Electronic Supplementary Information

Fast, Solvent-Free, Highly Enantioselective Three-Component Coupling of Aldehydes, Alkynes, and Amines Catalysed by Copper(II)pybox Complex under High-Vibration Ball-Milling

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1. General Information

All reagents were purchased from commercial source and were used without prior purification, unless otherwise indication. The reaction were conducted in a high-energy vibrational micromill (volume of stainless steel vial: 15 mL; 50 mL; diameter of stainless steel balls: 8.0 mm; diameter of copper balls: 8.0 mm). Melting points (mp) were measured on a digital melting point apparatus and uncorrected. ^{1}H and ^{13}C NMR were recorded at 400 and 100 MHz, respectively, and TMS was used as internal standard. IR spectra (KBr) were recorded on an FT-IR spectrophotometer. Mass spectra were measured with a HRMS-ESI instrument. Enantiomeric excess was determined with HPLC by using a Chiralcel OD column and 95/5 hexane/ isopropanol as eluent. The absolute configuration was assigned by analogy according to the reported HPLC retention times.

2. General experimental process for propargylamine derivatives

In a stainless steel ball milling vial, aldehydes (1.0 mmol, 1.0 equiv), amines (1.2 mmol, 1.2 equiv), alkynes (2.0 mmol, 2.0 equiv), $Cu(OTf)_2$ (0.07 mmol, 0.07 equiv), Ph-Pybox (0.07 mmol, 0.07 equiv), silica gel (0.8 g), along with two stainless steel balls (d = 8.0 mm) were added and screwed up. Then the vial was placed in a vibrational micromill, and grinded at 25 Hz. A pause was added after every 10 minutes grinding until the vital cool down. At the end of the experiment, all of contents was poured out for column chromatography separation directly using petroleum ether/ethyl acetate = 10/1 as eluent.

3. Detailed data for extractant screening

Table S1 Extractant screening [a]

No.	Solvent	1st run [b]		2nd run [c]	
		%yield [d]	%ee [e]	%yield[d]	%ee [e]
1	petroleum ether [f]	92	99	92	99
2	*n*-hexane [f]	96	99	96	99
3	*n*-heptane [f]	95	99	92	99
4	CH_2Cl_2 [g]	99	99	97	99
5	CH_2Cl_2 [f]	99	99	92	99
6	CH_2Cl_2 [h]	99	99	90	98
7	EtOAc [g]	98	99	75	95
8	EtOH [g]	99	99	n.d. [i]	-

[a] All the reactions were performed with **1a** (106 mg, 1.0 mmol), **2a** (112 mg, 1.2 mmol), **3a** (204 mg, 2.0 mmol), under Ball-Milling at 25 Hz. [b] $Cu(OTf)_2$ (36 mg, 0.1 mmol), $\mathbf{L_1}$ (36 mg, 0.1 mmol) with Silica gel (chromatography grade, 0.8 g) were used. [c] Catalyst system recovered from 1st run were used. [d] Isolated yields based on **1a**. [e] Determined by HPLC analysis of reaction mixture. [f] 50 mL of solvent were used. [g] 20 mL of solvent were used. [h] 100 mL of solvent were used. [i] Not detected.

4. General experimental process, detailed data and HPLC spectra for recycle experiment

The 1st run of reaction were performed as same as general process except the work-up process. At the end of the experiment, all of contents was washed out with 10 mL of dichloromethane, filtered and washed with another 10 mL of dichloromethane. The solvents were then combined and evaporated for column chromatography separation using petroleum ether : ethyl acetate = 10:1 as eluent. The residue was dried under air in laboratory oven (50 ºC, ambient pressure) for 3 hours, and used directly into the next run.

Due to the inevitable loss of catalyst system for monitoring the reaction and work-ups, after washing the products from the solid mixture, residue was dried in laboratory oven and weighted. Substance used for next run were calculated based on the residue weight.

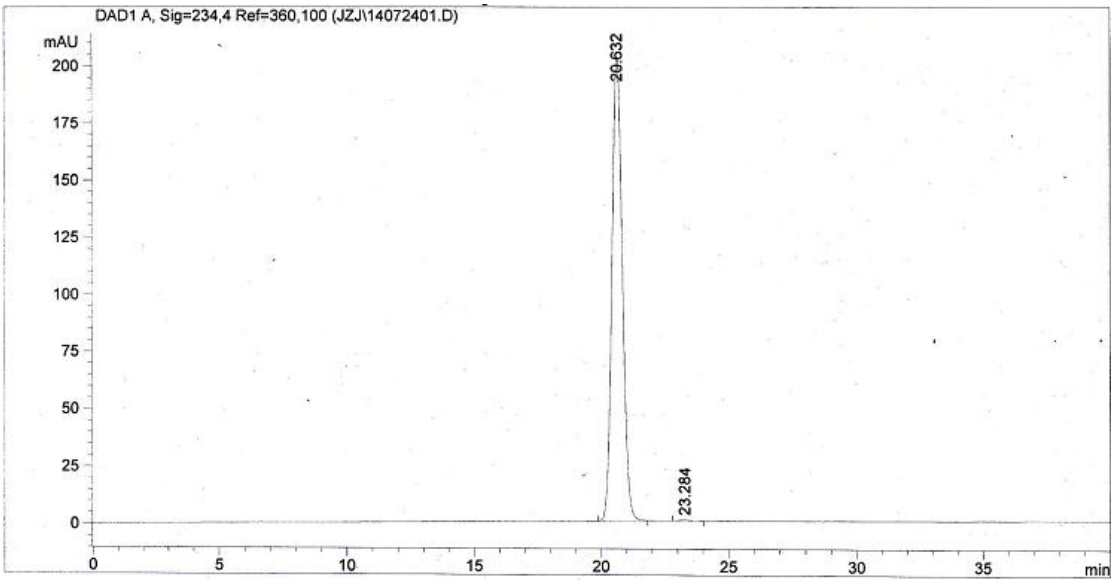
Table S2 Recycle Experiment [a]

No.	Run	Residue weight (mg)	Theoretical catalyst loading (mol %) [b]	Time (min)	%yield [c]	%ee [d]
1 [e]	1	-	10.0	40	98.6	99.5
2	2	830	9.5	30	96.7	99.2
3	3	801	9.2	30	99.0	99.1
4	4	768 [f]	8.7	30	98.6	99.4
5	5	830	8.4	30	94.0	94.3

[a] Unless mentioned otherwise, all the reactions were performed with **1a** (1.0 equiv.), **2a** (1.0 equiv.), **3a** (2.0 equiv.), and stainless steel balls (1.5cm*1) under Ball-Milling at 30Hz. [b] Theoretical catalyst loading = (Residue weight / 873 mg)*10 mol%. [c] Isolated yield based on **1**. [d] %ee were determined by HPLC analysis of crude mixture. [e] The reactions were performed with **1a** (106 mg, 1.0 mmol), **2a** (112 mg, 1.0 mmol), **3a** (204 mg, 2.0 mmol), $Cu(OTf)_2$ (36 mg, 10 mol%), $\mathbf{L_1}$ (36 mg, 10 mol%) with Silica gel (chromatography grade, 0.8 g) under Ball-Milling at 30Hz. [f] A portion of Silica gel (106 mg) were added into the mixture to increase the flowability of the powder.

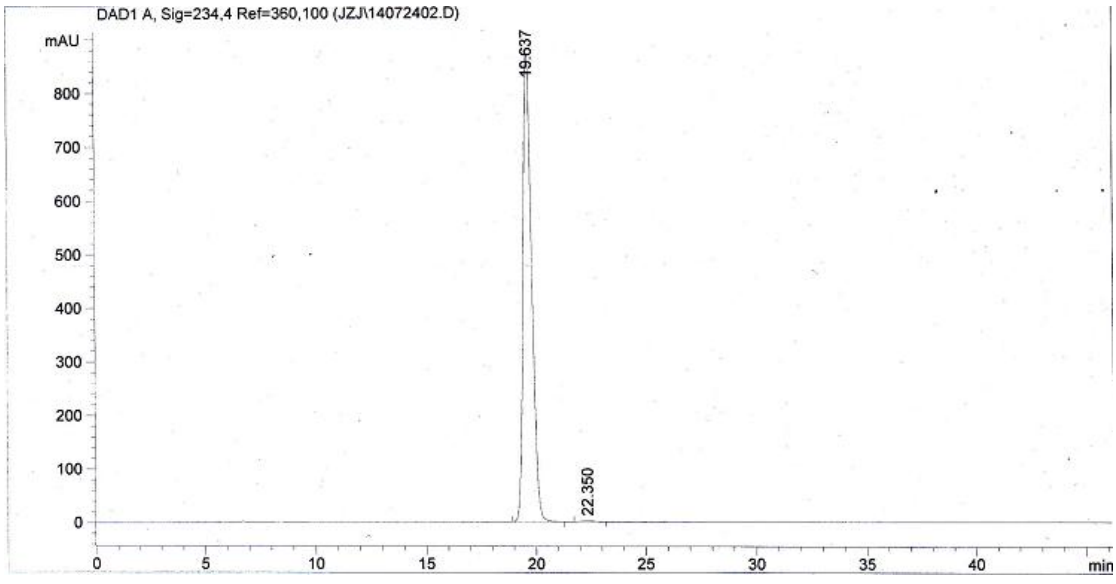
Copies of HPLC spectra for Recycle Experiment:

HPLC spectra for **run-1 (Table S1, entry 1)**



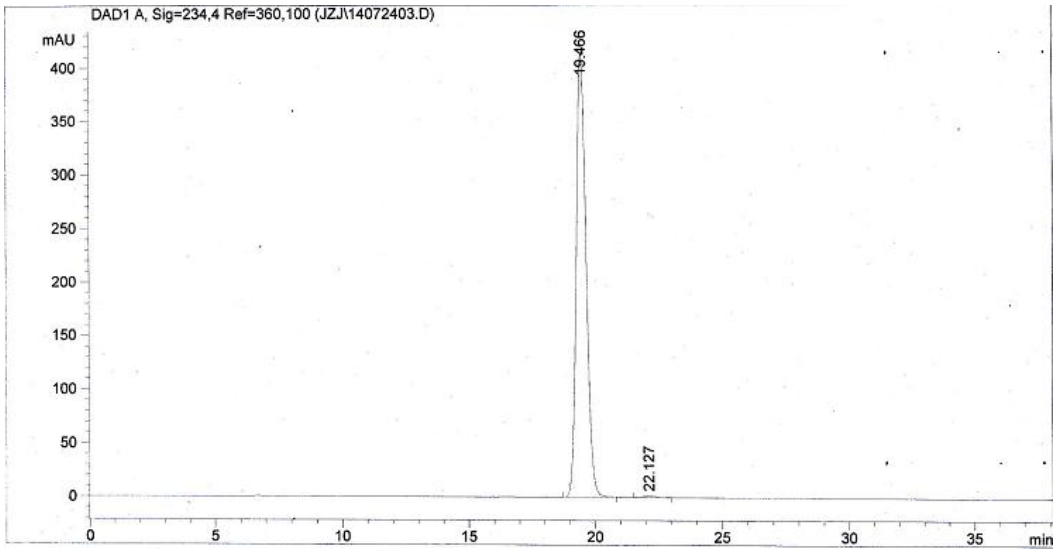
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.632	BB	0.4434	5743.14648	202.21242	99.7537
2	23.284	BP	0.3883	14.18085	4.64285e-1	0.2463

HPLC spectra for **run-2 (Table S1, entry 2)**



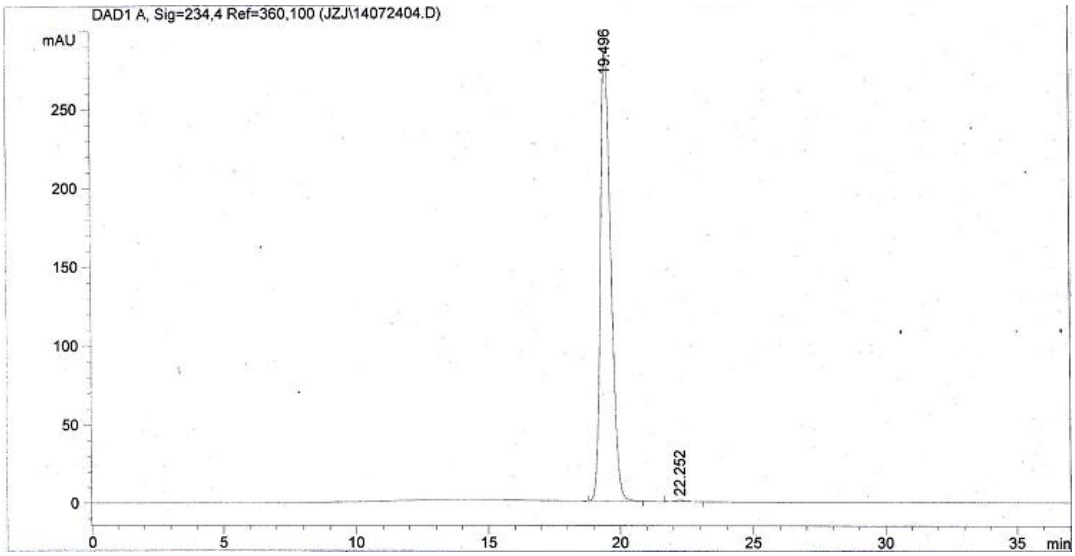
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.637	BB	0.4225	2.37448e4	869.87195	99.6103
2	22.350	BP	0.4756	92.88536	2.91620	0.3897

HPLC spectra for **run-3 (Table S1, entry 3)**



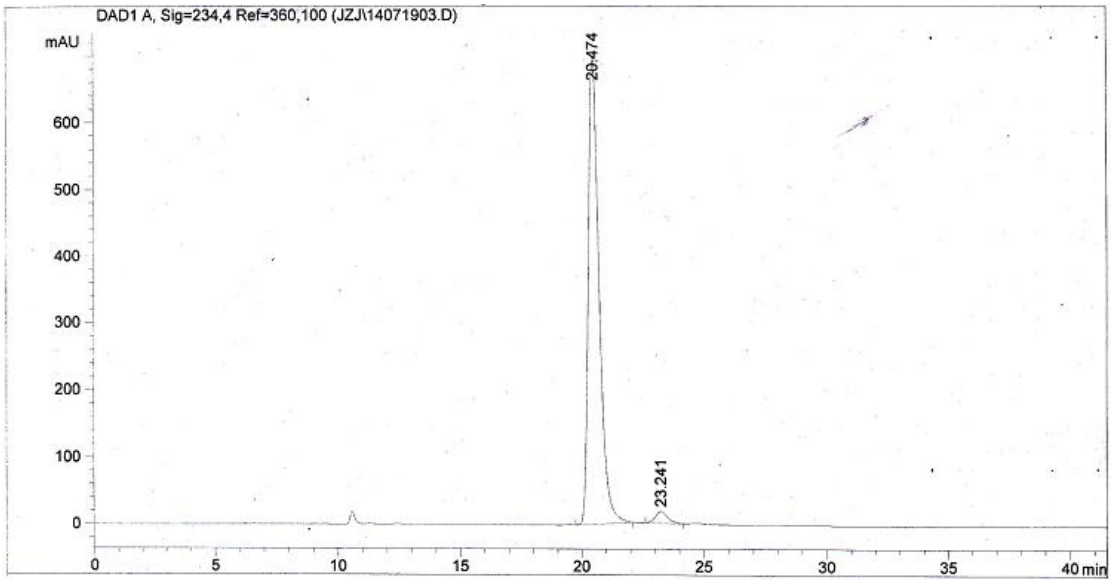
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.466	PB	0.4176	1.11259e4	413.91403	99.5264
2	22.127	PP	0.4474	52.94180	1.73782	0.4736

HPLC spectra for **run-4 (Table S1, entry 4)**



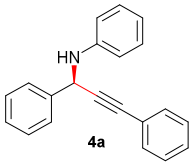
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.496	BB	0.4284	7811.49121	284.40112	99.6821
2	22.252	PP	0.3847	24.90881	8.05767e-1	0.3179

HPLC spectra for **run-5 (Table S1, entry 5)**

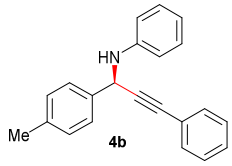


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.474	MM R	0.5449	2.13272e4	698.65851	97.1305
2	23.241	MM R	0.5925	630.05774	17.72272	2.8695

5. Characterization data for products 4a-4w

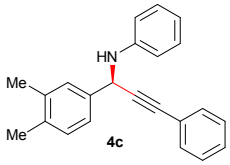


(*R*)-*N*-(1,3-diphenyl-prop-2-yn-1-yl)aniline **4a**[1, 2] (280 mg, 99% yield, 99% *ee*): white solid; mp 90.4-90.7 ˚C; $[\alpha]_D^{25}$ = +134.231 (*c* 0.52 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.46-7.10 (m, 10H), 6.78 (m, 3H), 5.50 (s, 1H), 4.05 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 139.6, 131.6, 129.0, 128.6, 128.1, 128.1, 127.9, 127.2, 122.7, 118.5, 114.0, 88.5, 85.0, 50.8. MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}N$, 284.1; found: 284.1; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 222 nm) major isomer: t_R = 18.6 min, minor isomer: t_R = 20.9 min.



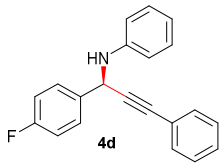
(*R*)-*N*-(3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)aniline **4b**[1] (293 mg, 99% yield, 98% *ee*): white solid; mp 120.5-121.0 ˚C; $[\alpha]_D^{25}$ = +140.784 (*c* 0.51 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.42-7.34 (m, 2H), 7.30-7.24 (m, 3H), 7.21-7.17 (m, 4H), 6.82-6.72 (m, 3H), 5.44 (s, 1H), 4.11 (br s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 137.7, 136.7, 131.6, 129.3, 129.0, 128.0, 127.1, 122.8, 118.4, 114.0, 88.7, 84.8, 50.5, 21.2; MS (ESI) m/z: $[M+H]^+$ calcd for

$C_{22}H_{19}N$, 298.2; found: 298.3; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 90:10, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 18.9 min, minor isomer: t_R = 21.2 min.



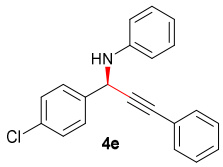
4c

(*R*)-*N*-(1-(3,4-dimethylphenyl)-3-phenylprop-2-yn-1-yl)aniline **4c*** (311 mg, 99% yield, 97% *ee*): white solid; mp 92.4-93.7 ˚C; $[\alpha]_D^{25}$ = +108.550 (*c* 0.54 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.33 (m, 4H), 7.27-7.25 (m, 3H), 7.22-7.12 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 3H), 5.41 (s, 1H), 4.21 (br s, 1H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 137.1, 137.0, 136.4, 131.7, 129.9, 129.1, 128.8, 128.5, 128.1, 124.6, 122.9, 118.4, 114.0, 88.9, 84.8, 50.5, 20.1, 19.7; IR (KBr) 3430, 2926, 1595, 1559, 1538, 1499, 1490, 755, 687 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}N$, 334.1572; found: 334.1566; HPLC (Chiralcel OD-H, hexane/i-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 17.5 min, minor isomer: t_R = 20.4 min.



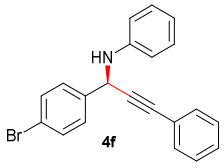
4d

(*R*)-*N*-(1-(4-fluorophenyl)-3-phenylprop-2-yn-1-yl)aniline **4d**[3] (292 mg, 97% yield, 95% *ee*); yellow solid; mp 86.1-86.7 ˚C; $[\alpha]_D^{25}$ = +140.266 (*c* 0.53 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J*= 8.0, 4.0 Hz, 2H), 7.42–7.34 (m, 2H), 7.28-7.17 (m, 5H), 7.06 (t, *J* = 8.0 Hz, 2H), 6.82-6.70 (m, 3H), 5.46 (s, 1H), 4.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.0, 146.2, 135.4, 131.6, 129.0, 128.9, 128.8, 128.3, 128.1, 122.4, 118.6, 115.6, 115.4, 114.0, 88.1, 85.2, 50.0; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NF$, 302.1; found: 302.3; HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 90:10, flow rate = 0.8 mL/min, λ = 242 nm) major isomer: t_R = 49.9 min, minor isomer t_R = 47.4 min.



4e

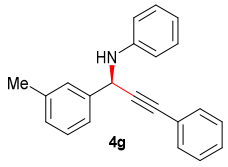
(*R*)-*N*-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)aniline **4e**[1, 2] (307 mg, 97% yield, 96% *ee*); yellow solid; mp 77.6-77.8 ˚C; $[\alpha]_D^{25}$ = +103.774 (*c* 0.53 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.40-7.31 (m, 4H), 7.30-7.25 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 2H), 6.88-6.68 (m, 3H), 5.46 (s, 1H), 4.20 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 138.3, 133.7, 131.6, 129.1, 128.8, 128.5, 128.3, 128.1, 122.4, 118.8, 114.1, 88.0, 85.4, 50.2; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NCl$, 318.1; found: 318.2; HPLC (Chiralcel OD-H, hexane/ *i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 30.6 min, minor isomer t_R = 33.6 min.



4f

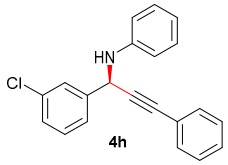
N-(1-(4-Bromophenyl)-3-phenylprop-2-yn-1-yl)aniline **4f**[1] (340 mg, 94% yield, 89% *ee*); yellow solid, mp 122.1-123.0 ˚C; $[\alpha]_D^{25}$ = +122.134 (*c* 0.51 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.46 (m, 3H), 7.42-7.35 (m, 2H), 7.31-7.24 (m, 3H), 7.23-7.14 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.83-6.69

(m, 3H), 5.44 (s, 1H), 4.25 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 138.7, 131.7, 129.1, 129.0, 128.8, 128.3, 128.1, 122.3, 121.8, 118.8, 118.7, 114.1, 114.0, 87.8, 85.3, 50.2; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NCl$, 362.1; found: 362.5; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 31.3 min, minor isomer t_R = 35.6 min.



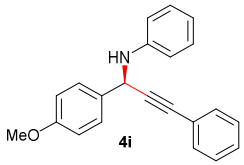
4g

(*R*)-*N*-(3-phenyl-1-(*m*-tolyl)prop-2-yn-1-yl)aniline **4g**[2] (295 mg, 99% yield, 99% *ee*); white solid; mp 111.6-112.8 ˚C; $[\alpha]_D^{25}$ = +134,783 (*c* 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.36 (m, 4H), 7.31-7.24 (m, 4H), 7.22-7.11 (m, 3H), 6.77 (m, 3H), 5.44 (s, 1H), 4.13 (br s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 139.5, 138.4, 131.6, 129.0, 128.7, 128.5, 128.1, 128.1, 127.9, 124.2, 122.7, 118.5, 114.0, 88.6, 84.9, 50.8, 21.6; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}N$, 298.2; found: 298.3; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 16.2 min, minor isomer t_R = 20.1 min.



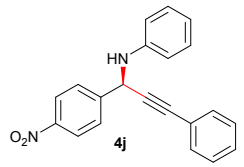
4h

(*R*)-*N*-(1-(3-chlorophenyl)-3-phenylprop-2-yn-1-yl)aniline **4h**[1] (314 mg, 99% yield, 99% *ee*); yellow solid; mp 63.9-67.2 ˚C; $[\alpha]_D^{25}$ = +90.698 (*c* 0.52 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.54-7.50 (m, 1H), 7.42-7.36 (m, 2H), 7.34-7.25 (m, 5H), 7.23-7.16 (m, 2H), 6.84-6.68 (m, 3H), 5.46 (s, 1H), 4.24 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 141.4, 134.2, 131.3, 129.6, 128.8, 128.1, 127.9, 127.0, 125.0, 122.1, 118.6, 113.9, 87.6, 85.4, 50.5; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NCl$, 318.1; found: 318.4; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 25.8 min, minor isomer t_R = 34.7 min.



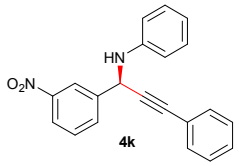
4i

(*R*)-*N*-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)aniline **4i**[3] (0.301mg, 96% yield, 85% *ee*); yellow oil; $[\alpha]_D^{25}$ = +78.761 (*c* 0.45 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.51 (m, 2H), 7.40-7.34 (dd, *J* = 4.0, 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 7.21-7.15 (dd, *J* = 4.0, 8.0 Hz, 2H), 6.92-6.87 (m, 2H), 6.76 (m, 3H), 5.42 (s, 1H), 4.12 (br, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 146.3, 131.6, 131.5, 128.9, 128.3, 128.0, 122.6, 118.3, 113.9, 88.7, 84.7, 55.3, 50.0; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}NO$, 314.2; found: 314.2; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.8 mL/min, λ = 250 nm) major isomer: t_R = 20.7 min, minor isomer t_R = 18.4 min.



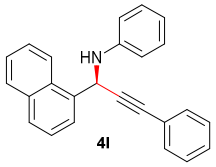
4j

(*R*)-*N*-(1-(4-nitrophenyl)-3-phenylprop-2-yn-1-yl)aniline **4j**[2, 3] (325 mg, 99% yield, 83% *ee*); yellow solid; mp 116.7-118.8 ˚C; $[\alpha]_D^{25}$ = +76.230 (*c* 0.49 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28-8.19 (m, 2H), 7.82 (m, 2H), 7.41-7.36 (m, 2H), 7.32-7.27 (m, 3H), 7.22-7.15 (m, 2H), 6.83-6.77 (m, 1H), 6.71-6.66 (m, 2H), 5.58 (s, 1H), 4.29 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.0, 145.6, 131.6, 129.1, 128.6, 128.2, 127.9, 123.9, 121.9, 119.1, 114.0, 86.8, 86.1, 50.3; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}N_2O_2$, 329.1; found: 329.2; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 90:10, flow rate = 0.7 mL/min, λ = 234 nm) major isomer: t_R = 37.6 min, minor isomer t_R = 33.4 min.



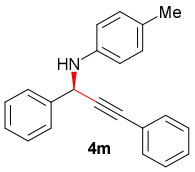
4k

(*R*)-*N*-(1-(3-nitrophenyl)-3-phenylprop-2-yn-1-yl)aniline **4k*** (312 mg, 95% yield, 88% *ee*); yellow oil; $[\alpha]_D^{25}$ = +101.894 (*c* 0.53 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (t, *J* = 4.0 Hz, 1H), 8.22-8.16 (m, 1H), 8.02-7.95 (m, 1H), 7.55 (m, 1H), 7.45-7.35 (m, 2H), 7.34-7.15 (m, 5H), 6.85-6.77 (m, 1H), 6.77-6.66 (m, 2H), 5.59 (s, 1H), 4.32 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 148.0, 145.3, 141.7, 132.8, 131.3, 129.3, 128.9, 128.3, 127.9, 122.7, 121.9, 118.9, 113.9, 86.8, 86.0, 50.3; IR (KBr) 3424, 2926, 1600, 1528, 1504, 1488, 1383, 1350, 757, 690 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}N_2O_2$, 351.1109; found: 351.1104; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 90:10, flow rate = 0.7 mL/min, λ = 234 nm) major isomer: t_R = 32.2 min, minor isomer t_R = 24.0 min.



4l

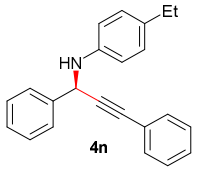
(*S*)-*N*-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)aniline **4l**[4] (310 mg, 93% yield, 97% *ee*); yellow solid; mp 86.8-88.4 ˚C; $[\alpha]_D^{25}$ = +86.794 (*c* 0.70 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.22-8.10 (m, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.92-7.79 (m, 2H), 7.57-7.46 (m, 3H), 7.44-7.34 (m, 2H), 7.30-7.18 (m, 5H), 6.88-6.70 (m, 3H), 6.11 (s, 1H), 4.25 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 134.4, 134.1, 131.7, 130.7, 129.1, 129.0, 128.8, 128.2, 128.1, 126.5, 125.8, 125.3, 123.5, 122.8, 118.5, 113.8, 88.4, 85.6, 48.5; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}N$, 334.1; found: 334.5; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 99.8:0.2, flow rate = 1.0 mL/min, λ = 234 nm) major isomer: t_R = 96.3 min, minor isomer t_R = 80.9 min.



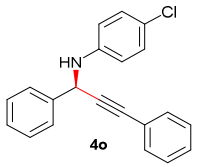
4m

(*R*)-*N*-(1,3-diphenylprop-2-yn-1-yl)-4-methylaniline **4m**[1] (294 mg, 99% yield, 99% *ee*); white solid; mp 77.5-77.6 ˚C; $[\alpha]_D^{25}$ = +148.074 (*c* 0.50 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 4.0 Hz, 2H), 7.43-7.20 (m, 8H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 5.45 (s, 1H), 4.10 (br s, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 139.6, 131.3, 129.2, 128.3, 127.8, 127.6, 127.5, 126.9, 122.6, 114.2, 88.7, 85.0, 51.4, 20.9; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}N$,

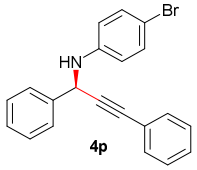
298.1; found: 298.2; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 25.5 min, minor isomer t_R = 22.6 min.



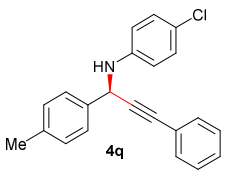
(*R*)-*N*-(1,3-diphenylprop-2-yn-1-yl)-4-ethylaniline **4n**[4] (292 mg, 94% yield, 90% *ee*); yellow oil; $[\alpha]_D^{25}$ = +134.122 (*c* 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.60 (m, 2H), 7.42-7.23 (m, 8H), 7.05-7.00 (m, 2H), 6.74-6.68 (m, 2H), 5.45 (s, 1H), 4.02 (br, 1H), 2.55 (q, *J* = 8.0 Hz, 2H), 1.19 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.7, 134.1, 131.5, 128.5, 128.2, 128.0, 127.8, 127.1, 122.6, 114.0, 88.7, 84.9, 50.8, 28.0, 16.0.; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}N$, 312.2; found: 312.3; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 234 nm) major isomer: t_R = 11.0 min, minor isomer t_R = 9.7 min.



(*R*)-4-Chloro-*N*-(1,3-diphenylprop-2-yn-1-yl)aniline **4o**[1] (292 mg, 92% yield, 98% *ee*); yellow solid; mp 88.4-89.3 ˚C; $[\alpha]_D^{25}$ = +152.672 (*c* 0.52 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.56 (m, 2H), 7.42-7.21 (m, 8H), 7.16-7.10 (m, 2H), 6.74-6.55 (m, 2H), 5.43 (s, 1H), 4.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.1, 131.6, 128.9, 128.8, 128.7, 128.3, 128.1, 127.1, 123.1, 122.4, 115.2, 87.8, 85.3, 50.8; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NCl$, 318.1; found: 318.6; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 21.3 min, minor isomer t_R = 25.4 min.

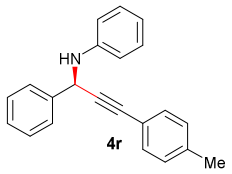


(*R*)-4-Bromo-*N*-(1,3-diphenylprop-2-yn-1-yl)aniline **4p**[1] (324mg, 90% yield, 97% *ee*); yellow solid; mp 83.0-83.8 ˚C; $[\alpha]_D^{25}$ = +147.177 (*c* 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.43-7.20 (m, 10H), 6.64 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 1H), 4.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 139.0, 131.7, 131.6, 128.7, 128.3, 128.1, 127.1, 122.4, 115.6, 110.2, 87.8, 85.3, 50.6, 29.8; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}NBr$, 362.1; found: 362.5; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 25.2 min, minor isomer t_R = 27.9 min.

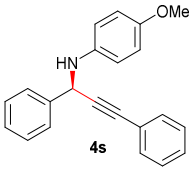


(*R*)-4-Chloro-*N*-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)aniline **4q** (311 mg, 94% yield, 95% *ee*); yellow solid; mp 78.5-80.3 ˚C; $[\alpha]_D^{25}$ = +116.863 (*c* 0.51 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ

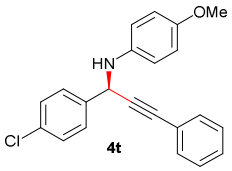
7.49 (d, J = 8.0 Hz, 2H), 7.41-7.36 (m, 2H), 7.30-7.10 (m, 7H), 6.73-6.61 (m, 2H), 5.40 (s, 1H), 4.249 (br s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 137.9, 136.2, 131.6, 129.4, 128.8, 128.2, 128.1, 127.0, 123.1, 122.5, 115.1, 88.1, 85.1, 50.5, 21.26.MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NCl$, 332.1; found: 332.3; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm, λ = 234 nm) major isomer: t_R = 14.5 min, minor isomer t_R = 16.0 min.



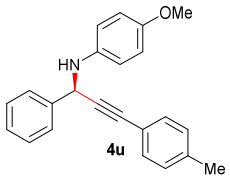
(*R*)-*N*-(1-phenyl-3-(*p*-tolyl)prop-2-yn-1-yl)aniline **4r** (295 mg, 99% yield, 99.7% *ee*); white solid; mp 111.2-111.7 °C; $[\alpha]_D^{25}$ = +63.162 (*c* 0.51 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.41-7.26 (m, 5H), 7.22-7.16 (m, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 3H), 5.48 (s, 1H), 4.24 (br s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 139.7, 138.2, 131.5, 129.0, 128.8, 128.6, 127.9, 127.2, 119.5, 118.4, 114.0, 87.7, 85.1, 50.7, 21.6; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}N$, 298.2; found: 298.2; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 16.7 min, minor isomer t_R = 19.0 min.



