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Highly diastereo- and enantioselective copper-catalyzed propargylic alkylation of acyclic ketone enamines for the construction of two vicinal stereocenters

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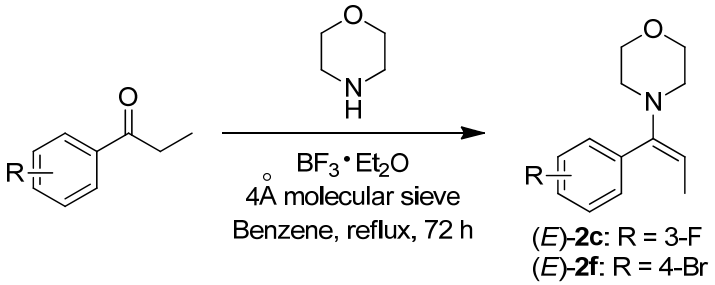
Supporting Information

General Information

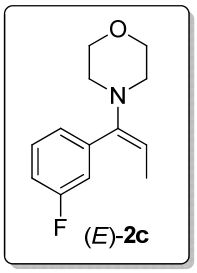
All reactions were carried out under a nitrogen atmosphere. Solvents were purified by standard procedure before use. Commercial reagents were used without further purification. Flash chromatography was performed on silica gel (40-63 μm, 60Å). Thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 with F254 indicator. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 or DMSO = δ 2.50). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 100 MHz spectrometer. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.23 or DMSO = 39.60). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Enantiomeric ratios were determined by chiral HPLC with *n*-hexane and *i*-PrOH as solvents. Optical rotations were recorded on a JASCO P-1020 polarimeter. Methanol was refluxed with magnesium ribbon and distilled under nitrogen atmosphere before use. Propargylic esters **1** were prepared following the method from the literature.[1] Enamines (*E*)-**2a-b**, (*E*)-**2d-e**, (*E*)-**2g-h** were prepared in the purity of *E*/*Z* >95/5 from the corresponding ketones with morpholine in the presence of boron trifluoride etherate according to the literature method.[2] Enamines (*E*)-**2j** (*E*/*Z* >95/5)[3], (*E*)-**2i** (*E*/*Z* >95/5)[5] and **4** (*E*/*Z* = 90/10)[2,4a] were prepared according to the literature method. Racemic products **3** were prepared using a combination of $Cu(OAc)_2{\cdot}H_2O$ and racemic (±)-**L4** as the catalyst.

Preparation of Morpholine-Derived Enamines 2c and 2f

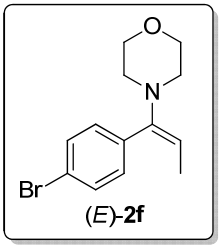


A mixture of acyclic ketone (50 mmol), morpholine (21.8 mL, 250 mmol), boron trifluoride etherate (0.628 mL, 5 mmol) and molecular sieves 4Å (1.0 g) as the dehydrating agent in anhydrous benzene (60 ml) was refluxed for 72 h using a Cope water separator. Then 4Å molecular sieves were removed by the filtration. The filtrate was concentrated under reduced pressure, and the residue was evaporated in vacuo to give the enamine (*E*)-**2c** or (*E*)-**2f**.

(*E*)-4-(1-(3-fluorophenyl)prop-1-en-1-yl)morpholine (2c). Yellow oil. *E*/*Z* >95/5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.27 (m, 1H), 7.12–7.09 (m, 1H), 7.07–7.04 (m, 1H), 7.00–6.95 (m, 1H), 4.72 (q, *J* = 6.9 Hz, 1H), 3.70–3.67 (m, 4H), 2.69–2.67 (m, 4H), 1.59 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, *J* = 245.6 Hz), 149.2 (d, *J* = 2.0 Hz), 140.2 (d, *J* = 7.5 Hz), 129.6 (d, *J* = 8.3 Hz), 125.8 (d, *J* = 2.8 Hz), 116.8 (d, *J* = 21.2 Hz), 114.5 (d, *J* = 21.1 Hz). 101.0, 67.3, 50.2, 13.9. HRMS calc. for $C_{13}H_{16}FNO$ $[M+H]^+$: 222.1294, found: 222.1293.



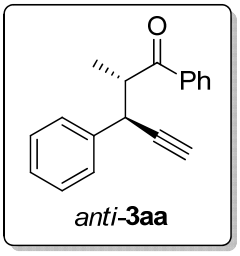
(*E*)-4-(1-(4-bromophenyl)prop-1-en-1-yl)morpholine (2f). Yellow solid, M.p.: 58-60 °C. *E*/*Z* >95/5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.72 (q, *J* = 6.9 Hz, 1H), 3.69–3.67 (m, 4H), 2.69–2.66 (m, 4H), 1.57 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 136.7, 131.7, 131.4, 121.6, 101.0, 67.3, 50.3, 13.9. HRMS calc. for $C_{13}H_{16}BrNO$ $[M+H]^+$: 282.0494, found: 282.0496.



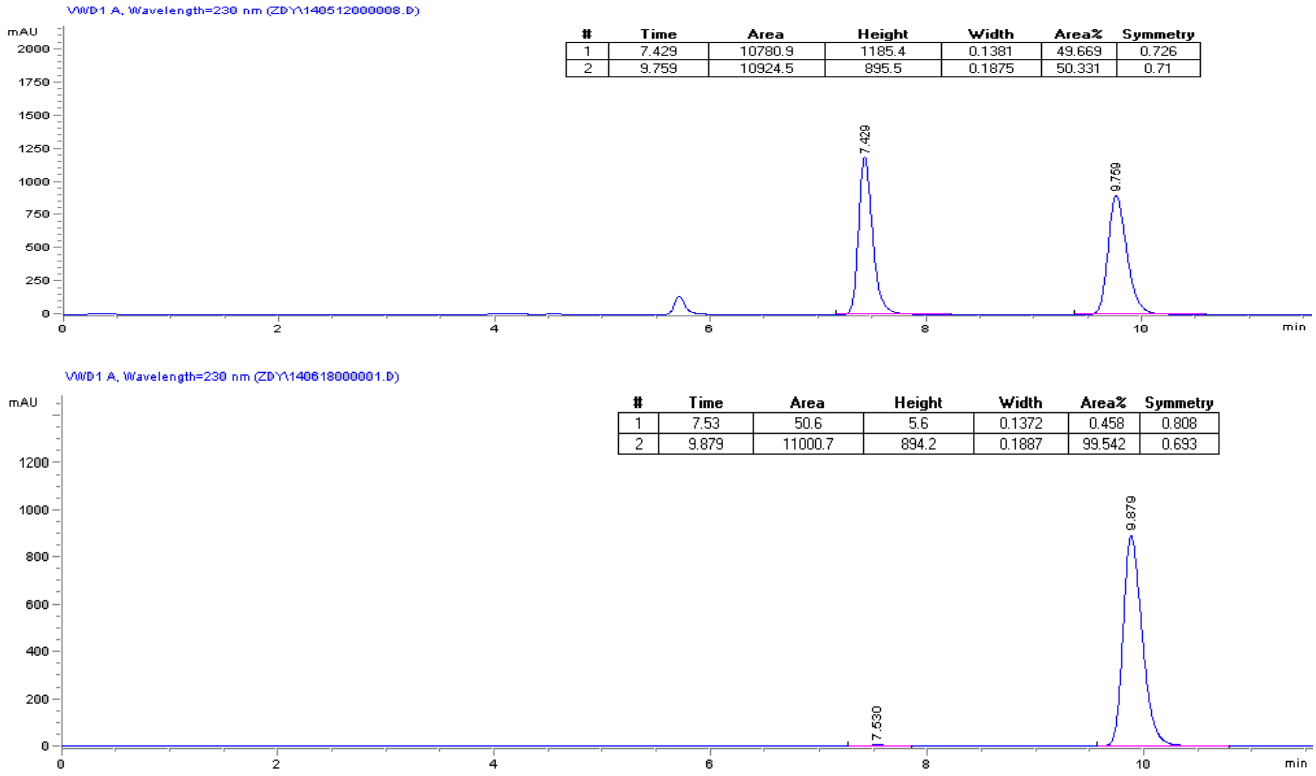
General Procedure for Copper-Catalyzed Propargylic Alkylation of Acyclic Ketone Enamines with Propargylic Esters

A solution of $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) and (*S*)-**L5** (7.8 mg, 0.0165 mmol) in 1 mL of anhydrous methanol was placed in an oven-dried Schlenk flask and stirred at 25 °C under a nitrogen atmosphere for 1 h. The reaction mixture was then cooled to -10 °C, and a solution of propargylic esters **1** (0.3 mmol) and acyclic ketone enamines **2** (0.36 mmol) in 2 mL of anhydrous methanol and ^{i}Pr$_2$NEt (63 uL, 0.36 mmol) were added successively. The mixture was stirred at -10 °C for 12 h. The reaction was then quenched by 3 mL of a buffer of NaOAc/AcOH, and extracted with CH_2Cl_2 (5 mL x 3). The combined extracts were dried over anhydrous Na_2SO_4, and concentrated under vaccum. The residue was passed over a short pad of silica using petroleum ether/EtOAc as eluent and then used for diastereoselective analysis by ^{1}H NMR or GC. After that, the crude mixture was purified by silica gel chromatography to afford products **3**.

(2*S*,3*S*)-2-Methyl-1,3-diphenylpent-4-yn-1-one (*anti*-3aa). White solid was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). M.p.: 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–8.00 (m, 2H), 7.60–7.55 (m, 1H), 7.50–7.46 (m, 2H), 7.39–7.32 (m, 4H), 7.29–7.25 (m, 1H), 4.01 (dd, *J* = 9.6, 2.4 Hz, 1H), 3.92–3.84 (m, 1H), 2.12 (d, *J* = 2.4 Hz, 1H), 0.99 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.7, 139.0, 137.0, 133.3, 128.9, 128.8, 128.7, 128.7, 127.6, 85.4, 71.5, 47.8, 40.4, 16.4. HRMS calc. for $C_{18}H_{16}O$ $[M+H]^+$: 249.1279, found: 249.1281.



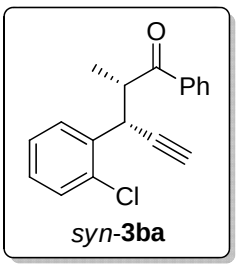
(2*S*,3*R*)-2-Methyl-1,3-diphenylpent-4-yn-1-one (*syn*-3aa). 94% yield, *syn/anti* >95/5. White solid was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). M.p.: 63-65 °C. >99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 7.5 min, t_R (major) = 9.9 min. $[\alpha]_D^{30}$ = 91.6 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.75 (m, 2H), 7.51–7.47 (m, 1H), 7.39–7.35 (m, 4H), 7.25–7.21 (m, 2H), 7.16–7.12 (m, 1H), 4.20 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.86–3.79 (m, 1H), 2.34 (d, *J* = 2.5 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 140.0, 136.7, 133.2, 128.8, 128.7, 128.3, 128.3, 127.3, 84.2, 72.9, 47.7, 40.7, 16.3. HRMS calc. for $C_{18}H_{16}O$ $[M+H]^+$: 249.1279, found: 249.1277.



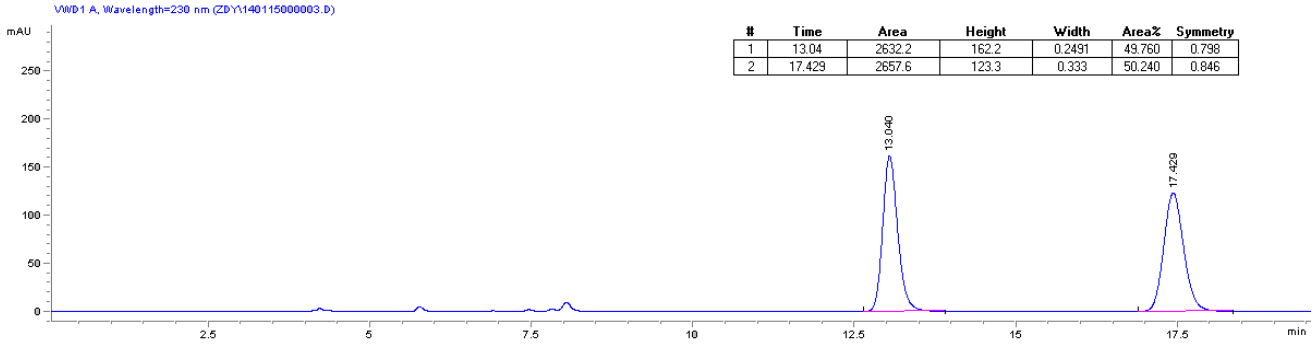
#	Time	Area	Height	Width	Area%	Symmetry
1	7.429	10780.9	1185.4	0.1381	49.669	0.726
2	9.759	10924.5	895.5	0.1875	50.331	0.71

#	Time	Area	Height	Width	Area%	Symmetry
1	7.53	50.6	5.6	0.1372	0.458	0.808
2	9.879	11000.7	894.2	0.1887	99.542	0.693

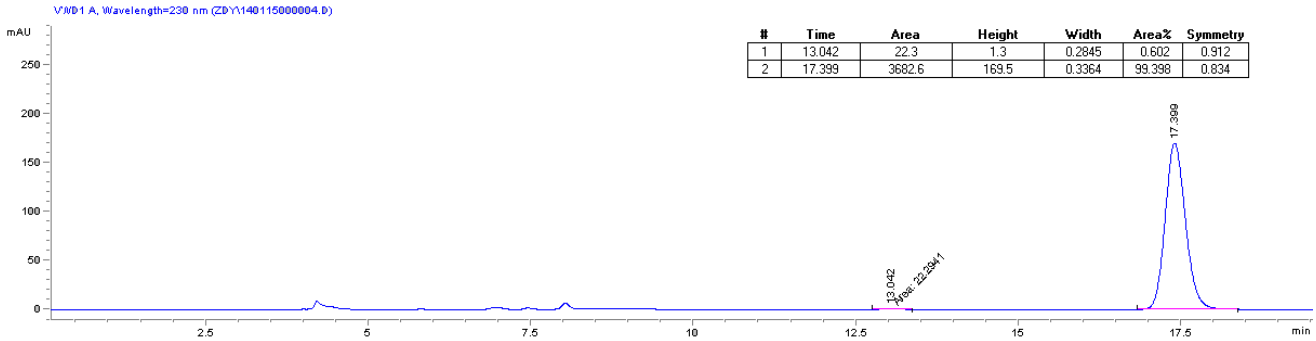
(2*S*,3*R*)-3-(2-Chlorophenyl)-2-methyl-1-phenylpent-4-yn-1-one (*syn*-3ba). 86% yield, *syn/anti* >95/5. Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). 99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 13.0 min, t_R (major) = 17.4 min. $[\alpha]_D^{29}$ = –12.0 (*c* 0.97, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.60 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56–7.52 (m, 1H), 7.46–7.42 (m, 2H), 7.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.25–7.15 (m, 2H), 4.66 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.01–3.94 (m, 1H), 2.33 (d, *J* = 2.5 Hz, 1H), 1.28 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100



MHz, $CDCl_3$): δ 201.6, 137.0, 136.6, 133.2, 133.1, 130.6, 130.1, 128.8, 128.8, 128.4, 127.1, 82.3, 73.5, 44.5, 37.5, 14.0. HRMS calc. for $C_{18}H_{15}ClO$ $[M+H]^+$: 283.0890, found: 283.0889.

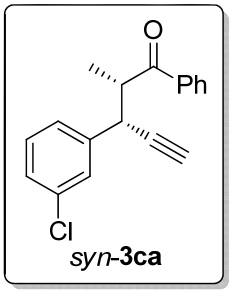


#	Time	Area	Height	Width	Area%	Symmetry
1	13.04	2632.2	162.2	0.2491	49.760	0.798
2	17.429	2657.6	123.3	0.333	50.240	0.846

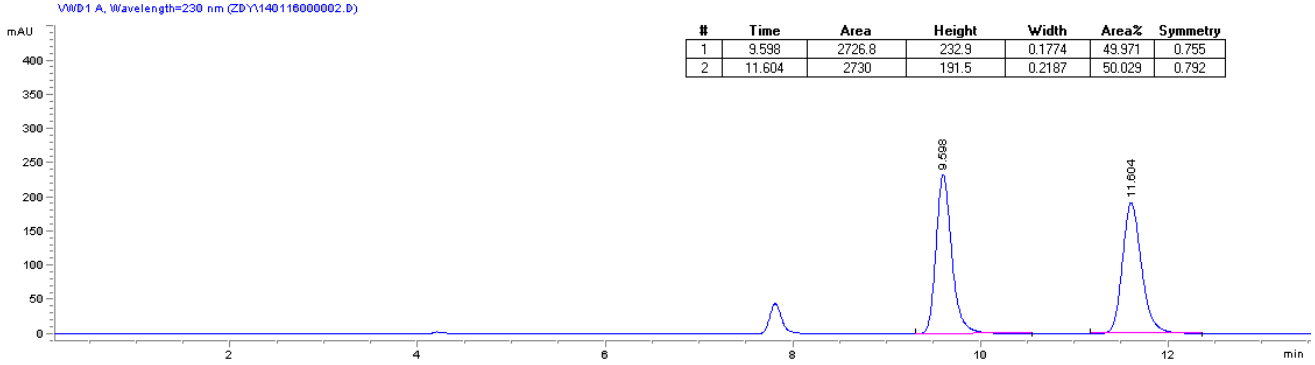


#	Time	Area	Height	Width	Area%	Symmetry
1	13.042	22.3	1.3	0.2845	0.602	0.912
2	17.399	3682.6	169.5	0.3364	99.398	0.834

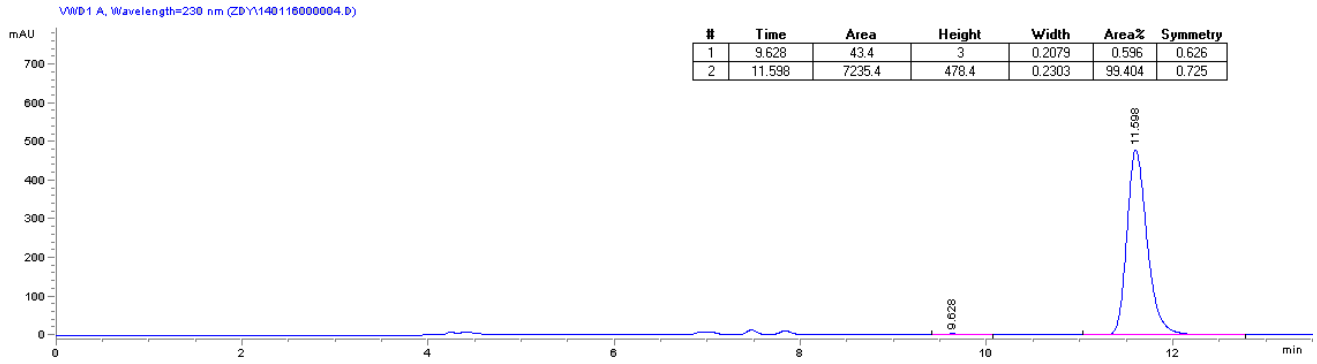
(2*S*,3*R*)-3-(3-Chlorophenyl)-2-methyl-1-phenylpent-4-yn-1-one (*syn*-3ca). 94% yield, *syn/anti* = 94/6.



Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). 99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 9.6 min, t_R (major) = 11.6 min. $[\alpha]_D^{29}$ = 87.8 (*c* 1.03, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.76 (m, 2H), 7.52–7.48 (m, 1H), 7.41–7.37 (m, 3H), 7.25–7.22 (m, 1H), 7.16–7.10 (m, 2H), 4.17 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.83–3.76 (m, 1H), 2.37 (d, *J* = 2.5 Hz, 1H), 1.41 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 142.1, 136.5, 134.5, 133.3, 129.9, 128.9, 128.4, 128.3, 127.6, 126.6, 83.5, 73.4, 47.6, 40.2, 16.5. HRMS calc. for $C_{18}H_{15}ClO$ $[M+H]^+$: 283.0890, found: 283.0888.

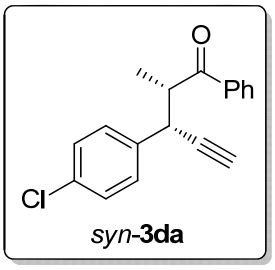


#	Time	Area	Height	Width	Area%	Symmetry
1	9.598	2726.8	232.9	0.1774	49.971	0.755
2	11.604	2730	191.5	0.2187	50.029	0.792

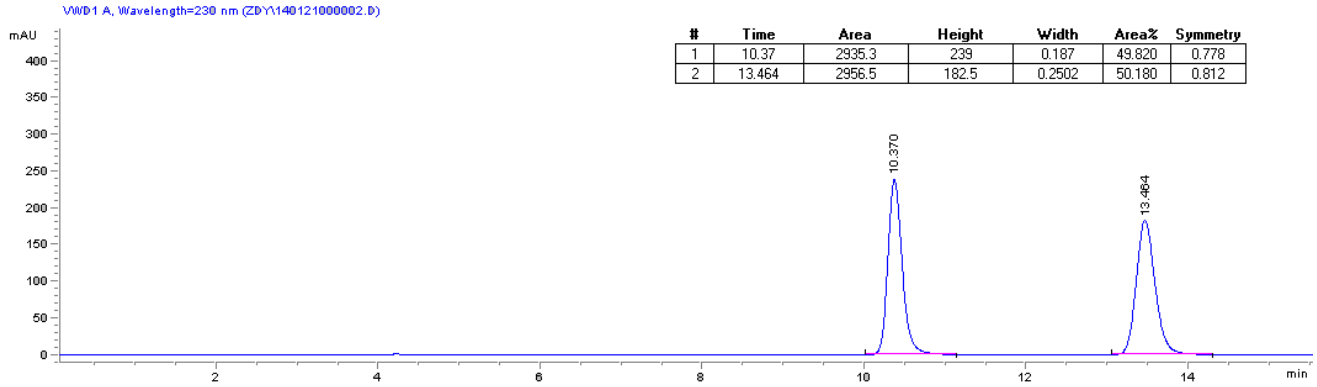


#	Time	Area	Height	Width	Area%	Symmetry
1	9.628	43.4	3	0.2079	0.596	0.626
2	11.598	7235.4	478.4	0.2303	99.404	0.725

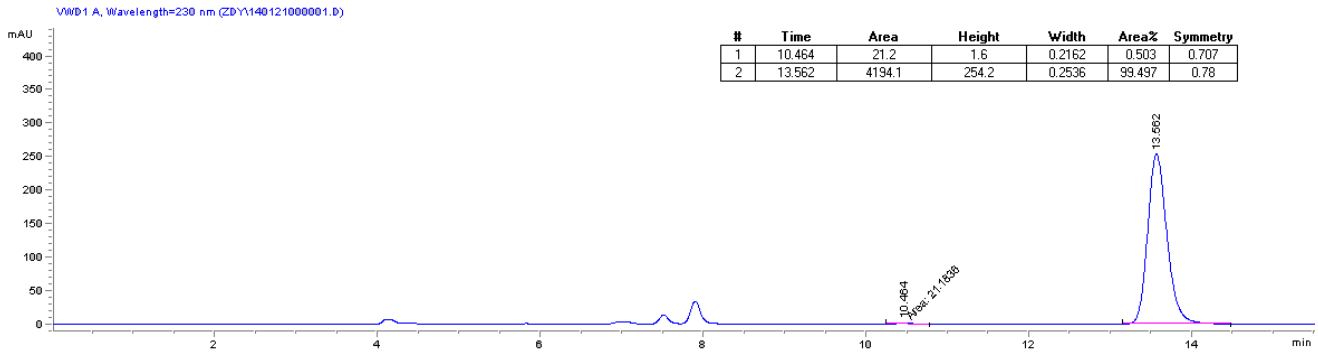
(2*S*,3*R*)-3-(4-Chlorophenyl)-2-methyl-1-phenylpent-4-yn-1-one (*syn*-3da). 93% yield, *syn*/*anti* >95/5.



Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). 99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 ^oC): t_R (minor) = 10.5 min, t_R (major) = 13.6 min. $[\alpha]_D^{30}$ = 85.7 (c 1.00, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.18 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.83–3.76 (m, 1H), 2.36 (d, *J* = 2.4 Hz, 1H), 1.42 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 201.9, 138.7, 136.5, 133.4, 133.1, 129.7, 128.9, 128.8, 128.3, 83.9, 73.1, 47.8, 40.0, 16.7. HRMS calc. for $C_{18}H_{15}ClO$ $[M+H]^+$: 283.0890, found: 283.0885.

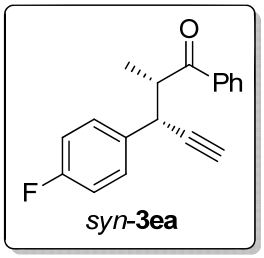


#	Time	Area	Height	Width	Area%	Symmetry
1	10.37	2935.3	239	0.187	49.820	0.778
2	13.464	2956.5	182.5	0.2502	50.180	0.812



#	Time	Area	Height	Width	Area%	Symmetry
1	10.464	21.2	1.6	0.2162	0.503	0.707
2	13.562	4194.1	254.2	0.2536	99.497	0.78

(2*S*,3*R*)-3-(4-Fluorophenyl)-2-methyl-1-phenylpent-4-yn-1-one (*syn*-3ea). 95% yield, *syn/anti* >95/5.



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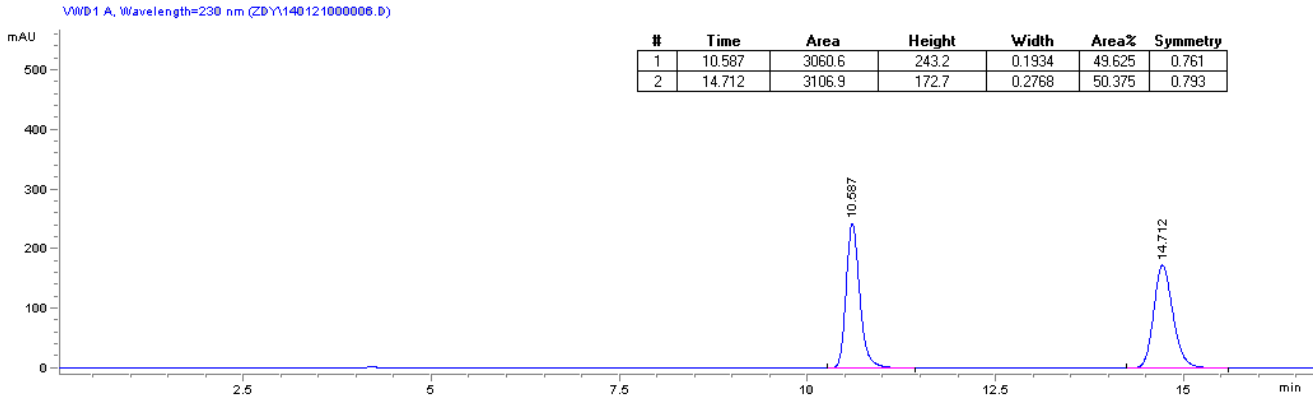
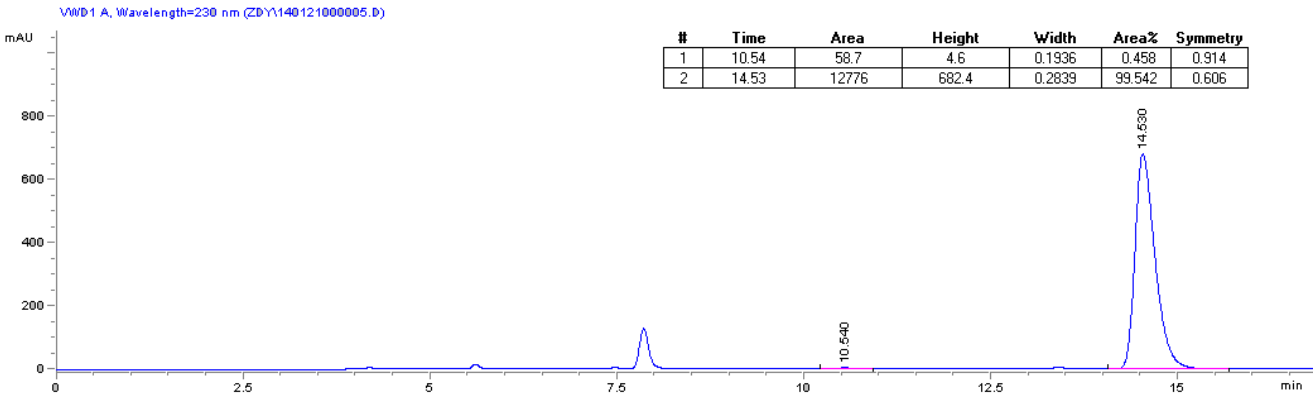
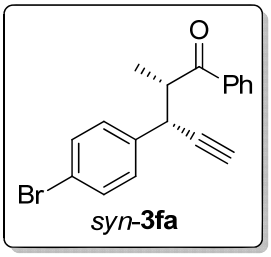


#	Time	Area	Height	Width	Area%	Symmetry
1	10.587	3060.6	243.2	0.1934	49.625	0.761
2	14.712	3106.9	172.7	0.2768	50.375	0.793



#	Time	Area	Height	Width	Area%	Symmetry
1	10.54	58.7	4.6	0.1936	0.458	0.914
2	14.53	12776	682.4	0.2839	99.542	0.606

(2*S*,3*R*)-3-(4-Bromophenyl)-2-methyl-1-phenylpent-4-yn-1-one (*syn*-3fa). 92% yield, *syn/anti* = 95/5.



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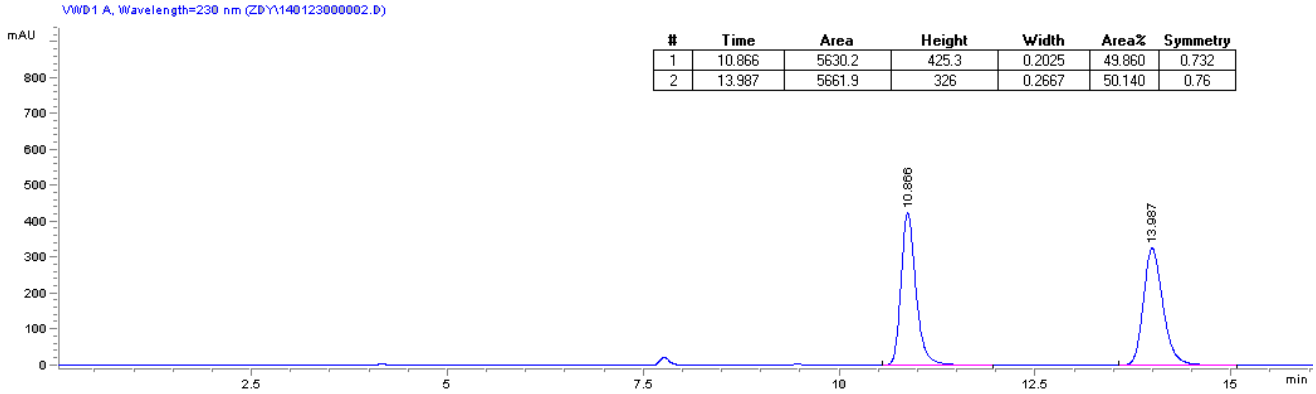
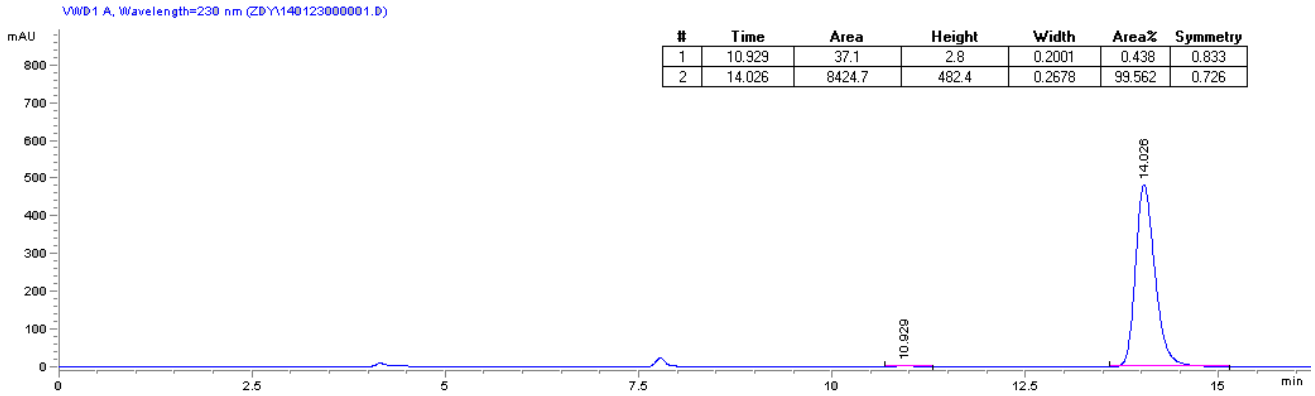
(m, 4H), 7.26–7.24 (m, 2H), 4.16 (dd, J = 8.9, 2.5 Hz, 1H), 3.82–3.75 (m, 1H), 2.35 (d, J = 2.5 Hz, 1H), 1.41 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 139.2, 136.4, 133.4, 131.7, 130.1, 128.9, 128.3, 121.2, 83.8, 73.2, 47.6, 40.0, 16.7. HRMS calc. for $C_{18}H_{15}BrO$ $[M+H]^+$: 327.0385, found: 327.0376.

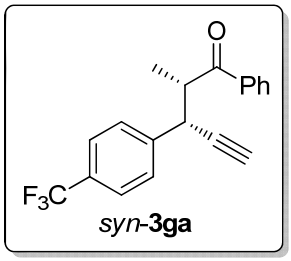


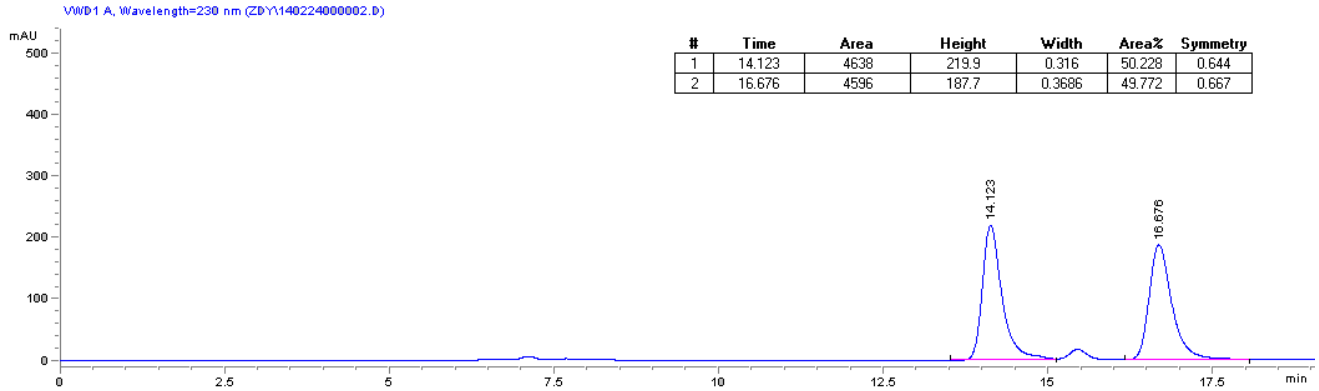
#	Time	Area	Height	Width	Area%	Symmetry
1	10.866	5630.2	425.3	0.2025	49.860	0.732
2	13.987	5661.9	326	0.2667	50.140	0.76



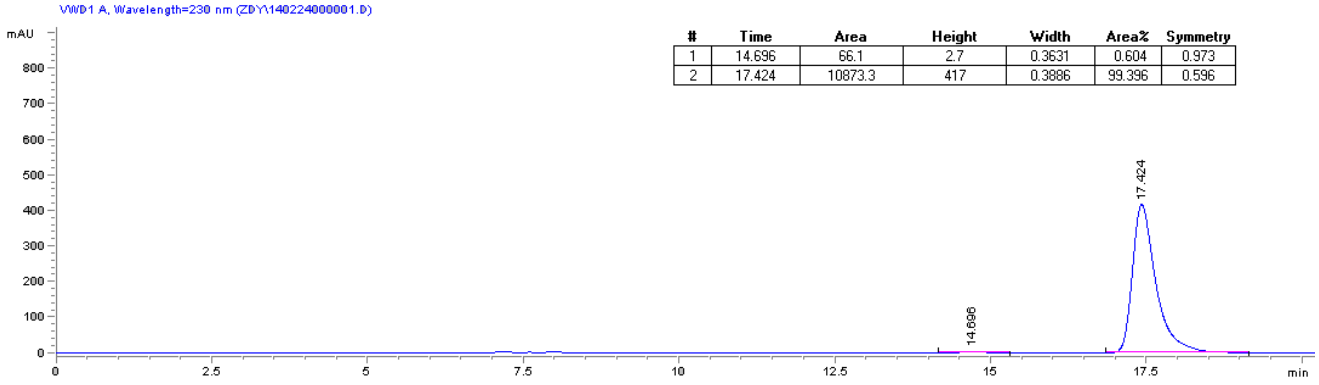
#	Time	Area	Height	Width	Area%	Symmetry
1	10.929	37.1	2.8	0.2001	0.438	0.833
2	14.026	8424.7	482.4	0.2678	99.562	0.726

(2*S*,3*R*)-2-Methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)pent-4-yn-1-one (*syn*-3ga). 93% yield, *syn*/*anti* = 94/6. Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). 99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 230 nm, 40 °C): t_R (minor) = 14.7 min, t_R (major) = 17.4 min. $[\alpha]_D^{29}$ = 66.5 (*c* 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.7 Hz, 2H), 7.53–7.48 (m, 5H), 7.39 (t, J = 7.7 Hz, 2H), 4.27 (dd, J = 8.9, 2.0 Hz, 1H), 3.88–3.80 (m, 1H), 2.38 (d, J = 2.3 Hz, 1H), 1.46 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 144.2, 136.4, 133.5, 129.6 (q, J = 32.5 Hz), 128.9, 128.8, 128.3, 125.7 (q, J = 3.8 Hz), 124.3 (q, J = 270.5 Hz), 83.5, 73.4, 47.64, 40.4, 16.8. HRMS calc. for $C_{19}H_{15}F_3O$ $[M+H]^+$: 317.1153, found: 317.1150.



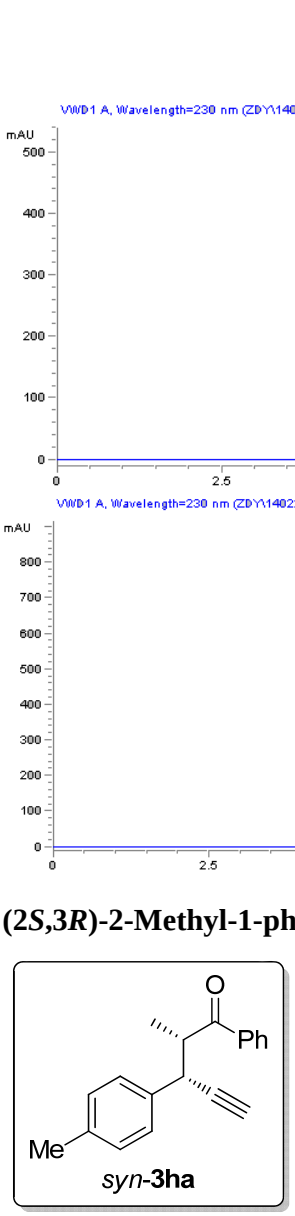


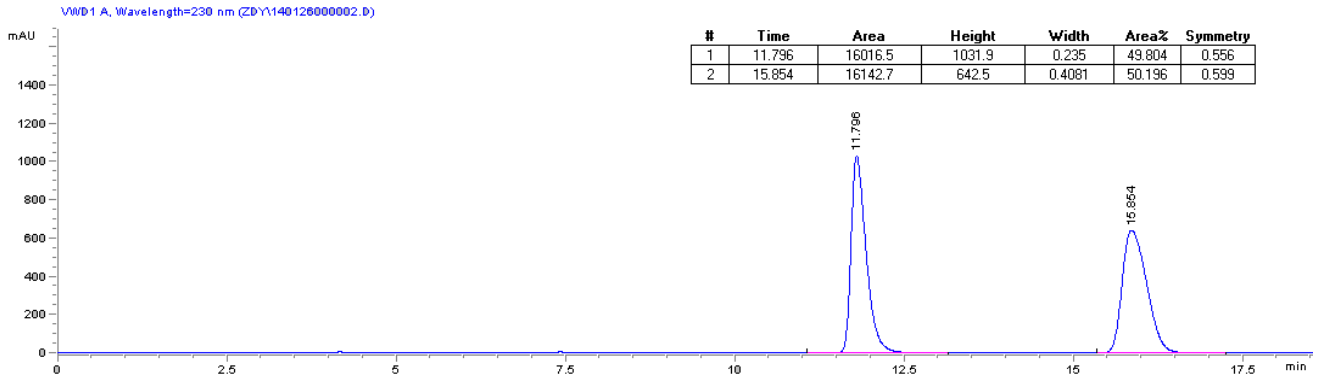
#	Time	Area	Height	Width	Area%	Symmetry
1	14.123	4638	219.9	0.316	50.228	0.644
2	16.676	4596	187.7	0.3686	49.772	0.667



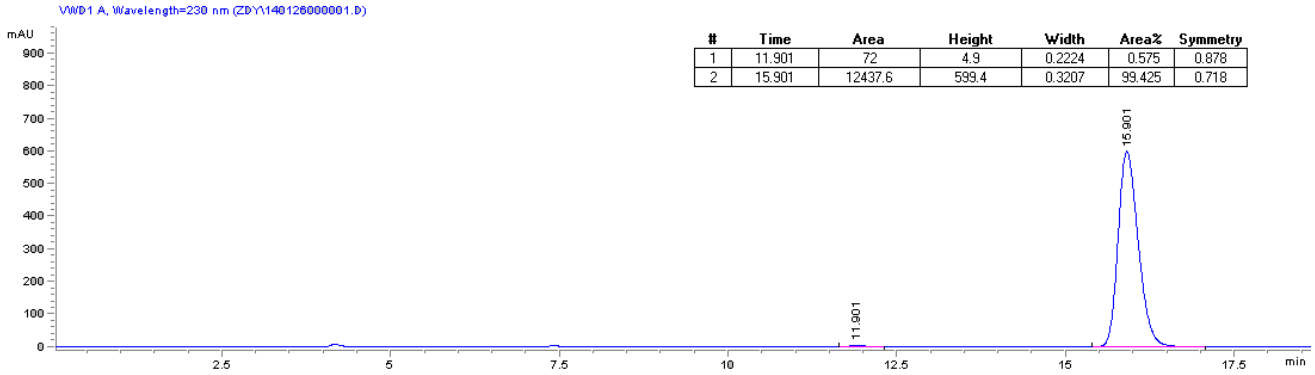
#	Time	Area	Height	Width	Area%	Symmetry
1	14.696	66.1	2.7	0.3631	0.604	0.973
2	17.424	10873.3	417	0.3886	99.396	0.596

(2*S*,3*R*)-2-Methyl-1-phenyl-3-(p-tolyl)pent-4-yn-1-one (*syn*-3ha). 93% yield, *syn/anti* >95/5. White solid was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). M.p.: 82–84 °C. 99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 11.9 min, t_R (major) = 15.9 min. $[\alpha]_D^{30}$ = 86.5 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.76 (m, 2H), 7.49–7.46 (m, 1H), 7.39–7.35 (m, 2H), 7.26–7.24 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.17 (d, *J* = 8.4 Hz, 1H), 3.84–3.77 (m, 1H), 2.32 (dd, *J* = 2.5, 1.0 Hz, 1H), 2.23 (s, 3H), 1.39 (dd, *J* = 6.9, 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 137.1, 136.8, 136.7, 133.1, 129.4, 128.7, 128.3, 128.1, 84.4, 72.7, 47.7, 40.2, 21.1, 16.3. HRMS calc. for $C_{19}H_{18}O$ $[M+H]^+$: 263.1436, found: 263.1430.



