Supplementary/Supporting Information:

Regioselective Synthesis of 2*H*-Indazoles through Ga/Al- and Al-Mediated Direct Alkylation Reactions of Indazoles

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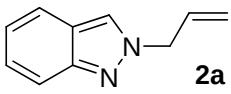
I. General Information and Materials:

All commercially available chemicals were used without further purification. TLC analyses were run on a TLC glass plate (Silica gel 60 F254) and were visualized using UV and a solution of phosphomolybdic acid in ethanol (5 wt%) or *p*-anisaldehyde stain. Flash chromatography was performed using silica gel (70-230 mesh). ^{1}H spectra were recorded on a 300 MHz spectrometer. ^{13}C NMR spectra were recorded on a 75 MHz with complete proton decoupling spectrometer. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.24, δ_C (central line) 77.0]. Mass spectra were recorded under electron spray interface (ESI) conditions and high-resolution mass spectra were recorded by electron impact ionization with magnetic sector analyzer.

II. Experimental Section:

General procedure for *N*-2 alkylation of indazole: A 25-mL flask was charged with gallium metal (104.6 mg, 1.5 mmol) in DMF/H_2O (0.75 mL/0.25 mL). To the solution, aluminium powder (325 mesh, 41.0 mg, 1.5 mmol), alkyl halide (3.0 mmol) and indazole (118.4 mg, 1.0 mmol) was successively added. The flask was sealed with a septum and heated to 55 ^oC for 19 h and cooled to rt. Et_2O (10 mL) and water (2 mL) was then added to the reaction and the mixture was transferred to a separatory funnel. The aqueous layer was back extracted with Et_2O (5 mL x 2). The combined organic layers were washed with 1*N* HCl aqueous solution (10 mL) and dried over $MgSO_4$, and concentrated in a rotary evaporator. The residue was purified by silica-gel chromatography. Procedure for purification of compounds **2c**, **2f-j**, **2q** and **2r** is as follows: The residue was dissolved in CH_2Cl_2 (2 mL), DMAP (12.0 mg, 0.1 mmol), triethylamine (0.21 mL, 1.5 mmol) and Ac_2O (0.14 mL, 1.5 mmol) was added and stirred at rt for 2 h. 1*N* HCl aqueous solution (3 mL) and CH_2Cl_2 (10 mL) was then added to the reaction and the mixture was transferred to a separatory funnel. The aqueous layer was back extracted with CH_2Cl_2 (5 mL x 3). The combined organic layers were dried over $MgSO_4$, and concentrated in a rotary evaporator. The residue was purified by silica-gel chromatography to give **2c**, **2f-j**, **2q** and **2r**.



2a

2-Allyl-2*H*-indazole (2a)[1] **:** 139 mg, 88% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.25; ^1H NMR (300 MHz, $CDCl_3$) δ 5.00 (d, *J* = 6.0 Hz, 2 H), 5.24-5.33 (m, 2 H), 6.03-6.16 (m, 1 H), 7.06 (t, *J* = 8.4 Hz, 1 H), 7.26 (t, *J* = 8.4 Hz, 1 H), 7.60 (d, *J* = 8.4 Hz, 1 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.91 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.0 (CH_2), 117.3 (CH), 119.3 (CH_2), 120.0 (CH), 121.6 (CH), 121.8 (C), 122.4 (CH), 125.8 (CH), 132.1 (CH), 148.8 (C); IR (neat) 3071, 1630, 1521 cm^{-1}; EI-MS *m/z* (rel intensity) 158 (M^+, 100), 157 (86), 131 (72), 118 (20); HRMS $[M]^+$ for $C_{10}H_{10}N_2$: 158.0844, found 158.0853.

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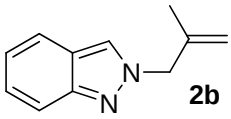
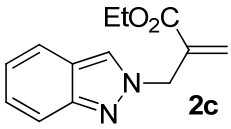
[1] Genung, N. E.; Wei, L.; Aspnes, G. E. *Org. Lett.* **2014**, *16*, 3114.



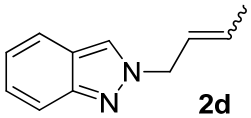
2b

2-(2-Methylallyl)-2*H*-indazole (2b): 145 mg, 84% yield; Solid, mp 41.7-42.3 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.38; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 3 H), 4.86-4.98 (m, 3 H), 4.98 (d, *J* = 0.6 Hz, 1 H), 7.04 (ddd, *J* = 8.5, 6.9, 0.9 Hz, 1 H), 7.24 (ddd, *J* = 8.5, 6.9, 0.9 Hz, 1 H), 7.61 (d, *J* = 8.5 Hz, 1 H), 7.70 (d, *J* = 8.5 Hz, 1 H), 7.86 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7 (CH_3), 59.7 (CH_2), 114.7 (CH_2), 117.4 (CH), 120.0 (CH), 121.6 (CH), 121.8 (C), 122.8 (CH), 125.8 (CH), 140.1 (C), 148.7 (C); IR (KBr) 2926, 1613, 1516 cm^{-1}; EI-MS *m/z* (rel intensity) 172 (M^+, 100), 157 (17), 131 (76), 118 (29); HRMS $[M]^+$ for $C_{11}H_{12}N_2$: 172.1000, found 172.0998.



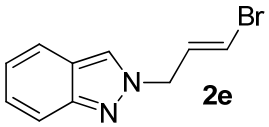
2c

Ethyl 2-((2*H*-indazol-2-yl)methyl)acrylate (2c): 189 mg, 82% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 5.24 (s, 2 H), 5.58 (t, *J* = 0.3 Hz, 1 H), 6.37 (s, 1 H), 7.05 (t, *J* = 8.4 Hz, 1 H), 7.25 (t, *J* = 8.4 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.95 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0 (CH_3), 53.8 (CH_2), 61.1 (CH_2), 117.3 (CH), 120.1 (CH), 121.7 (CH), 121.8 (C), 123.8 (CH), 126.0 (CH), 128.5 (CH_2), 135.7 (C), 149.0 (C), 165.1 (C); IR (neat) 2985, 1717, 1124 cm^{-1}; EI-MS *m/z* (rel intensity) 230 (M^+, 47), 185 (14), 131 (100), 118 (35); HRMS $[M]^+$ for $C_{13}H_{14}N_2O_2$: 230.1055, found 230.1049.

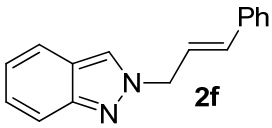


2d

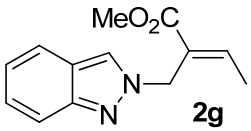
2-(But-2-enyl)-2*H*-indazole (2d): 122 mg, 71% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (d, *J* = 6.6 Hz, 2.25 H), 1.71 (d, *J* = 6.6 Hz, 0.75 H), 4.84 (d, *J* = 6.6 Hz, 1.5 H), 4.97 (d, *J* = 6.6 Hz, 0.5 H), 5.55-5.78 (m, 2 H), 6.98-7.03 (m, 1 H), 7.18-7.23 (m, 1 H), 7.57 (d, *J* = 8.7 Hz, 1 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.78 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 17.4, 49.5, 55.1, 117.0, 117.1, 119.8, 121.2, 121.5, 121.8, 121.9, 123.6, 124.7, 125.4, 129.5, 131.0, 148.4, 148.5; IR (neat) 2937, 1626, 1526 cm^{-1}; EI-MS *m/z* (rel intensity) 172 (M^+, 32), 157 (33), 131 (8), 118 (100); HRMS $[M]^+$ for $C_{11}H_{12}N_2$: 172.1000, found 172.0998.



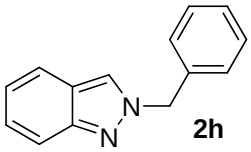
(*E*)-2-(3-Bromoallyl)-2*H*-indazole (2e): 213 mg, 90% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19 (d, *J* = 5.4 Hz, 2 H), 6.47 -6.57 (m, 2 H), 7.04-7.09 (m, 1 H), 7.24-7.29 (m, 1 H), 7.61-7.70 (m, 2 H), 7.95 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3 (CH_2), 111.7 (CH), 117.2 (CH), 120.0 (CH), 121.7 (CH), 121.8 (C), 122.7 (CH), 126.0 (CH), 129.0 (CH), 148.9 (C); IR (neat) 3009, 1623, 1288 cm^{-1}; EI-MS *m/z* (rel intensity) 238 ($[M+2]^+$, 22), 236 (M^+, 23), 157 (100), 130 (25); HRMS $[M]^+$ for $C_{10}H_9BrN_2$: 235.9949, found 235.9943.



2-Cinnamyl-2*H*-indazole (2f): 162 mg, 69% yield; Solid, mp 98-99 °C; TLC (EtOAc/hexanes (1:4)) R_f = 0.38; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.12 (d, *J* = 6.6 Hz, 2 H), 6.37-6.47 (m, 1 H), 6.63 (d, *J* = 15.9 Hz, 1 H), 7.09 (d, *J* = 7.8 Hz, 1 H), 7.22-7.38 (m, 6 H), 7.65 (d, *J* = 8.7 Hz, 1 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.91 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4 (CH_2), 117.2 (CH), 119.9 (CH), 121.5 (CH), 121.8 (C), 122.3 (CH), 122.9 (CH), 125.8 (CH), 126.4 (CH x 2), 128.0 (CH), 128.4 (CH x 2), 134.2 (CH), 135.6 (C), 148.7 (C); IR (KBr) 3122, 1514, 978 cm^{-1}; EI-MS *m/z* (rel intensity) 234 (M^+, 54), 157 (9), 131 (7), 117 (100); HRMS $[M]^+$ for $C_{16}H_{14}N_2$: 234.1157, found 234.1149.

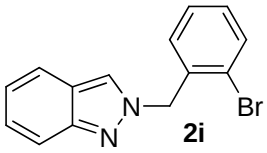


(*E*)-Methyl 2-((2*H*-indazol-2-yl)methyl)but-2-enoate (2g): 191 mg, 83% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.08 (d, *J* = 7.5 Hz, 3 H), 3.71 (s, 3 H), 5.31 (s, 2 H), 7.02 (t, *J* = 8.7 Hz, 1 H), 7.20-7.30 (m, 2 H), 7.61 (d, *J* = 8.7 Hz, 1 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.98 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.9 (CH_3), 48.2 (CH_2), 52.0 (CH_3), 117.3 (CH), 120.1 (CH), 121.4 (CH), 121.6 (C), 123.0 (CH), 125.7 (CH), 127.6 (C), 145.1 (CH), 148.6 (C), 166.7 (C); IR (neat) 2952, 1712, 1275 cm^{-1}; EI-MS *m/z* (rel intensity) 230 (M^+, 28), 215 (17), 131 (11), 118 (100); HRMS $[M]^+$ for $C_{13}H_{14}N_2O_2$: 230.1055, found 230.1059.



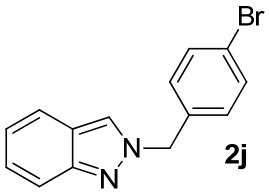
2h

2-Benzyl-2*H*-indazole (2h)[1]**:** 169 mg, 81% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (s, 2 H), 7.05-7.10 (m, 1 H), 7.23-7.35 (m, 6 H), 7.61 (d, *J* = 8.4 Hz, 1 H), 7.75 (d, *J* = 8.4 Hz, 1 H), 7.83 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.2 (CH_2), 117.3 (CH), 120.0 (CH), 121.5 (CH), 121.9 (C), 122.7 (CH), 125.8 (CH), 127.7 (CH x 2), 128.1 (CH), 128.7 (CH x 2), 135.6 (C), 148.7 (C); IR (neat) 3064, 1628, 1510 cm^{-1}; EI-MS *m/z* (rel intensity) 208 (M^+, 52), 207 (37), 180 (4), 91 (100); HRMS $[M]^+$ for $C_{14}H_{12}N_2$: 208.1000, found 208.0992.



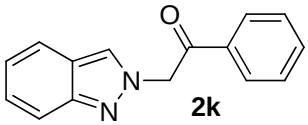
2i

2-(2-Bromobenzyl)-2*H*-indazole (2i): 258 mg, 90% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.50; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.59 (s, 2 H), 6.87-6.90 (m, 1 H), 7.02-7.15 (m, 3 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H)), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.88 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.6 (CH_2), 117.1 (CH), 119.9 (CH), 121.4 (CH), 121.6 (C), 122.7 (C), 123.3 (CH), 125.7 (CH), 127.6 (CH), 129.4 (CH x 2), 132.4 (CH), 134.9 (C), 148.6 (C); IR (neat) 3061, 1621, 1421 cm^{-1}; EI-MS *m/z* (rel intensity) 288 ($[M+2]^+$, 17), 286 (M^+, 18), 207 (100), 169 (26); HRMS $[M]^+$ for $C_{14}H_{11}BrN_2$: 286.0106, found 286.0111.



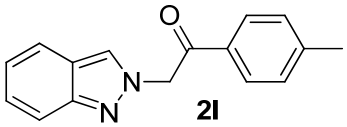
2j

2-(4-Bromobenzyl)-2*H*-indazole (2j): 218 mg, 76% yield; Solid, mp 112-113 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.41 (s, 2 H), 7.02-7.08 (m, 3 H), 7.25-7.29 (m, 1 H), 7.37-7.41 (m, 2 H), 7.59 (d, *J* = 8.7 Hz, 1 H), 7.73 (d, *J* = 8.7 Hz, 1 H), 7.79 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.3 (CH_2), 117.2 (CH), 119.9 (CH), 121.6 (CH), 121.8 (C), 122.0 (C), 122.7 (CH), 125.9 (CH), 129.2 (CH x 2), 131.6 (CH x 2), 134.5 (C), 148.7 (C); IR (KBr) 3115, 1486, 1348 cm^{-1}; EI-MS *m/z* (rel intensity) 288 ($[M+2]^+$, 70), 286 (M^+, 70), 207 (18), 169 (100); HRMS $[M]^+$ for $C_{14}H_{11}BrN_2$: 286.0106, found 286.0097.



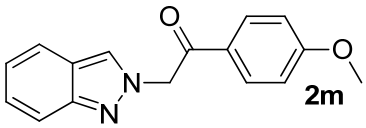
2k

2-(2*H*-Indazol-2-yl)-1-phenylethanone (2k): 180 mg, 76% yield; Solid, mp 122-124 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.08; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (s, 2 H), 7.02-7.08 (m, 1 H), 7.22-7.28 (m, 1 H), 7.34-7.39 (m, 2 H), 7.50-7.70 (m, 3 H), 7.82-7.93 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.9 (CH_2), 117.4 (CH), 120.3 (CH), 121.9 (CH), 122.3 (C), 124.7 (CH), 126.2 (CH), 128.1 (CH x 2), 129.0 (CH x 2), 134.2 (CH), 134.3 (C), 149.0 (C), 191.3 (C); IR (KBr) 2919, 1708, 1236 cm^{-1}; EI-MS *m/z* (rel intensity) 236 (M^+, 23), 207 (20), 146 (16), 105 (100); HRMS $[M]^+$ for $C_{15}H_{12}N_2O$: 236.0950, found 236.0952.



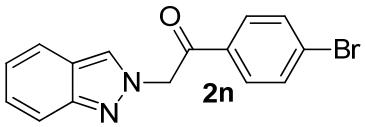
2l

2-(2*H*-Indazol-2-yl)-1-*p*-tolylethanone (2l): 195 mg, 78% yield; Solid, mp 200-201 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.44 (s, 3 H), 6.18 (s, 2 H), 7.08 (t, *J* = 8.4 Hz, 1 H), 7.29 (t, *J* = 8.4 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 8.02 (d, *J* = 8.4 Hz, 2 H), 8.42 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 22.2 (CH_3), 60.1 (CH_2), 117.9 (CH), 121.7 (CH), 122.0 (CH), 122.6 (C), 126.5 (CH), 126.7 (CH), 129.2 (CH x 2), 130.5 (CH x 2), 132.9 (C), 145.7 (C), 149.1 (C), 193.3 (C); IR (KBr) 2938, 1700, 1246 cm^{-1}; EI-MS *m/z* (rel intensity) 250 (M^+, 20), 222 (16), 119 (100), 91 (35); HRMS $[M]^+$ for $C_{16}H_{14}N_2O$: 250.1106, found 250.1115.

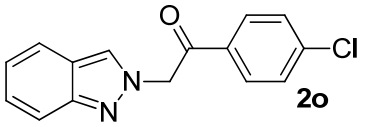


2m

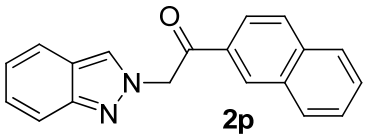
2-(2*H*-Indazol-2-yl)-1-(4-methoxyphenyl)ethanone (2m). 210 mg, 79% yield; Solid, mp 157-158 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.89 (s, 3 H), 6.17 (s, 2 H), 7.09 (t, *J* = 8.4 Hz, 1 H), 7.14 (t, *J* = 9.0 Hz, 2 H), 7.30 (t, *J* = 8.4 Hz, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.79 (d, *J* = 8.4 Hz, 1 H), 8.12 (d, *J* = 9.0 Hz, 2 H), 8.43 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 56.6 (CH_3), 59.9 (CH_2), 115.2 (CH x 2), 117.9 (CH), 121.7 (CH), 122.0 (CH), 122.7 (C), 126.5 (CH), 126.7 (CH), 128.3 (C), 131.5 (CH x 2), 149.2 (C), 164.8 (C), 192.1 (C); IR (KBr) 2938, 1680, 1597 cm^{-1}; EI-MS *m/z* (rel intensity) 266 (M^+, 16), 238 (15), 135 (100), 121 (55); HRMS $[M]^+$ for $C_{16}H_{14}N_2O_2$: 266.1055, found 266.1051.



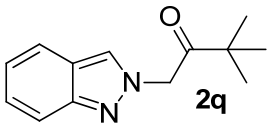
1-(4-Bromophenyl)-2-(2*H*-indazol-2-yl)ethanone (2n). 246 mg, 78% yield; Solid, mp 169-170 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.22 (s, 2 H), 7.09 (t, J = 8.4 Hz, 1 H), 7.29 (t, J = 8.4 Hz, 1 H), 7.64 (d, J = 8.4 Hz, 1 H), 7.78 (d, J = 8.4 Hz, 1 H), 7.85 (d, J = 8.4 Hz, 2 H), 8.05 (d, J = 8.4 Hz, 2 H), 8.42 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 60.2 (CH_2), 117.9 (CH), 121.7 (CH), 122.1 (CH), 122.7 (C), 126.6 (CH), 126.7 (CH), 129.3 (C), 131.1 (CH x 2), 133.1 (CH x 2), 134.4 (C), 149.2 (C), 193.2 (C); IR (KBr) 2965, 1702, 1578 cm^{-1}; EI-MS *m/z* (rel intensity) 316 ([M+2]$^{+}$, 26), 314 (M^{+}, 26), 250 (60), 183 (100); HRMS [M]$^{+}$ for $C_{15}H_{11}BrN_2O$: 314.0055, found 314.0061.



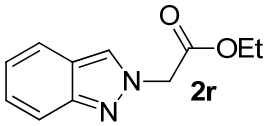
1-(4-Chlorophenyl)-2-(2*H*-indazol-2-yl)ethanone (2o). 200 mg, 74% yield; Solid, mp 152-153 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.23 (s, 2 H), 7.09 (t, J = 8.4 Hz, 1 H), 7.26.7.32 (m, 1 H), 7.63-7.71 (m, 3 H), 7.78 (d, J = 8.4 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 2 H), 8.43 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 60.2 (CH_2), 117.9 (CH), 121.7 (CH), 122.1 (CH), 122.7 (C), 126.6 (CH), 126.7 (CH), 130.1 (CH x 2), 131.0 (CH x 2), 134.1 (C), 140.0 (C), 149.2 (C), 193.0 (C); IR (KBr) 2956, 1701, 1228 cm^{-1}; EI-MS *m/z* (rel intensity) 272 ([M+2]$^{+}$, 8), 270 (M^{+}, 23), 241 (27), 139 (100); HRMS [M]$^{+}$ for $C_{15}H_{11}ClN_2O$: 270.0560, found 270.0565.



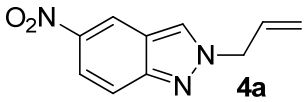
2-(2*H*-Indazol-2-yl)-1-(naphthalen-2-yl)ethanone (2p). 235 mg, 82% yield; Solid, mp 200-201 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.18; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.37 (s, 2 H), 7.10 (t, J = 7.8 Hz, 1 H), 7.30 (t, J = 7.8 Hz, 1 H), 7.64-7.82 (m, 4 H), 8.06-8.14 (m, 3 H), 8.21 (d, J = 7.8 Hz, 1 H), 8.48 (s, 1 H), 8.92 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 60.2 (CH_2), 117.9 (CH), 121.7 (CH), 122.0 (CH), 122.7 (C), 124.3 (CH), 126.6 (CH), 126.8 (CH), 128.2 (CH), 128.8 (CH), 129.6 (CH), 130.1 (CH), 130.7 (CH), 131.4 (CH), 132.7 (C), 133.1 (C), 136.4 (C), 149.2 (C), 193.8 (C); IR (KBr) 2938, 1690, 1394 cm^{-1}; EI-MS *m/z* (rel intensity) 286 (M^{+}, 23), 258 (30), 155 (100), 127 (67); HRMS [M]$^{+}$ for $C_{19}H_{14}N_2O$: 286.1106, found 286.1102.



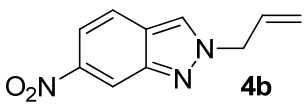
1-(2*H*-Indazol-2-yl)-3,3-dimethylbutan-2-one (2q). 203 mg, 94% yield; Solid, mp 100-101 ^{o}C; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (s, 9 H), 5.39 (s, 2 H), 7.05 (t, *J* = 8.4 Hz, 1 H), 7.25 (t, *J* = 8.4 Hz, 1 H), 7.64 (d, *J* = 8.4 Hz, 1 H), 7.67 (d, *J* = 8.4 Hz, 1 H), 7.91 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.9 (CH_3 x 3), 43.3 (C), 56.9 (CH_2), 117.1 (CH), 120.1 (CH), 121.5 (CH), 121.9 (C), 124.6 (CH), 125.9 (CH), 148.7 (C), 206.7 (C); IR (KBr) 2974, 1726, 1486 cm^{-1}; EI-MS *m/z* (rel intensity) 216 (M^+, 62), 131 (100), 118 (32), 77 (32); HRMS $[M]^+$ for $C_{13}H_{16}N_2O$: 216.1263, found 216.1268.



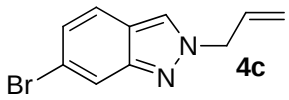
Ethyl 2-(2*H*-indazol-2-yl)acetate (2r). 167 mg, 82% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.20; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 5.14 (s, 2 H), 7.06 (t, *J* = 8.4 Hz, 1 H), 7.26 (t, *J* = 8.4 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 8.4 Hz, 1 H), 7.95 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7 (CH_3), 54.1 (CH_2), 61.8 (CH_2), 117.2 (CH), 120.1 (CH), 121.7 (CH), 121.8 (C), 124.3 (CH), 126.1 (CH), 148.8 (C), 166.9 (C); IR (neat) 2934, 1744, 1209 cm^{-1}; EI-MS *m/z* (rel intensity) 204 (M^+, 70), 131 (100), 118 (11), 103 (19); HRMS $[M]^+$ for $C_{11}H_{12}N_2O_2$: 204.0899, found 204.0894.



2-Allyl-5-nitro-2*H*-indazole (4a). 112 mg, 55% yield; An oil; TLC (EtOAc/hexanes (1:2)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.06 (d, *J* = 6.3 Hz, 2 H), 5.31-5.41 (m, 2 H), 6.04-6.18 (m, 1 H), 7.71 (d, *J* = 9.6 Hz, 1 H), 8.05 (d, *J* = 9.6 Hz, 1 H), 8.21 (s, 1 H), 8.68 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.6 (CH_2), 118.3 (CH), 119.3 (CH), 120.1 (C), 120.2 (CH), 120.6 (CH_2), 126.7 (CH), 131.1 (CH), 143.0 (C), 149.8 (C); IR (neat) 2928, 1496, 1329 cm^{-1}; EI-MS *m/z* (rel intensity) 203 ($[M]^+$, 100), 202 (71), 176 (41), 130 (25); HRMS $[M]^+$ for $C_{10}H_9N_3O_2$: 203.0695, found 203.0686.

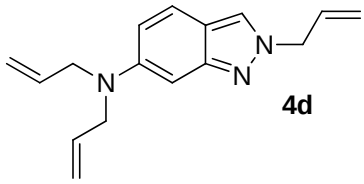


2-Allyl-6-nitro-2*H*-indazole (4b). 102 mg, 50% yield; An oil; TLC (EtOAc/hexanes (1:2)) R_f = 0.30; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.07 (d, *J* = 6.3 Hz, 2 H), 5.30-5.38 (m, 2 H), 6.03-6.16 (m, 1 H), 7.71 (d, *J* = 9.3 Hz, 1 H), 7.82 (d, *J* = 9.3 Hz, 1 H), 8.04 (s, 1 H), 8.62 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.7 (CH_2), 115.4 (CH), 115.6 (CH), 120.4 (CH_2), 121.4 (CH), 123.5 (CH), 124.3 (C), 131.2 (CH), 146.3 (C), 146.7 (C); IR (neat) 2938, 1523, 1338 cm^{-1}; EI-MS *m/z* (rel intensity) 203 ([M]$^+$, 100), 202 (64), 176 (40), 130 (21); HRMS [M]$^+$ for $C_{10}H_9N_3O_2$: 203.0695, found 203.0700.



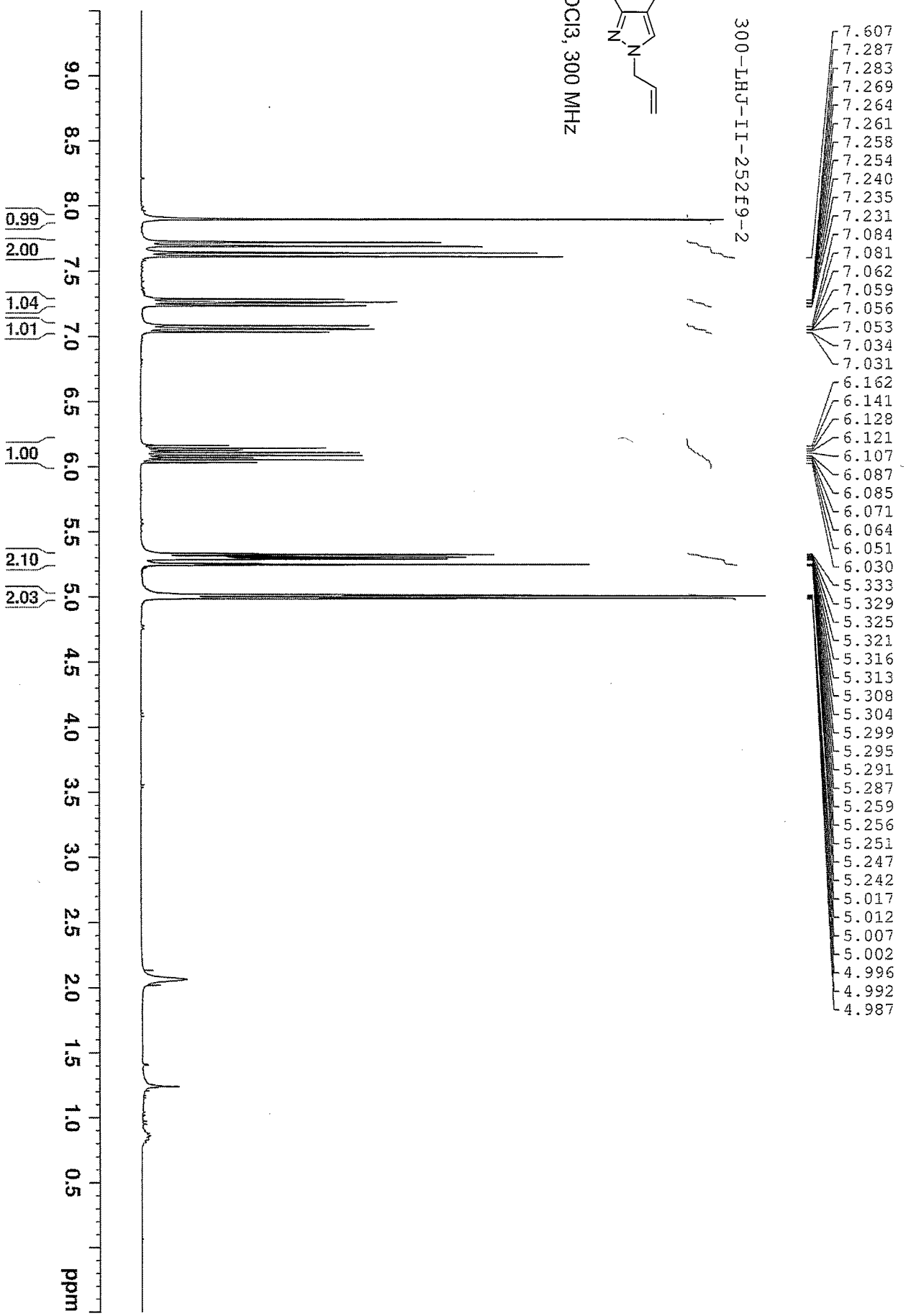
4c

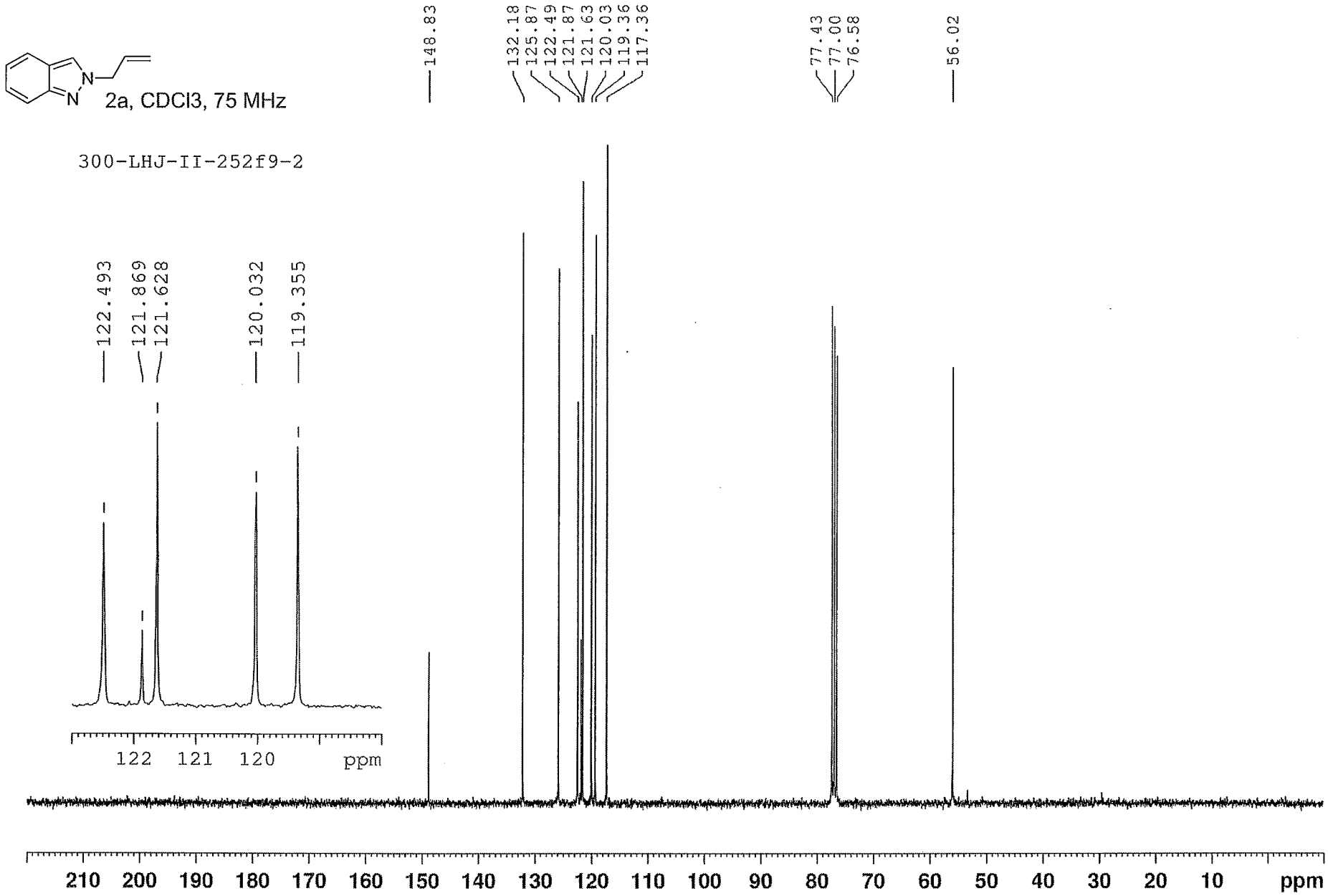
2-Allyl-6-bromo-2*H*-indazole (4c). 185 mg, 78% yield; An oil; TLC (EtOAc/hexanes (1:4)) R_f = 0.28; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.98 (d, *J* = 6.0 Hz, 2 H), 5.25-5.34 (m, 2 H), 6.01-6.14 (m, 1 H), 7.12 (d, *J* = 8.7 Hz, 1 H), 7.49 (d, *J* = 8.7 Hz, 1 H), 7.86 (s, 1 H), 7.88 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.0 (CH_2), 119.6 (CH), 119.7 (CH_2), 119.8 (C), 120.3 (C), 121.4 (CH), 123.0 (CH), 125.3 (CH), 131.7 (CH), 149.4 (C); IR (neat) 2934, 1612, 920 cm^{-1}; EI-MS *m/z* (rel intensity) 238 ([M+2]$^+$, 97), 236 (M$^+$, 100), 211 (64), 209 (66); HRMS [M]$^+$ for $C_{10}H_9BrN_2$: 235.9949, found 235.9956.

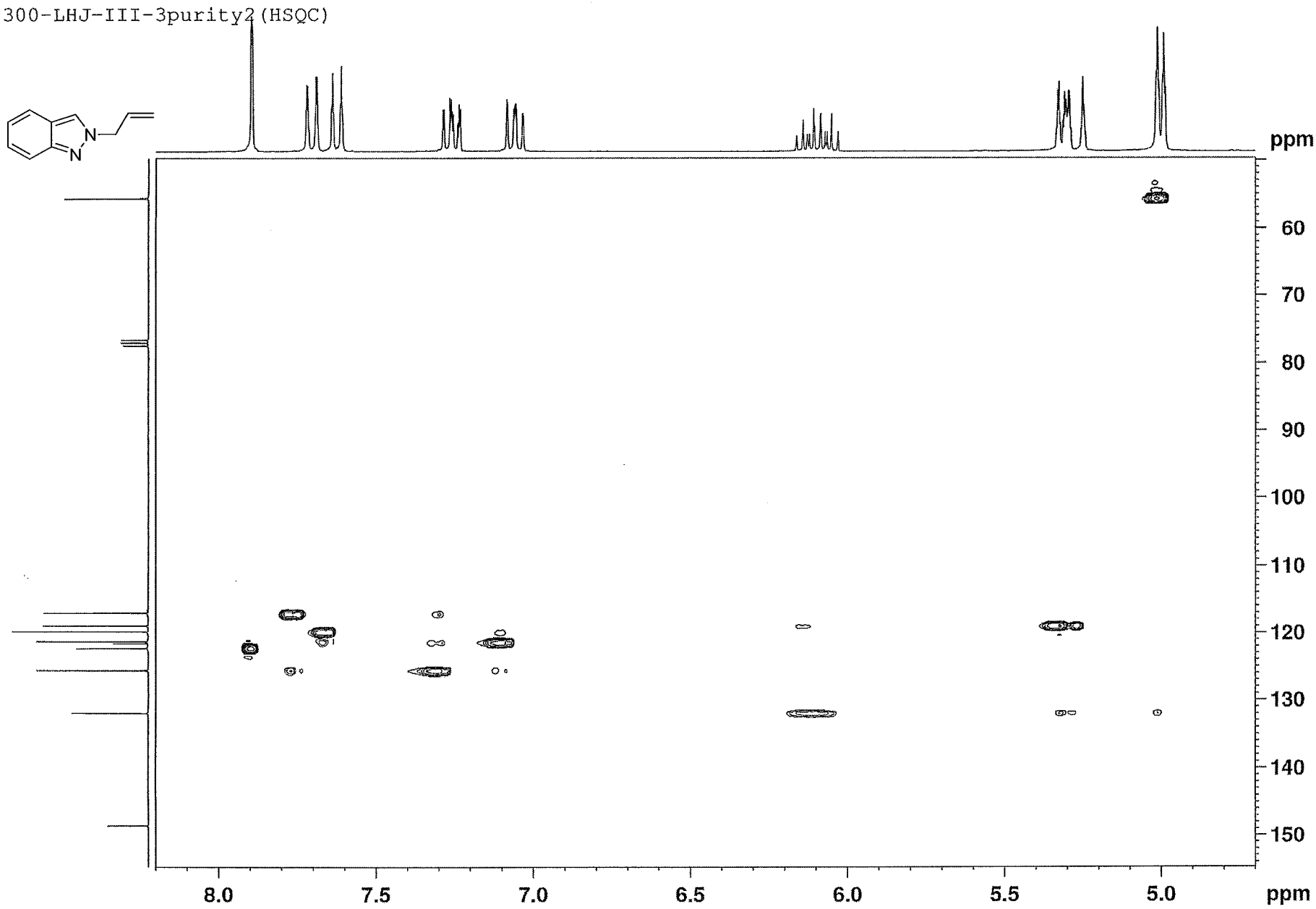


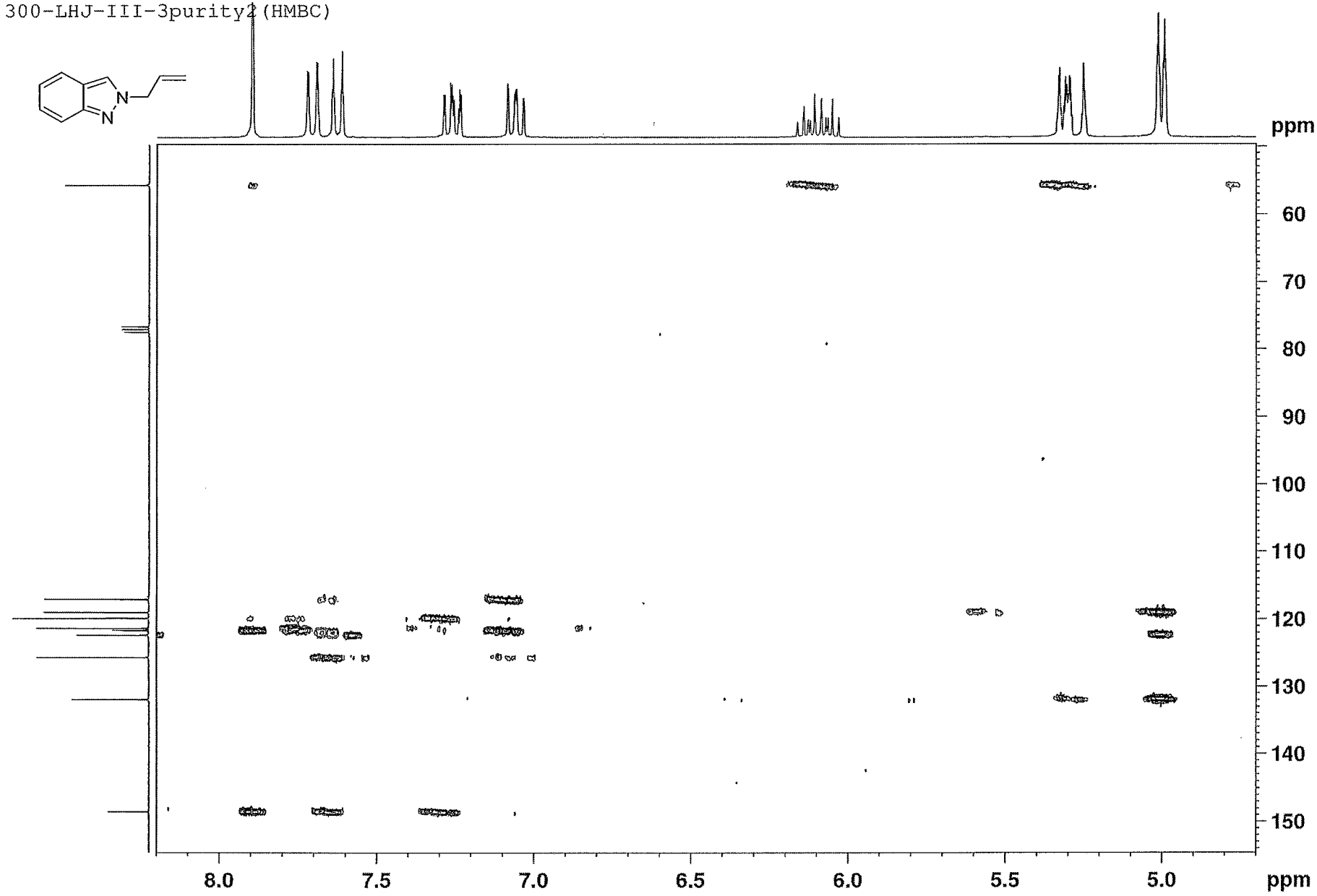
4d

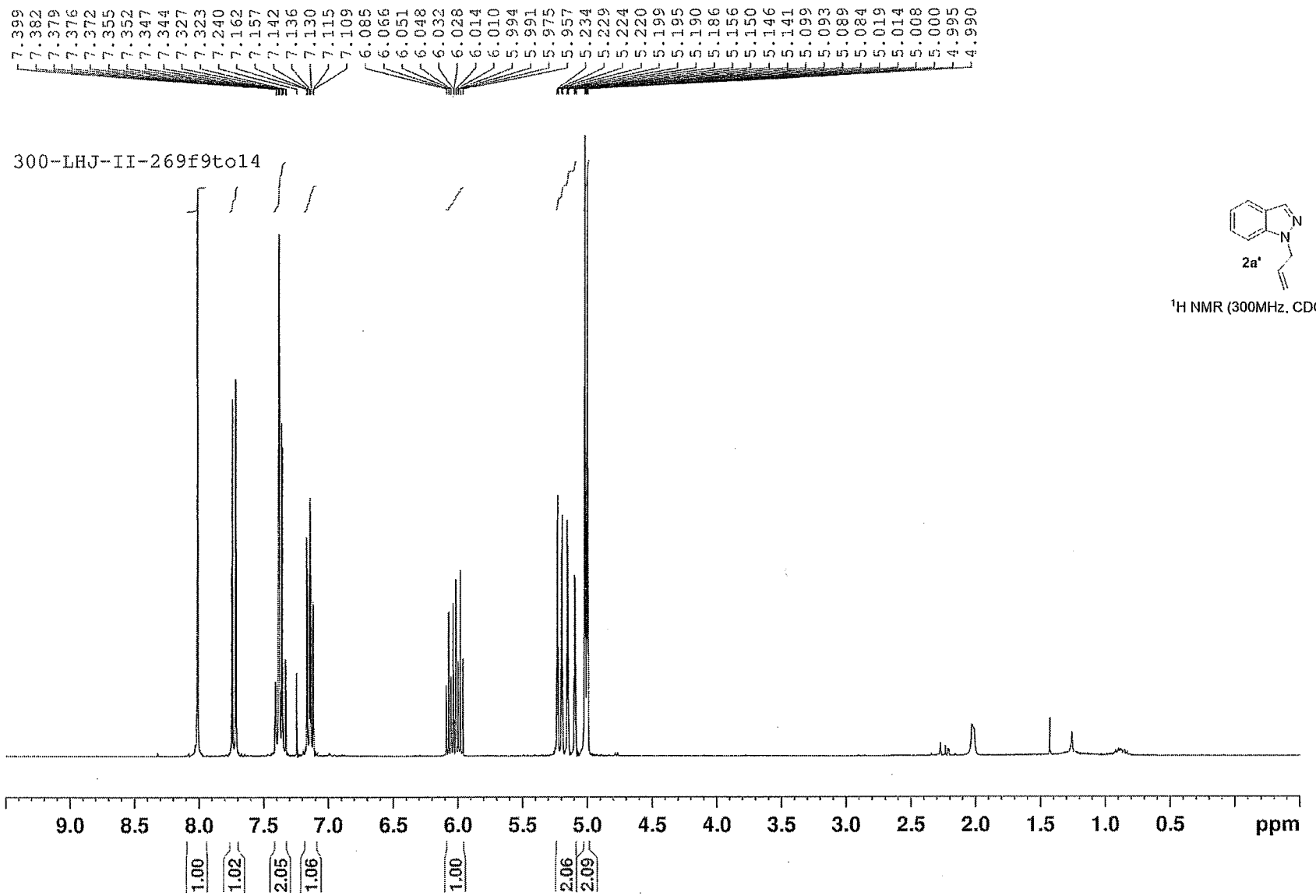
***N*,*N*,2-Triallyl-2*H*-indazol-6-amine (4d).** 203 mg, 80% yield; An oil; TLC (EtOAc/hexanes (1:2)) R_f = 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (d, *J* = 6.3 Hz, 4 H), 4.86 (d, *J* = 6.3 Hz, 2 H), 5.11-5.26 (m, 6 H), 5.79-5.91 (m, 2 H), 5.98-6.11 (m, 1 H), 6.74 (d, *J* = 9.0 Hz, 1 H), 6.77 (s, 1 H), 7.41 (d, *J* = 9.0 Hz, 1 H), 7.65 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.0 (CH_2 x 2), 55.4 (CH_2), 94.7 (CH), 114.3 (CH), 115.7 (C), 116.0 (CH_2 x 2), 118.7 (CH_2), 120.1 (CH), 122.1 (CH), 132.5 (CH), 133.9 (CH x 2), 147.3 (C), 150.5 (C); IR (neat) 2929, 1625, 1496 cm^{-1}; EI-MS *m/z* (rel intensity) 253 ([M]$^+$, 100), 238 (29), 212 (39), 184 (27); HRMS [M]$^+$ for $C_{16}H_{19}N_3$: 253.1579, found 253.1581.


