

## Supporting Information

### Copper-Catalyzed Amine-Mediated Yne-Propargylic Substitution

Chunyun Jiang,<sup>§a</sup> Defu Luo,<sup>§a</sup> Xiangjian Meng,<sup>c</sup> Qinqin Cui,<sup>d</sup> Lili Zhao,<sup>b</sup> Jinggong Liu,<sup>\*c</sup> Shuang Yang,<sup>b</sup> and Xinqiang Fang<sup>\*a,b</sup>

<sup>a</sup>College of Chemistry, Fuzhou University, Fuzhou 350116, China.

<sup>b</sup>State Key Laboratory of Structural Chemistry, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences, Fuzhou 350100, China.

<sup>c</sup>Orthopedics Department, Guangdong Provincial Hospital of Traditional Chinese Medicine, The Second Affiliated Hospital of Guangzhou University of Chinese Medicine, Guangzhou 510120, China.

<sup>d</sup>School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832000, China.

<sup>e</sup>Fujian Normal University, Fuzhou 350108, China.

<sup>§</sup>C. Jiang and D. Luo contributed equally to this work.

#### Table of Contents

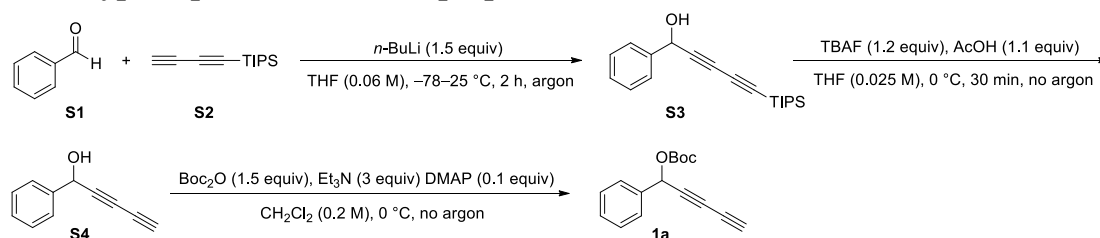
<b>I</b>	General information	S1
<b>II</b>	1. Typical procedure for the preparation of substrates	S2
	2. Typical procedure for the preparation of products	S2
<b>III</b>	Procedures for the derivatizations of products	S3
<b>IV</b>	Gram-scale reaction of <b>3a</b>	S4
<b>V</b>	Supplement of condition optimization	S4
<b>VI</b>	Characterizations of new compounds	S6
<b>VII</b>	<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of substrates and products	S25
<b>VIII</b>	HPLC analysis of <b>3a</b>	S26

#### I. General Information.

Commercially available materials were used as received, unless otherwise noted, all reactions and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. All solvents were purified and dried using standard procedures. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta = 0.00$  ppm) or chloroform ( $\delta = 7.26$  ppm). <sup>1</sup>H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplet), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Thermo Fisher Scientific LTQ FT Ultra mass spectrometer. X-ray crystallography analysis was

performed on Agilent SuperNova X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 5dm path length on an INESA SGW-1polarimeter and are reported as follows:  $[\alpha]_D^{rt}$  (c in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on WFH-203 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or 2,4-Dinitrophenylhydrazine or potassium permanganate stain.

## II. 1. Typical procedure for the preparation of substrates

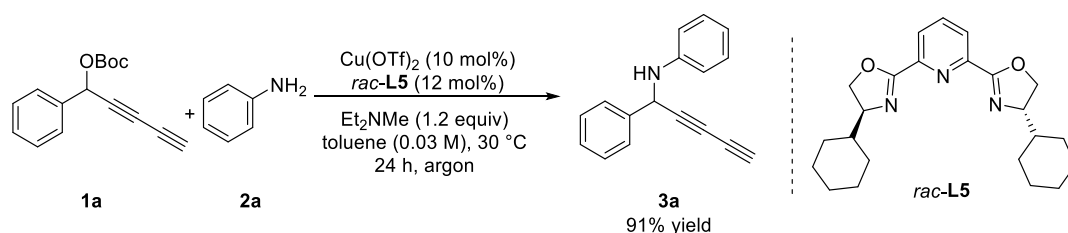


Generally, buta-1,3-diyne-1-yltriisopropylsilane **S2** (4 g, 19.2 mmol) in distilled THF (100 mL) was added to a Schlenk tube at  $-78$  °C under argon atmosphere. Then *n*-BuLi (2.5 M in hexane, 7.8 mL, 19.6 mmol) was added via syringe. After stirring for 30 min, then benzaldehyde **S1** (1.3 mL, 12.8 mmol) was added at  $-78$  °C and the reaction mixture was warmed to room temperature naturally. When the reaction was completed as monitored by TLC, the solution was quenched with saturated NH<sub>4</sub>Cl solution. The product was extracted with ethyl acetate (100 mL  $\times$  3), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1) to afford the product **S3** (3.6 g, 90% yield).

To a solution of **S3** (3.6 g, 11.5 mmol) in 460 mL of THF was added AcOH (0.72 mL, 12.8 mmol) and TBAF (3.6 g, 13.8 mmol) at 0 °C. When the reaction was completed as monitored by TLC, the solution was quenched with saturated NH<sub>4</sub>Cl solution. The product was extracted with ethyl acetate (100 mL  $\times$  3), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford the product **S4** (1.2 g, 67% yield).

To a solution of **S4** (1.2 g, 7.7 mmol) in 39 mL of CH<sub>2</sub>Cl<sub>2</sub> was added Et<sub>3</sub>N (3.2 mL, 23 mmol), DMAP (125 mg, 0.77 mmol) and Boc<sub>2</sub>O (2.5 g, 11.6 mmol) at 0 °C. When the reaction was completed as monitored by TLC, the solution was quenched with saturated NH<sub>4</sub>Cl solution. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  3), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 50:1) to afford the product **1a** (1.7 g, 85% yield).

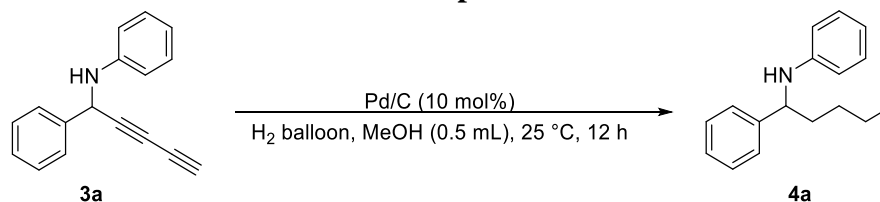
## 2. Typical procedure for the preparation of products



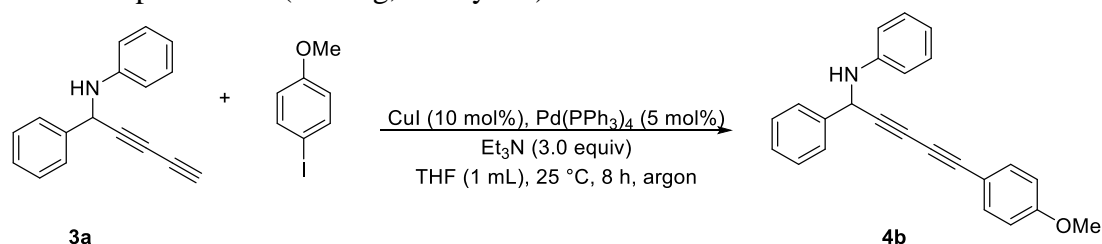
$\text{Cu(OTf)}_2$  (36 mg, 0.1 mmol) and *rac-L5* (46 mg, 0.12 mmol) in distilled toluene (5 mL) were added to a Schlenk tube at room temperature under argon atmosphere, and stirring for 1 h. Then a solution of **1a** (256 mg, 1 mmol), **2a** (140  $\mu\text{L}$ , 1.2 mmol) and  $\text{Et}_2\text{NMe}$  (145  $\mu\text{L}$ , 1.2 mmol) in distilled toluene (28 mL) was added via syringe. After stirring for 24 h, when the reaction was completed as monitored by TLC, the solution was quenched carefully with saturated  $\text{NH}_4\text{Cl}$  solution. The product was extracted with ethyl acetate (25 mL  $\times$  3), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1) to afford the product **3a** (210 mg, 91% yield).

**3x–3z'** were synthesized according to reported procedures.<sup>[1]</sup>

### III. Procedures for the derivatizations of products

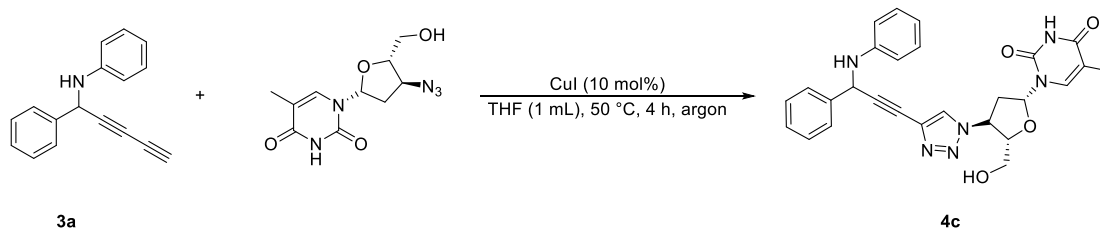


In a flask were placed **3a** (231 mg, 1 mmol), 10% Pd/C (42 mg) and 5 mL MeOH. Then the mixture was stirred using a magnetic stirrer at room temperature under a hydrogen atmosphere for 12 h. When the reaction was completed as monitored by TLC, the ethyl acetate was added, and then the mixture was passed through a membrane filter. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1) to afford the product **4a** (190 mg, 80% yield).



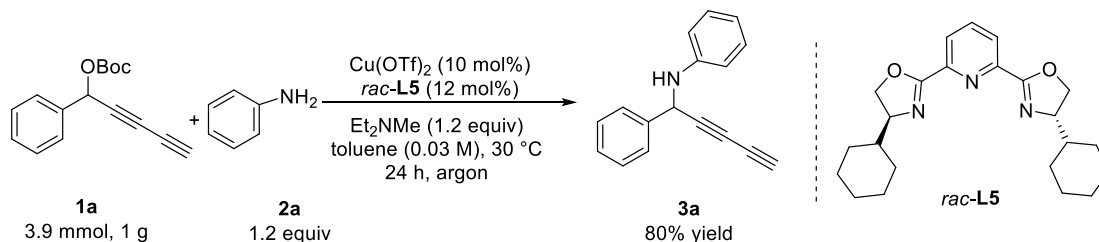
4-Iodoanisole (234 mg, 1 mmol) and **3a** (231 mg, 1 mmol) were dissolved in THF (10 mL), and  $\text{Et}_3\text{N}$  (420  $\mu\text{L}$ , 3 mmol),  $\text{Pd(PPh}_3)_4$  (58 mg, 0.05 mmol) and  $\text{CuI}$  (19 mg, 0.1 mmol) were added. The mixture was stirred at room temperature under argon atmosphere for 8 h. When the reaction was completed as monitored by TLC, the solution was quenched carefully with saturated  $\text{NH}_4\text{Cl}$  solution and then warmed to room temperature. The product was extracted with ethyl acetate (50 mL  $\times$  3), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation in vacuo, the residue

was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1) to afford the product **4b** (250 mg, 74% yield).



CuI (19 mg, 0.1 mmol) and **3a** (231 mg, 0.1 mmol) in distilled THF (5 mL) were added to a Schlenk tube at room temperature under argon atmosphere, then the solution of Zidovudine (400 mg, 1.5 mmol) in distilled THF (5 mL) was added via syringe. After stirring at 50 °C using an oil bath for 4 h, when the reaction was completed as monitored by TLC, the solution was quenched carefully with saturated  $\text{NH}_4\text{Cl}$  solution and then warmed to room temperature. The product was extracted with ethyl acetate (25 mL  $\times$  3), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 1:2) to afford the product **4c** (414 mg, 83% yield).

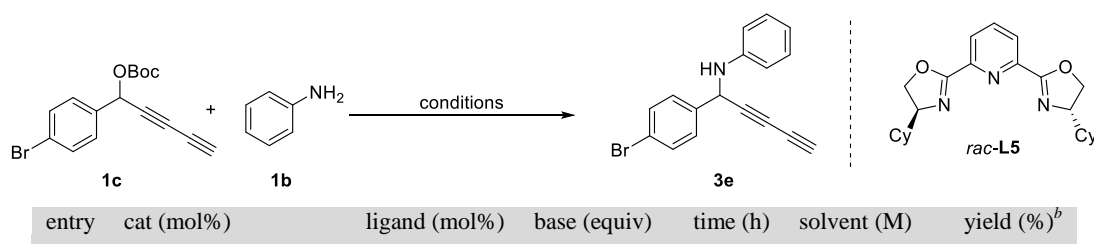
#### IV. Gram-scale Reaction of **3a**



$\text{Cu}(\text{OTf})_2$  (140 mg, 0.39 mmol) and *rac*-**L5** (179 mg, 0.468 mmol) in distilled toluene (20 mL) were added to a Schlenk tube at room temperature under argon atmosphere. The mixture was stirred for 1 h. Then a solution of **1a** (1 g, 3.9 mmol), **2a** (0.55 mL, 4.68 mmol) and  $\text{Et}_2\text{NMe}$  (0.57 mL, 4.68 mmol) in distilled toluene (110 mL) was added via syringe. After stirring for 24 h, when the reaction was completed as monitored by TLC, the solution was quenched carefully with saturated  $\text{NH}_4\text{Cl}$  solution. The product was extracted with ethyl acetate (50 mL  $\times$  3), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1) to afford the product **3a** (722 mg, 80% yield).

#### V. Supplementary tables of condition optimization

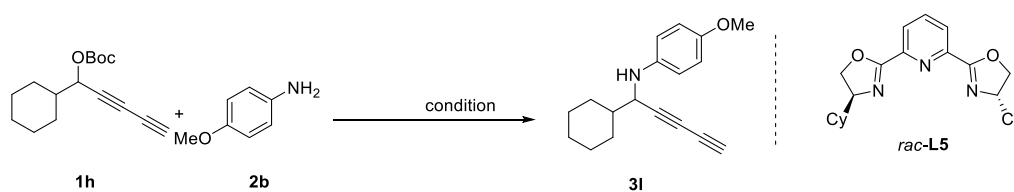
Table S1. Condition optimization of **3e**<sup>a</sup>



1	Cu(OTf) <sub>2</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	0
2	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	64
3	Cu(CH <sub>3</sub> CN) <sub>4</sub> BF <sub>4</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	0
4	CuI (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	0
5	Cu(ClO <sub>4</sub> ) <sub>4</sub> •6H <sub>2</sub> O (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	0
6	CuOAc (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	0
7	CuOTf(CH <sub>3</sub> CN) <sub>4</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	0
8	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub> (20)	<b>L5</b> (24)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.03)	75
9	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	16	toluene (0.06)	69
10	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	28	CH <sub>2</sub> Cl <sub>2</sub> (0.03)	0
11	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	28	THF (0.03)	0
12	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	4	MeOH (0.03)	92

<sup>a</sup>Reaction conditions: **1c** (0.1 mmol), **1b** (0.12 mmol), 24 h, under argon atmosphere. <sup>b</sup>All isolated yields were based on **1c**.

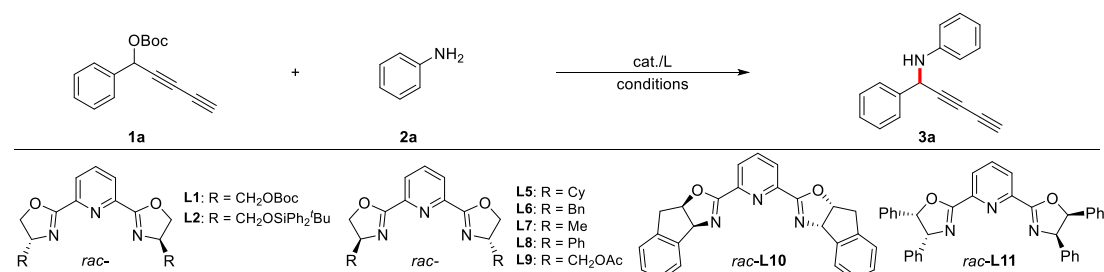
Table S2. Condition optimization of **31**<sup>a</sup>



entry	cat (mol%)	ligand (mol%)	base (equiv)	time (h)	solvent (M)	yield (%) <sup>b</sup>
1	Cu(OTf) <sub>2</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	22	toluene (0.03)	0
2	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	22	toluene (0.03)	0
3	Cu(CH <sub>3</sub> CN) <sub>4</sub> BF <sub>4</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	22	toluene (0.03)	12
4	CuOAc (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	22	toluene (0.03)	0
5	Cu(OAc) <sub>2</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	22	toluene (0.03)	0
6	CuTc (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	22	toluene (0.03)	19
7	CuClO <sub>4</sub> •6H <sub>2</sub> O (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	22	toluene (0.03)	28
8	Cu(ClO <sub>4</sub> ) <sub>4</sub> •6H <sub>2</sub> O (20)	<b>L5</b> (24)	Et <sub>2</sub> NMe (1.2)	20	toluene (0.03)	62

<sup>a</sup>Reaction conditions: **1h** (0.1 mmol), **2b** (0.12 mmol), 24 h, under argon atmosphere. <sup>d</sup>All isolated yields were based on **1h**.

Table S3. Asymmetric catalysis of the reaction of **1a** and **2a**<sup>a</sup>



entry	cat (mol%)	ligand (mol%)	base (equiv)	time (h)	solvent (M)	yield (%)	ee (%) <sup>b</sup>
1	Cu(OTf) <sub>2</sub> (10)	<b>L1</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	74	2
2	Cu(OTf) <sub>2</sub> (10)	<b>L2</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	61	19

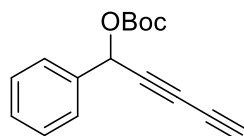
3	Cu(OTf) <sub>2</sub> (10)	<b>L5</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	91	22
4	Cu(OTf) <sub>2</sub> (10)	<b>L6</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	78	3
5	Cu(OTf) <sub>2</sub> (10)	<b>L7</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	69	1
6	Cu(OTf) <sub>2</sub> (10)	<b>L8</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	61	3
7	Cu(OTf) <sub>2</sub> (10)	<b>L9</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	43	9
8	Cu(OTf) <sub>2</sub> (10)	<b>L10</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	61	13
9	Cu(OTf) <sub>2</sub> (10)	<b>L11</b> (12)	Et <sub>2</sub> NMe (1.2)	24	toluene (0.03)	69	0

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), 24 h, under argon atmosphere. <sup>b</sup>All isolated yields were based on **1a**.

## References

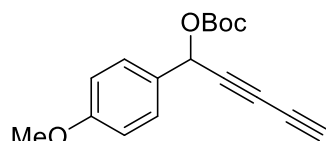
[1] Detz, R.; Delville, M.; Hiemstar, H.; Maarseveen, J. *Angew. Chem. Int. Ed.* **2008**, *47*, 3777–3780

## VI. Characterizations of new compounds



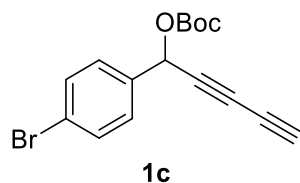
**1a**

**tert-butyl (1-phenylpenta-2,4-diyne-1-yl) carbonate (1a)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 50:1), yellow oil, 1.7 g, 85% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.53–7.49 (m, 2H), 7.42–7.36 (m, 3H), 6.26 (s, 1H), 2.62–2.50 (m, 1H), 1.49 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.4, 135.7, 129.5, 129.0, 127.9, 83.6, 72.3, 71.8, 69.8, 68.6, 67.4, 27.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>3</sub>Na 279.0992; Found 279.0992. IR (KBr thin film, cm<sup>-1</sup>): ν 3290, 2982, 1745, 1611, 1456, 1371, 1143, 1075, 708, 631.

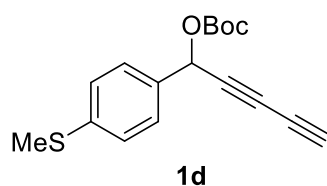


**1b**

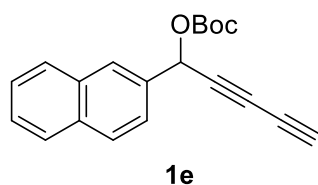
**tert-butyl (1-(4-methoxyphenyl)penta-2,4-diyne-1-yl) carbonate (1b)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 50:1), colorless oil, 772 mg, 35% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.21 (s, 1H), 3.81 (s, 3H), 2.25 (s, 1H), 1.48 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.5, 152.4, 129.6, 128.0, 114.3, 83.5, 72.5, 71.6, 69.7, 68.3, 67.4, 55.5, 27.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>Na 309.1097; Found 309.1103. IR (KBr thin film, cm<sup>-1</sup>): ν 3280, 2980, 2838, 1738, 1611, 1512, 1243, 1139, 831, 767.



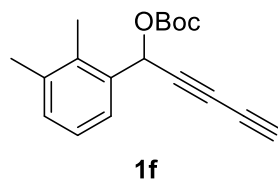
**1-(4-bromophenyl)penta-2,4-diyne-1-yl *tert*-butyl carbonate (1c):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 50:1), brown oil, 1.4 g, 54% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J$  = 8.4 Hz, 2H), 7.38 (d,  $J$  = 8.4 Hz, 2H), 6.21 (s, 1H), 2.27 (s, 1H), 1.49 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 134.9, 132.1, 129.5, 123.8, 83.9, 72.1, 71.7, 70.1, 67.8, 67.2, 27.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{16}\text{H}_{15}\text{O}_3\text{BrNa}$  357.0097; Found 357.0100. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3282, 2986, 1742, 1487, 1262, 1154, 1071, 749, 703.



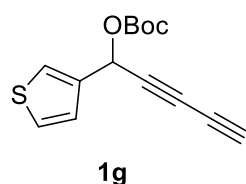
***tert*-butyl (1-(4-(methylthio)phenyl)penta-2,4-diyne-1-yl) carbonate (1d):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), colorless oil, 931 mg, 40% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J$  = 8.3 Hz, 2H), 7.23 (d,  $J$  = 8.3 Hz, 2H), 6.22 (s, 1H), 2.46 (s, 3H), 2.27 (s, 1H), 1.48 (s, 9H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 140.5, 132.2, 128.3, 126.3, 83.5, 72.1, 71.7, 69.9, 68.1, 67.2, 27.7, 15.4. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{SNa}$  325.0869; Found 325.0872. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3280, 2980, 2923, 1739, 1494, 1248, 1156, 1090, 868, 633.



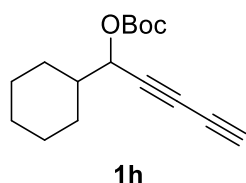
***tert*-butyl (1-(naphthalen-2-yl)penta-2,4-diyne-1-yl) carbonate (1e):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), brown solid, mp 72.9–75.3 °C, 944 mg, 40% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 1.2 Hz, 1H), 7.90–7.83 (m, 3H), 7.61 (dd,  $J$  = 8.6, 1.8 Hz, 1H), 7.55–7.48 (m, 2H), 6.44 (s, 1H), 2.29–2.27 (m, 1H), 1.50 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4, 133.7, 133.13, 133.08, 129.0, 128.5, 127.9, 127.5, 127.0, 126.7, 125.0, 83.7, 72.3, 72.1, 69.9, 68.7, 67.4, 27.9. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{20}\text{H}_{18}\text{O}_3\text{Na}$  329.1148; Found 329.1151. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3283, 2980, 1739, 1369, 1269, 1248, 1153, 846, 636.



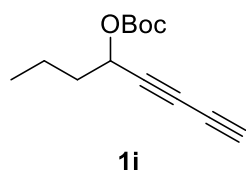
**tert-butyl (1-(2,3-dimethylphenyl)penta-2,4-diyn-1-yl) carbonate (1f):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), white solid, mp 67.9–68.8 °C, 1.2 g, 55% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46–7.42 (m, 1H), 7.21–7.12 (m, 2H), 6.48 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.28–2.25 (m, 1H), 1.52 (s, 9H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4, 137.7, 134.8, 133.7, 131.0, 126.0, 125.9, 83.4, 72.3, 71.6, 69.8, 67.4, 66.9, 27.8, 20.6, 15.2. HRMS (ESI-Quadrupole-Orbitrap) m/z:  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{20}\text{O}_3\text{Na}$  307.1305; Found 307.1309. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3291, 2983, 1742, 1264, 1146, 1076, 735, 636.



**tert-butyl (1-(thiophen-3-yl)penta-2,4-diyn-1-yl) carbonate (1g):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), brown oil, 1.5 g, 75% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 2.3$  Hz, 1H), 7.32 (dd,  $J = 4.8, 3.1$  Hz, 1H), 7.19 (d,  $J = 5.0$  Hz, 1H), 6.34 (s, 1H), 2.26 (s, 1H), 1.49 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 136.3, 126.9, 126.8, 125.4, 83.6, 71.9, 71.1, 69.8, 67.3, 63.9, 27.8. HRMS (ESI-Quadrupole-Orbitrap) m/z:  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{SNa}$  285.0556; Found 285.0558. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3288, 2981, 1740, 1457, 1370, 1250, 1156, 1074, 764, 644.

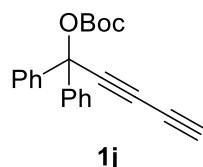


**tert-butyl (1-cyclohexylpenta-2,4-diyn-1-yl) carbonate (1h):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 50:1), yellow oil, 1.4 g, 69% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.02 (d,  $J = 6.1$  Hz, 1H), 2.18 (s, 1H), 1.87 (d,  $J = 11.4$  Hz, 1H), 1.82–1.69 (m, 4H), 1.66 (d,  $J = 13.4$  Hz, 1H), 1.48 (s, 9H), 1.29–1.05 (m, 5H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8, 83.1, 72.8, 71.3, 70.7, 68.6, 67.6, 42.0, 28.6, 28.1, 27.9, 26.1, 25.8, 25.7. HRMS (ESI-Quadrupole-Orbitrap) m/z:  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Na}$  285.1461; Found 285.1467. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3289, 2983, 2930, 2855, 1742, 1452, 1370, 1253, 1153, 1096, 857, 764.

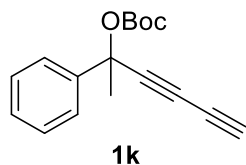




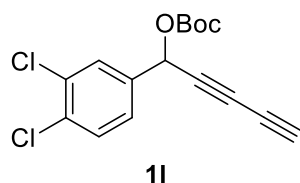
**tert-butyl octa-5,7-diyn-4-yl carbonate (1i):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 50:1), colorless oil, 1.1 g, 64% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.18 (t,  $J$  = 6.7 Hz, 1H), 2.19 (s, 1H), 1.85–1.72 (m, 2H), 1.52–1.42 (m, 11H), 0.94 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.6, 83.2, 73.5, 70.0, 68.9, 67.4, 66.8, 36.6, 27.8, 18.3, 13.6. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$  245.1148; Found 2245.1147. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3290, 2964, 1742, 1458, 1370, 1251, 1154, 1081, 764, 631.



**tert-butyl (1,1-diphenylpenta-2,4-diyn-1-yl) carbonate (1j):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), yellow oil, 511 mg, 20% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53–7.46 (m, 4H), 7.36–7.23 (m, 6H), 2.33 (s, 1H), 1.40 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 141.5, 128.5, 128.3, 126.3, 83.3, 80.7, 74.4, 73.8, 70.7, 67.5, 27.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_3\text{Na}$  355.1305; Found 355.1307. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3282, 2980, 1752, 1450, 1369, 1272, 11133, 696, 636.

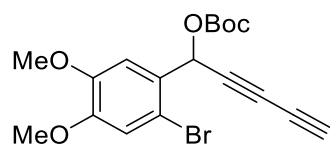


**tert-butyl (2-phenylhexa-3,5-diyn-2-yl) carbonate (1k):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), white solid mp 74.7–77.2  $^{\circ}\text{C}$ , 853 mg, 41% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J$  = 7.5 Hz, 2H), 7.40–7.34 (m, 2H), 7.33–7.28 (m, 1H), 2.31 (s, 1H), 1.89 (s, 3H), 1.40 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 141.9, 128.6, 128.3, 124.7, 83.2, 77.1, 75.0, 71.7, 69.8, 67.5, 32.3, 27.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Na}$  293.1148; Found 293.1156. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3294, 2985, 1751, 1371, 1263, 1154, 1071, 732, 634.



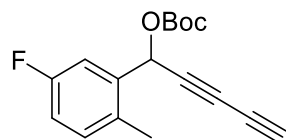
**tert-butyl (1-(3,4-dichlorophenyl)penta-2,4-diyn-1-yl) carbonate (1l):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 1.2 g, 48% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62–7.59 (m, 1H), 7.47 (d,  $J$  = 8.3 Hz 1H), 7.37–7.32 (m, 1H), 6.20 (s, 1H), 2.31–2.28 (m, 1H), 1.51–1.48 (m, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.0, 135.9, 133.8, 133.1, 130.9, 129.8, 127.0, 84.1, 72.4, 71.1, 70.4, 67.1, 67.0, 27.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$

Calcd for C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>3</sub>Na 347.0212; Found 347.0209. IR (KBr thin film, cm<sup>-1</sup>):  $\nu$  3290, 2981, 1745, 1471, 1271, 1252, 1144, 849, 767.



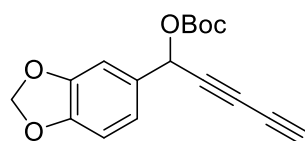
**1m**

**1-(2-bromo-4,5-dimethoxyphenyl)penta-2,4-diyne-1-yl tert-butyl carbonate (1m):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), brown oil, 2.6 g, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.16 (s, 1H), 7.00 (s, 1H), 6.53 (s, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 2.27 (d,  $J$  = 1.0 Hz, 1H), 1.49 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.9, 150.4, 148.9, 127.1, 115.4, 113.6, 111.7, 83.7, 71.8, 71.7, 70.0, 67.9, 67.3, 56.4, 56.3, 27.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ : [M + Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>19</sub>BrO<sub>5</sub>Na 417.0308; Found 417.0313. IR (KBr thin film, cm<sup>-1</sup>):  $\nu$  3291, 2982, 1747, 1509, 1249, 1209, 1072, 731, 634.



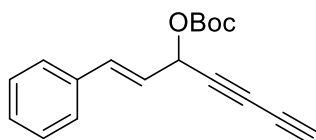
**1n**

**tert-butyl (1-(5-fluoro-2-methylphenyl)penta-2,4-diyne-1-yl) carbonate (1n):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 1.8 g, 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32–7.25 (m, 1H), 7.17–7.10 (m, 1H), 6.96 (td  $J$  = 8.3, 2.2 Hz, 1H), 6.35 (s, 1H), 2.36 (s, 3H), 2.26 (s, 1H), 1.50 (s, 9H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  161.4 (C-F, <sup>1</sup> $J_{C-F}$  = 244.5 Hz), 152.2, 135.7 (C-F, <sup>3</sup> $J_{C-F}$  = 7.0 Hz), 132.3 (C-F, <sup>3</sup> $J_{C-F}$  = 7.7 Hz), 131.5 (C-F, <sup>4</sup> $J_{C-F}$  = 2.9 Hz), 116.1 (C-F, <sup>2</sup> $J_{C-F}$  = 20.8 Hz), 114.7 (C-F, <sup>2</sup> $J_{C-F}$  = 23.2 Hz), 83.9, 71.8, 71.4, 70.0, 67.2, 65.7, 27.8, 18.4; <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -116.1. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ : [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>17</sub>FO<sub>3</sub>Na 311.1054; Found 311.1057. IR (KBr thin film, cm<sup>-1</sup>):  $\nu$  3291, 2983, 1746, 1498, 1252, 1155, 1073, 765, 627.



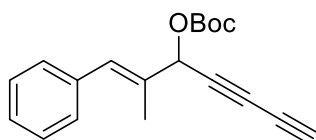
**1o**

**1-(benzo[d][1,3]dioxol-5-yl)penta-2,4-diyne-1-yl tert-butyl carbonate(1o):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 1.6 g, 69% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.02–6.94 (m, 2H), 6.78 (d,  $J$  = 7.9 Hz, 1H), 6.16 (s, 1H), 5.97 (s, 2H), 2.27 (d,  $J$  = 1.0 Hz, 1H), 1.48 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.3, 148.6, 148.1, 129.5, 122.1, 108.4, 101.5, 83.6, 72.2, 71.7, 69.9, 68.4, 67.3, 27.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ : [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>5</sub>Na 323.0890; Found 323.0889. IR (KBr thin film, cm<sup>-1</sup>):  $\nu$  3279, 2984, 1743, 1489, 1274, 1258, 1152, 764, 749.



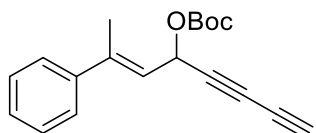
**1p**

**(E)-tert-butyl (1-phenylhepta-1-en-4,6-diyn-3-yl) carbonate (1p):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), brown oil, 847 mg, 39% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 7.0$  Hz, 2H), 7.37–7.27 (m, 3H), 6.85 (d,  $J = 15.8$  Hz, 1H), 6.22 (dd,  $J = 15.8, 6.9$  Hz, 1H), 5.87 (d,  $J = 6.9$  Hz, 1H), 2.27 (s, 1H), 1.51 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 135.7, 135.5, 128.84, 128.81, 127.2, 122.6, 83.6, 71.7, 71.5, 69.7, 67.4, 67.2, 27.9. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_3\text{Na}$  305.1148; Found 305.1153. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3289, 3005, 1745, 1275, 1258, 1153, 764, 711.



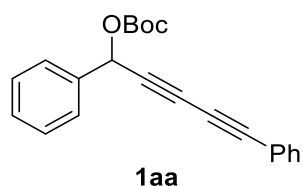
**1q**

**(E)-tert-butyl (2-methyl-1-phenylhepta-1-en-4,6-diyn-3-yl) carbonate (1q):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), brown oil, 1.9 g, 83% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.32 (m, 2H), 7.31–7.23 (m, 3H), 6.73 (s, 1H), 5.77 (s, 1H), 2.25 (s, 1H), 2.00 (d,  $J = 0.9$  Hz, 3H), 1.52 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4, 136.4, 132.2, 131.0, 129.2, 128.4, 127.4, 83.5, 72.4, 71.9, 71.3, 69.4, 67.5, 27.9, 14.4. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_3\text{Na}$  319.1305; Found 319.1308. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3280, 2983, 1742, 1457, 1370, 1249, 1066, 791, 637.

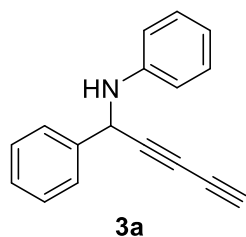


**1r**

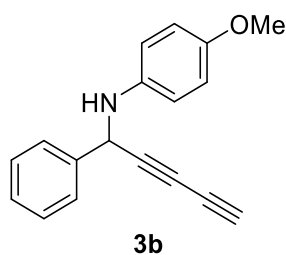
**(E)-tert-butyl (2-phenylocta-2-en-5,7-diyn-4-yl) carbonate (1r):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), brown oil, 1.9 g, 83% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44–7.38 (m, 2H), 7.38–7.28 (m, 3H), 6.07 (d,  $J = 8.7$  Hz, 1H), 5.84 (d,  $J = 8.9$  Hz, 1H), 2.24 (s, 1H), 2.18 (s, 3H), 1.51 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4, 141.8, 141.7, 128.5, 128.2, 126.2, 121.5, 83.5, 72.4, 70.4, 69.5, 67.5, 64.1, 27.9, 16.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_3\text{Na}$  319.1305; Found 319.1304. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3287, 2982, 1742, 1446, 1370, 1253, 1153, 1071, 750, 635.



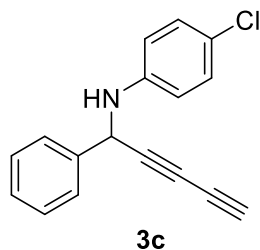
**tert-butyl (1,5-diphenylpenta-2,4-diyn-1-yl) carbonate (1aa):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), colorless oil, 2.4 g, 94% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60–7.54 (m, 2H), 7.53–7.47 (m, 2H), 7.45–7.28 (m, 6H), 6.38 (s, 1H), 1.52 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 136.1, 132.7, 129.6, 129.4, 128.9, 128.6, 127.9, 121.3, 83.4, 79.8, 78.3, 73.2, 72.4, 69.0, 27.8. HRMS (ESI-Quadrupole-Orbitrap) m/z:  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_3\text{Na}$  255.1305; Found 355.1307. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  2981, 2246, 1740, 1456, 1274, 1152, 1078, 1071, 735, 687.



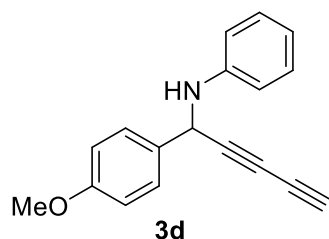
**N-(1-phenylpenta-2,4-diyn-1-yl)aniline (3a):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 42 mg, 91% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.4$  Hz, 2H), 7.44–7.30 (m, 3H), 7.21 (t,  $J = 7.2$  Hz, 2H), 6.81 (t,  $J = 7.4$  Hz, 1H), 6.72 (d,  $J = 7.9$  Hz, 2H), 5.32 (d,  $J = 7.4$  Hz, 1H), 4.03 (d,  $J = 7.1$  Hz, 1H), 2.13 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 138.3, 129.4, 129.1, 128.6, 127.4, 119.2, 114.1, 75.8, 69.2, 68.1, 67.8, 50.4. HRMS (ESI-Quadrupole-Orbitrap) m/z:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}$  232.1121; Found 232.1119. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3272, 3035, 1721, 1611, 1495, 1457, 1078, 721, 646.



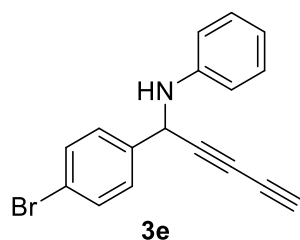
**4-methoxy-N-(1-phenylpenta-2,4-diyn-1-yl)aniline (3b):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 45 mg, 85% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 7.4$  Hz, 2H), 7.44–7.32 (m, 3H), 6.82 (d,  $J = 8.9$  Hz, 2H), 6.72 (d,  $J = 8.8$  Hz, 2H), 5.26 (s, 1H), 3.77 (s, 3H), 2.15 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 140.2, 138.6, 129.0, 128.6, 127.4, 116.0, 114.9, 76.2, 69.3, 68.0, 67.9, 55.8, 51.6. HRMS (ESI-Quadrupole-Orbitrap) m/z:  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{16}\text{NO}$  262.1226; Found 262.1227. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3281, 3003, 2833, 1510, 1275, 1242, 1032, 764, 634.



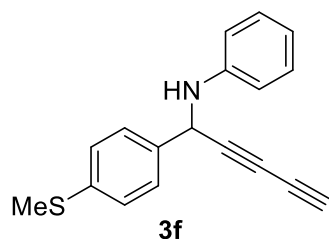
**4-chloro-*N*-(1-phenylpenta-2,4-diyne-1-yl)aniline (3c):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 43 mg, 81% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.2$  Hz, 2H), 7.46–7.32 (m, 3H), 7.17 (d,  $J = 8.7$  Hz, 2H), 6.65 (d,  $J = 8.7$  Hz, 2H), 5.29 (s, 1H), 4.07 (s, 1H), 2.17 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 137.9, 129.3, 129.2, 128.8, 127.4, 123.9, 115.3, 75.3, 69.5, 68.3, 67.7, 50.6. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{13}\text{ClN}$  266.0731; Found 266.0732. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3286, 2985, 1598, 1495, 1275, 1257, 764, 633.



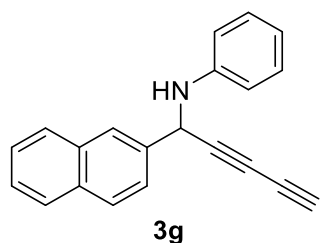
***N*-(1-(4-methoxyphenyl)penta-2,4-diyne-1-yl)aniline (3d):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 51 mg, 97% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.6$  Hz, 2H), 7.26–7.16 (m, 2H), 6.90 (d,  $J = 8.6$  Hz, 2H), 6.81 (t,  $J = 7.3$  Hz, 1H), 6.72 (d,  $J = 8.1$  Hz, 2H), 5.26 (s, 1H), 3.80 (s, 3H), 2.12 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 145.9, 130.3, 129.4, 128.7, 119.2, 114.3, 114.2, 76.0, 69.1, 68.1, 67.8, 55.5, 49.9. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{16}\text{NO}$  262.1226; Found 262.1229. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3394, 3276, 2931, 1600, 1499, 1245, 1029, 748, 691.



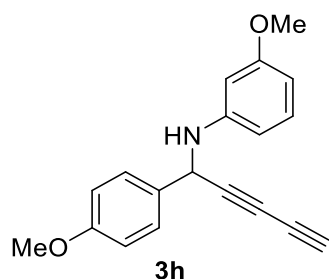
***N*-(1-(4-bromophenyl)penta-2,4-diyne-1-yl)aniline (3e):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 57 mg, 92% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 8.5$  Hz, 2H), 7.44 (d,  $J = 8.4$  Hz, 2H), 7.26–7.17 (m, 2H), 6.82 (t,  $J = 7.4$  Hz, 1H), 6.69 (d,  $J = 7.8$  Hz, 2H), 5.29 (s, 1H), 4.04 (s, 1H), 2.16 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 137.4, 132.2, 129.5, 129.0, 122.6, 119.4, 114.2, 75.1, 69.6, 68.5, 67.6, 49.4. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{13}\text{BrN}$  310.0226; Found 310.0229. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3287, 3005, 1601, 1500, 1485, 1275, 1261, 1011, 750, 631.



***N*-(1-(4-(methylthio)phenyl)penta-2,4-diyn-1-yl)aniline (3f)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), colorless oil, 40 mg, 72% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 5.29 (d, *J* = 7.1 Hz, 1H), 4.02 (d, *J* = 7.1 Hz, 1H), 2.49 (s, 3H), 2.15 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.0, 139.2, 135.1, 129.4, 127.8, 126.9, 119.2, 114.1, 75.7, 69.3, 68.2, 67.8, 50.0, 15.8. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>16</sub>NS 278.0998; Found 278.0997. IR (KBr thin film, cm<sup>-1</sup>): ν 3278, 2921, 1600, 1500, 1275, 11259, 1093, 764, 692.

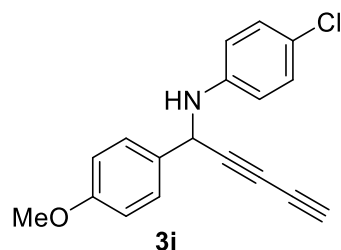


***N*-(1-(naphthalen-2-yl)penta-2,4-diyn-1-yl)aniline (3g)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), brown solid, mp 113.6–115.9 °C, 41 mg, 72% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 1H), 7.92–7.83 (m, 3H), 7.64 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.56–7.49 (m, 2H), 7.27–7.20 (m, 2H), 6.86–6.80 (m, 1H), 6.77 (d, *J* = 7.9 Hz, 2H), 5.51 (s, 1H), 4.16 (s, 1H), 2.18 (d, *J* = 0.5 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.1, 139.5, 135.7, 133.4, 133.3, 129.5, 129.0, 128.3, 127.9, 126.6, 126.3, 125.2, 119.2, 114.2, 75.7, 69.5, 68.3, 67.9, 50.6. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>16</sub>N 282.1277; Found 282.1279. IR (KBr thin film, cm<sup>-1</sup>): ν 3053, 1601, 1501, 1428, 1263, 895, 731, 702, 631.

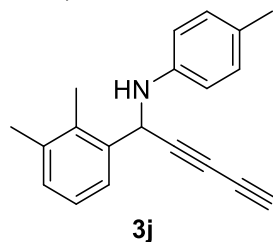


**3-methoxy-*N*-(1-(4-methoxyphenyl)penta-2,4-diyn-1-yl)aniline (3h)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), yellow oil, 51 mg, 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.35 (dd, *J* = 15.1, 8.1 Hz, 2H), 6.29 (s, 1H), 5.27 (s, 1H), 4.03 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.15 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.8, 159.8, 147.5, 130.4, 130.2, 128.6, 114.4, 106.9, 104.3, 100.2,

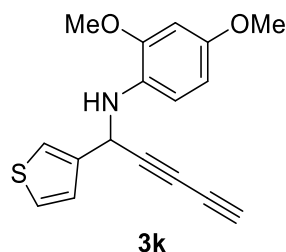
76.0 69.1, 68.1, 67.9, 55.5, 55.3, 49.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{19}H_{17}NO_2Na$  314.1151; Found 314.1150. IR (KBr thin film,  $cm^{-1}$ ):  $\nu$  3374, 3276, 1599, 1507, 1246, 1160, 1030, 736, 632.



**4-chloro-*N*-(1-(4-methoxyphenyl)penta-2,4-diyne-1-yl)aniline (3i)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 51 mg, 86% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.50–7.42 (m, 2H), 7.20–7.13 (m, 2H), 6.95–6.89 (m, 2H), 6.68–6.62 (m, 2H), 5.23 (s, 1H), 3.82 (s, 3H), 2.16 (d,  $J$  = 1.0 Hz, 1H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  159.9, 144.6, 130.0, 129.2, 128.6, 123.8, 115.3, 114.4, 75.6, 69.3, 68.3, 67.7, 55.5, 50.0. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{18}H_{15}ClNO$  296.0837; Found 296.0836. IR (KBr thin film,  $cm^{-1}$ ):  $\nu$  3399, 3281, 2932, 2836, 1597, 1493, 1246, 1174, 1029, 814, 631.

