

Trialkyl Methanetricarboxylate as Dialkyl Malonate

Surrogate in Copper-catalyzed Enantioselective

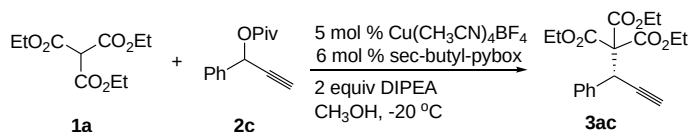
Propargylic Substitution

Guanxin Huang, Cang Cheng, Luo Ge, Beibei Guo, Long Zhao and Xiaoyu Wu*

General Information	S1
General Procedure for Copper-catalyzed Enantioselective Propargylic Substitution ---	S1-2
Screening of bases and solvents -----	S2
¹H NMR, ¹³C NMR, MS, Optical rotation and HPLC data of 3	S2-8
General procedure for decarboxylation of 3 -----	S8-9
¹H NMR, ¹³C NMR, MS, Optical rotation and HPLC data of 4	S9-11
Determination of absolute stereochemistry of 3ac by correlation	S11-12
General procedure for preparation of propargylic alcohol derivatives -----	S12-13
¹H NMR, ¹³C NMR and MS data of propargylic alcohol derivatives	S13-16
¹H NMR, ¹³C NMR and HPLC spectra of isolated compounds -----	S17-85

General Information: Thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates visualized with UV light and/or by staining with ethanolic phosphomolybdic acid (PMA) or iodine. Flash column chromatography was performed on silica gel (300-400 mesh). NMR spectra were recorded on Bruker AM500 (500 MHz). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. Optical rotations were taken on JASCO P1030. High-resolution mass spectra were recorded on Bruker ApeXIII 7.0 TESLA FTMS. Enantiomeric excesses were determined by chiral HPLC using a Shimadzu instrument.

General Procedure for Copper-catalyzed Enantioselective Propargylic Substitution:



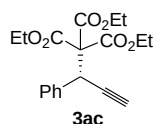
Under an atmosphere of nitrogen, a 25 mL dry Schlenk flask was placed with $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ (3.1 mg, 0.01 mmol) and ligand **A** (3.95 mg, 0.012 mmol). Anhydrous MeOH (0.5 mL) was added, and the mixture was magnetically stirred at $20\text{ }^\circ\text{C}$ for 15 min. Then the mixture was kept at $-20\text{ }^\circ\text{C}$ while stirring. Next, a solution of 1-phenylprop-2-ynyl pivalate **2c** (0.24 mmol), triethyl methanetricarboxylate **1a** (0.2 mmol) and diisopropylethylamine (0.07 mL, 0.4 mmol) in MeOH (0.5 mL) were added dropwise. The reaction flask was kept at $-20\text{ }^\circ\text{C}$ for 20 h. After **1a** was completely consumed as monitored by TLC, H_2O (10 mL) was added to quench the reaction. The resulted mixture was then extracted three times with diethyl ether (10 mL $\times$ 3). The combined organic layer was dried over Na_2SO_4 . After evaporation of the volatile solvent under reduced pressure, the residue was purified by flash chromatography on silica gel to afford pure **3ac** (66 mg, 0.19 mmol) as a pale yellow oil in a yield of 95%.

Screening of bases and solvents^a

entry	base	solvent	time (h)	yield (%) ^b	ee (%) ^c
1	DIPEA	MeOH	20	96	90
2	TEA	MeOH	30	89	82
3	DBU	MeOH	20	80	67
4 ^d	DIPEA	THF	48	-	-
5 ^d	DIPEA	DCM	48	-	-
6 ^d	DIPEA	Toluene	48	-	-
7	DIPEA	EtOH	40	43	54

^aGeneral conditions: **1a** (0.2 mmol), **2c** (0.24 mmol), Copper salt (10 mol %), ligand (12 mol %) and base (2 equiv) in solvent (1.5 mL). ^bIsolated yield. ^cDetermined by chiral HPLC analysis.

^dNo formation of **3ac** as determined by TLC.



(*R*)-triethyl 2-phenylbut-3-yn-1,1,1-tricarboxylate **3ac**: faint yellow oil, actual mass 66 mg, yield 95%.

¹H NMR (500 MHz, CDCl₃): δ 7.61-7.53 (m, 2H), 7.32-7.21 (m, 3H), 4.80 (s, 1H), 4.25-4.10 (m, 6H), 2.35 (s, 1H), 1.30-1.15 (m, 9H).

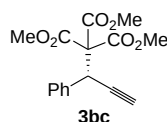
¹³C NMR (125 MHz, CDCl₃): δ 165.1, 135.4, 130.3, 128.0, 127.8, 82.0, 72.7, 69.9, 62.2, 40.7, 13.8.

HRMS (ESI) calcd. for (C₁₉H₂₂NaO₆)⁺ 369.1309, found 369.1317.

[α]_D²⁶ +18.21 (c 0.43, CHCl₃).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm):

t_R = 16.90 min (major enantiomer), t_R = 18.54 min (minor enantiomer).



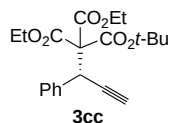
(*R*)-trimethyl 2-phenylbut-3-yn-1,1,1-tricarboxylate **3bc**: faint yellow oil, actual mass 53 mg, yield 87%. ¹H NMR (500 MHz, CDCl₃): δ 7.58-7.51 (m, 2H), 7.33-7.23 (m, 3H), 4.82 (m, 1H), 3.72 (s, 9H), 2.38 (s, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 165.4, 135.1, 130.1, 128.2, 127.9, 81.8, 72.8, 70.1, 53.1, 40.9.

HRMS (ESI) calcd. for (C₁₆H₁₆NaO₆)⁺ 327.0839, found 327.0844.

[α]_D²⁴ +9.15 (c 0.20, CHCl₃).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm):
 t_R = 16.06 min (major enantiomer), t_R = 26.84 min (minor enantiomer).



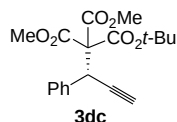
(*R*)-1-tert-butyl 1,1-diethyl 2-phenylbut-3-yn-1,1,1-tricarboxylate **3cc**: faint yellow oil, actual mass 65 mg, yield 87%. ^1H NMR (500 MHz, CDCl_3): δ 7.64-7.57 (m, 2H), 7.31-7.20 (m, 3H), 4.73 (s, 1H), 4.24-4.08 (m, 4H), 2.34 (s, 1H), 1.40 (s, 9H), 1.30-1.15 (m, 6H).

^{13}C NMR (125 MHz, CDCl_3): δ 165.42, 165.41, 163.8, 135.8, 130.5, 127.9, 127.8, 83.5, 82.4, 72.6, 70.2, 62.0, 61.9, 40.6, 27.6, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{21}\text{H}_{26}\text{NaO}_6)^+$ 397.1622, found 397.1630.

$[\alpha]_D^{24} +9.76$ (c 0.24, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm):
 t_R = 15.74 min (minor enantiomer), t_R = 16.91 min (major enantiomer).



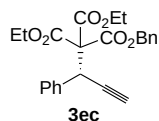
(*R*)-1-tert-butyl 1,1-dimethyl 2-phenylbut-3-yn-1,1,1-tricarboxylate **3dc**: faint yellow oil, actual mass 60 mg, yield 86%. ^1H NMR (500 MHz, CDCl_3): δ 7.61-7.55 (m, 2H), 7.35-7.28 (m, 3H), 4.75 (s, 1H), 3.72 (s, 6H), 2.36 (s, 1H), 1.41 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 165.96, 165.91, 163.6, 135.5, 130.3, 128.0, 127.9, 83.8, 82.2, 72.7, 70.6, 52.8, 40.6, 27.6.

HRMS (ESI) calcd. for $(\text{C}_{19}\text{H}_{22}\text{NaO}_6)^+$ 369.1309, found 369.1315.

$[\alpha]_D^{24} +12.05$ (c 0.10, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm):
 t_R = 18.77 min (major enantiomer), t_R = 23.80 min (minor enantiomer).



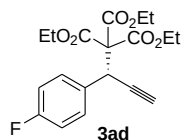
(*R*)-1-benzyl 1,1-diethyl 2-phenylbut-3-yn-1,1,1-tricarboxylate **3ec**: faint yellow oil liquid, actual mass 69 mg, yield 85%. ^1H NMR (500 MHz, CDCl_3): δ 7.60-7.52 (m, 2H), 7.40-7.22 (m, 7H), 5.20-5.10 (m, 2H), 4.83 (s, 1H), 4.22-4.05 (m, 6H), 2.33 (s, 1H), 1.17-1.08 (m, 6H).

^{13}C NMR (125 MHz, CDCl_3): δ 164.91, 164.88, 135.3, 134.8, 130.3, 128.45, 128.40, 128.1, 127.9, 81.9, 72.9, 69.9, 67.8, 62.3, 40.8, 13.7.

HRMS (ESI) calcd. for $(\text{C}_{24}\text{H}_{24}\text{NaO}_6)^+$ 431.1465, found 431.1469.

$[\alpha]_D^{24} +3.84$ (c 0.78, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm):
 t_R = 19.69 min (minor enantiomer), t_R = 22.18 min (major enantiomer).



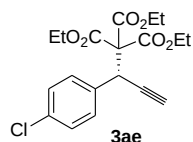
(*R*)-triethyl 2-(4-fluorophenyl)but-3-yn-1,1,1-tricarboxylate **3ad**: faint yellow oil, actual mass 67 mg, yield 92%. ^1H NMR (500 MHz, CDCl_3): δ 7.61-7.53 (m, 2H), 7.00-6.91 (m, 2H), 4.77 (s, 1H), 4.26-4.11 (m, 6H), 2.36 (s, 1H), 1.28-1.15 (m, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 164.9, 162.5(d, $J = 246$ Hz), 132.2 (d, $J = 8.3$ Hz), 131.2 (d, $J = 2.8$ Hz), 114.7 (d, $J = 21$ Hz), 81.8, 73.0, 69.8, 62.3, 39.9, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{19}\text{H}_{21}\text{FNaO}_6)^+$ 387.1214, found 387.1211.

$[\alpha]_{\text{D}}^{26} +15.5$ (c 0.23, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 19 : 1, Flow rate = 0.8 mL/min, $\lambda = 220$ nm): $t_{\text{R}} = 15.41$ min (major enantiomer), $t_{\text{R}} = 18.68$ min (minor enantiomer).



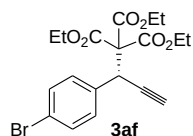
(*R*)-triethyl 2-(4-chlorophenyl)but-3-yn-1,1,1-tricarboxylate **3ae**: faint yellow oil, actual mass 71 mg, yield 94%. ^1H NMR (500 MHz, CDCl_3): δ 7.57-7.50 (m, 2H), 7.27-7.21 (m, 2H), 4.76 (s, 1H), 4.26-4.12 (m, 6H), 2.36 (s, 1H), 1.25-1.15 (m, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 164.9, 134.1, 134.0, 131.9, 128.0, 81.6, 73.1, 69.7, 62.4, 40.1, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{19}\text{H}_{21}\text{ClNaO}_6)^+$ 403.0919, found 403.0926.

$[\alpha]_{\text{D}}^{26} +10.01$ (c 0.24, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, $\lambda = 220$ nm): $t_{\text{R}} = 19.98$ min (major enantiomer), $t_{\text{R}} = 22.42$ min (minor enantiomer).



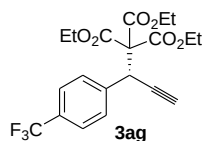
(*R*)-triethyl 2-(4-bromophenyl)but-3-yn-1,1,1-tricarboxylate **3af**: faint yellow oil, actual mass 81 mg, yield 96%. ^1H NMR (500 MHz, CDCl_3): δ 7.49-7.42 (m, 2H), 7.42-7.35 (m, 2H), 4.73 (s, 1H), 4.25-4.10 (m, 6H), 2.36 (s, 1H), 1.23-1.15 (m, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 164.9, 134.5, 132.2, 130.9, 122.3, 81.5, 73.1, 69.7, 62.4, 40.1, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{19}\text{H}_{21}\text{BrNaO}_6)^+$ 447.0414, found 447.0419.

$[\alpha]_{\text{D}}^{29} +17.05$ (c 0.46, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, $\lambda = 220$ nm): $t_{\text{R}} = 24.17$ min (minor enantiomer), $t_{\text{R}} = 25.46$ min (major enantiomer).



(*R*)-triethyl 2-(4-(trifluoromethyl)phenyl)but-3-yn-1,1,1-tricarboxylate **3ag**: faint yellow oil, actual mass 75 mg, yield 90%. ^1H NMR (500 MHz, CDCl_3): δ 7.76-7.72 (m, 2H), 7.60-7.54 (m, 2H), 4.84 (s, 1H), 4.28-4.12 (m, 6H), 2.39 (s, 1H), 1.25-1.19 (m, 9H).

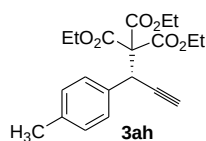
^{13}C NMR (125 MHz, CDCl_3): δ 164.8, 139.6, 130.9, 130.8, 130.3 (q, $J = 31$ Hz), 124.7 (q, $J = 3.6$ Hz), 124.0 (q, $J = 270$ Hz), 81.2, 73.4, 69.7, 62.4, 40.4, 13.7.

HRMS (ESI) calcd. for $(\text{C}_{20}\text{H}_{21}\text{F}_3\text{NaO}_6)^+$ 437.1182, found 437.1188.

$[\alpha]_{\text{D}}^{26} +9.77$ (c 0.22, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, $\lambda = 220$ nm):

$t_{\text{R}} = 16.53$ min (minor enantiomer), $t_{\text{R}} = 18.74$ min (major enantiomer).



(*R*)-triethyl 2-*p*-tolylbut-3-yn-1,1,1-tricarboxylate **3ah**: faint yellow oil liquid, actual mass 64 mg, yield 89%. ^1H NMR (500 MHz, CDCl_3): δ 7.44 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 4.76 (s, 1H), 4.26-4.11 (m, 6H), 2.36 (s, 1H), 2.28 (s, 3H), 1.25-1.17 (m, 9H).

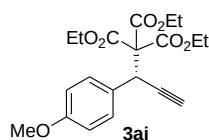
^{13}C NMR (125 MHz, CDCl_3): δ 165.1, 137.8, 132.4, 130.2, 128.6, 82.2, 72.6, 69.9, 62.2, 40.4, 21.1, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{20}\text{H}_{24}\text{NaO}_6)^+$ 383.1465, found 383.1472.

$[\alpha]_{\text{D}}^{26} +14.05$ (c 0.26, CHCl_3).

HPLC (Phenomenex cellulose-1, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, $\lambda = 220$ nm):

$t_{\text{R}} = 14.93$ min (minor enantiomer), $t_{\text{R}} = 17.39$ min (major enantiomer).



(*R*)-triethyl 2-(4-methoxyphenyl)but-3-yn-1,1,1-tricarboxylate **3ai**: faint yellow oil, actual mass 70 mg, yield 94%. ^1H NMR (500 MHz, CDCl_3): δ 7.52-7.45 (m, 2H), 6.83-6.76 (m, 2H), 4.74 (s, 1H), 4.25-4.11 (m, 6H), 3.76 (s, 3H), 2.34 (s, 1H), 1.25-1.17 (m, 9H).

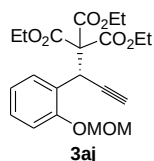
^{13}C NMR (125 MHz, CDCl_3): δ 165.1, 159.3, 131.5, 127.3, 113.2, 82.3, 72.6, 69.9, 62.2, 55.2, 40.0, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{20}\text{H}_{24}\text{NaO}_7)^+$ 399.1414, found 399.1422.

$[\alpha]_{\text{D}}^{26} +11.75$ (c 0.8, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, $\lambda = 220$ nm):

$t_{\text{R}} = 29.81$ min (minor enantiomer), $t_{\text{R}} = 33.18$ min (major enantiomer).



(*R*)-triethyl 2-(2-(methoxymethoxy)phenyl)but-3-yn-1,1,1-tricarboxylate **3aj**: faint yellow oil, actual mass 67 mg, yield 82%. ^1H NMR (500 MHz, CDCl_3): δ 7.83-7.78 (m, 1H), 7.24-7.16 (m, 1H),

7.07-7.02 (m, 1H), 6.99-6.94 (m, 1H), 5.36 (s, 1H), 5.21 (d, $J = 6.5$ Hz, 1H), 5.13 (d, $J = 6.5$ Hz, 1H), 4.24-4.15 (m, 6H), 3.50 (s, 3H), 2.22 (s, 1H), 1.22-1.14 (m, 9H).

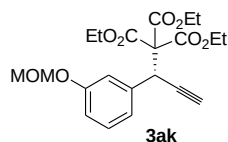
^{13}C NMR (125 MHz, CDCl_3): δ 165.5, 155.0, 130.4, 129.1, 126.1, 121.9, 114.1, 95.2, 82.8, 71.0, 69.3, 62.2, 56.3, 32.6, 13.7.

HRMS (ESI) calcd. for $(\text{C}_{21}\text{H}_{26}\text{NaO}_8)^+$ 429.1520, found 429.1527.

$[\alpha]_{\text{D}}^{26} -12.92$ (c 1.0, CHCl_3).

HPLC (Phenomenex cellulose-1, Hexane : Isopropanol = 49 : 1, Flow rate = 0.6 mL/min, $\lambda = 220$ nm):

$t_{\text{R}} = 15.77$ (minor enantiomer), $t_{\text{R}} = 16.92$ min (major enantiomer).



(*R*)-triethyl 2-(3-(methoxymethoxy)phenyl)but-3-yno-1,1,1-tricarboxylate **3ak**: faint yellow oil, actual mass 65 mg, yield 80%. ^1H NMR (500 MHz, CDCl_3): δ 7.28-7.14 (m, 3H), 6.94-6.90 (m, 1H), 5.13 (s, 2H), 4.76 (s, 1H), 4.25-4.11 (m, 6H), 3.44 (s, 3H), 2.35 (s, 1H), 1.24-1.17 (m, 9H).

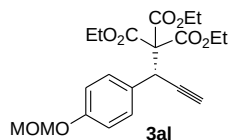
^{13}C NMR (125 MHz, CDCl_3): δ 165.0, 156.8, 136.9, 128.8, 123.9, 118.7, 115.7, 94.5, 81.9, 72.9, 69.8, 67.9, 62.2, 55.9, 40.6, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{21}\text{H}_{26}\text{NaO}_8)^+$ 429.1520, found 429.1531.

$[\alpha]_{\text{D}}^{26} +11.33$ (c 0.20, CHCl_3).

HPLC (Phenomenex cellulose-1, Hexane : Isopropanol = 49 : 1, Flow rate = 0.6 mL/min, $\lambda = 220$ nm):

$t_{\text{R}} = 17.85$ (minor enantiomer), $t_{\text{R}} = 26.39$ min (major enantiomer).



(*R*)-triethyl 2-(4-(methoxymethoxy)phenyl)but-3-yno-1,1,1-tricarboxylate **3al**: faint yellow oil, actual mass 68 mg, yield 84%. ^1H NMR (500 MHz, CDCl_3): δ 7.52-7.45 (m, 2H), 6.96-6.89 (m, 2H), 5.13 (s, 2H), 4.74 (s, 1H), 4.25-4.11 (m, 6H), 3.43 (s, 3H), 2.34 (s, 1H), 1.24-1.17 (m, 9H).

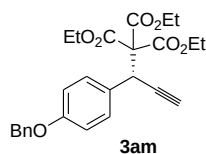
^{13}C NMR (125 MHz, CDCl_3): δ 165.1, 157.0, 131.5, 128.6, 115.4, 94.3, 82.2, 72.7, 69.90, 62.2, 40.0, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{21}\text{H}_{26}\text{NaO}_8)^+$ 429.1520, found 429.1526.

$[\alpha]_{\text{D}}^{26} +12.77$ (c 0.83, CHCl_3).

HPLC (Phenomenex cellulose-1, Hexane : Isopropanol = 49 : 1, Flow rate = 0.6 mL/min, $\lambda = 220$ nm):

$t_{\text{R}} = 17.85$ (minor enantiomer), $t_{\text{R}} = 26.17$ min (major enantiomer).



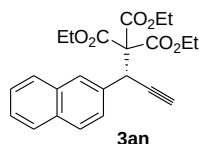
(*R*)-triethyl 2-(4-(benzyloxy)phenyl)but-3-yno-1,1,1-tricarboxylate **3am**: faint yellow oil, actual mass 80 mg, yield 89%. ^1H NMR (500 MHz, CDCl_3): δ 7.55-7.47 (m, 2H), 7.44-7.28 (m, 5H), 6.92-6.85 (m, 2H), 5.04 (s, 2H), 4.76 (s, 1H), 4.26-4.11 (m, 6H), 2.35 (s, 1H), 1.24-1.17 (m, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 165.1, 158.5, 136.9, 131.6, 128.6, 128.0, 127.6, 127.5, 114.1, 82.3, 72.6, 70.0, 70.0, 62.2, 40.0, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{26}\text{H}_{28}\text{NaO}_7)^+$ 475.1727, found 475.1722.

$[\alpha]_{\text{D}}^{25} +8.95$ (c 0.54, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm): t_{R} = 46.04 min (minor enantiomer), t_{R} = 53.37 min (major enantiomer).



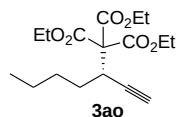
(*R*)-triethyl 2-(naphthalen-2-yl)but-3-yno-1,1,1-tricarboxylate **3an**: faint yellow oil, actual mass 74 mg, yield 94%. ^1H NMR (500 MHz, CDCl_3): δ 8.16-8.09 (m, 2H), 7.86-7.73 (m, 2H), 7.57-7.42 (m, 3H), 5.70 (s, 1H), 4.13-4.05 (m, 6H), 2.32 (s, 1H), 1.11-1.04 (m, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 165.4, 133.6, 132.6, 131.8, 128.9, 128.6, 128.1, 126.2, 125.4, 125.4, 123.0, 82.7, 72.0, 69.6, 62.3, 35.2, 13.6.

HRMS (ESI) calcd. for $(\text{C}_{23}\text{H}_{24}\text{NaO}_6)^+$ 419.1465, found 419.1472.

$[\alpha]_{\text{D}}^{26} -17.89$ (c 0.52, CHCl_3).

HPLC (Daicel CHIRALPAK OJ-H, Hexane : Isopropanol = 19 : 1, Flow rate = 0.5 mL/min, λ = 220 nm): t_{R} = 19.81 min (minor enantiomer), t_{R} = 22.99 min (major enantiomer).



(*R*)-triethyl 2-ethynylhexane-1,1,1-tricarboxylate **3ao**: faint yellow oil, actual mass 55 mg, yield 84%.

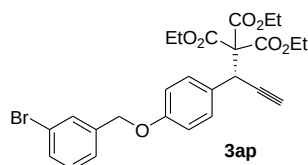
^1H NMR (500 MHz, CDCl_3): δ 4.27 (q, J = 7.0 Hz, 6H), 3.28-3.22 (m, 1H), 2.11-2.14 (m, 1H), 1.78-1.52 (m, 4H), 1.46-1.30 (m, 2H), 1.28 (t, J = 7.0 Hz, 9H), 0.90 (t, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 165.7, 83.0, 71.1, 68.5, 62.2, 35.7, 30.7, 30.1, 22.1, 13.9.

HRMS (ESI) calcd. for $(\text{C}_{17}\text{H}_{26}\text{NaO}_6)^+$ 349.1622, found 349.1633.

$[\alpha]_{\text{D}}^{28} +3.85$ (c 0.21, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm): t_{R} = 16.74 min (major enantiomer), t_{R} = 21.61 min (minor enantiomer).



(*R*)-triethyl 2-(4-(3-bromobenzyloxy)phenyl)but-3-yno-1,1,1-tricarboxylate **3ap**: faint yellow oil, actual mass 96 mg, yield 91%. ^1H NMR (500 MHz, CDCl_3): δ 7.58-7.55 (m, 1H), 7.54-7.47 (m, 2H), 7.45-7.42 (m, 1H), 7.34-7.30 (m, 1H), 7.27-7.21 (m, 1H), 6.89-6.82 (m, 2H), 5.00 (s, 2H), 4.75 (s, 1H), 4.26-4.11 (m, 6H), 2.35 (s, 1H), 1.21 (t, J = 7.5 Hz, 9H).

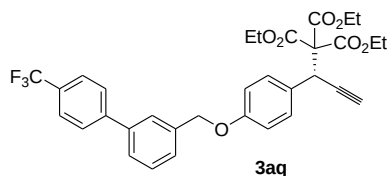
^{13}C NMR (126 MHz, CDCl_3): δ 165.1, 158.2, 139.3, 131.6, 131.0, 130.3, 130.2, 127.9, 125.8, 122.7, 114.1, 82.2, 72.7, 69.9, 69.0, 62.2, 40.0, 13.8.

HRMS (ESI) calcd. for $(C_{26}H_{27}BrNaO_7)^+$ 553.0832, found 553.0841.

$[\alpha]_D^{28} +8.75$ (c 0.2, $CHCl_3$).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm):

t_R = 44.87 min (major enantiomer), t_R = 52.23 min (minor enantiomer).



Compound **3aq**: faint yellow oil, actual mass 111 mg, yield 93%. 1H NMR (500 MHz, $CDCl_3$): δ 7.74-7.30 (m, 9H), 7.26-7.20 (m, 1H), 6.95-6.82 (m, 2H), 5.17-4.97 (m, 2H), 4.76 (s, 1H), 4.26-4.12 (m, 6H), 2.36 (s, 1H), 1.26-1.16 (m, 9H).

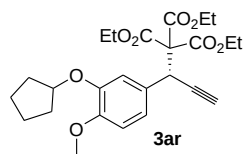
^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1, 158.4, 158.2, 144.4, 140.2, 139.3, 137.8, 131.6, 131.0, 130.3, 130.2, 129.5 (q, J = 31.8 Hz), 129.3, 128.6, 127.9, 127.3, 126.9, 126.5 (q, J = 271 Hz), 126.3, 125.8, 125.7 (q, J = 3.7 Hz), 122.7, 114.1, 82.2, 72.7, 69.9, 69.0, 62.2, 40.0, 13.8.

HRMS (ESI) calcd. for $(C_{33}H_{31}F_3NaO_7)^+$ 619.1914, found 619.1919.

$[\alpha]_D^{28} +7.92$ (c 0.47, $CHCl_3$).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 85 : 15, Flow rate = 1 mL/min, λ = 220 nm):

t_R = 10.40 min (major enantiomer), t_R = 12.40 min (minor enantiomer).



(*R*)-triethyl 2-(3-(cyclopentyloxy)-4-methoxyphenyl)but-3-yn-1,1,1-tricarboxylate **3ar**: faint yellow oil, actual mass 86 mg, yield 94%. 1H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, J = 2.2 Hz, 1H), 7.09 (dd, J = 8.4, 2.2 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 4.78-4.70 (m, 2H), 4.24-4.09 (m, 6H), 3.80 (s, 3H), 2.36 (s, 1H), 2.01-1.75 (m, 6H), 1.65-1.52 (m, 2H), 1.19 (t, J = 7.1 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.1, 149.7, 146.8, 127.6, 122.6, 117.2, 110.9, 82.3, 80.4, 72.7, 70.0, 62.2, 56.0, 40.3, 32.9, 32.7, 24.1, 13.8.

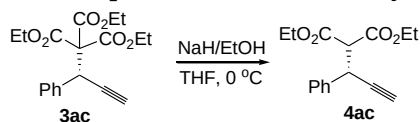
HRMS (ESI) calcd. for $(C_{25}H_{32}NaO_8)^+$ 483.1989, found 483.1996.

$[\alpha]_D^{28} +10.23$ (c 0.51, $CHCl_3$).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 19 : 1, Flow rate = 0.8 mL/min, λ = 220 nm):

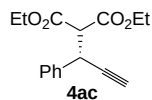
t_R = 10.64 min (major enantiomer), t_R = 11.73 min (minor enantiomer).

General procedure for decarboxylation of **3**



Dry ethanol (12 μ L, 0.2 mmol) was added dropwise to a suspension of NaH (8 mg, 60% dispersion in mineral oil, 0.2 mmol) in THF (1 mL), and the solution was stirred at rt for 30 min, then stirred at 0 $^{\circ}C$ for 5 min. A solution of **3ac** (35 mg, 0.1 mmol) in THF (1 mL) was added dropwise. The mixture was stirred at 0 $^{\circ}C$ for 1 h and acidified with 1N HCl and diluted with ether (20 mL),

washed with water, sat. NaHCO_3 and brine successively. The organic layer was dried over Na_2SO_4 . After evaporation of the volatile solvent under reduced pressure, the residue was purified by flash chromatography on silica gel to afford pure **4ac** (26 mg, 0.095 mmol) as a faint yellow oil in a yield of 95%.



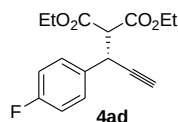
(*S*)-diethyl 2-(1-phenylprop-2-ynyl)malonate **4ac**: faint yellow oil, actual mass 26 mg, yield 95%. ^1H NMR (500 MHz, CDCl_3) δ 7.41-7.35 (m, 2H), 7.35-7.21 (m, 3H), 4.40 (dd, $J = 10.5, 2.5$ Hz, 1H), 4.25 (q, $J = 7.0$ Hz, 2H), 4.01-3.92 (m, 2H), 3.77 (d, $J = 10.5$ Hz, 1H), 2.29 (d, $J = 2.5$ Hz, 1H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.02 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 167.0, 166.6, 137.4, 128.6, 128.2, 127.8, 125.8, 82.8, 72.3, 61.8, 61.6, 59.1, 37.4, 14.1, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{16}\text{H}_{19}\text{O}_4)^+$ 275.1278, found 275.1286.

$[\alpha]_{\text{D}}^{28} +11.22$ (c 0.60, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, $\lambda = 220$ nm): $t_{\text{R}} = 21.06$ min (major enantiomer), $t_{\text{R}} = 24.42$ min (minor enantiomer).



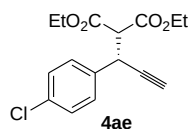
(*S*)-diethyl 2-(1-(4-fluorophenyl)prop-2-ynyl)malonate **4ad**: faint yellow oil, actual mass 27 mg, yield 93%. ^1H NMR (500 MHz, CDCl_3): δ 7.41-7.33 (m, 2H), 7.05-6.96 (m, 2H), 4.39 (dd, $J = 10.0, 2.5$ Hz, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 4.04-3.96 (m, 2H), 3.73 (d, $J = 10.0$ Hz, 1H), 2.31 (d, $J = 2.5$ Hz, 1H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.06 (q, $J = 7.0$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 166.8, 166.5, 162.3 (d, $J = 246$ Hz), 133.3, 130.0 (d, $J = 8.3$ Hz), 115.5 (d, $J = 21.9$ Hz), 82.6, 72.5, 61.9, 61.7, 59.1, 36.7, 14.0, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{16}\text{H}_{18}\text{FO}_4)^+$ 293.1184, found 293.1189.

$[\alpha]_{\text{D}}^{28} +6.95$ (c 0.30, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, $\lambda = 220$ nm): $t_{\text{R}} = 19.83$ min (major enantiomer), $t_{\text{R}} = 21.88$ min (minor enantiomer).



(*S*)-diethyl 2-(1-(4-chlorophenyl)prop-2-ynyl)malonate **4ae**: faint yellow oil, actual mass 29 mg, yield 96%. ^1H NMR (500 MHz, CDCl_3): δ 7.37-7.23 (m, 4H), 4.39 (dd, $J = 10.0, 2.5$ Hz, 1H), 4.30-4.18 (m, 2H), 4.08-3.94 (m, 2H), 3.73 (d, $J = 10.0$ Hz, 1H), 2.31 (d, $J = 2.5$ Hz, 1H), 1.33-1.19 (m, 3H), 1.09-1.02 (m, 3H).

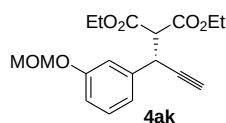
^{13}C NMR (125 MHz, CDCl_3): δ 166.8, 166.4, 136.0, 133.7, 129.7, 128.8, 82.3, 72.7, 62.0, 61.8, 58.9, 36.8, 14.1, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{16}\text{H}_{18}\text{ClO}_4)^+$ 309.0888, found 309.0897.

$[\alpha]_D^{28} +4.62$ (c 0.29, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.5 mL/min, λ = 220 nm):

t_R = 17.94 min (major enantiomer), t_R = 18.84 min (minor enantiomer).



(S)-diethyl 2-(1-(3-(methoxymethoxy)phenyl)prop-2-ynyl)malonate **4ak**: faint yellow oil, actual mass 30 mg, yield 91%. ^1H NMR (500 MHz, CDCl_3): δ 7.25-7.20 (m, 1H), 7.09-7.00 (m, 2H), 6.99-6.90 (m, 1H), 5.15 (s, 2H), 4.38 (dd, J = 10.0, 2.5 Hz, 1H), 4.25 (q, J = 7.0 Hz, 2H), 4.01 (q, J = 7.0 Hz, 2H), 3.77 (d, J = 10.0 Hz, 1H), 3.47 (s, 3H), 2.30 (d, J = 2.5 Hz, 1H), 1.27 (t, J = 7.0 Hz, 3H), 1.06 (t, J = 7.0 Hz, 3H).

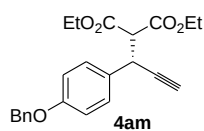
^{13}C NMR (125 MHz, CDCl_3): δ 166.9, 166.5, 157.4, 139.0, 129.6, 116.5, 115.5, 94.5, 82.6, 72.4, 61.9, 61.7, 59.0, 56.0, 37.3, 14.0, 13.8.

HRMS (ESI) calcd. for $(\text{C}_{18}\text{H}_{23}\text{O}_6)^+$ 335.1489, found 335.1496.

$[\alpha]_D^{28} -29.38$ (c 0.32, CHCl_3).

HPLC (Phenomenex cellulose-1, Hexane : Isopropanol = 49 : 1, Flow rate = 0.6 mL/min, λ = 220 nm):

t_R = 14.61 (minor enantiomer), t_R = 15.55 min (major enantiomer).



(S)-diethyl 2-(1-(4(benzyloxy)phenyl)prop-2-ynyl)malonate **4am**: faint yellow oil, actual mass 36 mg, yield 94%. ^1H NMR (500 MHz, CDCl_3): δ 7.45-7.27 (m, 7H), 6.96-6.89 (m, 2H), 5.04 (s, 2H), 4.37 (dd, J = 10.0, 2.5 Hz, 1H), 4.26 (q, J = 7.0 Hz, 2H), 4.05-3.94 (m, 2H), 3.74 (d, J = 10.0 Hz, 1H), 2.30 (d, J = 2.5 Hz, 1H), 1.30 (t, J = 7.0 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H).

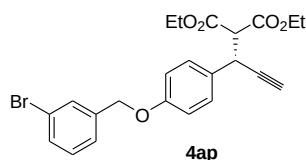
^{13}C NMR (125 MHz, CDCl_3): δ 167.0, 166.7, 158.3, 136.9, 129.7, 129.4, 128.6, 128.0, 127.5, 114.9, 83.1, 72.2, 70.0, 61.9, 61.6, 59.3, 36.7, 14.1, 13.9.

HRMS (ESI) calcd. for $(\text{C}_{23}\text{H}_{25}\text{O}_5)^+$ 381.1697, found 381.1710.

$[\alpha]_D^{28} +16.05$ (c 0.73, CHCl_3).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0. mL/min, λ = 220 nm):

t_R = 43.66 (minor enantiomer), t_R = 54.93 min (major enantiomer).



(S)-diethyl 2-(1-(4(3-bromobenzyloxy)phenyl)prop-2-ynyl)malonate **4ap**: faint yellow oil, actual mass 43 mg, yield 94%. ^1H NMR (500 MHz, CDCl_3): δ 7.58 (s, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.36-7.28 (m, 3H), 7.24 (t, J = 8.5 Hz, 1H), 6.93-6.86 (m, 2H), 5.01 (s, 2H), 4.36 (dd, J = 10.0, 2.5 Hz, 1H), 4.26 (q, J = 7.0 Hz, 2H), 4.02-3.95 (m, 2H), 3.74 (d, J = 10.0 Hz, 1H), 2.29 (d, J = 2.5 Hz, 1H), 1.29 (t, J = 7.0 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 167.0, 166.6, 158.0, 139.2, 131.1, 130.3, 130.2, 130.1, 129.5, 125.8,

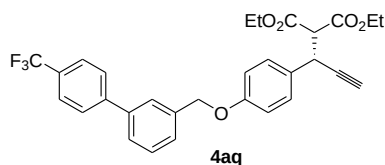
122.7, 114.9, 83.0, 72.2, 69.1, 61.9, 61.7, 59.2, 36.7, 14.1, 13.9.

HRMS (ESI) calcd. for $(C_{23}H_{24}BrO_5)^+$ 459.0802, found 459.0805.

$[\alpha]_D^{28} +26.05$ (c 0.24, $CHCl_3$).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 49 : 1, Flow rate = 0.3 mL/min, λ = 220 nm):

t_R = 72.55 (minor enantiomer), t_R = 91.64 min (major enantiomer).



Compound **4aq**: faint yellow oil, actual mass 48 mg, yield 92%. 1H NMR (500 MHz, $CDCl_3$): δ 7.72-7.62 (m, 5H), 7.59-7.42 (m, 3H), 7.36-7.28 (m, 2H), 6.98-6.87 (m, 2H), 5.12 (s, 2H), 4.38 (dd, J = 10.0, 2.5 Hz, 1H), 4.26 (q, J = 7.0 Hz, 2H), 4.03-3.93 (m, 2H), 3.75 (d, J = 7.0 Hz 1H), 2.29 (d, J = 2.5 Hz, 1H), 1.29 (t, J = 7.0 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H).

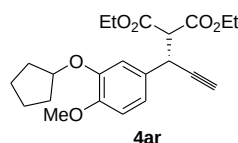
^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 166.6, 158.2, 144.4, 140.2, 137.8, 131.1, 130.3, 129.9, 129.55 (q, J = 31 Hz), 129.50, 129.3, 128.6, 127.5, 127.2, 127.0, 126.6 (q, J = 275 Hz), 126.3, 125.7 (q, J = 3.6 Hz), 125.4, 123.2, 122.7, 114.9, 83.0, 72.2, 69.9, 61.9, 61.6, 59.2, 36.7, 14.1, 13.8.

HRMS (ESI) calcd. for $(C_{30}H_{28}F_3O_5)^+$ 525.1883, found 525.1888.

$[\alpha]_D^{28} +11.52$ (c 0.42, $CHCl_3$).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 85 : 15, Flow rate = 1 mL/min, λ = 220 nm):

t_R = 8.94 (minor enantiomer), t_R = 10.45 min (major enantiomer).



(S)-diethyl 2-(1-(3-(cyclopentyloxy)-4-methoxyphenyl)prop-2-ynyl)malonate **4ar**: faint yellow oil, actual mass 37 mg, yield 95%. 1H NMR (500 MHz, $CDCl_3$): δ 6.93-6.85 (m, 2H), 6.79-6.76 (m, 1H), 4.78-4.72 (m, 1H), 4.32 (dd, J = 10.5, 2.5 Hz, 1H), 4.24 (q, J = 7.0 Hz, 2H), 4.02-3.93 (m, 2H), 3.80 (s, 3H), 3.72 (d, J = 10.5 Hz, 1H), 2.29 (d, J = 2.5 Hz, 1H), 1.99-1.76 (m, 6H), 1.66-1.54 (m, 2H), 1.28 (t, J = 7.0 Hz, 3H), 1.04 (t, J = 7.0 Hz, 3H).

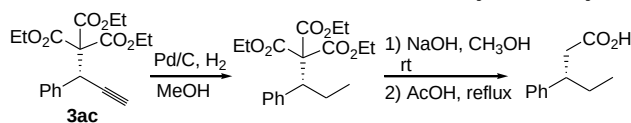
^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 166.6, 149.5, 147.6, 129.7, 120.4, 115.0, 111.8, 83.1, 80.4, 72.1, 61.8, 61.6, 59.3, 56.0, 37.1, 32.8, 32.7, 24.1, 24.0, 14.1, 13.8.

HRMS (ESI) calcd. for $(C_{22}H_{29}O_6)^+$ 389.1959, found 389.1969.

$[\alpha]_D^{29} +13.55$ (c 0.70, $CHCl_3$).

HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 19 : 1, Flow rate = 0.8 mL/min, λ = 220 nm): t_R = 10.71 (minor enantiomer), t_R = 11.75 min (major enantiomer).

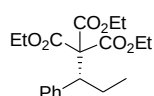
Determination of absolute stereochemistry of **3ac** by correlation



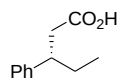
A solution of **3ac** (100 mg, 0.29 mmol) in MeOH (5 mL) was stirred under hydrogen atmosphere in the presence of 10% Pd/C (10 mg) at room temperature for 10 h. Then, the

reaction mixture was filtered through a short pad of silica gel eluting with EtOAc. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to afford pure triester (81 mg, 0.23 mmol) in a yield of 79%.

A solution of the triester in MeOH (2 mL) was treated with a solution 3 N NaOH (0.6 mL, 2 mmol) in water, the resulting mixture was stirred at room temperature and monitored by TLC. When no starting material remained, volatiles were removed in vacuo and the crude tris-acid was taken up in AcOH (2 mL) and heated to reflux. The reaction was monitored by TLC analysis, and when no starting material remained (12 hrs), solvent was concentrated in vacuo. The resultant crude acid was dissolved in water (3 mL), extracted with EtOAc (5 mL $\times$ 3), and the combined extracts were dried (Na₂SO₄) and concentrated in vacuo to give acid product (29 mg, 0.16 mmol) in a yield of 71%.



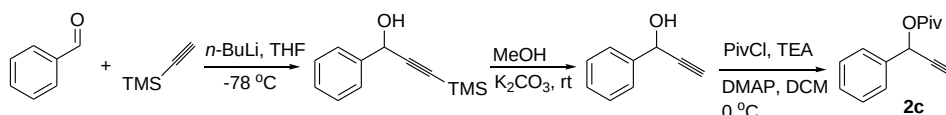
(*R*)-triethyl 2-phenylbutane-1,1,1-tricarboxylate: colourless oil, actual mass 81 mg, yield 79%. ¹H NMR (500 MHz, CDCl₃): δ 7.39-7.33 (m, 2H), 7.28-7.16 (m, 3H), 4.21-4.06 (m, 6H), 3.49-3.44 (m, 1H), 2.03-1.92 (m, 1H), 1.89-1.76 (m, 1H), 1.18 (t, *J* = 7.0 Hz, 9H), 0.73 (t, *J* = 7.0 Hz, 3H).



(*S*)-3-phenylpentanoic acid: colourless oil, actual mass 29 mg, yield 71%. ¹H NMR (500 MHz, CDCl₃): δ 7.33-7.15 (m, 5H), 3.02-2.95 (m, 1H), 2.72-2.52 (m, 2H), 1.85-1.55 (m, 2H), 0.82-0.75 (m, 3H).

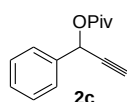
$[\alpha]_D^{25} +34.55$ (c 0.33, CHCl₃), {literature data: $[\alpha]_D^{20} -41.7$ (c 0.30, CHCl₃)} for *R*-isomer (*J. Org. Chem.* **2006**, *71*, 7763).

General procedure for preparation of propargylic alcohol derivatives:

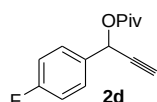


n-BuLi (19.7 mL, 31.5 mmol; 1.60 M solution in hexane) was added to a solution of trimethylsilylacetylene (4.67 mL, 33 mmol) in anhydrous THF (60 mL) at -70 °C and the mixture was stirred for 25 min. Benzaldehyde (3.18 g, 30 mmol) was then added dropwise, and the resulting solution was stirred for 0.5 h at -70 °C. After the reaction was warmed up to room temperature, water (30 mL) was added to quench the reaction. The organic materials were extracted with Et₂O (30 mL $\times$ 3). The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was dissolved in MeOH (50 mL), then K₂CO₃ (4.14 g, 30 mmol) was added while stirring. The reaction was allowed to stir at room temperature for 2 h. The solid was removed by filtration through a pad of celite and washed with DCM. The filtrate was washed with aqueous ammonium chloride and brine successively, and dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to afford the corresponding propargylic alcohol (3.3 g, 25 mmol) in 85% yield over 2 steps.

To a solution of propargylic alcohol (1.06 g, 8 mmol) in anhydrous DCM (20 mL), Et₃N (1.22 mL, 8.8 mmol) and DMAP (97 mg, 0.8 mmol) were added successively. The reaction mixture was cooled with an ice bath for 5 min. Then PivCl (1.03 mL, 8.4 mmol) was added dropwise. The reaction was gradually warmed to room temperature and stirred for 3 h at this temperature. After complete consumption of 1-phenylprop-2-yn-1-ol as followed by TLC, water (20 mL) was added to quench the reaction. The organic phase was isolated, and the aqueous phase was extracted with DCM (15 mL × 2). The combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford pure **2c** (1.50 g, 6.94 mmol) as a pale yellow oil in a yield of 87%.



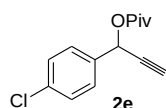
1-Phenylprop-2-ynyl pivalate **2c** (known compound: *Angew. Chem. Int. Ed.* **2013**, 52, 5880): a pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.55-7.48 (m, 2H), 7.43-7.32 (m, 3H), 6.44 (d, *J* = 2.5 Hz, 1H), 2.63 (d, *J* = 2.5 Hz, 1H), 1.23 (s, 9H).



