

Copper-Catalyzed Propargylic Substitution for Highly Selectively Constructing Multi-Substituted 1,4-Enynes

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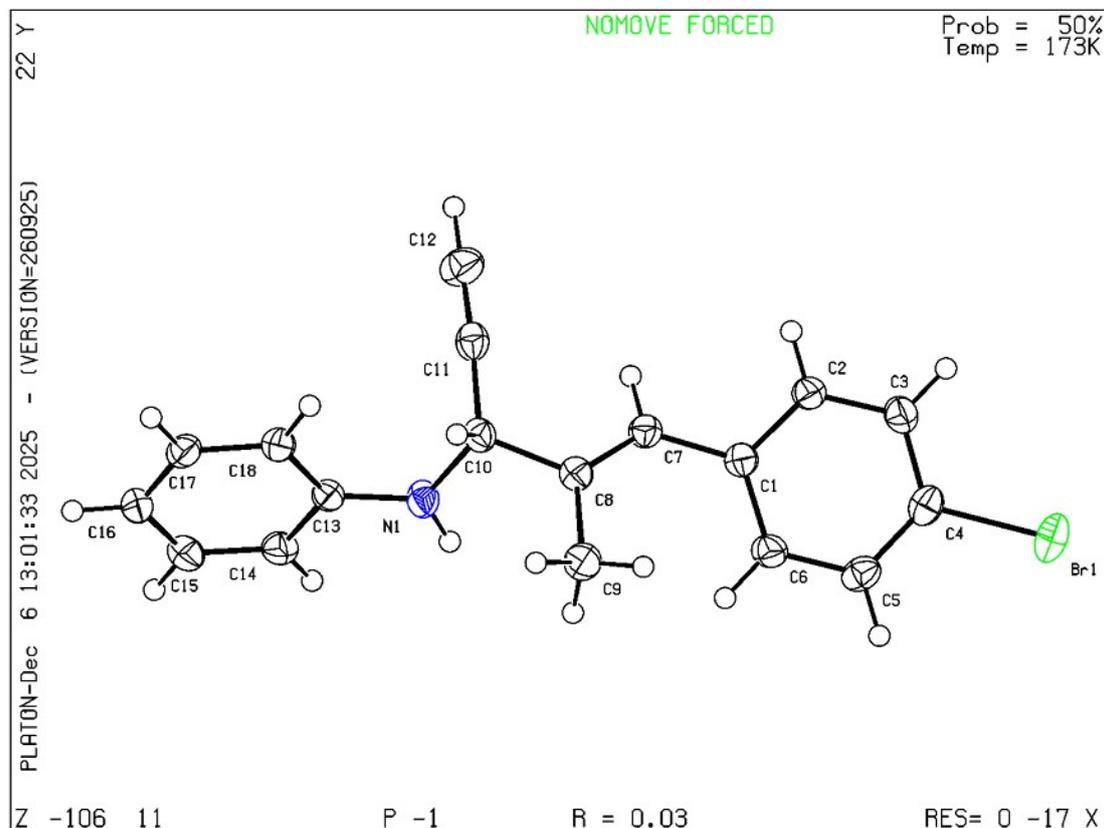
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I General Information.

Unless otherwise stated, commercially available reagents can be used without further purification. Unless otherwise stated, all reactions and operations involving air- or moisture-sensitive compounds were carried out using standard Schlenk techniques at room temperature. Unless otherwise specified, all heating reactions were performed using a heating module. Low-temperature reactions were conducted on a DHJF-8005 from Zhengzhou Great Wall Technology Industry and Trade Co., Ltd. Reactions were analyzed by thin-layer chromatography (TLC), and the plates were visualized under short-wave UV light (254 nm or 365 nm). High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific Q Exactive mass spectrometer equipped with an APCI source. The type of mass spectrometer used for HRMS measurements was Orbitrap. Crystal structure data were collected on a Supernova, TwinStar, Zero Cu, and Atlas diffractometer. ^1H , ^{13}C , and ^{19}F spectra of CDCl_3 were obtained at 400 MHz, 100 MHz, and 376 MHz, respectively, using a Bruker-BioSpin Avance III high-definition nuclear magnetic resonance spectrometer. Chemical shifts were reported in parts per million (δ values) and calibrated against residual solvent peaks (^1H NMR: δ 7.26, s; ^{13}C NMR: δ 77.16, t). The following abbreviations were used to indicate the multiplicity of chemical shifts: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

II. X-ray crystallographic analysis.

CCDC 2512208 (**4be**) suitable for X-ray crystallography was obtained by crystallization via evaporation from its hexane/DCM solution.



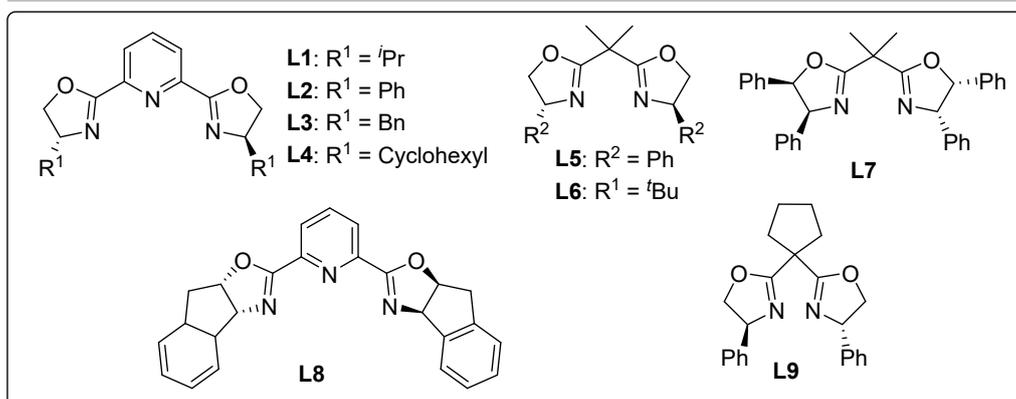
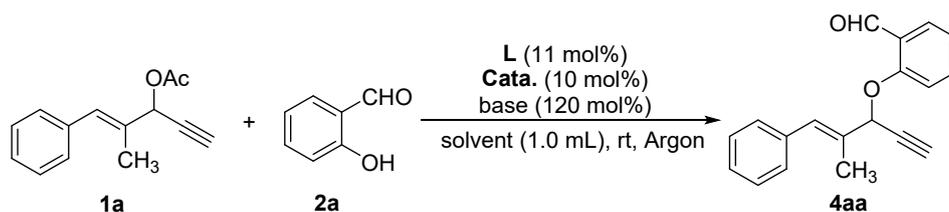
Crystal data and structure refinement for **4be**.

Table 1. Crystal data and structure refinement for C:\Users\11.

| | | |
|----------------------|---|----------------|
| Identification code | 11 | |
| Empirical formula | C ₁₉ H ₂₇ ClN ₂ O ₇ S | |
| Formula weight | 462.93 | |
| Temperature | 298.0 K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21/c 1 | |
| Unit cell dimensions | a = 18.3170(11) Å | a = 90° |
| | b = 6.4742(4) Å | b = 91.624(4)° |
| | c = 19.4174(11) Å | g = 90° |
| Volume | 2301.7(2) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.336 Mg/m ³ | |

| | |
|-----------------------------------|---|
| Absorption coefficient | 2.678 mm ⁻¹ |
| F(000) | 976 |
| Crystal size | 0.17 x 0.16 x 0.14 mm ³ |
| Theta range for data collection | 5.097 to 72.137° |
| Index ranges | -22<=h<=22, -7<=k<=6, -23<=l<=21 |
| Reflections collected | 17640 |
| Independent reflections | 4462 [R(int) = 0.0475] |
| Completeness to theta = 67.679° | 99.4 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7536 and 0.5721 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4462 / 1 / 278 |
| Goodness-of-fit on F ² | 1.025 |
| Final R indices [I>2sigma(I)] | R1 = 0.0418, wR2 = 0.0981 |
| R indices (all data) | R1 = 0.0625, wR2 = 0.1106 |
| Extinction coefficient | 0.0024(3) |
| Largest diff. peak and hole | 0.151 and -0.210 e.Å ⁻³ |

III. Attempts at chiral catalysts

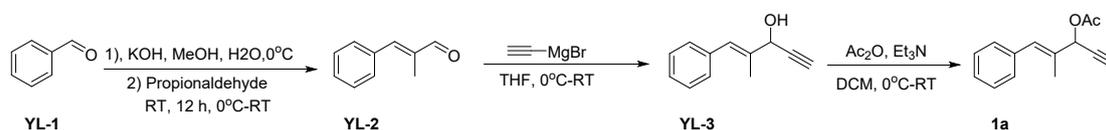


| Entry | L | Cata. | Base (mol%) | Solvent | T (°C) | <i>E/Z</i> | Yield (%) ^b | Ee% ^c |
|-------|----|--|---------------------------------|---------|--------|------------|------------------------|------------------|
| 1 | L1 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 70 | 7 |
| 2 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 75 | 57 |
| 3 | L3 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 79 | 7 |
| 4 | L4 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 67 | 13 |
| 5 | L5 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 60 | 7 |
| 6 | L6 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 55 | 5 |
| 7 | L7 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 45 | 23 |
| 8 | L8 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 80 | 45 |
| 9 | L9 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 55 | 29 |
| 10 | L2 | CuOTf | DIPEA | MeOH | 25 | >20:1 | 85 | 49 |
| 11 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 25 | >20:1 | 90 | 63 |
| 12 | L2 | CuBr | DIPEA | MeOH | 25 | >20:1 | 61 | 7 |
| 13 | L2 | Cu(OTf) ₂ | DIPEA | MeOH | 25 | >20:1 | 41 | 33 |
| 14 | L2 | CuTC | DIPEA | MeOH | 25 | >20:1 | 83 | 35 |
| 15 | L2 | CuAc | DIPEA | MeOH | 25 | >20:1 | 86 | 53 |
| 16 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | DBU | MeOH | 25 | >20:1 | 72 | 29 |
| 17 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | Cs ₂ CO ₃ | MeOH | 25 | >20:1 | 83 | 3 |

| | | | | | | | | |
|----|----|--|--------------------|--------------------|-----|-------|----|----|
| 18 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | NaHCO ₃ | MeOH | 25 | >20:1 | 50 | 45 |
| 19 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | KOH | MeOH | 25 | >20:1 | 89 | 29 |
| 20 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | CH ₃ CN | 25 | >20:1 | 71 | 53 |
| 21 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | EtOAc | 25 | >20:1 | 67 | 47 |
| 22 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | 0 | >20:1 | 82 | 53 |
| 23 | L2 | (CH ₃ CN) ₄ Cu]PF ₆ | DIPEA | MeOH | -10 | >20:1 | 78 | 60 |

IV. General procedure Preparation.

1. General procedure Preparation of (*E*)-2-methyl-1-phenylpent-1-en-4-yn-3-yl acetate.



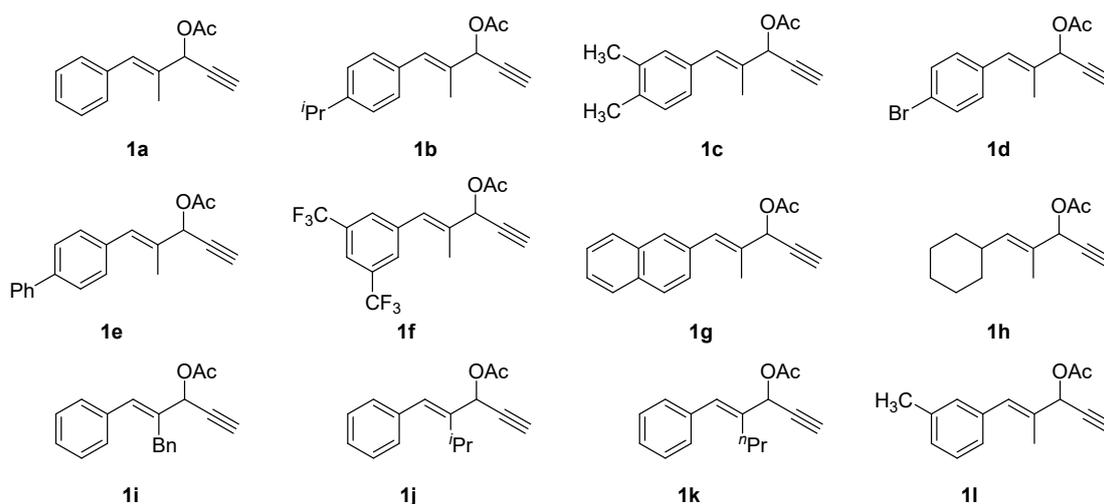
In a dry 100 mL round-bottom flask (5.3 g, 50 mmol), benzaldehyde was introduced using a syringe. Methanol and water were added to the flask in a 1:1 ratio, and the flask was sealed with a rubber stopper. The mixture was cooled to 0 °C in a low-temperature reactor. Then, KOH (2.8 g, 50 mmol) was added to the flask and stirred for 15 min. Next, n-propanal was added and the mixture was stirred at room temperature for 12 h. Then, HCl (10 mL, 1 M) was added to quench the reaction. The solution was extracted with CH₂Cl₂ (100 × 3 mL), and the combined organic phase was washed with brine, dried over Na₂SO₄, filter, and concentrate under reduced pressure by rotary evaporation. Purify the crude residue by flash column chromatography (200-300 mesh, PE/EtOAc *v/v* = 10:1) to obtain yellow oil **YL-2** (5.1 g, 70% yield).

The crude alcohol **YL-2** was dissolved in anhydrous THF (30 mL) and the solution was cooled to 0 °C under the low temperature reactor. Then ethynylmagnesium bromide (6.8 g, 52.5 mmol) was added in the round-bottom flask (250 mL). The resulting mixture was allowed to stir at room temperature for 1.5 h before adding aqueous solution of ammonium chloride (50 mL) to quench the reaction. The mixture was extracted with EA (50×3 mL), washed with brine (50×3 mL), dried

over Na₂SO₄, filtered and concentrated on rotavapor under reduced pressure. The **YL-3** was used directly for the next reaction without further purification.

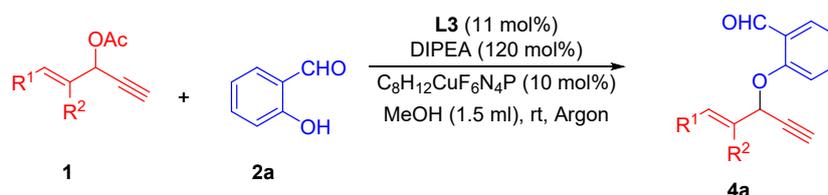
Dissolve crude alcohol **YL-3** in dichloromethane (200 mL) and cool to 0 °C in a low-temperature reactor. Then add triethylamine (8.4 mL, 60 mmol) and acetic anhydride (11.4 g, 60 mmol). Stir the resulting mixture at room temperature for 0.5 hours, then add 50 mL of water to quench the reaction. Extract the mixture with DCM (50 × 3 mL), wash with brine (50 × 3 mL), dry over Na₂SO₄, filter, and concentrate under reduced pressure by rotary evaporation. Purify the crude residue by flash column chromatography (200 - 300 mesh, PE/EtOAc v/v = 25:1) to obtain yellow oil **1a** (5.2 g, 70% yield).

Other (*E*)-2-methyl-1-phenylpent-1-en-4-yn-3-yl acetate products can be obtained using the same method^[1].



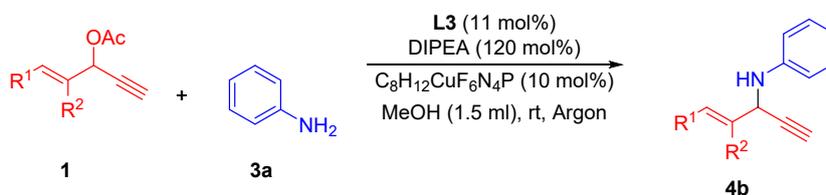
V. General procedure for synthesis of compounds

1. General procedure for synthesis of Compounds 4

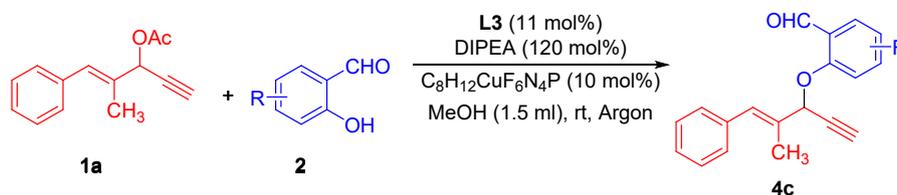


An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with (CH₃CN)₄Cu]PF₆ (7.5 mg, 10 mol%) and **L3** (5.2 mg, 12 mol%) in an Ar setting, followed by the addition of **1a-1k** (0.2 mmol, 1.0 equiv) and MeOH (1.5

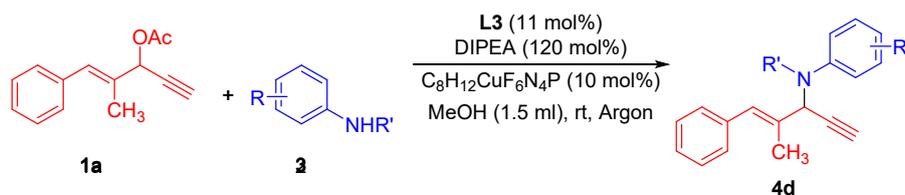
mL) and **2a** (29.3 mg, 0.24 mmol, 1.2 equiv) or were introduced into the Schlenk tube. The mixture being stirred at room temperature for an 12 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc $v/v = 25:1$ as the eluent) to produce the respective products **4a**.



An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with $(\text{CH}_3\text{CN})_4\text{Cu}[\text{PF}_6]$ (7.5 mg, 10 mol%) and **L3** (5.2 mg, 12 mol%) in an Ar setting, followed by the addition of **1a-1i** (0.2 mmol, 1.0 equiv) and MeOH (1.5 mL) and **3a** (22.4 mg, 0.24 mmol, 1.2 equiv) were introduced into the Schlenk tube. The mixture being stirred at room temperature for an 12 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc $v/v = 25:1$ as the eluent) to produce the respective products **4b**.

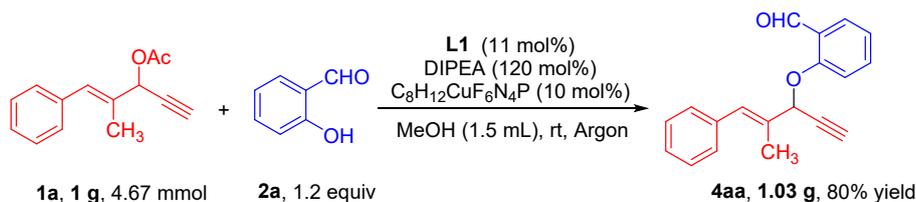


An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with $(\text{CH}_3\text{CN})_4\text{Cu}[\text{PF}_6]$ (7.5 mg, 10 mol%) and **L3** (5.2 mg, 12 mol%) in an Ar setting, followed by the addition of **1a** (31.6 mg, 0.2 mmol, 1.0 equiv) and MeOH (1.5 mL) and **2a-2h** (0.24 mmol, 1.2 equiv) or were introduced into the Schlenk tube. The mixture being stirred at room temperature for an 12 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc $v/v = 25:1$ as the eluent) to produce the respective products **4c**.

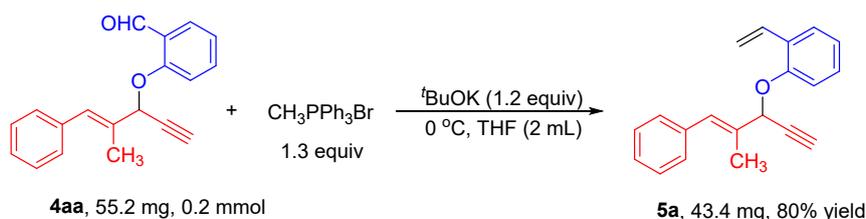


An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with $(\text{CH}_3\text{CN})_4\text{Cu}[\text{PF}_6]$ (7.5 mg, 10 mol%) and **L3** (5.2 mg, 12 mol%) in an Ar setting, followed by the addition of **1a** (31.6 mg, 0.2 mmol, 1.0 equiv) and MeOH (1.5 mL) and **3a-3i** (0.24 mmol, 1.2 equiv) were introduced into the Schlenk tube. The mixture being stirred at room temperature for an 12 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc $v/v = 25:1$ as the eluent) to produce the respective products **4d**.

2. General procedure for gram-scale experiments of product **4aa** and transformation.

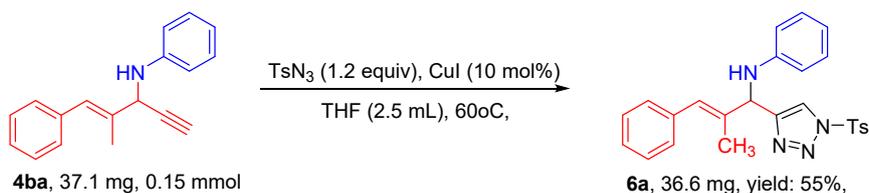


An oven-dried 100 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with $(\text{CH}_3\text{CN})_4\text{Cu}[\text{PF}_6]$ (0.17 g, 10 mol%) in an Ar setting, followed by the addition of **1a** (1.0 g, 4.67 mmol) and MeOH (15.0 mL) and **2a** (0.68 g, 5.6 mmol, 1.2 equiv) were introduced into the Schlenk tube. The mixture being stirred at room temperature for an 12 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc $v/v = 25:1$ as the eluent) to produce the respective products **4aa** (1.03 g, 80% yield).

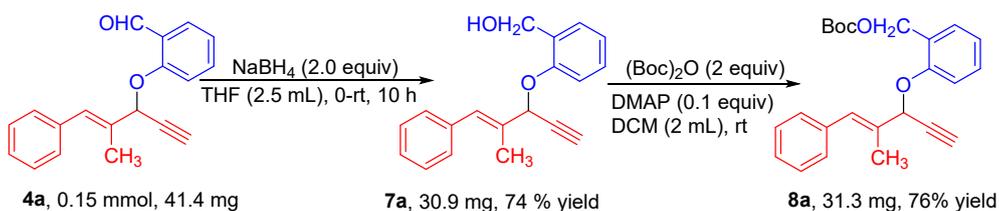


An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was

charged with **4aa** (55.2 mg, 0.2 mmol) in an Ar setting, followed by the addition of THF (2.0 mL, 0.1 M). The solution was cooled to 0 °C under the low temperature reactor and CH₃PPh₃Br (92.9 mg, 0.26 mmol), ^tBuOK (74 mg, 0.66 mmol) was added slowly into the Schlenk tube. The mixture being stirred at 0 °C for an 2 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc v/v = 15:1-10:1 as the eluent) to produce the respective products **5a** (80% yield).



An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with **4ba** (37.1 mg, 0.15 mmol) in an Ar setting, followed by the addition of THF (2.5 mL, 0.1 M). Then TsN₃ (35.5 mg, 0.18 mmol), CuI (2.9 mg, 10% mmol, 0.015mmol) was added slowly into the Schlenk tube. The mixture being stirred at 60 °C for an 4 h. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc v/v = 10:1-5:1 as the eluent) to produce the respective products **6a** (55% yield).



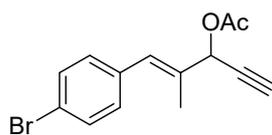
The solution was cooled to 0 °C. An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with **4aa** (41.4 mg, 0.15 mmol) in an Ar setting, followed by the addition of THF (2.5 mL, 0.13 M). Then, NaBH₄ (11.3 mg, 0.3 mmol) was added slowly into the Schlenk tube. Move the reaction to room temperature and stir for ten hours. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–

300 mesh, PE/EtOAc $v/v = 5:1-3:1$ as the eluent) to produce the respective products **7a** (74% yield). An oven-dried 25 mL Schlenk tube, fitted with a magnetic stirring bar, was charged with **7a** (30.9 mg, 0.11 mmol) in an Ar setting, followed by the addition of DCM (2.0 mL, M). Then, (Boc)₂O (48.0 mg, 0.22 mmol) was added slowly into the Schlenk tube. Stir the reaction at room temperature for ten hours. Following the completion of the reaction (monitored using TLC), the raw product underwent direct flash column chromatography on silica gel (200–300 mesh, PE/EtOAc $v/v = 10:1$ as the eluent) to produce the respective products **8a** (76% yield).

VI. Reference

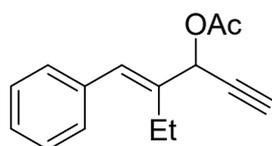
[1] M. A. Kacprzyński, A. H. Hoveyda, *J. Am. Chem. Soc.*, **2004**, *126*, 10676–10681.

VII. Characterization data of compounds



Y-1

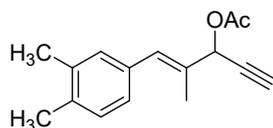
(E)-1-(4-bromophenyl)-2-methylpent-1-en-4-yn-3-yl acetate (Y-1). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 76% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.46 (d, $J = 8.5$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.67 (s, 1H), 5.93 (dd, $J = 2.3, 0.9$ Hz, 1H), 2.60 (d, $J = 2.2$ Hz, 1H), 2.13 (s, 3H), 1.95 (d, $J = 1.5$ Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 169.6, 135.4, 133.5, 131.4, 130.7, 128.8, 121.2, 79.5, 75.2, 68.8, 21.0, 14.3. HRMS (APCI) m/z calcd for C₁₄H₁₄BrO₂⁺ (M+H)⁺ 293.0172, found 293.0170.



Y-2

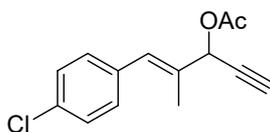
(E)-4-benzylidenehex-1-yn-3-yl acetate (Y-2). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 65% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.25–7.22 (m, 2H), 7.19–7.14 (m, 3H), 6.76 (s, 1H), 5.94 (dd, $J = 2.3, 1.0$ Hz, 1H), 2.52 (d, $J = 2.3$ Hz, 1H), 2.32–2.18 (m, 2H), 2.03 (s, 3H), 1.55–1.43 (m, 2H), 0.85–0.82 (m, 3H). ¹³C

NMR (100 MHz, Chloroform-*d*) δ : 169.6, 137.0, 136.7, 130.4, 128.7, 128.3, 127.1, 79.8, 75.3, 67.4, 31.5, 30.6, 30.0, 27.5, 21.9, 14.2. HRMS (APCI) m/z calcd for $C_{15}H_{17}O_2^+$ (M+H)⁺ 229.1223, found 229.1222.



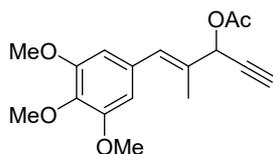
Y-3

(*E*)-1-(3,4-dimethylphenyl)-2-methylpent-1-en-4-yn-3-yl acetate (Y-3). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 77% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.14 – 7.02 (m, 3H), 6.15 (s, 1H), 5.68 (dt, *J* = 2.5, 1.3 Hz, 1H), 3.12 (d, *J* = 2.3 Hz, 1H), 2.26 (d, *J* = 4.2 Hz, 6H), 2.11 (s, 3H), 1.82 (d, *J* = 1.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 169.8, 137.2, 128.5, 80.2, 74.5, 69.1, 37.0, 32.7, 32.6, 26.1, 25.9, 21.2, 12.6. HRMS (APCI) m/z calcd for $C_{16}H_{19}O_2^+$ (M+H)⁺ 243.1380, found 243.1382.



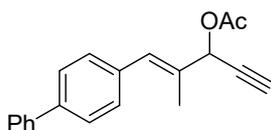
Y-4

(*E*)-1-(4-chlorophenyl)-2-methylpent-1-en-4-yn-3-yl acetate (Y-4). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 80% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.30 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.69 (s, 1H), 5.93 (dd, *J* = 2.3, 1.0 Hz, 1H), 2.60 (d, *J* = 2.2 Hz, 1H), 2.13 (s, 3H), 1.95 (d, *J* = 1.5 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 169.6, 135.0, 133.4, 133.0, 130.3, 128.8, 128.4, 79.5, 75.2, 68.8, 21.0, 14.2. HRMS (APCI) m/z calcd for $C_{14}H_{14}ClO_2^+$ (M+H)⁺ 249.0677, found 249.0675.



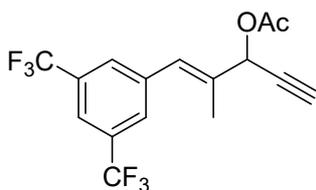
Y-5

(E)-2-methyl-1-(3,4,5-trimethoxyphenyl)pent-1-en-4-yn-3-yl acetate (Y-5). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 60% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ: 6.68 (s, 1H), 6.50 (s, 2H), 5.93 (dd, *J* = 2.2, 0.9 Hz, 1H), 3.84 (d, *J* = 1.8 Hz, 9H), 2.60 (d, *J* = 2.2 Hz, 1H), 2.13 (s, 3H), 1.99 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 169.8, 153.0, 137.4, 132.3, 132.2, 130.2, 106.4, 79.7, 75.1, 69.1, 61.0, 56.2, 21.1, 14.4. HRMS (APCI) *m/z* calcd for C₁₇H₂₁O₅⁺ (M+H)⁺ 305.1384, found 305.1382.



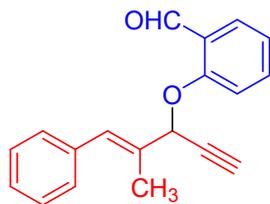
Y-6

(E)-1-([1,1'-biphenyl]-4-yl)-2-methylpent-1-en-4-yn-3-yl acetate (Y-6). White solid. (PE/EtOAc *v/v* = 10:1 as the eluent), 45% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.64–7.56 (m, 5H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 9.6, 7.7 Hz, 3H), 6.80 (s, 1H), 5.99 (d, *J* = 2.2 Hz, 1H), 2.61 (d, *J* = 2.2 Hz, 1H), 2.16 (s, 3H), 2.05 (d, *J* = 1.4 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 169.9, 140.8, 140.1, 135.7, 132.9, 129.8, 129.7, 129.0, 128.9, 127.5, 127.1, 127.0, 79.8, 75.1, 69.2, 21.2, 14.5. HRMS (APCI) *m/z* calcd for C₂₀H₁₉O₂⁺ (M+H)⁺ 291.1380, found 291.1382.



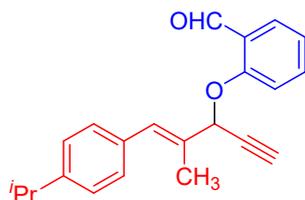
Y-7

(E)-1-(3,5-bis(trifluoromethyl)phenyl)-2-methylpent-1-en-4-yn-3-yl acetate (Y-7). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 70% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.77 (s, 1H), 7.71 (d, *J* = 1.7 Hz, 2H), 6.81 (s, 1H), 5.97 (dd, *J* = 2.3, 1.0 Hz, 1H), 2.63 (d, *J* = 2.3 Hz, 1H), 2.16 (s, 3H), 1.98 (d, *J* = 1.5 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 169.7, 138.7, 136.7, 132.0, 131.6, 129.1, 129.1, 127.0, 124.8, 122.1, 79.1, 75.7, 68.3, 21.1, 14.4. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ: 63.00. HRMS (APCI) *m/z* calcd for C₁₆H₁₃F₆O₂⁺ (M+H)⁺ 351.0814, found 351.0811.



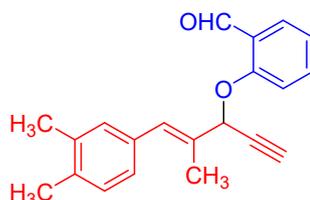
4aa

(E)-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4aa). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 49.9 mg, 90% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 10.59 (s, 1H), 7.84 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.47–7.30 (m, 6H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.81 (dt, *J* = 2.3, 1.2 Hz, 1H), 5.68 (s, 1H), 3.14 (d, *J* = 2.2 Hz, 1H), 1.91 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 189.34, 159.7, 150.1, 136.4, 135.9, 134.6, 129.2, 129.0, 128.1, 125.7, 121.7, 114.5, 107.6, 83.4, 83.0, 80.1, 15.7. HRMS (APCI) *m/z* calcd for C₁₉H₁₇O₂⁺ (M+H)⁺ 277.1223, found 277.1222.



4ab

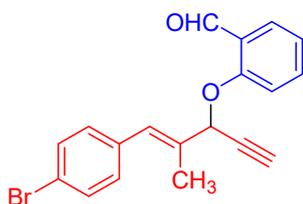
(E)-2-((1-(4-isopropylphenyl)-2-methylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4ab). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 47.9 mg, 75% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 10.59 (s, 1H), 7.84 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.45 (ddd, *J* = 8.5, 7.3, 1.9 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 3H), 7.24 (t, *J* = 8.2 Hz, 3H), 7.10–6.97 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 5.79 (dt, *J* = 2.3, 1.2 Hz, 2H), 5.65 (s, 2H), 3.13 (d, *J* = 2.3 Hz, 2H), 2.97–2.83 (m, 1H), 1.91 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 189.3, 159.7, 149.9, 136.9, 135.9, 132.1, 129.0, 128.4, 125.7, 122.6, 121.7, 114.5, 107.6, 83.4, 83.0, 80.1, 15.6. HRMS (APCI) *m/z* calcd for C₂₂H₂₃O₂⁺ (M+H)⁺ 319.1693, found 319.1690.



4ac

(*E*)-2-((1-(3,4-dimethylphenyl)-2-methylpent-1-en-4-yn-3-yl)oxy)benzaldehyde

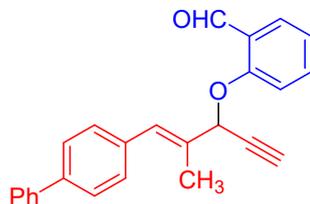
(4ac). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 34.8 mg, 57% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 10.53 (s, 1H), 7.96–7.84 (m, 4H), 7.51 (ddd, *J* = 8.8, 7.3, 1.8 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.88 (dt, *J* = 2.5, 1.2 Hz, 1H), 5.80 (s, 1H), 3.21 (d, *J* = 2.3 Hz, 1H), 1.88 (d, *J* = 1.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 189.4, 159.7, 150.1, 136.4, 135.9, 134.6, 129.2, 129.0, 128.1, 125.7, 121.8, 114.5, 107.6, 83.4, 83.0, 15.7. HRMS (APCI) *m/z* calcd for C₂₁H₂₁O₂⁺ (M+H)⁺ 305.1536, found 305.1537.



4ad

(*E*)-2-((1-(4-bromophenyl)-2-methylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4ad).

Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 39.1 mg, 55% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 10.46 (s, 1H), 7.75 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.45–7.40 (m, 2H), 7.39–7.33 (m, 1H), 7.21–7.16 (m, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 5.70 (dt, *J* = 2.3, 1.2 Hz, 1H), 5.55 (s, 1H), 3.07 (d, *J* = 2.2 Hz, 1H), 1.79 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 189.4, 159.7, 150.0, 137.0, 135.9, 132.1, 129.0, 128.4, 125.7, 122.7, 121.8, 114.5, 107.6, 83.4, 83.0, 80.1, 15.7. HRMS (APCI) *m/z* calcd for C₁₉H₁₆BrO₂⁺ (M+H)⁺ 355.0328, found 355.0325.

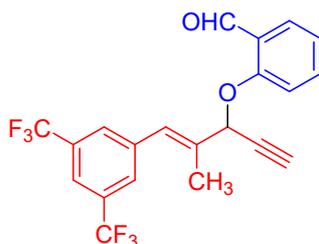


4ae

(*E*)-2-((1-([1,1'-biphenyl]-4-yl)-2-methylpent-1-en-4-yn-3-yl)oxy)benzaldehyde

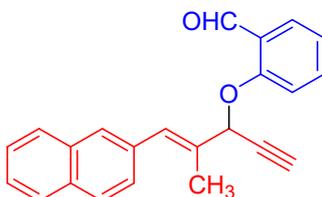
(4ae). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 35.3 mg, 50% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 10.63 (s, 1H), 7.87 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.66–7.54

(m, 5H), 7.52–7.42 (m, 6H), 7.41–7.33 (m, 1H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 5.85 (dt, $J = 2.6, 1.3$ Hz, 1H), 5.74 (s, 1H), 3.16 (d, $J = 2.3$ Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ : 189.6, 160.1, 150.6, 141.6, 140.5, 136.8, 135.9, 129.0, 128.8, 127.7, 127.7, 127.2, 127.2, 125.7, 121.5, 114.6, 107.2, 83.9, 82.8, 80.4, 15.8. HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{21}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 353.1536, found 353.1537.



4af

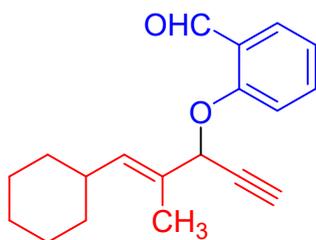
(*E*)-2-((1-(3,5-bis(trifluoromethyl)phenyl)-2-methylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4af). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 64.4 mg, 78% yield. ^1H NMR (400 MHz, Chloroform- d) δ : 10.53 (s, 1H), 7.93–7.85 (m, 4H), 7.51 (ddd, $J = 8.8, 7.3, 1.8$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 5.88 (dt, $J = 2.5, 1.2$ Hz, 1H), 5.80 (s, 1H), 3.21 (d, $J = 2.3$ Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ : 188.9, 159.0, 148.7, 140.9, 136.0, 129.8, 126.7, 125.9, 122.4, 114.4, 109.4, 83.9, 83.1, 79.6, 15.2. ^{19}F NMR (376 MHz, Chloroform- d) δ : 62.82. HRMS (APCI) m/z calcd for $\text{C}_{21}\text{H}_{15}\text{F}_6\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 413.0971, found 413.0970.



4ag

(*E*)-2-((2-methyl-1-(naphthalen-2-yl)pent-1-en-4-yn-3-yl)oxy)benzaldehyde (4ag). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 30.7 mg, 47% yield. ^1H NMR (400 MHz, Chloroform- d) δ : 10.56 (s, 1H), 8.04 (d, $J = 7.2$ Hz, 1H), 7.94–7.82 (m, 3H), 7.62 (d, $J = 7.2$ Hz, 1H), 7.58–7.52 (m, 2H), 7.50–7.45 (m, 1H), 7.38 (ddd, $J = 8.8,$

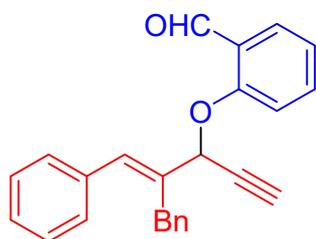
7.3, 1.9 Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 6.38 (s, 1H), 5.78 (dt, $J = 2.4, 1.2$ Hz, 1H), 3.17 (d, $J = 2.3$ Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 189.7, 160.3, 149.9, 136.0, 134.2, 132.8, 130.8, 129.6, 129.3, 128.7, 127.0, 126.1, 125.8, 125.7, 125.5, 123.0, 121.5, 114.4, 108.3, 83.2, 81.3, 80.5, 17.0. HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 327.1380, found 327.1383.



4ah

(*E*)-2-((1-cyclohexyl-2-methylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4ah).

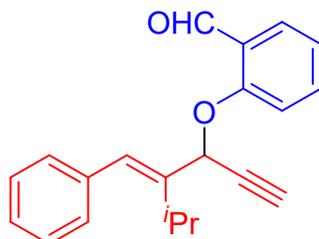
Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 33.4 mg, 59% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 10.58 (s, 1H), 7.82 (dd, $J = 7.7, 1.9$ Hz, 1H), 7.46 (ddd, $J = 8.8, 7.3, 1.9$ Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 8.5$ Hz, 1H), 5.52 (dt, $J = 2.4, 1.3$ Hz, 1H), 4.38 (d, $J = 6.6$ Hz, 1H), 3.13 (d, $J = 2.3$ Hz, 1H), 1.96 (dt, $J = 12.8, 2.6$ Hz, 1H), 1.90 (s, 3H), 1.88-1.70 (m, 3H), 1.69 (d, $J = 10.7$ Hz, 1H), 1.59 (d, $J = 12.7$ Hz, 1H), 1.30–1.07 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 189.7, 160.9, 149.9, 135.9, 128.4, 125.4, 120.9, 114.0, 108.0, 86.8, 82.6, 80.3, 41.0, 29.8, 28.6, 26.4, 26.2, 26.1, 15.6. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{23}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 283.1693, found 283.1690.



4ai

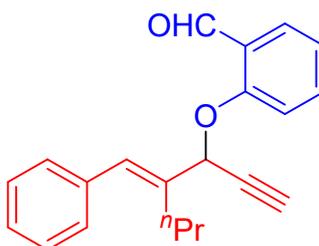
(*E*)-2-((2-benzyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4ai). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 53.0 mg, 75% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 10.21 (s, 1H), 7.32–7.26 (m, 4H), 7.25–7.11 (m, 9H), 6.84 (t, $J = 7.6$ Hz, 1H), 6.36 (d, $J = 8.5$ Hz, 1H), 5.49 (s, 1H), 3.08 (d, $J = 2.4$ Hz, 1H), 1.96 (s,

2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 189.6, 159.9, 152.9, 138.1, 137.5, 135.6, 129.0, 129.0, 128.9, 128.8, 128.5, 127.5, 126.9, 121.2, 114.1, 107.5, 82.6, 81.3, 80.7, 60.5, 37.0, 14.3. HRMS (APCI) m/z calcd for $\text{C}_{25}\text{H}_{21}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 353.1536, found 353.1535.



4aj

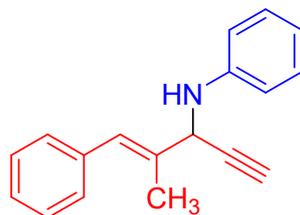
(*E*)-2-((4-benzylidene-5-methylhex-1-yn-3-yl)oxy)benzaldehyde (4aj). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 36.0 mg, 59% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 10.55 (s, 1H), 7.83 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.48–7.33 (m, 6H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 5.75 (s, 1H), 5.67 (dd, $J = 2.6, 1.2$ Hz, 1H), 3.27 (d, $J = 2.5$ Hz, 1H), 2.98 (p, $J = 7.1$ Hz, 1H), 1.18 (d, $J = 7.1$ Hz, 3H), 1.05 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 189.7, 160.2, 159.3, 137.9, 135.9, 128.9, 128.7, 128.6, 127.4, 125.6, 121.4, 114.5, 107.2, 85.1, 82.0, 80.5, 31.0, 21.1, 20.7. HRMS (APCI) m/z calcd for $\text{C}_{21}\text{H}_{21}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 305.1536, found 305.1533.



4ak

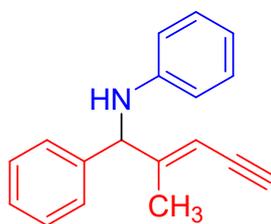
(*E*)-2-((4-benzylidenehept-1-yn-3-yl)oxy)benzaldehyde (4ak). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 36.0 mg, 59% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 10.56 (s, 1H), 7.83 (dd, $J = 7.7, 1.9$ Hz, 1H), 7.47–7.33 (m, 6H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 5.80–5.75 (m, 1H), 5.72 (s, 1H), 3.15 (d, $J = 2.3$ Hz, 1H), 2.43 (ddd, $J = 13.3, 9.4, 6.7$ Hz, 1H), 2.20 (ddd, $J = 13.3, 9.4, 6.3$ Hz, 1H), 1.52–1.43 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz,

Chloroform-*d*) δ : 189.7, 160.3, 154.6, 137.9, 135.9, 129.0, 128.7, 128.7, 127.2, 125.7, 121.5, 114.6, 107.3, 83.0, 82.9, 80.5, 32.9, 21.9, 14.4. HRMS (APCI) m/z calcd for $C_{21}H_{21}O_2^+$ (M+H)⁺ 305.1536, found 305.1533.



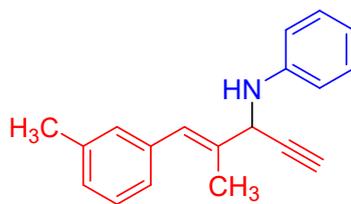
4ba

(*E*)-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)aniline (4ba). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 30.8 mg, 62% yield. 1H NMR (400 MHz, Chloroform-*d*) δ : 7.38–7.28 (m, 4H), 7.23 (td, $J = 8.9, 7.1$ Hz, 3H), 6.87 (s, 1H), 6.79 (t, $J = 7.4$ Hz, 1H), 6.74 (d, $J = 7.4$ Hz, 2H), 4.73 (s, 1H), 4.00 (s, 1H), 2.44 (d, $J = 2.3$ Hz, 1H), 2.02 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 146.7, 137.3, 135.2, 129.3, 129.1, 128.3, 128.0, 126.9, 118.8, 114.1, 82.7, 73.0, 53.8, 15.3. HRMS (APCI) m/z calcd for $C_{18}H_{18}N^+$ (M+H)⁺ 248.1434, found 248.1430.



