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Supporting Information

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An Efficient, Facile, and General Synthesis of 1*H*-Indazoles via 1,3-Dipolar Cycloaddition between Arynes and Diazoalkanes

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General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 300 MHz, 600 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CHCl_3$ at 7.26 ppm, DMSO-d^6 at 2.49 ppm integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spetra reported in ppm (d) relative to the central line of triplet for $CDCl_3$ at 77 ppm or cental line for DMSO-d^6 at 39.5 ppm. IR spectra were recorde on a SHIMADZU FTIR-8200A spectrometer; absorptions are reported in cm^{-1}. High-resolution mass spetra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing Slica gel 60 N (spherical, neutral, 40~100 μm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F_{254} (Merck).

Materials. Anhydrous acetonitrile (WAKO), Tetrahydrofuran (KANTO), KF, CsF (WAKO), 18-crown-6 (TCI), ethyl diazoacetate **2a**, *tert* butyl diazoacetate **2b**, trimethylsilyl diazomethane (2.0M solution in hexanes) **2c**, 2-trimethylsilylphenyl triflate **1a** (Aldrich), were purchased and used as received. Aryne precursors **1b**, **1c**, **1d**, **1f**,[1] **1e**,[2] phenyl diazomethane **2d**[3] and α-(4-trifluoromethylbenzoyl) diazomethane **2e**,[4] were prepared according to the literature procedure.

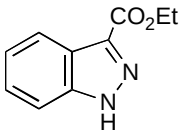
Typical procedure for the synthesis of 1*H*-indazole 3

Ethyl diazoacetate **2a** (62 ml, 0,6 mmol) was added to a THF (2 ml) solution of **1a** (125 μl, 0.5 mmol) and KF (87 mg, 1.5 mmol) and 18-crown-6 (462 mg, 1,75 mmol) under an Ar atmosphere in a pressured vial. After stirring at room temperature for 24 h, the reaction mixture was filtered through a short Florisil pad using ethyl acetate as an eluent. After concentration, the residue was purified with silica gel chromatography using hexane/EtOAc as an eluent, affording the product **3a** in 80% yield as a slight yellow solid (76.5 mg).

Typical procedure for the synthesis of 1-aryl-1*H*-indazole 4

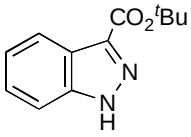
Ethyl diazoacetate **2a** (26 ml, 0,25 mmol) was added to a CH_3CN (2.0 ml) solution of **1a** (125 ml, 0.5 mmol) and CsF (228 mg, 1.5 mmol) under an Ar atmosphere in a pressured vial. After stirring at room temperature for 24 h, the reaction mixture was filtered through a short Florisil pad using ethyl acetate as an eluent. After concentration, the residue was purified with silica gel chromatography using hexane/EtOAc as an eluent, affording the product **4a** in 79% yield as a white solid (52.6 mg).

Analytical Data



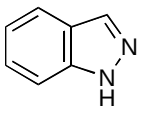
3a

3-Ethoxycarbonyl-1*H*-indazole (3a): slight yellow solid; ^{1}H NMR (300MHz, DMSO-d^6) δ 13.91 (1H, bs), 8.06 (1H, d, *J* = 7.8 Hz), 7.65 (1H, d, *J* = 8.4 Hz), 7.44 (1H, m), 7.30 (1H, m), 4.38 (2H, q, *J* = 7.2 Hz), 1.36 (1H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, DMSO-d^6) δ 14.27, 60.28, 111.09, 121.04, 122.16, 122.83, 126.64, 135.20, 140.93, 162.33; IR(neat) 3290, 3082, 1713, 1618, 1479, 1230 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{10}N_2O_2$ (M+Na) 213.0634. Found 213.0636.



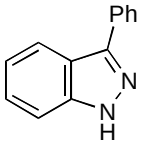
3b

3-*tert*-Butoxycarbonyl-1*H*-indazole (3b): white solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 13.40 (1H, s), 8.15 (1H, d, *J* = 8.1 Hz), 7.90 (1H, d, *J* = 8.4 Hz), 7.47-7.42 (1H, m), 7.30 (1H, m), 1.72 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.42, 81.98, 111.91, 121.63, 122.04, 122.81, 126.83, 137.39, 141.63, 162.54; IR(neat) 3258, 1710, 1621, 1235 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{14}N_2O_2$ (M+Na) 241.0947. Found 241.0946.



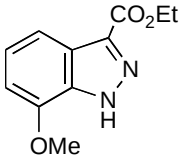
3c

1H-Indazole (3c): white solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.10 (1H, s), 7.77 (1H, d, *J* = 8.4 Hz), 7.51 (1H, d, *J* = 8.4 Hz), 7.40 (1H, m), 7.18 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 109.71, 120.86, 120.96, 123.13, 126.80, 134.77, 140.01; IR(neat) 3148, 1619, cm^{-1}; HRMS (EI) Calcd for $C_7H_6N_2$ (M+Na) 118.0530. Found 118.0529.

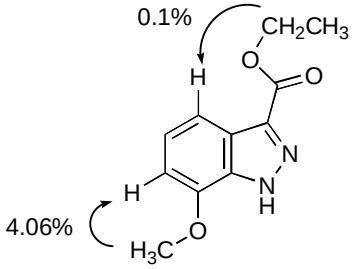


3d

3-Phenyl-1*H*-indazole (3d): slight yellow; ^{1}H NMR (300MHz, $CDCl_3$) δ 12.10 (1H, bs), 8.10-8.03 (3H, m), 7.60-7.46 (3H, m), 7.35-7.10 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.43, 120.82, 120.94, 121.24, 126.70, 127.81, 128.17, 128.98, 133.51, 141.63, 145.51; IR(neat) 3151, 2929, 1621, 1479 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{10}N_2$ (M+Na) 217.0736. Found 217.0735.

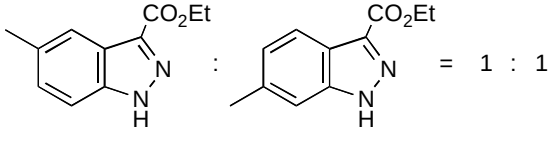


3e

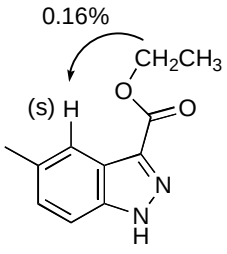


3e nOe analysis

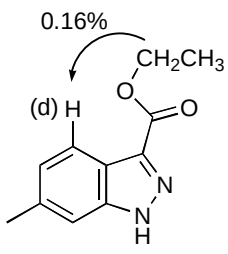
3-Ethoxycarbonyl-7-methoxy-1*H*-indazole (3e): slight yellow solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 10.90 (1H, bs), 7.77 (1H, d, *J* = 7.5 Hz), 7.23 (1H, dd, *J* = 7.5, 7.5 Hz), 6.77 (1H, d, *J* = 7.5 Hz), 4.51 (2H, q, *J* = 7.2 Hz), 3.98 (3H, s), 1.47 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.35, 55.51, 61.05, 105.45, 113.75, 124.08, 124.23, 133.23, 127.09, 145.24, 162.73; IR(neat) 3162, 2927, 1700, 1586, 1265, 1242 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}N_2O_3$ (M+Na) 243.0740. Found 243.0738.



3f : **3f'** = 1 : 1



3f nOe analysis



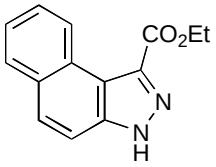
3f' nOe analysis

3-Ethoxycarbonyl-5-methyl-1*H*-indazole (3f): white solid; ^{1}H NMR (300MHz, $CDCl_3$)

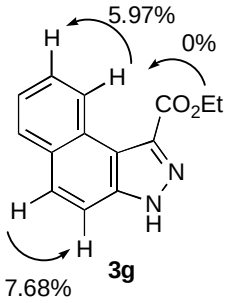
δ 12.70 (1H, bs), 7.97 (1H, s), 7.68 (1H, d, *J* = 8.7 Hz), 7.29-7.26 (1H, m), 4.55 (4.54) (2H, q, *J* = 7.2 Hz), 2.50 (3H, s), 1.46 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.40 (14.37), 21.93 (21.56), 61.02, 111.24, 120.53, 122.80, 129.37, 132.87, 135.59, 140.25, 1 63.26;

3-Ethoxycarbonyl-6-methyl-1*H*-indazole (3f'): white solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 12.70 (1H, bs), 8.06 (1H, d, *J* = 8.4 Hz), 7.52 (1H, s), 7.14 (1H, d, *J* = 8.4 Hz), 4.54 (4.55) (2H, q, *J* = 7.2 Hz), 2.50 (3H, s), 1.46 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.37 (14.40), 21.56 (21.93), 61.02, 110.74, 120.53, 121.16, 125.51, 136.18, 137.54, 142.09, 1 63.26;

IR(neat) 3278, 2922, 1708, 1626, 1417, 1280, 1231, 1133 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{12}N_2O_2$ (M+Na) 227.0791. Found 227.0792.

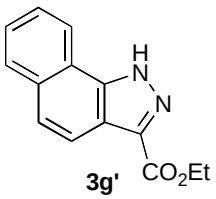


3g

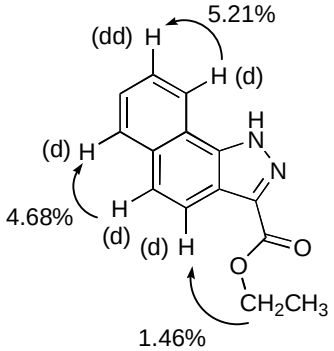


3g

3-Ethyl 1*H*-Benzo[e]indazole-3-carboxylate (3g): white solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.34-8.31 (1H, m), 7.93-7.79 (1H, m), 7.78 (1H, d, *J* = 9.0 Hz), 7.62-7.53 (2H, m), 7.50 (1H, d, *J* = 9.0 Hz), 4.24 (2H, q, *J* = 7.2 Hz), 1.27 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.24, 61.07, 119.11, 119.33, 120.52, 121.70, 125.14, 126.85, 127.17, 128.71, 132.44, 135.55, 139.61, 162.16; IR(neat) 3239, 2980, 1715, 1431, 1265 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{12}N_2O_2$ (M+Na) 263.0791. Found 263.0791.



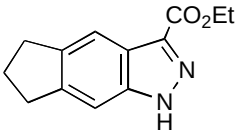
3g'



3g' nOe analysis

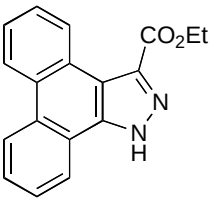
3-Ethyl 1*H*-Benzo[g]indazole-3-carboxylate (3g'): white solid; ^{1}H NMR (300MHz, $CDCl_3$)

δ 9.51 (1H, d, *J* = 8.4 Hz), 7.90 (1H, d, *J* = 7.8 Hz), 7.78 (1H, d, *J* = 9.0 Hz), 7.72-7.53 (3H, m), 4.58 (2H, q, *J* = 7.2 Hz), 1.48 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.36, 61.68, 111.60, 118.11, 125.88, 126.78, 126.95, 127.62, 128.78, 130.39, 131.04, 136.32, 141.66, 162.63; IR(neat) 3149, 2929, 1721, 1541, 1433 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{12}N_2O_2$ (M+Na) 263.0791. Found 263.0790.



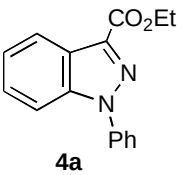
3h

Ethyl 1,5,6,7-tetrahydro-cyclopent[f]indazole-3-carboxylate (3h): white solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 12.10 (1H, bs), 7.95 (1H, s), 7.52 (1H, s), 4.53 (2H, q, *J* = 7.2 Hz), 3.03-2.97 (4H, m), 2.19-2.10 (2H, m), 1.45 (3H, t, *J* = 7.2 Hz) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.41, 26.56, 32.22, 32.76, 60.91, 106.01, 115.67, 122.04, 135.47, 140.82, 141.51, 145.36, 163.36; IR(neat) 3272, 2942, 1710, 1479 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{14}N_2O_2$ (M+Na) 253.0947. Found 253.0947.



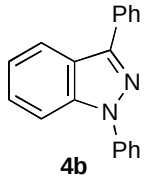
3i

3-Ethoxycarbonyl-1*H*-dibenzo[e,g]indazole (3i): slight blue solid; ^{1}H NMR (300MHz, DMSO-d^6) δ 14.74 (1H, bs), 9.34 (1H, d, *J* = 6.9 Hz), 8.86-8.78 (2H, m), 8.56-8.53 (1H, m), 7.75-7.60 (4H, m), 4.47 (2H, q, *J* = 7.2 Hz), 1.41 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, DMSO-d^6) δ 14.27, 60.89, 115.48, 120.39, 122.31, 123.90, 124.15, 126.01, 126.09, 126.36, 127.53, 127.74, 128.02, 128.08, 129.67, 137.79, 138.15, 163.84; IR(neat) 3165, 2969, 1715, 1447 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{14}N_2O_2$ (M+Na) 313.0947. Found 313.0945.



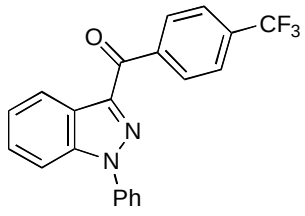
4a

3-Ethoxycarbonyl-1-phenyl-1H-indazole (4a): white solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.31 (1H, d, *J* = 8.1Hz), 7.73 (3H, dd, *J* = 7.8, 7.8 Hz), 760-7.30 (5H, m), 4.56 (2H, q, *J* = 6.9 Hz), 4.50 (3H, t, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.46, 61.17, 110.84, 122.46, 123.63, 123.90, 124.41, 127.56, 127.96, 129.48, 137.01, 139.22, 140.21, 162.67; IR(neat) 2925, 1723, 1593, 1473, 1414, 1196, 1129 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{14}N_2O_2$ (M+Na) 289.0947. Found 289.0945.



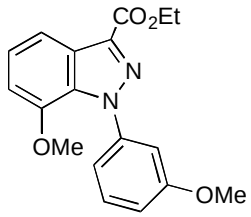
4b

1,3-Diphenyl-1*H*-indazole (4b): white solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.11-8.03 (3H, m), 7.82-7.78 (3H, m), 7.58-7.26 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.64, 121.55, 121.89, 122.96, 123.08, 126.64, 127.07, 127.73, 128.24, 128.80, 129.43, 133.17, 140.06, 140.27, 146.05; IR(neat) 2925, 1592, 1498, 1417, 1390, 1225, 1108 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{14}N_2$ (M+Na) 293.1049. Found 293.1046.

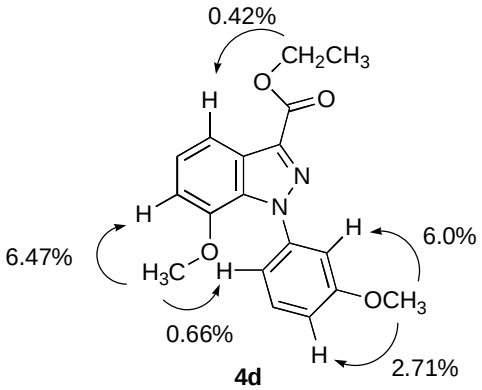


4c

1-Phenyl-3-(4'-trifluromethyl)benzoyl-1*H*-indazole (4c): slight yellow solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.60-8.50 (3H, m), 7.83-7.75 (5H, m), 7.60 (2H, dd, *J* = 7.8, 7.8 Hz), 7.57-7.47 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.77, 123.33, 123.54, 123.80 (q, ^{1}J (C, F) = 270 Hz), 124.55, 125.10 (q, ^{3}J (C, F) = 3.7 Hz), 125.31, 128.02, 128.07, 129.67, 130.87, 133.62 (q, ^{2}J (C, F) = 32 Hz), 139.28, 139.94, 140.62, 142.97, 187.40; IR(neat) 2925, 1646, 1595, 1495, 1465, 1315, 1201, 1108, 1061, 889, 758 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{13}F_3N_2O$ (M+Na) 389.0872. Found 389.0872.



4d



4d

3-Ethoxycarbonyl-1-(3'-methoxyphenyl)-7-methoxy-1*H*-indazole (4d): slight yellow solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.88 (1H, d, *J* = 7.5 Hz), 7.33-7.24 (2H, m), 7.20-7.10 (2H, m), 7.00-6.92 (1H, m), 6.82 (1H, d, *J* = 7.5 Hz), 4.52 (2H, q, *J* = 7.2 Hz), 3.83 (3H, s), 3.78 (3H, s), 1.47 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.43, 55.44, 55.48, 61.12, 106.89, 112.00, 114.09, 114.34, 118.96, 124.34, 126.43, 128.61, 131.80, 136.85, 141.66, 146.19, 159.23, 162.71; IR(neat) 2933, 1725, 1592, 1579, 1477, 1453, 1278, 1250, 1218, 1048, 1028 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}N_2O_4$ (M+Na) 349.1159. Found 349.1157.

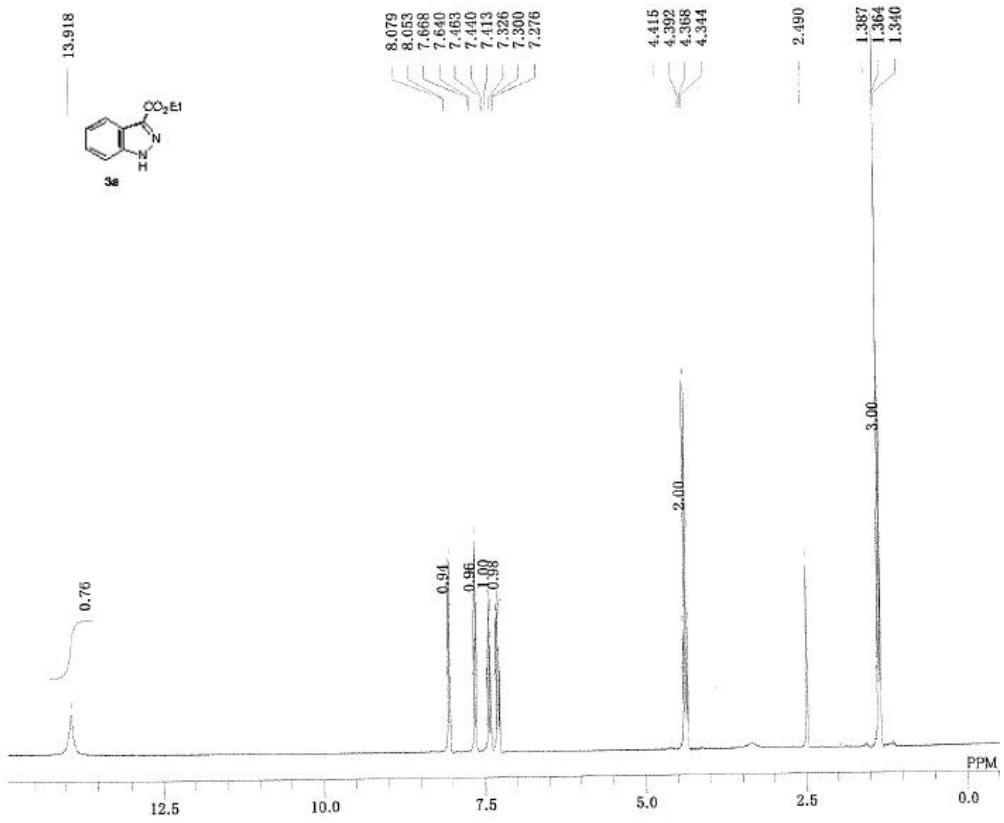
References

(1) a) D. Peña, D. Pérez, E. Guitián, L. Castedo, *J. Am. Chem. Soc*. **1999**, *121*, 5827-5828; b) D. Peña, D. Pérez, E. Guitián, L. Castedo, *J. Org. Chem*. **2000**, *65*, 6944-6950.

(2) H. Yoshida, S. Sugiura, A. Kunai, *Org. Lett.* **2002**, *4*, 2767-2769.

(3) S. Zrig, B. Andrioletti, E. Rose, J. Colin, *Tetrahedron Lett*. **2005**, *46*, 1103-1105.

