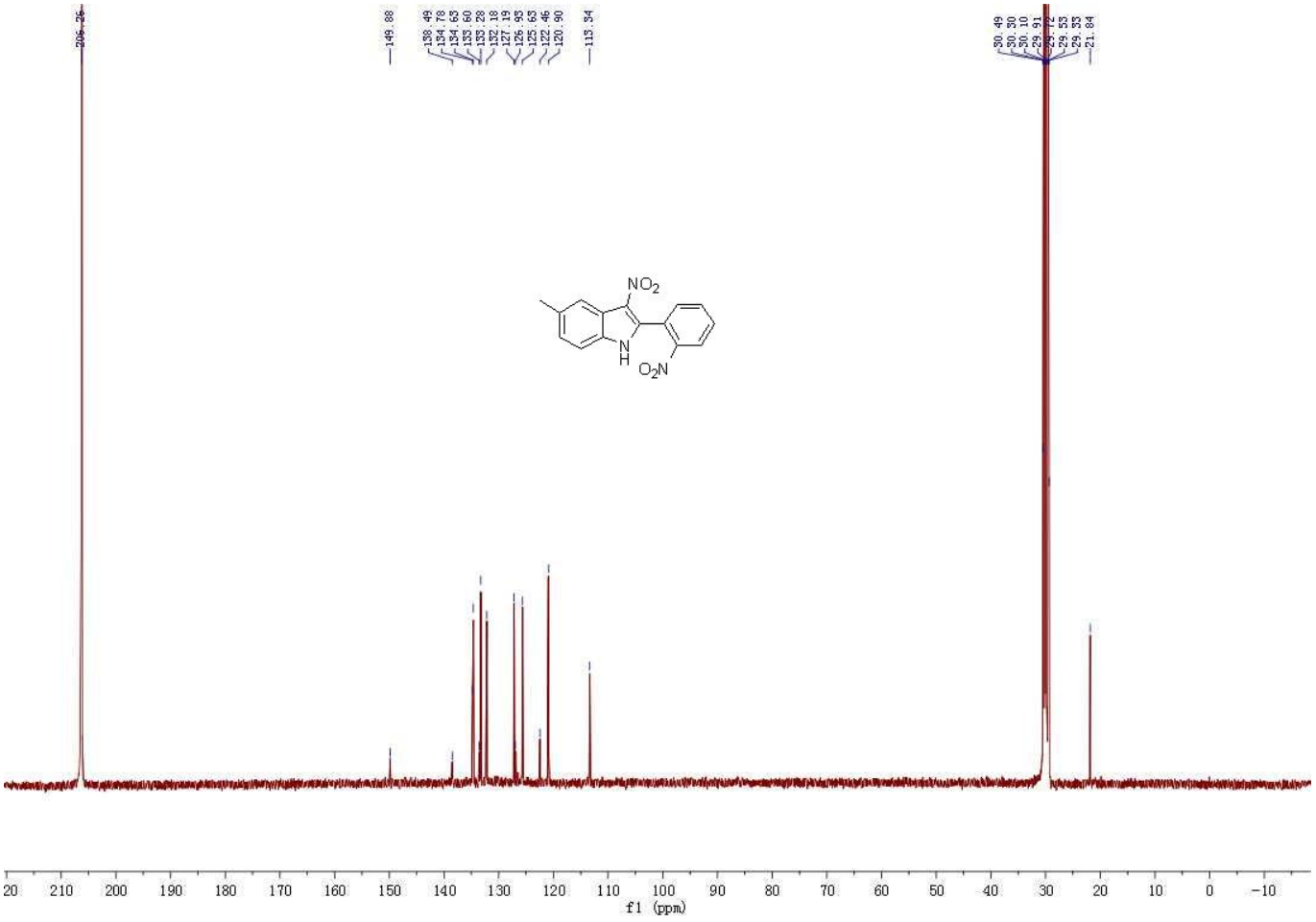
5-Methyl-3-nitro-2-(3-nitrophenyl)-1*H*-indole (3p)



