Supporting Information for:

Palladium–N-Heterocyclic Carbene (NHC)-Catalyzed Synthesis of 2-Ynamides via Oxidative Aminocarbonylation of Alkynes with Amines

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CONTENTS

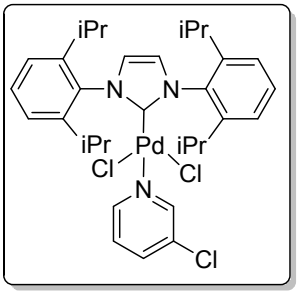
1. General methods

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. Aryl iodides were obtained from Alfa Aesar. Carbon monoxide (CO) with a purity of 99.99% was commercially available. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avance 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).

2. Synthesis of NHC palladium complexes

2.1 Synthesis of IPr-Pd-Peppsi-Cl_2 complex

IPr-Pd-Peppsi-Cl_2 was prepared according to the reported method [1].



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.88, 12H), 1.47 (d, *J* = 6.64, 12H), 3.12-3.19 (m, 4H), 7.01-7.04 (m, 1H), 7.14 (s, 2H), 7.34-7.52 (m, 7H), 8.49-8.58 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 26.4, 28.8, 124.1, 124.1, 124.4, 125.2, 130.4, 132.0, 135.0, 137.5, 146.7, 149.4, 150.4, 153.4.

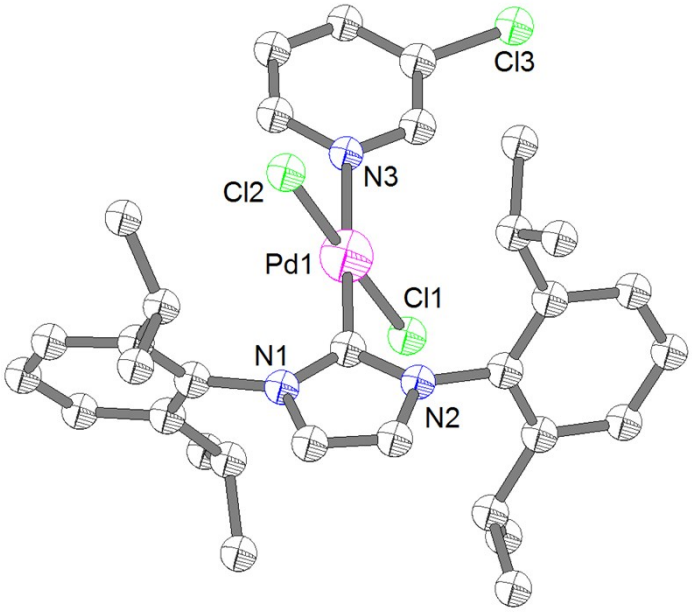
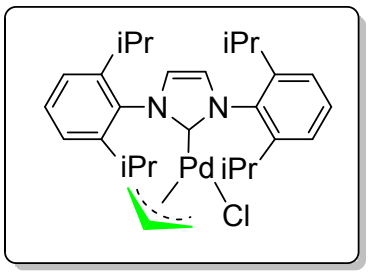


Figure S1. ORTEP drawing of IPr-Pd-Peppsi-Cl_2

2.2 Synthesis of IPr-Pd(allyl)Cl

IPr-Pd(allyl)Cl was prepared according to the reported method [2].

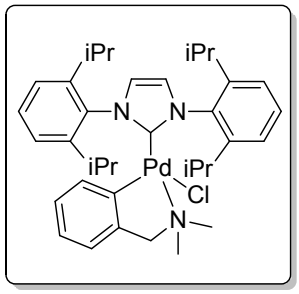


^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08-1.18 (m, 12H), 1.32-1.40 (m, 12H), 1.56 (d, J = 12 Hz, 1H), 2.75-3.16 (m, 6H), 3.88-3.91 (m, 1H), 4.76-4.86 (m, 1H), 7.16-7.44 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 22.9, 25.8, 26.5, 28.5, 28.6, 49.5, 72.5, 114.2, 123.8, 123.9, 124.1, 129.9, 135.8, 146.0, 146.2, 186.1.

2.3 Synthesis of IPr-Pd-dmba-Cl

IPr-Pd-dmba-Cl was prepared according to the reported method [3].

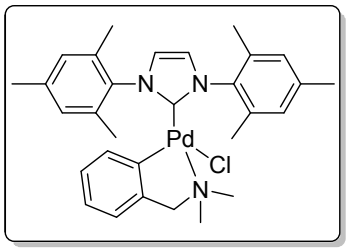


^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (d, *J* = 2.68, 6H), 1.01 (d, *J* = 6.84, 6H), 1.17 (d, *J* = 6.8, 6H), 1.48 (d, *J* = 6.56, 6H), 2.38 (s, 6H), 3.12-3.19 (m, 2H), 3.32-3.39 (m, 2H), 3.45 (s, 2H), 6.52-6.79 (m, 4H), 7.14-7.20 (m, 4H),7.29-7.41 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 23.3, 26.2, 26.4, 28.3, 29.0, 49.8, 72.6, 121.5, 122.6, 123.7, 124.0, 124.5, 125.4, 129.7, 136.2, 136.2, 144.7, 147.8, 147.8, 150.6, 177.6.

2.4 Synthesis of IMes-Pd-dmba-Cl

IMes-Pd-dmba-Cl was prepared according to the reported method [4].

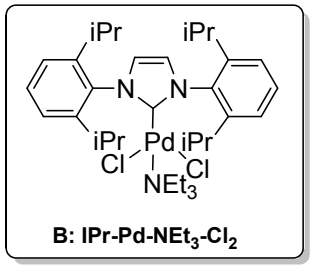


^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 6H), 2.27 (s, 6H), 2.42 (d, *J* = 4.0, 6H), 3.51 (s, 2H), 6.56-6.58 (m, 1H), 6.67-6.71 (m, 1H), 6.75-6.83 (m, 4H), 6.97 (s, 2H), 7.08 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.3, 21.1, 50.0, 72.3, 121.2, 122.9, 123.2, 123.9, 128.7, 129.4, 133.9, 136.2, 137.4, 138.3, 138.3, 147.6, 149.3, 175.7.

2.5 Synthesis of (IPr)$PdCl_2$(TEA) complex

(IPr)$PdCl_2$(TEA) was prepared according to the reported method [5].



^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, *J* = 4.0, 9H),1.05 (d, *J* = 8.0, 12H), 1.41 (d, *J* = 8.0, 12H), 2.50 (dd, J_1 = 4 Hz, J_2 = 8 Hz, 6H),3.13-3.19 (m, 4H), 7.11 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 4H), 7.48 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 22. 7, 26. 6, 28. 7, 46. 6, 123. 6, 124. 9, 130.0, 135. 2, 147. 1, 154. 3.

References

1) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.;Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem.−Eur. J.* 2006, **12**, 4743.

2) N. Marion, O. Navarro, J. -G. Mei, E. D. Stevens, N. M. Scott and S. P. Nolan, *J. Am. Chem. Soc.,* 2006, **128**, 4101.

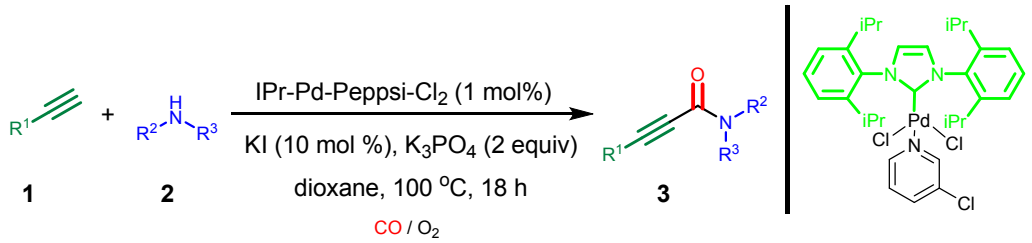
3) G.-R. Peh, E. Assen, B. Kantchev, C. Zhang, J. Y. Ying, *Org. Biomol. Chem.,* 2009, **7**, 2110.

4) E. Assen, B. Kantchev, J. Y. Ying, *Organometallics* 2009, **28**, 289.

5) M.-T. Chen, D. A. Vicic, M. L. Turner and O. Navarro, *Organometallics,* 2011, **30**, 5052;

3. General procedure for the carbonylation reaction

3.1 General procedure for the oxidative aminocarbonylation reaction

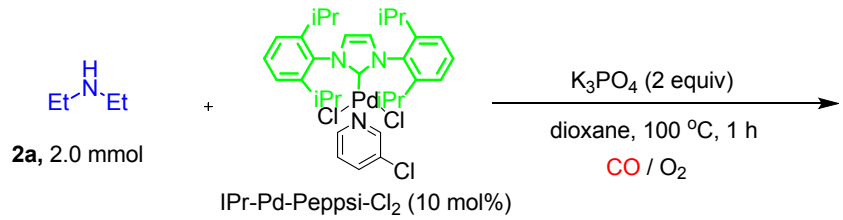


All carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, alkynes (1.0 mmol), amines (2.0 mmol), IPr-Pd-Peppsi-Cl_2 (1 mol%), K_3PO_4 (2.0 mmol), KI (10 mol%) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 ℃, and the whole reaction mixture was stirred for 18 hours. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by GC-MS. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1-1/1) to afford the desired product **3** as a white solid.

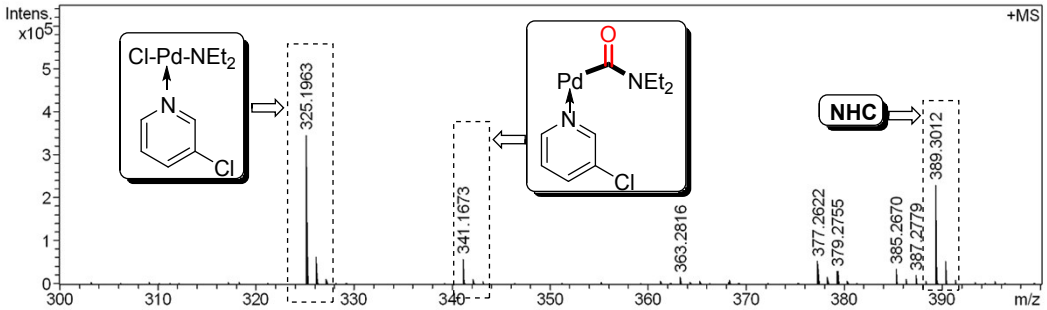
4. Preliminary Mechanistic Studies

4.1 Preliminary Mechanistic Studies :HRMS

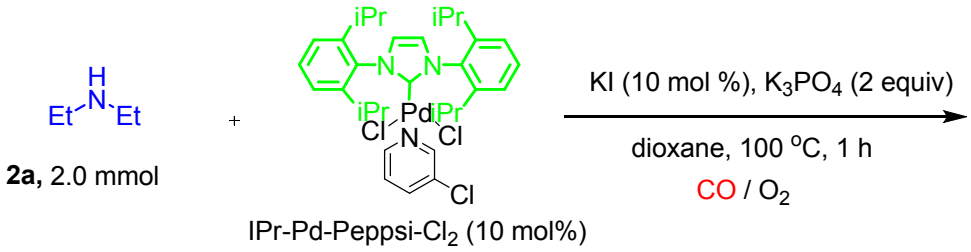
I: **2a** + [Pd] + K_3PO_4



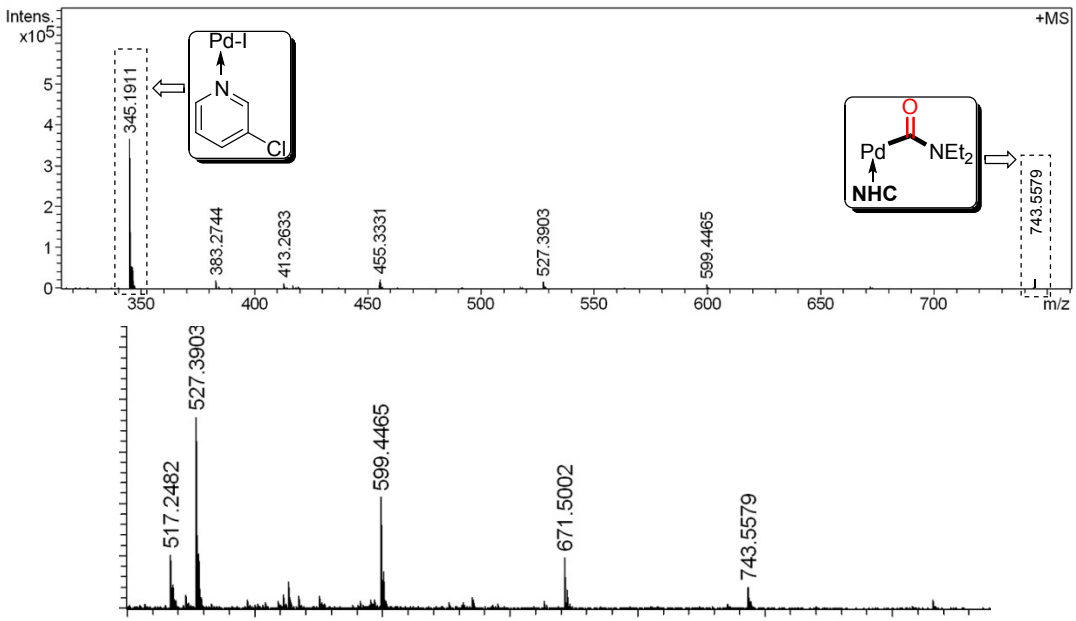
The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, **2a** (2.0 mmol), IPr-Pd-Peppsi-Cl_2 (10 mol%), K_3PO_4 (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 ℃, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by ESI-MS.



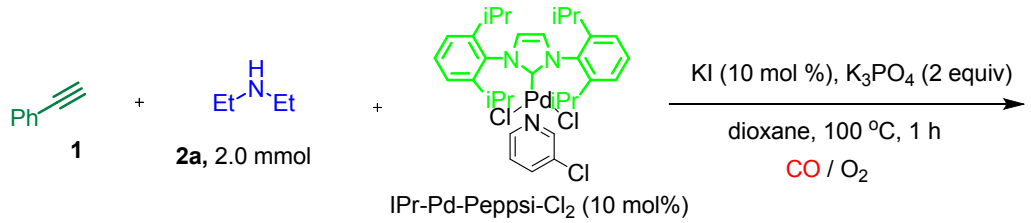
II: **2a** + [Pd] + K_3PO_4 + KI



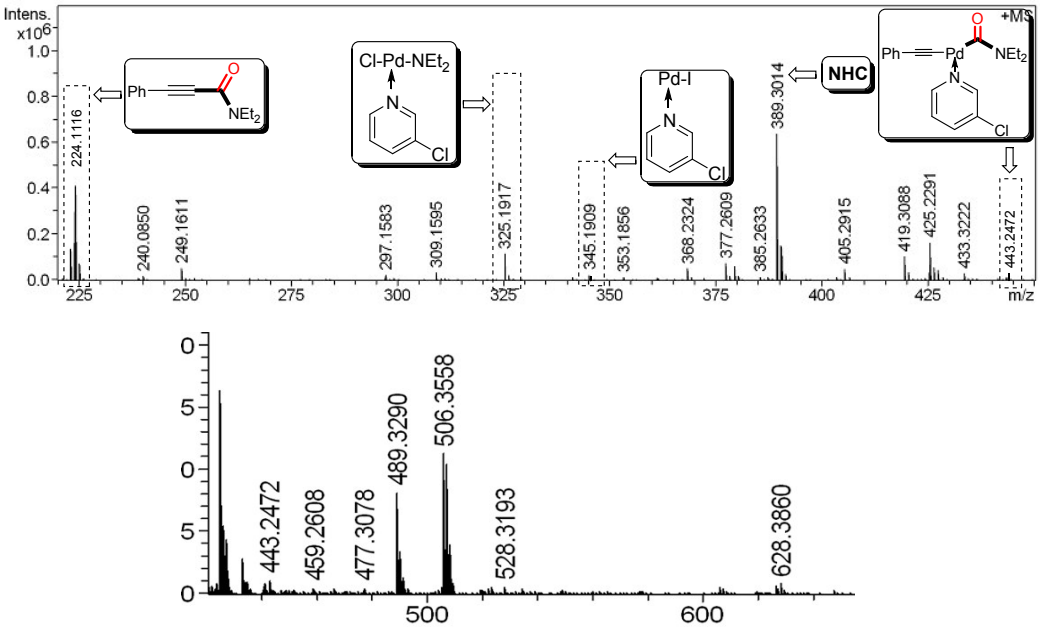
The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, **2a** (2.0 mmol), IPr-Pd-Peppsi-Cl_2 (10 mol%), KI (10 mol%), K_3PO_4 (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 ℃, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by ESI-MS.



III: **1a** + **2a** + [Pd] + K_3PO_4 + KI

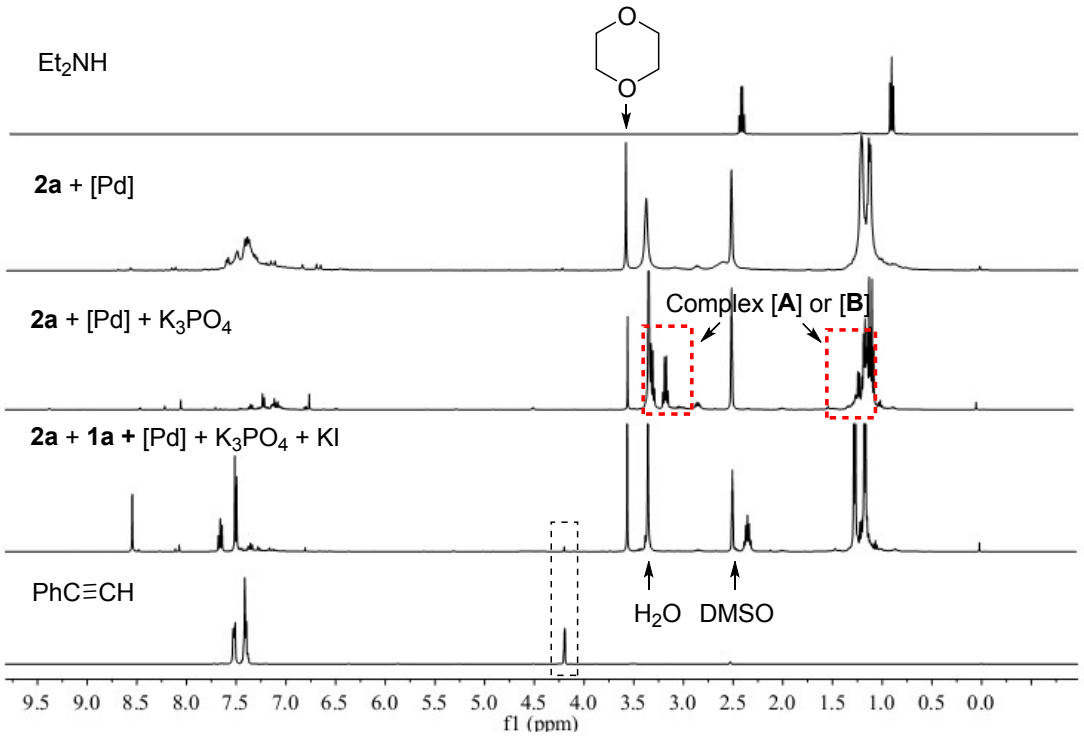


The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, **1a** (1.0 mmol), **2a** (2.0 mmol), IPr-Pd-Peppsi-Cl_2 (10 mol%), KI (10 mol%), K_3PO_4 (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 ℃, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. The reaction mixture was qualitatively and quantitatively analyzed by ESI-MS.



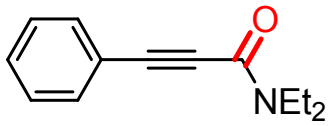
4.2 Preliminary Mechanistic Studies :NMR

The carbonylation experiments were carried out in a 75 mL autoclave equipped with magnetic stirring and automatic temperature control. In a typical experiment, **2a** (2.0 mmol), IPr-Pd-Peppsi-Cl_2 (10 mol%), K_3PO_4 (2.0 mmol) and 1,4-dioxane (5.0 ml) were charged into the reactor in the presence of air. Then the autoclave was purged three times with carbon monoxide, pressurized with carbon monoxide/dioxygen to a pressure of 3.0/0.5 MPa. The autoclave was placed in an oil bath pre-heated at 100 ℃, and the whole reaction mixture was stirred for an hour. After the reaction, the autoclave was cooled, and excess CO was discharged slowly at room temperature. After evaporation of the solvents under reduced pressure, the residue was directly analyzed by NMR in DMSO-d_6.



5. NMR, HRMS and IR datas of 2-ynamides

N,N-diethyl-3-phenylpropiolamide (3aa):



3aa

The products **3aa** were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.5 (petroleum ether/ethyl acetate = 10/1).

Yellowish oil, 95% yield.

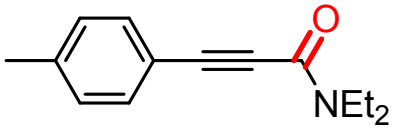
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 8.0 Hz, 3H), 1.28 (t, J = 8.0 Hz, 3H), 3.45 (dd, J_1 = 12 Hz, J_2 = 4 Hz, 2H), 3.63 (dd, J_1 = 12 Hz, J_2 = 8 Hz, 2H), 7.34-7.43 (m, 2H), 7.53-7.55 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 14.4, 39.3, 43.6, 81.9, 88.9, 120.7, 128.5, 129.9, 132.3, 153.9.

HRMS (ESI) calcd. for $C_{13}H_{15}NO$ [M+H]: 202.1226, found: 202.1232.

IR (KBr, cm^{-1}) 2970, 2209, 1635, 1139, 765.

N,N-diethyl-3-(p-tolyl)propiolamide (3ba):



3ba

The products **3ba** were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.45 (petroleum ether/ethyl acetate = 10/1).

Yellowish oil, 95% yield.

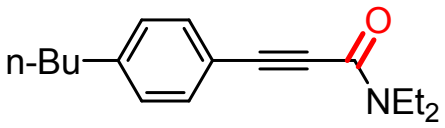
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 8.0 Hz, 3H), 1.28 (t, J = 8.0 Hz, 3H), 3.45 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 2.38 (s, 3H), 3.64 (dd, J_1 = 12 Hz, J_2 = 4 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 14.4, 21.6, 39.3, 43.6, 81.5, 89.4, 117.7, 129.3, 132.3, 140.3, 154.2.

HRMS (ESI) calcd. for $C_{14}H_{17}NO$ [M+H]: 216.1019, found: 216.1019.

IR (KBr, cm^{-1}) 2954, 2215, 1619, 1419, 759.

3-(4-butylphenyl)-N,N-diethylpropiolamide (3ca):



3ca

The products **3ca** were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.4 (petroleum ether/ethyl acetate = 10/1).

Yellowish oil, 92% yield.

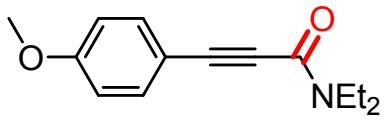
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 8.0 Hz, 3H), 1.10 (t, J = 8.0 Hz, 3H), 1.18-1.21 (m, 3H), 1.25-1.15 (m, 2H), 2.54 (t, J = 8.0 Hz, 2H), 3.37 (dd, J_1 = 12 Hz, J_2 = 8 Hz, 2H), 3.55 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 13.9, 14.4, 22.3, 33.3, 35.7, 39.3, 43.6, 81.5, 89.4, 1 17.8, 128.6, 132.3, 145.3, 154.2.

HRMS (ESI) calcd. for $C_{17}H_{23}NO$ [M+H]: 280.1672, found: 280.1663.

IR (KBr, cm^{-1}) 2934, 2201, 1635, 1425, 1139, 715.

N,N-diethyl-3-(4-methoxyphenyl)propiolamide (3da):



3da

The products **3da** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.4 (petroleum ether/ethyl acetate = 5/1).