300-LHJ-II-252f9-2
2a, CDCl3, 300 MHz
7.607
7.287
7.283
7.269
7.264
7.261
7.258
7.254
7.240
7.235
7.231
7.084
7.081
7.062
7.059
7.056
7.053
7.034
7.031
6.162
6.141
6.128
6.121
6.107
6.087
6.085
6.071
6.064
6.051
6.030
5.333
5.329
5.325
5.321
5.316
5.313
5.308
5.304
5.299
5.295
5.291
5.287
5.259
5.256
5.251
5.247
5.242
5.017
5.012
5.007
5.002
4.996
4.992
4.987
0.99
2.00
1.04
1.01
1.00
2.10
2.03
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
1.0
0.5
ppm


2a, CDCl3, 75 MHz
300-LHJ-II-252f9-2
148.83
132.18
125.87
122.49
121.87
121.63
120.03
119.36
117.36
77.43
77.00
76.58
56.02
122.493
121.869
121.628
120.032
119.355
122
121
120
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

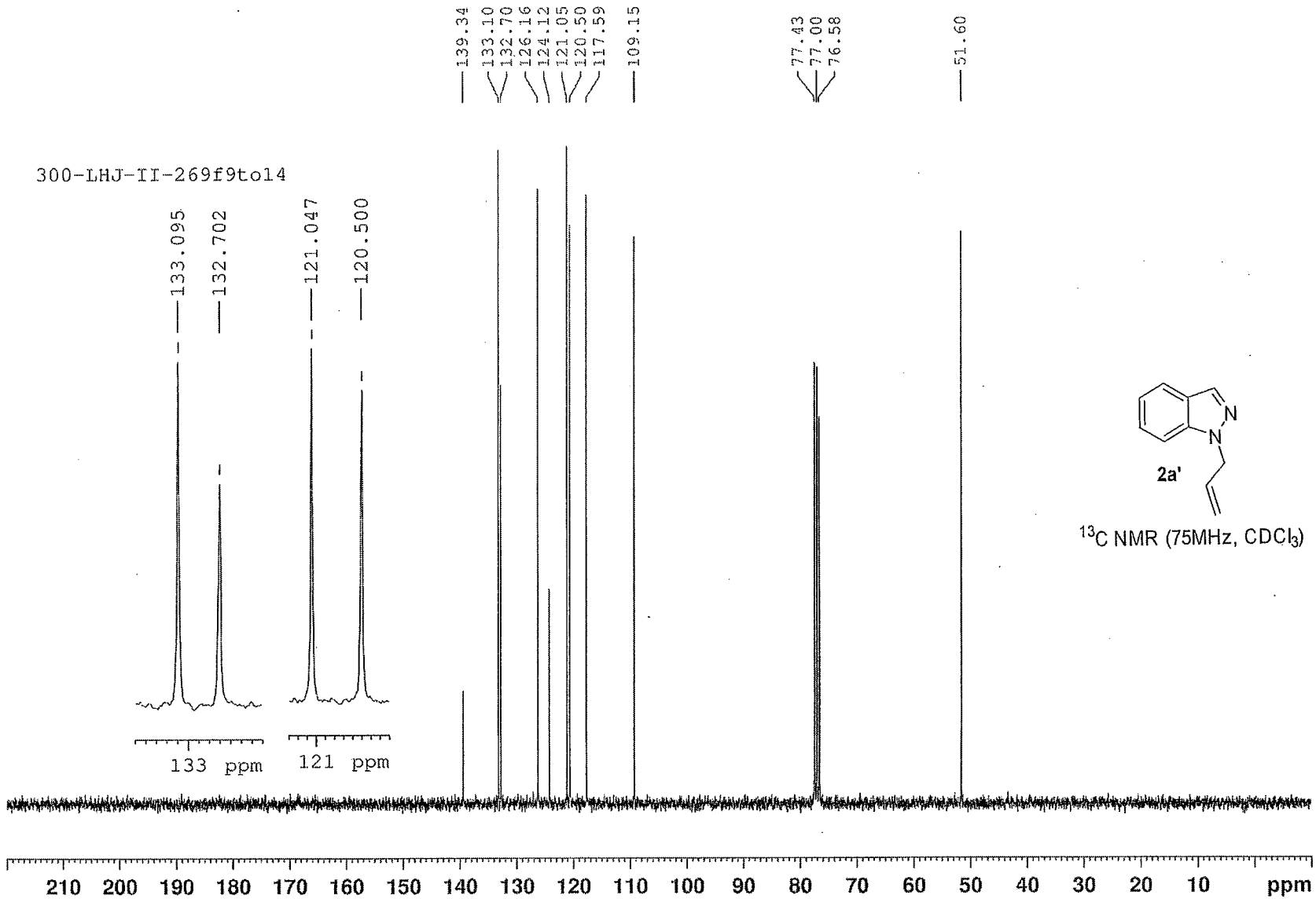

300-LHJ-III-3purity2(HSQC)
N
N
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm


300-LHJ-III-3purity2(HMBC)
N
N
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm



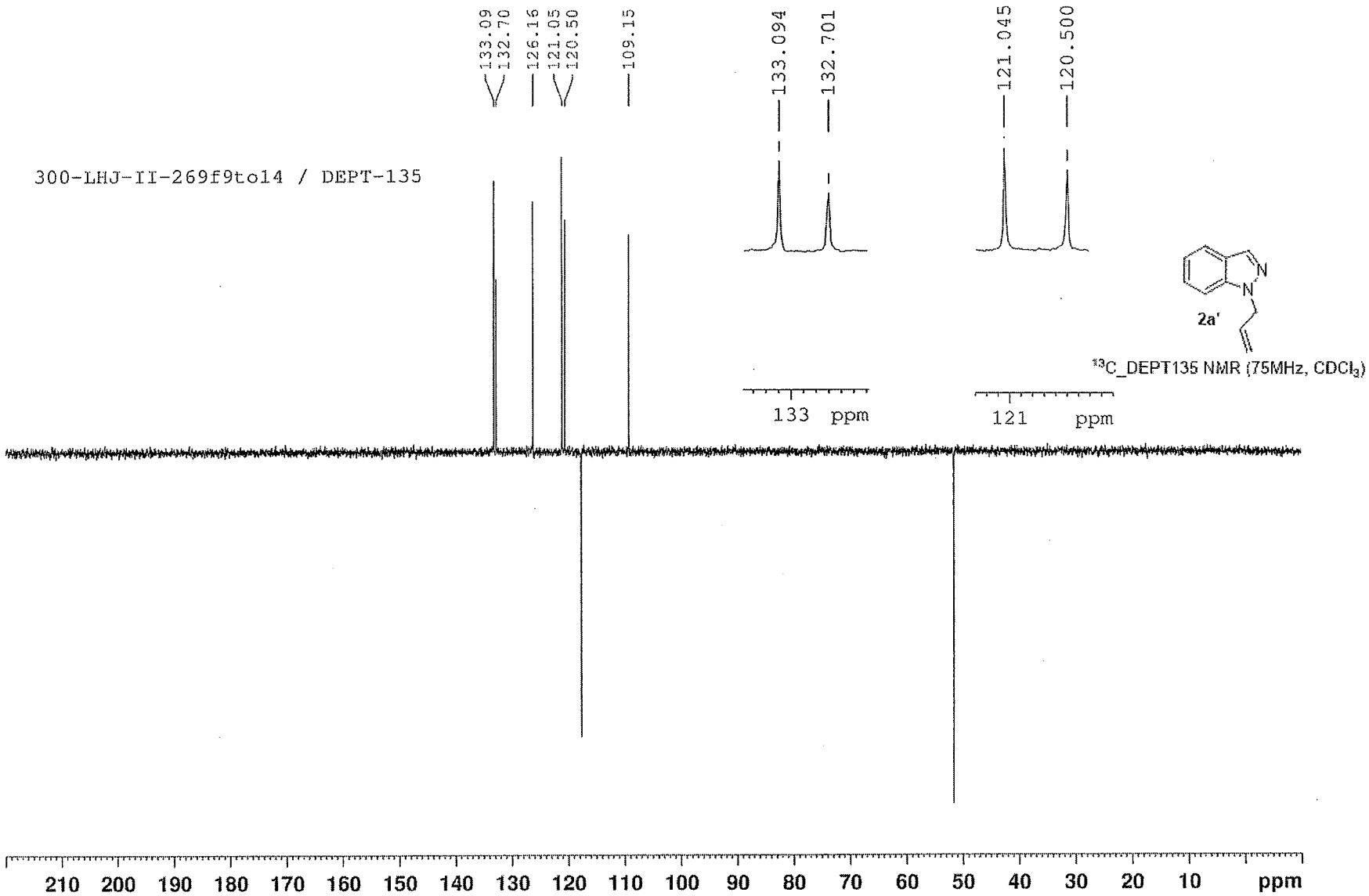
2a'

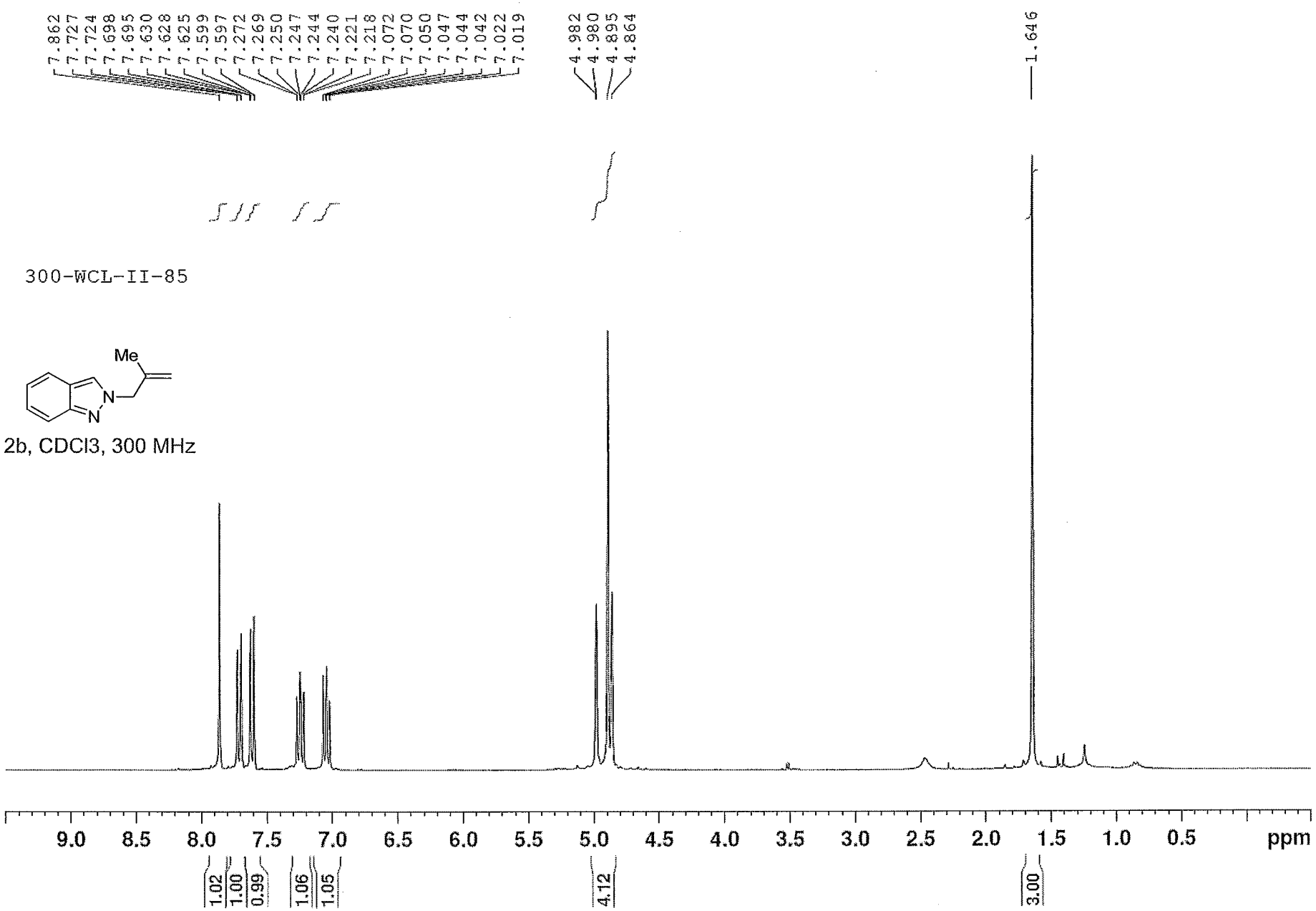
^{1}H NMR (300MHz, $CDCl_3$)

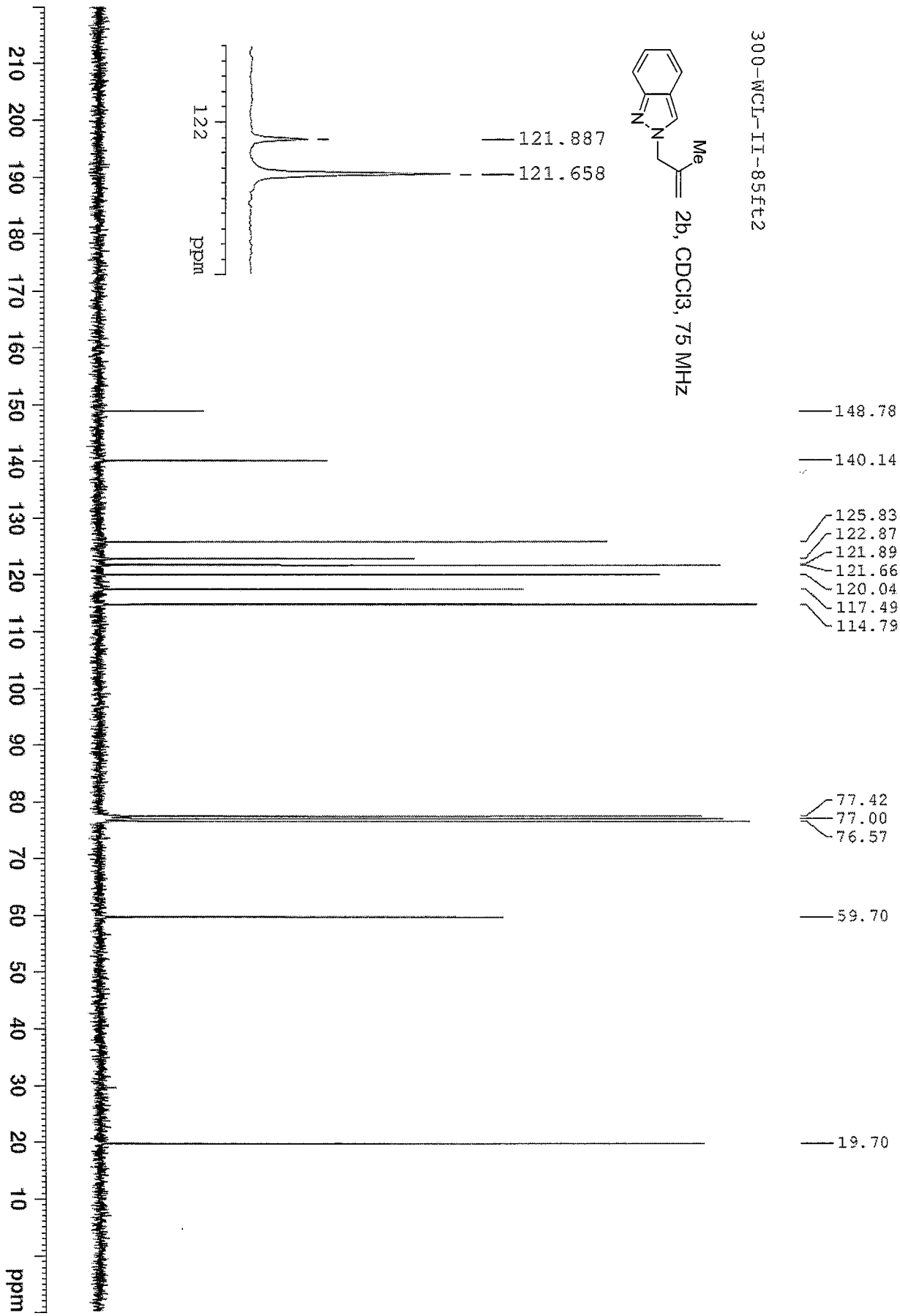


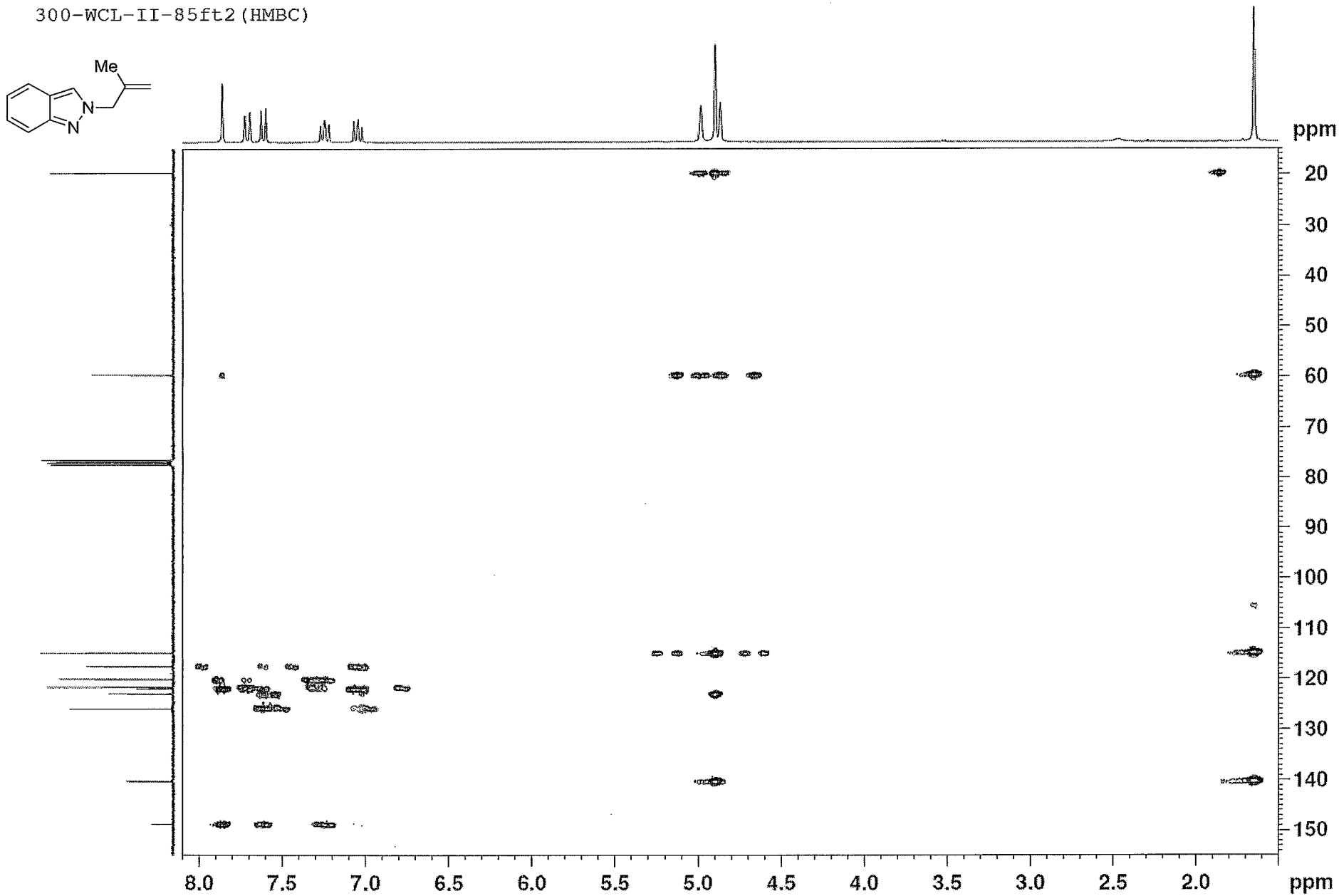
2a'

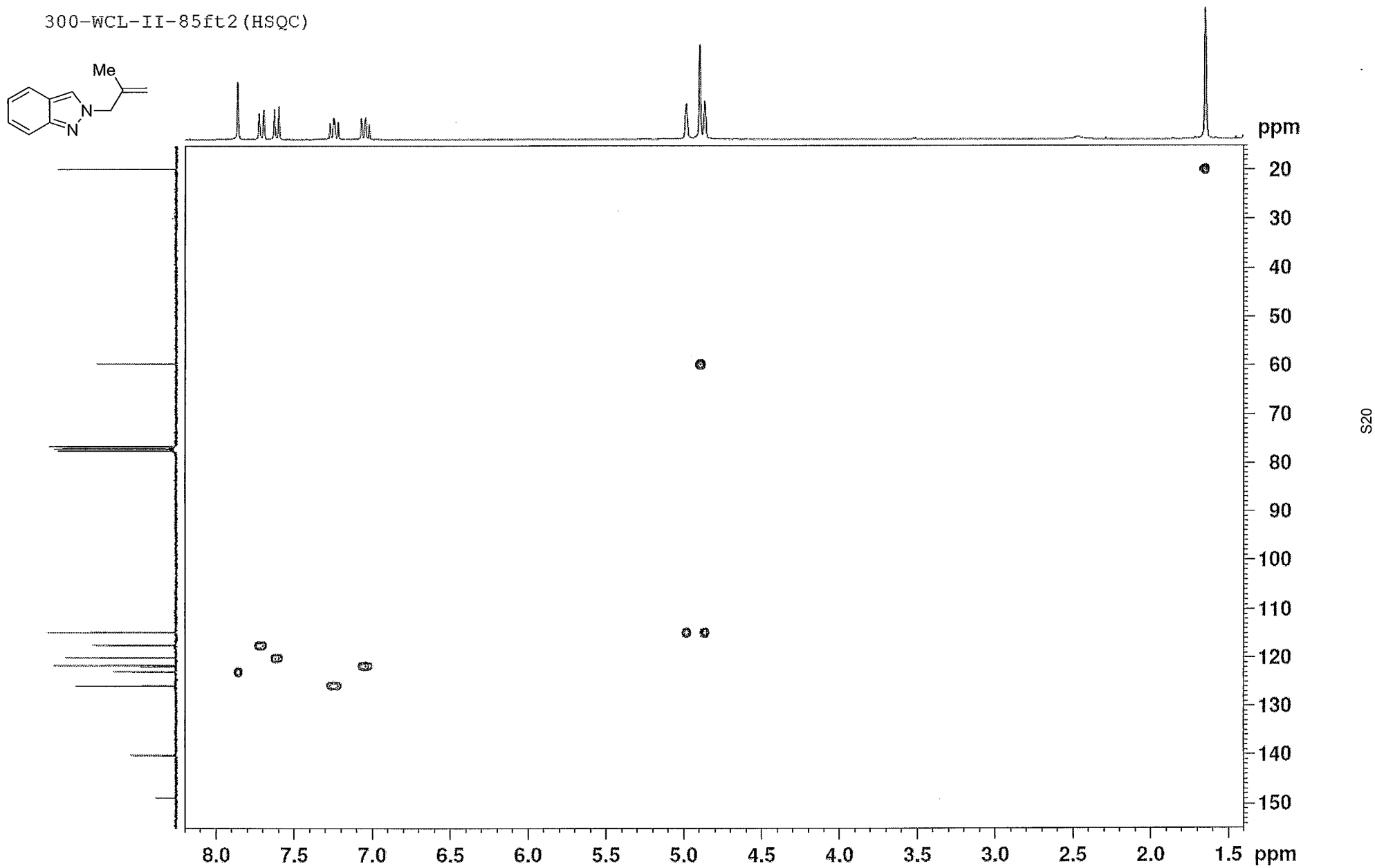
^{13}C NMR (75MHz, $CDCl_3$)

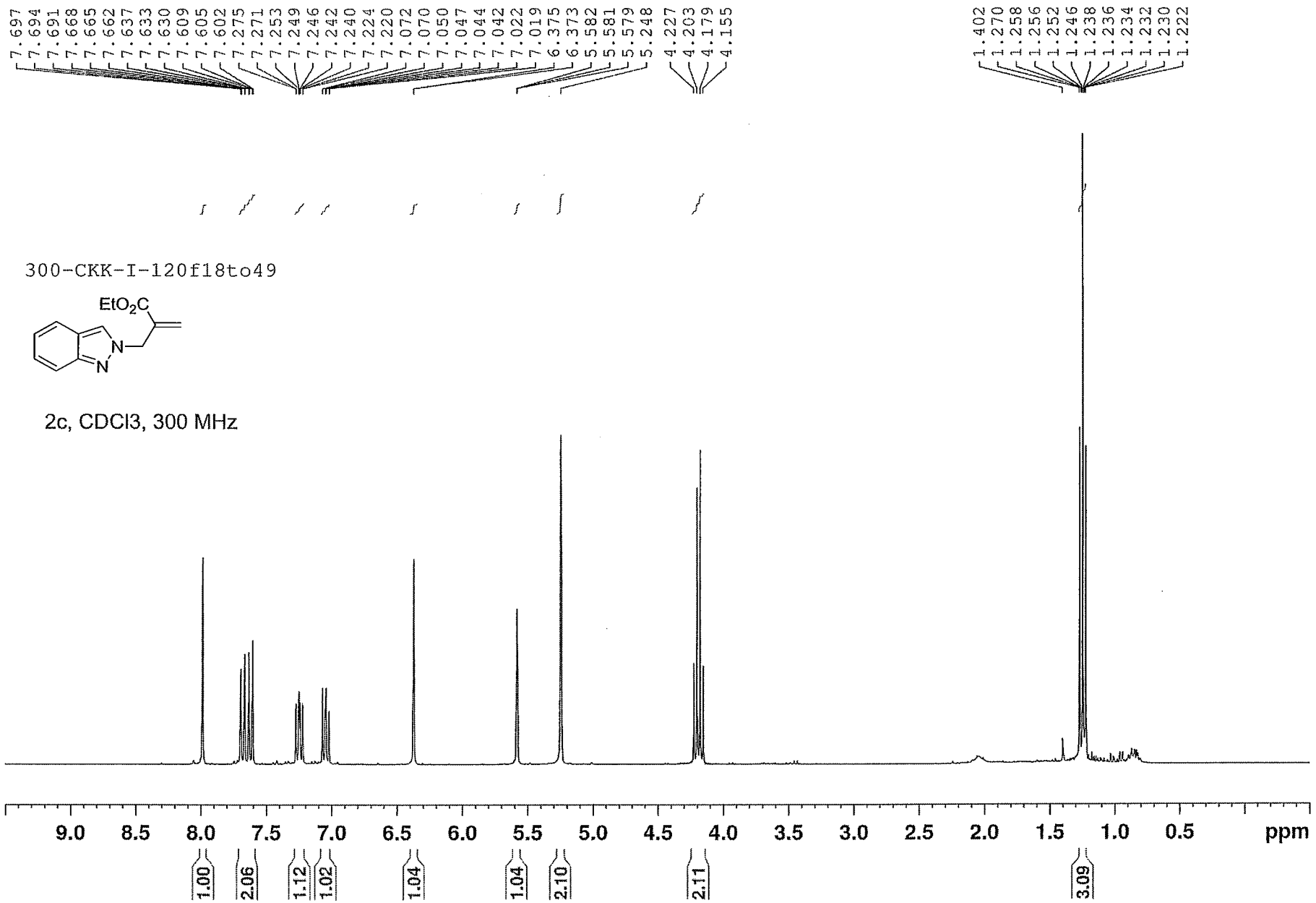

300-LHJ-II-269f9to14 / DEPT-135
133.09
132.70
126.16
121.05
120.50
109.15
133.094
132.701
121.045
120.500
133 ppm
121 ppm
2a'
13C_DEPT135 NMR (75MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.862
7.727
7.724
7.698
7.695
7.630
7.628
7.625
7.599
7.597
7.272
7.269
7.250
7.247
7.244
7.240
7.221
7.218
7.072
7.070
7.050
7.047
7.044
7.042
7.022
7.019
4.982
4.980
4.895
4.864
1.646
300-WCL-II-85
Me
N
N
2b, CDCl3, 300 MHz
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
1.0
0.5
ppm
1.02
1.00
0.99
1.06
1.05
4.12
3.00


300-WCL-II-85ft2
2b, CDCl3, 75 MHz
Me
N
N
121.887
121.658
122
ppm
148.78
140.14
125.83
122.87
121.89
121.66
120.04
117.49
114.79
77.42
77.00
76.57
59.70
19.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

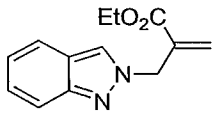

300-WCL-II-85ft2(HMBC)
Me
N
N
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


300-WCL-II-85ft2(HSQC)
Me
N
N
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
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

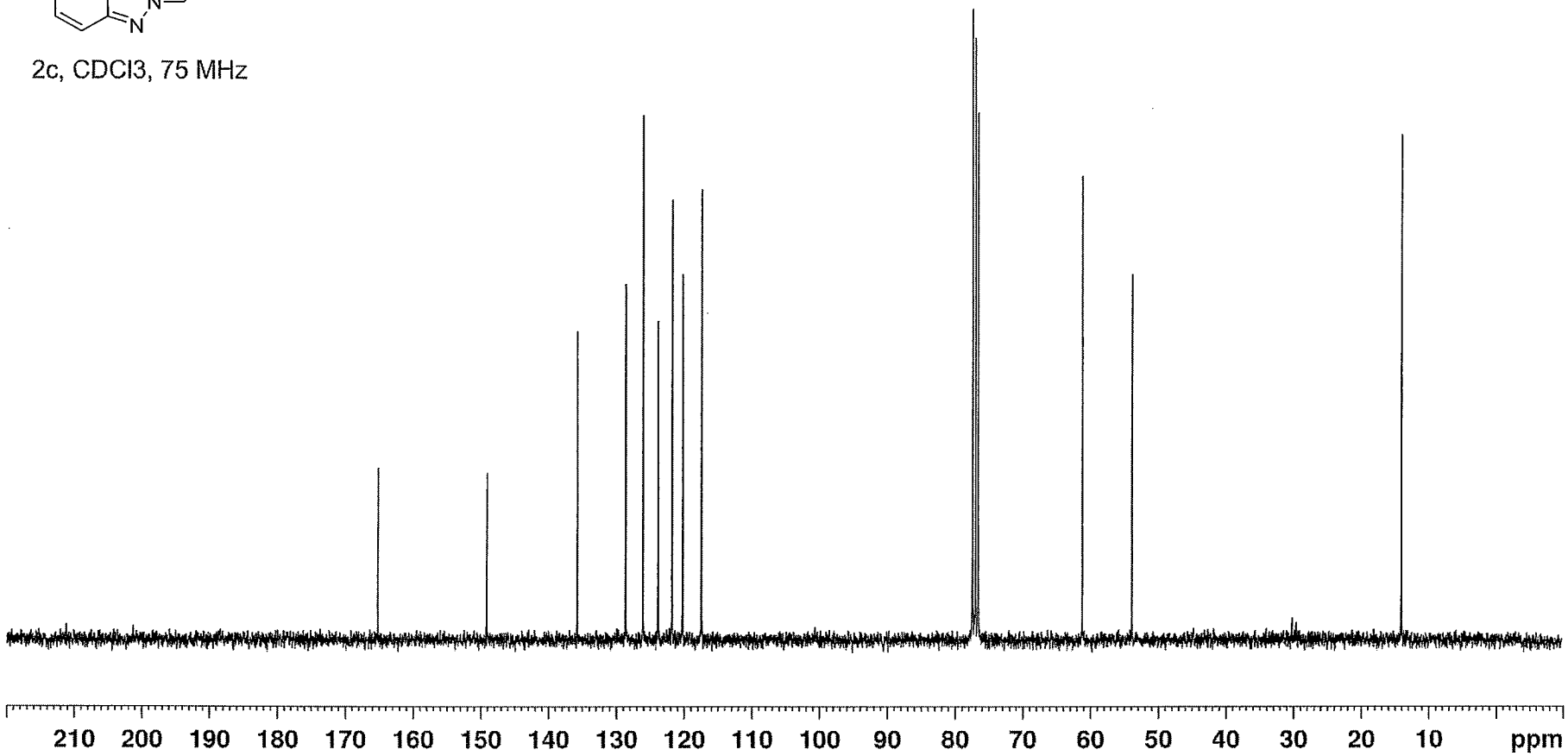

7.697
7.694
7.691
7.668
7.665
7.662
7.637
7.633
7.630
7.609
7.605
7.602
7.275
7.271
7.253
7.249
7.246
7.242
7.240
7.224
7.220
7.072
7.070
7.050
7.047
7.044
7.042
7.022
7.019
6.375
6.373
5.582
5.581
5.579
5.248
4.227
4.203
4.179
4.155
1.402
1.270
1.258
1.256
1.252
1.246
1.238
1.236
1.234
1.232
1.230
1.222
300-CKK-I-120f18to49
EtO2C
N
N
2c, CDCl3, 300 MHz
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
1.0
0.5
ppm
1.00
2.06
1.12
1.02
1.04
1.04
2.10
2.11
3.09

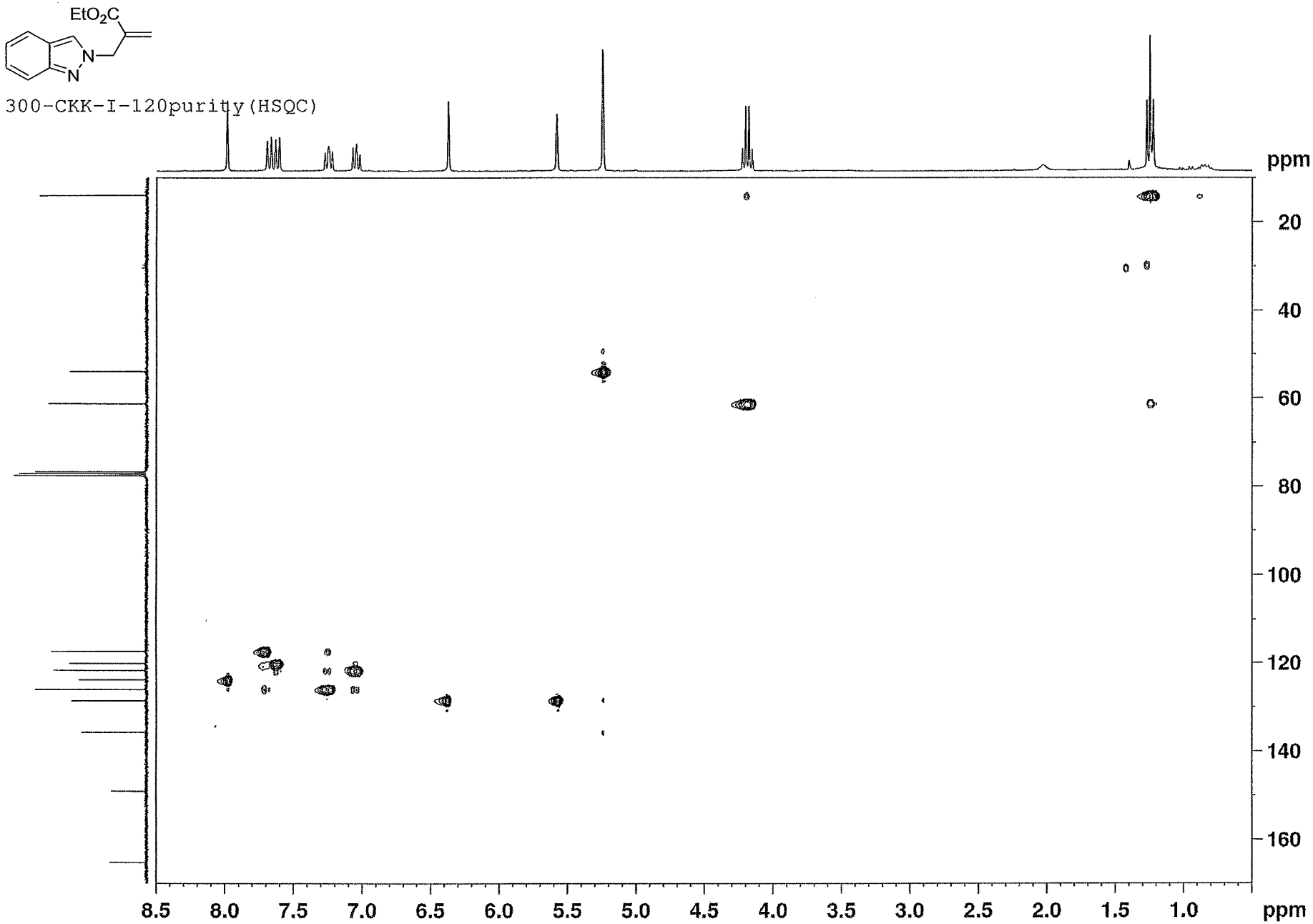
165.14
149.00
135.72
128.56
126.01
123.81
121.78
121.72
120.16
117.39
77.43
77.00
76.58
61.19
53.85
14.04

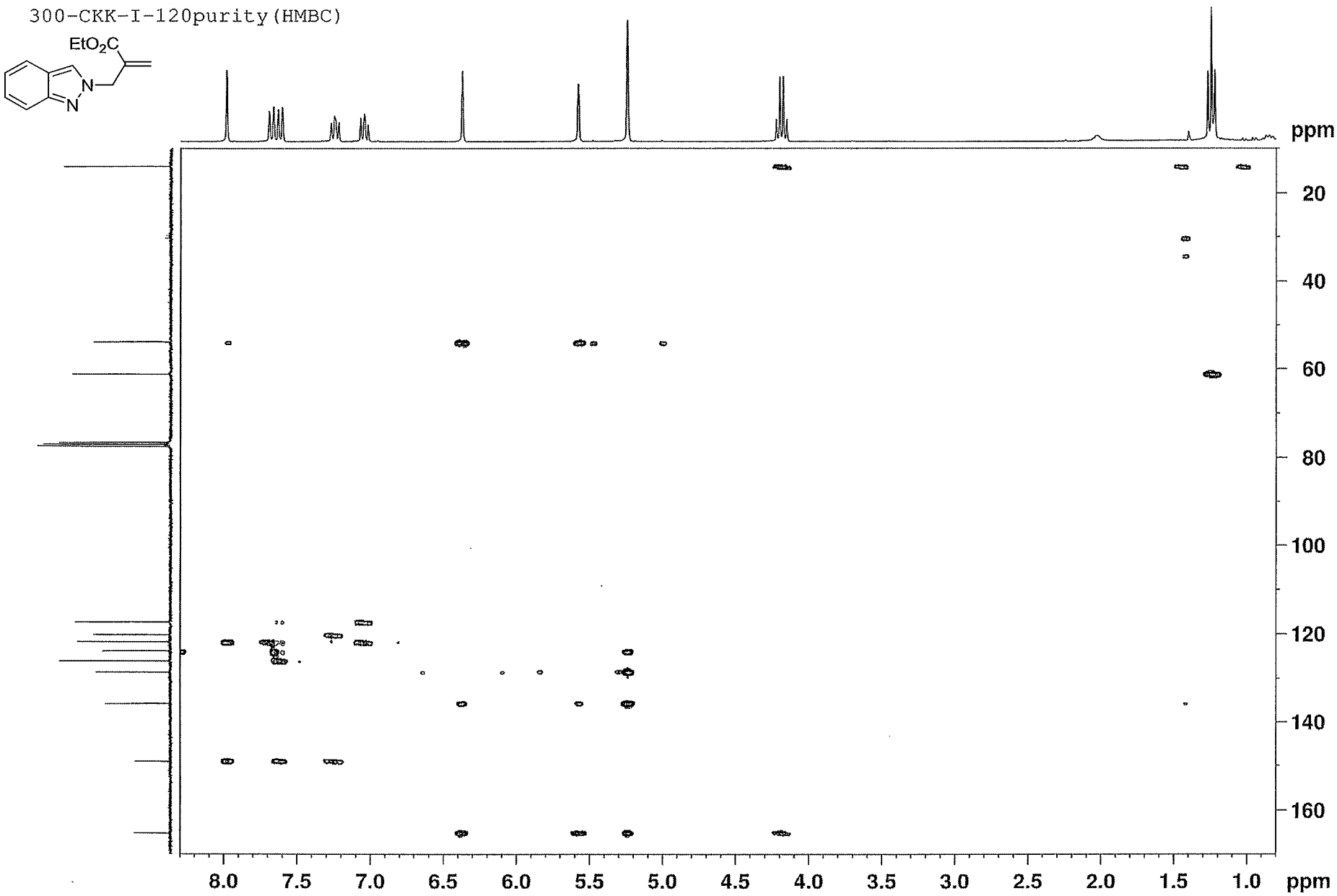
300-CKK-I-117purity(C13)

