Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Rh-Catalyzed Oxidative C-H Activation/Annulation: Converting Anilines to Indoles with Molecular Oxygen as Sole Oxidant

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CONTENTS

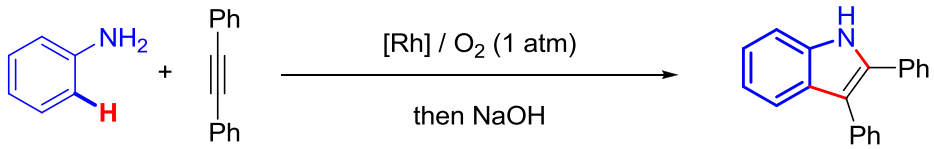
1. General experiment details and materials

Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents were purchased from Alfa Aesar, and before use were dried and degassed by standard methods and stored under argon atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI) or Waters GCT Premier mass spectrometer (EI). Anilines used here are known compounds. 1,2-diphenylethyne and prop-1-ynylbenzene were purchased from Alfa Aesar. The other alkynes used here are known compounds and synthesized according to the reported methods.[1] $Cp^*Rh(H_2O)_3(OTf)_2$, $Cp^*Rh(H_2O)(OAc)_2$ and $Cp^*Rh(CH_3CN)_3(SbF_6)_2$, $[\{RhCp^*Cl_2\}_2]$, used here are known compounds and synthesized according to the reported methods.[2]

2. Optimization of the reaction conditions

Diphenylethyne **2a** (71.3 mg, 0.4 mmol), [Rh] catalyst (0.02 mmol, 5 mol%), aniline **1a** (55.0 μL, 0.6 mmol), solvent (2.0 mL) and Ac_2O (57.0 μL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at design temperature for 24 hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH_3OH (2.0 mL) were added to the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **3aa** as a white solid.

Table 1. Optimization of the reaction conditions[a]

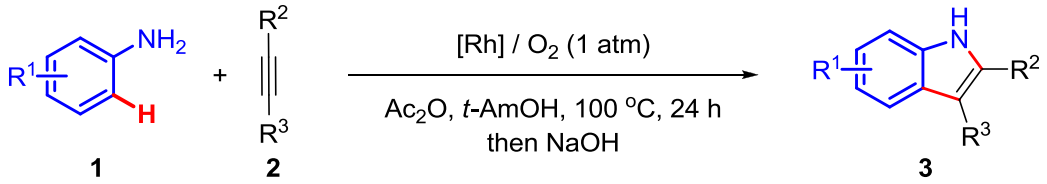


1a **2a** **3aa**

Entry	[Rh] (5 mol%)	Additive	T/ °C	Solvent	Yield (%)[b]
1	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	40	*t*-AmOH	70
2	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	40	*t*-BuOH	18
3	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	40	CH_3OH	<5
4	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	40	DMF	<5
5	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	40	$CH_3C(O)CH_3$	49
6	$Cp^*Rh(CH_3CN)_3(SbF_6)_2$	Ac_2O	40	*t*-AmOH	<5
7	$[\{RhCp^*Cl_2\}_2]$	Ac_2O	40	*t*-AmOH	0
8	$Cp^*Rh(H_2O)(OAc)_2$	Ac_2O	40	*t*-AmOH	<5
9	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	60	*t*-AmOH	80
10	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	80	*t*-AmOH	79
11	**$Cp^*Rh(H_2O)_3(OTf)_2$**	**Ac_2O**	**100**	***t*-AmOH**	**84**
12	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	120	*t*-AmOH	81
13	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	rt	*t*-AmOH	44
14	$Cp^*Rh(H_2O)_3(OTf)_2$	Ac_2O	100	*t*-AmOH	<5[c]
15	$Cp^*Rh(H_2O)_3(OTf)_2$	$(CF_3CO)_2O$	100	*t*-AmOH	0
16	$Cp^*Rh(H_2O)_3(OTf)_2$	$(CF_3SO_2)_2O$	100	*t*-AmOH	0
17	$Cp^*Rh(H_2O)_3(OTf)_2$	HOAc	100	*t*-AmOH	0
18	$Cp^*Rh(H_2O)_3(OTf)_2$	--	100	*t*-AmOH	0
19	--	Ac_2O	100	*t*-AmOH	0

[a] General conditions: **1a** (55.0 μL, 0.6 mmol), **2a** (71.3 mg, 0.4 mmol), [Rh] catalyst (0.02 mmol, 5mol %), additive (0.6 mmol), solvents (2.0 mL), oxygen (1 atm), for 24 h, unless otherwise noted. [b] Isolated yield. [c] Under argon.

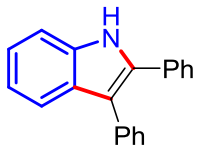
3. General procedure for the C-H activation/annulation



Alkynes **2** (0.4 mmol), Cp*Rh$(H_2O)_3(OTf)_2$ (11.8 mg, 0.02 mmol, 5 mol%), anilines **1** (0.6 mmol), *t*-AmOH (2.0 mL) and Ac_2O (57.0 μL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at 100 °C or 40 °C for 24 hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH_3OH (2.0 mL) were added to the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1 – 5:1) to afford the desired products **3**.

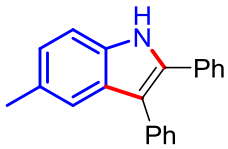
4. Experimental characterization data for products of 3.

2,3-Diphenyl-1H-indole (3aa):[3]



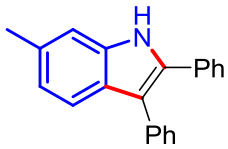
The title compound was prepared according to the general procedure as a white solid, 90.3 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.17 (m, 1H), 7.21-7.45 (m, 12H), 7.67 (d, *J* = 7.68, 1H), 8.18 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.9, 115.0, 119.7, 120.4, 122.7, 126.2, 127.7, 128.1, 128.5, 128.7, 128.7, 130.1, 132.7, 134.0, 135.0, 135.9. HRMS (EI) calcd. for $C_{20}H_{15}N$ [M]: 269.1204, found: 269.1205.

5-Methyl-2,3-diphenyl-1H-indole (3ba):[4]



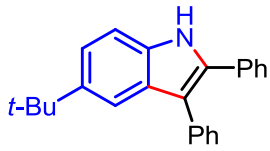
The title compound was prepared according to the general procedure as a white solid, 105.6 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.06-7.08 (m, 1H), 7.25-7.33 (m, 5H), 7.36-7.45 (m, 7H), 8.13 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 110.6, 114.7, 119.3, 124.3, 126.2, 127.6, 128.1, 128.5, 128.7, 129.1, 129.8, 130.2, 132.9, 134.2, 134.2, 135.2; HRMS (ESI) calcd. for $C_{21}H_{18}N$ [M+H]: 284.1434, found: 284.1436.

6-Methyl-2,3-diphenyl-1H-indole (3ca):[5]



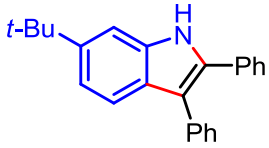
The title compound was prepared according to the general procedure as a white solid, 80.1 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.86-6.88 (m, 1H), 7.03 (s, 1H), 7.13-7.19 (m, 4H), 7.23-7.27 (m, 4H), 7.31-7.33 (m, 2H), 7.45 (d, *J* = 8.14, 1H), 7.86 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 110.8, 114.8, 119.3, 122.2, 126.1, 126.6, 127.4, 128.0, 128.5, 128.6, 130.1, 132.6, 132.8, 133.4, 135.2, 136.3; HRMS (ESI) calcd. for $C_{21}H_{18}N$ [M+H]: 284.1434, found: 284.1435.

5-tert-butyl-2,3-diphenyl-1H-indole (3da):



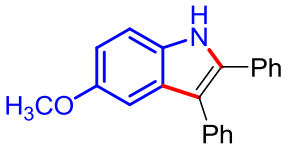
The title compound was prepared according to the general procedure as a white solid, 120.1 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 9H), 7.23-7.45 (m, 12H), 7.67 (s, 1H), 8.06 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.0, 34.8, 110.5, 115.2, 115.4, 121.2, 126.2, 127.6, 128.3, 128.5, 128.7, 128.7, 130.3, 133.0, 134.2, 134.5, 135.4, 143.6; HRMS (ESI) calcd. for $C_{24}H_{23}NNa$ [M+Na]: 348.1710, found: 348.1723.

6-tert-butyl-2,3-diphenyl-1H-indole (3ea):



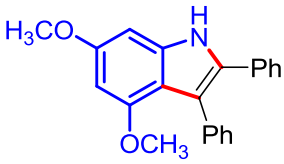
The title compound was prepared according to the general procedure as a white solid, 110.4 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 7.22-7.44 (m, 12H), 7.60 (d, J = 8.4 Hz, 1H), 8.13 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.8, 34.9, 107.2, 114.9, 118.8, 119.2, 126.1, 126.5, 127.5, 128.1, 128.5, 128.7, 130.1, 133.0, 133.9, 135.3, 136.1, 146.4; HRMS (EI) calcd. for $C_{24}H_{23}N$ [M]: 325.1830, found: 325.1833.

5-Methoxy-2,3-diphenyl-1H-indole (3fa):[5]



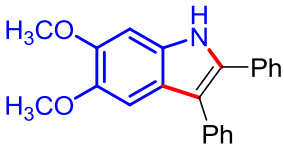
The title compound was prepared according to the general procedure as a white solid, 107.4 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.89 (dd, J_1 = 8.8 Hz, J_2 = 2.5 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.25-7.33 (m, 5H), 7.36-7.44 (m, 6H), 8.12 (b, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 101.3, 111.7, 113.0, 115.0, 126.2, 127.6, 128.1, 128.6, 128.7, 129.2, 130.1, 131.1, 132.8, 135.0, 135.2, 154.8; HRMS (ESI) calcd. for $C_{21}H_{18}NO$ [M+H]: 300.1383 found: 300.1384.

4,6-Dimethoxy-2,3-diphenyl-1H-indole (3ga):



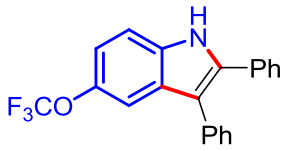
The title compound was prepared according to the general procedure as a white solid, 80.2 mg, 61% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.60 (s, 3H), 3.80 (s, 3H), 6.17 (d, J = 1.92 Hz, 1H), 6.56 (d, J = 1.92 Hz, 1H), 7.19-7.29 (m, 10H), 11.36 (br, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 54.9, 55.2, 86.8, 91.8, 112.2, 113.5, 125.7, 126.6, 127.2, 127.7, 128.2, 128.7, 131.1, 131.3, 131.6, 132.8, 136.4, 137.6,154.4, 156.9; HRMS (ESI) calcd. for $C_{22}H_{20}NO_2$ [M+H]: 330.1489, found: 330.1491.

5,6-Dimethoxy-2,3-diphenyl-1H-indole (3ha):[6]



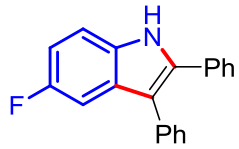
The title compound was prepared according to the general procedure as a white solid, 100.7 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 3.94 (s, 3H), 6.94 (s, 1H), 7.09 (s, 1H), 7.28-7.44 (m, 10H), 8.10 (br, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.7, 55.8, 94.9, 100.7, 113.3, 120.7, 125.9, 126.9, 127.7, 128.4, 128.7, 129.6, 130.6, 132.3, 132.8, 135.6, 145.1, 147.1. HRMS (EI) calcd. for $C_{22}H_{19}NO_2$ [M]: 329.1416, found: 329.1418.

2,3-Diphenyl-5-(trifluoromethoxy)-1H-indole (3ia):



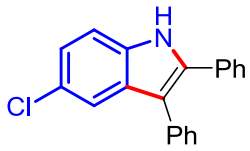
The title compound was prepared according to the general procedure as a white solid, 110.0 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98-7.01 (m, 1H), 7.17-7.29 (m, 11H), 7.42 (s, 1H), 8.13 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.5, 111.2, 114.3, 115.5, 116.0 (q, *J* = 254 Hz), 125.6, 127.1, 127.1, 127.5, 127.7, 127.7, 128.0, 128.9, 131.0, 133.1, 133.2, 135.0, 142.6, 142.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.88. HRMS (EI) calcd. for $C_{21}H_{14}F_3NO$ [M]: 353.1027, found: 353.1028.

5-Fluoro-2,3-diphenyl-1H-indole (3ja):[4]



The title compound was prepared according to the general procedure as a white solid, 87.3 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93-6.98 (m, 1H), 7.25-7.39 (m, 12H), 8.14 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.5 (d, *J* = 24 Hz), 110.9 (d, *J* = 27 Hz), 111.6 (d, *J* = 10 Hz), 115.2 (d, *J* = 5 Hz), 126.5, 128.0, 128.2, 128.7, 128.8, 129.2 (d, *J* = 10 Hz), 130.0, 132.4 (d, *J* = 4 Hz), 134.7, 135.9, 157.4 (d, *J* = 34 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.45. HRMS (EI) calcd. for $C_{20}H_{14}FN$ [M]: 287.1110, found: 287.1098.

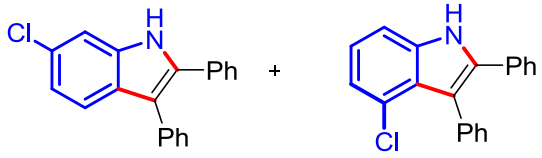
5-Chloro-2,3-diphenyl-1H-indole (3ka):[4]



The title compound was prepared according to the general procedure as a white solid, 109.7 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J_1 = 8.6 Hz, J_2 = 2.04 Hz, 1H), 7.27-7.34 (m, 5H), 7.35-7.41 (m, 6H), 7.62-7.63 (m, 1H), 8.21 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.9, 114.8, 119.2, 123.0, 126.2, 126.6, 128.1, 128.1, 128.7, 128.8, 129.9, 130.0, 132.2, 134.2, 134.4, 135.4. HRMS (EI) calcd. for $C_{20}H_{14}ClN$ [M]: 303.0815, found: 303.0813.

4-Chloro-2,3-diphenyl-1H-indole (3la) and

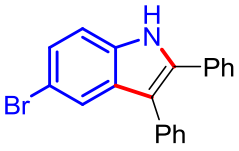
6-Chloro-2,3-diphenyl-1H-indole (3la') (1.08:1, Determined by NMR**):**[4]



The title compound was prepared according to the general procedure as a white solid, 59.2 mg, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 1.88 Hz, 0.48H), 7.11 (d, *J* = 1.88 Hz, 0.52H), 7.27-7.41 (m, 11H), 7.54 (s, 0.51H), 7.57 (s, 0.49H), 8.19 (br, 0.95H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.8, 115.1, 120.6, 121.2,

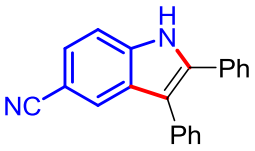
126.5, 127.4, 128.0, 128.1, 128.4, 128.7, 128.8, 130.1, 132.2, 134.5, 134.6, 136.2; HRMS (EI) calcd. for $C_{20}H_{14}ClN$ [M]: 303.0815, found: 303.0813.

5-Bromo-2,3-diphenyl-1H-indole (3ma):[5]



The title compound was prepared according to the general procedure as a white solid, 125.9 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.33 (m, 6H), 7.38-7.41 (m, 6H), 7.77 (t, *J* = 0.76 Hz, 1H), 8.24 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.3, 113.7, 114.7, 122.2, 125.5, 126.6, 128.1, 128.1, 128.7, 128.8, 130.1, 130.6, 132.1, 134.3, 134.5, 135.2. HRMS (EI) calcd. for $C_{20}H_{14}BrN$ [M]: 347.0310, found: 347.0308.

2,3-Diphenyl-1H-indole-5-carbonitrile (3na):[7]



The title compound was prepared according to the general procedure as a white solid, 36.0 mg, 31% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33-7.49 (m, 10H), 7.52-7.55 (m, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.90 (m, 1H), 12.21 (br, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 101.8, 112.8, 113.8, 120.5, 124.1, 124.7, 126.7, 127.7, 128.2, 128.3, 128.6, 128.8, 129.7, 131.4, 133.8, 136.6, 137.8; HRMS (ESI) calcd. for $C_{21}H_{15}N_2$ [M+H]: 295.1230, found: 295.1233.

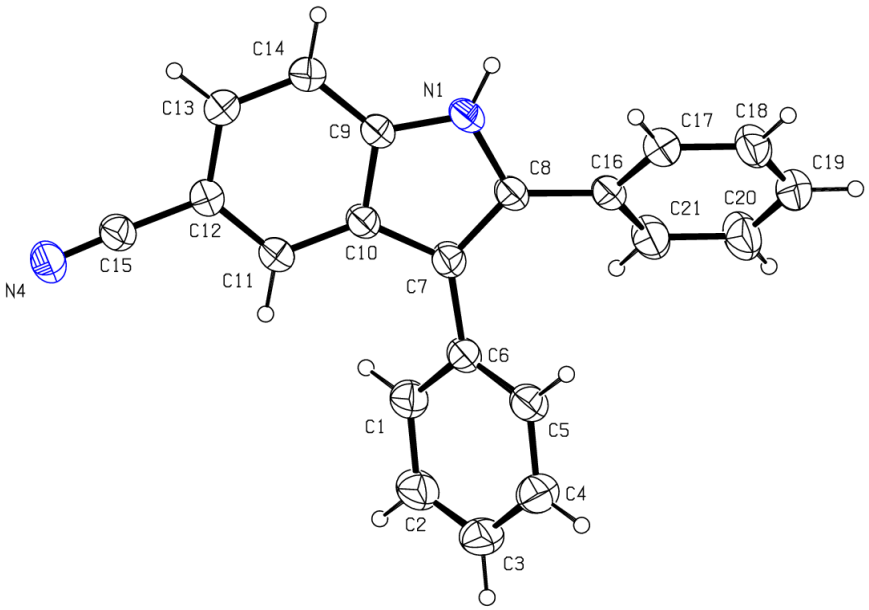
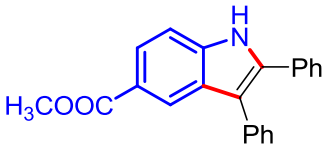


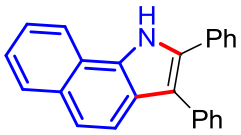
Figure S1. ORTEP drawing of product **3ma**

Methyl 2,3-diphenyl-1H-indole-5-carboxylate (3oa):[7]



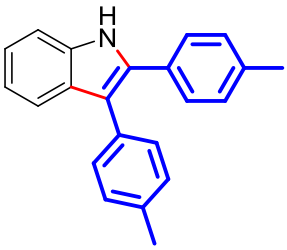
The title compound was prepared according to the general procedure as a white solid, 79.1 mg, 60% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.83 (s, 3H), 7.33-7.50 (m, 10H), 7.54 (d, J = 8.52, 1H), 7.81-7.84 (m, 1H), 8.15 (d, J = 1.36 Hz, 1H), 12.03 (br); ^{13}C NMR (100 MHz, DMSO-d_6) δ 51.7, 111.5, 114.5, 121.1, 121.1, 123.0,126.6, 127.7, 128.0, 128.2, 128.6, 128.8, 129.8, 131.8, 134.5, 135.8, 138.6, 167.1; HRMS (ESI) calcd. for $C_{22}H_{18}NO_2$ [M+H]: 328.1332, found: 328.1344.

2,3-Diphenyl-1H-benzo[g]indole (3pa):



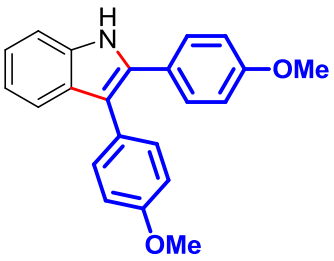
The title compound was prepared according to the general procedure as a white solid, 78.6 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.55 (m, 13H), 7.72 (d, J = 8.68, 1H), 7.91 (d, J = 8.04, 1H), 8.02 (d, J = 8.16, 1H), 8.87 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.9, 119.4, 119.5, 121.3, 121.5, 124.2, 124.6, 125.7, 126.4, 127.5, 128.1, 128.6, 128.8, 129.0, 130.3, 130.8, 132.5, 132.8, 135.0; HRMS (EI) calcd. for $C_{24}H_{17}N$ [M]: 319.1361, found: 319.1365.

2,3-Di-*p*-tolyl-1H-indole (3ab):[5]



The title compound was prepared according to the general procedure as a white solid, 96.0 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.28 (s, 3H), 6.99-7.13 (m, 6H), 7.18-7.26 (m, 5H), 7.56 (d, J = 7.96, 1H), 7.95 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 110.9, 114.6, 119.7, 120.4, 122.5, 128.1, 129.0, 129.4, 129.5, 130.0, 130.1, 132.2, 134.1, 135.8, 135.9, 137.6; HRMS (ESI) calcd. for $C_{22}H_{20}N$ [M+H]: 298.1590, found: 298.1595.

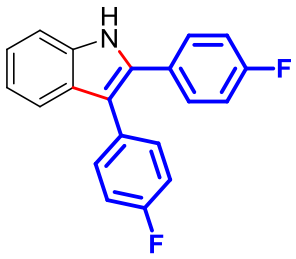
2,3-Bis(4-methoxyphenyl)-1H-indole (3ac):[5]



The title compound was prepared according to the general procedure as a white solid, 111.8 mg, 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.77 (s, 3H), 3.79 (s, 3H), 6.93-7.04 (m, 5H), 7.11-7.15 (m, 1H), 7.25-7.28 (m, 2H), 7.39-7.44 (m, 4H), 11.39 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 55.3, 110.7, 113.8, 114.0, 114.2, 119.5, 120.2, 122.3, 125.3, 127.6,

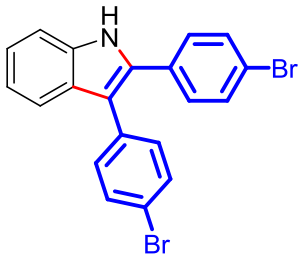
129.0, 129.3, 131.2, 133.7, 135.7, 158.7, 159.1; HRMS (ESI) calcd. for $C_{22}H_{20}NO_2$ [M+H]: 330.1489, found: 330.1487.

2,3-Bis(4-fluorophenyl)-1H-indole (3ad):[5]



The title compound was prepared according to the general procedure as a white solid, 93.0 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98-7.08 (m, 4H), 7.13-7.17 (m, 1H), 7.21-7.26 (m, 1H), 7.31-7.39 (m, 5H), 7.60 (d, *J* = 8.00, 1H), 8.12 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.0, 114.0, 115.5, 115.7 (d, *J* = 7 Hz), 116.0, 119.5, 120.7, 122.9, 128.6, 129.9, 130.0 (d, *J* = 8 Hz), 131.5 (d, *J* = 8 Hz), 133.2, 135.8, 160.4, 161.2 (d, *J* = 246 Hz), 162.9 (d, *J* = 244 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.2, -113.3; HRMS (EI) calcd. for $C_{20}H_{13}F_2N$ [M]: 305.1013, found: 305.1008.

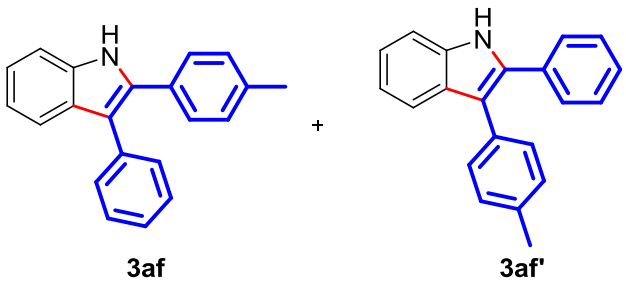
2,3-Bis(4-bromophenyl)-1H-indole (3ae):[5]



The title compound was prepared according to the general procedure as a white solid, 128.4 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.84, 1H), 7.24-7.29 (m, 5H), 7.40-7.51 (m, 5H), 7.61 (d, *J* = 7.96 Hz, 1H), 8.18 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.1, 114.3, 119.5, 120.4, 120.9, 122.1, 123.3, 128.4, 129.7, 131.3, 131.7, 131.9, 132.1, 133.1, 133.7, 136.0.HRMS (EI) calcd. for $C_{20}H_{13}Br_2N$ [M]: 424.9415, found: 424.9426.

2-Phenyl-3-*p*-tolyl-1H-indole (3af) and

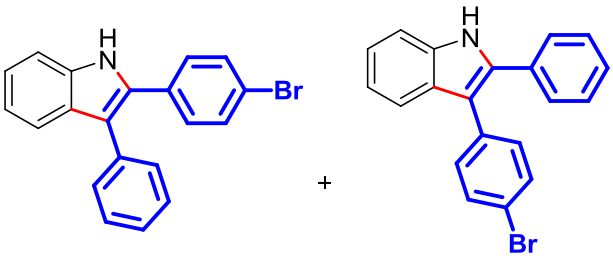
3-Phenyl-2-*p*-tolyl-1H-indole (3af') (1.14:1, Determined by NMR):[8]



The title compound was prepared according to the general procedure as a white solid, 90.0 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 1.36H), 2.36 (s, 1.64H), 7.07-7.44 (m, 12H), 7.65 (d, *J* = 7.92 Hz, 1H), 8.08 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 110.8, 119.6, 119.8, 120.4, 122.5, 122.7, 126.2, 127.6, 128.0, 128.1, 128.5, 128.7, 128.8, 129.3, 129.4,

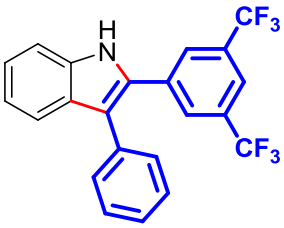
130.0, 130.2, 132.0, 132.8, 134.2, 135.8, 135.9, 137.6; HRMS (ESI) calcd. for $C_{21}H_{18}N$ [M+H]: 284.1434, found: 284.1436.

2-(4-Bromophenyl)-3-phenyl-1H-indole (3ag) and 3-(4-Bromophenyl)-2-phenyl-1H-indole (3ag') (1:1 Determined by NMR)**:**[7]



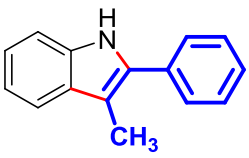
The title compound was prepared according to the general procedure as a white solid, 86.6 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.18 (m, 1H), 7.23-7.50 (m, 11H), 7.63-7.67 (m, 1H), 8.17 (br, 0.48H), 8.24 (br, 0.45H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.0, 111.0, 113.8, 115.7, 119.4, 119.8, 120.2, 120.6, 120.7, 121.8, 122.9, 123.1, 126.5, 128.0, 128.2, 128.4, 128.7, 128.7, 128.9, 129.6, 130.1, 131.6, 131.7, 131.9, 132.4, 132.8, 134.1, 134.4, 134.7, 135.9, 136.0; HRMS (ESI) calcd. for $C_{20}H_{18}N_2Br$ [M+NH_4]: 365.0648, found: 365.0634.

2-(4-Bromophenyl)-3-phenyl-1H-indole (3ah):



The title compound was prepared according to the general procedure as a white solid, 124.0 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.12 (m, 1H), 7.20-7.38 (m, 7H), 7.58 (d, *J* = 7.96 Hz, 1H), 7.66 (s, 1H), 7.72 (s, 2H), 8.21 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.2, 117.9, 120.3, 120.7 (heptet, *J* = 4 Hz), 121.1, 121.7 (q, *J* = 271 Hz), 124.0, 127.3, 127.7, 128.6, 129.0, 130.0, 130.5, 131.5 (q, *J* = 33 Hz), 133.7, 134.8, 136.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.2; HRMS (EI) calcd. for $C_{22}H_{13}F_6N$ [M]: 405.0952, found: 405.0945.

3-Methyl-2-phenyl-1H-indole (3ai):[8]

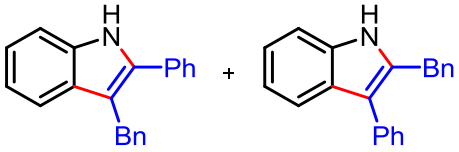


The title compound was prepared according to the general procedure as a white solid, 43.0 mg, 52% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.43 (s, 3H), 7.01-7.05 (m, 1H), 7.10-7.14 (m, 1H), 7.35-7.39 (m, 2H), 7.50-7.55 (m, 3H), 7.68-7.70 (m, 2H), 11.17 (br, 1H); ^{13}C

NMR (100 MHz, DMSO-d_6) δ 9.8, 106.7, 111.0, 118.4, 118.5, 121.5, 126.9, 127.5, 128.7, 129.4, 133.1, 133.7, 135.9; HRMS (ESI) calcd. for $C_{15}H_{14}N$ [M+H]: 208.1121, found: 208.1125.

3-Benzyl-2-phenyl-1H-indole (3aj) and

2-benzyl-3-phenyl-1H-indole (3aj') (12:1 Determined by NMR**):**[8]

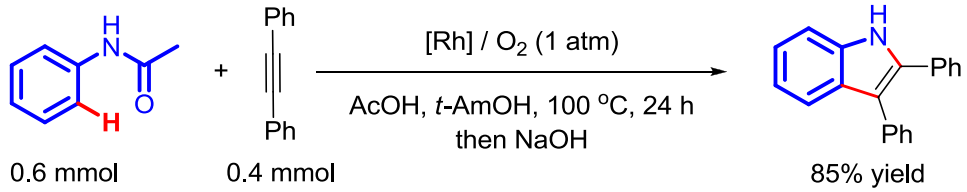


3aj **3aj'**

The title compound was prepared according to the general procedure as a white solid, 57.2 mg, 50% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.19 (s, 0.15H), 4.24 (s, 1.85H), 6.94-6.98 (m, 0.92H), 7.01-7.04 (m, 0.09H), 7.09-7.18 (m, 3.84H), 7.22-7.27 (m, 1.91H), 7.29-7.31 (m, 0.17H), 7.35-7.41 (m, 2.83H), 7.46-7.50 (m, 2.07H), 7.53-7.55 (m, 0.09H), 7.60-7.62 (m, 1.93H), 7.66-8.24 (m, 0.28H), 11.22 (br, 0.07H), 11.33 (br, 0.90); ^{13}C NMR (100 MHz, DMSO-d_6) δ 29.9, 109.7, 111.2, 118.7, 118.8, 121.6, 125.7, 127.4, 127.5, 127.9, 128.3, 128.6, 128.7, 128.8, 132.7, 134.9, 136.1, 141.5; HRMS (ESI) calcd. for $C_{21}H_{18}N$ [M+H]: 284.1428, found: 284.1434.