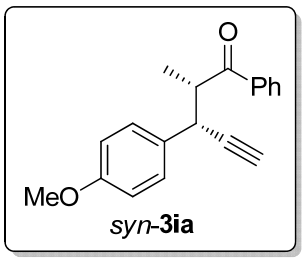


#	Time	Area	Height	Width	Area%	Symmetry
1	11.796	16016.5	1031.9	0.235	49.804	0.556
2	15.854	16142.7	642.5	0.4081	50.196	0.599

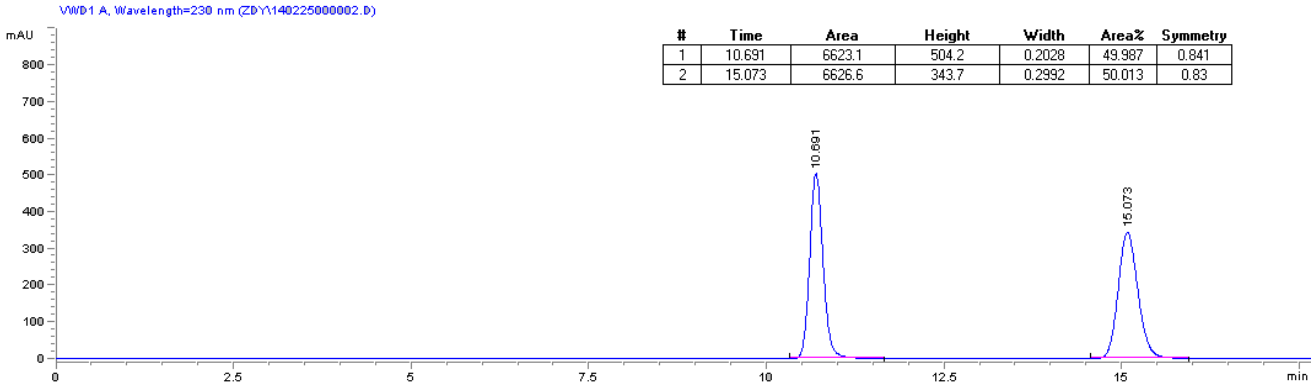


#	Time	Area	Height	Width	Area%	Symmetry
1	11.901	72	4.9	0.2224	0.575	0.878
2	15.901	12437.6	599.4	0.3207	99.425	0.718

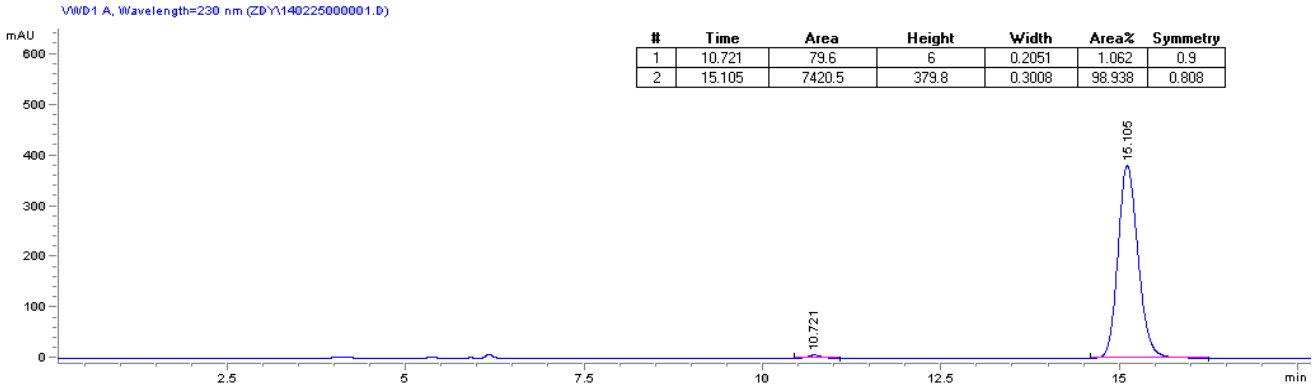
(2*S*,3*R*)-3-(4-Methoxyphenyl)-2-methyl-1-phenylpent-4-yn-1-one (*syn*-3ia). 87% yield, *syn/anti* >95/5.



White solid was obtained after purification with column chromatography on silica gel (petroleum ether/EtOAc, 100:1 to 60:1). M.p.: 72–74 °C. 98% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 70/30, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 10.7 min, t_R (major) = 15.1 min. $[\alpha]_D^{29}$ = 101.4 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.77 (m, 2H), 7.51–7.47 (m, 1H), 7.40–7.36 (m, 2H), 7.31–7.28 (m, 2H), 6.78–6.76 (m, 2H), 4.16 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.84–3.77 (m, 1H), 3.72 (s, 3H), 2.34 (d, *J* = 2.5 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3, 158.8, 136.8, 133.1, 132.1, 129.3, 128.7, 128.3, 114.1, 84.5, 72.6, 55.4, 47.8, 39.8, 16.4. HRMS calc. for $C_{19}H_{18}O_2$ $[M+Na]^+$: 301.1204, found: 301.1202.

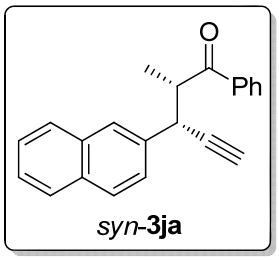


#	Time	Area	Height	Width	Area%	Symmetry
1	10.691	6623.1	504.2	0.2028	49.987	0.841
2	15.073	6626.6	343.7	0.2992	50.013	0.83

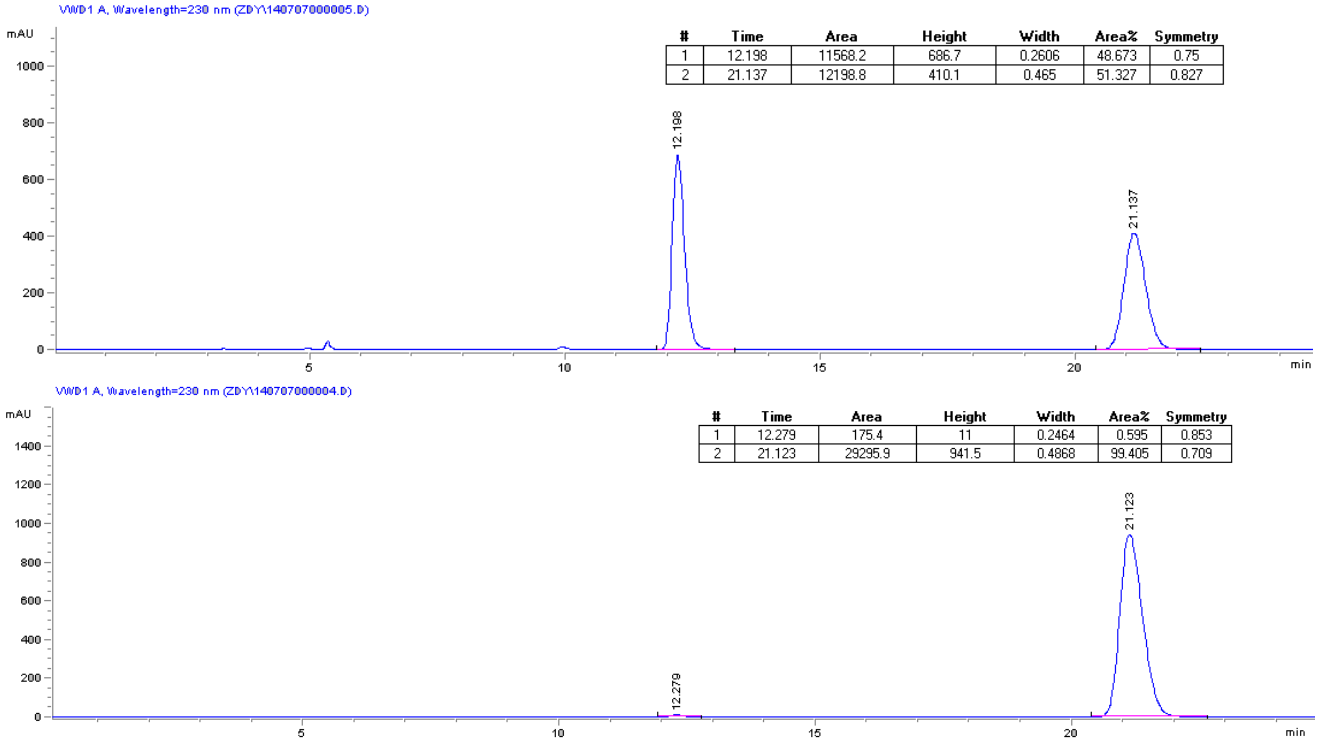


#	Time	Area	Height	Width	Area%	Symmetry
1	10.721	79.6	6	0.2051	1.062	0.9
2	15.105	7420.5	379.8	0.3008	98.938	0.808

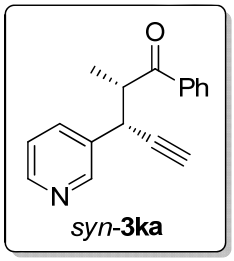
(2*S*,3*R*)-2-Methyl-3-(naphthalen-2-yl)-1-phenylpent-4-yn-1-one (*syn*-3ja). 90% yield, s*yn*/*anti* = 94/6.



Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/EtOAc, 150:1 to 100:1). 99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 230 nm, 40 °C): t_R (minor) = 12.3 min, t_R (major) = 21.1 min. $[\alpha]_D^{30}$ = 58.2 (*c* 1.04, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.81–7.75 (m, 5H), 7.56–7.54 (m, 1H), 7.48–7.40 (m, 3H), 7.37–7.34 (m, 2H), 4.42 (d, *J* = 8.4 Hz, 1H), 4.00–3.93 (m, 1H), 2.43 (d, *J* = 2.0 Hz, 1H), 1.48 (dd, *J* = 6.9, 0.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 137.4, 136.6, 133.5, 133.2, 132.7, 128.8, 128.5, 128.3, 128.1, 127.7, 127.3, 126.3, 126.1, 126.0, 84.1, 73.2, 47.6, 40.6, 16.4. HRMS calc. for $C_{22}H_{18}O$ $[M+H]^+$: 299.1436, found: 299.1430.

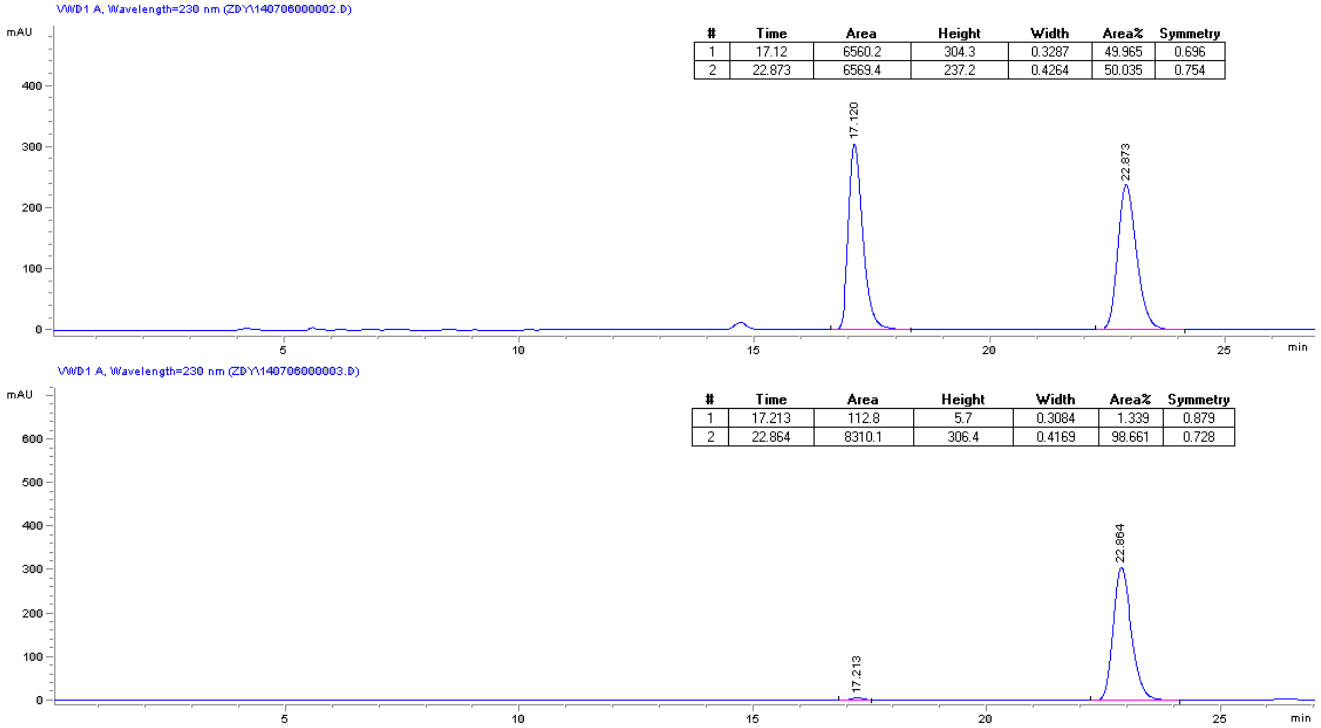


(2*S*,3*R*)-2-Methyl-1-phenyl-3-(pyridin-3-yl)pent-4-yn-1-one (*syn*-3ka). 74% yield, s*yn*/*anti* = 92/8.



Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/EtOAc, 10:1 to 2:1). 97% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 17.2 min, t_R (major) = 22.9 min. $[\alpha]_D^{29}$ = 75.1 (*c* 0.93, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.39 (d, *J* = 4.3 Hz, 1H), 7.78–7.76 (m, 2H), 7.70-7.68 (m, 1H), 7.51–7.48 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.14 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.20 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.86–3.78 (m, 1H), 2.37 (d, *J* = 2.5 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 149.8, 148.6, 136.3, 136.0, 135.8, 133.5, 128.9, 128.3, 123.5, 83.2, 73.4, 47.6,

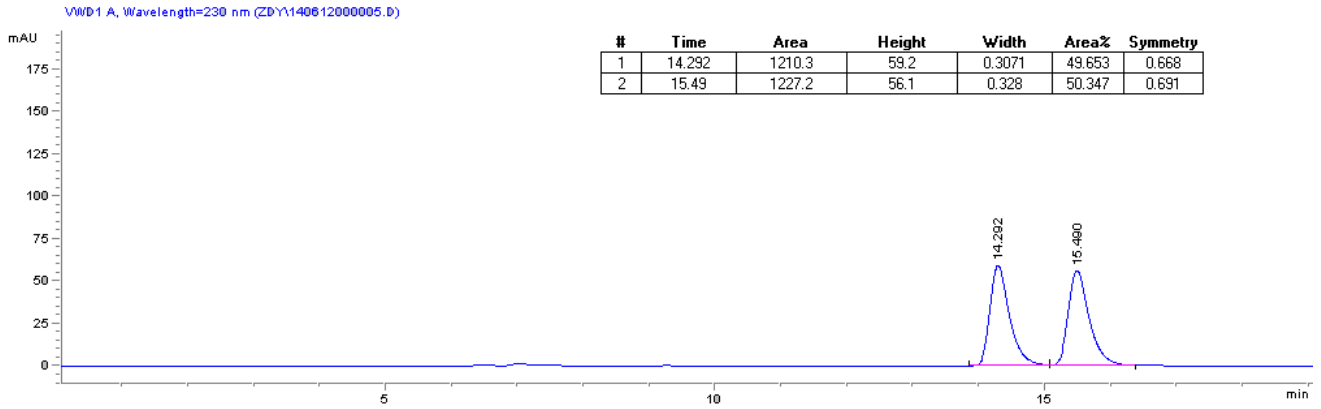
38.2, 16.8. HRMS calc. for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1232, found: 250.1230.



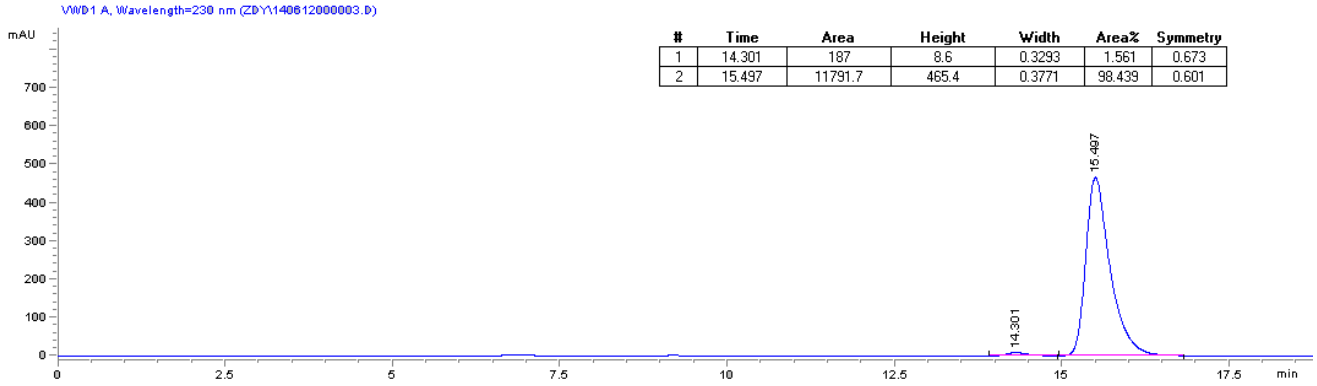
#	Time	Area	Height	Width	Area%	Symmetry
1	17.12	6560.2	304.3	0.3287	49.965	0.696
2	22.873	6569.4	237.2	0.4264	50.035	0.754

#	Time	Area	Height	Width	Area%	Symmetry
1	17.213	112.8	5.7	0.3084	1.339	0.879
2	22.864	8310.1	306.4	0.4169	98.661	0.728

(2*S*,3*R*)-2-Methyl-1-phenyl-3-(thiophen-2-yl)pent-4-yn-1-one (*syn*-3la). 96% yield, *syn*/*anti* >95/5. Pale yellow oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). 97% ee was determined by chiral HPLC (Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 230 nm, 40 °C): t_R (minor) = 14.3 min, t_R (major) = 15.5 min. $[\alpha]_D^{28}$ = 95.8 (*c* 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86–7.84 (m, 2H), 7.55–7.51 (m, 1H), 7.44–7.40 (m, 2H), 7.09 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.96 (d, *J* = 3.4 Hz, 1H), 6.82 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.54 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.92–3.85 (m, 1H), 2.41 (d, *J* = 2.5 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 143.1, 136.5, 133.3, 128.9, 128.4, 126.8, 126.0, 124.5, 83.4, 73.0, 48.3, 35.7, 16.6. HRMS calc. for $C_{16}H_{14}OS$ $[M+H]^+$: 255.0844, found: 255.0841.

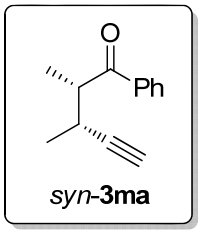


#	Time	Area	Height	Width	Area%	Symmetry
1	14.292	1210.3	59.2	0.3071	49.653	0.668
2	15.49	1227.2	56.1	0.328	50.347	0.691

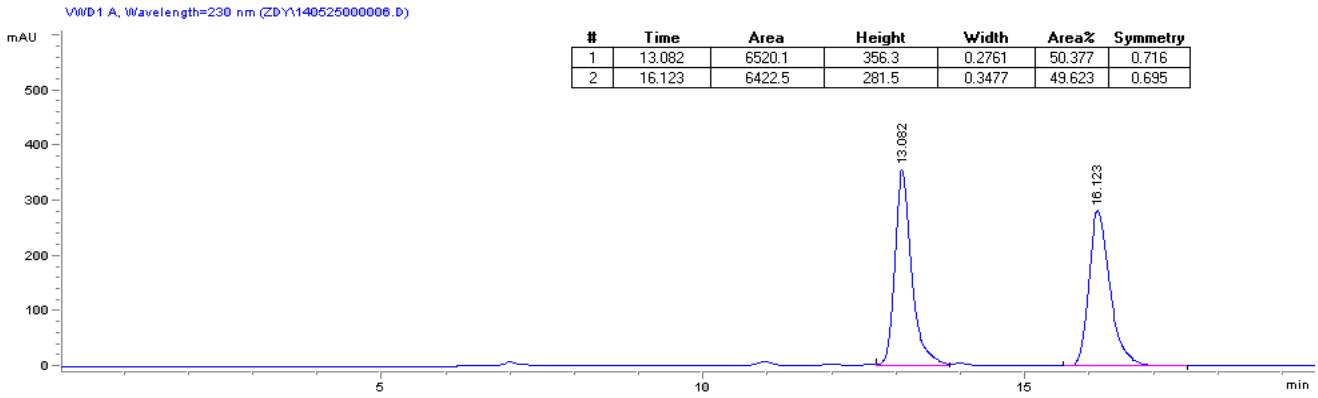


#	Time	Area	Height	Width	Area%	Symmetry
1	14.301	187	8.6	0.3293	1.561	0.673
2	15.497	11791.7	465.4	0.3771	98.439	0.601

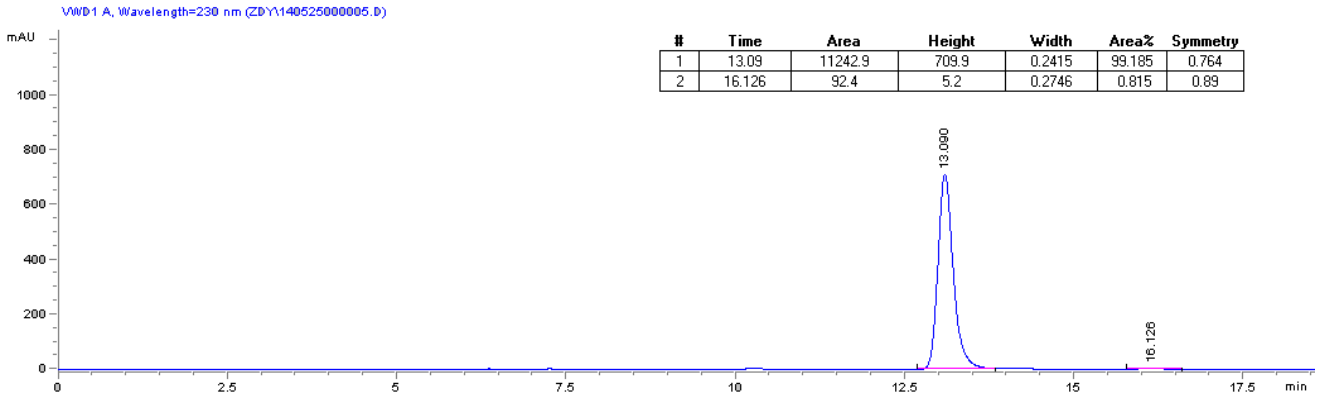
(2*S*,3*R*)-2,3-Dimethyl-1-phenylpent-4-yn-1-one (*syn*-3ma). 27% yield, *syn/anti* = 89/11. Colorless oil



was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). 98% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, 0.5 ml/min, 230 nm, 40 °C): t_R (major) = 13.1 min, t_R (minor) = 16.1 min. $[\alpha]_D^{29}$ = 72.0 (*c* 0.85, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.94 (m, 2H), 7.59–7.56 (m, 1H), 7.49–7.46 (m, 2H), 3.49–3.41 (m, 1H), 3.03–2.95 (m, 1H), 2.15 (d, *J* = 2.4 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.9, 136.9, 133.4, 128.9, 128.5, 87.0, 70.5, 46.1, 29.3, 20.0, 16.9. HRMS calc. for $C_{13}H_{14}O$ $[M+H]^+$: 187.1123, found: 187.1118.

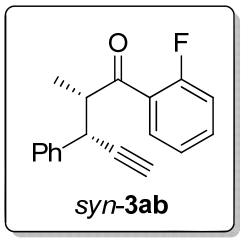


#	Time	Area	Height	Width	Area%	Symmetry
1	13.082	6520.1	356.3	0.2761	50.377	0.716
2	16.123	6422.5	281.5	0.3477	49.623	0.695



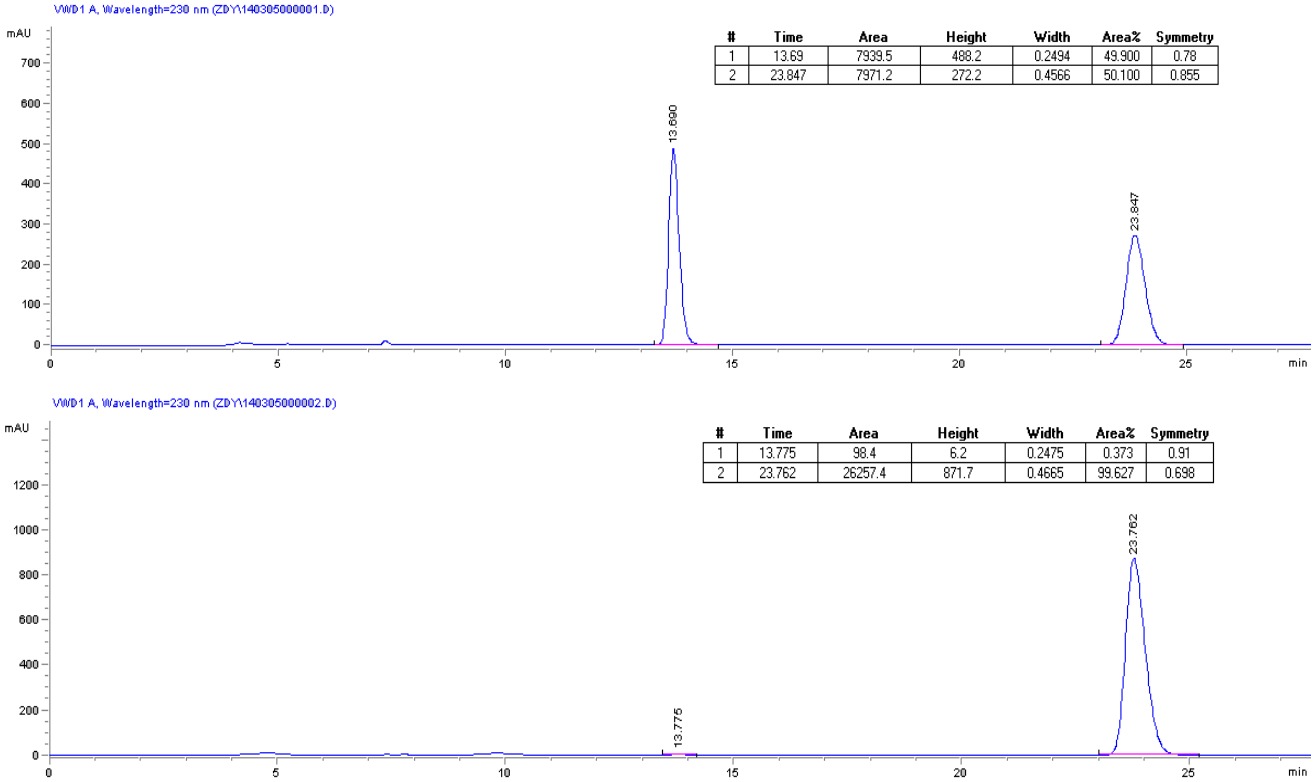
#	Time	Area	Height	Width	Area%	Symmetry
1	13.09	11242.9	709.9	0.2415	99.185	0.764
2	16.126	92.4	5.2	0.2746	0.815	0.89

(2*S*,3*R*)-1-(2-Fluorophenyl)-2-methyl-3-phenylpent-4-yn-1-one (*syn*-3ab). 92% yield, *syn/anti* >95/5.



syn-**3ab**

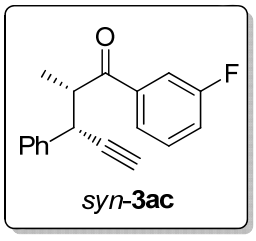
Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). >99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 13.8 min, t_R (major) = 23.8 min. $[\alpha]_D^{30}$ = 60.0 (*c* 1.03, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (td, *J* = 7.6, 1.7 Hz, 1H), 7.47–7.38 (m, 3H), 7.28–7.24 (m, 2H), 7.20–7.05 (m, 3H), 4.22 (d, *J* = 6.4 Hz, 1H), 3.72 (p, *J* = 6.9 Hz, 1H), 2.31 (d, *J* = 2.5 Hz, 1H), 1.32 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7 (d, *J* = 3.8 Hz), 161.0 (d, *J* = 252.7 Hz), 139.5, 134.3 (d, *J* = 8.9 Hz), 131.1 (d, *J* = 2.8 Hz), 128.6, 128.3, 127.3, 126.1 (d, *J* = 13.4 Hz), 124.8 (d, *J* = 3.3 Hz), 116.6 (d, *J* = 23.7 Hz), 83.2, 73.2 , 52.3 (d, *J* = 6.3 Hz), 40.3, 13.9. HRMS calc. for $C_{18}H_{15}FO$ $[M+H]^+$: 267.1185, found: 267.1181.



#	Time	Area	Height	Width	Area%	Symmetry
1	13.69	7939.5	488.2	0.2494	49.900	0.78
2	23.847	7971.2	272.2	0.4566	50.100	0.855

#	Time	Area	Height	Width	Area%	Symmetry
1	13.775	98.4	6.2	0.2475	0.373	0.91
2	23.762	26257.4	871.7	0.4665	99.627	0.698

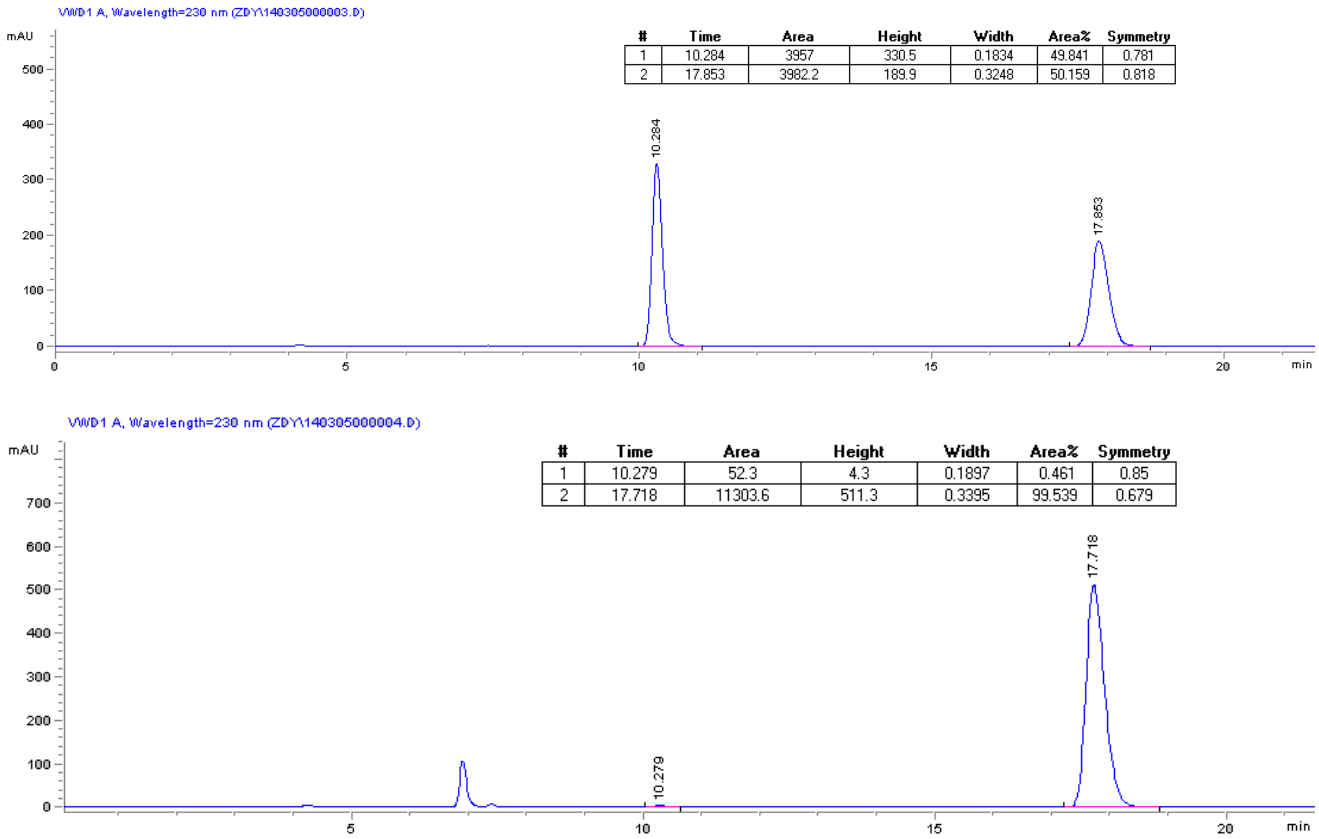
(2*S*,3*R*)-1-(3-Fluorophenyl)-2-methyl-3-phenylpent-4-yn-1-one (*syn*-3ac). 94% yield, *syn/anti* = 95/5.



syn-**3ac**

Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). >99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 10.3 min, t_R (major) = 17.7 min. $[\alpha]_D^{29}$ = 81.8 (*c* 0.94, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.44–7.41 (m, 1H), 7.36–7.31 (m, 3H), 7.25–7.21 (m, 2H), 7.20–7.13 (m, 2H), 4.16 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.79–3.72 (m, 1H), 2.35 (d,

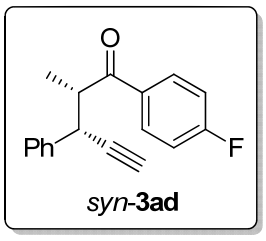
J = 2.5 Hz, 1H), 1.41 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0 (d, J = 2.0 Hz), 163.0 (d, J = 248.1 Hz), 139.8, 138.9 (d, J = 6.1 Hz), 130.4 (d, J = 7.6 Hz), 128.8, 128.2, 127.4, 123.9 (d, J = 3.0 Hz), 120.2 (d, J = 21.5 Hz), 115.1 (d, J = 22.4 Hz), 83.9, 73.0, 48.0, 40.8, 16.3. HRMS calc. for $C_{18}H_{15}FO$ $[M+H]^+$: 267.1185, found: 267.1180.



#	Time	Area	Height	Width	Area%	Symmetry
1	10.284	3957	330.5	0.1834	49.841	0.781
2	17.853	3982.2	189.9	0.3248	50.159	0.818

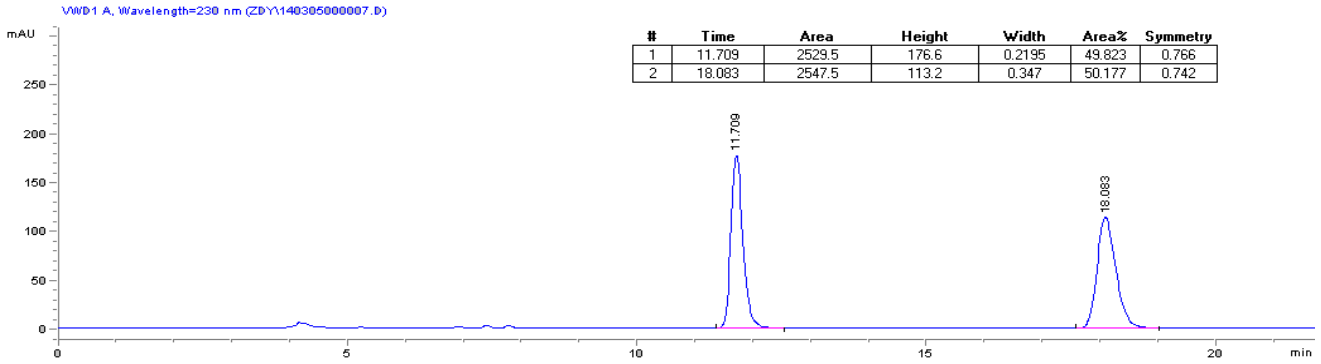
#	Time	Area	Height	Width	Area%	Symmetry
1	10.279	52.3	4.3	0.1897	0.461	0.85
2	17.718	11303.6	511.3	0.3395	99.539	0.679

(2*S*,3*R*)-1-(4-Fluorophenyl)-2-methyl-3-phenylpent-4-yn-1-one (*syn*-3ad). 95% yield, *syn*/*anti* >95/5.

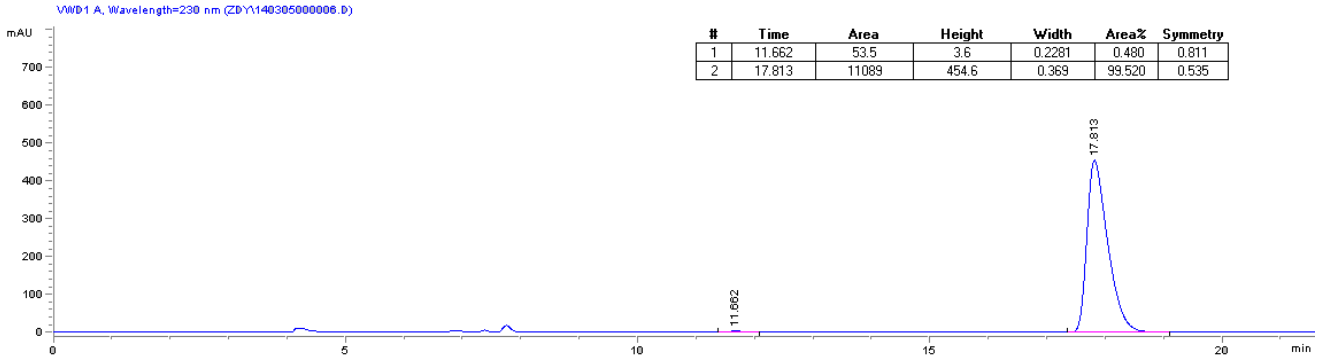


syn-3ad

Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). >99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 11.7 min, t_R (major) = 17.8 min. $[\alpha]_D^{29}$ = 108.9 (*c* 0.97, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.76 (m, 2H), 7.36 (d, J = 7.4 Hz, 2H), 7.25–7.21 (m, 2H), 7.16–7.13 (m, 1H), 7.05–7.01 (m, 2H), 4.16 (dd, J = 8.8, 2.4 Hz, 1H), 3.82–3.75 (m, 1H), 2.36 (d, J = 2.4 Hz, 1H), 1.42 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 165.8 (d, J = 254.9 Hz), 139.9, 133.2 (d, J = 3.0 Hz), 130.9 (d, J = 9.3 Hz), 128.7, 128.2, 127.4, 115.8 (d, J = 21.9 Hz), 84.1, 72.9, 47.7, 40.8, 16.5. HRMS calc. for $C_{18}H_{15}FO$ $[M+H]^+$: 267.1185, found: 267.1183.

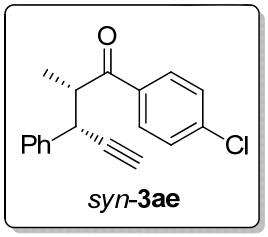


#	Time	Area	Height	Width	Area%	Symmetry
1	11.709	2529.5	176.6	0.2195	49.823	0.766
2	18.083	2547.5	113.2	0.347	50.177	0.742

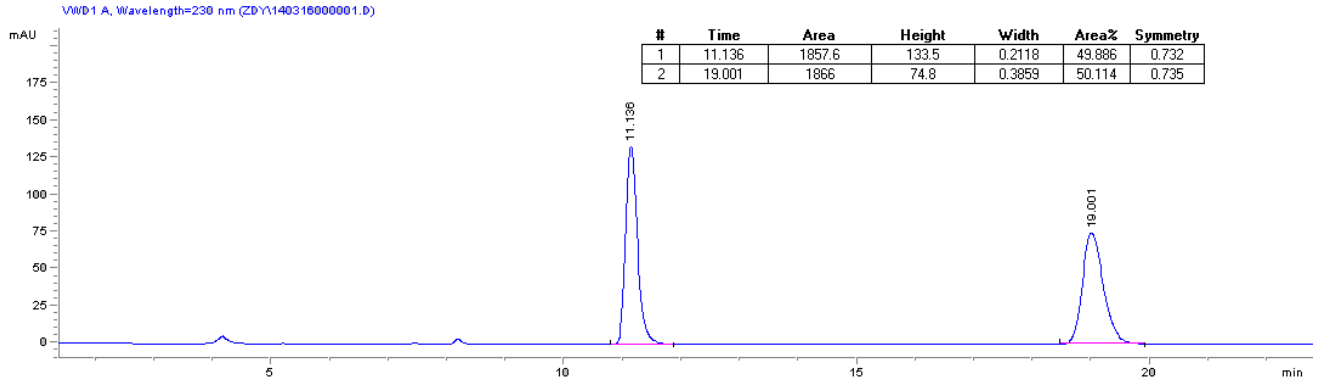


#	Time	Area	Height	Width	Area%	Symmetry
1	11.662	53.5	3.6	0.2281	0.480	0.811
2	17.813	11089	454.6	0.369	99.520	0.535

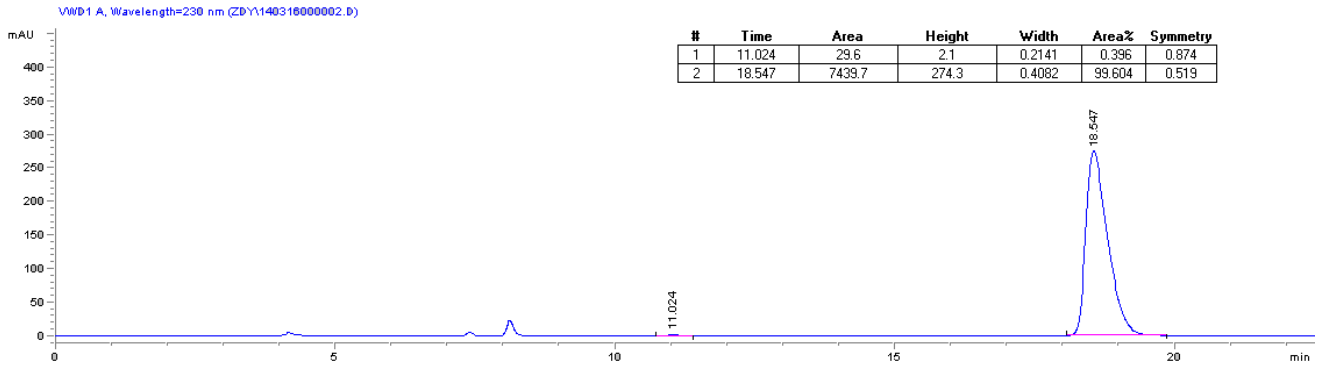
(2*S*,3*R*)-1-(4-Chlorophenyl)-2-methyl-3-phenylpent-4-yn-1-one (*syn*-3ae). 94% yield, s*yn/anti* >95/5.