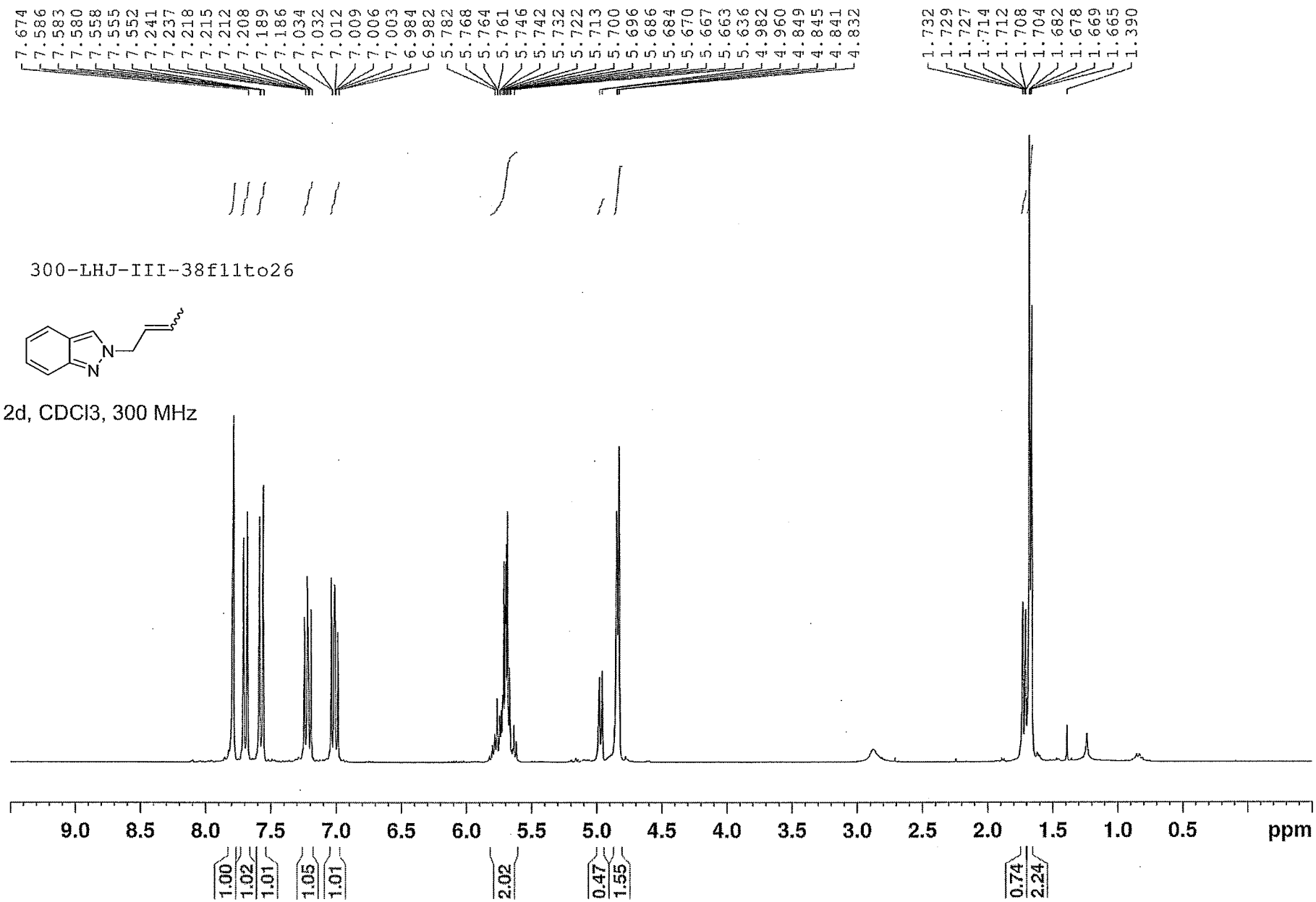


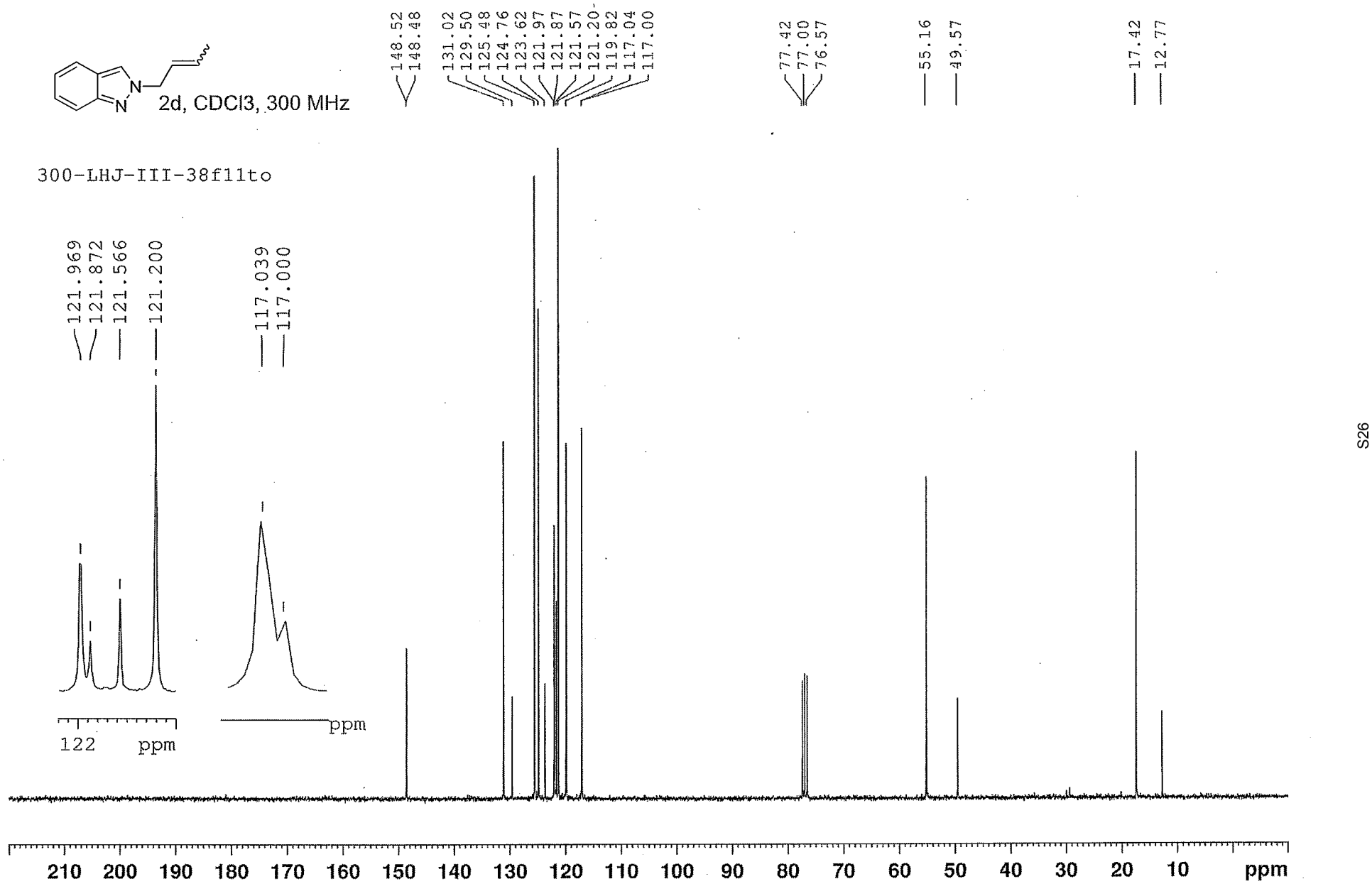
2c, CDCl3, 75 MHz

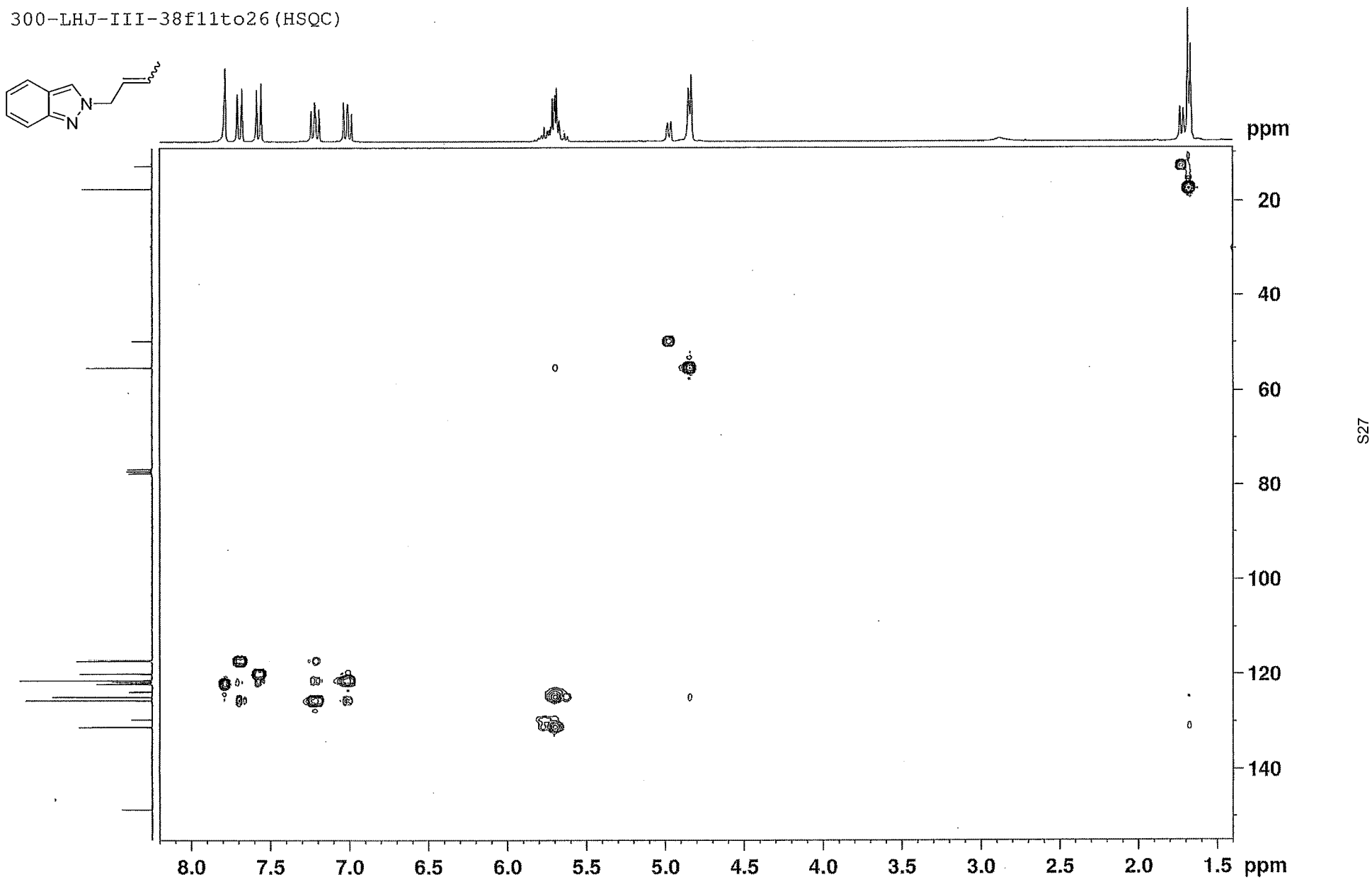


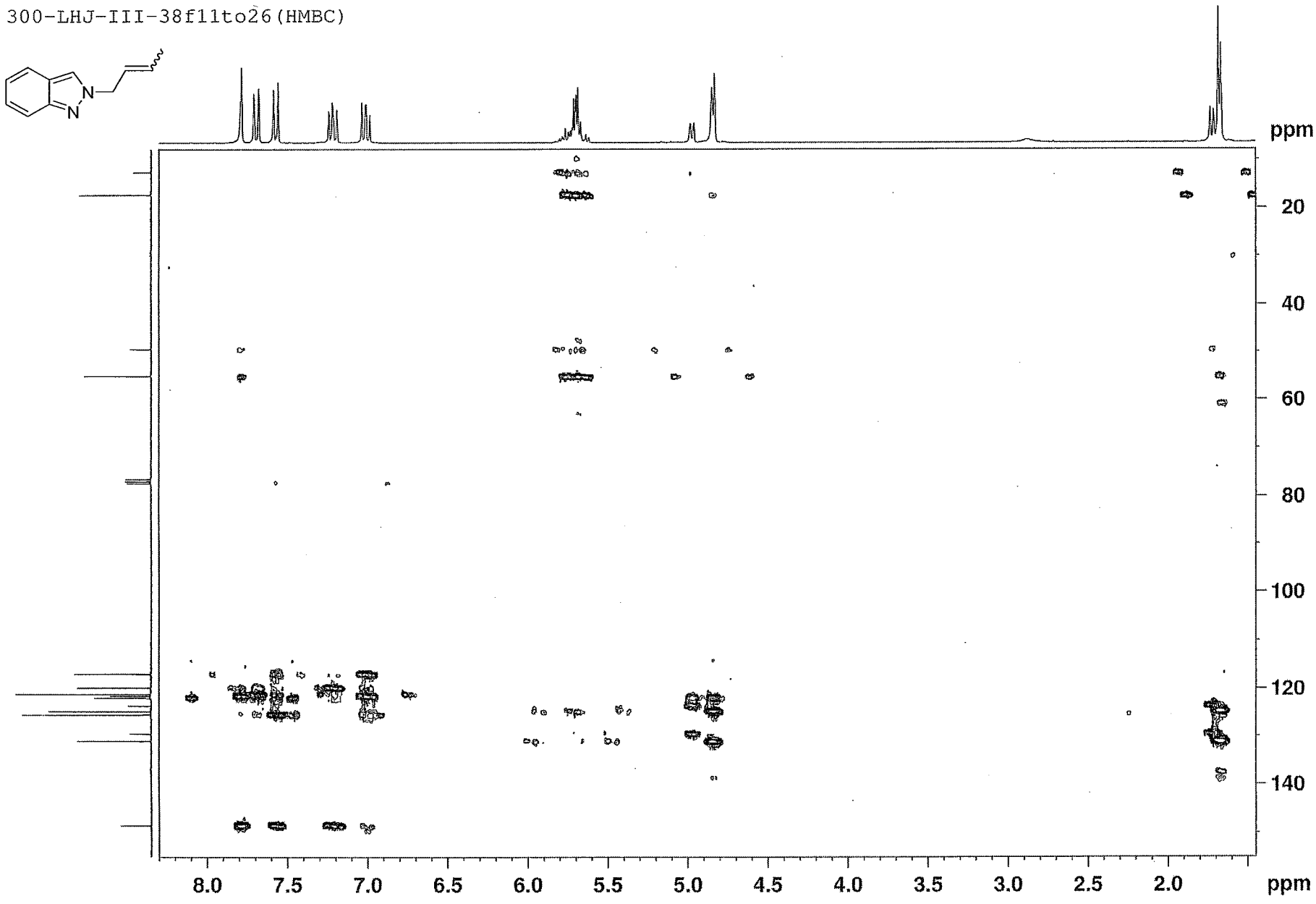

EtO2C
N
N
300-CKK-I-120purity(HSQC)
ppm
20
40
60
80
100
120
140
160
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

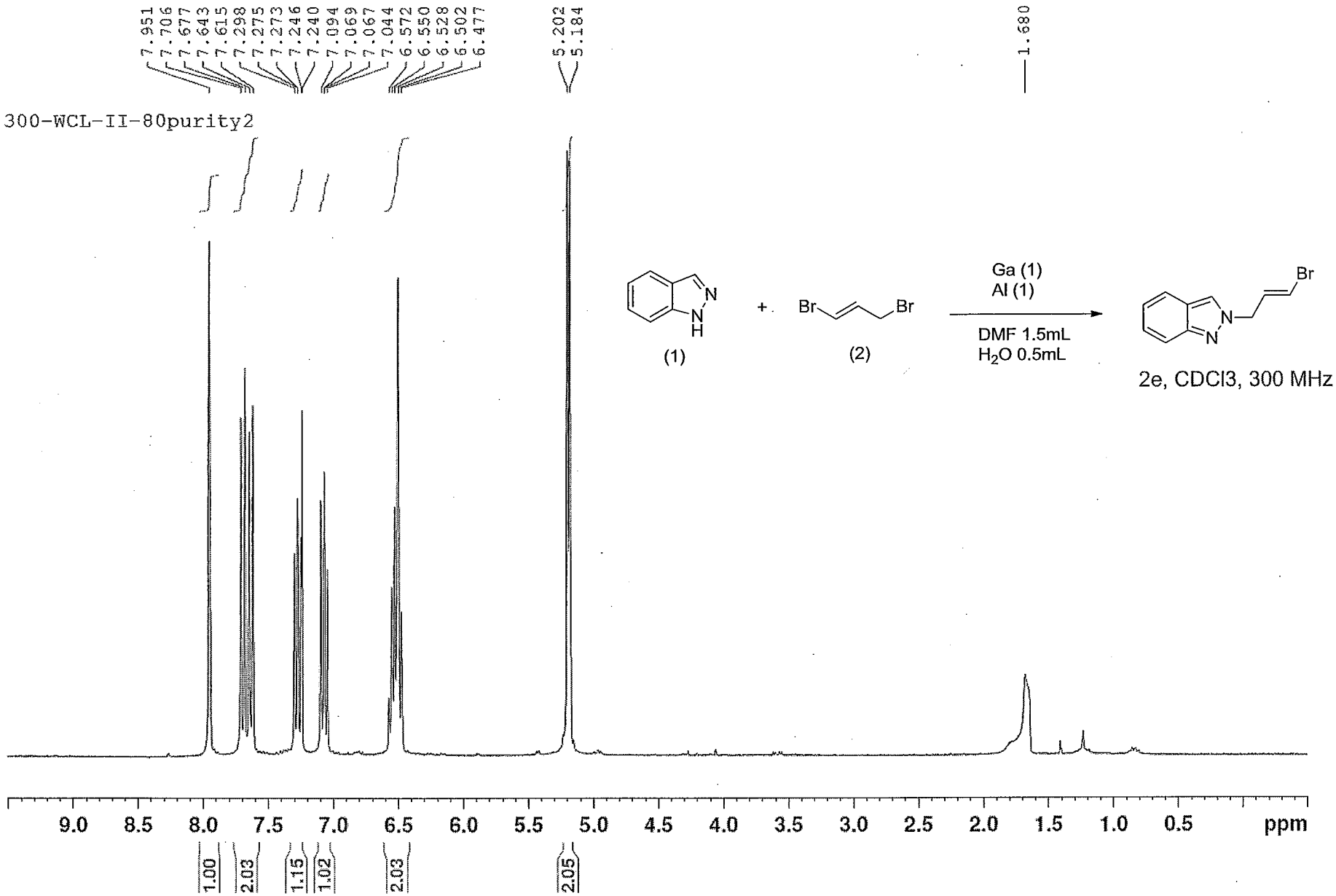

300-CKK-I-120purity(HMBC)
EtO2C
N
N
ppm
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

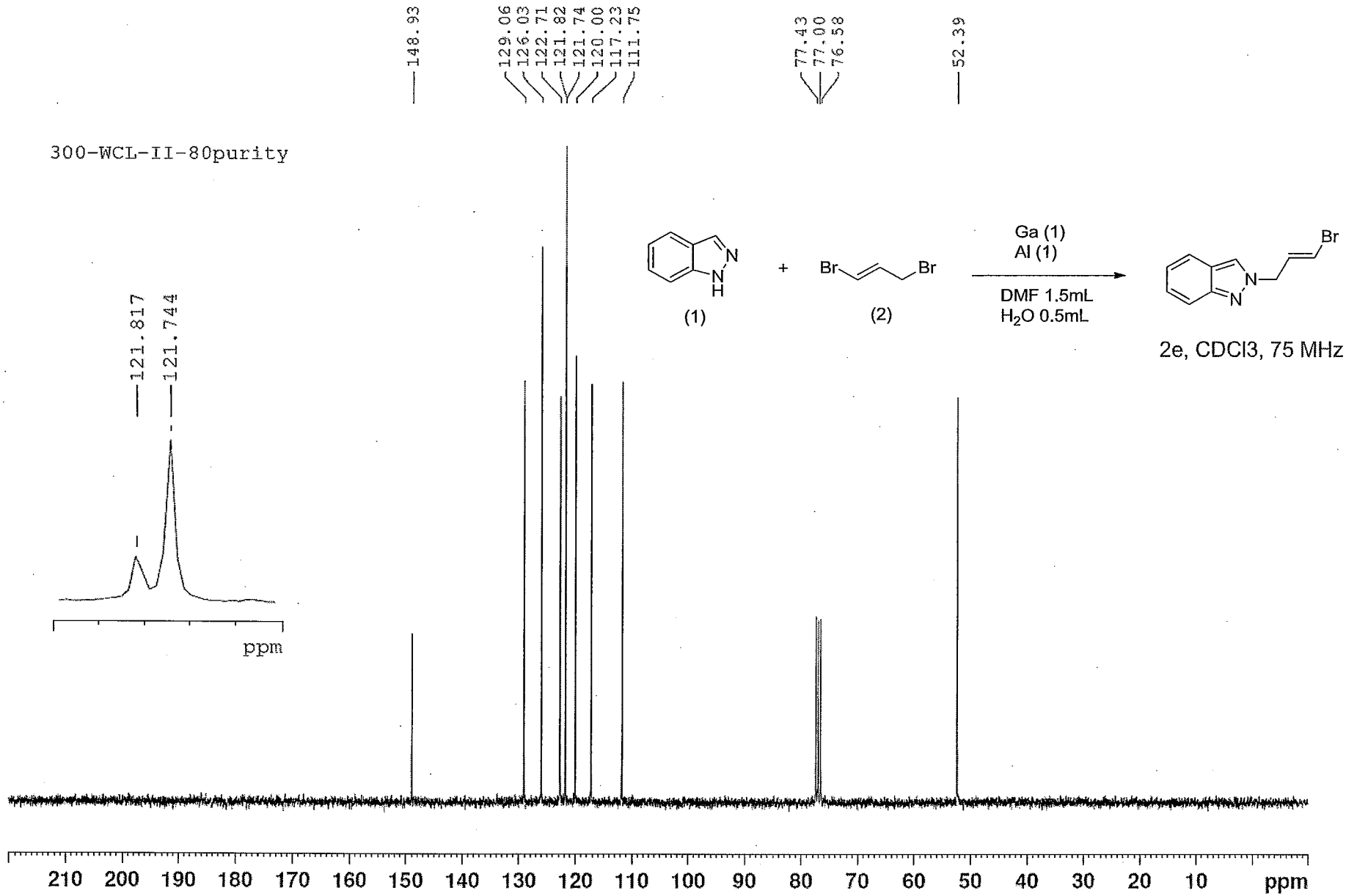

7.674
7.586
7.583
7.580
7.558
7.555
7.552
7.241
7.237
7.218
7.215
7.212
7.208
7.189
7.186
7.034
7.032
7.012
7.009
7.006
7.003
6.984
6.982
5.782
5.768
5.764
5.761
5.746
5.742
5.732
5.722
5.713
5.700
5.696
5.686
5.684
5.670
5.667
5.663
5.636
4.982
4.960
4.849
4.845
4.841
4.832
1.732
1.729
1.727
1.714
1.712
1.708
1.704
1.682
1.678
1.669
1.665
1.390
300-LHJ-III-38f11to26
N
N
2d, CDCl3, 300 MHz
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
1.0
0.5
ppm
1.00
1.02
1.01
1.05
1.01
2.02
0.47
1.55
0.74
2.24

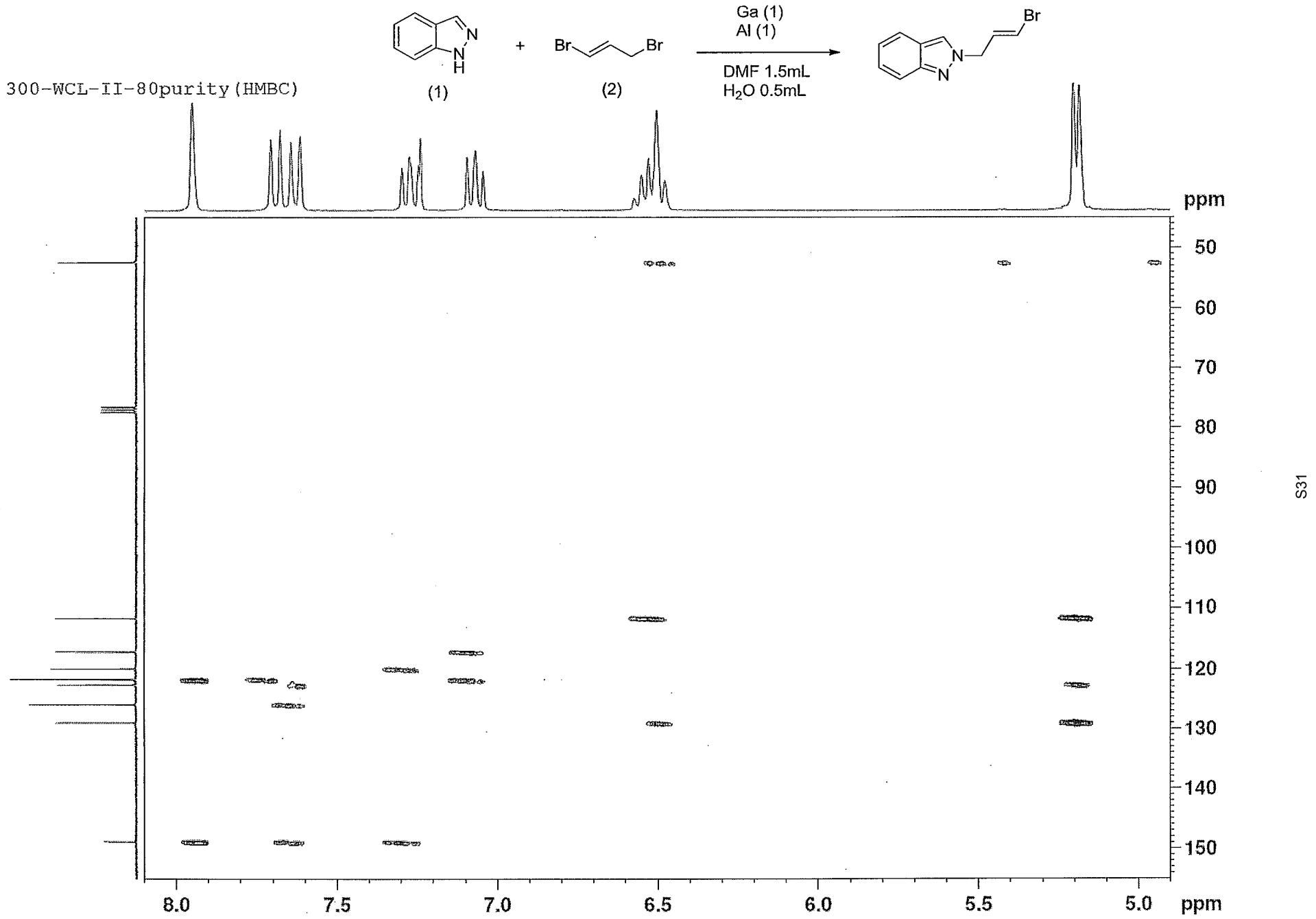

2d, CDCl3, 300 MHz
300-LHJ-III-38f11to
148.52
148.48
131.02
129.50
125.48
124.76
123.62
121.97
121.87
121.57
121.20
119.82
117.04
117.00
77.42
77.00
76.57
55.16
49.57
17.42
12.77
121.969
121.872
121.566
121.200
117.039
117.000
122 ppm
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

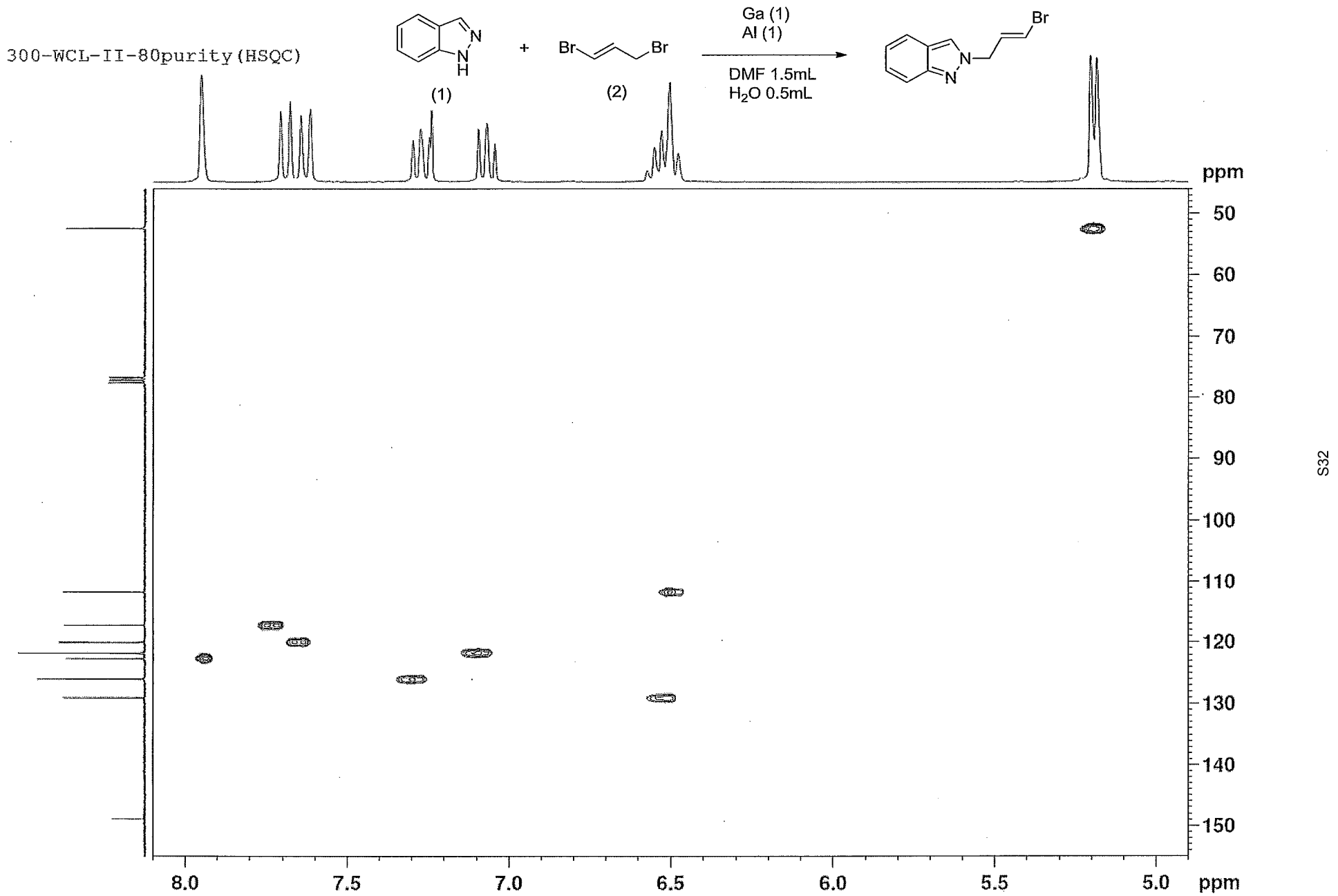

300-LHJ-III-38f11to26(HSQC)
N
N
ppm
20
40
60
80
100
120
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

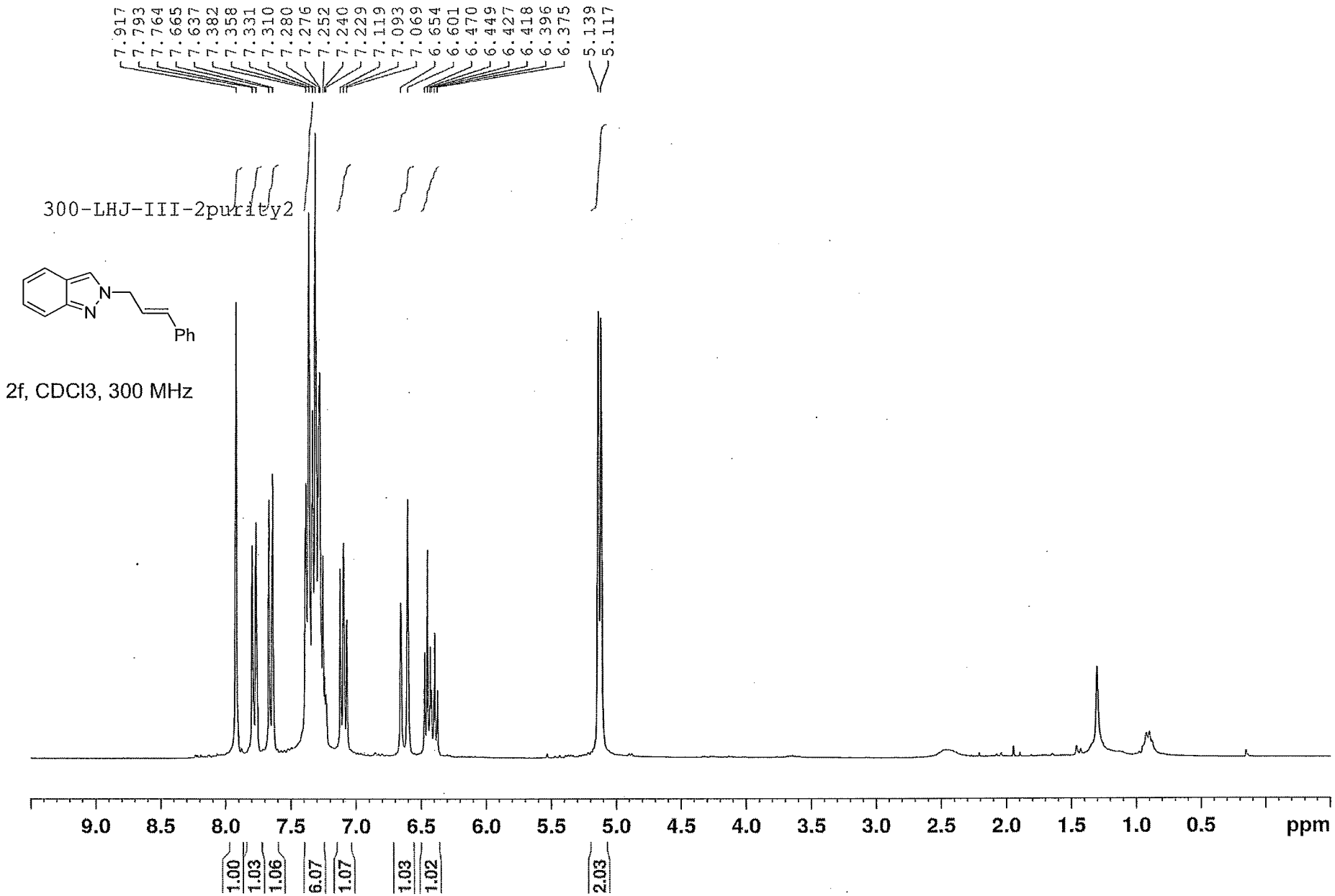

300-LHJ-III-38f11to26(HMBC)
N
N
ppm
20
40
60
80
100
120
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

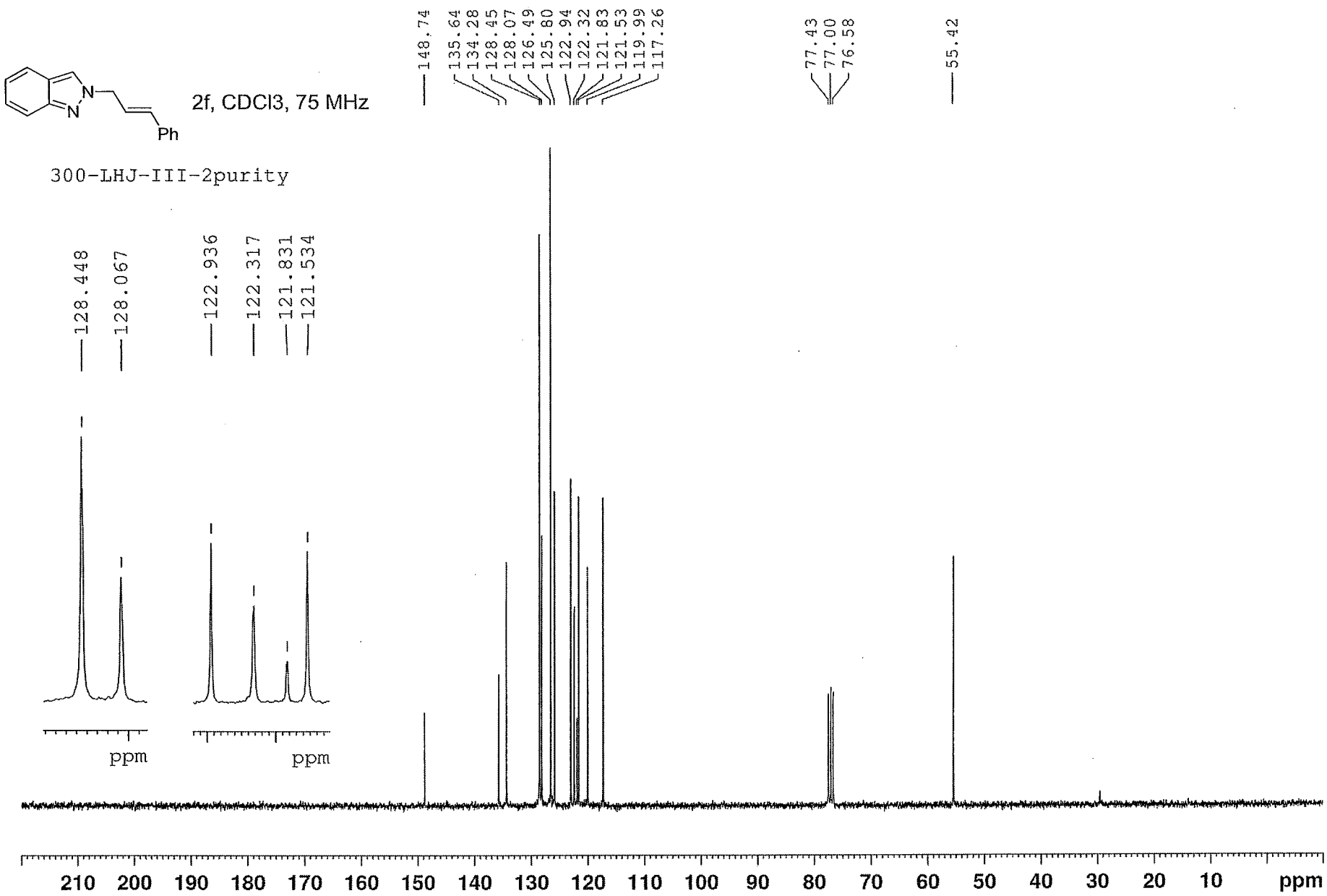

7.951
7.706
7.677
7.643
7.615
7.298
7.275
7.273
7.246
7.240
7.094
7.069
7.067
7.044
6.572
6.550
6.528
6.502
6.477
5.202
5.184
1.680
300-WCL-II-80purity2
(1)
(2)
Ga (1)
Al (1)
DMF 1.5mL
H2O 0.5mL
2e, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.03
1.15
1.02
2.03
2.05

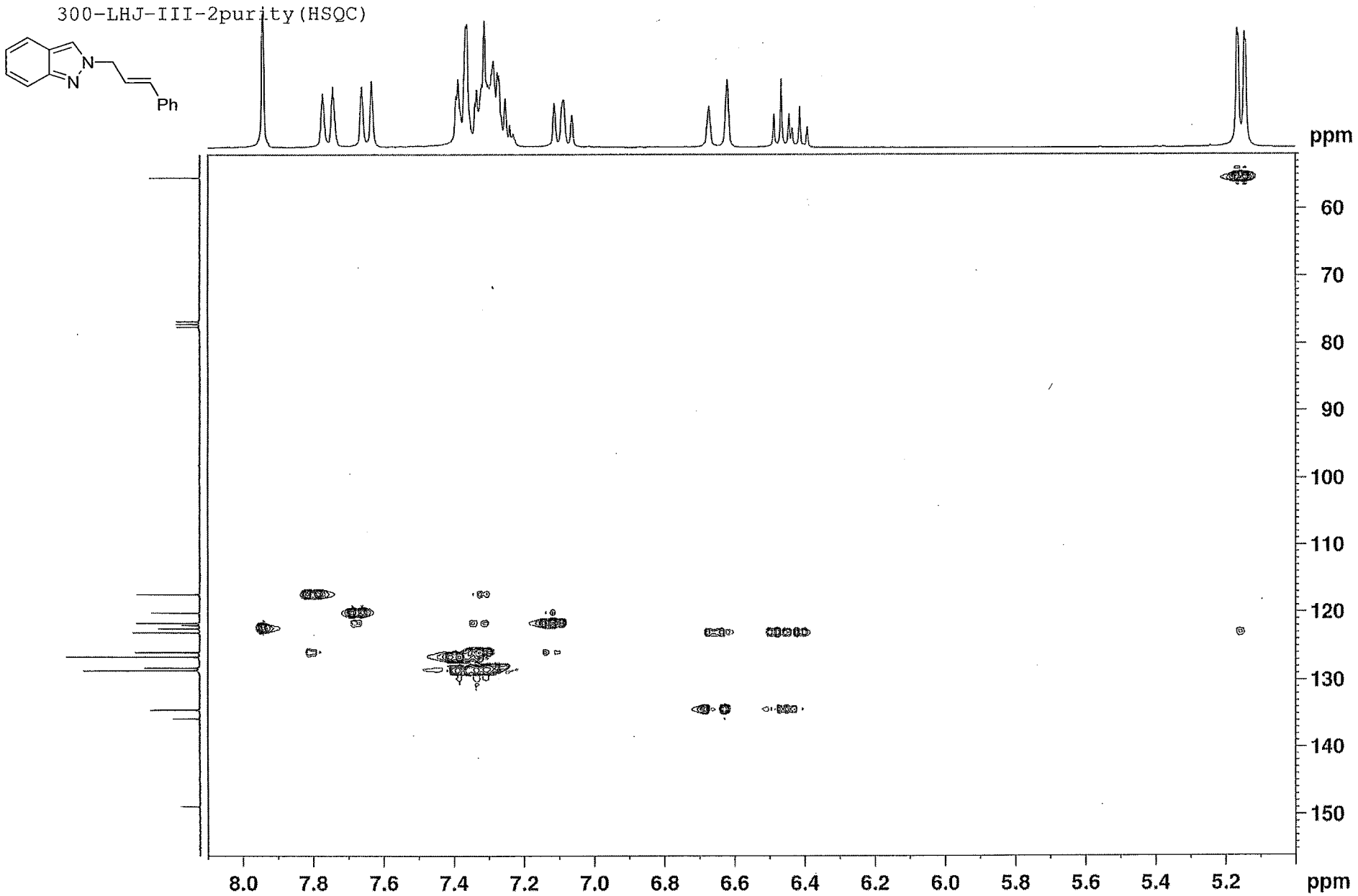

148.93
129.06
126.03
122.71
121.82
121.74
120.00
117.23
111.75
77.43
77.00
76.58
52.39
300-WCL-II-80purity
121.817
121.744
ppm
(1)
(2)
Ga (1)
Al (1)
DMF 1.5mL
H2O 0.5mL
Br
2e, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

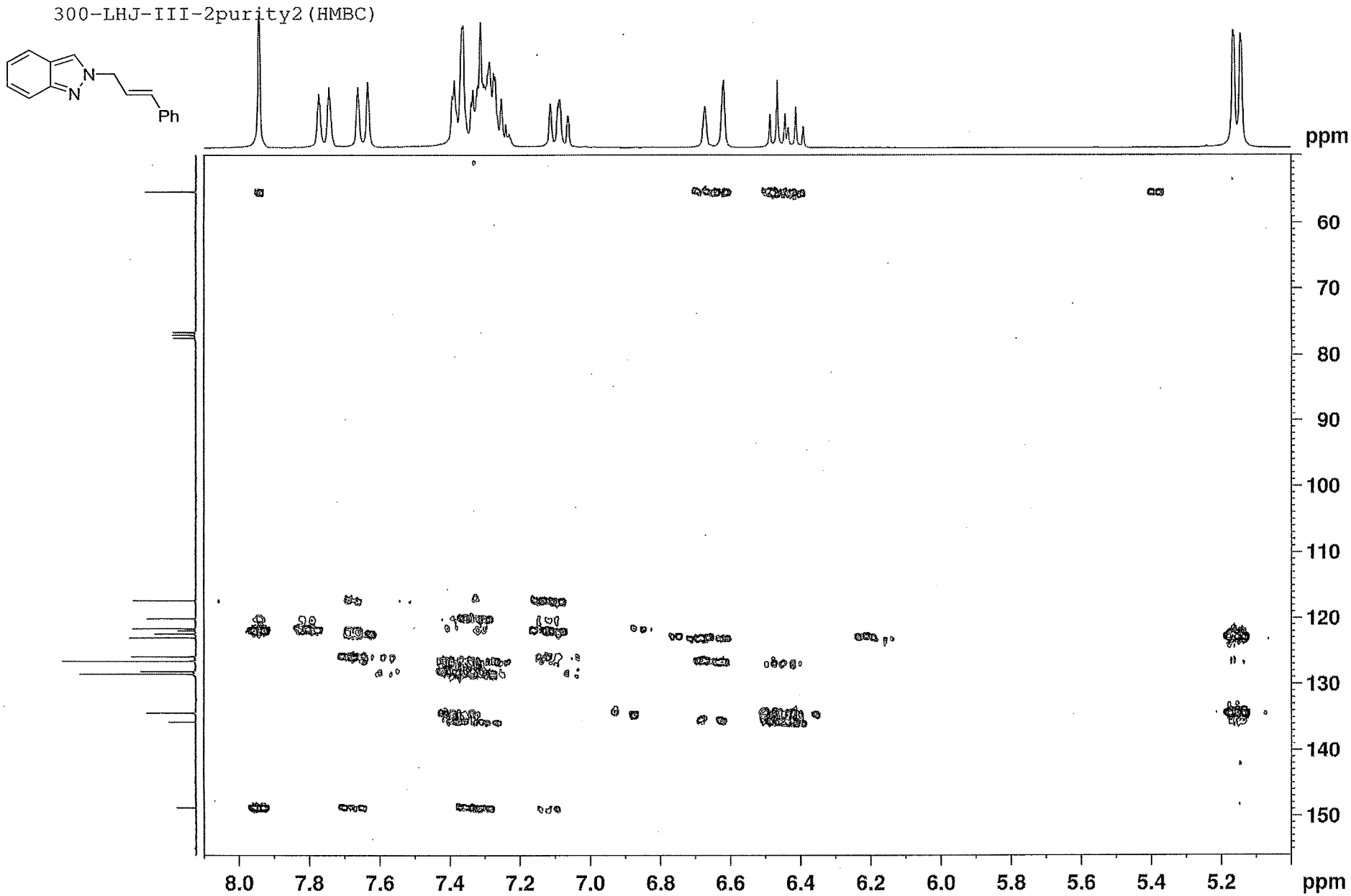

300-WCL-II-80purity(HMBC)
(1)
(2)
Ga (1)
Al (1)
DMF 1.5mL
H2O 0.5mL
Br
Br
Br
N
N
H
N
N
ppm
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm

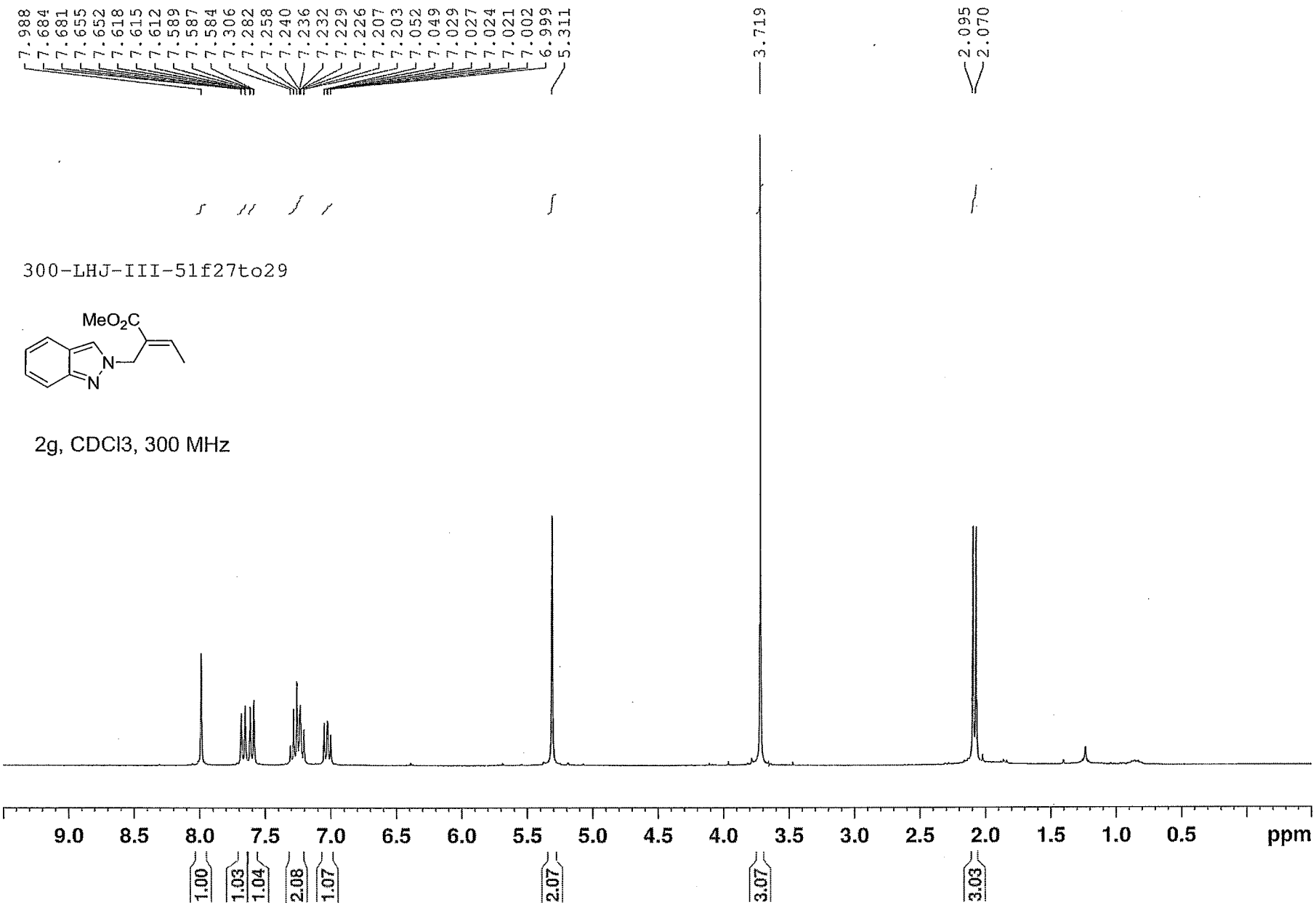

300-WCL-II-80purity(HSQC)
(1)
(2)
Ga (1)
Al (1)
DMF 1.5mL
H2O 0.5mL
Br
Br
Br
N
N
H
N
N
ppm
50
60
70
80
90
100
110
120
130
140
150
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm

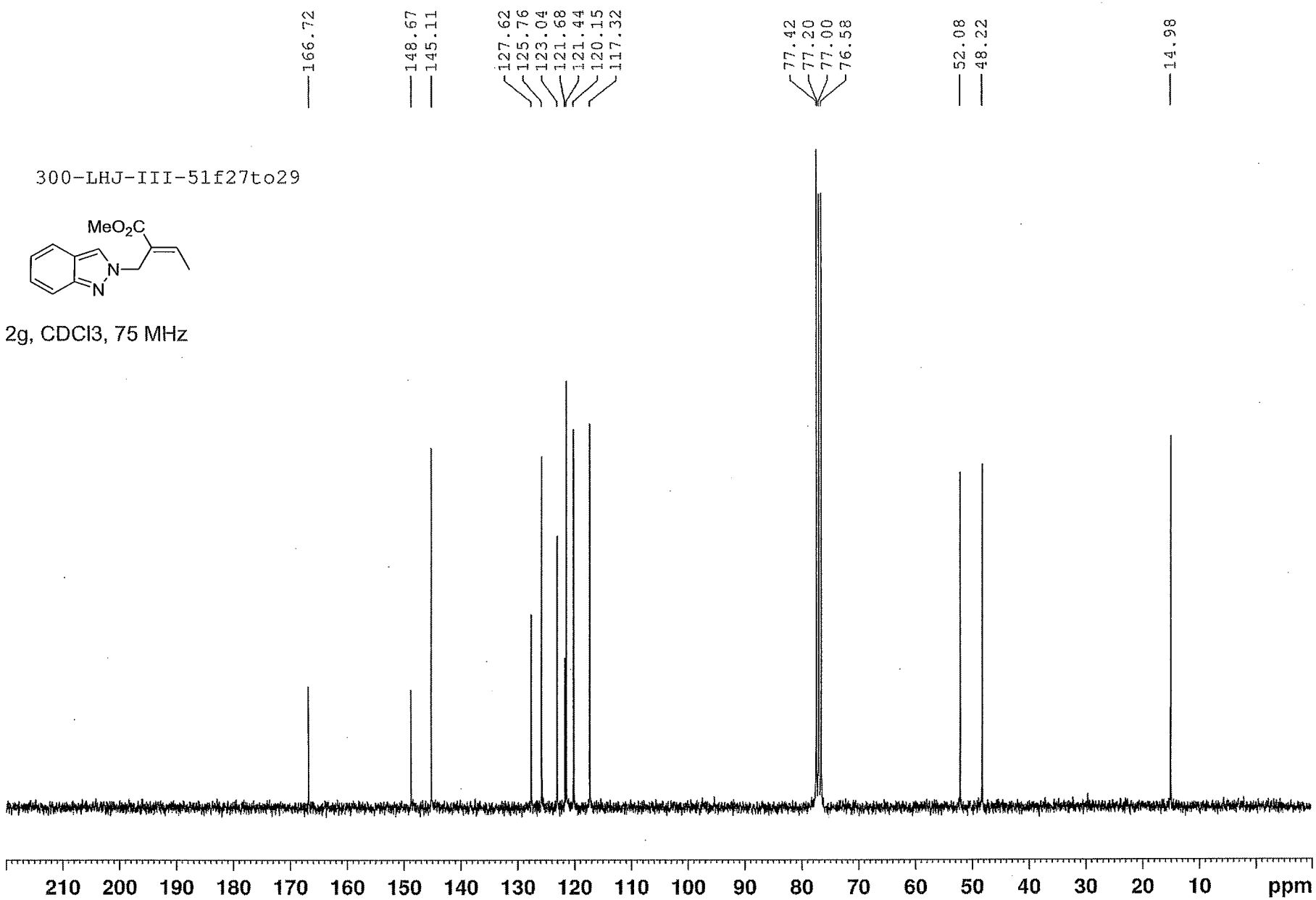

7.917
7.793
7.764
7.665
7.637
7.382
7.358
7.331
7.310
7.280
7.276
7.252
7.240
7.229
7.119
7.093
7.069
6.654
6.601
6.470
6.449
6.427
6.418
6.396
6.375
5.139
5.117
300-LHJ-III-2purity2
N
N
Ph
2f, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
1.06
6.07
1.07
1.03
1.02
2.03