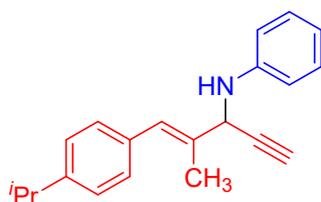
4ba'

(*E*)-N-(2-methyl-1-phenylpent-2-en-4-yn-1-yl)aniline (4ba') Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 15.0 mg, 30% yield. 1H NMR (400 MHz, Chloroform-*d*) δ : 7.36 (qd, $J = 6.1, 5.1, 2.4$ Hz, 5H), 7.22–7.15 (m, 2H), 6.76 (td, $J = 7.3, 1.1$ Hz, 1H), 6.56 (dt, $J = 7.6, 1.1$ Hz, 2H), 5.87 (dq, $J = 2.4, 1.2$ Hz, 1H), 4.79 (s, 1H), 3.89 (s, 1H), 3.13 (d, $J = 2.3$ Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 152.1, 147.1, 140.5, 129.3, 129.1, 128.2, 127.7, 118.1, 113.5, 105.8, 81.8, 81.4, 65.0, 17.4. HRMS (APCI) m/z calcd for $C_{18}H_{18}N^+$ (M+H)⁺ 248.1434, found 248.1432.



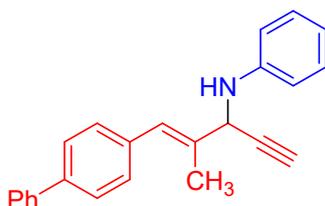
4bb

(E)-N-(2-methyl-1-(m-tolyl)pent-1-en-4-yn-3-yl)aniline (4bb). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 29.3 mg, 56% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.25–7.19 (m, 3H), 7.08 (dd, $J = 18.3, 7.1$ Hz, 3H), 6.83 (s, 1H), 6.79 (t, $J = 7.4$ Hz, 1H), 6.74 (d, $J = 6.1$ Hz, 2H), 4.72 (s, 1H), 3.47 (s, 1H), 2.44 (d, $J = 2.3$ Hz, 1H), 2.36 (s, 3H), 2.02 (d, $J = 1.4$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 146.7, 137.8, 137.3, 135.0, 129.8, 129.3, 128.2, 128.1, 127.7, 126.1, 118.7, 114.1, 82.7, 73.0, 53.8, 21.6, 15.3. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 262.1590, found 262.1592.



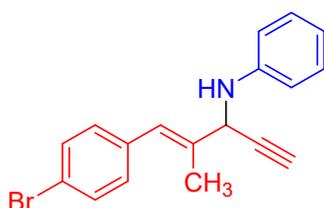
4bc

(E)-N-(1-(4-isopropylphenyl)-2-methylpent-1-en-4-yn-3-yl)aniline (4bc). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 29.0 mg, 50% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.29–7.12 (m, 6H), 6.88–6.57 (m, 4H), 4.73 (t, $J = 1.7$ Hz, 1H), 3.98 (s, 1H), 2.92 (p, $J = 6.9$ Hz, 1H), 2.44 (d, $J = 2.2$ Hz, 1H), 2.03 (d, $J = 1.4$ Hz, 3H), 1.27 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 147.6, 146.7, 134.8, 134.5, 129.3, 129.1, 127.9, 126.4, 118.7, 114.2, 82.8, 72.9, 53.9, 34.0, 24.1, 15.3. HRMS (APCI) m/z calcd for $\text{C}_{21}\text{H}_{24}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 290.1903, found 290.1901.



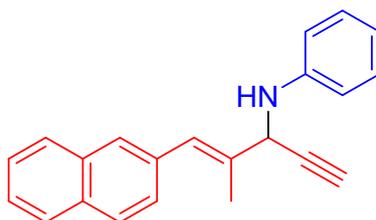
4bd

(E)-N-(1-([1,1'-biphenyl]-4-yl)-2-methylpent-1-en-4-yn-3-yl)aniline (4bd). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 37.6 mg, 58% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.63 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 2H), 7.59 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.41–7.34 (m, 3H), 7.25–7.20 (m, 2H), 6.90 (s, 1H), 6.80 (t, *J* = 6.9 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 2H), 4.76 (s, 1H), 4.02 (s, 1H), 2.47 (d, *J* = 2.2 Hz, 1H), 2.08 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 146.7, 140.9, 139.7, 136.4, 135.5, 129.6, 129.4, 128.9, 127.6, 127.4, 127.1, 127.0, 118.8, 114.2, 82.7, 73.1, 53.9, 15.5. HRMS (APCI) *m/z* calcd for C₂₄H₂₂N⁺ (M+H)⁺ 324.1747, found 324.1744.



4be

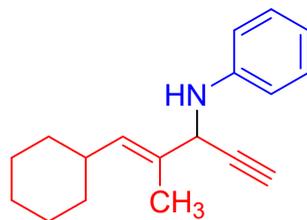
(E)-N-(1-(4-bromophenyl)-2-methylpent-1-en-4-yn-3-yl)aniline (4be). White solid, (PE/EtOAc *v/v* = 25:1 as the eluent), 36.5 mg, 56% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.48 (d, *J* = 8.4 Hz, 2H), 7.25–7.19 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.84–6.78 (m, 2H), 6.73 (d, *J* = 7.4 Hz, 2H), 4.72 (s, 1H), 3.96 (s, 1H), 2.46 (d, *J* = 2.3 Hz, 1H), 2.01 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 146.6, 136.2, 136.1, 131.4, 130.7, 129.4, 126.7, 120.8, 118.9, 114.1, 82.4, 73.2, 53.7, 15.3. HRMS (APCI) *m/z* calcd for C₁₈H₁₇BrN⁺ (M+H)⁺ 326.0539, found 326.0537.



4bf

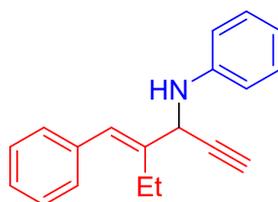
(E)-N-(2-methyl-1-(naphthalen-2-yl)pent-1-en-4-yn-3-yl)aniline (4bf). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 33.3 mg, 56% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.95–7.84 (m, 3H), 7.82–7.77 (m, 1H), 7.51–7.46 (m, 3H), 7.36 (dt, *J* = 7.1, 1.2 Hz, 1H), 7.29 (dd, *J* = 3.8, 1.5 Hz, 2H), 6.91–6.77 (m, 4H), 4.91 (dd, *J* = 2.3, 1.2 Hz, 1H), 3.81 (s, 1H), 2.53 (d, *J* = 2.3 Hz, 1H), 1.89 (d, *J* = 1.4 Hz, 3H). ¹³C

NMR (100 MHz, Chloroform-*d*) δ : 146.6, 136.9, 134.6, 133.6, 132.0, 129.43, 129.4, 128.5, 127.5, 126.6, 126.2, 126.0, 125.9, 125.3, 125.1, 118.9, 114.4, 113.8, 82.7, 73.1, 53.3, 15.2. HRMS (APCI) m/z calcd for $C_{22}H_{20}N^+$ ($M+H$)⁺ 297.1517, found 297.1515.



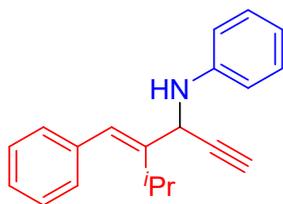
4bg

(*E*)-N-(1-cyclohexyl-2-methylpent-1-en-4-yn-3-yl)aniline (4bg). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 33.8 mg, 66% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 (dd, *J* = 8.5, 7.2 Hz, 2H), 6.80–6.74 (m, 1H), 6.72–6.68 (m, 2H), 6.55–6.42 (m, 1H), 5.60 (dt, *J* = 9.2, 1.4 Hz, 1H), 4.54 (d, *J* = 2.4 Hz, 1H), 2.37 (d, *J* = 2.2 Hz, 1H), 1.78 (d, *J* = 1.3 Hz, 3H), 1.74–1.61 (m, 6H), 1.32–1.23 (m, 5H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 146.8, 134.9, 130.3, 129.2, 118.5, 114.2, 113.2, 83.2, 72.4, 53.3, 37.1, 32.9, 32.9, 26.2, 26.0, 13.5. HRMS (APCI) m/z calcd for $C_{18}H_{24}N^+$ ($M+H$)⁺ 254.1903, found 254.1900.



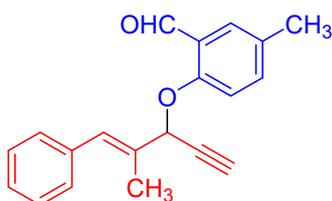
4bh

(*E*)-N-(4-benzylidenehex-1-yn-3-yl)aniline (4bh). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 25.4 mg, 46% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.37 (t, *J* = 7.6 Hz, 2H), 7.32–7.19 (m, 6H), 6.98 (s, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 2H), 4.82 (s, 1H), 2.51–2.35 (m, 3H), 1.62 (h, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 146.7, 139.6, 137.4, 129.2, 128.7, 128.2, 128.0, 126.8, 118.6, 114.0, 82.8, 73.0, 51.1, 31.3, 22.1, 14.3. HRMS (APCI) m/z calcd for $C_{20}H_{22}N^+$ ($M+H$)⁺ 276.1747, found 276.1746.



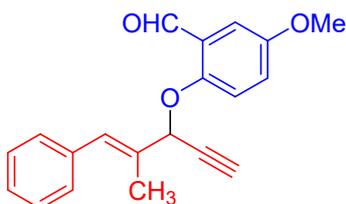
4bi

(E)-N-(4-benzylidene-5-methylhex-1-yn-3-yl)aniline (4bi). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 27.0 mg, 49% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 7.25–7.13 (m, 6H), 6.88–6.57 (m, 4H), 4.73 (t, $J = 1.7$ Hz, 1H), 3.98 (s, 1H), 2.92 (p, $J = 6.9$ Hz, 1H), 2.44 (d, $J = 2.2$ Hz, 1H), 2.04 (s, 1H), 1.27 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 147.6, 146.7, 134.8, 134.5, 129.3, 129.1, 127.9, 126.4, 118.7, 114.2, 82.8, 72.9, 53.9, 34.0, 24.1, 15.3. HRMS (APCI) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{N}^+$ ($\text{M}+\text{H}$) $^+$ 276.1747, found 276.1746.



4ca

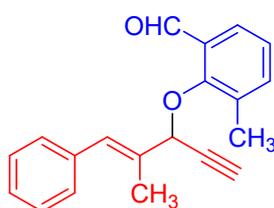
(E)-5-methyl-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4ca). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 79.7 mg, 56% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 10.46 (s, 1H), 7.54 (d, $J = 2.4$ Hz, 1H), 7.32–7.27 (m, 4H), 7.27–7.20 (m, 2H), 7.15 (dd, $J = 9.0, 2.9$ Hz, 1H), 6.70 (d, $J = 8.5$ Hz, 1H), 5.55 (s, 1H), 3.05 (d, $J = 2.3$ Hz, 1H), 2.19 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 189.8, 158.1, 150.8, 138.0, 136.6, 131.0, 128.9, 128.7, 128.6, 126.8, 125.4, 114.7, 107.0, 84.1, 82.6, 80.4, 20.4, 15.8. HRMS (APCI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 291.1380, found 291.1382.



4cb

(E)-5-methoxy-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4cb).

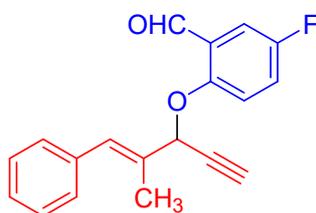
Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 31.8 mg, 52% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 10.51 (s, 1H), 7.41–7.29 (m, 6H), 7.03 (dd, *J* = 9.1, 3.3 Hz, 1H), 6.84 (d, *J* = 9.1 Hz, 1H), 5.81 (dt, *J* = 2.4, 1.2 Hz, 1H), 5.58 (s, 1H), 3.78 (s, 3H), 3.14 (d, *J* = 2.3 Hz, 1H), 1.88 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 189.4, 154.8, 154.2, 150.8, 138.0, 128.9, 128.6, 126.8, 126.1, 123.5, 116.8, 110.4, 107.0, 85.0, 82.6, 80.4, 55.9, 15.8. HRMS (APCI) *m/z* calcd for C₂₀H₁₉O₃⁺ (M+H)⁺ 307.1329, found 307.1328.



4cc

(E)-3-methyl-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4cc).

Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 29.1 mg, 50% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 9.67 (s, 1H), 7.52 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.32 (ddd, *J* = 7.4, 1.9, 0.9 Hz, 1H), 7.24 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.13–7.08 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.02 (dt, *J* = 2.5, 1.3 Hz, 1H), 5.04 (s, 1H), 3.11 (d, *J* = 2.3 Hz, 1H), 2.07 (s, 3H), 1.74 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 190.1, 159.3, 149.5, 137.6, 136.8, 132.6, 130.2, 129.1, 128.9, 128.0, 126.0, 124.5, 106.5, 90.1, 82.5, 80.7, 16.9, 16.5. HRMS (APCI) *m/z* calcd for C₂₀H₁₉O₂⁺ (M+H)⁺ 291.1380, found 291.1383.

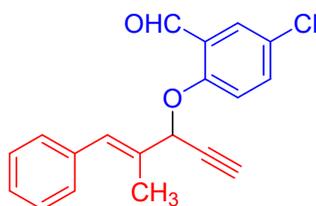


4cd

(E)-5-fluoro-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4cd).

Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 30.1 mg, 51% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 10.49 (s, 1H), 7.93 (d, *J* = 2.6 Hz, 1H), 7.51 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.40–7.32 (m, 5H), 6.79 (d, *J* = 8.9 Hz, 1H), 5.79 (dt, *J* = 2.4, 1.2 Hz, 1H),

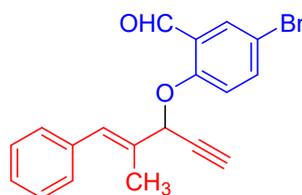
5.64 (s, 1H), 3.16 (d, $J = 2.3$ Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 188.5, 188.4, 150.3, 137.6, 123.0, 128.8, 126.8, 122.7, 122.4, 116.6, 116.5, 114.4, 114.2, 107.2, 84.9, 82.9, 80.3, 15.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ : 63.0. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{FO}_2^+$ ($\text{M}+\text{H}$) $^+$ 295.1129, found 295.1131.



4ce

(*E*)-5-chloro-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4ce).

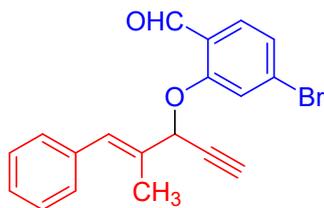
Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 56.0 mg, 90% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 10.51 (s, 1H), 7.78 (d, $J = 2.7$ Hz, 1H), 7.45–7.29 (m, 6H), 6.84 (d, $J = 8.9$ Hz, 1H), 5.79 (dt, $J = 2.3, 1.2$ Hz, 1H), 5.65 (s, 1H), 3.16 (d, $J = 2.3$ Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 188.2, 158.4, 150.1, 137.4, 135.4, 129.0, 128.8, 128.3, 127.2, 126.7, 126.6, 116.3, 107.3, 84.5, 82.9, 80.2, 15.8. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{ClO}_2^+$ ($\text{M}+\text{H}$) $^+$ 311.0388, found 311.0386.



4cf

(*E*)-5-bromo-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4cf).

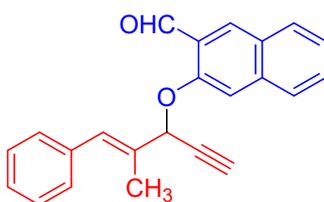
Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 42.6 mg, 60% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ : 10.49 (s, 1H), 7.93 (d, $J = 2.6$ Hz, 1H), 7.51 (dd, $J = 8.9, 2.7$ Hz, 1H), 7.46–7.29 (m, 5H), 6.79 (d, $J = 8.9$ Hz, 1H), 5.79 (dt, $J = 2.4, 1.2$ Hz, 1H), 5.64 (s, 1H), 3.16 (d, $J = 2.3$ Hz, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ : 188.1, 158.9, 150.1, 138.3, 137.3, 131.3, 129.0, 128.8, 127.0, 126.7, 116.7, 114.4, 107.4, 84.5, 83.0, 80.2, 15.8. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{BrO}_2^+$ ($\text{M}+\text{H}$) $^+$ 355.0328, found 355.0327.



4cg

(E)-4-bromo-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzaldehyde (4cg).

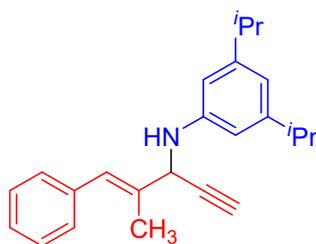
Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 36.9 mg, 52% yield. ^1H NMR (400 MHz, Chloroform- d) δ : 10.50 (s, 1H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.50–7.26 (m, 5H), 7.17 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.06 (d, $J = 1.7$ Hz, 1H), 5.85–5.73 (m, 1H), 5.66 (s, 1H), 1.90 (d, $J = 1.3$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ : 188.5, 160.2, 149.9, 137.2, 130.4, 129.9, 129.1, 128.9, 126.7, 125.1, 124.7, 118.1, 107.3, 84.5, 83.0, 80.2, 15.9. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{16}\text{BrO}_2^+$ ($\text{M}+\text{H}$) $^+$ 355.0328, found 355.0327.



4ch

(E)-3-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)-2-naphthaldehyde (4ch).

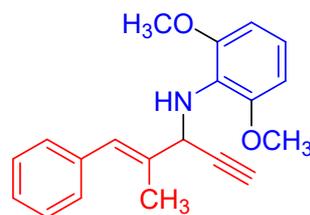
Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), (28.1 mg, 43% yield). ^1H NMR (400 MHz, Chloroform- d) δ : 11.00 (s, 1H), 9.27 (d, $J = 8.8$ Hz, 1H), 7.95 (d, $J = 9.1$ Hz, 1H), 7.74 (d, $J = 9.7$ Hz, 1H), 7.62 (ddd, $J = 8.6, 6.9, 1.4$ Hz, 1H), 7.52–7.32 (m, 6H), 7.17 (d, $J = 9.2$ Hz, 1H), 5.86 (dt, $J = 2.4, 1.2$ Hz, 1H), 5.83 (s, 1H), 3.16 (d, $J = 2.3$ Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ : 191.9, 162.3, 150.5, 137.7, 137.4, 131.6, 130.0, 129.0, 129.0, 128.8, 128.3, 126.9, 125.3, 125.1, 117.9, 115.1, 107.4, 85.0, 82.8, 80.3, 15.9. HRMS (APCI) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 327.1380, found 327.1381.



4da

(*E*)-3,5-diisopropyl-*N*-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)aniline (4da).

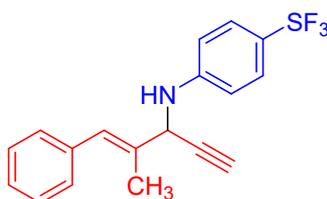
Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 29.9 mg, 45% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.26–7.23 (m, 1H), 7.23–7.18 (m, 2H), 7.08–7.03 (m, 2H), 7.01–6.93 (m, 3H), 6.12 (s, 1H), 4.27 (s, 1H), 3.11 (d, *J* = 2.2 Hz, 2H), 2.68 (hept, *J* = 6.8 Hz, 2H), 1.75 (s, 3H), 1.09 (d, *J* = 6.8 Hz, 6H), 0.90 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 153.4, 142.1, 142.0, 141.7, 128.7, 127.6, 127.1, 123.6, 123.4, 105.4, 81.8, 81.5, 71.2, 27.7, 24.3, 24.0, 18.1. HRMS (APCI) *m/z* calcd for C₂₄H₃₀N⁺ (M+H)⁺ 332.2373, found 332.2371.



4db

(*E*)-2,6-dimethoxy-*N*-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)aniline (4db).

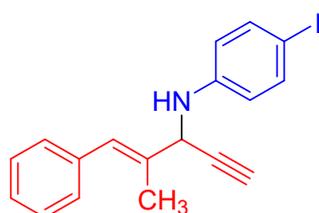
Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 41.3 mg, 67% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.38–7.02 (m, 7H), 6.76 (t, *J* = 8.3 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 6H), 3.61 (s, 1H), 3.03 (s, 1H), 1.80 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 154.5, 150.5, 128.4, 127.2, 127.2, 119.9, 105.6, 105.1, 104.1, 81.7, 80.9, 64.7, 56.1, 55.9, 16.7. HRMS (APCI) *m/z* calcd for C₂₀H₂₂NO₂⁺ (M+H)⁺ 308.1645, found 308.1644.



4dc

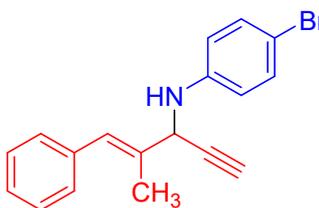
(E)-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)-4-(trifluoro-methylsulfanyl)aniline

(4dc). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 26.9 mg, 40% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.35 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.18 (s, 1H), 7.17 (s, 1H), 7.14 (s, 1H), 6.74 (s, 1H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.63 (s, 1H), 4.19 (s, 1H), 2.37 (d, *J* = 2.2 Hz, 1H), 1.90 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 148.8, 138.3, 137.0, 134.4, 129.1, 128.6, 128.4, 127.1, 114.3, 81.8, 73.5, 53.4, 15.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : 63.05. HRMS (APCI) *m/z* calcd for C₁₈H₁₇F₃NS⁺ (M+H)⁺ 336.1028, found 336.1026.



4dd

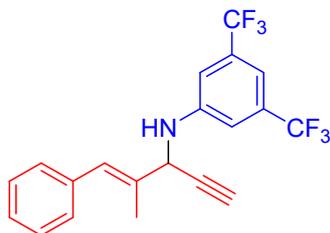
(E)-4-iodo-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)aniline (4dd). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 35.2 mg, 47% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.41–7.35 (m, 2H), 7.30–7.24 (m, 2H), 7.23–7.16 (m, 3H), 6.76 (s, 1H), 6.46–6.42 (m, 2H), 4.60 (s, 1H), 3.95 (s, 1H), 2.38 (d, *J* = 2.2 Hz, 1H), 1.92 (d, *J* = 1.5 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 146.2, 137.9, 137.1, 134.7, 129.1, 128.3, 128.3, 127.0, 116.3, 82.1, 73.4, 53.6, 15.2. HRMS (APCI) *m/z* calcd for C₁₈H₁₇IN⁺ (M+H)⁺ 374.0400, found 374.0402.



4de

(E)-4-bromo-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)aniline (4de). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 29.3 mg, 45% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.34 (t, *J* = 7.4 Hz, 2H), 7.30–7.26 (m, 4H), 7.24 (d, *J* = 1.4 Hz, 1H), 6.83 (s, 1H), 6.62–6.58 (m, 2H), 4.67 (s, 1H), 4.00 (s, 1H), 2.45 (d, *J* = 2.3 Hz, 1H), 1.99 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 145.6, 137.1, 134.7, 132.1, 129.1,

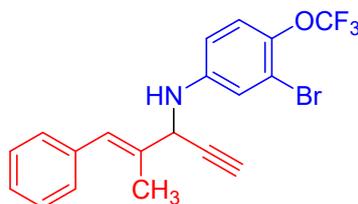
128.3, 128.3, 127.0, 115.8, 110.6, 82.2, 73.3, 53.8, 15.2. HRMS (APCI) m/z calcd for $C_{18}H_{17}BrNi^+$ ($M+H$)⁺ 326.04539, found 326.0538.



4df

(E)-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)-3,5-bis(trifluoromethyl)aniline

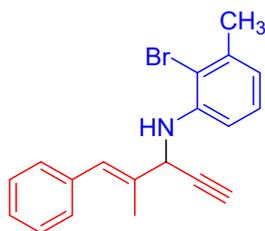
(4df). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 39.9 mg, 52% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ : 7.27 (dd, $J = 8.2, 6.8$ Hz, 2H), 7.22–7.14 (m, 5H), 7.02 (s, 2H), 6.80 (s, 1H), 4.36 (d, $J = 6.6$ Hz, 1H), 2.42 (d, $J = 2.3$ Hz, 1H), 1.91 (d, $J = 1.4$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 147.2, 136.8, 133.7, 129.4, 129.0, 128.4, 127.3, 113.4, 111.7, 81.0, 74.2, 53.5, 15.1. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : 63.05. HRMS (APCI) m/z calcd for $C_{20}H_{16}F_6N^+$ ($M+H$)⁺ 384.1181, found 384.1180.



4dg

(E)-3-bromo-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)-4-

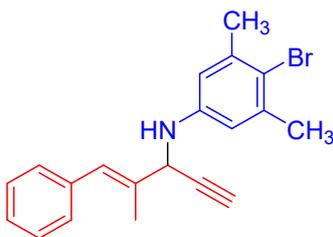
(trifluoromethoxy)aniline (4dg). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 35.3 mg, 43% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30–7.24 (m, 2H), 7.21 (s, 1H), 7.18 (d, $J = 9.0$ Hz, 2H), 7.04 (dd, $J = 8.9, 1.4$ Hz, 1H), 6.88 (d, $J = 2.8$ Hz, 1H), 6.77 (s, 1H), 6.55 (dd, $J = 8.9, 2.8$ Hz, 1H), 4.58 (s, 1H), 4.02 (s, 1H), 2.40 (d, $J = 2.3$ Hz, 1H), 1.91 (d, $J = 1.4$ Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ : 146.1, 137.0, 134.3, 129.1, 128.7, 128.4, 127.2, 123.5, 118.2, 113.4, 73.7, 53.7, 15.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ : 63.08. HRMS (APCI) m/z calcd for $C_{19}H_{16}BrF_3NO^+$ ($M+H$)⁺ 410.0362, found 410.0365.



4dh

(E)-2-bromo-3-methyl-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)aniline (4dh).

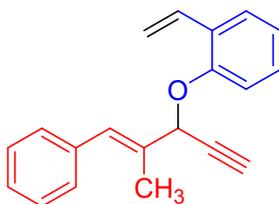
Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 52.3 mg, 77% yield. ^1H NMR (400 MHz, Chloroform- d) δ : 7.31–7.21 (m, 4H), 7.18 (t, $J = 3.4$ Hz, 1H), 7.02 (t, $J = 7.8$ Hz, 1H), 6.78 (s, 1H), 6.63–6.56 (m, 2H), 4.82–4.60 (m, 2H), 2.40 (d, $J = 2.1$ Hz, 1H), 2.33 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ : 143.6, 138.6, 137.1, 134.6, 129.0, 128.2, 128.1, 127.5, 126.9, 120.2, 113.1, 110.3, 82.1, 73.1, 53.7, 23.9, 15.0. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{19}\text{BrN}^+$ ($\text{M}+\text{H}$) $^+$ 340.0695, found 340.0693.



4di

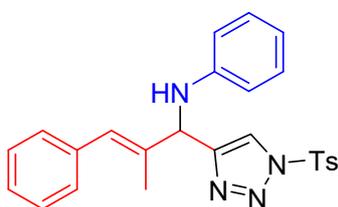
(E)-4-bromo-3,5-dimethyl-N-(2-methyl-1-phenylpent-1-en-4-yn-3-yl)aniline (4di).

Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 38.2 mg, 54% yield. ^1H NMR (400 MHz, Chloroform- d) δ : 7.35 (t, $J = 7.6$ Hz, 2H), 7.29 (s, 1H), 7.27 (d, $J = 6.2$ Hz, 1H), 7.25 (d, $J = 4.2$ Hz, 1H), 6.85 (s, 1H), 6.49 (s, 2H), 4.67 (s, 1H), 3.86 (s, 1H), 2.45 (d, $J = 2.2$ Hz, 1H), 2.34 (s, 6H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ : 151.6, 149.2, 148.8, 138.0, 137.4, 134.2, 132.0, 131.9, 129.1, 129.0, 128.9, 128.8, 128.3, 127.9, 126.9, 116.7, 114.5, 110.8, 109.1, 108.2, 82.6, 81.1, 75.8, 69.2, 59.7, 34.4, 33.2, 18.9, 16.1. HRMS (APCI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{BrN}^+$ ($\text{M}+\text{H}$) $^+$ 354.0852, found 354.0855.

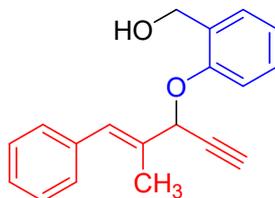


5a

(*E*)-1-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)-2-vinylbenzene (5a). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 43.4 mg, 80% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.51 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.43–7.31 (m, 5H), 7.21–7.09 (m, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.81–5.71 (m, 2H), 5.59 (s, 1H), 5.29 (dd, *J* = 11.1, 1.5 Hz, 1H), 3.12 (d, *J* = 2.2 Hz, 1H), 1.90 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ: 154.7, 151.6, 138.8, 131.6, 128.8, 128.7, 128.2, 127.7, 126.9, 126.6, 121.4, 114.7, 114.1, 106.5, 83.6, 82.1, 80.8, 15.9. HRMS (APCI) *m/z* calcd for C₂₀H₁₉O⁺ (M+H)⁺ 275.1430, found 275.1433.

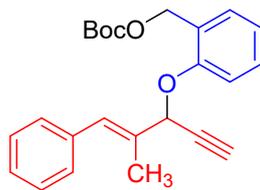
**6a**

(*E*)-N-(2-methyl-3-phenyl-1-(1-tosyl-1H-1,2,3-triazol-4-yl)allyl)aniline (6a). Yellow oil, (PE/EtOAc *v/v* = 10:1 as the eluent), 36.6 mg, 55% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 14.8 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.25–7.16 (m, 7H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.79 (s, 1H), 5.99 (s, 1H), 2.35 (s, 3H), 1.77 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 142.9, 140.4, 140.0, 136.7, 136.7, 134.2, 129.6, 129.6, 129.5, 128.5, 128.0, 126.5, 21.7, 13.8. HRMS (APCI) *m/z* calcd for C₂₅H₂₅N₄O₂S⁺ (M+H)⁺ 445.1693, found 445.1690.

**7a**

(*E*)-2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)phenylmethanol (7a). Yellow oil, (PE/EtOAc *v/v* = 25:1 as the eluent), 30.9 mg, 74% yield. ¹H NMR (400 MHz, Chloroform-*d*) δ: 7.42–7.30 (m, 6H), 7.18 (td, *J* = 7.9, 1.8 Hz, 1H), 6.95 (td, *J* = 7.4,

1.0 Hz, 1H), 6.79 (d, $J = 8.2$ Hz, 1H), 5.82–5.78 (m, 1H), 5.62 (s, 1H), 4.77 (qd, $J = 13.0, 4.1$ Hz, 2H), 3.14 (d, $J = 2.2$ Hz, 1H), 2.19 (s, 1H), 1.90 (d, $J = 1.2$ Hz, 3H). ^{13}C : NMR (100 MHz, Chloroform- d) δ : 155.4, 151.1, 138.5, 129.9, 128.9, 128.8, 128.4, 126.7, 121.4, 113.2, 106.6, 83.4, 82.4, 80.6, 62.0, 15.9. HRMS (APCI) m/z calcd for $\text{C}_{19}\text{H}_{19}\text{O}_2^+$ ($\text{M}+\text{H}$) $^+$ 279.1380, found 279.1382.

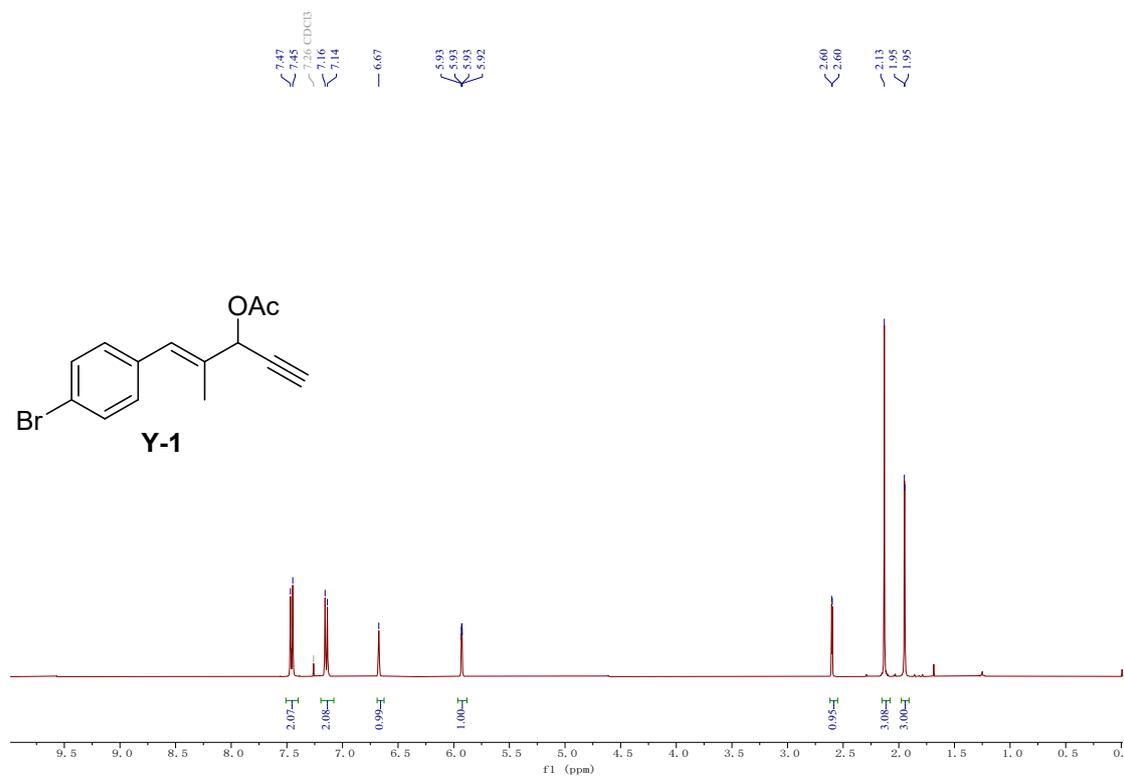


8a

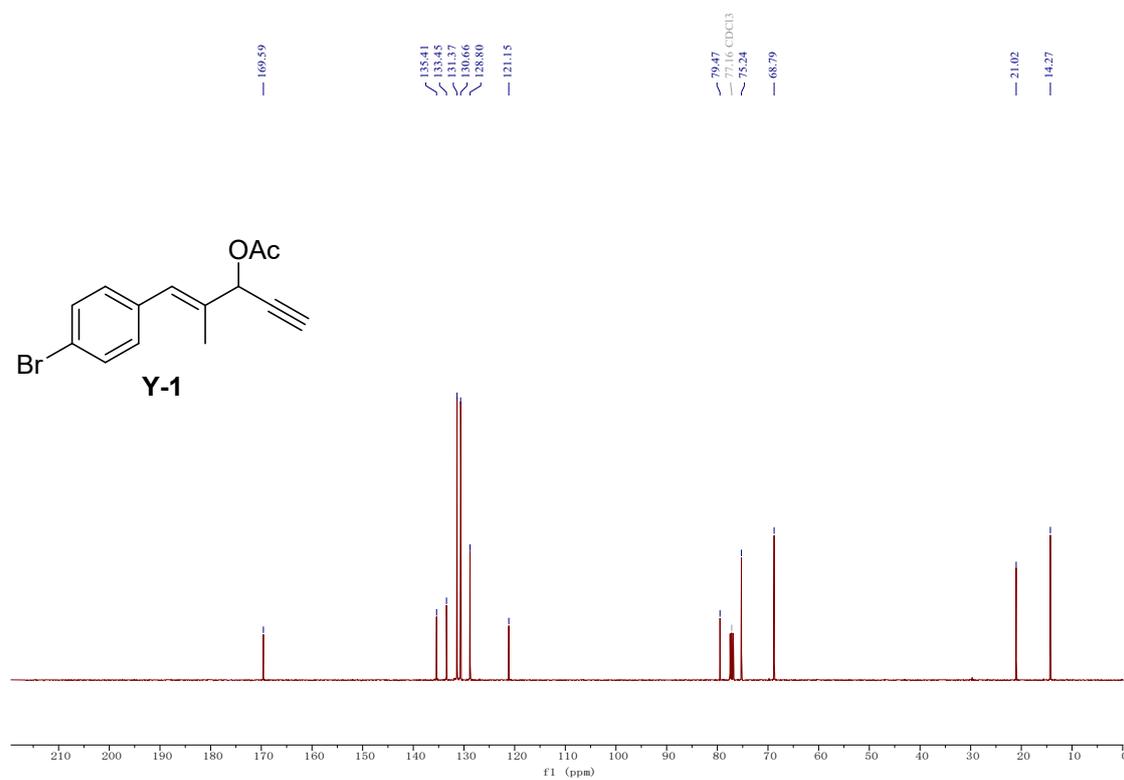
(*E*)-tert-butyl (2-((2-methyl-1-phenylpent-1-en-4-yn-3-yl)oxy)benzyl) carbonate (8a). Yellow oil, (PE/EtOAc $v/v = 25:1$ as the eluent), 31.3 mg, 76% yield. ^1H NMR (400 MHz, Chloroform- d) δ : 7.32 (dd, $J = 8.3, 1.6$ Hz, 2H), 7.29–7.24 (m, 3H), 7.23–7.17 (m, 2H), 6.83 (td, $J = 7.5, 1.0$ Hz, 1H), 6.71–6.65 (m, 1H), 5.70 (dt, $J = 2.5, 1.3$ Hz, 1H), 5.53 (s, 1H), 5.20–5.07 (m, 2H), 3.02 (d, $J = 2.2$ Hz, 1H), 1.79 (d, $J = 1.2$ Hz, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, Chloroform- d) δ : 155.4, 153.7, 151.5, 138.6, 130.1, 129.6, 128.7, 128.2, 126.8, 124.8, 121.1, 113.1, 106.5, 83.0, 82.1, 82.1, 80.8, 64.6, 28.0, 15.7. HRMS (APCI) m/z calcd for $\text{C}_{24}\text{H}_{27}\text{O}_4^+$ ($\text{M}+\text{H}$) $^+$ 379.1904, found 379.1901.