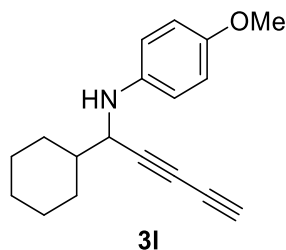


***N*-(1-(2,3-dimethylphenyl)penta-2,4-diyne-1-yl)-4-methylaniline (3j)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), white solid, mp 107.6–110.0 °C, 45 mg, 82% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.57 (dd,  $J$  = 6.4, 2.4 Hz, 1H), 7.21–7.13 (m, 2H), 7.06 (d,  $J$  = 8.2 Hz, 2H), 6.66 (d,  $J$  = 8.3 Hz, 2H), 5.43 (d,  $J$  = 3.9 Hz, 1H), 3.81 (s, 1H), 2.33 (s, 3H), 2.28 (s, 6H), 2.13 (s, 1H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  143.9, 137.8, 136.2, 134.9, 130.4, 129.9, 128.2, 126.1, 125.3, 113.9, 76.4, 69.0, 68.0, 67.7, 48.6, 20.8, 20.6, 14.9. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{20}N$  274.1590; Found 274.1593. IR (KBr thin film,  $cm^{-1}$ ):  $\nu$  3400, 3269, 2917, 1615, 1516, 1463, 1265, 748, 628.

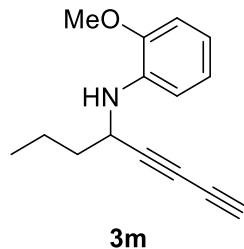


**2,4-dimethoxy-*N*-(1-(thiophen-3-yl)penta-2,4-diyne-1-yl)aniline (3k)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), brown oil, 48 mg, 81% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.47–7.43 (m, 1H), 7.34 (dd,  $J$  = 4.9, 3.1 Hz, 1H), 7.22 (d,  $J$  = 5.0 Hz, 1H), 6.72 (d,  $J$  = 8.5 Hz, 1H), 6.48 (d,  $J$  = 2.4

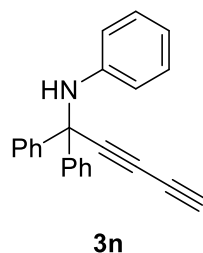
Hz, 1H), 6.43 (dd,  $J = 8.5, 2.5$  Hz, 1H), 5.34 (s, 1H), 4.32 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.12 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3, 148.9, 139.6, 129.9, 126.9, 126.7, 123.1, 112.9, 103.8, 99.4, 76.3, 68.1, 67.9, 67.8, 55.8, 55.7, 46.9. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{SNa}$  320.0716; Found 320.0718. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3273, 3003, 1600, 1514, 1463, 1276, 1207, 1158, 1032, 764, 629.



***N*-(1-cyclohexylpenta-2,4-diyne-1-yl)-4-methoxyaniline (3l)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate,  $v:v = 20:1$ ), colorless oil, 33 mg, 62% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.80 (d,  $J = 8.8$  Hz, 2H), 6.66 (d,  $J = 8.8$  Hz, 2H), 3.88 (d,  $J = 5.6$  Hz, 1H), 3.76 (s, 3H), 3.46 (s, 1H), 2.06 (s, 1H), 1.90 (d,  $J = 11.2$  Hz, 2H), 1.79 (d,  $J = 11.2$  Hz, 2H), 1.70 (d,  $J = 10.8$  Hz, 2H), 1.34–1.12 (m, 5H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 140.7, 115.9, 114.9, 77.5, 68.1, 67.9, 66.8, 55.8, 53.0, 42.6, 30.1, 28.9, 26.4, 26.1, 26.0. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{22}\text{NO}$  268.1696; Found 268.1700. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3299, 2926, 2852, 1742, 1509, 1275, 1036, 764, 624.

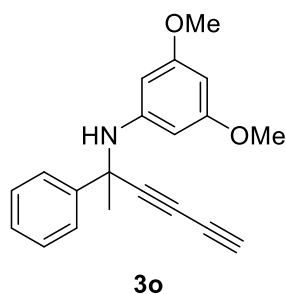


**2-methoxy-*N*-(octa-5,7-diyne-4-yl)aniline (3m)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate,  $v:v = 20:1$ ), yellow oil, 24 mg, 53% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (t,  $J = 7.5$  Hz, 1H), 6.83–6.69 (m, 3H), 4.32 (d,  $J = 8.2$  Hz, 1H), 4.15 (dd,  $J = 14.8, 7.2$  Hz, 1H), 3.85 (s, 3H), 2.05 (s, 1H), 1.84 (dd,  $J = 14.8, 7.5$  Hz, 2H), 1.67–1.53 (m, 2H), 0.99 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.2, 136.2, 121.3, 117.9, 111.4, 109.7, 78.2, 68.1, 66.9, 66.8, 55.6, 45.4, 37.7, 19.3, 13.9. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{18}\text{NO}$  228.1383; Found 228.1382. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3294, 2961, 1746, 1601, 1510, 1456, 1275, 1223, 1029, 764, 628.

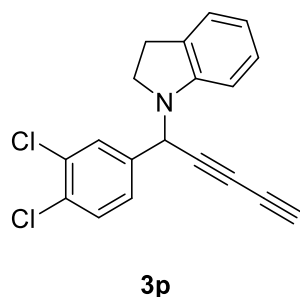




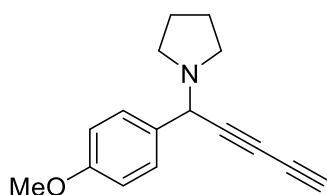
***N*-(1,1-diphenylpenta-2,4-diyn-1-yl)aniline (3n)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 36 mg, 58% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 7.4 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.30–7.23 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 4.42 (s, 1H), 2.16 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.7, 143.2, 128.9, 128.7, 128.1, 126.8, 119.0, 116.4, 78.1, 70.9, 68.4, 68.0, 63.6. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>18</sub>N 308.1434; Found 308.1432. IR (KBr thin film, cm<sup>-1</sup>): ν 3281, 2981, 1755, 1600, 1497, 1449, 1252, 1135, 1030, 753, 632.



**3,5-dimethoxy-*N*-(2-phenylhexa-3,5-diyn-2-yl)aniline (3o)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), brown oil, 44 mg, 72% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 7.6 Hz, 2H), 7.30–7.23 (m, 1H), 5.88 (t, *J* = 1.9 Hz, 1H), 5.71 (d, *J* = 2.0 Hz, 2H), 4.31 (s, 1H), 3.60 (s, 6H), 2.16 (s, 1H), 1.81 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 161.0, 146.6, 143.3, 128.9, 127.7, 125.4, 94.5, 91.5, 78.9, 68.8, 68.00, 67.97, 56.0, 55.2, 35.5. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>20</sub>NO<sub>2</sub> 306.1489; Found 306.1490. IR (KBr thin film, cm<sup>-1</sup>): ν 3388, 3278, 2932, 2838, 1595, 1447, 1201, 1149, 1063, 764, 628.

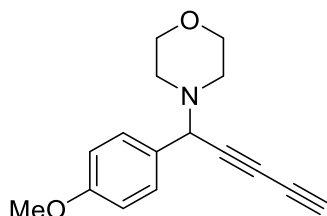


**1-(1-(3,4-dichlorophenyl)penta-2,4-diyn-1-yl)indoline (3p)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 53 mg, 81% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (s, 1H), 7.46 (s, 2H), 7.17–7.06 (m, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 5.58 (s, 1H), 3.38–3.28 (m, 1H), 3.21–3.11 (m, 1H), 3.06–2.87 (m, 2H), 2.13 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.9, 137.2, 132.9, 132.4, 130.8, 130.7, 129.7, 127.4, 127.1, 125.0, 119.8, 108.6, 72.3, 71.5, 67.9, 67.6, 52.8, 49.6, 28.3. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>14</sub>Cl<sub>2</sub>N 326.0498; Found 326.0503. IR (KBr thin film, cm<sup>-1</sup>): ν 3289, 2962, 2852, 1746, 1484, 1252, 1142, 748, 633.



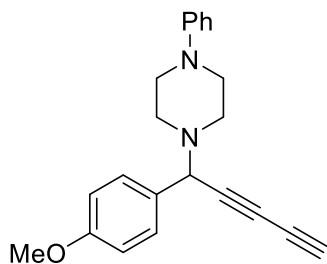
**3q**

**1-(1-(4-methoxyphenyl)penta-2,4-diyne-1-yl)pyrrolidine (3q):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 31 mg, 65% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 7.7$  Hz, 2H), 6.87 (d,  $J = 7.3$  Hz, 2H), 4.69 (s, 1H), 3.80 (s, 3H), 2.60 (s, 4H), 2.14 (s, 1H), 1.82–1.72 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 130.6, 129.4, 113.8, 75.3, 70.7, 68.1, 67.0, 58.3, 55.4, 50.3, 23.5. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}$  240.1383; Found 240.1385. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3283, 2961, 2835, 1610, 1509, 1246, 1173, 1103, 764, 631.



**3r**

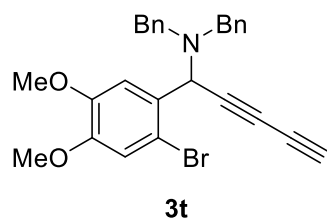
**1-(1-(4-methoxyphenyl)penta-2,4-diyne-1-yl)morpholine (3r):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), solid, mp 93.4–96.3  $^\circ\text{C}$ , 46 mg, 90% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.6$  Hz, 2H), 6.88 (d,  $J = 8.6$  Hz, 2H), 4.57 (s, 1H), 3.81 (s, 3H), 3.76–3.61 (m, 4H), 2.61–2.48 (m, 4H), 2.18 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 129.7, 128.7, 113.8, 73.8, 72.1, 67.8, 67.5, 67.2, 61.4, 55.4, 49.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}_2$  256.1332; Found 256.1335. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3287, 2960, 2834, 1611, 1509, 1453, 1249, 1114, 1032, 764, 631.



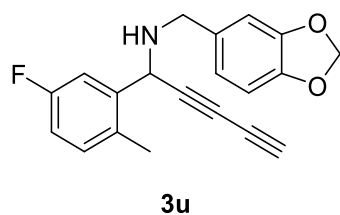
**3s**

**1-(1-(4-methoxyphenyl)penta-2,4-diyne-1-yl)-4-phenylpiperazine (3s):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 47 mg, 71% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 8.6$  Hz, 2H), 7.26–7.18 (m, 2H), 6.92–6.85 (m, 4H), 6.82 (t,  $J = 7.3$  Hz, 1H), 4.65 (s, 1H), 3.78 (s, 3H), 3.22–3.08 (m, 4H), 2.77–2.60 (m, 4H), 2.14 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 151.4, 129.7, 129.2, 128.9, 119.9, 116.3, 113.8, 73.8, 72.2, 67.9, 67.5, 61.0, 55.4, 49.5. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for

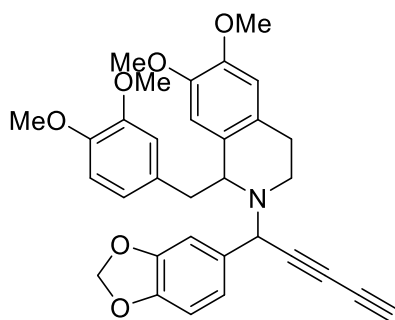
C<sub>22</sub>H<sub>23</sub>N<sub>2</sub>O 331.1805; Found 331.1808. IR (KBr thin film, cm<sup>-1</sup>): ν 3271, 2951, 2828, 1598, 1507, 1450, 1232, 1171, 757, 691.



***N,N*-dibenzyl-1-(2-bromo-4,5-dimethoxyphenyl)penta-2,4-diyne-1-amine (3t)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), brown oil, 68 mg, 72% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 7.2 Hz, 4H), 7.27 (t, *J* = 7.1 Hz, 4H), 7.24–7.17 (m, 3H), 6.96 (s, 1H), 4.94 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.77 (d, *J* = 13.3 Hz, 2H), 3.48 (d, *J* = 13.3 Hz, 2H), 2.26 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.2, 147.7, 138.5, 129.6, 128.6, 128.1, 127.3, 116.3, 115.0, 114.3, 73.8, 72.7, 67.9, 67.7, 57.0, 56.26, 56.25, 55.1. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>25</sub>BrNO<sub>2</sub> 474.1063; Found 474.1072. IR (KBr thin film, cm<sup>-1</sup>): ν 3281, 3027, 2933, 2837, 1748, 1601, 1504, 1453, 1376, 1259, 1207, 1029, 763, 633.

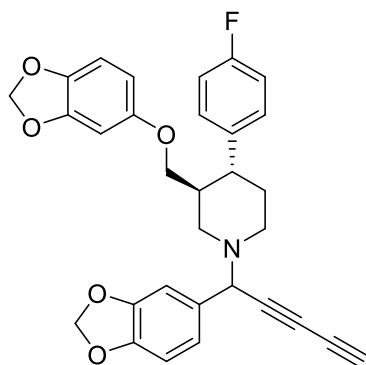


***N*-(benzo[*d*][1,3]dioxol-5-ylmethyl)-1-(5-fluoro-2-methylphenyl)penta-2,4-diyne-1-amine (3u)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 32 mg, 50% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (dd, *J* = 9.8, 2.6 Hz, 1H), 7.10 (dd, *J* = 8.2, 6.0 Hz, 1H), 6.93–6.85 (m, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 2H), 4.64 (s, 1H), 3.90 (d, *J* = 12.7 Hz, 1H), 3.81 (d, *J* = 12.7 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 1H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 161.4 (C-F, <sup>1</sup>*J*<sub>C-F</sub> = 243.7 Hz), 147.8, 146.9, 138.9 (C-F, <sup>3</sup>*J*<sub>C-F</sub> = 6.4 Hz), 133.0, 132.1 (C-F, <sup>3</sup>*J*<sub>C-F</sub> = 7.5 Hz), 131.8 (C-F, <sup>4</sup>*J*<sub>C-F</sub> = 2.5 Hz), 121.9, 114.8 (C-F, <sup>2</sup>*J*<sub>C-F</sub> = 20.8 Hz), 114.3 (C-F, <sup>2</sup>*J*<sub>C-F</sub> = 22.8 Hz), 109.2, 108.2, 101.1, 76.2, 69.9, 67.9, 67.8, 51.4, 50.4, 18.3; <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -116.5. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>FNO<sub>2</sub> 322.1238; Found 322.1241. IR (KBr thin film, cm<sup>-1</sup>): ν 3289, 2896, 1746, 1611, 1489, 1443, 1248, 766, 631.



**3v**  
1:1 dr

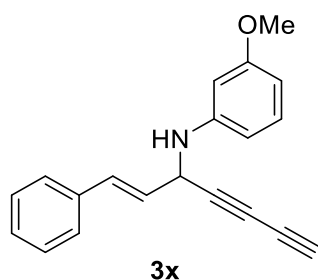
**2-(1-(benzo[*d*][1,3]dioxol-5-yl)penta-2,4-diyn-1-yl)-1-(3,4-dimethoxybenzyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (3v):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow oil, 89 mg, 85% yield, 1:1 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 1:1 dr)  $\delta$  6.95–6.82 (m, 4H), 6.77–6.68 (m, 4H), 6.60–6.46 (m, 6H), 6.30 (s, 1H), 6.10 (s, 1H), 5.96 (s, 2H), 5.95 (s, 2H), 4.81 (s, 1H), 4.64 (s, 1H), 4.18 (t,  $J$  = 6.8 Hz, 1H), 4.10 (t,  $J$  = 5.5 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 9H), 3.79 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.63 (s, 3H), 3.30–3.20 (m, 1H), 3.14–2.97 (m, 2H), 2.96–2.78 (m, 5H), 2.77–2.59 (m, 2H), 2.53–2.38 (m, 2H), 2.14 (s, 1H), 2.09 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.6, 148.5, 148.0, 147.9, 147.5, 147.4, 147.3, 146.8, 146.5, 132.6, 132.4, 132.3, 131.7, 129.6, 129.3, 127.8, 126.5, 122.2, 122.0, 121.62, 121.57, 112.7, 112.6, 111.2, 111.1, 110.9, 110.7, 108.9, 108.6, 107.8, 107.7, 101.32, 101.27, 76.6, 75.3, 71.1, 70.5, 67.9, 67.7, 67.6, 61.0, 60.6, 58.3, 57.4, 56.0, 55.9, 55.83, 55.76, 55.7, 42.5, 42.4, 42.0, 41.9, 27.3, 25.5. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{32}\text{H}_{32}\text{NO}_6$  526.2224; Found 526.2226. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3277, 2934, 2833, 1608, 1512, 1262, 1029, 733, 629.



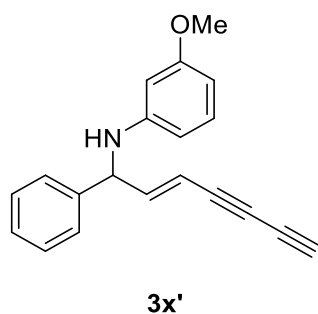
**3w**  
1.2:1

**(3*S*,4*R*)-1-(1-(benzo[*d*][1,3]dioxol-5-yl)penta-2,4-diyn-1-yl)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine (3w):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow oil, 72 mg, 70% yield, 1.2:1 dr.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 1:0.45 dr)  $\delta$  7.20–7.12 (m, 3H), 7.11–7.02 (m, 3H), 7.02–6.92 (m, 3H), 6.79 (d,  $J$  = 8.0 Hz, 1.43H), 6.64 (d,  $J$  = 8.5 Hz, 1H), 6.59 (d,  $J$  = 8.5 Hz, 0.44H), 6.36 (d,  $J$  = 2.5 Hz, 1H), 6.27 (d,  $J$  = 2.5 Hz, 0.44H), 6.15 (dd,  $J$  = 8.5, 2.5 Hz, 1H), 6.06 (dd,  $J$  = 8.5, 2.5 Hz, 0.44H), 6.00–5.96 (m, 3H), 5.88 (d,  $J$  = 7.6 Hz, 3H), 4.71 (s, 1H), 4.66 (s, 0.43H), 3.77–3.73

(m, 0.44H), 3.62–3.55 (m, 1H), 3.52–3.45 (m, 1.44H), 3.43–3.36 (m, 0.44H), 3.29 (dd,  $J = 11.1, 1.9$  Hz, 1H), 3.03–2.89 (m, 0.84H), 2.68 (d,  $J = 11.0$  Hz, 1H), 2.63–2.40 (m, 3H), 2.37–2.15 (m, 4H), 2.11–2.02 (m, 0.40H), 1.91–1.83 (m, 1H), 1.78–1.69 (m, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  161.63 (C-F,  $^1J_{\text{C-F}} = 244.3$  Hz), 161.59 (C-F,  $^1J_{\text{C-F}} = 243.9$  Hz), 154.42, 154.35, 148.3, 148.2, 147.9, 147.4, 141.7, 141.6, 139.7, 131.3, 131.0, 128.91, 128.86, 121.8, 121.7, 115.55 (C-F,  $^2J_{\text{C-F}} = 21.1$  Hz), 115.49 (C-F,  $^2J_{\text{C-F}} = 21.1$  Hz), 108.82, 108.78, 108.0, 107.91, 107.89, 105.8, 105.6, 101.3, 101.21, 101.16, 98.2, 98.1, 74.0, 73.8, 72.2, 72.0, 69.74, 69.65, 68.1, 67.9, 67.50, 67.46, 61.7, 61.6, 56.8, 53.0, 50.9, 47.1, 44.3, 44.0, 42.6, 42.2, 34.7, 34.4, 25.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.5. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{31}\text{H}_{27}\text{FNO}_5$  512.1868; Found 512.1871. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3282, 2896, 1605, 1485, 1181, 1036, 932, 737, 635.

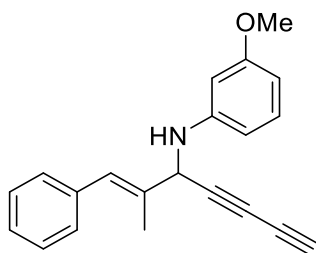


**(E)-3-methoxy-N-(1-phenylhepta-1-en-4,6-diyn-3-yl)aniline (3x)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 23 mg, 40% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 7.5$  Hz, 2H), 7.34 (t,  $J = 7.4$  Hz, 2H), 7.29 (d,  $J = 7.2$  Hz, 1H), 7.14 (t,  $J = 8.1$  Hz, 1H), 6.90 (d,  $J = 15.8$  Hz, 1H), 6.42–6.33 (m, 2H), 6.33–6.23 (m, 2H), 4.96 (t,  $J = 5.4$  Hz, 1H), 3.92 (d,  $J = 7.0$  Hz, 1H), 3.79 (s, 3H), 2.16 (s, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 147.3, 136.0, 133.1, 130.3, 128.8, 128.4, 126.9, 125.6, 107.2, 104.4, 100.5, 75.0, 69.2, 68.1, 67.8, 55.3, 48.0. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{18}\text{NO}$  288.1383; Found 288.1380. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3272, 3035, 1721, 1611, 1495, 1457, 1078, 721, 646.



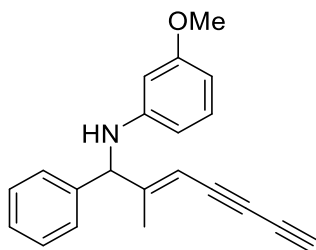
**(E)-3-methoxy-N-(1-phenylhepta-2-en-4,6-diyn-1-yl)aniline (3x')**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 13 mg, 21% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42–7.29 (m, 5H), 7.07 (t,  $J = 8.1$  Hz, 1H), 6.54 (dd,  $J = 15.9, 5.3$  Hz, 1H), 6.31 (dd,  $J = 8.1, 1.7$  Hz, 1H), 6.20 (d,  $J = 8.0$  Hz, 1H), 6.14 (s, 1H), 5.80 (d,  $J = 15.9$  Hz, 1H), 5.02–4.92 (m, 1H), 3.98 (d,  $J = 4.3$  Hz, 1H), 3.74 (s, 3H), 2.41 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 148.13, 148.07, 140.3, 130.1, 129.2, 128.3, 127.6, 109.6, 106.7, 103.3, 99.8, 74.8, 73.8, 71.4,

68.2, 60.4, 55.2. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{20}H_{17}NONa$  310.1202; Found 310.1198. IR (KBr thin film,  $cm^{-1}$ ):  $\nu$  3005, 1745, 1275, 1258, 1153, 764, 711.



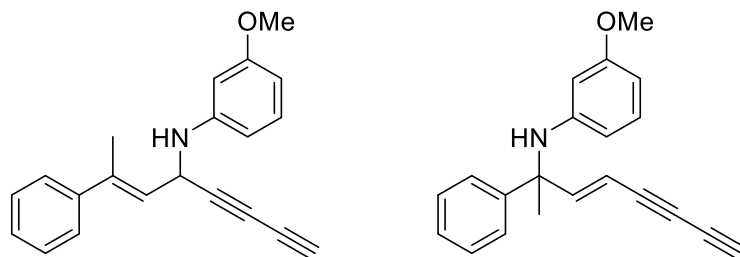
**3y**

**(E)-3-methoxy-N-(2-methyl-1-phenylhepta-1-en-4,6-diyn-3-yl)aniline (3y):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 29 mg, 48% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.38–7.31 (m, 2H), 7.31–7.20 (m, 3H), 7.12 (t,  $J = 8.1$  Hz, 1H), 6.82 (s, 1H), 6.39–6.30 (m, 2H), 6.30–6.24 (m, 1H), 4.76 (d,  $J = 7.3$  Hz, 1H), 3.99 (d,  $J = 7.3$  Hz, 1H), 3.77 (s, 3H), 2.16 (s, 1H), 2.00 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  160.8, 147.7, 137.1, 134.6, 130.2, 129.1, 128.6, 128.3, 127.1, 107.0, 104.2, 100.2, 75.3, 69.1, 68.1, 67.8, 55.3, 54.2, 15.5. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{21}H_{20}NO$  302.1539; Found 302.1540. IR (KBr thin film,  $cm^{-1}$ ):  $\nu$  3279, 3004, 1599, 1493, 1275, 1258, 1162, 764, 633.



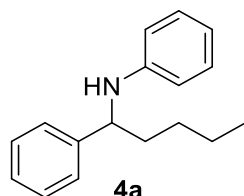
**3y'**

**(E)-3-methoxy-N-(2-methyl-1-phenylhepta-2-en-4,6-diyn-1-yl)aniline (3y'):** purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 19 mg, 32% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.41–7.28 (m, 5H), 7.08 (t,  $J = 8.1$  Hz, 1H), 6.31 (dd,  $J = 8.2, 2.3$  Hz, 1H), 6.14 (dd,  $J = 8.2, 2.1$  Hz, 1H), 6.07 (t,  $J = 2.1$  Hz, 1H), 5.92–5.87 (m, 1H), 4.74 (d,  $J = 3.5$  Hz, 1H), 3.98 (d,  $J = 3.4$  Hz, 1H), 3.75 (d,  $J = 0.8$  Hz, 3H), 2.47 (s, 1H), 1.90 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  160.8, 156.2, 148.3, 148.1, 130.1, 129.2, 128.4, 127.8, 106.6, 104.9, 103.2, 99.7, 77.9, 73.7, 71.6, 68.5, 65.2, 55.2, 18.0. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{21}H_{20}NO$  302.1539; Found 302.1537. IR (KBr thin film,  $cm^{-1}$ ):  $\nu$  3289, 3004, 1598, 1506, 1275, 1209, 1162, 750, 626.

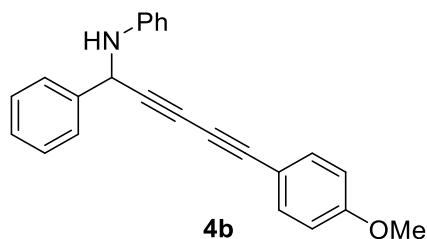


**3z and 3z'**  
2:1

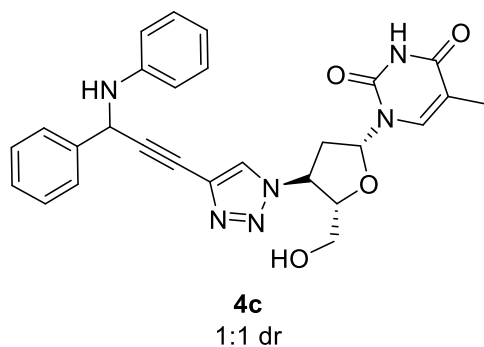
**(E)-3-methoxy-N-(2-phenylocta-2-en-5,7-diyn-4-yl)aniline and (E)-3-methoxy-N-(2-phenylocta-3-en-5,7-diyn-2-yl)aniline (3z and 3z')**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 30 mg, 50% yield and 15 mg, 25% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47–7.38 (m, 3H), 7.38–7.28 (m, 4H), 7.28–7.22 (m, 1H), 7.13 (t,  $J$  = 8.1 Hz, 1H), 6.98–6.88 (m, 1H), 6.41–6.33 (m, 2H), 6.33–6.28 (m, 1H), 6.22 (dd,  $J$  = 8.1, 2.0 Hz, 0.5H), 6.00 (dd,  $J$  = 8.1, 1.9 Hz, 0.5H), 5.92–5.72 (m, 2H), 5.00 (d,  $J$  = 7.8 Hz, 1H), 4.17 (s, 0.5H), 3.93 (s, 1H), 3.79 (s, 3H), 3.60 (s, 1.5H), 2.41 (s, 0.5H), 2.17 (s, 3H), 2.12 (s, 1H), 1.66 (s, 1.5H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.8, 160.2, 151.7, 147.4, 146.3, 144.1, 142.1, 140.0, 130.2, 129.6, 128.9, 128.5, 127.9, 127.4, 126.2, 126.1, 124.6, 108.8, 108.3, 107.1, 104.2, 103.3, 101.8, 100.3, 76.1, 74.6, 74.1, 71.3, 68.2, 67.9, 67.8, 67.4, 60.6, 55.3, 55.0, 44.9, 30.6, 16.8. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{20}\text{NO}$  302.1539; Found 302.1545. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3283, 2988, 1682, 1275, 1262, 1153, 764, 701.



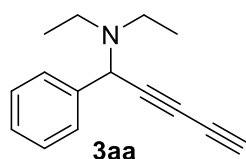
**N-(1-phenylpentyl)aniline (4a)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), colorless oil, 19 mg, 80% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.28 (m, 4H), 7.25–7.19 (m, 1H), 7.08 (dd,  $J$  = 8.4, 7.4 Hz, 2H), 6.63 (t,  $J$  = 7.3 Hz, 1H), 6.51 (d,  $J$  = 7.7 Hz, 2H), 4.29 (t,  $J$  = 6.8 Hz, 1H), 4.07 (s, 1H), 1.87–1.68 (m, 2H), 1.46–1.20 (m, 4H), 0.89 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.6, 144.5, 129.2, 128.7, 127.0, 126.5, 117.2, 113.3, 58.3, 38.9, 28.6, 22.7, 14.1. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{22}\text{N}$  240.1747; Found 240.1749. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  2930, 1601, 1503, 1317, 1179, 1077, 764, 711.



***N*-(5-(4-methoxyphenyl)-1-phenylpenta-2,4-diyne-1-yl)aniline (4b)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 25 mg, 74% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.46–7.38 (m, 4H), 7.38–7.32 (m, 1H), 7.28–7.18 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.80–6.72 (m, 2H), 5.42 (d, *J* = 7.2 Hz, 1H), 4.10 (d, *J* = 7.1 Hz, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.5, 146.3, 138.9, 134.3, 129.4, 129.0, 128.5, 127.5, 119.0, 114.2, 114.1, 113.5, 81.3, 78.4, 72.6, 70.0, 55.5, 50.8. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>19</sub>NONa 360.1359; Found 360.1355. IR (KBr thin film, cm<sup>-1</sup>): ν 2207, 1601, 1508, 1289, 1250, 1173, 1027, 831, 712.



**1-((2*R*,4*R*,5*S*)-5-(hydroxymethyl)-4-(4-(3-phenyl-3-(phenylamino)prop-1-yn-1-yl)-1*H*-1,2,3-triazol-1-yl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (4c)**: purified by flash chromatography on silica gel (ethyl acetate), yellow oil, 41 mg, 83% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.62 (s, 2H), 7.70 (s, 2H), 7.60 (d, *J* = 7.2 Hz, 4H), 7.44–7.28 (m, 8H), 7.16 (t, *J* = 7.5 Hz, 4H), 6.79–6.68 (m, 6H), 6.14 (t, *J* = 5.9 Hz, 2H), 5.48 (s, 2H), 5.42–5.32 (m, 2H), 4.30 (s, 4H), 3.92 (d, *J* = 10.8 Hz, 4H), 3.70 (d, *J* = 10.6 Hz, 2H), 2.86 (s, 4H), 1.83 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.1, 150.7, 146.4, 138.9, 138.0, 130.8, 129.4, 129.0, 128.9, 128.5, 127.9, 127.4, 126.6, 118.8, 114.1, 111.3, 92.8, 88.5, 85.2, 74.0, 61.5, 59.7, 50.5, 37.5, 27.9, 12.5. HRMS (ESI-Quadrupole-Orbitrap) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>26</sub>N<sub>6</sub>O<sub>4</sub>Na 521.1908; Found 521.1907. IR (KBr thin film, cm<sup>-1</sup>): ν 3005, 1688, 1472, 1275, 1259, 764, 750.

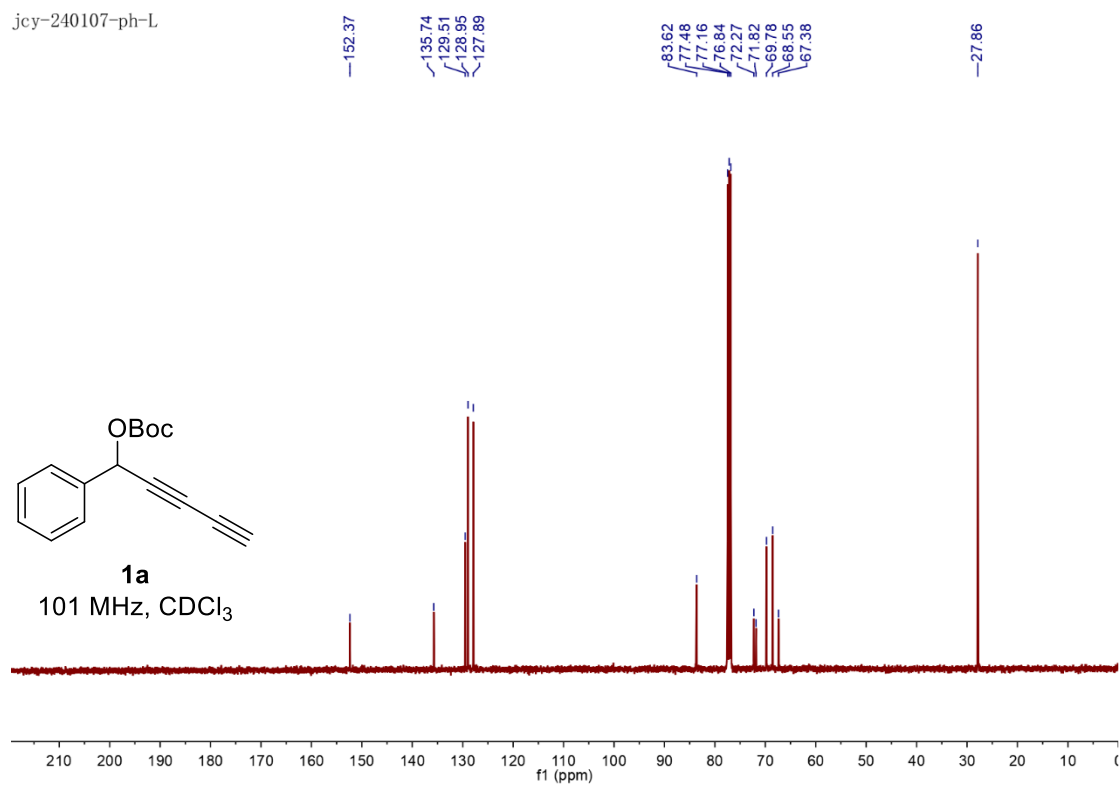
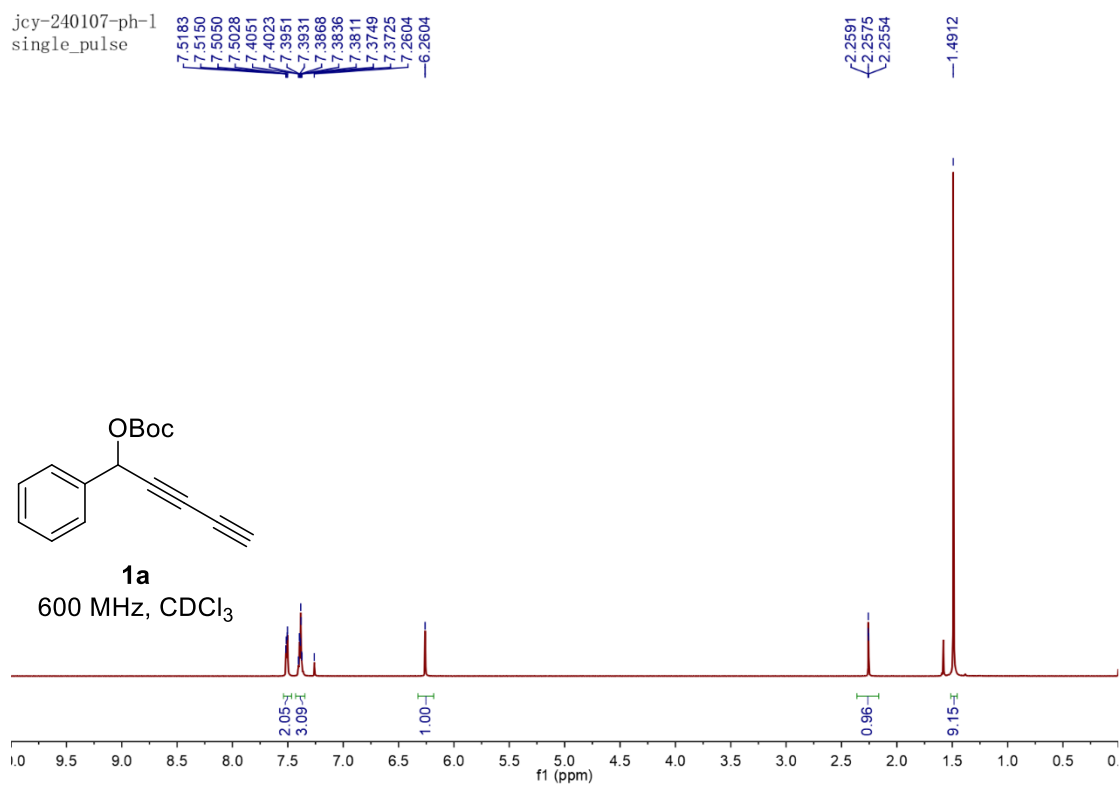


***N,N*-diethyl-1-phenylpenta-2,4-diyne-1-amine (3aa)**: purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 30:1), colorless oil,

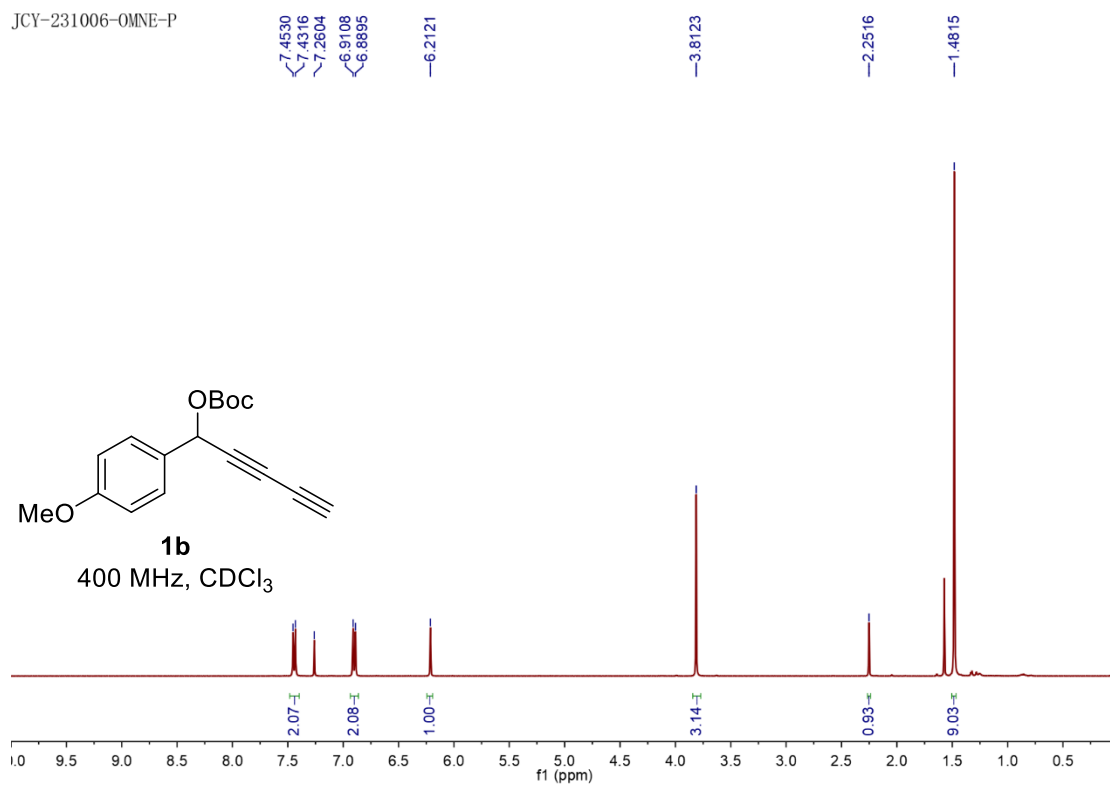


26.6 mg, 63% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 7.4$  Hz, 2H), 7.40–7.31 (m, 2H), 7.31–7.24 (m, 1H), 4.89 (s, 1H), 2.68–2.54 (m, 2H), 2.52–2.40 (m, 2H), 2.14 (s, 1H), 1.04 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 128.3, 128.2, 127.7, 74.9, 71.3, 68.1, 66.7, 57.1, 44.7, 13.7. HRMS (ESI-Quadrupole-Orbitrap)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{18}\text{N}$  212.1434; Found 212.1433. IR (KBr thin film,  $\text{cm}^{-1}$ ):  $\nu$  3005, 2120, 1469, 1276, 1259, 750, 721, 646.