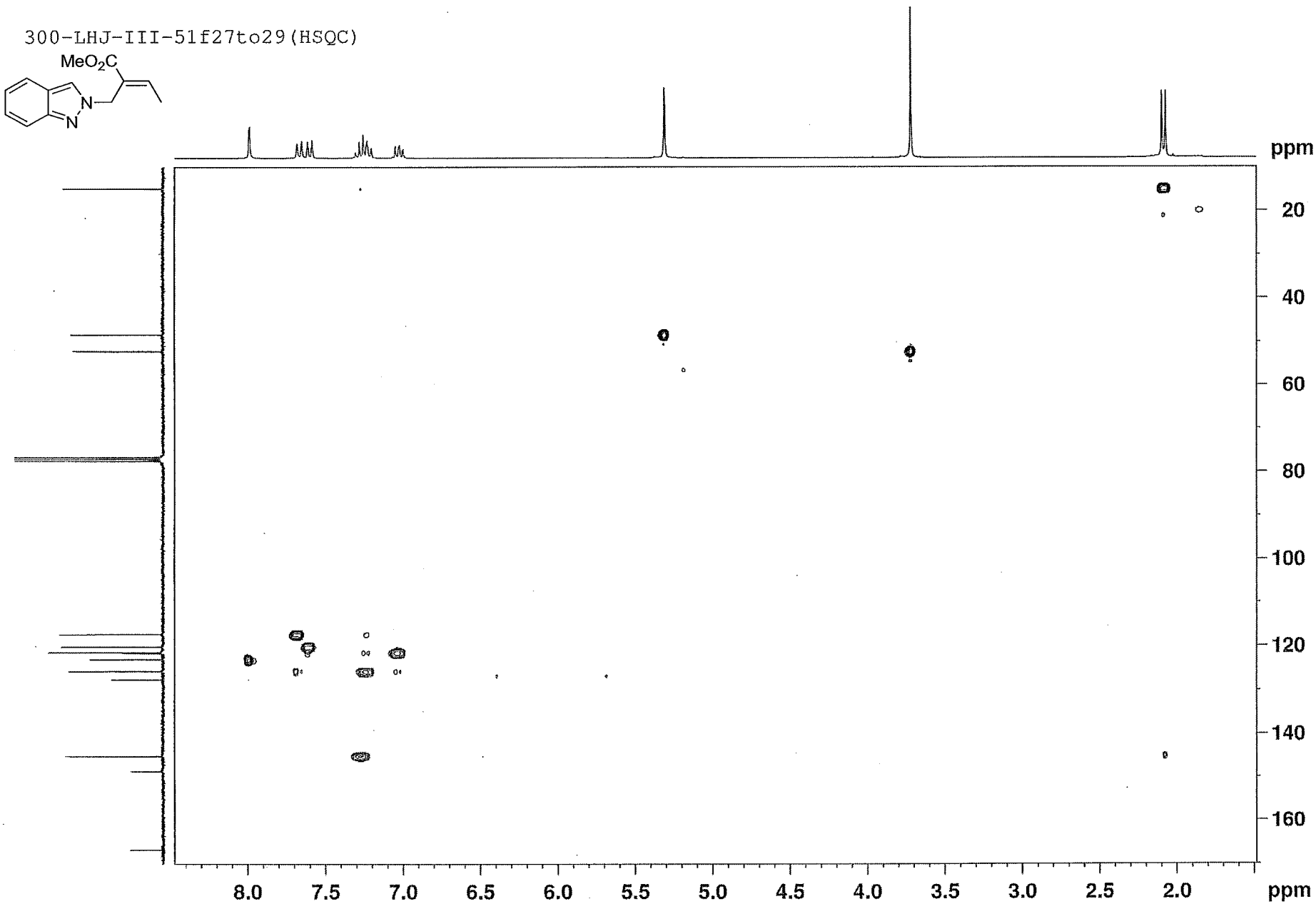

2f, CDCl3, 75 MHz
300-LHJ-III-2purity
148.74
135.64
134.28
128.45
128.07
126.49
125.80
122.94
122.32
121.83
121.53
119.99
117.26
77.43
77.00
76.58
55.42
128.448
128.067
122.936
122.317
121.831
121.534
ppm
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

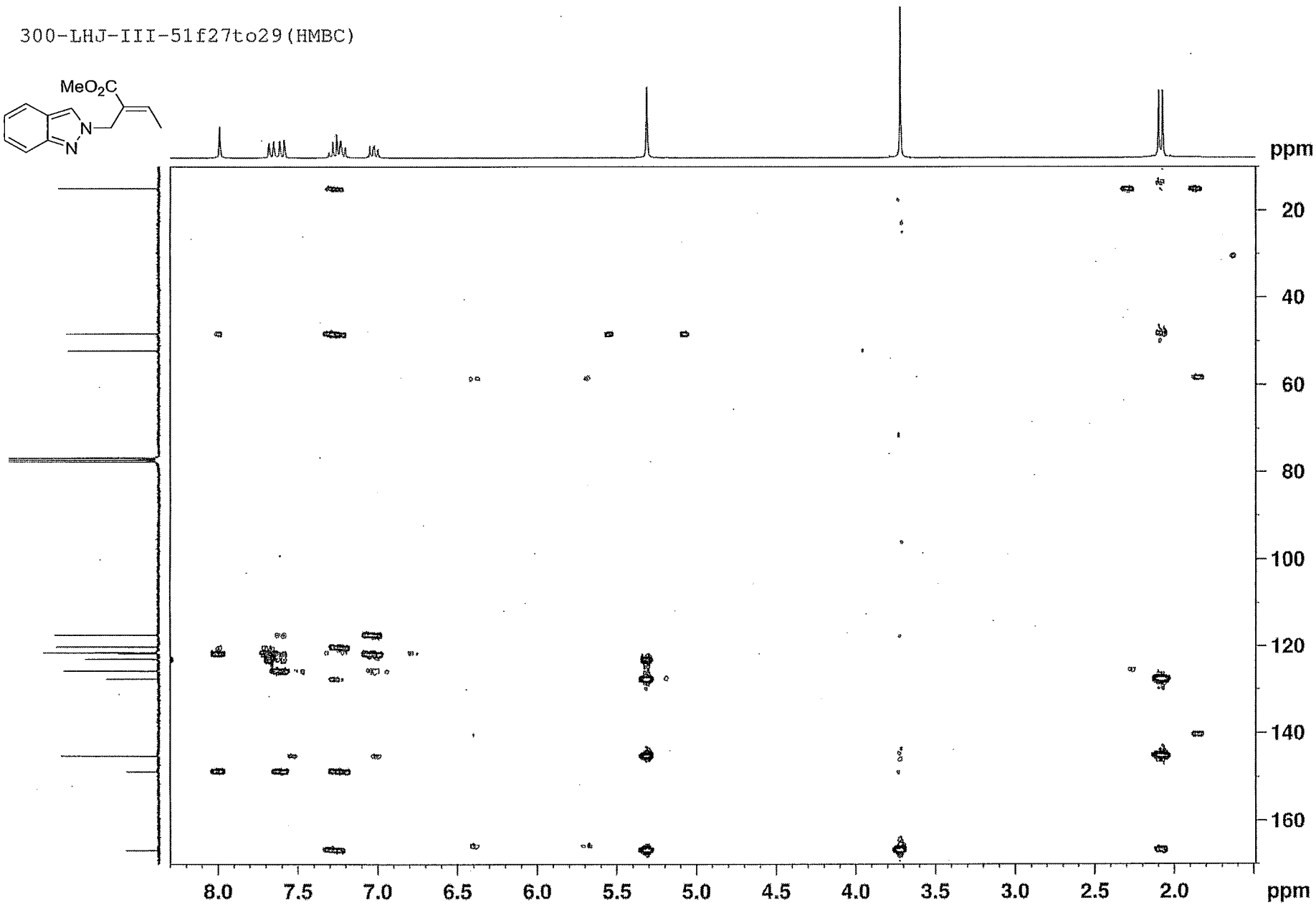

300-LHJ-III-2purity(HSQC)
N
N
Ph
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
ppm

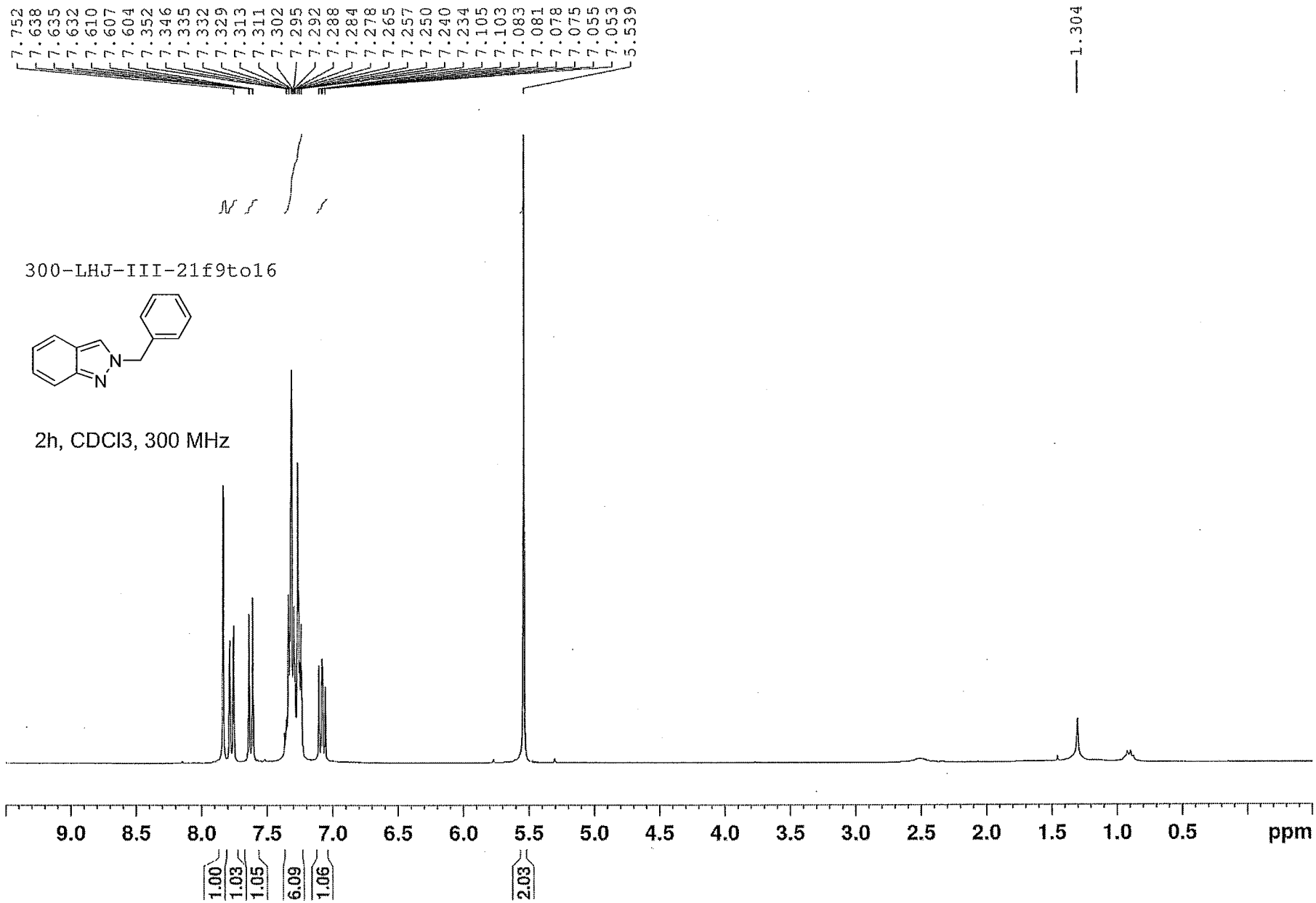

300-LHJ-III-2purity2(HMBC)
N
N
Ph
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
ppm

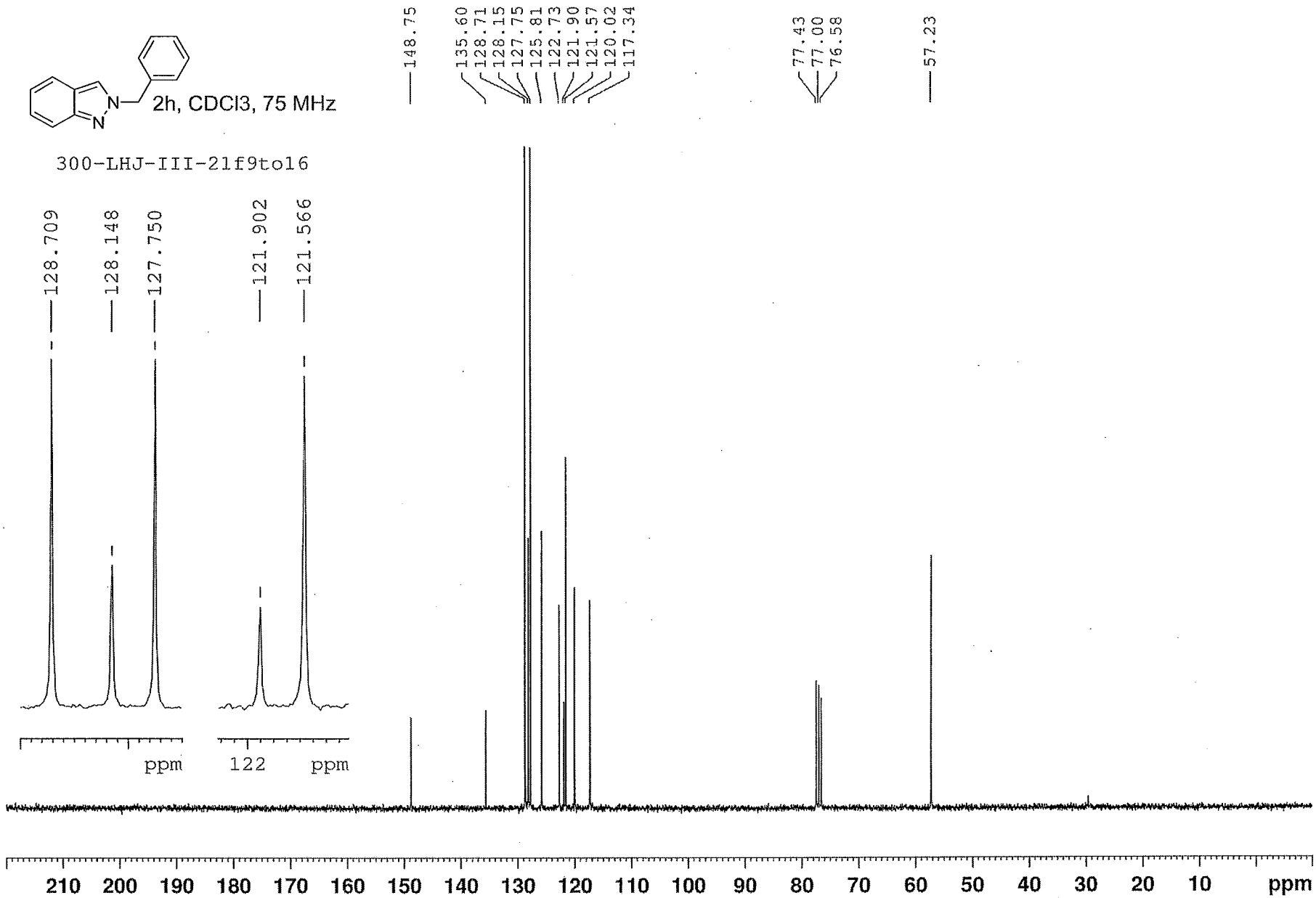

7.988
7.684
7.681
7.655
7.652
7.618
7.615
7.612
7.589
7.587
7.584
7.306
7.282
7.258
7.240
7.236
7.232
7.229
7.226
7.207
7.203
7.052
7.049
7.029
7.027
7.024
7.021
7.002
6.999
5.311
3.719
2.095
2.070
300-LHJ-III-51f27to29
MeO2C
N
N
2g, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
1.04
2.08
1.07
2.07
3.07
3.03

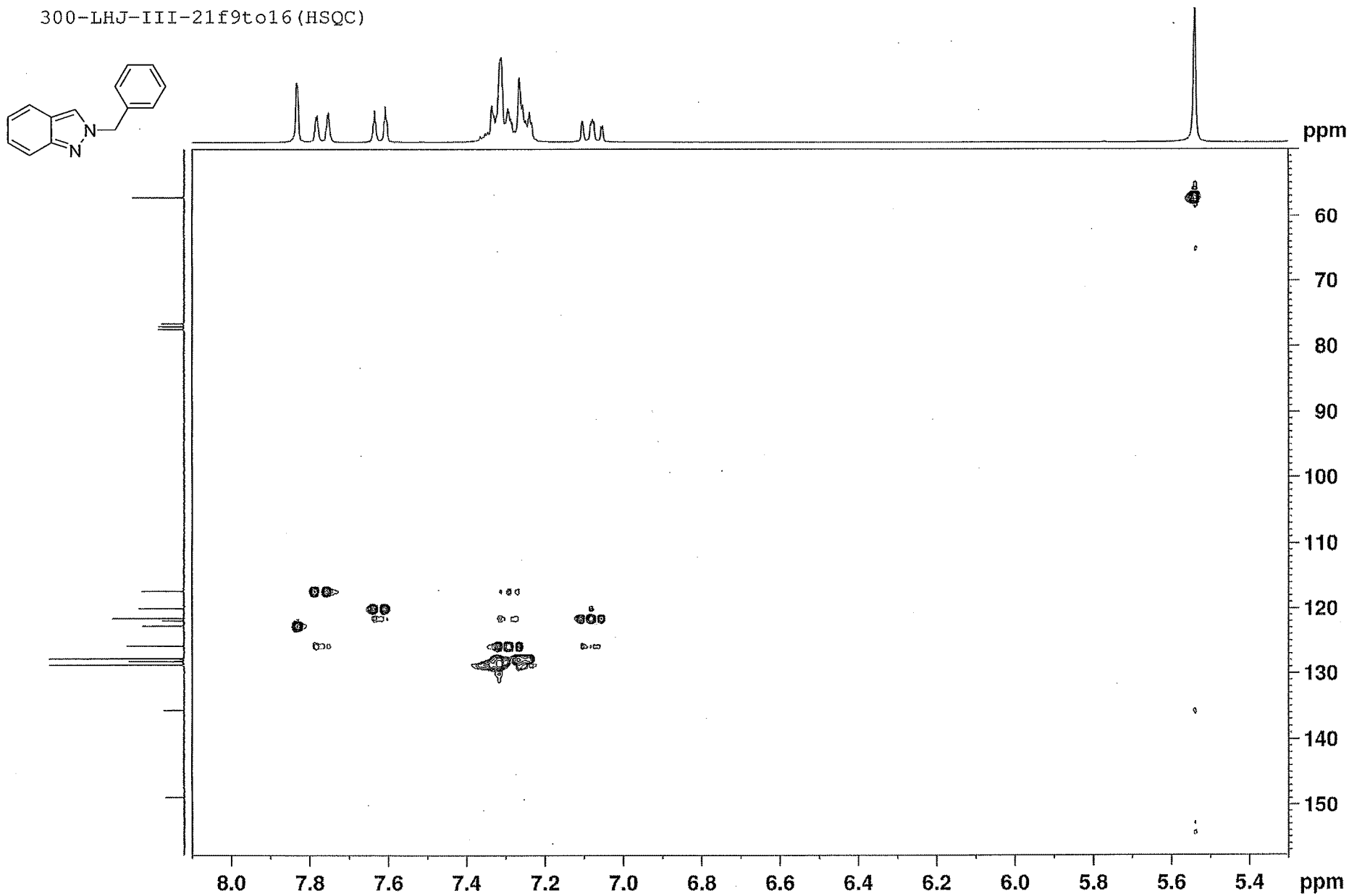

166.72
148.67
145.11
127.62
125.76
123.04
121.68
121.44
120.15
117.32
77.42
77.20
77.00
76.58
52.08
48.22
14.98
300-LHJ-III-51f27to29
MeO2C
N
N
2g, CDCl3, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

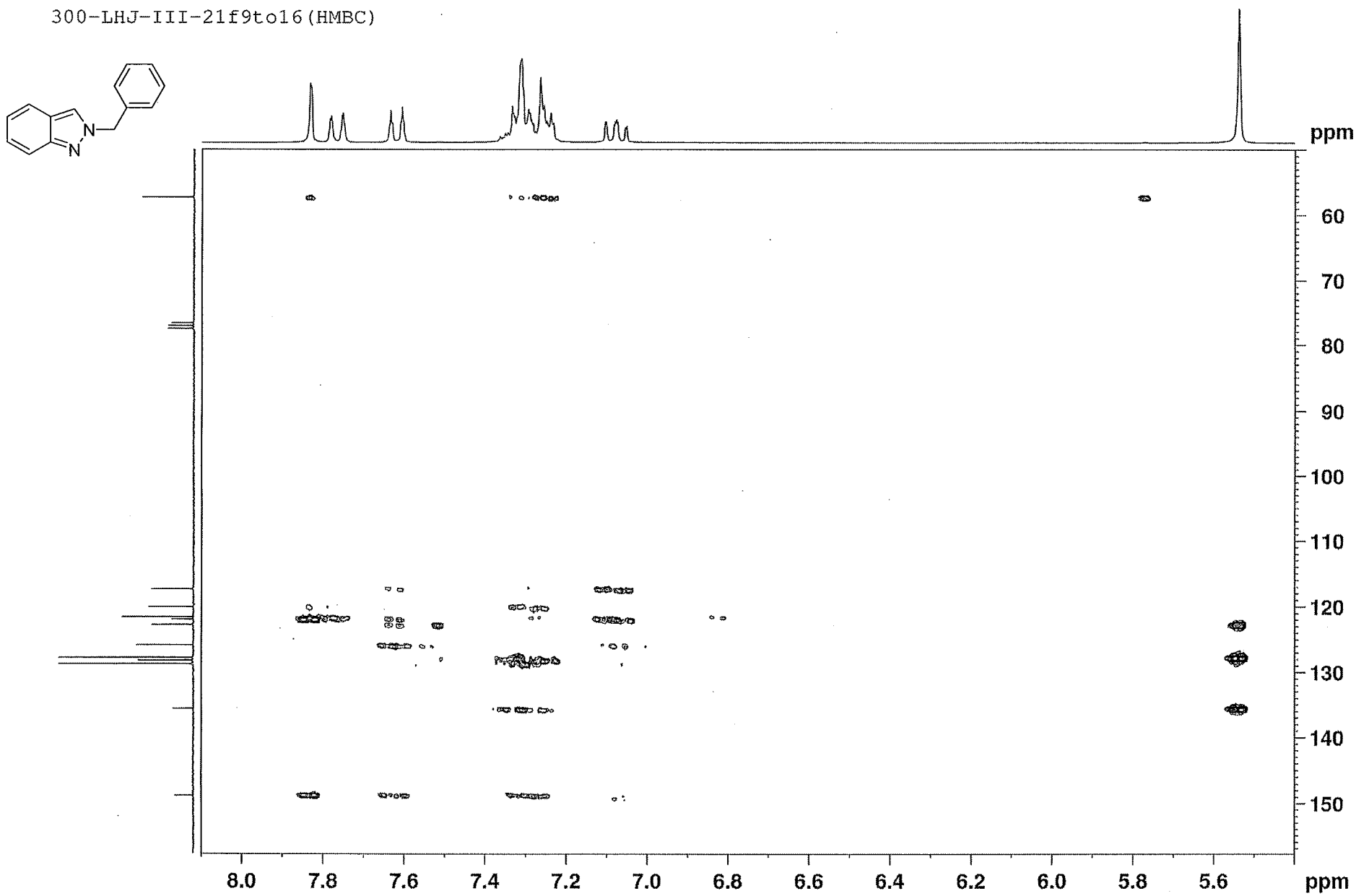

300-LHJ-III-51f27to29(HSQC)
MeO2C
N
N
ppm
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

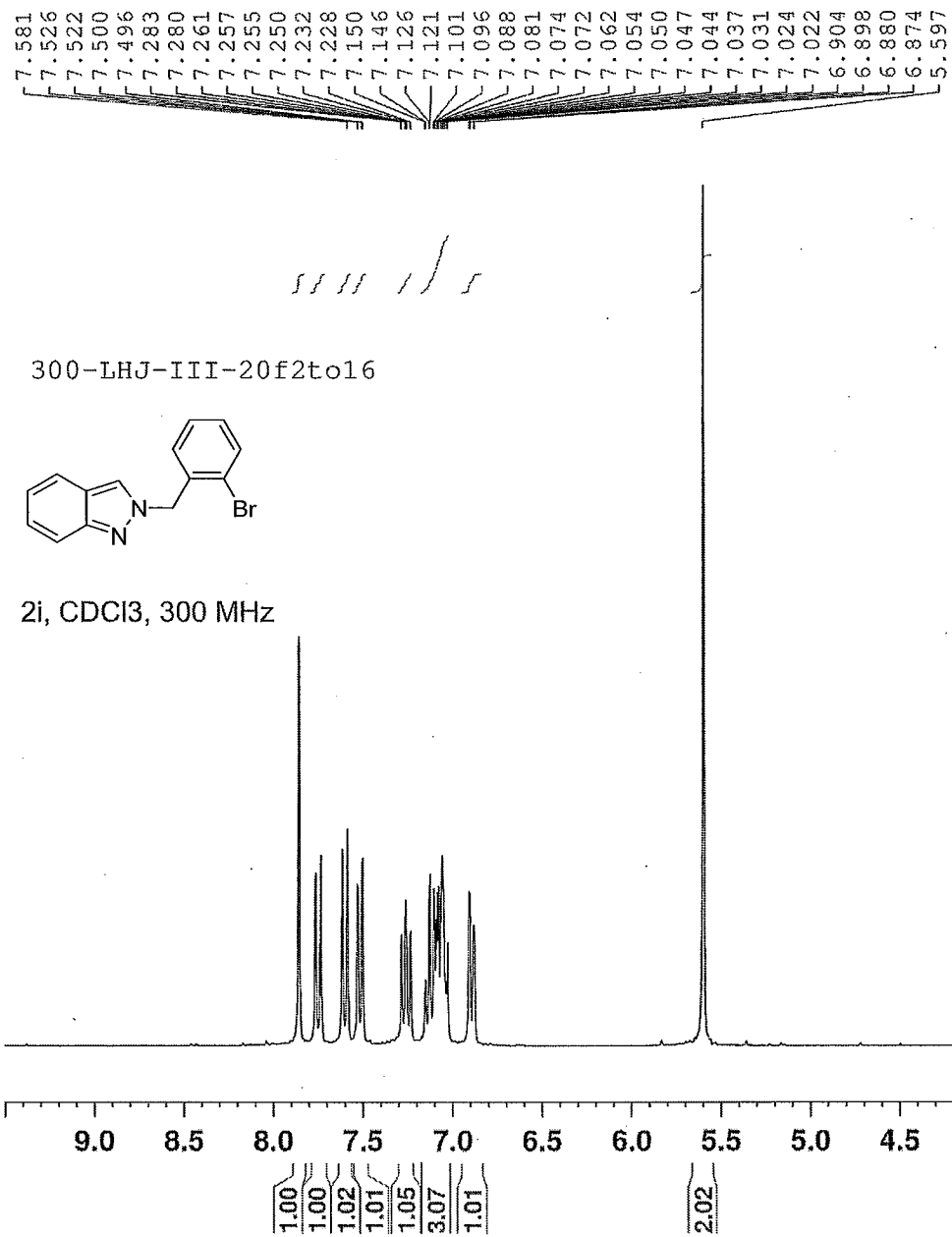

300-LHJ-III-51f27to29(HMBC)
MeO2C
N
N
ppm
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

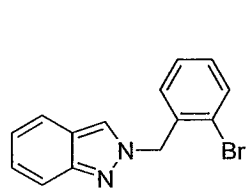

7.752
7.638
7.635
7.632
7.610
7.607
7.604
7.352
7.346
7.335
7.332
7.329
7.313
7.311
7.302
7.295
7.292
7.288
7.284
7.278
7.265
7.257
7.250
7.240
7.234
7.105
7.103
7.083
7.081
7.078
7.075
7.055
7.053
5.539
1.304
300-LHJ-III-21f9to16
2h, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.03
1.05
6.09
1.06
2.03


2h, CDCl3, 75 MHz
300-LHJ-III-21f9to16
148.75
135.60
128.71
128.15
127.75
125.81
122.73
121.90
121.57
120.02
117.34
77.43
77.00
76.58
57.23
128.709
128.148
127.750
121.902
121.566
ppm
122
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


300-LHJ-III-21f9to16(HSQC)
N
N
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm


300-LHJ-III-21f9to16(HMBC)
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
ppm

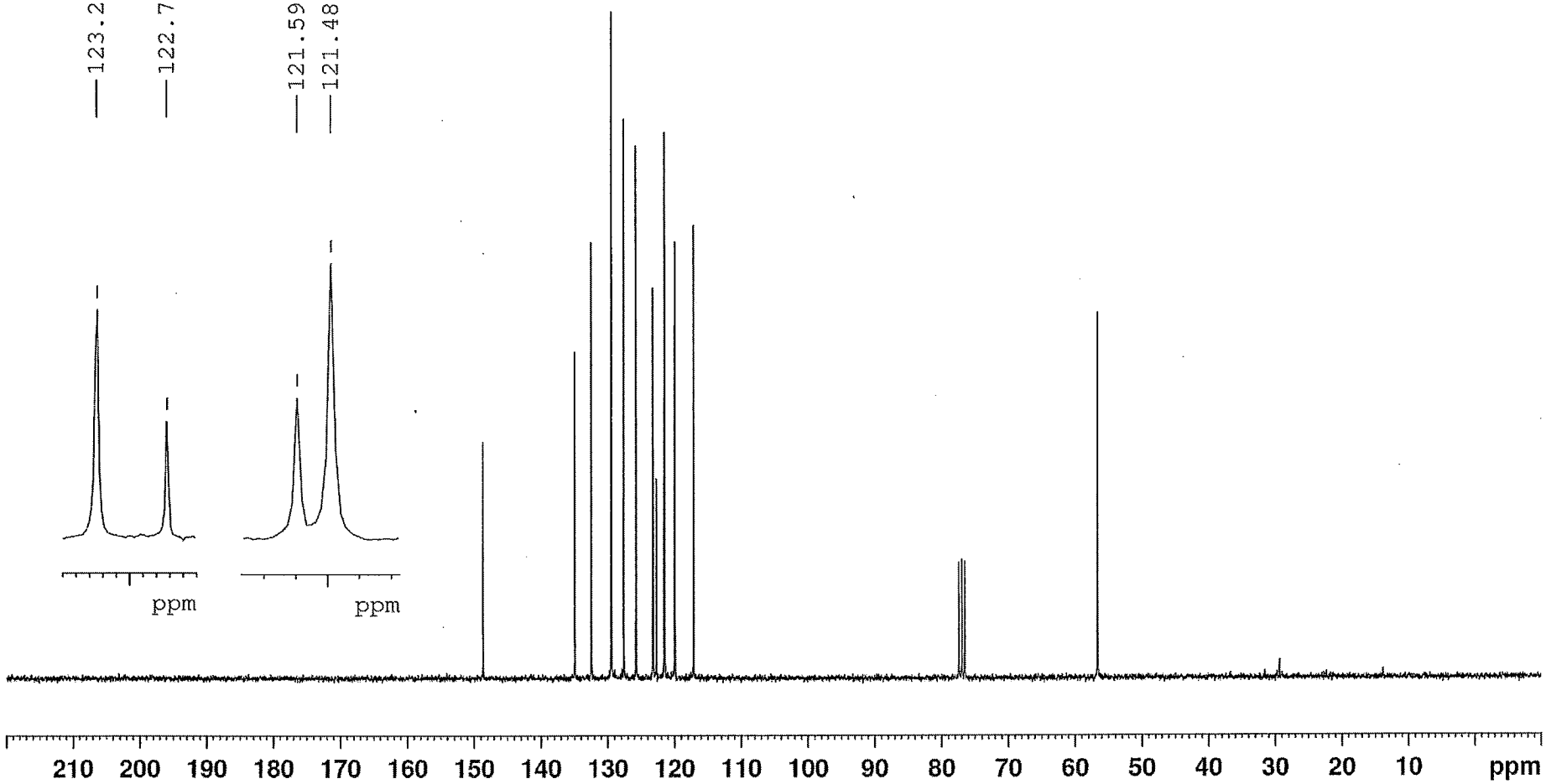

7.581
7.526
7.522
7.500
7.496
7.283
7.280
7.261
7.257
7.255
7.250
7.232
7.228
7.150
7.146
7.126
7.121
7.101
7.096
7.088
7.081
7.074
7.072
7.062
7.054
7.050
7.047
7.044
7.037
7.031
7.024
7.022
6.904
6.898
6.880
6.874
5.597
300-LHJ-III-20f2to16
N
N
Br
2i, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.00
1.02
1.01
1.05
3.07
1.01
2.02

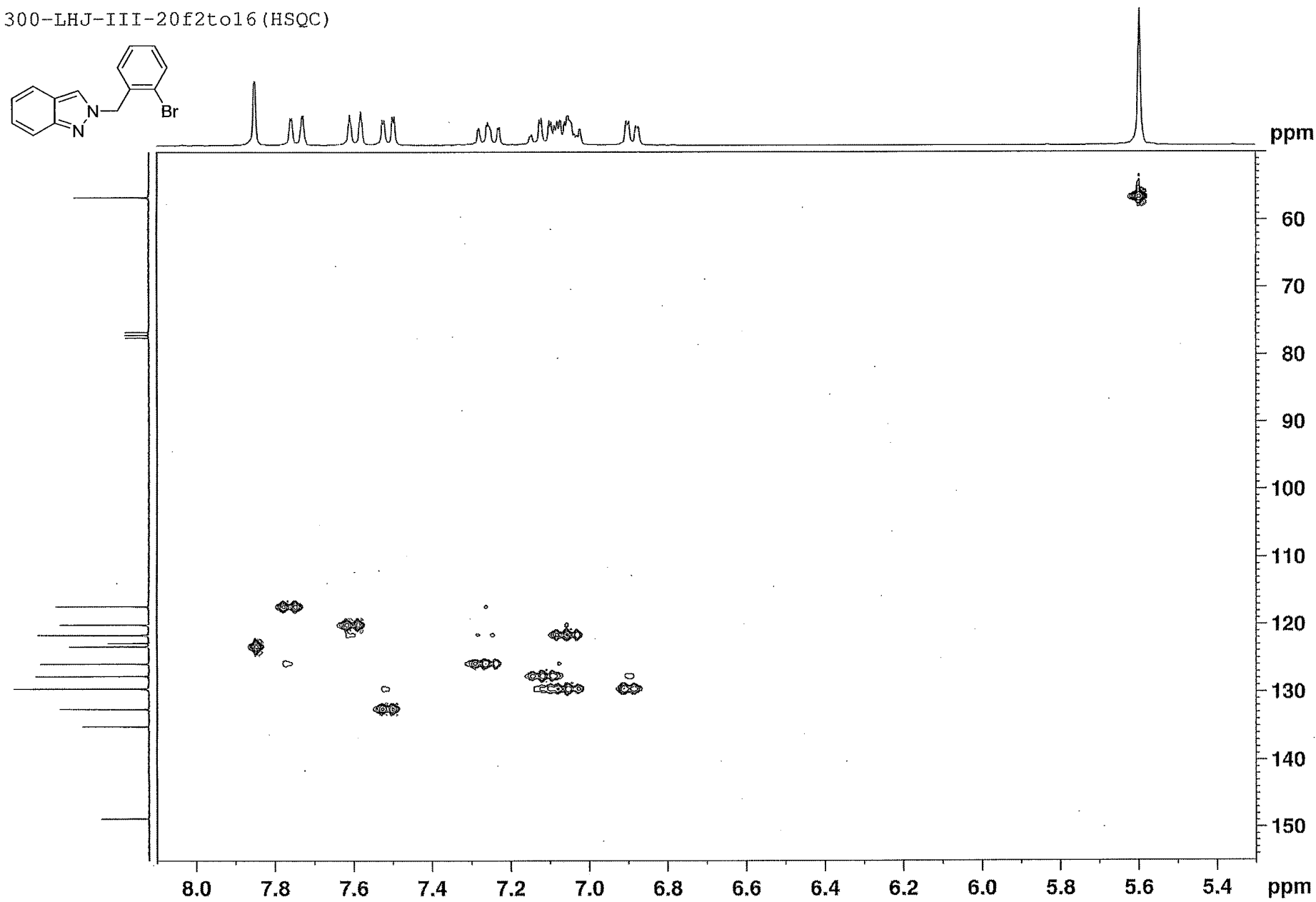


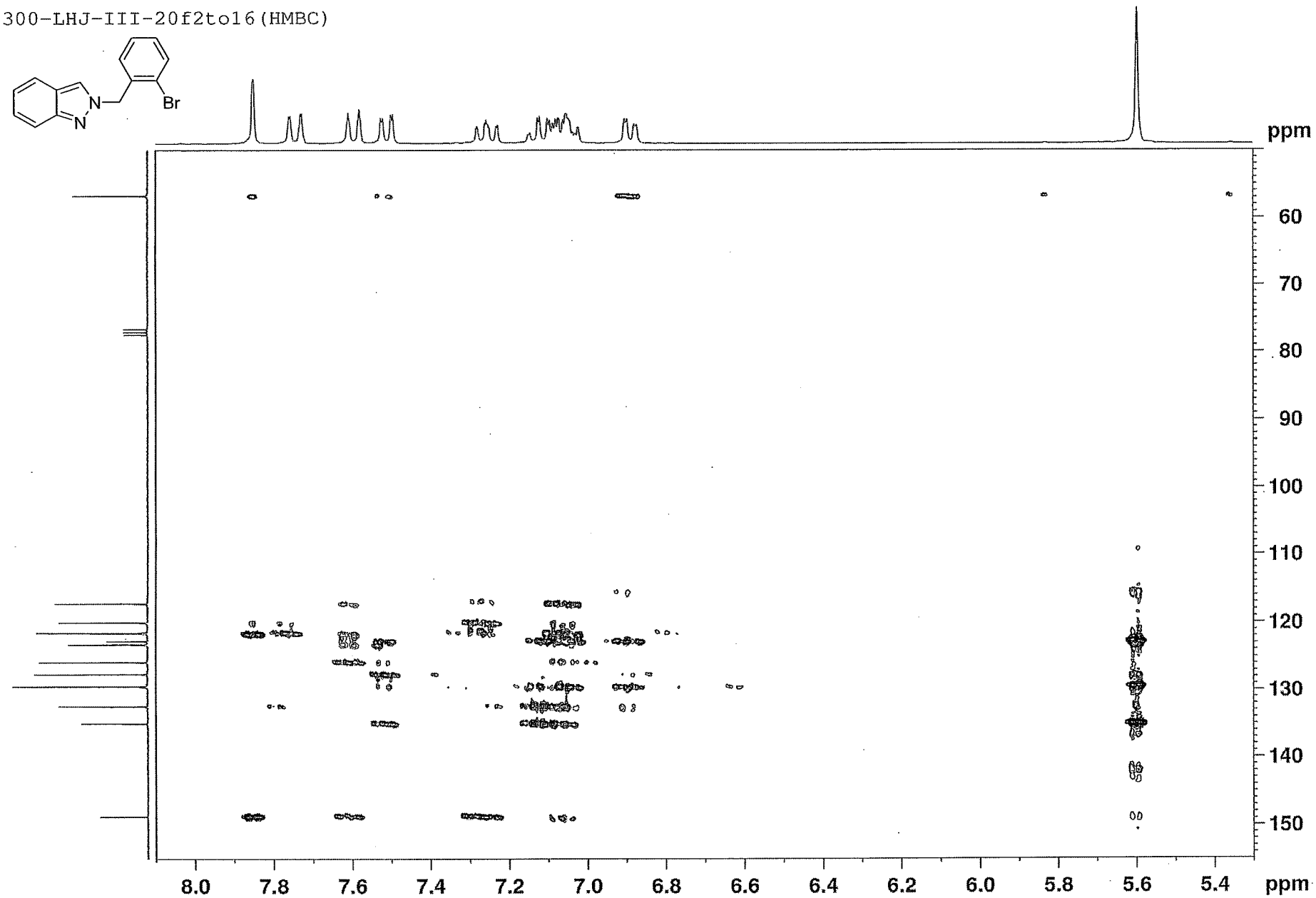
2i, CDCl3, 75 MHz

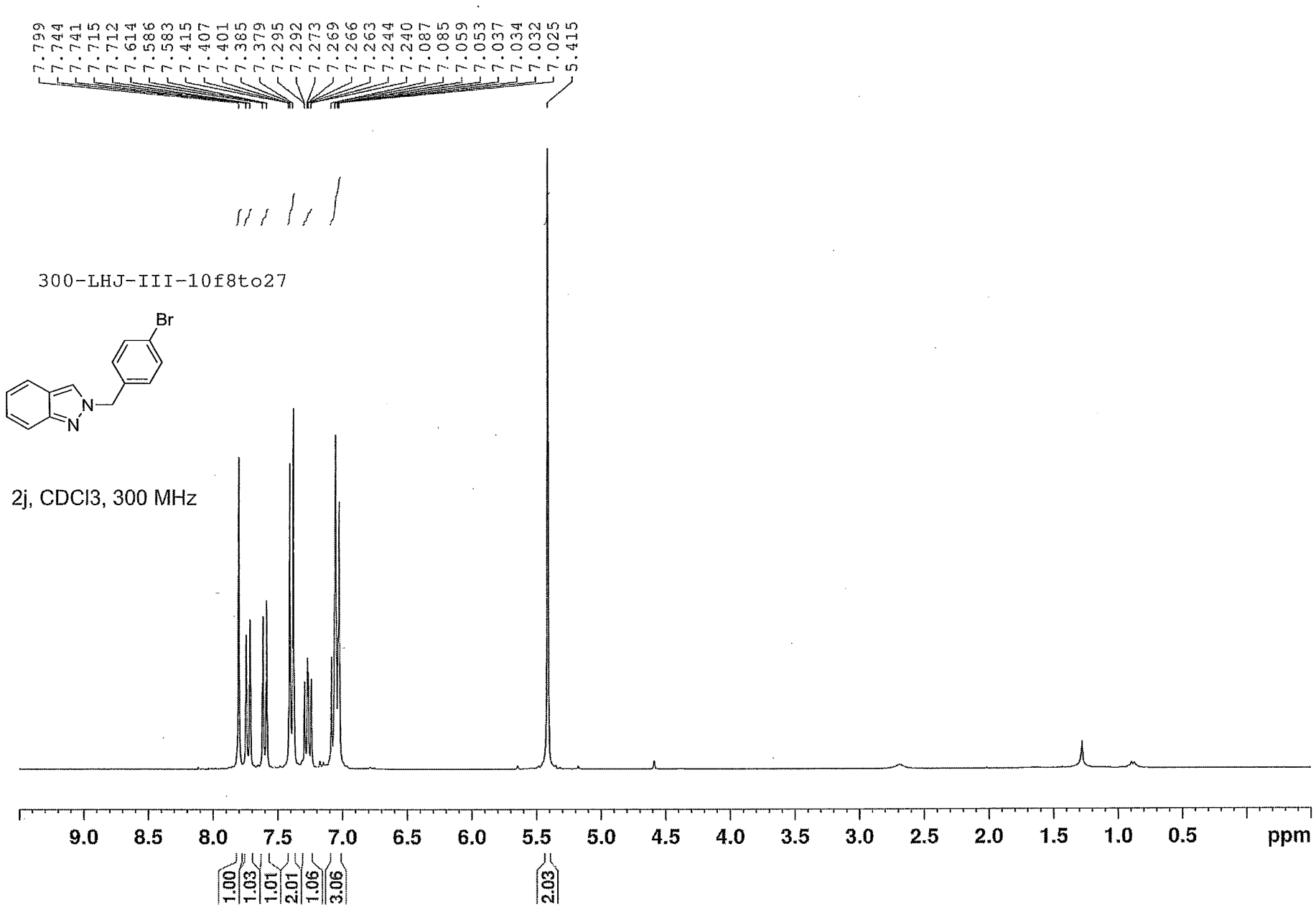
300-LHJ-III-20f2to16

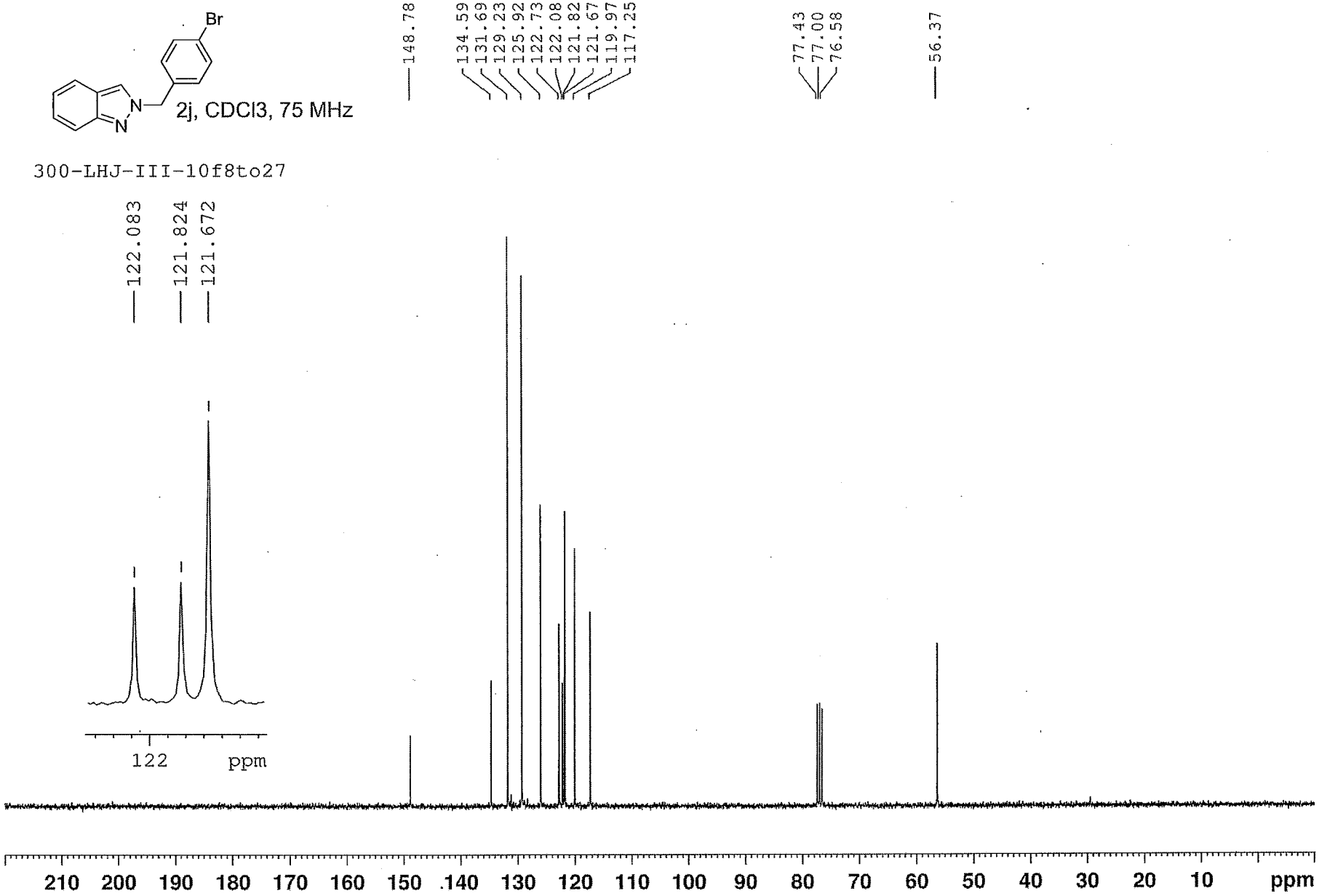
148.66
134.95
132.47
129.47
127.60
125.79
123.24
122.72
121.60
121.49
119.96
117.16
77.43
77.00
76.57
56.66
123.245
122.722
121.596
121.489