(4) G. Su, H. Mu, D. Za, L. Zeng, C. Cativiela, R. P. Hammer, K. Yu, *Synth. Commun.* **2003**, *33*, 2873-2884.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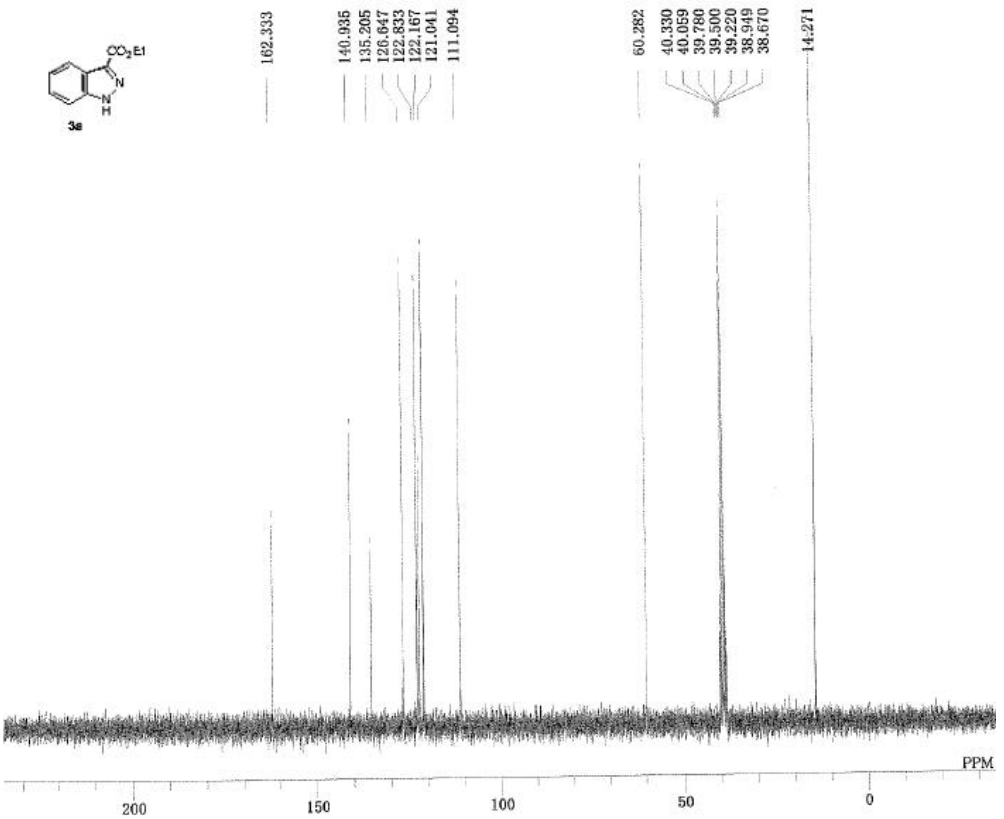
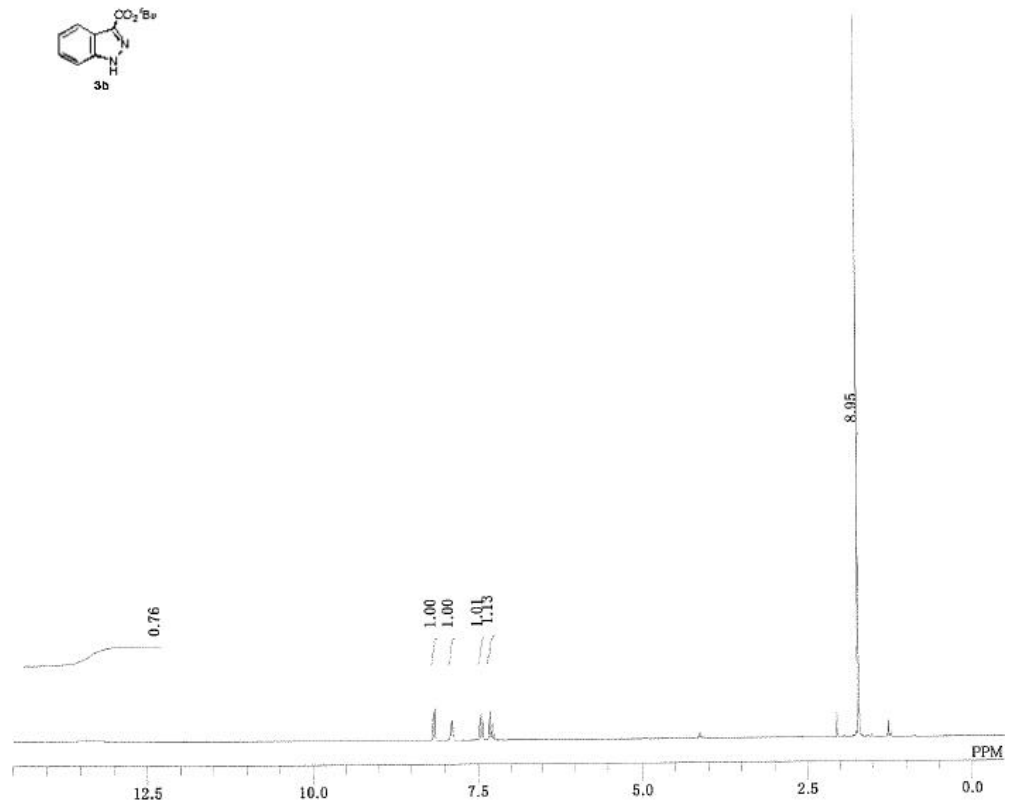
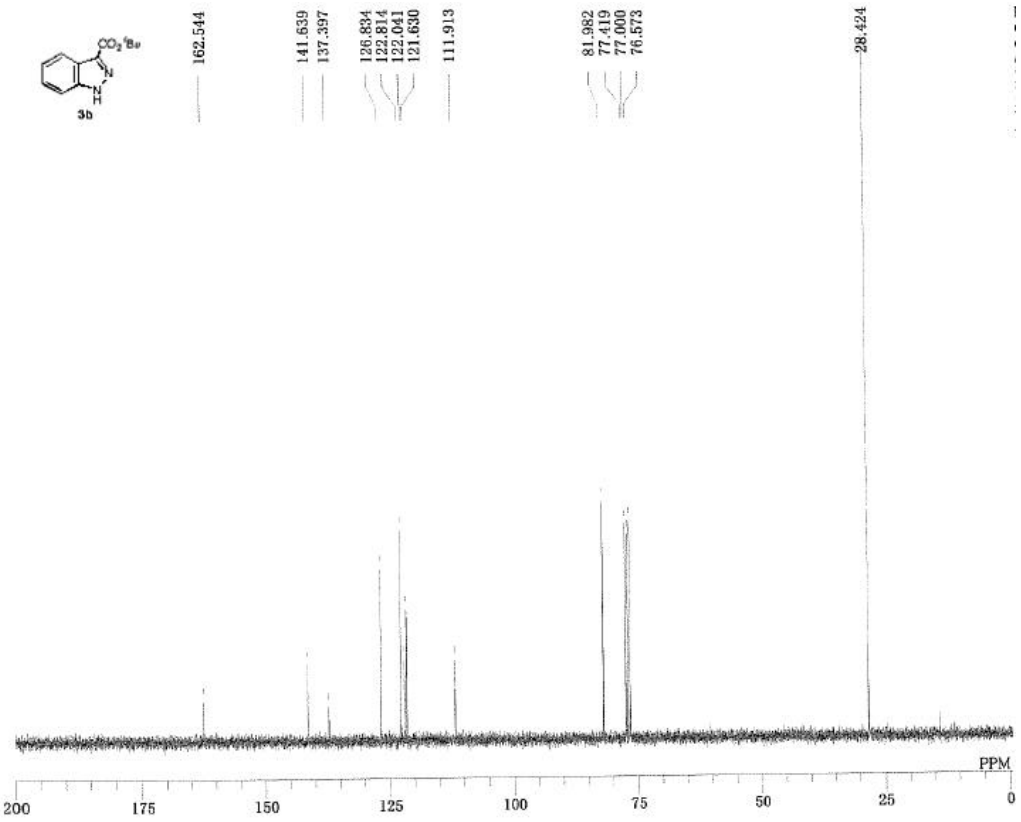
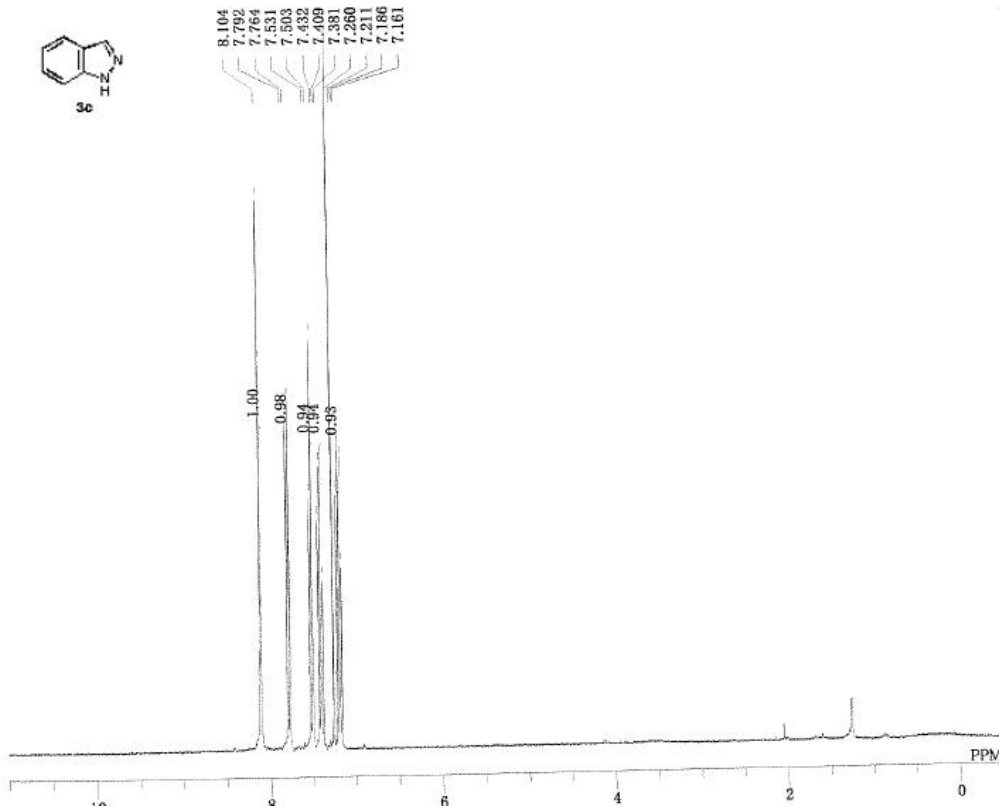
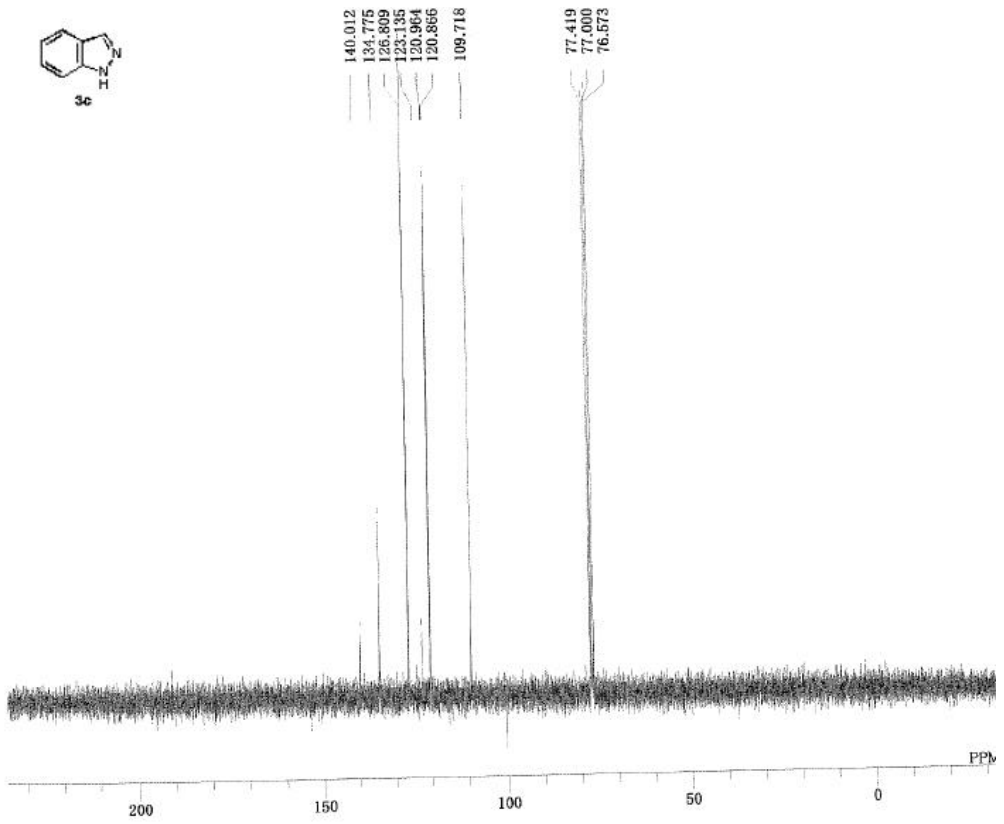
0.96
1.00
0.98
2.00
3.00
3a
PPM
12.5
10.0
7.5
5.0
2.5
0.0

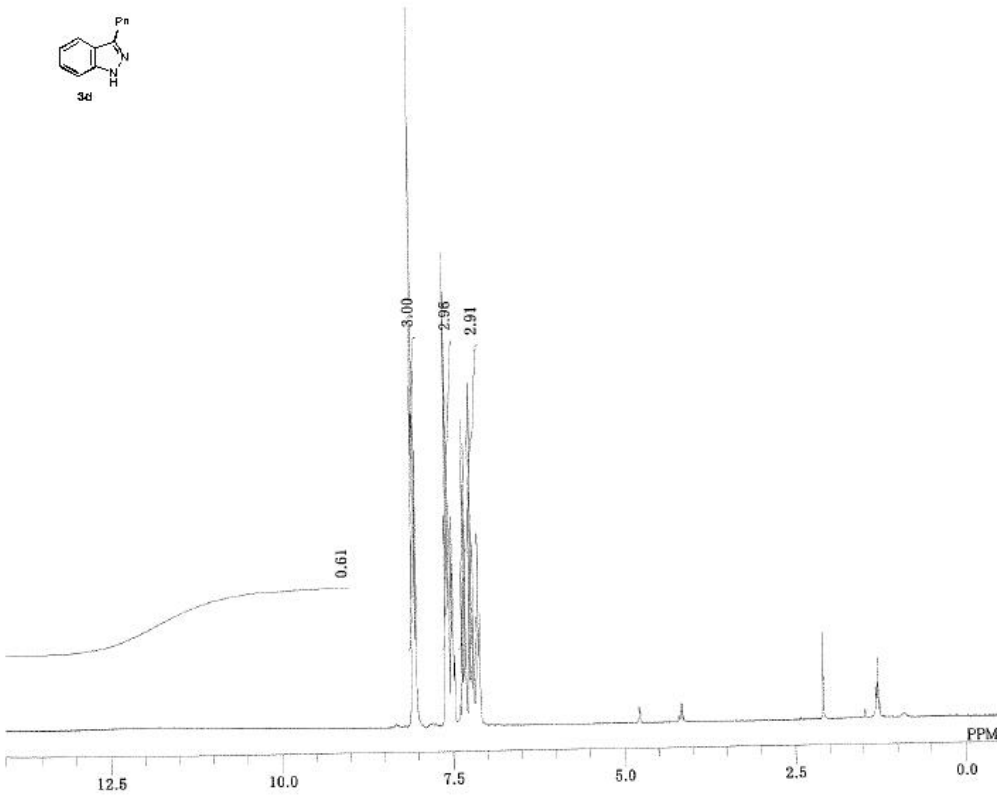

162.333
140.935
135.205
126.647
122.833
122.167
121.041
111.094
60.282
40.330
40.059
39.780
39.500
39.220
38.949
38.670
14.271
3a
PPM
200
150
100
50
0

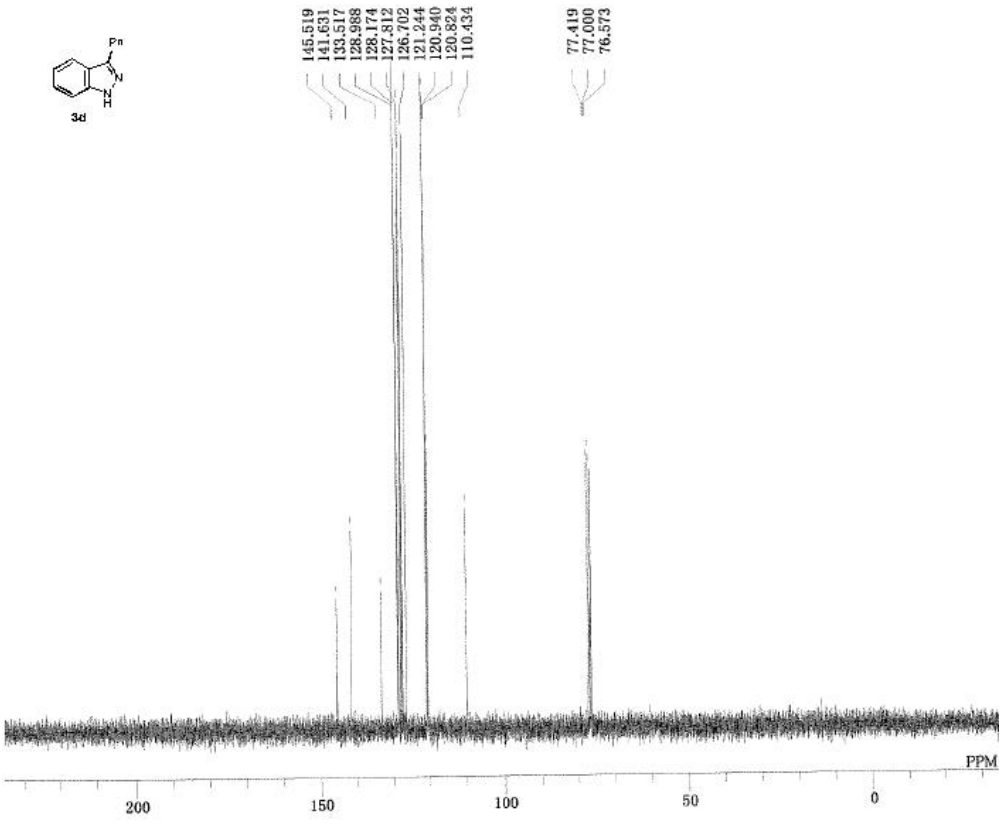

3b
0.76
1.00
1.00
1.01
1.13
8.95
PPM
12.5
10.0
7.5
5.0
2.5
0.0

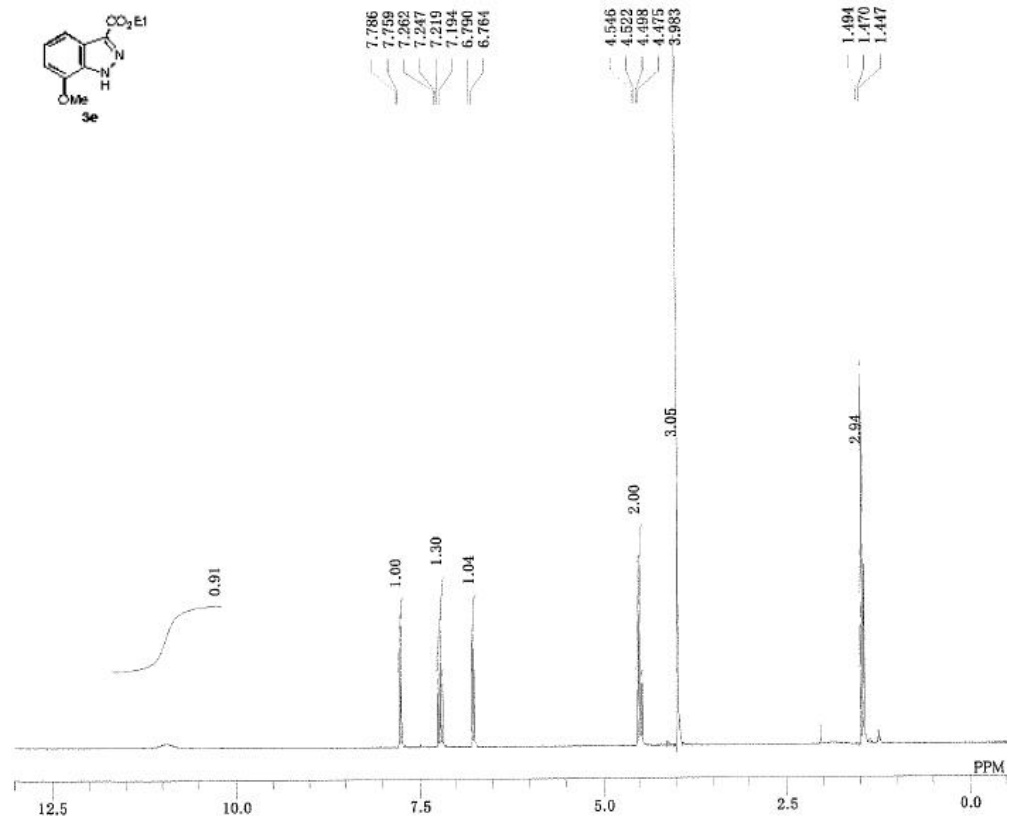

3b
162.544
141.639
137.397
126.834
123.814
122.041
121.630
111.913
81.982
77.419
77.000
76.573
28.424
PPM
200
175
150
125
100
75
50
25
0

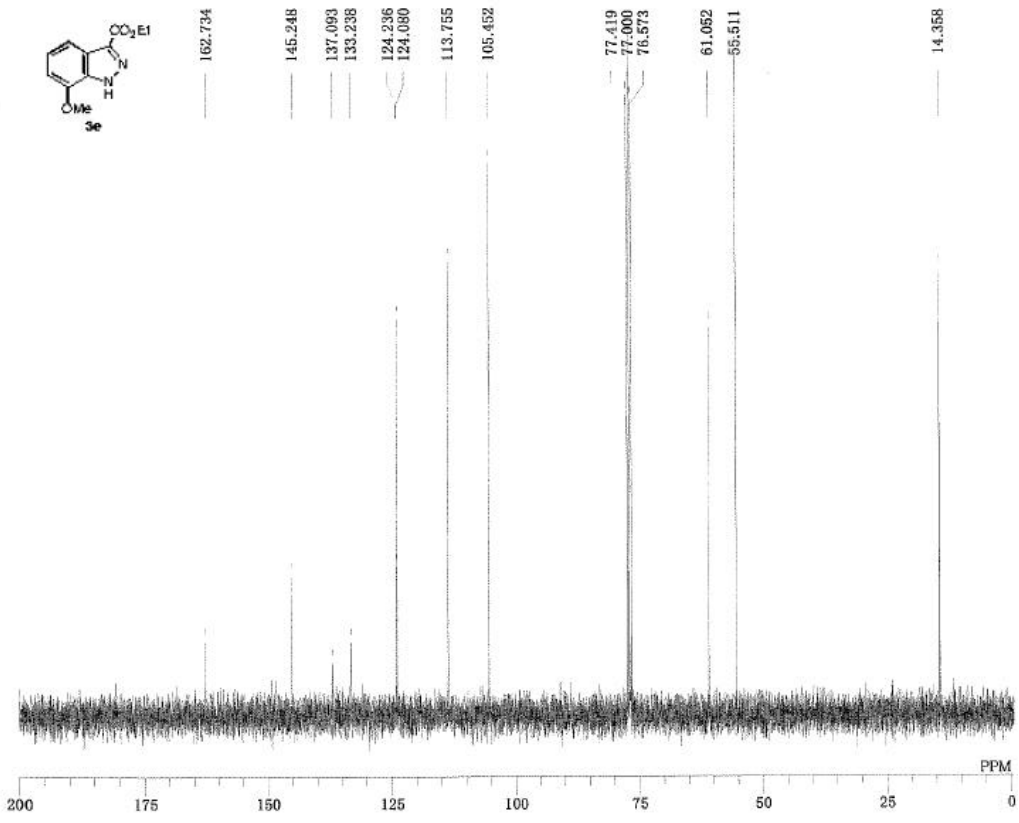

3c
8.104
7.792
7.764
7.531
7.503
7.432
7.409
7.381
7.260
7.211
7.186
7.161
1.00
0.98
0.94
0.94
0.93
PPM
6
4
2
0

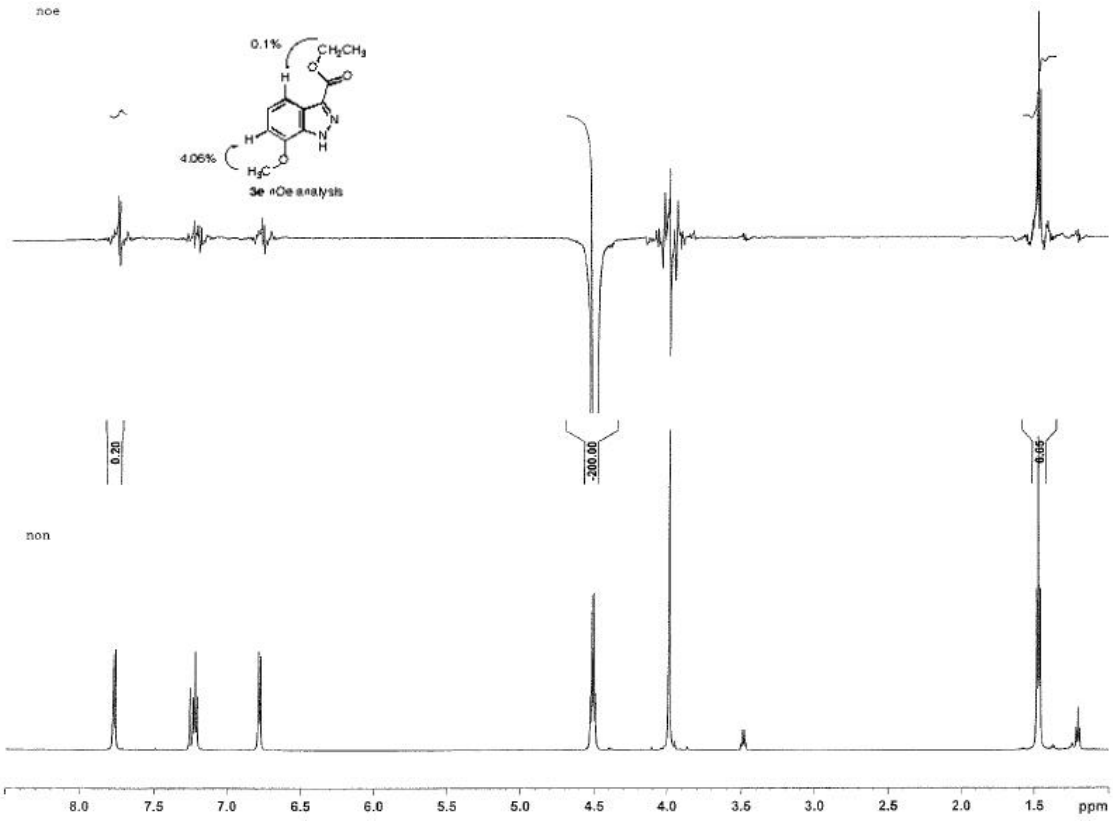

3c
140.012
134.775
126.809
123.135
120.964
120.866
109.718
77.419
77.000
76.573
PPM
200
150
100
50
0

