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Supporting Information

Copper-Catalyzed Asymmetric Propargylation of Imines Enabled by a Biphenol-Based Phosphoramidite Ligand

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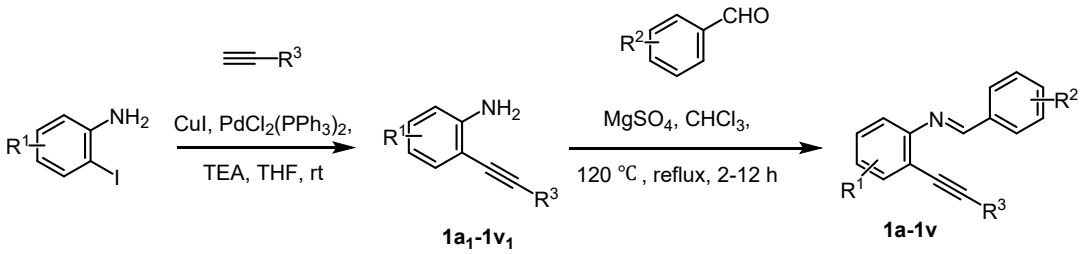
1. General Information

All reactions were carried out under the argon atmosphere in flame-dried glassware. Unless otherwise noted, all the reagents were obtained from commercial supplier and used as received without further purification. The solvents used in the reactions were distilled from appropriate drying agents prior to use. Flash column chromatography was performed using 200-300 mesh silica gel. **^{1}H NMR**, **^{13}C NMR** and **^{31}P NMR** spectra were recorded respectively on a Bruker 400 MHz or a Bruker 600 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Enantiomeric ratio (*er*) was determined by **HPLC** analysis on a Shimadzu LC-20A, using Daicel Chiralcel AD-H, AS-H, IC, IA or OD-H columns. or on an Agilent 1260 Infinity II LC System. Optical rotations were measured at PerkinElmer Model 341 LC Polarimeter. High resolution mass spectra were obtained on Bruker Daltonics micr OTOF-Q II spectrometer in ESI mode. The configurations of **1a** and **3a** were assigned by the X-ray analysis and the configurations of other products were assigned by analogy. The X-ray single-crystal determination was performed on Bruker D8 VENTURE X-ray single crystal diffractometer.

2. Preparation of Imines

The **$1a_1$-$1v_1$** were synthesized according to literature procedures. [1-2]



$1a_1$-$1v_1$ **1a-1v**

1a R^1= H, R^2 = 4-NO_2, R^3= Ph
1b R^1= H, R^2 = 3-NO_2, R^3= Ph
1c R^1= H, R^2 = 2-NO_2, R^3= Ph
1d R^1= H, R^2 = 3-Br, R^3 = Ph
1e R^1= H, R^2 = 4-CN, R^3 = 4-MePh
1f R^1= H, R^2 = 4-Me, R^3 = Ph
1g R^1 = 5-Cl, R^2 = 4-NO_2, R^3 = Ph
1h R^1 = 5-Br, R^2 = 4-NO_2, R^3 = Ph
1i R^1 = 5-Me, R^2 = 4-NO_2, R^3 = Ph
1j R^1 = H, R^2 = 4-NO_2, R^3 = 4-COOMePh
1k R^1 = H, R^2 = 4-NO_2, R^3 = 4-ClPh
1l R^1 = H, R^2 = 4-NO_2, R^3 = 4-BrPh

1m R^1 = H, R^2 = 4-NO_2, R^3 = Vinyl
1n R^1 = H, R^2 = 2, 4-NO_2, R^3 = Ph
1o R^1 = 3-Cl, R^2 = 2, 4-NO_2, R^3 = Ph
1p R^1 = 5-Cl, R^2 = 2, 4-NO_2, R^3 = Ph
1q R^1 = 5-Br, R^2 = 2, 4-NO_2, R^3 = Ph
1r R^1 = 4-Me, R^2 = 2, 4-NO_2, R^3 = Ph
1s R^1 = 5-Me, R^2 = 2, 4-NO_2, R^3 = Ph
1t R^1 = 4-OMe, R^2 = 2, 4-NO_2, R^3 = Ph
1u R^1 = Ph, R^2 = 2, 4-NO_2, R^3 = Ph
1v R^1 = H , R^2 = 2, 4-NO_2, R^3 = $C_{10}H_7$

Figure S1. The synthesis of alkynyl imines

Procedure 1 (1a-1v):

To a stirred solution of $MgSO_4$(10 g, 90 mmol) in $CHCl_3$ (50 mL) were added anilines (3 mmol), and corresponding aldehydes (3 mmol). The reaction mixture was refluxed at 120 ℃ for 2–12 h. Until the starting material disappeared on **^{1}H NMR**, the reaction mixture was filtered through short pad of celite and the filtrate was concentrated under reduced pressure to afford imines **1a-1v** which were used as such without further purification (**Figure S1**).

[1] Kusama, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc*. **2002**, *124*, 11592.
[2] Yuan, S.; Yan, Q.; Wang, D.; He, L.; He, C.; Chu, W.; Liu, Q. *Org. Lett*. **2021**, *23*, 4823.

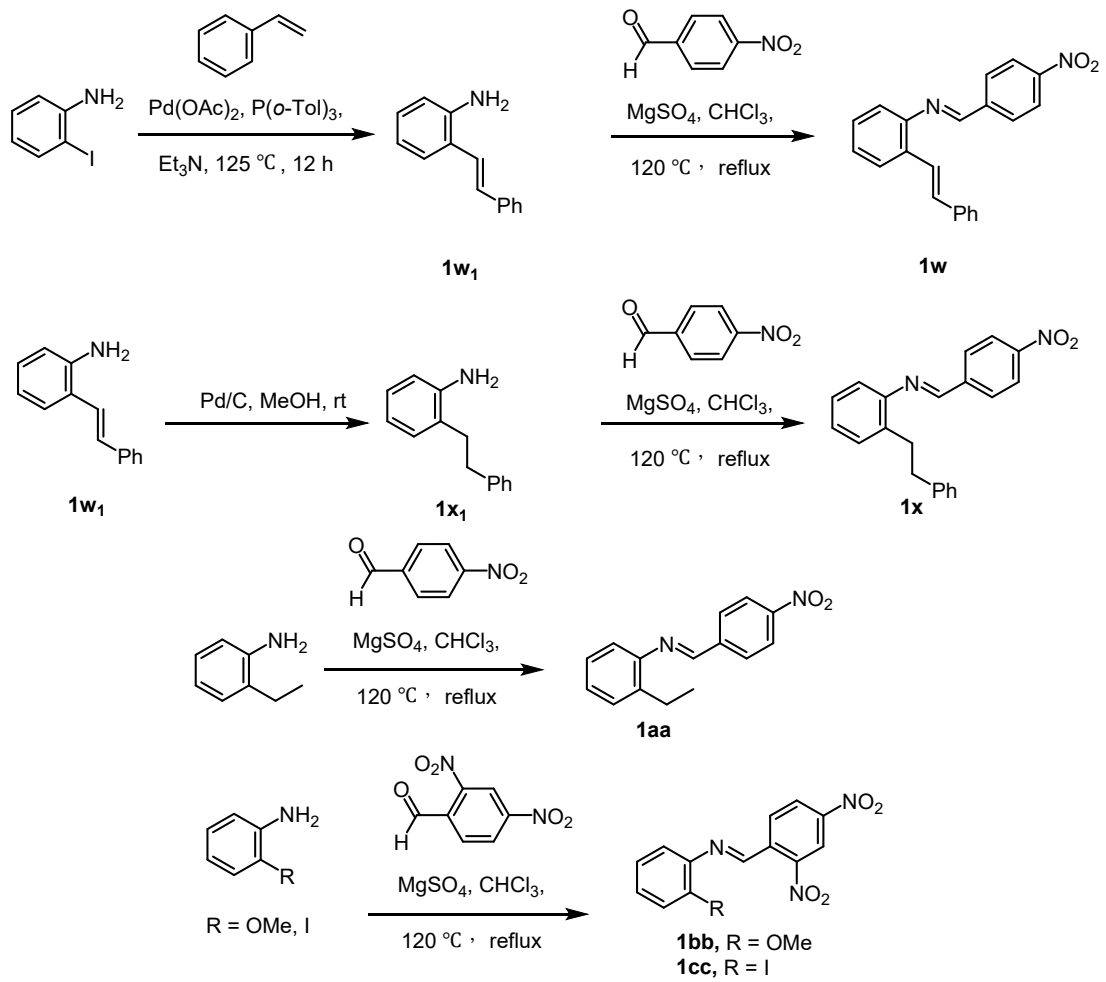


Figure S2. The synthesis of **1w, 1x, 1aa, 1bb, 1cc**

Procedures 2 (1w, 1x, 1aa, 1bb, 1cc):

To a dried round-bottom flask with the **1w$_1$** (975 mg, 5 mmol) and Pd/C (532 mg, 10 mol%) was added a solution of MeOH (20 mL), then purged with hydrogen 3 times and protected with hydrogen atmosphere. The reaction mixture was stirred at the room temperature for 12 h until starting material disappeared on TLC. The mixture was filtered through celite using CH_2Cl_2 (15 mL) and then concentrated in vacuo. The residue was purified by column chromatography on silica gel with a solution of hexane and ethyl acetate (10:1) to give the desired product **1x$_1$** in 90% yield. The synthesis of **1w**, **1x, 1aa, 1bb, 1cc** follows the procedure 1. (**1w$_1$** was synthesized according to the literature procedures.[3])

[3] Li, D. X.; Kim, J.; Yang, J. W.; Yun, J. *Chem. Asian J*. **2018**, *17*, 2365.

3. The Preparation of L10

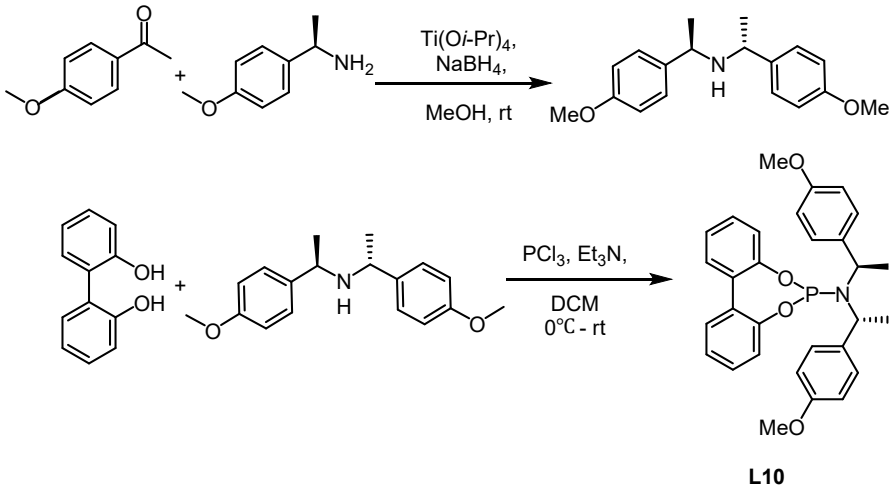


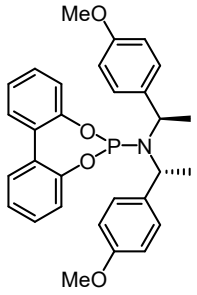
Figure S3. The synthesis of **L10**

A mixture of the 4-methoxyacetophenone (1.5 mL, 10 mmol), titanium (IV) isopropoxide (3.9 mL, 13 mmol) and (R)-phenylethylamine (4.4 mL, 30 mmol) in absolute MeOH (20 mL) was stirred under argon at room temperature for 5–6 h. Sodium borohydride (378 mg, 10 mmol) was then added at -78 ºC and the resulting mixture was stirred for an additional 2 h raising the temperature to 25 °C. The reaction was then quenched by adding water (10 mL). Stirring was maintained at room temperature for 20 min then the reaction mixture was acidified with hydrochloric acid (1 M, 5 mL). After filtration over a pad of celite, washing with water and ethyl acetate, the organic layer was separated and the remaining aqueous layer was extracted once with ethyl acetate. The acidic aqueous extracts were treated with aqueous sodium hydroxide (10% NaOH, 5–10 mL) to pH 10–12 and extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the expected crude amine which was recrystallized from MeOH and Et_2O until the dr was above 20:1 to give the desired (R, R)-amines product in 65% yield.

To a solution of triethylamine (30 mmol) in CH_2Cl_2 (5.0 mL) at 0 °C was added phosphorus trichloride (5 mmol). The resulting white solution was stirred at the same temperature for 30 min before the addition of (R, R)-amine (5 mmol). The resulting white suspension was warmed to room temperature and stirred for 4 h. The diphthol (5 mmol) was then added dropwise over 5 min at 0 °C. Then warming to room temperature and stirring for 18 h. The reaction was quenched via the addition of water (30 mL), extracted with CH_2Cl_2 (3 × 20 mL), dried over anhydrous magnesium sulfate and the

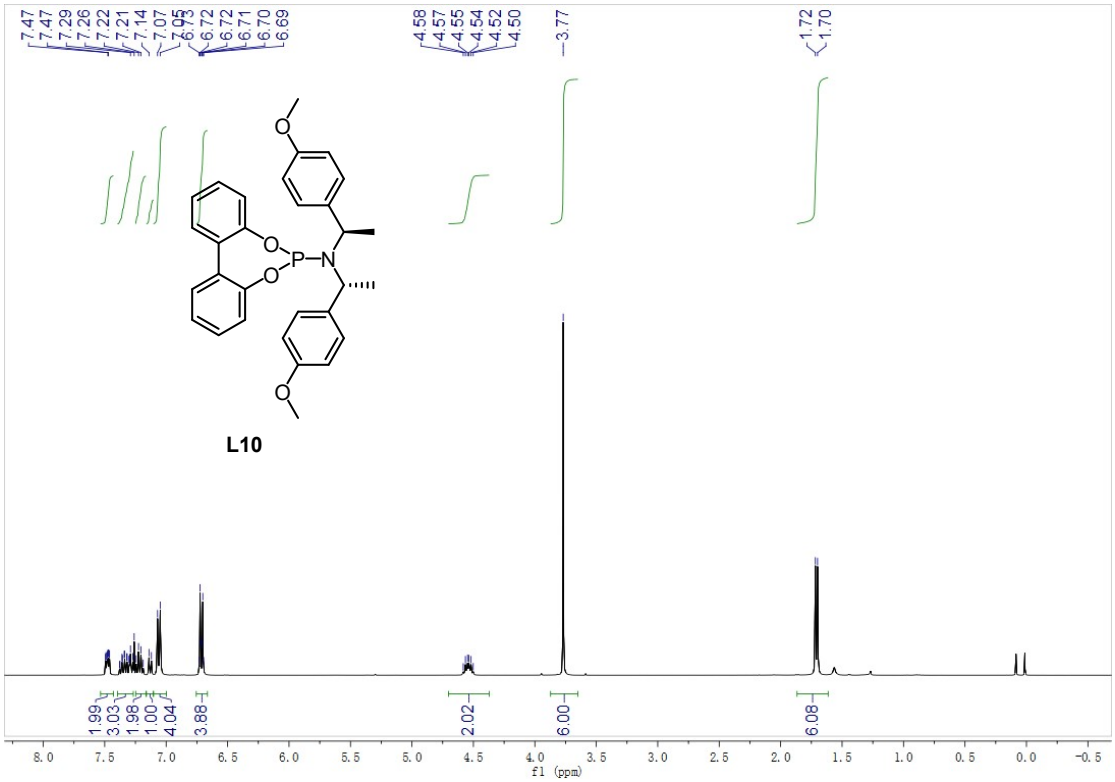
solvent removed in vacuo to afford the crude product as a white foam. The residue was purified by column chromatography on silica gel with hexane and ethyl acetate (60:1) to give the desired product **L10** in 75% yield. (**Figure S3**).

***N,N*-bis((R)-1-(4-methoxyphenyl)ethyl)dibenzo[d,f][1,3,2]dioxaphosphepin-6-amine**

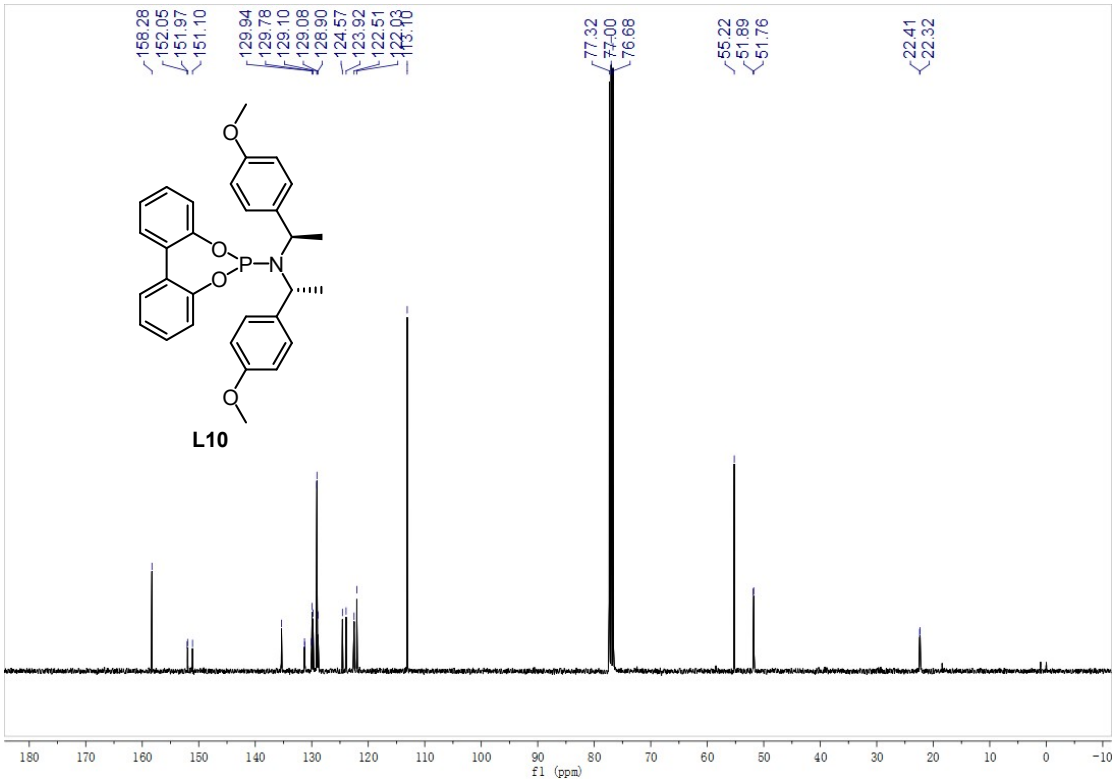


White solid, 75% yield, R_f = 0.3 (petroleum ether/ethyl acetate = 60:1), m. p. 109.2 – 110.7 ℃, $[\alpha]_D^{20}$ = + 343 ° (*c* = 1 mg/mL, THF). **^{1}H NMR (**400 MHz, $CDCl_3$, ppm). **^{1}C NMR** (400 MHz, $CDCl_3$, ppm) δ 7.48 (ddd, *J* = 7.6, 4.1, 1.6 Hz, 2H), 7.40 – 7.27 (m, 3H), 7.22 (dd, *J* = 15.3, 7.7 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 4H), 6.75 – 6.66 (m, 4H), 4.54 (dq, *J* = 14.1, 7.1 Hz, 2H), 3.77 (s, 6H), 1.71 (d, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 158.3, 151.5, 135.3, 131.3, 130.0, 129.1, 124.6, 122.5, 122.0, 113.1, 55.2, 51.8, 22.4. **^{31}P NMR** (162 MHz, $CDCl_3$, ppm) δ 147.0 (t, *J* = 11.4 Hz). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{30}H_{30}NO_4PH^+$ 500.1985; Found 500.1980.

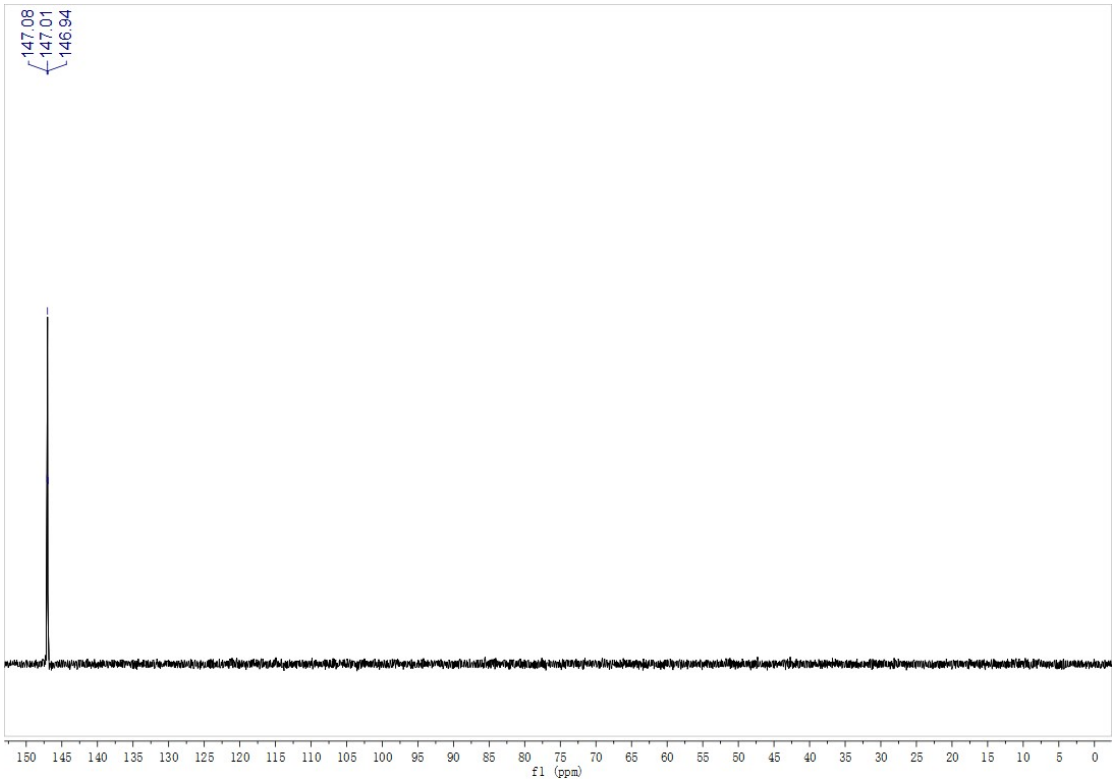
^{1}H NMR Spectra of **L10** (400 MHz, $CDCl_3$)



^{1}C NMR Spectra of **L10** (101 MHz, $CDCl_3$)



^{31}P NMR Spectra of **L10** (162 MHz, $CDCl_3$, ppm)



4. Cu-Catalyzed Asymmetric Propargylation of *N, 1*-diphenylmethanimines

4.1 Typical Procedure

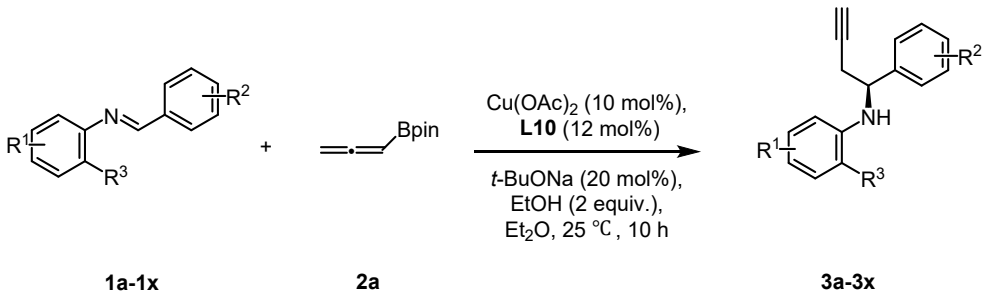
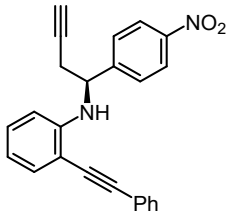


Figure S4. Cu-catalyzed asymmetric propargylation of *N, 1*-diphenylmethanimines

A dried tube filled with the imines **1a–1x** (0.1 mmol), $Cu(OAc)_2$ (2 mg, 0.01 mmol), *t*-BuONa (2 mg, 0.02 mmol) and **L10** (6 mg, 0.012 mmol) was evacuated and purged with argon three times. Afterwards, Et_2O (2 mL), **2a** (22 μL, 0.12 mmol) and EtOH (12 μL, 0.2 mmol) were added via syringe. The solution was kept at room temperature for 10 h. After TLC confirmed full conversion, filtration through a short celite, the solvent was evaporated in vacuo and the crude reaction mixture was purified by column chromatography on silica gel to give the corresponding product **3a-3x** (**Figure S4**). (NOTE: The racemic products were synthesized by using 12 mol% (±)-MonoPhos (CAS 157488-65-8) as ligand)

4.2 Characterization Data for the Products of 3a–3x

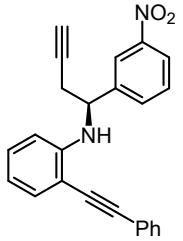
(S)-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3a)



Yellow solid, 95% yield, 90:10 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), m. p. 99.1 – 99.5 ℃, $[\alpha]_D^{20}$ = + 30.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 7.3, 1.7

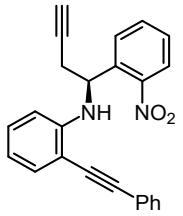
Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.35 (m, 5H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.3 Hz, 1H), 5.85 (s, 1H), 5.43 (d, *J* = 3.6 Hz, 1H), 3.13 (ddd, *J* = 17.1, 5.1, 2.6 Hz, 1H), 2.89 (ddd, *J* = 17.1, 4.5, 2.6 Hz, 1H), 2.10 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.3, 147.5, 146.8, 132.1, 131.5, 129.8, 128.4, 128.3, 127.4, 124.0, 123.1, 117.6, 110.9, 108.5, 95.9, 85.4, 78.5, 72.8, 55.2, 28.0. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 1 mL/min; Retention time: 11.3 min (major), 13.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{18}N_2O_2H^+$ 367.1441; Found 367.1440.

(S)-*N*-(1-(3-nitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3b)



Yellow oil, 75% yield, 82:18 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{20}$ = + 57.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.31 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 5.9 Hz, 2H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 14.2, 6.7 Hz, 4H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.26 (d, *J* = 8.3 Hz, 1H), 5.69 (s, 1H), 4.75 (s, 1H), 2.97 (d, *J* = 14.1 Hz, 1H), 2.77 (d, *J* = 13.6 Hz, 1H), 2.10 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 147.3, 147.3, 144.3, 131.9, 131.4, 130.8, 130.3, 129.8, 129.4, 128.4, 128.2, 125.0, 123.3, 122.8, 117.2, 111.0, 108.3, 95.7, 85.7, 72.3, 55.5, 28.3. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 13.4 min (major), 16.8 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{18}N_2O_2H^+$ 367.1441; Found 367.1439.

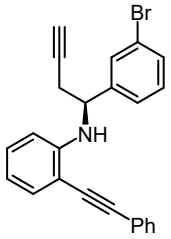
(S)-*N*-(1-(2-nitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3c)



Yellow oil, 86% yield, 83:17 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{20}$ = + 55.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 7.3, 1.7 Hz, 2H), 7.56 (t, *J* = 7.6

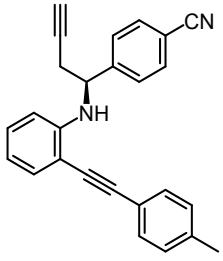
Hz, 1H), 7.46 – 7.32 (m, 5H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.3 Hz, 1H), 5.85 (s, 1H), 5.43 (d, *J* = 3.6 Hz, 1H), 3.13 (ddd, *J* = 17.1, 5.1, 2.6 Hz, 1H), 2.89 (ddd, *J* = 17.1, 4.5, 2.6 Hz, 1H), 2.10 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ148.8, 146.5, 136.9, 133.6, 132.0, 131.5, 130.0, 129.9, 128.9, 128.5, 128.4, 128.3, 125.0, 117.4, 110.6, 108.3, 95.8, 85.5, 78.8, 72.9, 50.2, 26.8. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 1 mL/min; Retention time: 7.9 min (major), 9.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{18}N_2O_2H^+$ 367.1441; Found 367.1442.

(S)-*N*-(1-(3-bromophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3d)



Yellow solid, 81% yield, 90:10 *er*, R_f = 0.4 (petroleum ether/ethyl acetate = 20:1), m. p. 122.2 – 122.9 ℃, $[\alpha]_D^{20}$ = – 54.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.59 (d, *J* = 7.7 Hz, 3H), 7.37 (dd, *J* = 12.9, 6.3 Hz, 6H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.31 (d, *J* = 8.3 Hz, 1H), 5.61 (d, *J* = 5.1 Hz, 1H), 4.59 (d, *J* = 5.6 Hz, 1H), 2.88 (d, *J* = 16.8 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.09 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) 147.2, 144.3, 131.9, 131.4, 130.8, 130.3, 129.7, 129.4, 128.4, 128.3, 124.9, 123.3, 122.8, 117.2, 111.0, 108.3, 95.7, 85.6, 79.2, 72.2, 55.4, 28.2. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 6.1 min (major), 7.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{18}BrNH^+$ 400.0696; Found 400.0696.

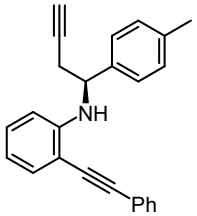
(S)-4-(1-((2-(p-tolylethynyl)phenyl)amino)but-3-yn-1-yl)benzonitrile (3e)



Yellow oil, 55% yield, 81:19 *er*, R_f = 0.3 (petroleum ether/dichloromethane = 10:1), $[\alpha]_D^{20}$ = + 26.3 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.72

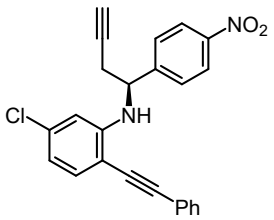
– 7.56 (m, 2H), 7.51 (dd, *J* = 18.8, 8.1 Hz, 4H), 7.40 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.94 (m, 1H), 6.67 (td, *J* = 7.5, 0.9 Hz, 1H), 6.21 (d, *J* = 8.2 Hz, 1H), 5.66 (d, *J* = 5.9 Hz, 1H), 4.75 – 4.60 (m, 1H), 2.94 (ddd, *J* = 16.8, 5.4, 2.7 Hz, 1H), 2.73 (ddd, *J* = 16.8, 5.8, 2.6 Hz, 1H), 2.39 (s, 3H), 2.09 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 147.3, 146.8, 138.5, 132.5, 131.9, 131.3, 129.6, 129.2, 127.3, 120.0, 118.7, 117.5, 111.5, 110.8, 108.7, 96.0, 84.8, 78.6, 72.6, 55.4, 27.9, 21.5. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 18.2 min (major), 31.2 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{26}H_{20}N_2H^+$ 361.1699; Found 361.1698.

(S)-2-(phenylethynyl)-*N*-(1-(p-tolyl)but-3-yn-1-yl)aniline (3f)



Yellow solid, 45% yield, 67:33 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), m. p. 84.3 – 84.7 ℃, $[\alpha]_D^{20}$ = + 32.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.59 (d, *J* = 6.3 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 8.3 Hz, 1H), 5.62 (d, *J* = 4.7 Hz, 1H), 4.62 (d, *J* = 5.4 Hz, 1H), 2.88 (dd, *J* = 16.8, 2.5 Hz, 1H), 2.73 (dd, *J* = 16.8, 4.3 Hz, 1H), 2.34 (s, 3H), 2.07 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 147.8, 138.8, 137.2, 131.9, 131.5, 129.8, 129.4, 128.4, 128.2, 126.2, 123.5, 116.8, 111.1, 108.1, 95.6, 86.0, 80.0, 71.8, 55.6, 28.4, 21.1. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 5.3 min (major), 6.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{25}H_{21}NH^+$ 336.1747; Found 336.1743.

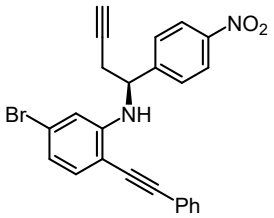
(S)-5-chloro-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3g)



Yellow solid, 94% yield, 90:10 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), m. p. 87.8 – 88.7 ℃, $[\alpha]_D^{20}$ = + 258.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz,

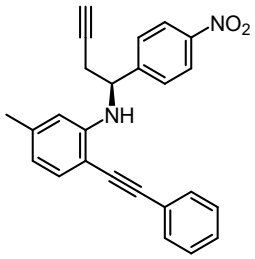
$CDCl_3$, ppm) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 4H), 7.42 – 7.35 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 6.20 (s, 1H), 5.75 (d, *J* = 6.0 Hz, 1H), 4.72 (q, *J* = 5.5 Hz, 1H), 3.04 – 2.92 (m, 1H), 2.82 – 2.69 (m, 1H), 2.10 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.4, 147.7, 147.6, 135.6, 132.9, 131.4, 128.6, 128.5, 127.3, 124.1, 122.8, 117.8, 110.9, 107.1, 96.7, 84.5, 78.2, 73.0, 55.0, 27.9. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 19.5 min (major), 23.9 min (minor). **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 19.5 min (major), 23.9 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{17}ClN_2O_2H^+$ 401.1052; Found 401.1052.

(S)-5-bromo-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3h)



Yellow solid, 91% yield, 91:9 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), m. p. 67.7 – 67.9 ℃, $[\alpha]_D^{20}$ = + 7.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 4H), 7.38 (d, *J* = 1.7 Hz, 3H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.37 (s, 1H), 5.74 (d, *J* = 6.0 Hz, 1H), 4.72 (q, *J* = 5.4 Hz, 1H), 2.98 (dd, *J* = 16.9, 2.6 Hz, 1H), 2.75 (dd, *J* = 16.9, 2.9 Hz, 1H), 2.11 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.3, 147.6, 147.6, 133.0, 131.4, 128.6, 128.5, 127.3, 124.1, 123.9, 122.7, 120.6, 113.7, 107.5, 96.8, 84.5, 78.2, 73.0, 54.8, 27.8. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 23.1 min (major), 26.0 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{17}BrN_2O_2H^+$ 445.0546; Found 445.0544.

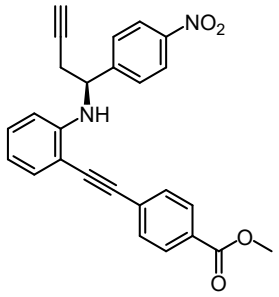
(S)-5-methyl-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3i)



Yellow solid, 80% yield, 78:22 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1),

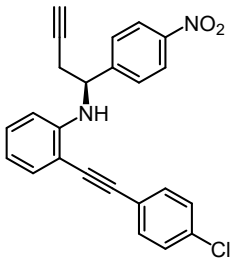
m. p. 125.3 – 126.1 ℃, $[\alpha]_D^{20}$ = + 6.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 8.2 Hz, 4H), 7.36 (d, *J* = 6.6 Hz, 3H), 7.30 (d, *J* = 7.7 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.05 (s, 1H), 5.62 (d, *J* = 5.7 Hz, 1H), 4.75 (d, *J* = 5.7 Hz, 1H), 3.02 – 2.88 (m, 1H), 2.75 (dd, *J* = 16.9, 3.1 Hz, 1H), 2.15 (s, 3H), 2.09 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.4, 147.5, 146.7, 140.2, 131.9, 131.4, 128.4, 128.2, 127.4, 124.0, 123.3, 118.7, 111.6, 105.7, 95.4, 85.7, 78.5, 72.7, 55.1, 28.0, 22.0. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 18.0 min (major), 23.5 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{25}H_{20}N_2O_2H^+$ 381.1598; Found 381.1600.

methyl (S)-4-((2-((1-(4-nitrophenyl)but-3-yn-1-yl)amino)phenyl)ethynyl)benzoate (3j)



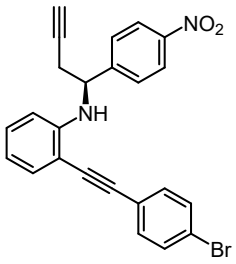
Yellow solid, 90% yield, 86:14 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 10:1), m. p. 59.3 – 60.5 ℃, $[\alpha]_D^{20}$ = + 24.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.22 (d, *J* = 8.1 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.62 (dd, *J* = 21.3, 8.0 Hz, 4H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.22 (d, *J* = 8.2 Hz, 1H), 5.68 (s, 1H), 4.76 (s, 1H), 3.95 (d, *J* = 9.5 Hz, 3H), 2.99 (d, *J* = 12.8 Hz, 1H), 2.77 (d, *J* = 16.6 Hz, 1H), 2.12 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 166.5, 149.1, 147.8, 146.9, 132.3, 131.3, 130.4, 129.6, 129.4, 127.8, 127.4, 124.0, 117.7, 111.0, 107.8, 95.4, 88.6, 78.5, 72.8, 55.1, 52.3, 27.9. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 31.8 min (major), 45.6 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{26}H_{20}N_2O_4H^+$ 425.1496; Found 425.1499.

(S)-2-((4-chlorophenyl)ethynyl)-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)aniline (3k)



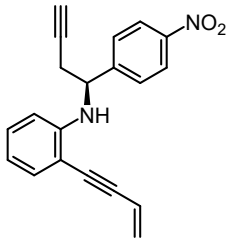
Yellow oil, 95% yield, 86:14 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{20}$ = + 245.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.55 (dd, *J* = 26.8, 8.5 Hz, 4H), 7.45 – 7.30 (m, 3H), 7.05 (dd, *J* = 11.4, 4.2 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 8.2 Hz, 1H), 5.64 (d, *J* = 5.5 Hz, 1H), 4.75 (q, *J* = 5.4 Hz, 1H), 2.97 (ddd, *J* = 16.9, 5.2, 2.6 Hz, 1H), 2.76 (ddd, *J* = 16.9, 5.7, 2.5 Hz, 1H), 2.10 (t, *J* = 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.1, 147.6, 146.8, 134.4, 132.6, 132.1, 130.0, 128.8, 127.4, 123.9, 121.6, 117.7, 110.9, 108.1, 94.8, 86.5, 78.54, 72.7, 55.2, 27.9. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 17.6 min (major), 28.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{17}ClN_2O_2H^+$ 401.1052; Found 401.1051.

(S)-2-((4-bromophenyl)ethynyl)-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)aniline (3l)



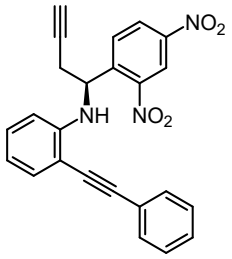
Yellow oil, 82% yield, 87:13 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{20}$ = - 21.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.30 – 8.08 (m, 2H), 7.68 – 7.29 (m, 7H), 7.03 (d, *J* = 6.2 Hz, 1H), 6.80 – 6.50 (m, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.63 (s, 1H), 4.81 – 4.60 (m, 1H), 3.05 – 2.84 (m, 1H), 2.75 (d, *J* = 14.1 Hz, 1H), 2.09 (d, *J* = 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.1, 147.6, 146.8, 132.8, 132.1, 131.7, 130.6, 127.4, 124.0, 122.6, 122.1, 117.7, 110.9, 108.1, 94.8, 86.7, 78.5, 72.8, 55.2, 27.9. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 18.7 min (major), 31.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{17}BrN_2O_2H^+$ 445.0546; Found 445.0547.

(S)-2-(but-3-en-1-yn-1-yl)-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)aniline (3m)



Yellow solid, 94% yield, 80:20 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), m. p. 81.7 – 82.3 ℃, $[\alpha]_D^{20}$ = + 100.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.32 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.08 – 6.88 (m, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.26 – 6.03 (m, 2H), 5.79 (dd, *J* = 17.5, 1.9 Hz, 1H), 5.59 (dd, *J* = 11.2, 1.9 Hz, 1H), 5.58 (s, 1H), 4.71 (t, *J* = 5.6 Hz, 1H), 2.93 (ddd, *J* = 16.8, 5.5, 2.6 Hz, 1H), 2.74 (ddd, *J* = 16.8, 5.7, 2.6 Hz, 1H), 2.14 (t, *J* = 2.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.2, 147.5, 146.8, 132.1, 129.8, 127.4 126.7, 123.9, 117.6, 117.0, 110.9, 108.4, 94.6, 85.9, 78.4, 72.6, 55.2, 27.9. **HPLC**: Chiralpak OD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 12.5 min (major), 42.3 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{20}H_{16}N_2O_2H^+$ 317.1285; Found 317.1283.

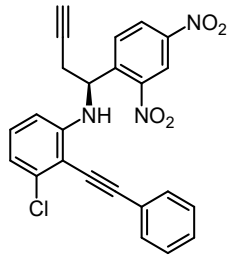
(S)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3n)



Yellow solid, 75% yield, 94:6 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), m. p. 62.9 – 64.4 ℃, $[\alpha]_D^{20}$ = + 68.7 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.87 (d, *J* = 2.3 Hz, 1H), 8.39 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.51 (m, 2H), 7.40 (tdd, *J* = 6.3, 5.1, 1.4 Hz, 4H), 7.03 (td, *J* = 8.3, 1.5 Hz, 1H), 6.70 (td, *J* = 7.6, 0.8 Hz, 1H), 6.16 (d, *J* = 8.2 Hz, 1H), 5.87 (s, 1H), 5.51 (t, *J* = 4.8 Hz, 1H), 3.18 (ddd, *J* = 17.2, 5.4, 2.7 Hz, 1H), 2.92 (ddd, *J* = 17.2, 4.2, 2.7 Hz, 1H), 2.14 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.8, 147.3, 145.7, 143.9, 132.2, 131.5, 130.9, 130.0, 128.5, 128.5, 127.4, 122.9, 120.5, 118.2, 110.4, 108.7, 96.1, 85.1, 77.8, 73.8, 50.4, 26.4. **HPLC**: Chiralpak OD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 21.7 min

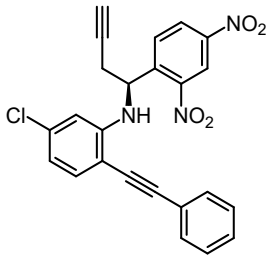
(major), 34.9 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{17}N_3O_4$ H^+ 412.1292; Found 412.1287.

(S)-3-chloro-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3o)



Yellow solid, 75% yield, 93:7 *er*, R_f = 0.3 (petroleum ether/dichloromethane = 5:1), m. p. 61.5 – 62.8 ℃, $[\alpha]_D^{20}$ = + 66.3 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.88 (d, *J* = 2.3 Hz, 1H), 8.40 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.72 – 7.55 (m, 2H), 7.45 – 7.29 (m, 3H), 6.93 (t, *J* = 8.1 Hz, 1H), 6.78 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.02 (dd, *J* = 26.2, 7.5 Hz, 2H), 5.60 – 5.42 (m, 1H), 3.18 (ddd, *J* = 17.2, 5.4, 2.7 Hz, 1H), 2.92 (ddd, *J* = 17.2, 4.1, 2.7 Hz, 1H), 2.13 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.8, 147.5, 146.9, 143.4, 136.6, 131.6, 130.8, 130.0, 128.9, 128.5, 127.5, 122.7, 120.6, 118.9, 108.9, 108.4, 101.0, 82.2, 77.5, 74.0, 50.5, 26.4. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 13.5 min (major), 45.9 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{16}ClN_3O_4H^+$ 446.0902; Found 446.0905.

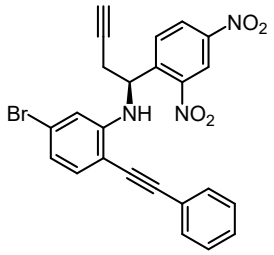
(S)-5-chloro-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3p)



Yellow solid, 88% yield, 94:6 *er*, R_f = 0.3 (petroleum ether/dichloromethane = 5:1), m. p. 53.8 – 54.9 ℃, $[\alpha]_D^{20}$ = + 72.0 ° (*c* = 1 mg / mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.90 (d, *J* = 2.3 Hz, 1H), 8.41 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.60 (ddd, *J* = 8.3, 4.0, 2.4 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.33 (dd, *J* = 7.4, 5.2 Hz, 1H), 6.68 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.17 (d, *J* = 1.9 Hz, 1H), 5.92 (d, *J* = 7.1 Hz, 1H), 5.51 (dd, *J* = 11.3, 5.3 Hz, 1H), 3.17 (ddd, *J* = 17.2, 5.5, 2.7 Hz, 1H), 2.90 (ddd, *J* = 17.2, 4.1, 2.7 Hz, 1H), 2.13 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ

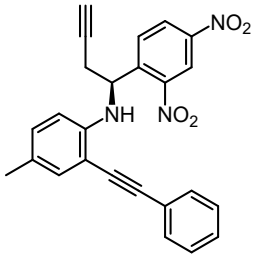
148.7, 147.5, 146.6, 143.1, 135.9, 133.0, 131.5, 130.7, 128.8, 128.5, 127.5, 122.6, 120.8, 118.4, 110.5, 107.2, 96.9, 84.2, 77.5, 74.0, 50.3, 26.4. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 22.2 min (major), 39.3 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{16}ClN_3O_4H^+$ 446.0902; Found 446.0895.

(S)-5-bromo-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-(phenylethynyl)aniline (3q)



Yellow oil, 86% yield, 95:5 *er*, R_f = 0.3 (petroleum ether/dichloromethane = 5:1). $[\alpha]_D^{20}$ = + 66.2 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.91 (d, *J* = 2.3 Hz, 1H), 8.43 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.99 (t, *J* = 6.8 Hz, 1H), 7.71 – 7.54 (m, 2H), 7.45 – 7.37 (m, 3H), 7.27 (d, *J* = 5.0 Hz, 1H), 6.92 – 6.76 (m, 1H), 6.35 (d, *J* = 1.7 Hz, 1H), 5.92 (d, *J* = 7.1 Hz, 1H), 5.53 (dd, *J* = 11.4, 5.3 Hz, 1H), 3.18 (ddd, *J* = 17.2, 5.5, 2.7 Hz, 1H), 2.92 (ddd, *J* = 17.2, 4.0, 2.7 Hz, 1H), 2.15 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.7, 147.5, 146.6, 143.1, 133.2, 131.5, 130.7, 128.8, 128.5, 127.5, 124.1, 122.6, 121.3, 120.7, 113.4, 107.7, 97.1, 84.2, 77.5, 74.0. 50.2, 26.4. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 26.2 min (major), 48.7 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{16}BrN_3O_4H^+$ 490.0397; Found 490.0391.