## VII. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of substrates and products

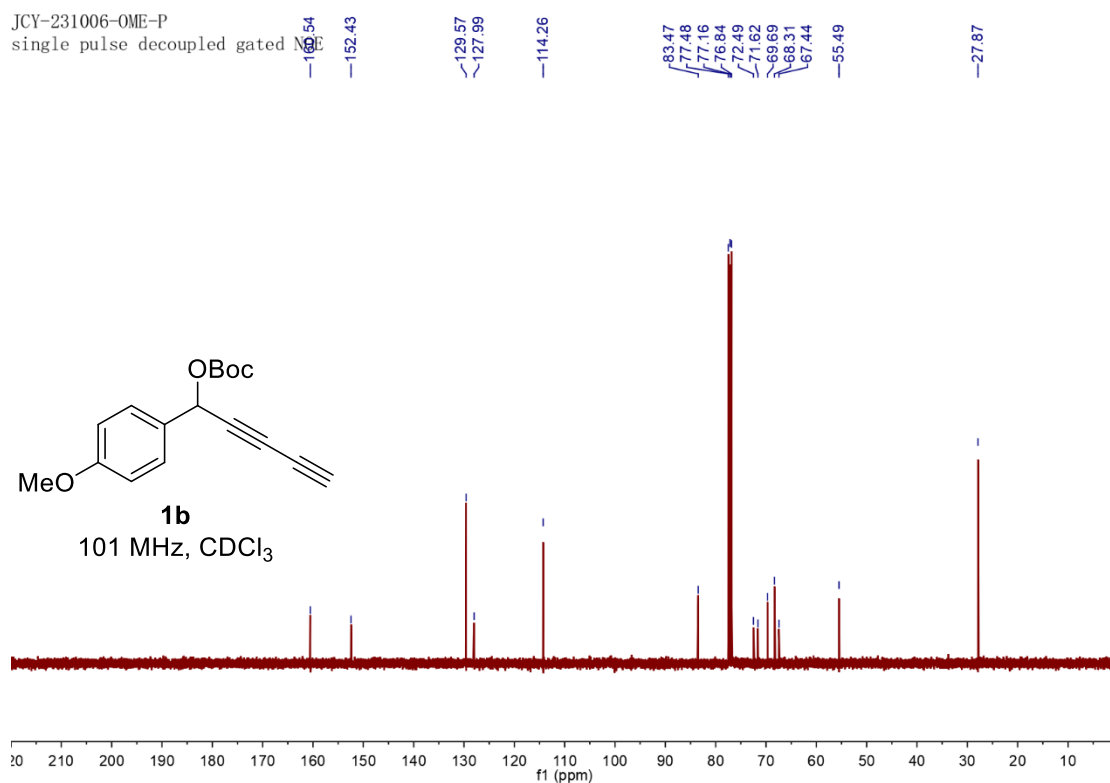


JCY-231006-OMNE-P

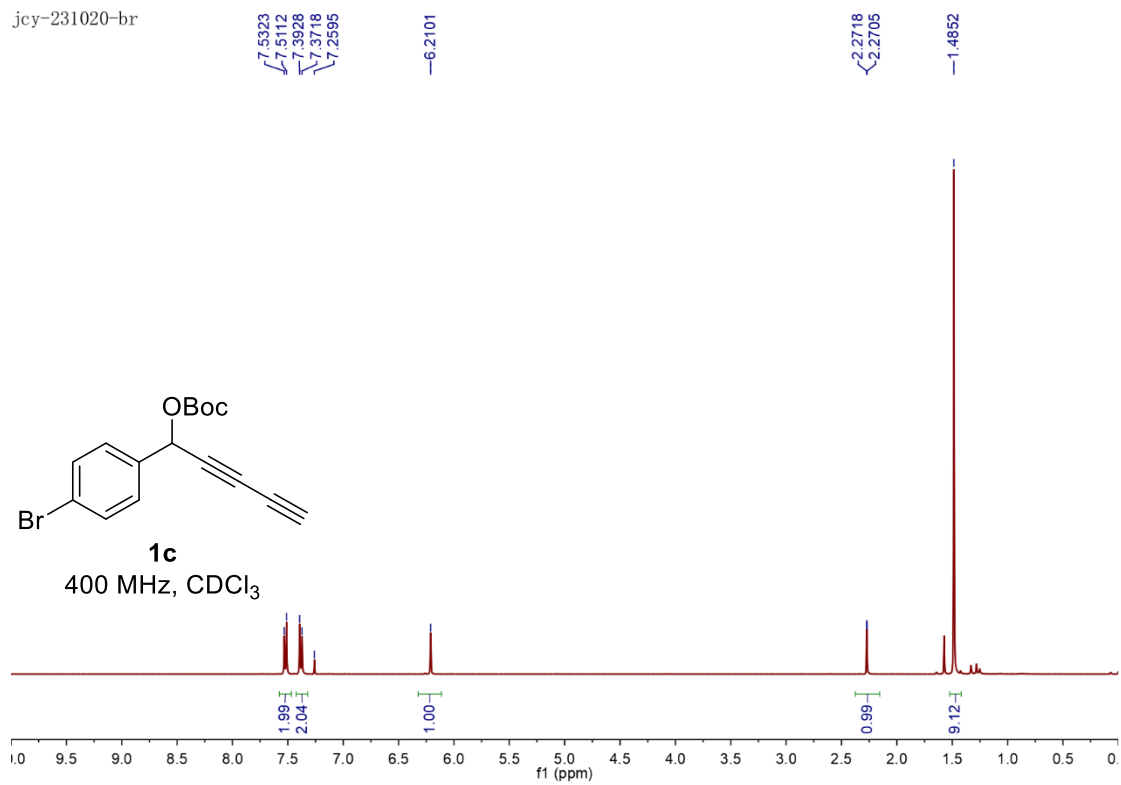


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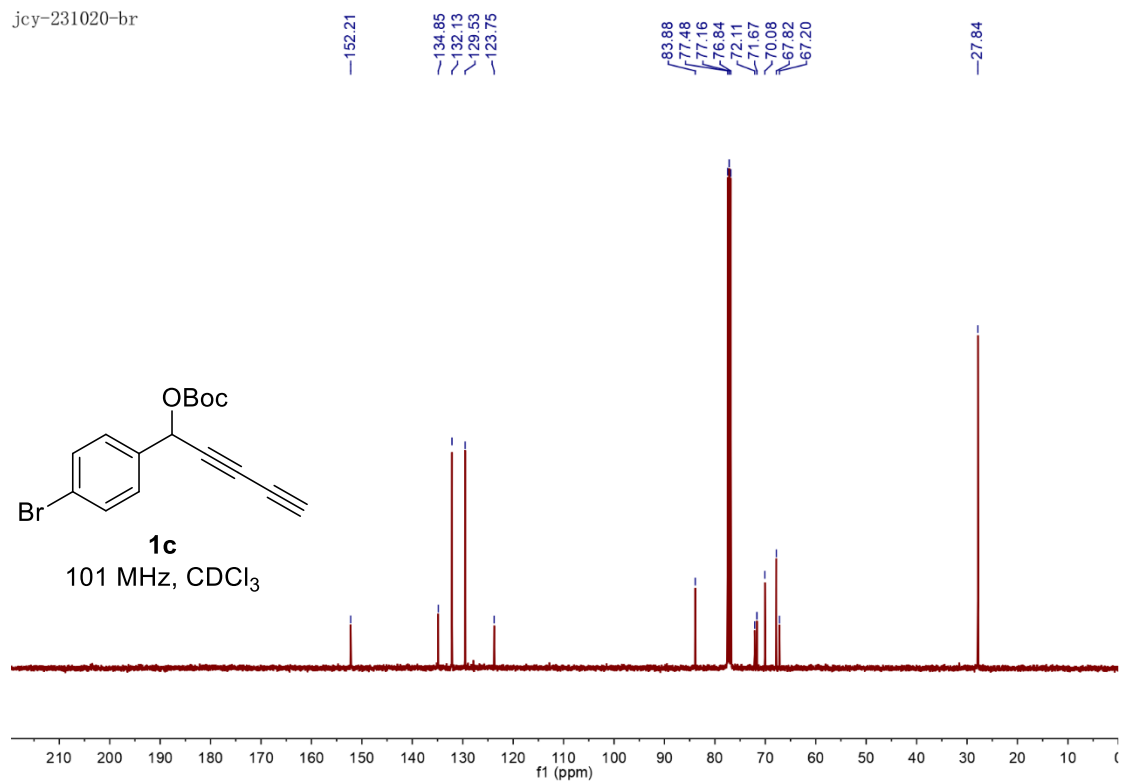
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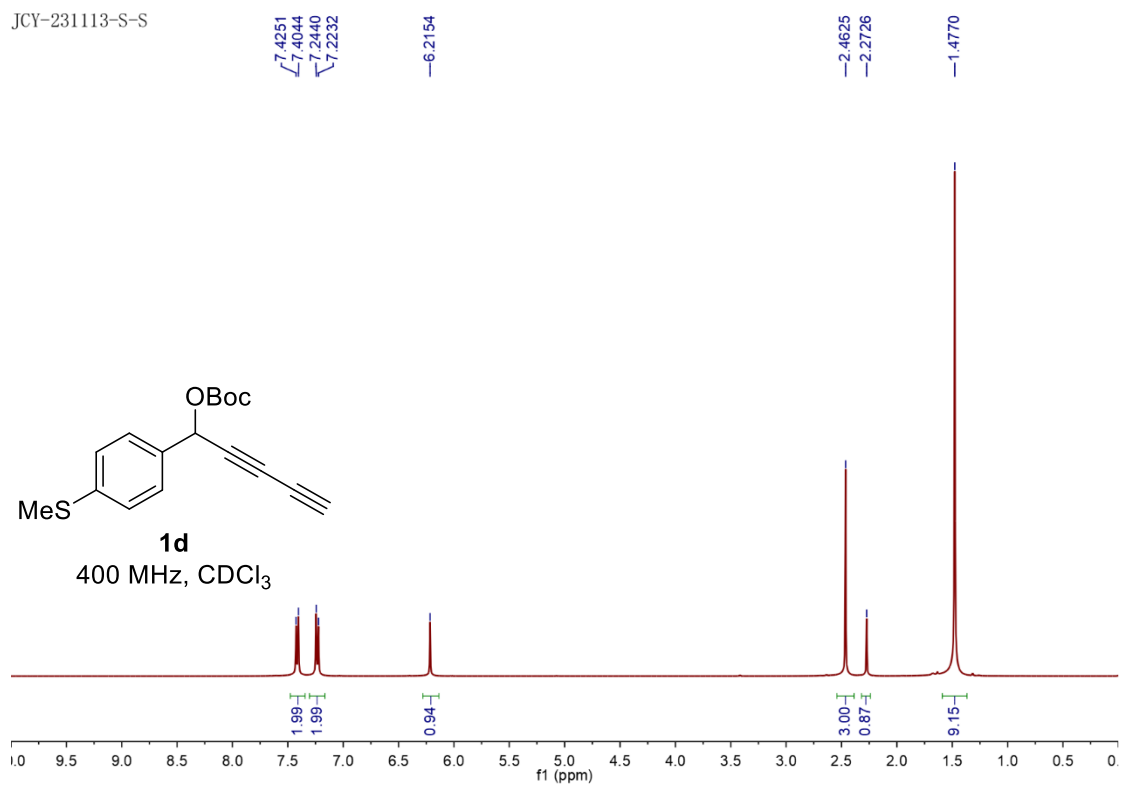
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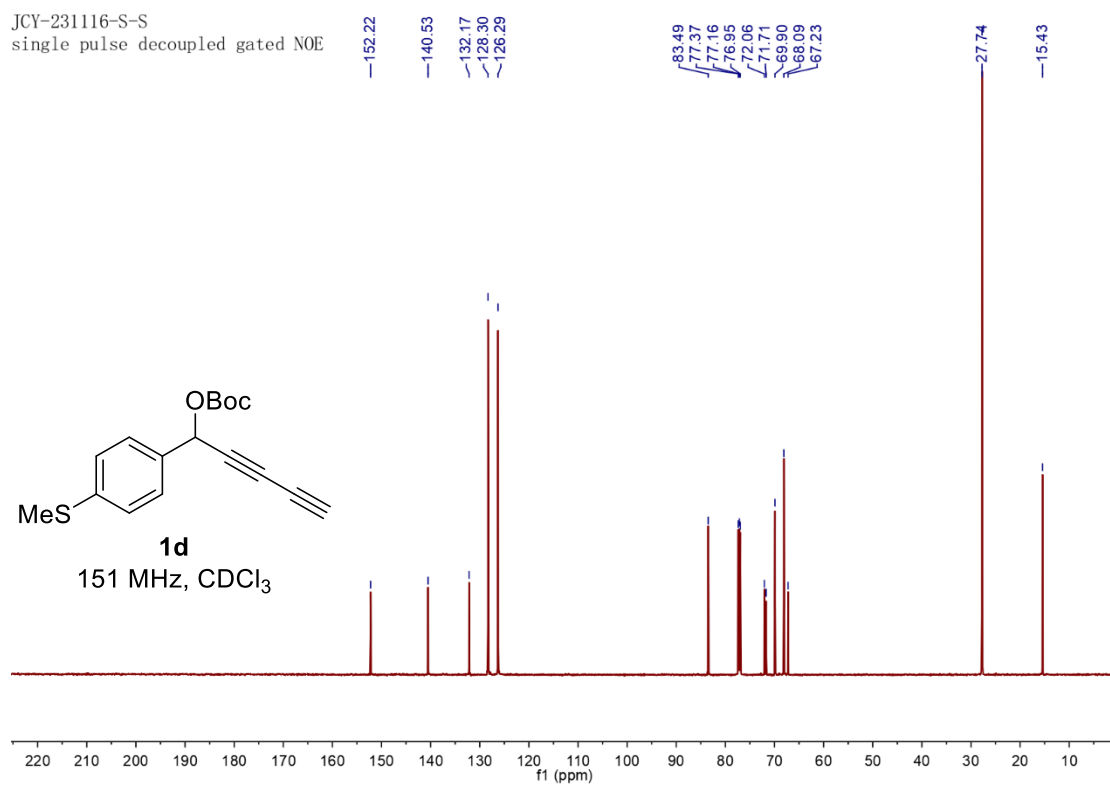
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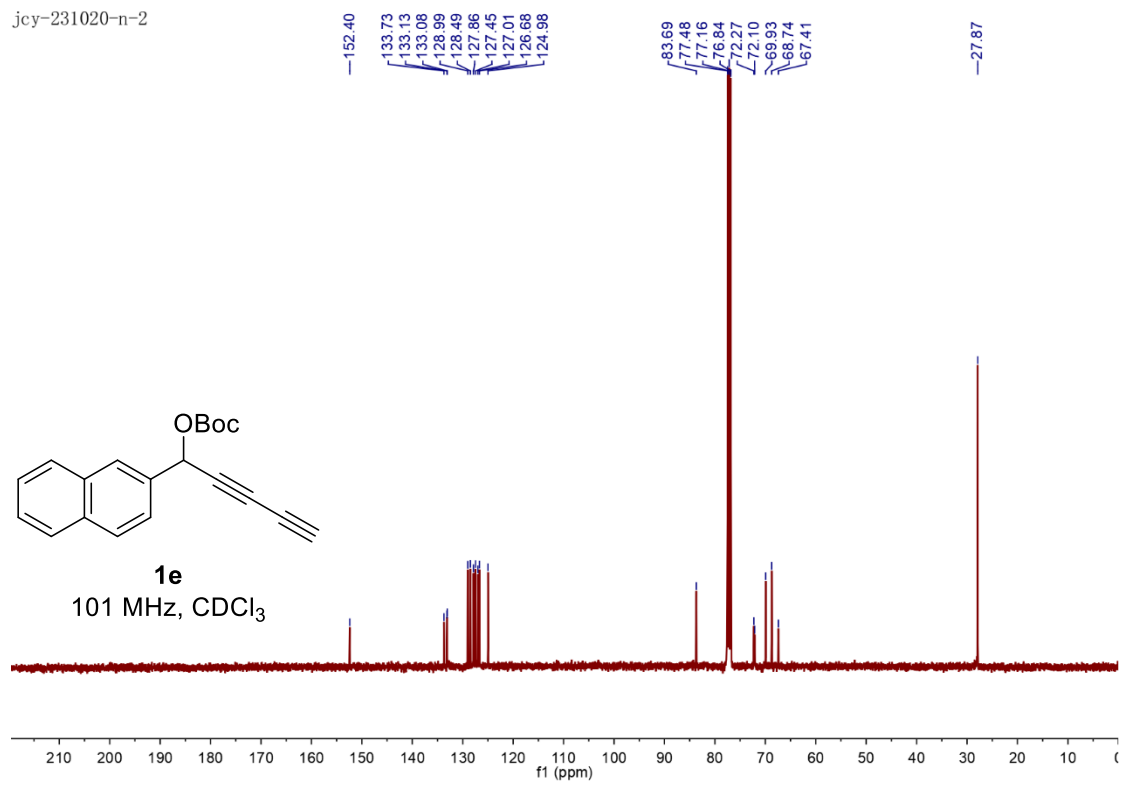
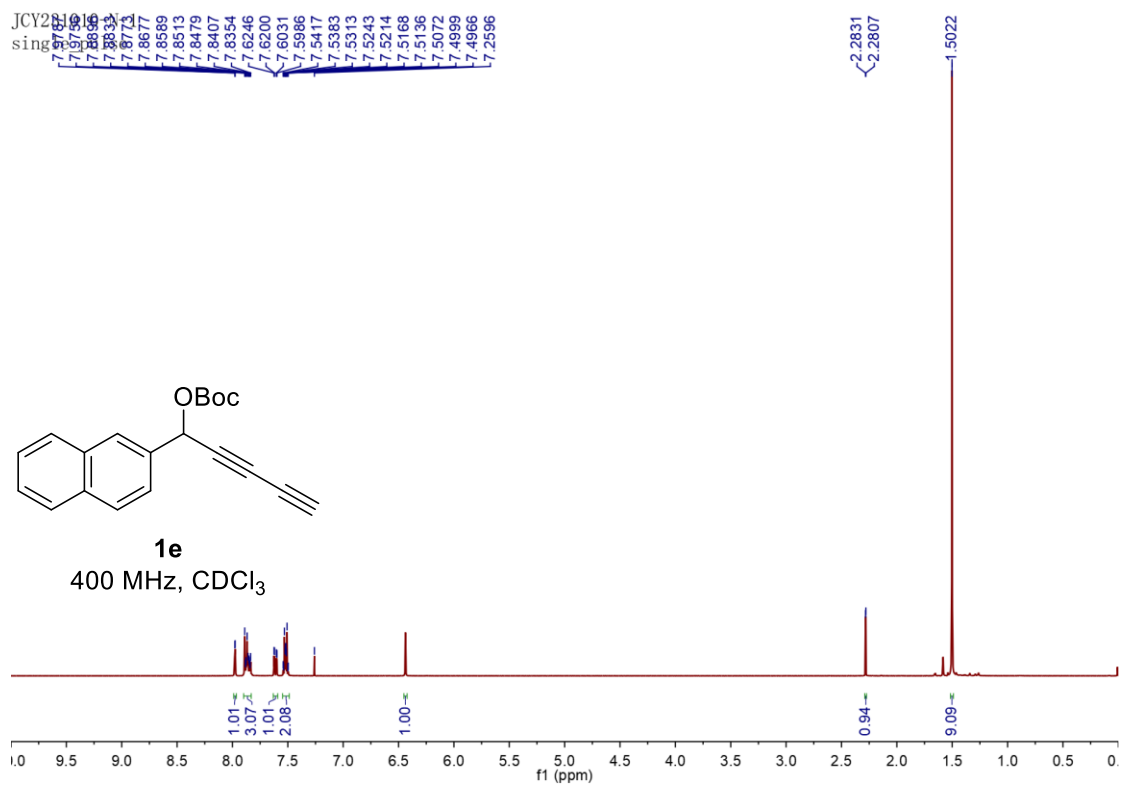


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JCY-231116-S-S  
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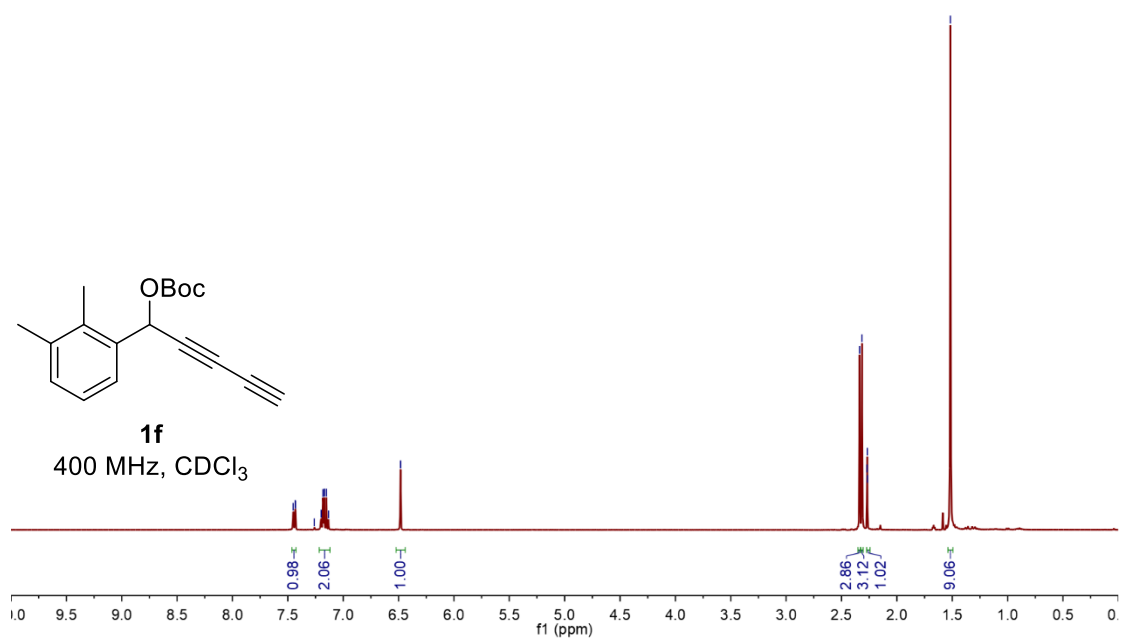




cqq-231114-2  
single\_pulse

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7.4335  
7.4305  
7.2602  
7.1984  
7.1832  
7.1699  
7.1513  
7.1326  
6.4819

2.3360  
2.3153  
2.2695  
2.2673  
2.2660  
1.5164

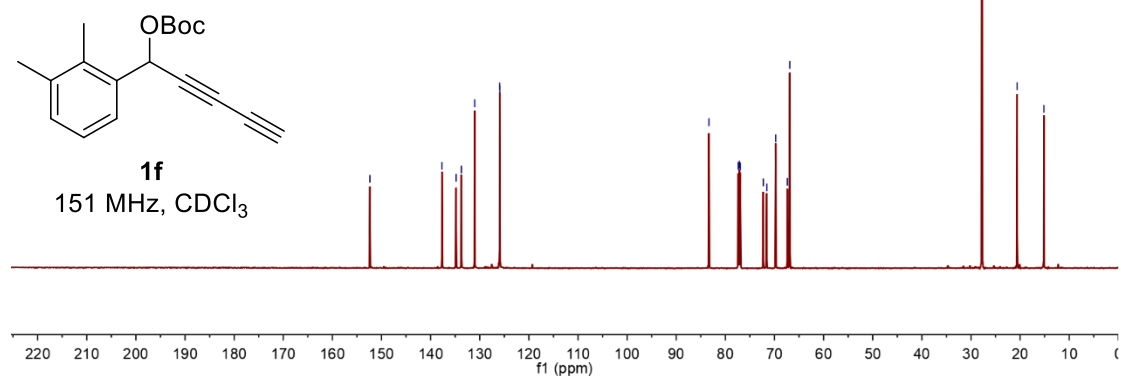


CQQ-231114-2  
single\_pulse decoupled gated NOE

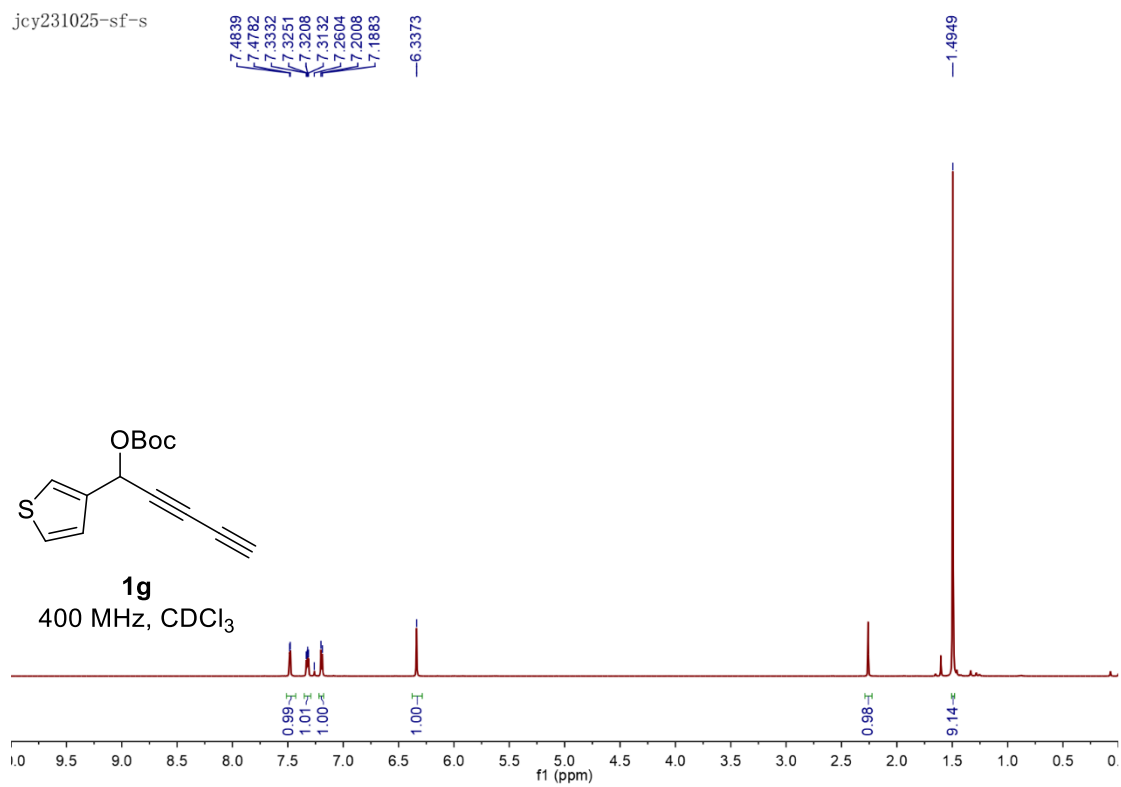
152.36  
137.69  
134.83  
133.74  
131.04  
125.95  
125.90

83.35  
77.37  
77.16  
76.95  
72.27  
71.58  
69.75  
67.39  
66.89

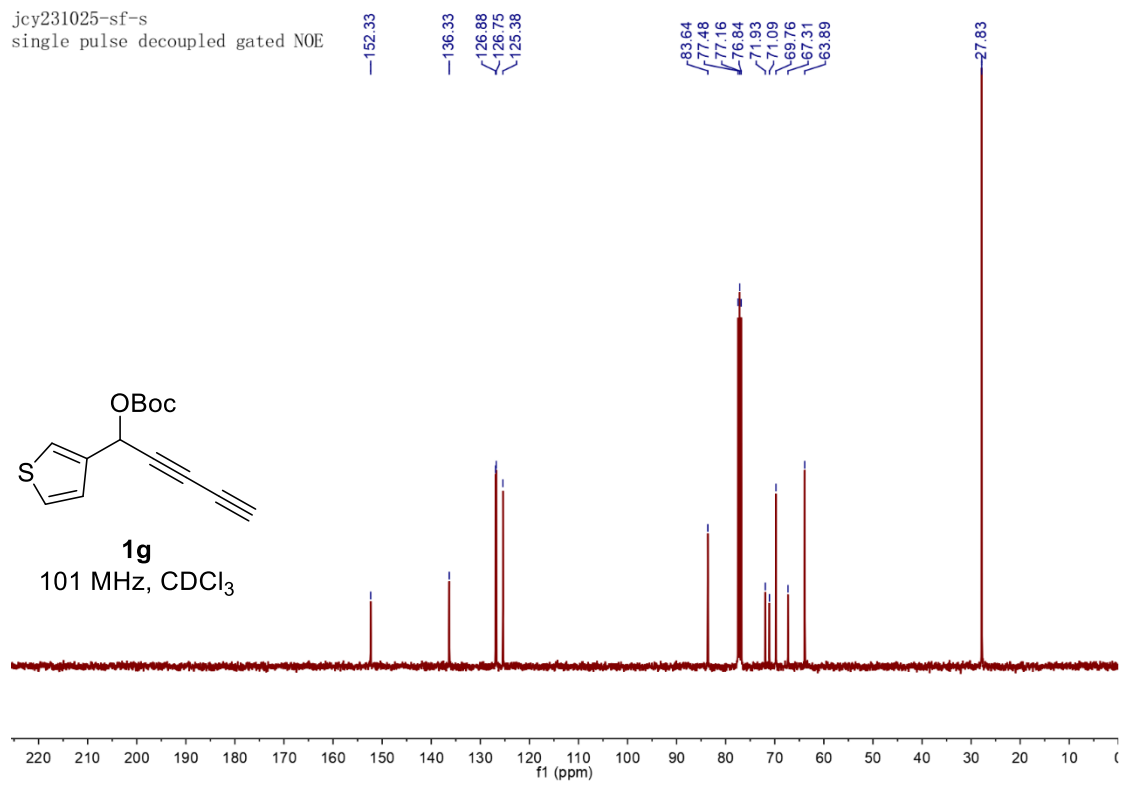
27.77  
20.60  
15.16



jcy231025-sf-s

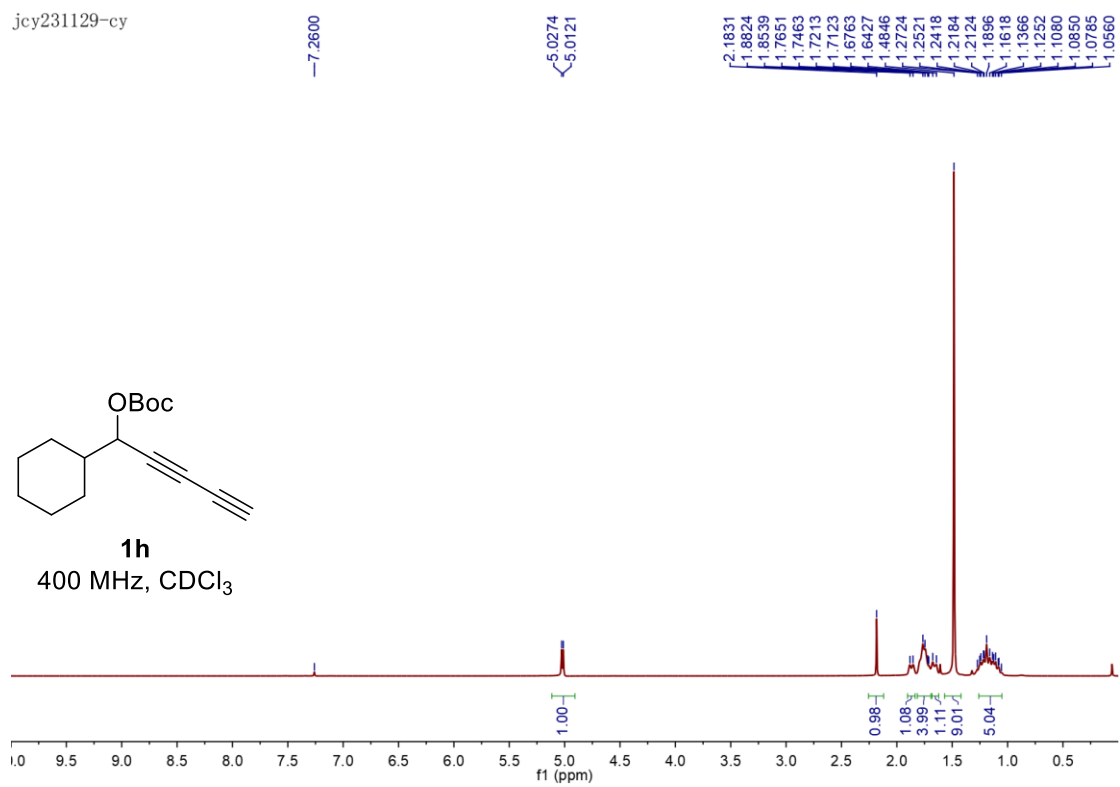


jcy231025-sf-s  
single pulse decoupled gated NOE

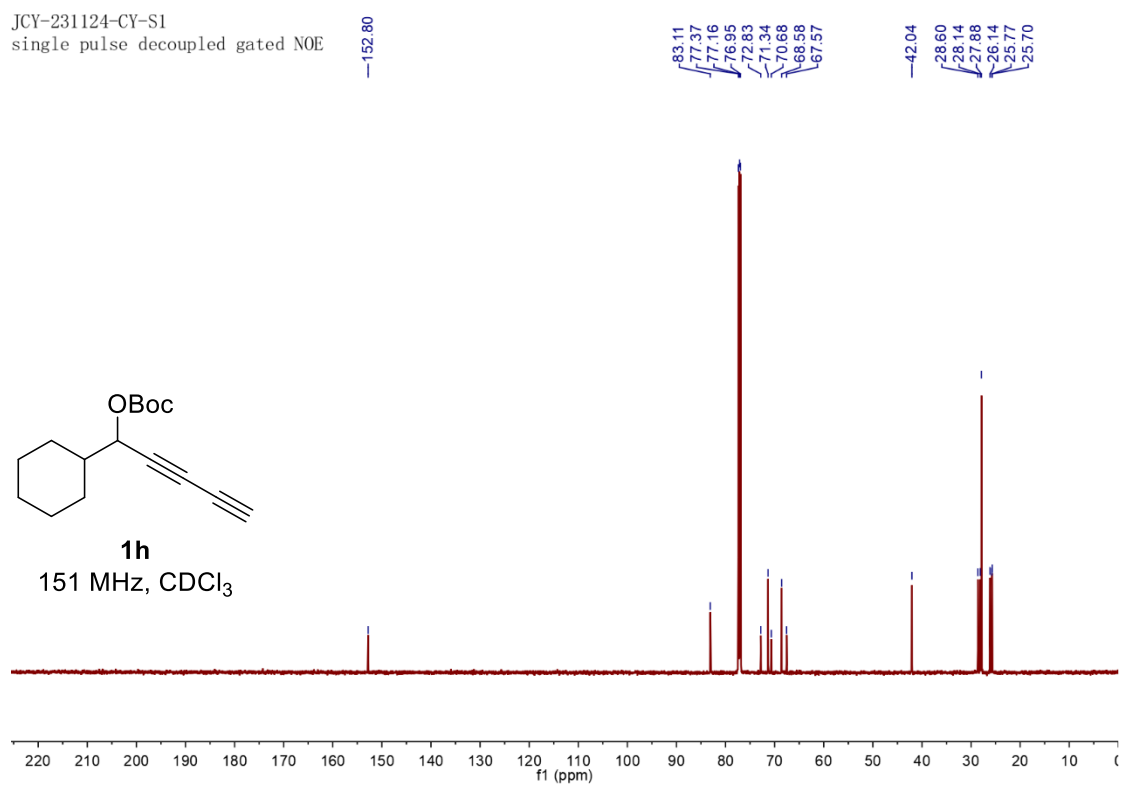




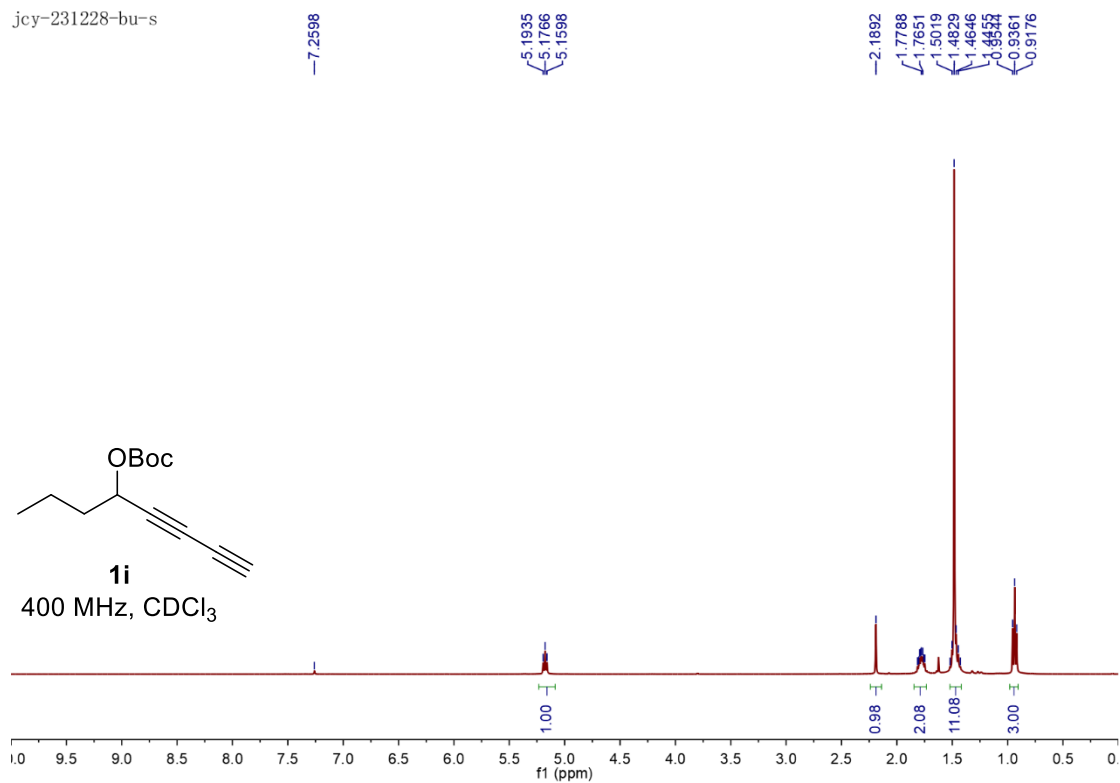
jcy231129-cy



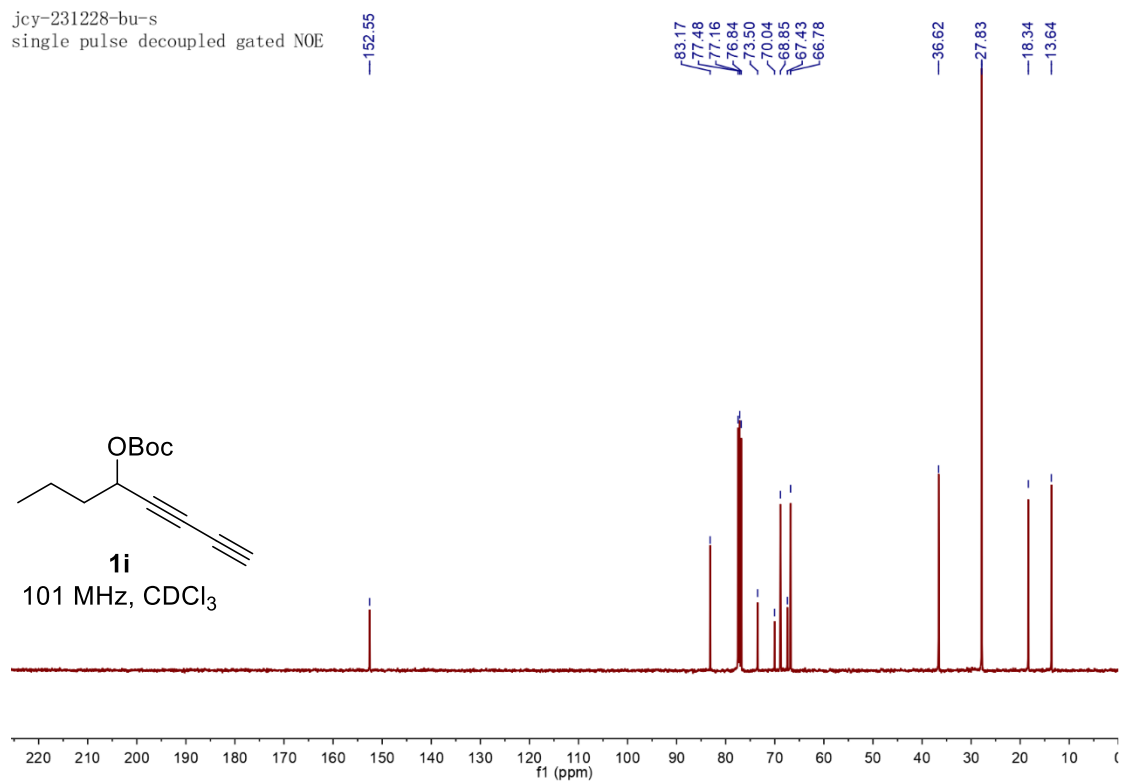
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single pulse decoupled gated NOE



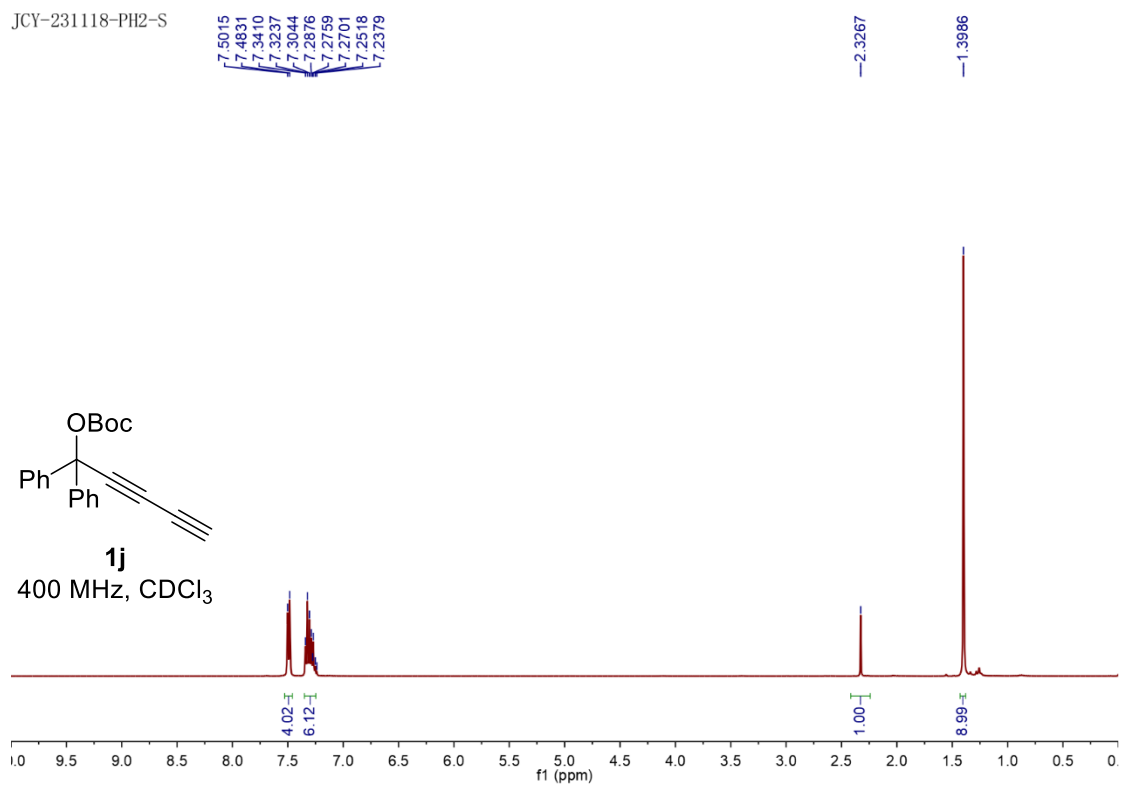
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jcy-231228-bu-s  
single pulse decoupled gated NOE

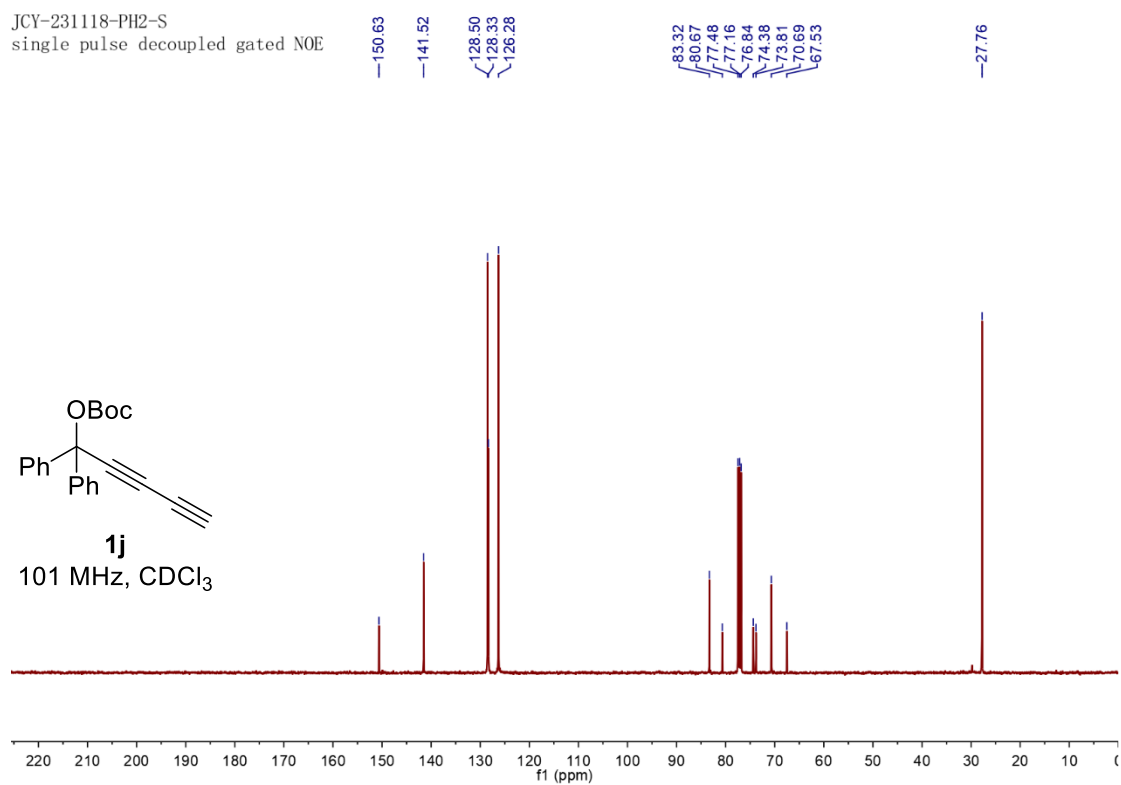


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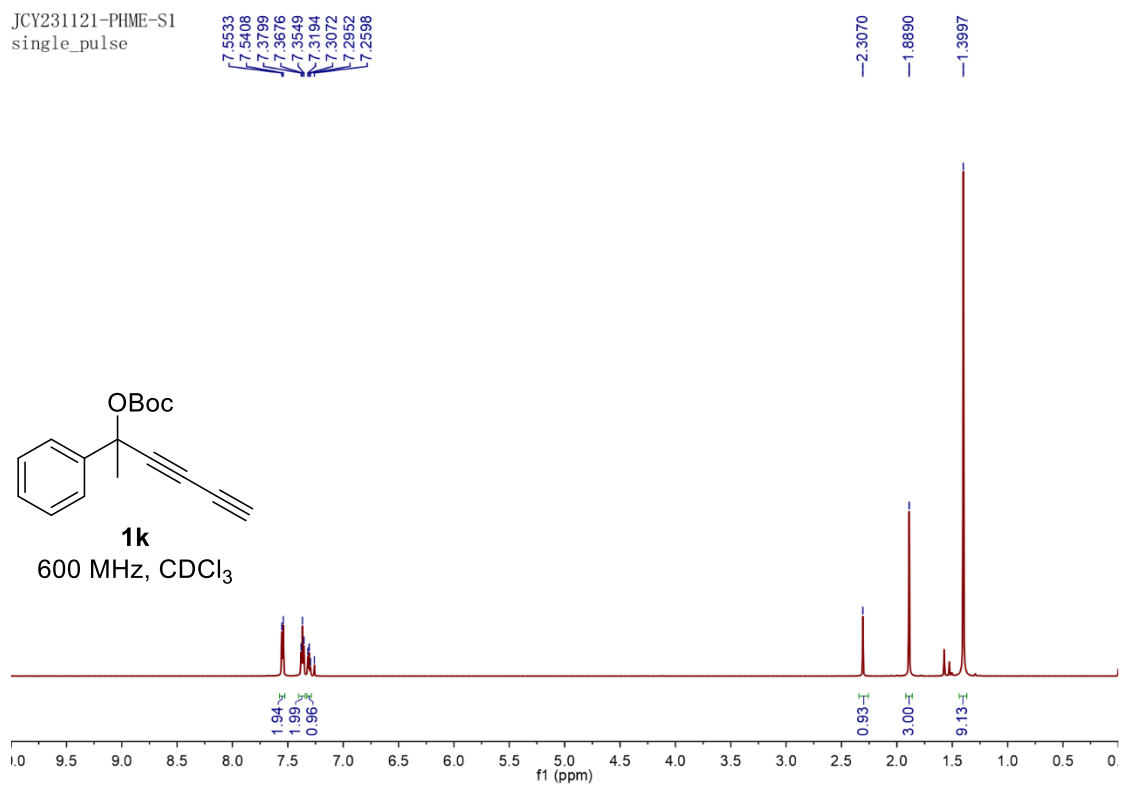