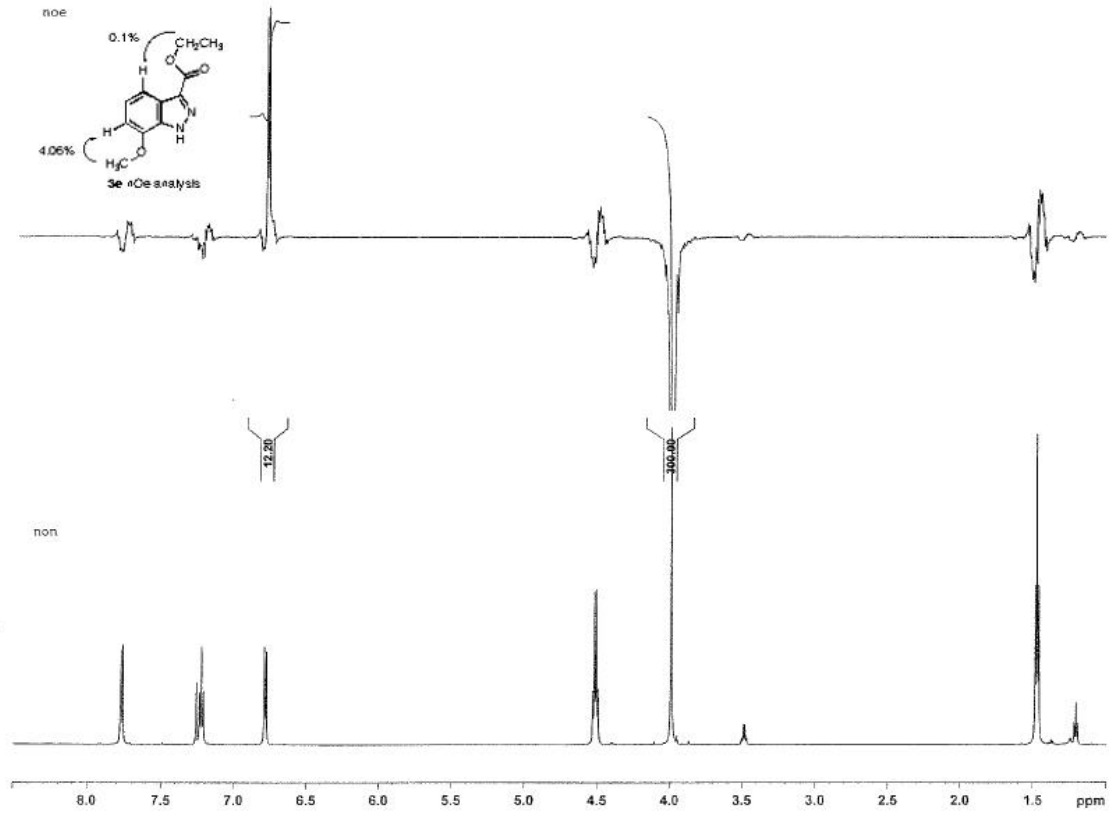

Pn
N
N
H
3d
0.61
3.00
2.96
2.91
PPM
12.5
10.0
7.5
5.0
2.5
0.0

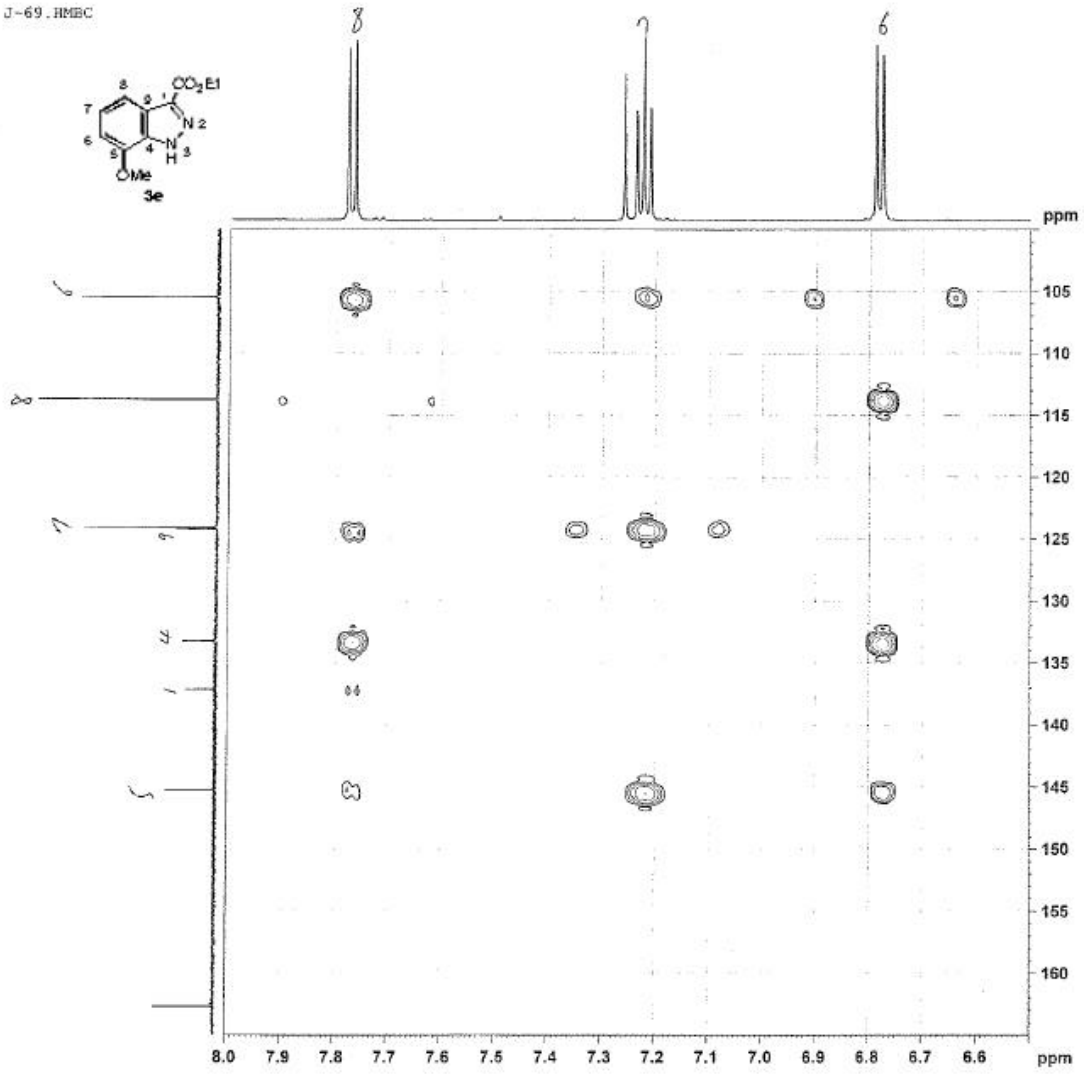

Pn
N
N
H
3d
145.519
141.631
133.517
128.988
128.174
127.812
126.702
121.244
120.940
120.824
110.434
77.419
77.000
76.573
PPM
200
150
100
50
0

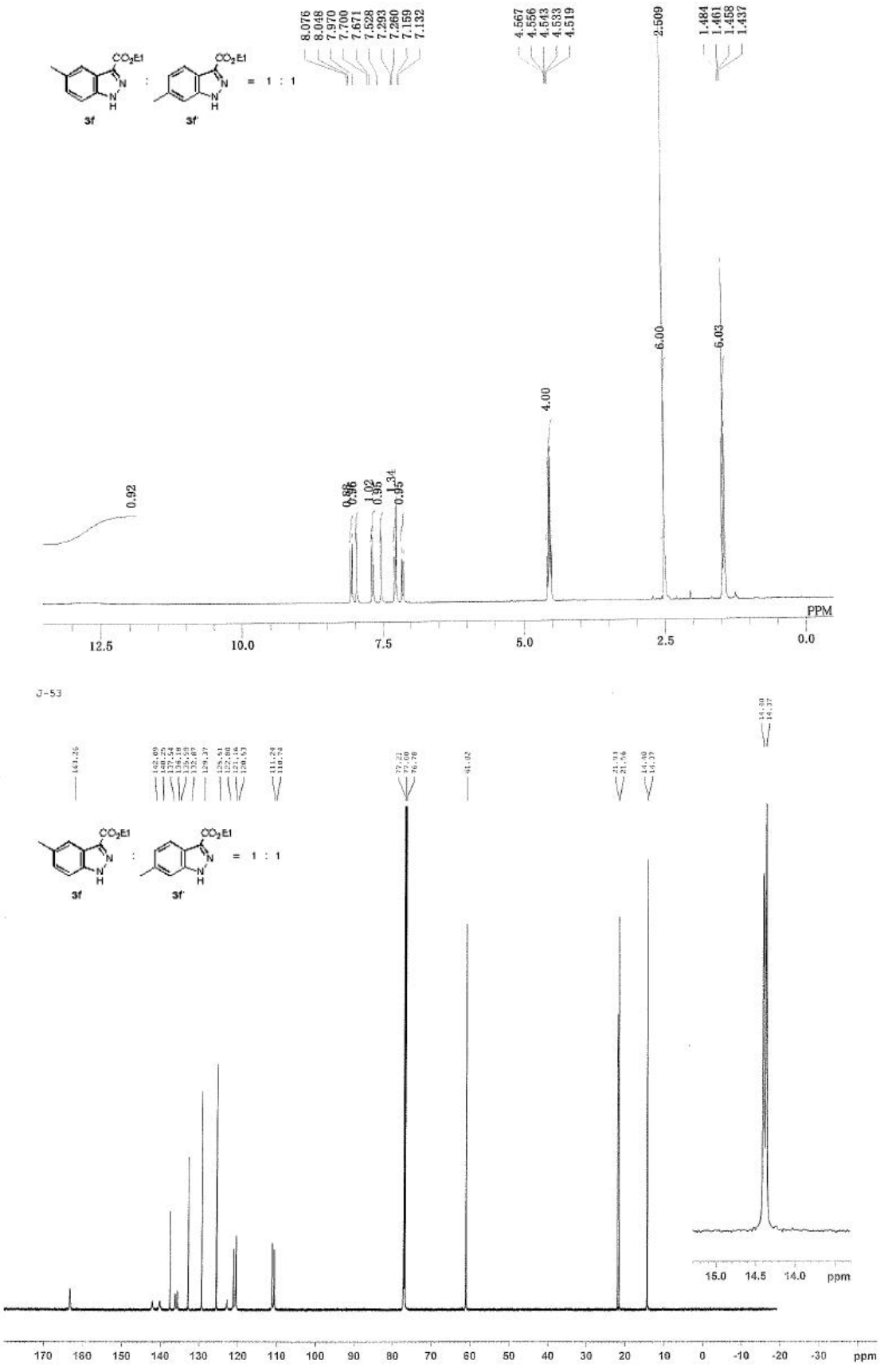

3e
7.786
7.759
7.262
7.247
7.219
7.194
6.790
6.764
4.546
4.522
4.498
4.475
3.983
1.494
1.470
1.447
0.91
1.00
1.30
1.04
2.00
3.05
2.94
PPM
12.5
10.0
7.5
5.0
2.5
0.0

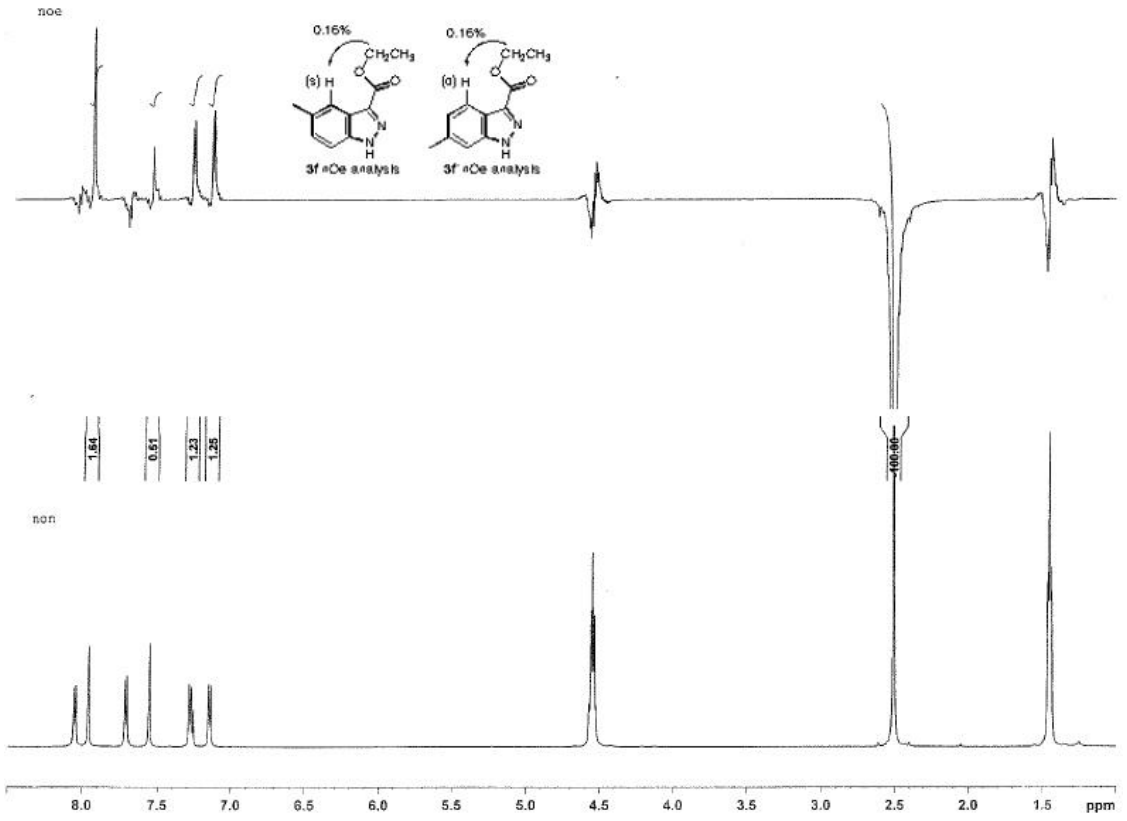

3e
162.734
145.248
137.093
133.238
124.236
124.080
113.755
105.452
77.419
77.000
76.573
61.052
55.511
14.358
PPM
200
175
150
125
100
75
50
25
0

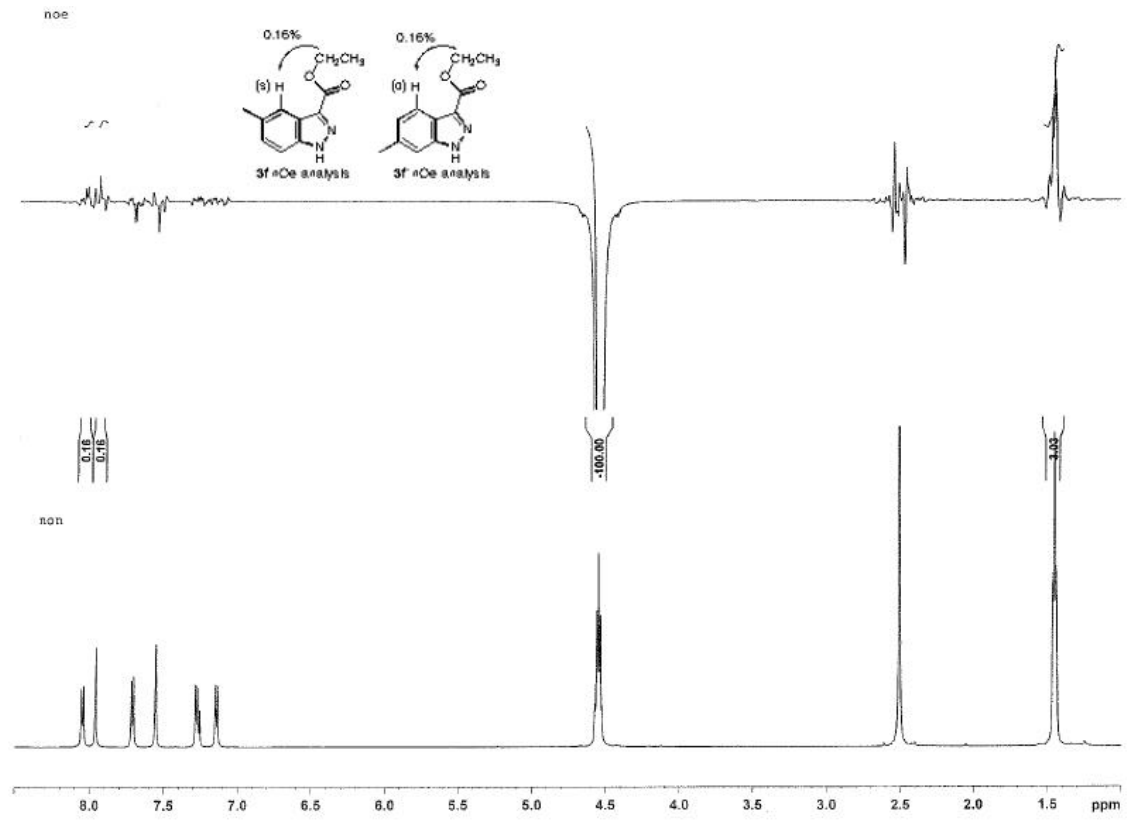

noe
0.1%
4.06%
3e nOe analysis
0.20
-200.00
0.65
non
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

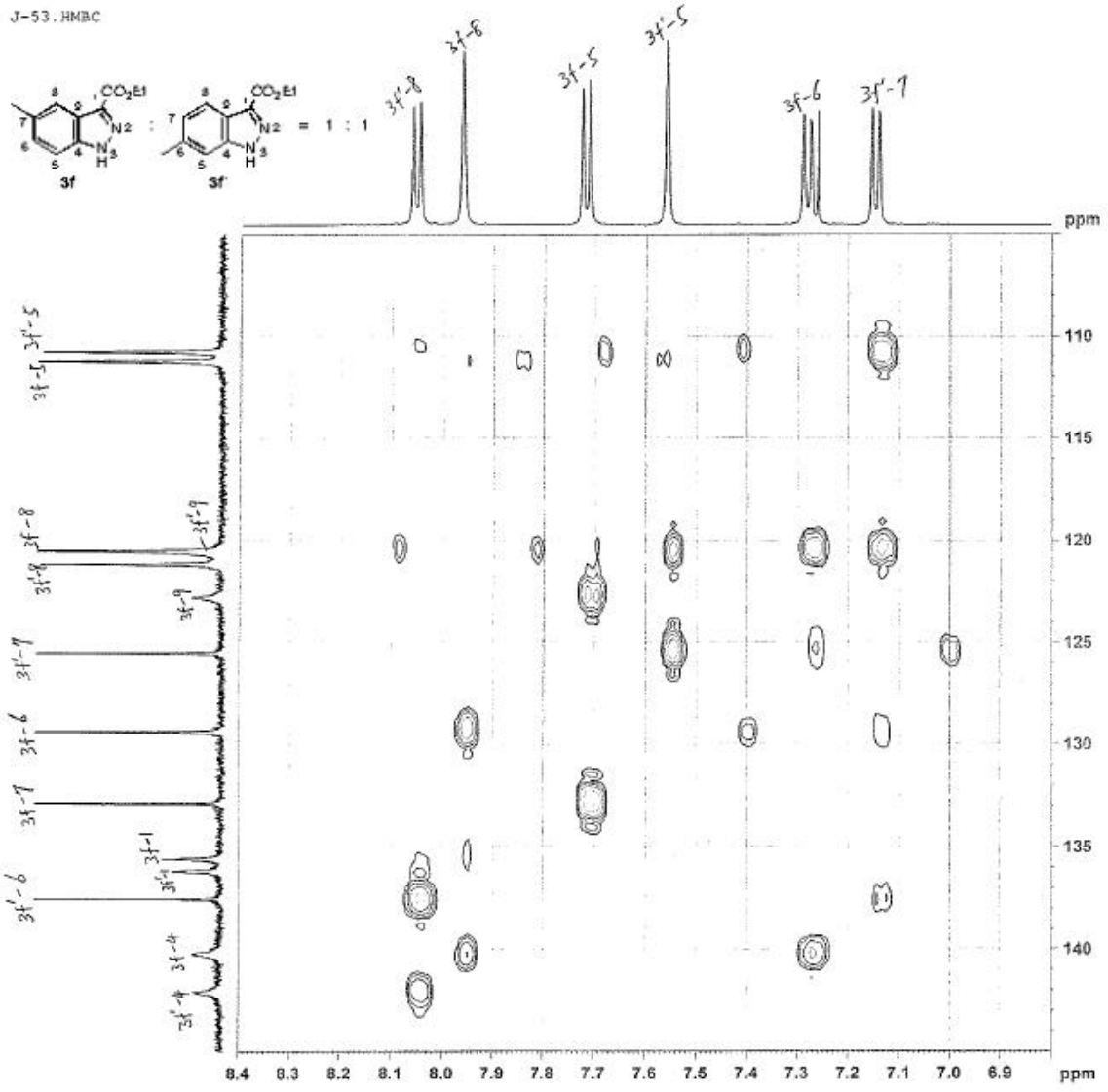

noe
0.1%
4.06%
3e nOe analysis
12.20
-300.00
non
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