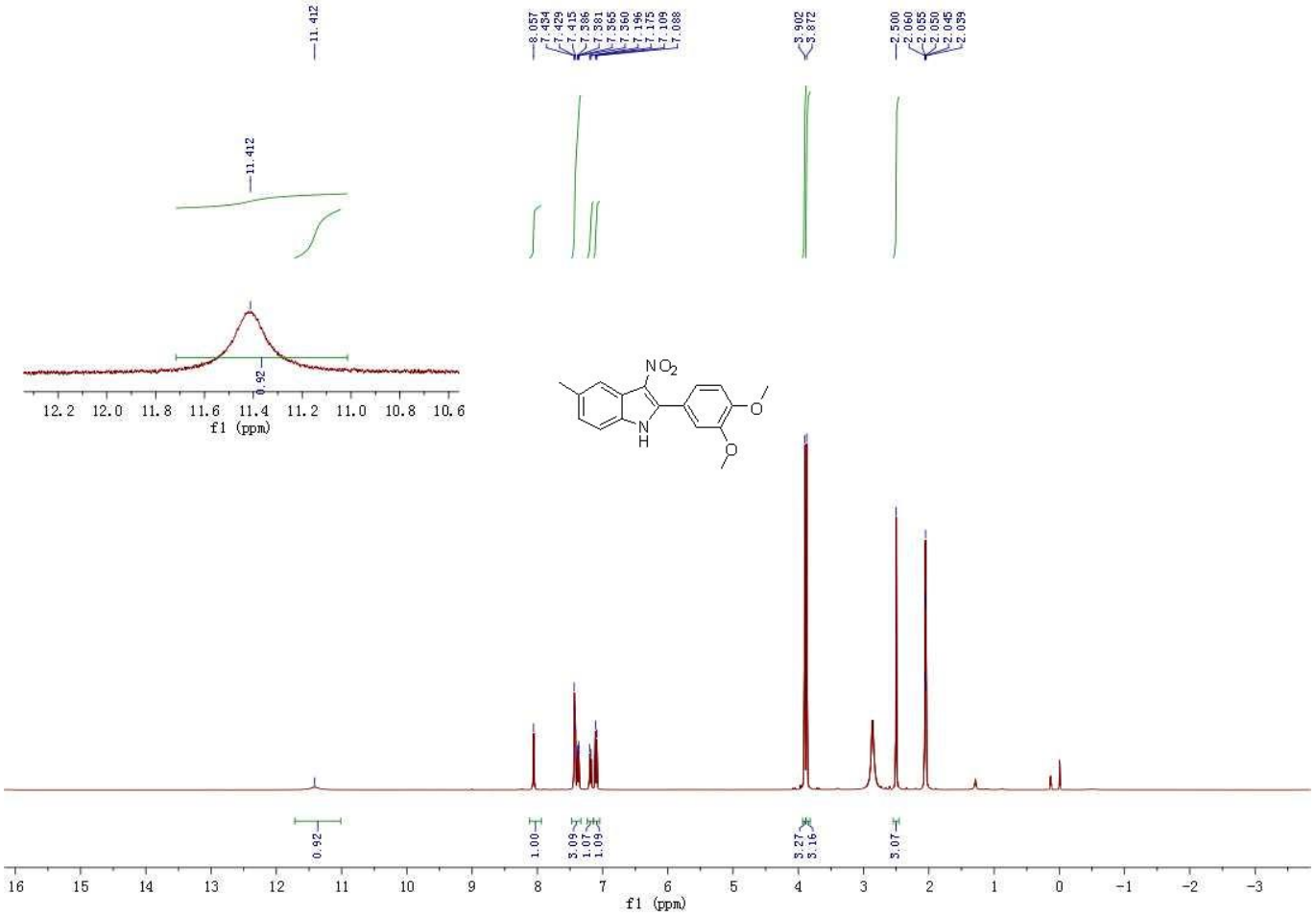


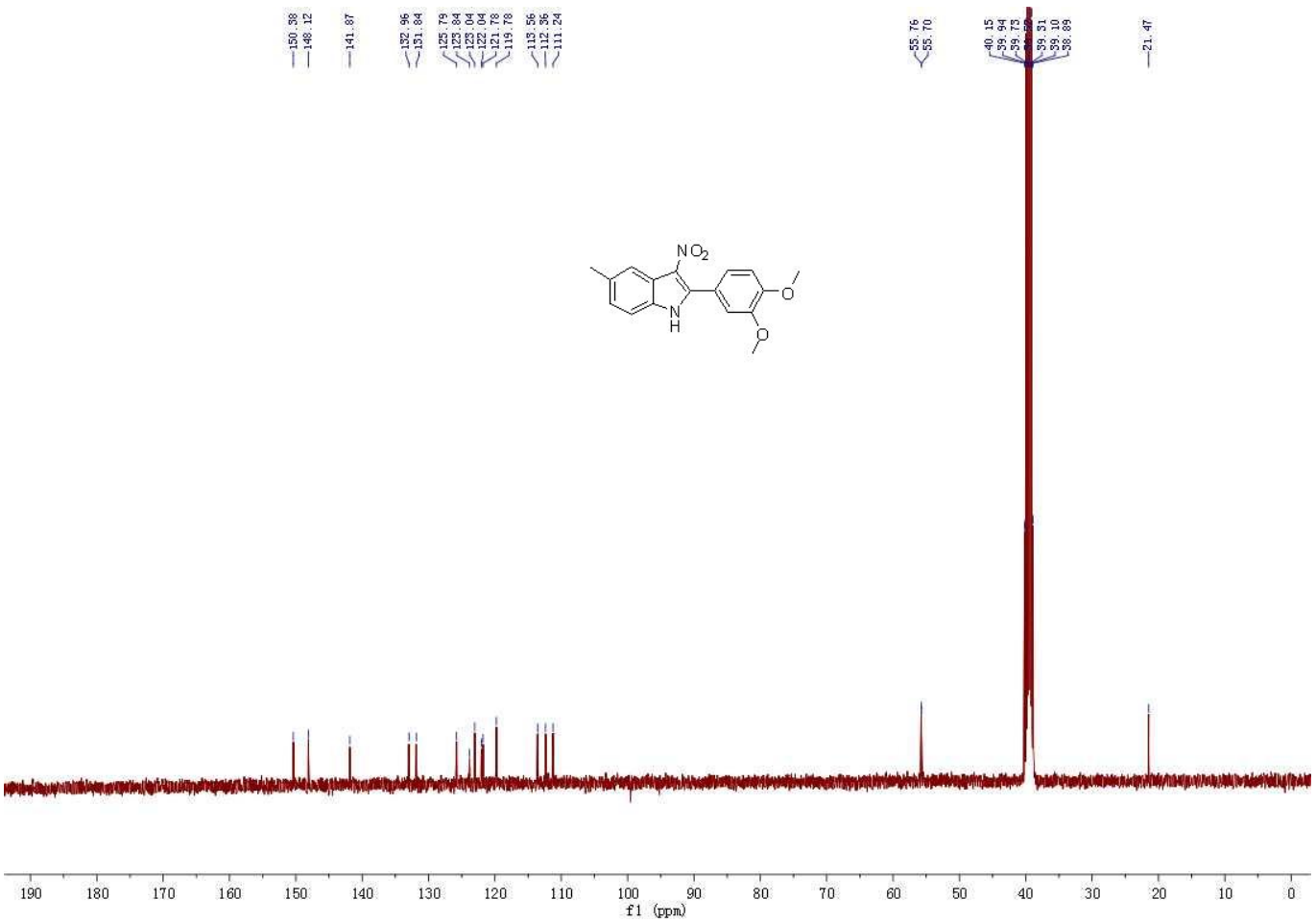