1-(4-Fluorophenyl)prop-2-ynyl pivalate **2d**: a pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.53-7.46 (m, 2H), 7.11-7.02 (m, 2H), 6.40 (d, *J* = 2.5 Hz, 1H), 2.63 (d, *J* = 2.5 Hz, 1H), 1.23 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ 177.1, 162.9 (d, *J* = 246 Hz), 132.8 (d, *J* = 2.5 Hz), 129.3 (d, *J* = 7.5 Hz), 115.6 (d, *J* = 22.5 Hz), 80.2, 75.3, 64.4, 38.7, 26.9.

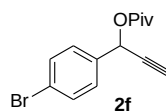
HRMS (ESI) calcd. for (C₁₄H₁₅FN₂O₂)⁺ 257.0948, found 257.0956.



1-(4-Chlorophenyl)prop-2-ynyl pivalate **2e**: a pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.49-7.41 (m, 2H), 7.39-7.32 (m, 2H), 6.39 (d, *J* = 2.5 Hz, 1H), 2.64 (d, *J* = 2.5 Hz, 1H), 1.21 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ 177.0, 135.4, 134.8, 128.9, 128.8, 80.0, 75.5, 64.4, 38.7, 26.9.

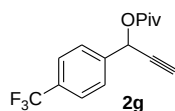
HRMS (ESI) calcd. for (C₁₄H₁₅ClNaO₂)⁺ 273.0653, found 273.0662.



1-(4-Bromophenyl)prop-2-ynyl pivalate **2f**: a pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.37 (d, *J* = 2.5 Hz, 1H), 2.63 (d, *J* = 2.5 Hz, 1H), 1.21 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ 177.0, 135.9, 131.8, 129.1, 123.0, 79.9, 75.5, 64.4, 38.7, 26.9.

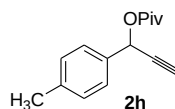
HRMS (ESI) calcd. for (C₁₄H₁₅BrNaO₂)⁺ 317.0148, found 317.0160.



1-(4-(Trifluoromethyl)phenyl)prop-2-ynyl pivalate **2g**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.68-7.60 (m, 4H), 6.46 (d, $J = 2.5$ Hz, 1H), 2.66 (d, $J = 2.5$ Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 176.9, 140.7, 131.0 (q, $J = 32.7$ Hz), 127.6, 127.1, 125.7 (q, $J = 3.6$ Hz), 123.9 (q, $J = 270.8$ Hz), 79.7, 75.8, 64.3, 38.8, 26.9.

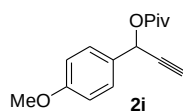
HRMS (ESI) calcd. for $(\text{C}_{15}\text{H}_{15}\text{F}_3\text{NaO}_2)^+$ 307.0916, found 307.0924.



1-*p*-Tolylprop-2-ynyl pivalate **2h**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.40 (d, $J = 8.0$ Hz, 2 H), 7.19 (d, $J = 8.0$ Hz, 2 H), 6.39 (d, $J = 2.5$ Hz, 1H), 2.61 (d, $J = 2.5$ Hz, 1H), 2.36 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 177.2, 138.7, 134.0, 129.3, 127.3, 80.7, 74.9, 65.0, 38.7, 27.0, 21.2.

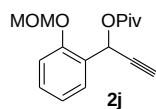
HRMS (ESI) calcd. for $(\text{C}_{15}\text{H}_{18}\text{NaO}_2)^+$ 253.1199, found 253.1205.



1-(4-Methoxyphenyl)prop-2-ynyl pivalate **2i**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.44 (d, $J = 8.5$ Hz, 2H), 6.90 (d, $J = 8.5$ Hz, 2H), 6.38 (d, $J = 2.0$ Hz, 1H), 3.81 (s, 3H), 2.62 (d, $J = 2.0$ Hz, 1H), 1.20 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 177.2, 160.0, 129.0, 128.9, 113.4, 80.7, 74.9, 64.8, 55.3, 38.7, 27.0.

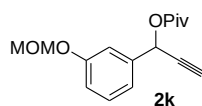
HRMS (ESI) calcd. for $(\text{C}_{15}\text{H}_{18}\text{NaO}_3)^+$ 269.1148, found 269.1158.



1-(2-(Methoxymethoxy)phenyl)prop-2-ynyl pivalate **2j**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.68-7.63 (m, 1H), 7.35-7.28 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.05 (t, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 2.0$ Hz, 1H), 5.25-5.15 (m, 2H), 3.47 (s, 3H), 2.57 (d, $J = 2.0$ Hz, 1H), 1.22 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 177.0, 154.3, 130.2, 128.3, 125.8, 121.8, 114.2, 94.4, 80.6, 74.32, 74.3, 60.2, 56.2, 38.7, 27.0.

HRMS (ESI) calcd. for $(\text{C}_{16}\text{H}_{20}\text{NaO}_4)^+$ 299.1254, found 299.1255.

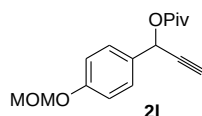


1-(3-(Methoxymethoxy)phenyl)prop-2-ynyl pivalate **2k**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.29 (t, $J = 7.9$ Hz, 1H), 7.21-7.11 (m, 2H), 7.05-7.00 (m, 1H), 6.39 (d, $J = 2.0$ Hz, 1H), 5.20-5.13 (m, 2H), 3.46 (s, 3H), 2.63 (d, $J = 2.0$ Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 176.9, 157.4, 138.3, 129.6, 120.6, 116.4, 115.1, 94.4, 80.3, 75.1, 64.7,

55.9, 38.7, 26.9.

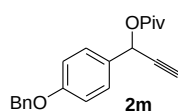
HRMS (ESI) calcd. for $(C_{16}H_{20}NaO_4)^+$ 299.1254, found 299.1259.



1-(4-(Methoxymethoxy)phenyl)prop-2-ynyl pivalate **2l**: a pale yellow oil liquid. 1H NMR (500 MHz, $CDCl_3$): δ 7.65 (dd, $J = 8.0, 2.0$ Hz, 1H), 7.33-7.28 (m, 1H), 7.12 (d, $J = 8.0$ Hz, 1H), 7.04 (t, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 2.0$ Hz, 1H), 5.24-5.15 (m, 2H), 3.46 (s, 3H), 2.56 (d, $J = 2.0$ Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.0, 154.3, 130.2, 128.3, 125.7, 121.8, 114.2, 94.4, 80.5, 74.4, 60.2, 56.1, 38.7, 27.0.

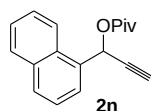
HRMS (ESI) calcd. for $(C_{16}H_{20}NaO_4)^+$ 299.1254, found 299.1260.



1-(4-(Benzyloxy)phenyl)prop-2-ynyl pivalate **2m**: a pale yellow oil. 1H NMR (500 MHz, $CDCl_3$): δ 7.50-7.31 (m, 7H), 7.03-6.96 (m, 2H), 6.40 (d, $J = 2.0$ Hz, 1H), 5.08 (s, 2H), 2.63 (d, $J = 2.0$ Hz, 1H), 1.23 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.2, 159.2, 136.8, 129.3, 128.9, 128.7, 128.1, 127.5, 114.9, 80.7, 74.9, 70.1, 64.8, 38.7, 27.0.

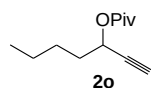
HRMS (ESI) calcd. for $(C_{21}H_{22}NaO_3)^+$ 345.1461, found 345.1466.



1-(Naphthalen-1-yl)prop-2-ynyl pivalate **2n**: a pale yellow oil. 1H NMR (500 MHz, $CDCl_3$): δ 8.25-8.19 (m, 1H), 7.94-7.84 (m, 3H), 7.64-7.47 (m, 3H), 7.10 (d, $J = 2.5$ Hz, 1H), 2.73 (d, $J = 2.5$ Hz, 1H), 1.27 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.2, 134.1, 132.1, 130.6, 130.0, 128.9, 126.6, 126.4, 126.1, 125.2, 123.8, 80.4, 75.9, 63.9, 39.0.

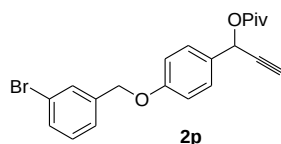
HRMS (ESI) calcd. for $(C_{18}H_{18}NaO_2)^+$ 289.1199, found 289.1209.



Hept-1-yn-3-yl pivalate **2o**: a pale yellow oil. 1H NMR (500 MHz, $CDCl_3$): δ 5.33-5.26 (m, 1H), 2.40 (d, $J = 2.5$ Hz, 1H), 1.82-1.70 (m, 2H), 1.46-1.28 (m, 4H), 1.20 (s, 9H), 0.89 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.4, 81.5, 73.0, 63.5, 38.7, 34.2, 27.0, 26.5, 22.2, 13.9.

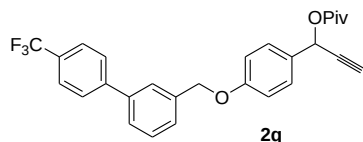
HRMS (ESI) calcd. for $(C_{12}H_{20}NaO_2)^+$ 219.1356, found 219.1363.



Compound **2p**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.60 (s, 1H), 7.48-7.43 (m, 3H), 7.37-7.33 (m, 1H), 7.28-7.23 (m 1H), 6.96 (d, J = 8.5 Hz, 2H), 6.38 (d, J = 2.0 Hz, 1H), 5.04 (s, 2H), 2.62 (d, J = 2.0 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 177.2, 158.9, 139.1, 131.1, 130.3, 130.2, 129.6, 129.0, 125.9, 122.7, 114.9, 80.6, 75.0, 69.1, 64.8, 38.7, 27.0.

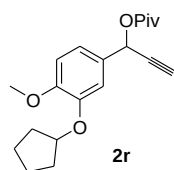
HRMS (ESI) calcd. for $(\text{C}_{21}\text{H}_{21}\text{BrNaO}_3)^+$ 423.0566, found 423.0571.



Compound **2q**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.70-7.48 (m, 10H), 7.42-6.94 (m, 2H), 6.9 (d, J = 2.0 Hz, 1H), 5.19-4.98 (m, 2H), 2.62 (d, J = 2.0 Hz, 1H), 1.22 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 177.2, 159.1, 158.9, 144.4, 140.2, 139.1, 137.6, 131.5, 130.4, 130.2, 130.19, 129.7, 129.6, 129.5, 129.43, 129.35, 129.0, 128.8 (q, J = 36.5 Hz), 128.1, 127.53, 127.48, 127.3, 127.1, 126.4, 125.86, 125.80 (q, J = 3.6 Hz), 124.3 (q, J = 269.7 Hz), 122.8, 114.91, 114.88, 80.63, 80.61, 74.9, 69.9, 69.2, 64.80, 38.7, 27.0.

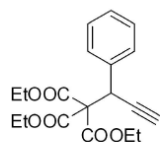
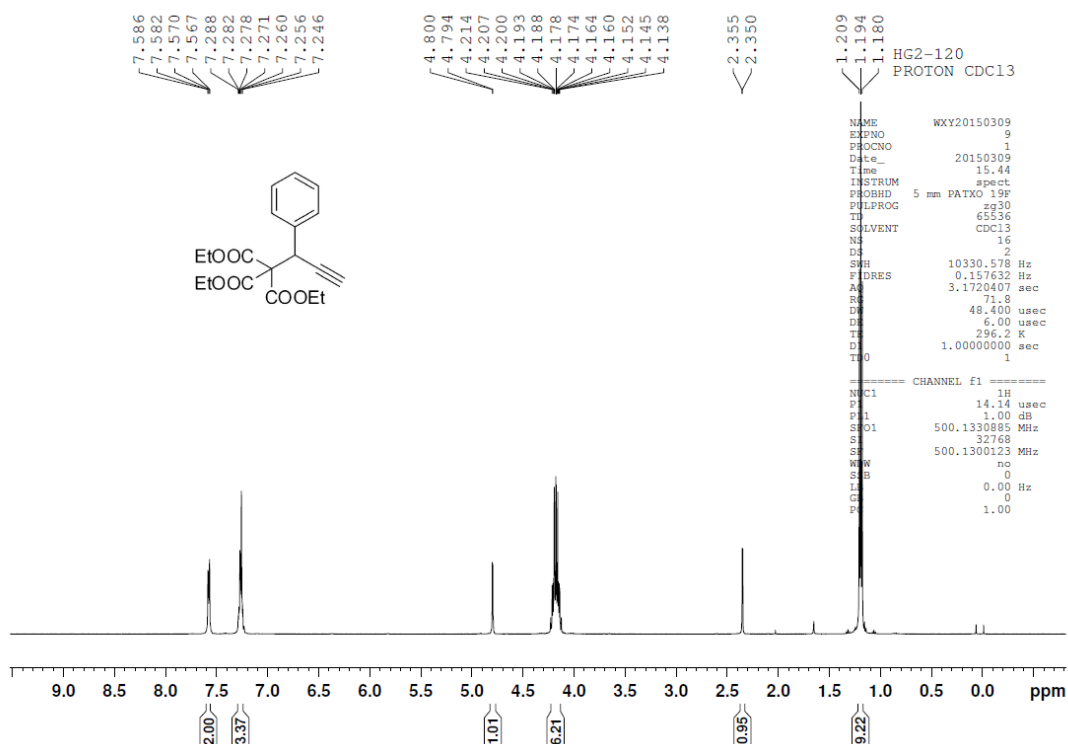
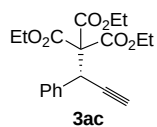
HRMS (ESI) calcd. for $(\text{C}_{28}\text{H}_{25}\text{F}_3\text{NaO}_3)^+$ 489.1648, found 489.1656.



1-(3-(Cyclopentyloxy)-4-methoxyphenyl)prop-2-ynyl pivalate **2r**: a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.08-6.99 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.36 (d, J = 2.5 Hz, 1H), 4.81-4.74 (m, 1H), 3.83 (s, 3H), 2.62 (d, J = 2.5 Hz, 1H), 1.99-1.77 (m, 6H), 1.66-1.54 (m, 2H), 1.20 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3): δ 177.2, 150.4, 147.6, 129.2, 119.9, 114.0, 111.5, 80.7, 74.9, 65.0, 56.0, 38.7, 32.8, 27.0, 24.1.

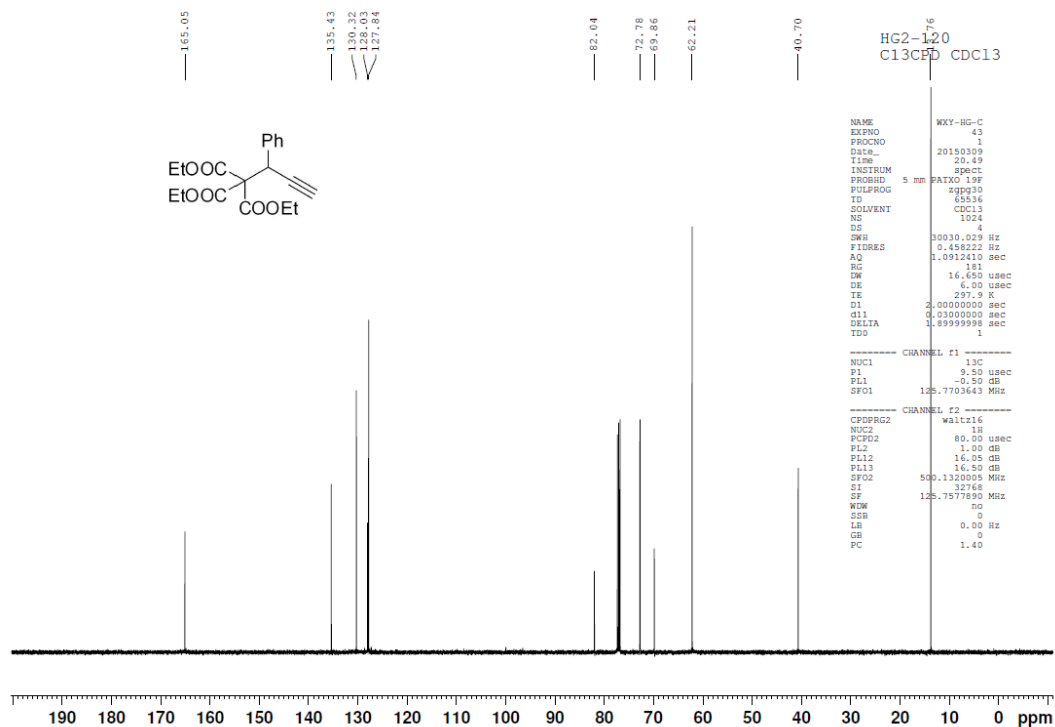
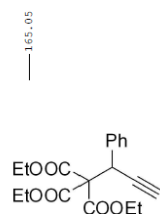
HRMS (ESI) calcd. for $(\text{C}_{20}\text{H}_{26}\text{NaO}_4)^+$ 353.1723, found 353.1732.



HG2-120
PROTON CDCl3

NAME WXY20150309
EXPNO 9
PROCNO 1
Date_ 20150309
Time_ 15.44
INSTRUM spect
PROBHD 5 mm PATKO 19F
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 71.8
DW 48.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 14.14 usec
PL1 1.00 dB
SFO1 500.1330885 MHz
SI 32768
SF 500.1300123 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

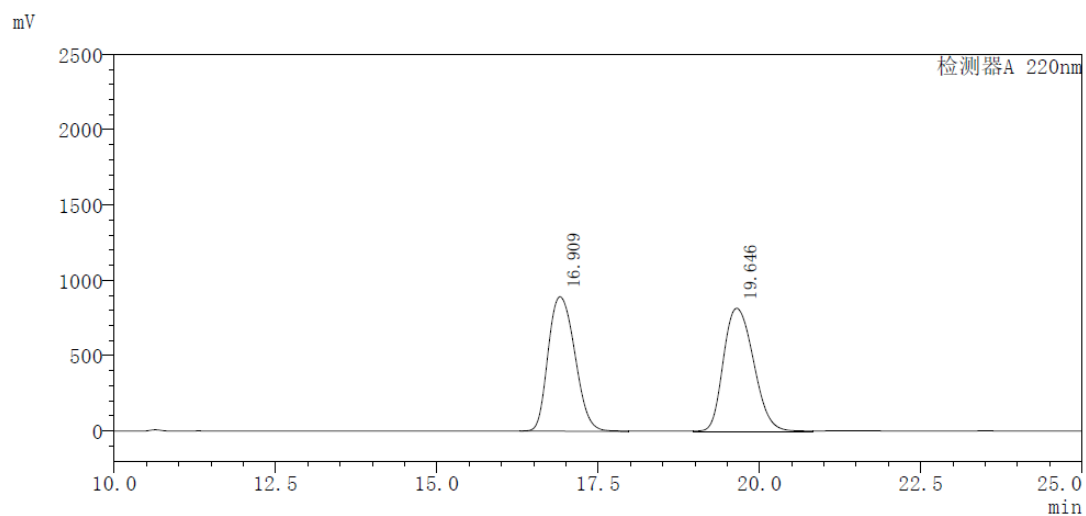
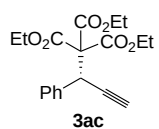


HG2-120
C13CD CDCl3

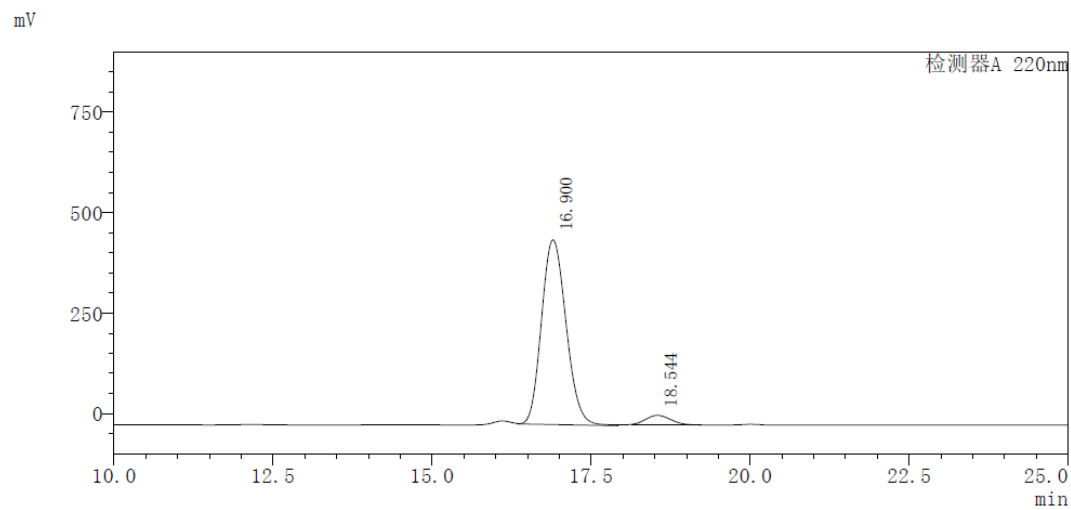
NAME WXY-HG-C
EXPNO 43
PROCNO 1
Date_ 20150309
Time_ 20.49
INSTRUM spect
PROBHD 5 mm PATKO 19F
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 181
DW 16.650 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 9.50 usec
PL1 -0.50 dB
SFO1 125.7703643 MHz

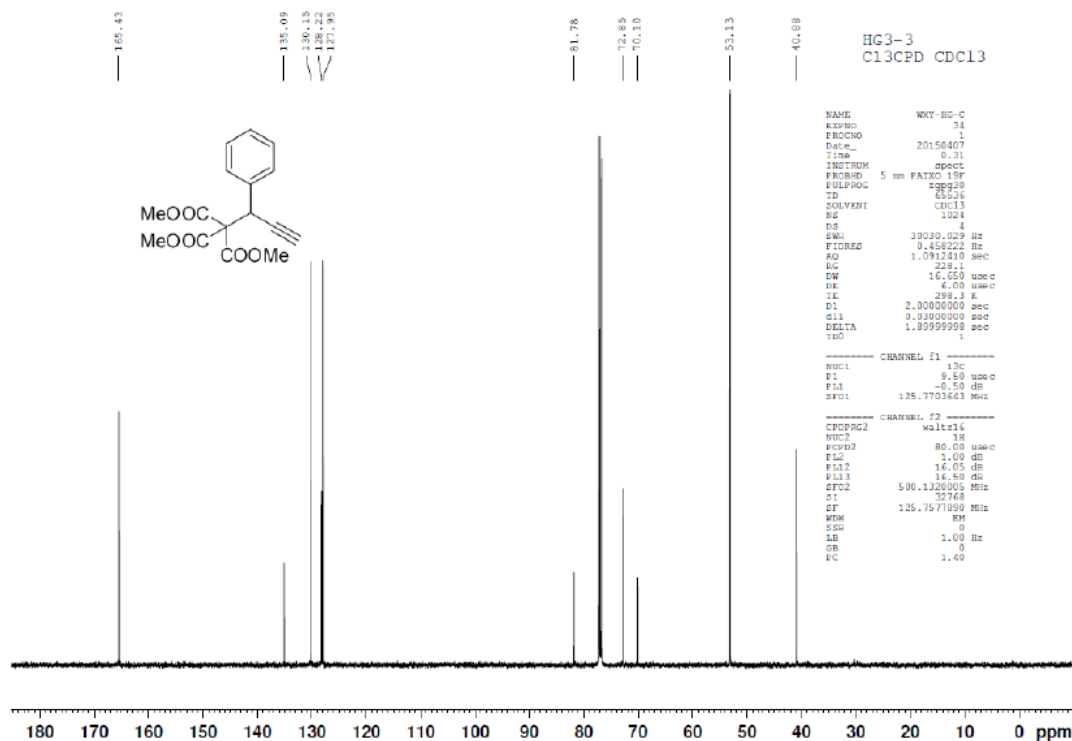
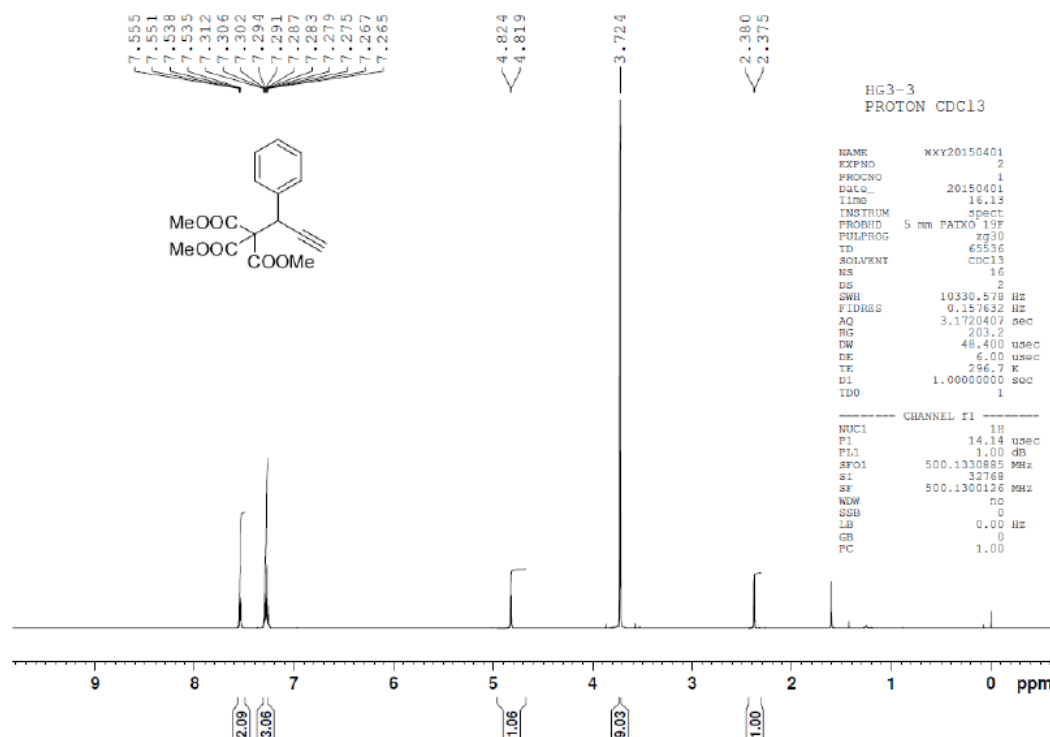
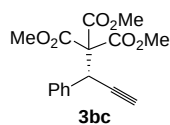
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.05 dB
PL13 16.50 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

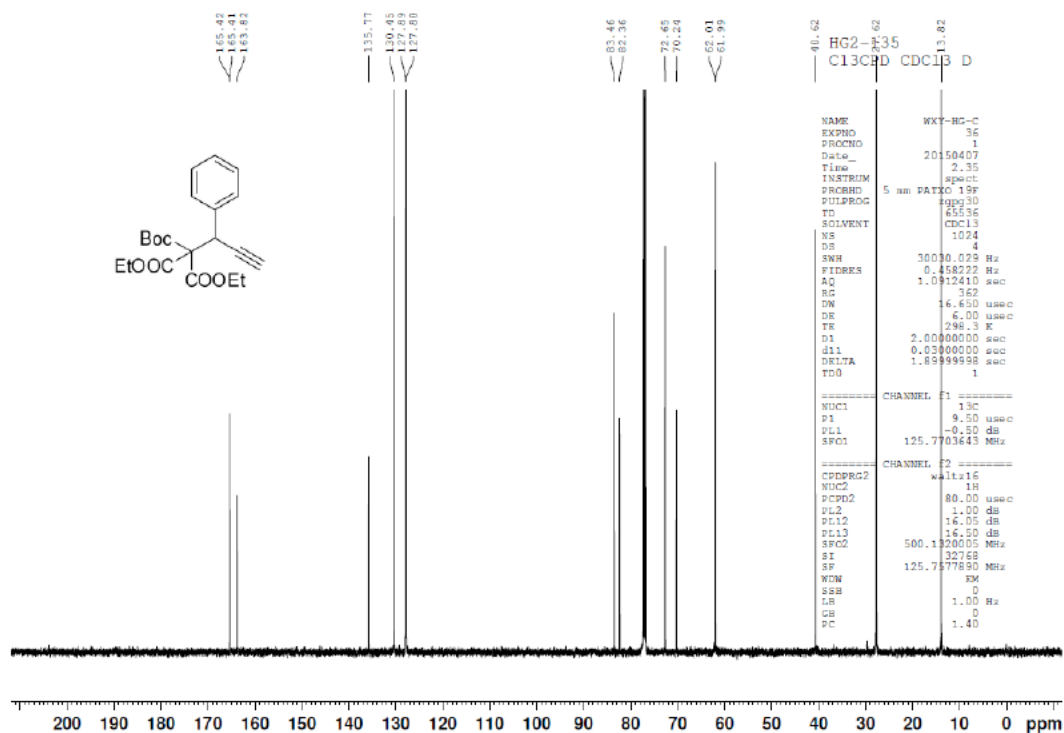
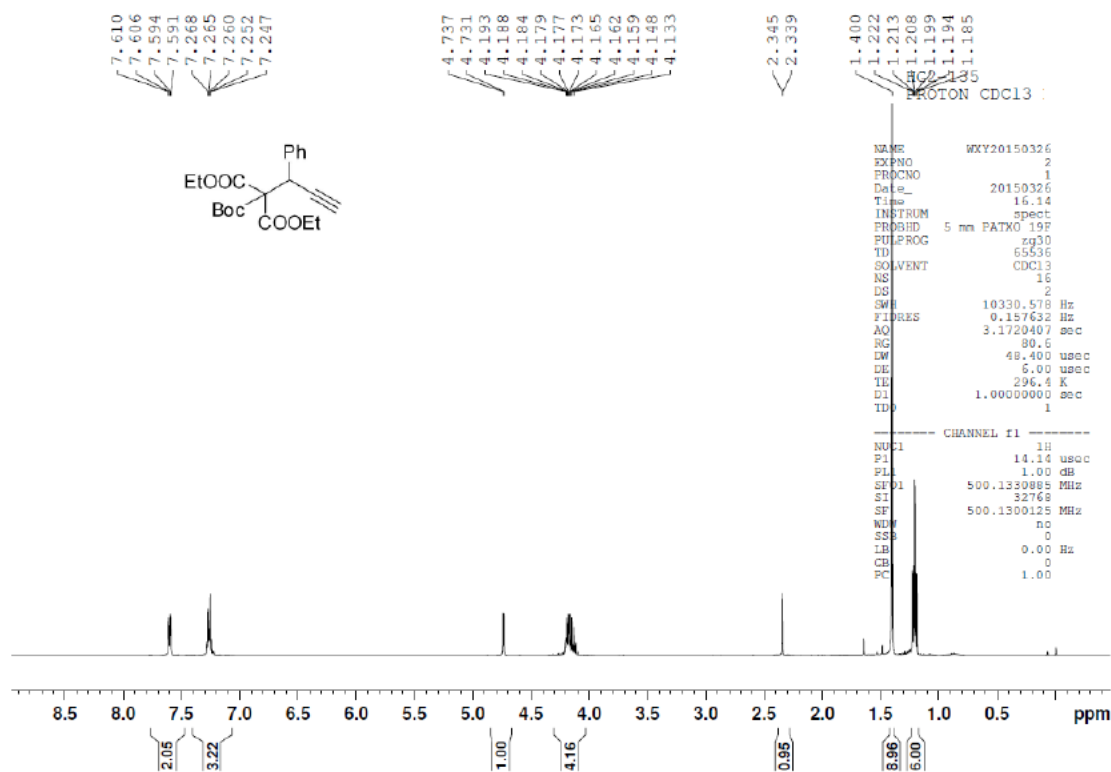
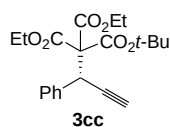


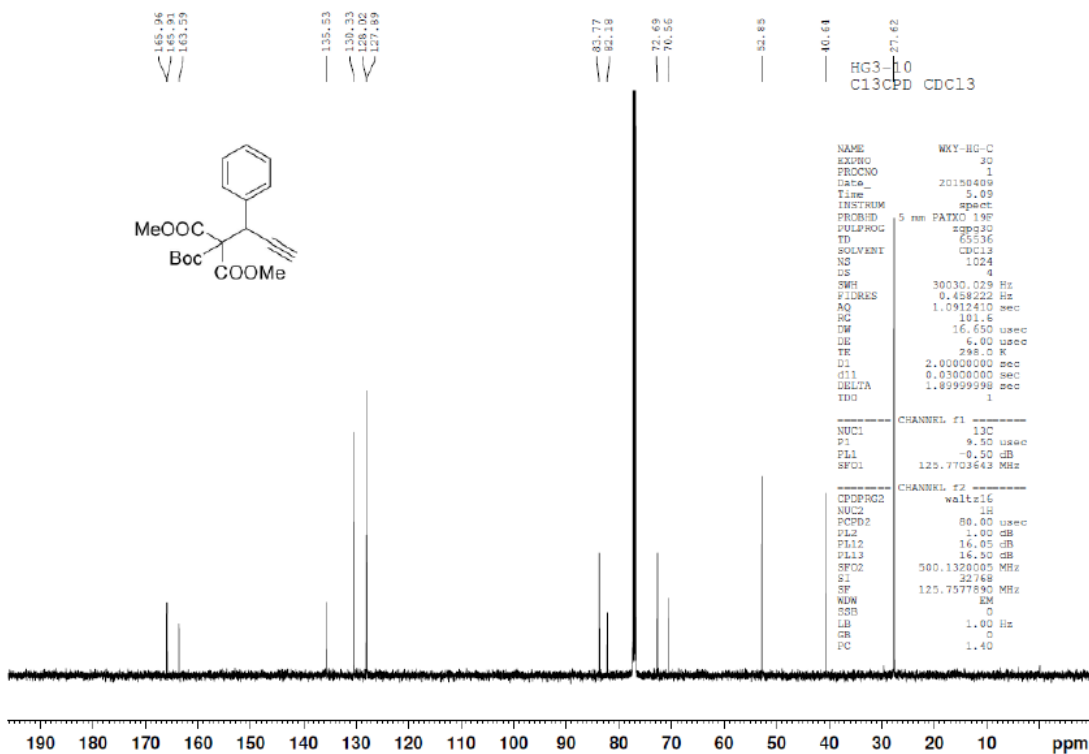
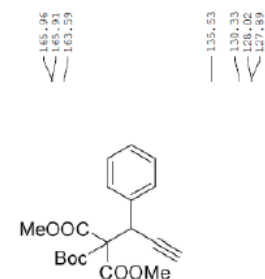
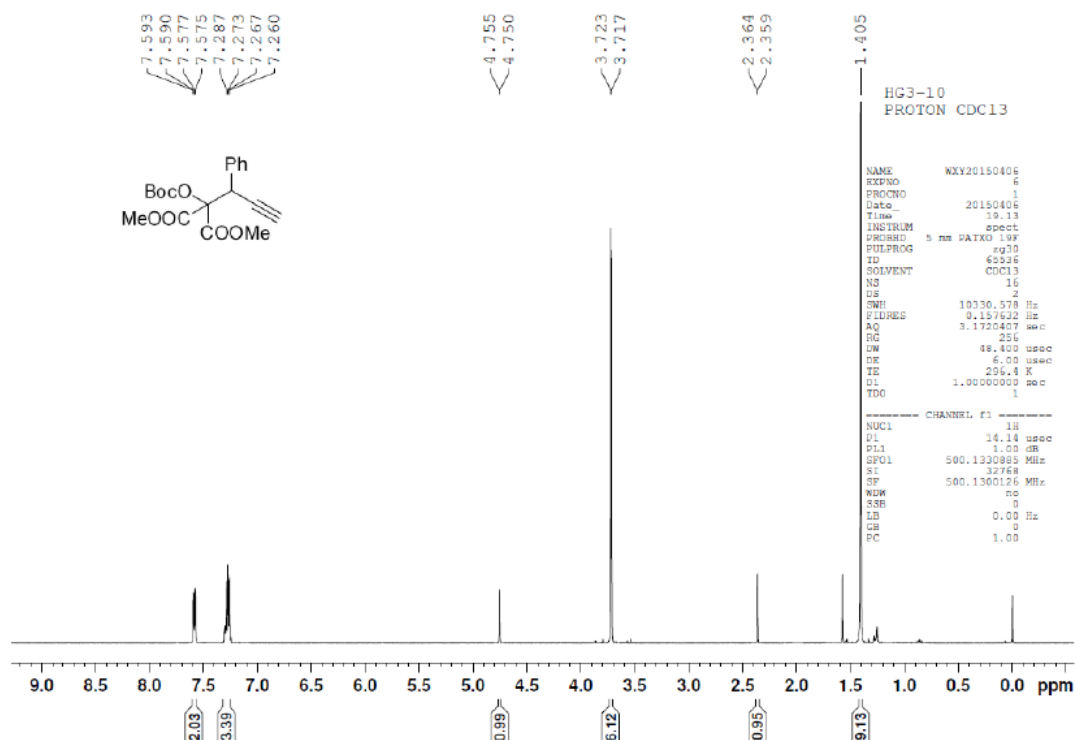
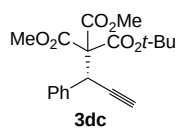
Peak#	Ret. Time	Area	Height	Area%
1	16.909	25799242	891200	49.098
2	19.646	26747118	817163	50.902
总计		52546360	1708363	100.000

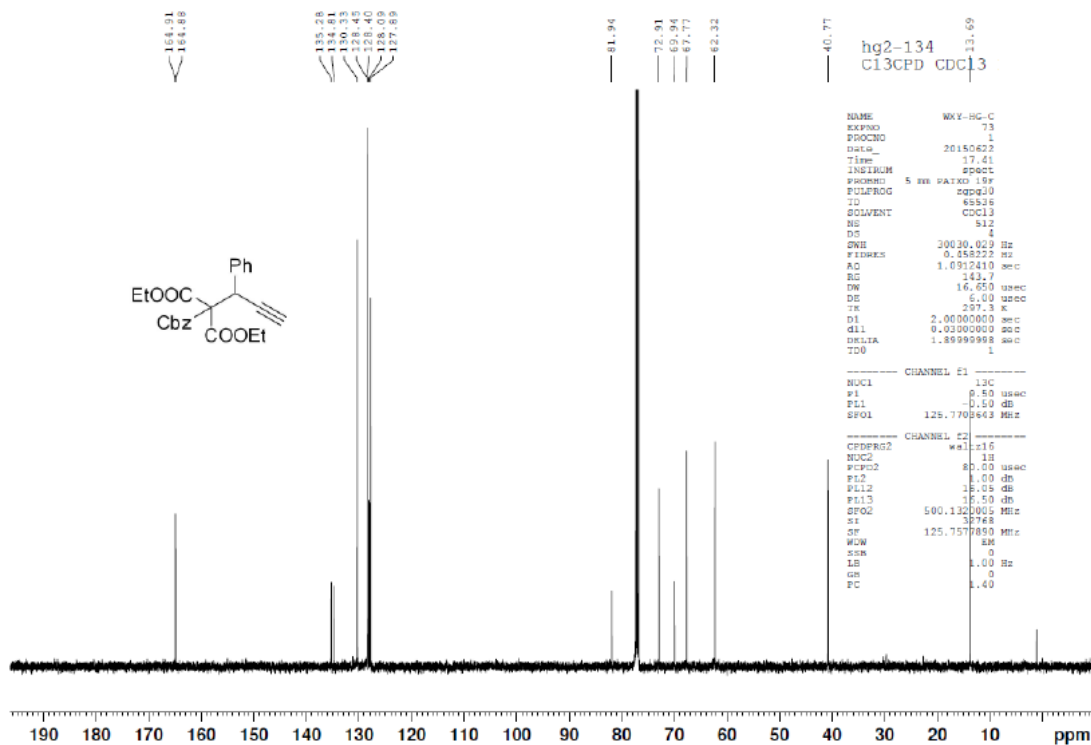
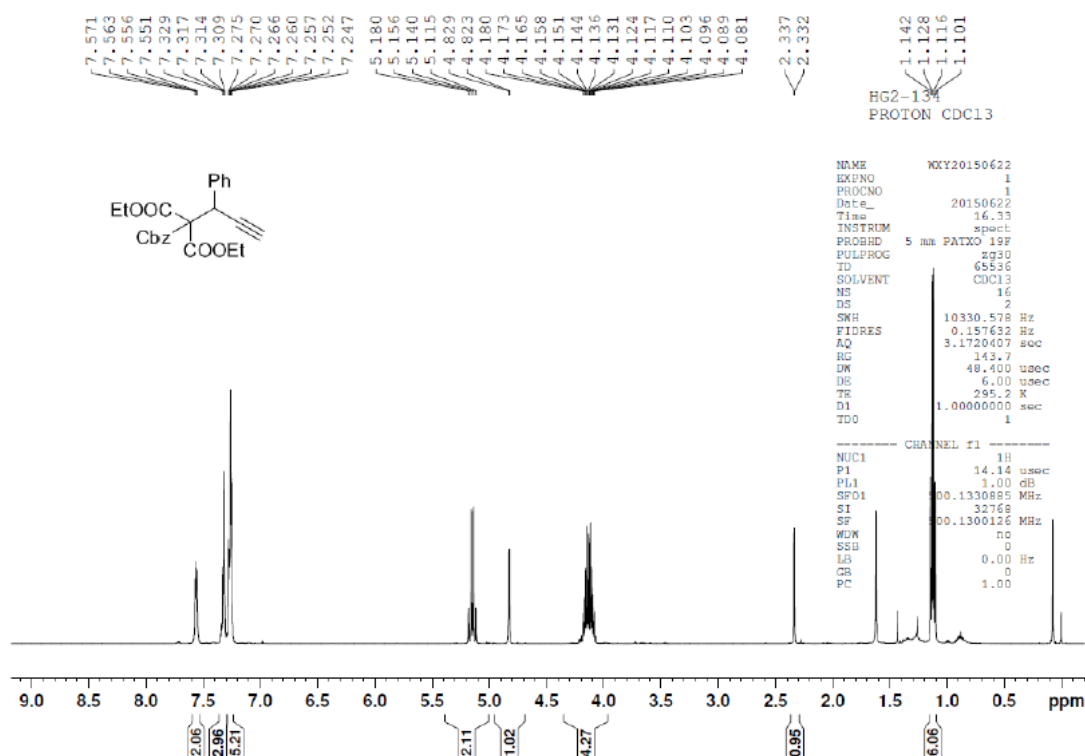
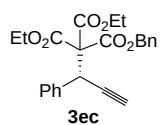


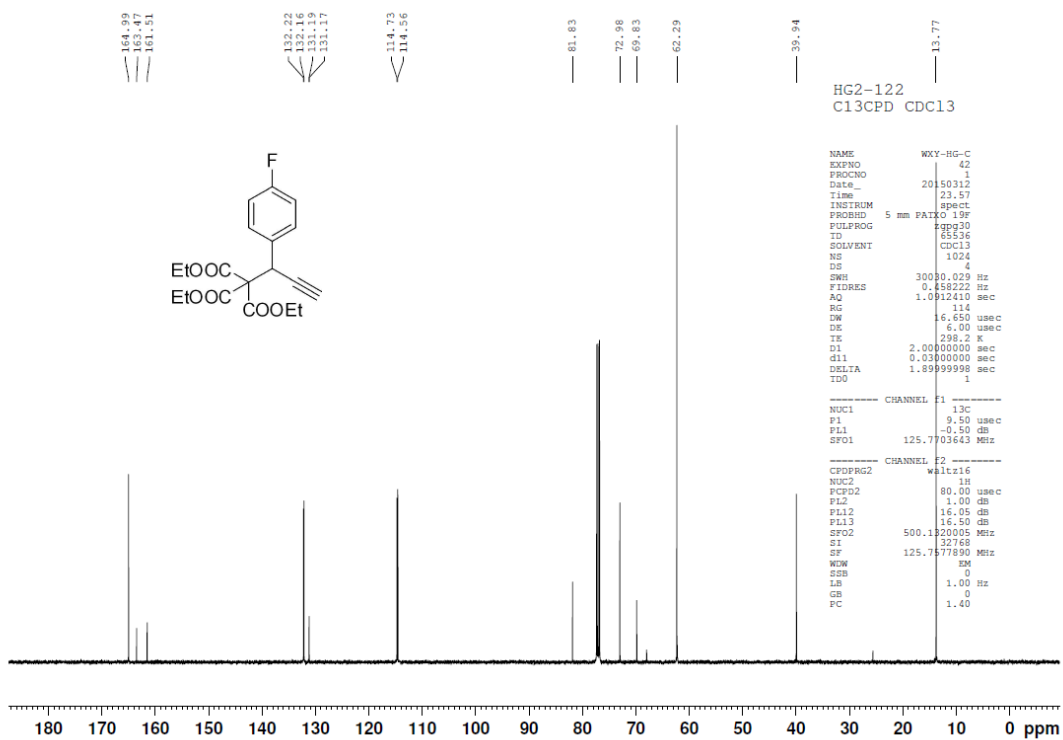
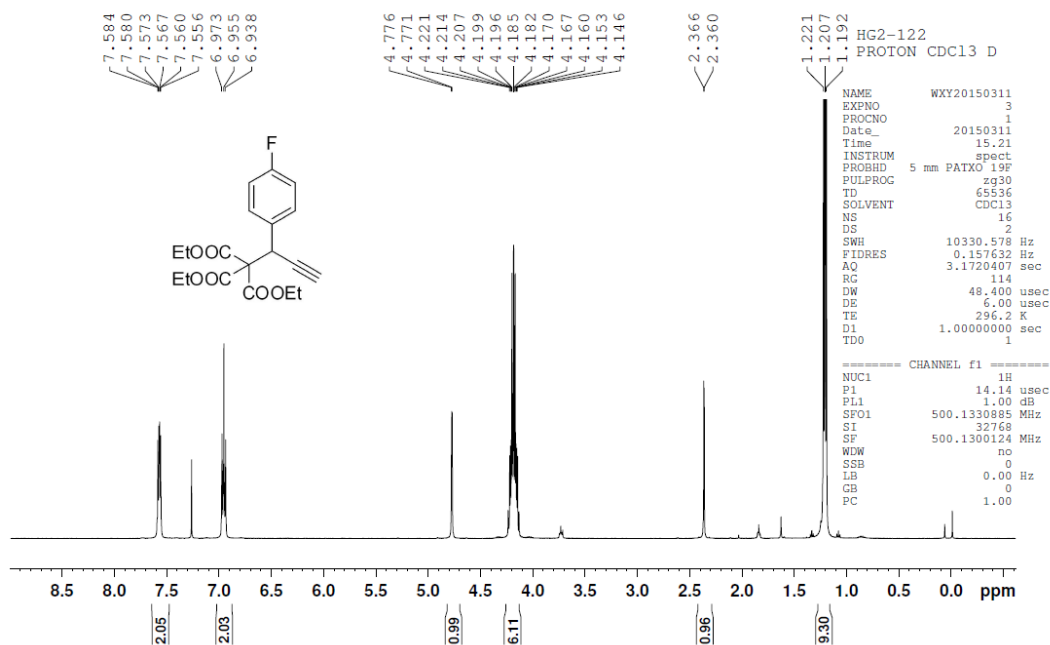
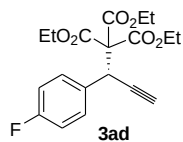
Peak#	Ret. Time	Area	Height	Area%
1	16.900	12356772	459895	94.929
2	18.544	660093	23742	5.071
总计		13016865	483637	100.000