Yellowish oil, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, J = 8 Hz, 3H), 1.28 (t, J = 8 Hz, 3H), 3.45 (dd, J_1 = 12 Hz, J_2 = 4 Hz, 2H), 3.63 (dd, J_1 = 12 Hz, J_2 = 4 Hz, 2H), 3.83 (s, 3H), 6.86-6.90 (m, 2H), 7.47-7.50 (m, 2H).

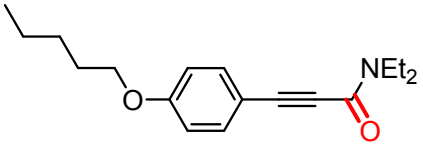
^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 14.4, 39.2, 43.6, 55.7, 81.2, 89.5, 112.6,

114.2,134.1, 154.3, 160.9.

HRMS (ESI) calcd. for $C_{14}H_{17}NO_2$ [M+H]: 232.1332, found: 232.1334.

IR (KBr, cm^{-1}) 2962, 2209, 1627, 1239, 1131, 823.

N,N-diethyl-3-(4-(pentyloxy)phenyl)propiolamide (3ea):



3ea

The products **3ea** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.5 (petroleum ether/ethyl acetate = 5/1).

White solid, 94% yield, m. p. =48 °C.

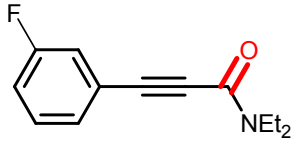
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 8 Hz, 3H), 1.07 (t, J = 8 Hz, 3H), 1.17 (t, J = 8 Hz, 3H), 1.28-1.33 (m, 4H), 1.64-1.71 (m, 2H), 3.34 (dd, J_1 = 16 Hz, J_2 = 4 Hz, 2H), 3.53 (dd, J_1 = 16 Hz, J_2 = 4 Hz, 2H), 3.84 (t, J = 8 Hz, 2H), 6.75 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.36 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ12.9, 14.0, 14.4, 22.4, 28.1, 28.8, 39.2, 43.6, 68.1,81.1, 89.6, 112.3, 114.6, 134.1, 154.3, 160.5.

HRMS (ESI) calcd. for $C_{18}H_{25}NO_2$ [M+H]: 288.1958, found: 288.1970.

IR (KBr, cm^{-1}) 3350, 2984, 2209, 1628, 1411, 1267, 787.

N,N-diethyl-3-(3-fluorophenyl)propiolamide (3fa):



3fa

The products **3fa** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.6 (petroleum ether/ethyl acetate = 5/1).

White solid, 87% yield, m. p. =48 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 8 Hz, 3H), 1.29 (t, J = 8 Hz, 3H), 3.46 (dd, J_1 = 12 Hz, J_2 = 4 Hz, 2H), 3.63 (dd, J_1 = 12 Hz, J_2 = 4 Hz, 2H), 7.10-7.22 (m, 2H),

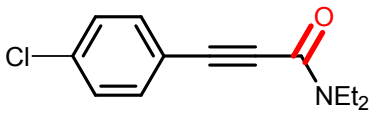
7.23-7.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 14.4, 39.4, 43.6, 76.7, 77.1, 77.4, 82.5, 87.4, 87.4, 117.2, 117.4, 118.9, 119.1, 122.5, 122.6, 128.2, 128.2, 130.2, 130.3, 153.6, 161.0, 163.5.

HRMS (ESI) calcd. for $C_{13}H_{14}FNO$ [M+H]: 242.0947, found: 242.0952.

IR (KBr, cm^{-1}) 2984, 2223, 1638, 1411, 1253, 1175, 787.

3-(4-chlorophenyl)-N,N-diethylpropiolamide (3ga):



3ga

The products **3ga** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.5 (petroleum ether/ethyl acetate = 5/1).

White solid, 93% yield, m. p. = 70 °C.

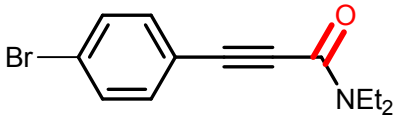
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 8 Hz, 3H), 1.28 (t, J = 8 Hz, 3H), 3.45 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 3.63 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 7.33-7.36 (m, 2H), 7.45-7.48 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 191.4. 12.8, 14.4, 39.3, 43.6, 76.8, 77.1, 77.4, 82.8, 87.7, 119.2, 128.9, 133.5, 136.1, 153.7.

HRMS (ESI) calcd. for $C_{13}H_{14}ClNO$ [M+H]: 236.0837, found: 236.0841.

IR (KBr, cm^{-1}) 2970, 2215, 1635, 1491, 1289, 1089, 845.

3-(4-bromophenyl)-N,N-diethylpropiolamide (3ha):



3ha

The products **3ha** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.4 (petroleum ether/ethyl acetate = 5/1).

White solid, 91% yield, m. p. =82 °C.

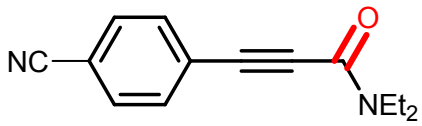
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, J = 4 Hz, 3H), 1.2 (t, J = 4 Hz, 3H), 3.37 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 3.55 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 7.30-7.33 (m, 2H), 7.41-7.45 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 14.4, 39.4, 43.6, 76.8, 77.1, 77.4, 82.9, 87.8, 119.7, 124.5, 131.9, 133.7, 153.7.

HRMS (ESI) calcd. for $C_{13}H_{14}BrNO$ [M+H]: 280.0322, found: 280.0324.

IR (KBr, cm^{-1}) 2934, 2202, 1618, 1413, 1297, 1055, 785.

3-(4-cyanophenyl)-N,N-diethylpropiolamide (3ia):



3ia

The products **3ia** were eluted with petroleum ether/ethyl acetate (5/1). Rf = 0.4 (petroleum ether/ethyl acetate = 2/1).

Yellowish solid, 50% yield, m.p. =40 °C.

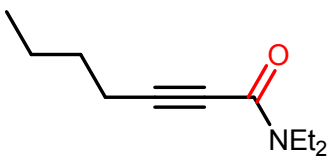
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 4 Hz, 3H), 1.29 (t, J = 4 Hz, 3H), 3.52 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 3.63 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 7.62-7.69 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 14.5, 39.4, 43.6, 76.8, 77.1, 77.4, 85.3, 86.6, 113.3, 118.0, 125.6, 132.2, 132.7, 153.2.

HRMS (ESI) calcd. for $C_{14}H_{14}N_2O$ [M+H]: 227.1179, found: 227.1178.

IR (KBr, cm^{-1}) 2927, 2209, 1441, 1289, 851.

N,N-diethylhept-2-ynamide (3ia):



3ja

The products **3ja** were eluted with petroleum ether/ethyl acetate (3/1). Rf = 0.4 (petroleum ether/ethyl acetate = 1/1).

Yellowish oil, 53% yield.

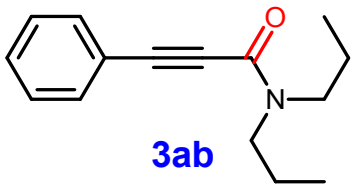
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 8 Hz, 3H), 1.11 (t, J = 8 Hz, 3H), 1.19 (t, J = 8 Hz, 3H), 1.45-1.55 (m, 2H), 1.56-1.57 (m, 2H), 3.38 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H), 3.54 (dd, J_1 = 16 Hz, J_2 = 8 Hz, 2H),.

^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 13.5, 14.3, 18.6, 21.9, 29.9, 39.1, 43.4, 74.3, 76.8, 77.1, 77.4, 91.8, 154.2.

HRMS (ESI) calcd. for $C_{11}H_{20}NO$ [M+H]: 182.1537, found: 182.1539.

IR (KBr, cm^{-1}) 2962, 2212, 1628, 1283, 759.

3-phenyl-N,N-dipropylpropiolamide (3ab):



3ab

The products **3ab** were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.4 (petroleum ether/ethyl acetate = 10/1)

Yellowish oil, 93% yield.

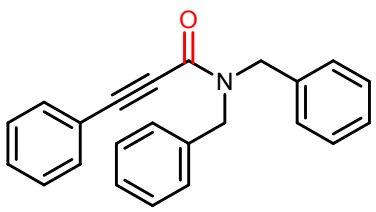
^{1}H NMR (400 MHz, $CDCl_3$) δ 091-1.00 (m, 6H), 1.59-1.70 (m, 4H), 3.35 (t, J = 8 Hz, 2H), 3.55 (t, J = 8 Hz, 2H), 7.33-7.41 (m, 3H), 7.51 (t, J = 4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 11.1, 20.5, 22.0, 46.3, 50.6, 76.7, 77.0, 77.3, 81.9, 89.0, 120.5, 128.3, 129.6, 132.0, 154.3.

HRMS (ESI) calcd. for $C_{15}H_{20}NO$ [M+H]: 230.1539, found: 230.1540.

IR (KBr, cm^{-1}) 3306, 2970, 2209, 1618, 1419, 1139, 759.

N,N-dibenzyl-3-phenylpropiolamide (3ac):



3ac

The products **3ac** were eluted with petroleum ether/ethyl acetate (20/1). Rf = 0.6

(petroleum ether/ethyl acetate = 10/1).

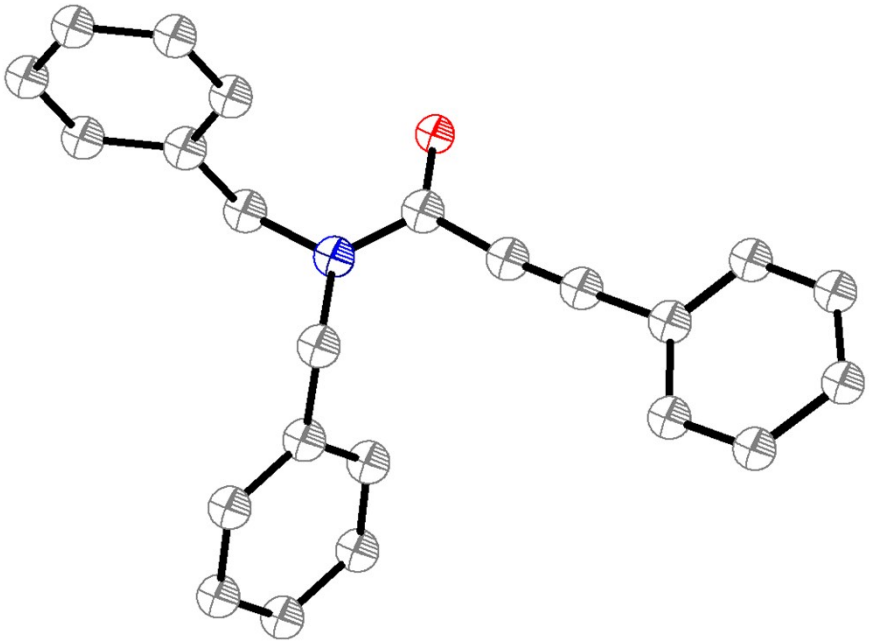
White solid, 91% yield, m.p. = 105 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (s, 2H), 4.76 (s, 2H), 1.10 (t, *J* = 4 Hz, 3H), 1.2 (t, *J* = 4 Hz, 3H), 7.27-7.50 (m, 12H), 7.52(s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 46.4, 51.5, 76.7, 77.0, 77.3, 81.7, 90.9, 120.4, 127.7, 127.8, 128.0, 128.5, 128.5, 128.7, 28.9, 130.2, 132.5, 136.1, 136.3, 155.0.

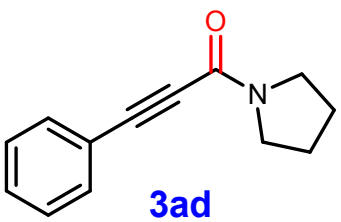
HRMS (ESI) calcd. for $C_{23}H_{19}NO$ [M+H]: 325.1467, found: 325.1469.

IR (KBr, cm^{-1}) 2962, 2352, 1655, 1455, 1267, 1023, 801.



3ac X-ray

3-phenyl-1-(pyrrolidin-1-yl)prop-2-yn-1-one (3ad):



3ad

The products **3ad** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.5

(petroleum ether/ethyl acetate = 5/1).

Yellowish oil, 89% yield.

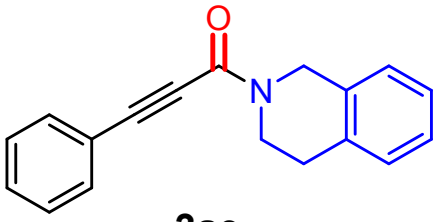
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.74 (t, *J* = 4 Hz, 2H), 3.84 (t, *J* = 8 Hz, 2H), 7.34-7.54 (m, 3H), 7.55-7.56 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 41.9, 47.3, 66.4, 66.8, 76.9, 77.2, 77.6, 80.8, 91.1, 120.2, 128.6, 130.2, 132.3, 153.1.

HRMS (ESI) calcd. for $C_{13}H_{13}NO$ [M+H]: 199.0997, found: 199.0999.

IR (KBr, cm^{-1}) 2934, 2202, 1618, 1413, 1297, 1055, 785.

1-(3,4-dihydroisoquinolin-2(1H)-yl)-3-phenylprop-2-yn-1-one (3ae)



3ae

The products **3ae** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.3 (petroleum ether/ethyl acetate = 5/1).

Yellowish oil, 89% yield.

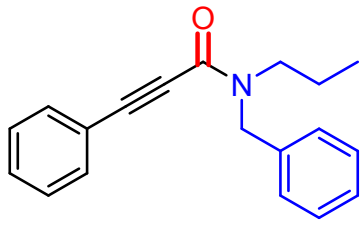
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90-2.99 (m, 2H), 3.91 (t, J = 4, 0.85H), 4.08 (t, J = 4, 1.25H), 4.82 (s, 1.23H), 4.98 (s, 0.83), 7.14-7.19 (m, 4H), 7.21-7.44 (m, 3H), 7.57-7.59 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 29.6, 39.7, 44.1, 44.7, 48.7, 81.4, 81.5, 90.4, 91.1, 126.1, 126.5, 126.6, 126.7, 126.8, 127.0, 128.6, 128.6, 129.0, 130.1, 132.4, 132.4, 133.9, 153.4, 153.7.

HRMS (ESI) calcd. for $C_{18}H_{15}NO$ [M+H]: 262.1226, found: 262.1224.

IR (KBr, cm^{-1}) 2934, 2202, 1618, 1413, 1297, 1055, 785.

N-benzyl-3-phenyl-N-propylpropiolamide (3af)



3af

The products **3af** were eluted with petroleum ether/ethyl acetate (10/1). Rf = 0.4 (petroleum ether/ethyl acetate = 5/1).

Yellowish oil, 83% yield.

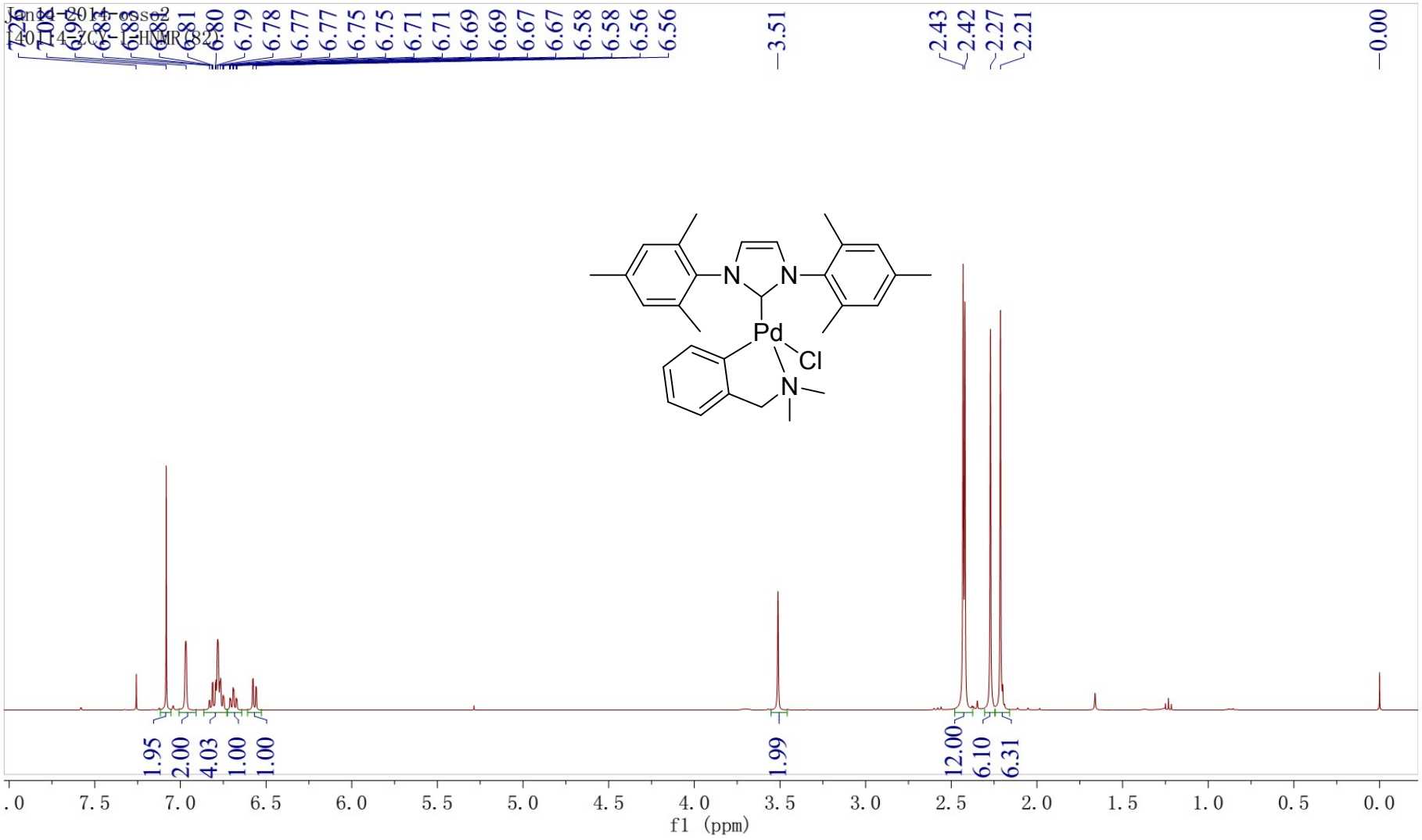
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87-0.97 (m, 3H), 1.56-1.68 (m, 3H), 3.33-3.55 (m, 2H), 4.68-4.87 (m, 2H), 7.28-7.56 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 11.4, 20.3, 21.7, 45.9, 47.4, 50.0, 52.7, 81.8, 82.0, 90.0, 90.2, 127.5, 127.6, 128.1, 128.5, 128.6, 128.7, 128.8, 130.0, 132.4, 132.4, 154.8, 155.0.

HRMS (ESI) calcd. for $C_{19}H_{19}NO$ [M+H]: 277.1467, found: 277.1462.

IR (KBr, cm^{-1}) 2934, 2202, 1618, 1413, 1297, 1055, 785.