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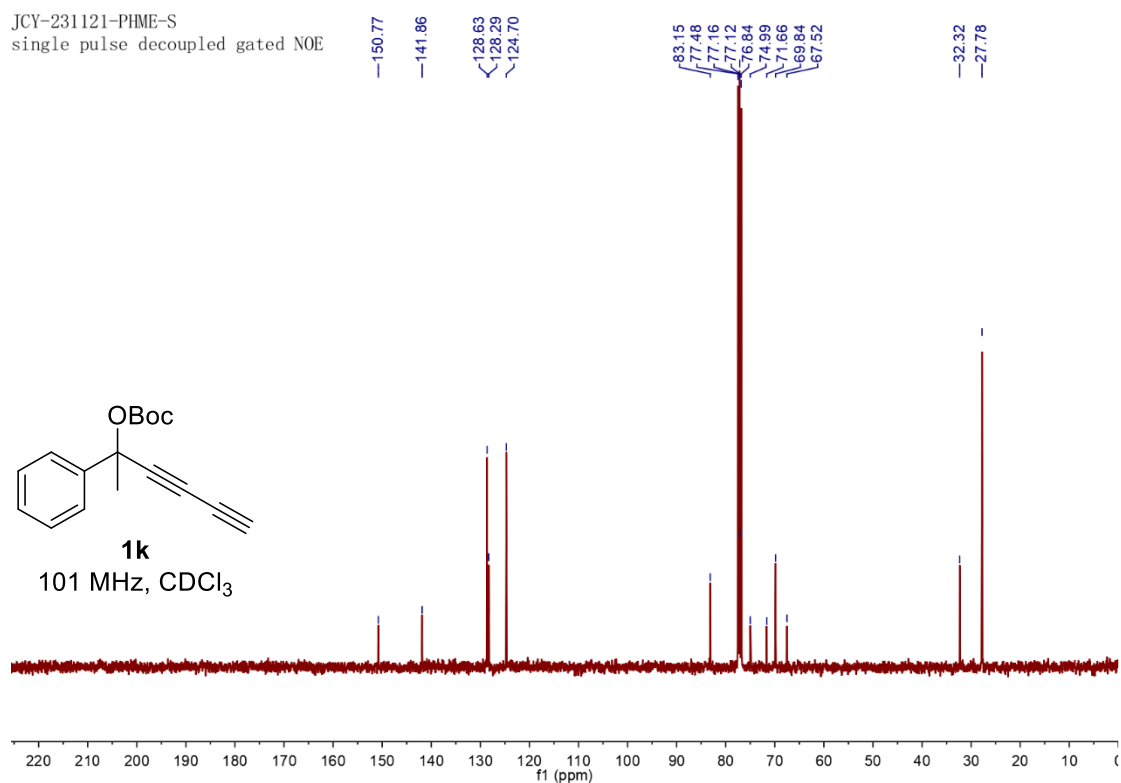
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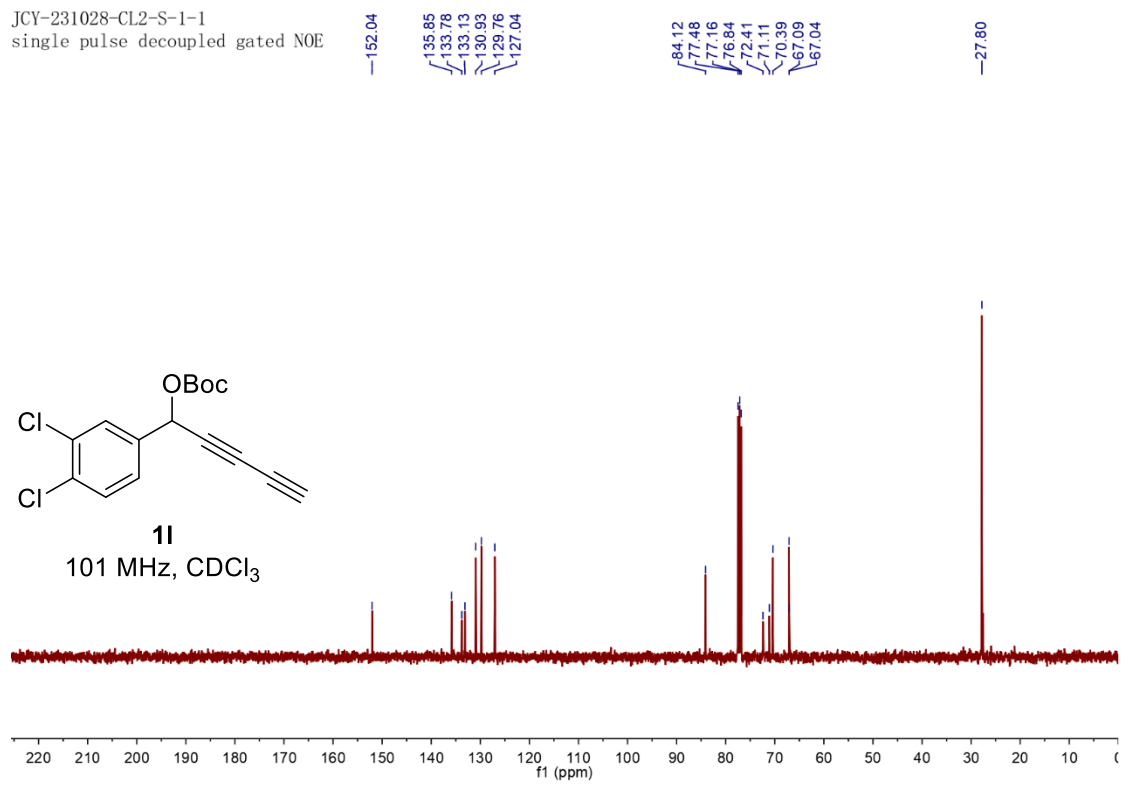
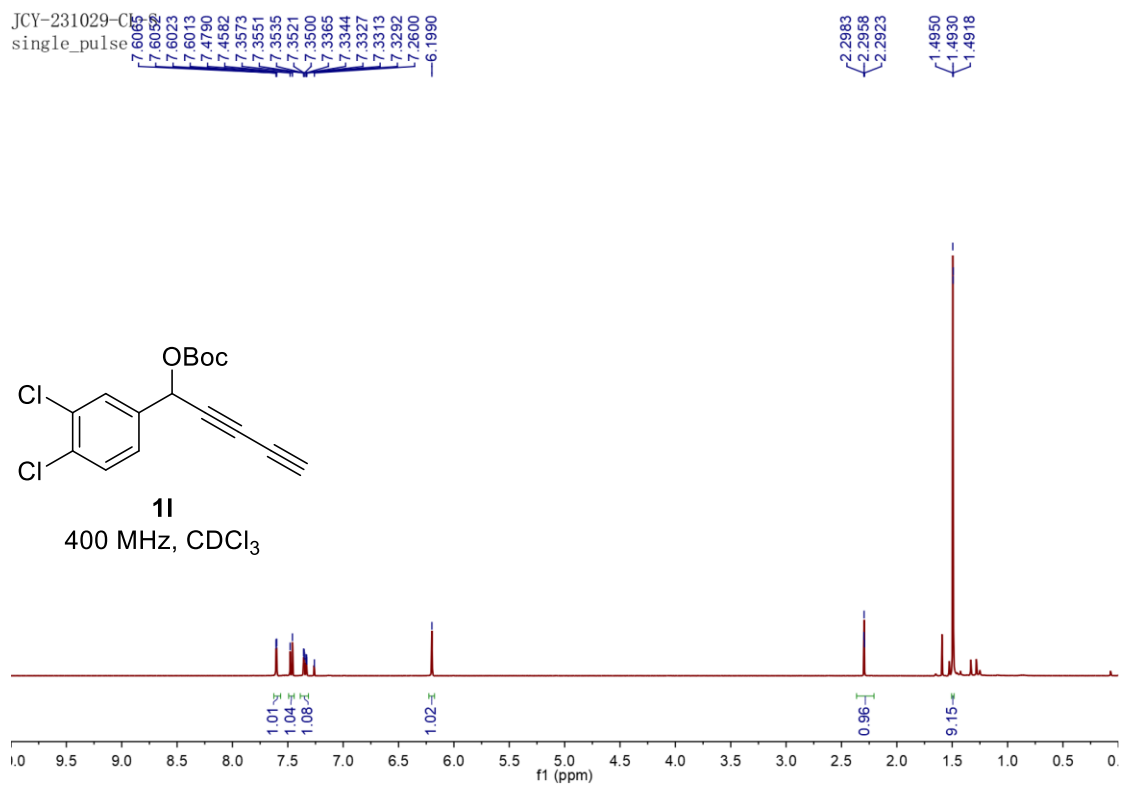


JCY231121-PHME-S1  
single\_pulse



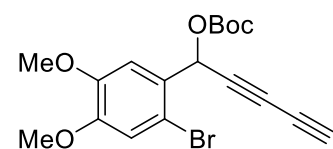
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single pulse decoupled gated NOE



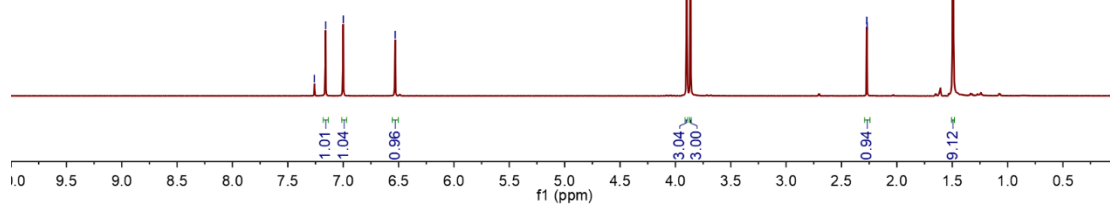


JCY-231101-BR-5  
single\_pulse

7.2589  
7.1589  
6.9893  
6.5305  
3.8877  
3.8630  
2.2718  
2.2694  
1.4922

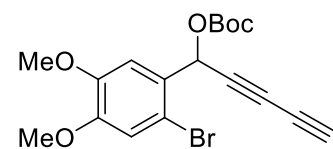


**1m**  
400 MHz, CDCl<sub>3</sub>

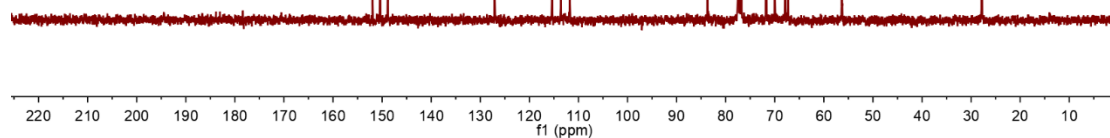


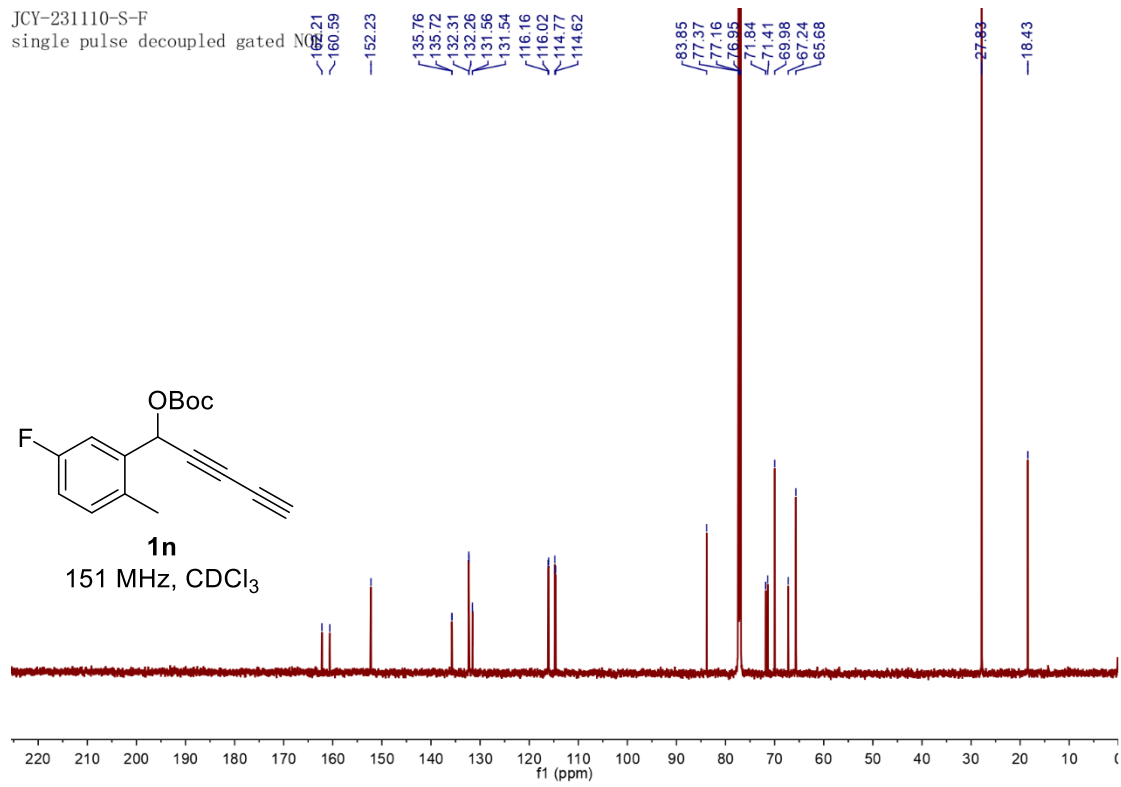
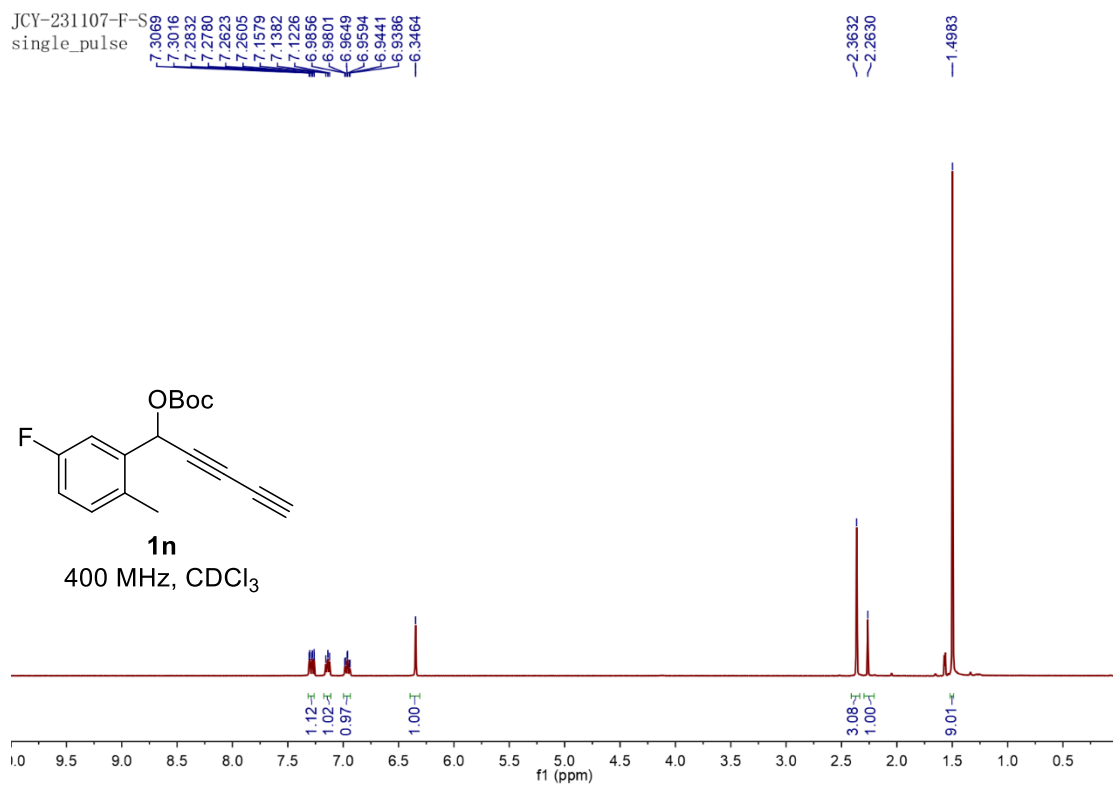
JCY-231101-BR6-S  
single pulse decoupled gated NOE

151.94  
150.40  
148.87  
127.07  
115.40  
113.61  
111.74  
83.73  
77.48  
77.16  
76.84  
71.82  
71.72  
69.98  
67.87  
67.30  
56.36  
56.32  
27.82

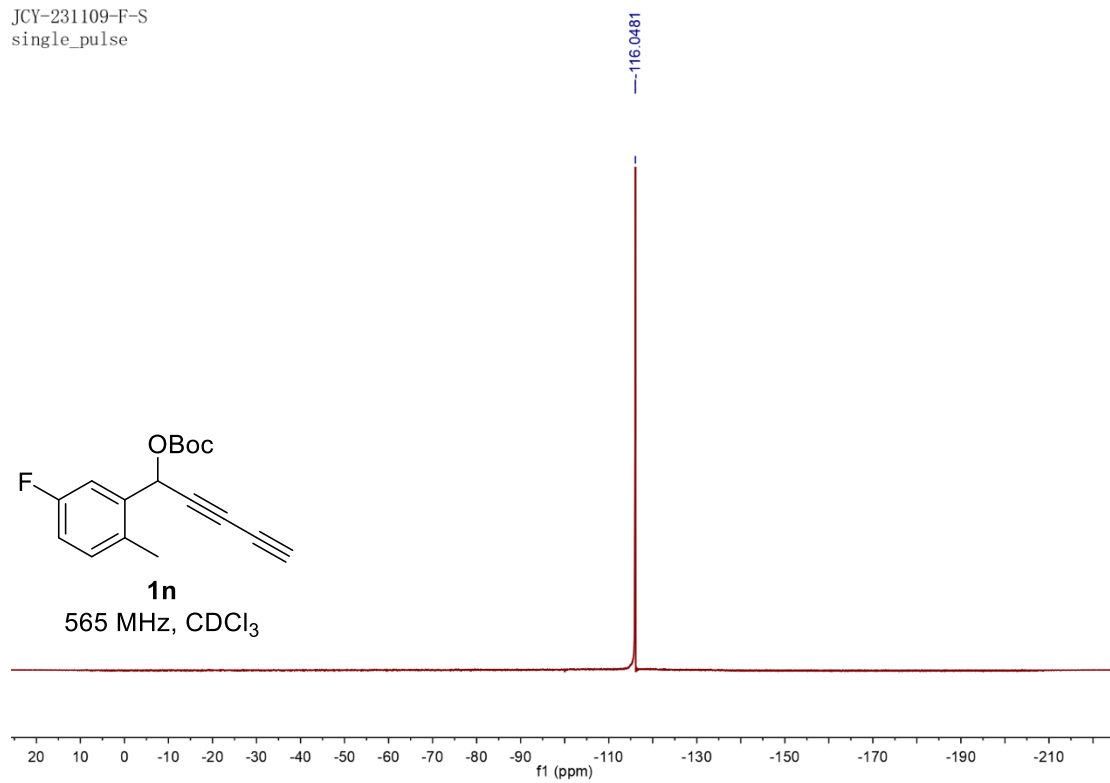
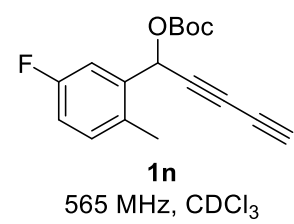


**1m**  
101 MHz, CDCl<sub>3</sub>



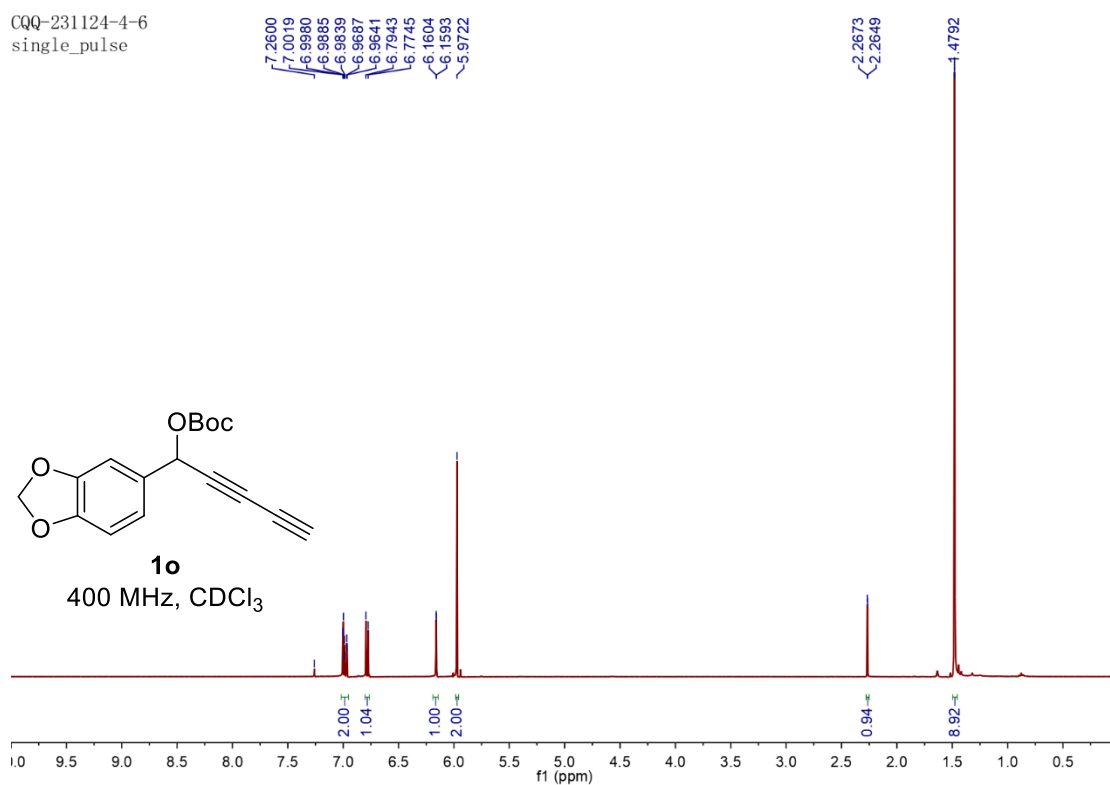


JCY-231109-F-S  
single\_pulse

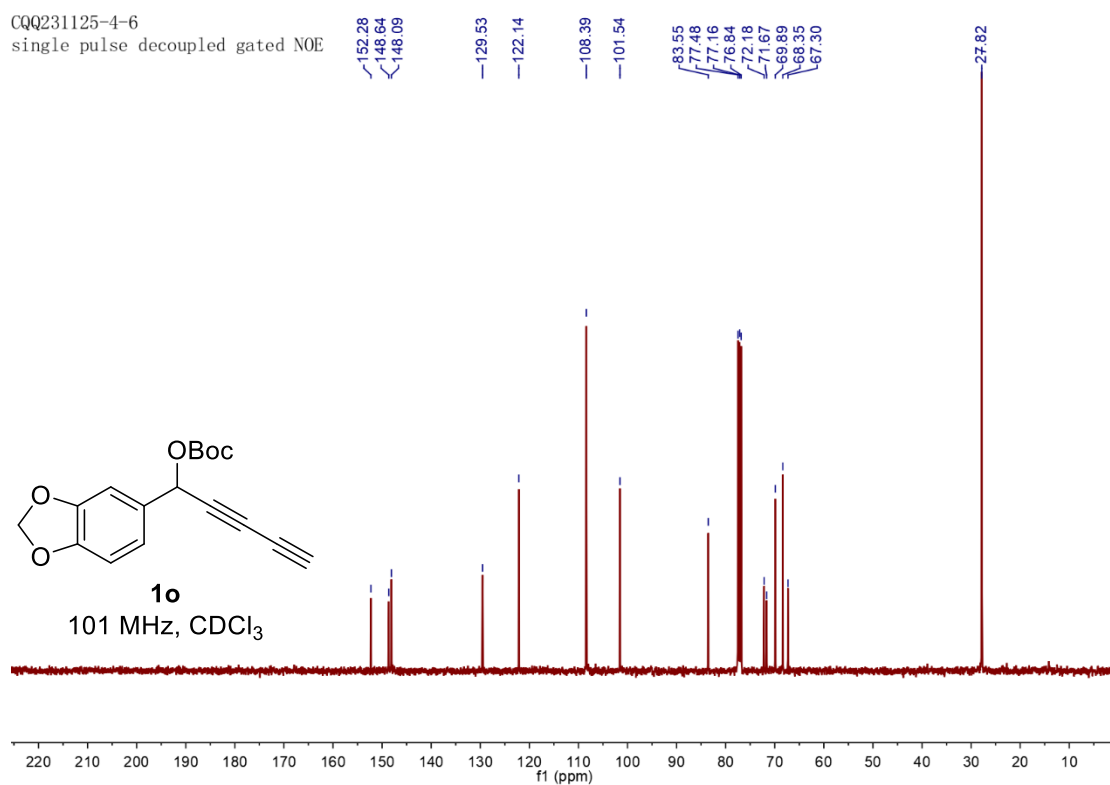




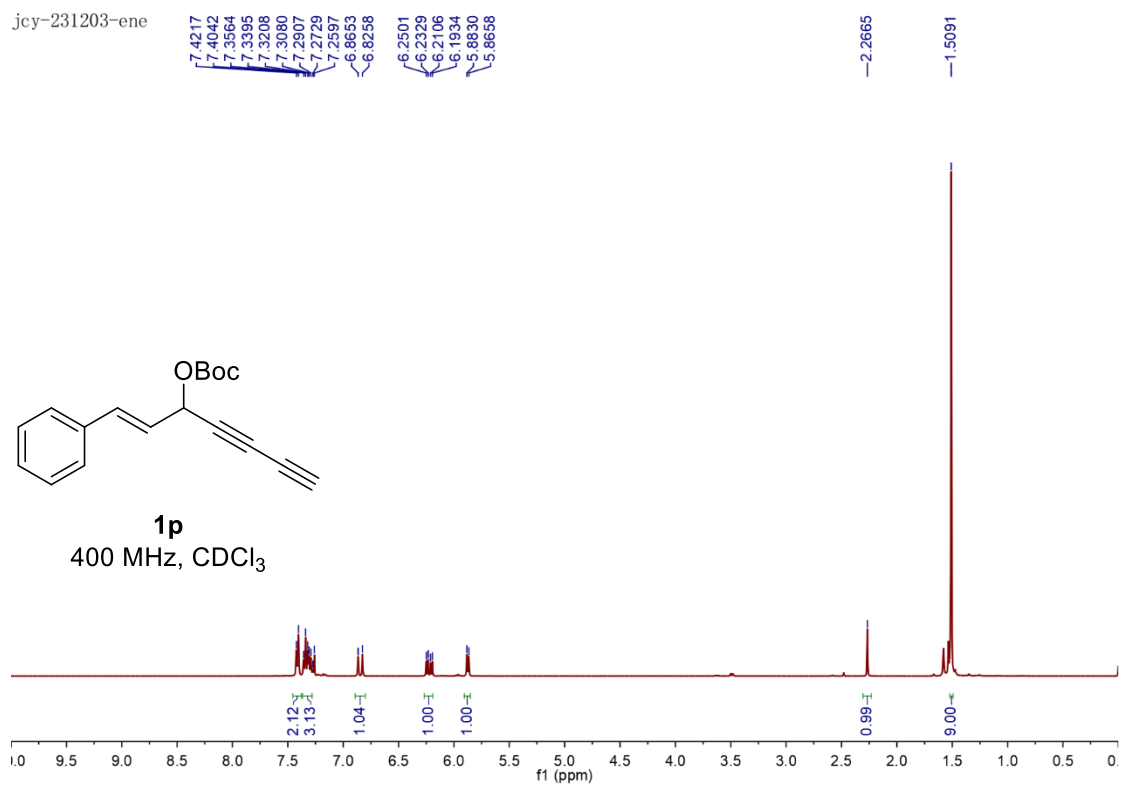
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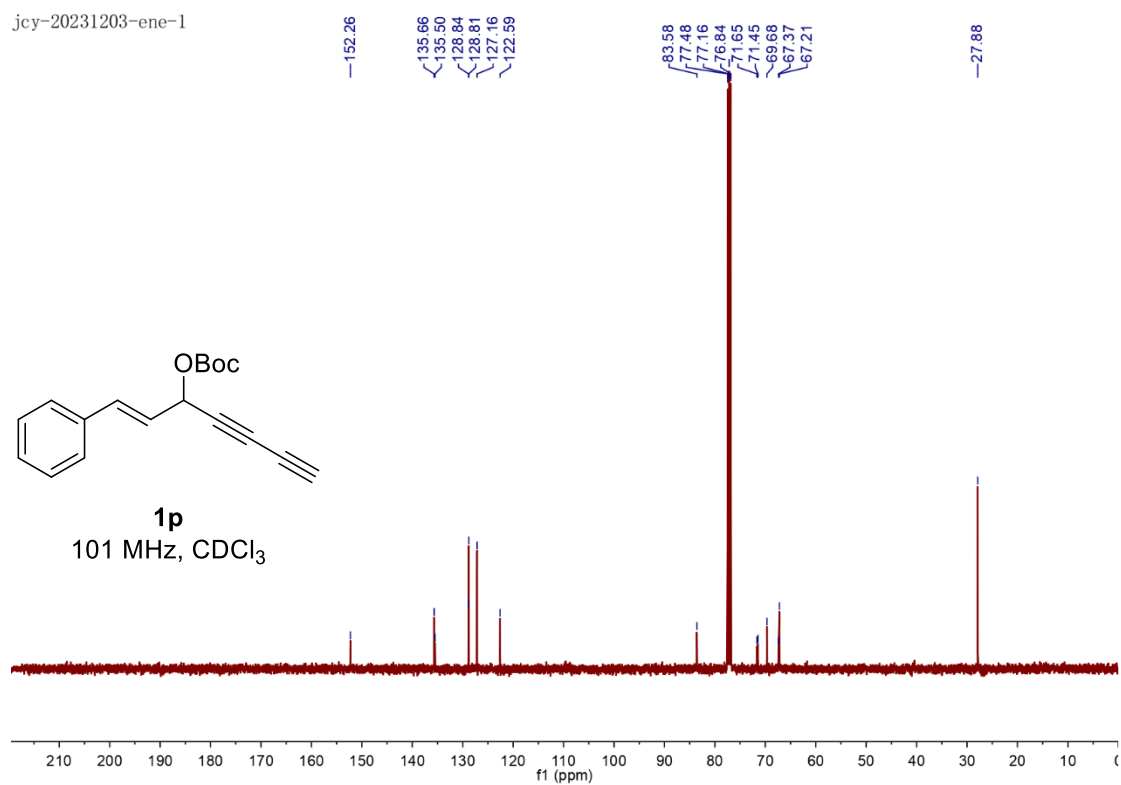
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single\_pulse decoupled gated NOE



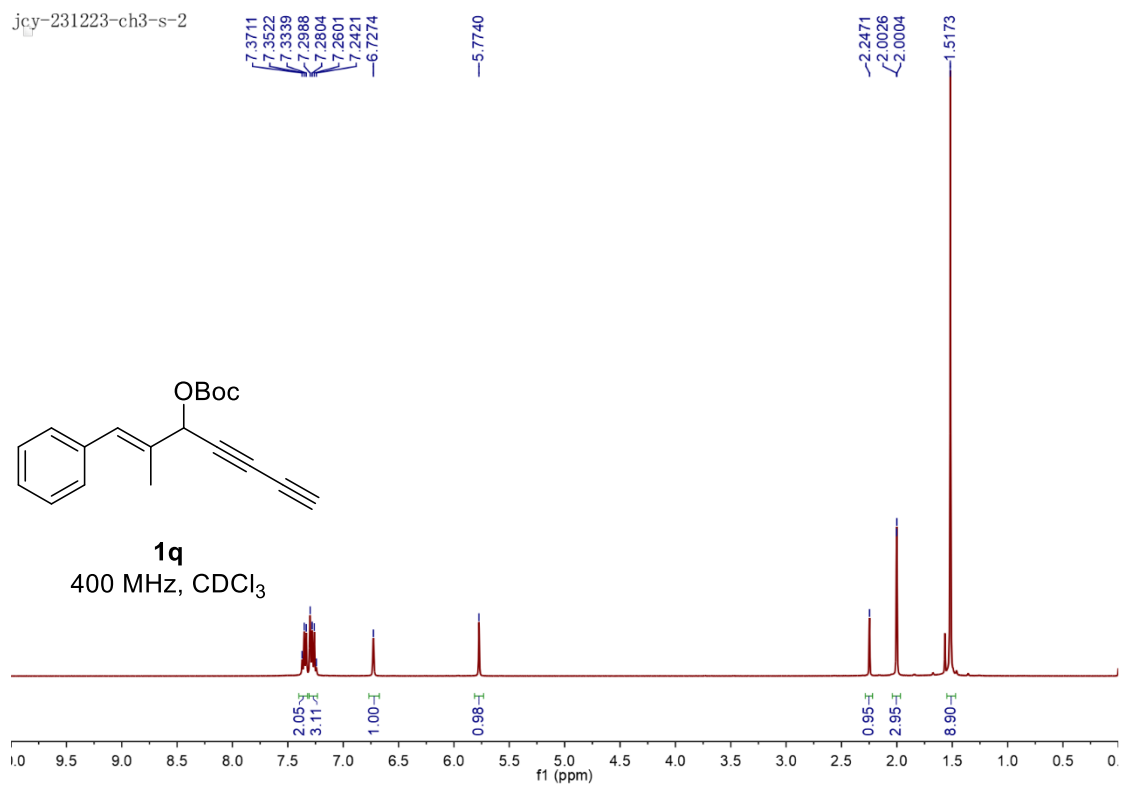
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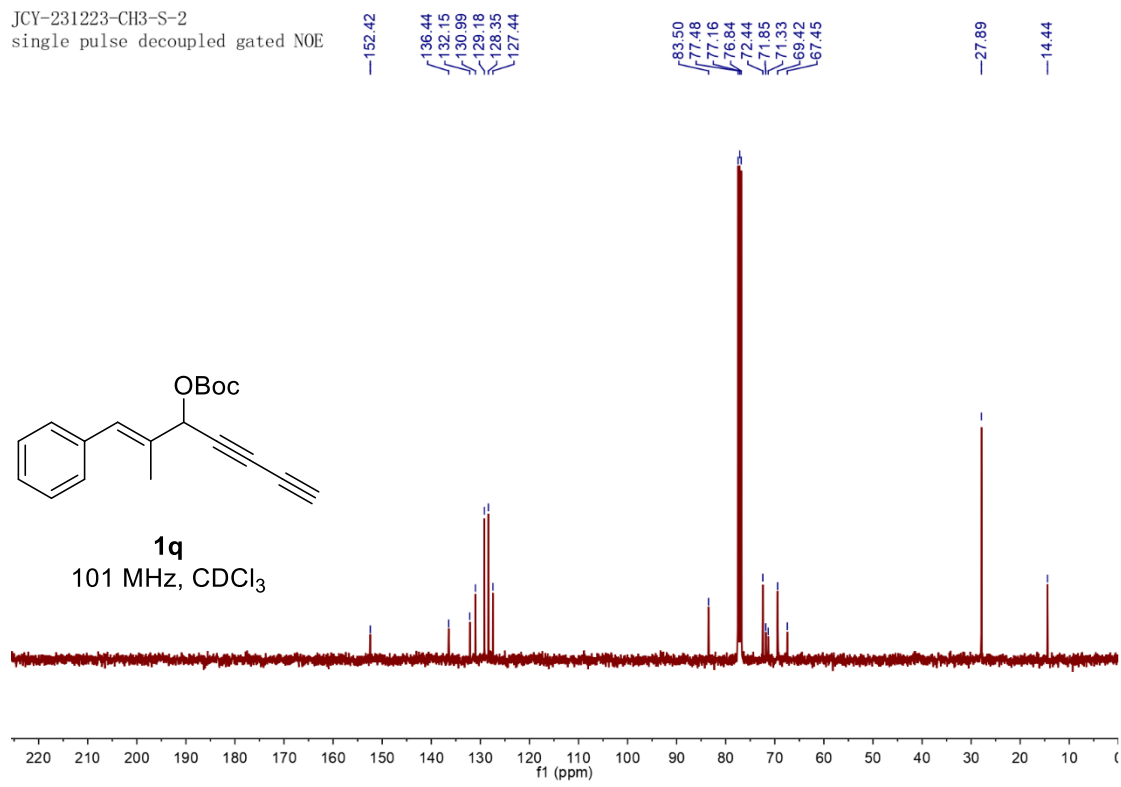
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jcy-231223-ch3-s-2



JCY-231223-CH3-S-2  
single pulse decoupled gated NOE



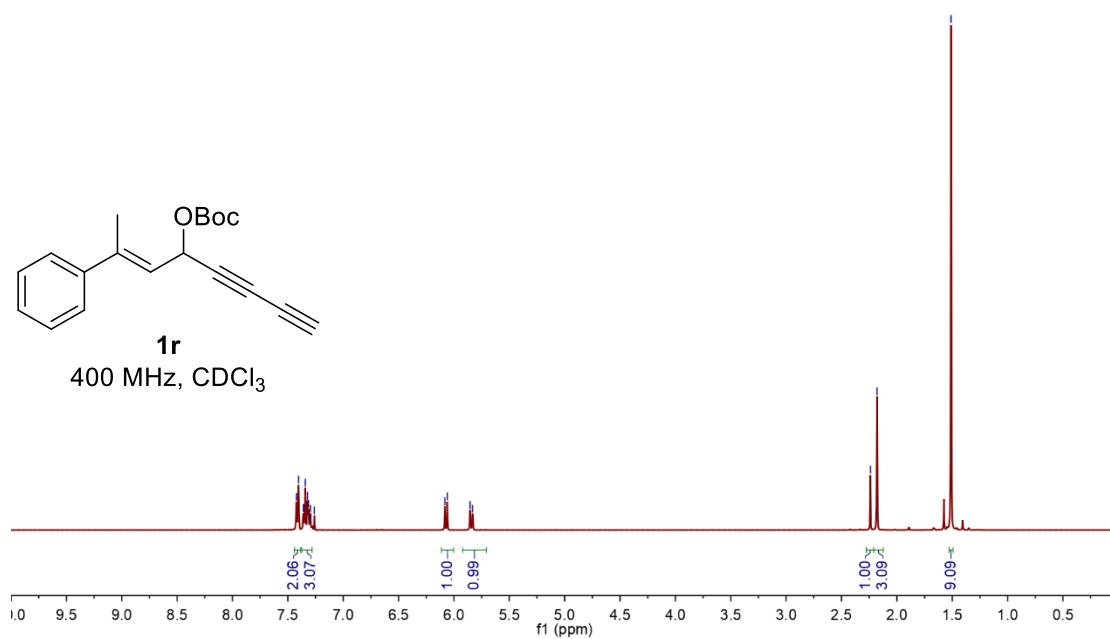
jcy240110-ch3-1  
single\_pulse

7.4212  
7.4036  
7.3587  
7.3419  
7.3230  
7.3131  
7.3027  
7.2960  
7.2602

6.0819  
6.0601  
5.8540  
5.8318

2.2388  
2.1793

1.5106



jcy2401110-ch3-1

152.36

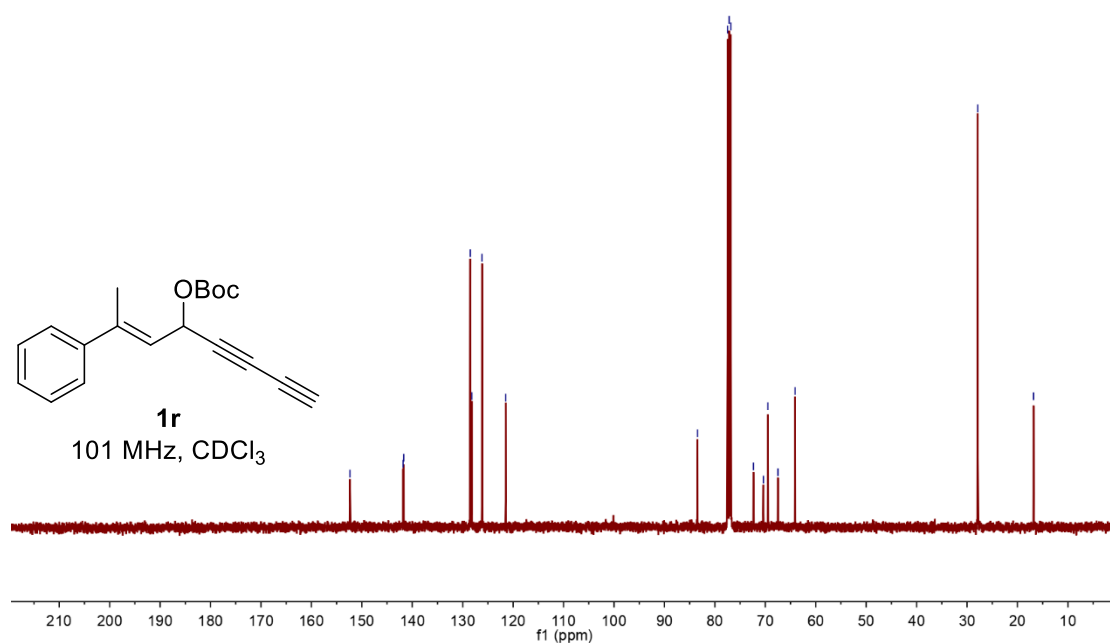
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141.69

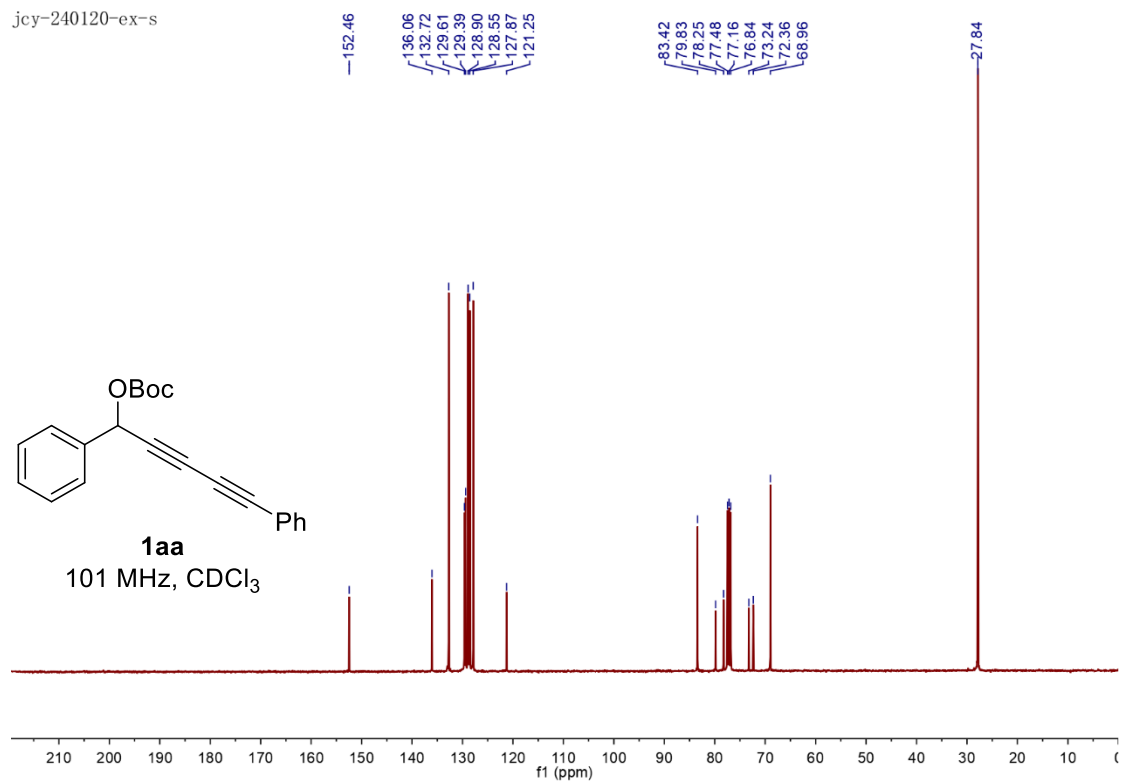
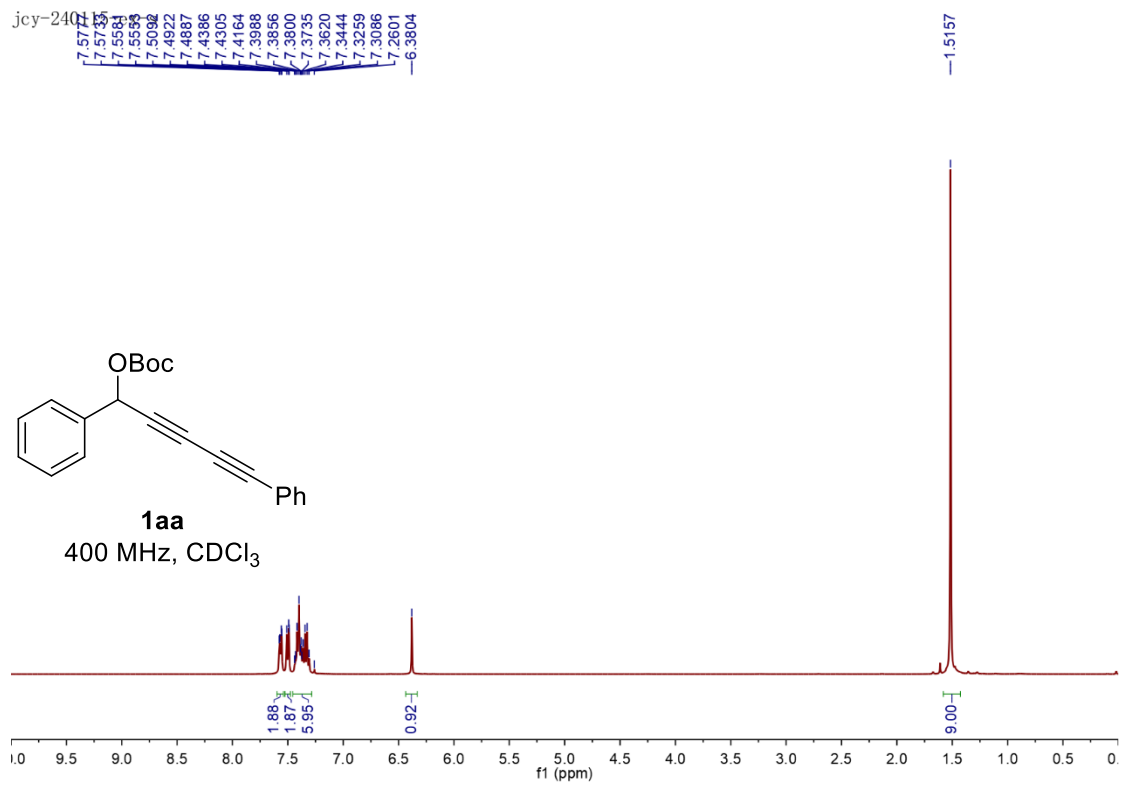
128.50  
128.19  
126.16  
121.47