Colorless oil was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). >99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 ^oC): t_R (minor) = 11.0 min, t_R (major) = 18.5 min. $[\alpha]_D^{29}$ = 80.1 (*c* 0.92, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.69–7.67 (m, 2H), 7.36–7.33 (m, 4H), 7.25–7.21 (m, 2H), 7.17–7.13 (m, 1H), 4.15 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.80–3.73 (m, 1H), 2.35 (d, *J* = 2.5 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 139.8, 139.7, 135.1, 129.7, 129.1, 128.7, 128.2, 127.4, 84.0, 73.0, 47.8, 40.8, 16.4. HRMS calc. for $C_{18}H_{15}ClO$ $[M+H]^+$: 283.0890, found: 283.0884.

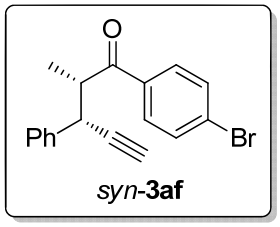


#	Time	Area	Height	Width	Area%	Symmetry
1	11.136	1857.6	133.5	0.2118	49.886	0.732
2	19.001	1866	74.8	0.3859	50.114	0.735

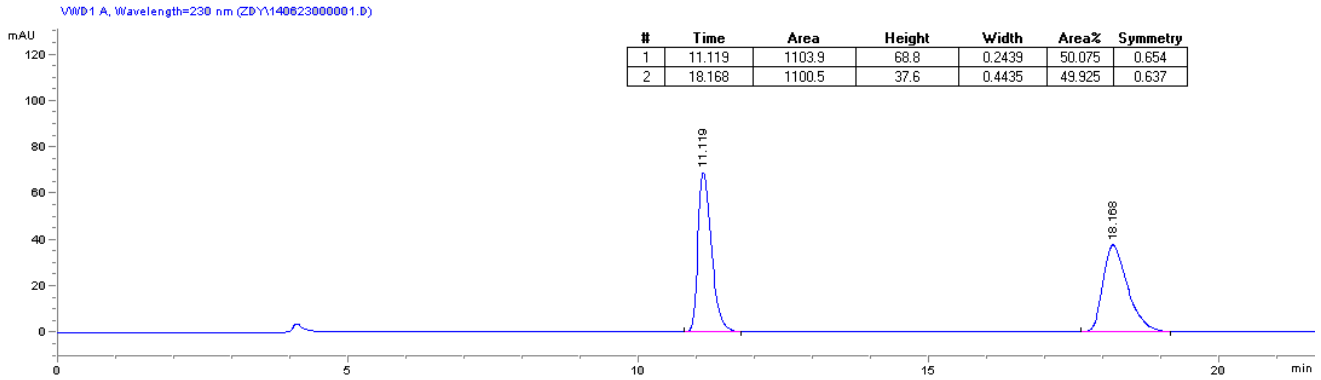


#	Time	Area	Height	Width	Area%	Symmetry
1	11.024	29.6	2.1	0.2141	0.396	0.874
2	18.547	7439.7	274.3	0.4082	99.604	0.519

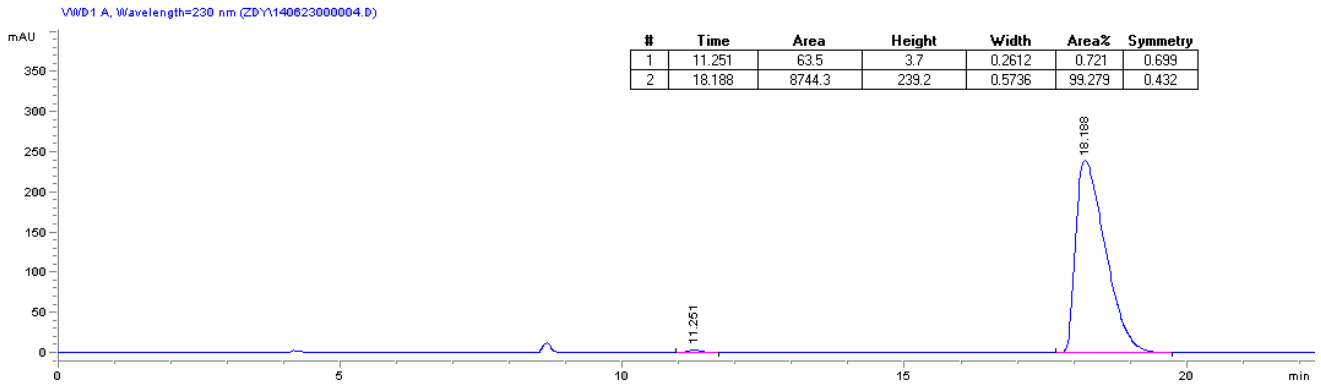
(2*S*,3*R*)-1-(4-Bromophenyl)-2-methyl-3-phenylpent-4-yn-1-one (*syn*-3af). 89% yield, *syn*/*anti* = 94/6.



White solid was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). M.p.: 77–79 °C. 98% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 11.3 min, t_R (major) = 18.2 min. $[\alpha]_D^{29}$ = 64.5 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 4.15 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.80–3.72 (m, 1H), 2.35 (d, *J* = 2.4 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 139.8, 135.5, 132.1, 129.8, 128.8, 128.4, 128.2, 127.4 , 84.0, 73.0, 47.8, 40.8, 16.4. HRMS calc. for $C_{18}H_{15}BrO$ $[M+H]^+$: 327.0385, found: 327.0376.

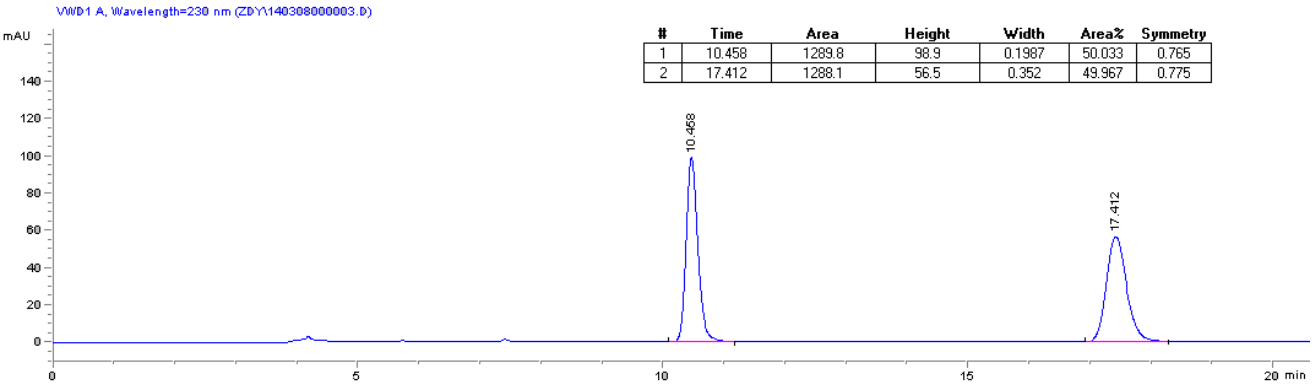


#	Time	Area	Height	Width	Area%	Symmetry
1	11.119	1103.9	68.8	0.2439	50.075	0.654
2	18.168	1100.5	37.6	0.4435	49.925	0.637

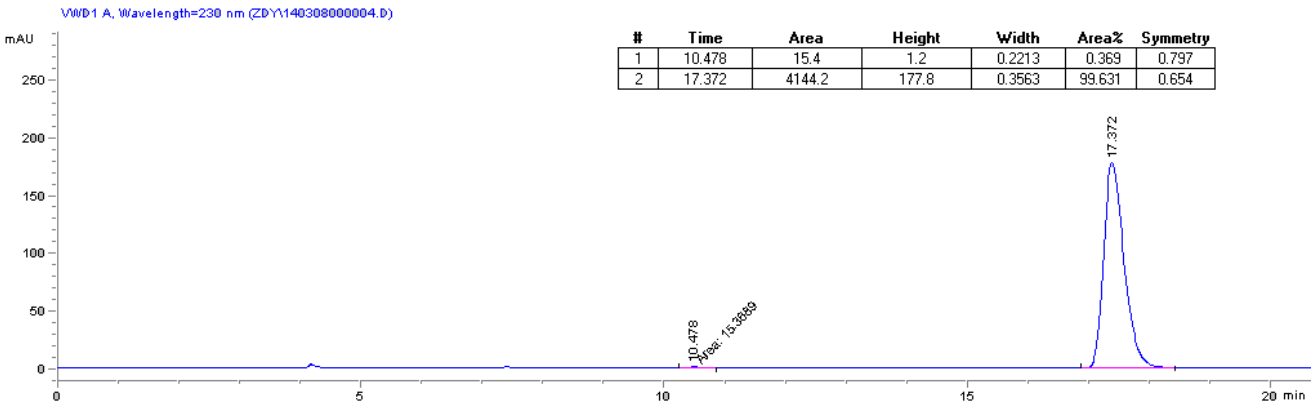


#	Time	Area	Height	Width	Area%	Symmetry
1	11.251	63.5	3.7	0.2612	0.721	0.699
2	18.188	8744.3	239.2	0.5736	99.279	0.432

(2*S*,3*R*)-2-Methyl-3-phenyl-1-(p-tolyl)pent-4-yn-1-one (*syn*-3ag). 93% yield, *syn/anti* = 93/7. White solid was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). M.p.: 61–62 °C. >99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 10.5 min, t_R (major) = 17.4 min. $[\alpha]_D^{30}$ = 95.4 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (m, 2H), 7.38–7.36 (m, 2H), 7.25–7.12 (m, 5H), 4.19 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.84–3.76 (m, 1H), 2.36 (s, 3H), 2.33 (d, *J* = 2.5 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 144.0, 140.2, 134.2, 129.5, 128.7, 128.5, 128.3, 127.3, 84.4, 72.8, 47.5, 40.7, 21.8, 16.4. HRMS calc. for $C_{19}H_{18}O$ $[M+H]^+$: 263.1436, found: 263.1443.



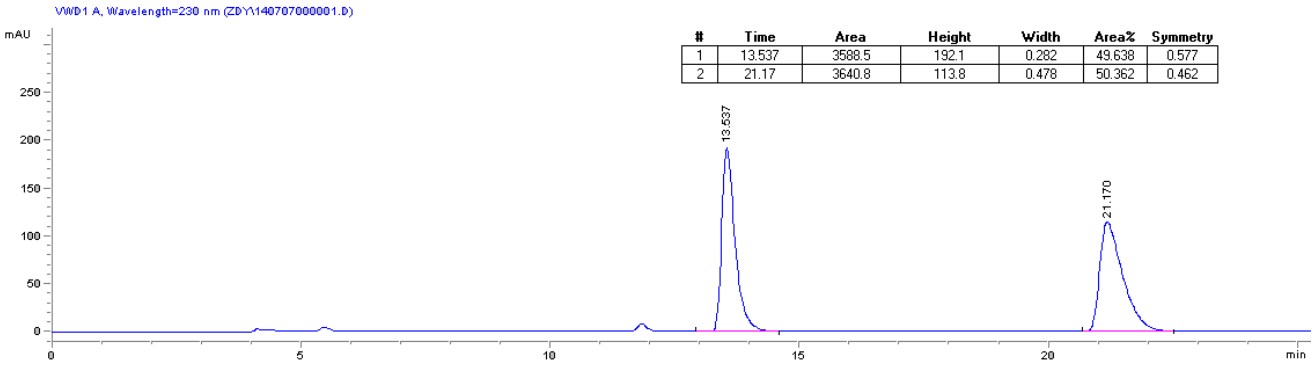
#	Time	Area	Height	Width	Area%	Symmetry
1	10.458	1289.8	98.9	0.1987	50.033	0.765
2	17.412	1288.1	56.5	0.352	49.967	0.775



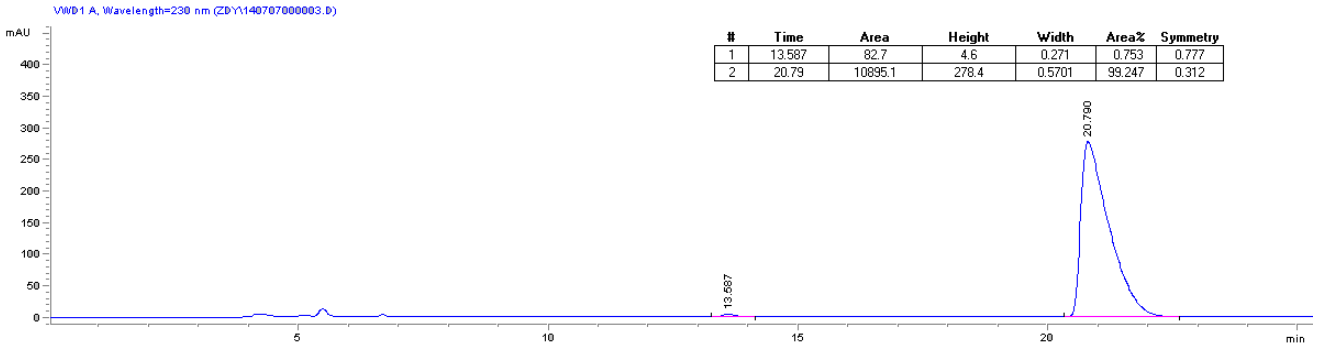
#	Time	Area	Height	Width	Area%	Symmetry
1	10.478	15.4	1.2	0.2213	0.369	0.797
2	17.372	4144.2	177.8	0.3563	99.631	0.654

(2*S*,3*R*)-1-(4-Methoxyphenyl)-2-methyl-3-phenylpent-4-yn-1-one (*syn*-3ah). 91% yield, *syn/anti* = 93/7. White solid was obtained after purification with column chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 30:1). M.p.: 56–58 °C. 98% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 13.6 min, t_R (major) = 20.8 min. $[\alpha]_D^{30}$ = 78.6 (*c* 0.98, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.76 (m, 2H), 7.37

(d, J = 7.3 Hz, 2H), 7.24–7.21 (t, J = 7.5 Hz, 2H), 7.15–7.12 (m, 1H), 6.85–6.83 (m, 2H), 4.19 (dd, J = 8.7, 2.3 Hz, 1H), 3.85–3.76 (m, 4H), 2.35 (d, J = 2.5 Hz, 1H), 1.42 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 163.6, 140.2, 130.6, 129.6, 128.6, 128.2, 127.2, 113.9, 84.5, 72.7, 55.6, 47.2, 40.7, 16.6. HRMS calc. for $C_{19}H_{18}O_2$ $[M+H]^+$: 279.1385, found: 279.1385.

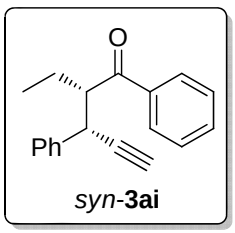


#	Time	Area	Height	Width	Area%	Symmetry
1	13.537	3588.5	192.1	0.282	49.638	0.577
2	21.17	3640.8	113.8	0.478	50.362	0.462

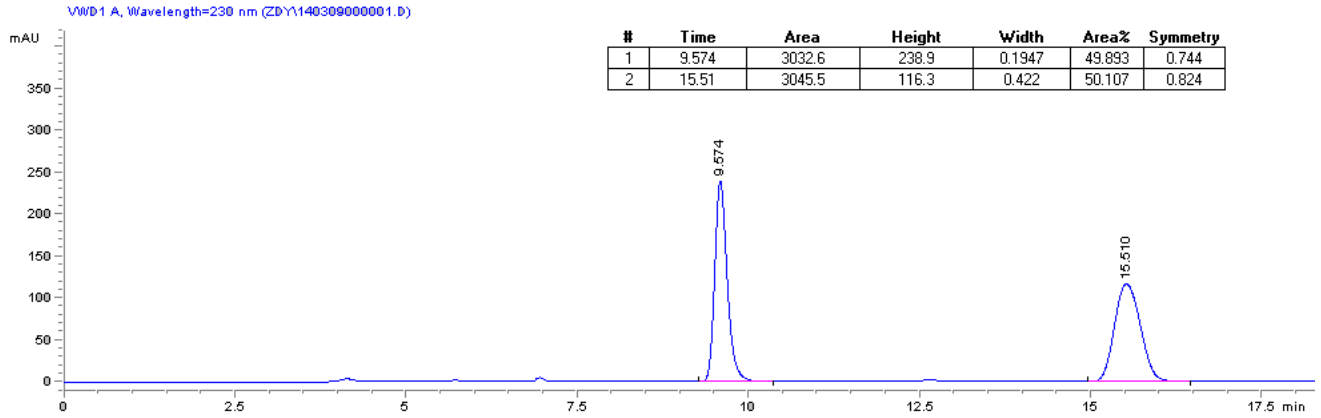


#	Time	Area	Height	Width	Area%	Symmetry
1	13.587	82.7	4.6	0.271	0.753	0.777
2	20.79	10895.1	278.4	0.5701	99.247	0.312

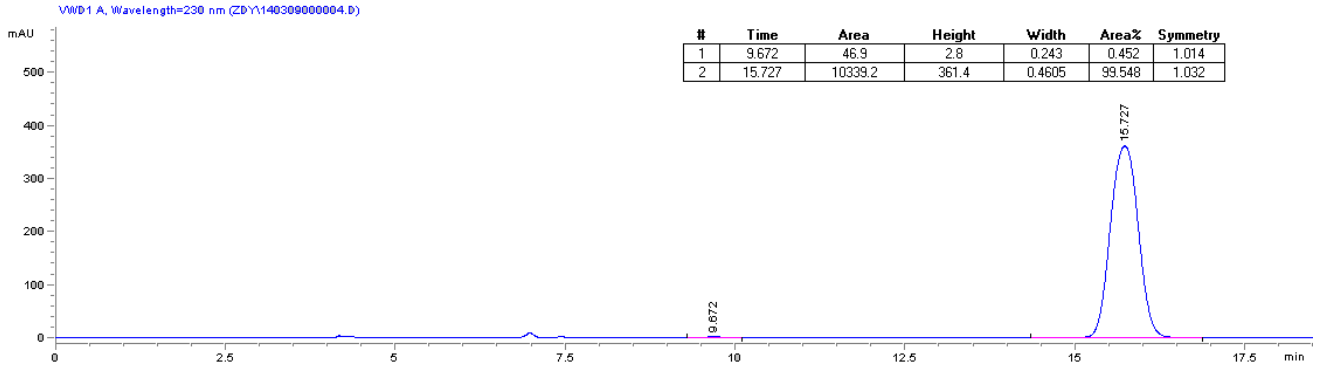
(2*S*,3*R*)-2-Ethyl-1,3-diphenylpent-4-yn-1-one (*syn*-3ai). 92% yield, *syn*/*anti* >95/5. White solid was obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 130:1). M.p.: 90–92 °C. >99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 9.7 min, t_R (major) = 15.7 min. $[\alpha]_D^{29}$ = 75.3 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.68 (m, 2H), 7.47–7.43 (m, 1H), 7.35–7.31 (m, 4H), 7.21–7.17 (m, 2H), 7.11–7.08 (m, 1H), 4.14 (dd, J = 9.7, 2.5 Hz, 1H), 3.83–3.78 (m, 1H), 2.34 (d, J = 2.5 Hz, 1H), 2.15–1.99 (m, 2H), 0.87 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.5, 139.9, 138.2, 133.0, 128.6, 128.6, 128.4, 128.1, 127.3, 84.7, 72.6, 54.1, 40.0, 24.8, 11.4. HRMS calc. for $C_{19}H_{18}O$ $[M+H]^+$: 263.1436, found: 263.1432.



syn-**3ai**

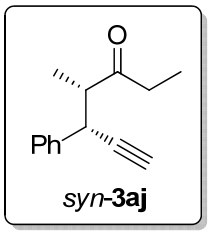


#	Time	Area	Height	Width	Area%	Symmetry
1	9.574	3032.6	238.9	0.1947	49.893	0.744
2	15.51	3045.5	116.3	0.422	50.107	0.824

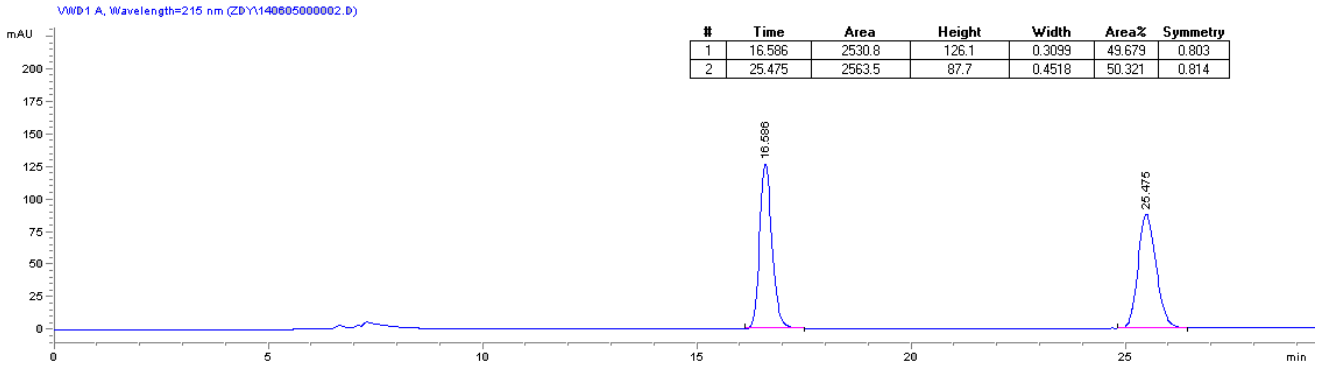


#	Time	Area	Height	Width	Area%	Symmetry
1	9.672	46.9	2.8	0.243	0.452	1.014
2	15.727	10339.2	361.4	0.4605	99.548	1.032

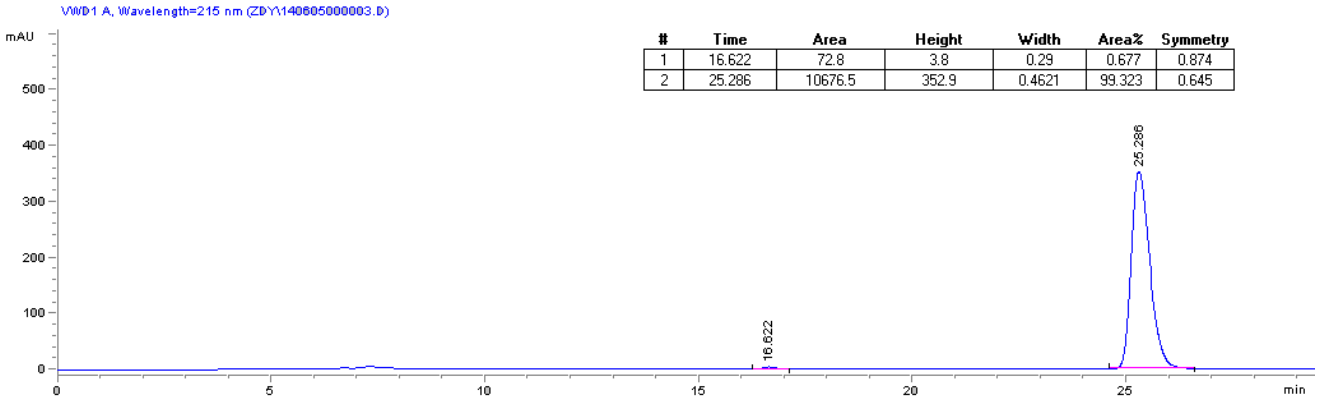
(2*S*,3*R*)-4-Methyl-5-phenylhept-6-yn-3-one (*syn*-3aj).[6] 60% yield, *syn*/*anti* = 81/19. Colorless oil was



obtained after purification with column chromatography on silica gel (petroleum ether/Et_2O, 150:1 to 110:1). 99% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 215 nm, 40 °C): t_R (minor) = 16.6 min, t_R (major) = 25.3 min. $[\alpha]_D^{28}$ = 94.2 (*c* 0.88, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.26 (m, 4H), 7.24–7.20 (m, 1H), 4.00 (dd, *J* = 8.4, 2.5 Hz, 1H), 2.90–2.83 (m, 1H), 2.40–2.32 (m, 1H), 2.30 (d, *J* = 2.5 Hz, 1H), 2.06–1.95 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.9, 139.8, 128.7, 128.2, 127.4, 83.9, 72.7, 52.7, 40.5, 36.1, 14.9, 7.5. HRMS calc. for $C_{14}H_{16}O$ $[M+H]^+$: 201.1279, found: 201.1273.

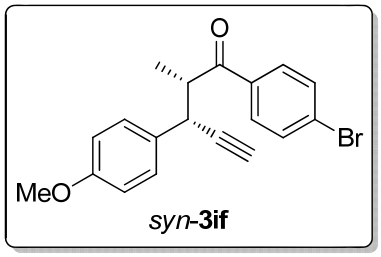


#	Time	Area	Height	Width	Area%	Symmetry
1	16.586	2530.8	126.1	0.3099	49.679	0.803
2	25.475	2563.5	87.7	0.4518	50.321	0.814

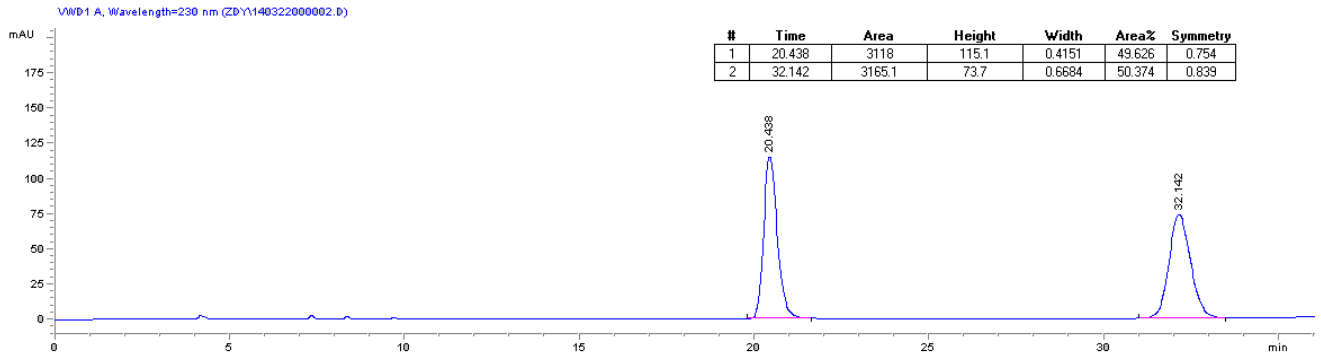


#	Time	Area	Height	Width	Area%	Symmetry
1	16.622	72.8	3.8	0.29	0.677	0.874
2	25.286	10676.5	352.9	0.4621	99.323	0.645

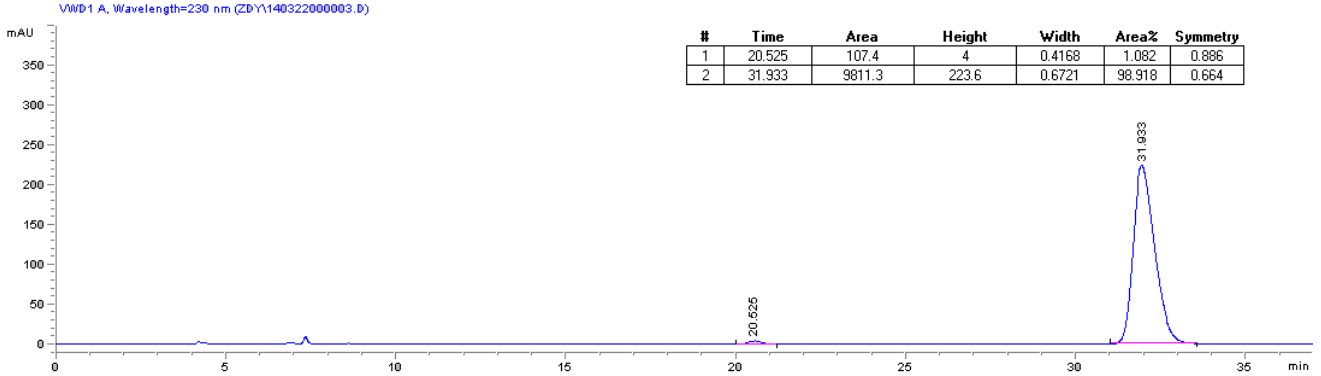
(2*S*,3*R*)-3-(4-Methoxyphenyl)-1-(4-bromophenyl)pent-4-yn-1-one (*syn*-3if). 92% yield, s*yn*/*anti* = 93/7.



White solid was obtained after purification with column chromatography on silica gel (petroleum ether/EtOAc, 120:1 to 80:1). M.p.: 76–78 °C. 98% ee was determined by chiral HPLC (Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, 230 nm, 40 °C): t_R (minor) = 20.5 min, t_R (major) = 31.9 min. $[\alpha]_D^{30}$ = 52.7 (*c* 1.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.60 (m, 2H), 7.52–7.50 (m, 2H), 7.26–7.24 (m, 2H), 6.76–6.74 (m, 2H), 4.09 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.76–3.69 (m, 4H), 2.33 (d, *J* = 2.4 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 158.9, 135.5, 132.1, 131.9, 129.8, 129.2, 128.4, 114.1, 84.4, 72.8, 55.4, 47.9, 40.0, 16.5. HRMS calc. for $C_{19}H_{17}BrO_2$ $[M+Na]^+$: 379.0310, found: 379.0307.

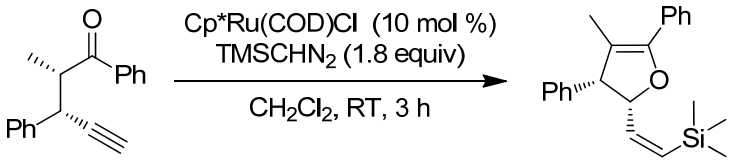


#	Time	Area	Height	Width	Area%	Symmetry
1	20.438	3118	115.1	0.4151	49.626	0.754
2	32.142	3165.1	73.7	0.6684	50.374	0.839



#	Time	Area	Height	Width	Area%	Symmetry
1	20.525	107.4	4	0.4168	1.082	0.886
2	31.933	9811.3	223.6	0.6721	98.918	0.664

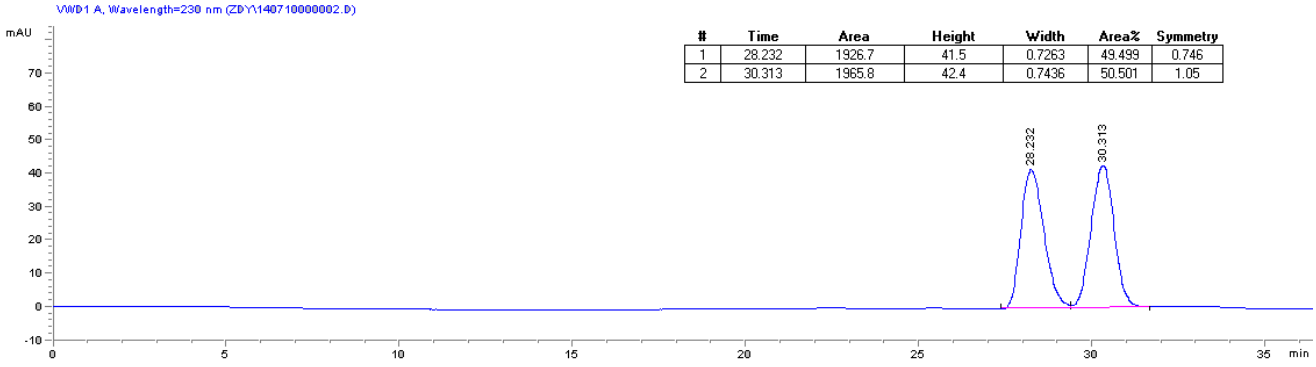
Synthesis of Compound 5



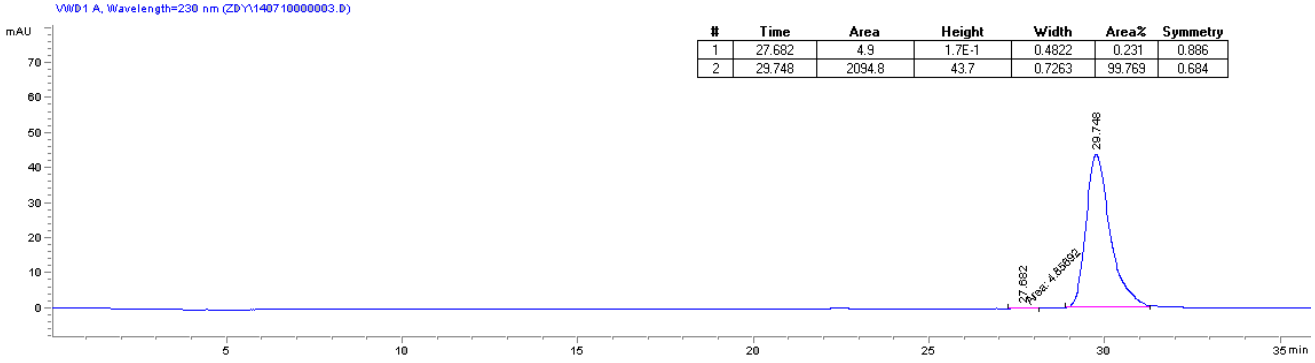
>99% ee
(2*S*,3*R*)-**3aa**

>95/5 dr, >99% ee
5

Under an N_2 atmosphere, to an oven-dried Schlenk flask charged with (2*S*,3*R*)-**3aa** (37.2 mg, 0.150 mmol, >99% ee) and anhydrous CH_2Cl_2 (2.0 mL), was added $TMSCHN_2$ (2M in hexanes) (0.135 mL, 0.270 mmol, 1.8 equiv) and Cp*Ru(COD)Cl (5.7 mg, 0.015 mmol, 0.1 equiv) at room temperature. The mixture was stirred at room temperature for 3 h and then concentrated under reduced pressure. The crude obtained was directly purified with column chromatography on silica gel (petroleum ether/EtOAc, 400:1 to 300:1), affording trimethyl{(*Z*)-2-[(2*S*,3*R*)-4-methyl-3,5-diphenyl-2,3-dihydrofuran-2-yl]vinyl}silane (**5**) as a colorless oil (38 mg, 76% yield). >99% ee was determined by chiral HPLC (Chiralcel 2*OJ-H, *n*-hexane/*i*-PrOH = 99/1, 0.5 mL/min, 230 nm, 40 °C): t_R (minor) = 27.7 min, t_R (major) = 29.7 min. $[\alpha]_D^{29}$ = –160.1 (*c* 0.83, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d^6): δ 7.60–7.57 (m, 2H), 7.46–7.42 (m, 2H), 7.38–7.30 (m, 3H), 7.24–7.20 (m, 1H), 7.09–7.07 (m, 2H), 5.84 (dd, *J* = 14.4, 8.8 Hz, 1H), 5.53 (d, *J* = 14.4 Hz, 1H), 5.28 (t, *J* = 9.1 Hz, 1H), 4.08 (d, *J* = 9.4 Hz, 1H), 1.75 (s, 3H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d^6): δ 148.8, 144.5, 138.3, 133.1, 131.2, 128.9, 128.4, 128.4, 128.2, 127.0, 126.9, 110.1, 82.3, 58.8, 11.8, 0.3. HRMS calc. for $C_{22}H_{26}OSi$ $[M+H]^+$: 335.1831, found: 335.1824.



#	Time	Area	Height	Width	Area%	Symmetry
1	28.232	1926.7	41.5	0.7263	49.499	0.746
2	30.313	1965.8	42.4	0.7436	50.501	1.05



#	Time	Area	Height	Width	Area%	Symmetry
1	27.682	4.9	1.7E-1	0.4822	0.231	0.886
2	29.748	2094.8	43.7	0.7263	99.769	0.684

References

1. P. Fang and X.-L. Hou, *Org. Lett.*, 2009, **11**, 4612.
2. K. Funabiki, K. Matsunaga, H. Gonda, H. Yamamoto, T. Arima, Y. Kubota and M. Matsui, *J. Org. Chem.*, 2011, **76**, 285.
3. W.-J. Zhao, M. Yan, D. Huang and S.-J. Ji, *Tetrahedron*, 2005, **61**, 5585.
4. (*a*) R. Stradi, D. Pocar and C. Cassio, *J. Chem. Soc., Perkin Trans. I*, 1974, 2671; (*b*) N. Kawai and T. Shioiri, *Chem. Pharm. Bull.*, 1983, **31**, 2564.
5. T. Izawa, Y. Terao and K. Suzuki, *Tetrahedron: Asymmetry*, 1997, **8**, 2645.
6. Y. Nishibayashi, I. Wakiji, Y. Ishii, S. Uemura and M. Hidai, *J. Am. Chem. Soc.*, 2001, **123**, 3393.

Crystal Data and Structure Refinement for (2*S*,3*R*)-3if

Crystals of **3if** suitable for X-ray analysis were obtained, and subsequent structure elucidation and refinement resulted in an unambiguous absolute structure determination, with the Flack parameter (absolute structure parameter) 0.024 (11) (Table 1) for the model shown in the following figure. The chemical structure of **3if** is non-centrosymmetric with a Br-atom heavier than silicon, then it is expected that Friedel pairs will be used in the refinement and that the absolute structure will be determined. The Flack parameter value should be 0.0 for the correct absolute structure and +1.0 for the inverted enantiomer.[1] Therefore the absolute stereochemistry of chiral centers C2 and C3 can be established as *S* and *R* respectively.

Ref: 1. H. D. Flack, G. Bernardinelli, *Acta Crystallogr.*, A55 (1999) 908–915.

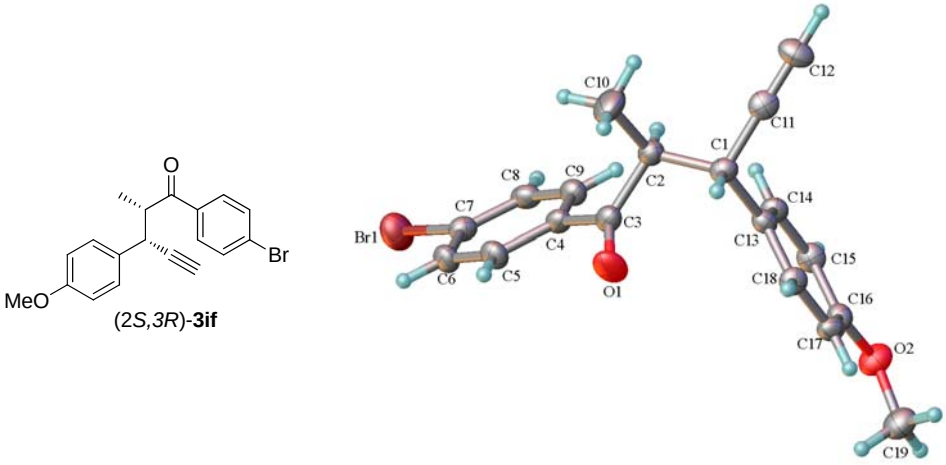


Table 1. Crystal data and structure refinement for **(2*S*,3*R*)-3if**.

Identification code	sa3346	
Empirical formula	C19 H17 Br O2	
Formula weight	357.23	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.5798(14) Å	α= 90°.
	b = 15.675(4) Å	β= 90°.
	c = 19.082(5) Å	γ = 90°.
Volume	1669.1(8) Å^3	
Z	4	
Density (calculated)	1.422 Mg/m^3	

Absorption coefficient	2.467 mm^{-1}
F(000)	728
Crystal size	0.34 x 0.13 x 0.06 mm^3
Theta range for data collection	3.364 to 27.475°.
Index ranges	-6<=h<=7, -20<=k<=20, -24<=l<=24
Reflections collected	10540
Independent reflections	3797 [R(int) = 0.0572]
Completeness to theta = 26.000°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.5550
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3797 / 0 / 201
Goodness-of-fit on F^2	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1008
R indices (all data)	R1 = 0.0542, wR2 = 0.1048
Absolute structure parameter	0.024(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.469 and -0.341 $e.Å^{-3}$

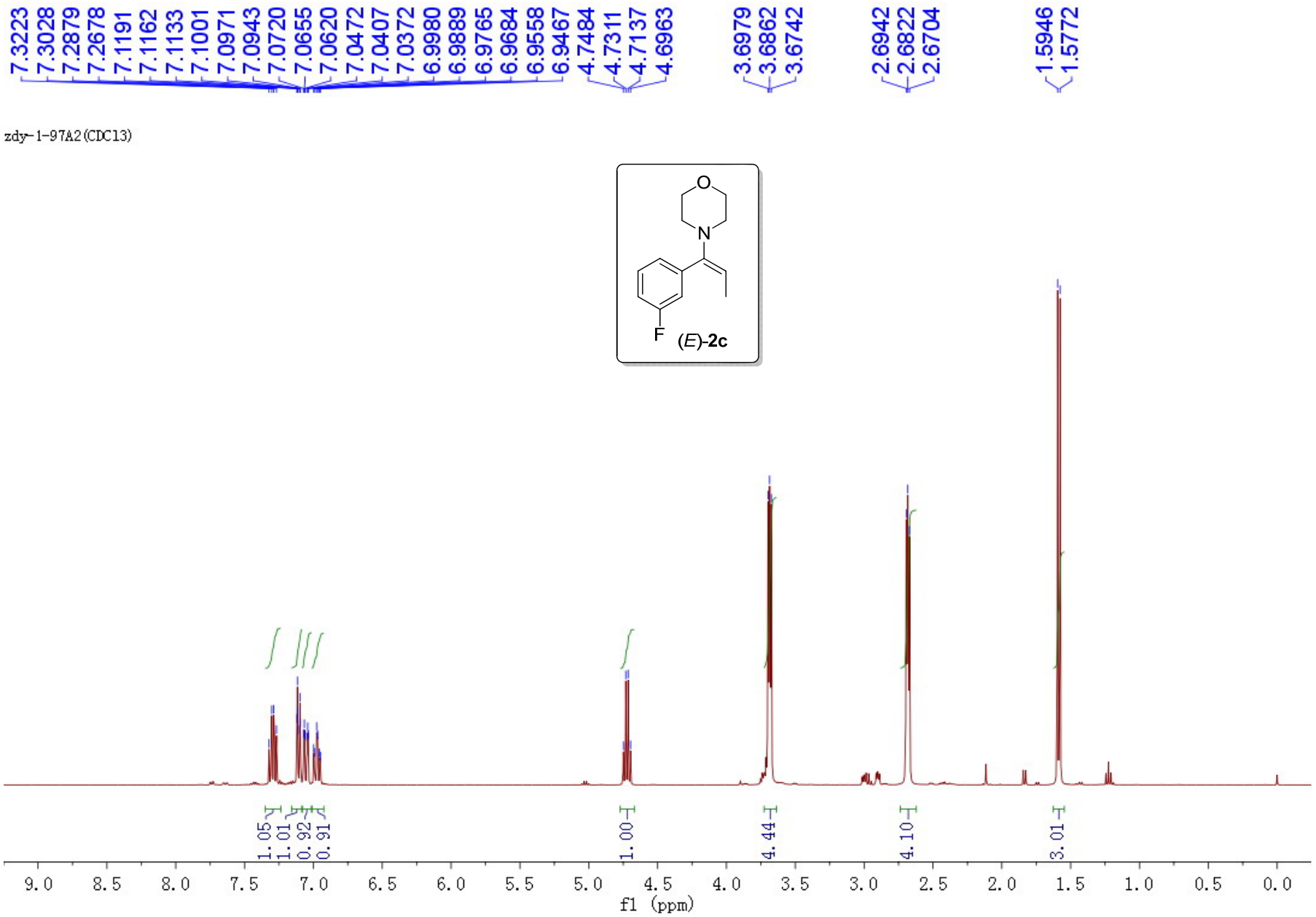
Table 2. Bond lengths [Å] and angles [°] for **(2*S*,3*R*)-3if**.