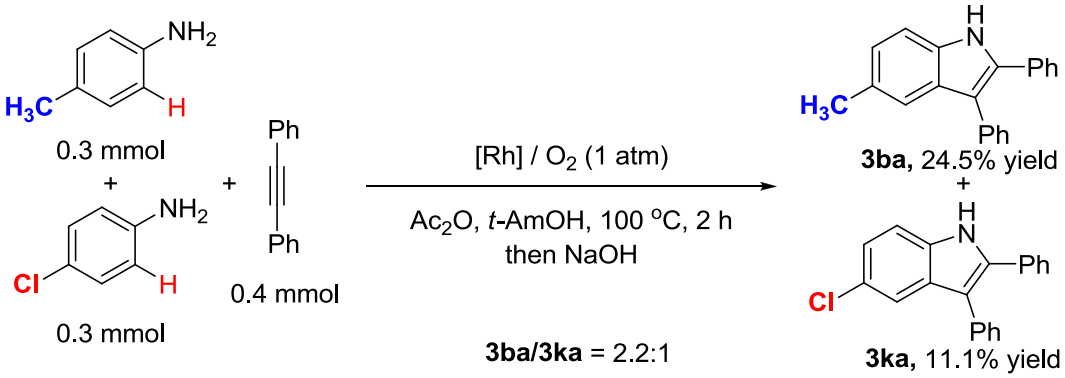
5. Mechanistic studies

5.1 Rh/O_2 catalytic system catalyzed aerobic C-H activation



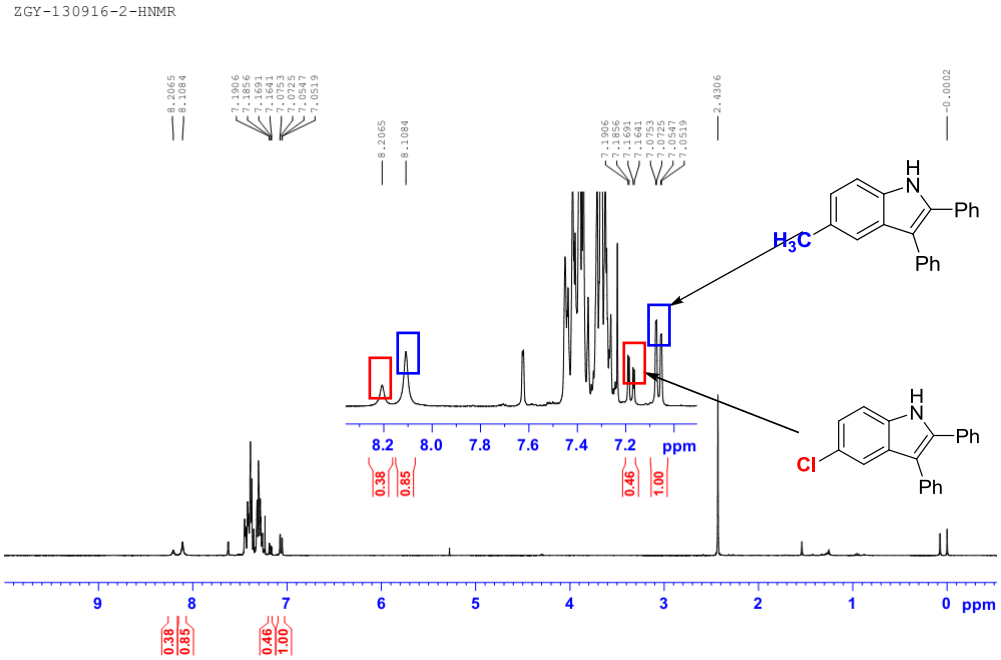
Following our general procedure: 1,2-diphenylethyne **2a** (71.3 mg, 0.4 mmol), Cp*Rh$(H_2O)_3(OTf)_2$ (11.8 mg, 0.02 mmol, 5 mol%), acetanilide (81.1mg, 0.6 mmol), *t*-AmOH (2.0 mL) and AcOH (35 μL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at 100 °C for 24 hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH_3OH (2.0 mL) were added into the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product **3aa** in 85% yield (91.2 mg).

5.2 Substrate Competition Experiments

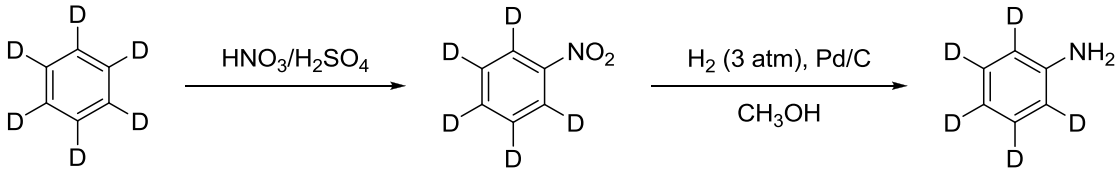


Following our general procedure: 1,2-diphenylethyne **2a** (71.3 mg, 0.4 mmol), Cp*Rh$(H_2O)_3(OTf)_2$ (11.8 mg, 0.02 mmol, 5 mol%), *p*-toluidine **1b**, (32.2mg, 0.3 mmol), 4-chloroaniline **1k** (38.3 mg, 0.3 mmol), *t*-AmOH (2.0 mL) and Ac_2O (57.0 μL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of oxygen, and then stirred at 100 °C for two hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH_3OH (2.0 mL) were added into the reaction mixture, and then stirred

at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired products **3ba** (24.5% yield) and **3ka** (11.1% yield), respectively.



5.3 Synthesis of aniline (D$_5$-1a'):[9]



Synthesis of D$_5$-nitrobenzene:

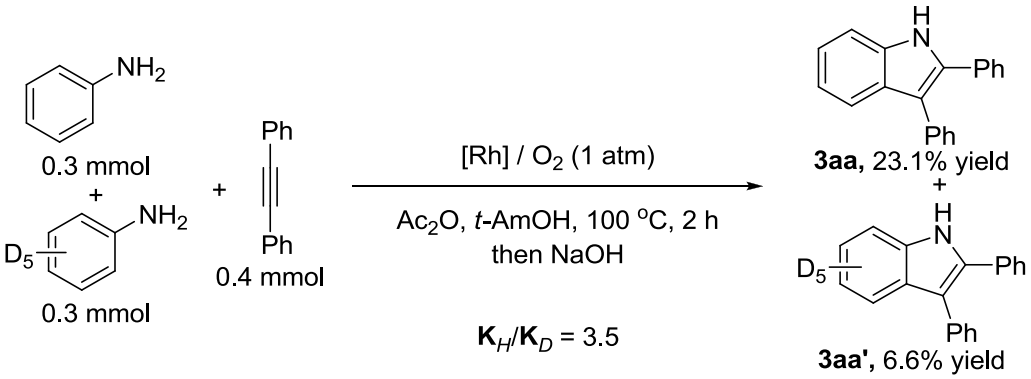
Concentrated nitric acid (12.0 mL) and concentrated sulfuric acid (13.6 mL) were mixed together in a 250 mL round-bottom flask held in 30-50 ^{o}C. Benzene-*d*$_6$ (10.0 mL, 112 mmol) was added drop-wise at 80 ^{o}C and the mixture was allowed to stir at 60 ^{o}C for an additional 45 minutes. Then the reaction mixture was poured into ice-water (100 mL) and extracted with DCM (3×50 mL). The combined organic layer was washed with ice water (2×50 mL), sat. aq. $NaHCO_3$ solution (2×50 mL), brine (2×40 mL), and dried with anhydrous Na_2SO_4 for 24 hours. After distilling, faint yellow oil of D$_5$-nitrobenzene was obtained in 81 % yield, (11.7 g).

Synthesis of D$_5$-aniline (D$_5$-1a'):

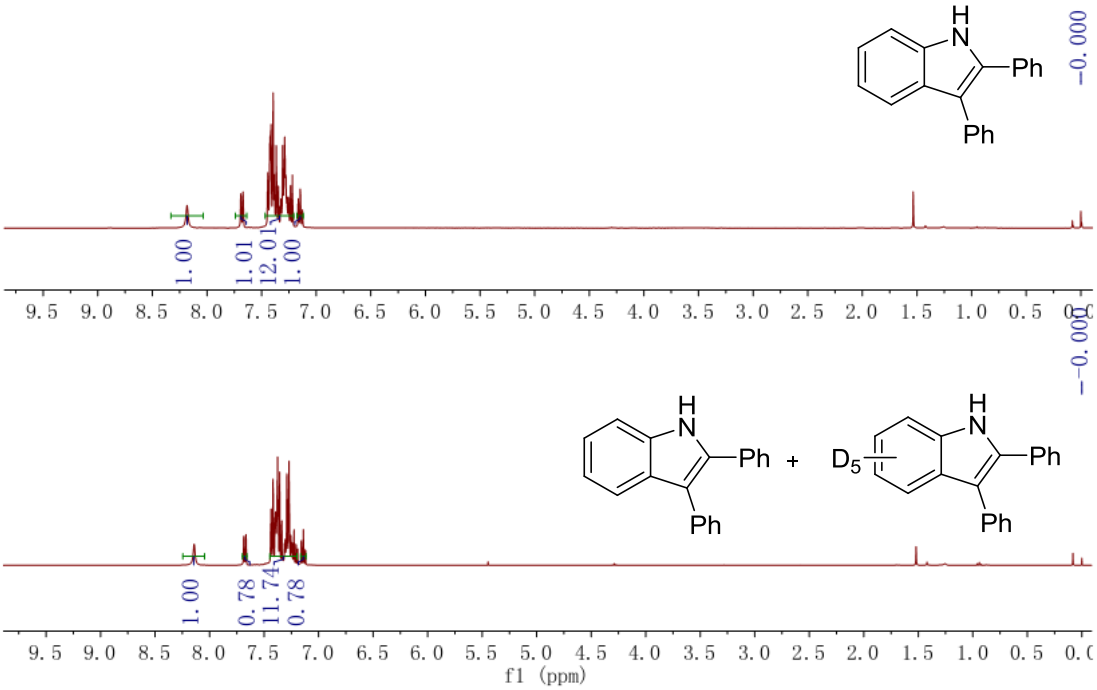
D$_5$-nitrobenzene (2.55 g), Pd/C (200 mg), MeOH (5 mL) were added to a teflon tube which was placed in an autoclave. Then the autoclave was purged and charged with H_2

at 3 atm. The reaction mixture was stirred at room temperature for 16 hours, and then H_2 was carefully released. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the colorless oil desired product D_5-aniline in 92 % yield (1.8 g).

5.4 Experimental detail for determination of the intramolecular KIE



Following our general procedure: 1,2-diphenylethyne (71.3 mg, 0.4 mmol), $Cp^*Rh(H_2O)_3(OTf)_2$ (11.8 mg, 0.02 mmol, 5 mol%), D_5-aniline (29.4 mg, 0.3 mmol), aniline (27.5 mg, 0.3 mmol), *t*-AmOH (2.0 mL) and Ac_2O (57.0 μL, 0.6 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of O_2, and then stirred at 100 ^oC for two hours. After cooling to room temperature, NaOH (48.0 mg, 1.2 mmol) and CH_3OH (2.0 mL) were added into the reaction mixture, and then stirred at room temperature for another one hour. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired products **3aa** (23.1% yield) and **3aa'** (6.6 % yield), respectively.


H
N
Ph
Ph
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1.00
1.01
12.01
1.00
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 1.0 0.5 0.0
-0.000
H
N
Ph
Ph
+
D5
H
N
Ph
Ph
1.00
0.78
11.74
0.78
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 1.0 0.5 0.0
f1 (ppm)

6. References

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6 J.-D. Charrier, C. Landreau, D. Deniaud, F. Reliquet, A. Reliquet and J. C. Meslin, *Tetrahedron*, 2001, **57**, 4195.

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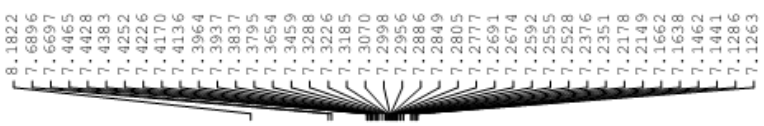
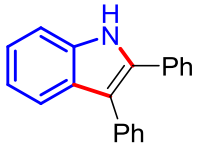
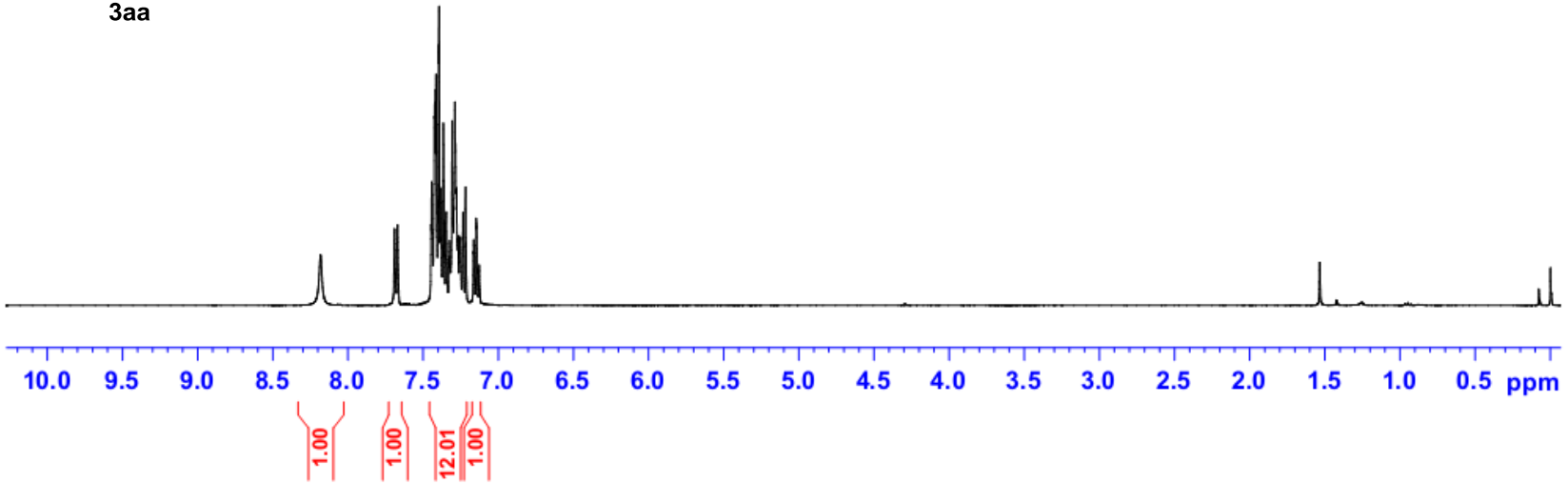
7. Copies for ^{1}H NMR and ^{13}C NMR of the indole products

911-9-ZhangCY-HNMR

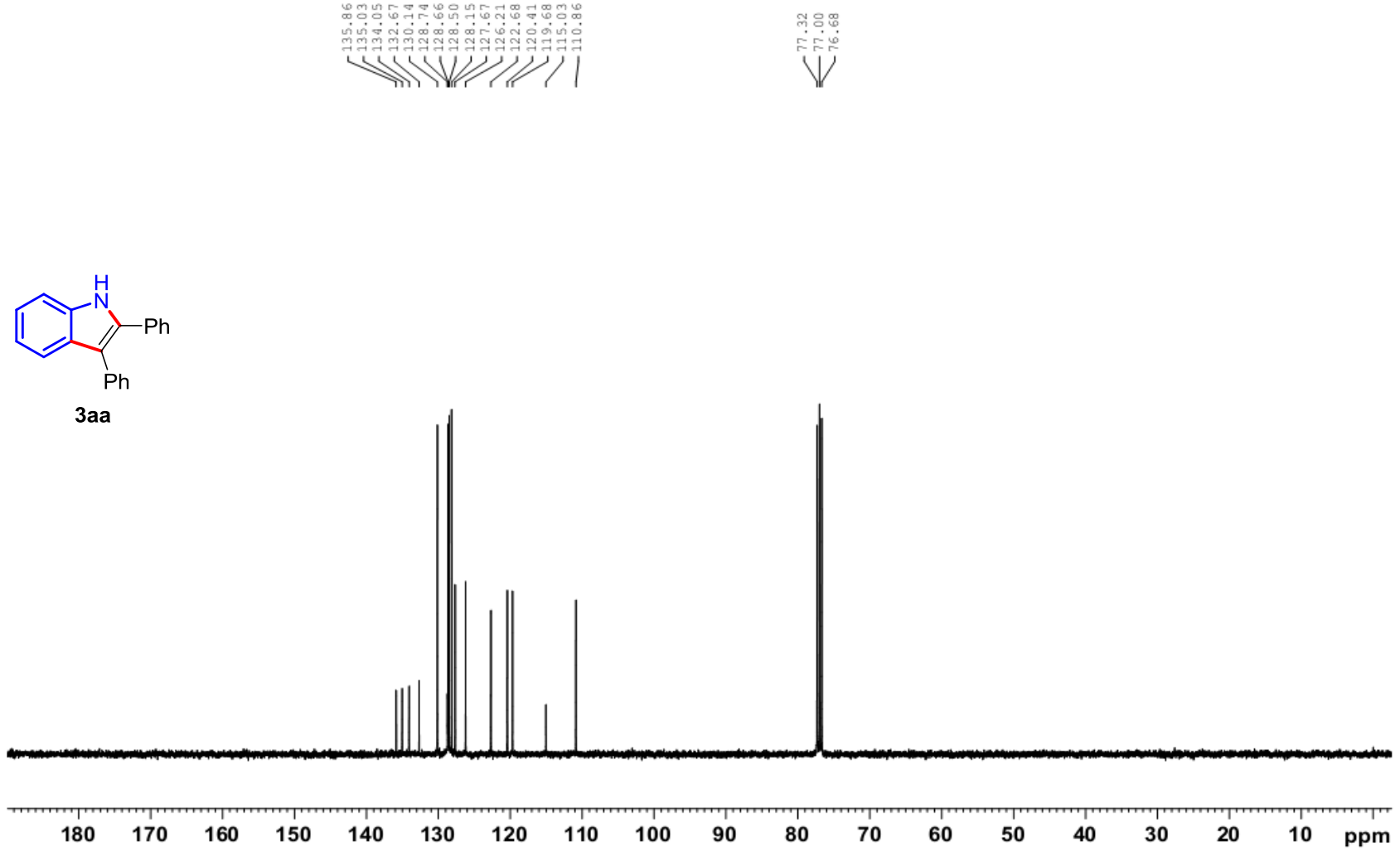




3aa

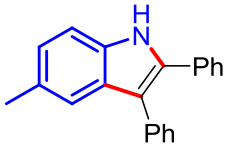


130911-9-ZhangCY-CNMR(18)



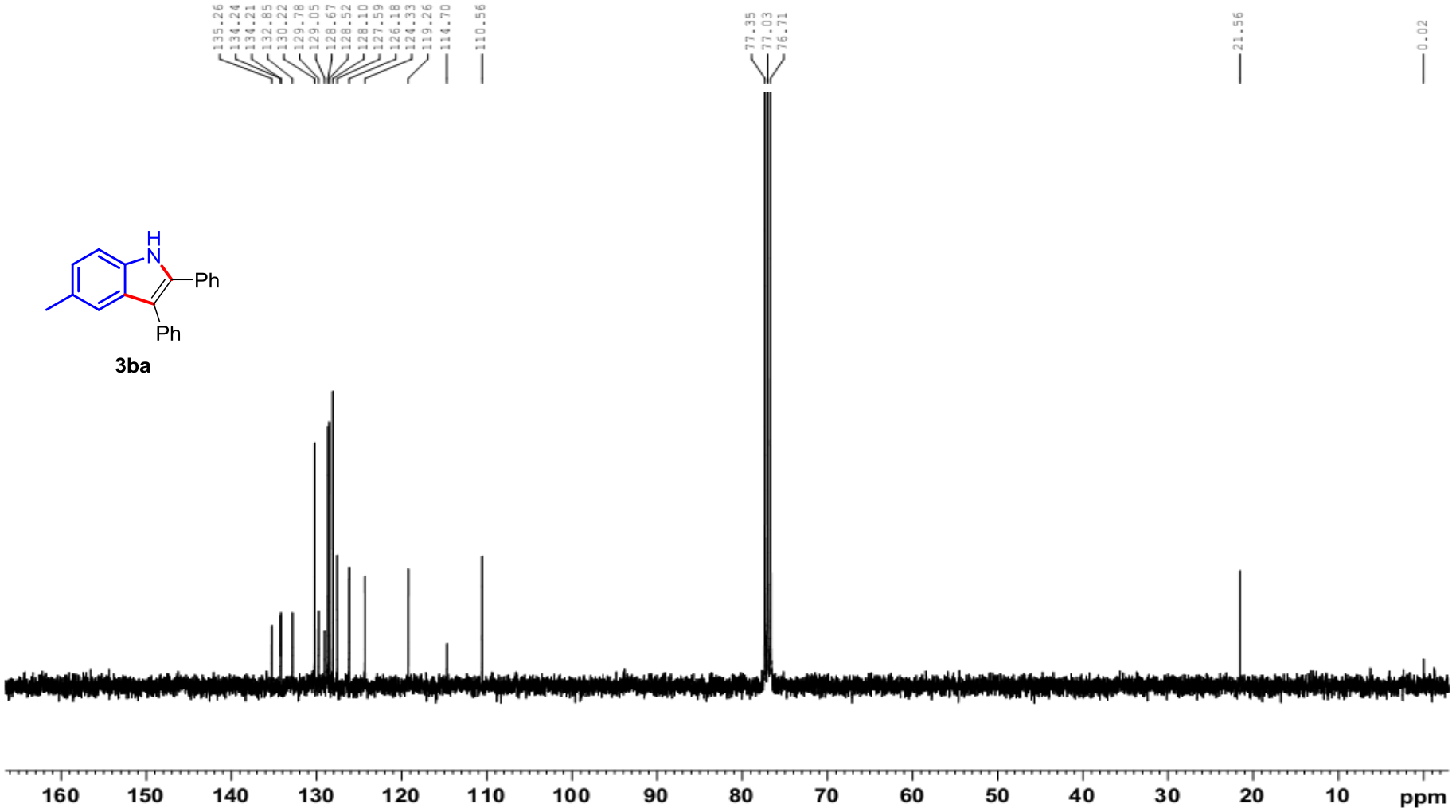
3aa

ZGY-130826-3-HNMR



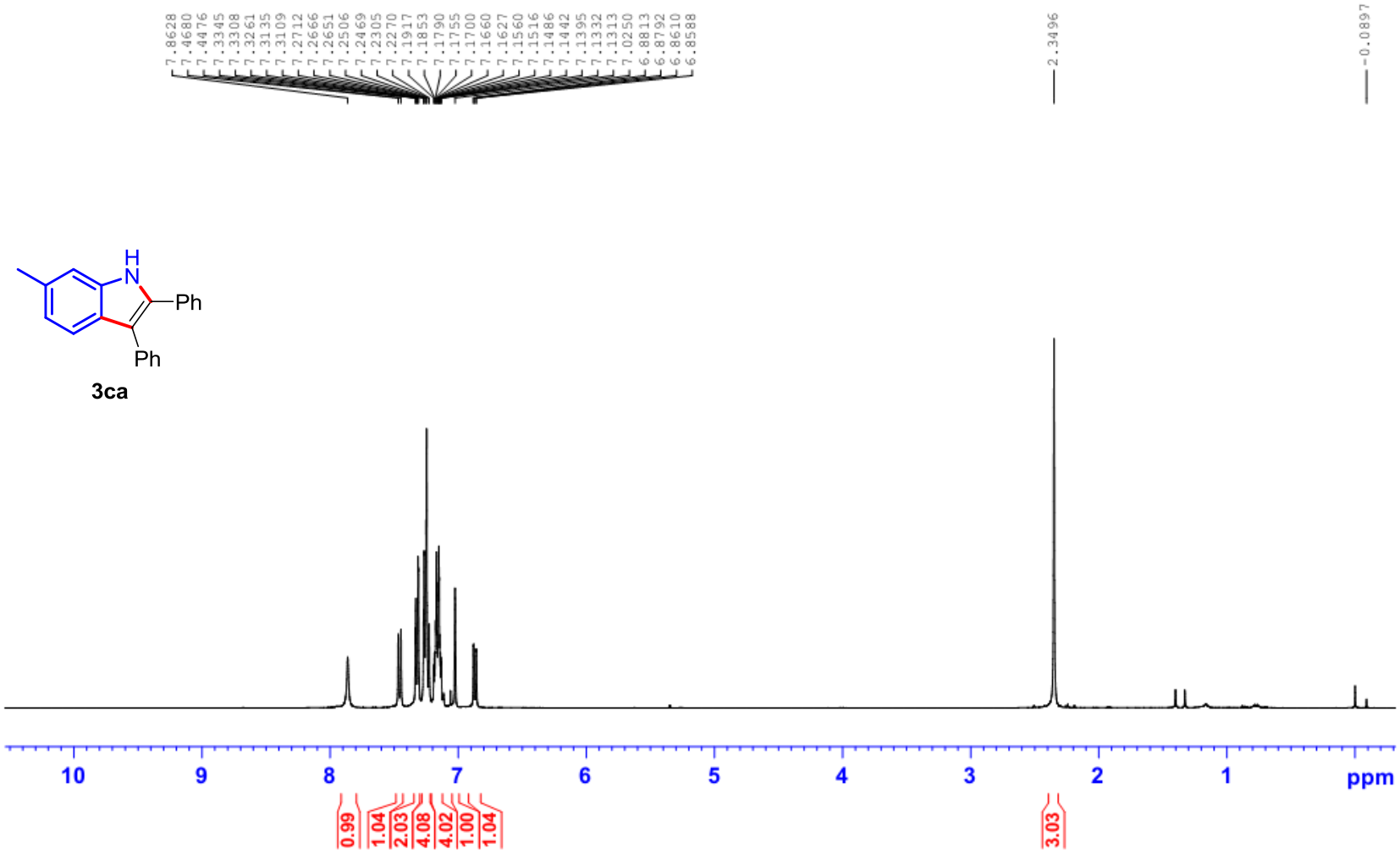
3ba

ZGY-130826-3-CNMR

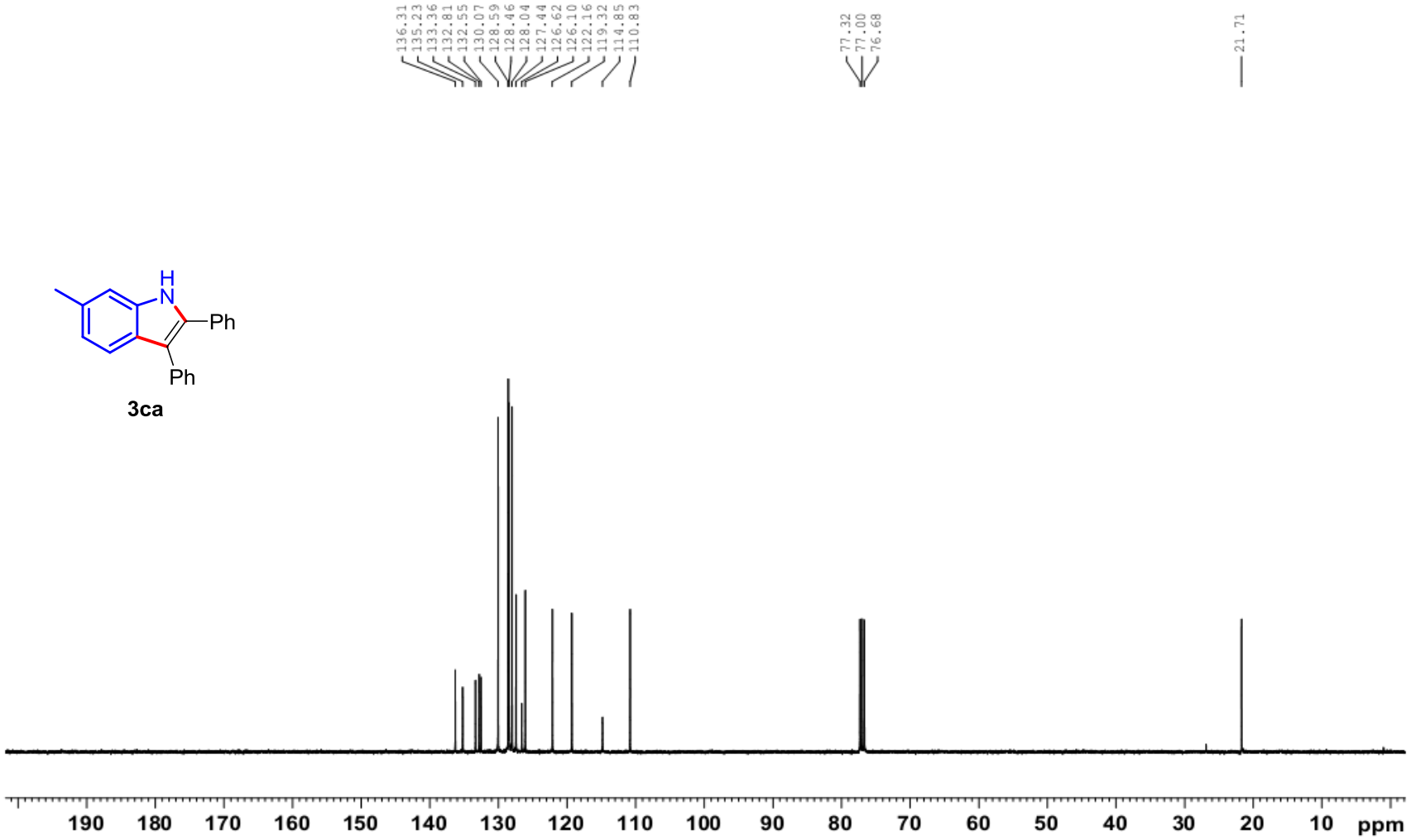


3ba

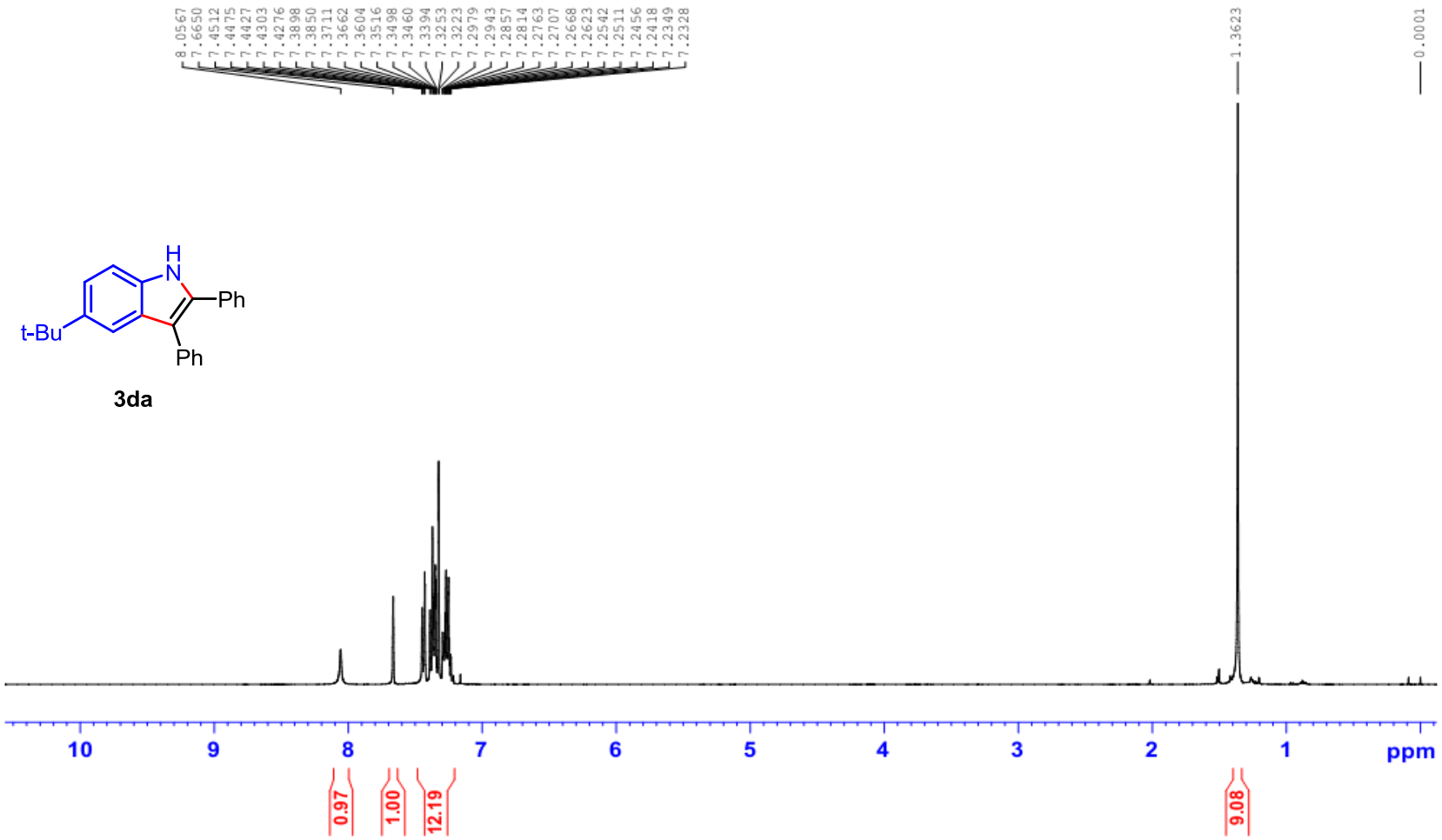
911-6-ZhangCY-HNMR



130911-6-ZhangCY-CNMR(12)