5-Methyl-3-nitro-2-(2-nitrophenyl)-1*H*-indole (3q)



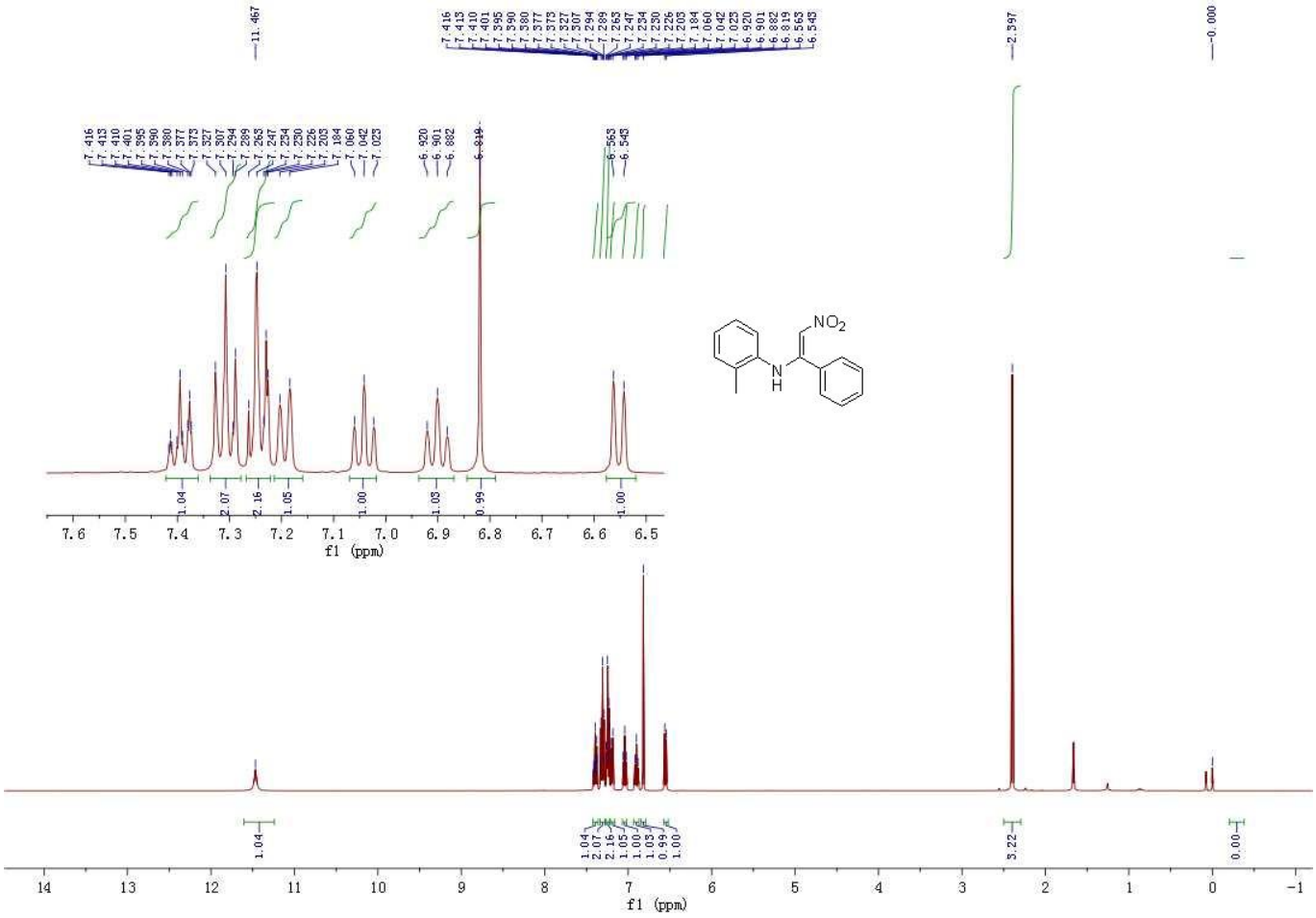