Br1-C7	1.898(4)
O1-C3	1.210(6)
O2-C16	1.366(6)
O2-C19	1.410(7)
C1-C2	1.550(6)
C1-C11	1.481(7)
C1-C13	1.518(6)
C2-C3	1.518(7)
C2-C10	1.534(6)
C3-C4	1.500(6)
C4-C5	1.396(6)
C4-C9	1.389(7)
C5-C6	1.378(7)
C6-C7	1.388(7)
C7-C8	1.378(6)
C8-C9	1.388(6)
C11-C12	1.183(7)
C13-C14	1.400(6)

C13-C18	1.378(6)
C14-C15	1.380(6)
C15-C16	1.389(6)
C16-C17	1.380(6)
C17-C18	1.398(6)
C16-O2-C19	117.7(4)
C11-C1-C2	109.4(4)
C11-C1-C13	110.9(4)
C13-C1-C2	112.8(3)
C3-C2-C1	110.9(4)
C3-C2-C10	107.1(4)
C10-C2-C1	111.4(4)
O1-C3-C2	121.3(4)
O1-C3-C4	120.4(4)
C4-C3-C2	118.1(4)
C5-C4-C3	118.5(4)
C9-C4-C3	122.8(4)
C9-C4-C5	118.7(4)
C6-C5-C4	120.9(5)
C5-C6-C7	118.9(4)
C6-C7-Br1	119.7(3)
C8-C7-Br1	118.6(4)
C8-C7-C6	121.7(4)
C7-C8-C9	118.7(4)
C8-C9-C4	121.1(4)
C12-C11-C1	178.3(5)
C14-C13-C1	121.0(4)
C18-C13-C1	121.0(4)
C18-C13-C14	118.0(4)
C15-C14-C13	120.9(4)
C14-C15-C16	120.3(4)
O2-C16-C15	115.5(4)
O2-C16-C17	124.8(4)
C17-C16-C15	119.8(4)
C16-C17-C18	119.4(4)
C13-C18-C17	121.7(4)

Table 3. Torsion angles [°] for **(2*S*,3*R*)-*3if***.

Br1-C7-C8-C9	177.6(3)
O1-C3-C4-C5	31.9(7)
O1-C3-C4-C9	-147.6(5)
O2-C16-C17-C18	179.8(4)
C1-C2-C3-O1	38.8(6)
C1-C2-C3-C4	-147.4(4)
C1-C13-C14-C15	-180.0(4)
C1-C13-C18-C17	-180.0(4)
C2-C1-C13-C14	52.3(6)
C2-C1-C13-C18	-128.5(4)
C2-C3-C4-C5	-142.0(4)
C2-C3-C4-C9	38.5(6)
C3-C4-C5-C6	-179.9(5)
C3-C4-C9-C8	178.8(4)
C4-C5-C6-C7	0.2(7)
C5-C4-C9-C8	-0.7(7)
C5-C6-C7-Br1	-178.5(4)
C5-C6-C7-C8	1.0(7)
C6-C7-C8-C9	-2.0(7)
C7-C8-C9-C4	1.8(7)
C9-C4-C5-C6	-0.4(7)
C10-C2-C3-O1	-82.8(6)
C10-C2-C3-C4	91.0(5)
C11-C1-C2-C3	-179.8(4)
C11-C1-C2-C10	-60.7(5)
C11-C1-C13-C14	-70.8(5)
C11-C1-C13-C18	108.5(5)
C13-C1-C2-C3	56.3(5)
C13-C1-C2-C10	175.5(4)
C13-C14-C15-C16	-0.6(7)
C14-C13-C18-C17	-0.7(6)
C14-C15-C16-O2	-179.8(4)
C14-C15-C16-C17	0.3(7)
C15-C16-C17-C18	-0.2(6)
C16-C17-C18-C13	0.5(7)
C18-C13-C14-C15	0.8(6)
C19-O2-C16-C15	-174.2(4)
C19-O2-C16-C17	5.8(7)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7.0720
7.0655
7.0620
7.0472
7.0407
7.0372
6.9980
6.9889
6.9765
6.9684
6.9558
6.9467
4.7484
4.7311
4.7137
4.6963
3.6979
3.6862
3.6742
2.6942
2.6822
2.6704
1.5946
1.5772
zdy-1-97A2(CDC13)
O
N
F
(E)-2c
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1.01
0.92
0.91
1.00
4.44
4.10
3.01
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
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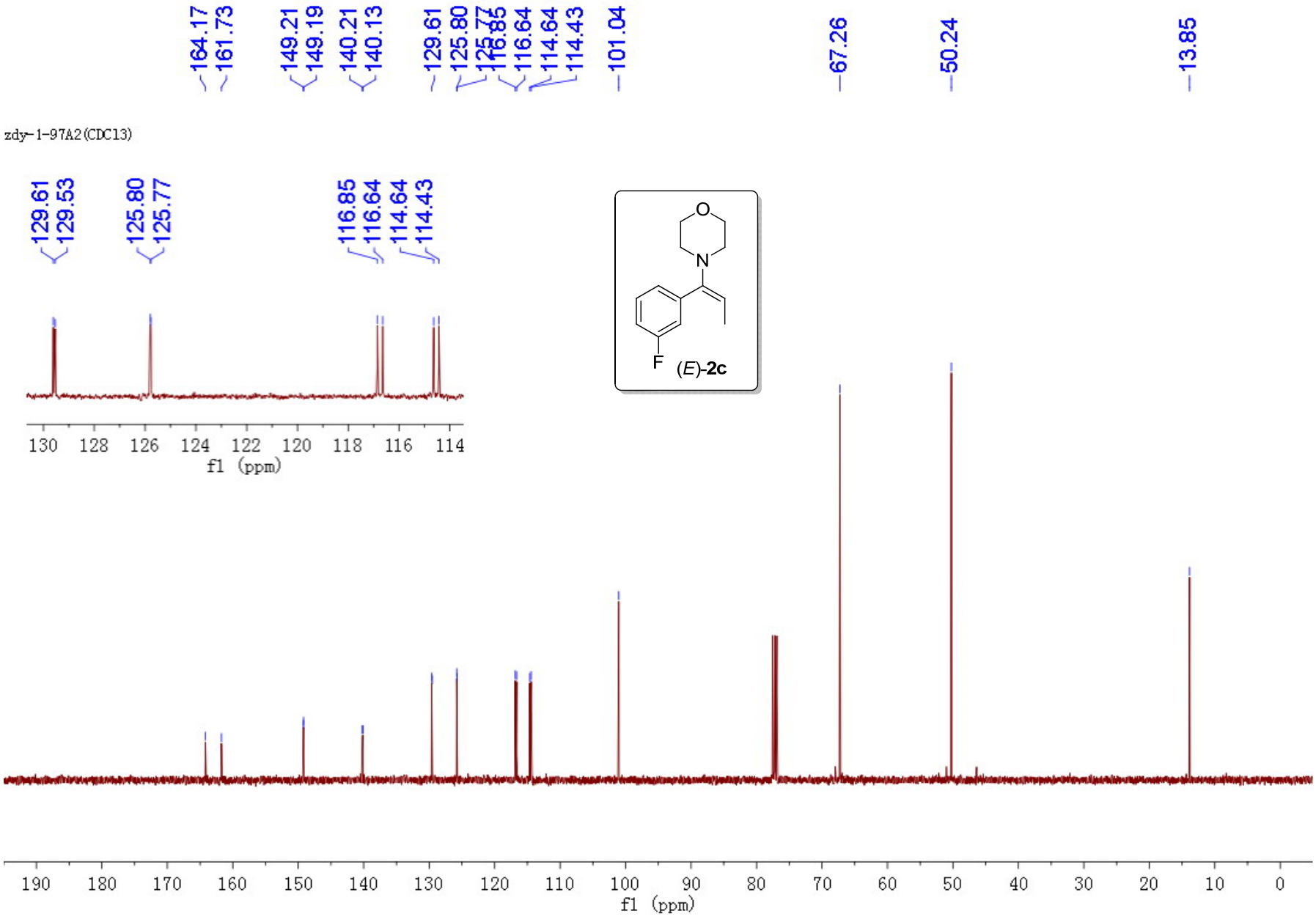
1.5
1.0
0.5
0.0
f1 (ppm)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140.13
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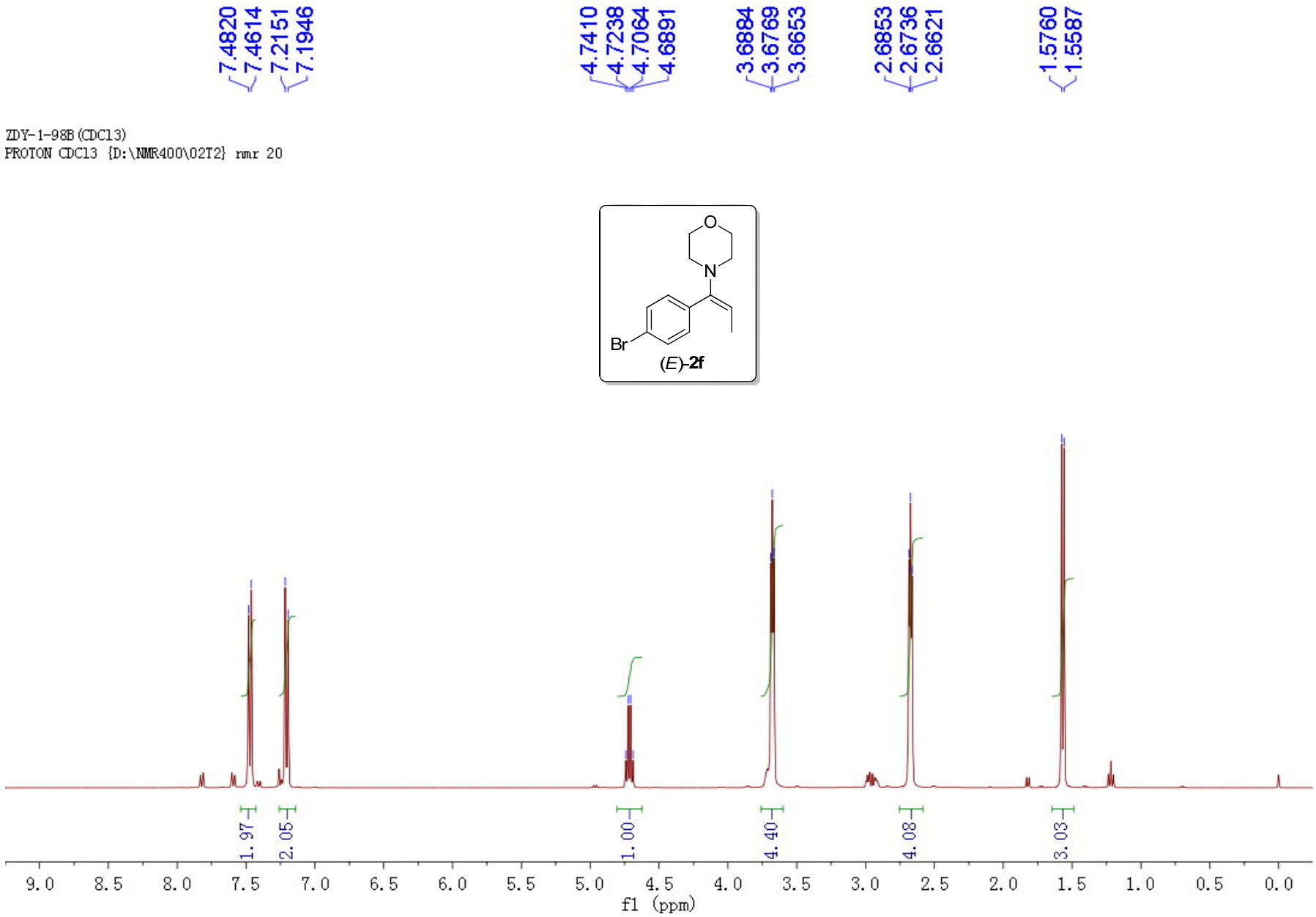
116.64
114.64
114.43
101.04
67.26
50.24
13.85
zdy-1-97A2(CDC13)
129.61
129.53
125.80
125.77
116.85
116.64
114.64
114.43
130 128 126 124 122 120 118 116 114
f1 (ppm)
O
N
F
(E)-2c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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2.6736
2.6621
1.5760
1.5587
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N
Br
(E)-2f
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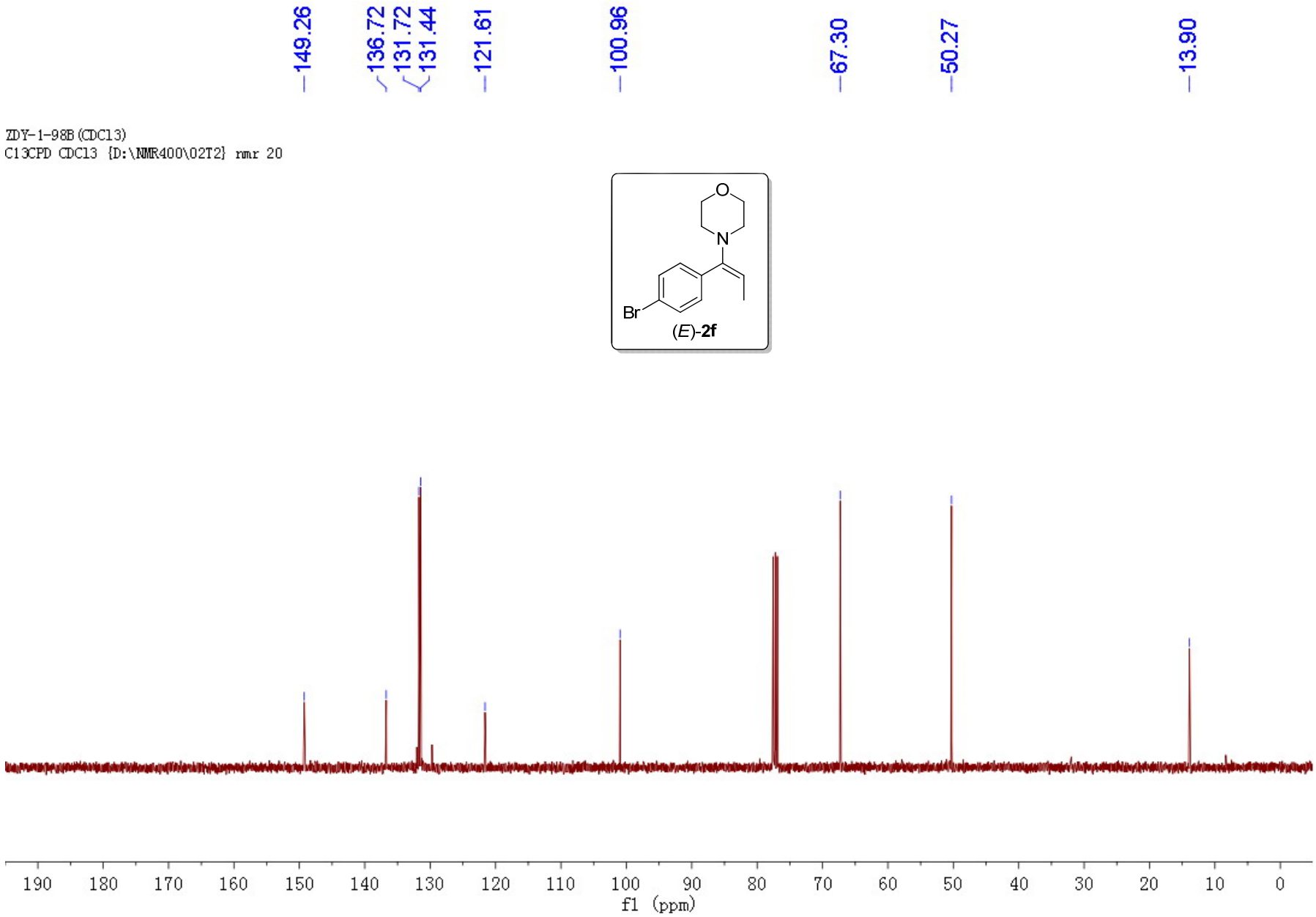
1.00
4.40
4.08
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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50.27
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N
Br
(E)-2f
190
180
170
160
150
140
130
120
110
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90
80
70
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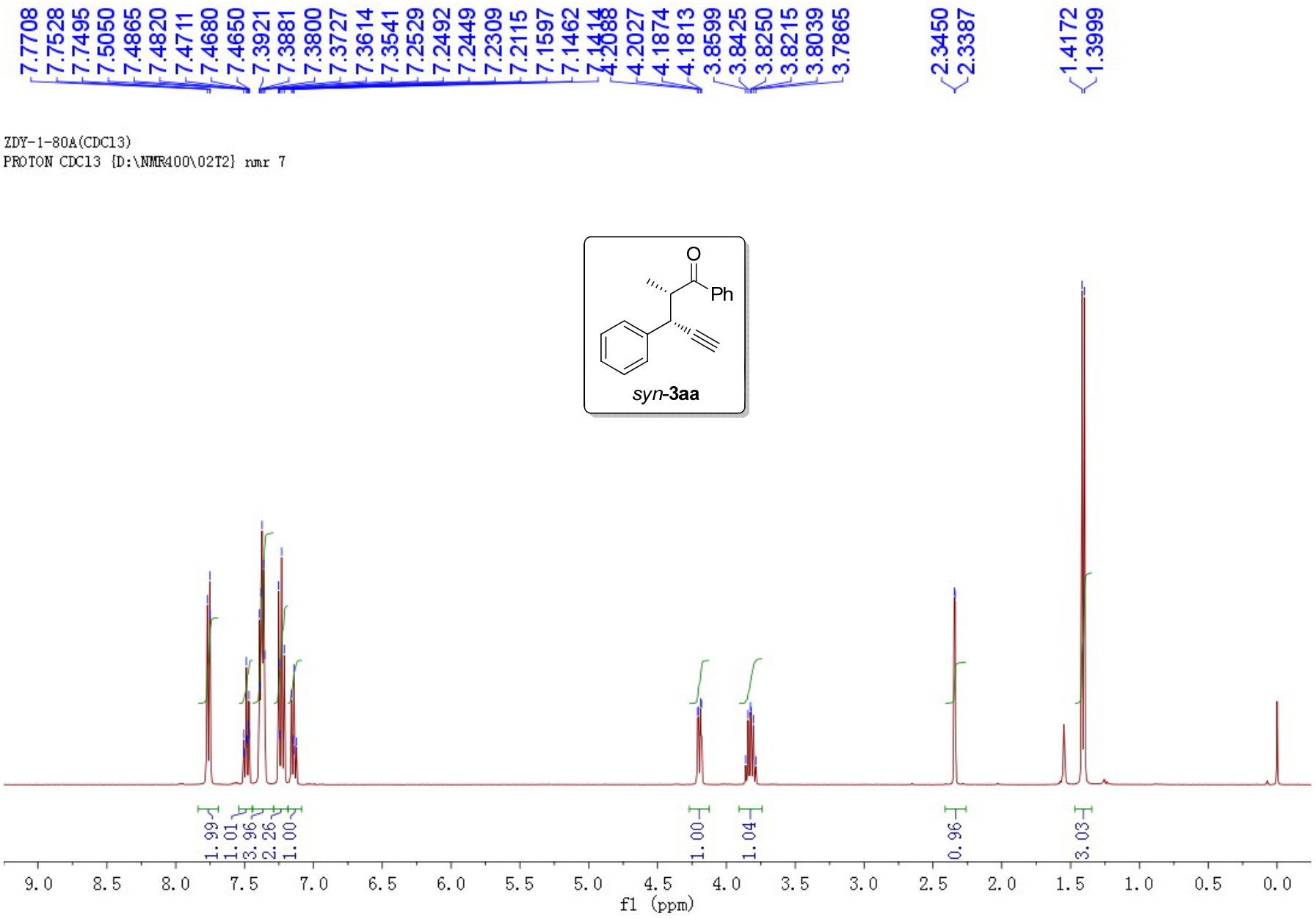
50
40
30
20
10
0
f1 (ppm)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7.3800
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7.3541
7.2529
7.2492
7.2449
7.2309
7.2115
7.1597
7.1462
7.1414
4.2088
4.2027
4.1874
4.1813
3.8599
3.8425
3.8250
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3.96
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1.00
1.04
0.96
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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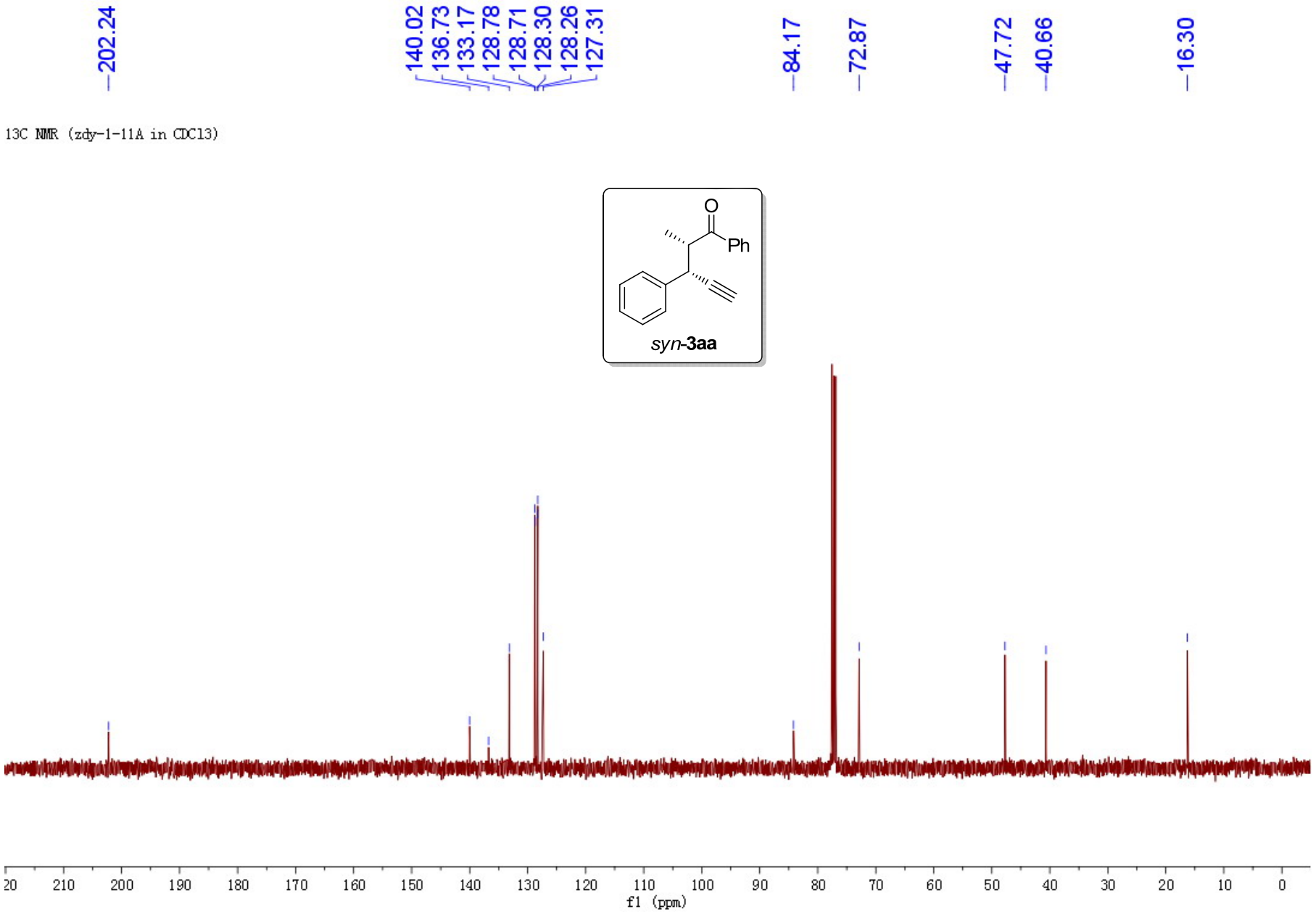
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.73
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128.26
127.31
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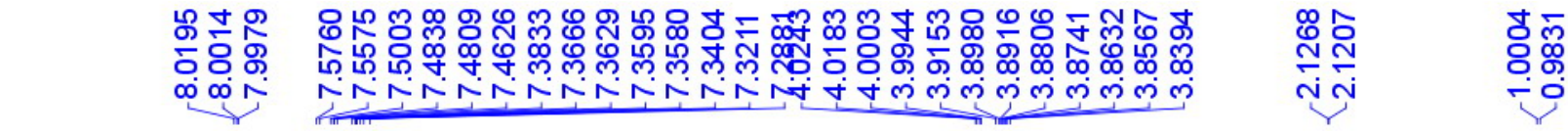
47.72
40.66
16.30
13C NMR (zdy-1-11A in CDCl3)
O
Ph
syn-3aa
f1 (ppm)



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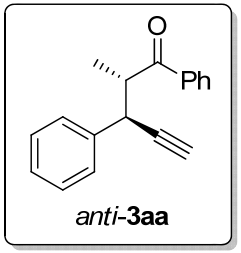
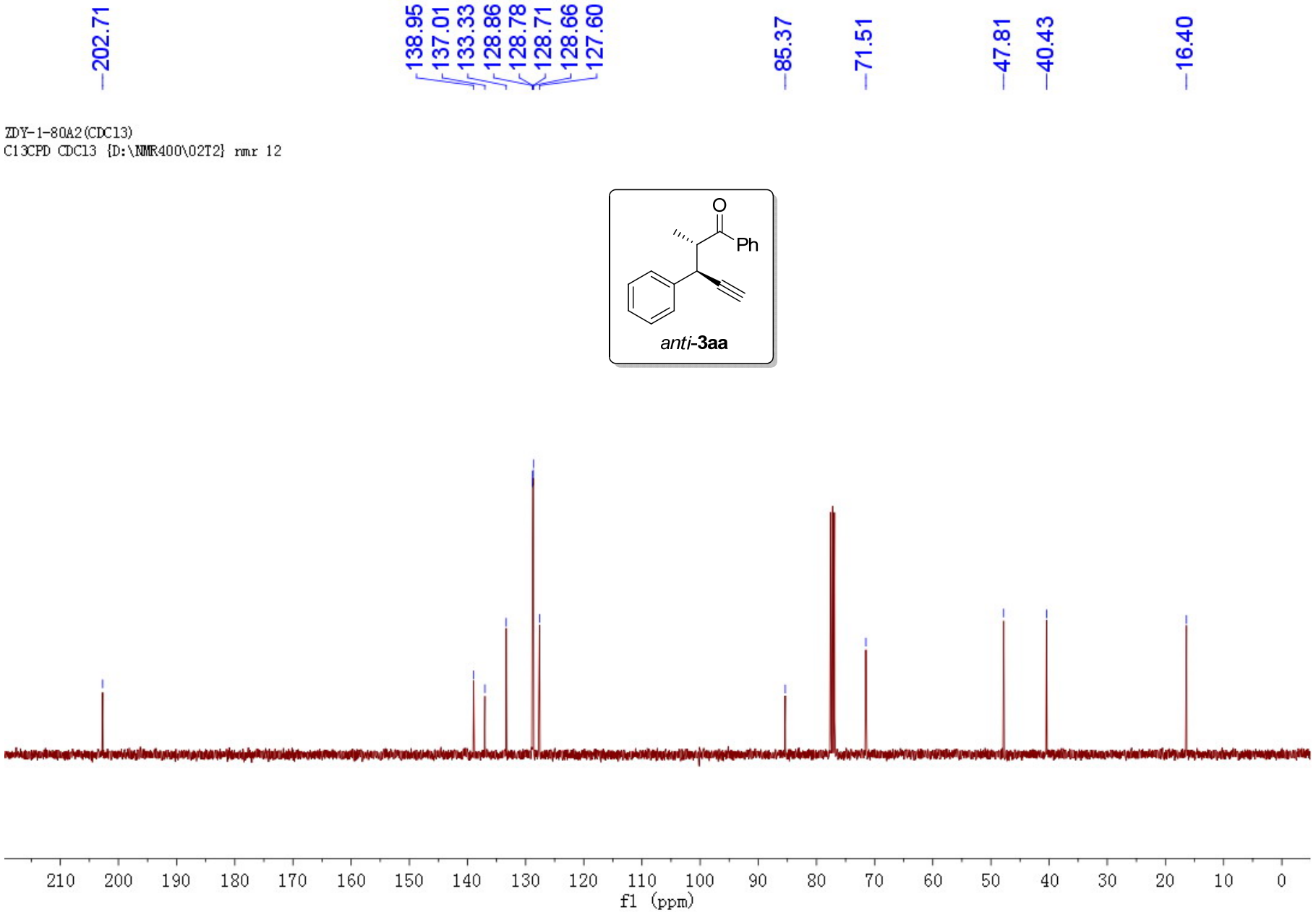