VIII. ^1H NMR and ^{13}C NMR spectra of new compounds

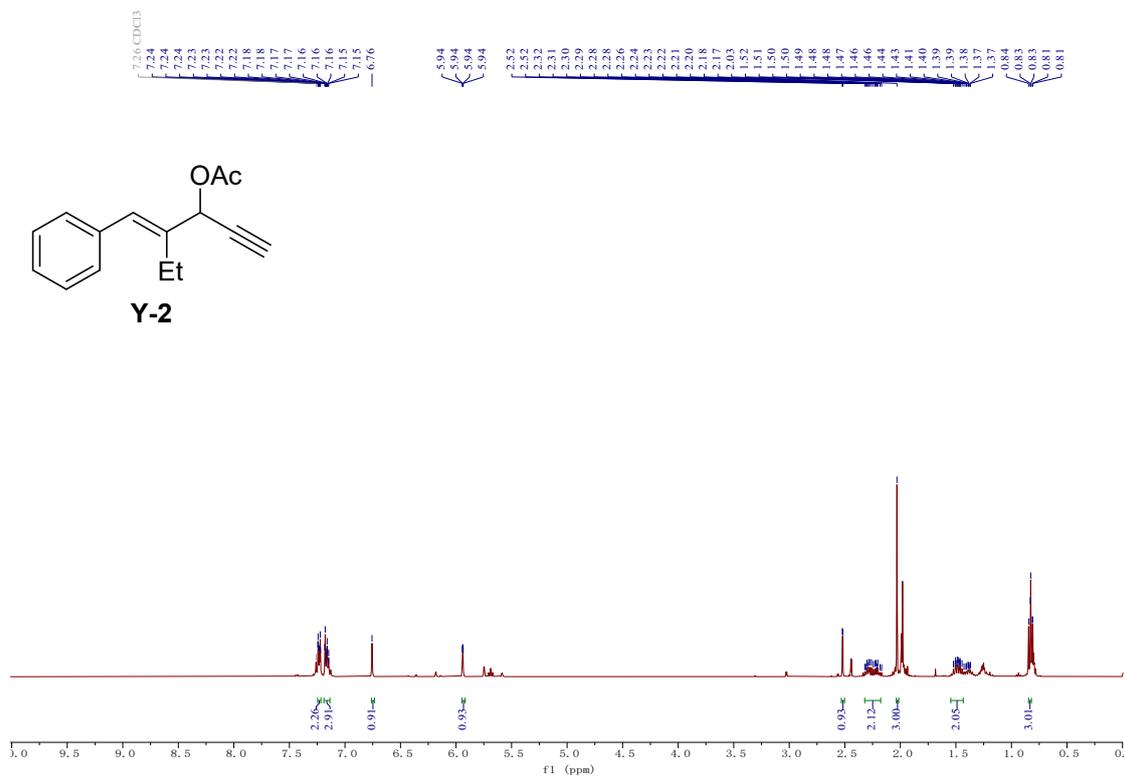
^1H NMR-Y-1 (400 MHz, CDCl_3)



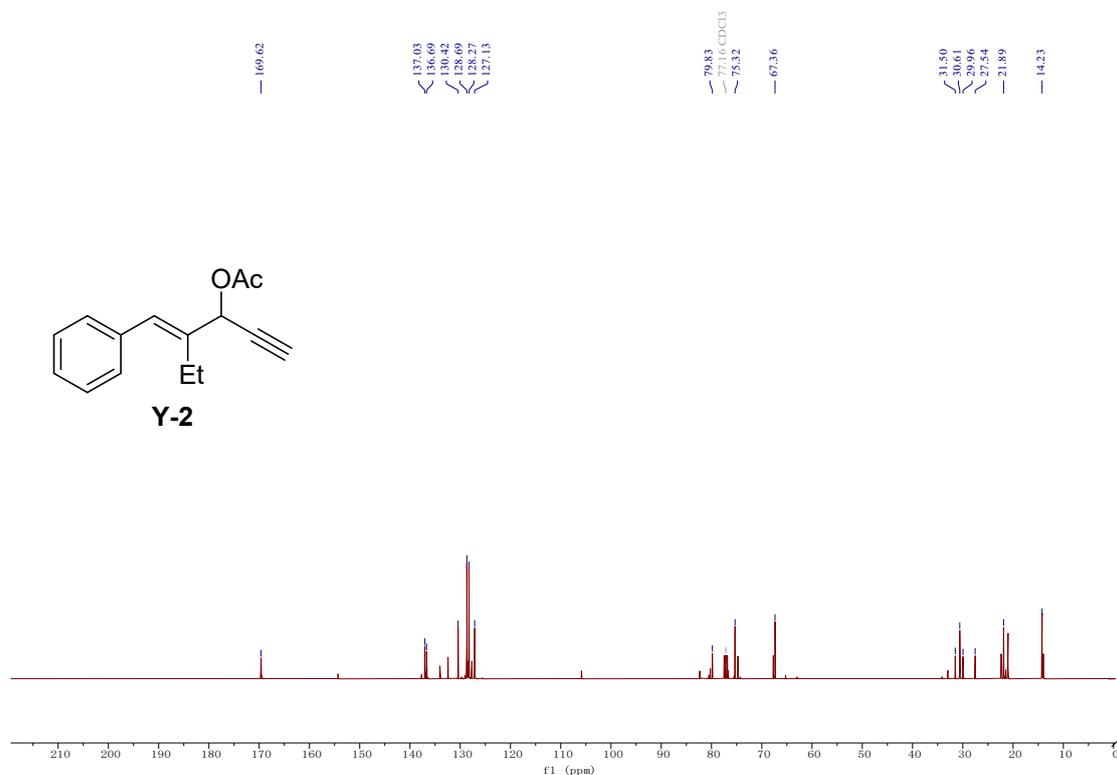
^{13}C NMR-Y-1 (100 MHz, CDCl_3)



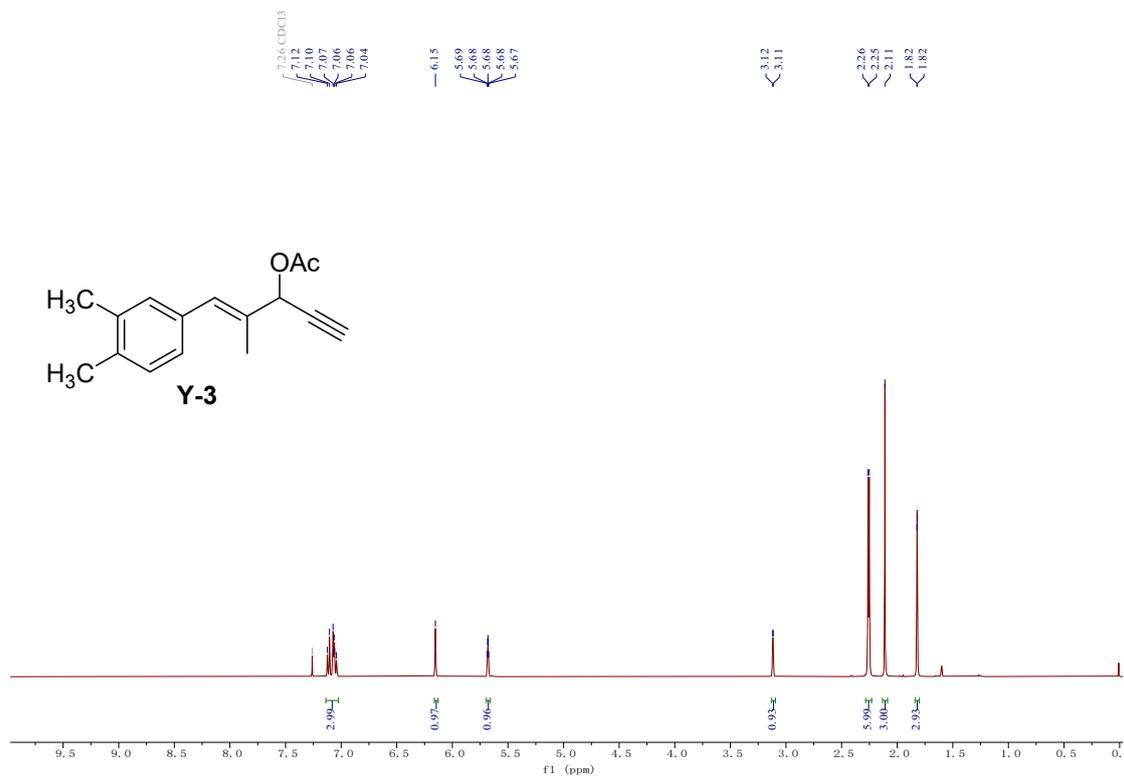
¹H NMR-Y-2 (400 MHz, CDCl₃)



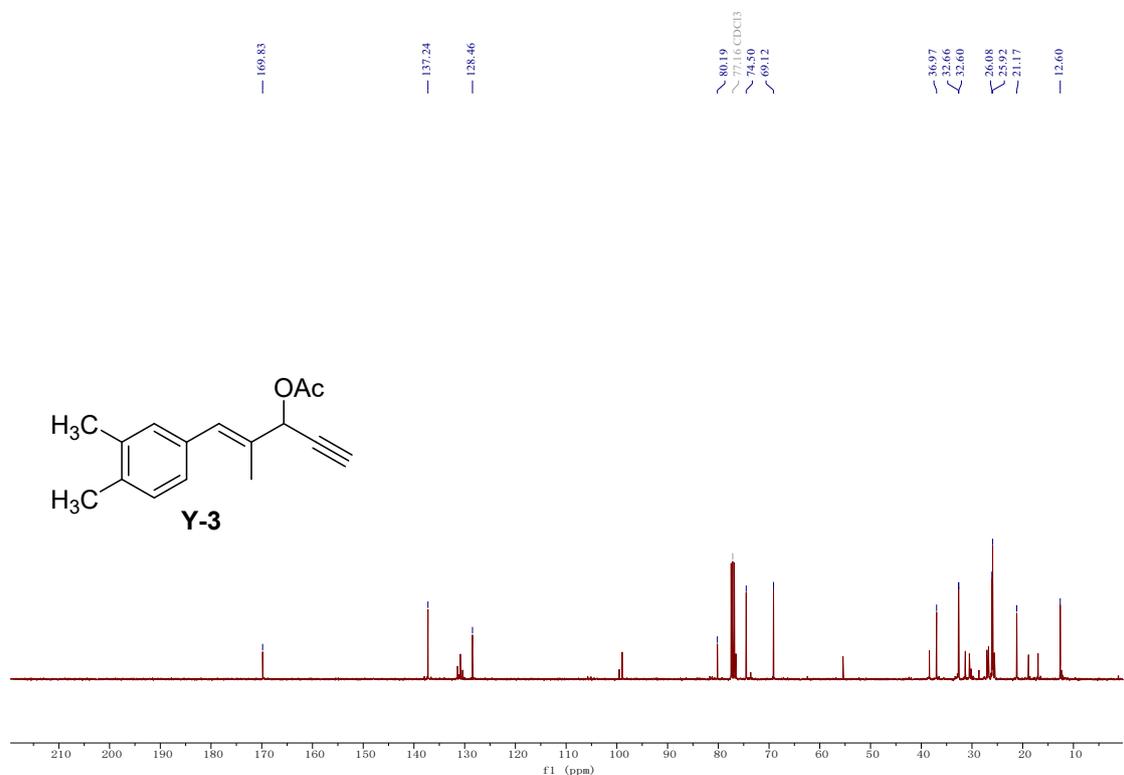
¹³C NMR-Y-2 (100 MHz, CDCl₃)



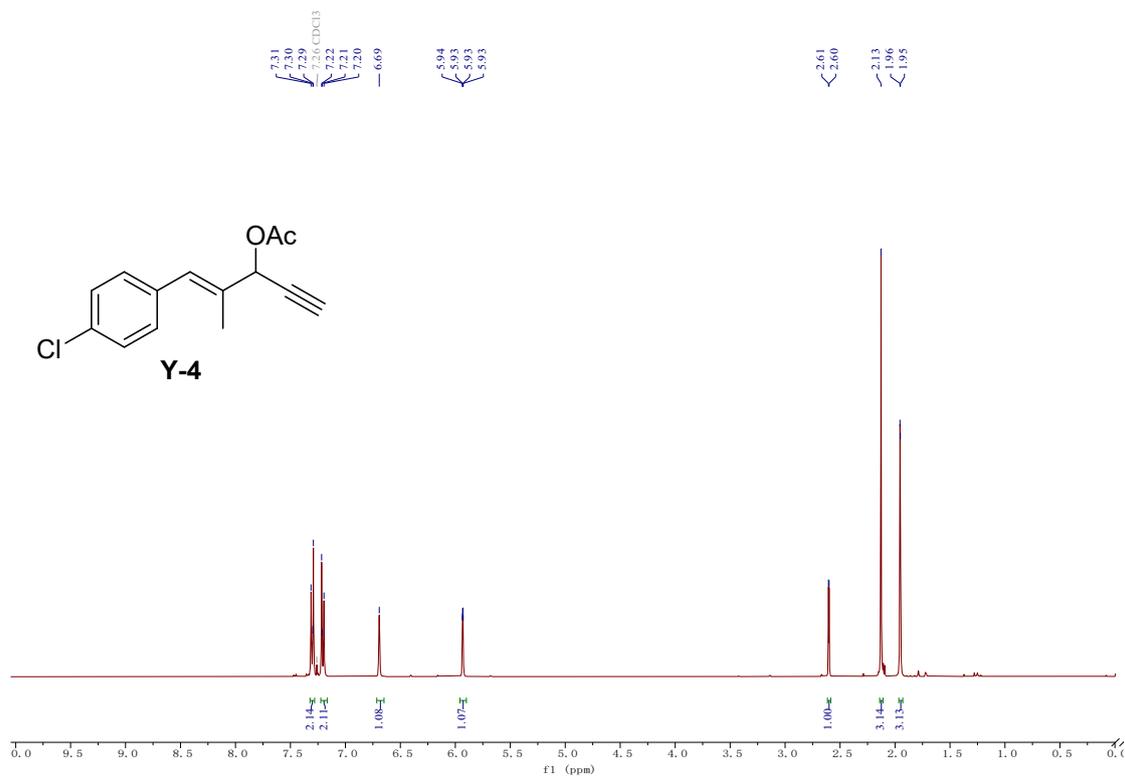
¹H NMR-Y-3 (400 MHz, CDCl₃)



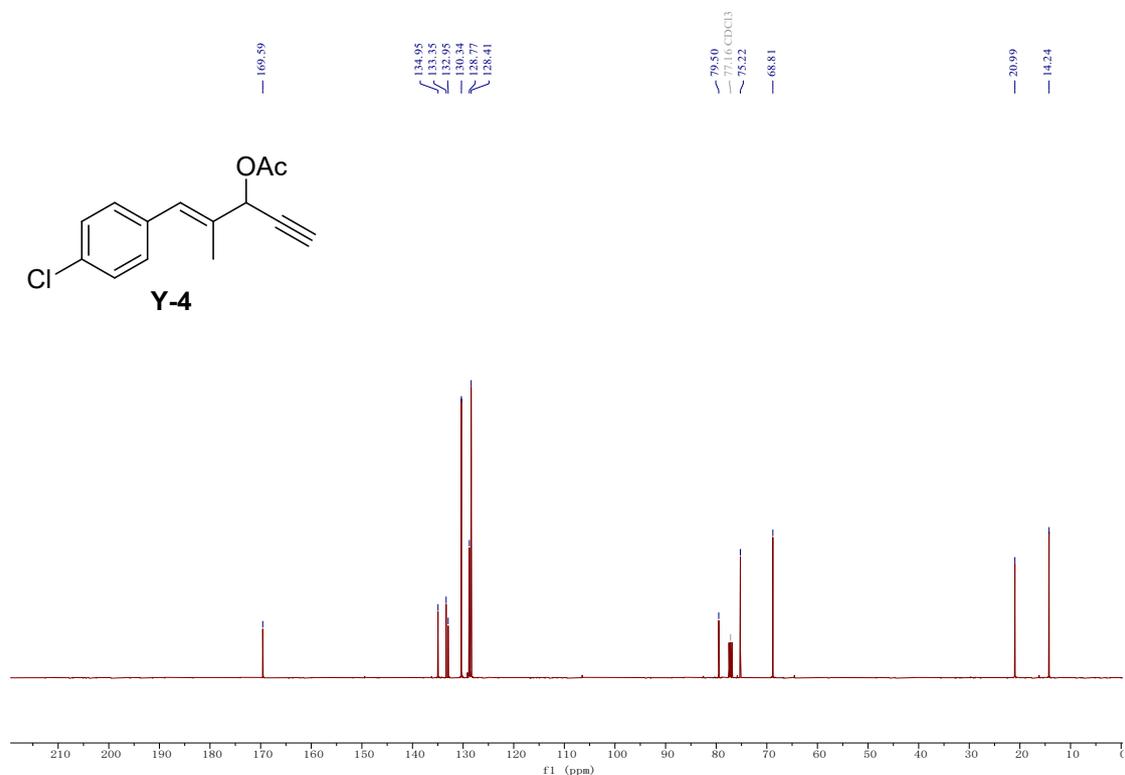
¹³C NMR-Y-3 (100 MHz, CDCl₃)



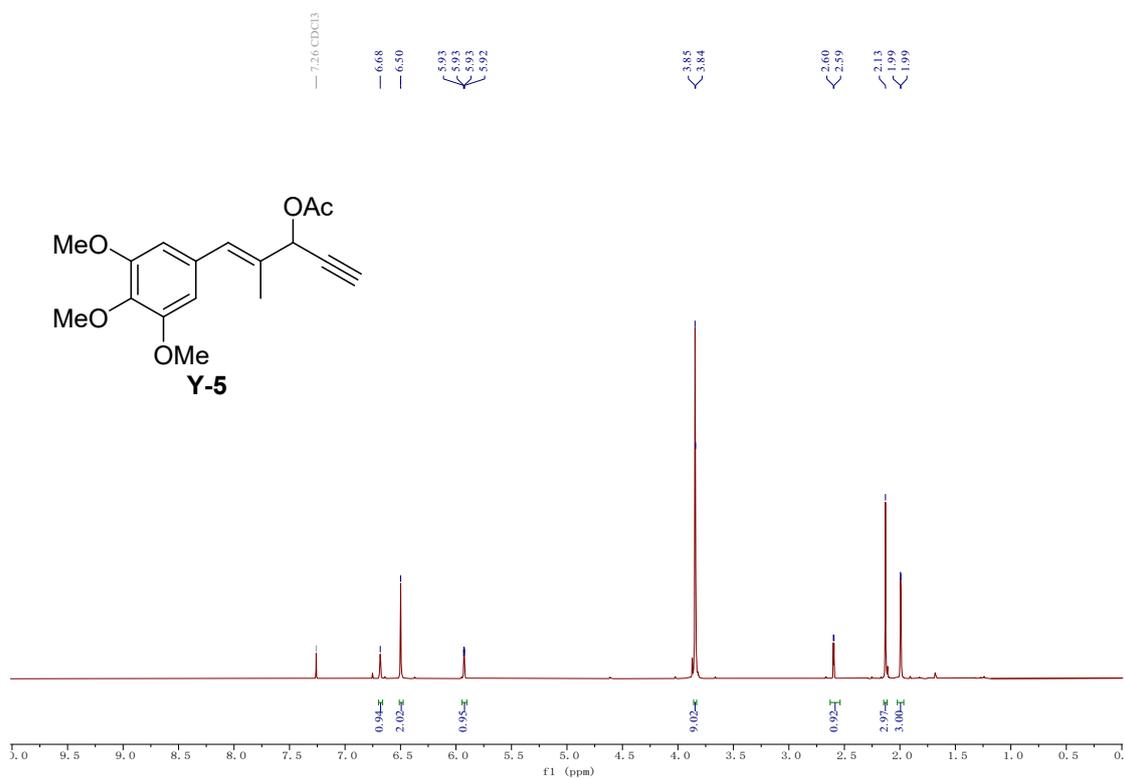
¹H NMR-Y-4 (400 MHz, CDCl₃)



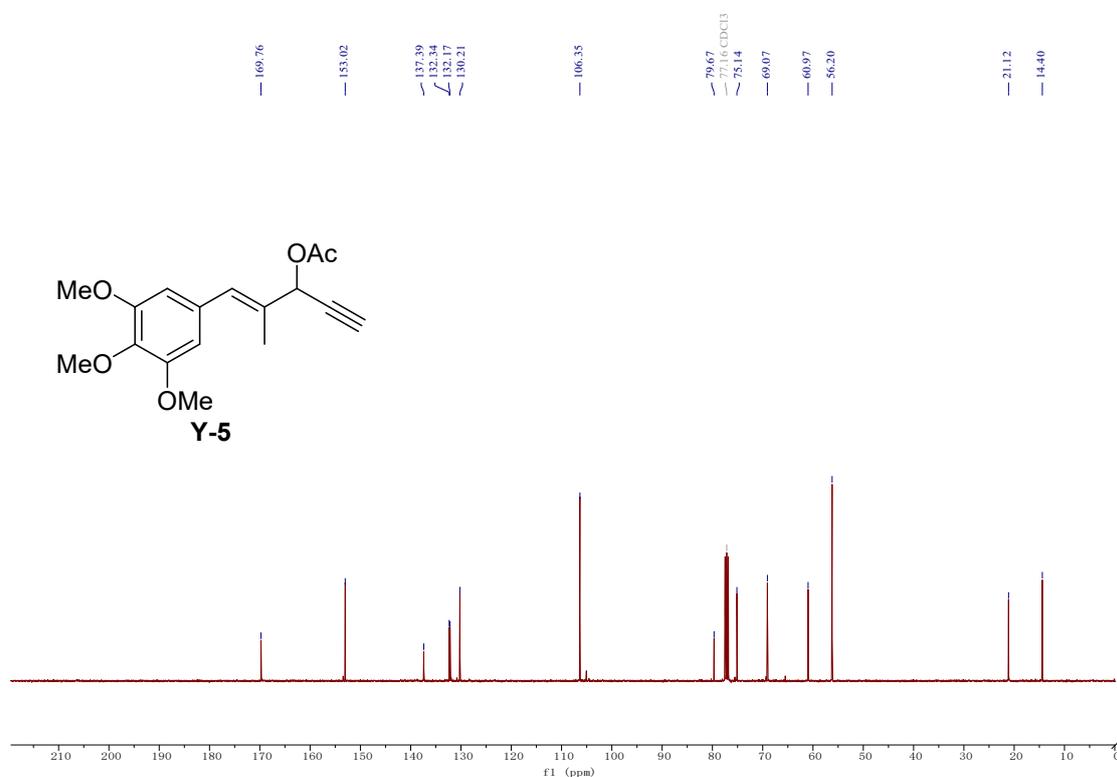
¹³C NMR-Y-4 (100 MHz, CDCl₃)



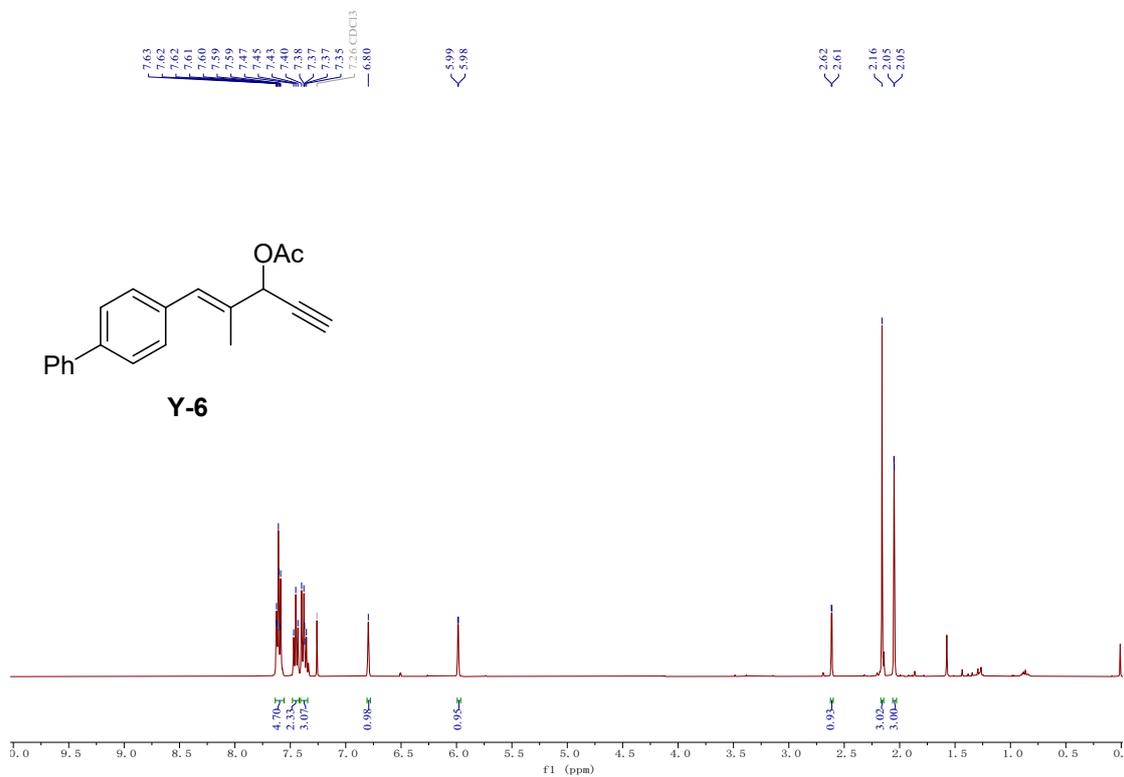
¹H NMR-Y-5 (400 MHz, CDCl₃)



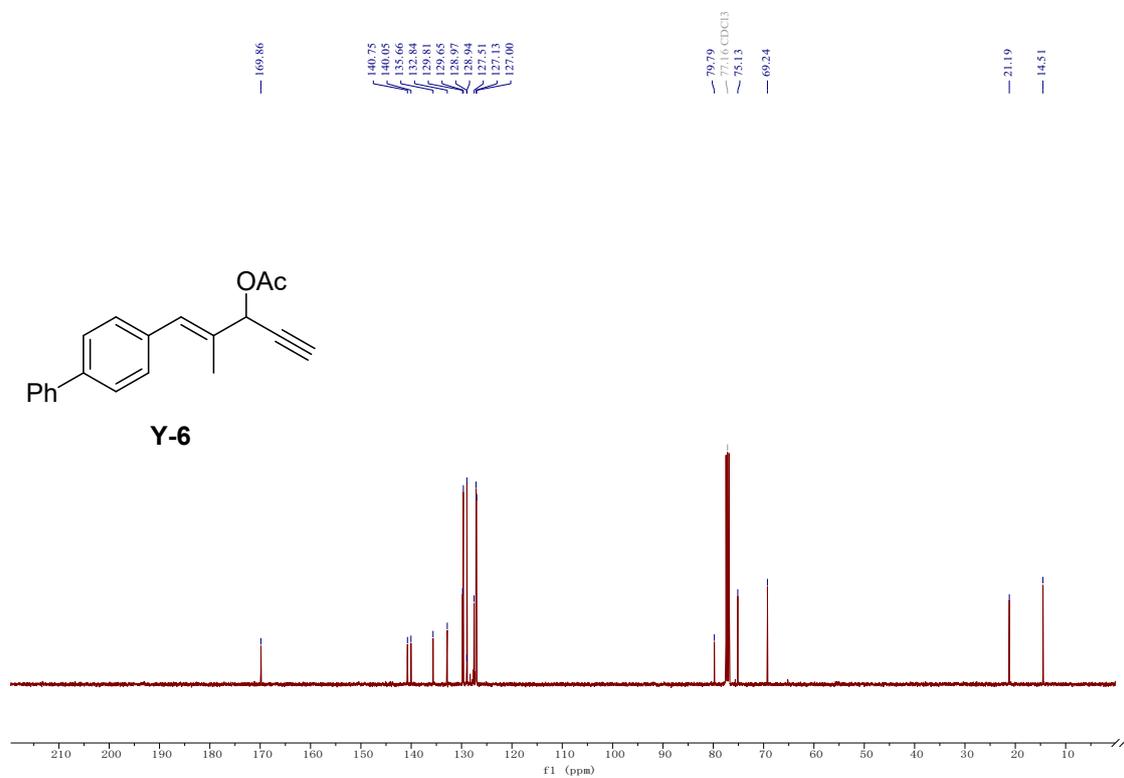
¹³C NMR-Y-5 (100 MHz, CDCl₃)



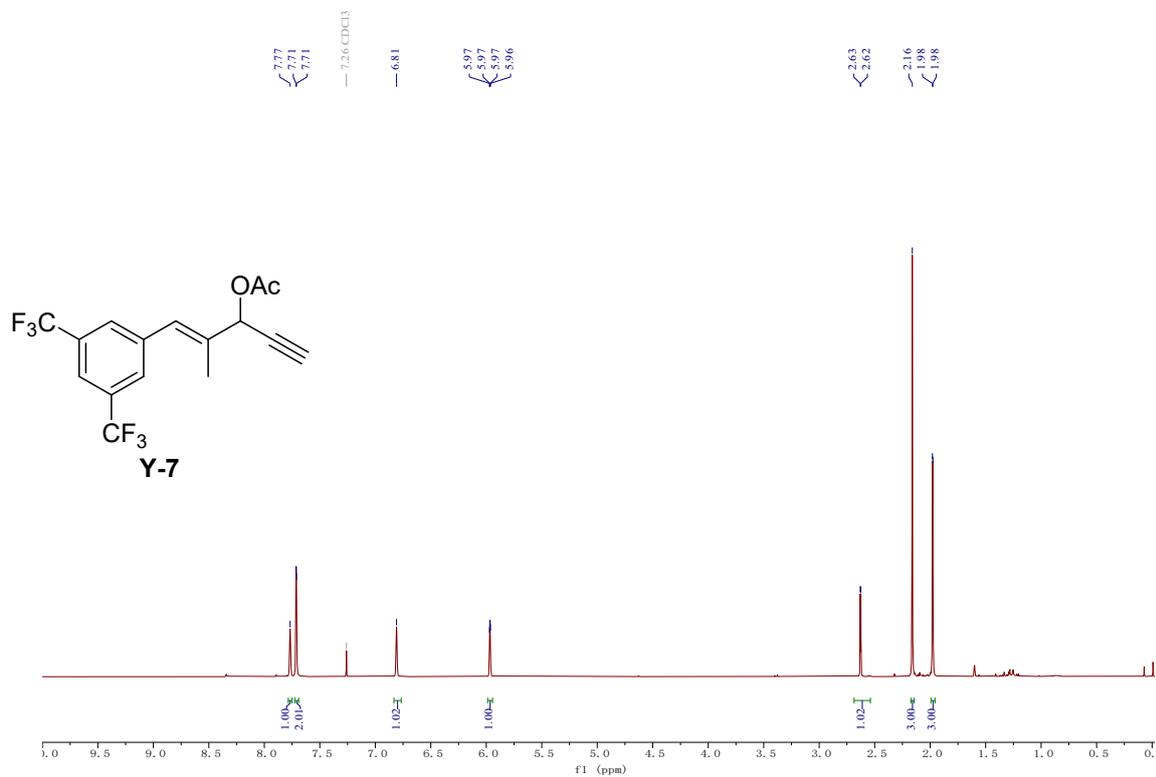
¹H NMR-Y-6 (400 MHz, CDCl₃)



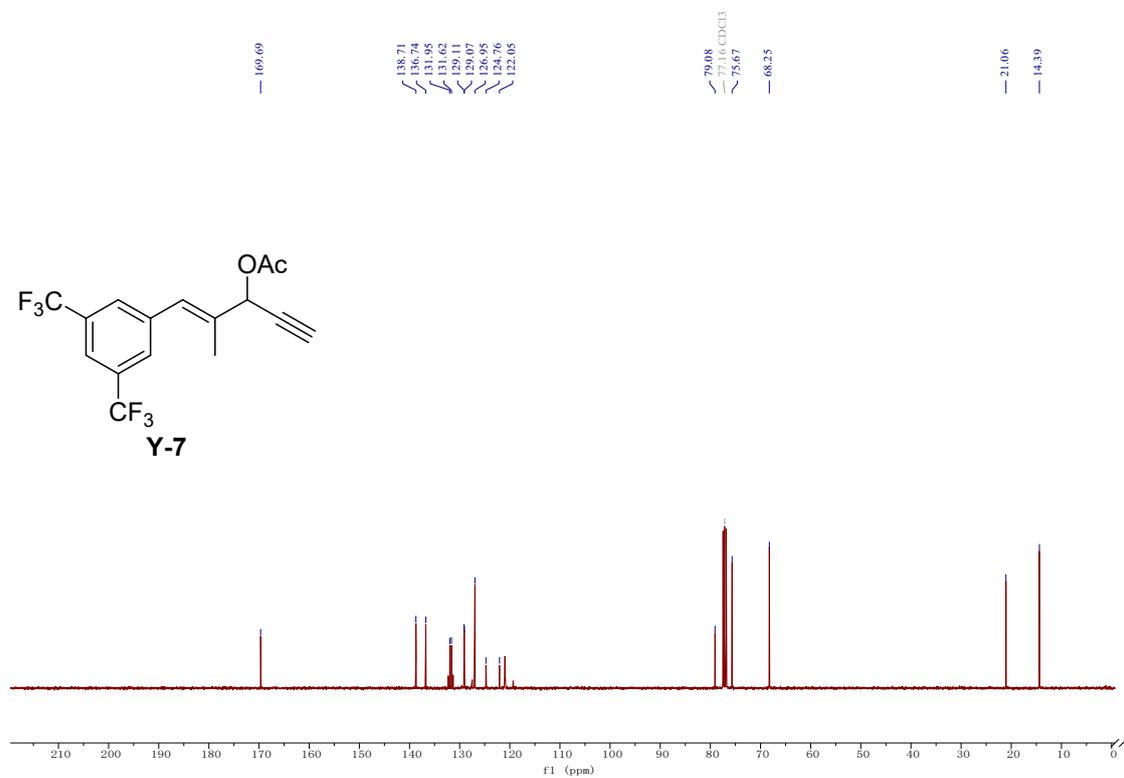
¹³C NMR-Y-6 (100 MHz, CDCl₃)



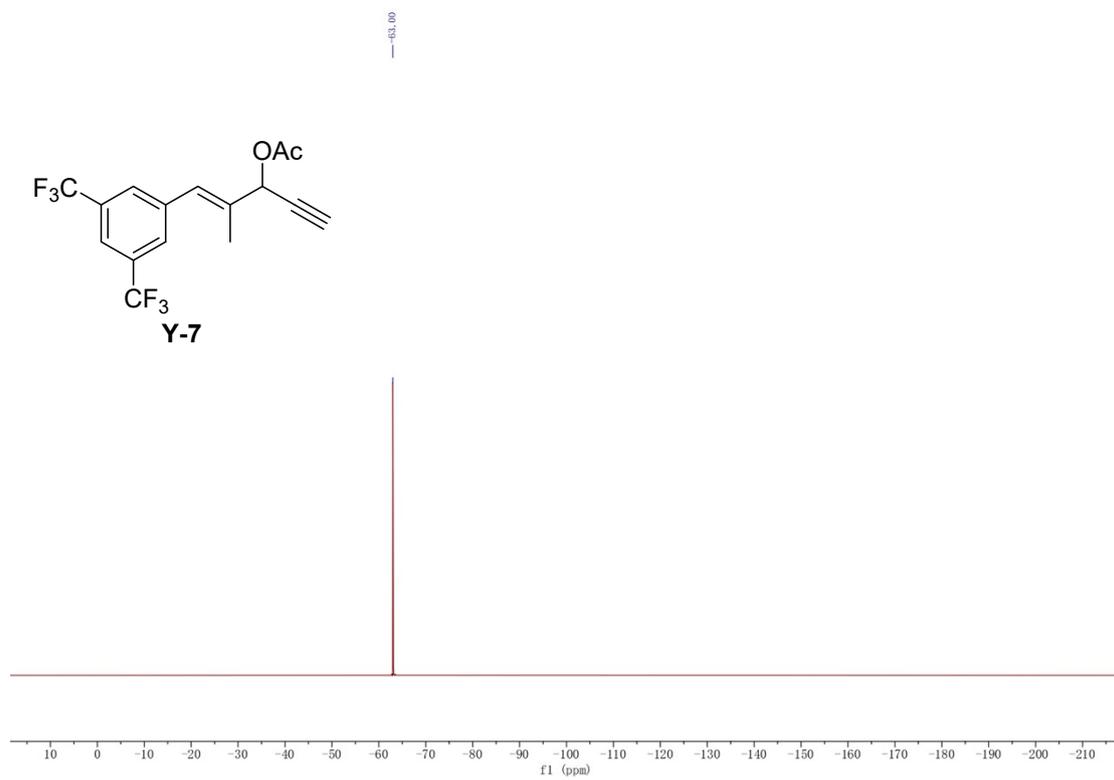
^1H NMR-Y-7 (400 MHz, CDCl_3)



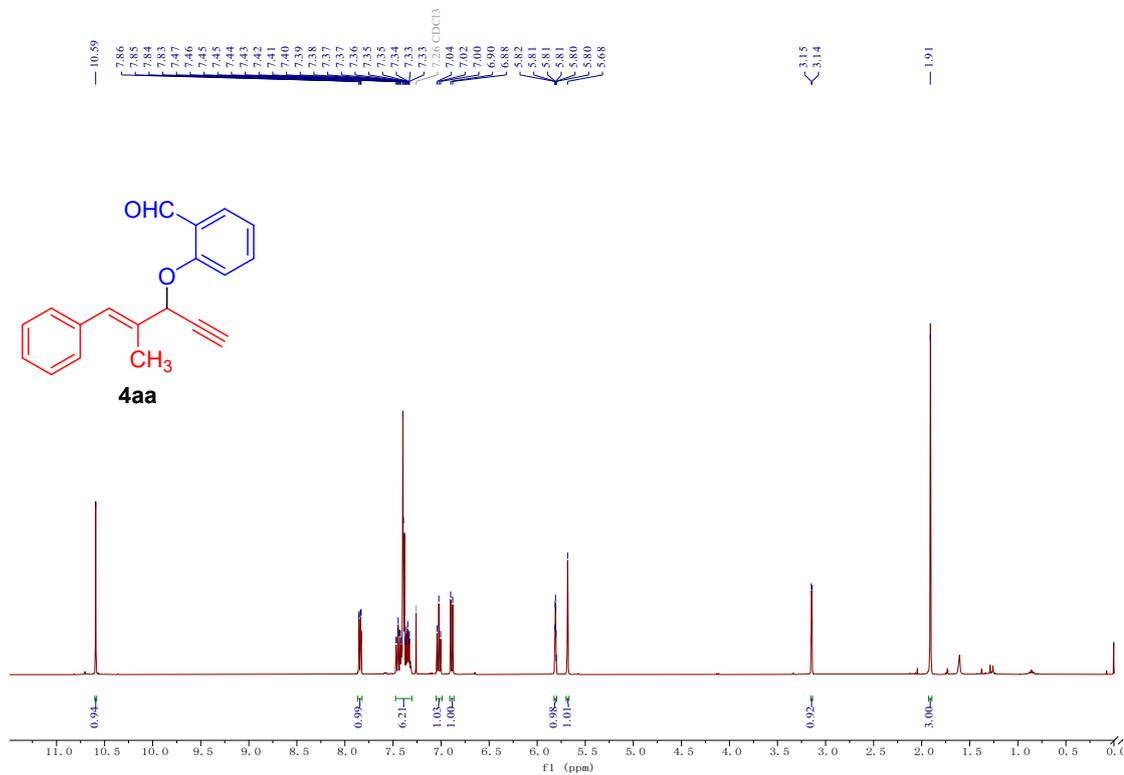
^{13}C NMR-Y-7 (100 MHz, CDCl_3)



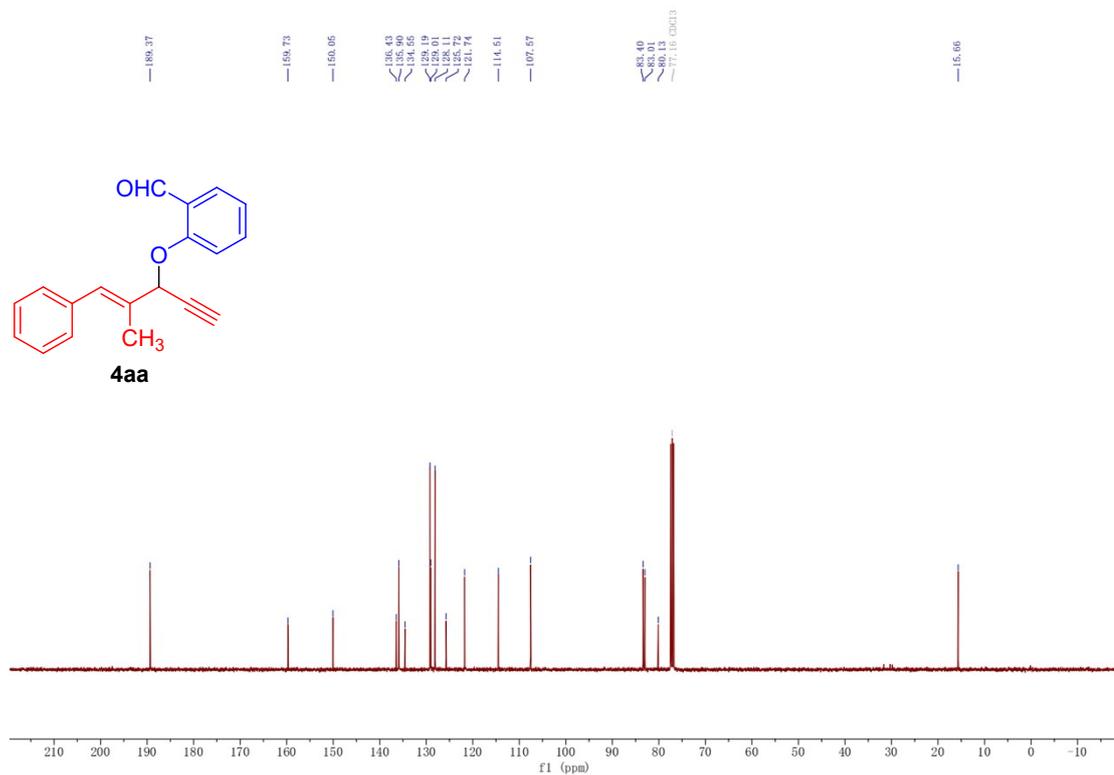
^{19}F NMR-Y-7 (376 MHz, CDCl_3)



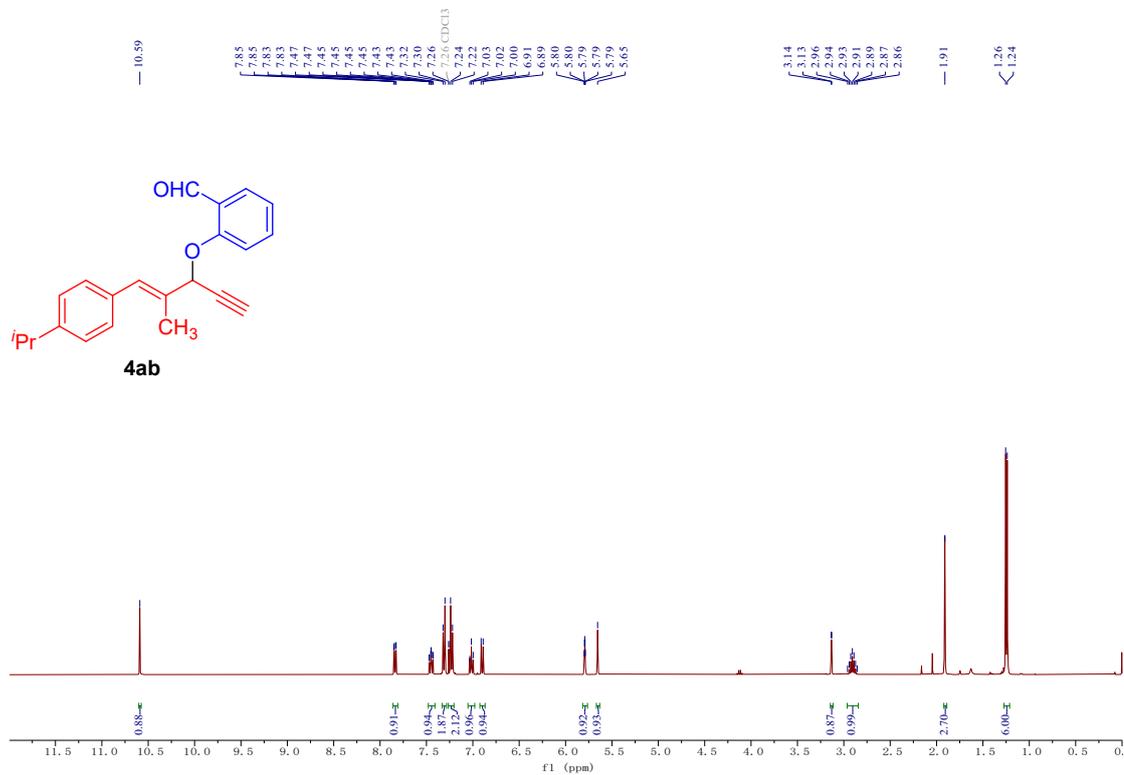
¹H NMR-4aa (400 MHz, CDCl₃)



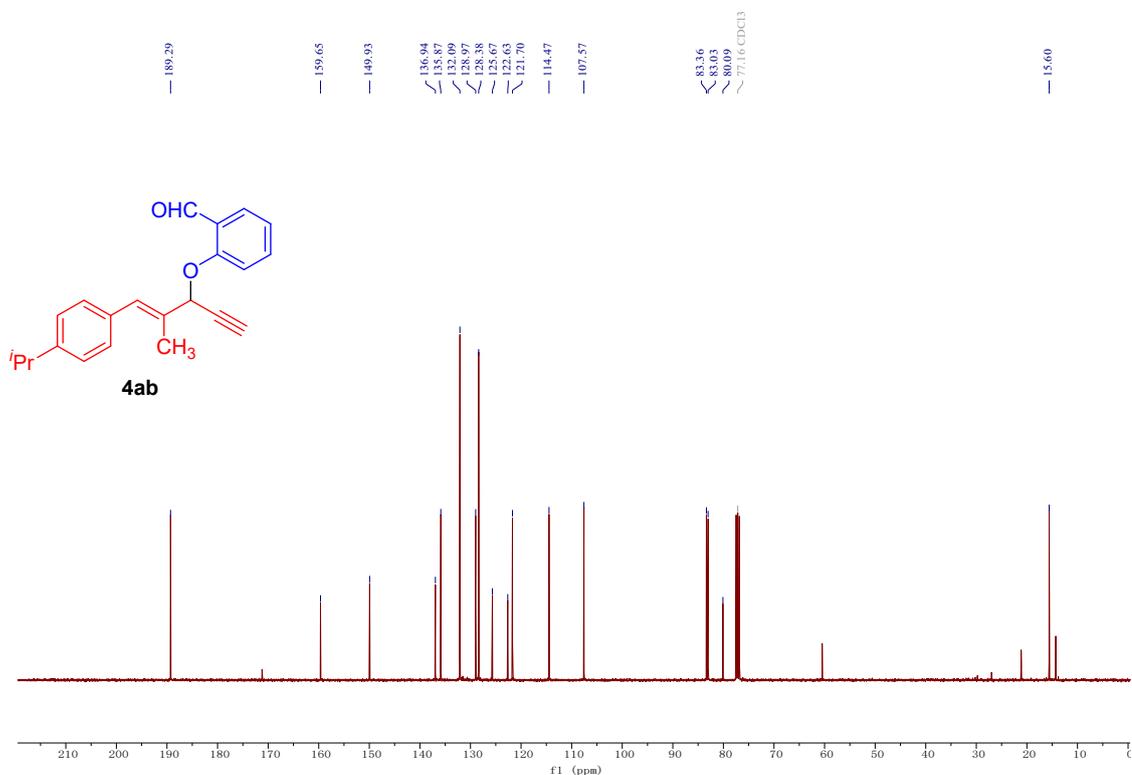
¹³C NMR-4aa (100 MHz, CDCl₃)



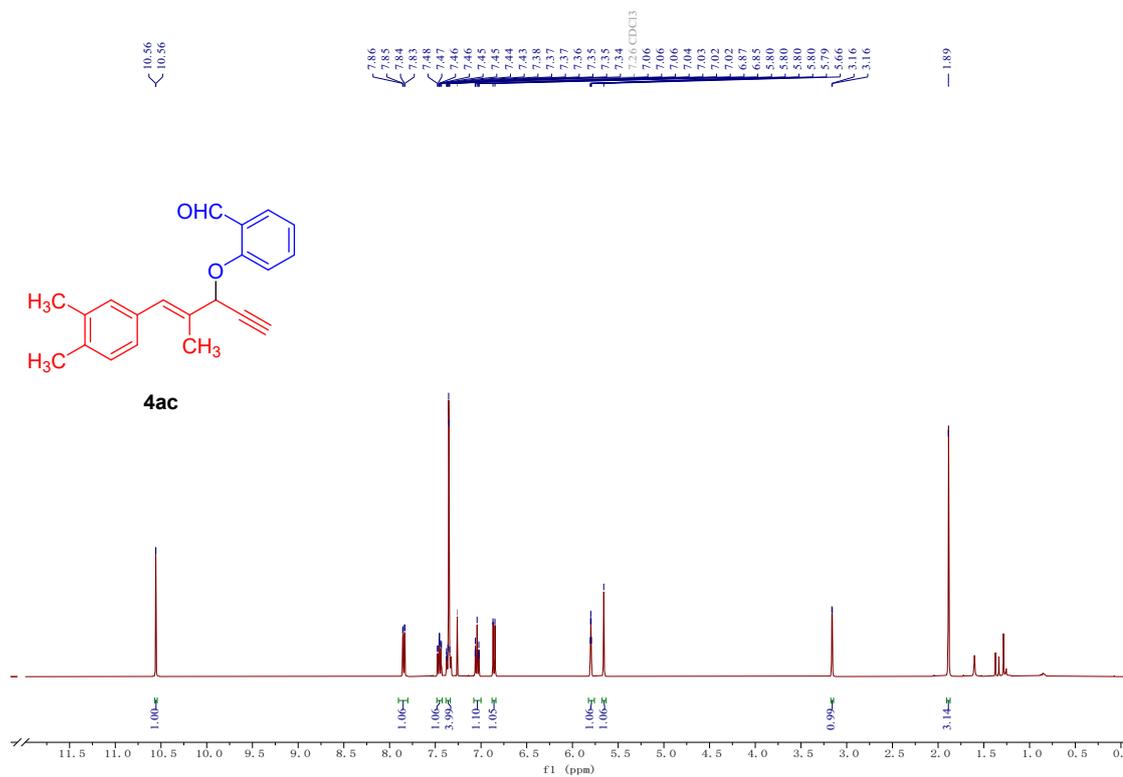
¹H NMR-4ab (400 MHz, CDCl₃)