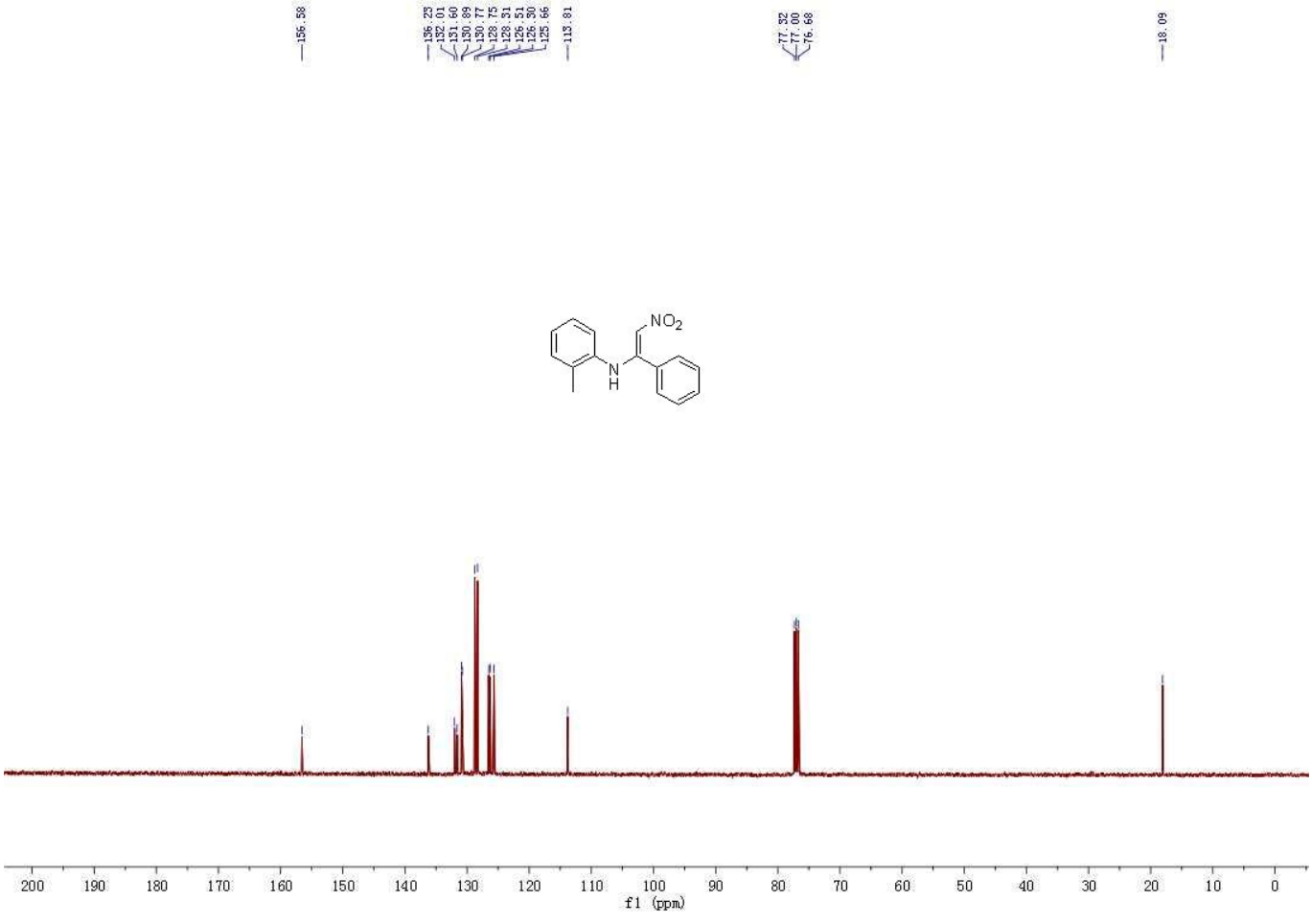
2-(3,4-Dimethoxyphenyl)-5-methyl-3-nitro-1*H*-indole (3r)