anti-**3aa**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40.43
16.40
ZDY-1-80A2(CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 12
O
Ph
anti-3aa
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200
190
180
170
160
150
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130
120
110
100
90
80
70
60
50
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20
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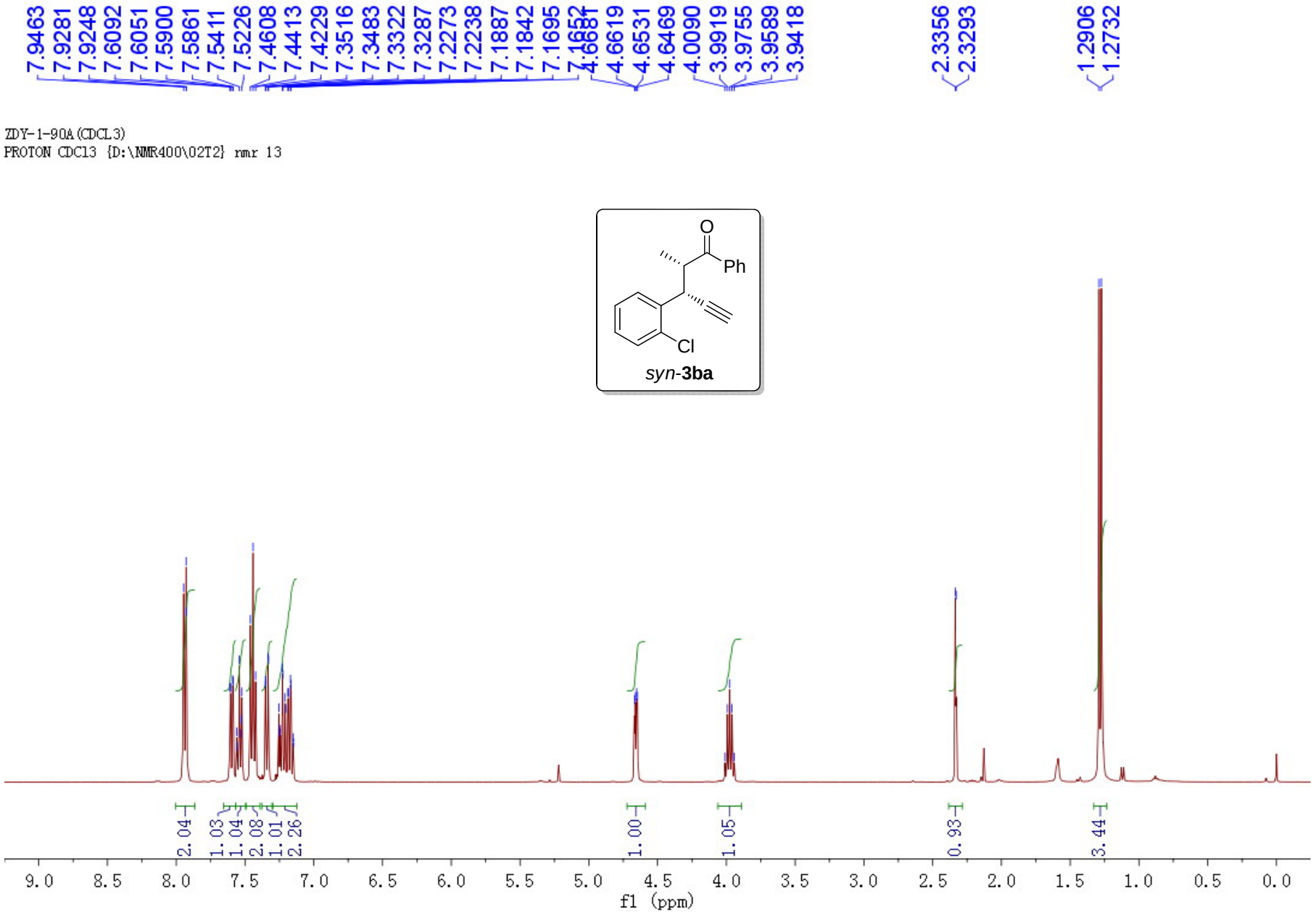
f1 (ppm)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7.5226
7.4608
7.4413
7.4229
7.3516
7.3483
7.3322
7.3287
7.2273
7.2238
7.1887
7.1842
7.1695
4.6619
4.6531
4.6469
4.0090
3.9919
3.9755
3.9589
3.9418
2.3356
2.3293
1.2906
1.2732
ZDY-1-90A(CDCL3)
PROTON CDCl3 {D:\NMR400\02T2} rmr 13
O
Ph
Cl
syn-3ba
2.04
1.03
1.04
2.08
1.01
2.26
1.00
1.05
0.93
3.44
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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2.5
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1.0
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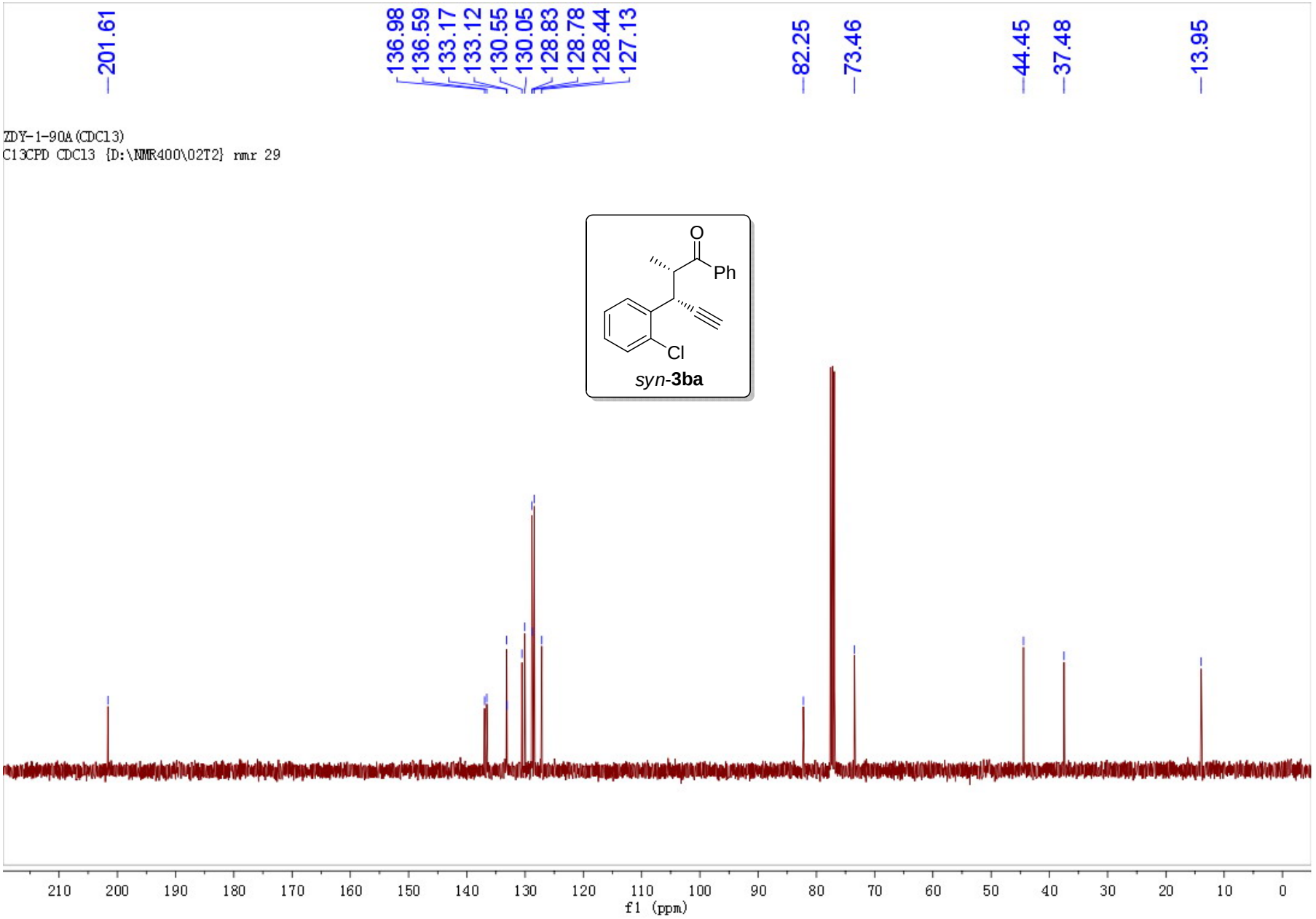
0.0
f1 (ppm)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133.12
130.55
130.05
128.83
128.78
128.44
127.13
82.25
73.46
44.45
37.48
13.95
ZDY-1-90A(CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 29
O
Ph
Cl
syn-3ba
210
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
40
30
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10
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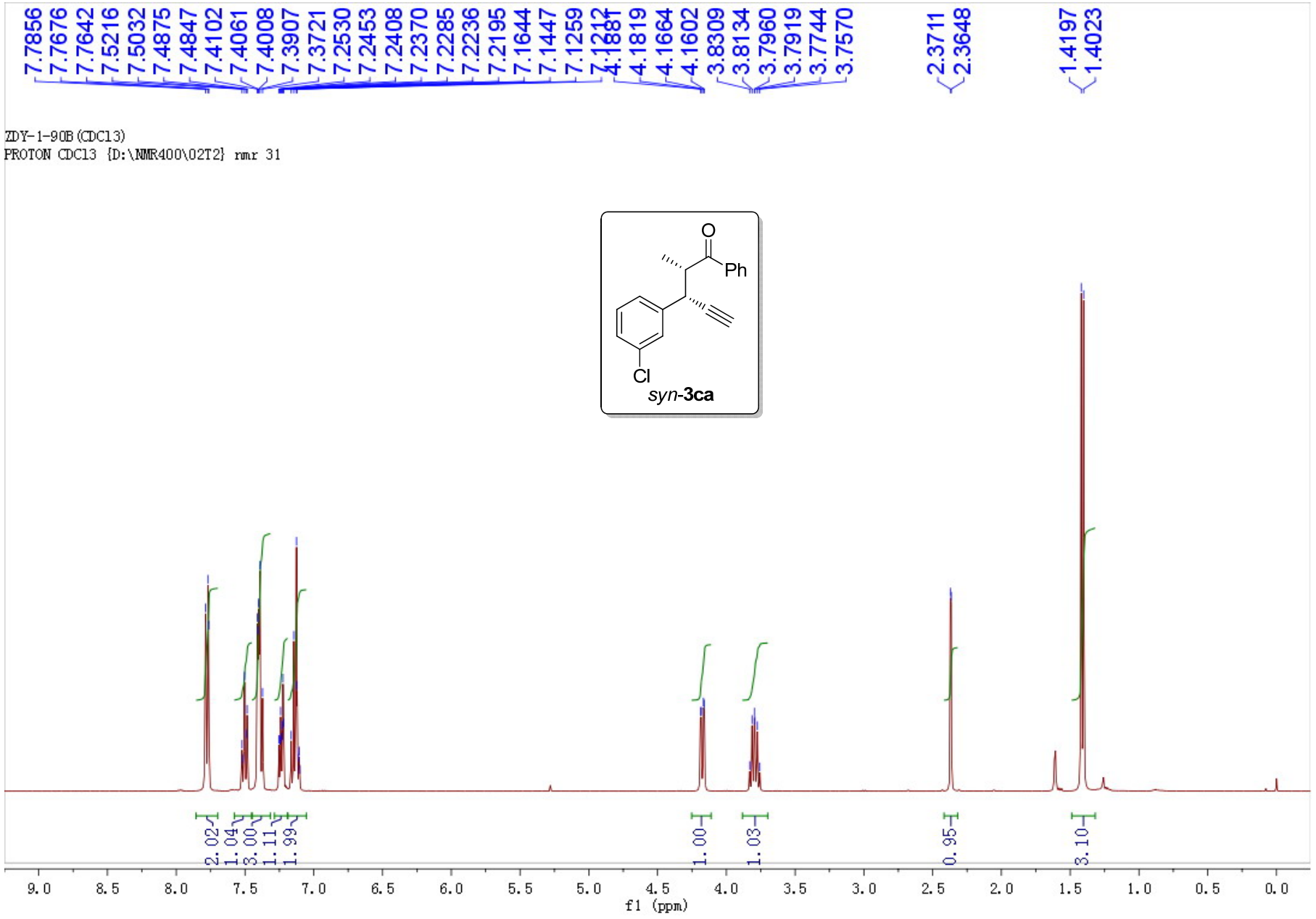
f1 (ppm)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7.5032
7.4875
7.4847
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7.4061
7.4008
7.3907
7.3721
7.2530
7.2453
7.2408
7.2370
7.2285
7.2236
7.2195
7.1644
7.1447
7.1259
7.1212
4.1881
4.1819
4.1664
4.1602
3.8309
3.8134
3.7960
3.7919
3.7744
3.7570
2.3711
2.3648
1.4197
1.4023
ZDY-1-90B(CDCl3)
PROTON CDCl3 {D:\NMR400\02T2} rmr 31
O
Ph
Cl
syn-3ca
2.02
1.04
3.00
1.11
1.99
1.00
1.03
0.95
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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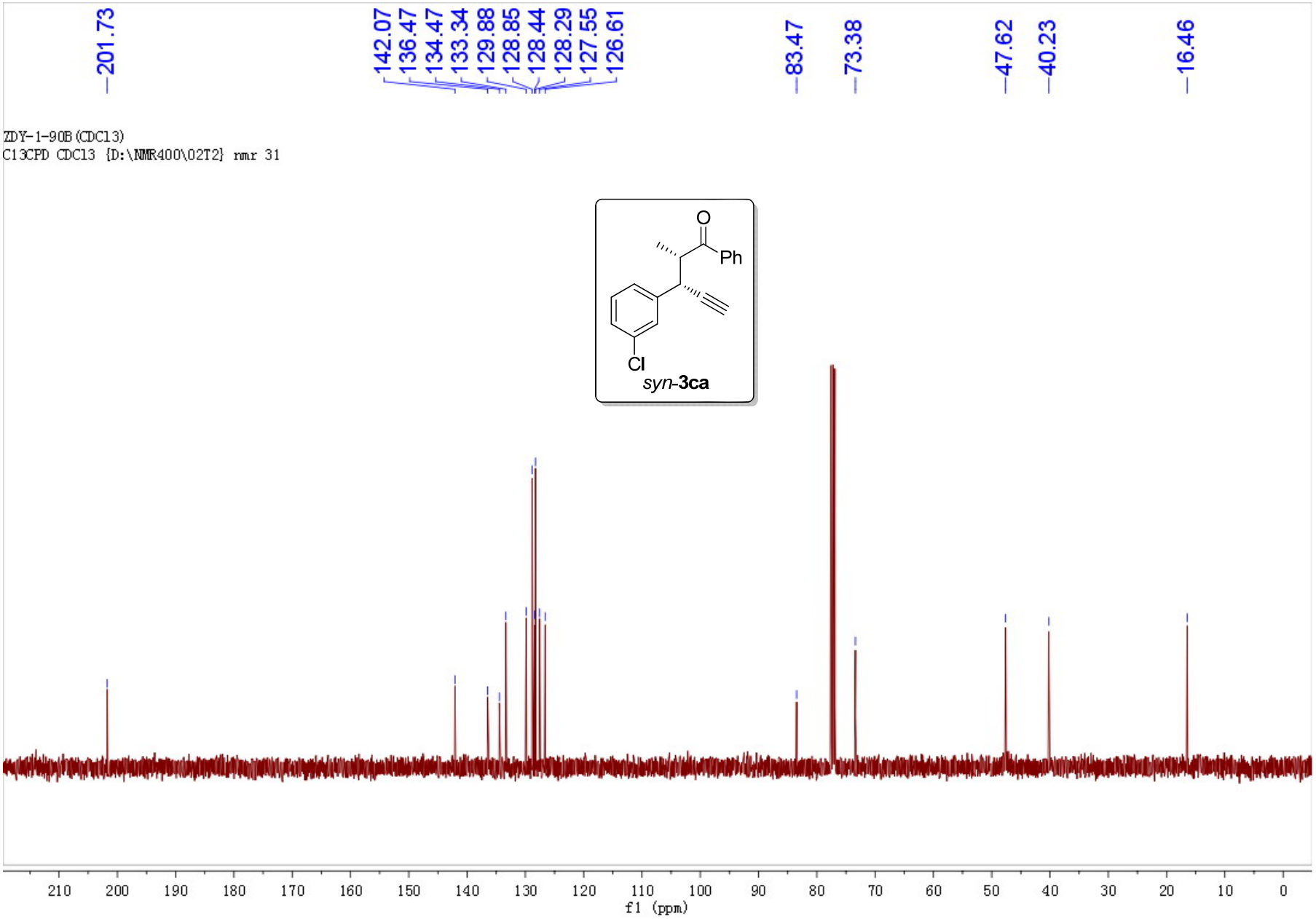
0.0
f1 (ppm)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136.47
134.47
133.34
129.88
128.85
128.44
128.29
127.55
126.61
83.47
73.38
47.62
40.23
16.46
ZDY-1-90B(CDC13)
C13CPD CDC13 {D:\NMR400\02T2} rmr 31
O
Ph
Cl
syn-3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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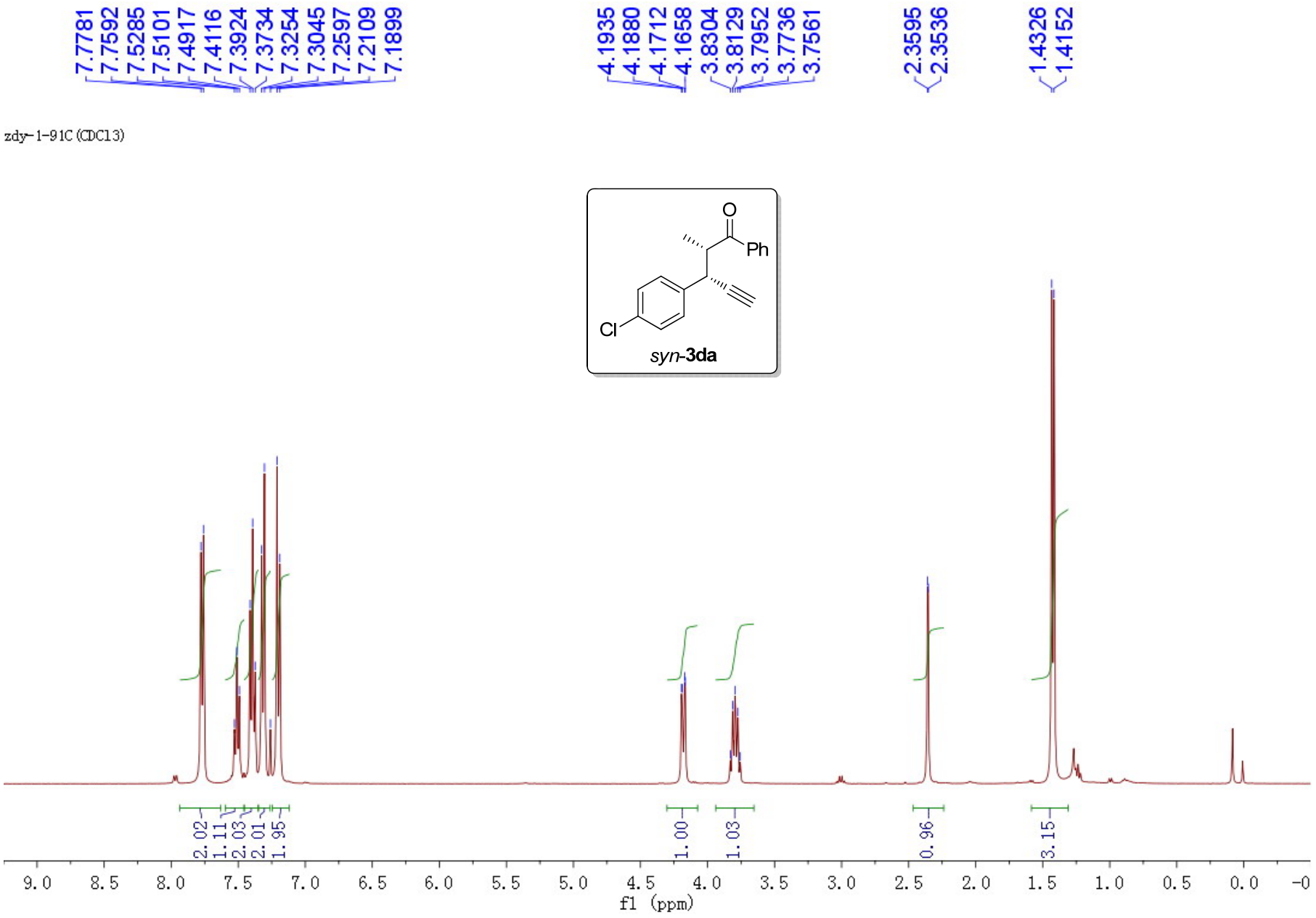
f1 (ppm)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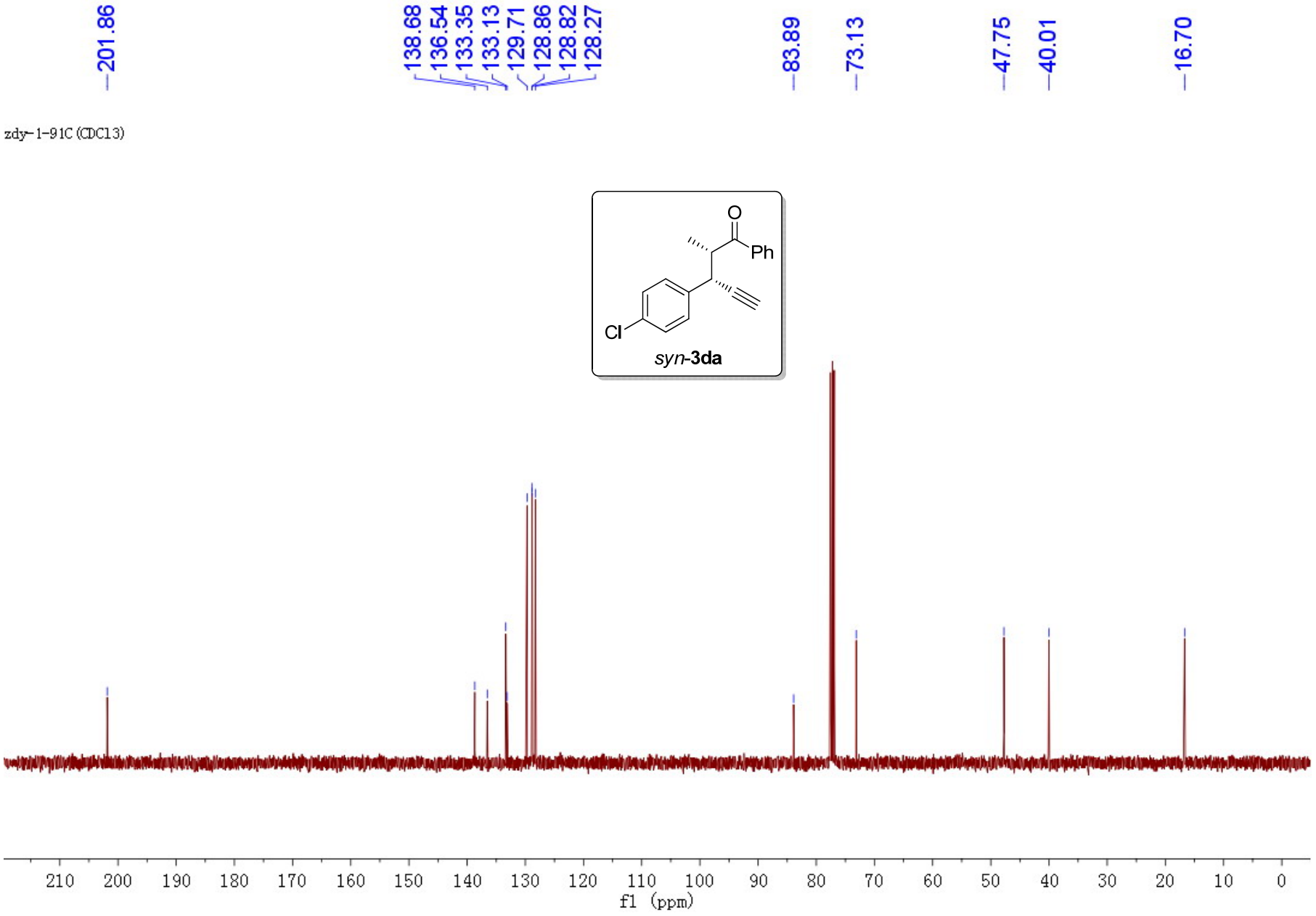
7.5285
7.5101
7.4917
7.4116
7.3924
7.3734
7.3254
7.3045
7.2597
7.2109
7.1899
4.1935
4.1880
4.1712
4.1658
3.8304
3.8129
3.7952
3.7736
3.7561
2.3595
2.3536
1.4326
1.4152
zdy-1-91C (CDCl3)
O
Ph
Cl
syn-3da
2.02
1.11
2.03
2.01
1.95
1.00
1.03
0.96
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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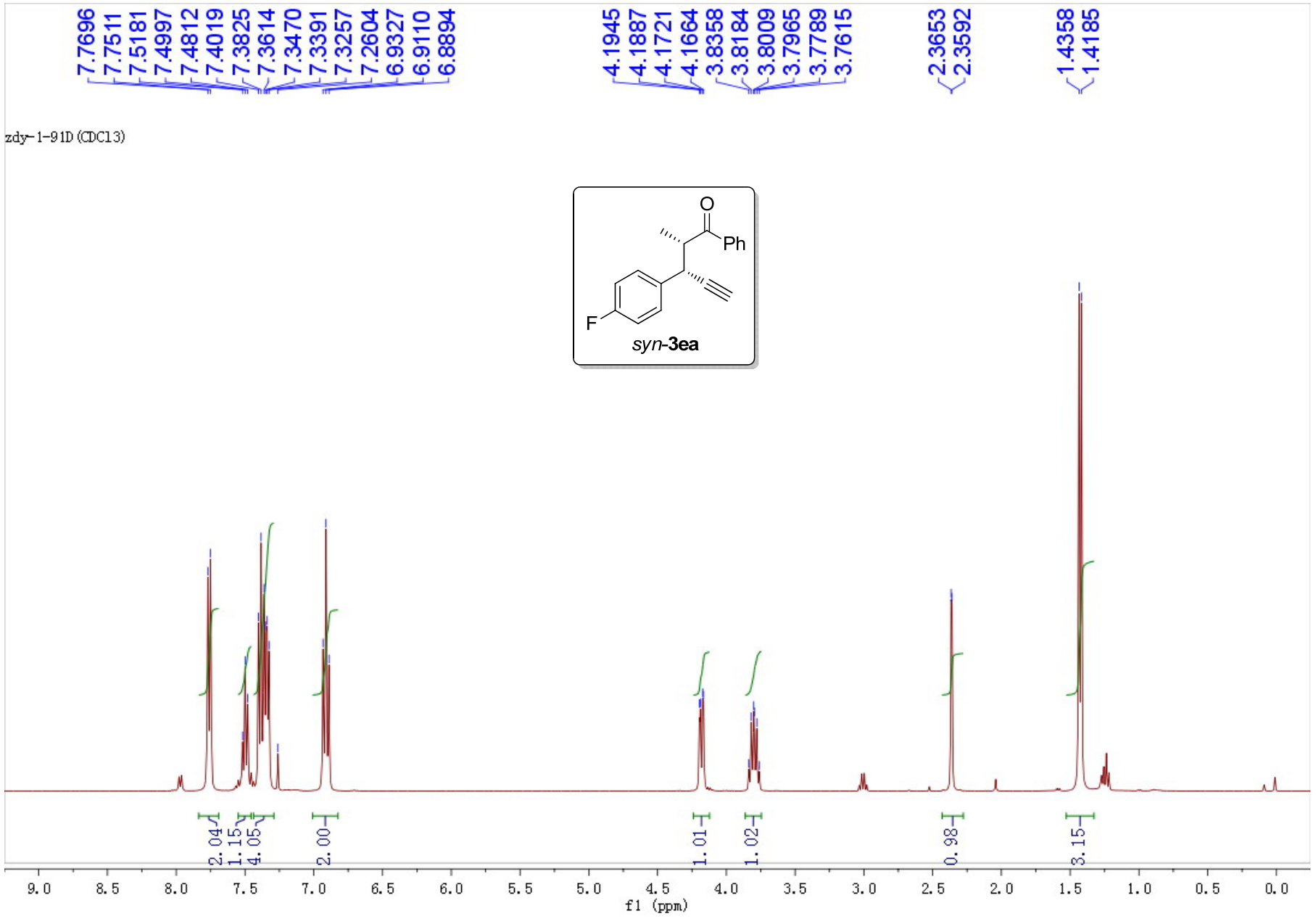
136.54
133.35
133.13
129.71
128.86
128.82
128.27
83.89
73.13
47.75
40.01
16.70
zdy-1-91C (CDCl3)
O
Ph
Cl
syn-3da
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.5181
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7.4812
7.4019
7.3825
7.3614
7.3470
7.3391
7.3257
7.2604
6.9327
6.9110
6.8894
4.1945
4.1887
4.1721
4.1664
3.8358
3.8184
3.8009
3.7965
3.7789
3.7615
2.3653
2.3592
1.4358
1.4185
zdy-1-91D (CDCl3)
O
Ph
F
syn-3ea
2.04
1.15
4.05
2.00
1.01
1.02
0.98
3.15
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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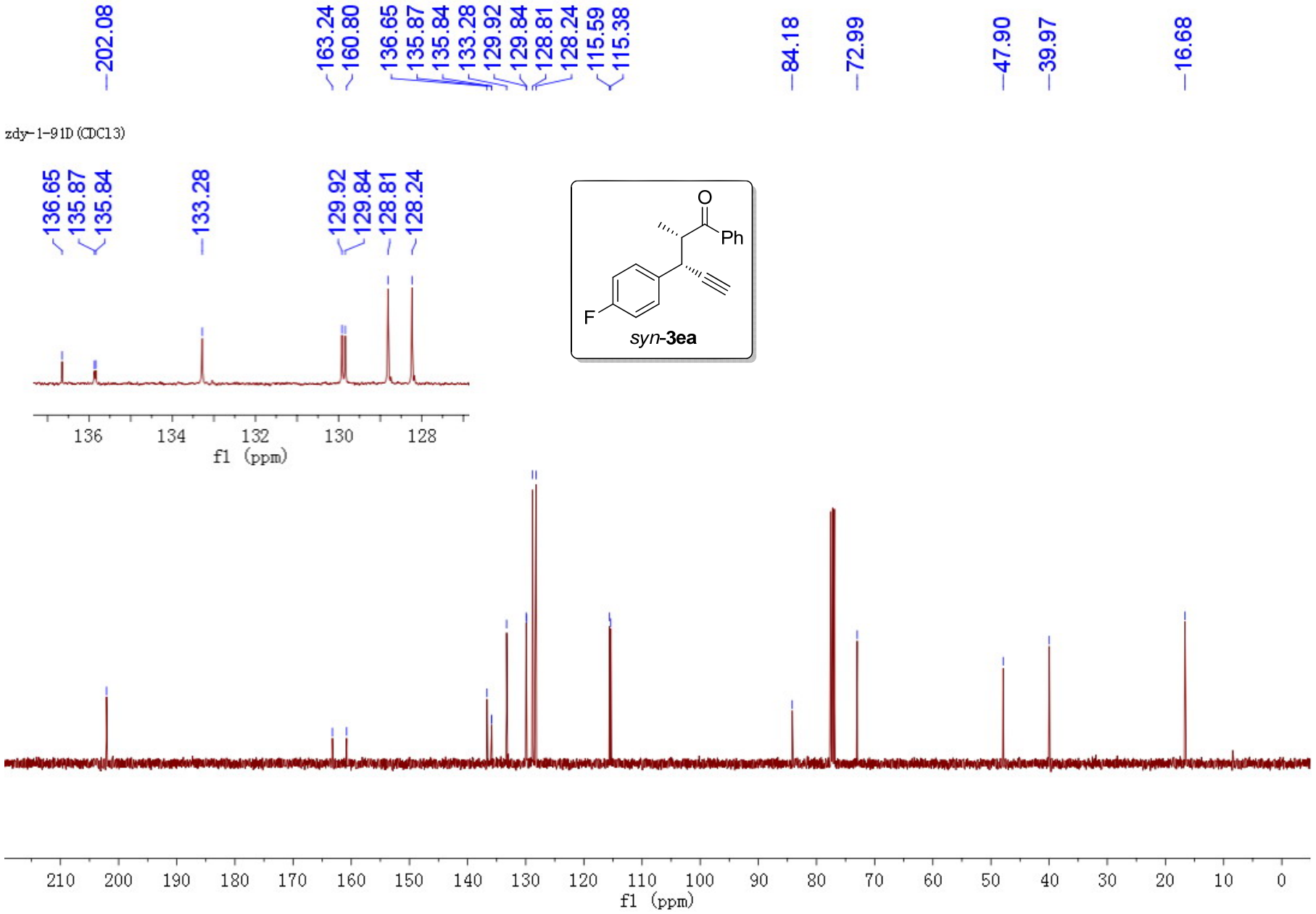
0.0
f1 (ppm)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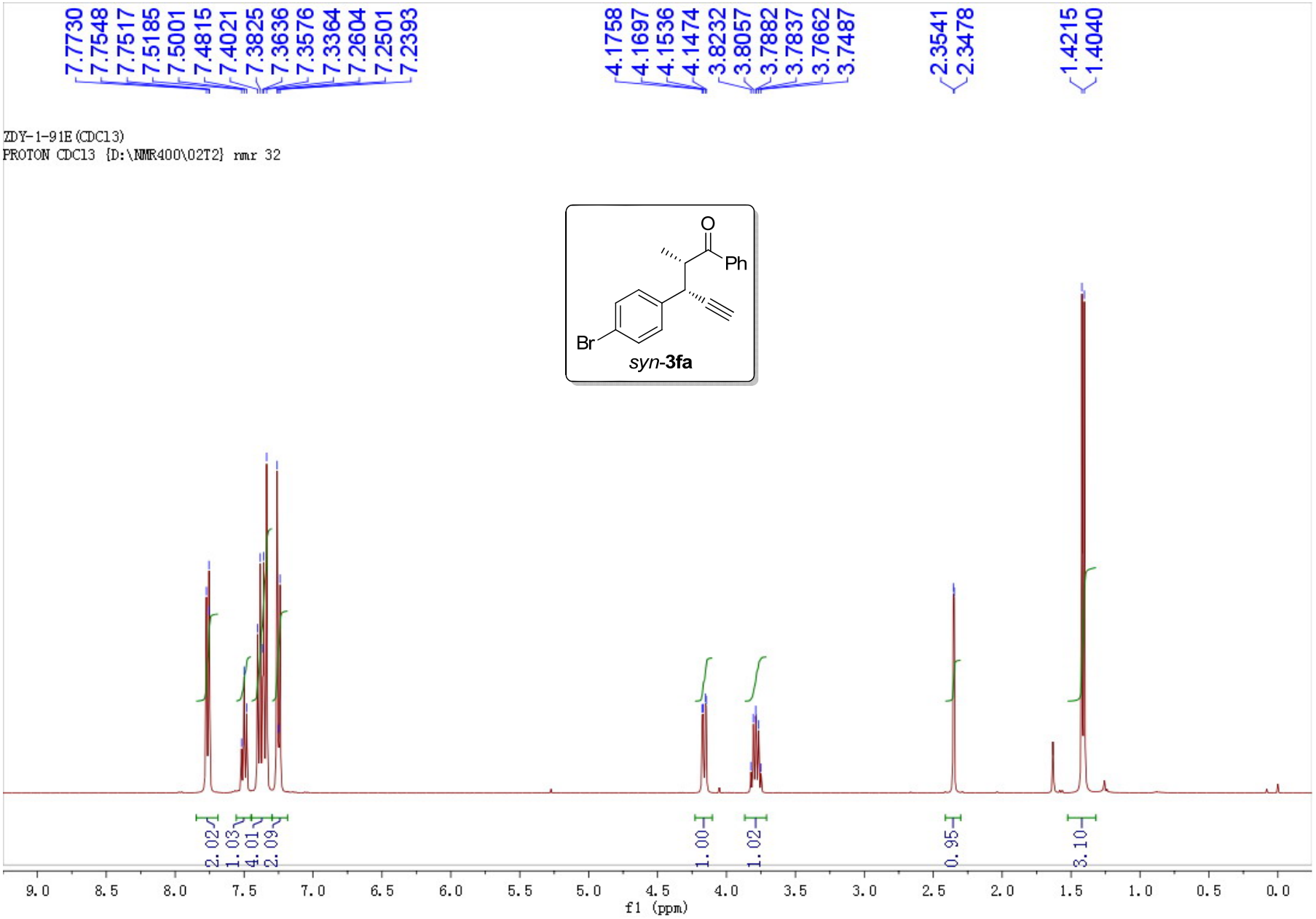
163.24
160.80
136.65
135.87
135.84
133.28
129.92
129.84
128.81
128.24
115.59
115.38
84.18
72.99
47.90
39.97
16.68
zdy-1-91D (CDCl3)
136.65
135.87
135.84
133.28
129.92
129.84
128.81
128.24
136
134
132
130
128
f1 (ppm)
O
Ph
F
syn-3ea
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.5001
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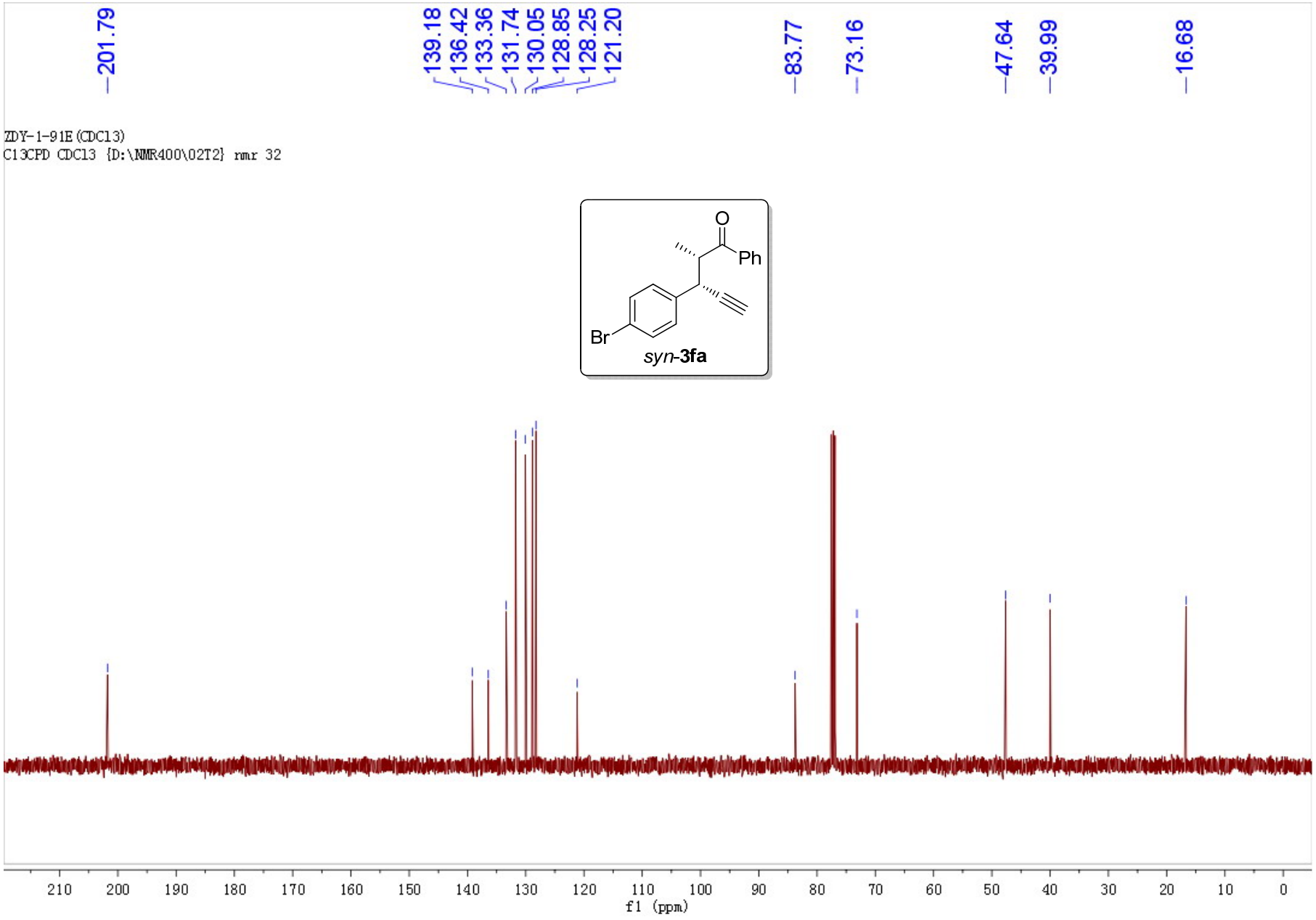
7.3636
7.3576
7.3364
7.2604
7.2501
7.2393
4.1758
4.1697
4.1536
4.1474
3.8232
3.8057
3.7882
3.7837
3.7662
3.7487
2.3541
2.3478
1.4215
1.4040
ZDY-1-91E(CDCl3)
PROTON CDCl3 {D:\NMR400\02T2} nmr 32
O
Ph
Br
syn-3fa
2.02
1.03
4.01
2.09
1.00
1.02
0.95
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.42
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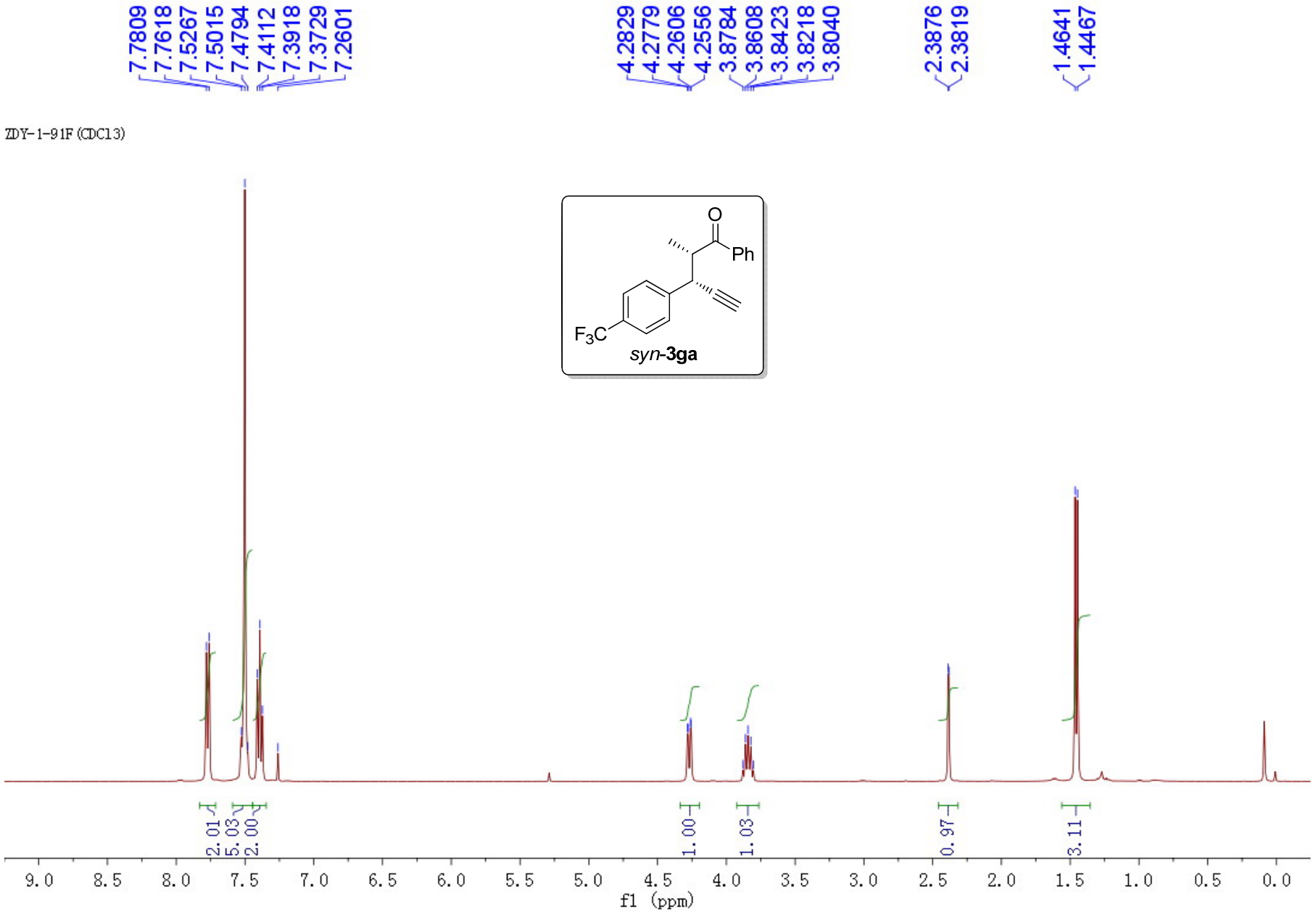
131.74
130.05
128.85
128.25
121.20
83.77
73.16
47.64
39.99
16.68
ZDY-1-91E(CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 32
O
Ph
Br
syn-3fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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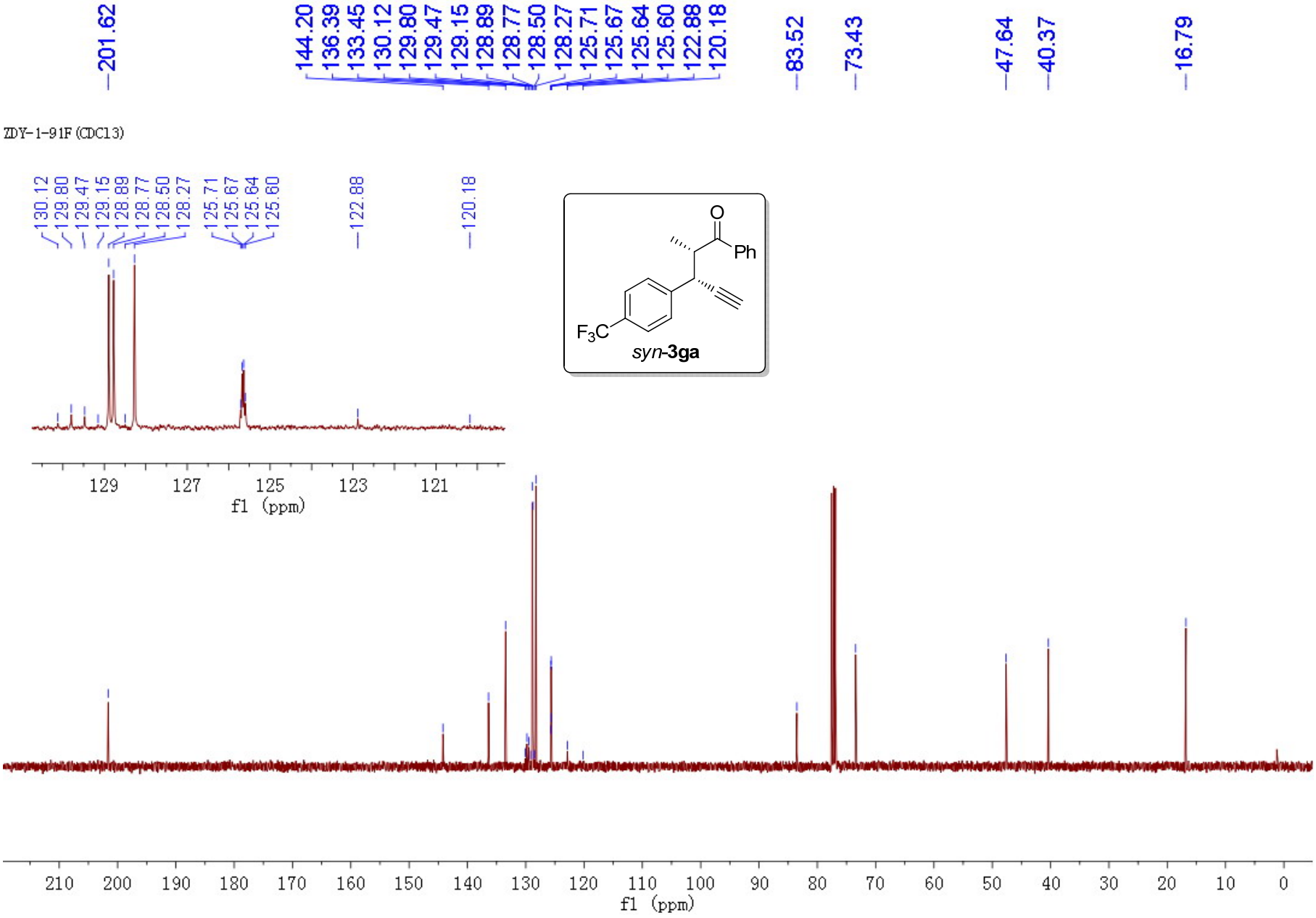
7.4794
7.4112
7.3918
7.3729
7.2601
4.2829
4.2779
4.2606
4.2556
3.8784
3.8608
3.8423
3.8218
3.8040
2.3876
2.3819
1.4641
1.4467
ZDY-1-91F (CDCl3)
O
Ph
F3C
syn-3ga
2.01
5.03
2.00
1.00
1.03
0.97
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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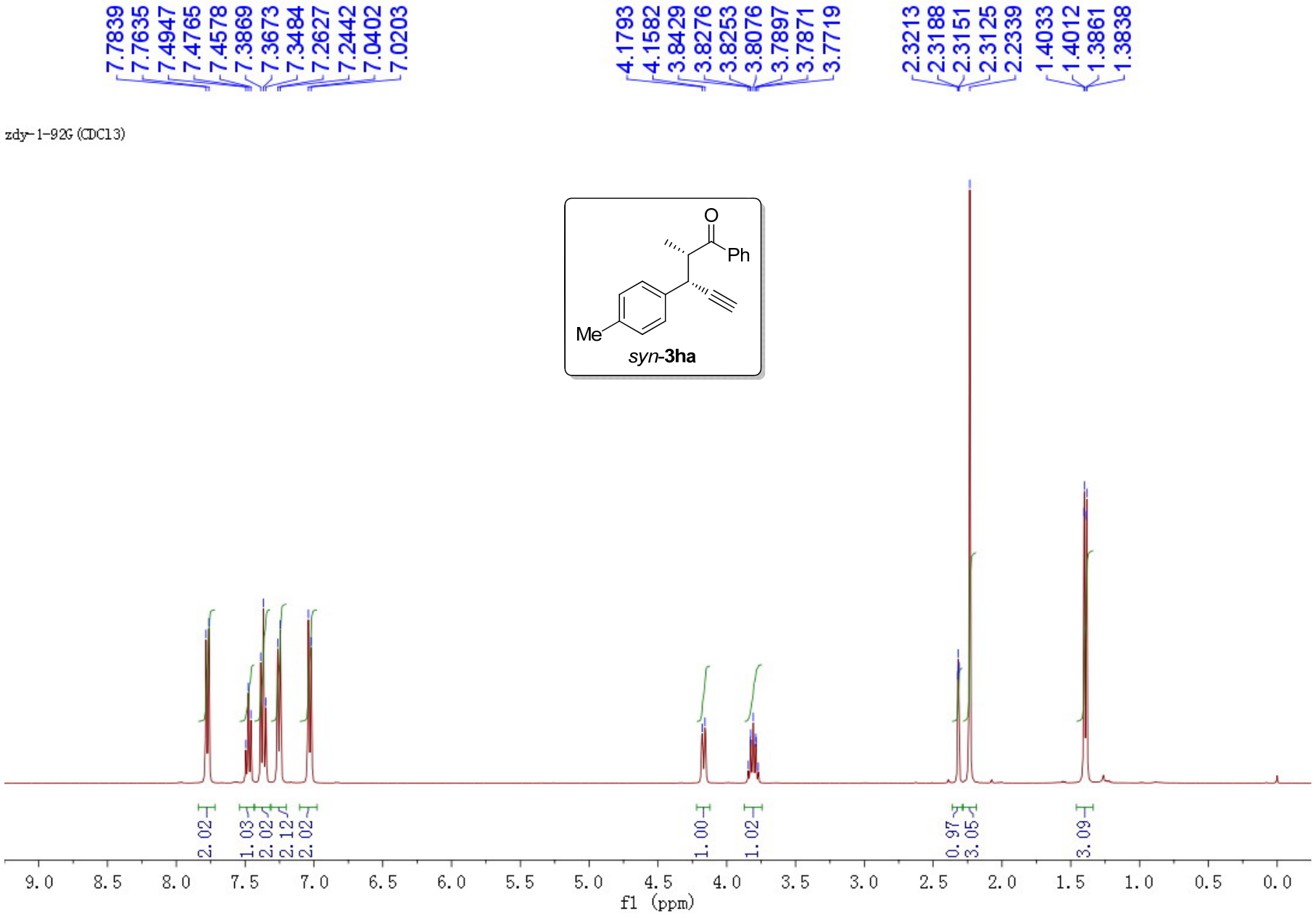
129.80
129.47
129.15
128.89
128.77
128.50
128.27
125.71
125.67
125.64
125.60
122.88
120.18
83.52
73.43
47.64
40.37
16.79
ZDY-1-91F (CDCl3)
O
Ph
F3C
syn-3ga
f1 (ppm)
f1 (ppm)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7.4765
