Supporting Information for

Asymmetric Copper-Catalyzed Alkynylallylic Dimethylamination

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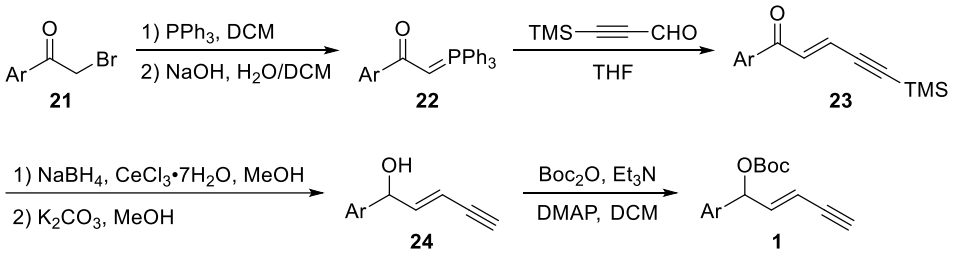
1. General information

All air-sensitive procedures were conducted by Schlenk techniques under argon. Unless otherwise indicated, all commercially available starting materials and dry solvents were purchased and used directly without further purification. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on 400 MHz Bruker or 500 MHz Agilent instruments at Shanghai Institute of Organic Chemistry. For High-resolution mass spectra: ESI mass spectra were recorded on Thermo Scientific Q Exactive HF Orbitrap-FTMS; MALDI was measured on Voyager-DE STR; EI mass spectra were recorded on Waters Premier GC-TOF MS; FI mass spectra were recorded on JEOL-AccuTOF-GCv4G-GCT MS. Optical rotation was measured using a 1 mL cell with 1.0 dm path length on a JASCO P-1030 polarimeter. HPLC analysis was conducted on a Shimadzu HPLC system equipped with Daicel or Chiralpak chiral-stationary-phase columns (ϕ 4.6 mm×250 mm). Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard or $CHCl_3$ in $CDCl_3$ (7.26 ppm) for ^{1}H NMR, $CDCl_3$ (δ = 77.10 ppm) for ^{13}C NMR, and $CFCl_3$ (0 ppm) for ^{19}F NMR. Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Column chromatography was performed with 300-400 mesh silica gel using flash column chromatography technique.

2. Synthesis of substrates

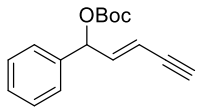
2.1 Synthesis of enyne esters



General procedure: To a solution of **21** (10 mmol) in DCM (20 mL) were added the solution of PPh_3 (10 mmol) in DCM (20 mL) dropwise at 0 °C. The reaction mixture was then allowed to stir at room temperature for 24 hours followed by the addition of aqueous NaOH (1.2 M, 10 mL). The new mixture was allowed to stir at room temperature for another 2 hours. After this time, the resulting mixture was quenched with water (20 mL), extracted with DCM (20 mL × 3), washed by brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford Wittig reagent **22** without further purification. Then, to a solution of **22** in THF (50 mL) was added 3-(trimethylsilyl) propiolaldehyde (10 mmol) dropwise at 0 °C. The reaction mixture was allowed to stir at room temperature for 4 hours. After this time, the resulting mixture was concentrated and purified by flash column chromatography on silica gel to give **23**.

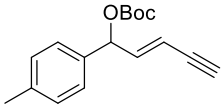
To a solution of **23** (1.0 equiv) and $CeCl_3{\cdot}7H_2O$ (1.2 equiv) in MeOH (0.5 M) was added $NaBH_4$ (1.3 equiv) slowly at 0 °C. The reaction mixture was then allowed to stir at room temperature for 4

hours. After this time, the resulting mixture was quenched with water (10 mL), extracted with EtOAc (20 mL × 3), washed by brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude alcohol. To a solution of the crude alcohol in MeOH (0.5 M) was added K_2CO_3 (1.2 equiv). The reaction mixture was then allowed to stir at room temperature for 1 hours. After this time, the resulting mixture was quenched with water (20 mL), extracted with DCM (20 mL × 3), washed by brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford crude products **24**. Next, to a solution of **24** (1.0 equiv) in DCM (0.5 M) was added DMAP (0.1 equiv), Et_3N (2.0 equiv) and Boc_2O (1.5 equiv) sequentially. The reaction mixture was allowed to stir at room temperature for 12 hours. After this time, the resulting mixture was quenched with saturated aqueous NH_4Cl (10 mL), extracted with DCM (20 mL × 3), washed by brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was finally purified by flash column chromatography on silica gel to give pure **1**.



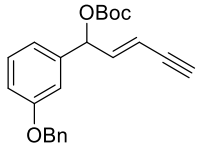
(*E*)-*tert*-Butyl (1-phenylpent-2-en-4-yn-1-yl) carbonate (**1a**)

Known compound[1]. White solid, 66% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.41 – 7.28 (m, 5H), 6.36 (dd, *J* = 15.9, 6.1 Hz, 1H), 6.06 (dd, *J* = 6.1, 1.3 Hz, 1H), 5.73 (ddd, *J* = 15.9, 2.2, 1.6 Hz, 1H), 2.92 (d, *J* = 2.3 Hz, 1H), 1.47 (s, 9H).



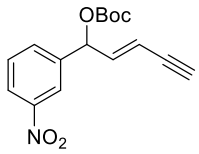
(*E*)-*tert*-Butyl (1-(p-tolyl)pent-2-en-4-yn-1-yl) carbonate (**1b**)

Yellow solid, 70% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.35 (dd, *J* = 15.9, 6.1 Hz, 1H), 6.03 (d, *J* = 6.1 Hz, 1H), 5.75 – 5.67 (m, 1H), 2.91 (d, *J* = 2.1 Hz, 1H), 2.34 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 142.4, 138.5, 134.7, 129.5, 127.2, 111.0, 82.7, 81.2, 79.1, 77.9, 27.8, 21.3. HRMS (FI): $[M]^+$ calcd for $C_{17}H_{20}O_3^+$ 272.1407, found 272.1405.



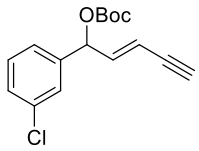
(*E*)-1-(3-(Benzyloxy)phenyl)pent-2-en-4-yn-1-yl *tert*-butyl carbonate (**1c**)

Known compound[1]. Yellow solid, 80% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.49 – 7.22 (m, 6H), 7.02 – 6.86 (m, 3H), 6.33 (dd, *J* = 15.9, 6.1 Hz, 1H), 6.02 (dd, *J* = 6.2, 1.5 Hz, 1H), 5.77 – 5.66 (m, 1H), 5.06 (s, 2H), 2.93 (d, *J* = 2.3 Hz, 1H), 1.47 (s, 9H).



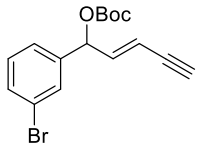
(*E*)-*tert*-Butyl (1-(3-nitrophenyl)pent-2-en-4-yn-1-yl) carbonate (**1d**)

Known compound[1]. Brown oil, 34% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.23 (s, 1H), 8.22 – 8.17 (m, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 6.31 (dd, *J* = 15.9, 6.4 Hz, 1H), 6.13 (d, *J* = 6.3 Hz, 1H), 5.85 – 5.77 (m, 1H), 2.98 (d, *J* = 2.0 Hz, 1H), 1.48 (s, 9H).



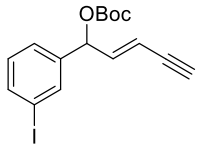
(*E*)-*tert*-Butyl (1-(3-chlorophenyl)pent-2-en-4-yn-1-yl) carbonate (**1e**)

Known compound[1]. Yellow oil, 57% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.35 (s, 1H), 7.30 (d, *J* = 5.1 Hz, 2H), 7.23 (dd, *J* = 6.1, 2.7 Hz, 1H), 6.30 (dd, *J* = 15.9, 6.2 Hz, 1H), 6.01 (d, *J* = 6.2 Hz, 1H), 5.75 (dt, *J* = 15.8, 1.6 Hz, 1H), 2.95 (d, *J* = 2.0 Hz, 1H), 1.48 (s, 9H).



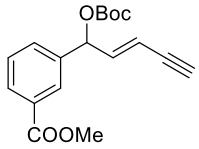
(*E*)-1-(3-Bromophenyl)pent-2-en-4-yn-1-yl *tert*-butyl carbonate (**1f**)

Known compound[1]. Yellow oil, 42% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.50 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.20 (m, 2H), 6.30 (dd, *J* = 15.9, 6.2 Hz, 1H), 6.01 (d, *J* = 6.3 Hz, 1H), 5.72 (d, *J* = 15.9 Hz, 1H), 2.95 (d, *J* = 2.0 Hz, 1H), 1.48 (s, 9H).



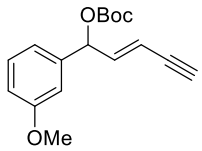
(*E*)-*tert*-Butyl (1-(3-iodophenyl)pent-2-en-4-yn-1-yl) carbonate (**1g**)

Known compound[1]. Yellow solid, 80% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.31 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.29 (ddd, *J* = 15.8, 6.2, 0.6 Hz, 1H), 5.97 (dd, *J* = 6.3, 1.5 Hz, 1H), 5.74 (ddd, *J* = 15.9, 2.3, 1.5 Hz, 1H), 2.95 (d, *J* = 2.3 Hz, 1H), 1.47 (s, 9H).



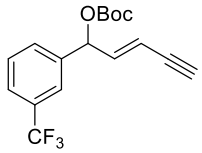
Methyl (*E*)-3-(1-((*tert*-butoxycarbonyl)oxy)pent-2-en-4-yn-1-yl)benzoate (**1h**)

Known compound[1]. White solid, 33% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.01 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 6.34 (dd, *J* = 15.9, 6.2 Hz, 1H), 6.09 (d, *J* = 6.2 Hz, 1H), 5.75 (d, *J* = 15.9 Hz, 1H), 3.92 (s, 3H), 2.94 (s, 1H), 1.47 (s, 9H).



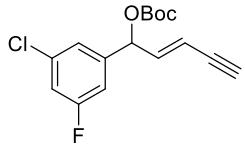
(*E*)-*tert*-Butyl (1-(3-methoxyphenyl)pent-2-en-4-yn-1-yl) carbonate (**1i**)

Known compound[1]. Yellow oil, 60% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.90 – 6.82 (m, 2H), 6.34 (ddd, *J* = 15.9, 6.2, 0.7 Hz, 1H), 6.03 (d, *J* = 6.1 Hz, 1H), 5.77 – 5.68 (m, 1H), 3.81 (s, 3H), 2.92 (d, *J* = 2.3 Hz, 1H), 1.47 (s, 9H).



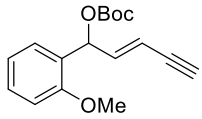
(*E*)-*tert*-Butyl (1-(3-(trifluoromethyl)phenyl)pent-2-en-4-yn-1-yl) carbonate (**1j**)

Known compound[1]. Yellow oil, 44% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.72 – 7.42 (m, 4H), 6.32 (dd, *J* = 15.9, 6.3 Hz, 1H), 6.10 (d, *J* = 6.2 Hz, 1H), 5.77 (d, *J* = 15.9 Hz, 1H), 2.96 (d, *J* = 2.3 Hz, 1H), 1.48 (s, 9H).



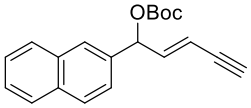
(*E*)-*tert*-Butyl (1-(3-chloro-5-fluorophenyl)pent-2-en-4-yn-1-yl) carbonate (**1k**)

Known compound[1]. Yellow solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.14 (s, 1H), 7.05 (dt, *J* = 8.3, 2.2 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.3 Hz, 1H), 6.03 – 5.94 (m, 1H), 5.77 (dd, *J* = 18.2, 1.4 Hz, 1H), 2.97 (d, *J* = 2.3 Hz, 1H), 1.48 (s, 9H).



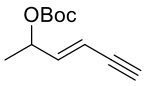
(*E*)-*tert*-Butyl (1-(2-methoxyphenyl)pent-2-en-4-yn-1-yl) carbonate (**1l**)

Known compound[1]. White solid, 93% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.35 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.96 (td, *J* = 7.5, 1.1 Hz, 1H), 6.88 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.49 (dd, *J* = 6.1, 1.4 Hz, 1H), 6.35 (ddd, *J* = 15.8, 6.1, 0.7 Hz, 1H), 5.69 (ddd, *J* = 15.9, 2.3, 1.4 Hz, 1H), 3.84 (s, 3H), 2.89 (d, *J* = 2.2 Hz, 1H), 1.47 (s, 9H).



(*E*)-*tert*-Butyl (1-(naphthalen-2-yl)pent-2-en-4-yn-1-yl) carbonate (**1m**)

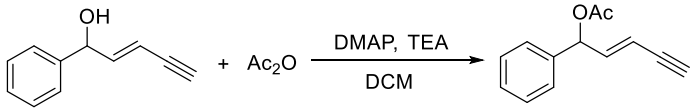
Yellow solid, 85% yield. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.84 (q, *J* = 6.9, 5.4 Hz, 4H), 7.49 (dd, *J* = 6.3, 3.1 Hz, 2H), 7.45 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.43 (dd, *J* = 15.9, 6.1 Hz, 1H), 6.23 (d, *J* = 6.1 Hz, 1H), 5.78 (dt, *J* = 15.9, 1.7 Hz, 1H), 2.93 (d, *J* = 2.1 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 142.1, 135.1, 133.4, 133.2, 128.7, 128.2, 127.8, 126.5, 126.5, 126.5, 124.7, 111.5, 82.9, 81.1, 79.3, 78.1, 27.8. HRMS (FI): $[M]^+$ calcd for $C_{20}H_{20}O_3^+$ 308.1412, found 308.1411.



(*E*)-*tert*-Butyl hex-3-en-5-yn-2-yl carbonate (**1n**)

Known compound[1]. Yellow oil, 67% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.19 (dd, *J* = 16.0, 6.3 Hz, 1H), 5.70 (ddd, *J* = 16.1, 2.3, 1.4 Hz, 1H), 5.16 (td, *J* = 6.5, 1.4 Hz, 1H), 2.90 (d, *J* = 2.3 Hz, 1H), 1.48 (s, 9H), 1.35 (d, *J* = 6.6 Hz, 3H).

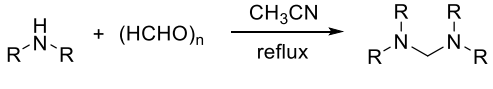
2.2 Synthesis of OAc-easter



24 **25**

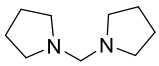
(*E*)-1-phenylpent-2-en-4-yn-1-ol (**25**). To a solution of **24** (10 mmol) in DCM (20 mL) were added DMAP (0.1 equiv), Et_3N (2.0 equiv) and Ac_2O (1.5 equiv) sequentially. The reaction mixture was then allowed to stir at room temperature for 12 hours. After this time, the resulting mixture was quenched with saturated aqueous NH_4Cl (10 mL), extracted with DCM (20 mL × 3), washed by brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was finally purified by flash column chromatography on silica gel (hexane/EtOAc = 20/1) to give **25** as a yellow oil in 96% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.35 (q, *J* = 6.5, 6.0 Hz, 5H), 6.37 – 6.29 (m, 2H), 5.73 – 5.68 (m, 1H), 2.93 (d, *J* = 1.9 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 142.3, 137.9, 128.8, 128.6, 127.3, 111.2, 81.1, 79.2, 75.0, 21.2. HRMS (FI): $[M]^+$ calcd for $C_{13}H_{12}O_2^+$ 200.0827, found 200.0832.

2.3 Synthesis of methanediamine nucleophiles



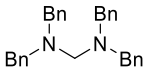
26 **2**

General procedure: to a solution of **26** (10 mmol) in CH_3CN (50 mL) was added paraformaldehyde (5 mmol). The reaction mixture was then allowed to stir under reflux for 4 hours. After this time, the resulting mixture was cooled to room temperature, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford **2**.



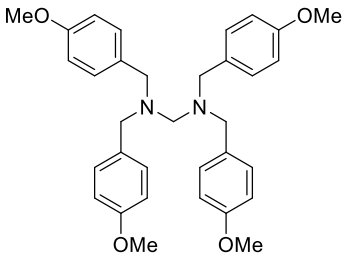
Di(pyrrolidin-1-yl)methane (**2c**)

Known compound[2]. Yellow oil, 77% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 3.22 (s, 2H), 2.58 (d, *J* = 6.3 Hz, 9H), 1.78 (d, *J* = 6.3 Hz, 8H).



***N,N,N′,N′*-Tetrabenzylmethanediamine** (**2e**)

Known compound[2]. White solid, 90% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.31 – 7.20 (m, 20H), 3.61 (s, 8H), 3.09 (s, 2H).

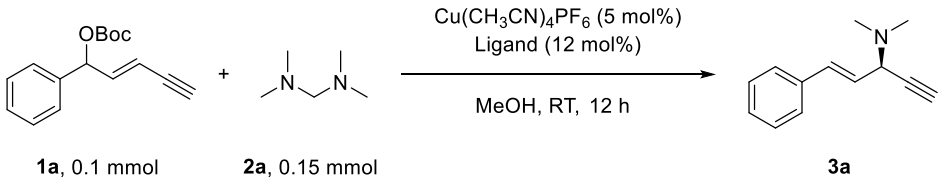


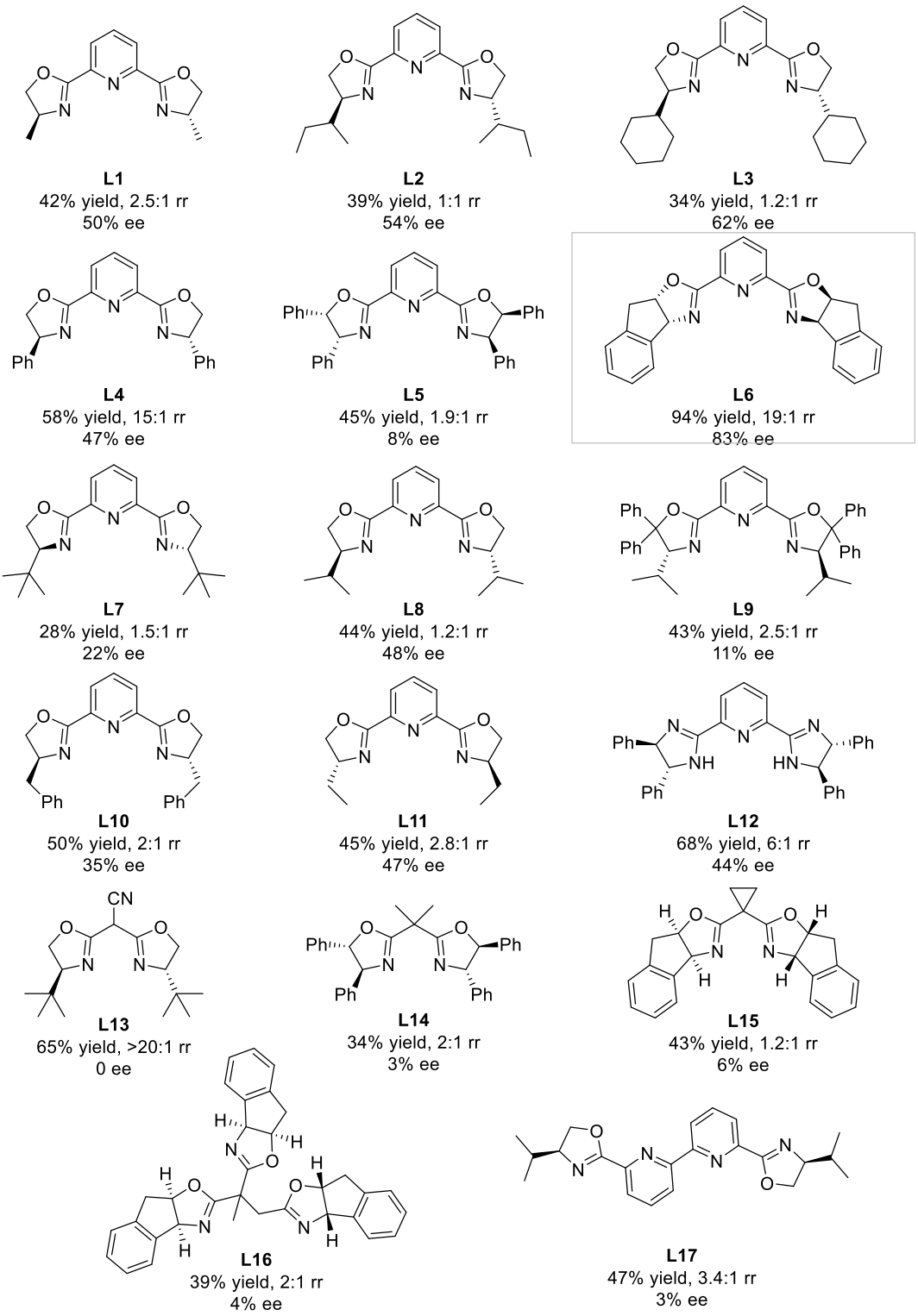
***N,N,N′,N′*-Tetrakis(4-methoxybenzyl)methanediamine (2f)**

Known compound[3]. White solid, 90% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.19 (d, *J* = 8.5 Hz, 8H), 6.80 (d, *J* = 8.5 Hz, 8H), 3.70 (s, 12H), 3.52 (s, 8H), 3.05 (s, 2H).

3. Development of reaction conditions

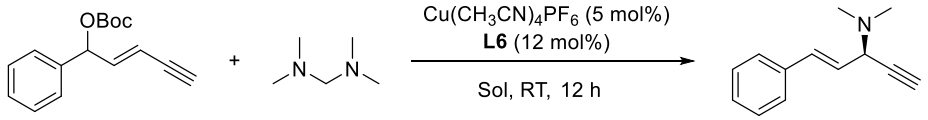
3.1 Evaluation of chiral ligands





The yields and rr values were determined by crude ^{1}H NMR. The ee values were determined by HPLC analysis.

3.2 Evaluation of solvents

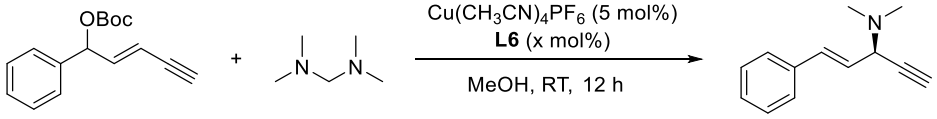


1a, 0.1 mmol **2a**, 0.15 mmol **3a**

Entry	Solvent	Yield	rr	ee
1	MeOH	94%	19:1	83%
2	EtOH	66%	13:1	72%
3	DCM	21%	>20:1	12%
4	MeCN	9%	1:2.6	70%
5	DCE	39%	3.5:1	10%
6	dioxane	41%	2.7:1	60%
7	MeOH:Tol = 2:5	77%	>20:1	80%

The yields and rr values were determined by crude ^{1}H NMR. The ee values were determined by HPLC analysis.

3.3 Evaluation of the ratios of catalysts

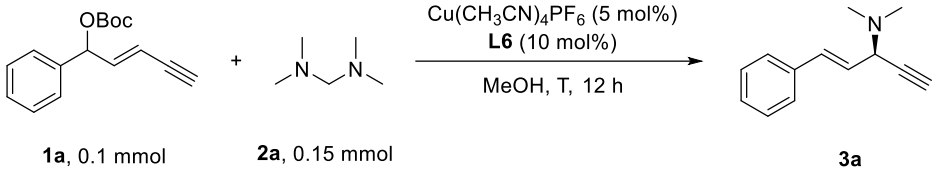


1a, 0.1 mmol **2a**, 0.15 mmol **3a**

Entry	x	Yield	rr	ee
1	3	94%	19:1	72%
2	6	95%	>20:1	82%
3	9	89%	>20:1	85%
4	10	90%	>20:1	86%
5	12	94%	19:1	83%

The yields and rr values were determined by crude ^{1}H NMR. The ee values were determined by HPLC analysis.

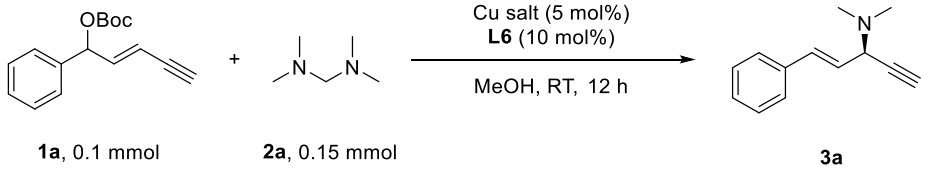
3.4 Evaluation of the temperatures



Entry	T	Yield	rr	ee
1	-20℃	72%	10:1	81%
2	-10℃	79%	>20:1	80%
3	0℃	77%	>20:1	83%
4	RT	90%	>20:1	86%
5	40℃	81%	>20:1	80%
6	60℃	55%	11:1	75%

The yields and rr values were determined by crude ^{1}H NMR. The ee values were determined by HPLC analysis.

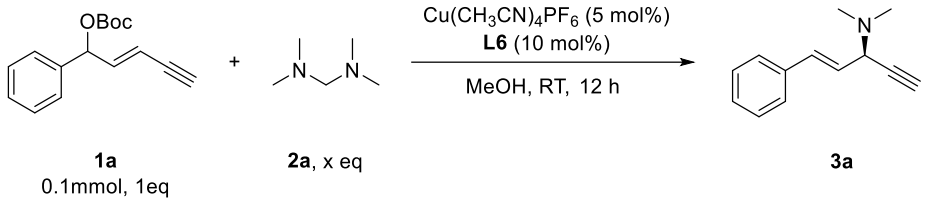
3.5 Evaluation of the copper sources



Entry	Cu salt	Yield	rr	ee
1	$Cu(CH_3CN)_4PF_6$	90%	>20:1	86%
2	$Cu(CH_3CN)_4BF_4$	66%	>20:1	82%
3	$Cu(CH_3CN)_4OTf$	76%	19:1	83%
4	$(CuOTf)_2Tol$	96%	>20:1	75%
5	Cu(TC)	76%	>20:1	81%
6	$Cu(OAc)_2{\cdot}H_2O$	77%	>20:1	81%

The yields and rr values were determined by crude ^{1}H NMR. The ee values were determined by HPLC analysis.

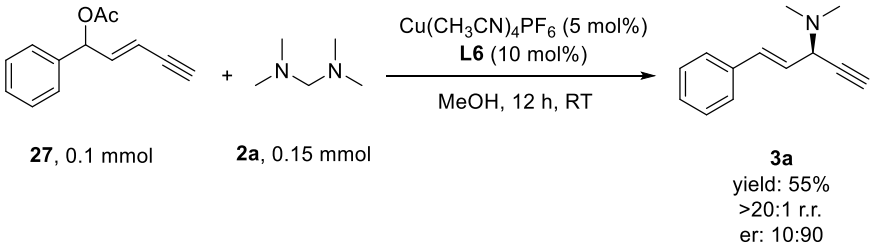
3.6 Evaluation of the ratios of reactants



Entry	x	Yield	rr	ee
1	1	65%	>20:1	84%
2	1.5	90%	>20:1	86%
3	2	70%	>20:1	78%
4	2.5	72%	>20:1	78%
5	5	65%	>20:1	68%

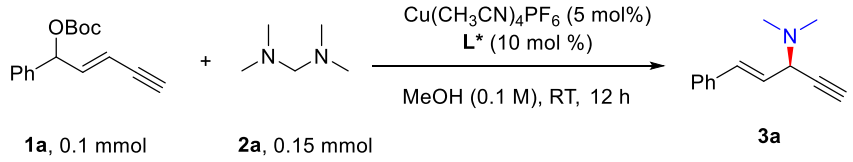
The yields and rr values were determined by crude ^{1}H NMR. The ee values were determined by HPLC analysis.

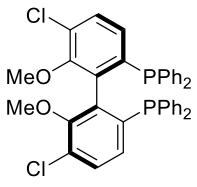
3.7 Evaluation of leaving groups



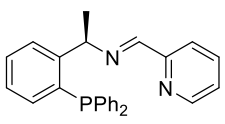
The yields and rr values were determined by crude ^{1}H NMR. The ee values were determined by HPLC analysis.

3.8 Evaluation of additional chiral ligands





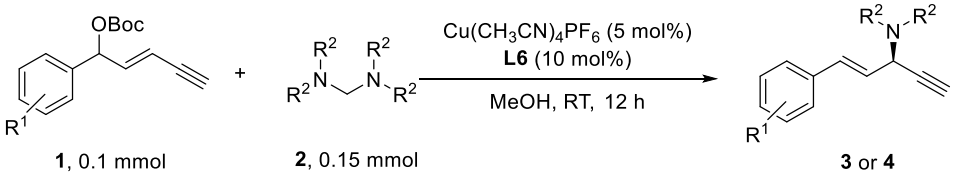
L18
47% yield
3.3:1 rr, 58% er



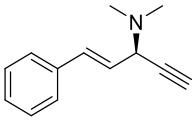
Hu's ligand

L19
43% yield
2:1 rr, 2% er

4. General procedure for Cu-catalyzed alkynylallylic dimethylamination

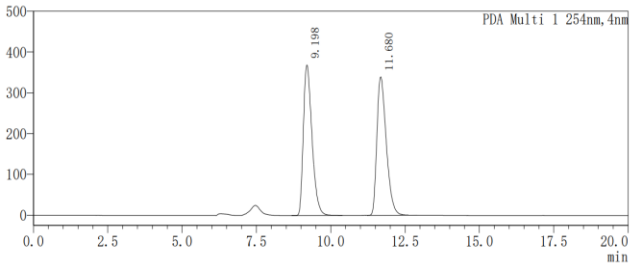


General procedure: In a N_2-filled glovebox, $Cu(CH_3CN)_4PF_6$ (1.9 mg, 0.005 mmol), **L6** (3.9 mg, 0.010 mmol) and anhydrous MeOH (0.5 mL) were added sequentially to a 4 ml vial. The reaction mixture was then allowed to stir at room temperature for 1 h, followed by the addition of enyne **1** (0.10 mmol) and nucleophiles **2** (0.15 mmol). The reaction was allowed to stir at room temperature for 12 h. After this time, the reaction was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford product **3** or **4**.

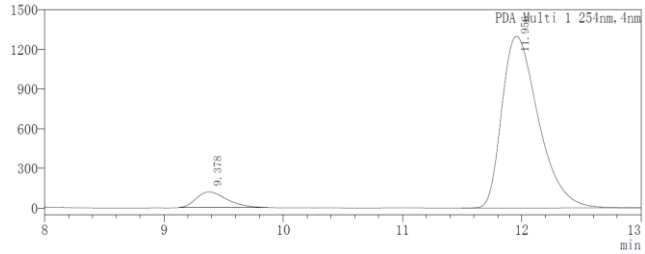


(*R*,*E*)-*N*,*N*-Dimethyl-1-phenylpent-1-en-4-yn-3-amine (**3a**)

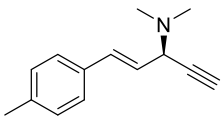
Yellow oil, 90% yield, >20:1 rr. $[\alpha]_D^{25}$ +3.2 (*c* 1.0, $CHCl_3$) for 93:7 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.44 – 7.39 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.22 (m, 1H), 6.85 (dd, *J* = 15.9, 1.6 Hz, 1H), 6.22 (dd, *J* = 15.9, 5.0 Hz, 1H), 4.23 (dt, *J* = 4.4, 1.9 Hz, 1H), 2.52 (d, *J* = 2.2 Hz, 1H), 2.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 132.8, 128.7, 127.9, 127.2, 126.7, 78.2, 76.0, 59.3, 41.4. HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{16}N^+$ 186.5708, found 186.5709. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 24.2 min (minor), 33.8 min (major).



Entry	Retention time/min	Area	Area%
1	9.198	7475618	50.038
2	11.680	7464228	49.962

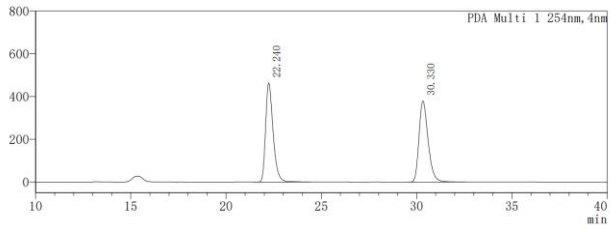


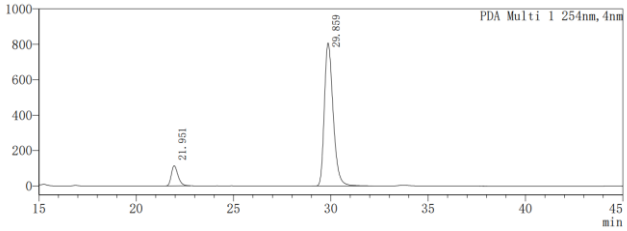
Entry	Retention time/min	Area	Area%
1	9.378	2116105	7.128
2	11.956	27569262	92.872



(*R*,*E*)-*N*,*N*-Dimethyl-1-(p-tolyl)pent-1-en-4-yn-3-amine (**3b**)

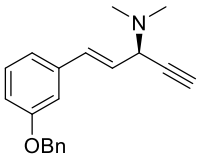
Yellow oil, 93% yield, >20:1 rr. $[\alpha]_D^{25}$ +3.0 (*c* 0.40, $CHCl_3$) for 90:10 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.86 – 6.76 (m, 1H), 6.16 (dd, *J* = 15.9, 5.1 Hz, 1H), 4.24 – 4.17 (m, 1H), 2.51 (d, *J* = 2.2 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 133.8, 132.7, 129.4, 126.6, 126.1, 78.4, 75.9, 59.3, 41.4, 21.3. HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{18}N^+$ 200.1351, found 200.1359. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 22.0 min (minor), 29.8 min (major).





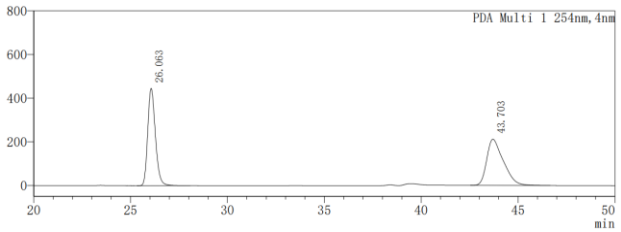
Entry	Retention time/min	Area	Area%
1	22.240	12680045	50.148
2	30.330	12605275	49.852

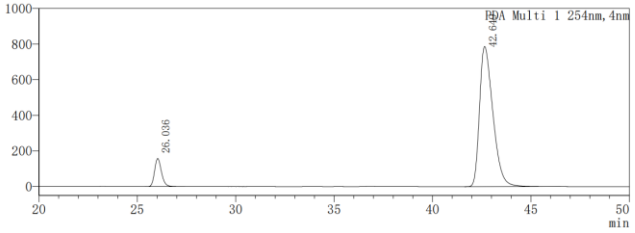
Entry	Retention time/min	Area	Area%
1	21.951	2696117	9.636
2	29.859	25284868	90.364



(*R*,*E*)-1-(3-(Benzyloxy)phenyl)-*N*,*N*-dimethylpent-1-en-4-yn-3-amine (**3c**)

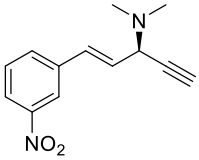
Colorless oil, 90% yield, >20:1 rr. $[\alpha]_D^{25}$ +14 (*c* 0.90, $CHCl_3$) for 91:9 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.38 (ddd, *J* = 25.1, 17.0, 7.0 Hz, 5H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.91 – 6.77 (m, 2H), 6.21 (dd, *J* = 15.9, 4.9 Hz, 1H), 5.07 (s, 2H), 4.25 – 4.19 (m, 1H), 2.52 (s, 1H), 2.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 138.1, 137.0, 132.7, 129.7, 128.7, 128.0, 127.7, 127.6, 119.7, 114.5, 112.9, 78.2, 76.0, 70.0, 59.2, 41.4. HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{21}NO^+$ 292.1696, found 292.1690. HPLC analysis: chiral AD-H + AD-H column (the two columns were connected to each other in this order); detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 26.0 min (minor), 42.6 min (major).





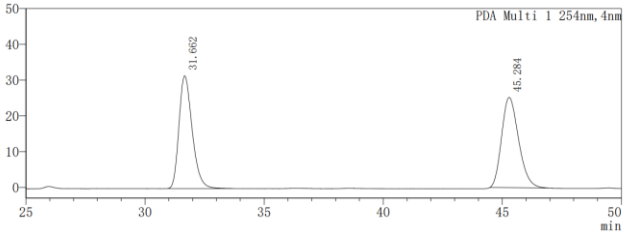
Entry	Retention time/min	Area	Area%
1	26.063	12256426	49.371
2	43.703	12568767	50.629

Entry	Retention time/min	Area	Area%
1	26.036	3868408	9.418
2	42.649	37206613	90.582

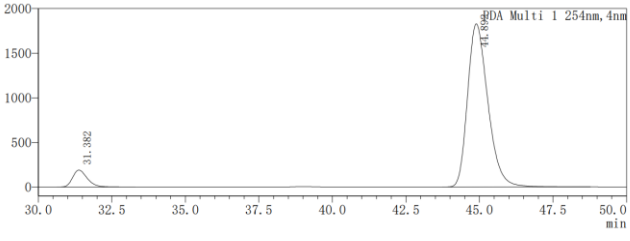


(*R*,*E*)-*N*,*N*-Dimethyl-1-(3-nitrophenyl)pent-1-en-4-yn-3-amine (**3d**)

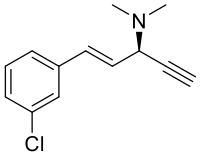
Yellow oil, 89% yield, >20:1 rr. $[\alpha]_D^{25}$ +3.3 (*c* 1.2, $CHCl_3$) for 93:7 er. ^1H NMR (400 MHz, chloroform-*d*) δ 8.26 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.37 (dd, *J* = 15.9, 4.8 Hz, 1H), 4.32 – 4.22 (m, 1H), 2.56 (d, *J* = 2.2 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 138.3, 132.4, 130.8, 130.6, 129.6, 122.4, 121.4, 77.6, 76.5, 59.1, 41.5. HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{15}N_2O_2^+$ 231.1128, found 231.1130. HPLC analysis: chiral AD-H + AD-H column (the two columns were connected to each other in this order); detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 31.4 min (minor), 44.9 min (major).



Entry	Retention time/min	Area	Area%
1	31.662	1219896	49.320
2	45.284	1253524	50.680

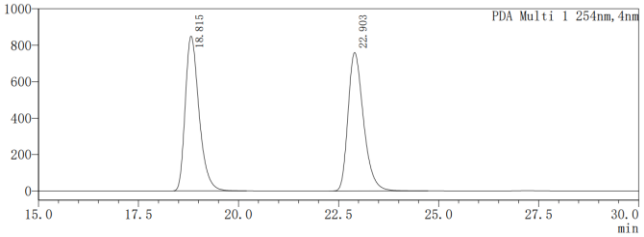


Entry	Retention time/min	Area	Area%
1	31.382	6530209	6.914
2	44.892	87925179	93.086

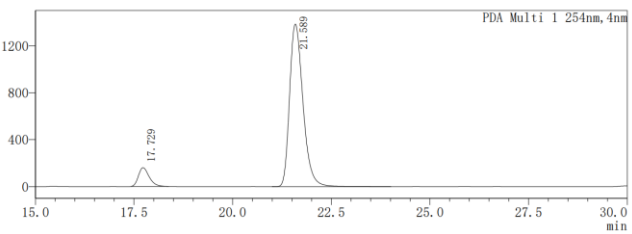


(*R*,*E*)-1-(3-Chlorophenyl)-*N*,*N*-dimethylpent-1-en-4-yn-3-amine (**3e**)

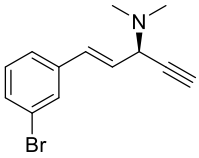
Colorless oil, 76% yield, >20:1 rr. $[\alpha]_D^{25}$ -0.22 (*c* 0.46, $CHCl_3$) for 92:8 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.39 (s, 1H), 7.31 – 7.19 (m, 3H), 6.80 (d, *J* = 16.1 Hz, 1H), 6.23 (dd, *J* = 15.9, 4.9 Hz, 1H), 4.25 – 4.19 (m, 1H), 2.53 (d, *J* = 1.9 Hz, 1H), 2.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.4, 134.6, 131.6, 129.9, 128.8, 127.8, 126.7, 124.8, 77.9, 76.2, 59.2, 41.4. HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{15}NCl^+$ 220.0888, found 220.0885. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 18.8 min (minor), 22.9 min (major).



Entry	Retention time/min	Area	Area%
1	18.815	20332363	49.833
2	22.903	20468743	50.167

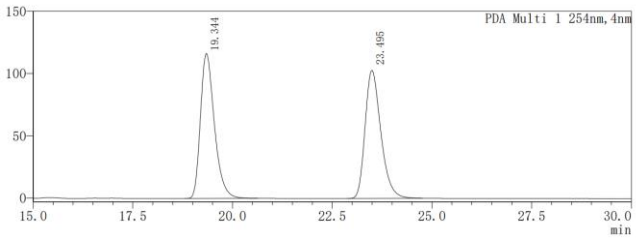


Entry	Retention time/min	Area	Area%
1	17.729	3003420	8.415
2	21.589	32687034	91.585

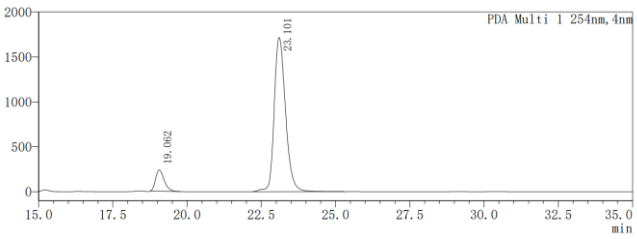


(*R*,*E*)-1-(3-Bromophenyl)-*N*,*N*-dimethylpent-1-en-4-yn-3-amine (**3f**)

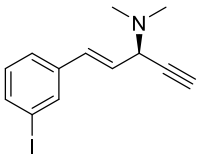
Yellow oil, 93% yield, >20:1 rr. $[\alpha]_D^{25}$ -41.0 (*c* 0.49, $CHCl_3$) for 91:9 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.76 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 4.9 Hz, 1H), 4.26 – 4.16 (m, 1H), 2.52 (s, 1H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 131.4, 130.7, 130.2, 129.7, 128.9, 125.2, 122.8, 77.9, 76.2, 59.1, 41.4. HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{15}NBr^+$ 264.0382, found 264.0378. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 19.1 min (minor), 23.1 min (major).



Entry	Retention time/min	Area	Area%
1	19.344	2833930	50.056
2	23.495	2827617	49.944

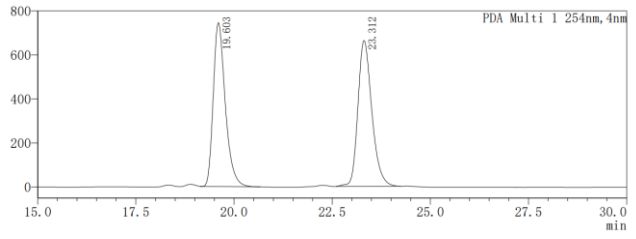


Entry	Retention time/min	Area	Area%
1	19.062	4778243	9.493
2	23.101	45555276	90.507

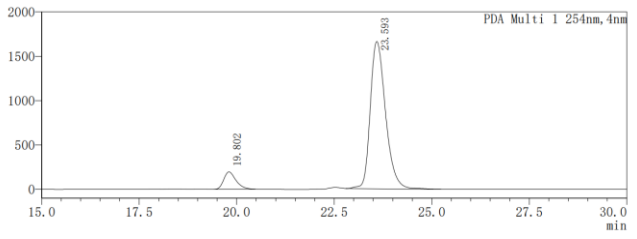


(*R*,*E*)-1-(3-Iodophenyl)-*N*,*N*-dimethylpent-1-en-4-yn-3-amine (**3g**)

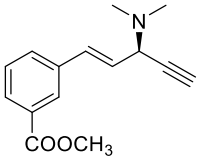
Yellow oil, 67% yield, >20:1 rr. $[\alpha]_D^{25}$ +5.7 (*c* 1.2, $CHCl_3$) for 91:9 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.76 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 4.9 Hz, 1H), 4.25 – 4.18 (m, 1H), 2.52 (s, 1H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 136.7, 135.7, 131.3, 130.3, 128.8, 125.8, 94.7, 78.0, 76.2, 59.1, 41.4. HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{15}NI^+$ 312.0243, found 312.0241. HPLC analysis: chiral AD-H; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 23.6 min (major), 19.8 min (minor).



Entry	Retention time/min	Area	Area%
1	19.603	15860691	49.289
2	23.312	16318338	50.711

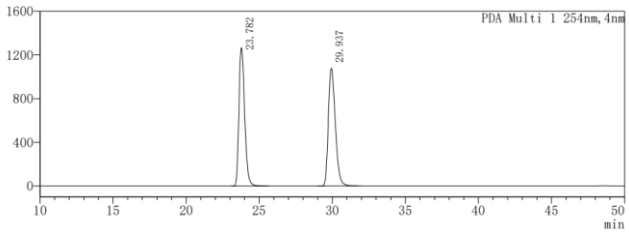


Entry	Retention time/min	Area	Area%
1	19.802	4281166	8.634
2	23.593	45302183	91.366

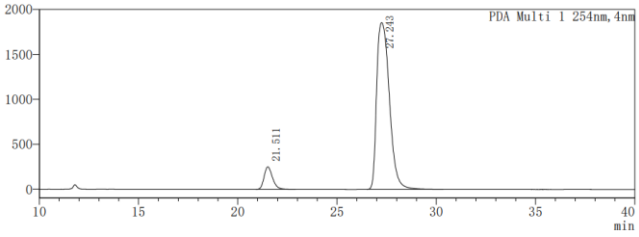


Methyl (*R*,*E*)-3-(3-(dimethylamino)pent-1-en-4-yn-1-yl)benzoate (**3h**)

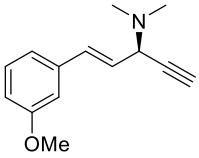
Colorless oil, 80% yield, >20:1 rr. $[\alpha]_D^{25}$ +2.3 (*c* 0.60, $CHCl_3$) for 92:8 er. ^1H NMR (400 MHz, chloroform-*d*) δ 8.09 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 15.9, 4.9 Hz, 1H), 4.25 (d, *J* = 4.9 Hz, 1H), 3.92 (s, 3H), 2.55 (d, *J* = 2.1 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 136.8, 131.9, 130.9, 130.6, 128.9, 128.8, 128.5, 127.9, 77.9, 76.3, 59.2, 52.2, 41.4. HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{18}NO_2^+$ 244.1332, found 244.1333. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 27.2 min (major), 21.5 min (minor).



Entry	Retention time/min	Area	Area%
1	23.782	34584378	49.093
2	29.937	35861921	50.907

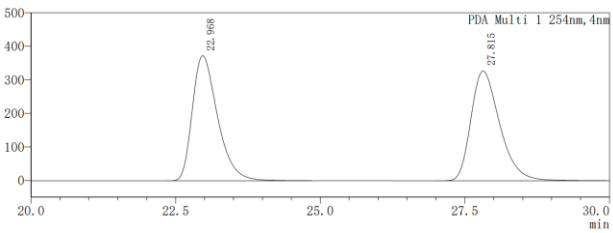


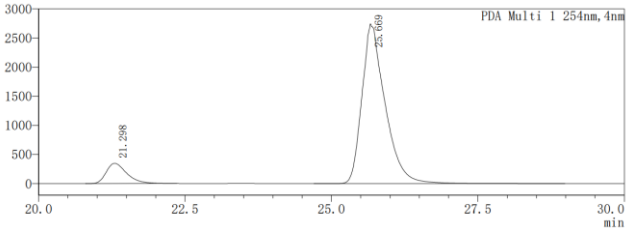
Entry	Retention time/min	Area	Area%
1	21.511	7396641	8.238
2	27.243	82389731	91.762



(*R*,*E*)-1-(3-Methoxyphenyl)-*N*,*N*-dimethylpent-1-en-4-yn-3-amine (**3i**)

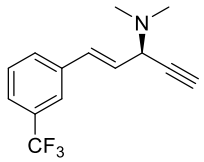
Yellow oil, 75% yield, >20:1 rr. [α]D25 +12.1 (c 0.38, CHCl3) for 90:10 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.22 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.95 (s, 1H), 6.85 – 6.77 (m, 2H), 6.21 (dd, *J* = 15.9, 5.0 Hz, 1H), 4.27 – 4.18 (m, 1H), 3.81 (s, 3H), 2.52 (d, *J* = 2.0 Hz, 1H), 2.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 138.0, 132.8, 129.6, 127.5, 119.4, 113.7, 111.8, 78.2, 76.1, 59.2, 55.3, 41.4. HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{17}NO^+$ 216.1381, found 216.1384. HPLC analysis: chiral AD-H + AD-H column (the two columns were connected to each other in this order); detected at 254 nm, 40 ℃, flow = 0.7 mL/min, n-hexane: *i*-PrOH = 95:5; Retention time: 21.3 min (minor), 25.7 min (major).





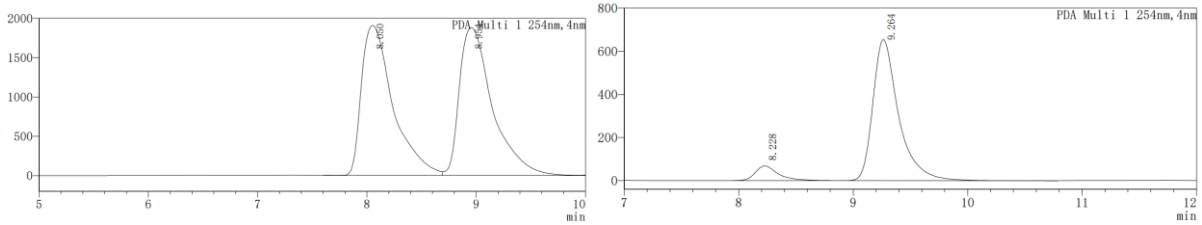
Entry	Retention time/min	Area	Area%
1	22.968	11325858	49.970
2	27.815	11339566	50.030

Entry	Retention time/min	Area	Area%
1	21.298	8480791	10.133
2	25.669	75211051	89.867



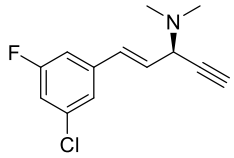
(*R*,*E*)-*N*,*N*-Dimethyl-1-(3-(trifluoromethyl)phenyl)pent-1-en-4-yn-3-amine (**3j**)

Yellow oil, 64% yield, >20:1 rr. $[\alpha]_D^{25}$ +27.1 (*c* 0.14, $CHCl_3$) for 92:8 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.65 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 15.9 Hz, 1H), 6.30 (dd, *J* = 15.9, 4.8 Hz, 1H), 4.29 – 4.20 (m, 1H), 2.54 (s, 1H), 2.32 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 131.5, 131.1 (q, J_{CF} = 31.5 Hz), 129.7, 129.4, 129.3, 124.4 (d, J_{CF} = 2.5 Hz), 123.5 (d, J_{CF} = 2.5 Hz), 77.8, 76.4, 59.1, 41.5 (the carbon signal of CF_3 was not observed). ^{19}F NMR (376 MHz, $CDCl_3$) δ -49.47 (s, 3F). HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{17}NO^+$ 253.1078, found 253.1076. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 8.2 min (minor), 9.3 min (major).



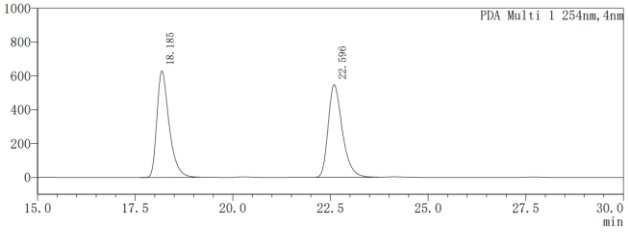
Entry	Retention time/min	Area	Area%
1	8.050	38299273	49.170
2	8.954	39592958	50.830

Entry	Retention time/min	Area	Area%
1	8.228	945953	8.475
2	9.264	10215590	91.525

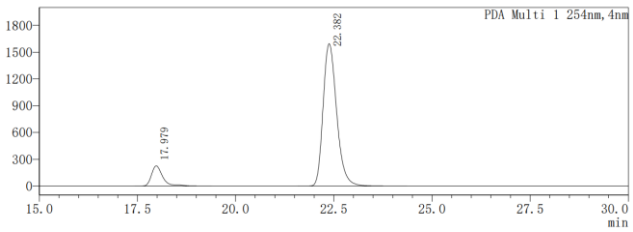


(*R*,*E*)-1-(3-Chloro-5-fluorophenyl)-*N*,*N*-dimethylpent-1-en-4-yn-3-amine (**3k**)

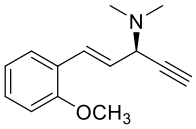
Yellow oil, 71% yield, >20:1 rr. $[\alpha]_D^{25}$ +5.7 (*c* 1.75, $CHCl_3$) for 89:11 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.18 (s, 1H), 6.99 (t, *J* = 9.3 Hz, 2H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 4.7 Hz, 1H), 4.26 – 4.18 (m, 1H), 2.53 (s, 1H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 249.5 Hz), 139.9 (d, J_{CF} = 8.1 Hz), 135.2 (d, J_{CF} = 11.1 Hz), 130.6 (d, J_{CF} = 3.0 Hz), 130.4, 122.9 (d, J_{CF} = 3.0 Hz), 115.4 (d, J_{CF} = 25.2 Hz), 111.7 (d, J_{CF} = 21.1 Hz), 77.7, 76.4, 59.0, 41.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.01 (s, 1F). HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{17}NO^+$ 237.0721, found 237.0722. HPLC analysis: chiral AD-H + AD-H column (the two columns were connected to each other in this order); detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 18.0 min (minor), 22.4 min (major).



Entry	Retention time/min	Area	Area%
1	18.185	13685797	49.675
2	22.596	13865074	50.325

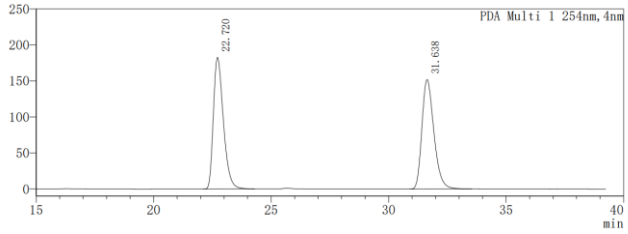


Entry	Retention time/min	Area	Area%
1	17.979	4553629	10.643
2	22.382	38232590	89.357

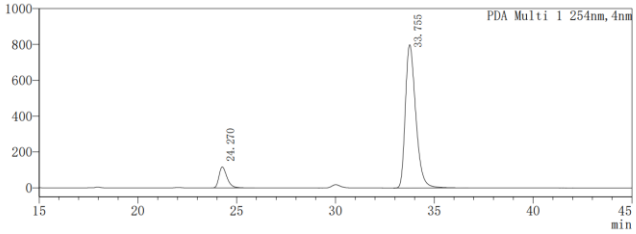


(*R*,*E*)-1-(2-Methoxyphenyl)-*N*,*N*-dimethylpent-1-en-4-yn-3-amine (**3l**)

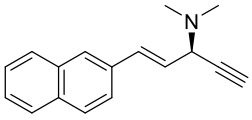
Yellow oil, 86% yield, >20:1 rr. $[\alpha]_D^{25}$ +9.0 (*c* 0.50, $CHCl_3$) for 90:10 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 14.9 Hz, 1H), 6.96 – 6.84 (m, 2H), 6.26 (dd, *J* = 16.0, 5.2 Hz, 1H), 4.26 – 4.18 (m, 1H), 3.85 (s, 3H), 2.51 (d, *J* = 2.1 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 157.0, 128.9, 127.9, 127.9, 127.4, 125.6, 120.7, 111.0, 78.6, 75.8, 59.7, 55.5, 41.5. HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{17}NO^+$ 216.1381, found 216.1383. HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 24.2 min (minor), 33.8 min (major).



Entry	Retention time/min	Area	Area%
1	22.720	5429929	50.107
2	31.638	5406632	49.893



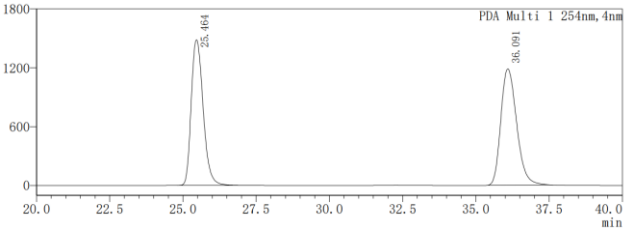
Entry	Retention time/min	Area	Area%
1	24.270	3290177	10.115
2	33.755	29238438	89.885

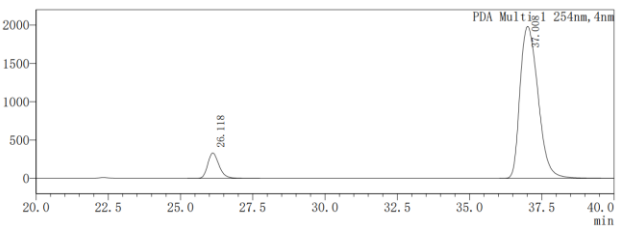


(*R*,*E*)-*N*,*N*-Dimethyl-1-(naphthalen-2-yl)pent-1-en-4-yn-3-amine (3m)

Yellow solid, 90% yield, >20:1 rr. $[\alpha]_D^{25}$ +21.1 (*c* 0.56, $CHCl_3$) for 91:9 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.87 – 7.75 (m, 4H), 7.62 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.02 (dd, *J* = 15.9, 1.6 Hz, 1H), 6.35 (dd, *J* = 15.9, 5.0 Hz, 1H), 4.29 (dt, *J* = 4.4, 1.9 Hz, 1H), 2.56 (d, *J* = 2.2 Hz, 1H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 134.0, 133.6, 133.2, 132.9, 128.3, 128.1, 127.7, 127.6, 126.8, 126.4, 126.0, 123.7, 78.3, 76.1, 59.4, 41.5. HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{17}NO^+$ 216.1381, found 216.1383. HPLC analysis: chiral AD-H + AD-H column (the two columns were

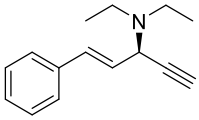
connected to each other in this order); detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 26.1 min (minor), 37.0 min (major).





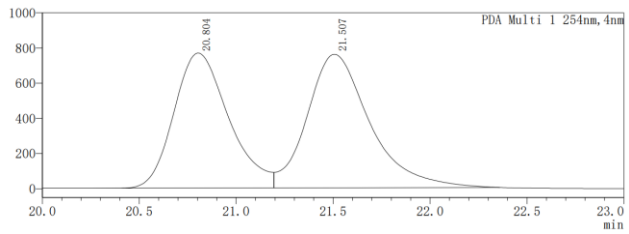
Entry	Retention time/min	Area	Area%
1	25.464	41964203	48.555
2	36.091	44461096	51.445

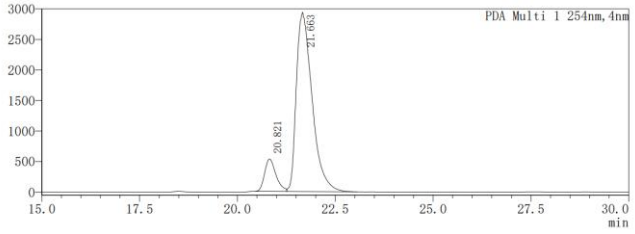
Entry	Retention time/min	Area	Area%
1	26.118	8995045	9.471
2	37.008	85978841	90.529



(*R*,*E*)-*N*,*N*-Diethyl-1-phenylpent-1-en-4-yn-3-amine (**4a**)

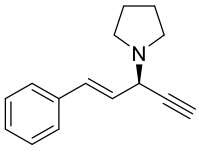
Known compound[1]. Yellow oil, 66% yield, >20:1 rr. $[\alpha]_D^{25}$ +4.8 (*c* 0.15, $CHCl_3$) for 89:11 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.41 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 4.5 Hz, 1H), 4.45 (s, 1H), 2.72 (dt, *J* = 13.3, 7.3 Hz, 2H), 2.54 – 2.41 (m, 3H), 1.10 (t, *J* = 7.1 Hz, 6H). HPLC analysis: chiral AD-H + AD-H column (the two columns were connected to each other in this order); detected at 254 nm, 40 ℃, flow = 0.5 mL/min, *n*-hexane: *i*-PrOH = 99:1; Retention time: 21.7 min (major), 20.8 min (minor).





Entry	Retention time/min	Area	Area%
1	20.804	15092269	46.997
2	21.507	17020943	53.003

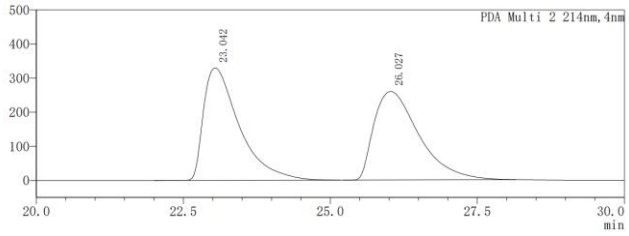
Entry	Retention time/min	Area	Area%
1	20.821	10664530	11.484
2	21.663	82201607	88.516



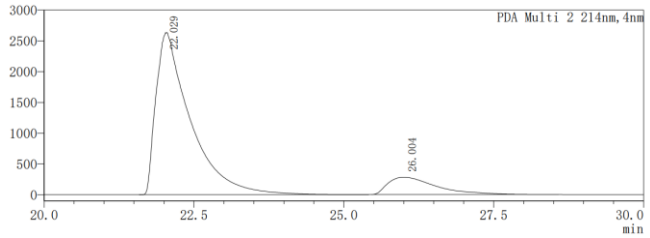
(*R*,*E*)-1-(1-Phenylpent-1-en-4-yn-3-yl)pyrrolidine (**4b**)

Yellow oil, 91% yield, >20:1 rr. $[\alpha]_D^{25}$ +12 (*c* 0.45, $CHCl_3$) for 87:13 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.40 (m, *J* = 7.3 Hz, 2H), 7.32 (m, *J* = 7.4 Hz, 2H), 7.23 (m, *J* = 7.1 Hz, 1H), 6.82 (d, *J* = 15.9 Hz, 1H), 6.29 (dd, *J* = 15.8, 5.7 Hz, 1H), 4.38 – 4.31 (m, 1H), 2.70 (dt, *J* = 13.5, 6.8 Hz, 4H), 2.47 (d, *J* = 2.0 Hz, 1H), 1.82 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 132.1, 128.6, 127.8, 127.6, 126.7, 79.8, 75.0, 55.9, 49.8, 23.5. HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{18}N^+$ 212.0244, found 212.0240. HPLC analysis: chiral OJ-H + OJ-H column (the two columns were connected to each other

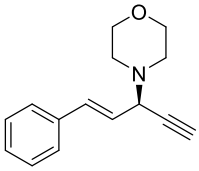
in this order); detected at 214 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 97:3; Retention time: 22.0 min (major), 26.0 min (minor).



Entry	Retention time/min	Area	Area%
1	23.042	13965692	50.162
2	26.027	13875656	49.838

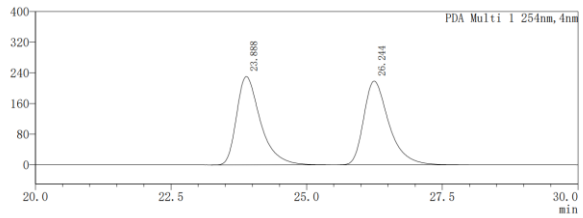


Entry	Retention time/min	Area	Area%
1	22.029	105645225	87.053
2	26.004	15712811	12.947

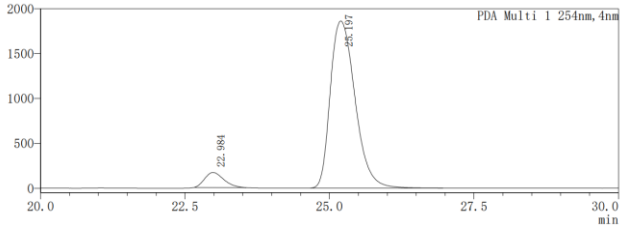


(*R*,*E*)-4-(1-Phenylpent-1-en-4-yn-3-yl)morpholine (**4c**)

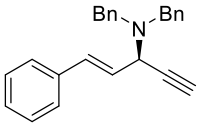
Known compound[1]. Yellow oil, 84% yield, >20:1 rr. $[\alpha]_D^{25}$ +12 (*c* 0.64, $CHCl_3$) for 94:6 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 14.3 Hz, 1H), 6.86 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 5.2 Hz, 1H), 4.22 – 4.16 (m, 1H), 3.81 – 3.69 (m, 4H), 2.75 – 2.48 (m, 5H). HPLC analysis: chiral AD-H column; detected at 254 nm, 40 ℃, flow = 0.5 mL/min, *n*-hexane: *i*-PrOH = 95:5; Retention time: 25.2 min (major), 23.0 min (minor).



Entry	Retention time/min	Area	Area%
1	23.888	7072789	50.039
2	26.244	7061756	49.961

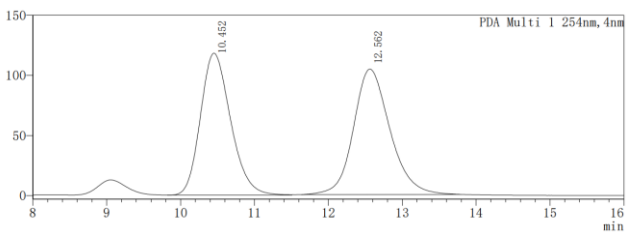


Entry	Retention time/min	Area	Area%
1	22.984	3838870	6.474
2	25.197	55457336	93.526

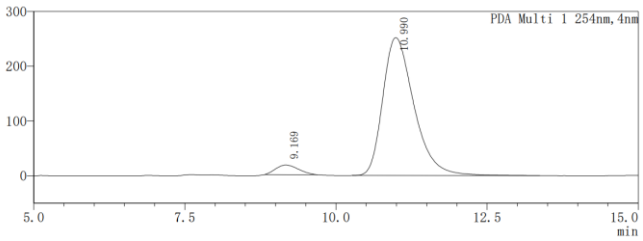


(*R*,*E*)-*N*,*N*-Dibenzyl-1-phenylpent-1-en-4-yn-3-amine (**4d**)

Known compound[1]. White solid, 91% yield, >20:1 rr. $[\alpha]_D^{25}$ -9.7 (*c* 0.60, $CHCl_3$) for 95:5 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.45 – 7.18 (m, 15H), 6.90 (dd, *J* = 16.0, 1.8 Hz, 1H), 6.21 (dd, *J* = 15.9, 4.3 Hz, 1H), 4.35 – 4.25 (m, 1H), 3.86 (d, *J* = 13.7 Hz, 2H), 3.47 (d, *J* = 13.7 Hz, 2H), 2.58 (d, *J* = 2.2 Hz, 1H). HPLC analysis: chiral OJ-H column; detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 97:3; Retention time: 11.0 min (major), 9.17 min (minor).



Entry	Retention time/min	Area	Area%
1	10.452	3355798	48.381
2	12.562	3580325	51.619



Entry	Retention time/min	Area	Area%
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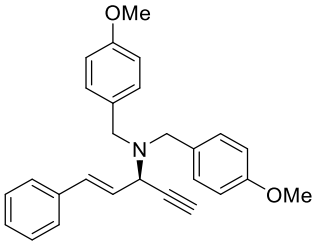
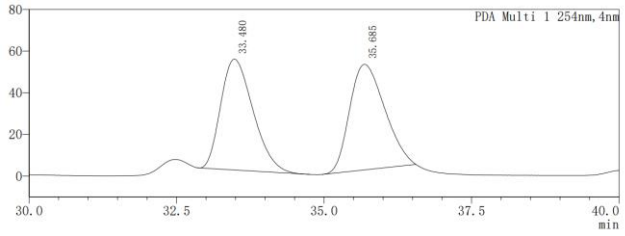
2	10.990	9044140	95.225



(*R*,*E*)-*N*,*N*-Bis(4-methoxybenzyl)-1-phenylpent-1-en-4-yn-3-amine (**4e**)

White solid, 50% yield, >20:1 rr. $[\alpha]_D^{25}$ -36 (*c* 1.0, $CHCl_3$) for 96:4 er. ^1H NMR (400 MHz, chloroform-*d*) δ 7.39 – 7.18 (m, 9H), 6.91 – 6.82 (m, 5H), 6.18 (dd, *J* = 16.0, 4.4 Hz, 1H), 4.30 (dt, *J* = 4.2, 2.1 Hz, 1H), 3.79 (s, 8H), 3.37 (d, *J* = 13.4 Hz, 2H), 2.57 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6, 136.7, 132.7, 128.9, 128.6, 128.4, 128.1, 127.7, 127.1, 126.6, 79.0, 75.7, 54.7, 53.7. (one carbon signal was not observed). HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{28}NO_2^+$ 398.2114, found 398.2107. HPLC analysis: chiral OD-H + OD-H column (the two columns were connected to each other in this order); detected at 254 nm, 40 ℃, flow = 0.7 mL/min, *n*-hexane: *i*-PrOH = 99:1; Retention time: 34.8 min (major), 33.2 min (minor).



Entry	Retention time/min	Area	Area%
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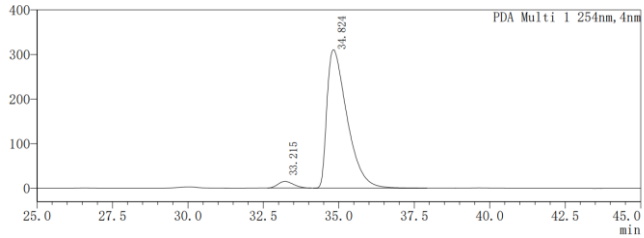
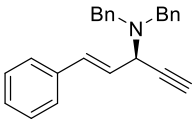
2	35.685	2096771	50.739



Entry	Retention time/min	Area	Area%
1	33.215	528586	3.540
2	34.824	14401417	96.460

5. Determination of absolute configuration

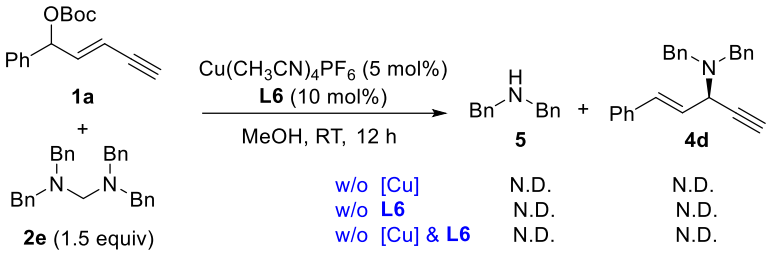


4d

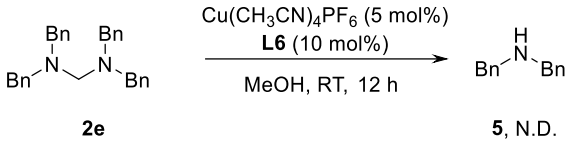
Compounds **4d** are known compounds[1]. By comparing the corresponding data of optical rotation and HPLC spectra under similar conditions, the absolute configuration of compound **4d** was determined to be (*R*)-**4d**.

6. Control experiments and Mechanistic studies

6.1 Control experiments

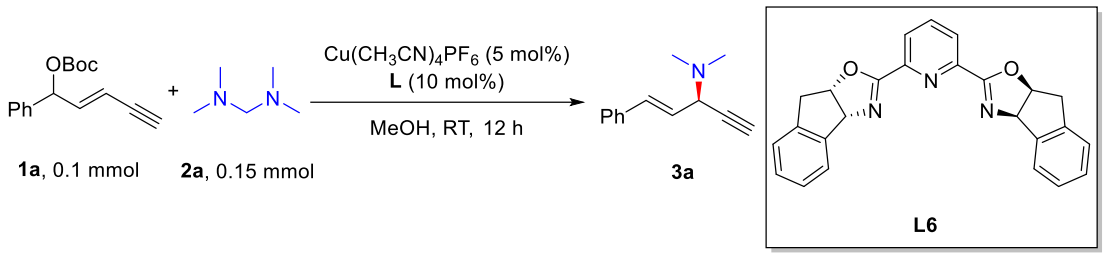


The procedure for these control experiments were same to that described in section 4 titled "General procedure for Cu-catalyzed alkynylallylic dimethylamination", except that special requirements were followed for each case. For all these cases, no amine **5** and product **4d** were detected.

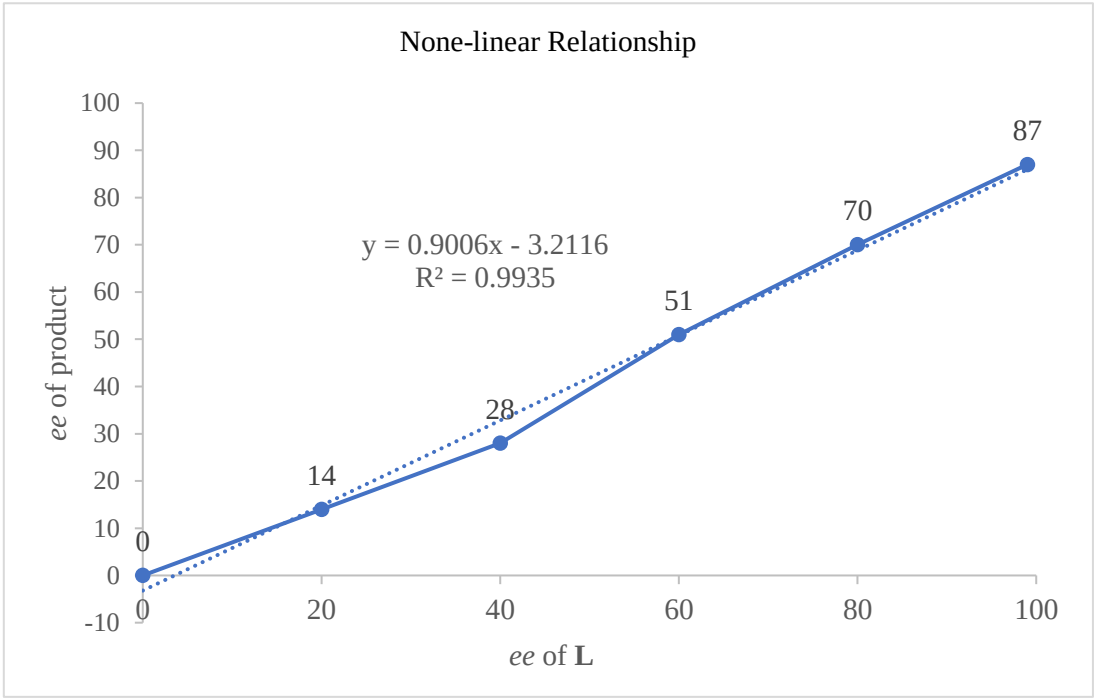


The procedure for this experiment was same to that described in section 4 titled "General procedure for Cu-catalyzed alkynylallylic dimethylamination", except that electrophile **1a** was not used. After the reaction time, no amine **5** was detected.

6.2 Non-linear effect experiments



Entry	ee of **L6** (%)	Yield of **3a** (%)	ee of **3a** (%)
1	0	76%	0
2	20	65%	14
3	40	74%	28
4	60	73%	51
5	80	87%	70
6	99	92%	87



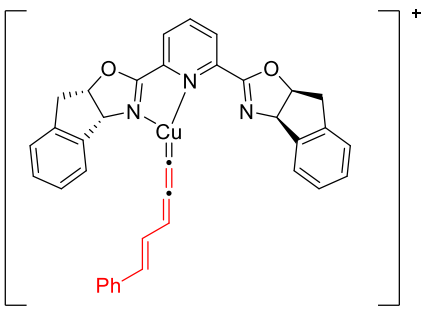
The procedure for these experiments were same to that described in section 4 titled “General procedure for Cu-catalyzed alkynylallylic dimethylamination”, except that special requirements for substrates and ligands were followed for each case.

7. Computational details

7.1 Computational methods

All density functional theory (DFT) calculations were performed using the Gaussian 09 software package[4]. Geometries were optimized using the B3LYP functional and Grimme's D3(BJ) dispersion correction with the basis set of SDD for all atoms. Vibrational frequencies were calculated for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. Solvation energy corrections were calculated in methanol solvent with the SMD continuum solvation model based on the gas phase optimized geometries. The BP86 functional with the basis set of def2-TZVP for all atoms was used for single-point energy calculations. The DFRT analysis based on the Hirshfeld charge calculation were obtained by Multiwfn 3.8 (dev)[5, 6]. The isosurface picture was rendered by VMD.

7.2 Cartesian coordinates of optimized structures



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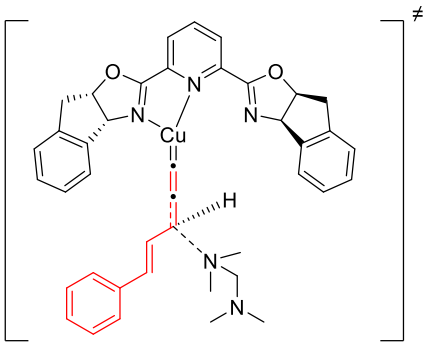

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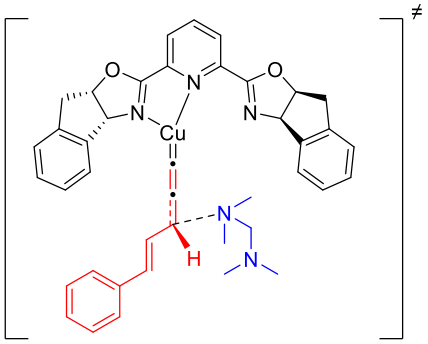

TS 1

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H	-1.09540263	1.25825085	-0.31850000
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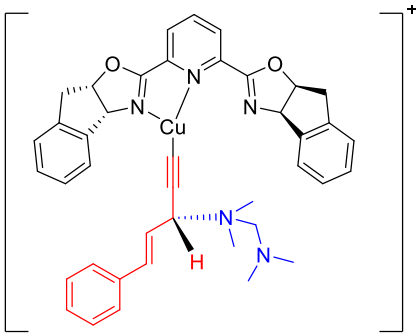
C	0.49237837	-0.95405715	-0.57237300
N	1.33853737	-1.90994915	-0.73950600
C	3.90086037	1.71436985	1.39628900
N	4.68683237	0.72415685	1.57139300
C	5.71630137	2.82094085	2.15994300
C	5.99992837	1.32097785	1.86426200

H	5.66633337	3.08146485	3.22014200
N	2.10046637	0.45676685	0.43565100
O	4.36740637	2.97552785	1.62120100
O	-0.77295063	-1.16699415	-0.94659900
H	6.46996237	0.79540985	2.70099900
Cu	3.18064637	-1.91009815	-0.12257400
C	0.33765037	2.62148185	0.57774200
H	-0.34382863	3.46400685	0.63438600
C	0.59195137	-3.07994515	-1.25705000
H	1.09328637	-3.45259415	-2.15433800
C	0.39152937	-4.13795115	-0.19630300
C	1.37019537	-4.88900115	0.45287600
C	-0.96217863	-4.27978215	0.12160100
C	0.97190337	-5.79190315	1.44019700
H	2.42036737	-4.76698515	0.20234600
C	-1.35745063	-5.18456315	1.10613600
C	-0.38213863	-5.93710015	1.76408400
H	1.71681737	-6.38841115	1.95837400
H	-2.40712563	-5.30581415	1.35874900
H	-0.67836363	-6.64459715	2.53284000
C	-1.83622963	-3.39239415	-0.73760300
H	-2.52588863	-2.76721715	-0.16071400
H	-2.44593263	-3.98208315	-1.43290400
C	-0.84019063	-2.51856115	-1.51767400
H	-1.09641663	-2.38848315	-2.56966500
C	6.87055637	1.36626185	0.62334600
C	7.18052237	0.31714885	-0.24033900
C	7.29536737	2.67132585	0.35638500
C	7.98906537	0.57828685	-1.34959700
H	6.75014437	-0.66565615	-0.08056700
C	8.10393337	2.92995285	-0.75017300
C	8.46038137	1.87388885	-1.59305600
H	8.22961937	-0.22265315	-2.04402500
H	8.44028037	3.94026185	-0.96647700
H	9.08373737	2.06679585	-2.46128400
C	6.73974537	3.64962885	1.36973300
H	6.26955537	4.52559785	0.91104200
H	7.51876237	4.02223085	2.04743600
C	4.85435337	-2.56818615	0.26538400
C	5.93473337	-3.08940415	0.56818800
C	8.36570137	-3.24510015	0.27207700
H	8.35151937	-2.26182915	-0.18444700
C	9.45679537	-4.04040315	0.16140500
H	9.40646537	-5.04324915	0.58617400

C	10.70558937	-3.70525415	-0.50787700
C	10.98421537	-2.41038215	-0.99251900
C	11.67821437	-4.70942915	-0.66897700
C	12.19156837	-2.14154415	-1.62441600
H	10.26125737	-1.61024315	-0.86548100
C	12.88639637	-4.43790015	-1.30475600
H	11.47493437	-5.71003115	-0.29614700
C	13.14542337	-3.15322815	-1.78504400
H	12.39606037	-1.14031515	-1.99126100
H	13.62424937	-5.22500115	-1.42463300
H	14.08756137	-2.93705315	-2.27943600
C	6.07811137	-2.78004915	3.45993200
H	5.47466637	-2.33415415	2.66726800
H	5.70323937	-3.80092015	3.63718000
C	8.30110837	-3.93050415	3.52391300
H	7.72576137	-4.83707615	3.72558800
H	9.13125537	-4.16622015	2.85128400
H	8.71968737	-3.55167115	4.46232900
C	8.13441337	-1.64157515	2.73731200
H	9.11090237	-1.81124915	2.28132600
H	7.54532237	-0.99306015	2.09035500
H	8.24997237	-1.16795715	3.71511600
C	4.78608037	-1.12586715	4.65142900
H	4.65652537	-0.60367415	3.69957800
H	3.88188437	-1.73260715	4.83894800
H	4.86441237	-0.38374815	5.45249100
N	6.01083037	-1.92908615	4.62349500
C	6.21475737	-2.62880315	5.88878200
H	7.17790637	-3.14387115	5.89901300
H	6.21916037	-1.90307715	6.70715900
H	5.42296137	-3.37253915	6.09257400
C	7.15607737	-3.64490115	0.96570900
H	7.13920637	-4.67557215	1.32236400
N	7.44243237	-2.93005115	2.88184500

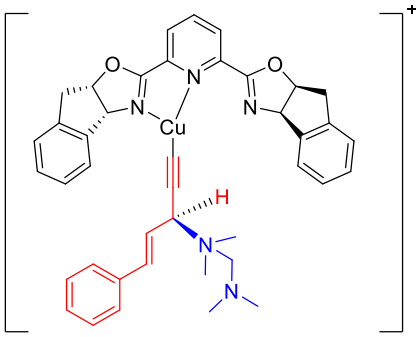


int-2

C	0.01552662	-0.27950310	-0.00020325
C	-0.57721538	0.97750890	0.14534575
C	1.40589162	1.64754590	1.32554675
C	1.91196062	0.35317290	1.12646175
H	-1.56188238	1.17048890	-0.26355425
H	2.00138462	2.37727890	1.86010675
C	-0.65391138	-1.38107110	-0.71025625
N	-0.11695938	-2.53460410	-0.91028125
C	3.24574262	-0.02860610	1.63371175
N	3.76389662	-1.18720010	1.53464875
C	5.17675462	0.34868690	2.74180675
C	5.12093162	-1.06898410	2.08886375
H	5.11178862	0.35403090	3.83238475
N	1.22665762	-0.59132610	0.47530475
O	3.95140962	0.96677590	2.24599075
O	-1.89182138	-1.17916710	-1.17877525
H	5.29816462	-1.88819410	2.79363575
Cu	1.59218162	-3.12340010	-0.19445625
C	0.14395062	1.95735990	0.82654675
H	-0.27322638	2.94953590	0.96515275
C	-1.12365938	-3.38311010	-1.58291025
H	-0.67816338	-3.81958910	-2.48123125
C	-1.71719538	-4.41351410	-0.64899025
C	-1.06085938	-5.46544210	-0.01179225
C	-3.07740938	-4.17340510	-0.43549025
C	-1.79131238	-6.28341010	0.85148875
H	0.00179462	-5.62735110	-0.17160425
C	-3.80585338	-4.99458110	0.42459375
C	-3.15447438	-6.04958510	1.06700075
H	-1.30037538	-7.10631010	1.36288175
H	-4.86398038	-4.81782010	0.59605175
H	-3.71139738	-6.69359510	1.74109175
C	-3.57358138	-2.99634610	-1.24737225
H	-4.09373838	-2.24285310	-0.64664125
H	-4.27005338	-3.31555910	-2.03214325
C	-2.30140738	-2.40263910	-1.87516125
H	-2.41698338	-2.12896510	-2.92458225
C	6.16681062	-1.00551010	0.99568575
C	6.40979862	-1.94804810	-0.00060825
C	6.88660462	0.19158690	1.05274275
C	7.41602462	-1.69017710	-0.93397725
H	5.81311162	-2.85253110	-0.05191825
C	7.89269862	0.44614290	0.12098775
C	8.15632762	-0.50459110	-0.86807925

H	7.63055562	-2.41368310	-1.71350225
H	8.46116362	1.37175290	0.15838075
H	8.93954362	-0.32006610	-1.59775125
C	6.42614262	1.06368890	2.20137275
H	6.18717462	2.08875390	1.89870075
H	7.18954462	1.13261890	2.98701975
C	3.00192462	-4.22960910	0.24706075
C	3.92344162	-4.98864610	0.54055675
C	6.18434862	-5.63783910	-0.08986025
H	5.94372462	-5.53736510	-1.14406925
C	7.41397462	-5.34849510	0.36757175
H	7.58007562	-5.36348610	1.44532375
C	8.55544562	-4.90885610	-0.43590125
C	9.60299862	-4.22245110	0.19836175
C	8.61578062	-5.09338510	-1.82873225
C	10.66421162	-3.70228910	-0.53865425
H	9.56477362	-4.07041510	1.27367575
C	9.67837162	-4.57938310	-2.56425025
H	7.83118562	-5.64659510	-2.33652825
C	10.70271962	-3.87522710	-1.92249825
H	11.45761162	-3.15982110	-0.03390425
H	9.71334262	-4.72997810	-3.63908625
H	11.52971962	-3.47294910	-2.49963925
N	4.50581262	-7.38912810	0.71987775
C	3.34193962	-7.54234510	1.73411475
H	3.79643462	-7.32441310	2.70550775
H	2.65921362	-6.73168310	1.47545675
C	5.60472262	-8.33253210	1.06553275
H	6.42383962	-8.19621210	0.36054575
H	5.95600062	-8.11245610	2.07591075
H	5.21437762	-9.34886410	1.01389975
C	4.00990062	-7.67556010	-0.65880925
H	3.29494662	-6.89686510	-0.92747925
H	4.85561062	-7.66065810	-1.34599425
H	3.54615662	-8.66111110	-0.65043825
N	2.73891462	-8.82890610	1.67526175
C	2.95597262	-9.68190310	2.84452875
H	2.38383462	-9.34470810	3.72440875
H	2.64799162	-10.70433810	2.60798775
H	4.01642562	-9.70328810	3.10790975
C	1.34226862	-8.82790610	1.23660075
H	1.03676162	-9.85068510	0.99819275
H	0.66056162	-8.43509910	2.00914575
H	1.23068362	-8.22096510	0.33446675

C	5.02102762	-5.88326410	0.82384975
H	5.35472962	-5.82787110	1.86829075



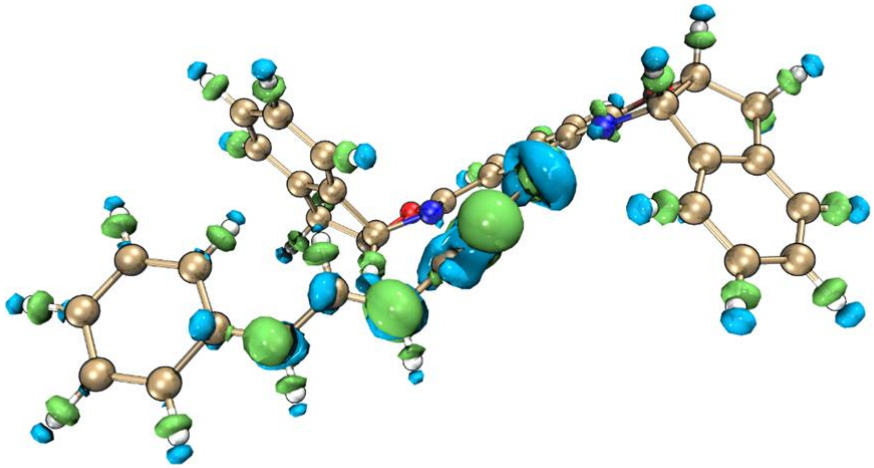
int-3

C	-0.21739132	0.43478260	0.00000000
C	0.35218268	-0.66361040	0.65127800
C	-1.81883932	-1.09221540	1.58671500
C	-2.28859932	0.04106660	0.90512200
H	1.40192868	-0.89644740	0.51724800
H	-2.50020932	-1.66930840	2.19987700
C	0.57167068	1.29758960	-0.89649300
N	0.06384168	2.18877660	-1.67608000
C	-3.69927932	0.46610660	1.02313600
N	-4.16651032	1.59409960	0.65172300
C	-5.84072932	0.21578460	1.69442000
C	-5.62459932	1.47960960	0.81404000
H	-5.99023632	0.41325460	2.75922800
N	-1.50298332	0.78613060	0.12092800
O	-4.54764132	-0.45326940	1.56574300
O	1.90263068	1.15786960	-0.89393900
H	-6.02680932	2.39417060	1.26354100
Cu	-1.75910932	2.82189660	-1.63297900
C	-0.47751632	-1.44195740	1.45704000
H	-0.08307632	-2.30987040	1.97539900
C	1.18373768	2.90802260	-2.32566300
H	1.03931268	2.88775060	-3.40911400
C	1.35032668	4.30423660	-1.76905800
C	0.46649368	5.37737660	-1.88137400
C	2.54370568	4.41881760	-1.05061900
C	0.79555168	6.58067160	-1.25369200
H	-0.46024332	5.27721760	-2.43864400
C	2.86768168	5.62078960	-0.42111000
C	1.98670068	6.69978660	-0.52642200
H	0.12949868	7.43463560	-1.34117900
H	3.79484468	5.72269360	0.13585600

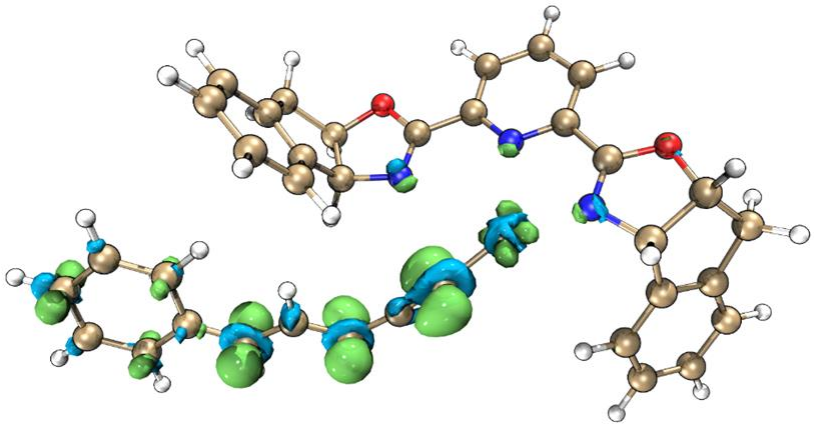
H	2.23447068	7.64320760	-0.04856800
C	3.36082368	3.14587660	-1.11169700
H	3.64500768	2.76336460	-0.12568300
H	4.28936068	3.29548860	-1.67539100
C	2.45032468	2.13792460	-1.83722500
H	2.96062768	1.56303960	-2.61011800
C	-6.31525232	1.12213960	-0.48944900
C	-6.21423932	1.76815560	-1.72136200
C	-7.08615932	-0.03617440	-0.34121100
C	-6.95306832	1.27077160	-2.79800600
H	-5.55564332	2.62063560	-1.84702900
C	-7.82177832	-0.52941240	-1.41781400
C	-7.76024232	0.13849960	-2.64384600
H	-6.89263632	1.76388160	-3.76356300
H	-8.42478732	-1.42720840	-1.31179100
H	-8.32888332	-0.23715540	-3.48943900
C	-6.96859332	-0.60549740	1.05614400
H	-6.73461032	-1.67505740	1.06926600
H	-7.89440032	-0.47311740	1.63105100
C	-3.21675632	3.94781760	-1.63852300
C	-4.05874132	4.80800960	-1.39180600
C	-6.35053932	5.17985660	-0.62493400
H	-6.39780032	4.14859260	-0.29574400
C	-7.46732432	5.83369960	-0.98562200
H	-7.37930732	6.86805760	-1.32149500
C	-8.82651732	5.28724760	-0.98218900
C	-9.08244432	3.90656060	-0.88196700
C	-9.91553832	6.16821860	-1.09191900
C	-10.38910032	3.43124660	-0.87440700
H	-8.26115832	3.19954560	-0.84850700
C	-11.22420632	5.69058560	-1.07688800
H	-9.73037532	7.23559160	-1.18493000
C	-11.46475232	4.32020360	-0.96600800
H	-10.56736532	2.36175460	-0.81219900
H	-12.05435932	6.38567360	-1.15833800
H	-12.48371332	3.94491660	-0.96348500
N	-4.36170032	6.12900960	0.65926300
C	-2.90989232	6.64351260	0.44231500
H	-2.42144632	5.84011060	-0.10627400
H	-3.02461632	7.50889360	-0.21753200
C	-5.18106032	7.20293360	1.28568700
H	-5.17778332	8.07920860	0.63365700
H	-6.20170232	6.84234360	1.40763900
H	-4.74002832	7.45036960	2.25124000

C	-4.33847632	4.92985960	1.55275400
H	-5.36551332	4.67477360	1.81274300
H	-3.86908232	4.09883060	1.02266600
H	-3.78524732	5.19986160	2.45139500
C	-1.12965332	6.09129860	2.00259600
H	-1.40540532	5.04401360	1.85474900
H	-0.24171432	6.30402860	1.38818100
H	-0.86880632	6.23099260	3.05605200
N	-2.26339032	6.95918860	1.66827800
C	-1.96521632	8.37439460	1.87955600
H	-2.84860132	8.98477760	1.67459900
H	-1.68188332	8.53344560	2.92411200
H	-1.13847932	8.73126960	1.24250200
C	-4.97000232	5.74555660	-0.77020500
H	-5.00817732	6.71730560	-1.27758900

7.3 Condensed dual descriptor and condensed Fukui function of int-1



Isosurface of condensed dual descriptor



Isosurface of condensed f^+ Fukui function

7.4 Wave functions analysis of int-1

Hirshfeld charges, condensed Fukui functions and condensed dual descriptors (CDD)
Units used below are "e" (elementary charge)

Atom	$q_{(N)}$	$q_{(N+1)}$	$q_{(N-1)}$	f^-	f^+	f^0	CDD
1(C)	0.0594	0.0552	0.0619	0.0025	0.0043	0.0034	0.0018
2(C)	-0.0135	-0.0284	0.0035	0.0171	0.0149	0.0160	-0.0022
3(C)	-0.0118	-0.0233	0.0060	0.0177	0.0115	0.0146	-0.0062
4(C)	0.0721	0.0715	0.0787	0.0067	0.0006	0.0036	-0.0061
5(H)	0.0665	0.0566	0.0777	0.0111	0.0100	0.0106	-0.0011
6(H)	0.0653	0.0577	0.0767	0.0114	0.0076	0.0095	-0.0038
7(C)	0.1601	0.1502	0.1731	0.0130	0.0099	0.0115	-0.0031
8(N)	-0.1537	-0.1493	-0.1616	-0.0079	-0.0044	-0.0061	0.0035
9(C)	0.1370	0.1270	0.1426	0.0056	0.0100	0.0078	0.0045
10(N)	-0.1558	-0.1385	-0.1629	-0.0071	-0.0173	-0.0122	-0.0102
11(C)	0.0684	0.0646	0.0734	0.0050	0.0038	0.0044	-0.0013
12(C)	0.0198	0.0251	0.0193	-0.0005	-0.0053	-0.0029	-0.0048
13(H)	0.0458	0.0402	0.0523	0.0065	0.0056	0.0061	-0.0009
14(N)	-0.1011	-0.0979	-0.0996	0.0015	-0.0032	-0.0008	-0.0048
15(O)	-0.1340	-0.1478	-0.1215	0.0124	0.0139	0.0132	0.0014
16(O)	-0.1091	-0.1217	-0.0897	0.0194	0.0126	0.0160	-0.0068
17(H)	0.0367	0.0466	0.0349	-0.0018	-0.0098	-0.0058	-0.0080
18(Cu)	0.2477	0.1576	0.4726	0.2249	0.0902	0.1575	-0.1348
19(C)	0.0057	-0.0106	0.0266	0.0210	0.0163	0.0186	-0.0047
20(H)	0.0711	0.0598	0.0845	0.0134	0.0113	0.0123	-0.0021
21(C)	0.0313	0.0308	0.0339	0.0025	0.0005	0.0015	-0.0020
22(H)	0.0537	0.0508	0.0604	0.0067	0.0030	0.0048	-0.0037
23(C)	-0.0187	-0.0144	-0.0203	-0.0016	-0.0043	-0.0030	-0.0027
24(C)	-0.0361	-0.0285	-0.0267	0.0094	-0.0076	0.0009	-0.0170
25(C)	-0.0047	-0.0082	0.0117	0.0164	0.0035	0.0099	-0.0129
26(C)	-0.0319	-0.0336	-0.0096	0.0223	0.0017	0.0120	-0.0207
27(H)	0.0449	0.0514	0.0447	-0.0001	-0.0065	-0.0033	-0.0064
28(C)	-0.0364	-0.0460	-0.0091	0.0273	0.0096	0.0184	-0.0177
29(C)	-0.0276	-0.0363	-0.0102	0.0174	0.0087	0.0131	-0.0087
30(H)	0.0518	0.0503	0.0624	0.0105	0.0015	0.0060	-0.0091
31(H)	0.0516	0.0439	0.0657	0.0141	0.0077	0.0109	-0.0064
32(H)	0.0535	0.0464	0.0663	0.0128	0.0072	0.0100	-0.0056
33(C)	-0.0442	-0.0480	-0.0374	0.0068	0.0038	0.0053	-0.0030
34(H)	0.0490	0.0442	0.0579	0.0089	0.0048	0.0069	-0.0041
35(H)	0.0507	0.0432	0.0635	0.0128	0.0075	0.0101	-0.0053
36(C)	0.0786	0.0738	0.0873	0.0087	0.0048	0.0068	-0.0039
37(H)	0.0543	0.0474	0.0655	0.0111	0.0069	0.0090	-0.0042
38(C)	-0.0132	-0.0044	-0.0151	-0.0019	-0.0089	-0.0054	-0.0070

39(C)	-0.0381	-0.0278	-0.0435	-0.0054	-0.0103	-0.0079	-0.0049
40(C)	-0.0033	-0.0059	0.0021	0.0054	0.0026	0.0040	-0.0028
41(C)	-0.0359	-0.0380	-0.0302	0.0057	0.0021	0.0039	-0.0036
42(H)	0.0451	0.0515	0.0396	-0.0055	-0.0064	-0.0059	-0.0009
43(C)	-0.0369	-0.0463	-0.0262	0.0107	0.0094	0.0101	-0.0013
44(C)	-0.0337	-0.0417	-0.0202	0.0135	0.0080	0.0108	-0.0055
45(H)	0.0506	0.0458	0.0555	0.0049	0.0048	0.0048	-0.0002
46(H)	0.0510	0.0418	0.0595	0.0086	0.0092	0.0089	0.0006
47(H)	0.0515	0.0427	0.0604	0.0088	0.0088	0.0088	-0.0001
48(C)	-0.0453	-0.0491	-0.0415	0.0038	0.0037	0.0038	-0.0001
49(H)	0.0489	0.0402	0.0564	0.0075	0.0087	0.0081	0.0012
50(H)	0.0465	0.0418	0.0529	0.0064	0.0047	0.0055	-0.0018
51(C)	-0.1483	-0.2683	-0.1506	-0.0023	0.1199	0.0588	0.1222
52(C)	-0.0618	-0.1071	-0.0131	0.0486	0.0454	0.0470	-0.0033
53(C)	0.0511	-0.0463	0.0700	0.0189	0.0974	0.0581	0.0785
54(H)	0.0715	0.0377	0.0860	0.0145	0.0337	0.0241	0.0192
55(C)	-0.0275	-0.0490	0.0009	0.0284	0.0215	0.0249	-0.0069
56(H)	0.0484	0.0346	0.0552	0.0068	0.0138	0.0103	0.0070
57(C)	0.0312	-0.0587	0.0655	0.0344	0.0899	0.0621	0.0556
58(H)	0.0598	0.0309	0.0744	0.0146	0.0288	0.0217	0.0143
59(C)	-0.0006	-0.0081	0.0189	0.0195	0.0075	0.0135	-0.0119
60(C)	-0.0139	-0.0506	0.0124	0.0263	0.0366	0.0315	0.0103
61(C)	-0.0169	-0.0482	0.0017	0.0187	0.0313	0.0250	0.0126
62(C)	-0.0243	-0.0516	-0.0011	0.0232	0.0273	0.0252	0.0041
63(H)	0.0552	0.0368	0.0686	0.0134	0.0184	0.0159	0.0049
64(C)	-0.0247	-0.0494	-0.0059	0.0188	0.0247	0.0218	0.0059
65(H)	0.0415	0.0305	0.0469	0.0053	0.0111	0.0082	0.0057
66(C)	-0.0019	-0.0572	0.0419	0.0438	0.0553	0.0496	0.0115
67(H)	0.0599	0.0387	0.0755	0.0156	0.0212	0.0184	0.0055
68(H)	0.0561	0.0377	0.0681	0.0119	0.0184	0.0152	0.0065
69(H)	0.0616	0.0350	0.0805	0.0189	0.0266	0.0228	0.0077

Condensed local electrophilicity/nucleophilicity index (e*eV)

Atom	Electrophilicity	Nucleophilicity
1(C)	0.02322	0.00161
2(C)	0.08113	0.01103
3(C)	0.06302	0.01148
4(C)	0.00324	0.00431
5(H)	0.05458	0.00719
6(H)	0.04138	0.00735
7(C)	0.05417	0.00842
8(N)	-0.02395	-0.00510
9(C)	0.05489	0.00360

10(N)	-0.09459	-0.00458
11(C)	0.02051	0.00326
12(C)	-0.02904	-0.00032
13(H)	0.03076	0.00421
14(N)	-0.01765	0.00099
15(O)	0.07580	0.00804
16(O)	0.06880	0.01255
17(H)	-0.05376	-0.00117
18(Cu)	0.14544	
19(C)	0.08879	0.01355
20(H)	0.06166	0.00866
21(C)	0.00276	0.00163
22(H)	0.01615	0.00431
23(C)	-0.02347	-0.00105
24(C)	-0.04132	0.00608
25(C)	0.01917	0.01059
26(C)	0.00918	0.01444
27(H)	-0.03577	-0.00008
28(C)	0.05228	0.01766
29(C)	0.04767	0.01128
30(H)	0.00812	0.00682
31(H)	0.04196	0.00911
32(H)	0.03929	0.00825
33(C)	0.02057	0.00440
34(H)	0.02646	0.00576
35(H)	0.04082	0.00827
36(C)	0.02616	0.00565
37(H)	0.03781	0.00719
38(C)	-0.04851	-0.00123
39(C)	-0.05638	-0.00348
40(C)	0.01409	0.00347
41(C)	0.01140	0.00367
42(H)	-0.03502	-0.00354
43(C)	0.05148	0.00693
44(C)	0.04380	0.00872
45(H)	0.02595	0.00319
46(H)	0.05001	0.00553
47(H)	0.04792	0.00572
48(C)	0.02025	0.00247
49(H)	0.04756	0.00488
50(H)	0.02543	0.00415
51(C)	0.65516	-0.00148
52(C)	0.24776	0.03145
53(C)	0.53204	0.01223

54(H)	0.18419	0.00938
55(C)	0.11758	0.01835
56(H)	0.07527	0.00440
57(C)	0.49123	0.02222
58(H)	0.15760	0.00942
59(C)	0.04121	0.01260
60(C)	0.20000	0.01701
61(C)	0.17099	0.01208
62(C)	0.14895	0.01499
63(H)	0.10028	0.00868
64(C)	0.13499	0.01217
65(H)	0.06057	0.00345
66(C)	0.30220	0.02833
67(H)	0.11558	0.01010
68(H)	0.10057	0.00772
69(H)	0.14533	0.01222

8. Referances

1. J.-S. Ma, H.-Y. Lu, Y.-W. Chen, W.-C. Zhao, Y.-Z. Sun, R.-P. Li, H.-X. Wang, G.-Q. Lin and Z.-T. He, Copper-catalysed convergent regio- and enantioselective alkynylallylic substitution, *Nat. Synth.*, 2022, **2**, 37–48.

2. Y.-J. Xie, J.-H. Hu, Y.-Y. Wang, C.-G. Xia and H.-M. Huang, Palladium-Catalyzed Vinylation of Aminals with Simple Alkenes: A New Strategy to Construct Allylamines, *J. Am. Chem. Soc.*, 2012, **134**, 20613–20616.

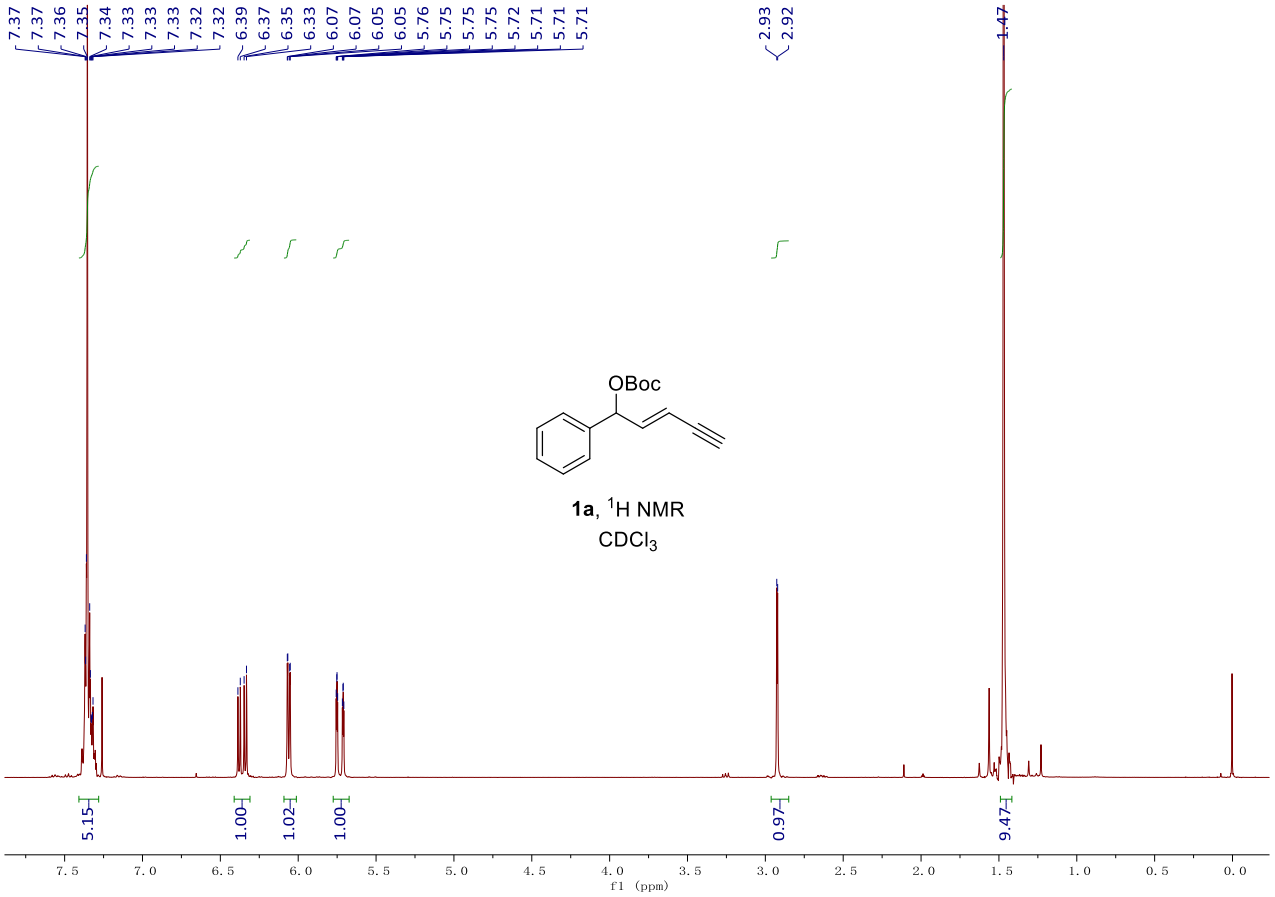
3. Y. Liu, Y.-J. Xie, H.-L. Wang and H.-M. Huang, Enantioselective Aminomethylamination of Conjugated Dienes with Aminals Enabled by Chiral Palladium Complex-Catalyzed C–N Bond Activation, *J. Am. Chem. Soc.*, 2016, **138**, 4314–4317.

4. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

5. T. Lu and F.-W. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, *J. Comput. Chem.*, 2012, **33**, 580–592.

6. T. Lu and Q. Chen, Realization of conceptual density functional theory and information-theoretic approach in Multiwfn program. In: Liu S, ed. Conceptual Density Functional Theory. Wiley-VCH; 2022, 631–647.

9. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMRspectra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7.37
7.36
7.35
7.34
7.33
7.33
7.33
7.32
7.32
6.39
6.37
6.35
6.33
6.07
6.07
6.05
6.05
5.76
5.75
5.75
5.75
5.72
5.71
5.71
5.71
2.93
2.92
1.47
OBoc
1a, 1H NMR
CDCl3
5.15
1.00
1.02
1.00
0.97
9.47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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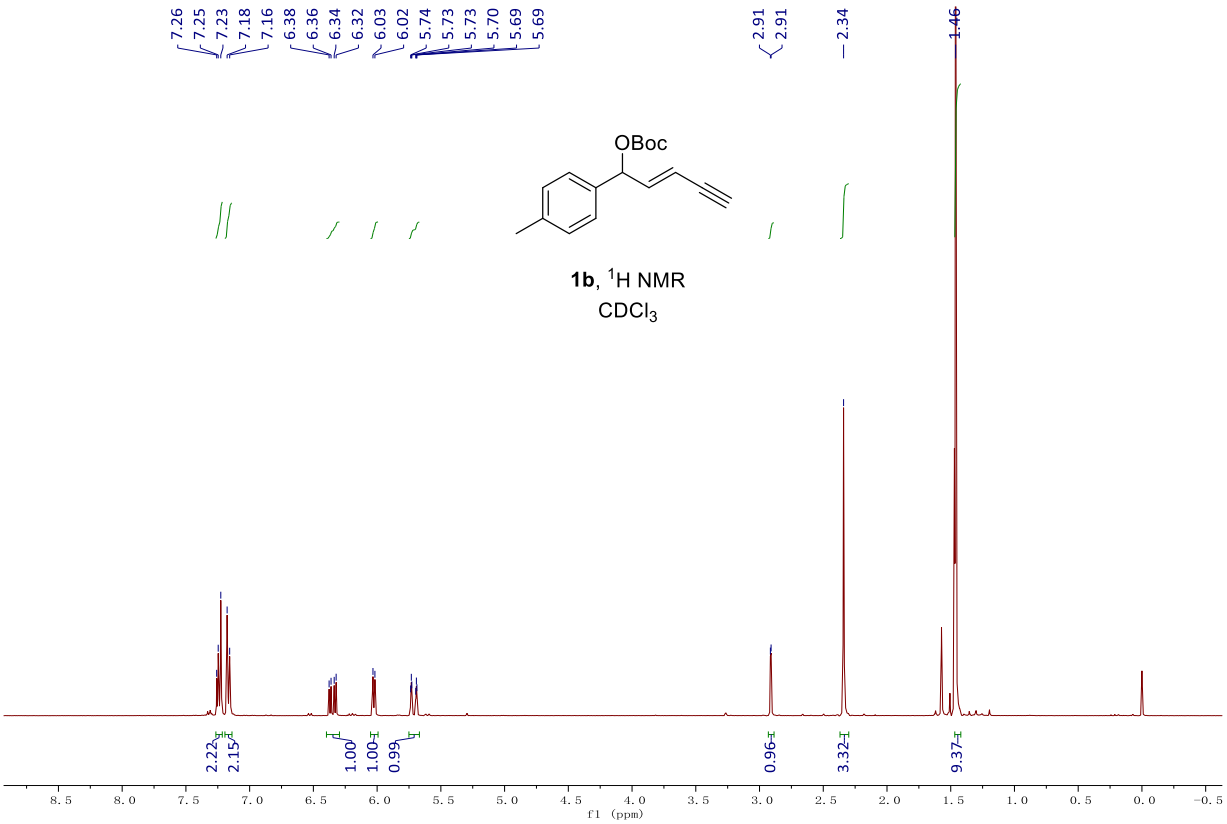
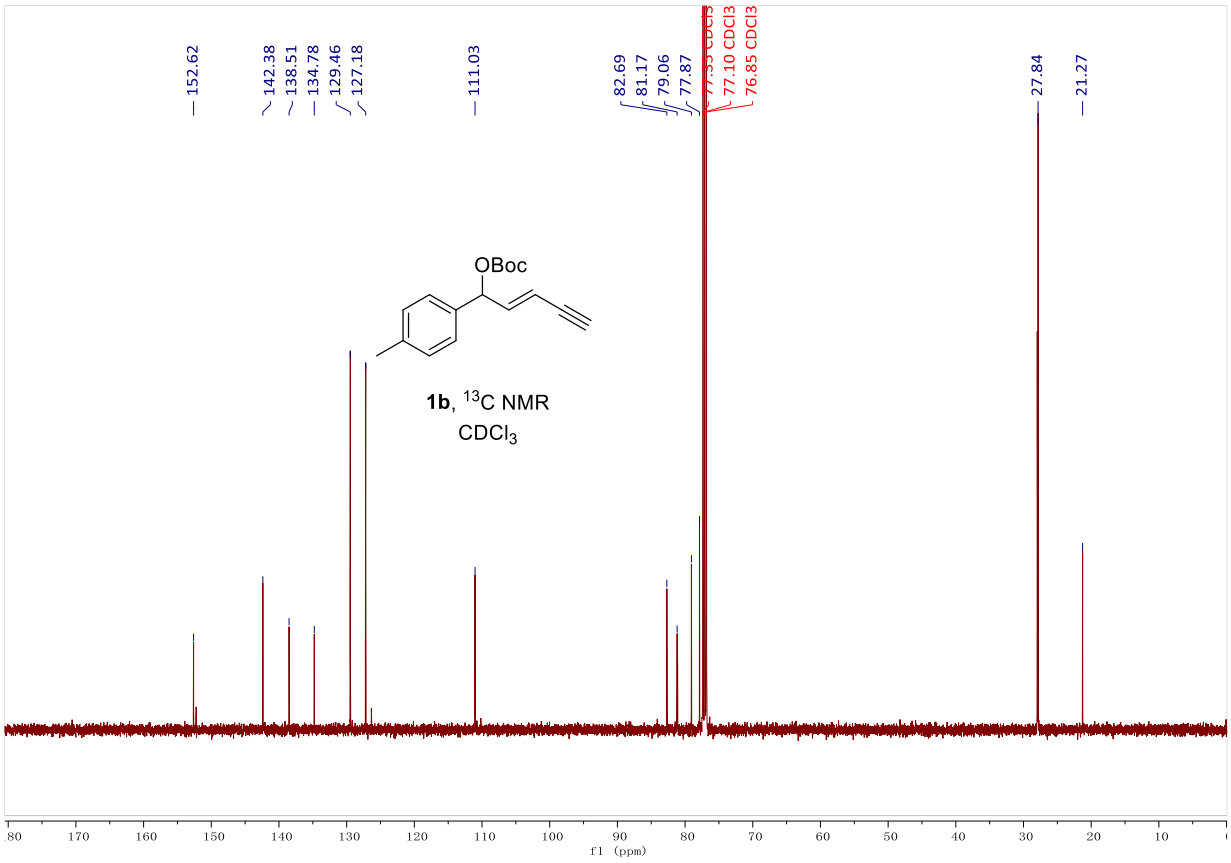
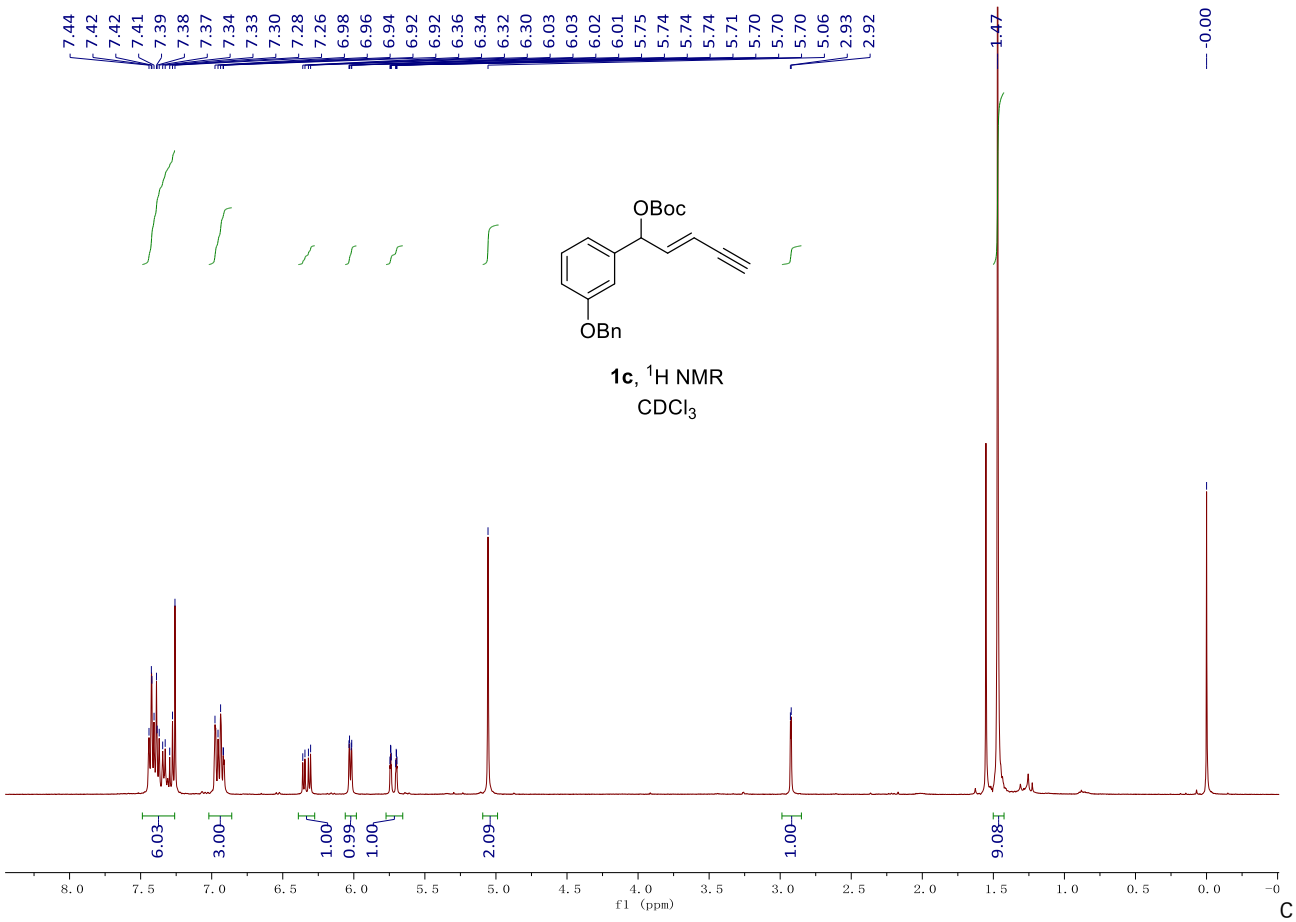
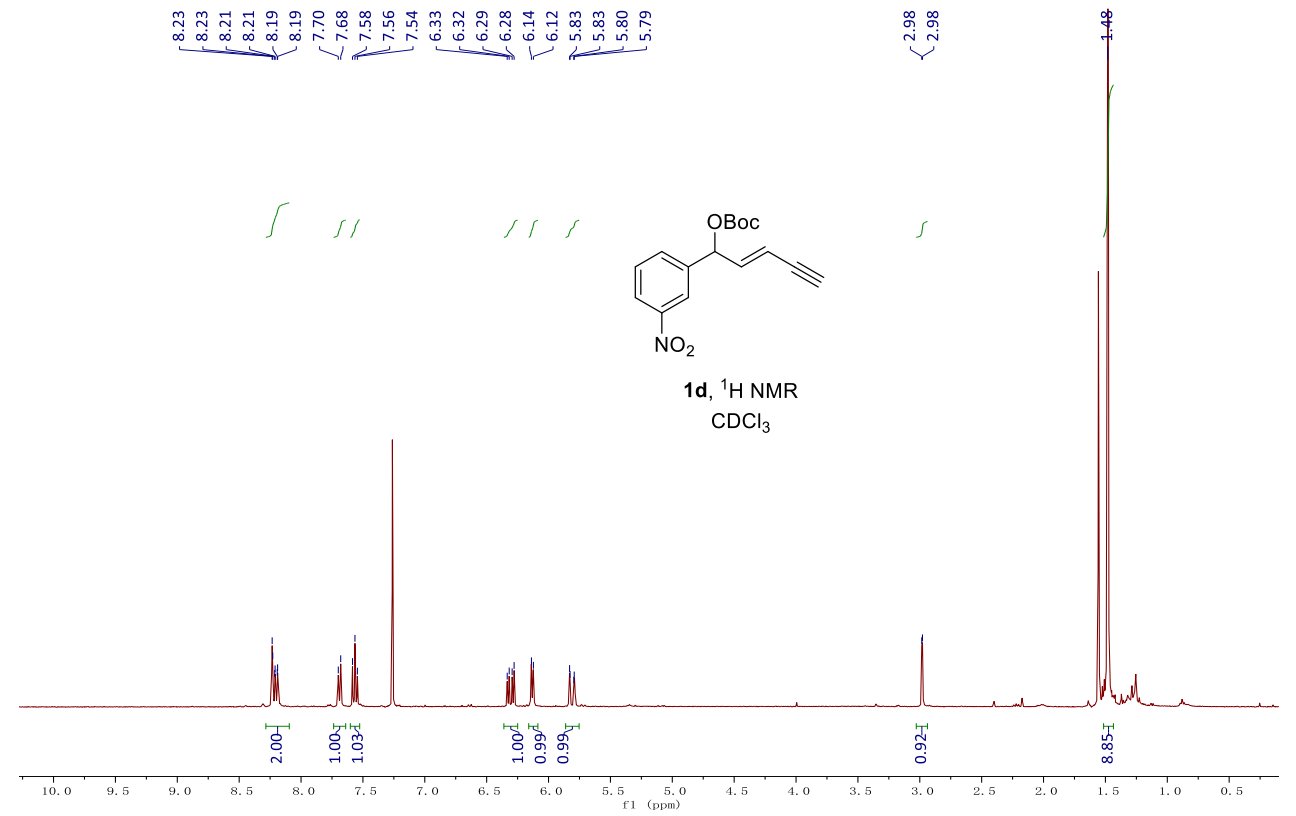
0.0
f1 (ppm)


7.26
7.25
7.23
7.18
7.16
6.38
6.36
6.34
6.32
6.03
6.02
5.74
5.73
5.73
5.70
5.69
5.69
2.91
2.91
2.34
1.46
OBoc
1b, 1H NMR
CDCl3
2.22
2.15
1.00
1.00
0.99
0.96
3.32
9.37
f1 (ppm)

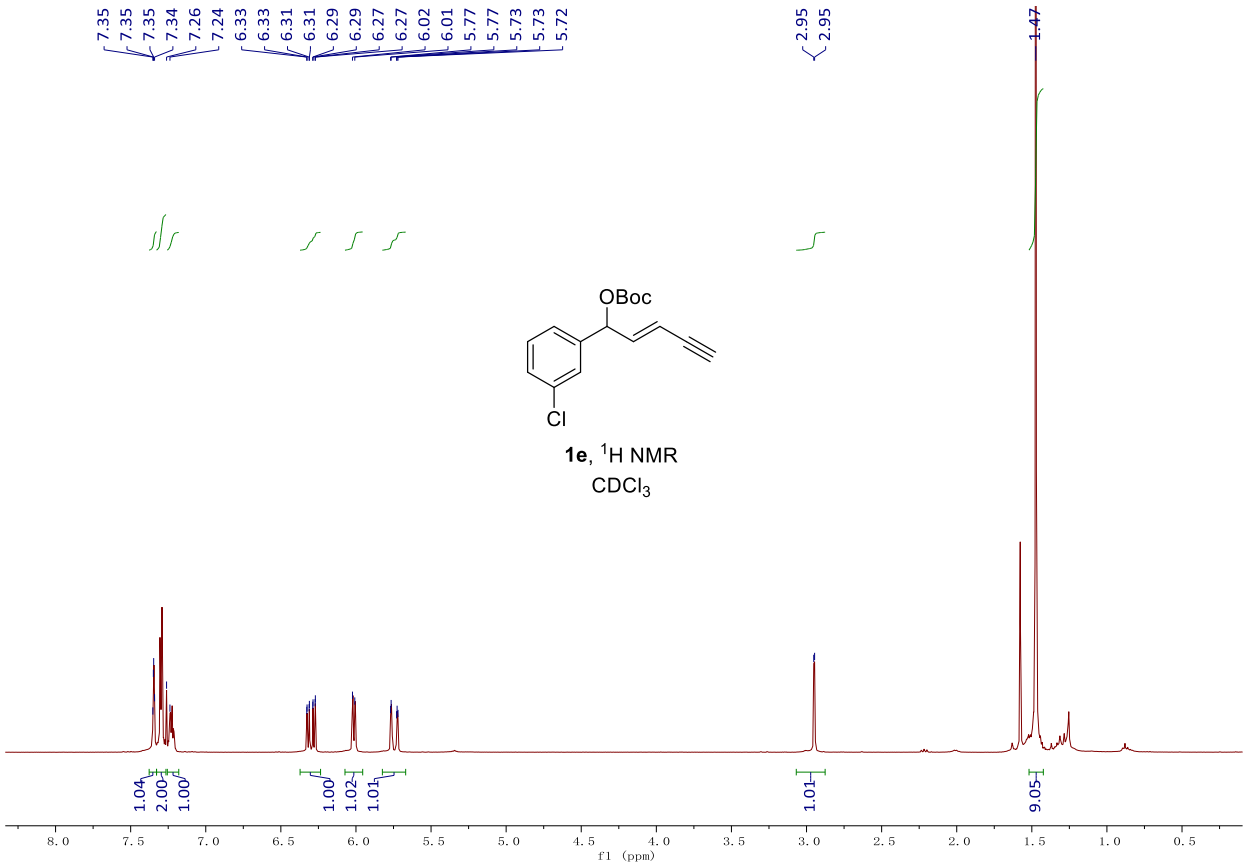

152.62
142.38
138.51
134.78
129.46
127.18
111.03
82.69
81.17
79.06
77.87
77.10 CDCl3
76.85 CDCl3
27.84
21.27
OBoc
1b, 13C NMR
CDCl3
f1 (ppm)



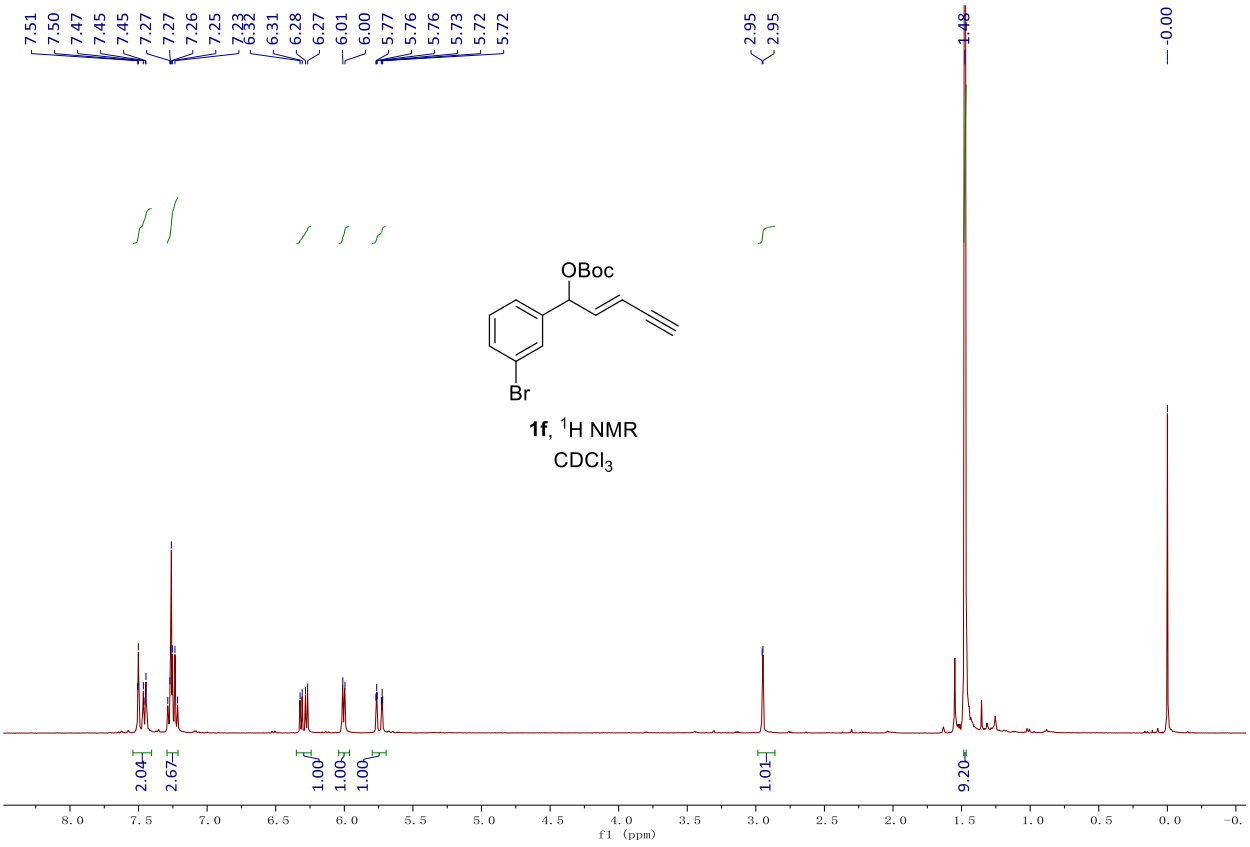
1c, ^{1}H NMR
$CDCl_3$



1d, ^{1}H NMR
$CDCl_3$



1e, ^{1}H NMR
$CDCl_3$



1f, ^{1}H NMR
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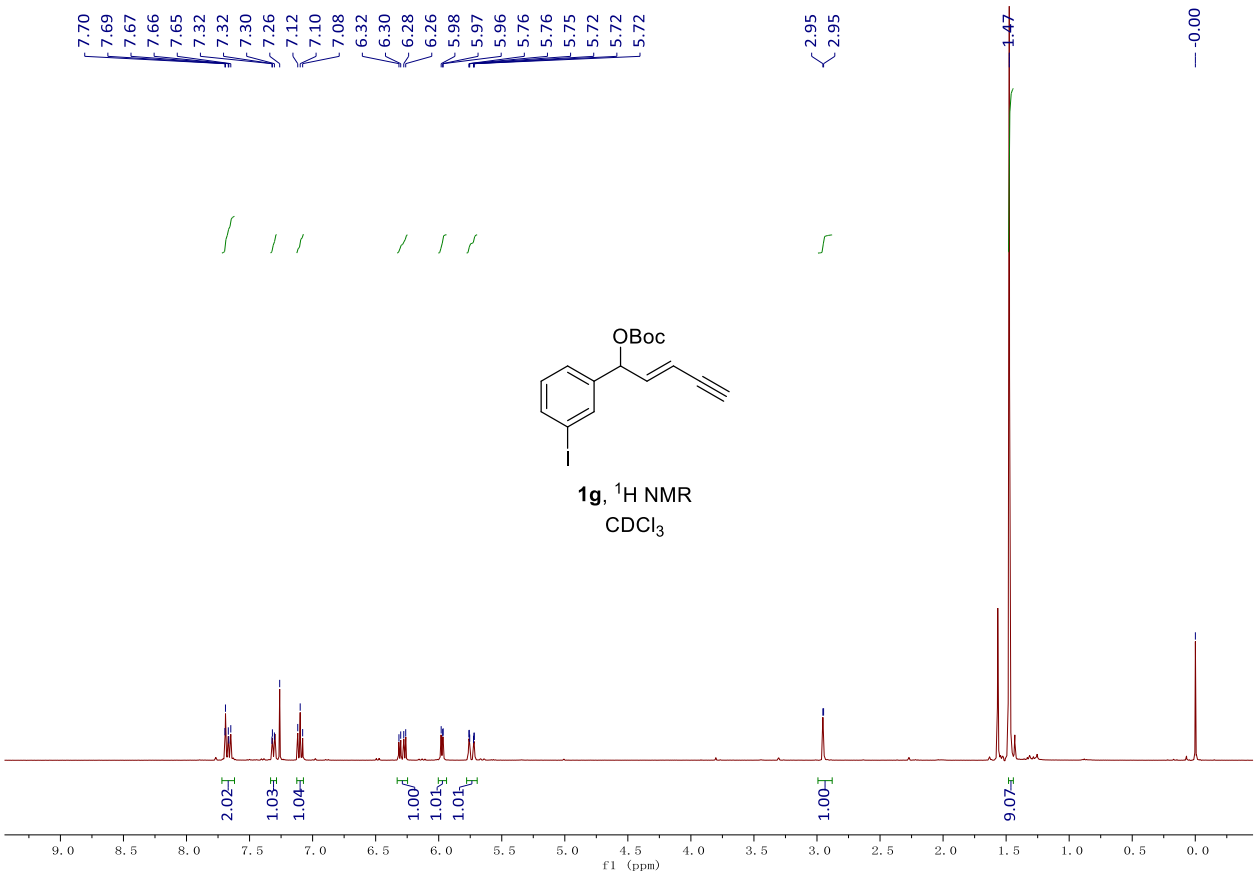

1g, ^{1}H NMR
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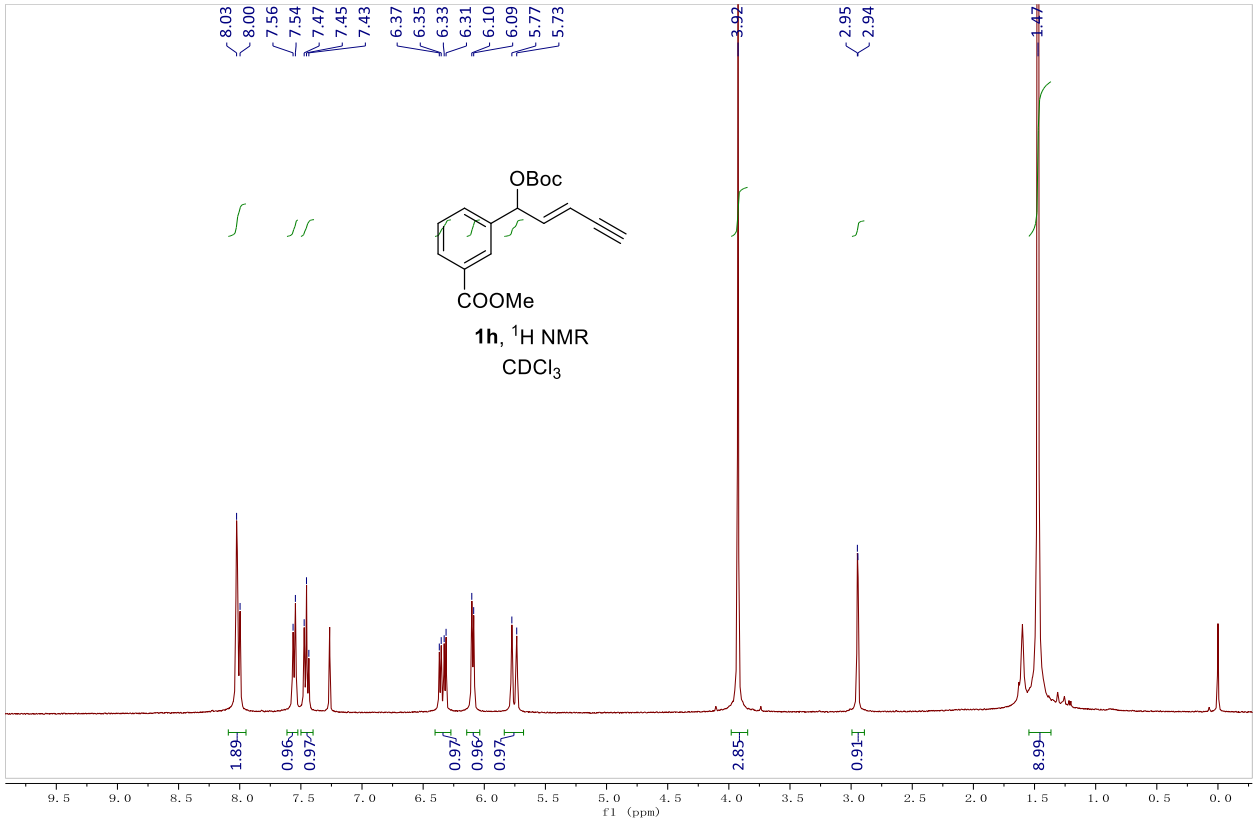

1h, ^{1}H NMR
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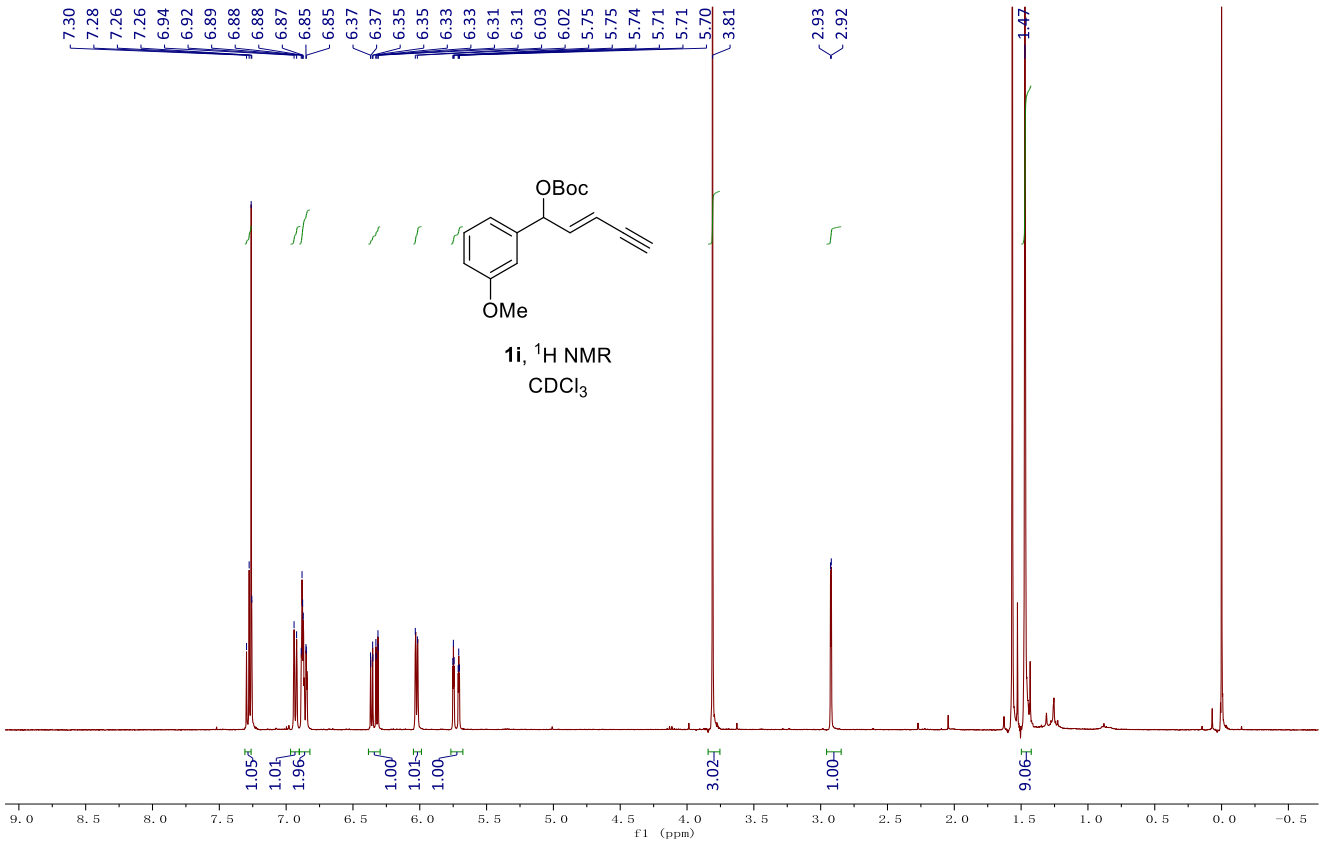
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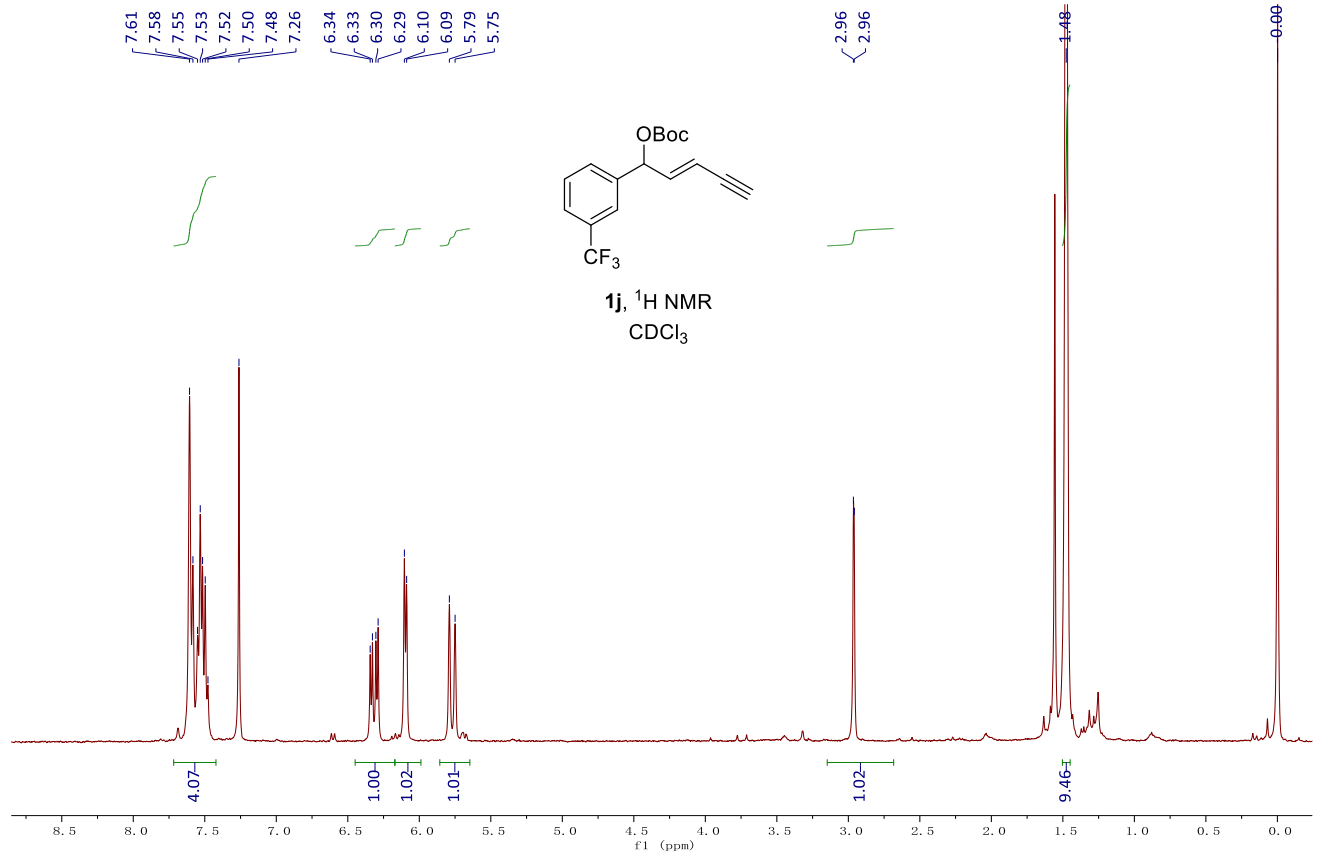
OMe
1i, 1H NMR
CDCl3
f1 (ppm)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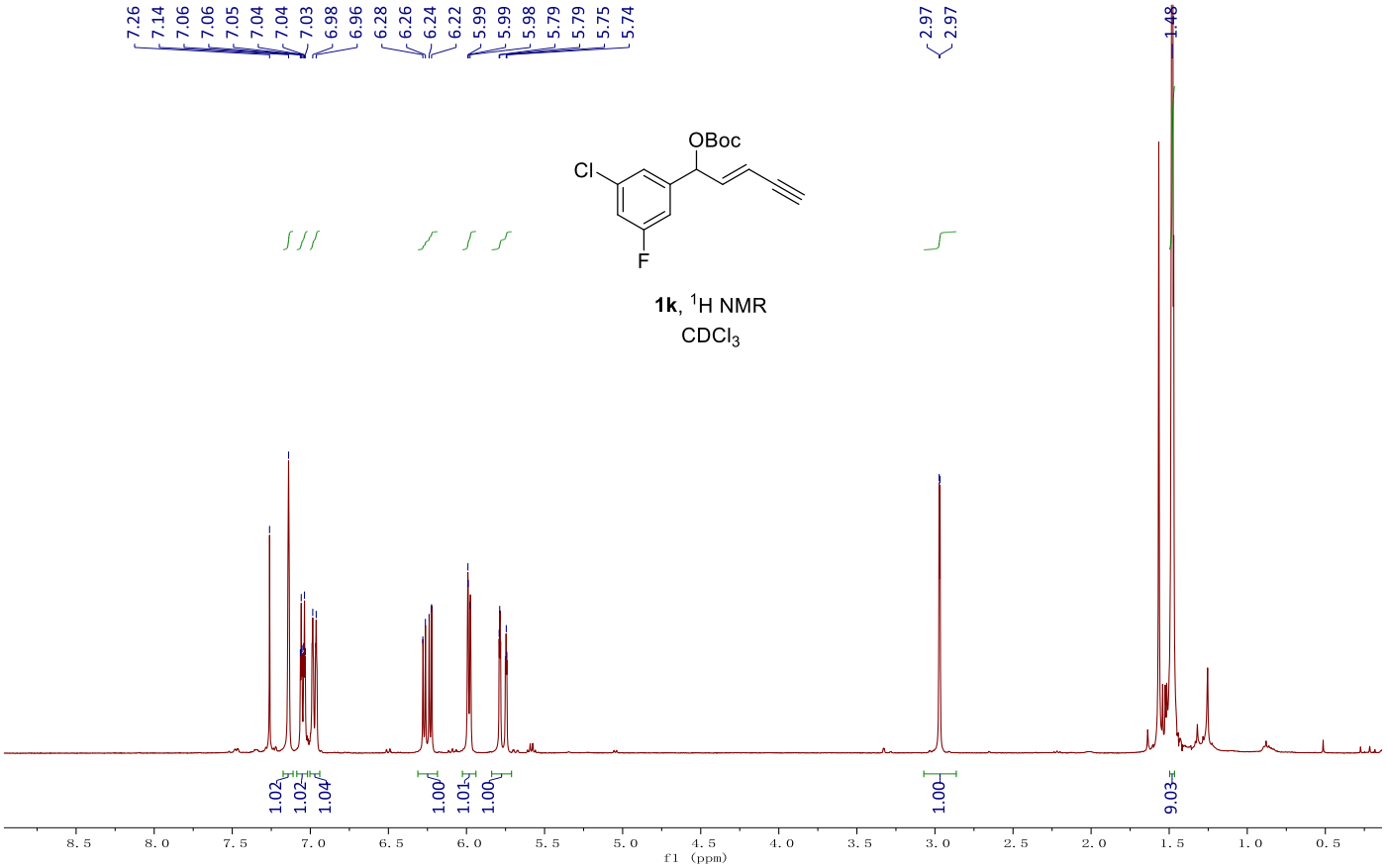
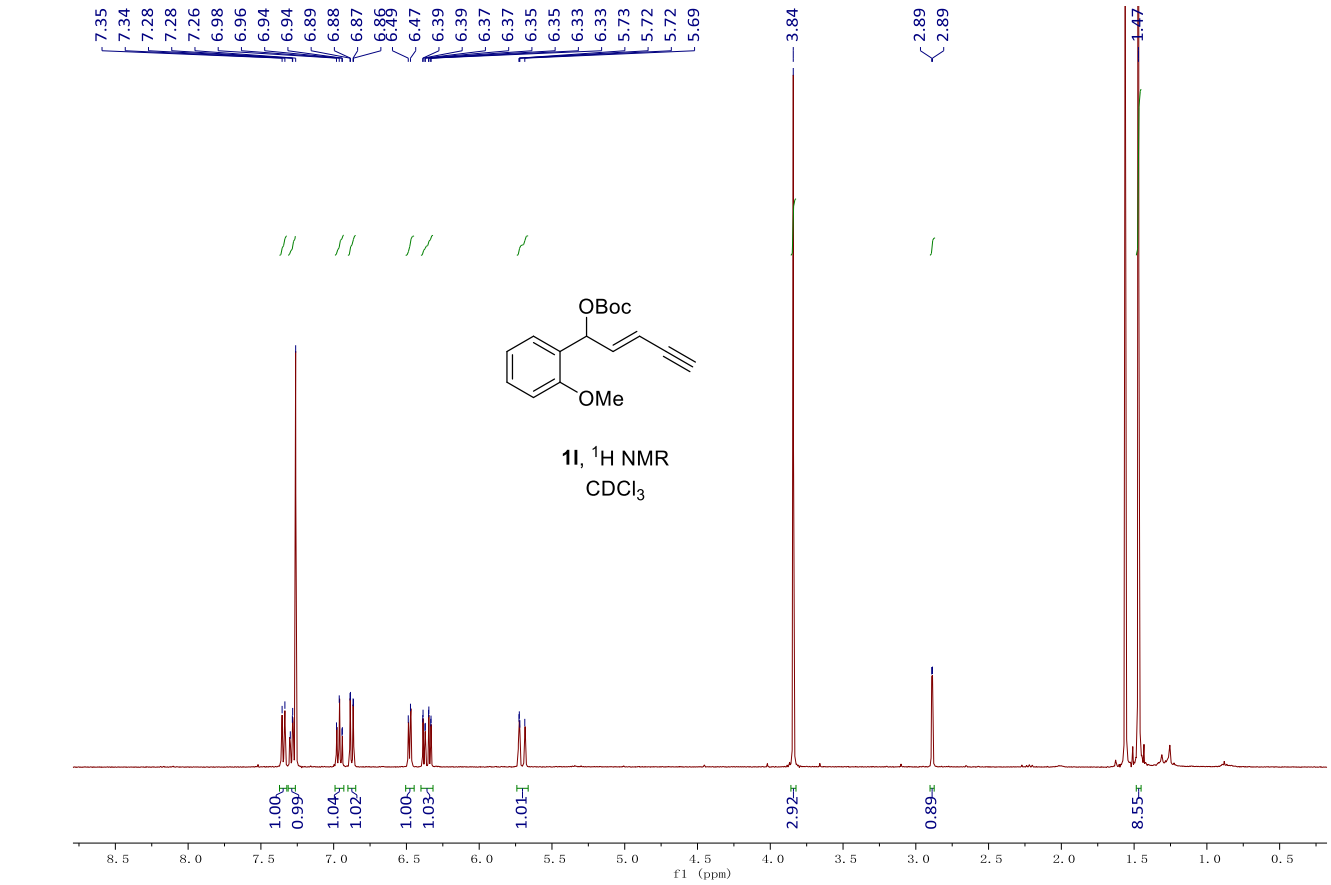
CF3
1j, 1H NMR
CDCl3
f1 (ppm)



1k, ^{1}H NMR
$CDCl_3$



1l, ^{1}H NMR
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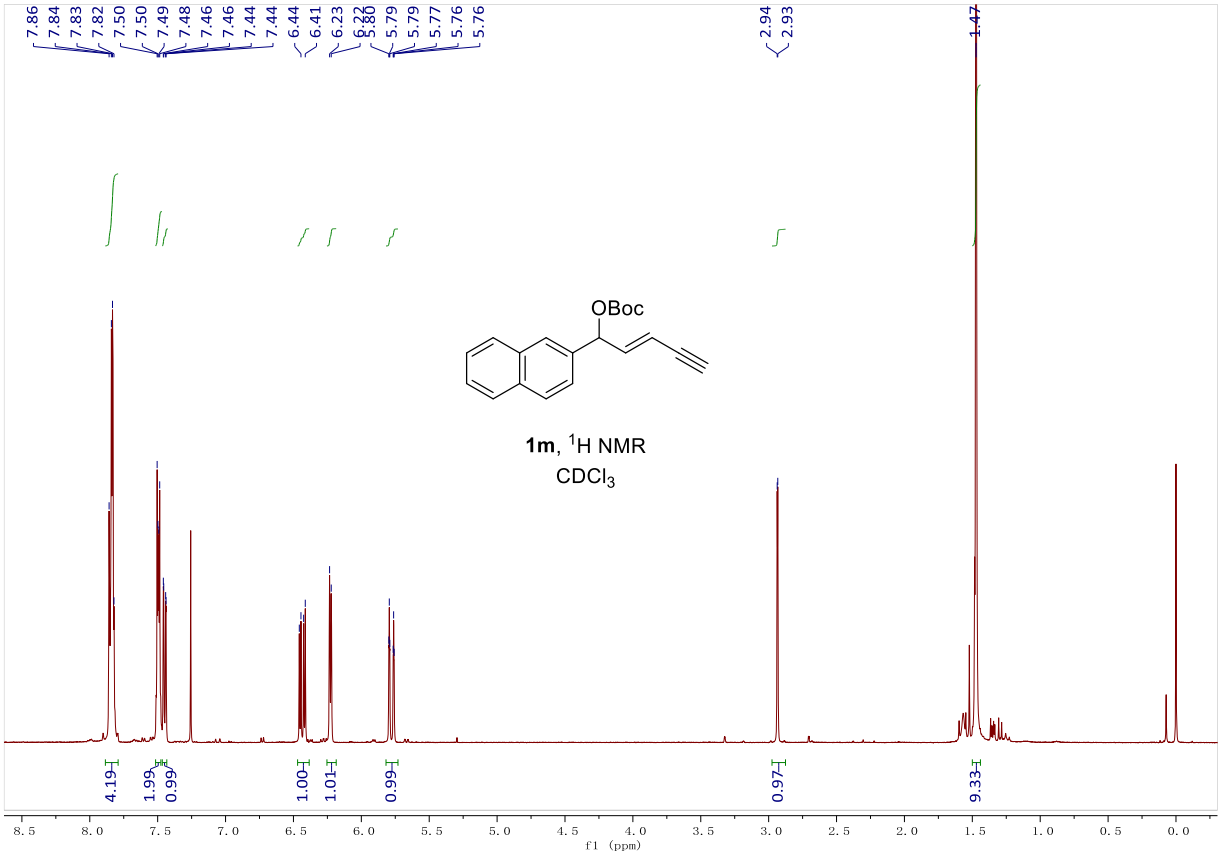

1m, ^{1}H NMR
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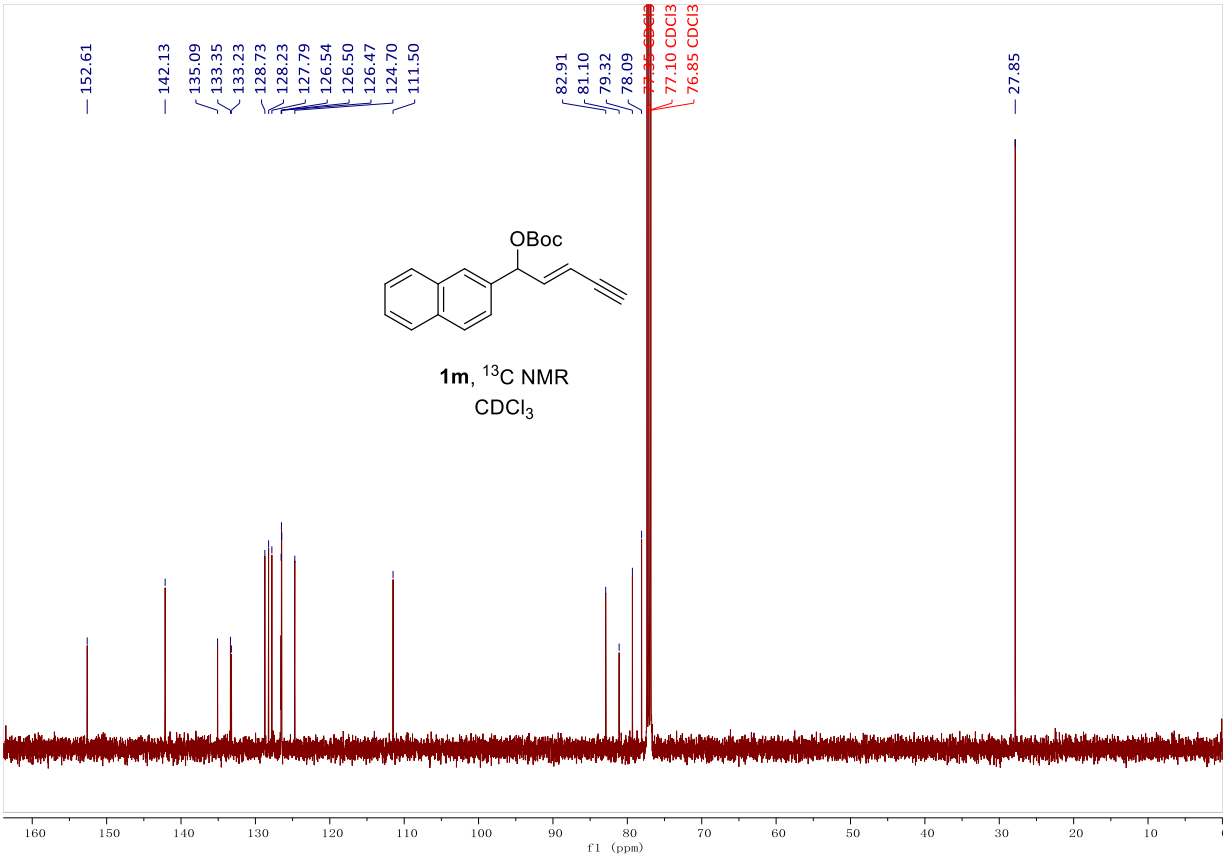

1m, ^{13}C NMR
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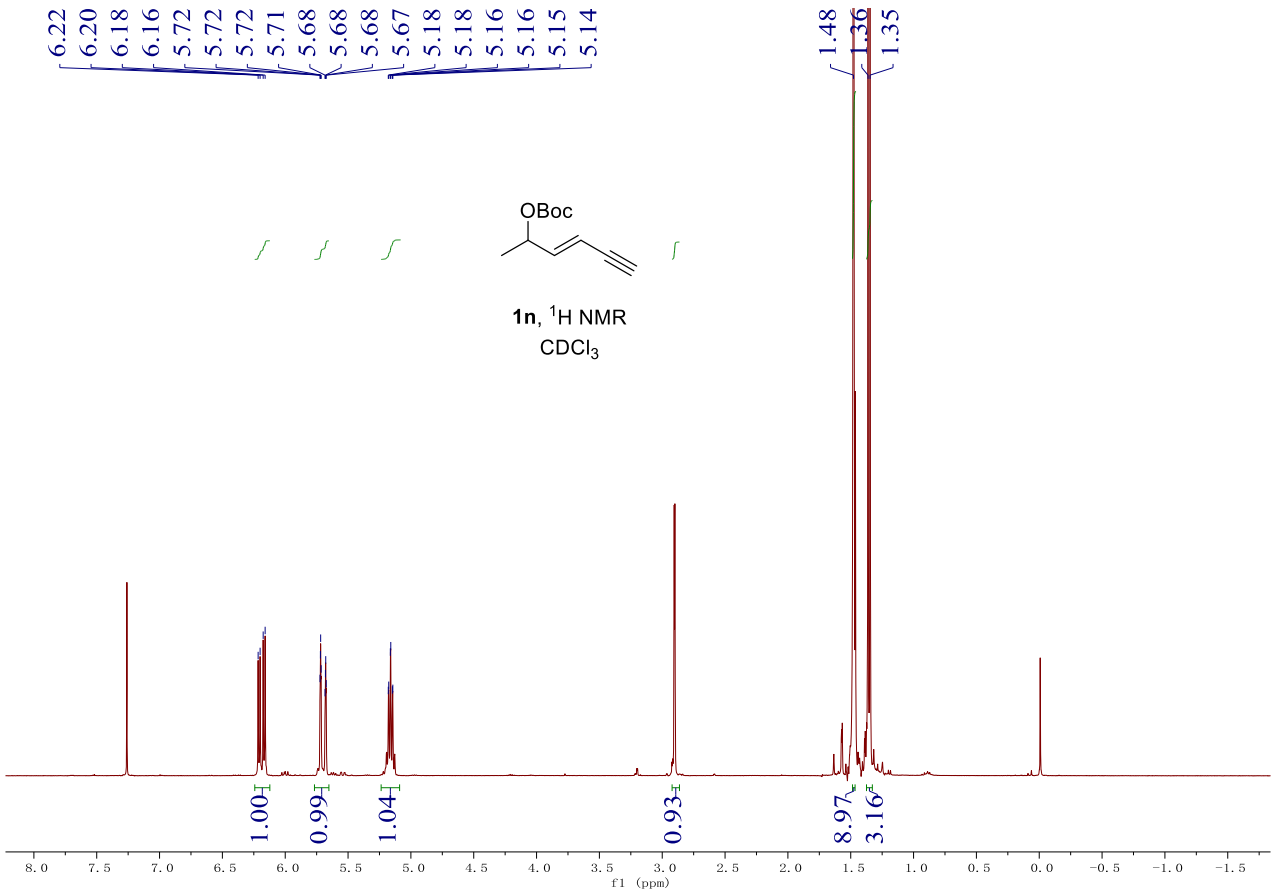
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5.18
5.16
5.16
5.15
5.14
1.48
1.36
1.35
OBoc
1n, 1H NMR
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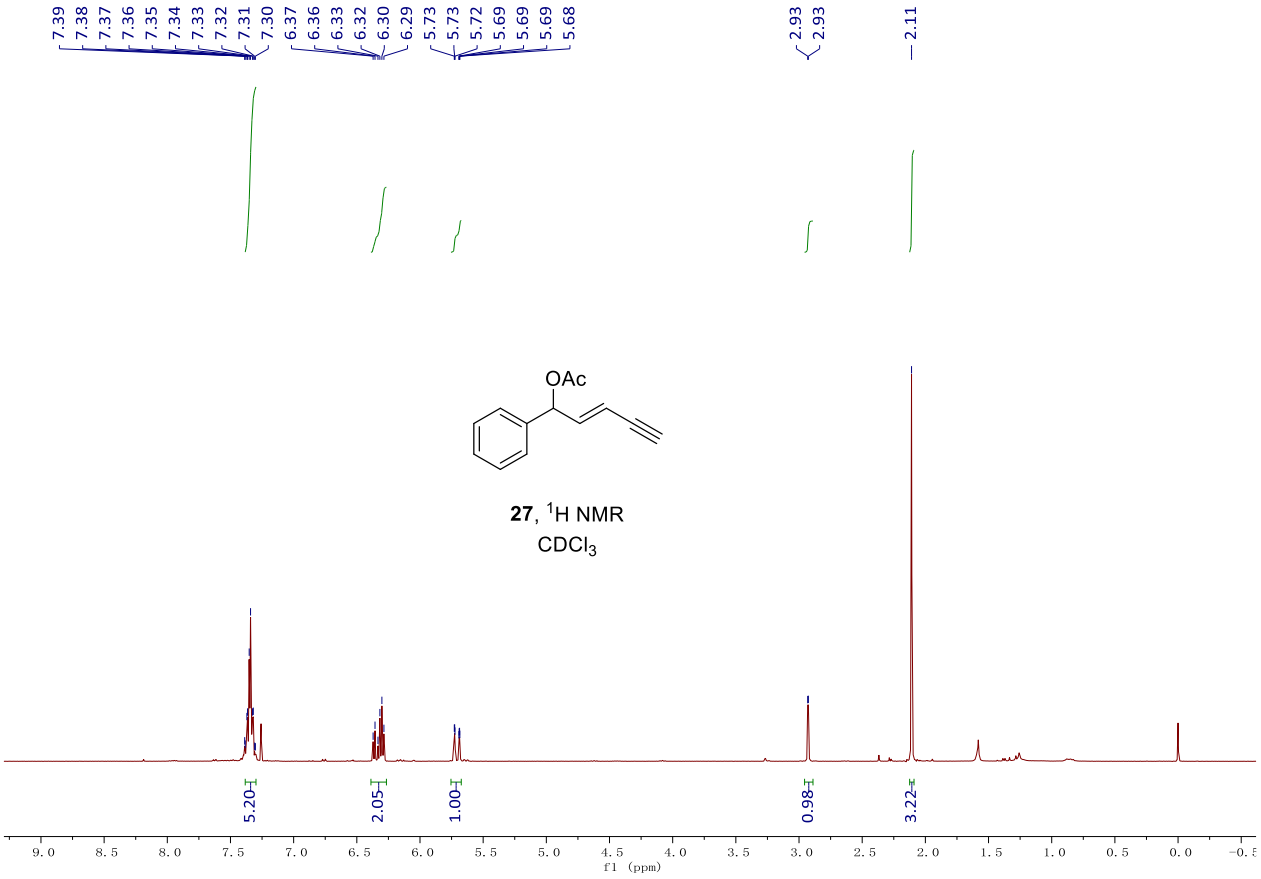
0.93
8.97
3.16
f1 (ppm)



27, ^{1}H NMR
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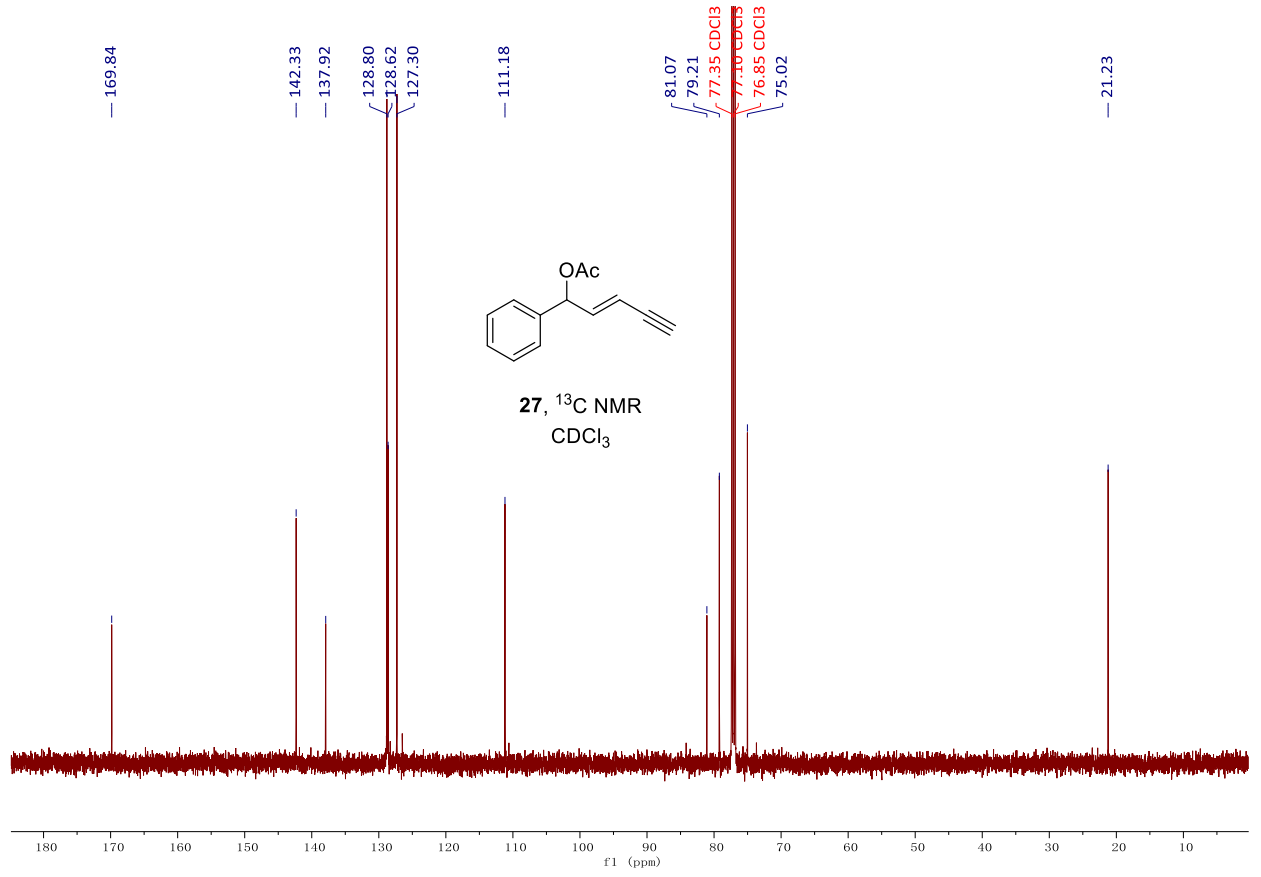

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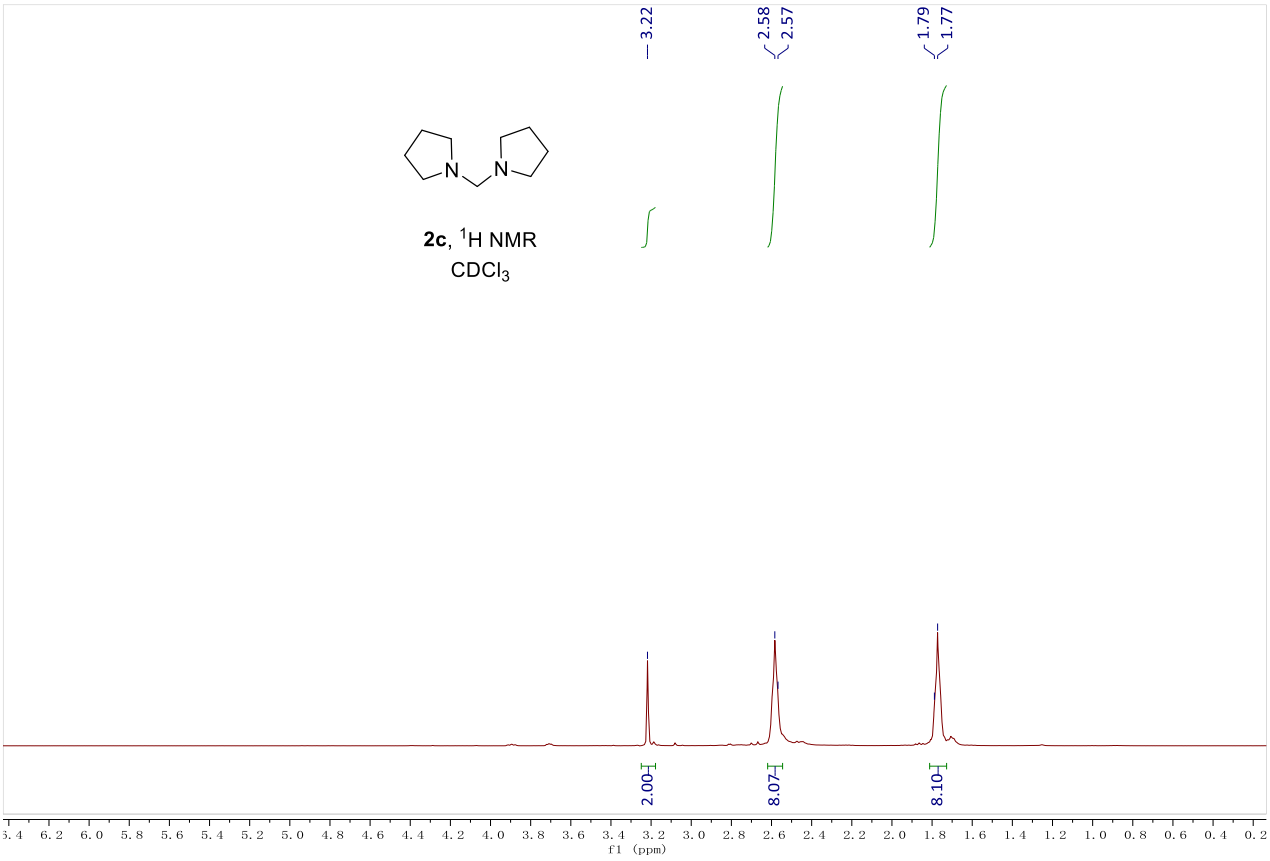

2c, ^{1}H NMR
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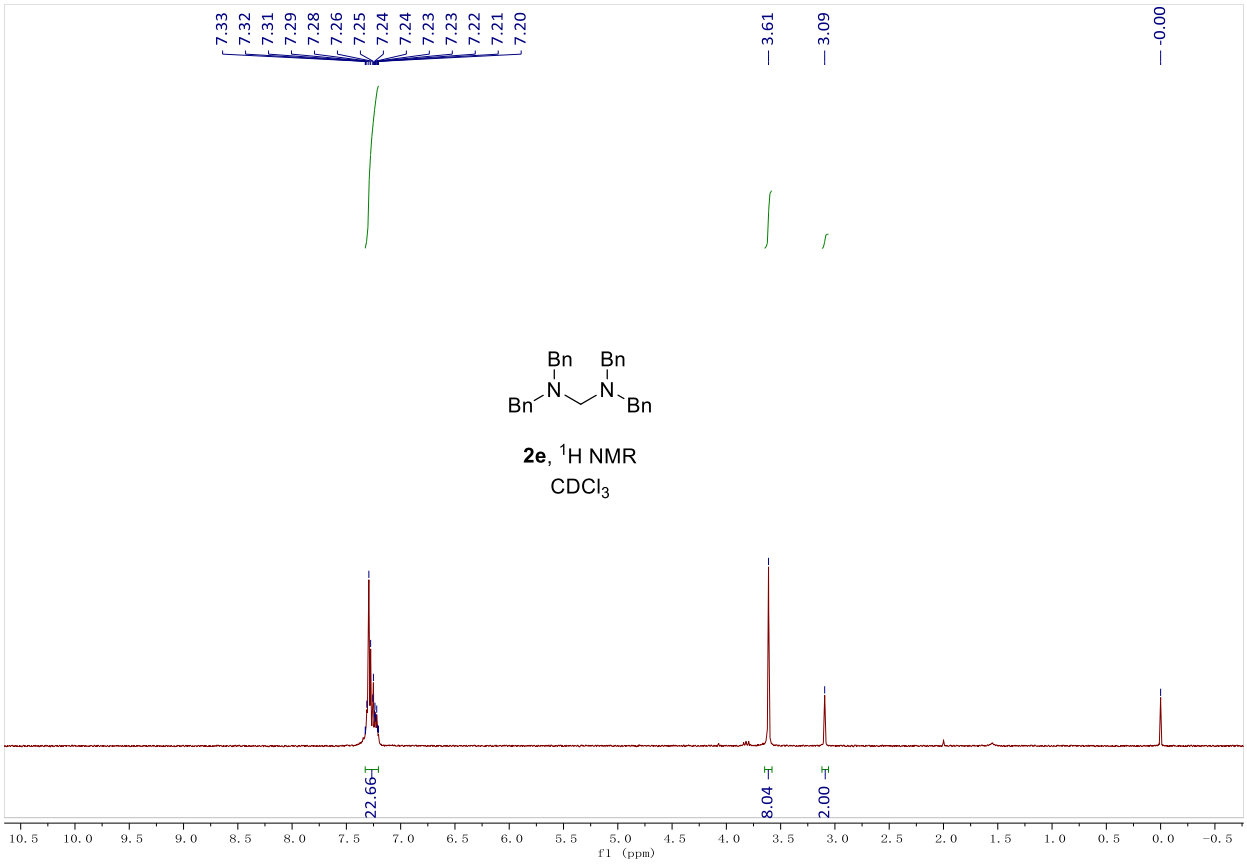

2e, ^{1}H NMR
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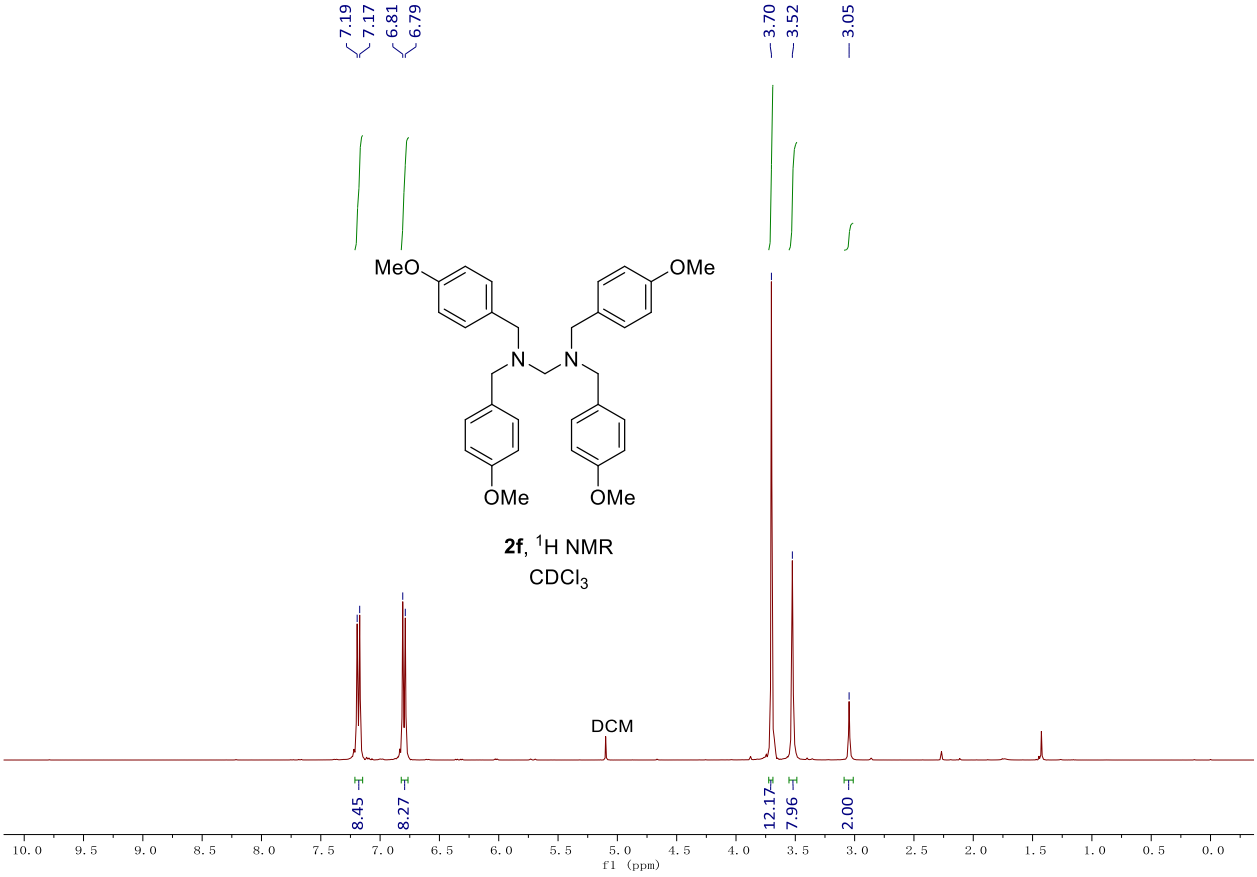
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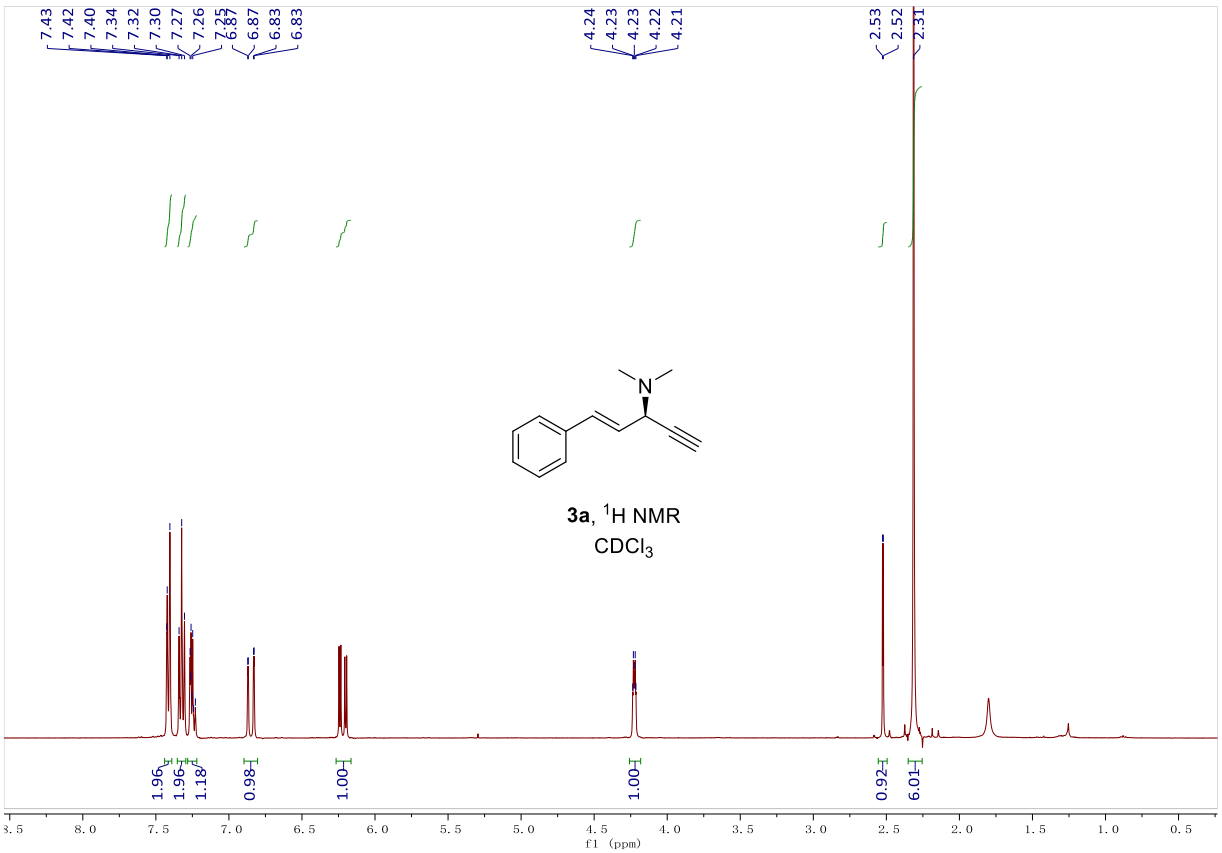
MeO
OMe
N
N
OMe
OMe
2f, 1H NMR
CDCl3
DCM
8.45
8.27
12.17
7.96
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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4.23
4.22
4.21
2.53
2.52
2.31
N
3a, 1H NMR
CDCl3
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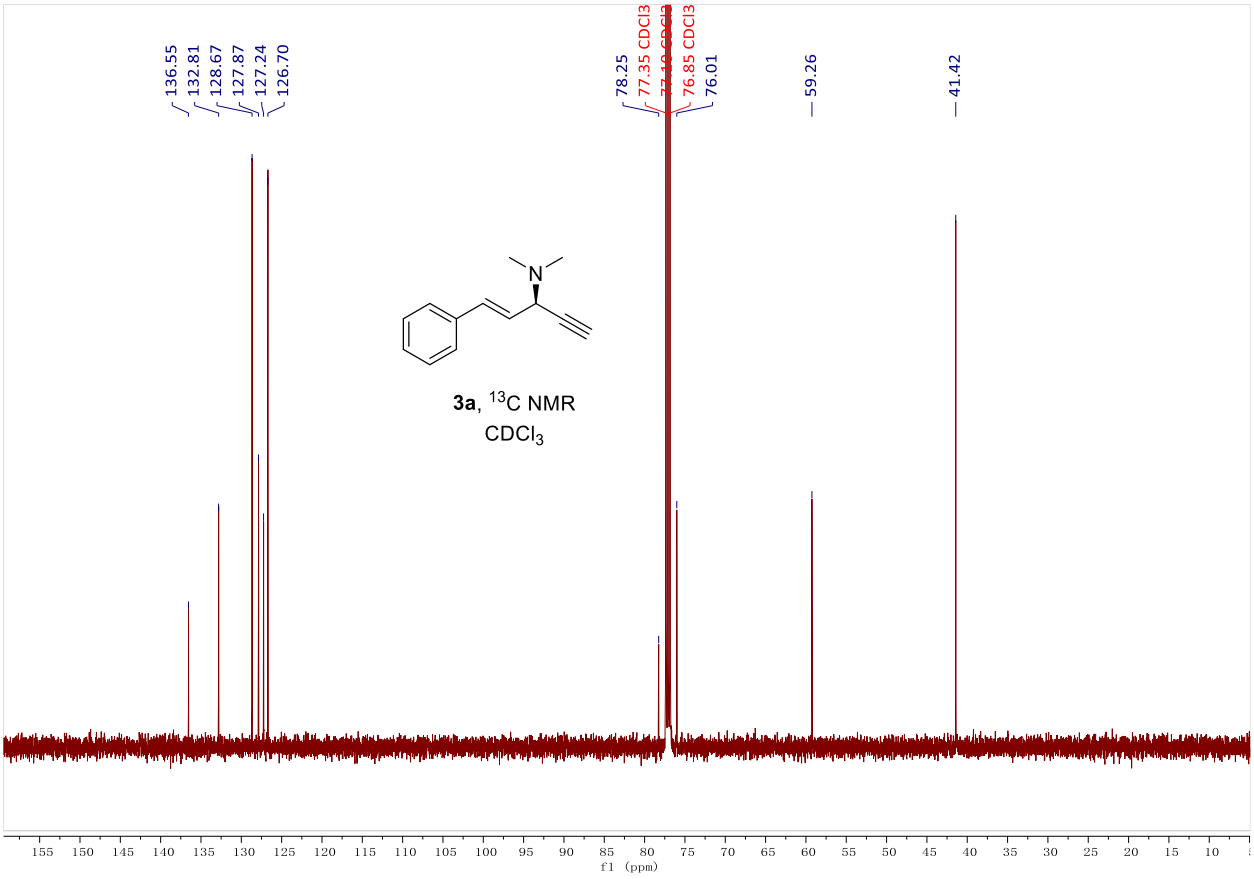
1.18
0.98
1.00
1.00
0.92
6.01
f1 (ppm)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126.70
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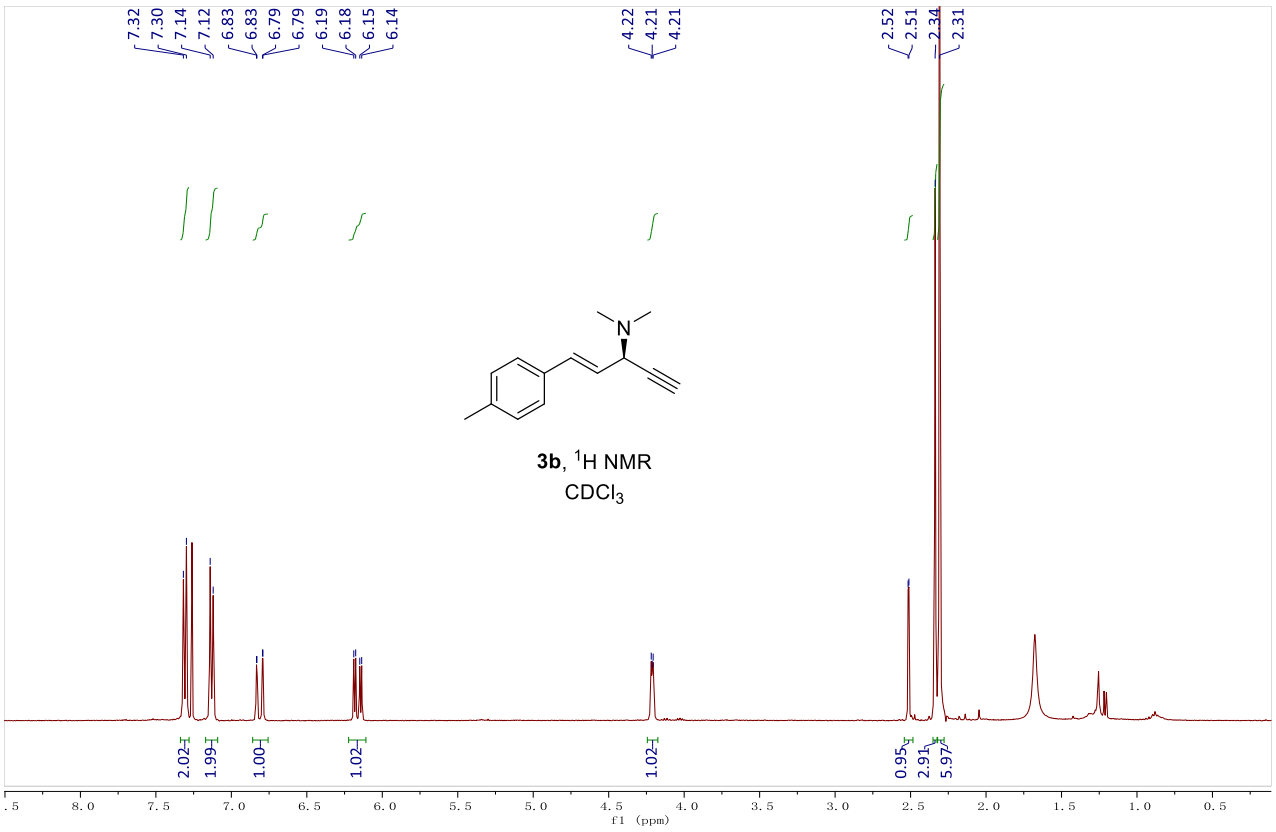
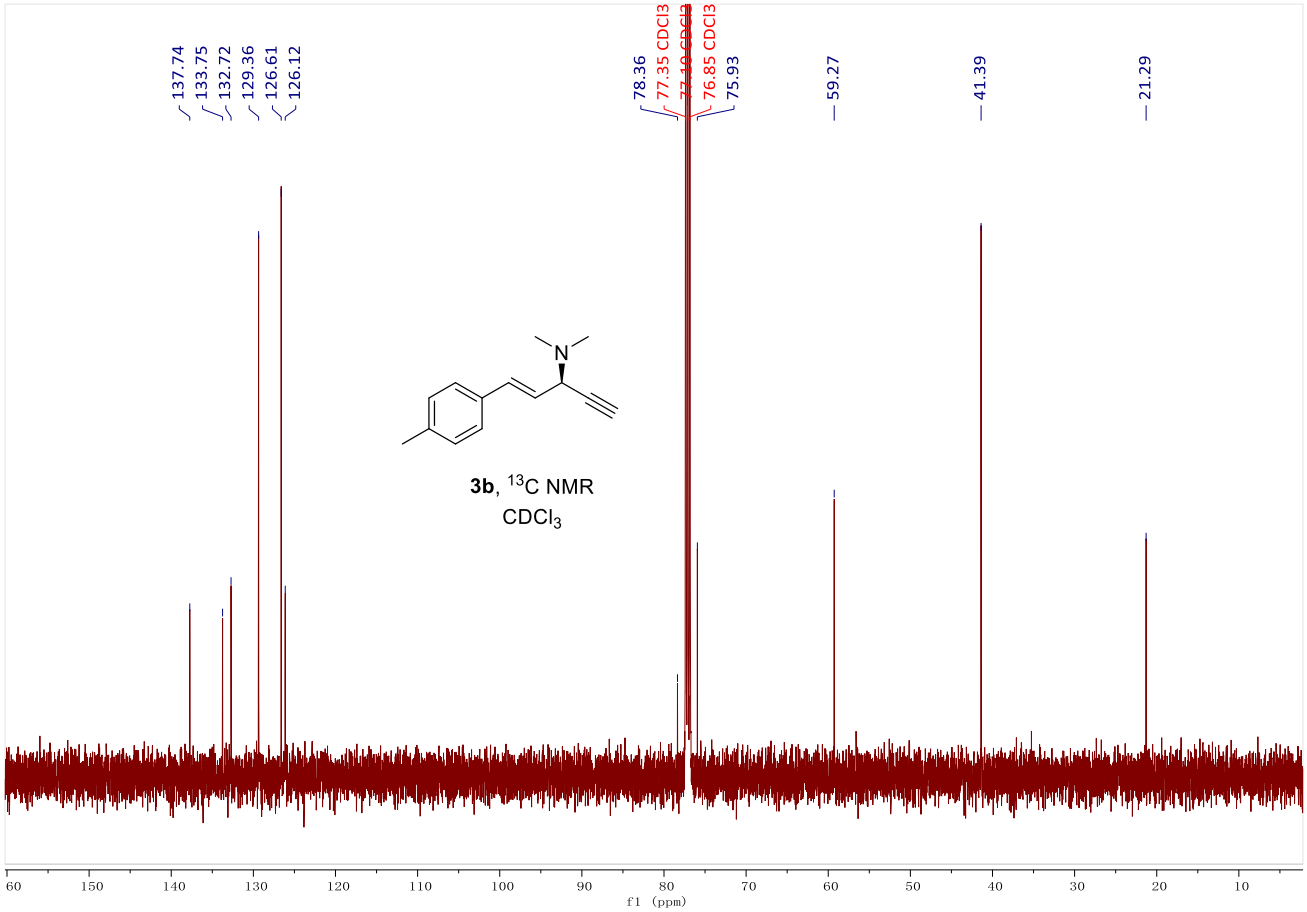
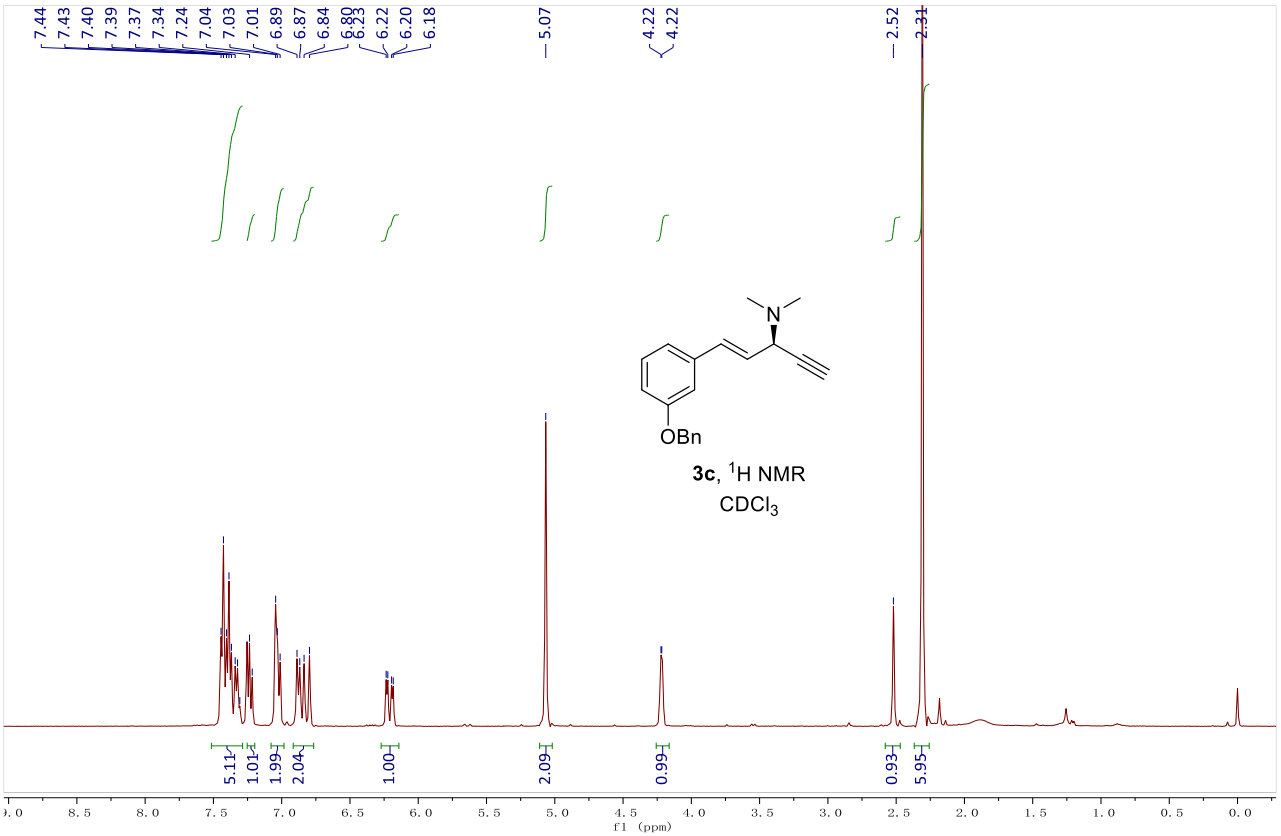
77.35 CDCl3
76.85 CDCl3
76.01
59.26
41.42
N
3a, 13C NMR
CDCl3
f1 (ppm)



3b, ^{1}H NMR
$CDCl_3$



3b, ^{13}C NMR
$CDCl_3$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7.43
7.40
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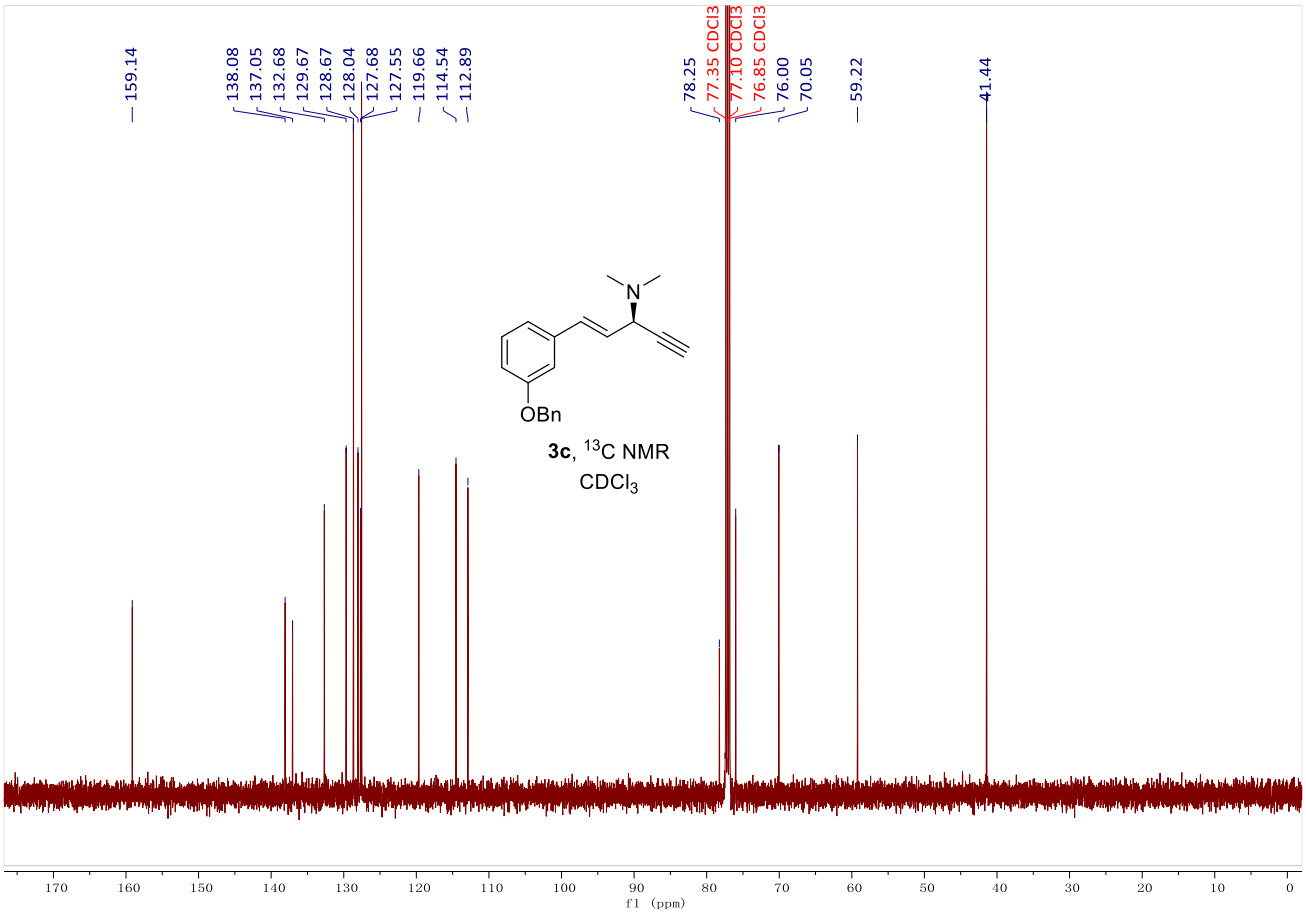
7.37
7.34
7.24
7.04
7.03
7.01
6.89
6.87
6.84
6.80
6.23
6.22
6.20
6.18
5.07
4.22
4.22
2.52
2.31
N
OBn
3c, 1H NMR
CDCl3
5.11
1.01
1.99
2.04
1.00
2.09
0.99
0.93
5.95
f1 (ppm)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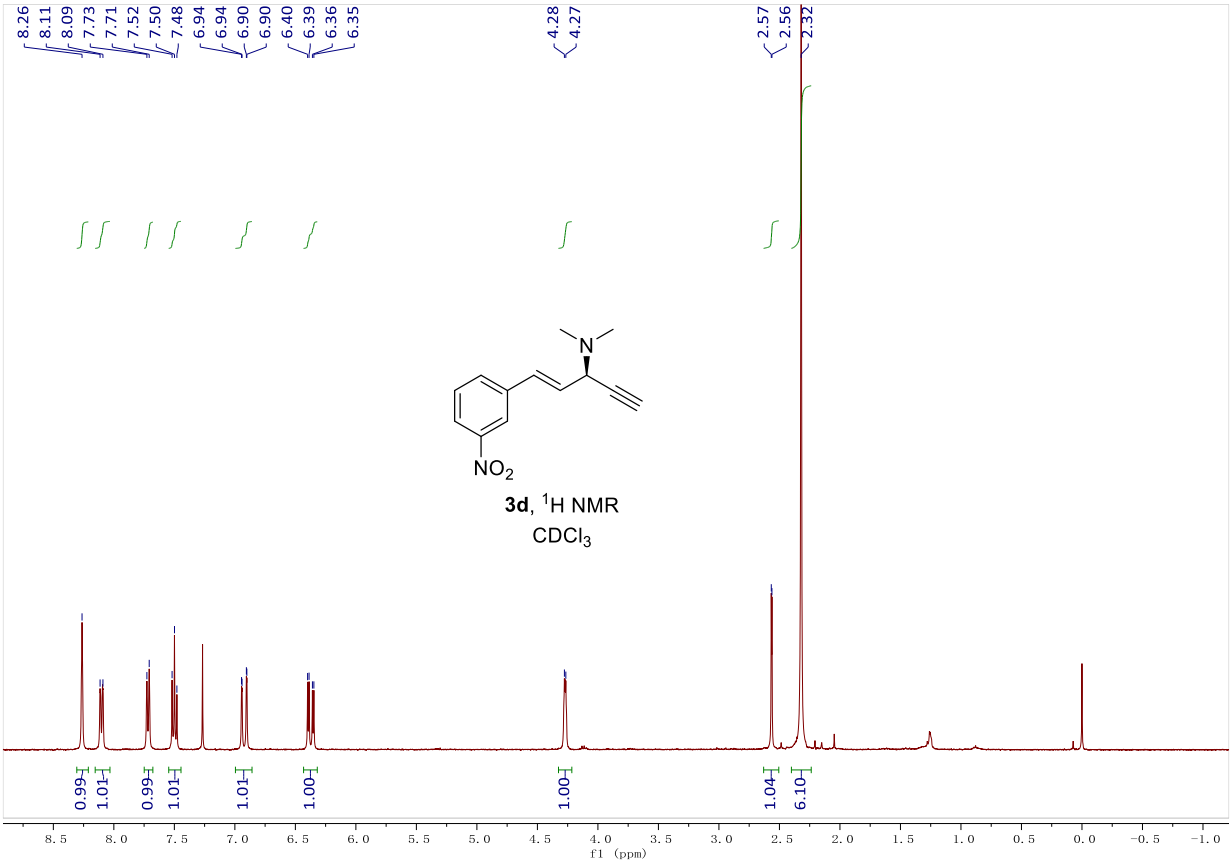
128.04
127.68
127.55
119.66
114.54
112.89
78.25
77.35 CDCl3
77.10 CDCl3
76.85 CDCl3
76.00
70.05
59.22
41.44
N
OBn
3c, 13C NMR
CDCl3
f1 (ppm)


8.26
8.11
8.09
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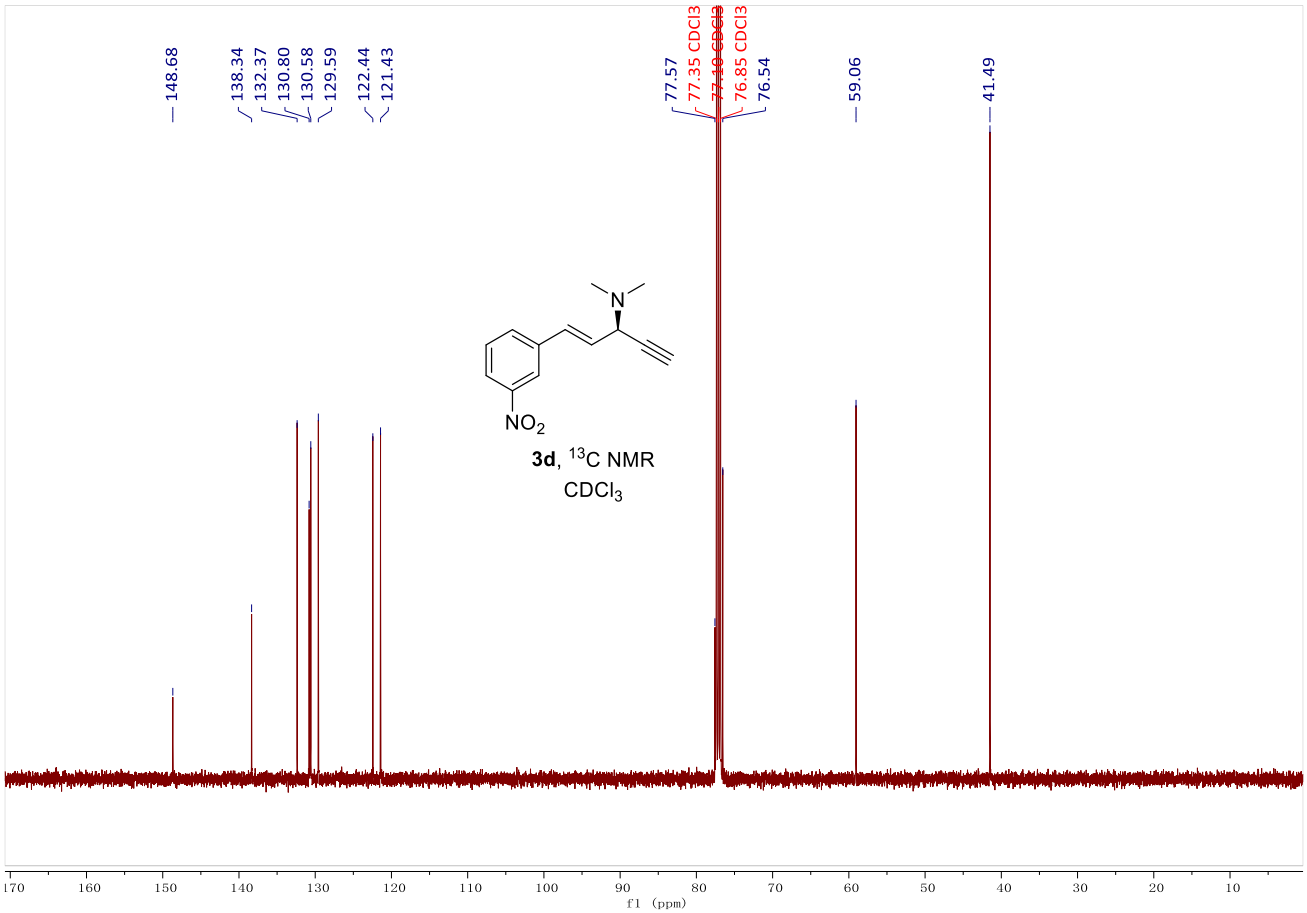
7.71
7.52
7.50
7.48
6.94
6.94
6.90
6.90
6.40
6.39
6.36
6.35
4.28
4.27
2.57
2.56
2.32
N
NO2
3d, 1H NMR
CDCl3
0.99
1.01
0.99
1.01
1.01
1.00
1.00
1.04
6.10
f1 (ppm)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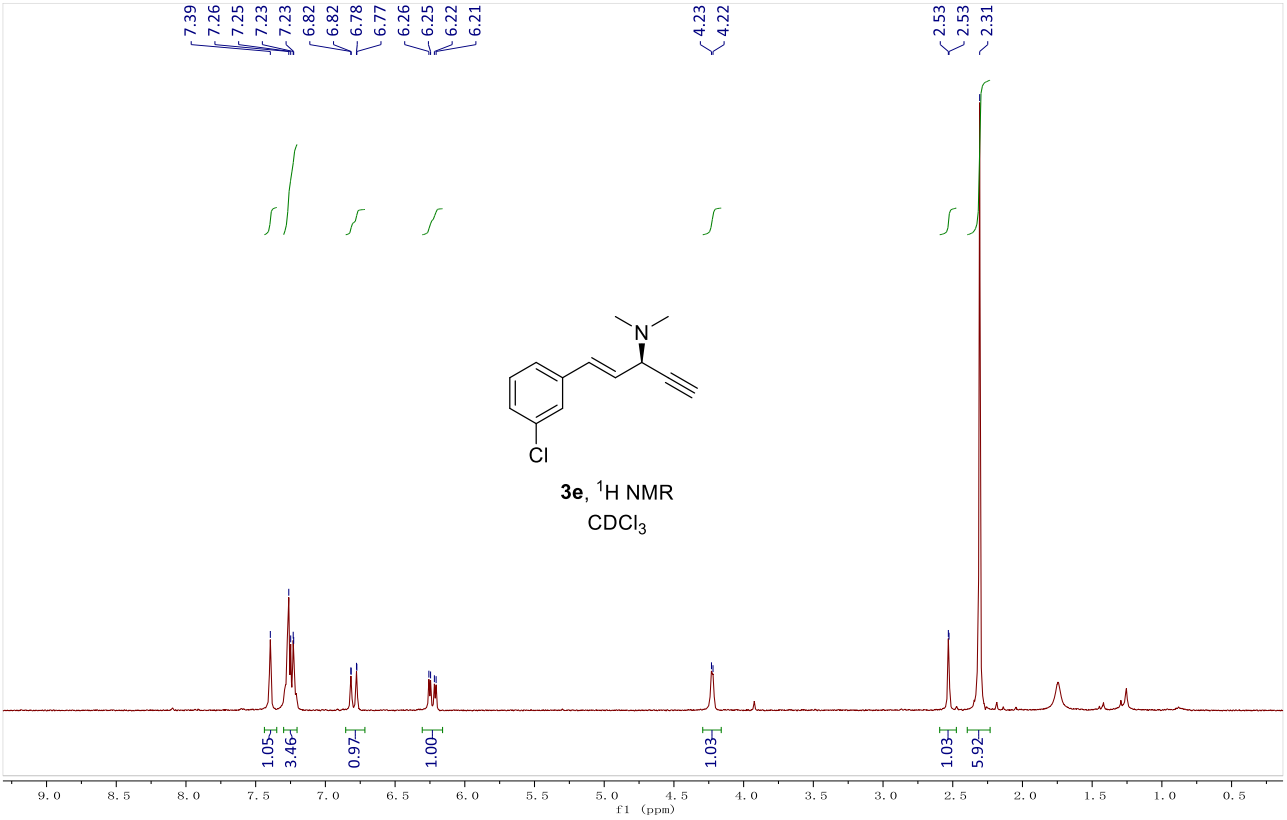
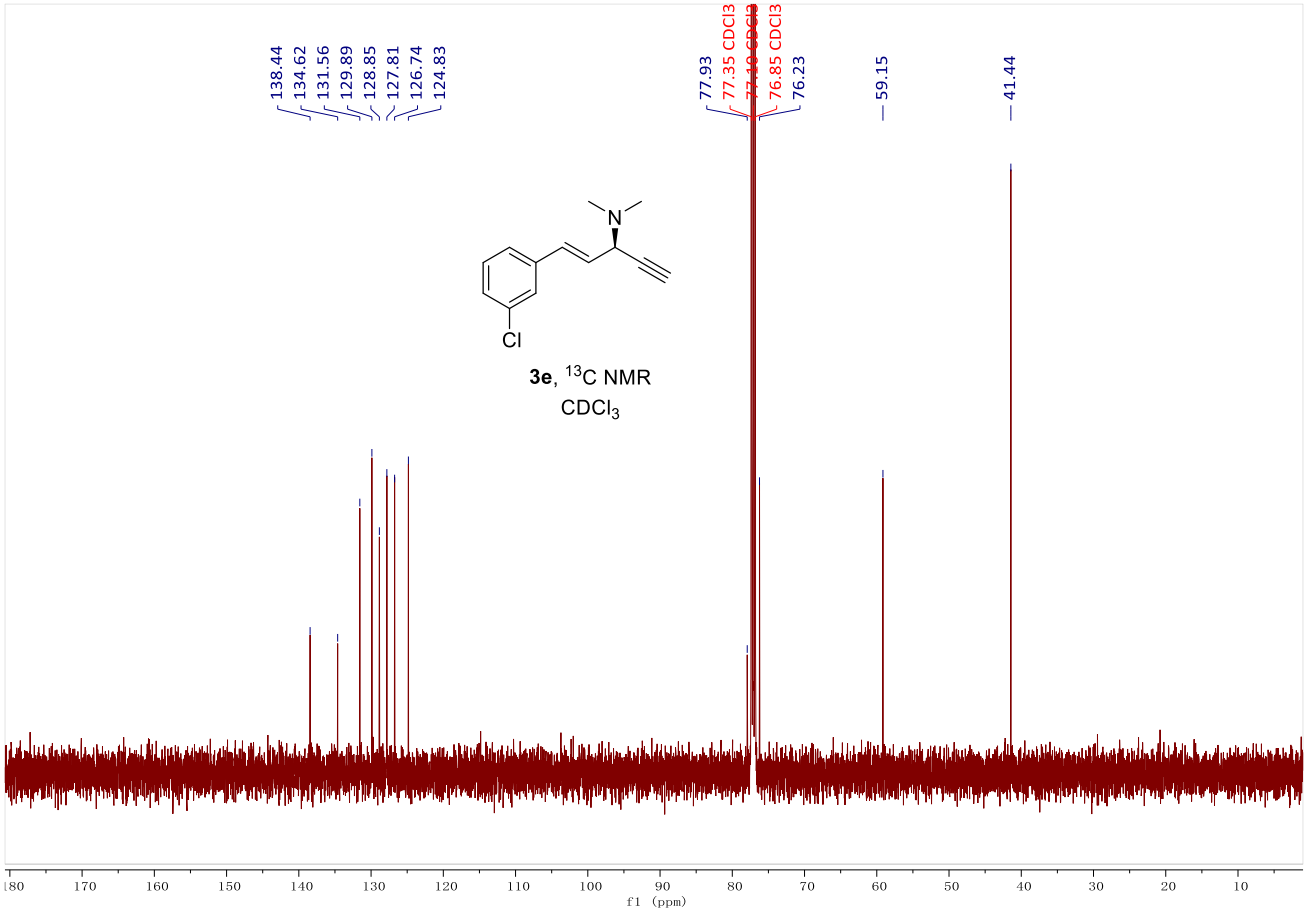
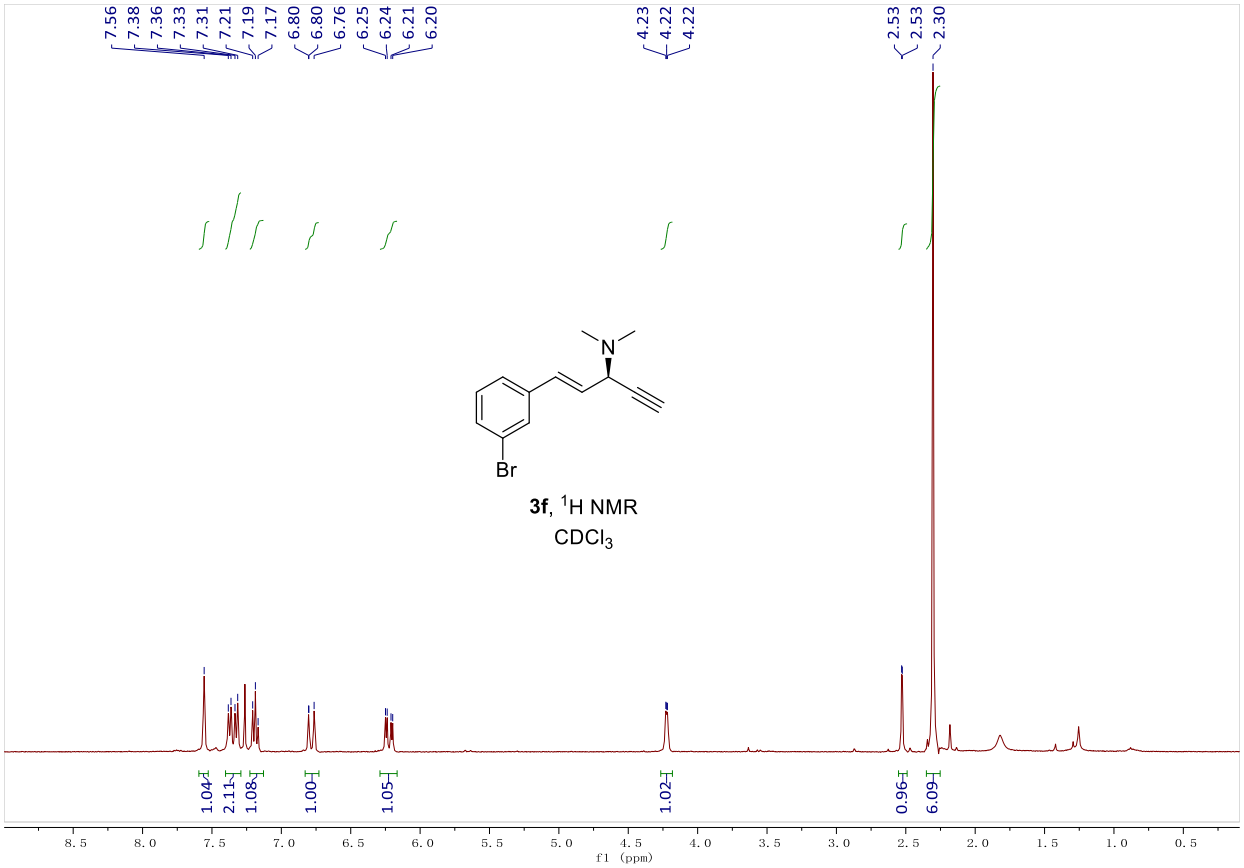
138.34
132.37
130.80
130.58
129.59
122.44
121.43
77.57
77.35 CDCl3
77.10 CDCl3
76.85 CDCl3
76.54
59.06
41.49
N
NO2
3d, 13C NMR
CDCl3
f1 (ppm)



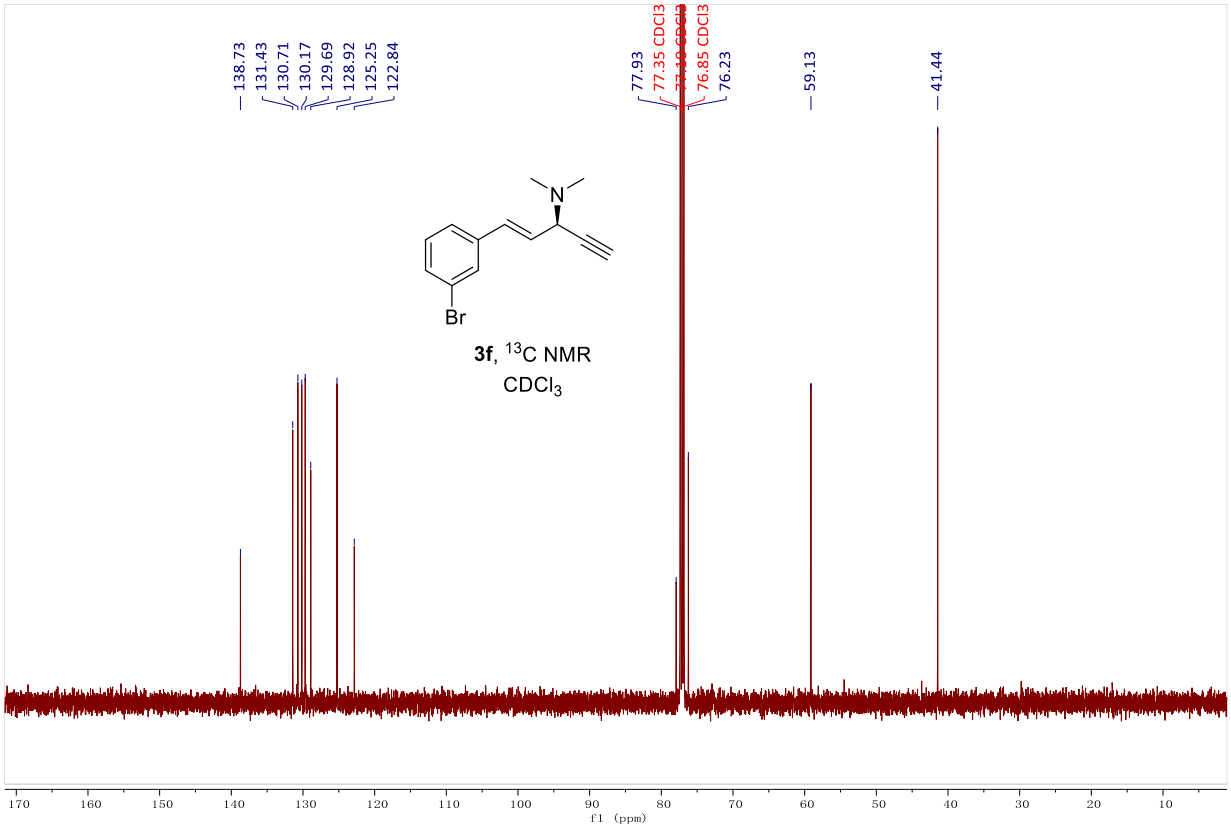
3e, ^{1}H NMR
$CDCl_3$



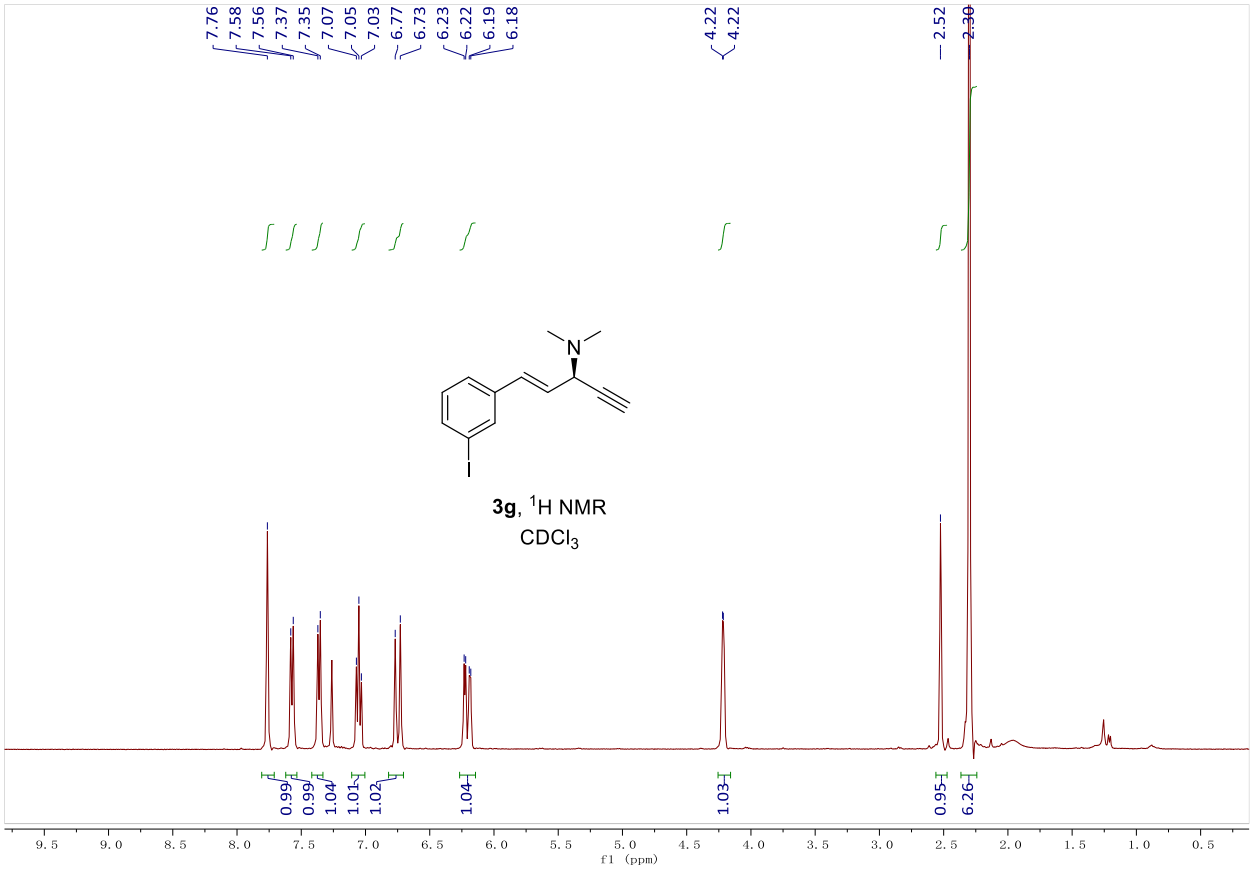
3e, ^{13}C NMR
$CDCl_3$



3f, ^{1}H NMR
$CDCl_3$



3f, ^{13}C NMR
$CDCl_3$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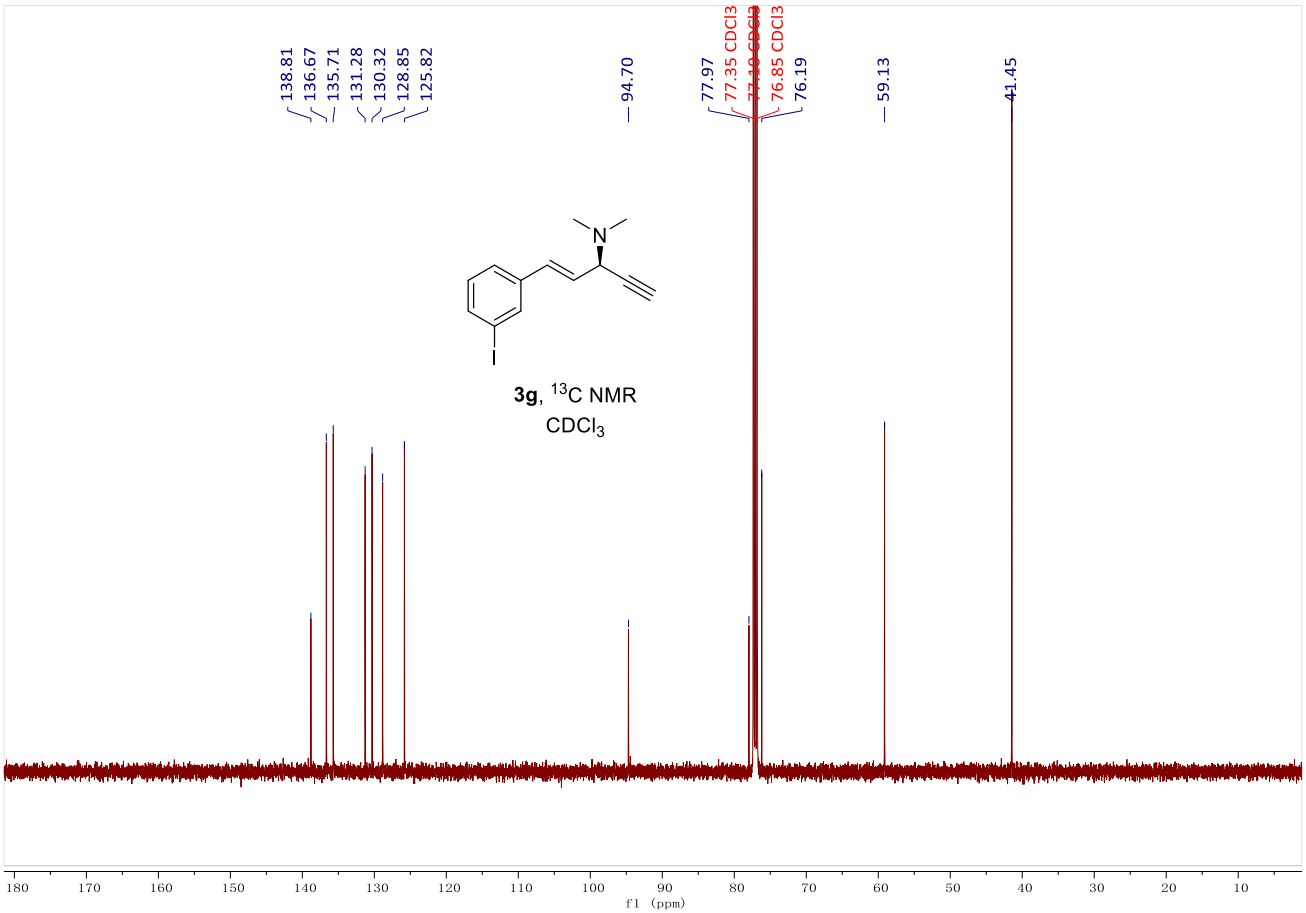
7.58
7.56
7.37
7.35
7.07
7.05
7.03
6.77
6.73
6.23
6.22
6.19
6.18
4.22
4.22
2.52
2.30
N
I
3g, 1H NMR
CDCl3
0.99
0.99
1.04
1.01
1.02
1.04
1.03
0.95
6.26
f1 (ppm)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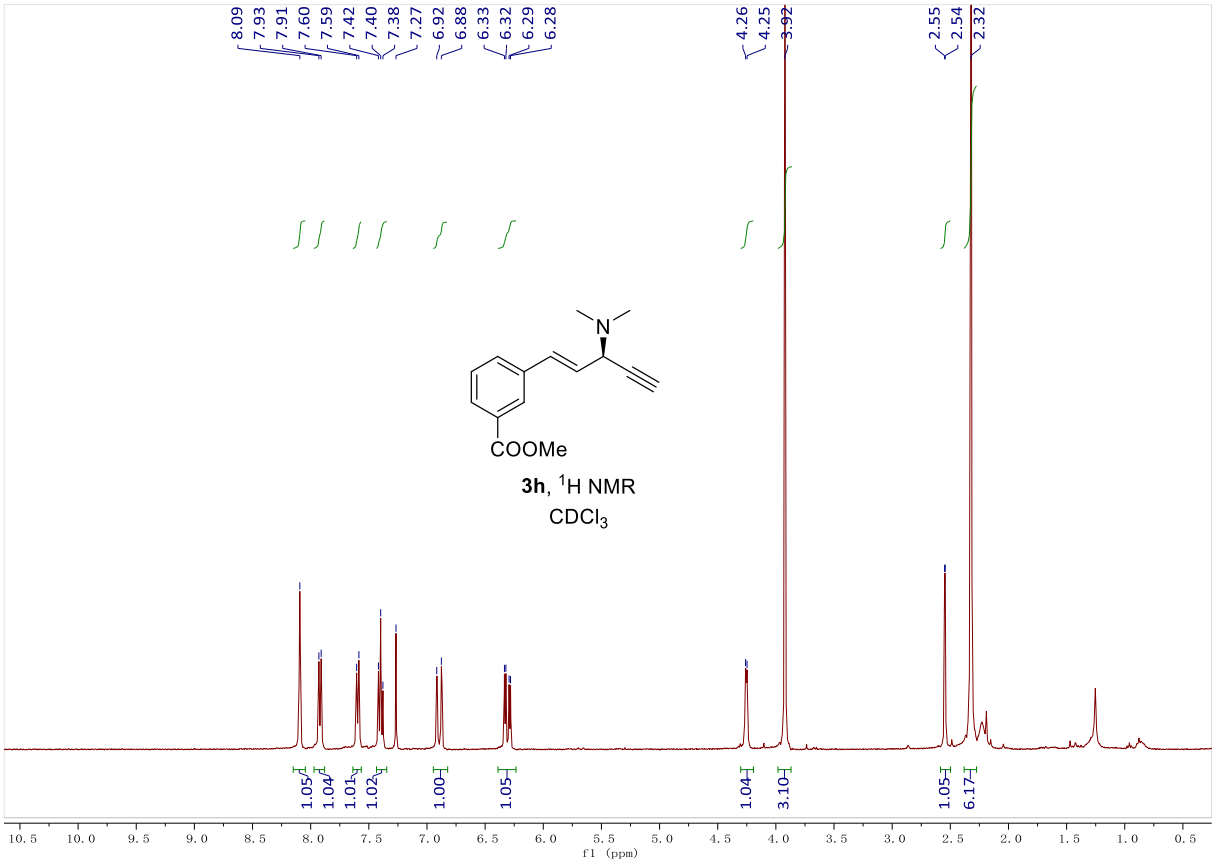
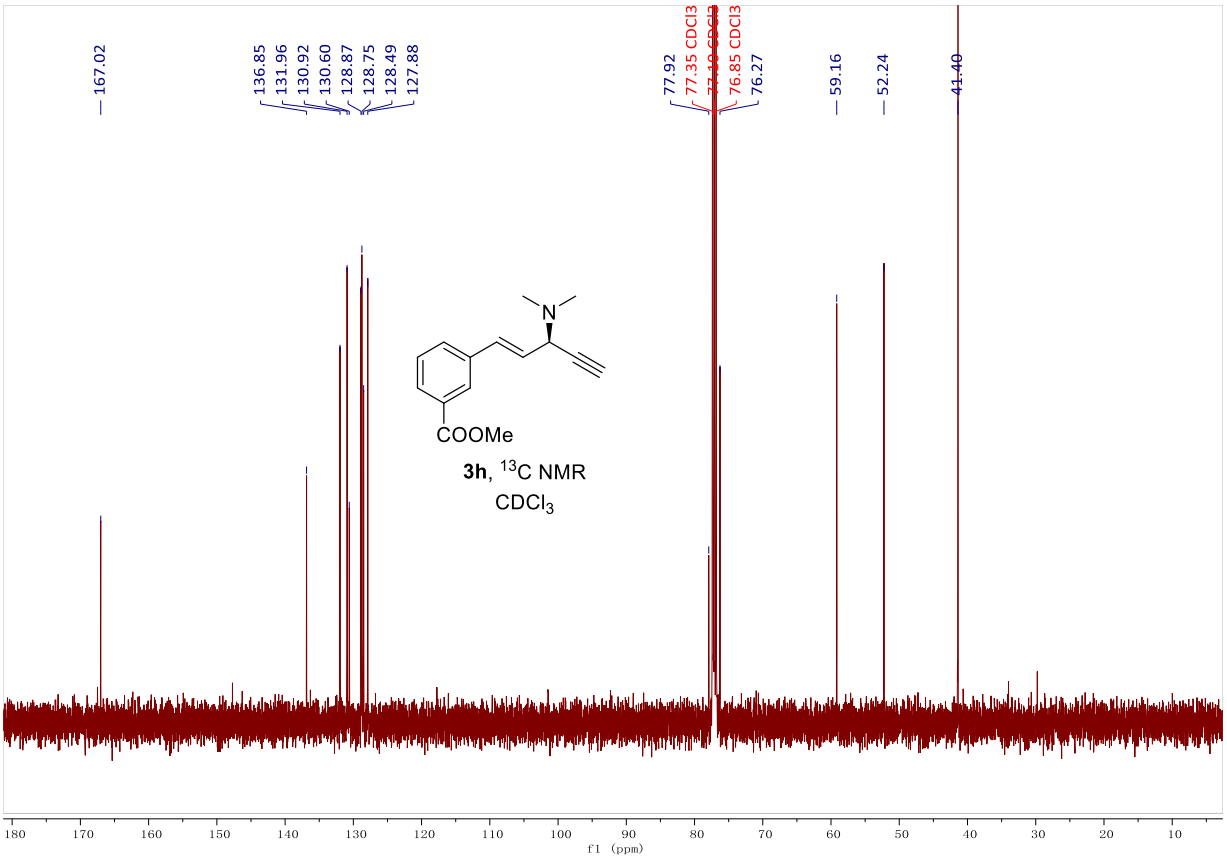
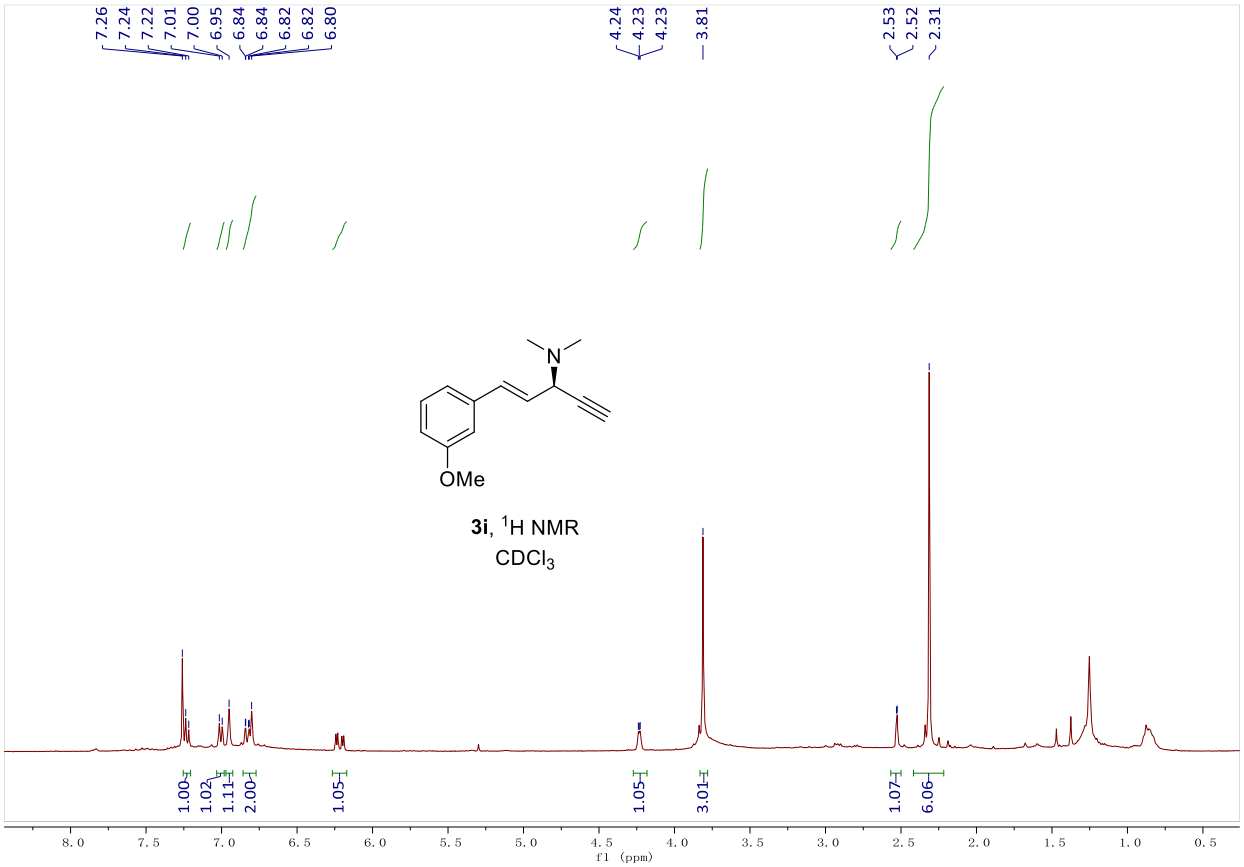
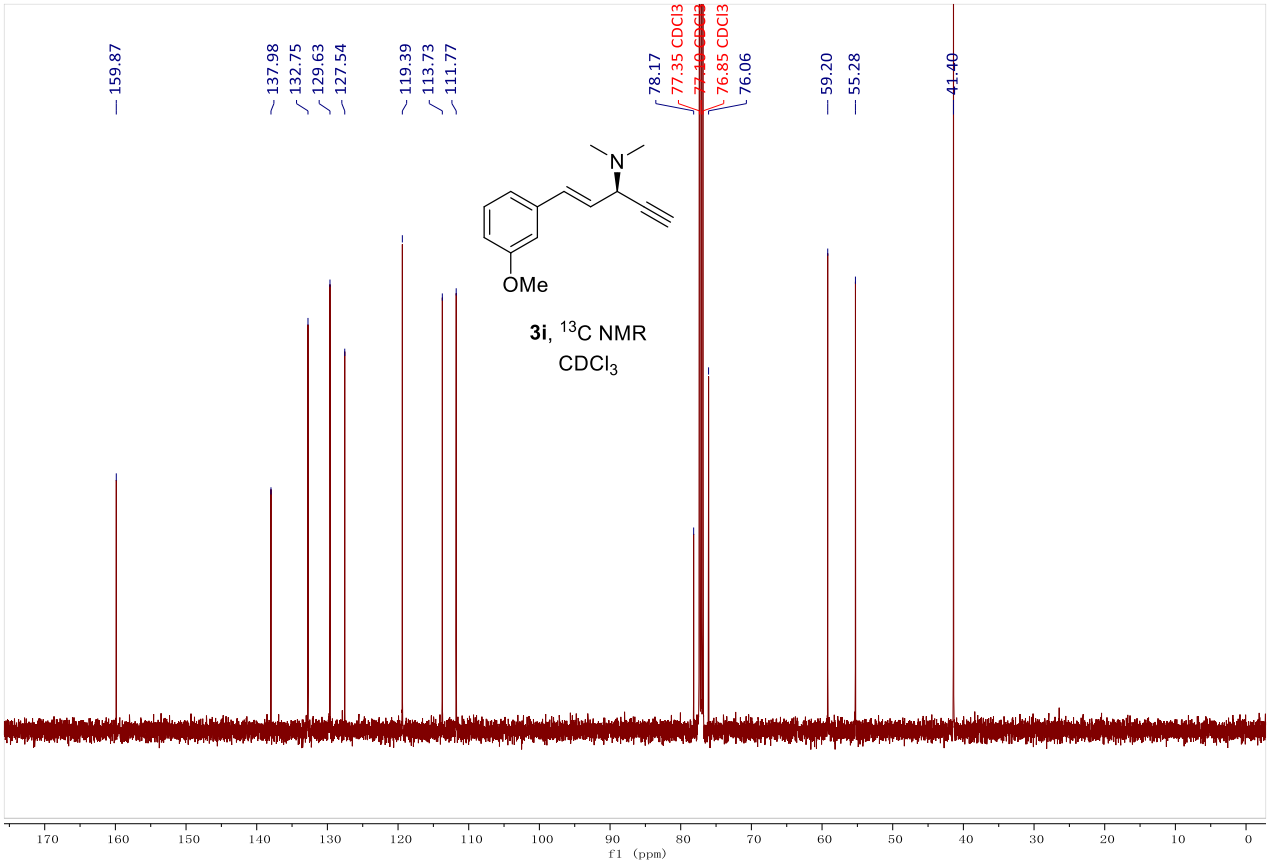
136.67
135.71
131.28
130.32
128.85
125.82
94.70
77.97
77.35 CDCl3
76.85 CDCl3
76.19
59.13
41.45
N
I
3g, 13C NMR
CDCl3
f1 (ppm)


8.09
7.93
7.91
7.60
7.59
7.42
7.40
7.38
7.27
6.92
6.88
6.33
6.32
6.29
6.28
4.26
4.25
3.92
2.55
2.54
2.32
N
COOMe
3h, 1H NMR
CDCl3
1.05
1.04
1.01
1.02
1.00
1.05
1.04
3.10
1.05
6.17
f1 (ppm)


167.02
136.85
131.96
130.92
130.60
128.87
128.75
128.49
127.88
77.92
77.35 CDCl3
76.85 CDCl3
76.27
59.16
52.24
41.40
N
COOMe
3h, 13C NMR
CDCl3
f1 (ppm)


7.26
7.24
7.22
7.01
7.00
6.95
6.84
6.84
6.82
6.82
6.80
4.24
4.23
4.23
3.81
2.53
2.52
2.31
N
OMe
3i, 1H NMR
CDCl3
1.00
1.02
1.11
2.00
1.05
1.05
3.01
1.07
6.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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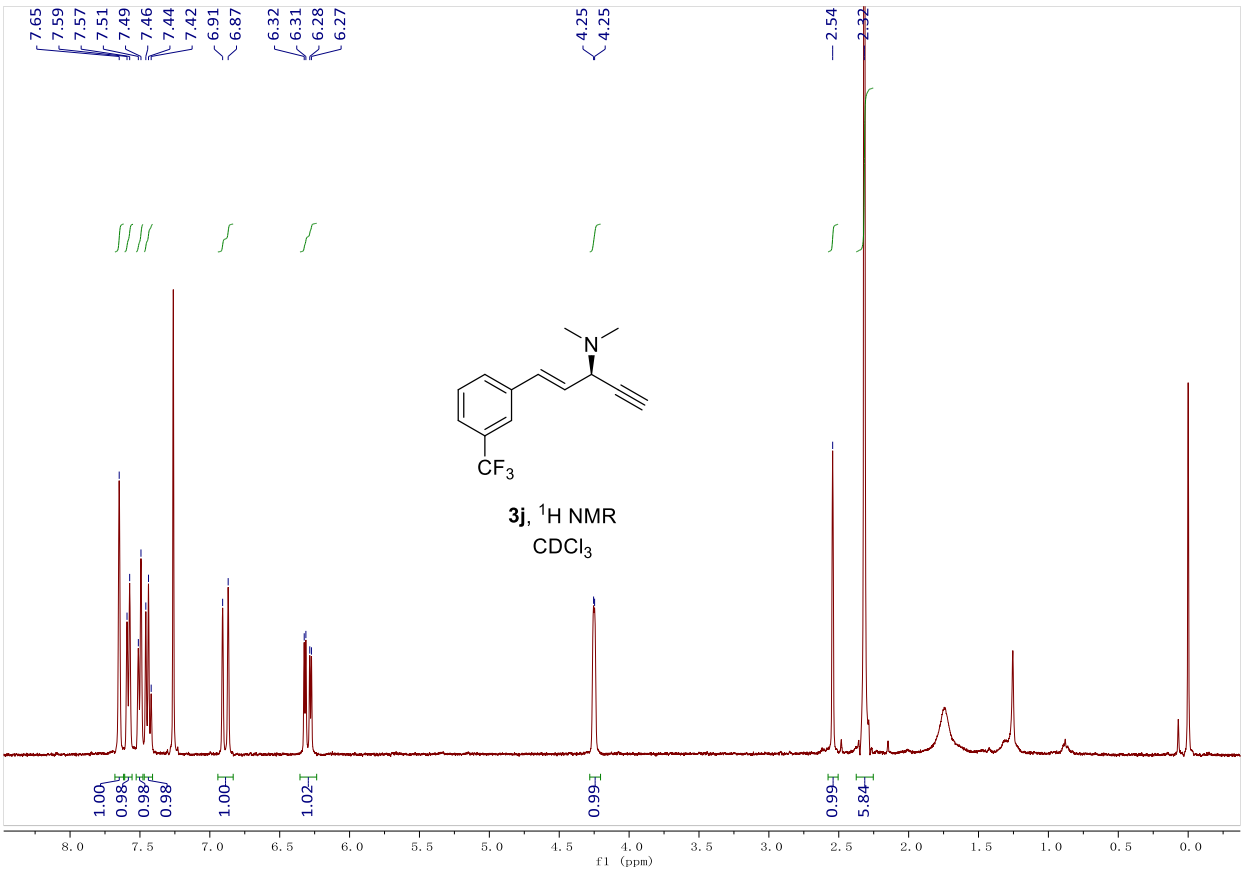
119.39
113.73
111.77
78.17
77.35 CDCl3
77.10 CDCl3
76.85 CDCl3
76.06
59.20
55.28
41.40
N
OMe
3i, 13C NMR
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.65
7.59
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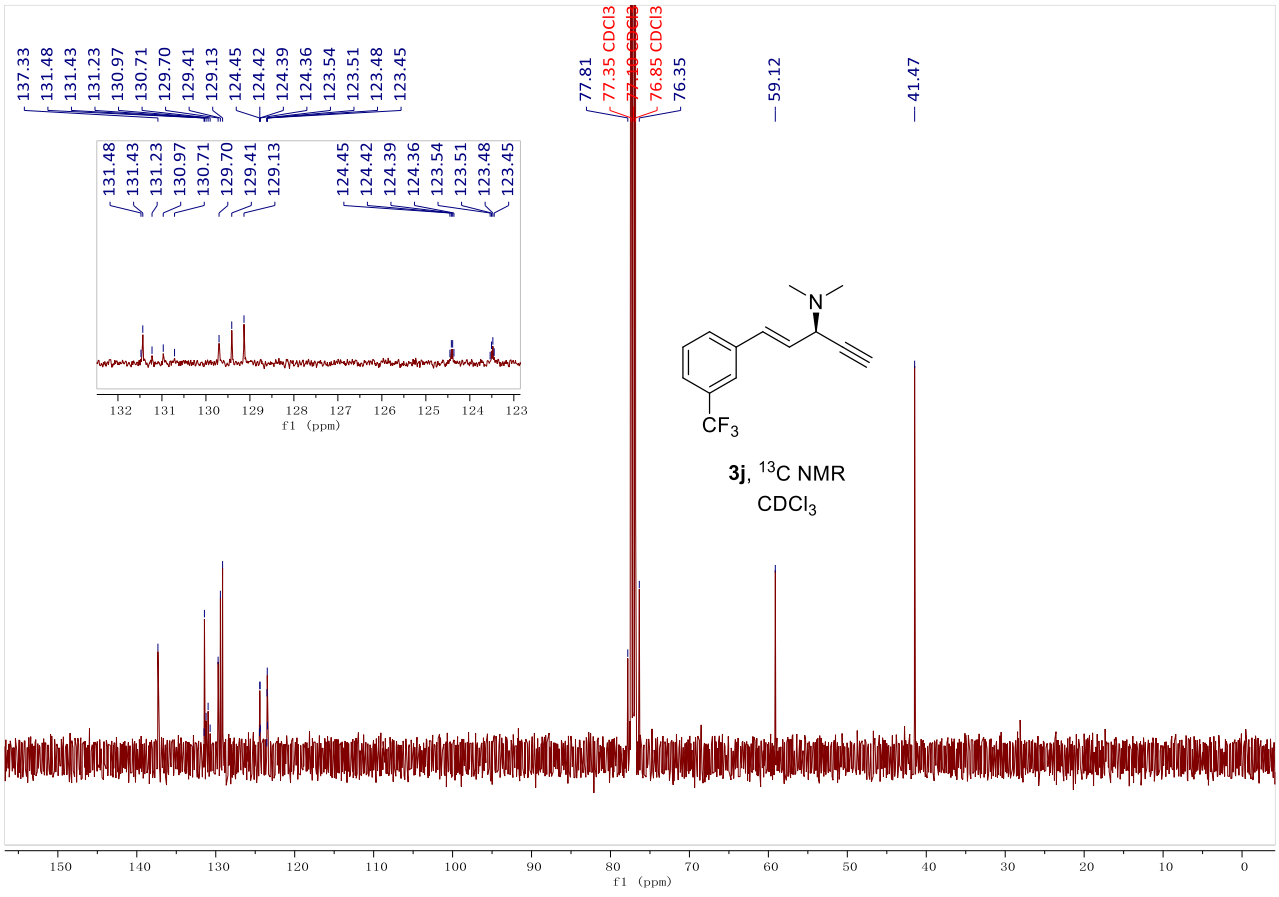
7.49
7.46
7.44
7.42
6.91
6.87
6.32
6.31
6.28
6.27
4.25
4.25
2.54
2.32
N
CF3
3j, 1H NMR
CDCl3
1.00
0.98
0.98
0.98
1.00
1.02
0.99
0.99
5.84
f1 (ppm)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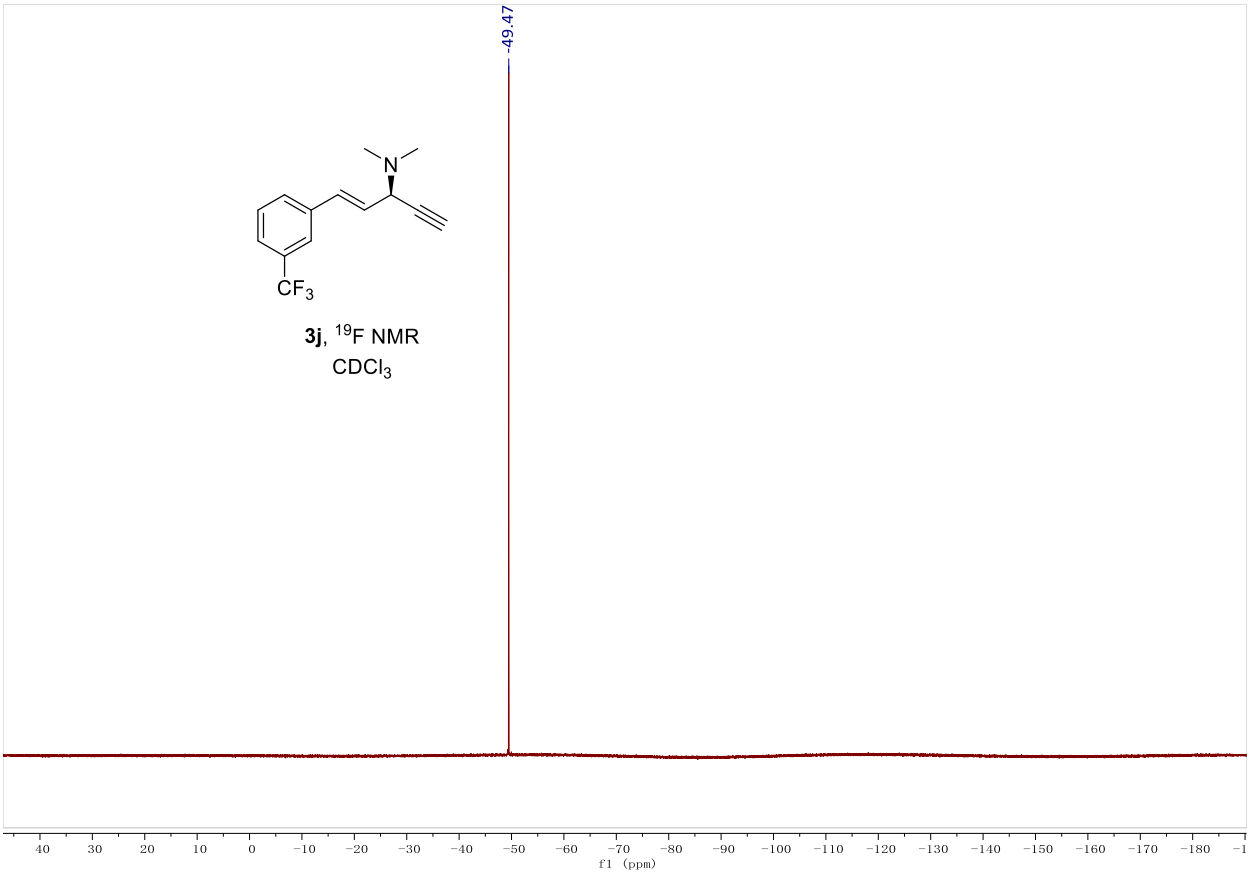
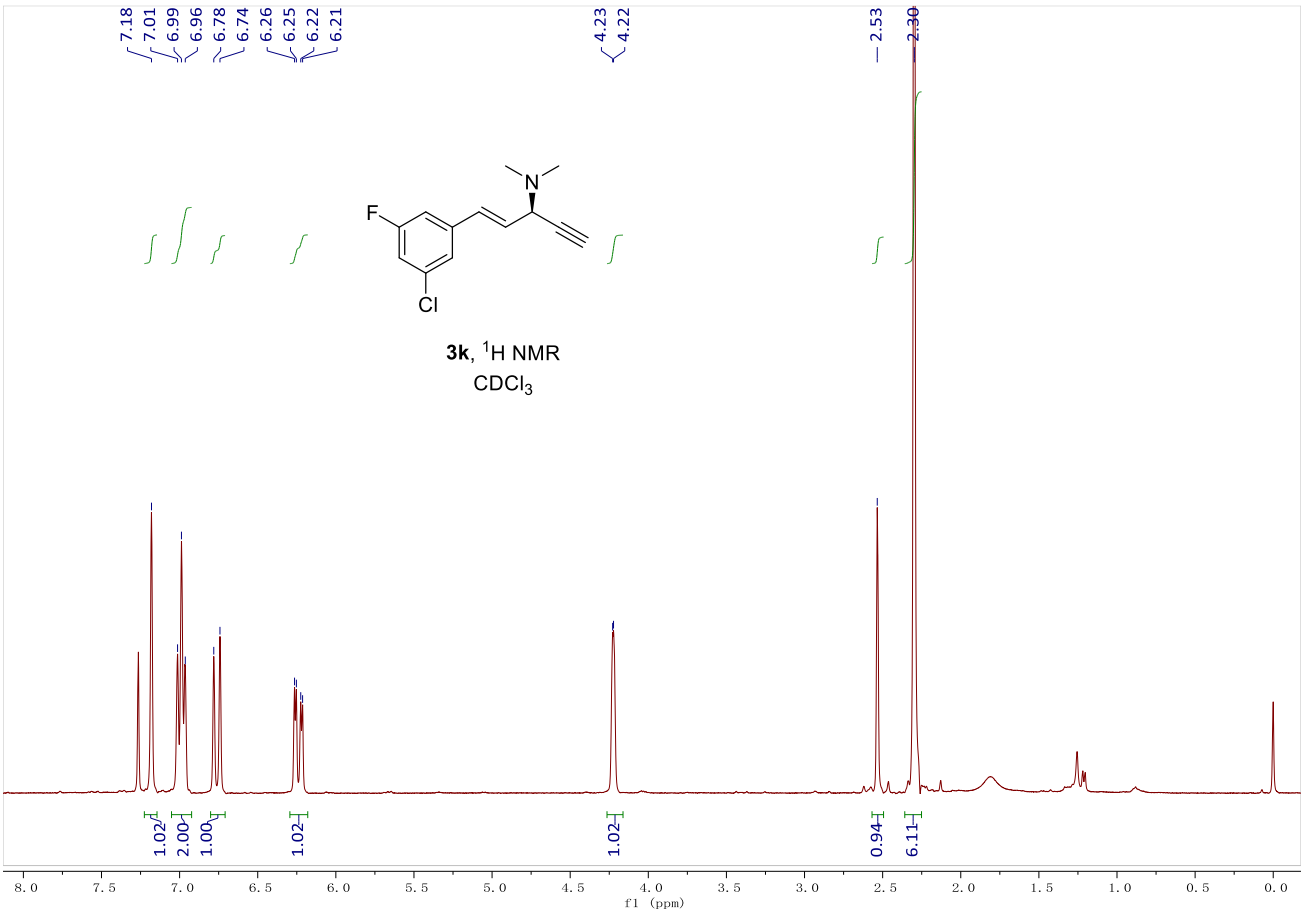
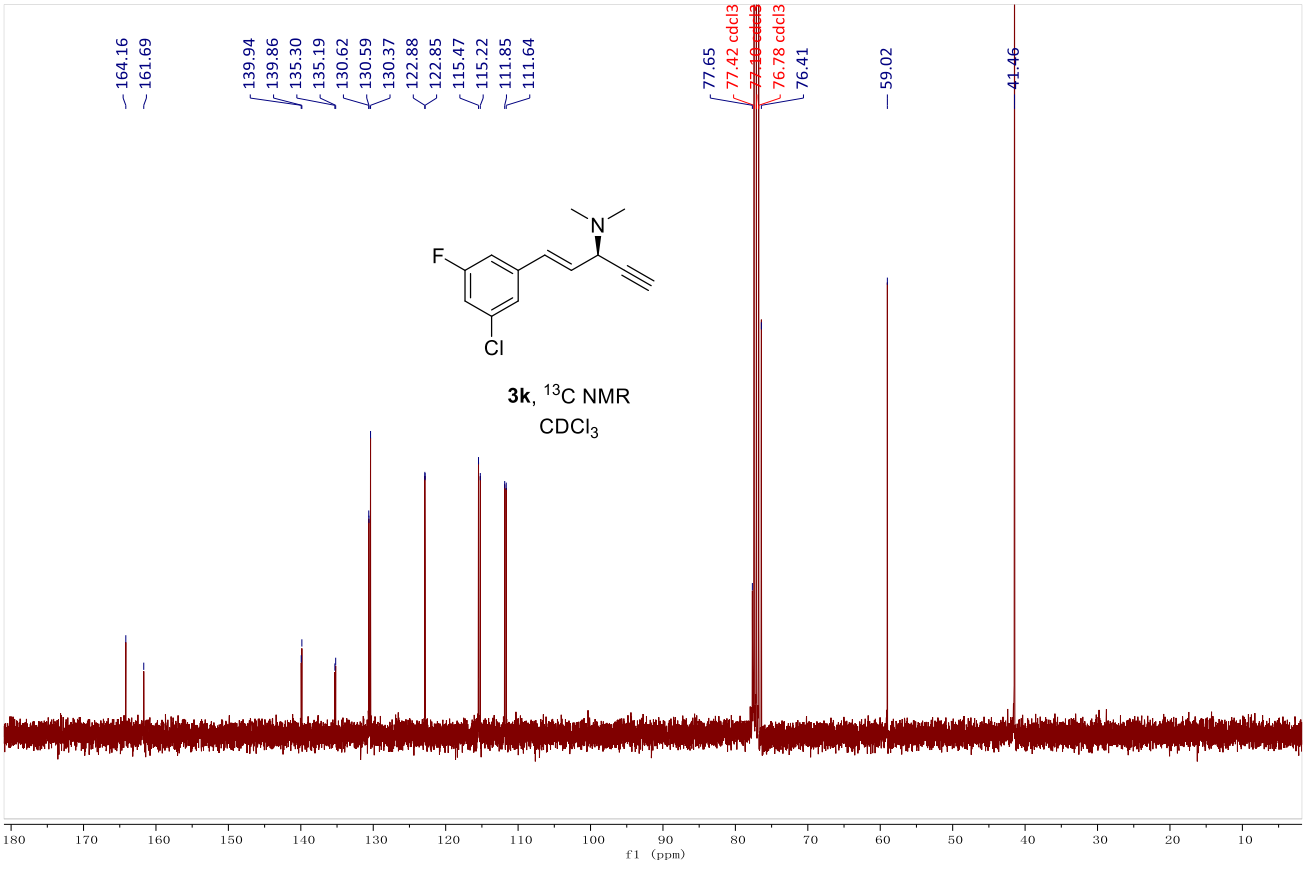
130.97
130.71
129.70
129.41
129.13
124.45
124.42
124.39
124.36
123.54
123.51
123.48
123.45
77.81
77.35 CDCl3
76.85 CDCl3
76.35
59.12
41.47
N
CF3
3j, 13C NMR
CDCl3
f1 (ppm)

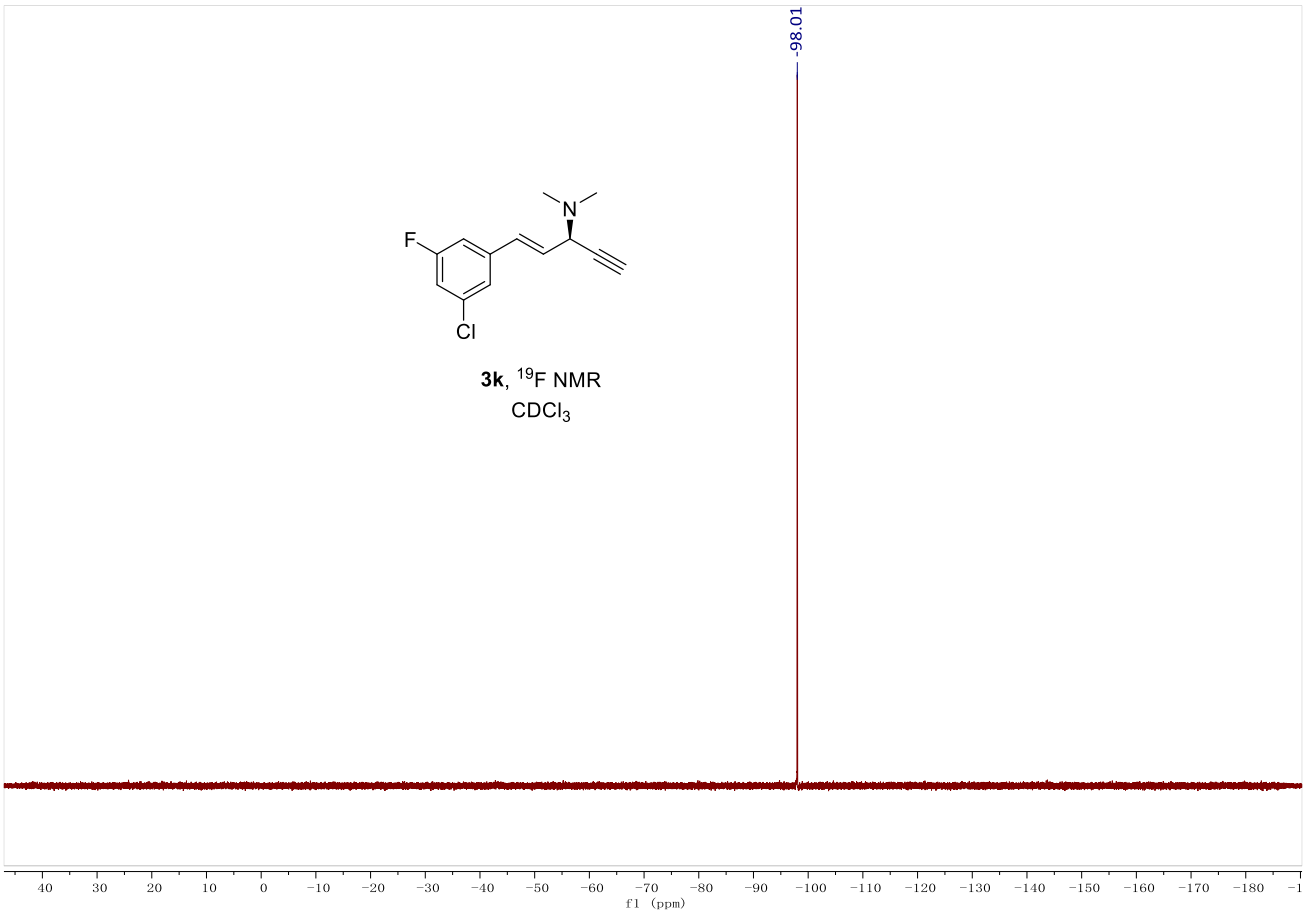

-49.47
N
CF3
3j, 19F NMR
CDCl3
40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −1
f1 (ppm)



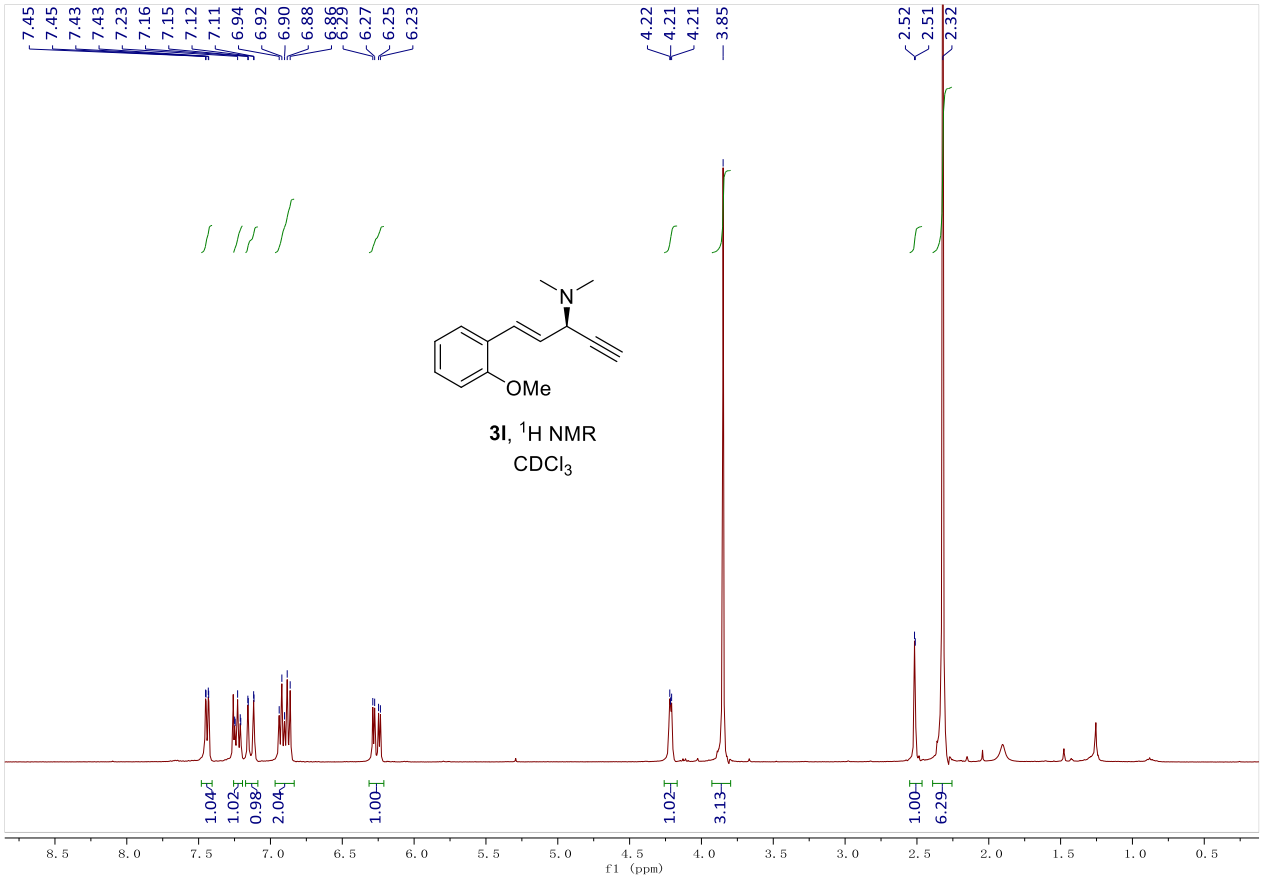
3k, ^{1}H NMR
$CDCl_3$



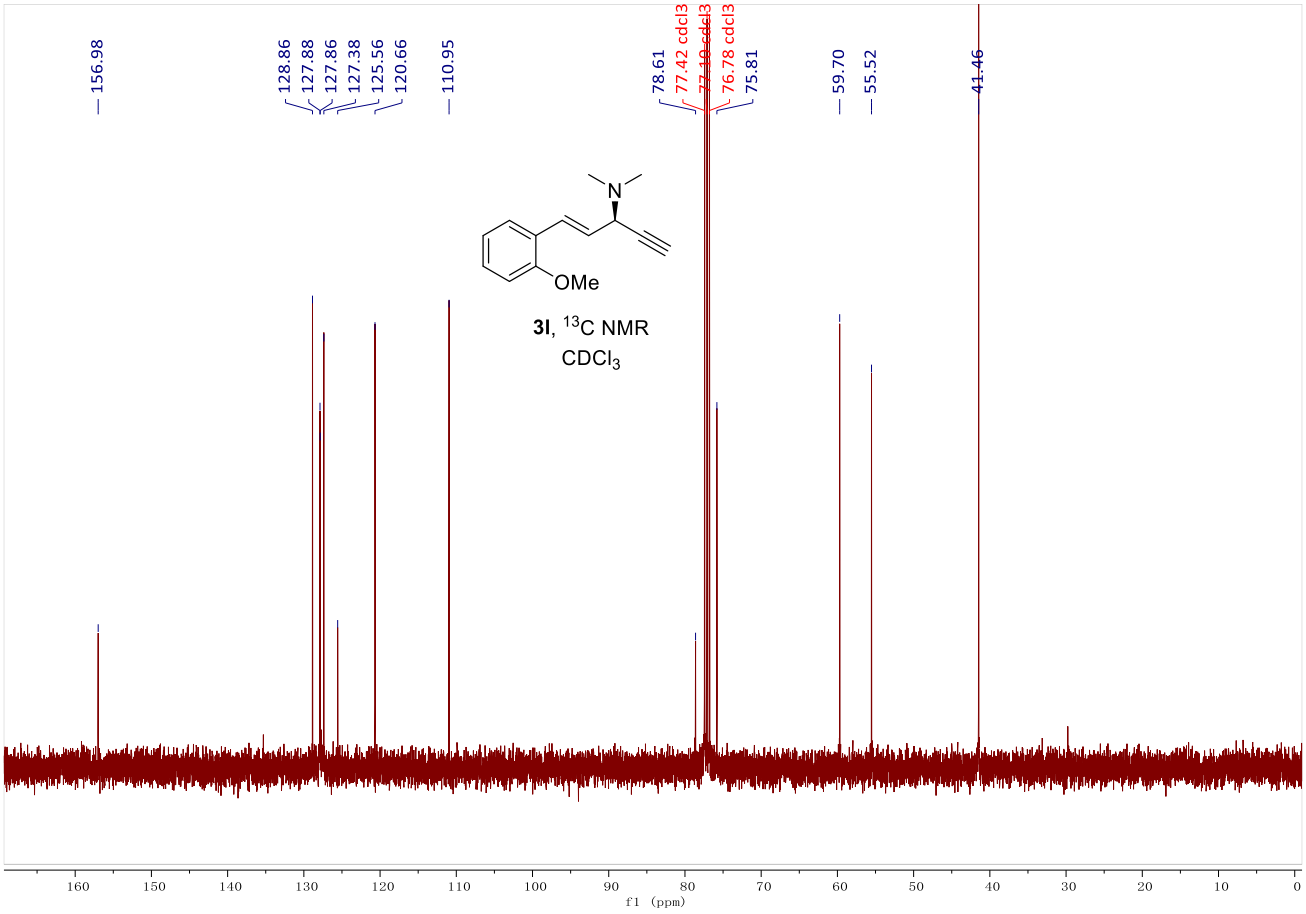
3k, ^{13}C NMR
$CDCl_3$



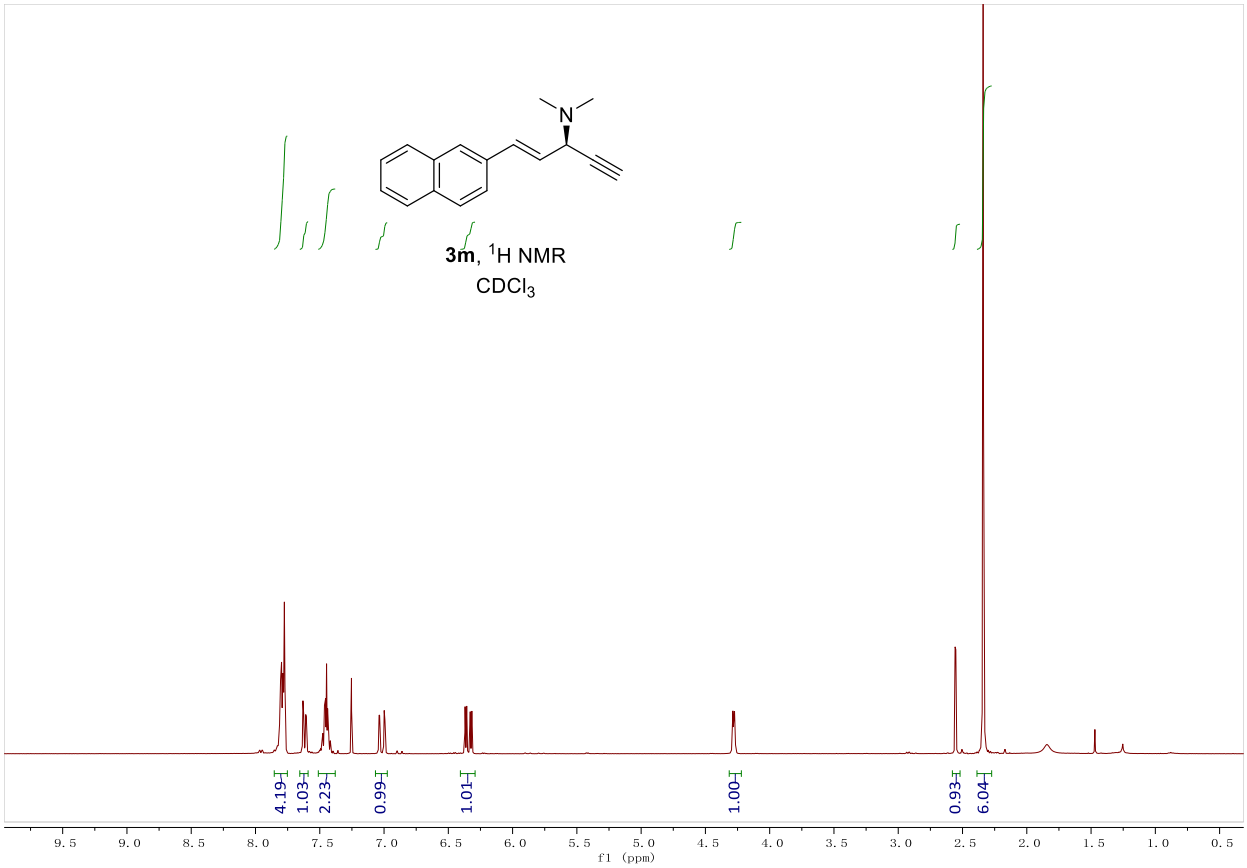
3k, ^{19}F NMR
$CDCl_3$

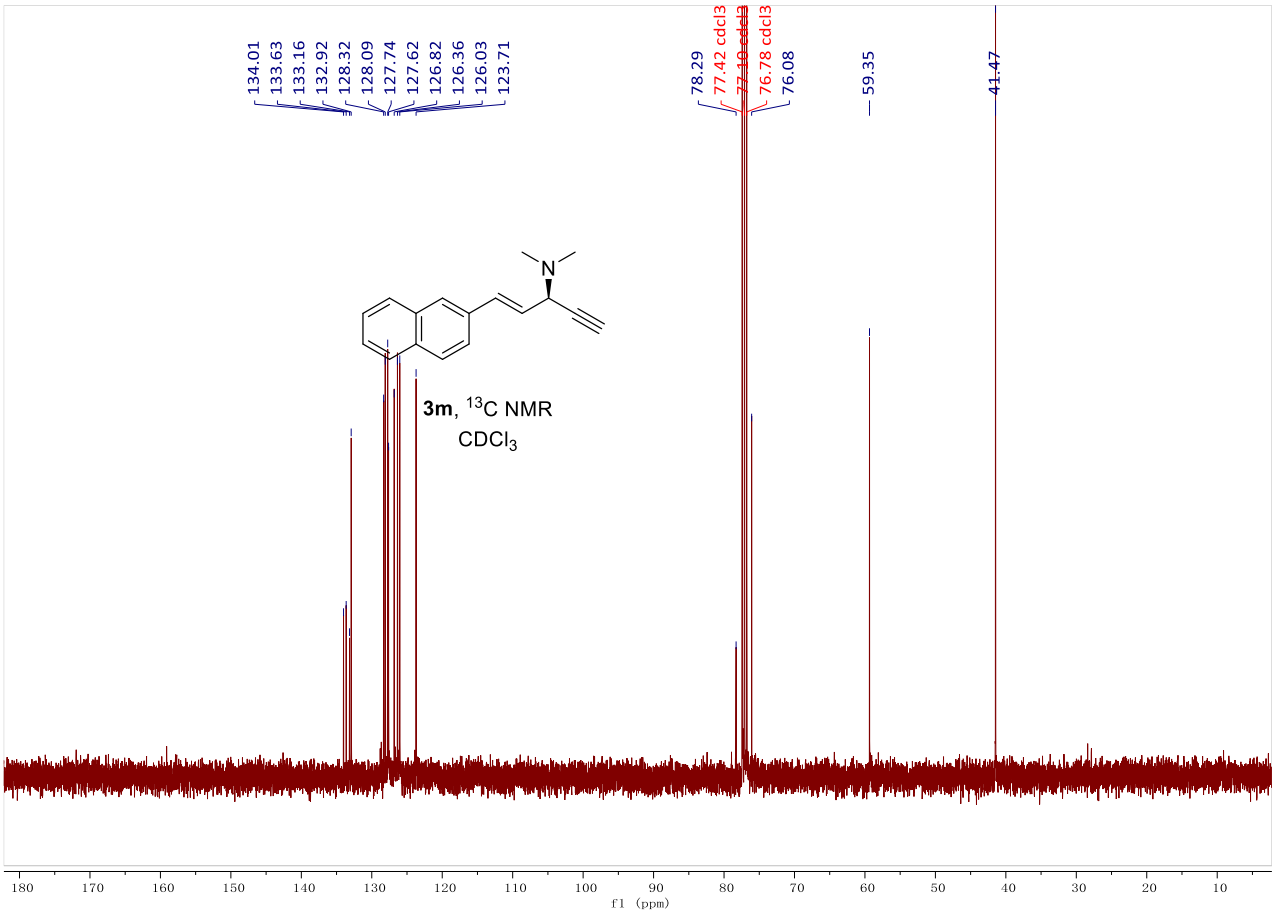


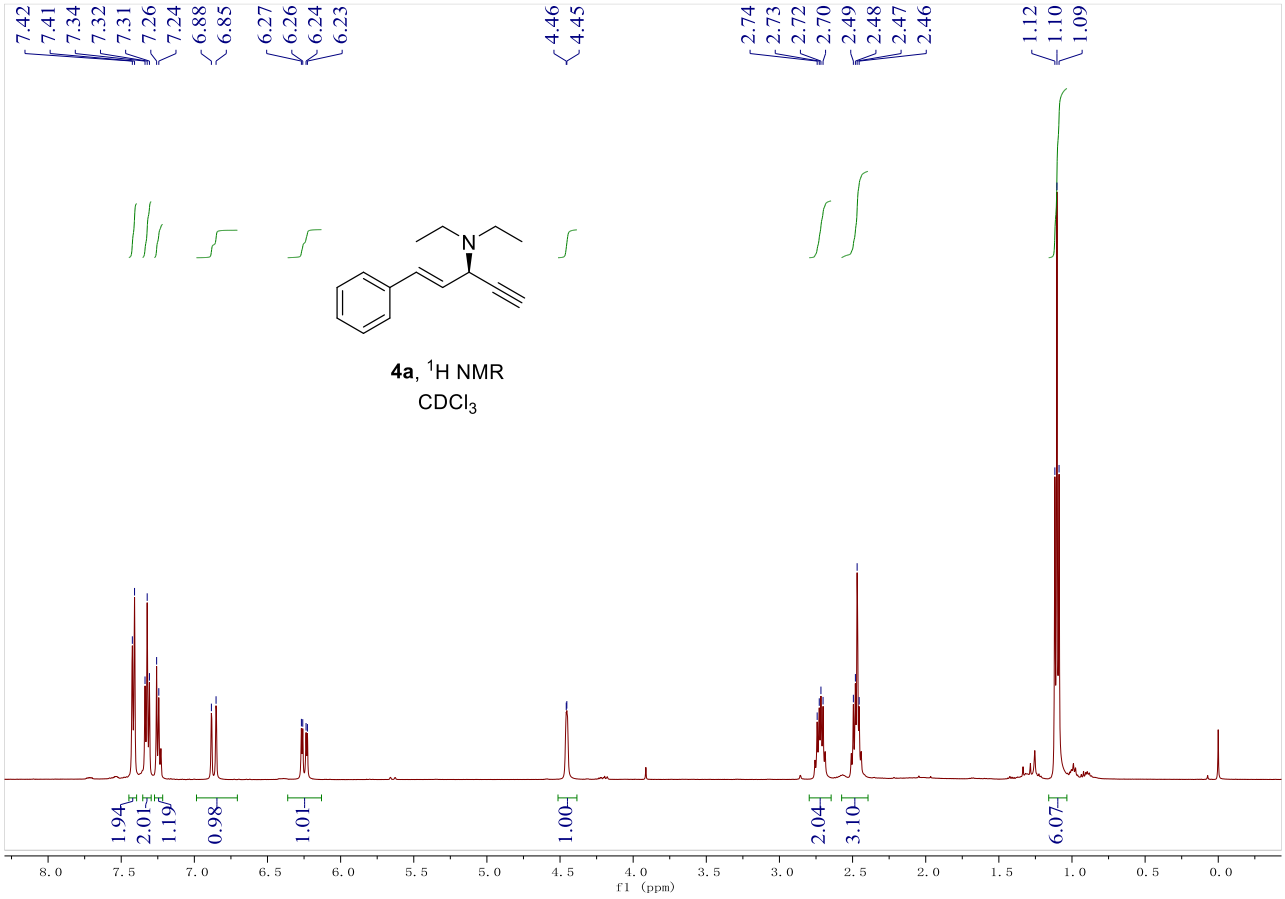
3l, ^{1}H NMR
$CDCl_3$



3l, ^{13}C NMR
$CDCl_3$


N
3m, 1H NMR
CDCl3
4.19
1.03
2.23
0.99
1.01
1.00
0.93
6.04
f1 (ppm)


134.01
133.63
133.16
132.92
128.32
128.09
127.74
127.62
126.82
126.36
126.03
123.71
78.29
77.42 cdcl3
76.78 cdcl3
76.08
59.35
41.47
N
3m, 13C NMR
CDCl3
f1 (ppm)


7.42
7.41
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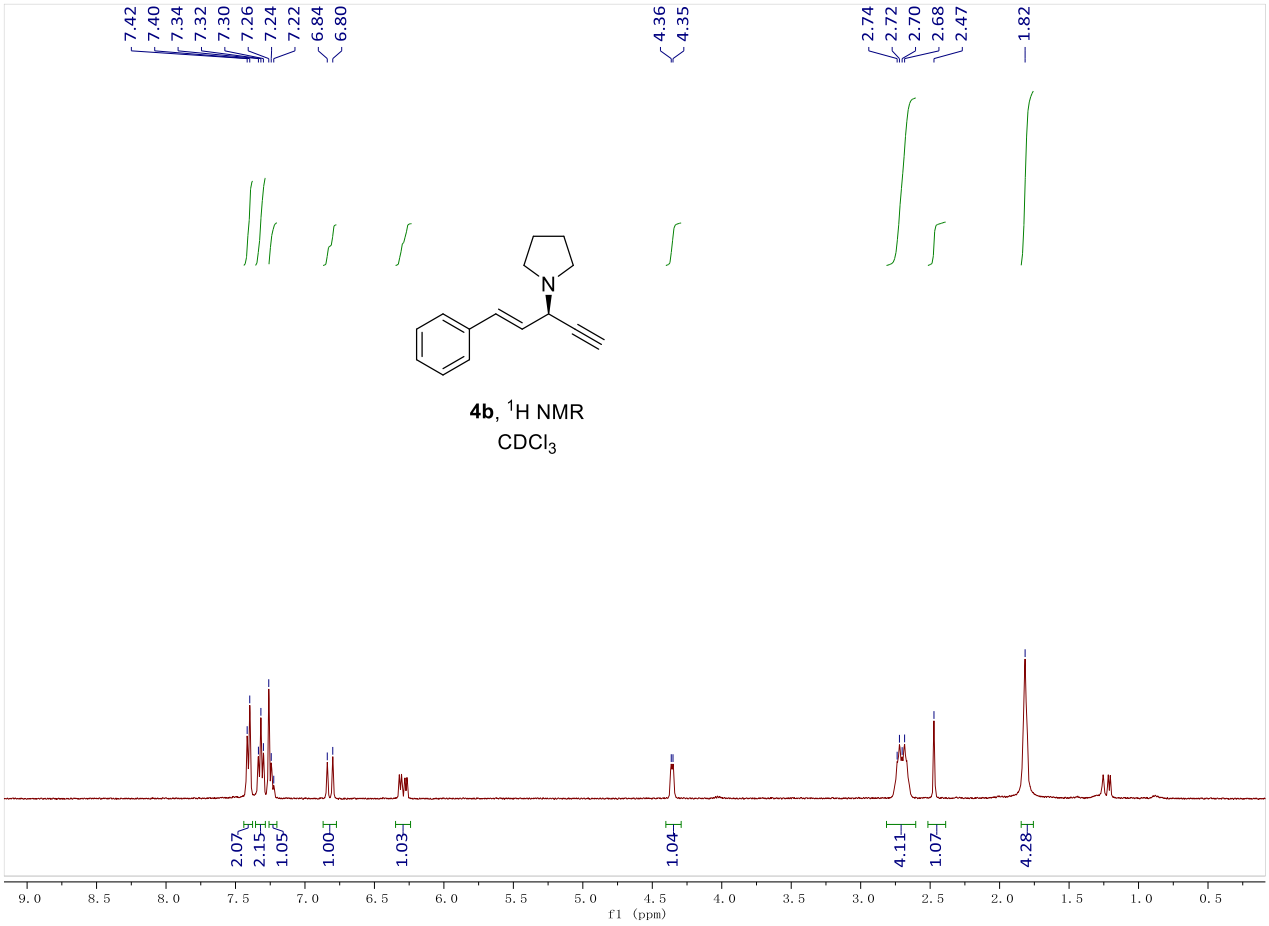
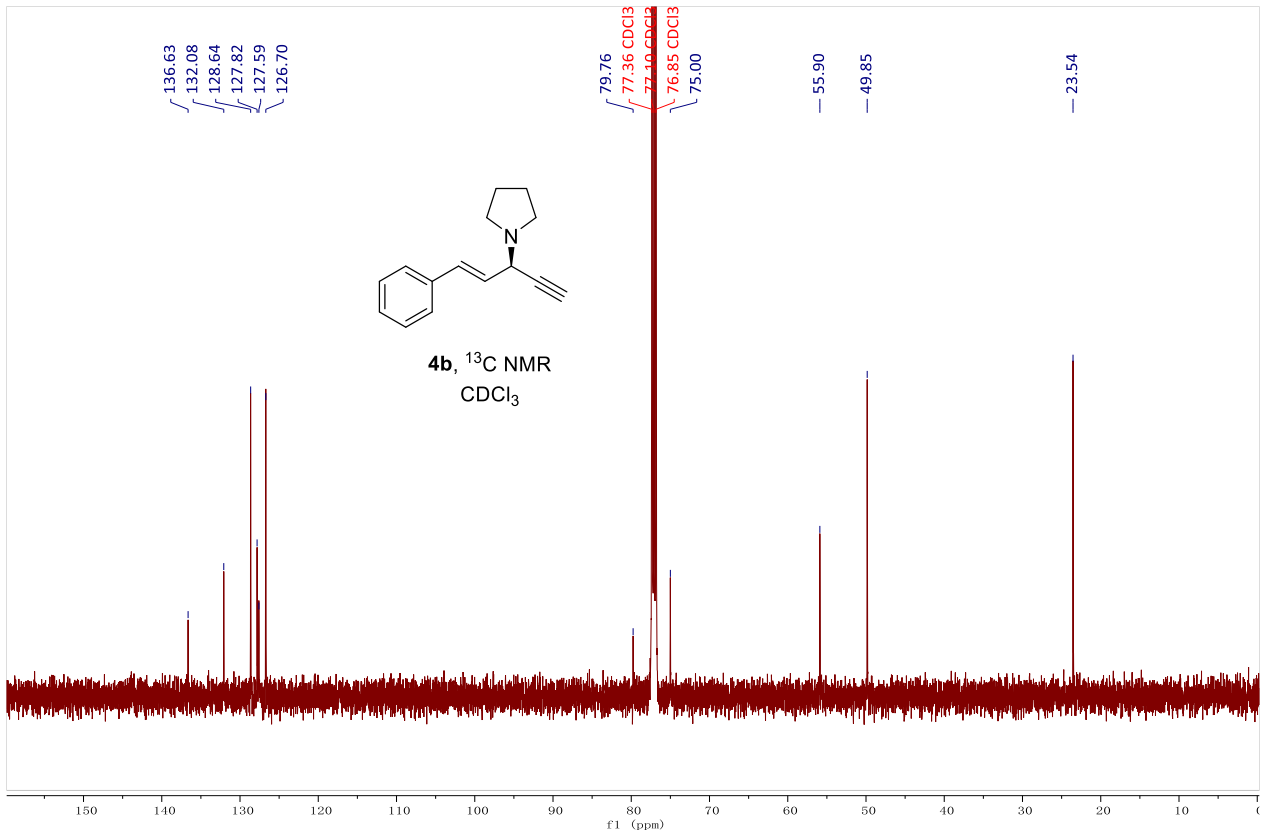
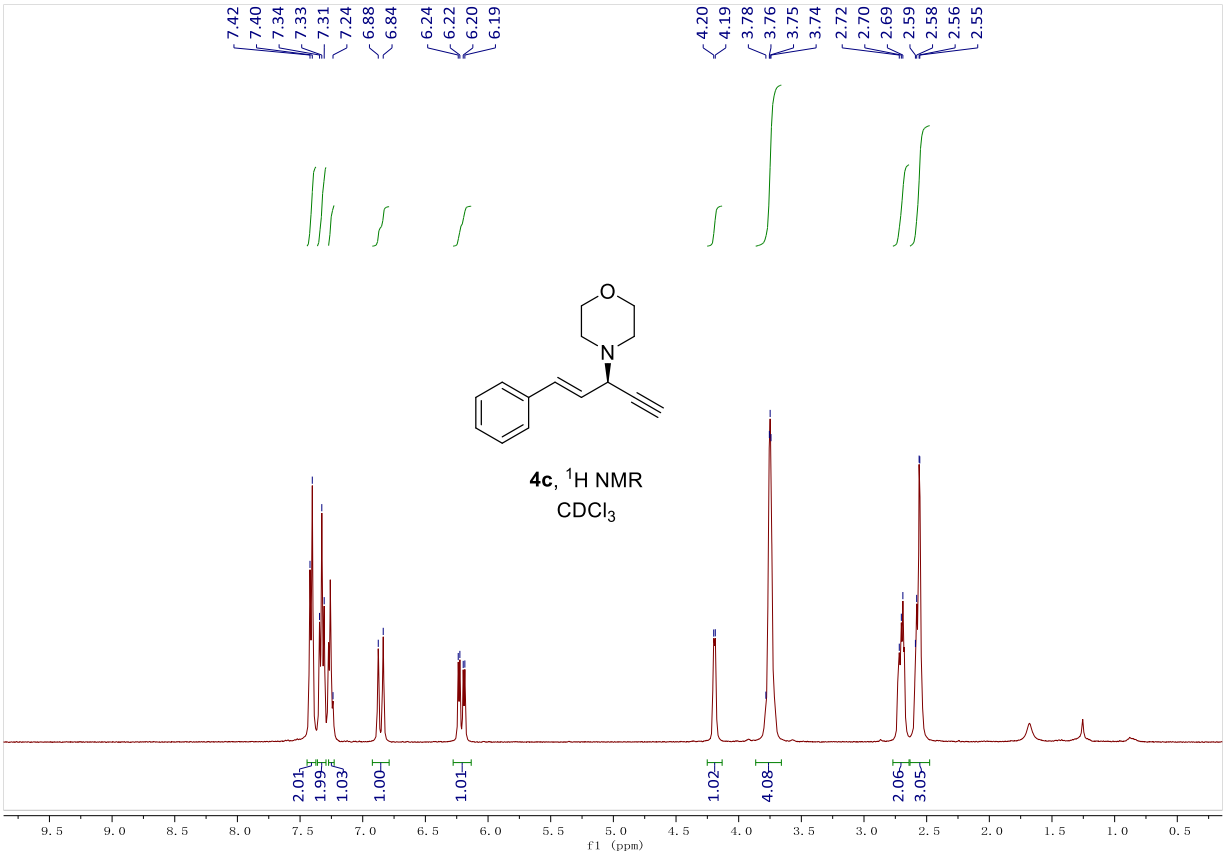
7.32
7.31
7.26
7.24
6.88
6.85
6.27
6.26
6.24
6.23
4.46
4.45
2.74
2.73
2.72
2.70
2.49
2.48
2.47
2.46
1.12
1.10
1.09
N
4a, 1H NMR
CDCl3
1.94
2.01
1.19
0.98
1.01
1.00
2.04
3.10
6.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



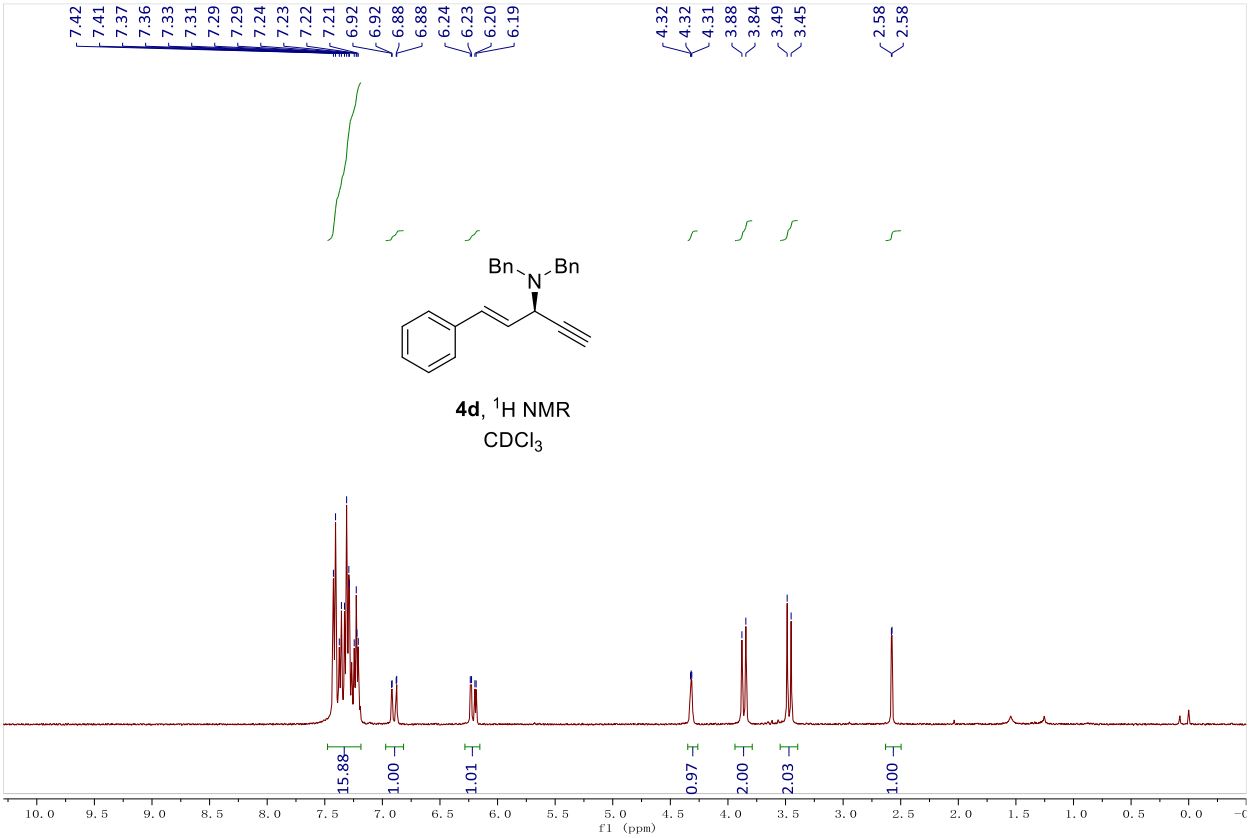
4b, ^{1}H NMR
$CDCl_3$



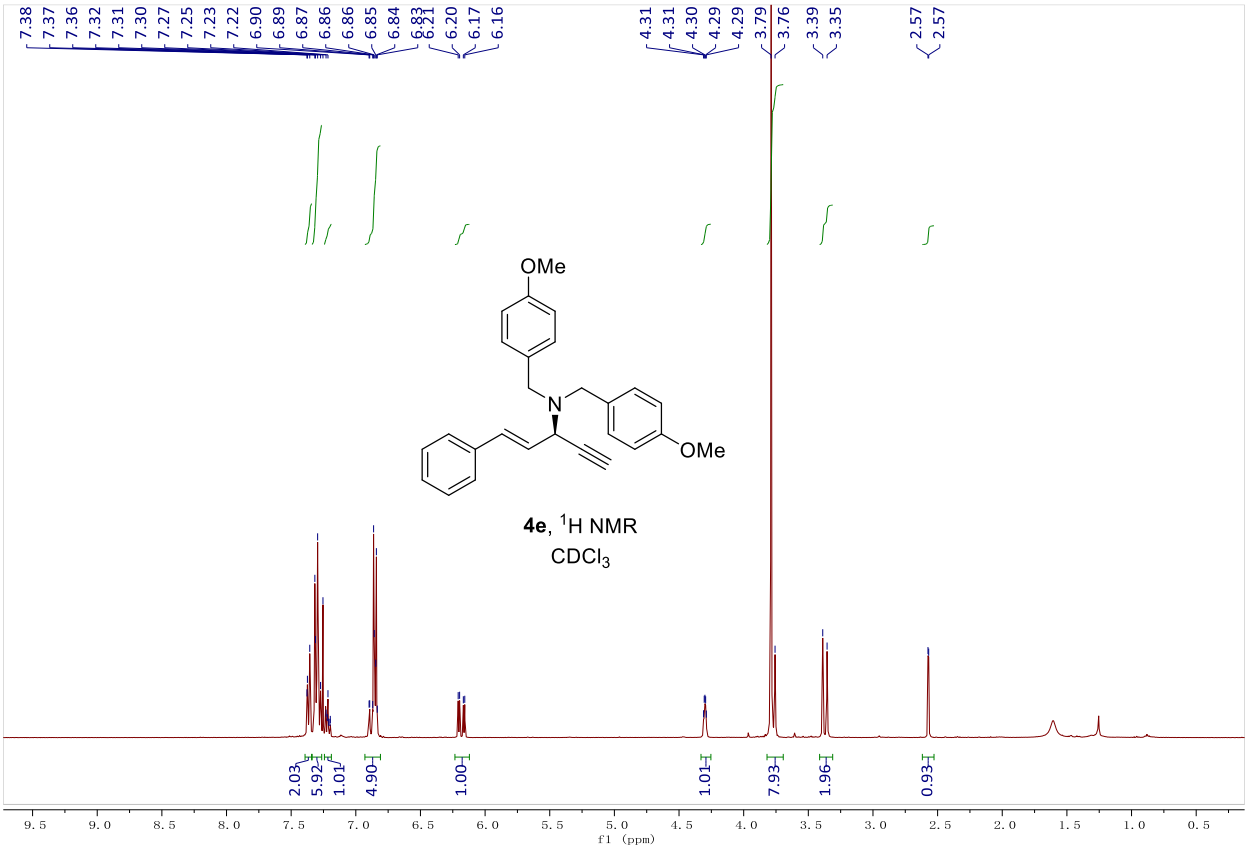
4b, ^{13}C NMR
$CDCl_3$



4c, ^{1}H NMR
$CDCl_3$



4d, ^{1}H NMR
$CDCl_3$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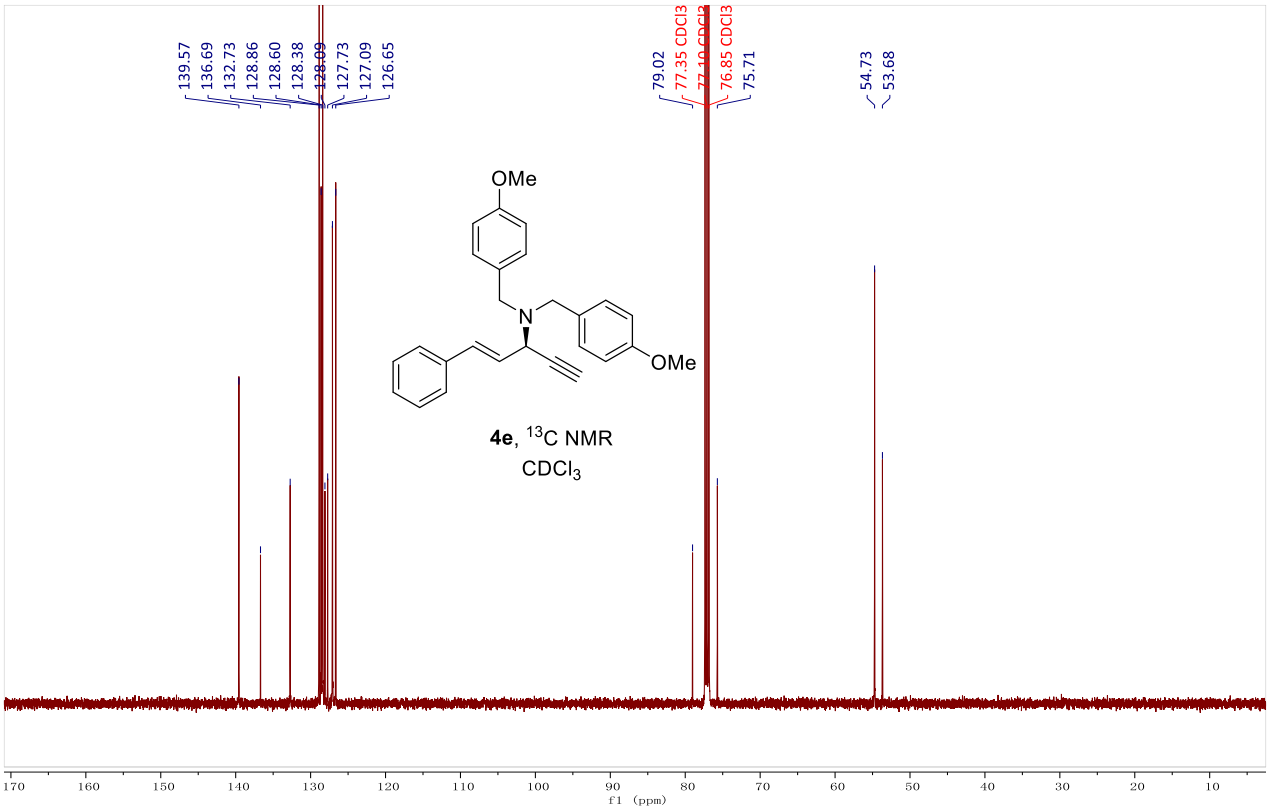
7.37
7.36
7.32
7.31
7.30
7.27
7.25
7.23
7.22
6.90
6.89
6.87
6.86
6.86
6.85
6.84
6.83
6.21
6.20
6.17
6.16
4.31
4.31
4.30
4.29
4.29
3.79
3.76
3.39
3.35
2.57
2.57
OMe
N
OMe
4e, 1H NMR
CDCl3
2.03
5.92
1.01
4.90
1.00
1.01
7.93
1.96
0.93
f1 (ppm)


139.57
136.69
132.73
128.86
128.60
128.38
128.09
127.73
127.09
126.65
79.02
77.35 CDCl3
77.10 CDCl3
76.85 CDCl3
75.71
54.73
53.68
OMe
N
OMe
4e, 13C NMR
CDCl3
f1 (ppm)