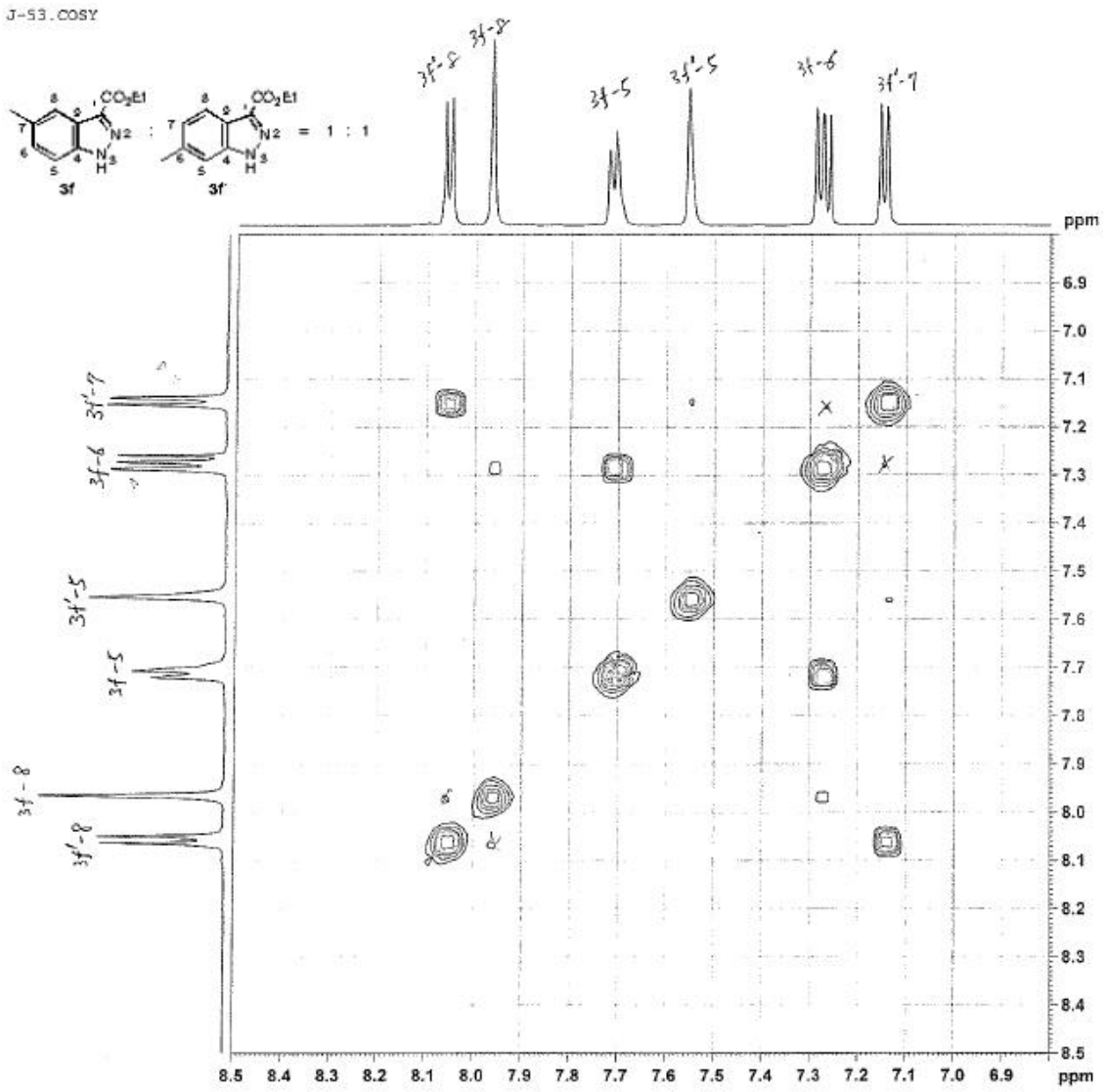

J-69.HMBC
3e
ppm
105
110
115
120
125
130
135
140
145
150
155
160
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm


8.076
8.048
7.970
7.700
7.671
7.528
7.293
7.260
7.159
7.132
4.567
4.556
4.543
4.533
4.519
2.509
1.484
1.461
1.458
1.437
3f
3f'
= 1 : 1
0.92
4.00
6.00
6.03
PPM
12.5
10.0
7.5
5.0
2.5
0.0
J-53
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
15.0
14.5
14.0

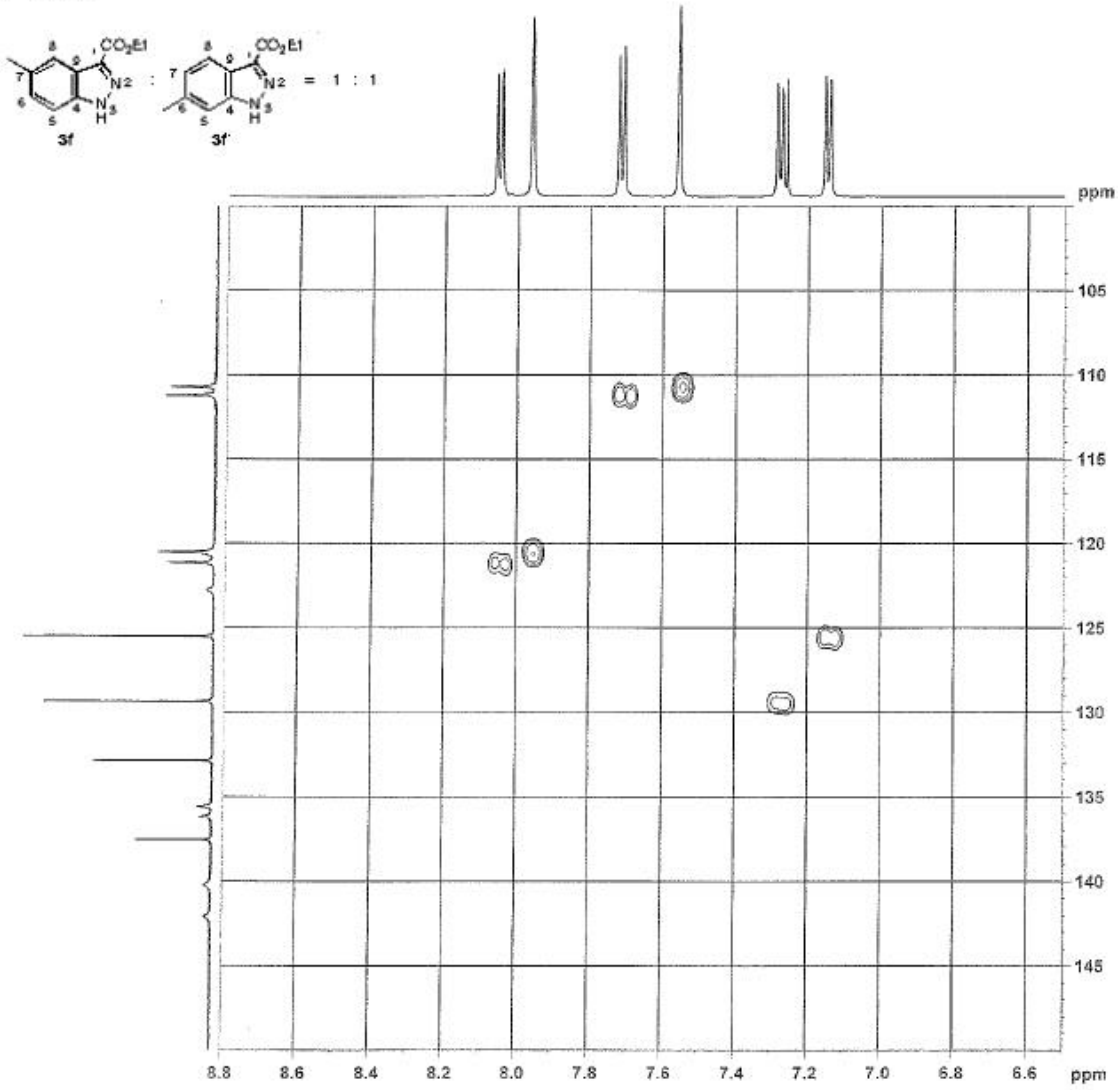

noe
0.16%
(s) H
3f nOe analysis
0.16%
(a) H
3f nOe analysis
1.64
0.51
1.23
1.25
100.00
non
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

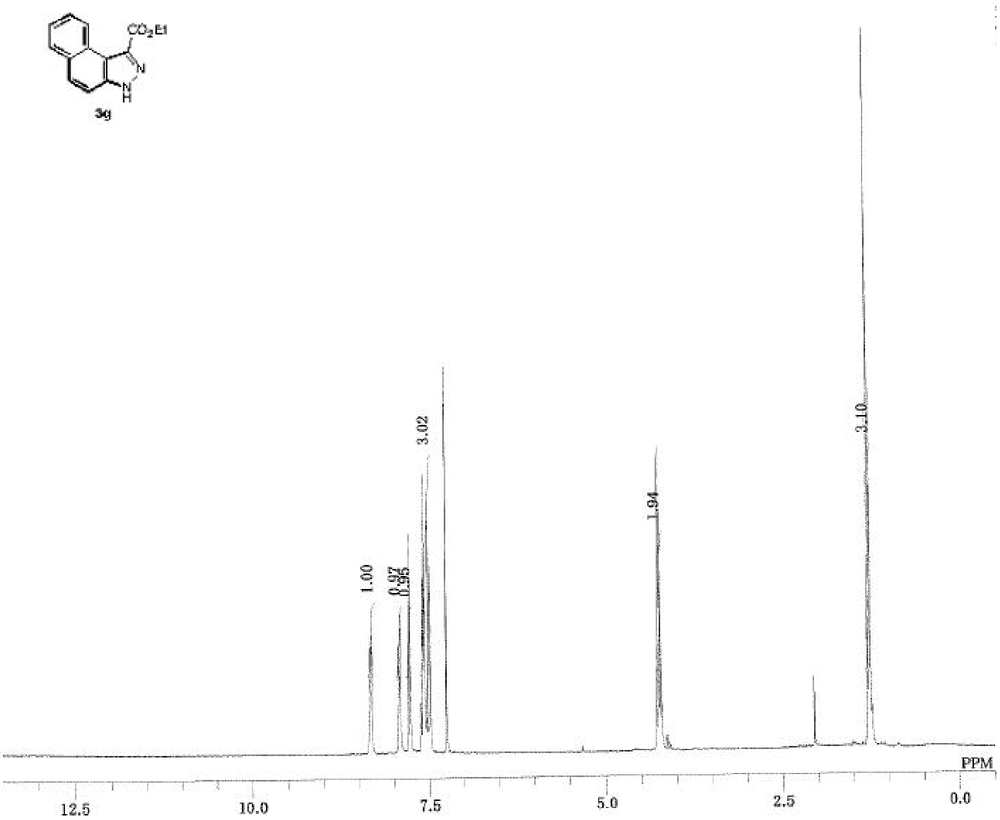

noe
0.16%
(s) H
3f nOe analysis
0.16%
(a) H
3f nOe analysis
0.16
0.16
100.00
3.03
non
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


J-53.HMBC
3f : 3f' = 1 : 1
3f-8
3f-6
3f-5
3f-5
3f-6
3f-7
ppm
110
115
120
125
130
135
140
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm

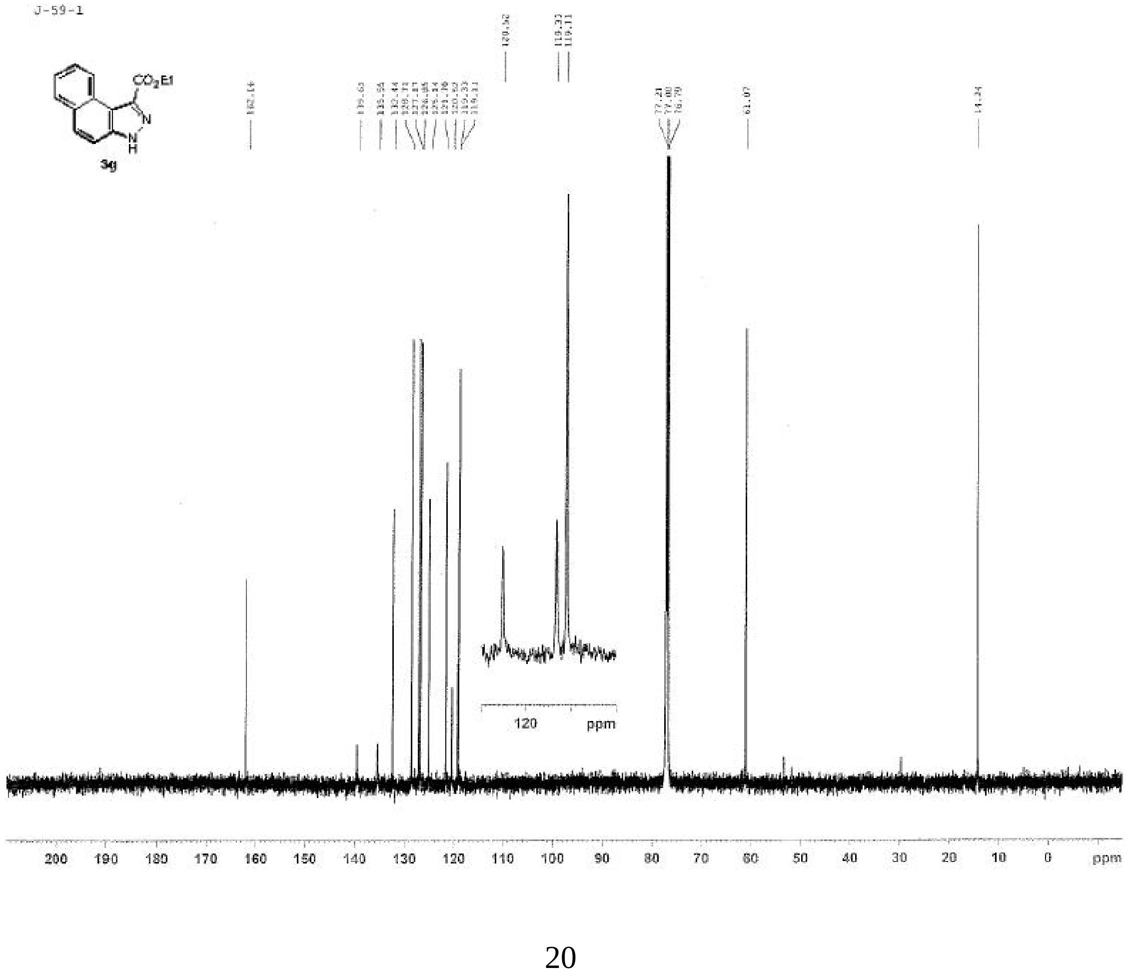

J-53.COSY
3f : 3f' = 1 : 1
3f
3f'
3f'-8
3f-8
3f-5
3f'-5
3f-6
3f'-7
ppm
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 ppm

J-53 . HMQC

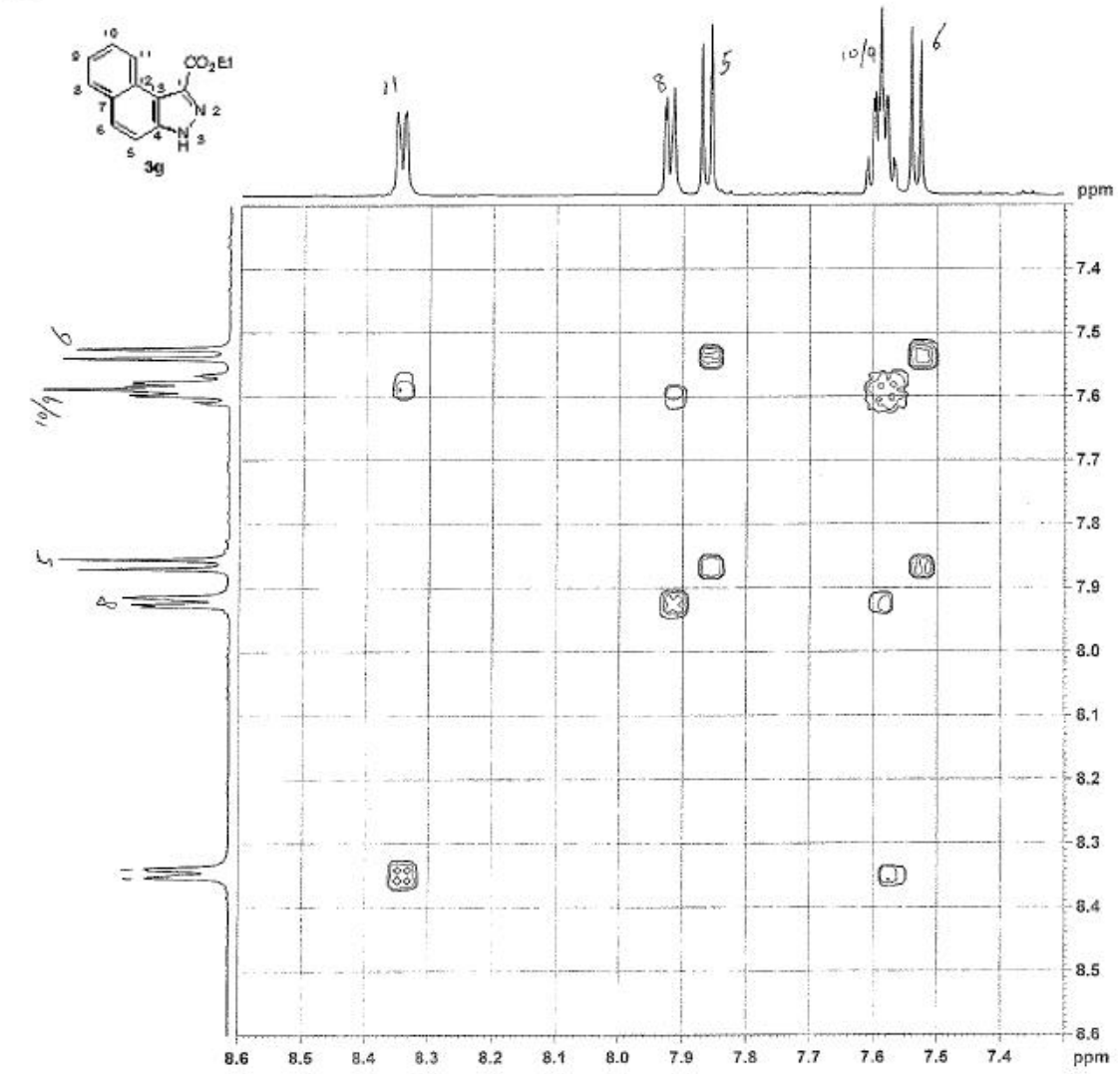

3f
3f'
= 1 : 1
ppm
105
110
115
120
125
130
135
140
145
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm

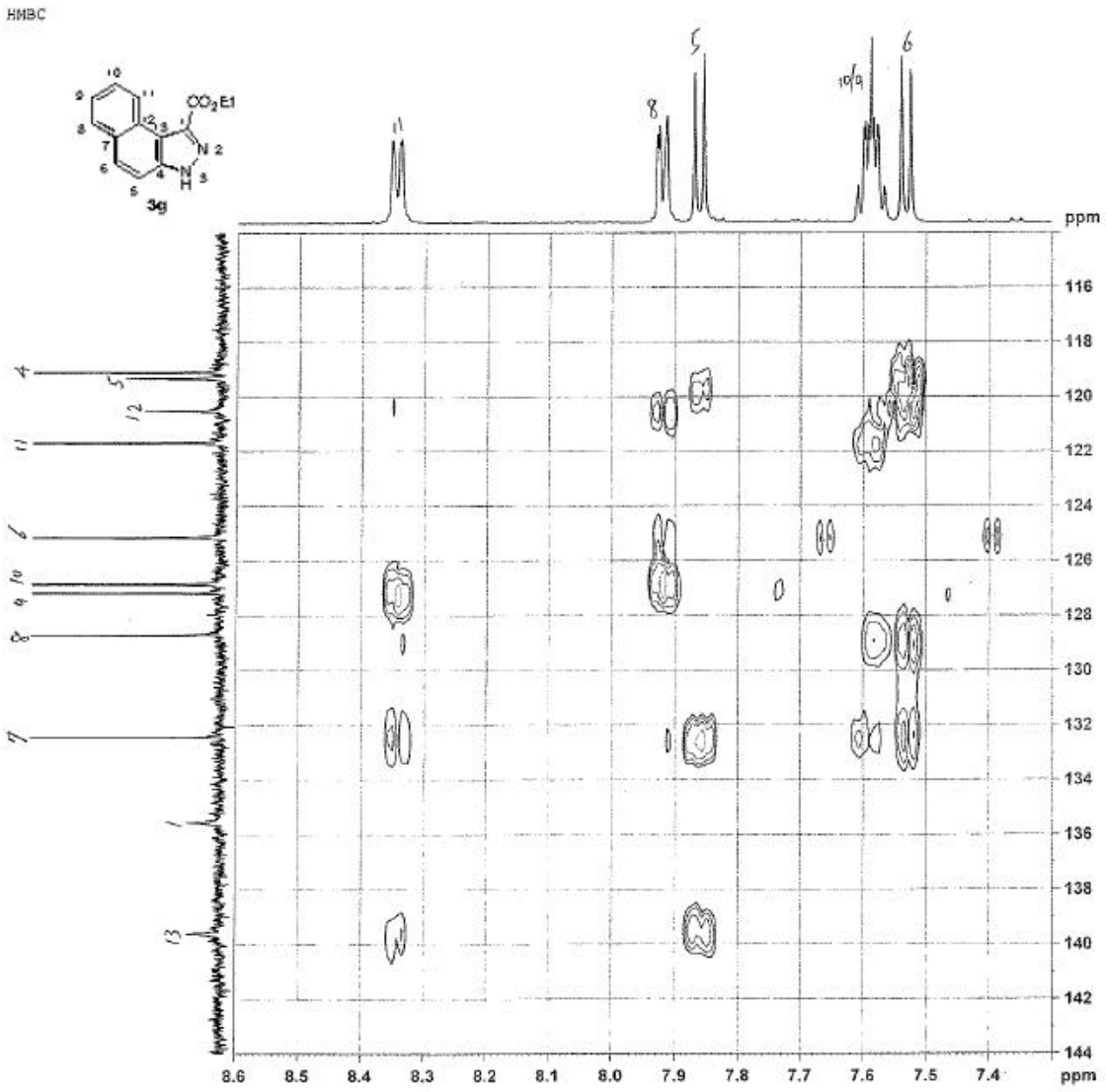

CO2Et
N
H
3g
1.00
0.97
0.95
3.02
1.94
3.10
PPM
12.5
10.0
7.5
5.0
2.5
0.0

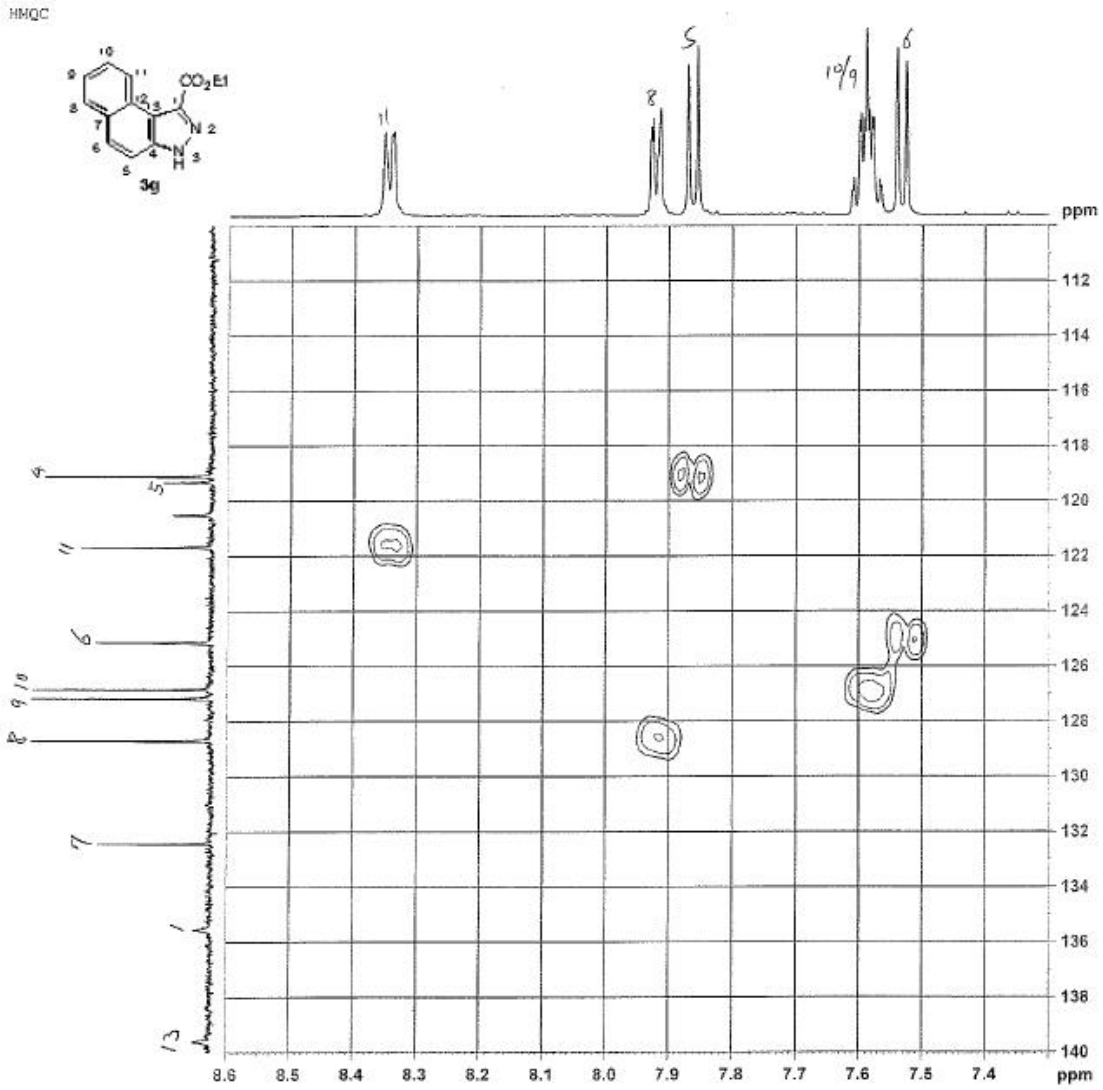
J-59-1

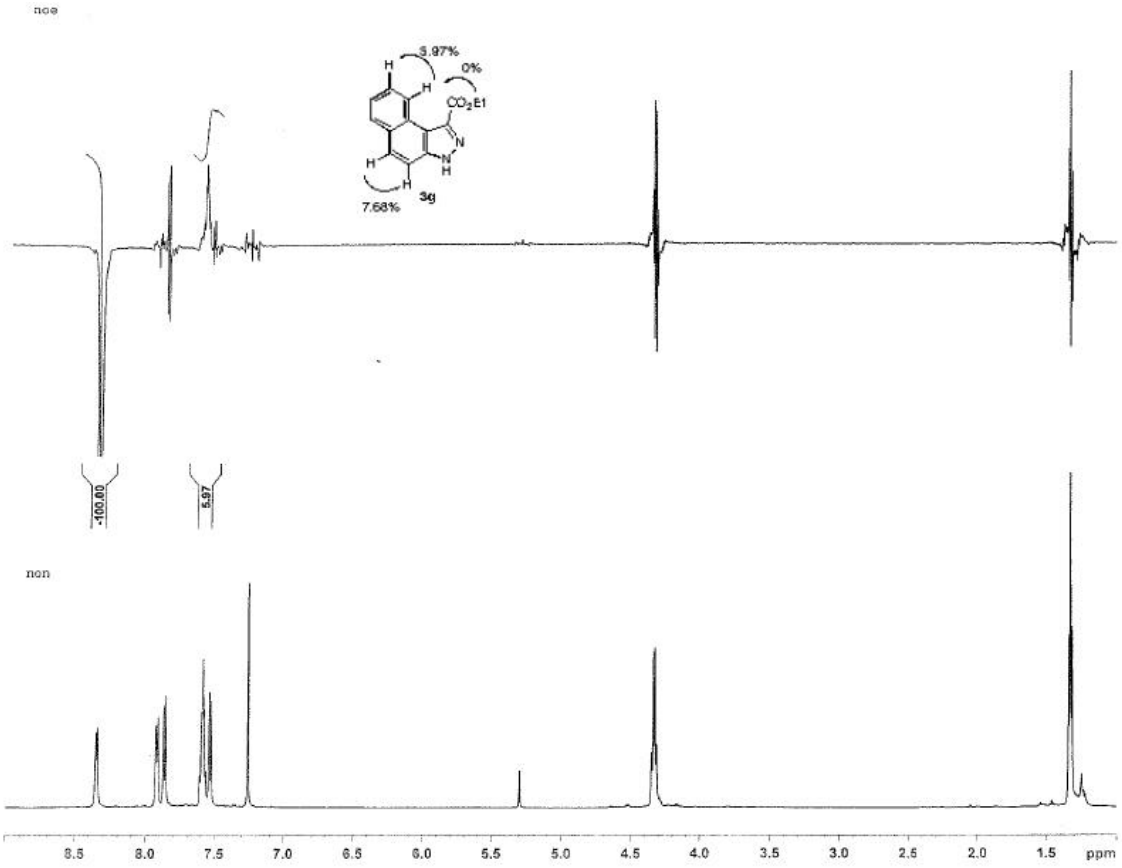

CO2Et
N
H
3g
120
ppm
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

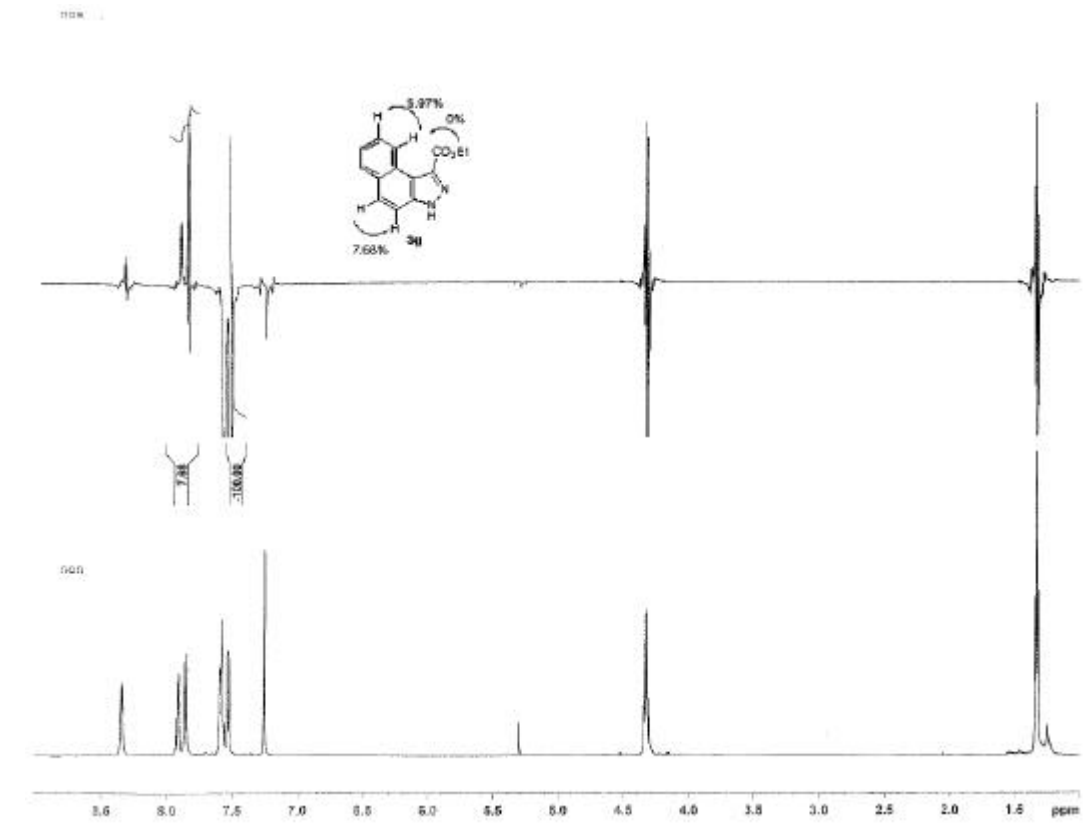
COSY

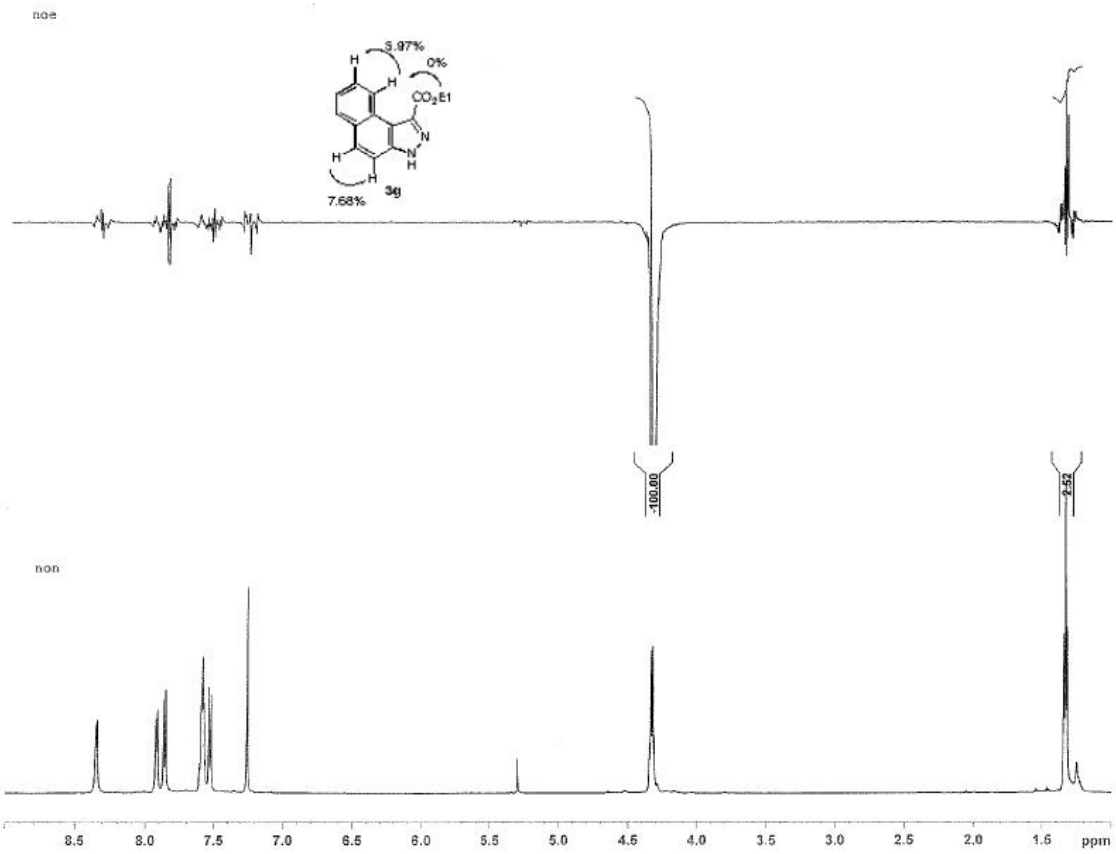

3g
CO2Et
N
H
11
8
5
10/9
6
ppm
7.4
7.5
7.6
7.7
7.8
7.9
8.0
8.1
8.2
8.3
8.4
8.5
8.6
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 ppm

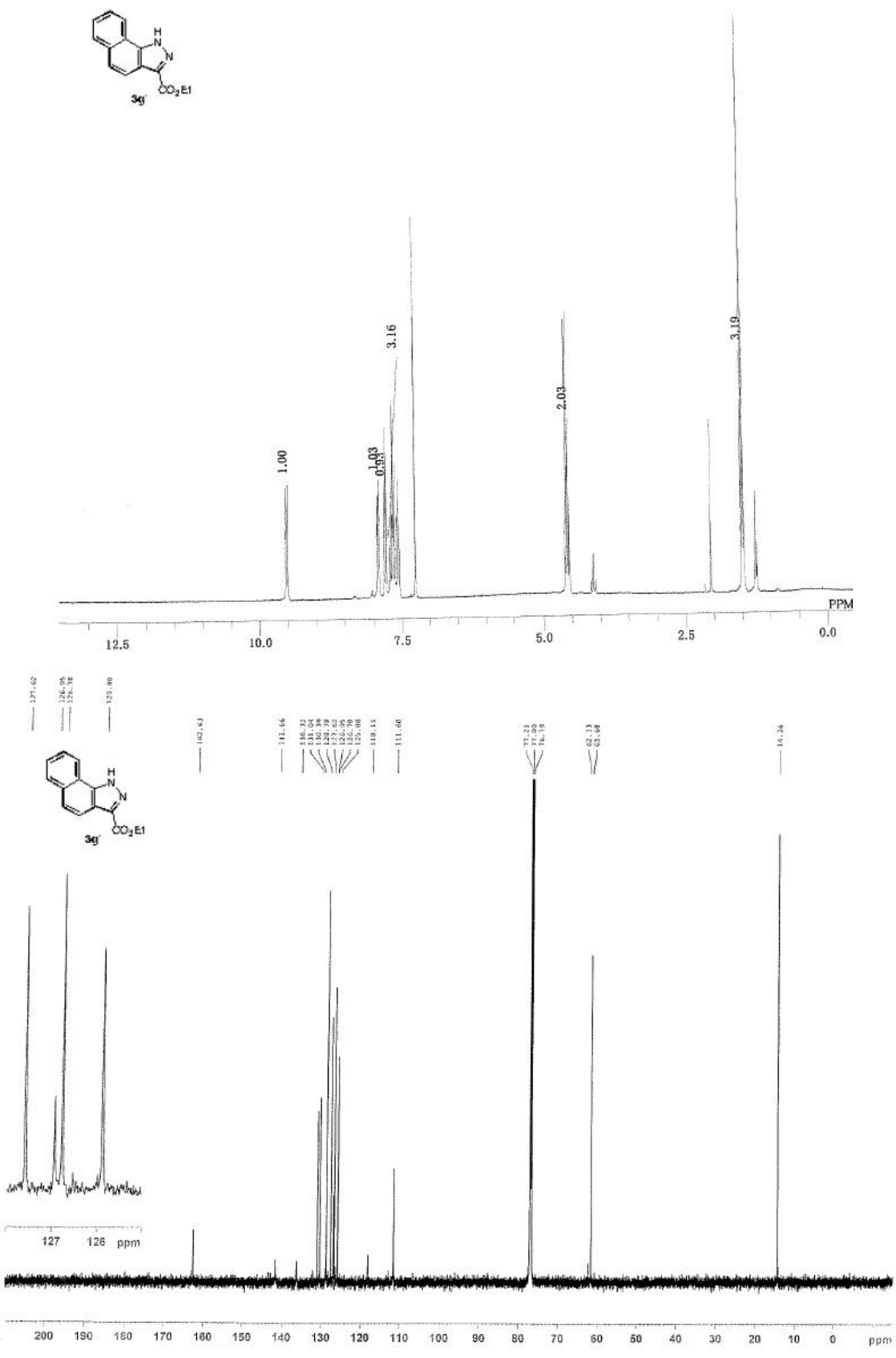

HMBC
3g
ppm
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
116
118
120
122
124
126
128
130
132
134
136
138
140
142
144

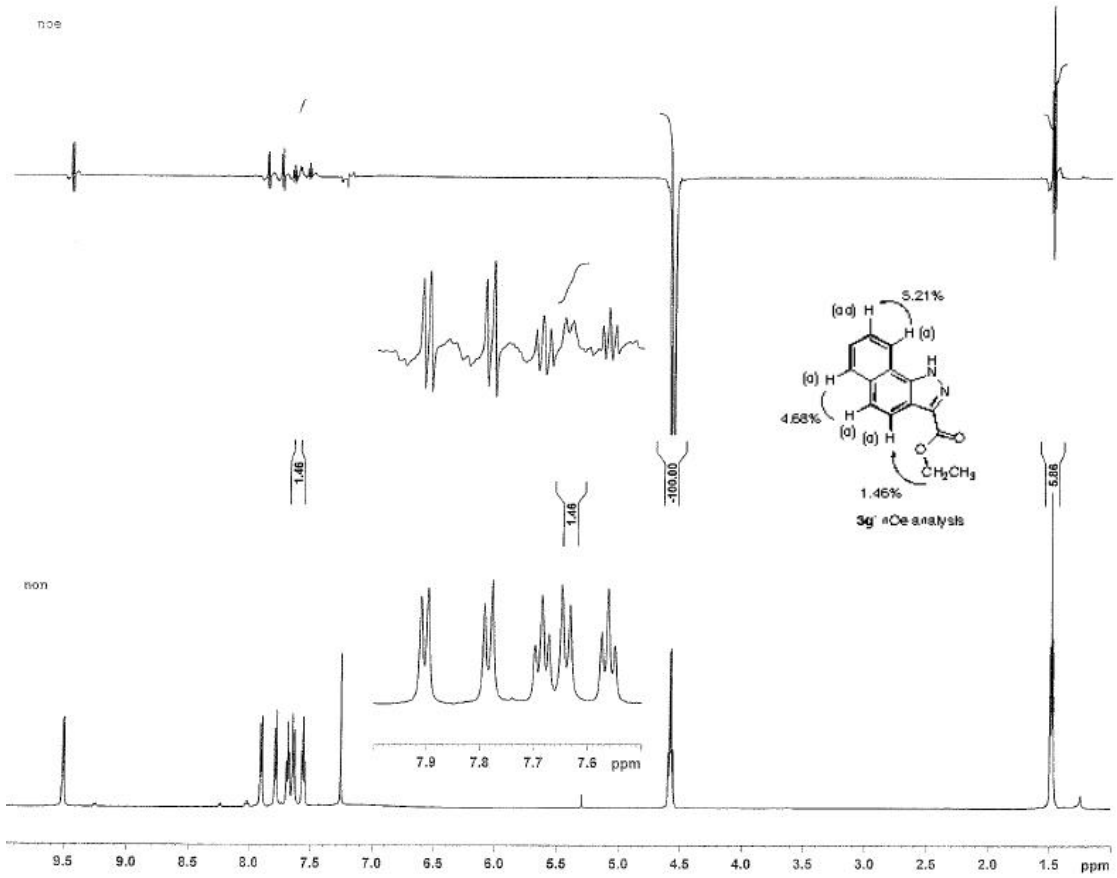

HMQC
3g
ppm
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
ppm
112
114
116
118
120
122
124
126
128
130
132
134
136
138
140

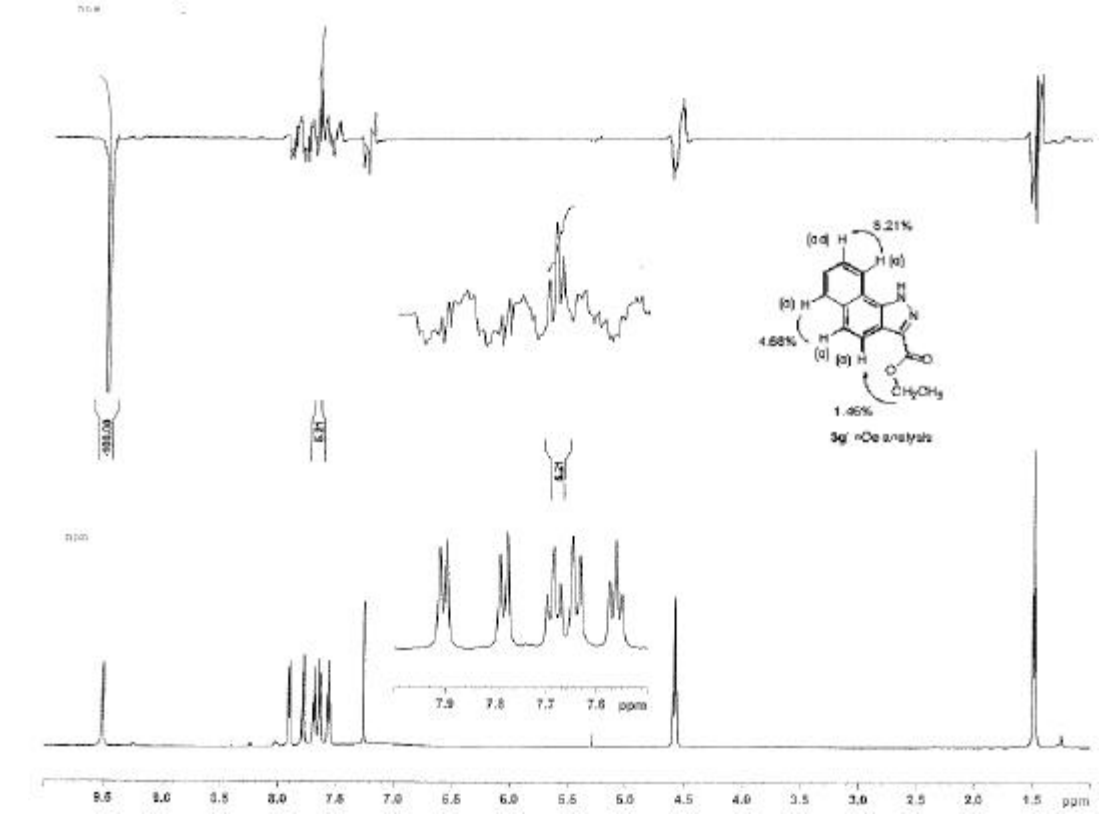

noe
5.97%
0%
CO_2Et
7.68%
3g
-100.00
5.97
non
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