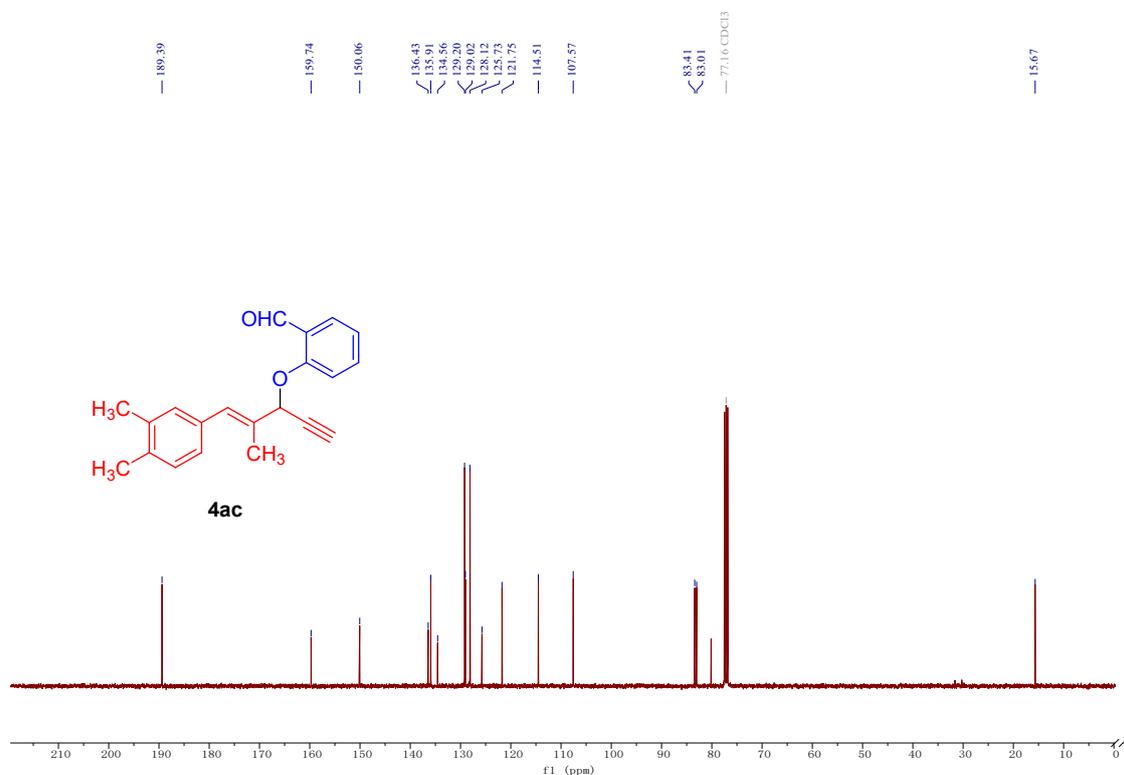
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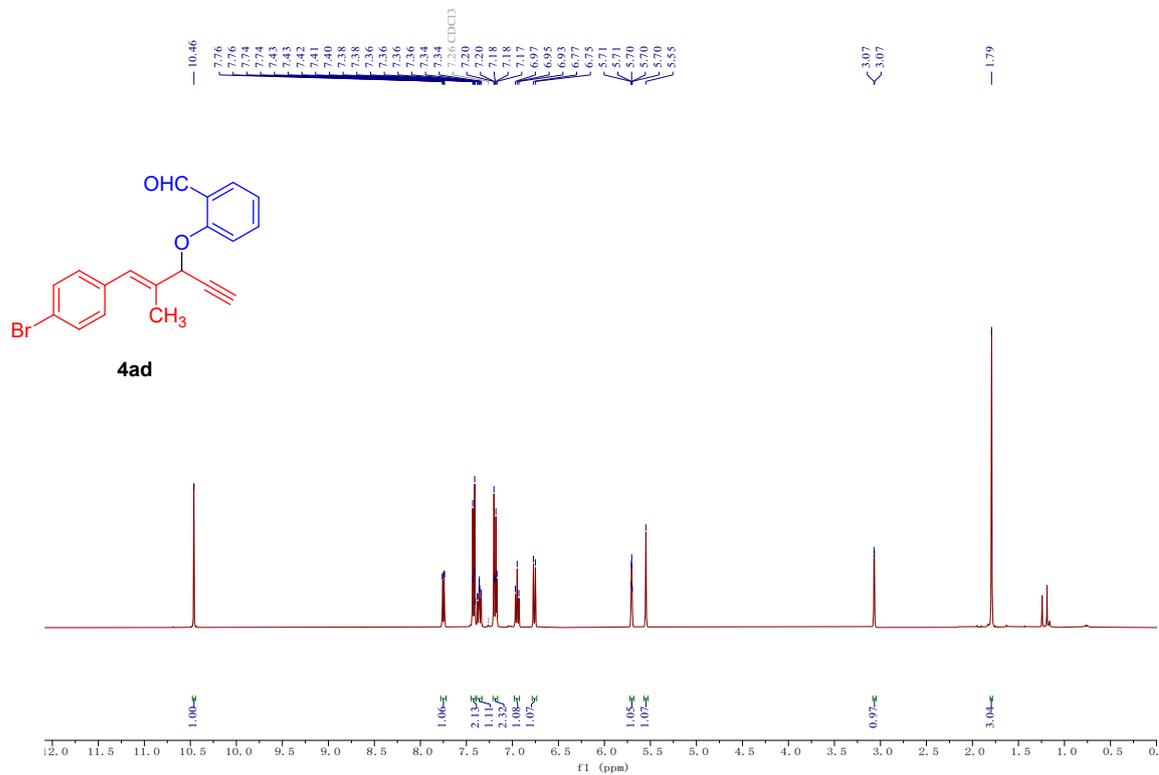
¹H NMR-4ac (400 MHz, CDCl₃)



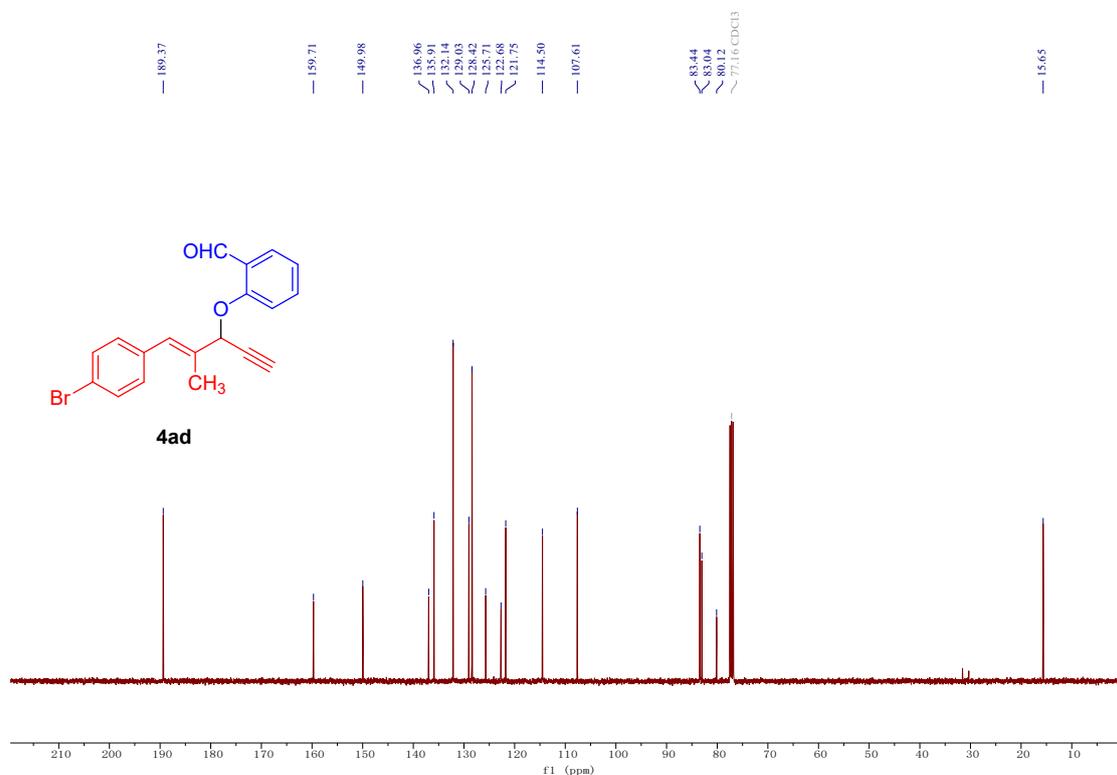
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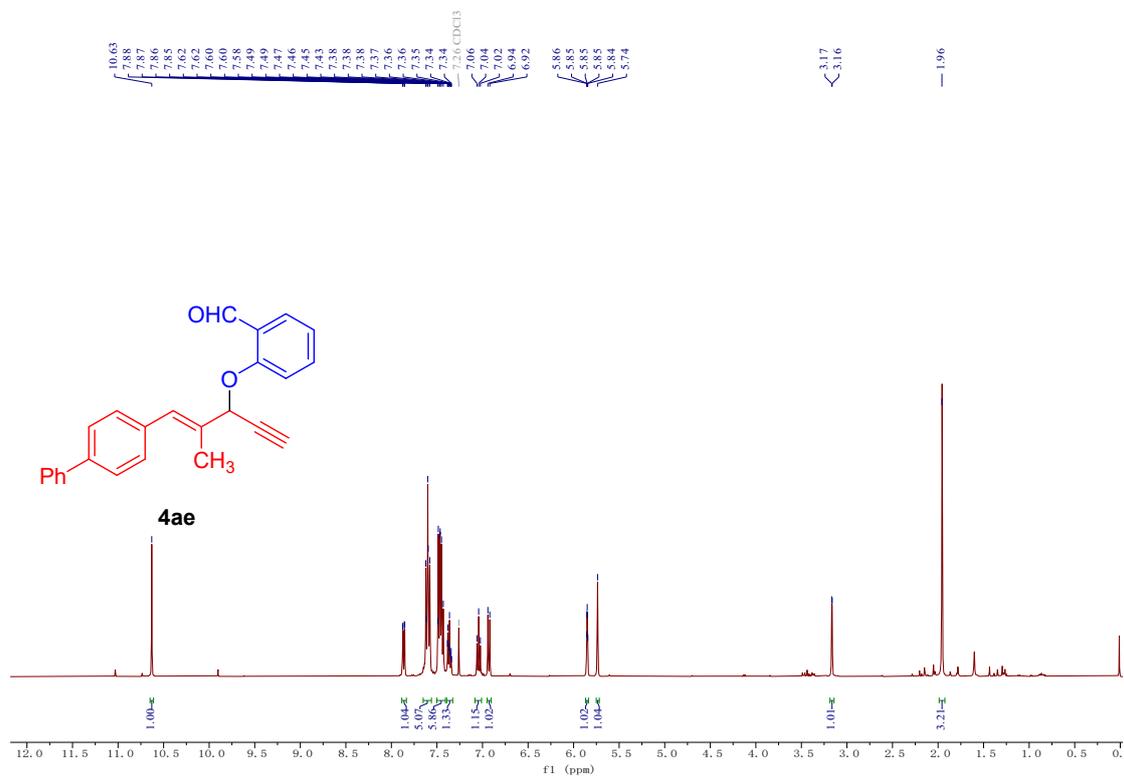
¹H NMR-4ad (400 MHz, CDCl₃)



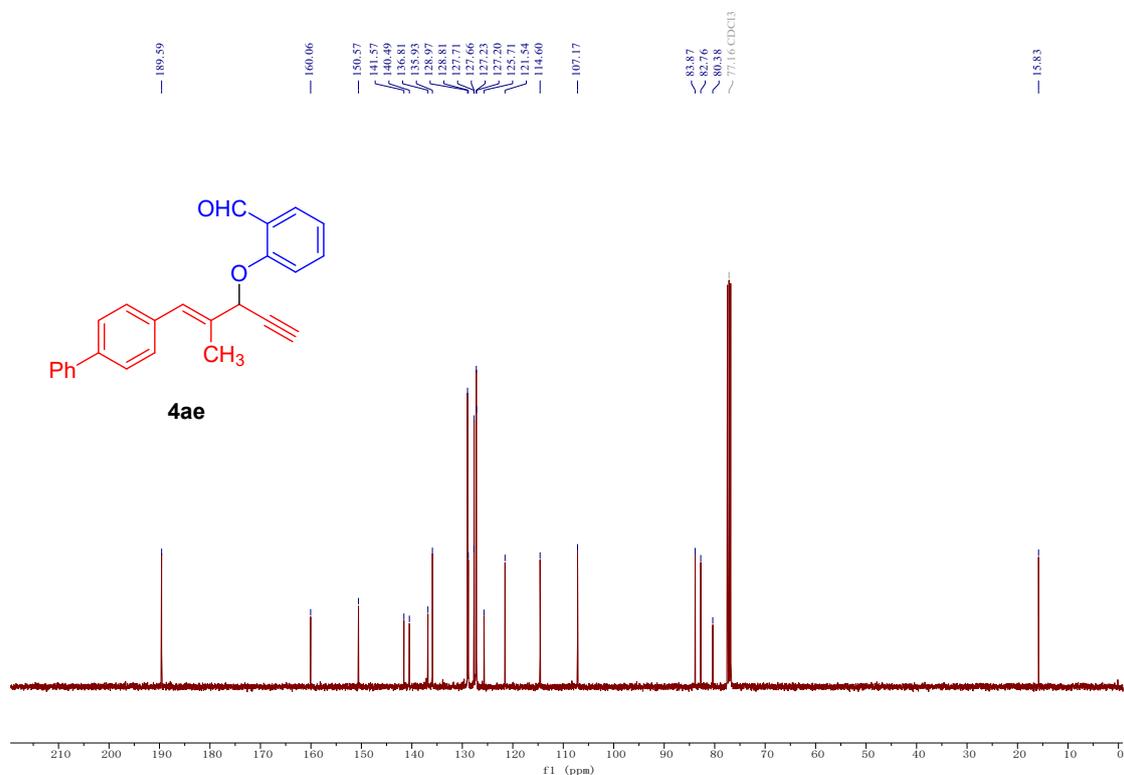
¹³C NMR-4ad (100 MHz, CDCl₃)



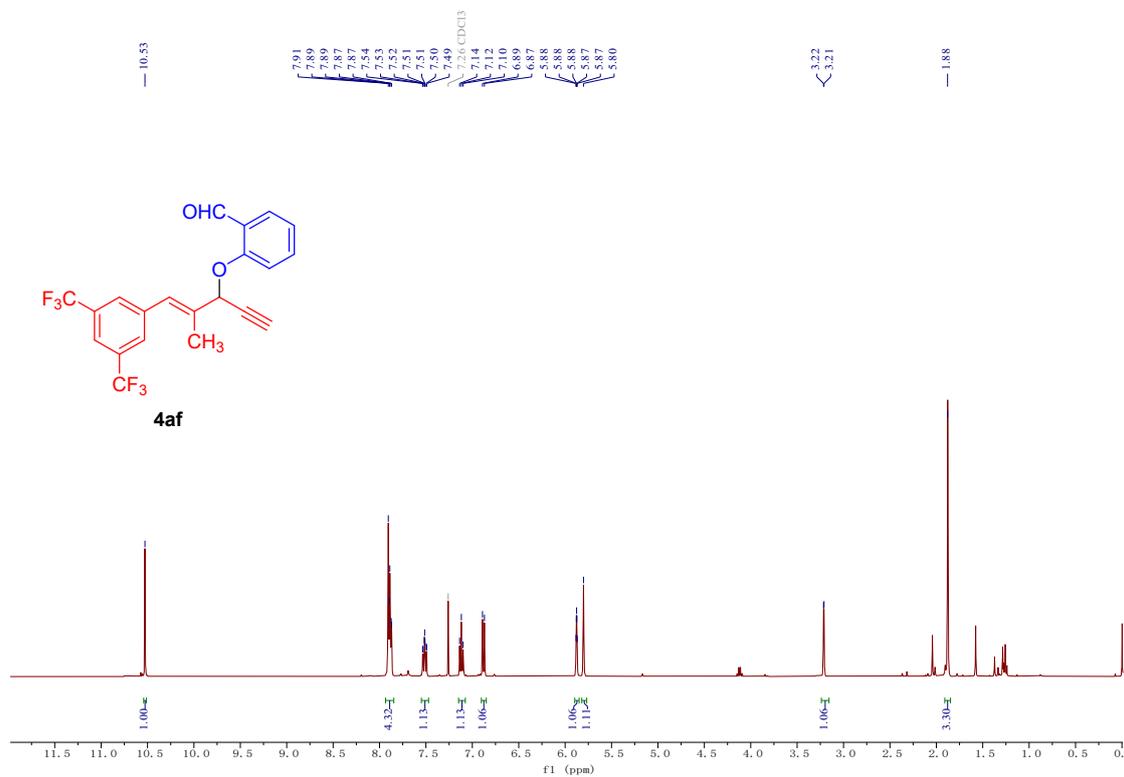
¹H NMR-4ae (400 MHz, CDCl₃)



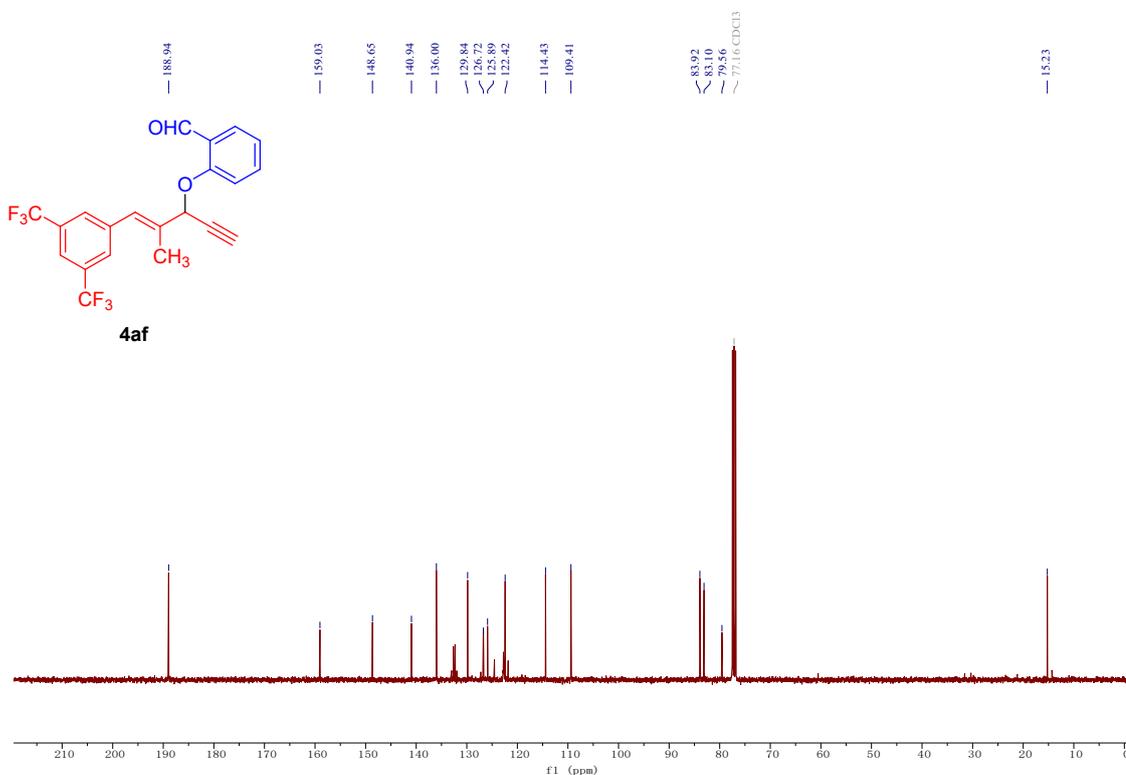
¹³C NMR-4ae (100 MHz, CDCl₃)



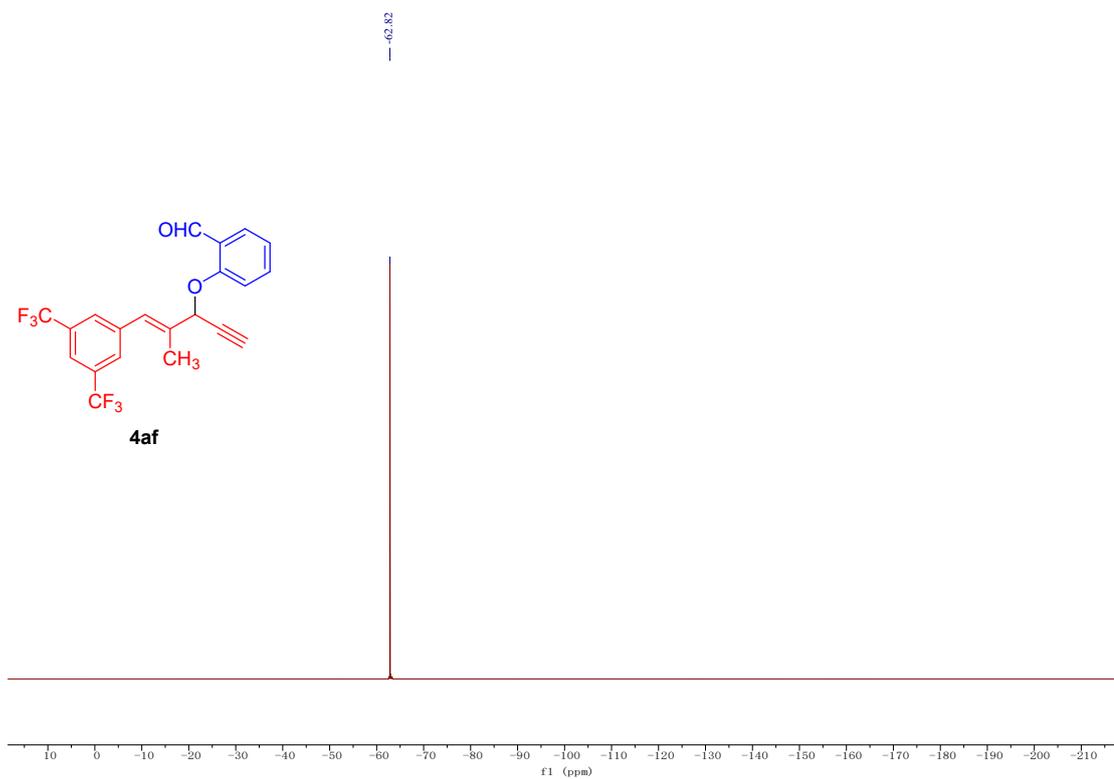
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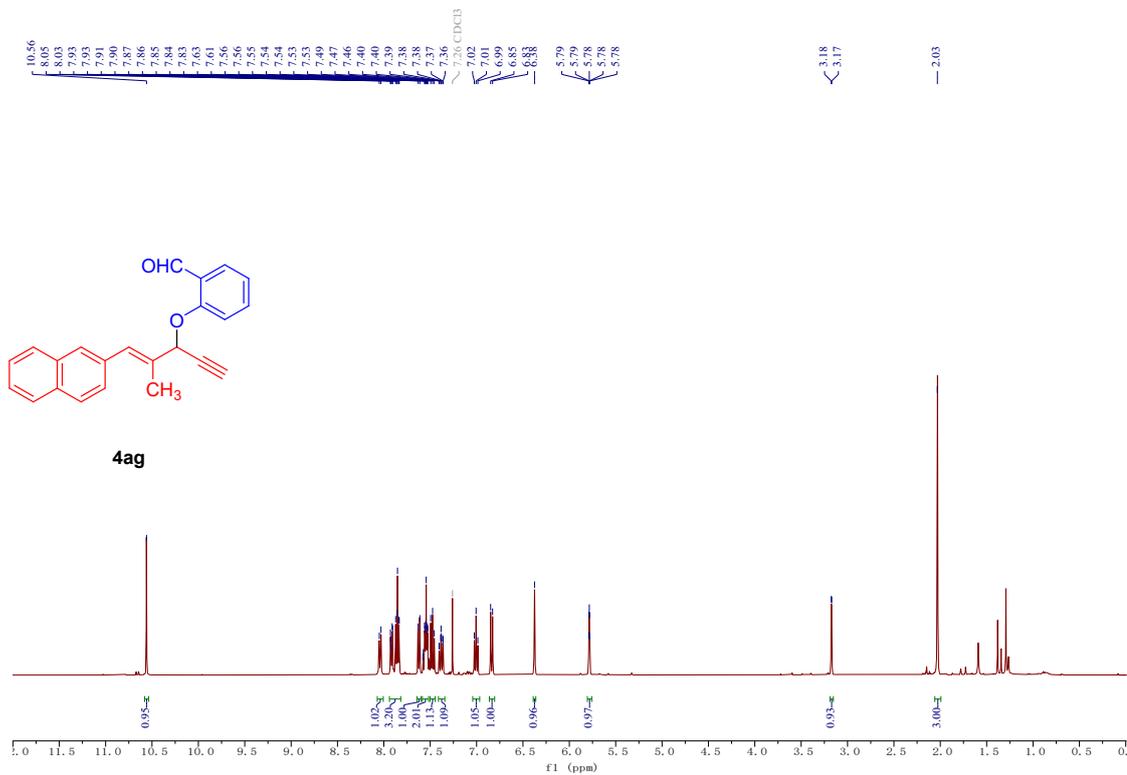
¹³C NMR-4af (100 MHz, CDCl₃)



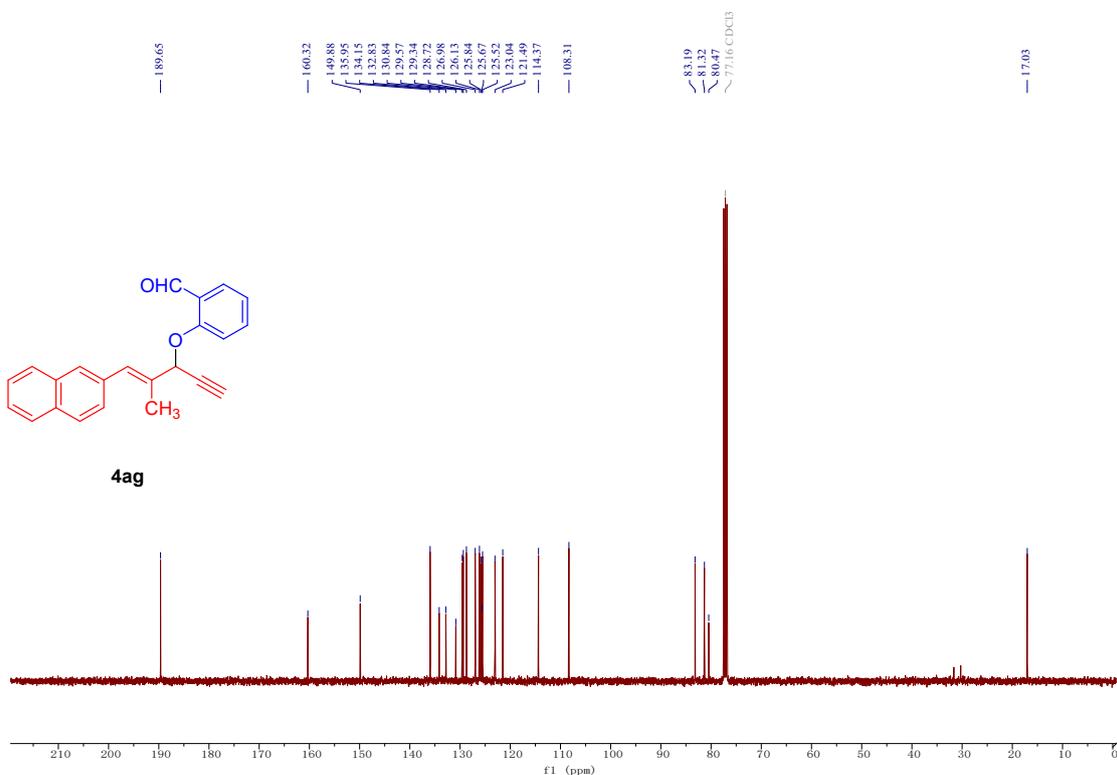
^{19}F NMR-**4af** (376 MHz, CDCl_3)



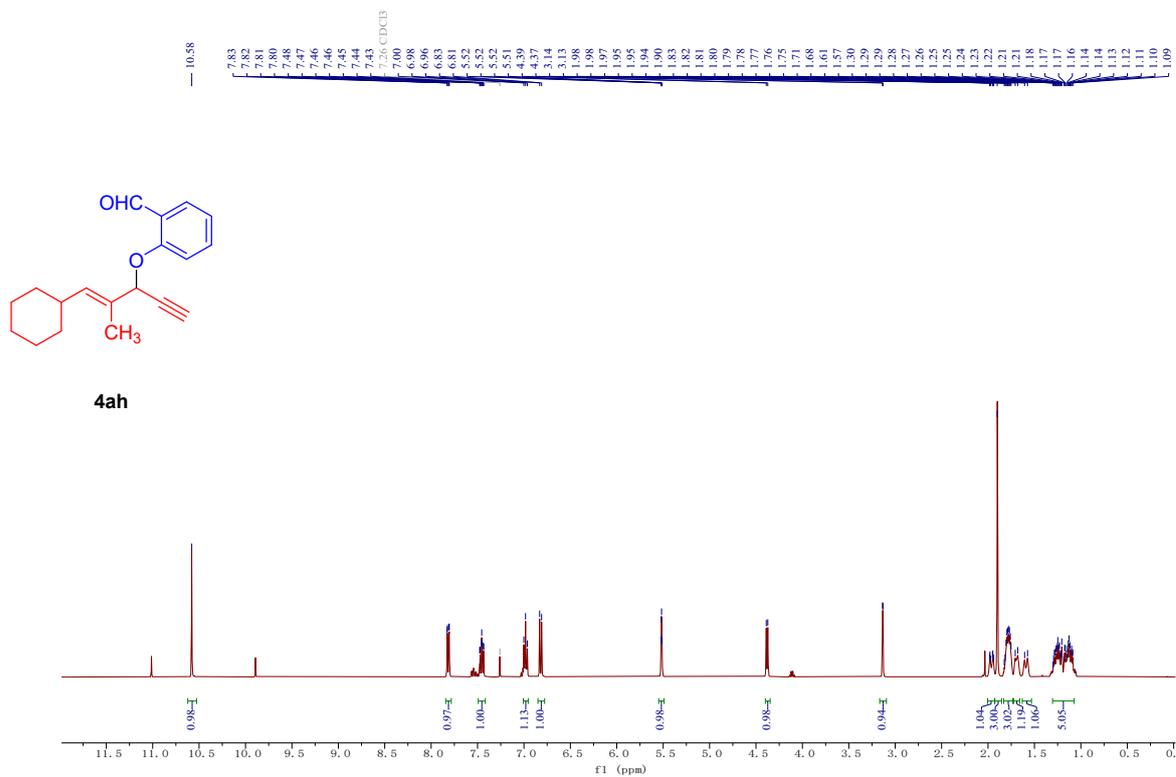
¹H NMR-4ag (400 MHz, CDCl₃)



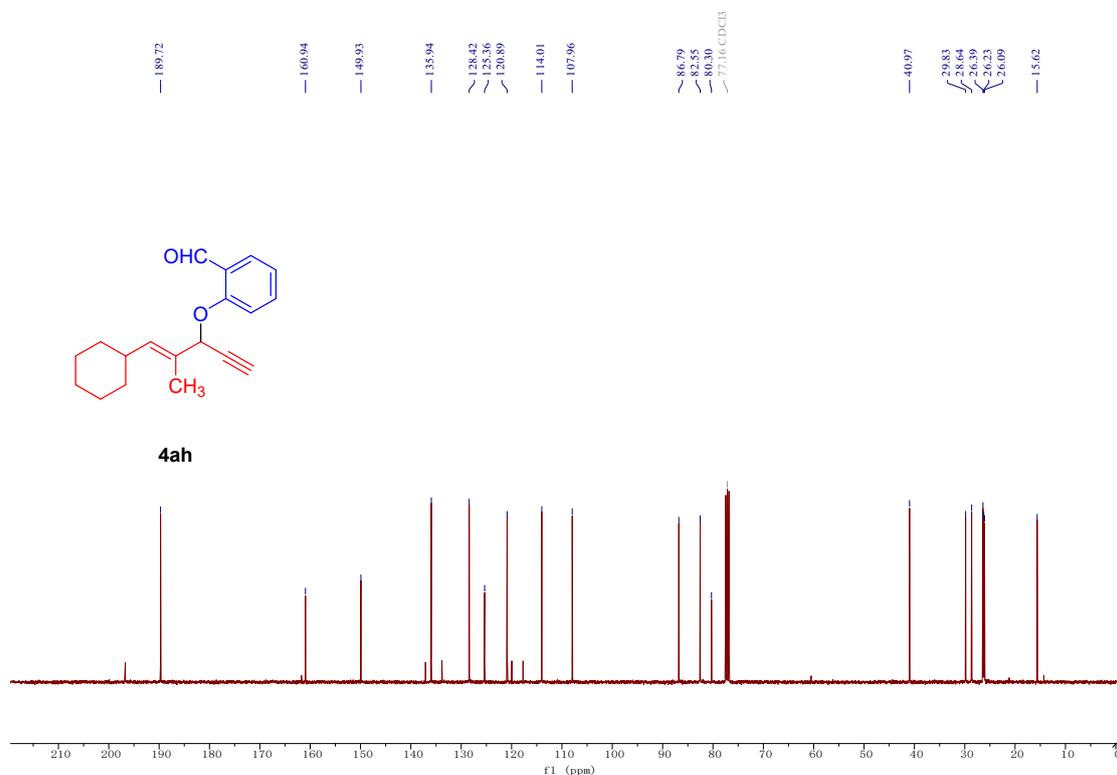
¹³C NMR-4ag (100 MHz, CDCl₃)



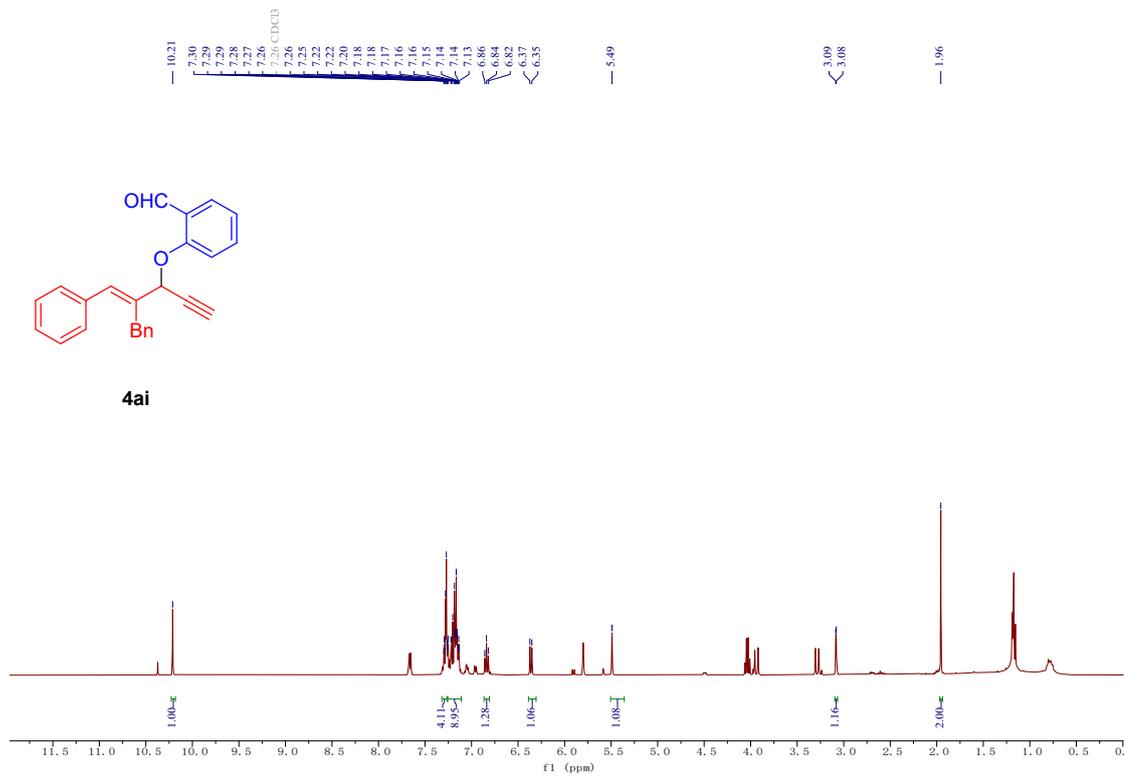
¹H NMR-4ah (400 MHz, CDCl₃)



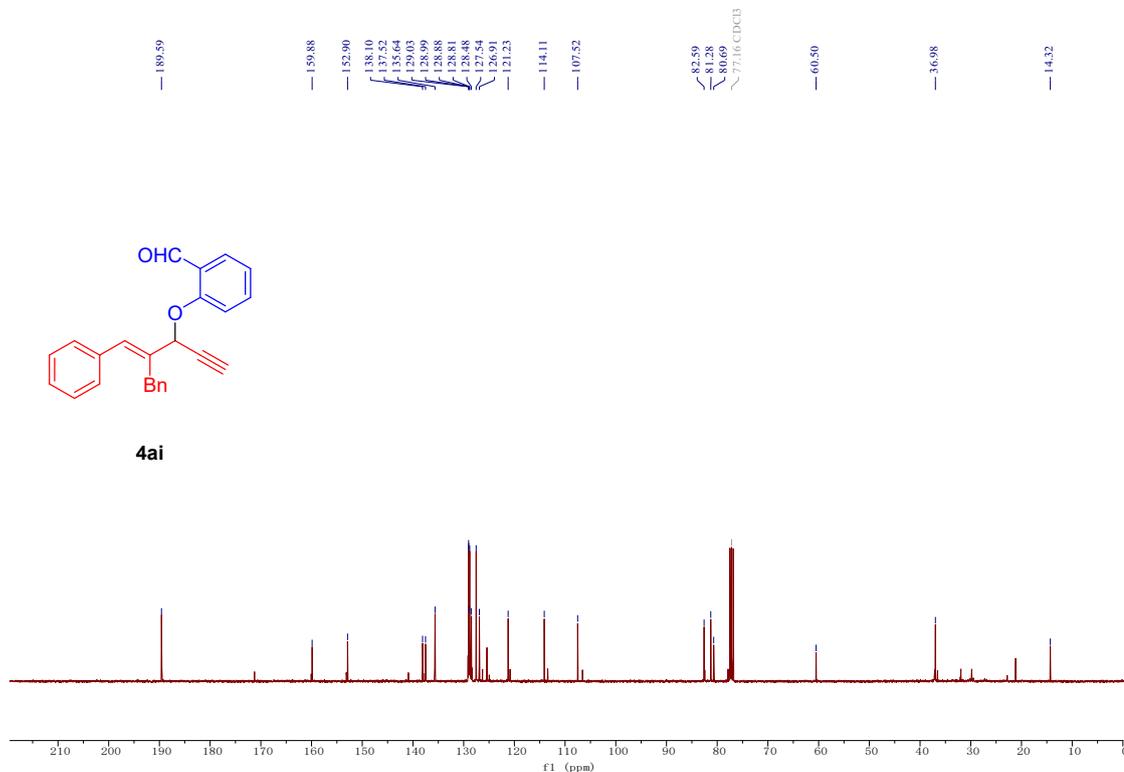
¹³C NMR-4ah (100 MHz, CDCl₃)



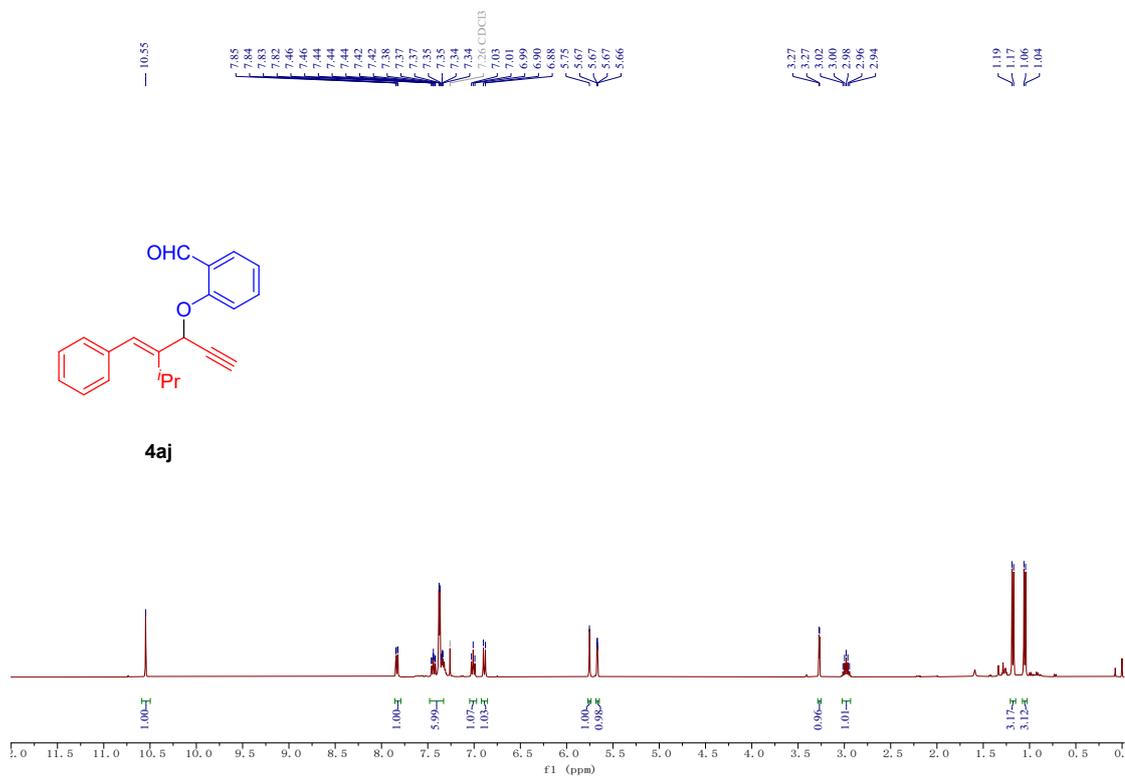
¹H NMR-4ai (400 MHz, CDCl₃)



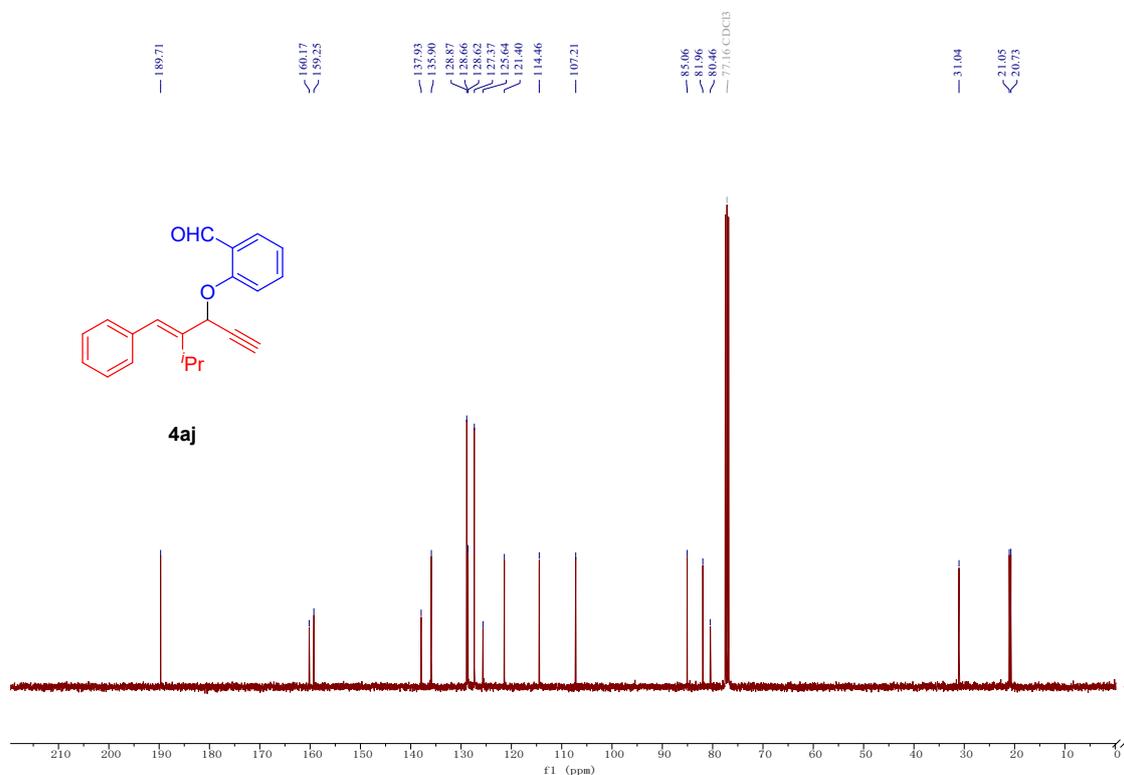
¹³C NMR-4ai (100 MHz, CDCl₃)