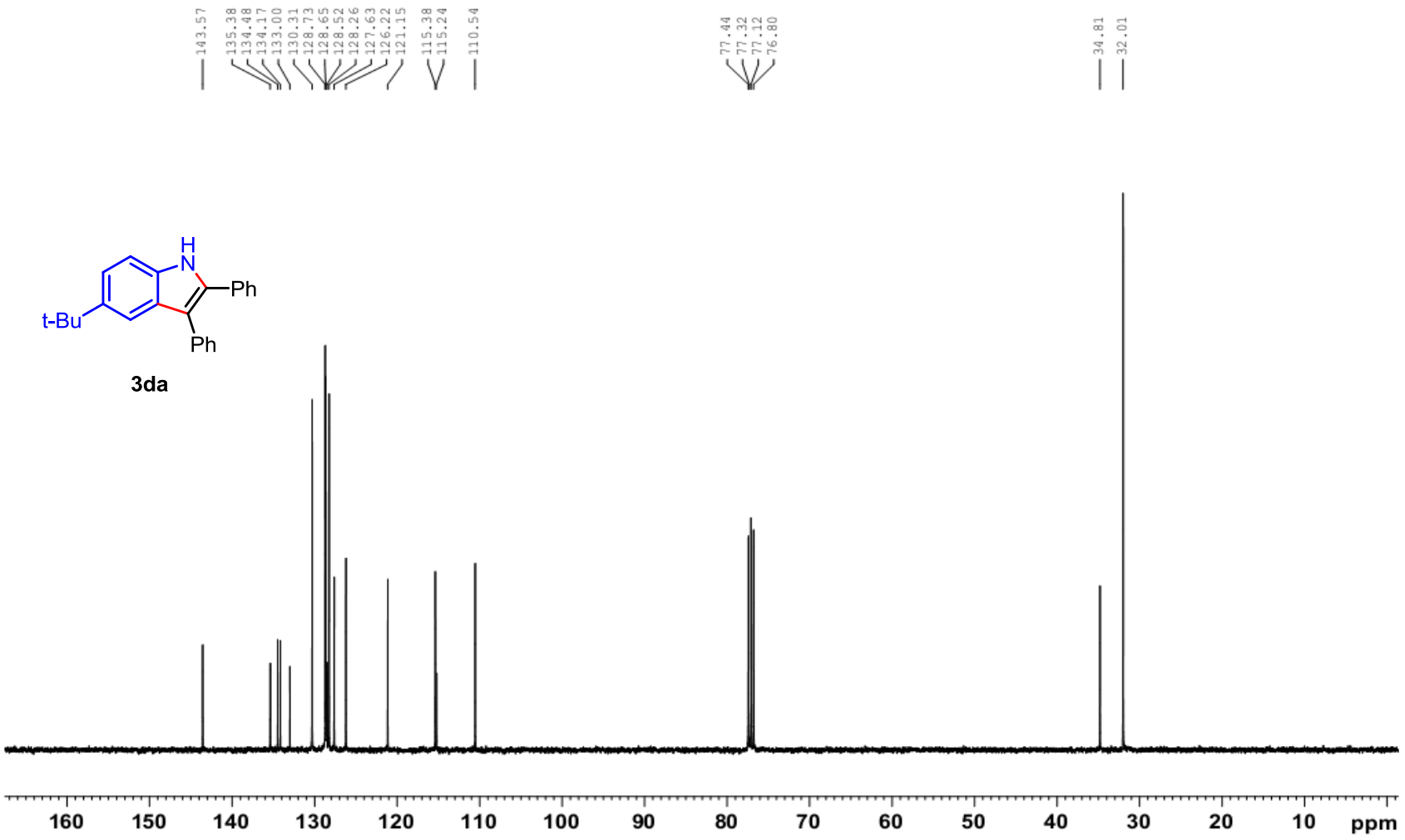


ZGY-131104-1-HNMR

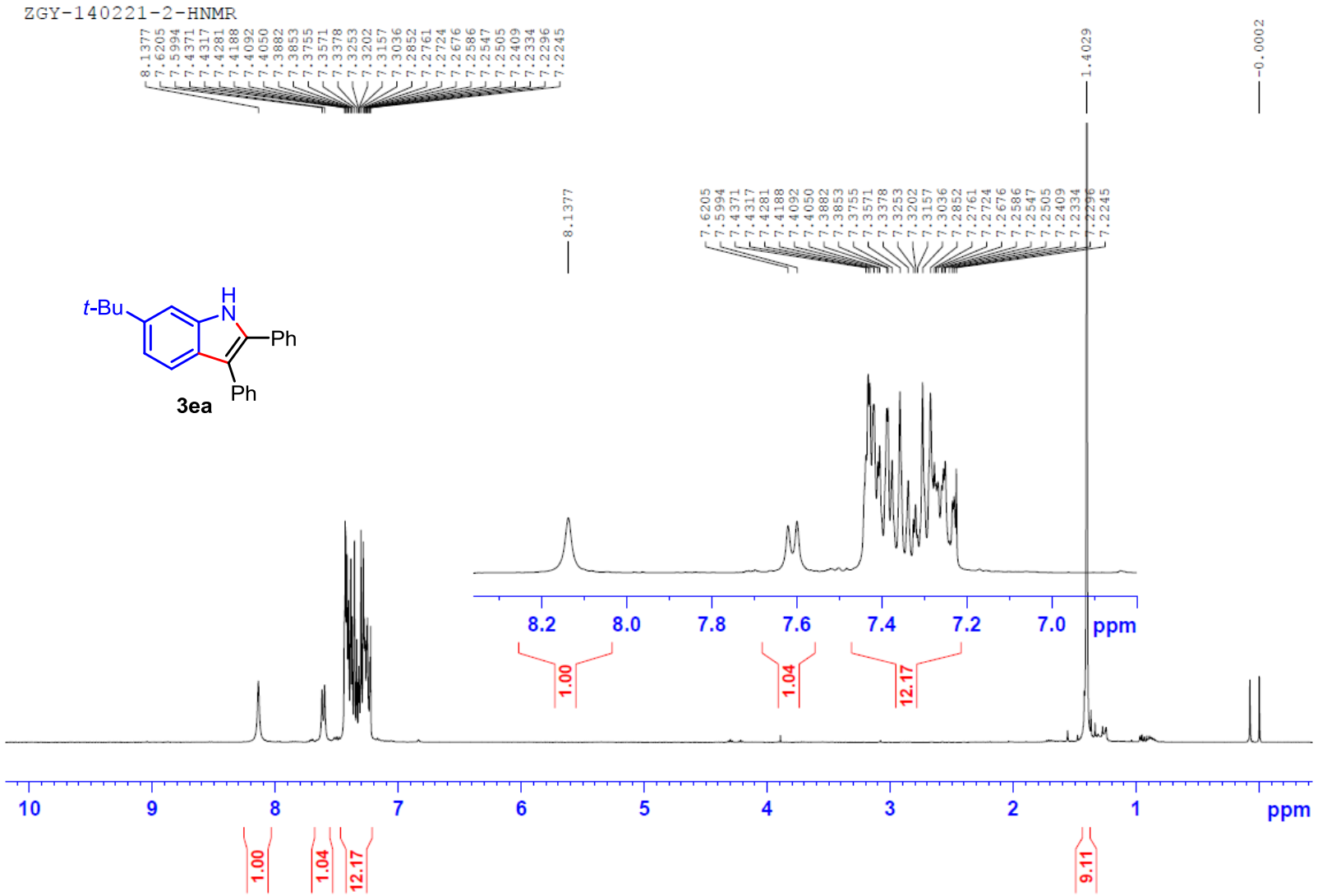


3da

ZGY-131104-1-CNMR



3da


ZGY-140221-2-HNMR
8.1377
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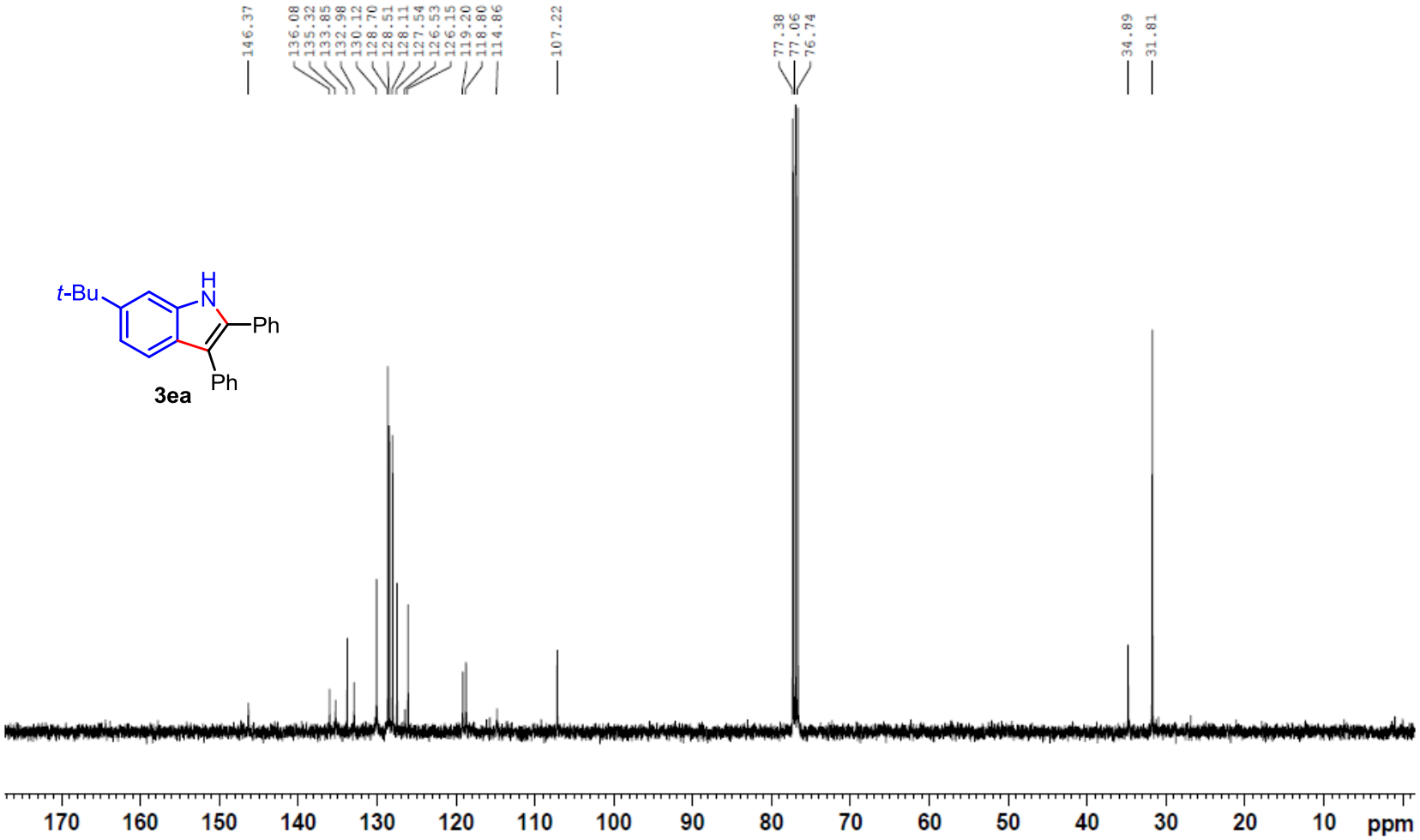
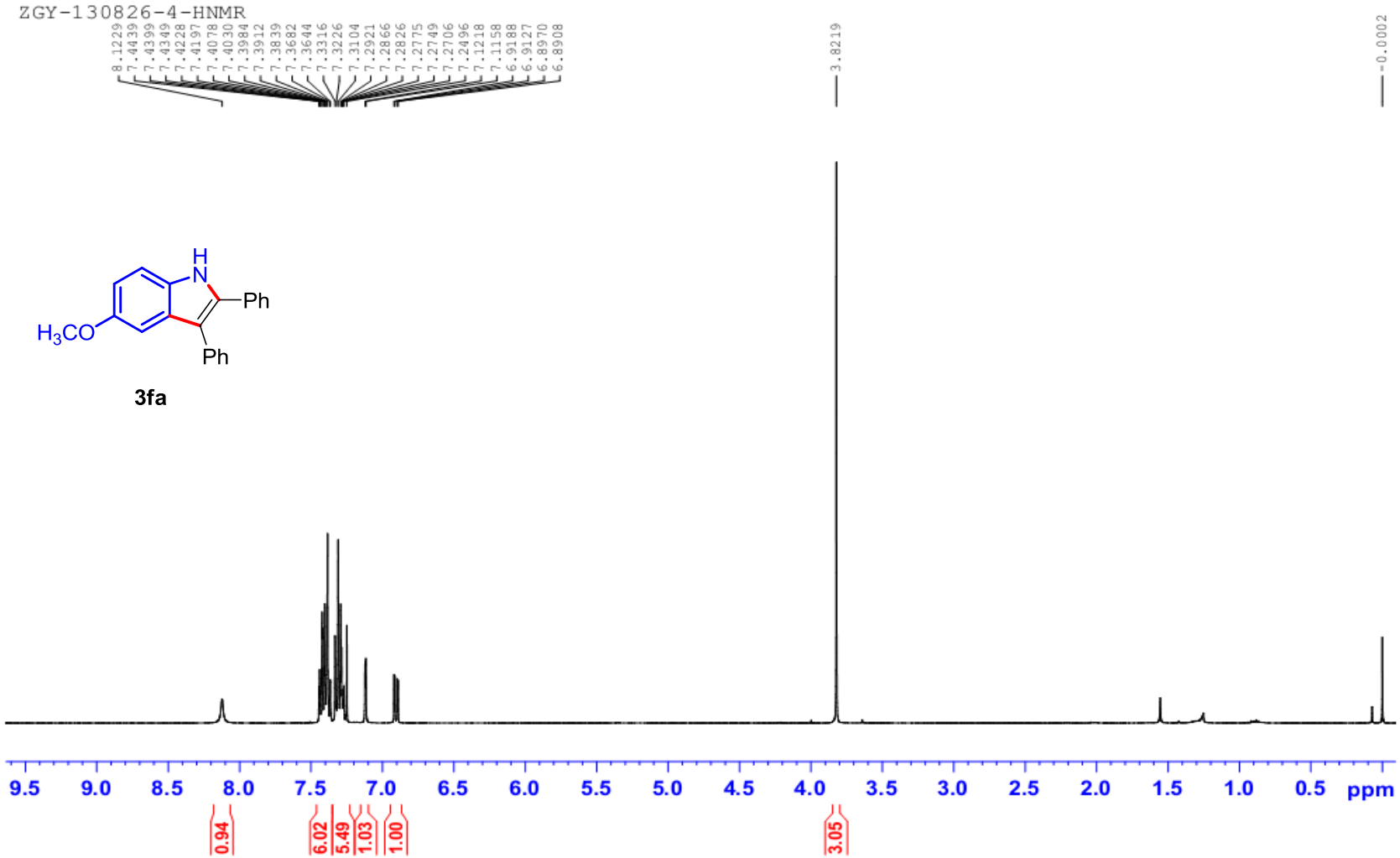
7.5994
7.4371
7.4317
7.4281
7.4188
7.4092
7.4050
7.3882
7.3853
7.3755
7.3571
7.3378
7.3253
7.3202
7.3157
7.3036
7.2852
7.2761
7.2724
7.2676
7.2586
7.2547
7.2505
7.2409
7.2334
7.2296
7.2245
1.4029
-0.0002
t-Bu
H
N
Ph
Ph
3ea
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.00
1.04
12.17
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.04
12.17
9.11

ZGY-140221-2-CNMR




ZGY-130826-4-HNMR
8.1229
7.4439
7.4399
7.4349
7.4228
7.4197
7.4078
7.4030
7.3984
7.3912
7.3839
7.3682
7.3644
7.3316
7.3226
7.3104
7.2921
7.2866
7.2826
7.2775
7.2749
7.2706
7.2496
7.1218
7.1158
6.9188
6.9127
6.8970
6.8908
3.8219
-0.0002
H
N
Ph
Ph
H3CO
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
1.0
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ppm
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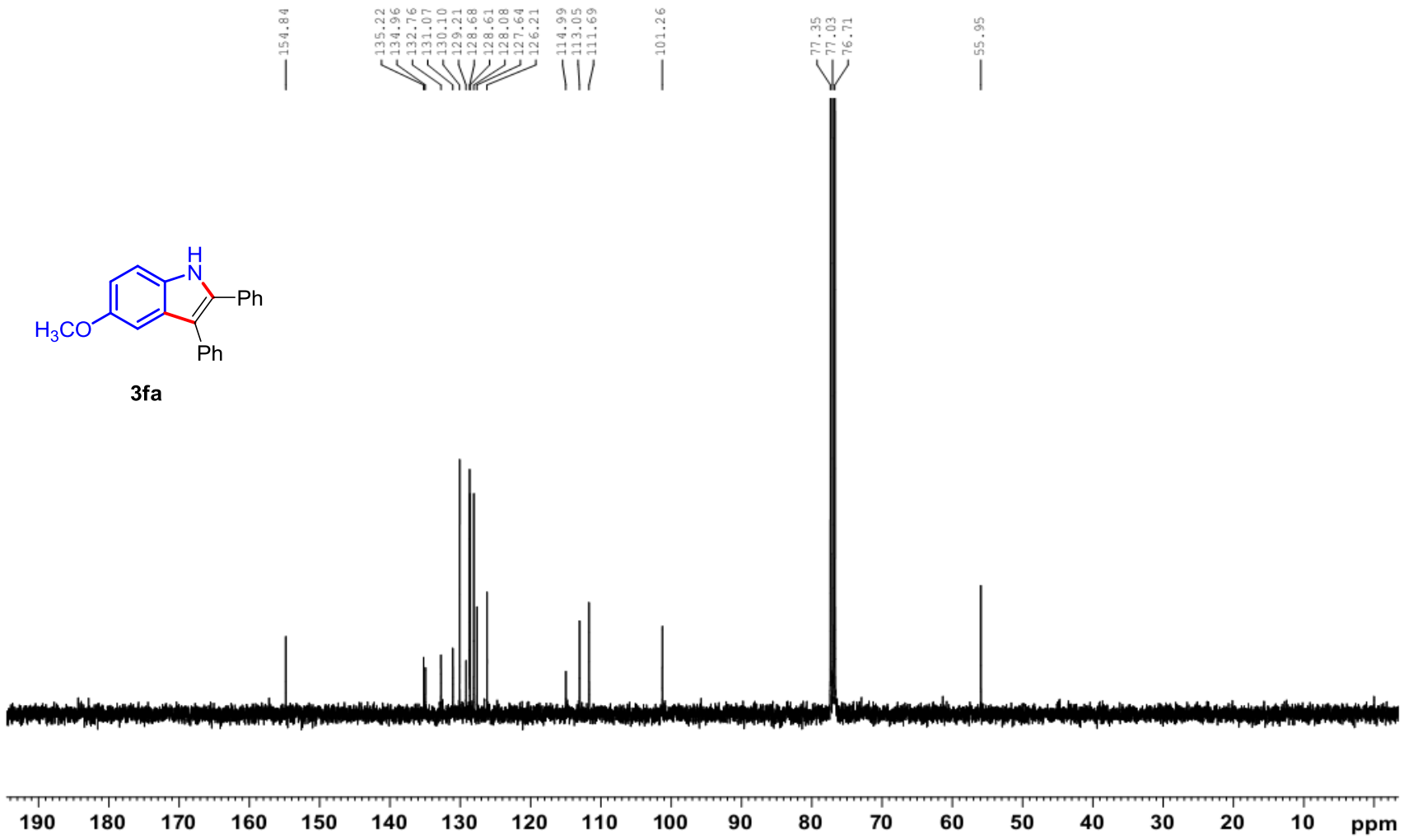
6.02
5.49
1.03
1.00
3.05