(*R*)-*N*-(1,3-diphenylprop-2-yn-1-yl)-4-methoxyaniline **4s**[2] (310 mg, 99% yield, 98% *ee*); yellow oil; $[\alpha]_D^{25}$ = +123.904 (*c* 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.60 (m, 2H), 7.41-7.24 (m, 8H), 6.88-6.64 (m, 4H), 5.40 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 140.4, 139.6, 131.5, 128.5, 128.3, 128.0, 127.8, 127.1, 122.6, 115.7, 114.5, 88.7, 85.0, 55.6, 51.7; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}NO$, 314.2; found: 314.1; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 90:10, flow rate = 0.5 mL/min, λ = 234 nm) major isomer: t_R = 28.9 min, minor isomer t_R = 24.2 min.

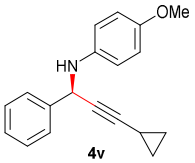


(*R*)-*N*-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)-4-methoxyaniline **4t**[2] (320 mg, 92% yield, 88% *ee*); yellow oil; $[\alpha]_D^{25}$ = +84.524 (*c* 0.50 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.39-7.32 (m, 4H), 7.29-7.24 (m, 3H), 6.81-6.75 (dt, J = 4.0, 12.0 Hz, 2H), 6.73-6.68 (dt, J = 4.0, 12.0 Hz, 2H), 5.37 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 140.1, 138.3, 133.6, 131.6, 128.7, 128.5, 128.3, 128.1, 122.4, 115.9, 114.6, 88.1, 85.4, 55.7, 51.3; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}ClNO$, 347.1; found: 348.2; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 234 nm) major isomer: t_R = 23.5 min, minor isomer t_R = 22.5 min.



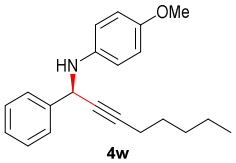
4u

(*R*)-4-Methoxy-*N*-(1-phenyl-3-(*p*-tolyl)prop-2-yn-1-yl)aniline **4u**[2] (325 mg, 99% yield, 95.0% *ee*); white solid; mp 72.4-72.7 ˚C; $[\alpha]_D^{25}$ = +129.457 (*c* 0.52 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.60 (m, 2H), 7.41-7.25 (m, 5H), 7.06 (m, 2H), 6.81-6.71 (m, 4H), 5.38 (s, 1H), 3.74 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 140.5, 139.8, 138.2, 131.4, 128.7, 128.6, 127.8, 127.2, 119.6, 115.8, 114.5, 88.0, 85.2, 55.7, 51.8, 21.6; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}NO$, 328.2; found: 328.3; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 80:20, flow rate = 0.8 mL/min, λ= 254 nm) major isomer: t_R = 16.9 min, minor isomer t_R = 14.1 min.



4v

(*R*)-*N*-(3-cyclopropyl-1-phenylprop-2-yn-1-yl)-4-methoxyaniline **4v**[5] (248 mg, 90% yield, 88% *ee*); yellow oil; $[\alpha]_D^{25}$ = +94.603 (*c* 0.63 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.34-7.22 (m, 3H), 6.79-6.68 (dt, *J* = 4.0, 8.0 Hz, 2H), 6.67-6.56 (dt, *J* = 4.0, 8.0 Hz, 2H), 5.09 (s, 1H), 3.70 (s, 3H), 1.28-1.17 (m, 1H), 0.76-0.66 (m, 2H), 0.65-0.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 140.6, 140.3, 128.4, 127.6, 127.0, 115.5, 114.4, 88.5, 74.7, 55.6, 51.2, 8.4, -0.3; MS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}NO$, 278.2; found: 278.3; HPLC (Chiralcel AD-H, hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, λ = 234 nm) major isomer: t_R = 15.1 min, minor isomer t_R = 12.8 min.



4w

(*R*)-4-Methoxy-*N*-(1-phenyloct-2-yn-1-yl)aniline **4w*** (293 mg, 92% yield, 88% *ee*); yellow solid; mp 77.6-77.8 ˚C; $[\alpha]_D^{25}$ = +86.498 (*c* 0.47 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.37-7.25 (m, 3H), 6.79-6.73 (m, 2H), 6.70-6.65 (m, 2H), 5.14 (s, 1H), 3.73 (s, 3H), 2.20 (td, *J* = 8.0, 4.0 Hz, 2H), 1.53-1.43 (m, 2H), 1.36-1.22 (m, 4H), 0.87 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 138.3, 133.7, 131.6, 129.1, 128.8, 128.5, 128.3, 128.1, 122.4, 118.8, 114.1, 88.0, 85.4, 50.2; IR (KBr) 3435, 2925, 1633, 1511, 1456, 1385, 1241, 1029, 826, 701 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}NO$, 330.1834; found: 330.1828; HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate = 0.5 mL/min, λ = 254 nm) major isomer: t_R = 30.6 min, minor isomer t_R = 33.6 min.

Additional References

1. C. Wei, J. T. Mague and C.-J. Li, *Proc. Natl. Acad. Sci. U.S.A.*, 2004, **101**, 5749-5754.
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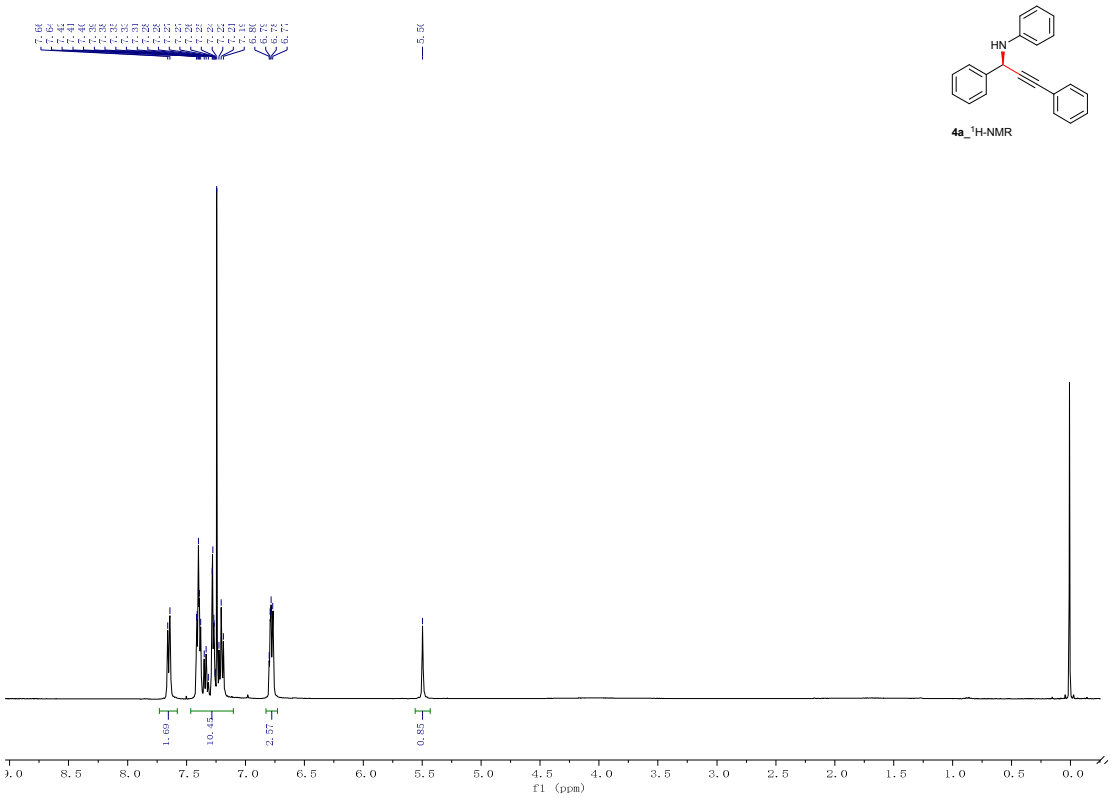
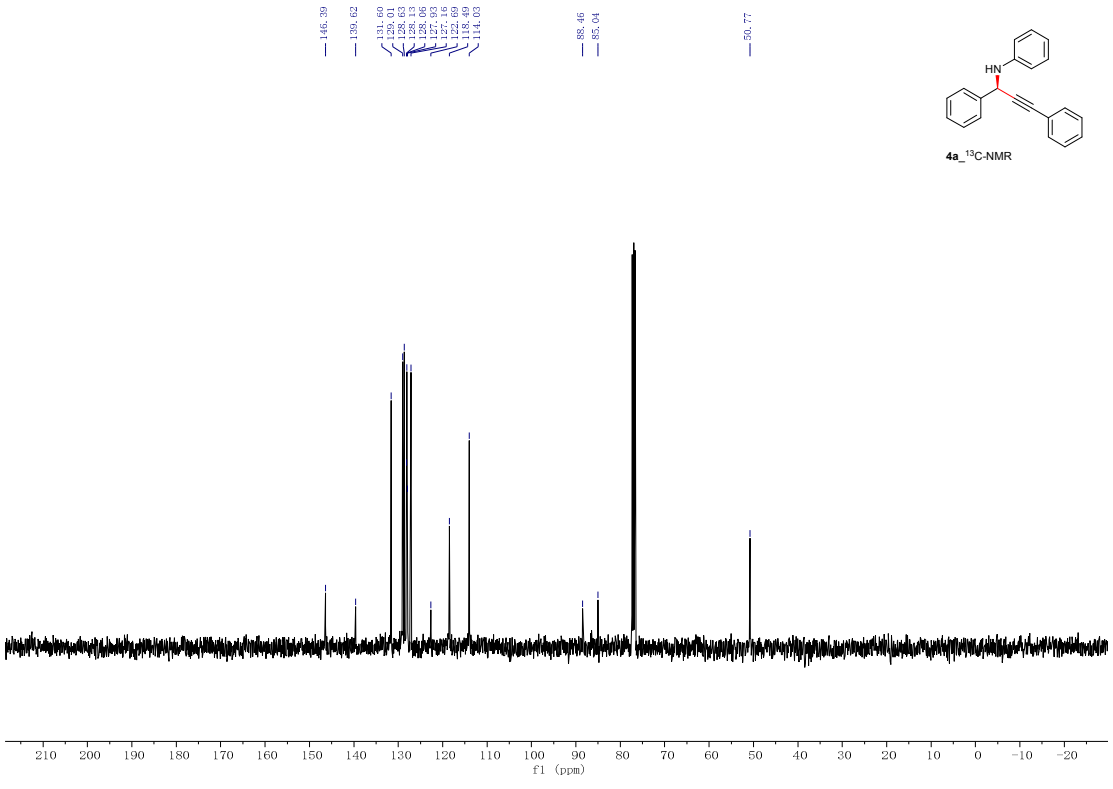
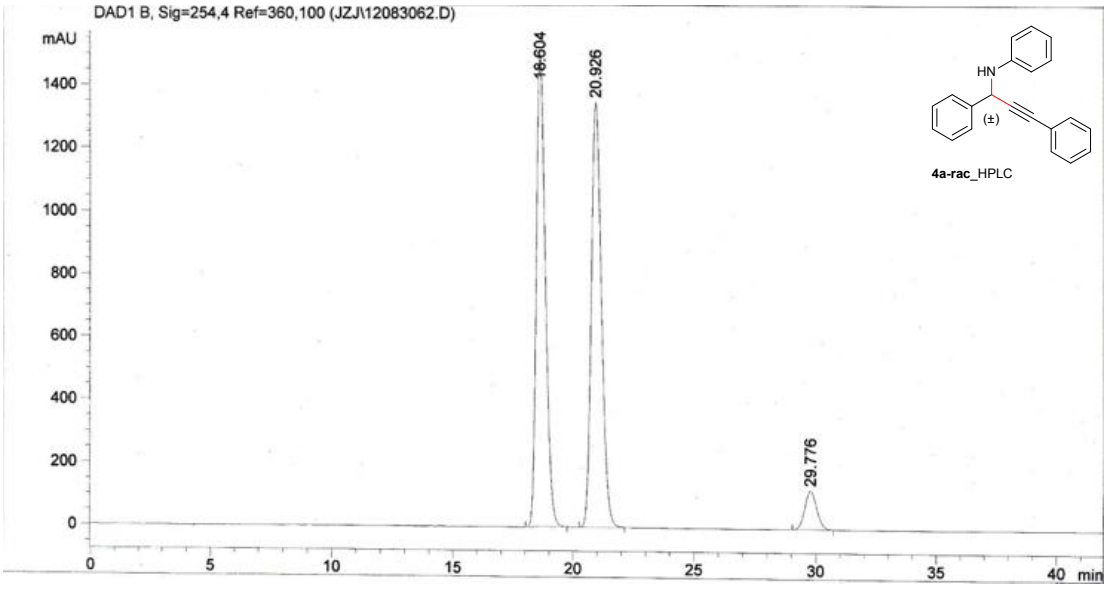
5. S. Nakamura, M. Ohara, Y. Nakamura, N. Shibata and T. Toru, *Chem. - Eur. J.*, 2010, **16**, 2360-

2362.

6. Copies of 1H NMR, 13C NMR, and HPLC spectra for 4a-4w







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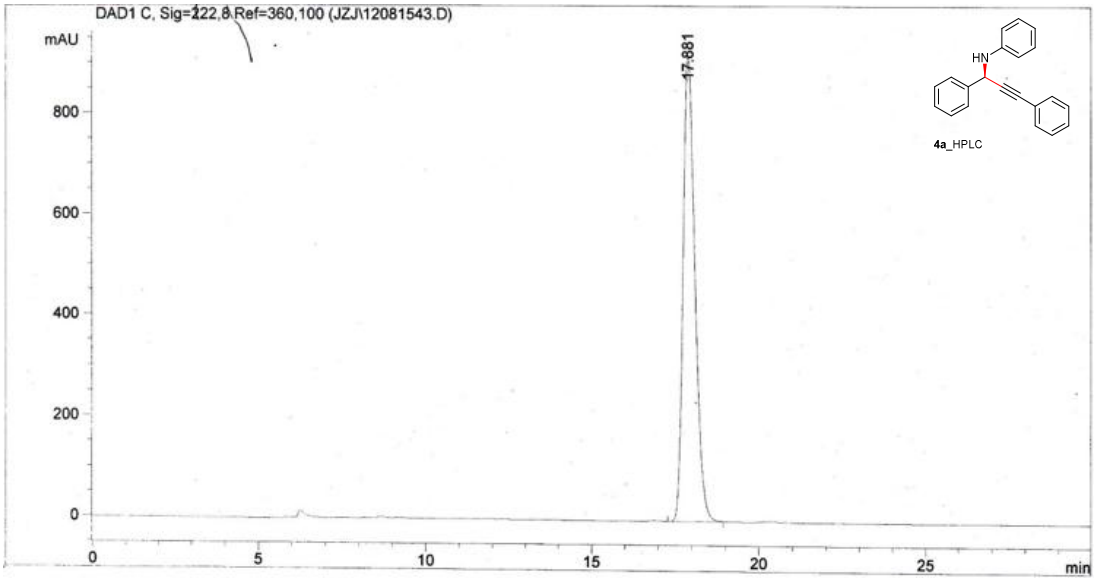
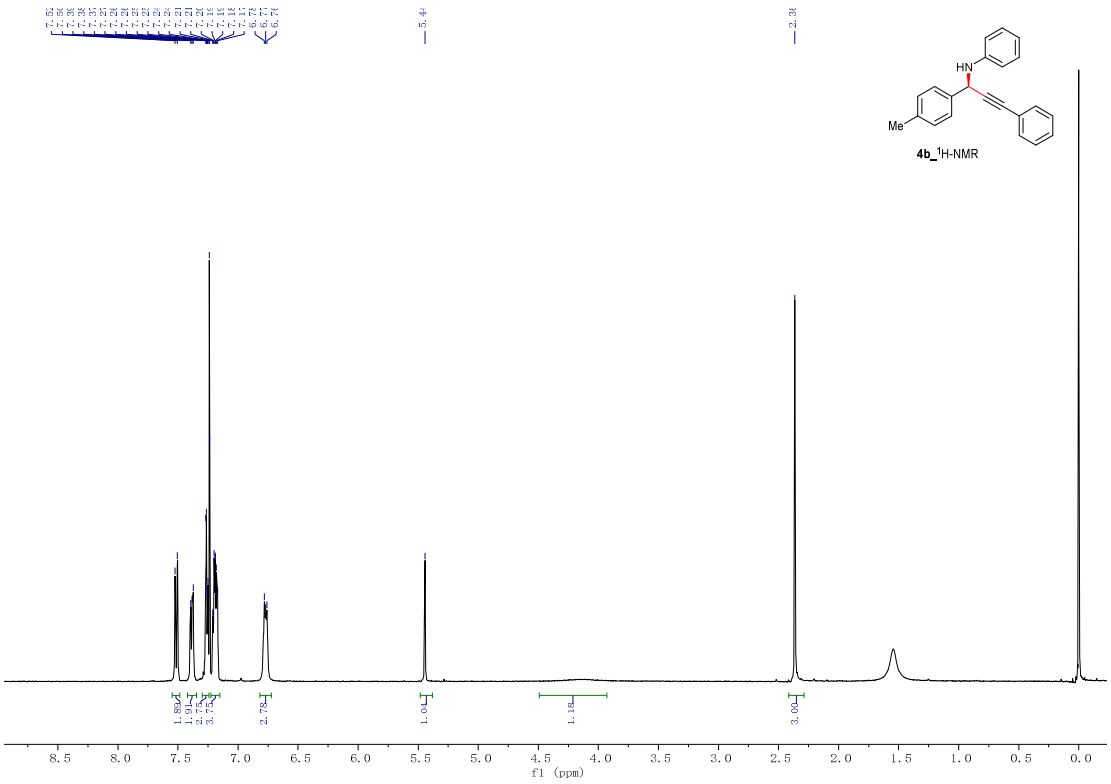
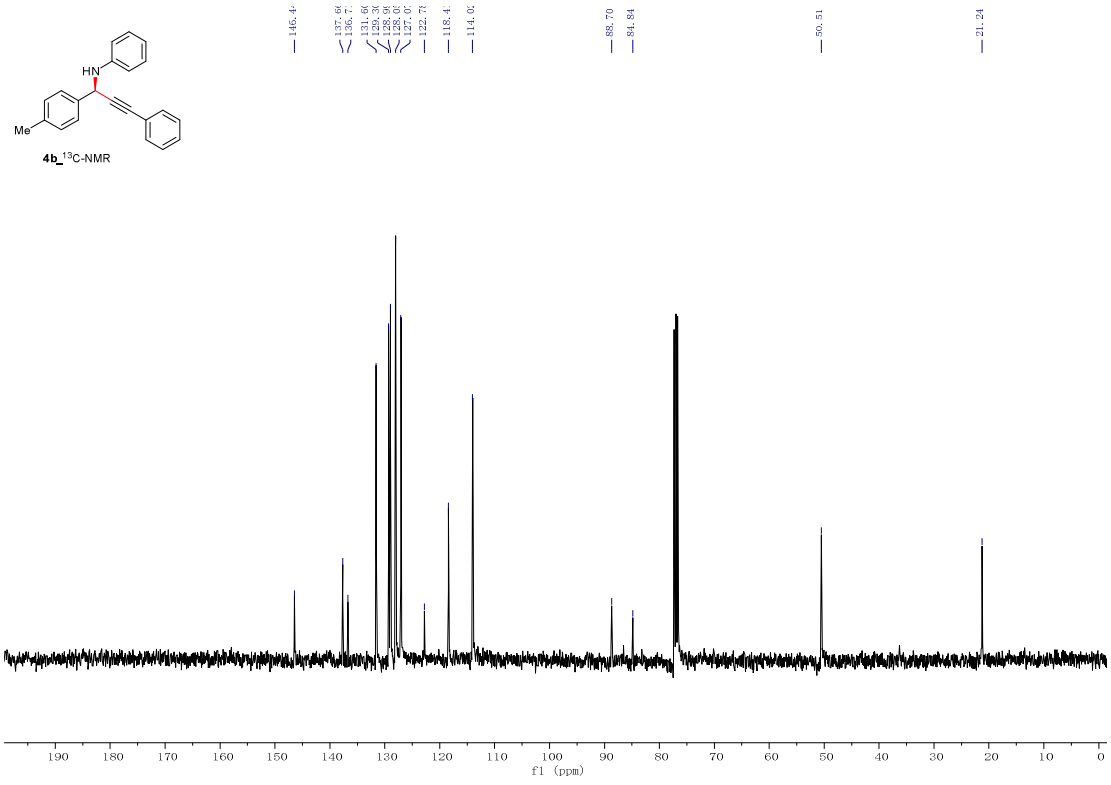
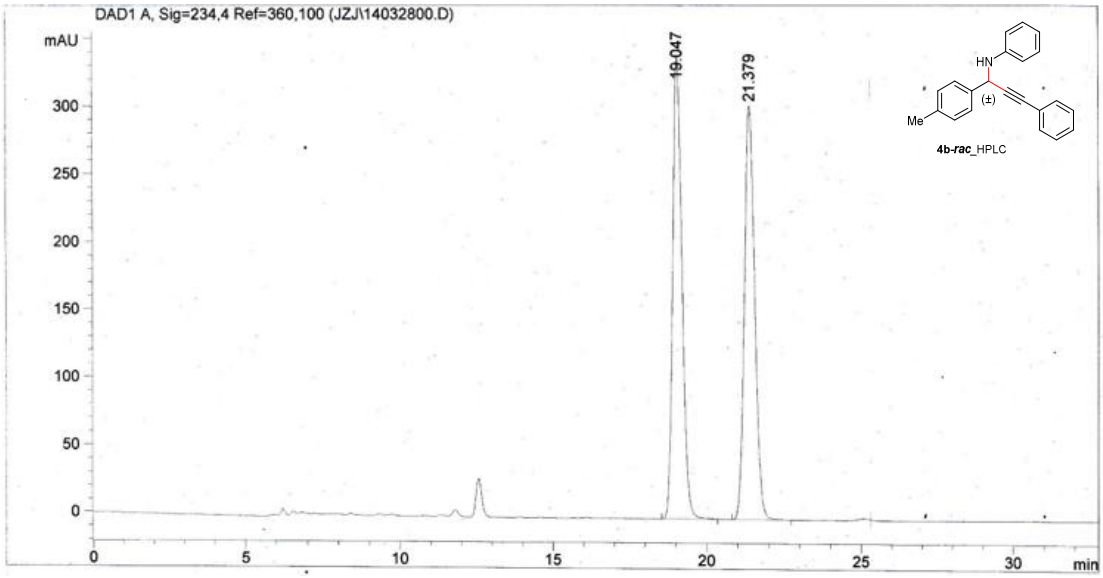
Totals :				8.27587e4	2962.85599	



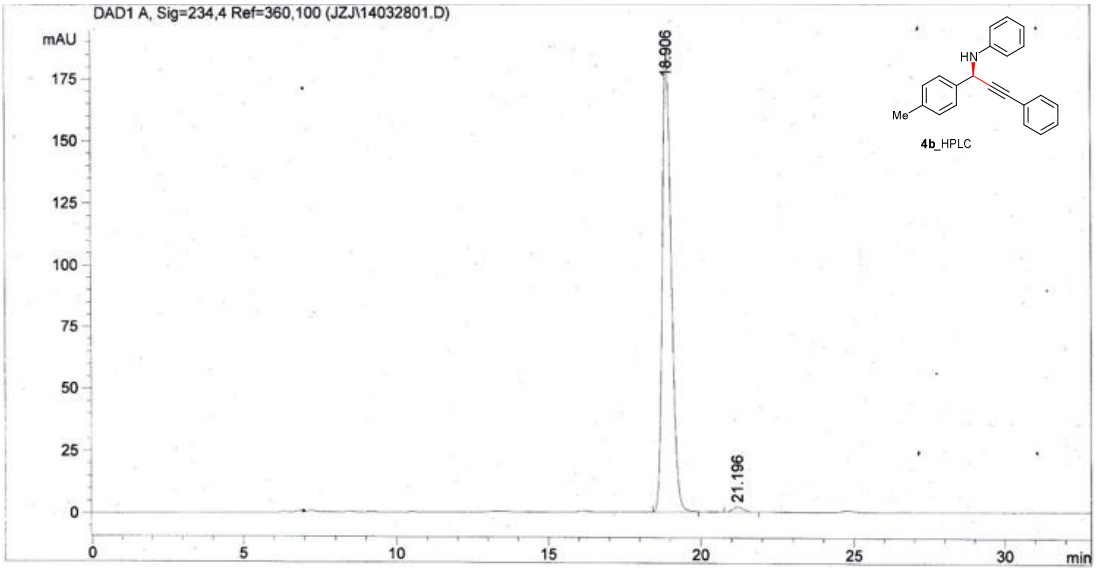
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.881	VB	0.3745	2.24066e4	918.70538	100.0000
Totals :				2.24066e4	918.70538	


HN
Me
4b_1H-NMR
f1 (ppm)

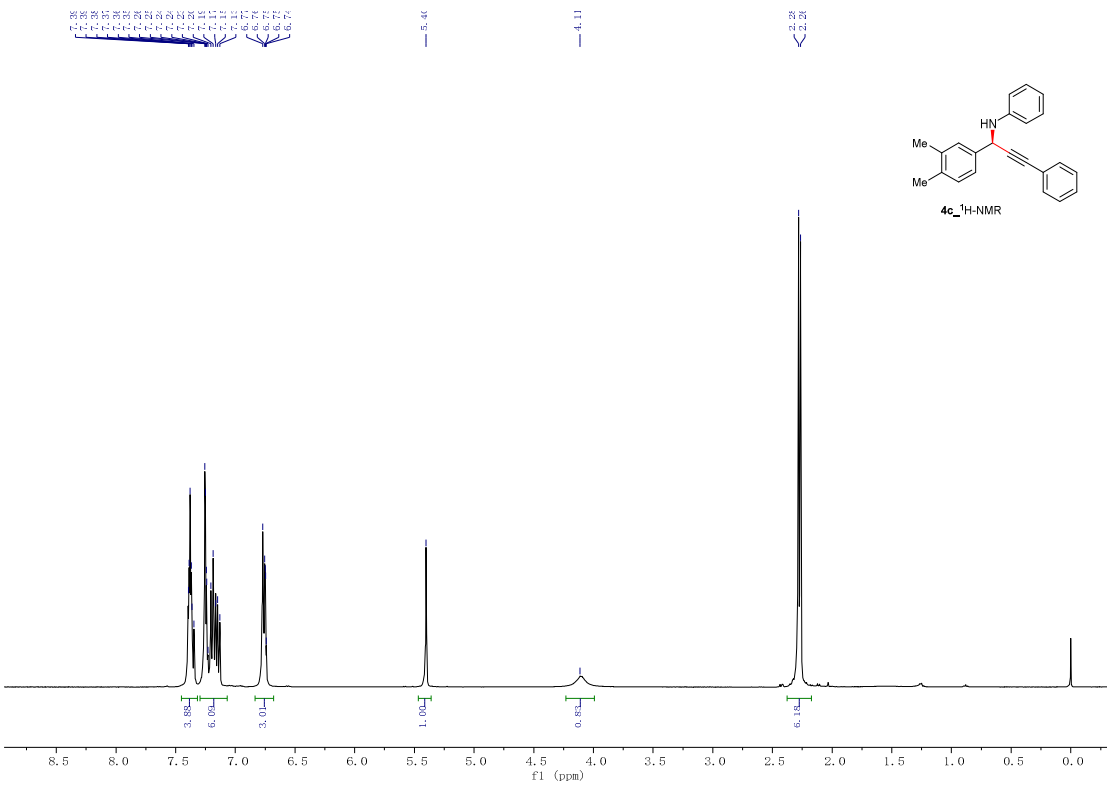

HN
Me
4b_13C-NMR
f1 (ppm)

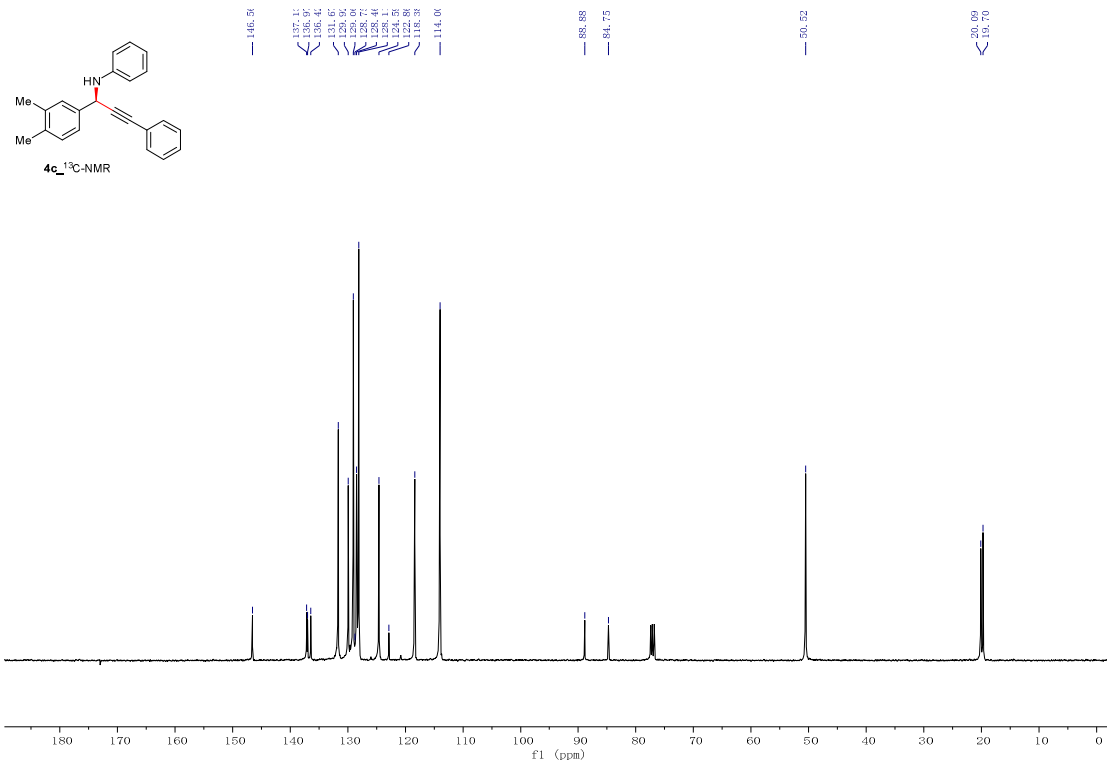


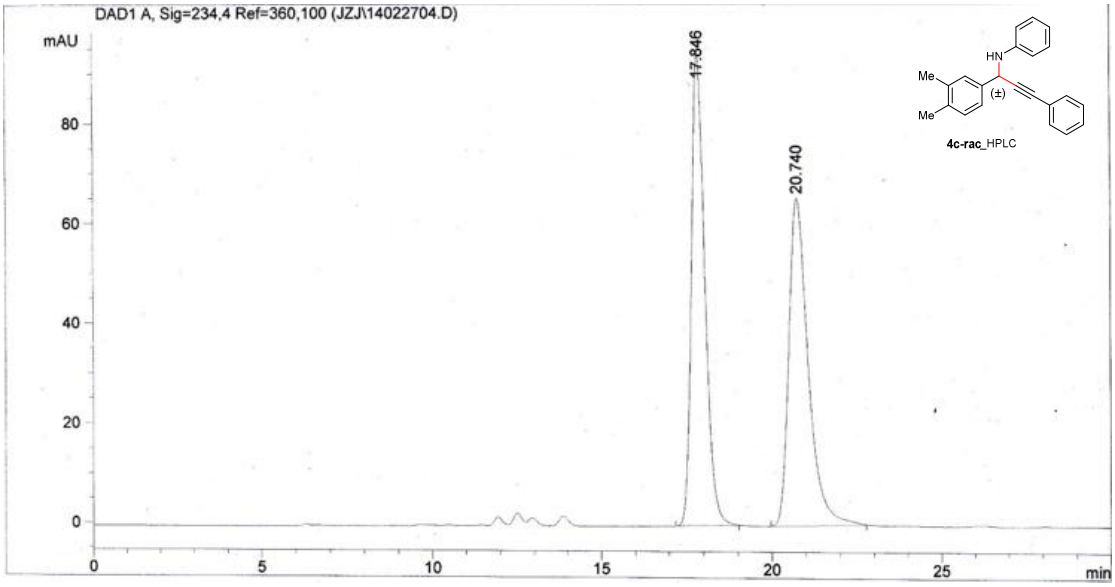
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.047	BB	0.3223	7084.92627	341.15991	50.2735
2	21.379	PB	0.3571	7007.83301	303.84702	49.7265
Totals :				1.40928e4	645.00693	