6. Copies for ^{1}H NMR and ^{13}C NMR of the Compounds and 2-Ynamides products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6.67
6.67
6.58
6.58
6.56
6.56
3.51
2.43
2.42
2.27
2.21
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N
Pd
Cl
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4.03
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1.99
12.00
6.10
6.31
.0
7.5
7.0
6.5
6.0
5.5
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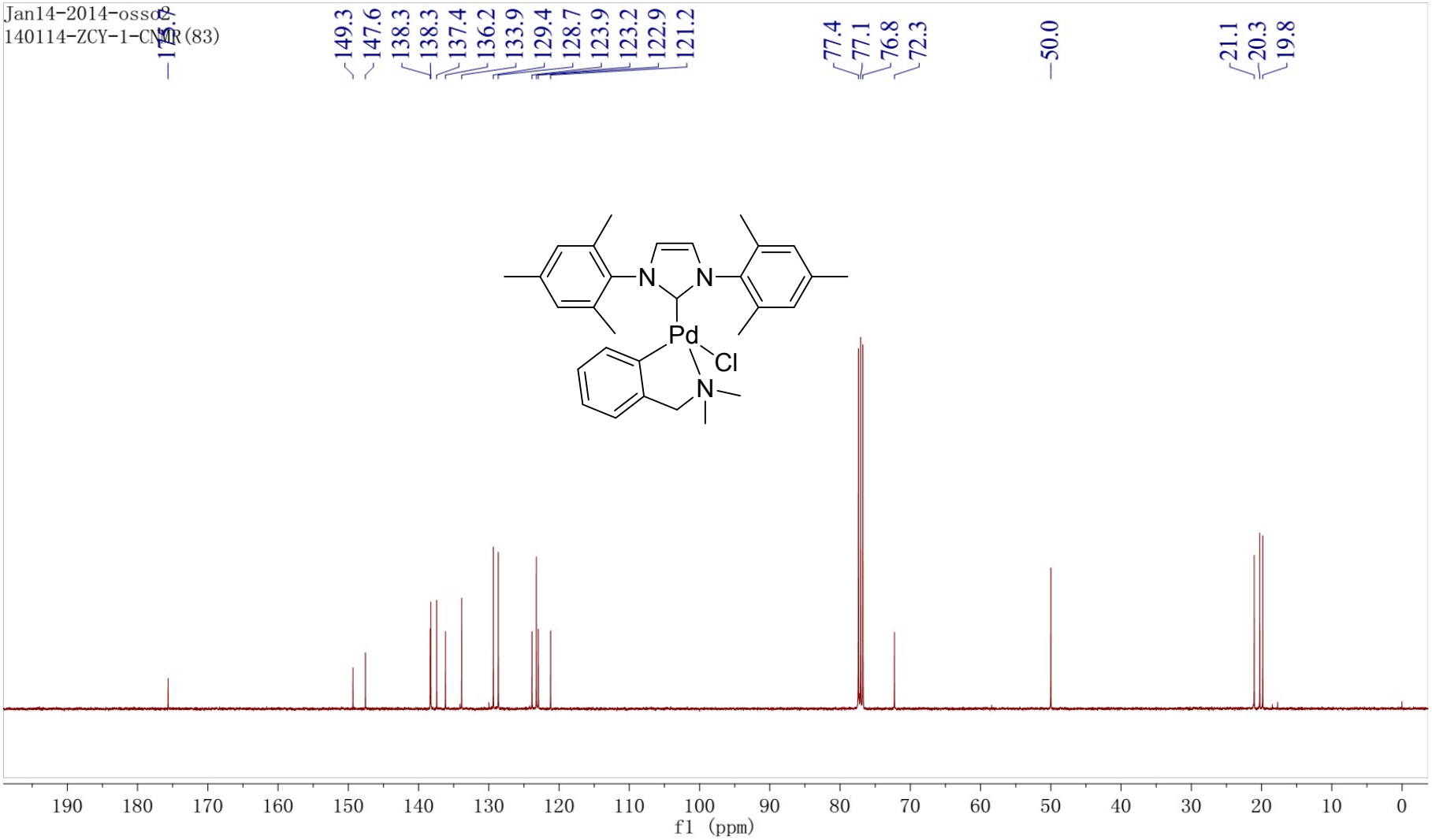
0.0
f1 (ppm)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133.9
129.4
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123.9
123.2
122.9
121.2
77.4
77.1
76.8
72.3
50.0
21.1
20.3
19.8
N
N
Pd
Cl
N
190
180
170
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130
120
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100
90
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10
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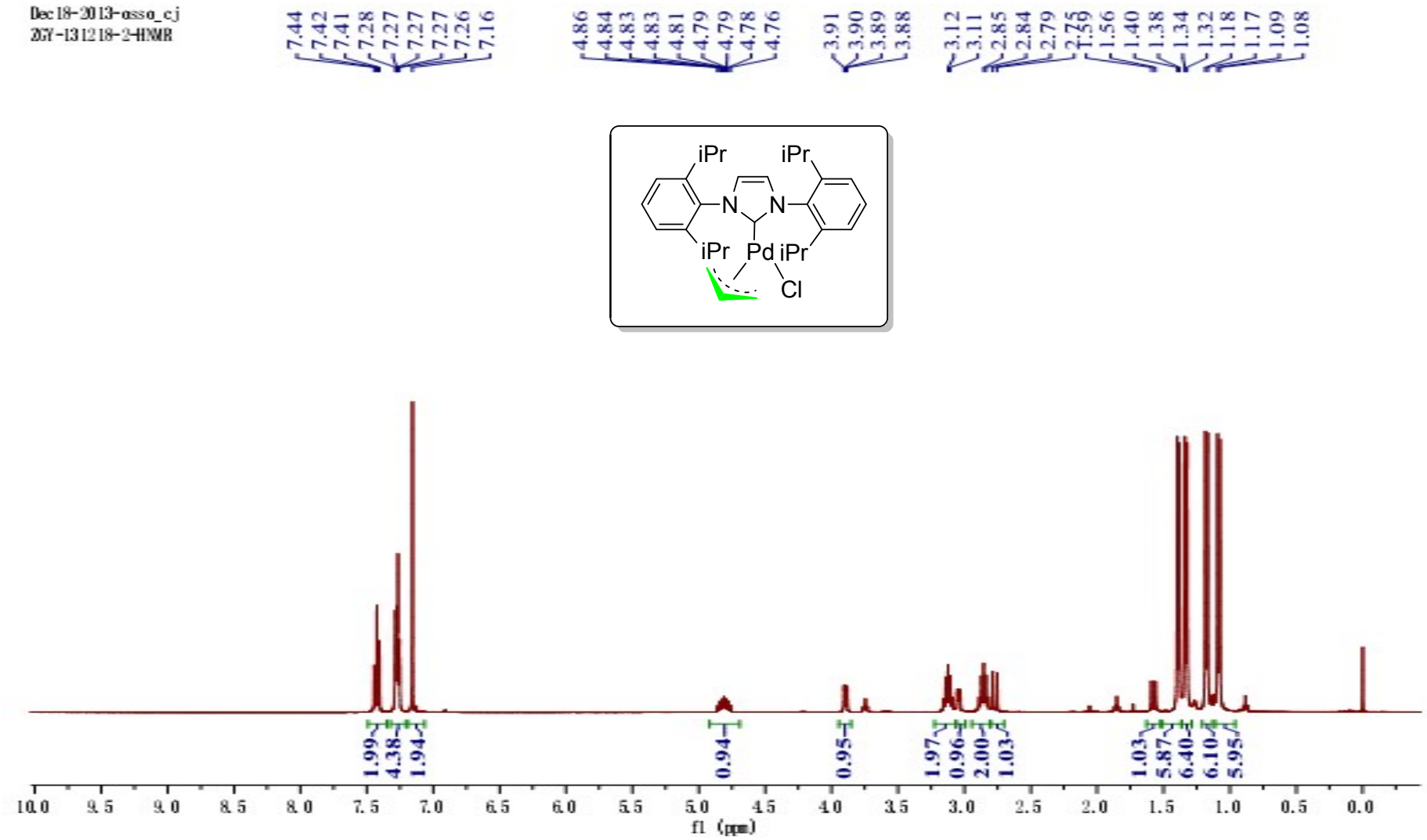
f1 (ppm)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4.83
4.81
4.79
4.79
4.78
4.76
3.91
3.90
3.89
3.88
3.12
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2.79
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1.34
1.32
1.18
1.17
1.09
1.08
iPr
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iPr
Pd
iPr
Cl
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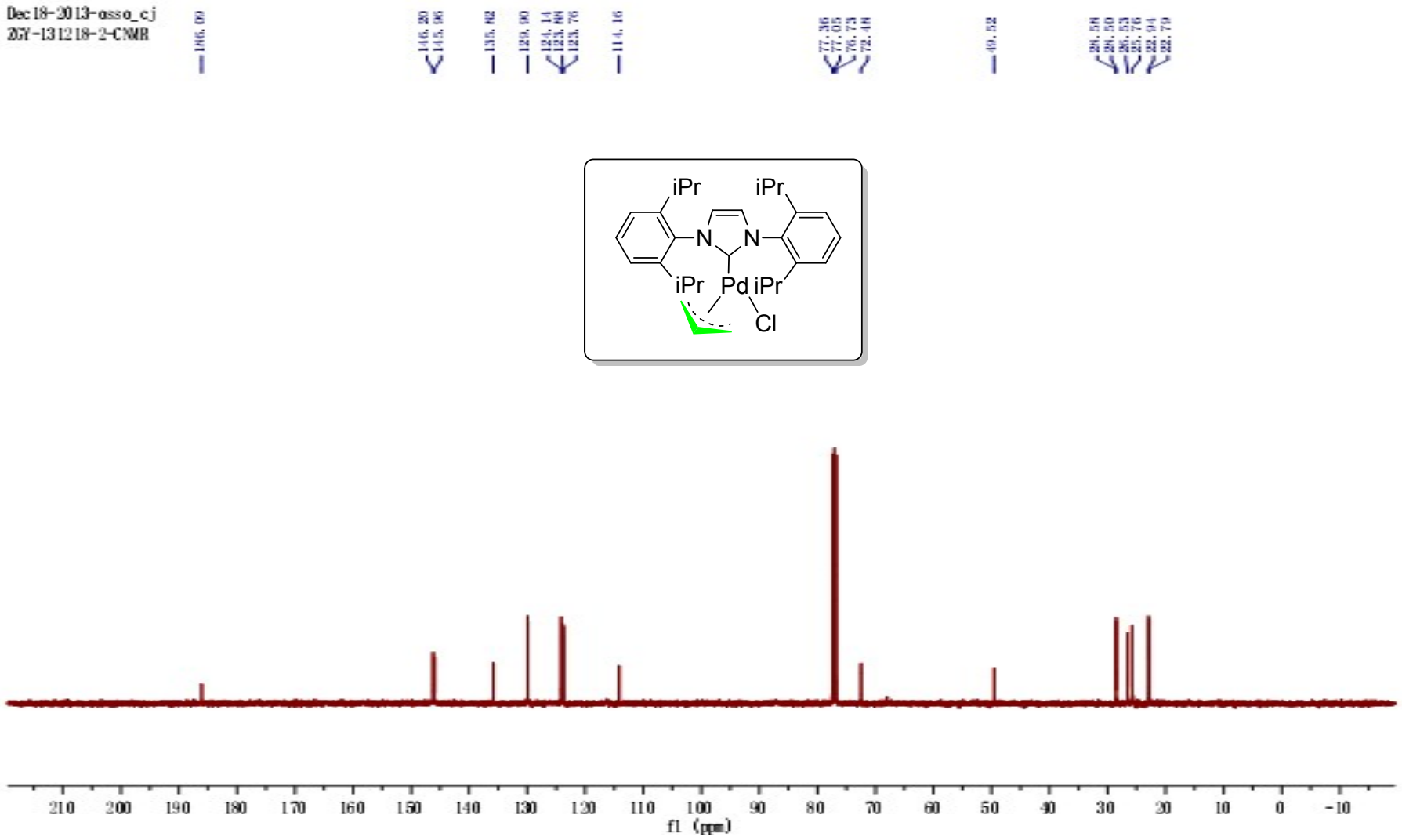
f1 (ppm)


Dec18-2013-asso_cj
267-131218-2-CNMR
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77.05
76.73
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49.52
28.58
28.50
26.53
25.76
22.94
22.79
iPr
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iPr
Pd
iPr
Cl
210
200
190
180
170
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100
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80
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30
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10
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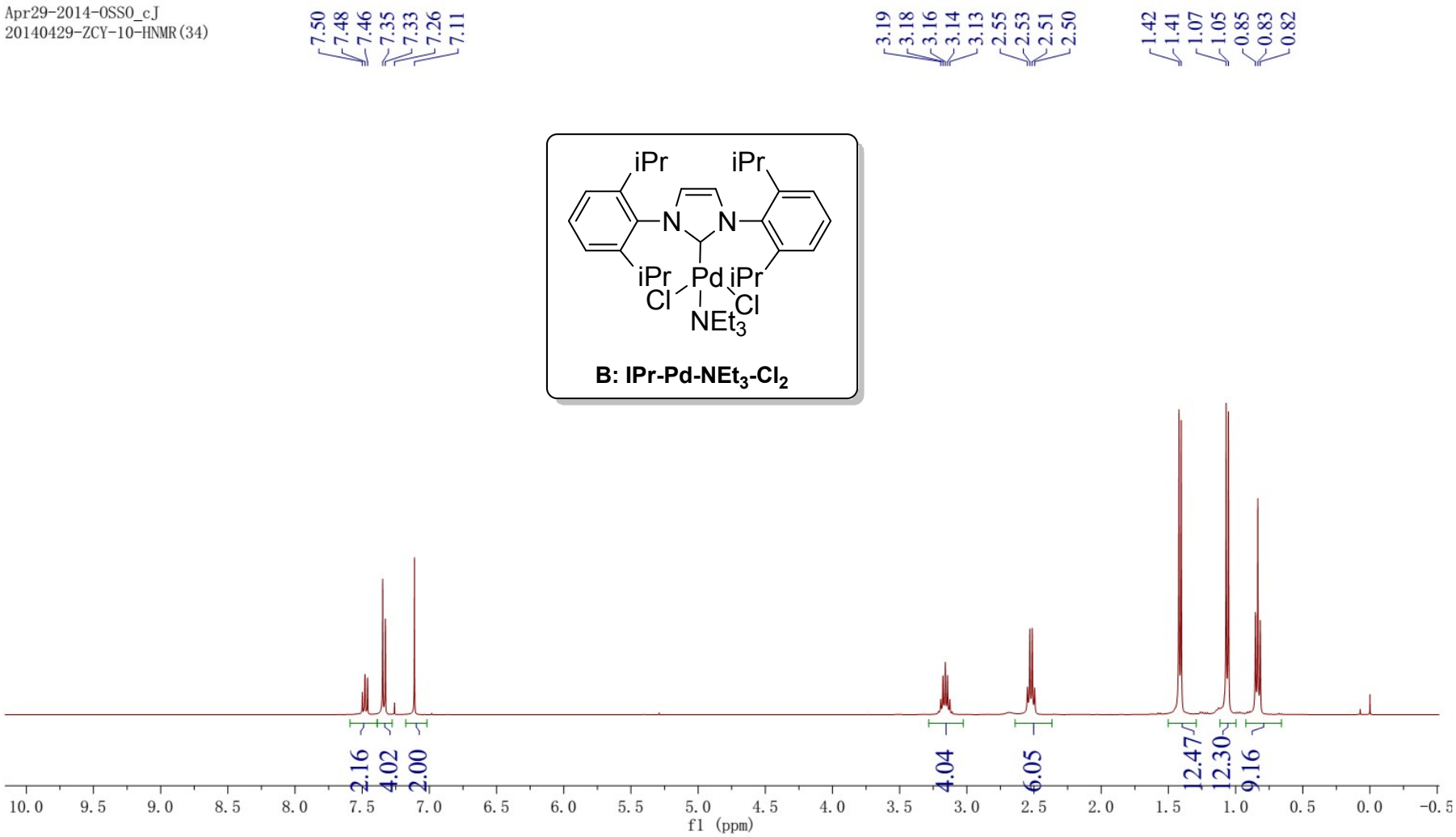
f1 (ppm)


Apr29-2014-OSSO_cJ
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3.14
3.13
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2.53
2.51
2.50
1.42
1.41
1.07
1.05
0.85
0.83
0.82
iPr
iPr
N
N
iPr
Pd
iPr
Cl
Cl
NEt3
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2.00
4.04
6.05
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12.30
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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
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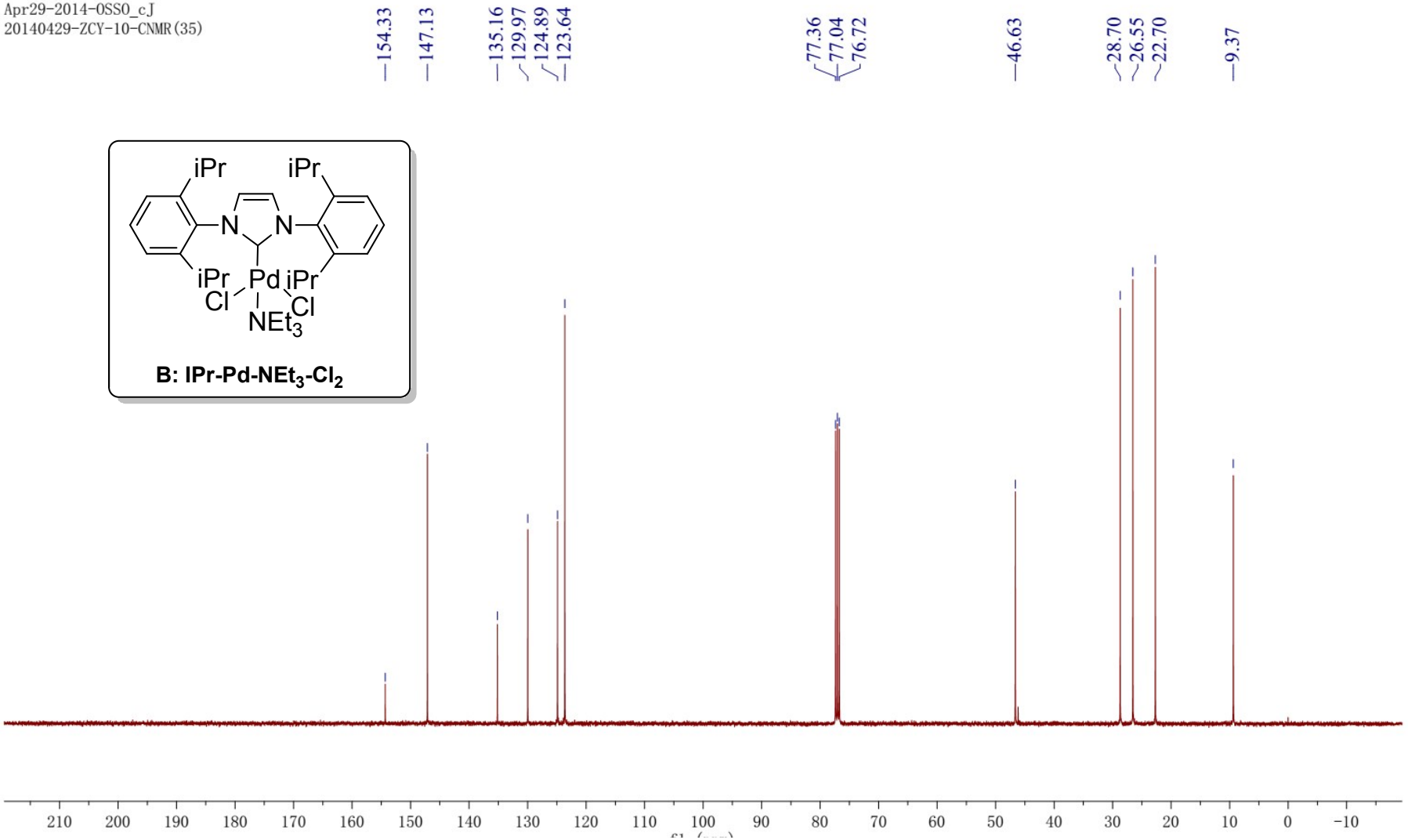
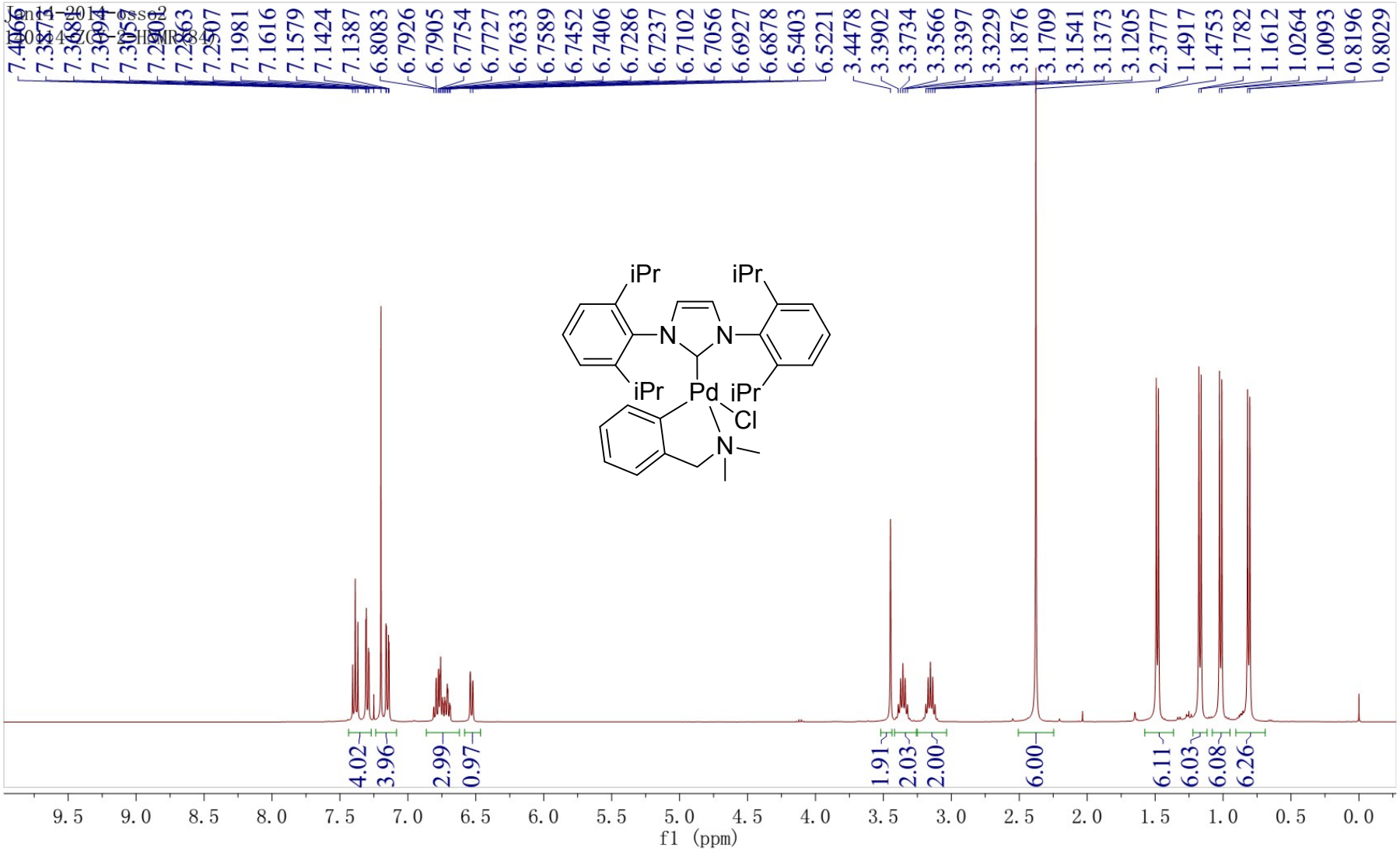
0.0
-0.5
f1 (ppm)

Apr29-2014-OSSO_cJ
20140429-ZCY-10-CNMR(35)

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Cl
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2.03
2.00
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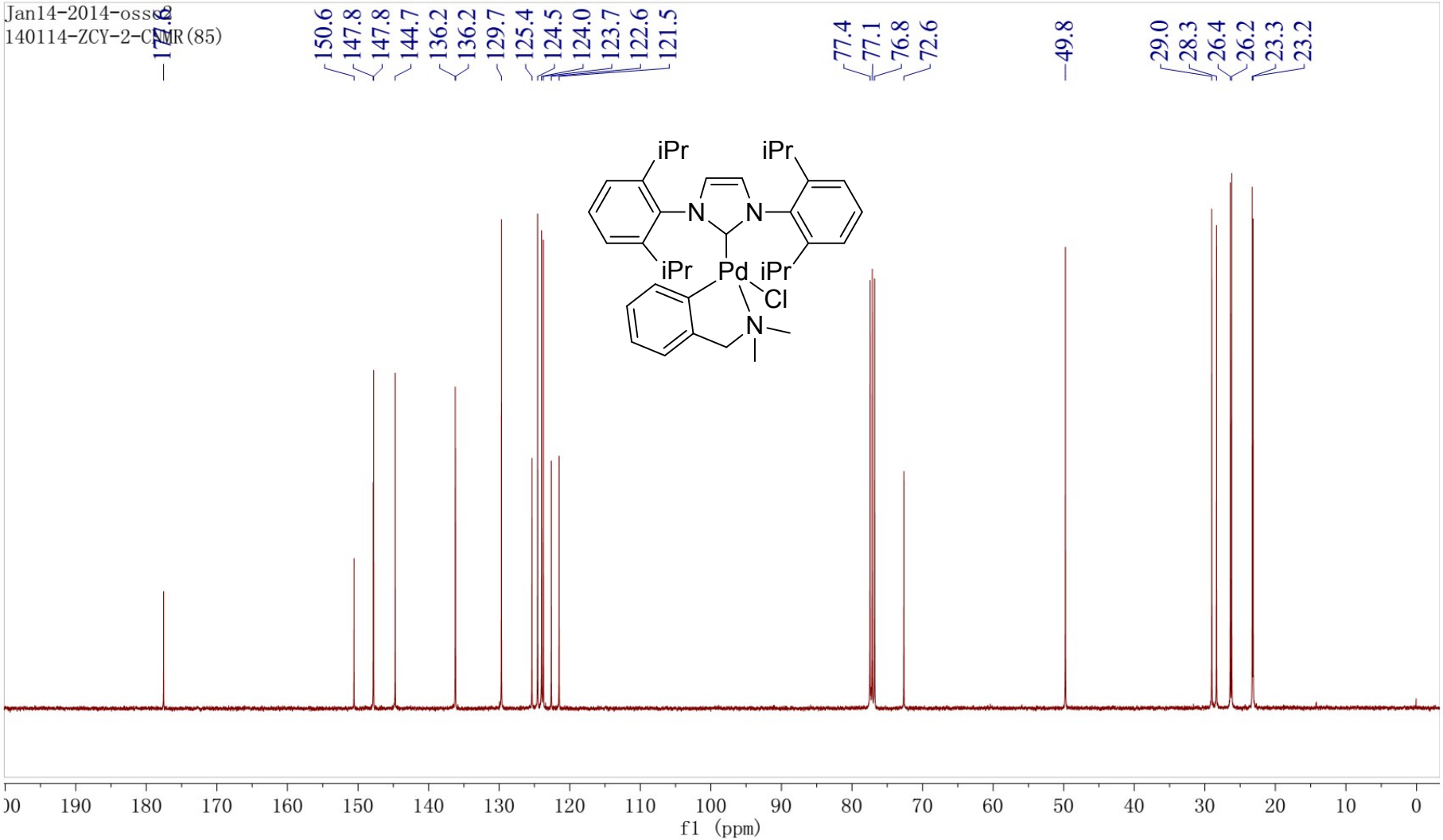
6.03
6.08
6.26
f1 (ppm)