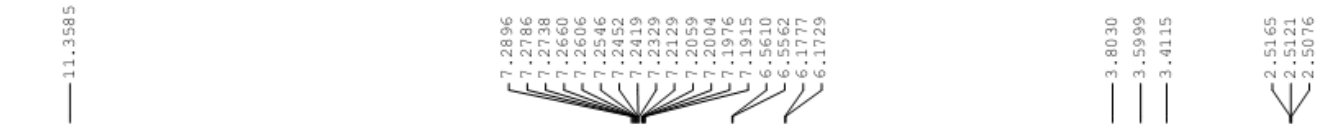
3fa

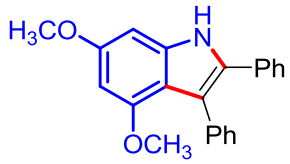
ZGY-130826-4-CNMR



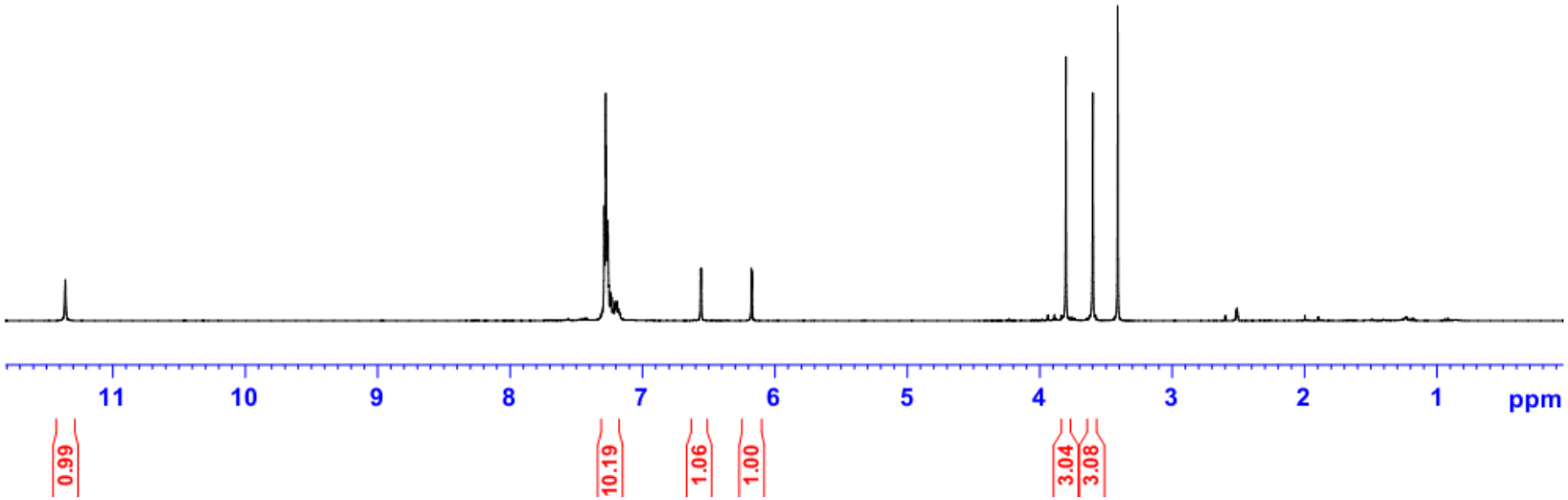
3fa

ZGY-130909-7-HNMR

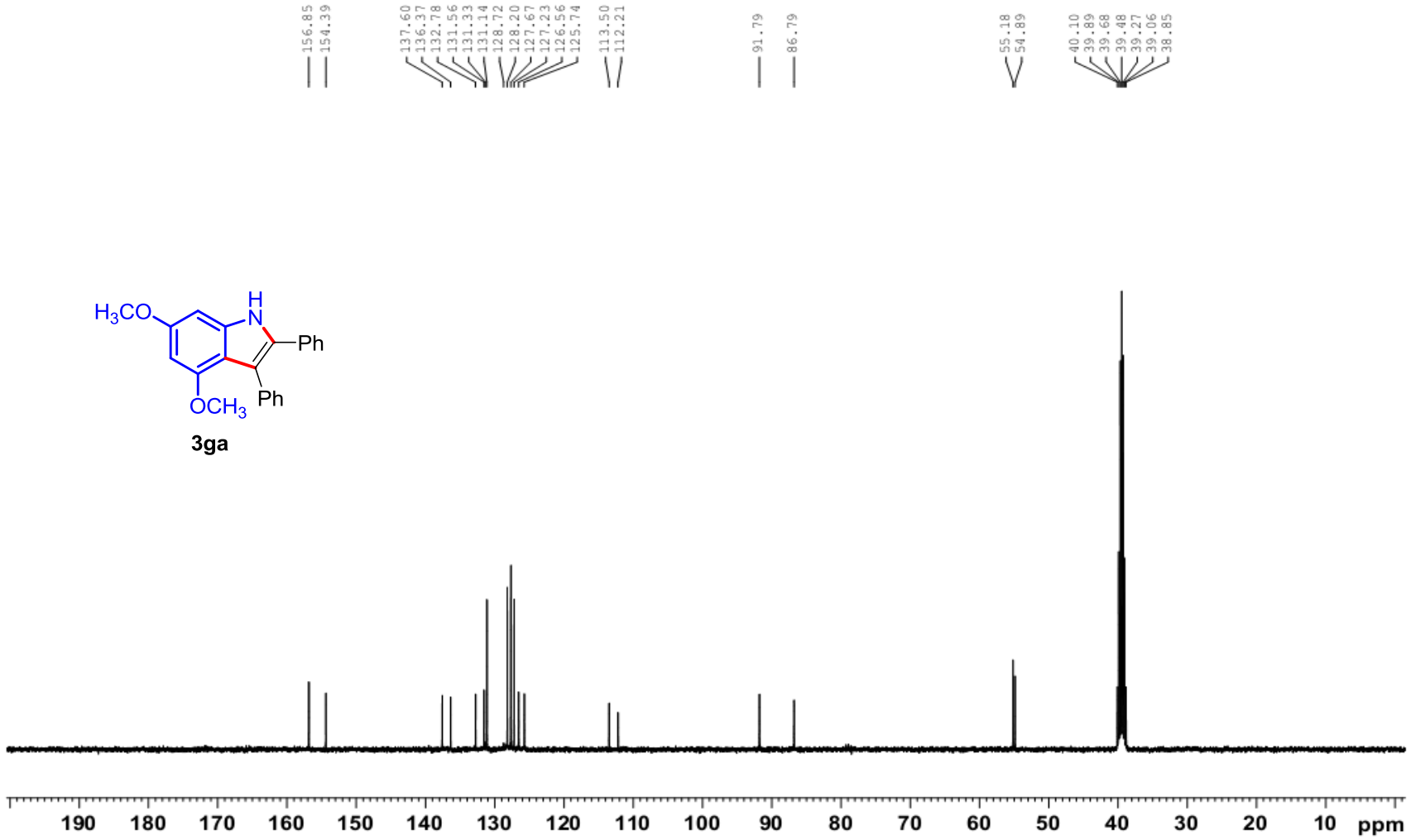




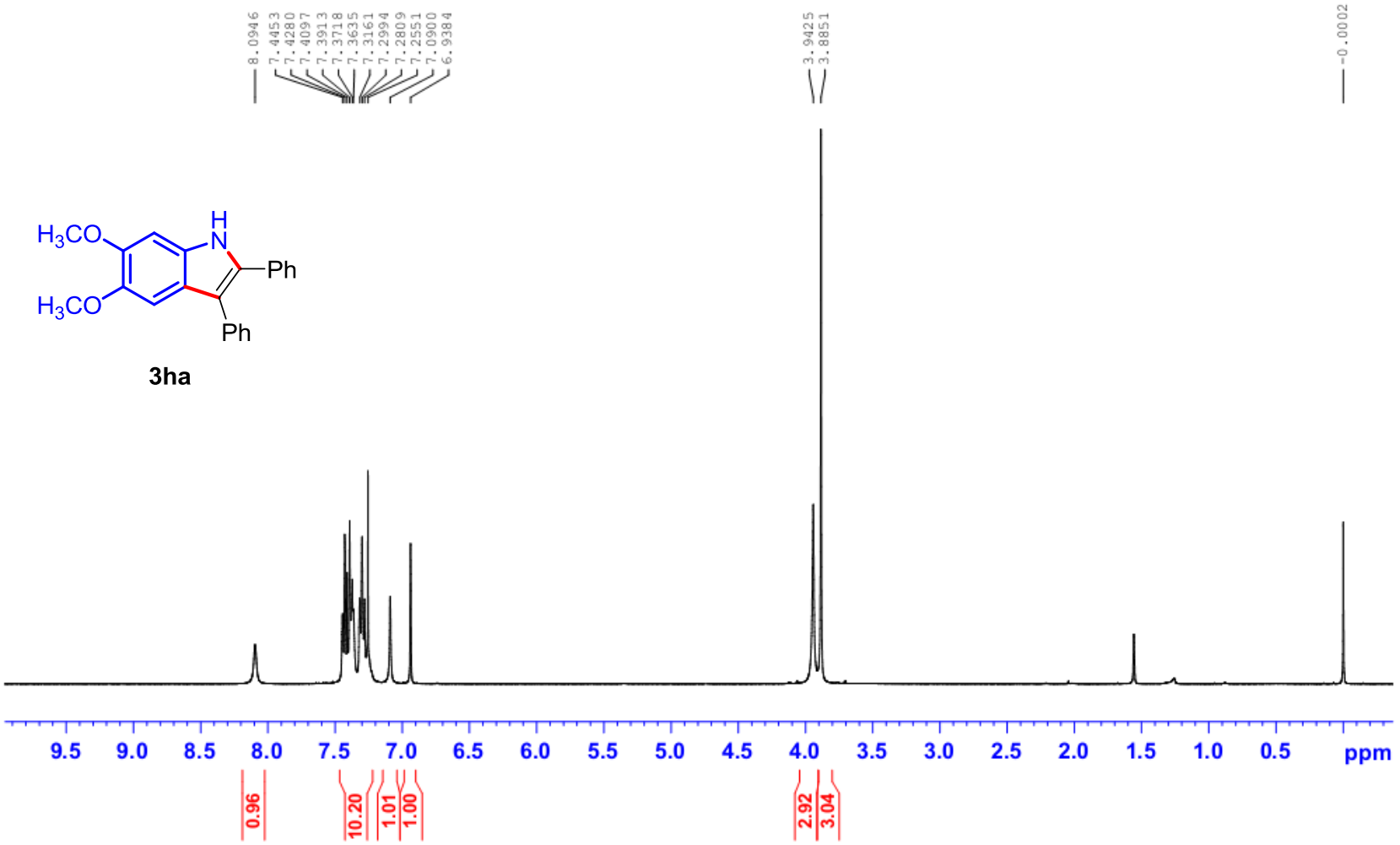
3ga



ZGY-130909-7-CNMR

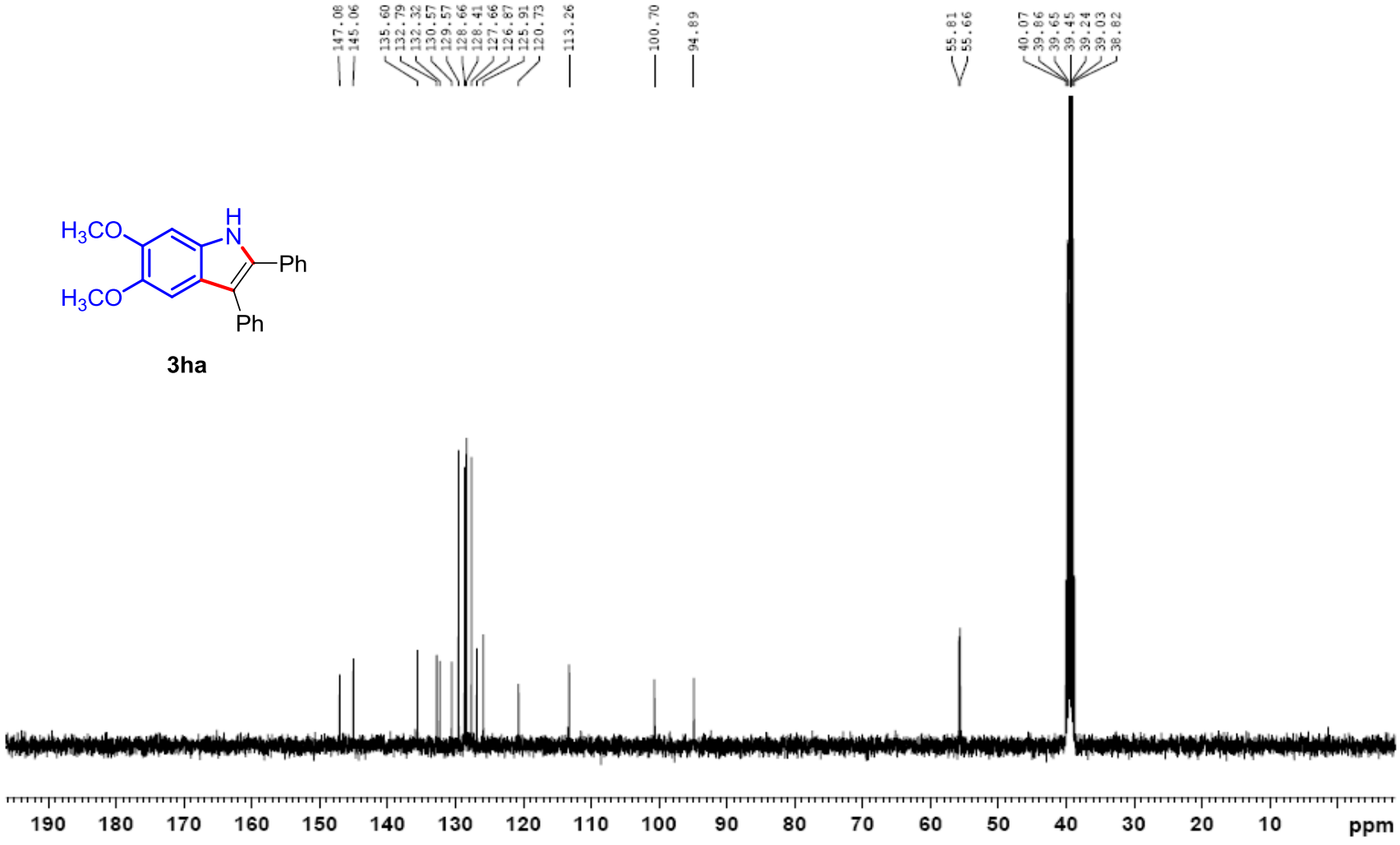


ZGY-130916-4-HNMR



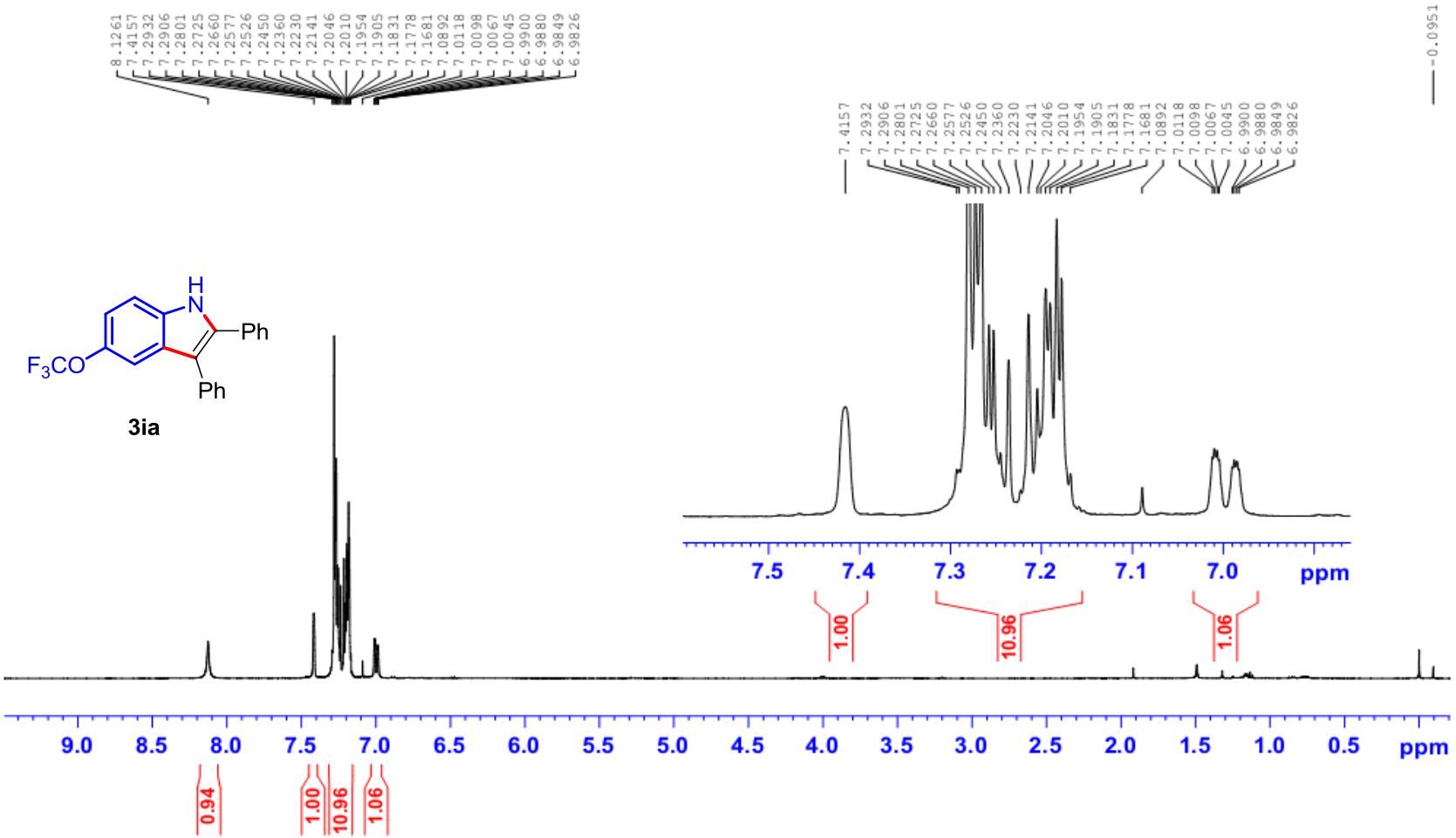
3ha

ZGY-131009-4-CNMR

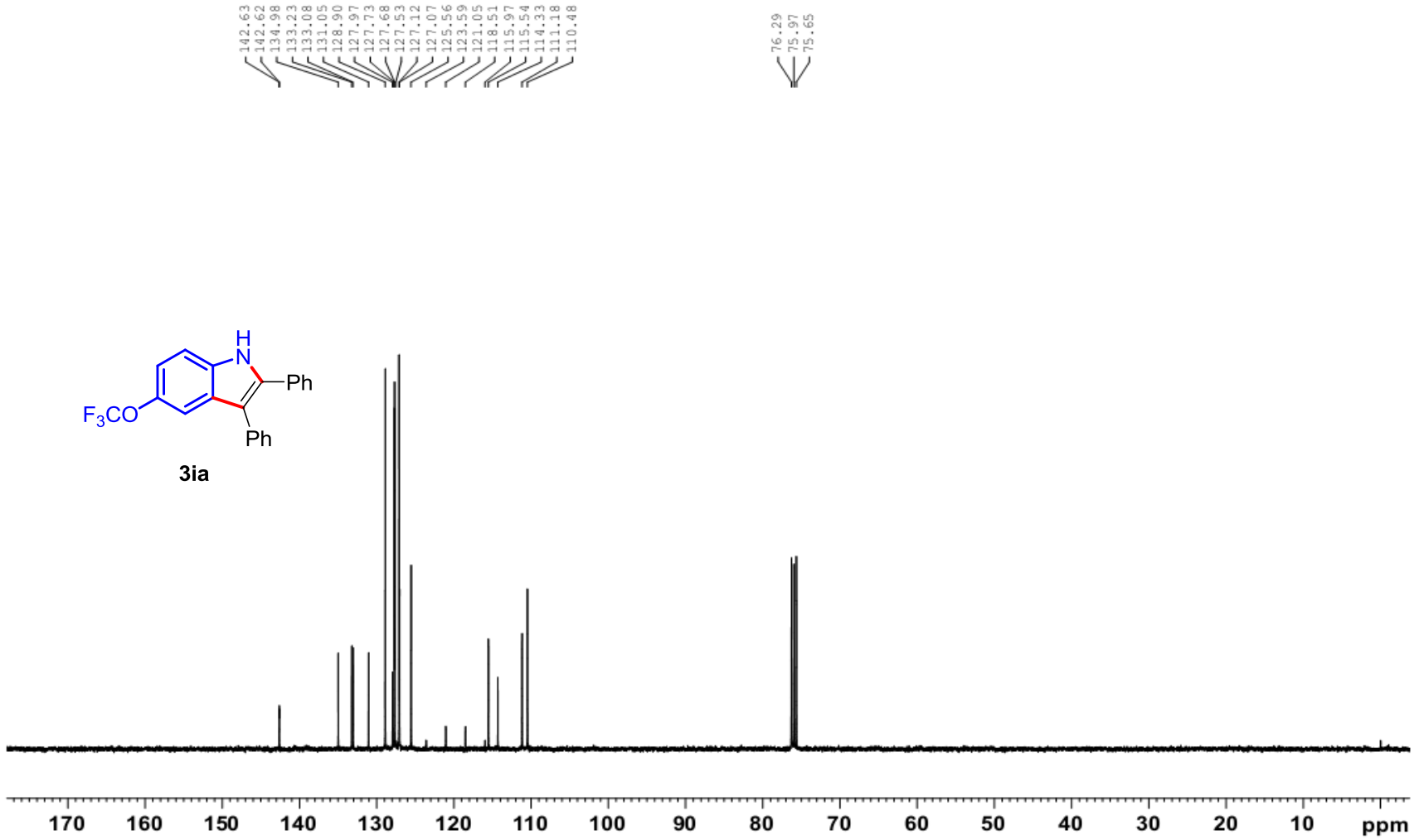


3ha

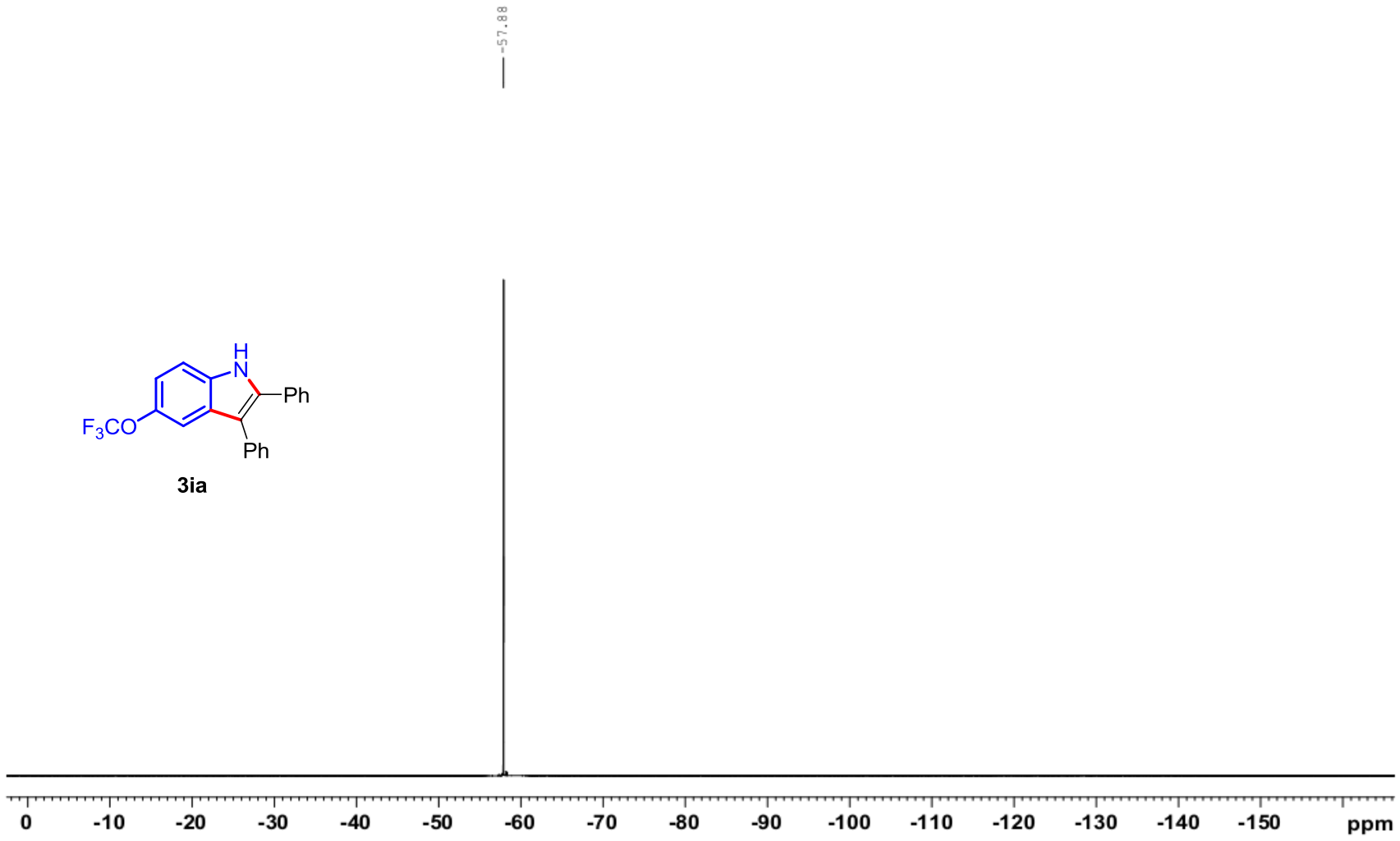
ZGY-130902-8-HNMR



ZGY-130902-8-CNMR

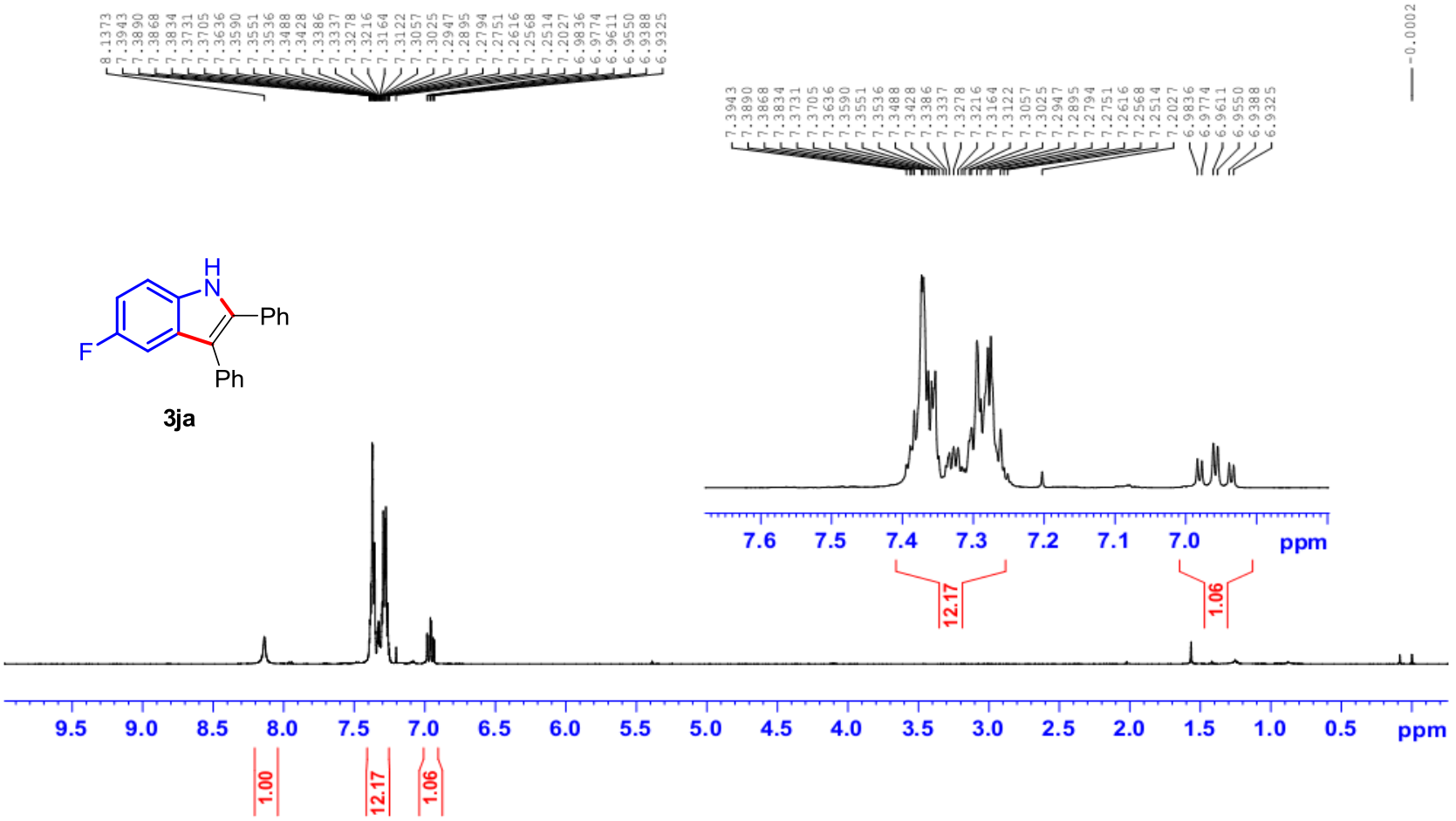


ZGY-X130911-1-FNMR

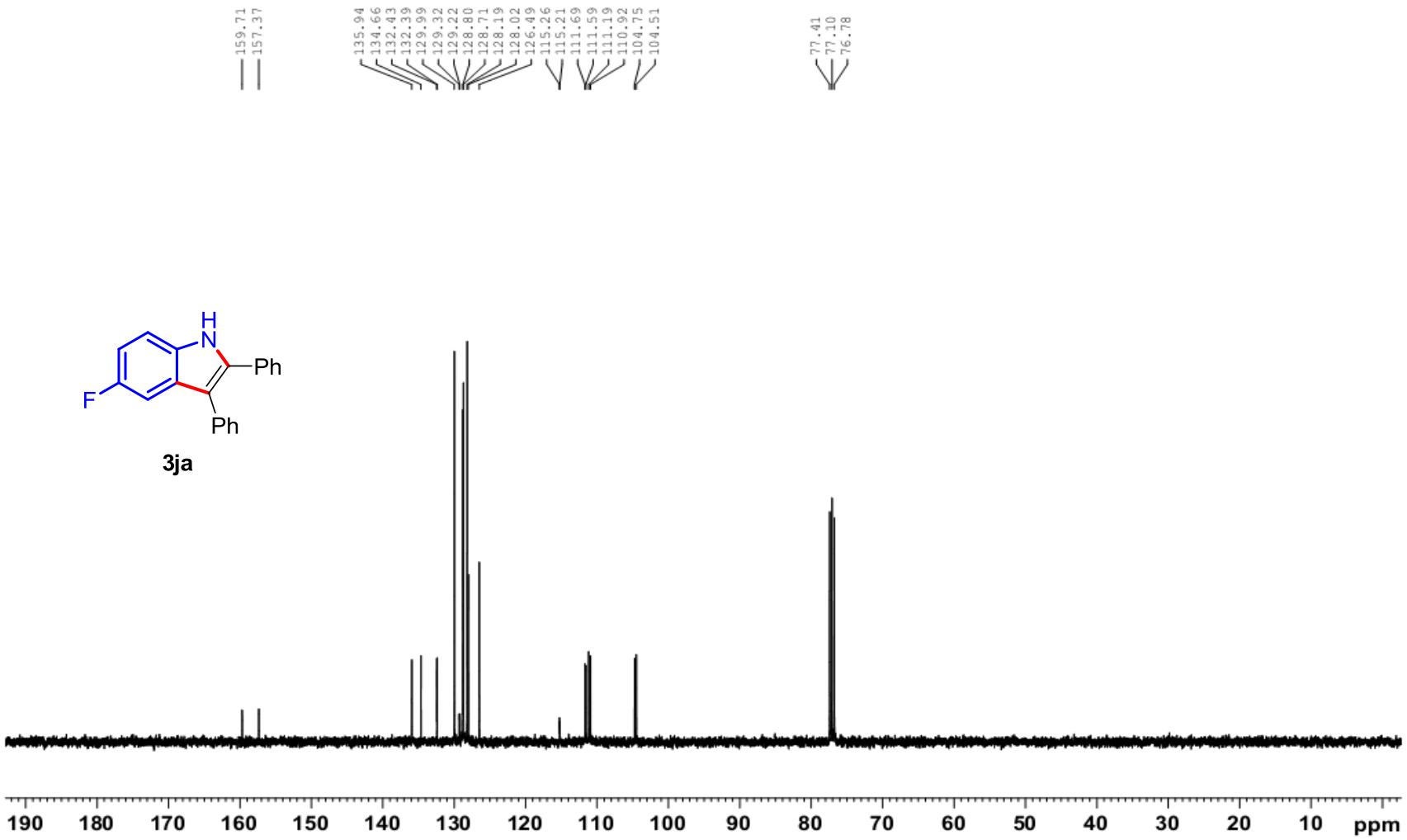


3ia

ZGY-130826-6-HNMR

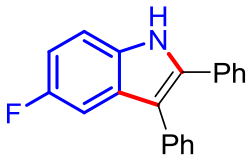


ZGY-130826-6-CNMR



3ja

ZGY-130826-6-FNMR



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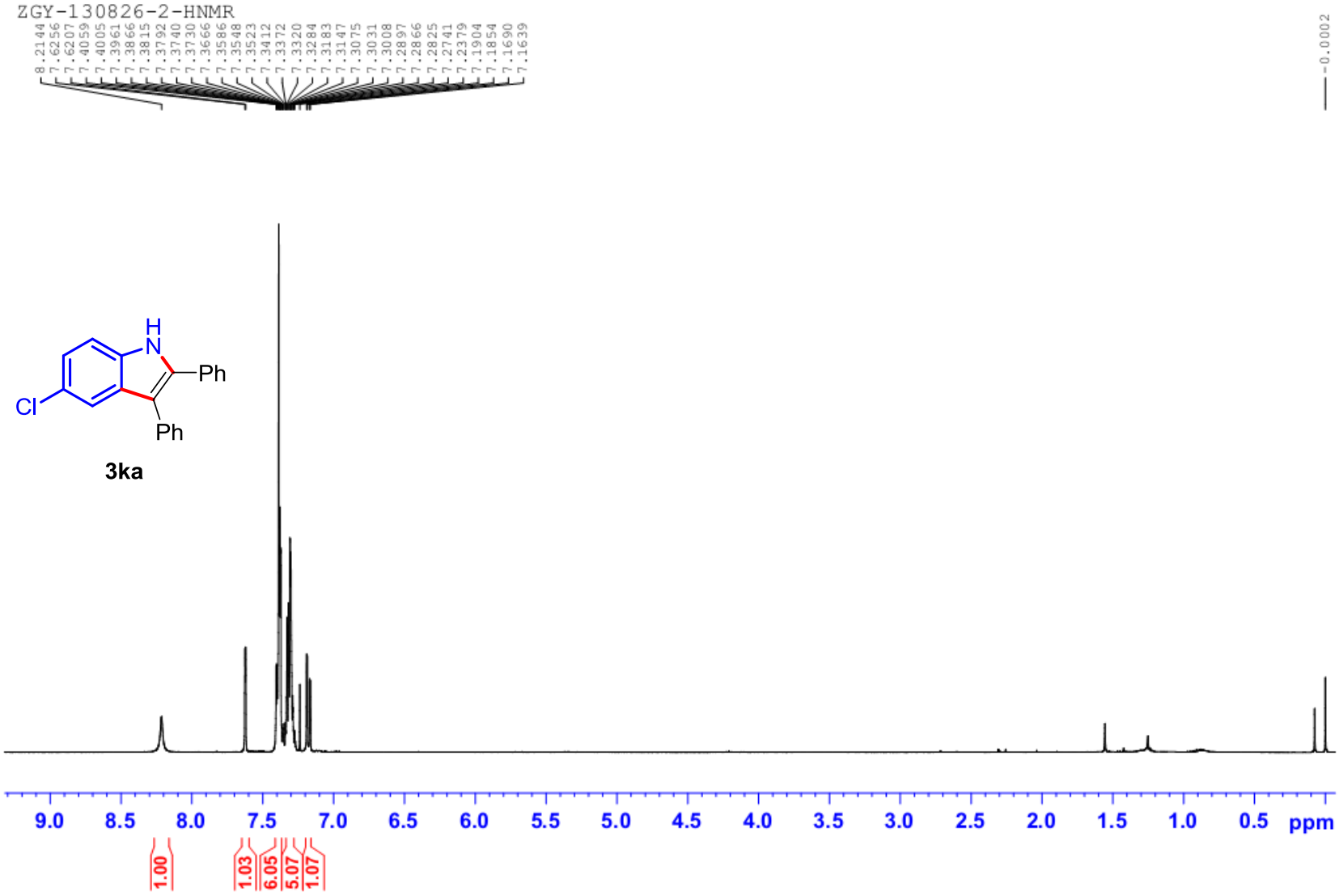
ZGY-130826-2-HNMR
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7.6207
7.4059
7.4005
7.3961
7.3866
7.3815
7.3792
7.3740
7.3730
7.3666
7.3586
7.3548
7.3523
7.3412
7.3372
7.3320
7.3284
7.3183
7.3147
7.3075
7.3031
7.3008
7.2897