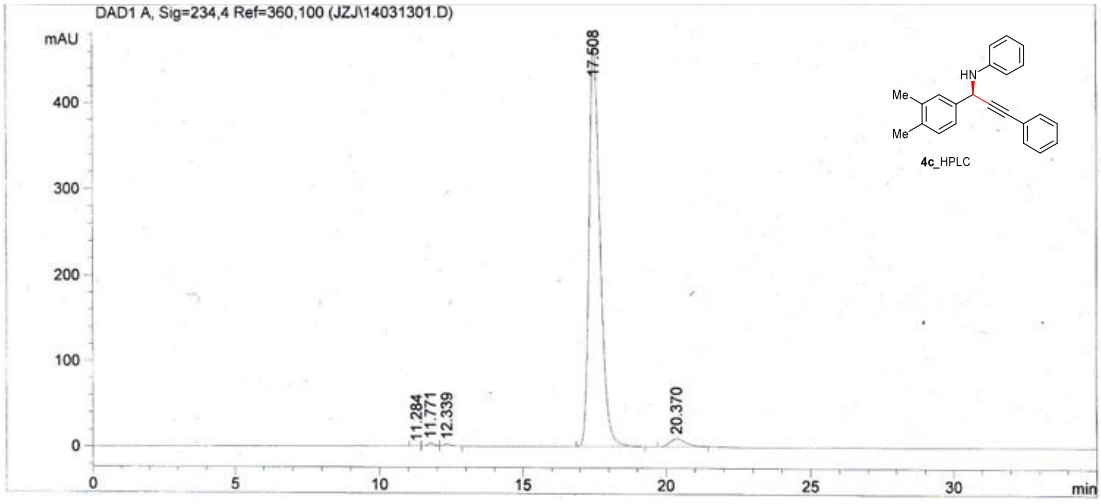
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.906	BB	0.3134	3745.23511	184.04599	98.7490
2	21.196	PB	0.3517	47.44709	2.03737	1.2510
Totals :				3792.68220	186.08336	


HN
Me
Me
4c_1H-NMR
f1 (ppm)

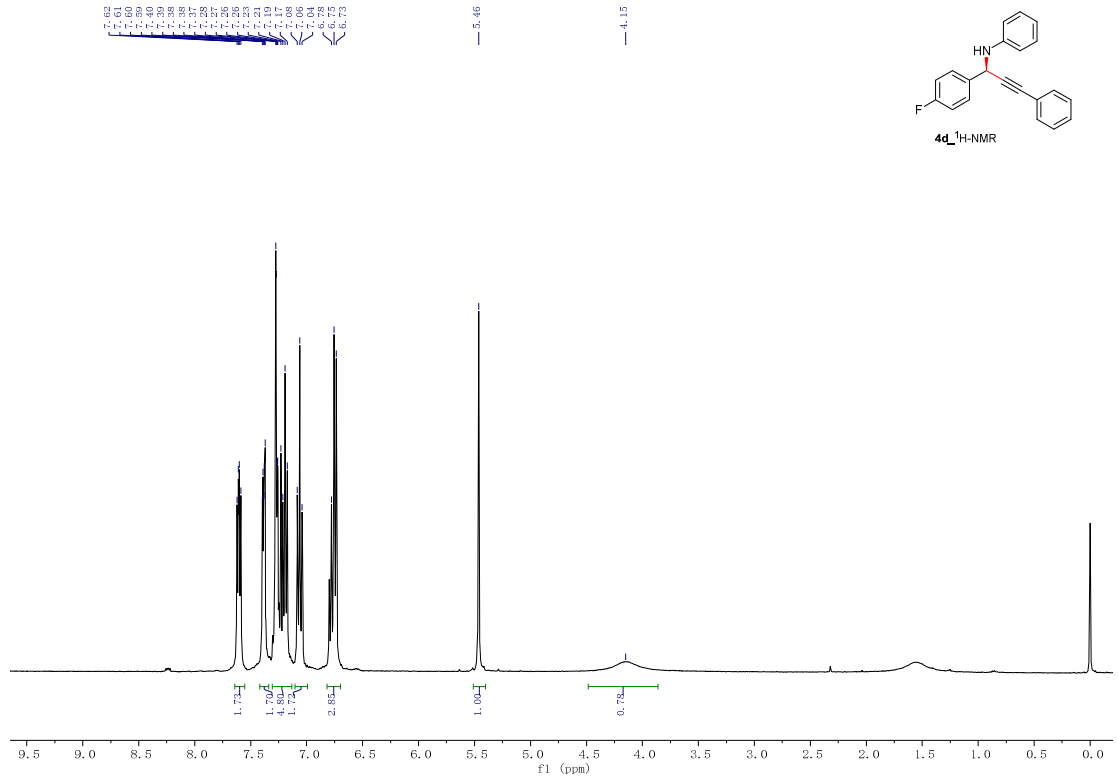

HN
Me
Me
4c_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.846	BB	0.4166	2570.31226	94.12095	50.0188
2	20.740	BB	0.5940	2568.38379	65.14193	49.9812
Totals :				5138.69604	159.26288	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.284	BV	0.2227	3.04048	1.98546e-1	0.0237
2	11.771	VV	0.2570	53.87199	3.25642	0.4202
3	12.339	VB	0.2813	44.02587	2.40843	0.3434
4	17.508	BB	0.4132	1.23510e4	460.09940	96.3395
5	20.370	BB	0.5818	368.34476	9.47062	2.8731
Totals :				1.28203e4	475.43342	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7.59
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7.39
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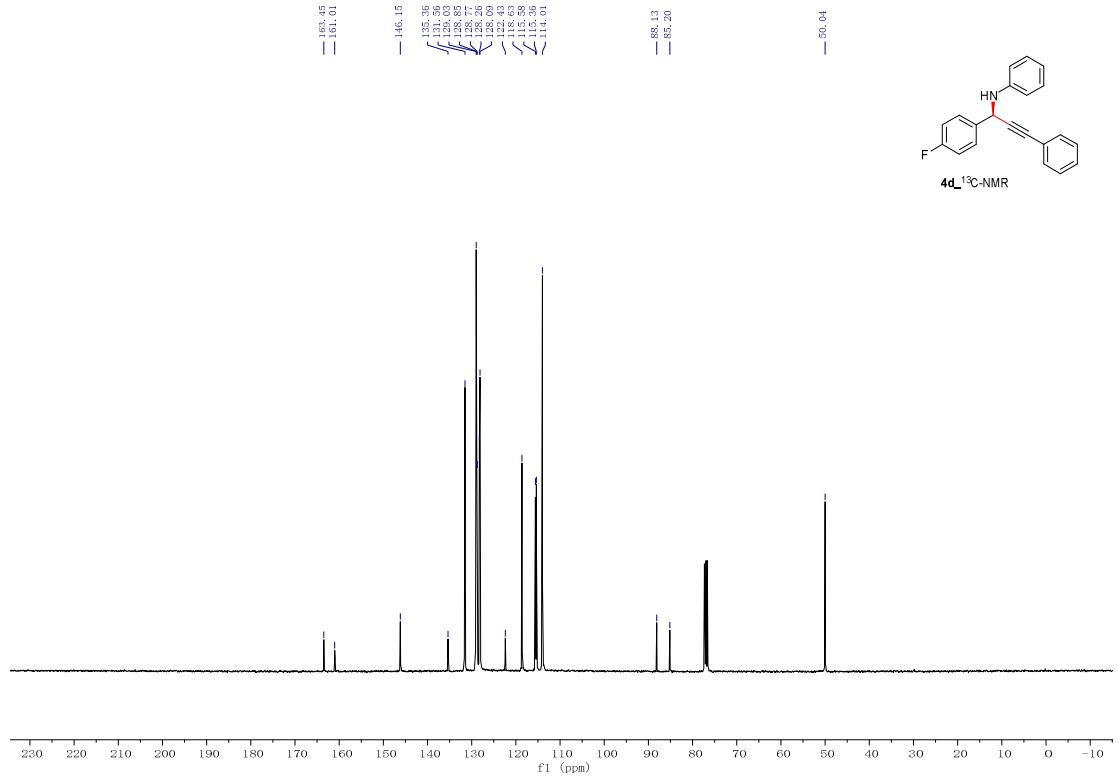
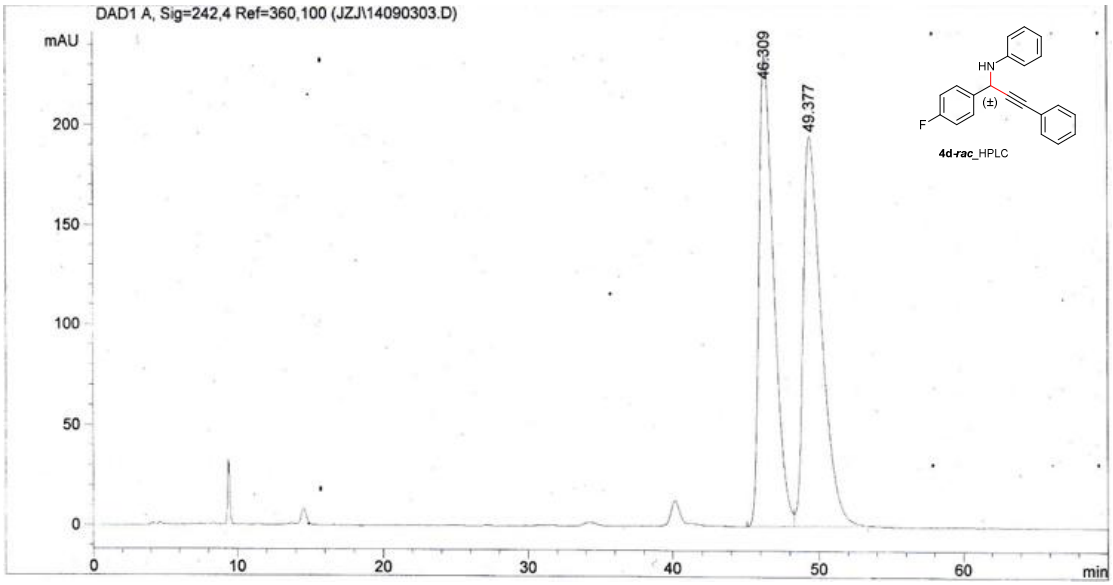
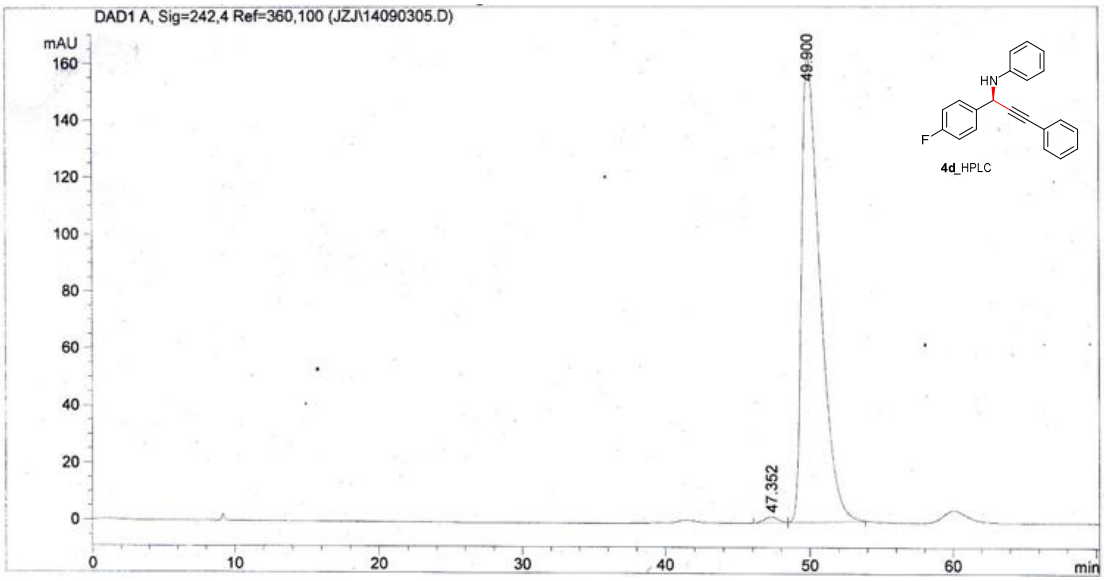
7.37
7.28
7.27
7.26
7.25
7.23
7.21
7.17
7.08
7.04
6.78
6.75
6.73
5.46
4.15
HN
F
4d_1H-NMR
1.74
1.70
4.80
1.74
2.85
1.00
0.78
f1 (ppm)

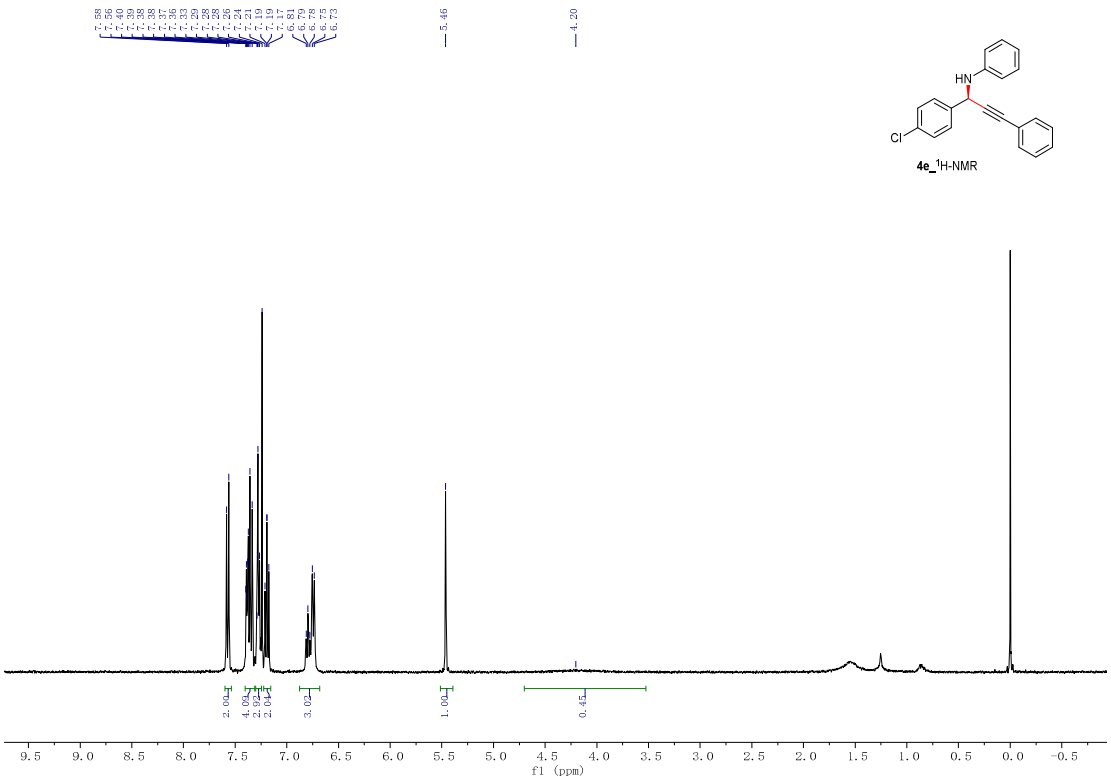

163.45
161.01
146.15
135.36
131.56
129.03
128.85
128.77
128.26
128.09
122.43
118.63
115.58
115.36
114.01
88.13
85.20
50.04
HN
F
4d_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.309	BV	1.0835	1.67124e4	234.47879	49.6475
2	49.377	VB	1.3231	1.69497e4	193.28320	50.3525
Totals :				3.36621e4	427.76199	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.352	BV	0.8341	142.02116	2.05546	0.9714
2	49.900	VB	1.3323	1.44786e4	162.36597	99.0286
Totals :				1.46206e4	164.42143	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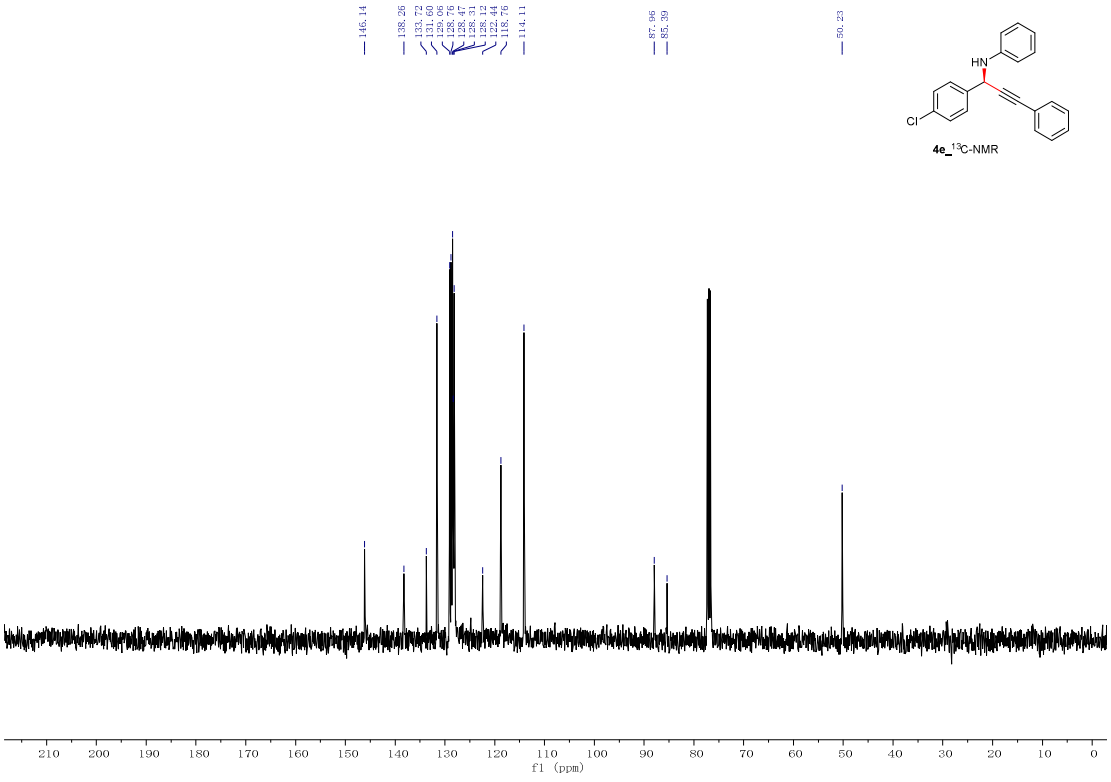
7.28
7.28
7.25
7.24
7.21
7.19
7.19
7.17
6.81
6.79
6.78
6.75
6.73
5.46
4.20
HN
Cl
4e_1H-NMR
2.00
4.09
2.99
2.04
3.02
1.00
0.45
f1 (ppm)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128.12
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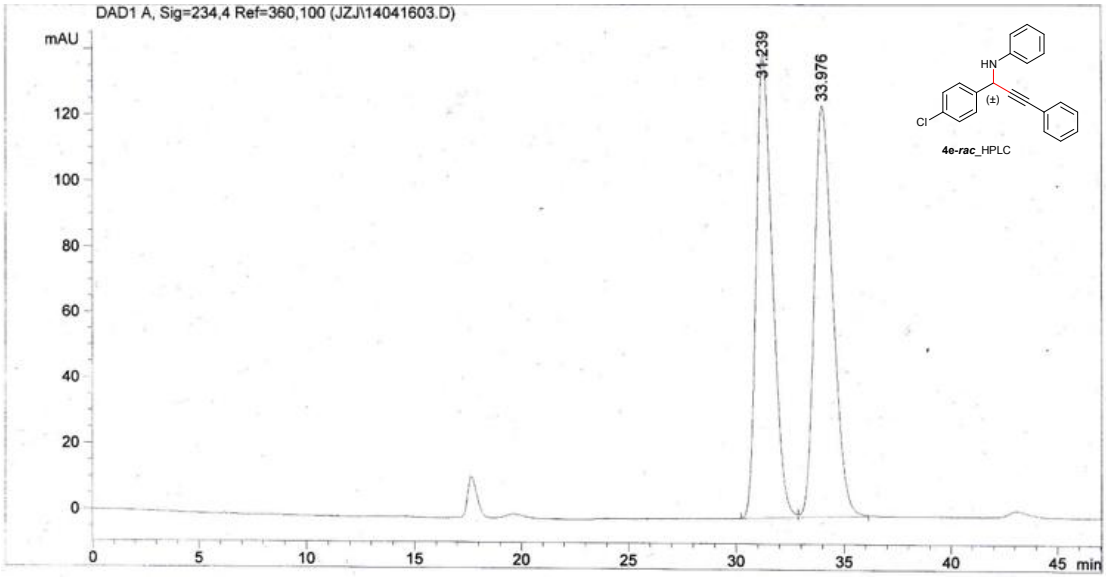
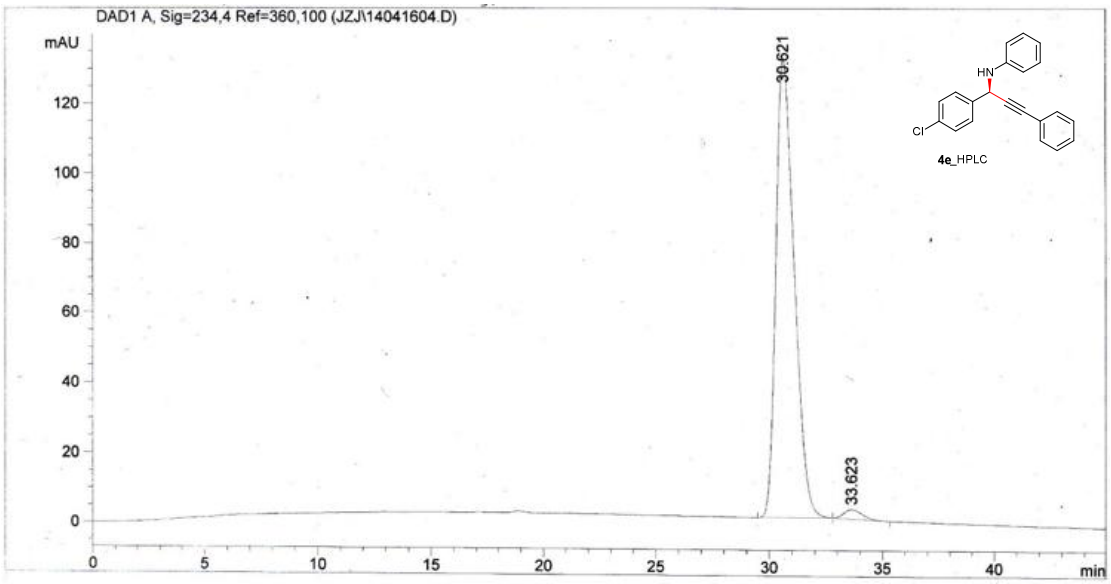
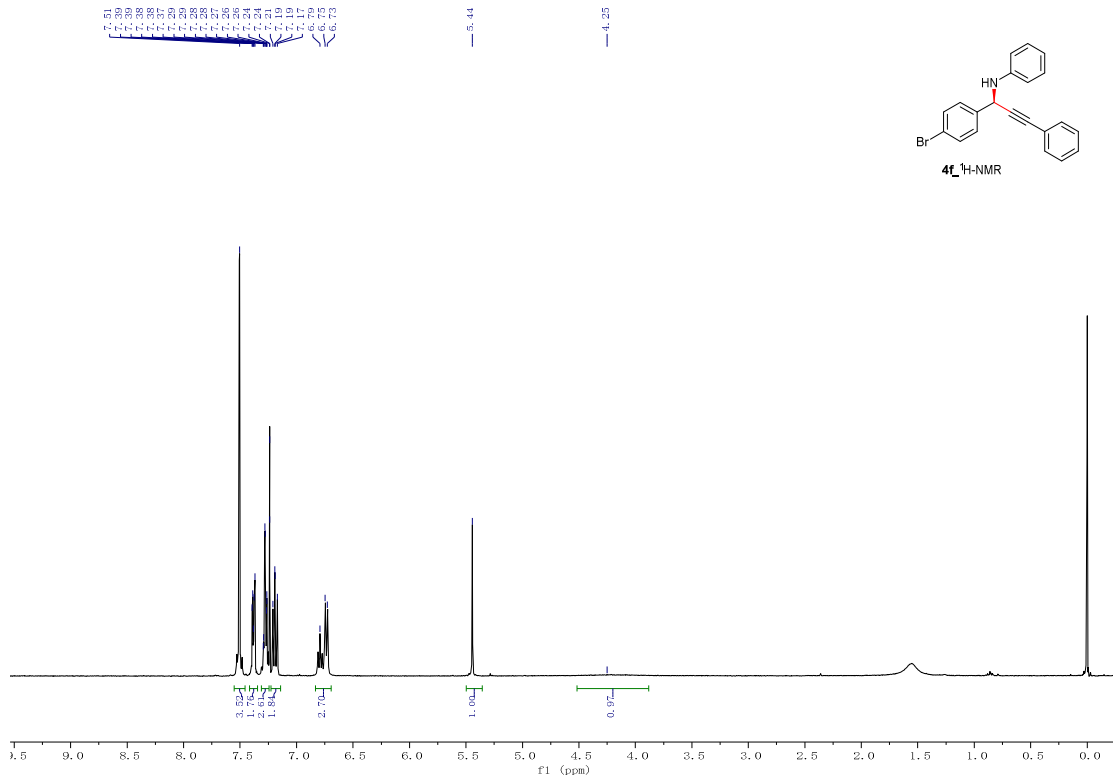
118.76
114.11
87.96
85.39
50.23
HN
Cl
4e_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.239	BV	0.8133	7419.72949	140.22141	49.9109
2	33.976	VB	0.9158	7446.21484	124.13836	50.0891
Totals :				1.48659e4	264.35976	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.621	MM R	0.7885	7288.13818	130.89549	97.8201
2	33.623	MM R	0.9648	162.41176	2.80551	2.1799
Totals :				7450.54994	133.70100	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7.28
7.28
7.27
7.26
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7.21
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6.79
6.75
6.73
5.44
4.25
HN
Br
4f_1H-NMR
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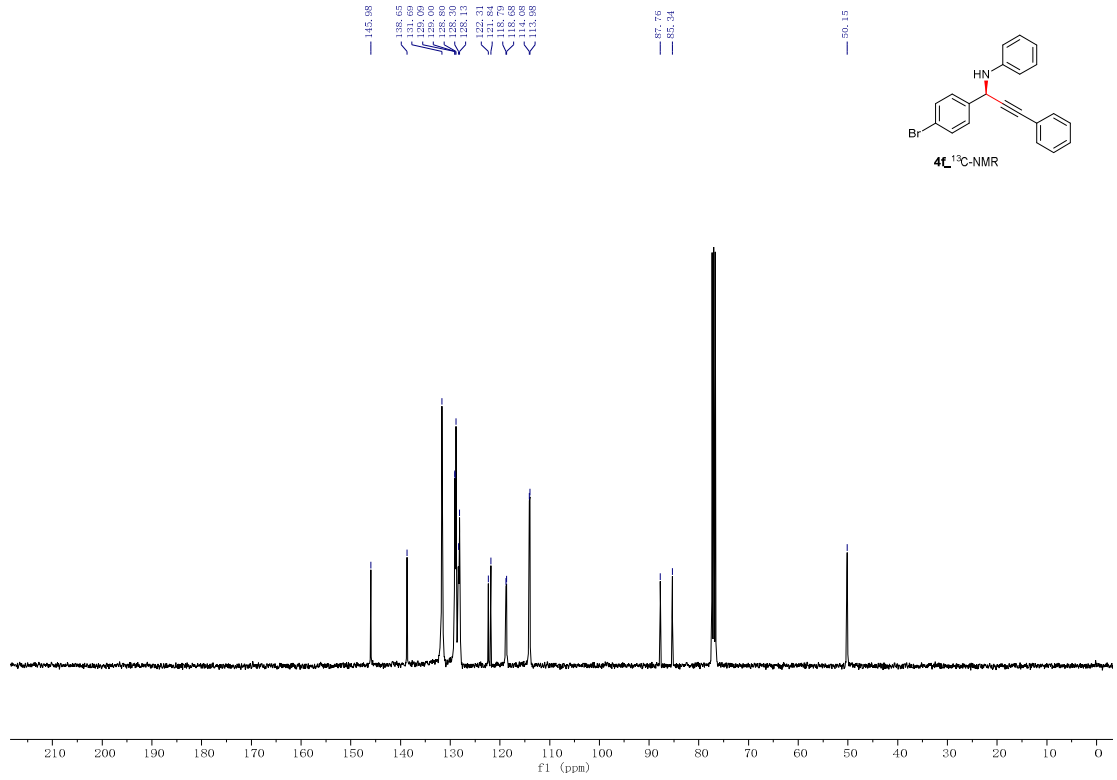
1.76
2.81
1.93
2.70
1.00
0.97
f1 (ppm)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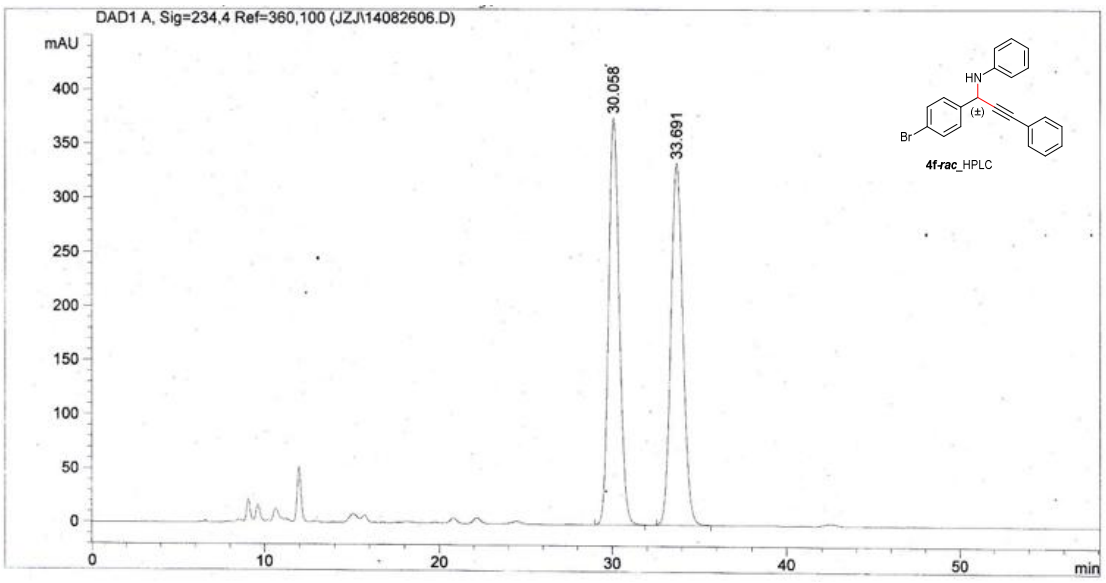
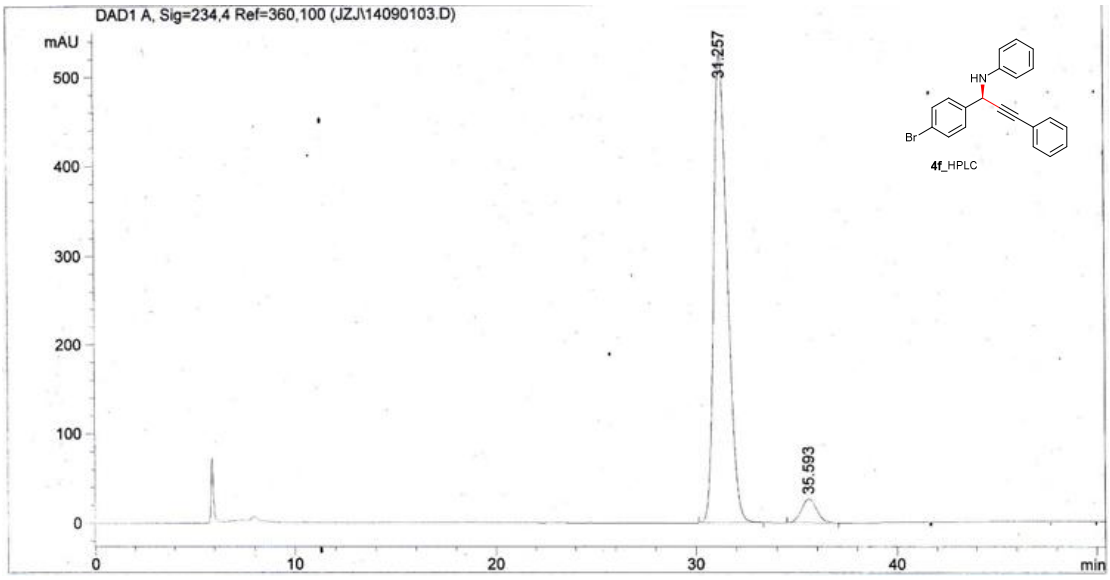
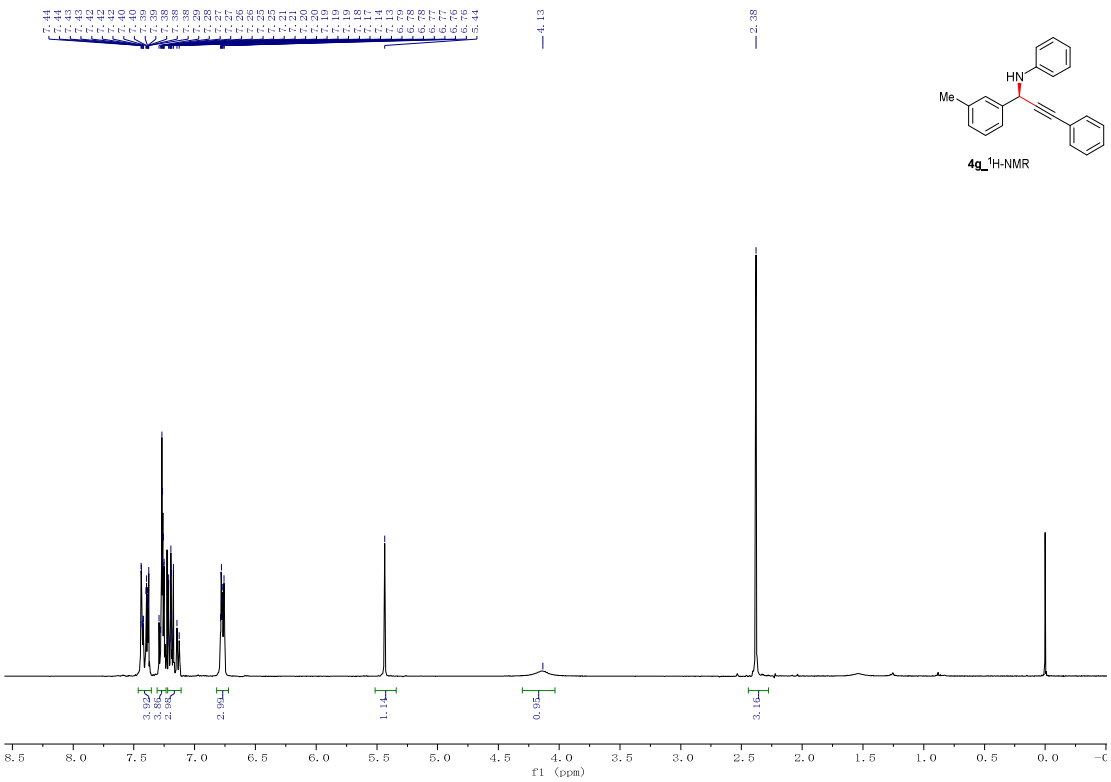
122.31
121.84
118.79
113.68
114.08
113.98
87.76
85.34
50.15
HN
Br
4f_13C-NMR
f1 (ppm)