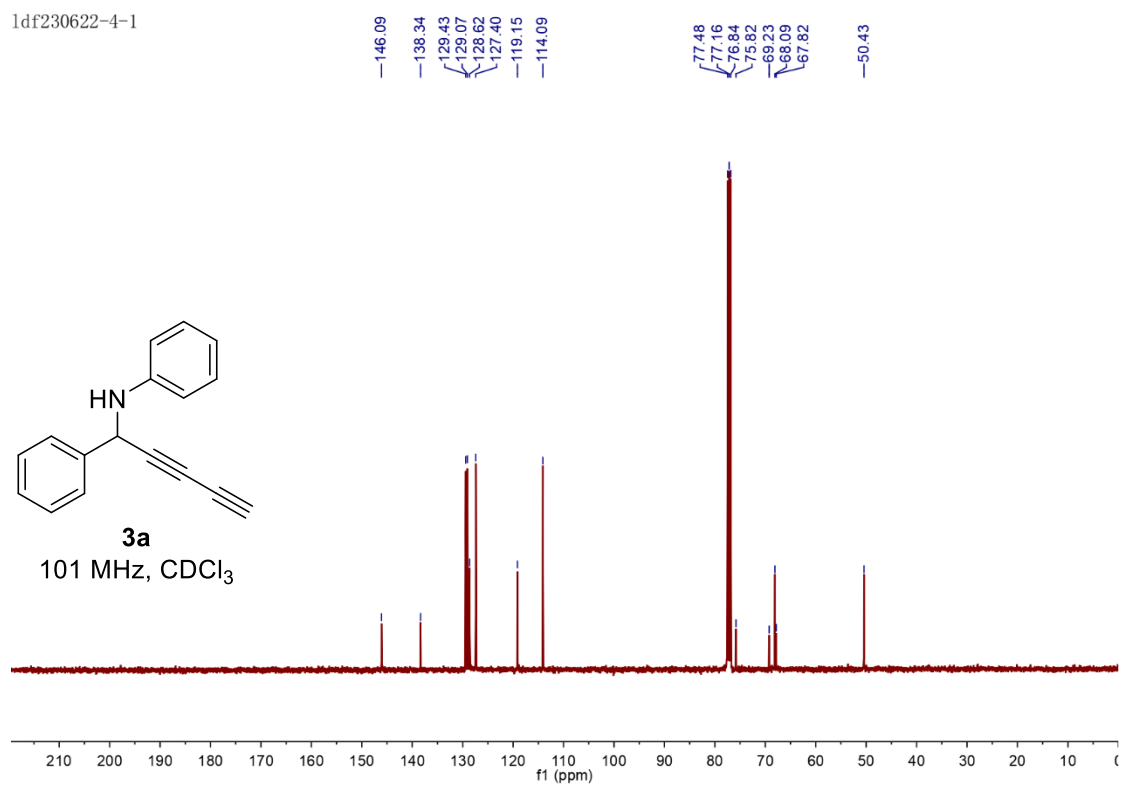
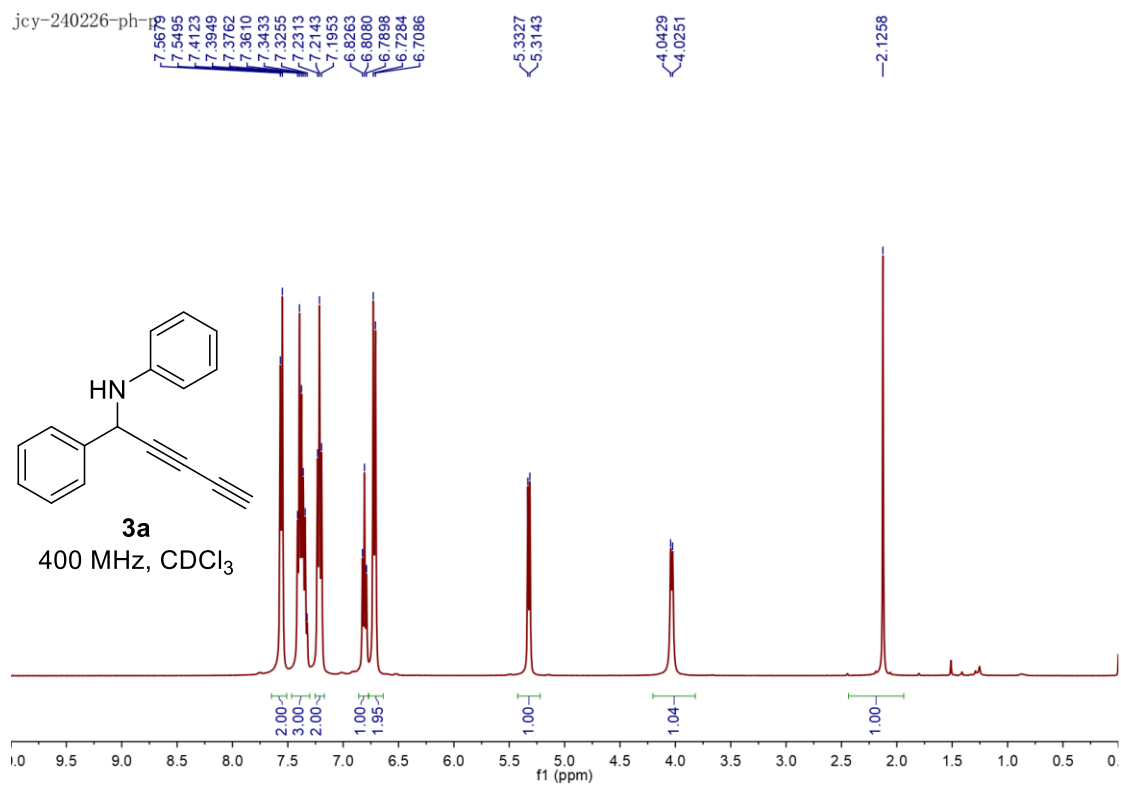
83.45  
77.46  
77.16  
76.84  
72.35  
70.37  
69.49  
67.49  
64.09

27.87

16.81







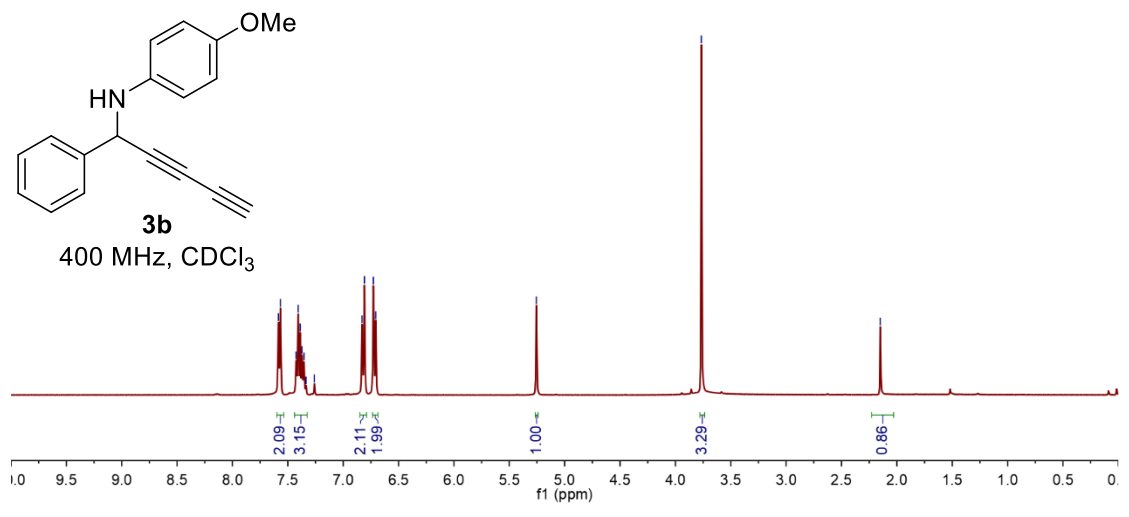
jcy-240312-ome

7.5847  
7.5662  
7.4248  
7.4070  
7.3884  
7.3718  
7.3545  
7.3362  
7.2600  
6.8303  
6.8081  
6.7279  
6.7059

-5.2552

-3.7654

-2.1495

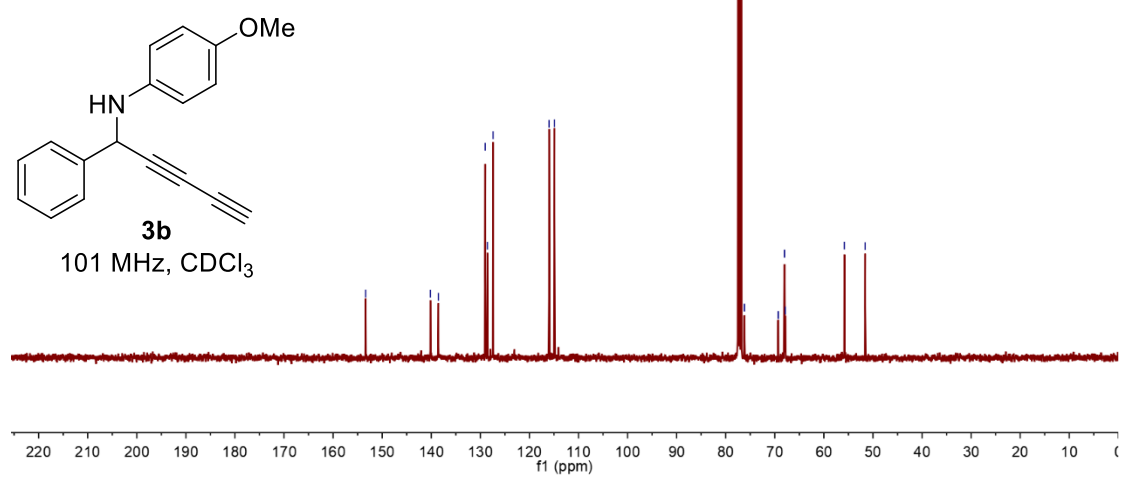


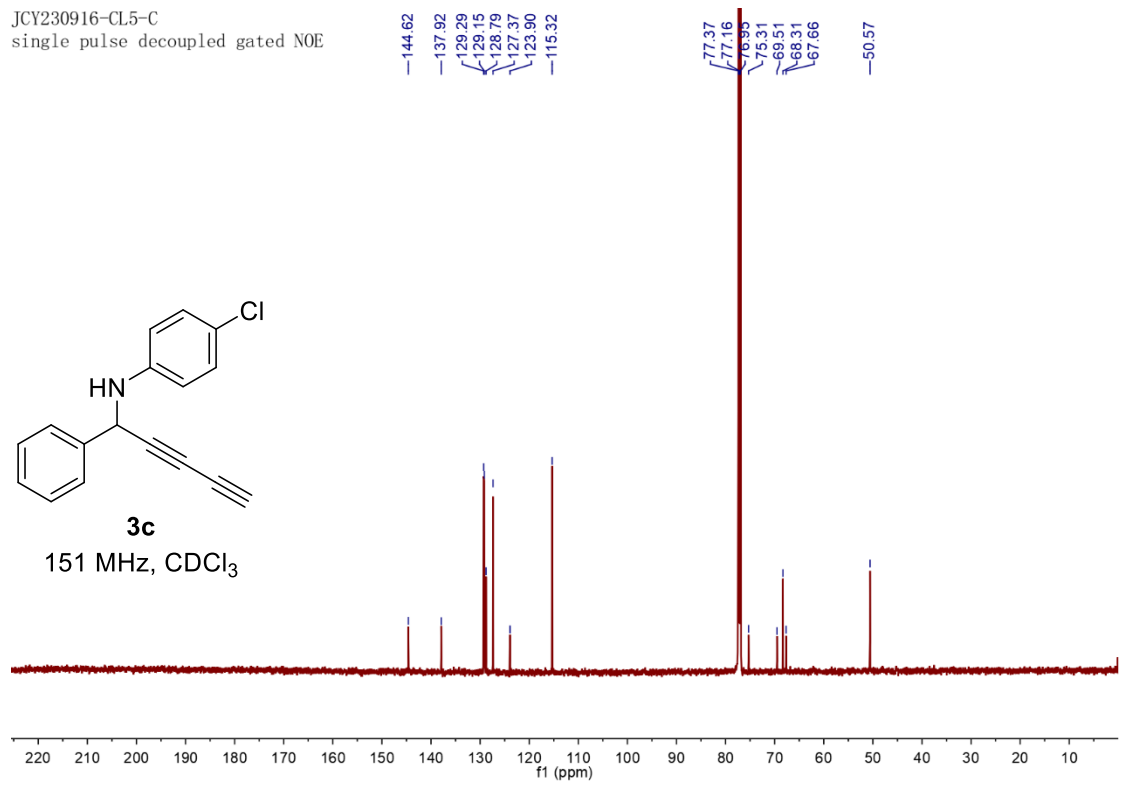
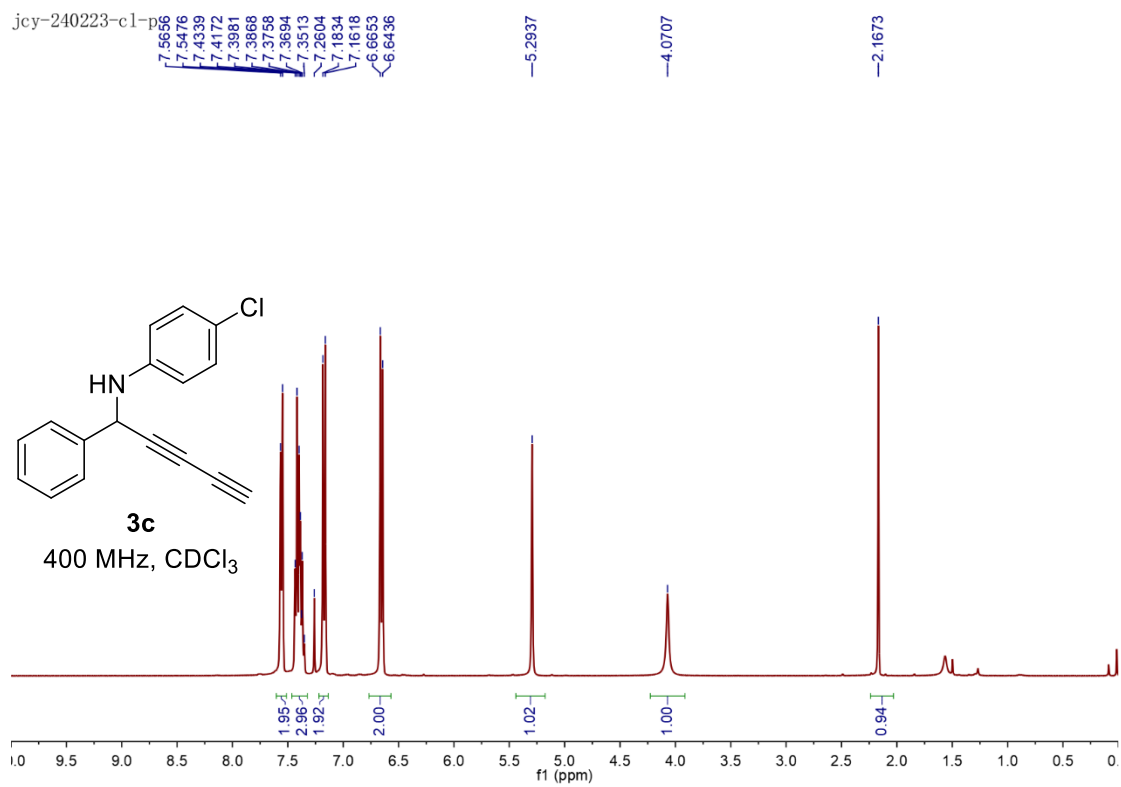
JCY-230916-OME7

single pulse decoupled gated NOE

-153.37  
140.16  
138.55  
129.00  
128.55  
127.41  
115.98  
114.90

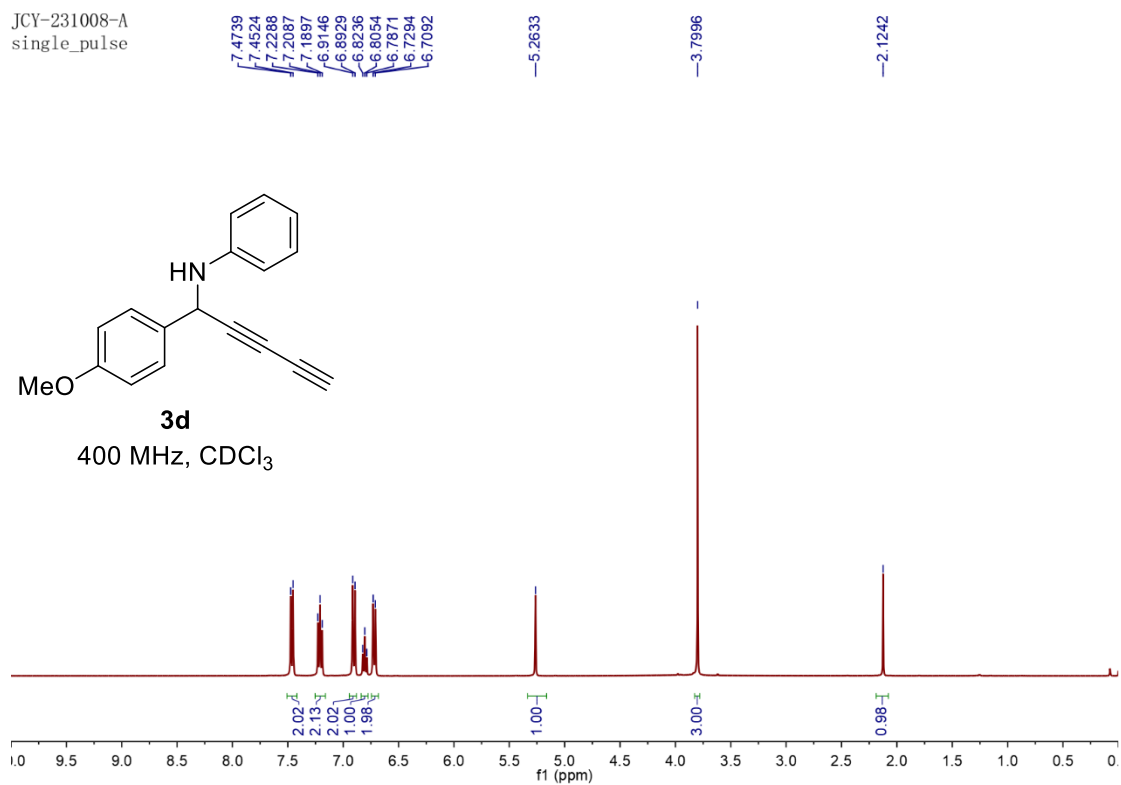
77.48  
77.16  
76.84  
76.19  
69.30  
68.02  
67.87  
55.81  
51.58



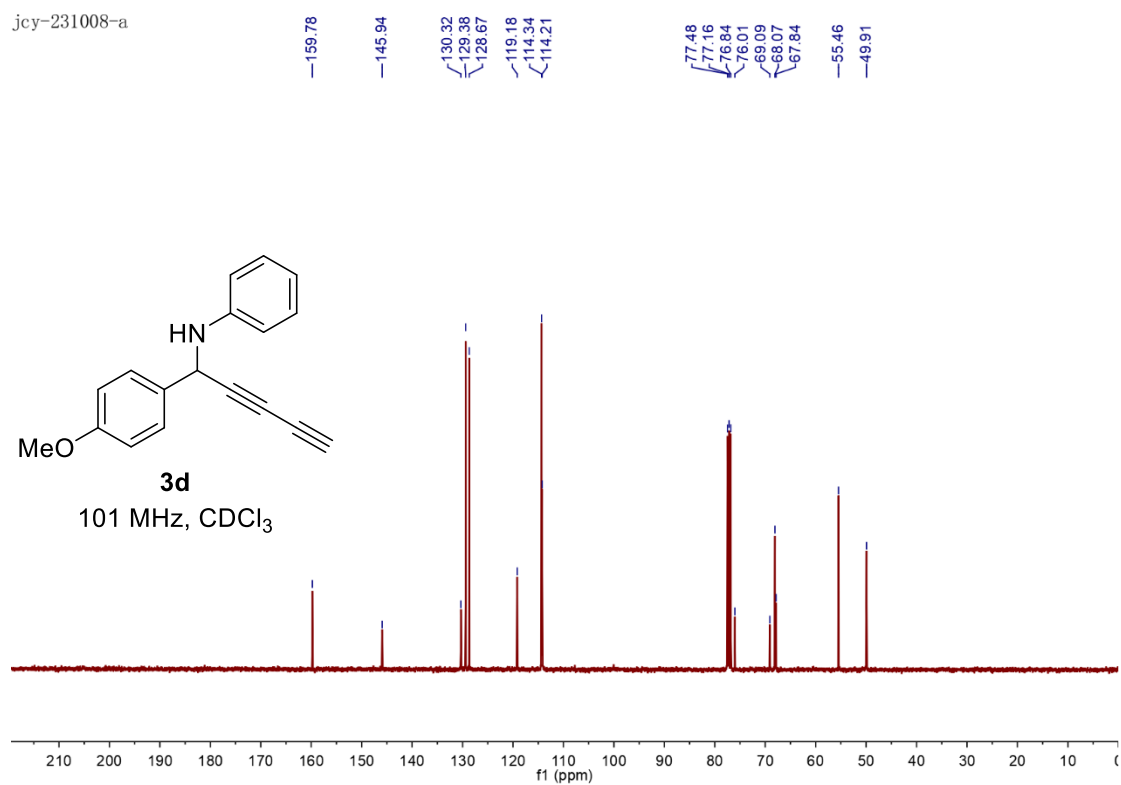




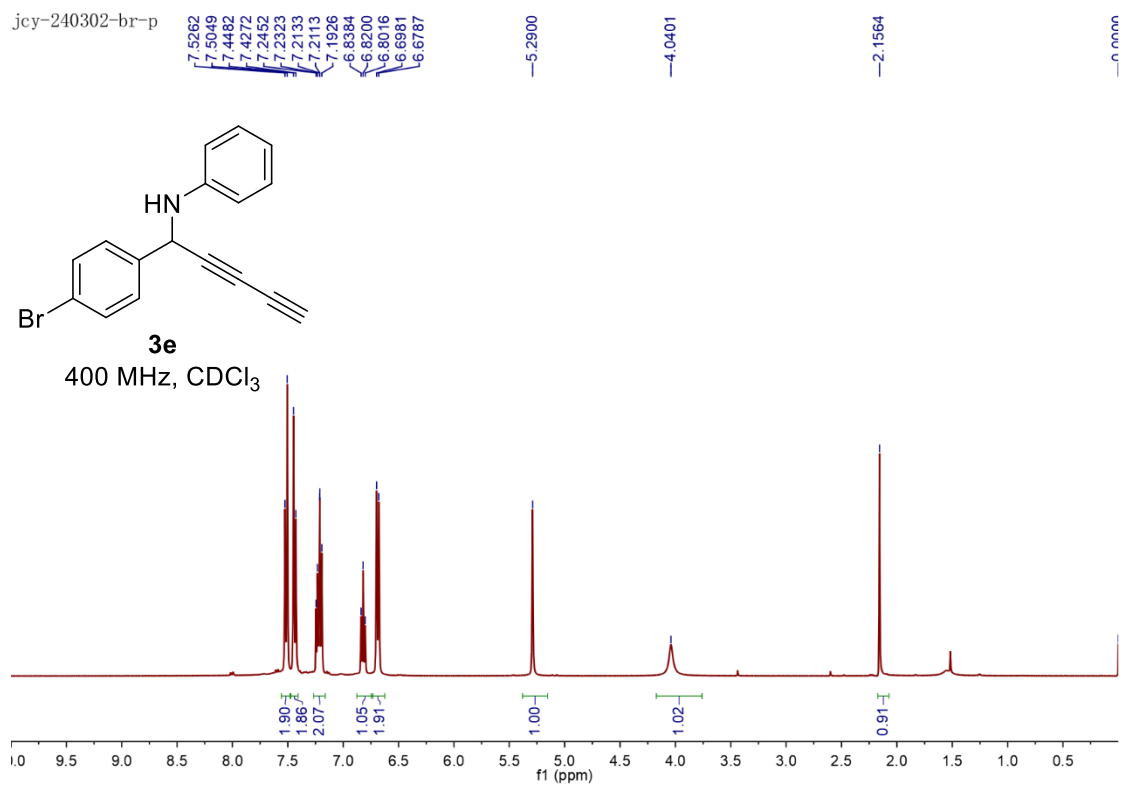
JCY-231008-A  
single\_pulse



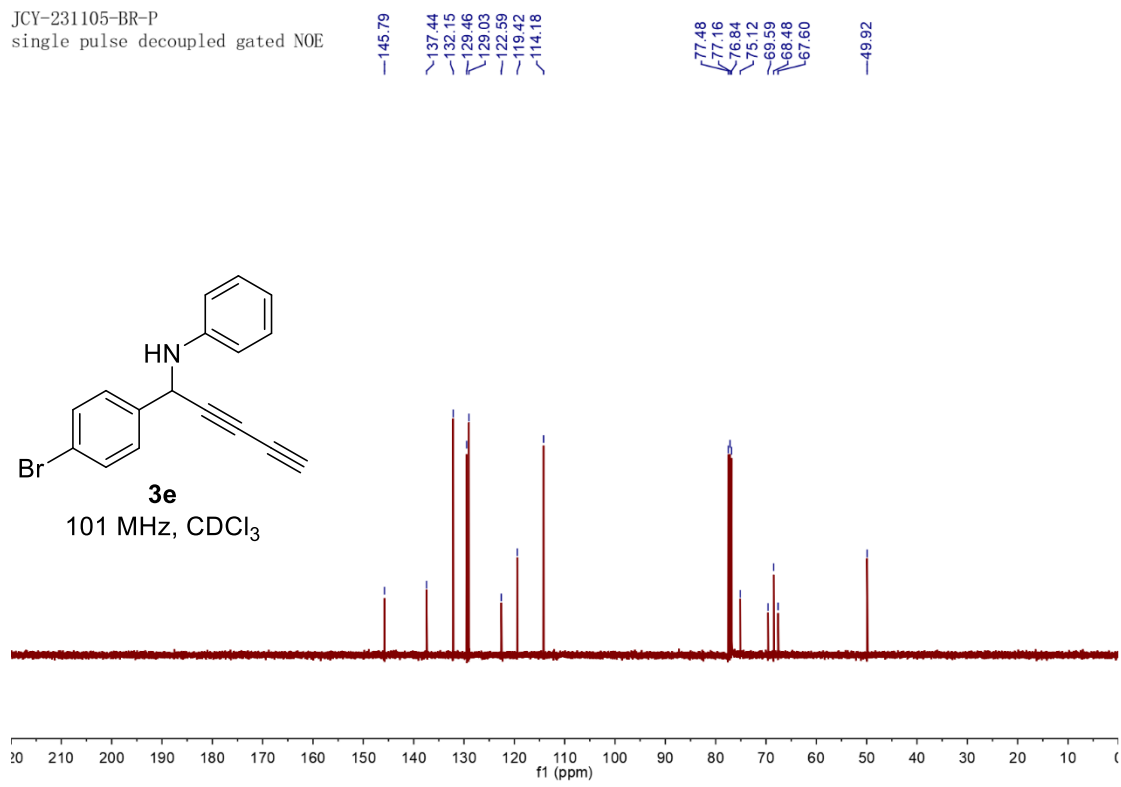
jcy-231008-a



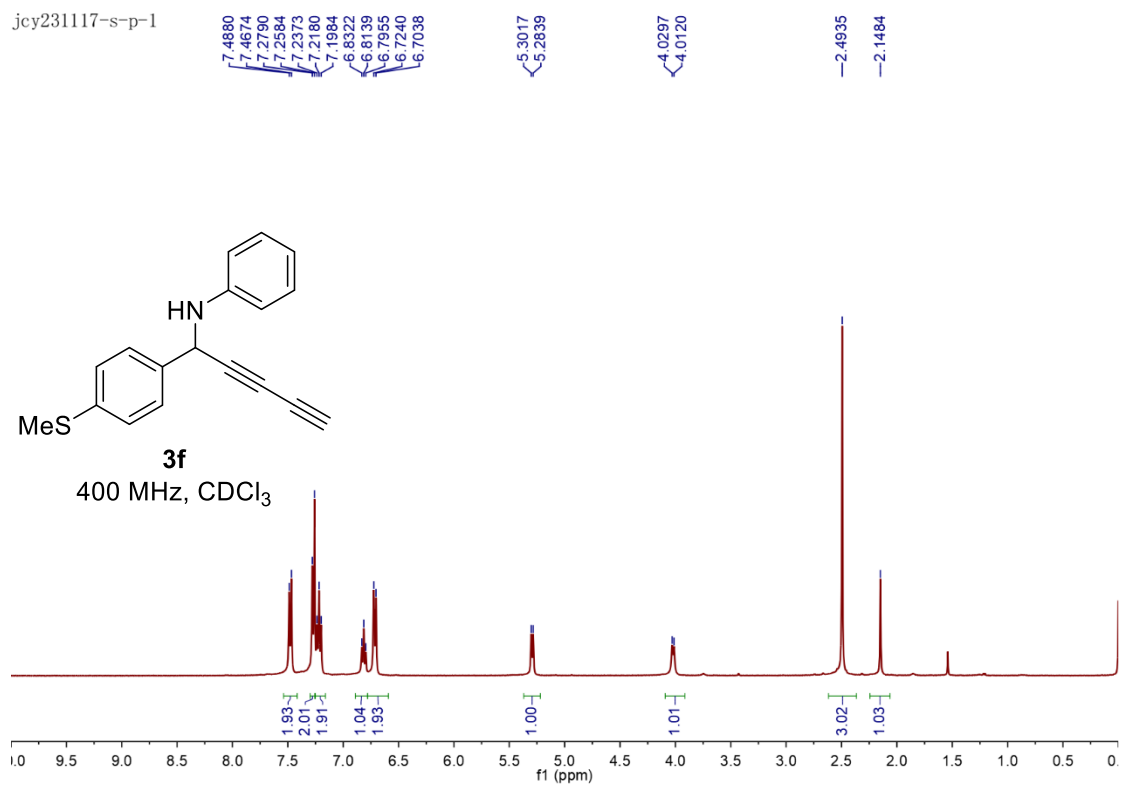
jcy-240302-br-p



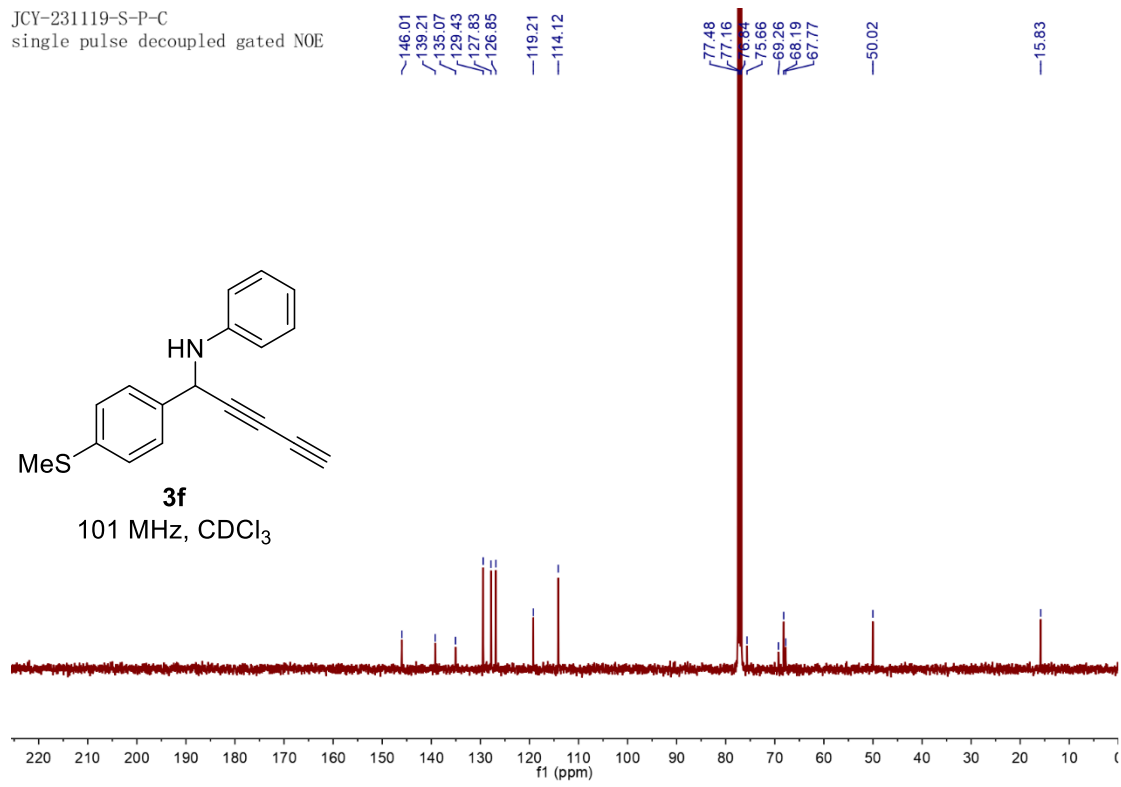
JCY-231105-BR-P  
single pulse decoupled gated NOE

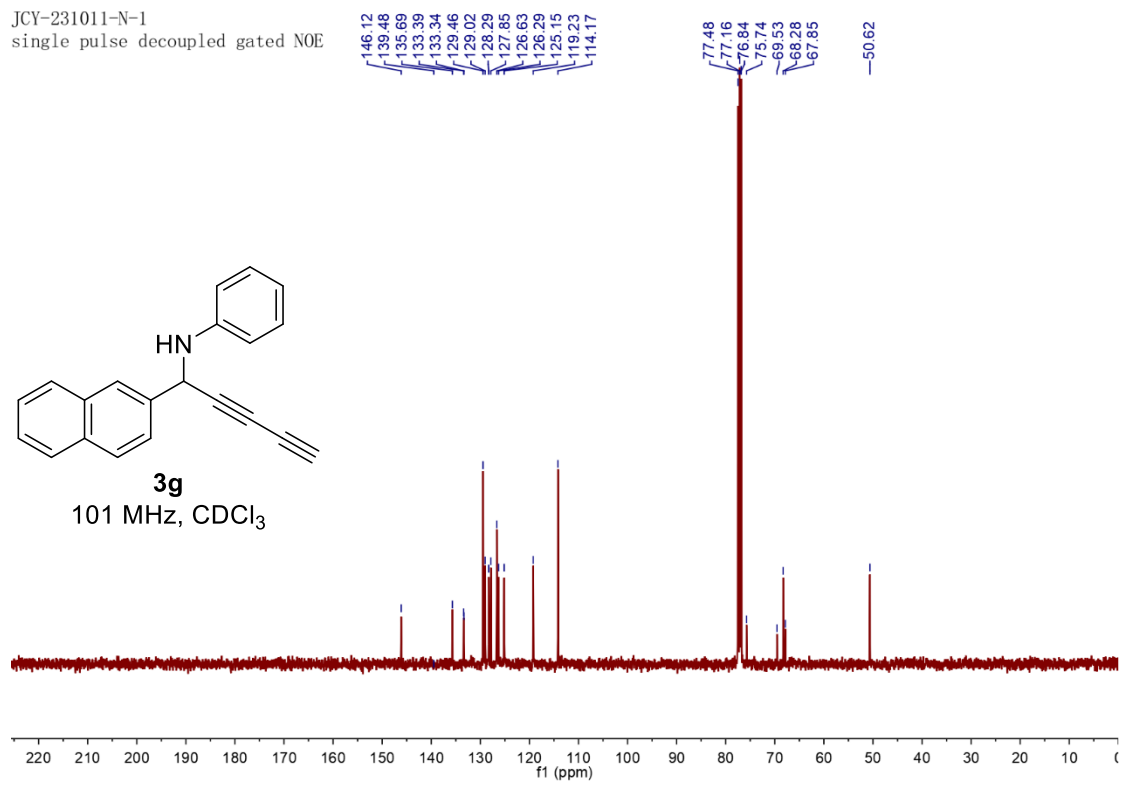
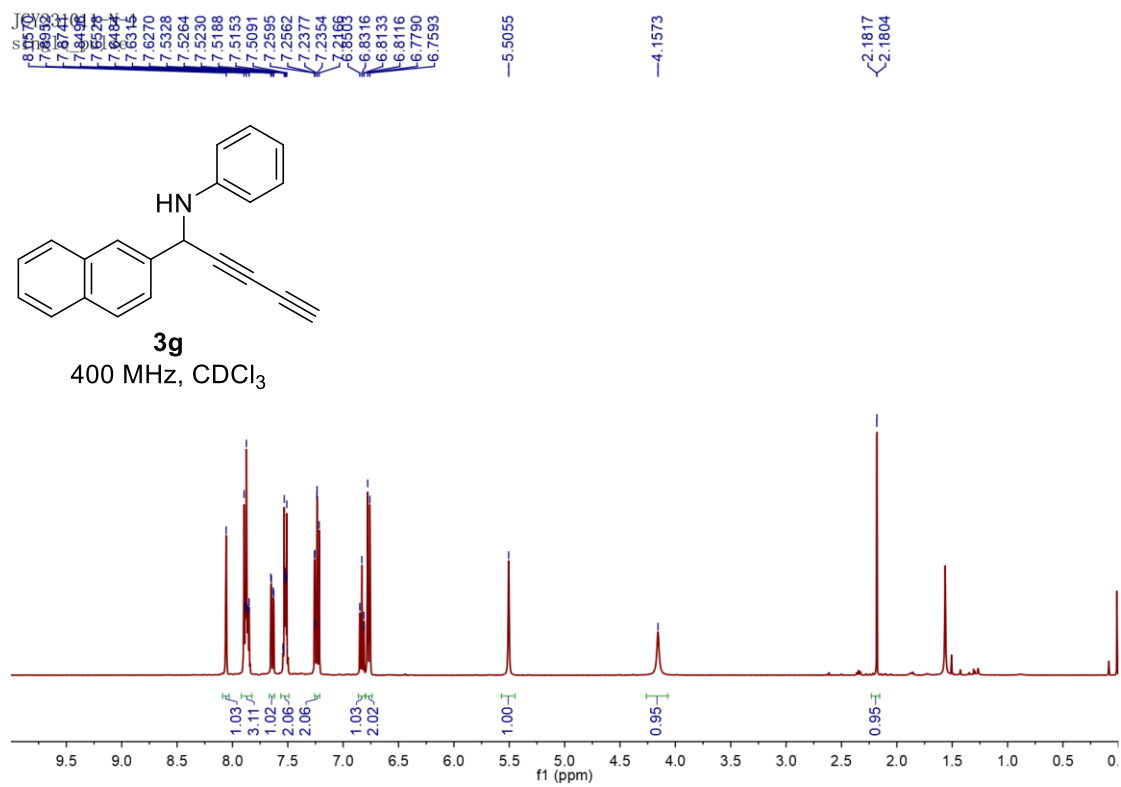


jcy231117-s-p-1

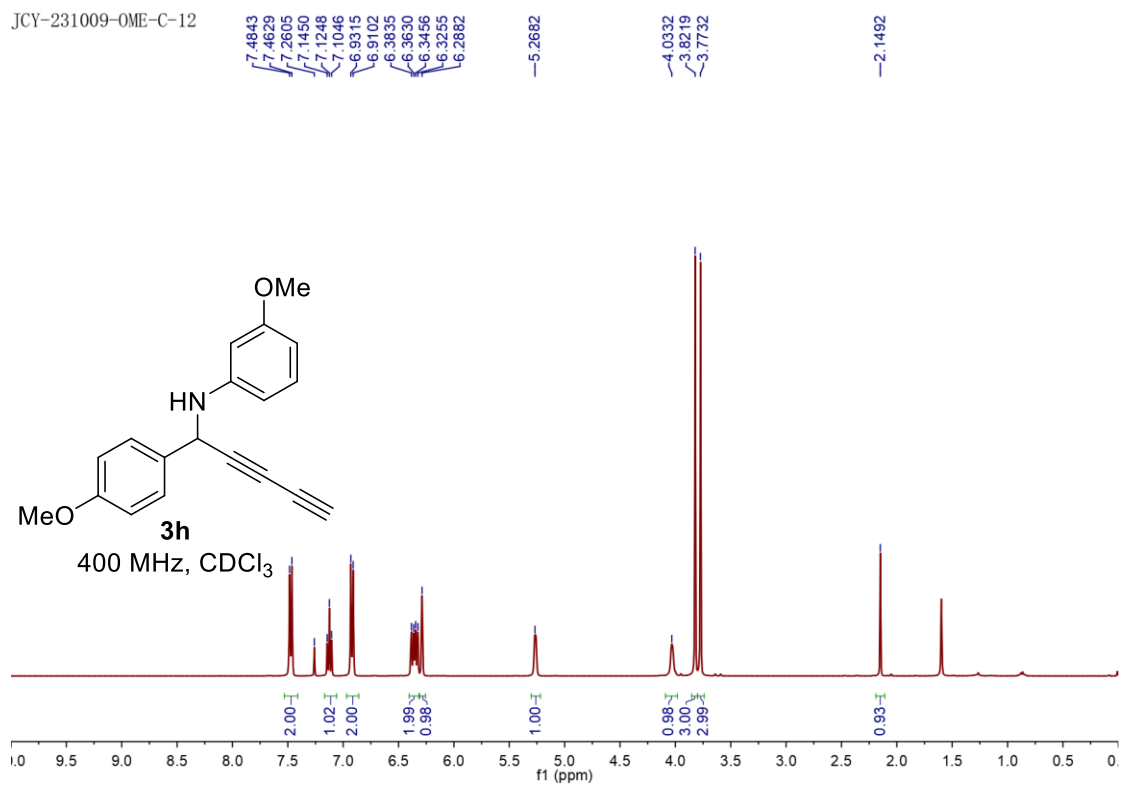


JCY-231119-S-P-C  
single pulse decoupled gated NOE



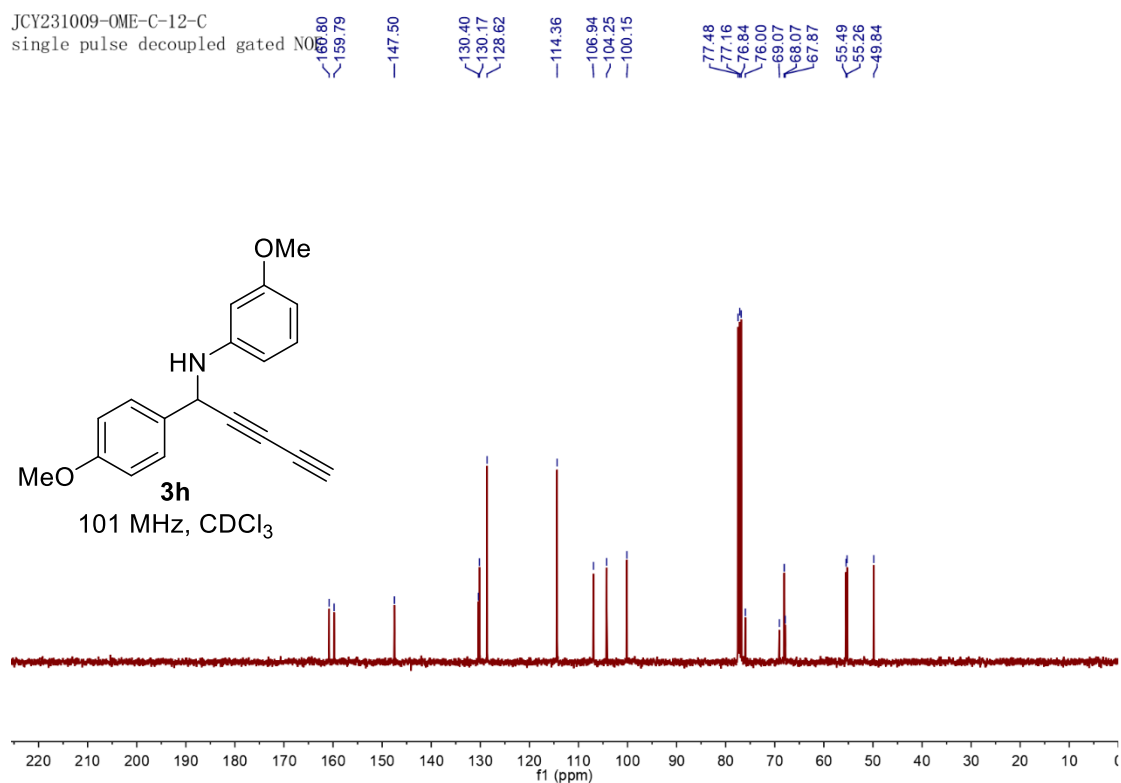


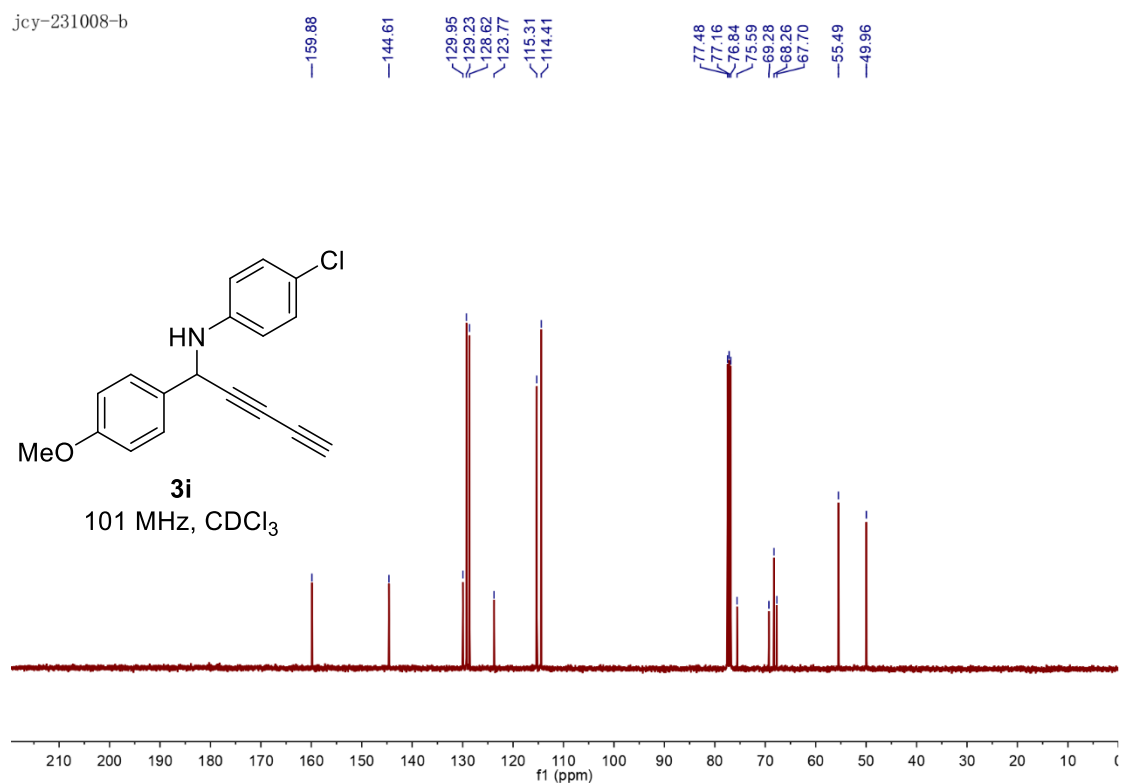
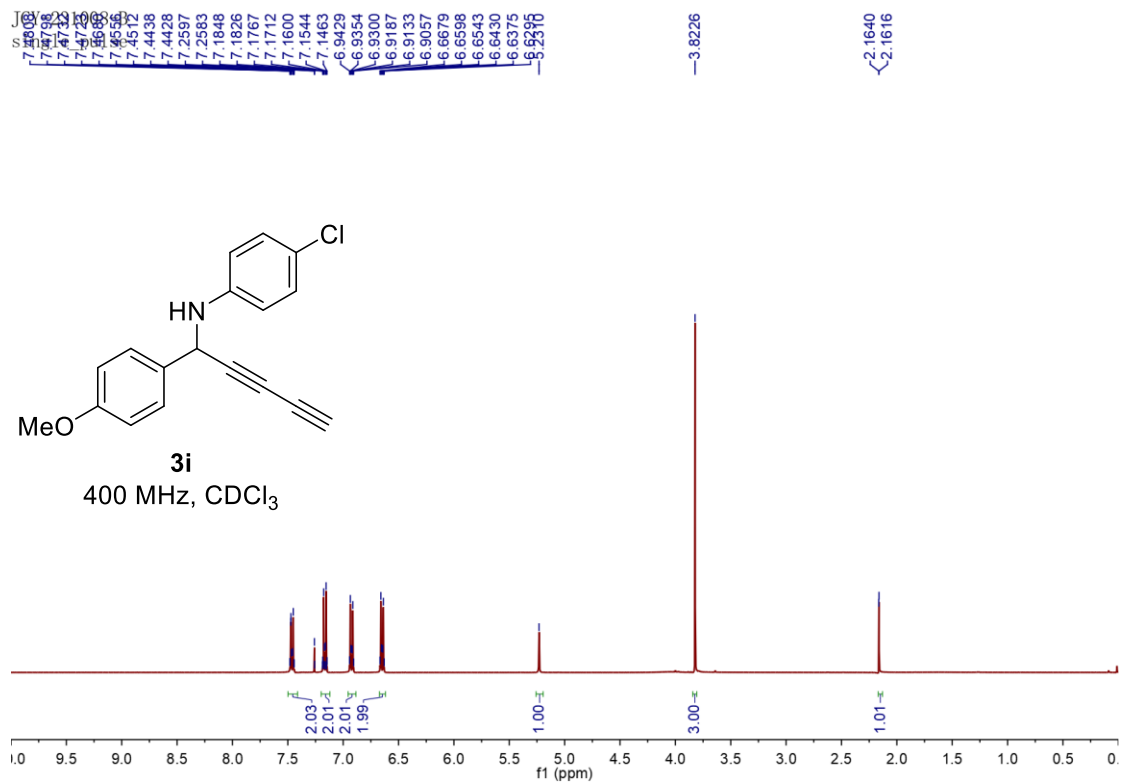
JCY-231009-OME-C-12