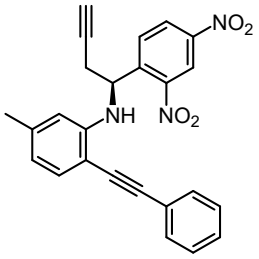
(S)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-4-methyl-2-(phenylethynyl)aniline (3r)



Yellow solid, 80% yield, 93:7 *er*, R_f = 0.2 (petroleum ether/dichloromethane = 5:1), m. p. 52.1 – 53.5 ℃, $[\alpha]_D^{20}$ = + 79.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.85 (d, *J* = 2.3 Hz, 1H), 8.37 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.60 (dt, *J* = 4.7, 2.8 Hz, 2H), 7.44 – 7.33 (m, 3H), 7.24 (d, *J* = 1.8 Hz, 1H),

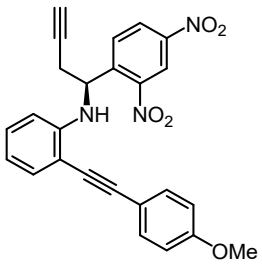
6.84 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.09 (d, *J* = 8.3 Hz, 1H), 5.73 (d, *J* = 6.6 Hz, 1H), 5.48 (d, *J* = 4.9 Hz, 1H), 3.17 (ddd, *J* = 17.2, 5.4, 2.7 Hz, 1H), 2.92 (ddd, *J* = 17.2, 4.2, 2.7 Hz, 1H), 2.18 (s, 3H), 2.13 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.9, 147.3, 144.2, 143.5, 132.5, 131.4, 130.9, 130.7, 128.5, 127.4, 127.3, 127.3, 123.0, 120.4, 110.6, 108.7, 95.8, 85.3, 77.9, 77.3, 50.6, 26.4, 20.1. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 23.3 min (major), 55.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{25}H_{19}N_3O_4H^+$ 426.1448; Found 426.1451.

(S)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-5-methyl-2-(phenylethynyl)aniline (3s)



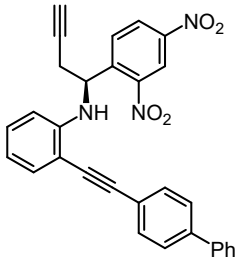
Yellow oil, 75% yield, 95:5 *er*, R_f = 0.3 (petroleum ether/dichloromethane = 5:1). $[\alpha]_D^{20}$ = + 84.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.87 (d, *J* = 2.3 Hz, 1H), 8.39 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.41 – 7.34 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.52 (dd, *J* = 7.8, 0.6 Hz, 1H), 5.99 (s, 1H), 5.81 (s, 1H), 5.51 (s, 1H), 3.16 (ddd, *J* = 17.2, 5.4, 2.7 Hz, 1H), 2.90 (ddd, *J* = 17.2, 4.1, 2.7 Hz, 1H), 2.17 – 2.09 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.9, 147.3, 145.7, 144.0, 140.5, 132.1, 131.4, 130.9, 128.4, 128.3, 127.4, 123.2, 120.4, 119.3, 111.2, 105.9, 95.6, 85.4, 77.8, 73.8, 50.3, 26.5, 22.0. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 25.1 min (major), 38.8 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{25}H_{19}N_3O_4H^+$ 426.1448; Found 426.1451.

(S)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-((4-methoxyphenyl)ethynyl)aniline (3t)



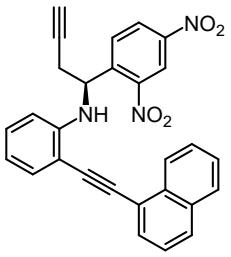
Yellow oil, 85% yield, 94:6 *er*, R_f = 0.4 (petroleum ether/dichloromethane = 5:1), $[\alpha]_D^{20}$ = + 74.6 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.86 (d, *J* = 2.3 Hz, 1H), 8.38 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.45 (m, 2H), 7.38 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.01 (td, *J* = 8.3, 1.5 Hz, 1H), 6.96 – 6.82 (m, 2H), 6.68 (td, *J* = 7.5, 0.7 Hz, 1H), 6.15 (d, *J* = 8.2 Hz, 1H), 5.86 (s, 1H), 5.50 (t, *J* = 4.7 Hz, 1H), 3.85 (s, 3H), 3.17 (ddd, *J* = 17.2, 5.4, 2.7 Hz, 1H), 2.92 (ddd, *J* = 17.2, 4.2, 2.7 Hz, 1H), 2.13 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 159.8, 148.8, 147.3, 145.5, 143.9, 132.9, 131.9, 130.9, 129.6, 127.4, 120.5, 118.2, 115.0, 114.1, 110.4, 109.1, 96.1, 83.8, 77.8, 73.8, 55.3, 50.4, 26.4. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 34.2 min (major), 64.4 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{25}H_{19}N_3O_5$ H^+ 442.1397; Found 442.1399.

(S)-2-([1,1'-biphenyl]-4-ylethynyl)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)aniline (3u)



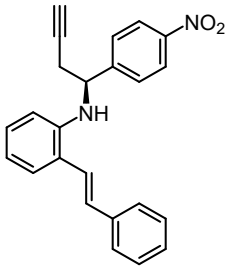
Yellow oil, 89% yield, 94:6 *er*, R_f = 0.3 (petroleum ether/dichloromethane = 5:1), $[\alpha]_D^{20}$ = + 72.3 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.88 (d, *J* = 2.3 Hz, 1H), 8.39 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.65 – 7.59 (m, 4H), 7.45 (ddd, *J* = 13.6, 7.4, 1.6 Hz, 3H), 7.42 – 7.35 (m, 1H), 7.12 – 6.97 (m, 1H), 6.71 (td, *J* = 7.6, 0.8 Hz, 1H), 6.17 (d, *J* = 8.2 Hz, 1H), 5.89 (d, *J* = 6.9 Hz, 1H), 5.52 (dd, *J* = 11.3, 5.1 Hz, 1H), 3.20 (ddd, *J* = 17.2, 5.4, 2.7 Hz, 1H), 2.94 (ddd, *J* = 17.2, 4.2, 2.7 Hz, 1H), 2.17 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.8, 147.3, 145.7, 143.9, 141.3, 140.2, 132.3, 131.9, 130.9, 130.0, 128.9, 127.8, 127.4, 127.1, 127.0, 121.8, 120.5, 118.2, 110.4, 108.8, 96.1, 85.8, 77.8, 73.8, 50.4, 26.5. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 32.1 min (major), 75.6 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{30}H_{21}N_3O_4H^+$ 488.1605; Found 488.1603.

(S)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-(naphthalen-1-ylethynyl)aniline (3v)



Yellow oil, 82% yield, 94:6 *er*, R_f = 0.3 (petroleum ether/dichloromethane = 5:1), $[\alpha]_D^{20}$ = + 40.5 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.88 (d, *J* = 2.3 Hz, 1H), 8.53 – 8.28 (m, 1H), 8.14 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.83 (dd, *J* = 15.9, 8.8 Hz, 3H), 7.74 – 7.60 (m, 1H), 7.60 – 7.36 (m, 3H), 7.14 – 6.93 (m, 1H), 6.87 – 6.57 (m, 1H), 6.18 (d, *J* = 8.2 Hz, 1H), 5.95 (d, *J* = 6.9 Hz, 1H), 5.53 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.22 (ddd, *J* = 17.2, 5.4, 2.7 Hz, 1H), 2.95 (ddd, *J* = 17.2, 4.1, 2.7 Hz, 1H), 2.16 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 148.8, 147.3, 145.8, 143.9, 133.0, 132.9, 132.3, 132.3, 131.4, 130.9, 130.1, 128.2, 127.8, 127.7, 127.4, 126.9, 126.8, 120.5, 120.2, 118.3, 110.4, 108.7, 96.6, 85.5, 77.9, 73.9, 50.4, 26.5. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 27.7 min (major), 53.6 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{19}N_3O_4H^+$ 462.1448; Found 462.1446.

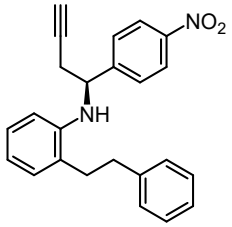
(S, E)-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)-2-styrylaniline (3w)



Yellow oil, 78% yield, 91:9 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{20}$ = + 25.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.57 (dd, *J* = 18.8, 8.1 Hz, 4H), 7.40 (t, *J* = 7.7 Hz, 3H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.03 (dd, *J* = 20.8, 11.7 Hz, 2H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.28 (d, *J* = 8.1 Hz, 1H), 4.70 (t, *J* = 5.9 Hz, 2H), 2.88 (ddd, *J* = 16.8, 5.3, 2.6 Hz, 1H), 2.73 (ddd, *J* = 16.9, 6.5, 2.5 Hz, 1H), 2.13 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.5, 147.5, 143.5, 137.5, 131.7, 128.8, 127.7, 127.8, 127.7, 127.4, 126.5, 124.8, 124.0, 123.8, 118.8, 112.6, 78.9, 72.6, 56.0, 28.1. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 42.0 min (major), 55.5 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{20}N_2O_2H^+$

369.1598; Found 369.1596.

(S)-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)-2-phenethylaniline (3x)



Yellow solid, 83% yield, 92:8 *er*, R_f = 0.4 (petroleum ether/ethyl acetate = 20:1), m. p. 38.1 – 39.5 ℃, $[\alpha]_D^{20}$ = + 69.9 ° (*c* = 1 mg/mL, THF). **^{1}H NMR (**400 MHz, $CDCl_3$, ppm) δ 8.23 – 8.12 (m, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.28 (d, *J* = 2.1 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.11 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.02 – 6.89 (m, 1H), 6.71 (td, *J* = 7.4, 0.8 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 4.71 – 4.56 (m, 1H), 4.46 (d, *J* = 4.0 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.93 (dd, *J* = 9.4, 5.6 Hz, 2H), 2.81 (ddd, *J* = 16.9, 5.3, 2.6 Hz, 1H), 2.65 (ddd, *J* = 16.9, 6.7, 2.6 Hz, 1H), 2.13 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 149.8, 147.5, 143.6, 141.7, 129.5, 128.5, 128.5, 127.3, 127.2, 126.3, 126.2, 123.9, 118.4, 111.8, 79.2, 72.5, 55.7, 35.7, 33.6, 28.1. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 14.5 min (major), 22.3 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{22}N_2O_2H^+$ 371.1754; Found 371.1758.

5. Synthetic Transformations

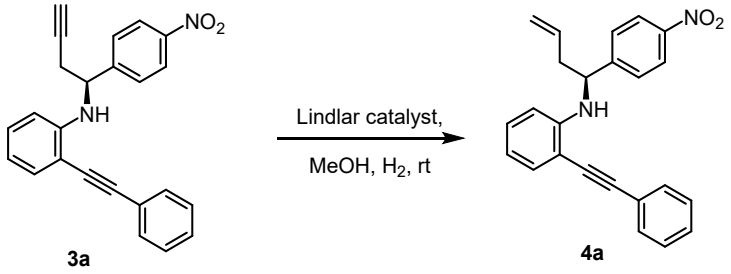
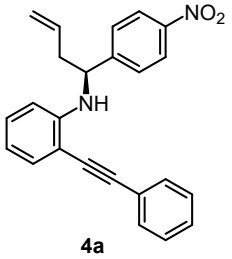


Figure S5. The synthesis of **4a**

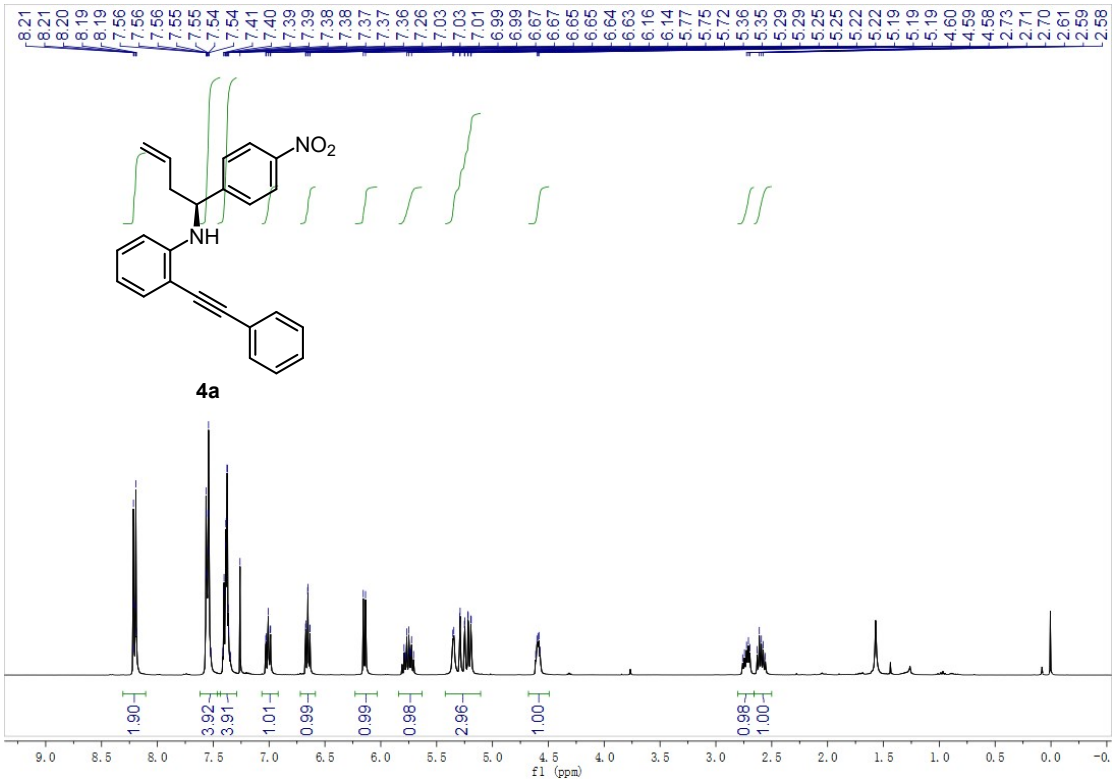
Procedure: To a dried tube filled with the **3a** (37 mg, 0.1 mmol) and Lindlar catalyst (10 mg, 0.01 mmol) was added MeOH (2 mL) under the argon atmosphere, then purged with hydrogen three times and protected with hydrogen. The reaction mixture was stirred at room temperature for 6 h until starting material disappeared on TLC. The mixture was filtered through celite using CH_2Cl_2 (15 mL) and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane and ethyl acetate (30:1) to give the desired product **4a** in 68% yield (**Figure S5**).

(S)-*N*-(1-(4-nitrophenyl)but-3-en-1-yl)-2-(phenylethynyl)aniline (4a)

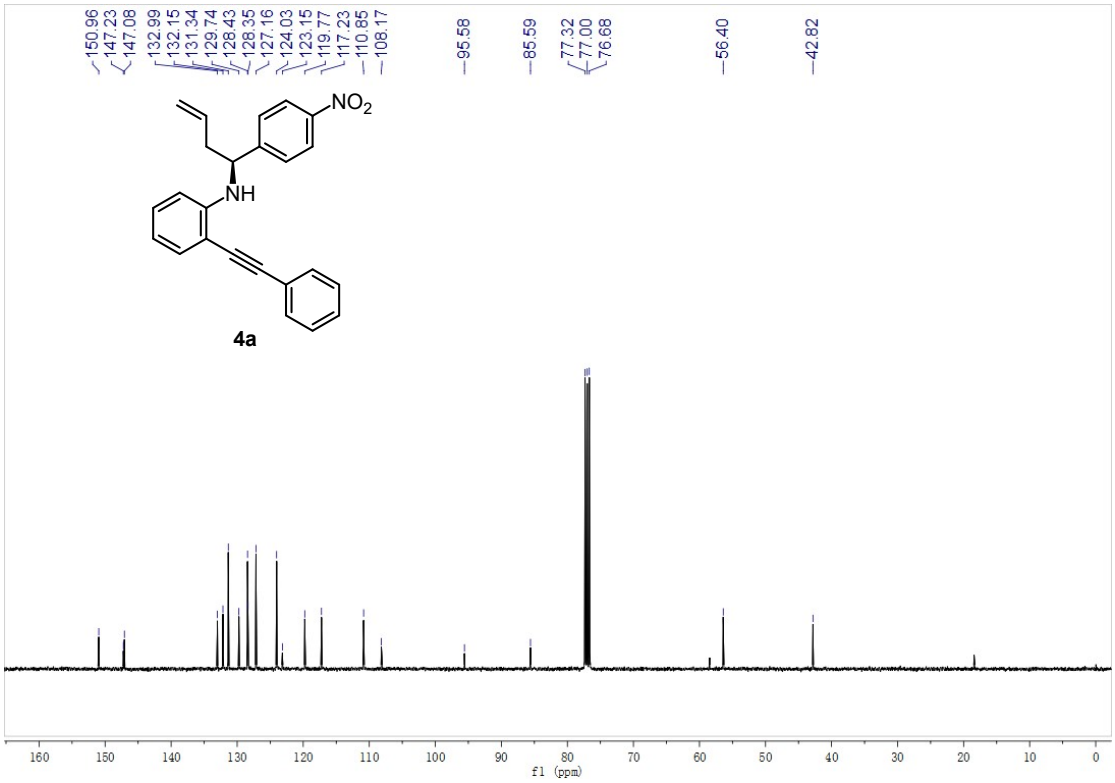


Yellow solid, 68% yield, 89:11 *er*, R_f = 0.5 (petroleum ether/ethyl acetate = 15:1), m. p. 43.1 – 44.5 ℃, $[\alpha]_D^{20}$ = + 225.2 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.31 – 8.10 (m, 2H), 7.55 (ddd, *J* = 10.6, 6.1, 4.0 Hz, 4H), 7.46 – 7.29 (m, 4H), 7.06 – 6.92 (m, 1H), 6.65 (td, *J* = 7.5, 0.9 Hz, 1H), 6.15 (d, *J* = 8.2 Hz, 1H), 5.84 – 5.63 (m, 1H), 5.42 – 5.11 (m, 3H), 4.68 – 4.49 (m, 1H), 2.81 – 2.66 (m, 1H), 2.66 – 2.50 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 151.0, 147.2, 147.1, 133.0, 132.2, 131.3, 129.7, 128.4, 128.4, 127.2, 124.0, 123.2, 119.8, 117.2, 110.9, 108.2, 95.6, 85.6, 56.4, 42.8. **HPLC**: AD-3; detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 6.9 min (major), 8.3 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{20}N_2O_2H^+$ 369.1598; Found 369.1600.

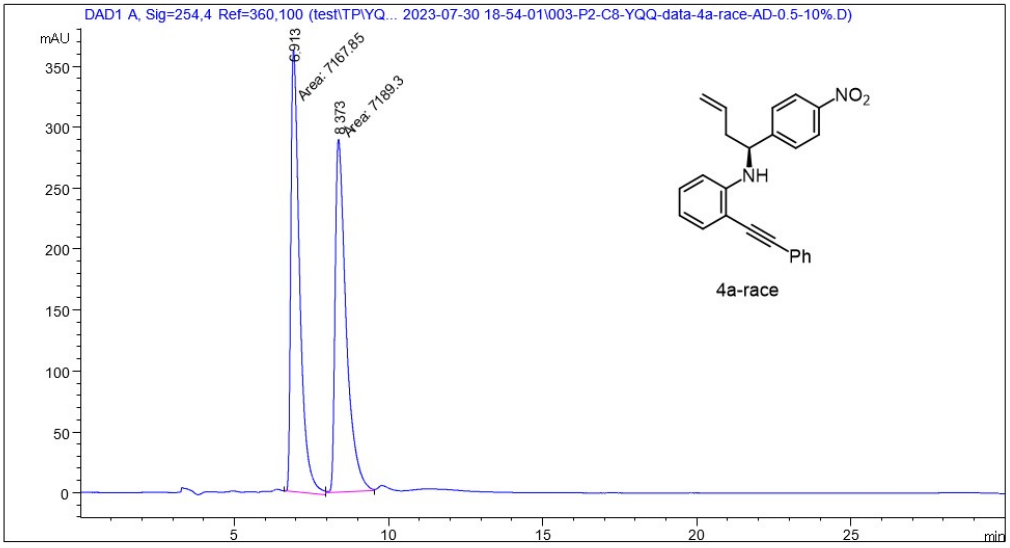
^{1}H NMR Spectra of **4a** (400 MHz, $CDCl_3$)



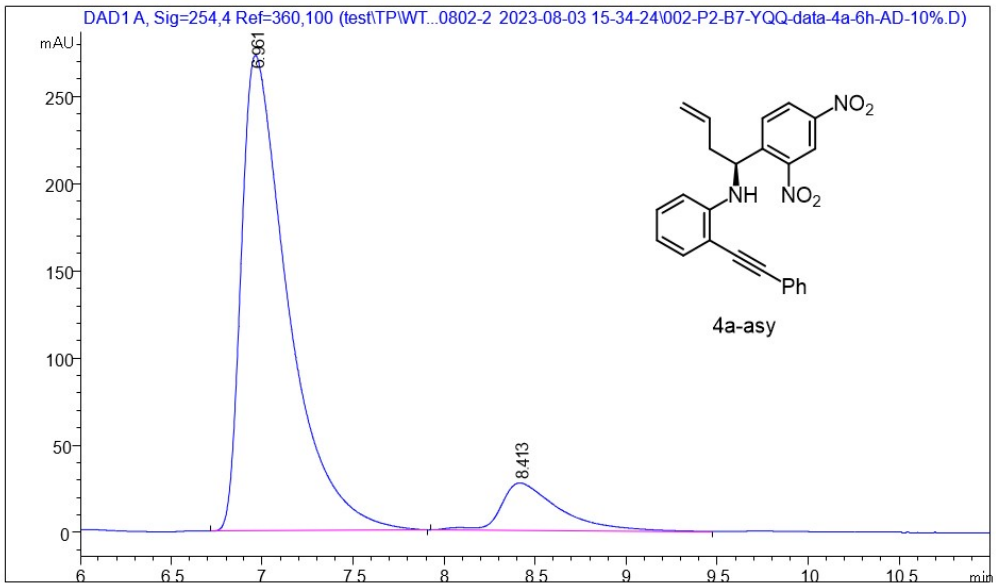
^{1}C NMR Spectra of **4a** (101 MHz, $CDCl_3$)



HPLC Spectra of **4a** (by Agilent 1260 Infinity II LC System)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.913	MM	0.3301	7167.84570	361.85895	49.9253
2	8.373	MM	0.4145	7189.30420	289.10687	50.0747

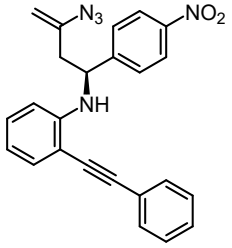


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.961	BB	0.2648	4867.90918	272.64914	88.9968
2	8.413	VB R	0.2904	601.84686	27.17982	11.0032

Figure S6. The synthesis of **5a**

Procedure: To a dried tube filled with the Ag_2CO_3 (2.8 mg, 0.01 mmol) and $TMSN_3$ (27 mg, 0.2 mmol) was added DMSO (1 mL) under the argon atmosphere. The reaction mixture was stirred at 80 °C for 5 min, and then **3a** (37 mg, 0.1 mmol) and H_2O (3.6 μL, 0.2 mmol) were added to the reaction system and continued to react at 80 °C for 90 min until starting material disappeared on TLC. To reaction mixture were added CH_2Cl_2 (2 mL) and saturated ammonium chloride solution, and phases were separated in separatory funnel. Aqueous phase was additionally extracted with CH_2Cl_2 (2 × 10 mL). Organic phases were combined and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane and ethyl acetate (30:1) to give the desired product **5a** in 70% yield (**Figure S6**).

(S)-*N*-(3-azido-1-(4-nitrophenyl)but-3-en-1-yl)-2-(phenylethynyl)aniline (5a)

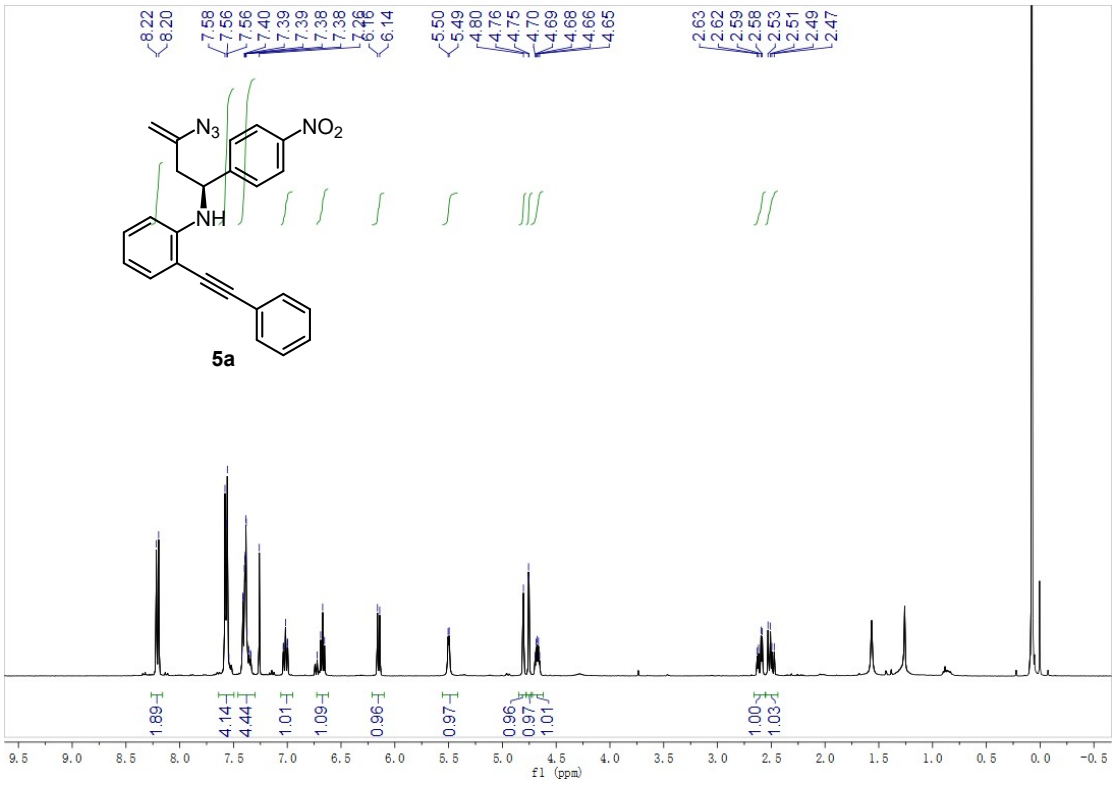


5a

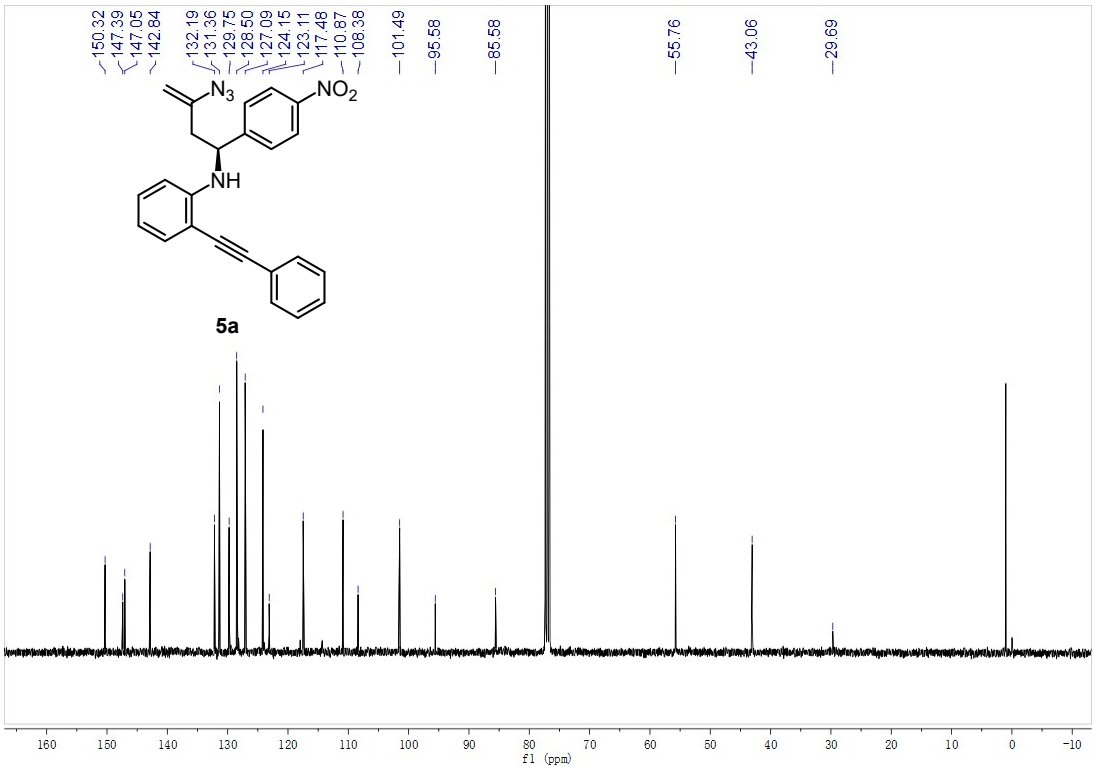
Yellow oil, 70% yield, 85:15 *er*, R_f = 0.5 (petroleum ether/ethyl acetate = 10:1), $[\alpha]_D^{20}$ = + 182.0 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.56 (dd, *J* = 8.1, 6.6 Hz, 4H), 7.46 – 7.30 (m, 4H), 7.06 – 6.95 (m, 1H), 6.68 (dd, *J* = 17.6, 10.1 Hz, 1H), 6.15 (d, *J* = 8.2 Hz, 1H), 5.50 (d, *J* = 3.9 Hz, 1H), 4.80 (s, 1H), 4.75 (d, *J* = 1.9 Hz, 1H), 4.68 (dt, *J* = 8.8, 4.3 Hz, 1H), 2.61 (dd, *J* = 14.1, 4.7 Hz, 1H), 2.50 (dd, *J* = 14.3, 8.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 150.3, 147.4, 147.1, 142.8, 132.2, 131.4, 129.8, 128.5, 127.1, 124.2, 123.1, 117.5, 110.9, 108.4, 101.5, 95.6, 85.6, 55.8, 43.1, 29.7. **HPLC**: Chiralpak OD-H (250 mm); detected

at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 8.0 min (major), 23.6 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{19}N_5O_2H^+$ 410.1612; Found 410.1610.

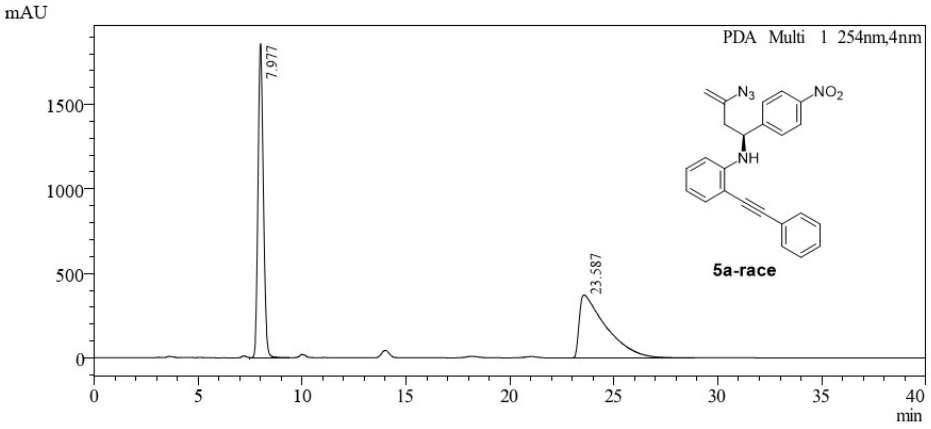
^{1}H NMR Spectra of **5a** (400 MHz, $CDCl_3$)



^{1}C NMR Spectra of **5a** (101 MHz, $CDCl_3$)



HPLC Spectra of **5a**



<PeakTable>
PDA Ch1 254nm

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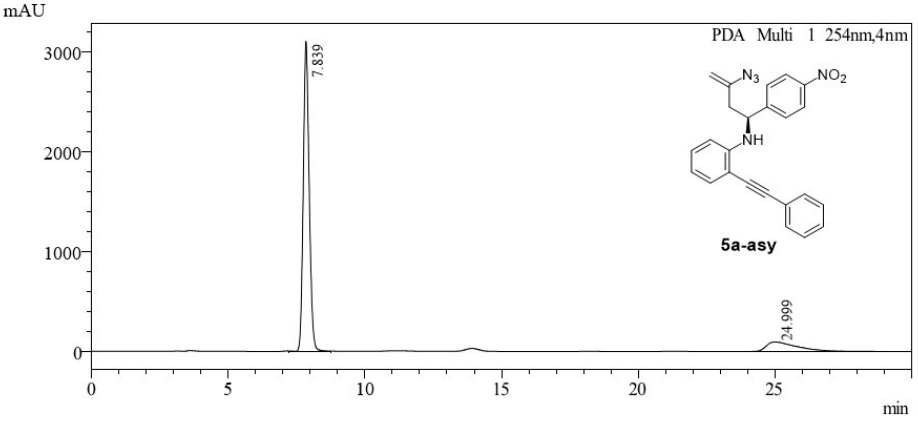
2	23.587	33129778	372331	50.078
Total		66156336	2234393	100.000



<PeakTable>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	7.839	46178882	3104076	85.220
2	24.999	8009230	102476	14.780
Total		54188112	3206552	100.000

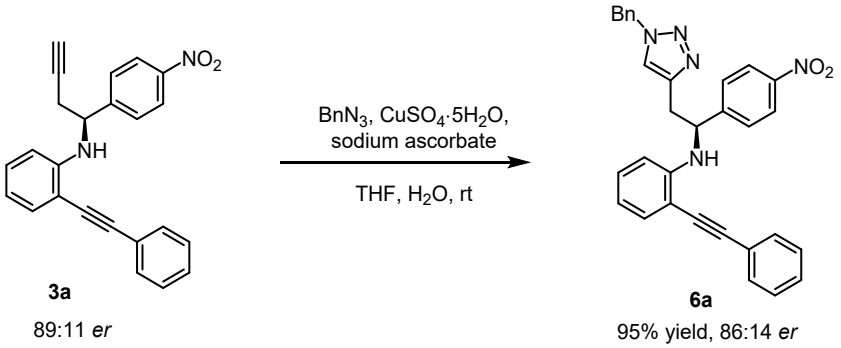
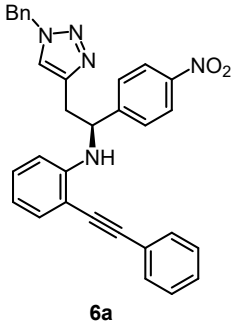


Figure S7. The synthesis of **6a**

Procedure: To a dried tube filled with the **3a** (37 mg, 0.1 mmol) and BnN_3 (12.5 μL, 0.1 mmol) was added THF (1 mL) and a solution of $CuSO_4 \times 5H_2O$ (12.5 mg, 0.05 mmol) and sodium ascorbate (20 mg, 0.1 mmol) in H_2O (1 mL) under the argon atmosphere. The reaction mixture was stirred at room temperature for 10 h until starting material disappeared on TLC. Reduced pressure in vacuo to remove the THF. To reaction mixture were added CH_2Cl_2 (2 mL) and saturated ammonium chloride solution. Aqueous phase was additionally extracted with CH_2Cl_2 (2 × 10 mL). Organic phases were combined and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give the desired product **6a** in 95% yield without further purification (**Figure S7**).

(S)-*N*-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-1-(4-nitrophenyl)ethyl)-2-(phenylethynyl) aniline (6a)

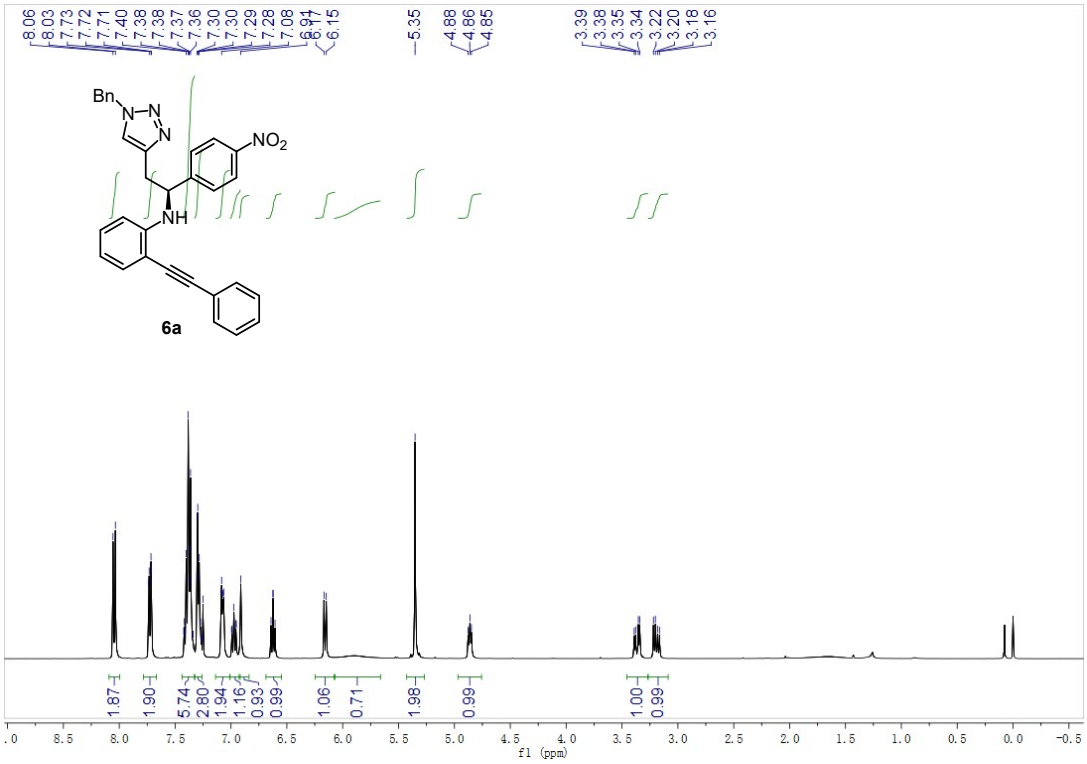


6a

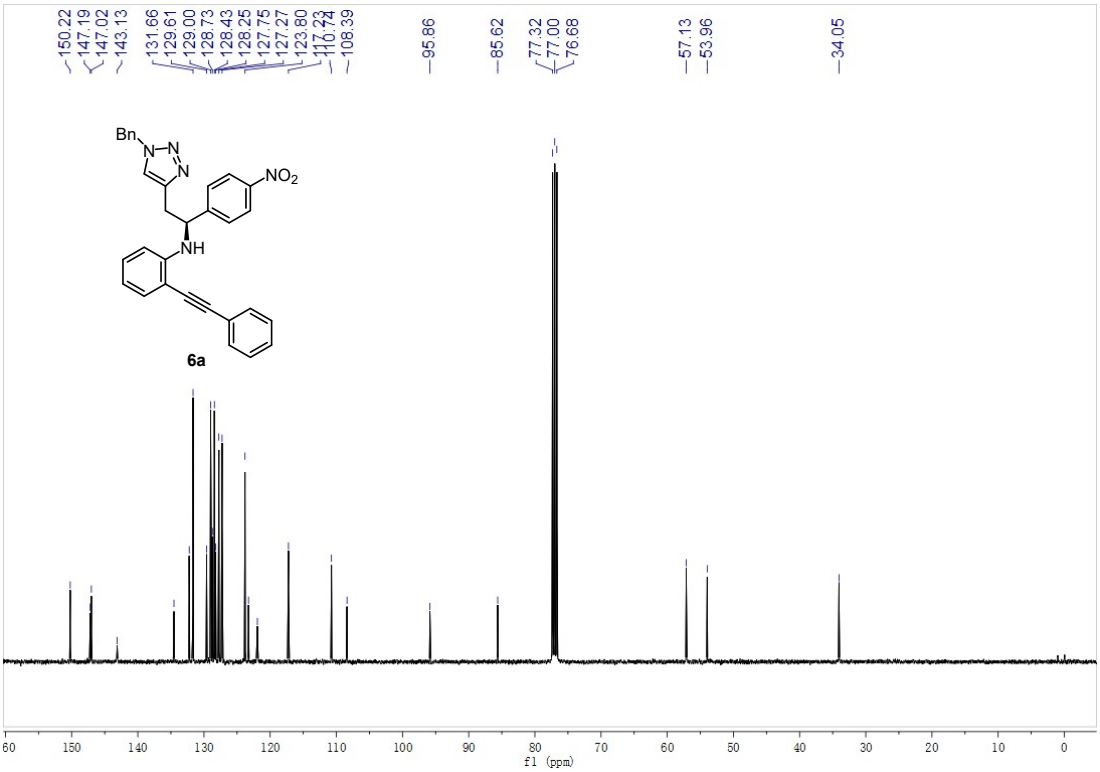
Yellow solid, 95% yield, 86:14 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 5:1), m. p. 146.6 – 147.9 ℃, $[\alpha]_D^{20}$ = + 231 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.72 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.44 – 7.32 (m, 6H), 7.33 – 7.26 (m, 3H), 7.08 (dd, *J* = 7.1, 2.1 Hz, 2H), 7.01 – 6.92 (m, 1H), 6.91 (s, 1H), 6.62 (dd, *J* = 7.4, 7.0 Hz, 1H), 6.16 (d, *J* = 8.2 Hz, 1H), 5.92 (d, *J* = 19.4 Hz, 1H), 5.35 (s, 2H), 4.97 – 4.76 (m, 1H), 3.37 (dd, *J* = 14.7, 5.0 Hz, 1H), 3.19 (dd, *J* = 14.7, 7.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 150.2, 147.1, 147.0, 143.1, 134.5,

132.2, 131.7, 129.6, 129.0, 128.7, 128.4, 128.3, 127.8, 127.3, 123.8, 123.3, 121.9, 117.2, 110.7, 108.4, 95.9, 85.6, 57.1, 54.0, 34.1. **HPLC**: Chiralpak AS-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 1 mL/min; Retention time: 67.1 min (major), 97.2 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{31}H_{25}N_5O_2H^+$ 500.2081; Found 500.2086.

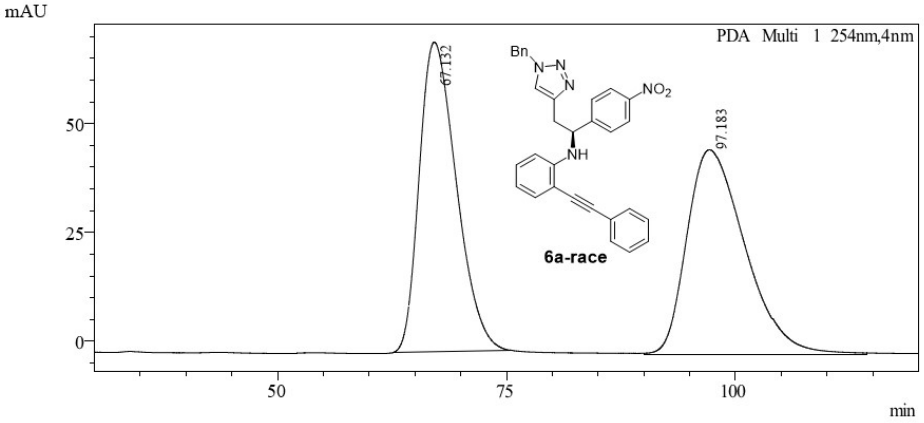
^{1}H NMR Spectra of **6a** (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of **6a** (101 MHz, $CDCl_3$)



HPLC Spectra of **6a**



<PeakTable>

PDA Ch1 254nm

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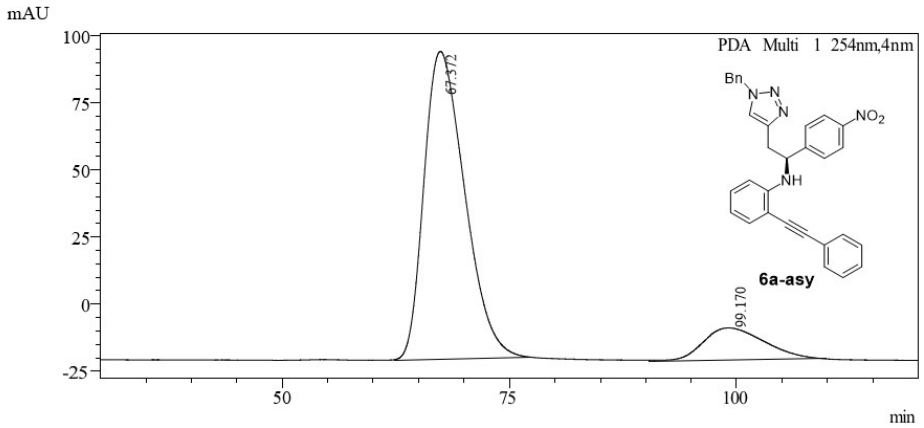
2	97.183	20621974	47016	50.591
Total		40762425	118318	100.000



<PeakTable>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
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2	99.170	5589874	12119	13.539
Total		41287837	126885	100.000

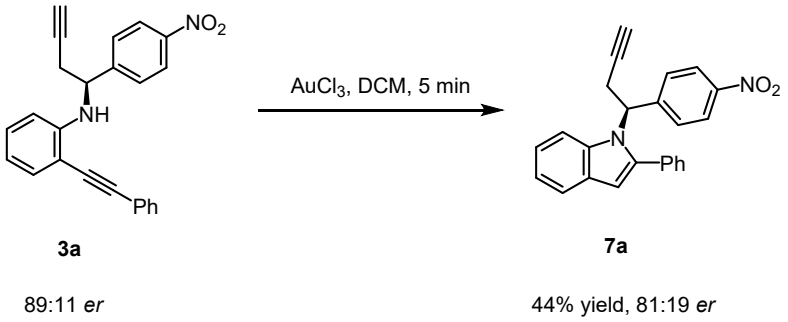
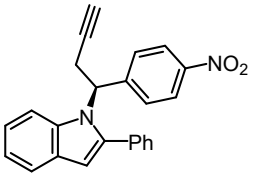


Figure S8. The Synthesis of **7a**

Procedure: To a tube filled with the **3a** (37 mg, 0.1 mmol) and $AuCl_3$ (3 mg, 0.01 mmol) was added CH_2Cl_2 (2 mL). The reaction mixture was stirred at 0 ℃ for 5 min. The reaction was quenched by the addition of the saturated ammonium chloride solution. To reaction mixture were added CH_2Cl_2 (2 mL) and saturated ammonium chloride solution, and phases were separated in separatory funnel. Aqueous phase was additionally extracted with CH_2Cl_2 (2 × 10 mL). Organic phases were combined and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane and ethyl acetate (30:1) to give the desired product **7a** in 44% yield (**Figure S8**).