7.4578
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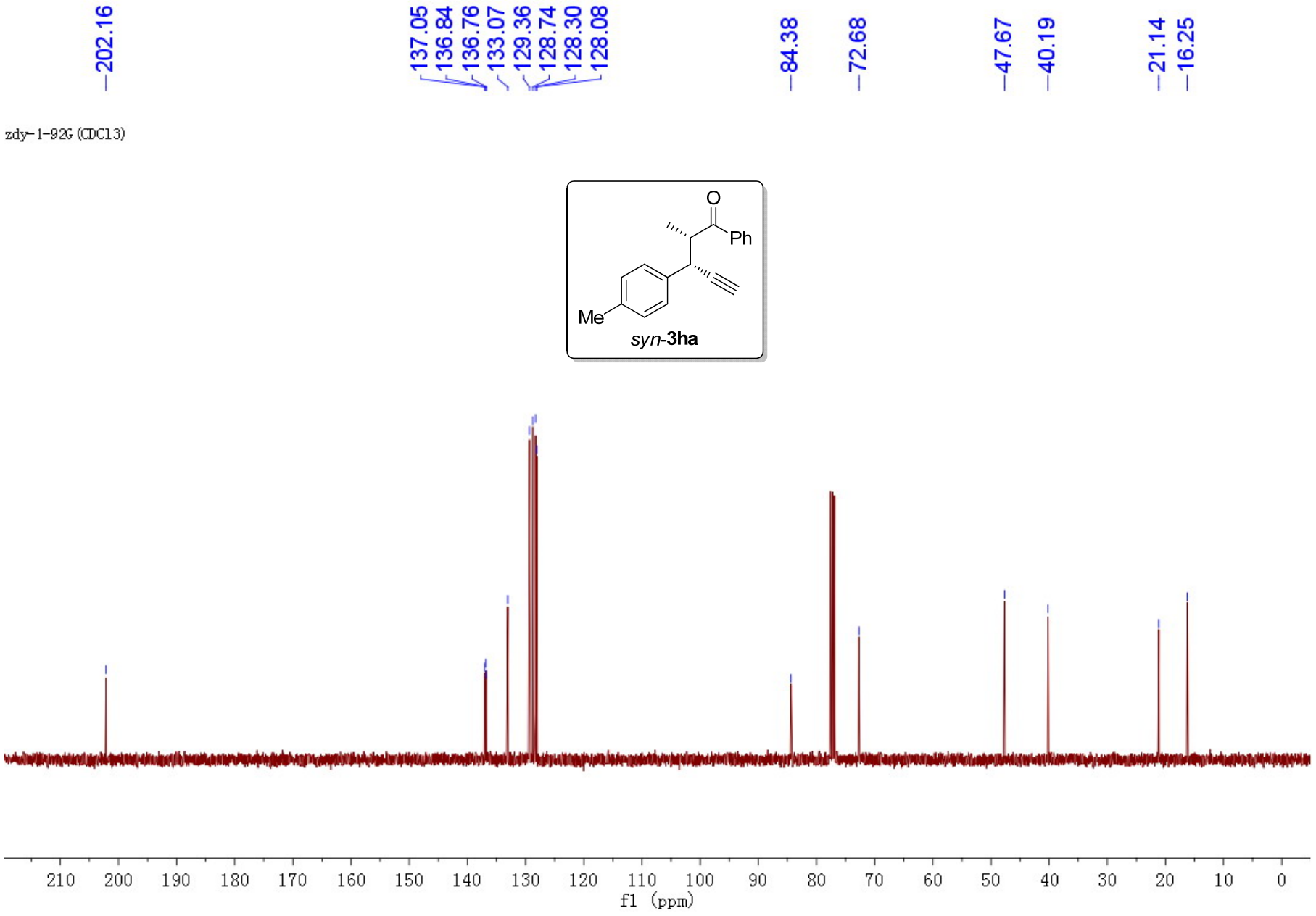
7.3673
7.3484
7.2627
7.2442
7.0402
7.0203
4.1793
4.1582
3.8429
3.8276
3.8253
3.8076
3.7897
3.7871
3.7719
2.3213
2.3188
2.3151
2.3125
2.2339
1.4033
1.4012
1.3861
1.3838
zdy-1-92G (CDCl3)
O
Ph
Me
syn-3ha
2.02
1.03
2.02
2.12
2.02
1.00
1.02
0.97
3.05
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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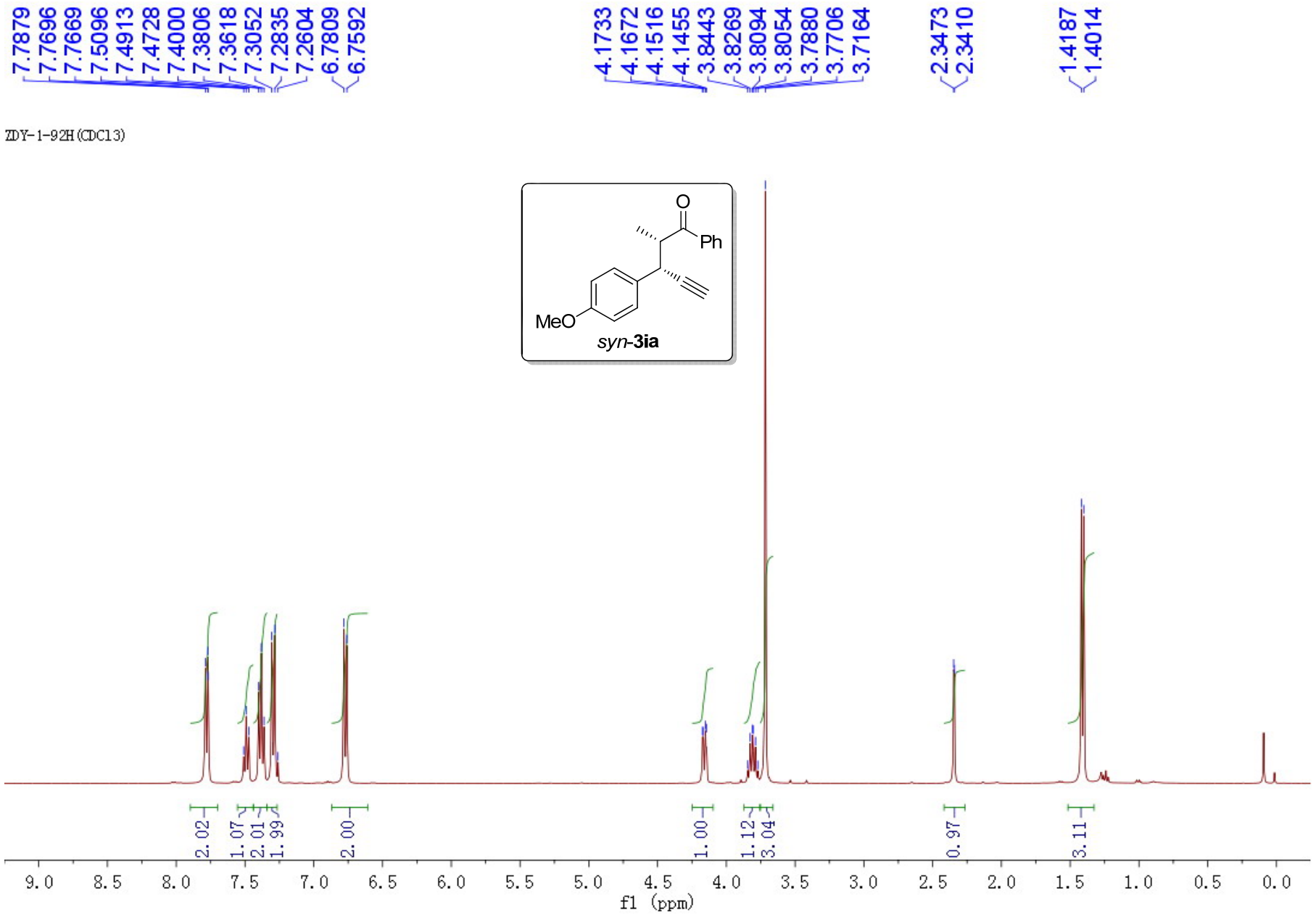
129.36
128.74
128.30
128.08
84.38
72.68
47.67
40.19
21.14
16.25
zdy-1-92G (CDCl3)
O
Ph
Me
syn-3ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.4000
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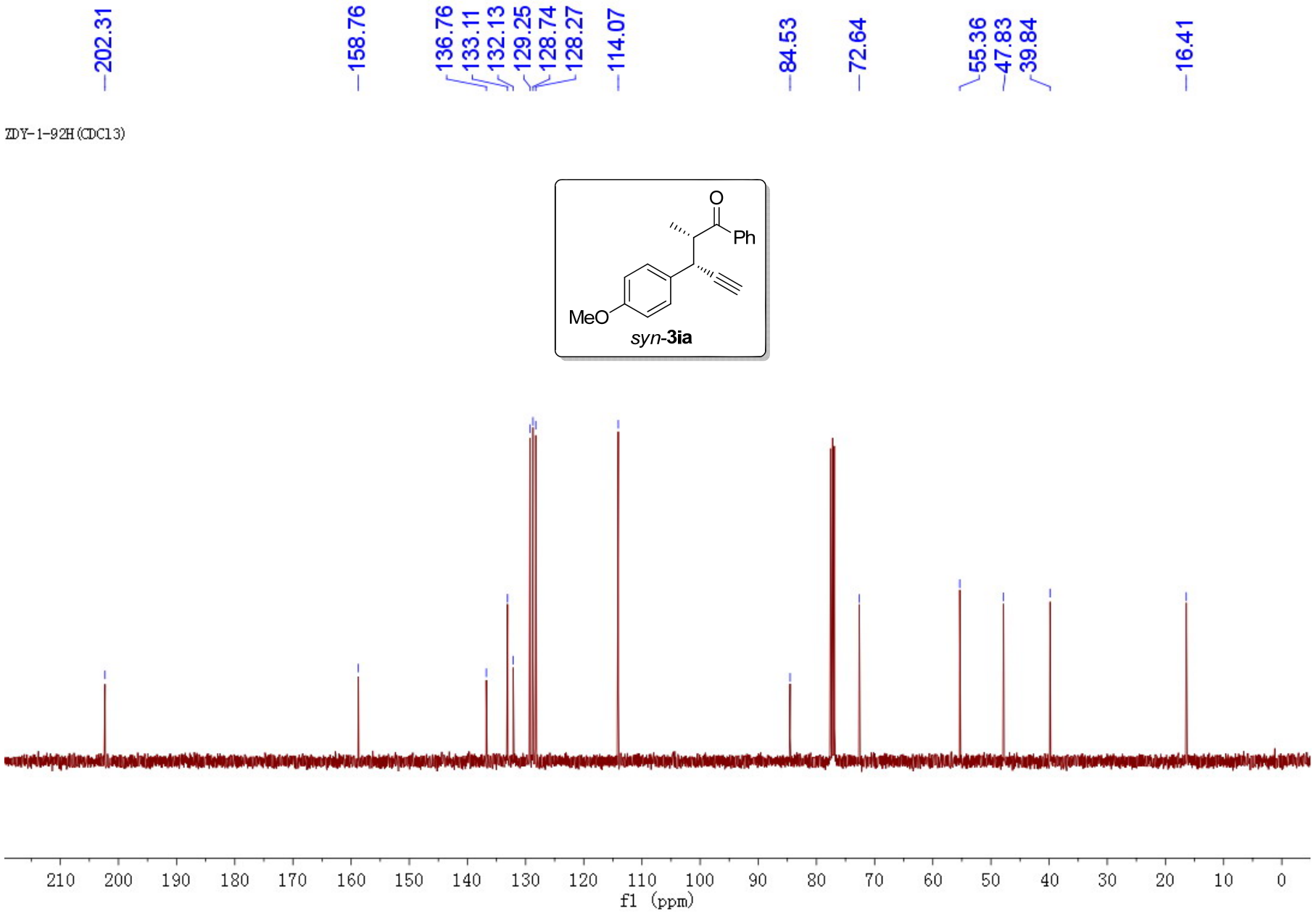
7.3052
7.2835
7.2604
6.7809
6.7592
4.1733
4.1672
4.1516
4.1455
3.8443
3.8269
3.8094
3.8054
3.7880
3.7706
3.7164
2.3473
2.3410
1.4187
1.4014
ZDY-1-92H(CDCl3)
O
Ph
MeO
syn-3ia
2.02
1.07
2.01
1.99
2.00
1.00
1.12
3.04
0.97
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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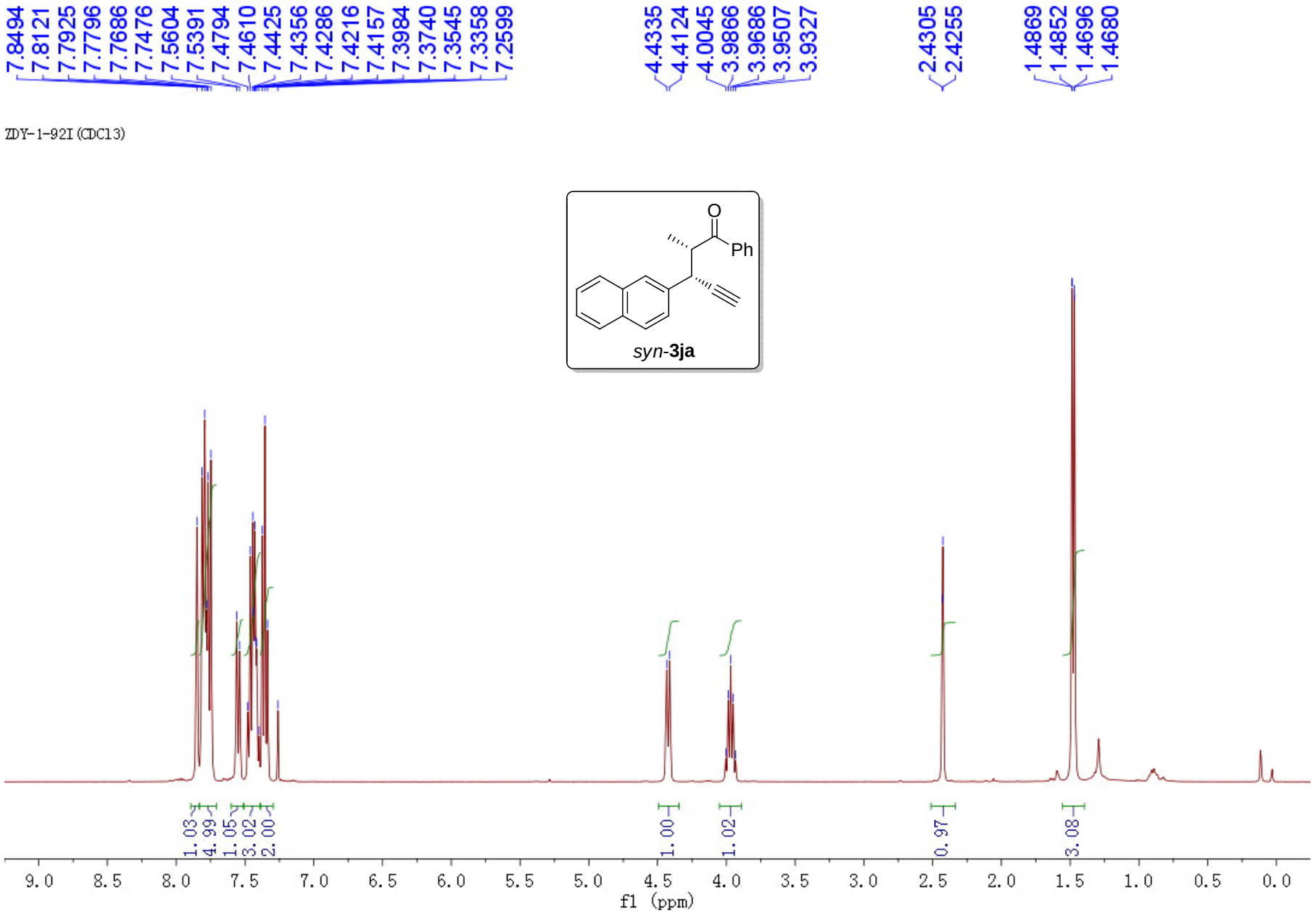
128.74
128.27
114.07
84.53
72.64
55.36
47.83
39.84
16.41
ZDY-1-92H(CDCl3)
O
Ph
MeO
syn-3ia
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.7796
7.7686
7.7476
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7.4610
7.4425
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7.4286
7.4216
7.4157
7.3984
7.3740
7.3545
7.3358
7.2599
4.4335
4.4124
4.0045
3.9866
3.9686
3.9507
3.9327
2.4305
2.4255
1.4869
1.4852
1.4696
1.4680
ZDY-1-92I(CDCl3)
O
Ph
syn-3ja
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4.99
1.05
3.02
2.00
1.00
1.02
0.97
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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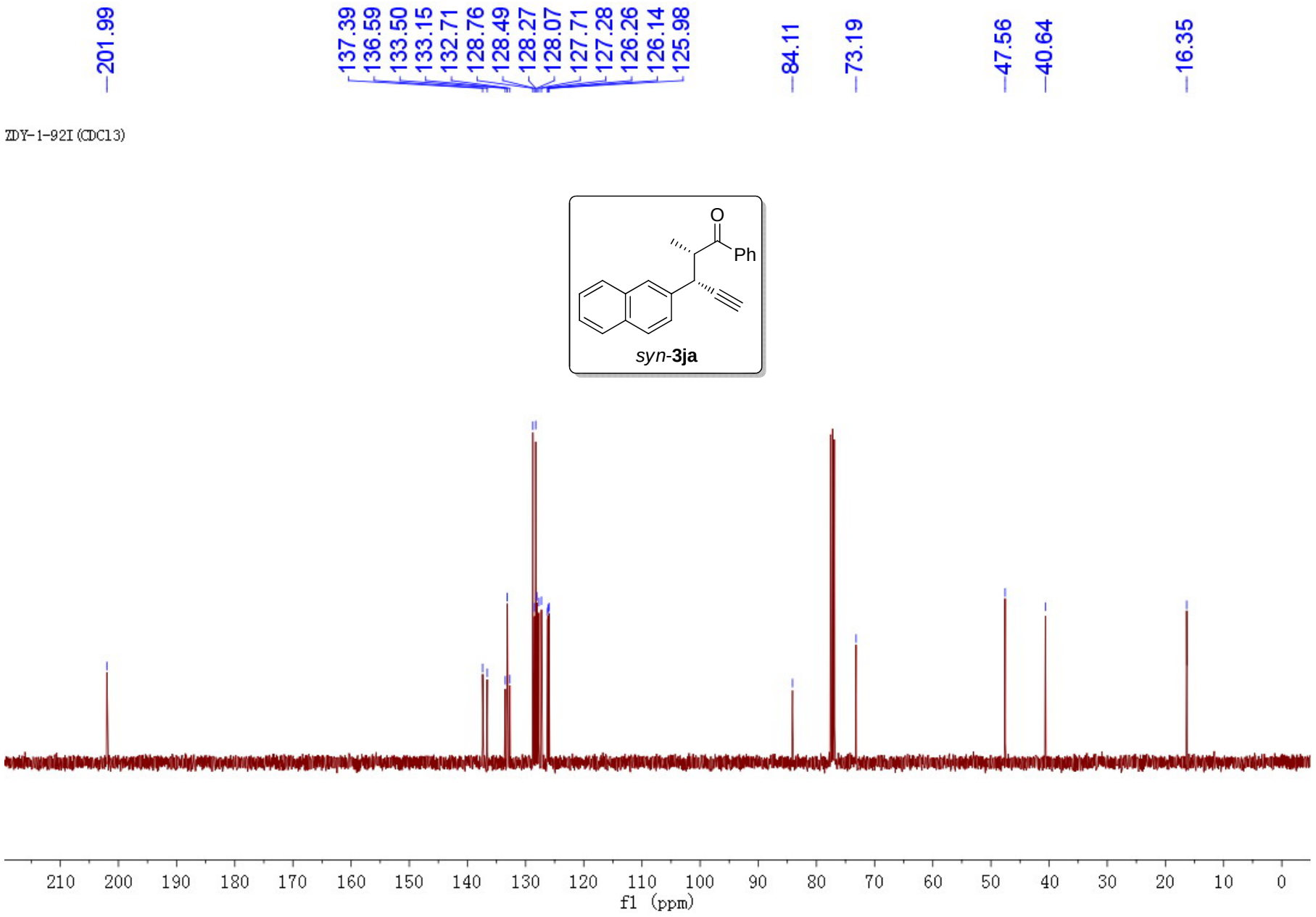
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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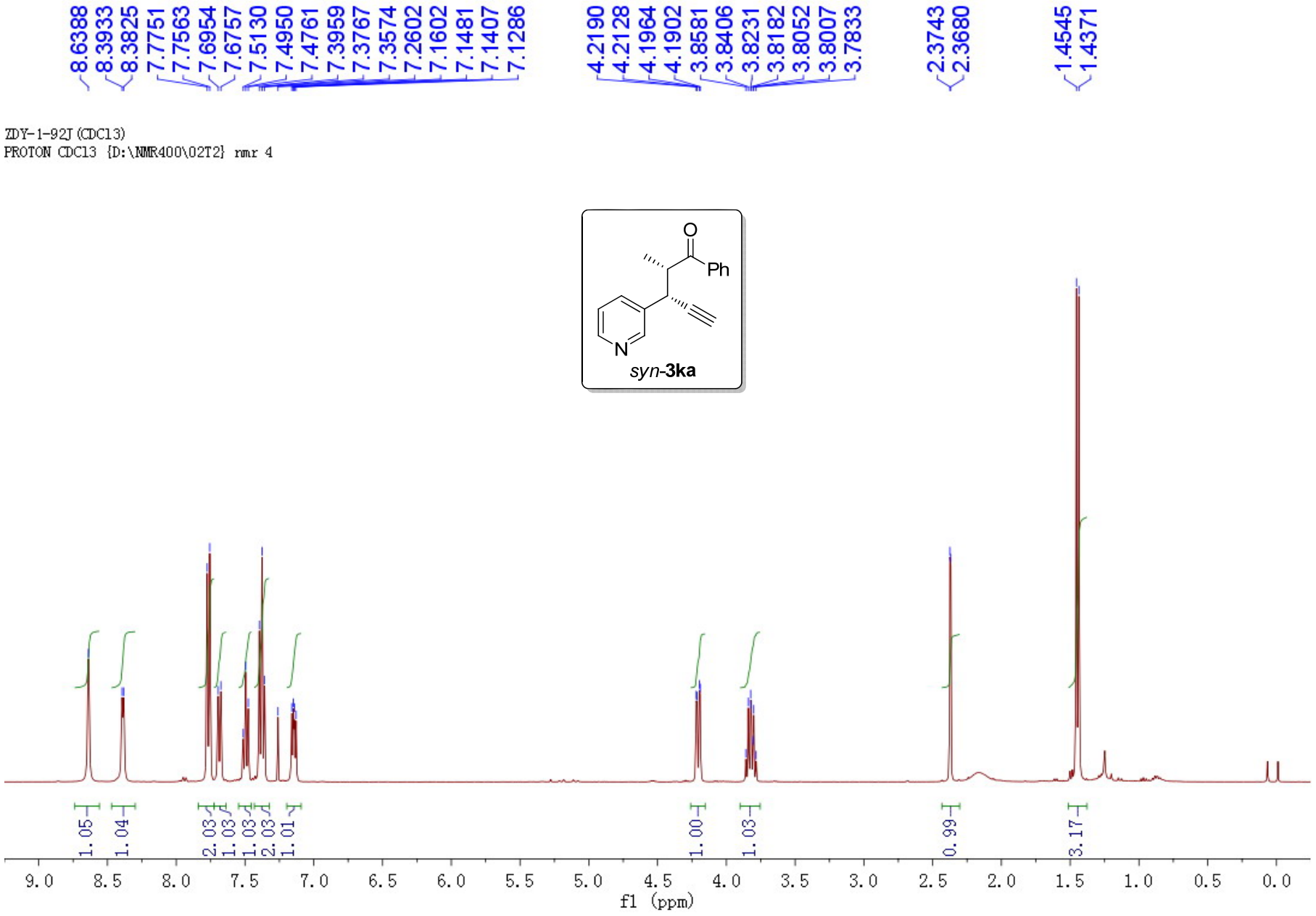
128.49
128.27
128.07
127.71
127.28
126.26
126.14
125.98
84.11
73.19
47.56
40.64
16.35
ZDY-1-92I(CDCl3)
O
Ph
syn-3ja
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.3825
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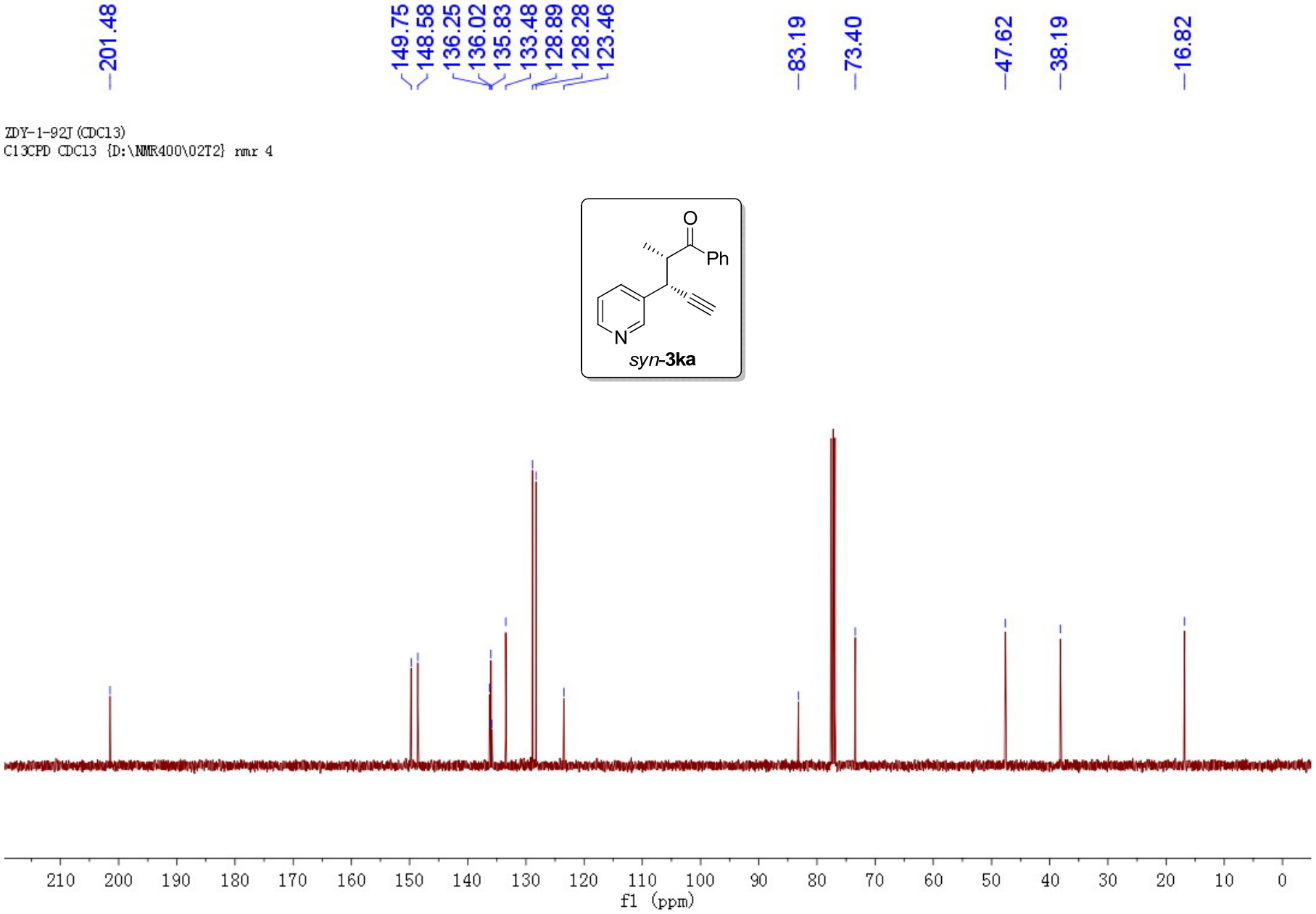
7.3959
7.3767
7.3574
7.2602
7.1602
7.1481
7.1407
7.1286
4.2190
4.2128
4.1964
4.1902
3.8581
3.8406
3.8231
3.8182
3.8052
3.8007
3.7833
2.3743
2.3680
1.4545
1.4371
ZDY-1-92J (CDCl3)
PROTON CDCl3 {D:\NMR400\02T2} rmr 4
O
Ph
N
syn-3ka
1.05
1.04
2.03
1.03
1.03
2.03
1.01
1.00
1.03
0.99
3.17
9.0
8.5
8.0
7.5
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)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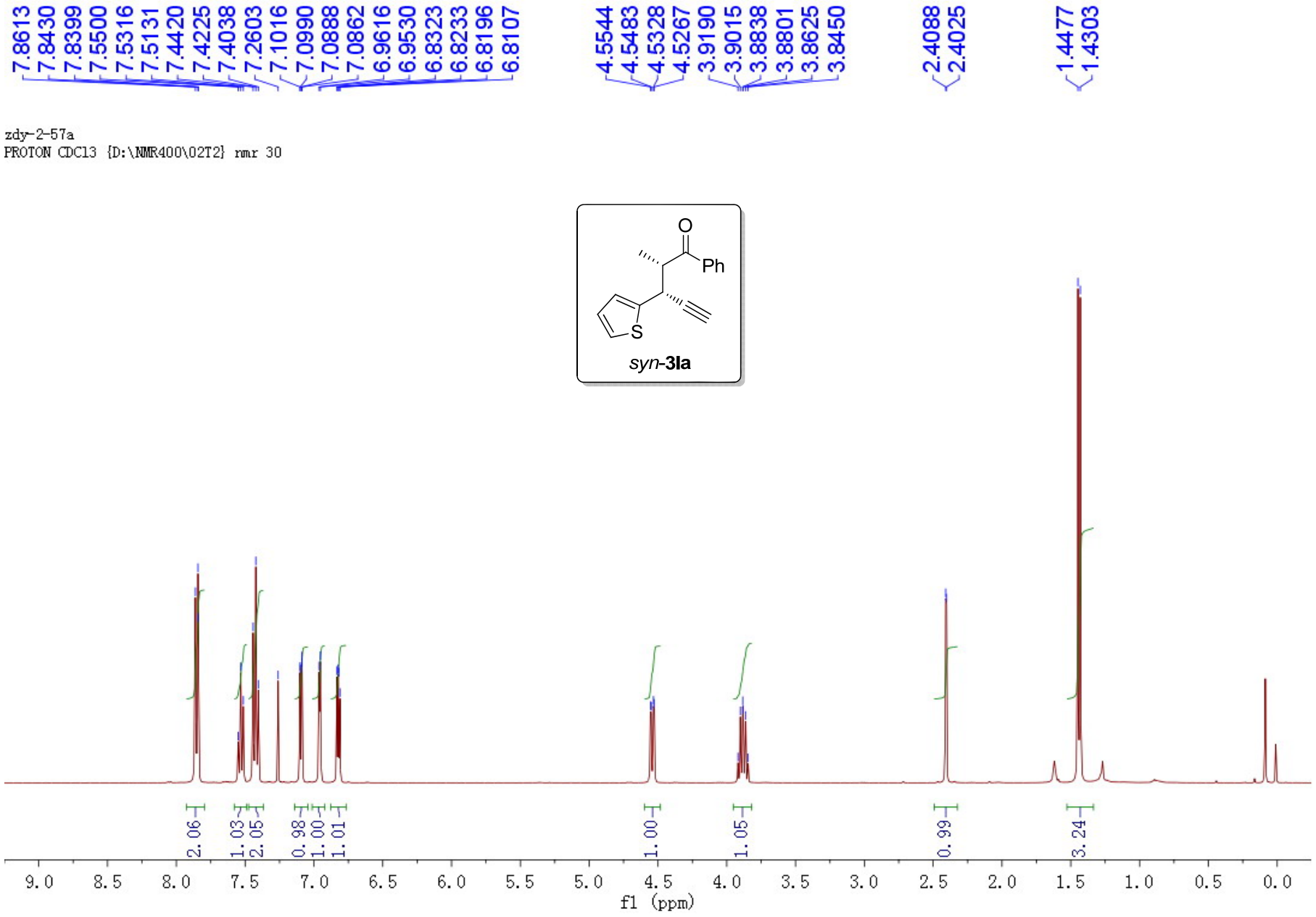
136.02
135.83
133.48
128.89
128.28
123.46
83.19
73.40
47.62
38.19
16.82
ZDY-1-92J (CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 4
O
Ph
N
syn-3ka
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4225
7.4038
7.2603
7.1016
7.0990
7.0888
7.0862
6.9616
6.9530
6.8323
6.8233
6.8196
6.8107
4.5544
4.5483
4.5328
4.5267
3.9190
3.9015
3.8838
3.8801
3.8625
3.8450
2.4088
2.4025
1.4477
1.4303
zdy-2-57a
PROTON CDCl3 {D:\NMR400\02T2} rmr 30
O
Ph
S
syn-3la
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1.03
2.05
0.98
1.00
1.01
1.00
1.05
0.99
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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1.0
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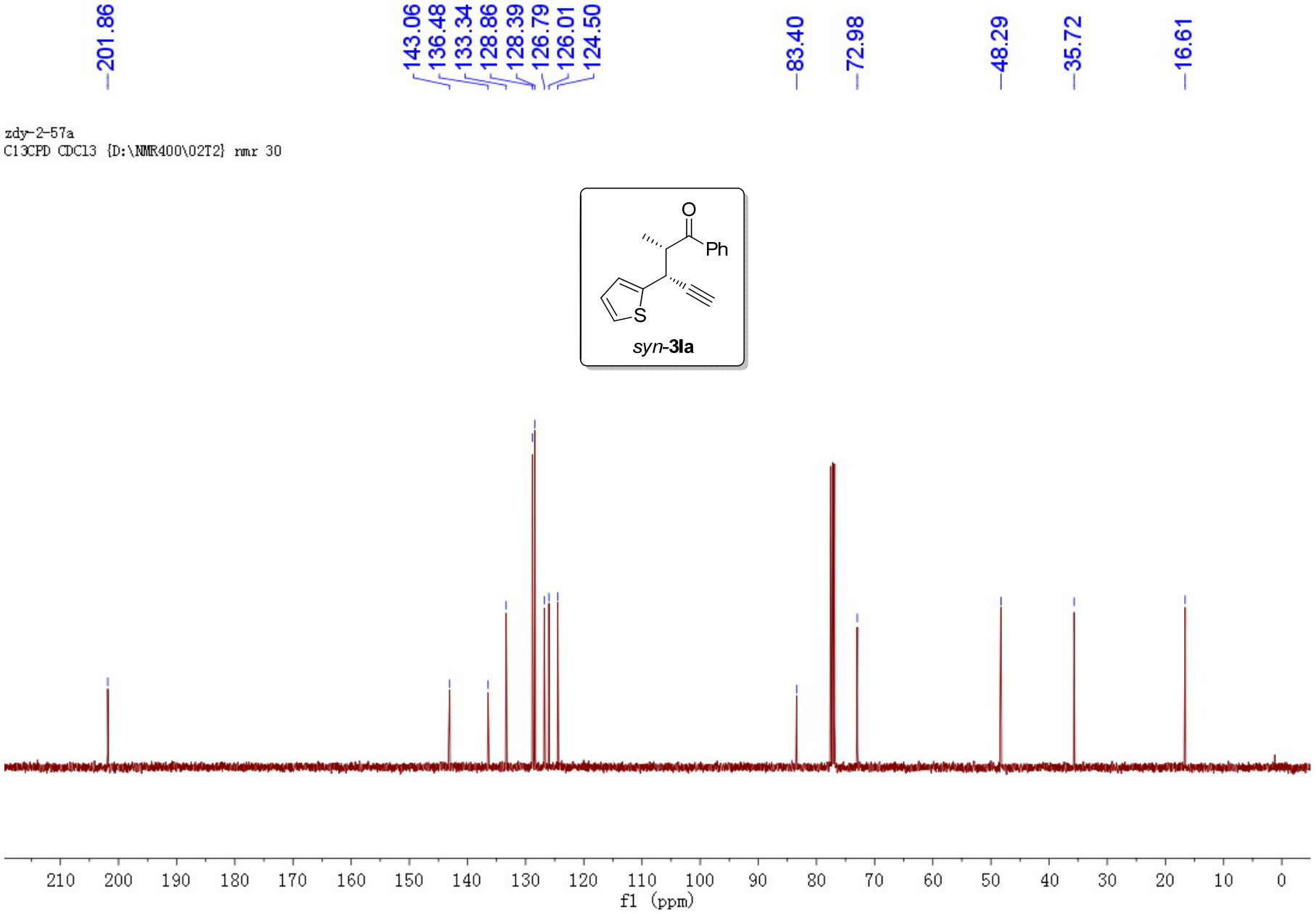
0.0
f1 (ppm)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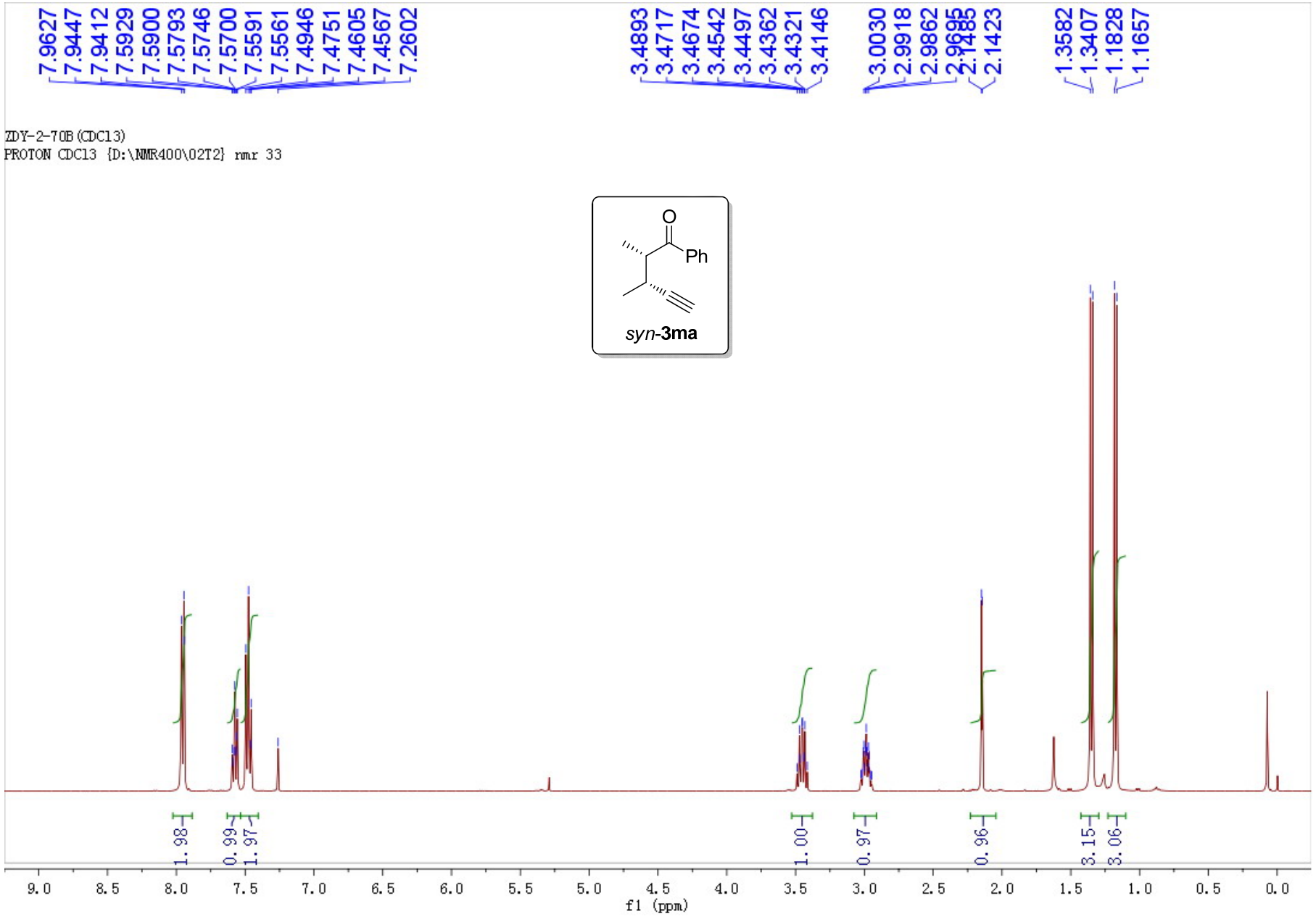
48.29
35.72
16.61
zdy-2-57a
C13CPD CDCl3 {D:\NMR400\02T2} rmr 30
O
Ph
S
syn-3la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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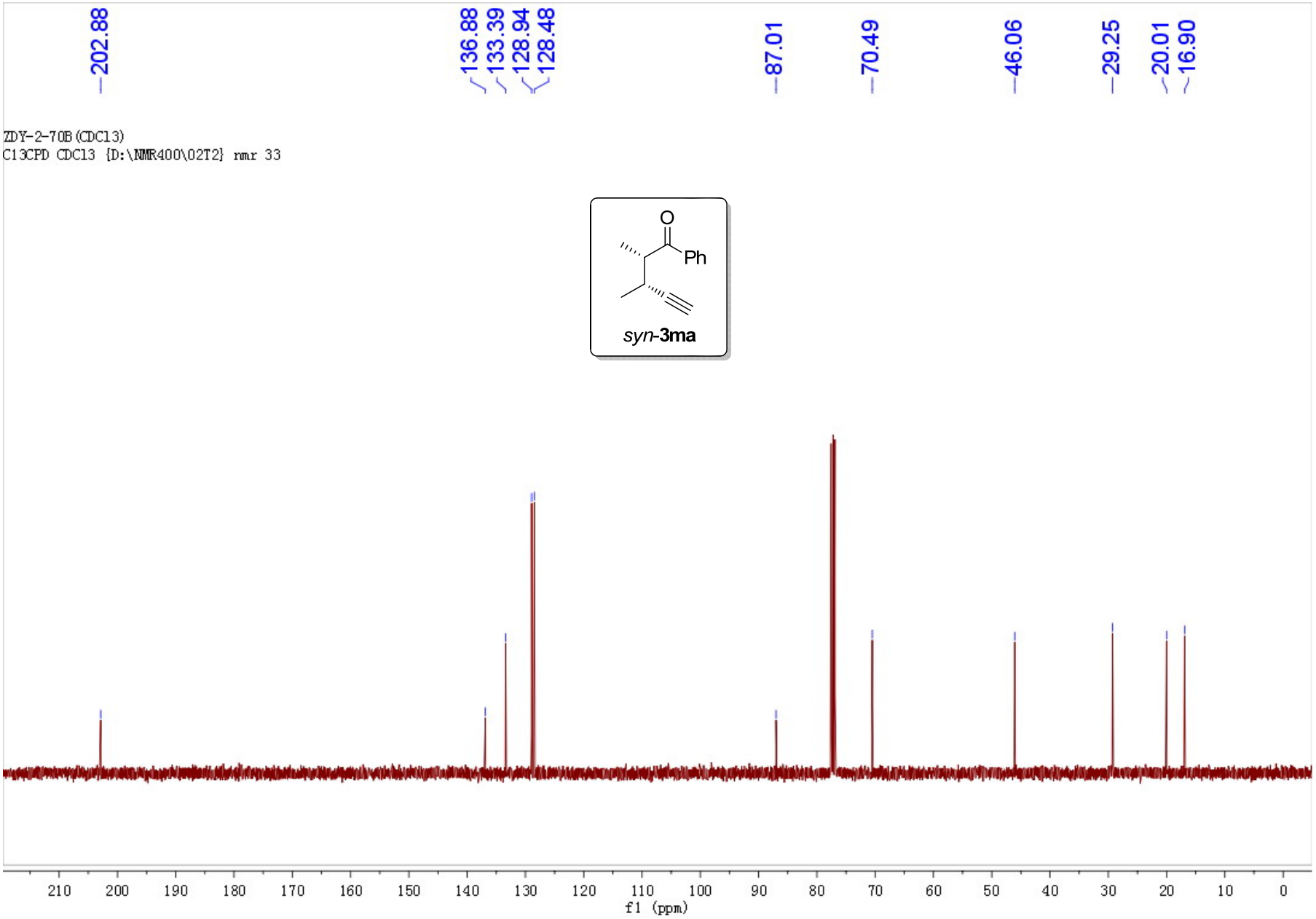
7.5561
7.4946
7.4751
7.4605
7.4567
7.2602
3.4893
3.4717
3.4674
3.4542
3.4497
3.4362
3.4321
3.4146
3.0030
2.9918
2.9862
2.1485
2.1423
1.3582
1.3407
1.1828
1.1657
ZDY-2-70B(CDCl3)
PROTON CDCl3 {D:\NMR400\02T2} rmr 33
O
Ph
syn-3ma
1.98
0.99
1.97
1.00
0.97
0.96
3.15
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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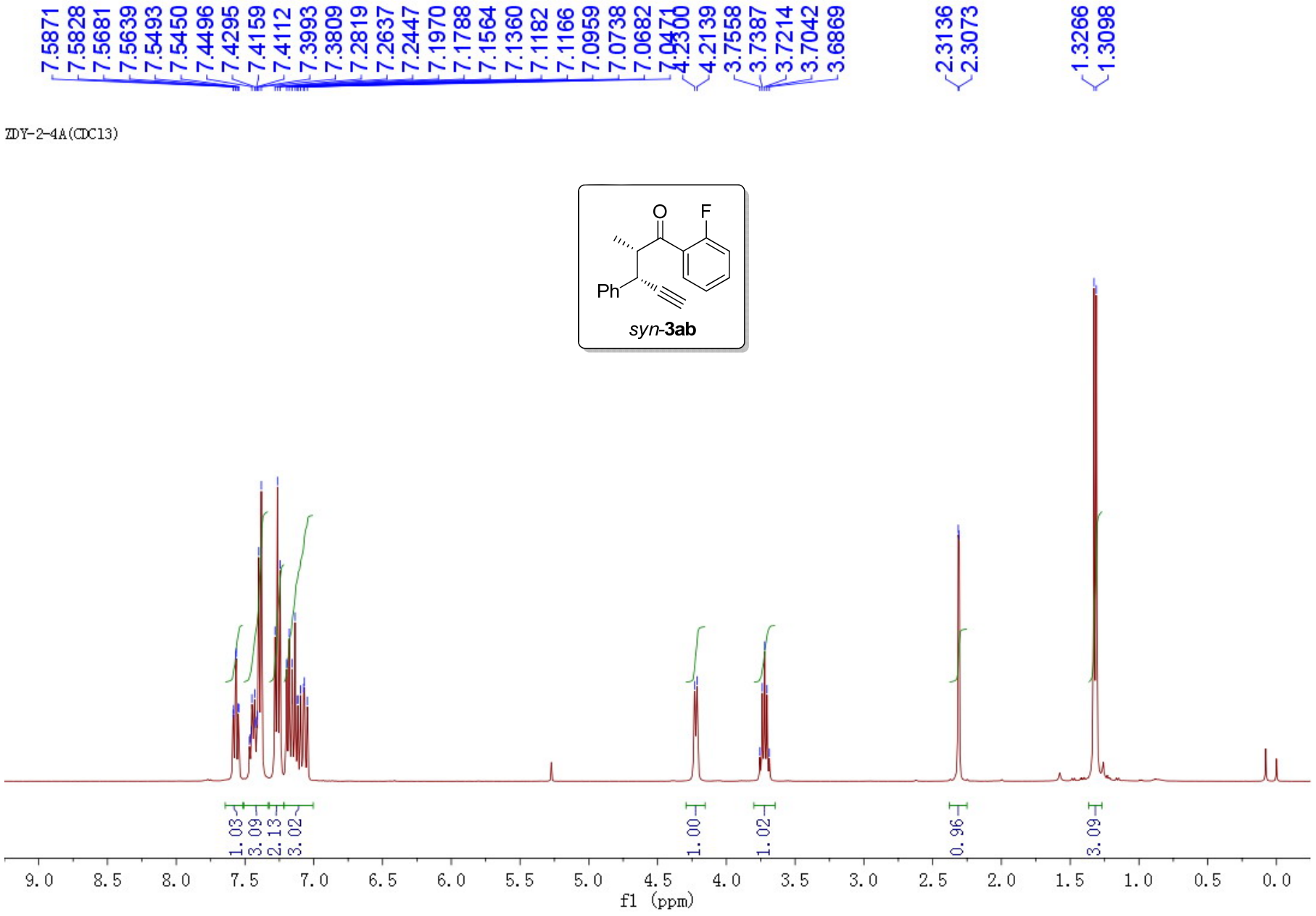
70.49
46.06
29.25
20.01
16.90
ZDY-2-70B(CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 33
O
Ph
syn-3ma
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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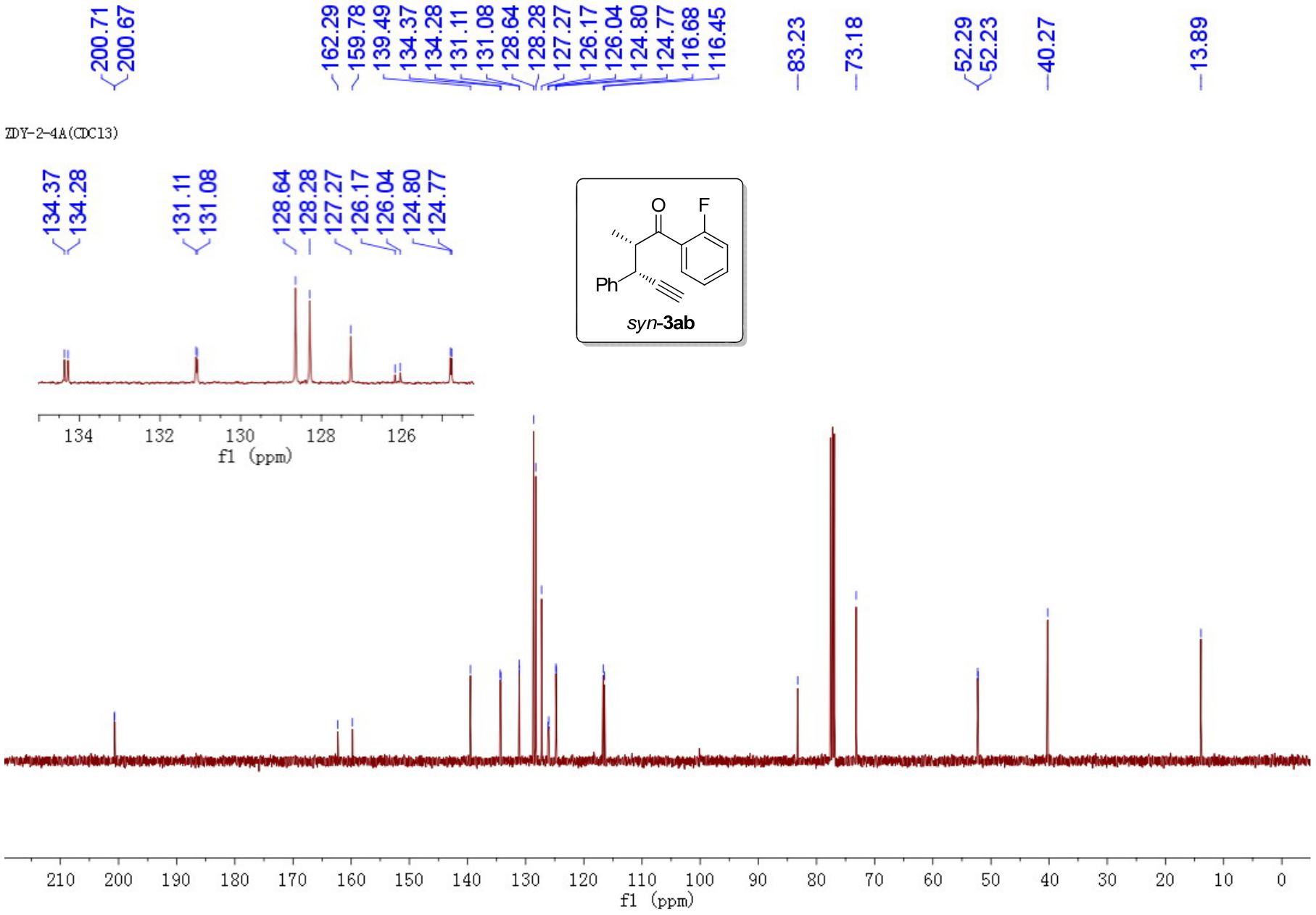
7.3993
7.3809
7.2819
7.2637
7.2447
7.1970
7.1788
7.1564
7.1360
7.1182
7.1166
7.0959
7.0738
7.0682
4.2300
4.2139
3.7558
3.7387
3.7214
3.7042
3.6869
2.3136
2.3073
1.3266
1.3098
ZDY-2-4A(CDCl3)
O
F
Ph
syn-3ab
1.03
3.09
2.13
3.02
1.00
1.02
0.96
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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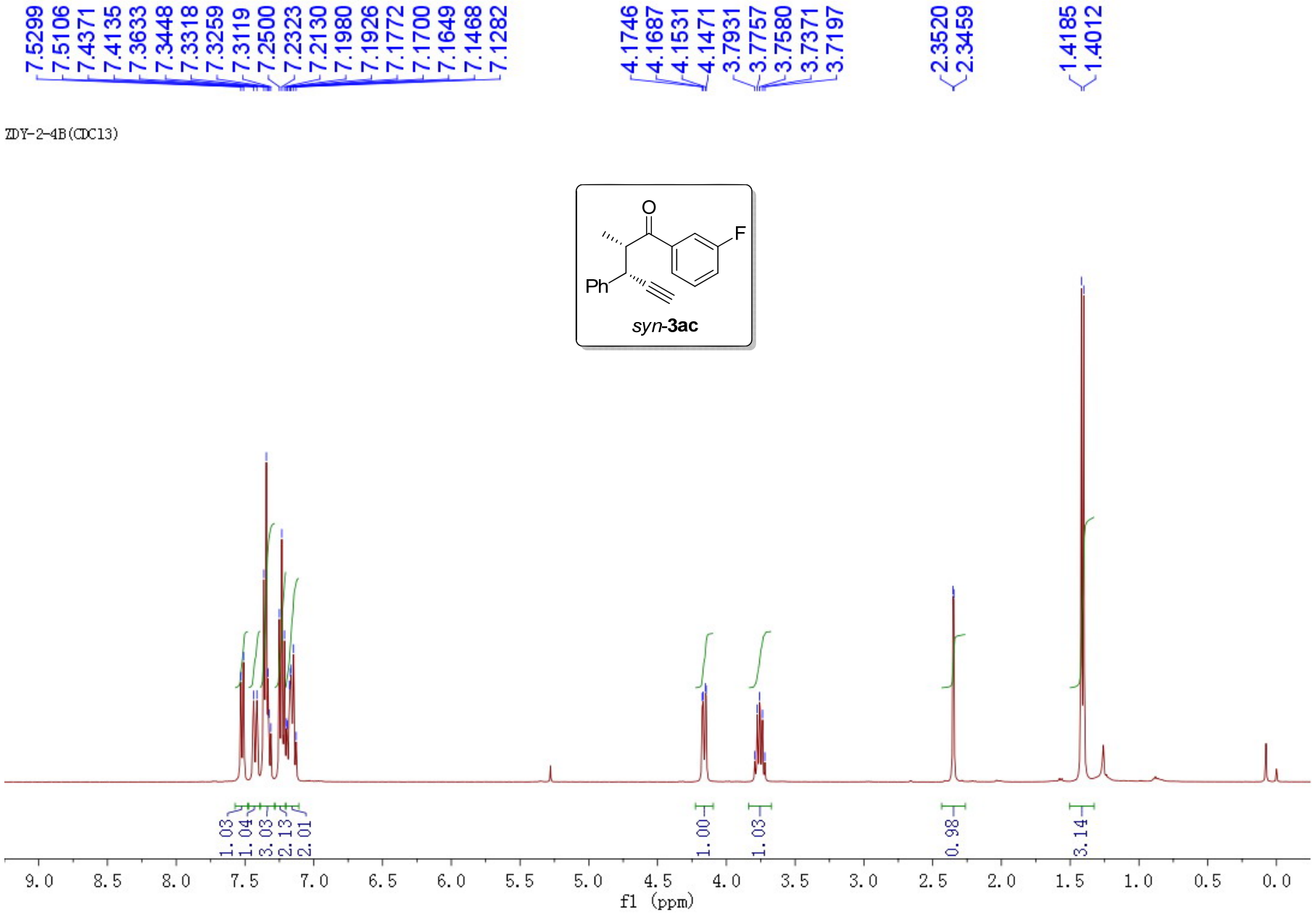
134.37
134.28
131.11
131.08
128.64
128.28
127.27
126.17
126.04
124.80
124.77
116.68
116.45
83.23
73.18
52.29
52.23
40.27
13.89
ZDY-2-4A(CDC13)
O
F
Ph
syn-3ab
f1 (ppm)
f1 (ppm)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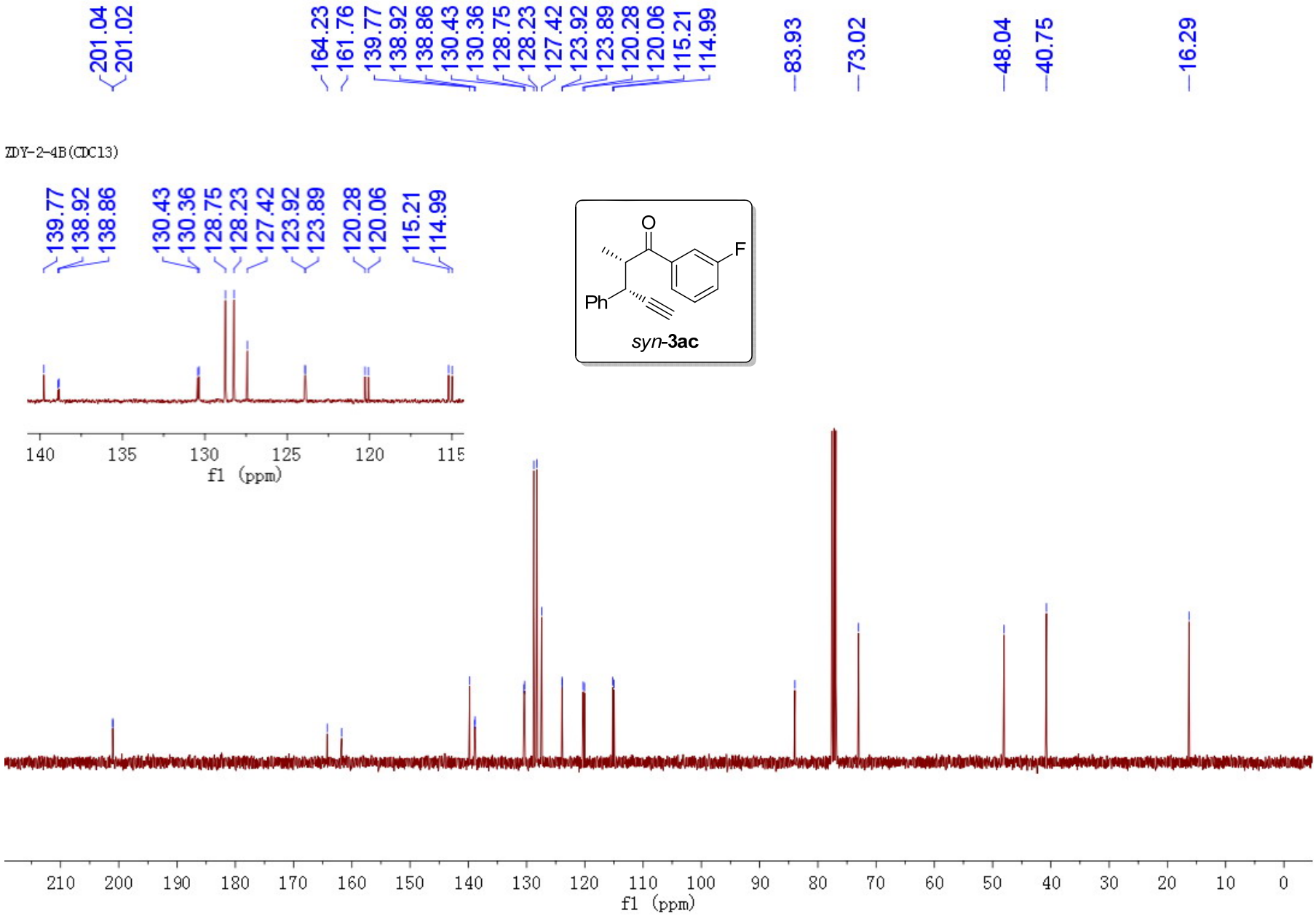
7.3633
7.3448
7.3318
7.3259
7.3119
7.2500
7.2323
7.2130
7.1980
7.1926
7.1772
7.1700
7.1649
7.1468
7.1282
4.1746
4.1687
4.1531
4.1471
3.7931
3.7757
3.7580
3.7371
3.7197
2.3520
2.3459
1.4185
1.4012
ZDY-2-4B(CDCl3)
O
F
Ph
syn-3ac