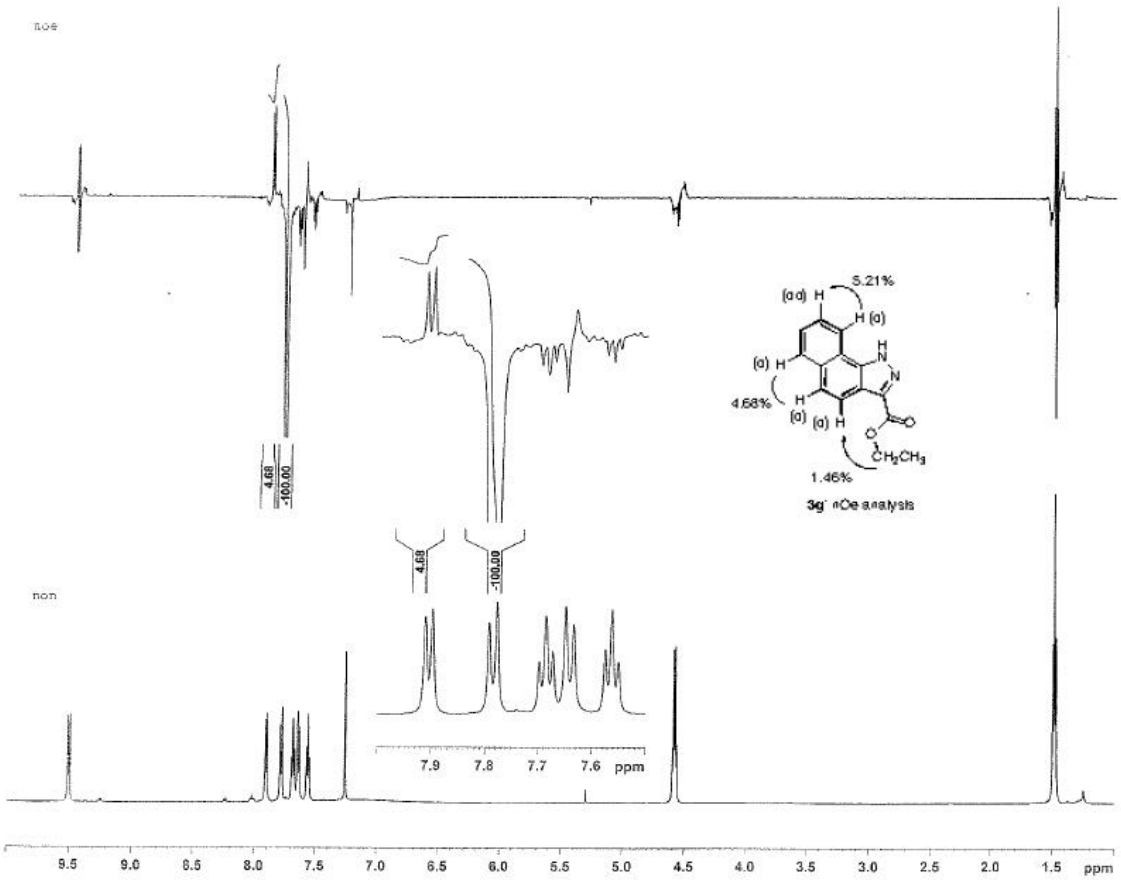

5.97%
0%
CO_2Et
7.68%
3g
non
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

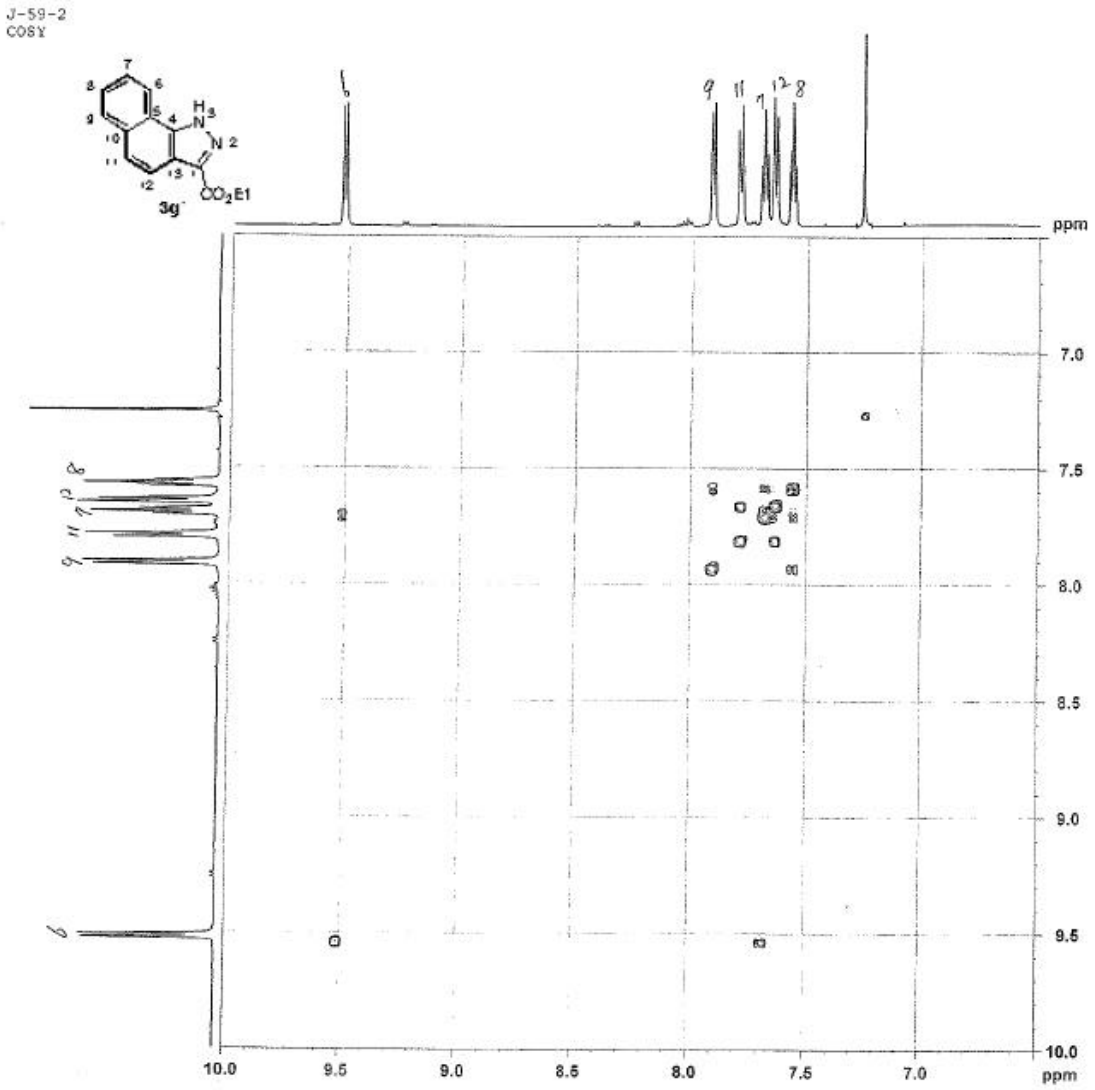

noe
3.97%
0%
CO_2Et
7.68%
3g
-100.00
2.52
non
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

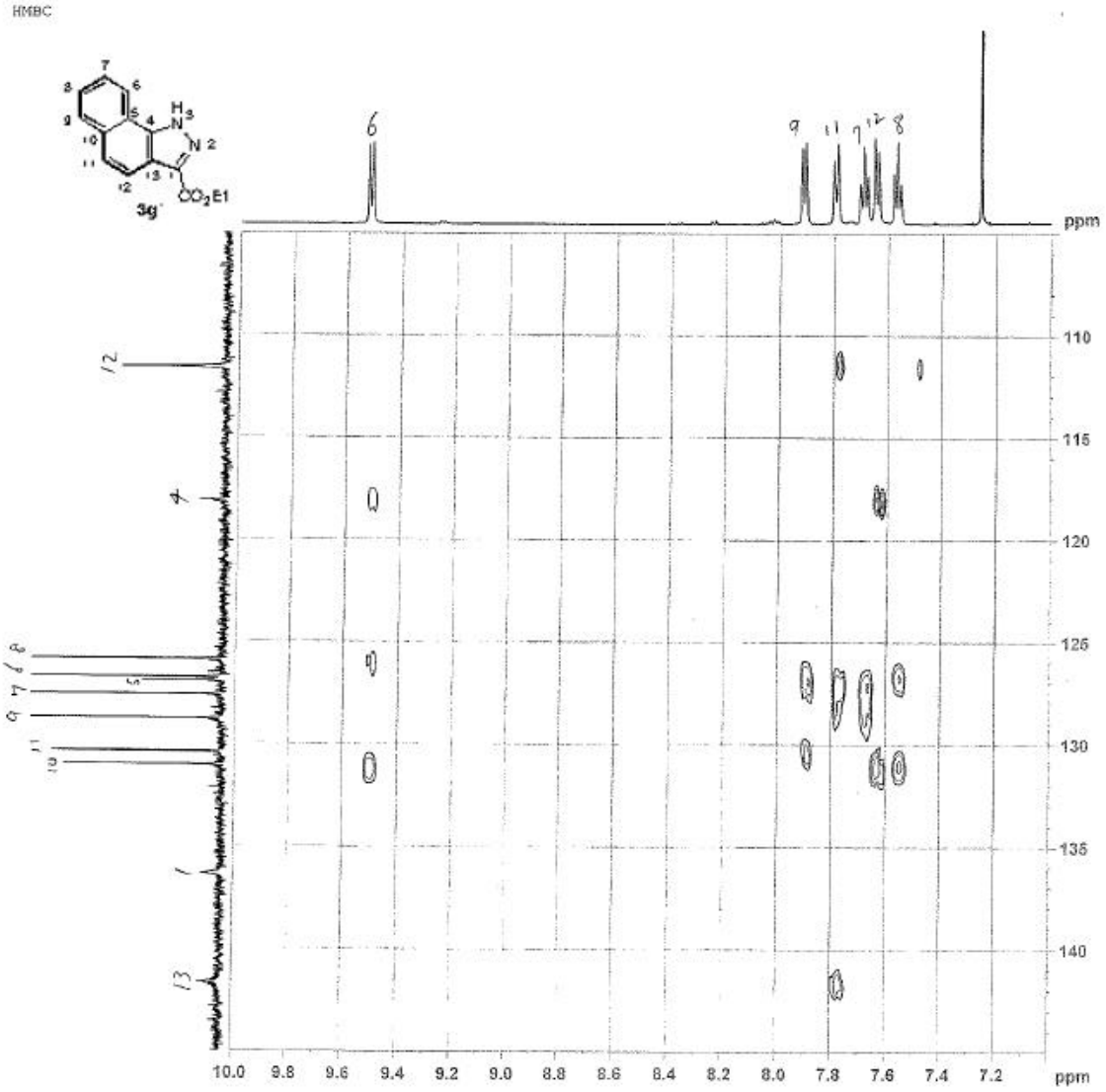

3g
CO2Et
1.00
1.03
0.99
3.16
2.03
3.19
PPM
12.5
10.0
7.5
5.0
2.5
0.0
127
126
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

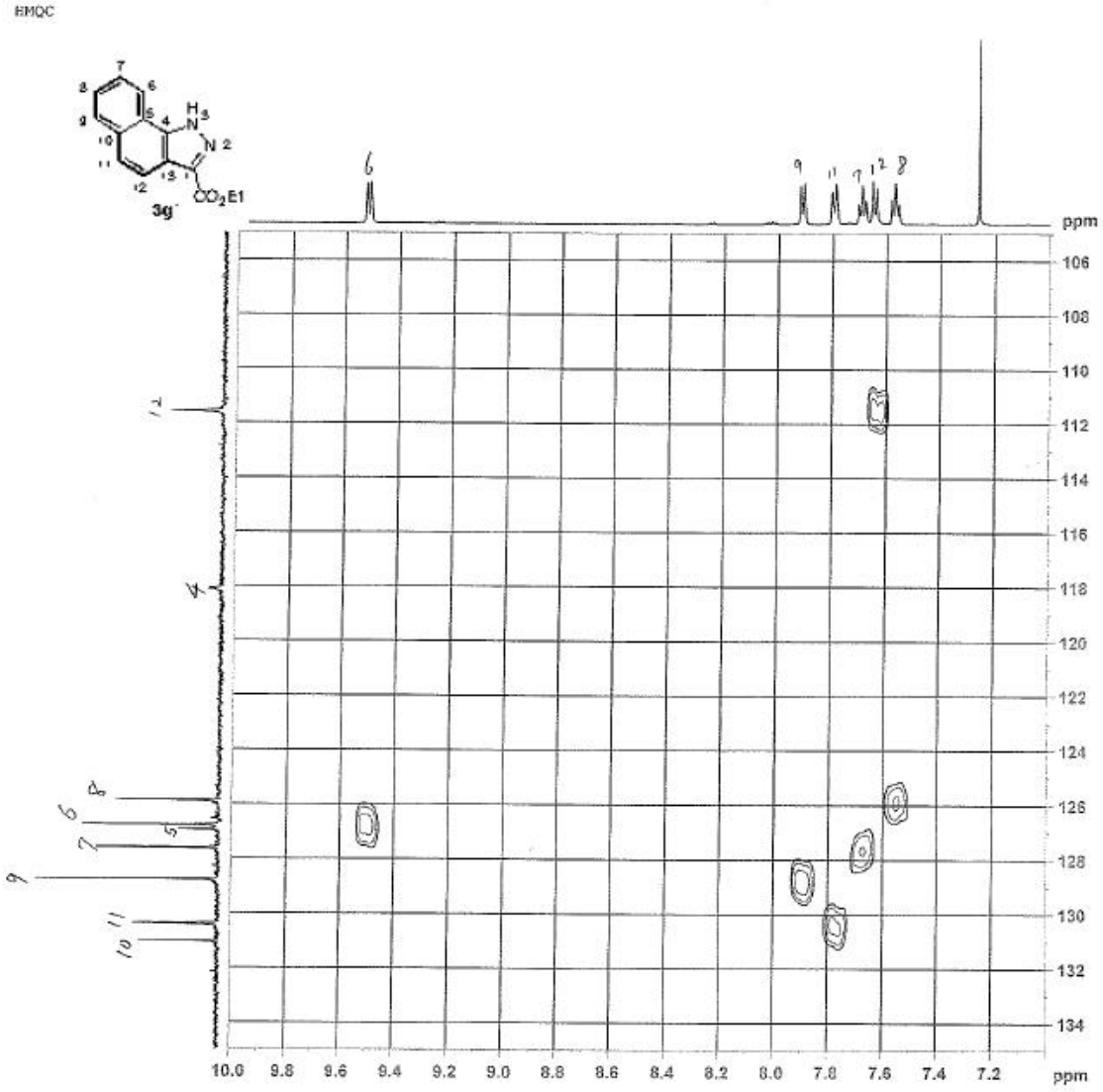

noe
1.46
1.46
-100.00
5.86
5.21%
(aa) H
H (a)
(a) H
4.68%
(a)
(a) H
1.46%
3g' nOe analysis
non
7.9
7.8
7.7
7.6 ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5 ppm

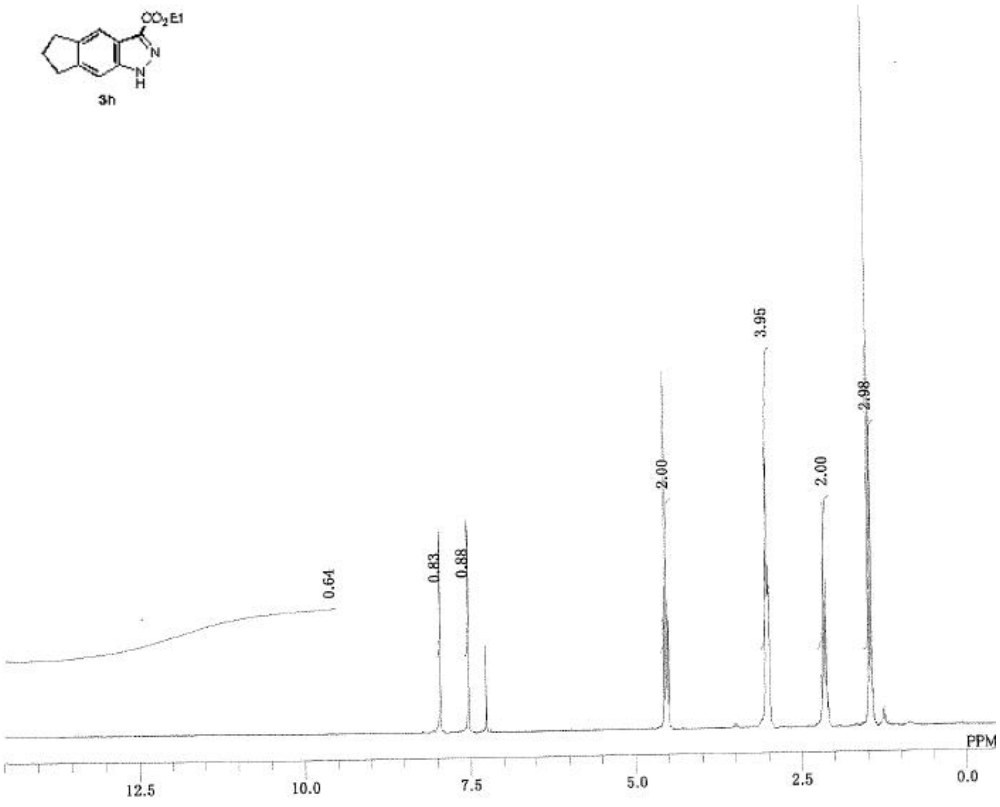

5.21%
(aa) H
H (a)
(a) H
4.68%
(a)
(a) H
1.46%
3g' nOe analysis
7.9
7.8
7.7
7.6 ppm
9.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5 ppm

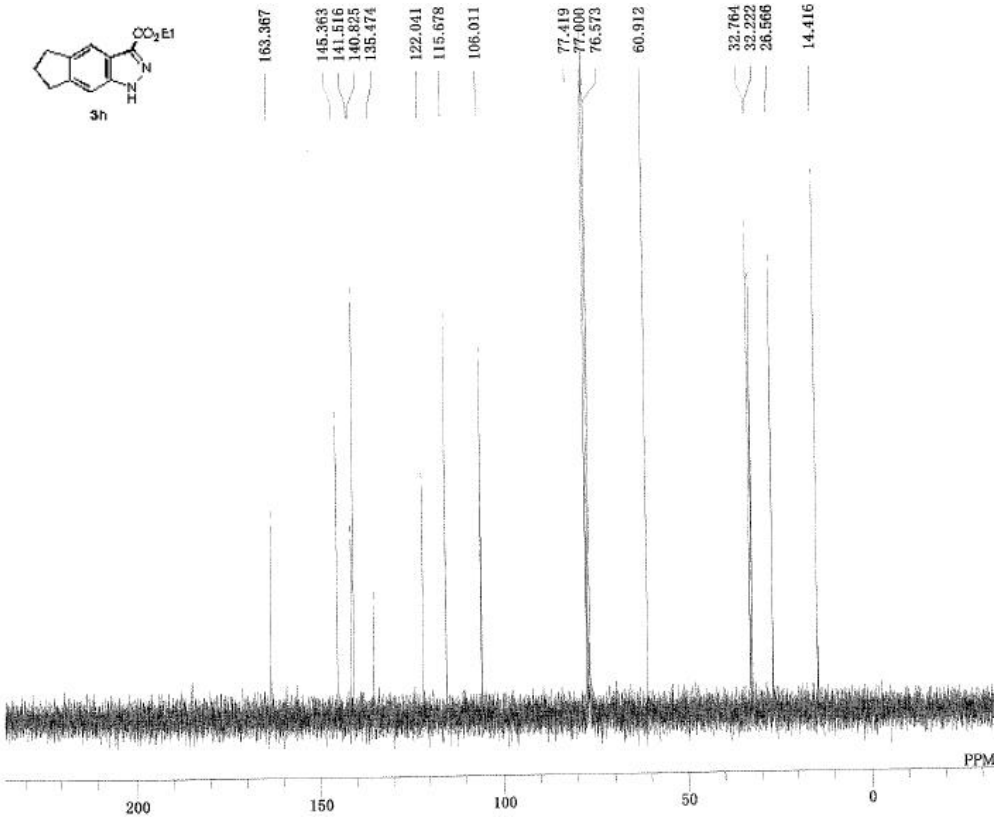

noe
4.68
-100.00
5.21%
(a) H
H (a)
(a) H
4.68%
(a) (a) H
1.46%
3g' nOe analysis
non
4.68
-100.00
7.9 7.8 7.7 7.6 ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm


J-59-2
COSY
3g
CO2Et
ppm
10.0
9.5
9.0
8.5
8.0
7.5
7.0


HMBC
3g
ppm
10.0
9.8
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
110
115
120
125
130
135
140

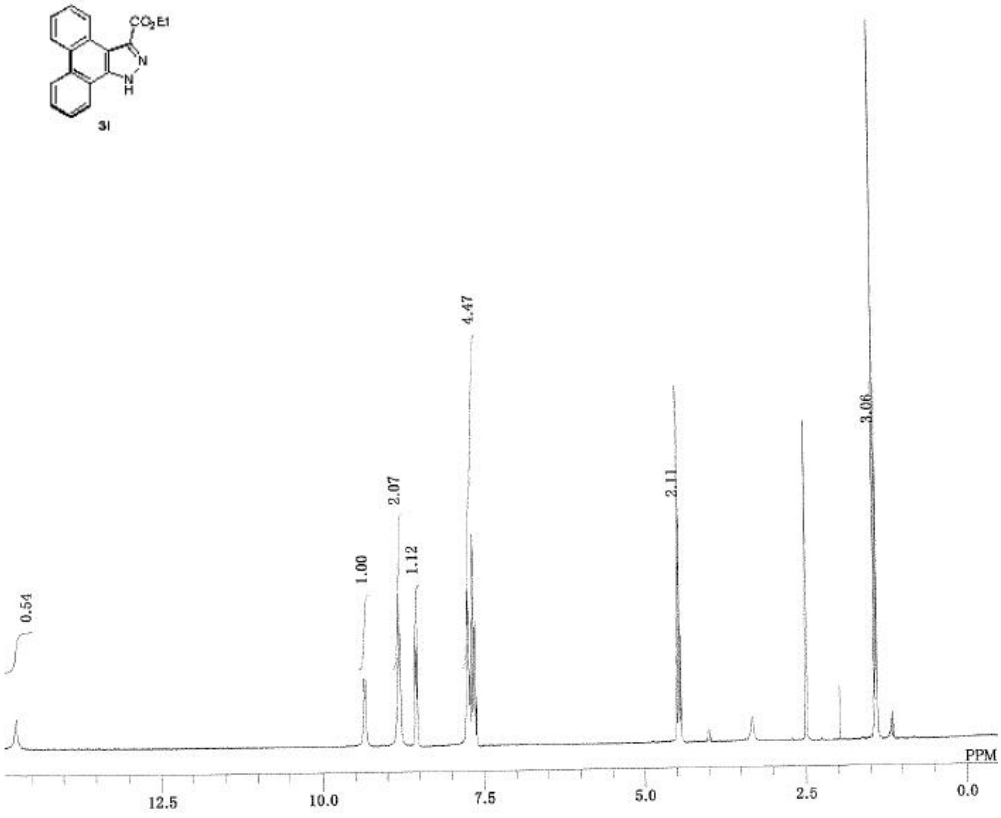

HMQC
3g
CO2Et
ppm
106
108
110
112
114
116
118
120
122
124
126
128
130
132
134
10.0
9.8
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm

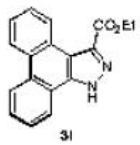

CO2Et
N
H
3h
0.64
0.83
0.88
2.00
3.95
2.00
2.98
PPM
12.5
10.0
7.5
5.0
2.5
0.0


CO2Et
N
H
3h
163.367
145.363
141.516
140.825
135.474
122.041
115.678
106.011
77.419
77.000
76.573
60.912
32.764
32.222
26.566
14.416
PPM
200
150
100
50
0