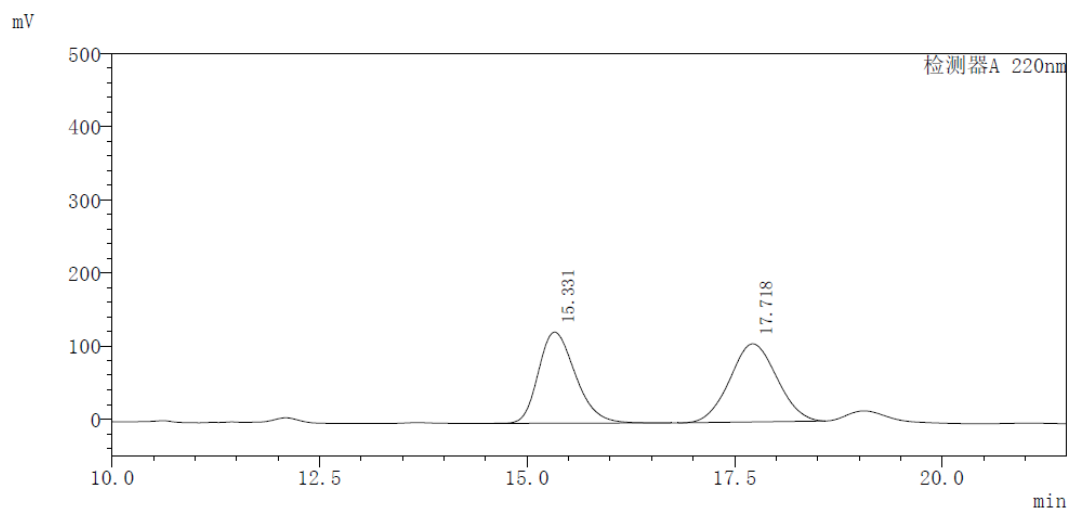
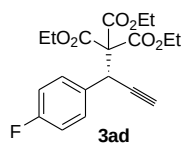




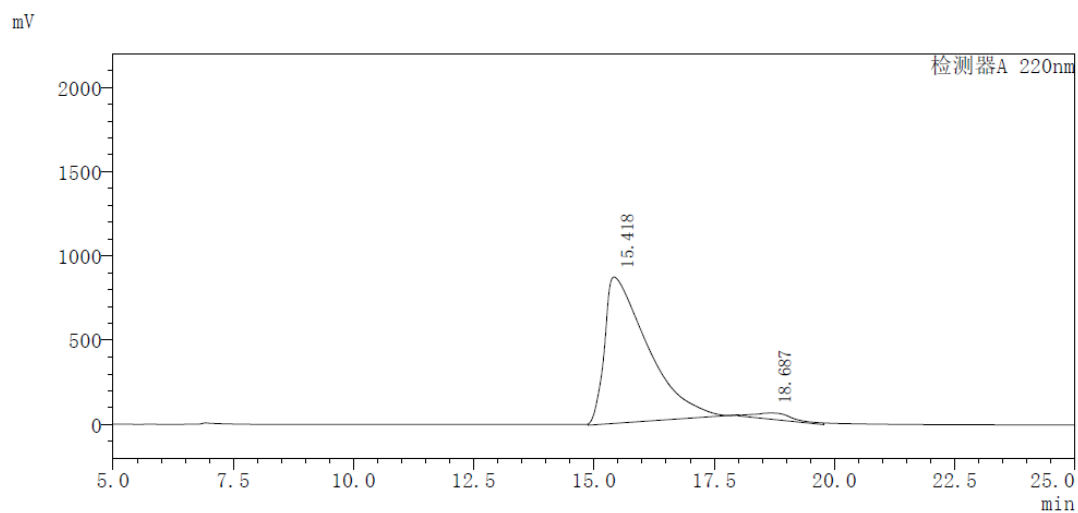




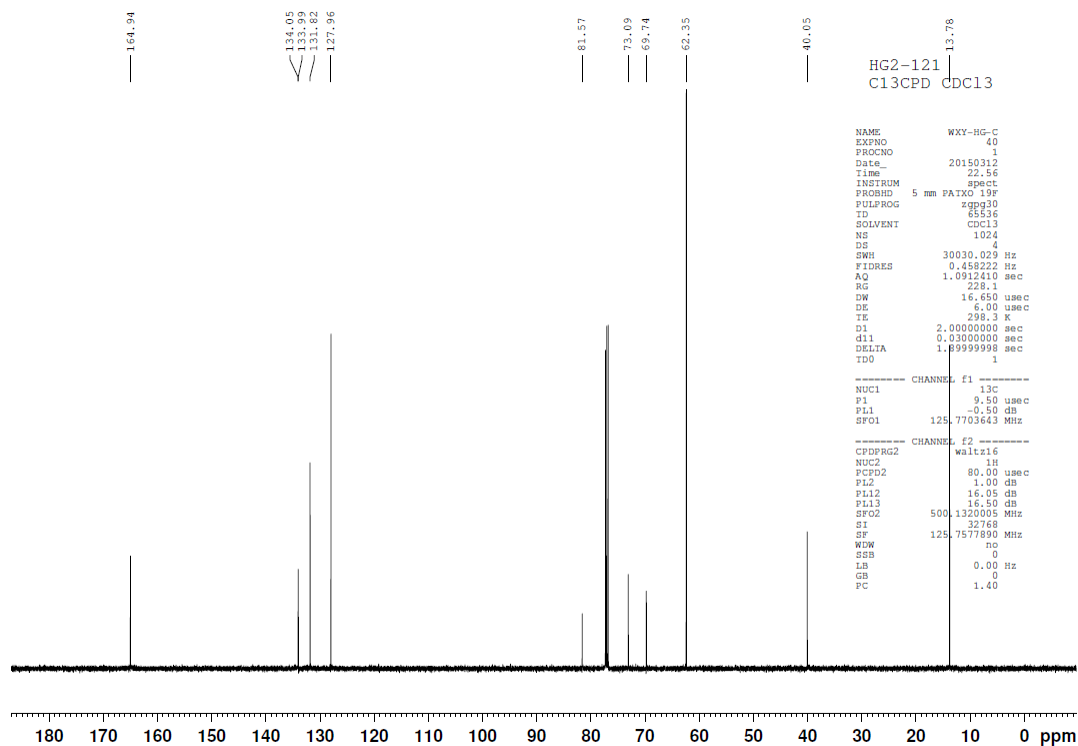
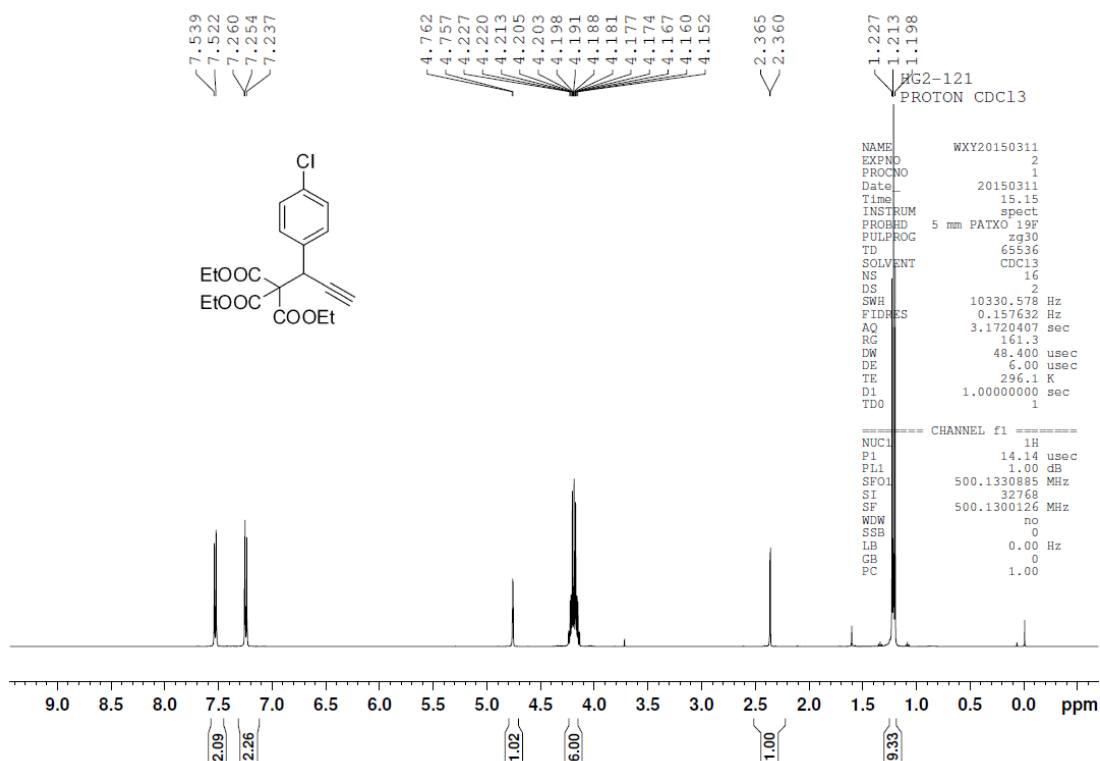
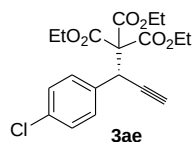


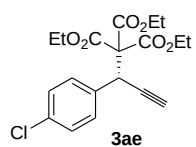


Peak#	Ret. Time	Area	Height	Area%
1	15.331	3862629	124500	47.836
2	17.718	4212119	106754	52.164
总计		8074748	231254	100.000

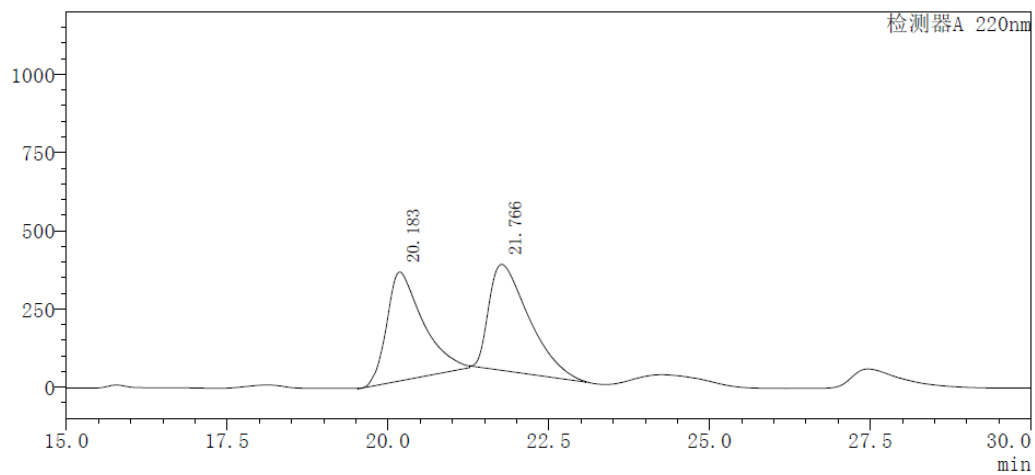


Peak#	Ret. Time	Area	Height	Area%
1	15.418	54319130	868814	96.215
2	18.687	2136736	37179	3.785
总计		56455867	905994	100.000



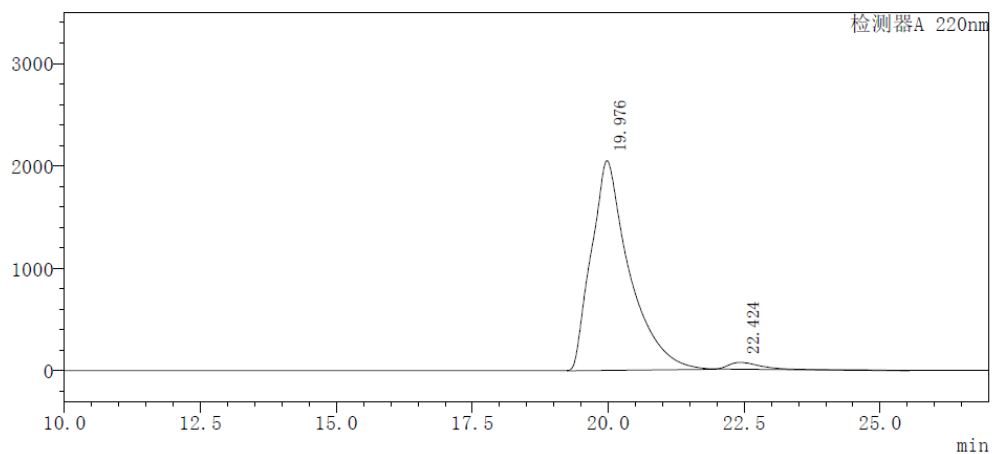


mV

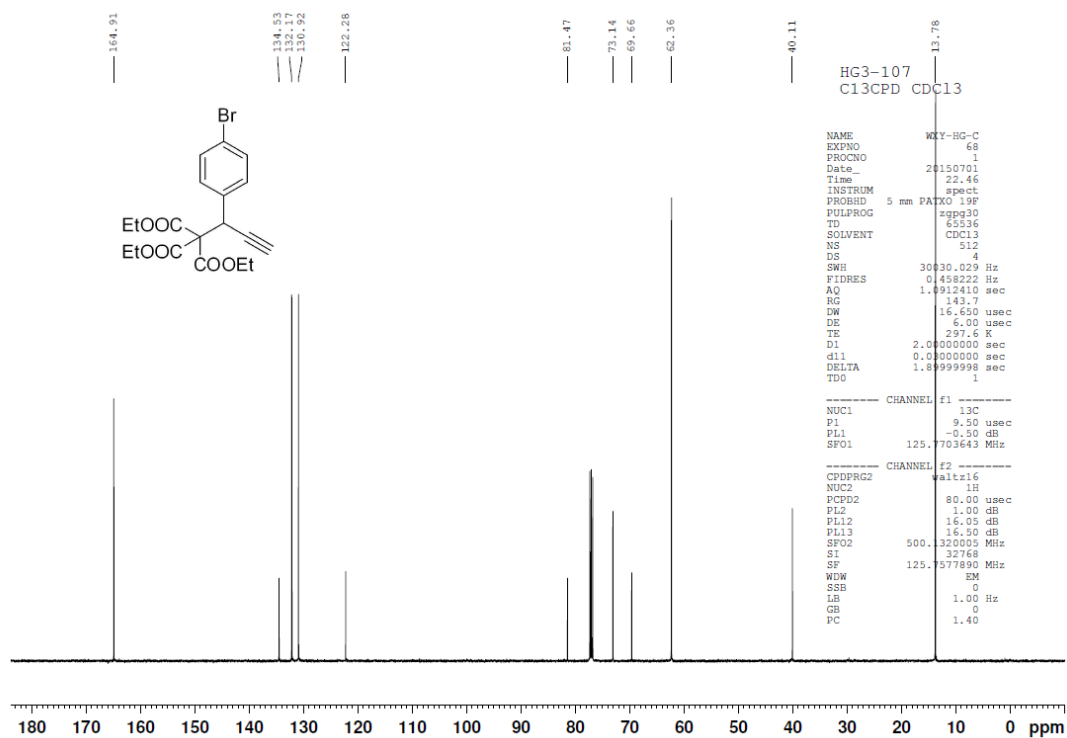
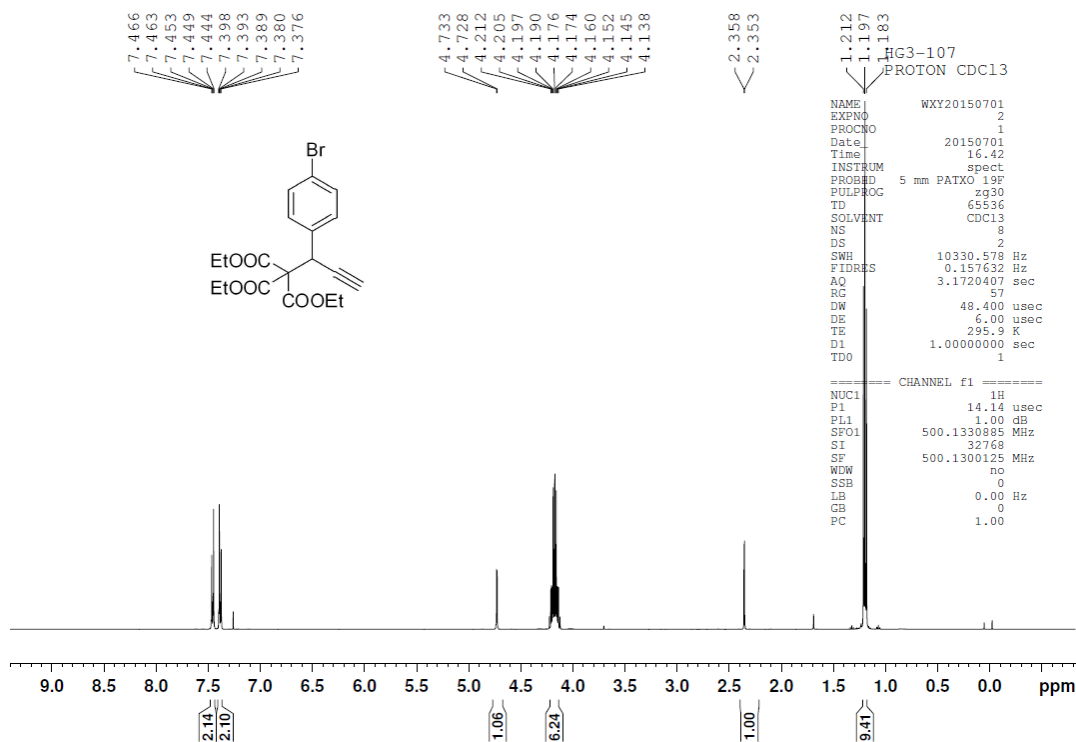
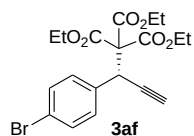


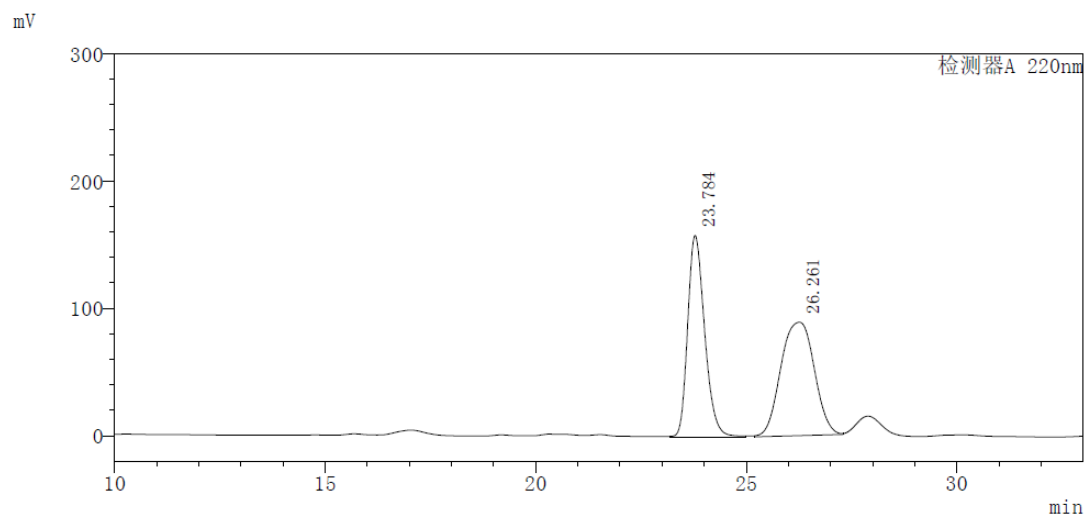
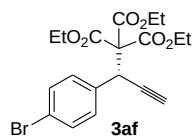
Peak#	Ret. Time	Area	Height	Area%
1	20.183	13647625	347956	47.965
2	21.766	14805781	338874	52.035
总计		28453406	686831	100.000

mV

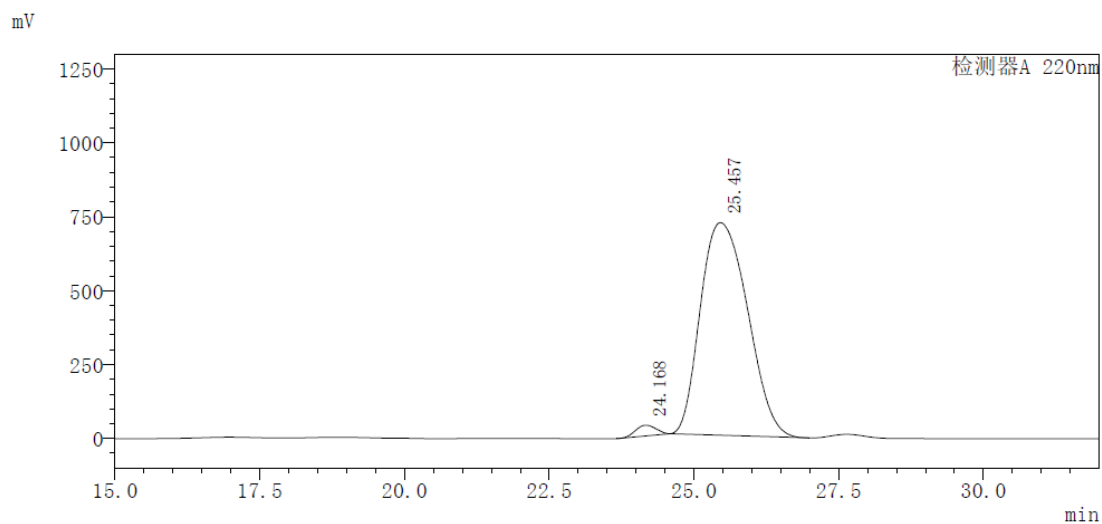


Peak#	Ret. Time	Area	Height	Area%
1	19.976	99766355	2047760	96.888
2	22.424	3204754	68030	3.112
总计		102971109	2115790	100.000

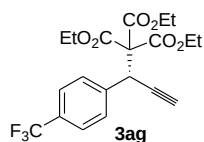




Peak#	Ret. Time	Area	Height	Area%
1	23.784	4418263	158066	47.267
2	26.261	4929279	88997	52.733
总计		9347543	247063	100.000



Peak#	Ret. Time	Area	Height	Area%
1	24.168	891284	36394	2.133
2	25.457	40885633	719479	97.867
总计		41776917	755873	100.000

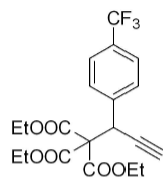


7.742
7.726
7.547
7.531

4.846
4.841
4.230
4.223
4.216
4.209
4.202
4.193
4.185
4.178
4.171
4.164
4.157

2.392
2.387

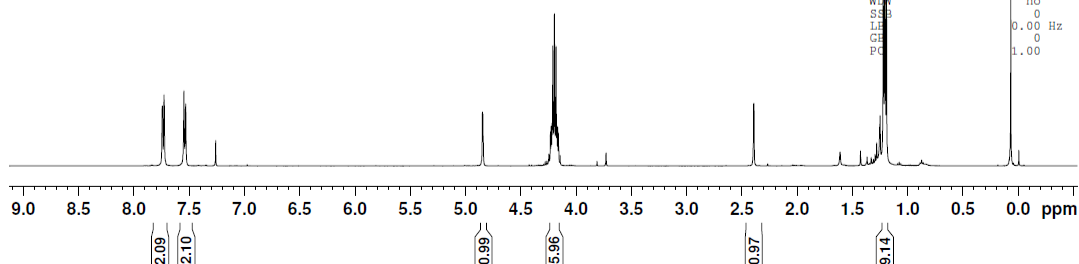
1.218
1.204
1.190
HG3-75-6
PROTON CDC13



```

NAME      WXY20150603
EXPNO     3
PROCNO    1
Date_     20150603
Time      19.06
INSTRUM   spect
PROBHD    5 mm PATXO 19F
PULPROG   zg30
TD        65536
SOLVENT   CDC13
NS        16
DS        2
SWH        10330.578 Hz
FIDRES     0.157632 Hz
AQ         3.1720407 sec
RG         114
DW         48.400 usec
DE         6.00 usec
TE         295.5 K
D1         1.00000000 sec
TD0        1
===== CHANNEL f1 =====
NUC1       1H
P1         14.14 usec
PL1        1.00 dB
SFO1       500.1330885 MHz
SI         32768
SF         500.1300127 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.00

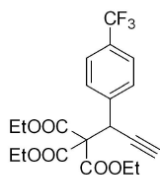
```



164.85
139.56
139.90
139.25
130.10
129.83
129.18
124.73
124.70
124.67

81.20
73.41
69.66
62.44

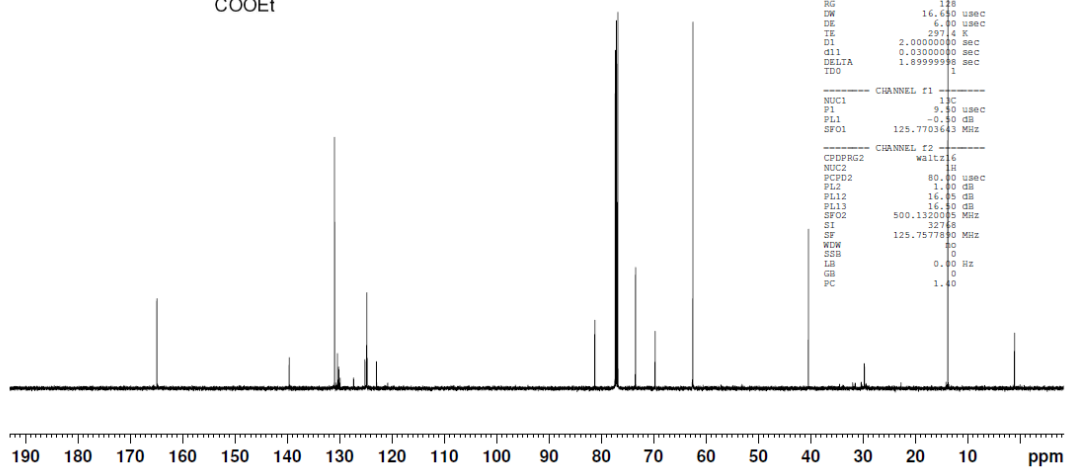
40.37
13.73
HG3-75-6
C13CPD CDC13

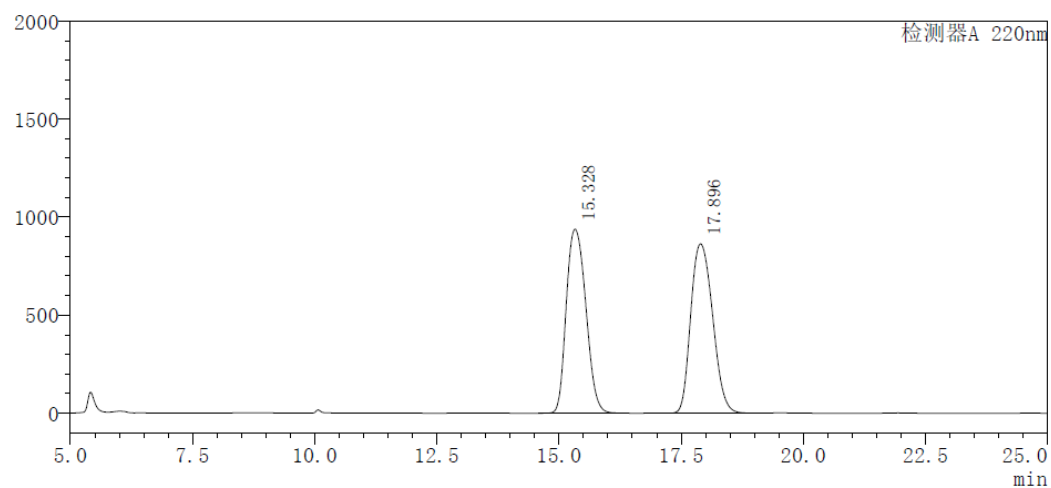
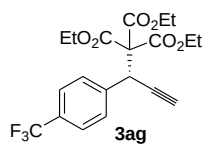


```

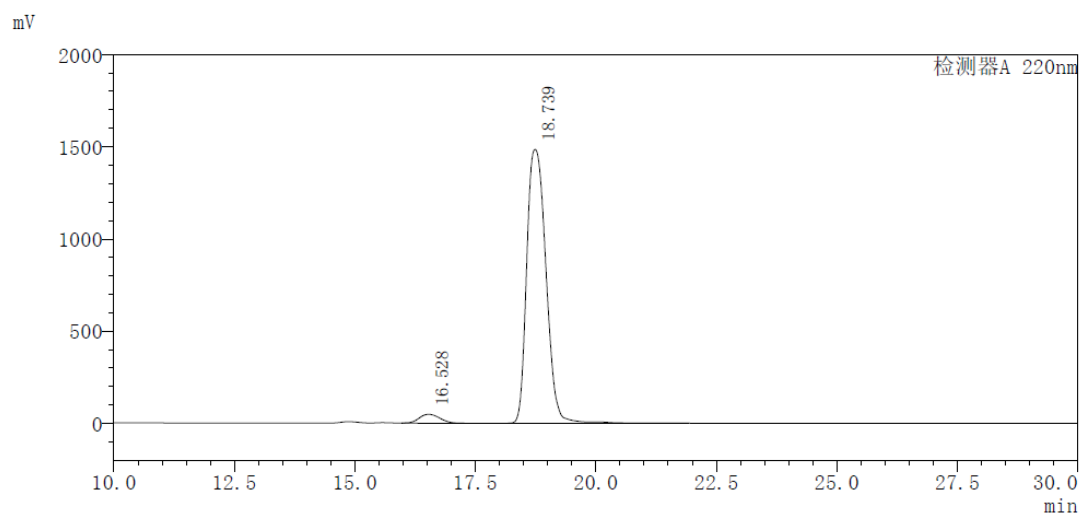
NAME      WXY-HG-C
EXPNO     41
PROCNO    1
Date_     20150606
Time      8.42
INSTRUM   spect
PROBHD    5 mm PATXO 19F
PULPROG   zgpg30
TD        65536
SOLVENT   CDC13
NS        4
DS        4
SWH        30030.028 Hz
FIDRES     0.458222 Hz
AQ         1.0912410 sec
RG         128
DW         16.640 usec
DE         6.40 usec
TE         297.4 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999998 sec
TD0        1
===== CHANNEL f1 =====
NUC1       13C
P1         9.40 usec
PL1        -0.40 dB
SFO1       125.7703643 MHz
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.80 usec
PL2        1.40 dB
PL12       16.85 dB
PL13       16.80 dB
SFO2       500.1330085 MHz
SI         32768
SF         125.7577890 MHz
WDW        80
SSB        0
LB         0.40 Hz
GB         0
PC         1.40

```

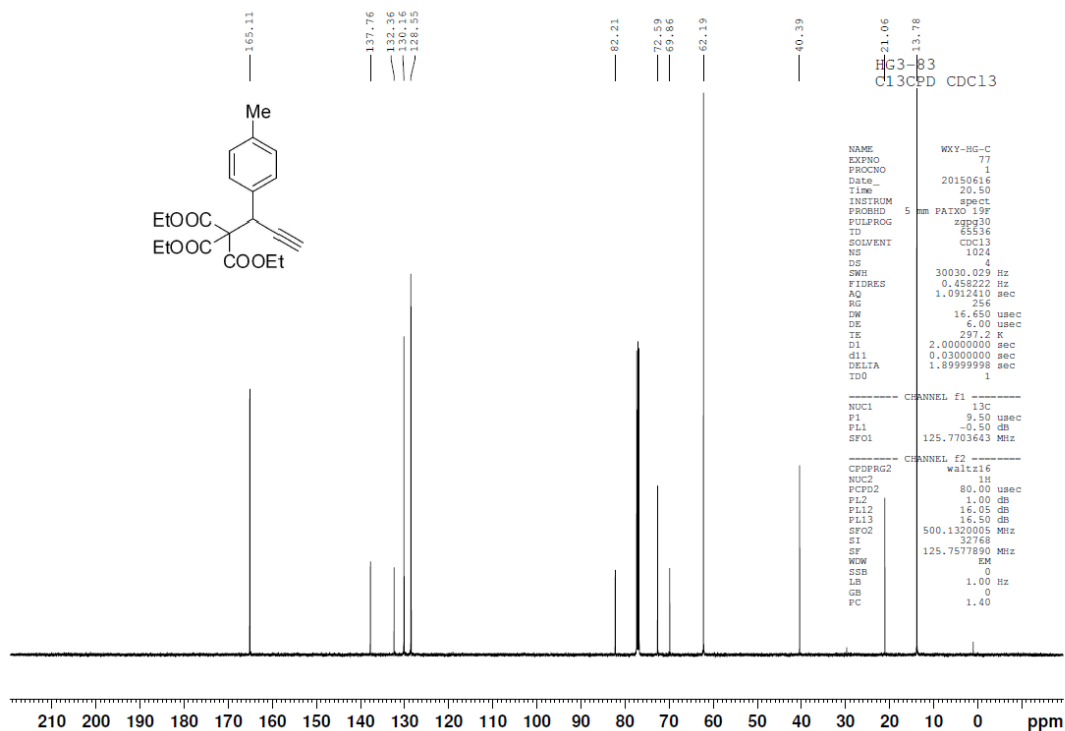
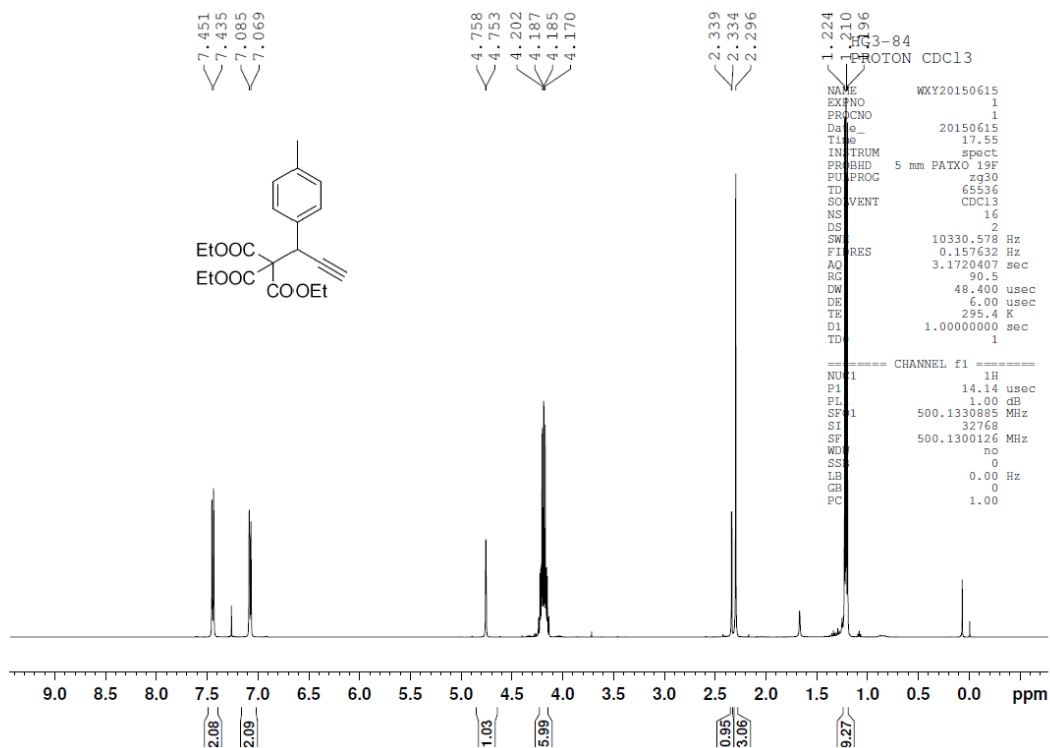
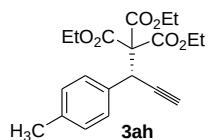


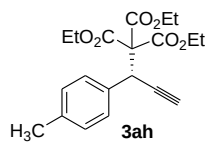


Peak#	Ret. Time	Area	Height	Area%
1	15.328	26306239	939225	49.358
2	17.896	26990960	863672	50.642
总计		53297200	1802897	100.000

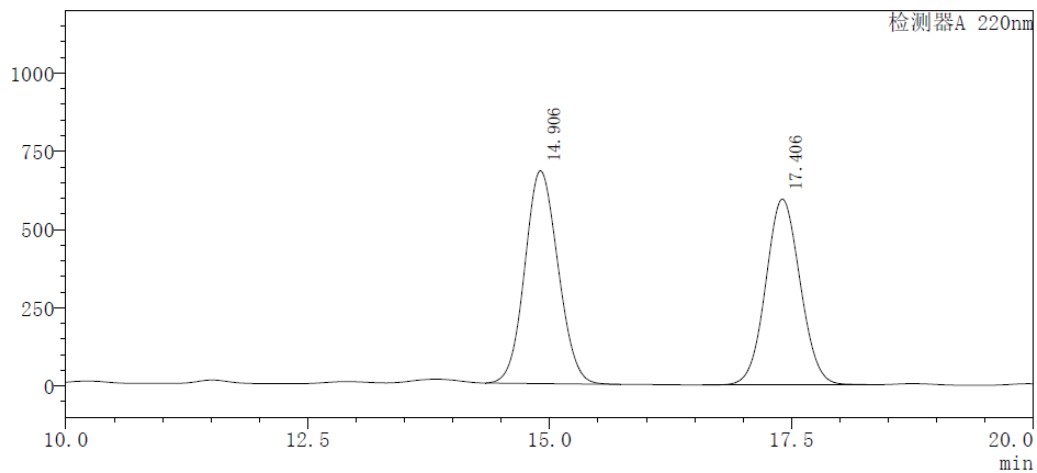


Peak#	Ret. Time	Area	Height	Area%
1	16.528	1431847	48383	3.349
2	18.739	41325278	1484776	96.651
总计		42757125	1533159	100.000



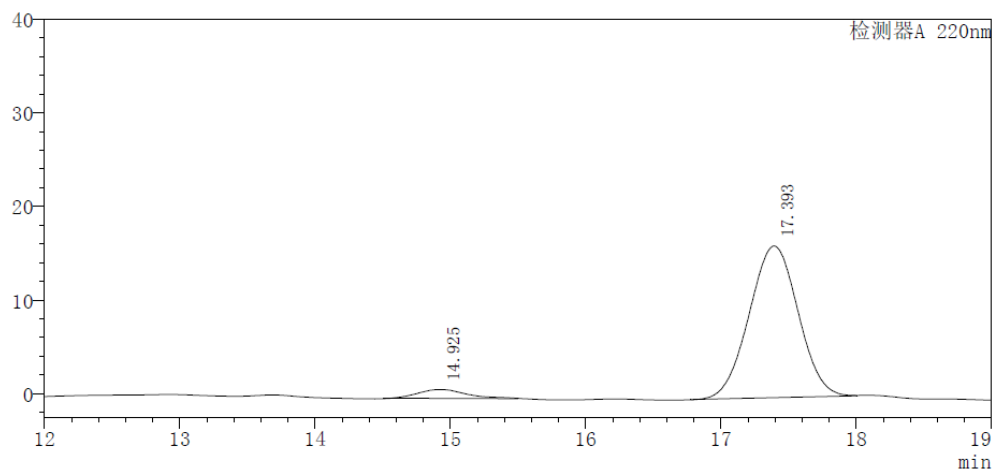


mV

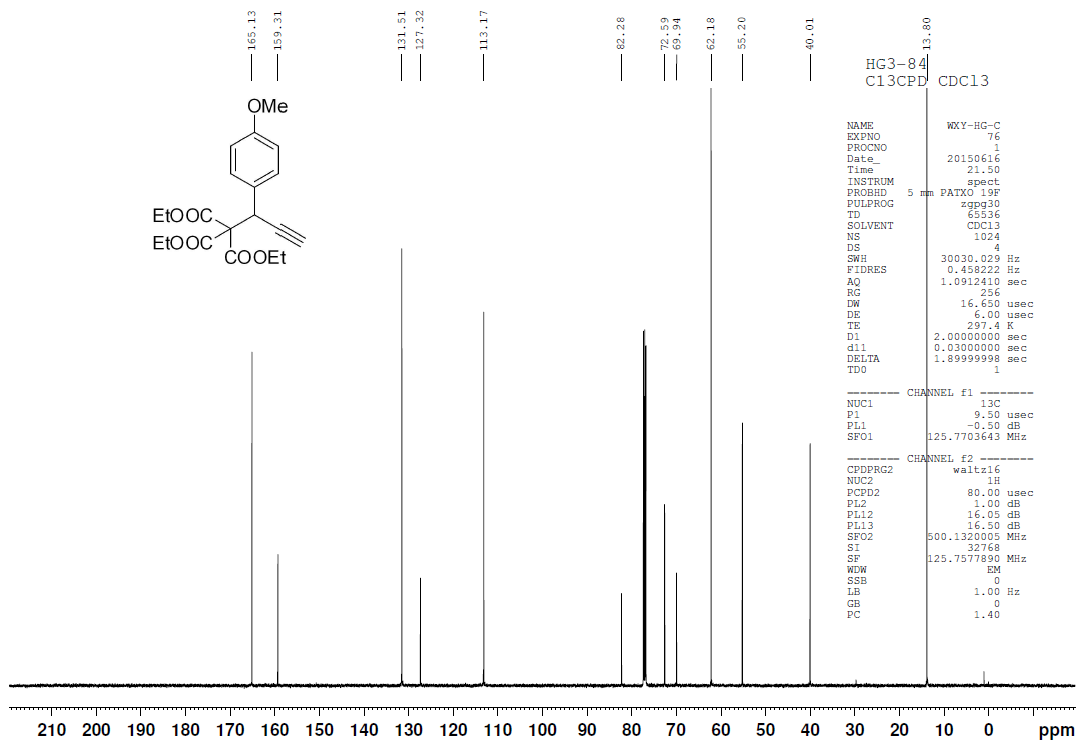
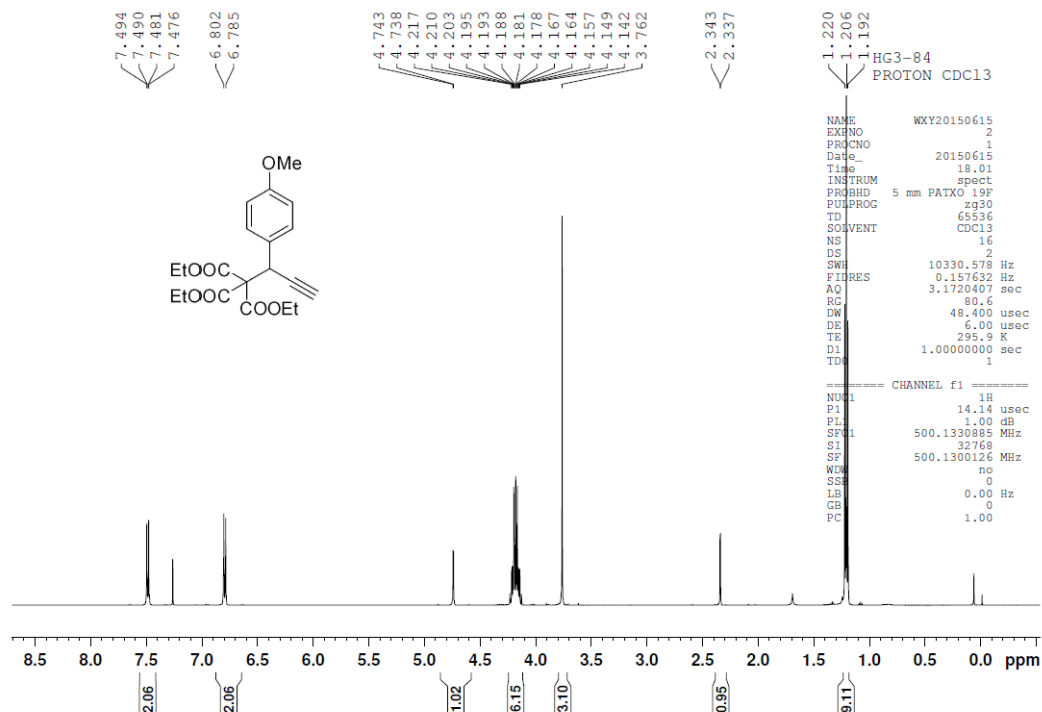
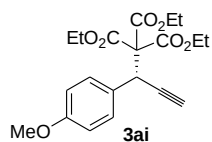