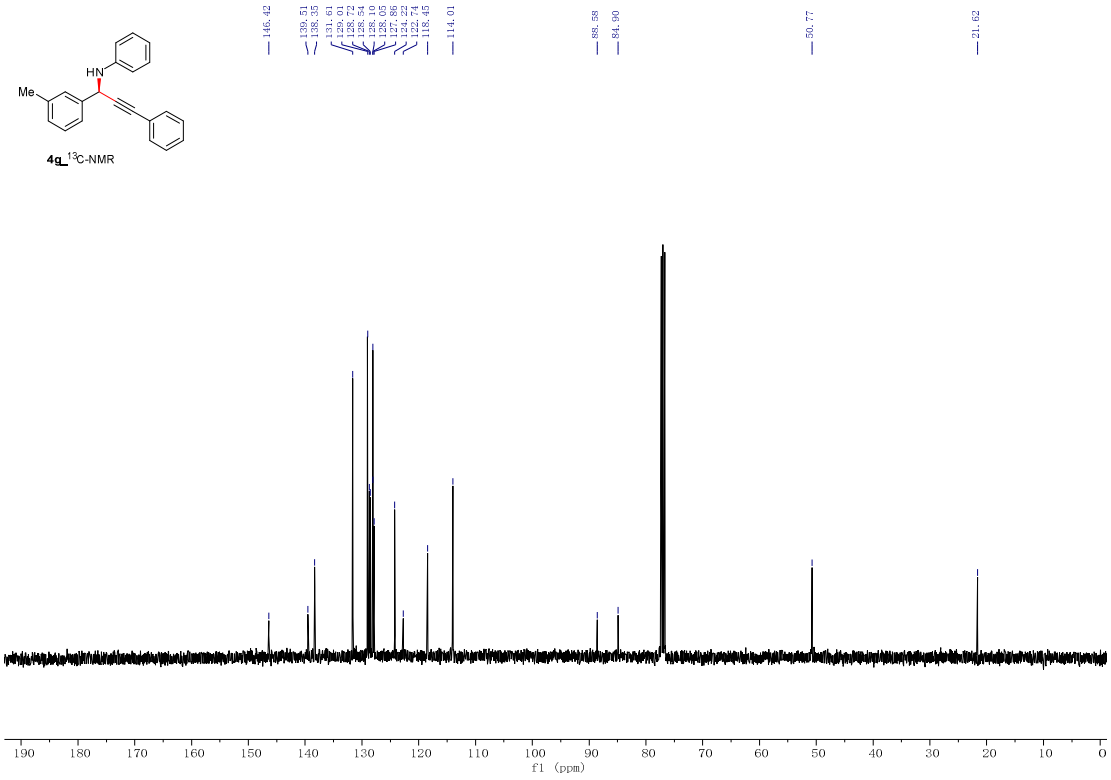


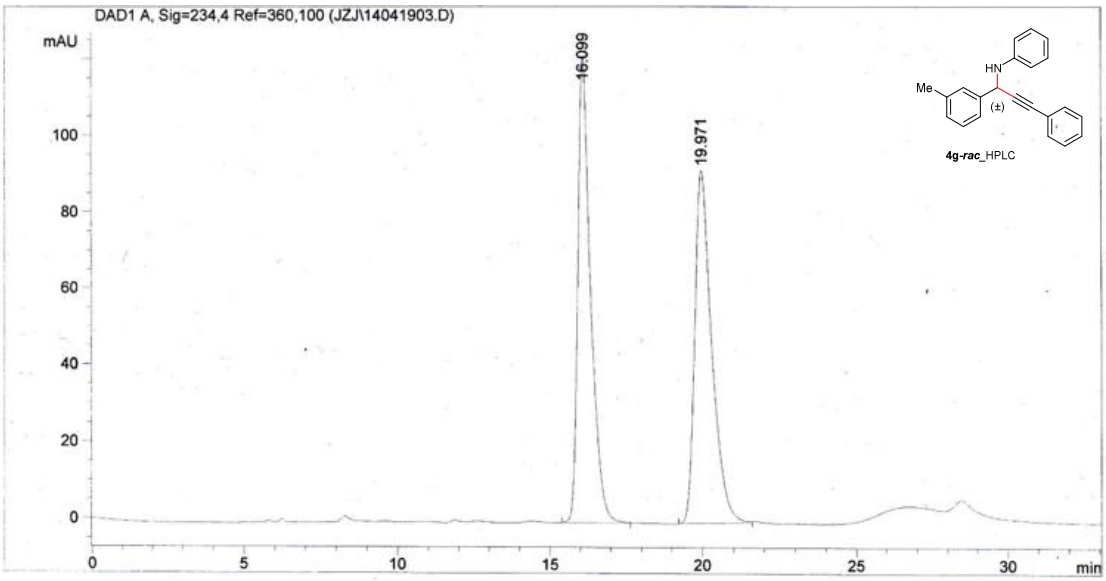
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.058	BB	0.6626	1.59988e4	374.34927	49.9897
2	33.691	BB	0.7452	1.60054e4	332.72415	50.0103
Totals :				3.20042e4	707.07343	



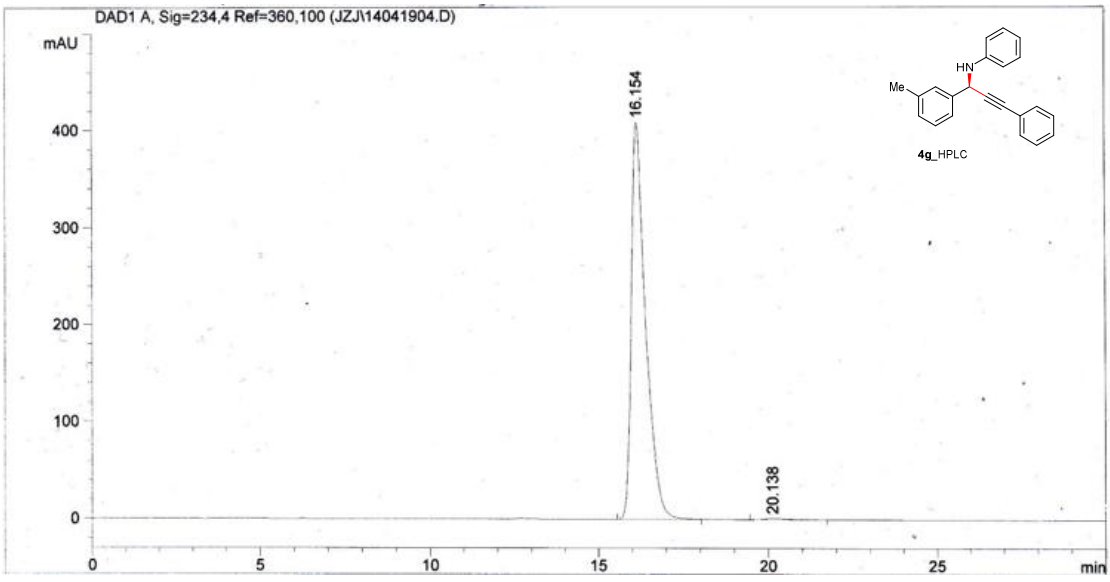
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.257	BB	0.7253	2.44689e4	523.48938	94.6328
2	35.593	BP	0.8155	1387.78577	26.47578	5.3672
Totals :				2.58567e4	549.96516	


HN
Me
4g_1H-NMR
f1 (ppm)

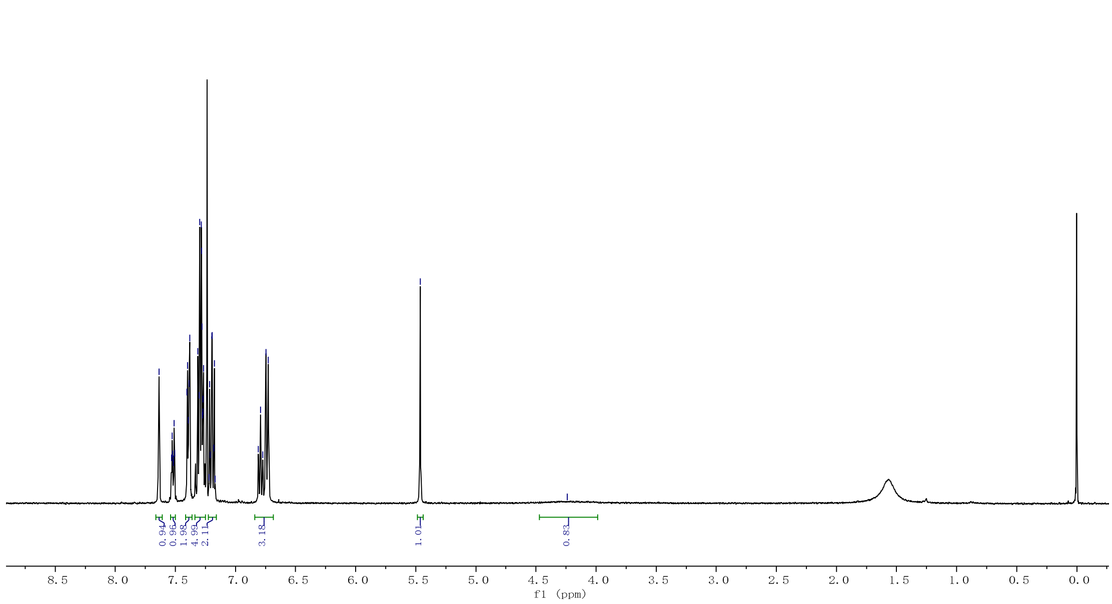

HN
Me
4g_13C-NMR
f1 (ppm)

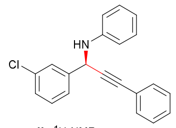


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.099	BB	0.4238	3543.46167	121.65050	50.2045
2	19.971	PB	0.5618	3514.59229	91.98058	49.7955
Totals :				7058.05396	213.63108	

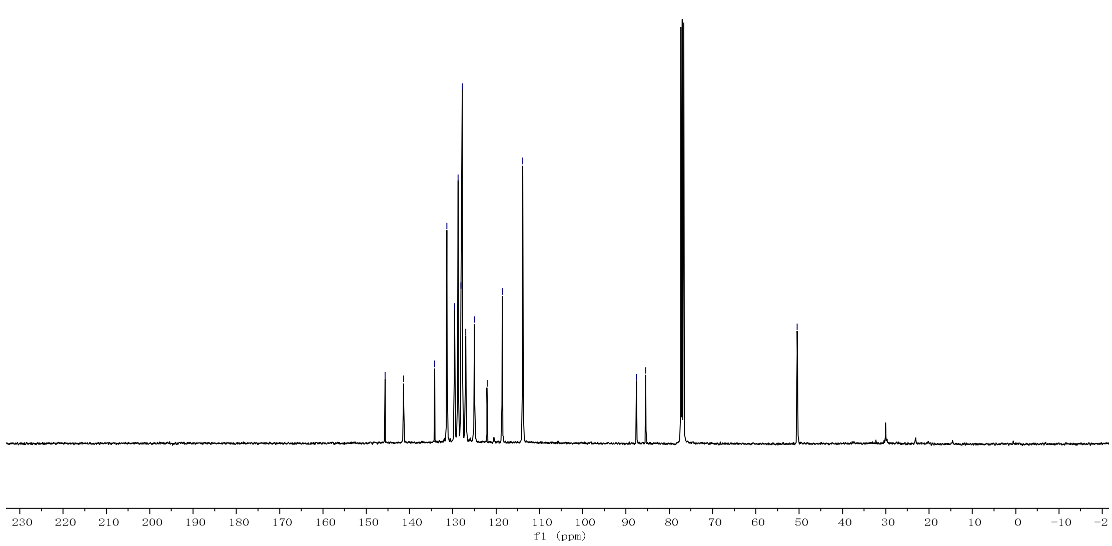


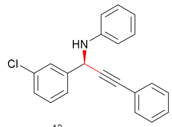
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.154	BB	0.4257	1.19585e4	408.29361	99.3804
2	20.138	PB	0.7694	74.55544	1.17954	0.6196
Totals :				1.20330e4	409.47315	



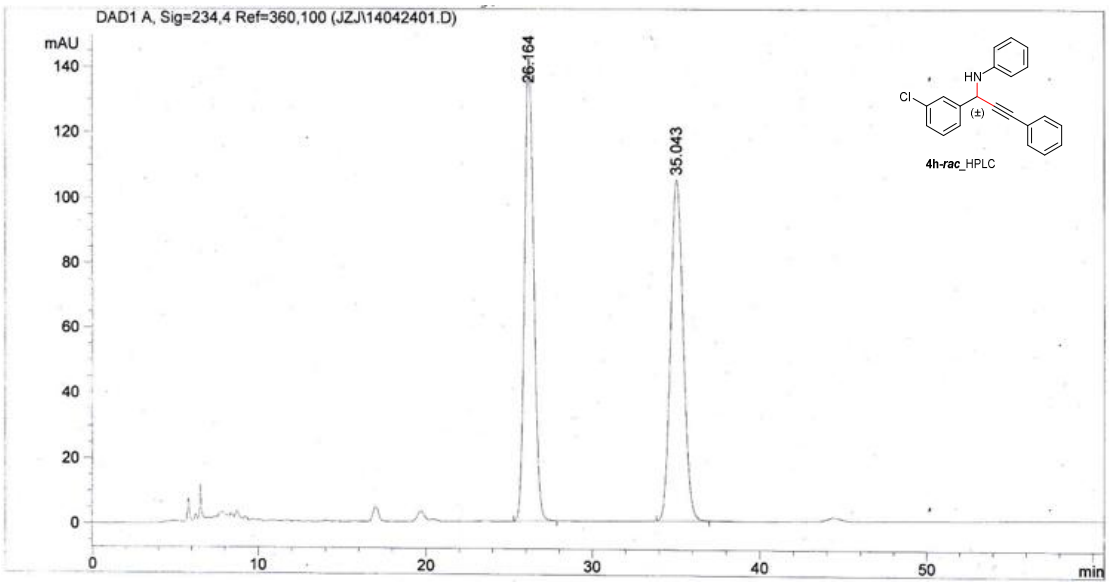


4h_1H-NMR

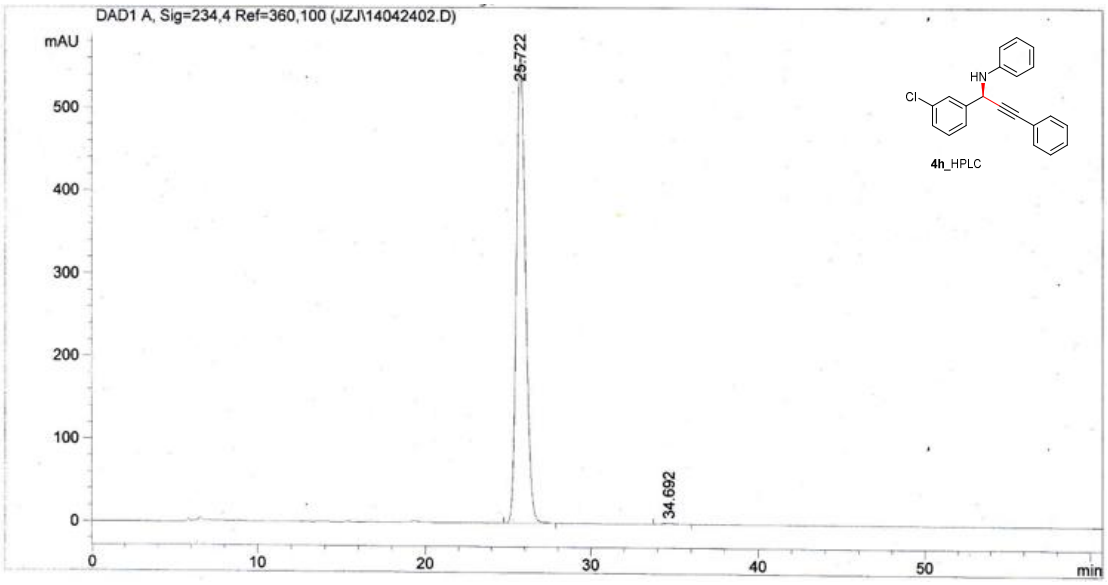




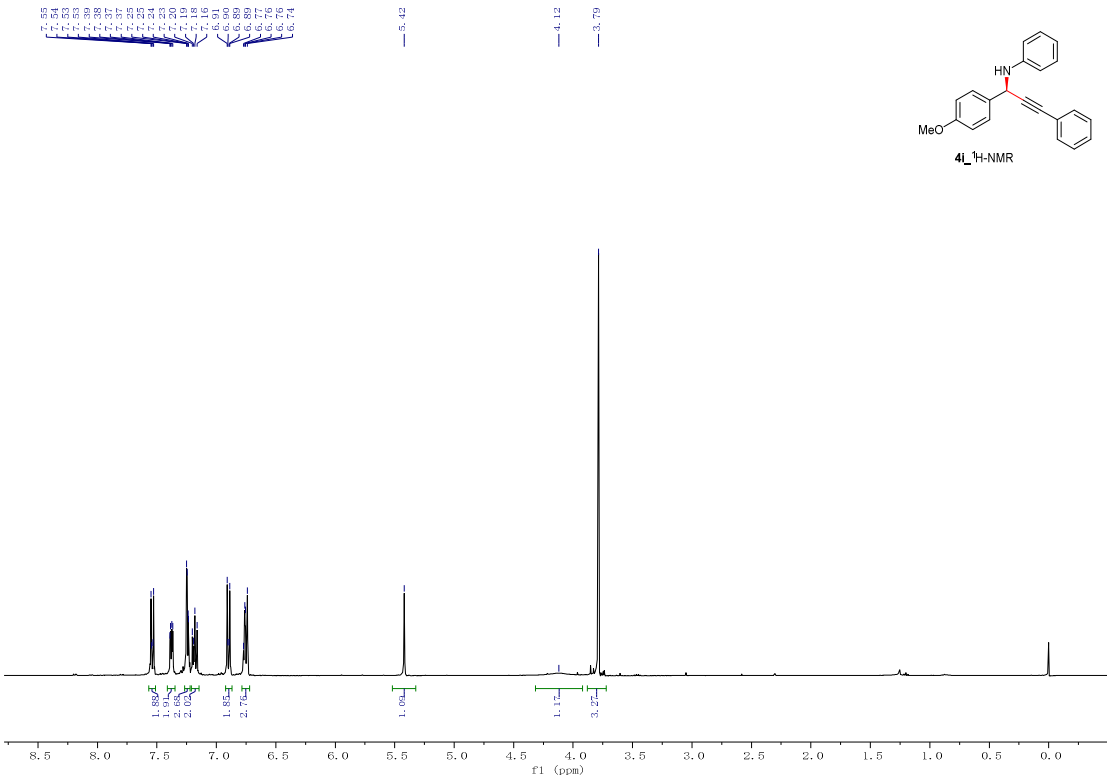
4h_13C-NMR



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.164	BB	0.6016	5441.67383	141.21989	49.8848
2	35.043	BB	0.8205	5466.79883	104.13400	50.1152
Totals :				1.09085e4	245.35390	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.722	PB	0.6008	2.15820e4	561.05762	99.7126
2	34.692	BB	0.7207	62.19881	1.21617	0.2874
Totals :				2.16442e4	562.27379	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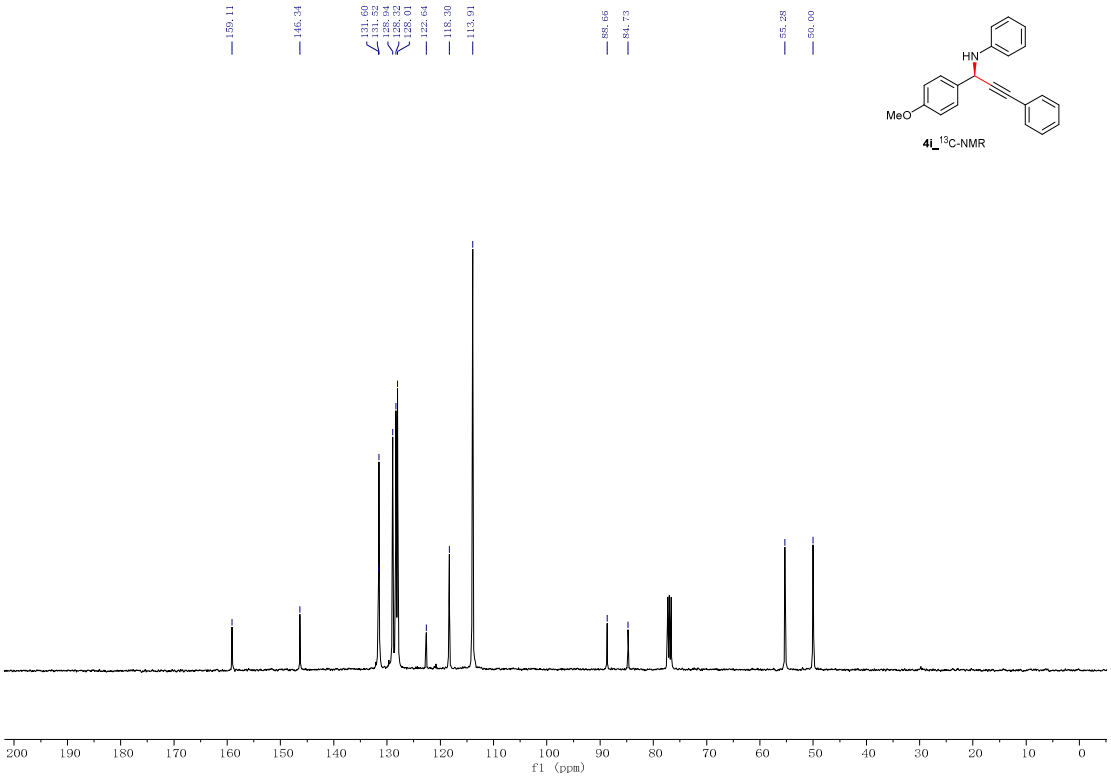
7.20
7.19
7.18
7.16
6.91
6.90
6.89
6.77
6.76
6.75
6.74
5.42
4.12
3.79
HN
MeO
4i_1H-NMR
1.88
1.91
2.68
2.05
1.85
2.76
1.00
1.17
3.27
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.11
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131.52
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113.91
88.66
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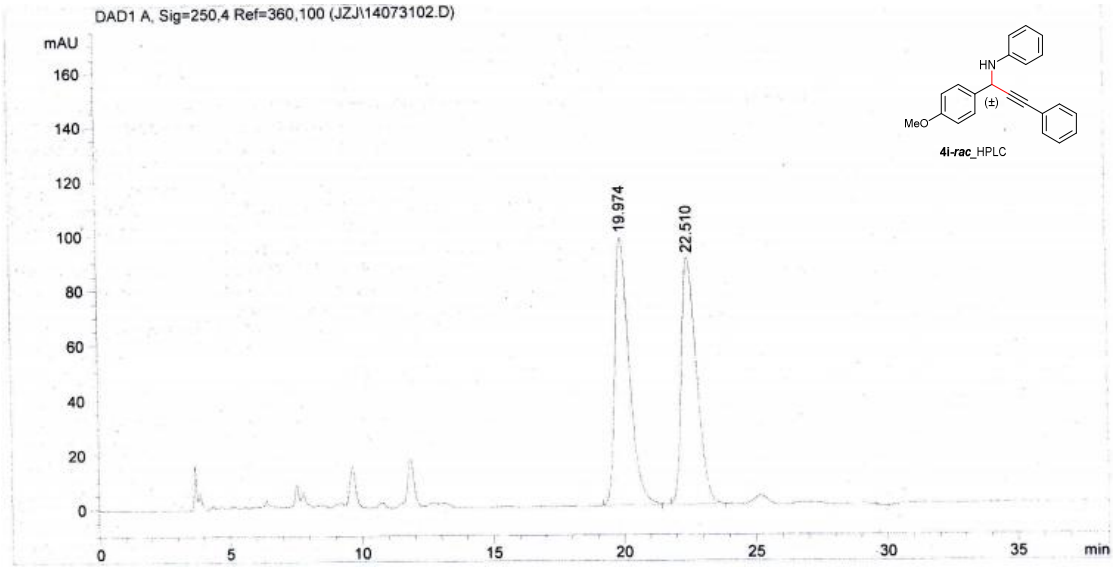
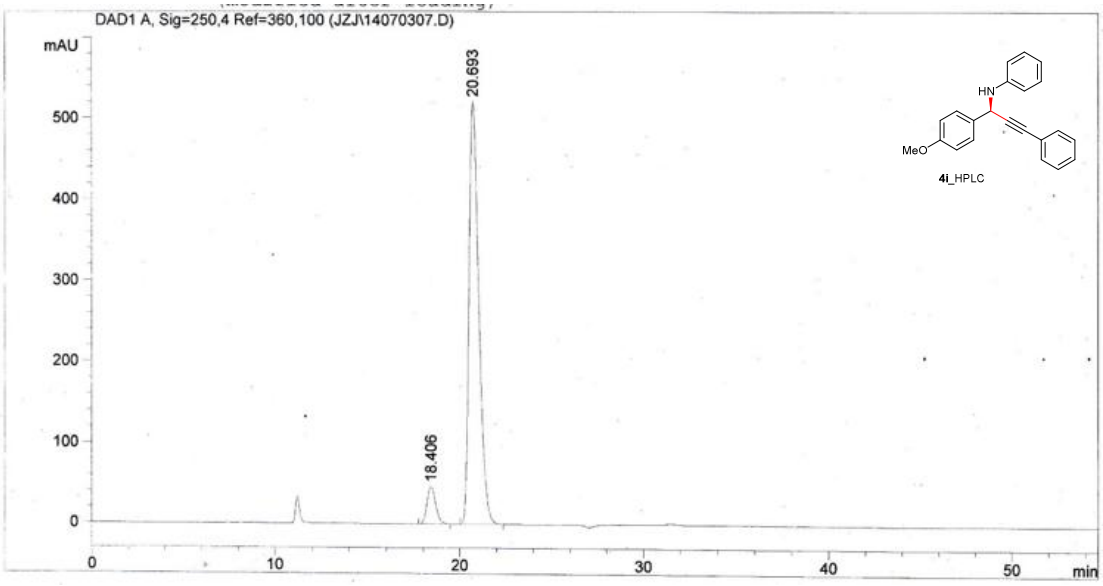
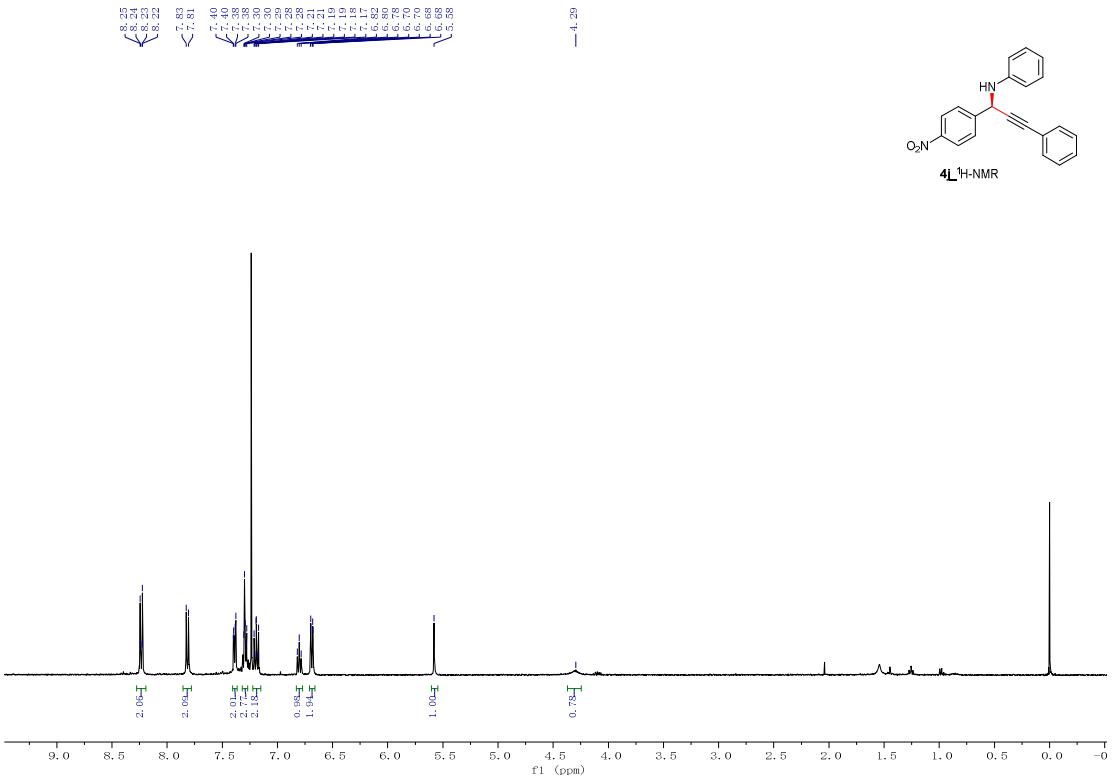
55.28
50.00
HN
MeO
4i_13C-NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.974	MM R	0.5646	3721.50757	97.38279	51.1535
2	22.509	MM R	0.6556	3553.66260	89.49030	48.8465
Totals :				7275.17017	186.87309	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.406	BB	0.4932	1508.04431	46.64791	7.2879
2	20.693	PB	0.5654	1.91844e4	521.26874	92.7121
Totals :				2.06924e4	567.91665	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8.22
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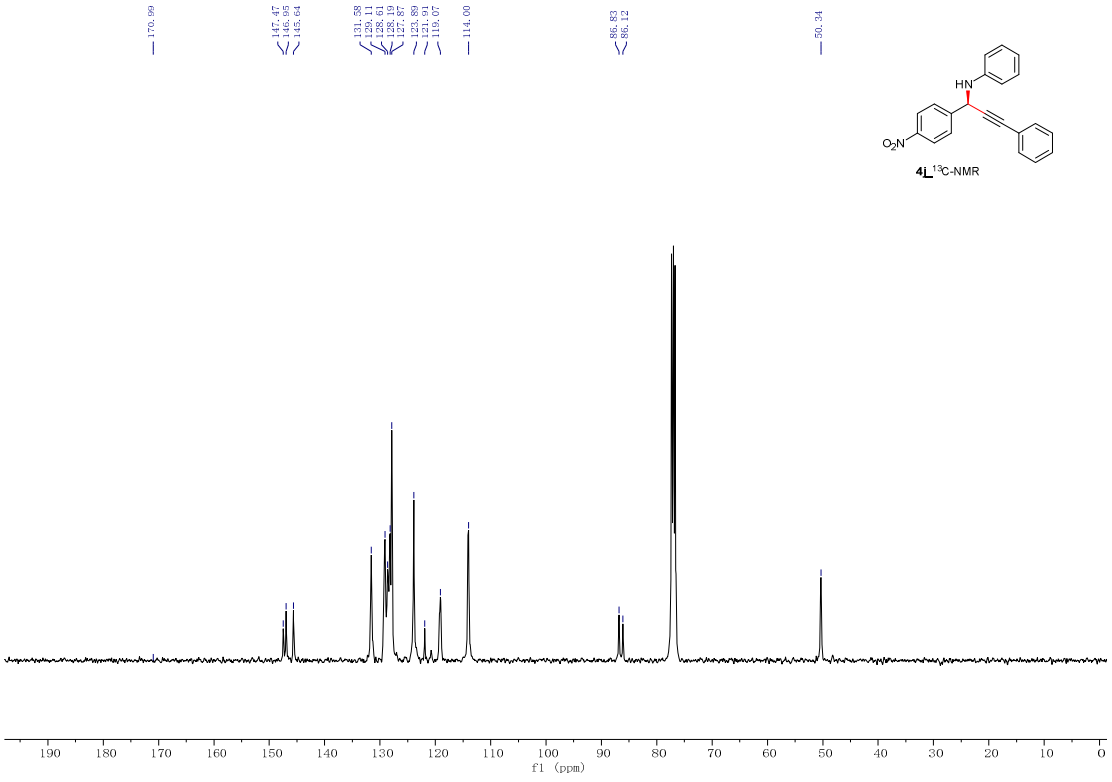
7.17
6.82
6.80
6.78
6.70
6.70
6.68
6.68
5.58
4.29
HN
O2N
4iL 1H-NMR
2.06
2.00
2.01
2.75
2.18
0.98
1.94
1.00
0.78
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)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114.00
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HN
O2N
4iL 13C-NMR
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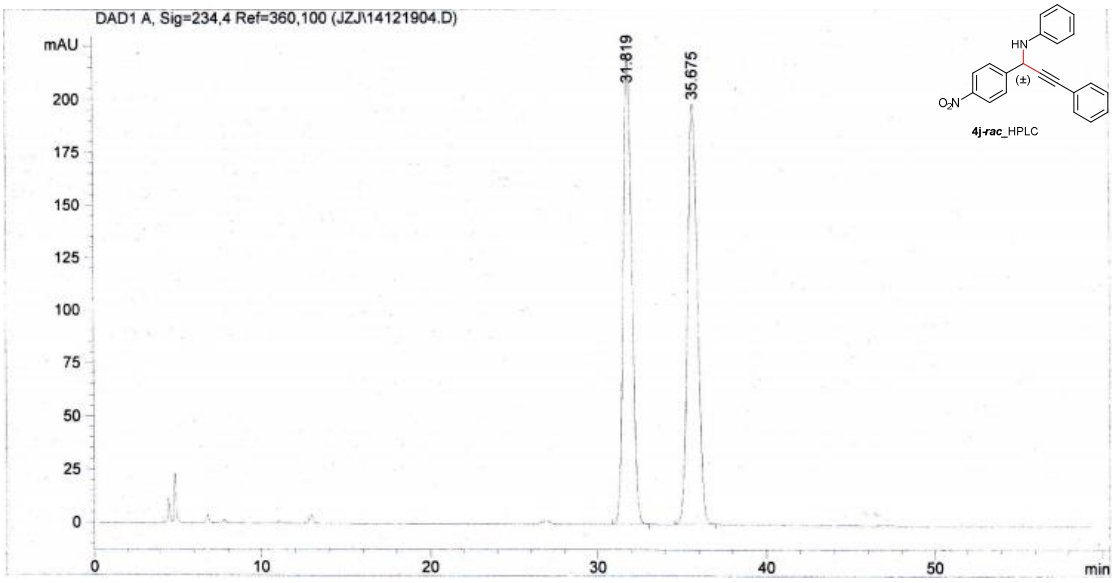
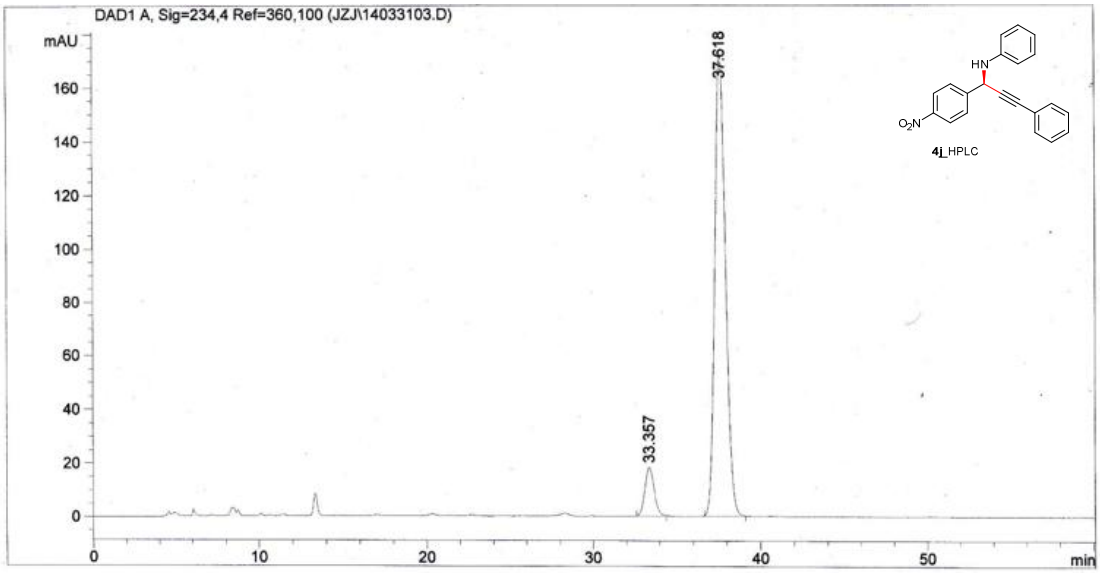
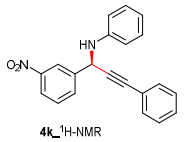
f1 (ppm)