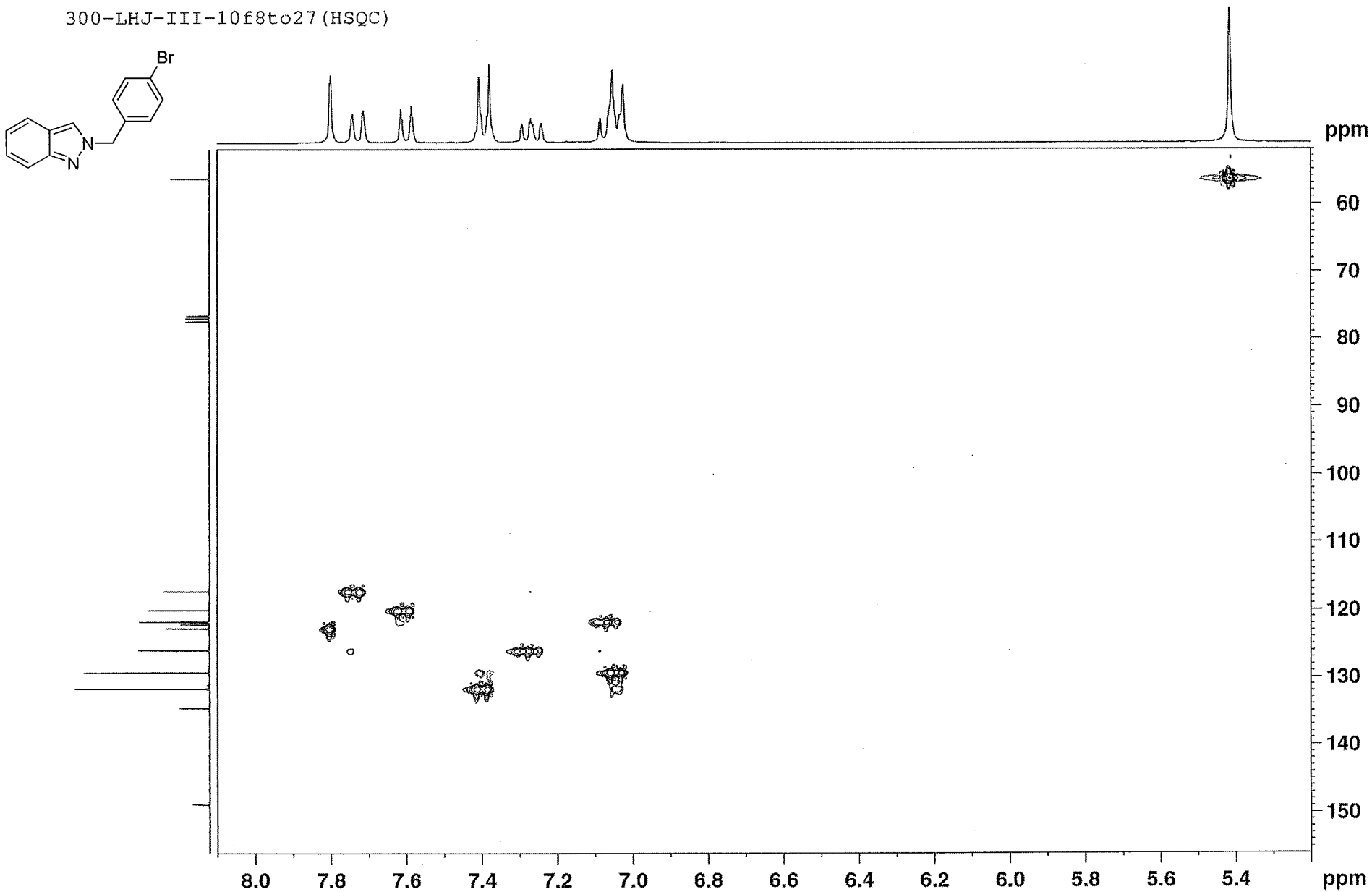


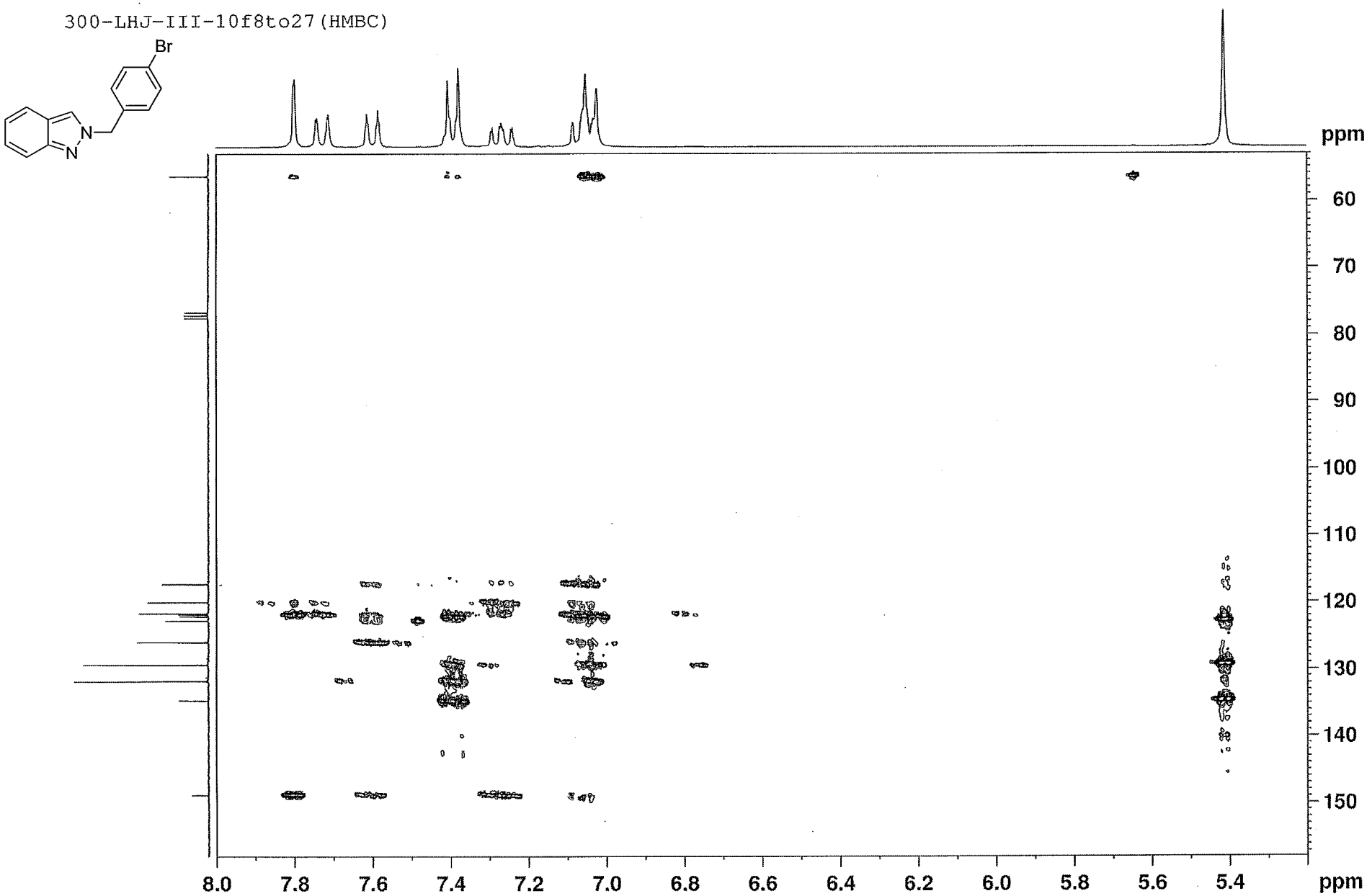

300-LHJ-III-20f2to16(HSQC)
N
N
Br
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm

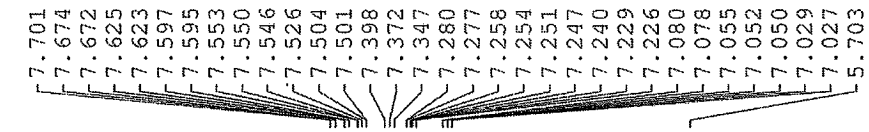

300-LHJ-III-20f2to16(HMBC)
N
N
Br
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm


7.799
7.744
7.741
7.715
7.712
7.614
7.586
7.583
7.415
7.407
7.401
7.385
7.379
7.295
7.292
7.273
7.269
7.266
7.263
7.244
7.240
7.087
7.085
7.059
7.053
7.037
7.034
7.032
7.025
5.415
300-LHJ-III-10f8to27
Br
N
N
2j, CDCl3, 300 MHz
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
1.0
0.5
ppm
1.00
1.03
1.01
2.01
1.06
3.06
2.03


Br
N
N
2j, CDCl3, 75 MHz
300-LHJ-III-10f8to27
148.78
134.59
131.69
129.23
125.92
122.73
122.08
121.82
121.67
119.97
117.25
77.43
77.00
76.58
56.37
122.083
121.824
121.672
122
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

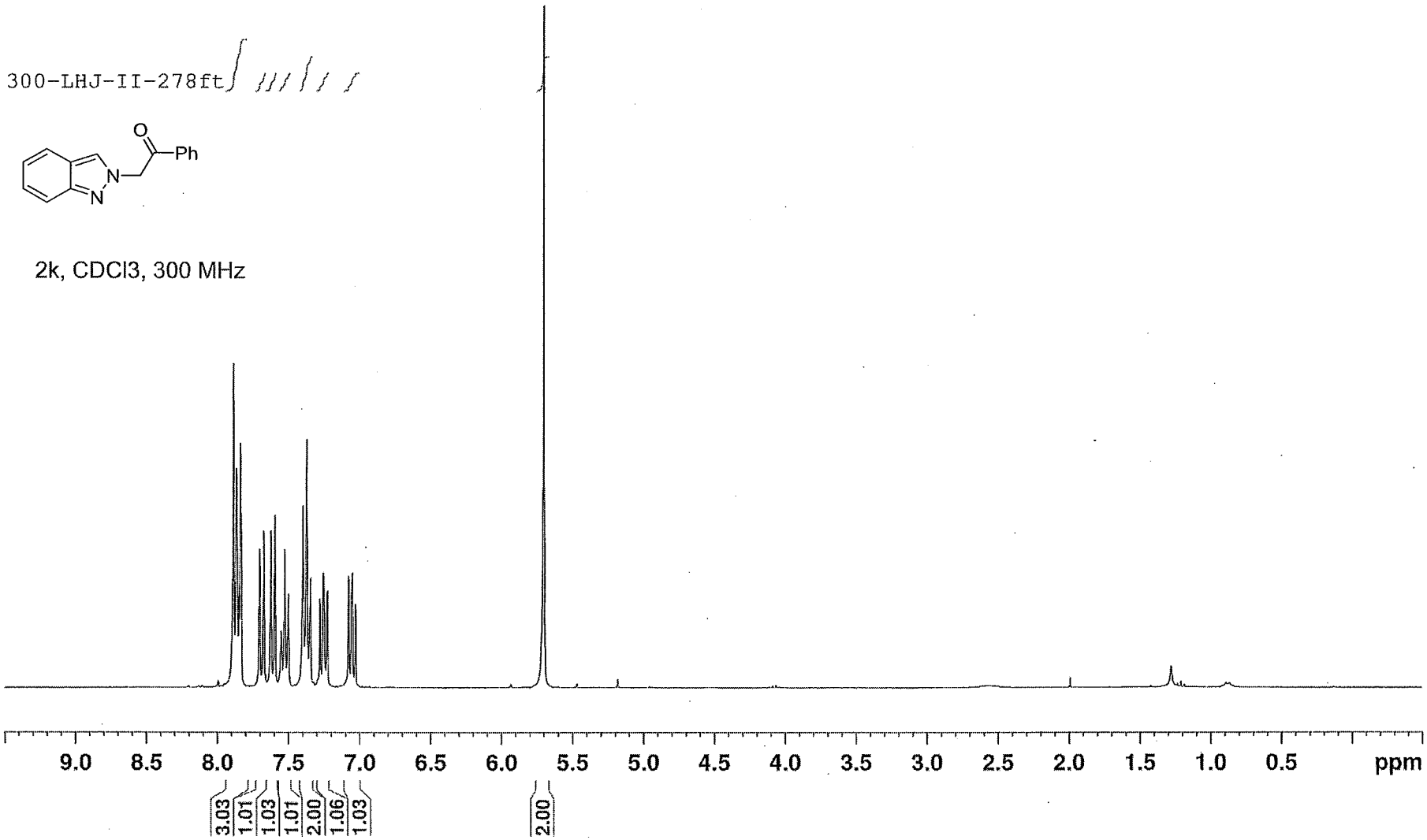

300-LHJ-III-10f8to27(HSQC)
Br
N
N
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm

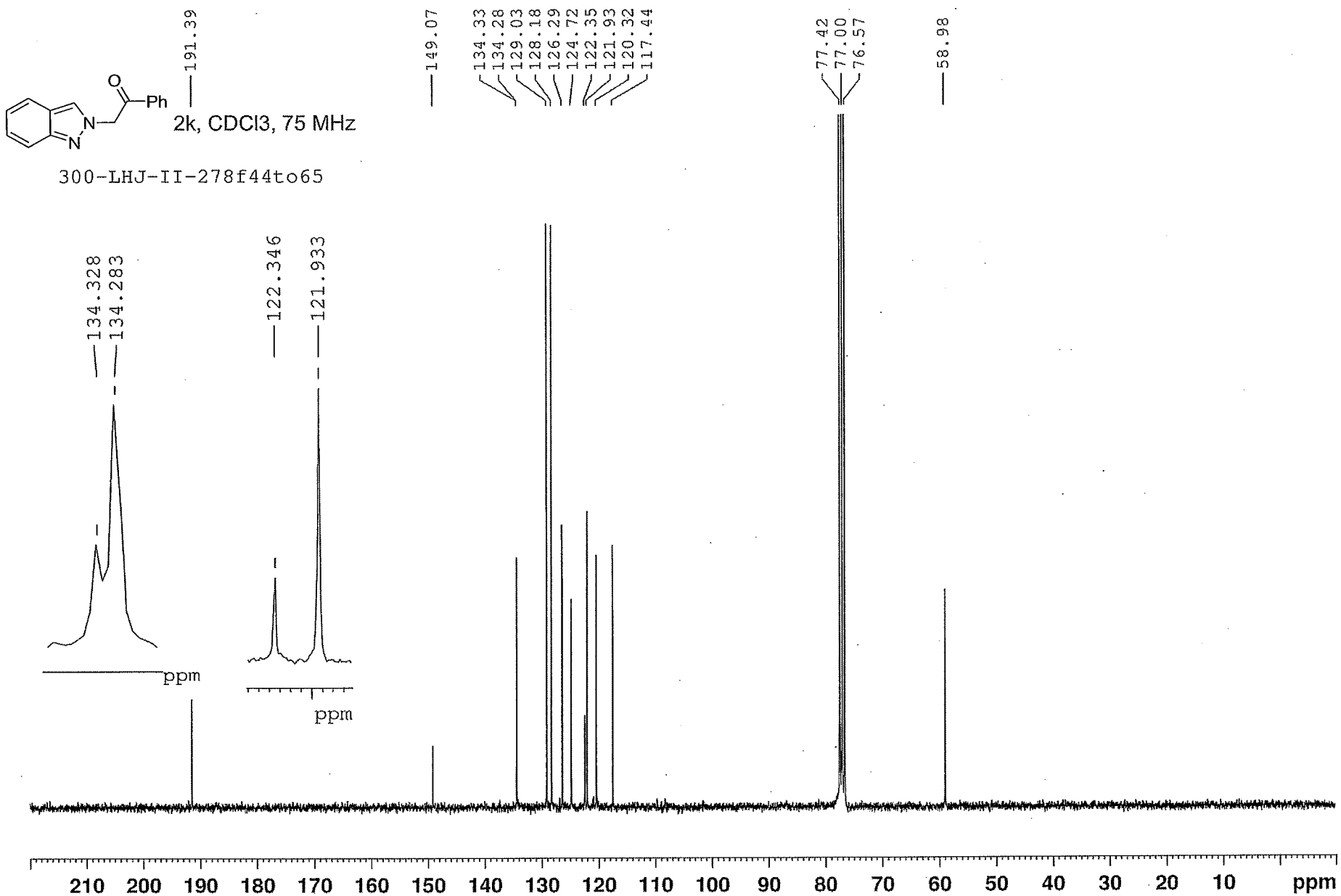

300-LHJ-III-10f8to27(HMBC)
Br
N
N
ppm
60
70
80
90
100
110
120
130
140
150
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm

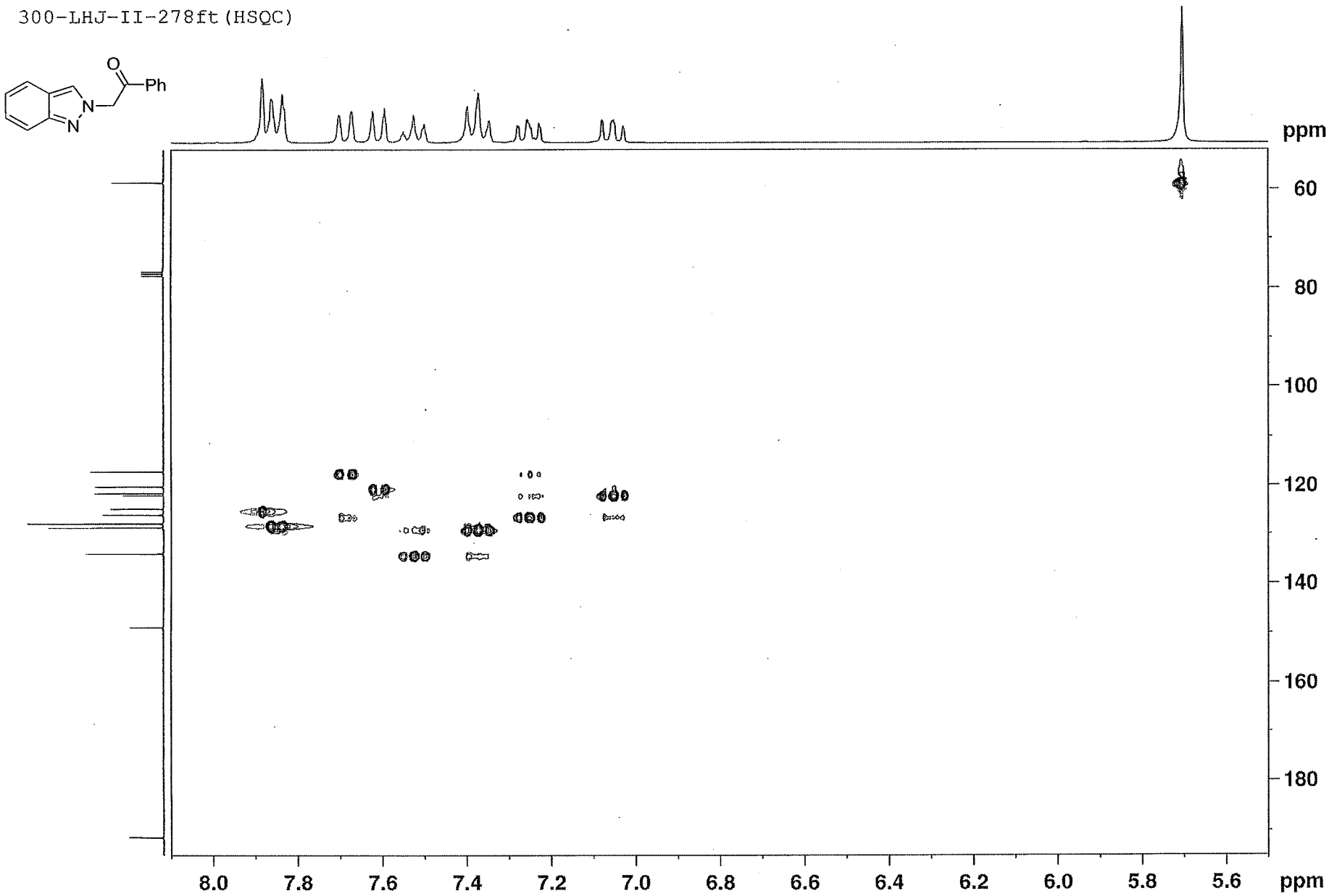


300-LHJ-II-278ft

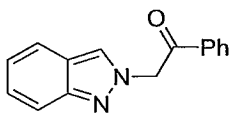
2k, CDCl3, 300 MHz

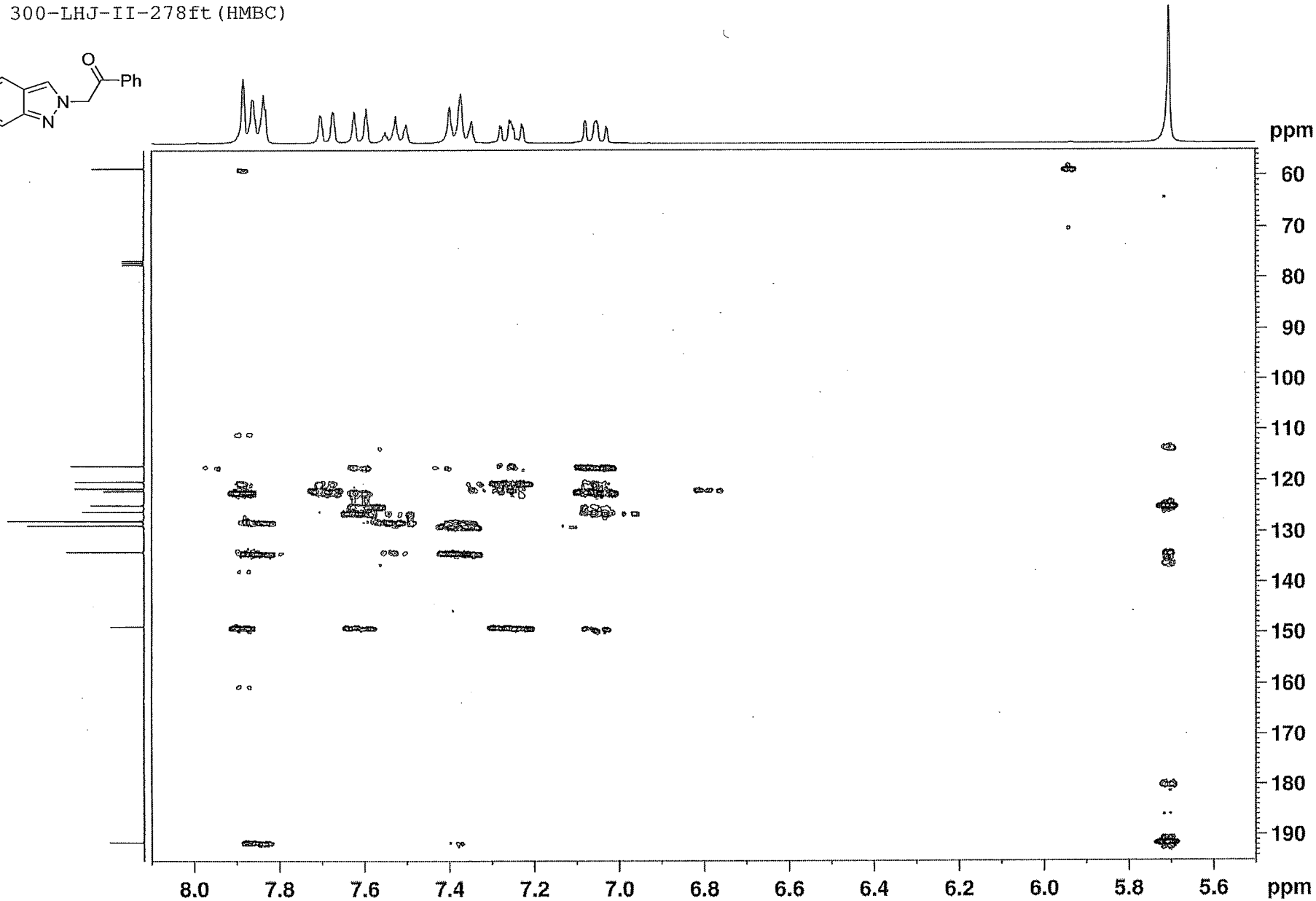


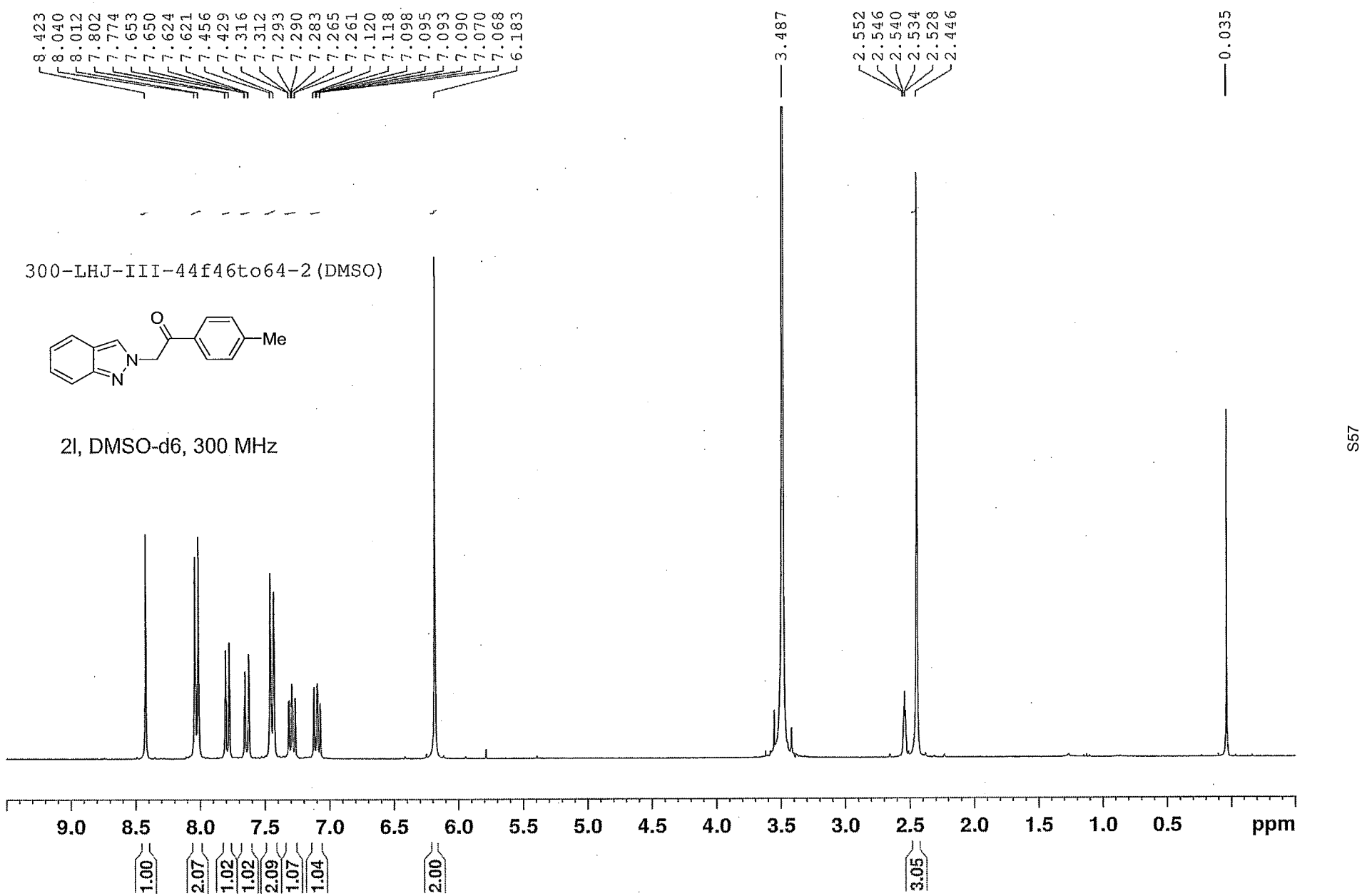

191.39
149.07
134.33
134.28
129.03
128.18
126.29
124.72
122.35
121.93
120.32
117.44
77.42
77.00
76.57
58.98
O
Ph
N
N
2k, CDCl3, 75 MHz
300-LHJ-II-278f44to65
134.328
134.283
122.346
121.933
ppm
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

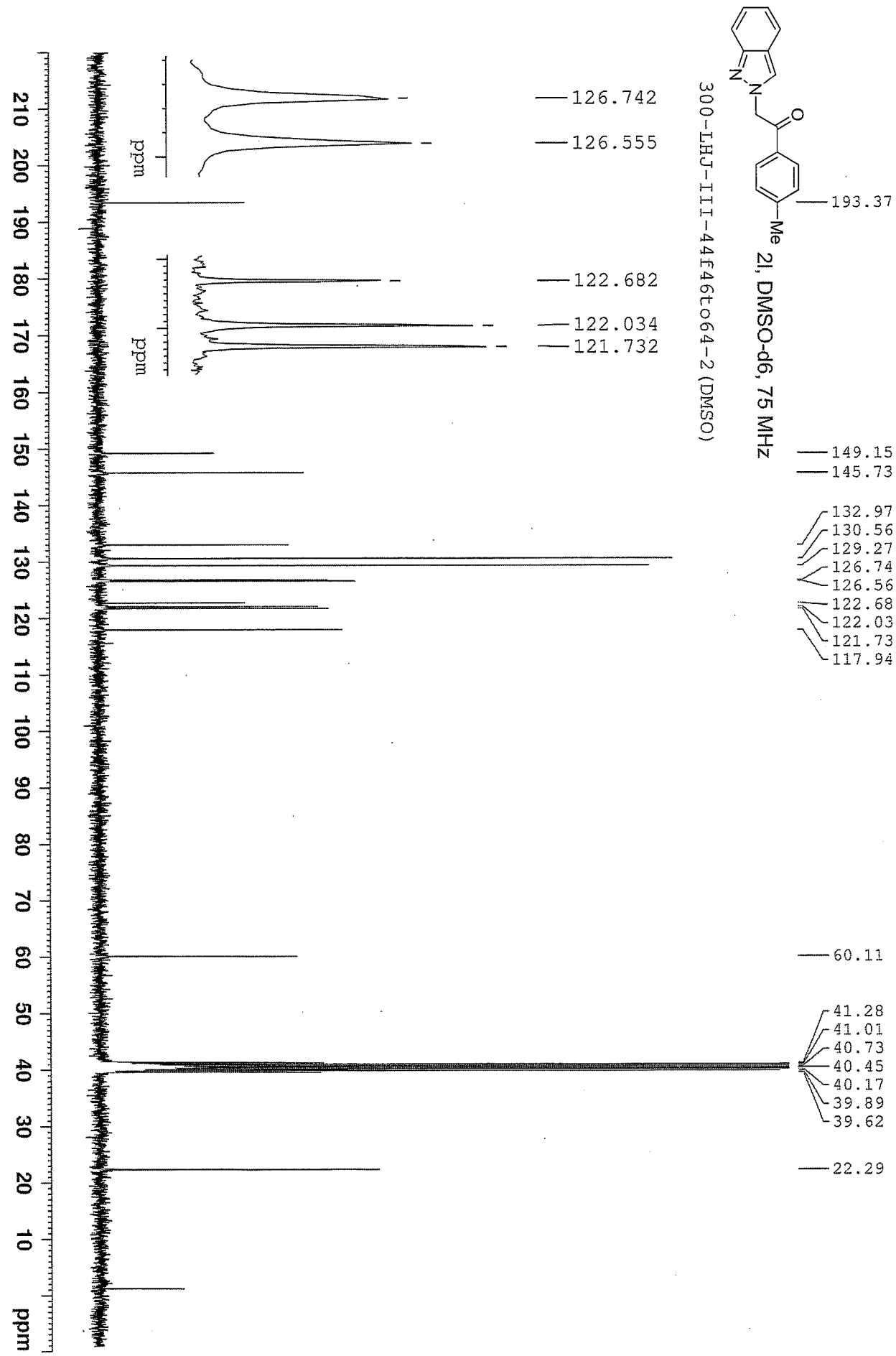

300-LHJ-II-278ft(HSQC)
O
Ph
N
N
ppm
60
80
100
120
140
160
180
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
ppm

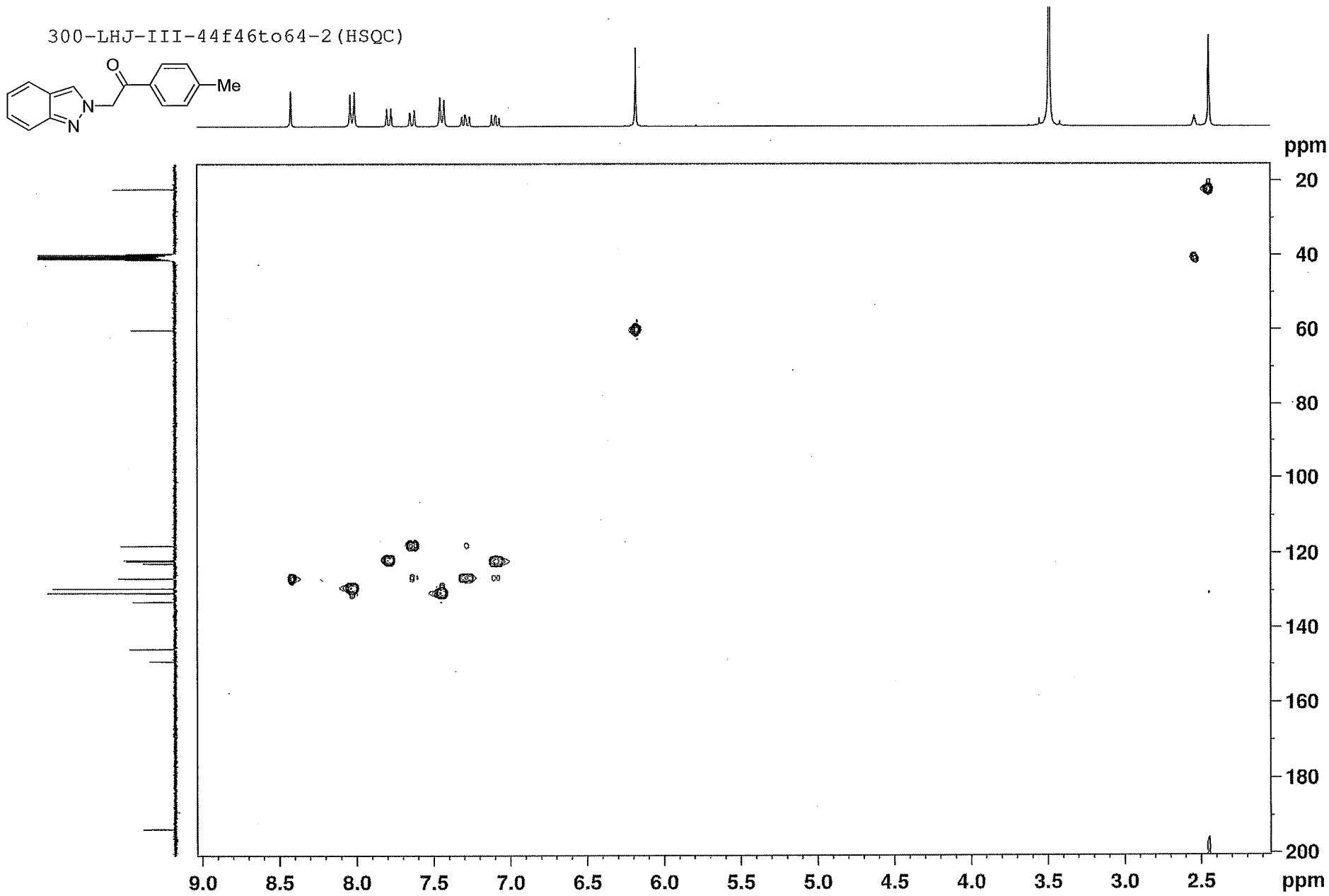
300-LHJ-II-278ft(HMBC)

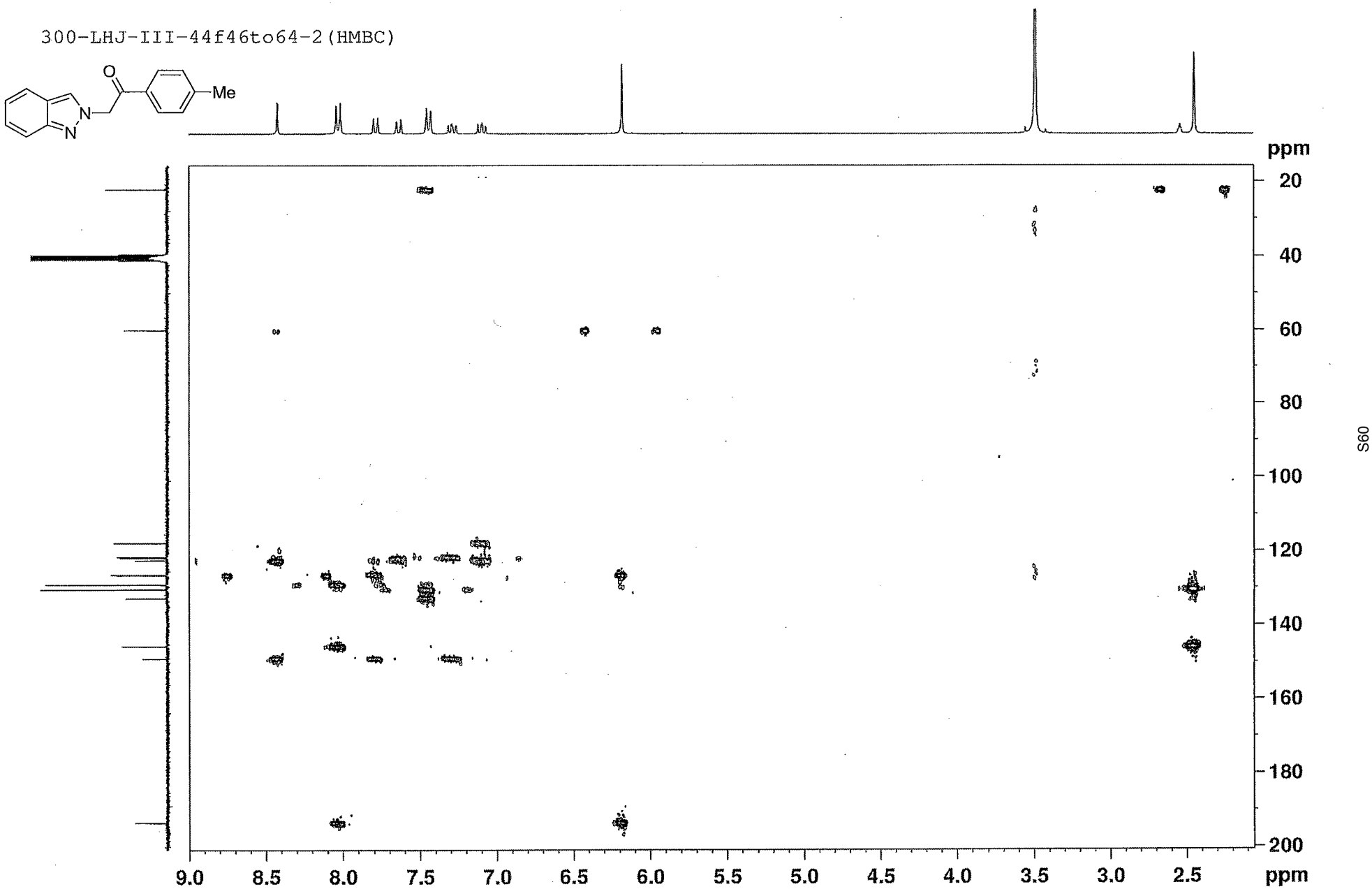


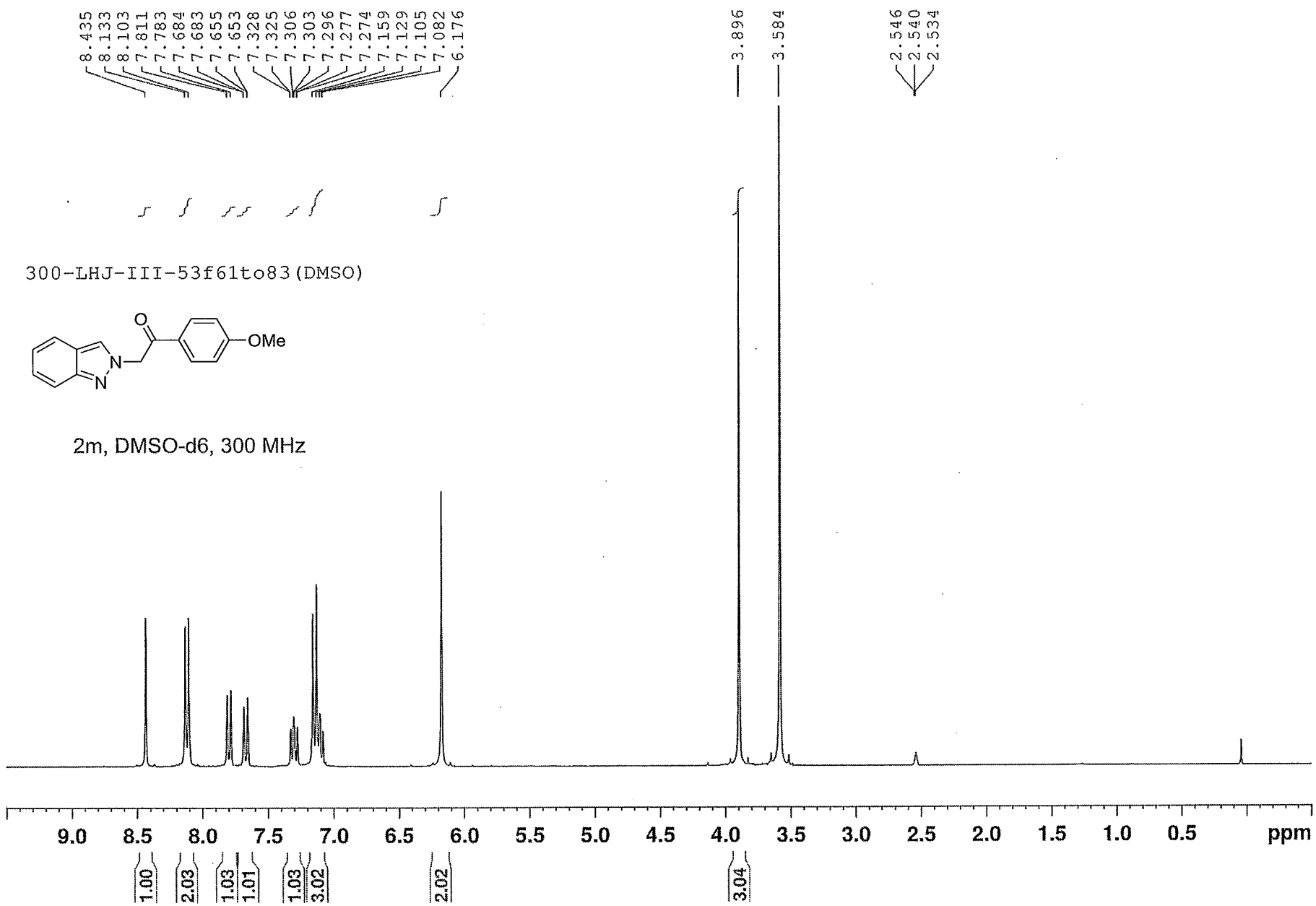


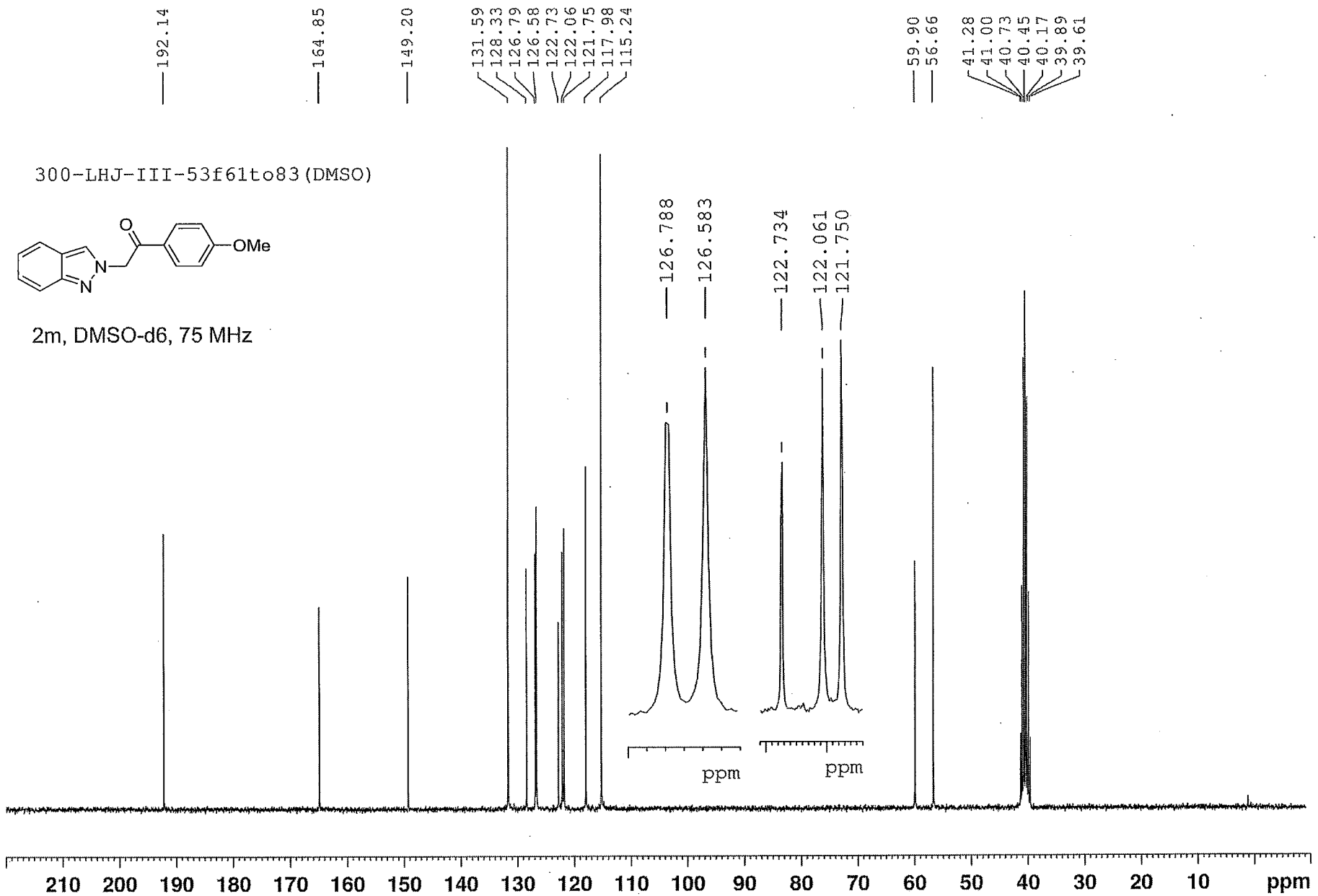

8.423
8.040
8.012
7.802
7.774
7.653
7.650
7.624
7.621
7.456
7.429
7.316
7.312
7.293
7.290
7.283
7.265
7.261
7.120
7.118
7.098
7.095
7.093
7.090
7.070
7.068
6.183
3.487
2.552
2.546
2.540
2.534
2.528
2.446
0.035
300-LHJ-III-44f46to64-2(DMSO)
O
Me
N
N
2l, DMSO-d6, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.07
1.02
1.02
2.09
1.07
1.04
2.00
3.05