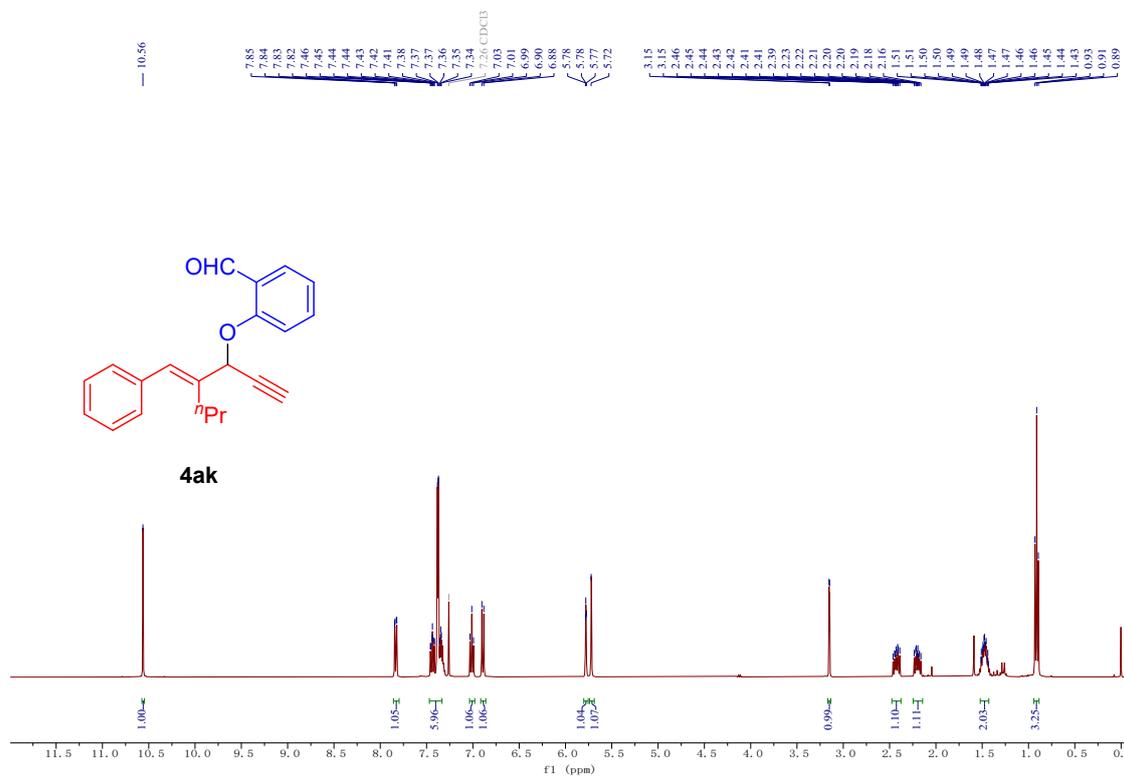
^1H NMR-4aj (400 MHz, CDCl_3)



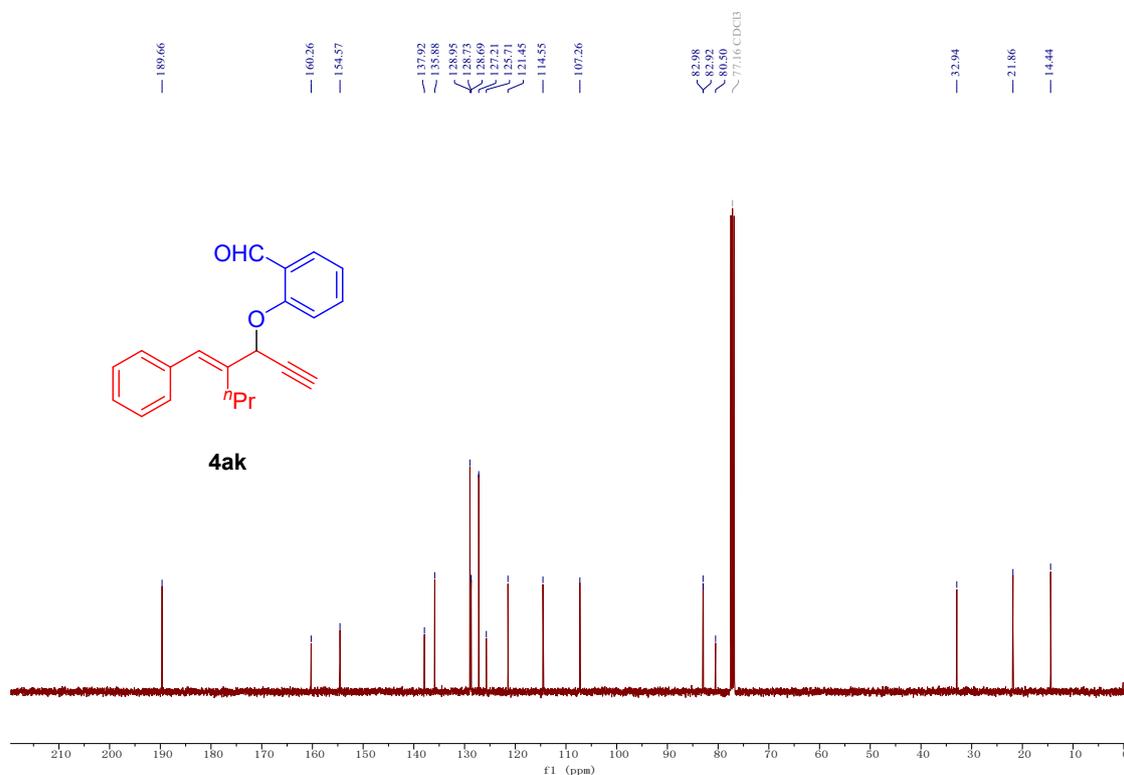
^{13}C NMR-4aj (100 MHz, CDCl_3)



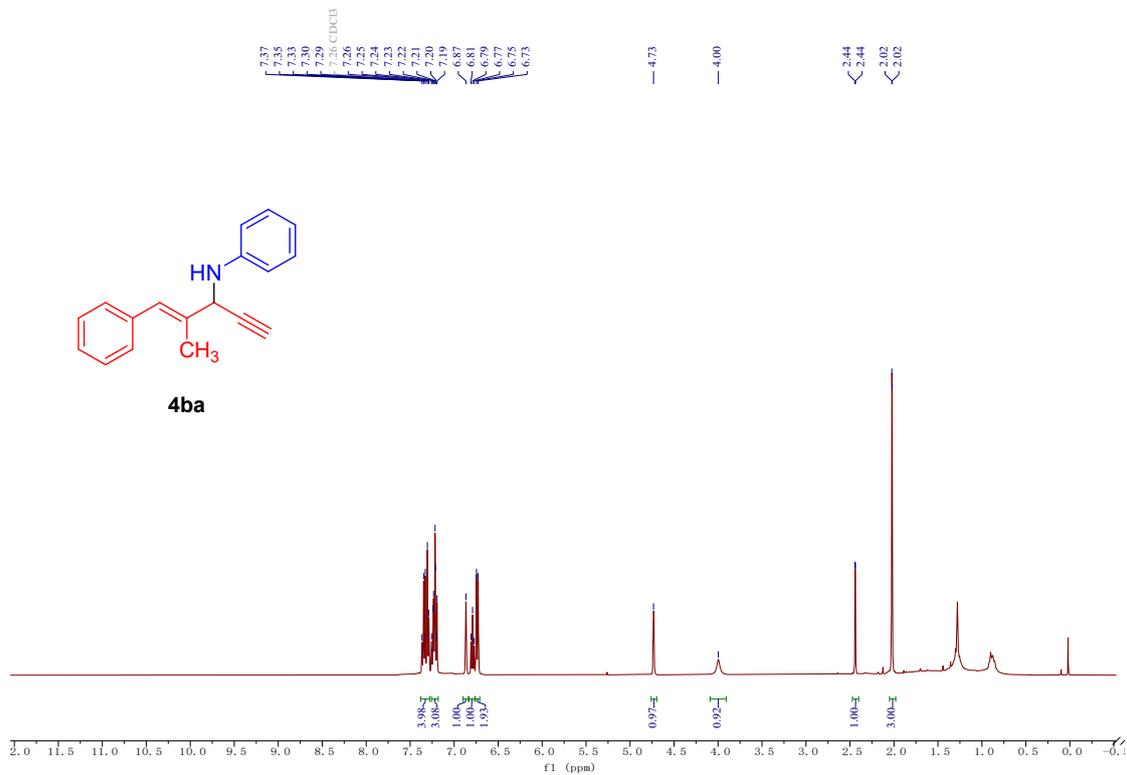
¹H NMR-4ak (400 MHz, CDCl₃)



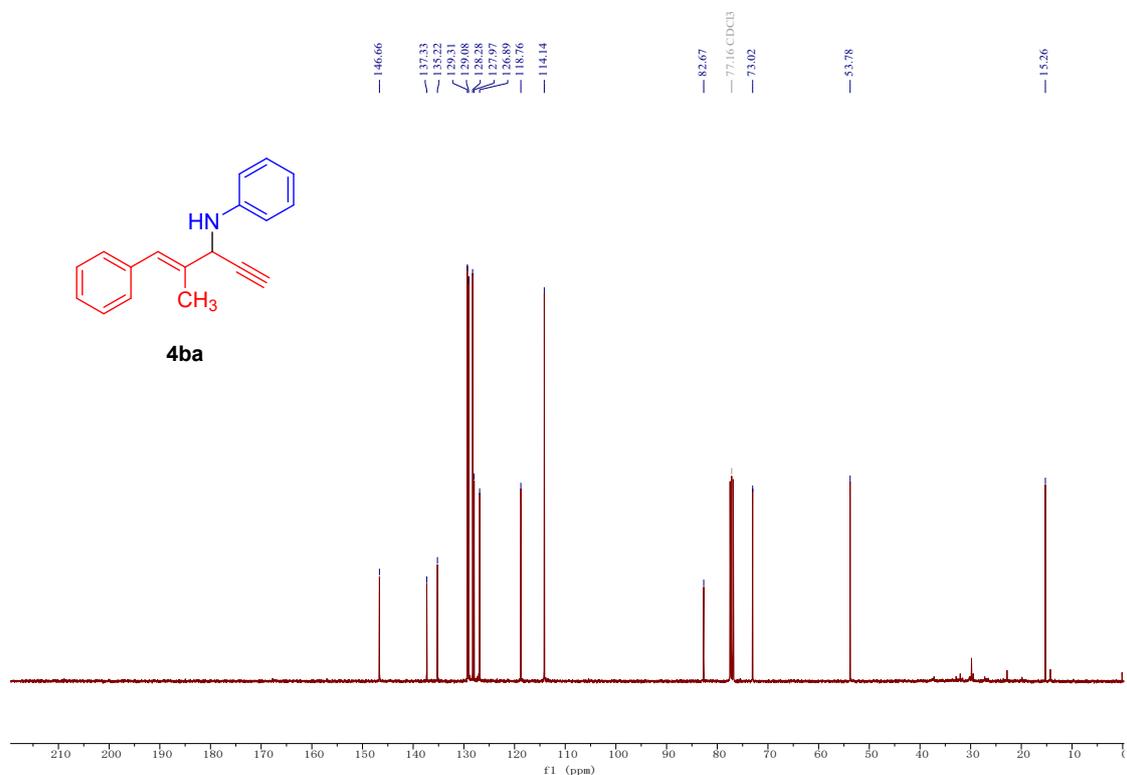
¹³C NMR-4ak (100 MHz, CDCl₃)



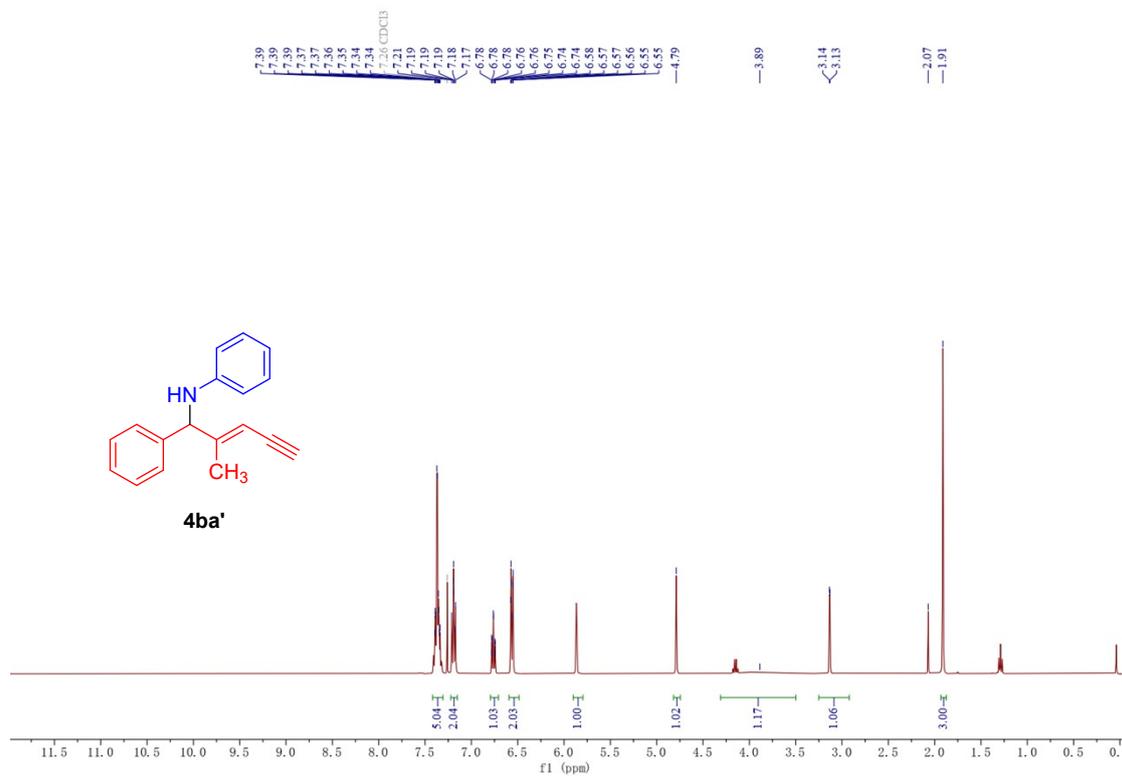
¹H NMR-4ba (400 MHz, CDCl₃)



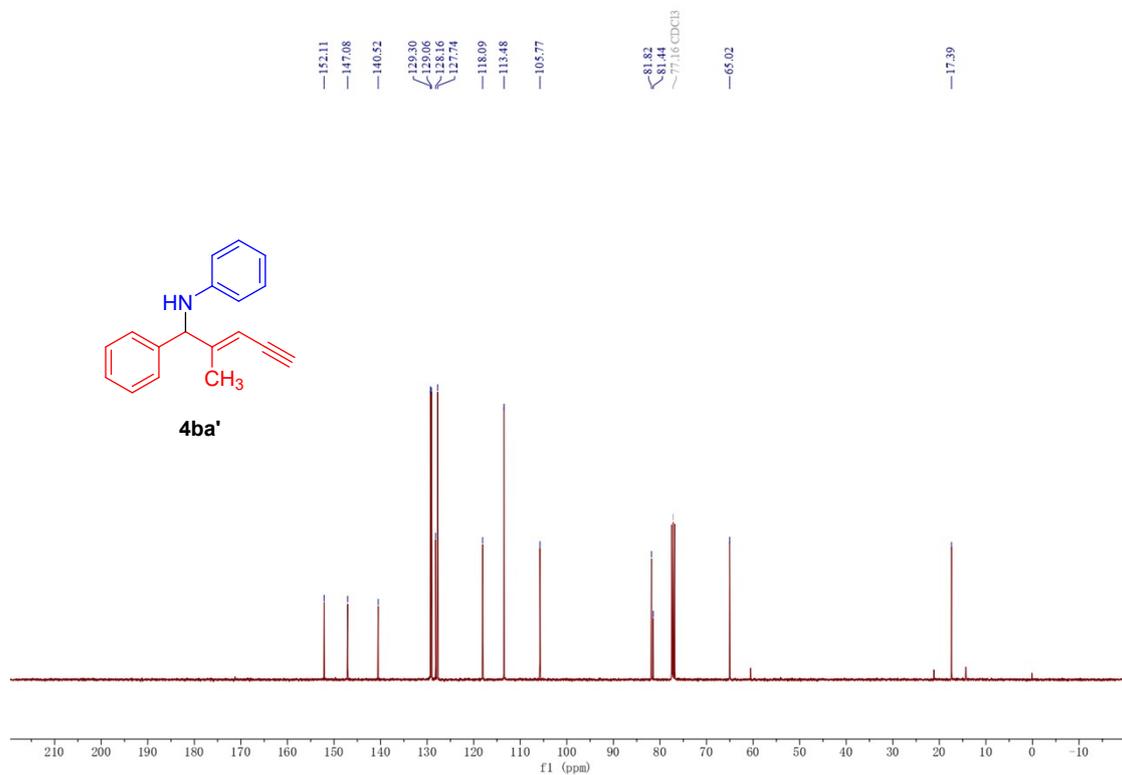
¹³C NMR-4ba (100 MHz, CDCl₃)



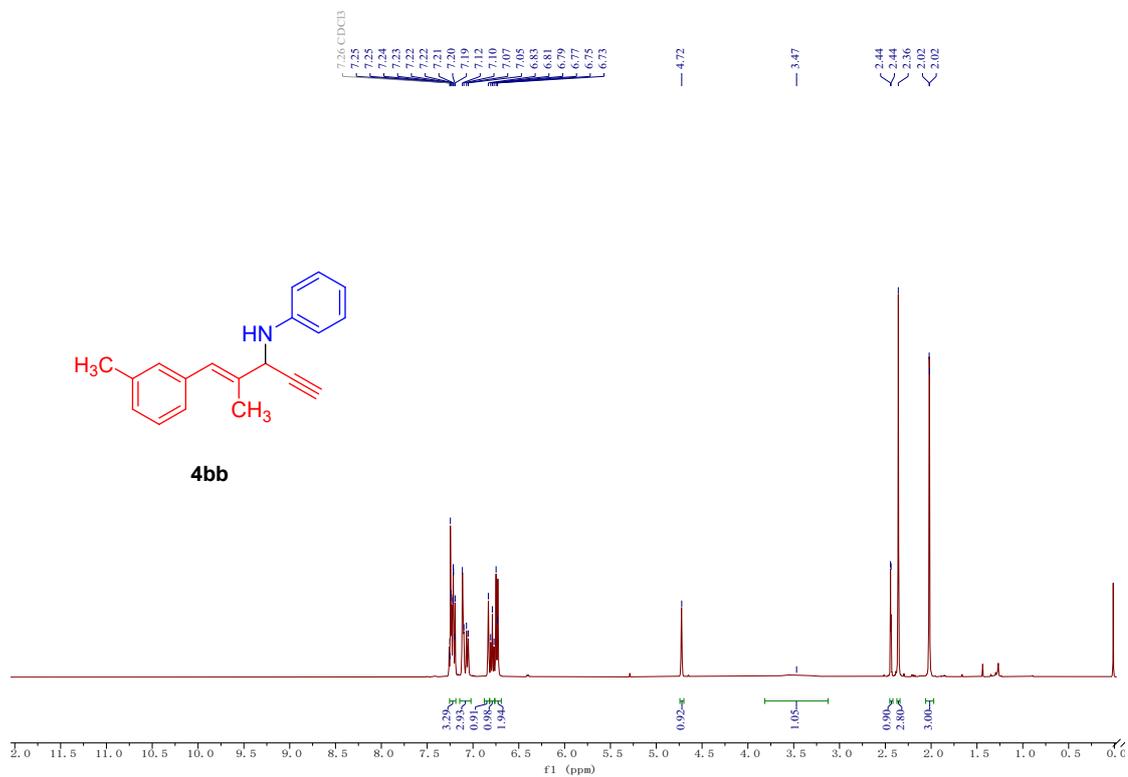
^1H NMR-4ba' (400 MHz, CDCl_3)



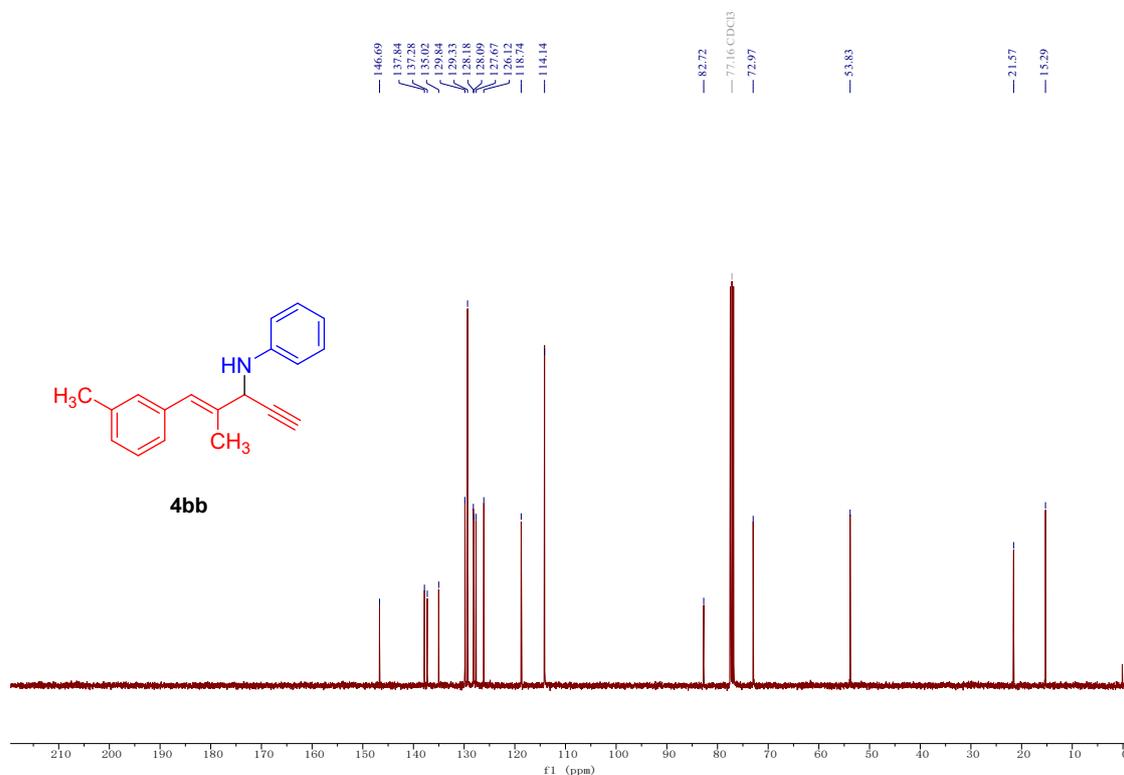
^{13}C NMR-4ba' (100 MHz, CDCl_3)



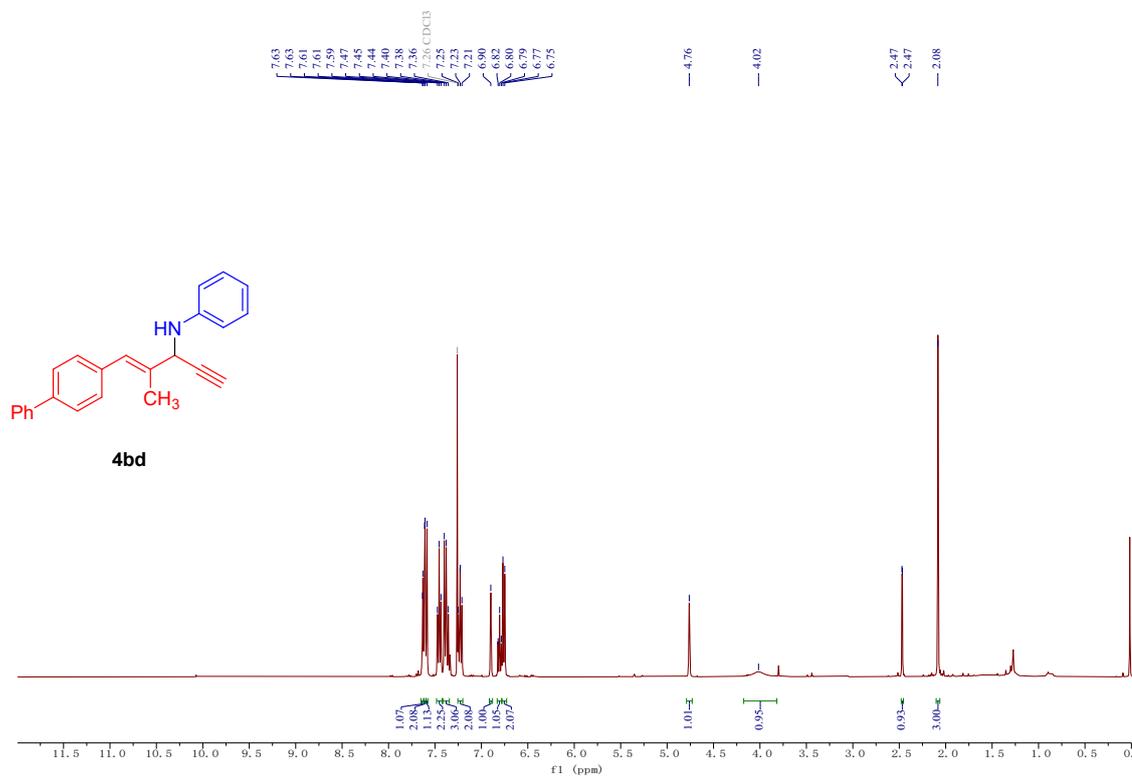
^1H NMR-**4bb** (400 MHz, CDCl_3)



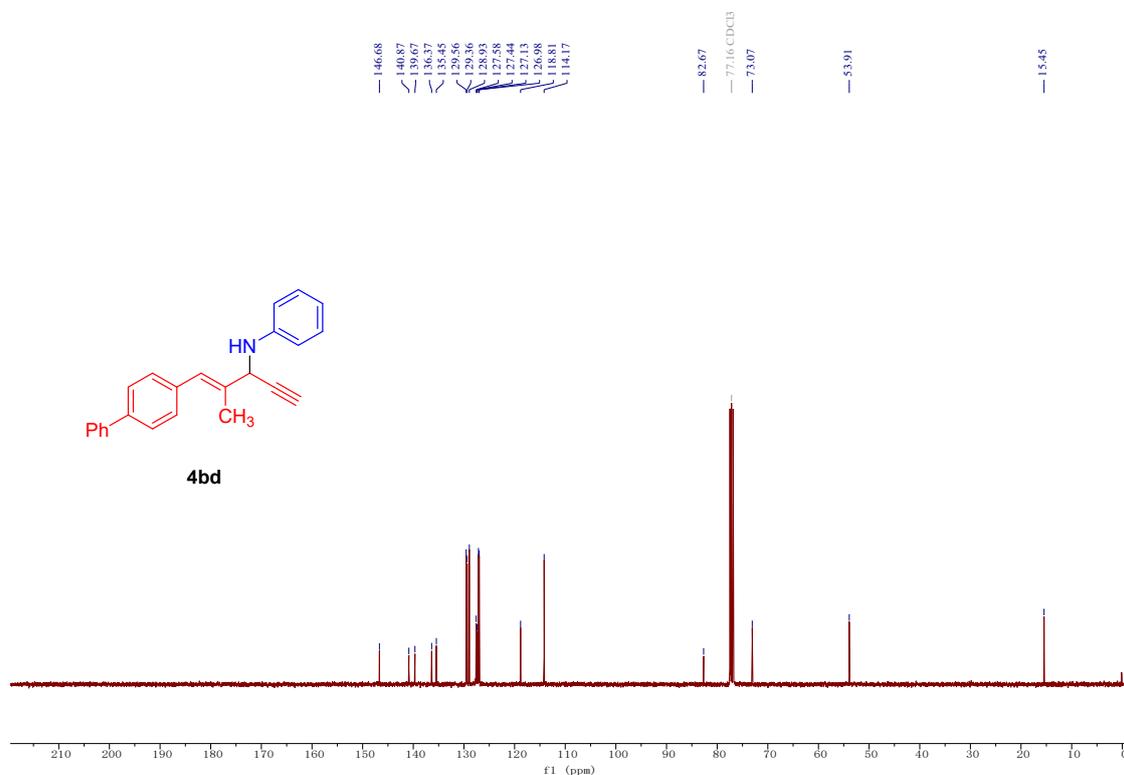
^{13}C NMR-**4bb** (100 MHz, CDCl_3)



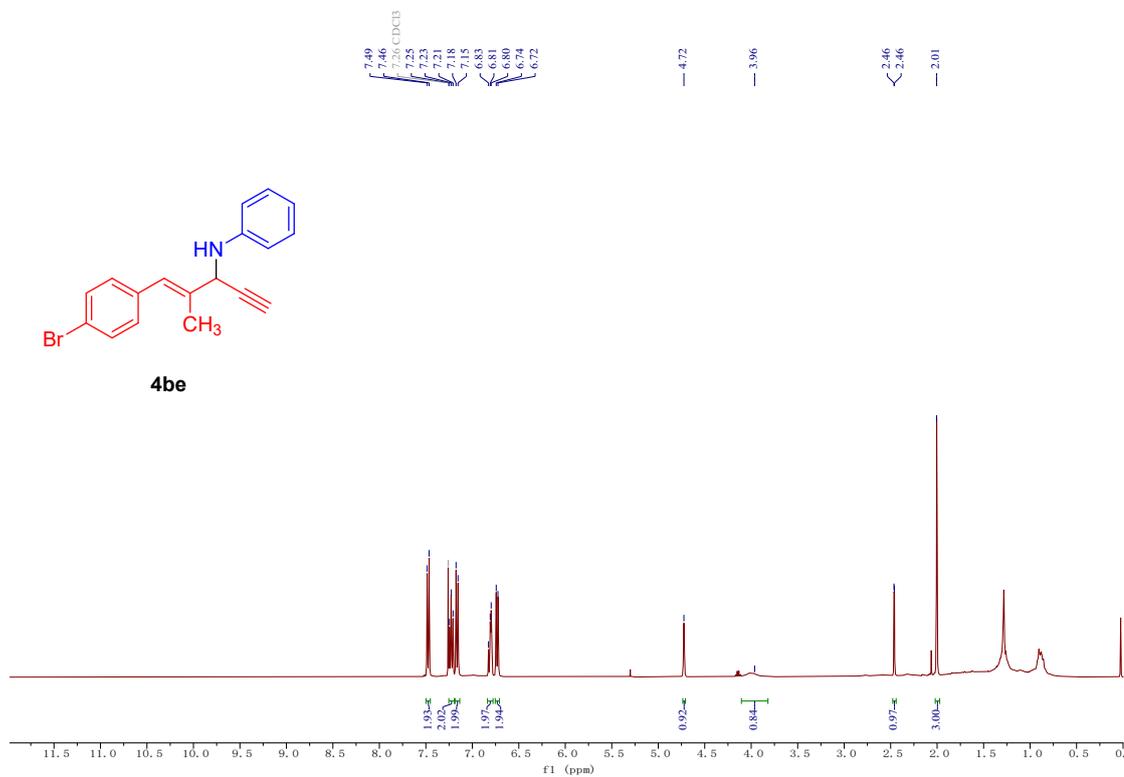
¹H NMR-4bd (400 MHz, CDCl₃)



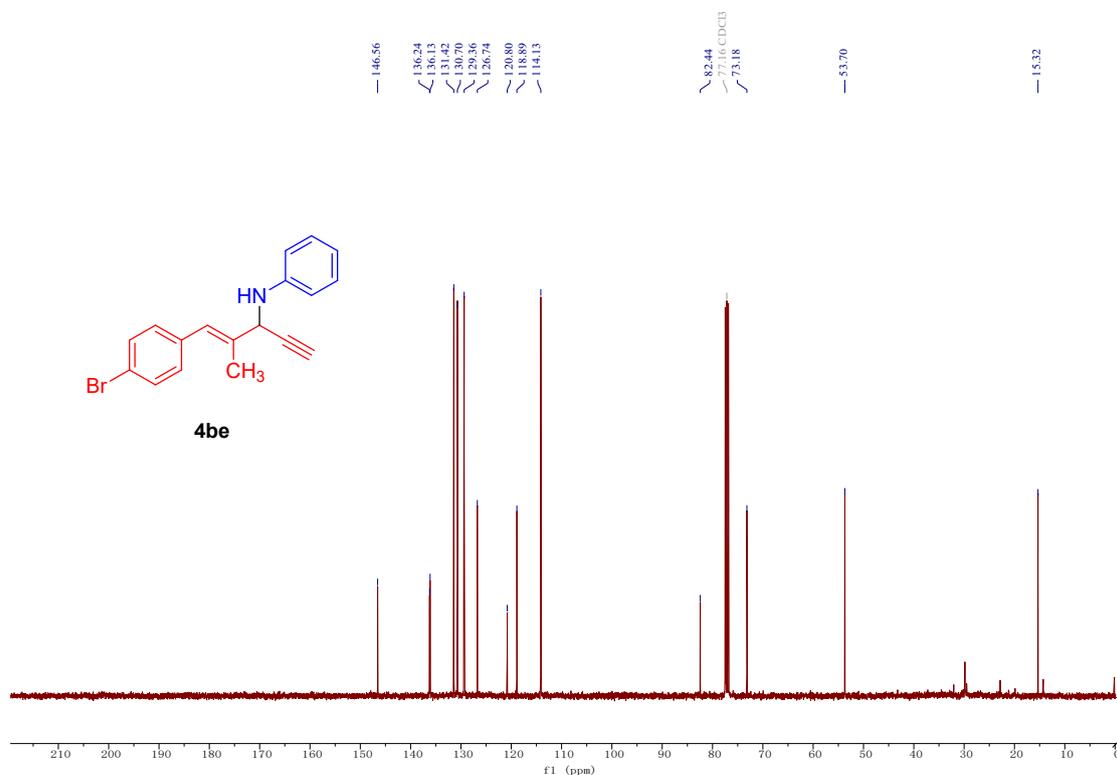
¹³C NMR-4bd (100 MHz, CDCl₃)



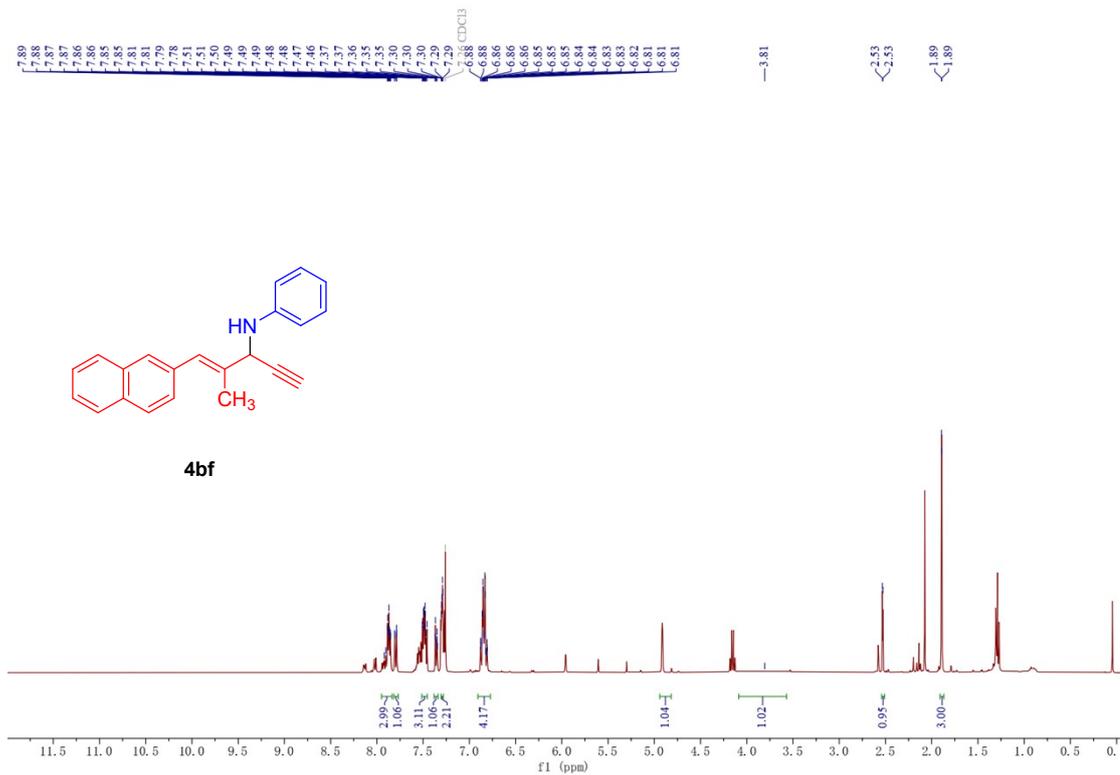
^1H NMR-**4be** (400 MHz, CDCl_3)



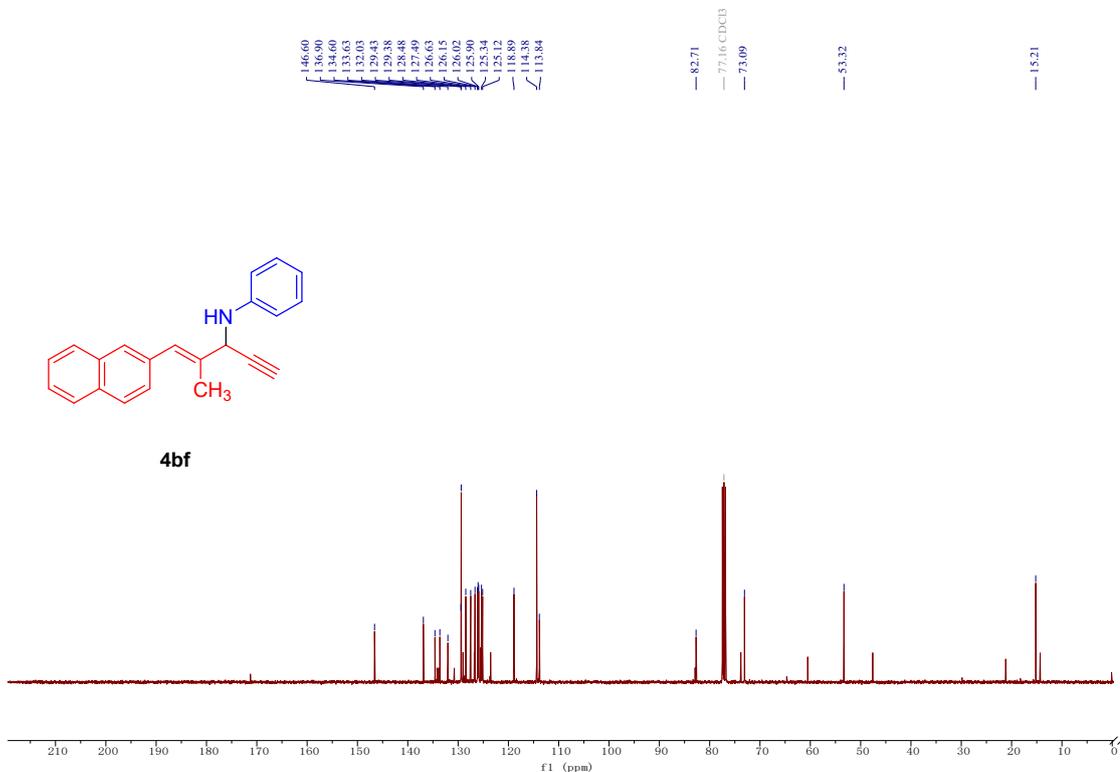
^{13}C NMR-**4be** (100 MHz, CDCl_3)



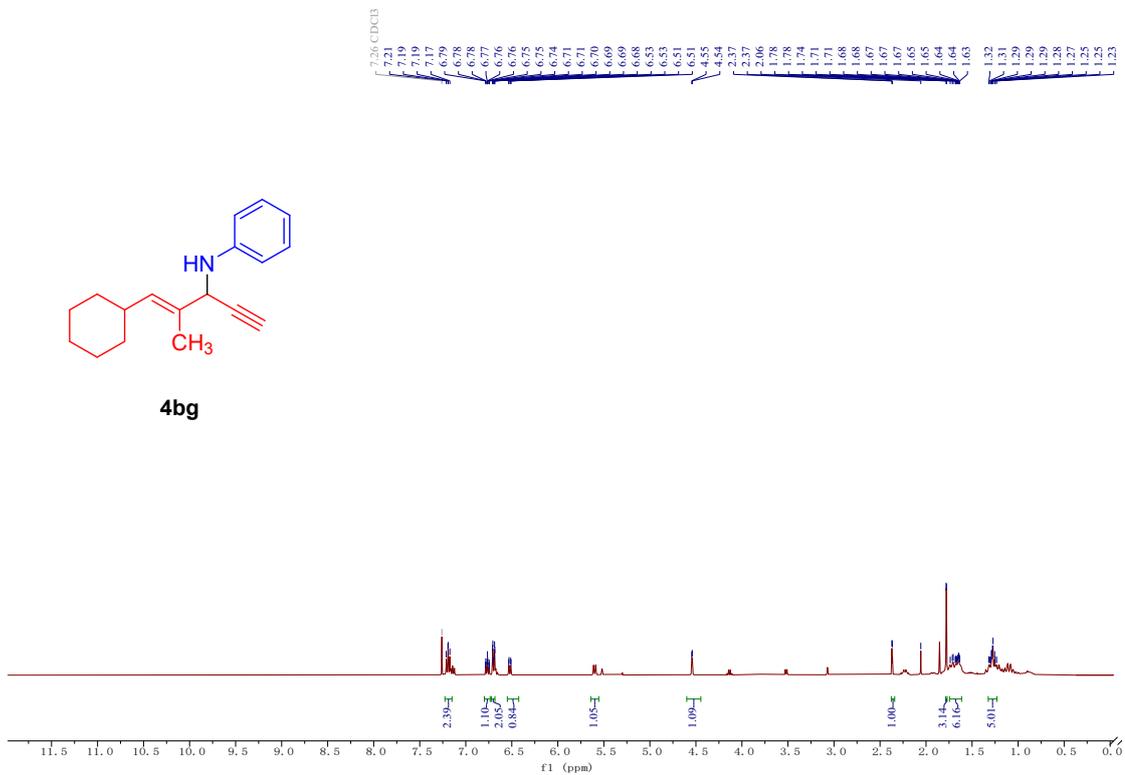
^1H NMR-**4bf** (400 MHz, CDCl_3)