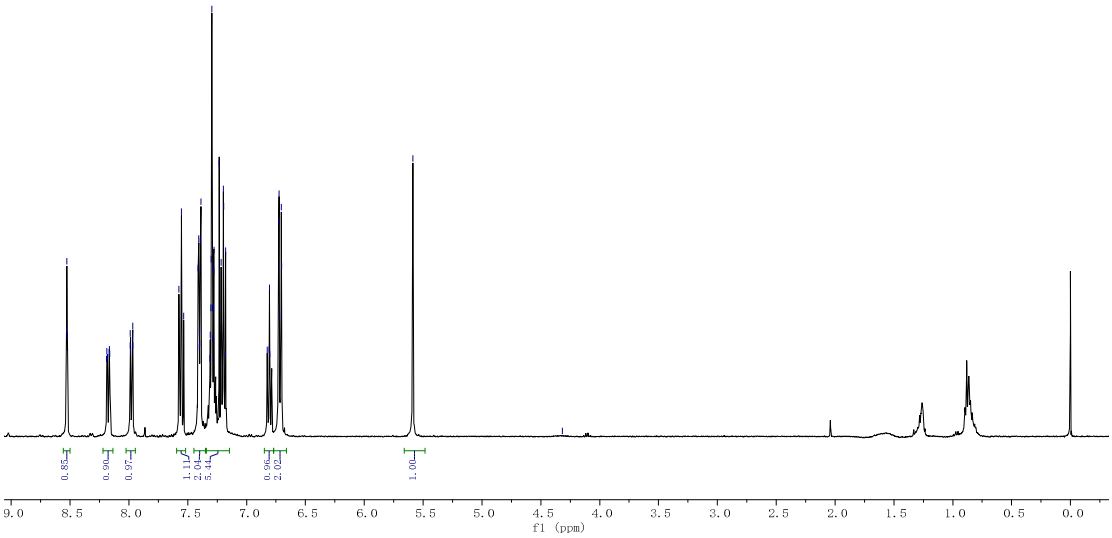
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.819	BB	0.5494	7783.53613	219.65318	49.3025
2	35.675	BB	0.6313	8003.77588	198.11304	50.6975
Totals :				1.57873e4	417.76622	

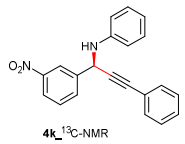


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.357	BB	0.6098	714.64722	18.21256	8.5949
2	37.618	BB	0.6881	7600.16455	171.80377	91.4051
Totals :				8314.81177	190.01633	

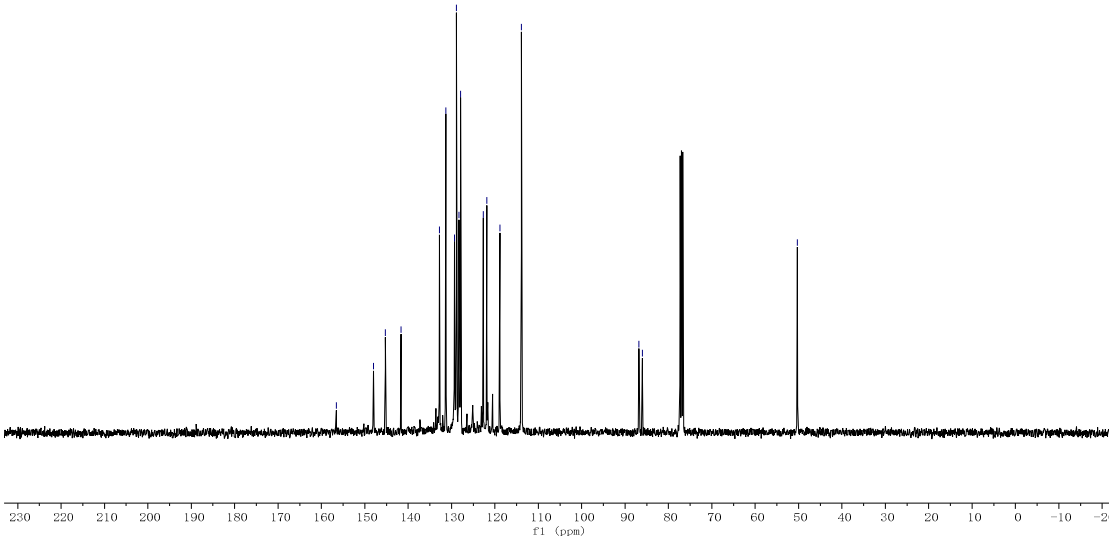


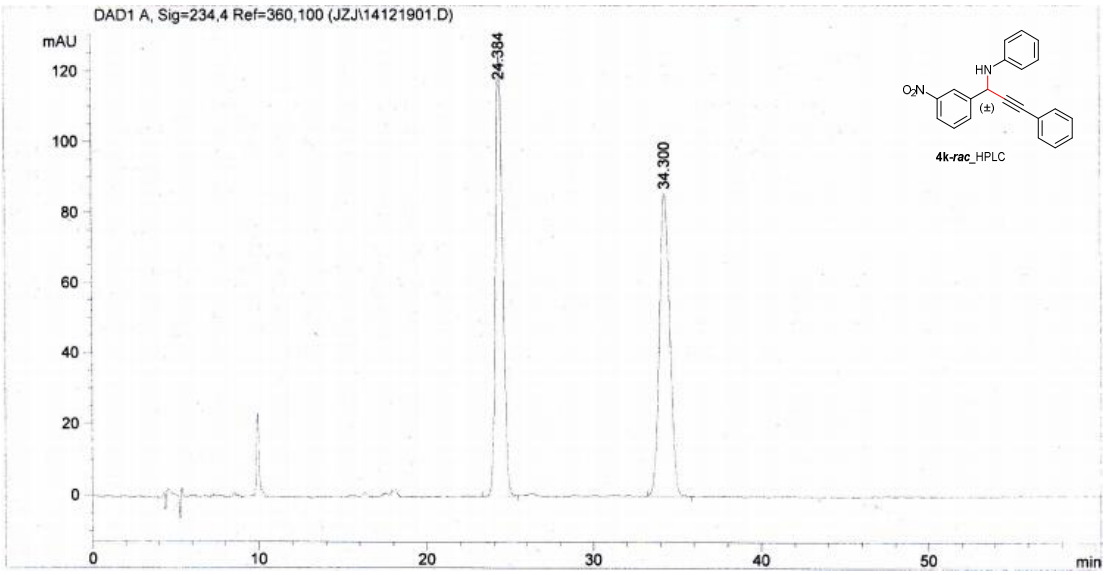
4k_^{1}H-NMR



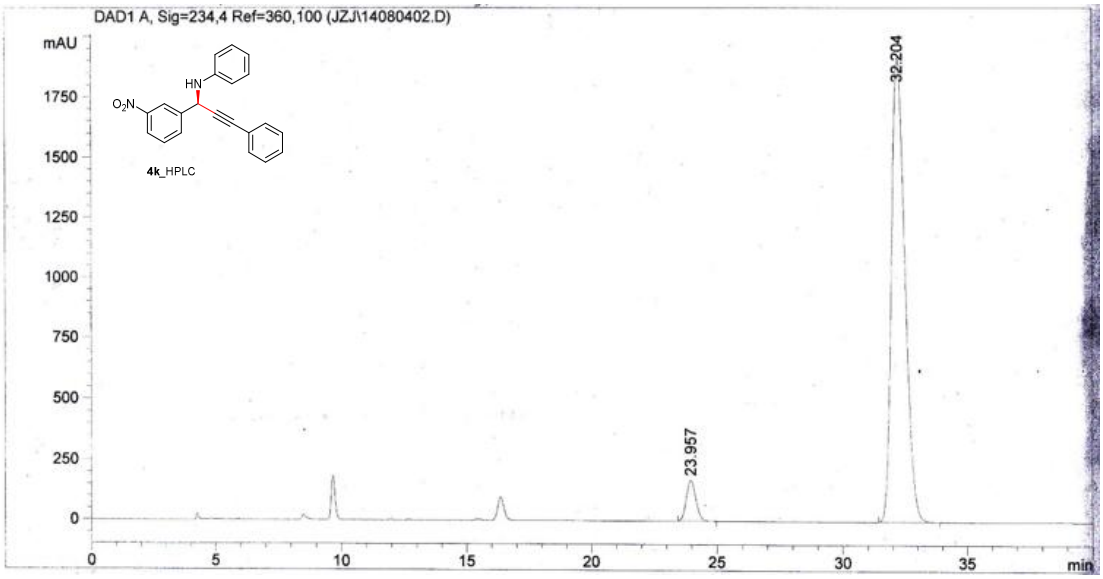


4k_^{13}C-NMR

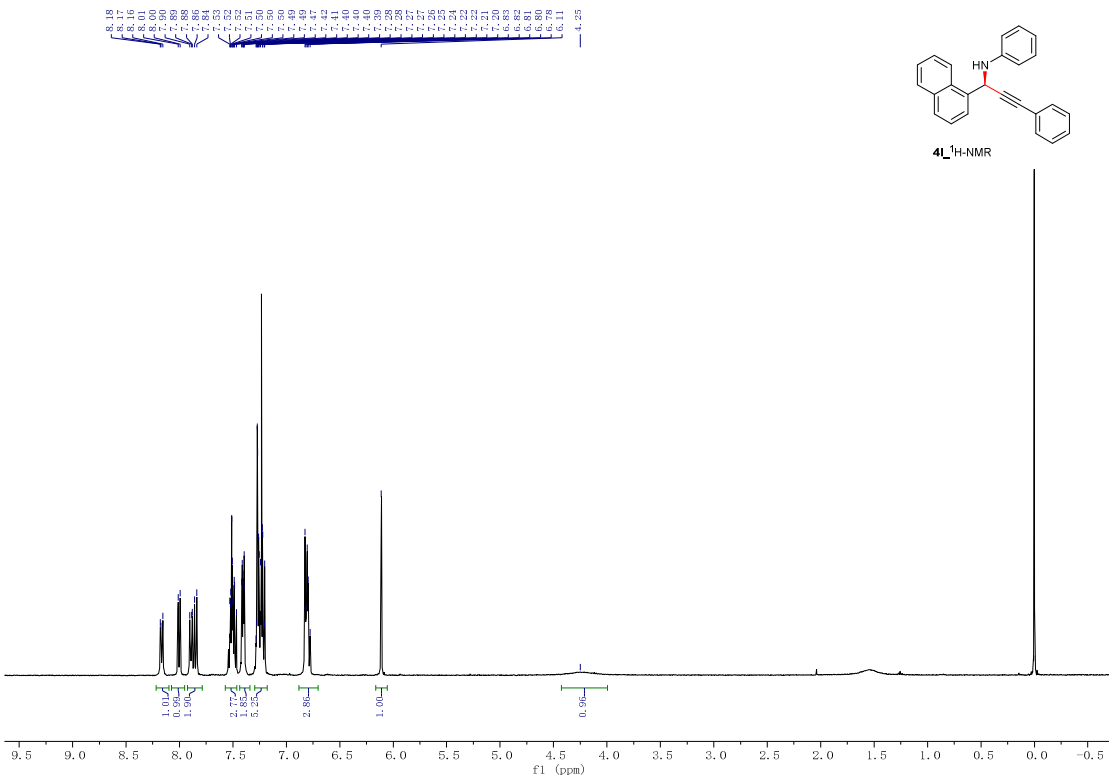




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.384	BB	0.4762	3758.87158	124.50810	50.1083
2	34.300	BP	0.6844	3742.62500	85.22110	49.8917
Totals :				7501.49658	209.72920	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.957	BB	0.4147	4495.41602	168.78981	5.8946
2	32.204	BB	0.5893	7.17681e4	1914.57678	94.1054
Totals :				7.62635e4	2083.36659	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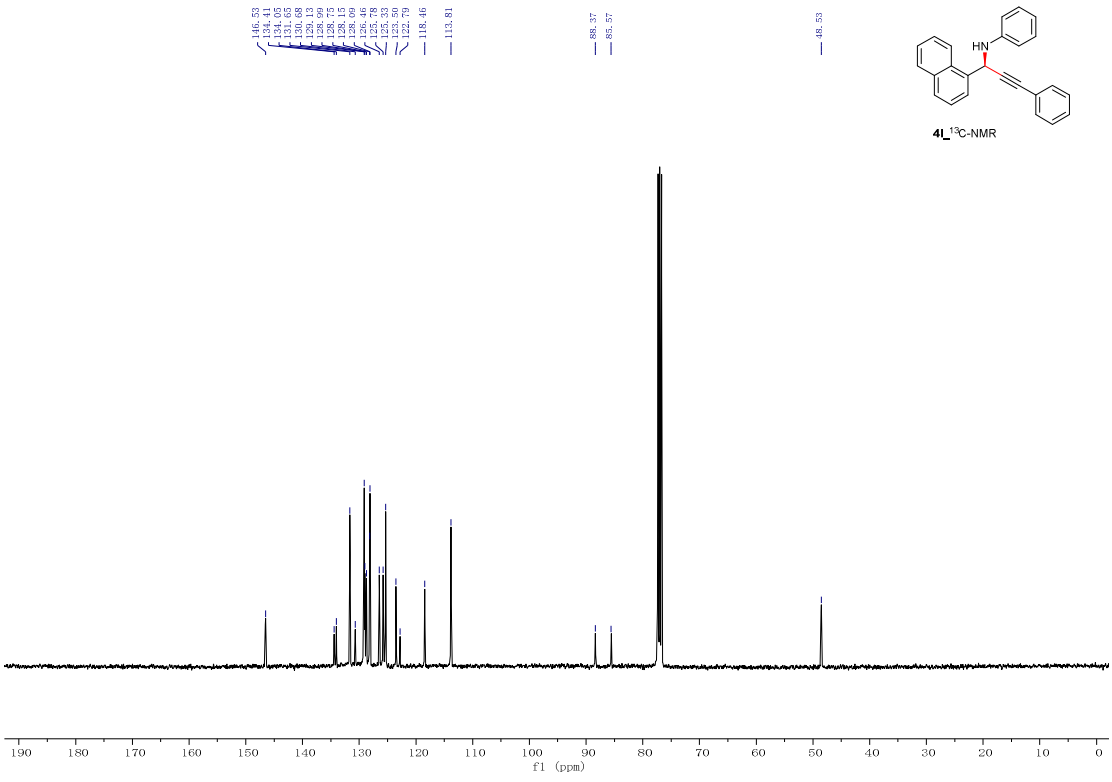
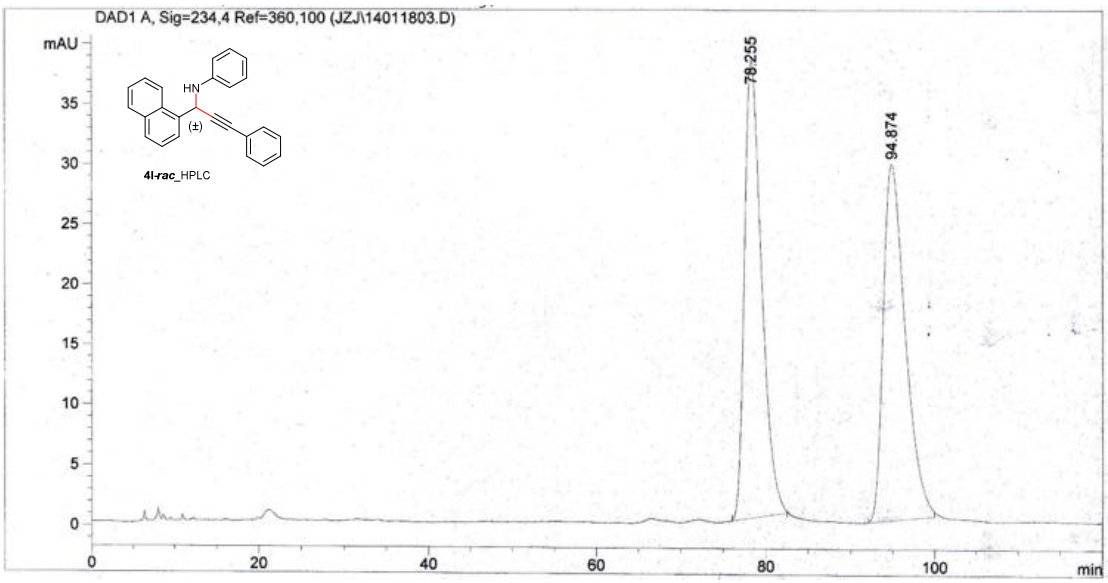
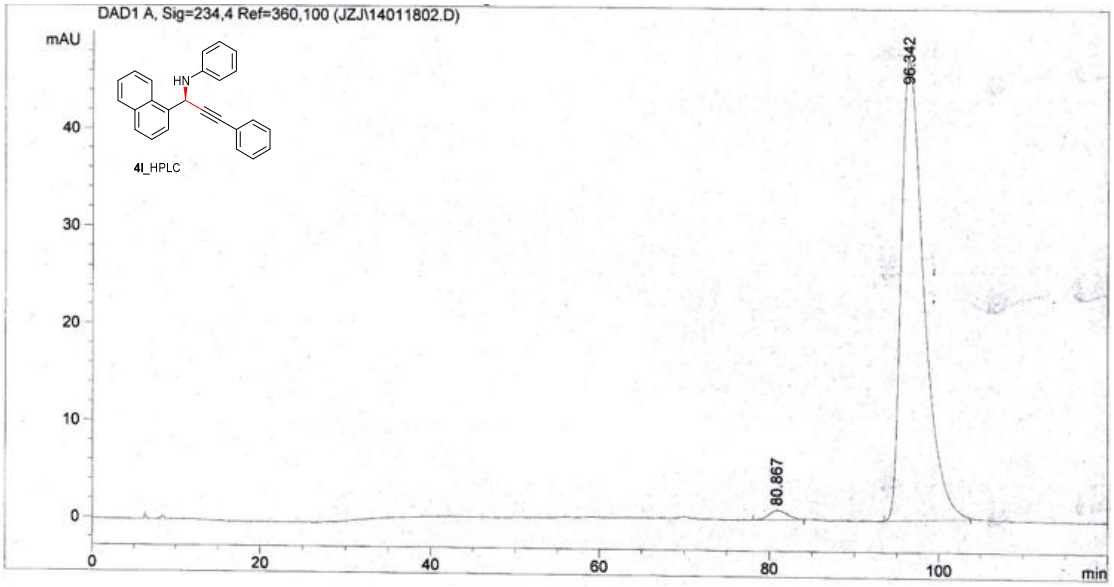
f1 (ppm)

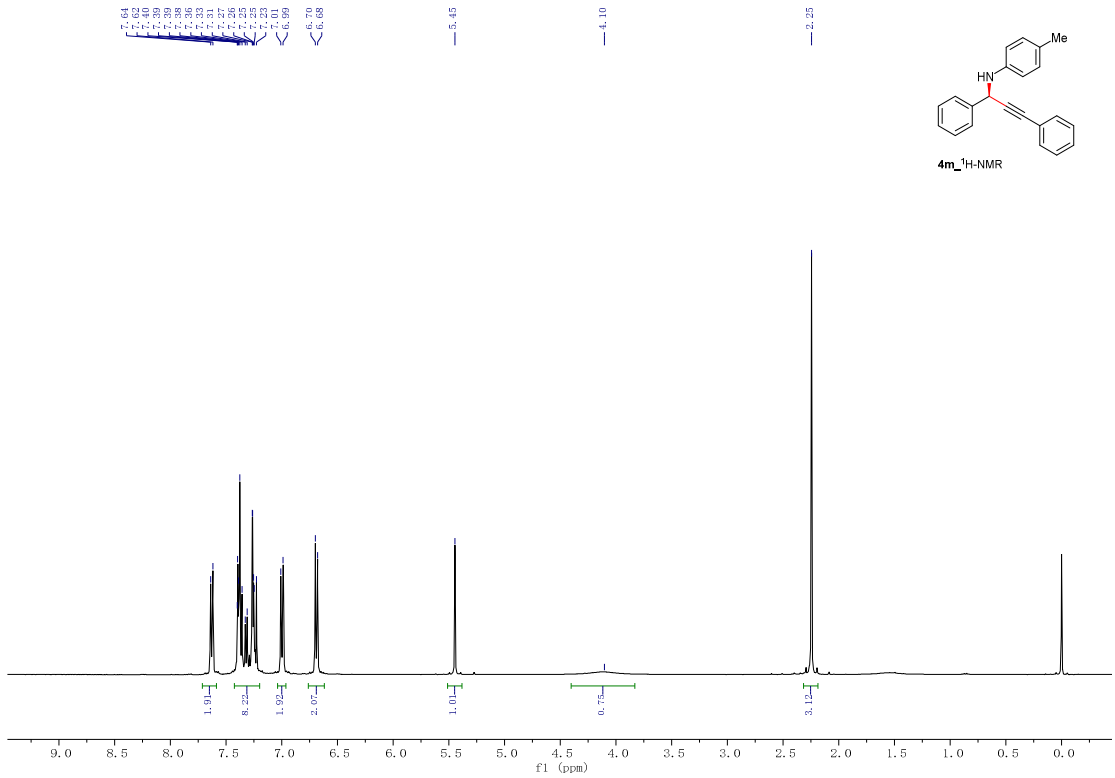

HN
4l_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	78.255	BB	1.6430	5289.83691	37.93120	49.6426
2	94.874	BB	2.1369	5366.00977	29.46171	50.3574
Totals :				1.06558e4	67.39291	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	80.867	VV	1.8170	151.61581	9.82149e-1	1.6862
2	96.342	BB	2.4823	8839.94727	47.17232	98.3138
Totals :				8991.56308	48.15447	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7.27
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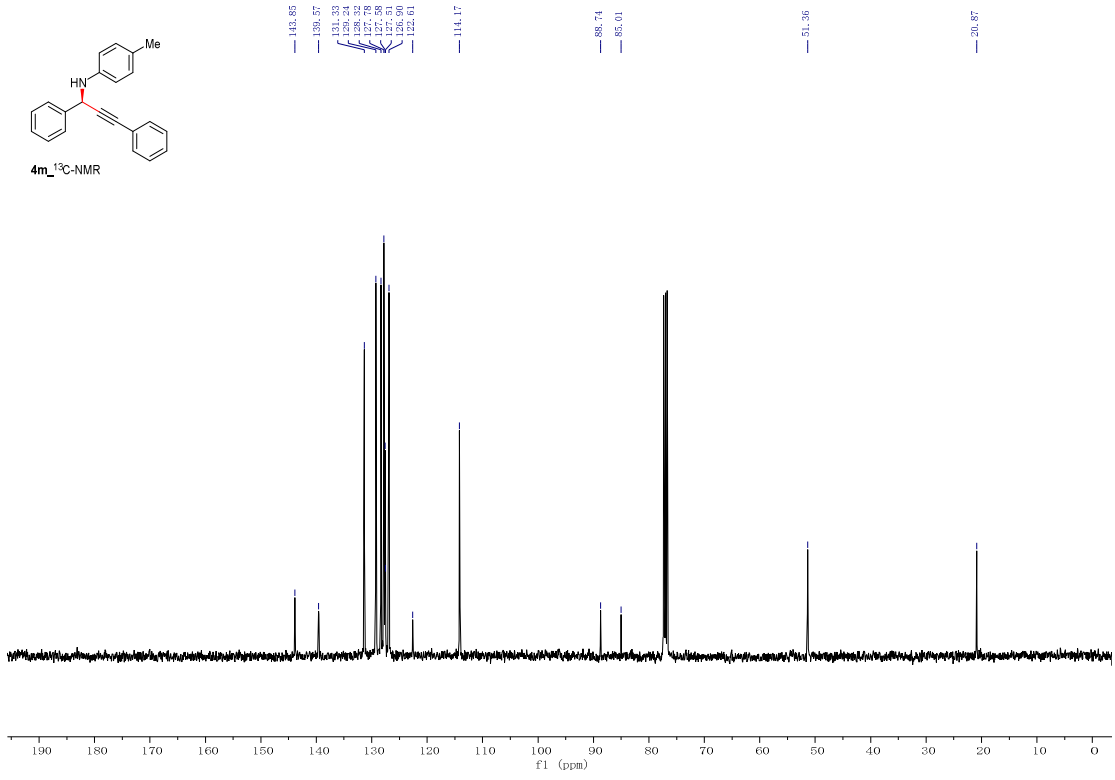
7.25
7.23
7.01
6.99
6.70
6.68
5.45
4.10
2.25
Me
HN
4m_1H-NMR
1.91
8.22
1.92
2.07
1.01
0.75
3.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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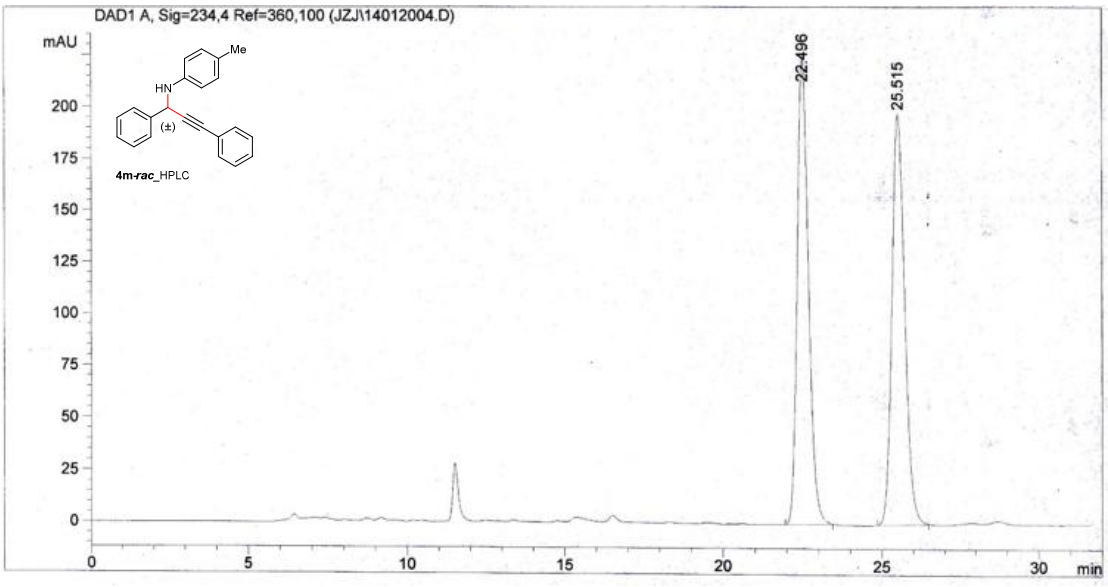
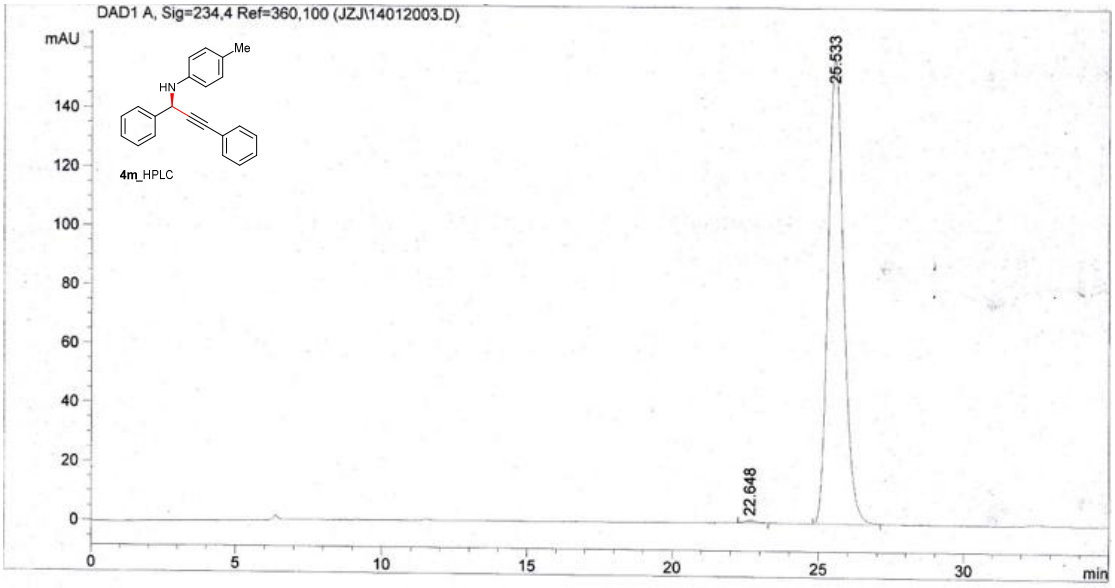
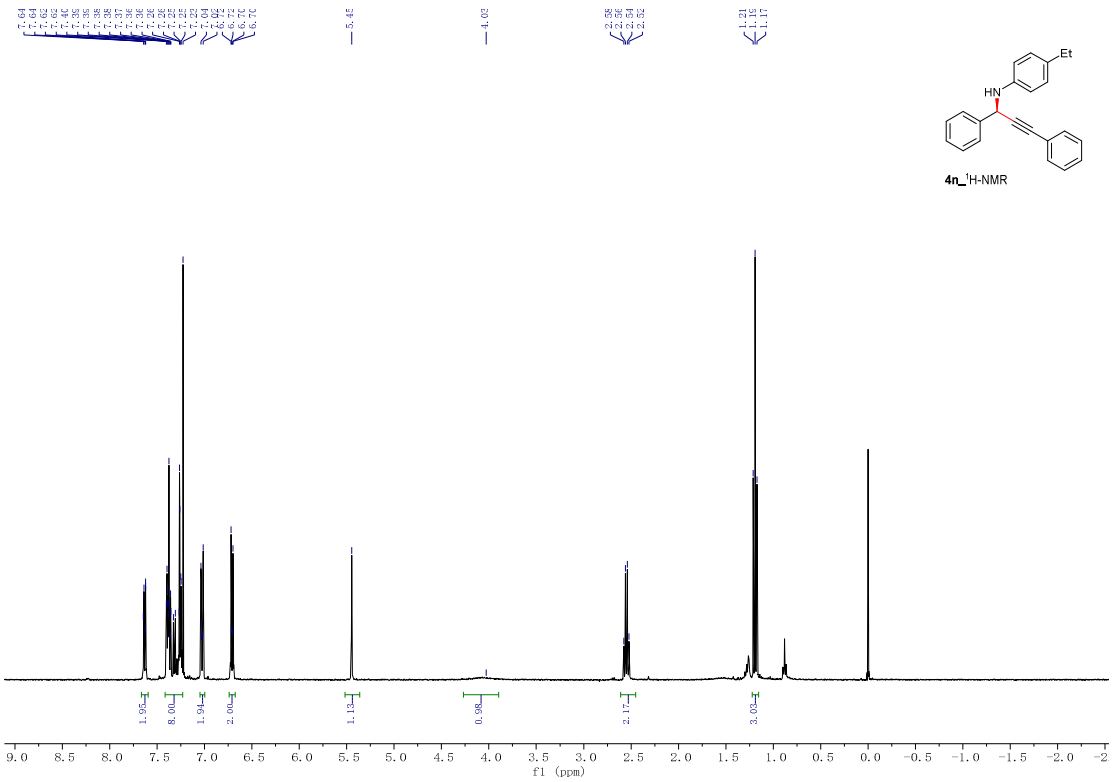
122.61
114.17
88.74
85.01
51.36
20.87
Me
HN
4m_13C-NMR
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