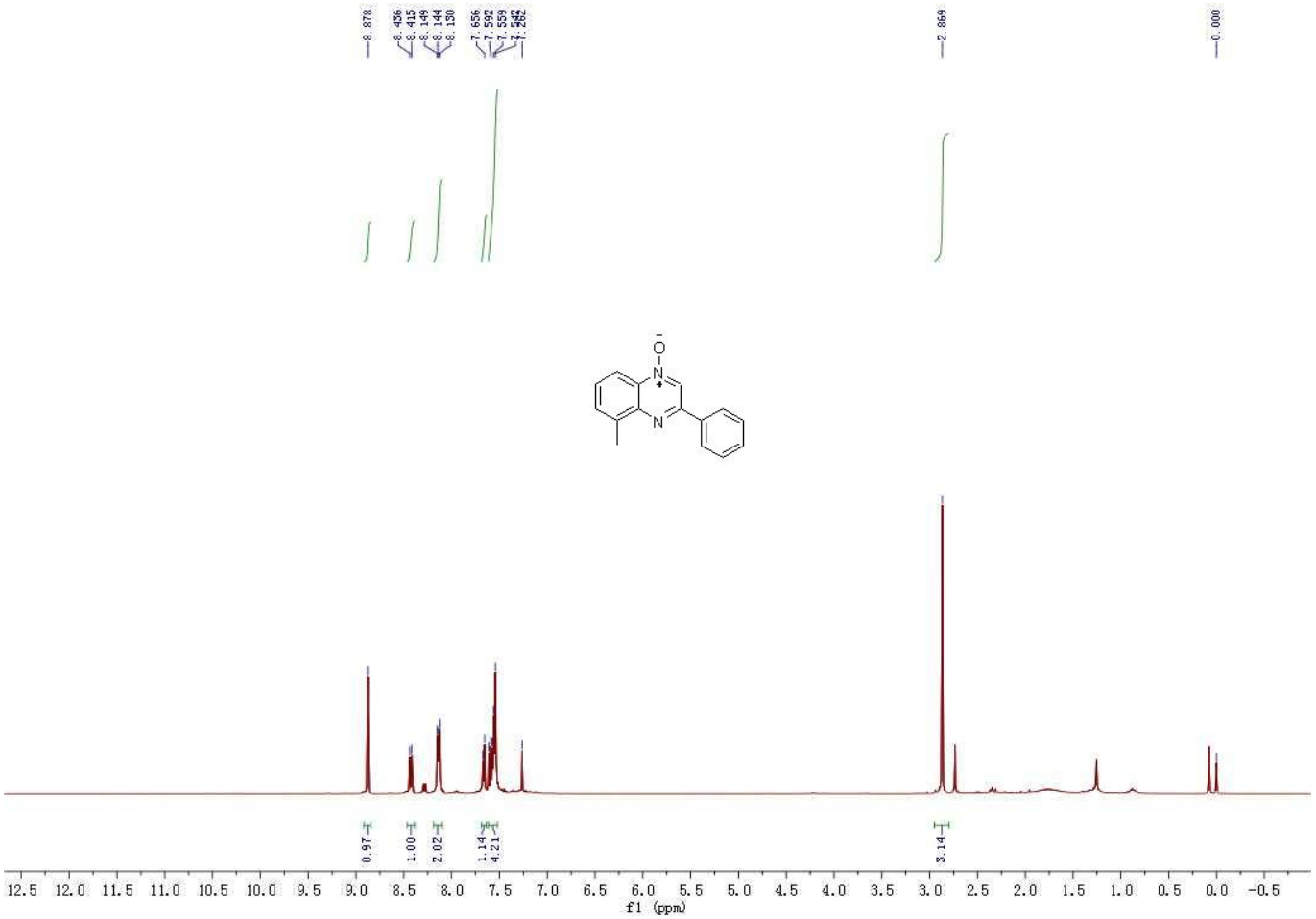


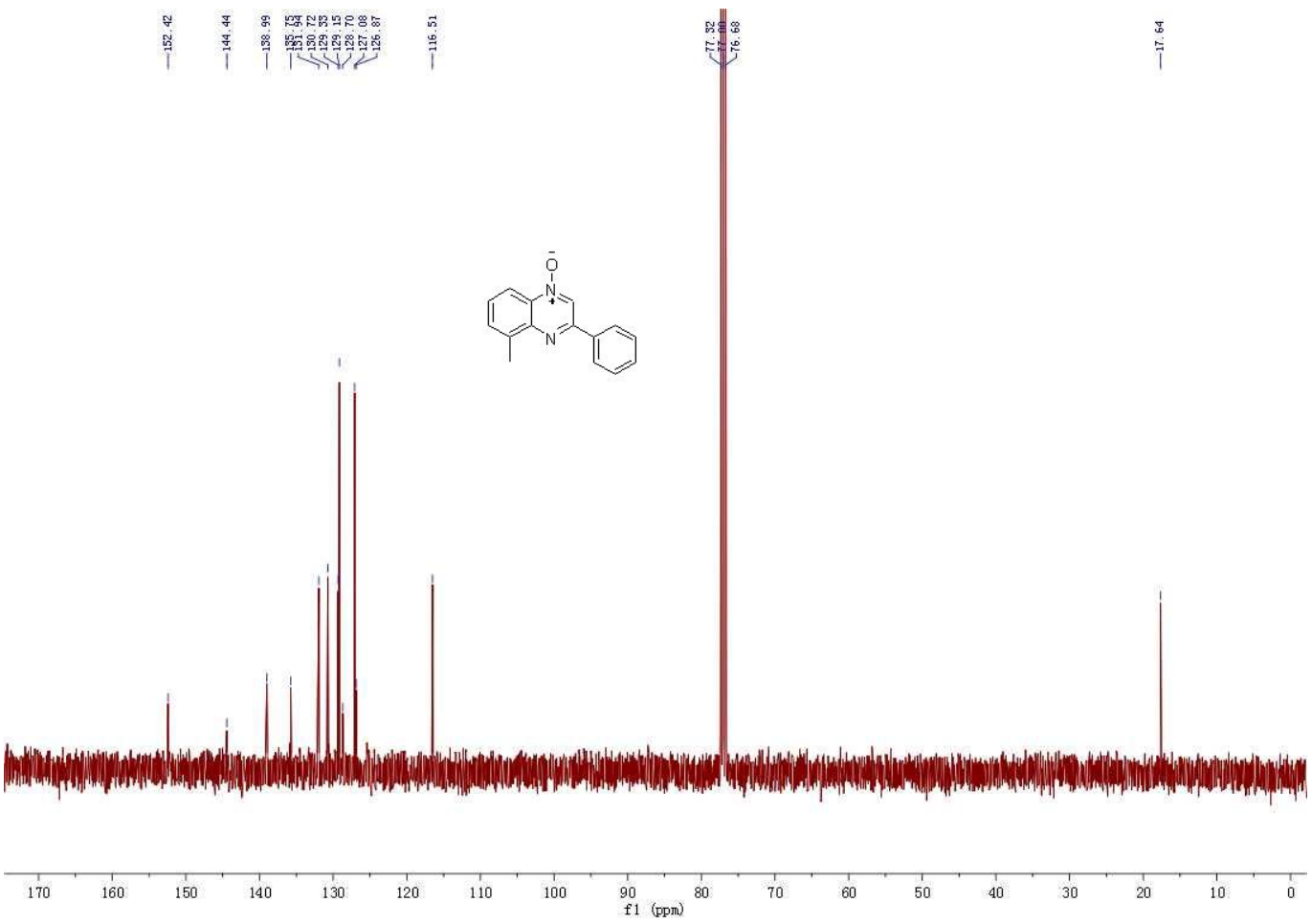
(*E*)-2-Methyl-*N*-(