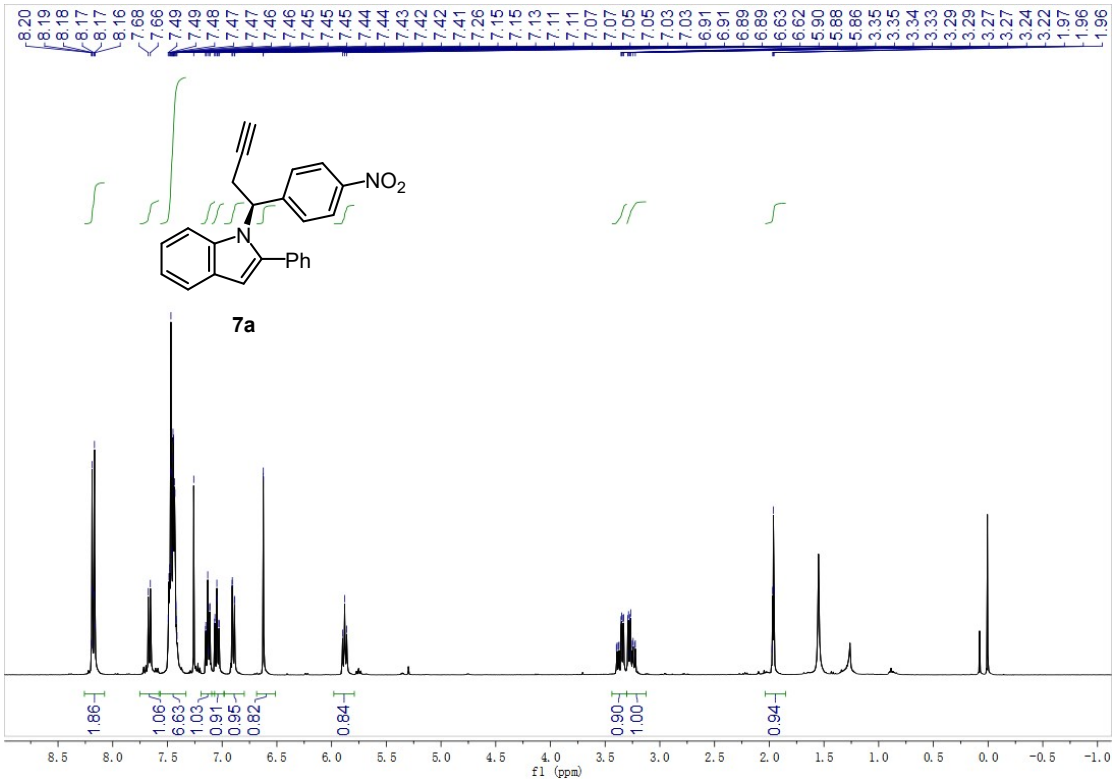
(S)-1-(1-(4-nitrophenyl)but-3-yn-1-yl)-2-phenyl-1H-indole (7a)



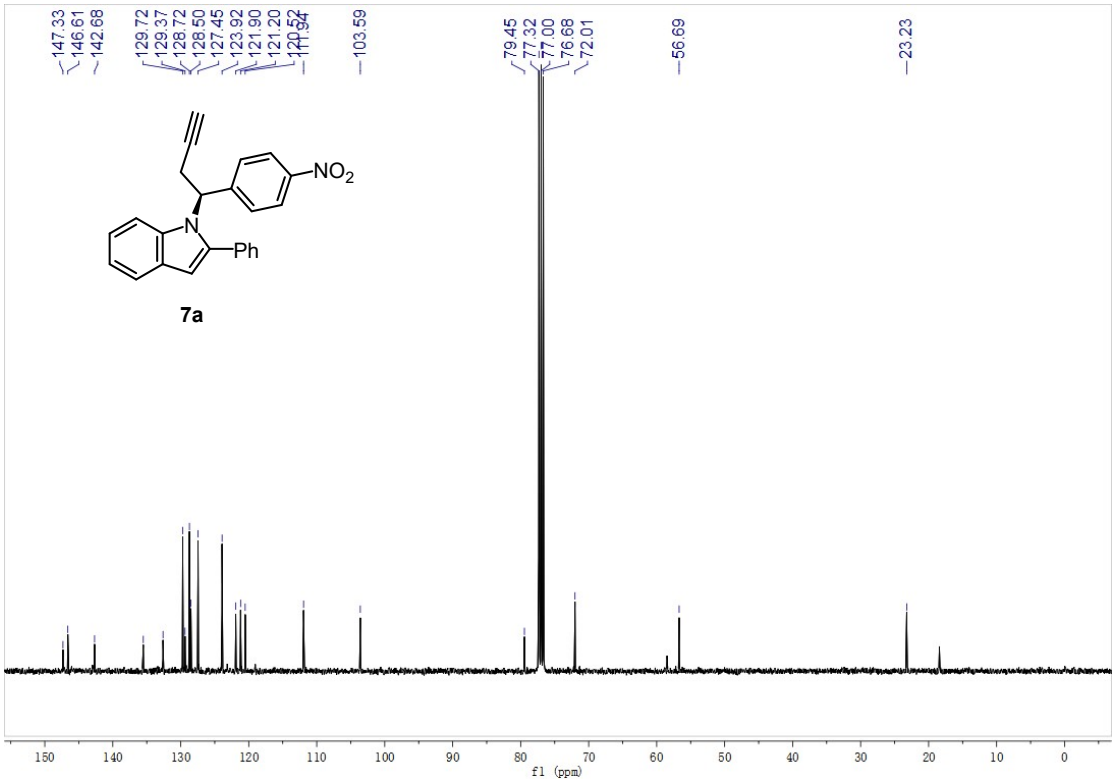
7a

Yellow oil, 44% yield, 81:19 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 15:1), $[\alpha]_D^{20}$ = + 65 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.26 – 8.07 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.33 (m, 7H), 7.19 – 7.07 (m, 1H), 7.10 – 6.98 (m, 1H), 6.90 (dd, *J* = 8.3, 0.6 Hz, 1H), 6.62 (d, *J* = 0.7 Hz, 1H), 5.88 (t, *J* = 7.6 Hz, 1H), 3.36 (ddd, *J* = 17.0, 7.2, 2.6 Hz, 1H), 3.30 – 3.13 (m, 1H), 1.97 (dd, *J* = 5.0, 2.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 147.3, 146.6, 142.7, 135.5, 132.6, 129.7, 129.4, 128.7, 128.5, 127.5, 123.9, 121.9, 121.2, 120.5, 111.9, 103.6, 79.5, 72.0, 56.7, 23.2. **HPLC**: Chiralpak IC (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 1 mL/min; Retention time: 9.1 min (major), 10.7 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{24}H_{18}N_2O_2H^+$ 367.1441; Found 367.1439.

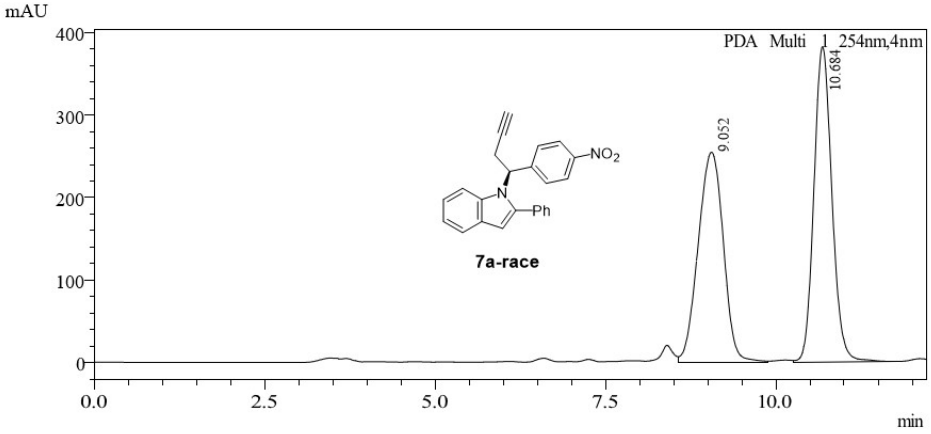
^{1}H NMR Spectra of **7a** (400 MHz, $CDCl_3$)



^{1}C NMR Spectra of **7a** (101 MHz, $CDCl_3$)



HPLC Spectra of **7a**



<PeakTabl>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
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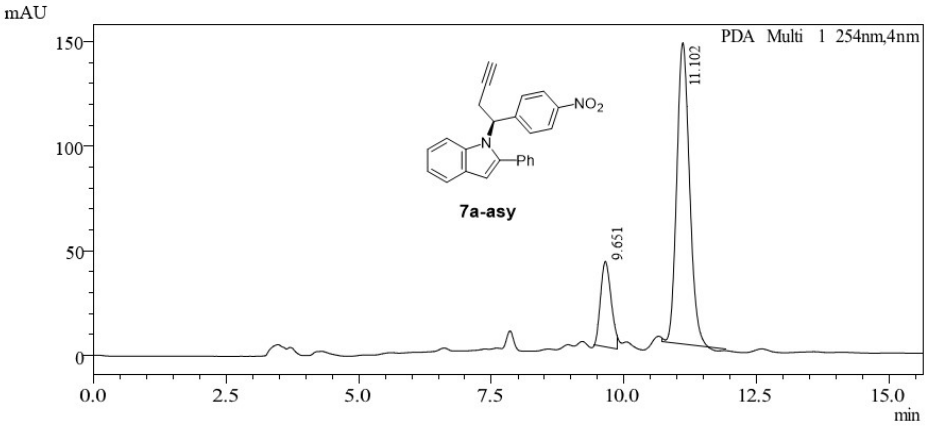
2	10.684	7008436	382095	51.851
Total		13516565	636104	100.000

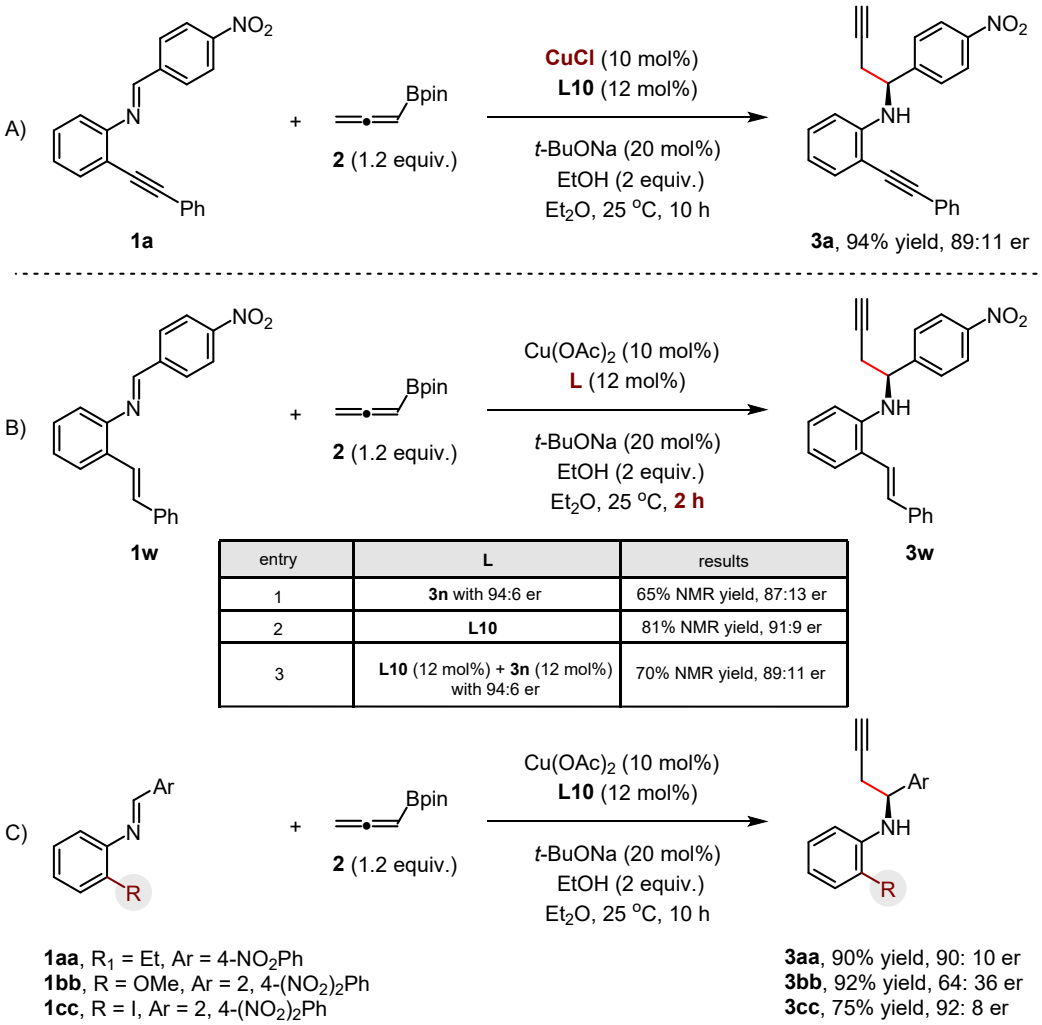


<PeakTabl>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	9.651	560829	40925	18.914
2	11.102	2404300	144104	81.086
Total		2965129	185029	100.000

6. Control Experiments



entry	L	results
1	**3n** with 94:6 er	65% NMR yield, 87:13 er
2	**L10**	81% NMR yield, 91:9 er
3	**L10** (12 mol%) + **3n** (12 mol%) with 94:6 er	70% NMR yield, 89:11 er

Figure S9. The control experiments

Procedure: The procedure of control experiments is given below (**Figure S9**).

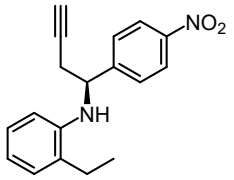
A) A dried tube filled with the imines **1a** (33 mg, 0.1 mmol), CuCl (1 mg, 0.01 mmol), *t*-BuONa (2 mg, 0.02 mmol) and **L10** (6 mg, 0.012 mmol) was evacuated and purged with argon three times. Afterwards, Et_2O (2 mL), **2a** (22 μL, 0.12 mmol) and EtOH (12 μL, 0.2 mmol) were added via syringe. The solution was kept at room temperature for 10 h. After TLC confirmed full conversion, filtration through a short celite, the solvent was evaporated in vacuo and the crude reaction mixture was purified by column chromatography on silica gel to give the product **3a.**

B) A dried tube filled with the imines **1w** (33 mg, 0.1 mmol), $Cu(OAc)_2$ (2 mg, 0.01

mmol), *t*-BuONa (2 mg, 0.02 mmol) and **L** (0.012 mmol) was evacuated and purged with argon three times. Afterwards, Et_2O (2 mL), **2** (22 μL, 0.12 mmol) and EtOH (12 μL, 0.2 mmol) were added via syringe. The solution was kept at room temperature for 2 h. Then filtration through a short celite, the solvent was evaporated in vacuo and the crude reaction mixture was purified by column chromatography on silica gel to give the product **3w.** The yield on the table in **6B** were obtained through NMR using CH_2Br_2 as the internal standard.

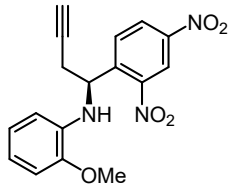
C) A dried tube filled with the imines **1aa-1cc** (0.1 mmol), $Cu(OAc)_2$ (1 mg, 0.01 mmol), *t*-BuONa (2 mg, 0.02 mmol) and **L10** (6 mg, 0.012 mmol) was evacuated and purged with argon three times. Afterwards, Et_2O (2 mL), **2** (22 μL, 0.12 mmol) and EtOH (12 μL, 0.2 mmol) were added via syringe. The solution was kept at room temperature for 10 h. After TLC confirmed full conversion, filtration through a short celite, the solvent was evaporated in vacuo and the crude reaction mixture was purified by column chromatography on silica gel to give the corresponding products **3aa-3cc.**

(S)-2-ethyl-*N*-(1-(4-nitrophenyl)but-3-yn-1-yl)aniline (3aa)



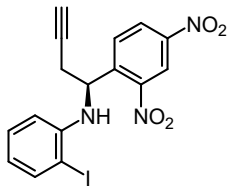
Yellow solid, 90% yield, 90:10 *er*, R_f = 0.4 (petroleum ether/ethyl acetate = 30:1), m. p. 118.8 – 119.9 ℃, $[\alpha]_D^{20}$ = + 80.1 ° (*c* = 1 mg/mL, THF). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 – 8.09 (m, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.94 (td, *J* = 7.9, 1.5 Hz, 1H), 6.71 (td, *J* = 7.4, 0.9 Hz, 1H), 6.20 (d, *J* = 7.6 Hz, 1H), 4.75 – 4.59 (m, 1H), 4.52 (s, 1H), 2.87 (ddd, *J* = 16.9, 5.2, 2.7 Hz, 1H), 2.79 – 2.57 (m, 3H), 2.14 (t, *J* = 2.6 Hz, 1H), 1.36 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 147.5, 143.5, 128.3, 128.3, 127.3, 126.8, 124.0, 118.3, 111.5, 79.1, 72.4, 55.8, 28.1, 24.0, 13.1. **HPLC**: Chiralpak AD-H (250 mm); detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1 mL/min; Retention time: 9.3 min (major), 11.6 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{18}H_{18}N_2O_2H^+$ 295.1441; Found 295.1440.

(S)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-methoxyaniline (3bb)



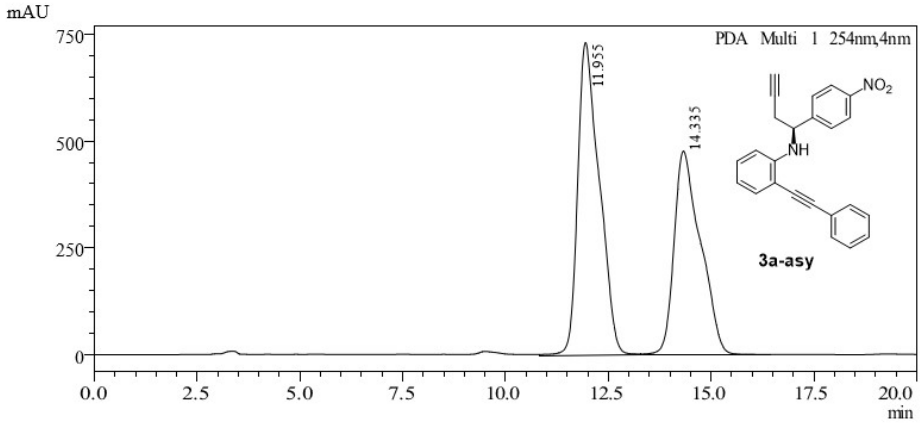
Brown oil, 92% yield, 64:36 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{20}$ = + 18.0 ° (*c* = 1 mg / mL, THF). **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 8.83 (d, *J* = 2.3 Hz, 1H), 8.35 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 6.87 – 6.73 (m, 1H), 6.75 – 6.55 (m, 2H), 6.28 – 6.03 (m, 1H), 5.40 (q, *J* = 5.5 Hz, 1H), 5.24 (d, *J* = 6.0 Hz, 1H), 3.93 (s, 3H), 3.03 (ddd, *J* = 17.1, 5.5, 2.7 Hz, 1H), 2.88 (ddd, *J* = 17.1, 5.1, 2.7 Hz, 1H), 2.15 (t, *J* = 2.6 Hz, 1H).**^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ148.9, 147.2, 146.9, 144.6, 135.0, 130.8, 127.2, 121.2, 120.4, 118.2, 110.7, 109.8, 78.1, 73.2, 55.6, 51.0, 26.5. **HPLC**: AD-3; detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 12.98 min (major), 21.77 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{17}H_{15}N_3O_5H^+$ 342.1084; Found 342.1088.

(S)-*N*-(1-(2,4-dinitrophenyl)but-3-yn-1-yl)-2-iodoaniline (3cc)



Yellow oil, 75% yield, 92:8 *er*, R_f = 0.3 (petroleum ether/ethyl acetate = 20:1), $[\alpha]_D^{20}$ = + 77.0 ° (*c* = 1 mg / mL, THF). **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 8.86 (d, *J* = 2.3 Hz, 1H), 8.39 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.07 – 6.89 (m, 1H), 6.47 (td, *J* = 7.7, 1.4 Hz, 1H), 6.12 (dd, *J* = 8.2, 1.3 Hz, 1H), 5.48 (dd, *J* = 11.1, 5.5 Hz, 1H), 5.31 (d, *J* = 6.5 Hz, 1H), 3.11 (ddd, *J* = 17.2, 5.6, 2.7 Hz, 1H), 2.87 (ddd, *J* = 17.2, 4.6, 2.7 Hz, 1H), 2.24 (t, *J* = 2.7 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ 148.9, 147.4, 144.2, 143.6, 139.4, 130.8, 129.6, 127.5, 120.5, 120.3, 111.5, 85.8, 77.6, 74.0, 51.4, 26.5. **HPLC**: AD-3; detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 10.09 min (major), 13.92 min (minor). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{12}IN_3O_4H^+$ 437.9945; Found 437.9944.

HPLC Spectra of **3a** in the **Scheme 4 A**



<PeakTable>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
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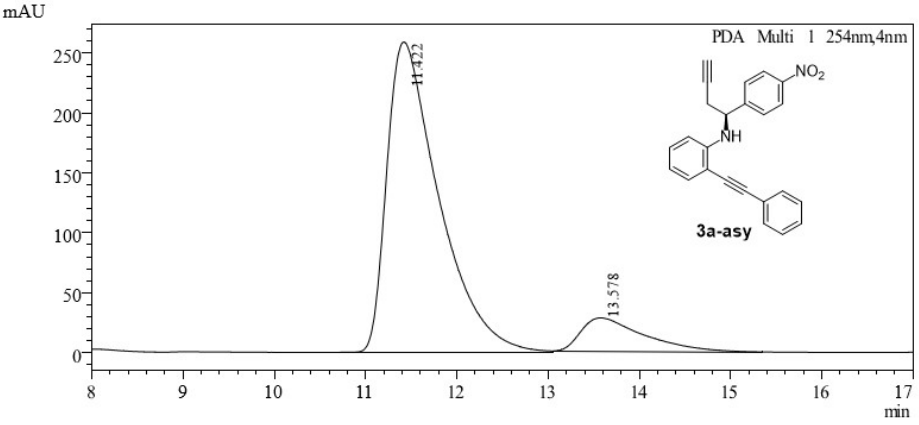
2	14.335	21265684	476850	44.434
Total		47859346	1205291	100.000



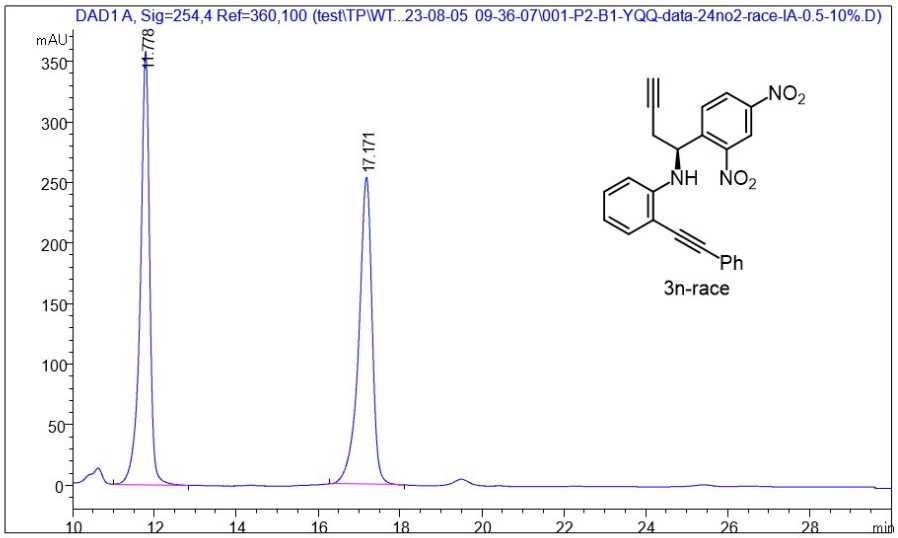
<PeakTable>

PDA Ch1 254nm

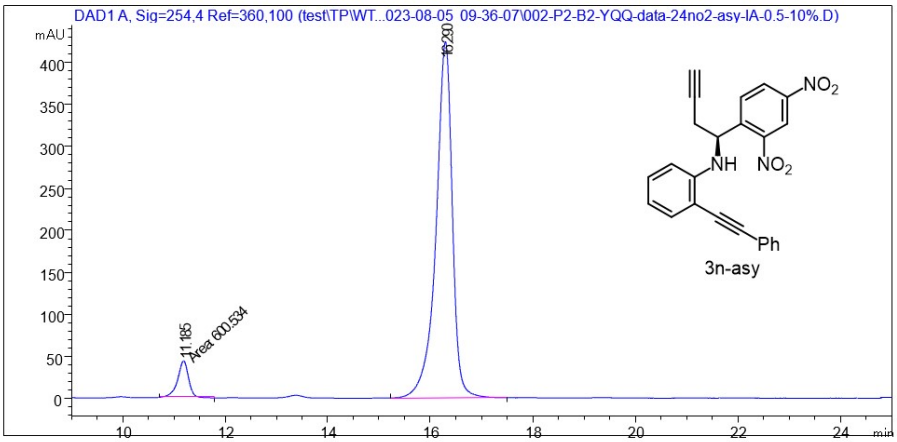
Peak#	Ret. Time	Area	Hight	Area%
1	11.422	10292284	259395	88.586
2	13.578	1326107	28062	11.414
Total		11618391	287457	100.000

HPLC Spectra in the **Scheme 4 B**

HPLC Spectra of **3n**. (IA; detected at 254 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.5 mL/min)



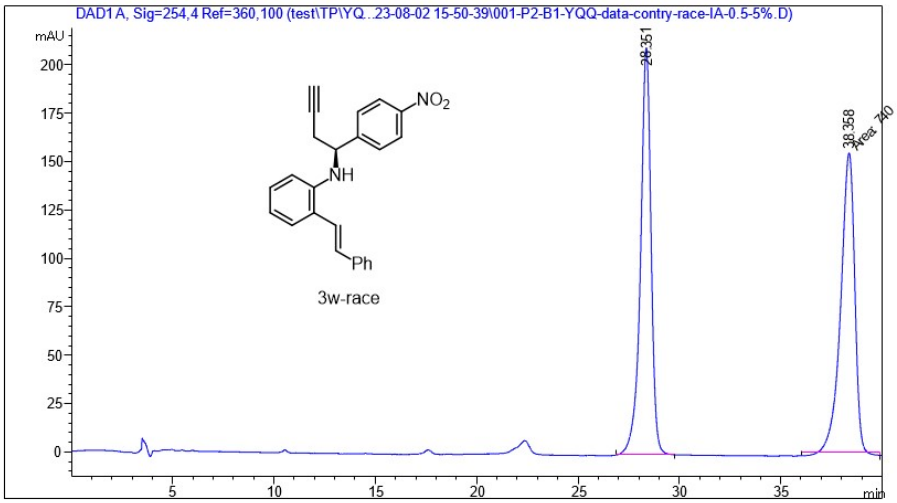
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.778	BB	0.2351	5677.21436	357.89926	49.6899
2	17.171	BB	0.3387	5748.08301	253.80292	50.3101



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.185	MM	0.2359	600.53400	42.42539	6.0118
2	16.290	BB	0.3300	9388.75488	423.65442	93.9882

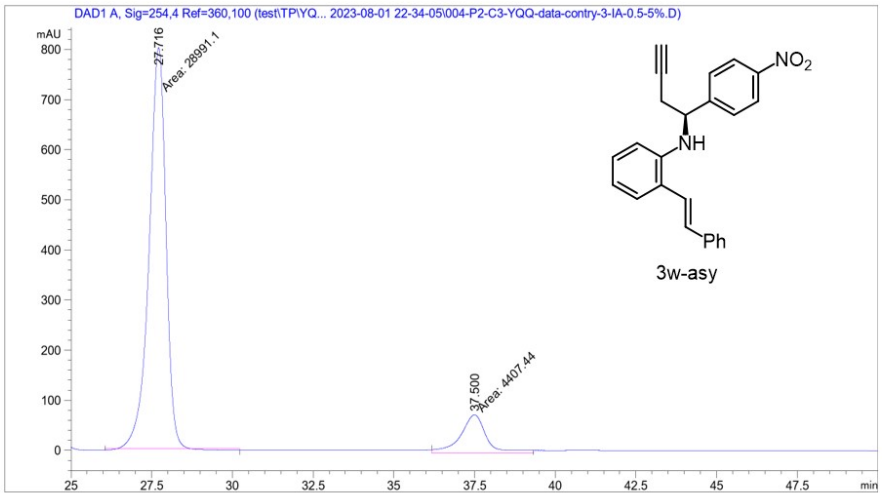
HPLC Spectra of **3w**

The racemic spectra. (IA; detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow = 0.5 mL/min)



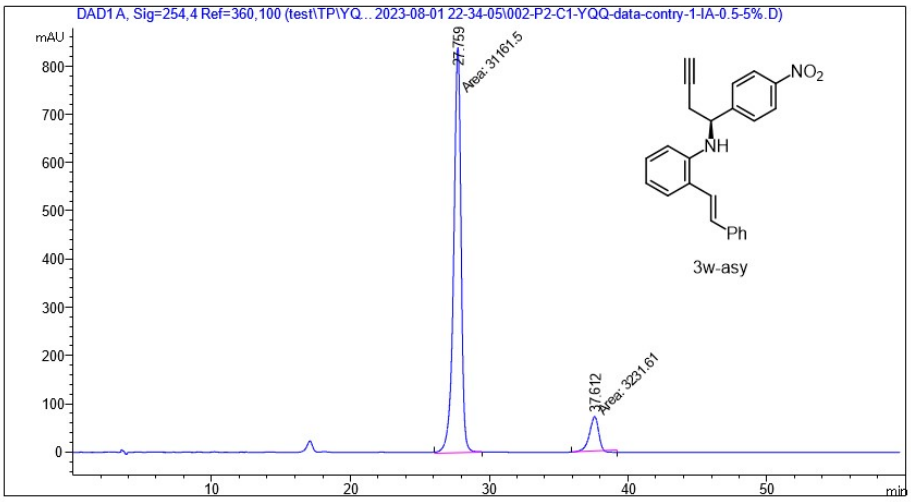
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.351	BB	0.5196	7626.32422	210.03429	50.7432
2	38.358	MM	0.7977	7402.91895	154.67326	49.2568

Entry 1 (Ligand = **3n**)



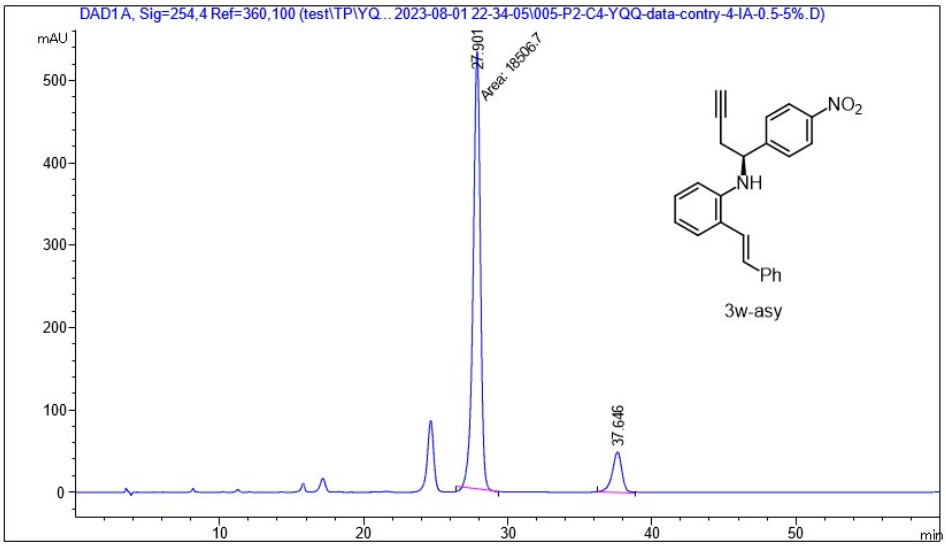
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.716	MM	0.6038	2.89911e4	800.19885	86.8035
2	37.500	MM	0.9585	4407.43750	76.63668	13.1965

Entry 2 (Ligand = **L10**)



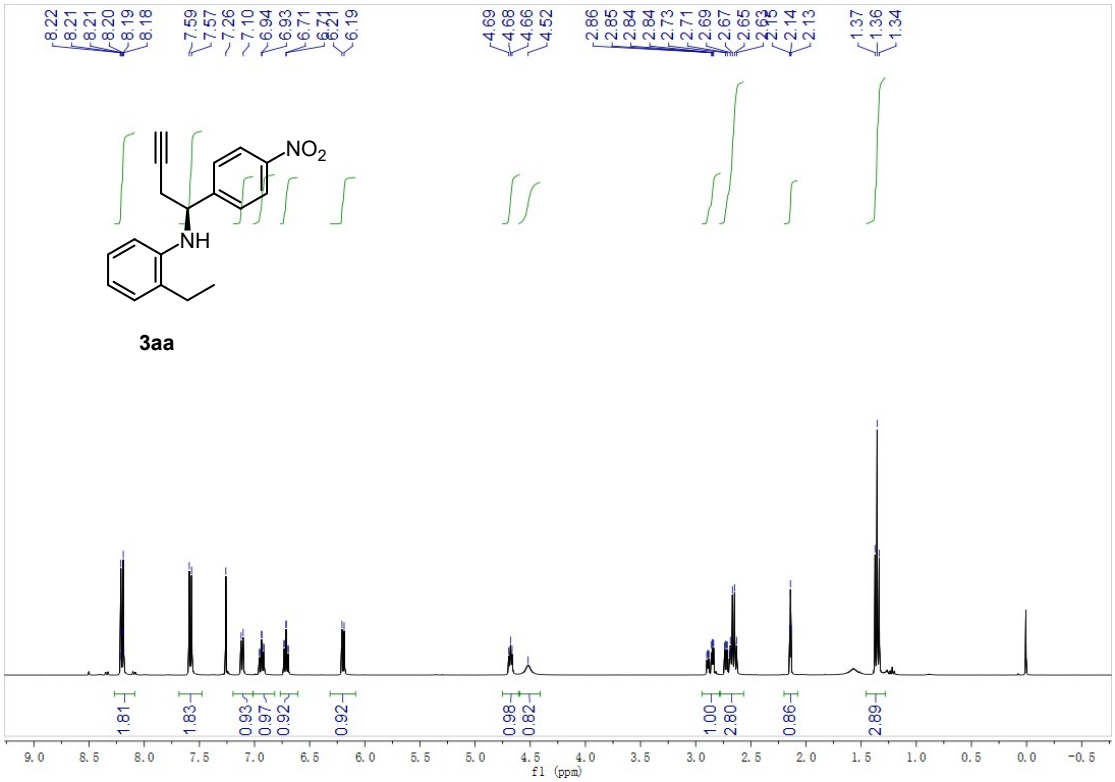
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.759	MM	0.6196	3.11615e4	838.17175	90.6039
2	37.612	MM	0.7543	3231.61377	71.40480	9.3961

Entry 3 (Ligand = **L10** + **3n**)

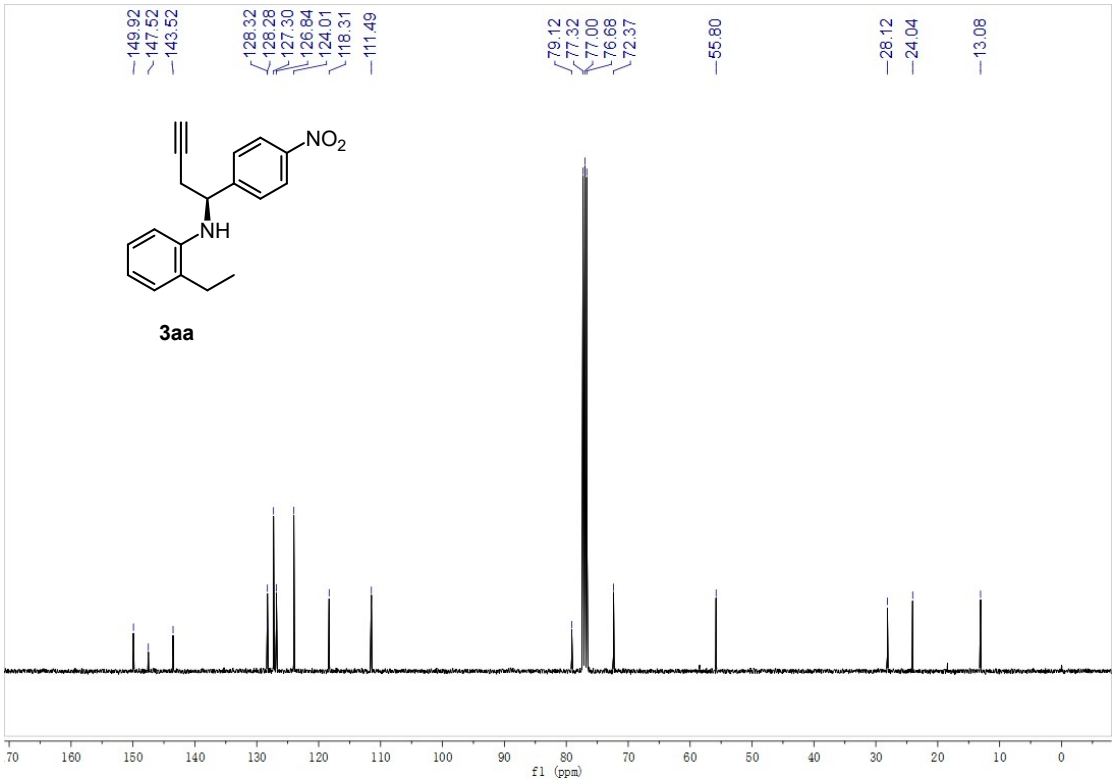


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.901	MM	0.5810	1.85067e4	530.89331	89.3352
2	37.646	BB	0.5346	2209.30908	48.53116	10.6648

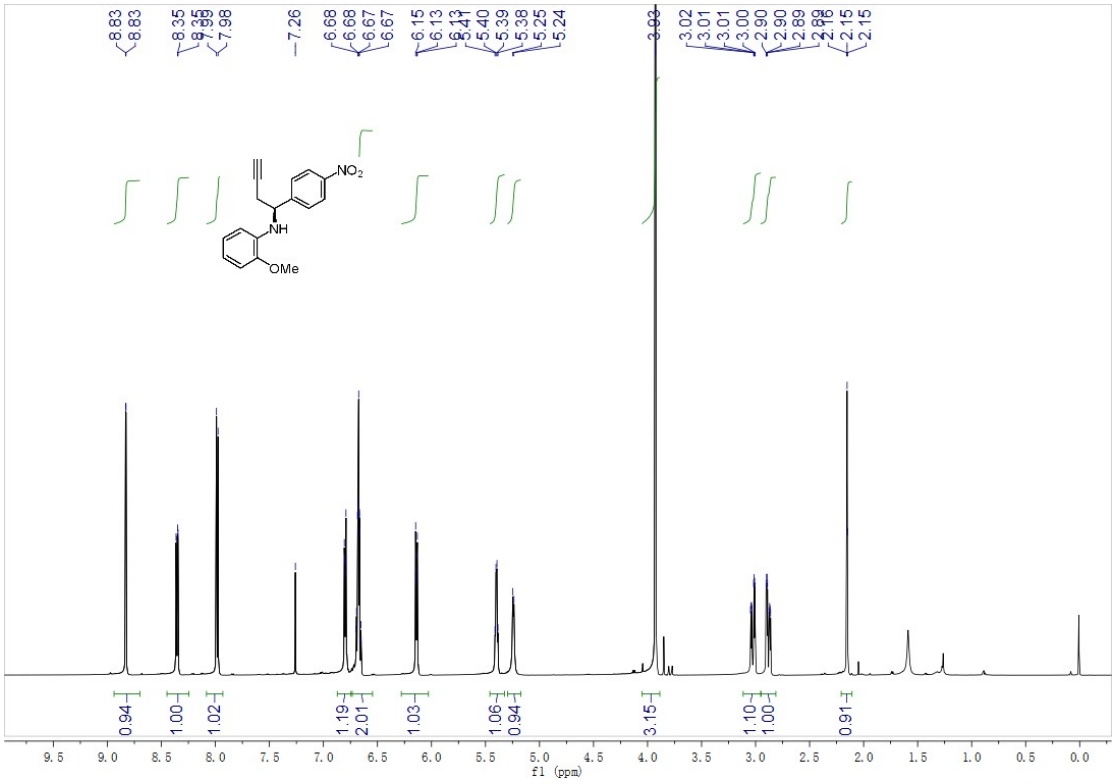
[1]H NMR Spectra of **3aa** in the **Scheme 4 C** (400 MHz, $CDCl_3$)



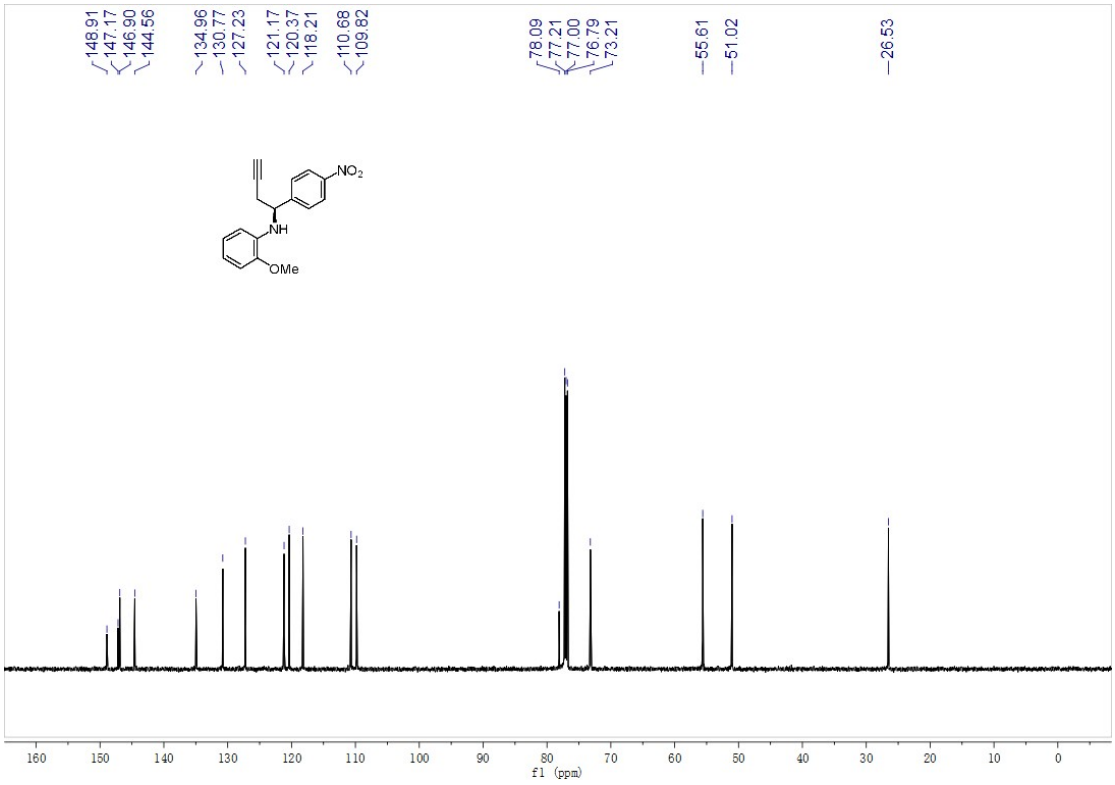
[1]C NMR Spectra of **3aa** in the **Scheme 4 C** (101 MHz, $CDCl_3$)