7.2866
7.2825
7.2741
7.2379
7.1904
7.1854
7.1690
7.1639
-0.0002
H
N
Ph
Cl
Ph
3ka
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
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1.0
0.5
ppm
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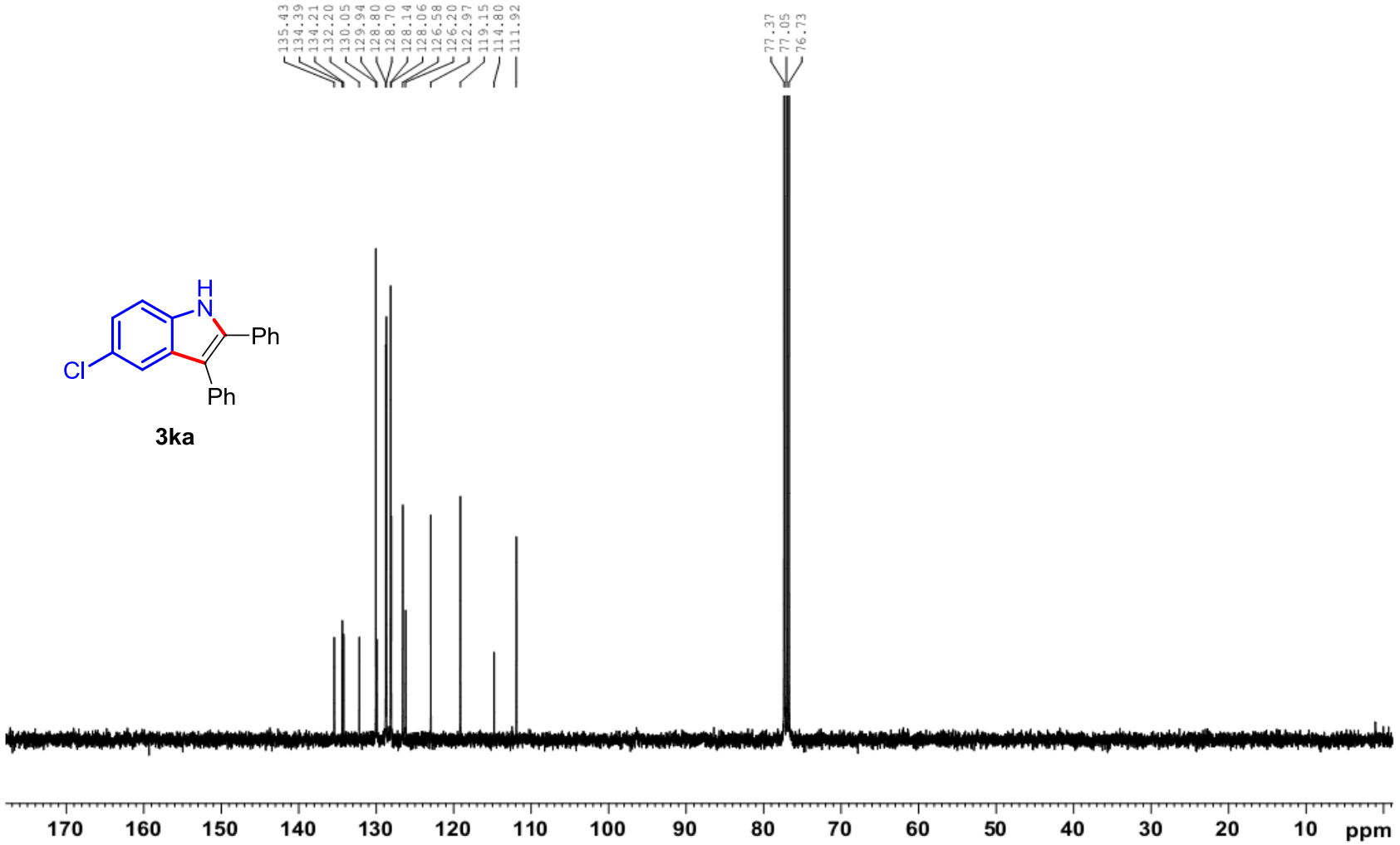
1.03
6.05
5.07
1.07

ZGY-130826-2-CNMR



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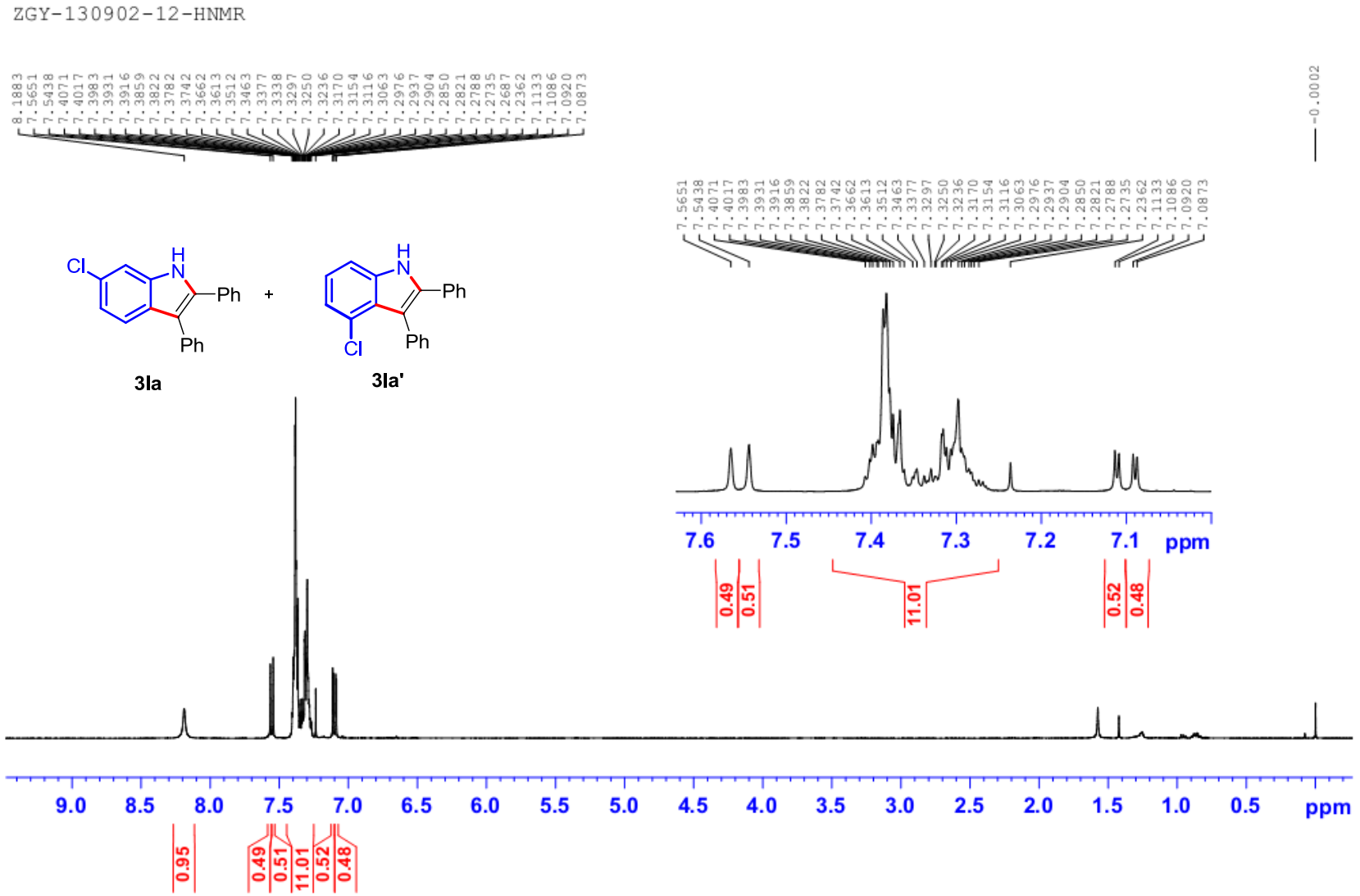
ZGY-130902-12-HNMR
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7.3983
7.3931
7.3916
7.3859
7.3822
7.3782
7.3742
7.3662
7.3613
7.3512
7.3463
7.3377
7.3338
7.3297
7.3250
7.3236
7.3170
7.3154
7.3116
7.3063
7.2976
7.2937
7.2904
7.2850
7.2821
7.2788
7.2735
7.2687
7.2362
7.1133
7.1086
7.0920
7.0873
-0.0002
Cl
H
N
Ph
Ph
+
Cl
H
N
Ph
Ph
3la
3la'
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
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0.49
0.51
11.01
0.52
0.48
7.6
7.5
7.4
7.3
7.2
7.1
ppm
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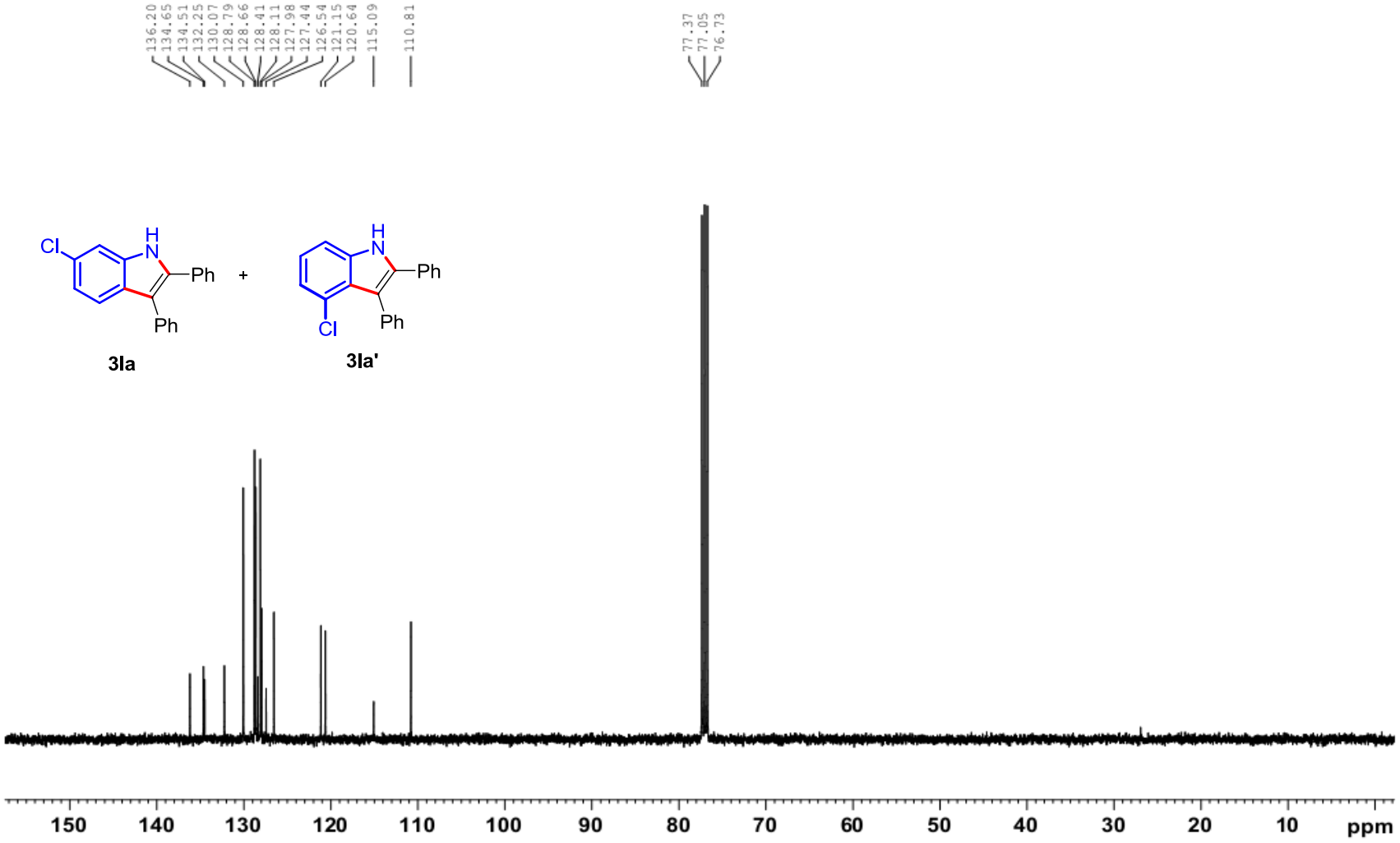
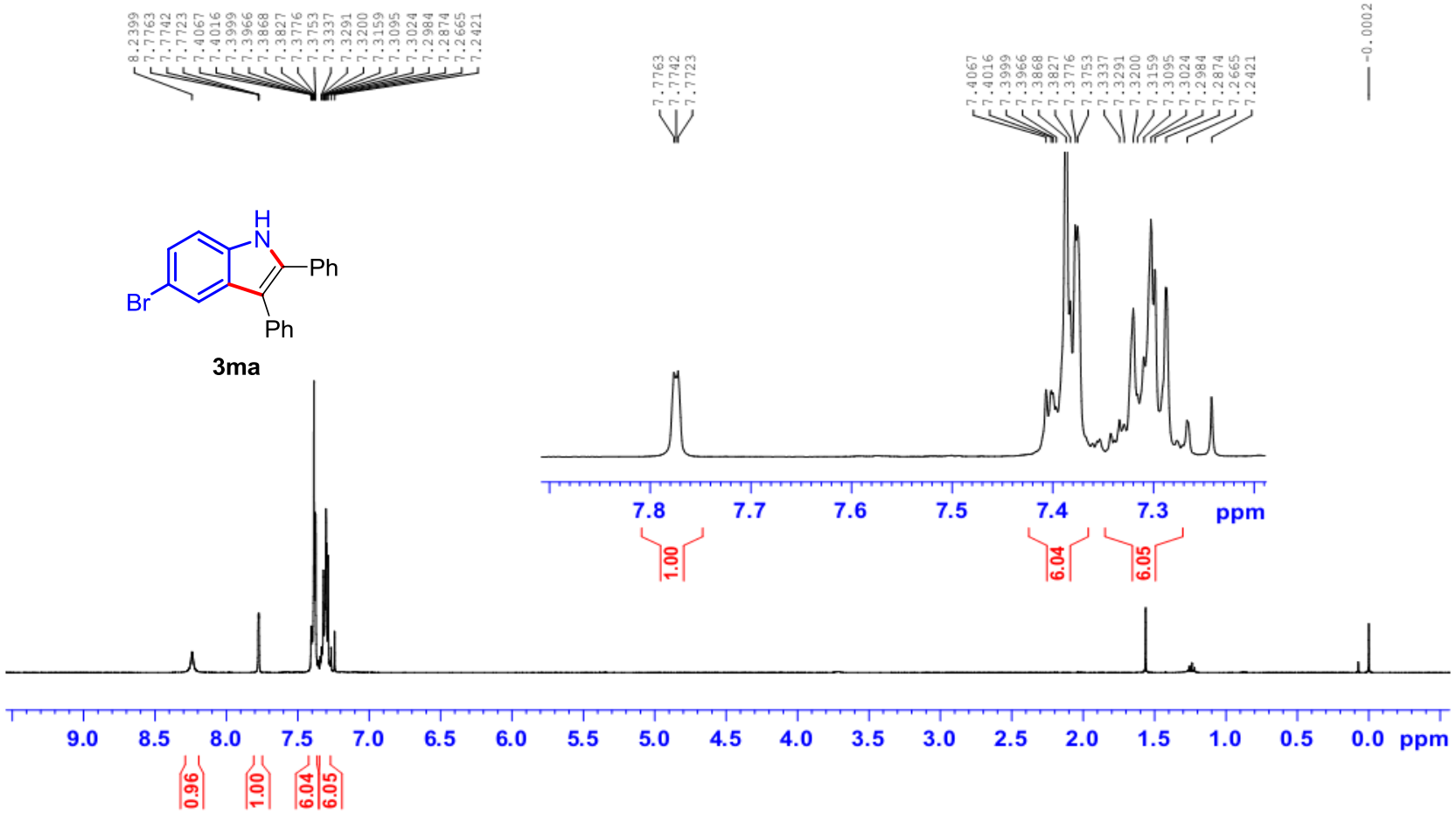
0.51
11.01
0.52
0.48