1.03
1.04
3.03
2.13
2.01
1.00
1.03
0.98
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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201.02
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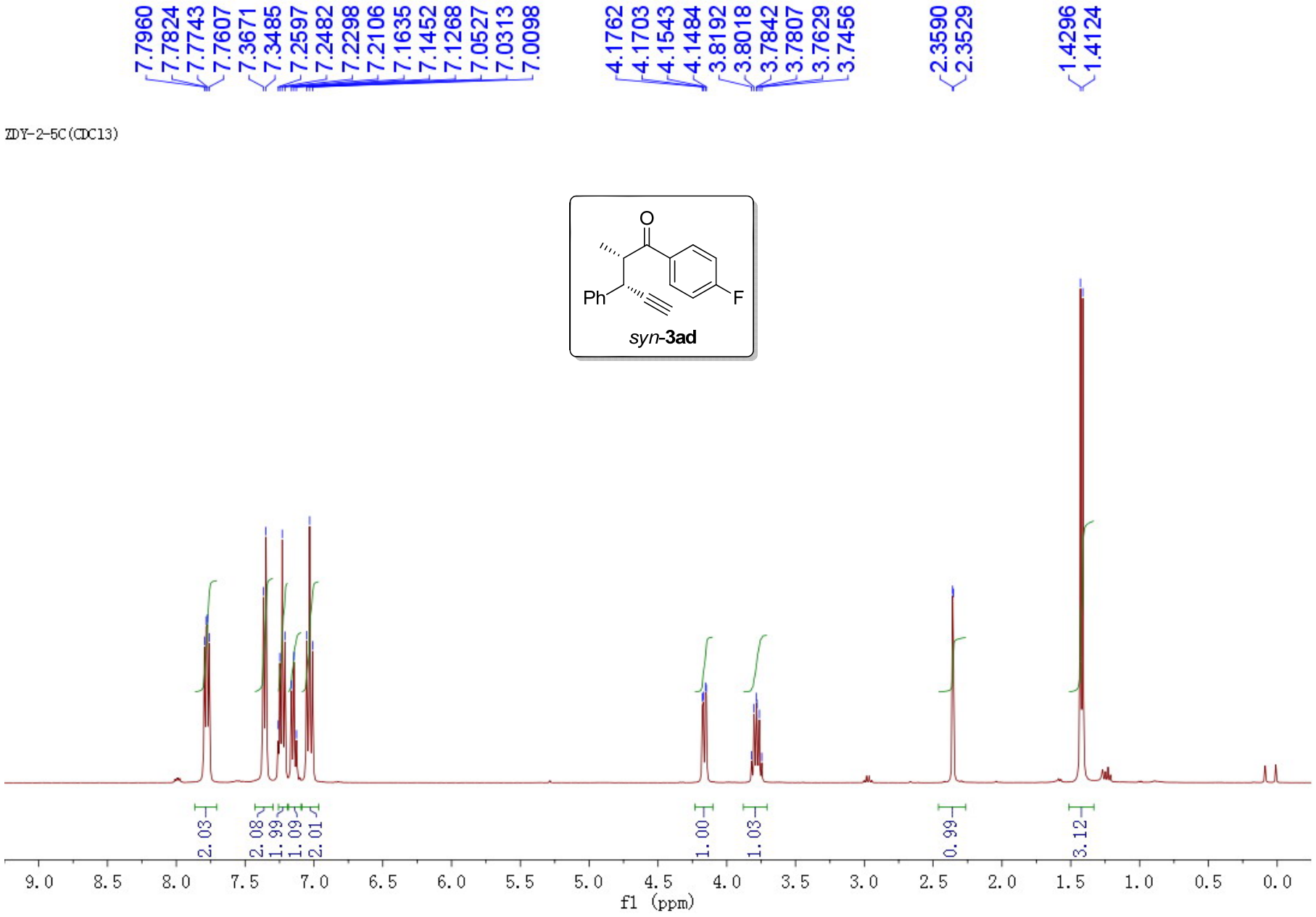
138.92
138.86
130.43
130.36
128.75
128.23
127.42
123.92
123.89
120.28
120.06
115.21
114.99
83.93
73.02
48.04
40.75
16.29
ZDY-2-4B(CDCl3)
O
F
Ph
syn-3ac
f1 (ppm)
f1 (ppm)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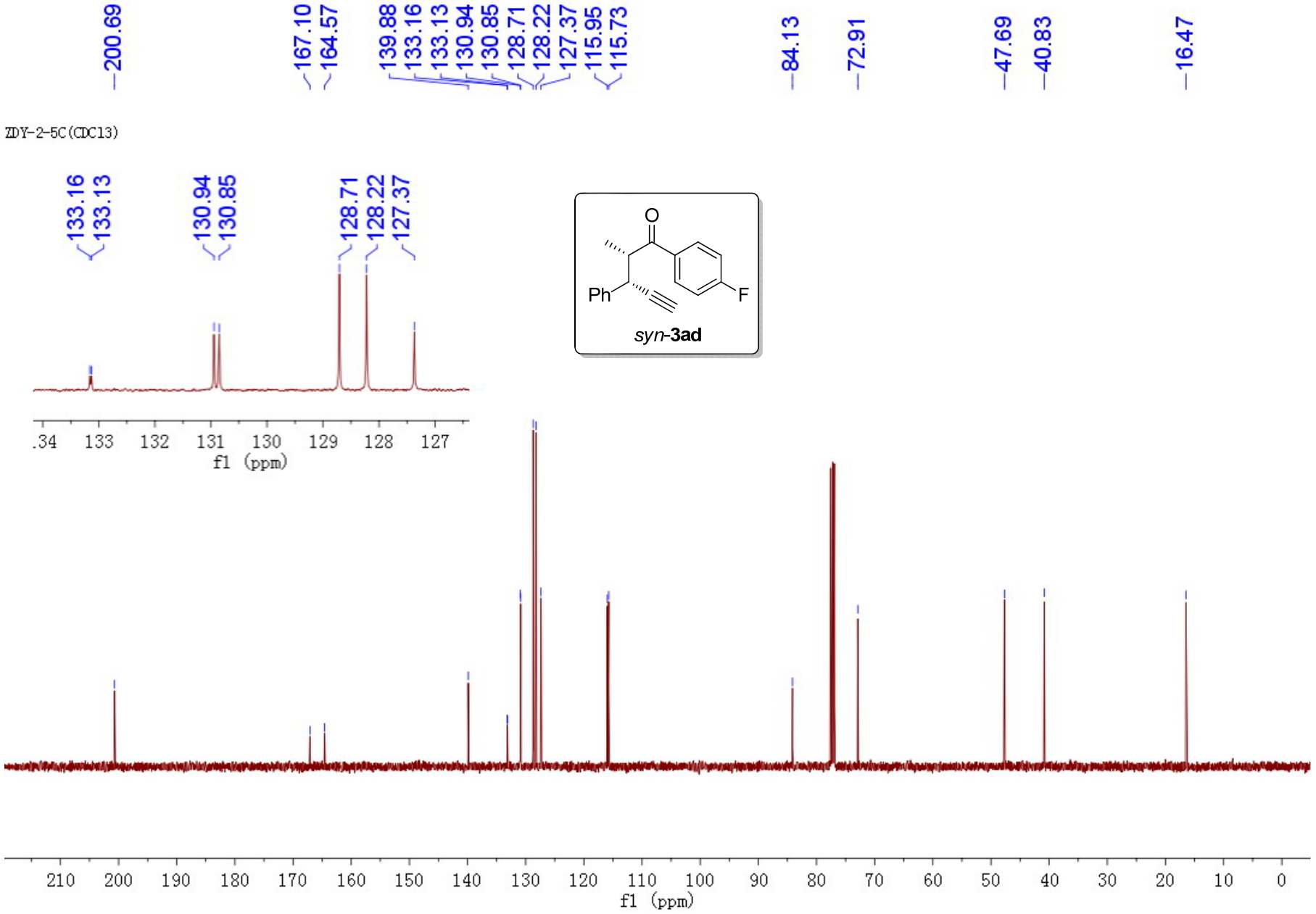
7.7607
7.3671
7.3485
7.2597
7.2482
7.2298
7.2106
7.1635
7.1452
7.1268
7.0527
7.0313
7.0098
4.1762
4.1703
4.1543
4.1484
3.8192
3.8018
3.7842
3.7807
3.7629
3.7456
2.3590
2.3529
1.4296
1.4124
ZDY-2-5C(CDCl3)
O
Ph
F
syn-3ad
2.03
2.08
1.99
1.09
2.01
1.00
1.03
0.99
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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130.85
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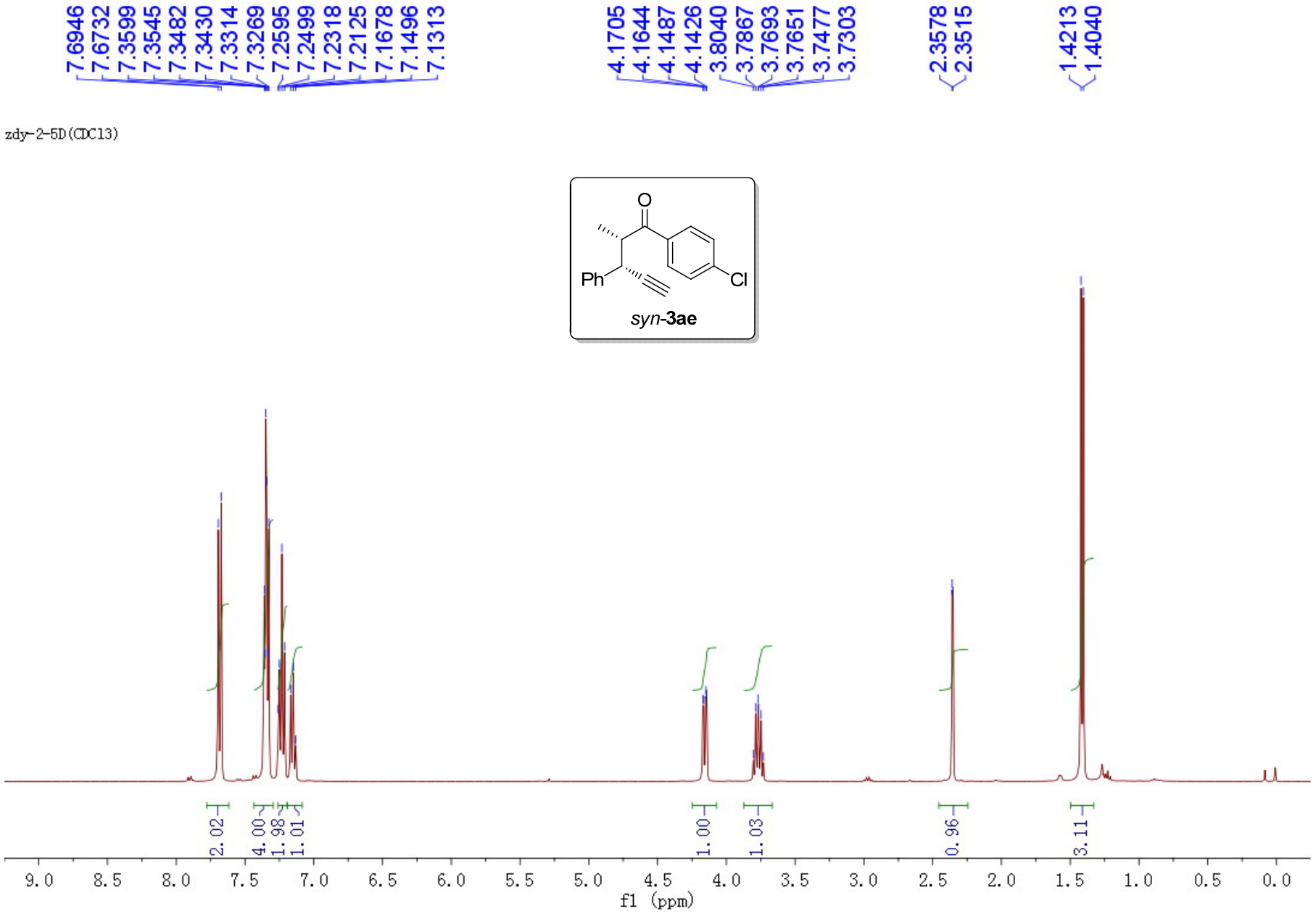
128.22
127.37
115.95
115.73
84.13
72.91
47.69
40.83
16.47
ZDY-2-5C(CDCl3)
133.16
133.13
130.94
130.85
128.71
128.22
127.37
O
Ph
F
syn-3ad
f1 (ppm)
f1 (ppm)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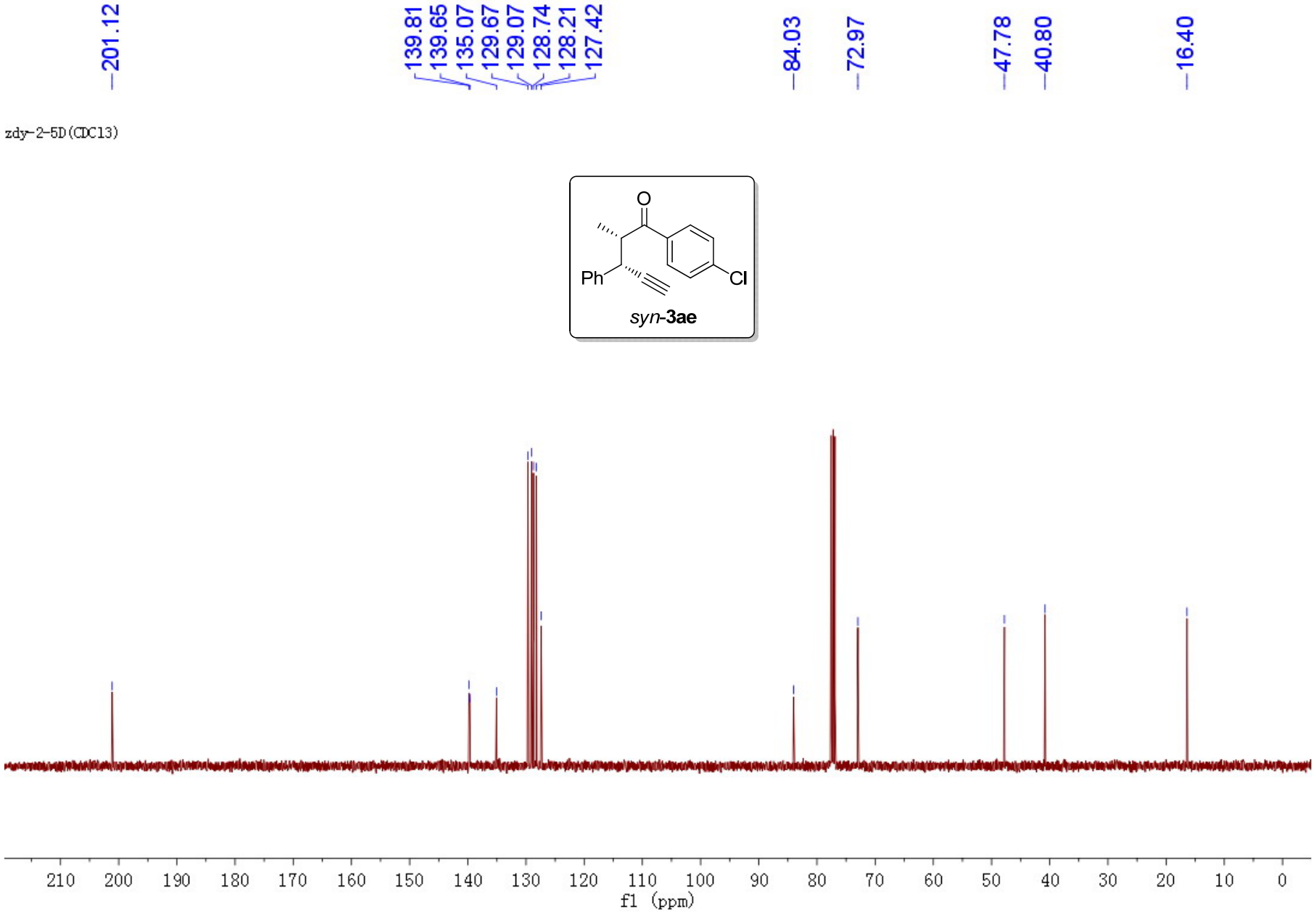
7.1678
7.1496
7.1313
4.1705
4.1644
4.1487
4.1426
3.8040
3.7867
3.7693
3.7651
3.7477
3.7303
2.3578
2.3515
1.4213
1.4040
zdy-2-5D(CDC13)
O
Ph
Cl
syn-3ae
2.02
4.00
1.98
1.01
1.00
1.03
0.96
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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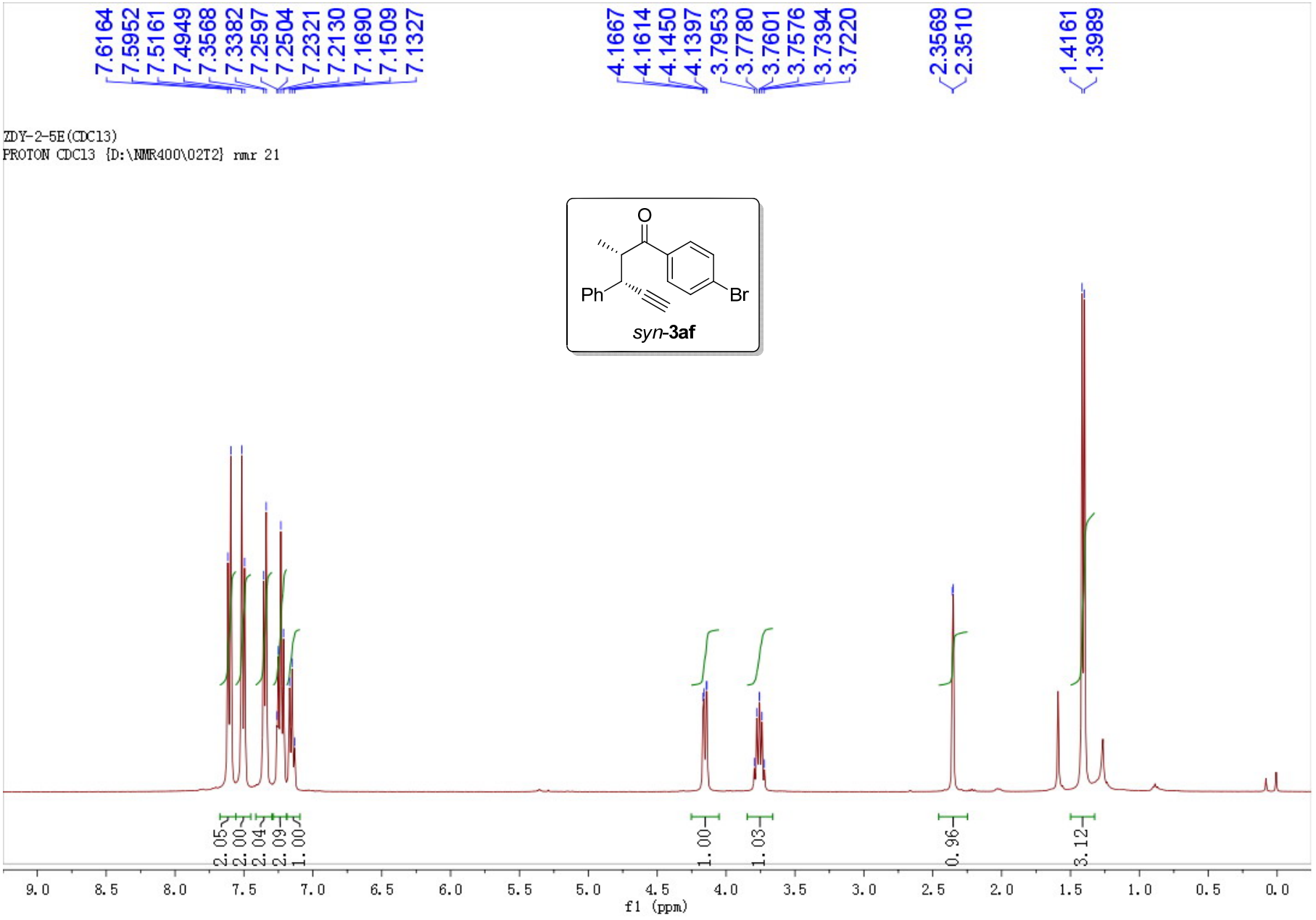
128.21
127.42
84.03
72.97
47.78
40.80
16.40
zdy-2-5D(CDCl3)
O
Ph
Cl
syn-3ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.2130
7.1690
7.1509
7.1327
4.1667
4.1614
4.1450
4.1397
3.7953
3.7780
3.7601
3.7576
3.7394
3.7220
2.3569
2.3510
1.4161
1.3989
ZDY-2-5E(CDCl3)
PROTON CDCl3 {D:\NMR400\02T2} rmr 21
O
Ph
Br
syn-3af
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2.00
2.04
2.09
1.00
1.00
1.03
0.96
3.12
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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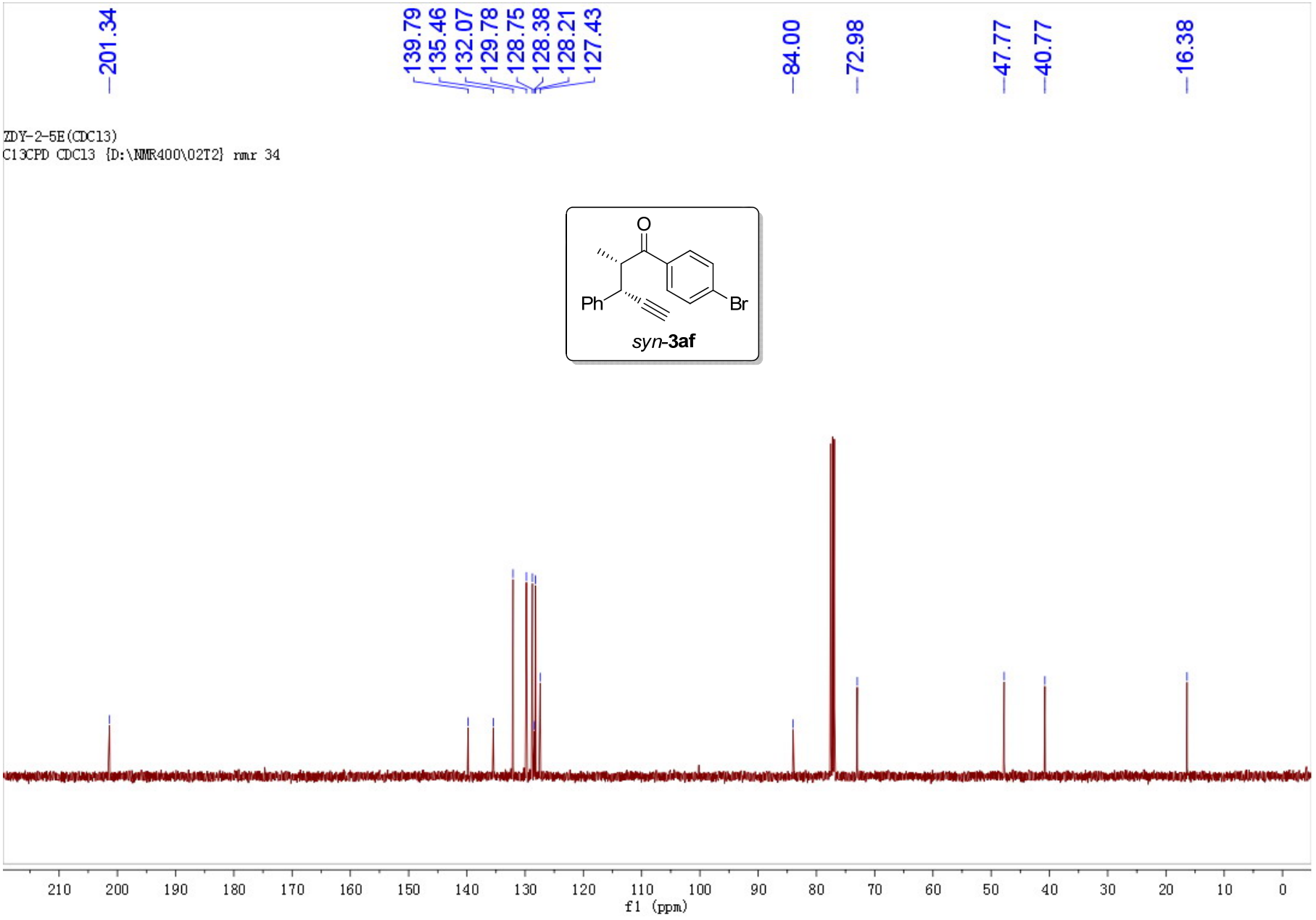
0.0
f1 (ppm)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128.21
127.43
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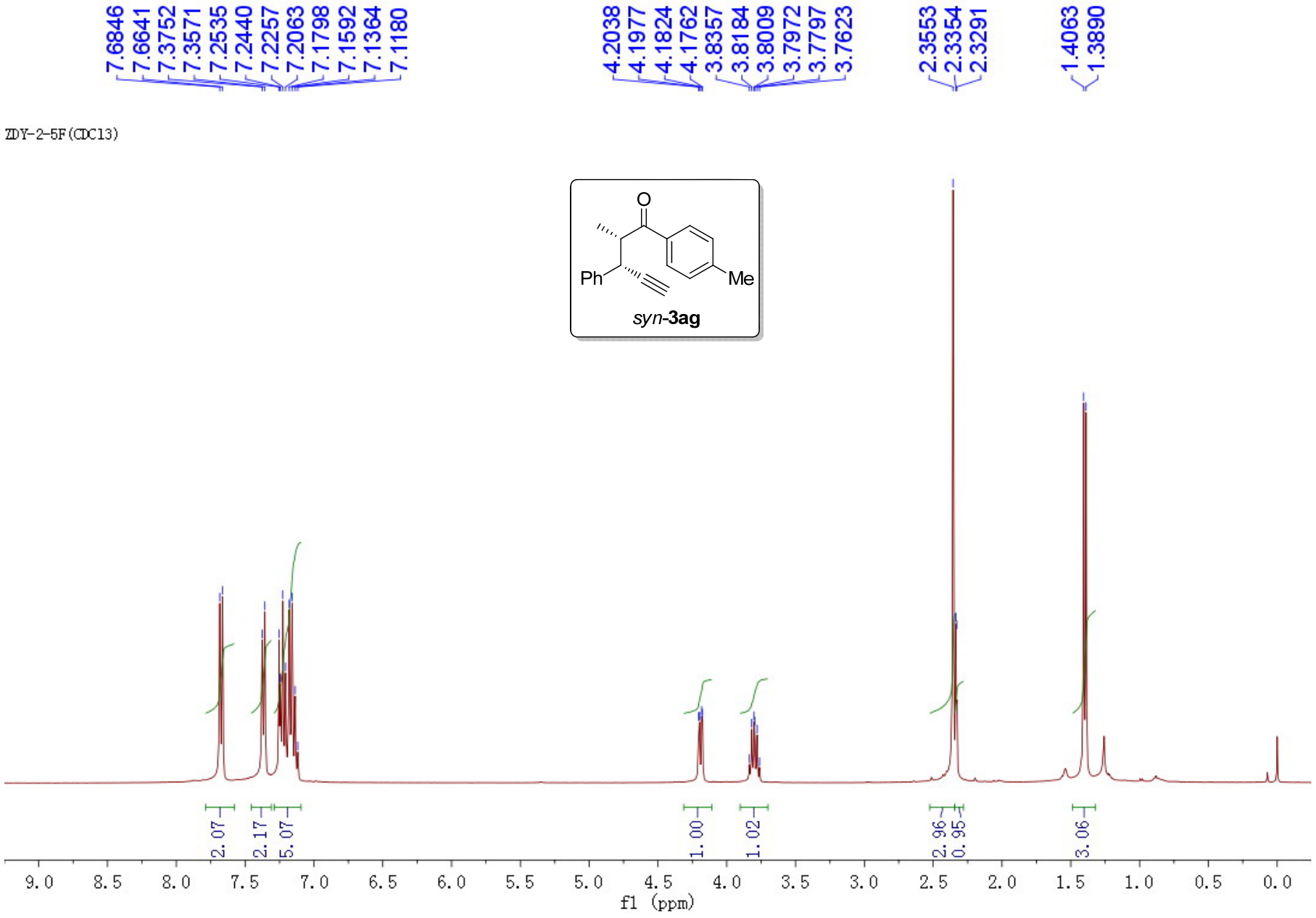
72.98
47.77
40.77
16.38
ZDY-2-5E(CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 34
O
Ph
Br
syn-3af
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.1180
4.2038
4.1977
4.1824
4.1762
3.8357
3.8184
3.8009
3.7972
3.7797
3.7623
2.3553
2.3354
2.3291
1.4063
1.3890
ZDY-2-5F(CDCl3)
O
Ph
Me
syn-3ag
2.07
2.17
5.07
1.00
1.02
2.96
0.95
3.06
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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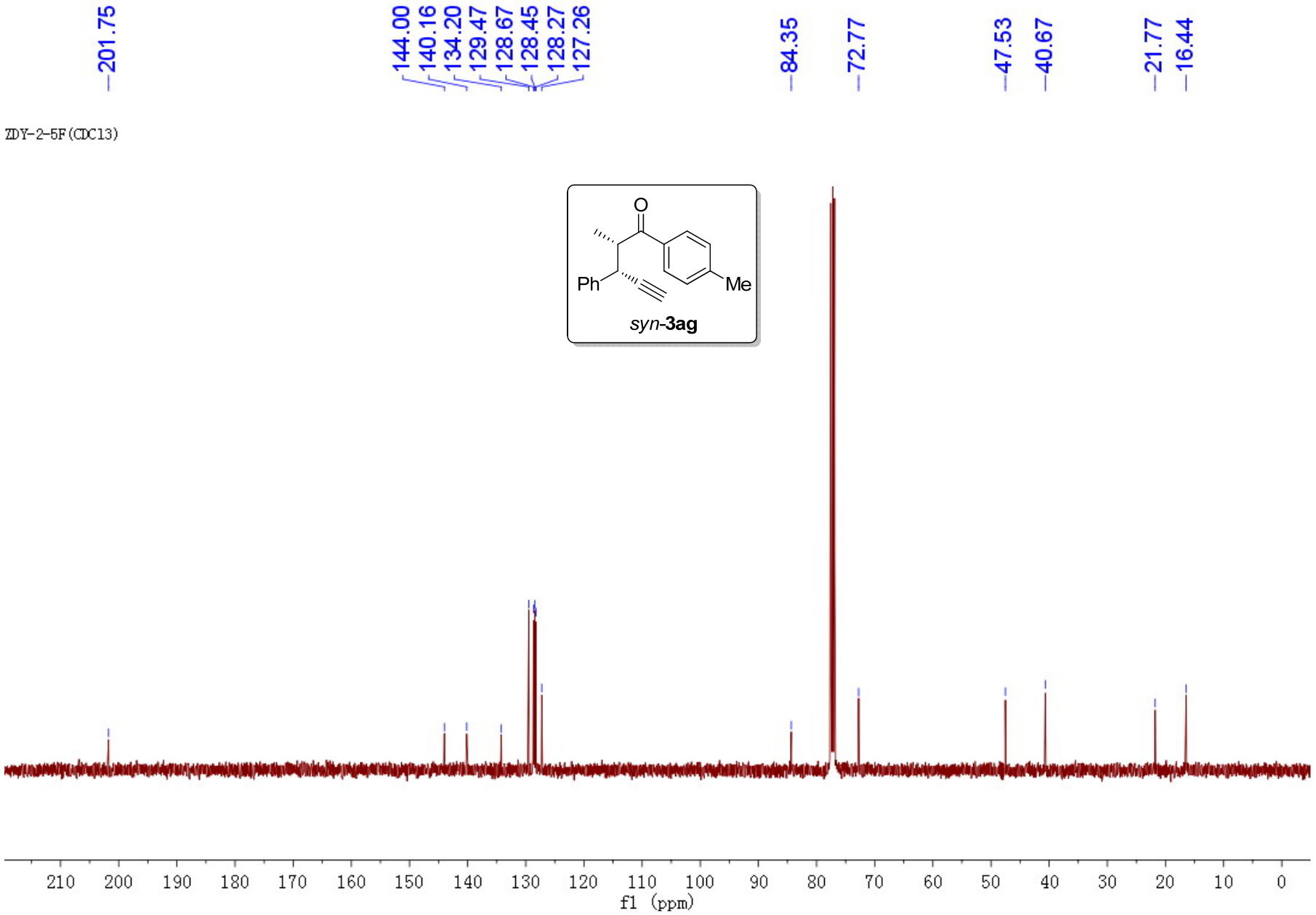
0.0
f1 (ppm)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128.27
127.26
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72.77
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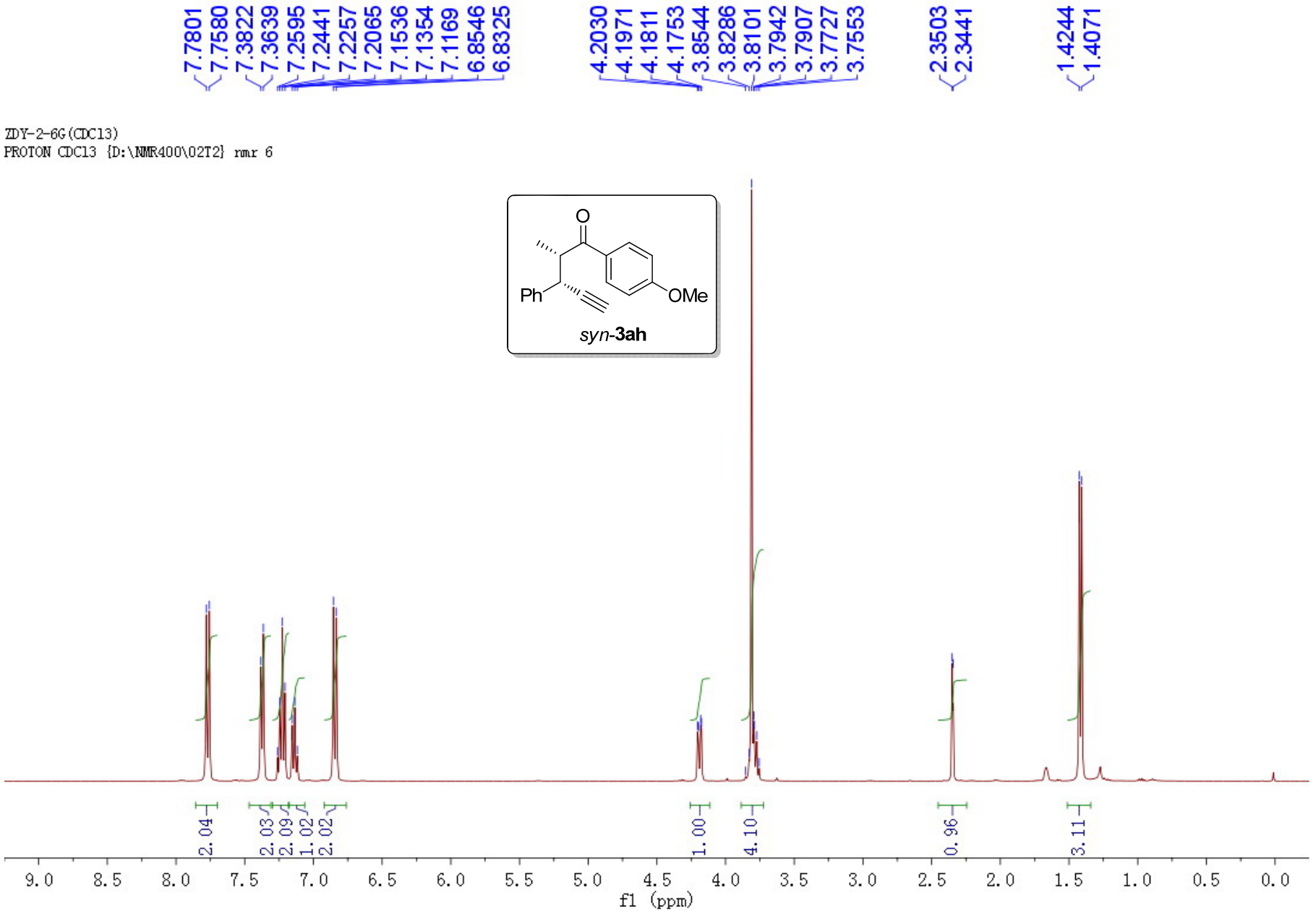
40.67
21.77
16.44
ZDY-2-5F(CDC13)
O
Ph
Me
syn-3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.1169
6.8546
6.8325
4.2030
4.1971
4.1811
4.1753
3.8544
3.8286
3.8101
3.7942
3.7907
3.7727
3.7553
2.3503
2.3441
1.4244
1.4071
ZDY-2-6G(CDCl3)
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O
Ph
OMe
syn-3ah
2.04
2.03
2.09
1.02
2.02
1.00
4.10
0.96
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
2.0
1.5
1.0
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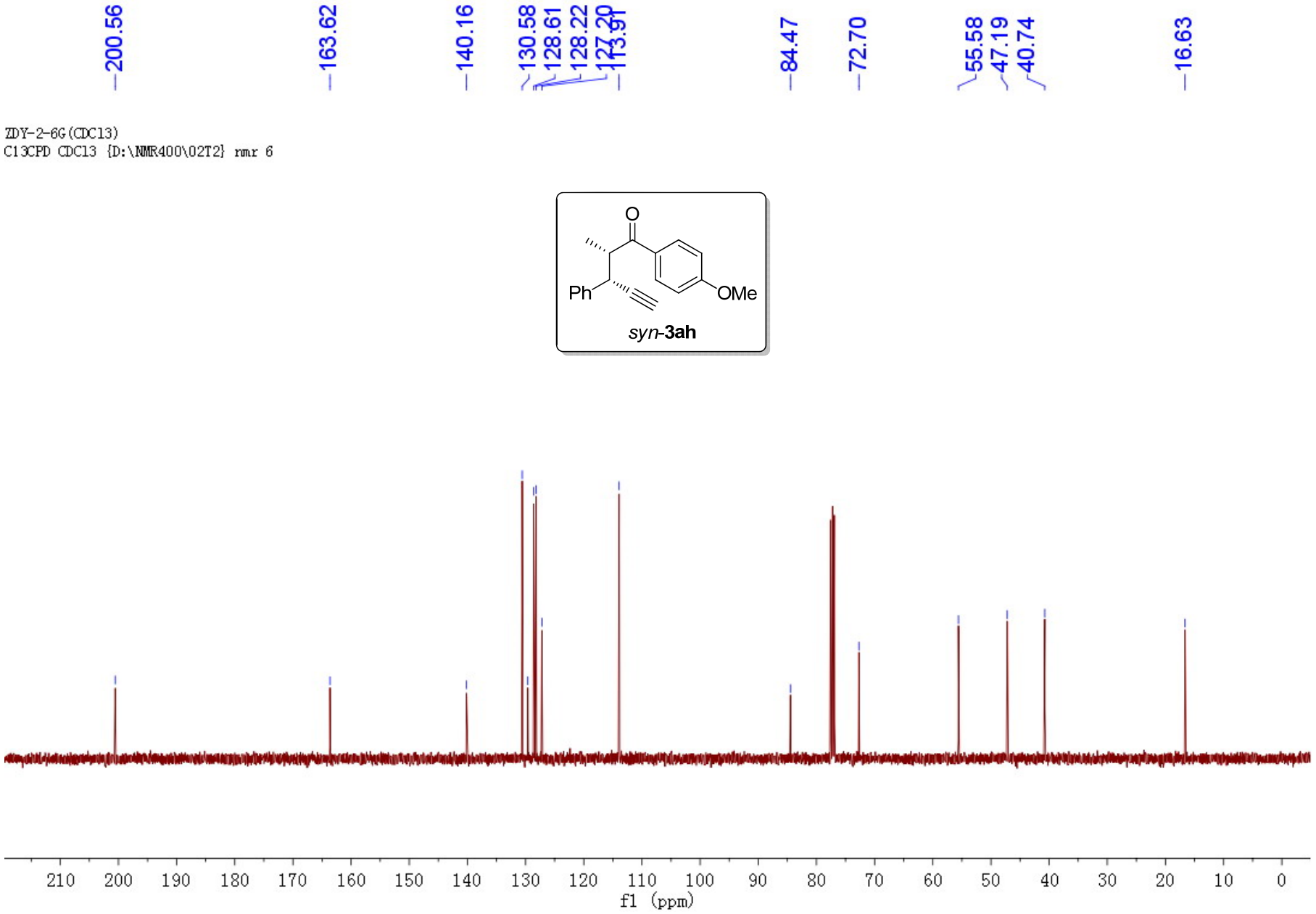
0.0
f1 (ppm)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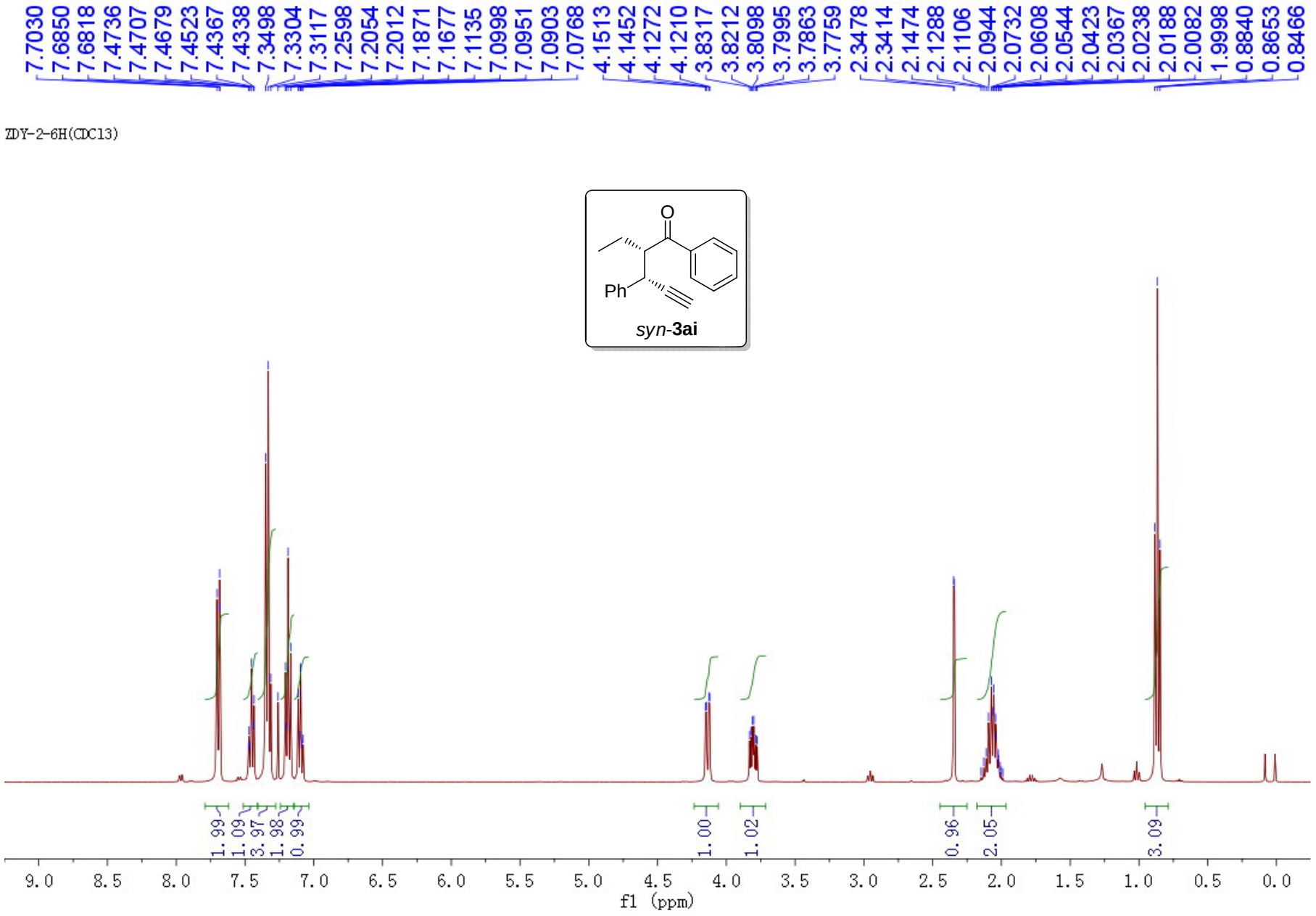
47.19
40.74
16.63
ZDY-2-6G(CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 6
O
Ph
OMe
syn-3ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.0903
7.0768
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4.1452
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4.1210
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3.7863
3.7759
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2.3414
2.1474
2.1288
2.1106
2.0944
2.0732
2.0608
2.0544
2.0423
2.0367
2.0238
2.0188
2.0082
1.9998
0.8840
0.8653
0.8466
ZDY-2-6H(CDCl3)
O
Ph
syn-3ai
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1.09
3.97
1.98
0.99
1.00
1.02
0.96
2.05
3.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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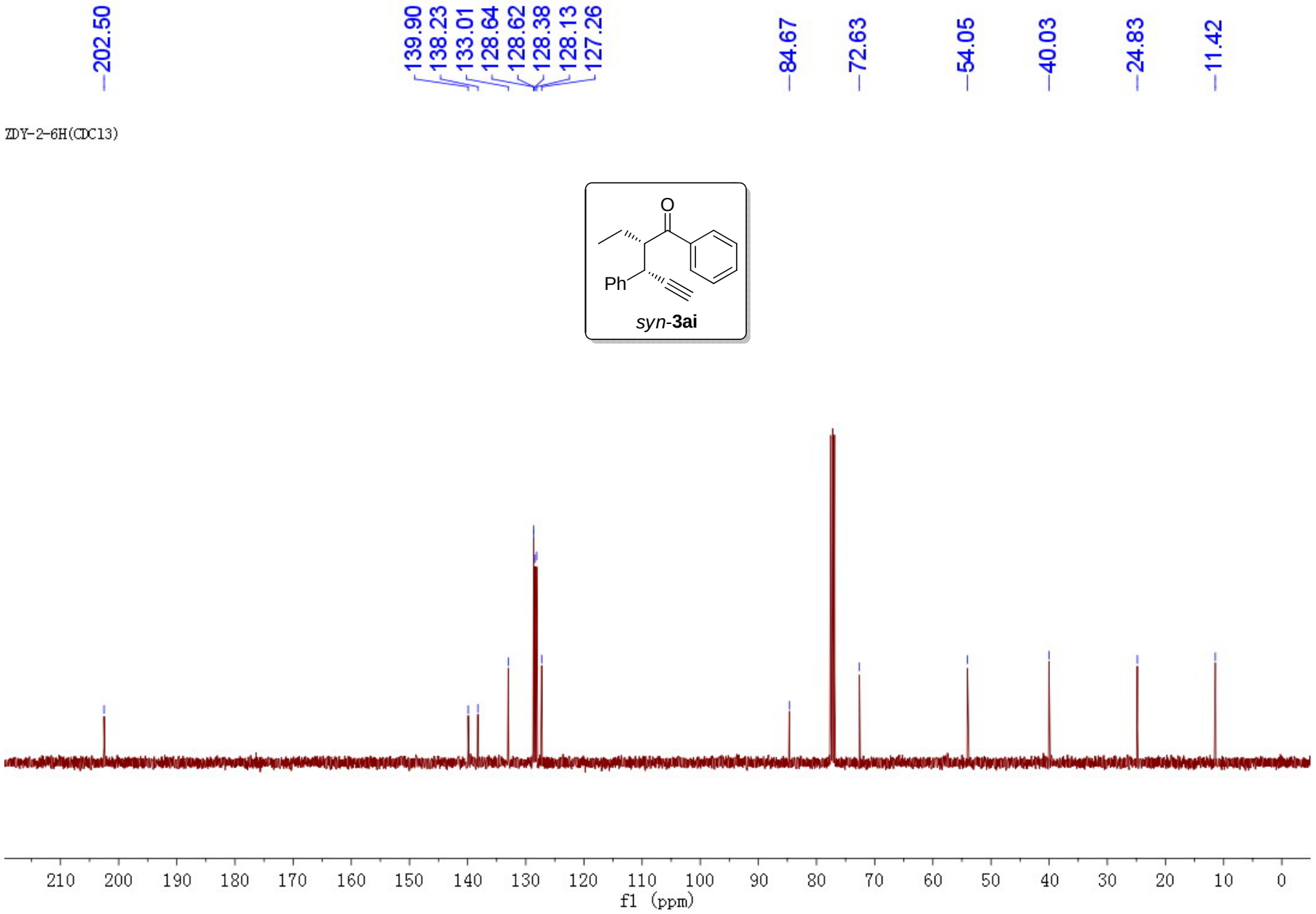
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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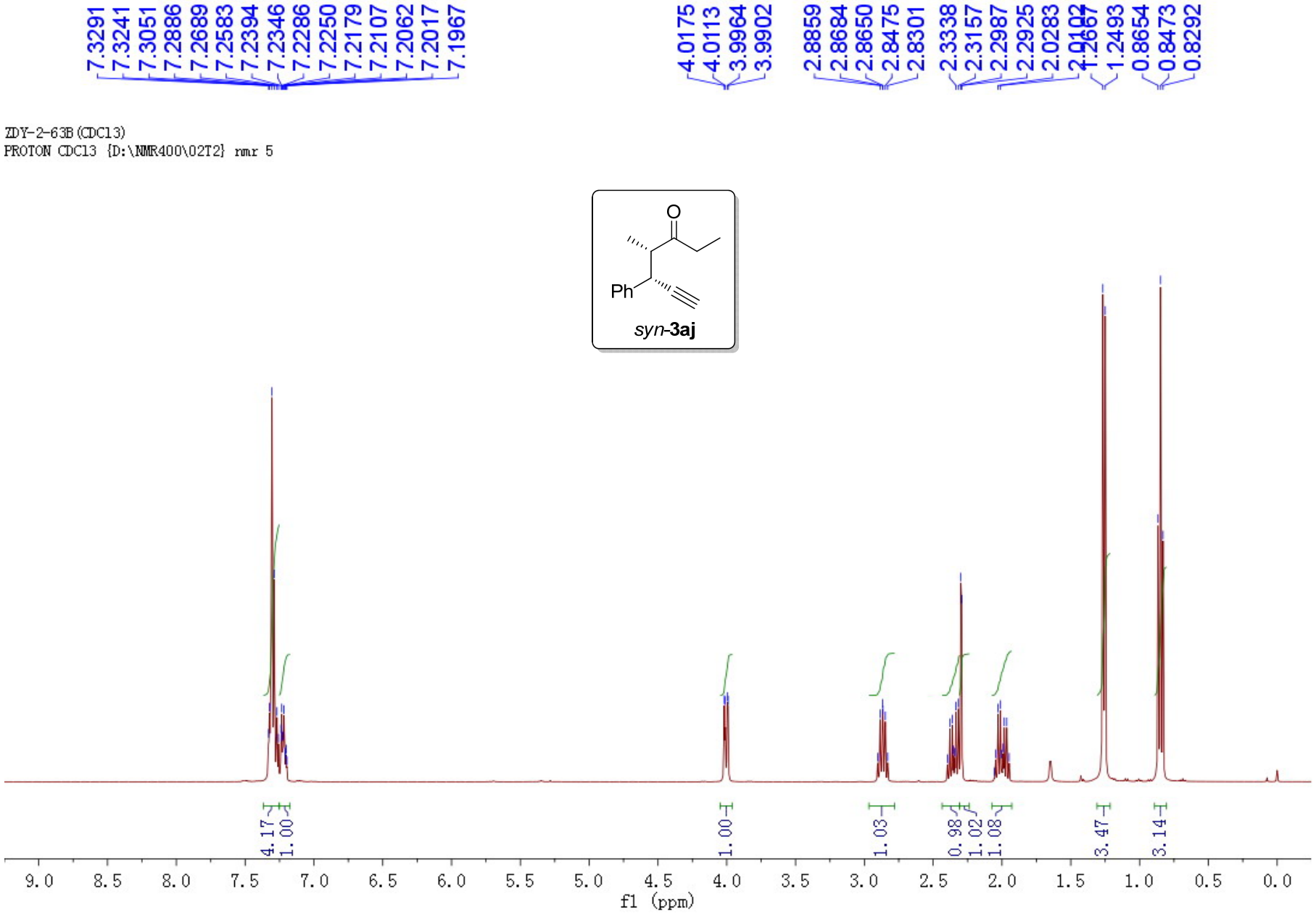
128.62
128.38
128.13
127.26
84.67
72.63
54.05
40.03
24.83
11.42
ZDY-2-6H(CDCl3)
O
Ph
syn-3ai
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.2107
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7.2017
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3.9902
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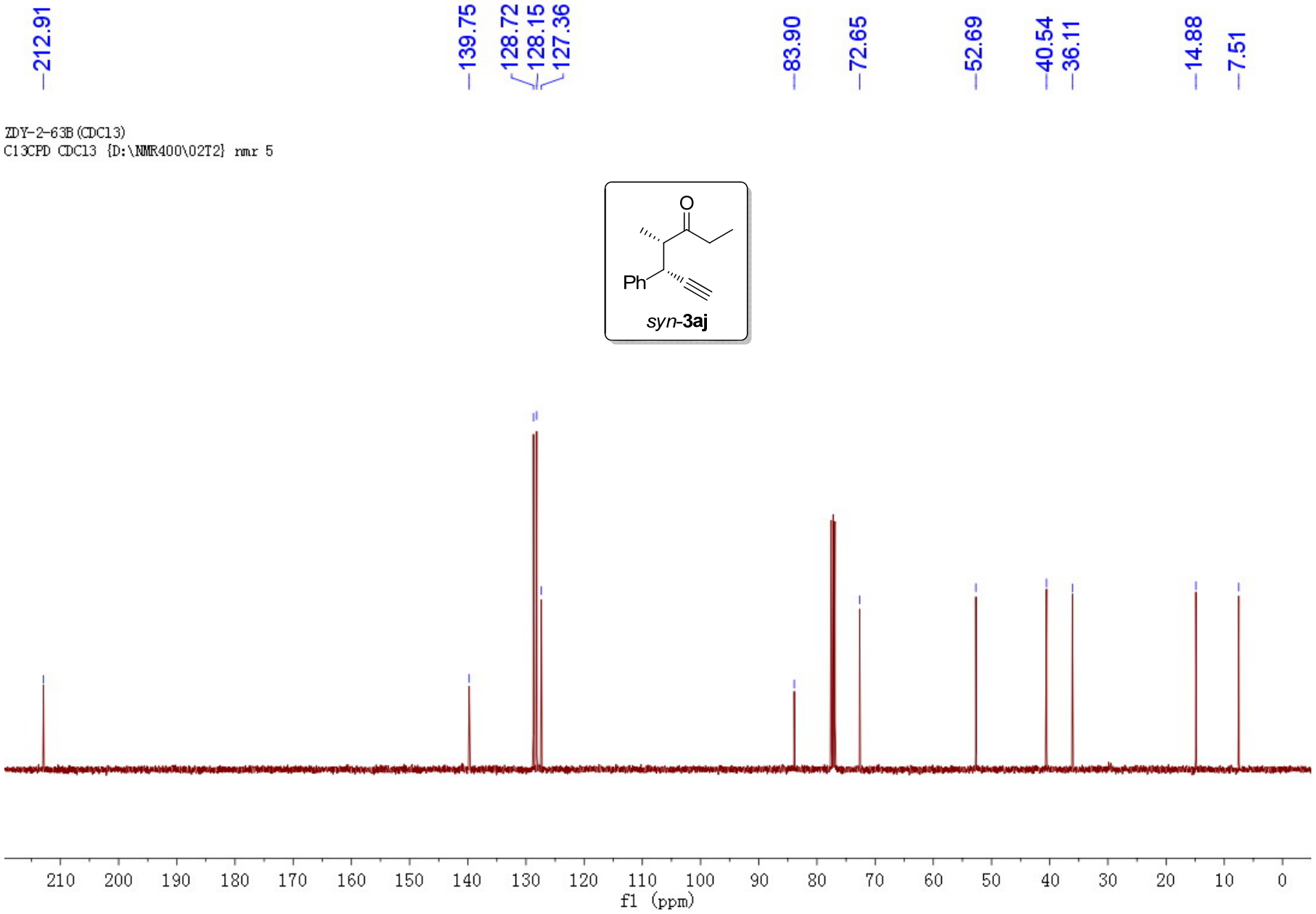
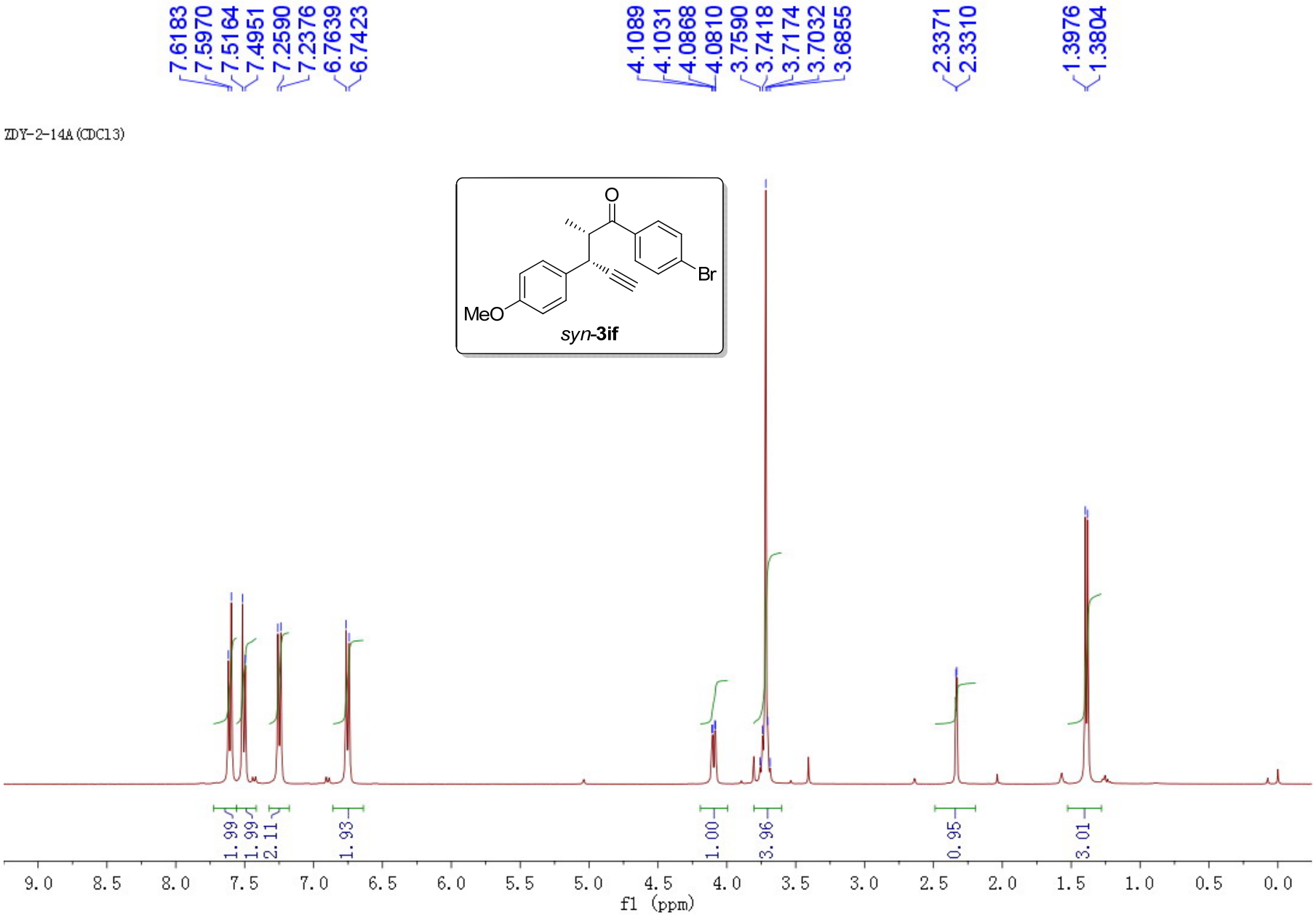
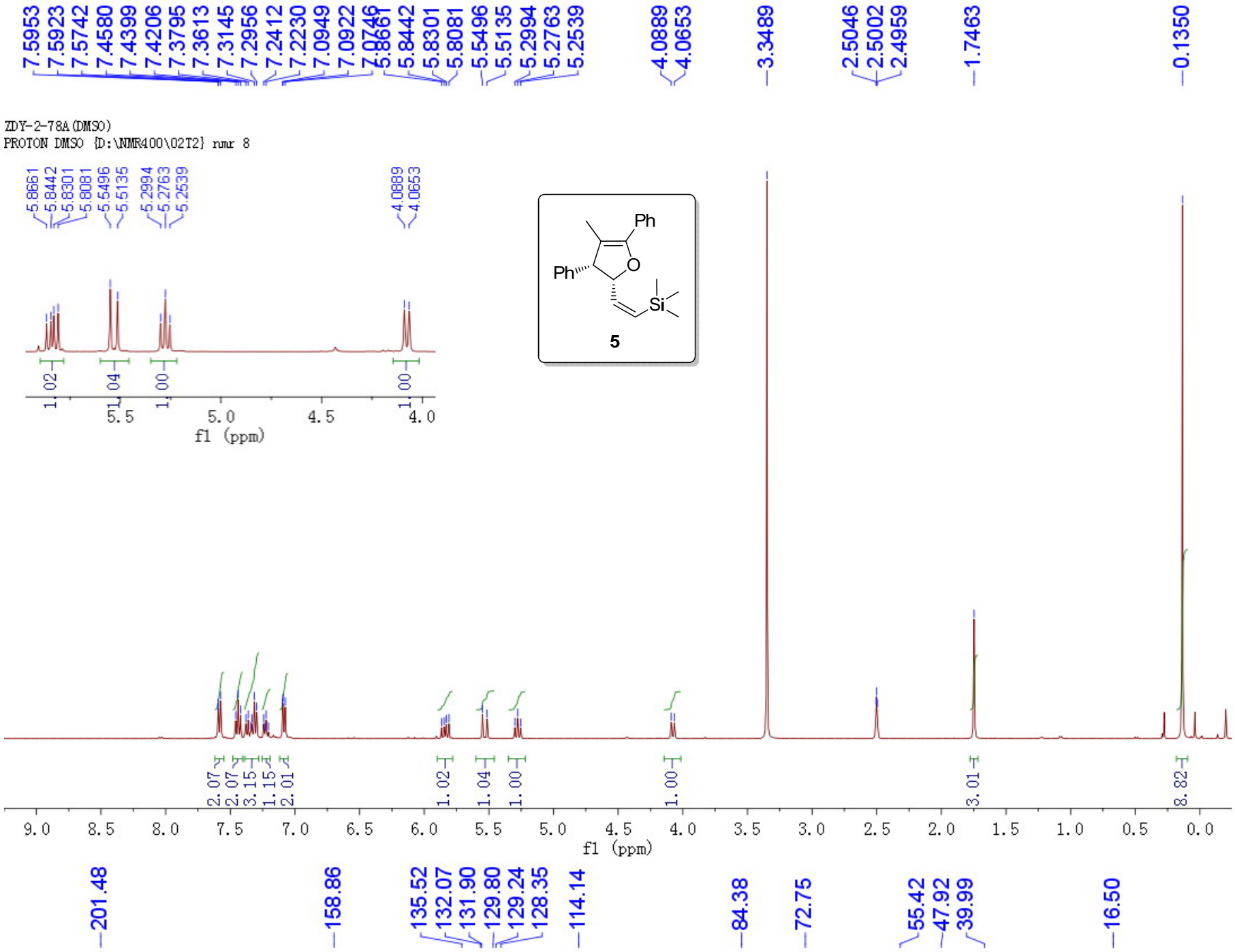
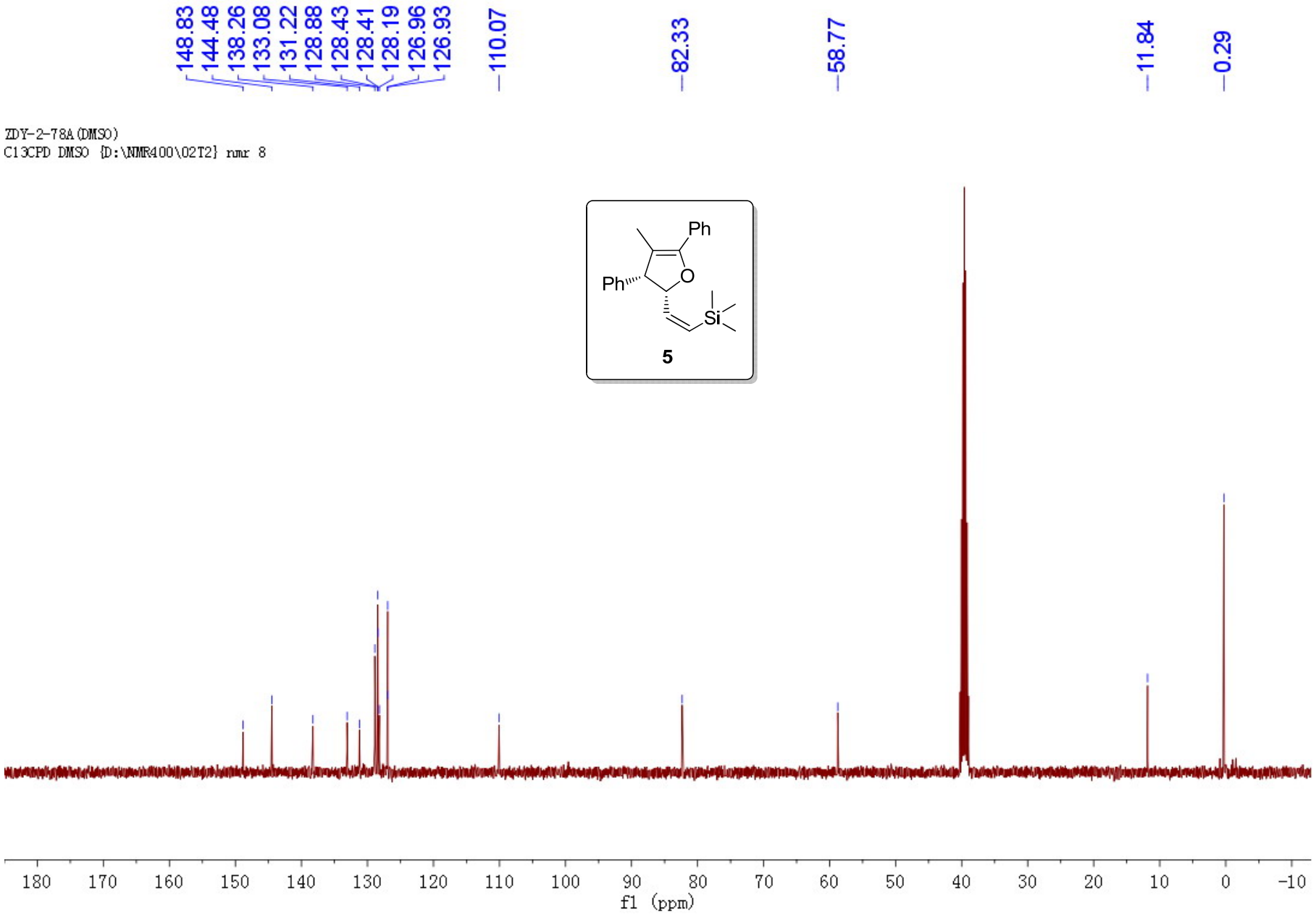
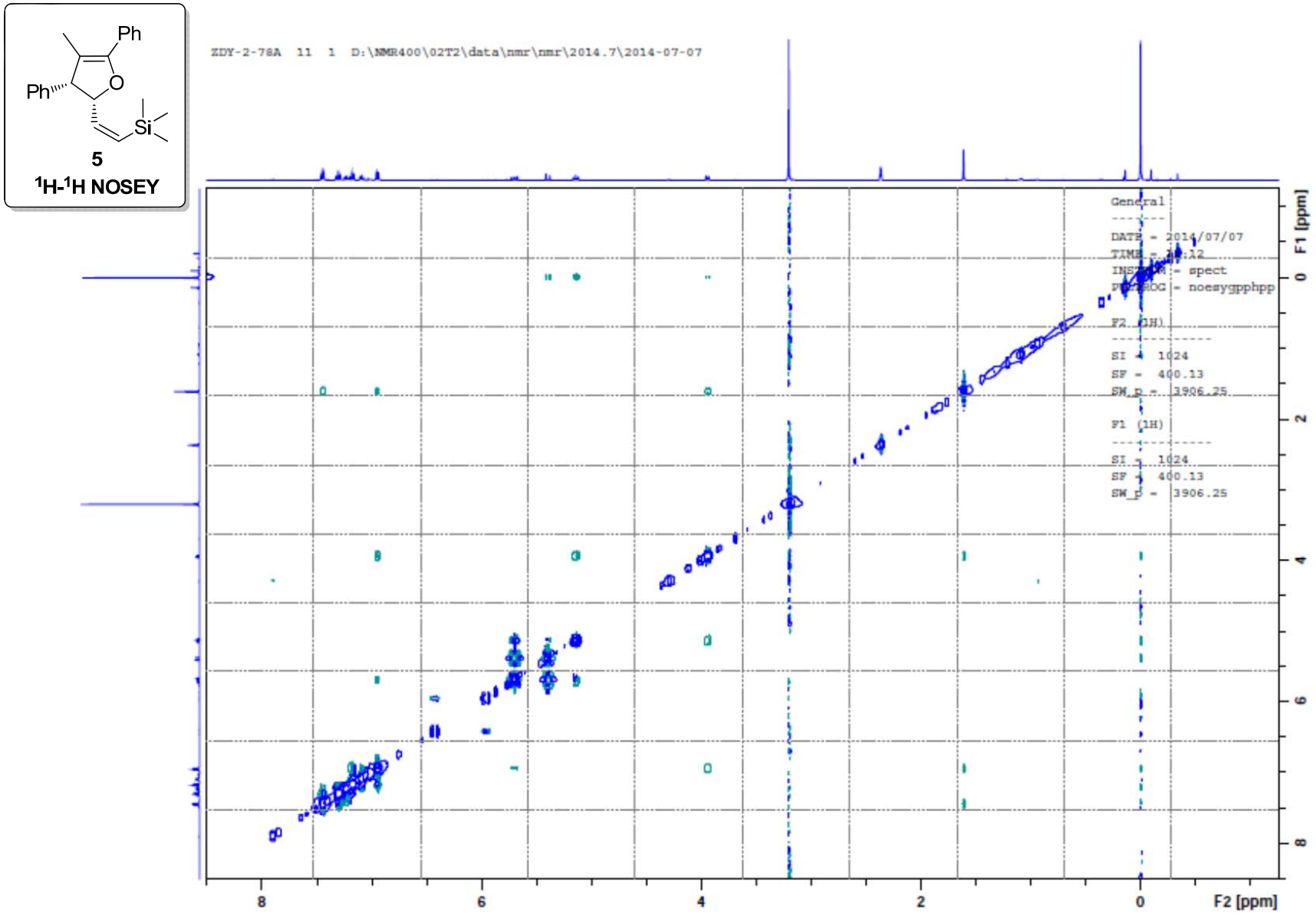
2.3338
2.3157
2.2987
2.2925
2.0283
1.2667
1.2493
0.8654
0.8473
0.8292
ZDY-2-63B(CDCl3)
PROTON CDCl3 {D:\NMR400\02T2} rmr 5
O
Ph
syn-3aj
4.17
1.00
1.00
1.03
0.98
1.02
1.08
3.47
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