2-nitro-1-phenylvinyl)aniline (4a)



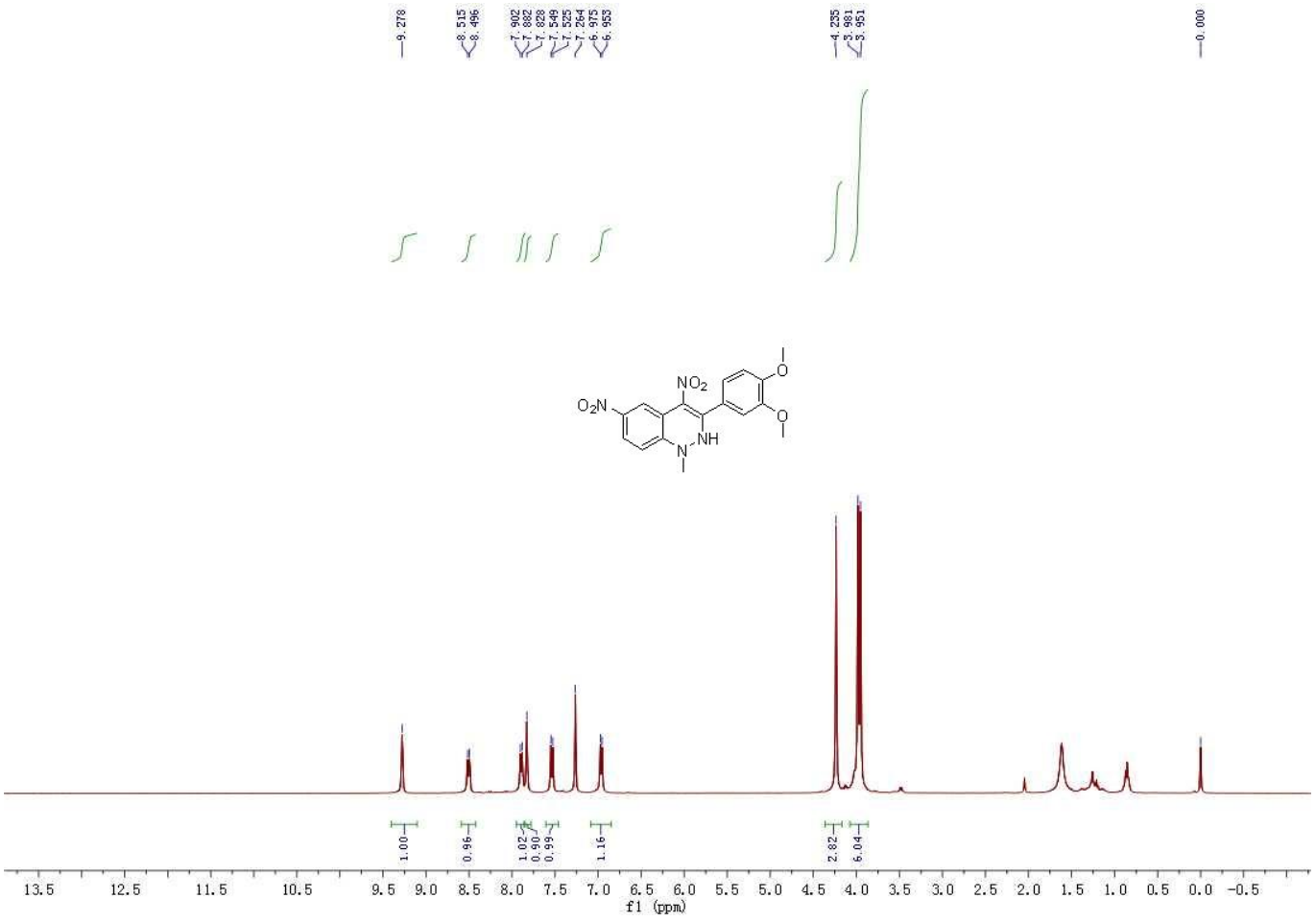