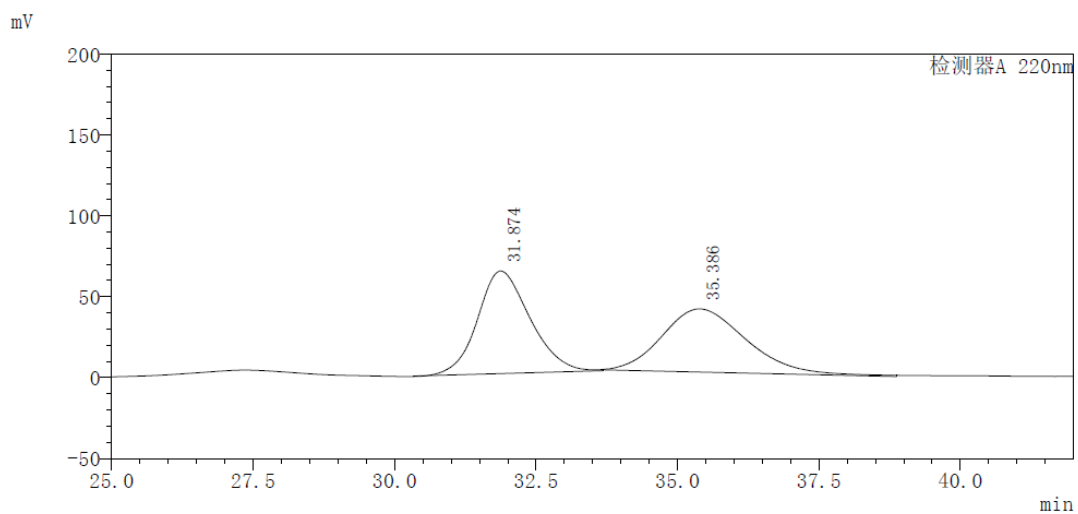
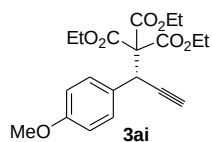
Peak#	Ret. Time	Area	Height	Area%
1	14.906	16313489	680307	52.459
2	17.406	14784086	594110	47.541
总计		31097576	1274417	100.000

mV

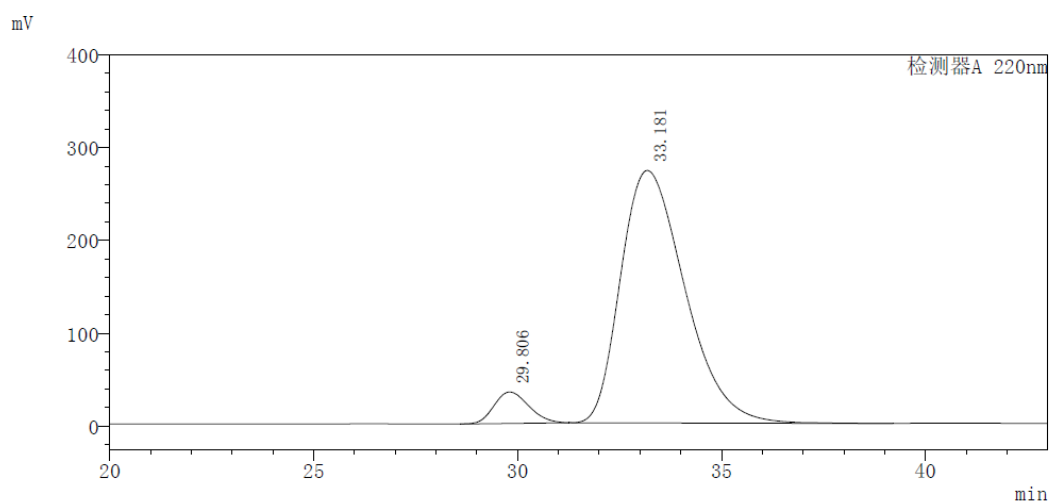


Peak#	Ret. Time	Area	Height	Area%
1	14.925	24145	964	5.591
2	17.393	407752	16194	94.409
总计		431897	17158	100.000

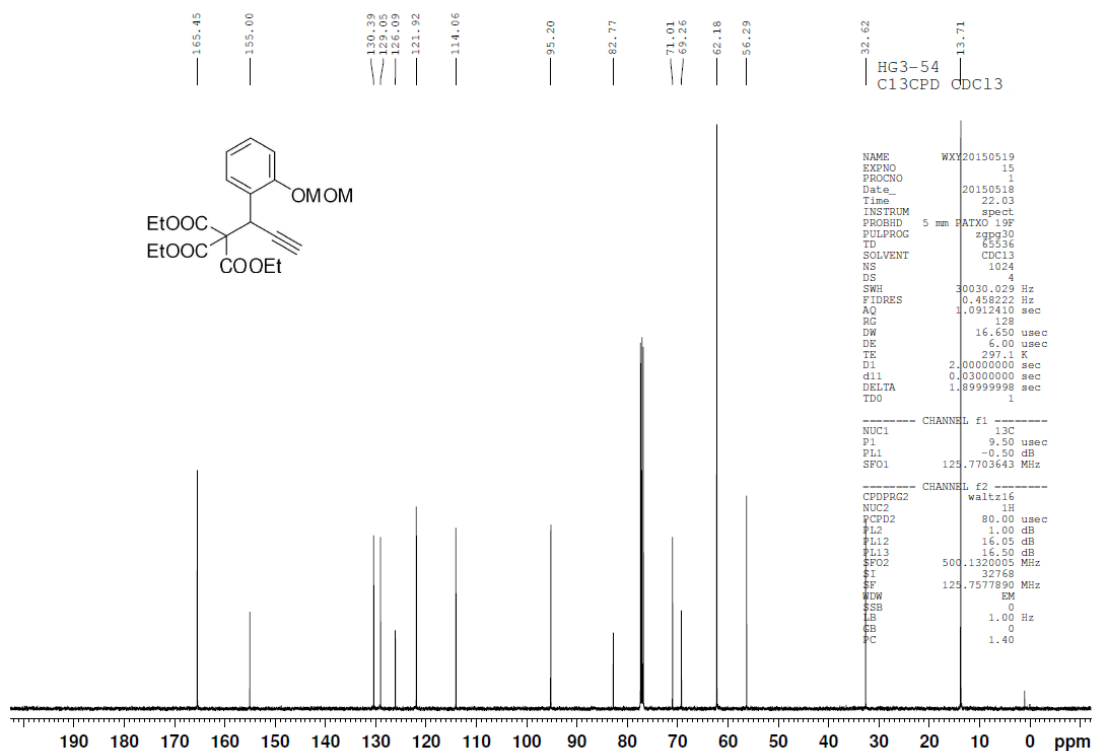
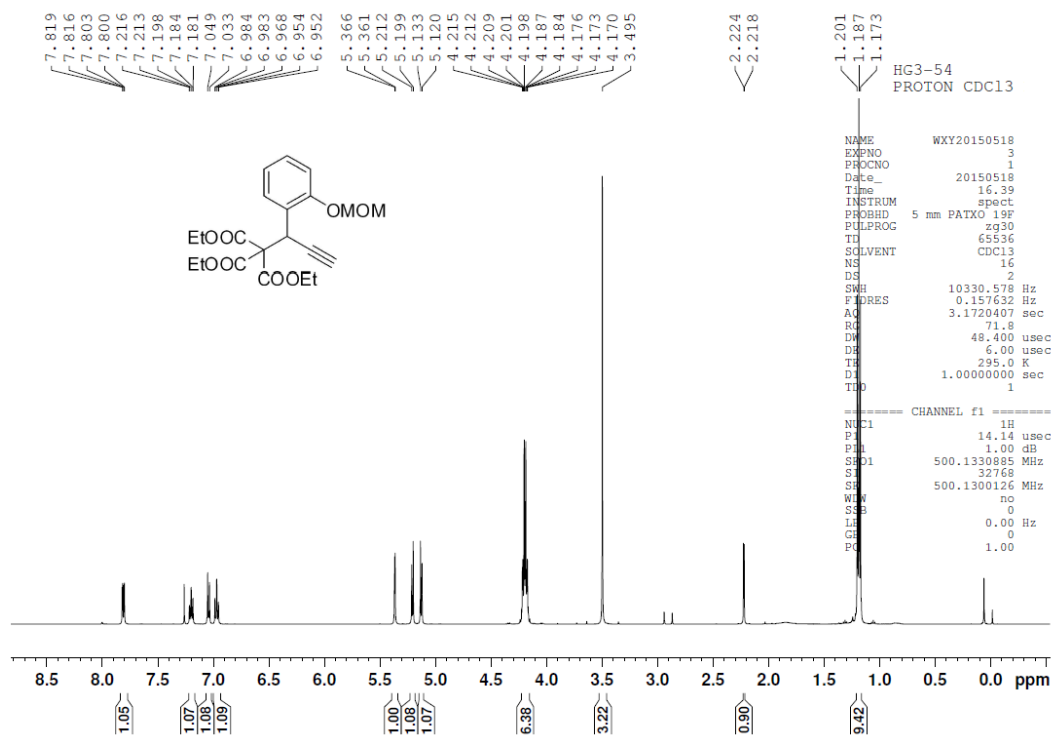
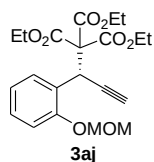


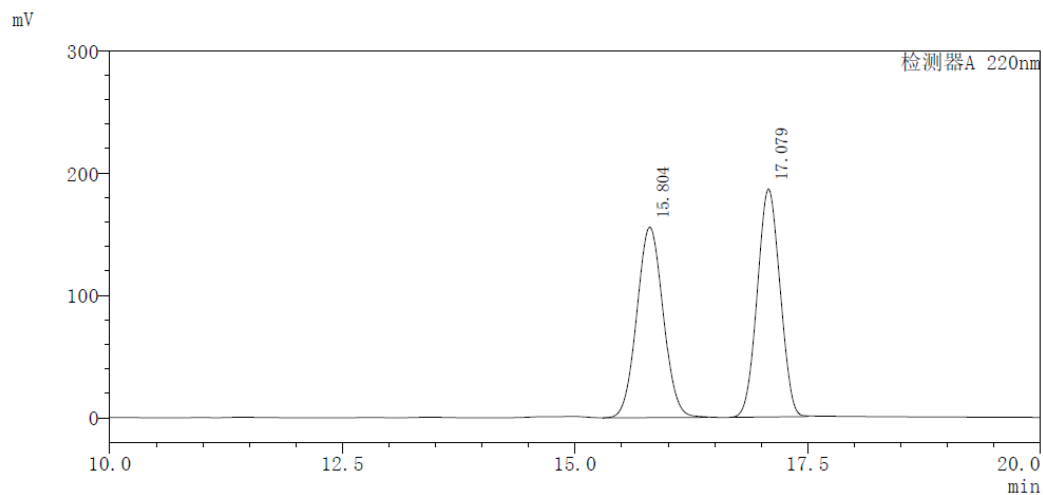
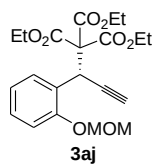


Peak#	Ret. Time	Area	Height	Area%
1	31.874	4090417	63352	50.210
2	35.386	4056164	39013	49.790
总计		8146582	102365	100.000

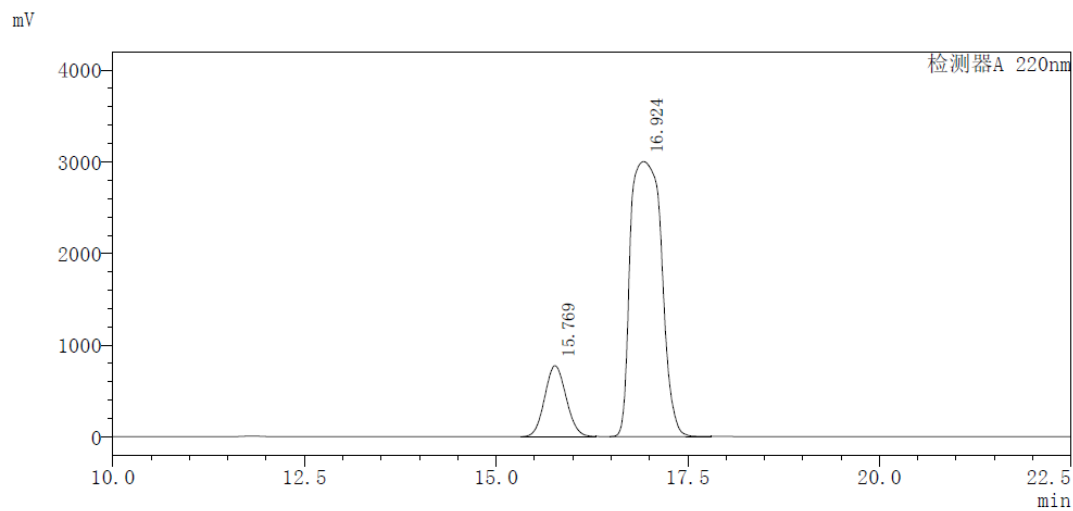


Peak#	Ret. Time	Area	Height	Area%
1	29.806	1996799	33797	6.279
2	33.181	29804669	271687	93.721
总计		31801468	305484	100.000

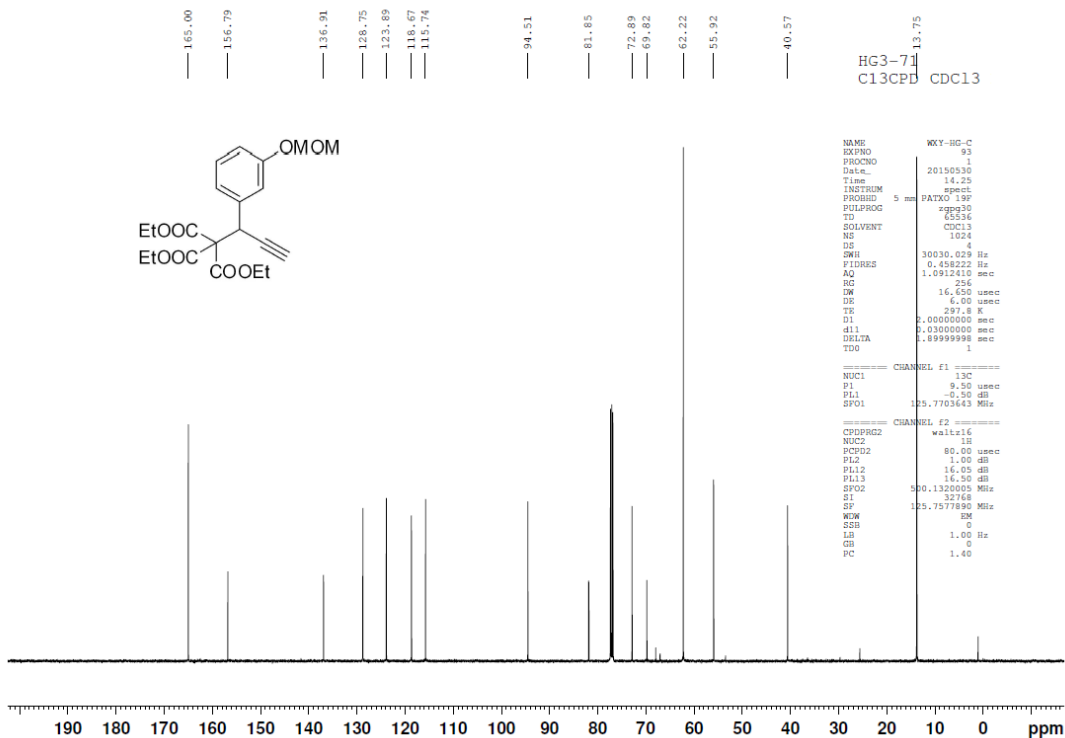
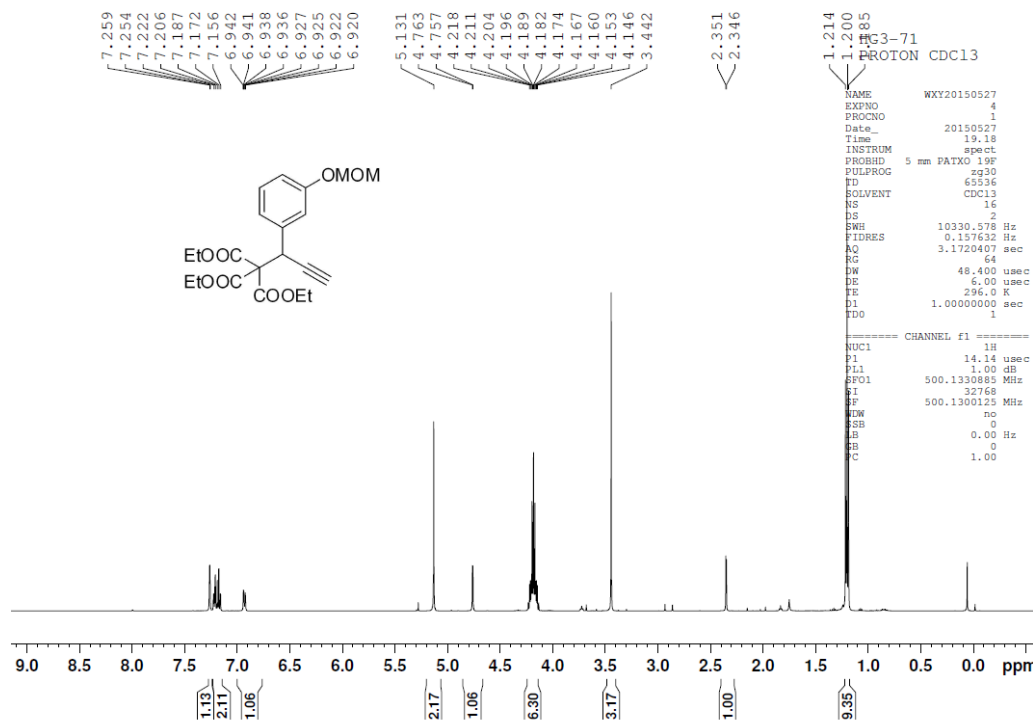
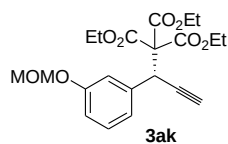


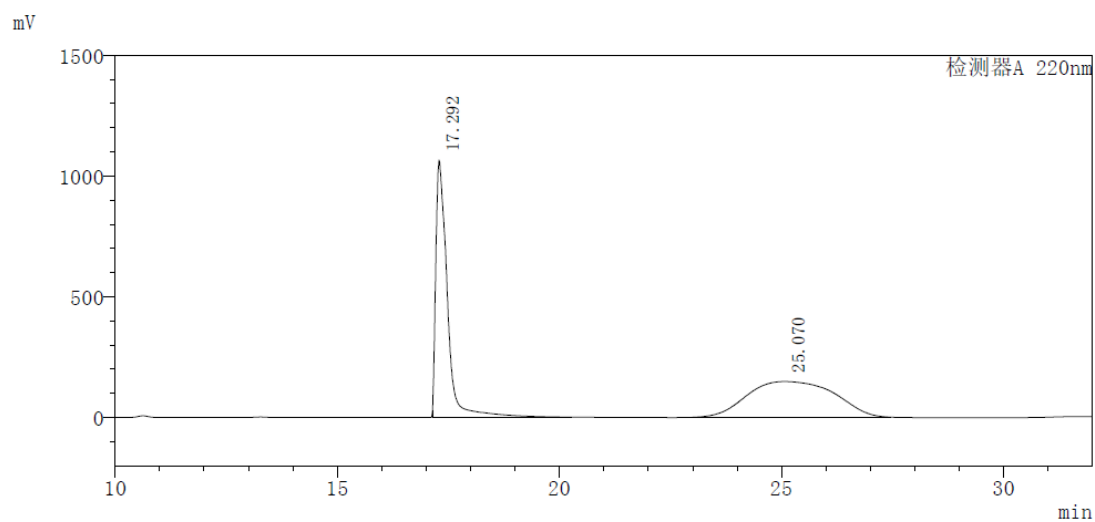
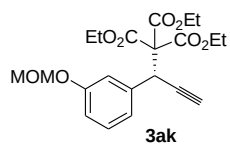


Peak#	Ret. Time	Area	Height	Area%
1	15.804	3062589	155703	49.097
2	17.079	3175262	186311	50.903
总计		6237851	342014	100.000

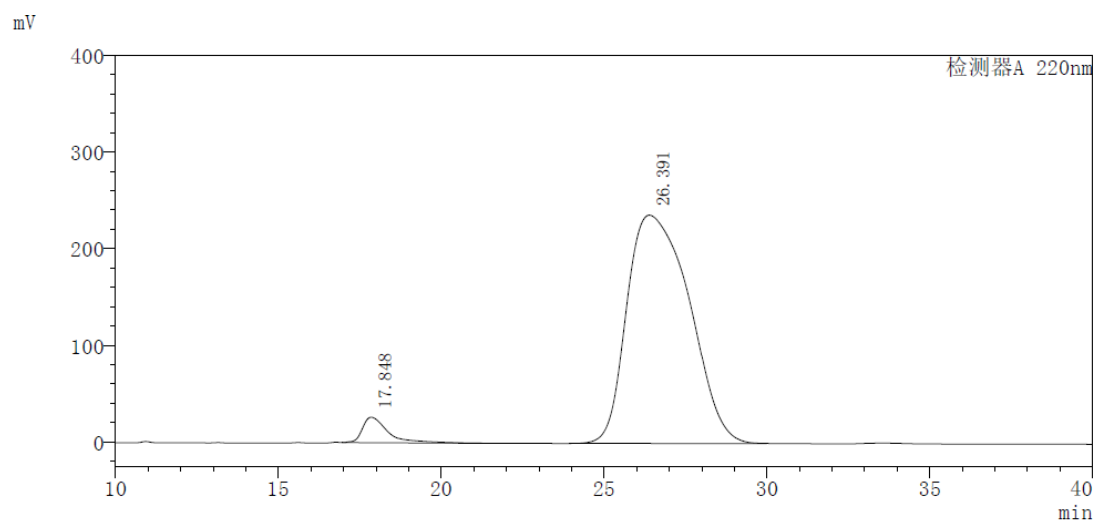


Peak#	Ret. Time	Area	Height	Area%
1	15.769	15059822	773196	15.063
2	16.924	84918491	3002555	84.937
总计		99978313	3775751	100.000

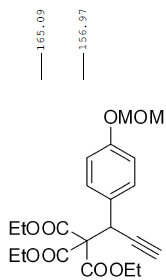
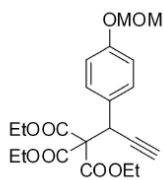
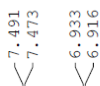


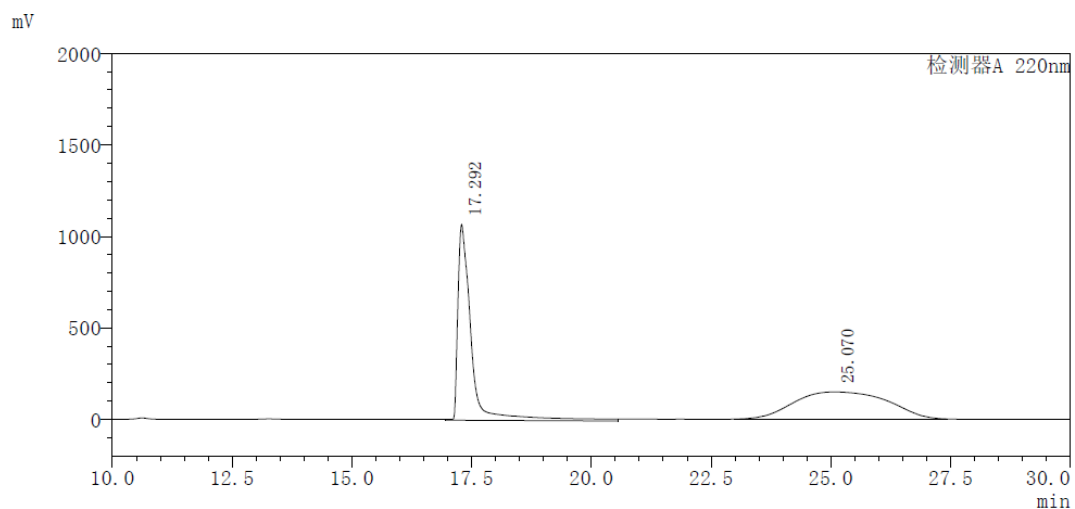
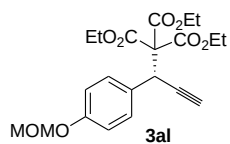


Peak#	Ret. Time	Area	Height	Area%
1	17.292	19359472	1063838	48.183
2	25.070	20819651	150183	51.817
总计		40179123	1214021	100.000

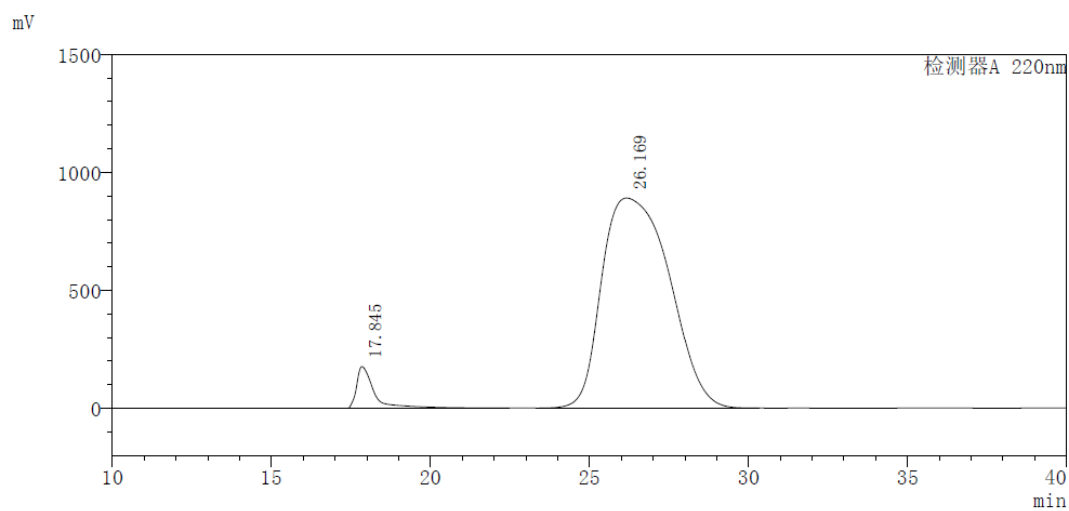


Peak#	Ret. Time	Area	Height	Area%
1	17.848	1438914	26307	4.364
2	26.391	31532001	236101	95.636
总计		32970915	262408	100.000

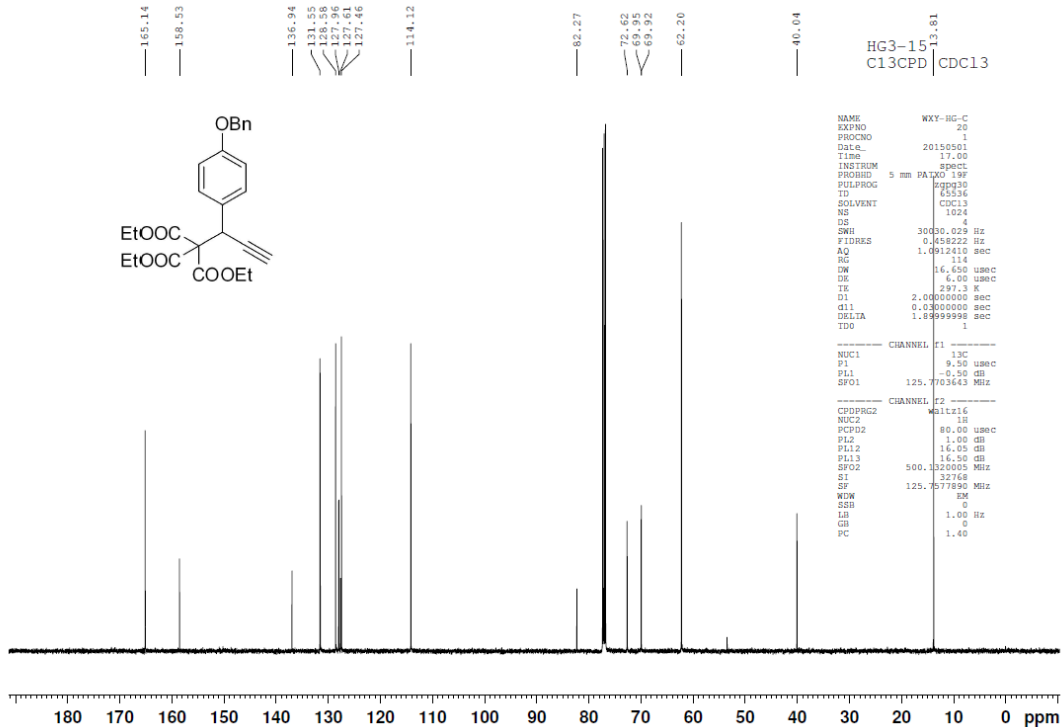
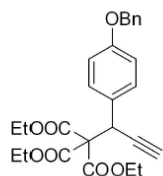
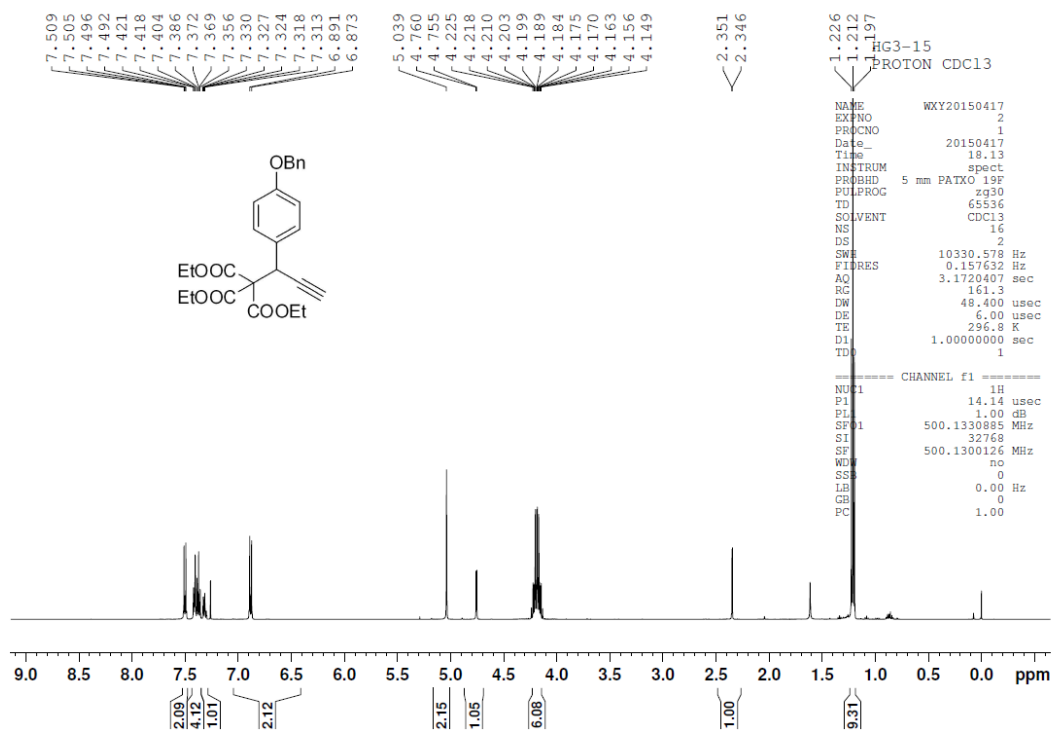
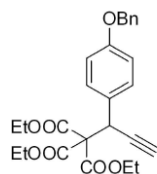
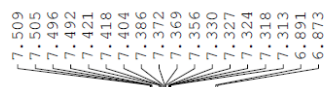


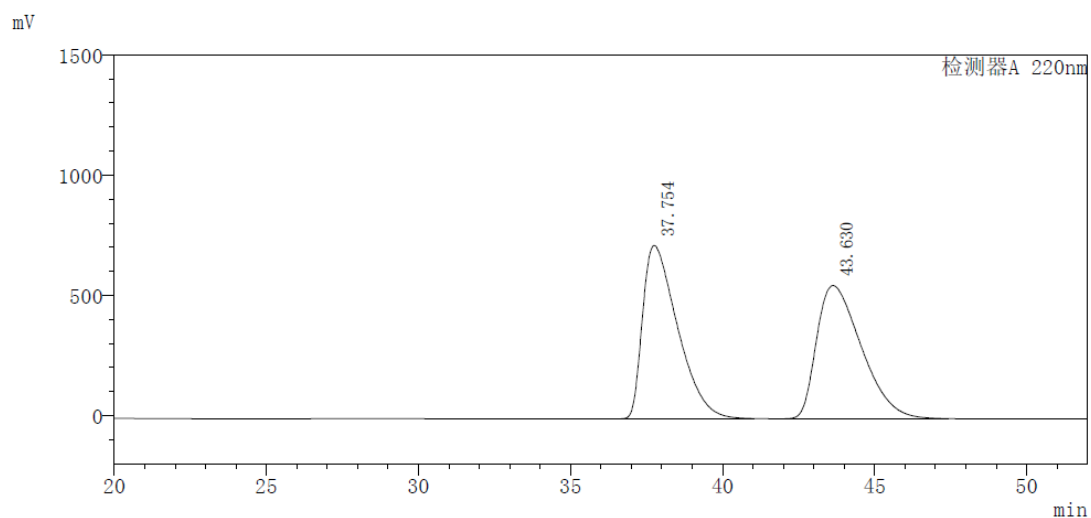
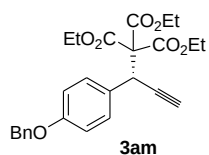


Peak#	Ret. Time	Area	Height	Area%
1	17.292	21017809	1070124	50.237
2	25.070	20819651	150183	49.763
总计		41837461	1220307	100.000

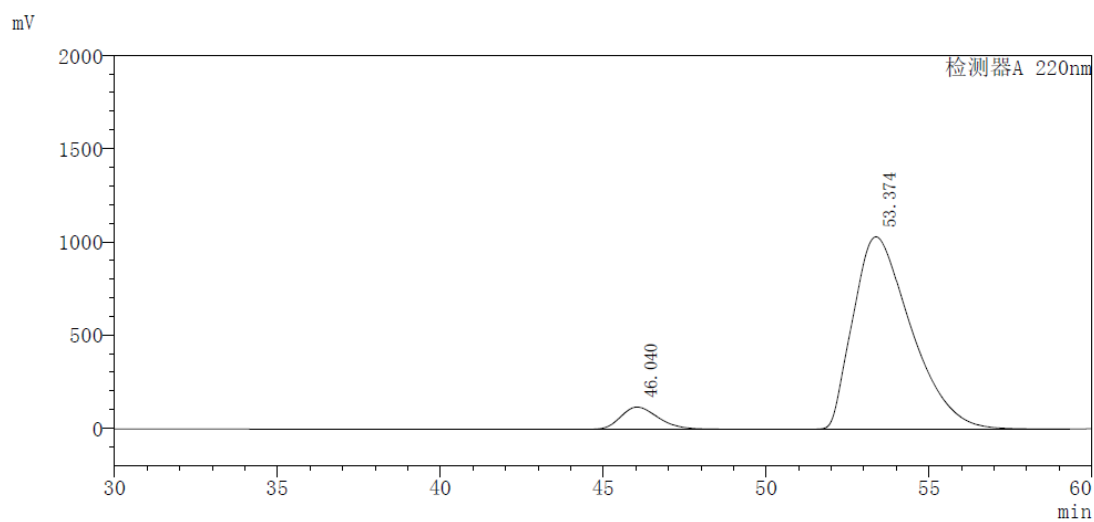


Peak#	Ret. Time	Area	Height	Area%
1	17.845	6842053	176861	4.908
2	26.169	132577099	891892	95.092
总计		139419152	1068753	100.000

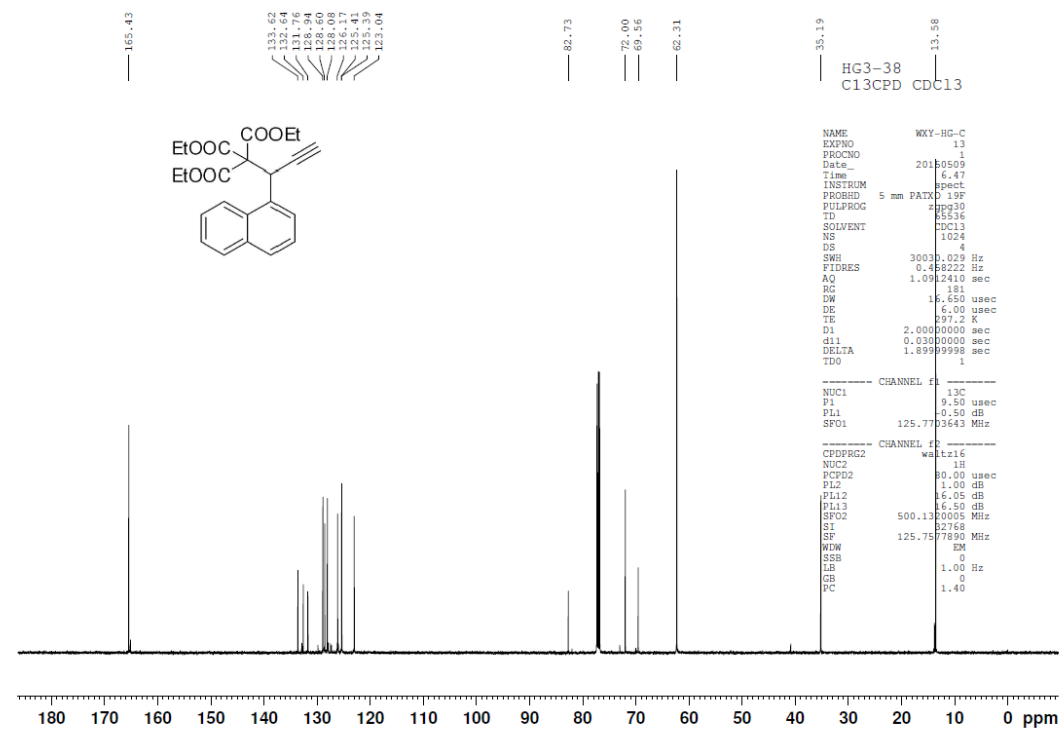
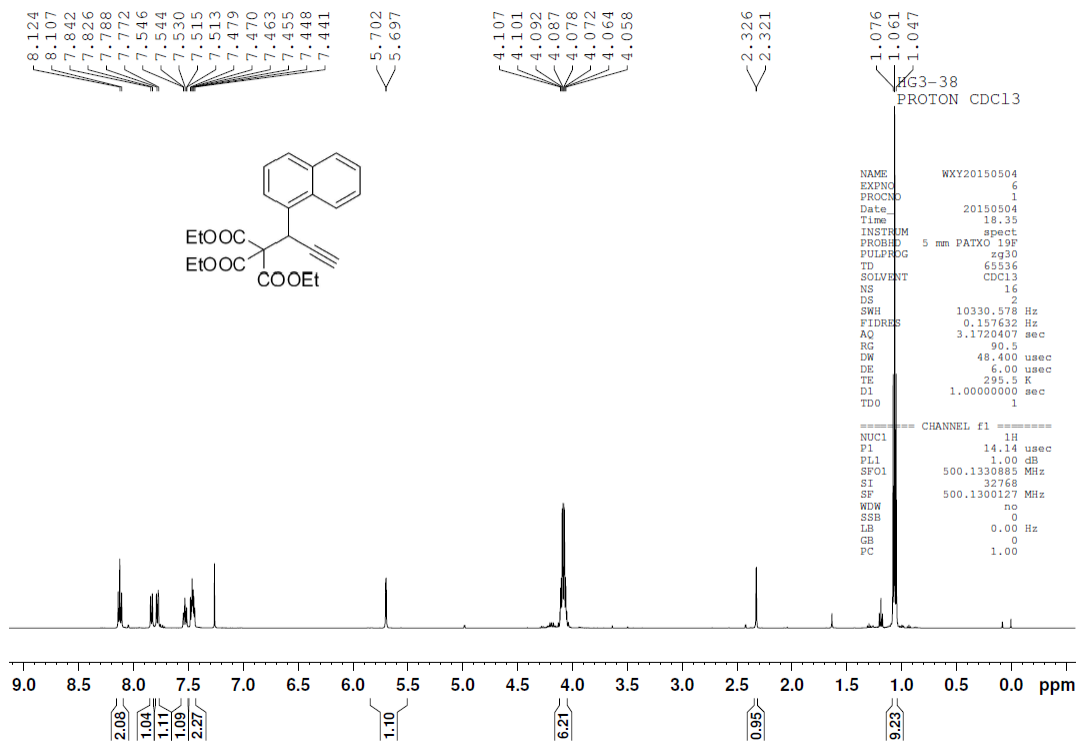
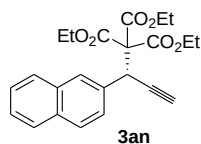


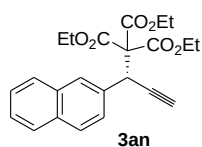


Peak#	Ret. Time	Area	Height	Area%
1	37.754	57639339	719882	50.454
2	43.630	56602430	552962	49.546
总计		114241769	1272845	100.000

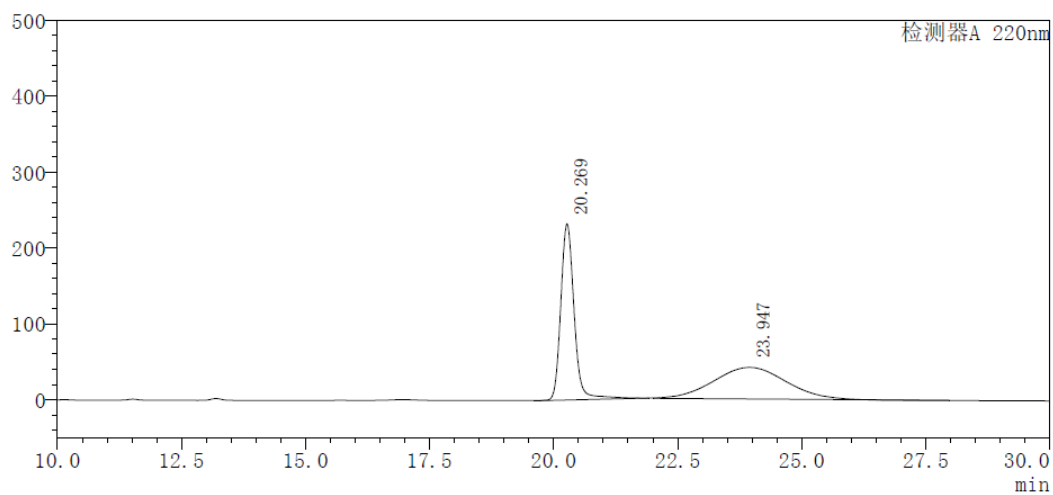


Peak#	Ret. Time	Area	Height	Area%
1	46.040	9525942	119200	6.932
2	53.374	127894462	1032186	93.068
总计		137420404	1151385	100.000