Jan14-2014-osss2
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125.4
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124.0
123.7
122.6
121.5
77.4
77.1
76.8
72.6
49.8
29.0
28.3
26.4
26.2
23.3
23.2
iPr
iPr
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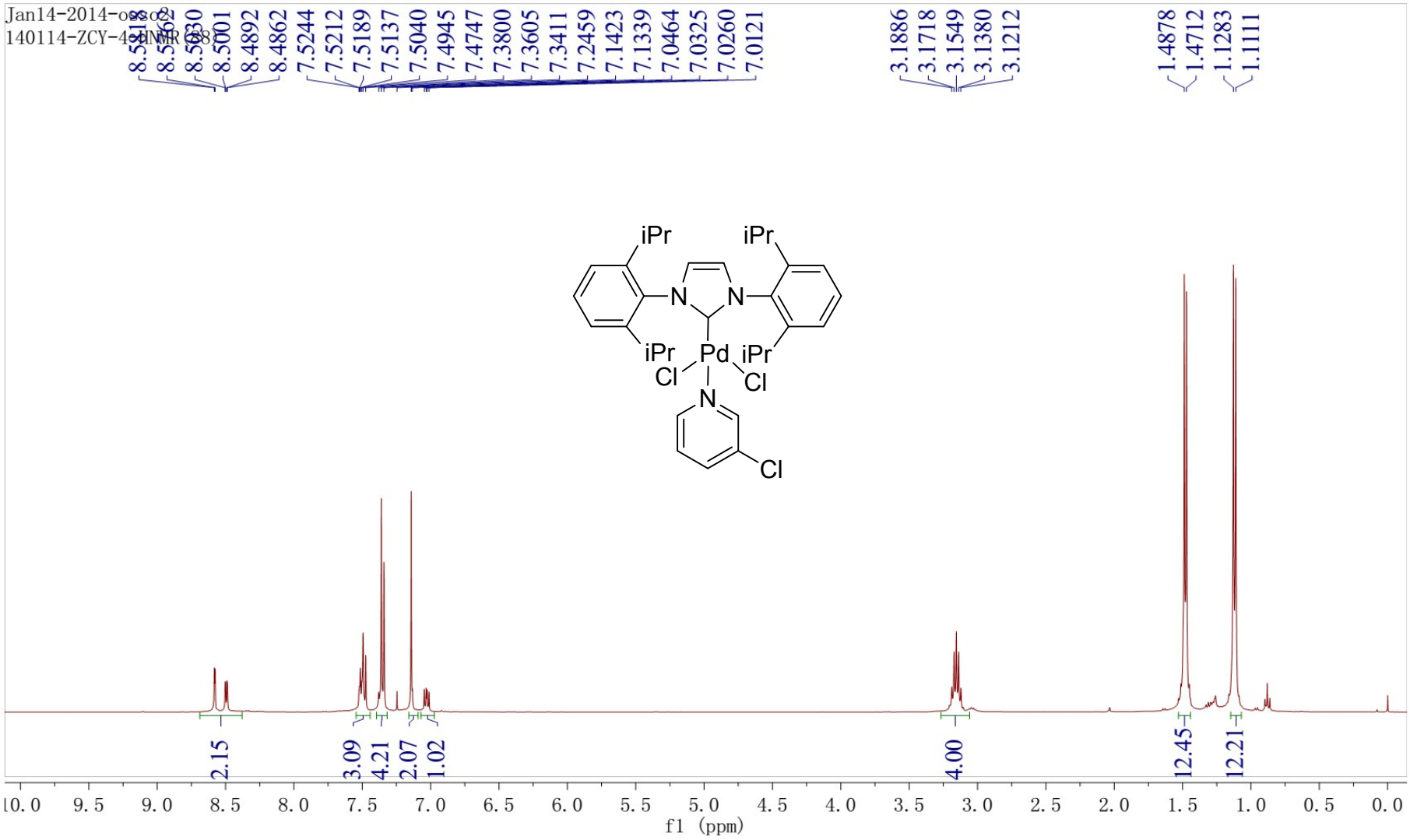
N
iPr
Pd
iPr
Cl
N
f1 (ppm)


Jan14-2014-ossoo2
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Pd
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Cl
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Cl
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3.09
4.21
2.07
1.02
4.00
12.45
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9.0
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8.0
7.5
7.0
6.5
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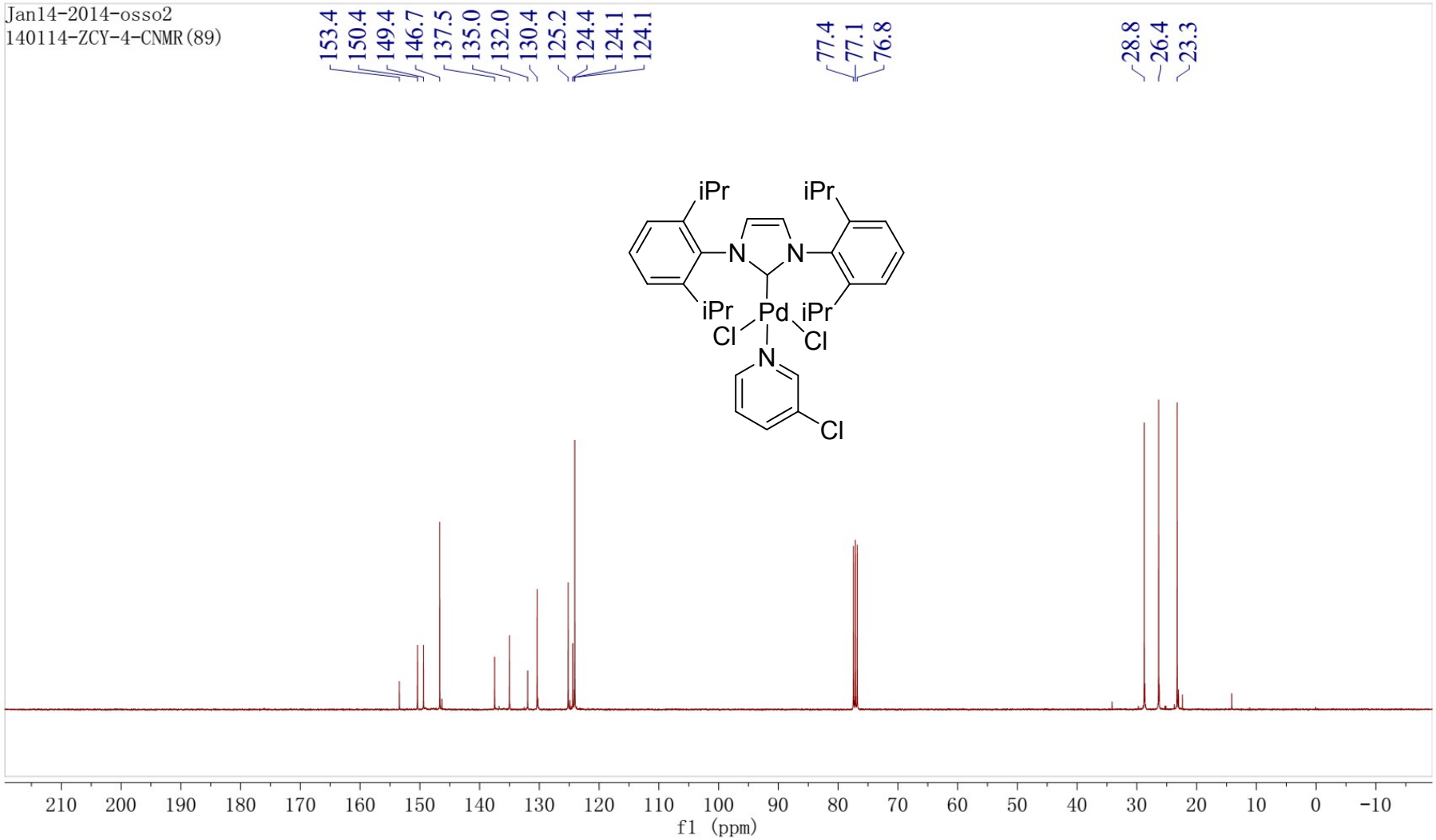
0.0
f1 (ppm)


Jan14-2014-osso2
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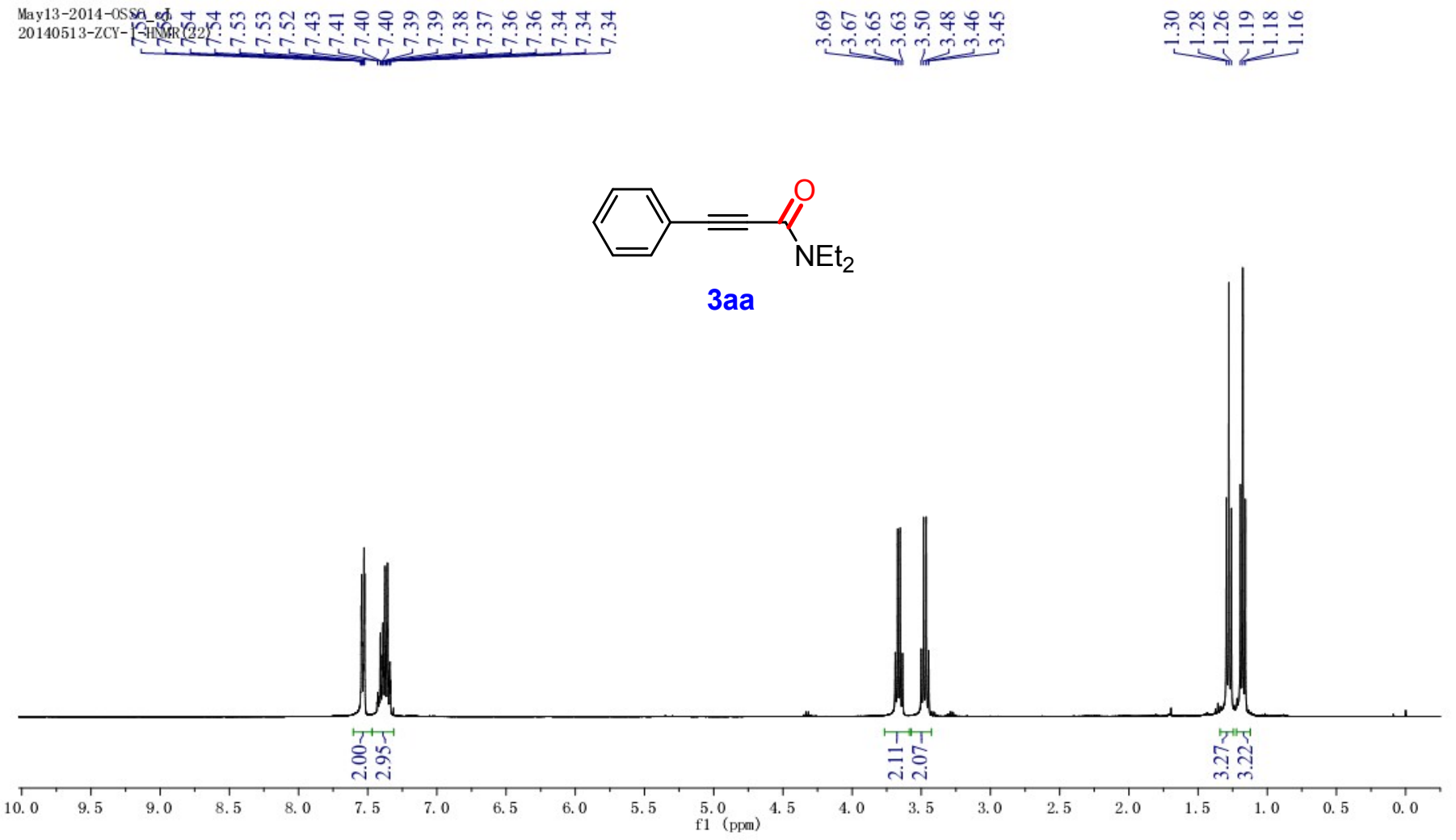
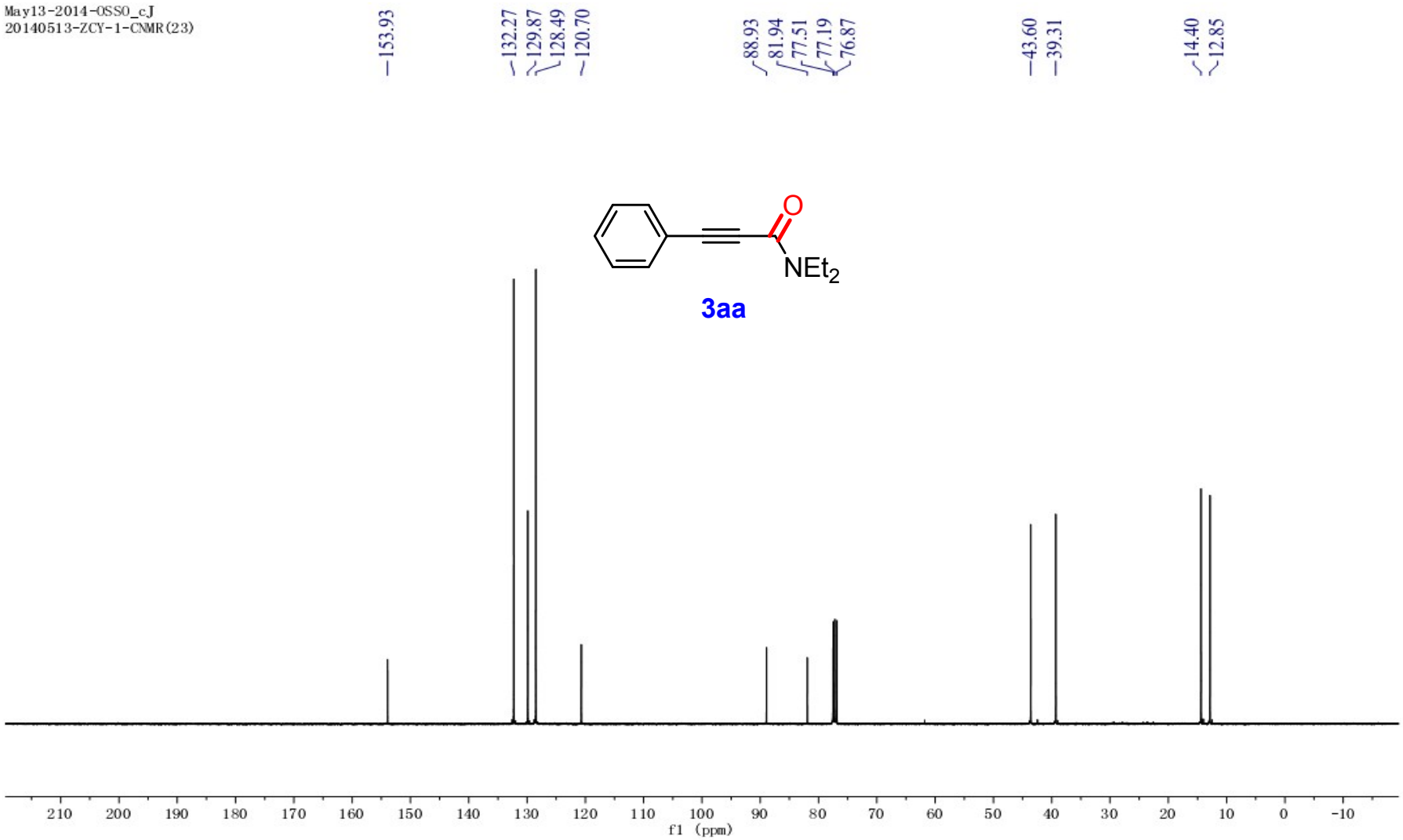
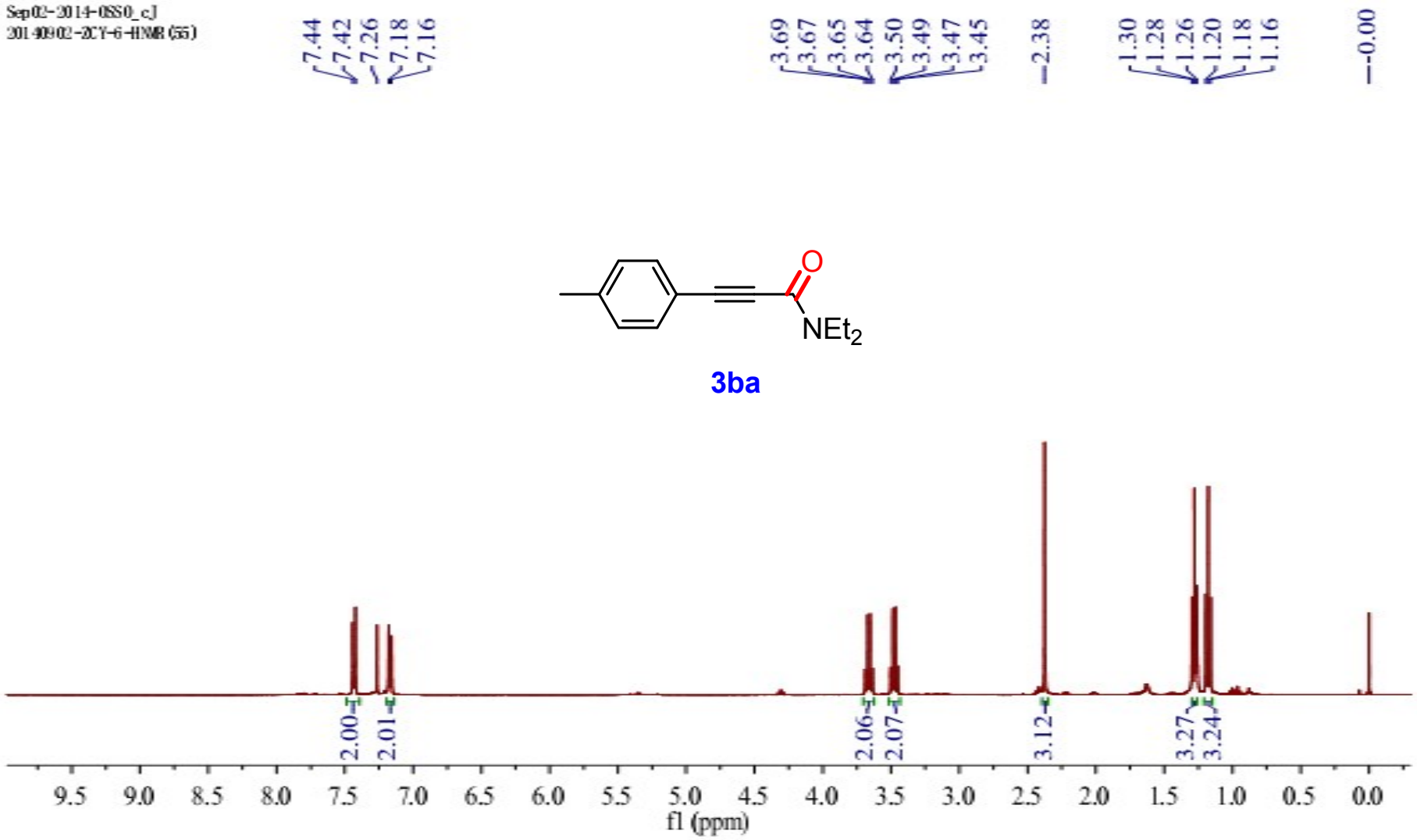
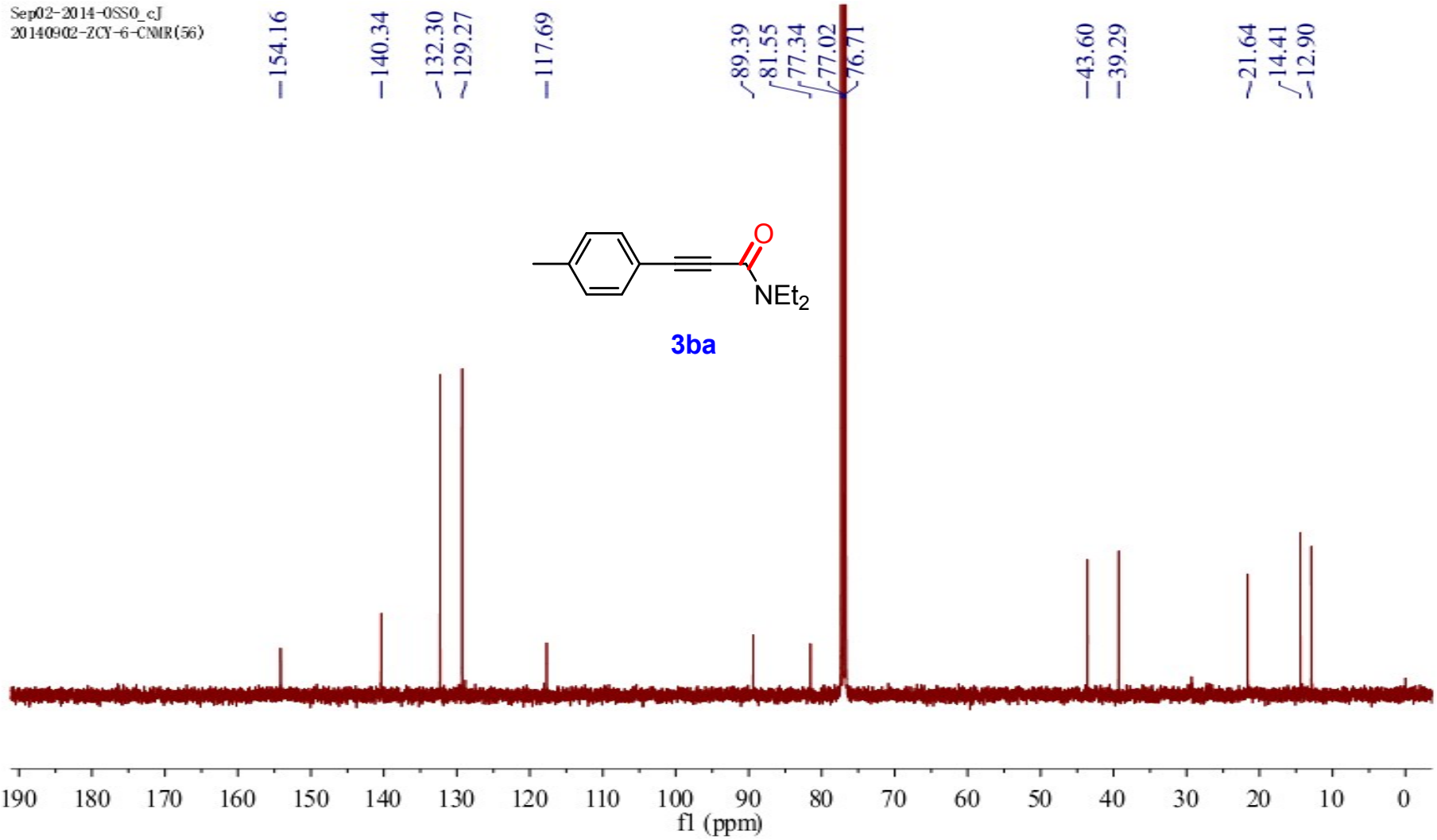
76.8
28.8
26.4
23.3
iPr
iPr
N
N
iPr
Pd
iPr
Cl
Cl
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


May13-2014-OSSO ed
20140513-ZCY-1-1HNMR(22)
7.56
7.54
7.54
7.53
7.53
7.52
7.43
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.34
7.34
7.34
3.69
3.67
3.65
3.63
3.50
3.48
3.46
3.45
1.30
1.28
1.26
1.19
1.18
1.16
O
NEt2
3aa
2.00
2.95
2.11
2.07
3.27
3.22
10.0
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)