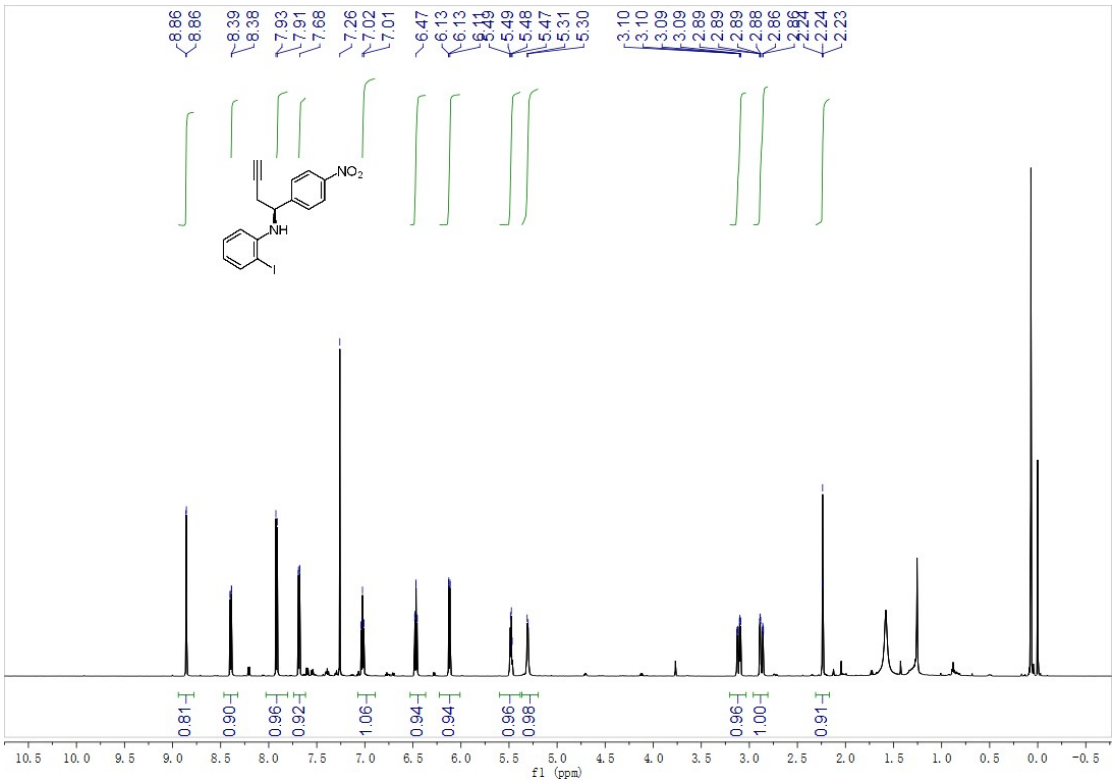
^{1}H NMR Spectra of **3bb** in the **Scheme 4 C** (600 MHz, $CDCl_3$)



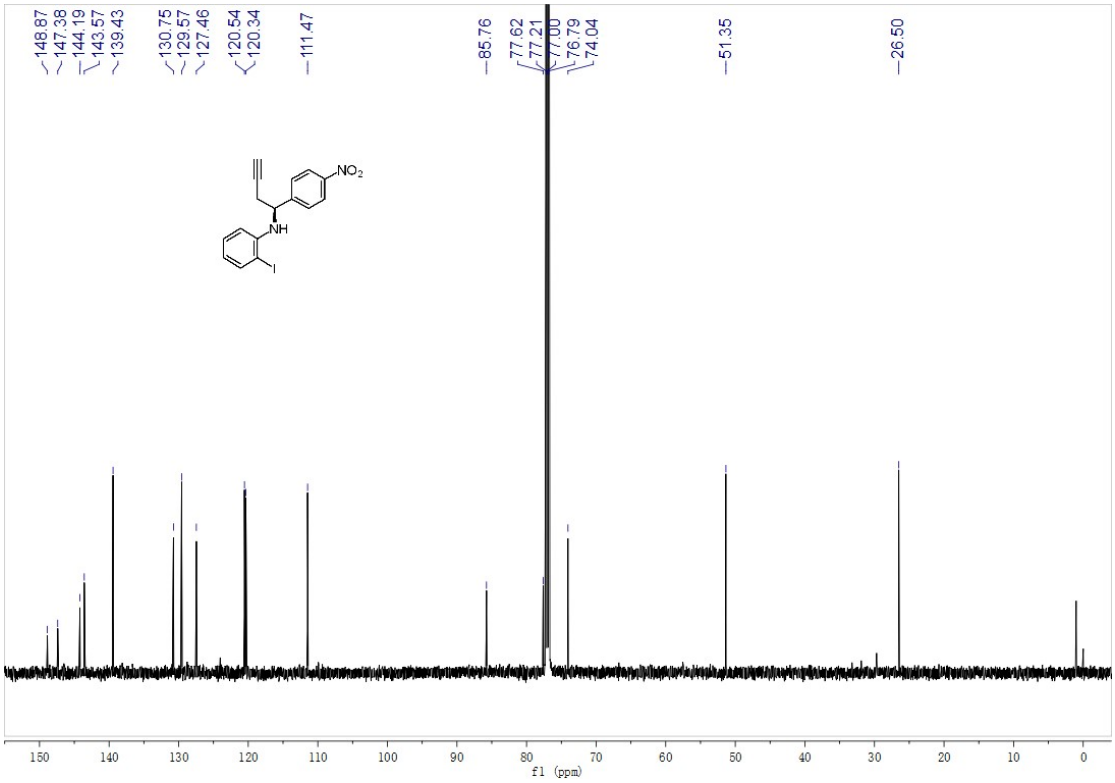
^{1}C NMR Spectra of **3bb** in the **Scheme 4 C** (151 MHz, $CDCl_3$)



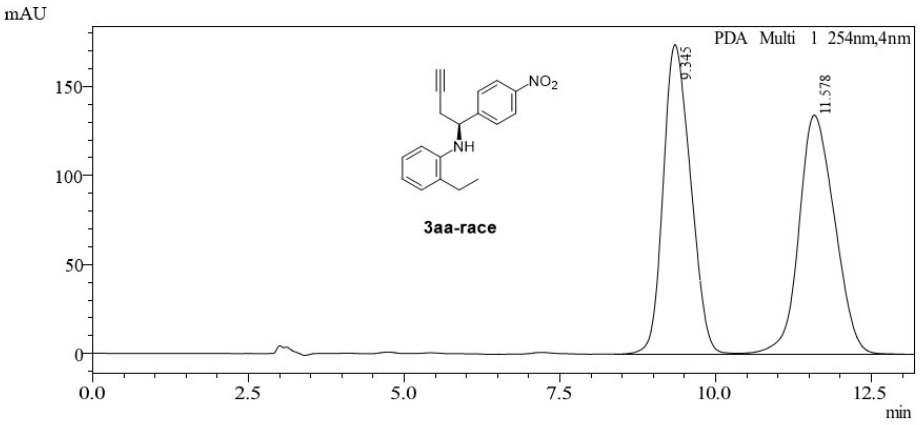
^{1}H NMR Spectra of **3cc** in the **Scheme 4 C** (600 MHz, $CDCl_3$)



^{1}C NMR Spectra of **3cc** in the **Scheme 4 C** (151 MHz, $CDCl_3$)

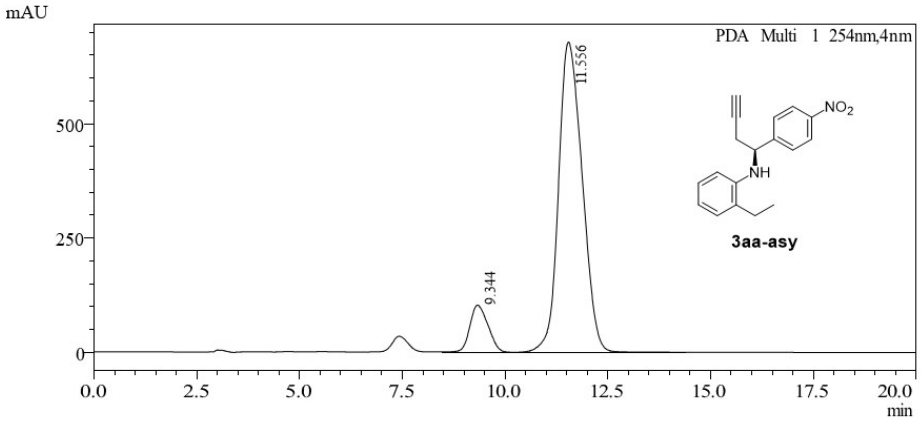


HPLC Spectra of **3aa** in the **Scheme 4 C**



<PeakTable>
PDA Ch1 254nm

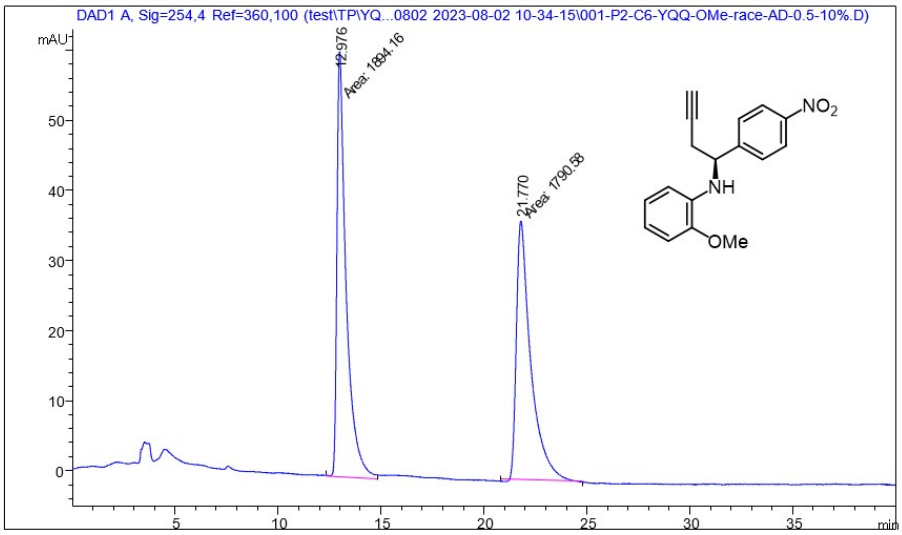
Peak#	Ret. Time	Area	Hight	Area%
1	9.345	5327564	174177	49.837
2	11.578	5362456	134143	50.163
Total		10690020	308320	100.000



<PeakTable>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	9.344	3117617	101880	10.275
2	11.556	27222829	679207	89.725
Total		30340446	781087	100.000

HPLC Spectra of **3bb** in the **Scheme 4 C**



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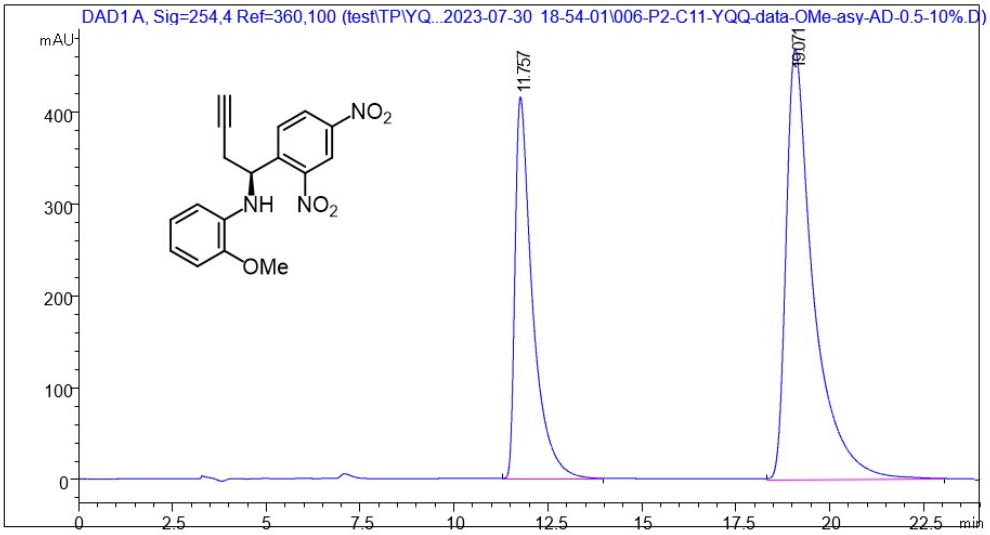
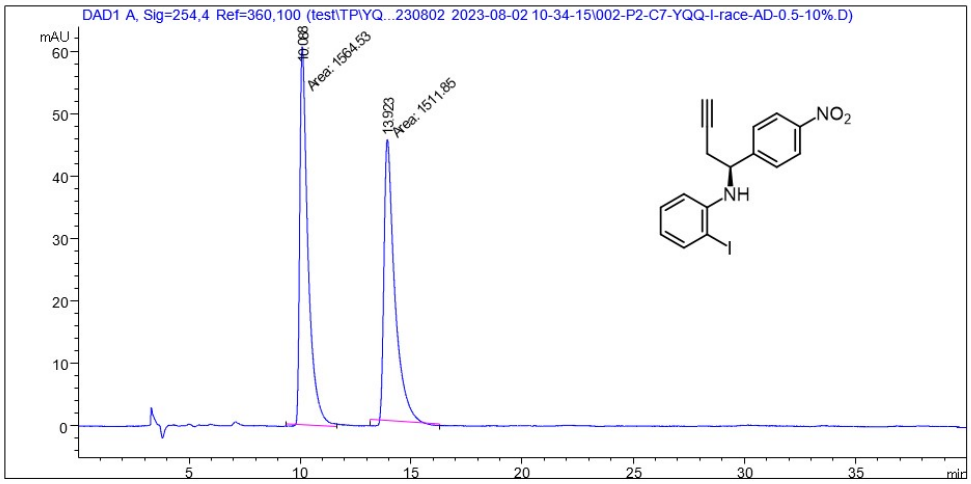
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.976	MM	0.5193	1894.16187	60.78710	51.4056
2	21.770	MM	0.8089	1790.57996	36.89495	48.5944

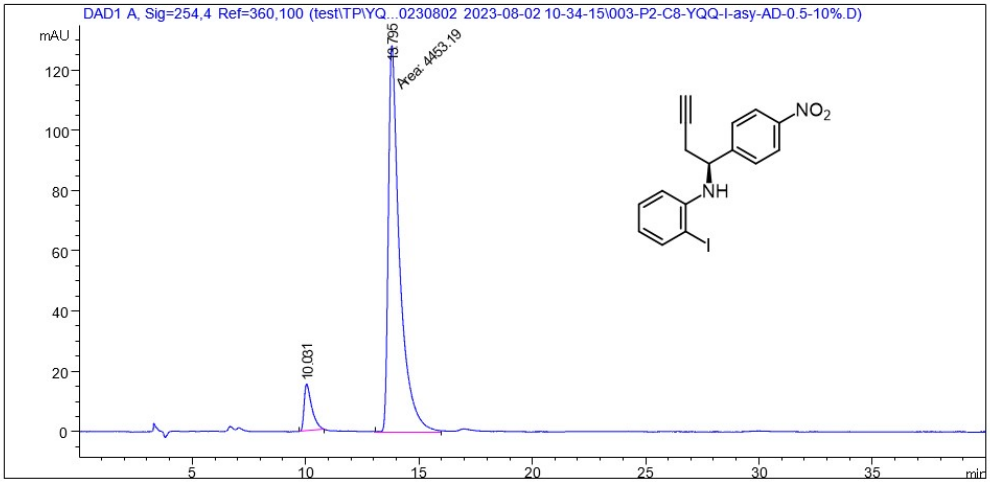


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.757	BB	0.4632	1.34506e4	415.48282	36.4195
2	19.071	BB	0.7102	2.34818e4	467.74744	63.5805

HPLC Spectra of **3cc** in the **Scheme 4 C**



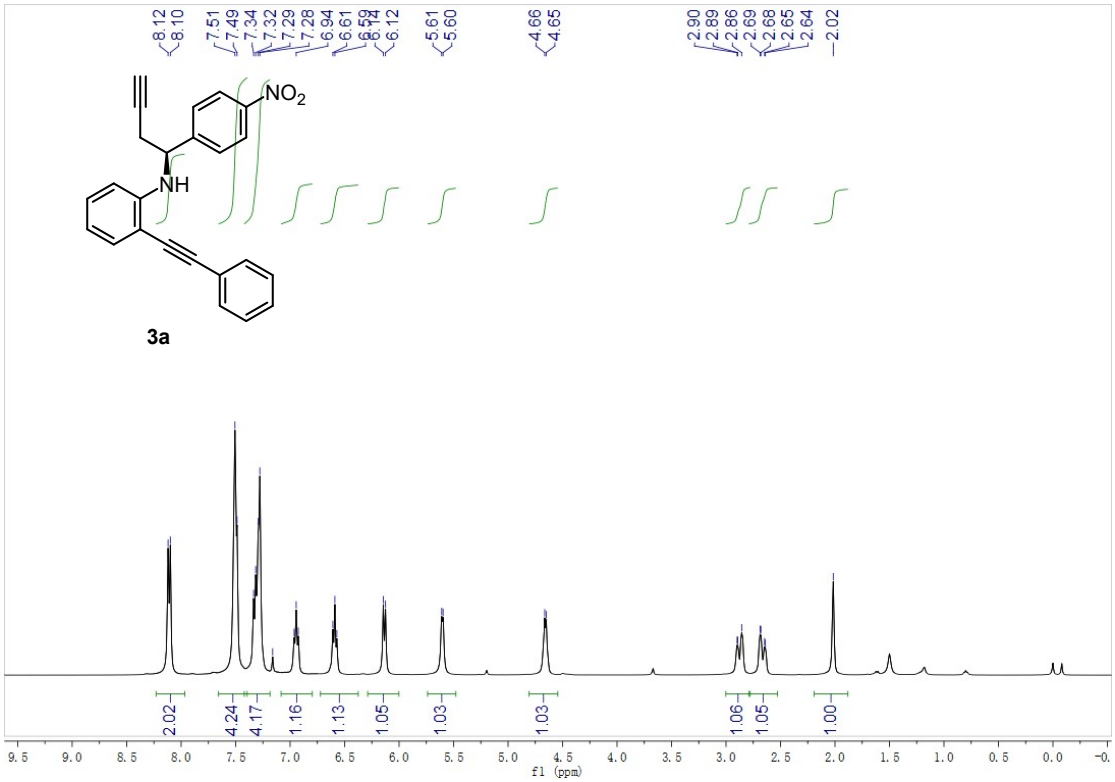
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.088	MM	0.4303	1564.52905	60.59906	50.8561
2	13.923	MM	0.5583	1511.85425	45.12960	49.1439



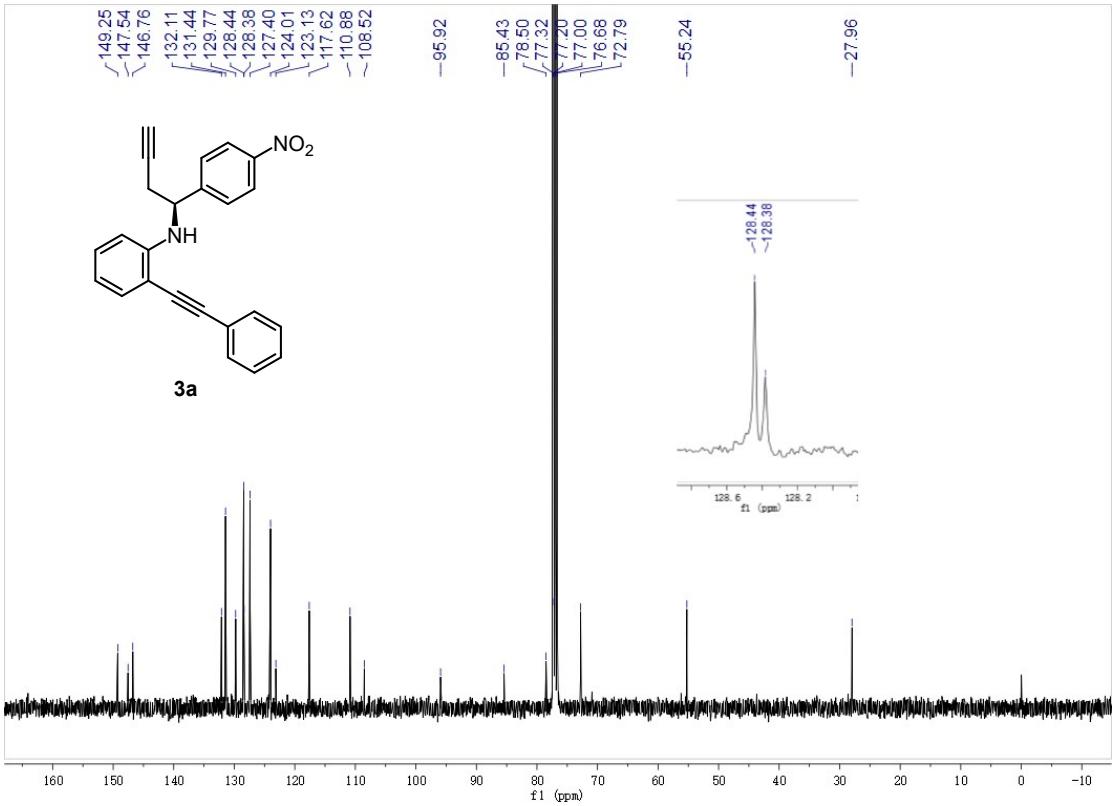
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.031	BBA	0.3120	361.43997	15.50064	7.5071
2	13.795	MM	0.5783	4453.18701	128.35004	92.4929

7. NMR Spectra of Products 3a–3x

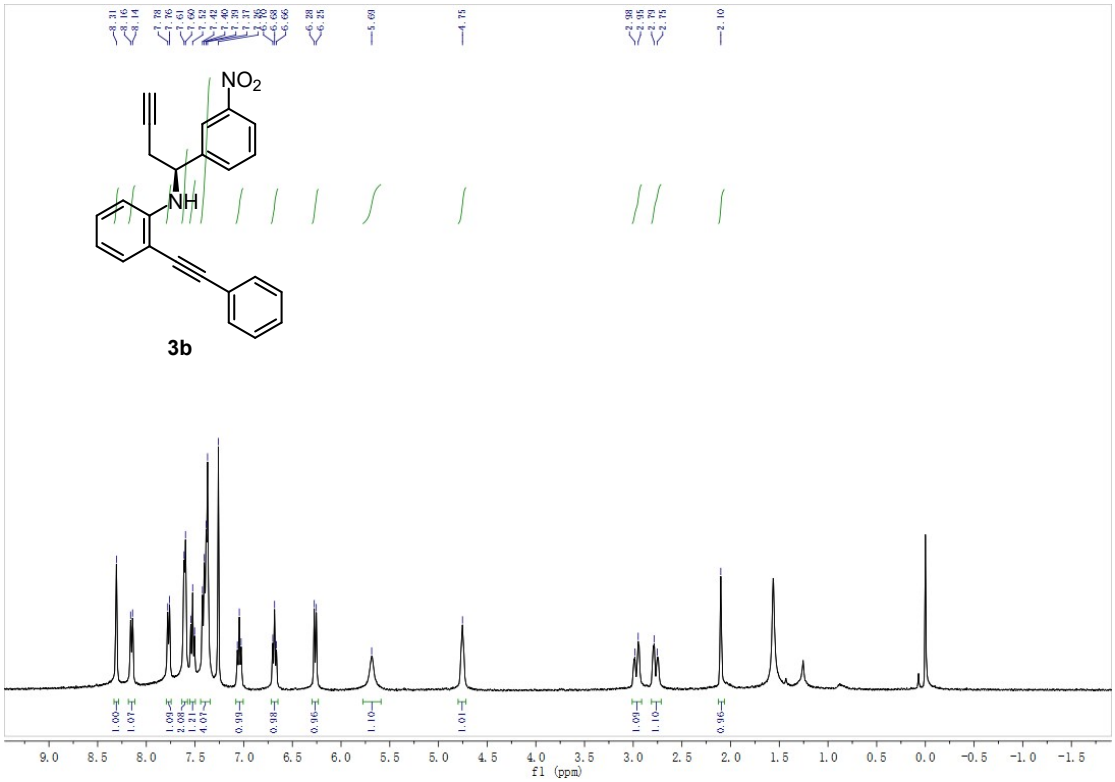
^{1}H NMR Spectra of **3a** (400 MHz, $CDCl_3$)



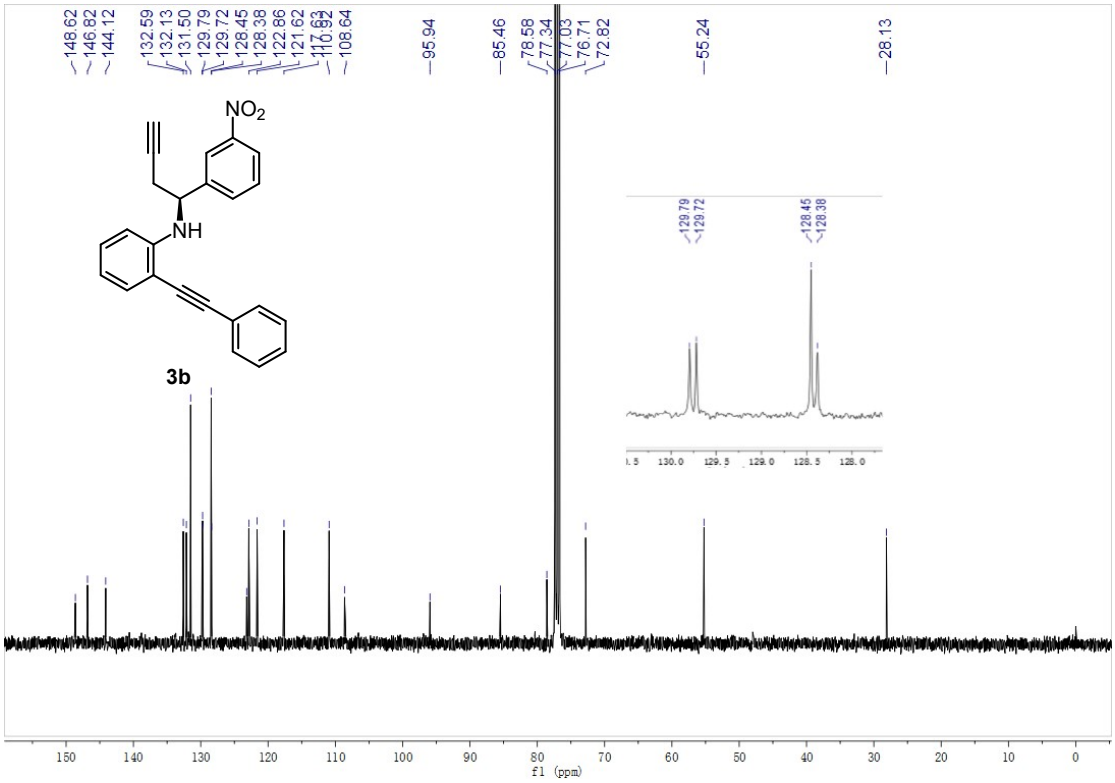
^{1}C NMR Spectra of **3a** (101 MHz, $CDCl_3$)



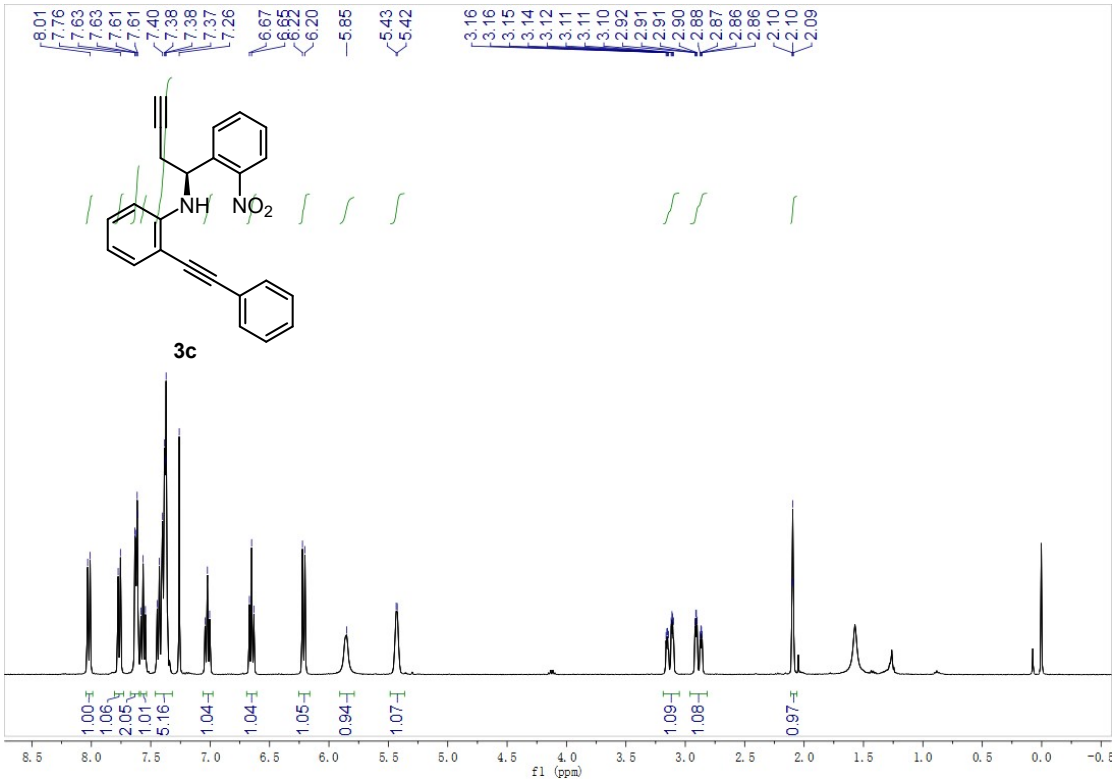
^{1}H NMR Spectra of **3b** (400 MHz, $CDCl_3$)



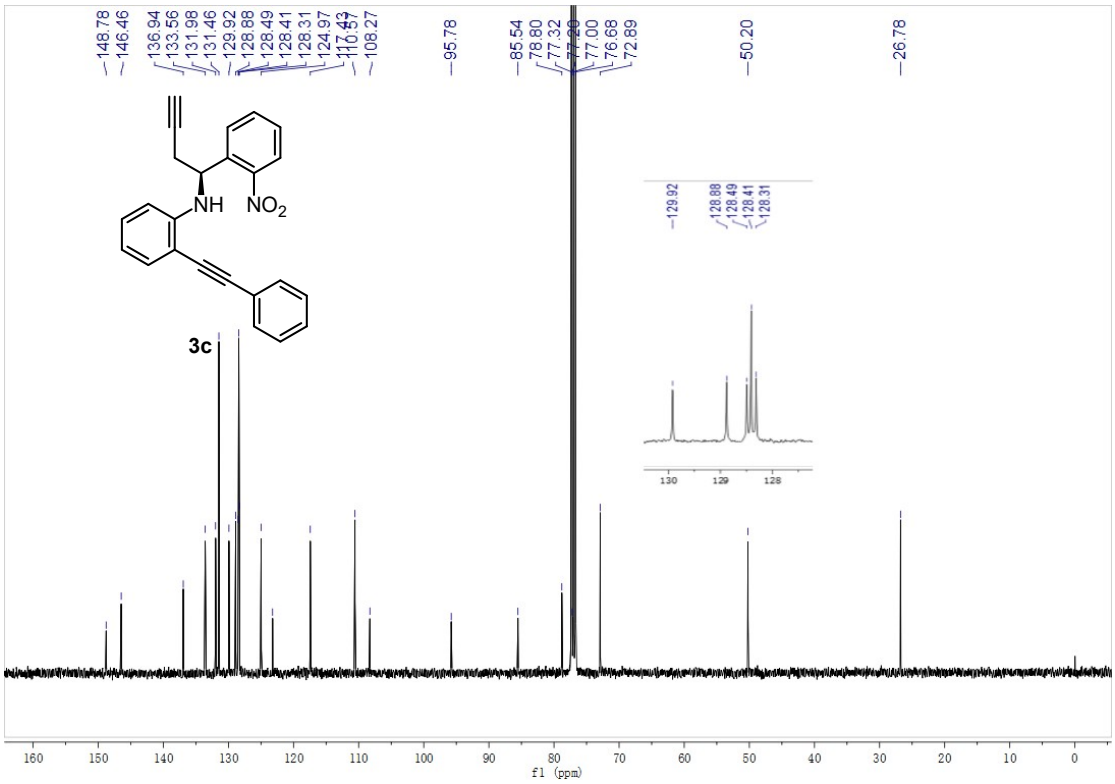
^{1}C NMR Spectra of **3b** (101 MHz, $CDCl_3$)



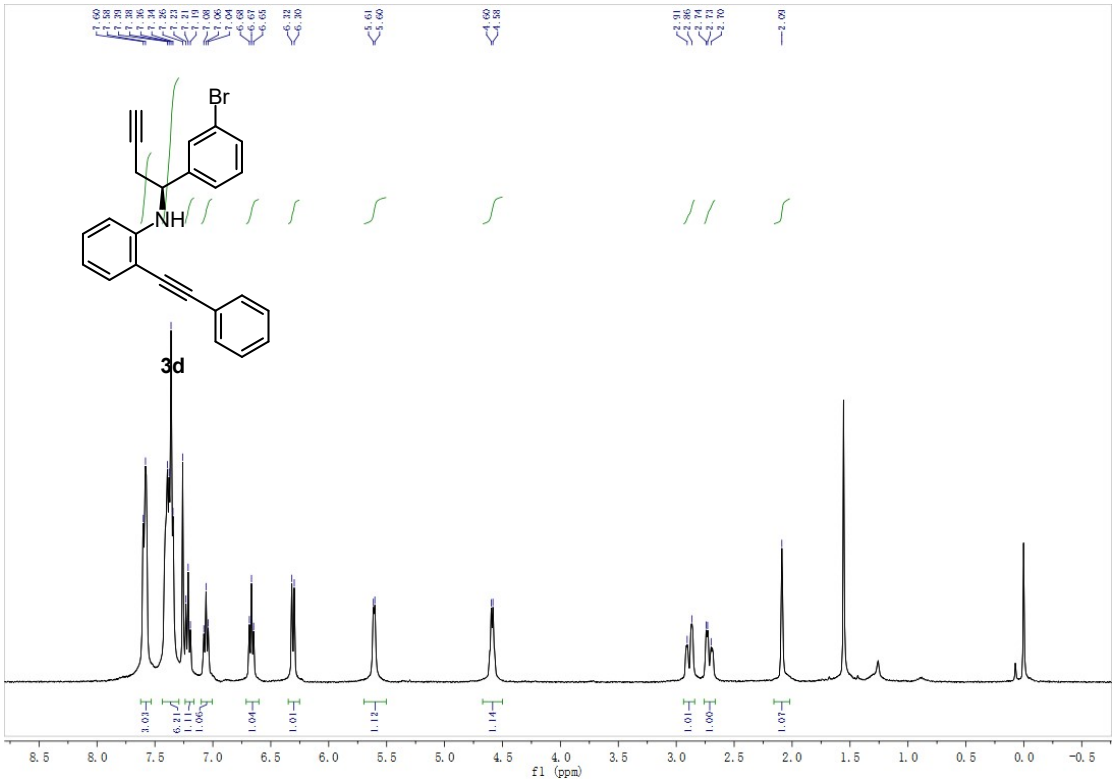
^{1}H NMR Spectra of **3c** (400 MHz, $CDCl_3$)



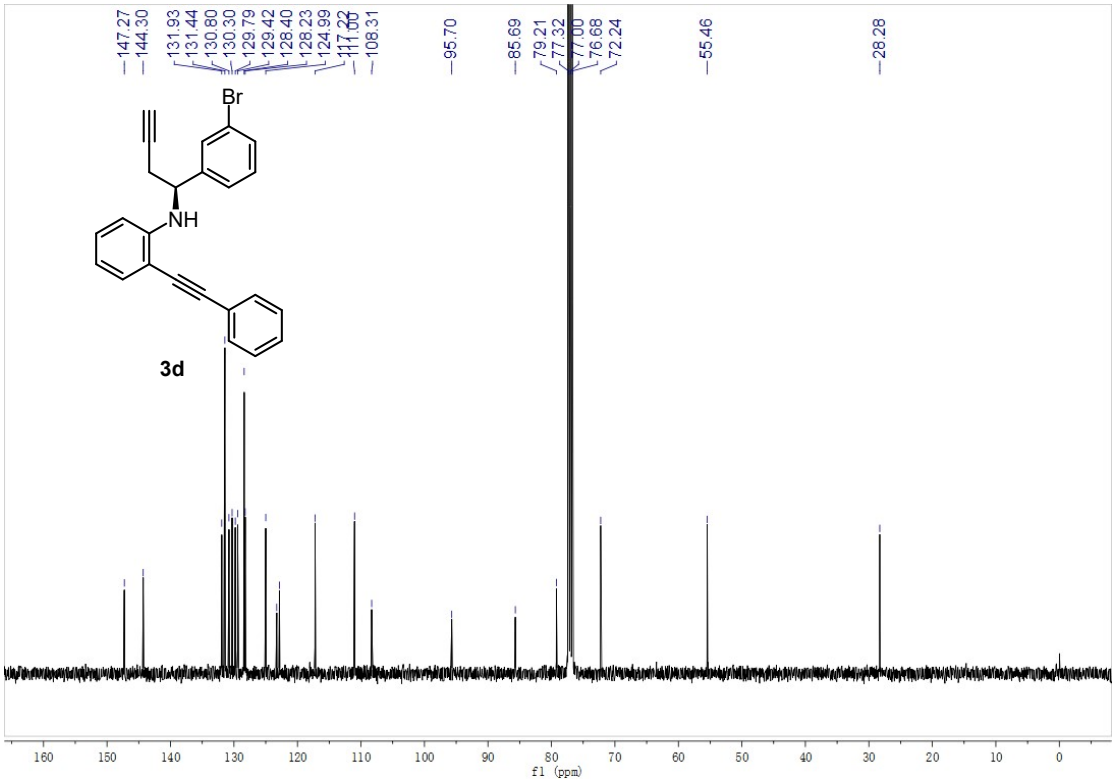
^{1}C NMR Spectra of **3c** (101 MHz, $CDCl_3$)



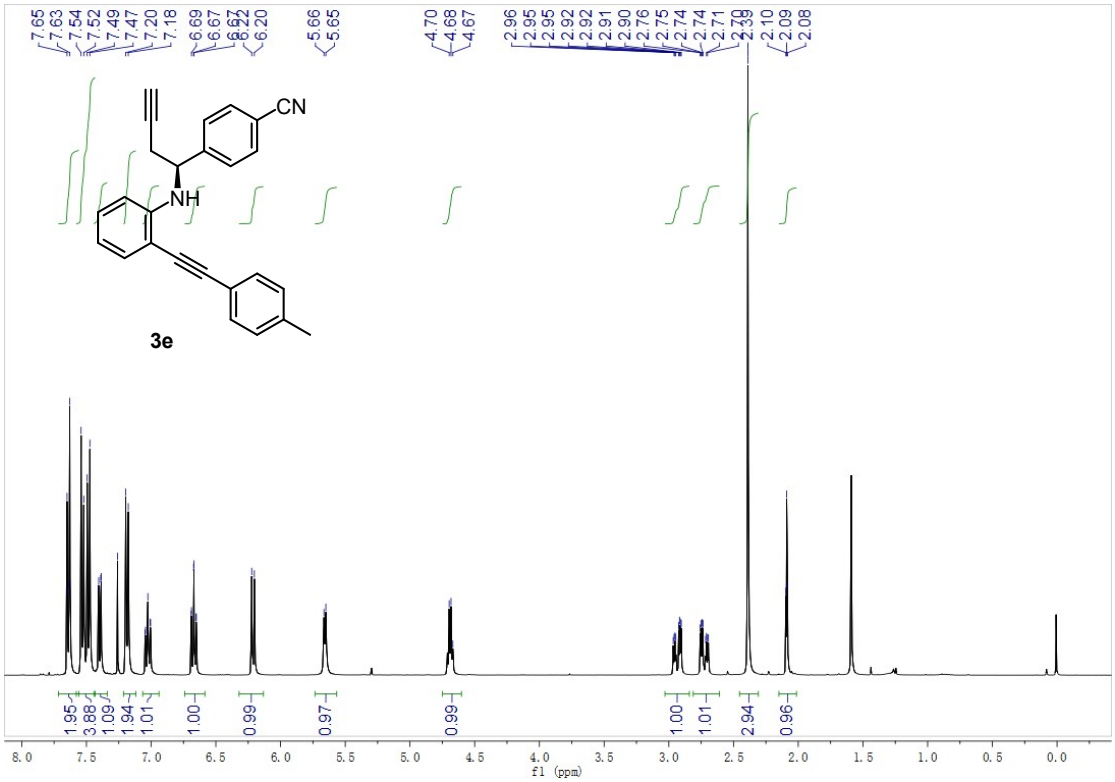
^{1}H NMR Spectra of **3d** (400 MHz, $CDCl_3$)



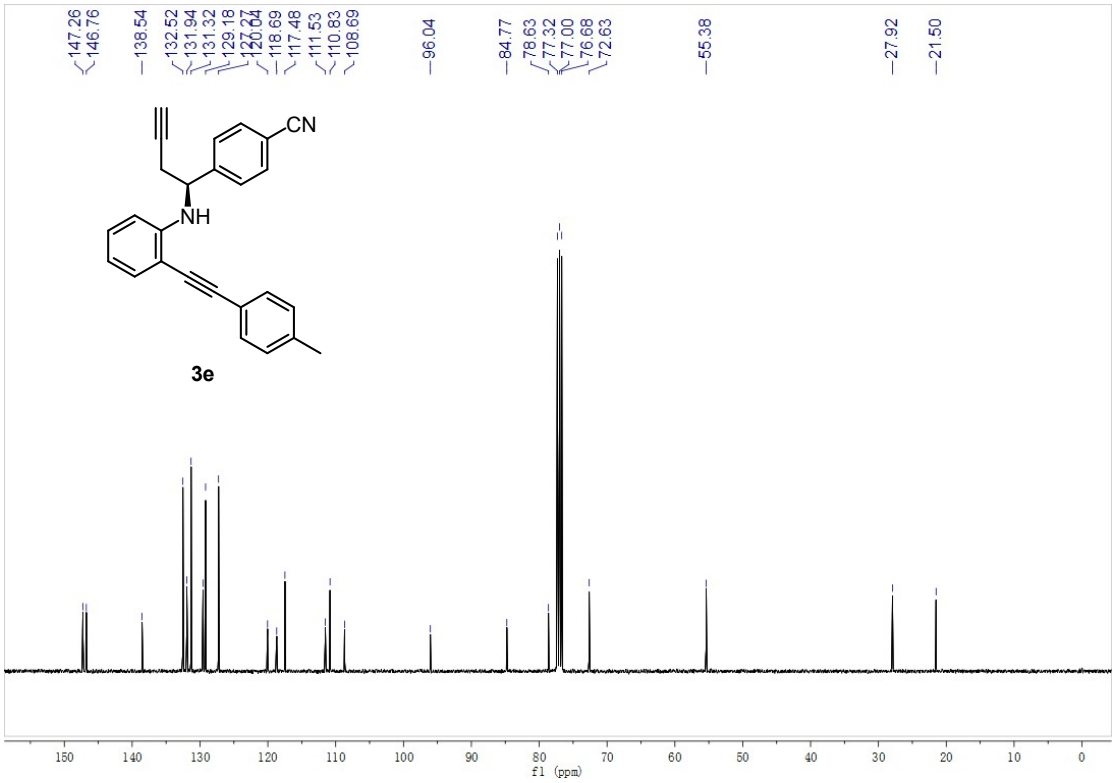
^{1}C NMR Spectra of **3d** (101 MHz, $CDCl_3$)



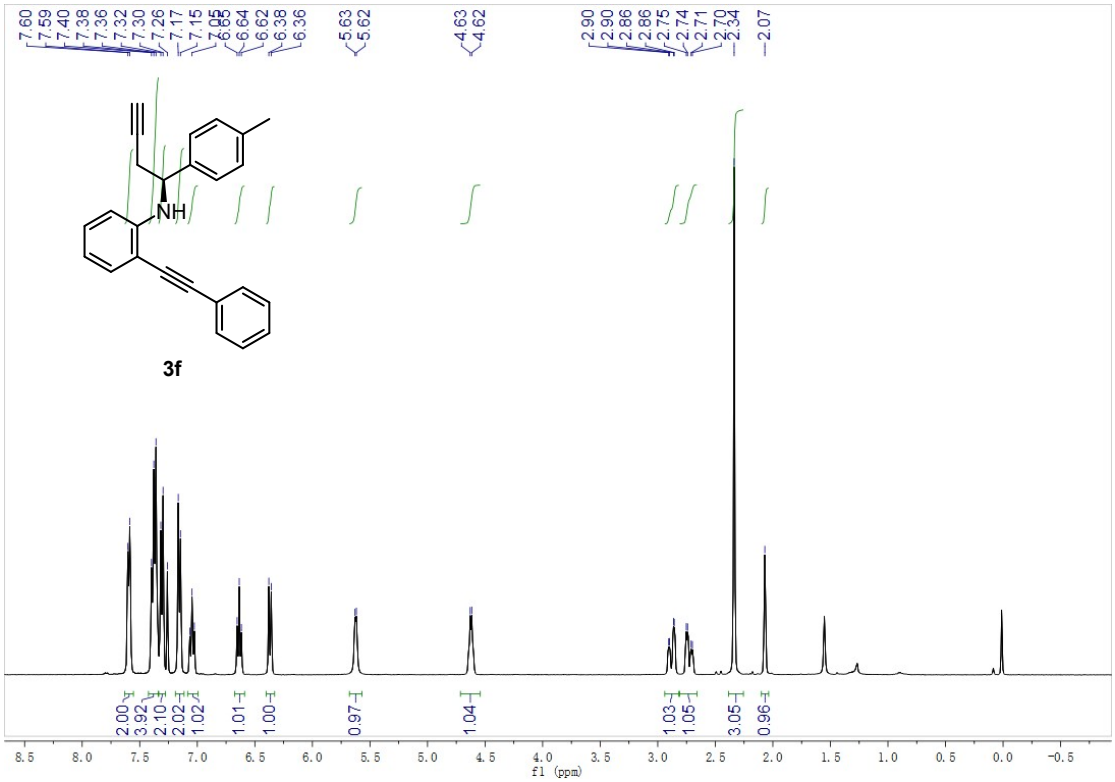
^{1}H NMR Spectra of **3e** (400 MHz, $CDCl_3$)