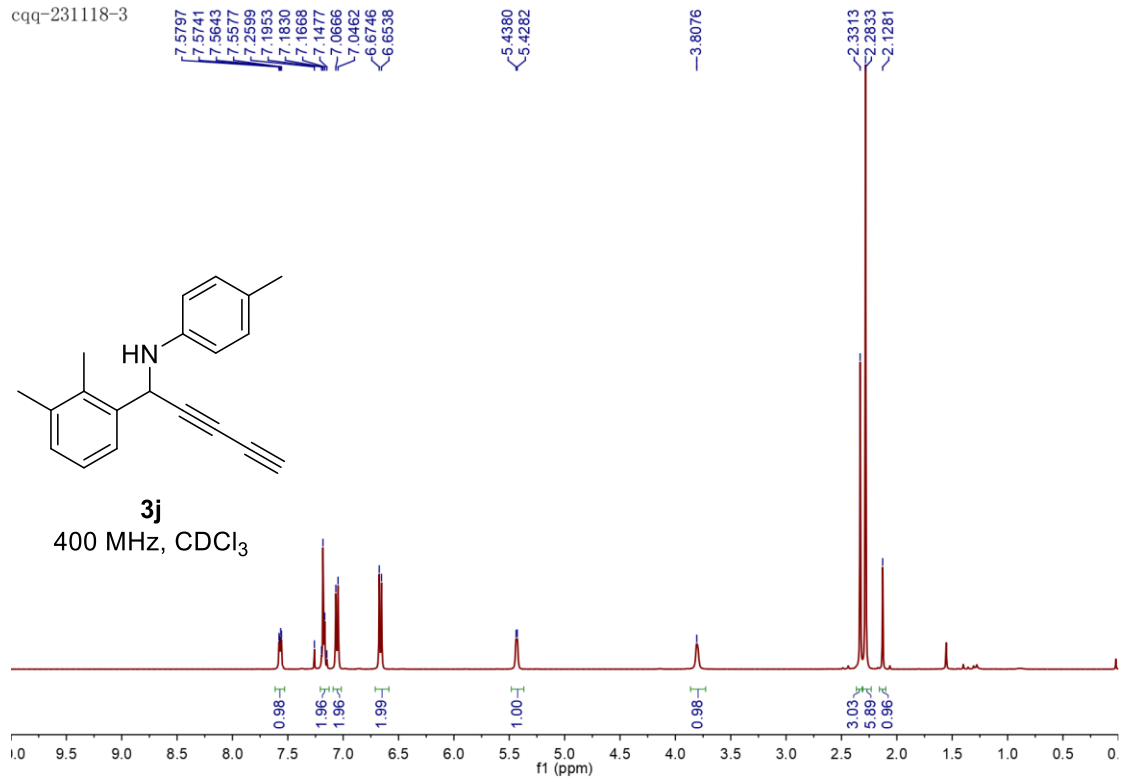
JCY231009-OME-C-12-C

single pulse decoupled gated NOE



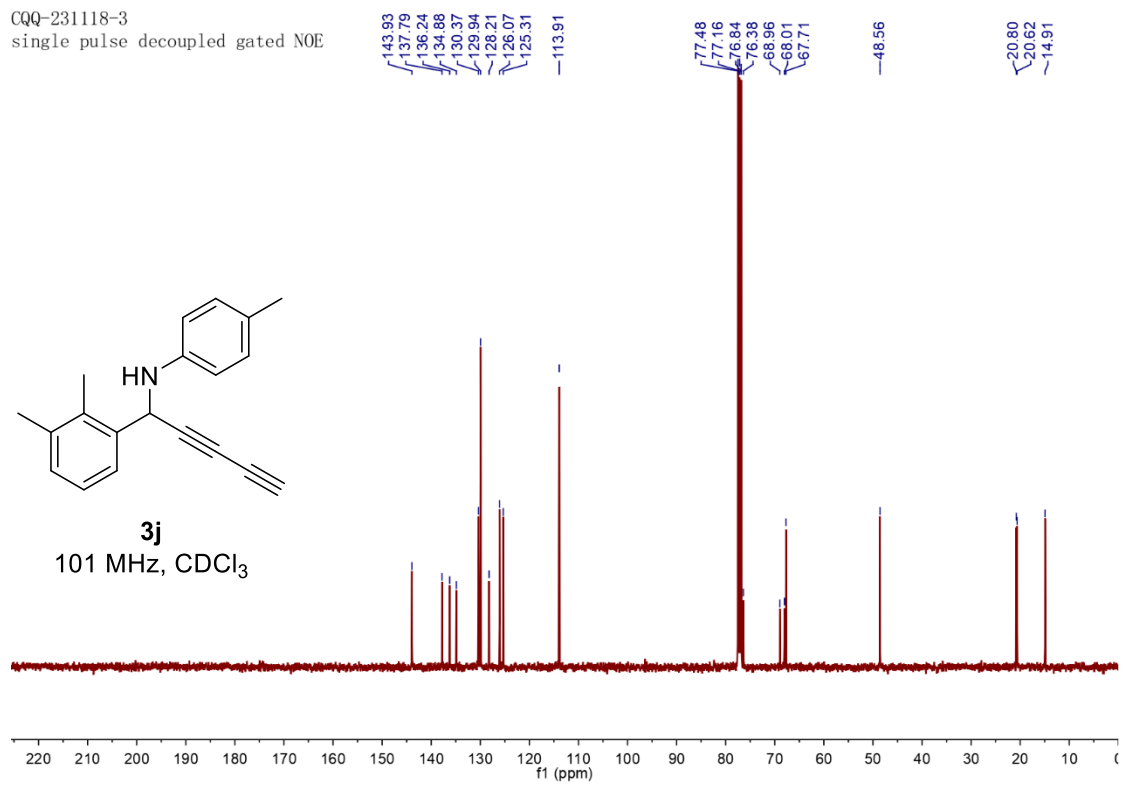


cqq-231118-3

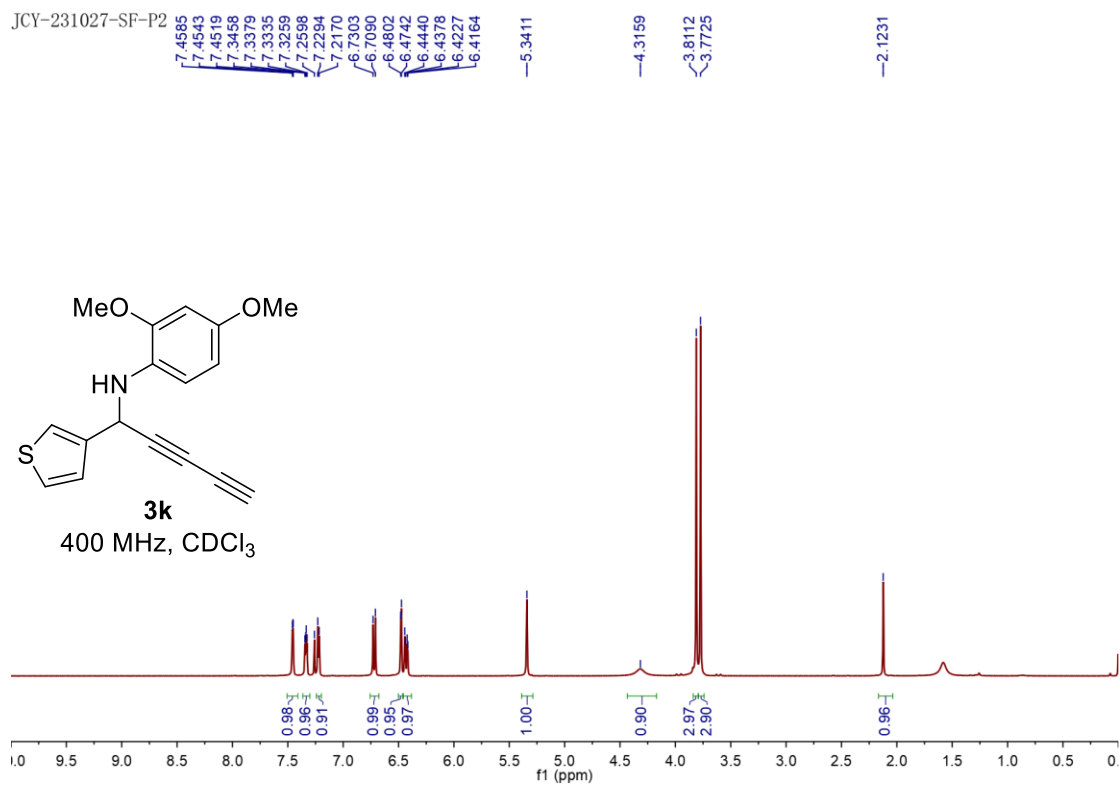


CQQ-231118-3

single pulse decoupled gated NOE

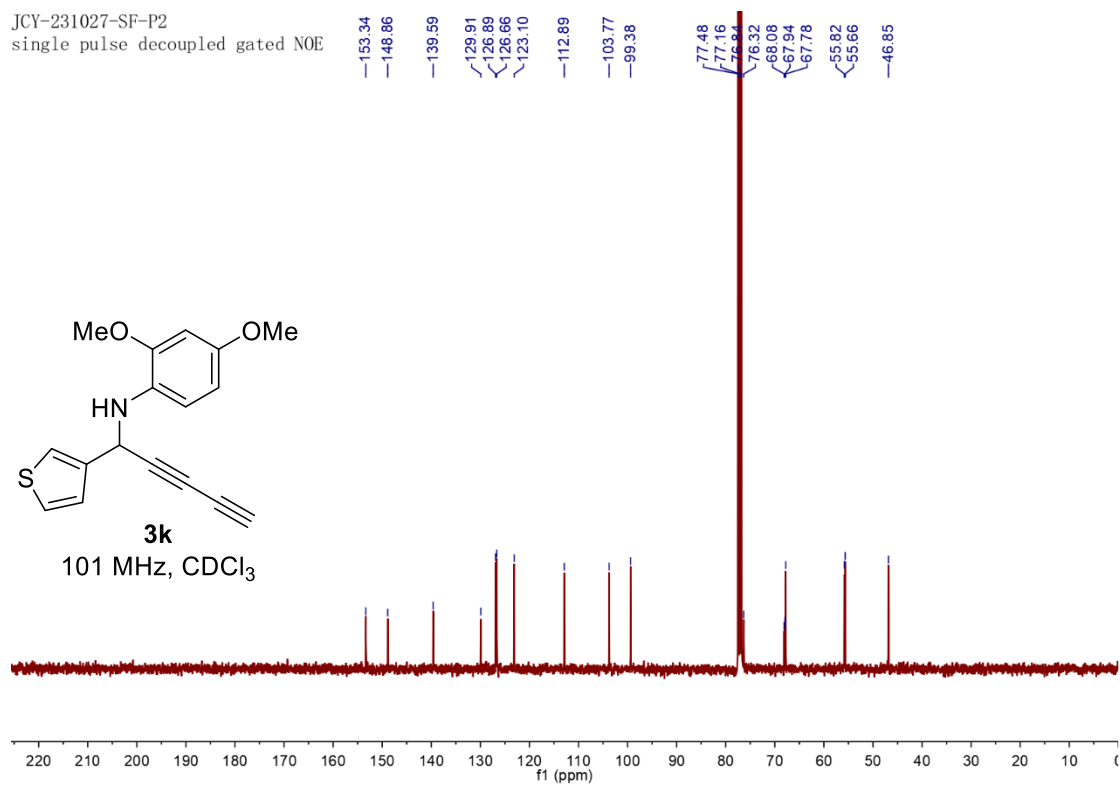


JCY-231027-SF-P2



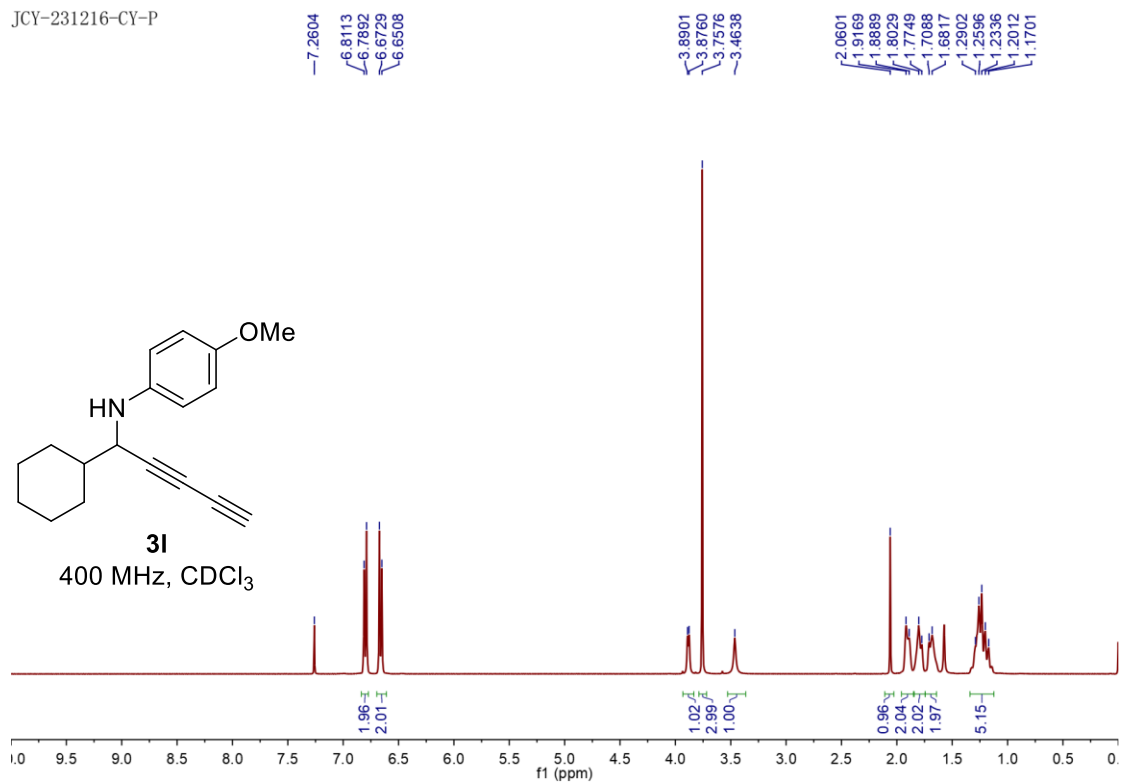
JCY-231027-SF-P2

single pulse decoupled gated NOE



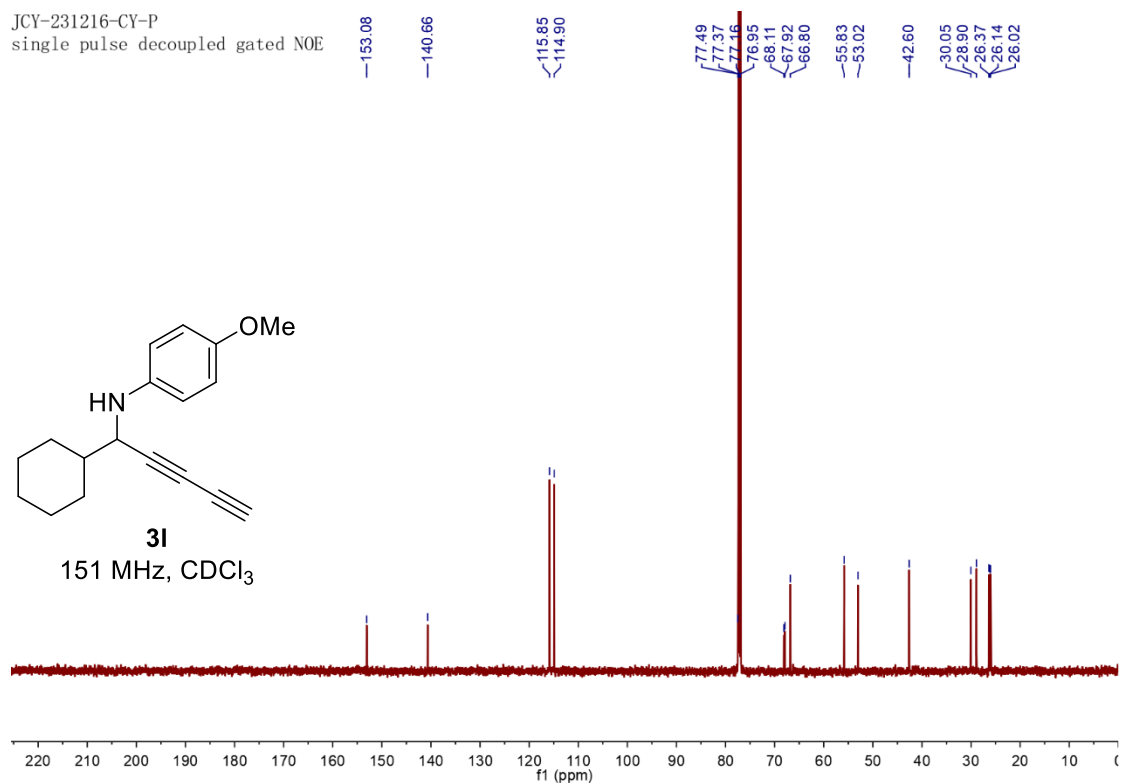


JCY-231216-CY-P

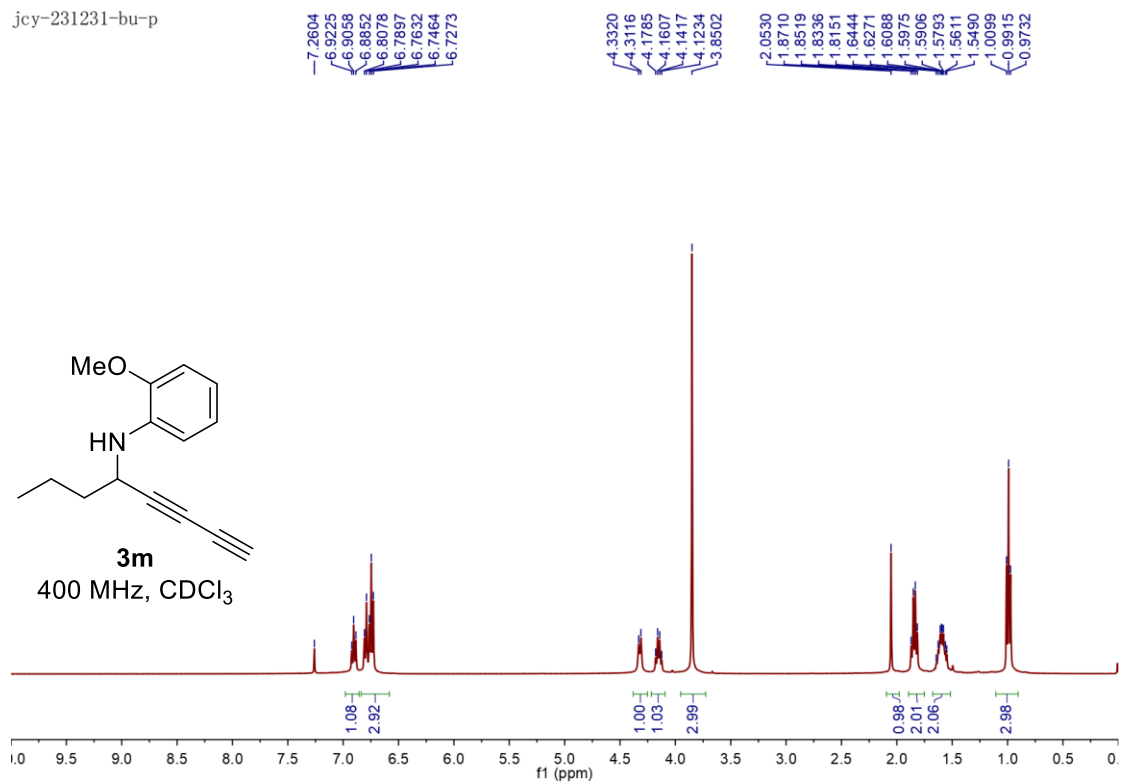


JCY-231216-CY-P

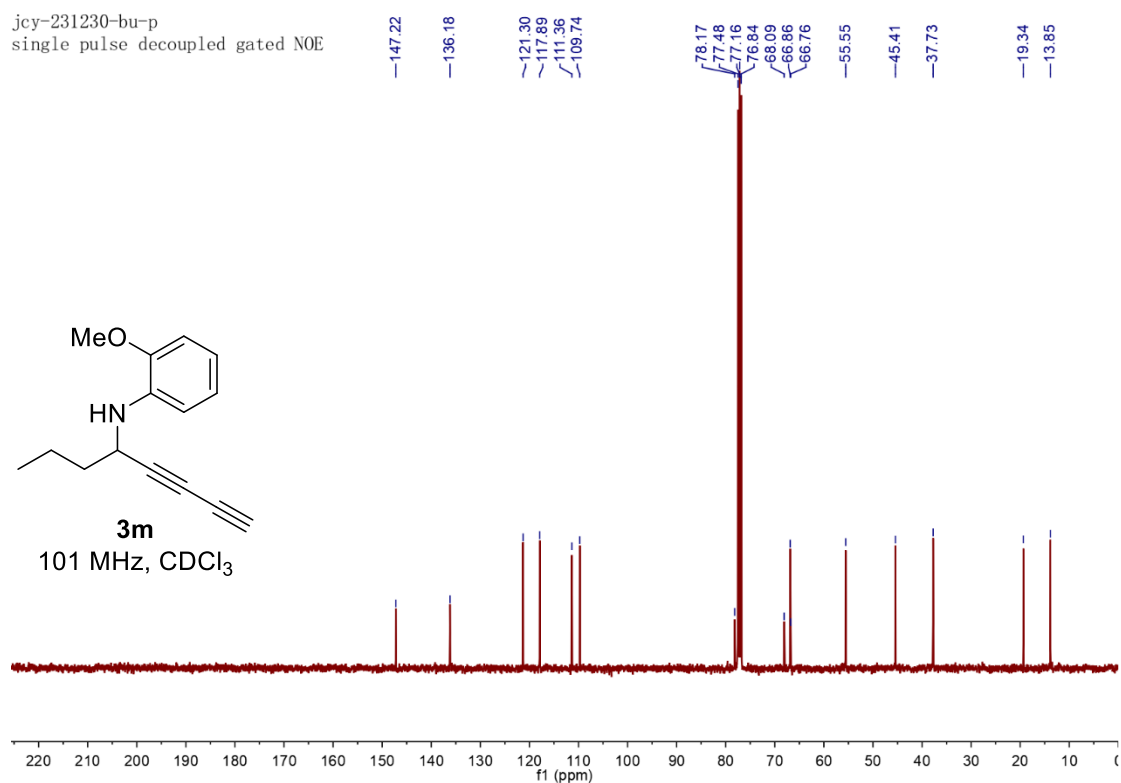
single pulse decoupled gated NOE



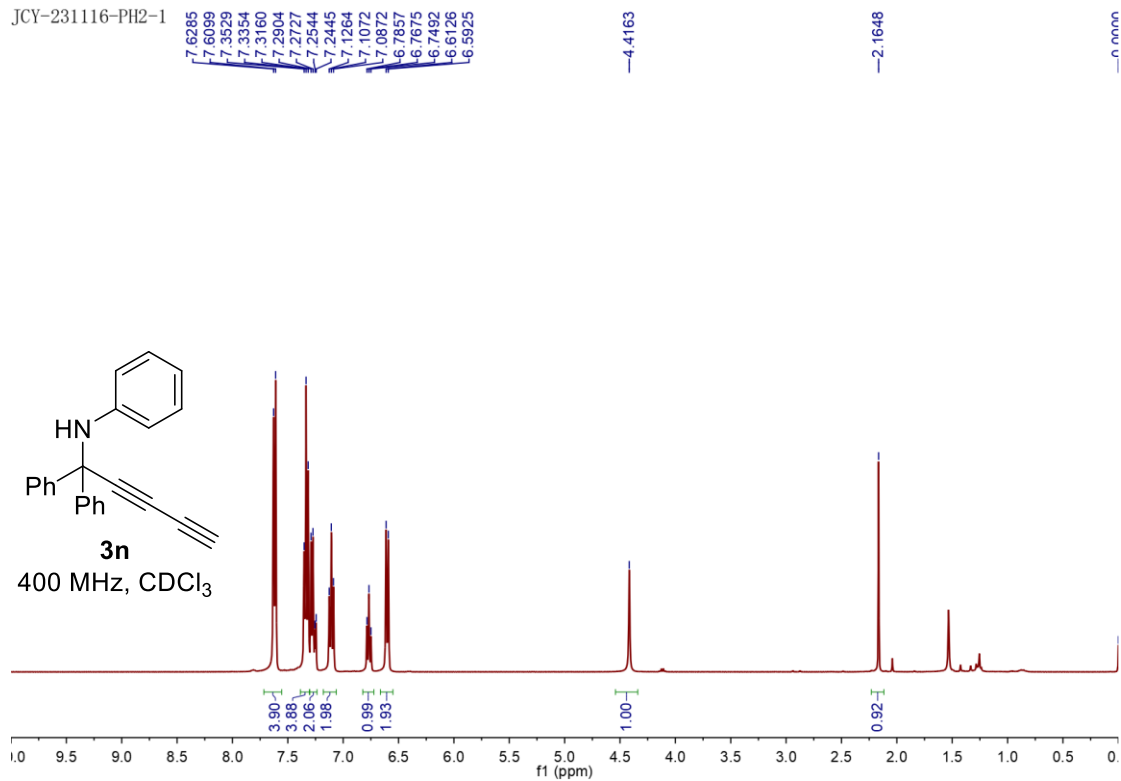
jcy-231231-bu-p



jcy-231230-bu-p  
single pulse decoupled gated NOE

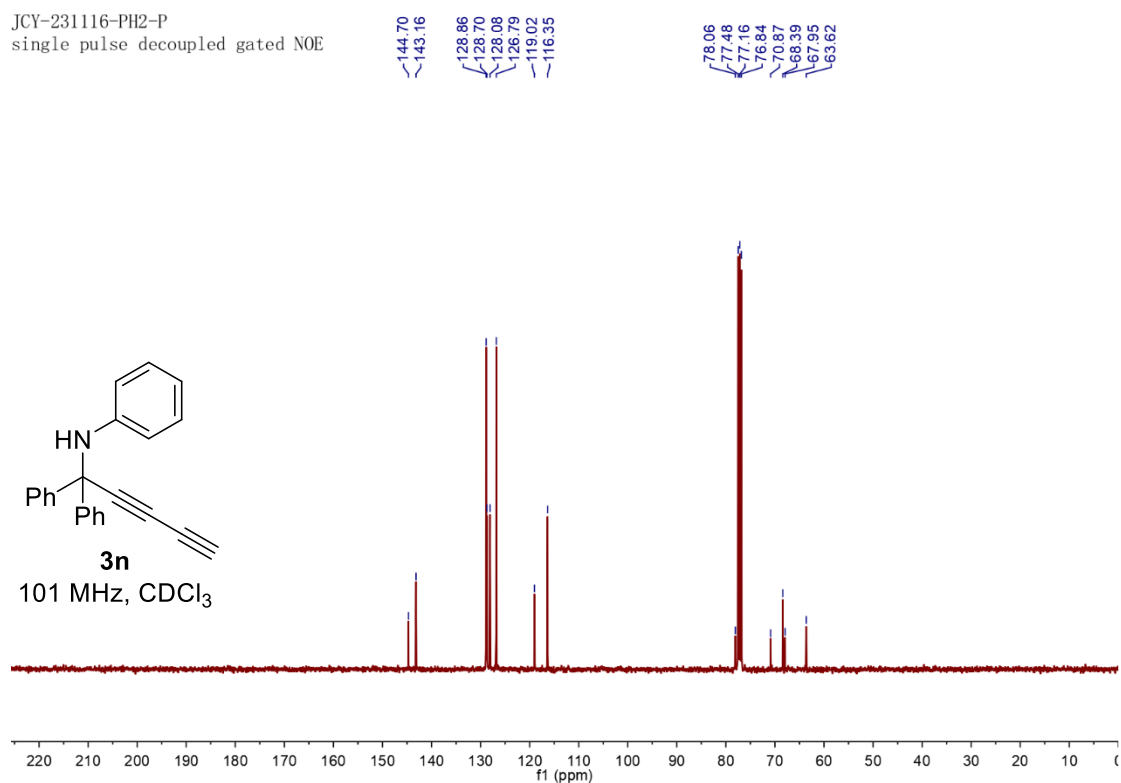


JCY-231116-PH2-1

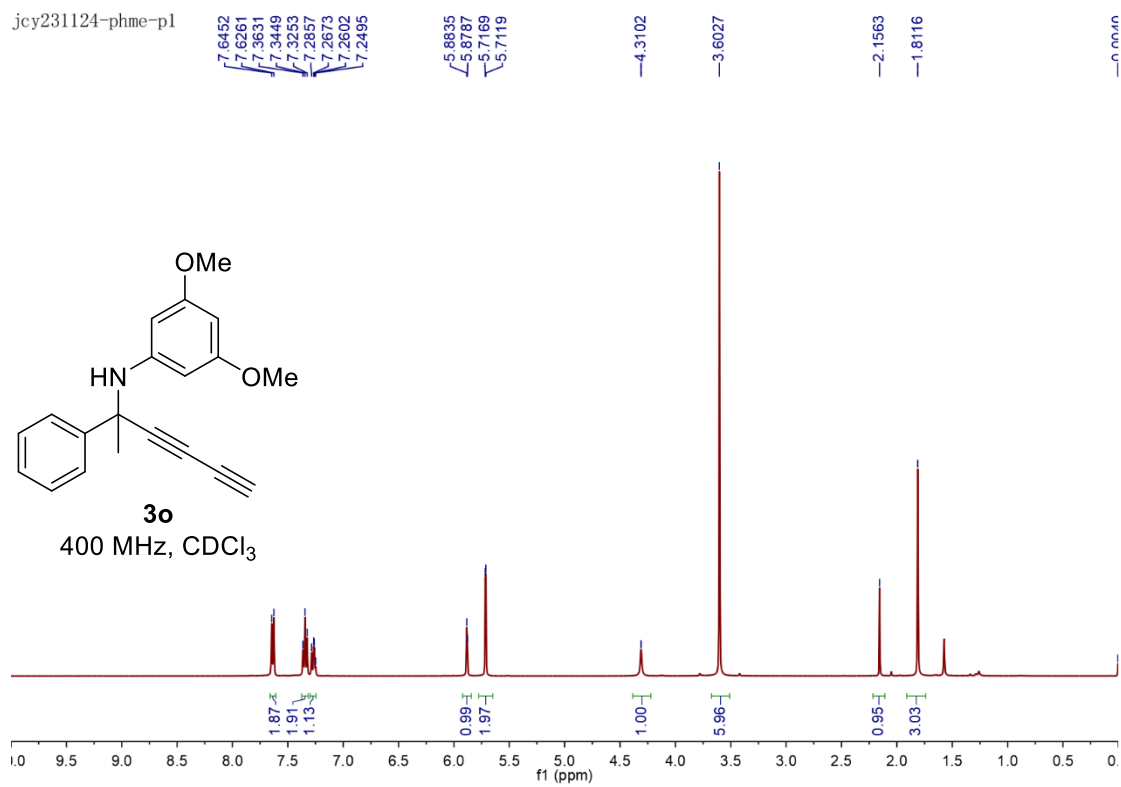


JCY-231116-PH2-P

single pulse decoupled gated NOE

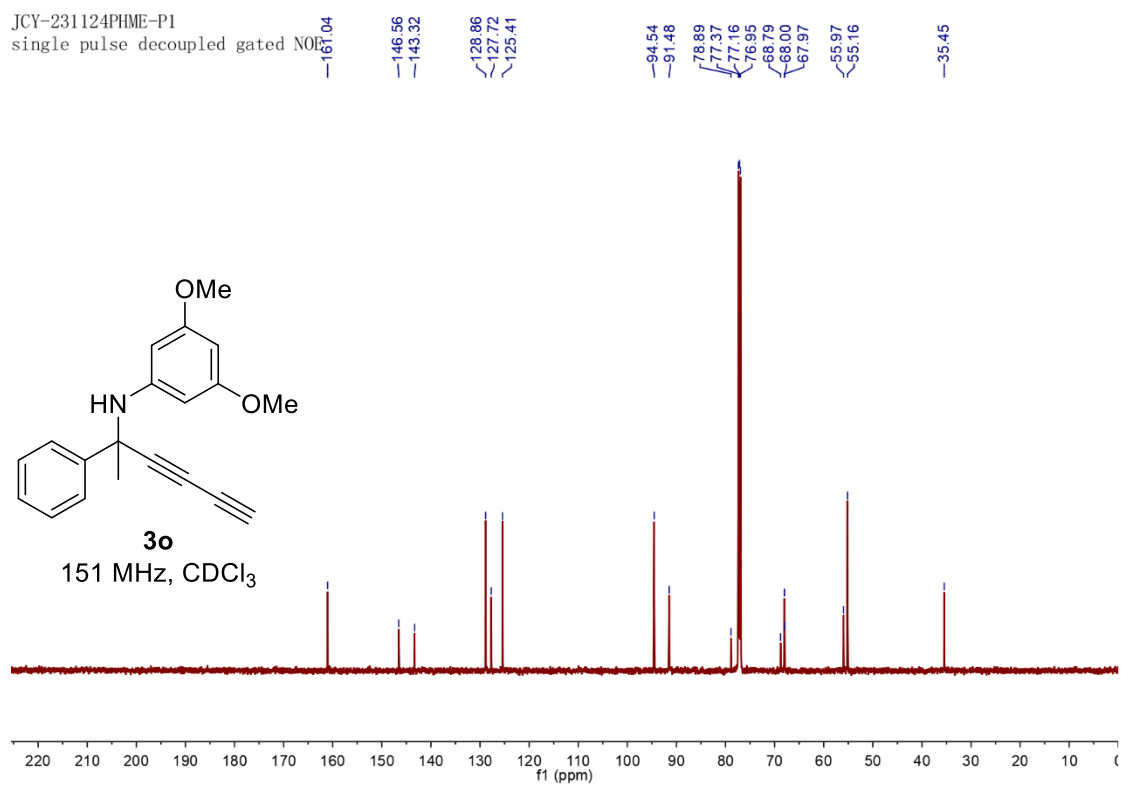


jcy231124-phme-p1

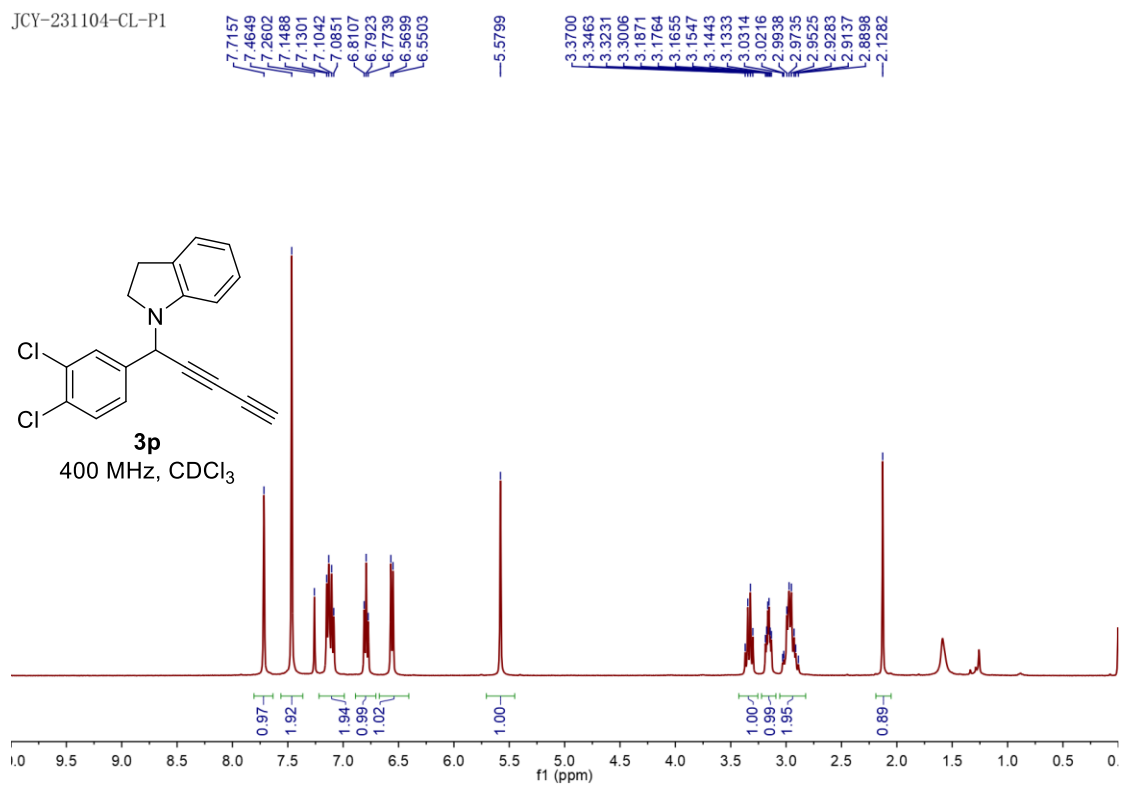


JCY-231124PHME-P1

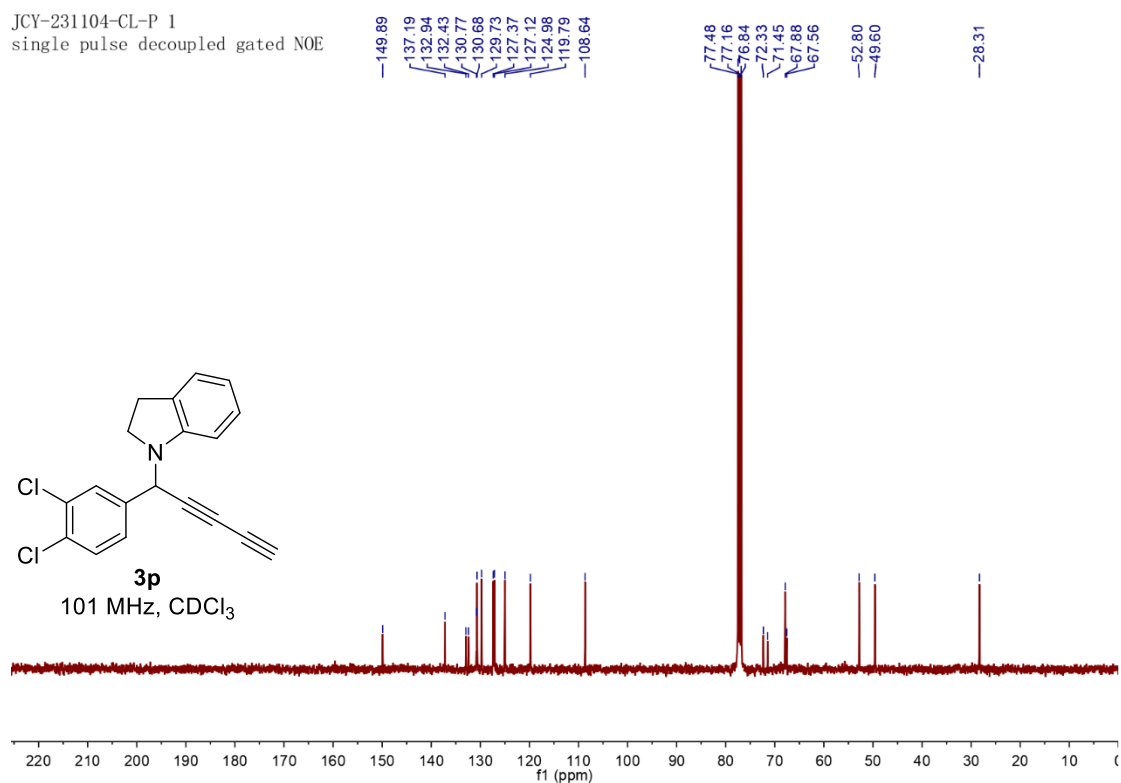
single pulse decoupled gated NMR



JCY-231104-CL-P1



JCY-231104-CL-P 1  
single pulse decoupled gated NOE



JCY-231018-A-P  
single\_pulse

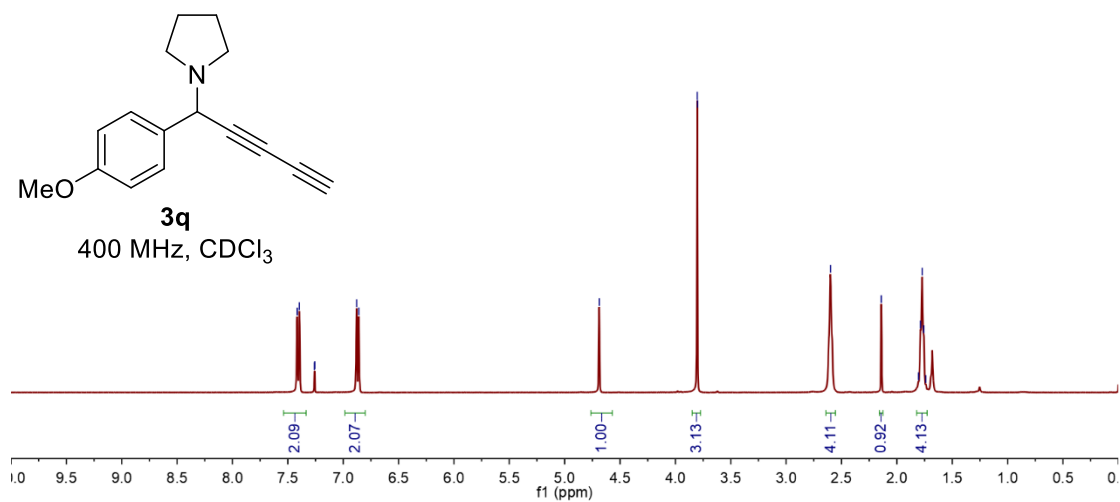
7.4152  
7.3860  
7.2597  
7.2566  
6.8780  
6.8598