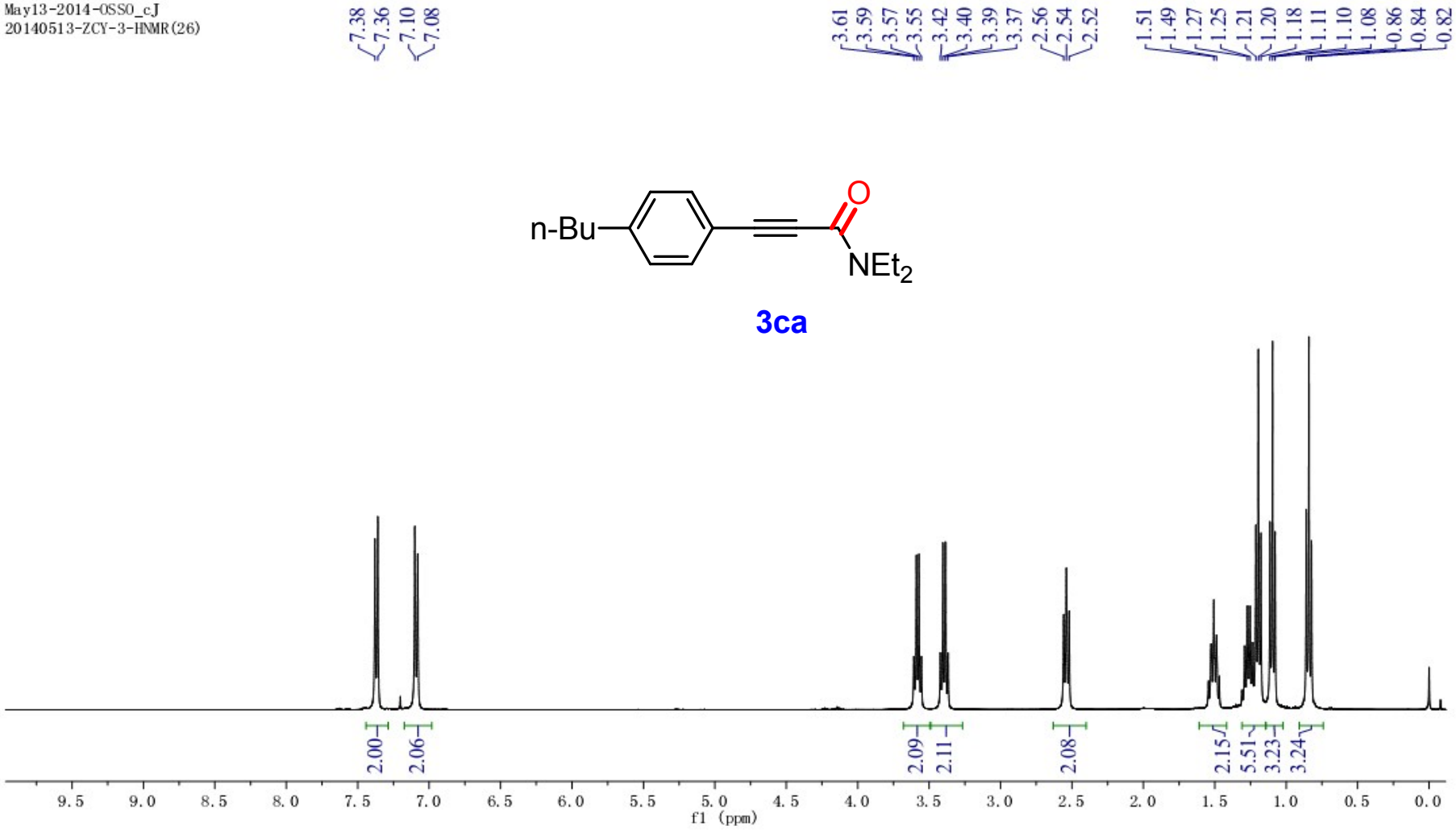

May13-2014-OSSO_cJ
20140513-ZCY-1-CNMR(23)
153.93
132.27
129.87
128.49
120.70
88.93
81.94
77.51
77.19
76.87
43.60
39.31
14.40
12.85
O
NEt2
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Sep02-2014-0SS0_c]
20140902-2CY-6-HNMR (55)
7.44
7.42
7.26
7.18
7.16
3.69
3.67
3.65
3.64
3.50
3.49
3.47
3.45
2.38
1.30
1.28
1.26
1.20
1.18
1.16
0.00
O
NEt2
2.00
2.01
2.06
2.07
3.12
3.27
3.24
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)

3ba


Sep02-2014-0SS0_cJ
20140902-ZCY-6-CNMR(56)
154.16
140.34
132.30
129.27
117.69
89.39
81.55
77.34
77.02
76.71
43.60
39.29
21.64
14.41
12.90
O
NEt2
3ba
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

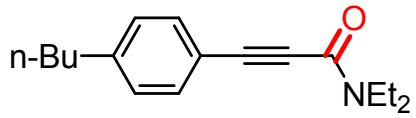
May13-2014-OSSO_cJ
20140513-ZCY-3-HNMR(26)



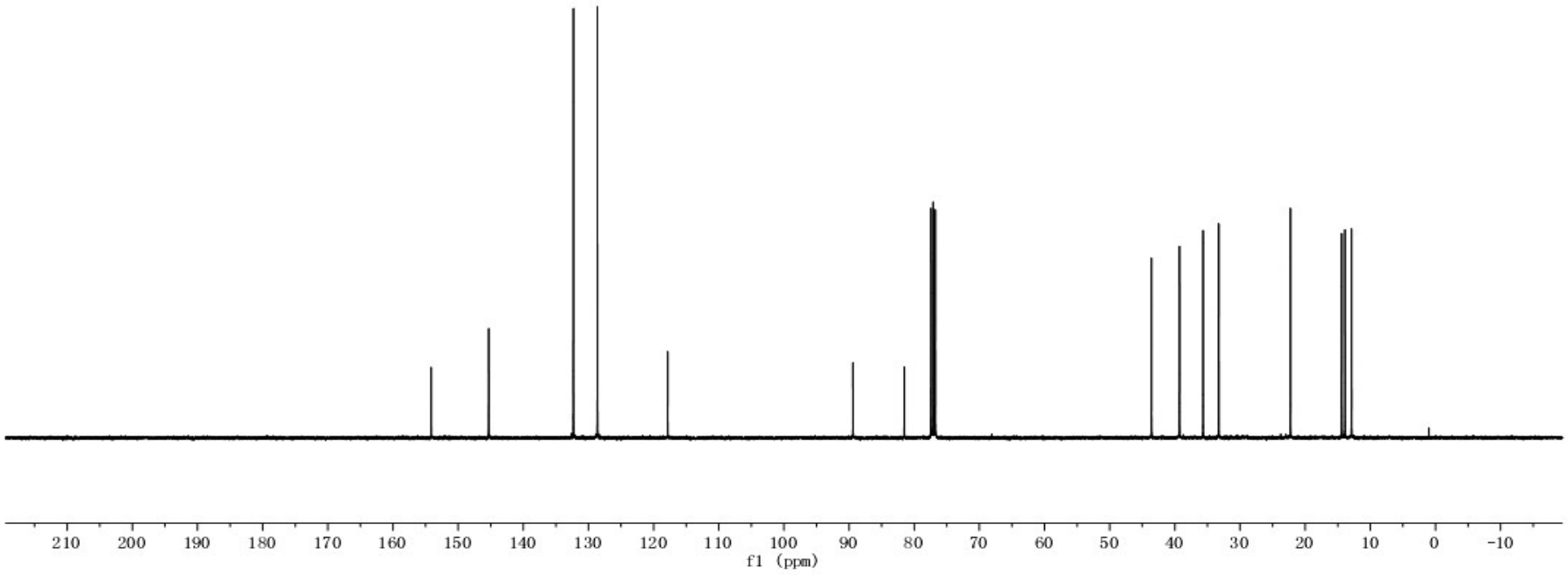
3ca

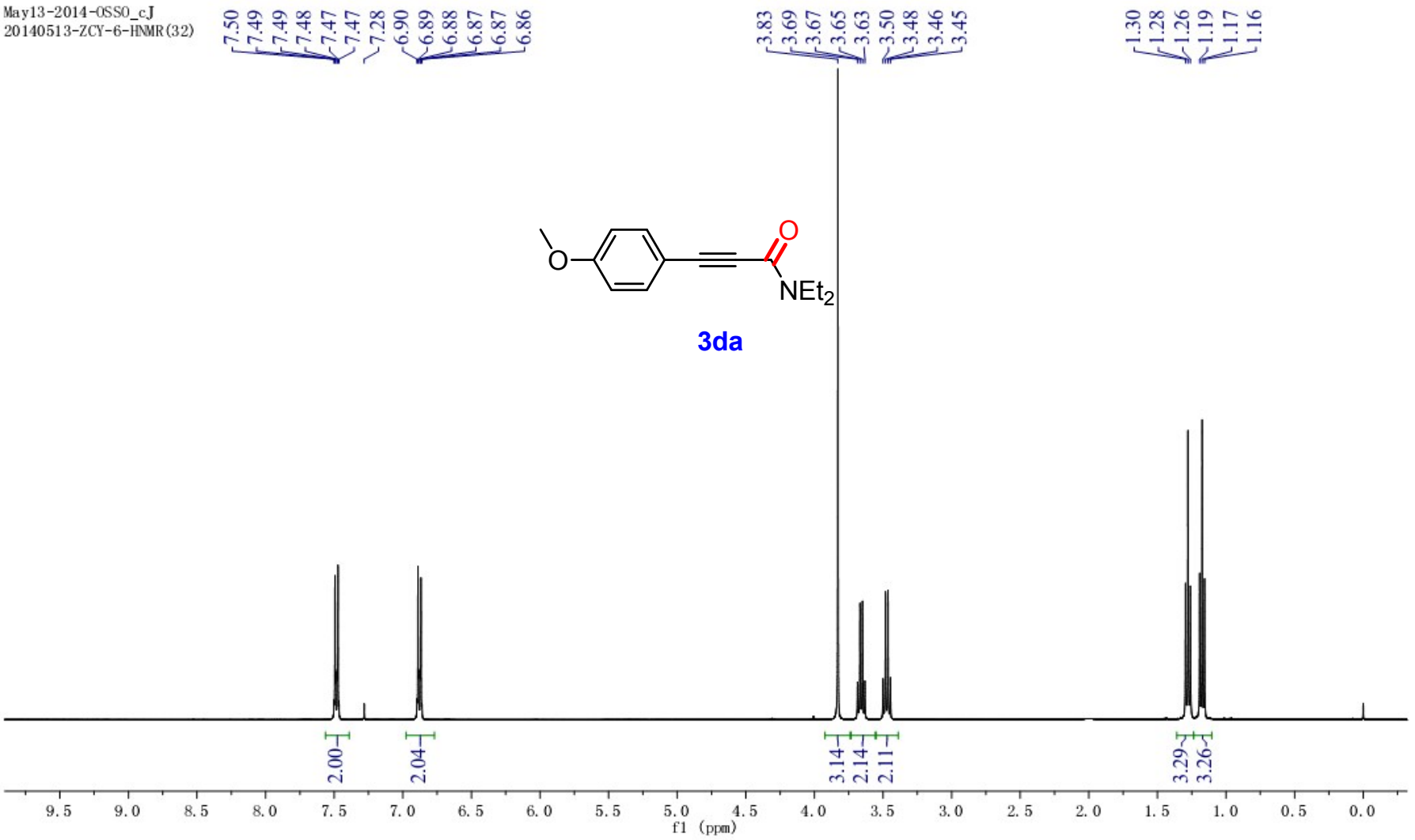
May13-2014-OSSO_cJ
20140513-ZCY-3-CNMR(27)

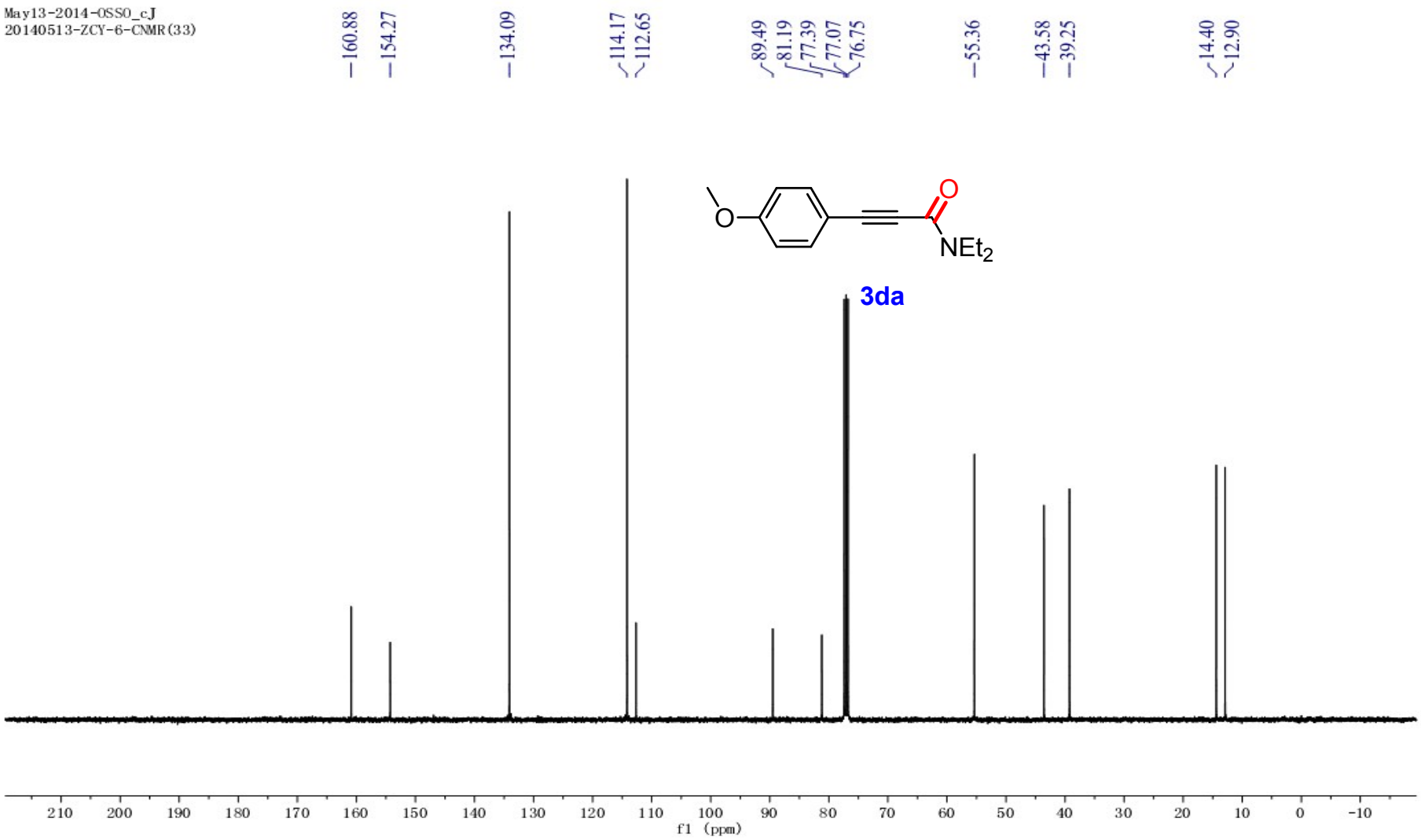
154.15
145.30
132.31
128.62
117.84
89.40
81.53
77.41
77.09
76.78
43.60
39.29
35.67
33.27
22.27
14.41
13.89
12.89

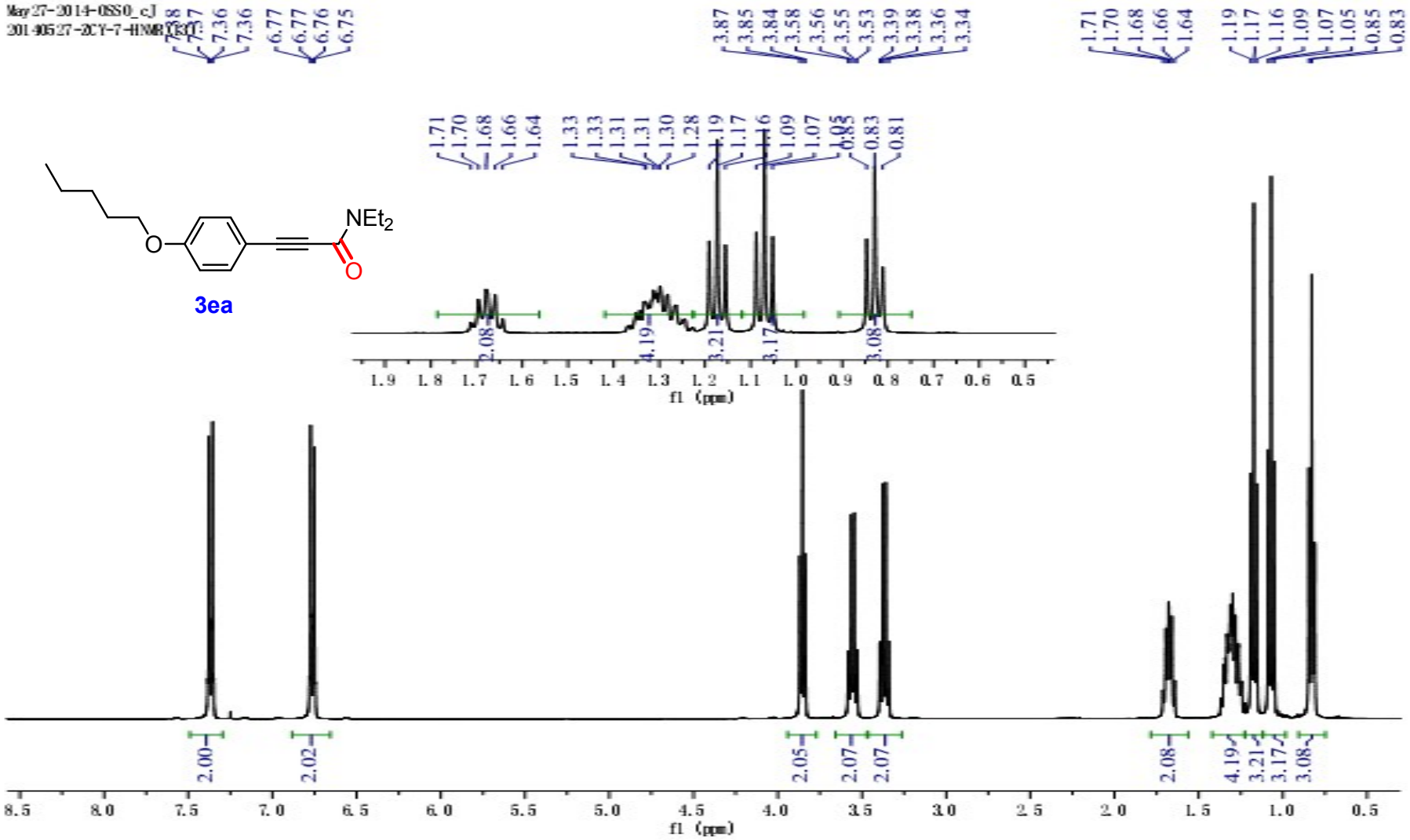


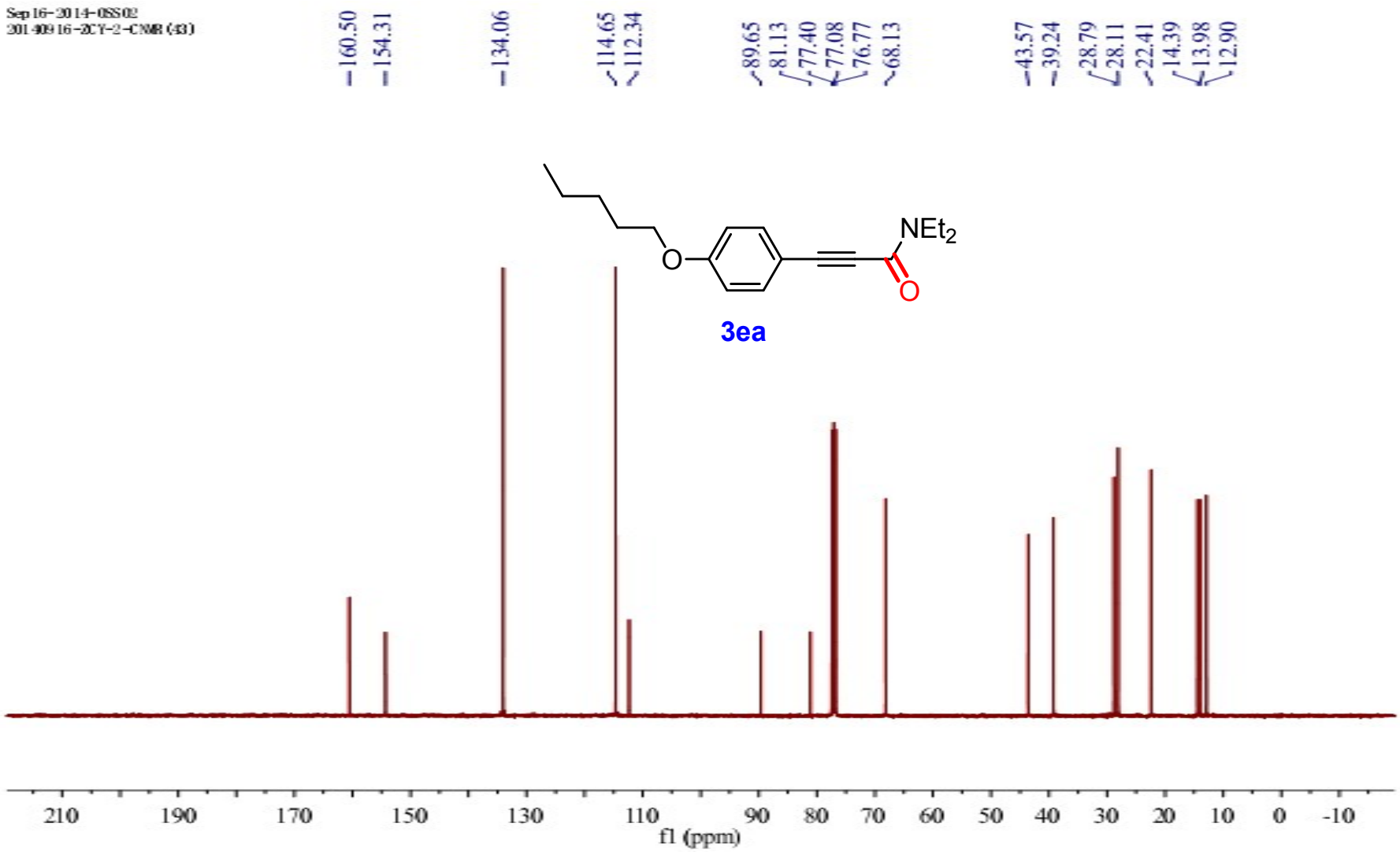
3ca

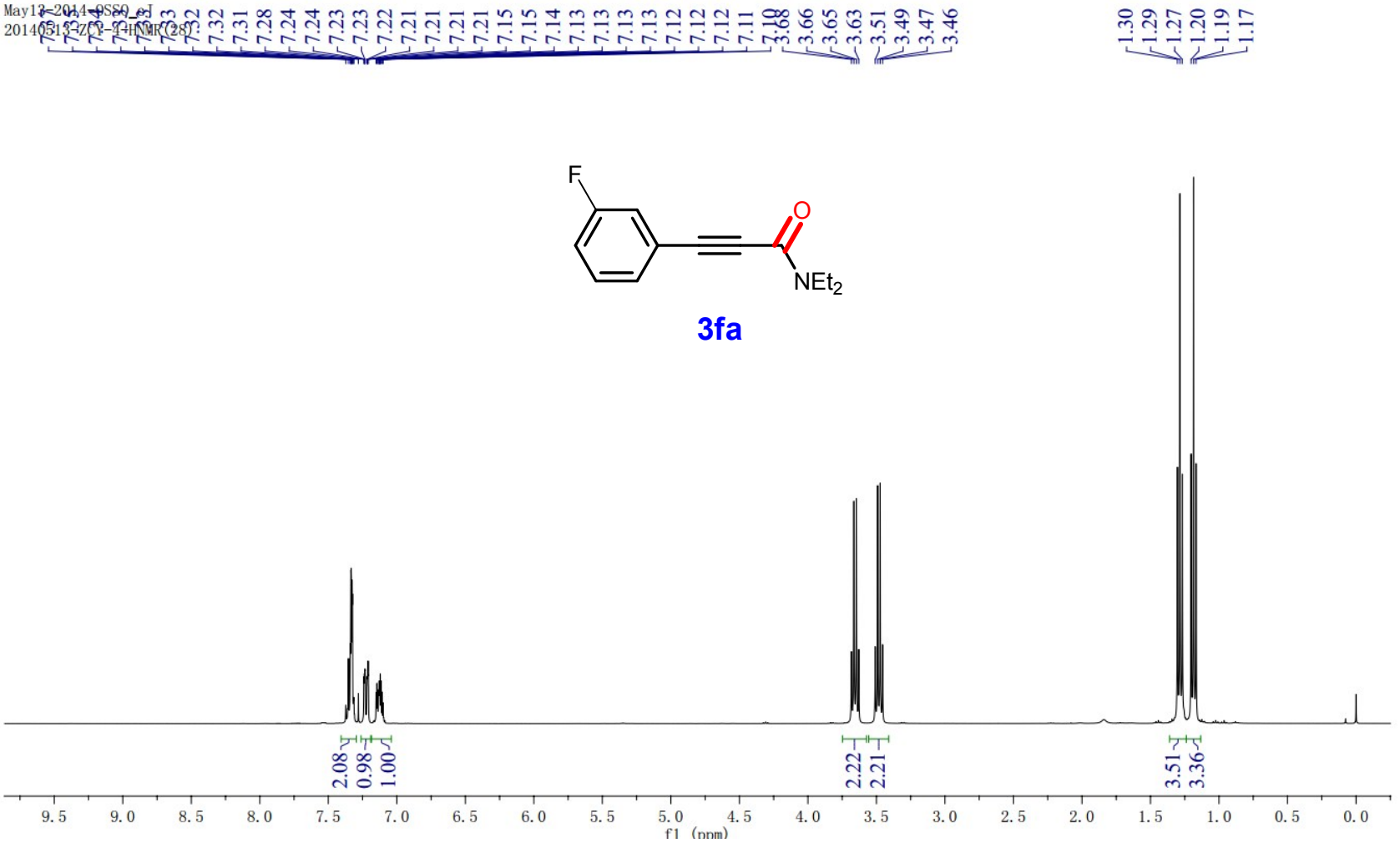



May13-2014-OSSO_cJ
20140513-ZCY-6-HNMR(32)
7.50
7.49
7.49
7.48
7.47
7.47
7.28
6.90
6.89
6.88
6.87
6.87
6.86
3.83
3.69
3.67
3.65
3.63
3.50
3.48
3.46
3.45
1.30
1.28
1.26
1.19
1.17
1.16
O
O
NEt2
3da
2.00
2.04
3.14
2.14
2.11
3.29
3.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