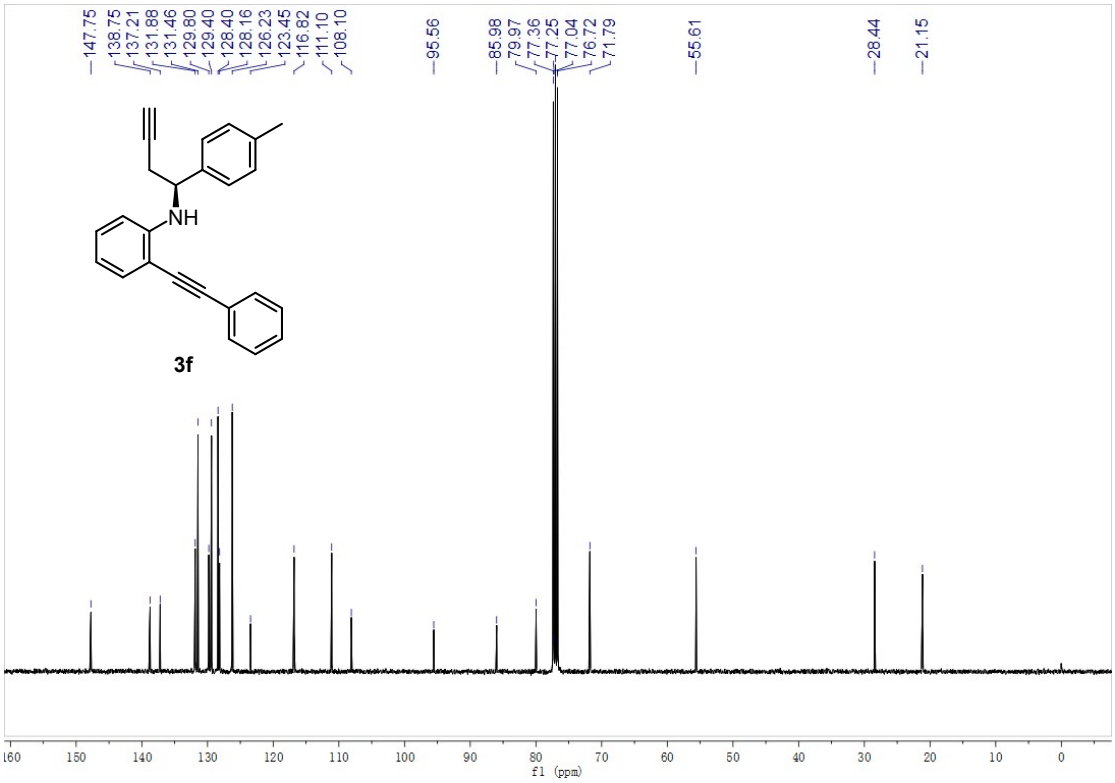
^{1}C NMR Spectra of **3e** (101 MHz, $CDCl_3$)



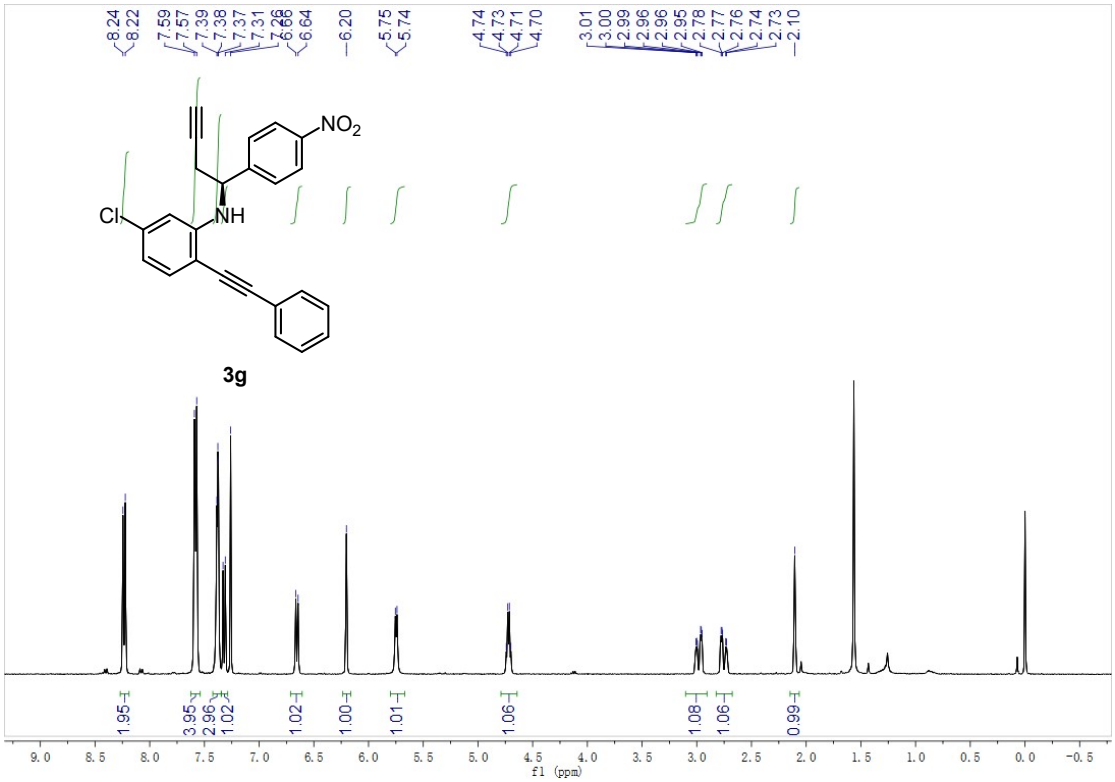
^{1}H NMR Spectra of **3f** (400 MHz, $CDCl_3$)



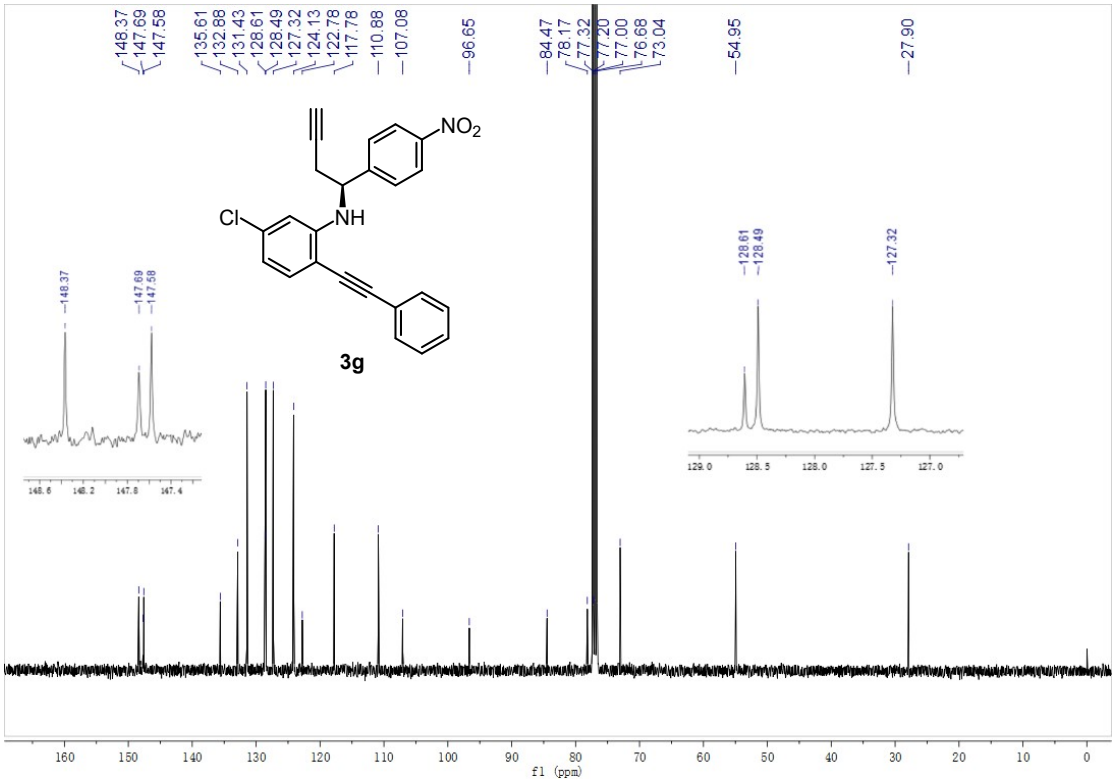
^{1}C NMR Spectra of **3f** (101 MHz, $CDCl_3$)



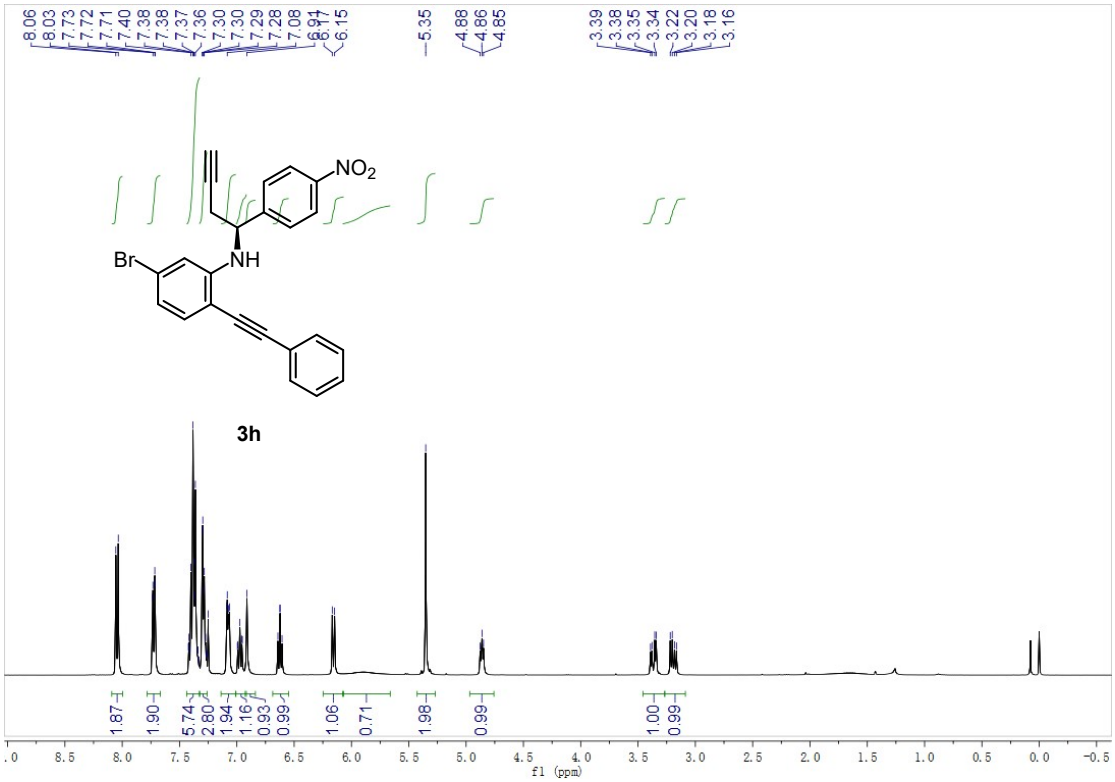
^{1}H NMR Spectra of **3g** (400 MHz, $CDCl_3$)



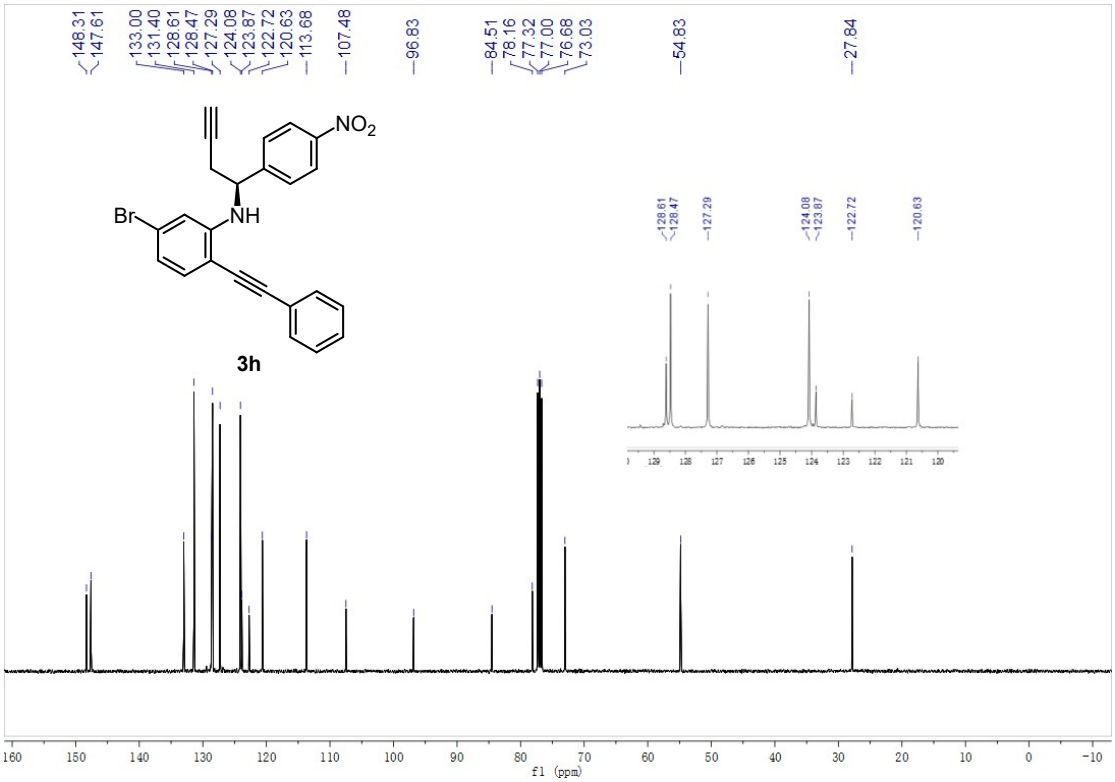
^{1}C NMR Spectra of **3g** (101 MHz, $CDCl_3$)



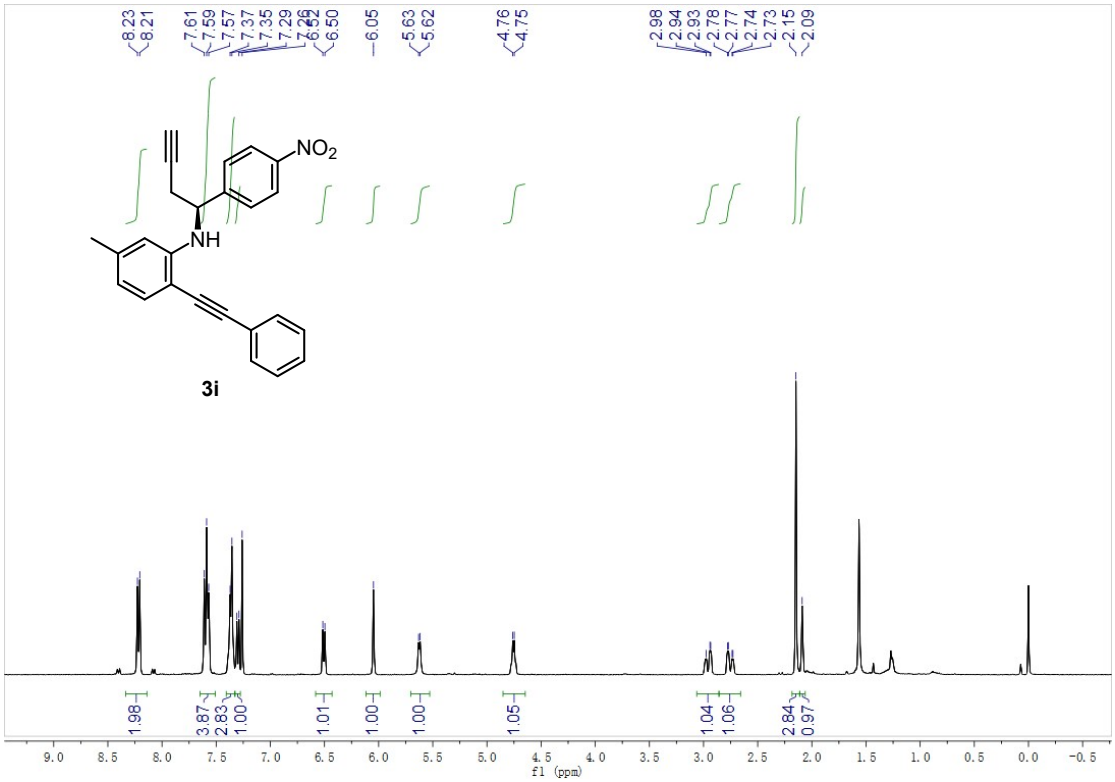
^{1}H NMR Spectra of **3h** (400 MHz, $CDCl_3$)



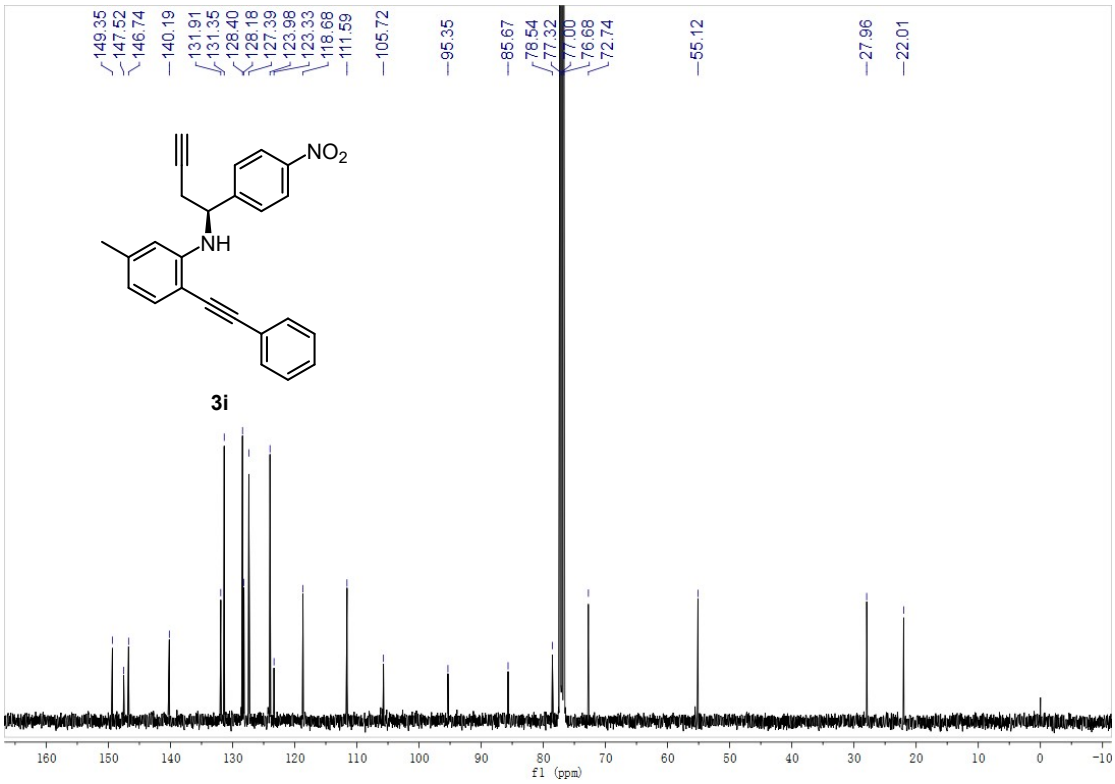
^{1}C NMR Spectra of **3h** (101 MHz, $CDCl_3$)



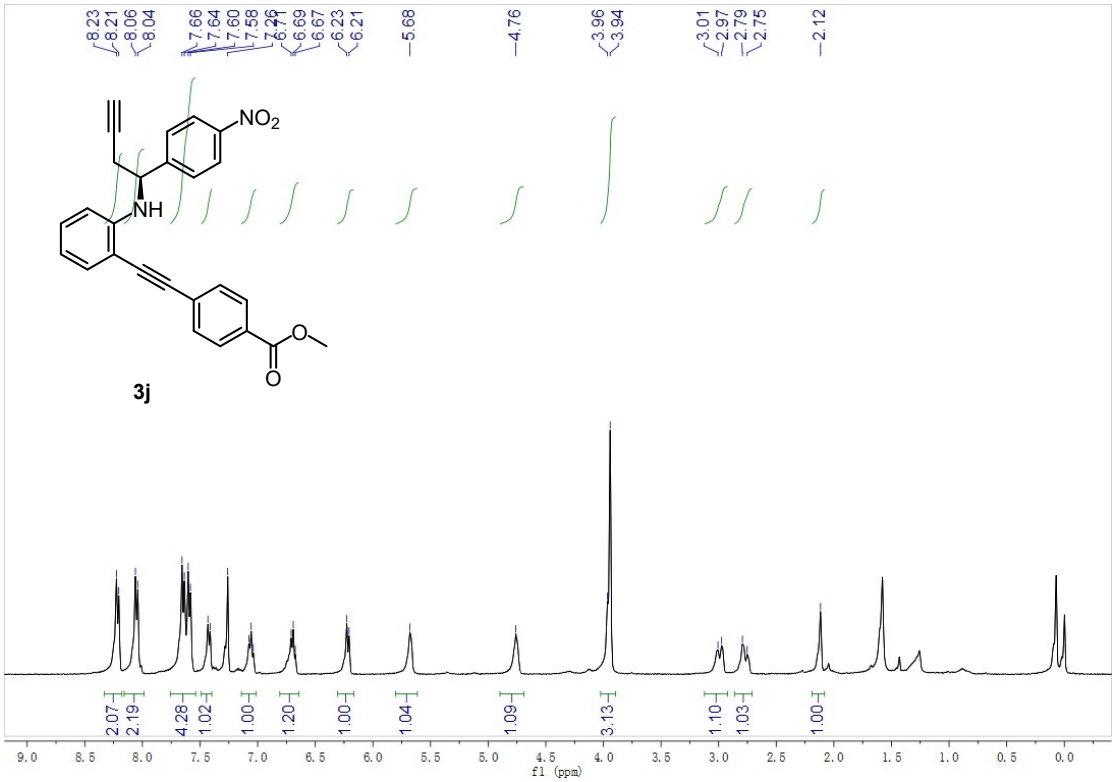
^{1}H NMR Spectra of **3i** (400 MHz, $CDCl_3$)



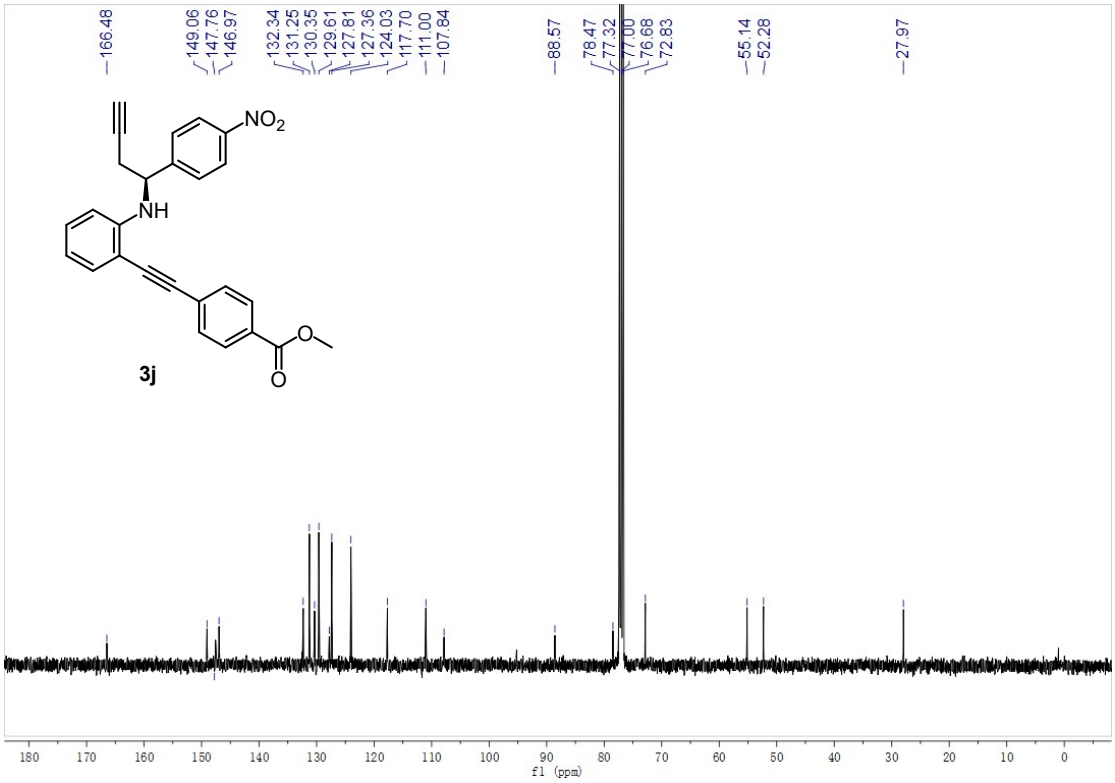
^{1}C NMR Spectra of **3i** (101 MHz, $CDCl_3$)



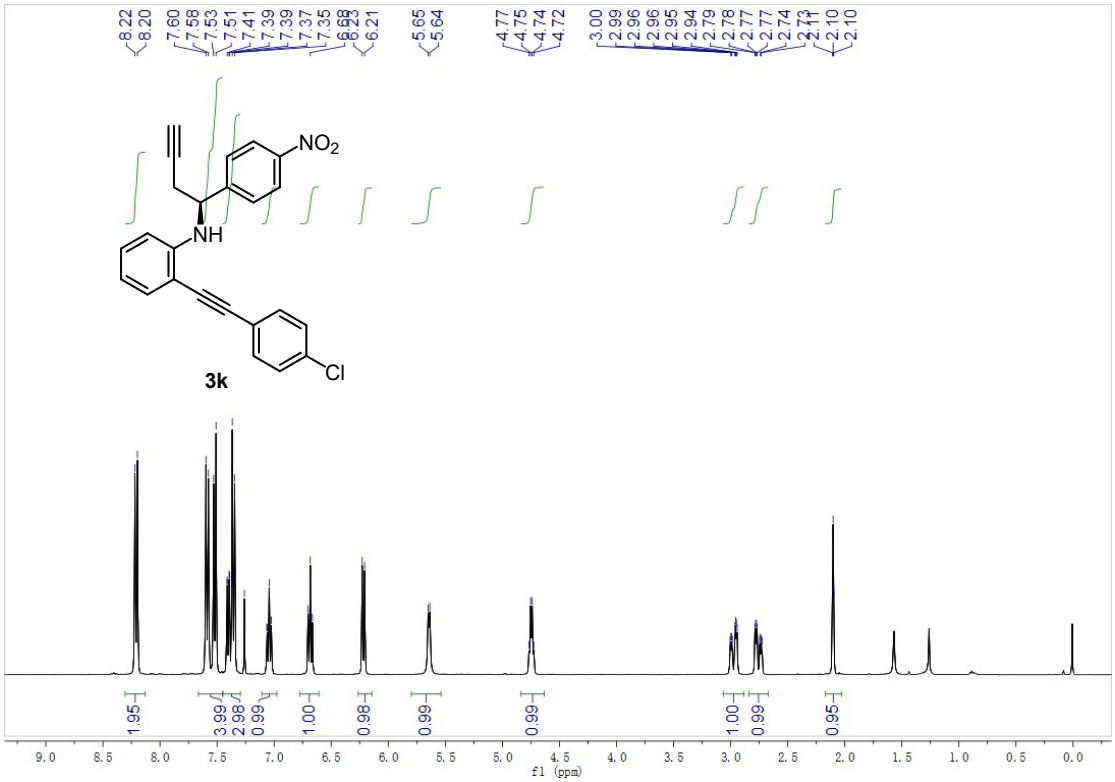
^{1}H NMR Spectra of **3j** (400 MHz, $CDCl_3$)



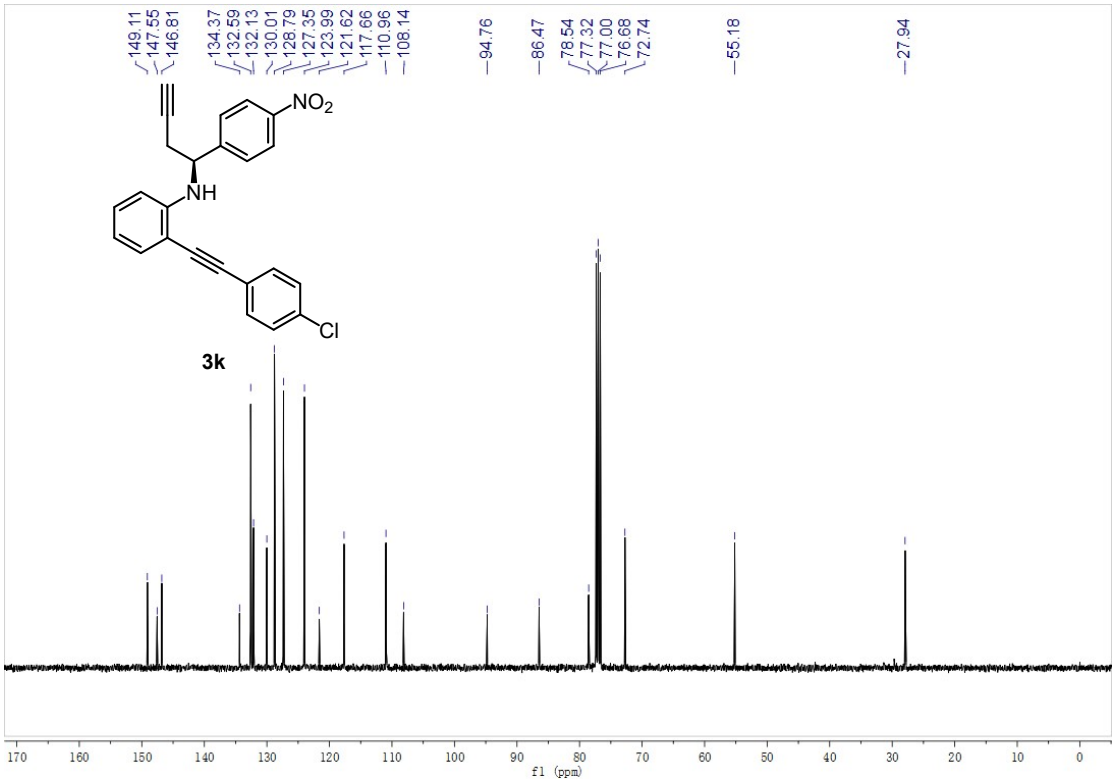
^{1}C NMR Spectra of **3j** (101 MHz, $CDCl_3$)



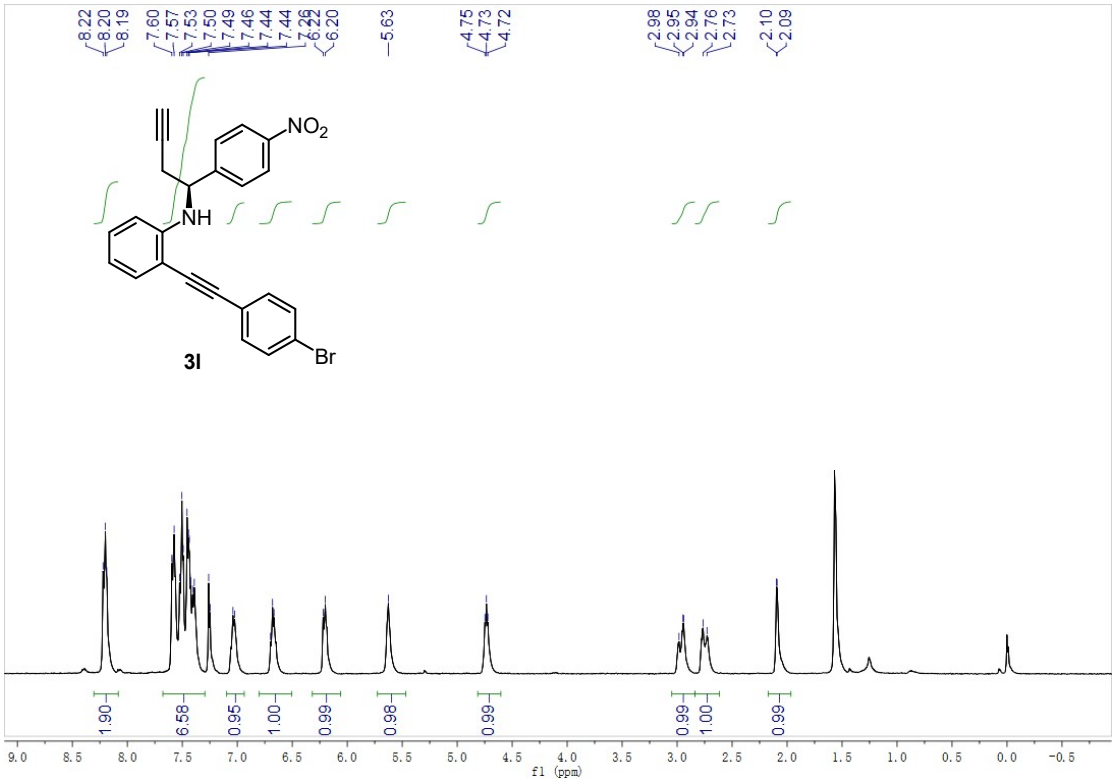
^{1}H NMR Spectra of **3k** (400 MHz, $CDCl_3$)



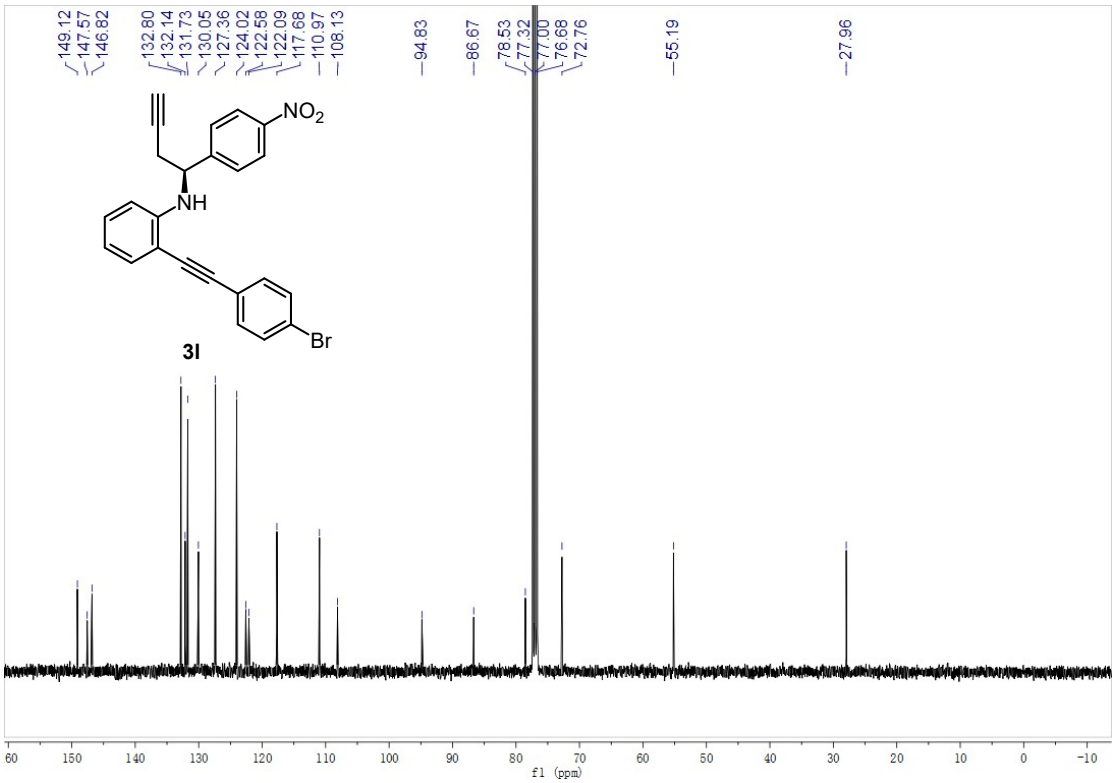
^{1}C NMR Spectra of **3k** (101 MHz, $CDCl_3$)



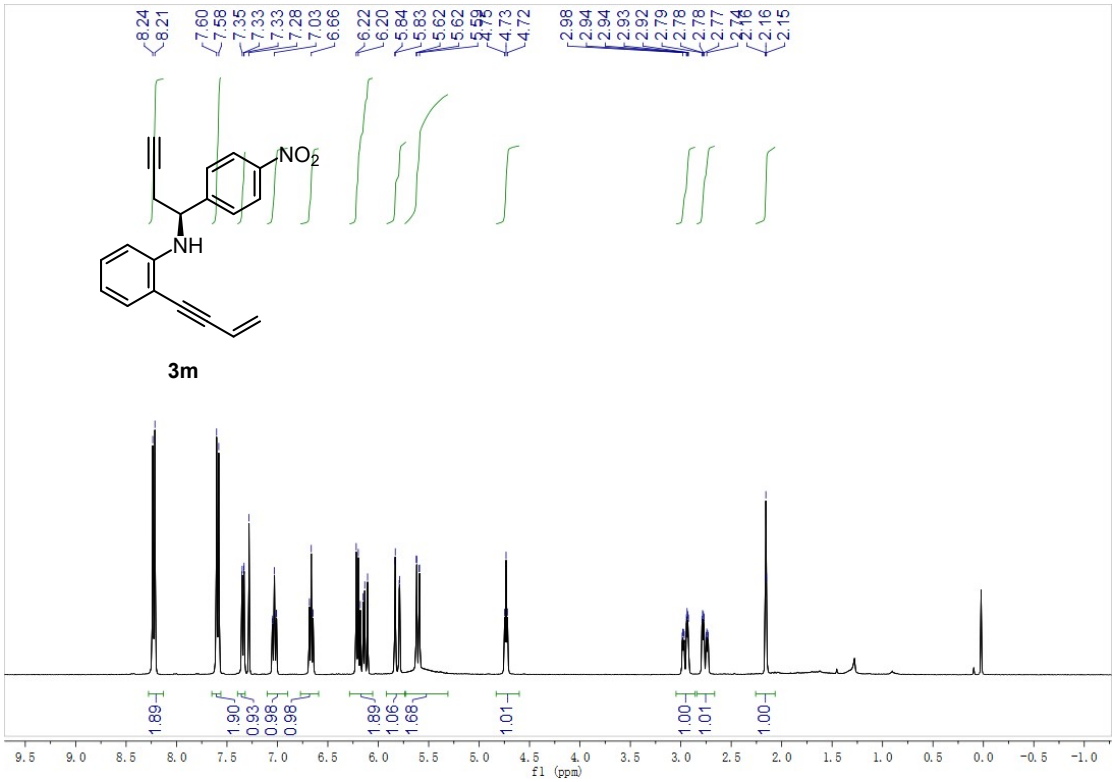
^{1}H NMR Spectra of **3l** (400 MHz, $CDCl_3$)



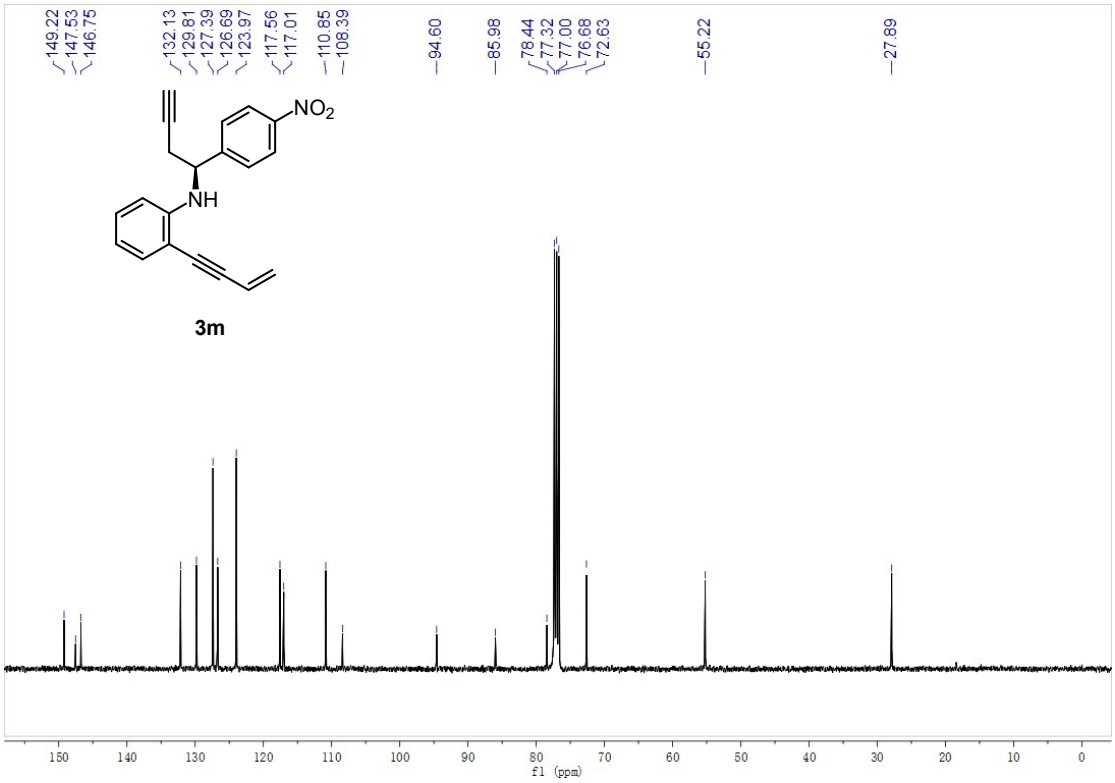
^{1}C NMR Spectra of **3l** (101 MHz, $CDCl_3$)



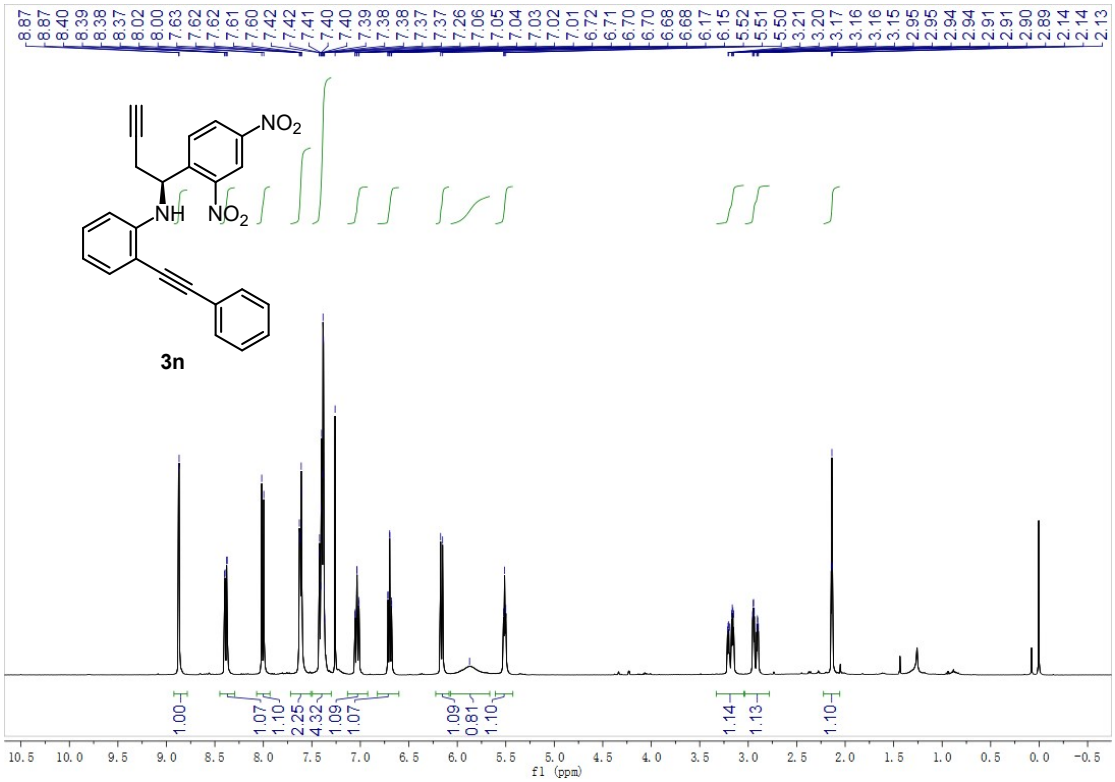
^{1}H NMR Spectra of **3m** (400 MHz, $CDCl_3$)