212.91
139.75
128.72
128.15
127.36
83.90
72.65
52.69
40.54
36.11
14.88
7.51
ZDY-2-63B(CDCl3)
C13CPD CDCl3 {D:\NMR400\02T2} rmr 5
O
Ph
syn-3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.6183
7.5970
7.5164
7.4951
7.2590
7.2376
6.7639
6.7423
4.1089
4.1031
4.0868
4.0810
3.7590
3.7418
3.7174
3.7032
3.6855
2.3371
2.3310
1.3976
1.3804
ZDY-2-14A(CDCl3)
O
Br
MeO
syn-3if
1.99
1.99
2.11
1.93
1.00
3.96
0.95
3.01
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)


7.5953
7.5923
7.5742
7.4580
7.4399
7.4206
7.3795
7.3613
7.3145
7.2956
7.2412
7.2230
7.0949
7.0922
7.0746
5.8661
5.8442
5.8301
5.8081
5.5496
5.5135
5.2994
5.2763
5.2539
4.0889
4.0653
3.3489
2.5046
2.5002
2.4959
1.7463
0.1350
ZDY-2-78A(DMSO)
PROTON DMSO {D:\NMR400\02T2} rmr 8
Ph
Ph
O
Si
5
f1 (ppm)
f1 (ppm)
201.48
158.86
135.52
132.07
131.90
129.80
129.24
128.35
114.14
84.38
72.75
55.42
47.92
39.99
16.50


148.83
144.48
138.26
133.08
131.22
128.88
128.43
128.41
128.19
126.96
126.93
110.07
82.33
58.77
11.84
0.29
ZDY-2-78A(DMSO)
C13CPD DMSO {D:\NMR400\02T2} rmr 8
Ph
Ph
O
Si
5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
Ph
O
Si
5
^{1}H-^{1}H NOSEY
ZDY-2-78A 11 1 D:\NMR400\02T2\data\nmr\nmr\2014.7\2014-07-07
General
DATE = 2014/07/07
INSTRUM = spect
PULPROG = noesygpphpp
F2 (1H)
SI = 1024
SF = 400.13
SW_p = 3906.25
F1 (1H)
SI = 1024
SF = 400.13
SW_p = 3906.25
F1 [ppm]
F2 [ppm]
0
2
4
6
8