CO2Et
N
N
H

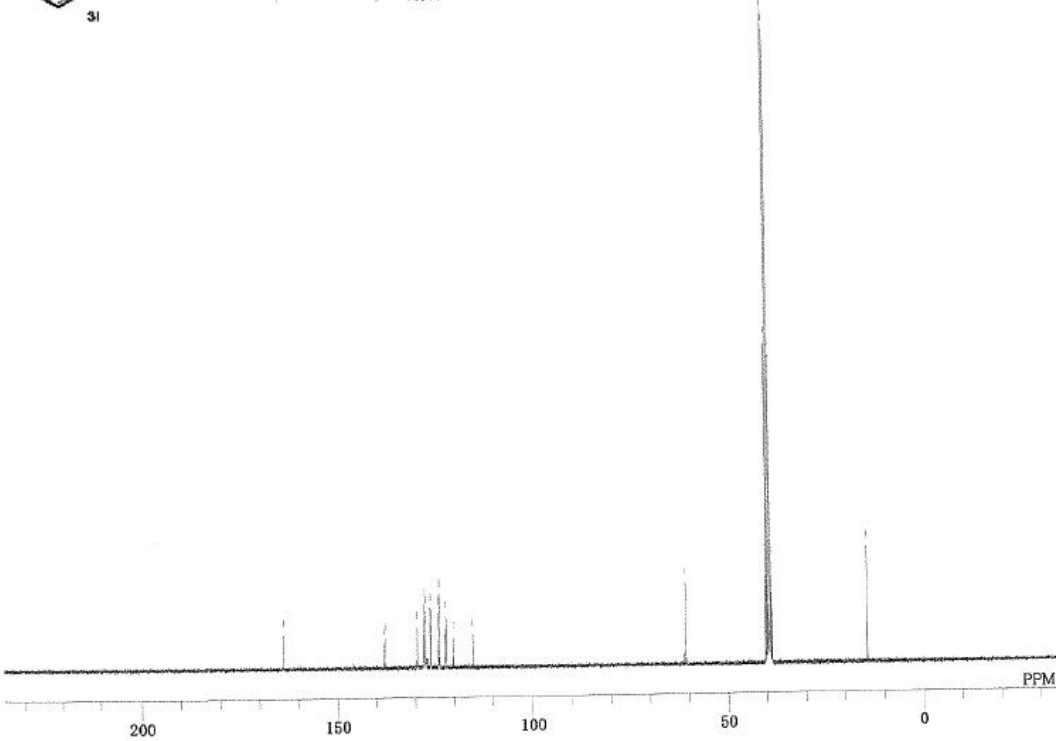
3l

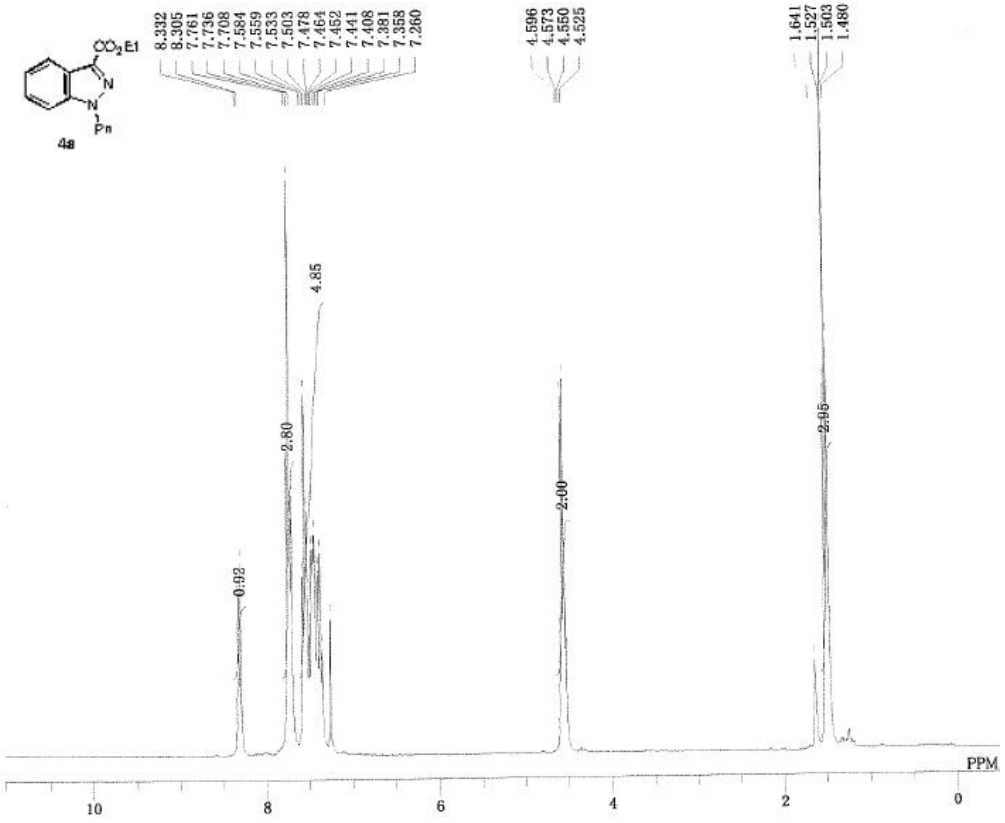

0.54
1.00
2.07
1.12
4.47
2.11
3.06
PPM
12.5
10.0
7.5
5.0
2.5
0.0

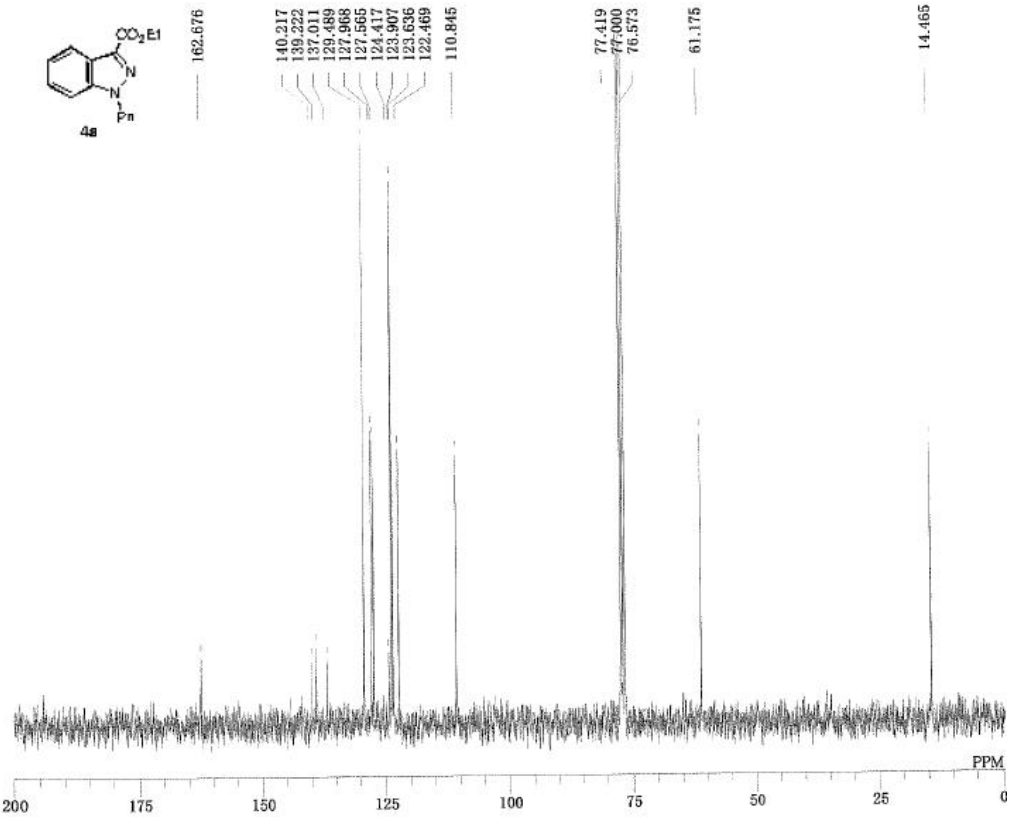

CO2Et
N
N
H

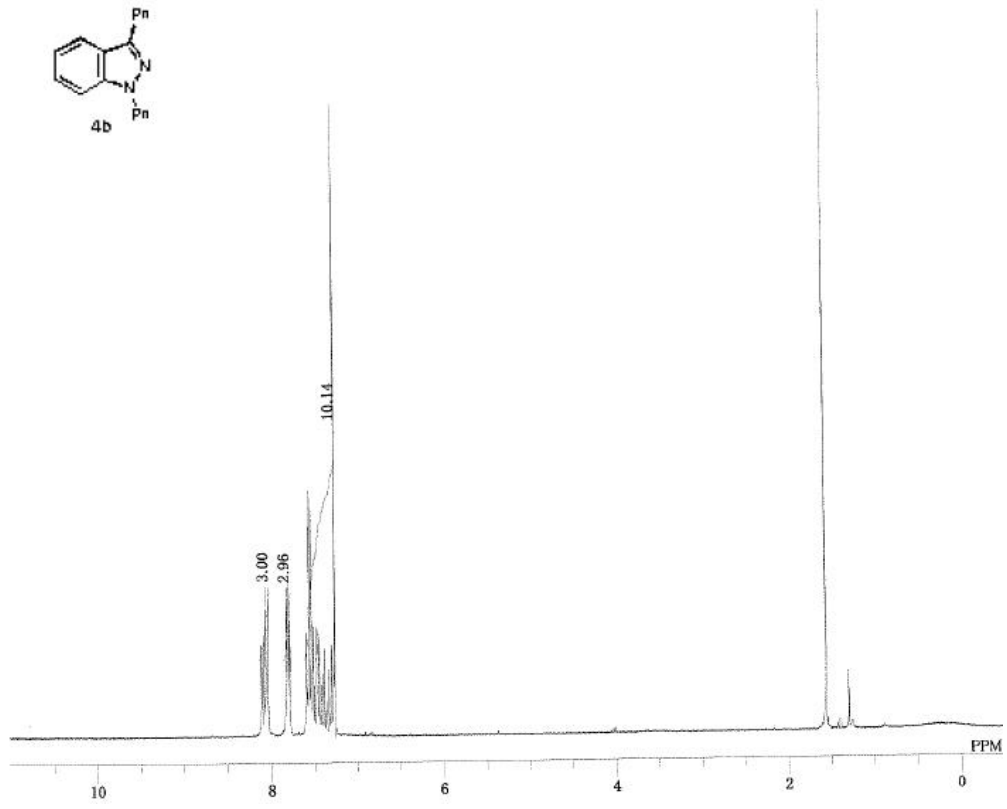
3l

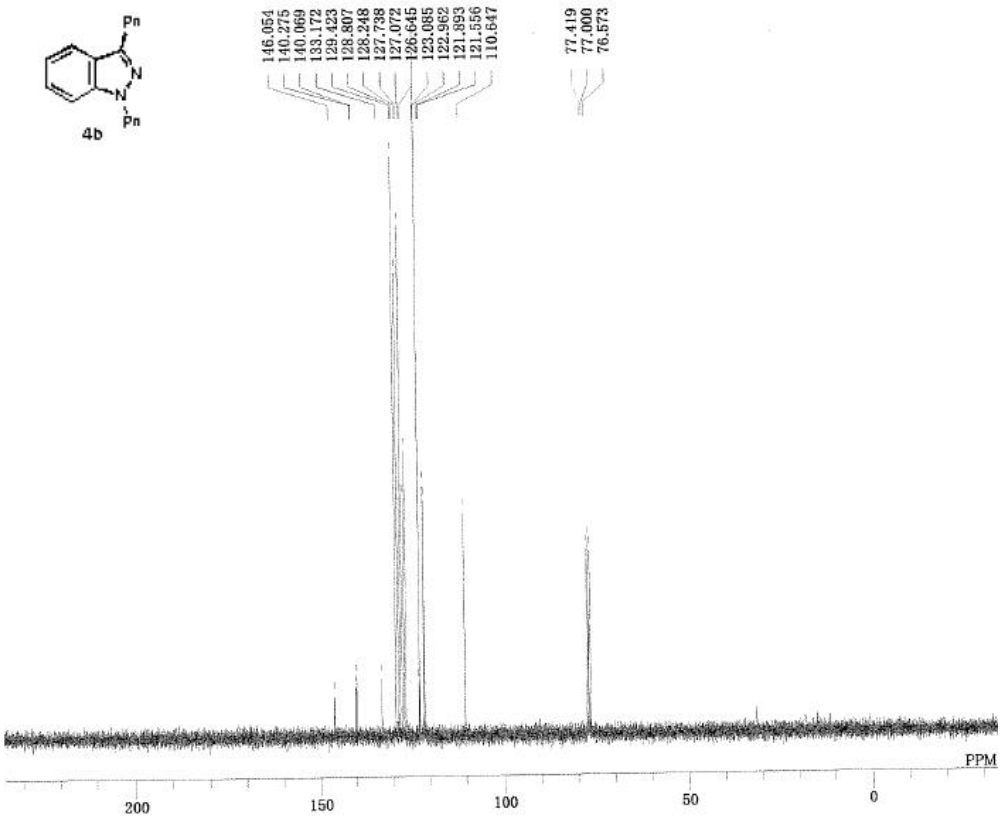

163.846
138.156
137.795
129.673
128.086
128.020
127.749
127.535
126.368
126.097
126.014
124.157
123.902
122.315
120.392
115.484
60.890
40.330
40.059
39.760
39.500
39.220
38.949
38.670
14.279

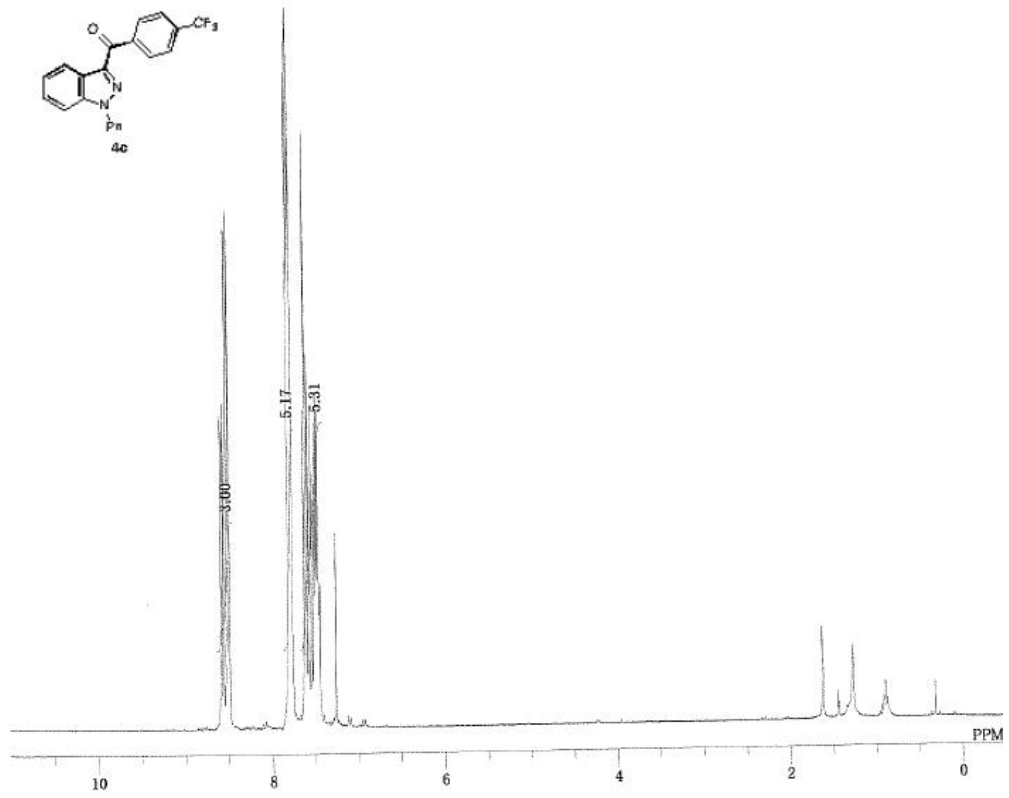

PPM
200
150
100
50
0

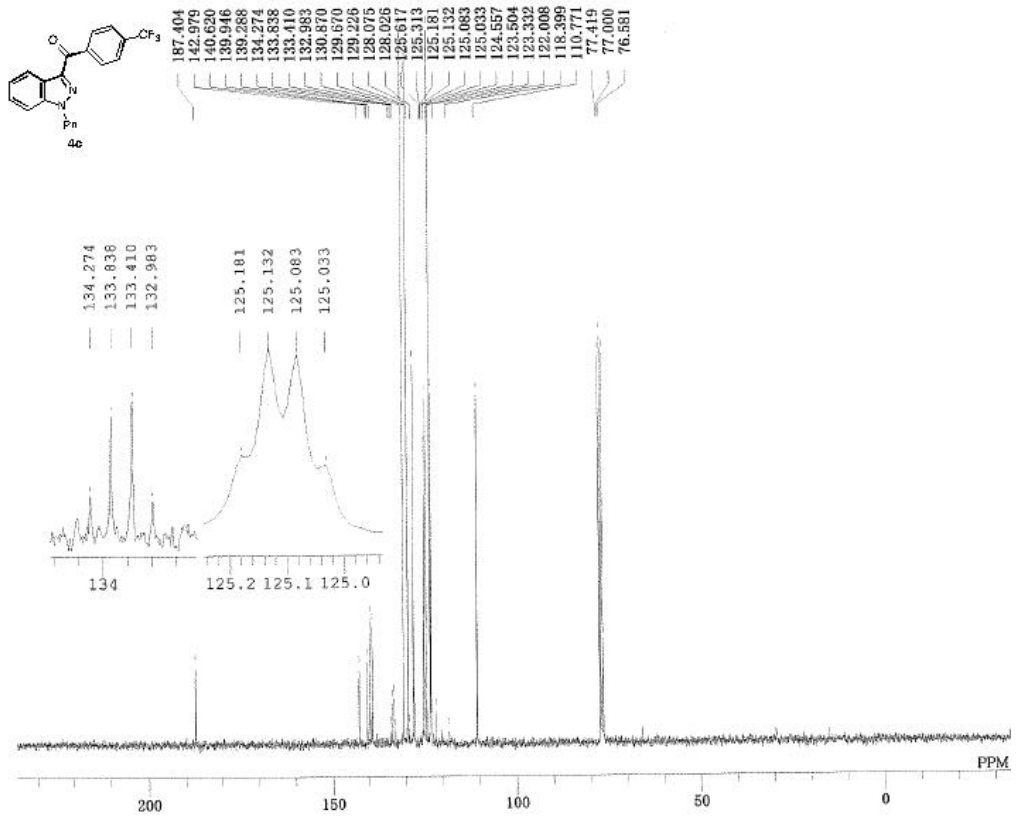

8.332
8.305
7.761
7.736
7.708
7.584
7.559
7.533
7.503
7.478
7.464
7.452
7.441
7.408
7.381
7.358
7.260
4.596
4.573
4.550
4.525
1.641
1.527
1.503
1.480
0.92
2.80
4.85
2.00
2.95
PPM
10
8
6
4
2
0
4a

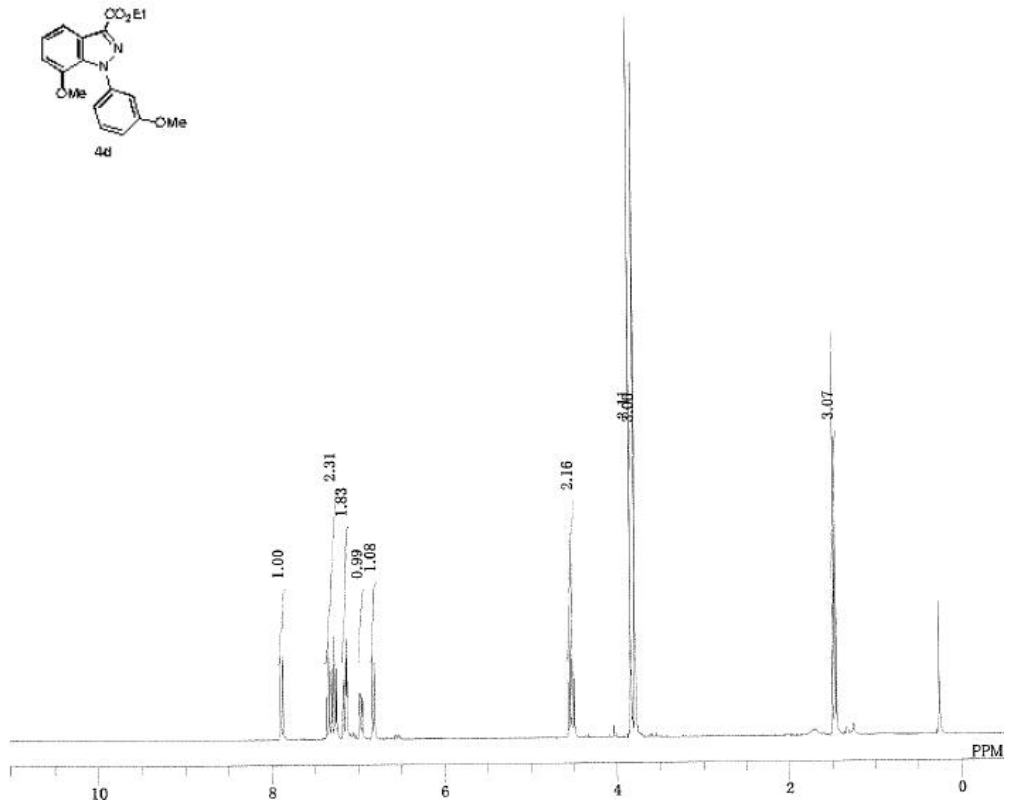

162.676
140.217
139.222
137.011
129.489
127.968
127.565
124.417
123.907
123.636
122.469
110.845
77.419
77.000
76.573
61.175
14.465
PPM
200
175
150
125
100
75
50
25
0
4a