300-LHJ-III-44f46to64-2 (DMSO)
2l, DMSO-d6, 75 MHz
Me
193.37
149.15
145.73
132.97
130.56
129.27
126.74
126.56
122.68
122.03
121.73
117.94
126.742
126.555
122.682
122.034
121.732
60.11
41.28
41.01
40.73
40.45
40.17
39.89
39.62
22.29
ppm
ppm
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

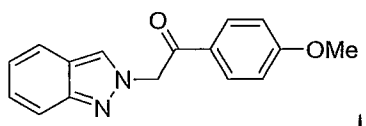

300-LHJ-III-44f46to64-2(HSQC)
O
N
N
Me
ppm
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

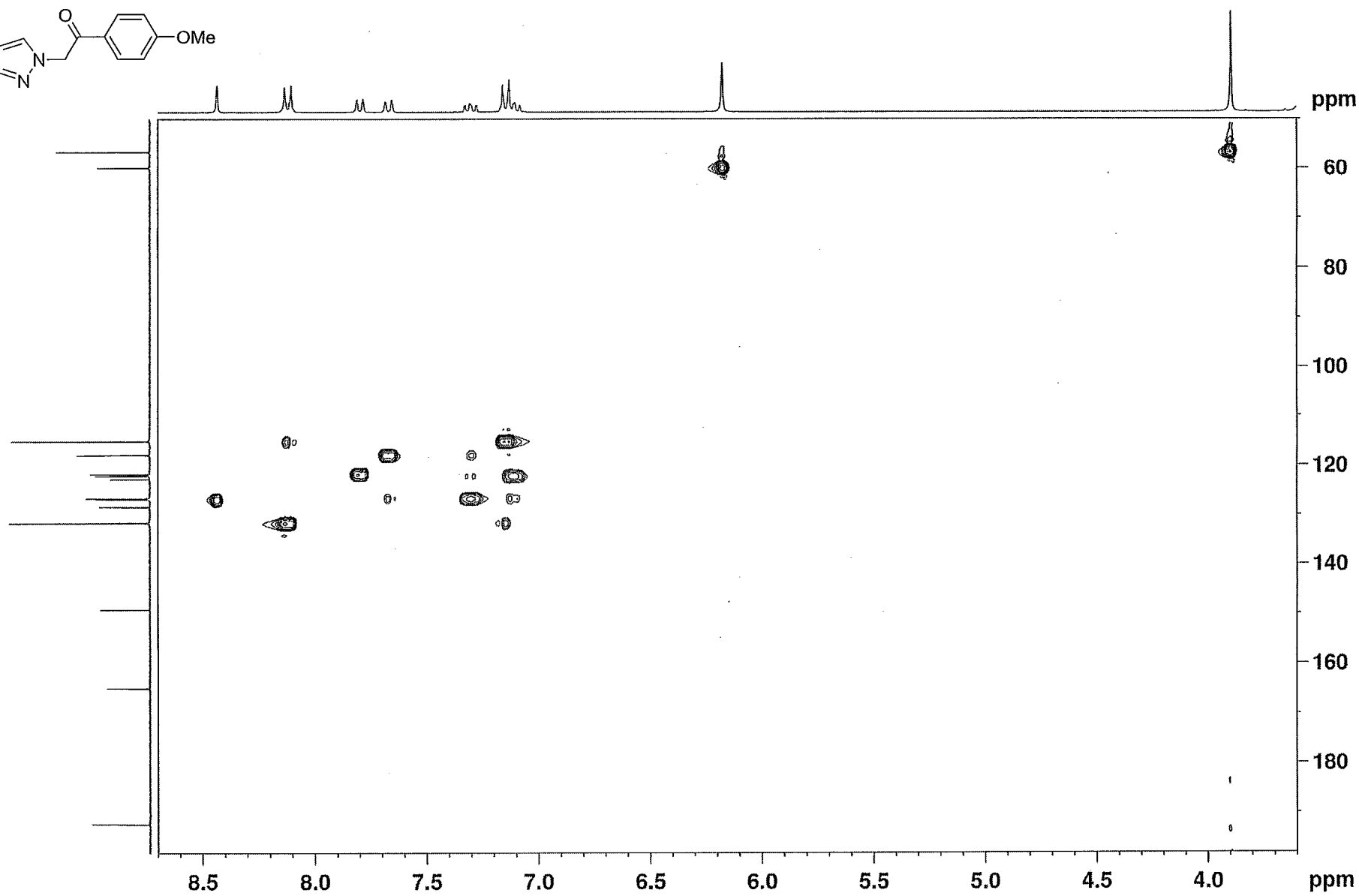

300-LHJ-III-44f46to64-2(HMBC)
O
Me
N
N
ppm
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm


8.435
8.133
8.103
7.811
7.783
7.684
7.683
7.655
7.653
7.328
7.325
7.306
7.303
7.296
7.277
7.274
7.159
7.129
7.105
7.082
6.176
3.896
3.584
2.546
2.540
2.534
300-LHJ-III-53f61to83(DMSO)
O
OMe
N
N
2m, DMSO-d6, 300 MHz
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
1.0
0.5
ppm
1.00
2.03
1.03
1.01
1.03
3.02
2.02
3.04

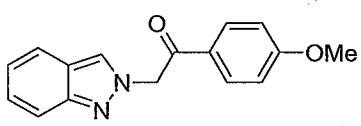

192.14
164.85
149.20
131.59
128.33
126.79
126.58
122.73
122.06
121.75
117.98
115.24
59.90
56.66
41.28
41.00
40.73
40.45
40.17
39.89
39.61
300-LHJ-III-53f61to83(DMSO)
O
OMe
N
N
2m, DMSO-d6, 75 MHz
126.788
126.583
122.734
122.061
121.750
ppm
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

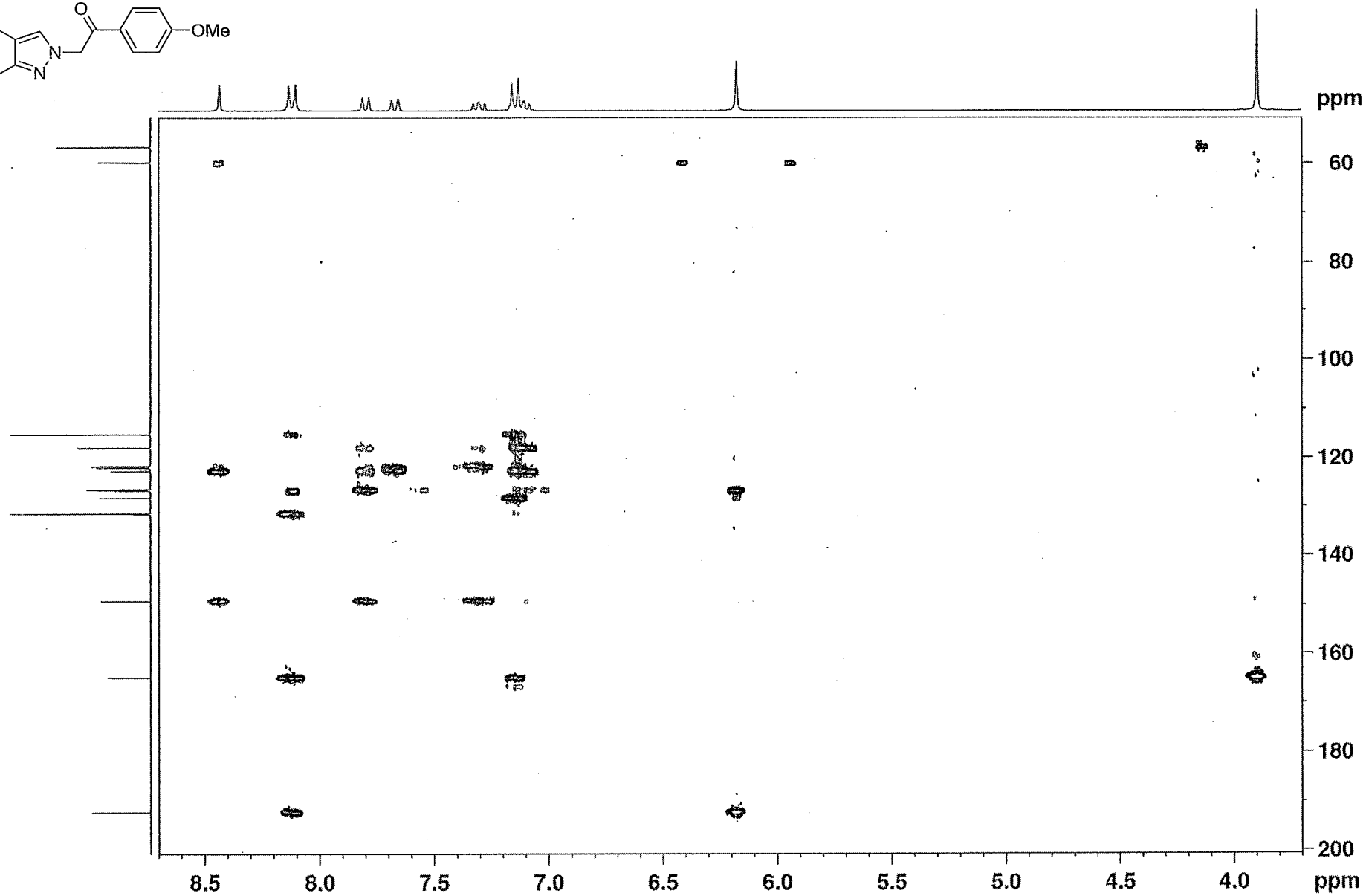
300-LHJ-III-53f61to83(HSQC)

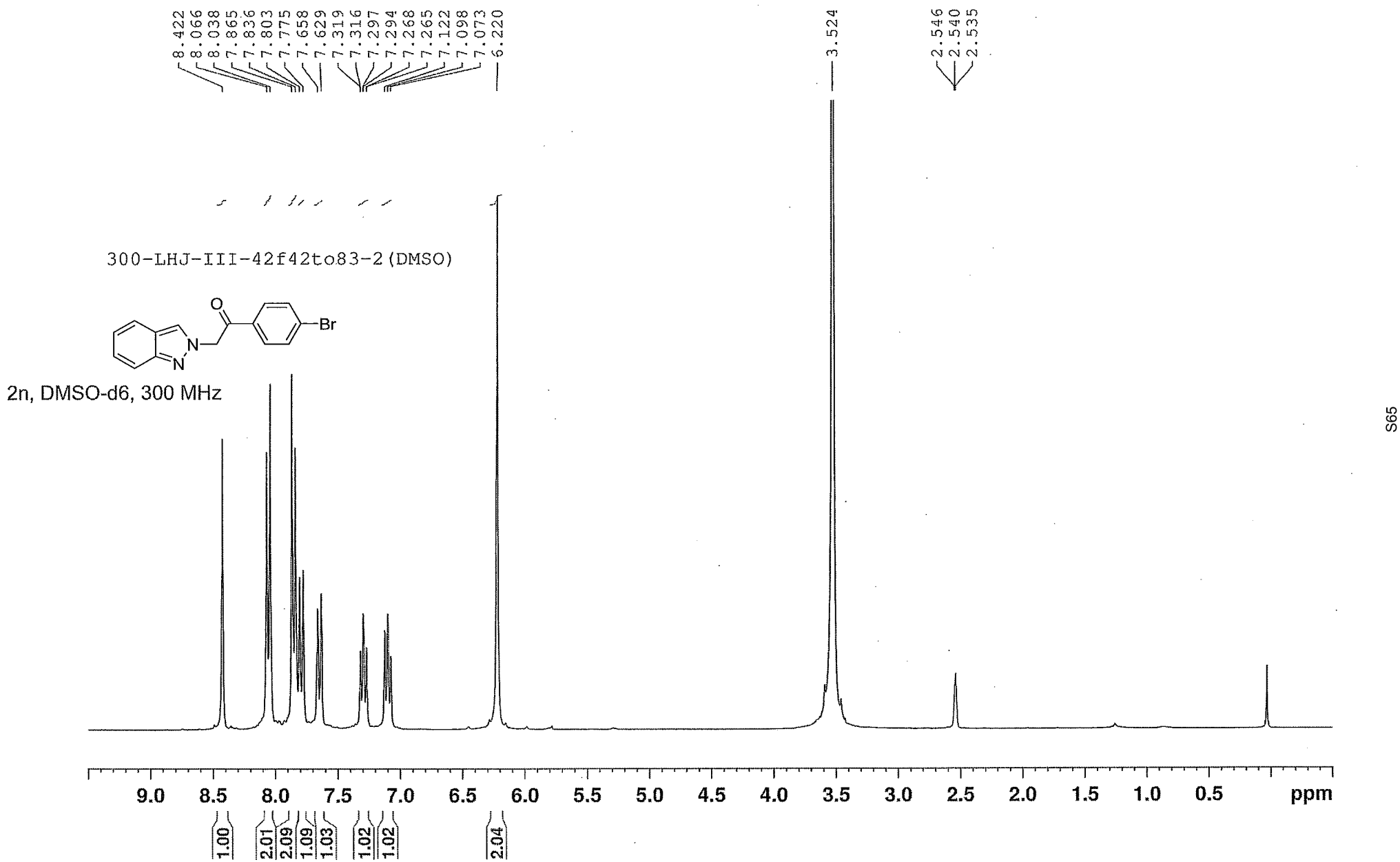


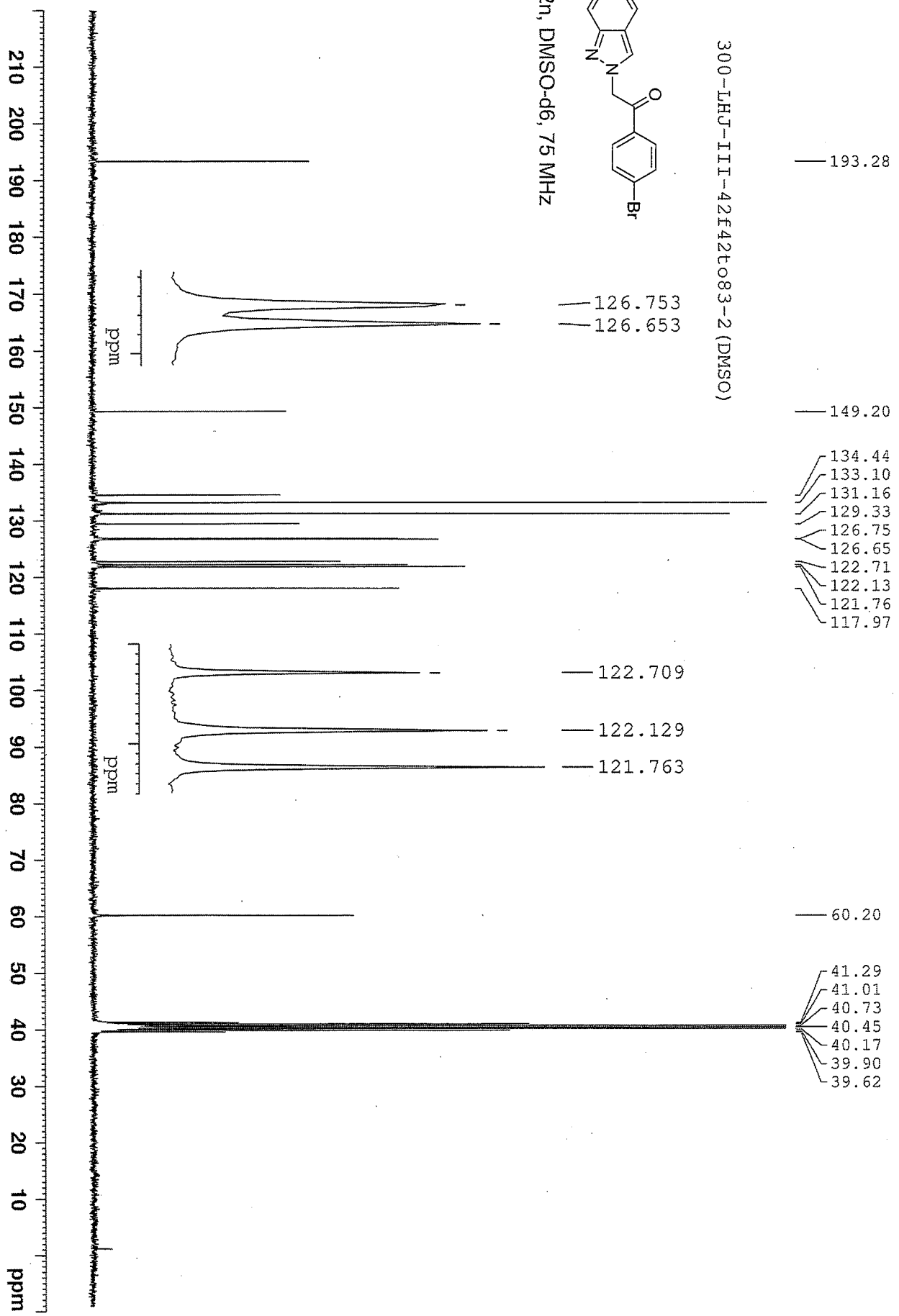


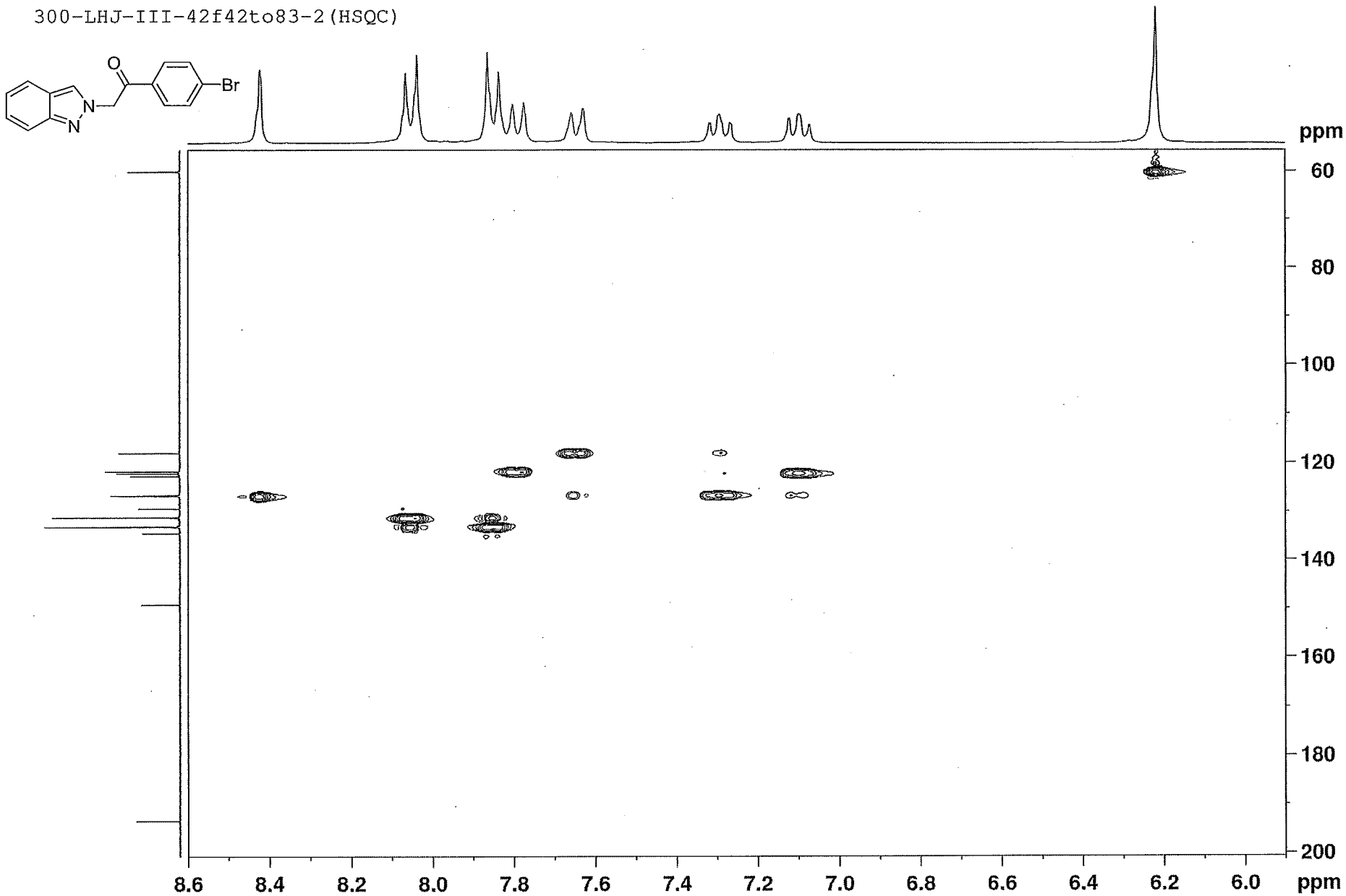
300-LHJ-III-53f61to83(HMBC)

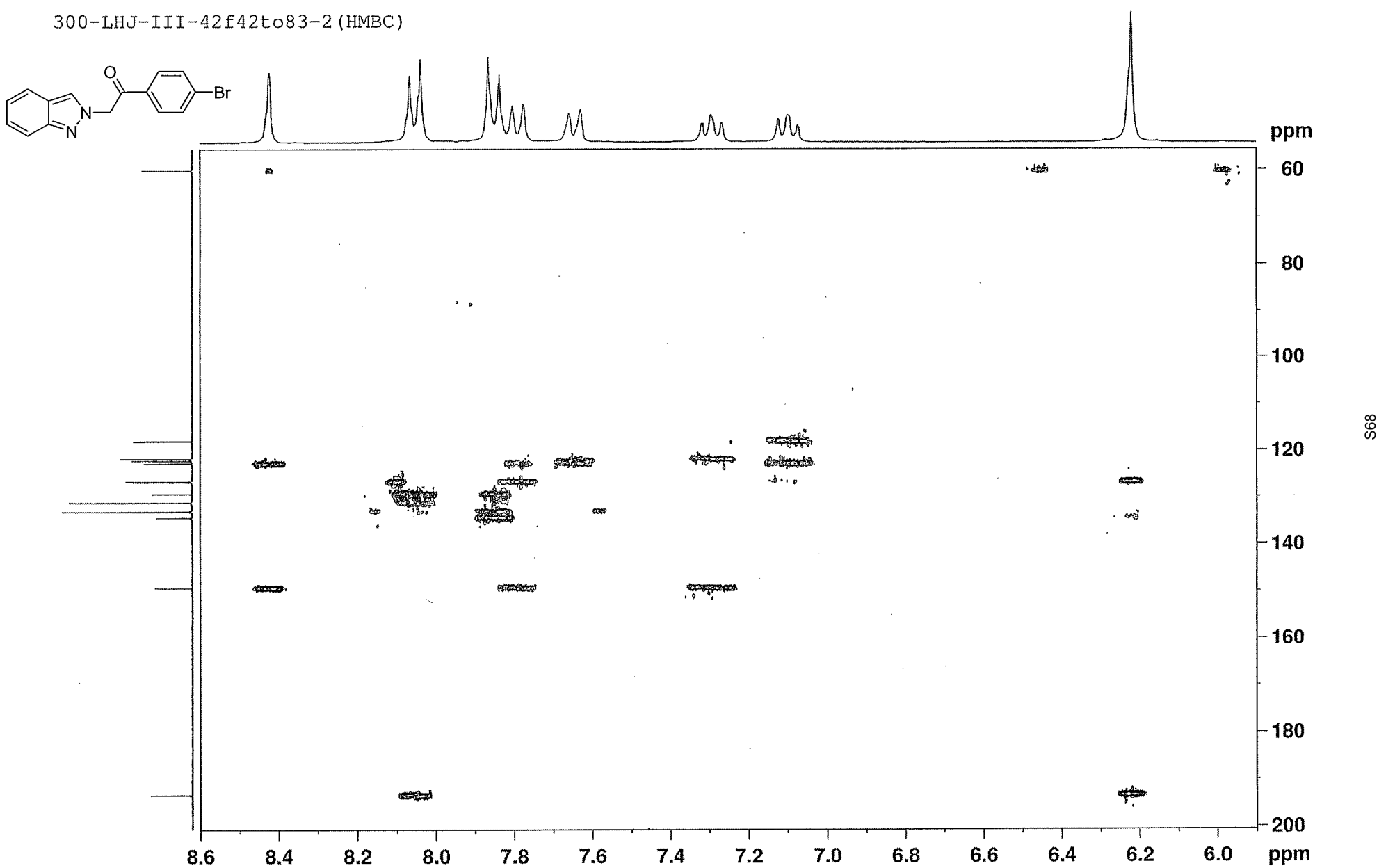


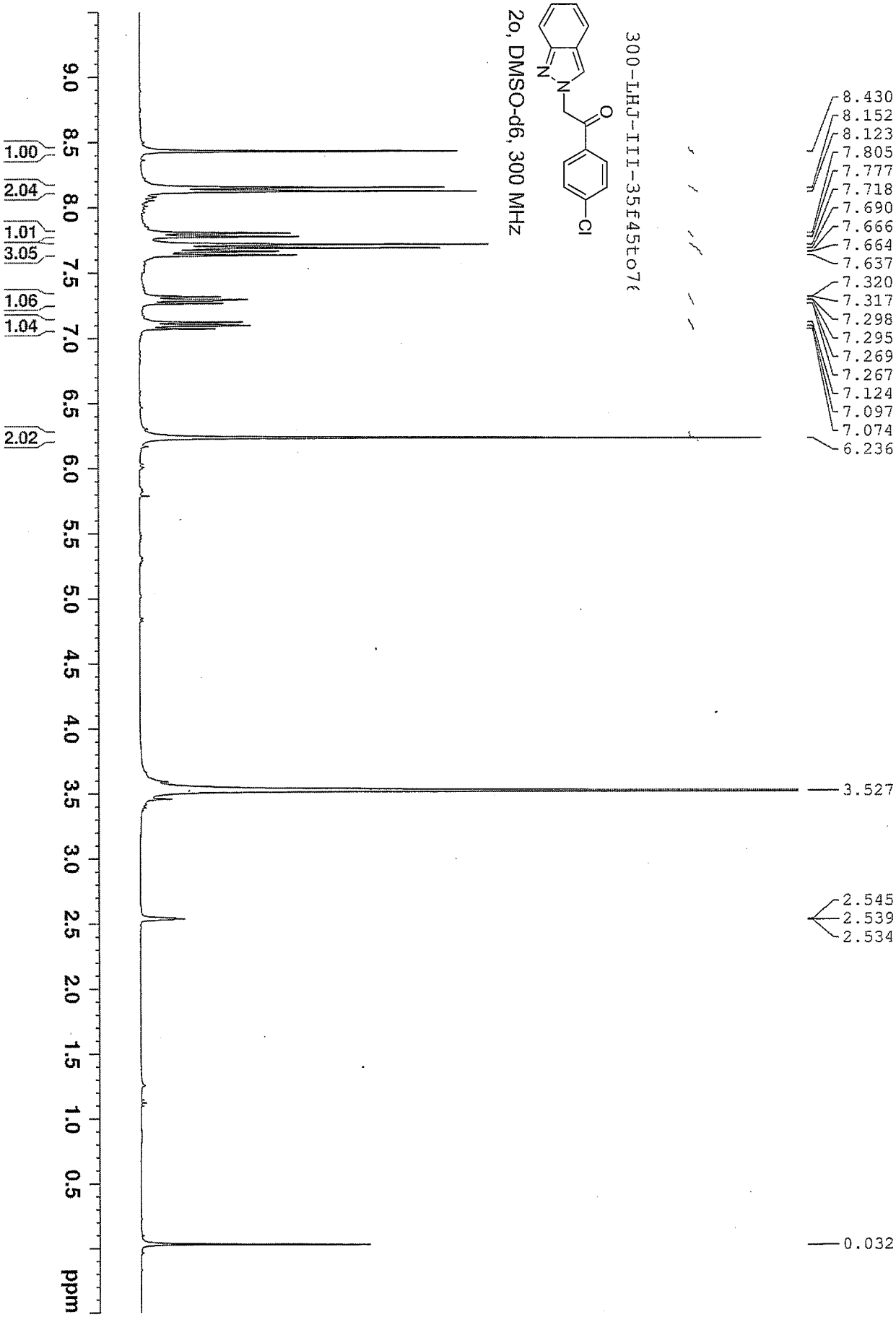


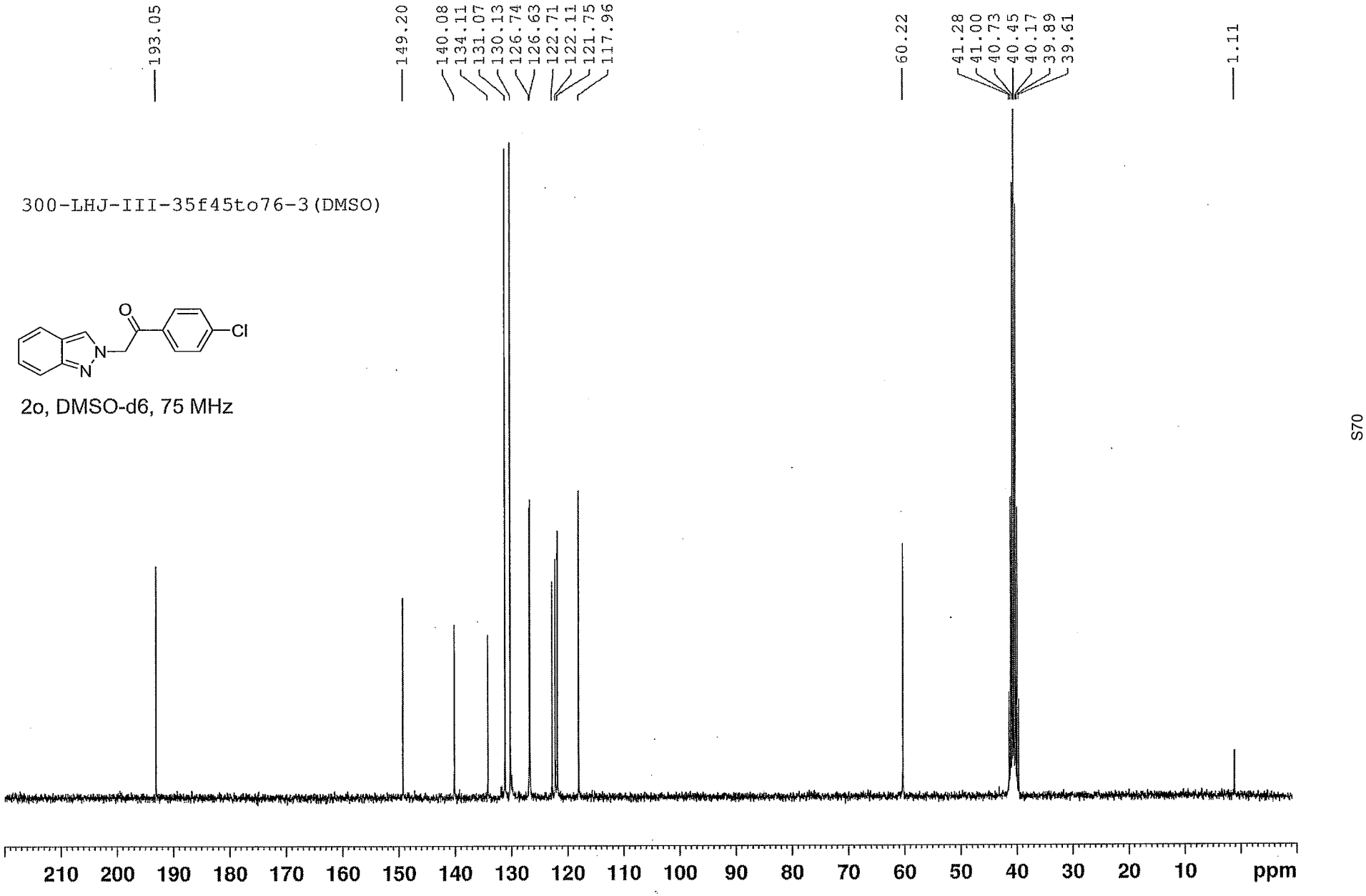

8.422
8.066
8.038
7.865
7.836
7.803
7.775
7.658
7.629
7.319
7.316
7.297
7.294
7.268
7.265
7.122
7.098
7.073
6.220
3.524
2.546
2.540
2.535
300-LHJ-III-42f42to83-2(DMSO)
O
Br
N
N
2n, DMSO-d6, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.01
2.09
1.09
1.03
1.02
1.02
2.04

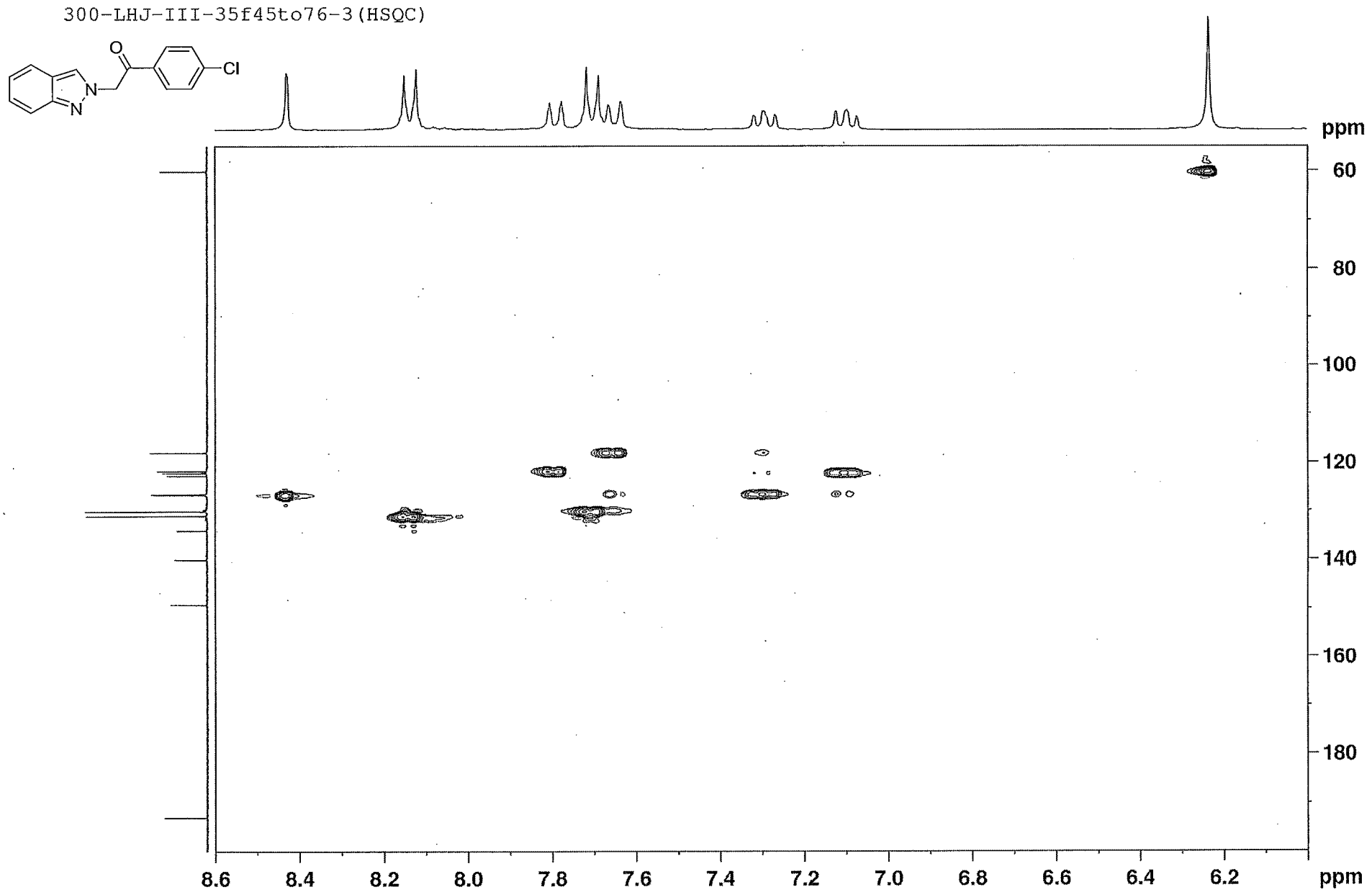

300-LHJ-III-42f42to83-2 (DMSO)
2n, DMSO-d6, 75 MHz
193.28
149.20
134.44
133.10
131.16
129.33
126.75
126.65
122.71
122.13
121.76
117.97
60.20
41.29
41.01
40.73
40.45
40.17
39.90
39.62
126.753
126.653
122.709
122.129
121.763
ppm


300-LHJ-III-42f42to83-2(HSQC)
O
Br
N
N
ppm
60
80
100
120
140
160
180
200
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
ppm

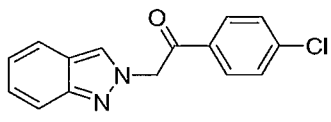

300-LHJ-III-42f42to83-2(HMBC)
O
Br
N
N
ppm
60
80
100
120
140
160
180
200
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
ppm

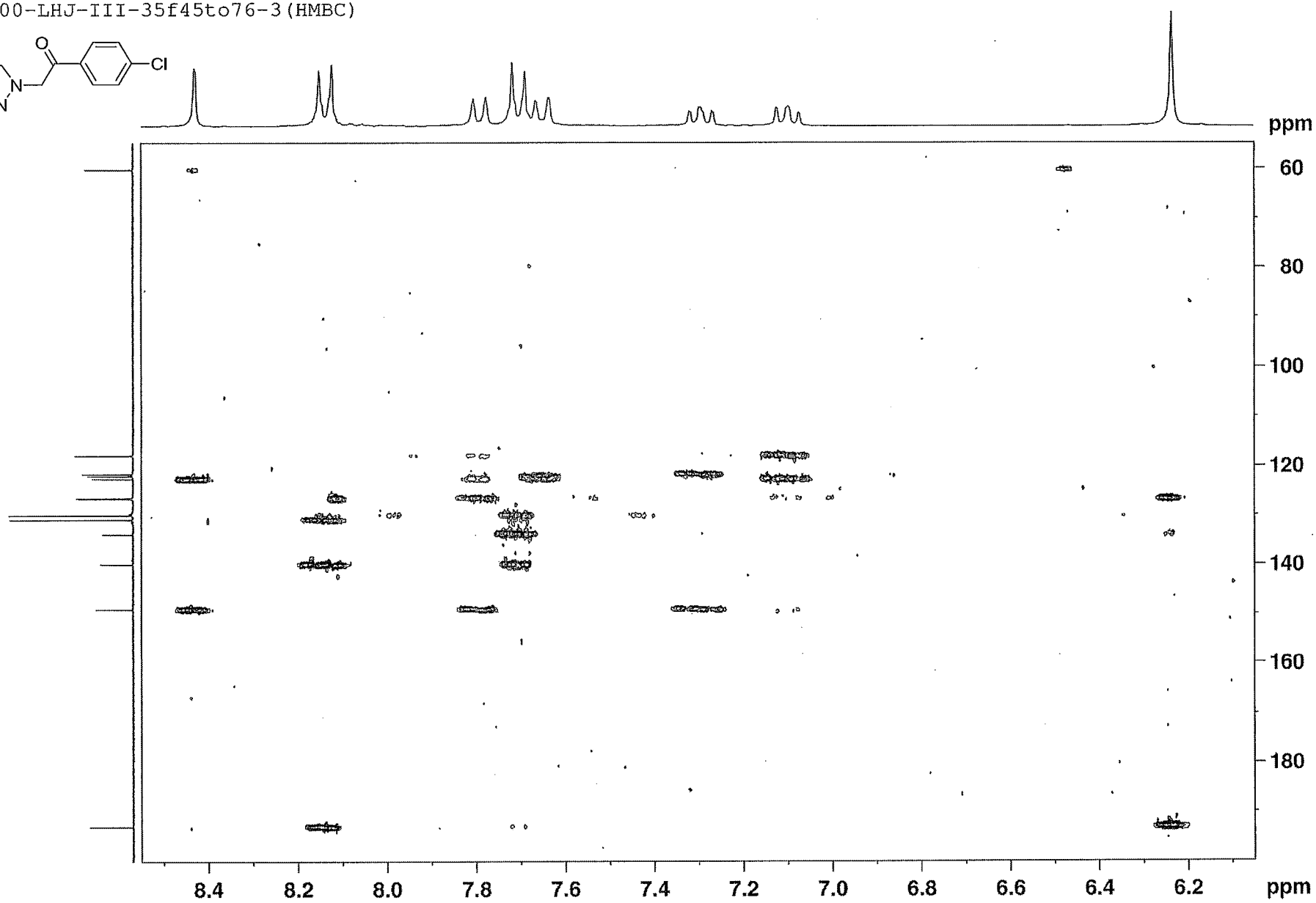

300-LHJ-III-35f45to7(
2o, DMSO-d6, 300 MHz
8.430
8.152
8.123
7.805
7.777
7.718
7.690
7.666
7.664
7.637
7.320
7.317
7.298
7.295
7.269
7.267
7.124
7.097
7.074
6.236
3.527
2.545
2.539
2.534
0.032
1.00
2.04
1.01
3.05
1.06
1.04
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

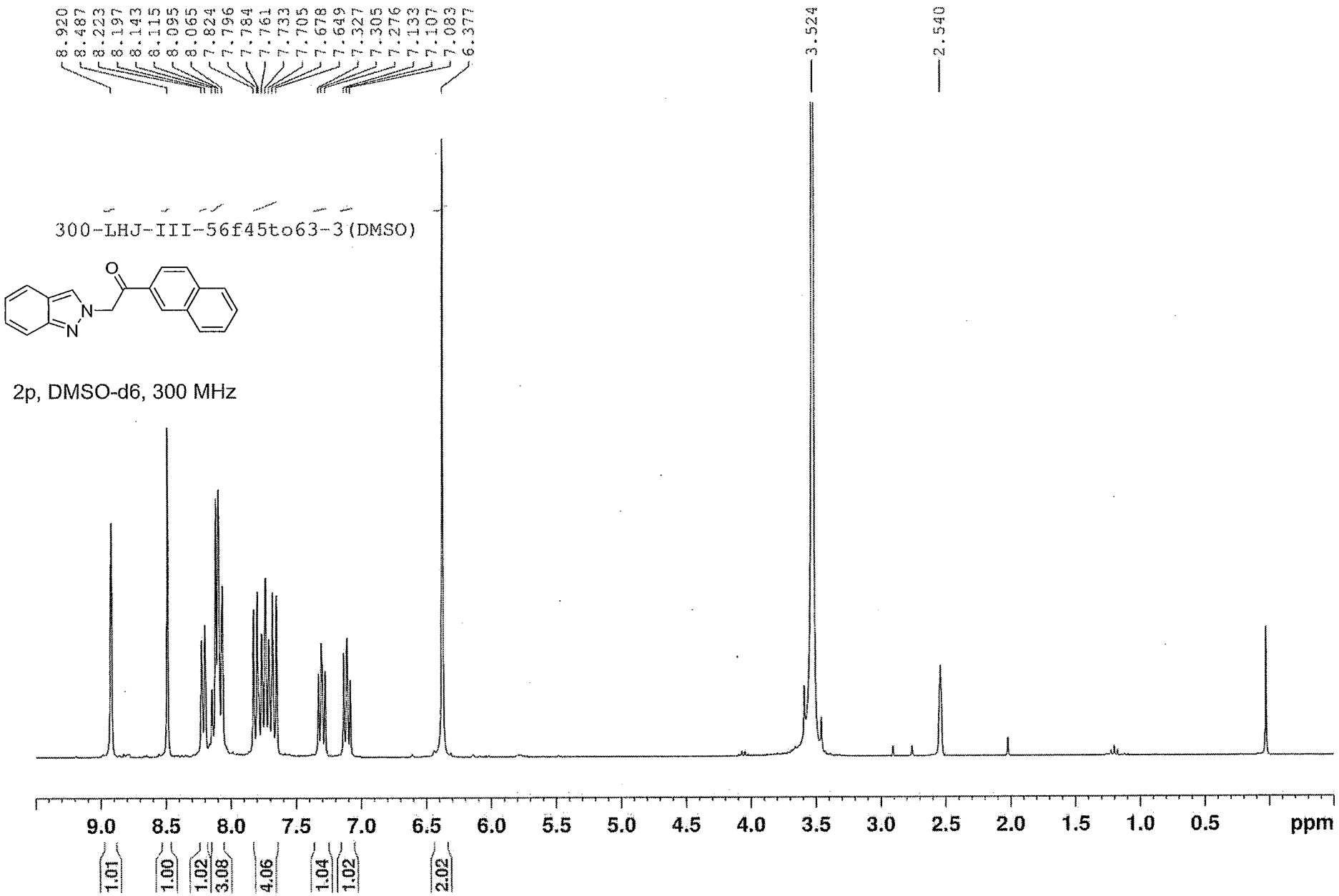

193.05
149.20
140.08
134.11
131.07
130.13
126.74
126.63
122.71
122.11
121.75
117.96
60.22
41.28
41.00
40.73
40.45
40.17
39.89
39.61
1.11
300-LHJ-III-35f45to76-3(DMSO)
O
Cl
N
N
2o, DMSO-d6, 75 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