May13-2014-OSSO_cJ
20140513-ZCY-6-CNMR(33)
160.88
154.27
134.09
114.17
112.65
89.49
81.19
77.39
77.07
76.75
55.36
43.58
39.25
14.40
12.90
O
O
NEt2
3da
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

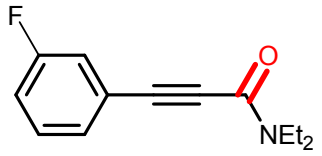

NEt2
O
O
3ea
f1 (ppm)


Sep 16-2014-0SS02
20140916-2CY-2-CNMR (43)
160.50
154.31
134.06
114.65
112.34
89.65
81.13
77.40
77.08
76.77
68.13
43.57
39.24
28.79
28.11
22.41
14.39
13.98
12.90
NEt2
O
O
3ea
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

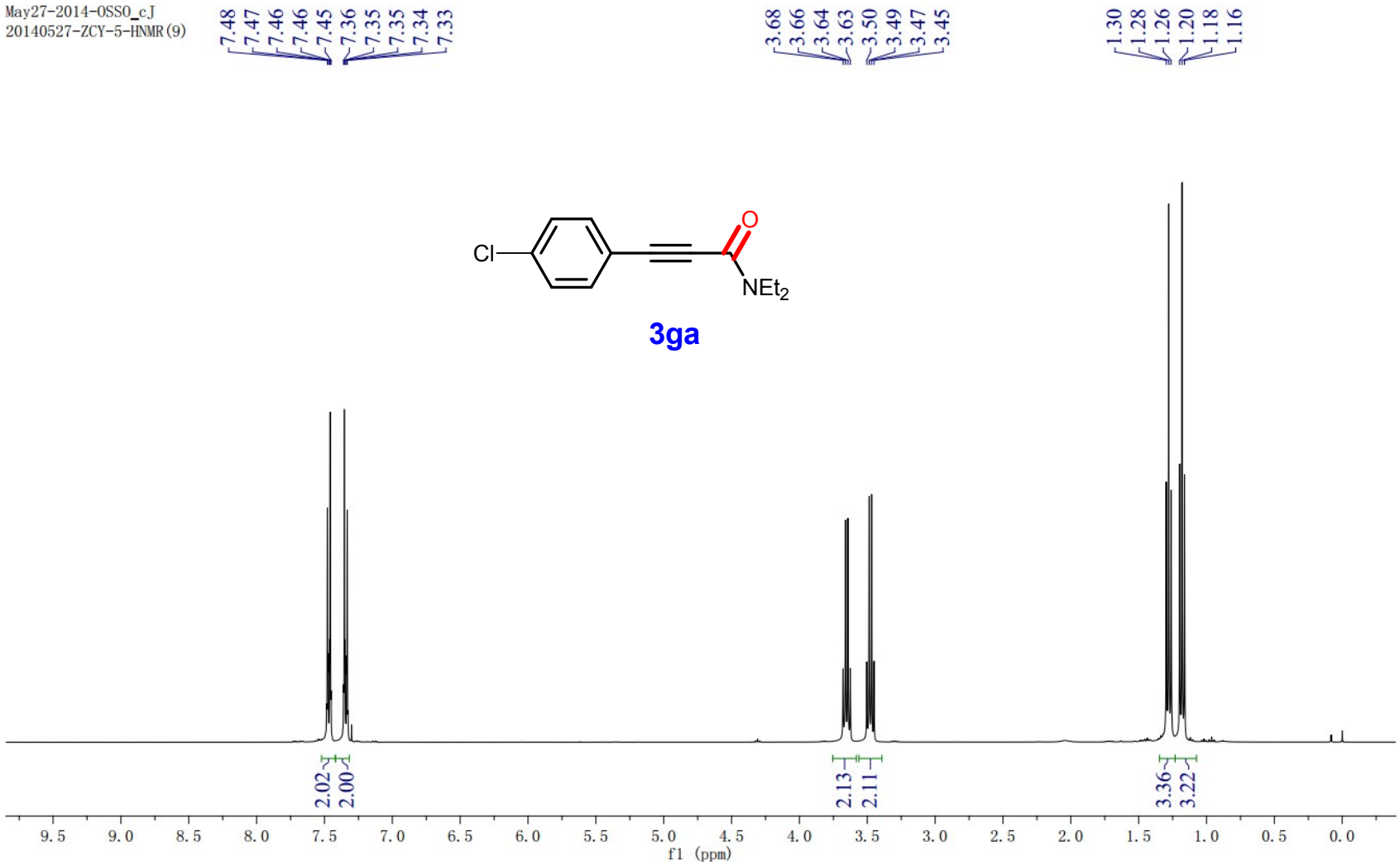

May13-2014-QSS0_ej
20140513-ZCJ-1-1HNMR(28)
7.33
7.32
7.32
7.31
7.28
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.21
7.21
7.15
7.15
7.14
7.13
7.13
7.13
7.13
7.12
7.12
7.12
7.11
7.10
3.68
3.66
3.65
3.63
3.51
3.49
3.47
3.46
1.30
1.29
1.27
1.20
1.19
1.17
F
O
NEt2
3fa
2.08
0.98
1.00
2.22
2.21
3.51
3.36
9.5
9.0
8.5
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)

May13-2014-OSSO_cJ
20140513-ZCY-4-CNMR(29)

163.48
161.01
153.59
130.27
130.18
128.24
128.21
122.61
122.51
119.14
118.90
117.42
117.21
87.41
87.37
82.52
77.37
77.06
76.74
43.61
39.37
14.42
12.83

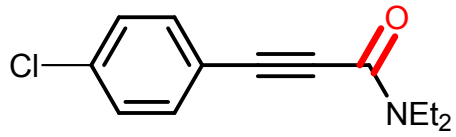


3fa

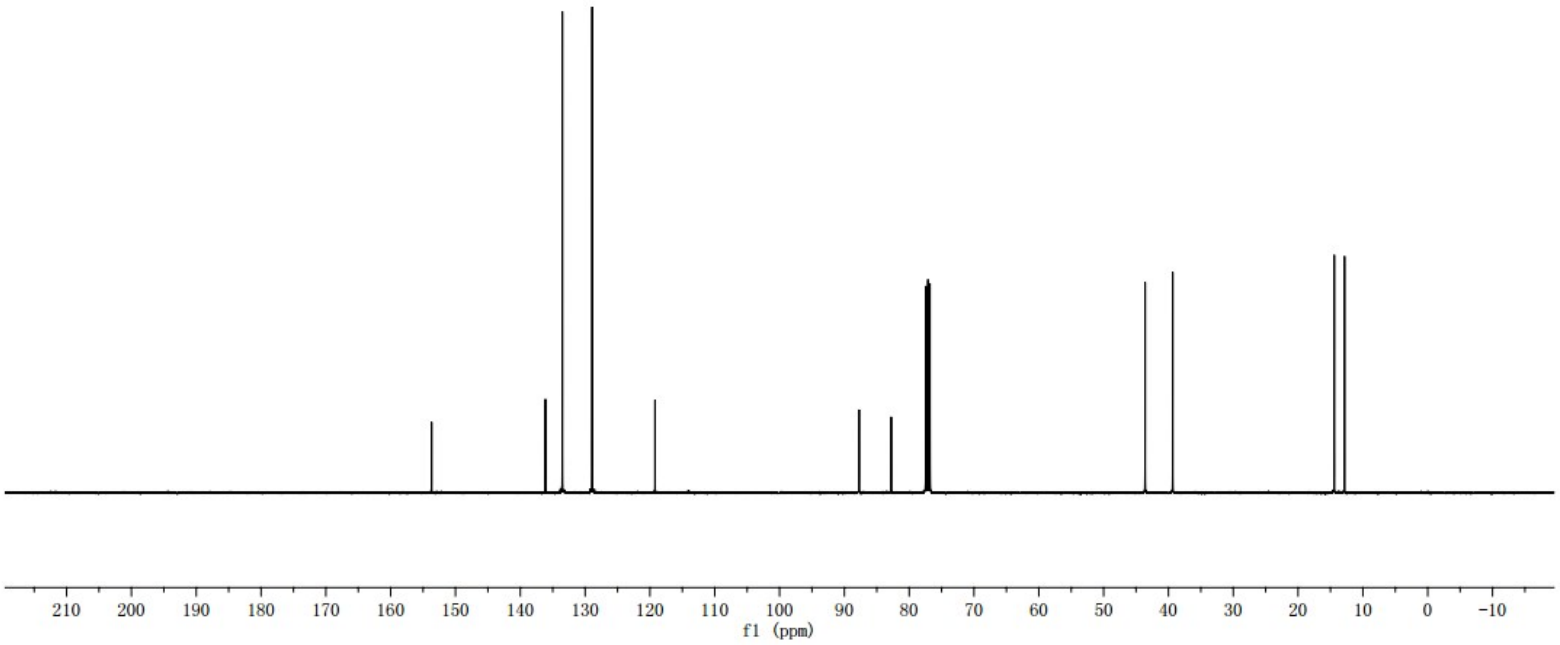

May27-2014-OSSO_cJ
20140527-ZCY-5-HNMR(9)
7.48
7.47
7.46
7.46
7.45
7.36
7.35
7.35
7.34
7.33
3.68
3.66
3.64
3.63
3.50
3.49
3.47
3.45
1.30
1.28
1.26
1.20
1.18
1.16
Cl
O
NEt2
3ga
2.02
2.00
2.13
2.11
3.36
3.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

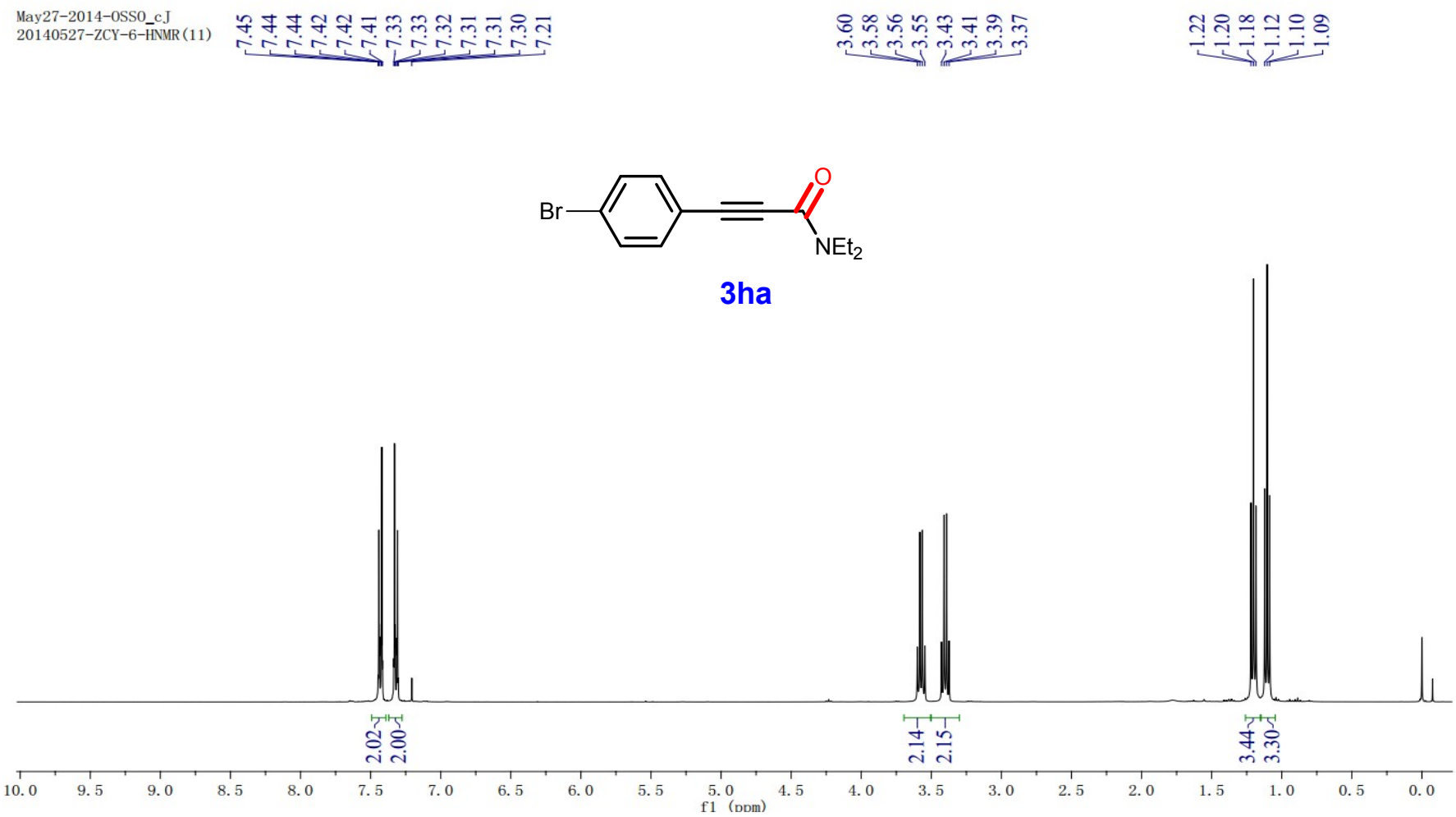
May27-2014-OSSO_c.J
20140527-ZCY-5-CNMR(10)

153.69
136.12
133.51
128.92
119.21
87.72
82.77
77.43
77.11
76.79
43.59
39.33
14.42
12.83



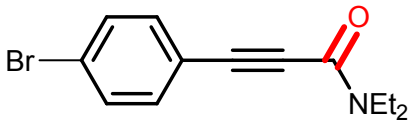
3ga



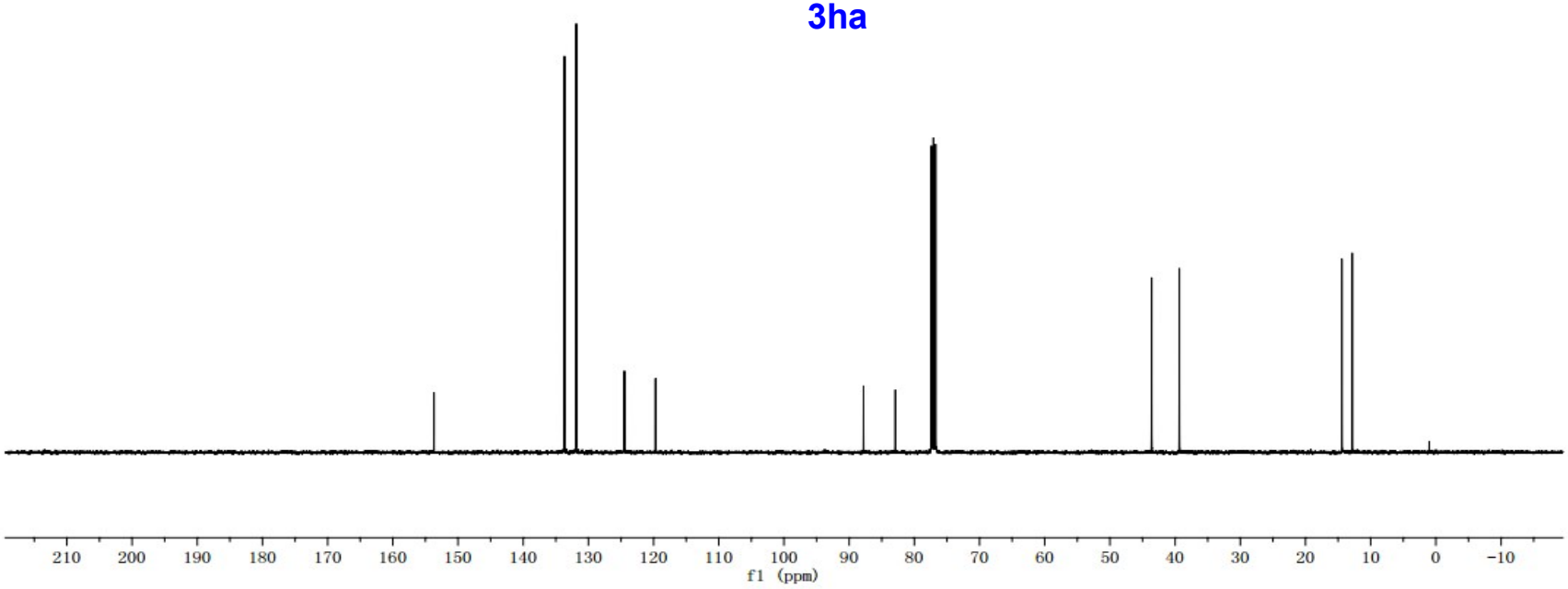

May27-2014-OSSO_cJ
20140527-ZCY-6-HNMR(11)
7.45
7.44
7.44
7.42
7.42
7.41
7.33
7.33
7.32
7.31
7.31
7.30
7.21
3.60
3.58
3.56
3.55
3.43
3.41
3.39
3.37
1.22
1.20
1.18
1.12
1.10
1.09
Br
O
NEt2
3ha
2.02
2.00
2.14
2.15
3.44
3.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

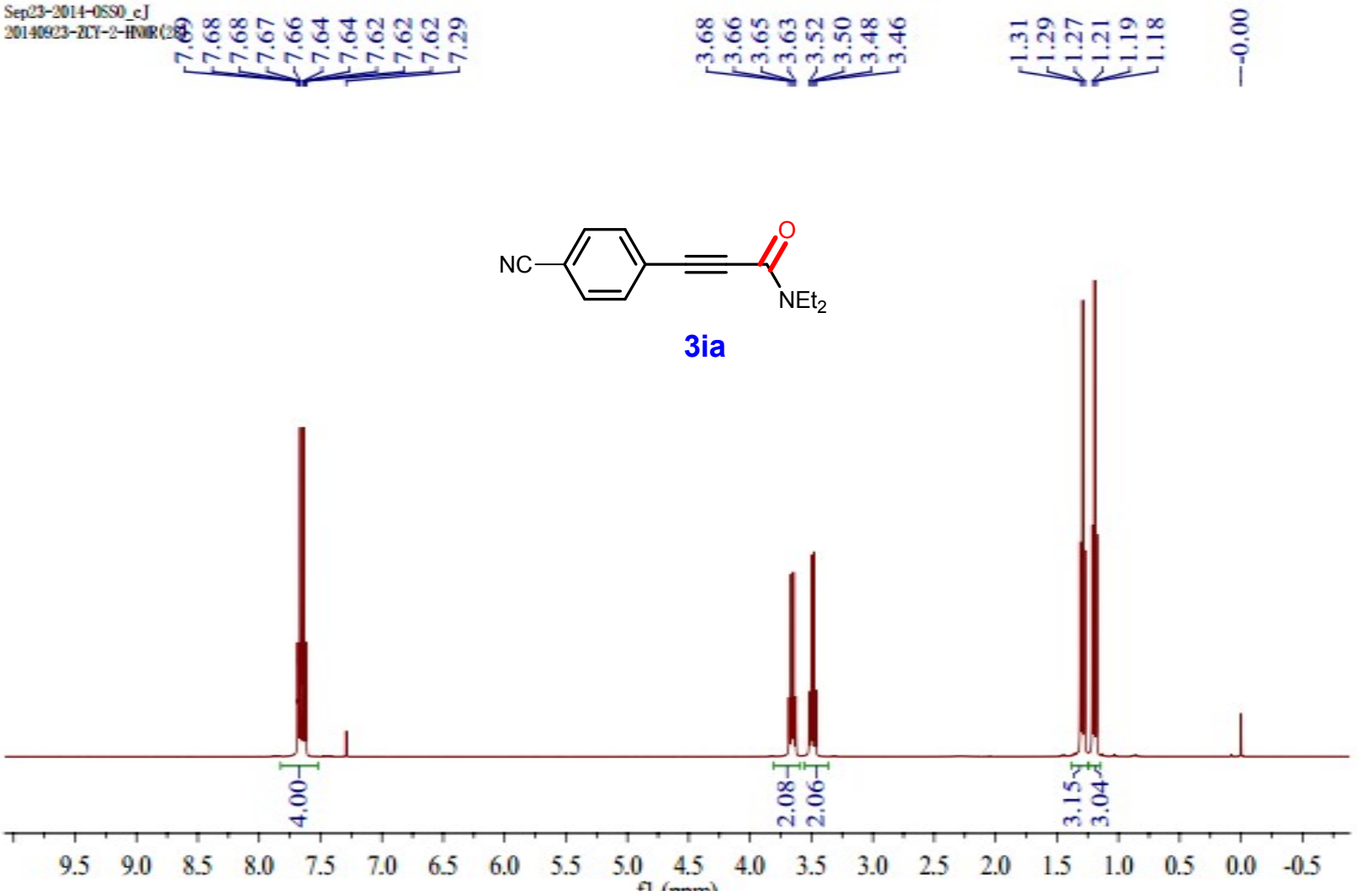
May27-2014-OSSO_cJ
20140527-ZCY-6-CNMR(12)