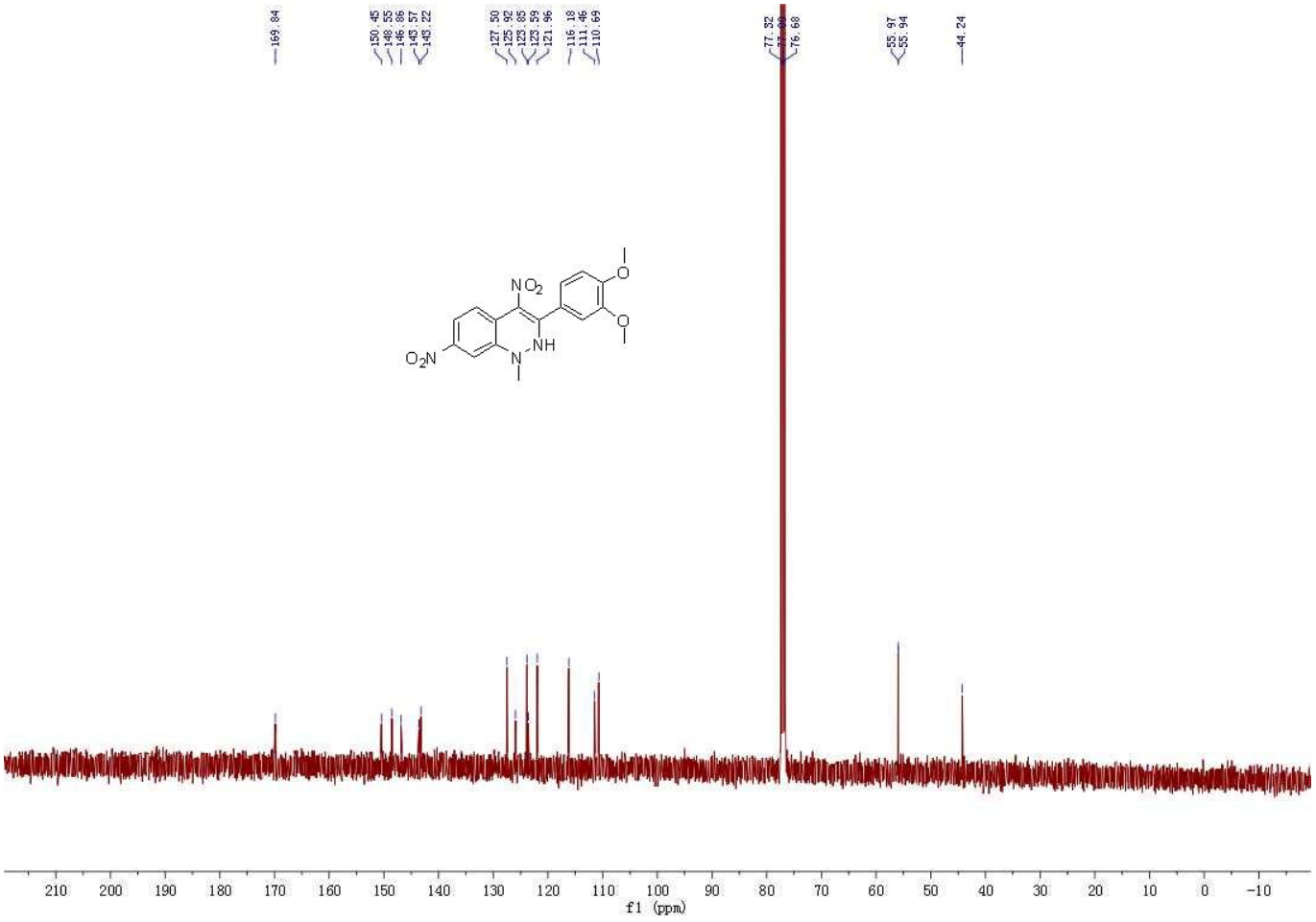
5-Methyl-3-phenylquinoxaline 1-oxide (5a)





3-(3,4-Dimethoxyphenyl)-1-methyl-4,6-dinitro-1,2-dihydrocinnoline (6t)





7-Methyl-3,5-dinitro-2-phenyl-1H-indole (7a):