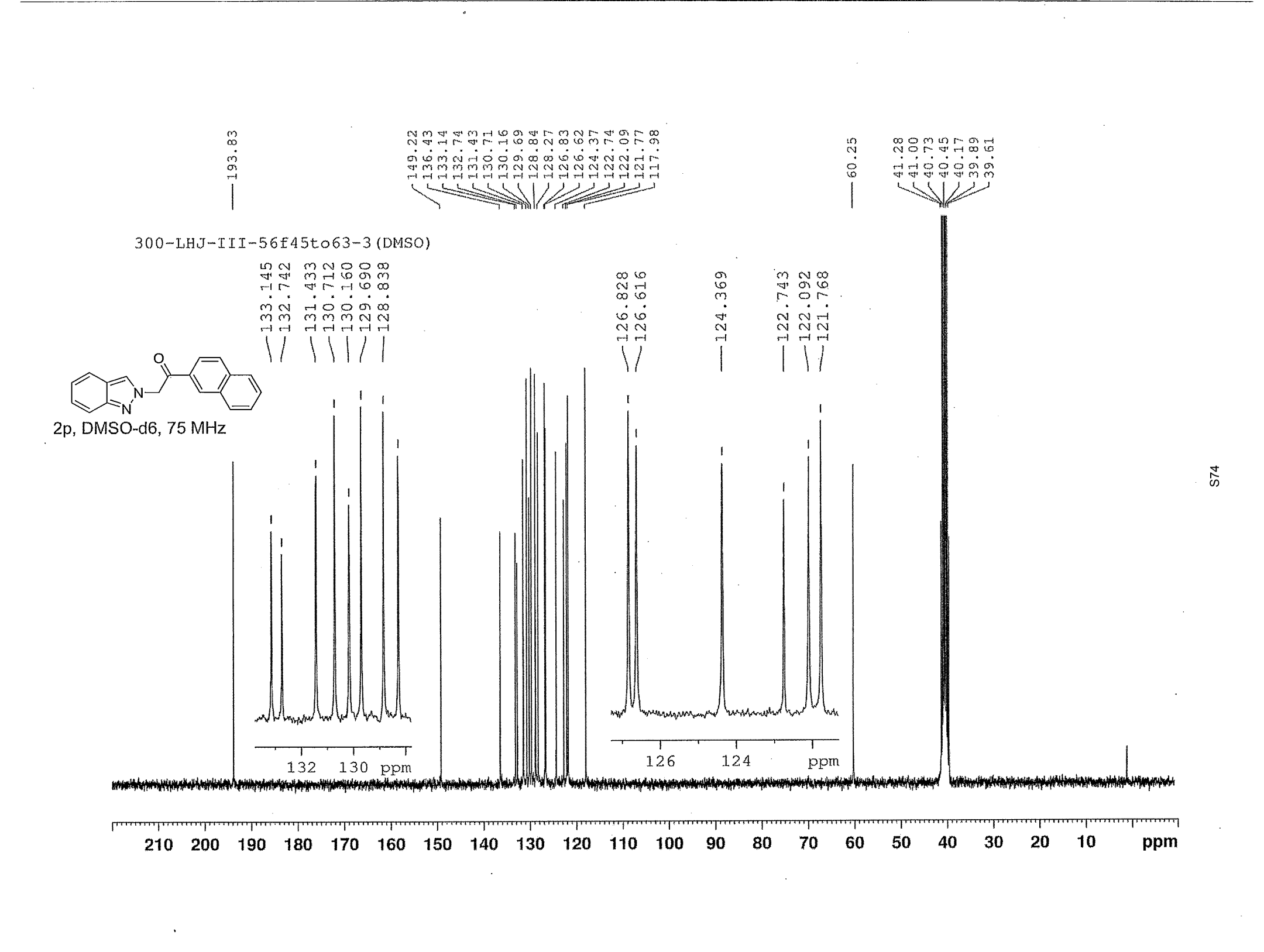

300-LHJ-III-35f45to76-3(HSQC)
O
Cl
N
N
ppm
60
80
100
120
140
160
180
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm

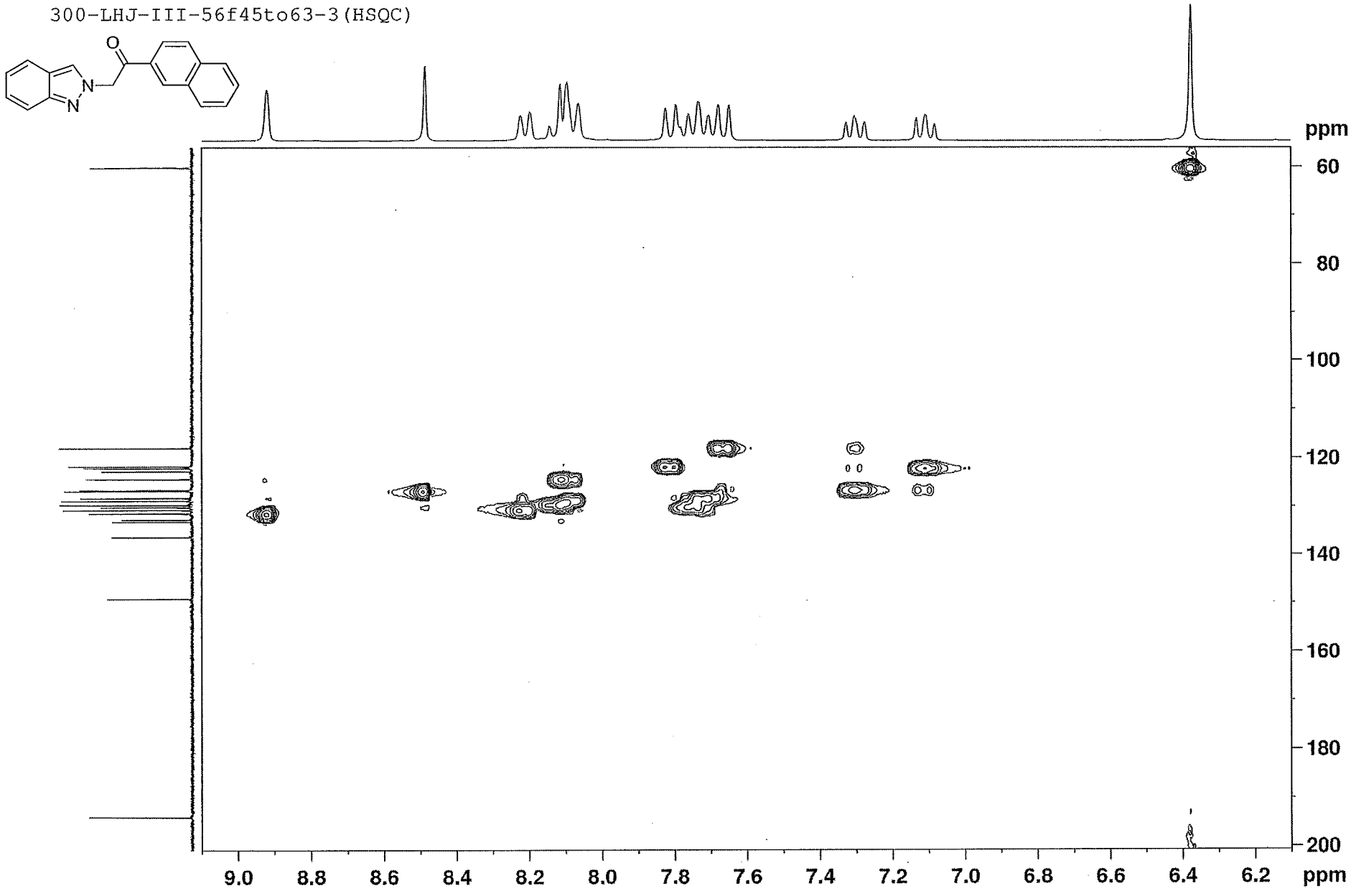
300-LHJ-III-35f45to76-3(HMBC)

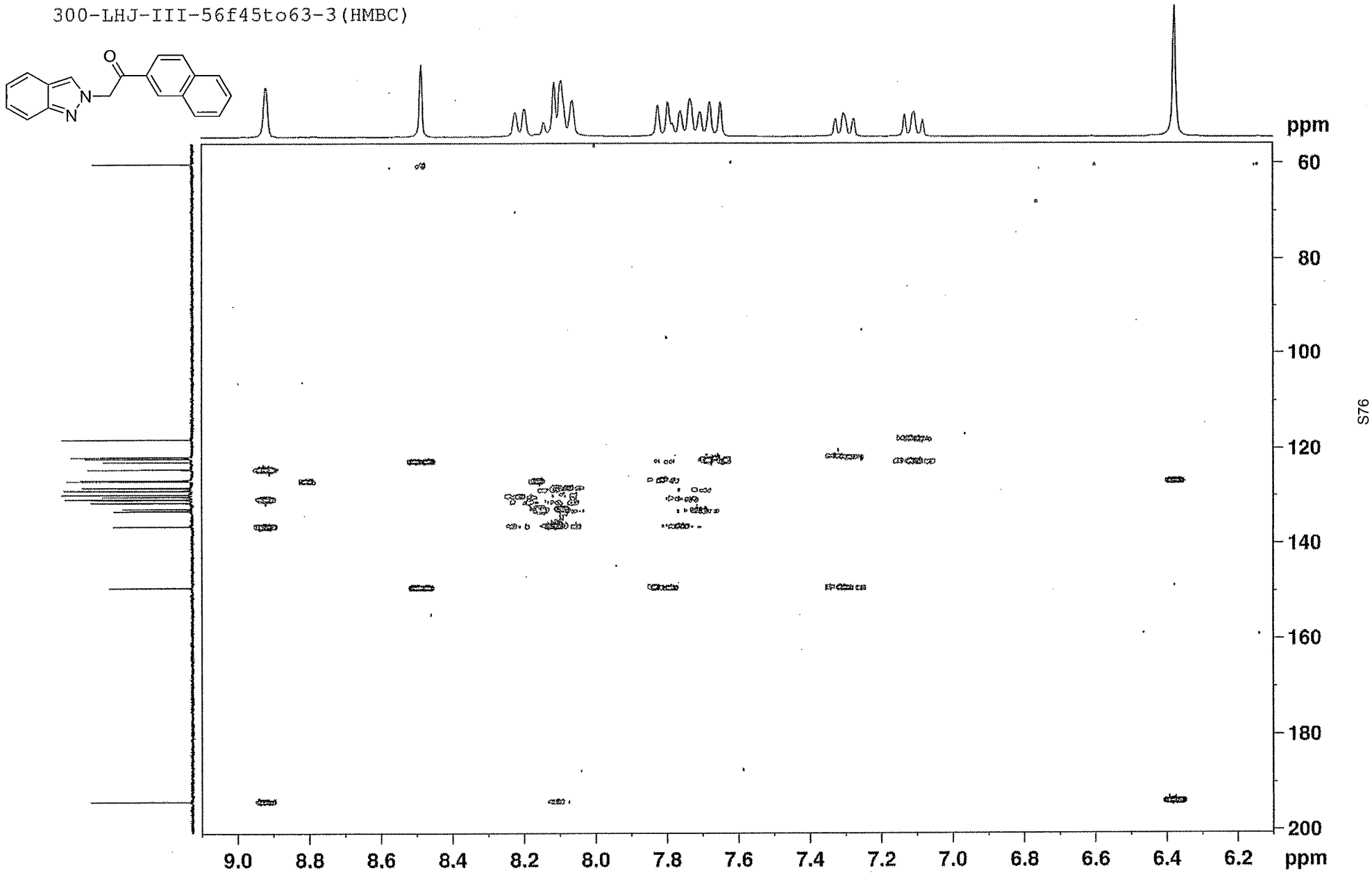


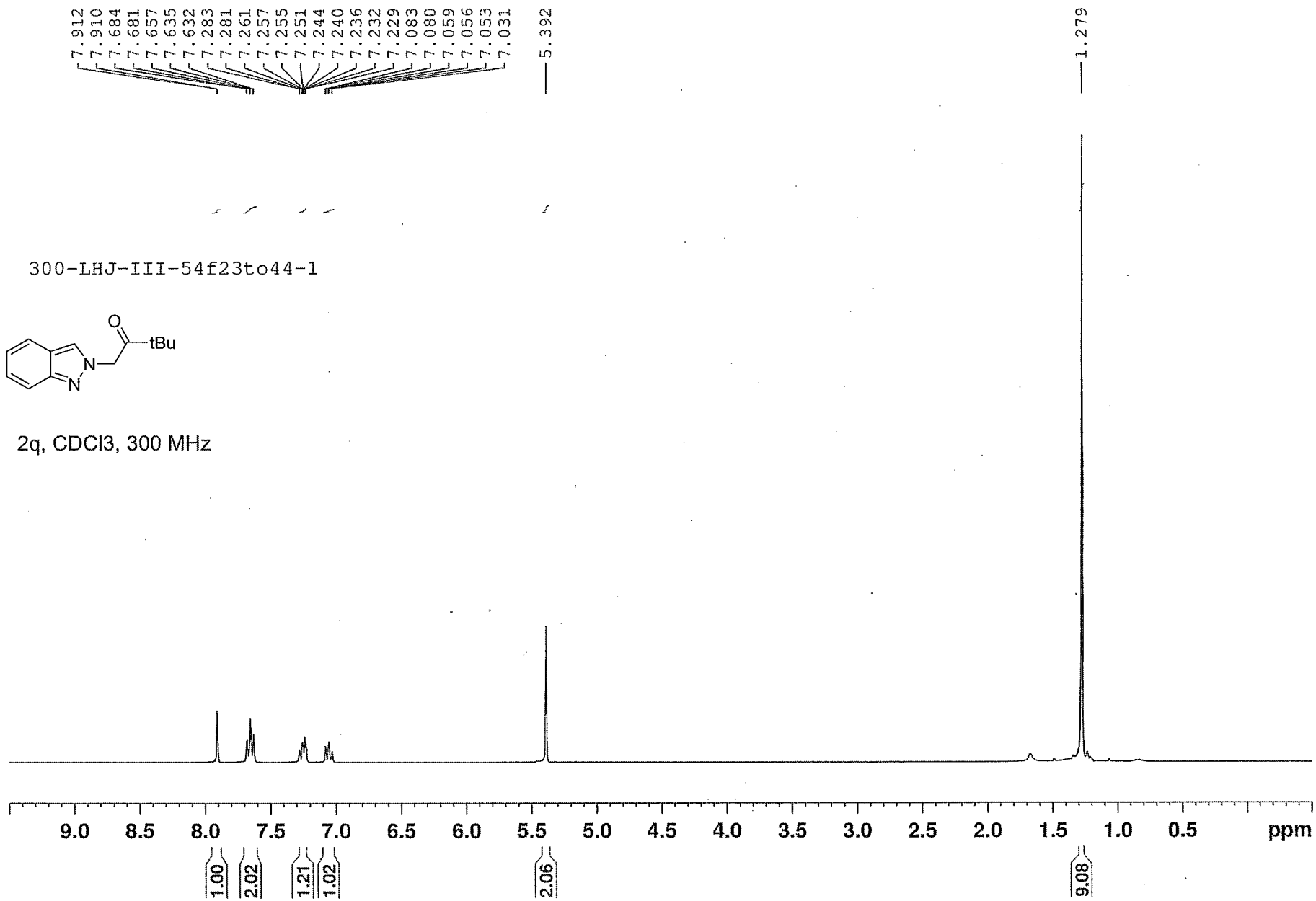


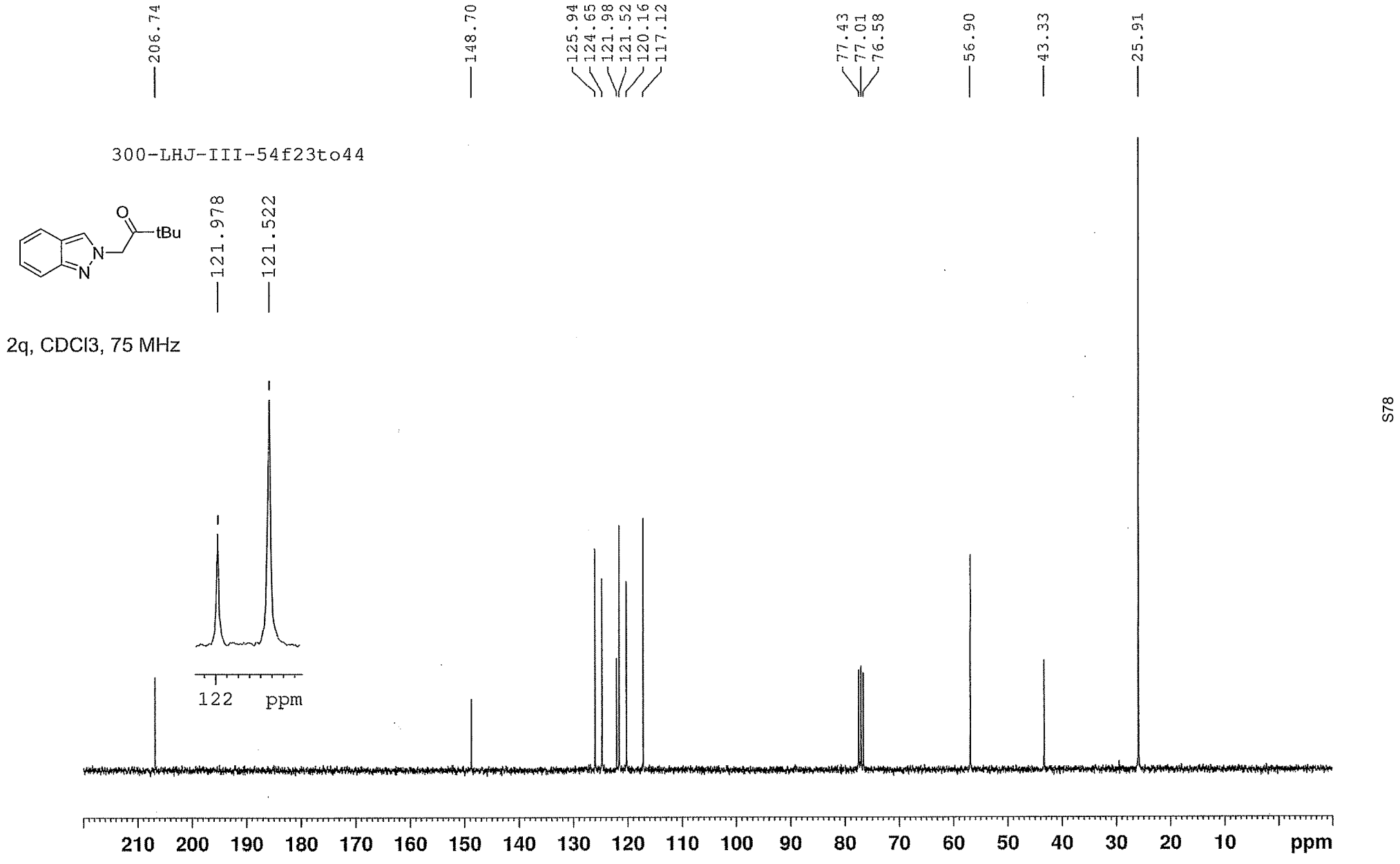

8.920
8.487
8.223
8.197
8.143
8.115
8.095
8.065
7.824
7.796
7.784
7.761
7.733
7.705
7.678
7.649
7.327
7.305
7.276
7.133
7.107
7.083
6.377
3.524
2.540
300-LHJ-III-56f45to63-3(DMSO)
O
N
N
2p, DMSO-d6, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
1.00
1.02
3.08
4.06
1.04
1.02
2.02

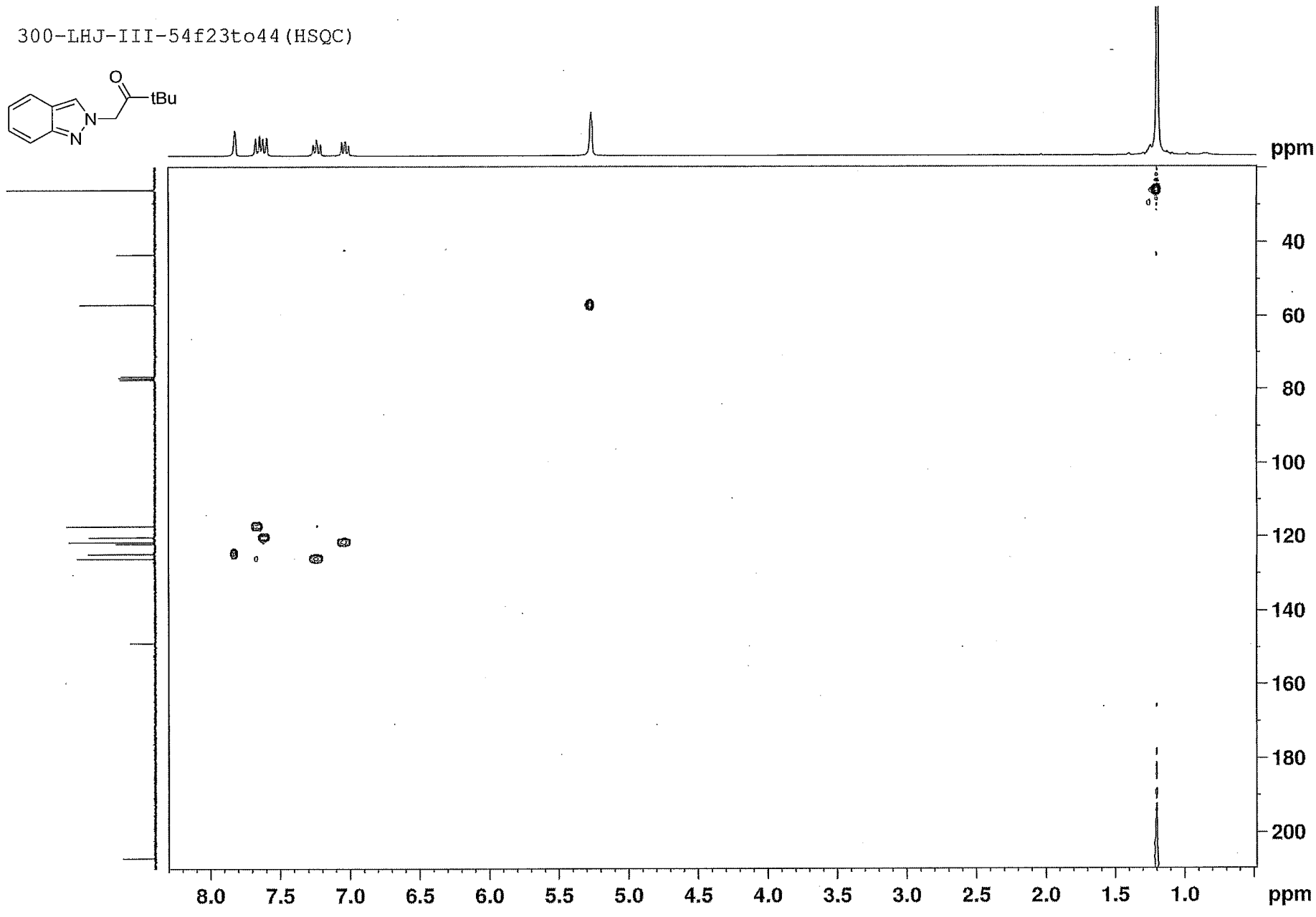

193.83
149.22
136.43
133.14
132.74
131.43
130.71
130.16
129.69
128.84
128.27
126.83
126.62
124.37
122.74
122.09
121.77
117.98
60.25
41.28
41.00
40.73
40.45
40.17
39.89
39.61
300-LHJ-III-56f45to63-3(DMSO)
133.145
132.742
131.433
130.712
130.160
129.690
128.838
126.828
126.616
124.369
122.743
122.092
121.768
O
N
N
2p, DMSO-d6, 75 MHz
132 130 ppm
126 124 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


300-LHJ-III-56f45to63-3(HSQC)
O
N
N
ppm
60
80
100
120
140
160
180
200
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm

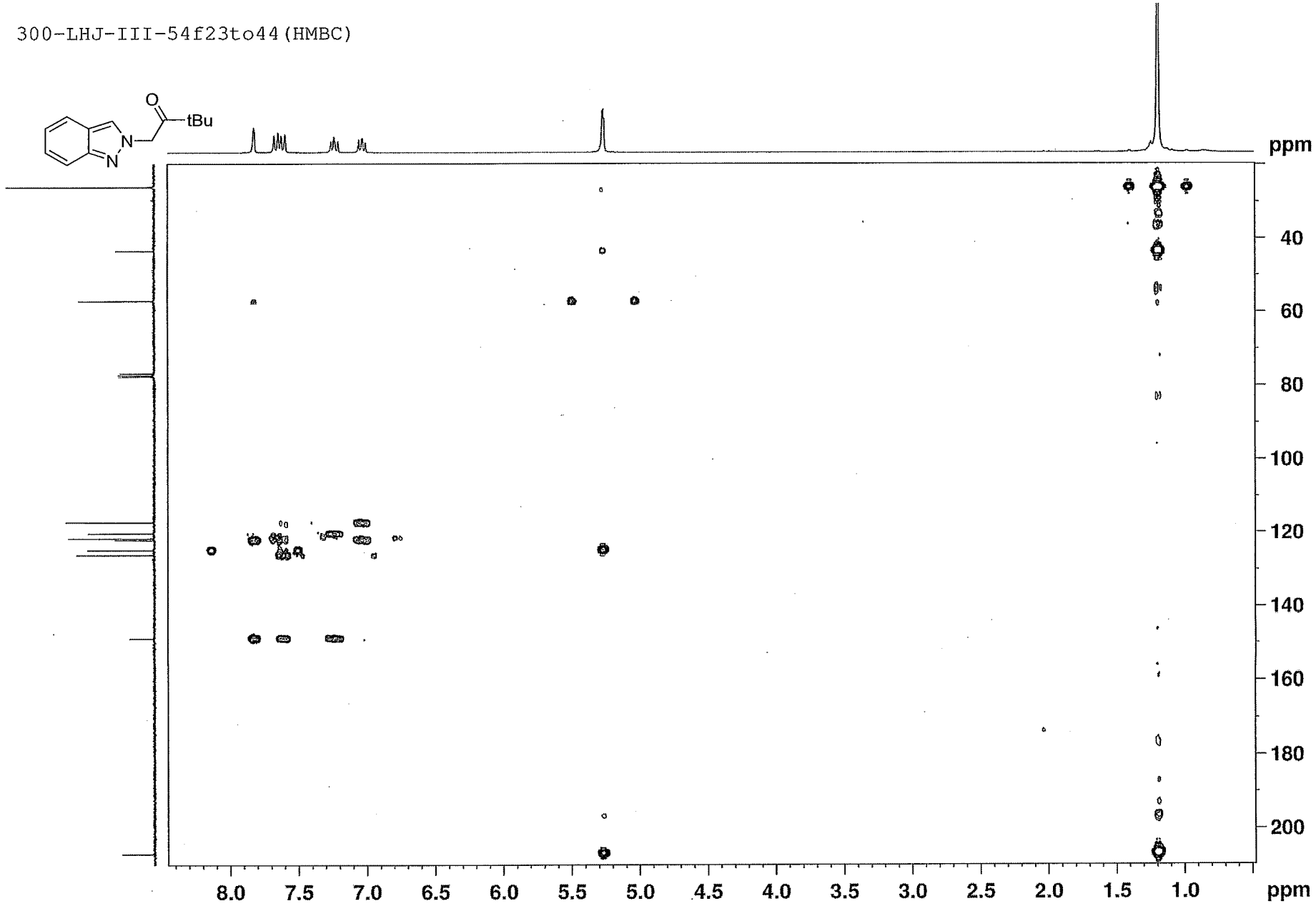

300-LHJ-III-56f45to63-3(HMBC)
O
N
N
ppm
60
80
100
120
140
160
180
200
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm

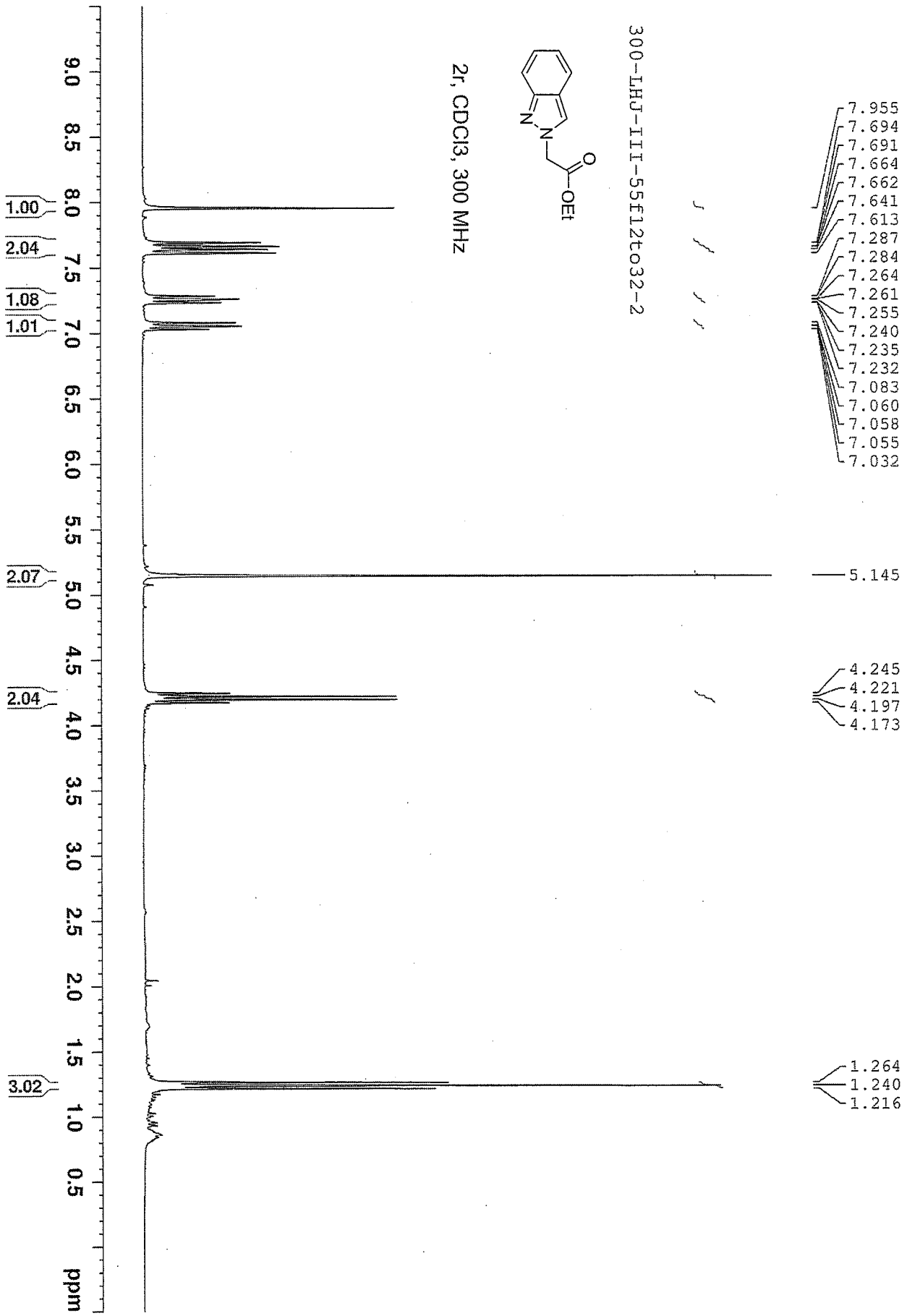

7.912
7.910
7.684
7.681
7.657
7.635
7.632
7.283
7.281
7.261
7.257
7.255
7.251
7.244
7.240
7.236
7.232
7.229
7.083
7.080
7.059
7.056
7.053
7.031
5.392
1.279
300-LHJ-III-54f23to44-1
O
tBu
N
N
2q, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.02
1.21
1.02
2.06
9.08

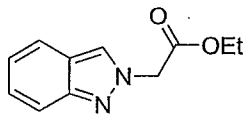

206.74
148.70
125.94
124.65
121.98
121.52
120.16
117.12
77.43
77.01
76.58
56.90
43.33
25.91
300-LHJ-III-54f23to44
121.978
121.522
O
tBu
N
N
2q, CDCl3, 75 MHz
122 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


300-LHJ-III-54f23to44(HSQC)
O
tBu
N
N
ppm
40
60
80
100
120
140
160
180
200
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
ppm

300-LHJ-III-54f23to44(HMBC)




300-LHJ-III-55f12to32-2
2r, CDCl3, 300 MHz
OEt
7.955
7.694
7.691
7.664
7.662
7.641
7.613
7.287
7.284
7.264
7.261
7.255
7.240
7.235
7.232
7.083
7.060
7.058
7.055
7.032
5.145
4.245
4.221
4.197
4.173
1.264
1.240
1.216
1.00
2.04
1.08
1.01
2.07
2.04
3.02
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
1.0
0.5
ppm



2r, CDCl3, 75 MHz

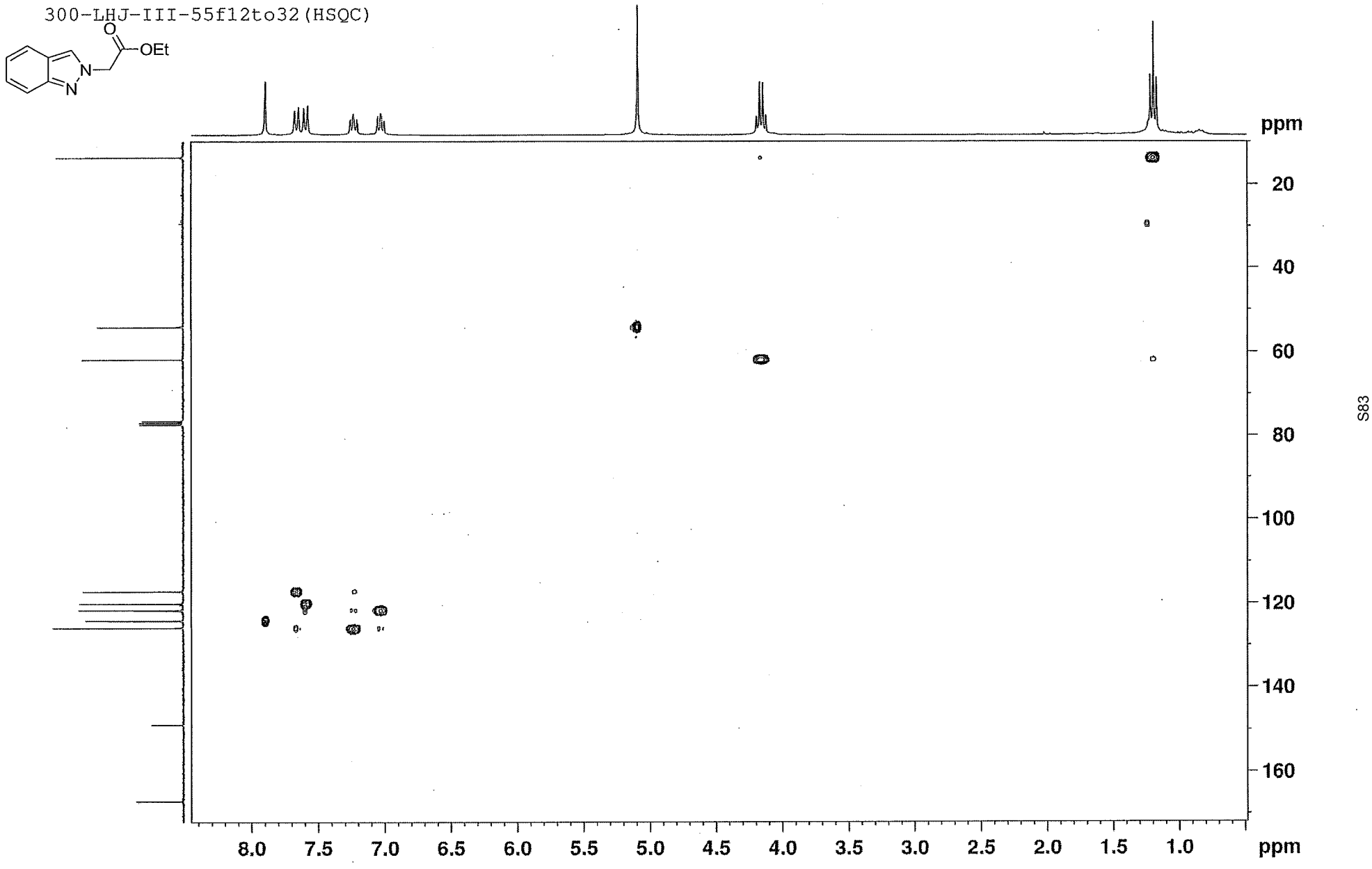
300-LHJ-III-55f12to32

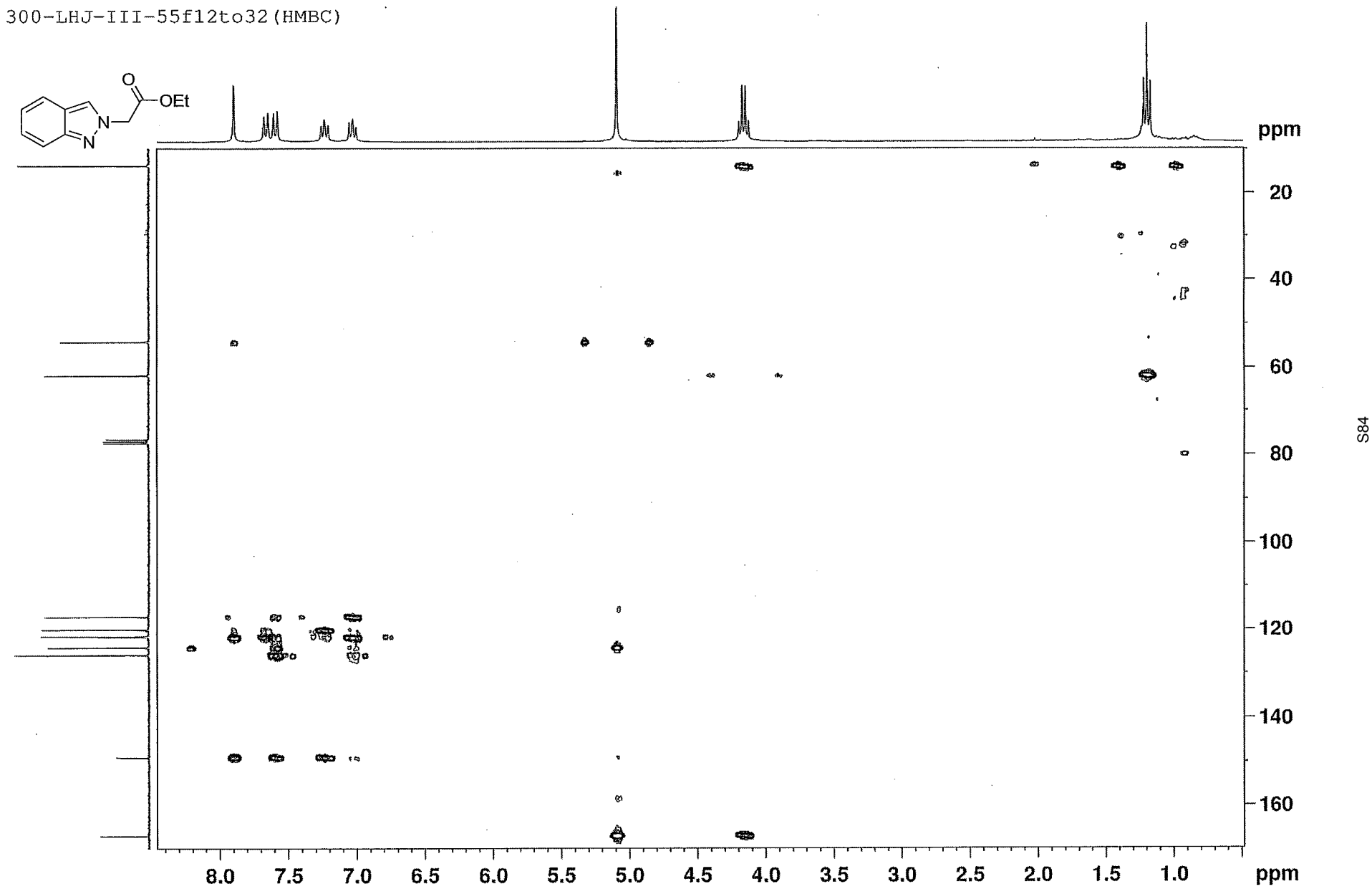
166.93
148.86
126.13
124.30
121.89
121.73
120.13
117.20
77.43
77.00
76.58
61.81
54.14
13.78

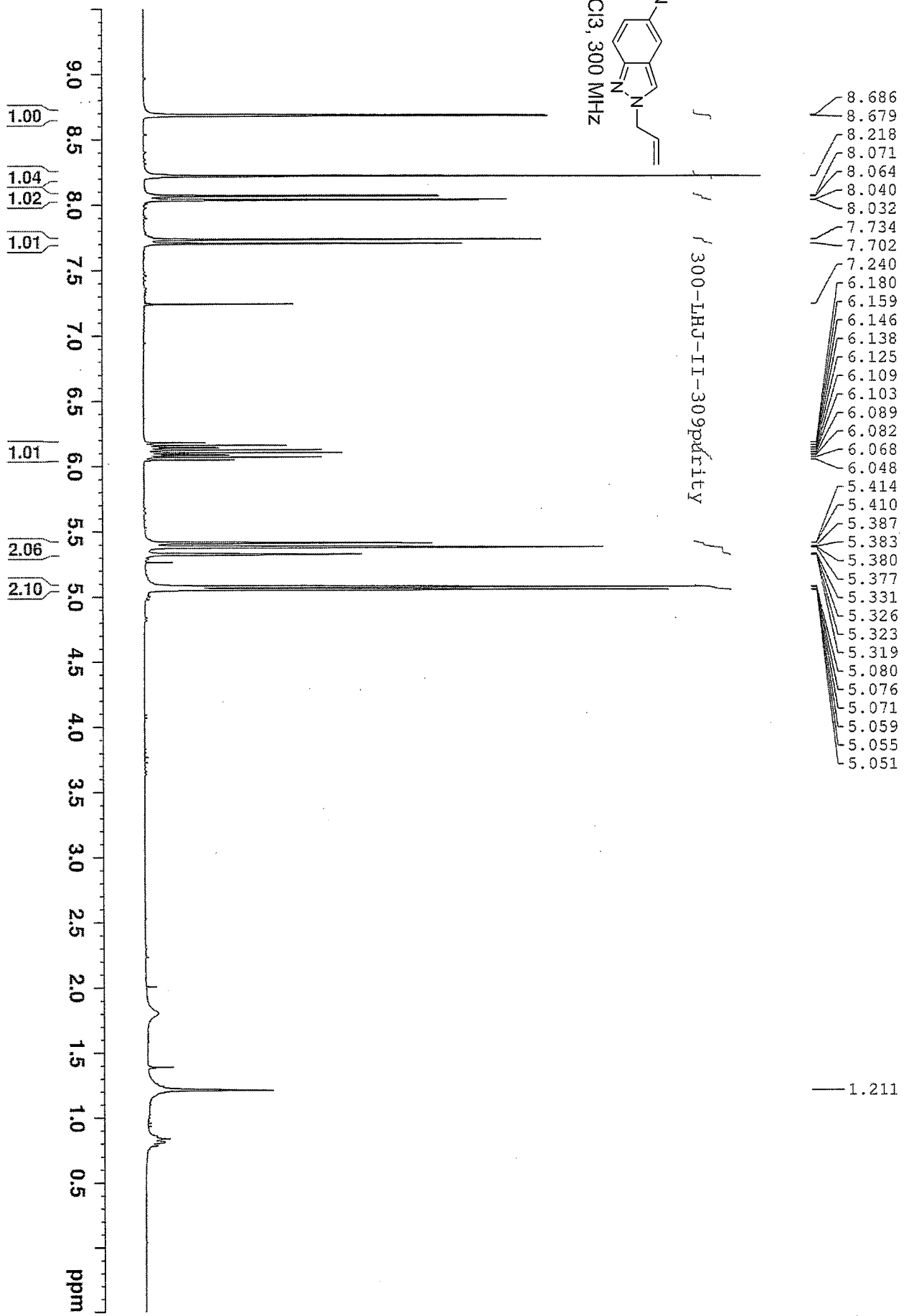
121.886
121.729

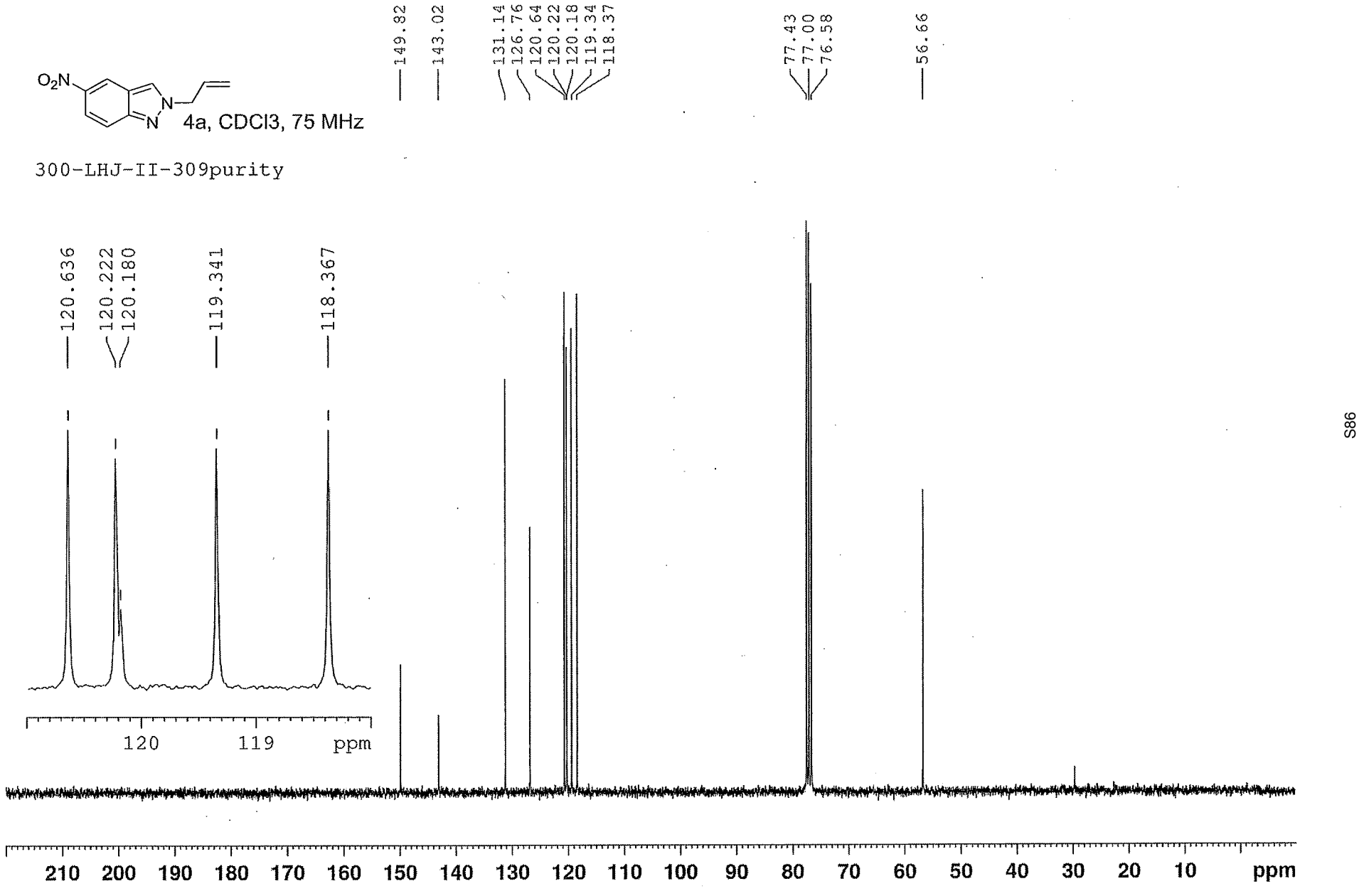
ppm

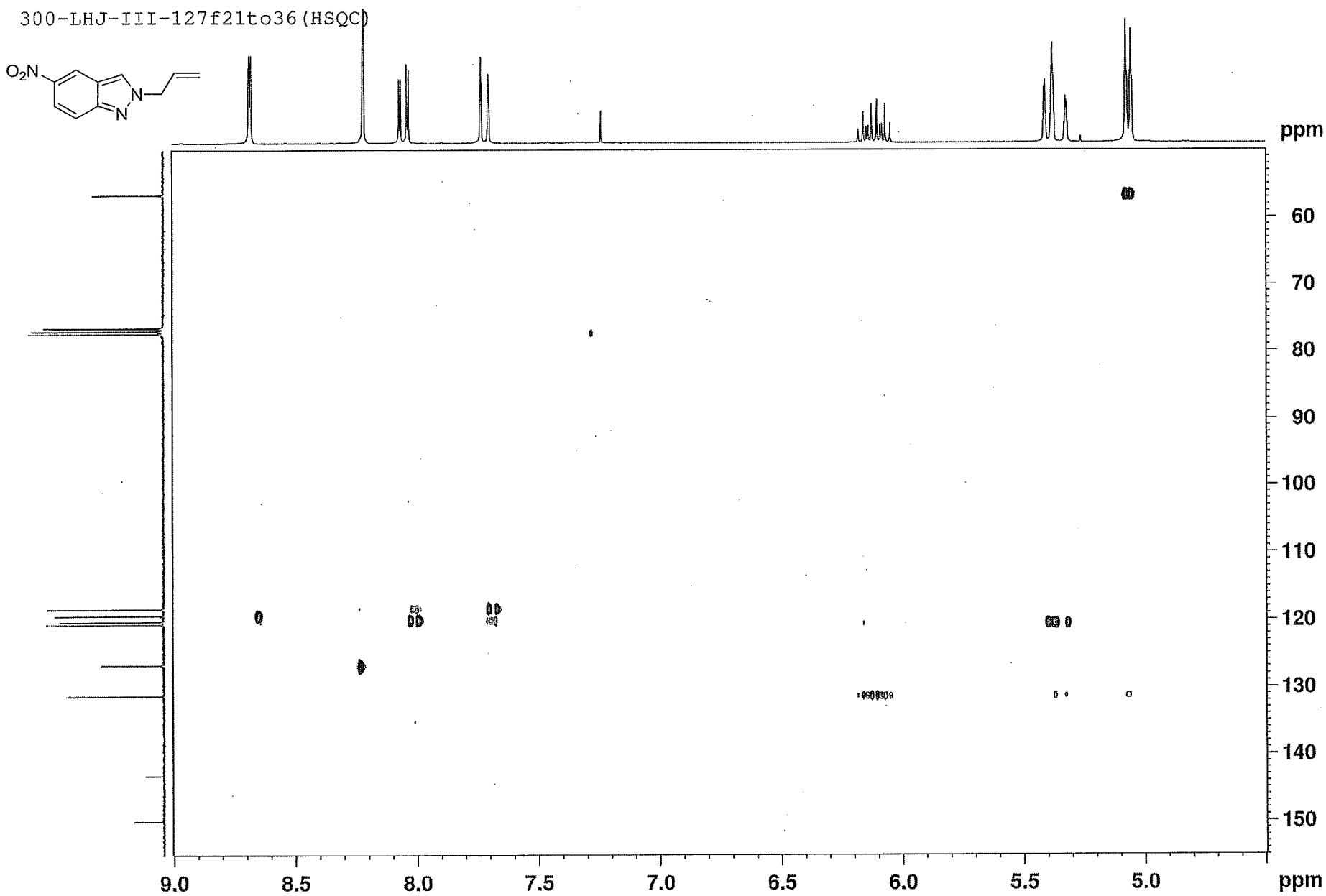
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