4.6682

3.8031  
3.8003

2.5998

2.1407  
1.8047  
1.7863  
1.7716  
1.7572  
1.7386



JCY-231018-A-P

159.3250

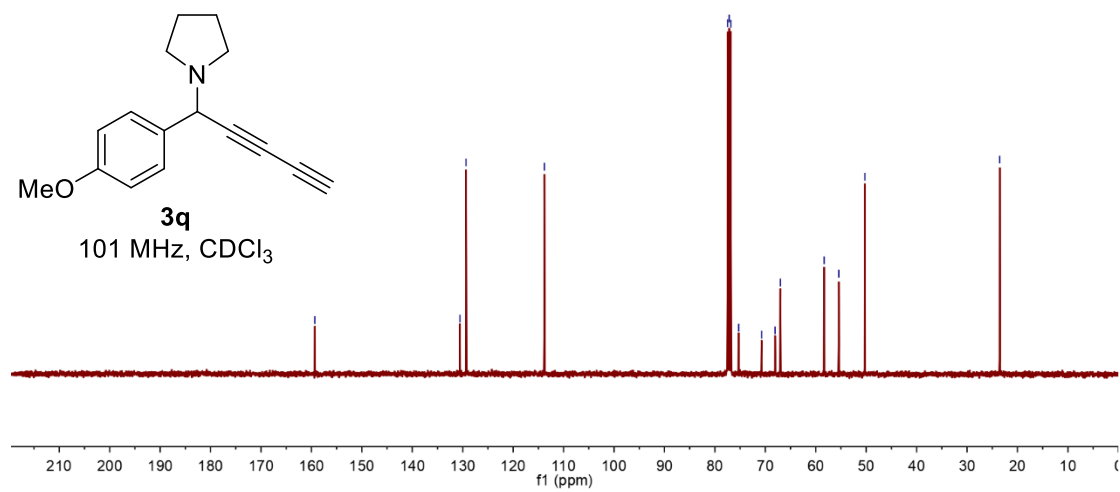
130.5522  
129.3484

113.8106

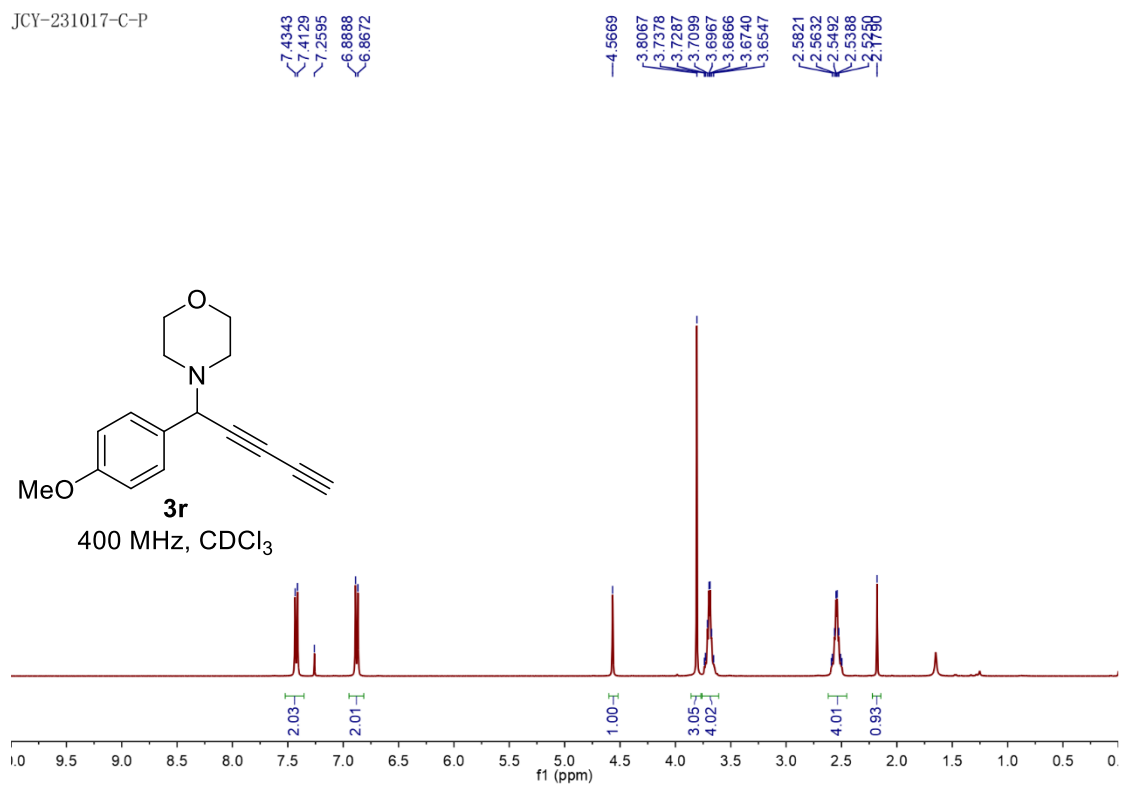
77.4777  
77.1601  
76.8425  
75.2884  
70.7226  
68.0656  
67.0115

56.3371  
55.4250  
50.2545

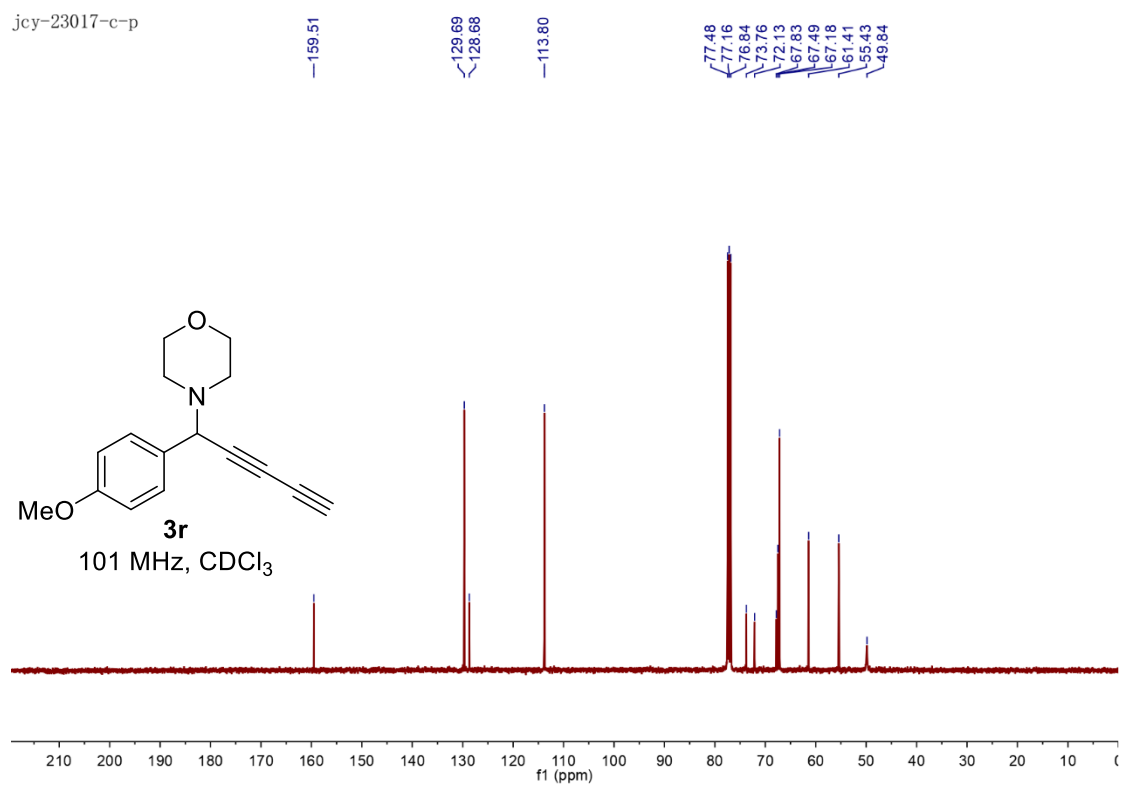
23.5212



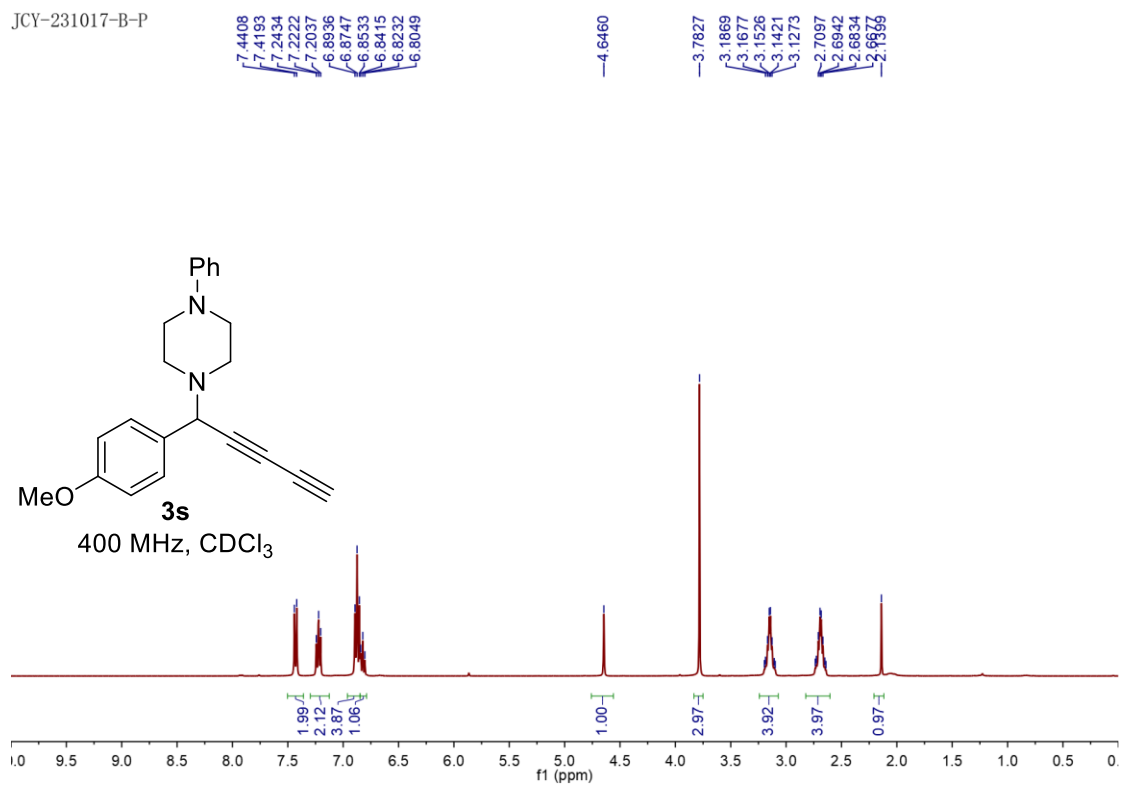
JCY-231017-C-P



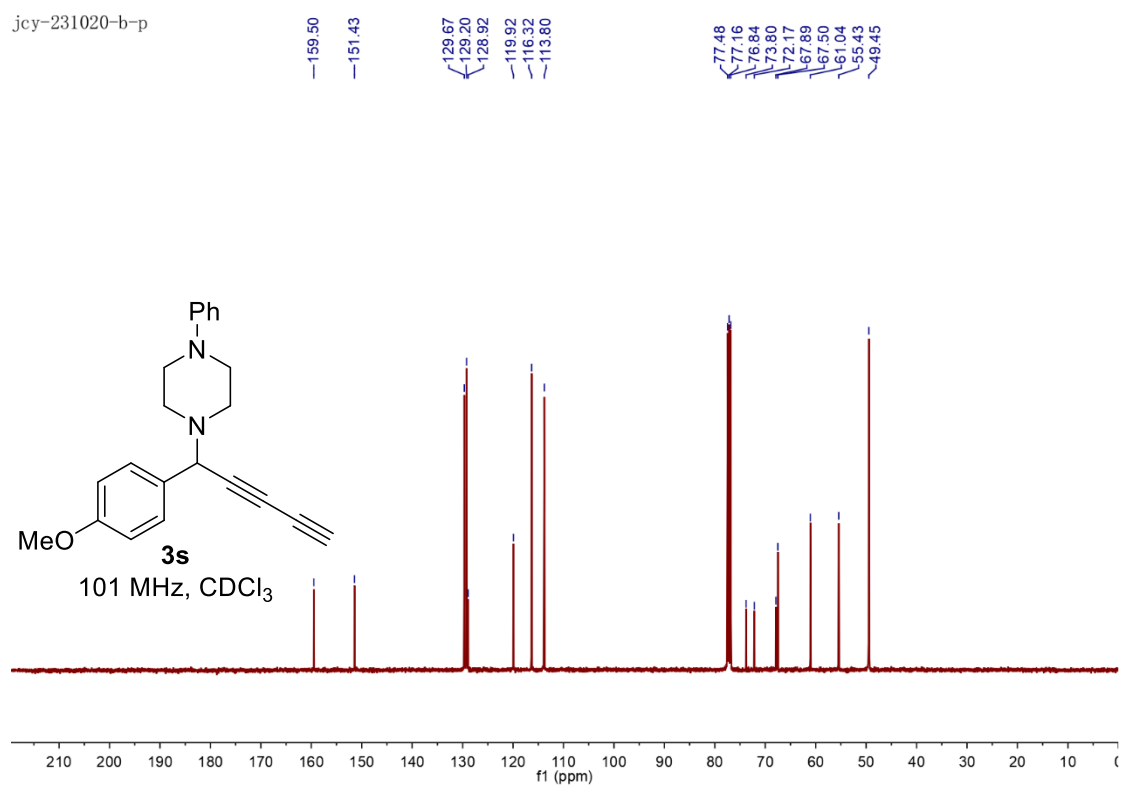
jcy-23017-c-p



JCY-231017-B-P

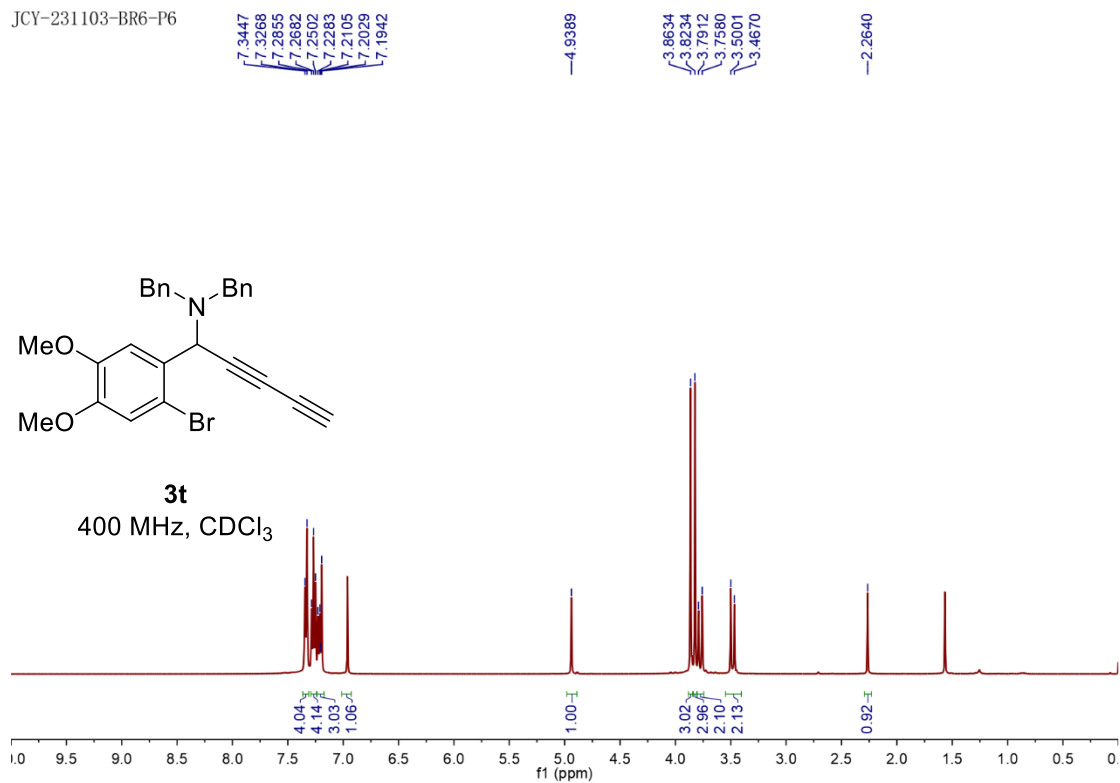


jcy-231020-b-p



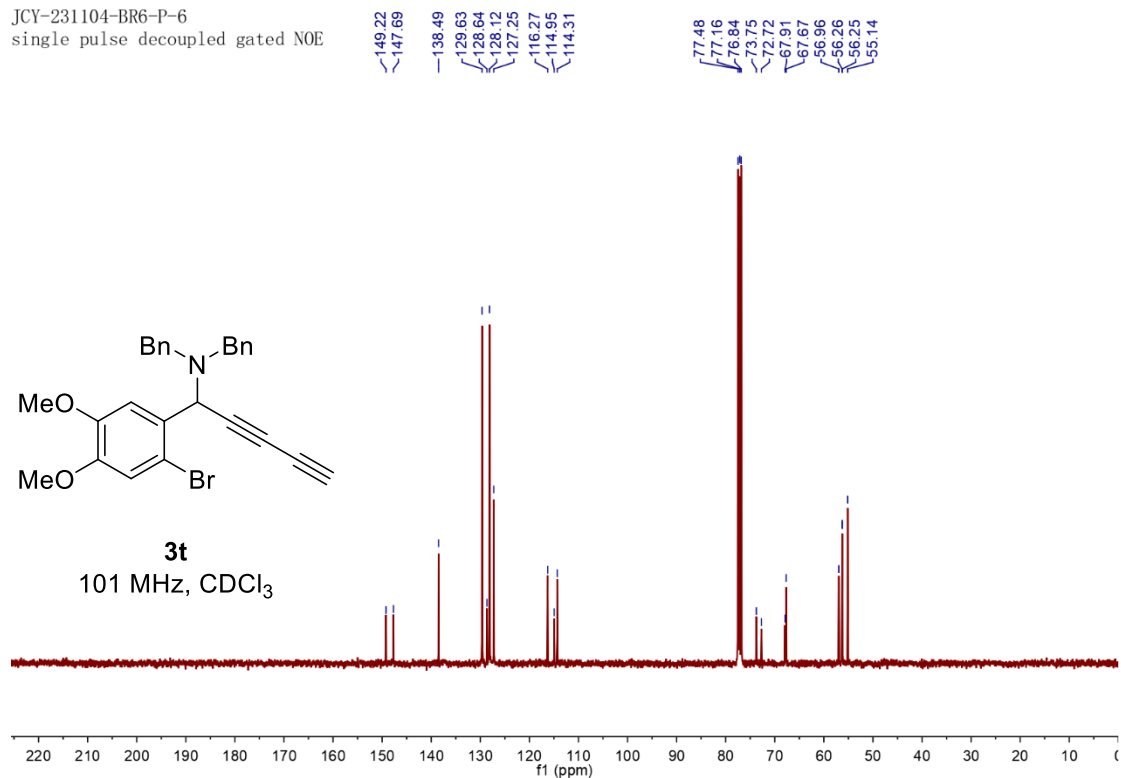


JCY-231103-BR6-P6



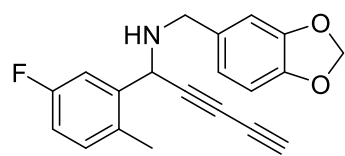
JCY-231104-BR6-P-6

single pulse decoupled gated NOE

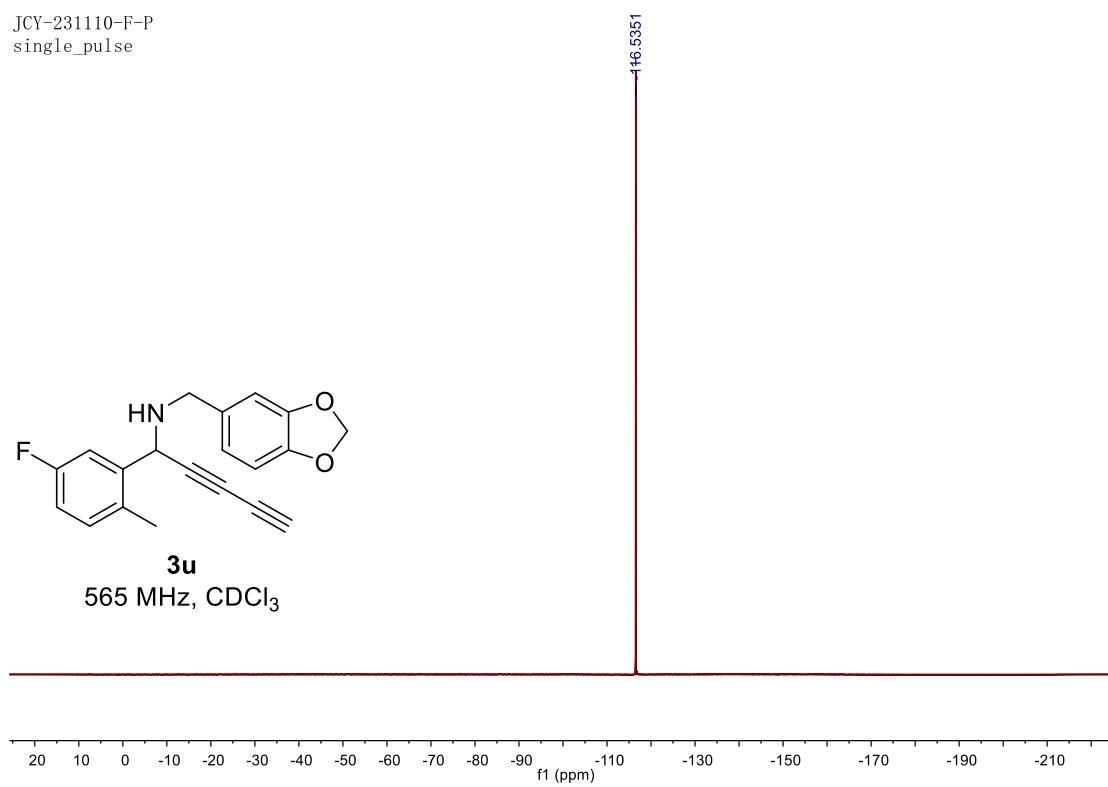


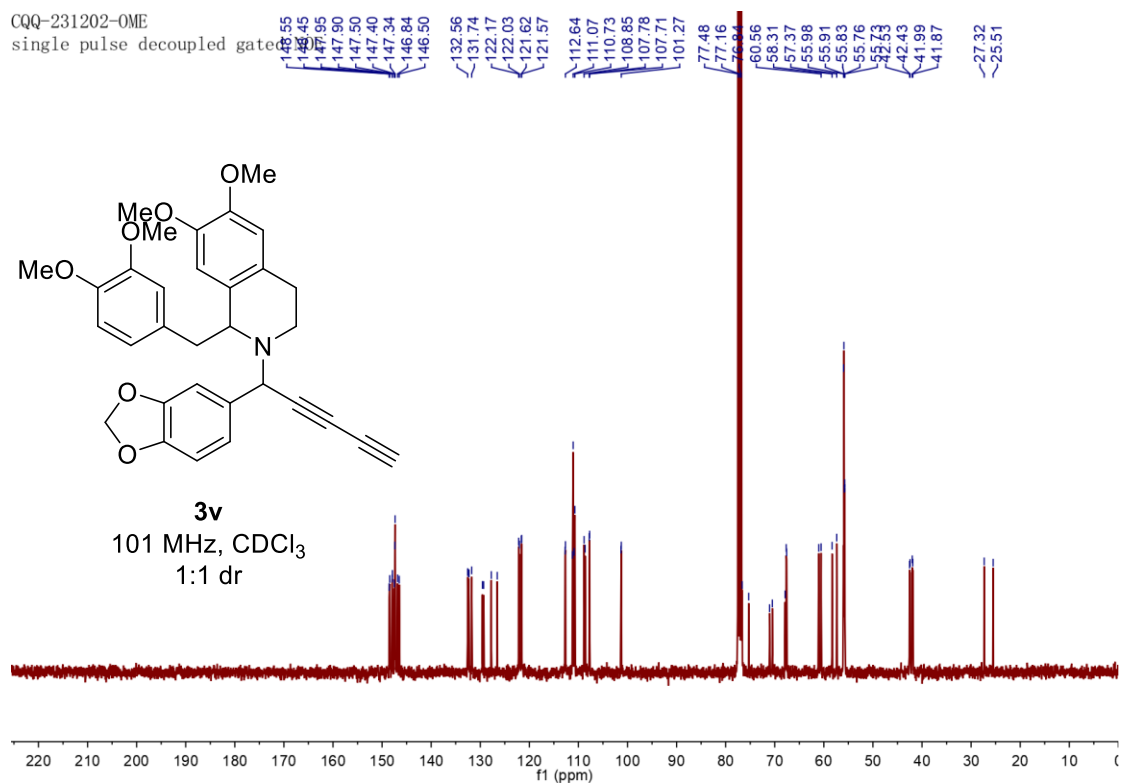
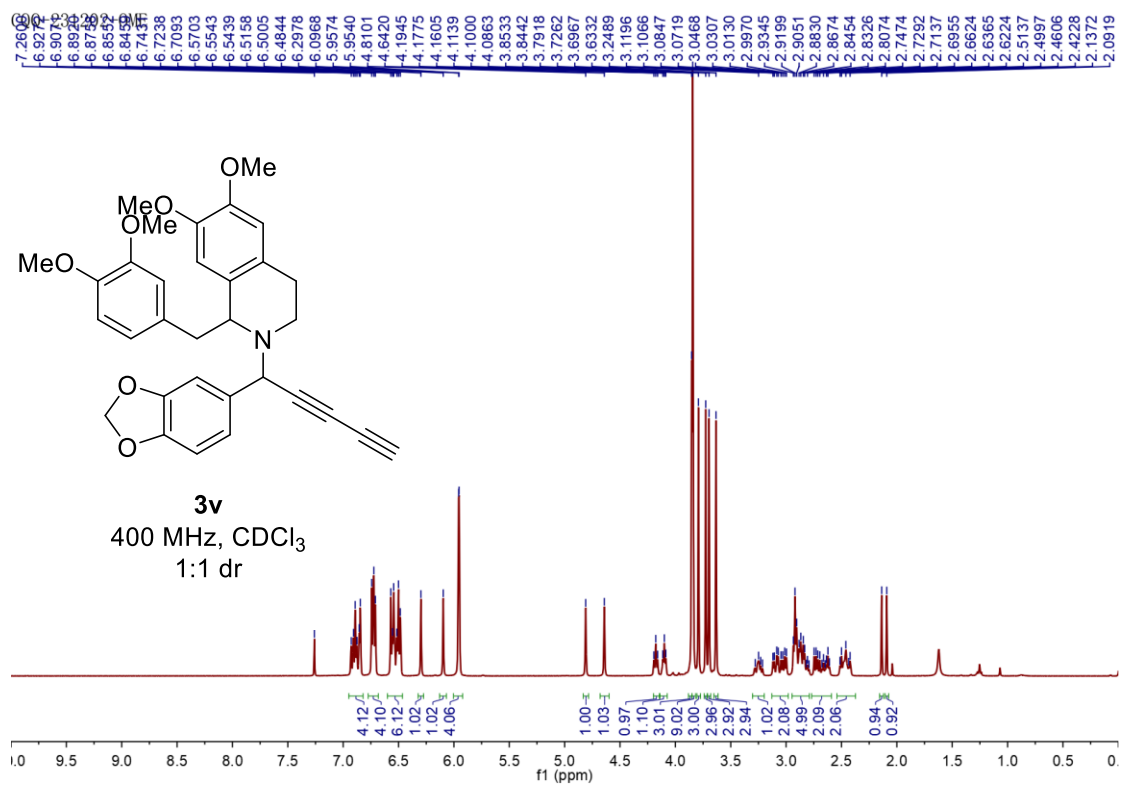


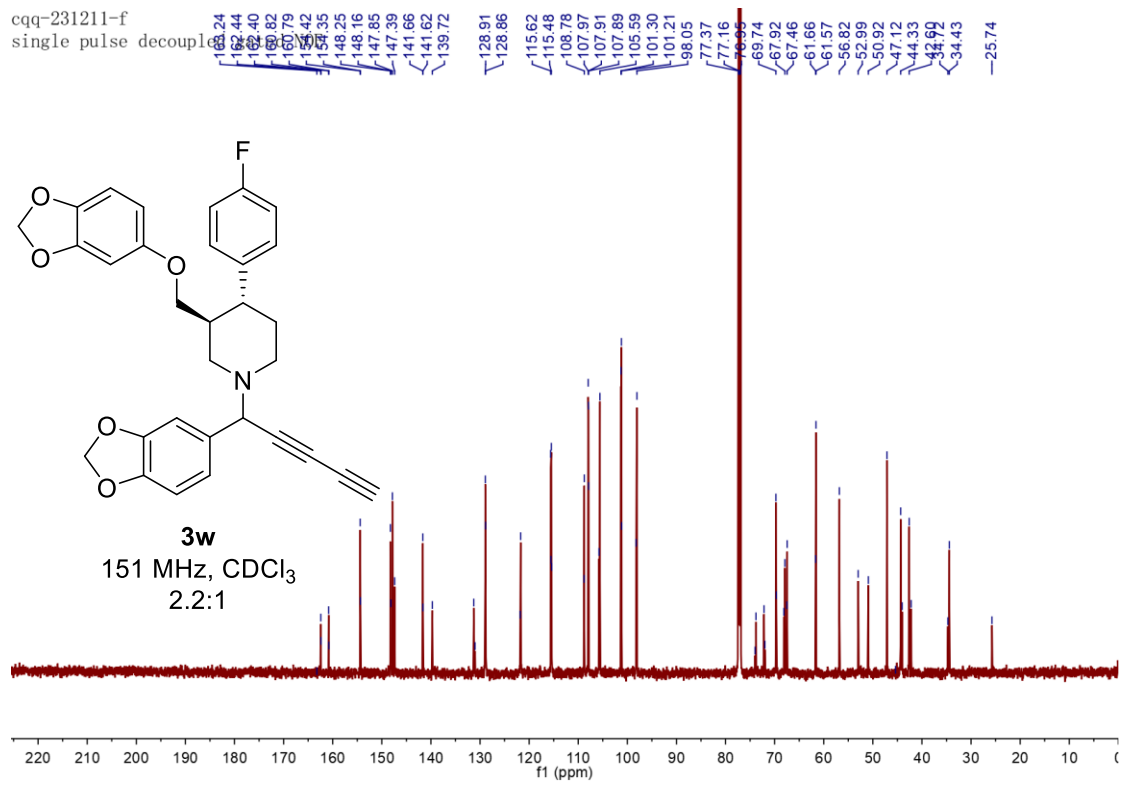
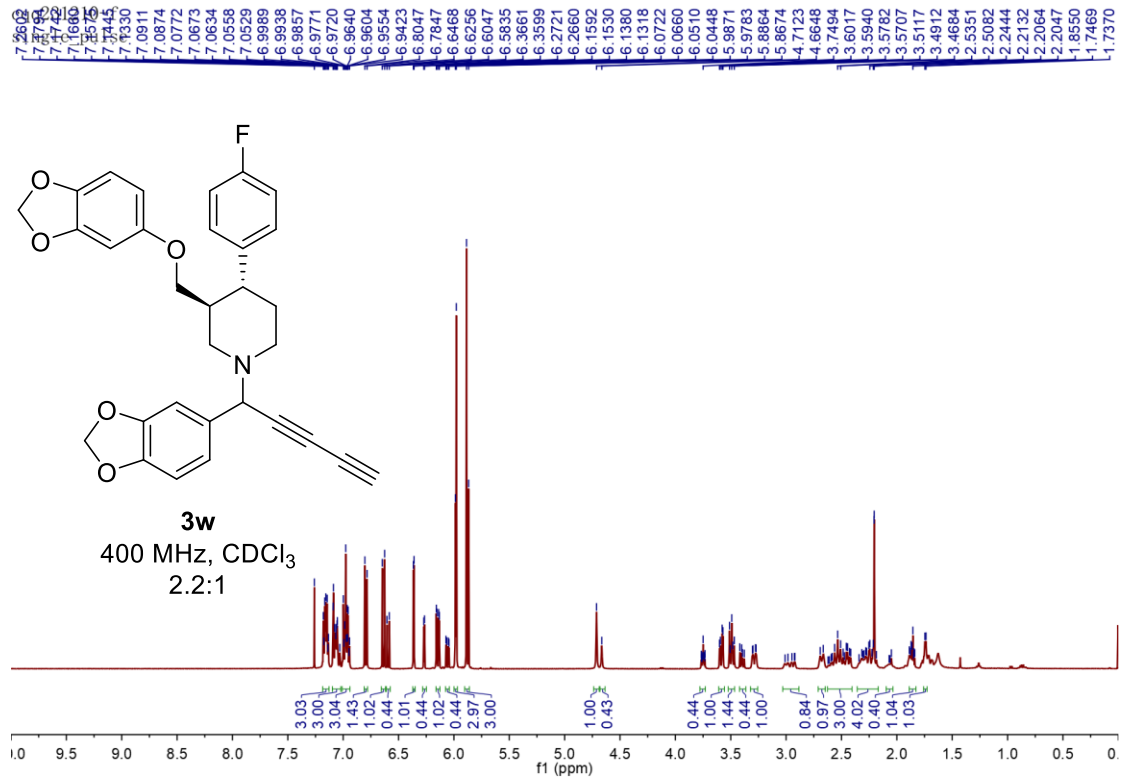
JCY-231110-F-P  
single\_pulse



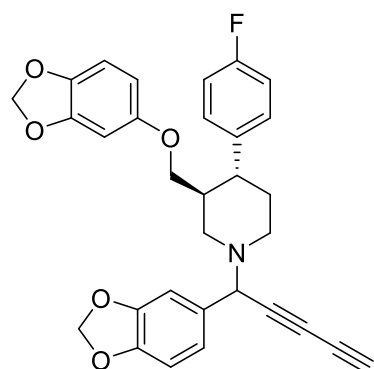
**3u**  
565 MHz, CDCl<sub>3</sub>



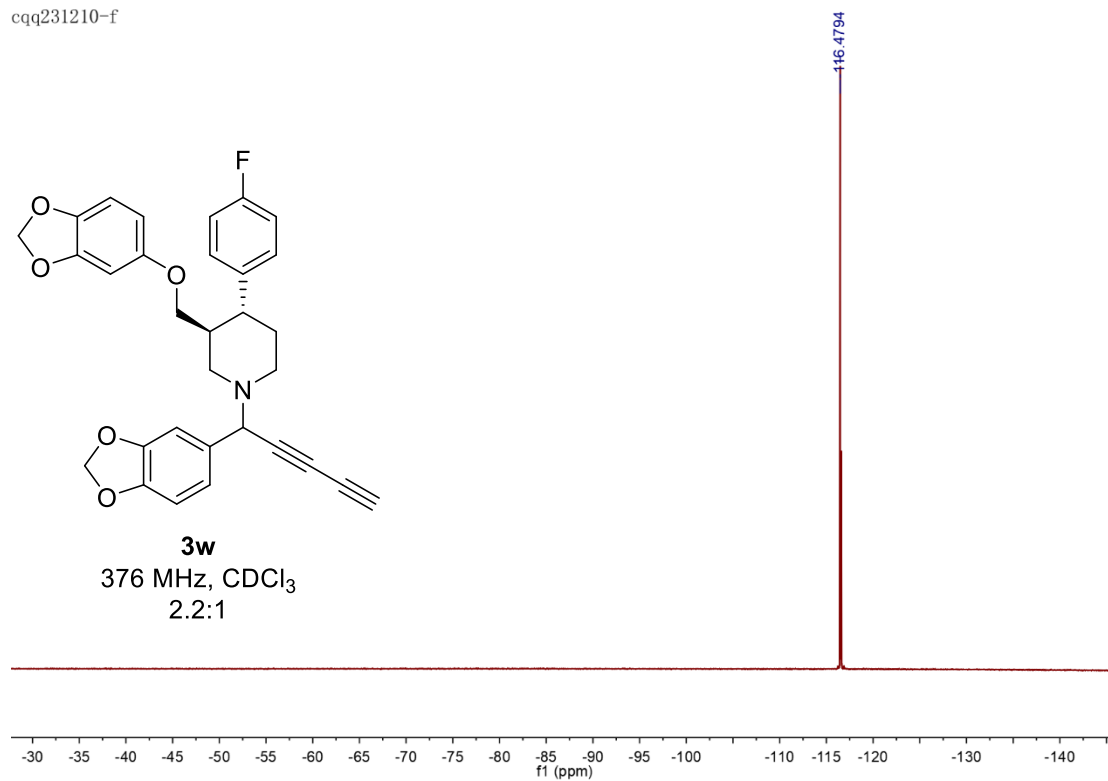




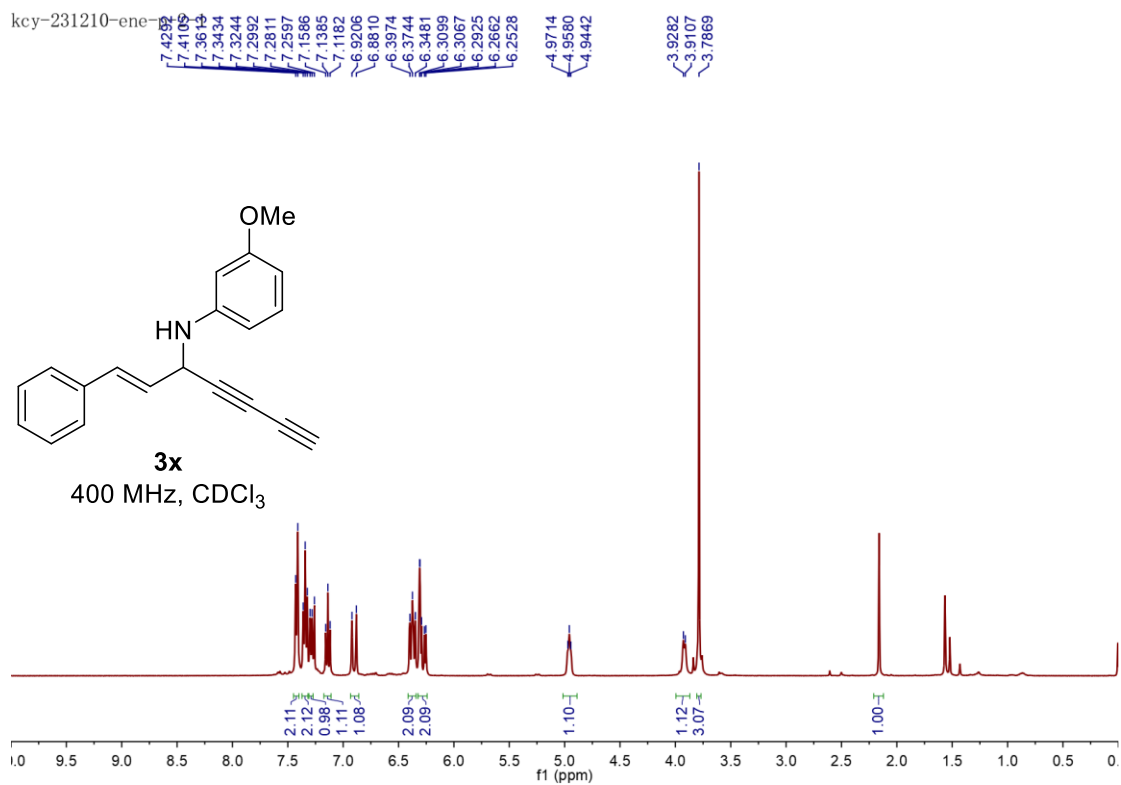
cqq231210-f



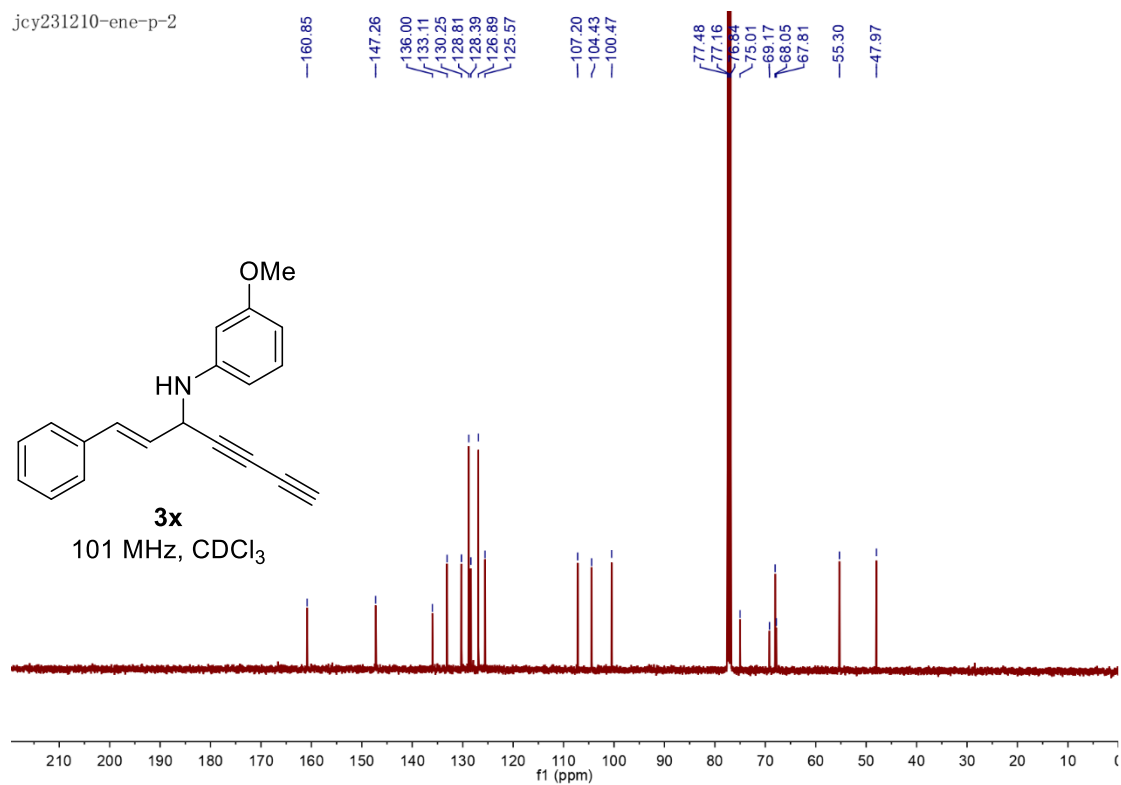
**3w**  
376 MHz, CDCl<sub>3</sub>  
2.2:1