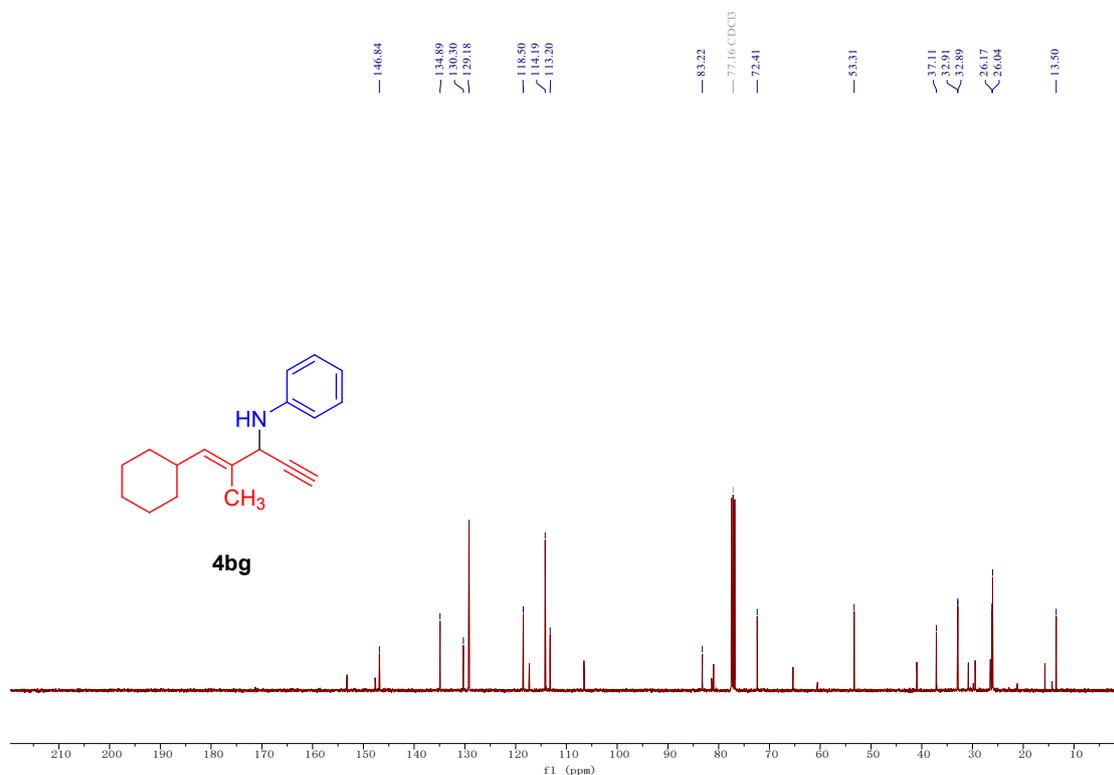
^{13}C NMR-**4bf** (100 MHz, CDCl_3)



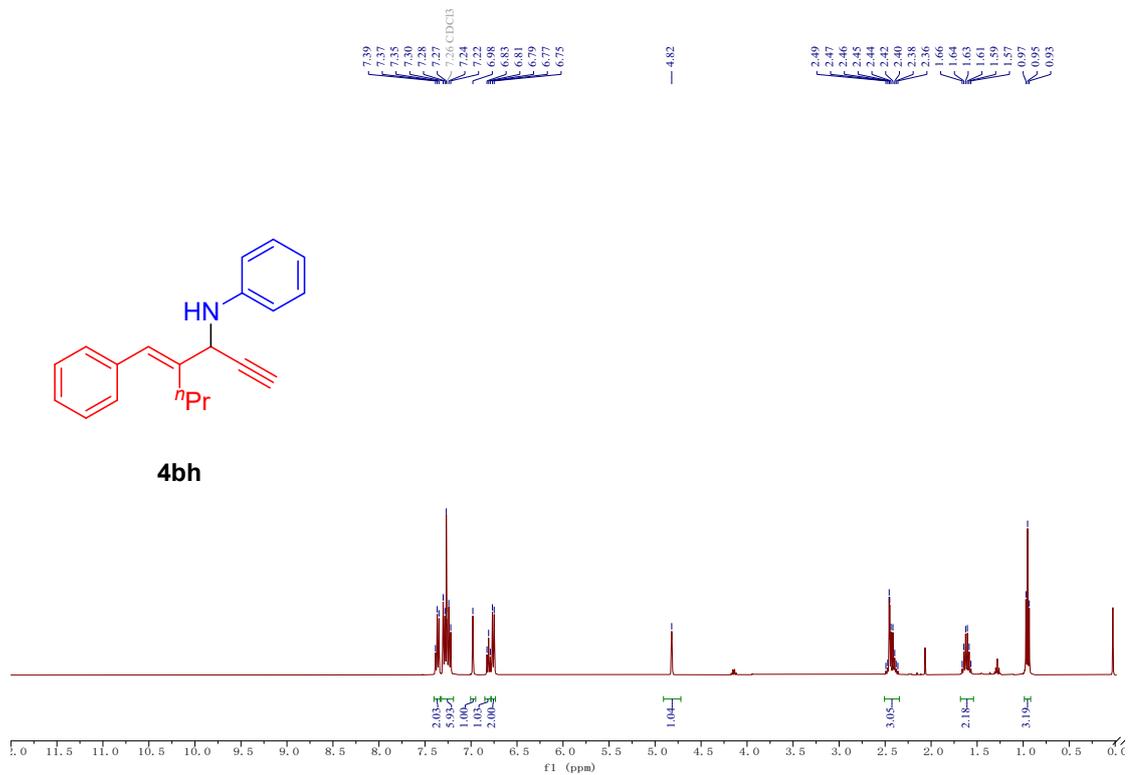
¹H NMR-4bg (400 MHz, CDCl₃)



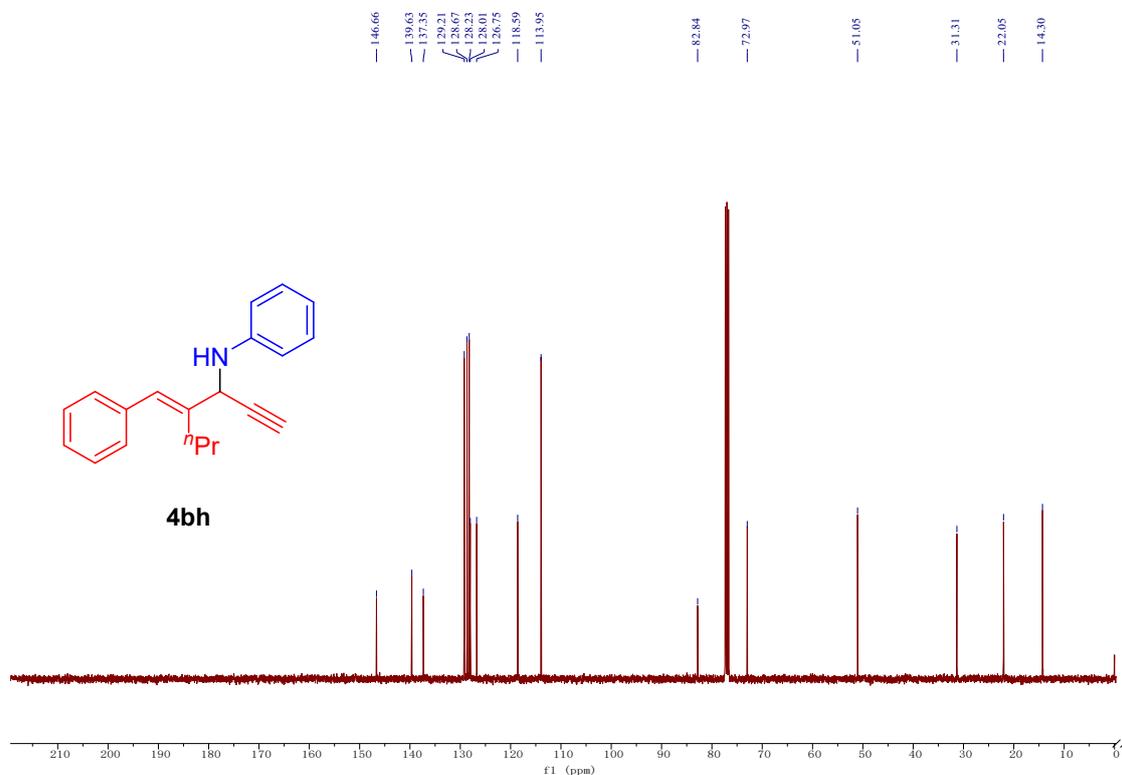
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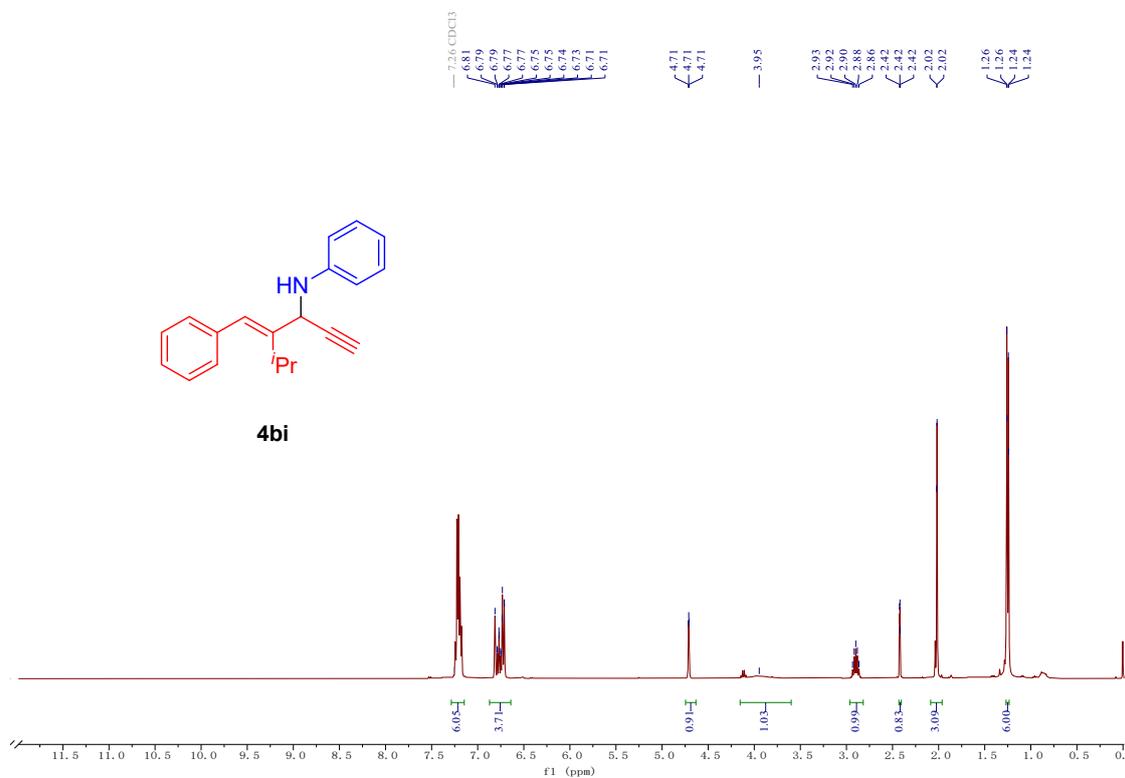
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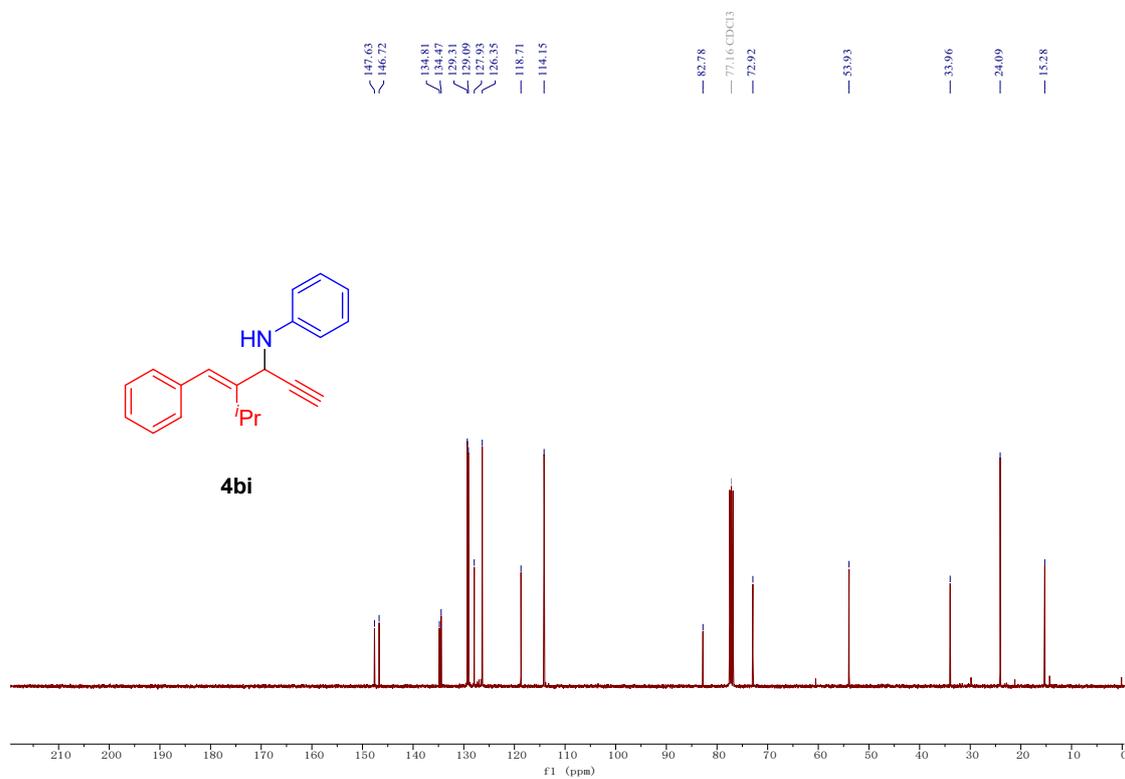
^{13}C NMR-4bh (100 MHz, CDCl_3)



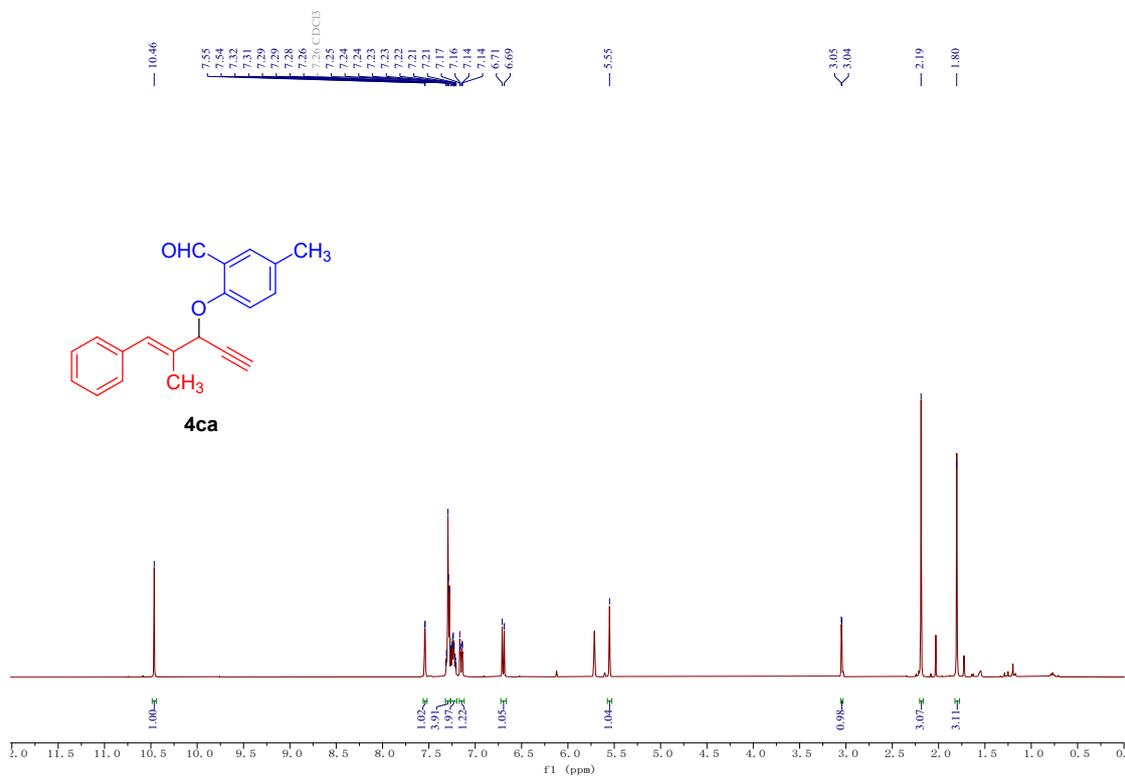
¹H NMR-4bi (400 MHz, CDCl₃)



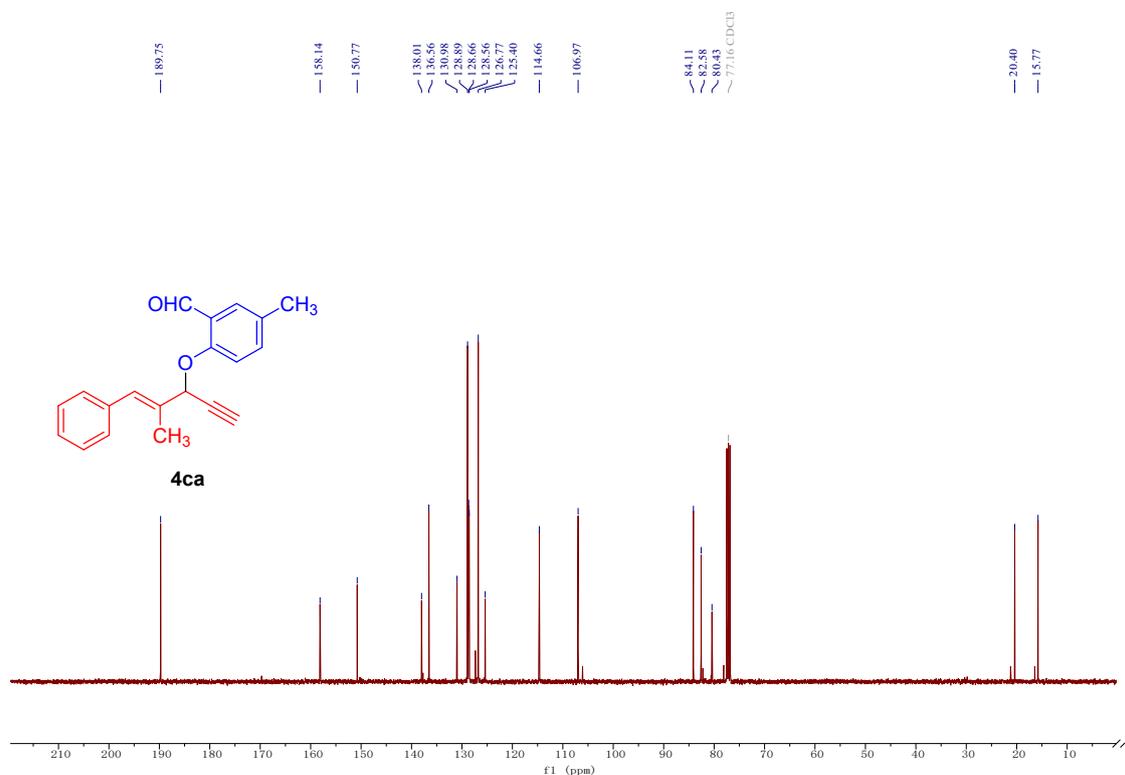
¹³C NMR-4bi (100 MHz, CDCl₃)



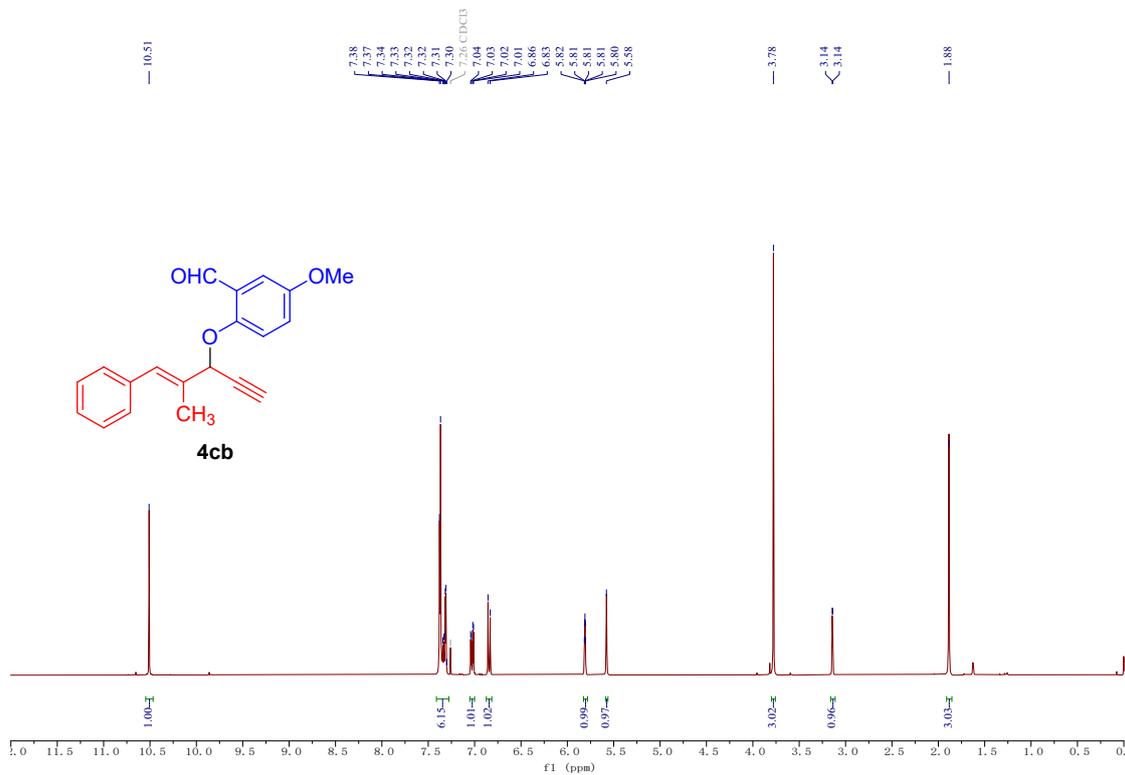
¹H NMR-4ca (400 MHz, CDCl₃)



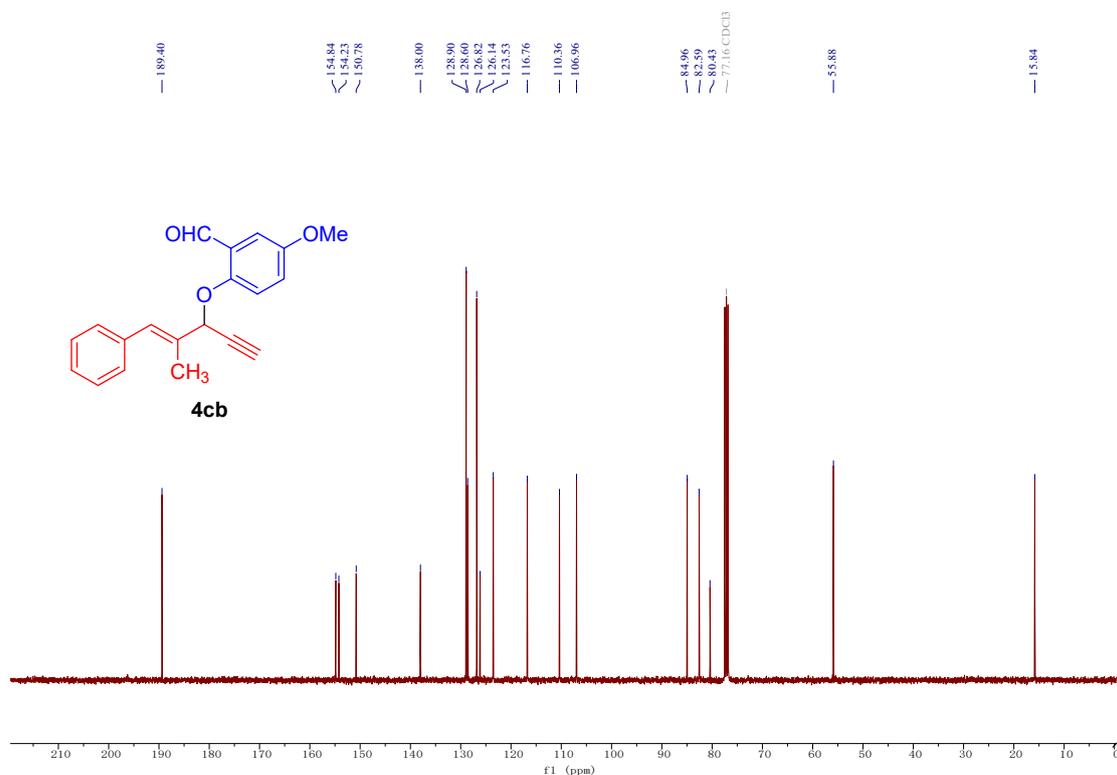
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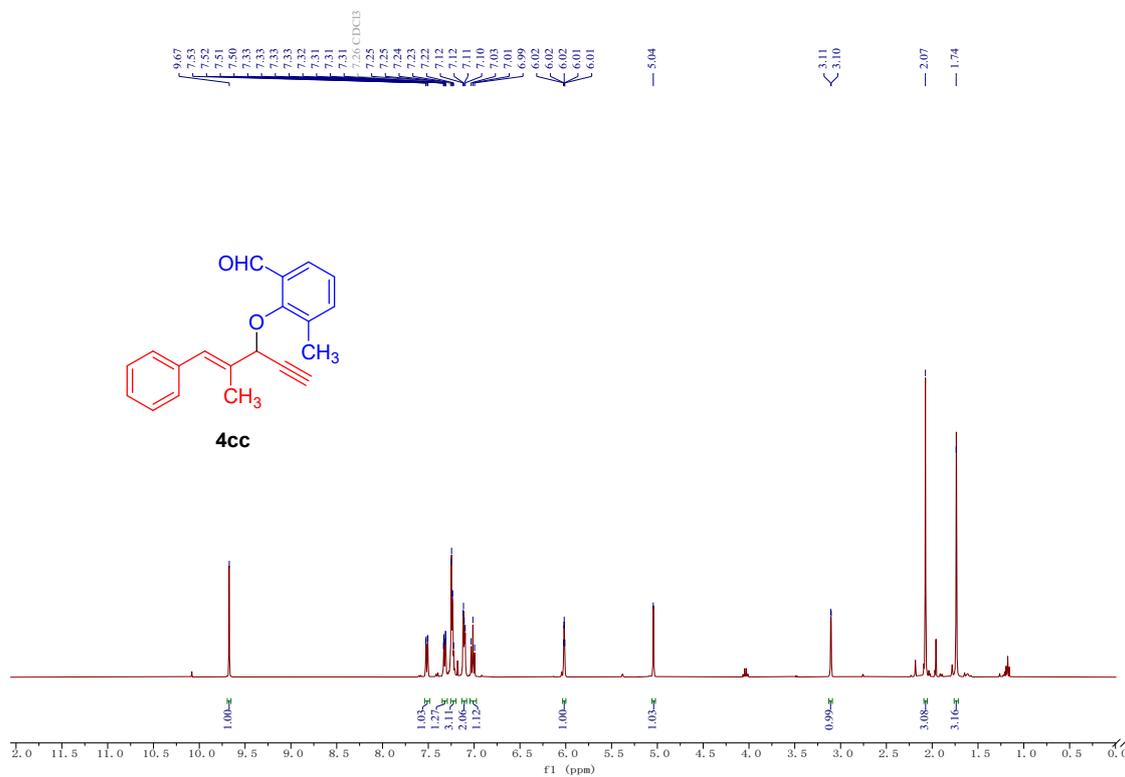
¹H NMR-4cb (400 MHz, CDCl₃)



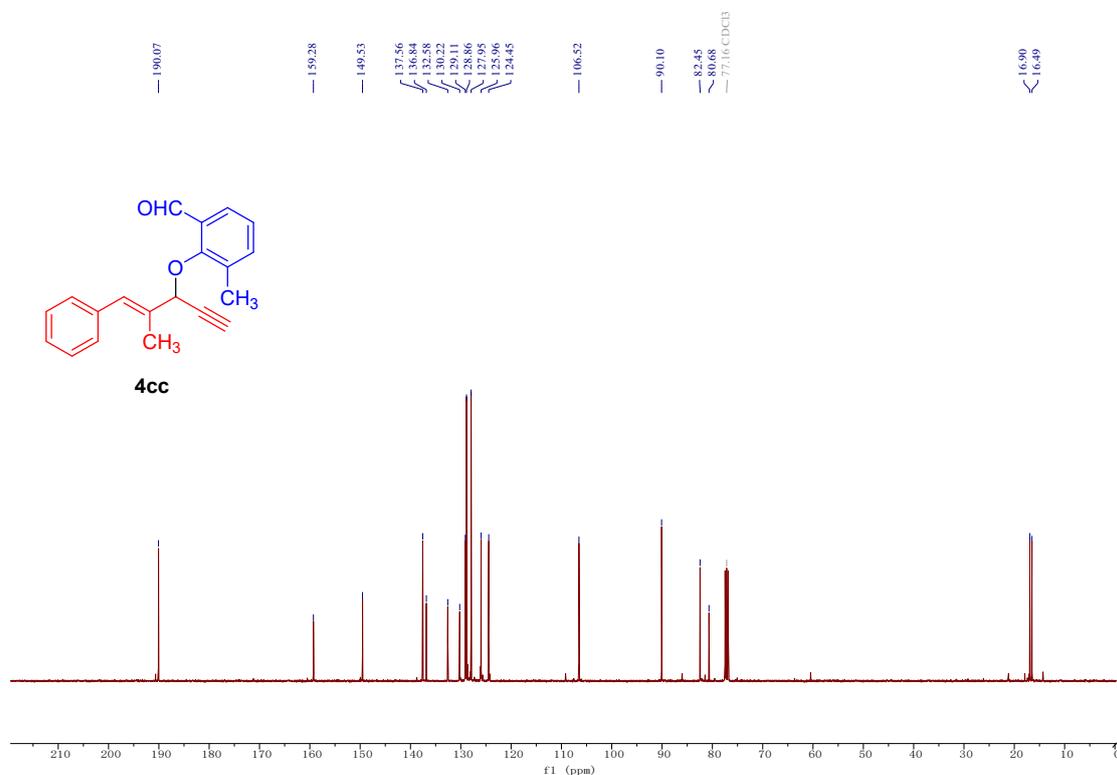
¹³C NMR-4cb (100 MHz, CDCl₃)



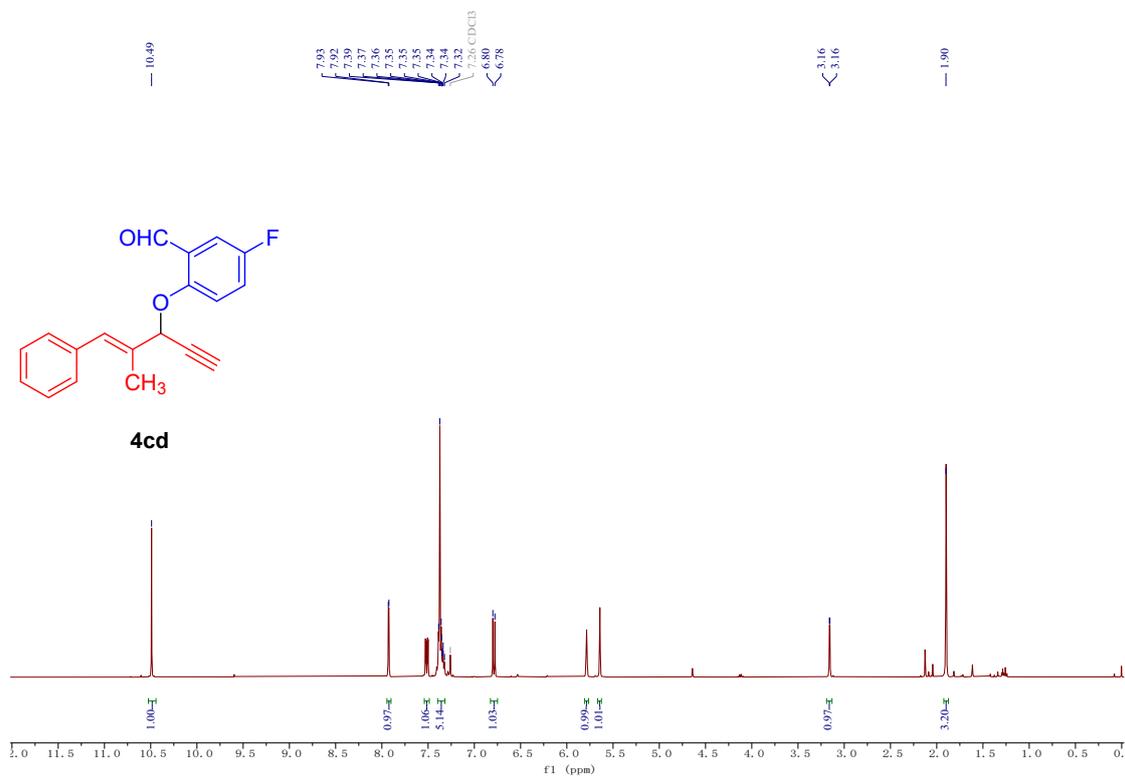
¹H NMR-4cc (400 MHz, CDCl₃)



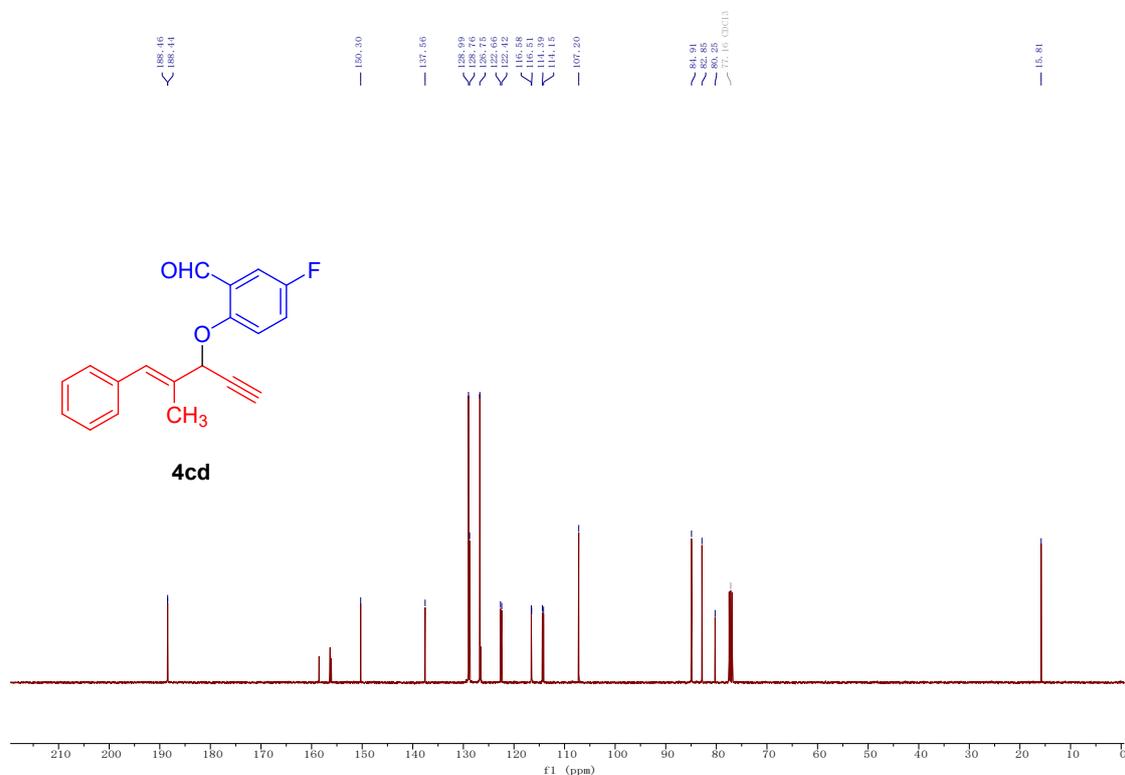
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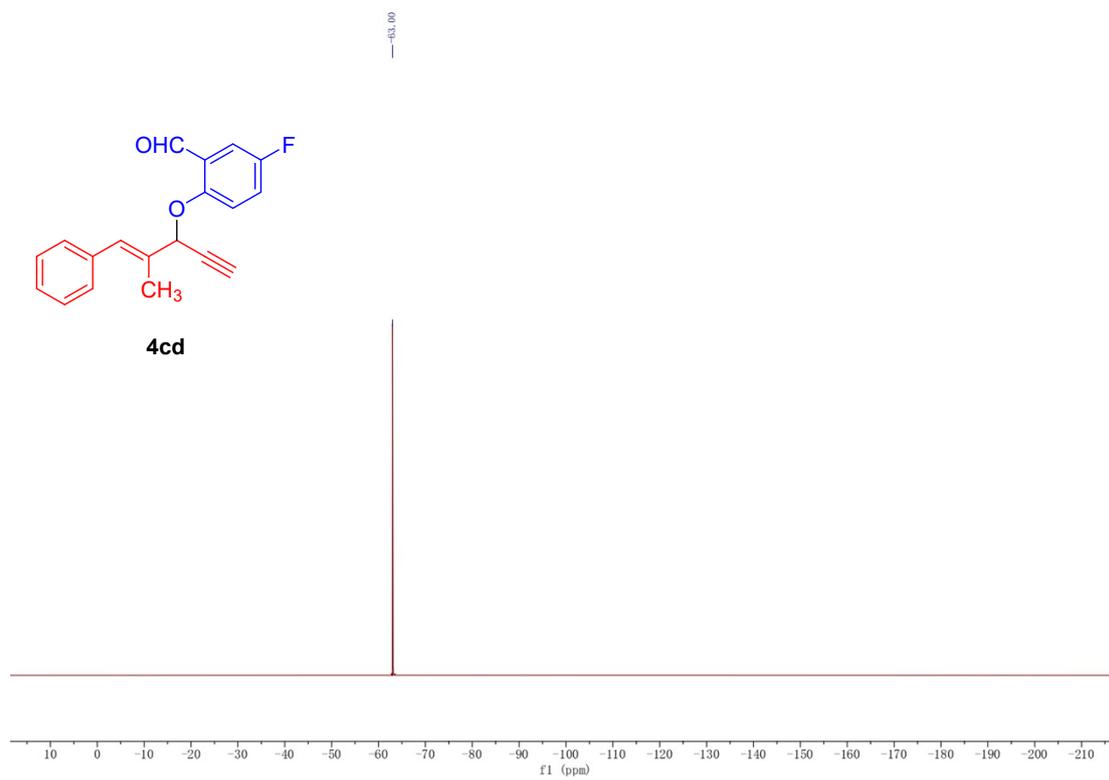
¹H NMR-4cd (400 MHz, CDCl₃)



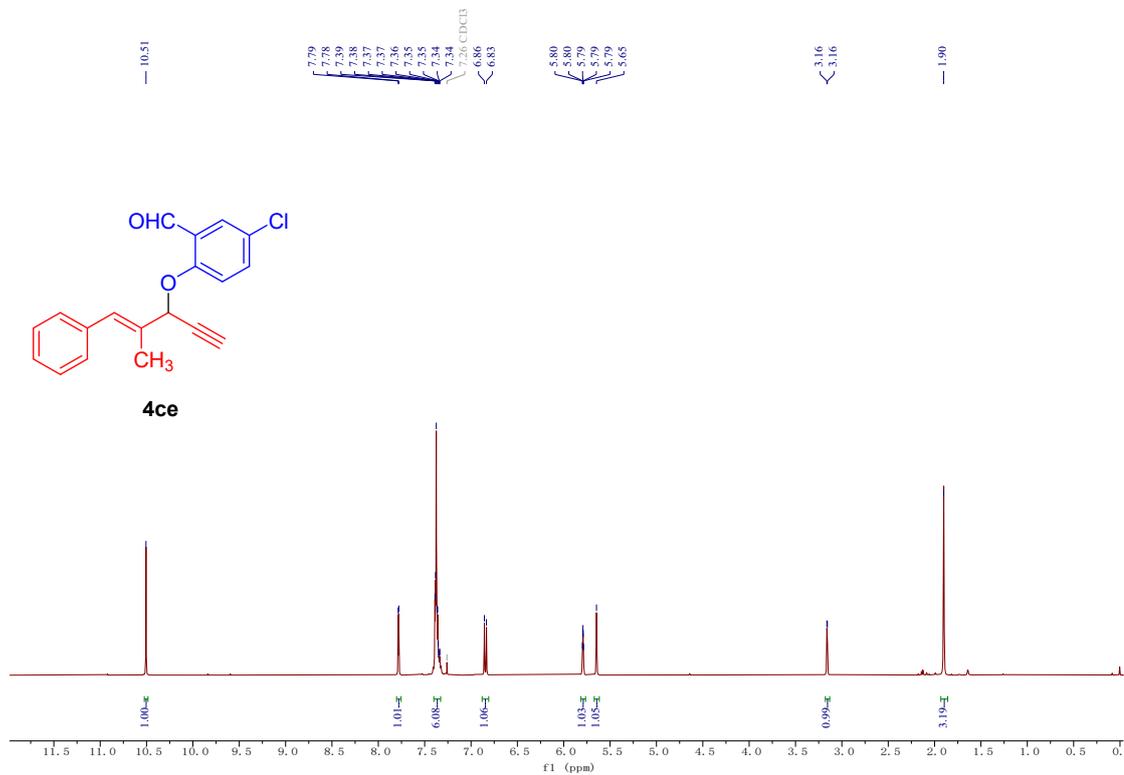
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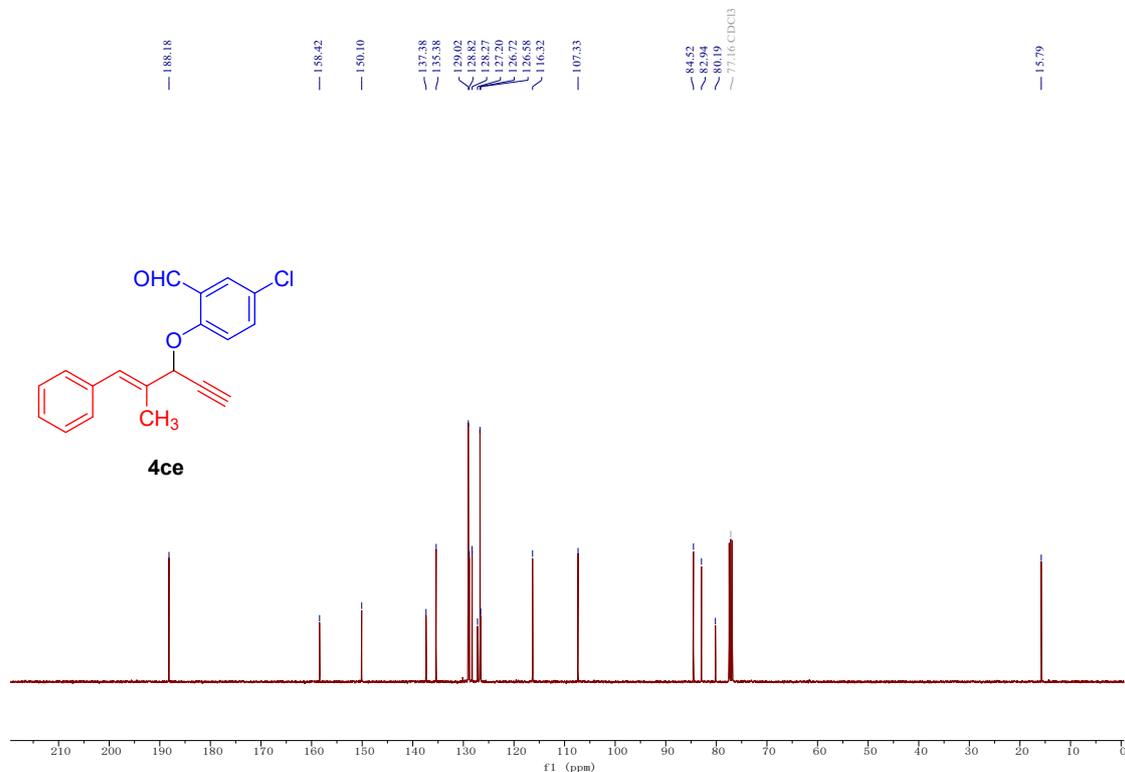
^{19}F NMR-**4cd** (376 MHz, CDCl_3)