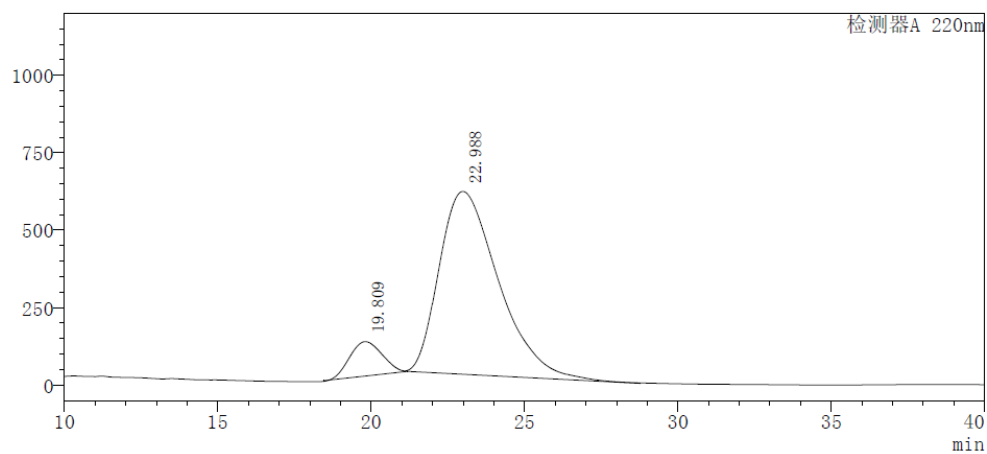


mV

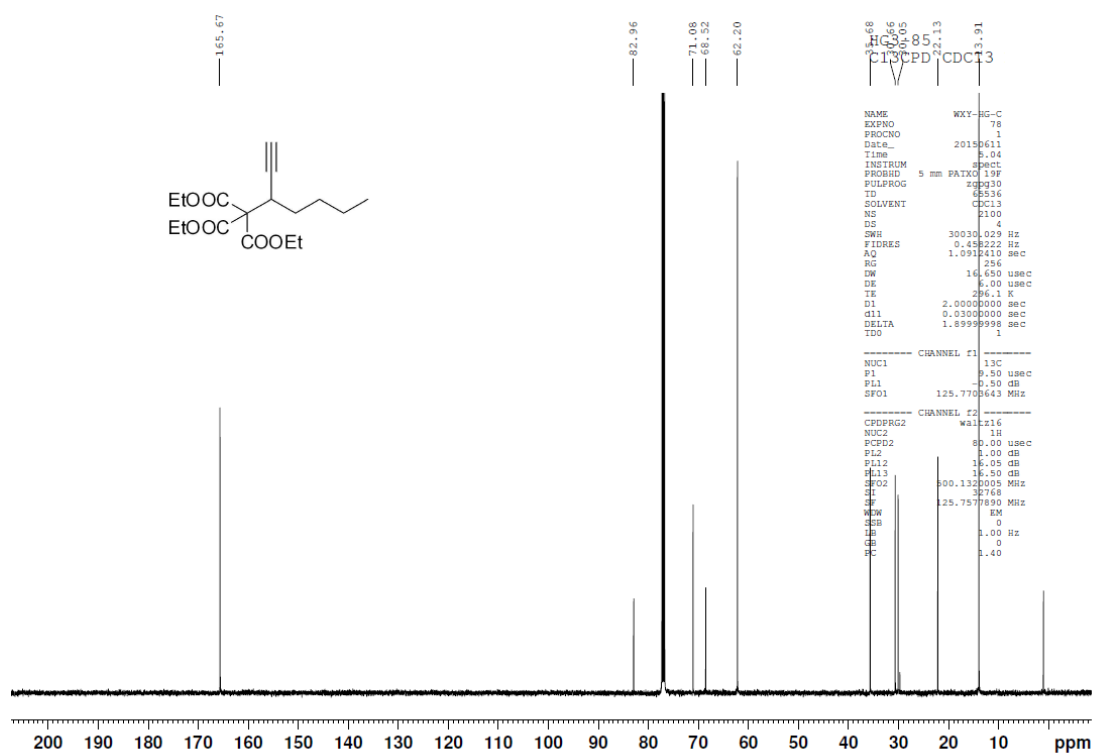
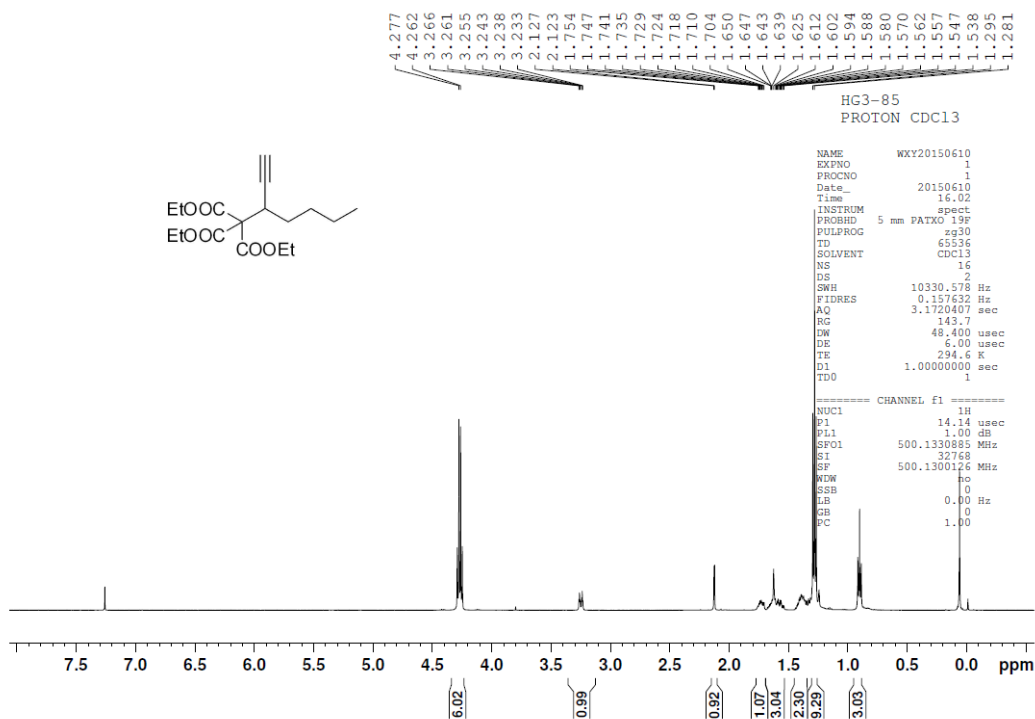
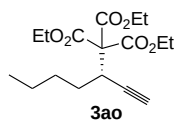


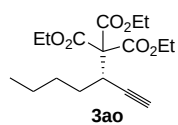
Peak#	Ret. Time	Area	Height	Area%
1	20.269	4331189	232039	50.593
2	23.947	4229667	41761	49.407
总计		8560856	273800	100.000

mV

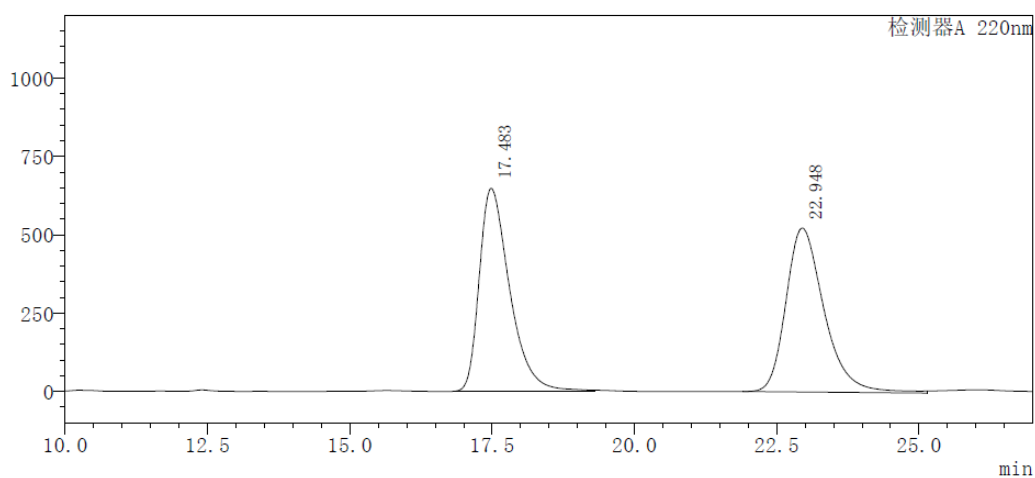


Peak#	Ret. Time	Area	Height	Area%
1	19.809	8147229	110725	9.319
2	22.988	79279064	589715	90.681
总计		87426293	700439	100.000



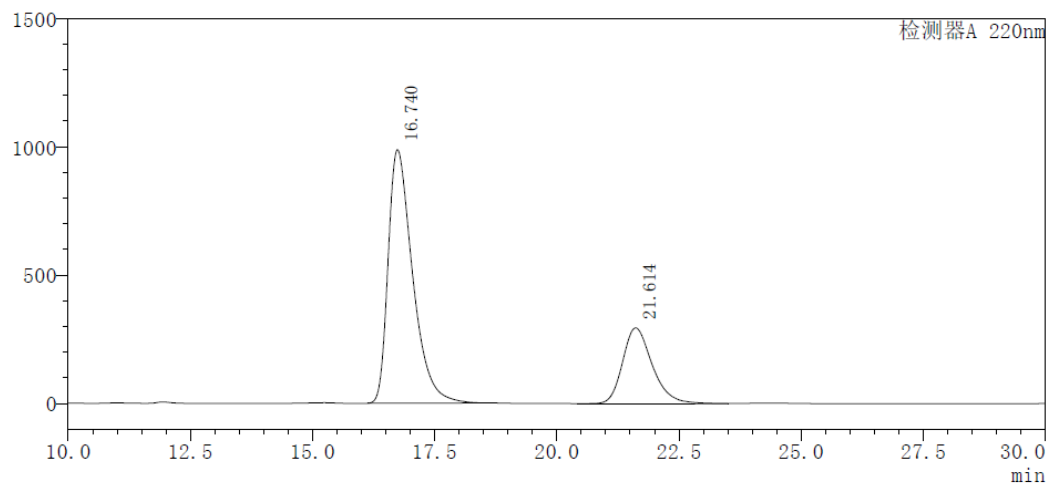


mV

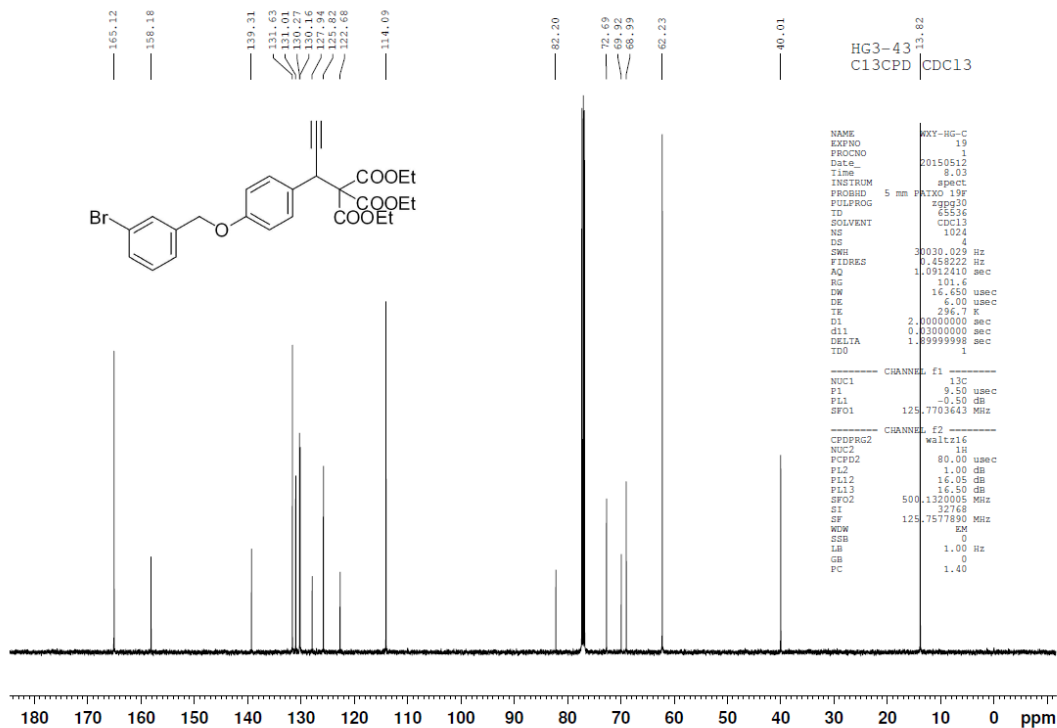
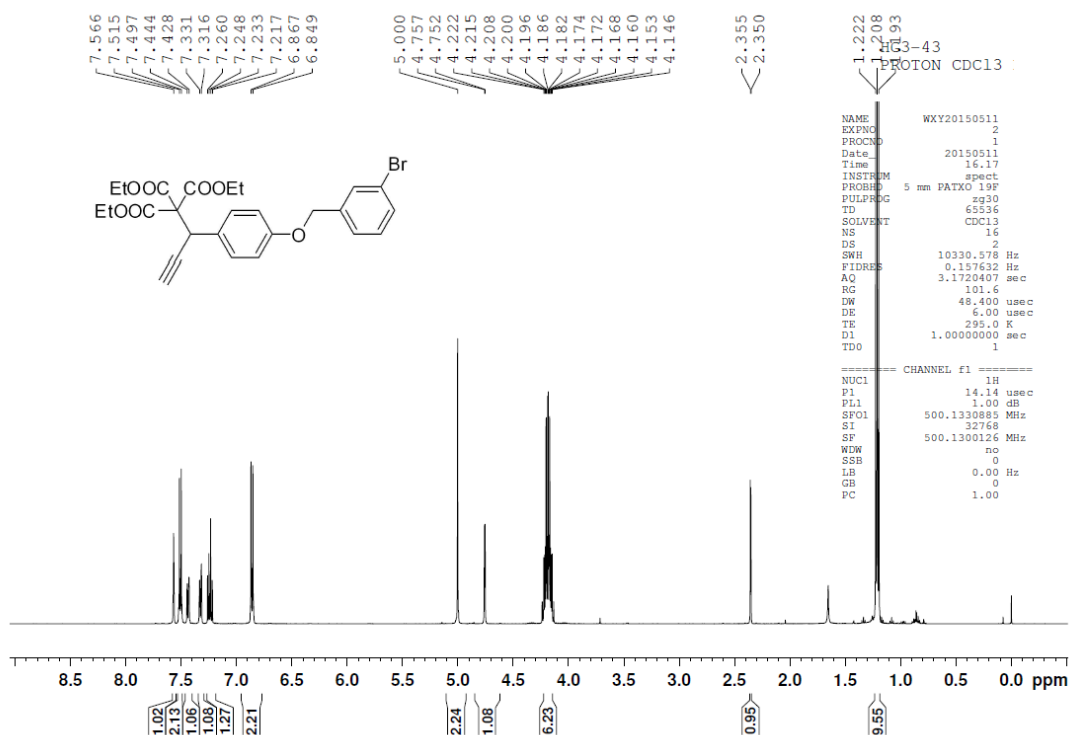
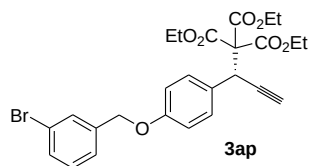


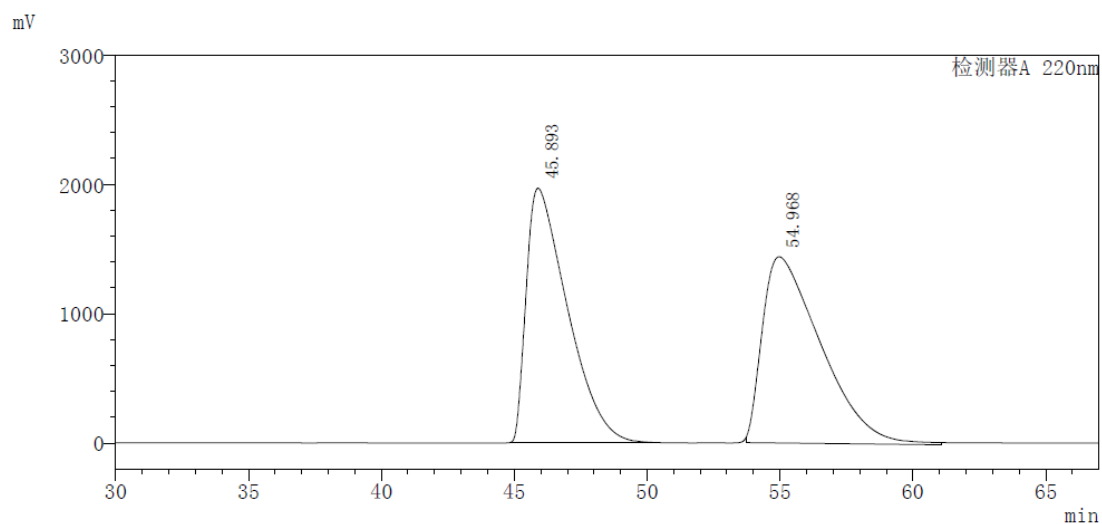
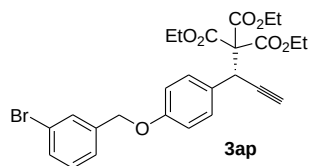
Peak#	Ret. Time	Area	Height	Area%
1	17.483	24172813	648331	49.701
2	22.948	24463848	523324	50.299
总计		48636662	1171655	100.000

mV

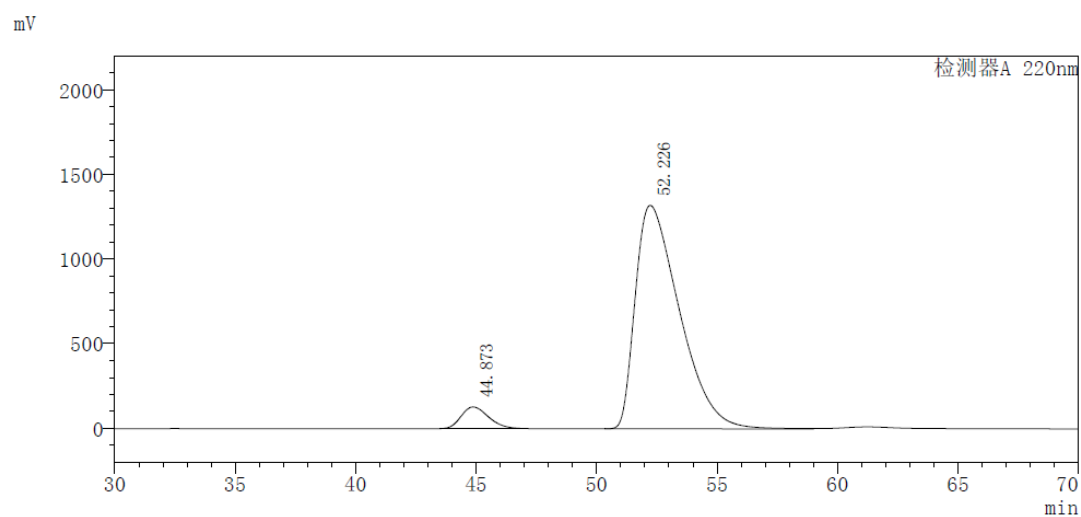


Peak#	Ret. Time	Area	Height	Area%
1	16.740	34490746	987899	73.231
2	21.614	12607770	296348	26.769
总计		47098516	1284247	100.000

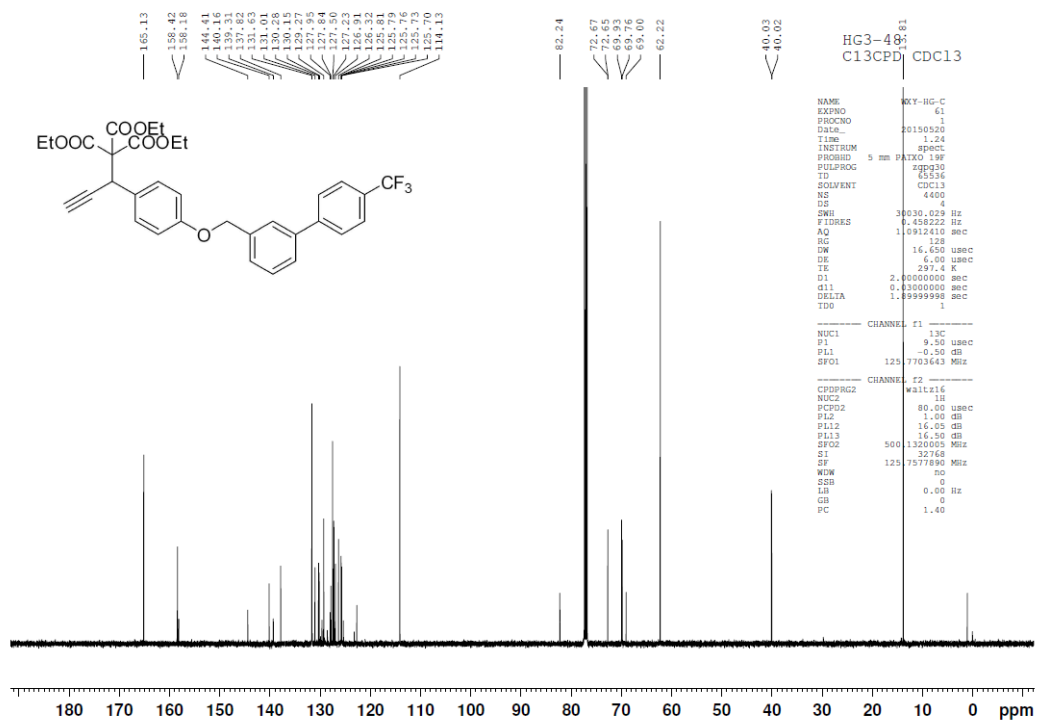
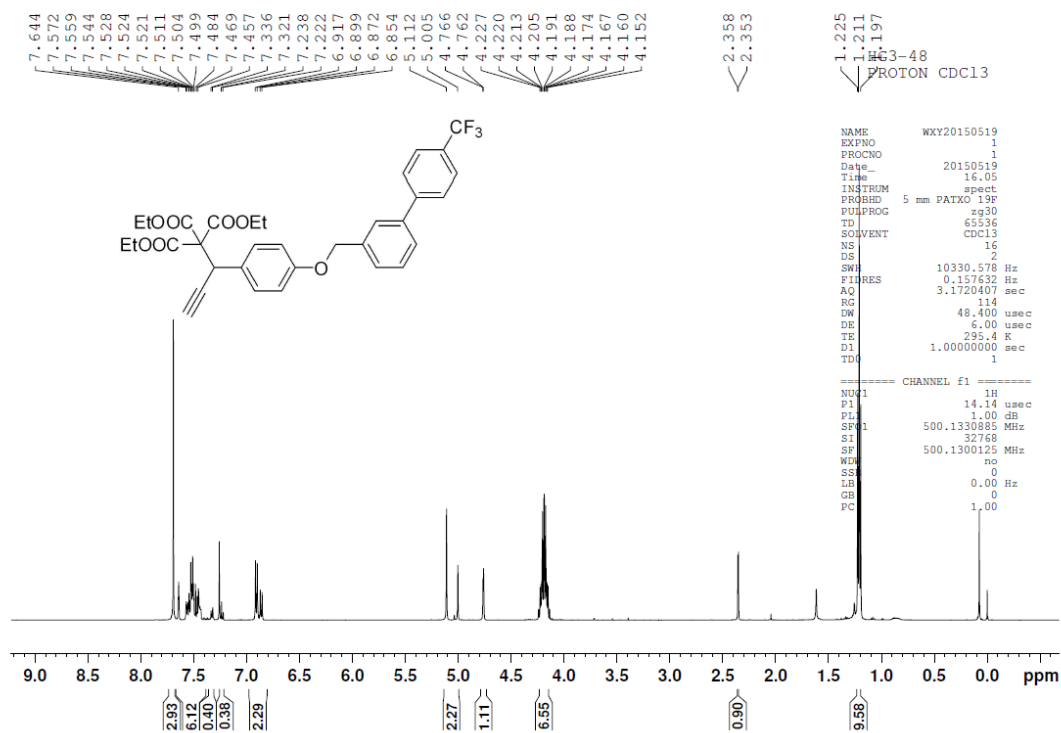
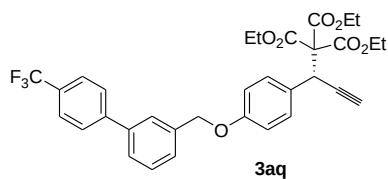


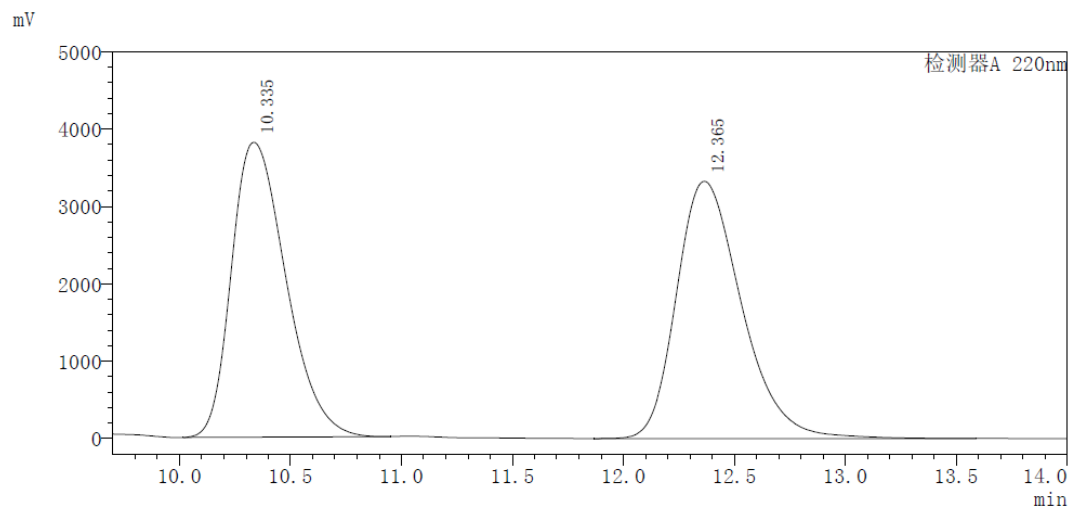
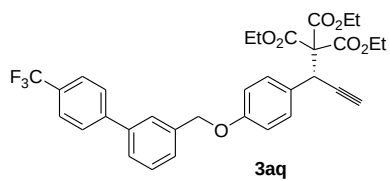


Peak#	Ret. Time	Area	Height	Area%
1	45.893	211832868	1966173	48.997
2	54.968	220502840	1439259	51.003
总计		432335707	3405432	100.000

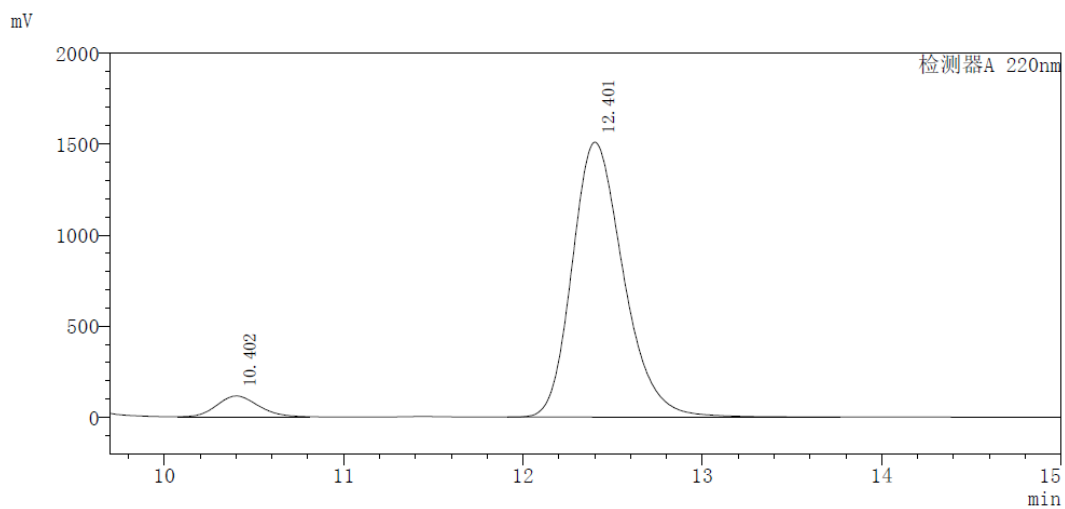


Peak#	Ret. Time	Area	Height	Area%
1	44.873	10545162	130242	5.889
2	52.226	168523323	1320563	94.111
总计		179068485	1450805	100.000

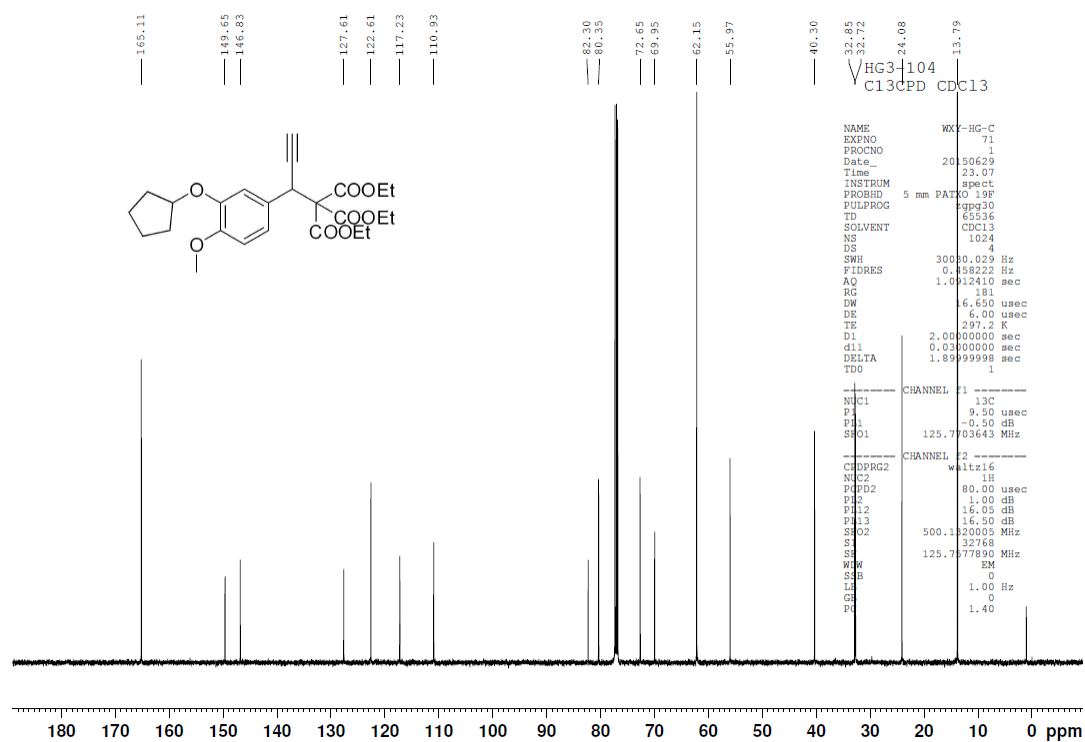
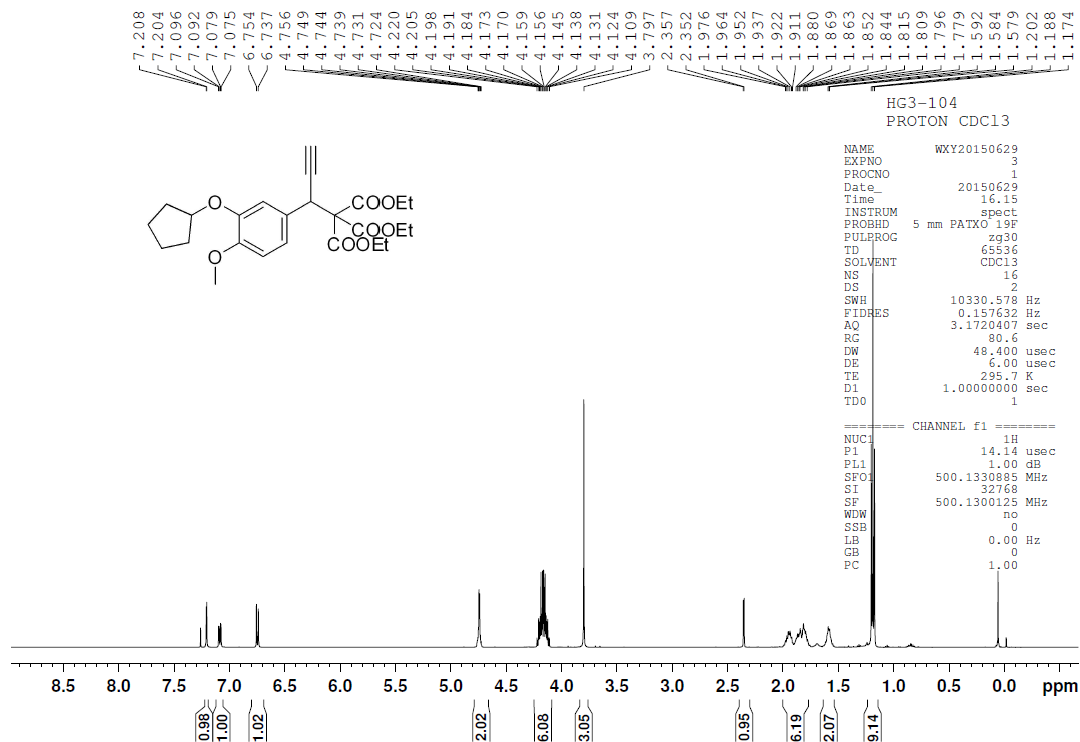
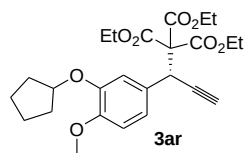


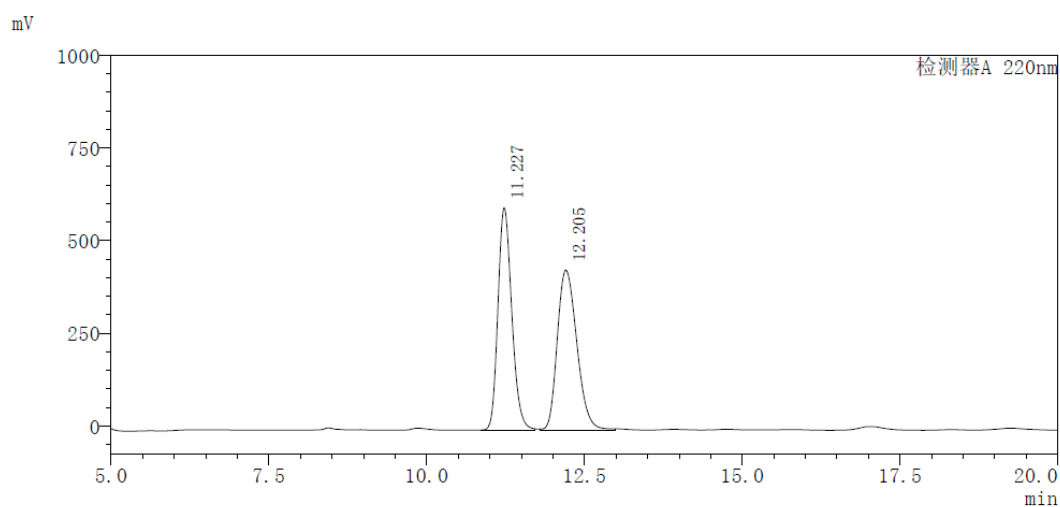
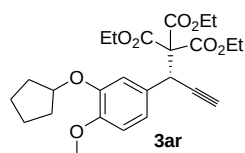


Peak#	Ret. Time	Area	Height	Area%
1	10.335	65335710	3810862	49.051
2	12.365	67862794	3325655	50.949
总计		133198504	7136517	100.000

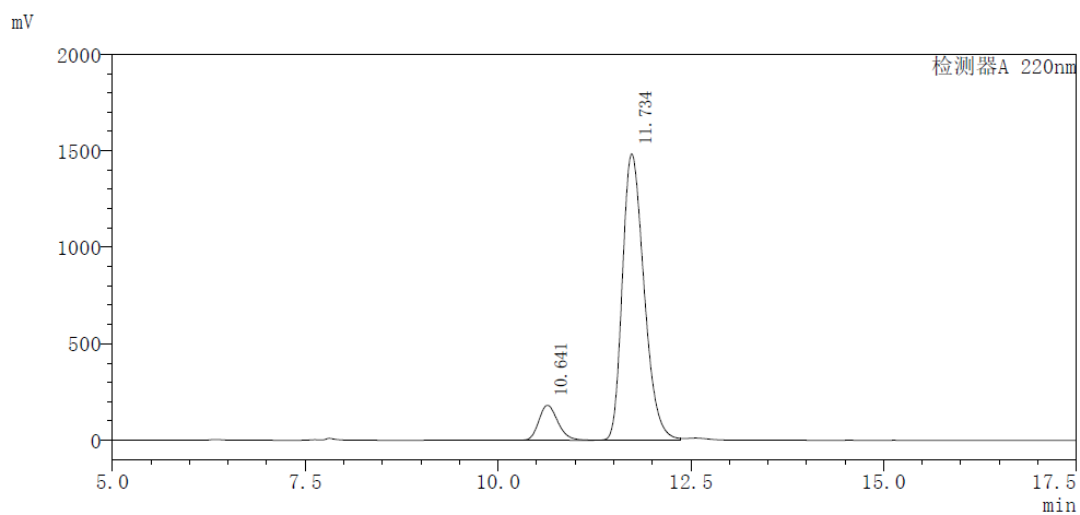


Peak#	Ret. Time	Area	Height	Area%
1	10.402	1832010	114445	5.744
2	12.401	30060598	1509744	94.256
总计		31892608	1624189	100.000

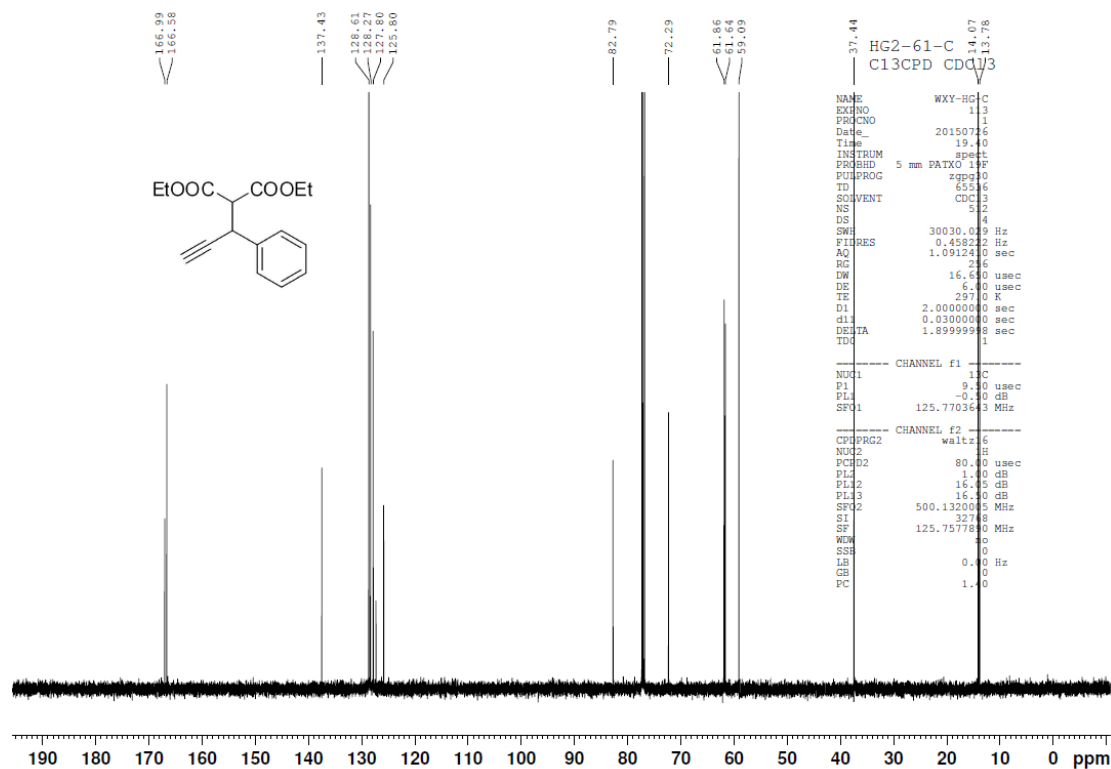
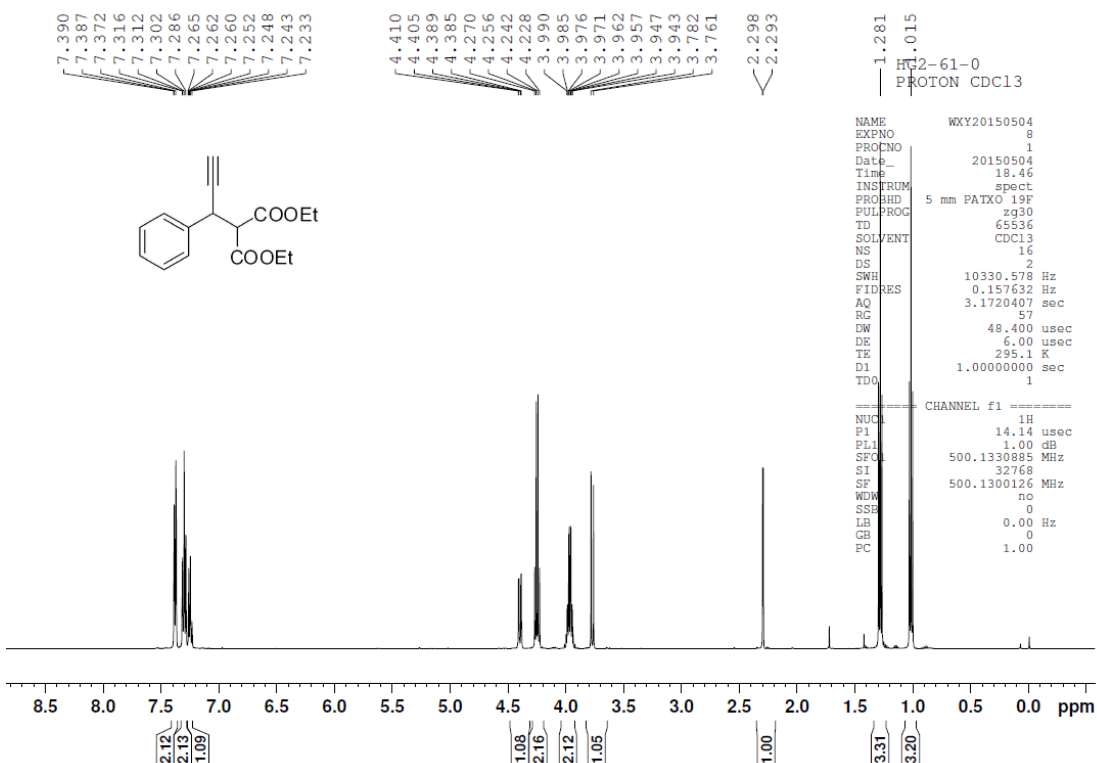
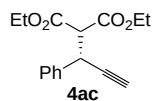


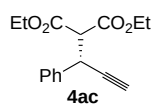


Peak#	Ret. Time	Area	Height	Area%
1	11.227	9212088	601023	49.448
2	12.205	9417888	432719	50.552
总计		18629975	1033742	100.000

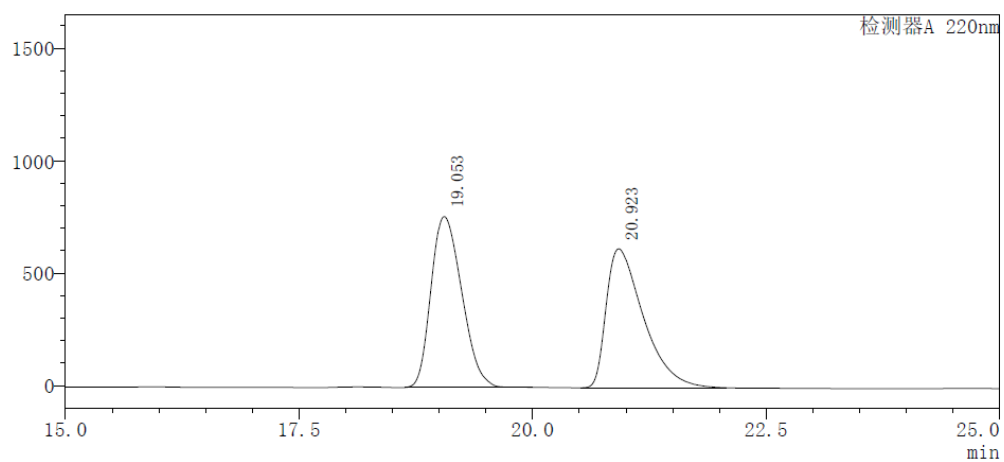


Peak#	Ret. Time	Area	Height	Area%
1	10.641	3128444	181544	9.698
2	11.734	29130225	1485726	90.302
总计		32258669	1667270	100.000



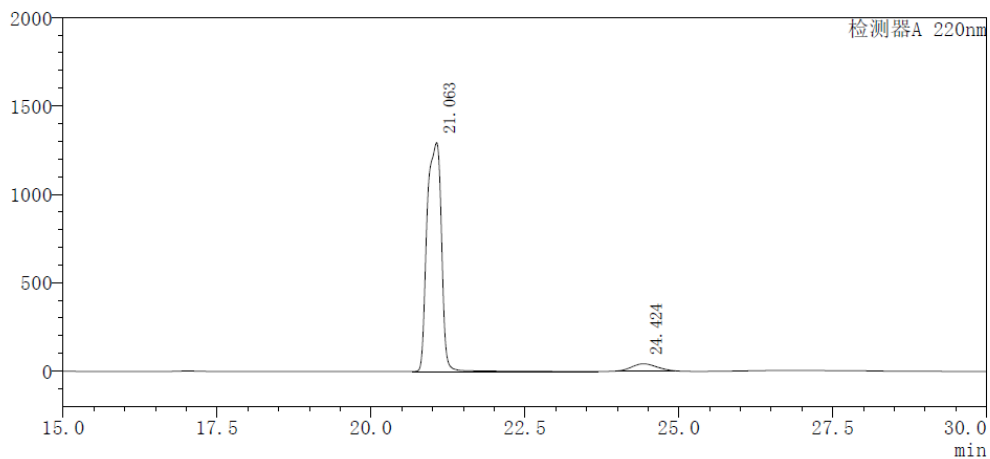


mV

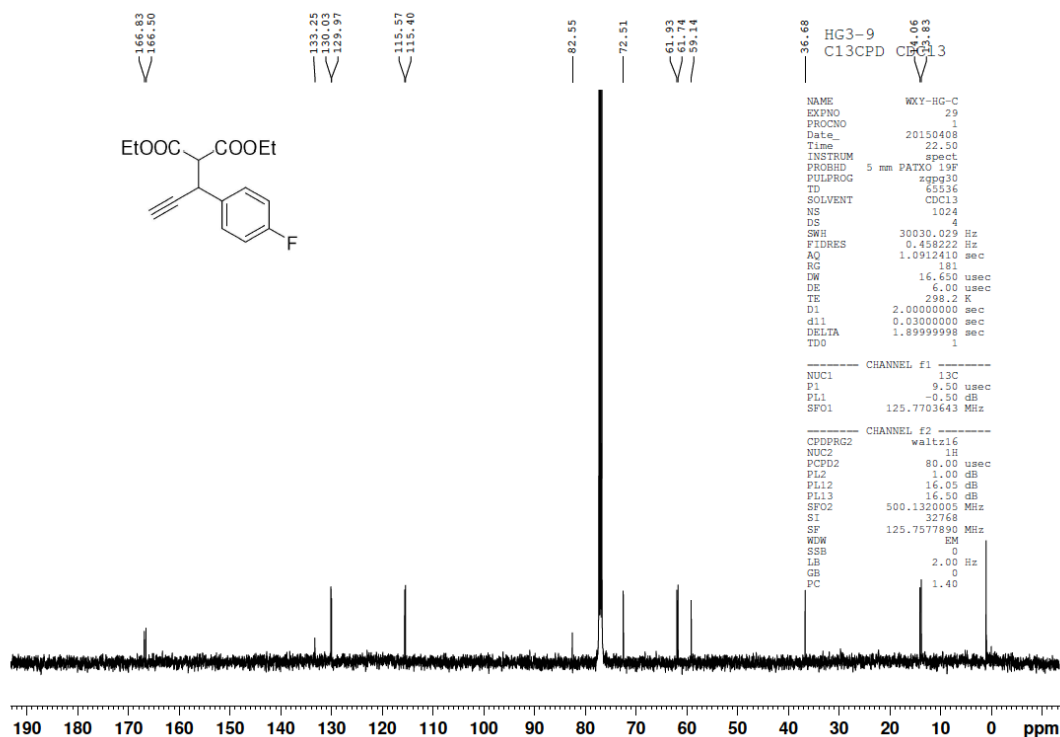
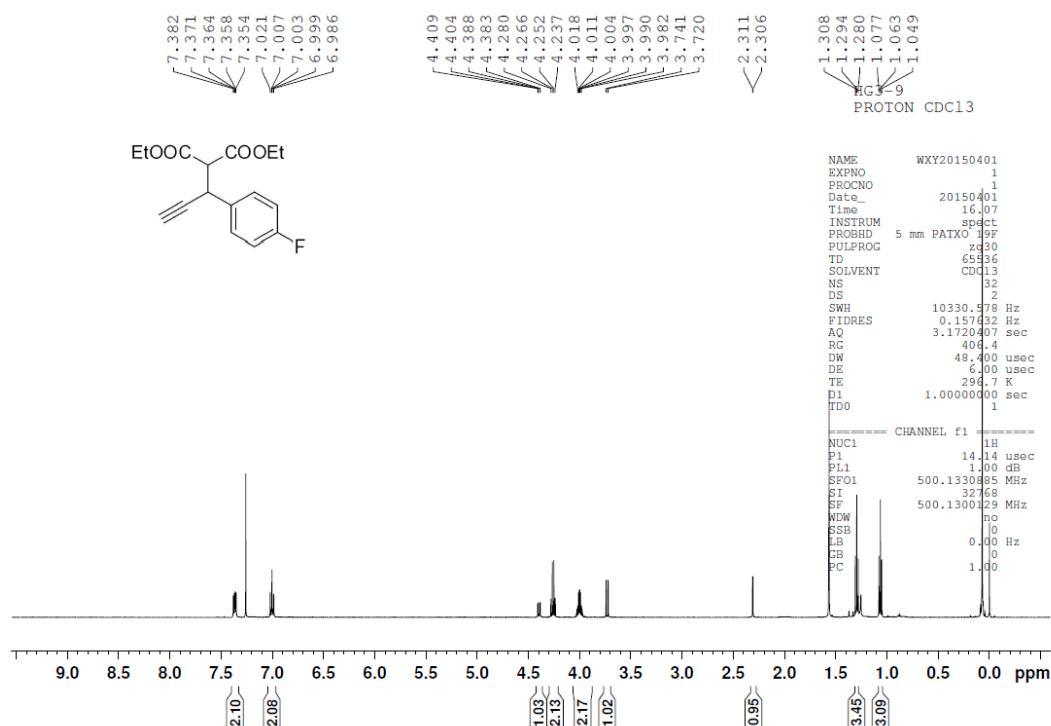
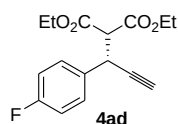