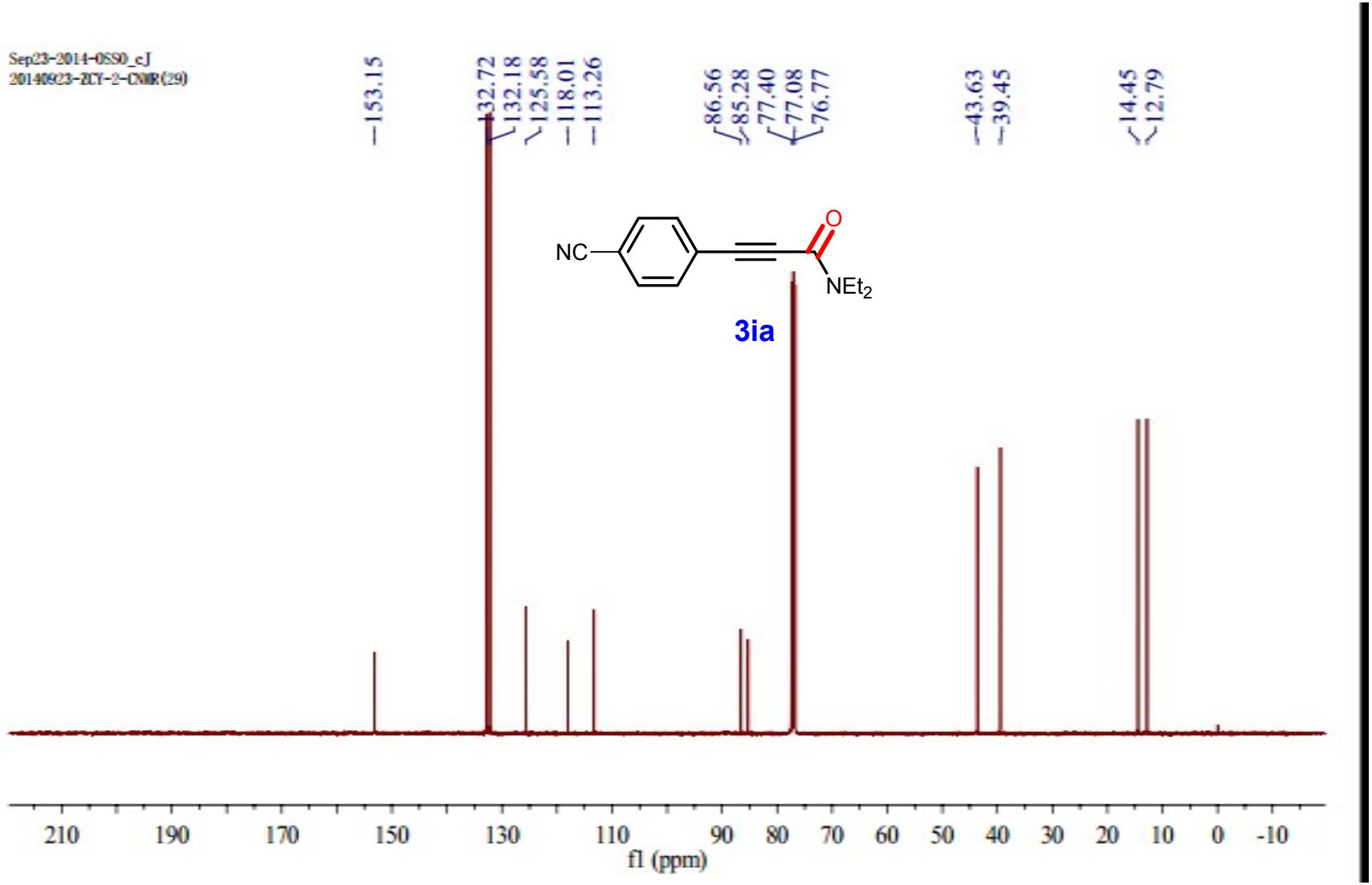
153.70
133.66
131.86
124.47
119.69
87.79
82.91
77.39
77.07
76.75
43.60
39.35
14.43
12.84



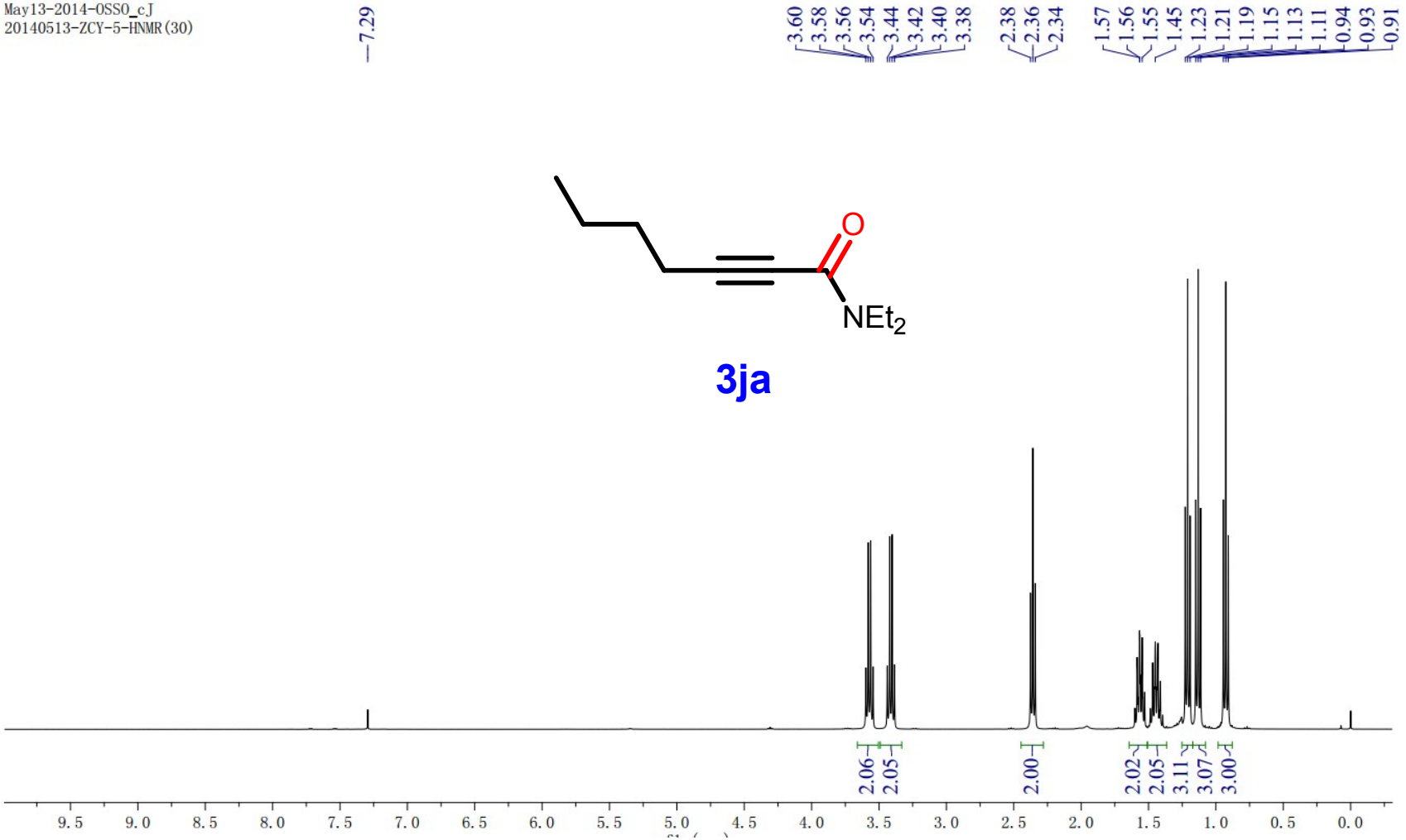
3ha



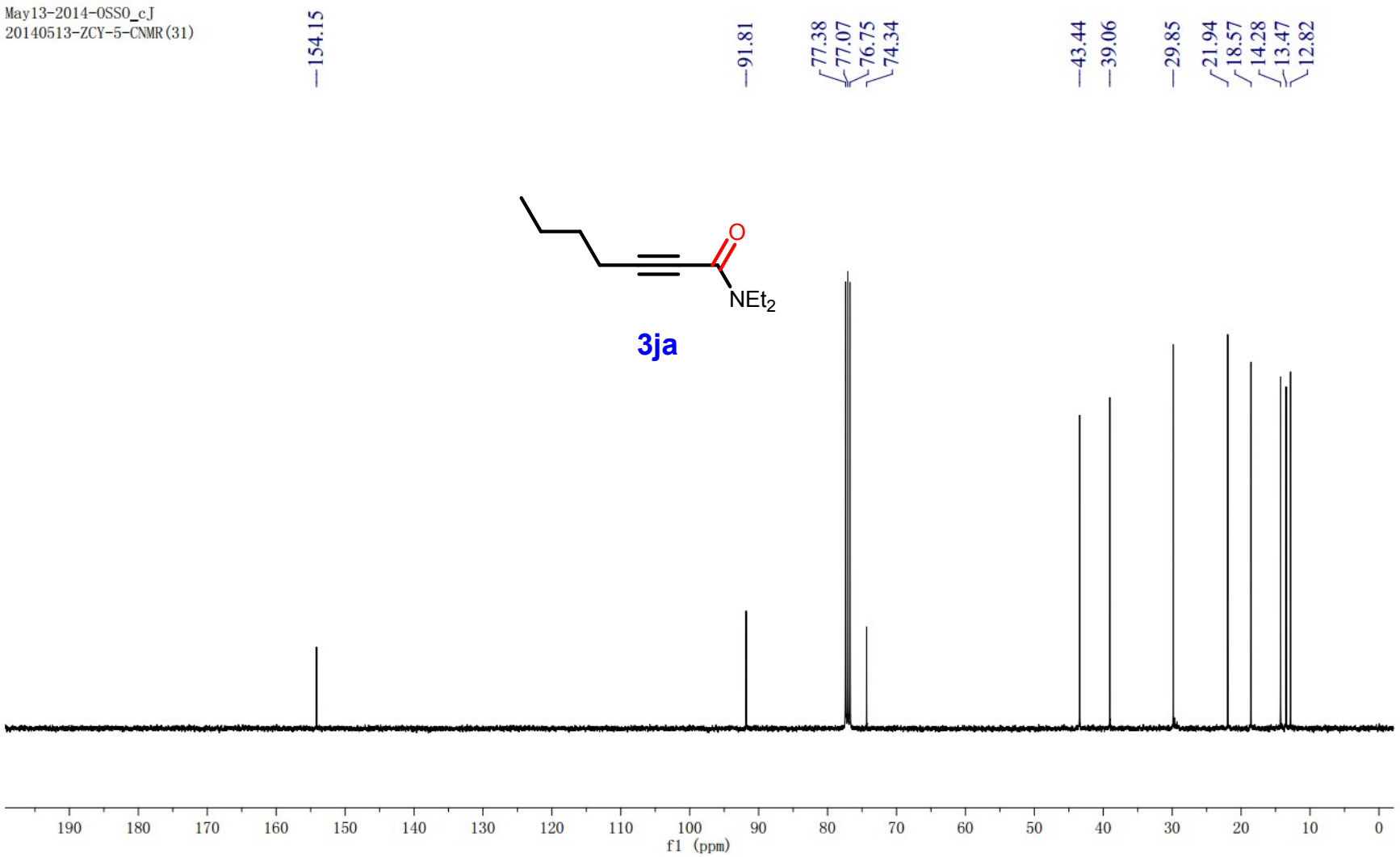

Sep23-2014-0SS0_cJ
20140923-ZCY-2-H NMR(28
7.69
7.68
7.68
7.67
7.66
7.64
7.64
7.62
7.62
7.62
7.29
3.68
3.66
3.65
3.63
3.52
3.50
3.48
3.46
1.31
1.29
1.27
1.21
1.19
1.18
0.00
NC
O
NEt2
3ia
4.00
2.08
2.06
3.15
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

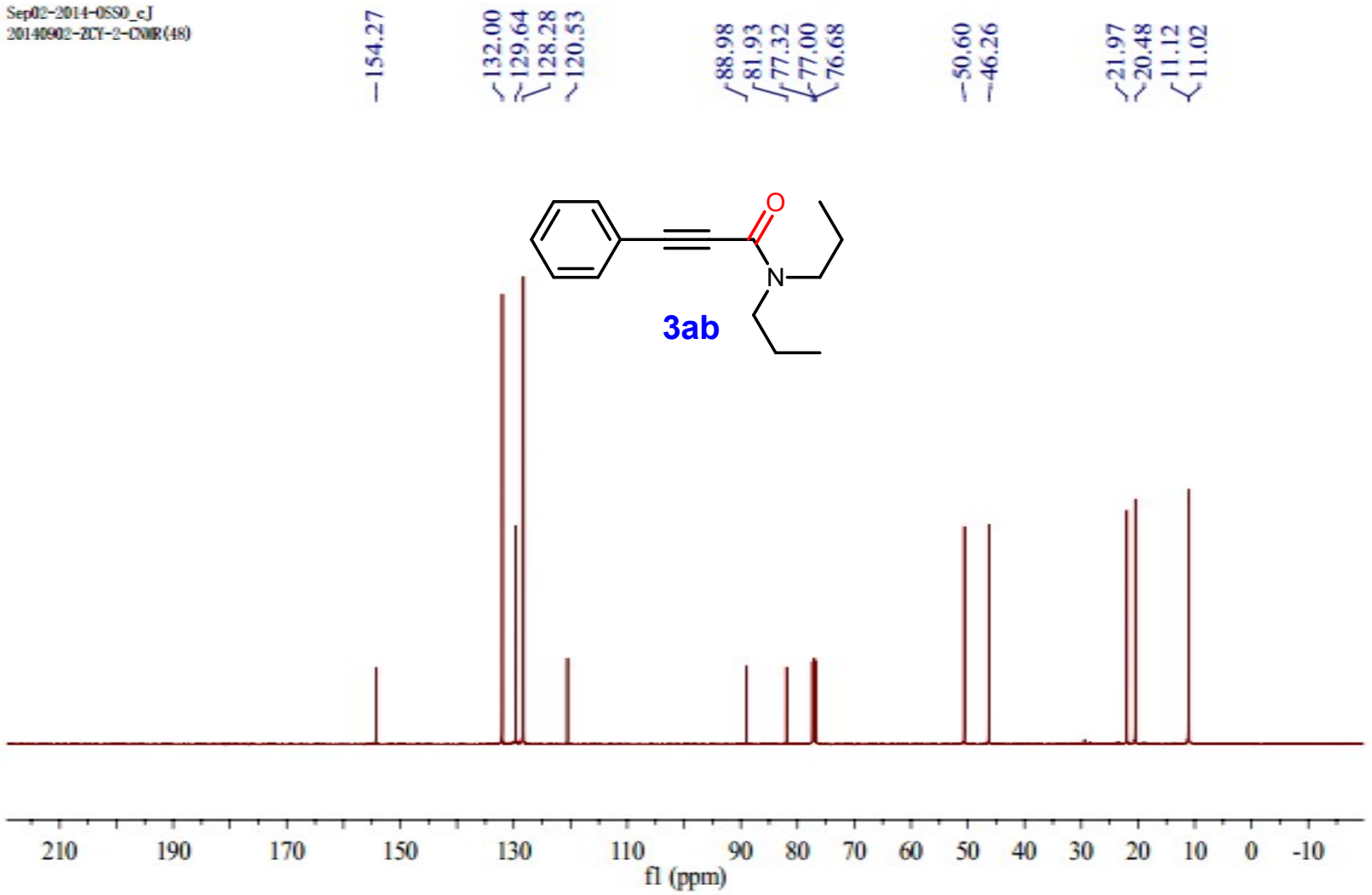

Sep23-2014-0SS0_cJ
20140923-ZCY-2-C0IR(29)
153.15
132.72
132.18
125.58
118.01
113.26
86.56
85.28
77.40
77.08
76.77
43.63
39.45
14.45
12.79
NC
O
NEt2
3ia
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

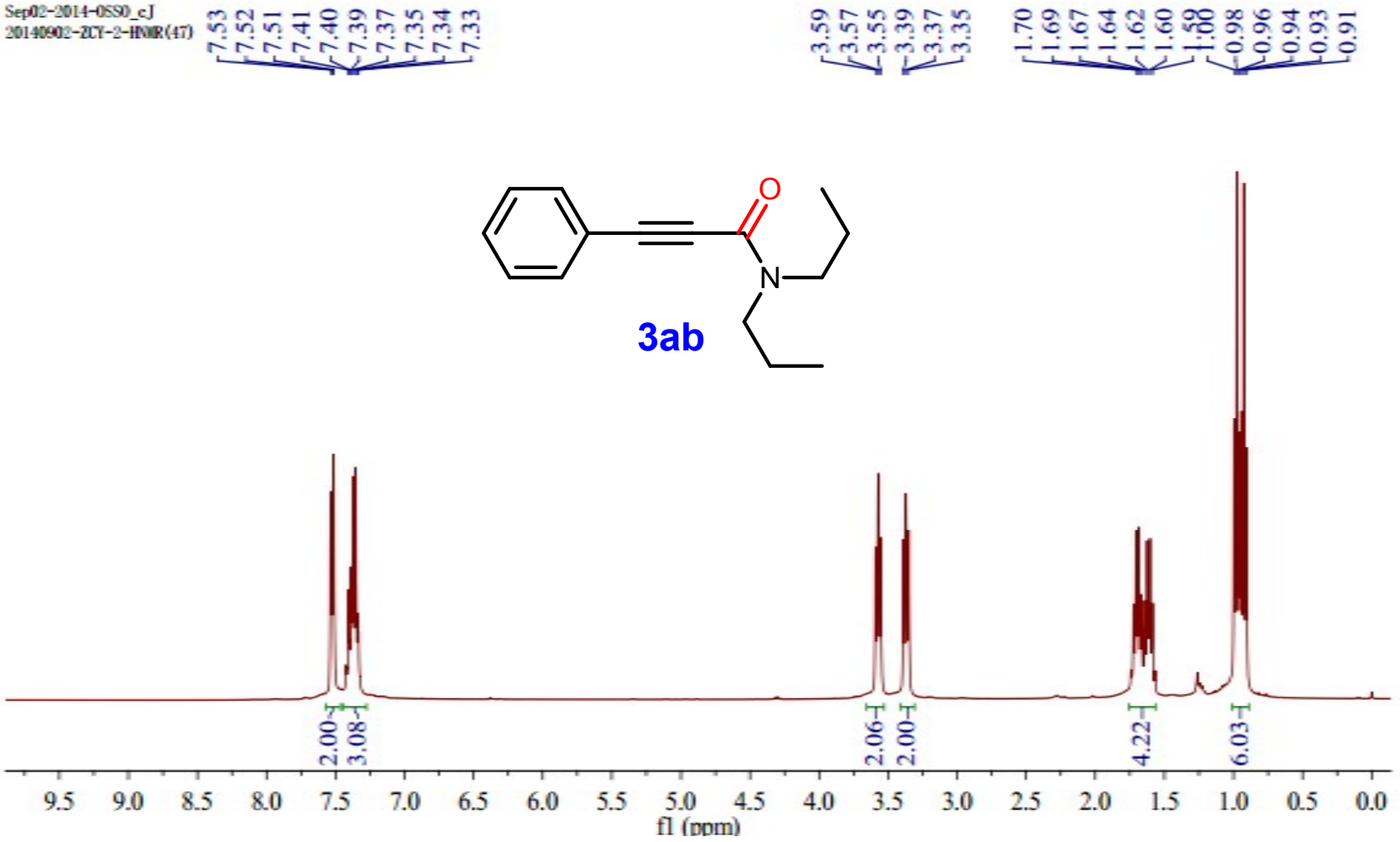
May13-2014-OSSO_cJ
20140513-ZCY-5-HNMR(30)



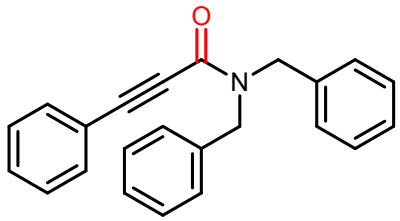
3ja


May13-2014-OSSO_cJ
20140513-ZCY-5-CNMR(31)
154.15
91.81
77.38
77.07
76.75
74.34
43.44
39.06
29.85
21.94
18.57
14.28
13.47
12.82
O
NEt2
3ja
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

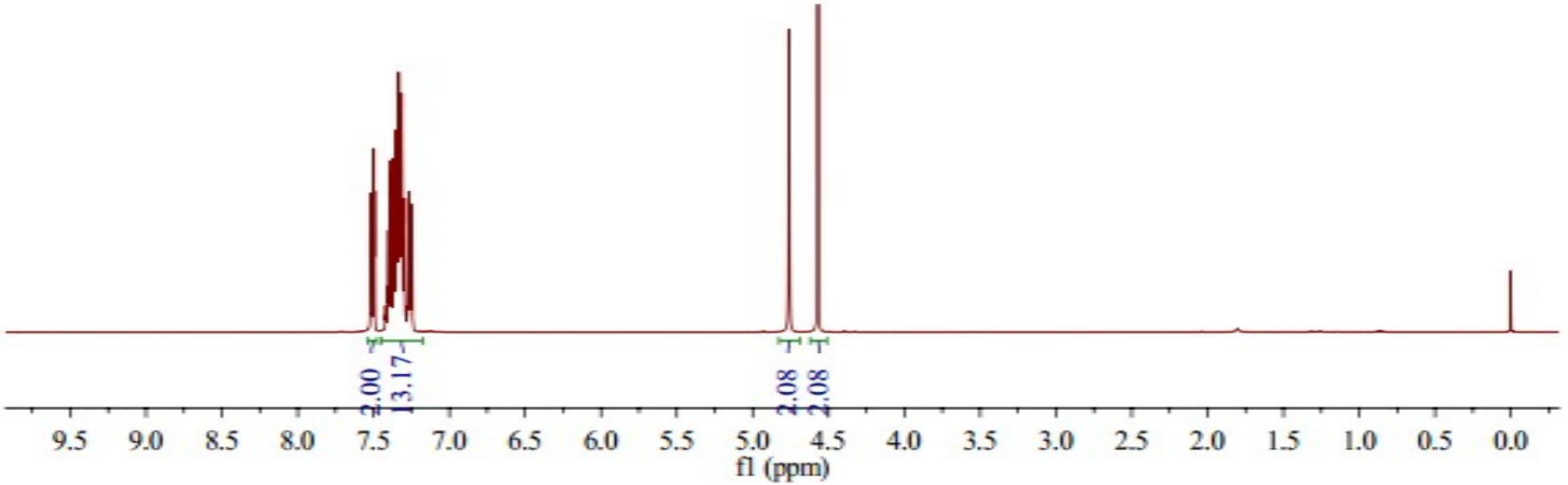

Sep02-2014-0SS0_cJ
20140902-2CY-2-CNMR(48)
154.27
132.00
129.64
128.28
120.53
88.98
81.93
77.32
77.00
76.68
50.60
46.26
21.97
20.48
11.12
11.02
O
N
3ab
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

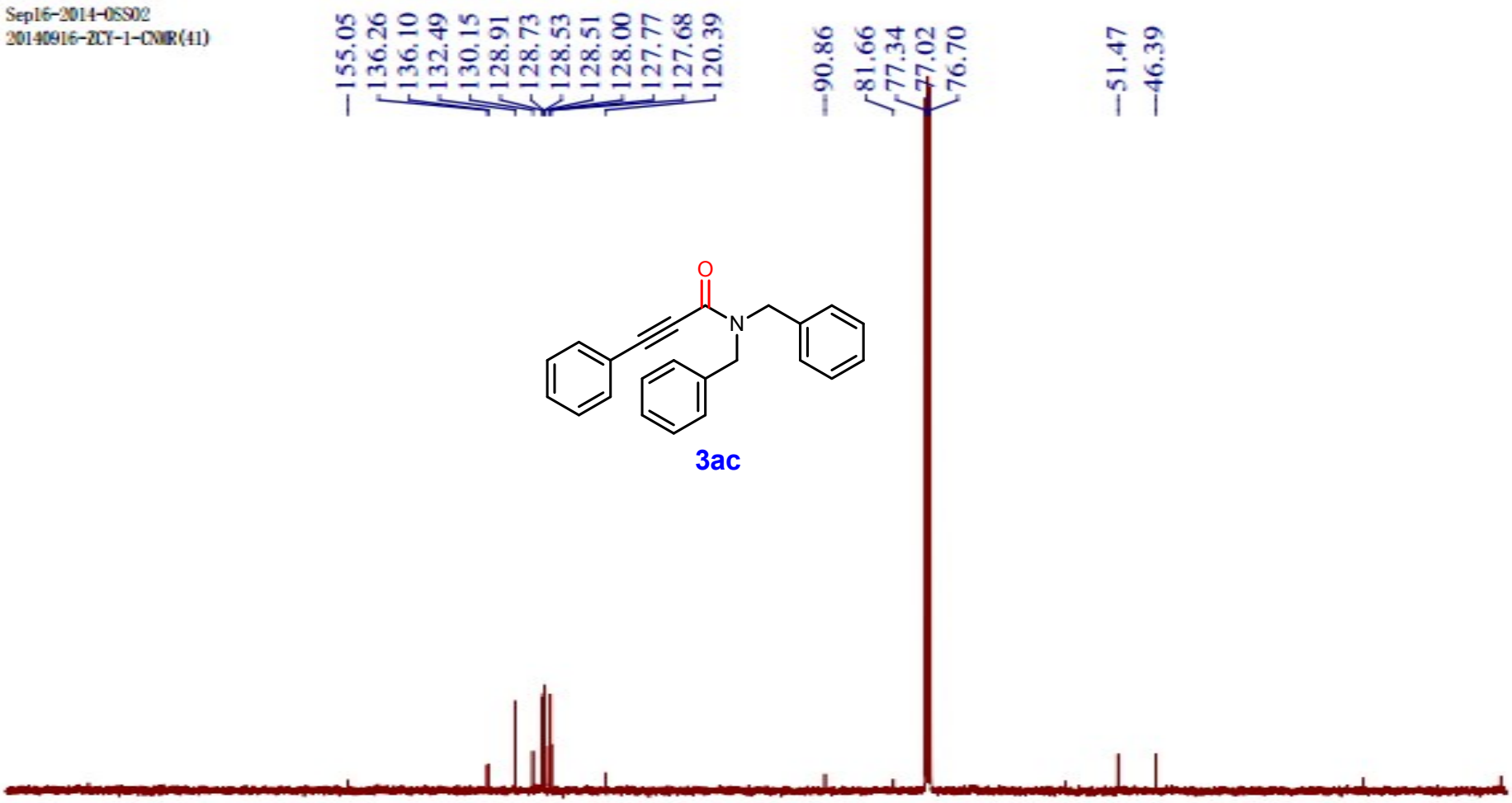

Sep02-2014-0SS0_cJ
20140902-2CY-2-HNMR(47)
7.53
7.52
7.51
7.41
7.40
7.39
7.37
7.35
7.34
7.33
3.59
3.57
3.55
3.39
3.37
3.35
1.70
1.69
1.67
1.64
1.62
1.60
0.98
0.96
0.94
0.93
0.91
O
N
3ab
2.00
3.08
2.06
2.00
4.22
6.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