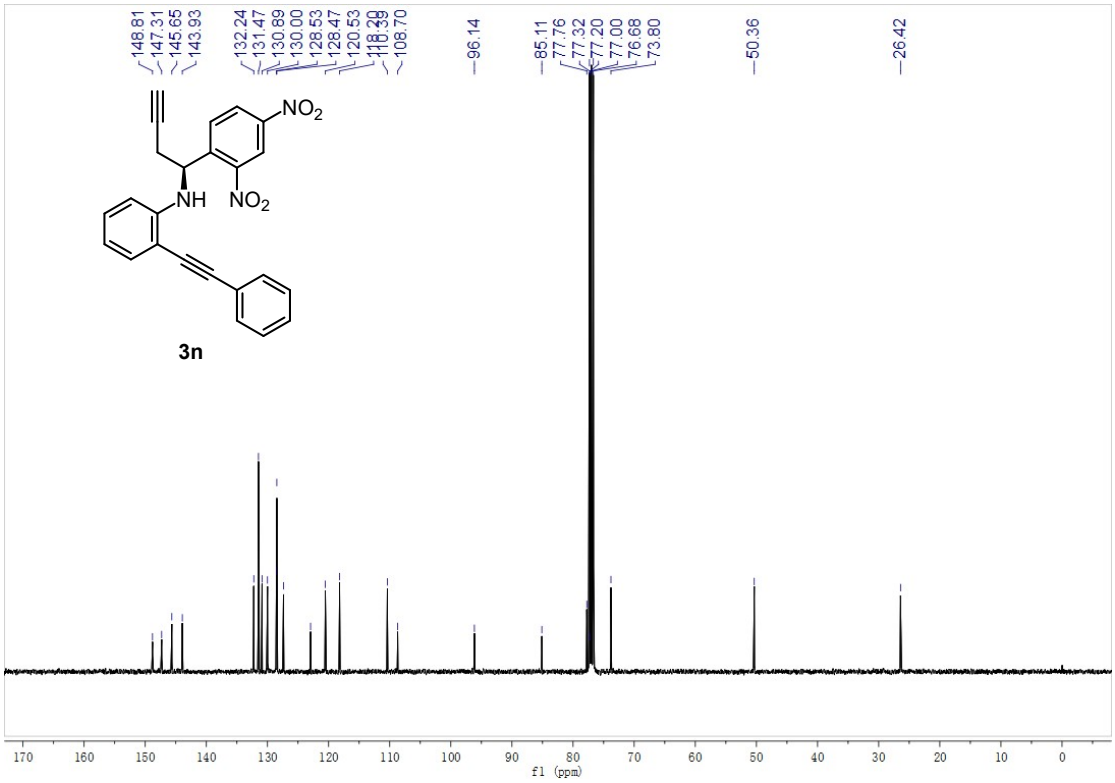
^{1}C NMR Spectra of **3m** (101 MHz, $CDCl_3$)



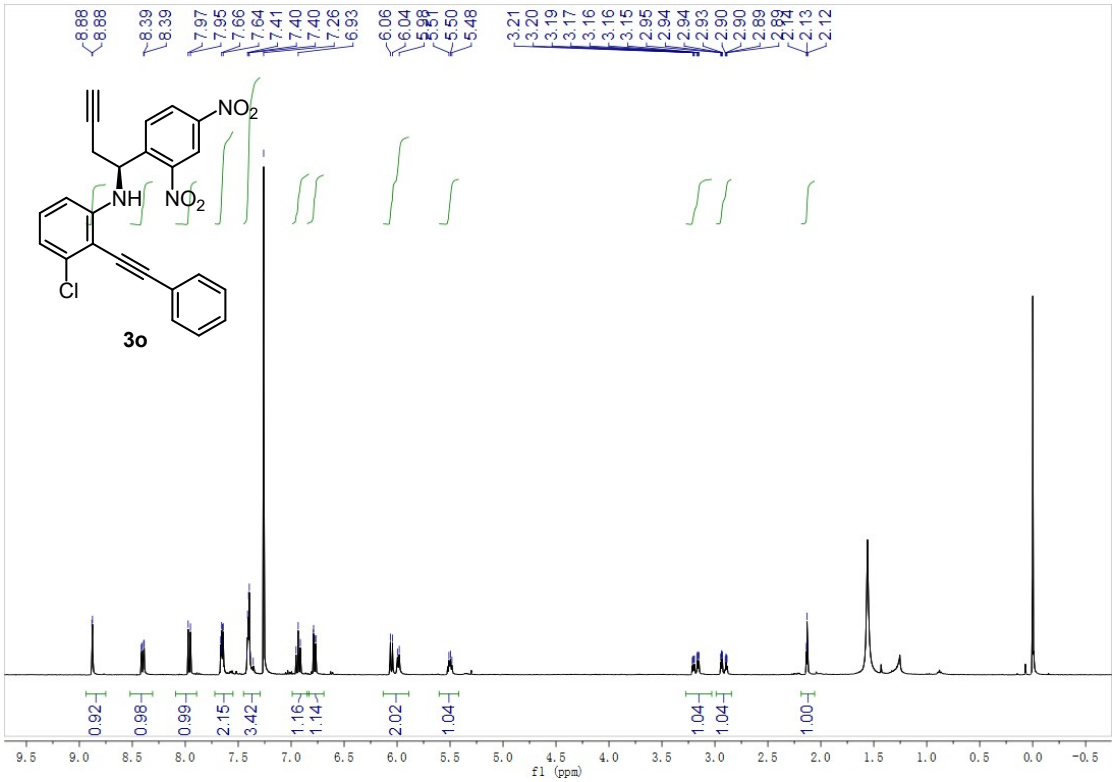
^{1}H NMR Spectra of **3n** (400 MHz, $CDCl_3$)



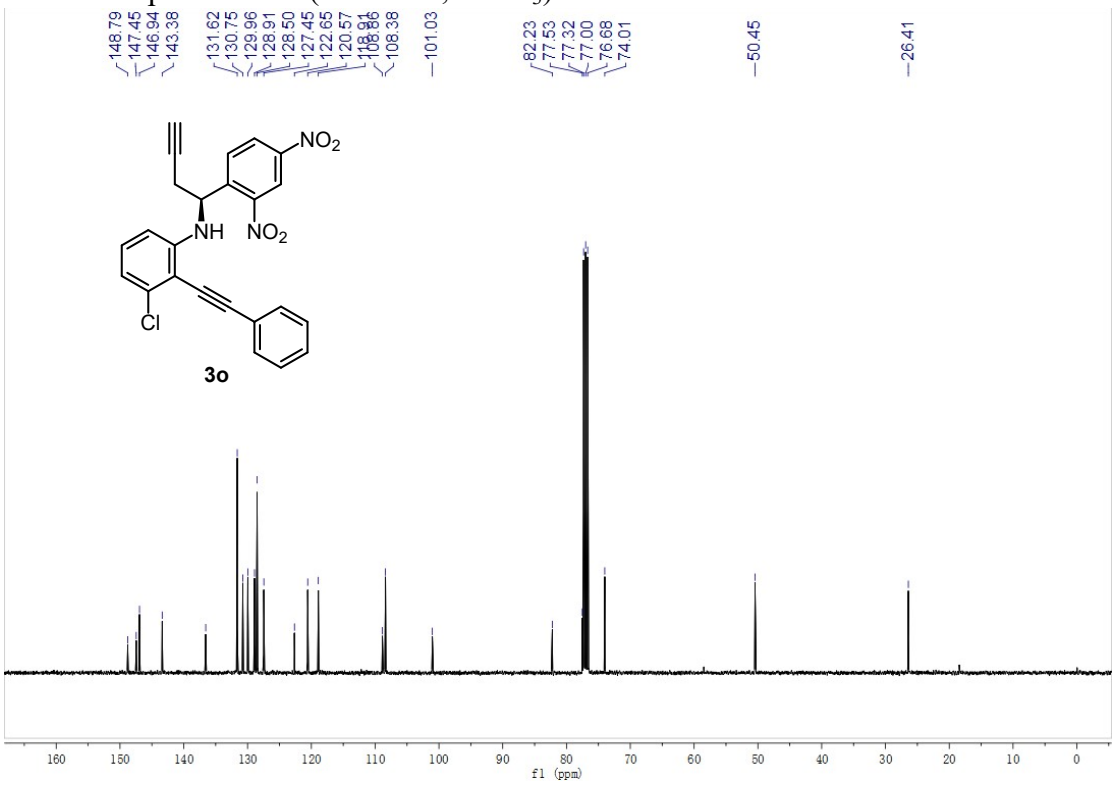
^{1}C NMR Spectra of **3n** (101 MHz, $CDCl_3$)



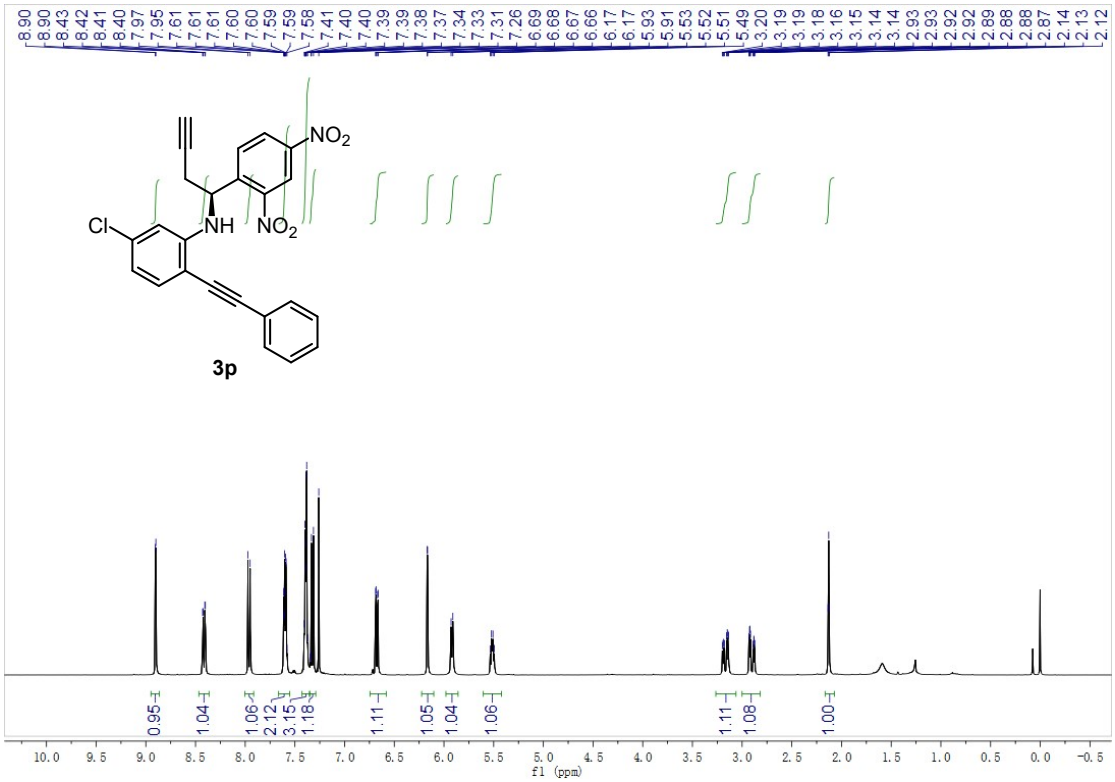
^{1}H NMR Spectra of **3o** (400 MHz, $CDCl_3$)



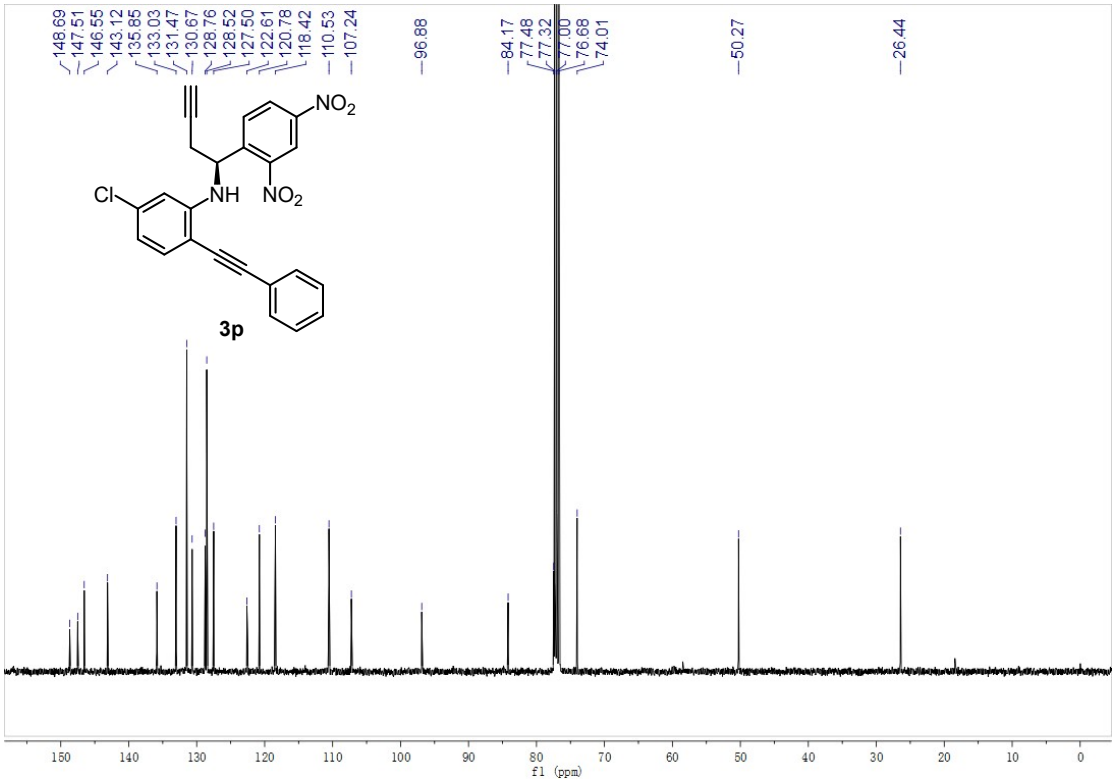
^{1}C NMR Spectra of **3o** (101 MHz, $CDCl_3$)



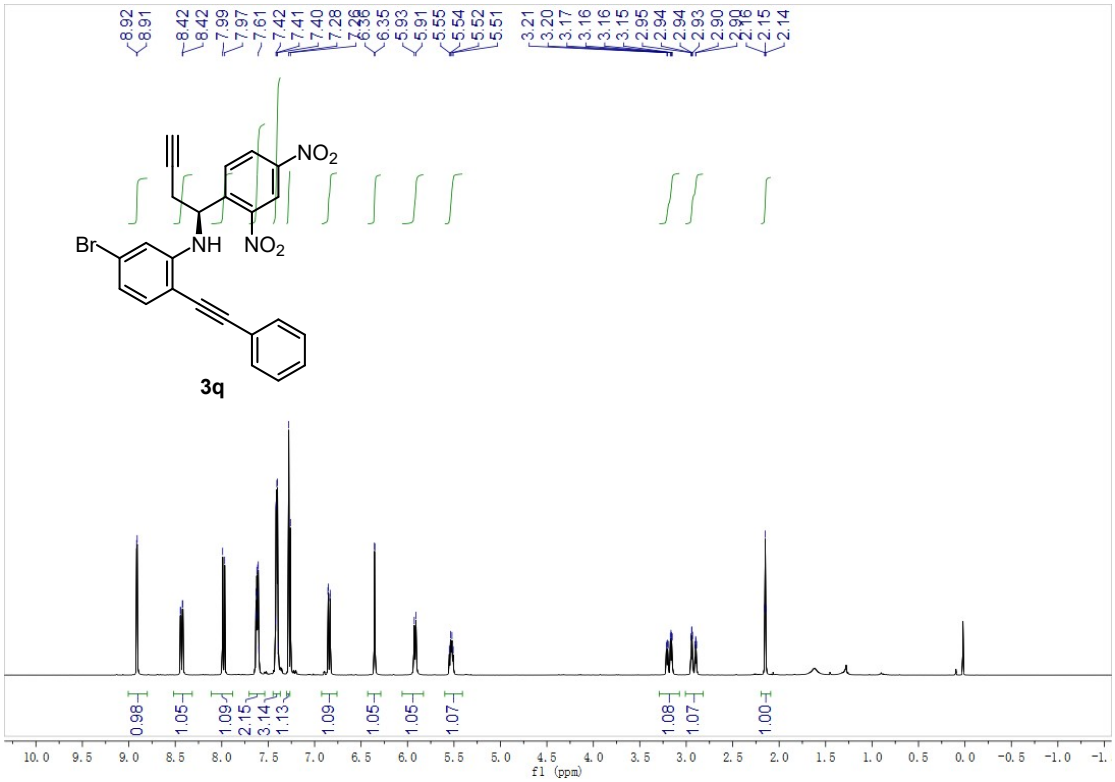
^{1}H NMR Spectra of **3p** (400 MHz, $CDCl_3$)



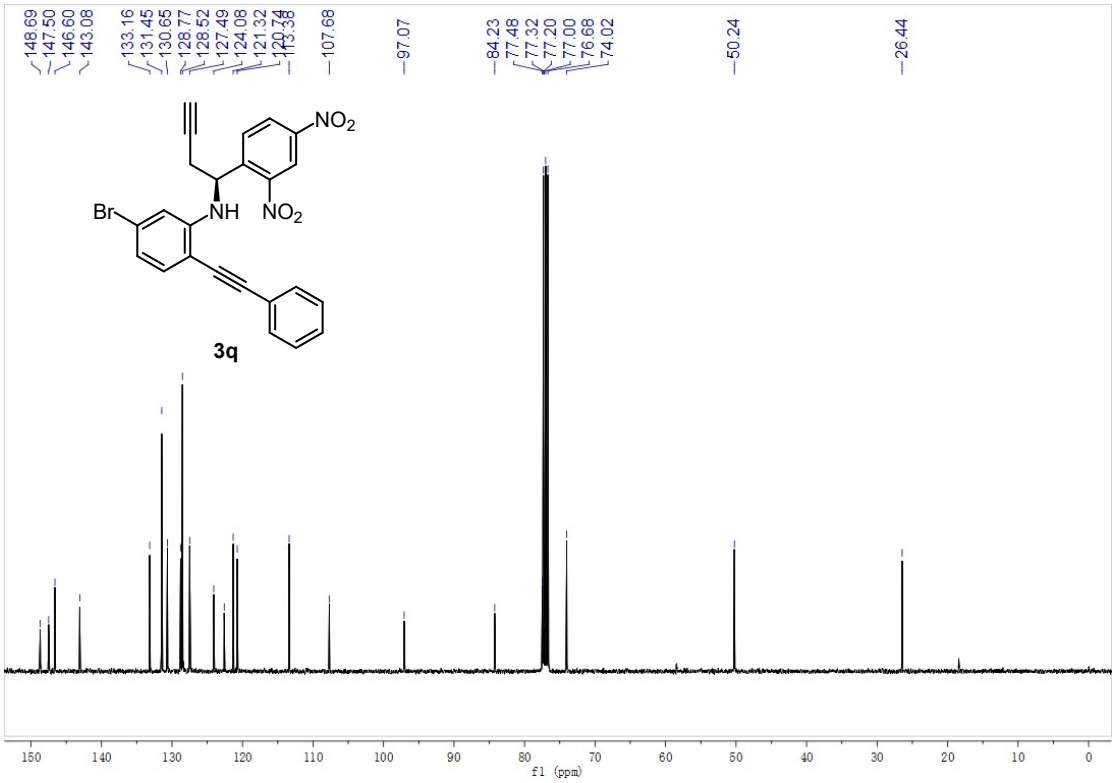
^{1}C NMR Spectra of **3p** (101 MHz, $CDCl_3$)



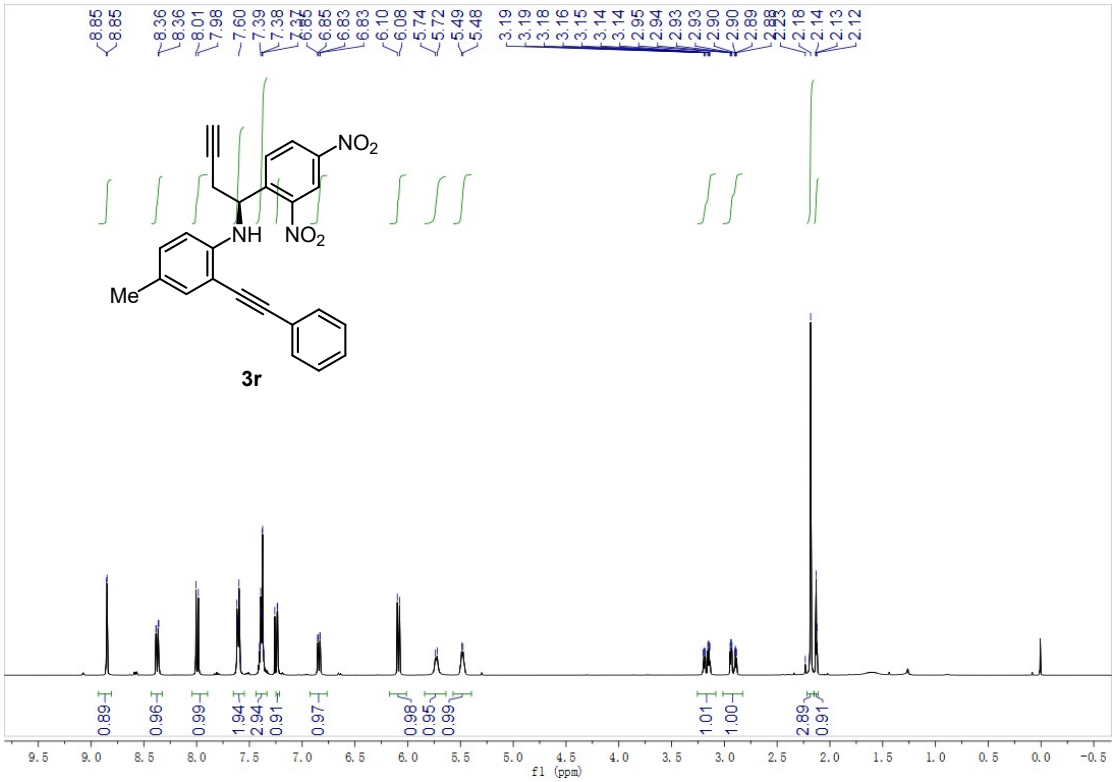
^{1}H NMR Spectra of **3q** (400 MHz, $CDCl_3$)



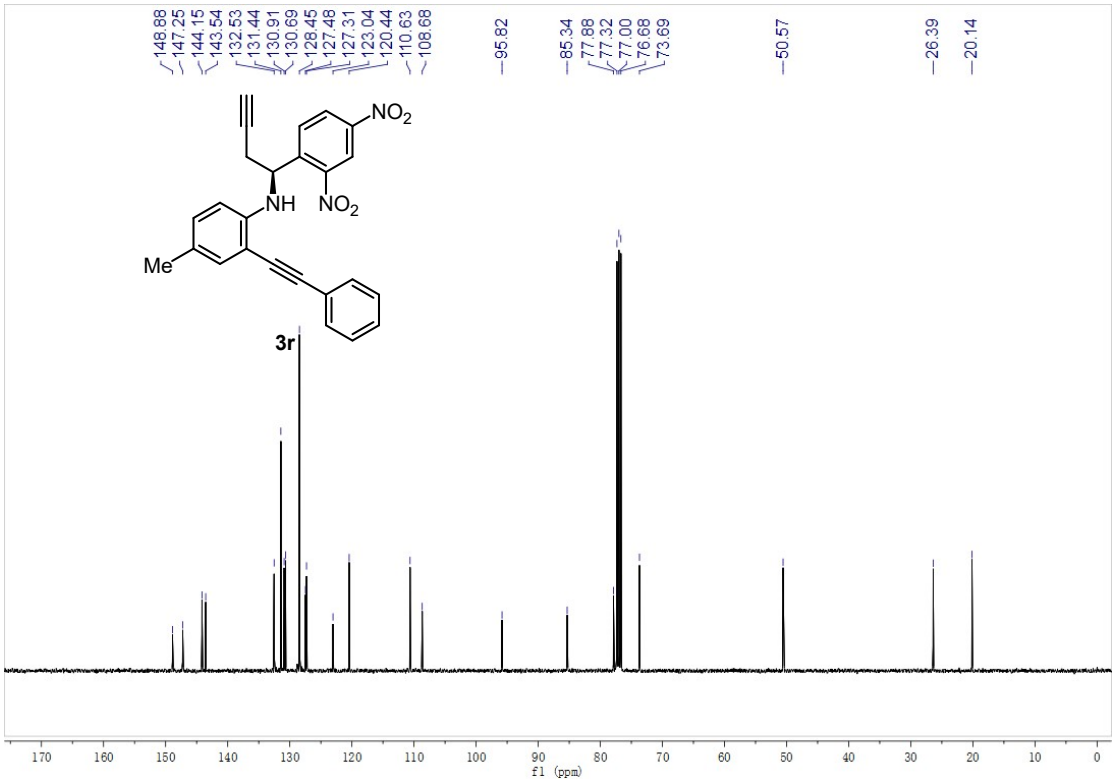
^{1}C NMR Spectra of **3q** (101 MHz, $CDCl_3$)



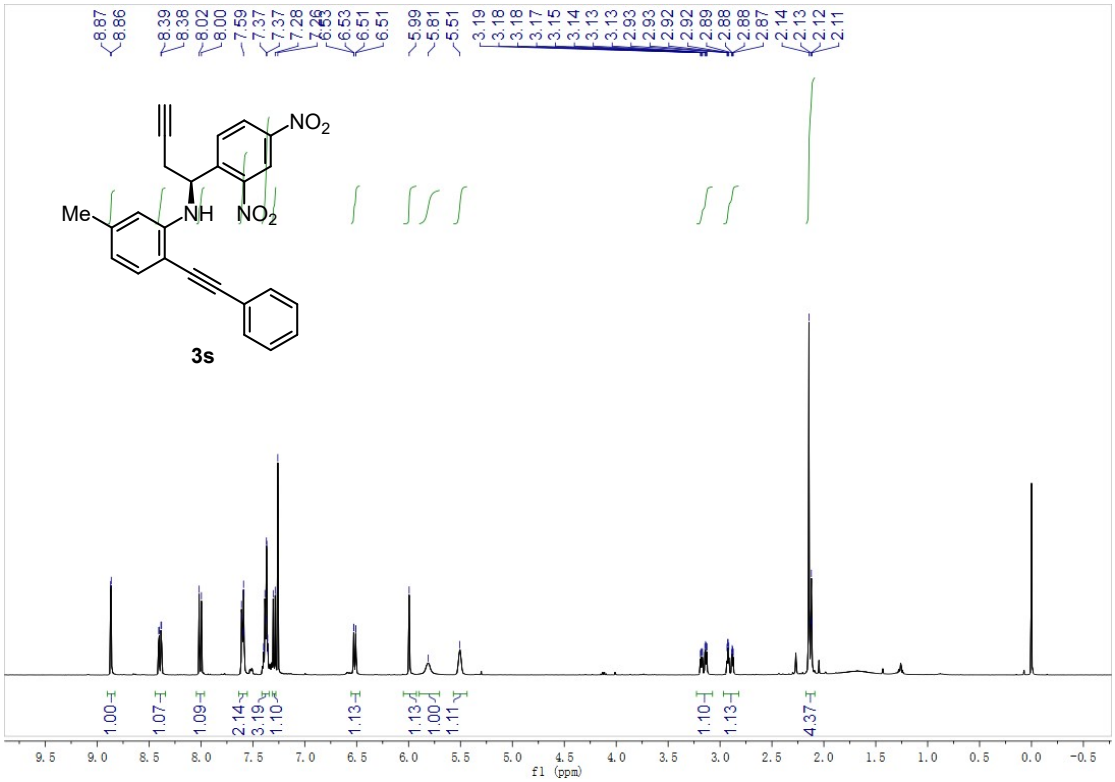
^{1}H NMR Spectra of **3r** (400 MHz, $CDCl_3$)



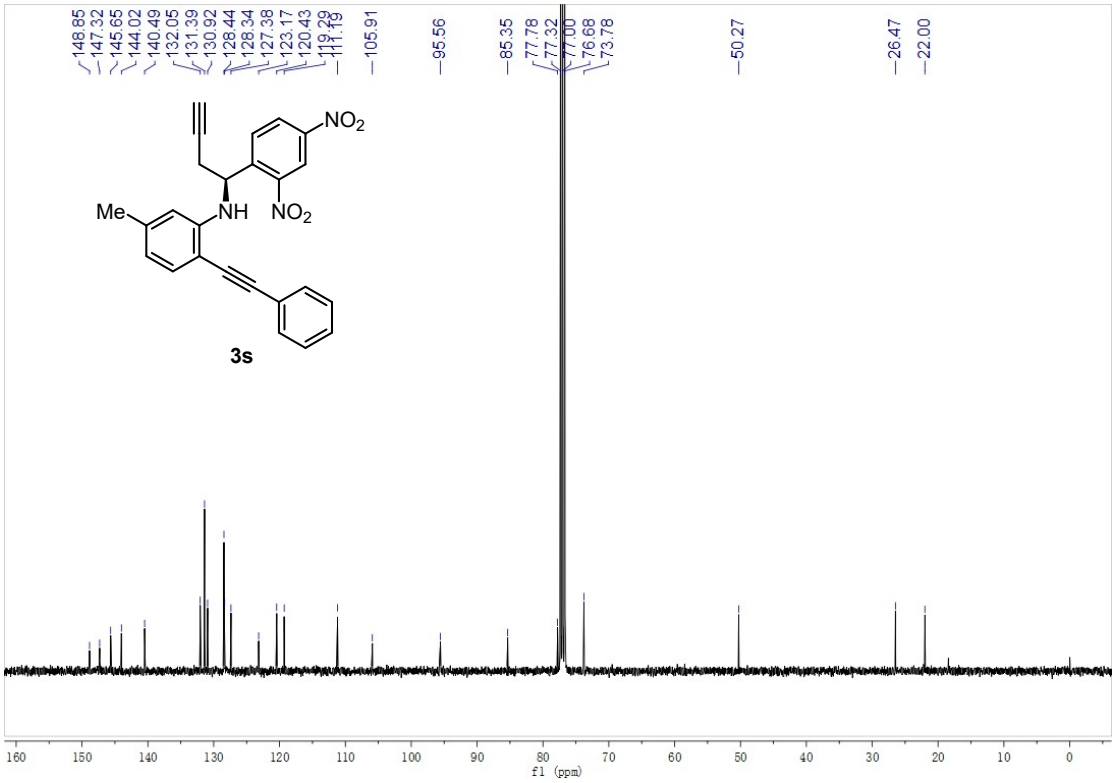
^{1}C NMR Spectra of **3r** (101 MHz, $CDCl_3$)



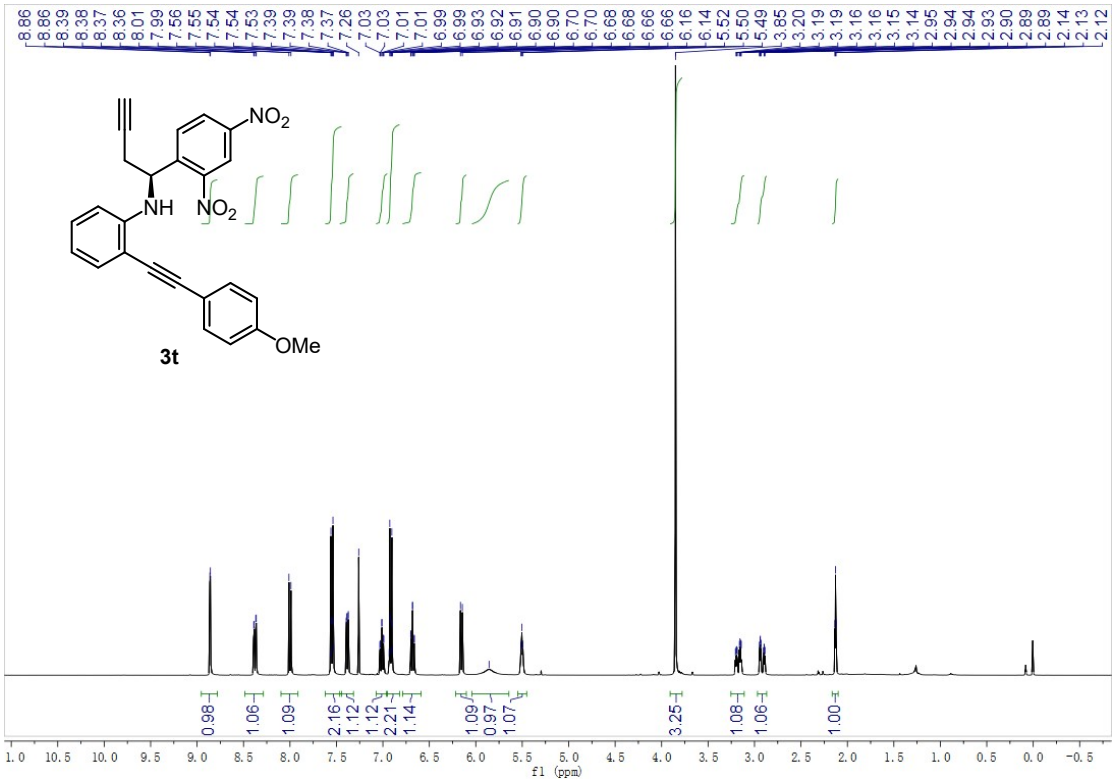
^{1}H NMR Spectra of **3s** (400 MHz, $CDCl_3$)



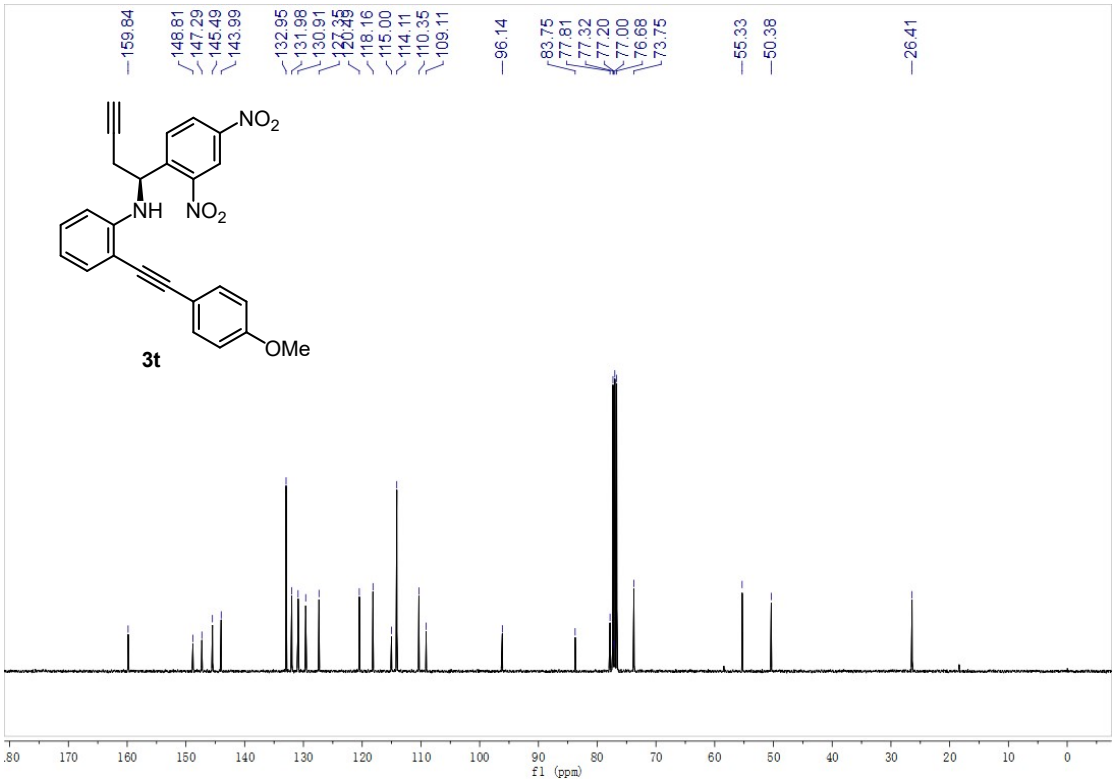
^{1}C NMR Spectra of **3s** (101 MHz, $CDCl_3$)



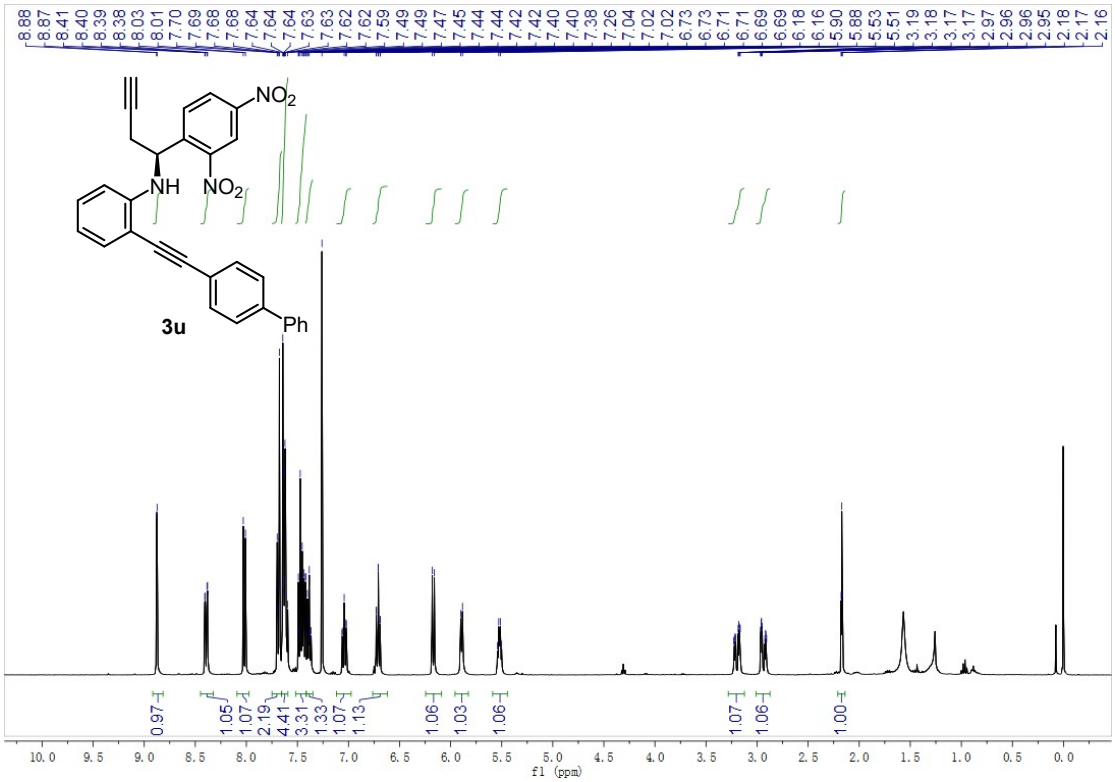
^{1}H NMR Spectra of **3t** (400 MHz, $CDCl_3$)



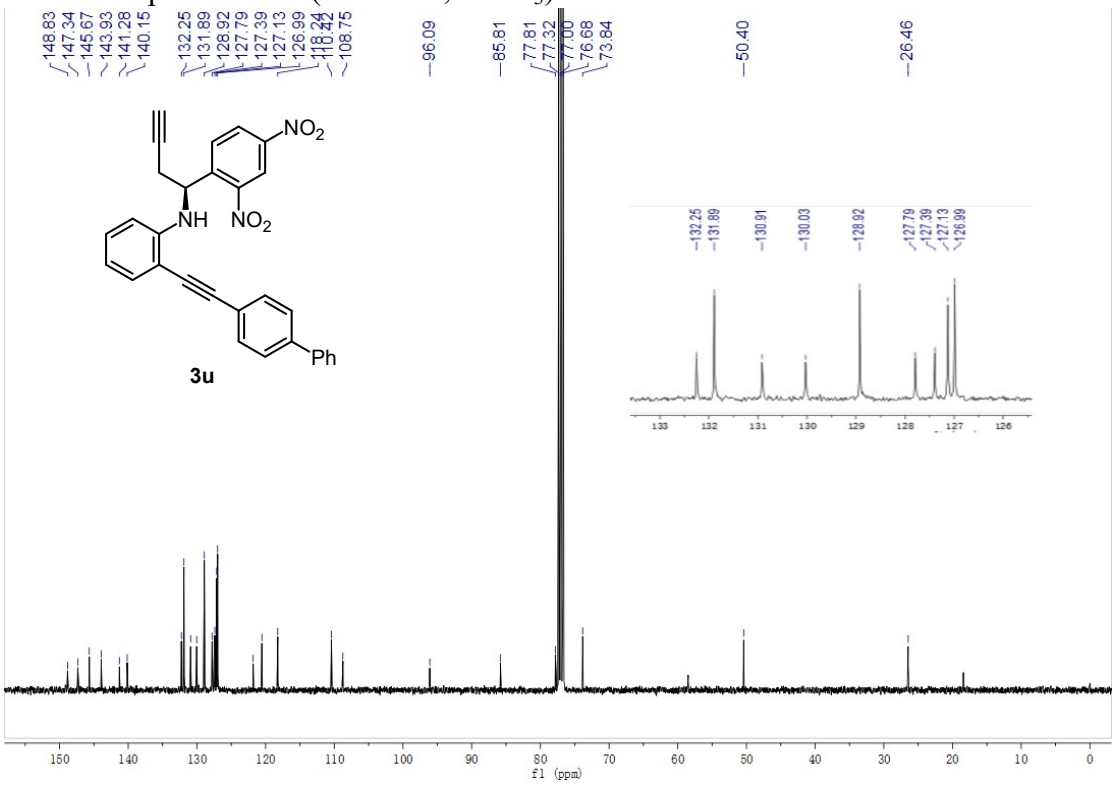
^{1}C NMR Spectra of **3t** (101 MHz, $CDCl_3$)



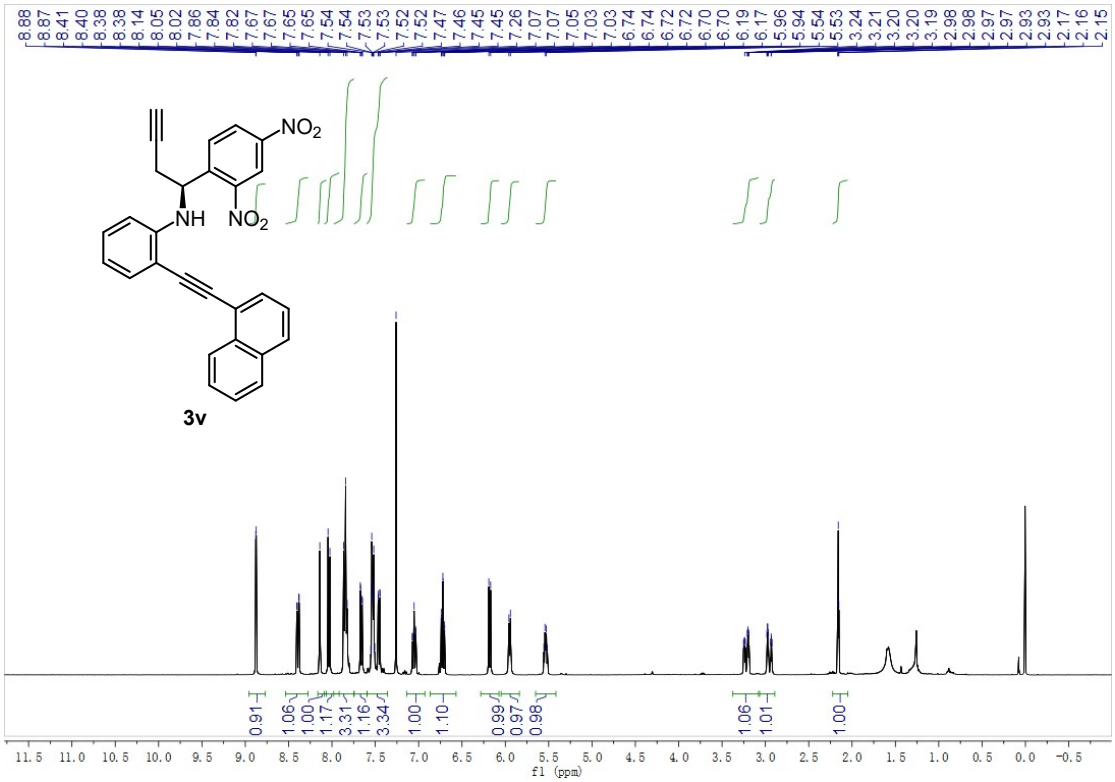
^{1}H NMR Spectra of **3u** (400 MHz, $CDCl_3$)



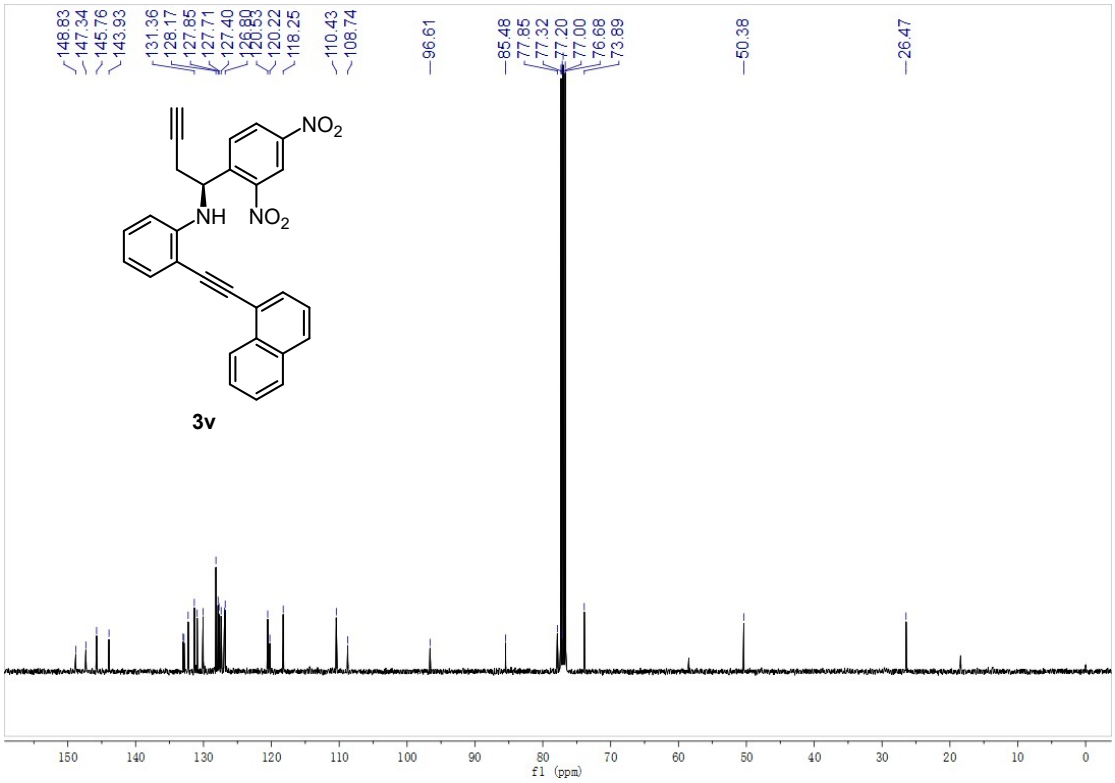
^{1}C NMR Spectra of **3u** (101 MHz, $CDCl_3$)