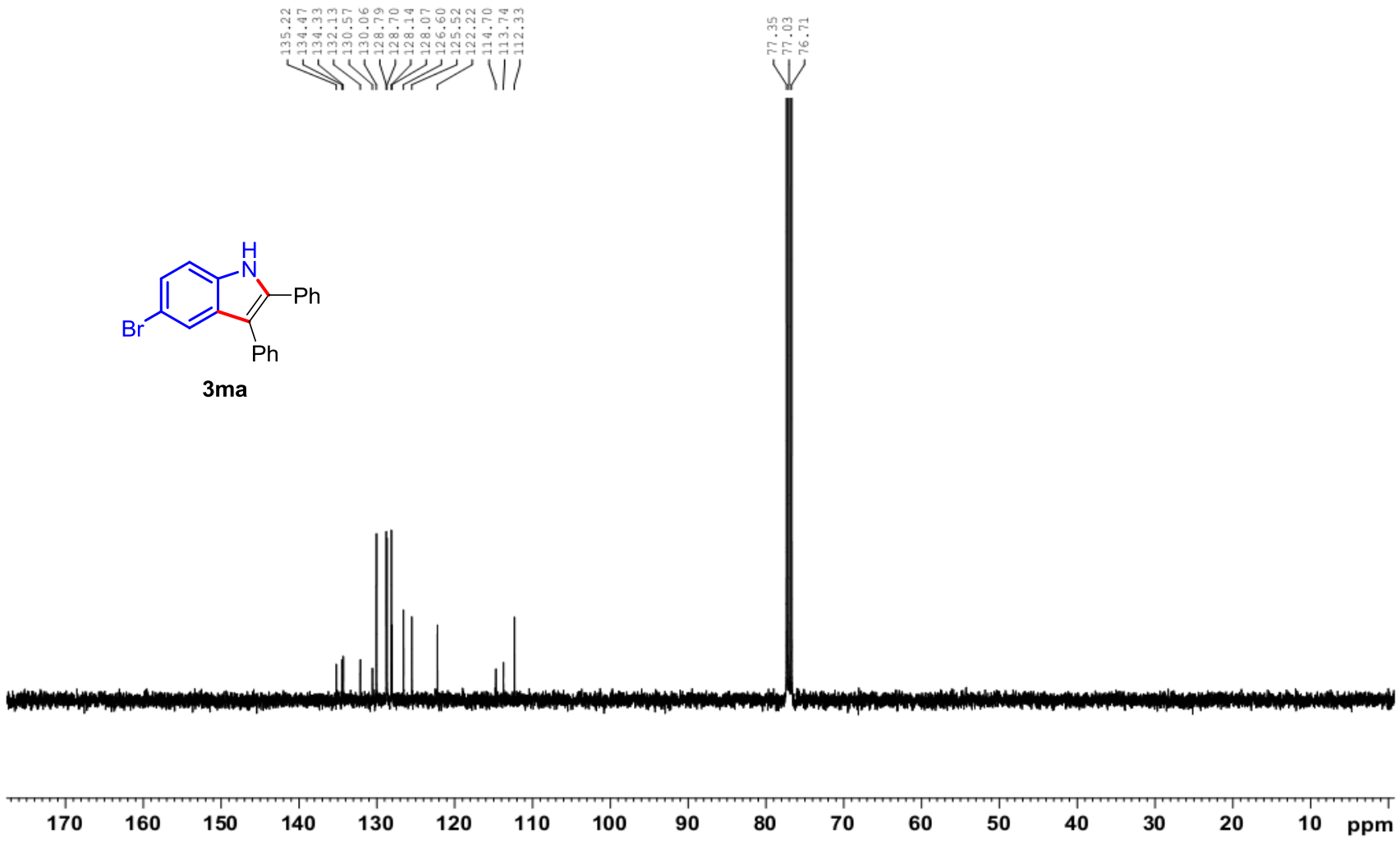
ZGY-130902-12-CNMR



04-13-ZhangCY-HNMR

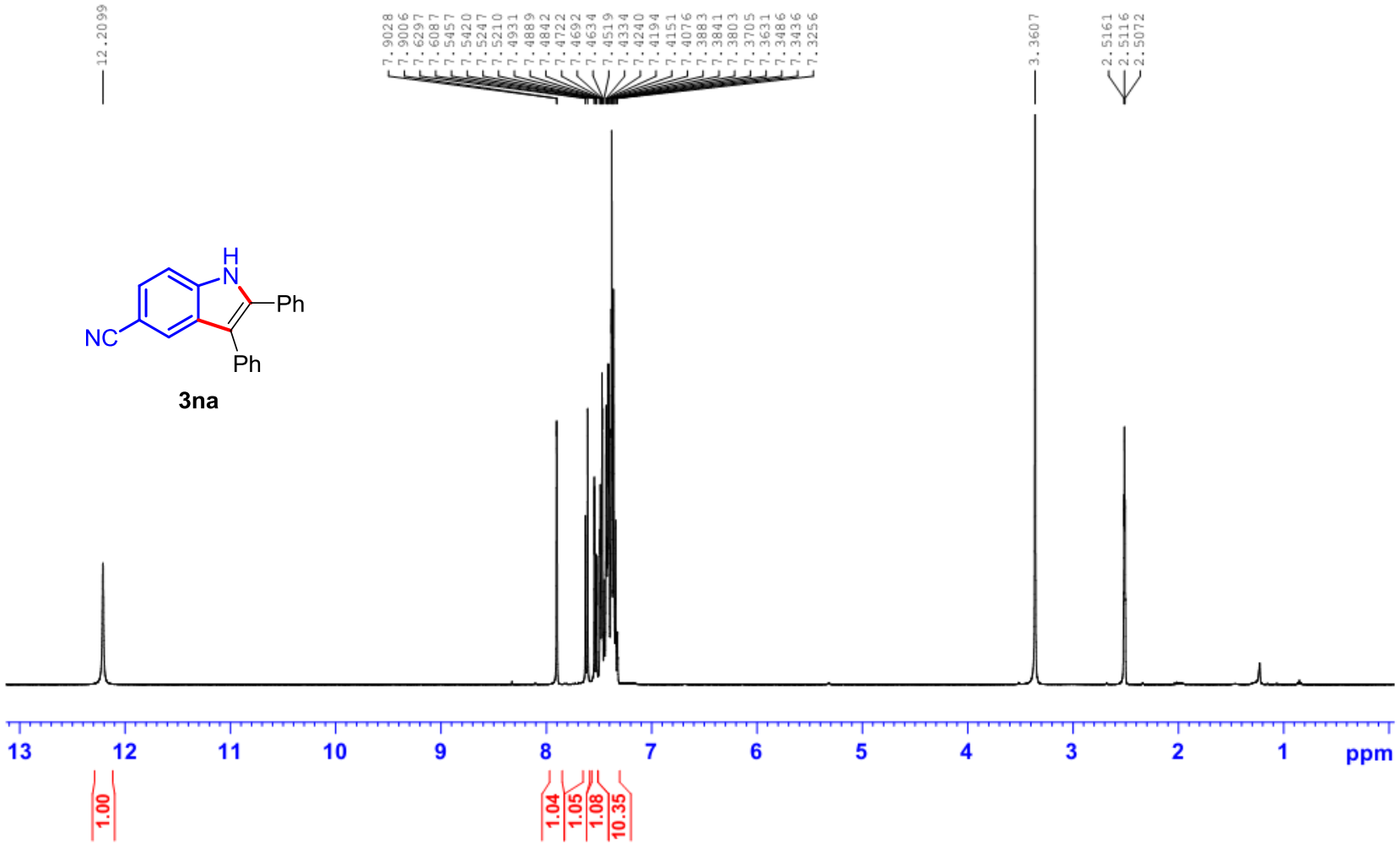


ZGY-130902-1-CNMR



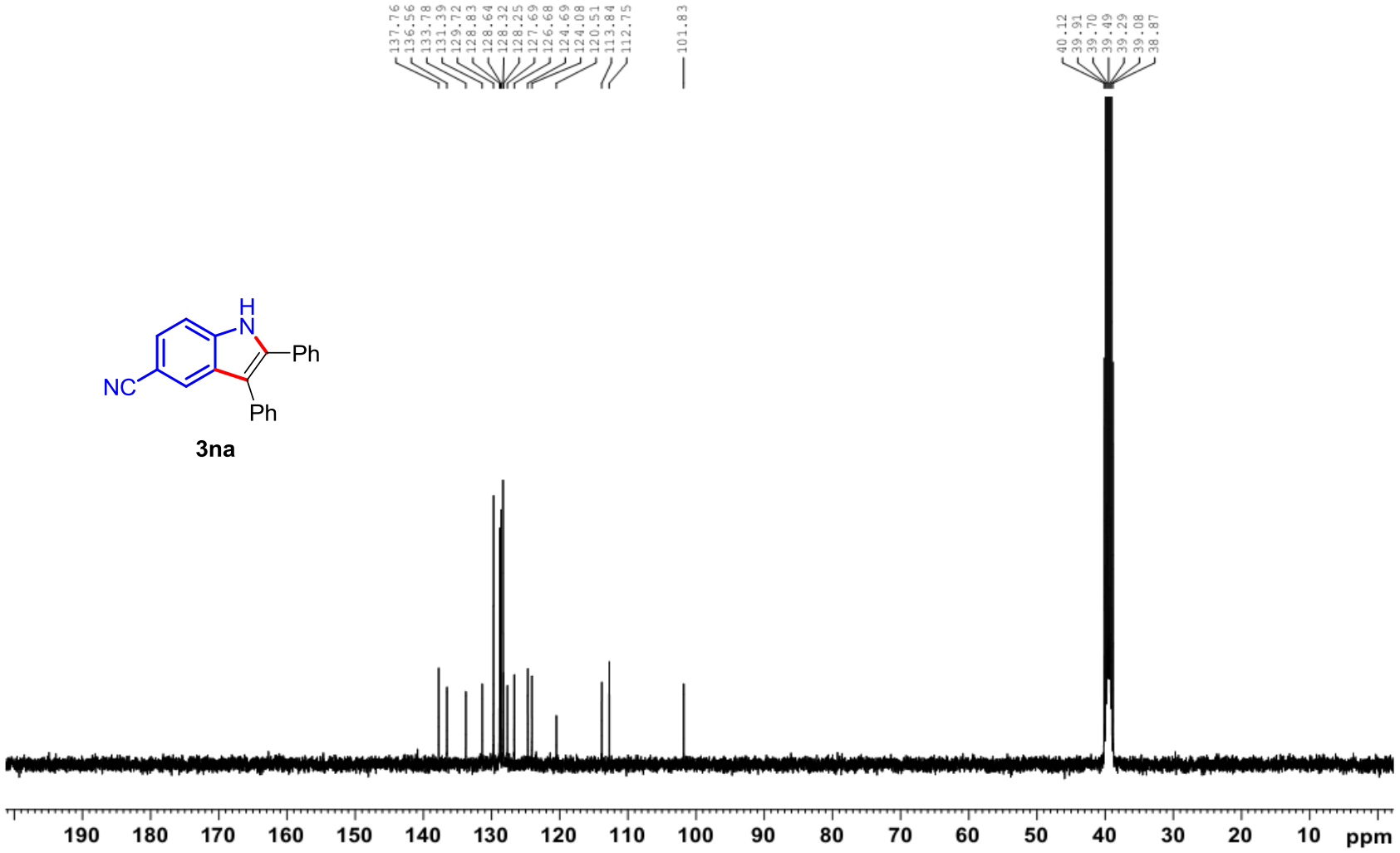
3ma

ZGY-130909-8-HNMR

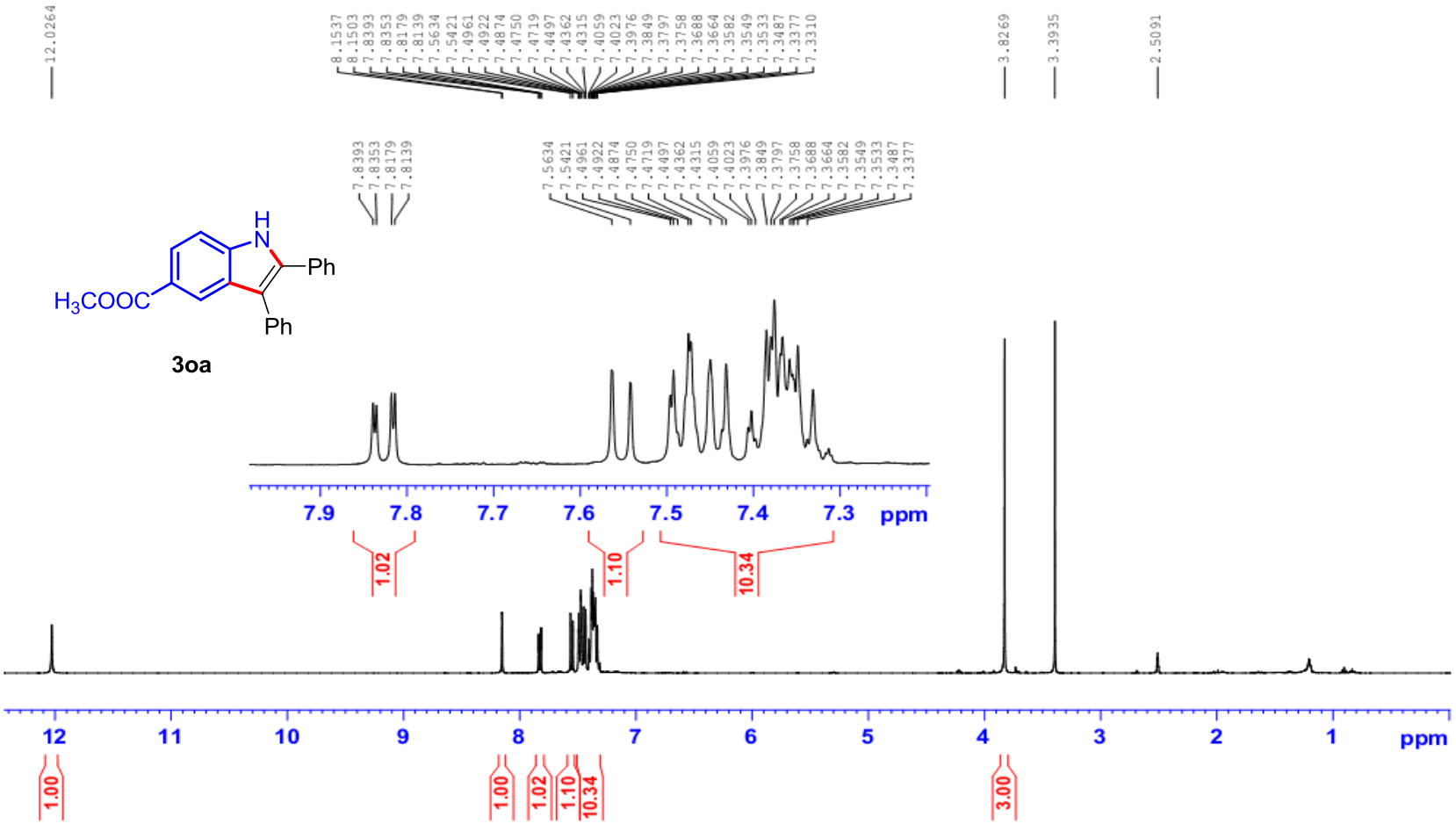


3na

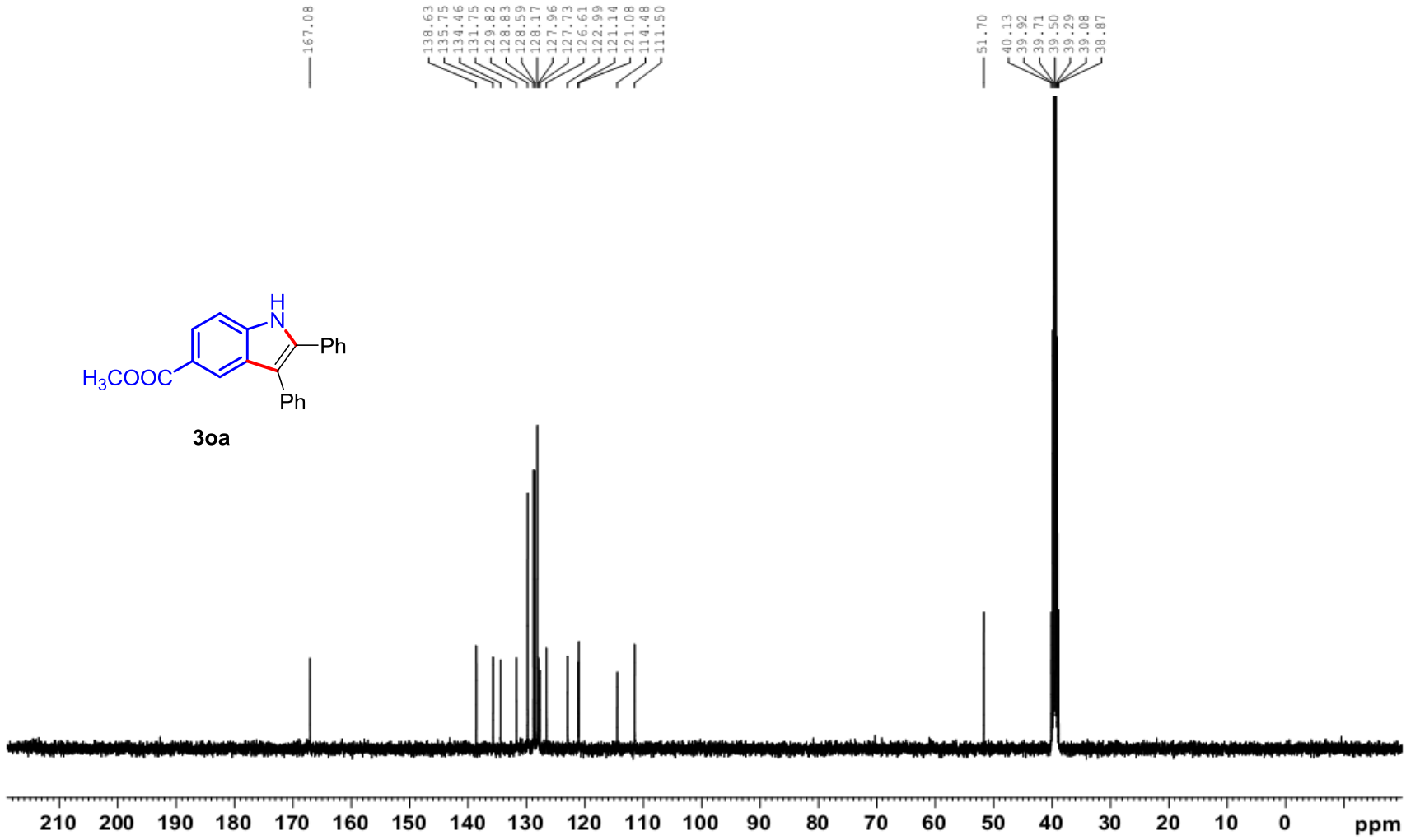
ZGY-130909-8-CNMR



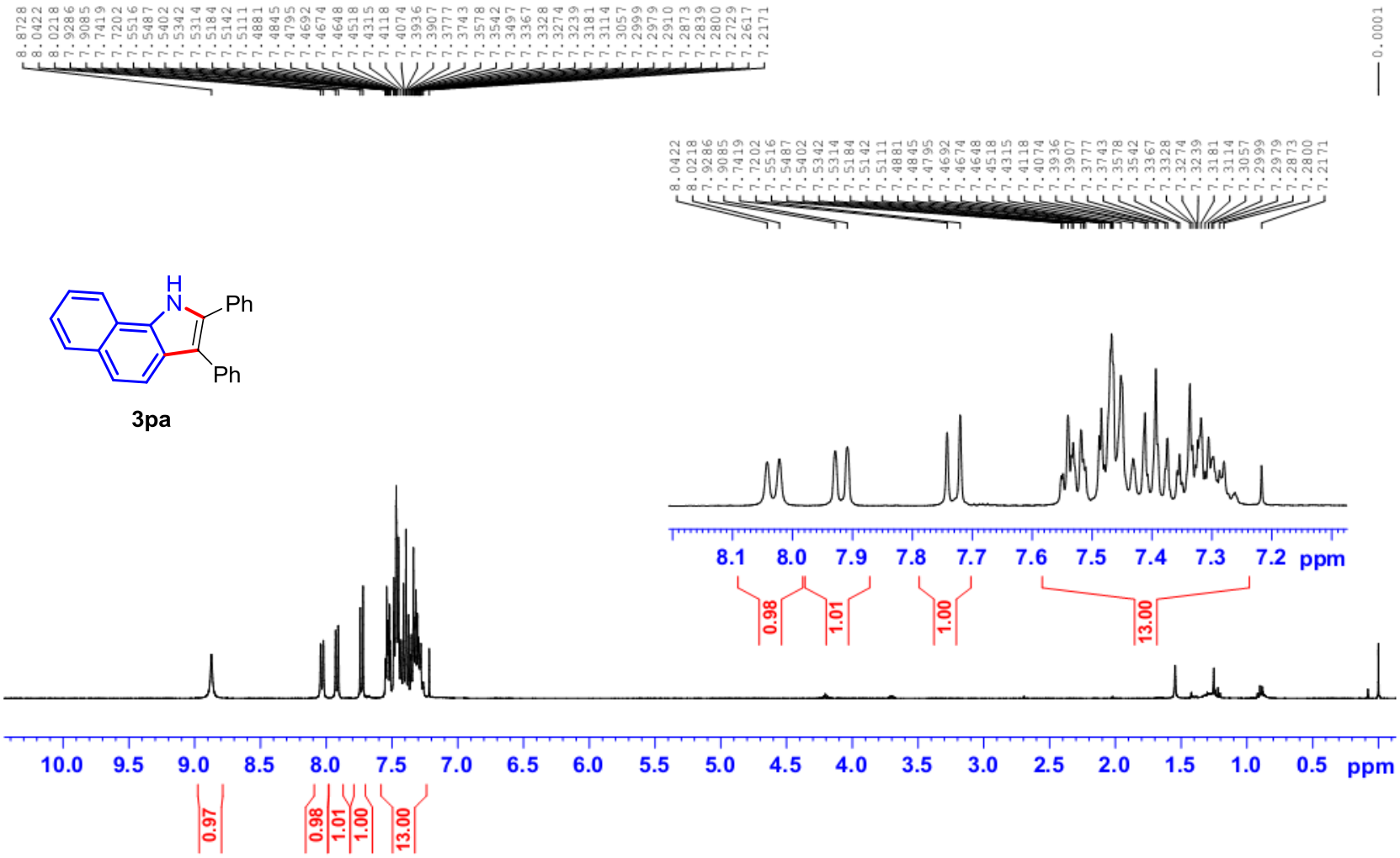
ZGY-130922-1-HNMR



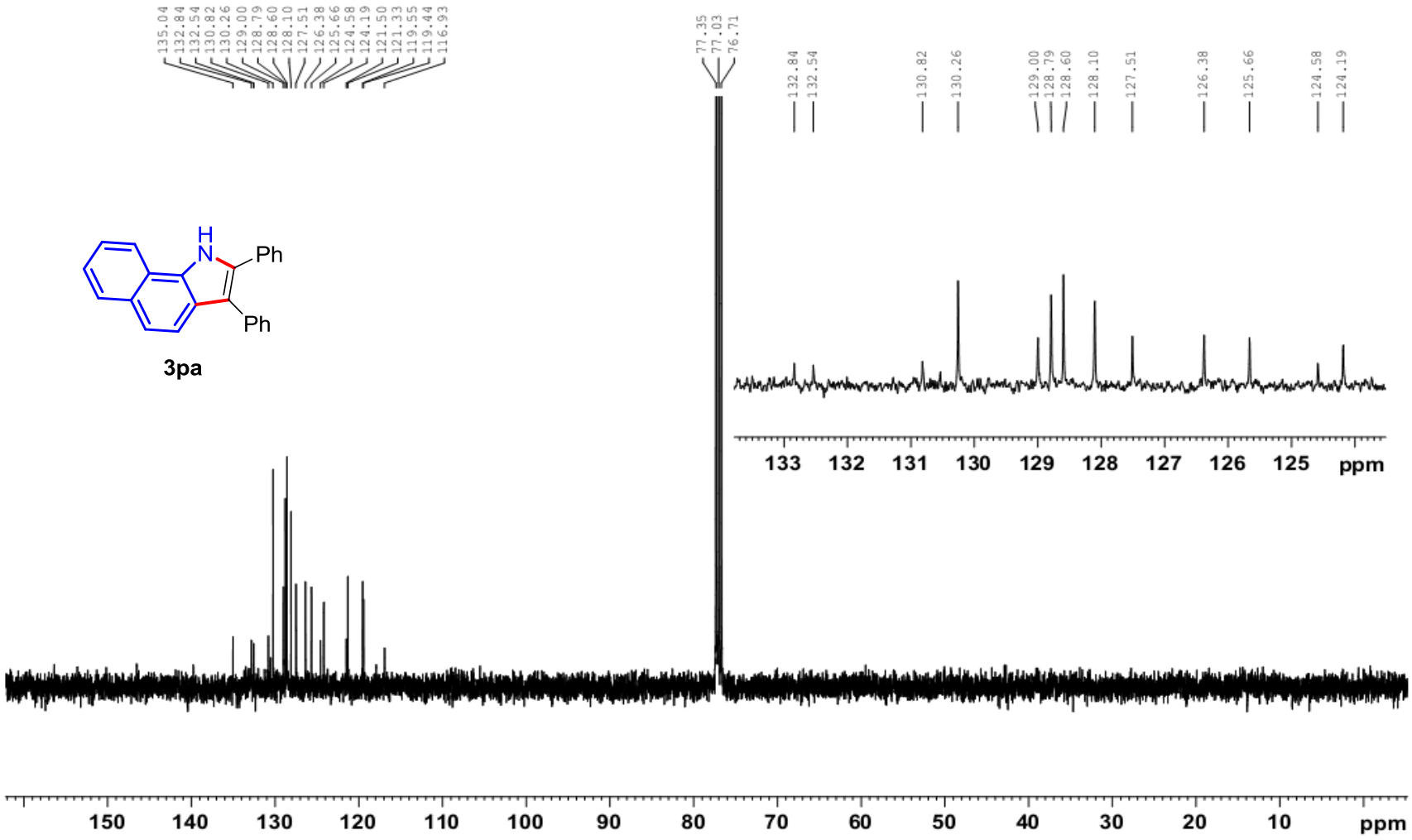
HJH-130922-1-CNMR

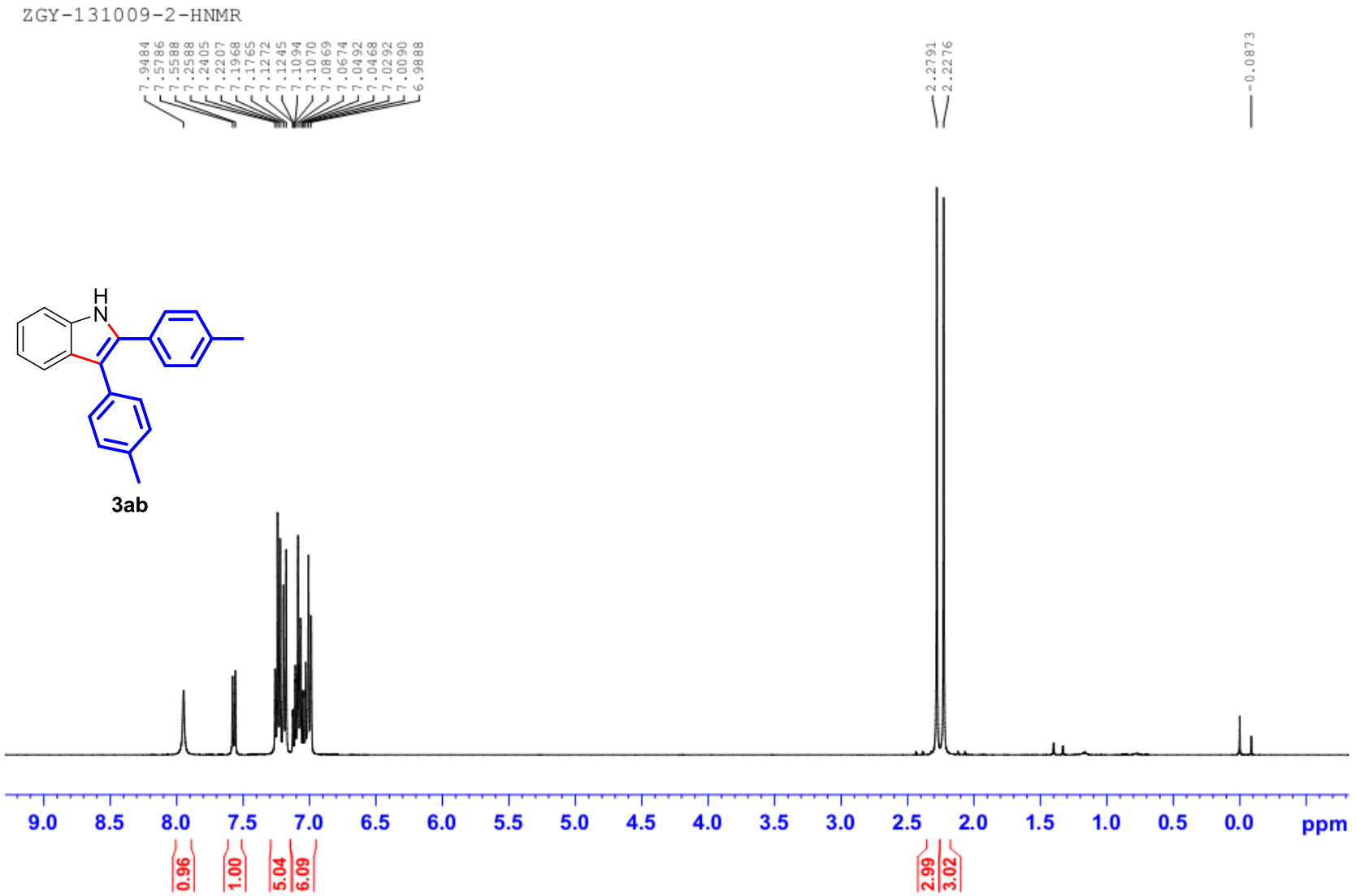


04-11-ZhangCY-HNMR



ZGY-130902-6-CNMR




ZGY-131009-2-HNMR
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7.5588
7.2588
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7.2207
7.1968
7.1765
7.1272
7.1245
7.1094
7.1070
7.0869
7.0674
7.0492
7.0468
7.0292
7.0090
6.9888
2.2791
2.2276
-0.0873
H
N
3ab
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
0.0
ppm
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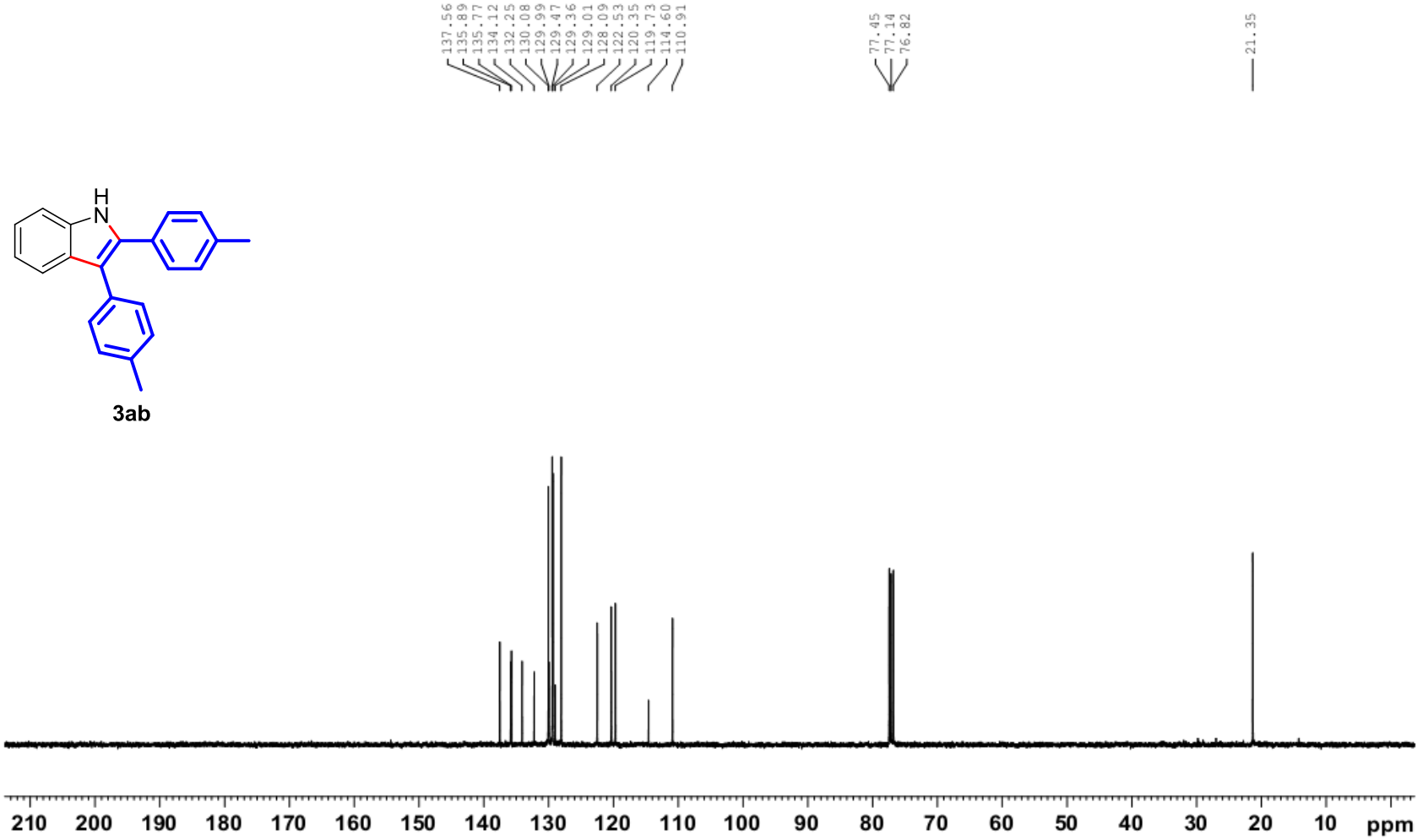
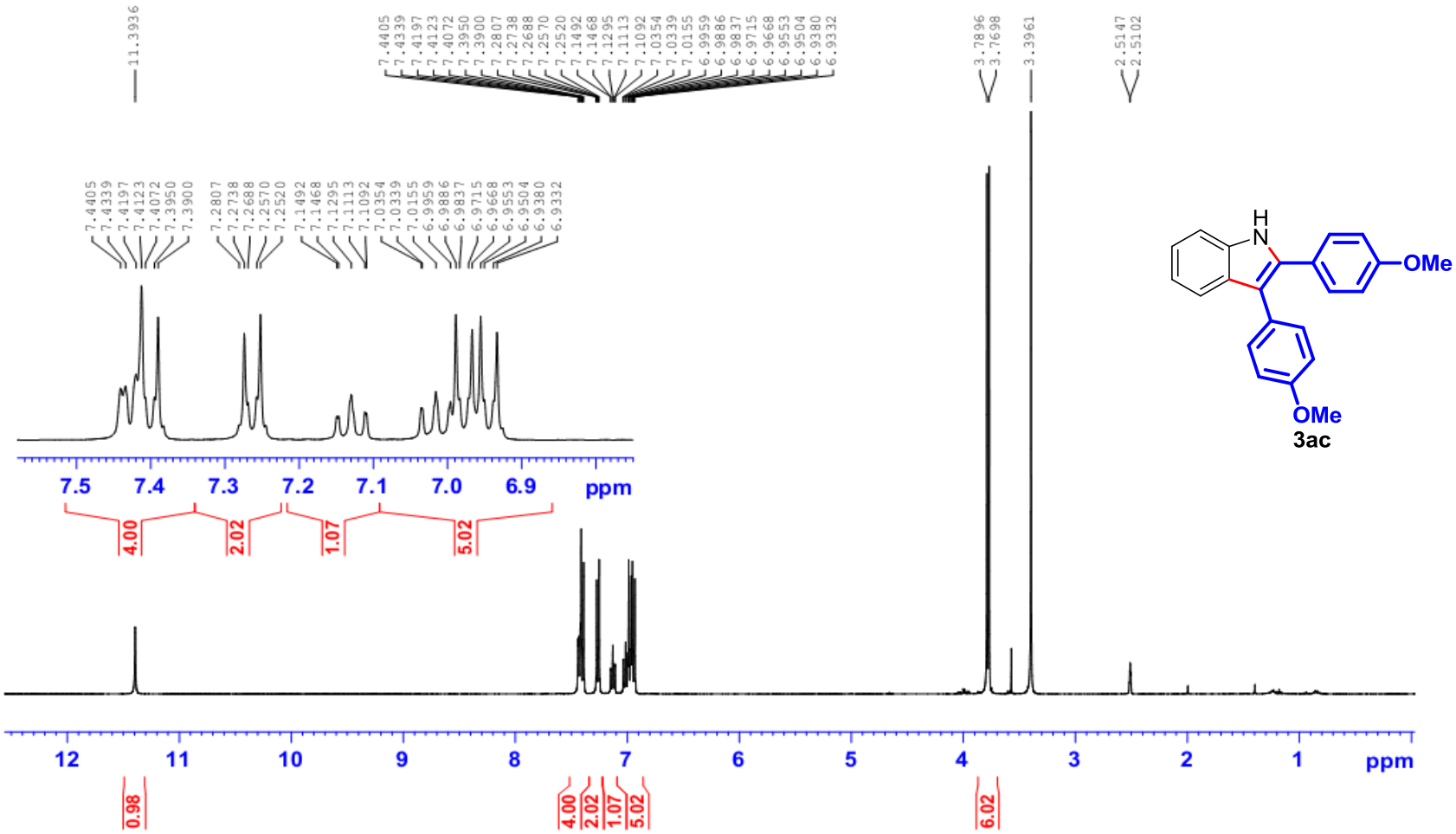
5.04
6.09
2.99
3.02

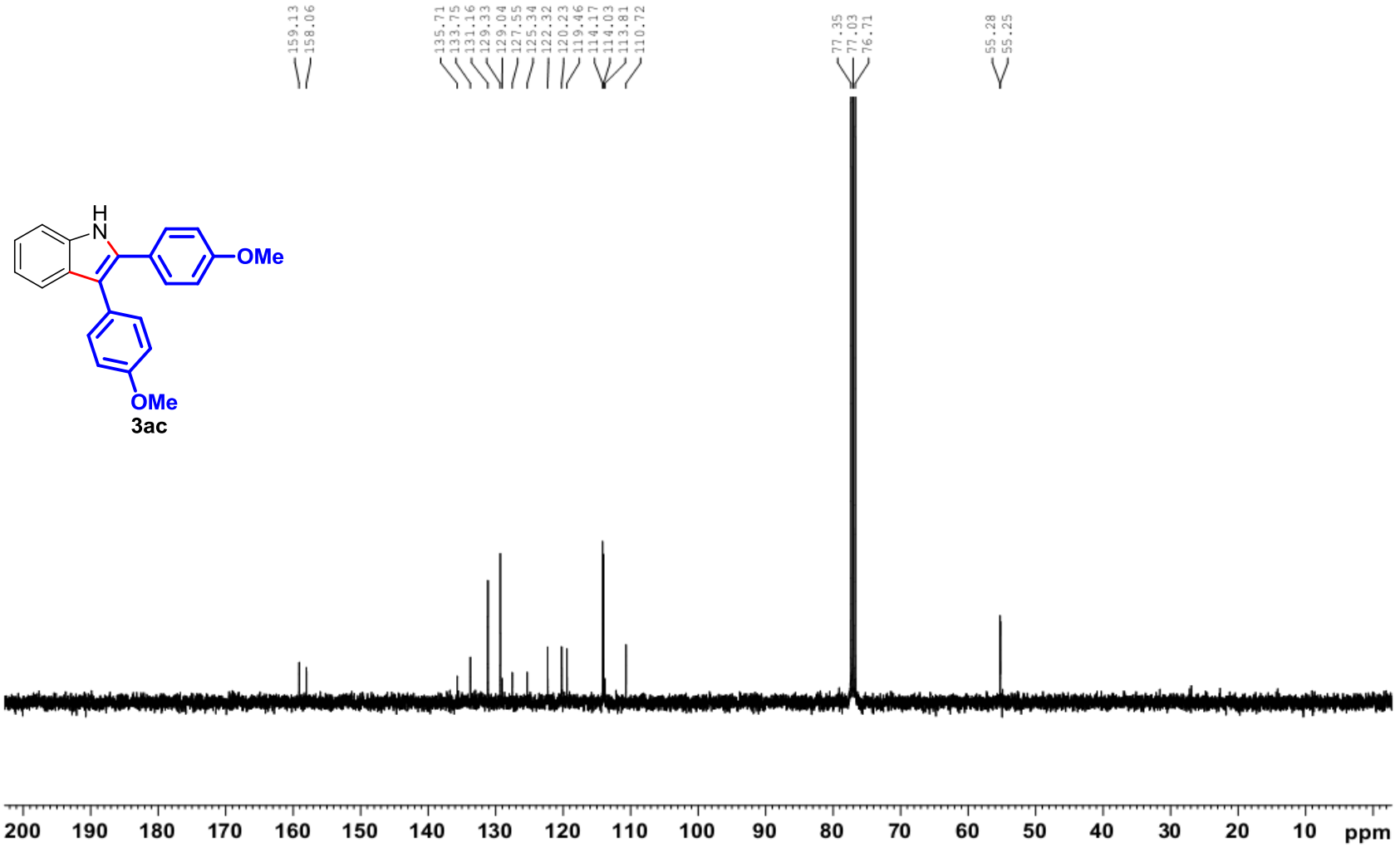
ZGY-130902-2-CNMR



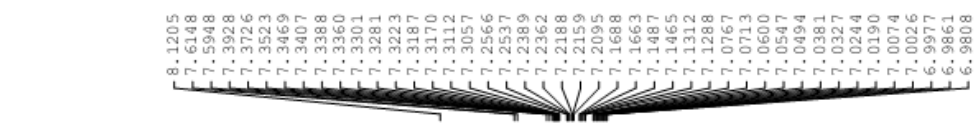
ZGY-131106-4-HNMR

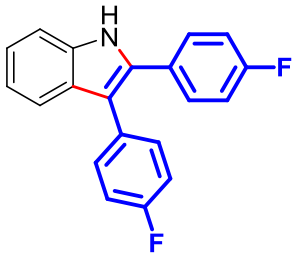


ZGY-130902-3-CNMR

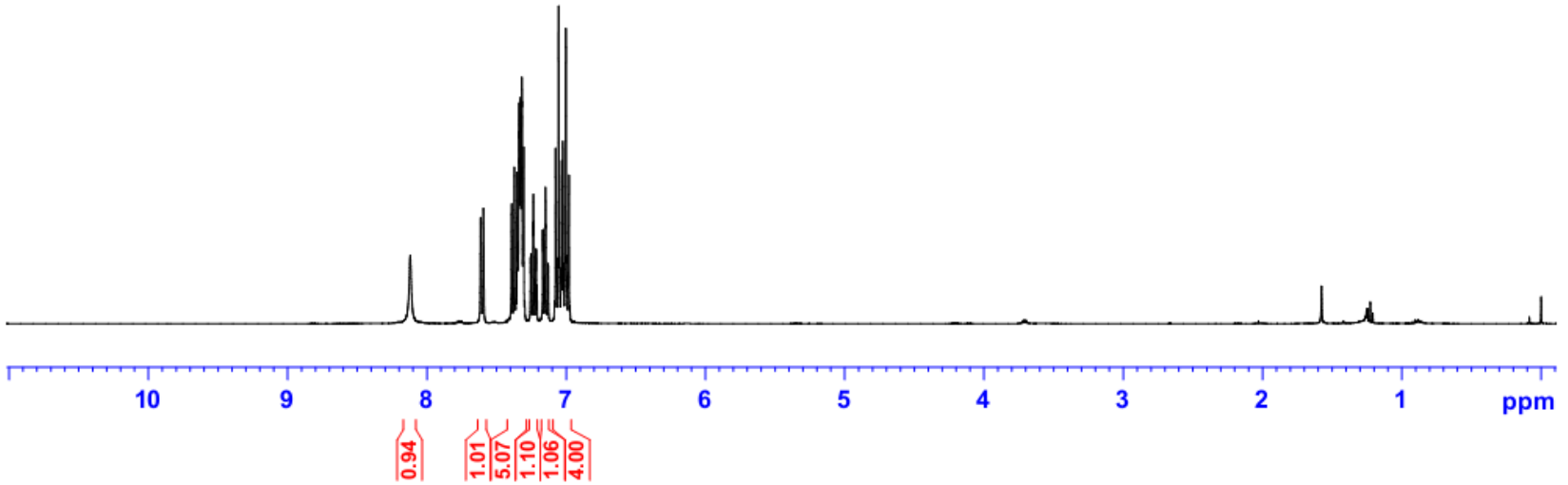


04-14-ZhangCY-HNMR

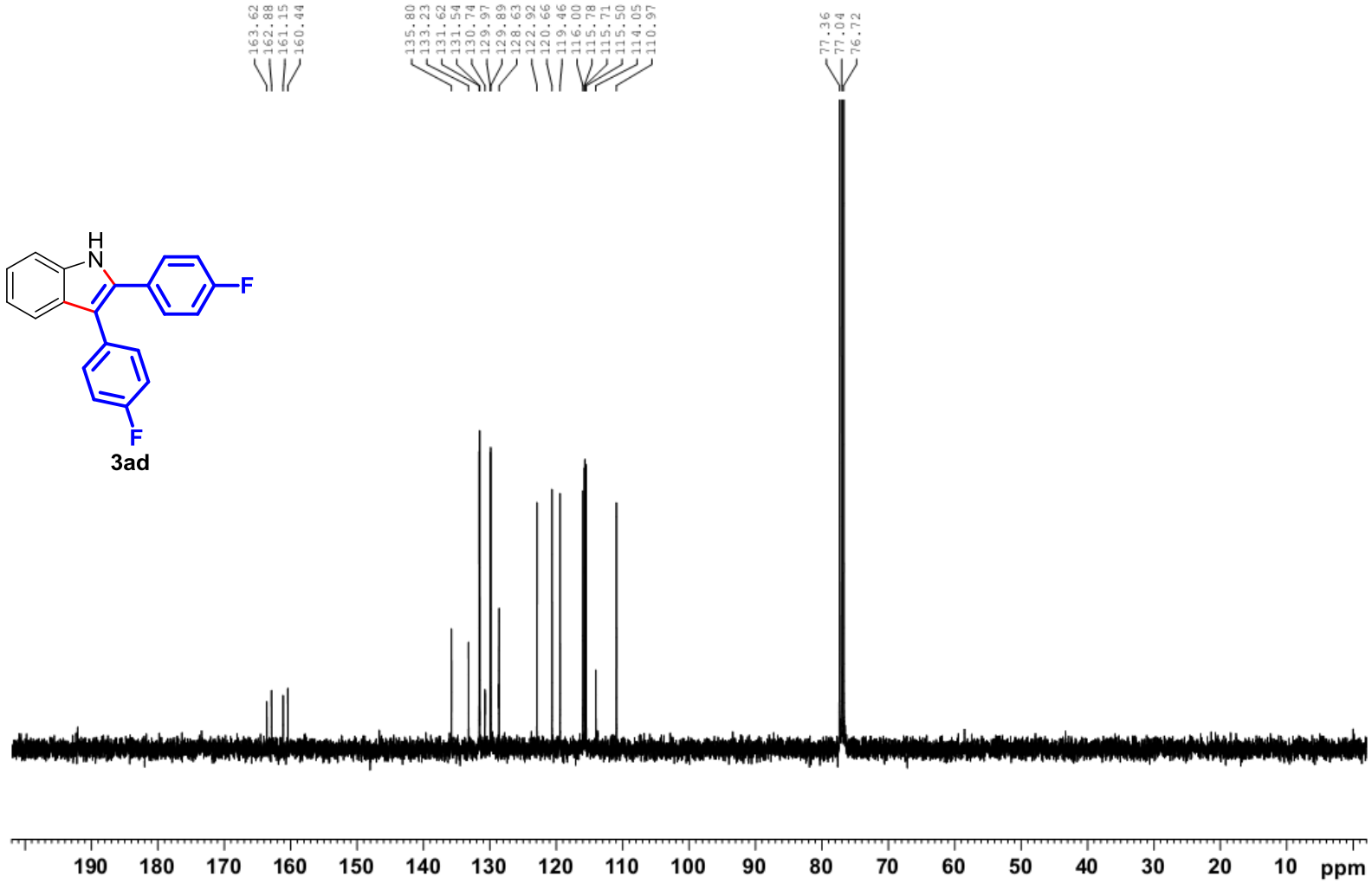




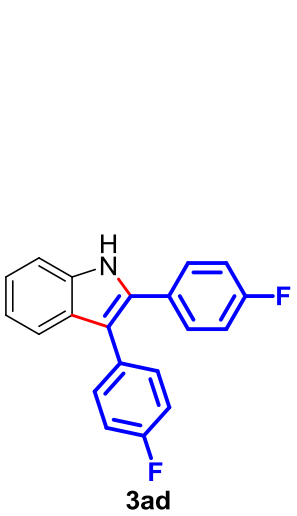
3ad



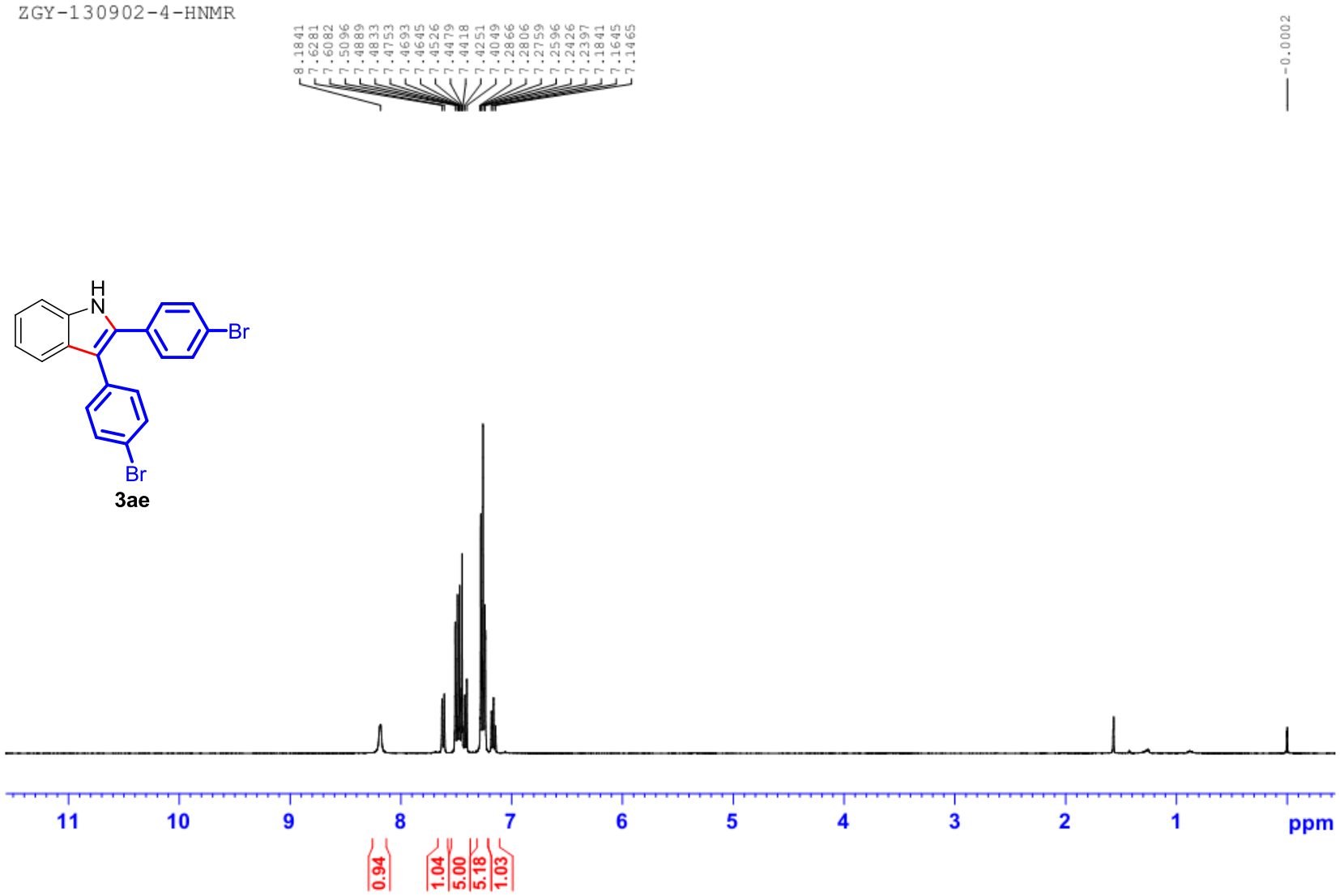
ZGY-130902-5-CNMR



ZGY-130902-5-FNMR



3ad


ZGY-130902-4-HNMR
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7.6281
7.6082
7.5096
7.4889
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7.4753
7.4693
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7.4526
7.4479
7.4418
7.4251
7.4049
7.2866
7.2806
7.2759
7.2596
7.2426
7.2397
7.1841
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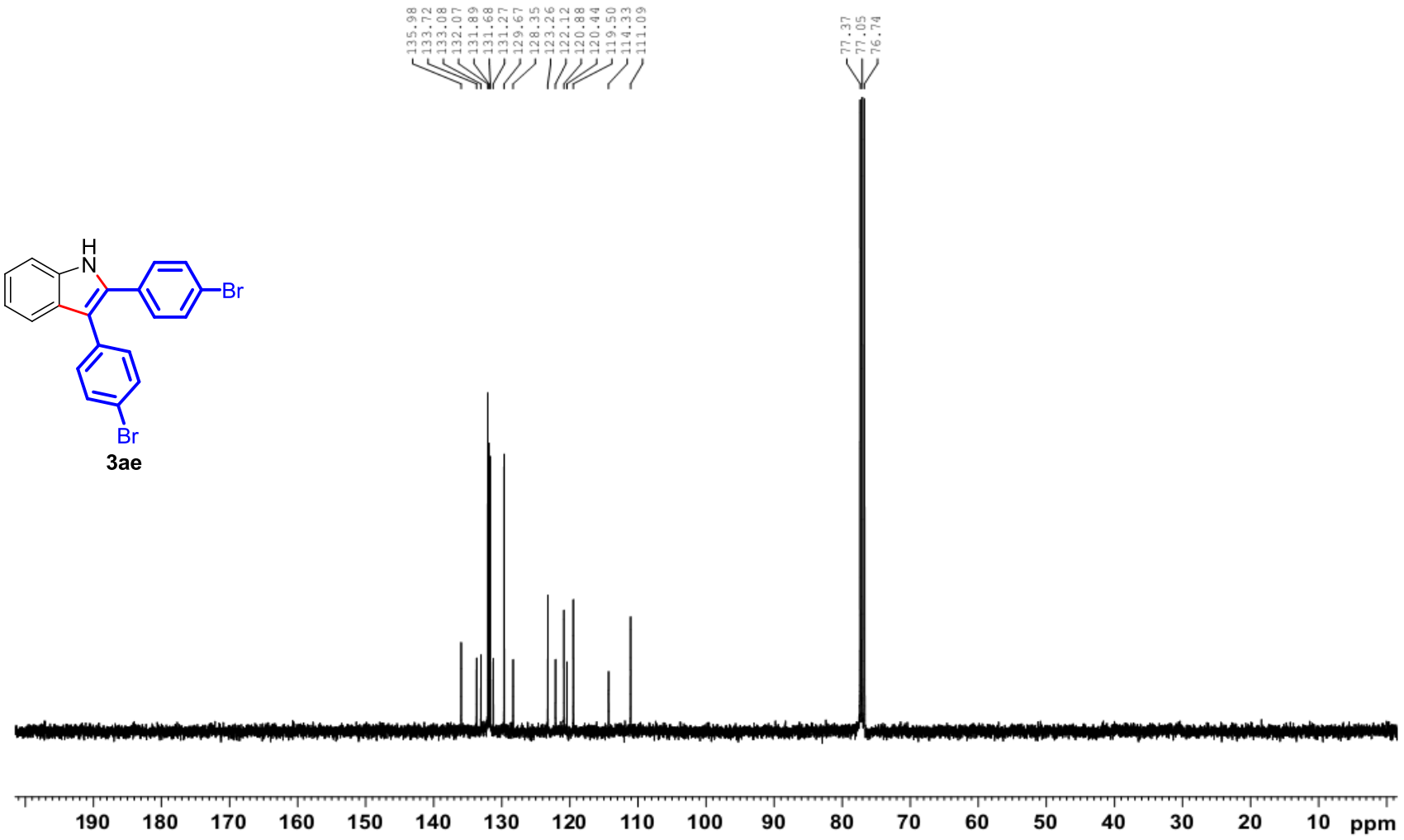
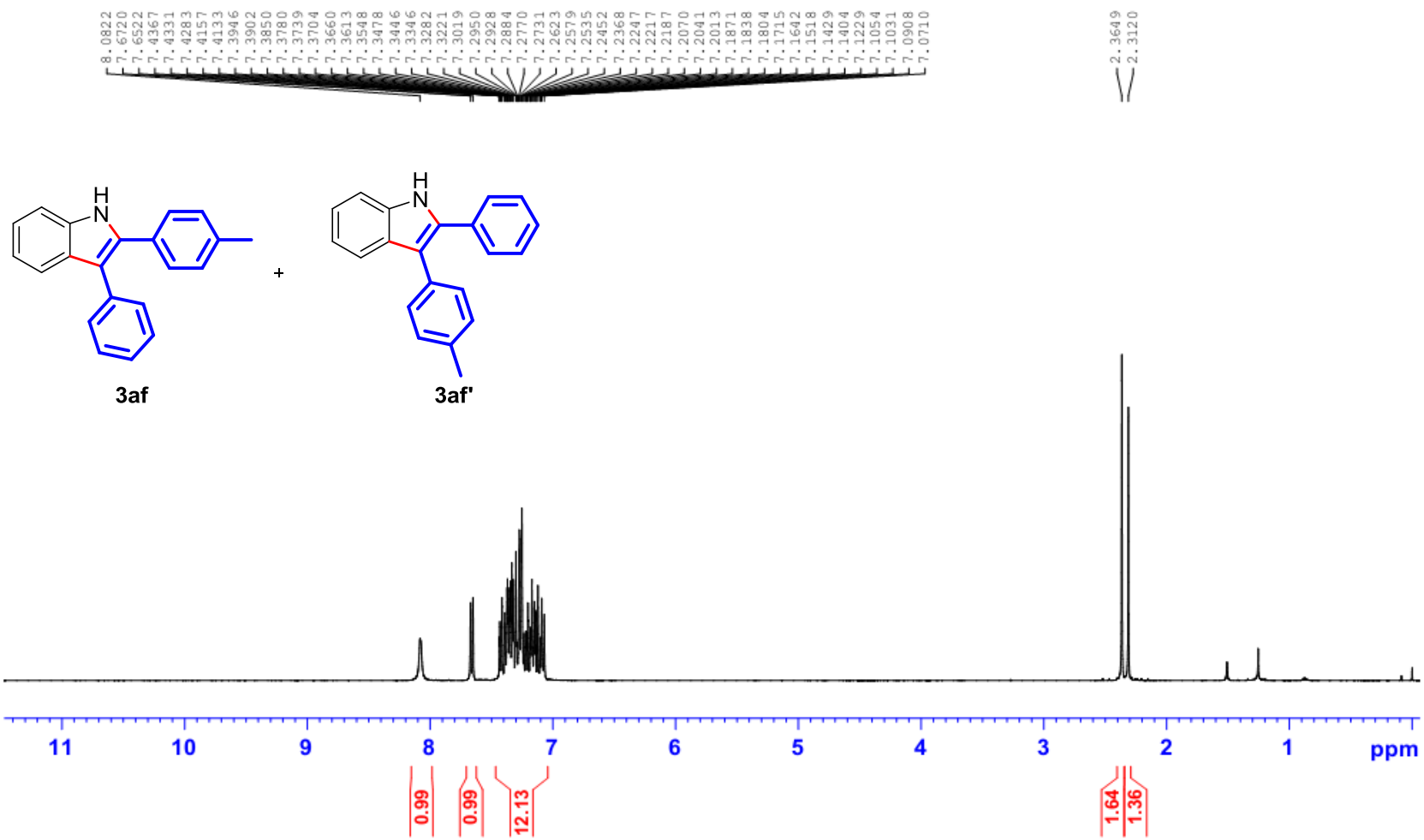
9
8
7
6
5
4
3
2
1
ppm
0.94
1.04
5.00
5.18
1.03

ZGY-130902-4-CNMR



04-10-ZhangCY-HNMR



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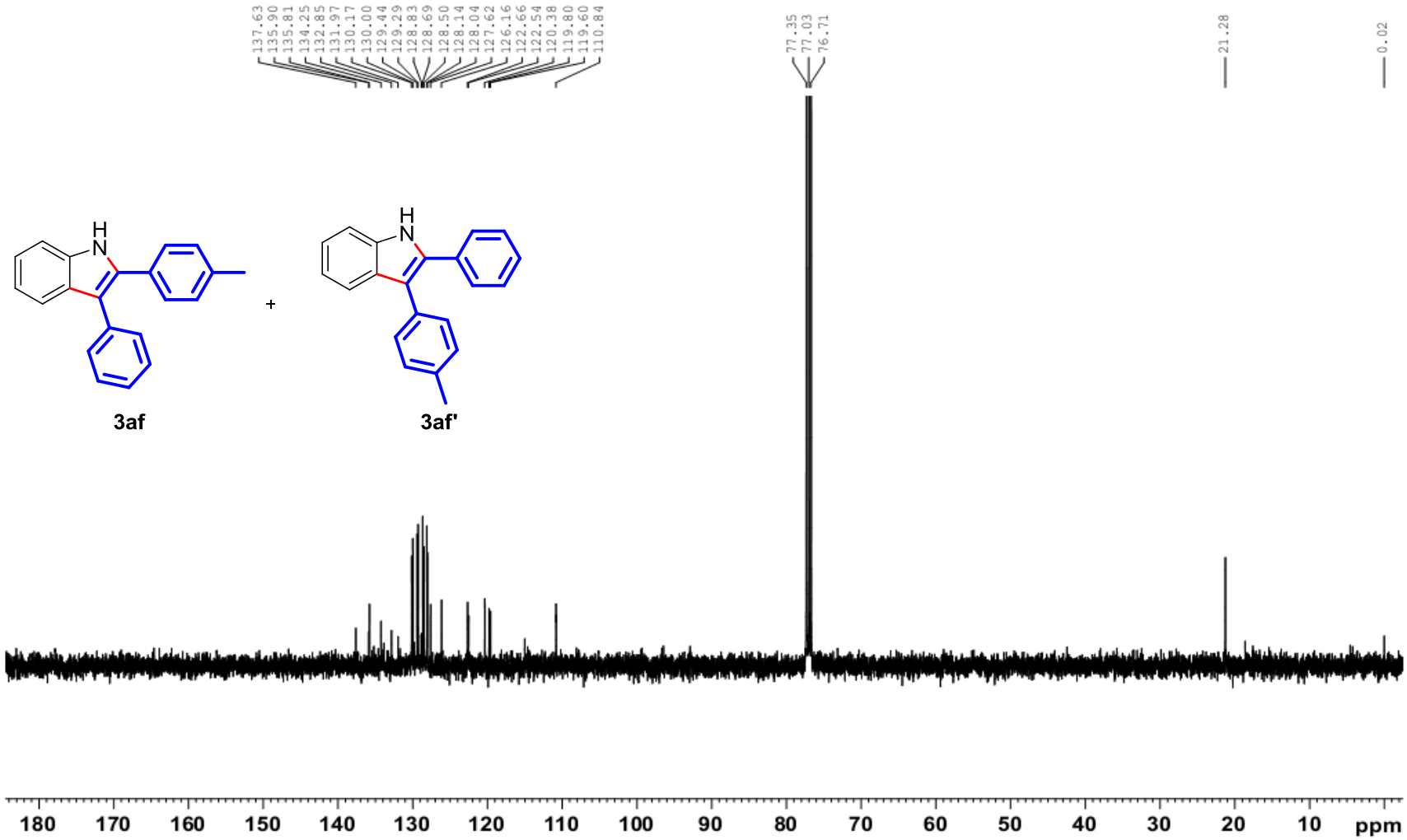
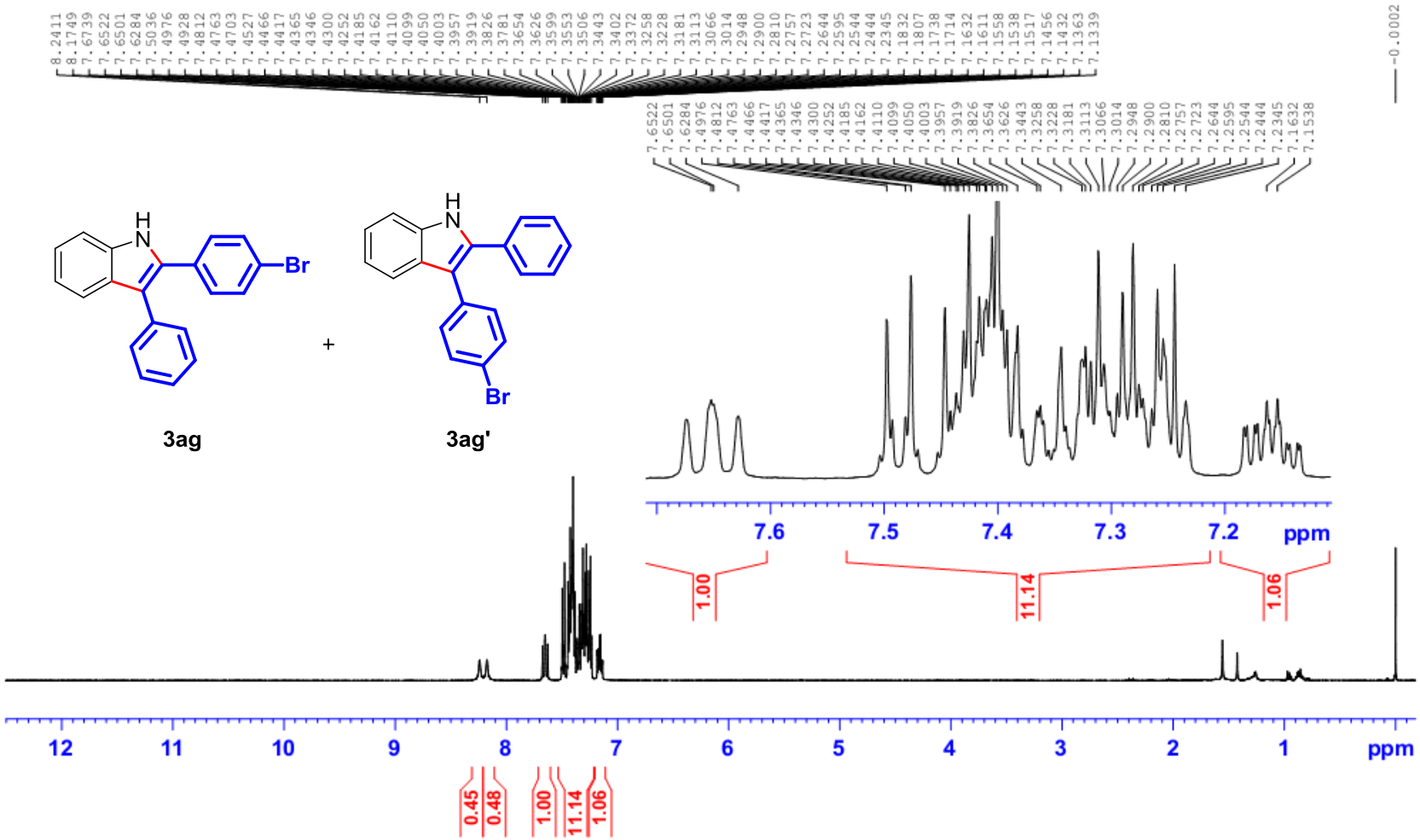


ZGY-130902-11-HNMR



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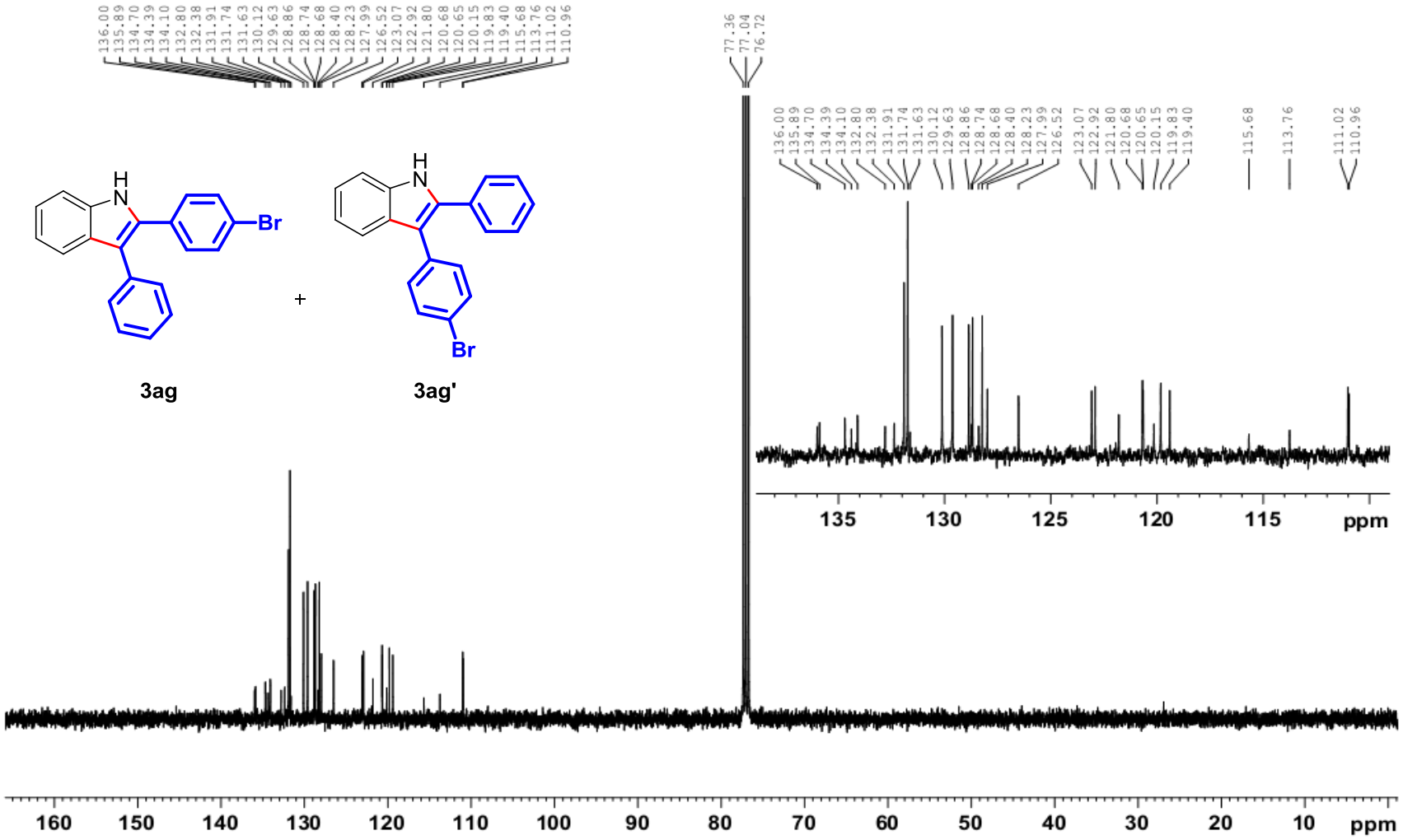
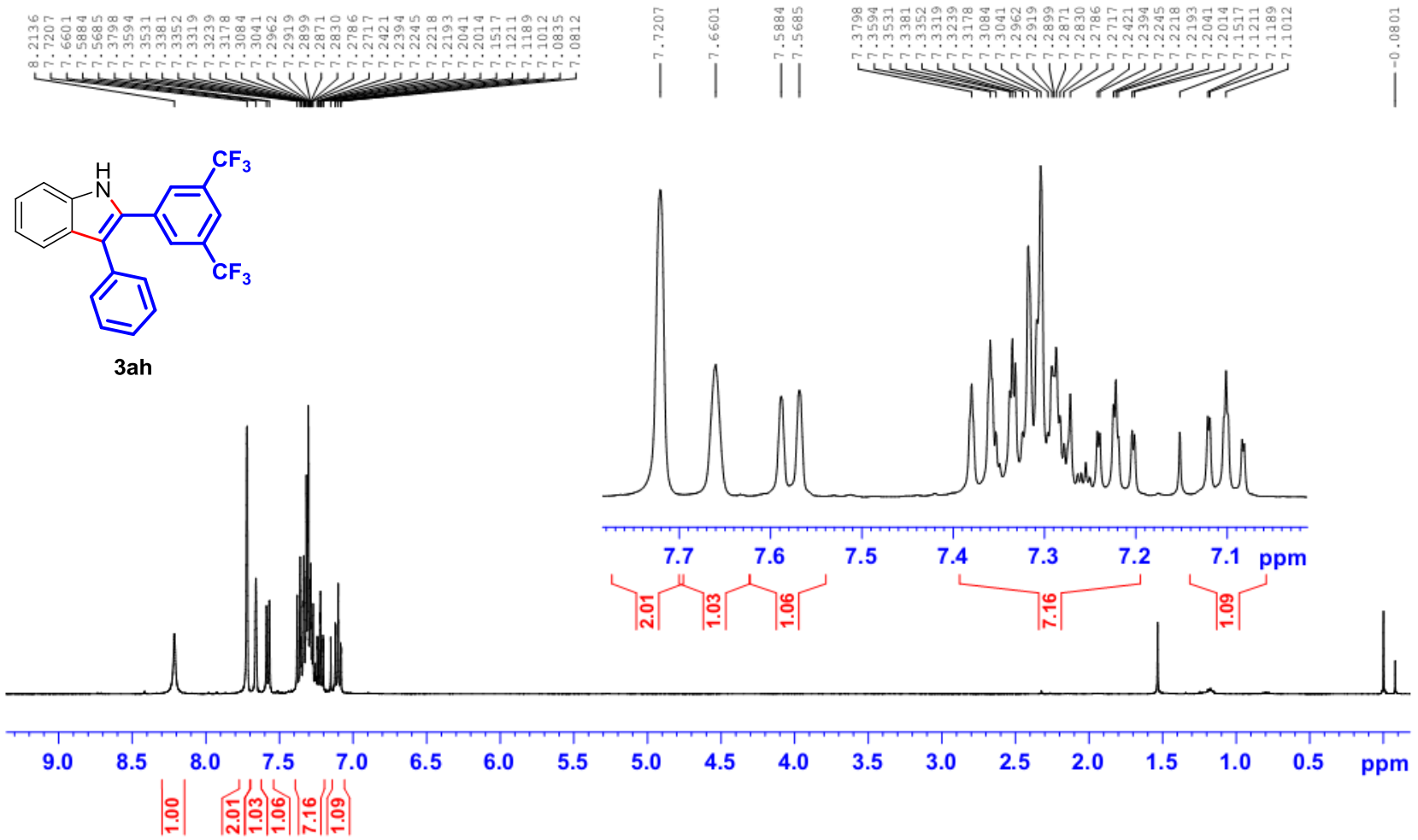