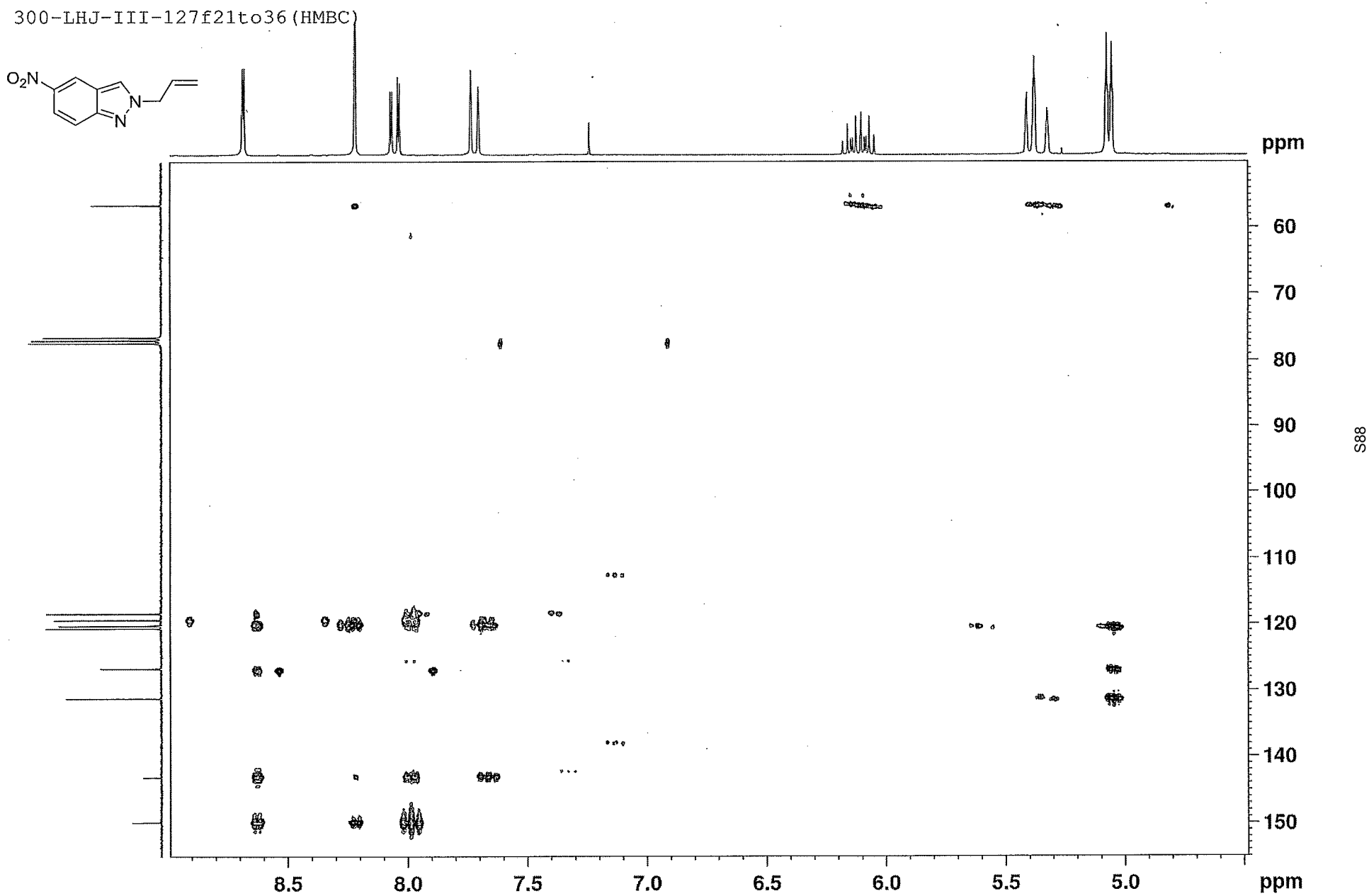

300-LHJ-III-55f12to32(HSQC)
O
OEt
N
N
ppm
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

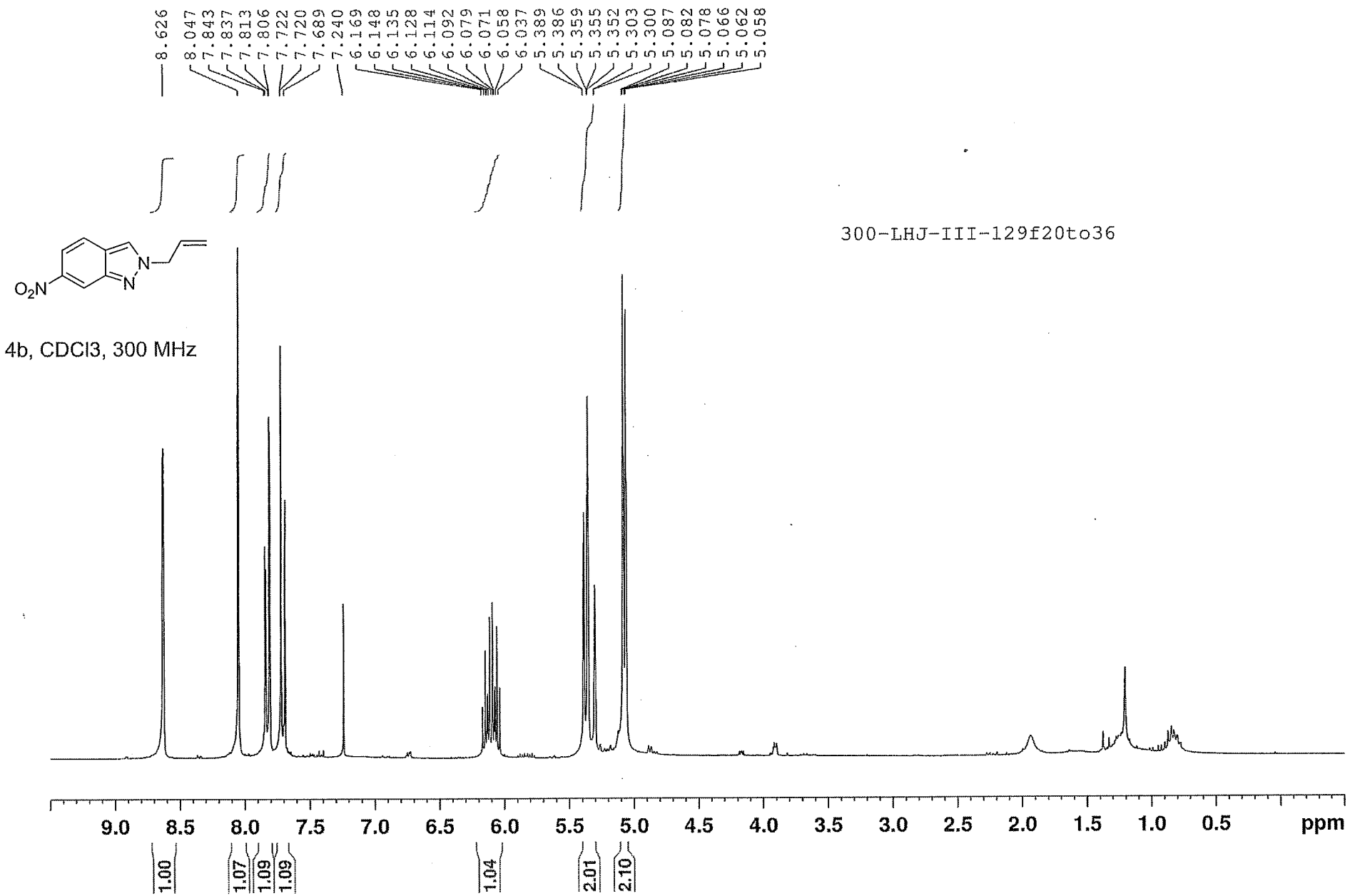

300-LHJ-III-55f12to32(HMBC)
O
OEt
N
N
ppm
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

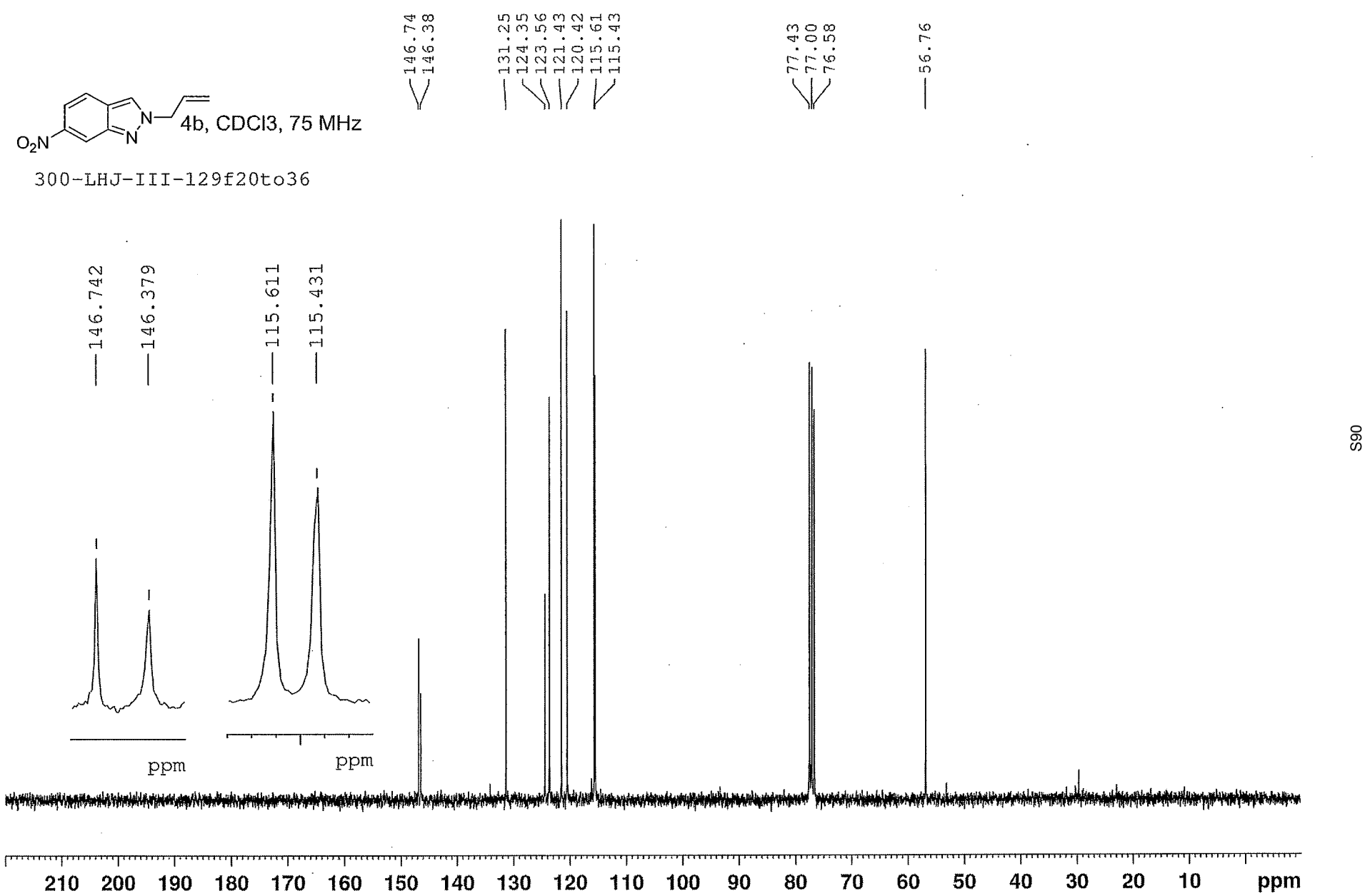

4a, CDCl3, 300 MHz
300-LHJ-II-309purity
8.686
8.679
8.218
8.071
8.064
8.040
8.032
7.734
7.702
7.240
6.180
6.159
6.146
6.138
6.125
6.109
6.103
6.089
6.082
6.068
6.048
5.414
5.410
5.387
5.383
5.380
5.377
5.331
5.326
5.323
5.319
5.080
5.076
5.071
5.059
5.055
5.051
1.211
1.00
1.04
1.02
1.01
1.01
2.06
2.10
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
1.0
0.5
ppm

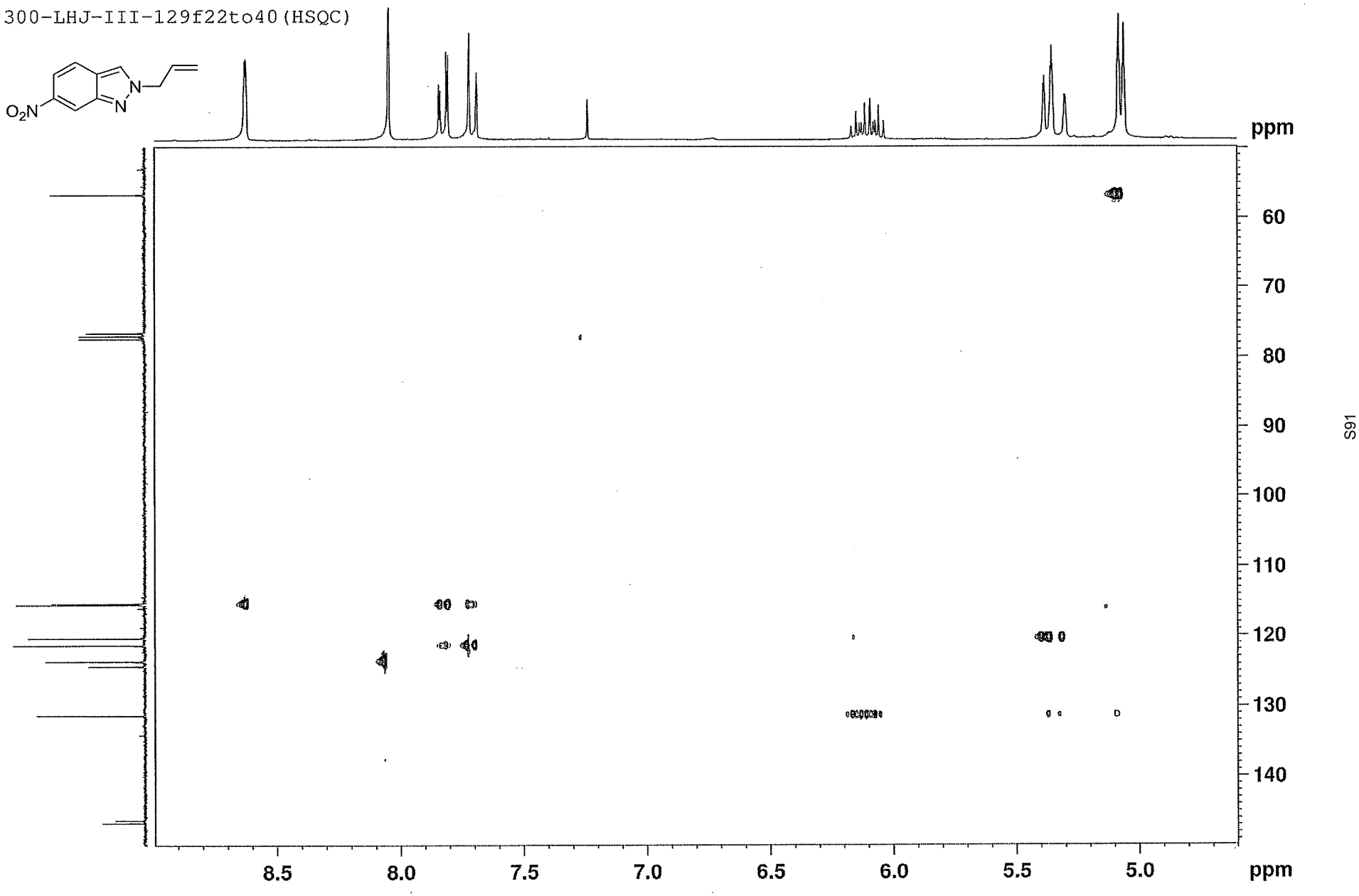

O2N
N
N
4a, CDCl3, 75 MHz
300-LHJ-II-309purity
149.82
143.02
131.14
126.76
120.64
120.22
120.18
119.34
118.37
77.43
77.00
76.58
56.66
120.636
120.222
120.180
119.341
118.367
120
119
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

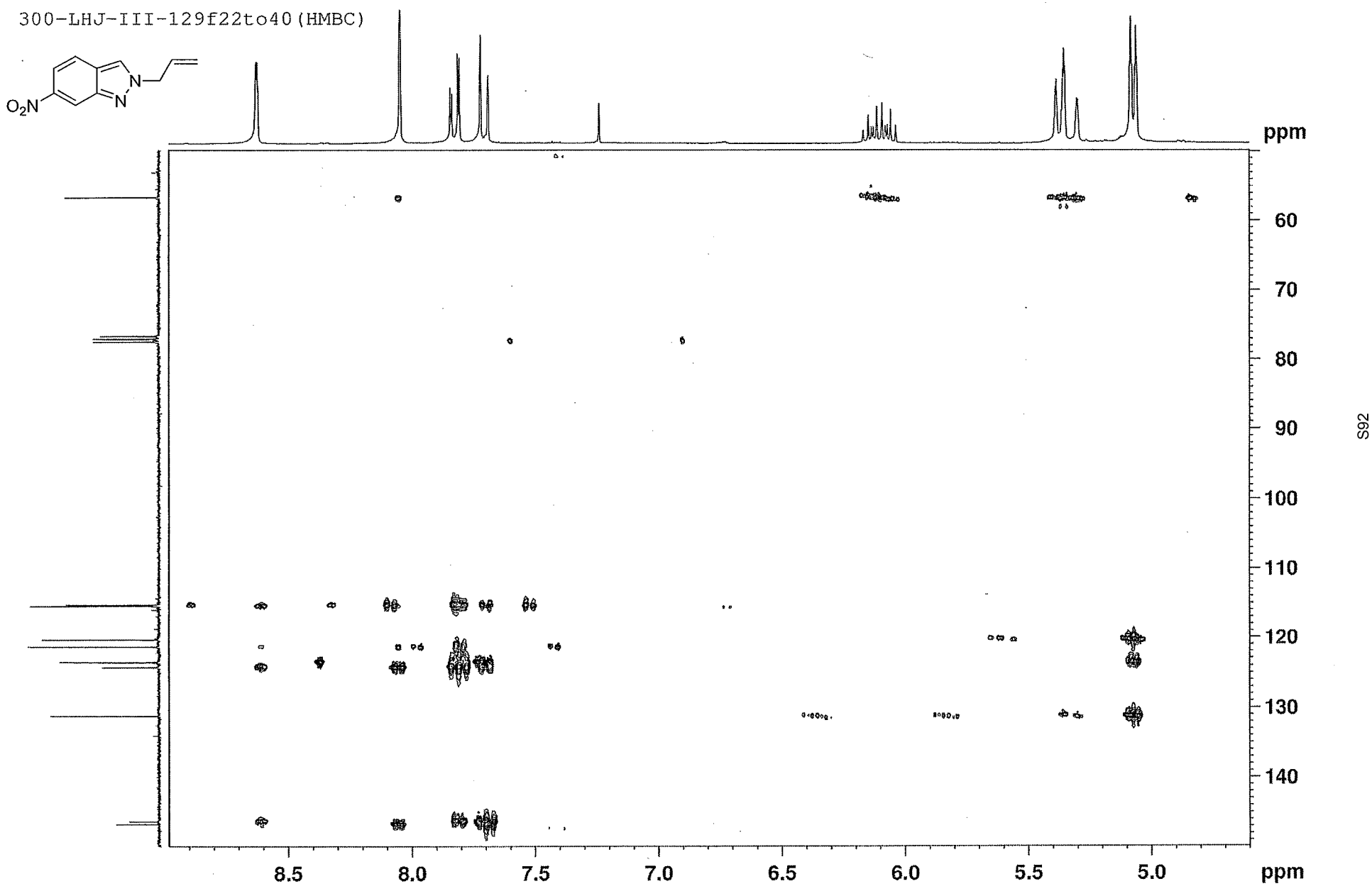

300-LHJ-III-127f21to36(HSQC)
O2N
N
N
ppm
60
70
80
90
100
110
120
130
140
150
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm

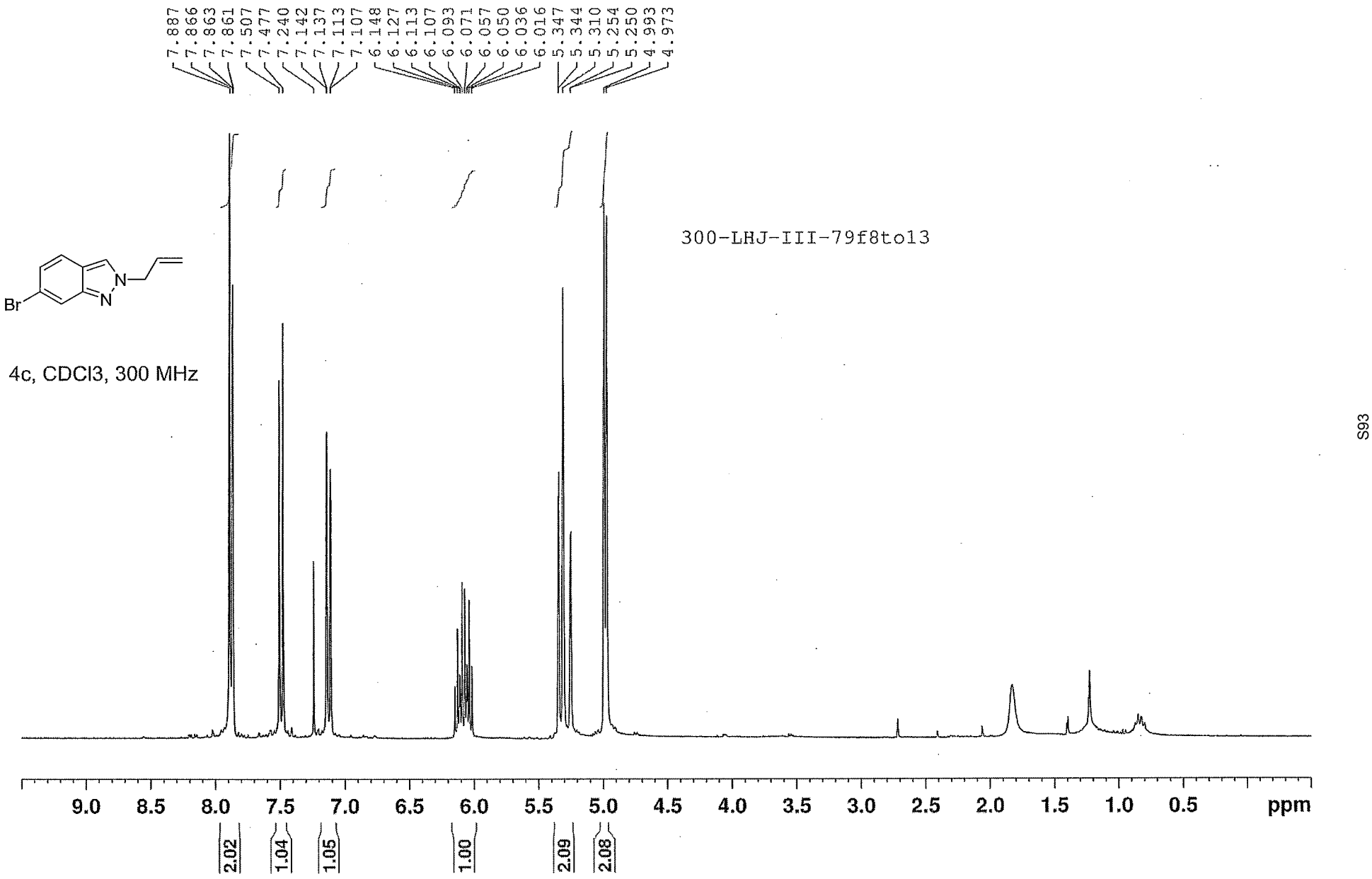

300-LHJ-III-127f21to36(HMBC)
O2N
N
N
ppm
60
70
80
90
100
110
120
130
140
150
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm

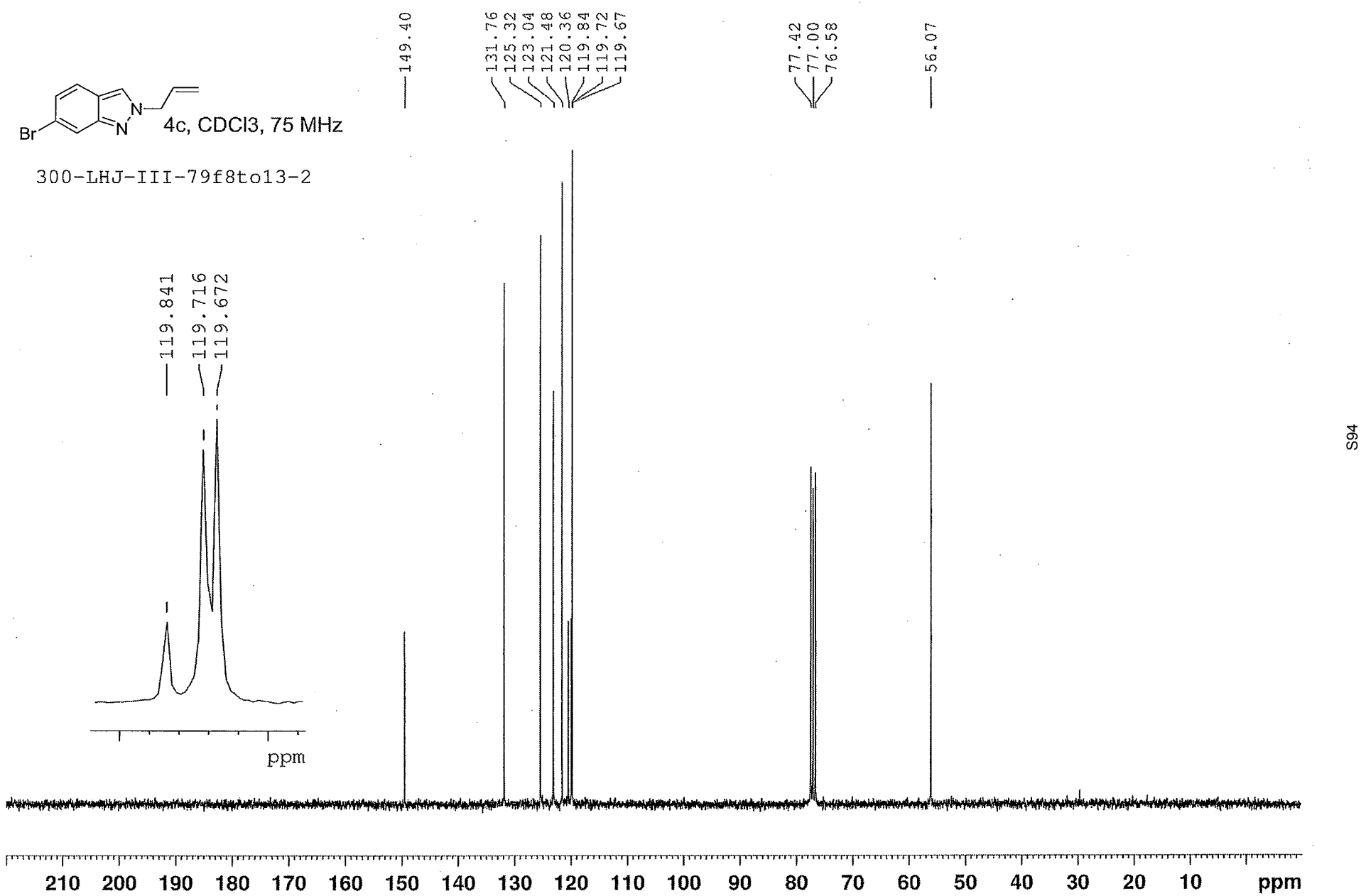

8.626
8.047
7.843
7.837
7.813
7.806
7.722
7.720
7.689
7.240
6.169
6.148
6.135
6.128
6.114
6.092
6.079
6.071
6.058
6.037
5.389
5.386
5.359
5.355
5.352
5.303
5.300
5.087
5.082
5.078
5.066
5.062
5.058
300-LHJ-III-129f20to36
4b, CDCl3, 300 MHz
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.07
1.09
1.09
1.04
2.01
2.10

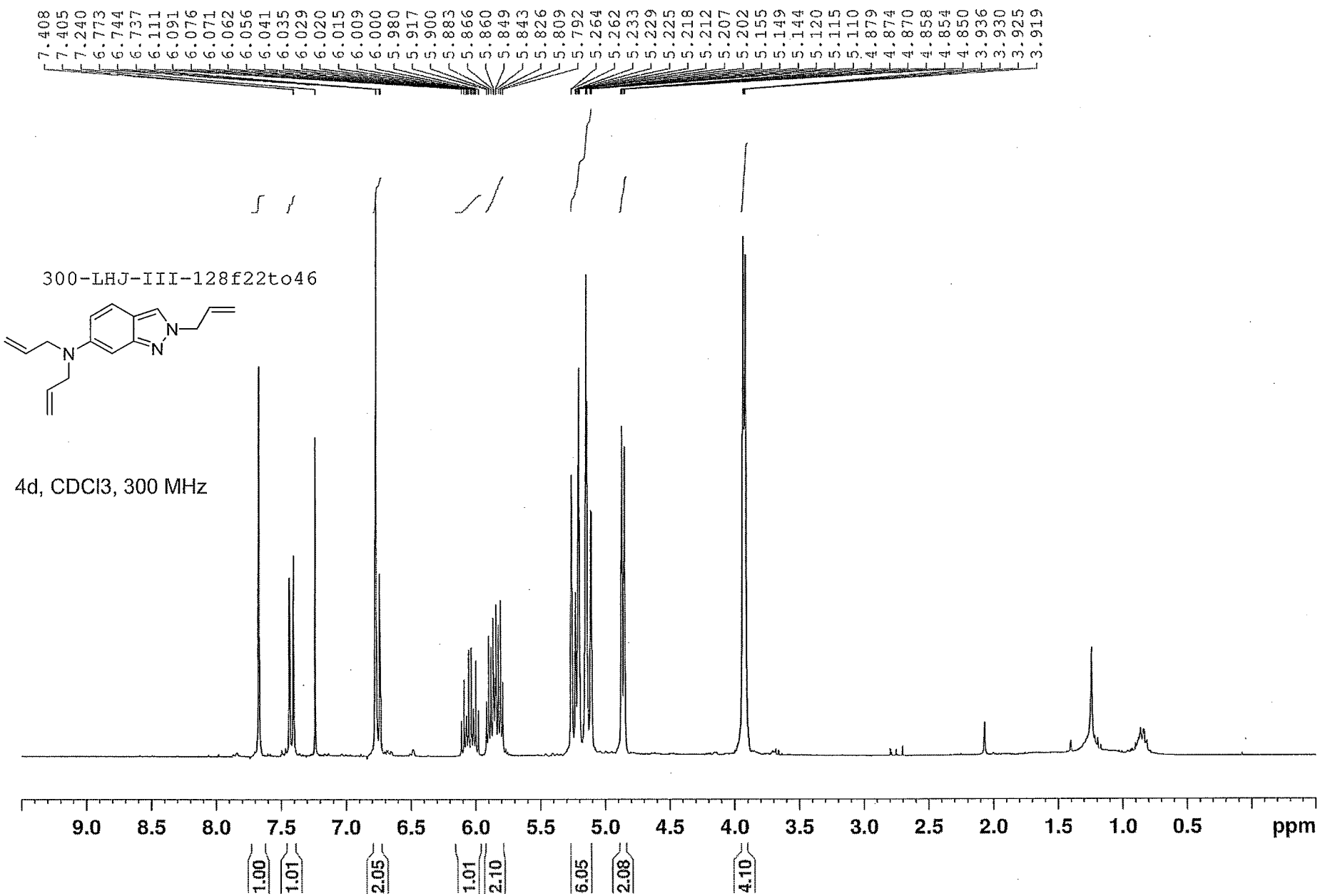

4b, CDCl3, 75 MHz
300-LHJ-III-129f20to36
146.74
146.38
131.25
124.35
123.56
121.43
120.42
115.61
115.43
77.43
77.00
76.58
56.76
146.742
146.379
115.611
115.431
ppm
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

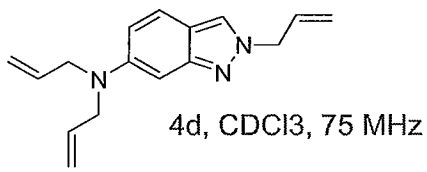

300-LHJ-III-129f22to40(HSQC)
O2N
N
N
ppm
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm


300-LHJ-III-129f22to40(HMBC)
O2N
N
N
ppm
60
70
80
90
100
110
120
130
140
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm


7.887
7.866
7.863
7.861
7.507
7.477
7.240
7.142
7.137
7.113
7.107
6.148
6.127
6.113
6.107
6.093
6.071
6.057
6.050
6.036
6.016
5.347
5.344
5.310
5.254
5.250
4.993
4.973
300-LHJ-III-79f8to13
Br
N
N
4c, CDCl3, 300 MHz
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
1.0
0.5
ppm
2.02
1.04
1.05
1.00
2.09
2.08


4c, CDCl3, 75 MHz
300-LHJ-III-79f8to13-2
149.40
131.76
125.32
123.04
121.48
120.36
119.84
119.72
119.67
77.42
77.00
76.58
56.07
119.841
119.716
119.672
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.408
7.405
7.240
6.773
6.744
6.737
6.111
6.091
6.076
6.071
6.062
6.056
6.041
6.035
6.029
6.020
6.015
6.009
6.000
5.980
5.917
5.900
5.883
5.866
5.860
5.849
5.843
5.826
5.809
5.792
5.264
5.262
5.233
5.229
5.225
5.218
5.212
5.207
5.202
5.155
5.149
5.144
5.120
5.115
5.110
4.879
4.874
4.870
4.858
4.854
4.850
3.936
3.930
3.925
3.919
300-LHJ-III-128f22to46
4d, CDCl3, 300 MHz
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
1.0
0.5
ppm
1.00
1.01
2.05
1.01
2.10
6.05
2.08
4.10



4d, CDCl3, 75 MHz

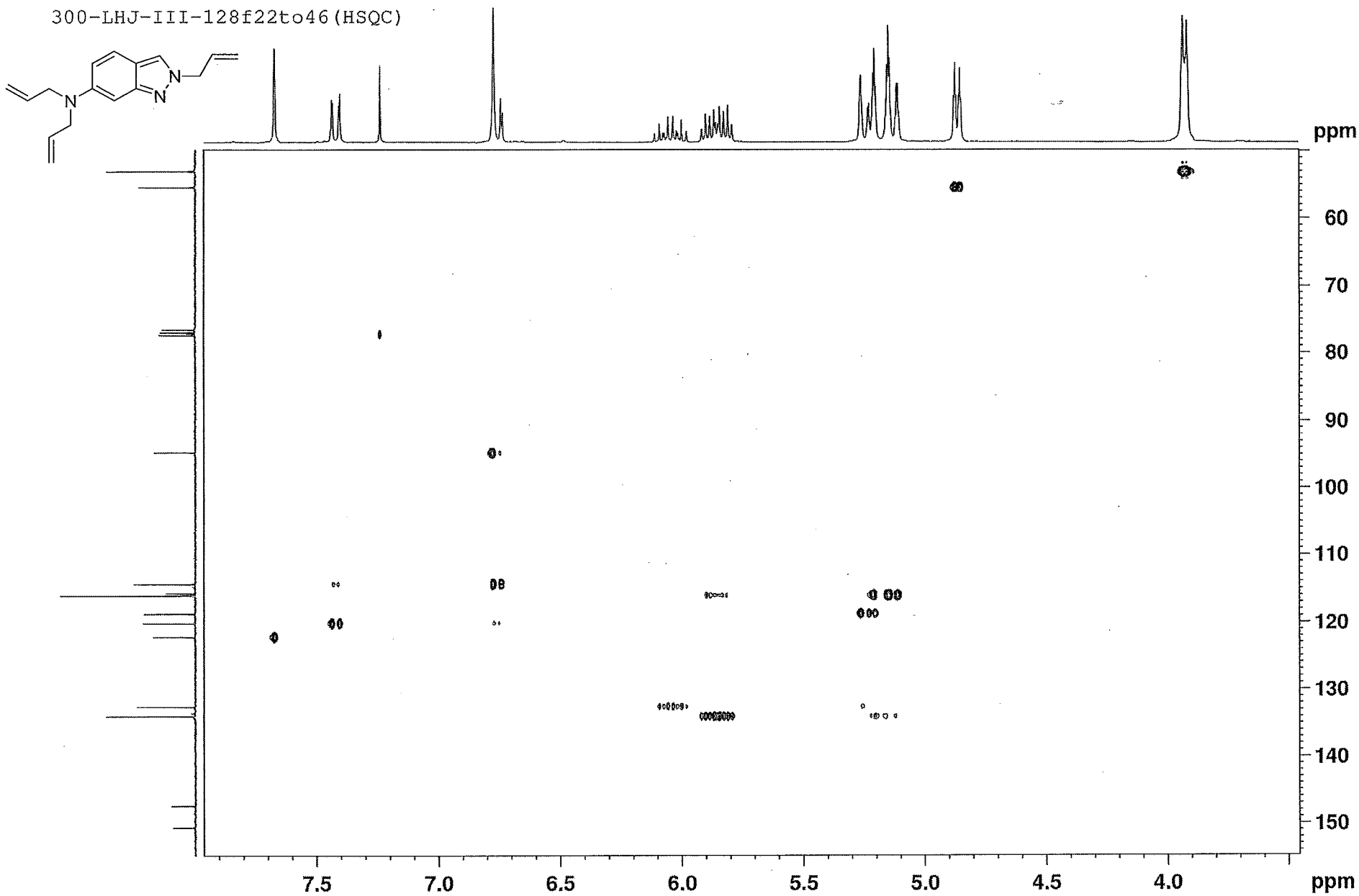
300-LHJ-III-128f22to46

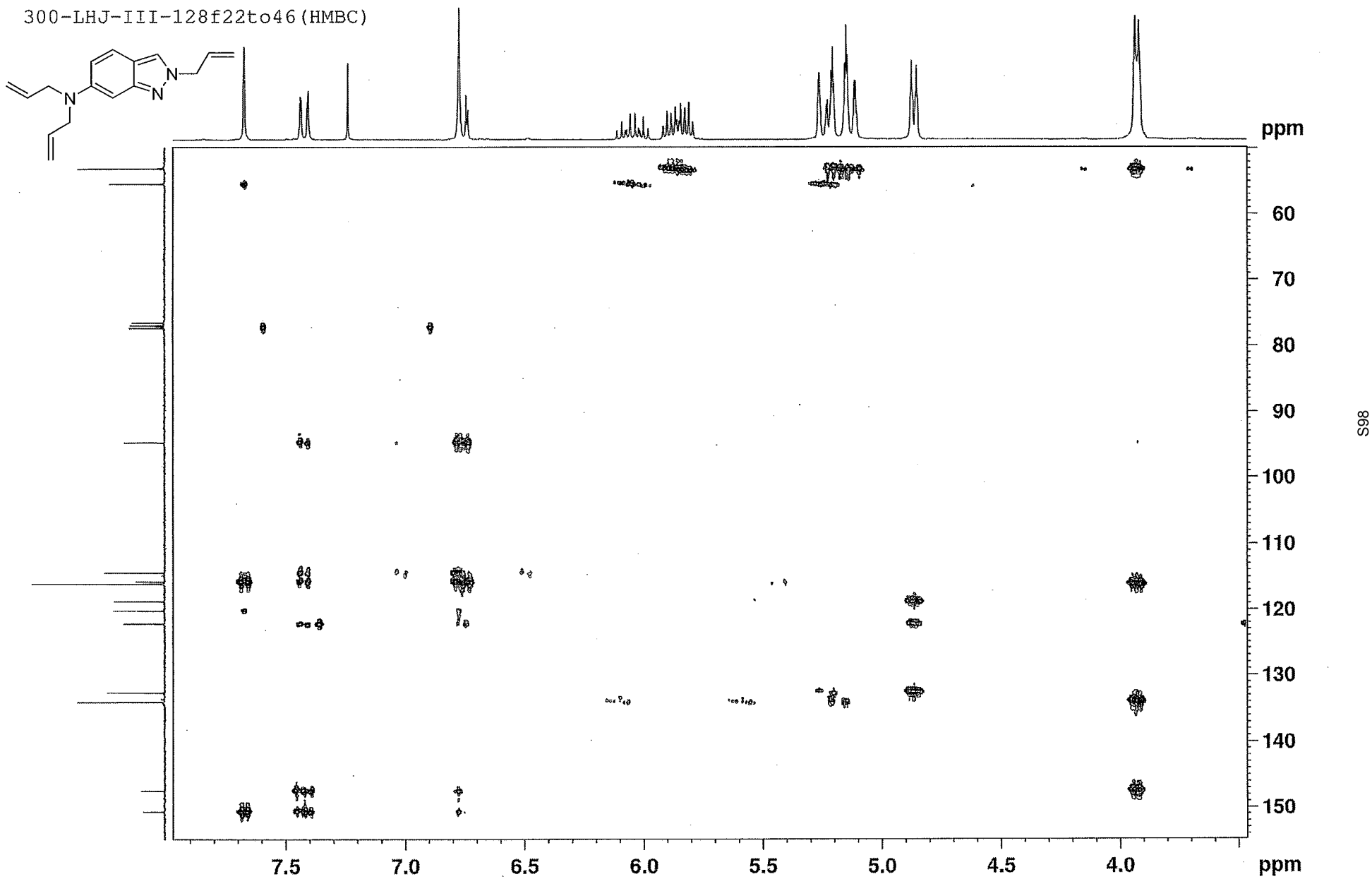
150.57
147.37
133.95
132.52
122.15
120.14
118.72
116.02
115.72
114.36
94.73
77.43
77.00
76.58
55.42
53.05

116.022
115.717

116.0 ppm

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


300-LHJ-III-128f22to46(HSQC)
N
N
N
ppm
60
70
80
90
100
110
120
130
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm


300-LHJ-III-128f22to46(HMBC)
N
N
N
ppm
60
70
80
90
100
110
120
130
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm