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Supporting information

New Reactivity of Ethynyl Benziodoxolone: Modulating Iron-Catalyzed Dehydration of Propargyl Alcohols

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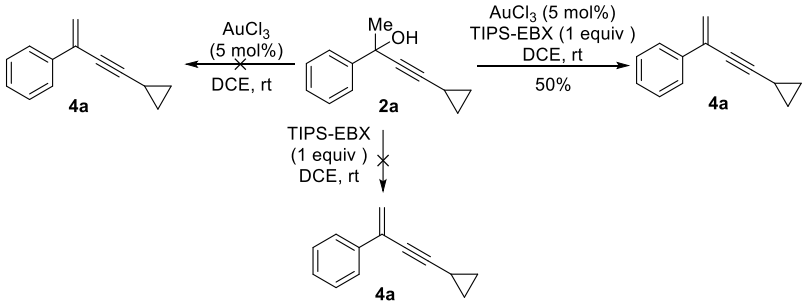
Materials and methods

All the chemicals were commercially, and used without further purification unless otherwise noted. $FeCl_3$ and other starting materials were purchased from Alfa Aesar, Energy Chemical, Adamas and other companies. All reactions were carried out under nitrogen atmosphere unless specified. 1,2-dichloroethane, dichloromethane, and acetonitrile were distilled from calcium hydride. Toluene was distilled from sodium. Thin-layer chromatography (TLC) was carried out on 0.25 mm Huanghai silica gel plates (HSGF-254) and visualized by exposure to UV light (254 nm) and/or $KMnO_4$ (aq.) was used as revealing system. Flash column chromatography was performed on Tsingdao silica gel (60, particle size 0.040–0.063 mm). ^{1}H NMR, and ^{13}C NMR spectra were recorded on Bruker spectrometers (at 300, 400 or 500 MHz for ^{1}H NMR, at 75, 100 or 125 MHz for ^{13}C NMR) and were reported relative to deuterated solvent or tetramethylsilane internal standard signals. Data for ^{1}H NMR spectra were reported as following: chemical shift (δ/ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J*/Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift and coupling constant (*J*/Hz) when necessary. High Resolution Mass Spectrometry was conducted on Bruker Apex IV RTMS.

Propagyl alcohols were prepared according to known procedures. [1-3] R-EBX were prepared according to Waser's procedures.[4] Arylbenziodoxolone was prepared according to Zhdankin and co-workers' procedure.[5]

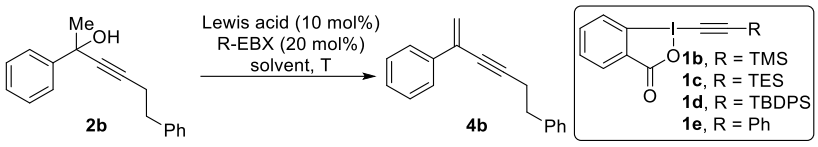
General Procedure for the Discovery of Dehydration



In a 10 mL flask with a magnetic stirring bar under N_2 atmosphere were placed a solution of propargyl alcohol **2a** (0.3 mmol, 55.8 mg, 1.0 equiv) in dry DCE (1.5 mL), then TIPS-EBX (0.3 mmol, 129 mg, 1.0 equiv) was added followed by addition of $AuCl_3$ (0.015 mmol, 4.5 mg, 0.05 equiv) quickly. The solution was stirred at room temperature for about 12 h and followed by TLC. After that, the solvent was removed in vacuo and the residue was subjected to column chromatography (SiO_2, Hexanes) to afford enyne **4a** as colorless oil (25.5 mg, 50%).

The control experiments were conducted under the similar condition without $AuCl_3$ or TIPS-EBX.

Optimization of the Reaction Conditions



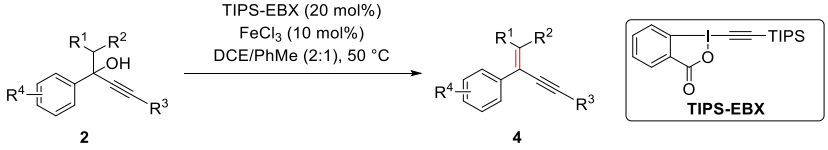
entry	Lewis Acid (10 mol%)	R-EBX (20 mol%)	additive	solvent	temp (°C)	time (h)	yield[a] (%)

1	$FeCl_3$	TIPS-EBX	-	DCM	rt	6	54
2	$FeBr_3$	TIPS-EBX	-	DCM	rt	12	53
3	$FeCl_2$	TIPS-EBX	-	DCM	rt	12	<10
4	$InCl_3$	TIPS-EBX	-	DCM	rt	12	trace
5	$Ce(OTf)_3$	TIPS-EBX	-	DCM	rt	12	trace
6	$La(OTf)_3$	TIPS-EBX	-	DCM	rt	12	trace
7	$Dy(OTf)_3$	TIPS-EBX	-	DCM	rt	12	trace
8	$Cu(OTf)_2$	TIPS-EBX	-	DCM	rt	24	<30
9	$(CuOTf)_2$•Ph	TIPS-EBX	-	DCM	rt	24	<30
10	$FeCl_3$	TIPS-EBX	4 Å MS	DCM	rt	>36	-[b]
11	$FeCl_3$	TIPS-EBX	$MgSO_4$	ACN	rt	24	44
12	$FeCl_3$	TIPS-EBX	Na_2SO_4	ACN	rt	24	48
13	$FeCl_3$	TIPS-EBX	$MgSO_4$	ACN	50	5	63
14	$FeCl_3$	TIPS-EBX	-	DCE	50	2	76
15	$FeCl_3$ (5 mol %)	TIPS-EBX (10 mol %)	-	DCE	50	3	68
16	$Cu(OTf)_2$	TIPS-EBX	-	DCE	50	3	64
17	$FeCl_3$	TIPS-EBX	-	PhMe	50	12	13
18	$FeCl_3$	TMS-EBX	-	DCE	50	7	58
19	$FeCl_3$	TES-EBX	-	DCE	50	1	65
20	$FeCl_3$	Ph-EBX	-	DCE	50	5	55
21	$FeCl_3$	TBDPS-EBX	-	DCE	50	1.2	76
22	$FeCl_3$	TIPS-EBX	-	DCE/PhMe (v/v = 2:1)	50	5	88(83[c])

[a] NMR yield using 1,3,5-trimethoxybenzene as the internal standard. [b] Propargyl alcohol could not be fully converted and the yield was not determined. [c] Isolated yield.

Reaction conditions: unless otherwise noted, **2b** (0.1 mmol), R-EBX (0.02 mmol), Lewis acid (0.01 mmol), solvent (1mL or 1.5 mL).

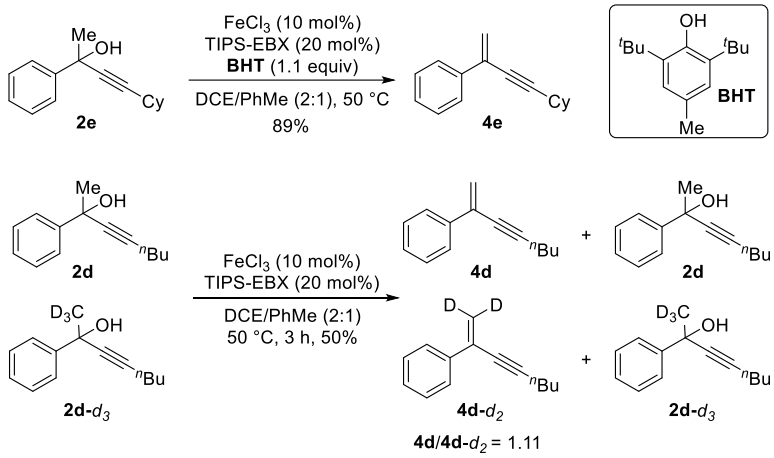
General Procedures for the Dehydration Reaction



A 25 mL oven-dried round bottom flask was charged with a stir bar, $FeCl_3$ (4.8 mg, 0.03 mmol, 0.1 equiv) and DCE/PhMe (3 mL/1.5 mL) unless otherwise specified. Then TIPS-EBX (25.6 mg, 0.06 mmol, 0.2 equiv) was added and the resulting mixture was stirred for about 5 min at room temperature. To the resulting yellow solution was added progargyl alcohol **2** (0.3 mmol, 1.0 equiv). Or progargyl alcohol **2**

and TIPS-EBX was premixed in solution, then added $FeCl_3$ quickly. The reaction solution was allowed to stir at 50 °C until progargyl alcohol **2** disappeared from the TLC, followed by evaporation of the solvent under reduced pressure. The residue was purified by column chromatography on silica gel (Hexanes) to afford the desired pure product **4** in 60-95% yield (most of the enynes are not stable at neat state).

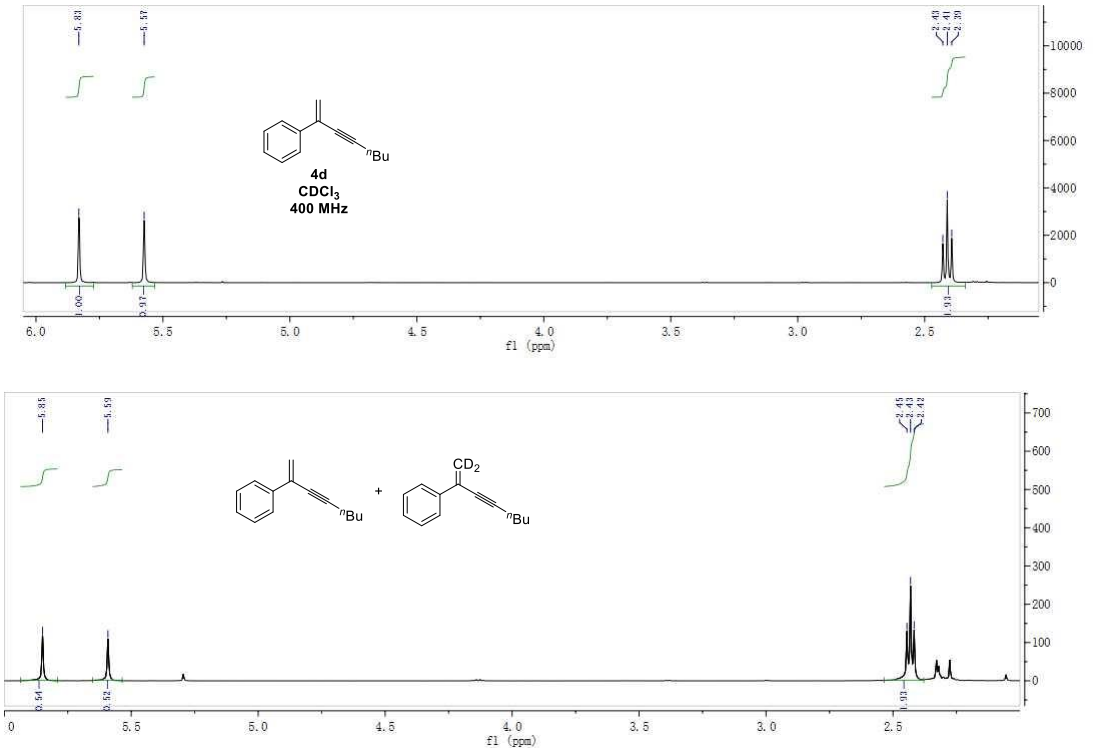
Radical Trapping and Kinetic Isotopic Effect



Radical Trapping Experiment: A 10 mL oven-dried round bottom flask was charged with a stir bar, $FeCl_3$ (1.6 mg, 0.01 mmol, 0.1 equiv) and DCE/PhMe (1 mL/0.5 mL), then TIPS-EBX (8.4 mg, 0.02 mmol, 0.2 equiv) and BHT (24.2 mg, 0.11 mmol, 1.1 equiv) were added and the resulting mixture was stirred for 5 min. Then **2e** (20.2 mg, 0.1 mmol, 1.0 equiv) was added and the resulting mixture was warmed to 50 °C and stirred for 1.5 h at this temperature. Upon completion of the reaction indicated by TLC, the reaction mixture was cooled to room temperature. Remove $FeCl_3$ through a short pad of silica gel (DCM eluted) and added 1,3,5-trimethoxybenzene (11.2 mg, 0.066 mmol) as the internal standard for NMR analysis. Then remove the solvent in vacuo and the residue was subjected to NMR analysis in $CDCl_3$.

Intermolecular Kinetic Isotopic Effect Experiment: A 10 mL oven-dried round bottom flask was charged with a stir bar, $FeCl_3$ (4.8 mg, 0.03 mmol, 0.1 equiv) and DCE/PhMe (2 mL/1 mL), then TIPS-EBX (25.6 mg, 0.06 mmol, 0.2 equiv) was added and the resulting mixture was stirred for 5 min. In another 25 mL oven-dried round bottom flask was placed **2d** (32.2 mg, 0.159 mmol) and **2d-d3** (30.8 mg, 0.150 mmol) in DCE/PhMe (1 mL/0.5 mL). The mixture in the first flask was transferred into the second one and the resulting mixture was allowed to warm to 50 °C and stirred for 3 h. After cooling down to room temperature, the solvent was removed and the resulting residue was subjected to silica gel (Hexanes to EtOAc/Hexanes = 20: 1) to afford enyne (28.4 mg, with some impurity, KIE = 1.11) and the recovered alcohol (34.3 mg).

In the starting material: H : D = 0.159 : 0.150 = 1.06; In the product：H : D = 0.54 : 0.46 = 1.174；So $1.06k_H/k_D = 1.174$; $k_H/k_D = 1.11$.



Copy for NMR analysis of intermolecular kinetic isotopic effect experiment

UV-Vis absorption experiment:

Materials and instrument: MeCN (99.9% for HPLC, BCR international trading Ltd. Co), $FeCl_3$ (Alfa Aesar). UV-Vis absorption spectrums were recorded on Shimadzu UV-2600 UV-Vis spectrophotometer. TIPS-EBX, **2a** and $FeCl_3$ were prepared as a MeCN solution (2.664×10^{-5} M), respectively. TIPS-EBX+ **2a**, TIPS-EBX+ $FeCl_3$ were prepared as a 1:1 mixture in MeCN (2.664×10^{-5} M), respectively.

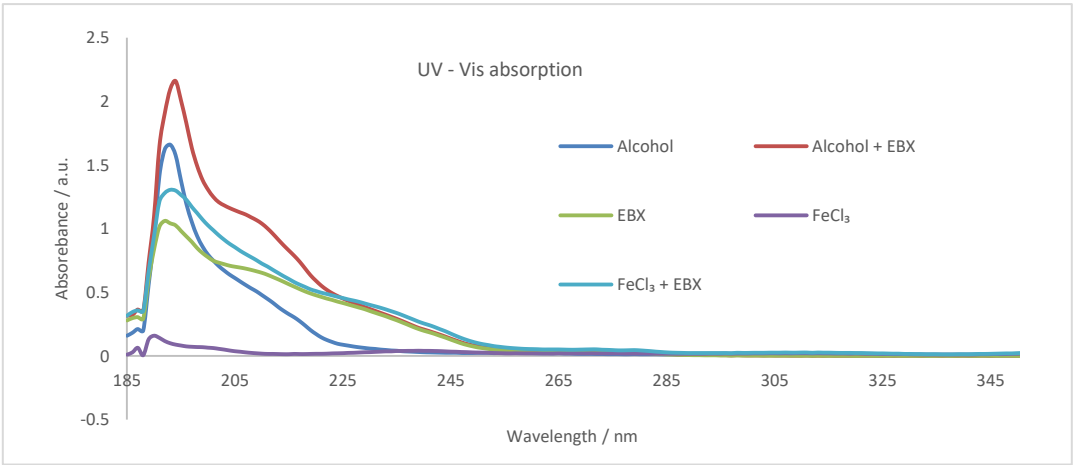
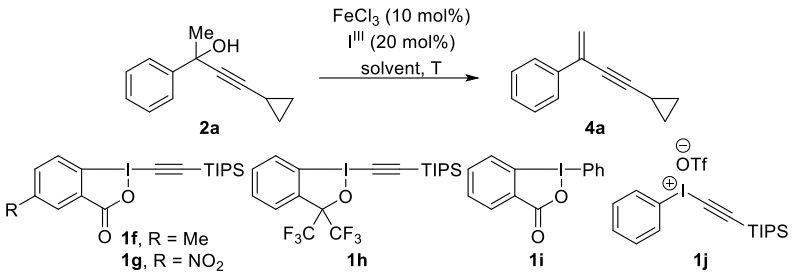


Figure S1 UV-Vis absorption spectrum

Control Experiments

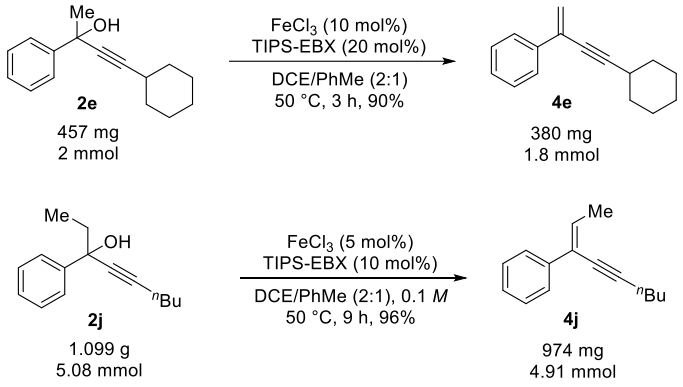


entry	I^{III} (20 mol %)	T(°C)	t (h)	yield (%)[a,b]
1[c]	**1a**	50	24	NR
2[d]	**-**	rt-50	24	**4a** (trace), **2a** (70)[e]
3	**1f**	50	5	88
4	**1g**	50	1	44
5	**1h**	50	12	trace
6	**1i**	50	12	**4a** (trace), **2a** (>90)[e]
7	**1j**	50	24	49

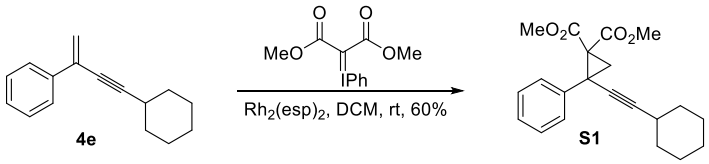
[a] NMR yield using 1,3,5-trimethoxybenzene as the internal standard. [b] DCE/PhMe (v/v = 2:1) was used as solvent. [c] Without $FeCl_3$. [d] Without I^{III}. [e] Isolated yield.

Reaction conditions: **2a** (0.1 mmol), R-EBX (0.02 mmol), $FeCl_3$ (0.01 mmol), DCE/PhMe (1 mL/0.5 mL), 50 °C.

Millimole Scale Reaction and Derivation of Enyne 4e and 4j



Follow the general procedures for the dehydration reaction described above.



Enyne **4e** (128 mg, 0.61 mmol, 1.0 equiv) was dissolved in freshly distilled DCM (5 mL), and the solution was bubbled for 10 min with Ar and cooled to 0 °C using an ice/water bath. Then To the solution was added bis[rhodium(α，α，α’，α’, -tetramethyl-1,3-benzenedipropionic acid)] (0.92 mg, 0.0012 mmol, 0.02 mol%). After that, the iodonium ylide (203 mg, 0.61 mmol, 1.0 equiv) was added in one portion at 0 °C. After 10 min, the ice/water bath was removed and the reaction mixture was stirred at room

temperature for another 1 h. Another portion of iodonium ylide (203 mg, 0.61 mmol, 1.0 equiv) was added and stirred for another hour. When TLC showed the completion of the reaction, DCM was removed in vacuo. The residue was purified by flash chromatography on silica gel (Hexanes/EtOAc = 50:1 to 20:1) to afford the desired product as yellowish oil (124 mg, 60%).

References:

(1) C.-F. Xu, M. Xu, L.-Q. Yang and C.-Y. Li, *J. Org. Chem.*, 2012, **77**, 3010-3016.

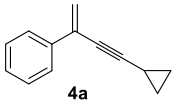
(2) H. Chen, J. Zhang and D. Z. Wang, *Org. Lett.*, 2015, **17**, 2098-2101.

(3) W. Yan, X. Ye, N. G. Akhmedov, J. L. Petersen and X. Shi, *Org. Lett.*, 2012, **14**, 2358-2361.

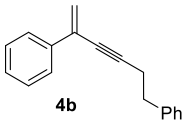
(4) S. Nicolai, C. Piemontesi and J. Waser, *Angew. Chem., Int. Ed.*, 2011, **50**, 4680-4683.

(5) M. S. Yusubov, R. Y. Yusubova, V. N. Nemykin and V. V. Zhdankin, *J. Org. Chem.*, 2013, **78**, 3767-3773.

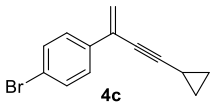
Characterization Data for Compounds



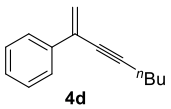
(4-cyclopropylbut-1-en-3-yn-2-yl)benzene (4a): 5 h, yellowish oil (42.4 mg, 84% yield); **^{1}H NMR** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 5.82 (d, *J* = 1.1 Hz, 1H), 5.56 (d, *J* = 0.9 Hz, 1H), 1.48 – 1.41 (m, 1H), 0.88 – 0.83 (m, 1H), 0.82 – 0.78 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.9, 130.9, 128.3, 128.1, 126.1, 119.4, 95.1, 75.0, 8.7, 0.2; **HRMS** calculated for $C_{13}H_{13}$ ($M + H^+$): 169.1012, found: 169.1014.



hex-5-en-3-yne-1,5-diyldibenzene (4b): 5 h, yellowish oil (57.7 mg, 83% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 2H), 7.36 – 7.17 (m, 8H), 5.83 (d, *J* = 0.9 Hz, 1H), 5.56 (s, 1H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 137.5, 130.8, 128.6, 128.4, 128.2, 128.1, 126.3, 126.0, 119.5, 91.0, 80.5, 35.0, 21.6; **HRMS** calculated for $C_{18}H_{17}$ ($M + H^+$): 233.1325, found: 233.1324.

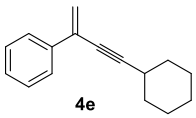


1-bromo-4-(4-cyclopropylbut-1-en-3-yn-2-yl)benzene (4c): 2 h, DCE as solvent**,** yellowish oil (67.0 mg, 90% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.41 (m, 4H), 5.81 (d, *J* = 0.6 Hz, 1H), 5.58 (s, 1H), 1.49 – 1.41 (m, 1H), 0.92 – 0.84 (m, 2H), 0.84 – 0.76 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.8, 131.3, 129.9, 127.7, 122.2, 119.8, 95.6, 74.5, 8.7, 0.2; **HRMS** calculated for $C_{13}H_{12}Br$ ($M + H^+$): 247.0122, found: 247.0116.



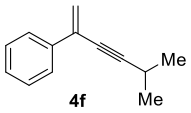
oct-1-en-3-yn-2-ylbenzene (4d): 5 h, colorless oil (47.5 mg, 85% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.40 – 7.25 (m, 3H), 5.83 (s, 1H), 5.57 (s, 1H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.59 (dq, *J* = 12.1, 6.9 Hz, 2H), 1.54 – 1.41 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 131.0, 128.2, 128.0, 126.0, 119.3, 92.0, 79.7, 30.8, 22.0, 19.1, 13.6; **HRMS**

calculated for $C_{14}H_{17}$ (M + H^+): 185.1325, found: 185.1325.



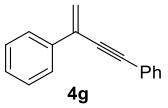
4e

(4-cyclohexylbut-1-en-3-yn-2-yl)benzene (4e): 2 h, colorless oil (59 mg, 93% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.60 (m, 2H), 7.39 – 7.25 (m, 3H), 5.84 (d, *J* = 1.2 Hz, 1H), 5.58 (d, *J* = 0.8 Hz, 1H), 2.71 – 2.53 (m, 1H), 1.93 – 1.85 (m, 2H), 1.81 – 1.69 (m, 2H), 1.64 – 1.48 (m, 3H), 1.45 – 1.27 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 130.9, 128.2, 128.0, 126.0, 119.1, 96.0, 79.6, 32.6, 29.7, 25.9, 24.9; **HRMS** calculated for $C_{16}H_{19}$ (M + H^+): 211.1487, found: 211.1480.



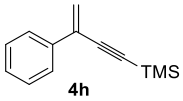
4f

(5-methylhex-1-en-3-yn-2-yl)benzene (4f): 4 h, colorless oil (48.4 mg, 90%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 – 7.62 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 5.86 (d, *J* = 1.1 Hz, 1H), 5.61 (d, *J* = 0.6 Hz, 1H), 2.81 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.9, 130.9, 128.3, 128.09, 126.1, 119.3, 97.4, 79.0, 23.0, 21.2; **HRMS** calculated for $C_{13}H_{15}$ (M + H^+): 171.1174, found: 171.1168.



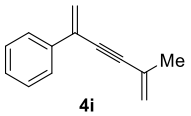
4g

but-3-en-1-yne-1,3-diyldibenzene (4g): 11 h, colorless oil (50.4 mg, 82%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.58 – 7.53 (m, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 4H), 6.00 (d, *J* = 0.9 Hz, 1H), 5.78 (d, *J* = 0.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.3, 131.7, 130.7, 128.4, 128.4, 126.1, 123.2, 120.6, 90.8, 88.6; **HRMS** calculated for $C_{16}H_{13}$ (M + H^+): 205.1017, found: 205.1011.



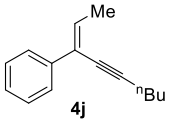
4h

trimethyl(3-phenylbut-3-en-1-yn-1-yl)silane (4h): 24 h, yellowish oil (52.7 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 2H), 7.44 – 7.29 (m, 3H), 5.95 (d, *J* = 0.9 Hz, 1H), 5.73 (d, *J* = 0.9 Hz, 1H), 0.27 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.9, 130.6, 128.4, 128.3, 126.0, 121.4, 104.1, 95.9, -0.1; **HRMS** calculated for $C_{13}H_{17}Si$ (M + H^+): 201.1100, found: 201.1092.



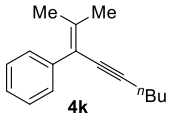
4i

(5-methylhexa-1,5-dien-3-yn-2-yl)benzene (4i): 12 h, yellowish oil (51.2 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.41 – 7.27 (m, 3H), 5.92 (d, *J* = 0.9 Hz, 1H), 5.66 (d, *J* = 0.8 Hz, 1H), 5.40 (dd, *J* = 1.8, 0.9 Hz, 1H), 5.34 – 5.28 (m, 1H), 2.00 – 1.98 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.2, 130.5, 128.3, 128.2, 126.7, 126.0, 122.2, 120.5, 92.0, 87.5, 23.4; **HRMS** calculated for $C_{13}H_{13}$ (M + H^+): 169.1017, found: 169.1011.



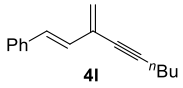
4j

(*Z*)-non-2-en-4-yn-3-ylbenzene (4j): 5 h, colorless oil (58.9 mg, 95%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dt, *J* = 3.2, 1.9 Hz, 2H), 7.40 – 7.28 (m, 2H), 7.28 – 7.19 (m, 1H), 6.40 (q, *J* = 6.9 Hz, 1H), 2.48 (t, *J* = 7.0 Hz, 2H), 2.05 (d, *J* = 6.9 Hz, 3H), 1.67 – 1.57 (m, 2H), 1.56 – 1.44 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.9, 131.5, 128.2, 127.1, 125.8, 124.7, 96.7, 77.6, 31.0, 22.0, 19.3, 16.7, 13.6; **HRMS** calculated for $C_{15}H_{19}$ ($M + H^+$): 199.1487, found: 199.1482.



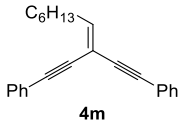
4k

(2-methylnon-2-en-4-yn-3-yl)benzene (4k): 5 h, colorless oil (42.9 mg, 66%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.27 – 7.21 (m, 1H), 2.38 (t, *J* = 7.0 Hz, 2H), 2.12 (s, 3H), 1.79 (s, 3H), 1.62 – 1.51 (m, 2H), 1.50 – 1.38 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 (MHz, $CDCl_3$) δ 140.8, 140.2, 129.1, 127.9, 126.5, 119.4, 93.1, 81.3, 31.1, 23.8, 22.0, 21.3, 19.3, 13.6; **HRMS** calculated for $C_{16}H_{21}$ ($M + H^+$): 213.1643, found: 213.1636.



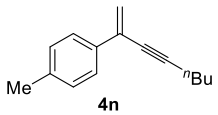
4l

(*E*)-(3-methylenenon-1-en-4-yn-1-yl)benzene (4l): 23 h, PhMe as solvent, room temperature, colorless oil (41.4 mg, 60%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.22 (m, 1H), 6.98 (d, *J* = 15.7 Hz, 1H), 6.76 (d, *J* = 15.7 Hz, 1H), 5.48 (d, *J* = 15.1 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.58 – 1.47 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 136.9, 132.5, 130.2, 128.9, 128.6, 127.8, 126.8, 122.6, 92.9, 77.4, 30.8, 22.0, 19.0, 13.6; **HRMS** calculated for $C_{16}H_{19}$ ($M + H^+$): 211.1487, found: 211.1471.



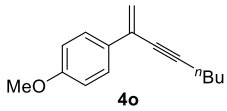
4m

(3-heptylidenepenta-1,4-diyne-1,5-diyl)dibenzene (4m): 24 h, colorless oil (51.8 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 4H), 7.37 – 7.27 (m, 6H), 6.47 (t, *J* = 7.8 Hz, 1H), 2.49 (q, *J* = 7.5 Hz, 2H), 1.55 – 1.45 (m, 2H), 1.42 – 1.34 (m, 2H), 1.34 – 1.23 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7, 131.6, 131.6, 128.4, 128.3, 128.2, 128.2, 123.0, 105.6, 92.7, 87.5, 86.5, 84.9, 31.6, 31.0, 28.9, 28.6, 22.6, 14.1; **HRMS** calculated for $C_{24}H_{25}$ ($M + H^+$): 313.1956, found: 313.1948.



4n

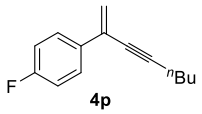
1-methyl-4-(oct-1-en-3-yn-2-yl)benzene (4n): 3 h, yellowish oil (53.3 mg, 82%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.80 (d, *J* = 0.5 Hz, 1H), 5.53 (s, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.64 – 1.56 (m, 21H), 1.49 (dq, *J* = 14.3, 7.2 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ137.9, 135.1, 130.8, 128.9, 126.0, 118.4, 91.8, 79.9, 49.4, 30.9, 22.0, 21.1, 19.1, 13.6; **HRMS** calculated for $C_{15}H_{19}$ ($M + H^+$): 199.1487, found: 199.1480.



4o

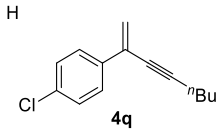
1-methoxy-4-(oct-1-en-3-yn-2-yl)benzene (4o): 4 h, PhMe was used as solvent, yellowish oil (65.0

mg, 88%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 2H), 6.95 – 6.79 (m, 2H), 5.75 (d, *J* = 0.7 Hz, 1H), 5.49 (s, 1H), 3.82 (d, *J* = 6.0 Hz, 3H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.56 – 1.43 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.7, 130.5, 130.4, 127.3, 117.4, 113.6, 91.7, 80.0, 55.3, 30.9, 22.1, 19.1, 13.6; **HRMS** calculated for $C_{15}H_{19}O$ ($M + H^+$): 215.1436, found: 215.1431.



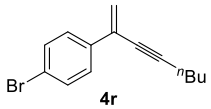
4p

1-fluoro-4-(oct-1-en-3-yn-2-yl)benzene (4p): 7 h, colorless oil (4p): 7 h, colorless oil (54.6 mg, 90%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H), 7.09 – 6.99 (m, 2H), 5.78 (s, 1H), 5.56 (s, 1H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.66 – 1.55 (m, 2H), 1.55 –1.43 (m, 8.3, 5.9 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.3 Hz), 133.9 (d, *J* = 3.2 Hz), 129.9, 127.8 (d, *J* = 8.1 Hz), 119.0, 115.1 (d, *J* = 21.6 Hz), 92.2, 79.6, 30.8, 22.0, 19.1, 13.6; **HRMS** calculated for $C_{14}H_{16}F$ ($M + H^+$): 203.1236, found: 203.1227.



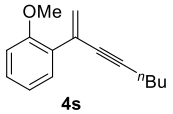
4q

1-chloro-4-(oct-1-en-3-yn-2-yl)benzene (4q): 15 h, colorless oil (55.6 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 2H), 7.34 – 7.27 (m, 2H), 5.80 (d, *J* = 0.8 Hz, 1H), 5.57 (s, 1H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.52 – 1.40 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.3, 133.9, 129.9, 128.3, 127.3, 119.6, 92.4, 79.3, 30.7, 22.0, 19.0, 13.6; **HRMS** calculated for $C_{14}H_{16}Cl$ ($M + H^+$): 219.0941, not found; calculated for $C_{14}H_{16}Cl$ ($M + H^+$): 219.0941, found: 219.0935.



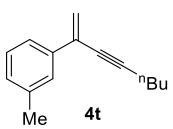
4r

1-bromo-4-(oct-1-en-3-yn-2-yl)benzene (4r): 5 h, colorless oil (70 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 2H), 5.81 (d, *J* = 0.8 Hz, 1H), 5.58 (s, 1H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.52 – 1.40 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.7, 131.3, 123.0, 127.7, 122.1, 119.7, 92.5, 79.2, 30.7, 22.0, 19.0, 13.6; **HRMS** calculated for $C_{14}H_{16}Br$ ($M + H^+$): 263.0435, found: 263.0425.



4s

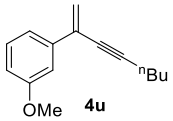
1-methoxy-2-(oct-1-en-3-yn-2-yl)benzene (4s): 0.5 h, colorless oil (58.0 mg, 90%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.33 – 7.15 (m, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.87 (d, *J* = 2.1 Hz, 1H), 5.75 (d, *J* = 2.0 Hz, 1H), 3.86 (s, 3H), 2.36 (t, *J* = 7.0 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.51 – 1.40 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.0, 130.3, 128.9, 128.3, 128.0, 124.3, 120.5, 111.4, 90.0, 81.0, 55.6, 30.8, 22.0, 19.1, 13.6; **HRMS** calculated for $C_{15}H_{19}O$ ($M + H^+$): 215.1436, found: 215.1429.



4t

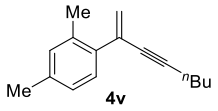
1-methyl-3-(oct-1-en-3-yn-2-yl)benzene (4t): 1 h, colorless to yellowish oil (57.4 mg, 90%); **^{1}H NMR**

(500 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.9, 0.5 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 5.81 (d, *J* = 1.1 Hz, 1H), 5.55 (s, 1H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 1.65 – 1.54 (m, 2H), 1.54 – 1.44 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.8, 137.8, 131.1, 128.9, 128.2, 126.8, 123.2, 119.2, 91.9, 79.9, 30.86, 22.07, 21.5, 19.1, 13.6; **HRMS** calculated for $C_{15}H_{19}$ (M + H^+): 199.1487, found: 199.1481.



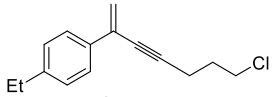
4u

1-methoxy-3-(oct-1-en-3-yn-2-yl)benzene (4u): 5 h, colorless oil (51.1 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.22 – 7.20 (m, 1H), 6.87 – 6.81 (m, 1H), 5.83 (d, *J* = 1.0 Hz, 1H), 5.58 (s, 1H), 3.82 (s, 3H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.55 – 1.41 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 139.3, 130.8, 129.2, 119.5, 118.4, 113.6, 111.9, 91.9, 79.7, 55.2, 30.8, 22.0, 19.0, 13.6; **HRMS** calculated for $C_{15}H_{19}O$ (M + H^+): 215.1436, found: 215.1431.



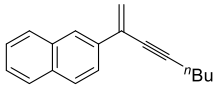
4v

2,4-dimethyl-1-(oct-1-en-3-yn-2-yl)benzene (4v): 0.5 h, colorless oil (57.8 mg, 90%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 10.1, 2.3 Hz, 2H), 5.66 (d, *J* = 2.0 Hz, 1H), 5.37 (d, *J* = 2.0 Hz, 1H), 2.41 (s, 3H), 2.37 – 2.29 (m, 5H), 1.60 – 1.50 (m, 21H), 1.49 – 1.37 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.3, 137.2, 135.2, 132.2, 131.1, 128.6, 126.4, 123.4, 91.6, 80.8, 30.8, 22.0, 21.0, 20.1, 19.1, 13.6; **HRMS** calculated for $C_{16}H_{21}$ (M + H^+): 213.1643, found: 213.1636.



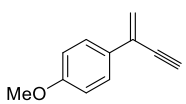
4w

1-(7-chlorohept-1-en-3-yn-2-yl)-4-ethylbenzene (4w): 3 h, colorless oil (61.5 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.83 (d, *J* = 1.0 Hz, 1H), 5.56 (s, 1H), 3.78 – 3.65 (m, 2H), 2.77 – 2.57 (m, 4H), 2.06 (dq, *J* = 13.2, 6.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.5, 135.0, 130.5, 127.8, 126.0, 119.1, 89.4, 80.9, 43.7, 31.4, 28.5, 16.8, 15.5; **HRMS** calculated for $C_{15}H_{18}Cl$ (M + H^+): 233.1097, found: 233.1097.



4x

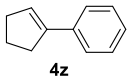
2-(oct-1-en-3-yn-2-yl)naphthalene (4x): 4 h, PhMe/DCE (1:2) as solvent, yellowish oil (53.6 mg, 76%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.91 – 7.74 (m, 4H), 7.56 – 7.43 (m, 2H), 6.00 (s, 1H), 5.70 (s, 1H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.72 –1.61 (m, 2H), 1.62 – 1.44 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.0, 133.2, 133.1, 130.8, 128.4, 127.8, 127.5, 126.2, 126.1, 125.9, 123.4, 119.7, 92.2, 79.7, 30.8, 22.1, 19.1, 13.7; **HRMS** calculated for $C_{18}H_{19}$ (M + H^+): 235.1487, found: 235.1482.



4y

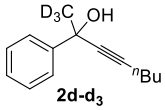
1-(but-1-en-3-yn-2-yl)-4-methoxybenzene (4y): 6 h, white solid (36.3 mg, 77%); **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.67 – 7.54 (m, 2H), 6.97 – 6.81 (m, 2H), 5.89 (s, 1H), 5.67 (s, 1H), 3.83 (s, 3H), 3.11 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 129.2, 129.0, 127.2, 120.2, 113.7, 83.0, 78.3, 55.3; **HRMS** calculated for $C_{11}H_{11}O$ ($M + H^+$): 159.0810, found: 159.0806.



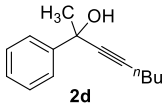
4z

cyclopent-1-en-1-ylbenzene (4z): 10 h, white solid (38.1 mg, 88%); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.40 (m, 2H), 7.38 – 7.28 (m, 2H), 7.24 (dd, *J* = 14.1, 6.7 Hz, 1H), 6.30 – 6.14 (m, 1H), 2.77 – 2.70 (m, 2H), 2.59 – 2.51 (m, 2H), 2.14 – 1.96 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 136.9, 128.3, 126.8, 126.1, 125.6, 33.4, 33.2, 23.4; **HRMS** calculated for $C_{11}H_{13}$ ($M + H^+$): 145.1017, found: 145.1013.



2d-d$_3$

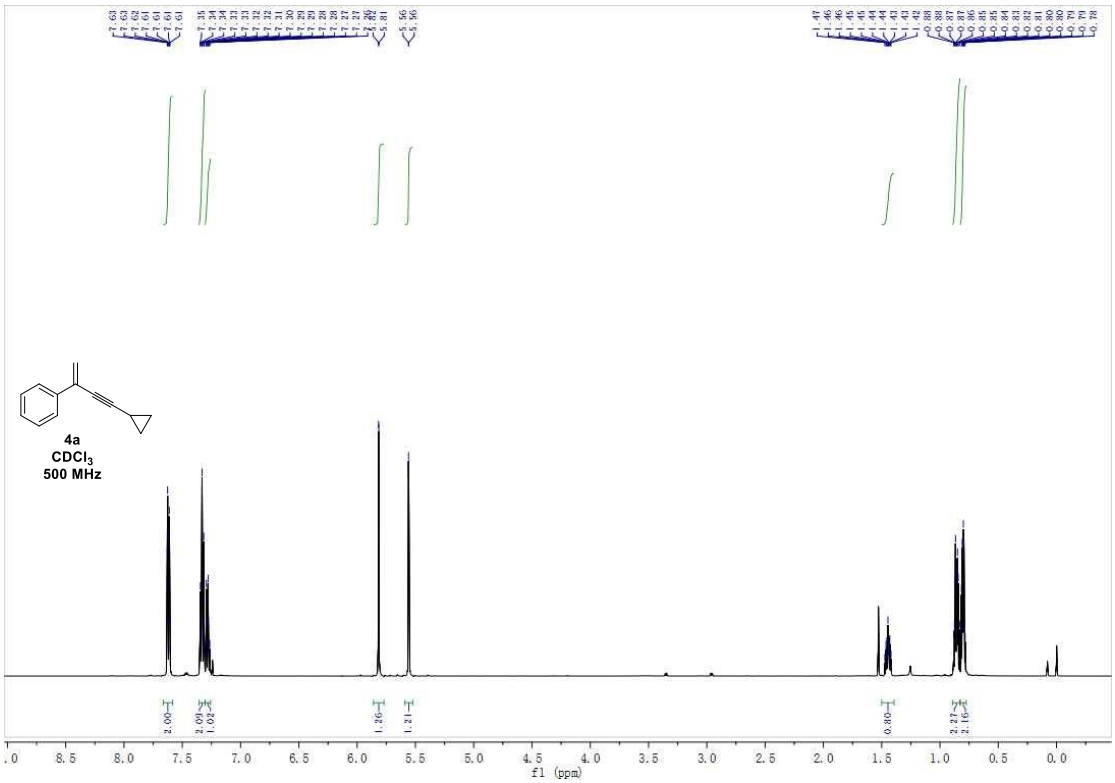
2-phenyloct-3-yn-1,1,1-d3-2-ol (2d-d$_3$): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.59 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 13.9, 6.5 Hz, 1H), 2.38 (s, 1H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.50 – 1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.2, 128.2, 127.5, 125.0, 85.7, 83.8, 69.9, 30.8, 22.0, 18.4, 13.6; **HRMS** calculated for $C_{14}H_{15}D_3ONa$ ($M + Na^+$): 228.1444, found: 228.1445.

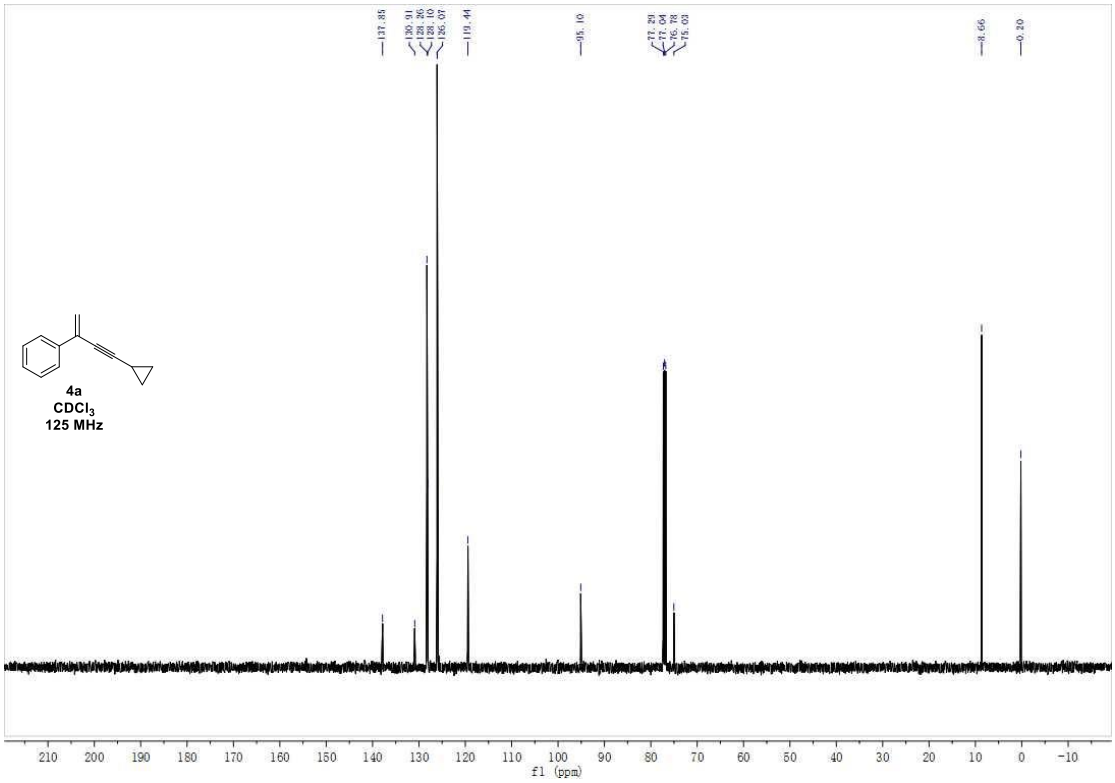


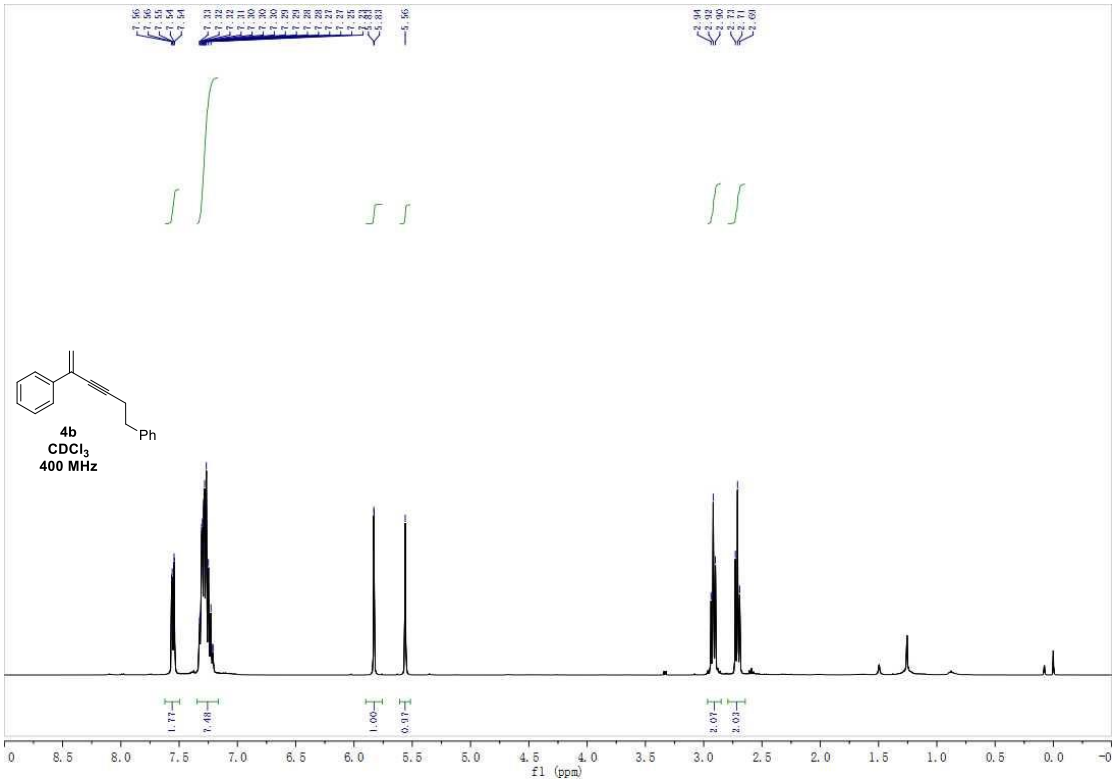
2d

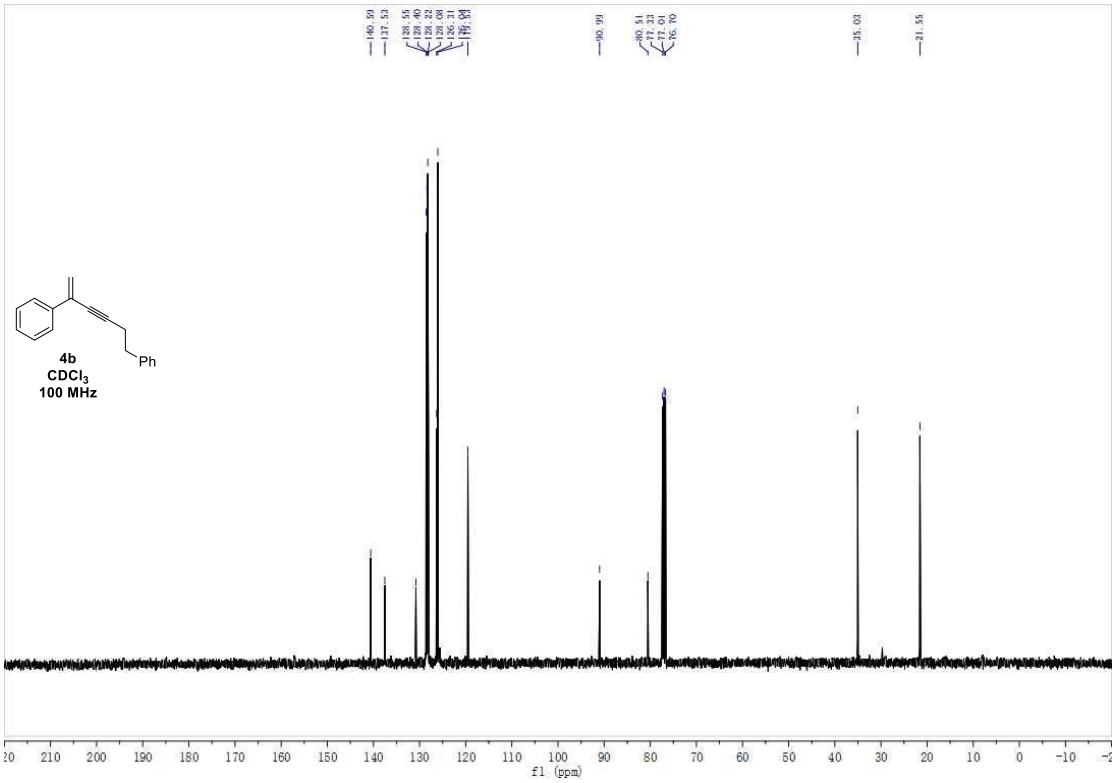
2-phenyloct-3-yn-2-ol (2d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.26 (m, 1H), 2.45 (s, 1H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.76 (s, 3H), 1.57 (dq, *J* = 11.9, 6.9 Hz, 2H), 1.46 (dq, *J* = 14.0, 7.0 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 128.2, 127.5, 125.0, 85.6, 83.8, 70.0, 33.6, 30.7, 22.0, 18.4, 13.6.

Copies of ^{1}H NMR and ^{13}C NMR Spectra






4b
CDCl3
400 MHz
Ph
f1 (ppm)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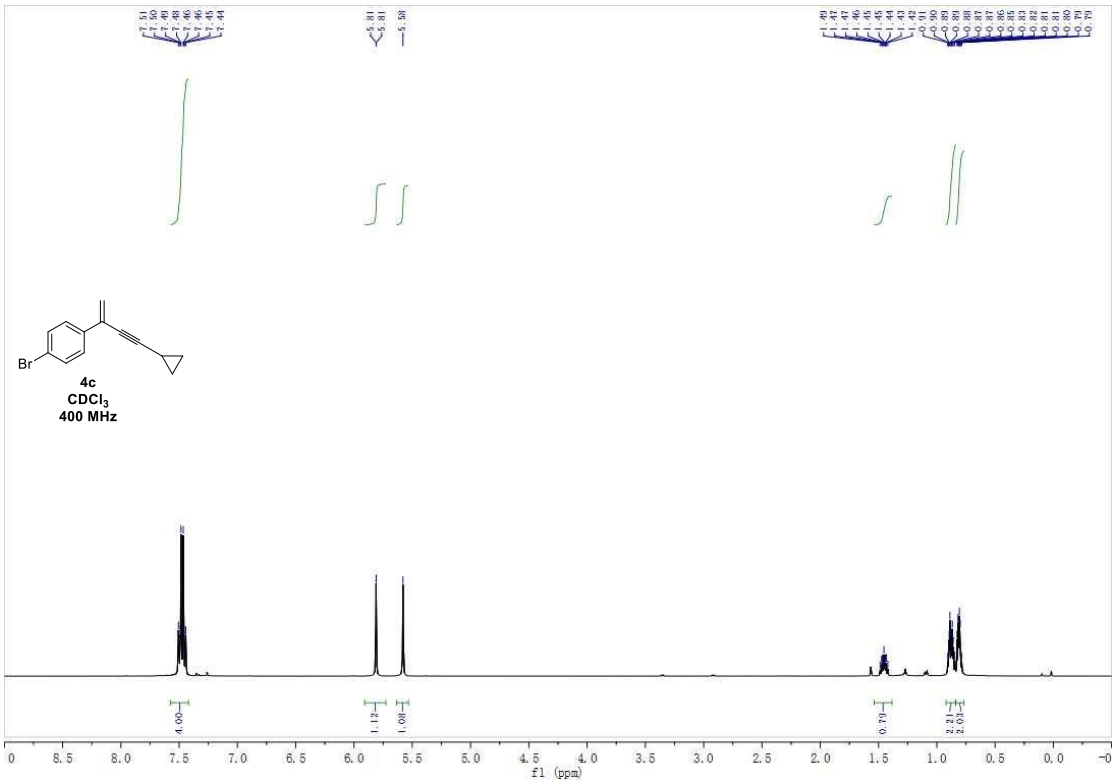
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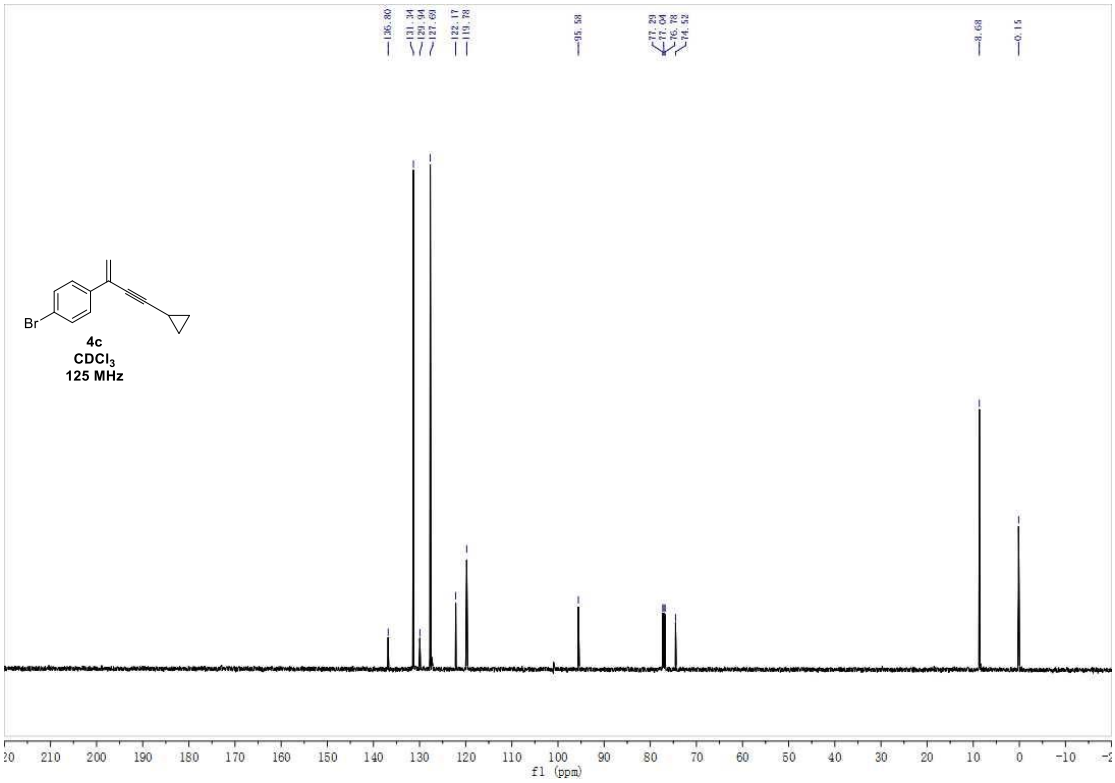
CDCl3
400 MHz
f1 (ppm)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4c
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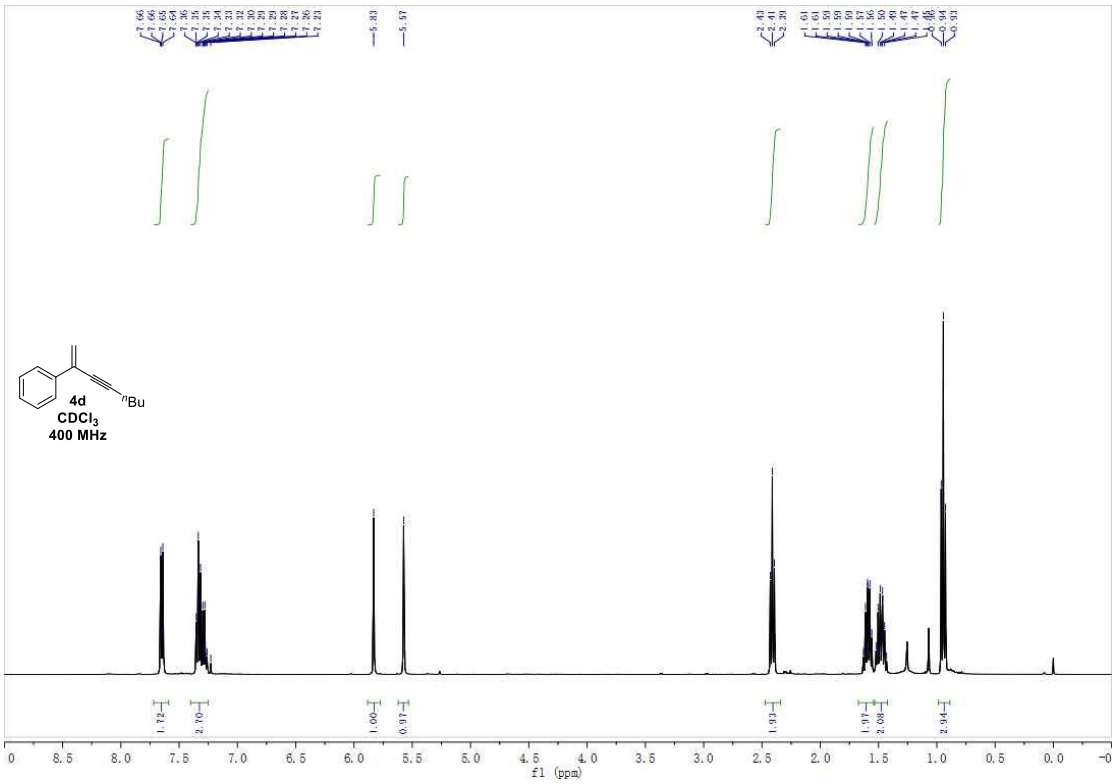
125 MHz
f1 (ppm)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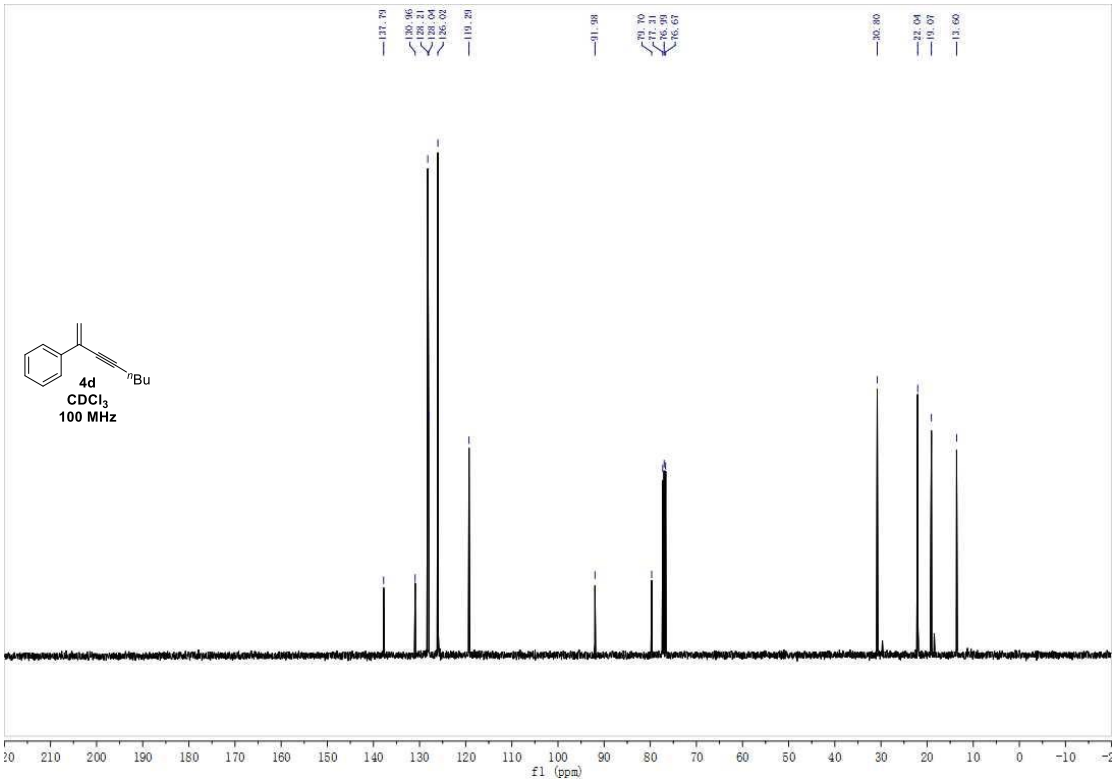
CDCl3
400 MHz
nBu
f1 (ppm)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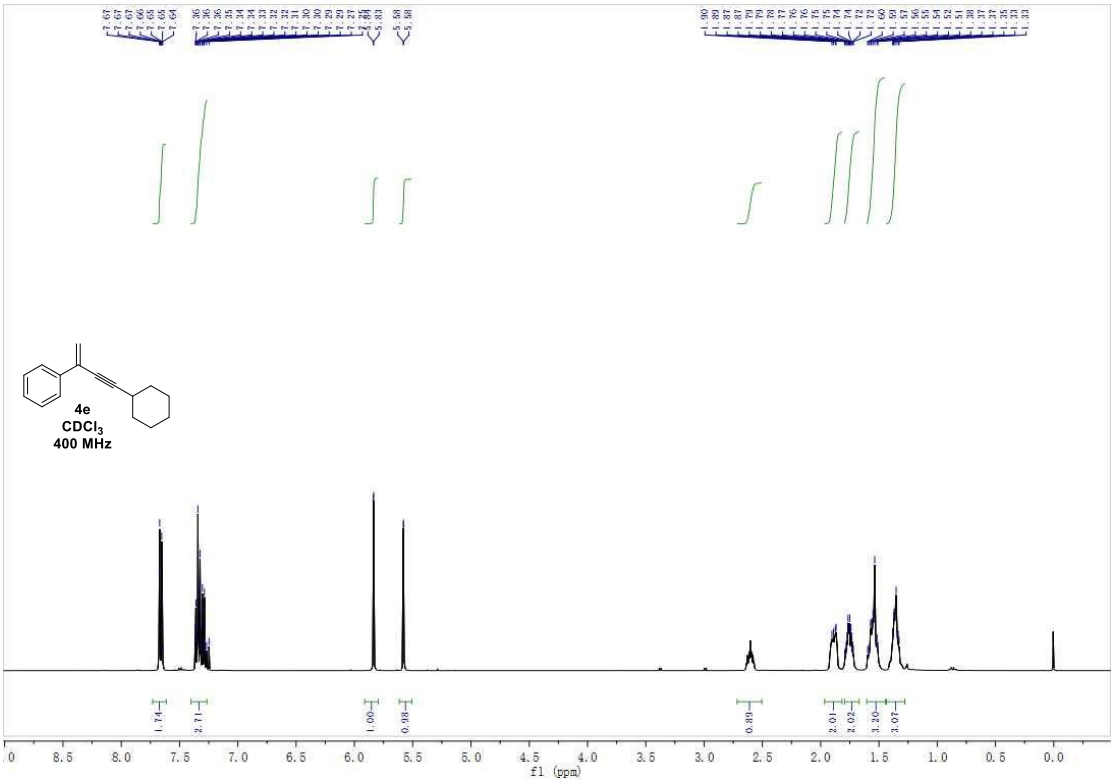
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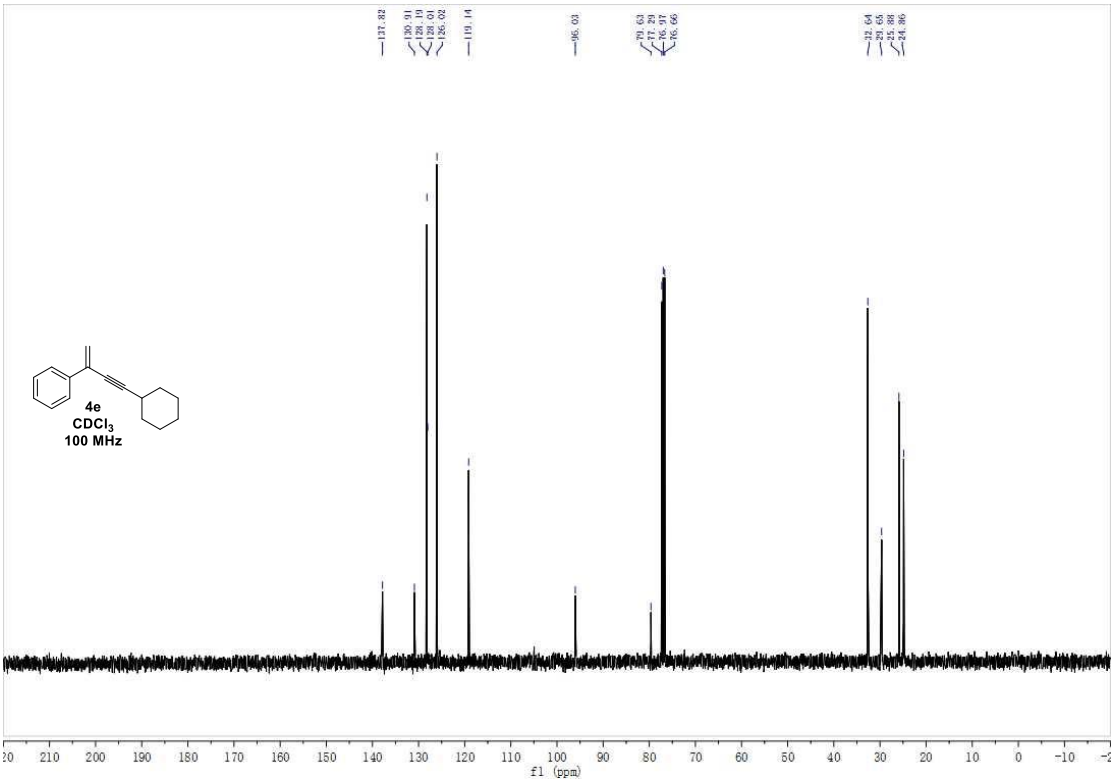
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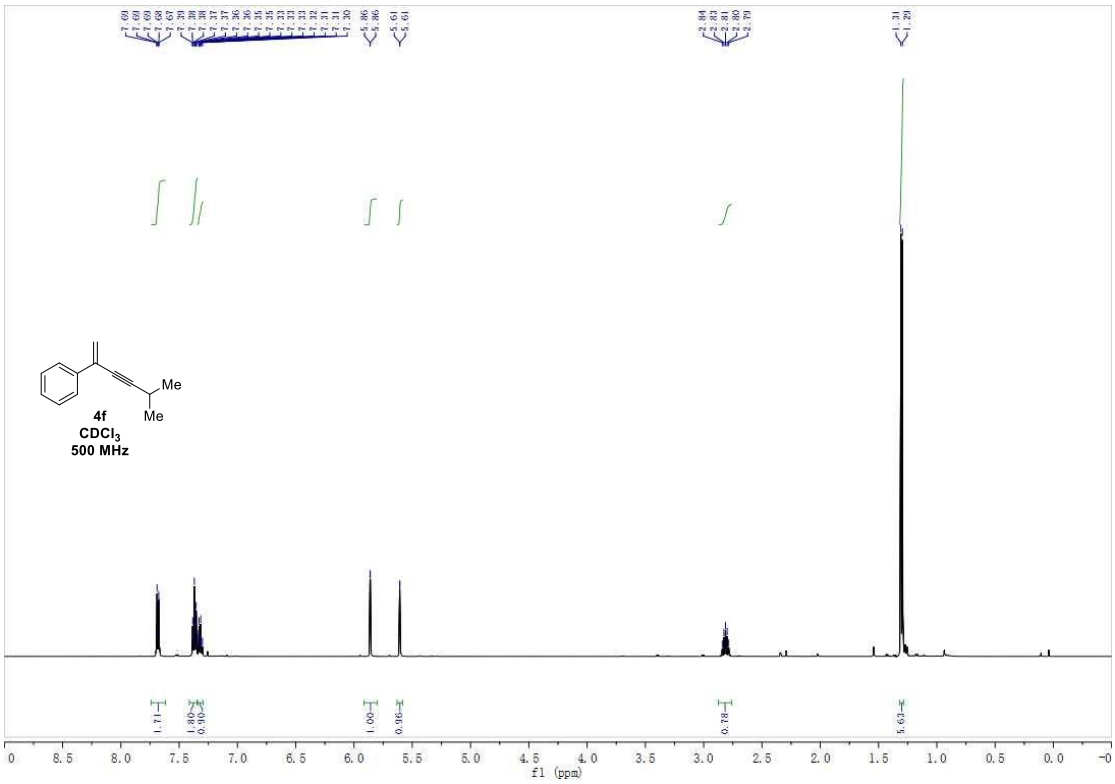
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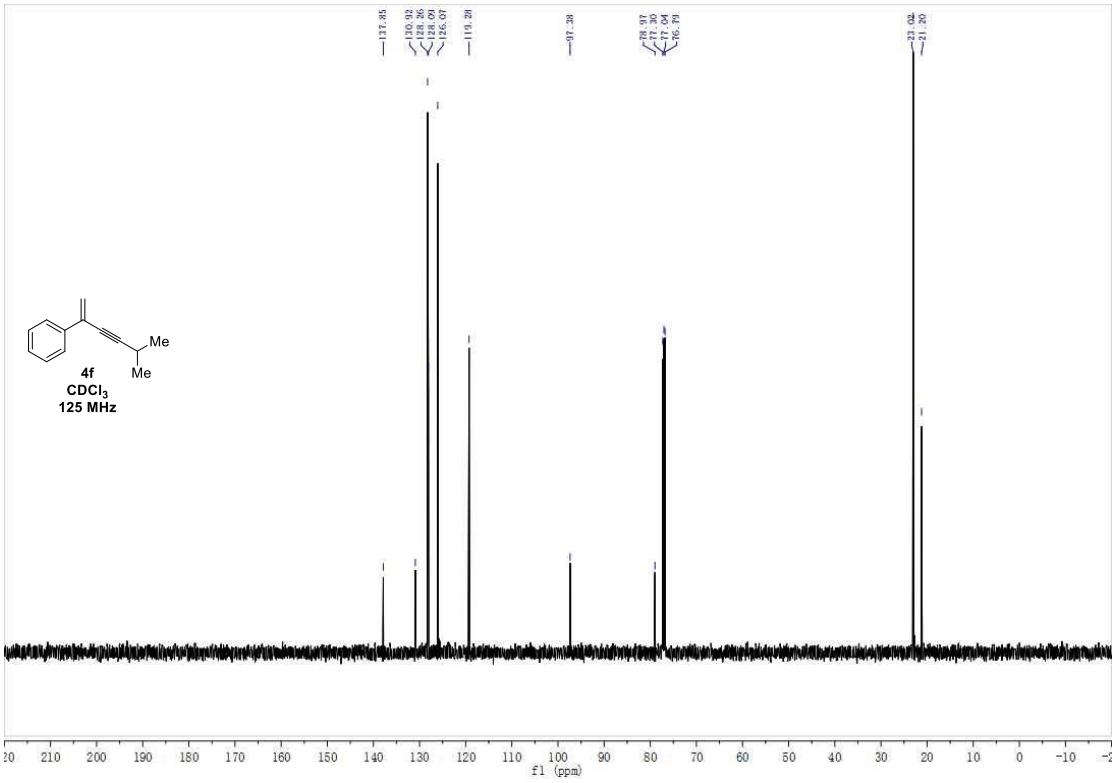
Me
4f
CDCl3
500 MHz
f1 (ppm)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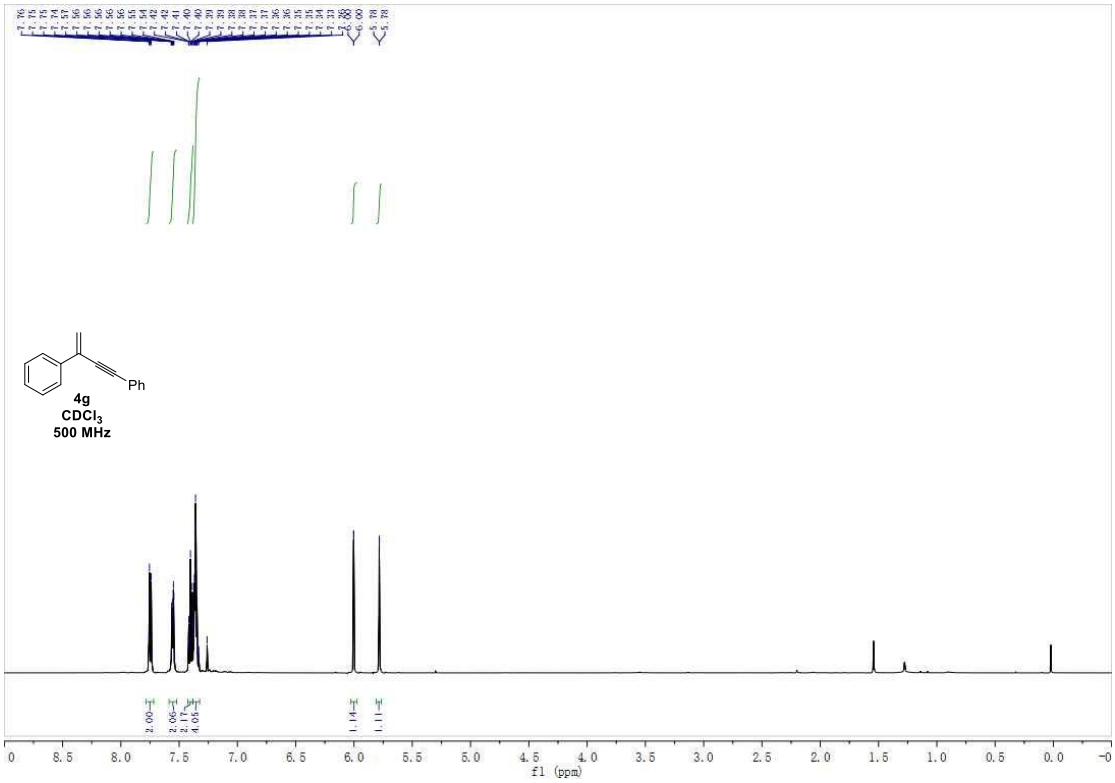
Me
4f
CDCl3
125 MHz
f1 (ppm)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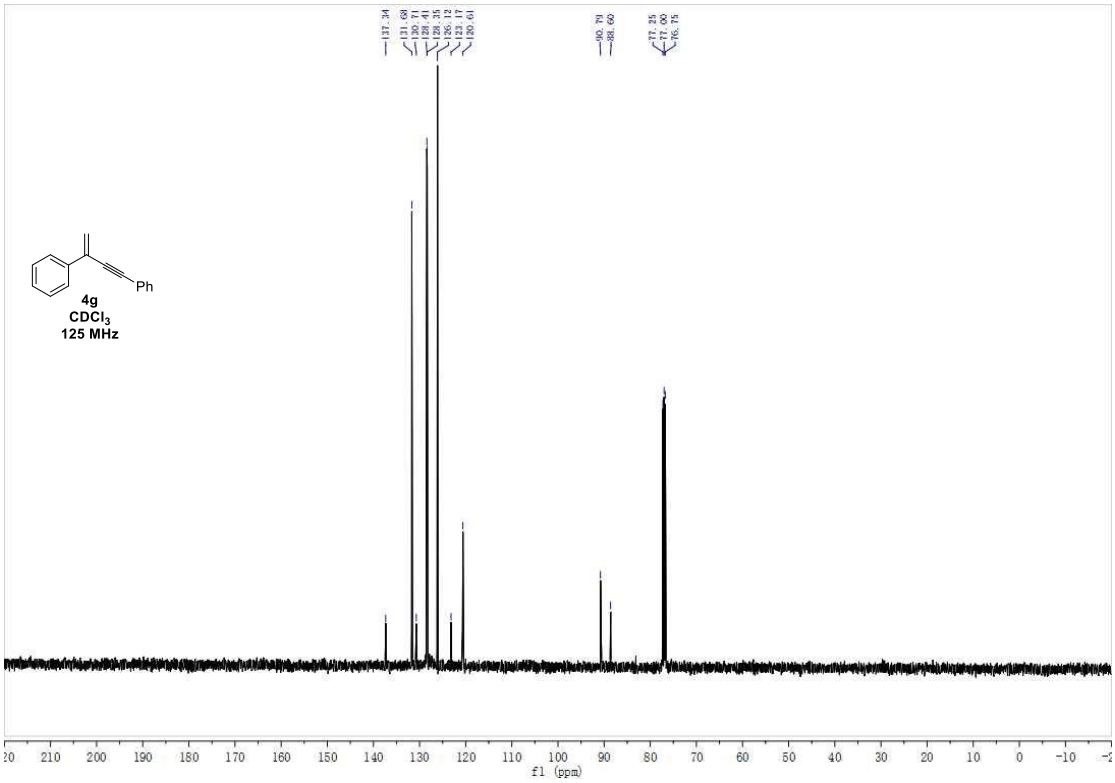
4g
CDCl3
500 MHz
f1 (ppm)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125 MHz
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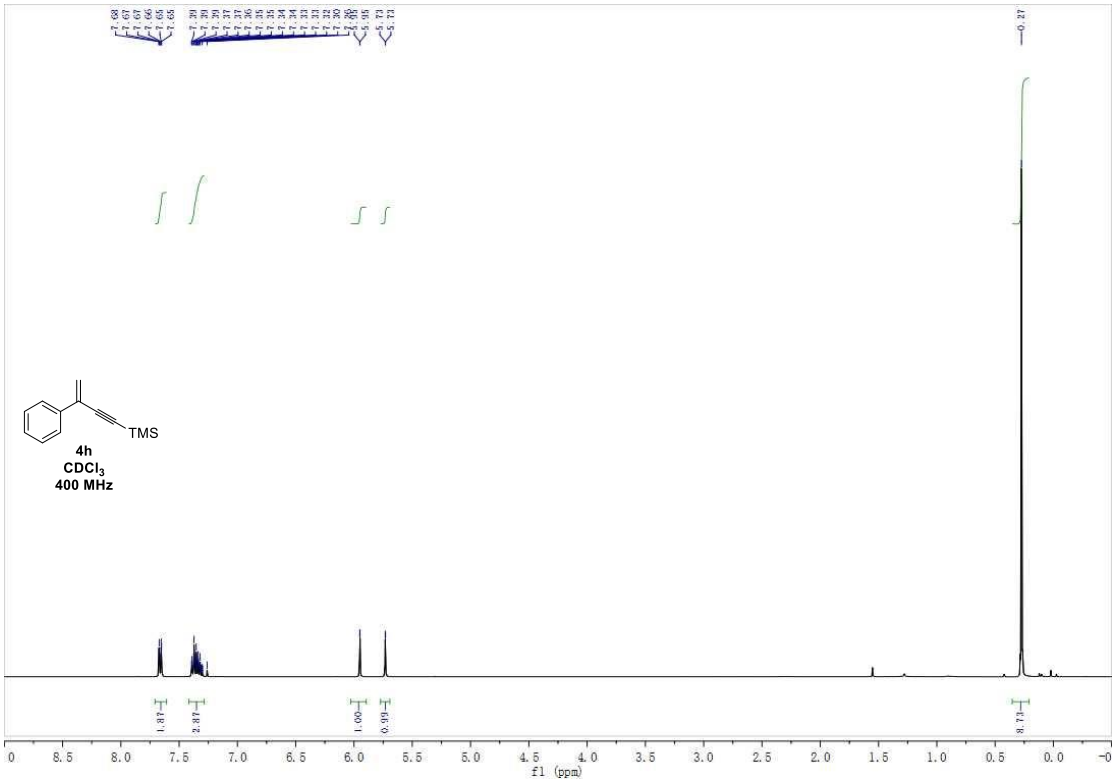
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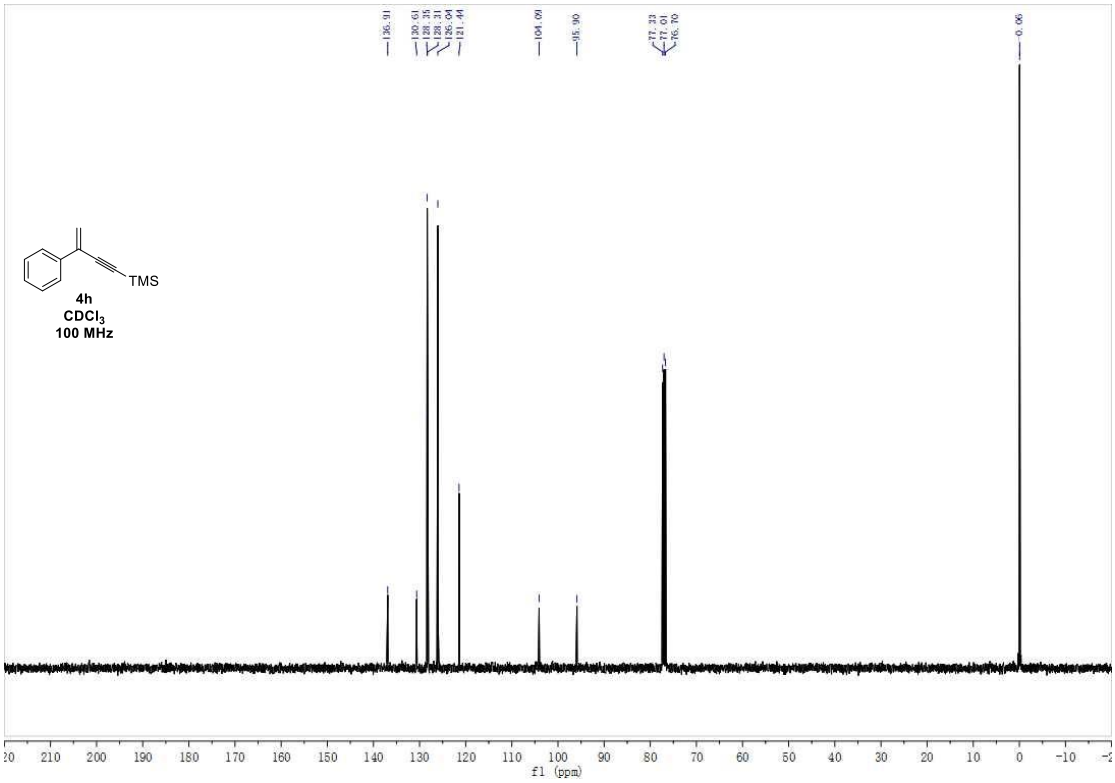
4h
CDCl3
400 MHz
f1 (ppm)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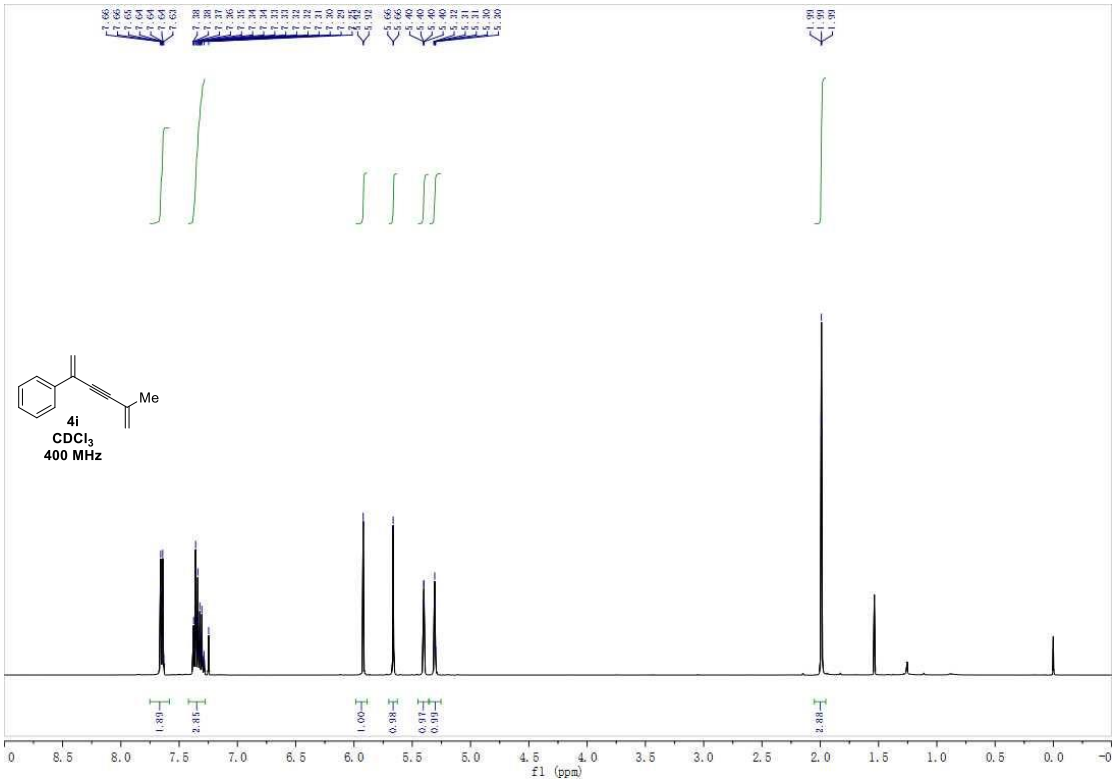
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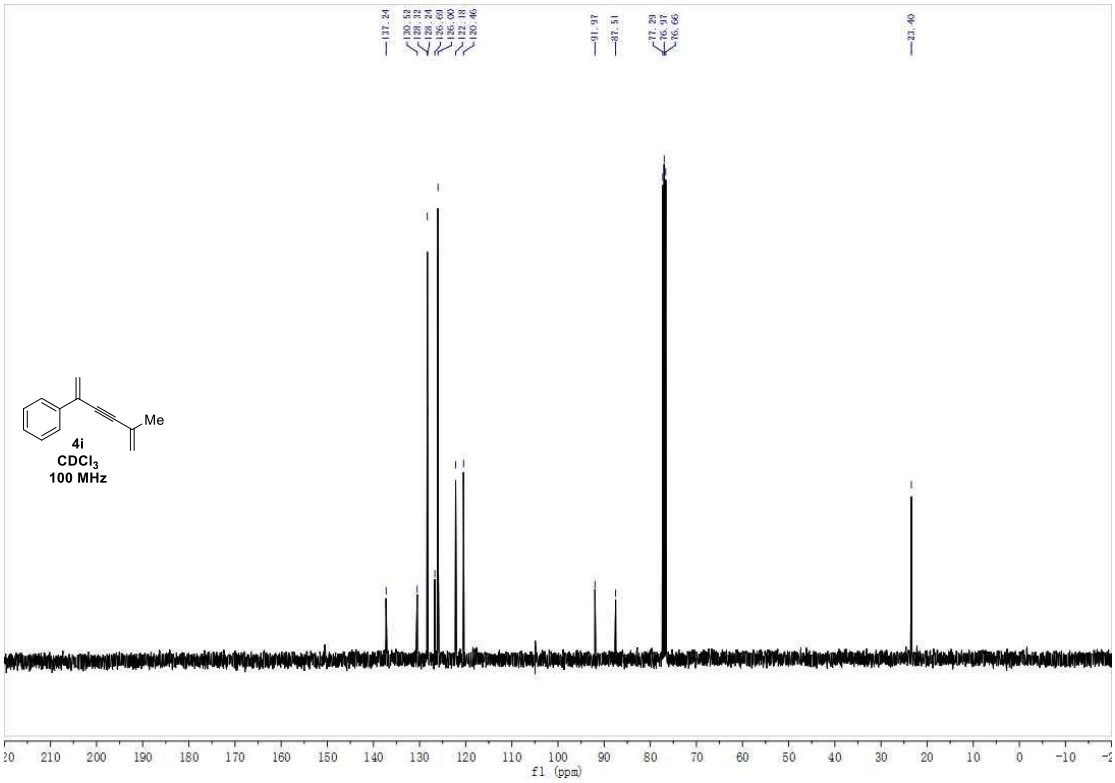
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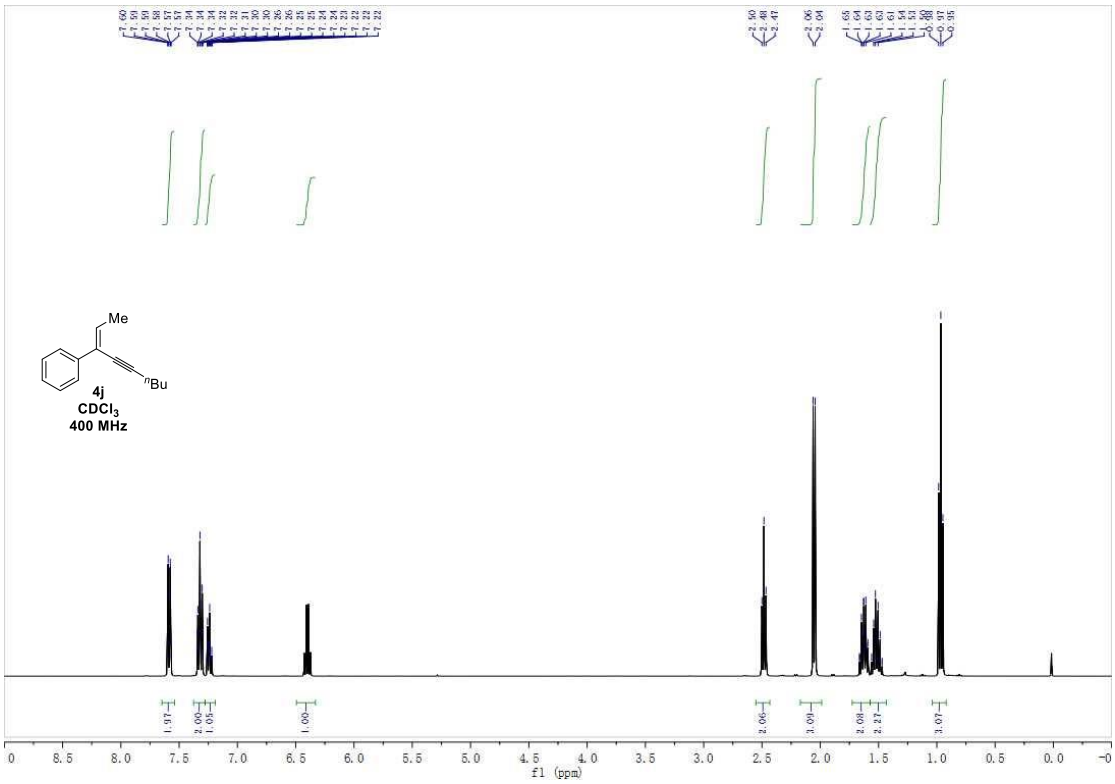
f1 (ppm)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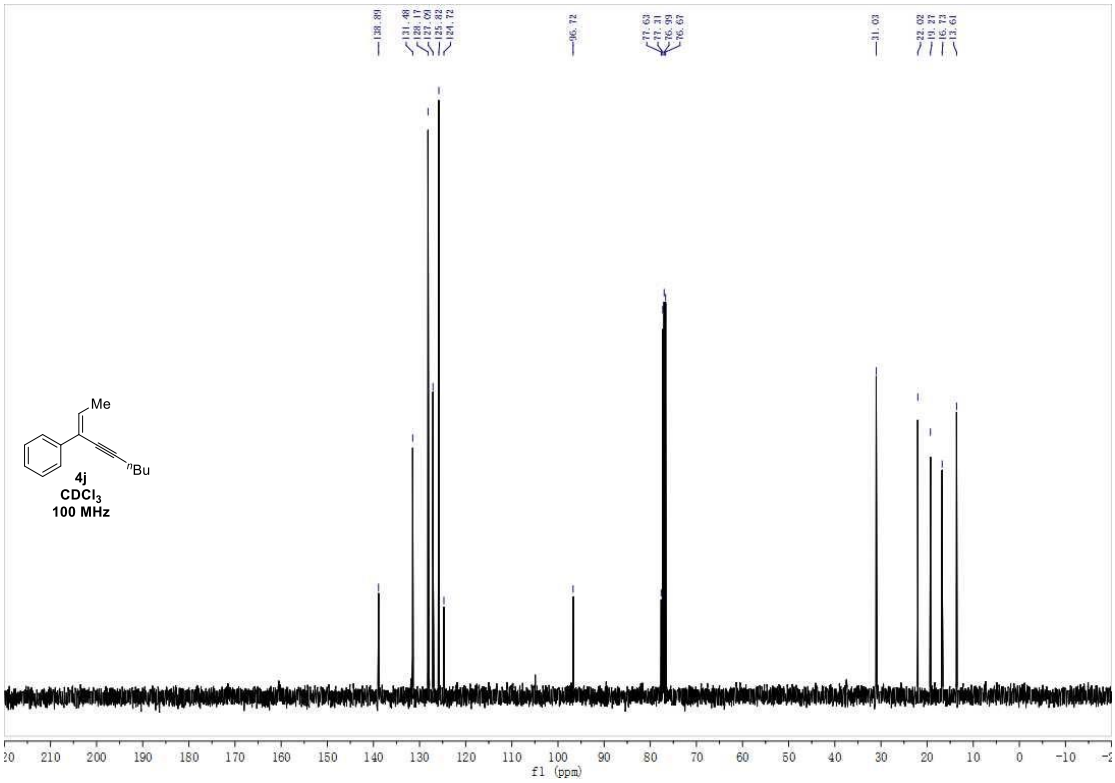
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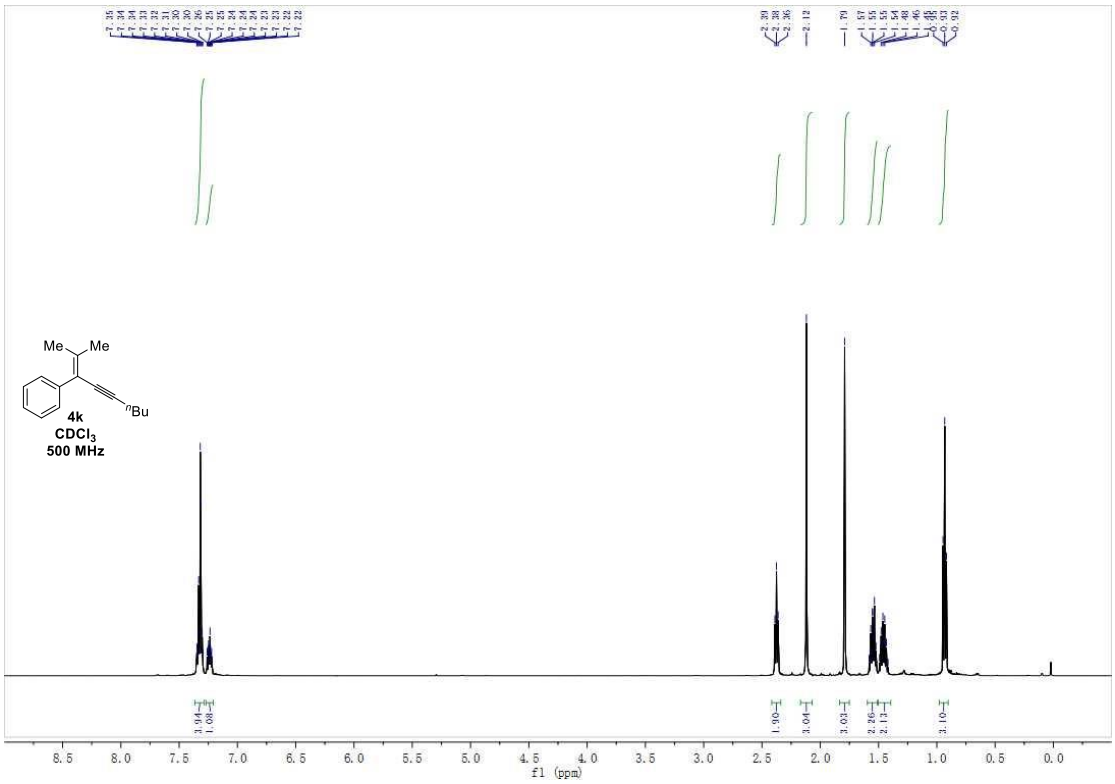
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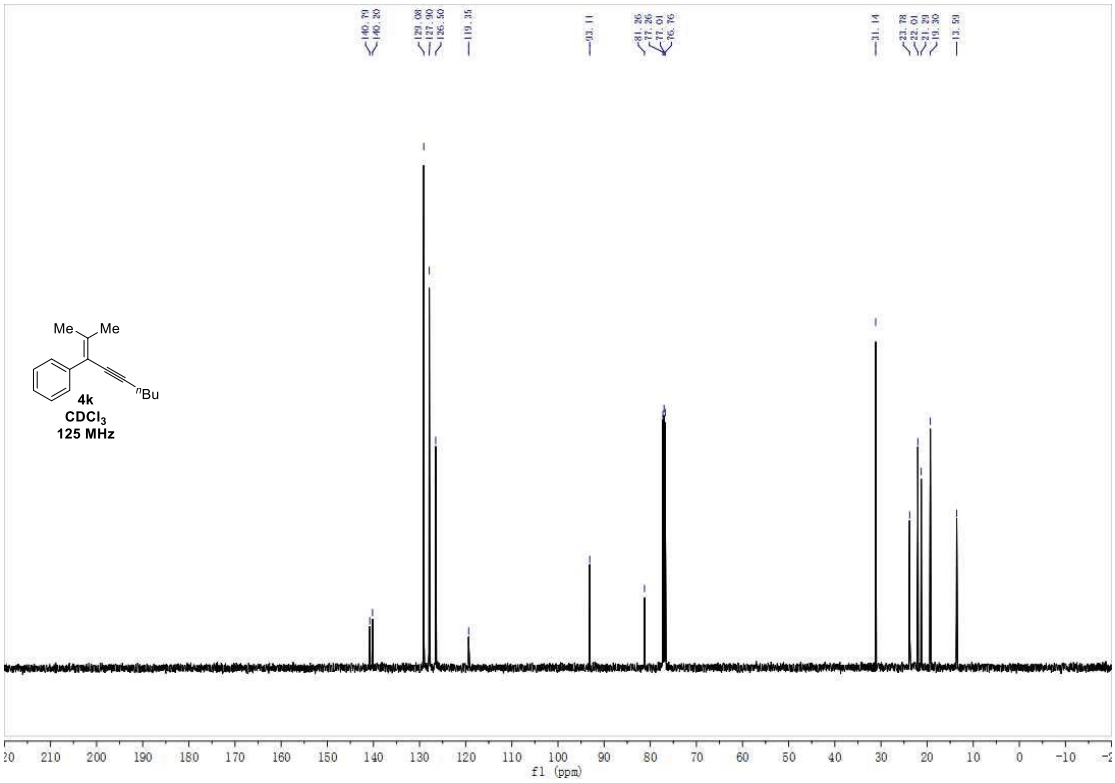
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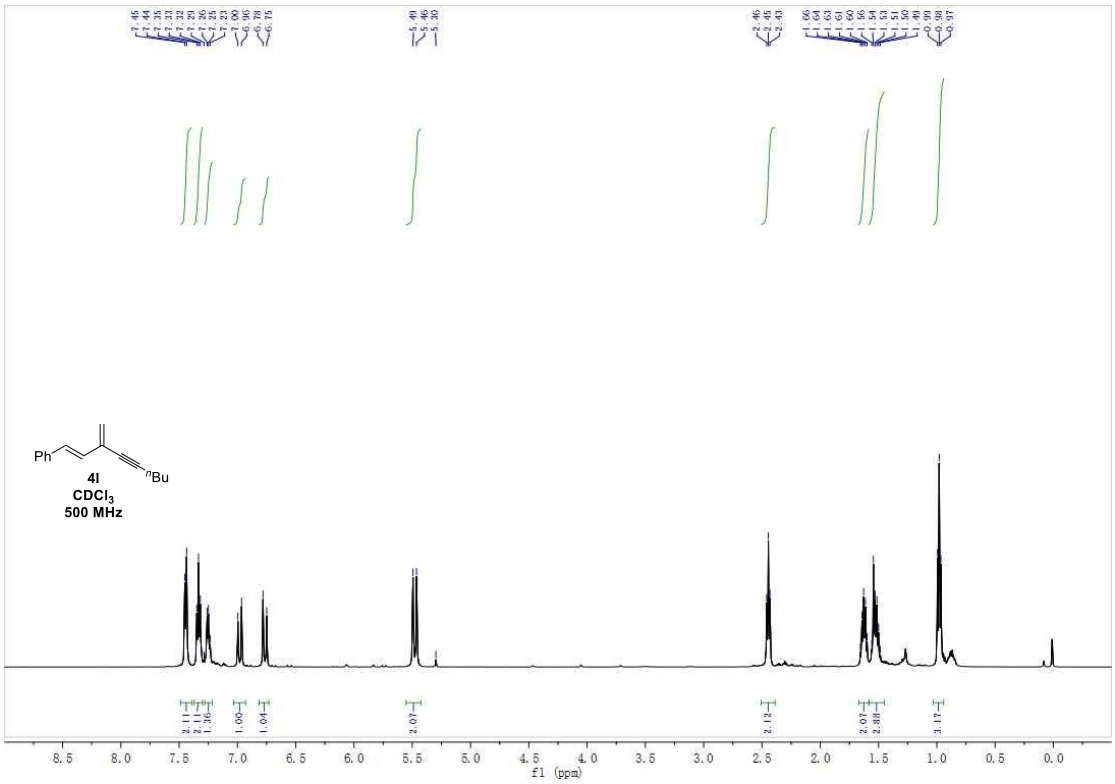
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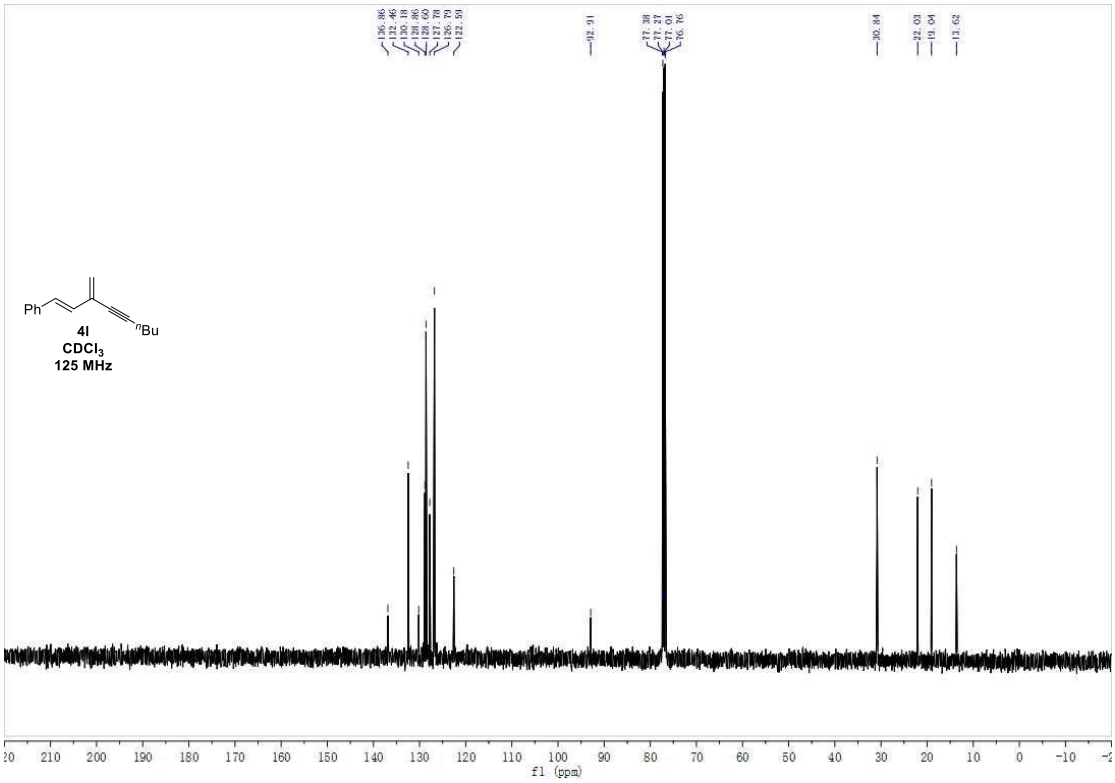
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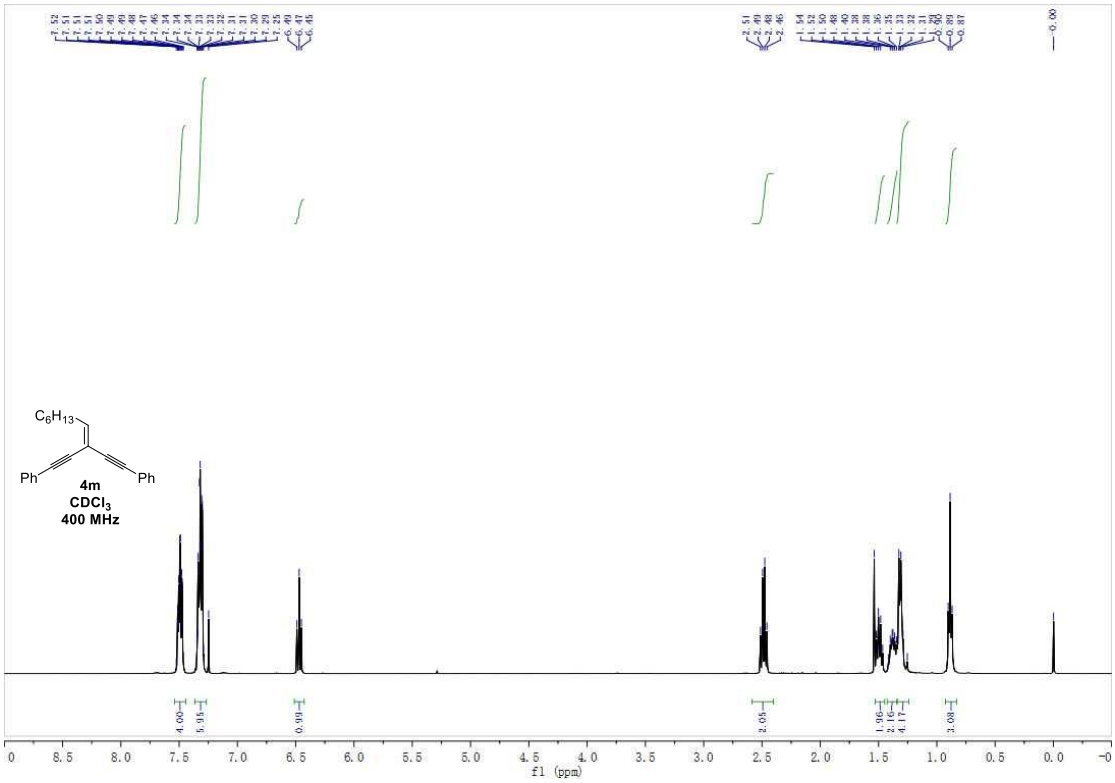
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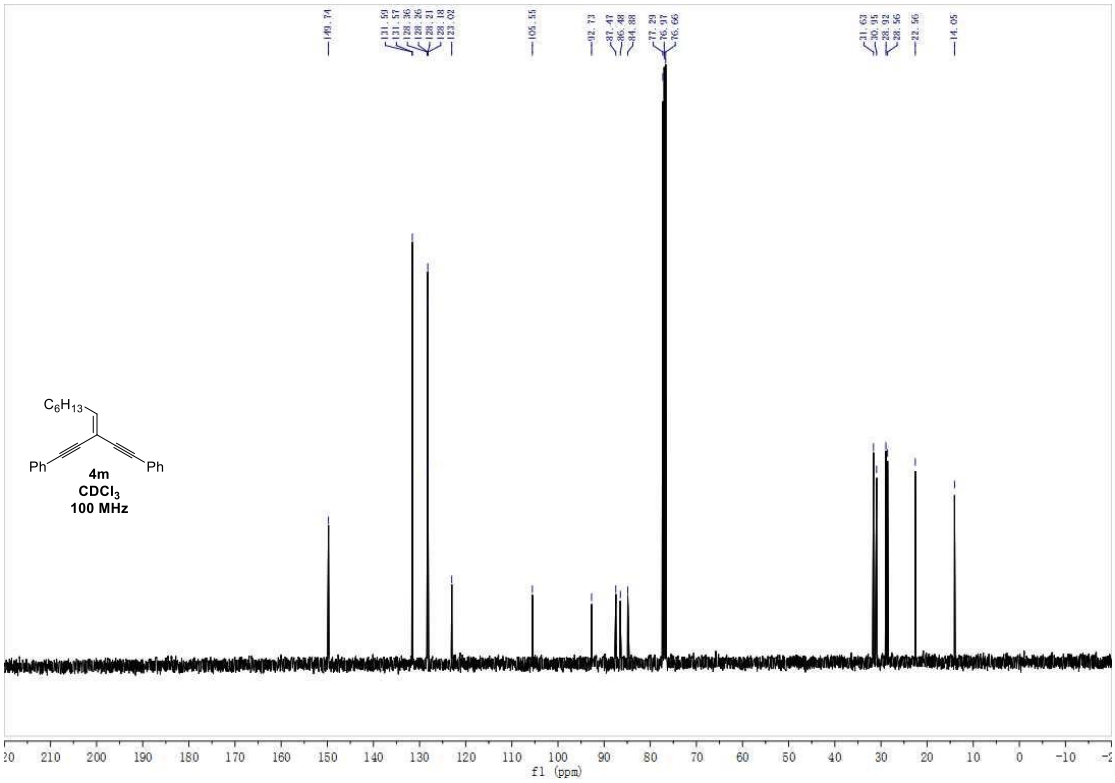
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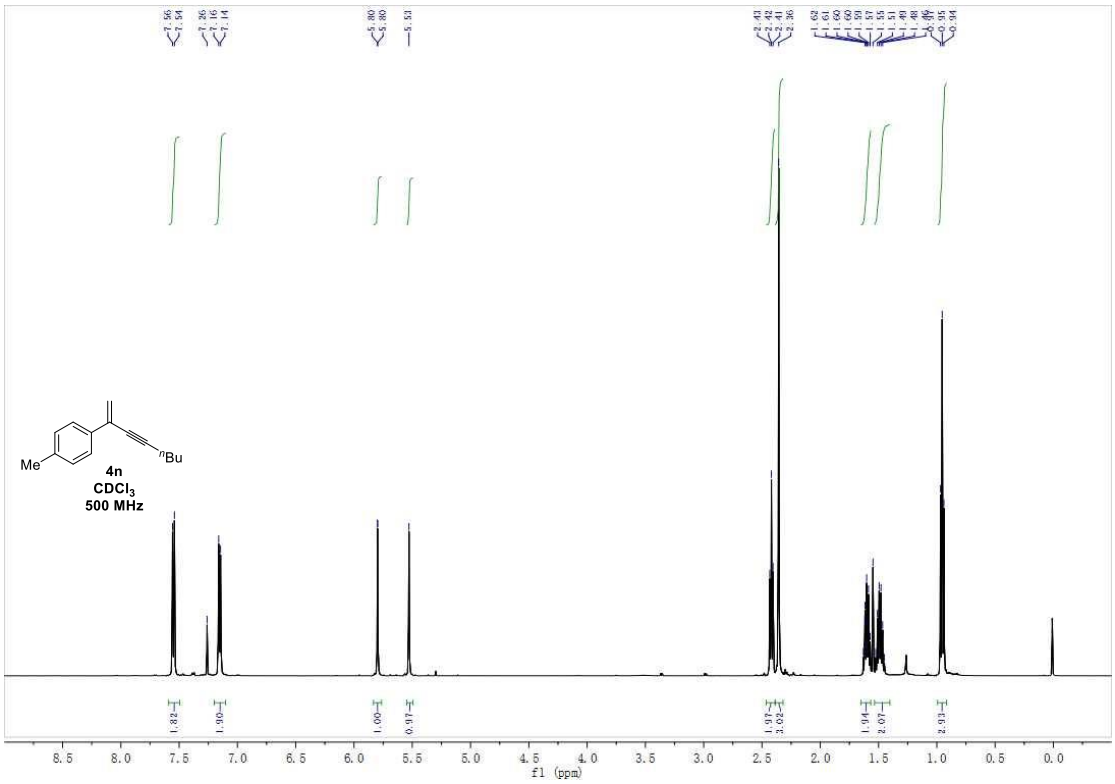
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4n
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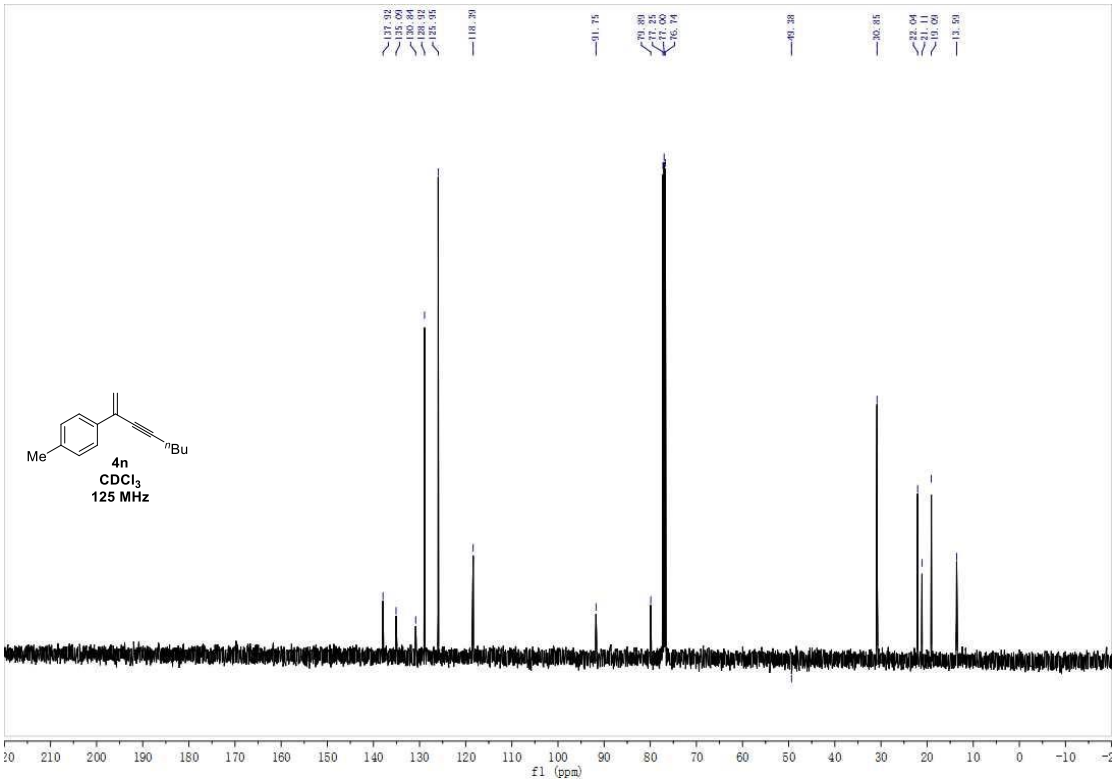
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125 MHz
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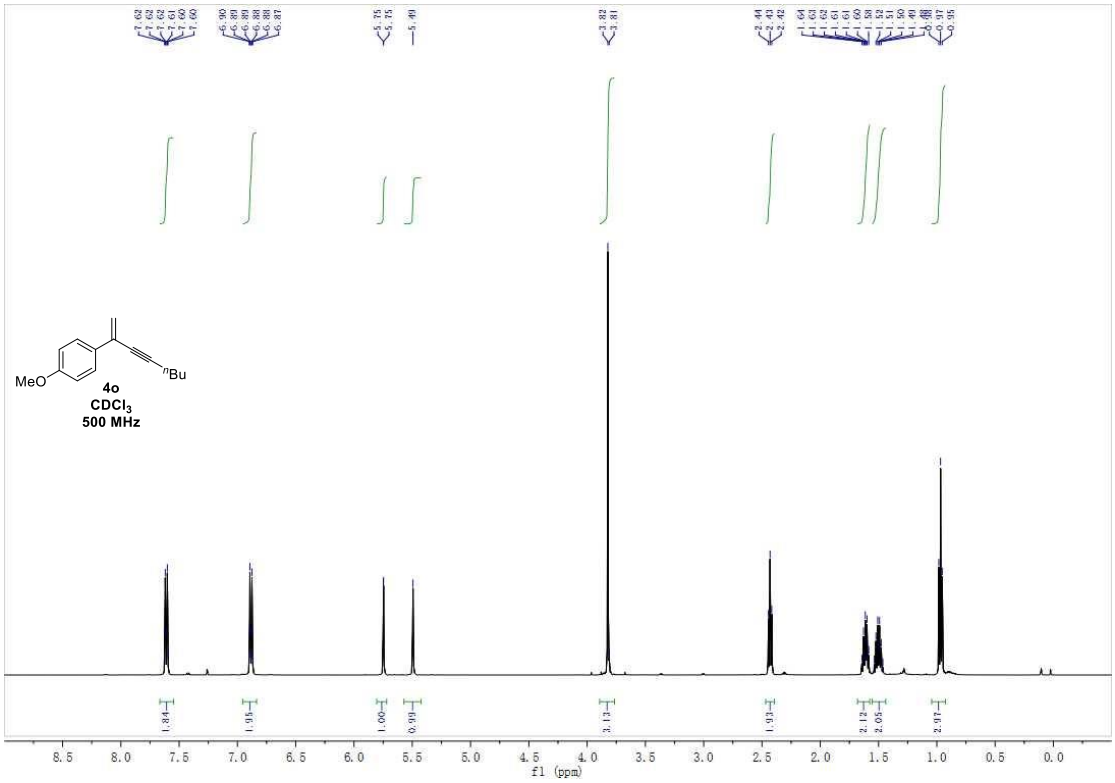
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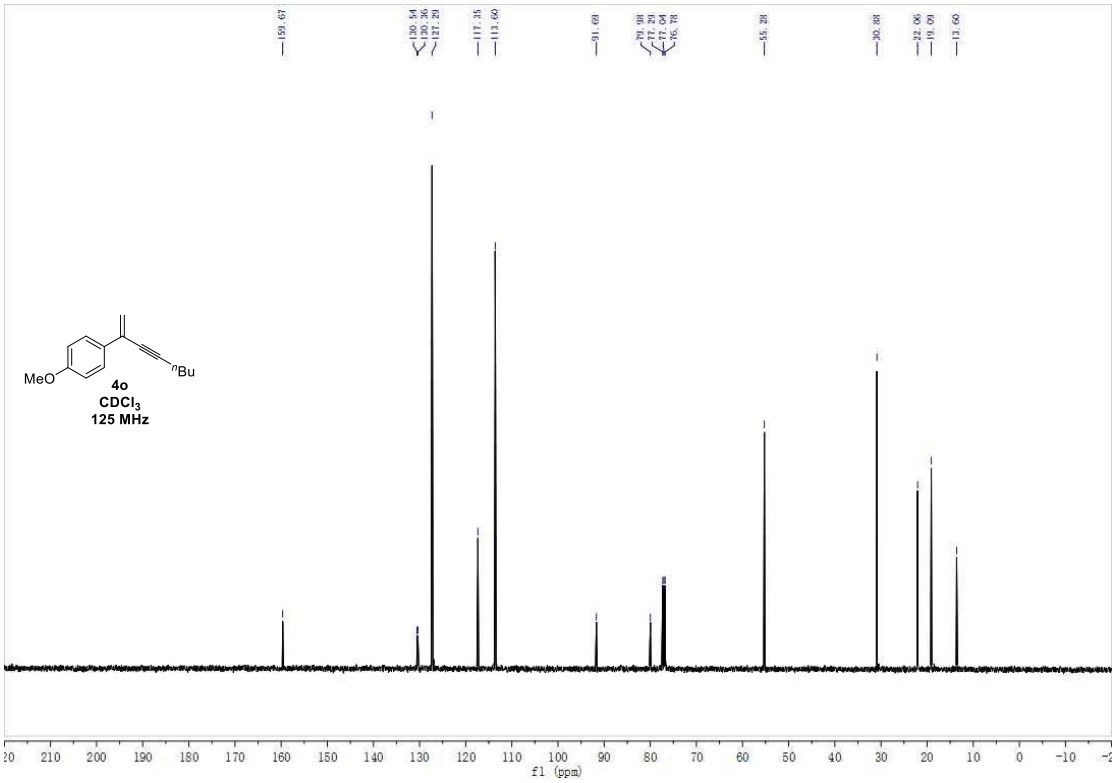
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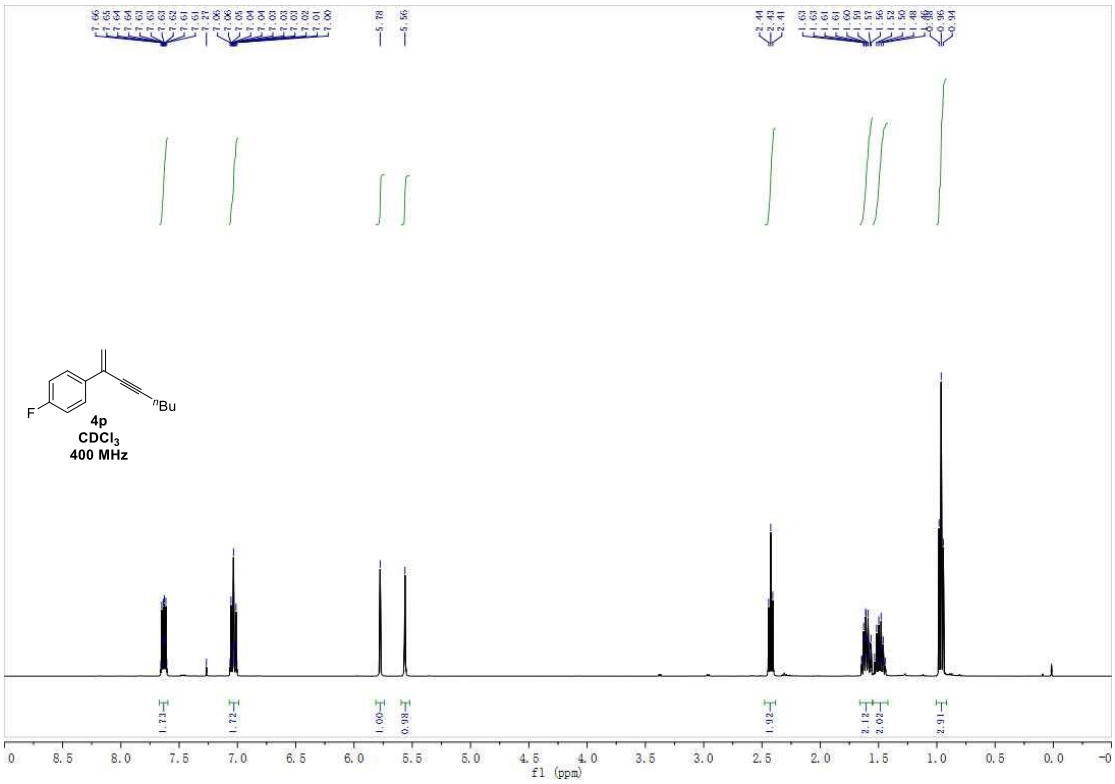
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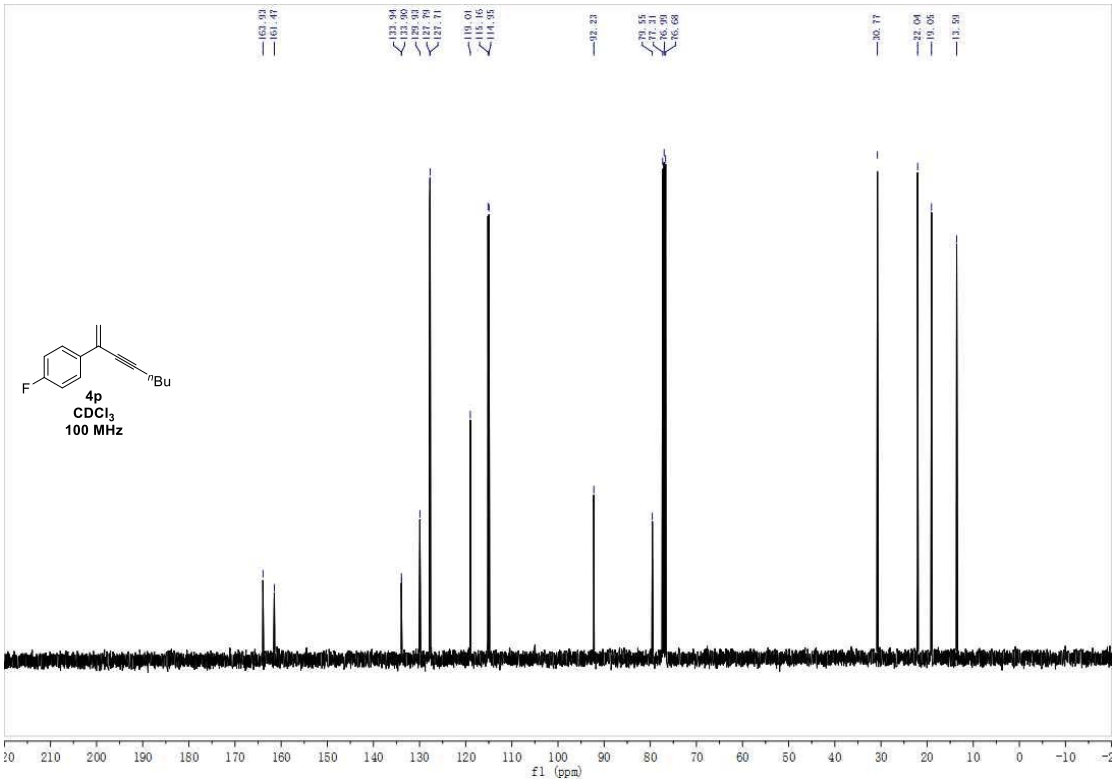
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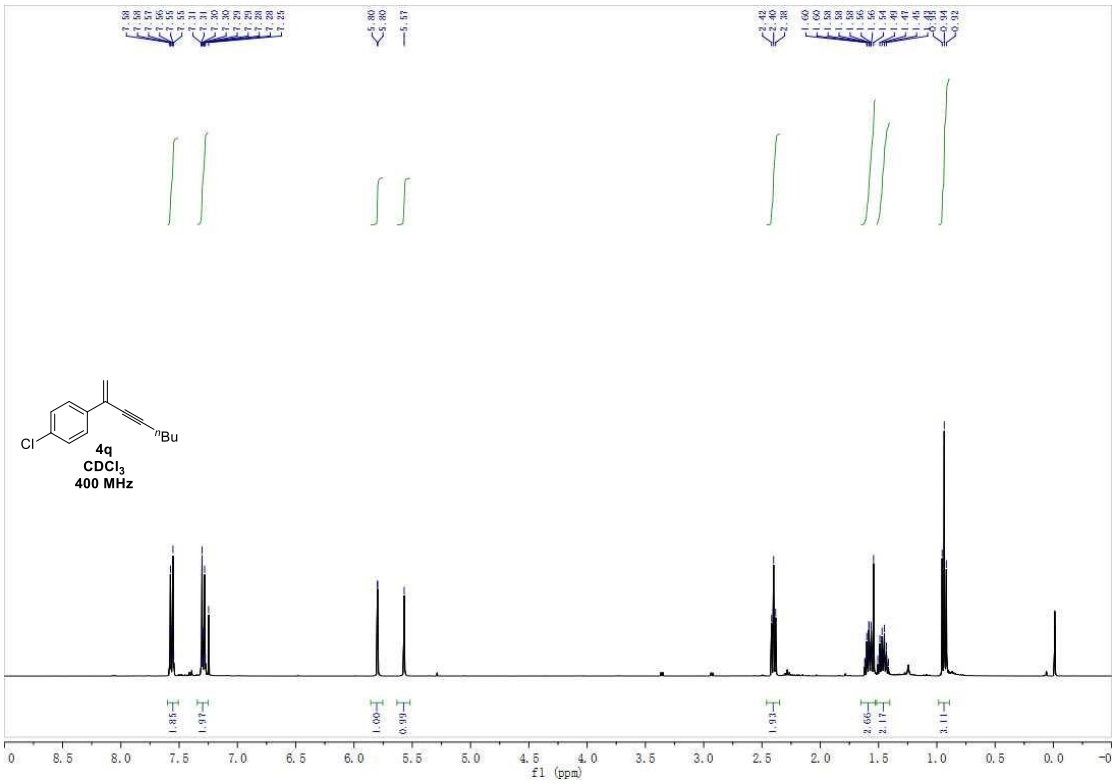
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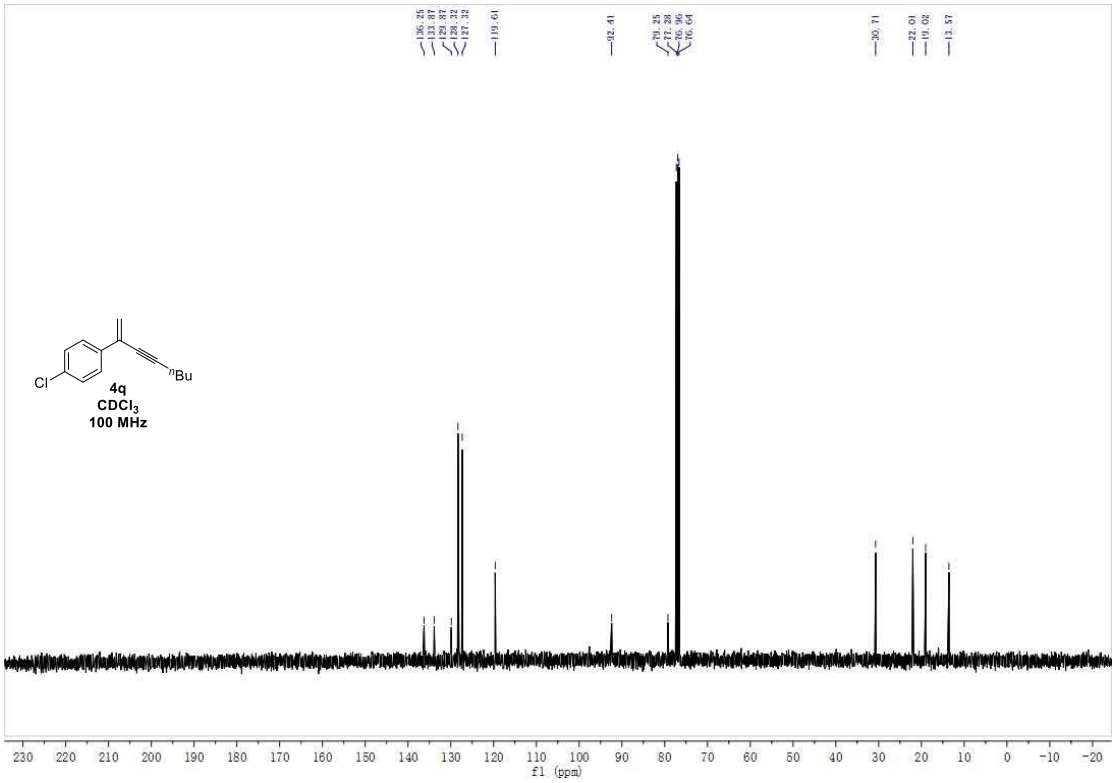
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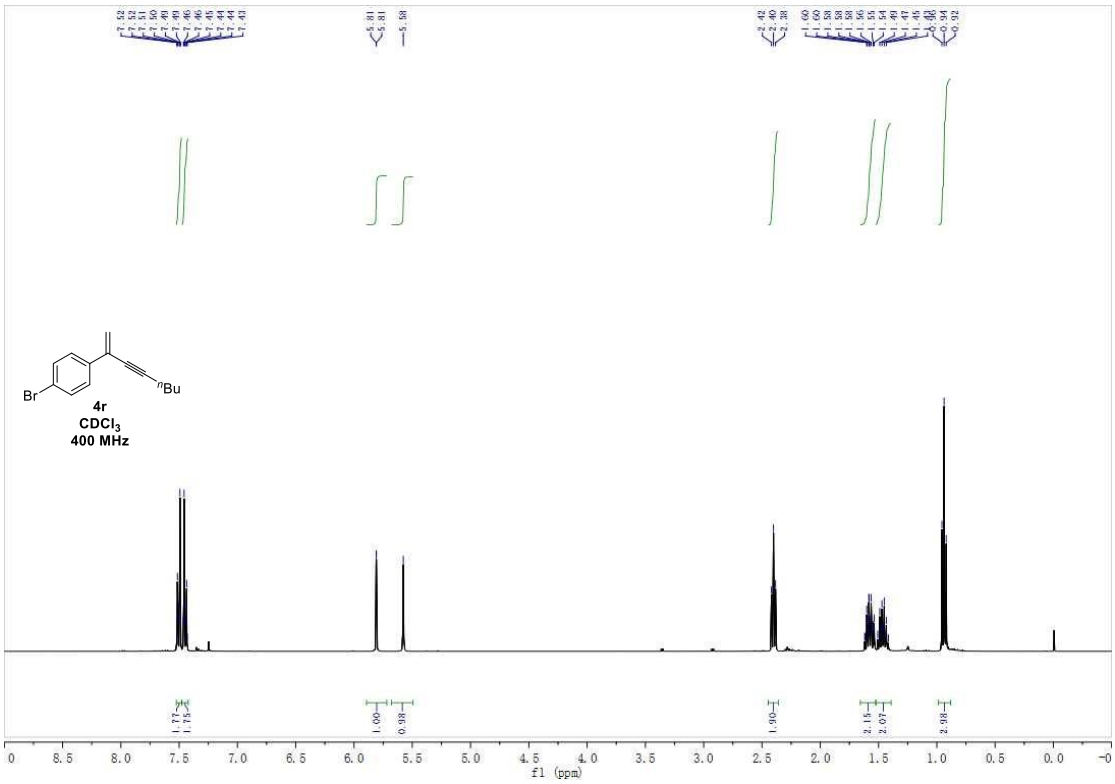
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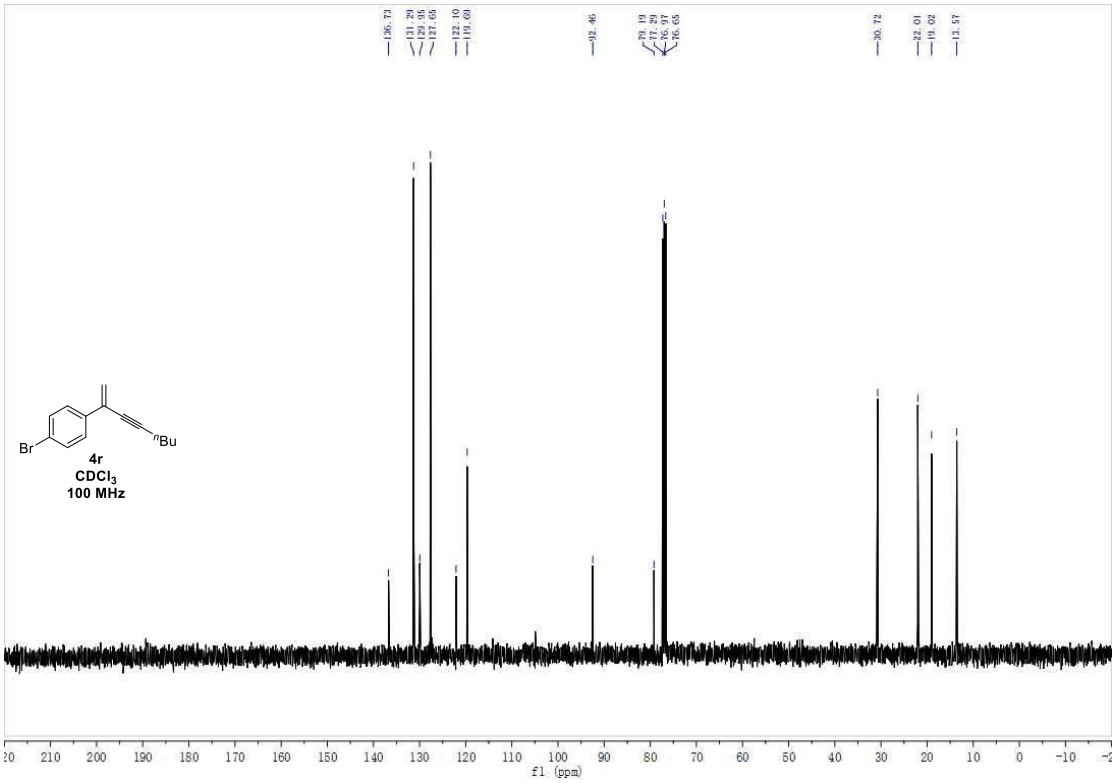
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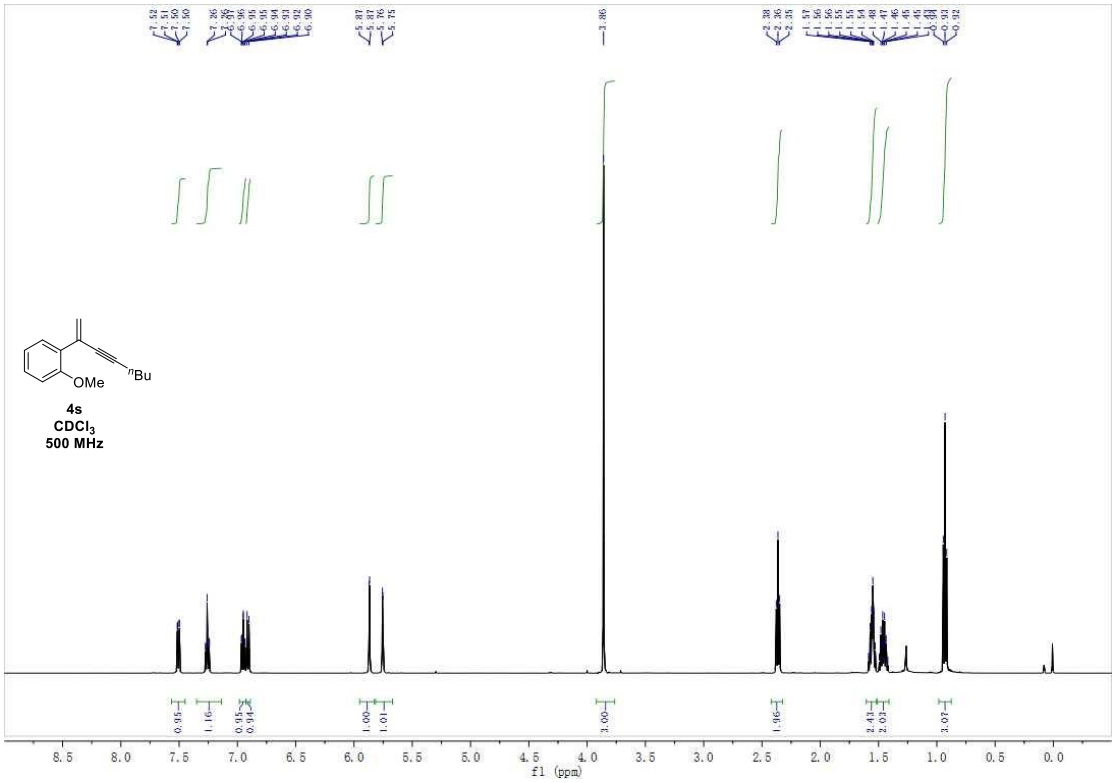
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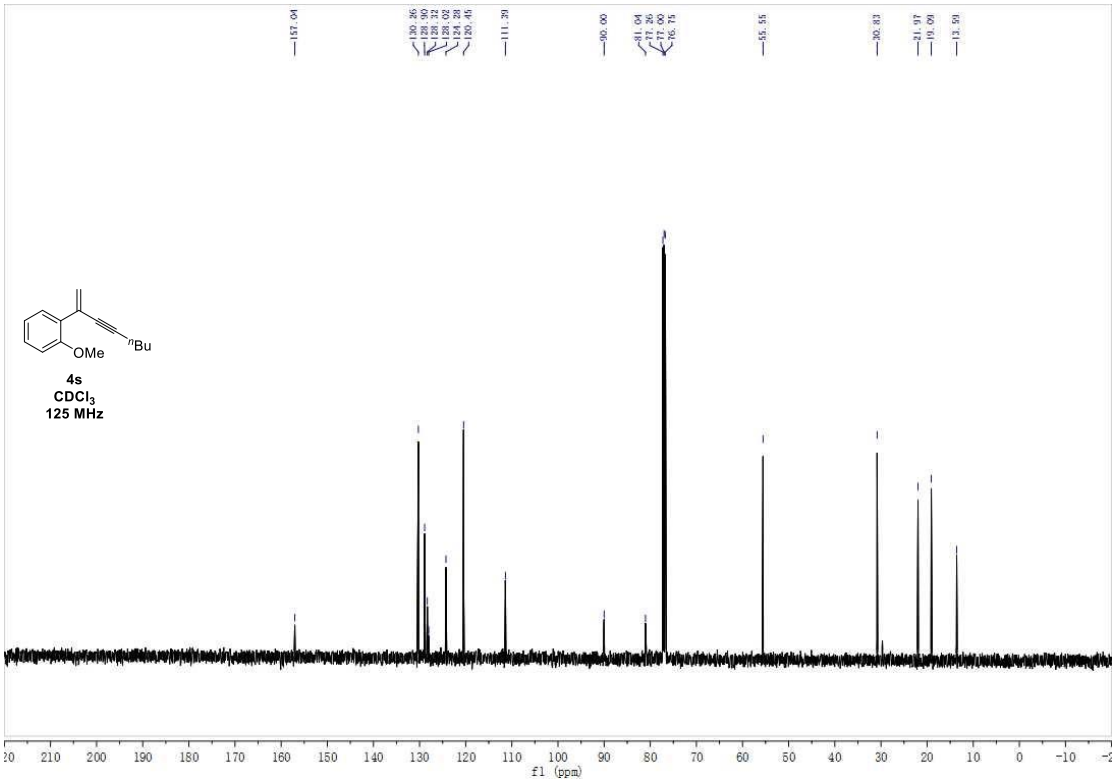
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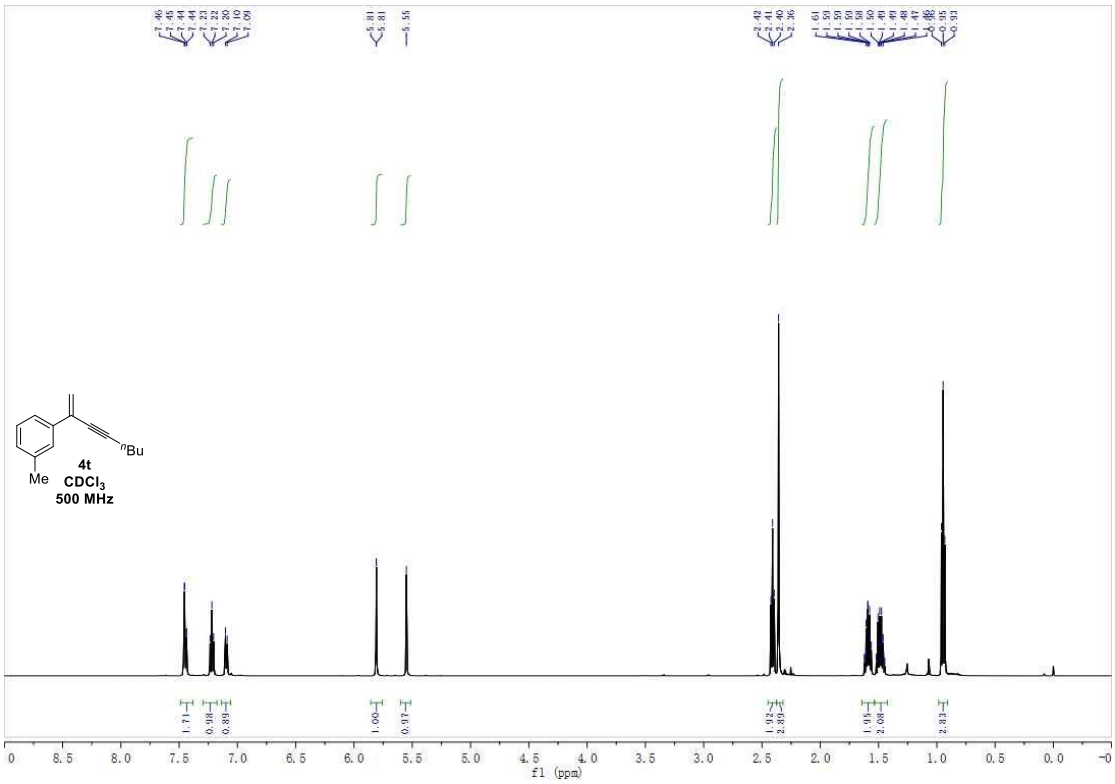
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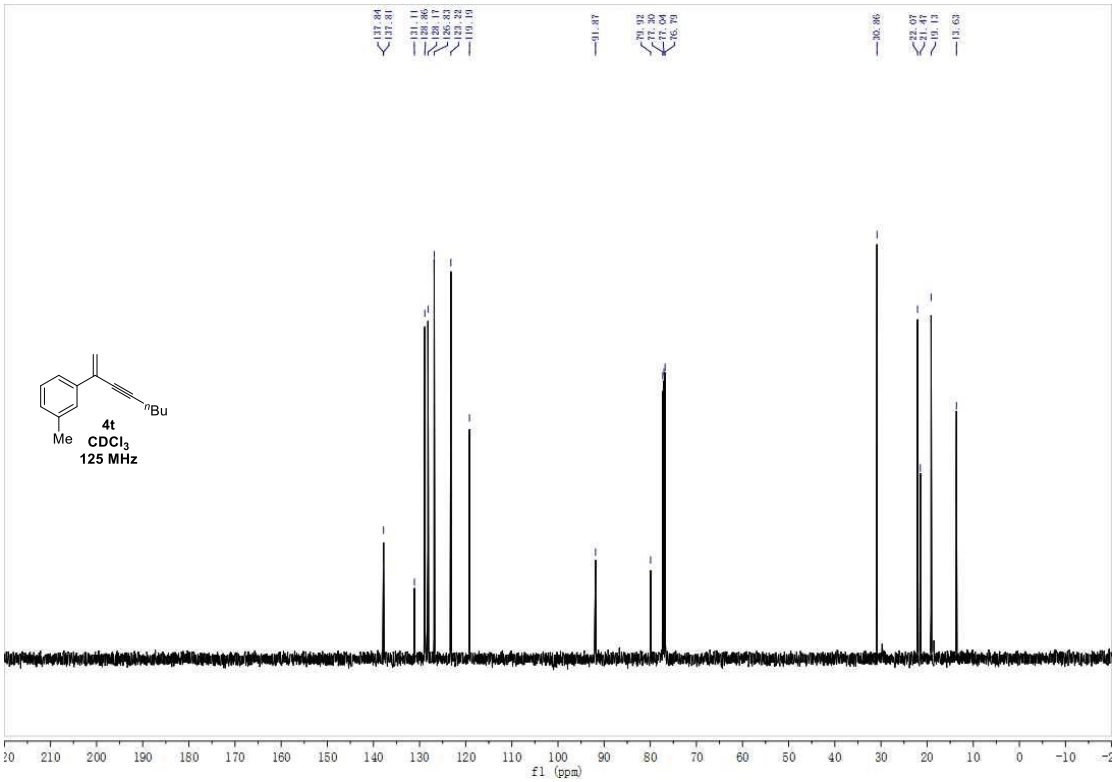
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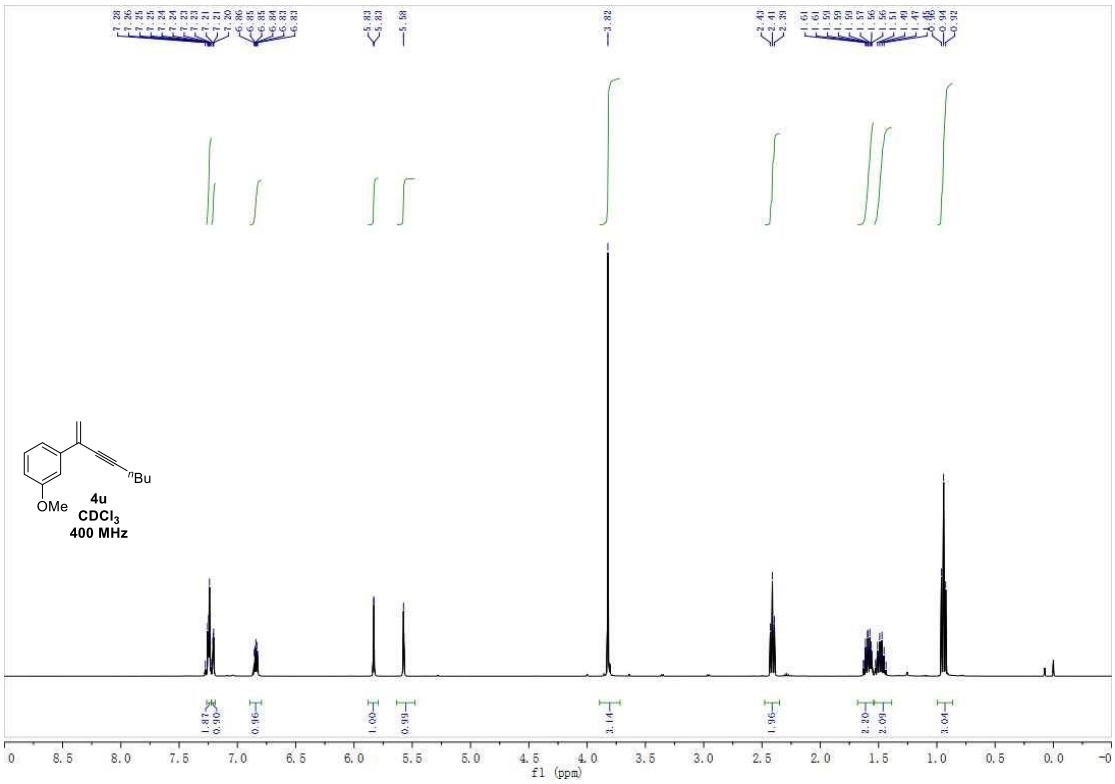
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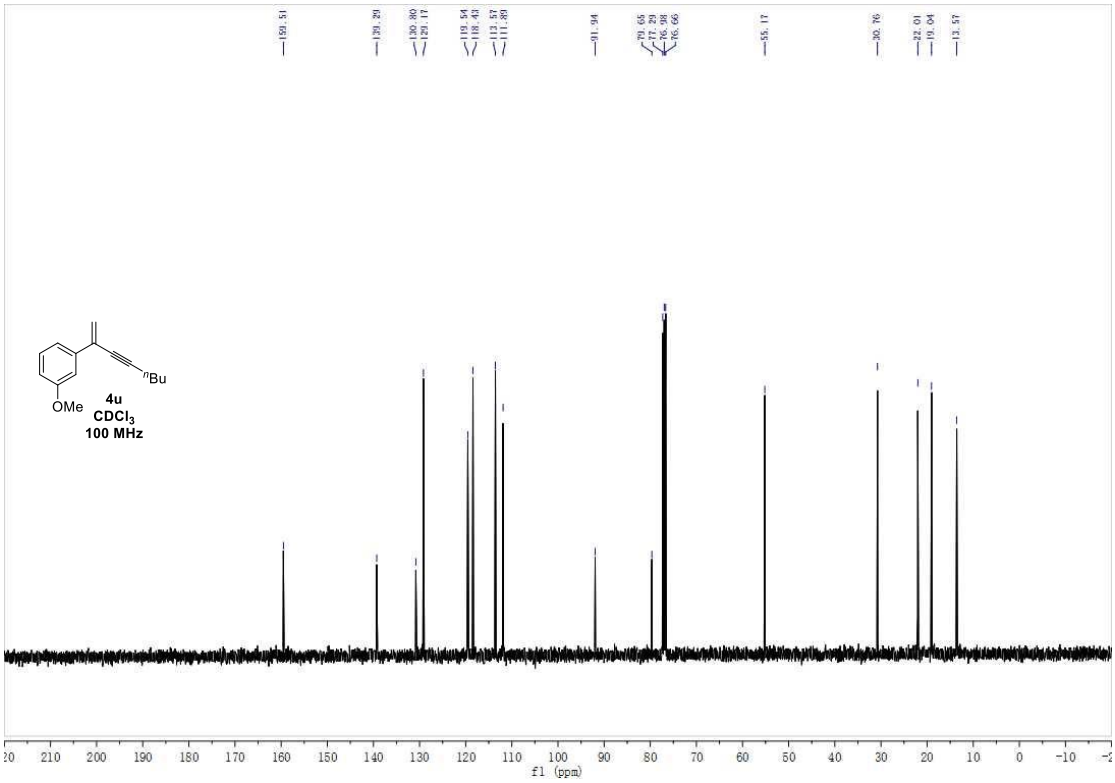
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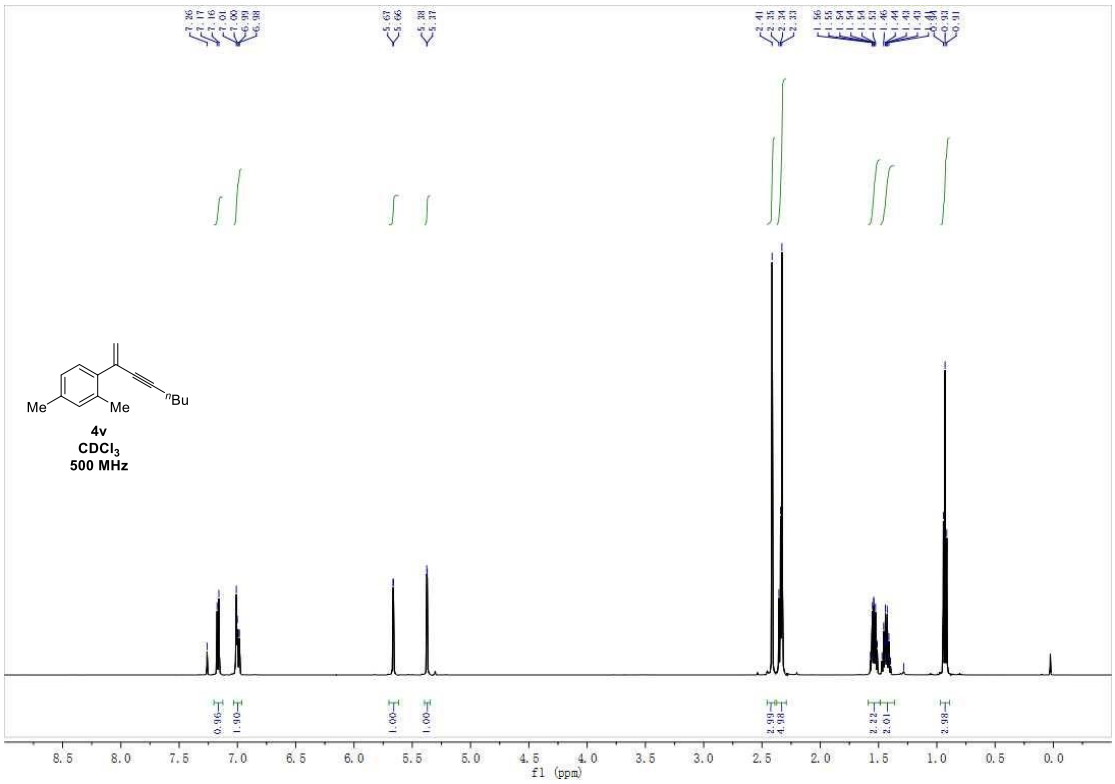
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Me
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500 MHz
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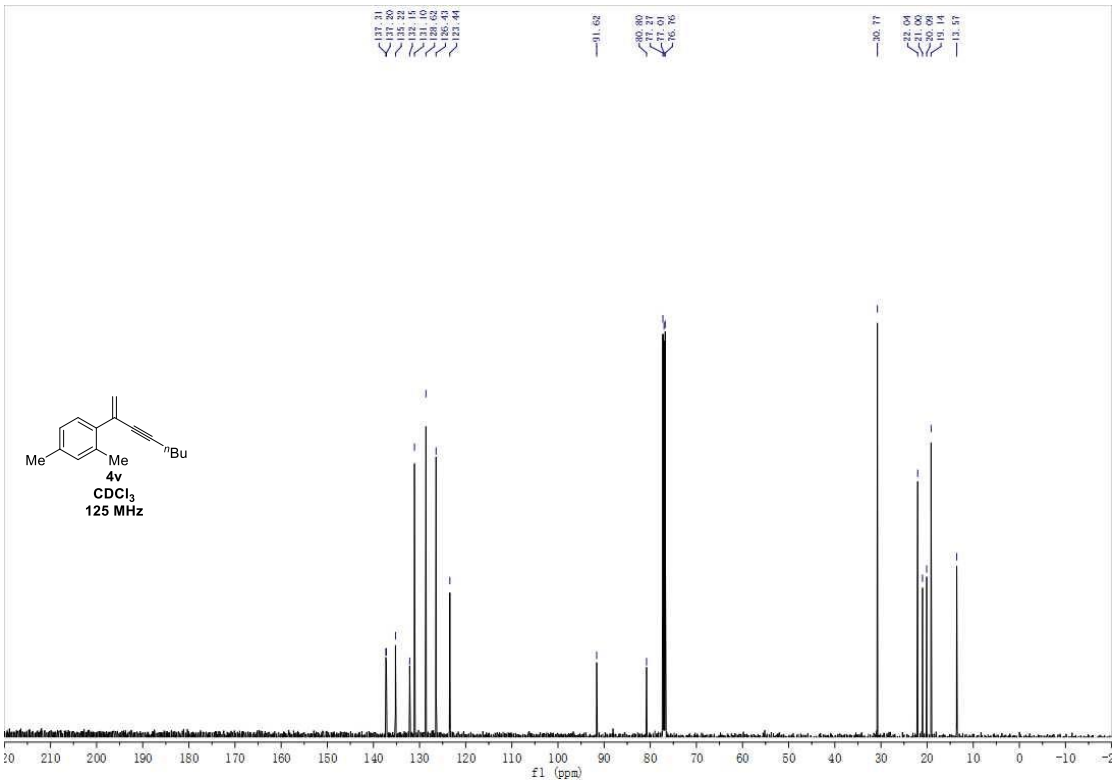
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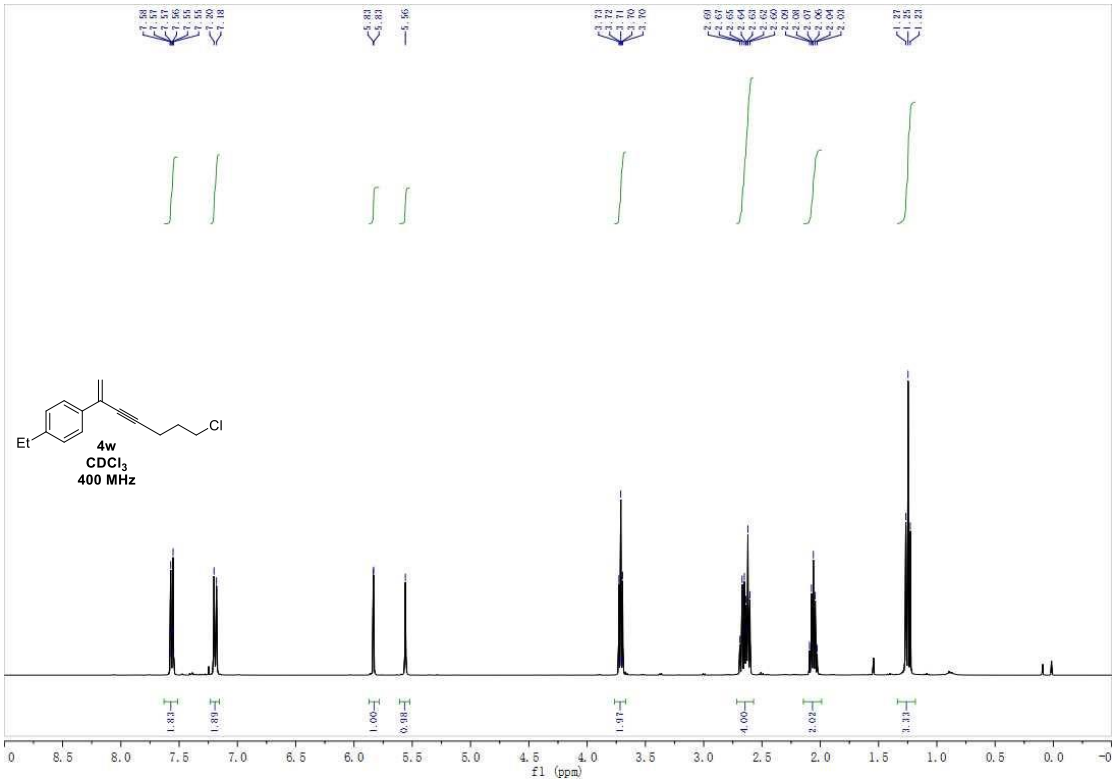
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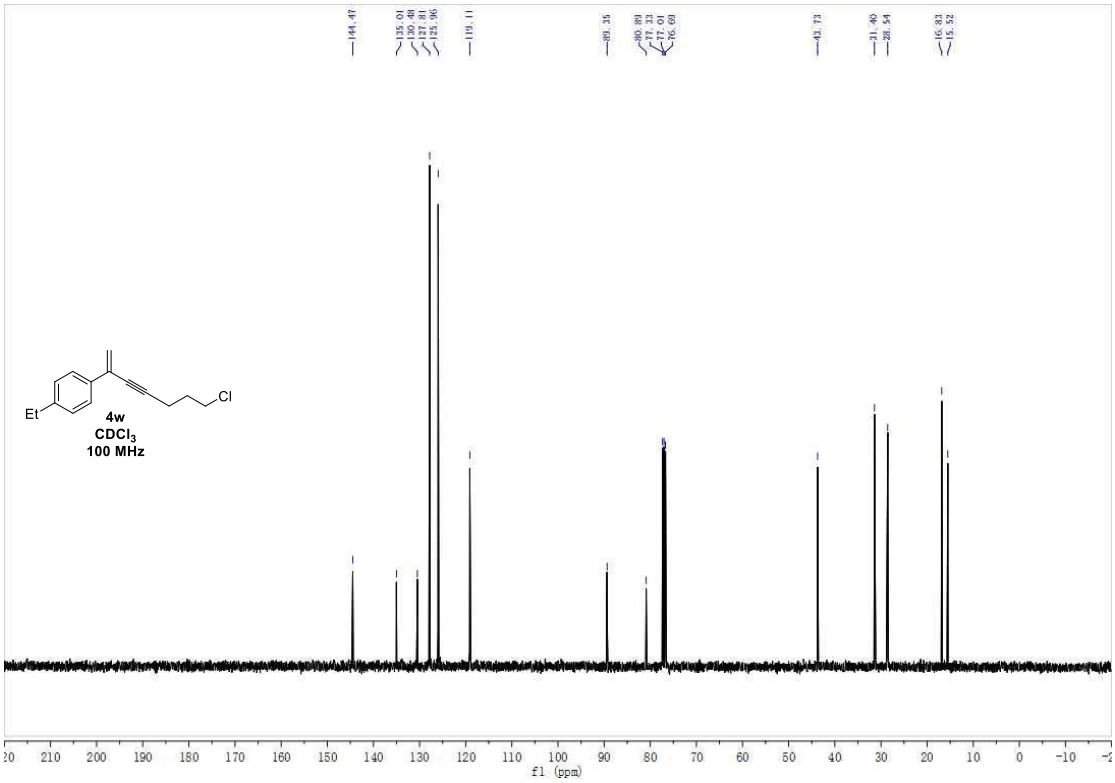
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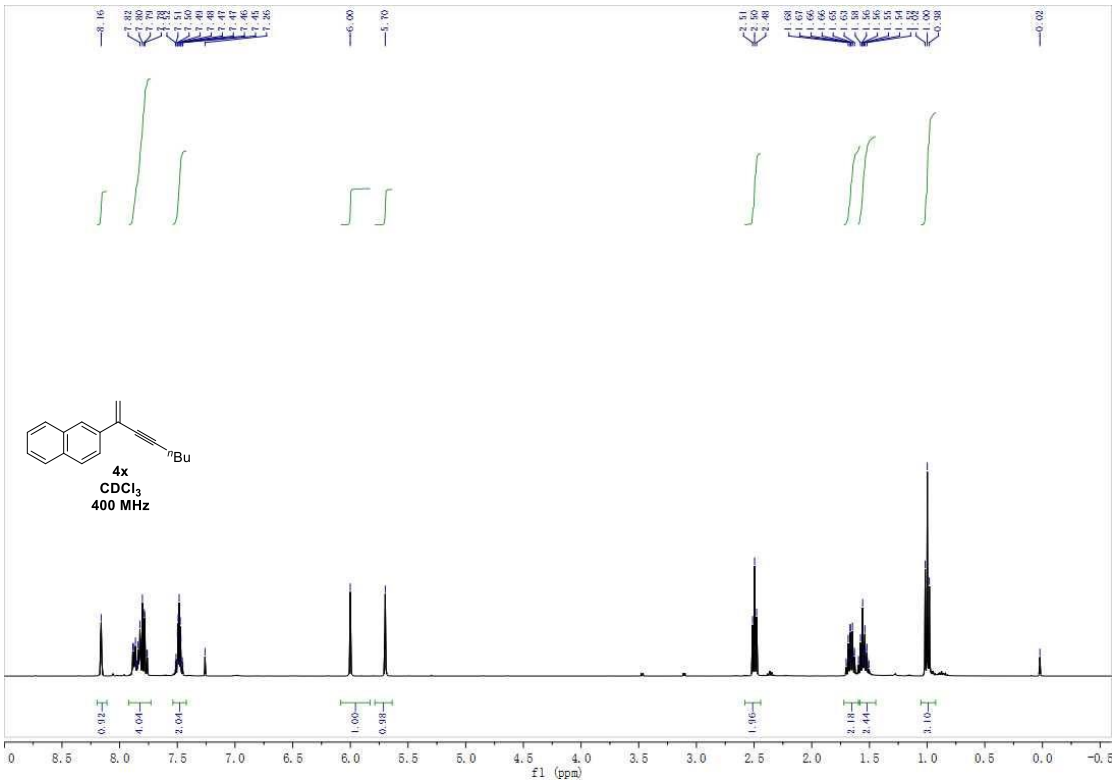
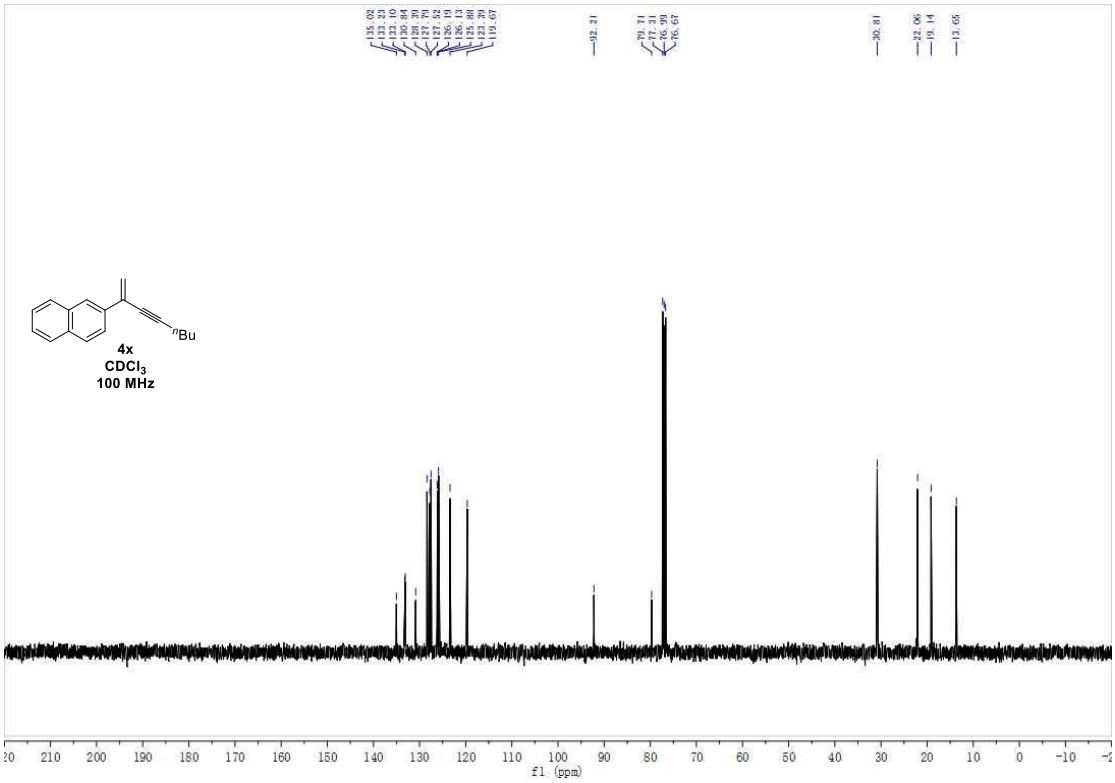
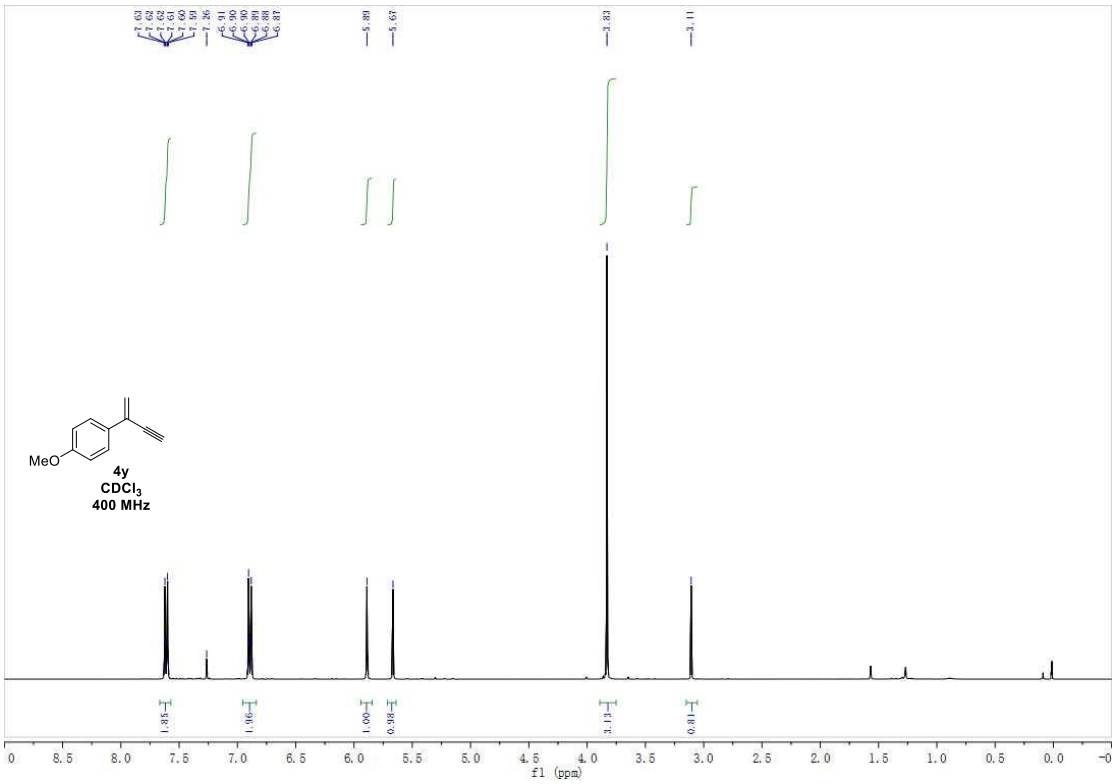
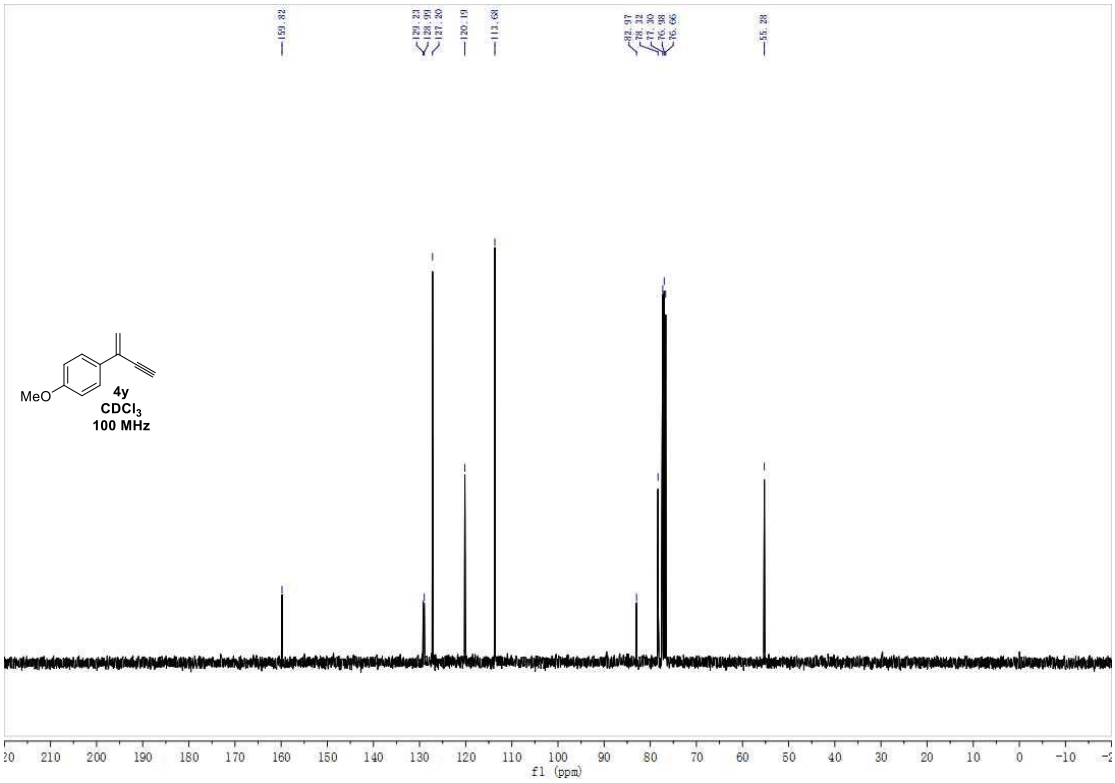
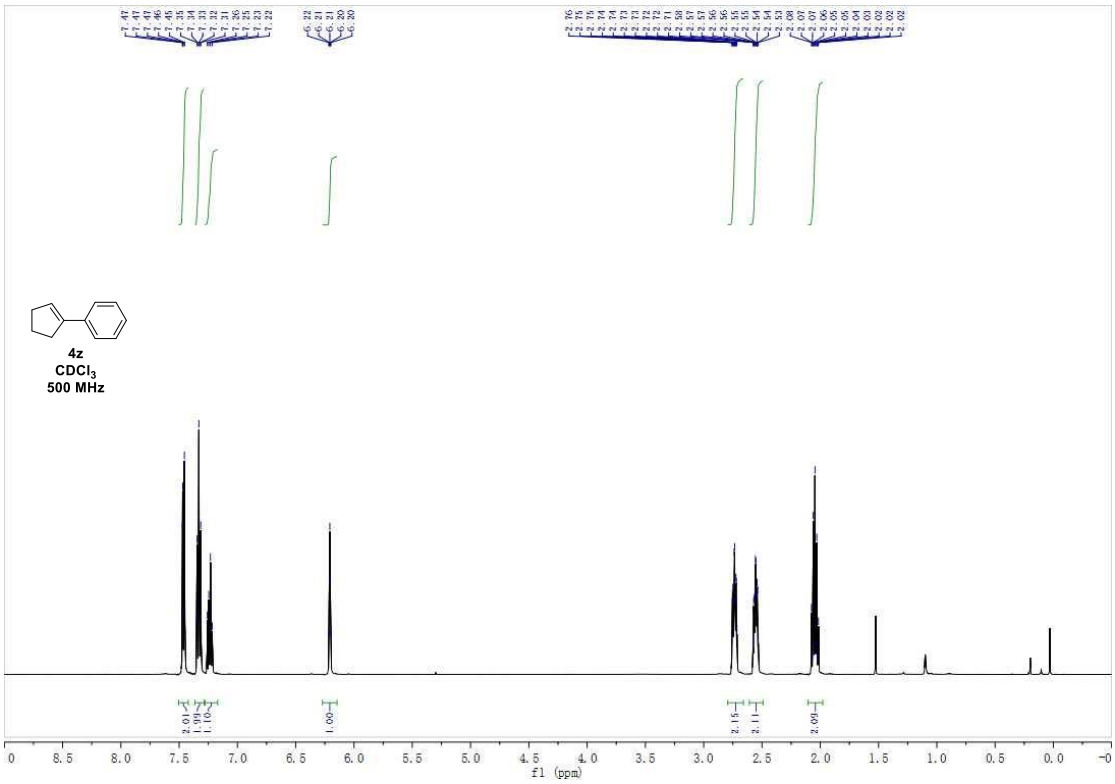
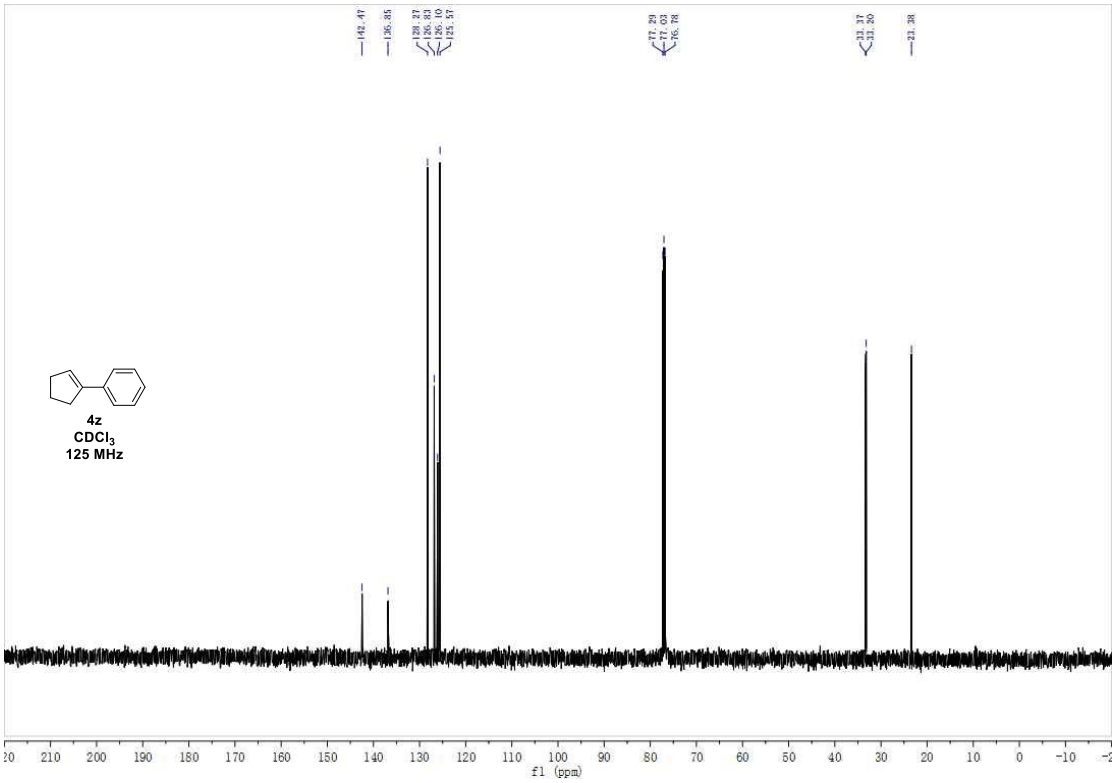

nBu
4x
CDCl3
400 MHz
f1 (ppm)

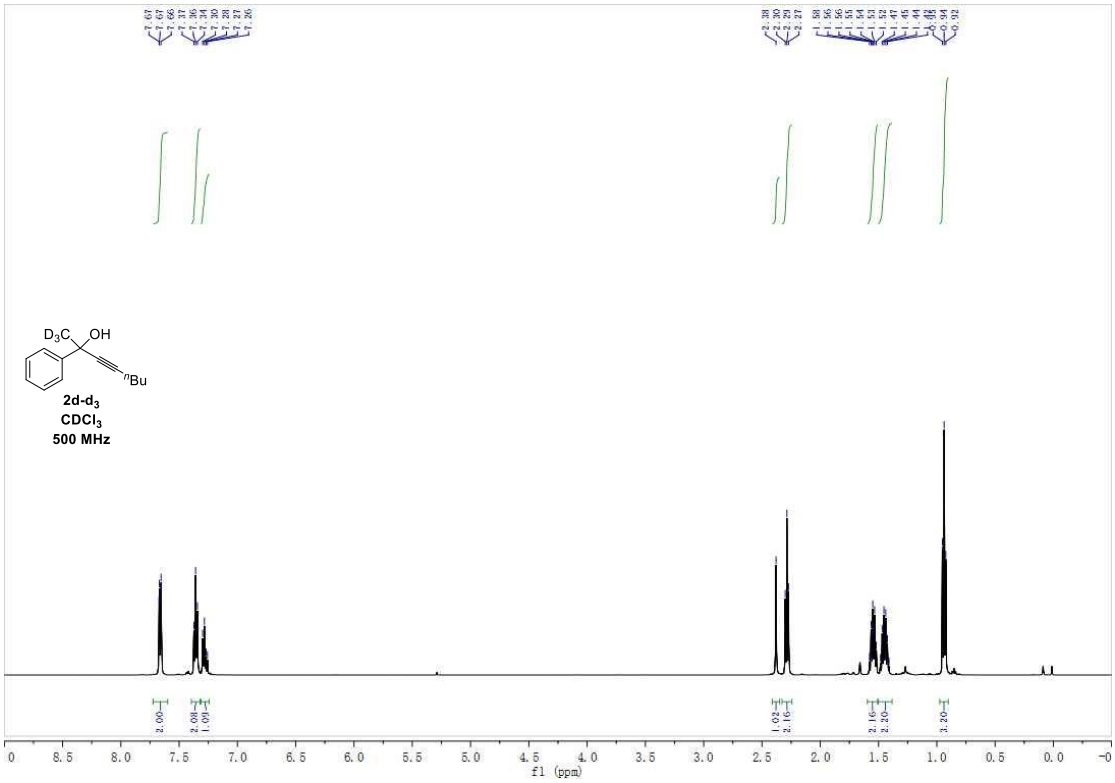

nBu
4x
CDCl3
100 MHz
f1 (ppm)

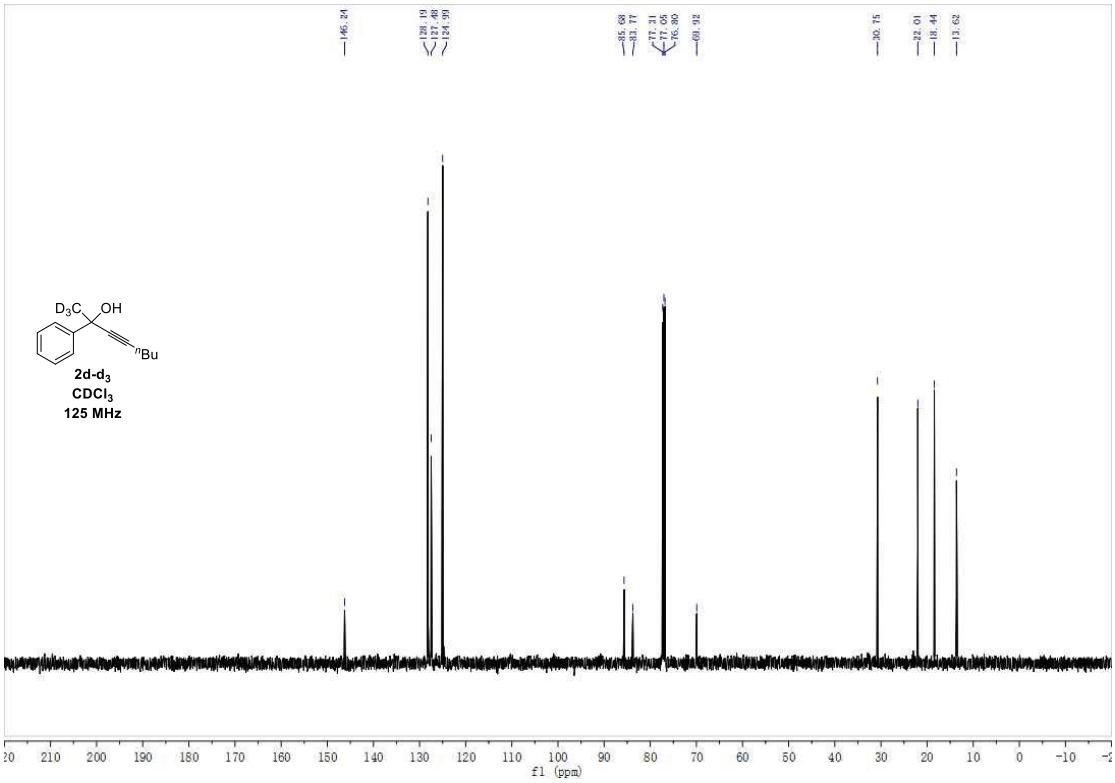

MeO
4y
CDCl3
400 MHz
f1 (ppm)

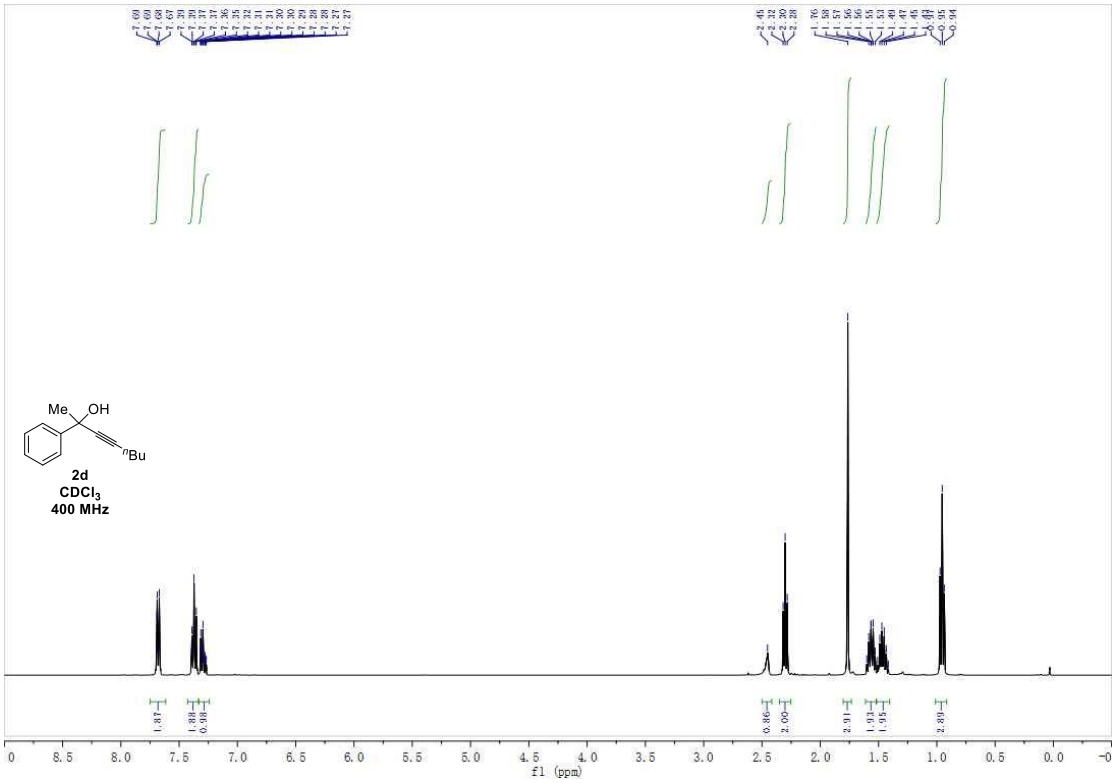

MeO
4y
CDCl3
100 MHz
f1 (ppm)

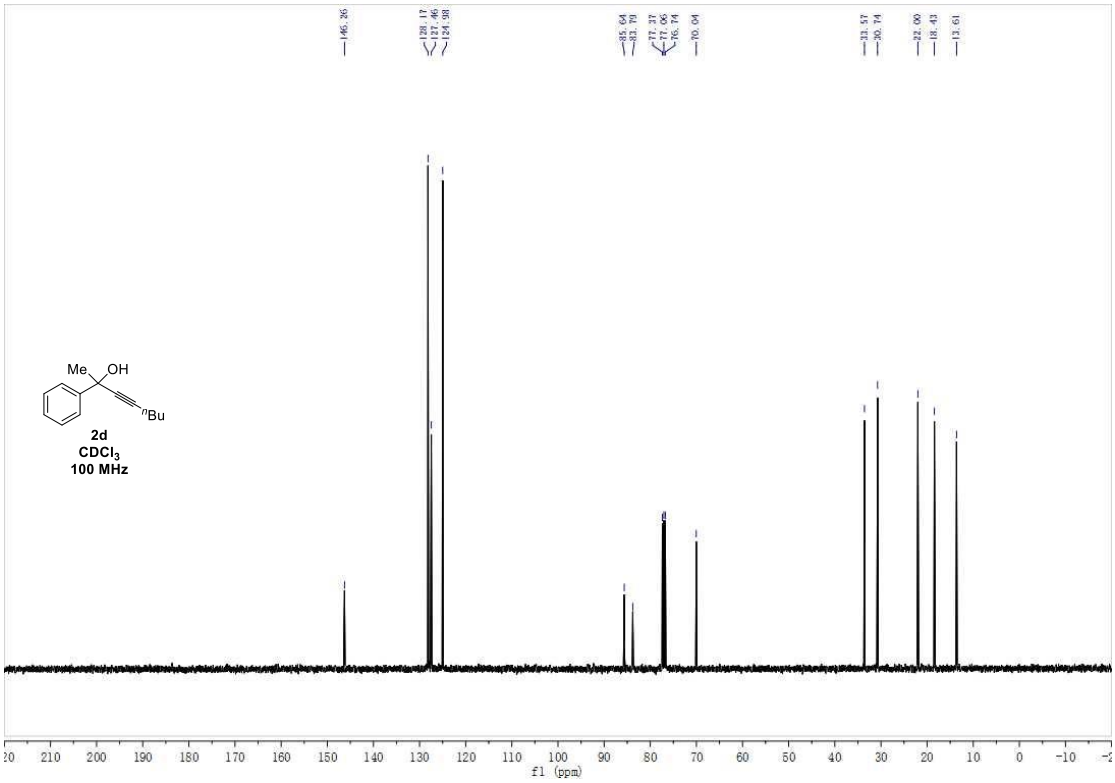

4z
CDCl3
500 MHz
f1 (ppm)


4z
CDCl3
125 MHz
f1 (ppm)


D3C
OH
nBu
2d-d3
CDCl3
500 MHz
f1 (ppm)


D3C
OH
nBu
2d-d3
CDCl3
125 MHz
f1 (ppm)


Me
OH
nBu
2d
CDCl3
400 MHz
f1 (ppm)


Me
OH
nBu
2d
CDCl3
100 MHz
f1 (ppm)