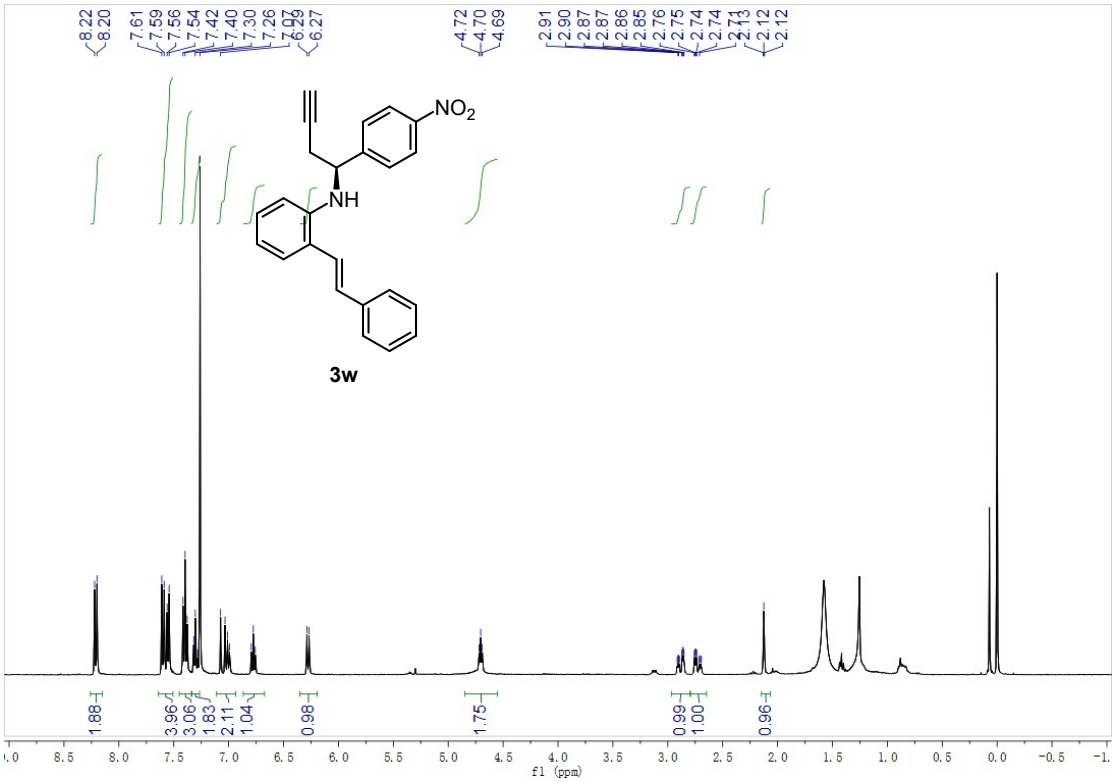
^{1}H NMR Spectra of **3v** (400 MHz, $CDCl_3$)



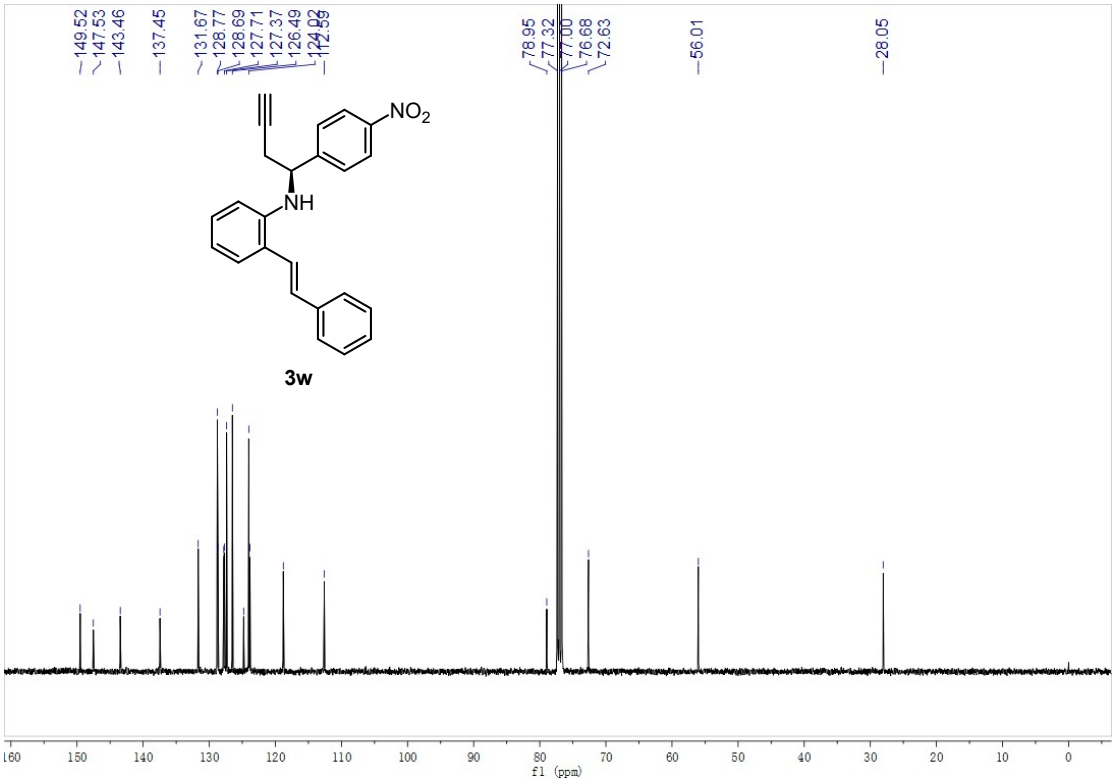
^{1}C NMR Spectra of **3v** (101 MHz, $CDCl_3$)



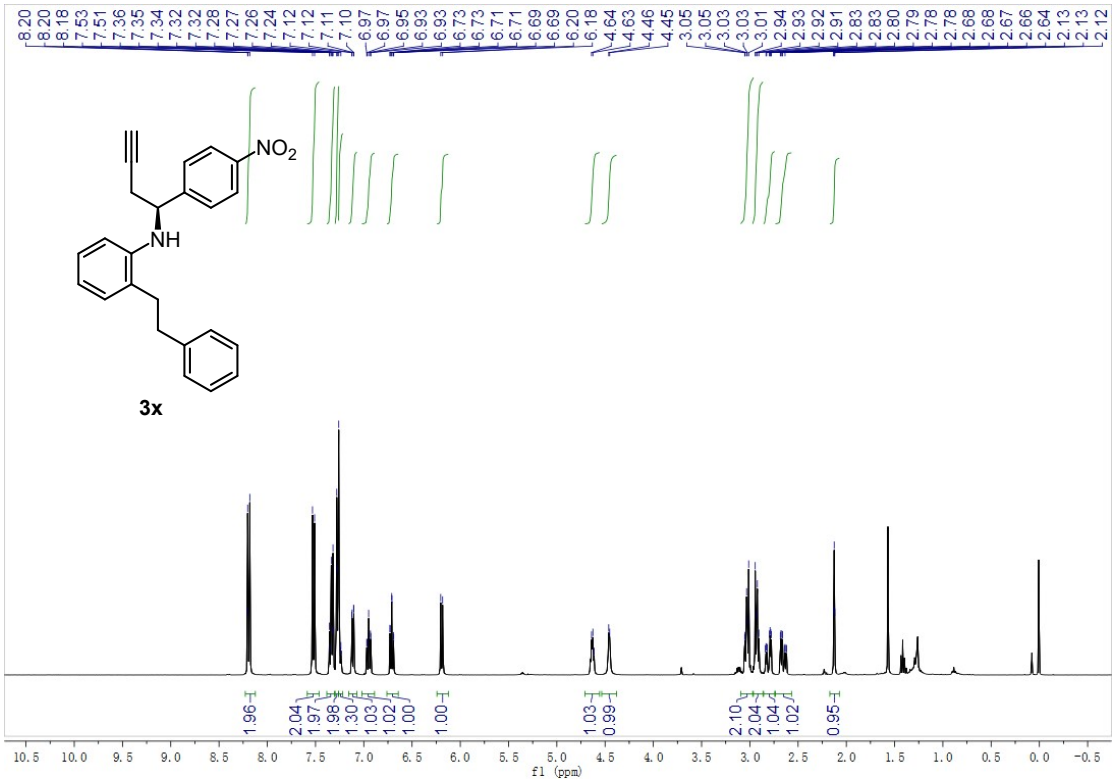
^{1}H NMR Spectra of **3w** (400 MHz, $CDCl_3$)



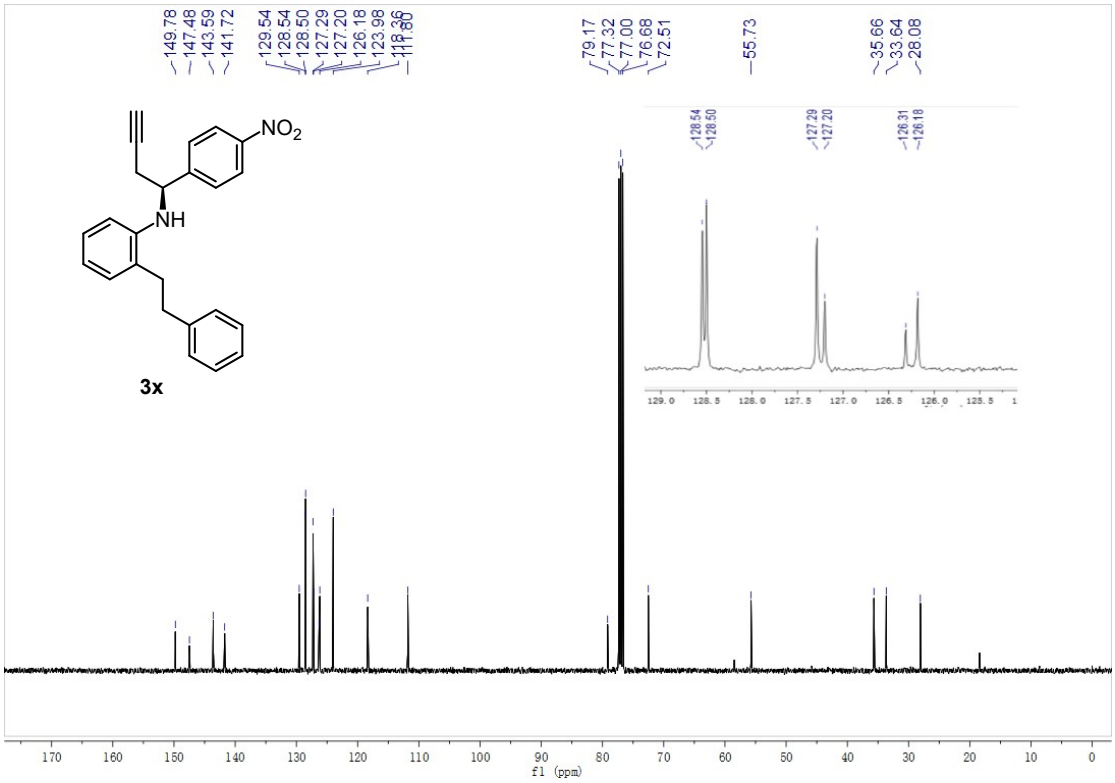
^{1}C NMR Spectra of **3w** (101 MHz, $CDCl_3$)



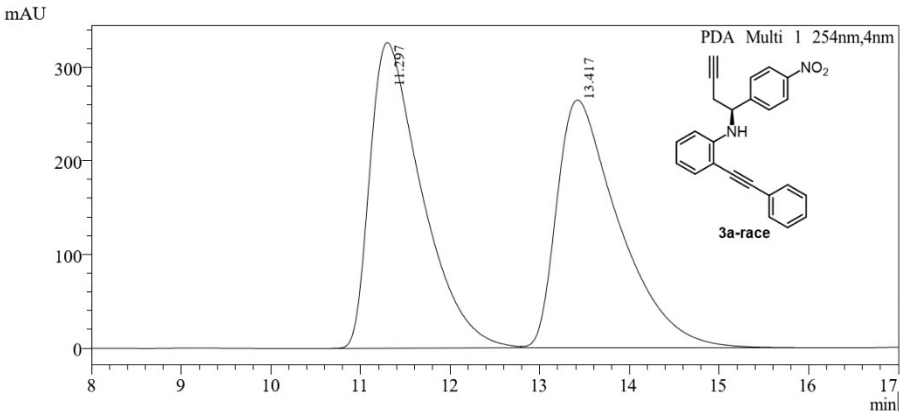
^{1}H NMR Spectra of **3x** (400 MHz, $CDCl_3$)



^{1}C NMR Spectra of **3x** (101 MHz, $CDCl_3$)

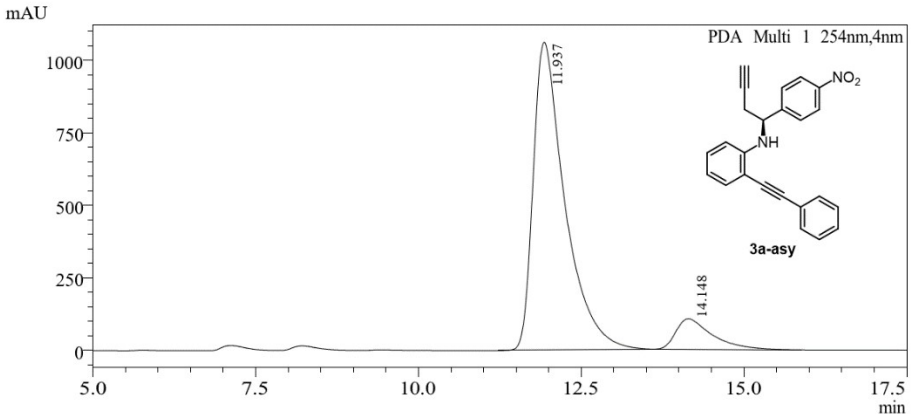


8. HPLC Spectra of Products 3a–3x



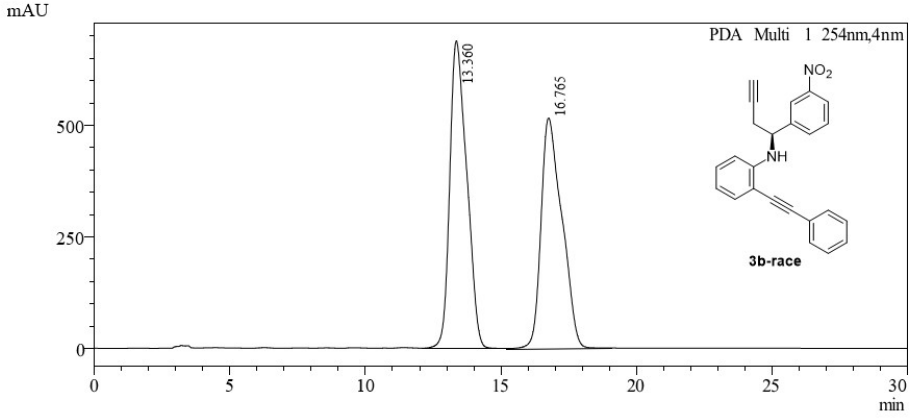
<PeakTable>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	11.297	13136777	326185	50.617
2	13.417	12816625	265212	49.383
Total		25953402	591397	100.000



<PeakTable>
PDA Ch1 254nm

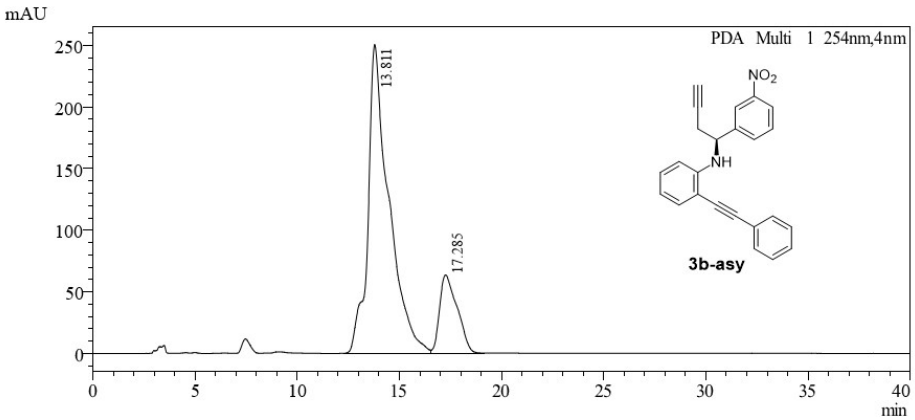
Peak#	Ret. Time	Area	Hight	Area%
1	11.937	35882229	1061394	89.765
2	14.148	4091099	105434	10.235
Total		39973329	1166829	100.000



<PeakTable>

PDA Ch1 254nm

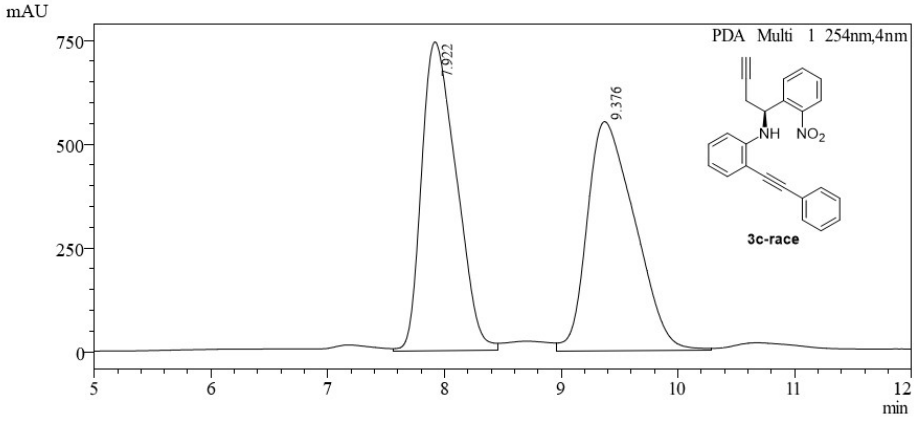
Peak#	Ret. Time	Area	Hight	Area%
1	13.360	30541096	689902	52.501
2	16.765	27630844	516252	47.499
Total		58171940	1206154	100.000



<PeakTable>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	13.811	17904256	250768	82.416
2	17.285	3819966	63621	17.584
Total		21724222	314389	100.000



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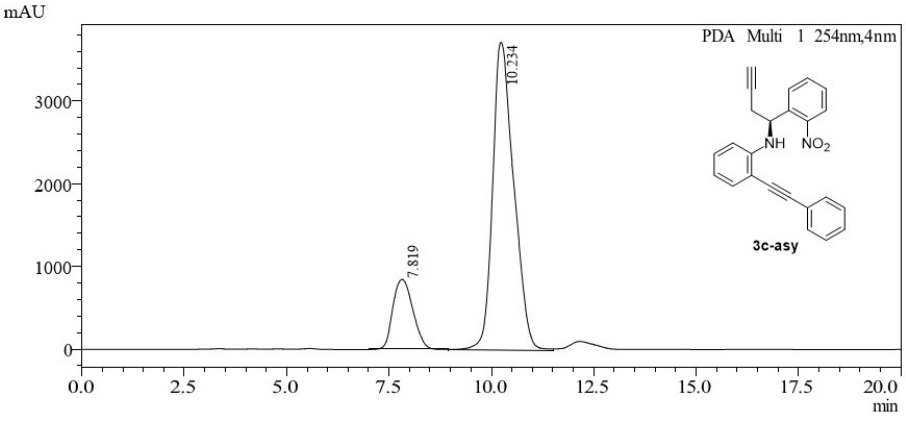
PDA Ch1 254nm

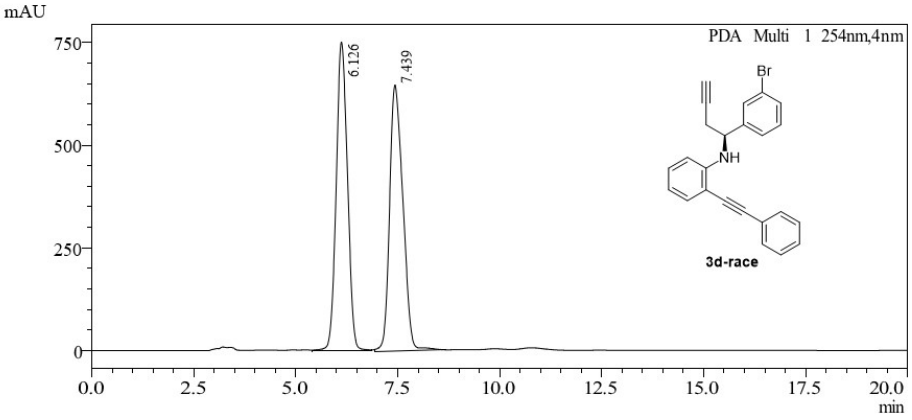
Peak#	Ret. Time	Area	Hight	Area%
1	7.922	15387264	744638	49.781
2	9.376	15522538	550404	50.219
Total		30909802	1295042	100.000



<PeakTable>

PDA Ch1 254nm

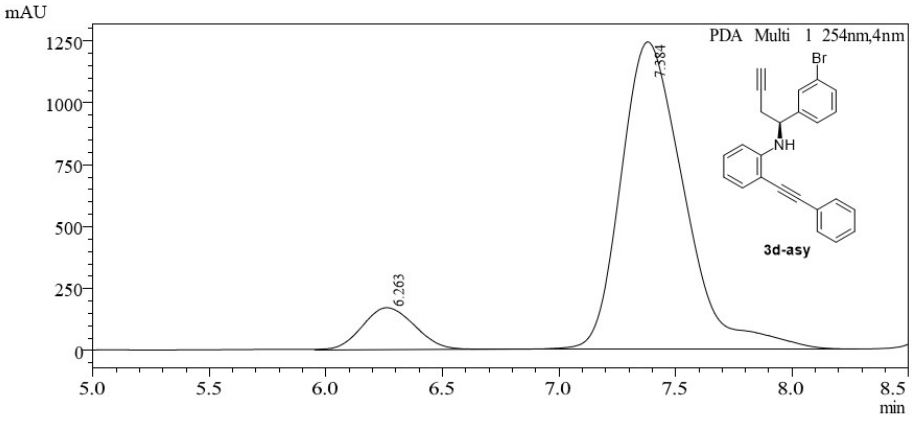
Peak#	Ret. Time	Area	Hight
7.819	27634542	836553	17.212
10.234	132921735	3720510	82.788
Total	160556277	4557063	100.000



<PeakTable>

PDA Ch1 254nm

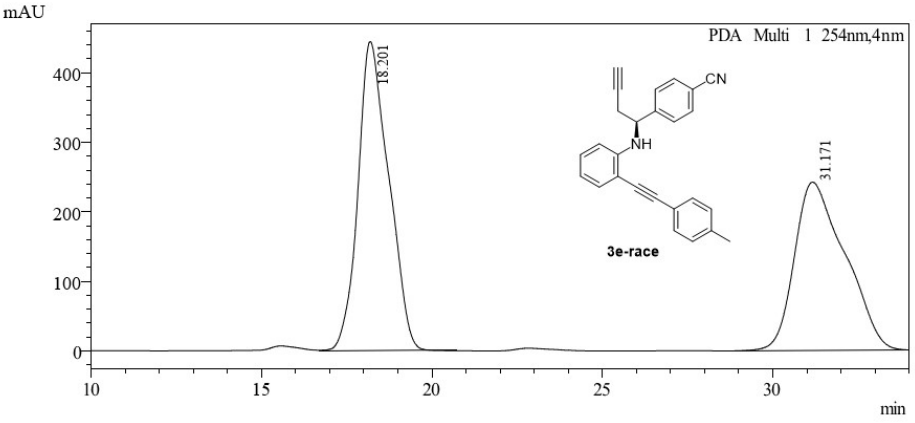
Peak#	Ret. Time	Area	Hight	Area%
1	6.126	14496202	751850	49.884
2	7.439	14563503	646063	50.116
Total		29059705	1397913	100.000



<PeakTable>

PDA Ch1 254nm

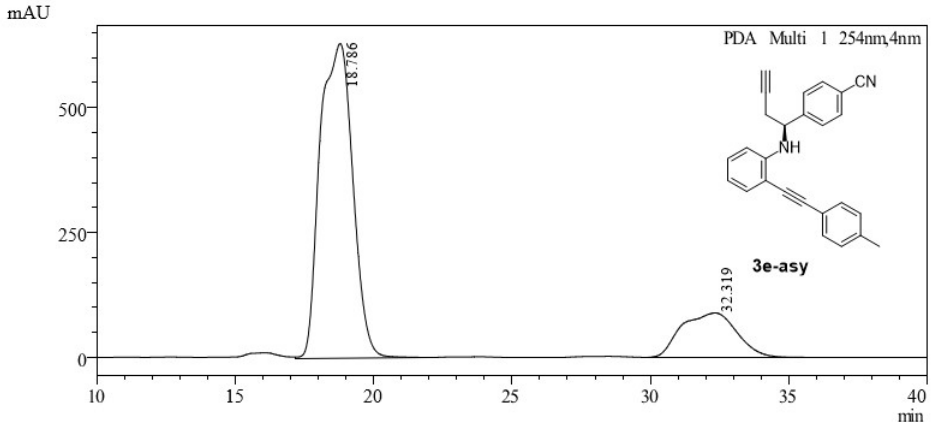
Peak#	Ret. Time	Area	Hight	Area%
1	6.263	2591727	168552	9.987
2	7.384	23358775	1244270	90.013
Total		25950502	1412822	100.000



<Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	18.201	27985450	444699	52.746
2	31.171	25071243	242256	47.254
Total		53056692	686955	100.000



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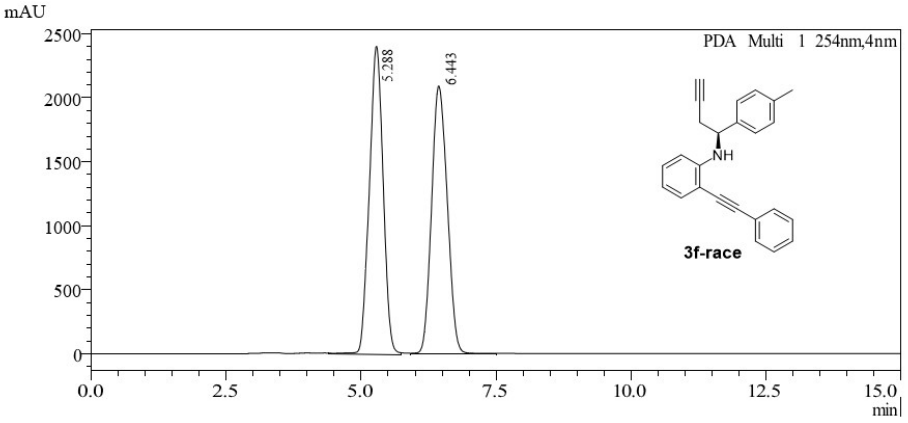
PDA Ch1 254nm

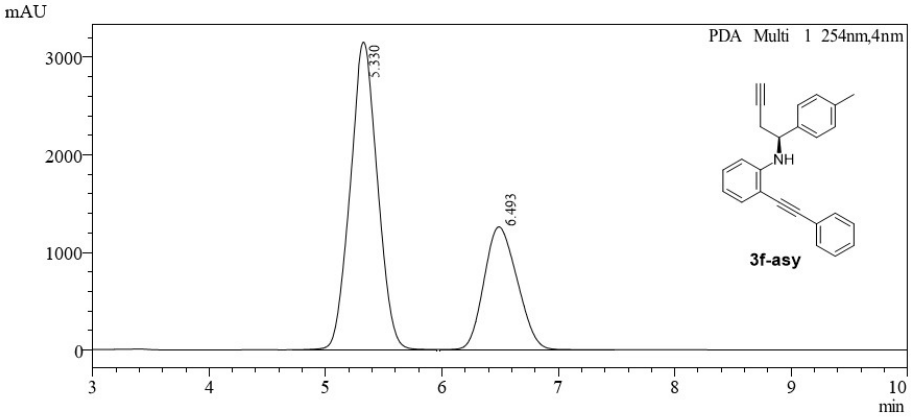
Peak#	Ret. Time	Area	Hight	Area%
1	18.786	51413012	627714	80.801
2	32.319	12216249	88374	19.199
Total		63629261	716088	100.000



<PeakTabl>

PDA Ch1 254nm

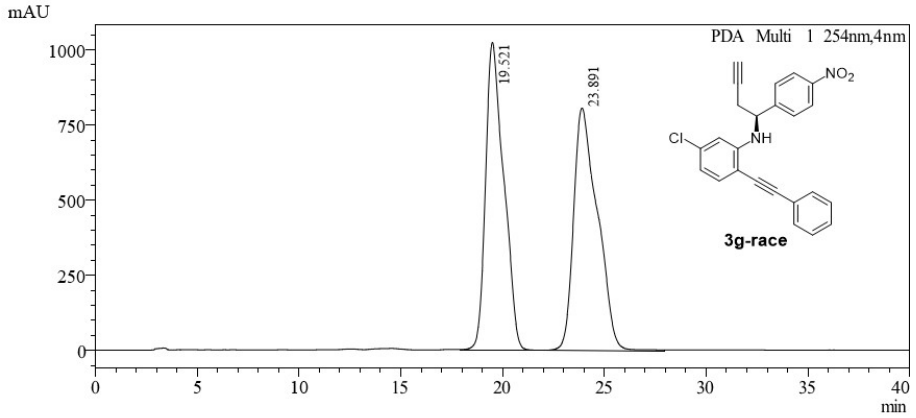
Peak#	Ret. Time	Area	Hight	Area%
1	5.288	42969116	2406133	50.328
2	6.443	42409687	2090713	49.672
Total		85378802	4496846	100.000



<PeakTable>

PDA Ch1 254nm

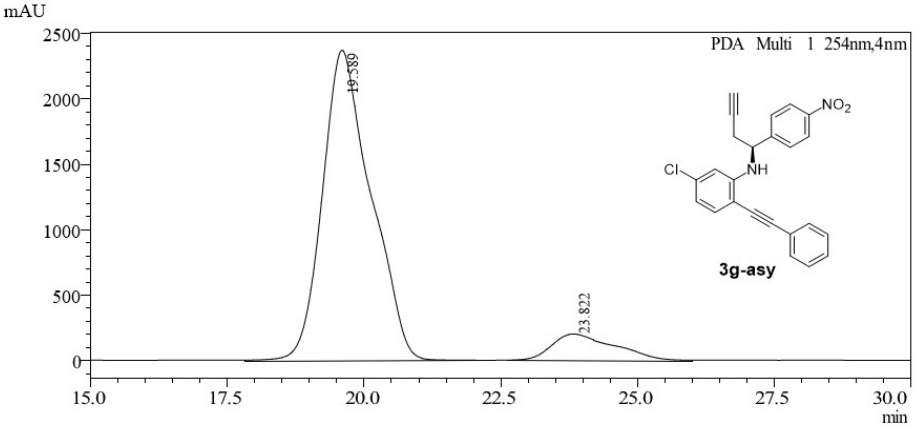
Peak#	Ret. Time	Area	Hight	Area%
1	5.330	51228479	3156439	67.156
2	6.493	25054870	1261688	32.844
Total		76283349	4418127	100.000



<PeakTabl>

PDA Ch1 254nm

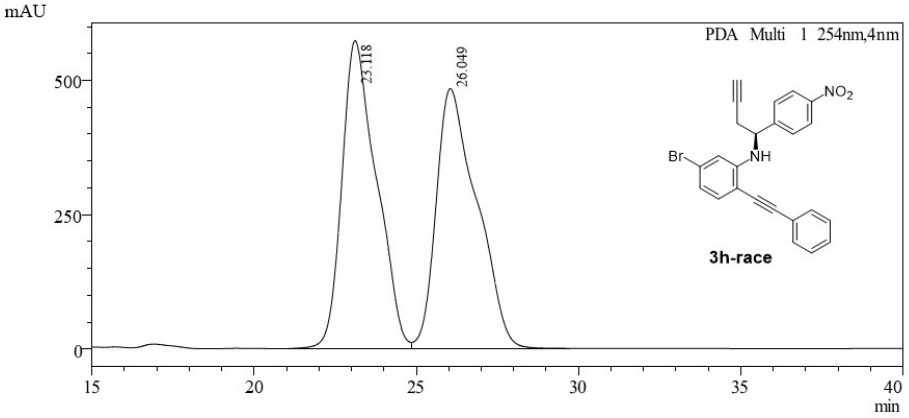
Peak#	Ret. Time	Area	Hight	Area%
1	19.521	63605009	1024025	49.479
2	23.891	64945209	806184	50.521
Total		128550218	1830209	100.000



<PeakTable>

PDA Ch1 254nm

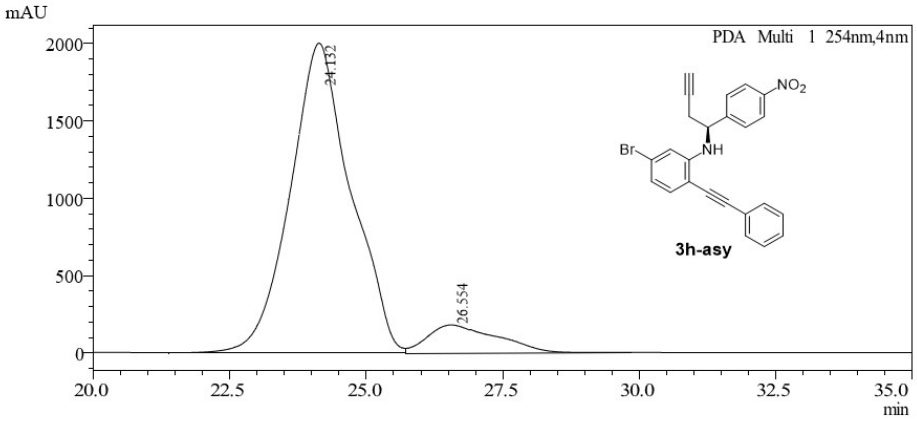
Peak#	Ret. Time	Area	Hight	Area%
1	19.589	146324938	2373016	90.336
2	23.822	15654223	198464	9.664
Total		161979161	2571480	100.000



<PeakTabl>

PDA Ch1 254nm

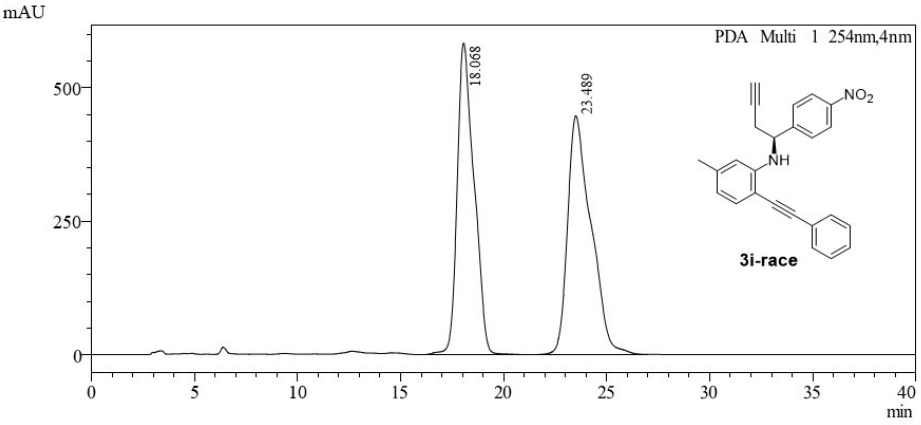
Peak#	Ret. Time	Area	Hight	Area%
1	23.118	42166536	574020	49.779
2	26.049	42540985	484611	50.221
Total		84707520	1058631	100.000



<PeakTable>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	24.132	156016037	2005549	90.737
2	26.554	15926798	182960	9.263
Total		171942835	2188509	100.000



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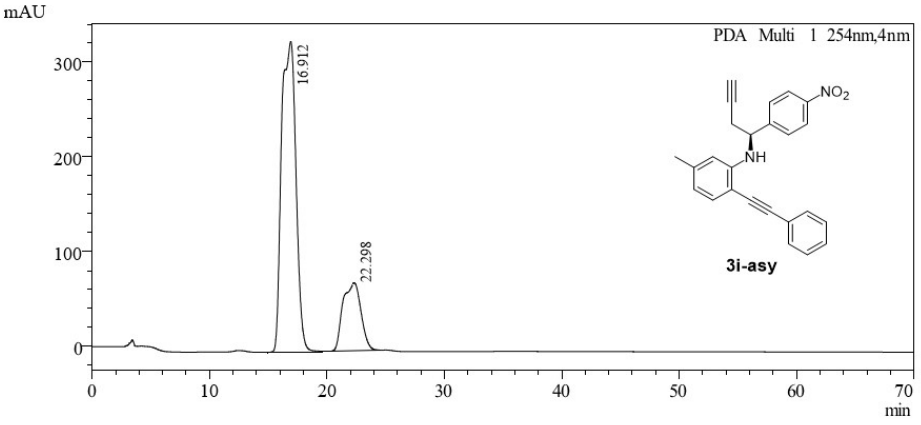
PDA Ch1 254nm

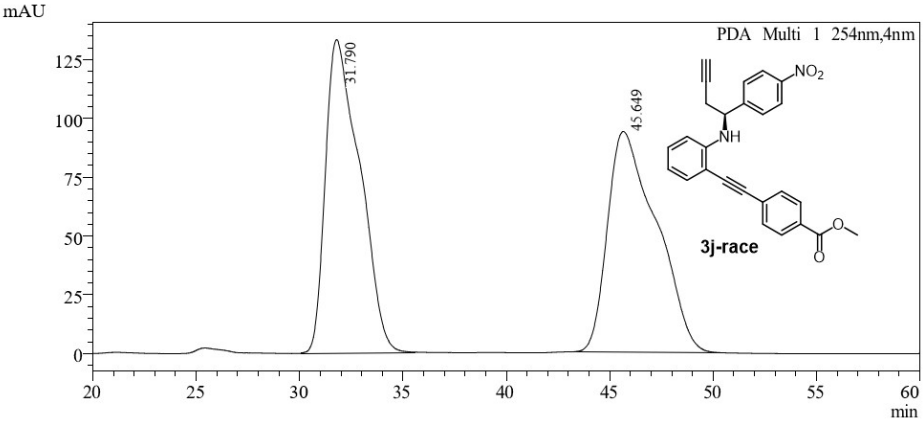
Peak#	Ret. Time	Area	Hight	Area%
1	18.068	33387423	583569	48.573
2	23.489	35349045	446668	51.427
Total		68736468	1030237	100.000



<PeakTable>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	16.912	27608995	328048	78.166
2	22.298	7711786	71795	21.834
Total		35320781	399843	100.000



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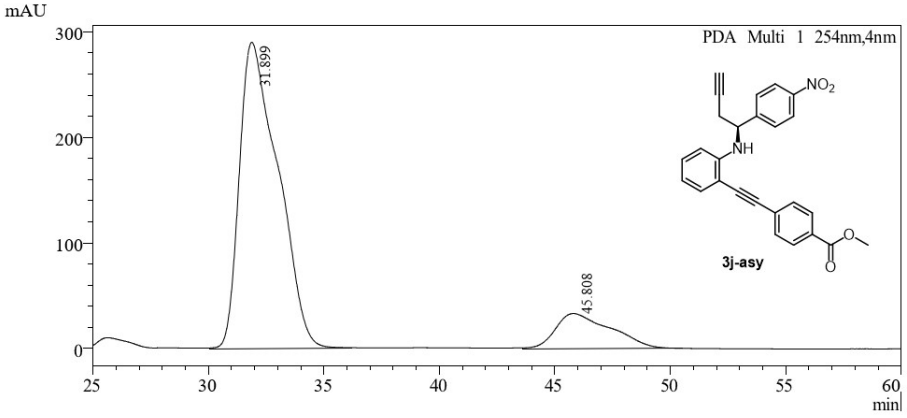
PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	31.790	15465604	133162	50.138
2	45.649	15380210	93856	49.862
Total		30845815	227017	100.000



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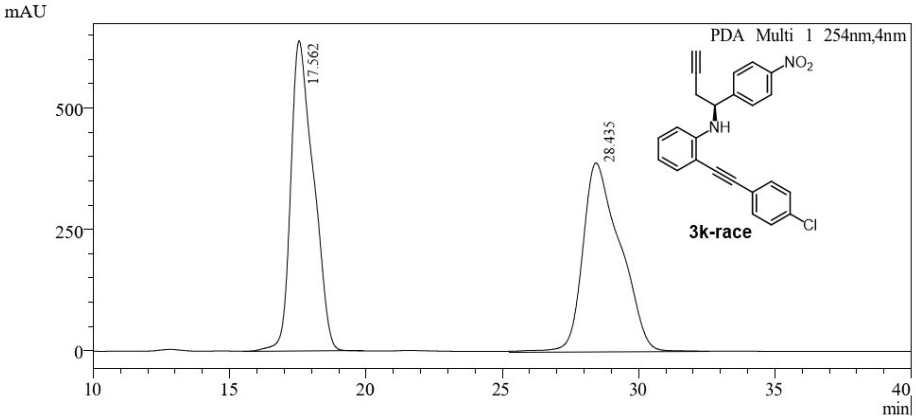
PDA Ch1 254nm

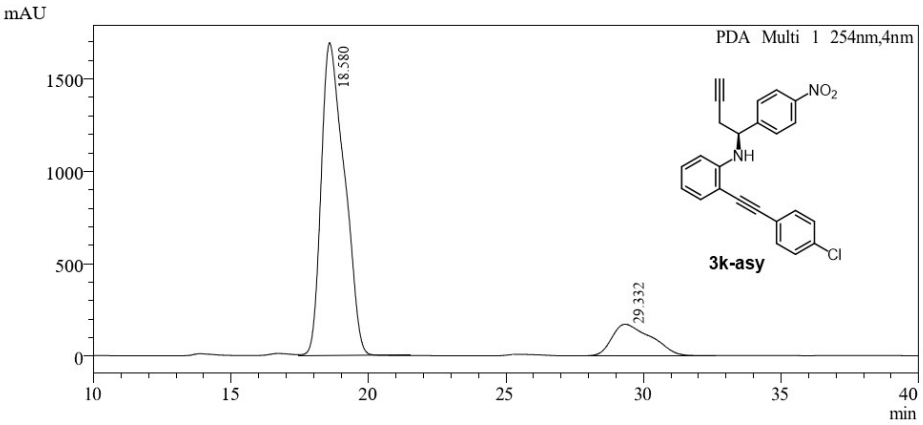
Peak#	Ret. Time	Area	Hight	Area%
1	31.899	33555842	289901	86.173
2	45.808	5384459	32430	13.827
Total		38940300	322331	100.000



<PeakTable>

PDA Ch1 254nm

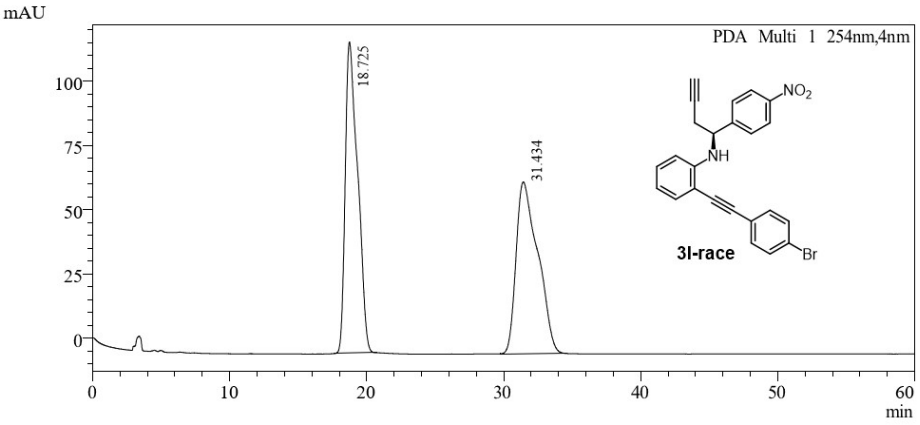
Peak#	Ret. Time	Area	Hight	Area%
1	17.562	37079527	638549	50.137
2	28.435	36877552	387868	49.863
Total		73957079	1026417	100.000



<PeakTable>

PDA Ch1 254nm

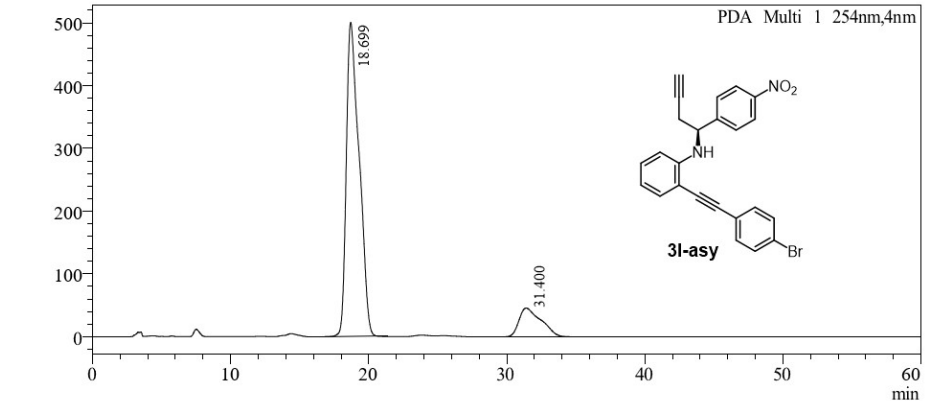
Peak#	Ret. Time	Area	Hight	Area%
1	18.580	99586053	1690918	85.525
2	29.332	16854227	170340	14.475
Total		116440280	1861258	100.000