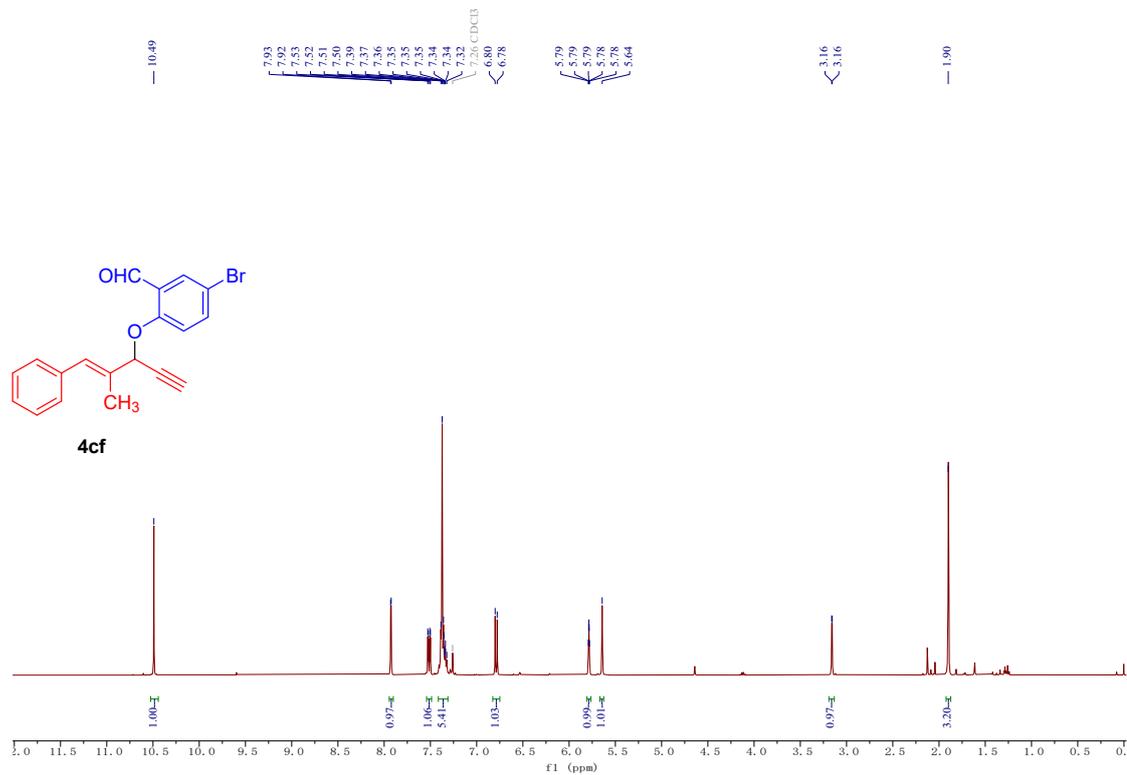
^1H NMR-4ce (400 MHz, CDCl_3)



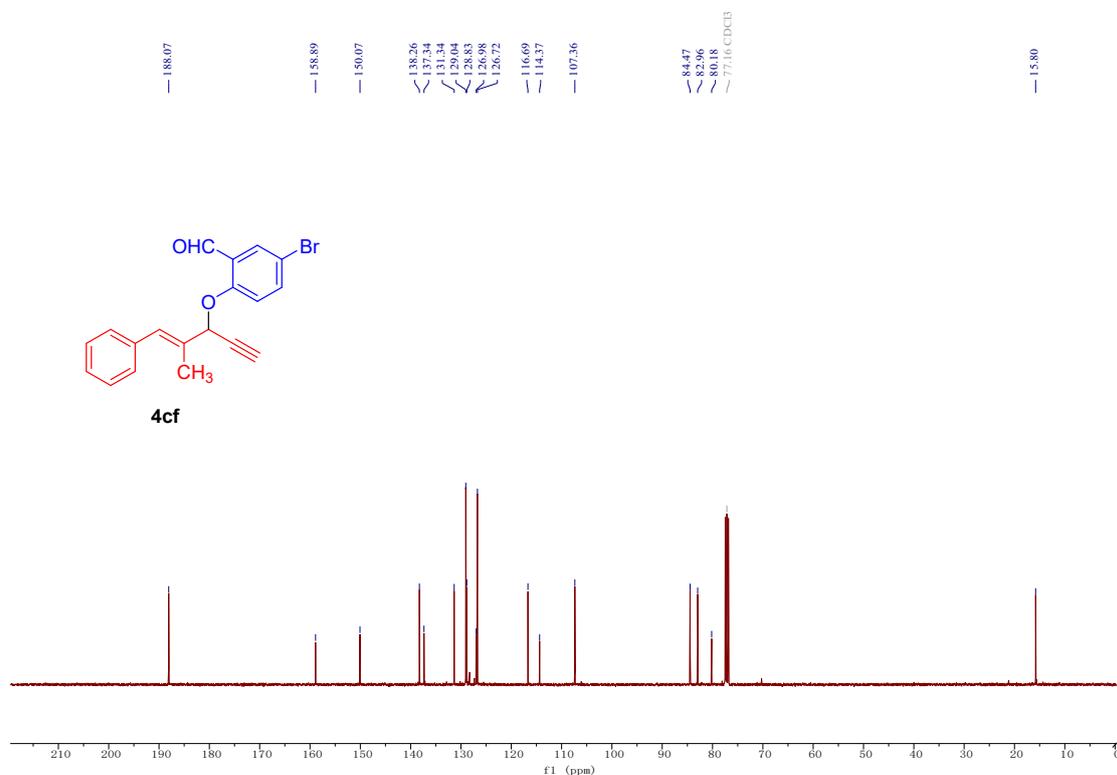
^{13}C NMR-4ce (100 MHz, CDCl_3)



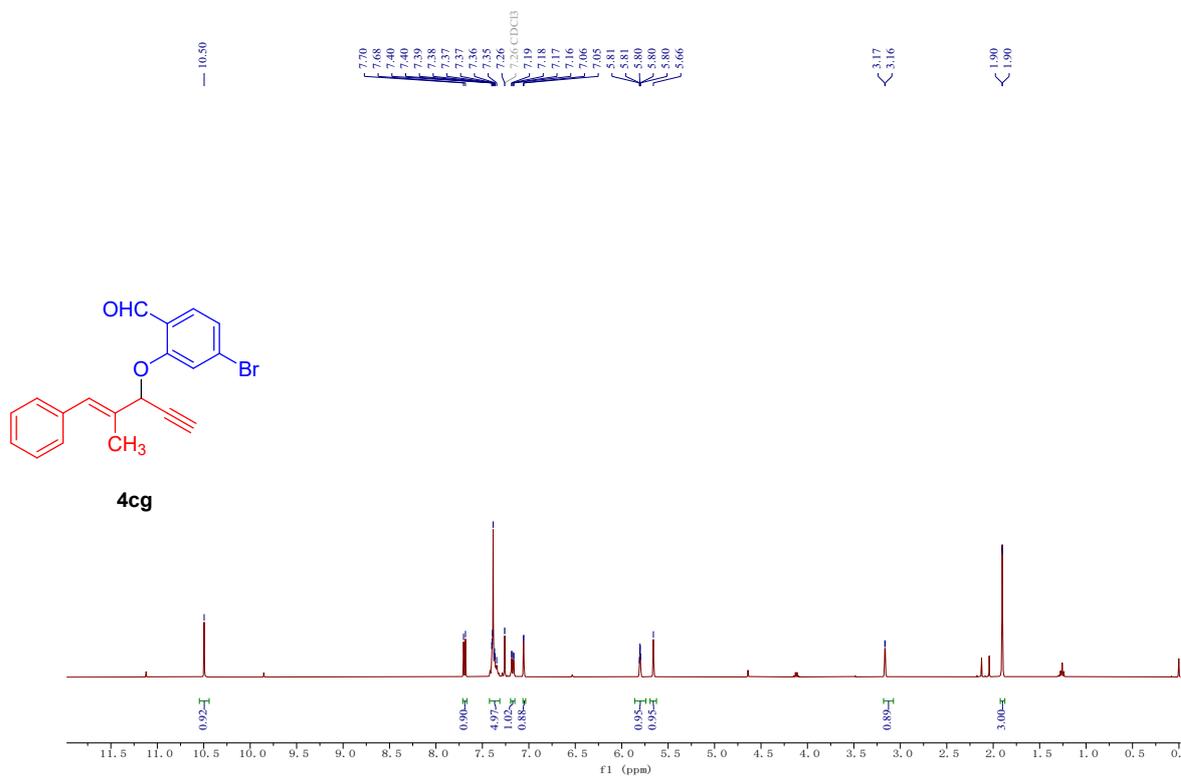
¹H NMR-4cf (400 MHz, CDCl₃)



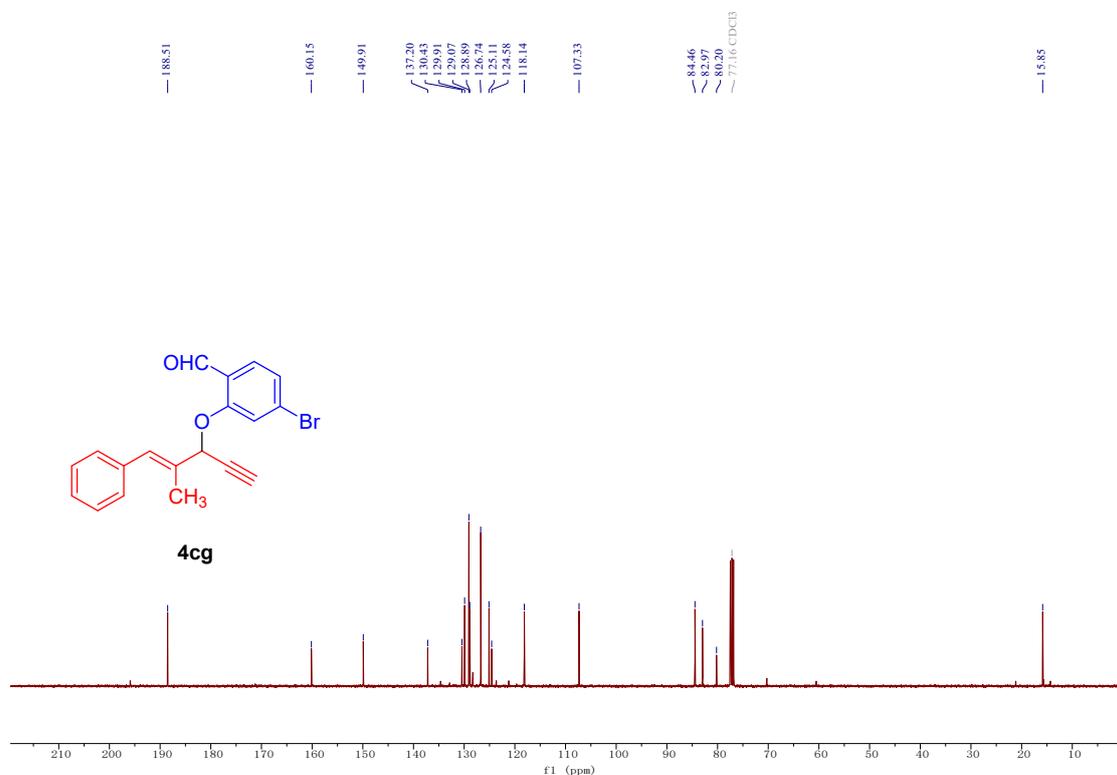
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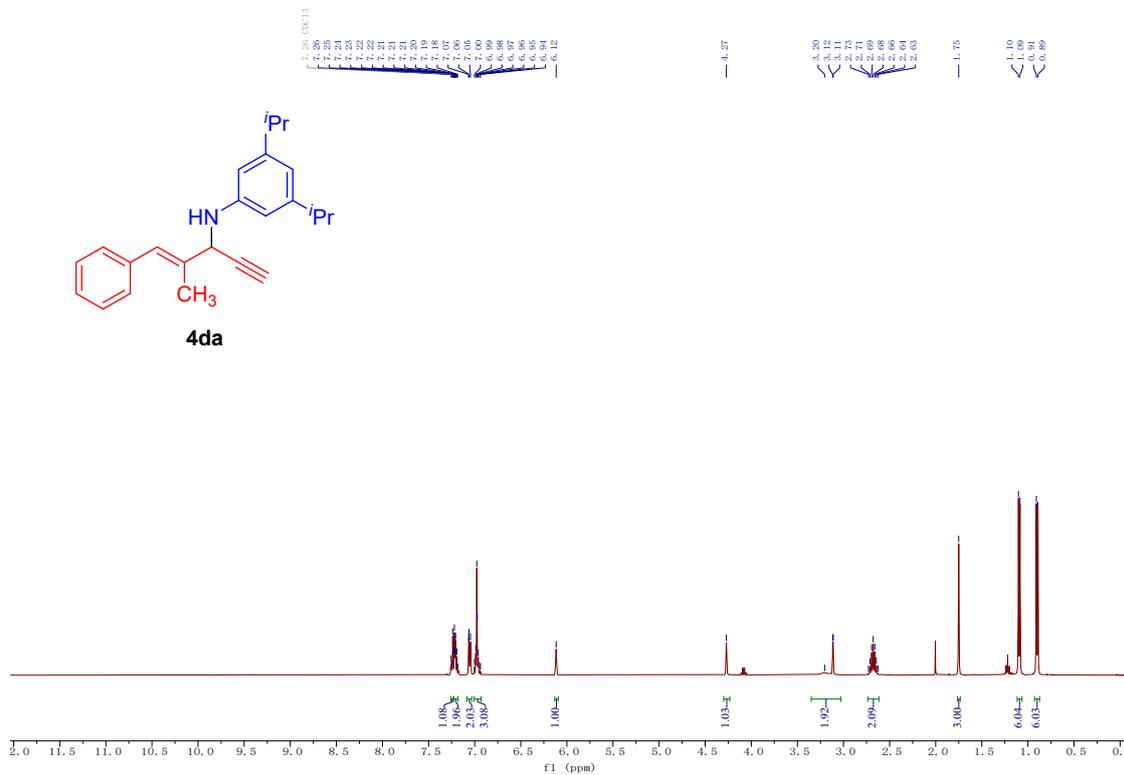
¹H NMR-4cg (400 MHz, CDCl₃)



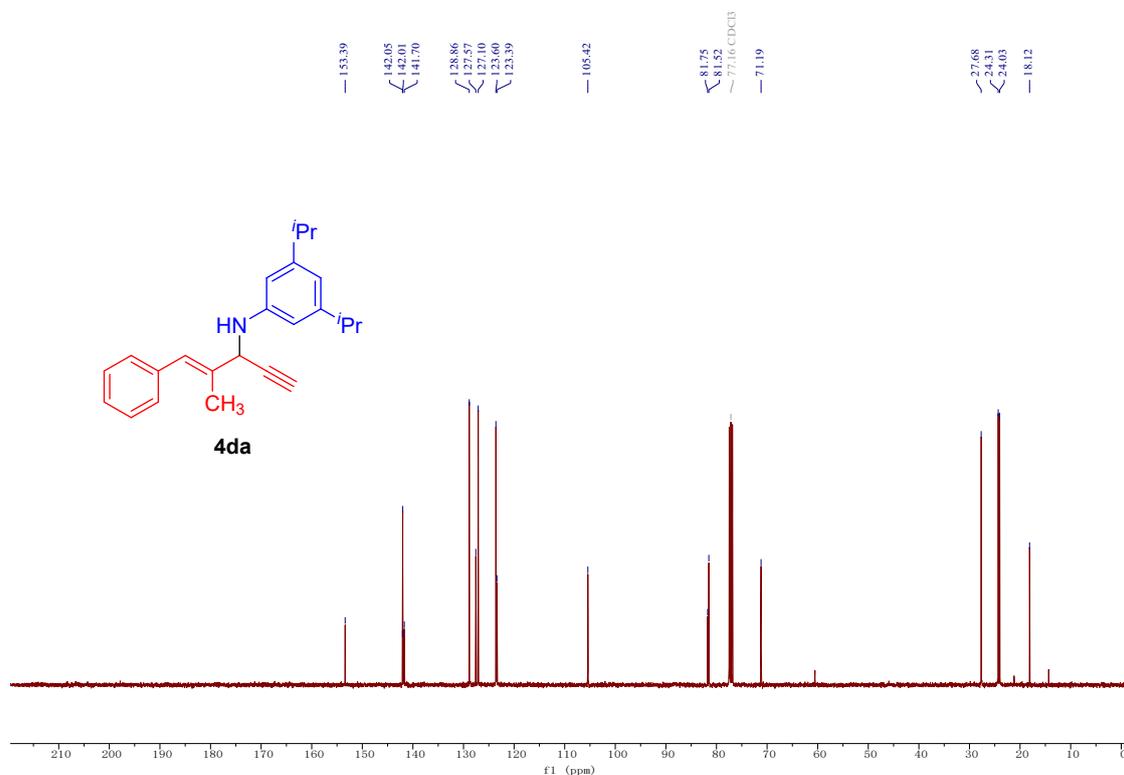
¹³C NMR-4cg (100 MHz, CDCl₃)



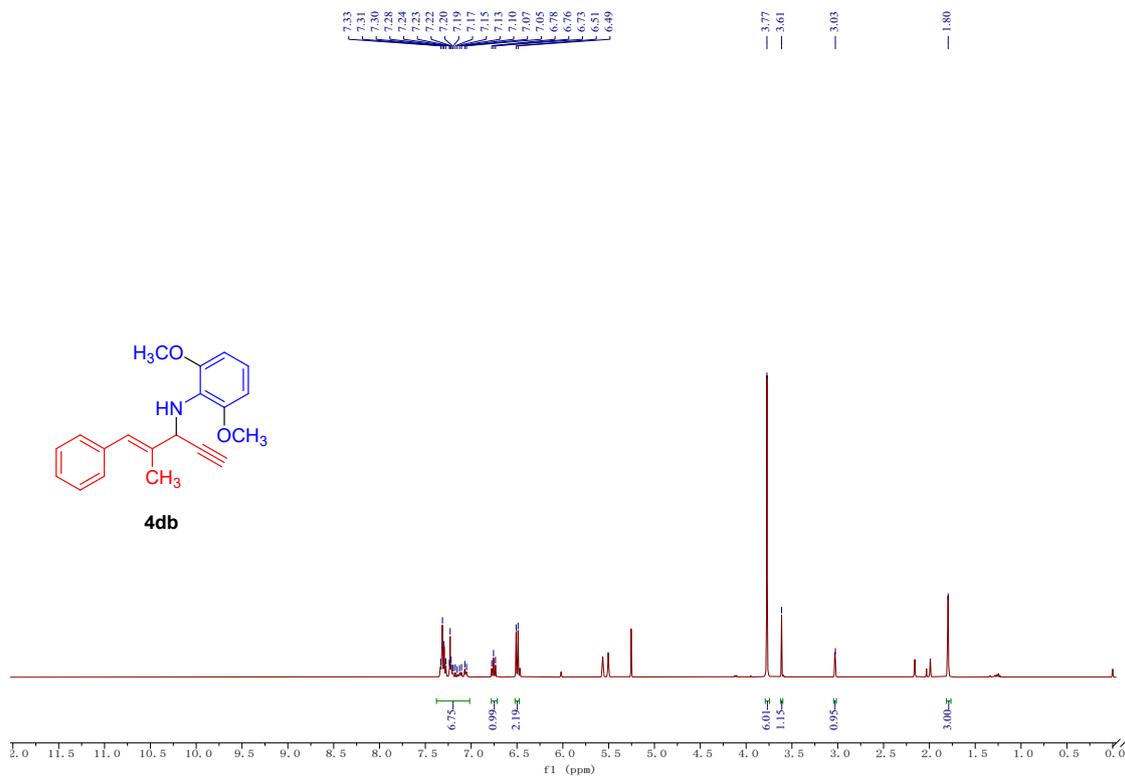
^1H NMR-4da (400 MHz, CDCl_3)



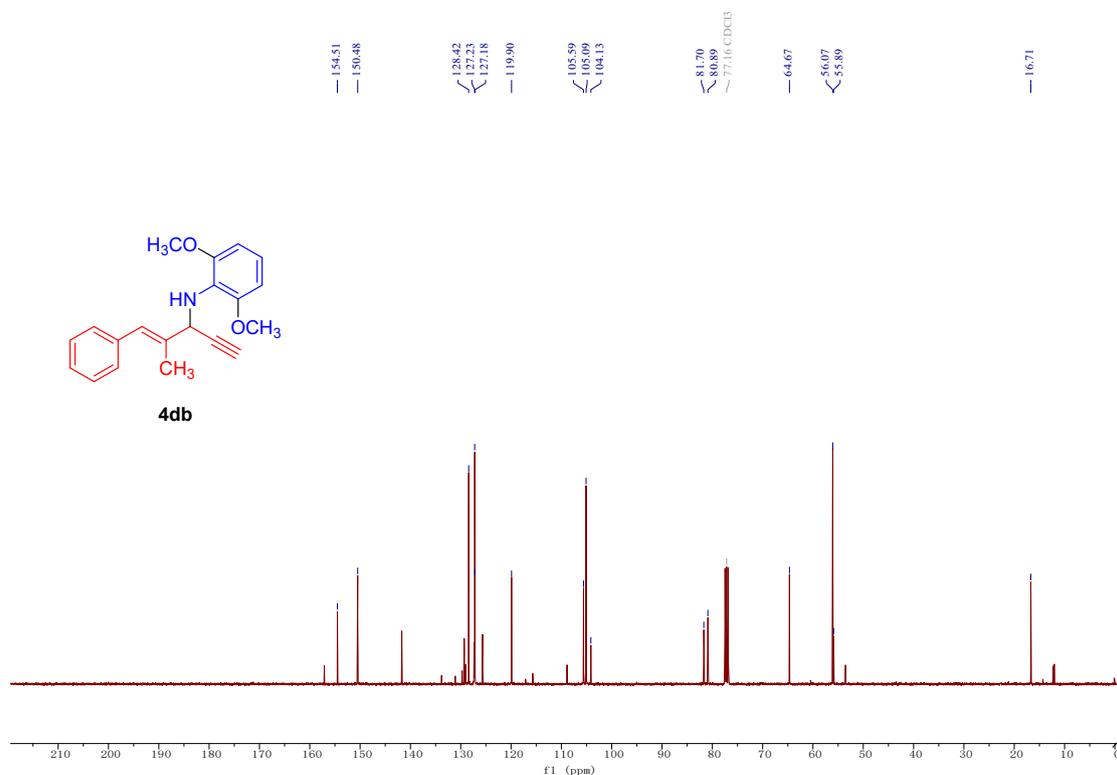
^{13}C NMR-4da (100 MHz, CDCl_3)



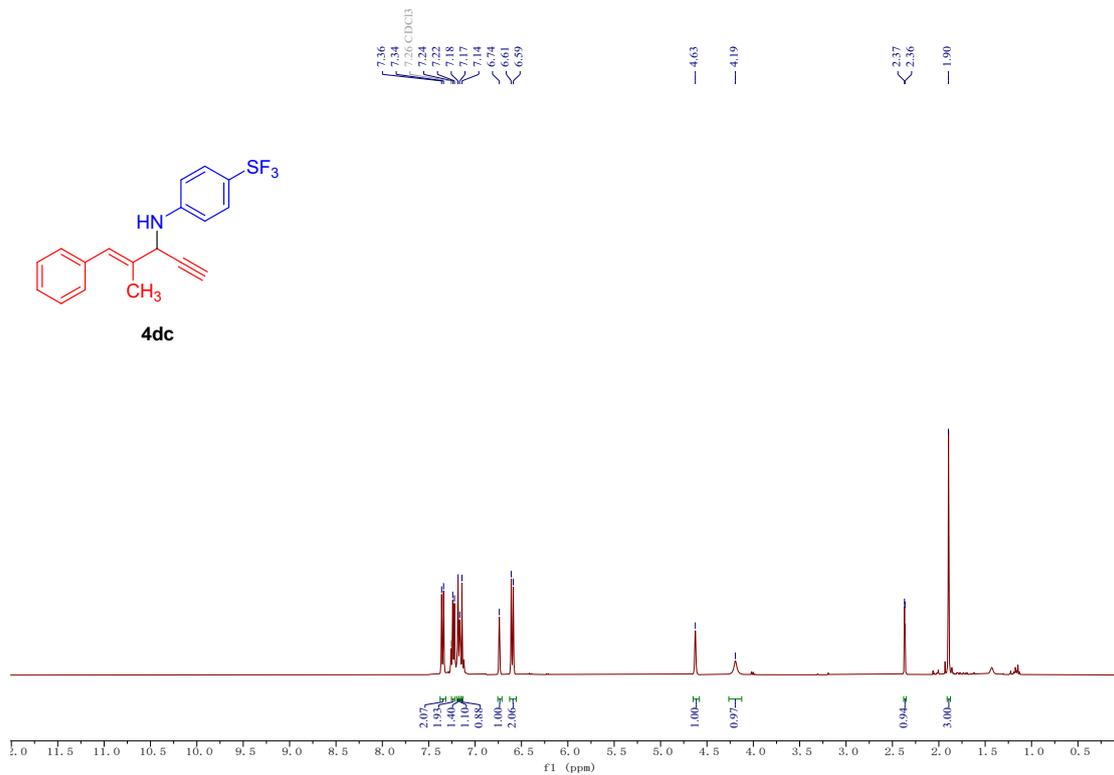
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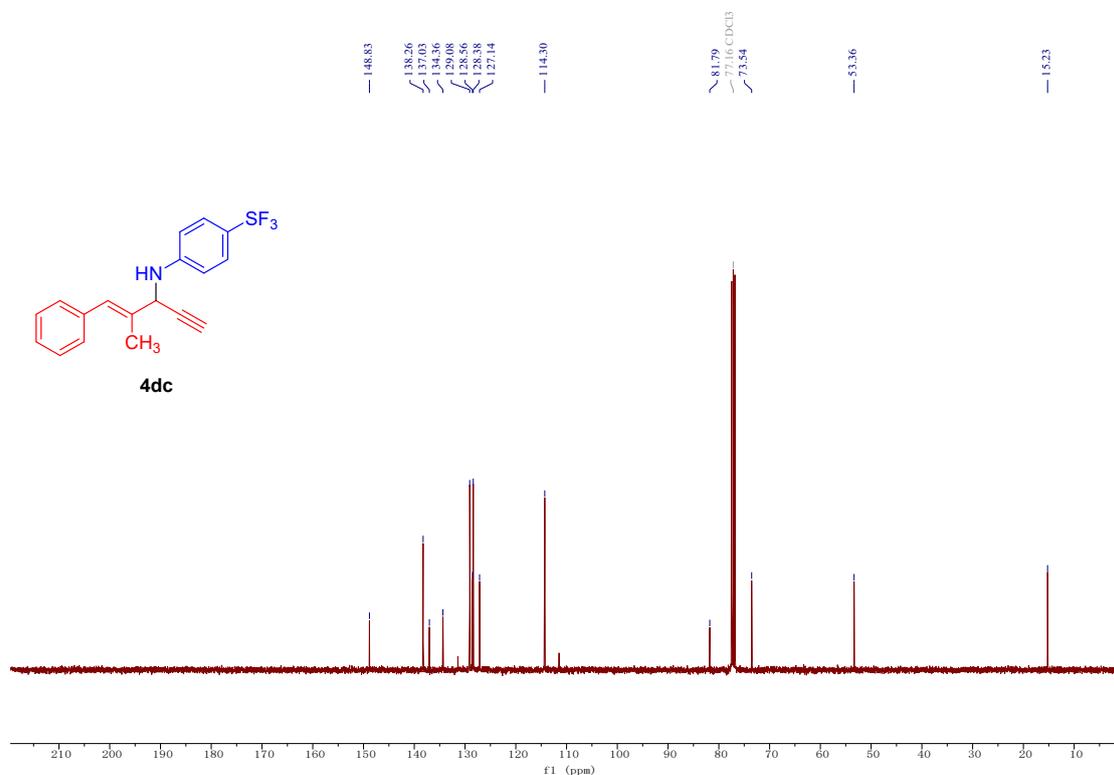
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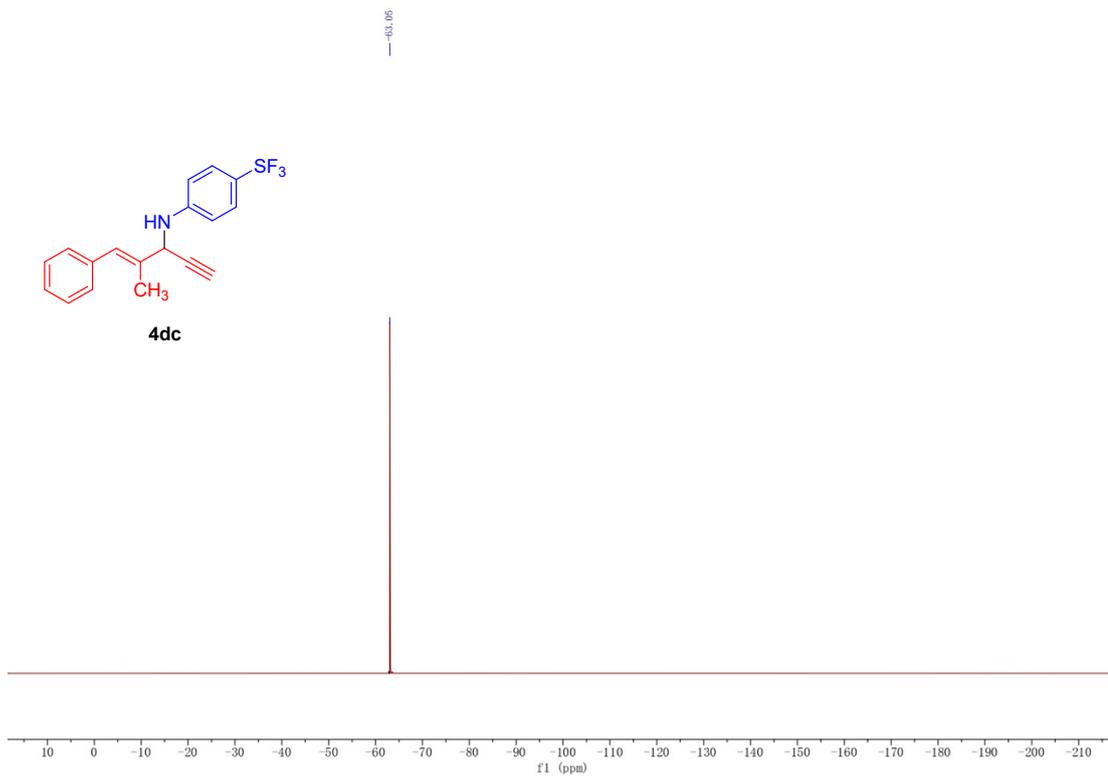
¹H NMR-4dc (400 MHz, CDCl₃)



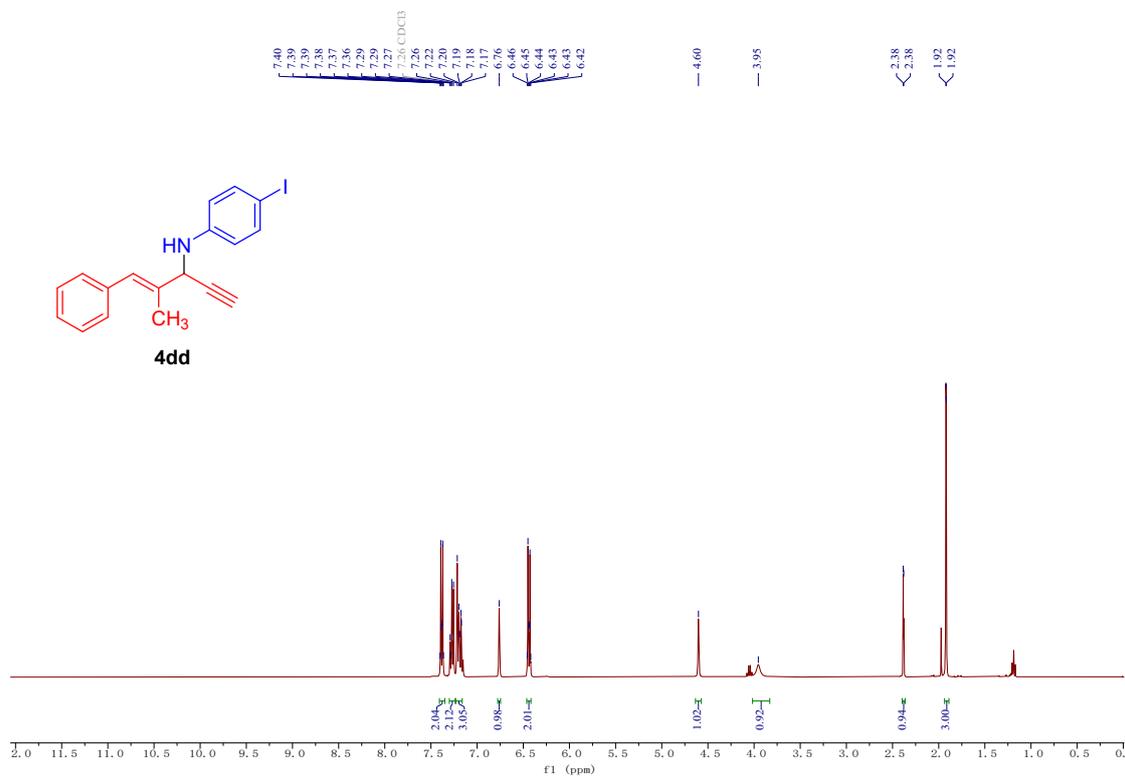
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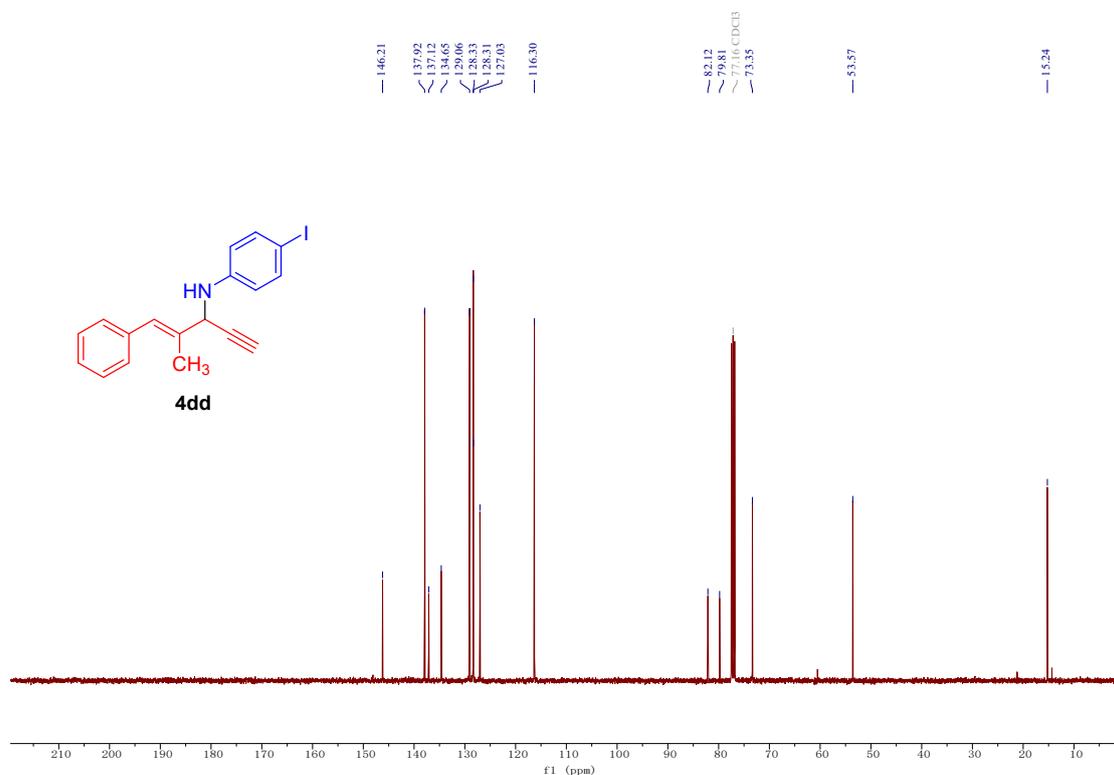
^{19}F NMR-**4dc** (376 MHz, CDCl_3)



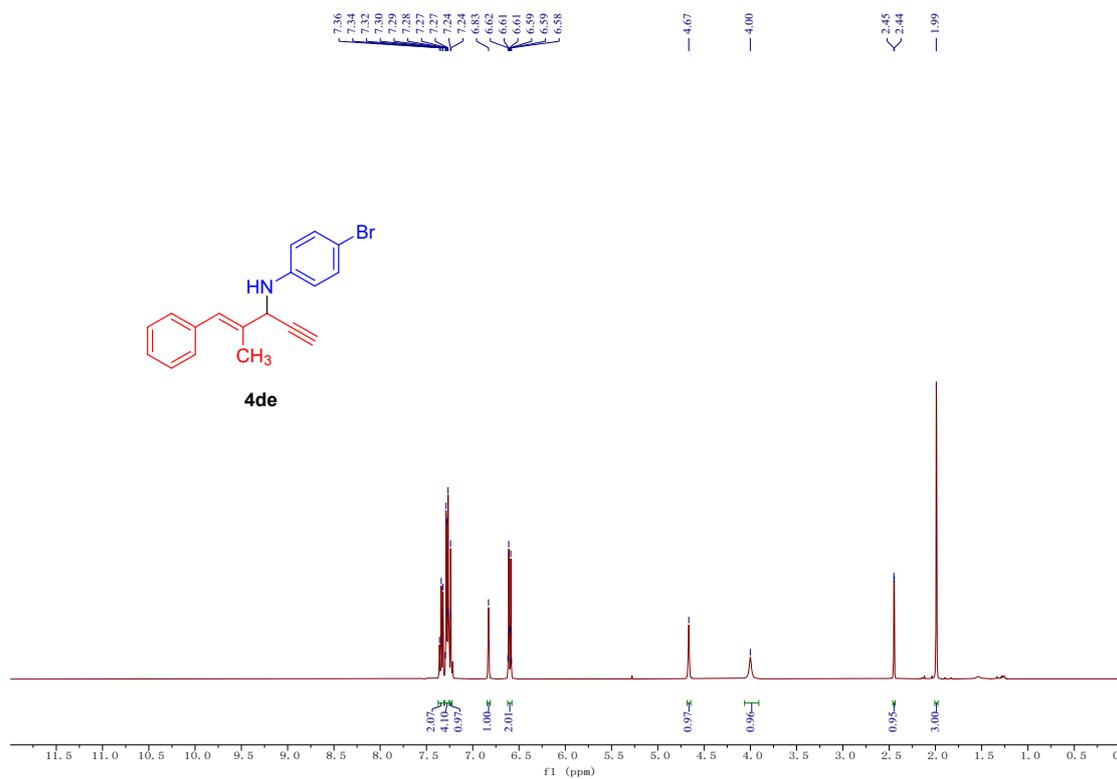
^1H NMR-4dd (400 MHz, CDCl_3)



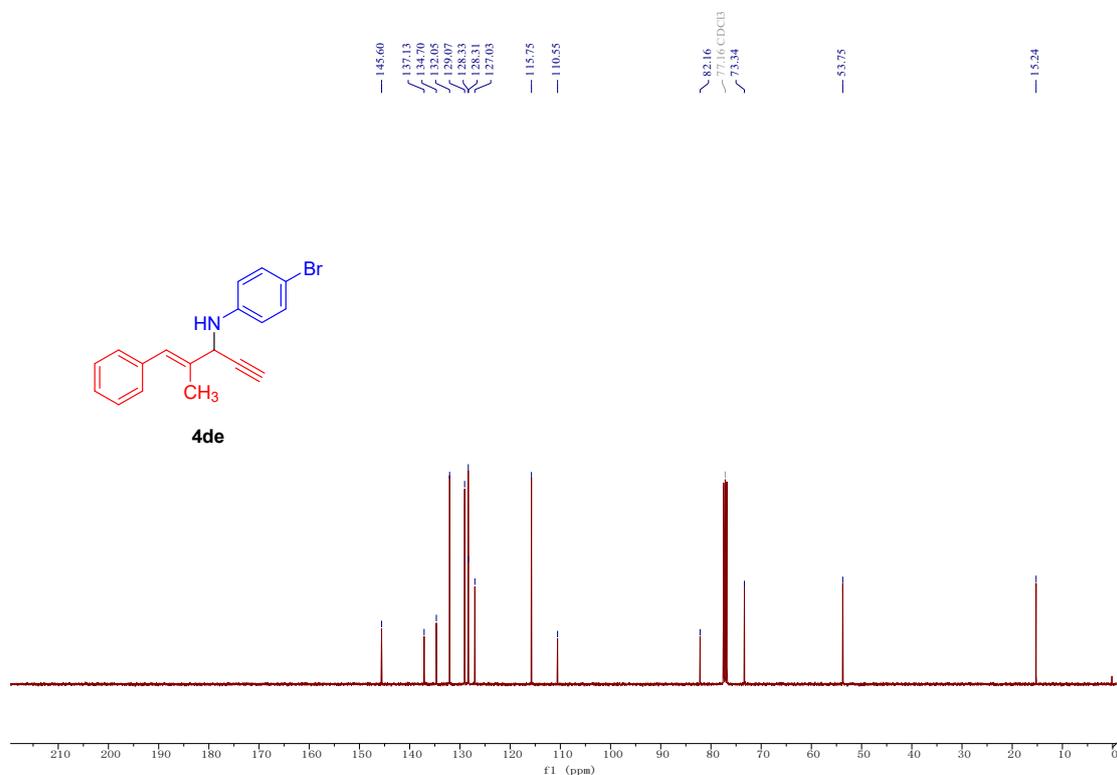
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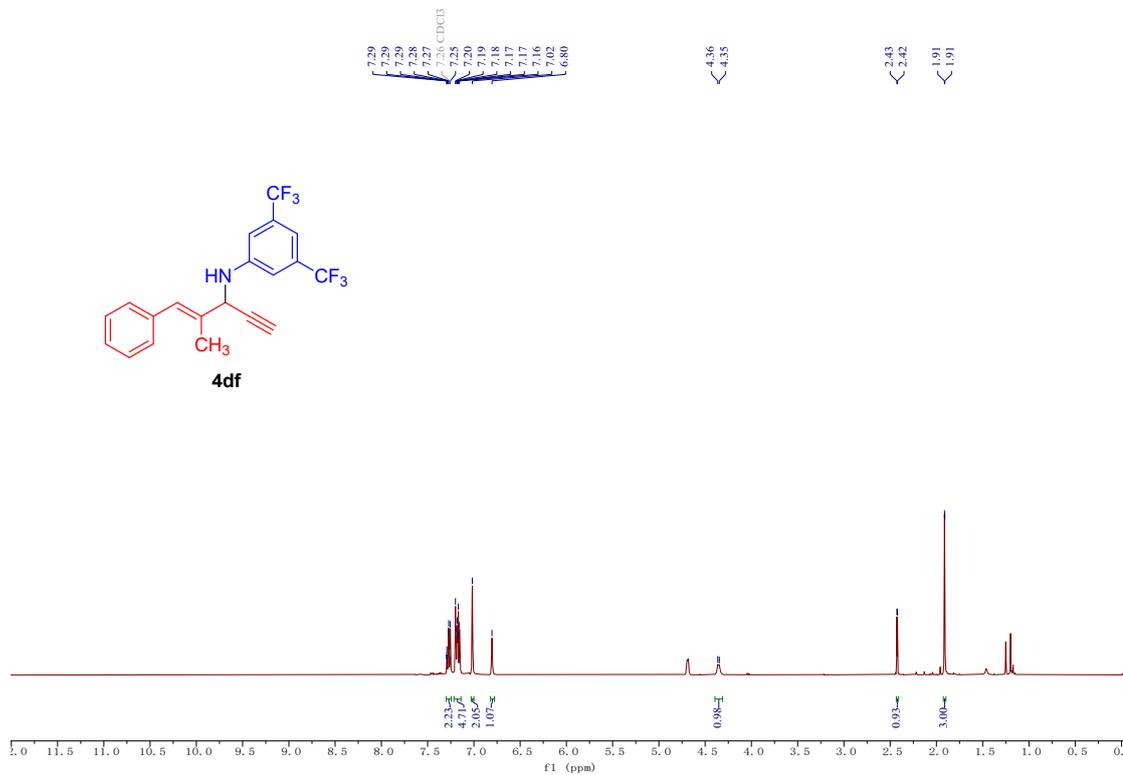
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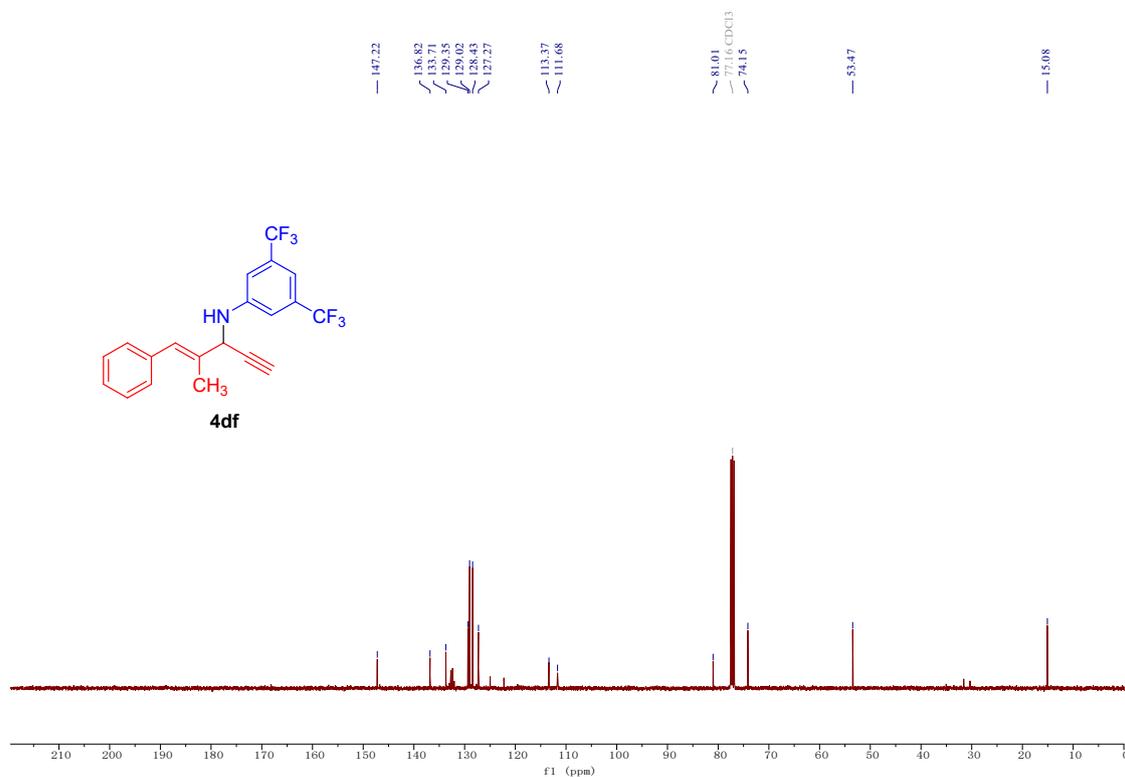
^{13}C NMR-4de (100 MHz, CDCl_3)