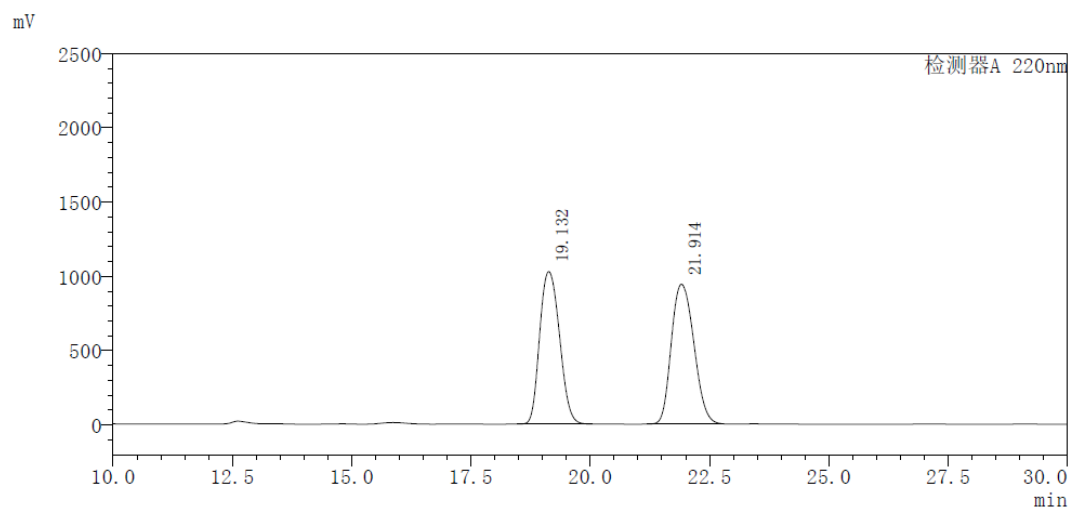
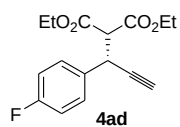
Peak#	Ret. Time	Area	Height	Area%
1	19.053	17353901	760136	50.170
2	20.923	17236286	620009	49.830
总计		34590187	1380146	100.000

mV

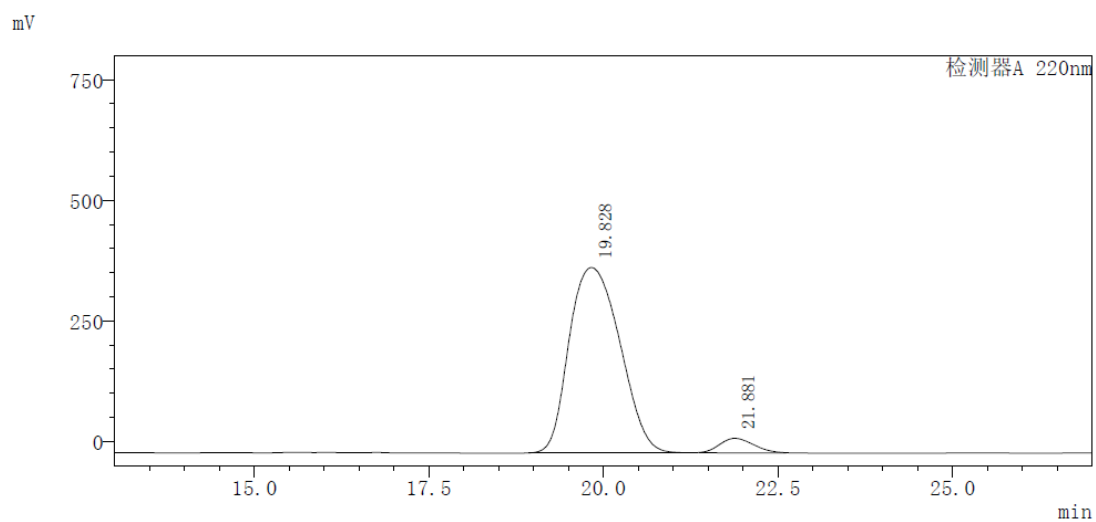


Peak#	Ret. Time	Area	Height	Area%
1	21.063	20743605	1295617	94.760
2	24.424	1147050	40873	5.240
总计		21890654	1336490	100.000

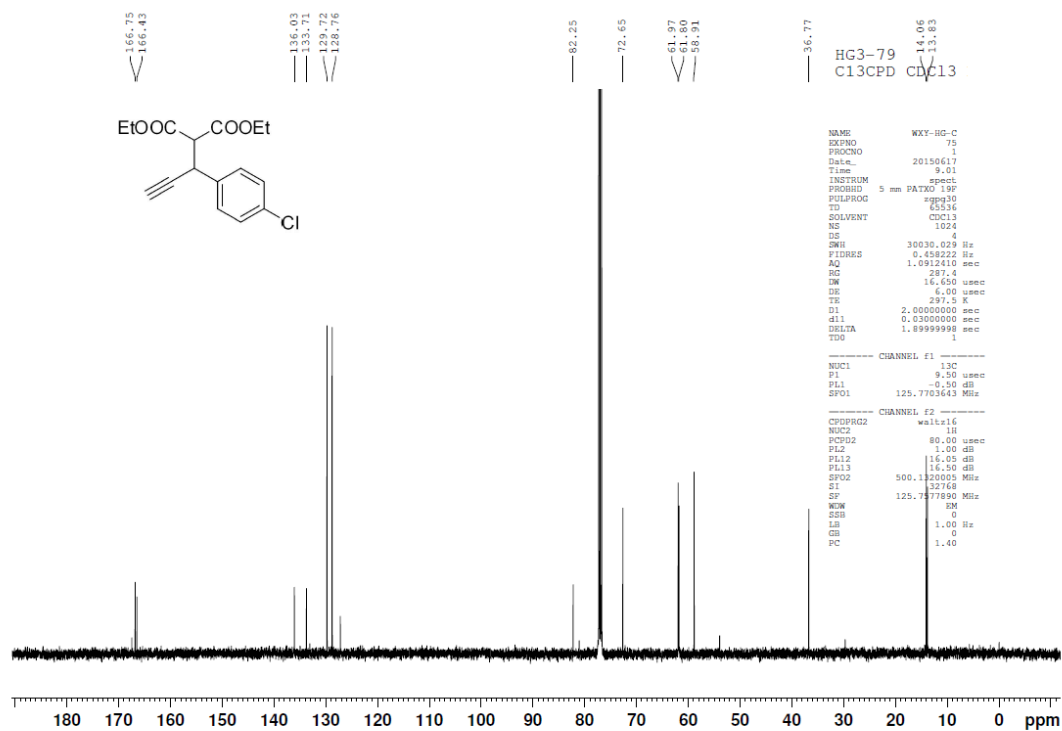
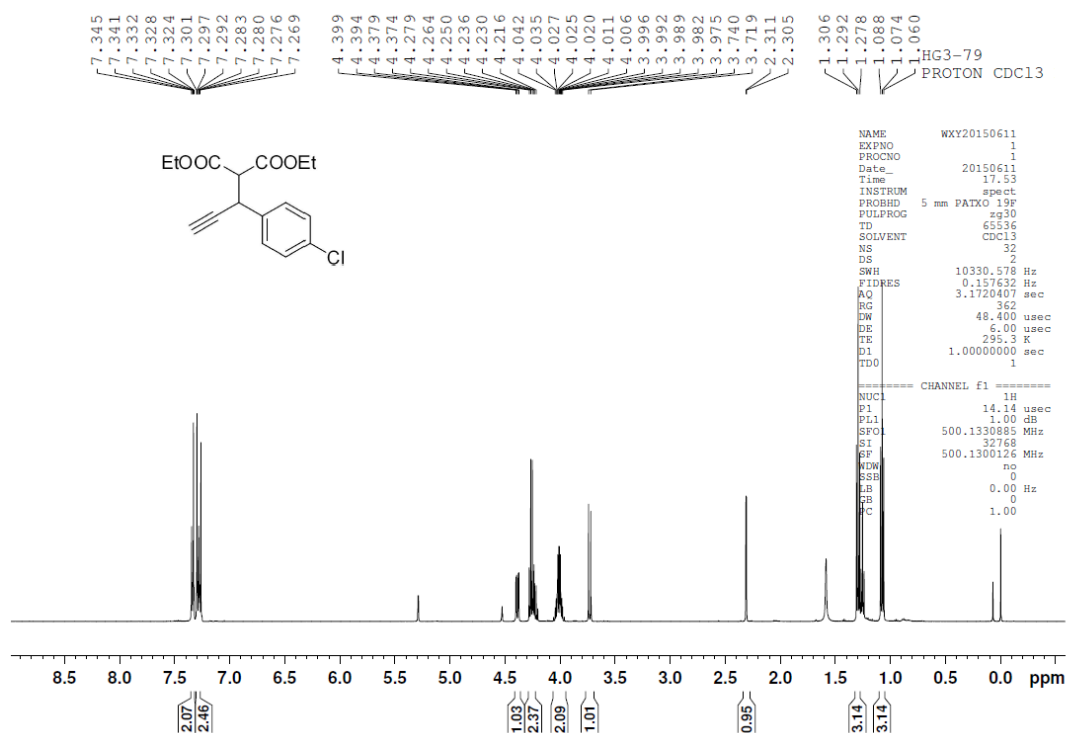
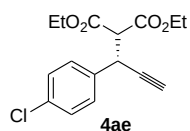


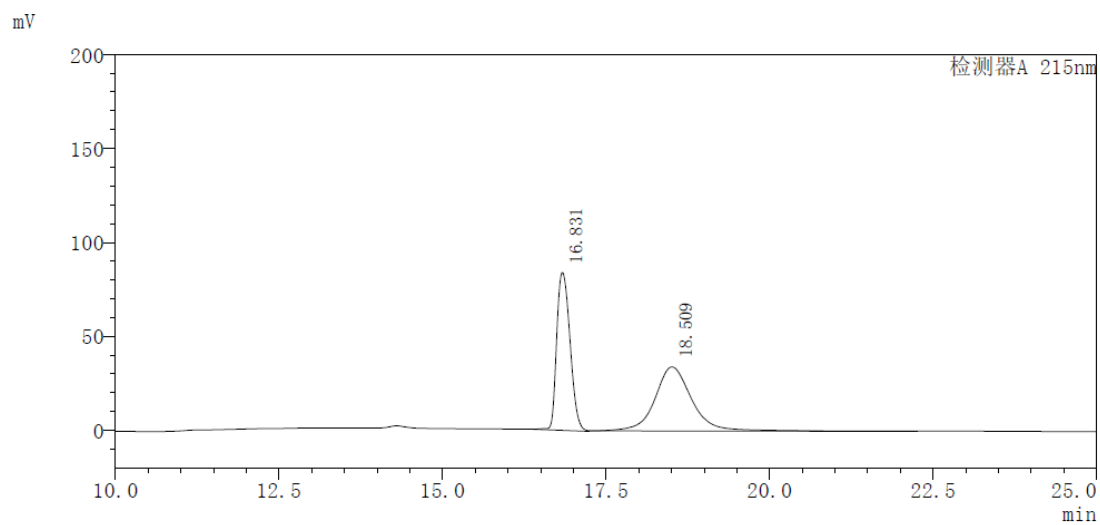
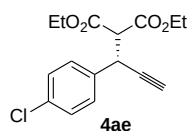


Peak#	Ret. Time	Area	Height	Area%
1	19.132	29884586	1027402	49.195
2	21.914	30862724	940529	50.805
总计		60747310	1967932	100.000

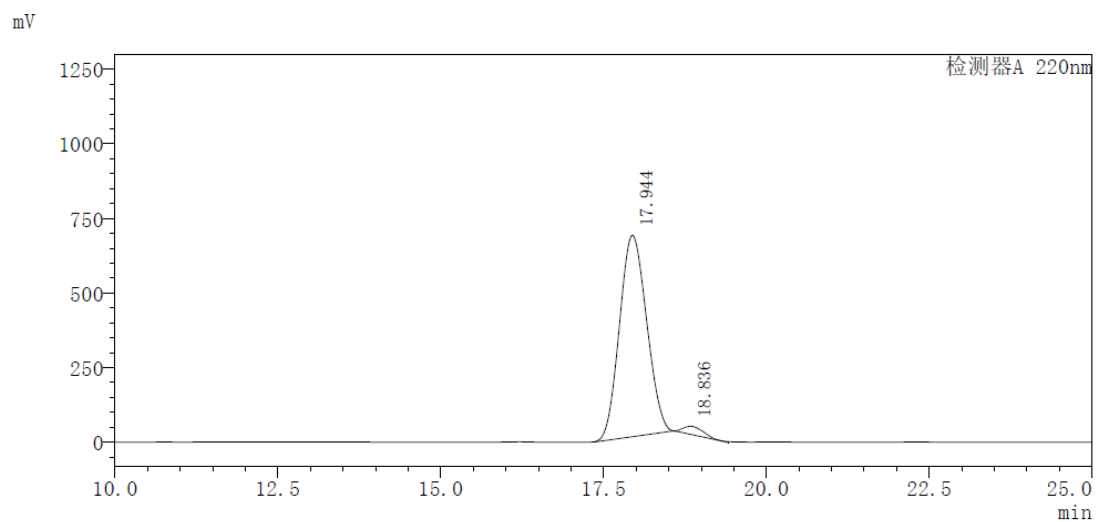


Peak#	Ret. Time	Area	Height	Area%
1	19.828	19490475	384663	95.035
2	21.881	1018360	29925	4.965
总计		20508835	414588	100.000

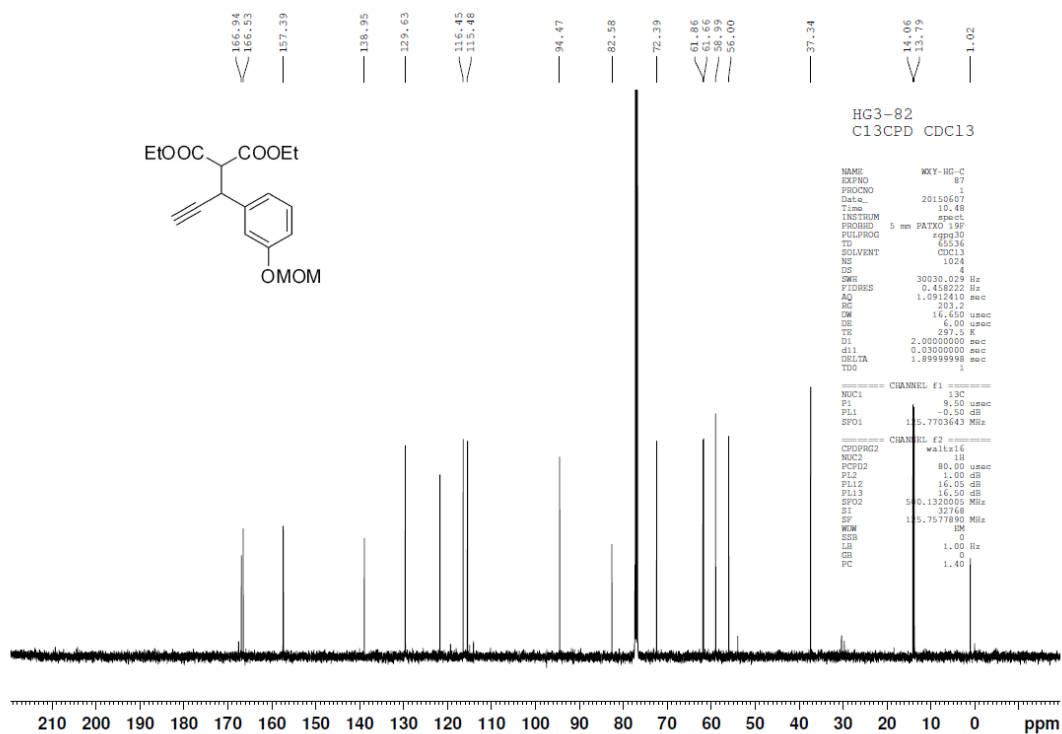
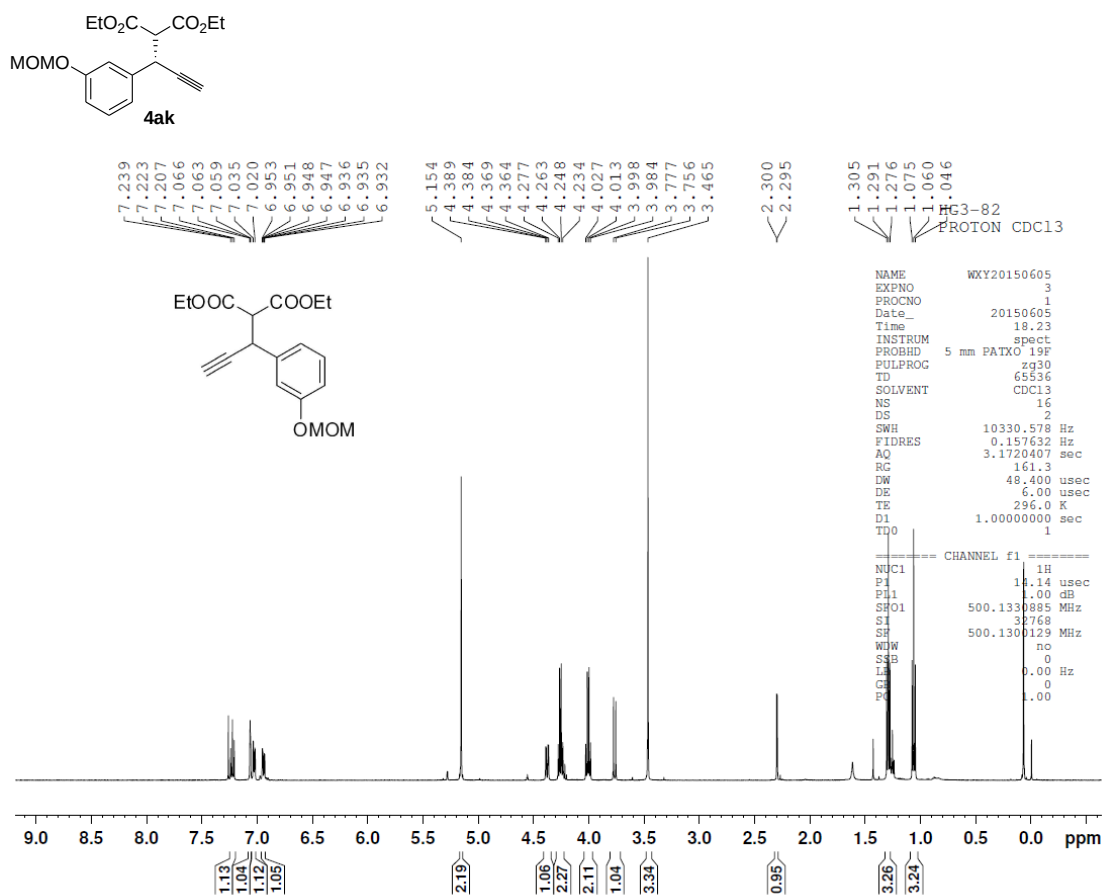


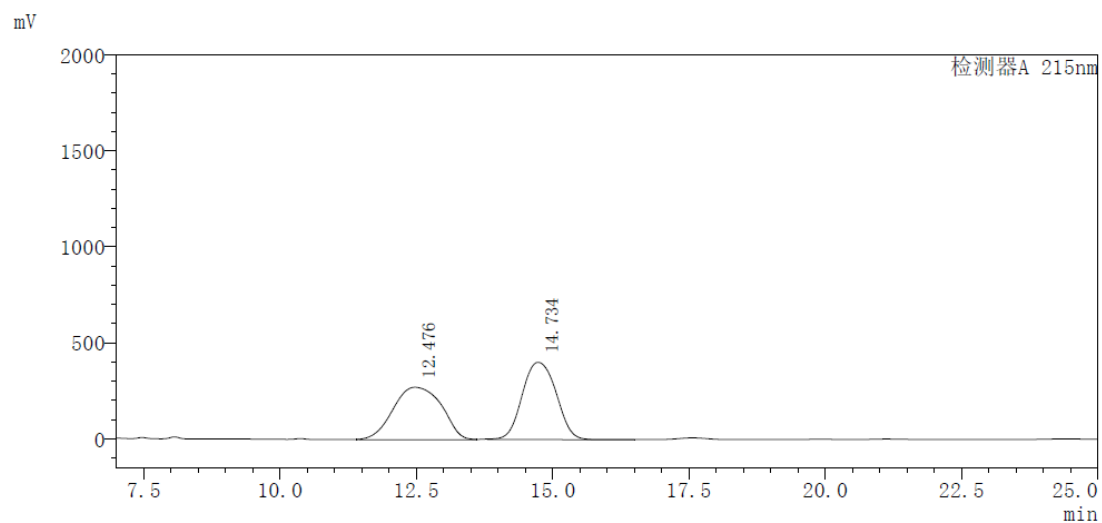
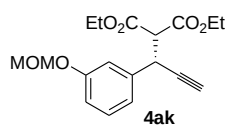


Peak#	Ret. Time	Area	Height	Area%
1	16.831	1192706	84071	46.712
2	18.509	1360592	34144	53.288
总计		2553298	118215	100.000

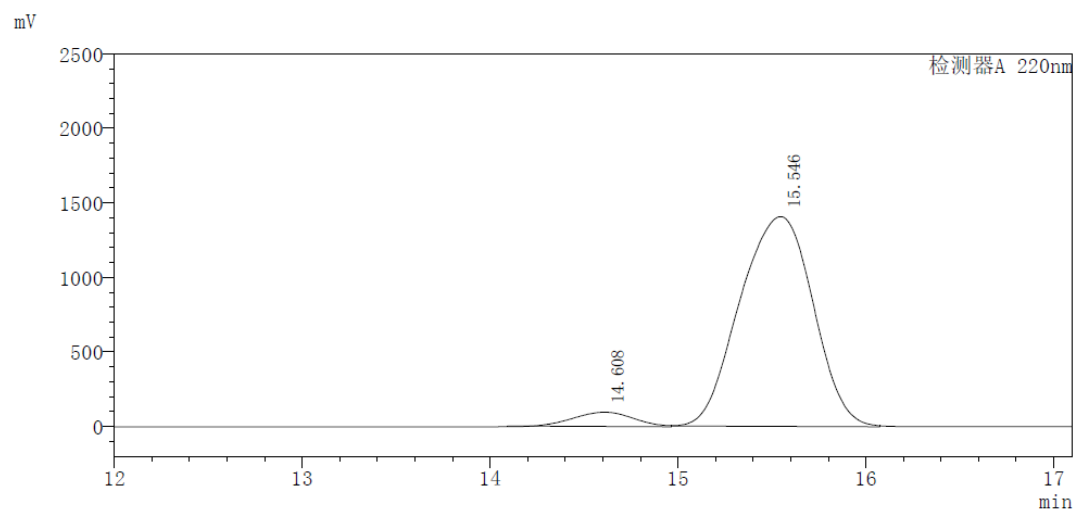


Peak#	Ret. Time	Area	Height	Area%
1	17.944	19561367	674649	96.983
2	18.836	608555	27170	3.017
总计		20169922	701819	100.000

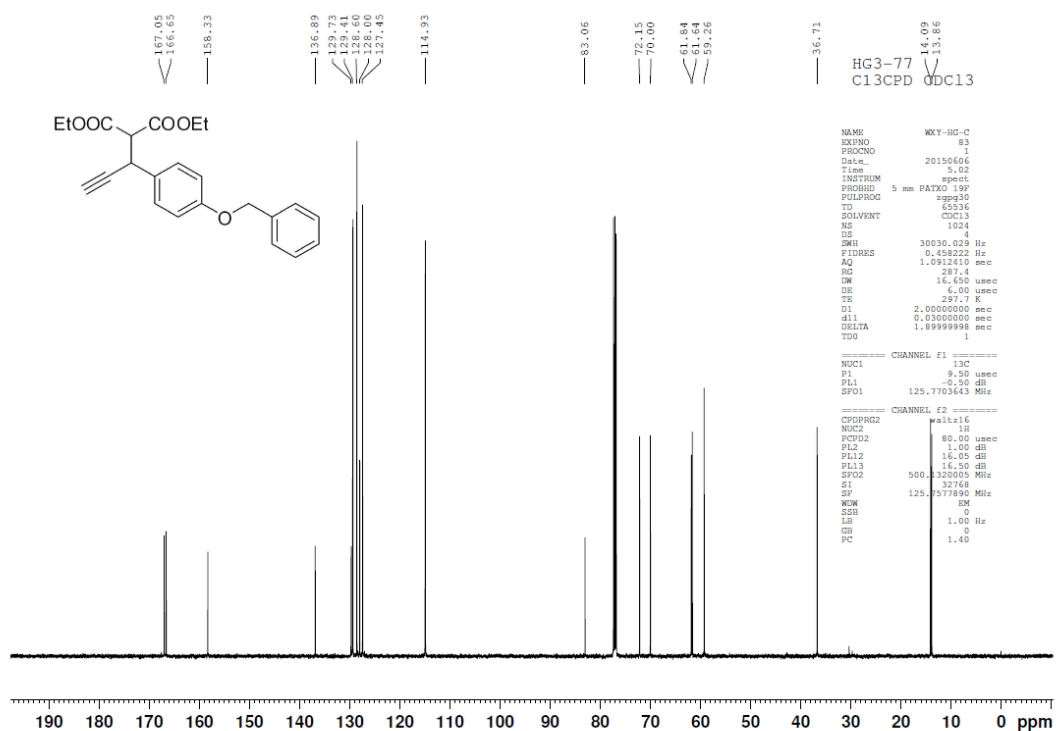
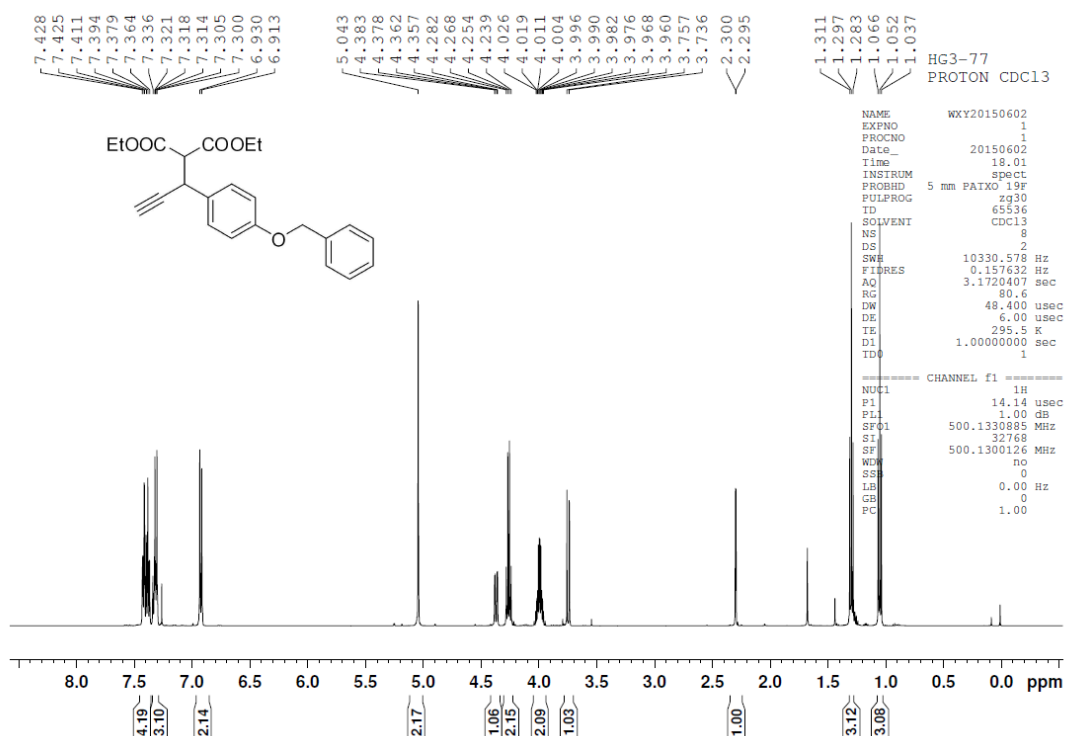
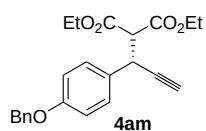


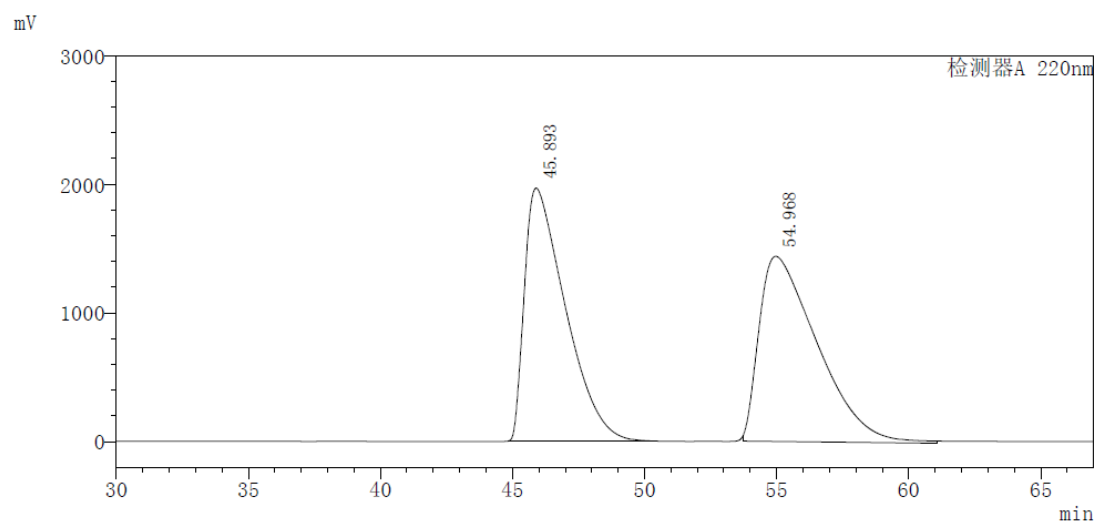
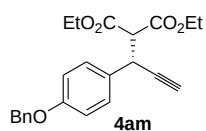


Peak#	Ret. Time	Area	Height	Area%
1	12.476	16971153	274265	49.161
2	14.734	17550336	402077	50.839
总计		34521489	676343	100.000

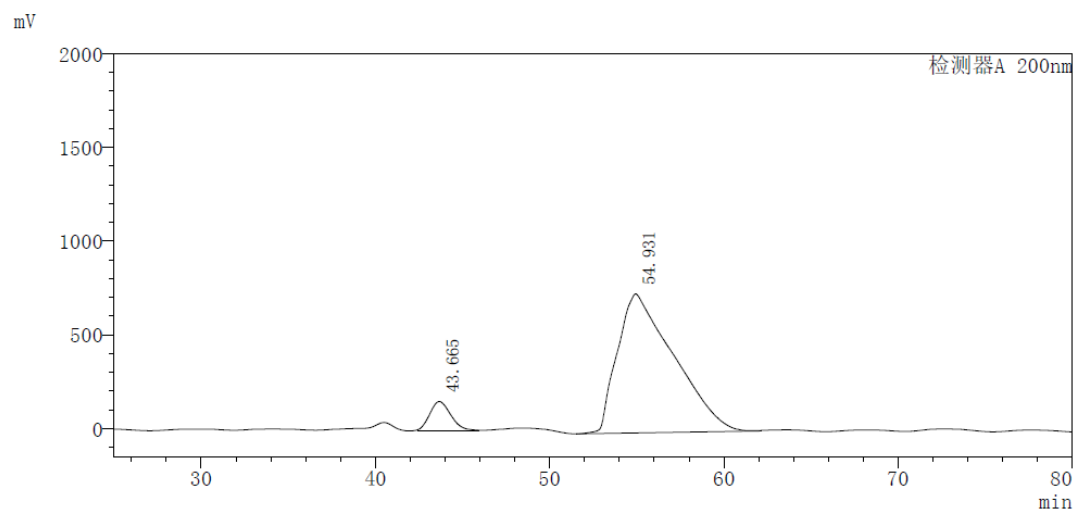


Peak#	Ret. Time	Area	Height	Area%
1	14.608	2112227	96030	5.240
2	15.546	38200352	1406994	94.760
总计		40312579	1503024	100.000

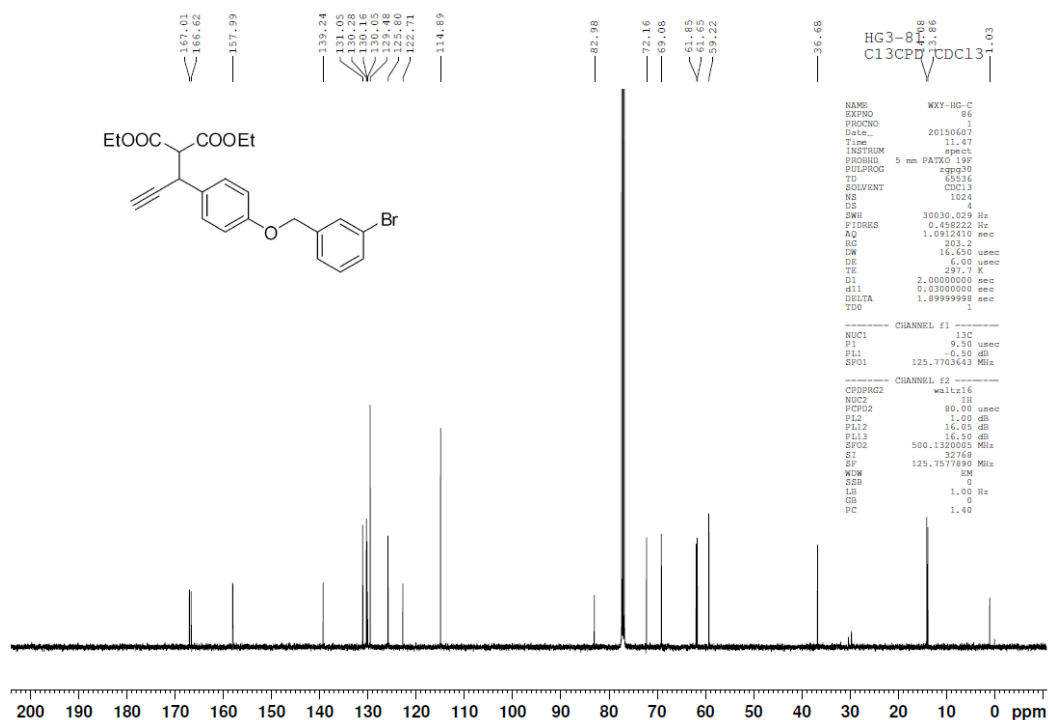
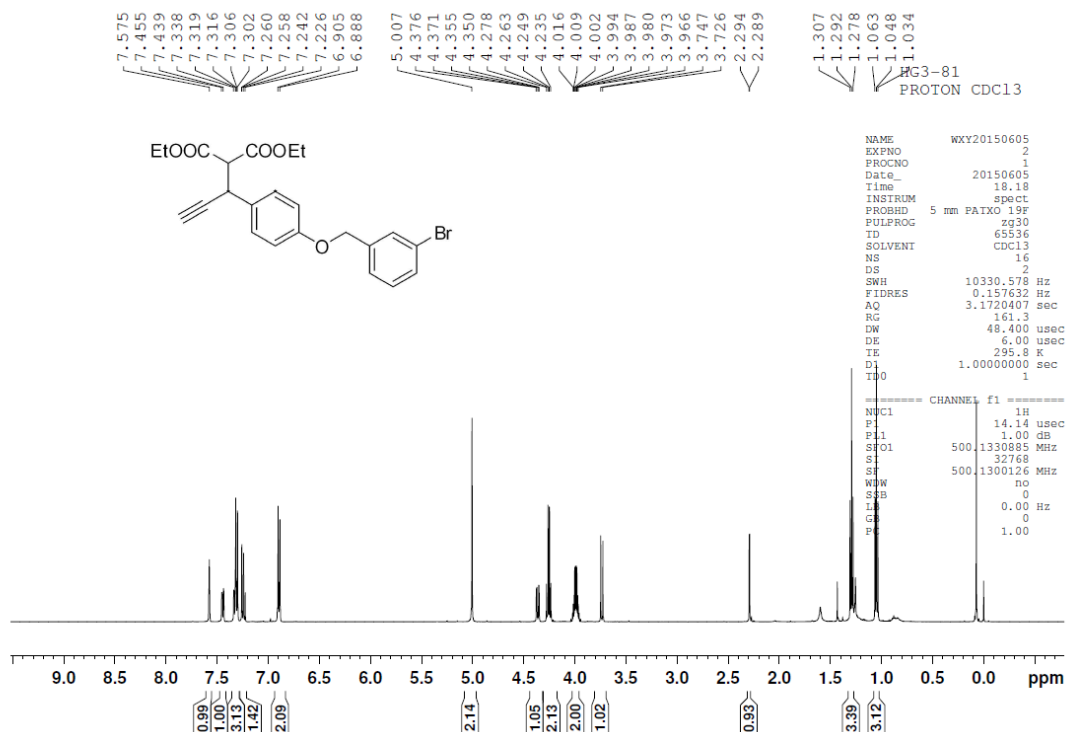
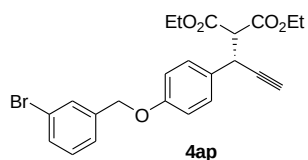


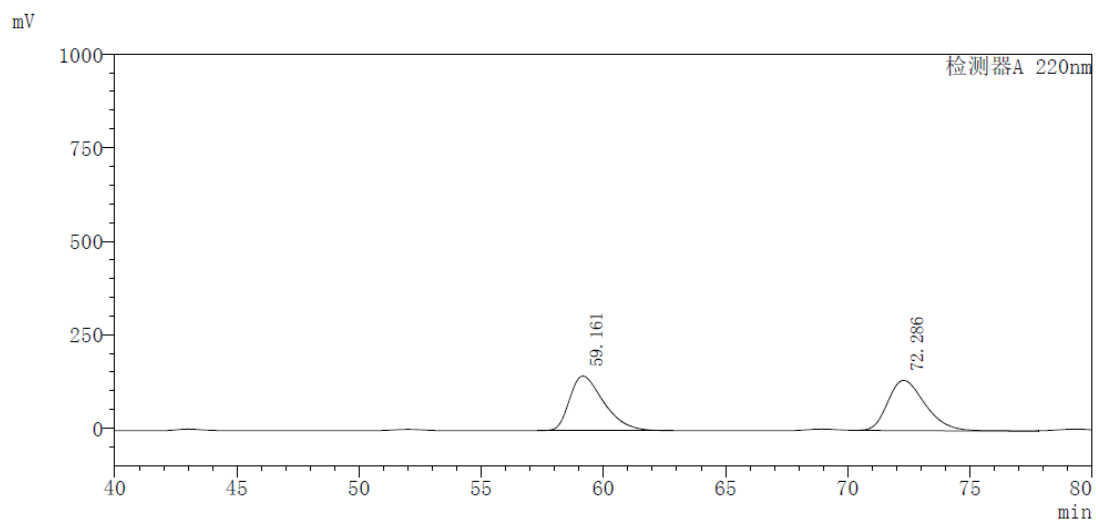
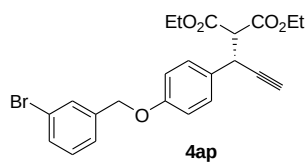


Peak#	Ret. Time	Area	Height	Area%
1	45.893	211832868	1966173	48.997
2	54.968	220502840	1439259	51.003
总计		432335707	3405432	100.000

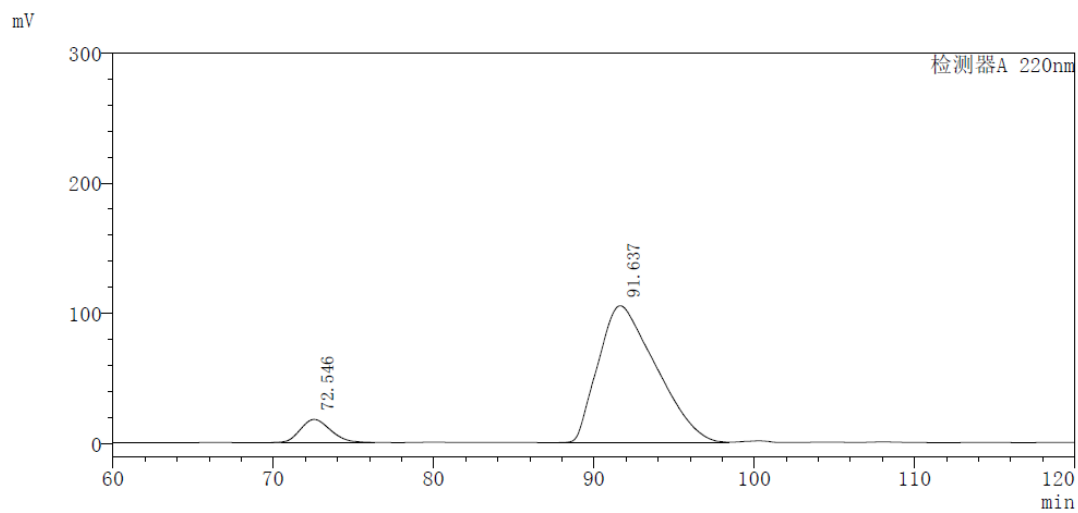


Peak#	Ret. Time	Area	Height	Area%
1	43.665	13061179	155519	7.258
2	54.931	166901491	741301	92.742
总计		179962670	896820	100.000

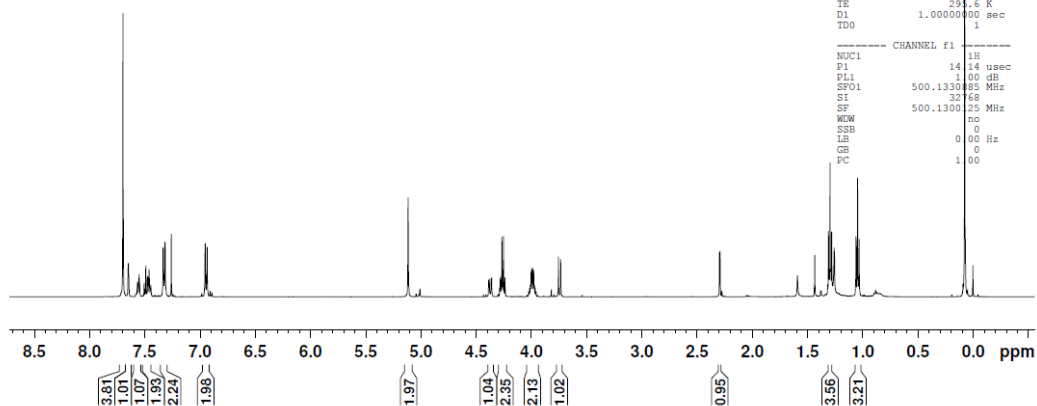
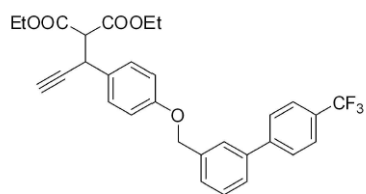
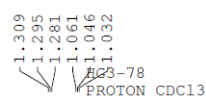
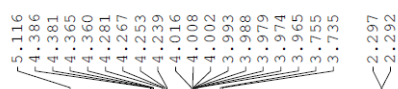
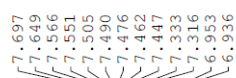
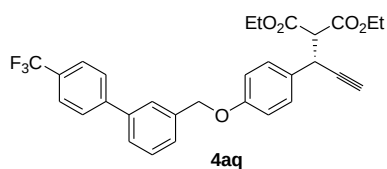