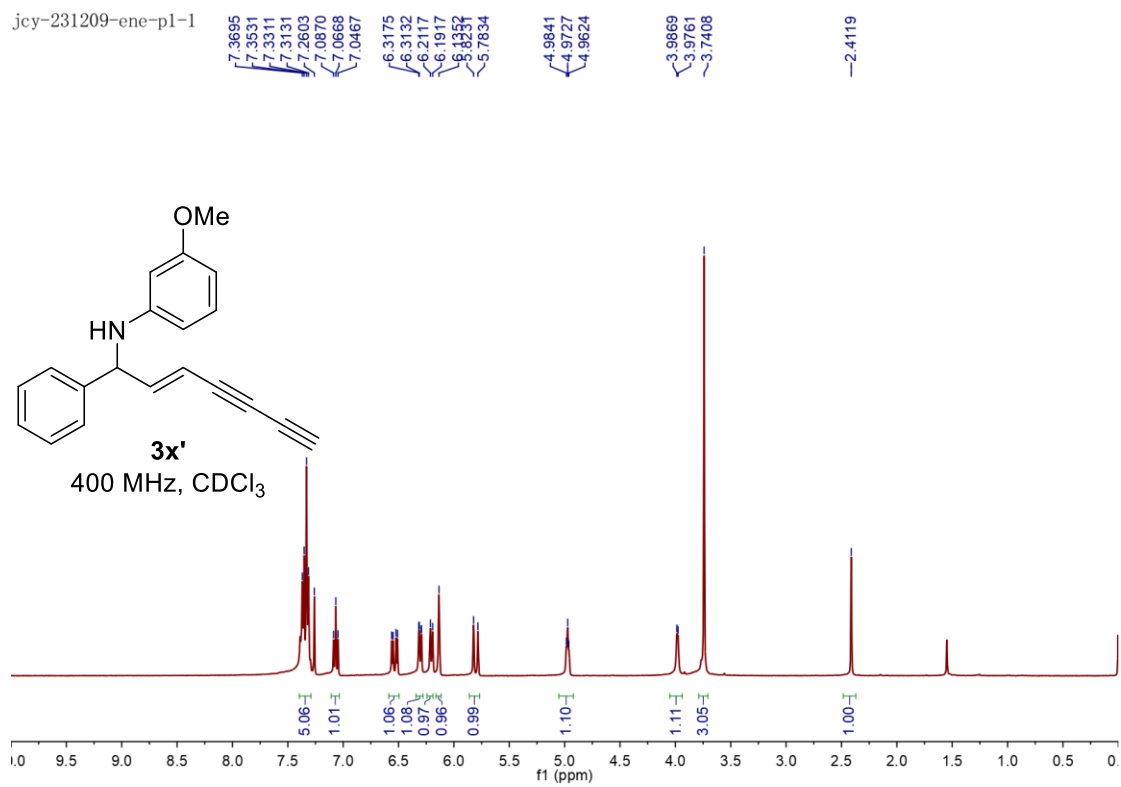
key-231210-ene



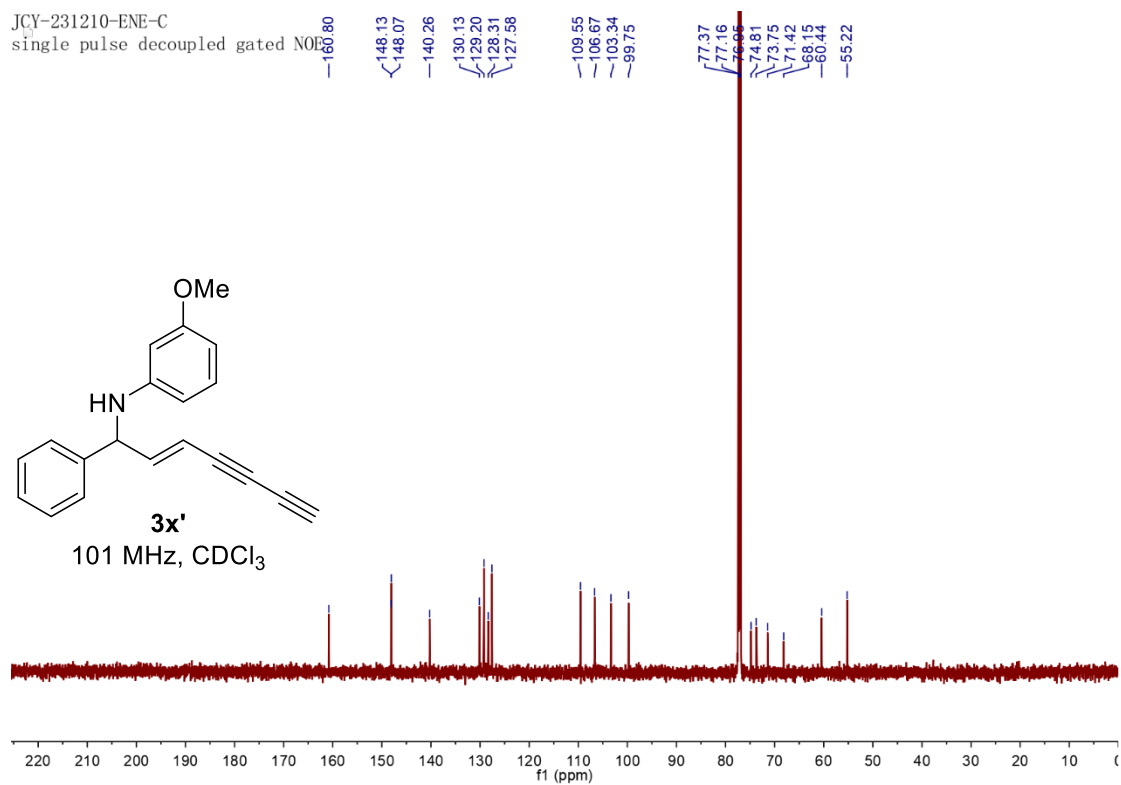
jcy231210-ene-p-2



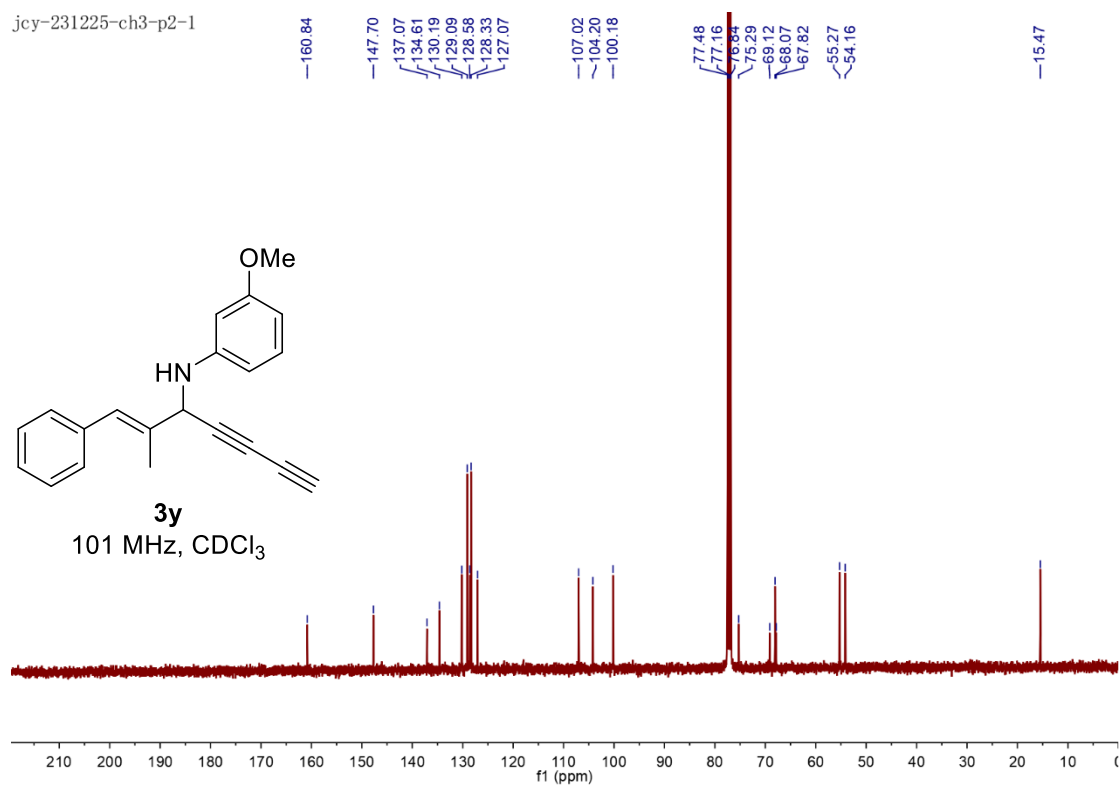
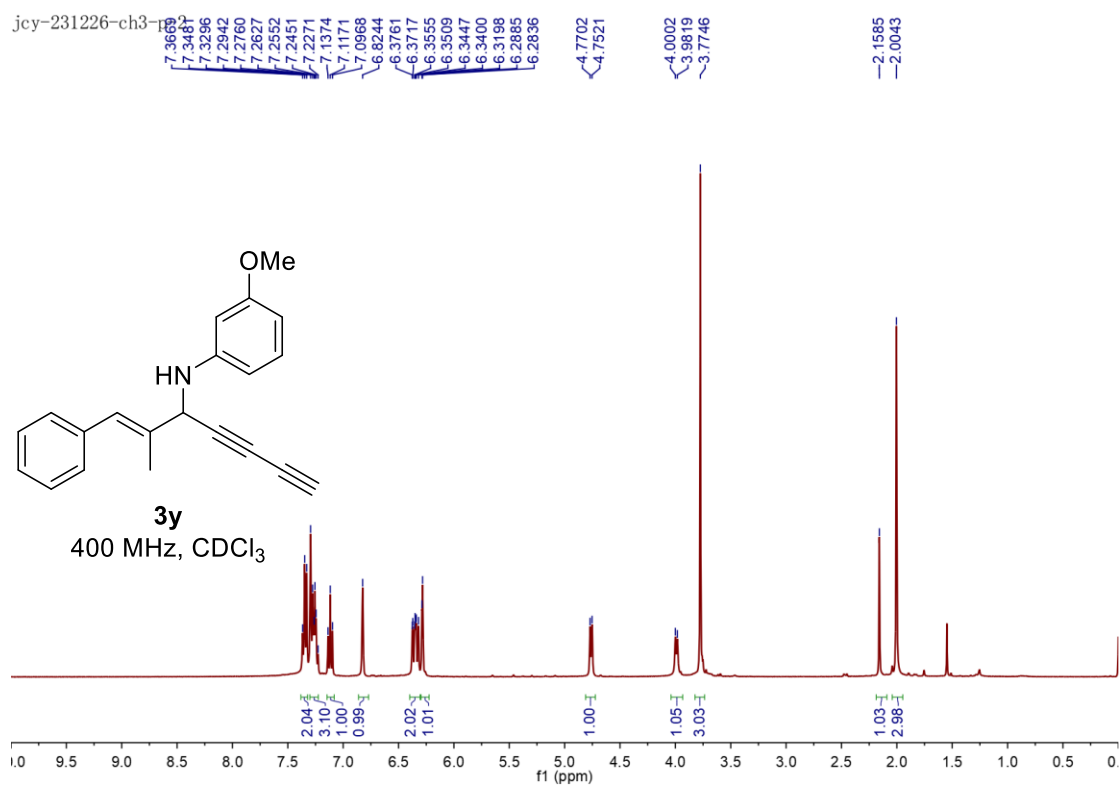
jcy-231209-ene-pl-1



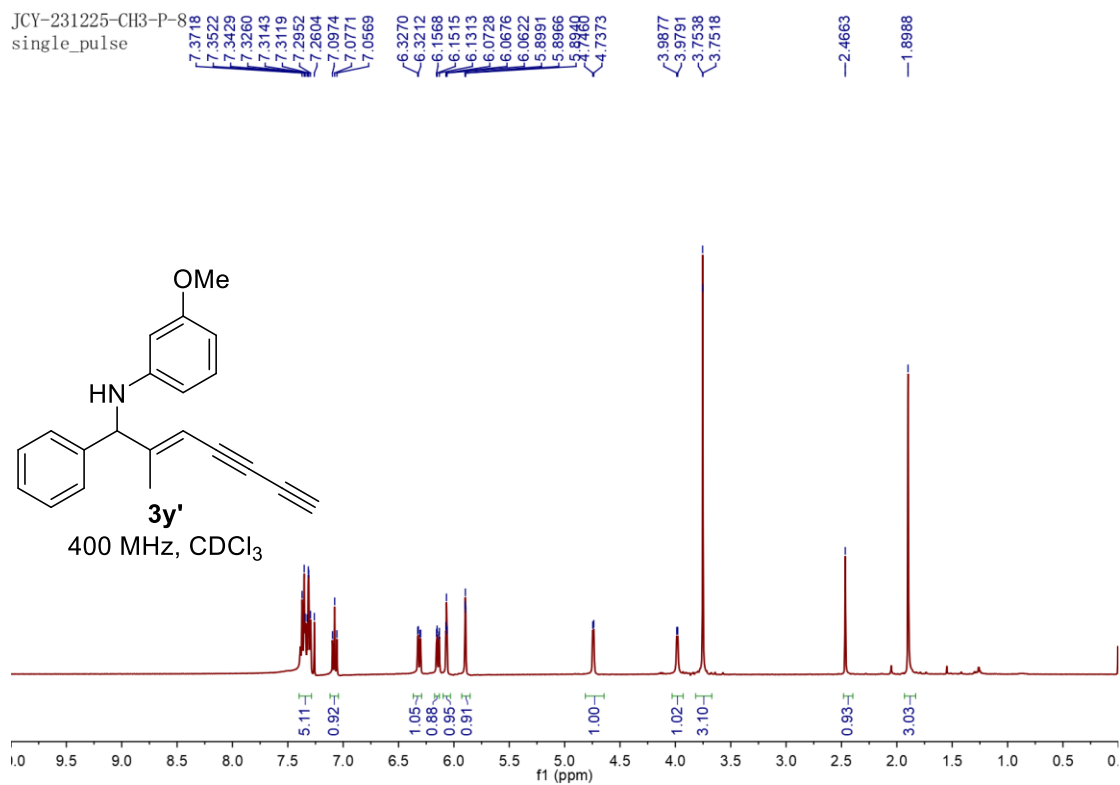
JCY-231210-ENE-C  
single pulse decoupled gated NOE



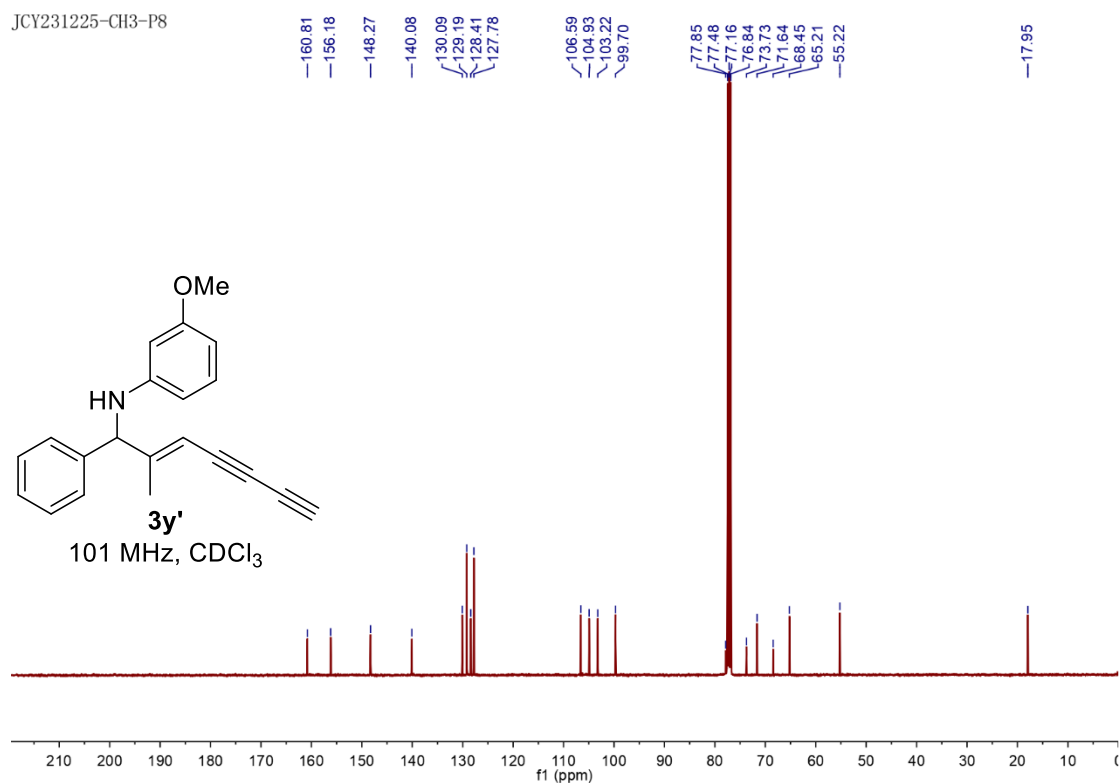


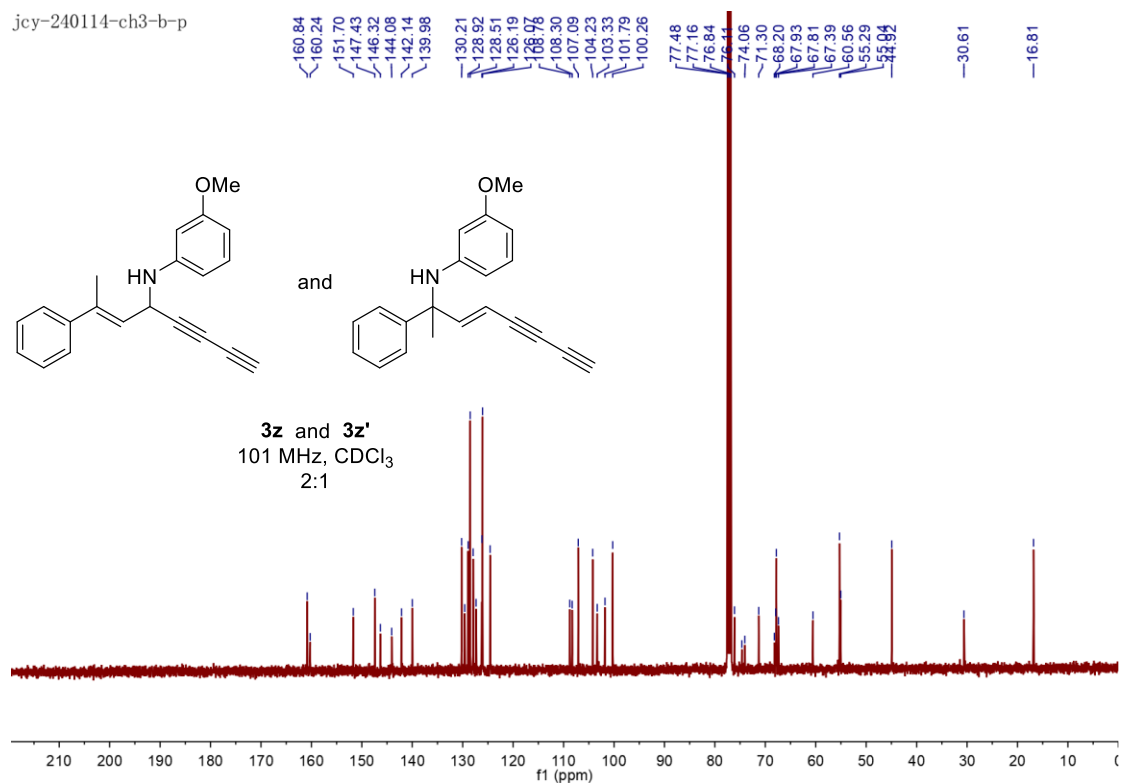
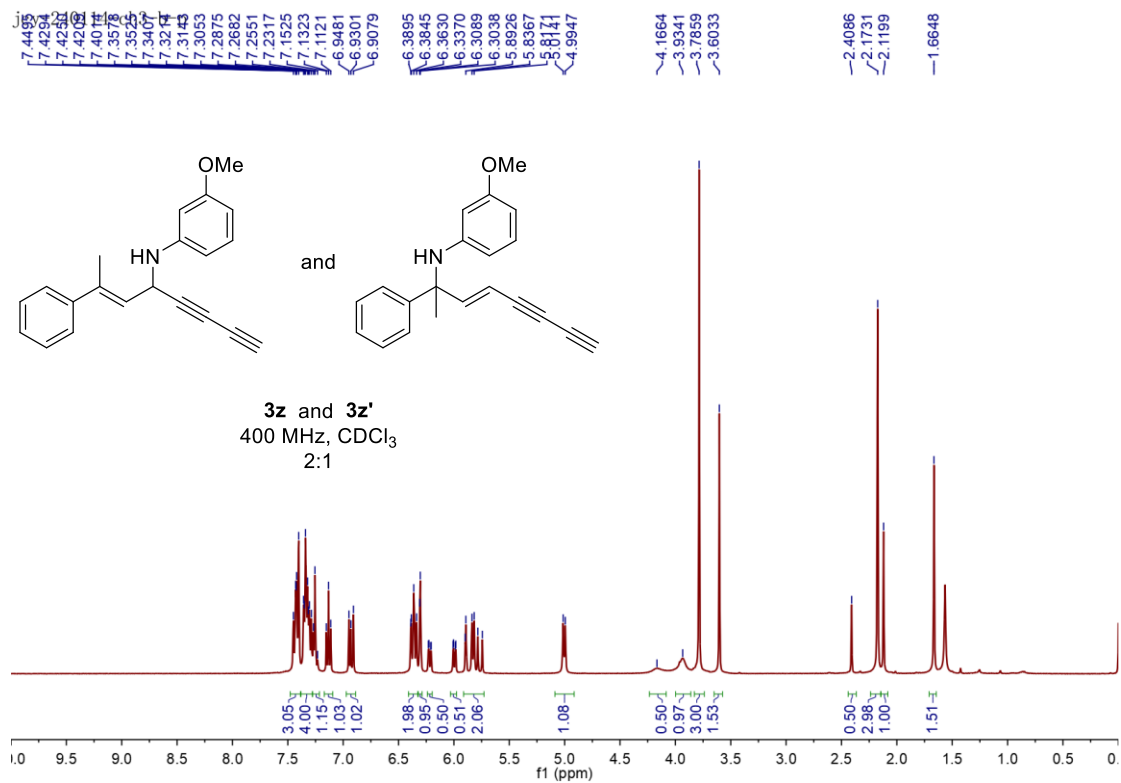


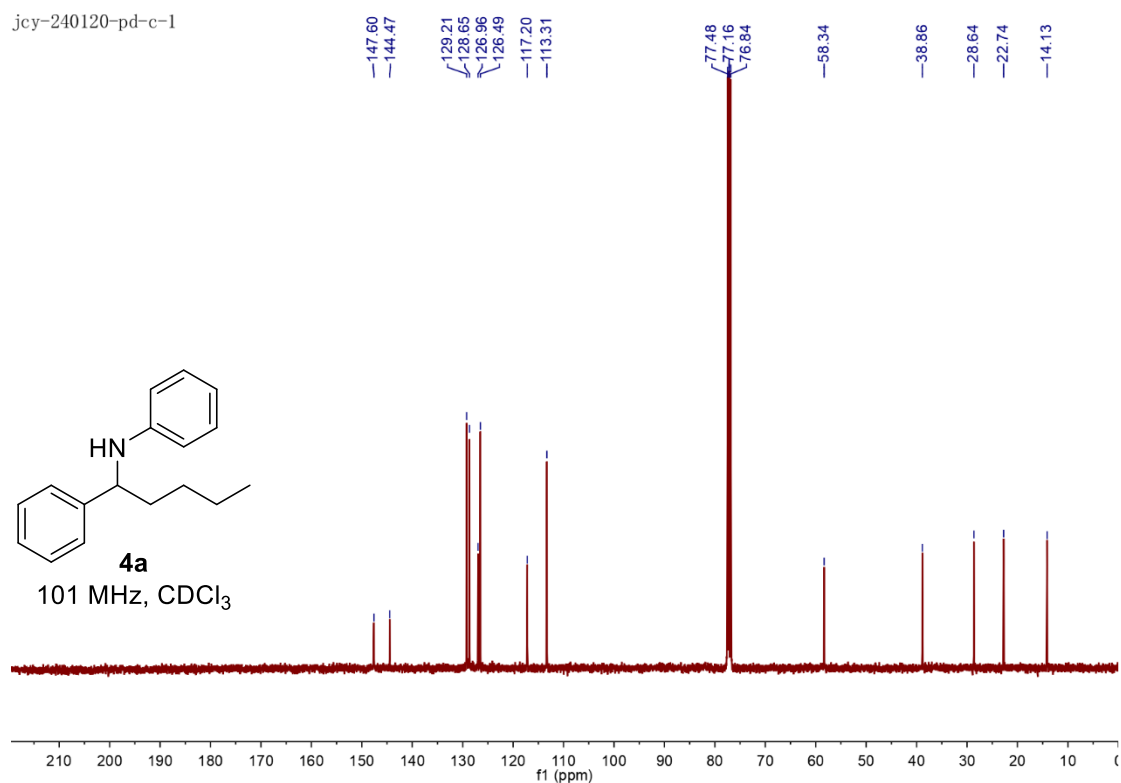
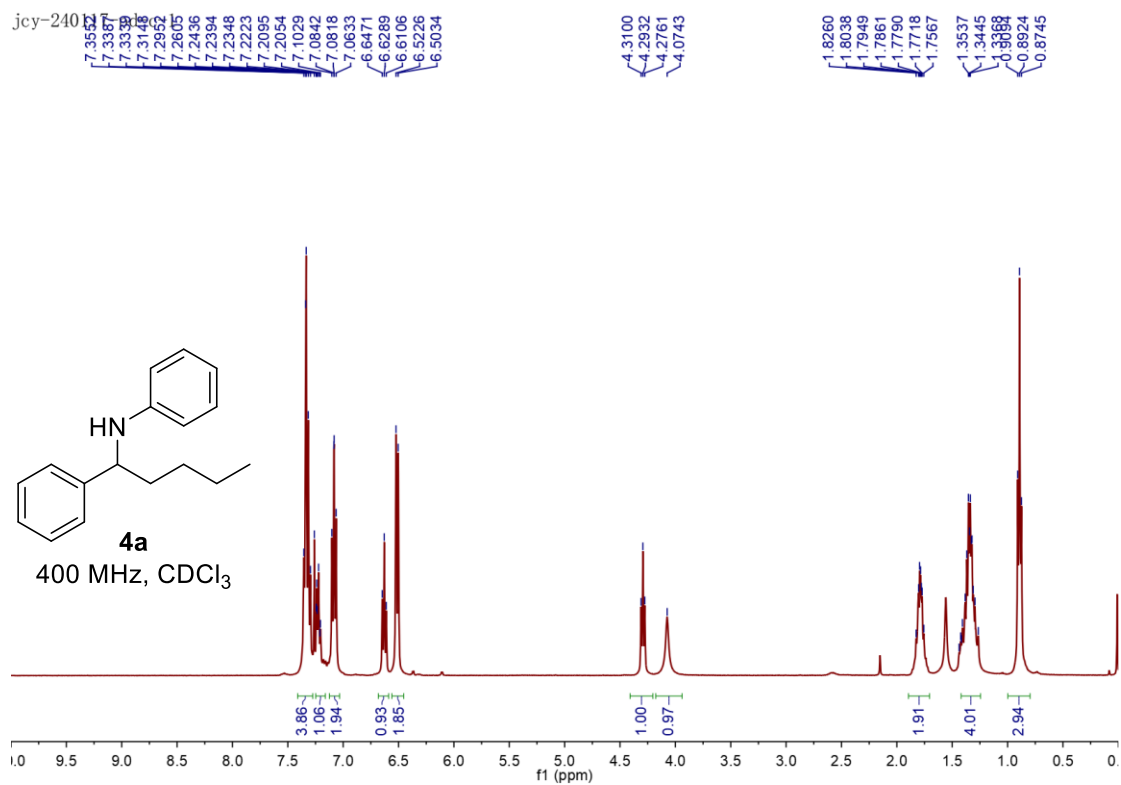
JCY-231225-CH3-P-8  
single\_pulse

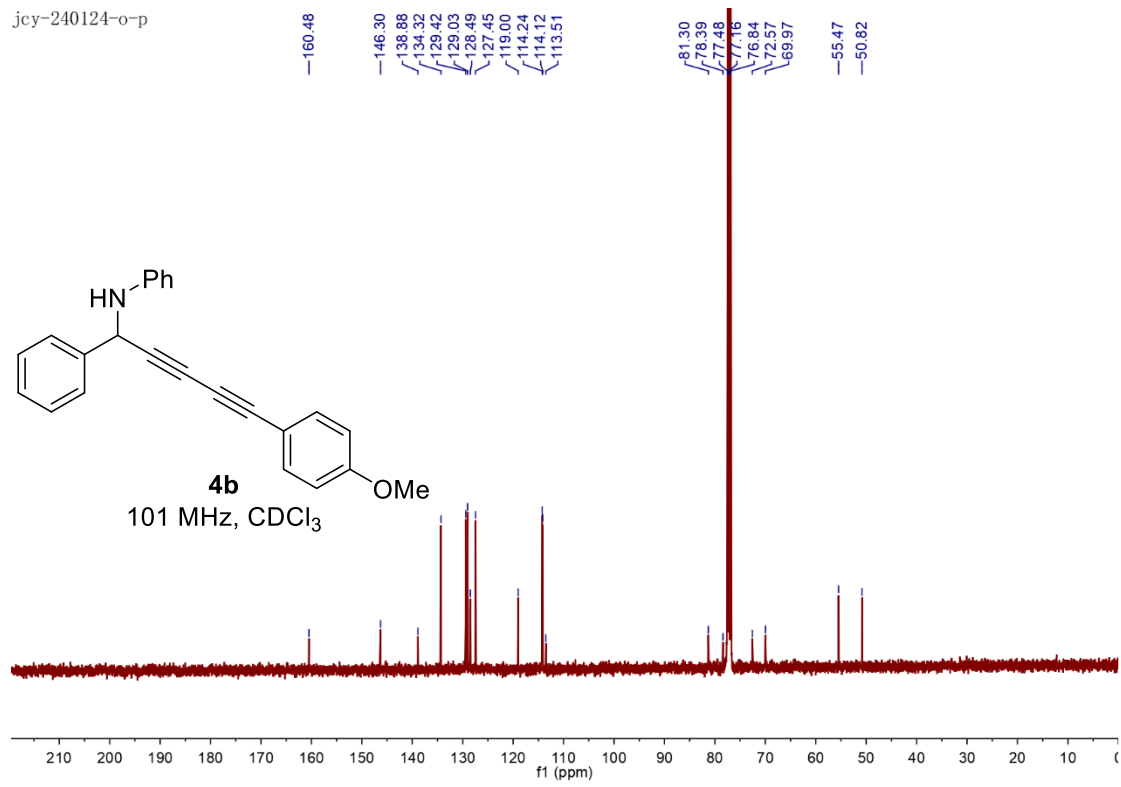
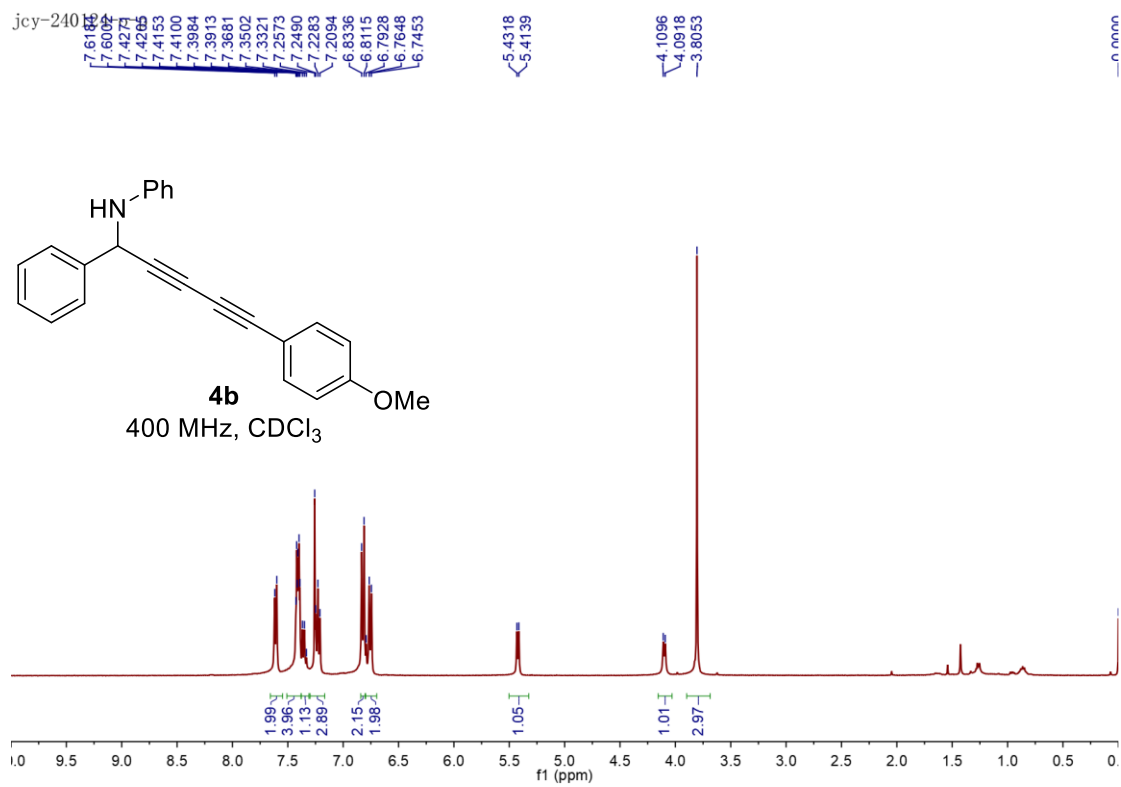


JCY231225-CH3-P8

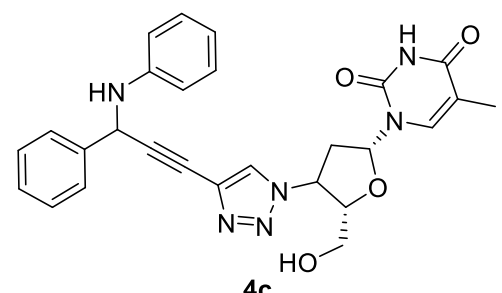




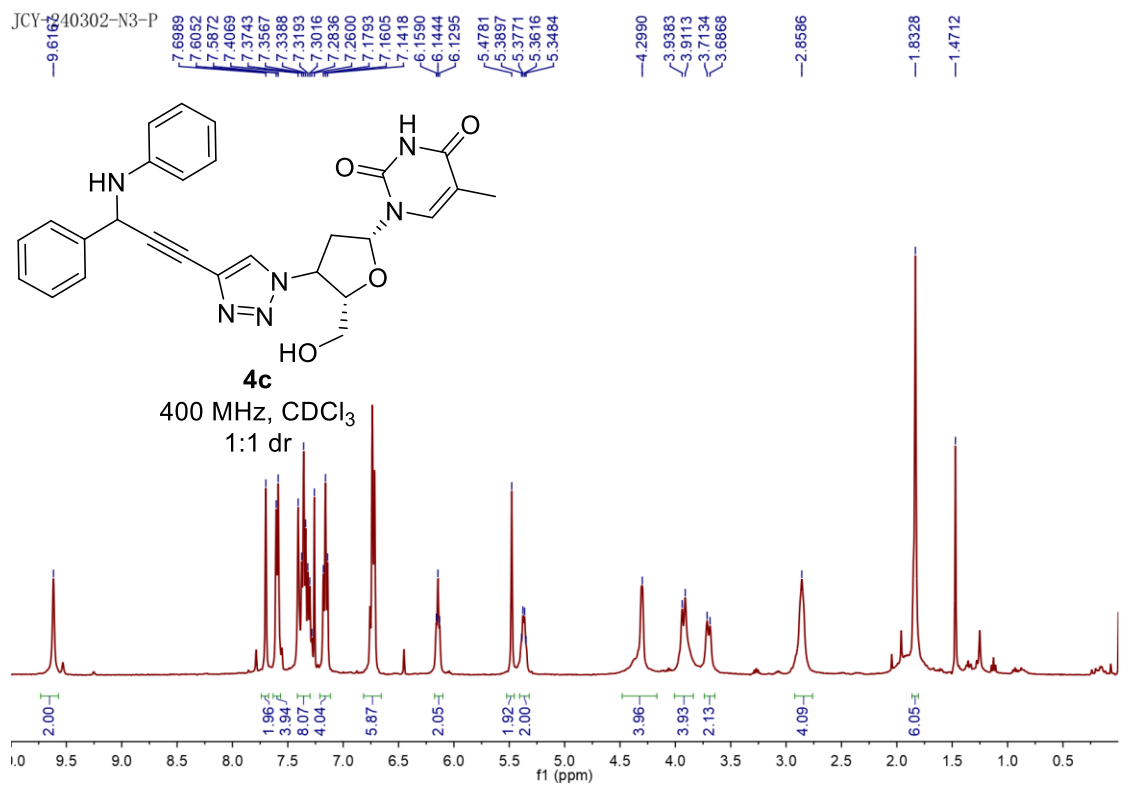




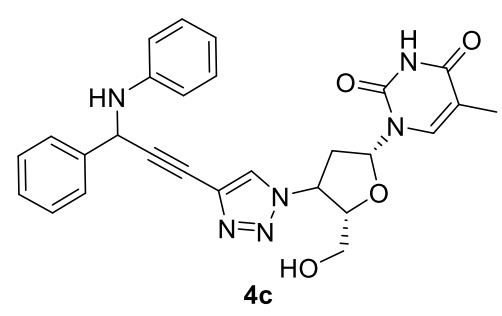
JCY-240302-N3-P



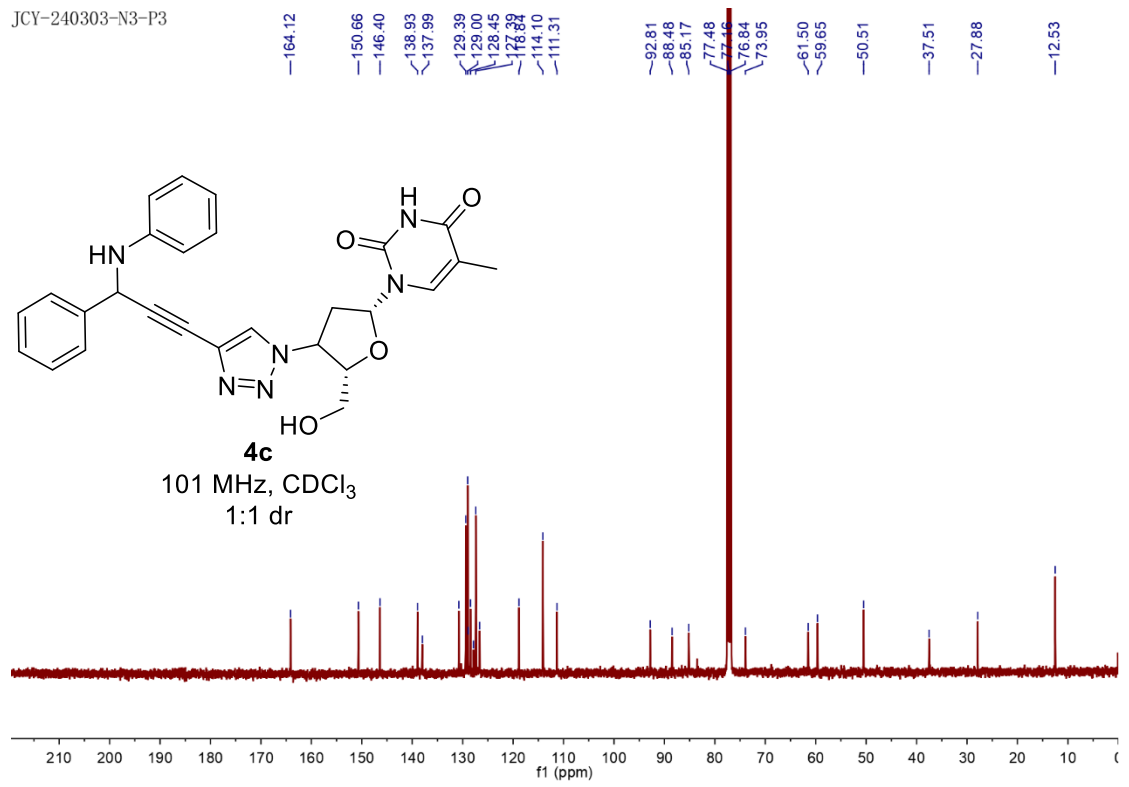
400 MHz, CDCl<sub>3</sub>  
1:1 dr



JCY-240303-N3-P3



101 MHz, CDCl<sub>3</sub>  
1:1 dr

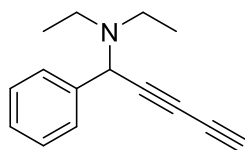


jcy-240503-et2nh-1

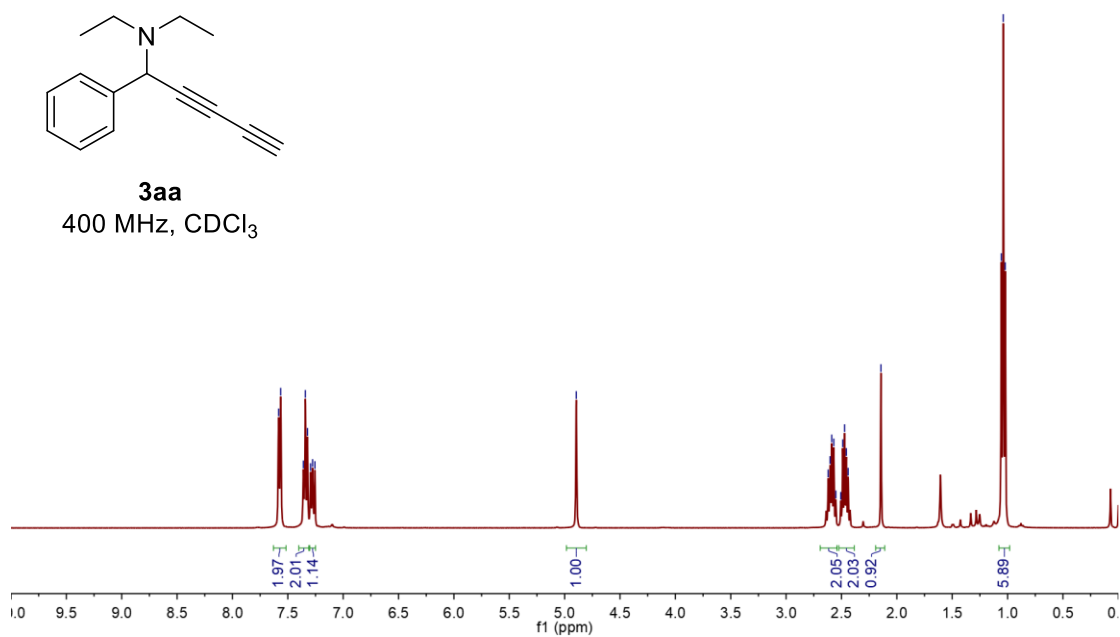
7.5828  
7.5642  
7.3600  
7.3421  
7.3228  
7.2943  
7.2763  
7.2564

4.8950

2.6205  
2.6026  
2.5884  
2.5701  
2.5517  
2.5067  
2.4896  
2.4725  
2.4562  
2.4403  
2.1437  
1.0569  
1.0390  
1.0213



**3aa**  
400 MHz, CDCl<sub>3</sub>



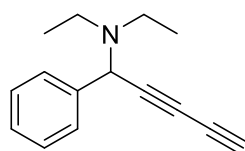
JCY-240503-ET2NH-1-1  
single pulse decoupled gated NOE

138.70  
128.28  
128.22  
127.68

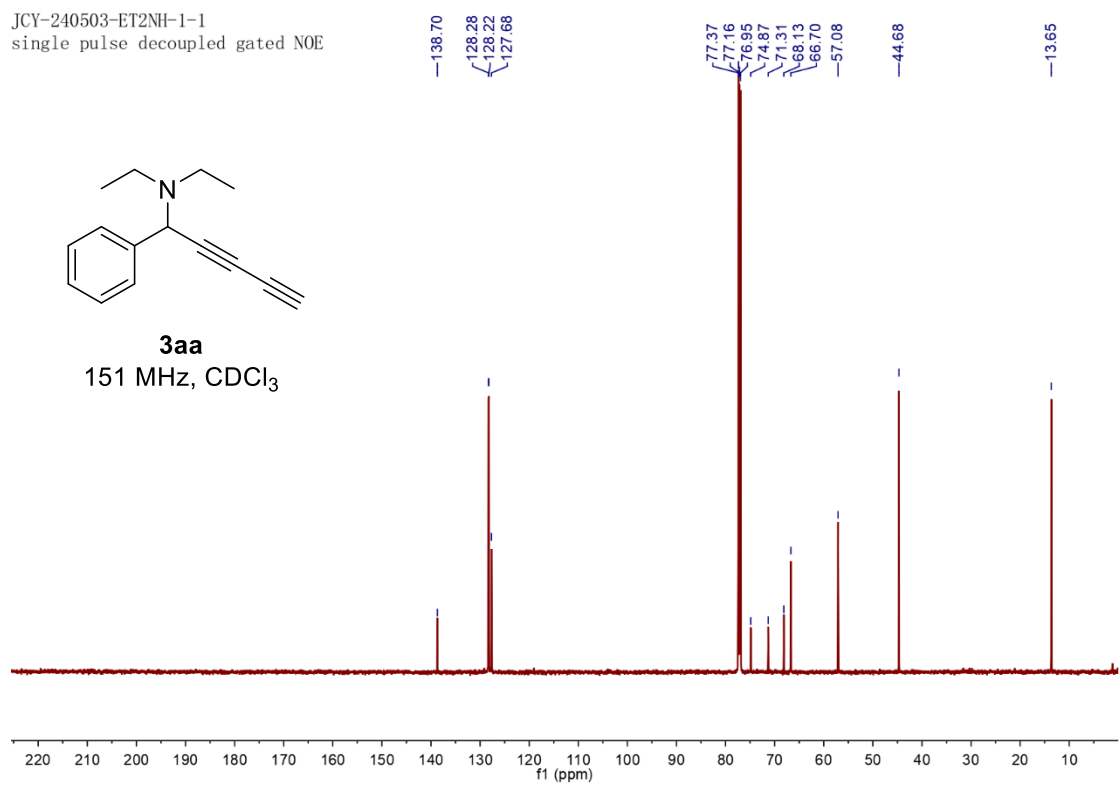
77.37  
77.16  
76.95  
74.87  
71.31  
68.13  
66.70  
57.08

44.68

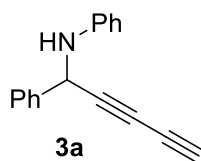
13.65



**3aa**  
151 MHz, CDCl<sub>3</sub>

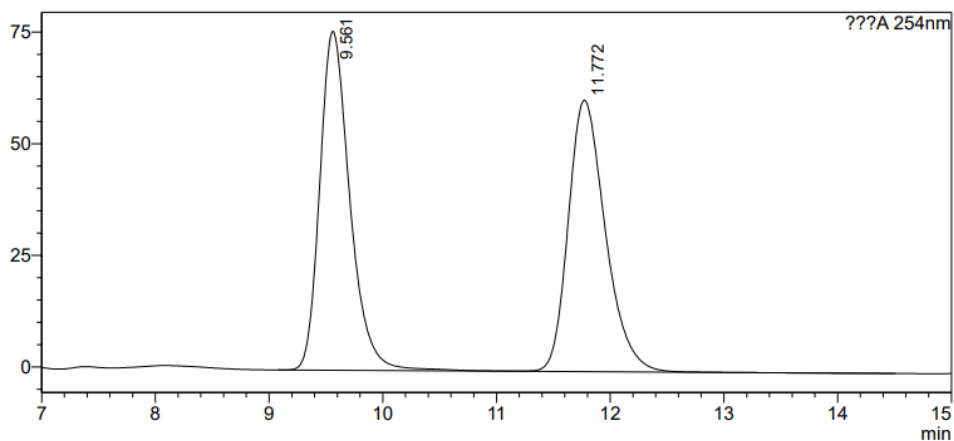


### VIII. HPLC analysis of 3a.



#### <Chromatogram>

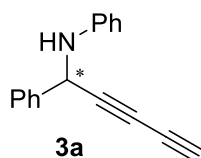
mV



#### <Peak Table>

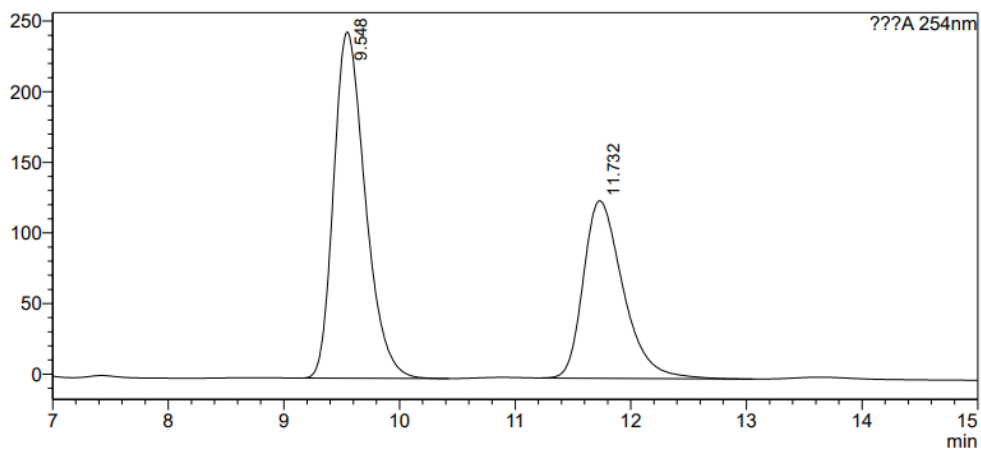
??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.561	1399737	75876	50.332			
2	11.772	1381265	60799	49.668		SV	
Total		2781002	136675				



#### <Chromatogram>

mV



#### <Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.548	4666054	245156	60.813			
2	11.732	3006737	125756	39.187			
Total		7672791	370911				