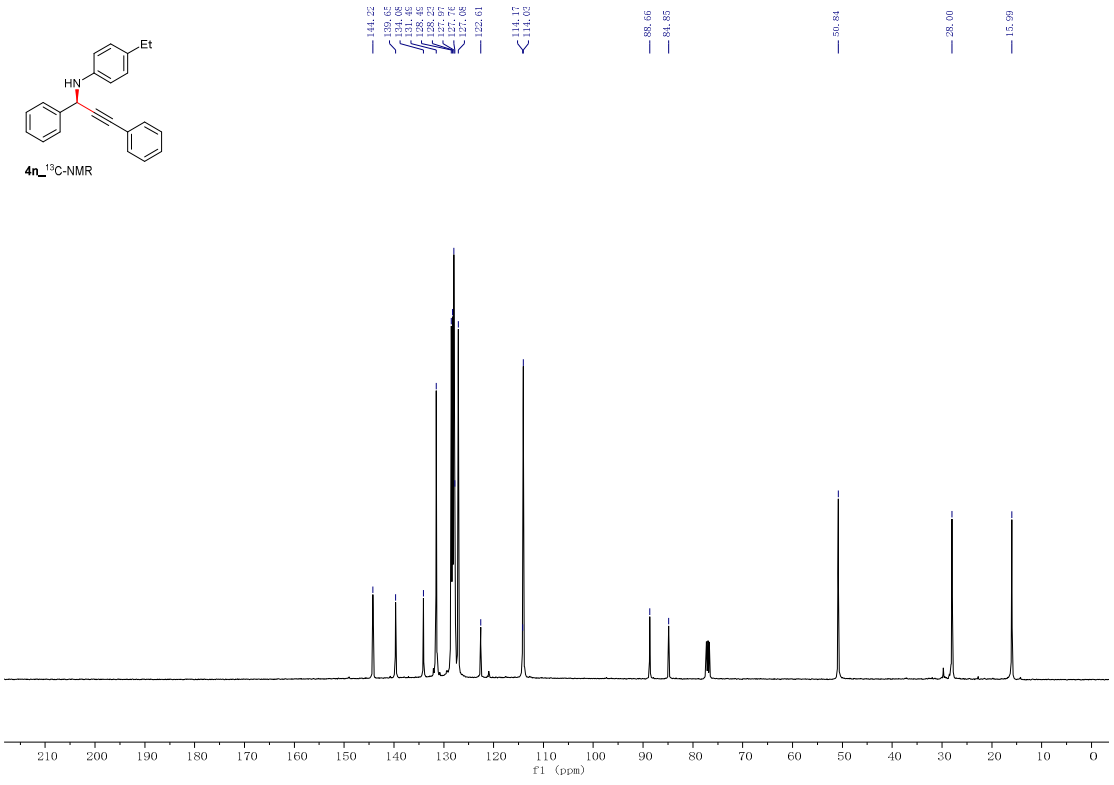


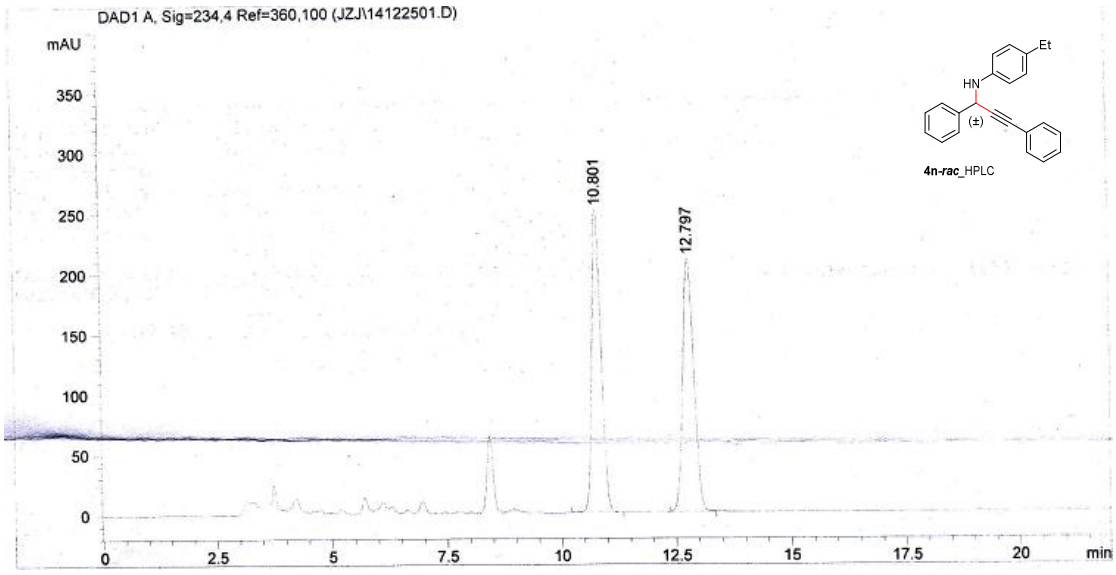
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.496	BB	0.3745	5507.11670	224.26443	49.8255
2	25.515	BB	0.4326	5545.68359	196.90877	50.1745
Totals :				1.10528e4	421.17320	



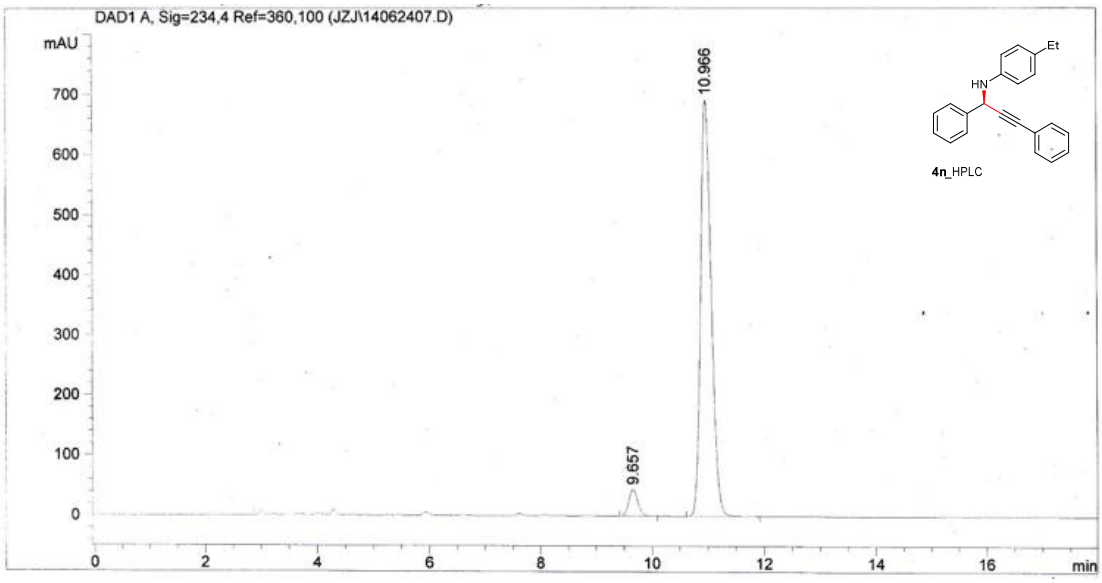
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.648	BB	0.3696	22.21836	8.37303e-1	0.3821
2	25.533	BB	0.5671	5792.66992	156.77869	99.6179
Totals :				5814.88829	157.61599	


Et
HN
4n_1H-NMR
f1 (ppm)