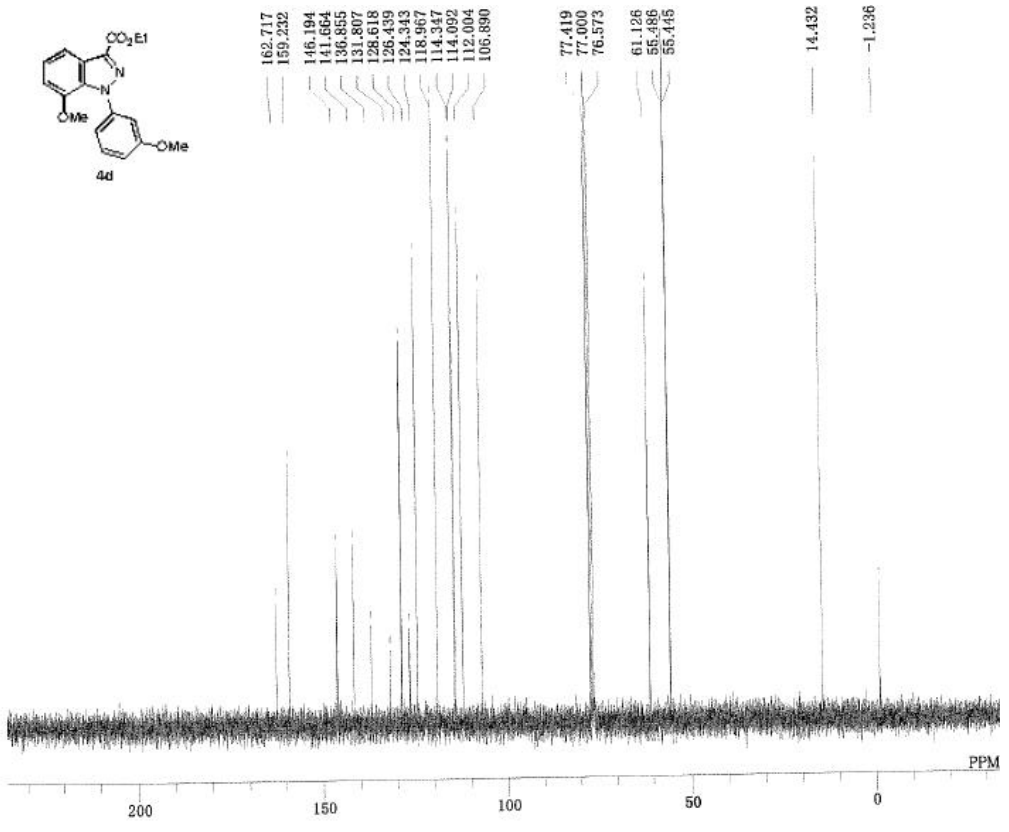

Pn
Pn
4b
10.14
3.00
2.96
PPM
10
8
6
4
2
0

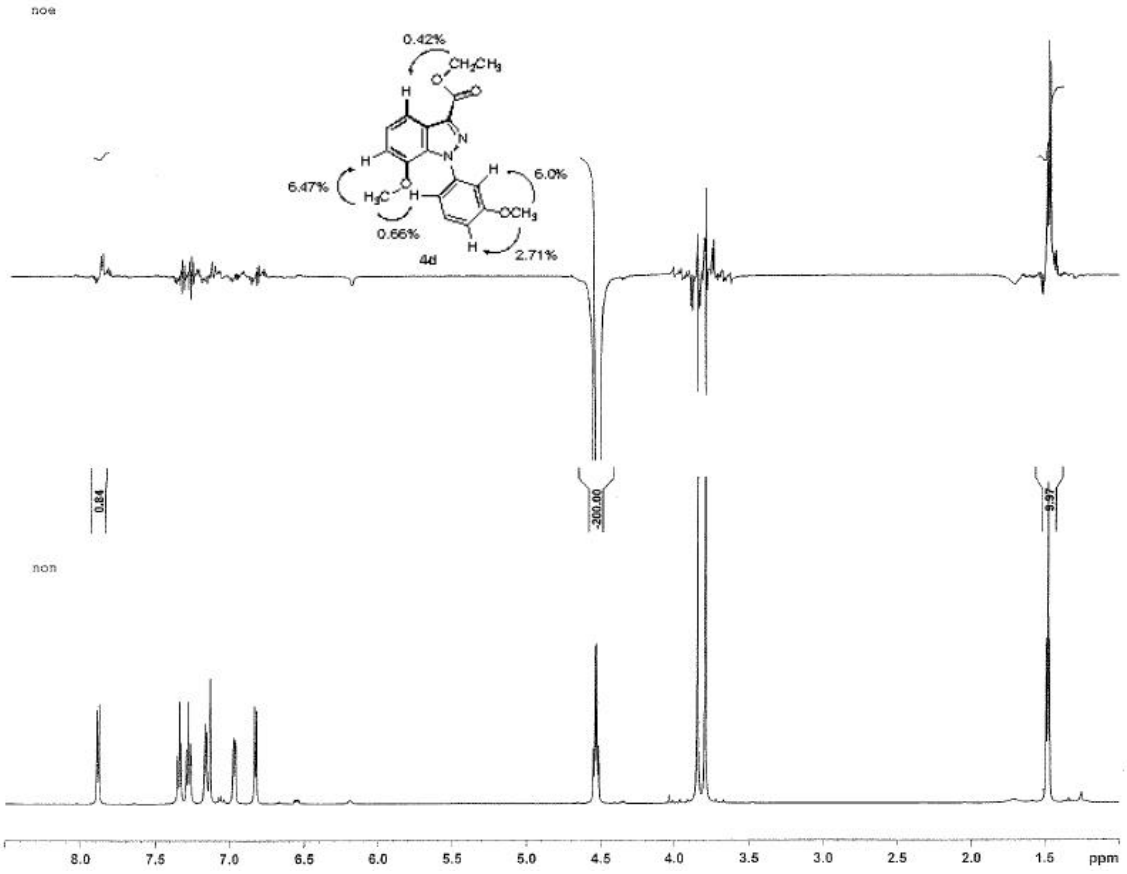

Pn
Pn
4b
146.054
140.275
140.069
133.172
129.423
128.807
128.248
127.738
127.072
126.645
123.085
122.962
121.993
121.556
110.647
77.419
77.000
76.573
PPM
200
150
100
50
0

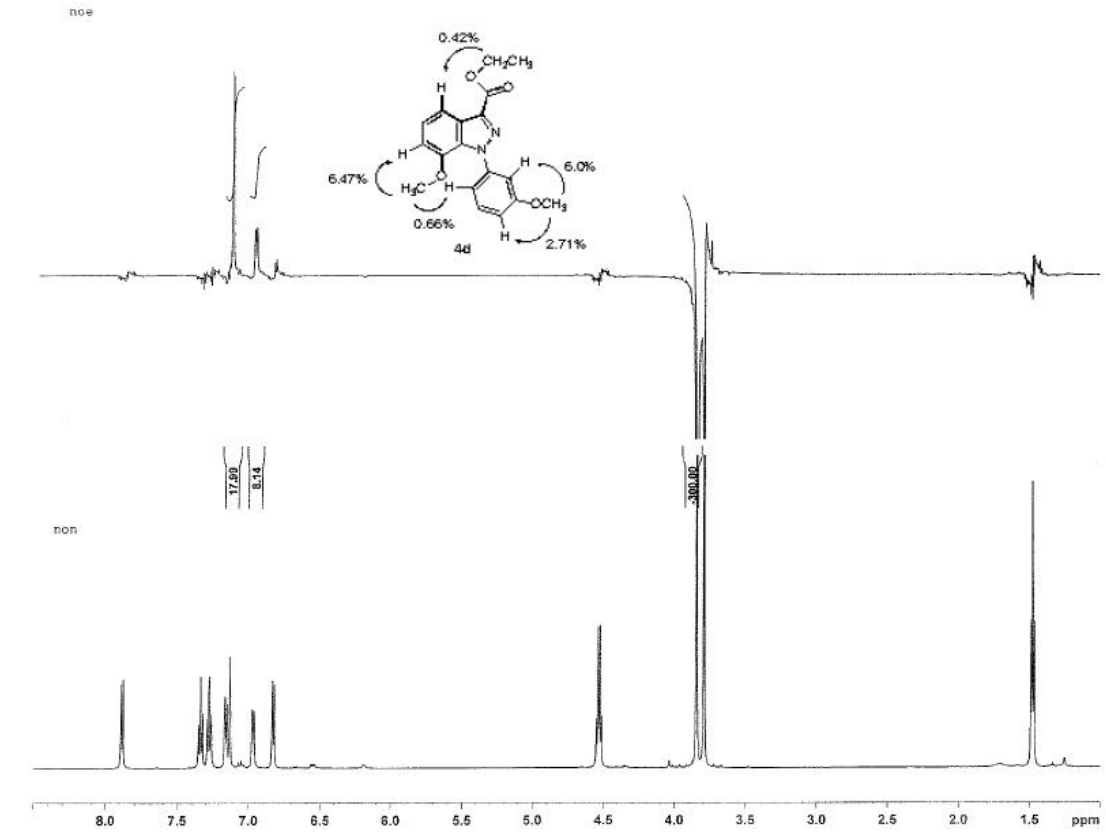

4c
3.00
5.17
5.31
PPM
10
8
6
4
2
0

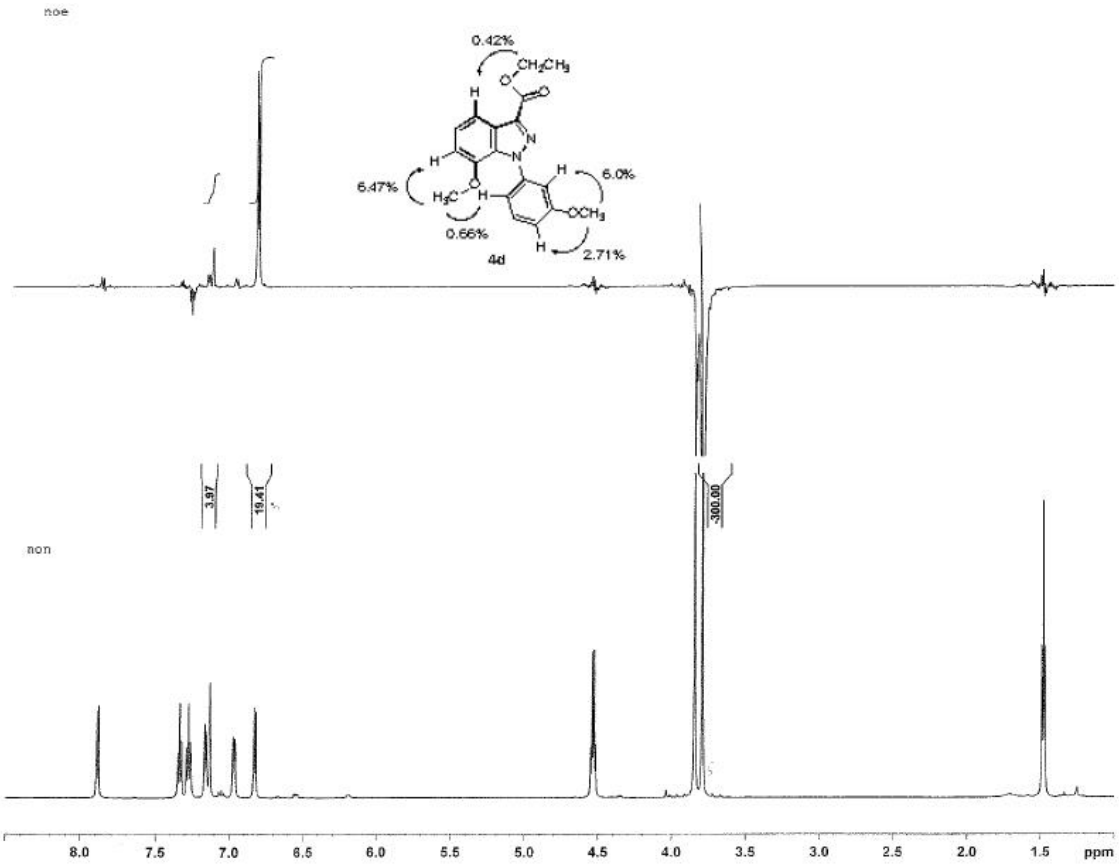

4c
187.404
142.979
140.620
139.946
139.288
134.274
133.838
133.410
132.983
130.870
129.670
129.226
128.075
128.026
125.617
125.313
125.181
125.132
125.083
125.033
124.557
123.504
123.332
122.008
118.399
110.771
77.419
77.000
76.581
134.274
133.838
133.410
132.983
125.181
125.132
125.083
125.033
134
125.2 125.1 125.0
PPM
200
150
100
50
0

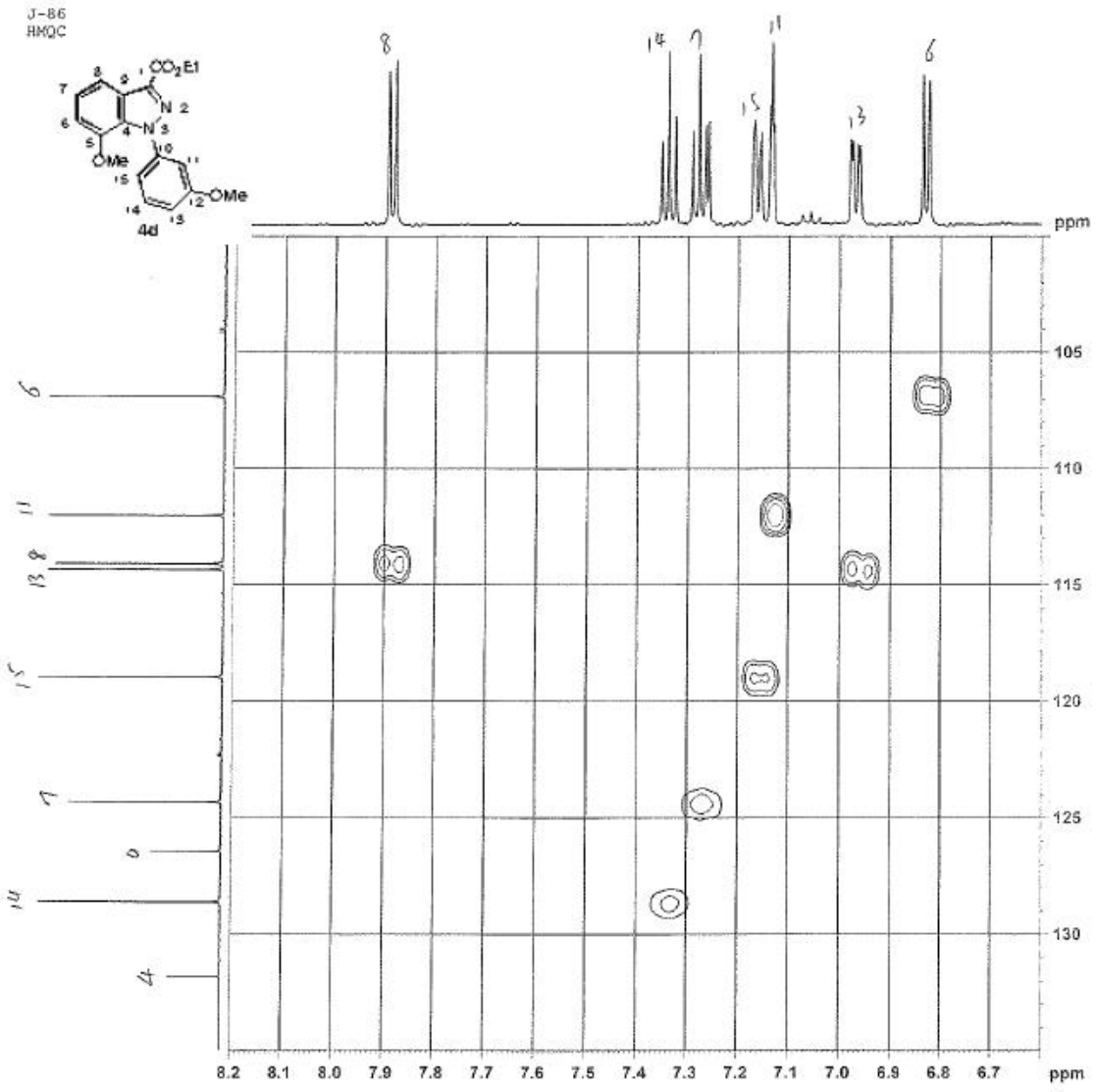

CO2Et
N
N
OMe
OMe
4d
1.00
2.31
1.83
0.99
1.08
2.16
3.01
3.07
PPM
10
8
6
4
2
0

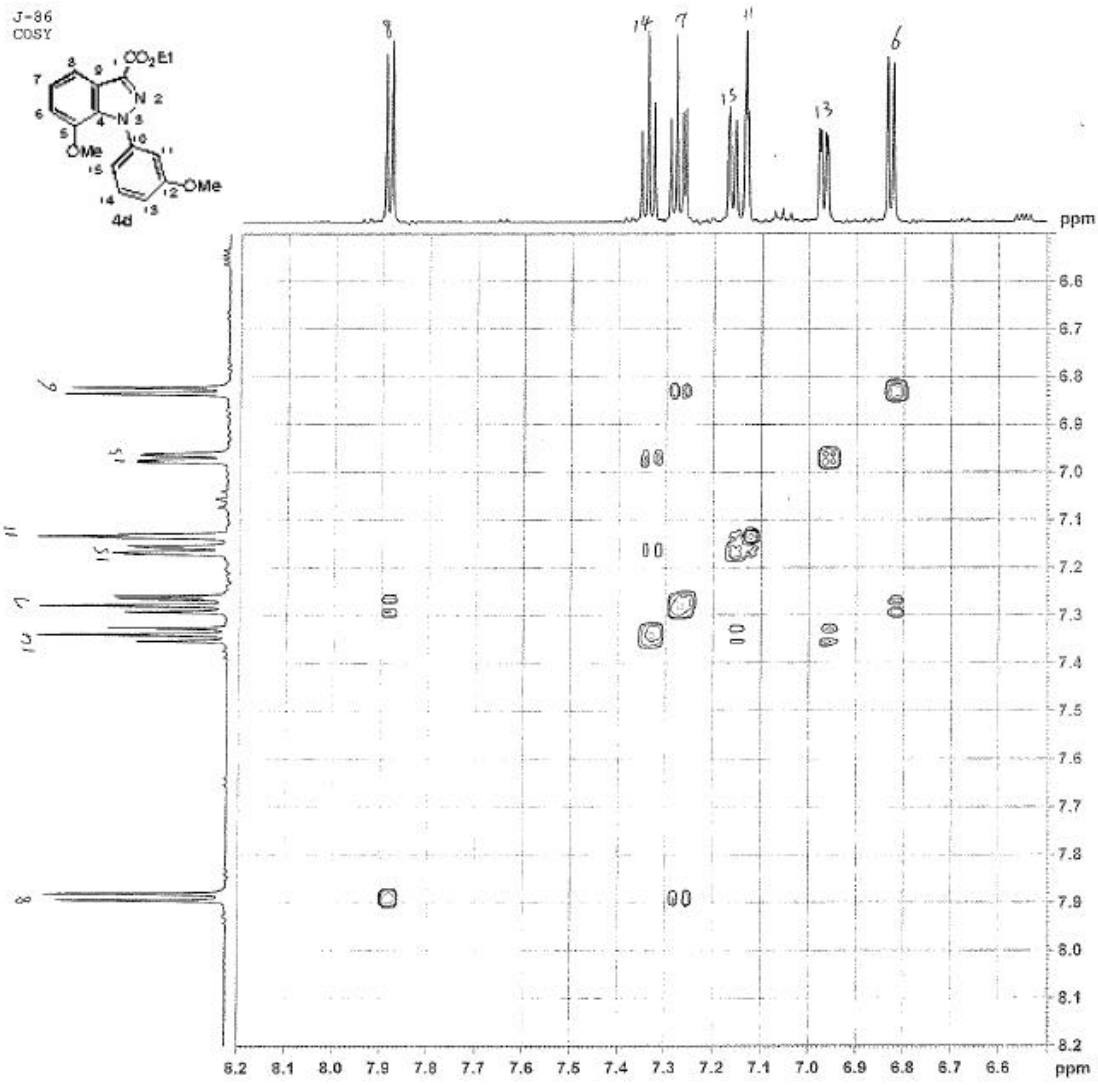

CO2Et
N
N
OMe
OMe
4d
162.717
159.232
146.194
141.664
136.855
131.807
128.618
126.439
124.343
118.967
114.347
114.092
112.004
106.890
77.419
77.000
76.573
61.126
55.486
55.445
14.432
-1.236
PPM
200
150
100
50
0

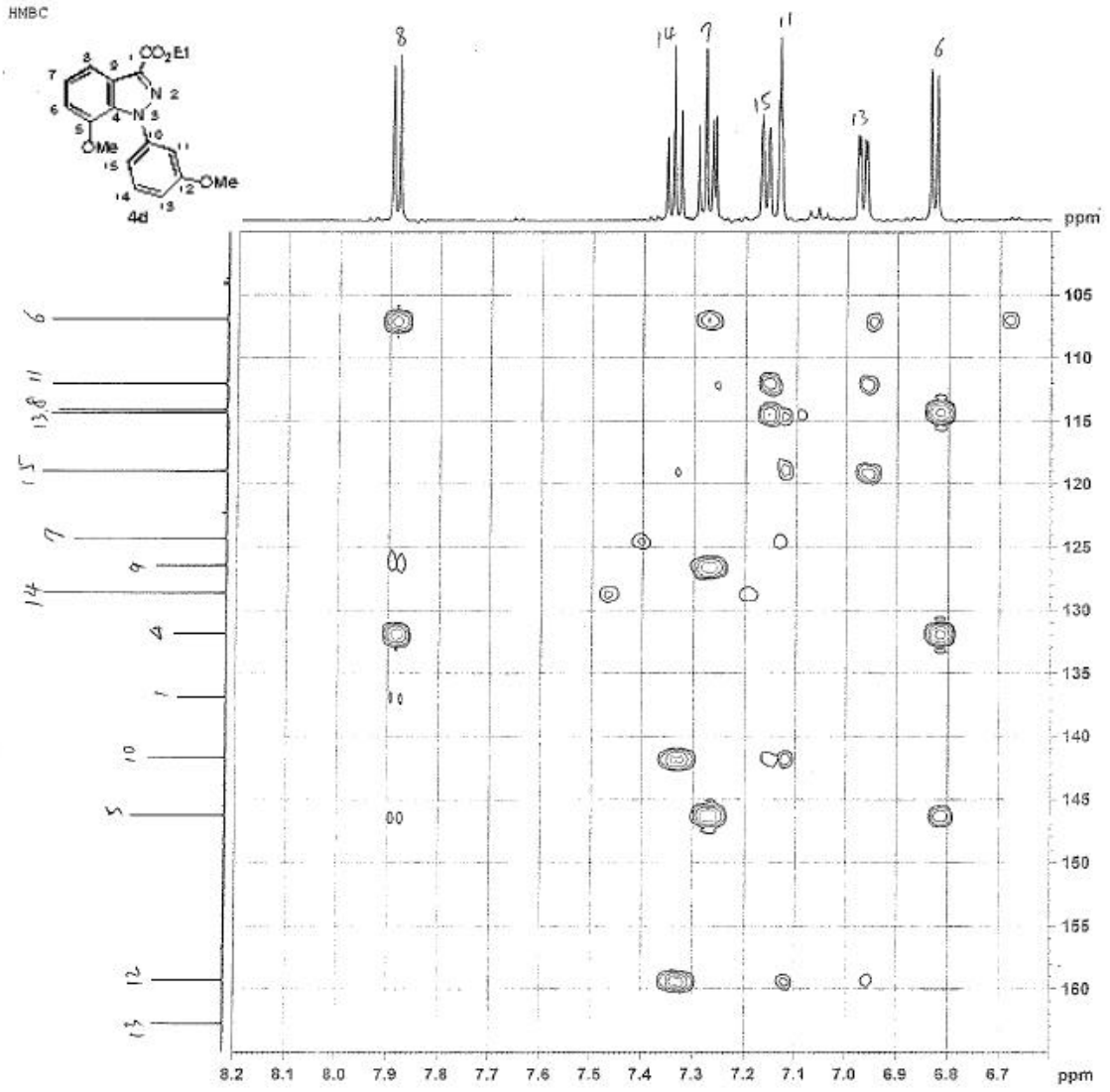

noe
0.42%
6.47%
6.0%
0.66%
2.71%
4d
0.84
200.00
9.97
non
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


noe
0.42%
6.47%
6.0%
0.66%
2.71%
4d
17.99
8.14
300.00
non
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
ppm


noe
0.42%
CH2CH3
6.47%
6.0%
0.66%
2.71%
4d
3.97
19.41
300.00
non
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
ppm


J-86
HMQC
4d
8
14
7
15
11
13
6
ppm
105
110
115
120
125
130
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
ppm


J-86
COSY
4d
ppm
6.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
ppm


HMBC
4d
8
14
9
11
15
13
6
ppm
105
110
115
120
125
130
135
140
145
150
155
160
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
ppm