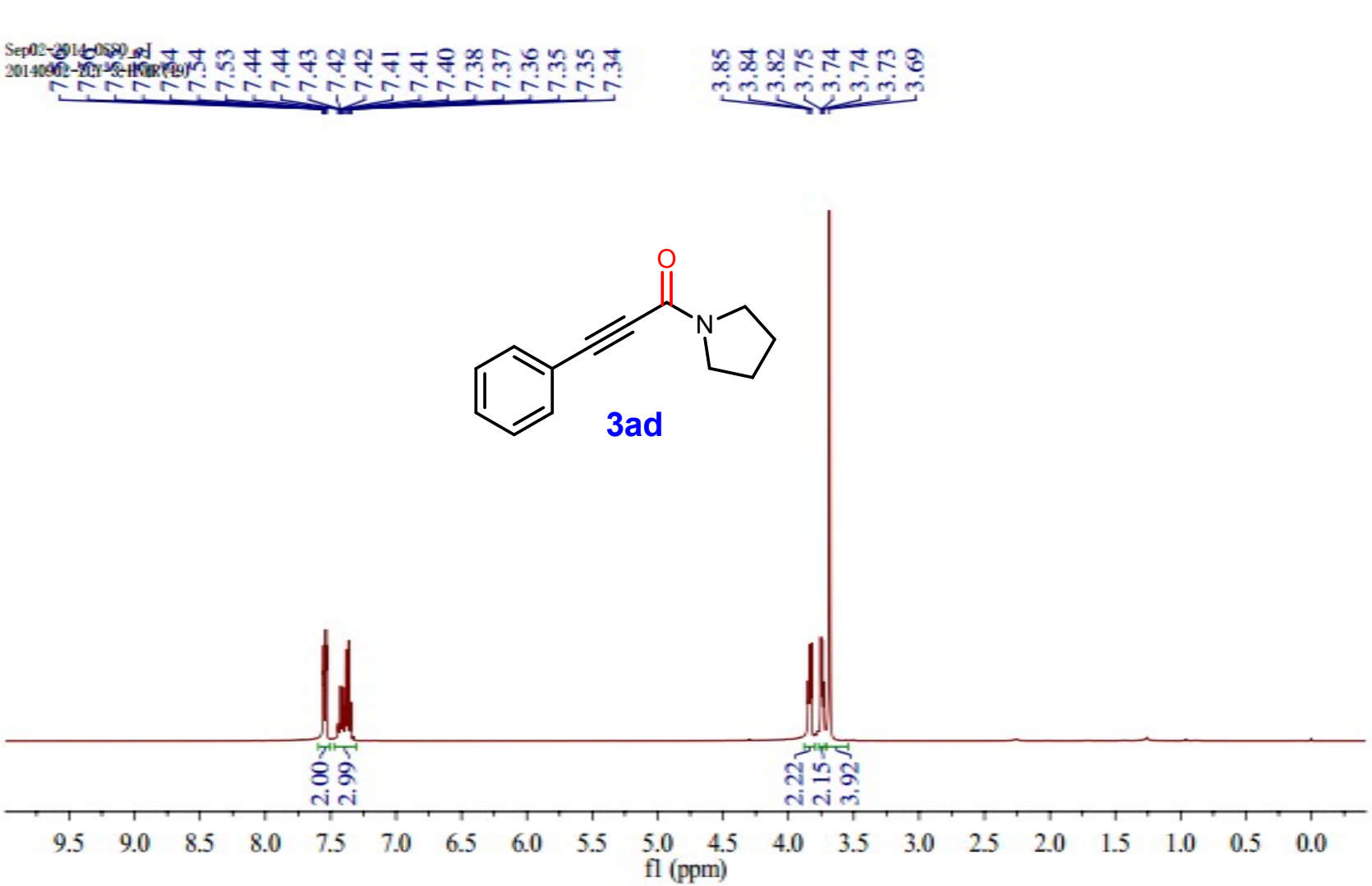

7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.27
7.26
7.25
4.76
4.57

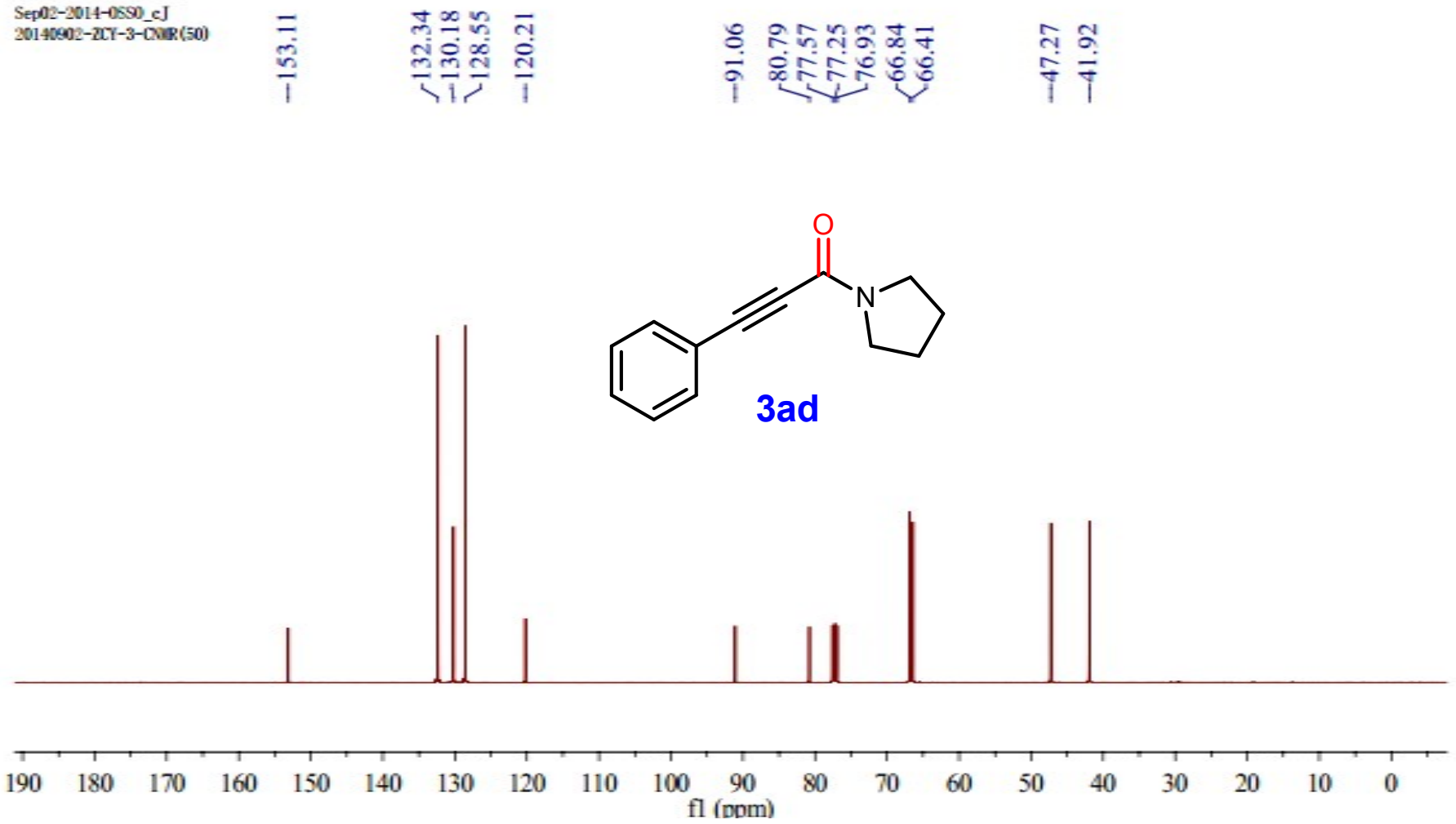

O
N

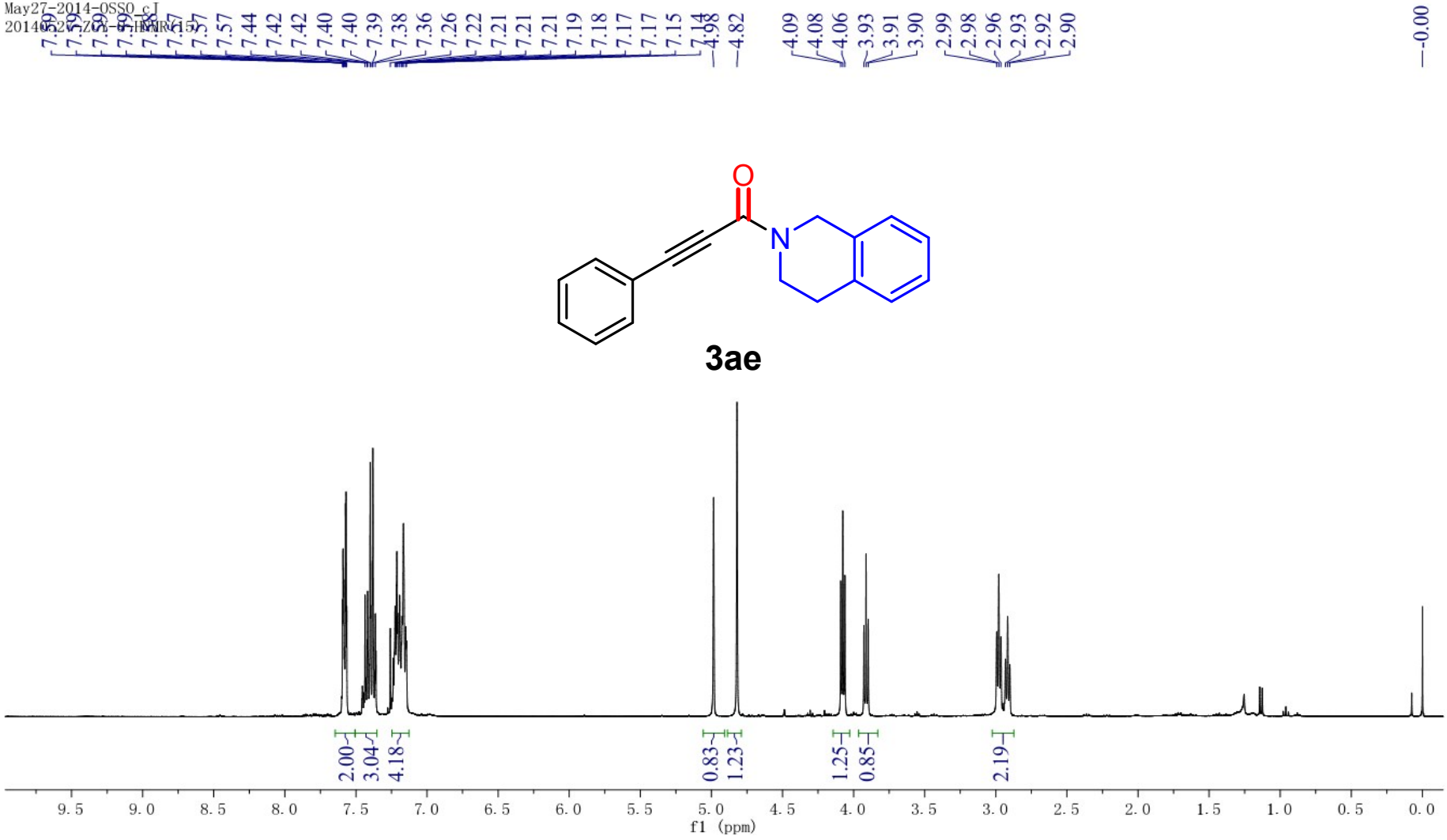
3ac


2.00
3.17
2.08
2.08
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)


Sep16-2014-OSS02
20140916-ZCY-1-CNMR(41)
155.05
136.26
136.10
132.49
130.15
128.91
128.73
128.53
128.51
128.00
127.77
127.68
120.39
90.86
81.66
77.34
77.02
76.70
51.47
46.39
O
N
3ac

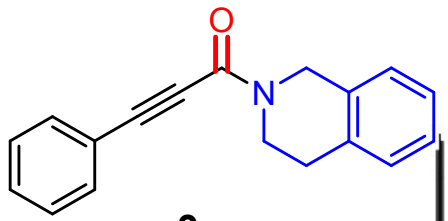

7.54
7.53
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.38
7.37
7.36
7.35
7.35
7.34
3.85
3.84
3.82
3.75
3.74
3.74
3.73
3.69
O
N
3ad
2.00
2.99
2.22
2.15
3.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Sep02-2014-0SS0_cJ
20140902-ZCY-3-CN0R(50)
153.11
132.34
130.18
128.55
120.21
91.06
80.79
77.57
77.25
76.93
66.84
66.41
47.27
41.92
O
N
3ad
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

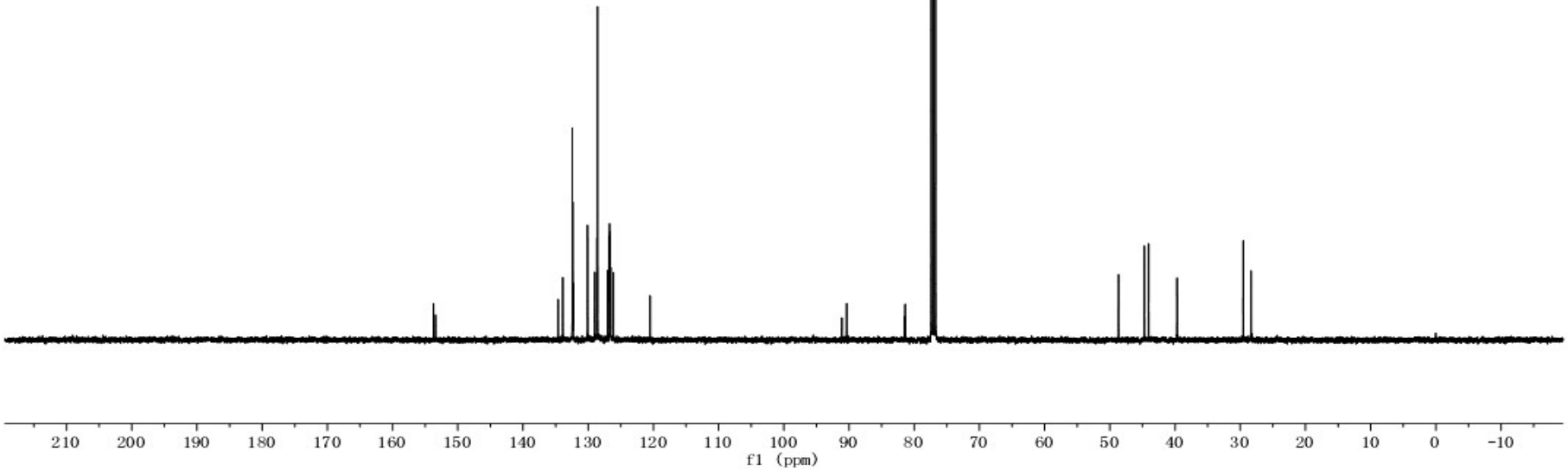

May27-2014-OSSO_cJ
7.59
7.57
7.44
7.42
7.40
7.39
7.38
7.36
7.26
7.22
7.21
7.19
7.18
7.17
7.15
4.98
4.82
4.09
4.08
4.06
3.93
3.91
3.90
2.99
2.98
2.96
2.93
2.92
2.90
-0.00
O
N
3ae
2.00
3.04
4.18
0.83
1.23
1.25
0.85
2.19
f1 (ppm)

May27-2014-OSSO_cJ
20140527-ZCY-8-CNMR(16)

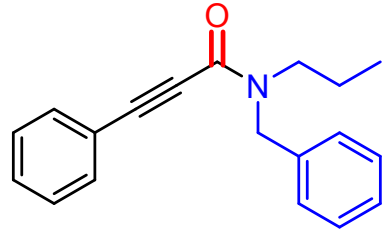
153.73
153.41
133.89
132.44
132.37
130.10
129.00
128.65
128.57
127.05
126.75
126.72
126.65
126.54
126.14
91.10
90.35
81.49
81.39
77.38
77.06
76.74
48.66
44.70
44.07
39.68
29.55
28.35



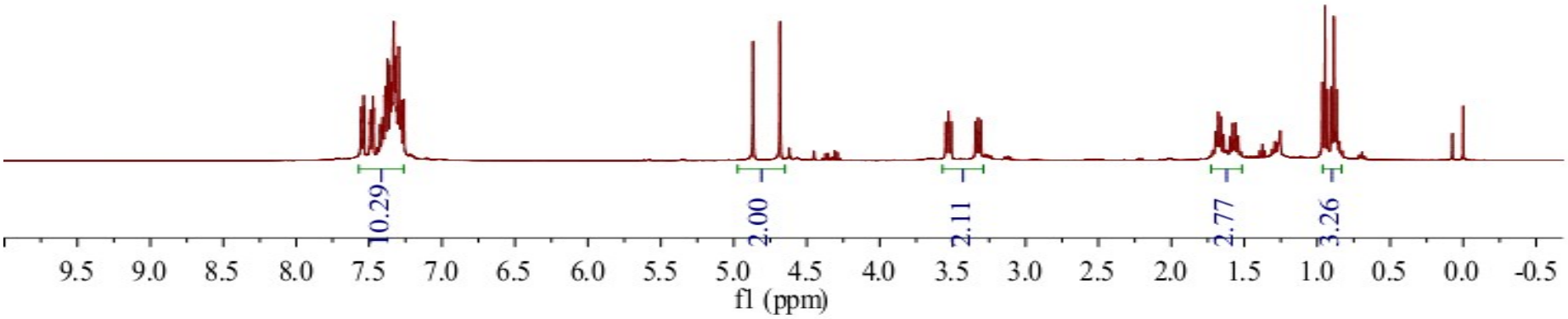
3ae

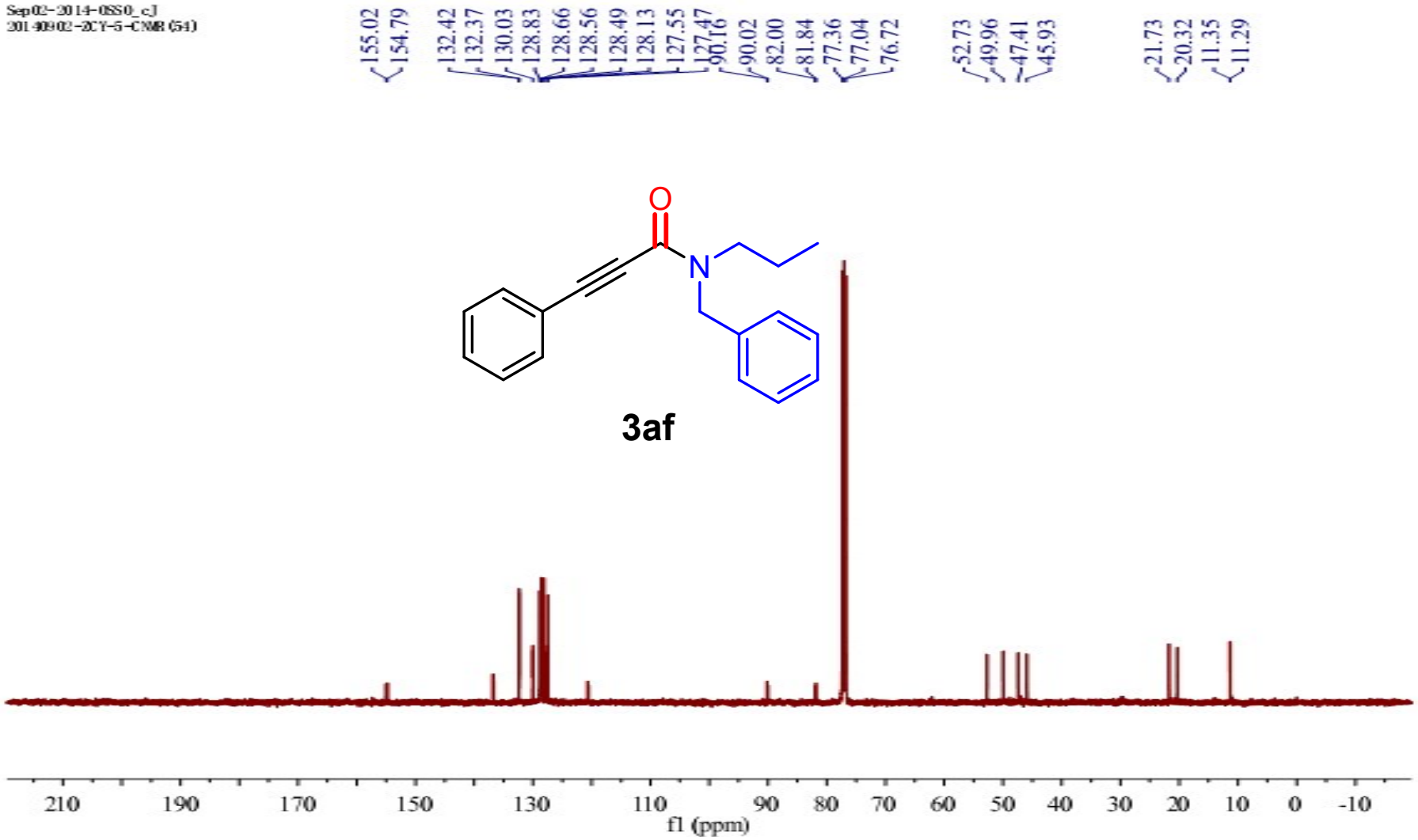



7.47
7.47
7.43
7.41
7.41
7.39
7.39
7.37
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.26
4.87
4.68
3.55
3.53
3.51
3.34
3.33
3.32
3.31
1.68
1.66
1.58
1.56
0.97
0.95
0.93
0.90
0.89
0.87


O
N

3af


10.29
2.00
2.11
2.77
3.26
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
-0.5
f1 (ppm)


Sep02-2014-0SS0_cJ
20140902-ZCY-5-CNMR (54)
155.02
154.79
132.42
132.37
130.03
128.83
128.66
128.56
128.49
128.13
127.55
127.47
90.16
90.02
82.00
81.84
77.36
77.04
76.72
52.73
49.96
47.41
45.93
21.73
20.32
11.35
11.29
O
N
3af
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)