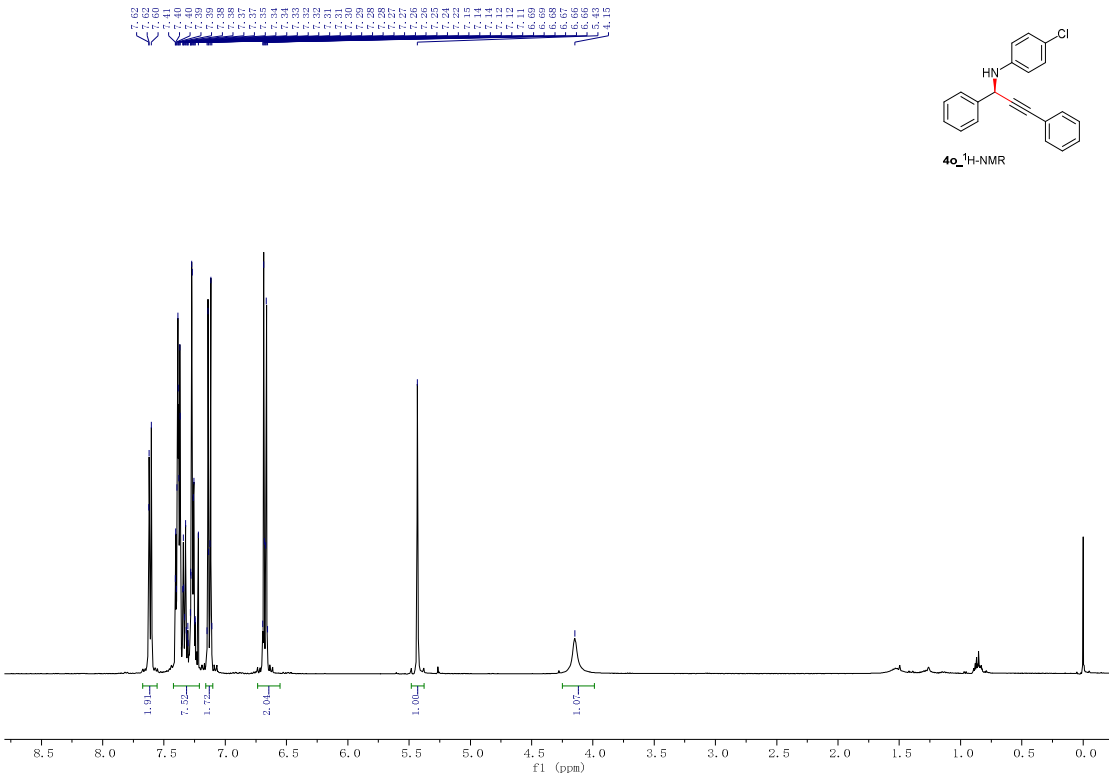

Et
HN
4n_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.801	BB	0.2151	3477.79907	248.73000	50.0729
2	12.797	BB	0.2587	3467.67944	207.75609	49.9271
Totals :				6945.47852	456.48608	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.657	BB	0.1759	500.19601	44.25336	5.2438
2	10.966	BB	0.2007	9038.69629	690.35638	94.7562
Totals :				9538.89230	734.60975	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7.12
7.11
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6.68
6.67
6.66
6.66
5.43
4.15
Cl
HN
4o_1H-NMR
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1.00
1.07
8.5
8.0
7.5
7.0
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6.0
5.5
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3.0
2.5
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1.0
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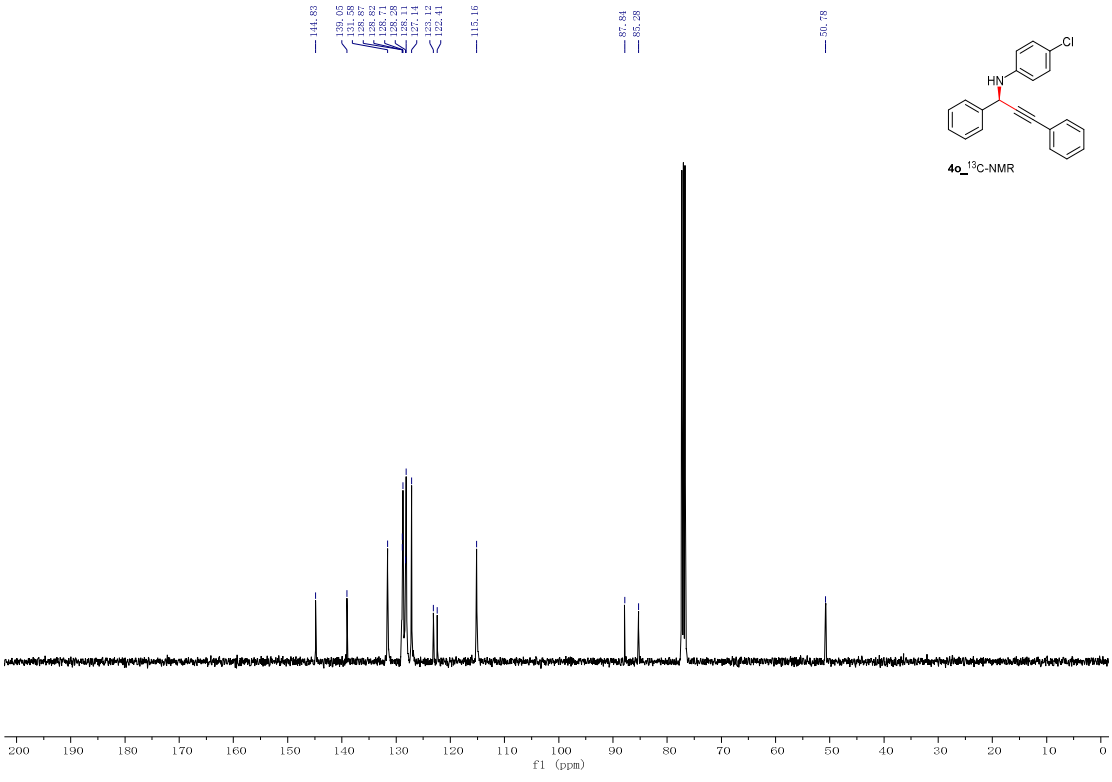
0.0
f1 (ppm)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50.78
Cl
HN
4o_13C-NMR
200
190
180
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130
120
110
100
90
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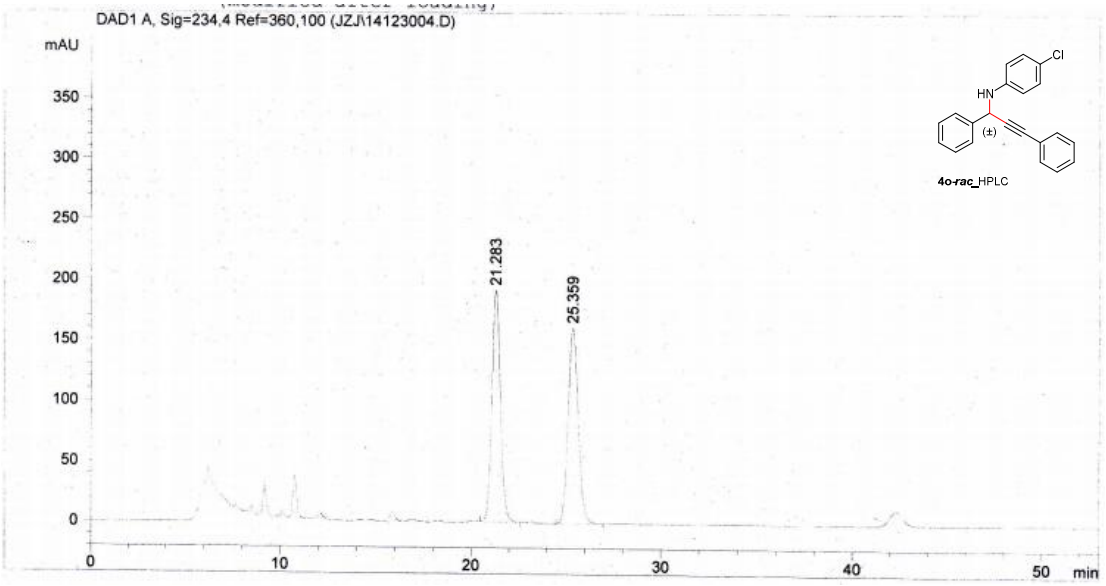
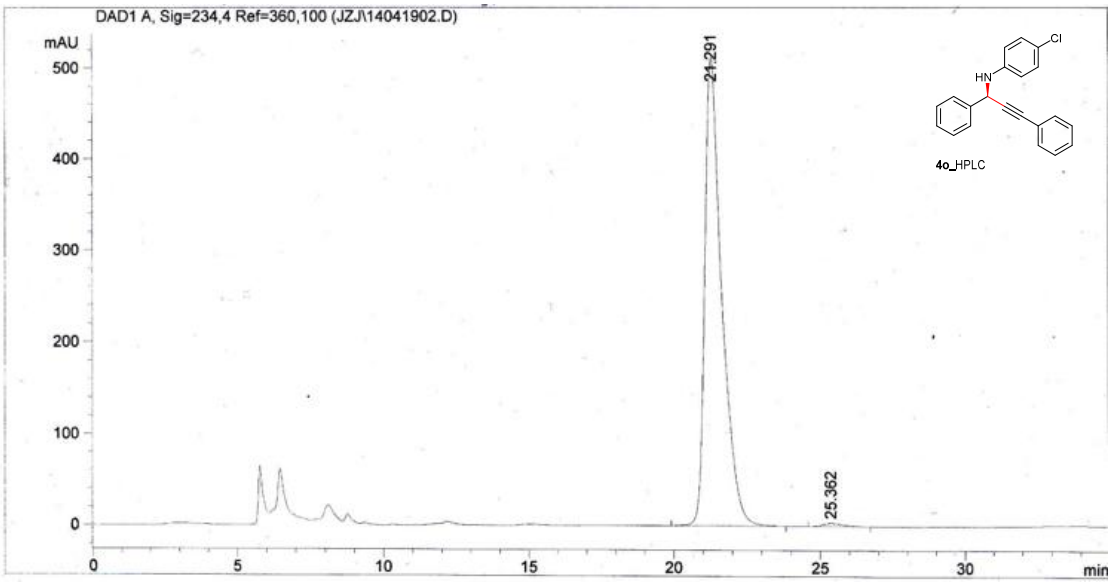
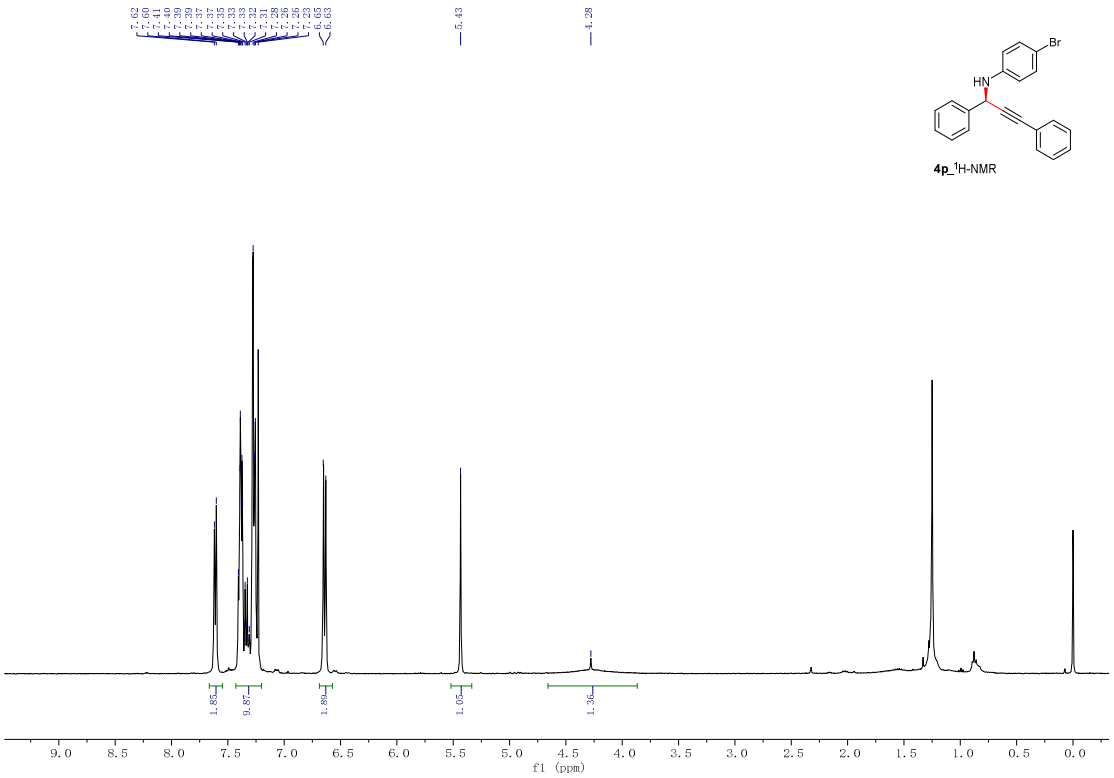
50
40
30
20
10
0
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.283	VB	0.4849	5979.54639	191.19867	50.0995
2	25.359	BB	0.5721	5955.79053	160.79886	49.9005
Totals :				1.19353e4	351.99753	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.291	BB	0.5861	2.06013e4	511.24457	99.1967
2	25.362	PP	0.6778	166.83995	3.64620	0.8033
Totals :				2.07681e4	514.89077	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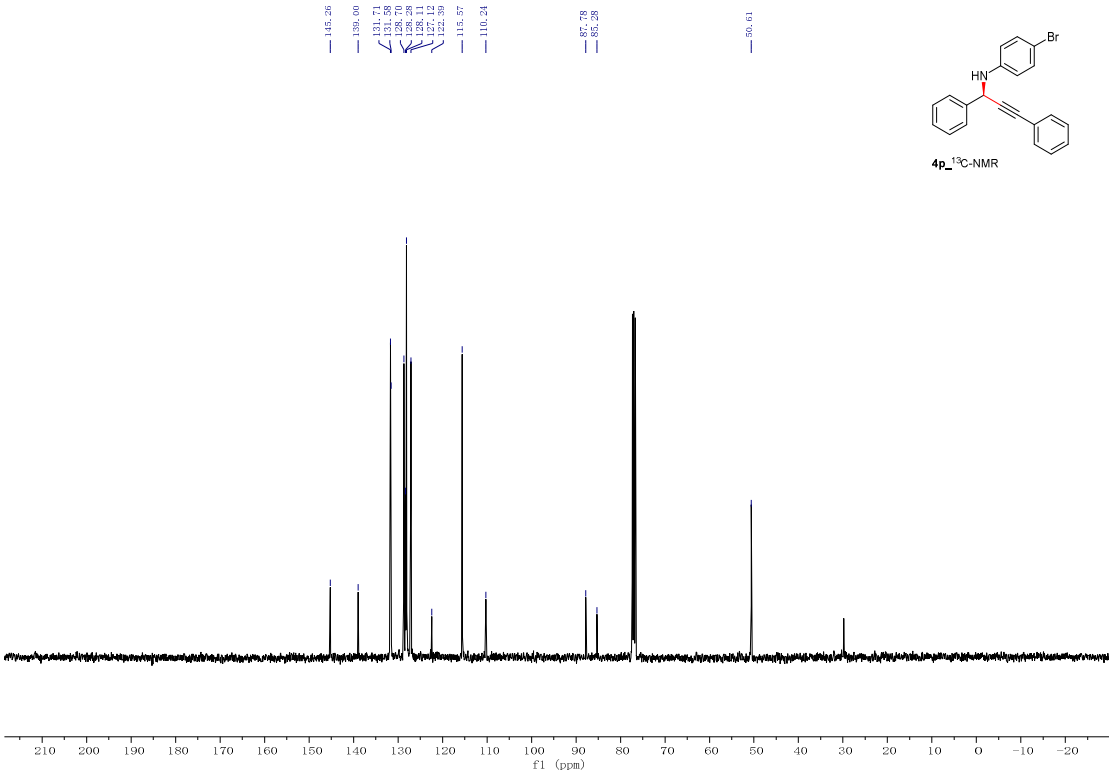
7.28
7.26
7.25
7.23
6.65
6.63
5.43
4.28
Br
HN
4p_1H-NMR
1.85
9.87
1.80
1.05
1.36
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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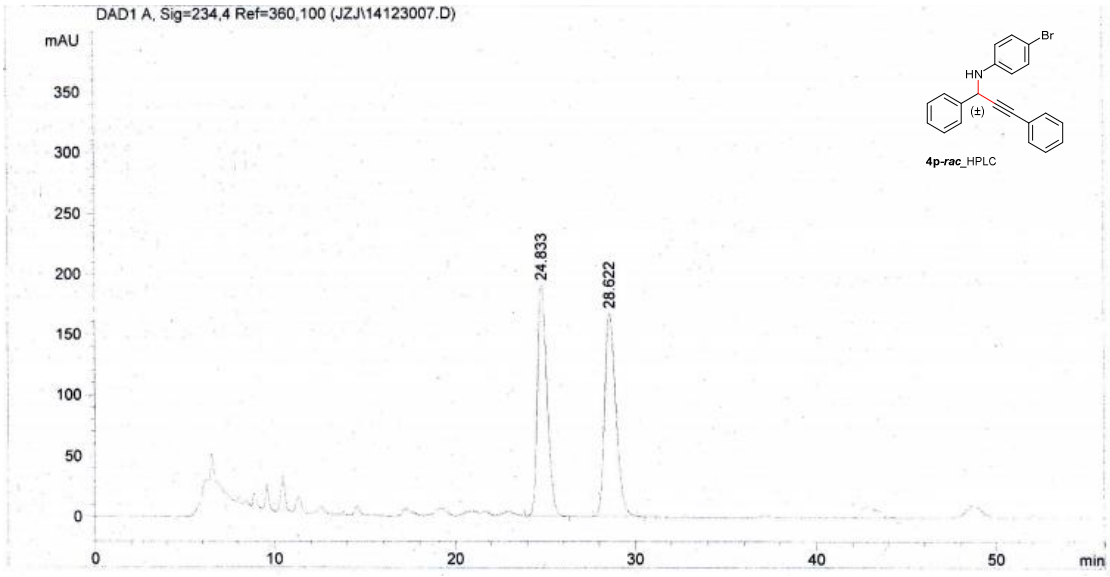
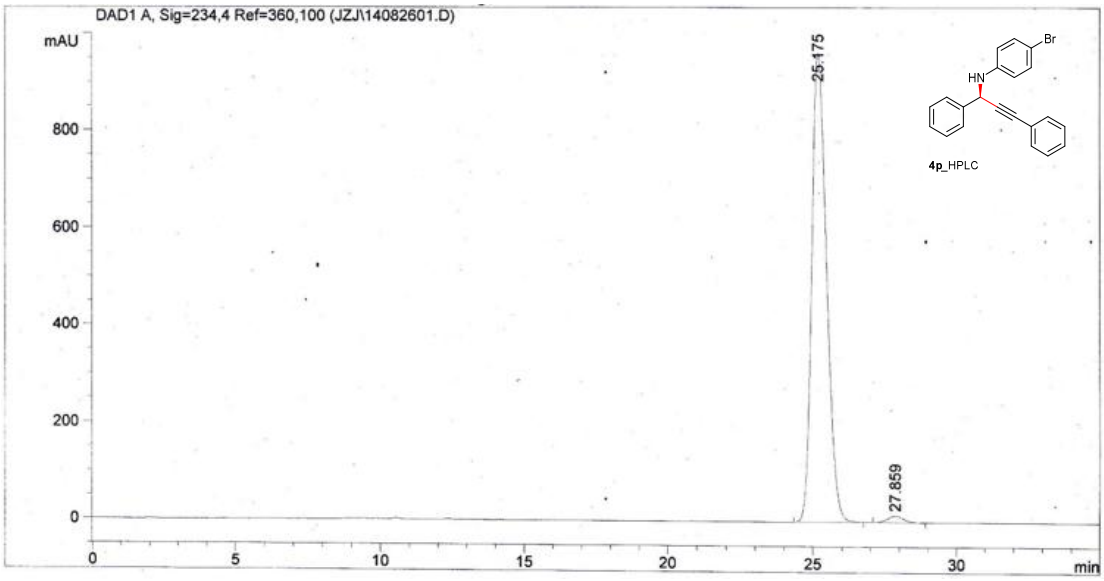
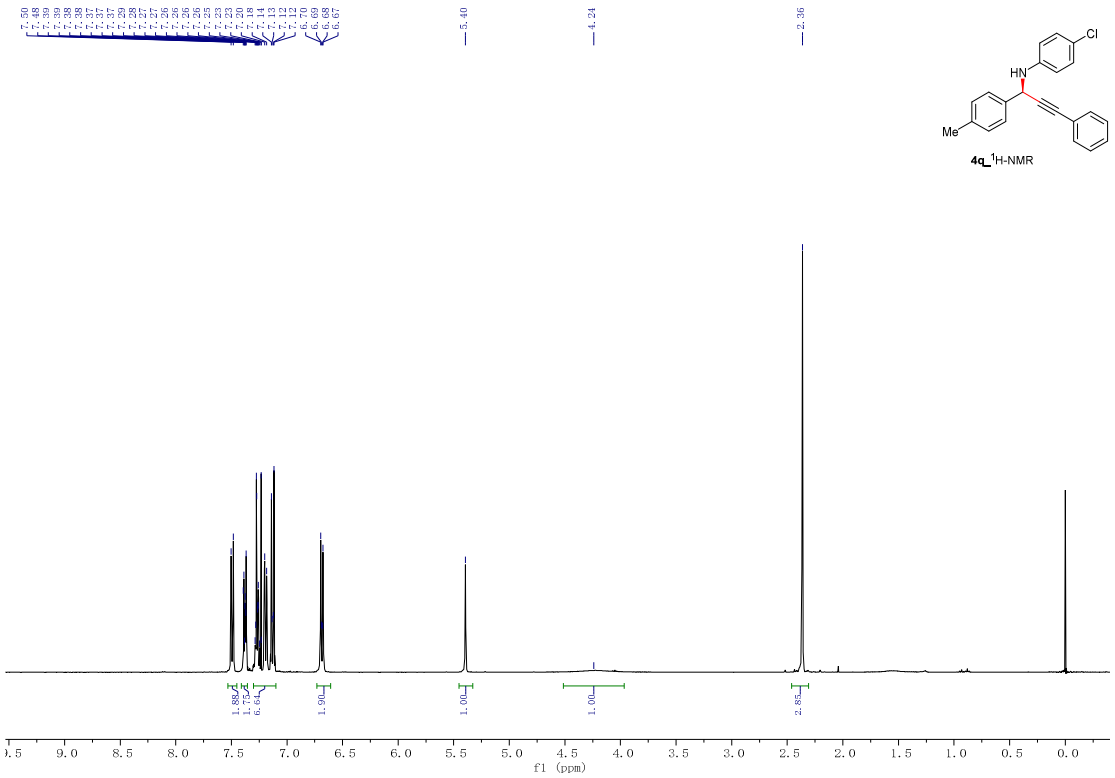
Br
HN
4p_13C-NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.833	VB	0.5754	7087.32959	189.91766	49.4665
2	28.622	BB	0.6704	7240.20703	166.80516	50.5335
Totals :				1.43275e4	356.72282	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.175	BB	0.5457	3.40493e4	960.28058	98.3955
2	27.859	BB	0.6096	555.21844	13.91331	1.6045
Totals :				3.46046e4	974.19389	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7.25
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7.23
7.20
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7.12
7.12
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6.68
6.67
5.40
4.24
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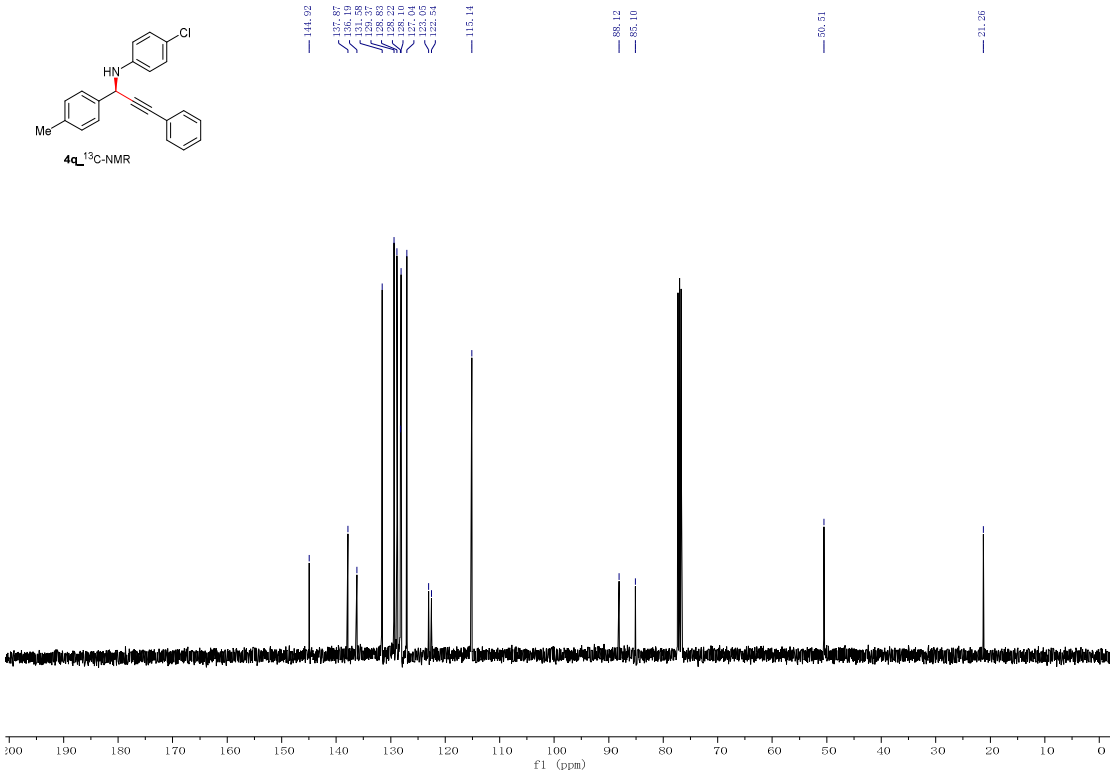
f1 (ppm)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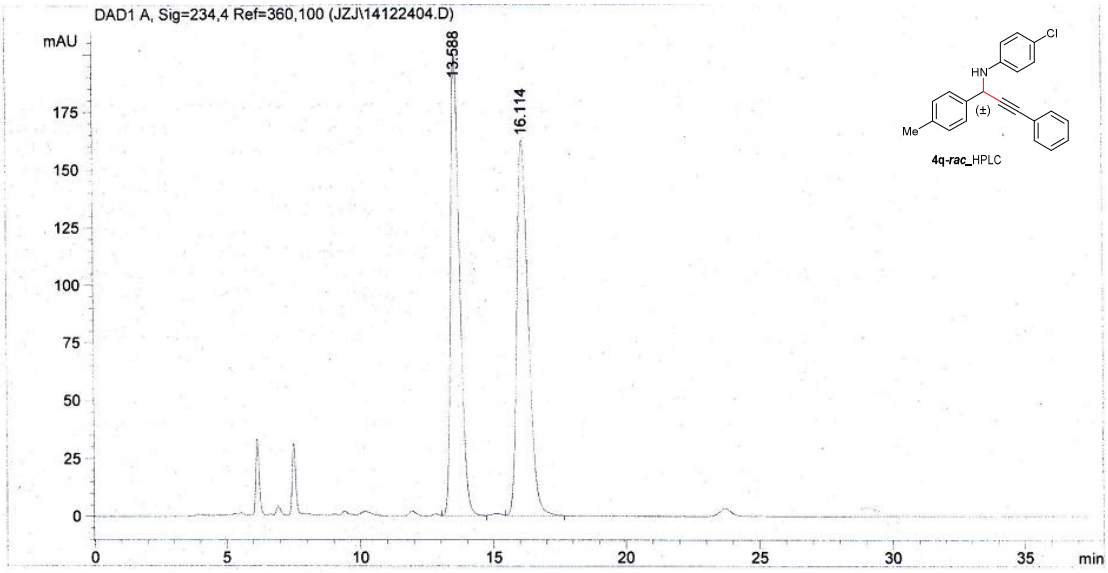
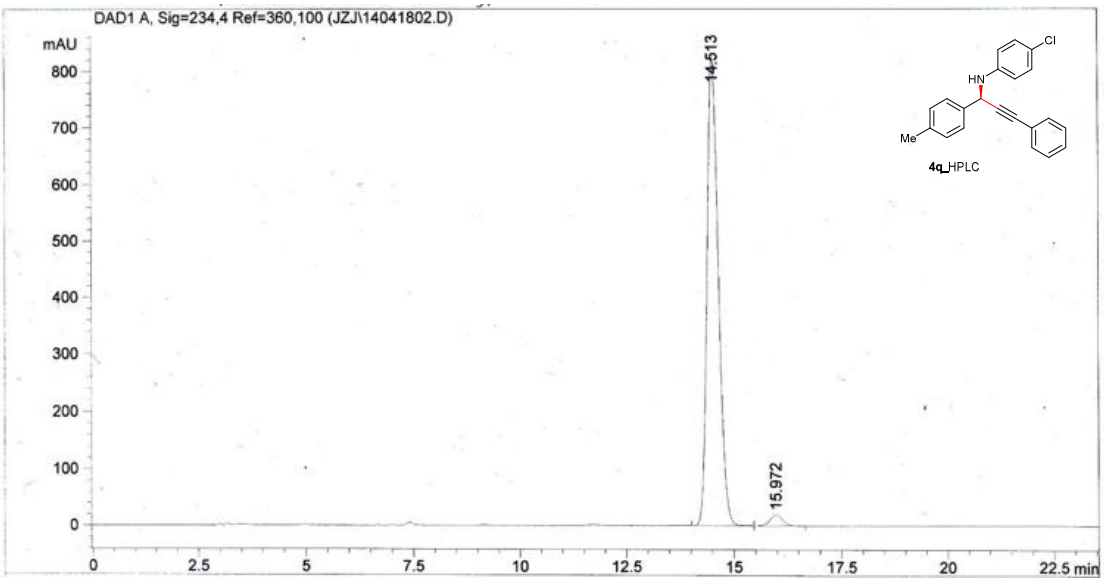
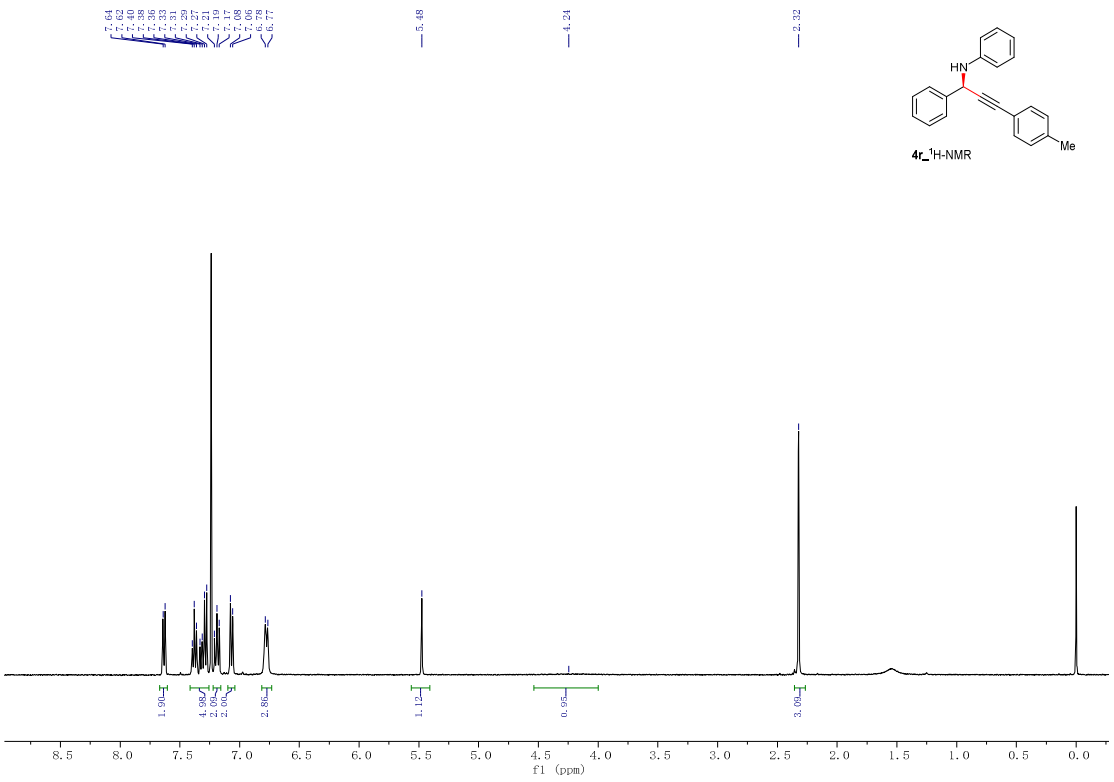
Cl
HN
Me
4q_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.588	VB	0.3723	4796.81299	199.62189	49.6653
2	16.114	VB	0.4616	4861.47461	162.22475	50.3347
Totals :				9658.28760	361.84663	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.513	VV	0.2849	1.49866e4	821.22845	97.4241
2	15.972	VB	0.3098	396.25226	19.77369	2.5759
Totals :				1.53829e4	841.00214	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7.08
7.06
6.78
6.77
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4.24
2.32
HN
Me
4r_1H-NMR
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2.06
2.04
2.86
1.12
0.96
3.04
8.5
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7.5
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6.5
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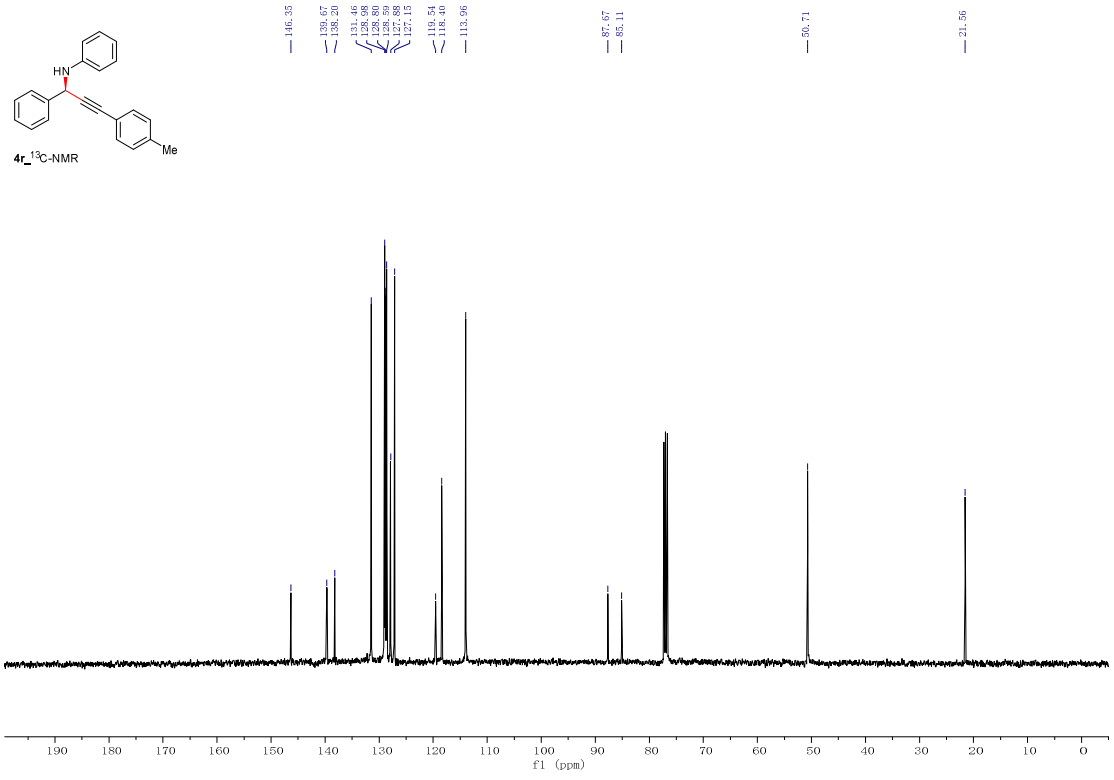
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21.56
HN
Me
4r_13C-NMR
190
180
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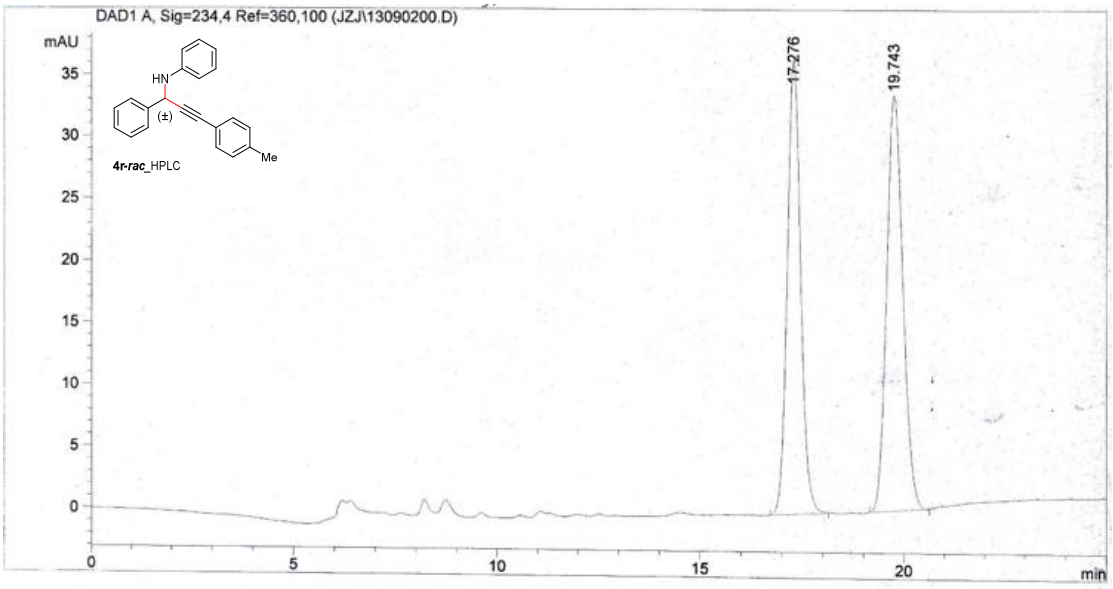
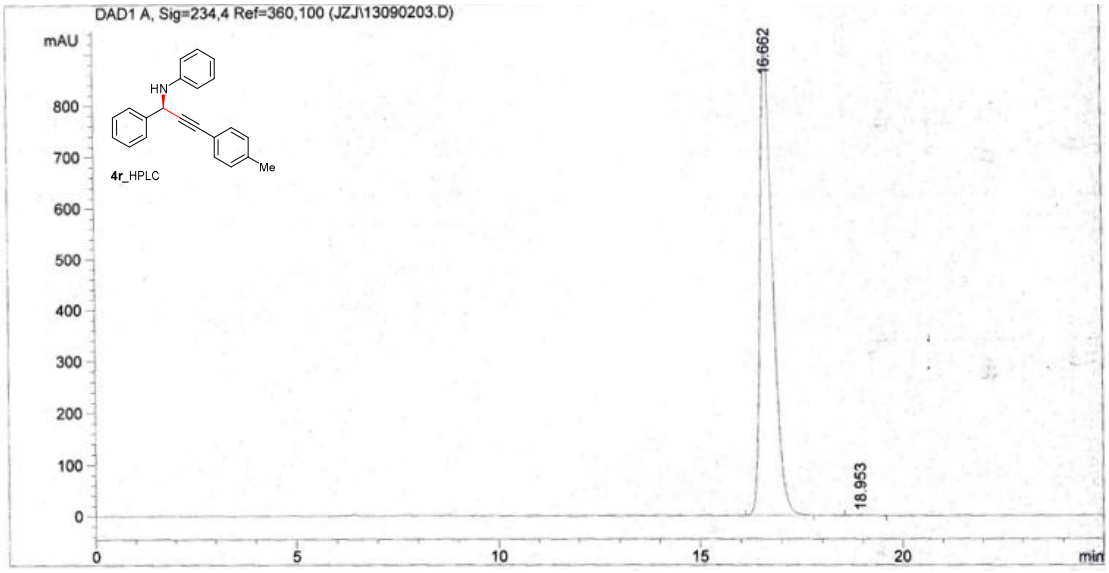
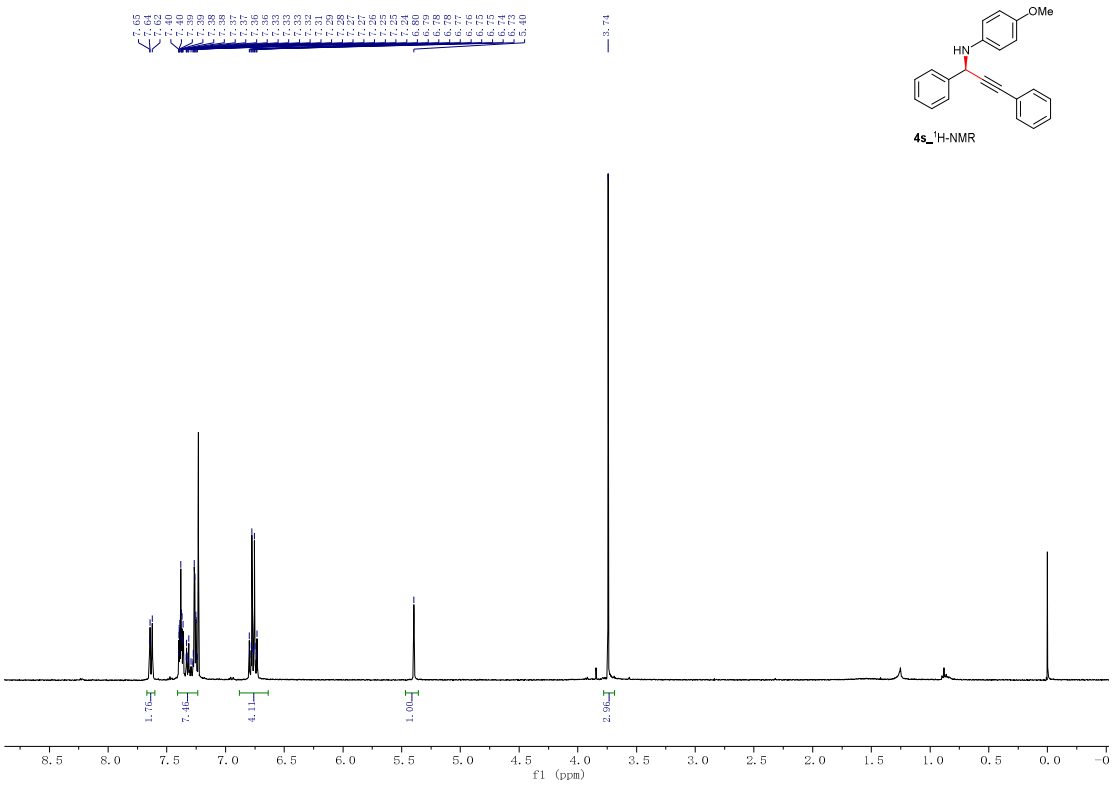
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.276	PB	0.3479	823.91992	36.41933	47.0738
2	19.743	BP	0.4295	926.35162	33.19777	52.9262
Totals :				1750.27155	69.61710	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.662	BB	0.3358	1.97532e4	900.85382	99.8368
2	18.953	BP	0.3647	32.28425	1.40155	0.1632
Totals :				1.97854e4	902.25537	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6.77
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6.75
6.75
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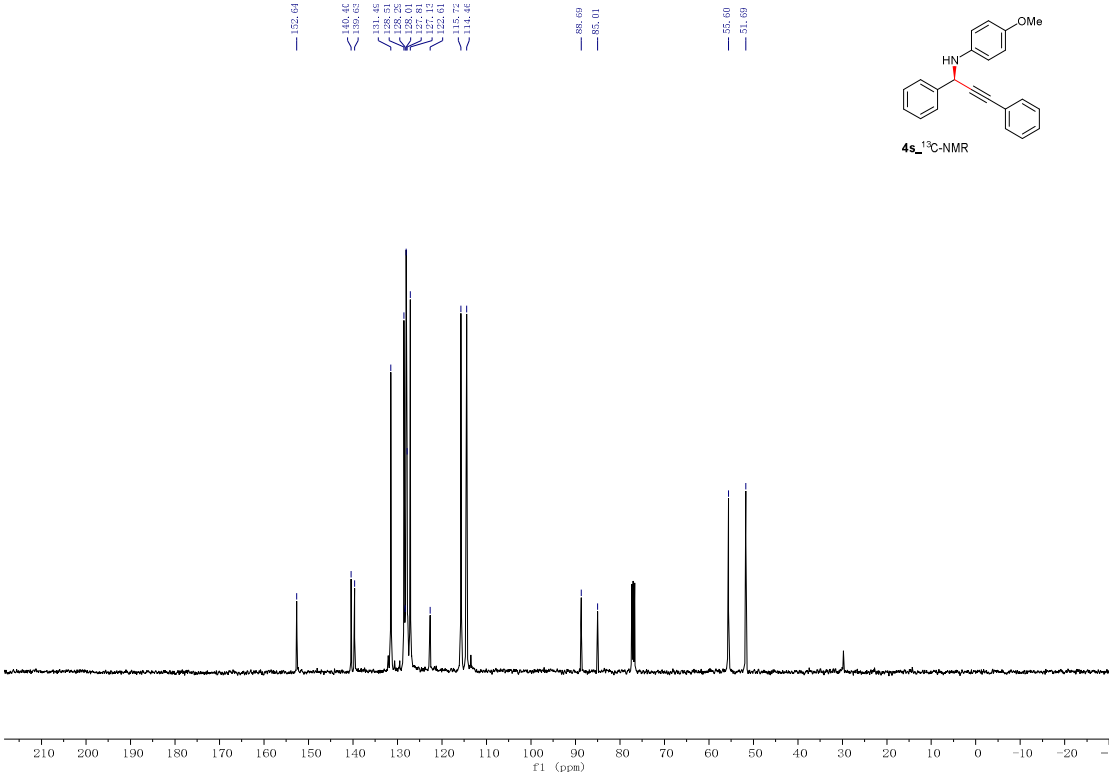
f1 (ppm)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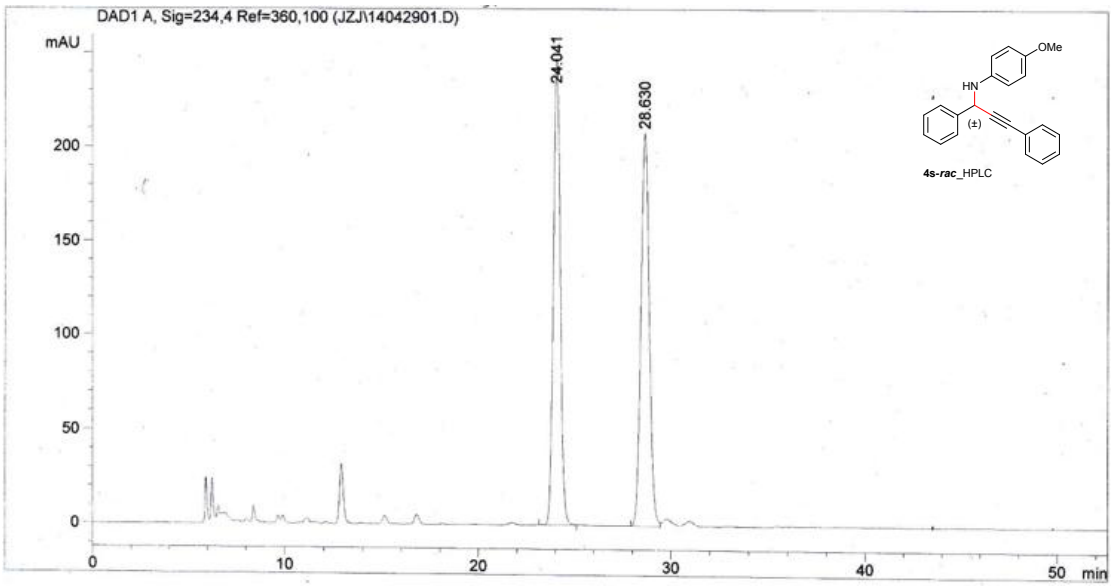
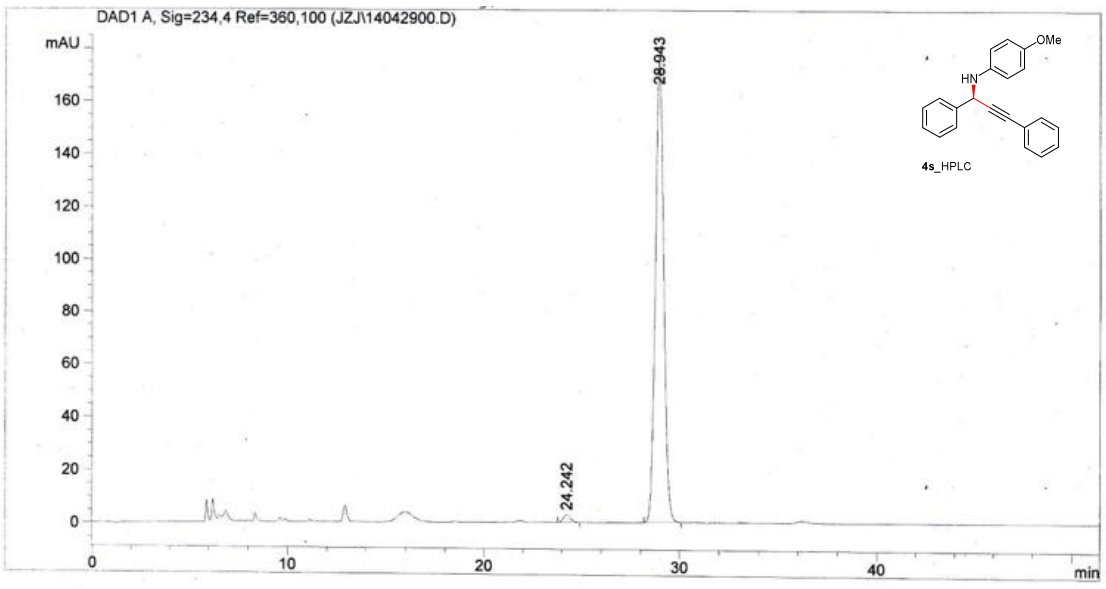
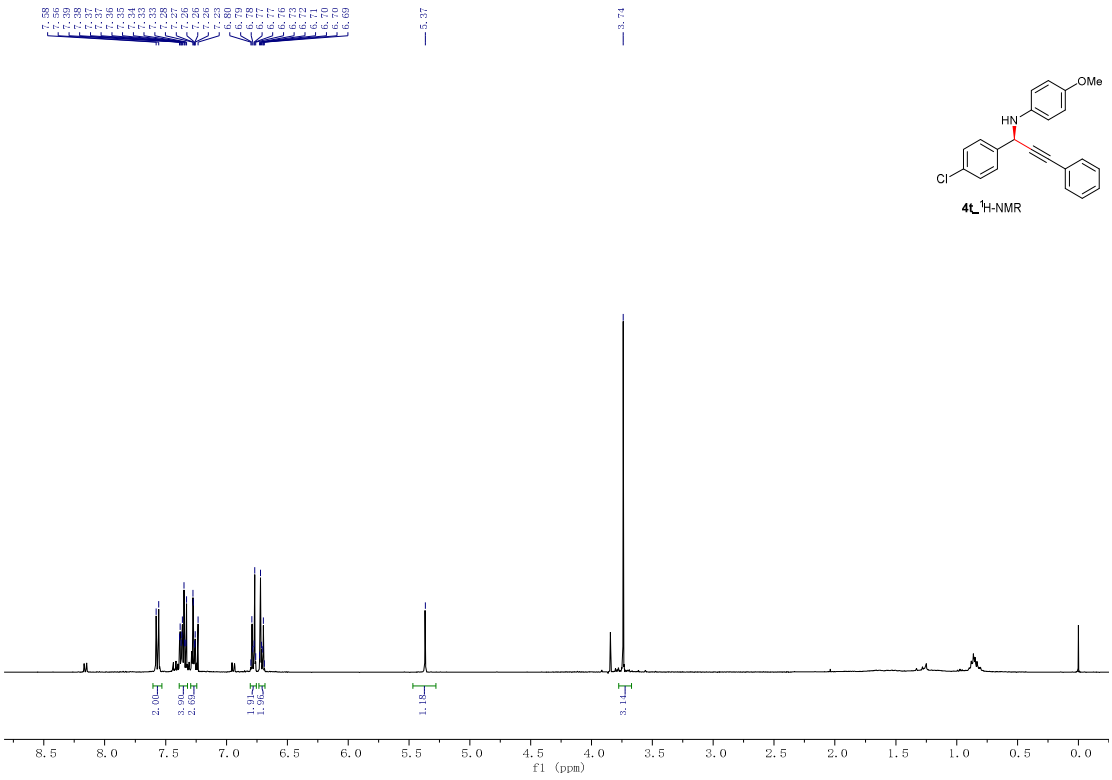
OMe
HN
4s_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.041	BB	0.3899	6212.96289	246.63480	50.0028
2	28.630	BV	0.4656	6212.27295	207.32950	49.9972
Totals :				1.24252e4	453.96429	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.242	BB	0.3925	72.78056	2.86333	1.3542
2	28.943	BB	0.4702	5301.74365	174.62524	98.6458
Totals :				5374.52421	177.48857	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5.37
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OMe
HN
Cl
4t 1H-NMR
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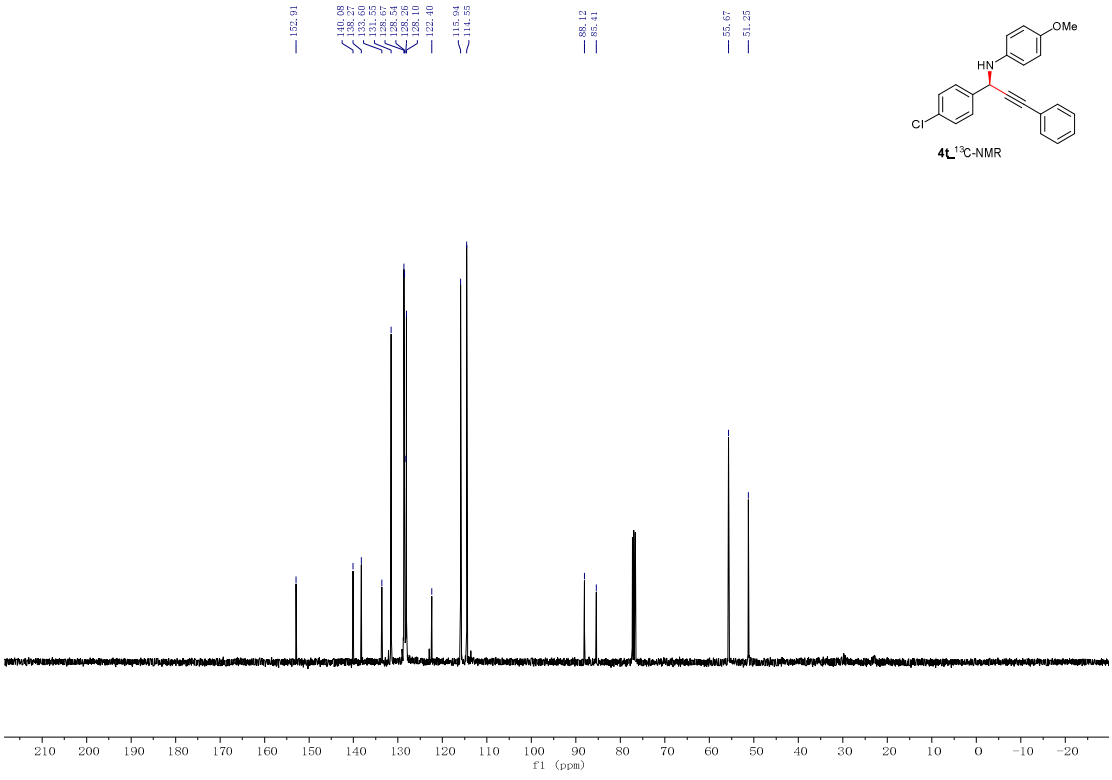
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55.67
51.25
OMe
HN
Cl
4t 13C-NMR
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200
190
180
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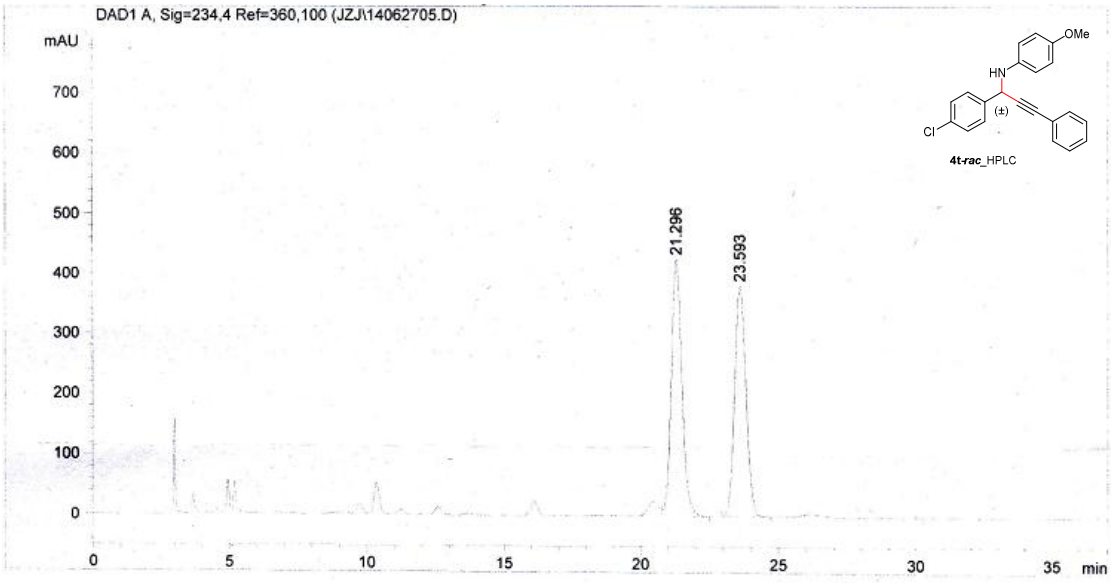
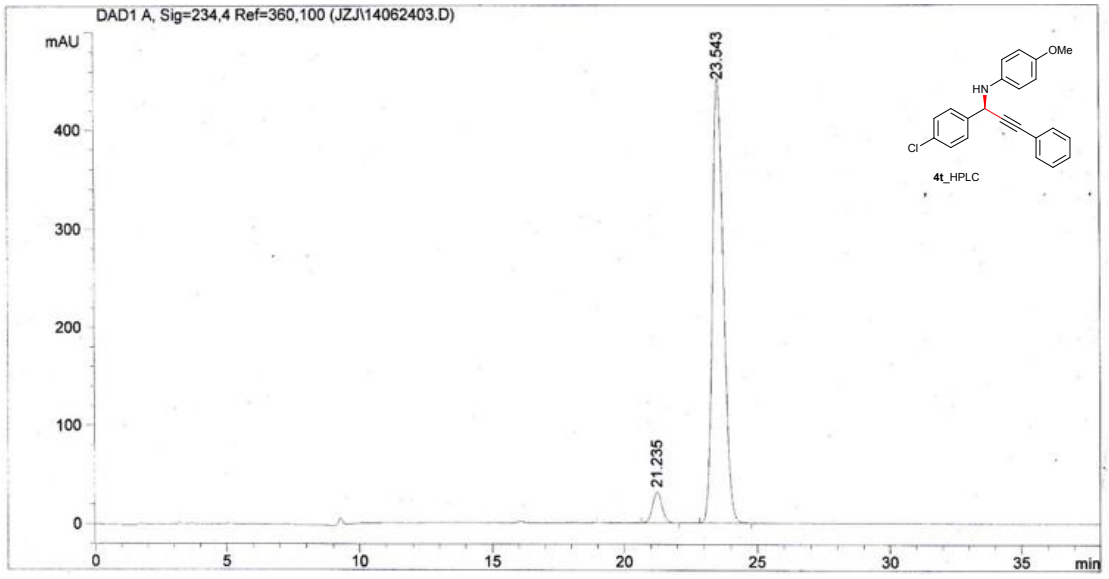
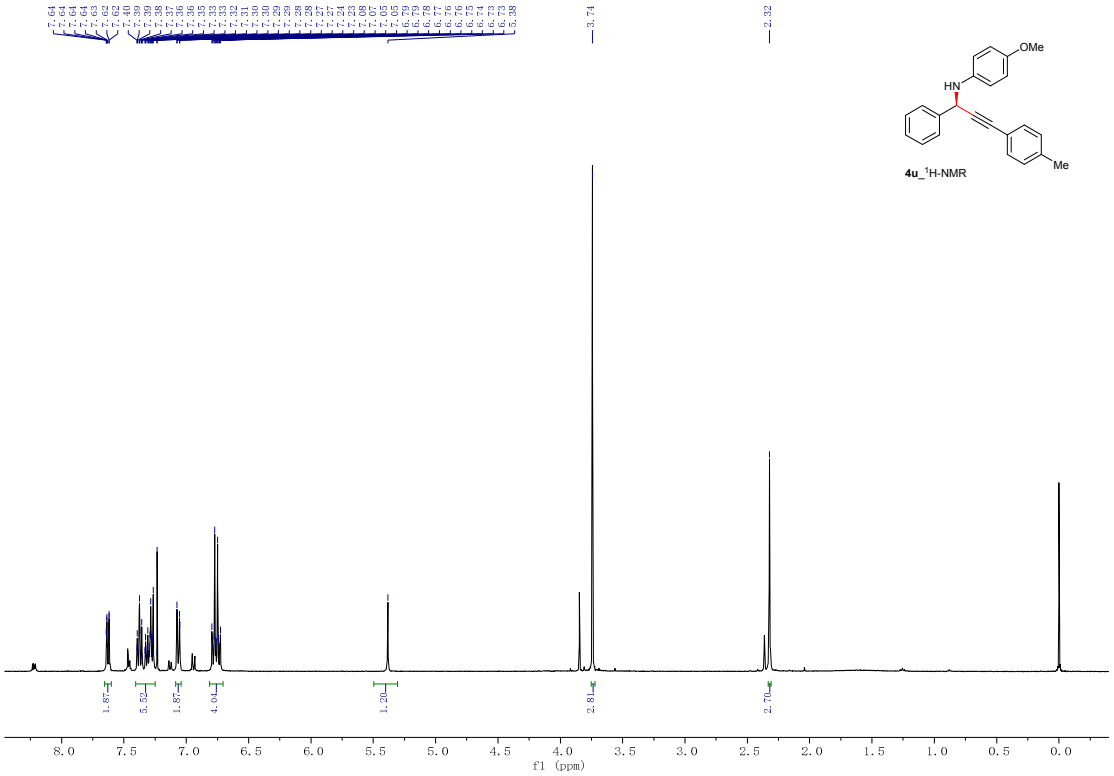