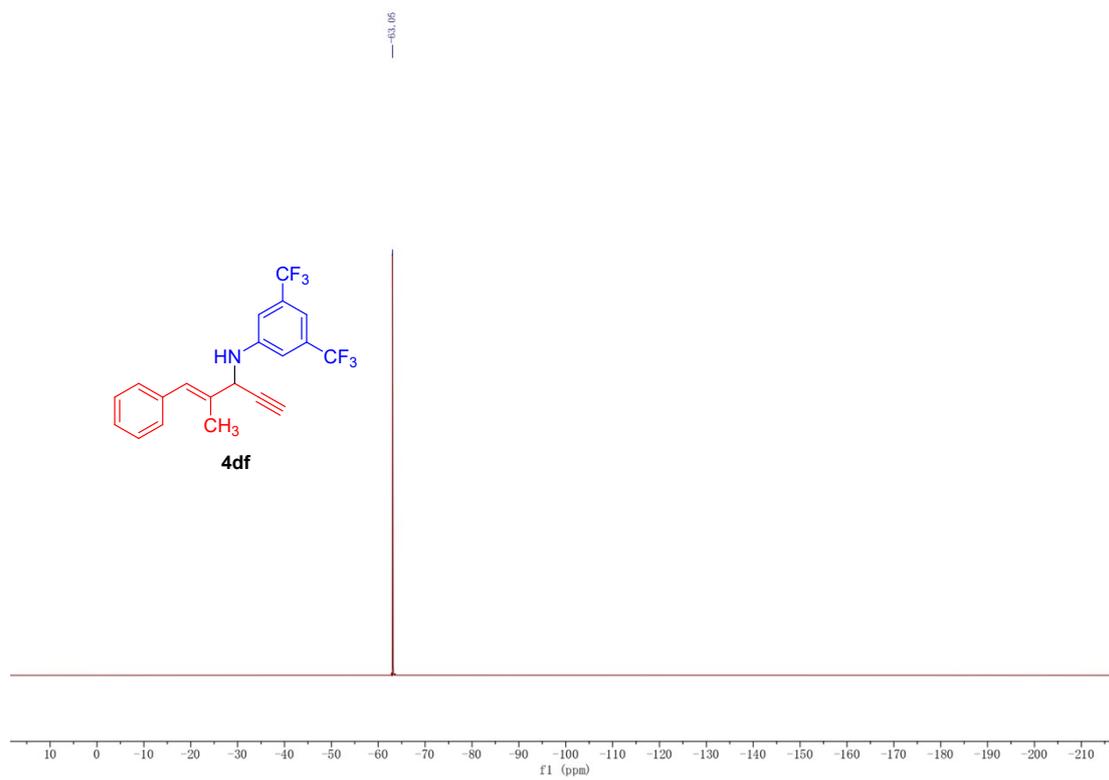
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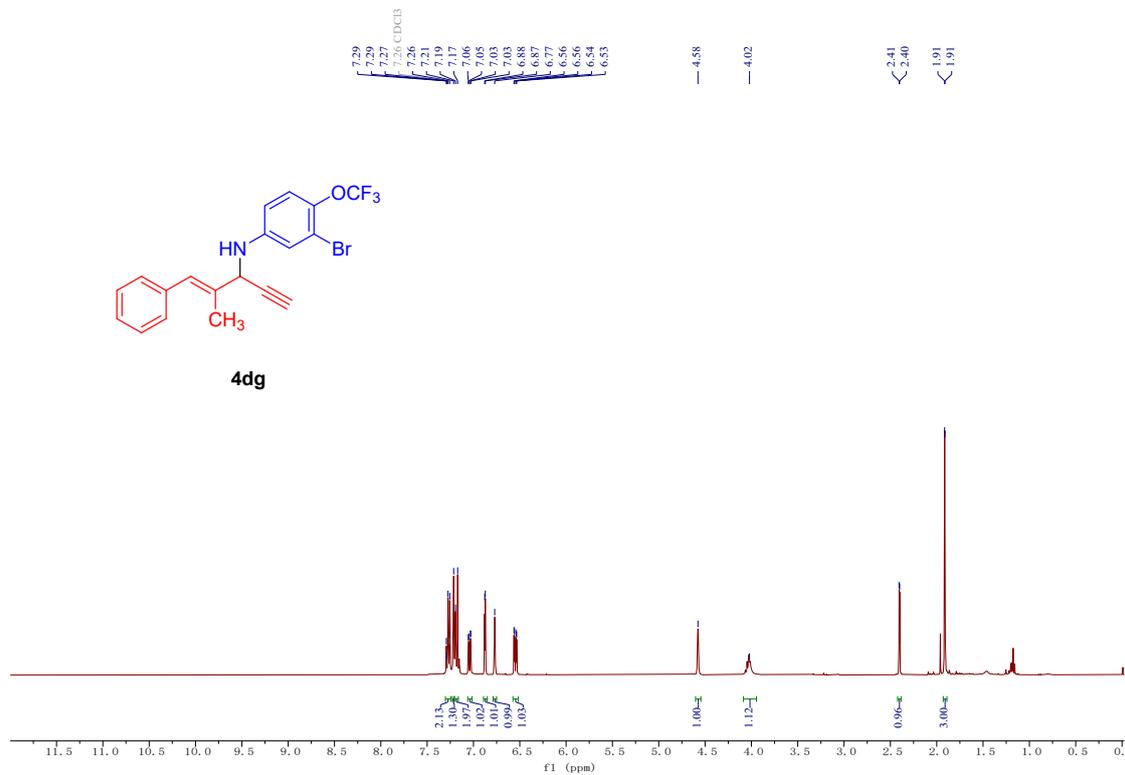
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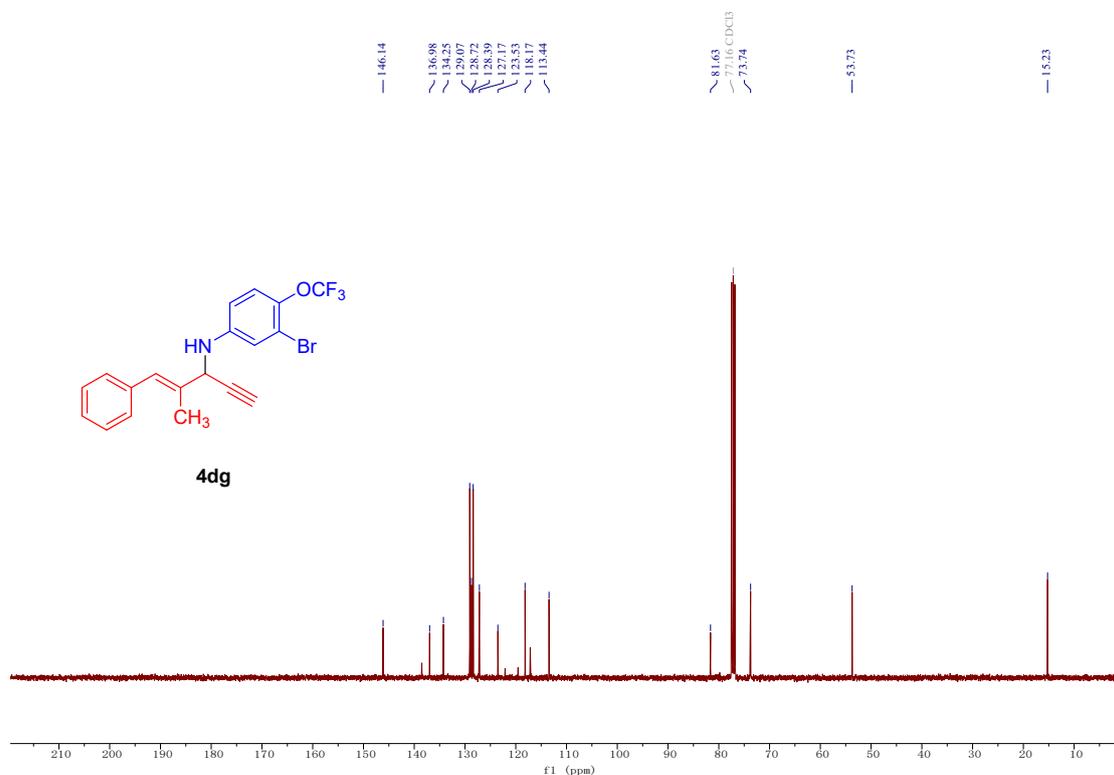
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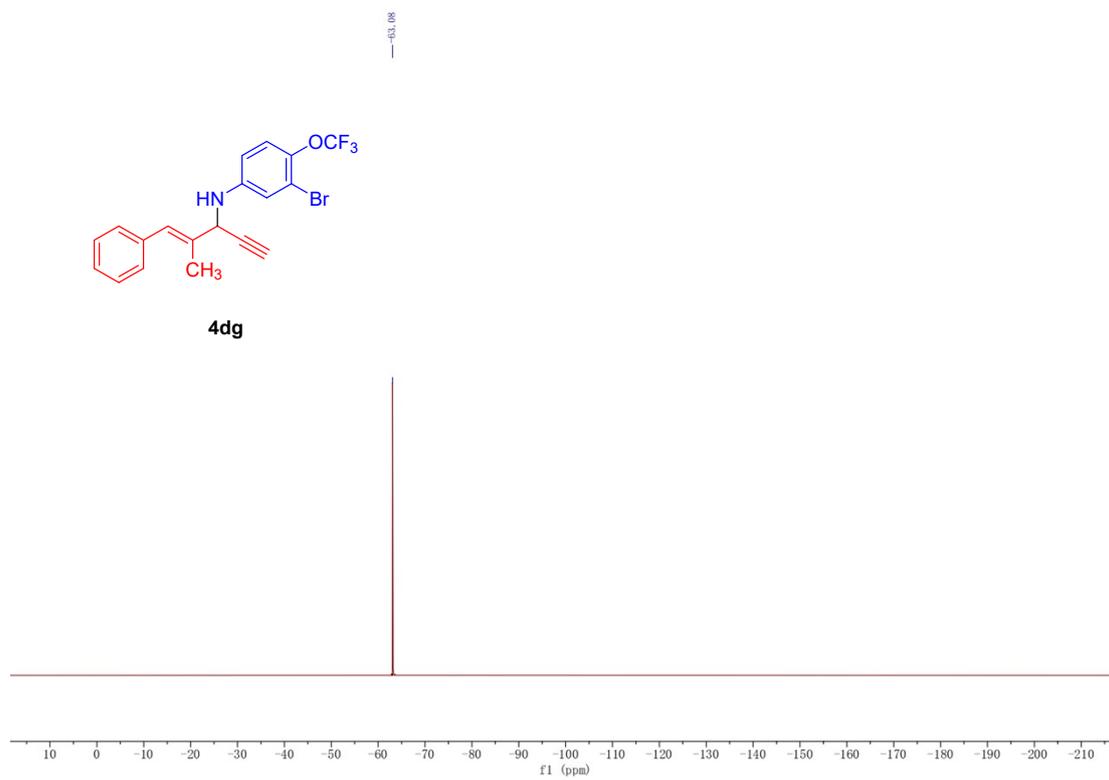
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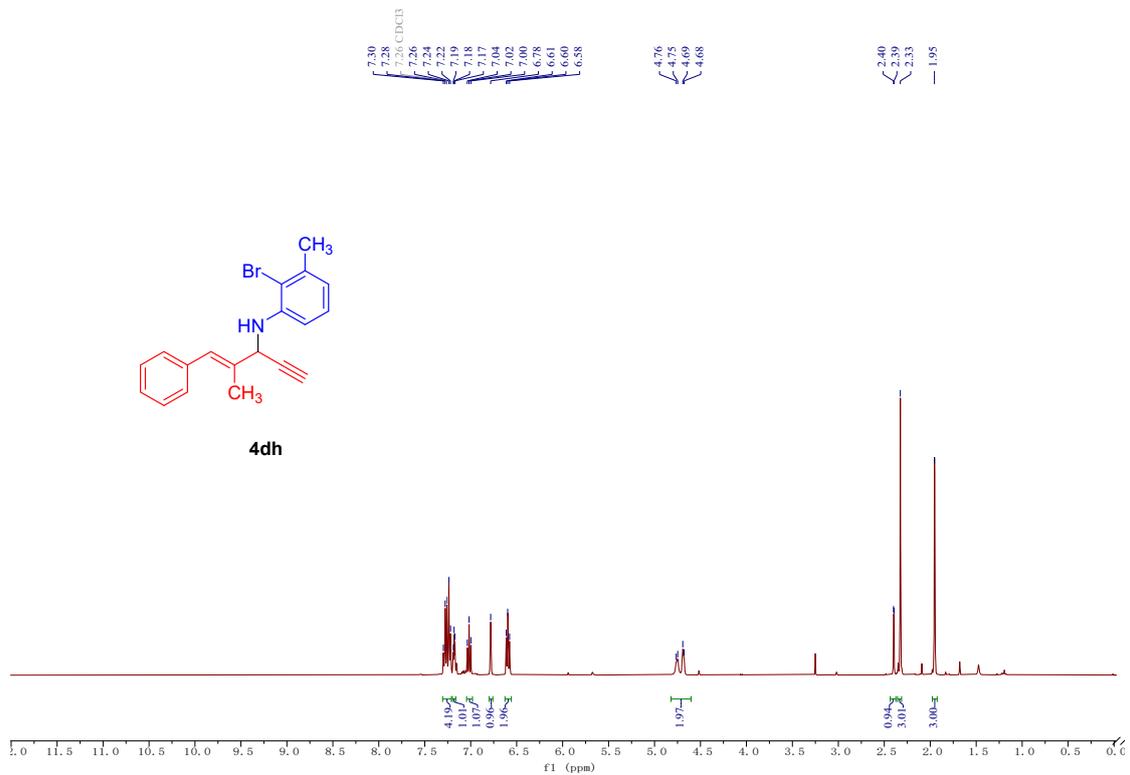
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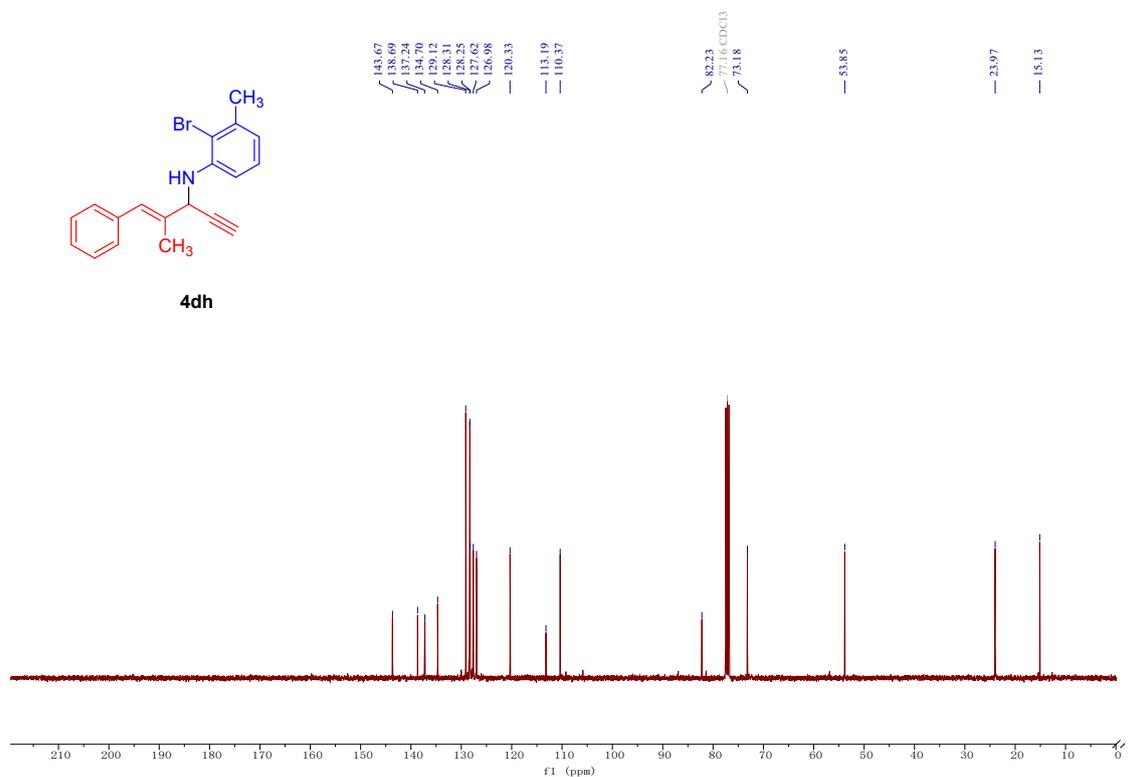
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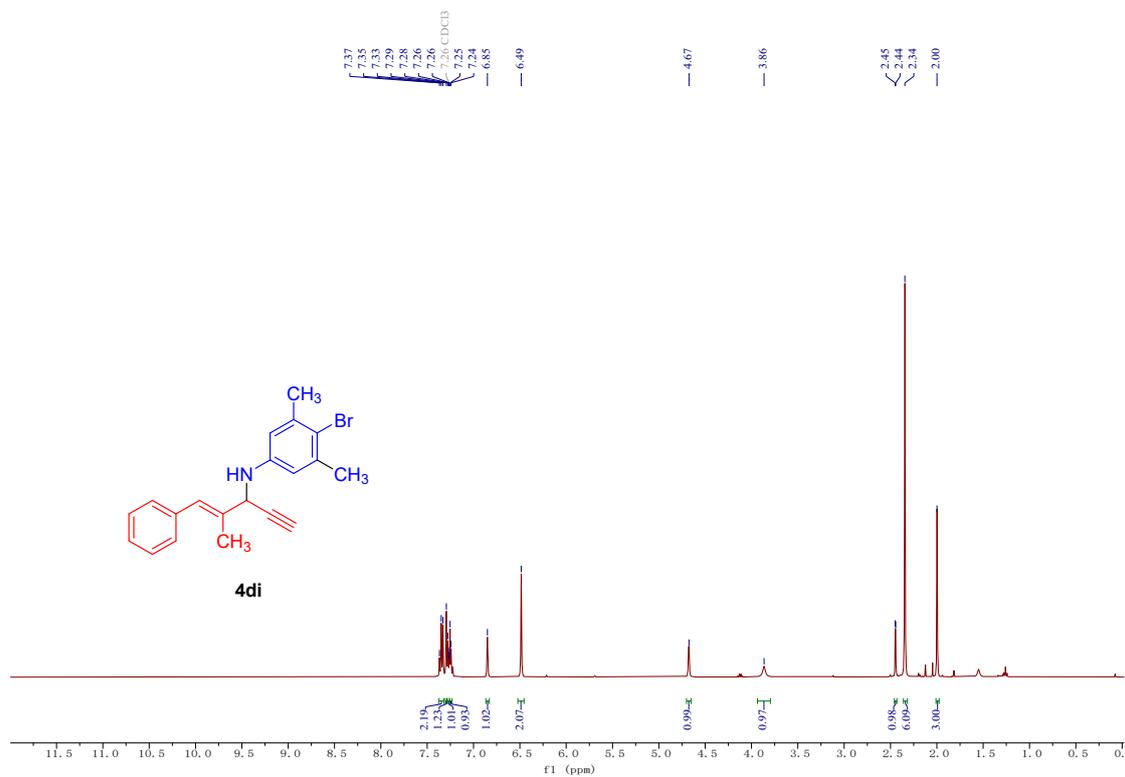
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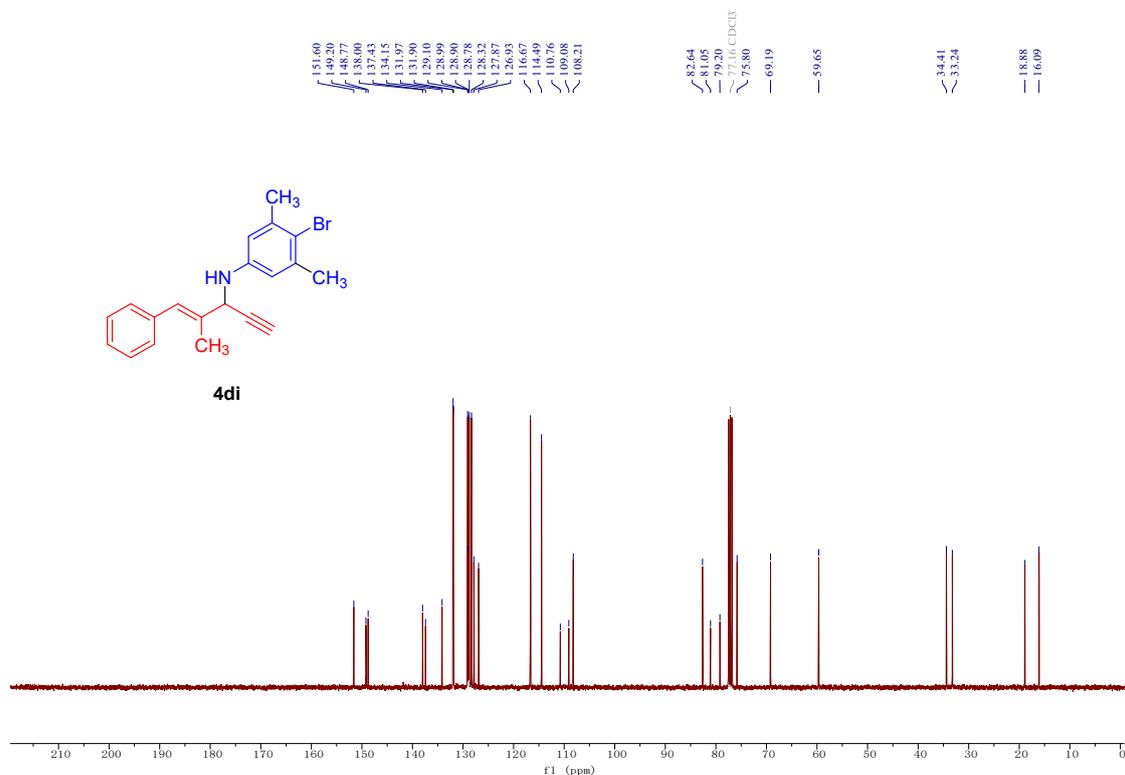
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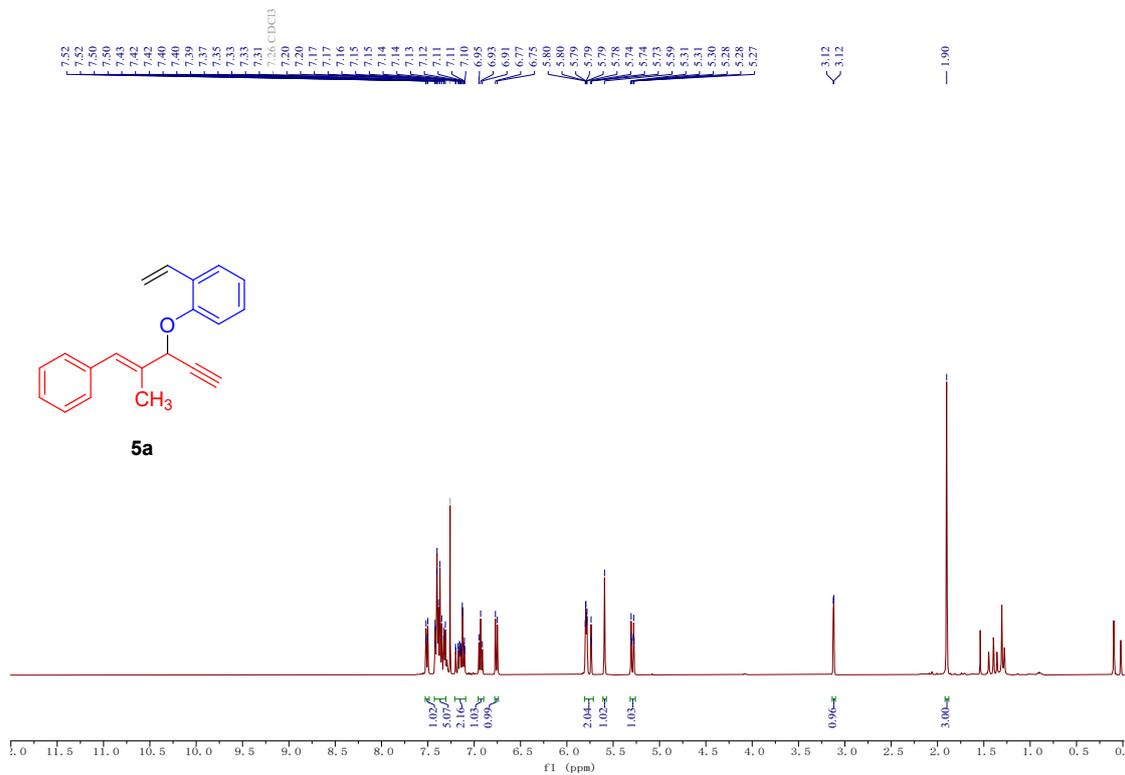
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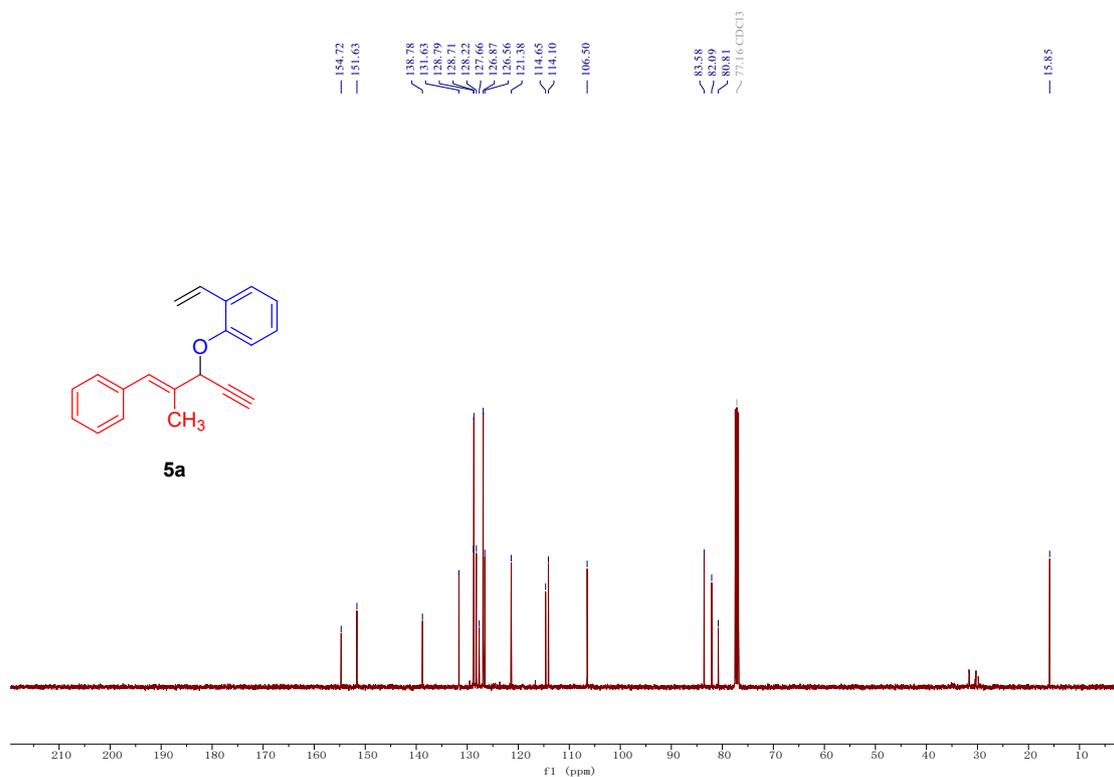
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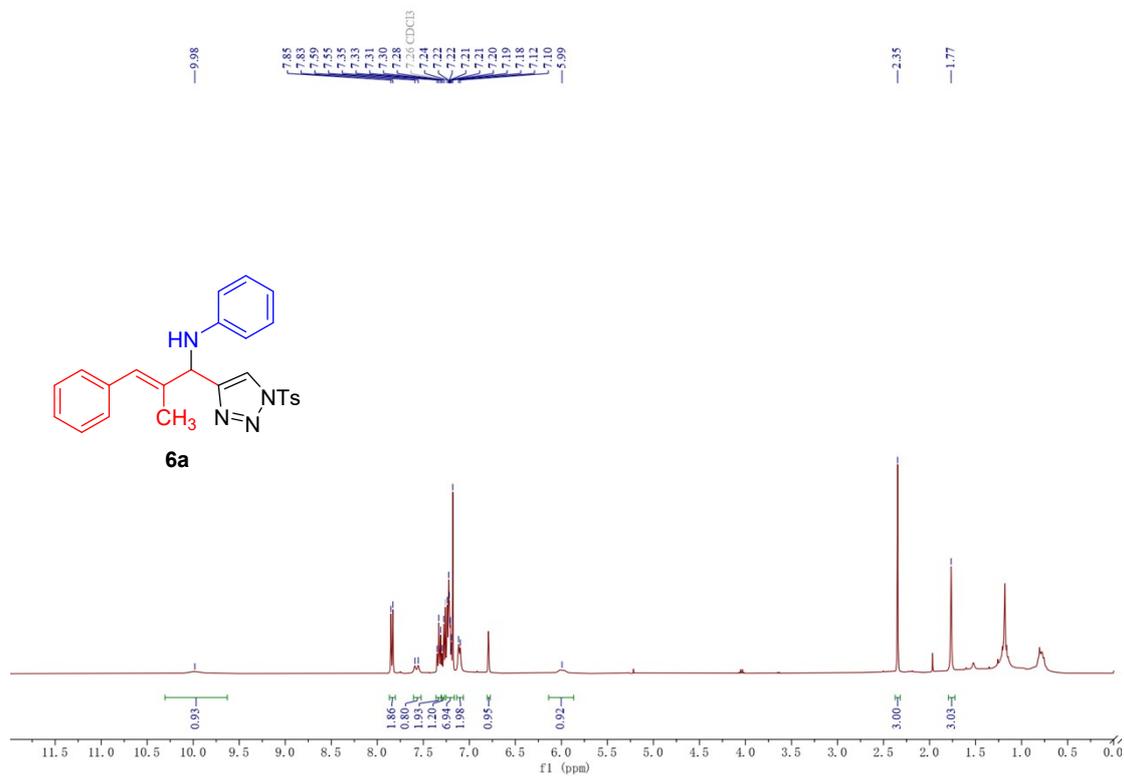
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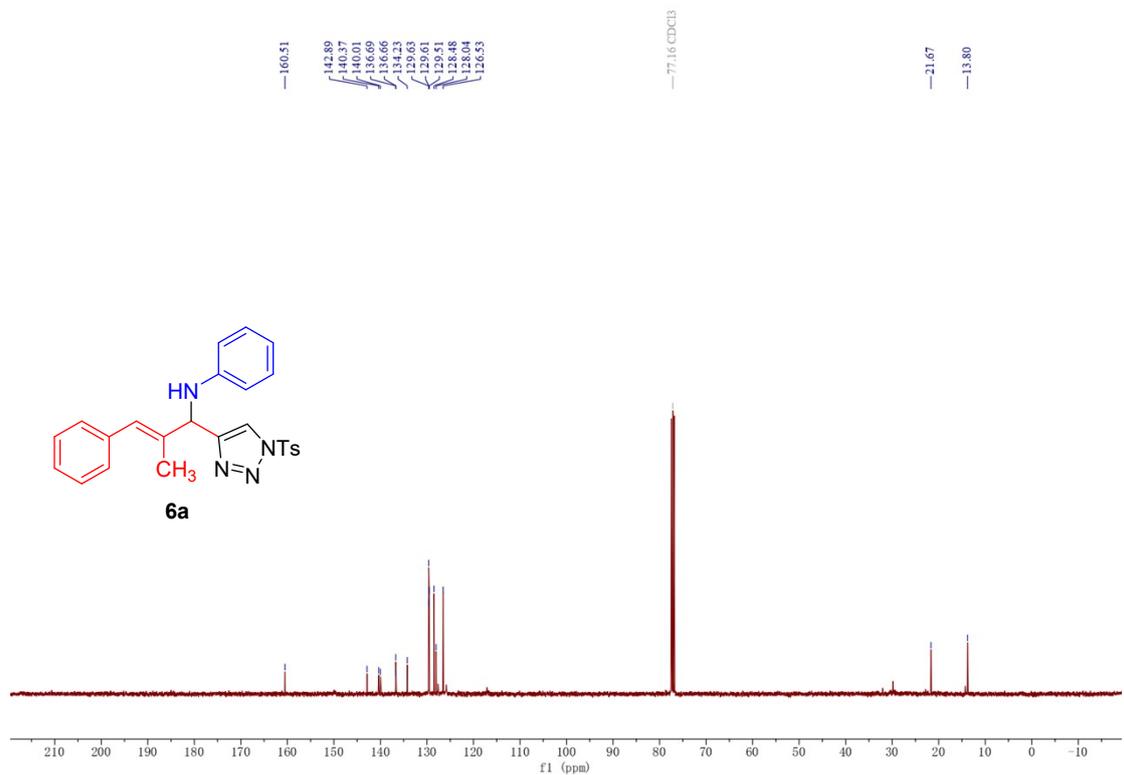
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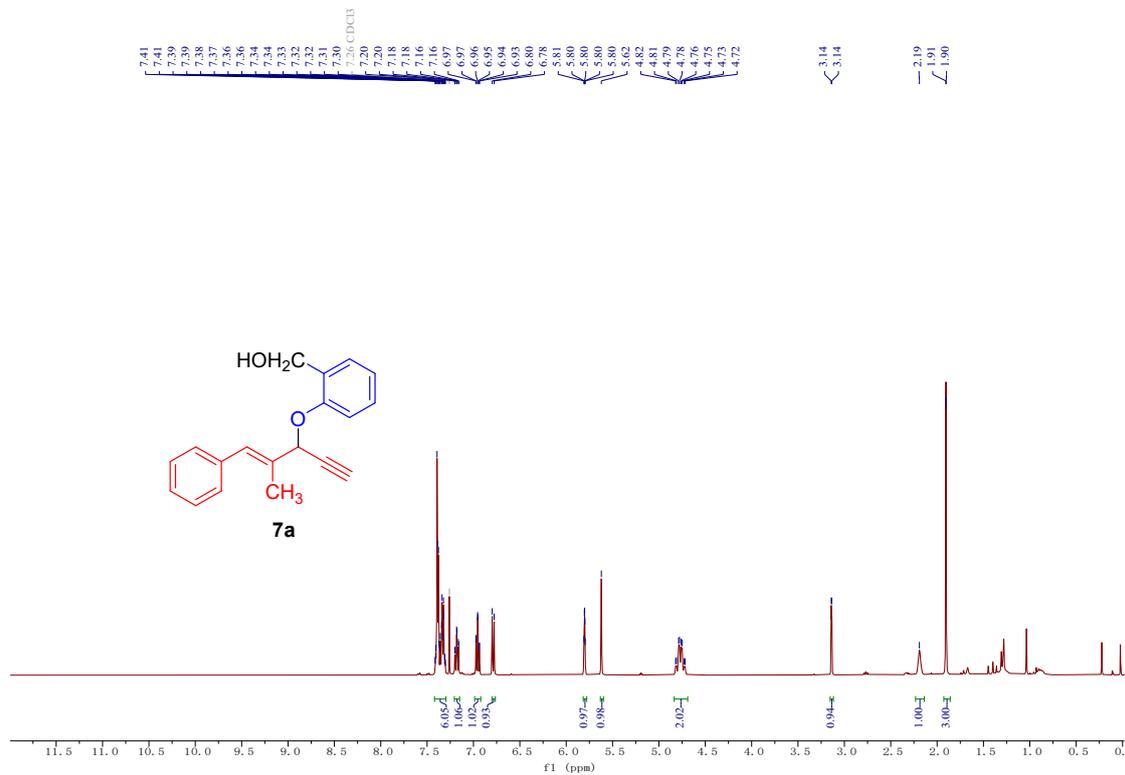
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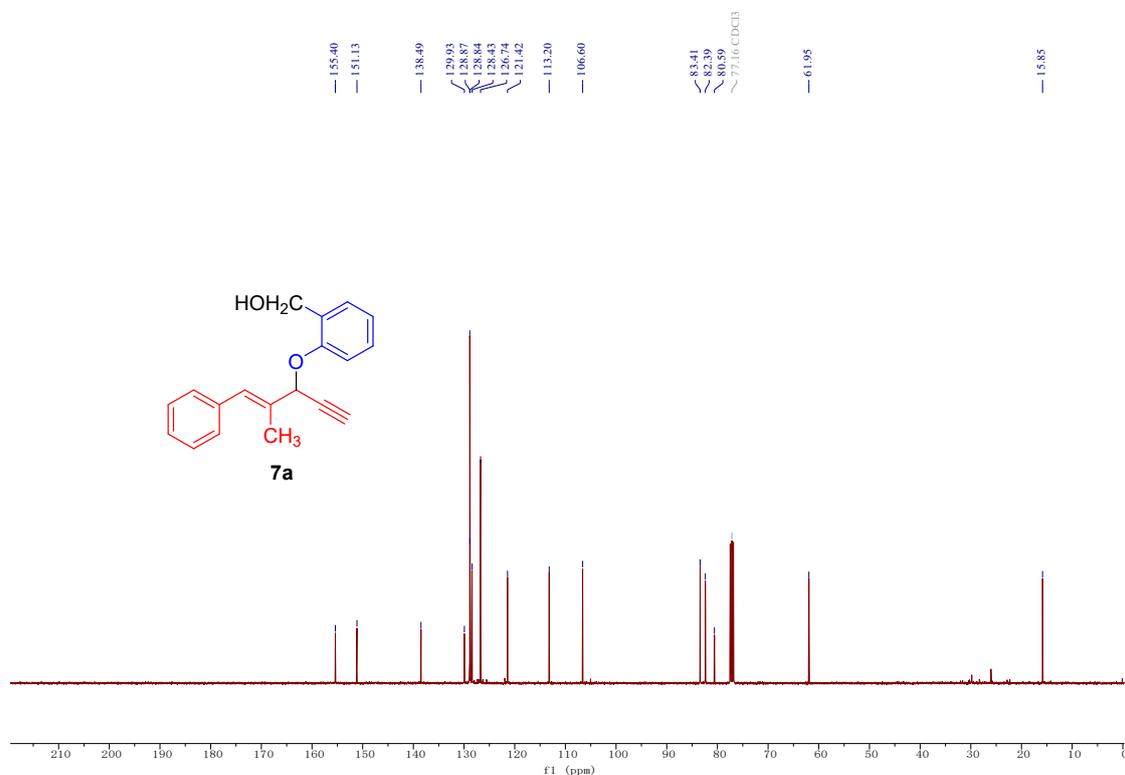
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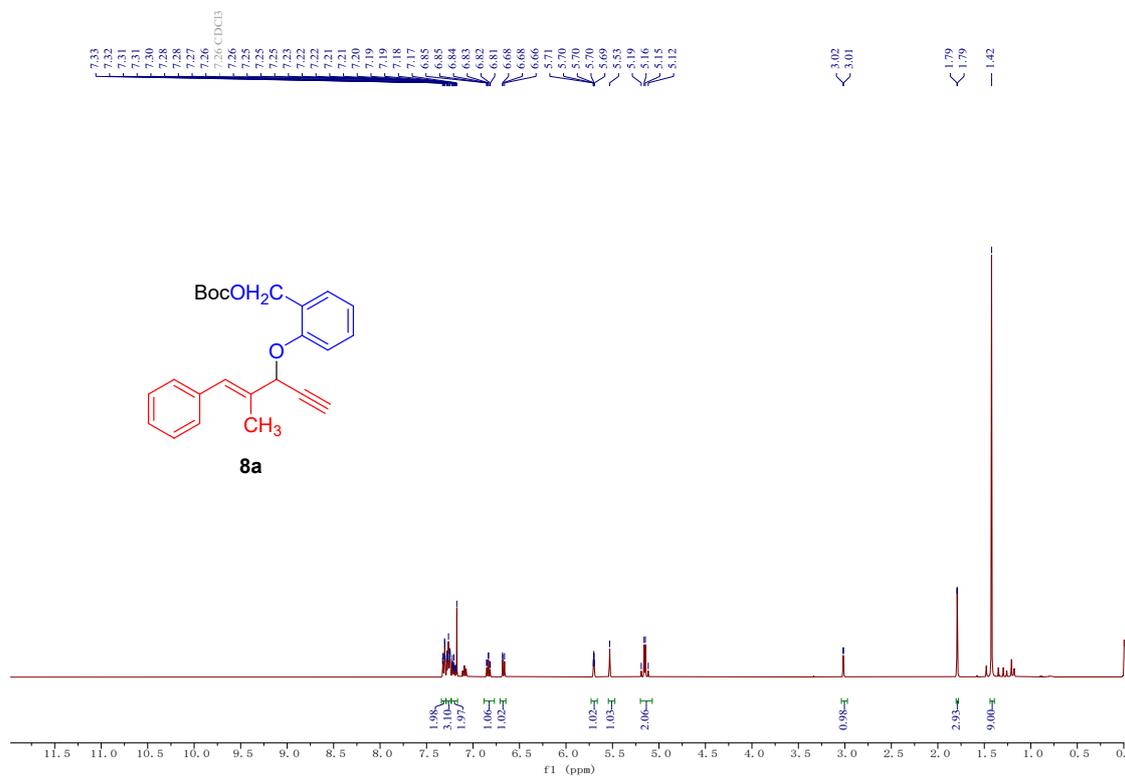
¹H NMR-7a (400 MHz, CDCl₃)



¹³C NMR-7a (100 MHz, CDCl₃)



¹H NMR-8a (400 MHz, CDCl₃)



¹³C NMR-8a (100 MHz, CDCl₃)