Peak#	Ret. Time	Area	Height	Area%
1	59.161	14170577	145757	49.528
2	72.286	14440867	134485	50.472
总计		28611444	280242	100.000



Peak#	Ret. Time	Area	Height	Area%
1	72.546	2347735	17790	8.180
2	91.637	26351554	104989	91.820
总计		28699290	122779	100.000



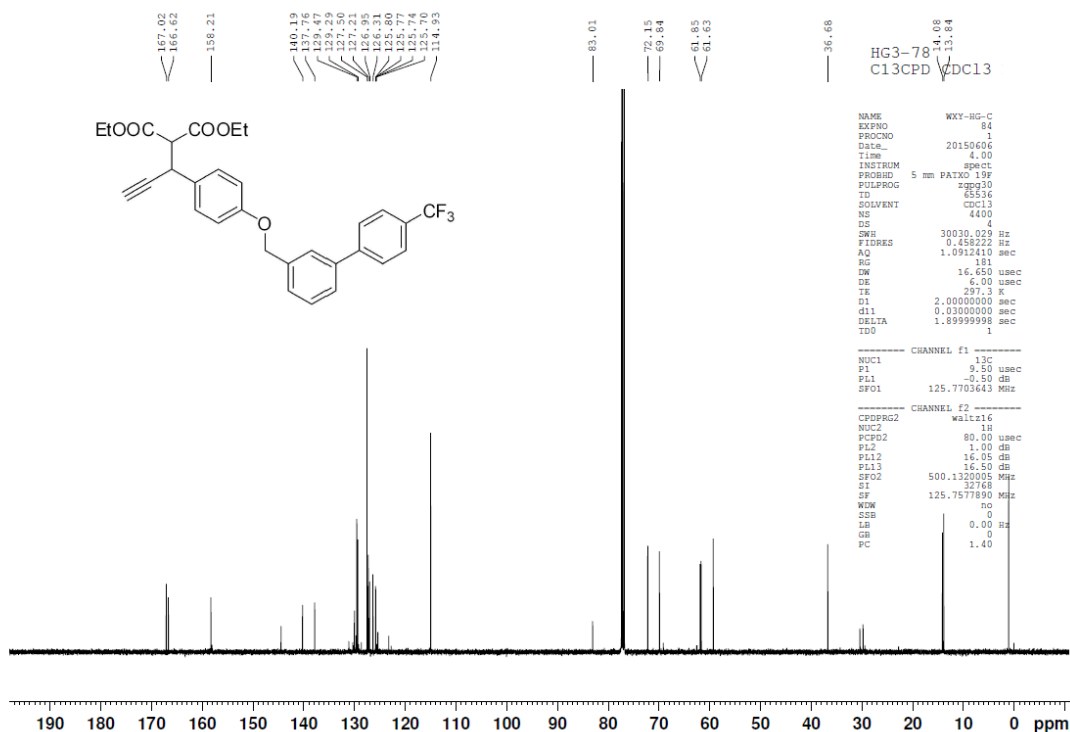
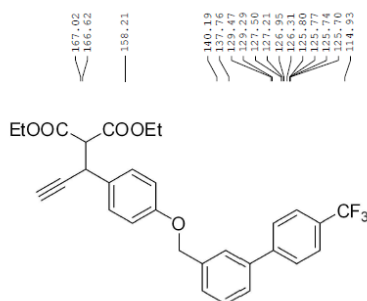
```

NAME      WXY20150603
EXPNO     4
PROCNO    1
Date_     20150603
Time      19:12
INSTRUM   spect
PROBHD    5 mm PATXO 19F
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        10330.578 Hz
FIDRES     0.157632 Hz
AQ         3.1720407 sec
RG         141.7
DW         48.400 usec
DE         6.00 usec
TE         294.6 K
D1         1.00000000 sec
TD0        1
  
```

----- CHANNEL f1 -----

```

NUC1      13C
P1        14.14 usec
PL1       1.00 dB
SFO1      500.130085 MHz
SI        32768
SF        500.130085 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.00
  
```



```

NAME      WXY-HG-C
EXPNO     84
PROCNO    1
Date_     20150606
Time      4:00
INSTRUM   spect
PROBHD    5 mm PATXO 19F
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         4
DS         4
SWH        30030.028 Hz
FIDRES     0.458222 Hz
AQ         1.0912110 sec
RG         181
DW         16.650 usec
DE         6.00 usec
TE         297.3 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA     1.89999998 sec
TD0        1
  
```

----- CHANNEL f1 -----

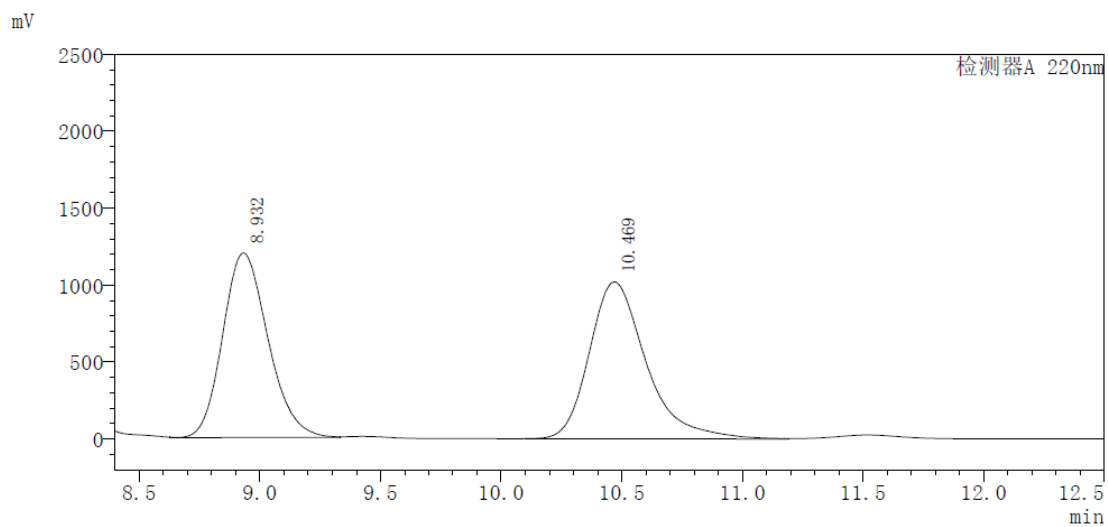
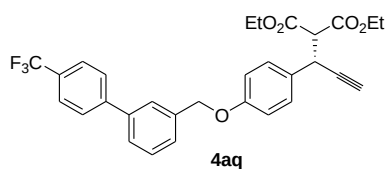
```

NUC1      13C
P1        9.50 usec
PL1       -4.50 dB
SFO1      125.7703643 MHz
  
```

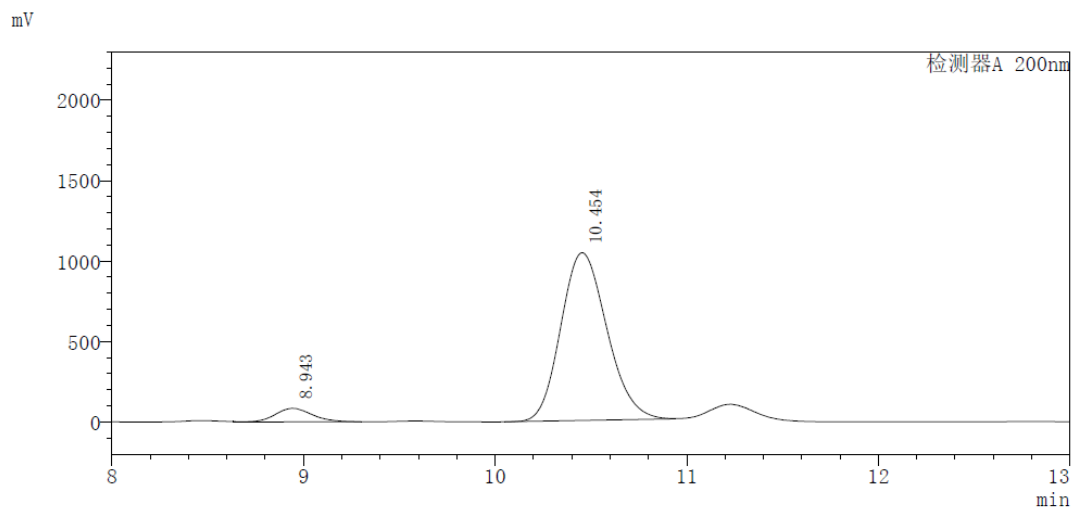
----- CHANNEL f2 -----

```

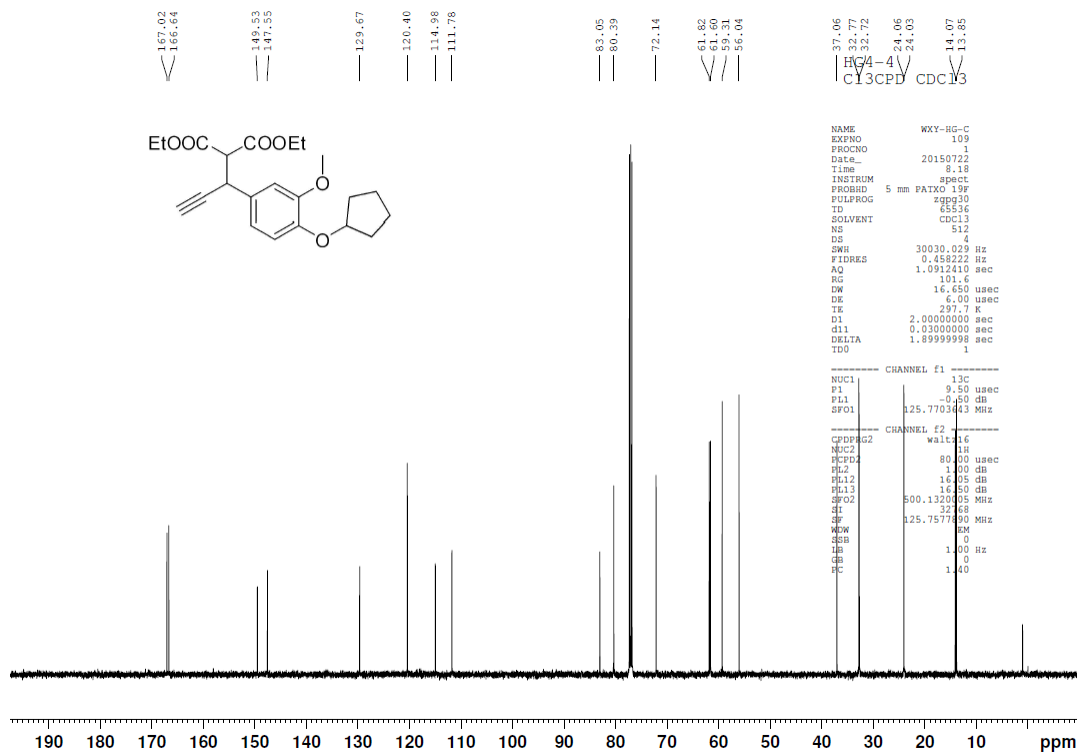
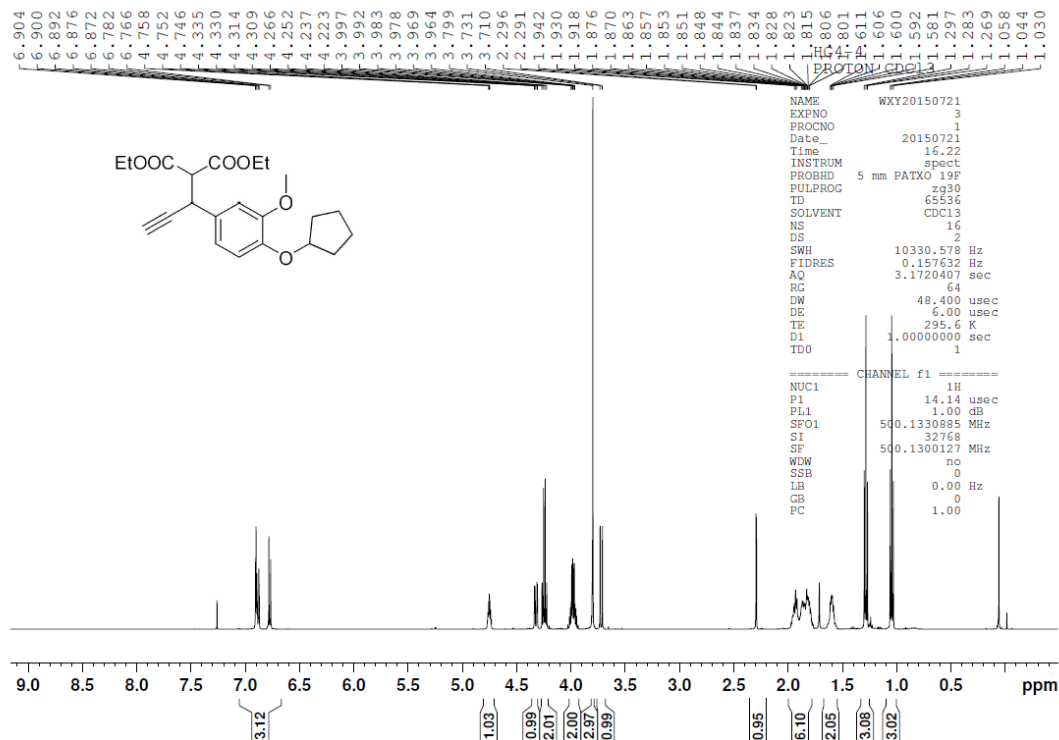
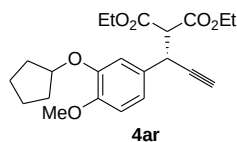
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       1.00 dB
PL12      16.05 dB
PL13      16.50 dB
SFO2      500.1320005 MHz
SI        32768
SF        125.7577890 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.40
  
```

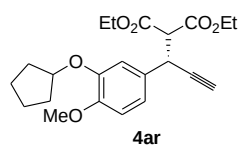


Peak#	Ret. Time	Area	Height	Area%
1	8.932	15658634	1199532	48.424
2	10.469	16677580	1019685	51.576
总计		32336213	2219217	100.000

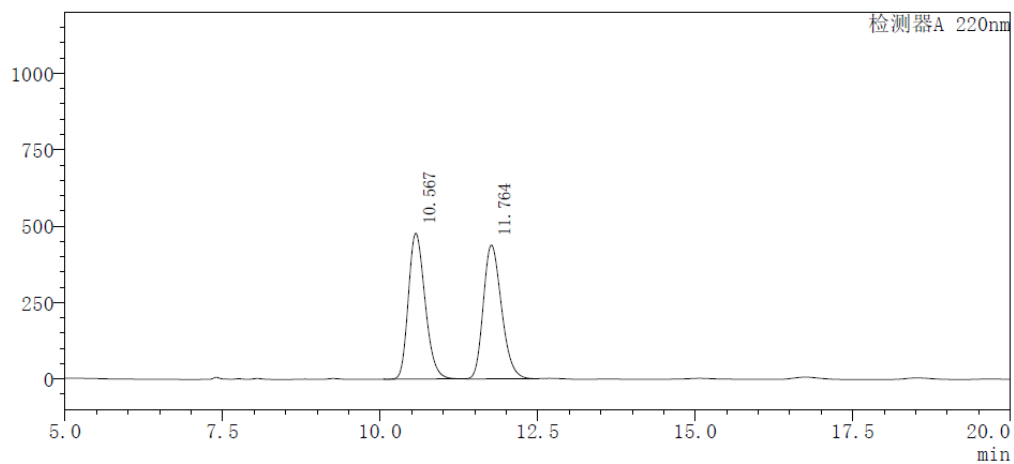


Peak#	Ret. Time	Area	Height	Area%
1	8.943	1125630	84104	6.052
2	10.454	17472225	1042381	93.948
总计		18597855	1126486	100.000



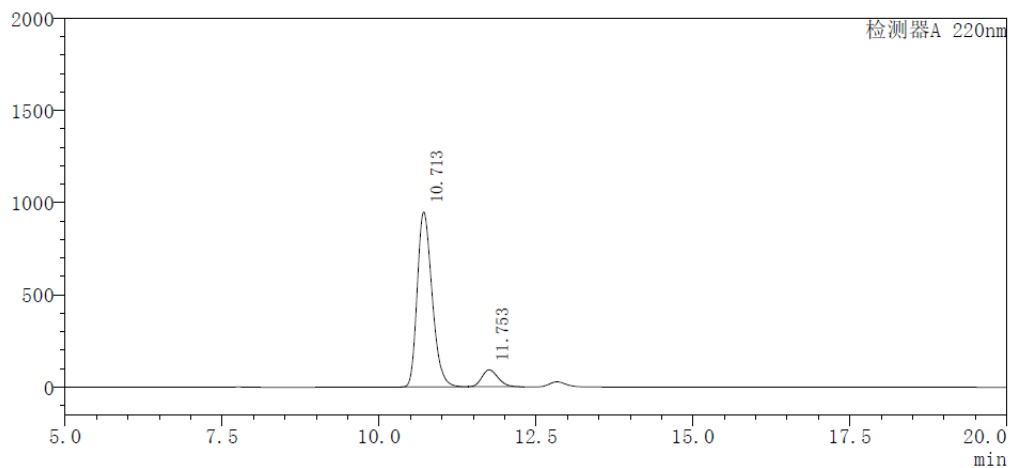


mV

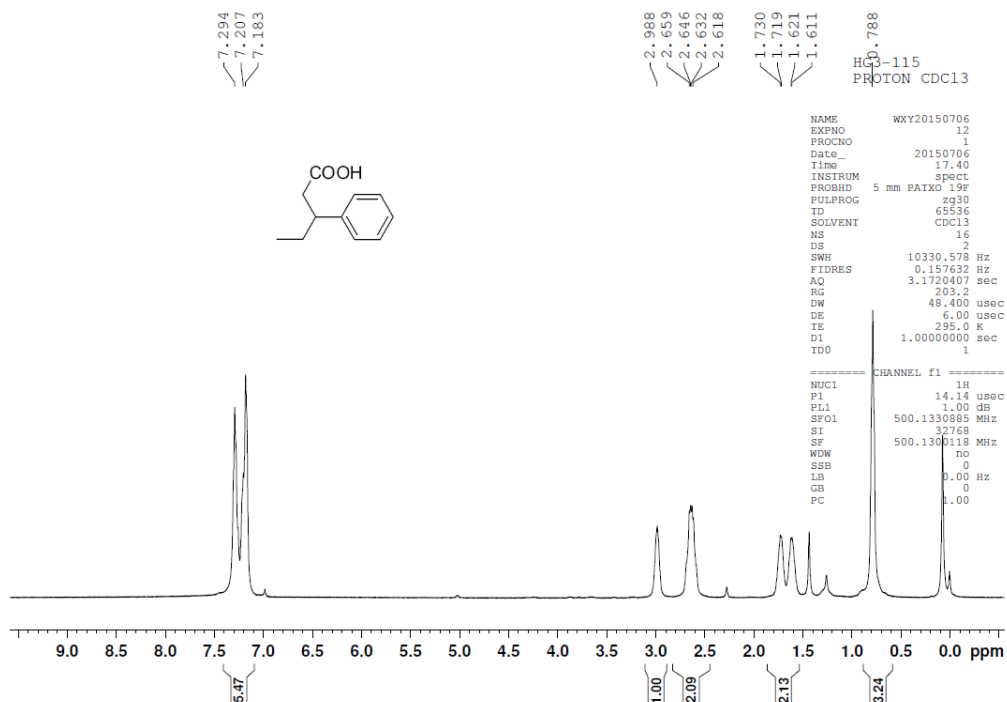
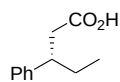
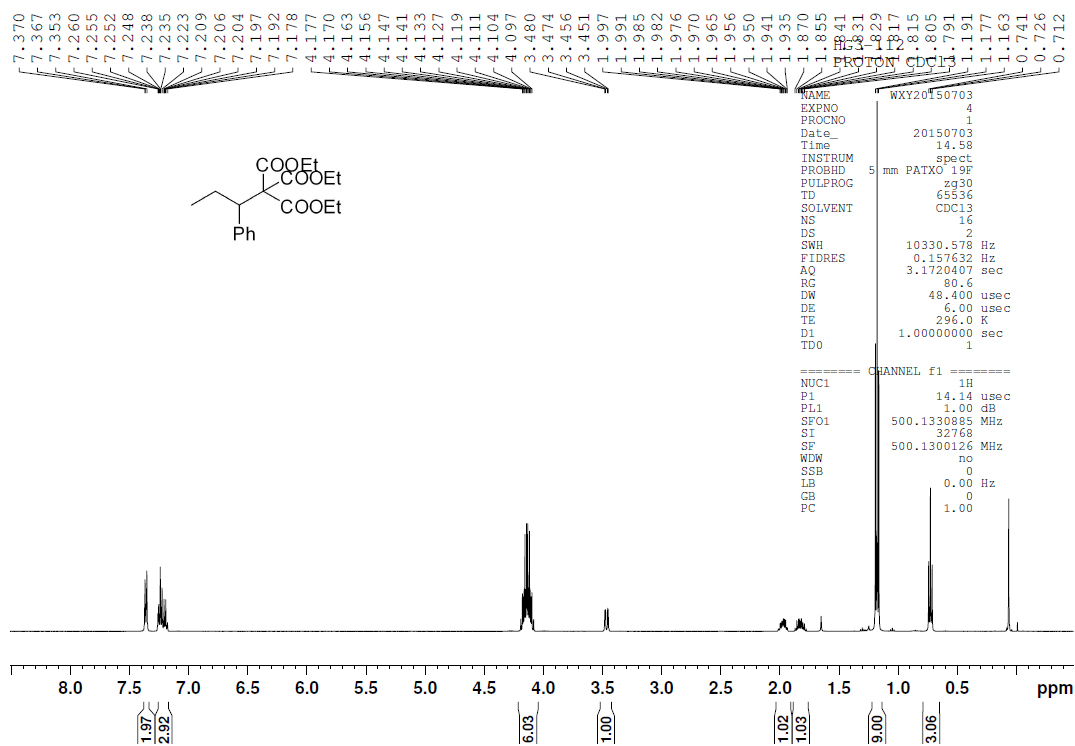
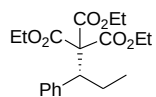


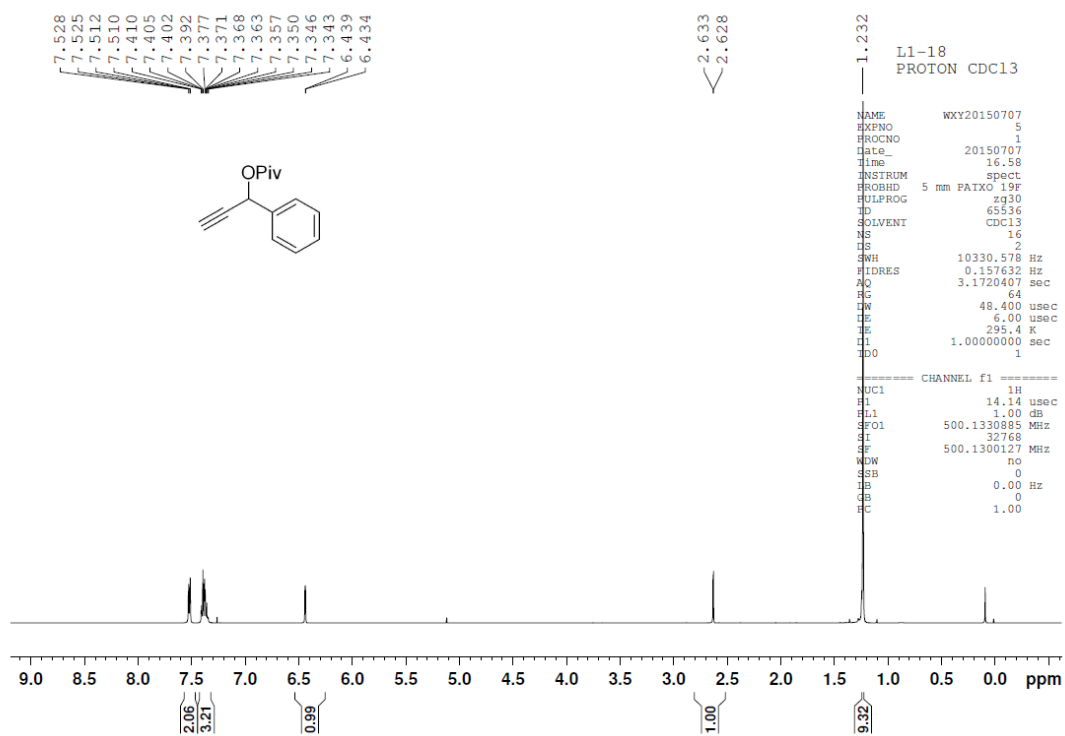
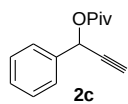
Peak#	Ret. Time	Area	Height	Area%
1	10.567	8820983	476943	50.070
2	11.764	8796161	437595	49.930
总计		17617144	914538	100.000

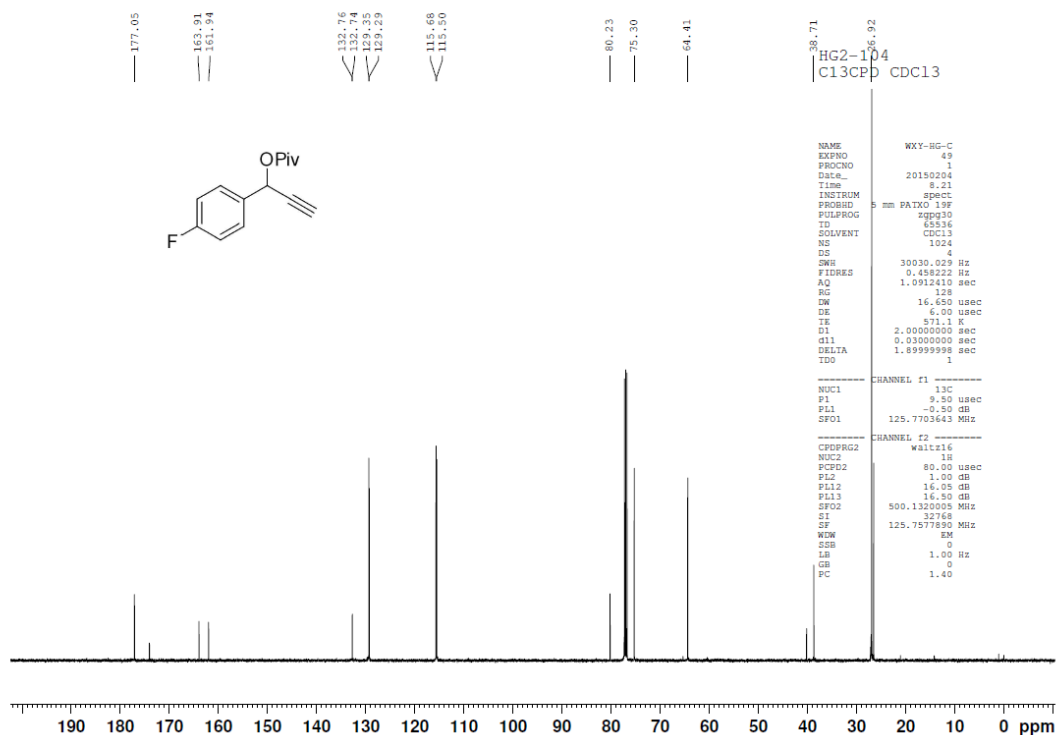
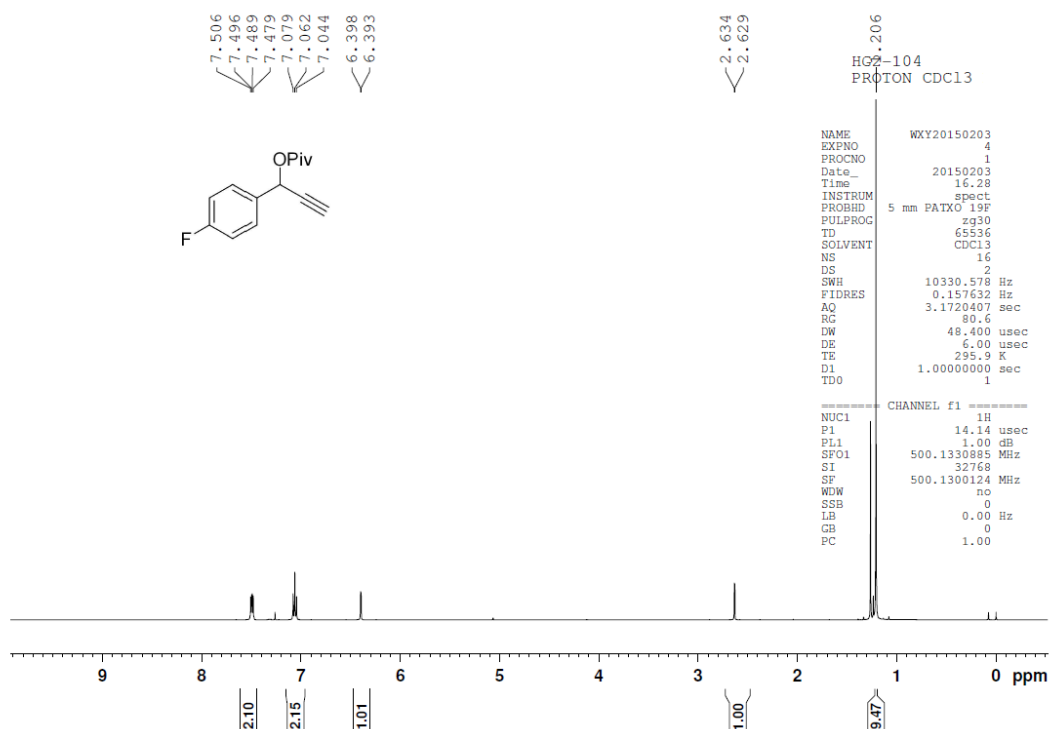
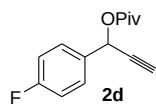
mV

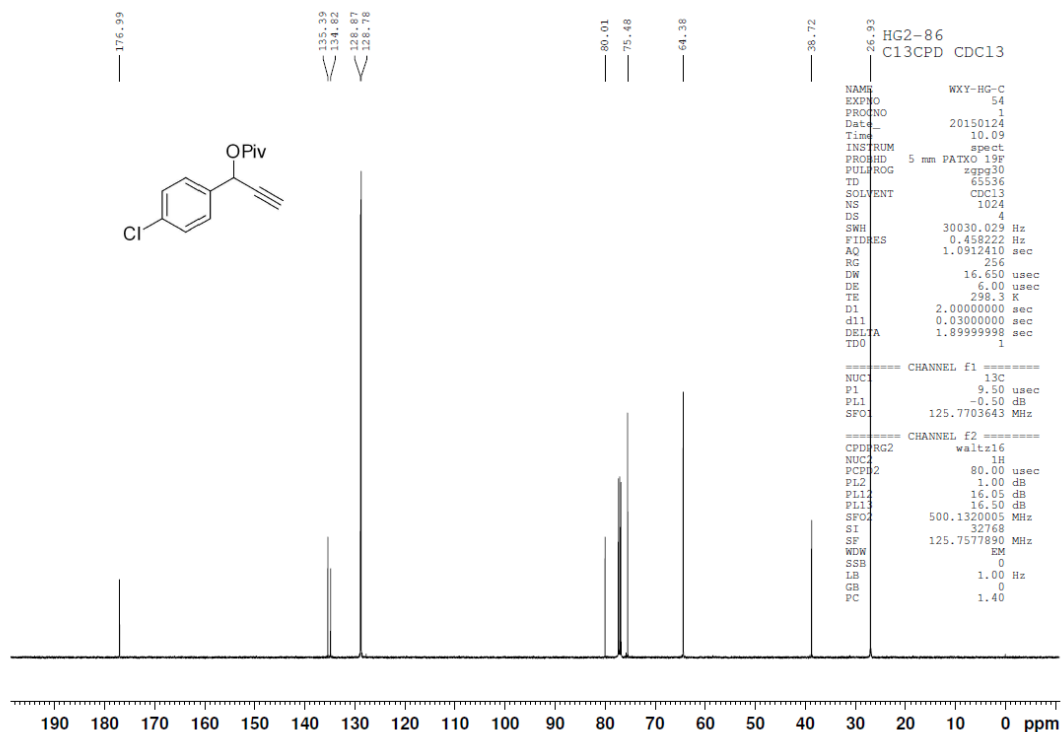
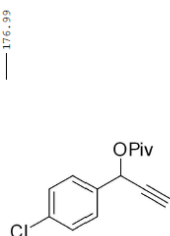
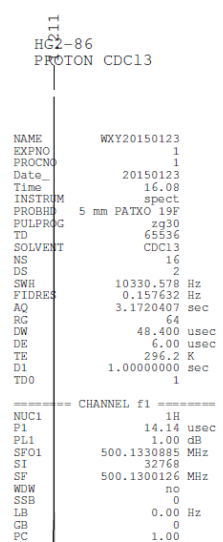
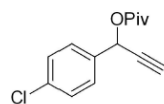


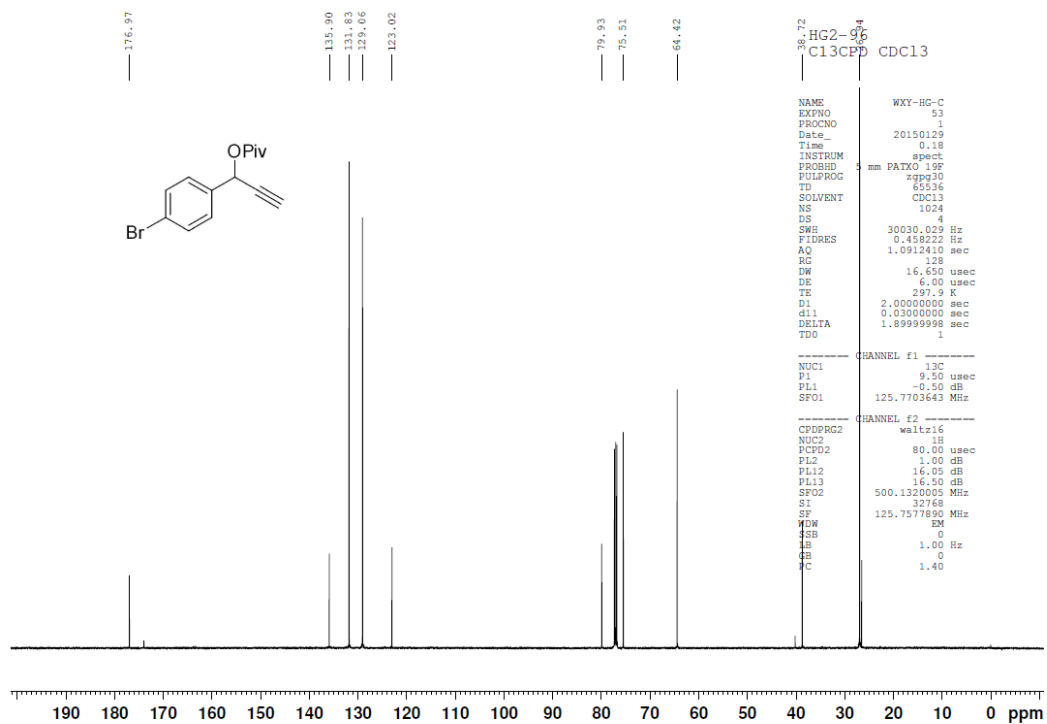
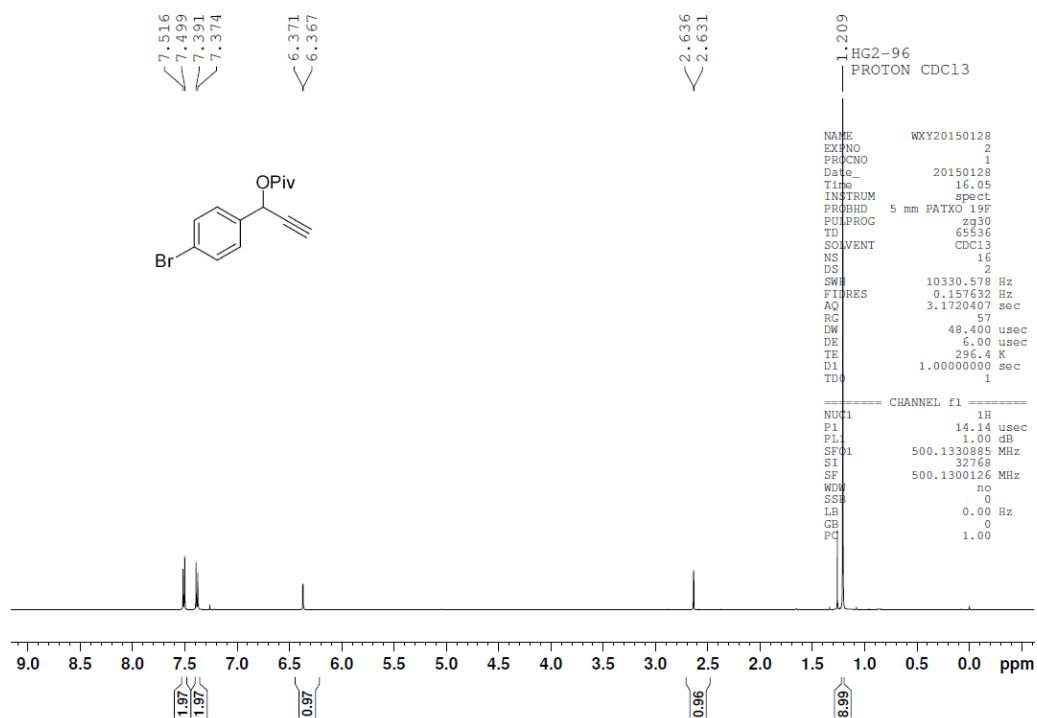
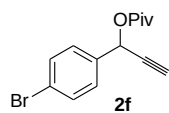
Peak#	Ret. Time	Area	Height	Area%
1	10.713	15634160	948780	90.443
2	11.753	1652091	91421	9.557
总计		17286252	1040201	100.000

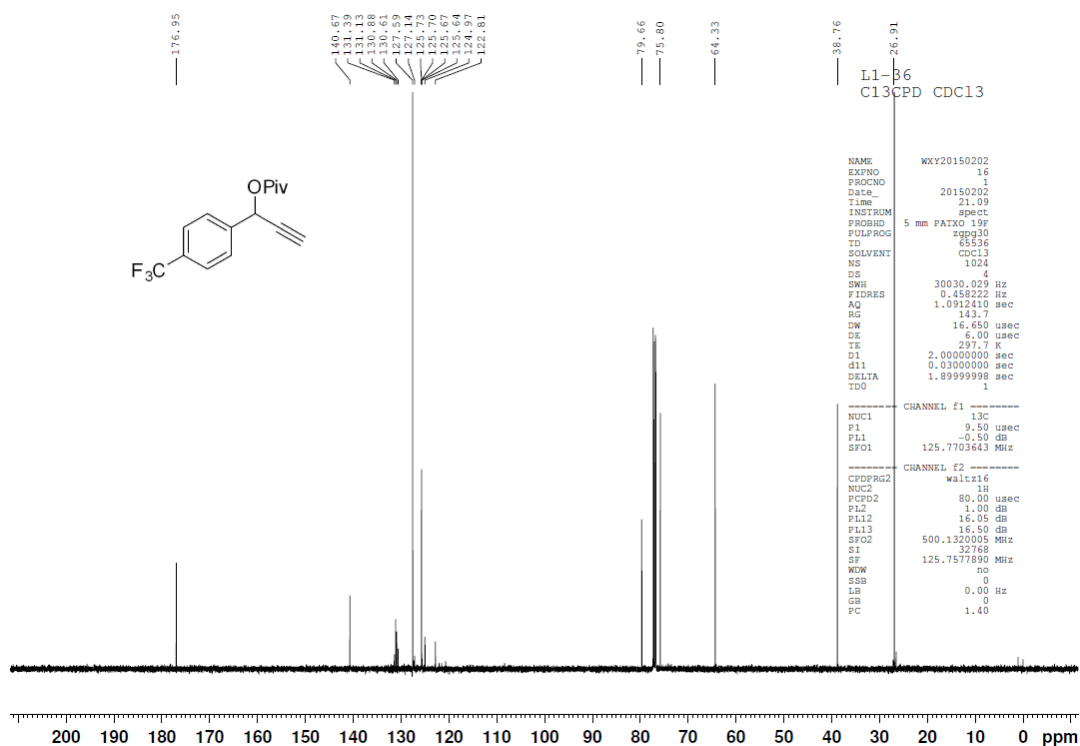
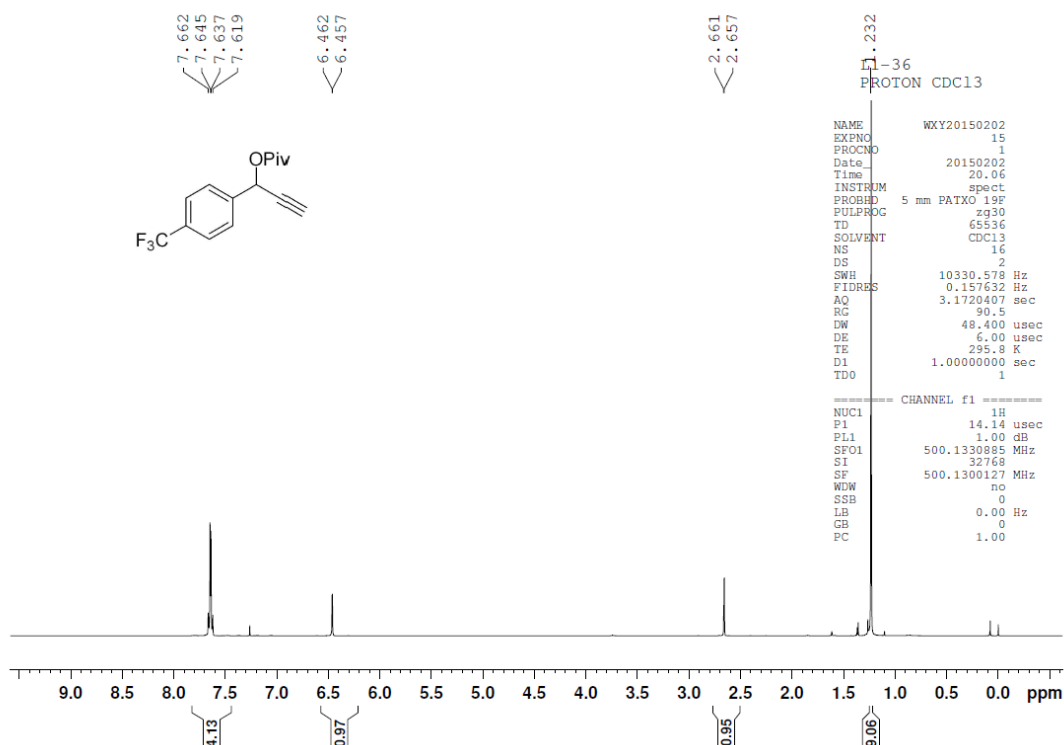
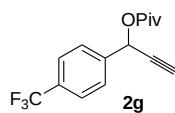