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.296	VB	0.4071	1.13233e4	424.66837	51.0669
2	23.593	BB	0.4447	1.08502e4	380.52472	48.9331
Totals :				2.21735e4	805.19308	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.235	BP	0.3974	791.64600	31.05952	5.7898
2	23.543	BB	0.4410	1.28814e4	451.30472	94.2102
Totals :				1.36730e4	482.36424	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6.73
5.38
3.74
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HN
Me
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6.5
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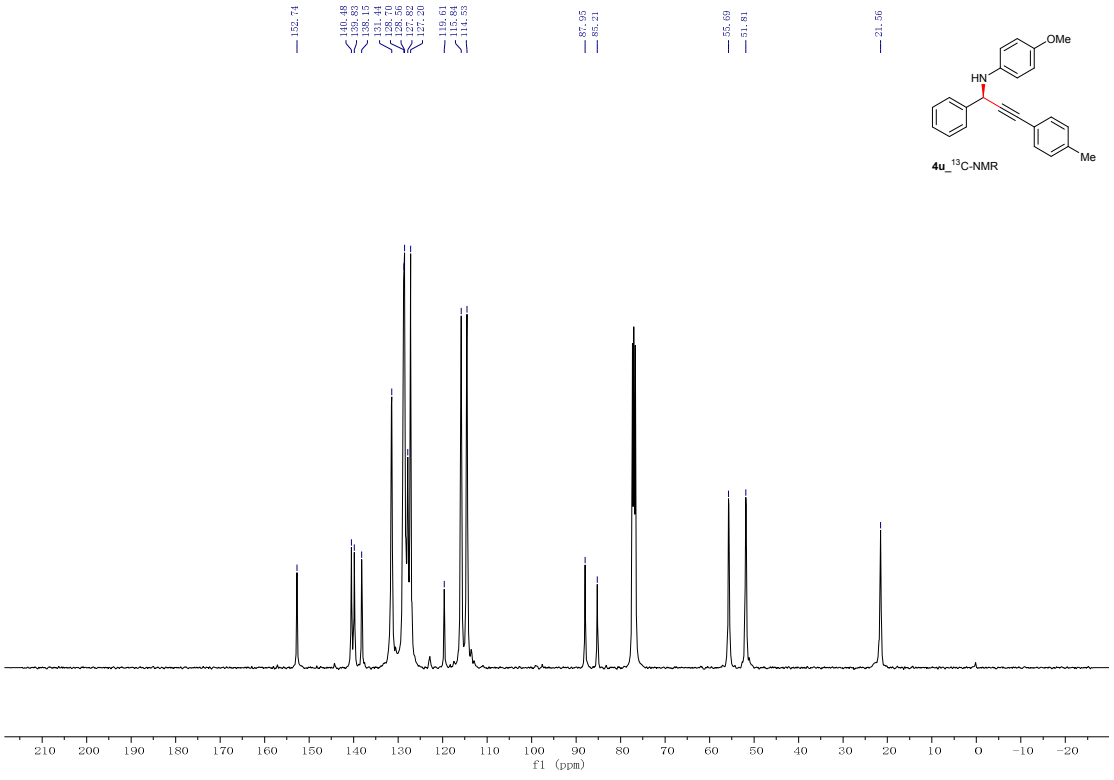
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HN
Me
4u_13C-NMR
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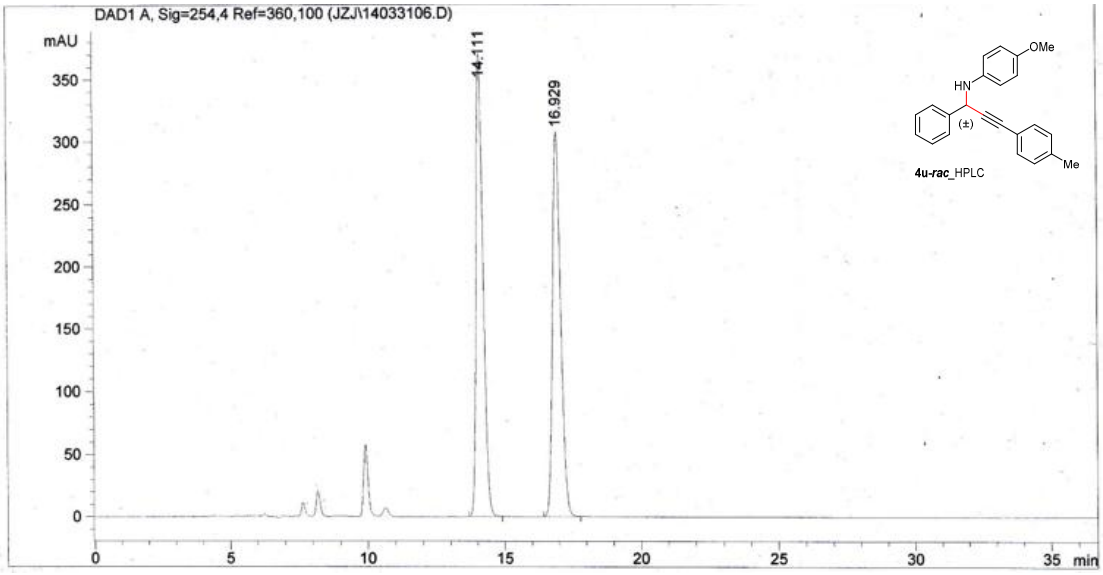
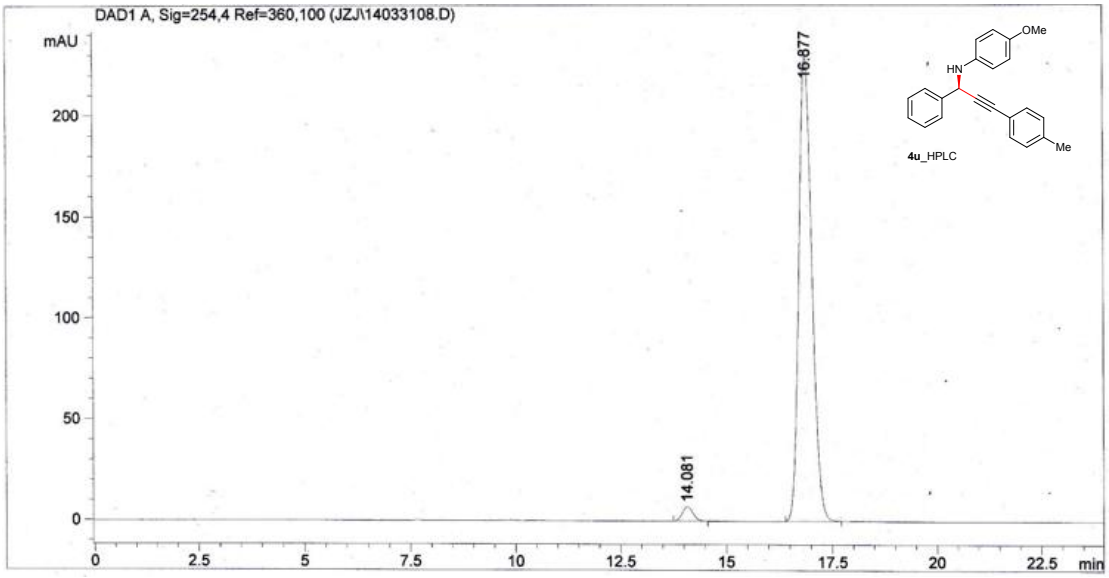
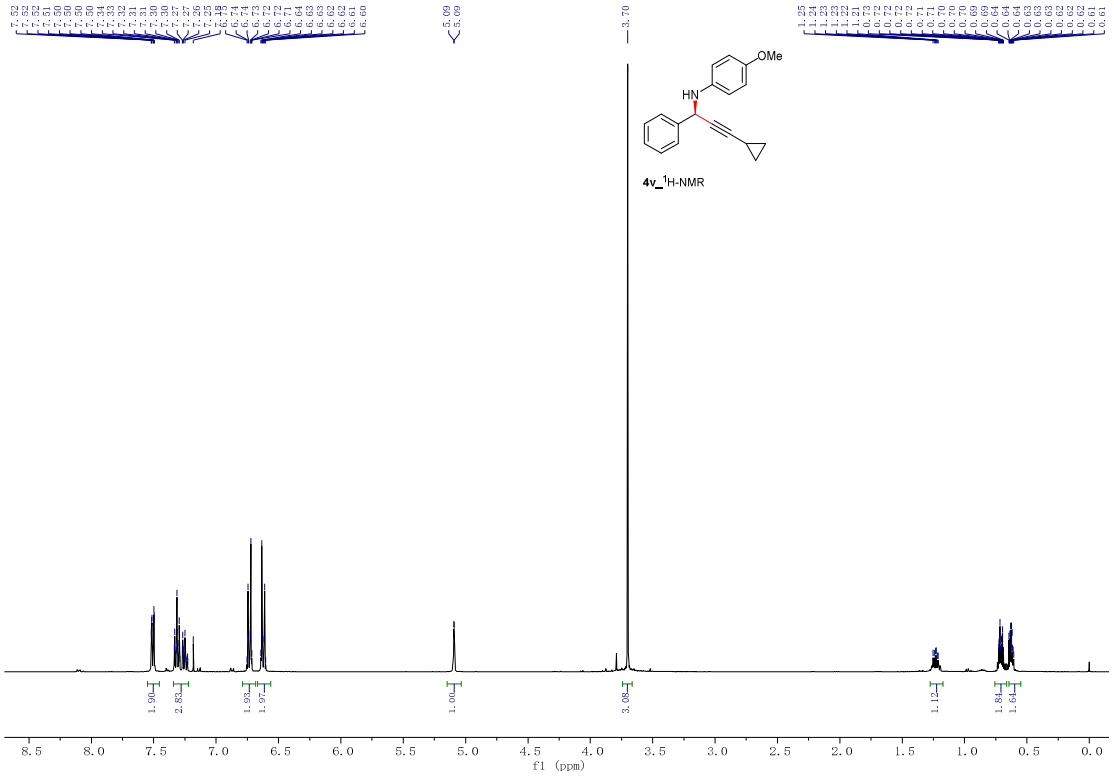
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.111	BB	0.2787	6551.59814	369.82031	50.0024
2	16.929	BB	0.3331	6550.97803	306.75696	49.9976
Totals :				1.31026e4	676.57727	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.081	BB	0.2715	125.77978	7.21120	2.5064
2	16.877	BB	0.3279	4892.46777	230.26598	97.4936
Totals :				5018.24755	237.47718	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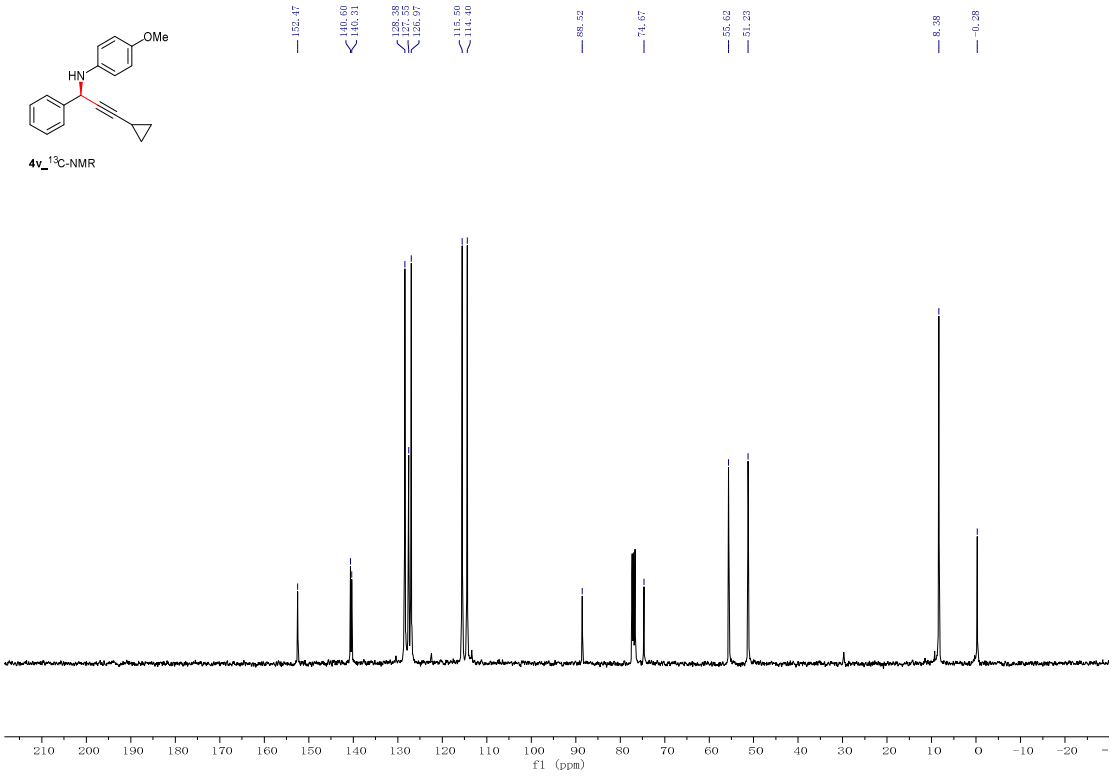
f1 (ppm)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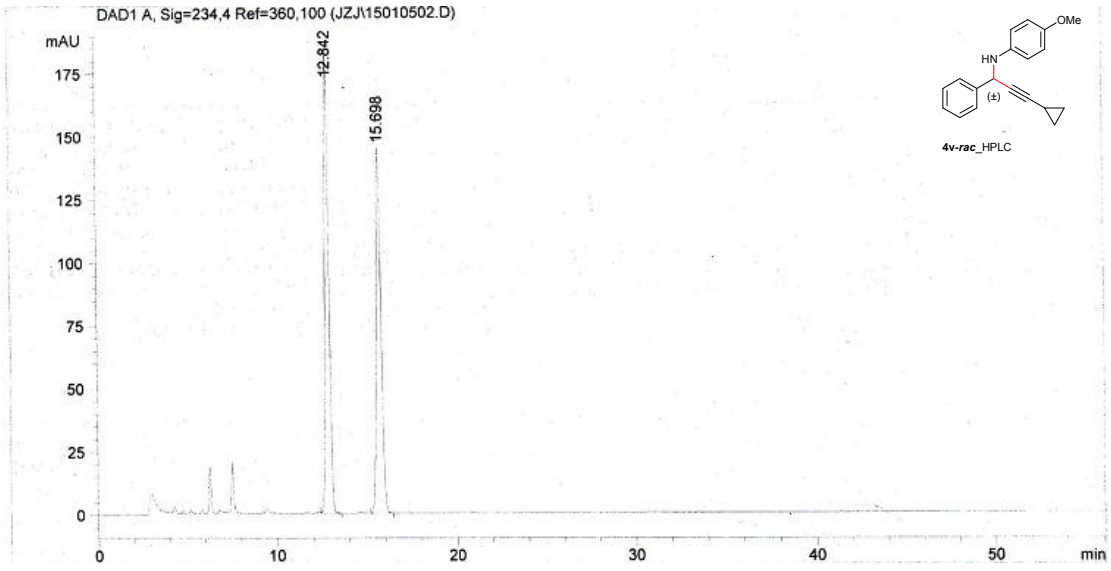
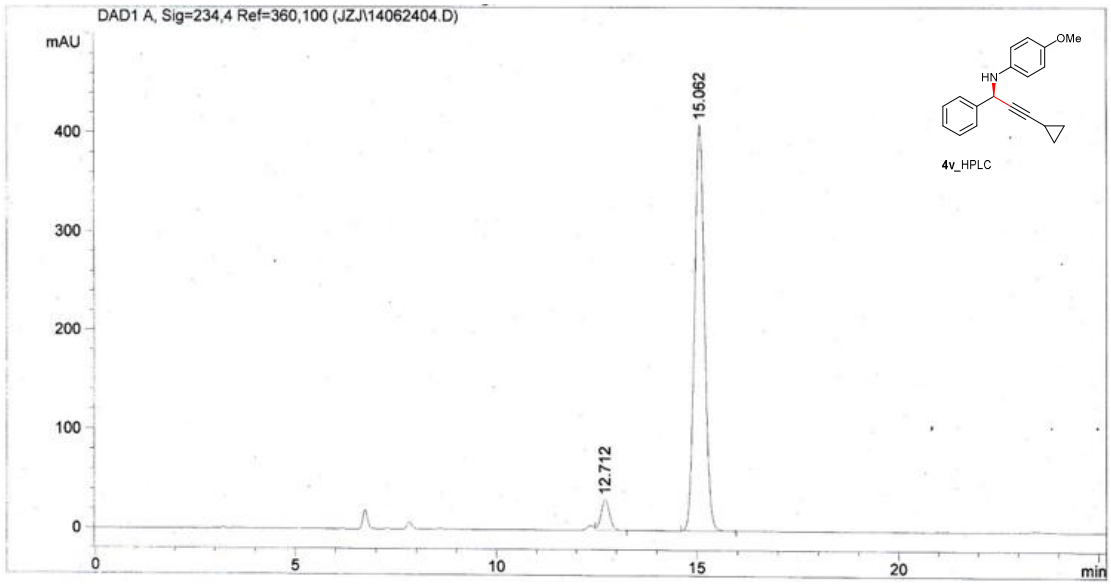
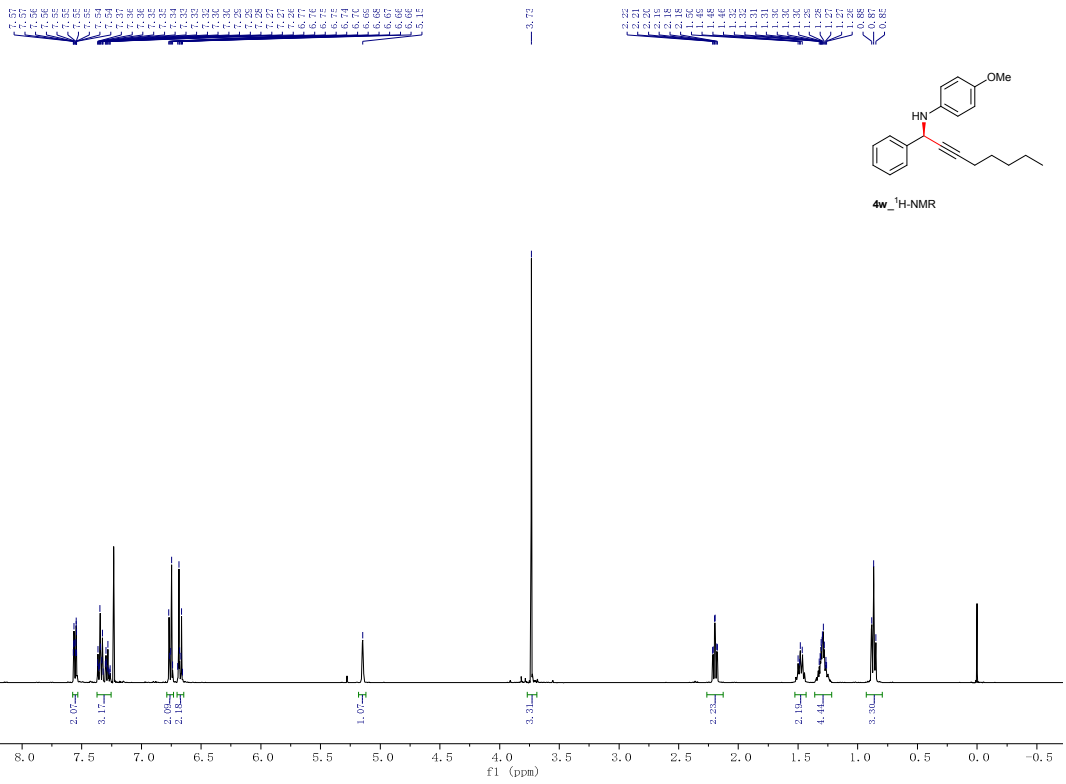
4v_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.842	VB	0.2370	2764.66162	182.19524	50.0849
2	15.698	BB	0.2981	2755.28662	144.70485	49.9151
Totals :				5519.94824	326.90009	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.712	VB	0.2279	458.79721	31.14288	6.1357
2	15.062	BB	0.2646	7018.66064	408.13318	93.8643
Totals :				7477.45786	439.27605	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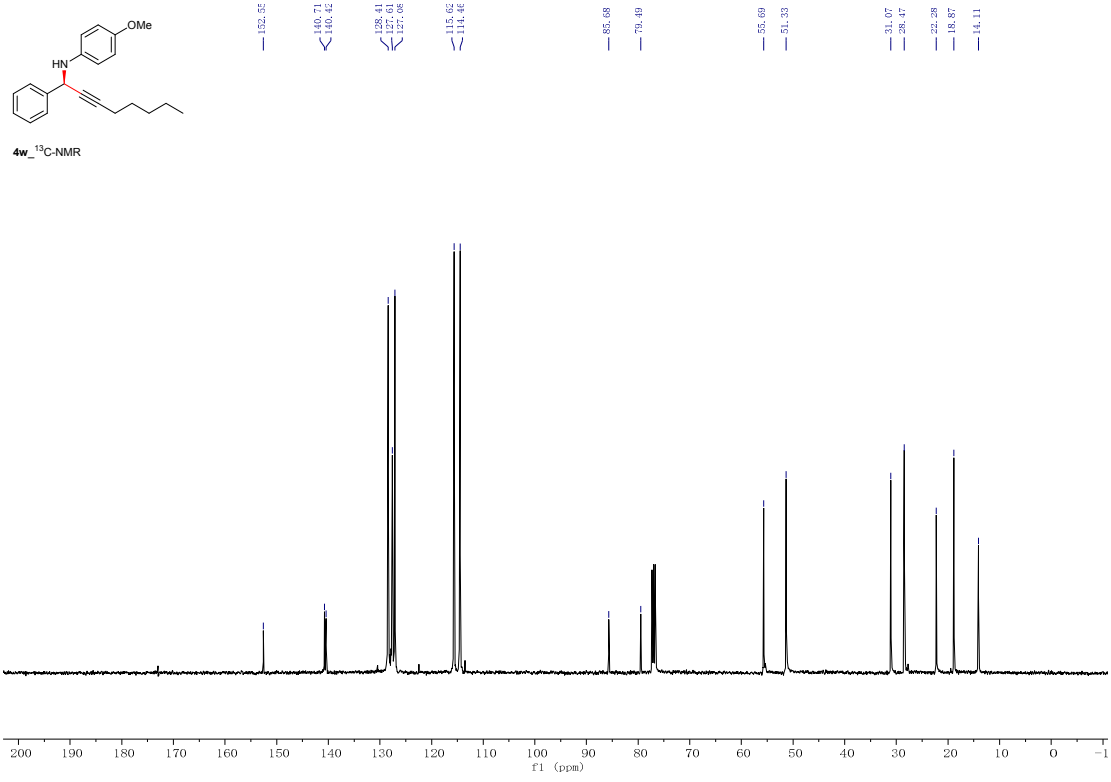
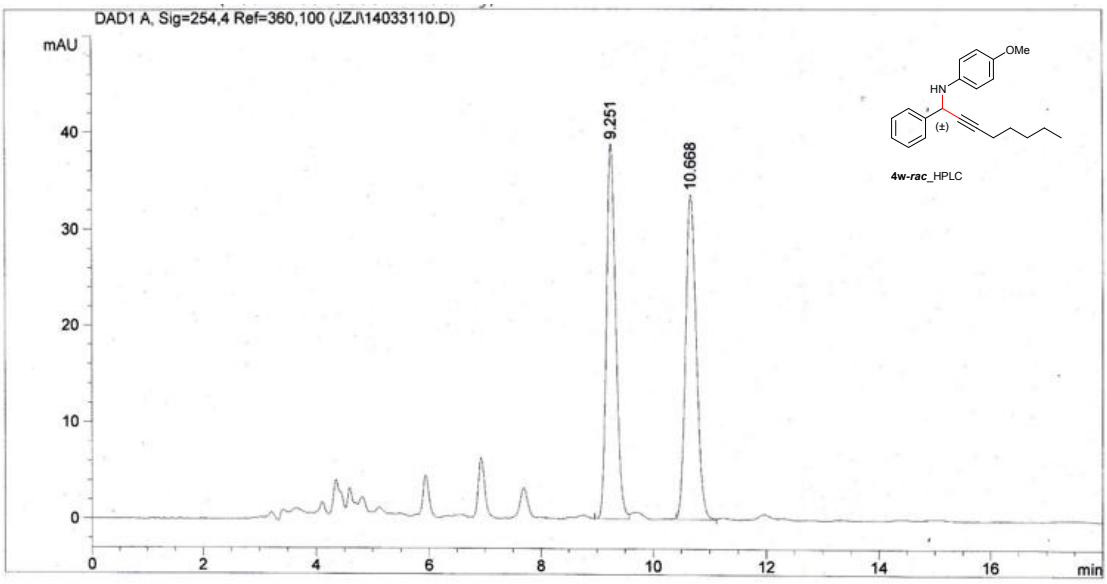
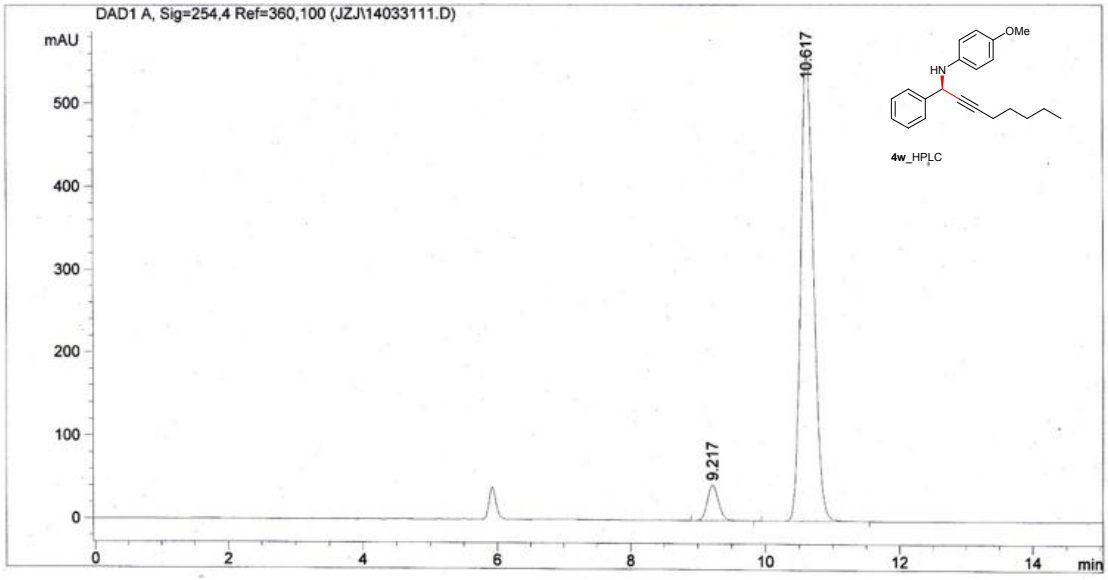
4w_1H-NMR
f1 (ppm)


OMe
HN
4w_13C-NMR
f1 (ppm)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.251	VV	0.1775	442.25922	38.65802	50.0923
2	10.668	BB	0.2056	440.63022	33.46254	49.9077
Totals :				882.88943	72.12056	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.217	VV	0.1777	488.64297	42.65104	6.1814
2	10.617	VV	0.2070	7416.37158	558.25519	93.8186
Totals :				7905.01456	600.90623	