ZGY-130909-2-HNMR



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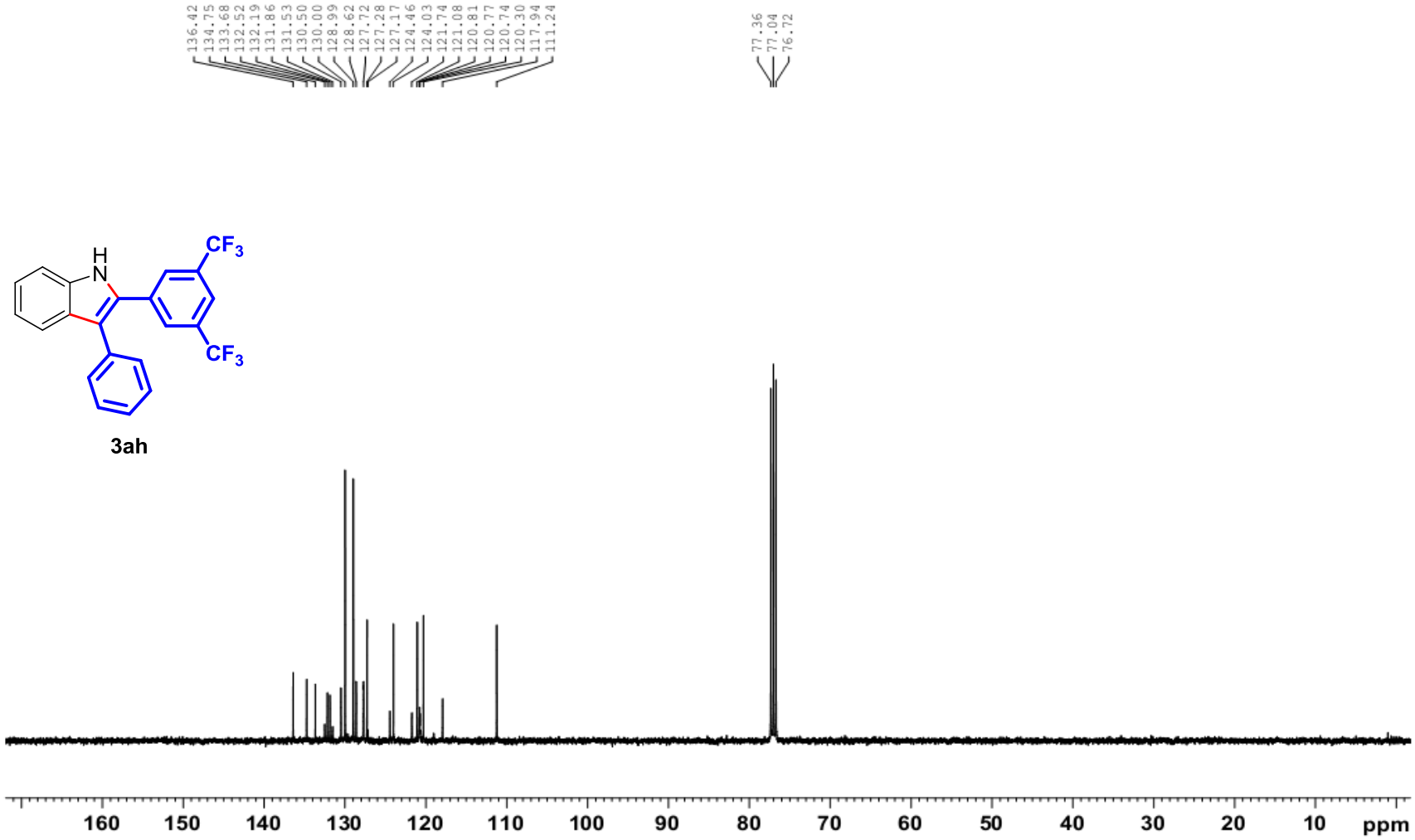

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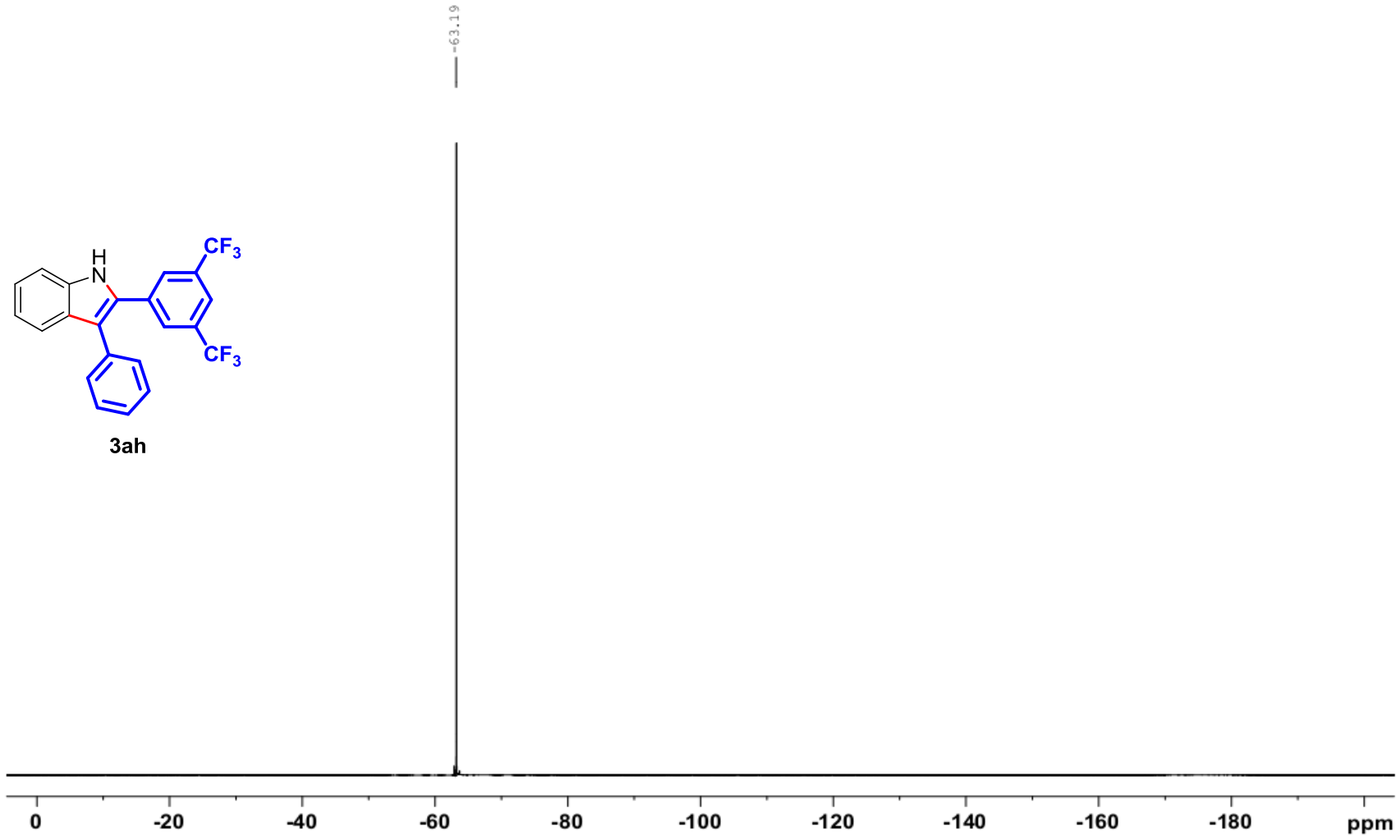

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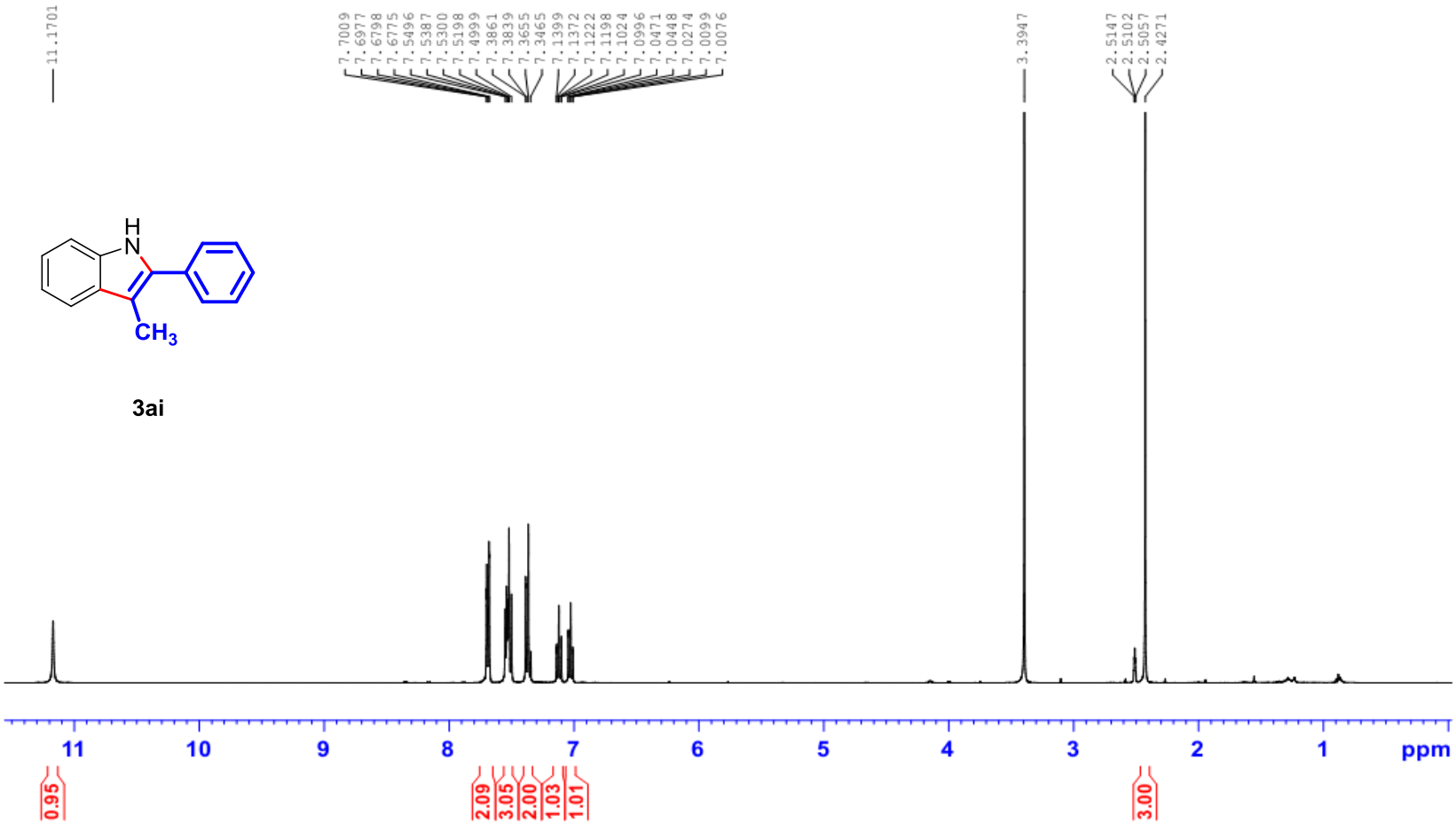
ZGY-131106-3-HNMR



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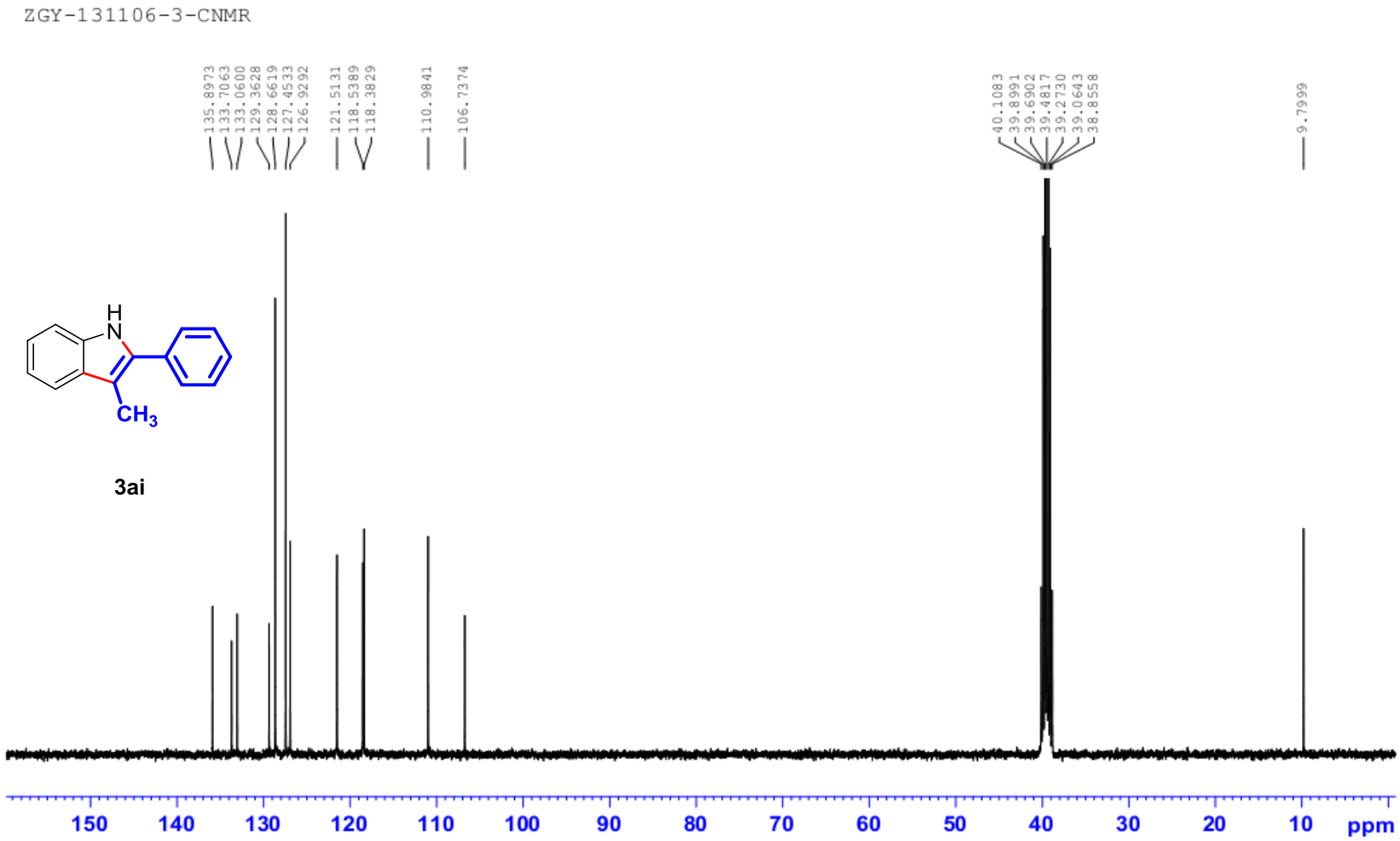
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39.6902
39.4817
39.2730
39.0643
38.8558
9.7999
H
N
CH3
3ai
150
140
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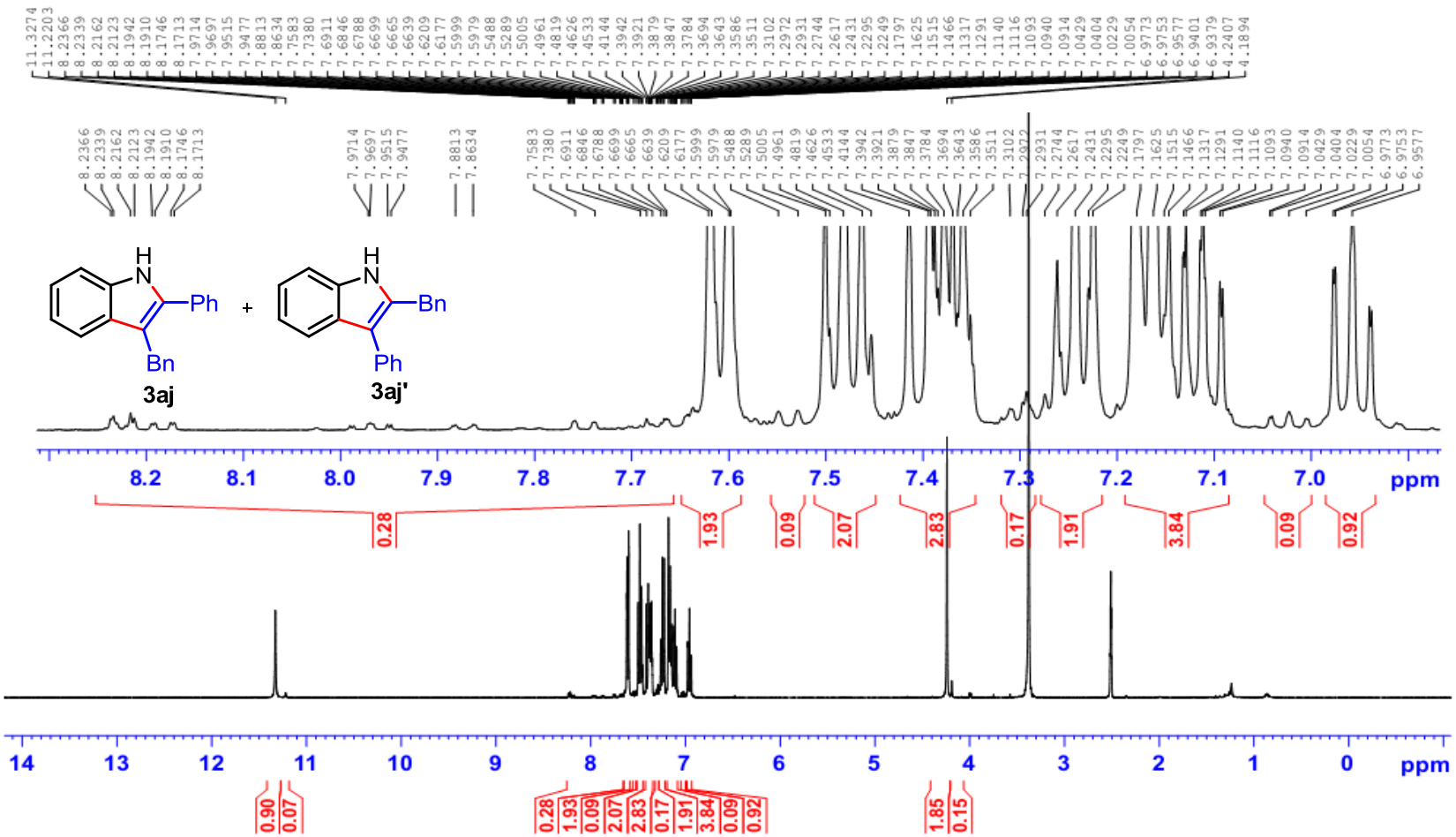
110
100
90
80
70
60
50
40
30
20
10
ppm

ZGY-131106-5-HNMR



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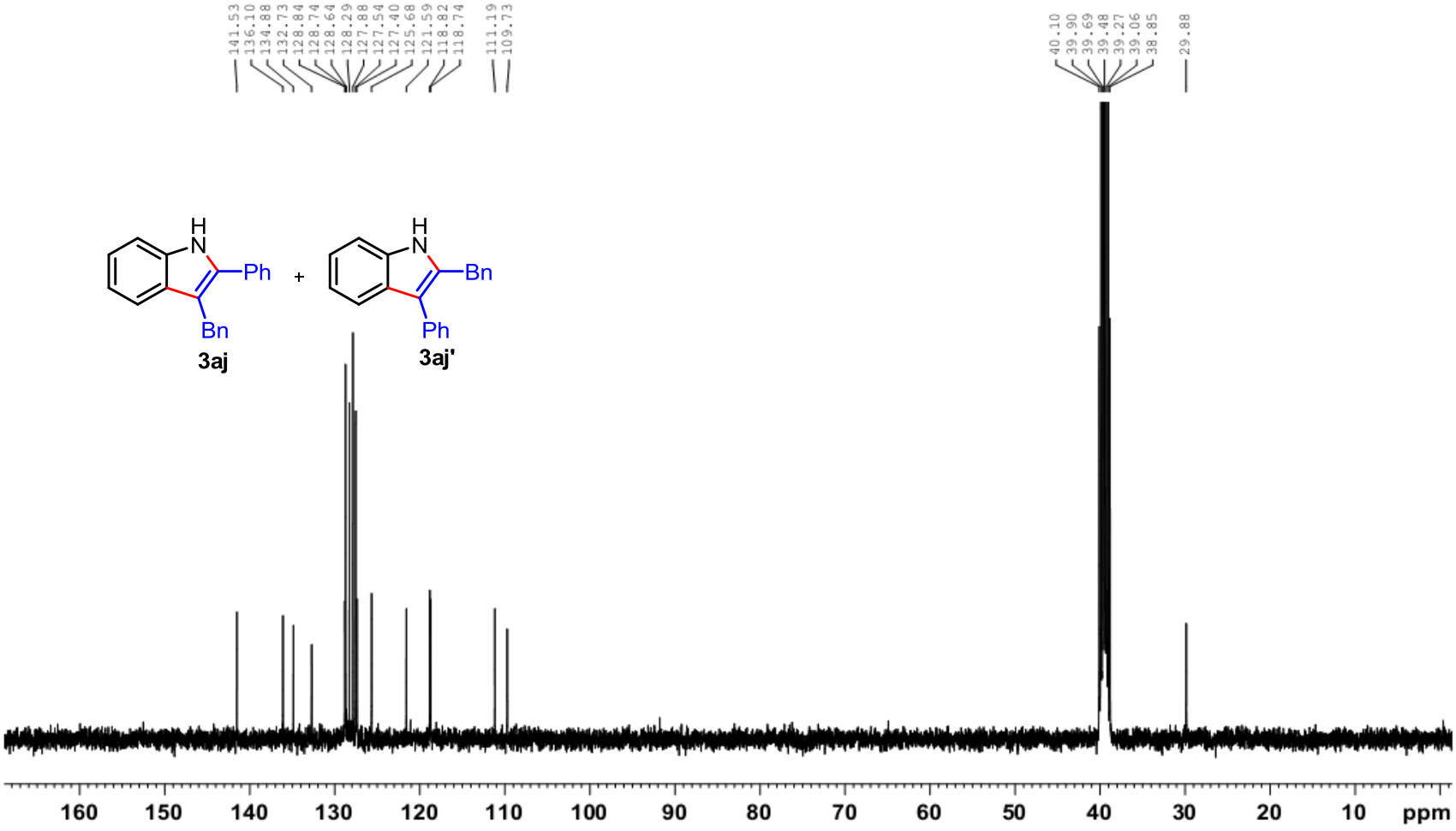

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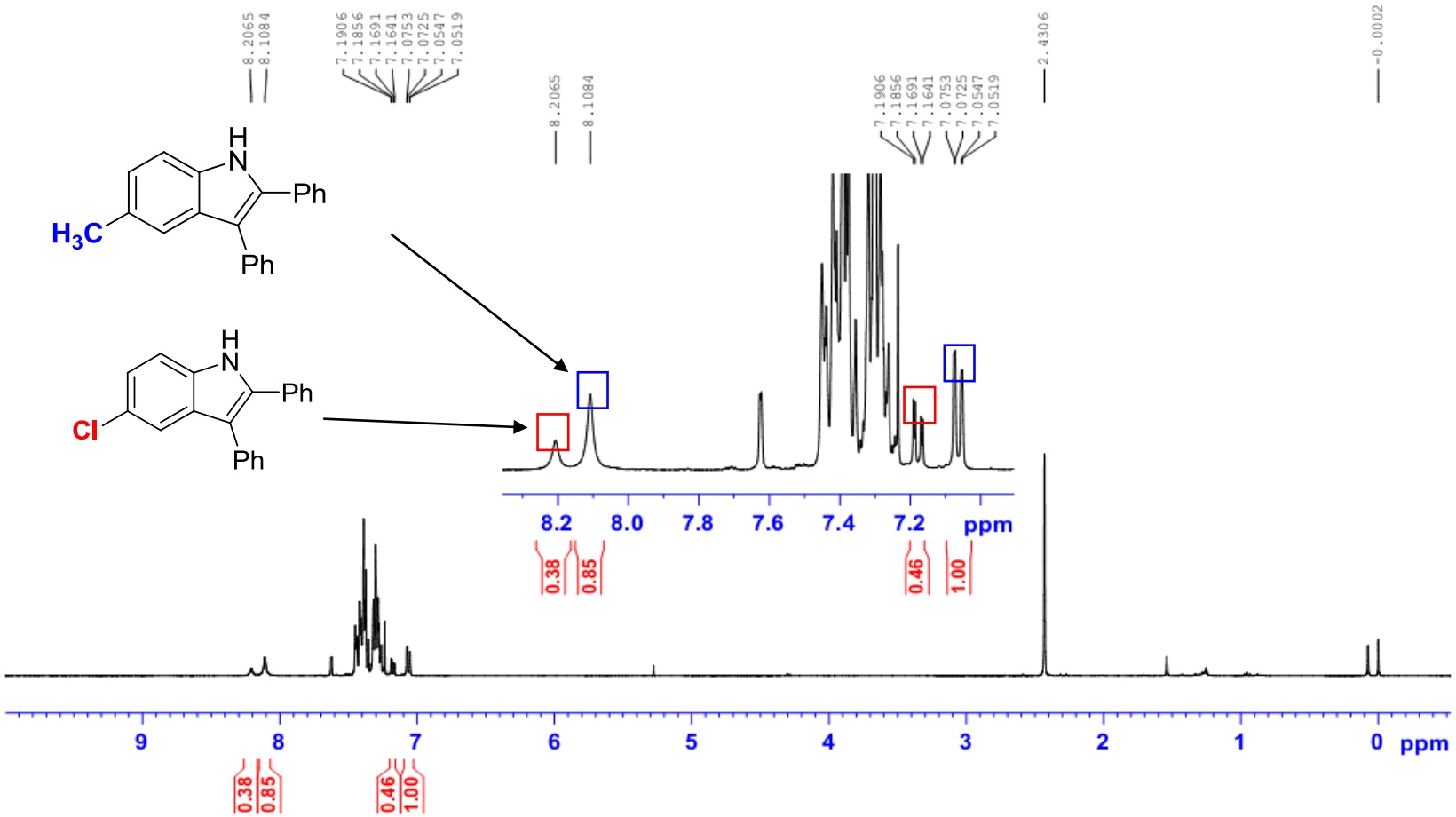

11-10-ZhangCY-HNMR