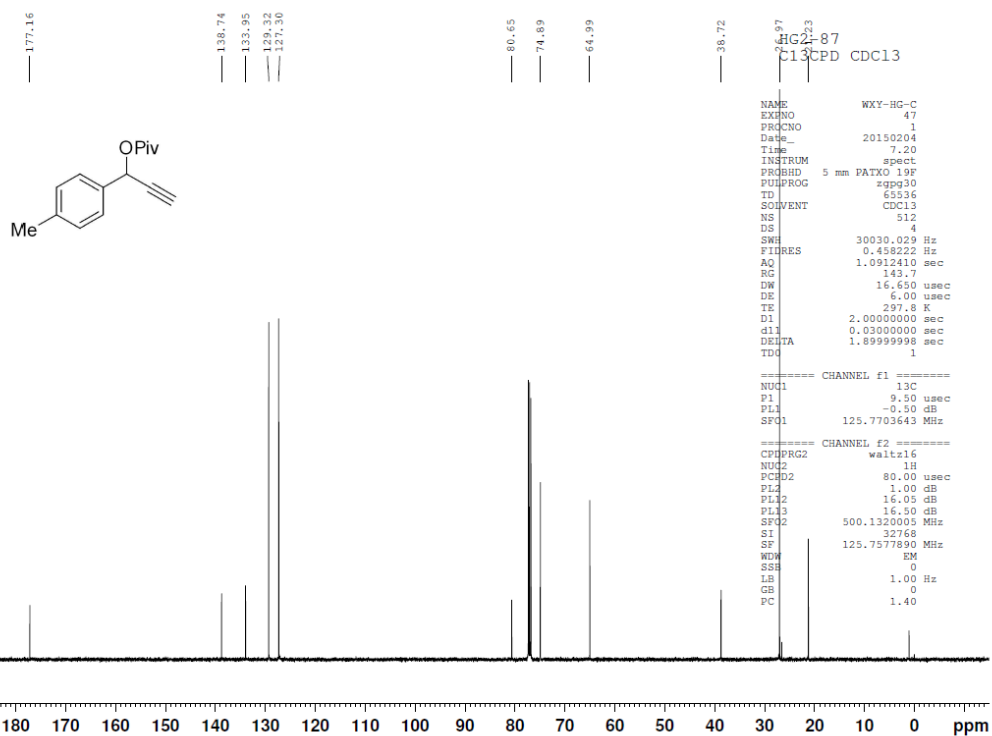
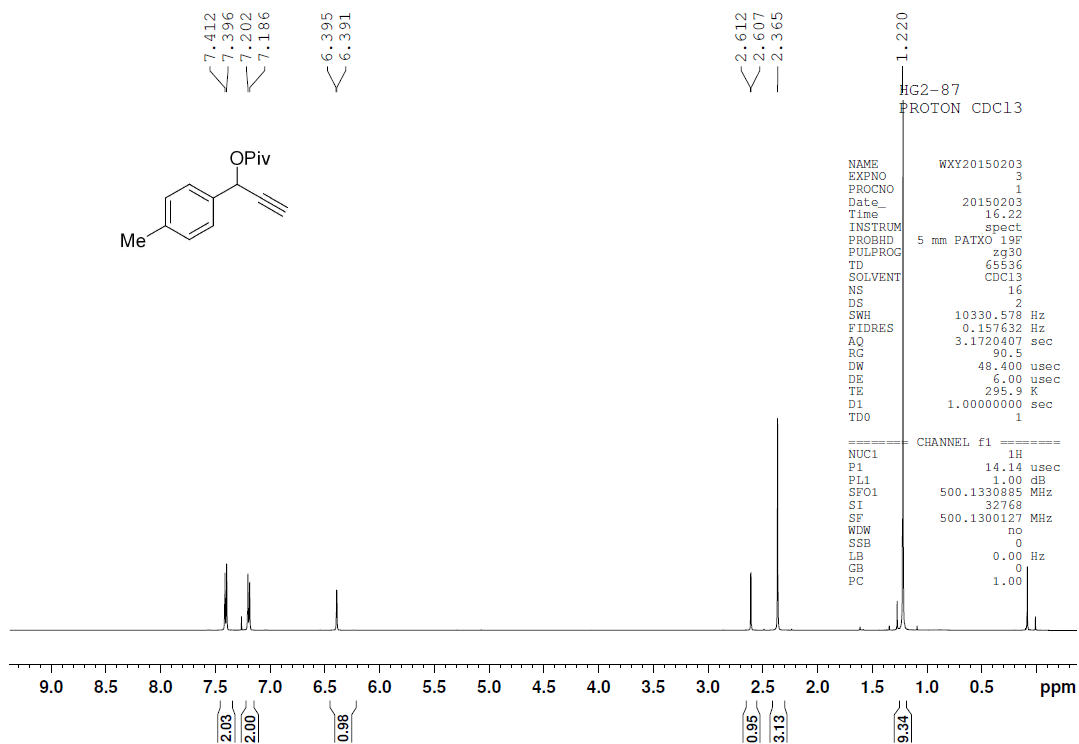
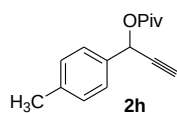


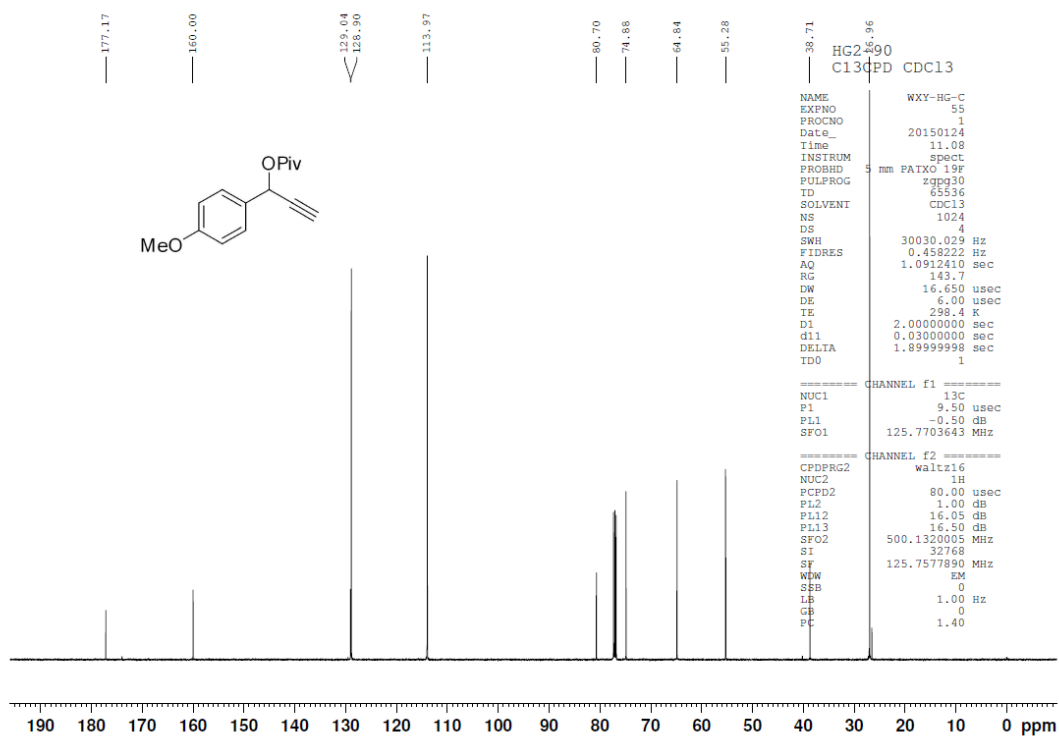
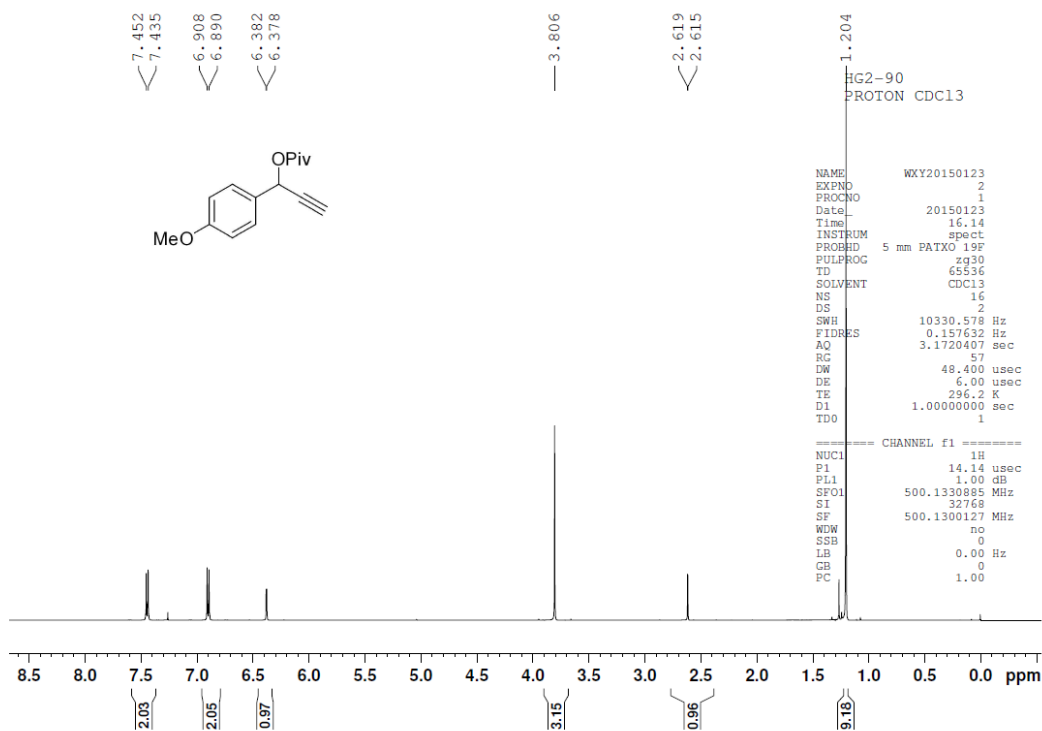
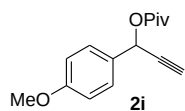


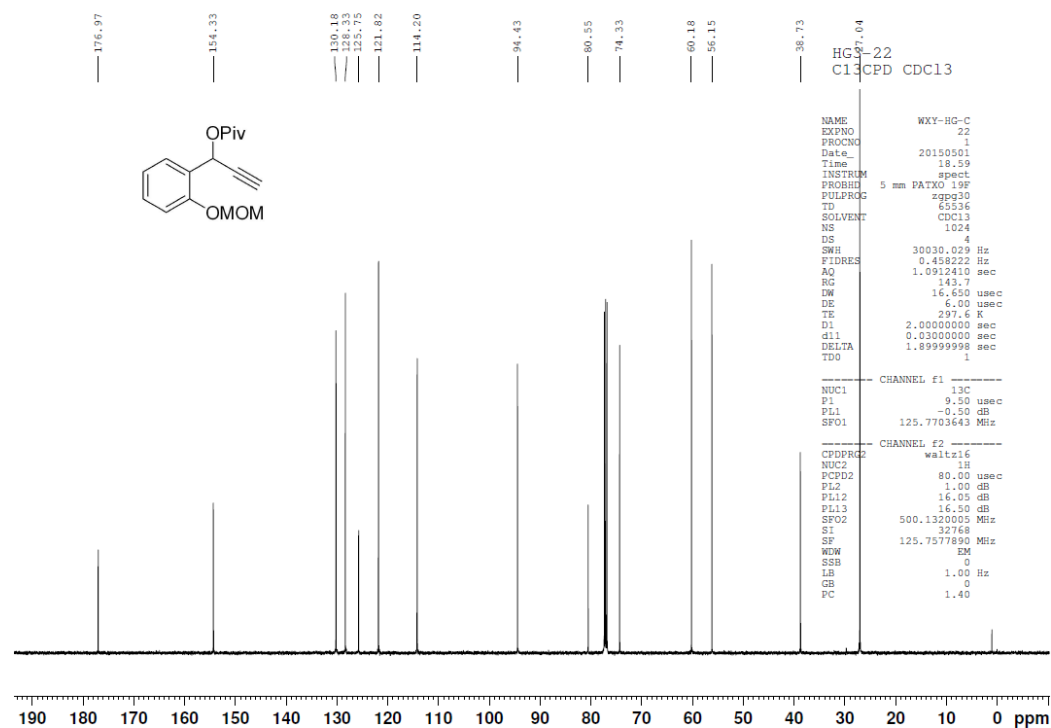
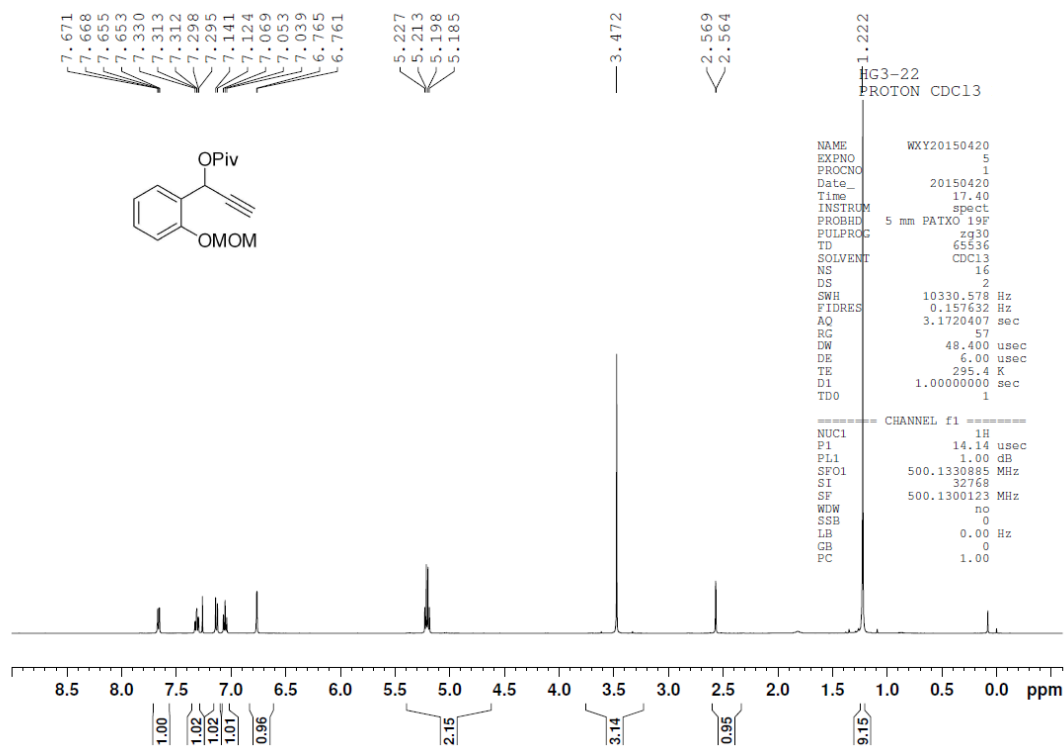
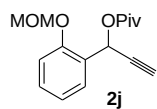


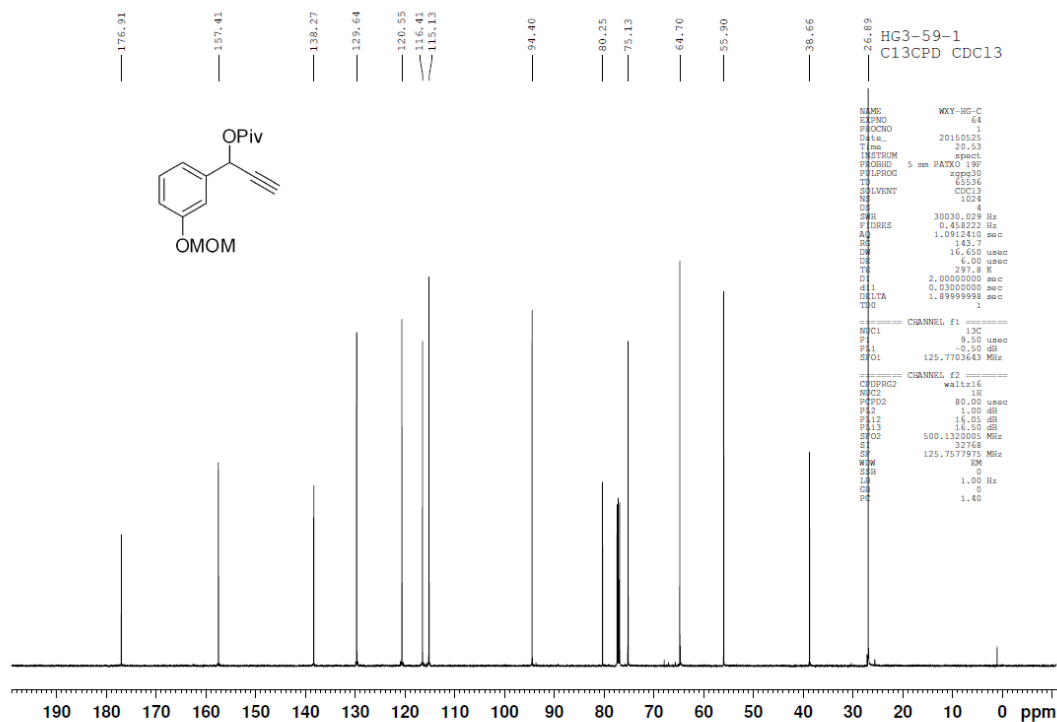
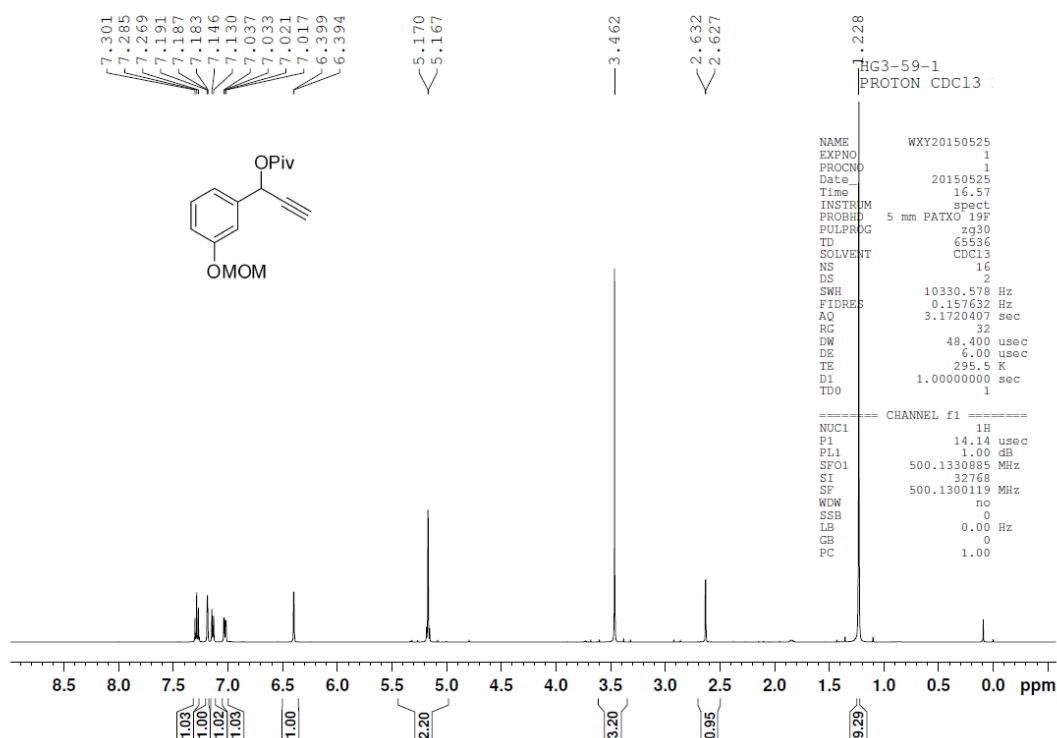
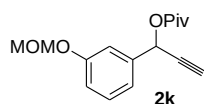


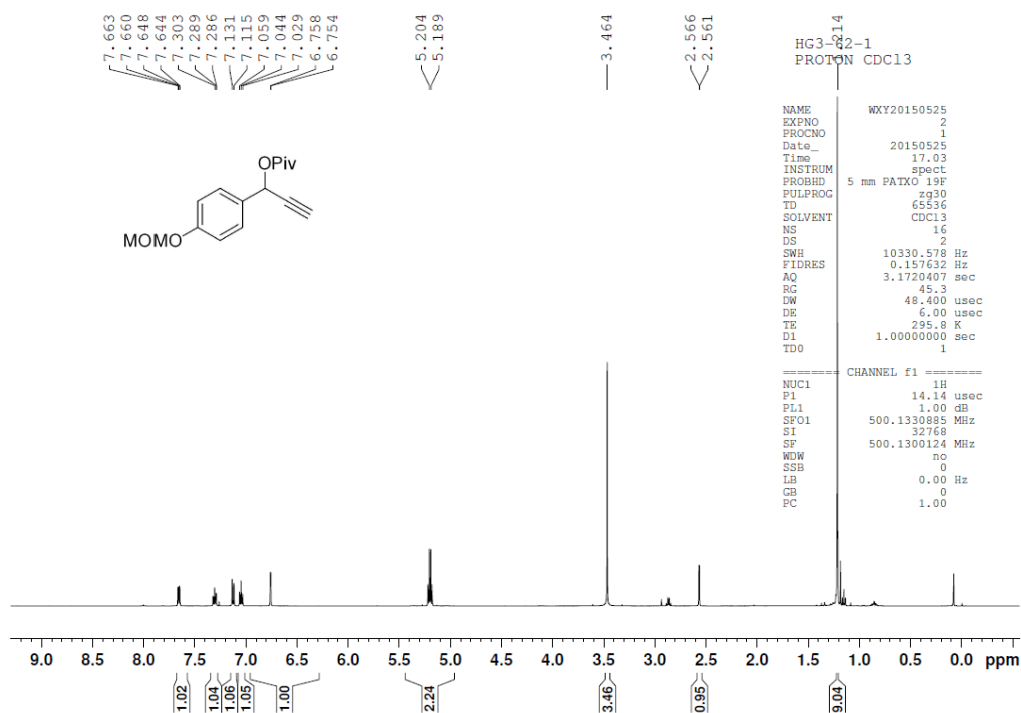
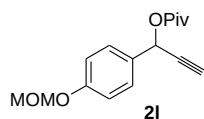




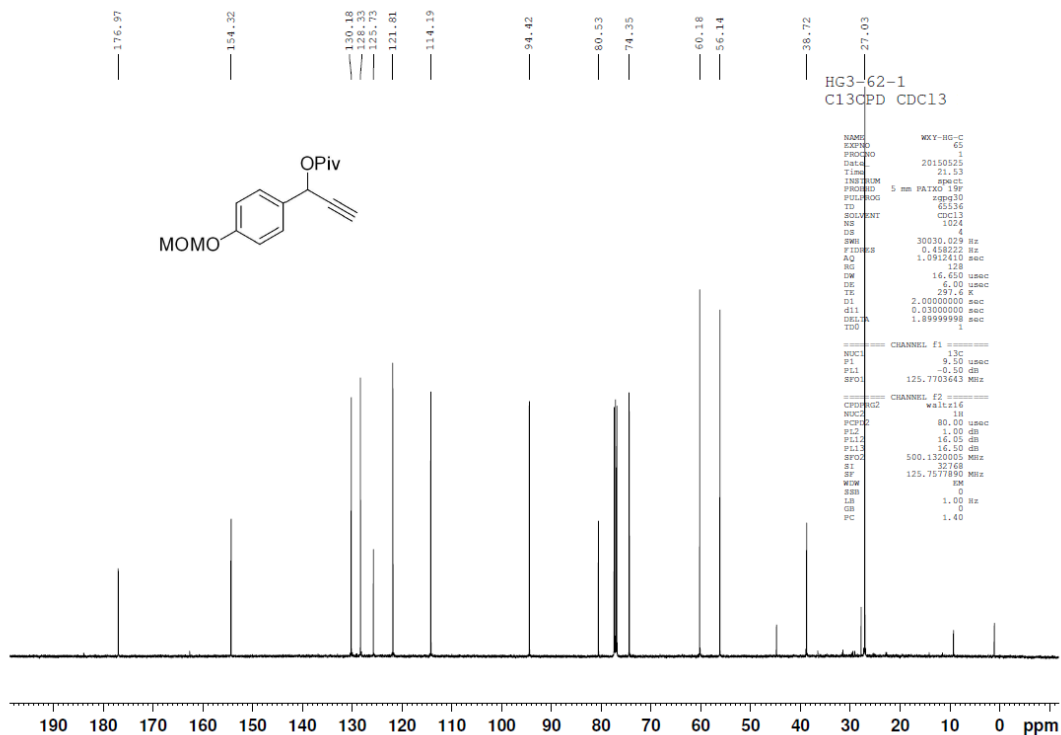
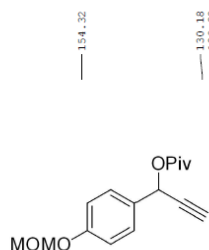




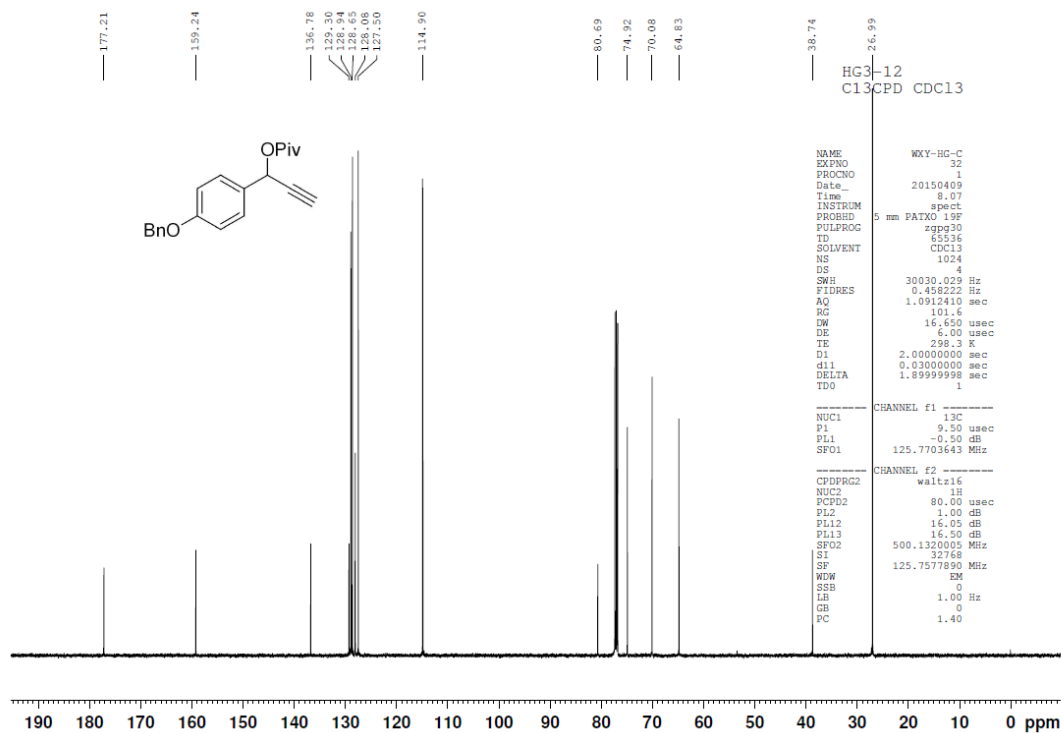
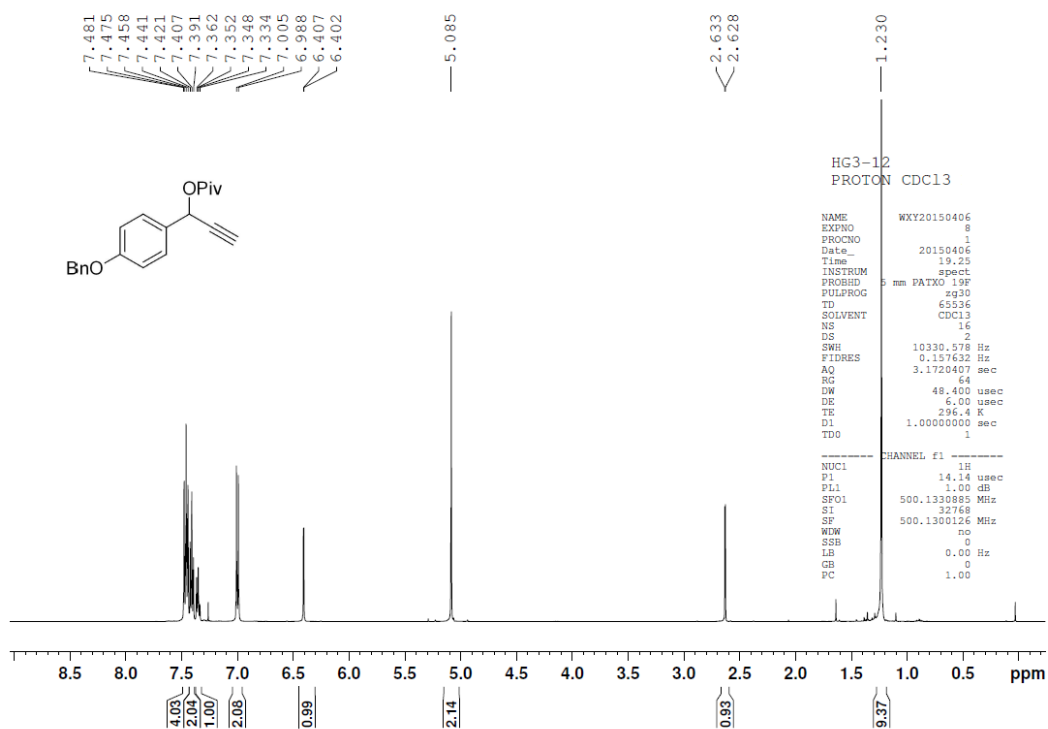
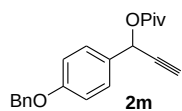


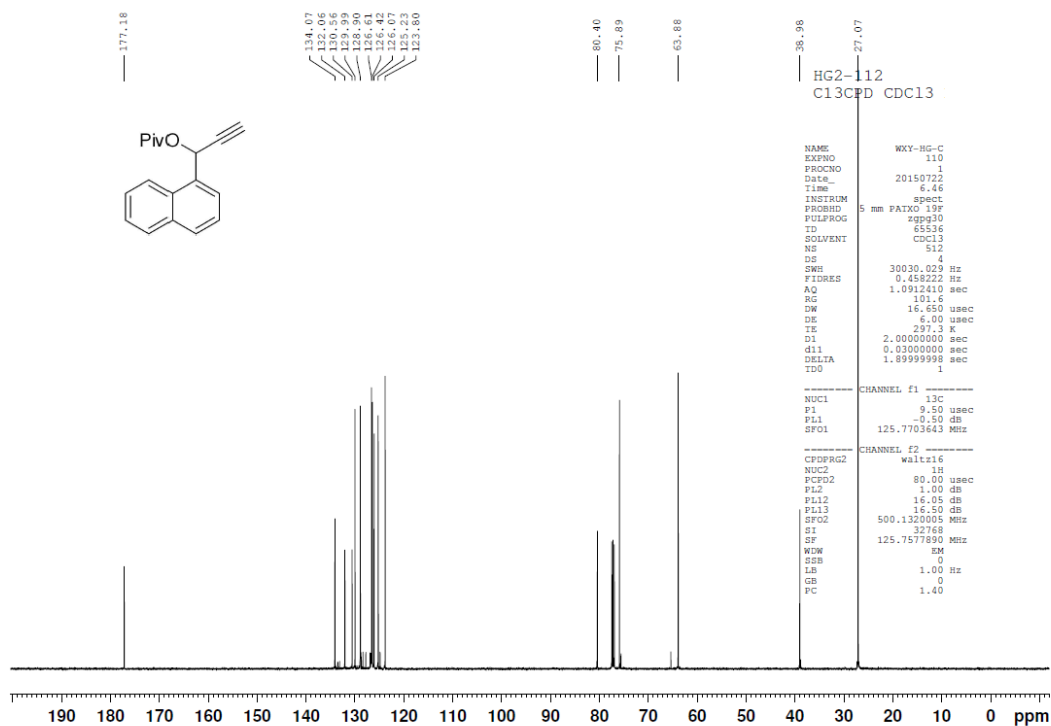
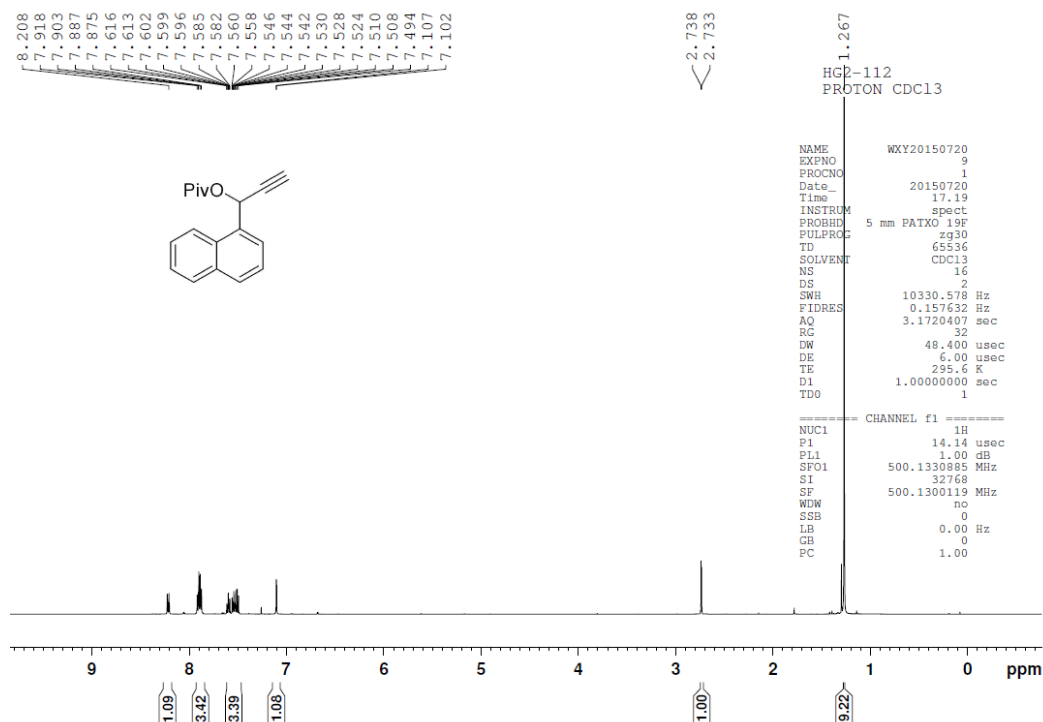
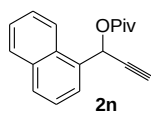


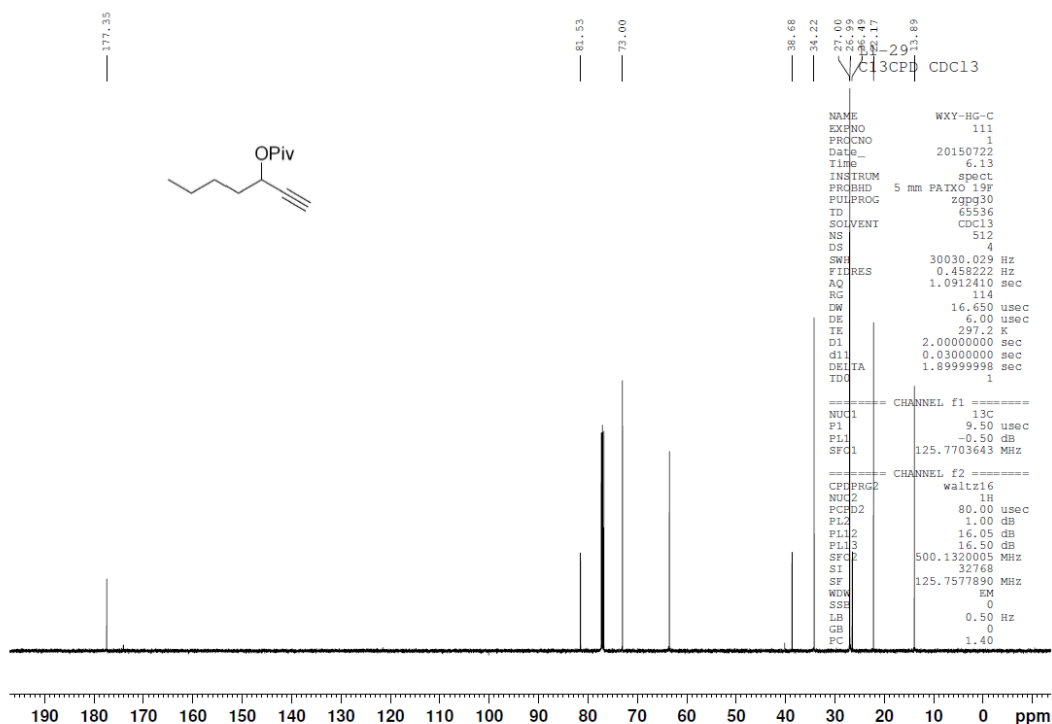
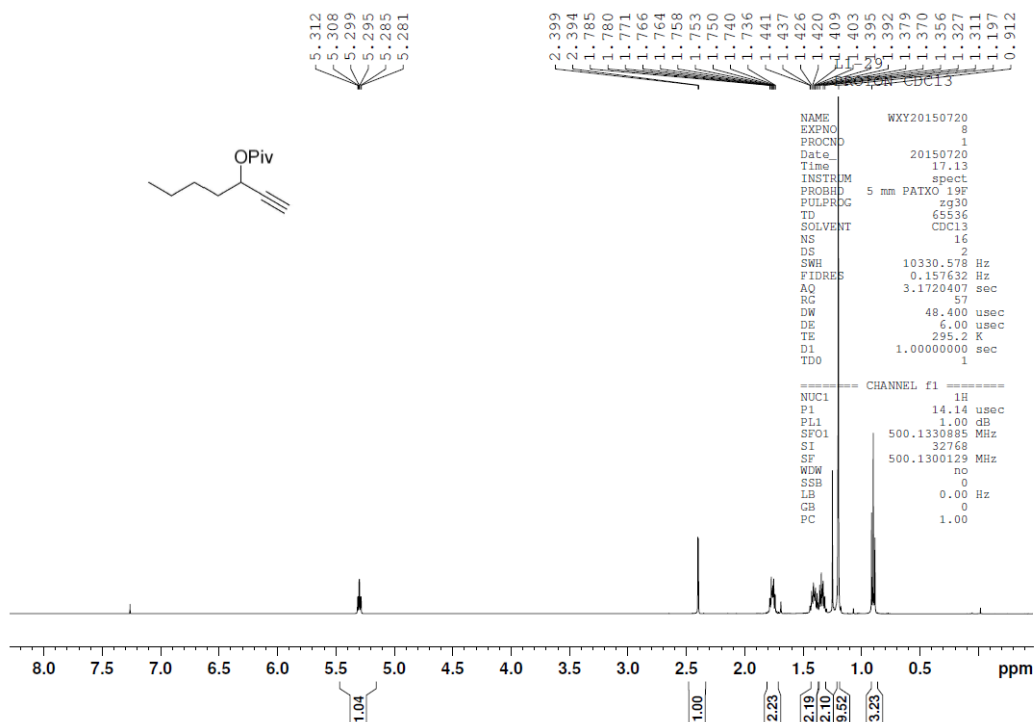
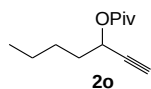
HG3-62-1
 PROTON CDC13
 NAME WXY20150525
 EXPNO 2
 PROCNO 1
 Date_ 20150525
 Time 17.03
 INSTRUM spect
 PROBHD 5 mm PATXO 19F
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 16
 DS 2
 SWH 10330.578 Hz
 FIDRES 0.157632 Hz
 AQ 3.1720407 sec
 RG 45.3
 DW 48.400 usec
 DE 6.00 usec
 TE 295.8 K
 D1 1.00000000 sec
 TDO 1
 CHANNEL f1 =====
 NUC1 1H
 P1 14.14 usec
 PL1 1.00 dB
 SFO1 500.1330895 MHz
 SI 32768
 SF 500.1300124 MHz
 WDW no
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

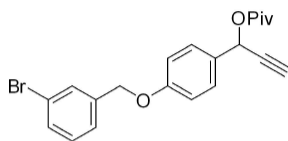
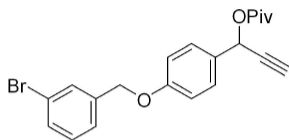


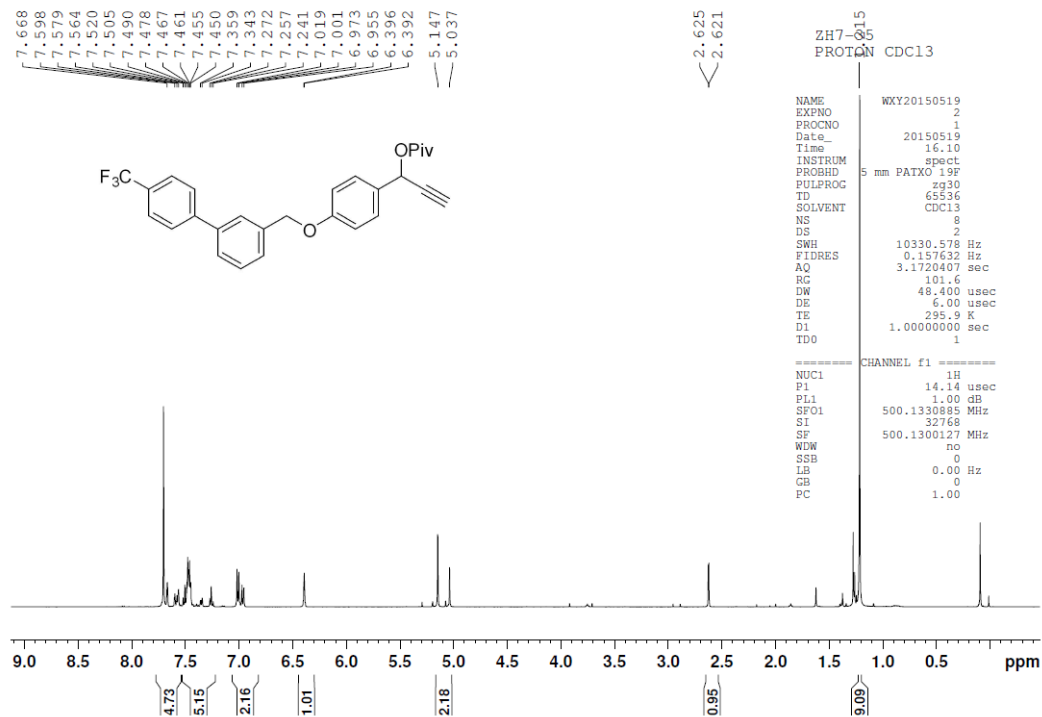
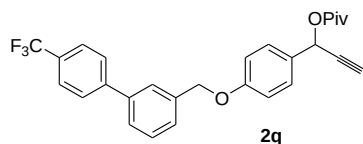
HG3-62-1
 C13CPD CDC13
 NAME WXY-HG-C
 EXPNO 65
 PROCNO 1
 Date_ 20150525
 Time 21.53
 INSTRUM spect
 PROBHD 5 mm PATXO 19F
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 1024
 DS 4
 SWH 30030.029 Hz
 FIDRES 0.498222 Hz
 AQ 1.0912410 sec
 RG 128
 DW 16.650 usec
 DE 6.00 usec
 TE 297.6 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TDO 1
 CHANNEL f1 =====
 NUC1 13C
 P1 9.50 usec
 PL1 -0.50 dB
 SFO1 125.7703643 MHz
 CHANNEL f2 =====
 NUC2 1H
 P2 14.14 usec
 PL2 1.00 dB
 SFO2 500.1330895 MHz
 SI 32768
 SF 125.7577890 MHz
 WDW RM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40









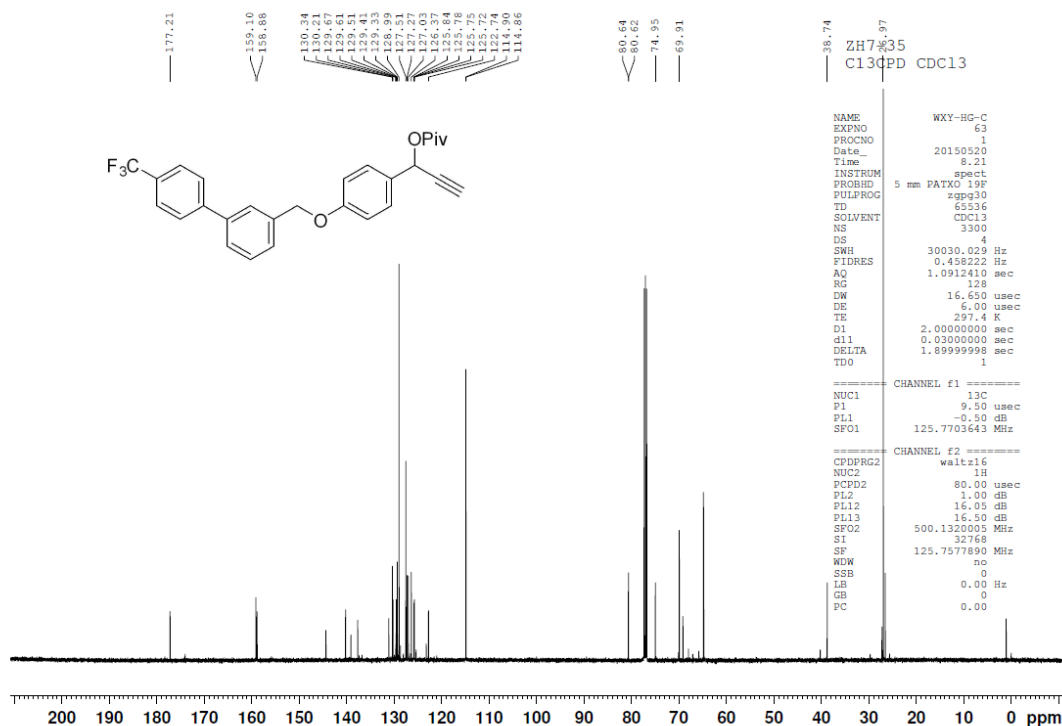


ZH7-05
PROTON CDC13

NAME	WXY20150519
EXPNO	2
PROCNO	1
Date_	20150519
Time	16.10
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1720407 sec
RG	101.6
DW	48.400 usec
DE	6.00 usec
TE	295.9 K
D1	1.00000000 sec
TD0	1

===== CHANNEL f1 =====

NUC1	1H
P1	14.14 usec
PL1	1.00 dB
SFO1	500.1330885 MHz
SI	32768
SF	500.1300127 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



ZH7-05
C13CPD CDC13

NAME	WXY-HG-C
EXPNO	63
PROCNO	1
Date_	20150520
Time	8.21
INSTRUM	spect
PROBHD	5 mm PATXO 19F
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	3300
DS	4
SWH	30030.029 Hz
FIDRES	0.458222 Hz
AQ	1.0912410 sec
RG	128
DW	16.650 usec
DE	6.00 usec
TE	297.4 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.69999998 sec
TD0	1

===== CHANNEL f1 =====

NUC1	13C
P1	9.50 usec
PL1	0.50 dB
SFO1	125.7703643 MHz

===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	16.05 dB
PL13	16.50 dB
SFO2	500.1320005 MHz
SI	32768
SF	125.7577890 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	0.00