<PeakTable>

PDA Ch1 254nm

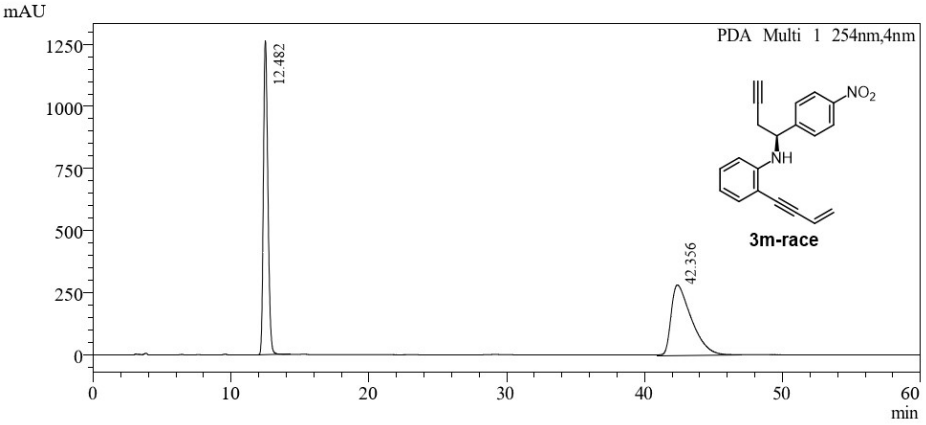
Peak#	Ret. Time	Area	Hight	Area%
1	18.725	7828749	121014	51.490
2	31.434	7375697	66859	48.510
Total		15204446	187872	100.000



<PeakTabl>

PDA Ch1 254nm

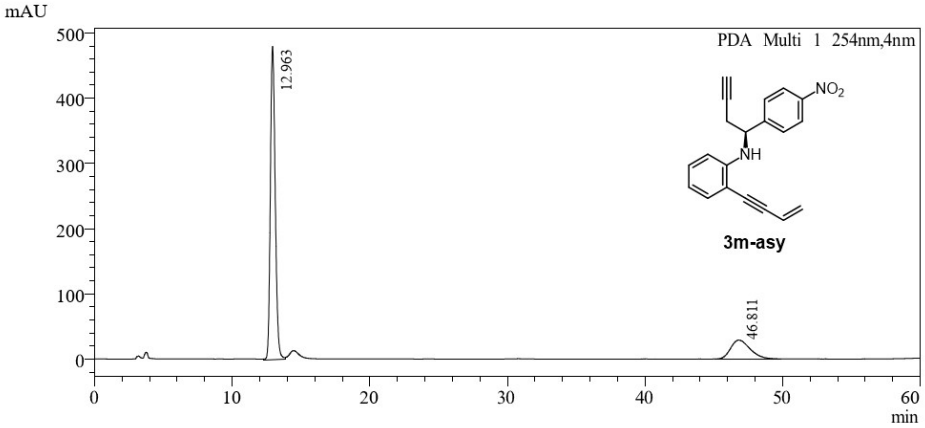
Peak#	Ret. Time	Area	Hight	Area%
1	18.699	32509816	499890	86.645
2	31.400	5010847	45302	13.355
Total		37520662	545193	100.000



<PeakTabl>

PDA Ch1 254nm

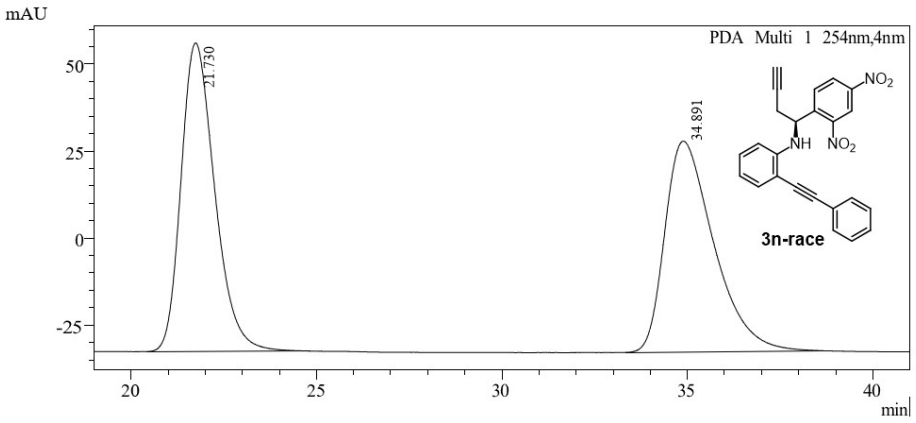
Peak#	Ret. Time	Area	Hight	Area%
1	12.482	28486120	1262384	49.920
2	42.356	28577309	282151	50.080
Total		57063429	1544534	100.000



<PeakTable>

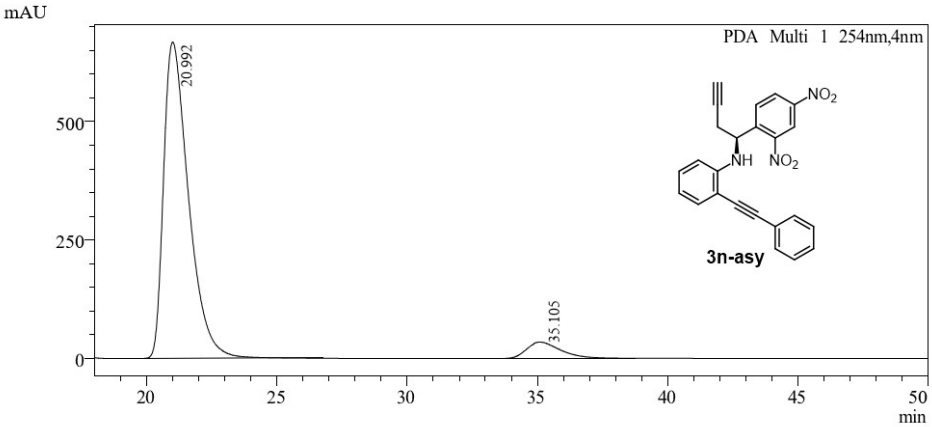
PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	12.963	11732368	479880	80.477
2	46.811	2846182	29134	19.523
Total		14578550	509014	100.000



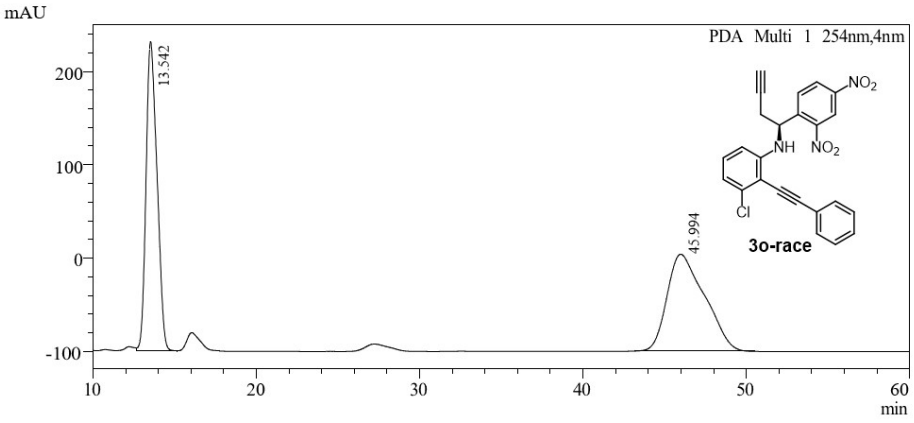
<PeakTable>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	21.730	5589380	88618	50.111
2	34.891	5564541	60648	49.889
Total		11153921	149266	100.000



<PeakTable>
PDA Ch1 254nm

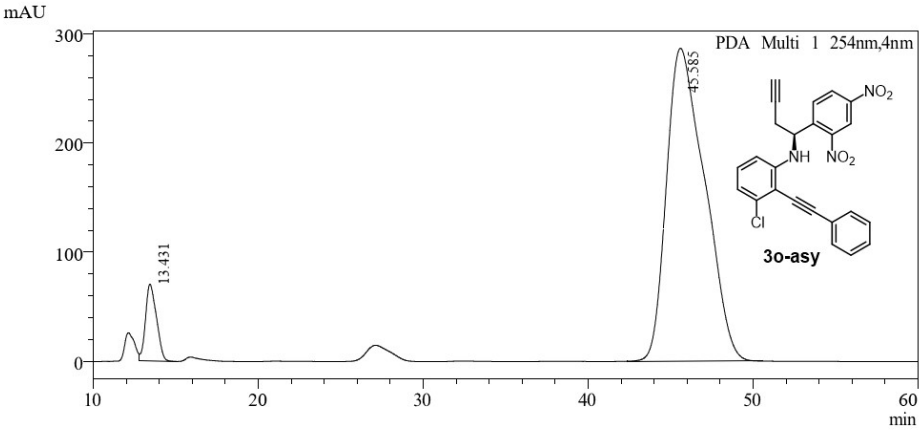
Peak#	Ret. Time	Area	Hight	Area%
1	20.992	44594245	666967	93.610
2	35.105	3043876	33347	6.390
Total		47638121	700314	100.000



<Table>

PDA Ch1 254nm

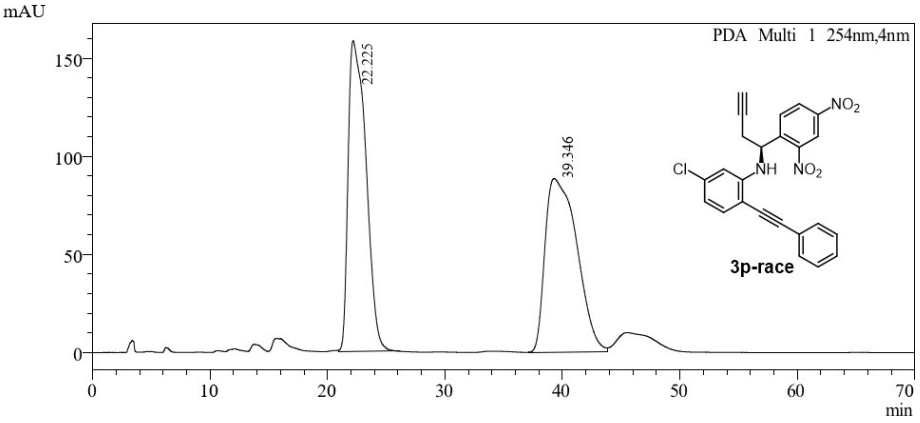
Peak#	Ret. Time	Area	Hight	Area%
1	13.542	15519511	331076	48.315
2	45.994	16602165	103498	51.685
Total		32121676	434574	100.000



<Table>

PDA Ch1 254nm

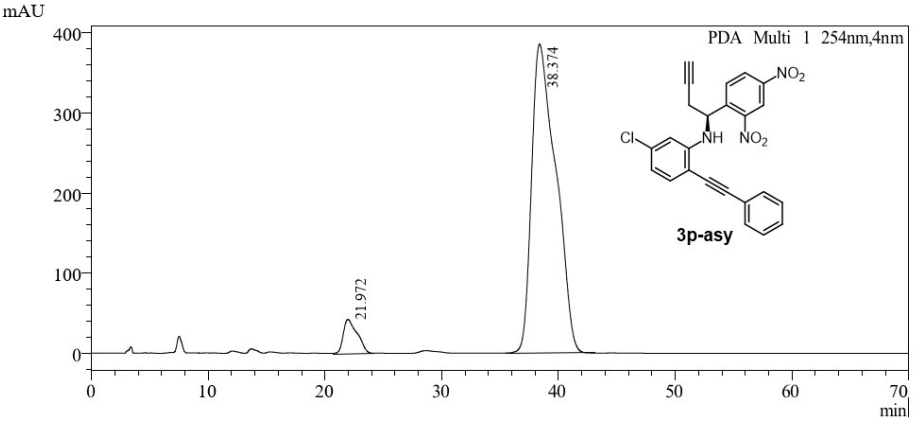
Peak#	Ret. Time	Area	Hight	Area%
1	13.431	3294704	70127	6.679
2	45.585	46033101	286163	93.321
Total		49327805	356290	100.000



<PeakTable>

PDA Ch1 254nm

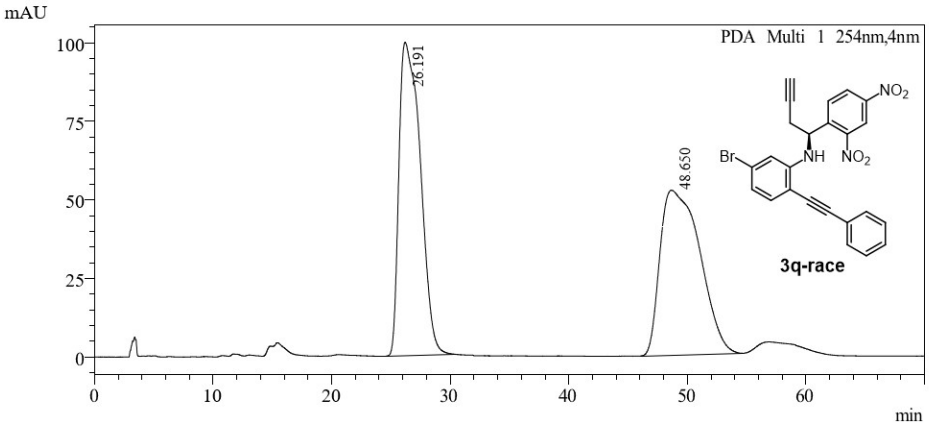
Peak#	Ret. Time	Area	Hight	Area%
1	22.225	16600287	158378	50.112
2	39.346	16526320	88342	49.888
Total		33126607	246720	100.000



<PeakTable>

PDA Ch1 254nm

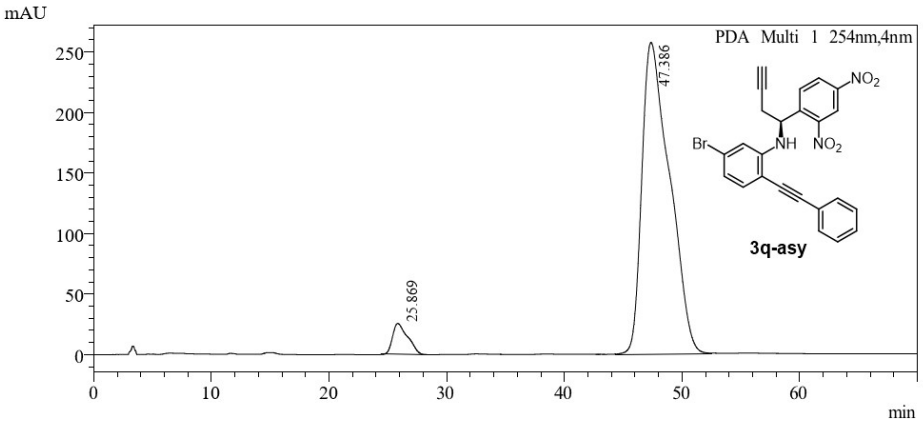
Peak#	Ret. Time	Area	Hight	Area%
1	21.972	3485984	42028	5.924
2	38.374	55363270	385554	94.076
Total		58849254	427582	100.000



<PeakTable>

PDA Ch1 254nm

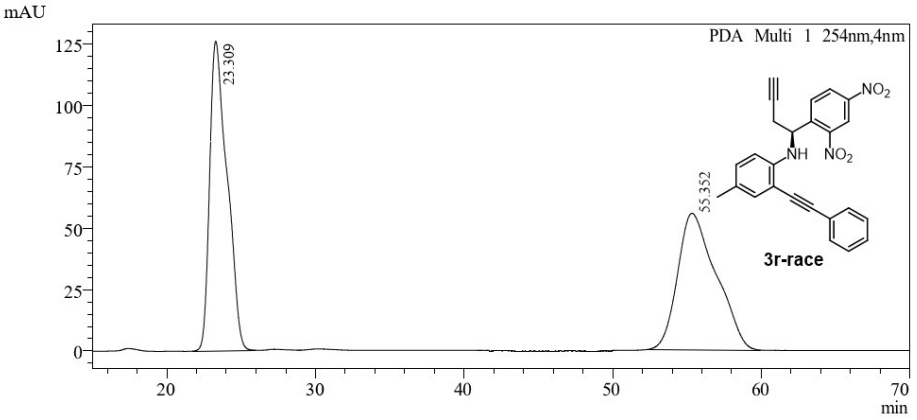
Peak#	Ret. Time	Area	Hight	Area%
1	26.191	12440586	99738	50.479
2	48.650	12204631	52643	49.521
Total		24645217	152381	100.000



<PeakTable>

PDA Ch1 254nm

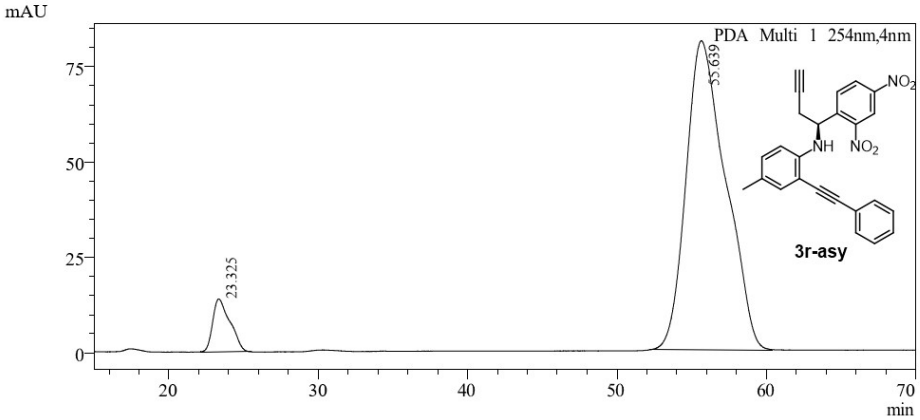
Peak#	Ret. Time	Area	Hight	Area%
1	25.869	2309994	25866	5.154
2	47.386	42512164	256984	94.846
Total		44822158	282850	100.000



<PeakTable>

PDA Ch1 254nm

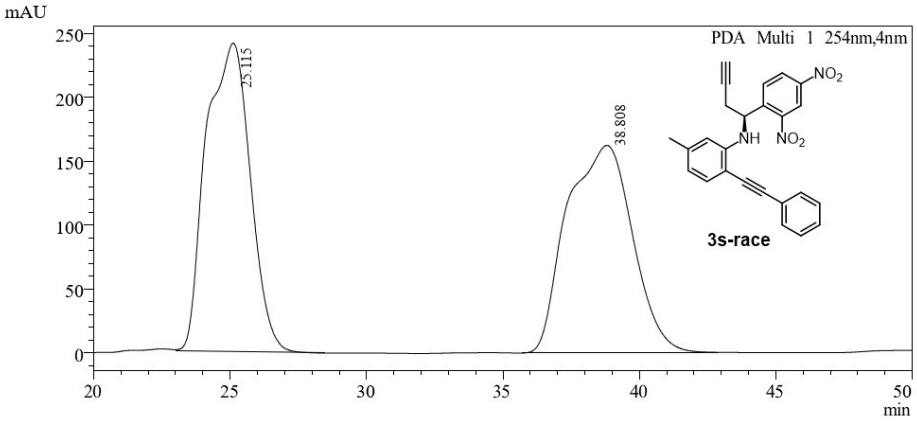
Peak#	Ret. Time	Area	Hight	Area%
1	23.309	10264009	126206	50.336
2	55.352	10126815	55603	49.664
Total		20390824	181810	100.000



<PeakTable>

PDA Ch1 254nm

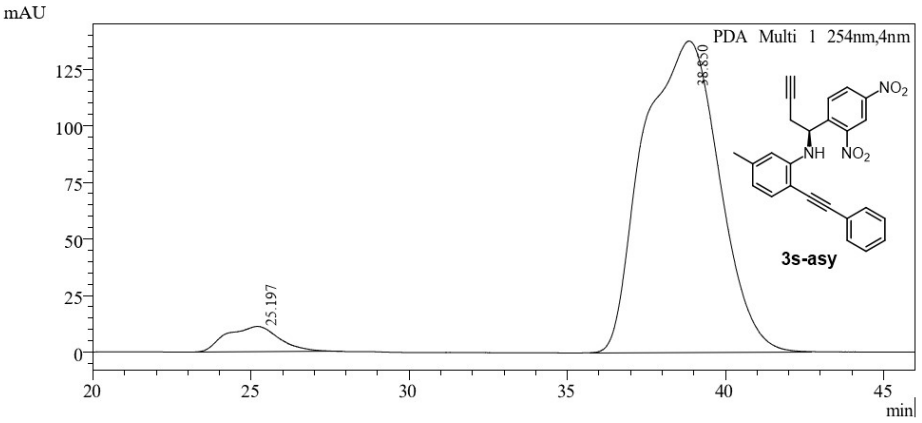
Peak#	Ret. Time	Area	Hight	Area%
1	23.325	1111638	13762	6.959
2	55.639	14861400	80895	93.041
Total		15973038	94657	100.000



<Table>

PDA Ch1 254nm

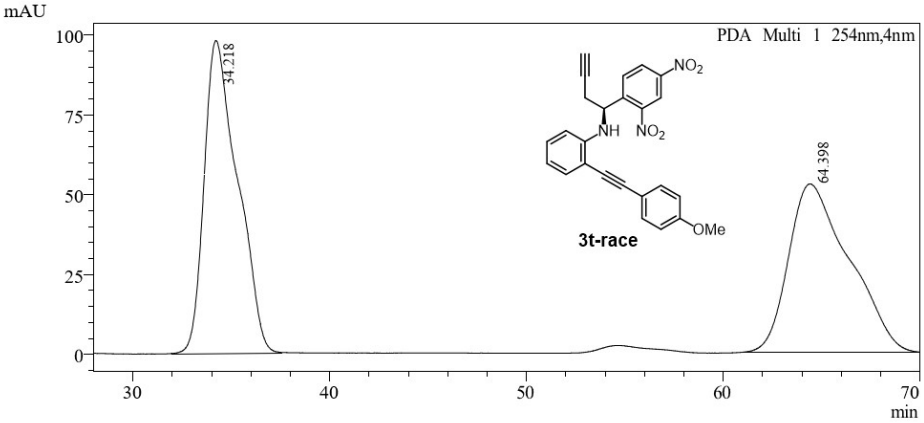
Peak#	Ret. Time	Area	Hight	Area%
1	25.115	27198535	241400	49.962
2	38.808	27239698	162177	50.038
Total		54438232	403577	100.000



<Table>

PDA Ch1 254nm

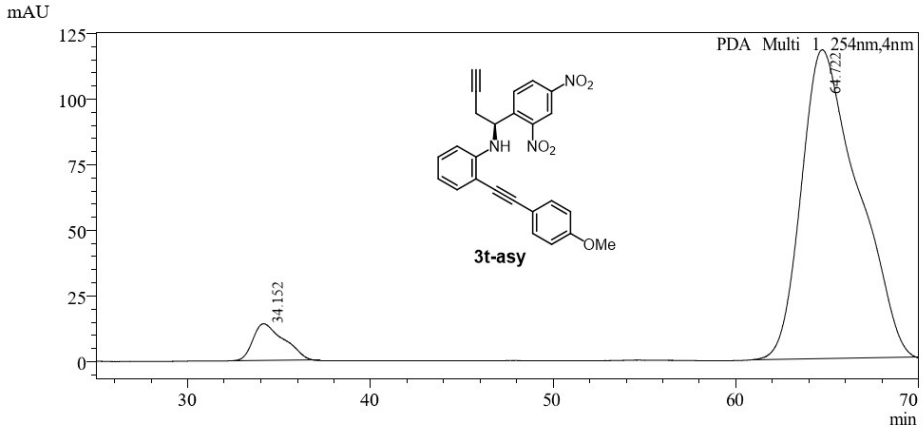
Peak#	Ret. Time	Area	Hight	Area%
1	25.197	1293736	11068	5.334
2	38.850	22961501	137277	94.666
Total		24255236	148345	100.000



<PeakTable>

PDA Ch1 254nm

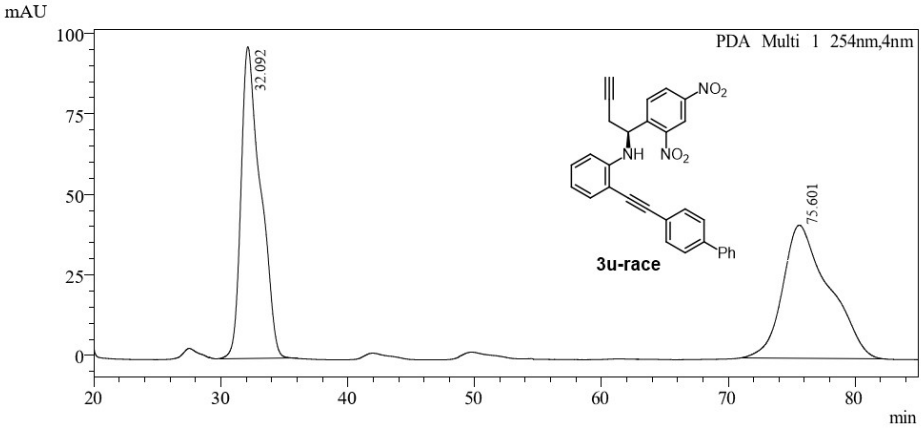
Peak#	Ret. Time	Area	Hight	Area%
1	34.218	11462110	97841	50.219
2	64.398	11362068	52858	49.781
Total		22824179	150699	100.000



<PeakTable>

PDA Ch1 254nm

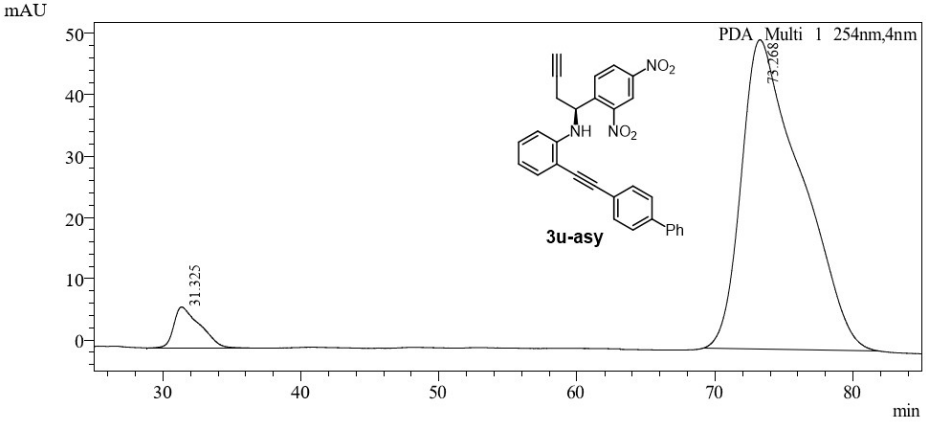
Peak#	Ret. Time	Area	Hight	Area%
1	34.152	1626010	13849	6.048
2	64.722	25259496	117667	93.952
Total		26885506	131517	100.000



<PeakTabl>

PDA Ch1 254nm

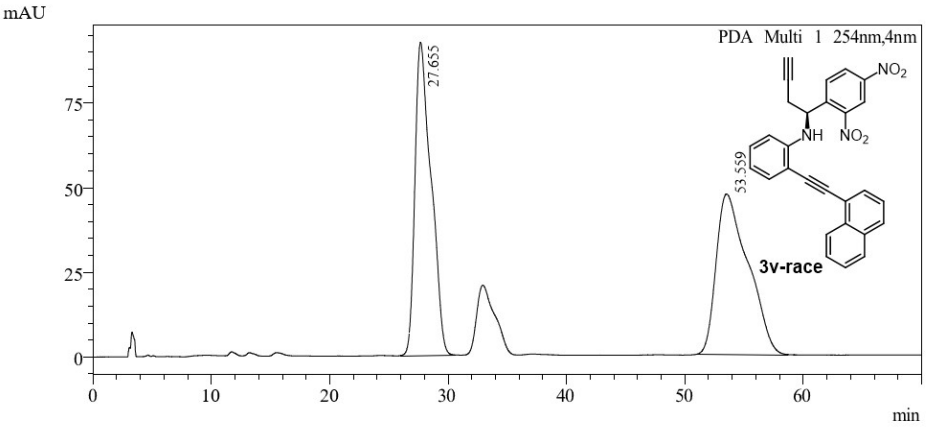
Peak#	Ret. Time	Area	Hight	Area%
1	32.092	10318945	96667	49.485
2	75.601	10533635	41266	50.515
Total		20852580	137933	100.000



<PeakTabl>

PDA Ch1 254nm

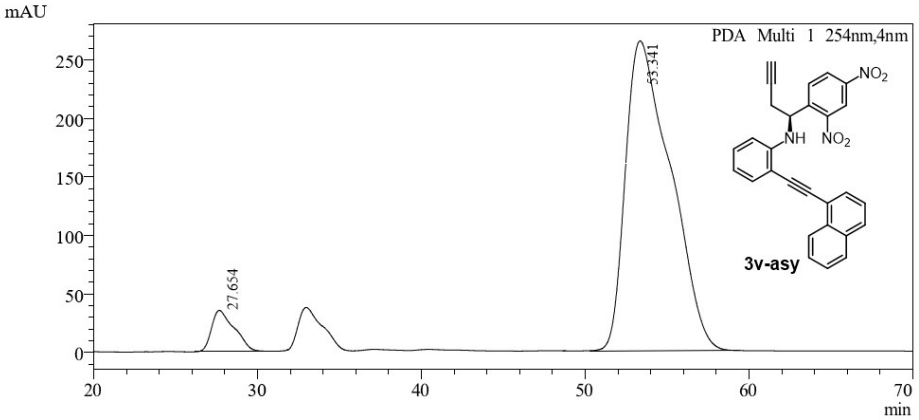
Peak#	Ret. Time	Area	Hight	Area%
1	31.325	885775	6699	5.513
2	73.268	15182356	50393	94.487
Total		16068131	57092	100.000



<PeakTable>

PDA Ch1 254nm

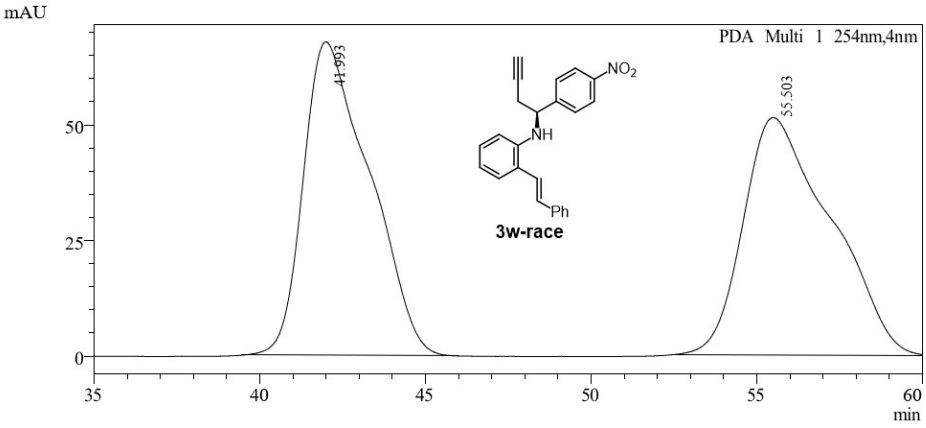
Peak#	Ret. Time	Area	Hight	Area%
1	27.655	8840851	92310	50.128
2	53.559	8795838	47243	49.872
Total		17636689	139553	100.000



<PeakTable>

PDA Ch1 254nm

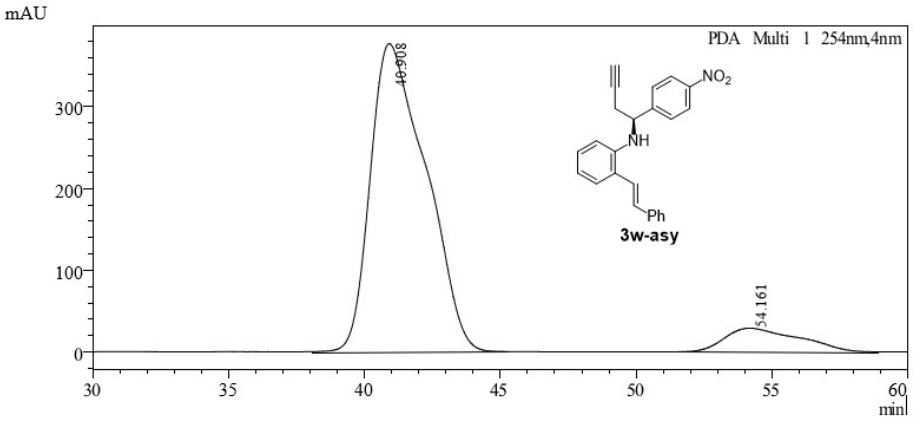
Peak#	Ret. Time	Area	Hight	Area%
1	27.654	3419993	35651	6.279
2	53.341	51050839	264708	93.721
Total		54470831	300359	100.000



<PeakTable>

PDA Ch1 254nm

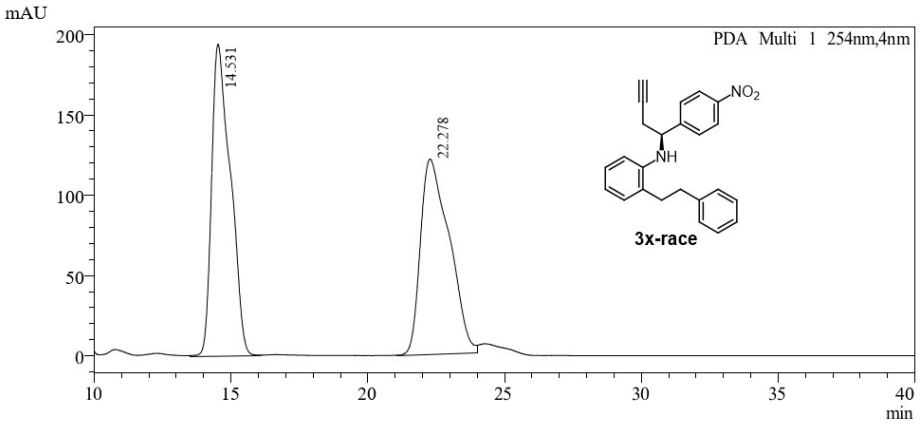
Peak#	Ret. Time	Area	Hight	Area%
1	41.993	9450603	67719	50.241
2	55.503	9359891	51273	49.759
Total		18810494	118992	100.000



<PeakTable>

PDA Ch1 254nm

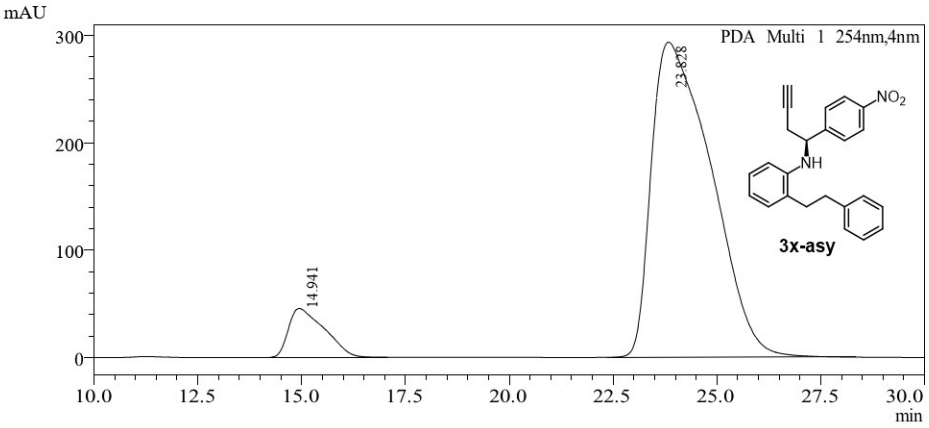
Peak#	Ret. Time	Area	Hight	Area%
1	40.908	54015958	377481	90.775
2	54.161	5489157	29029	9.225
Total		59505115	406511	100.000



<PeakTable>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	14.531	9194432	193479	50.360
2	22.278	9063076	121518	49.640
Total		18257508	314997	100.000



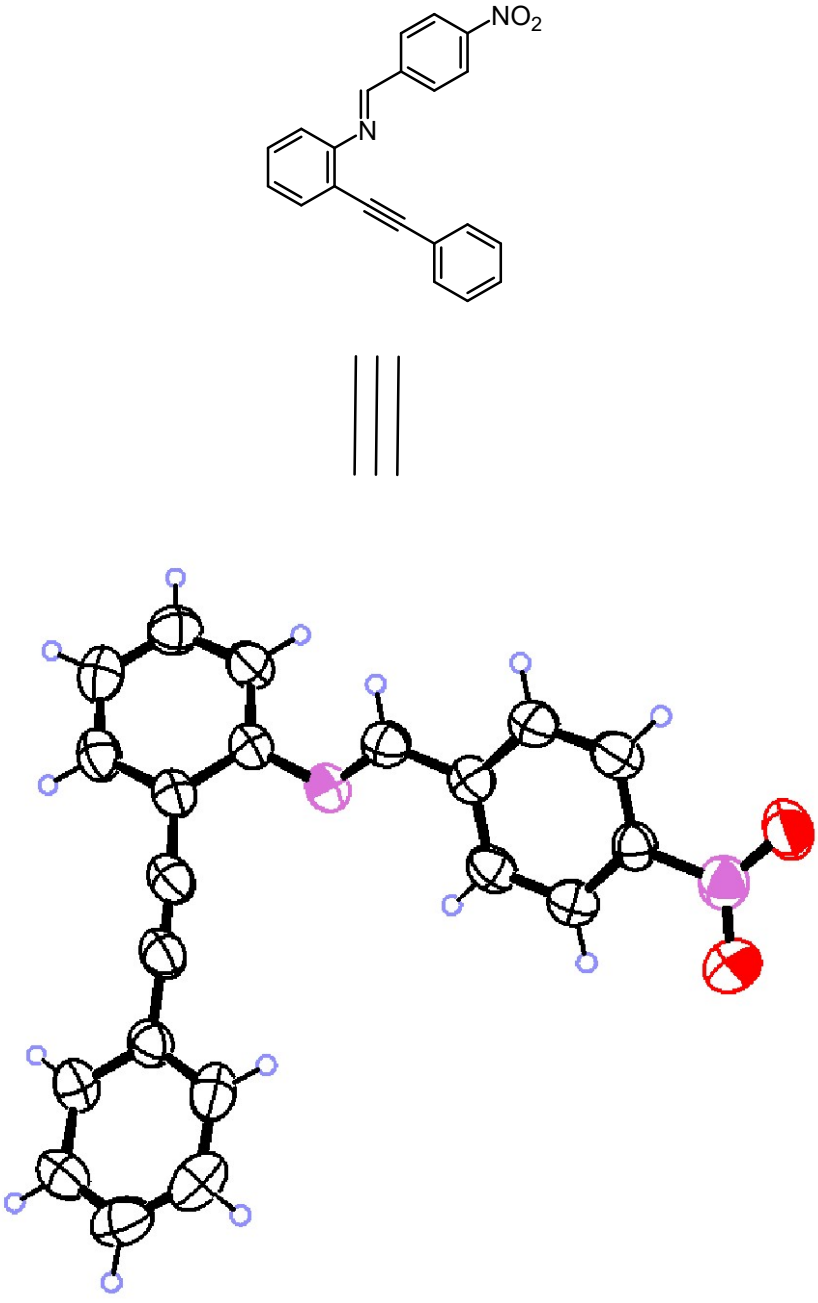
<PeakTable>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Hight	Area%
1	14.941	2728221	45430	8.441
2	23.828	29592980	293228	91.559
Total		32321200	338658	100.000

9. X-ray Crystallographic Data of **1a** and **3a**

The structure of **1a** (CCDC: 2267478) was determined by the X-ray diffraction analysis of single crystal, which recrystallized from a mixed solution of CH_2Cl_2 and hexane. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

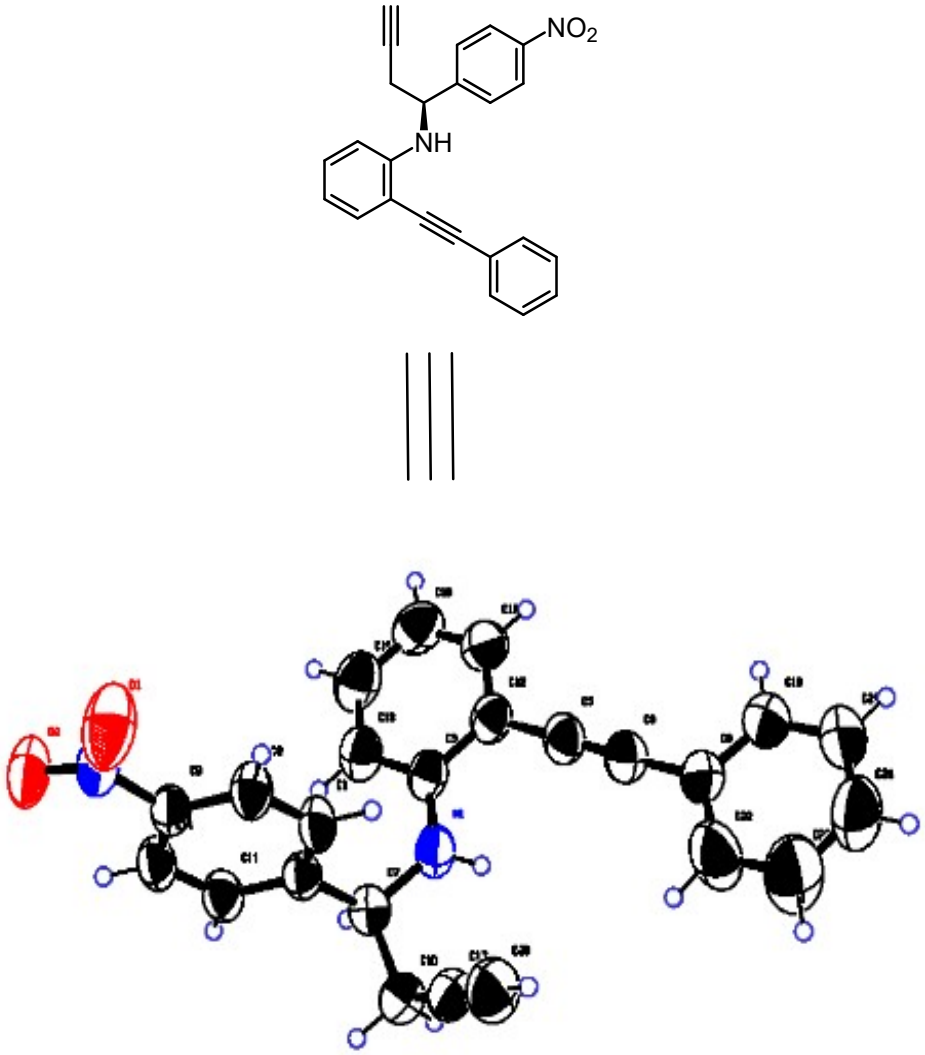


ORTEP of **1a** (CCDC: 2267478)

Identification code	**1a**
CCDC Deposit number	2267478
Empirical formula	$C_{24}H_{14}N_2O_2$
Formula weight	326.34
Temperature/K	296.4(3)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	24.7258 (4)
b/Å	10.9717 (2)
c/Å	12.8034 (2)
α/°	90
β/°	104.793 (2)
γ/°	90
Volume/Å^3	3358.23 (10)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.679
F(000)	1360.0
Crystal size/mm^3	0.2 × 0.15 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.396 to 153.748
Index ranges	-31 ≤ h ≤ 31, -13≤ k ≤ 12, -15≤ l ≤ 10
Reflections collected	24894
Independent reflections	6683 [R_{int} = 0.0272, R_{sigma} = 0.0257]
Data/restraints/parameters	6683/0/452
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0918, wR_2 = 0.2592
Final R indexes [all data]	R_1 = 0.0978, wR_2 = 0.2629
Largest diff. peak/hole / e Å^{-3}	0.32/-0.25

The structure of **3a** (CCDC: 2265065) was determined by the X-ray diffraction

analysis of single crystal, which recrystallized from a mixed solution of CH_2Cl_2 and hexane. The crystal of **3a** was cultured using the sample after recrystallization (with > 99:1 *er*). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



ORTEP of **3a** (CCDC: 2265065)

Identification code	**3a**
CCDC Deposit number	2265065
Empirical formula	$C_{24}H_{18}N_2O_2$

Formula weight	366.40
Temperature/K	297.64(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6789(2)
b/Å	9.7371(2)
c/Å	10.6182(4)
α/°	90
β/°	93.927(2)
γ/°	90
Volume/Å^3	998.36(3)
Z	2
ρ_{calc}g/cm^3	1.219
μ/mm^{-1}	0.626
F(000)	384.0
Crystal size/mm^3	0.16 × 0.15 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.346 to 152.61
Index ranges	-11 ≤ h ≤ 11, -12≤ k ≤ 12, -13≤ l ≤ 13
Reflections collected	12022
Independent reflections	3963 [R_{int} = 0.0312, R_{sigma} = 0.0264]
Data/restraints/parameters	3963/1/253
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1211
Final R indexes [all data]	R_1 = 0.0443, wR_2 = 0.1253
Largest diff. peak/hole / e Å^{-3}	0.12/-0.12
Flack parameter	0.03(12)