Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Zinc(II)-catalyzed Intramolecular Hydroarylation-Redox Cross-Dehydrogenative Coupling of *N*-Propargylanilines with Diverse Carbon Pronucleophiles: Facile Access to Functionalized Tetrahydroquinolines

Guangzhe Li, [*a,b] *Chengdong Wang,* [a] *Yueqing Li,* [a,b] *Kun Shao,* [b] *Guo Yu,* [c] *Shisheng Wang,* [a,b] *Xiuhan Guo,* [a,b] *Weijie Zhao* [a,b] *and Hiroyuki Nakamura* [c]

[a] Department of Pharmacy, School of Chemical Engineering, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, China.
[b] State Key Laboratory of Fine Chemicals, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, China.
[c] Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan.

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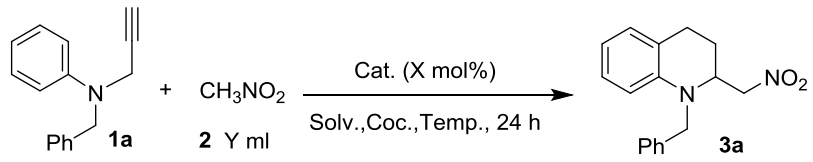
1. General information

General Solvents and chemicals were reagent grade or better and obtained from commercial sources. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on 400 MHz NMR Spectrometer instrument (Bruker Avance II, Vaian DLG400), 500 MHz NMR Spectrometer instrument (Bruker AVANCE III 500) and 600 MHz NMR Spectrometer instrument (Bruker Avance NEO 600M NMR Spectroscopy). Tetramethylsilane (δ 0.00) was used as internal standard for ^{1}H-NMR. ^{13}C-NMR was referenced to the residual solvent ($CDCl_3$, δ 77.0). IR spectra were measured on a ThermoFisher-6700 spectrophotometer. Melting points were determined with a X6 melting point apparatus (Beijing Take Co., Ltd). Analytical thin layer chromatography (TLC) was performed on silica gel plates produced by Qingdao Haiyang Chemical Co. Ltd (200 × 200 mm, 0.2-0.25 mm). Detection: under 254 nm UV light. HRMS/MS data were detected with LTQ Orbitrap XL ETD Mass Spectrometer instrument (Thermo Scientific).

2. Optimization of the reaction conditions

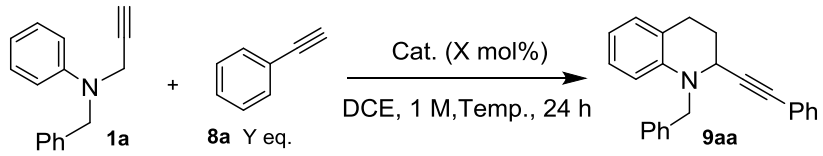
2.1 Optimization of the reaction conditions for nitromethane (Table S1)



Entry	Cat.	X	Solv.	Coc. (M)	Y (ml)	Temp. (^{o}C)	**3a**[a] (%)	Rec.**1a**[a] (%)
1	ZnI_2	20	DCE	1	0.04	100	13	N.D.
2	$Zn(ClO_4)_2$	20	DCE	1	0.04	100	N.D.	46
3	$ZnSO_4$	20	DCE	1	0.04	100	N.D.	96
4	$ZnCl_2$	20	DCE	1	0.04	100	40	N.D.
5	$Zn(OAc)_2$	20	DCE	1	0.04	100	N.D.	84
6	$ZnBr_2$	20	DCE	1	0.04	100	65	N.D.
7	$Zn(OAc)_2{\cdot}2H_2O$	20	DCE	1	0.04	100	N.D.	81
8	$ZnBr_2$	20	Toluene	0.5	0.04	100	27	52
9	$ZnBr_2$	20	Aceton	0.5	0.04	100	31	4
10	$ZnBr_2$	20	DCE	0.5	0.04	100	48	N.D.
11	$ZnBr_2$	20	THF	0.5	0.04	100	48	N.D.
12	$ZnBr_2$	20	MeOH	0.5	0.04	100	22	5
13	$ZnBr_2$	20	DME	0.5	0.04	100	N.D.	N.D.
14	$Zn(OAc)_2$	20	Neat	-	0.5	100	10	67
15	$ZnBr_2$	20	Neat	-	0.5	100	71(65)[b]	N.D.
16	$ZnCl_2$	20	Neat	-	0.5	100	46	15
17	ZnI_2	20	Neat	-	0.5	100	51	N.D.
18	$ZnSO_4$	20	Neat	-	0.5	100	4	90
19	$CuBr_2$	20	Neat	-	0.5	100	24	N.D.
20	CuBr	20	Neat	-	0.5	100	38	N.D.
21	$Cu(OAc)_2$	20	Neat	-	0.5	100	N.D.	N.D.
22	$CuSO_4$	20	Neat	-	0.5	100	20	N.D.
23	$Cu(OTf)_2$	20	Neat	-	0.5	100	N.D.	N.D.
24	$PtCl_2$	20	Neat	-	0.5	100	N.D.	N.D.
25	$Pd(OAc)_2$	20	Neat	-	0.5	100	N.D.	N.D.
26	$Fe(OAc)_3$	20	Neat	-	0.5	100	N.D.	N.D.
27	$NiCl_2$	20	Neat	-	0.5	100	N.D.	N.D.
28	$In(OTf)_3$	20	Neat	-	0.5	100	N.D.	N.D.
29	$Vo(OAc)_2$	20	Neat	-	0.5	100	N.D.	N.D.
30	$Yb(OTf)_2$	20	Neat	-	0.5	100	N.D.	N.D.
31	$Sc(OTf)_3$	20	Neat	-	0.5	100	N.D.	N.D.
32	$Zr(OAc)_4$	20	Neat	-	0.5	100	N.D.	N.D.
33	$RuCl_2$	20	Neat	-	0.5	100	N.D.	N.D.
34	$FeCl_2$	20	Neat	-	0.5	100	N.D.	N.D.
35	$FeCl_3$	20	Neat	-	0.5	100	N.D.	N.D.
36	$ZnBr_2$	30	Neat	-	0.5	100	28	18
37	$ZnBr_2$	20	Neat	-	0.5	100	70	8
38	$ZnBr_2$	10	Neat	-	0.5	100	74	N.D.
39	$ZnBr_2$	5	Neat	-	0.5	100	70	trace
40	$ZnBr_2$	20	Neat	-	0.25	100	58	N.D.
41	$ZnBr_2$	20	Neat	-	0.5	100	70	N.D.
42	$ZnBr_2$	20	Neat	-	1.0	100	71	N.D.
43	$ZnBr_2$	20	Neat	-	1.5	100	48	N.D.
44	$ZnBr_2$	20	Neat	-	0.5	50	15	N.D.
45	$ZnBr_2$	20	Neat	-	0.5	80	53	N.D.
46	$ZnBr_2$	20	Neat	-	0.5	100	71	8
47	$ZnBr_2$	20	Neat	-	0.5	120	28	12

[a] ^{1}H-NMR yield; [b] Isolated yield

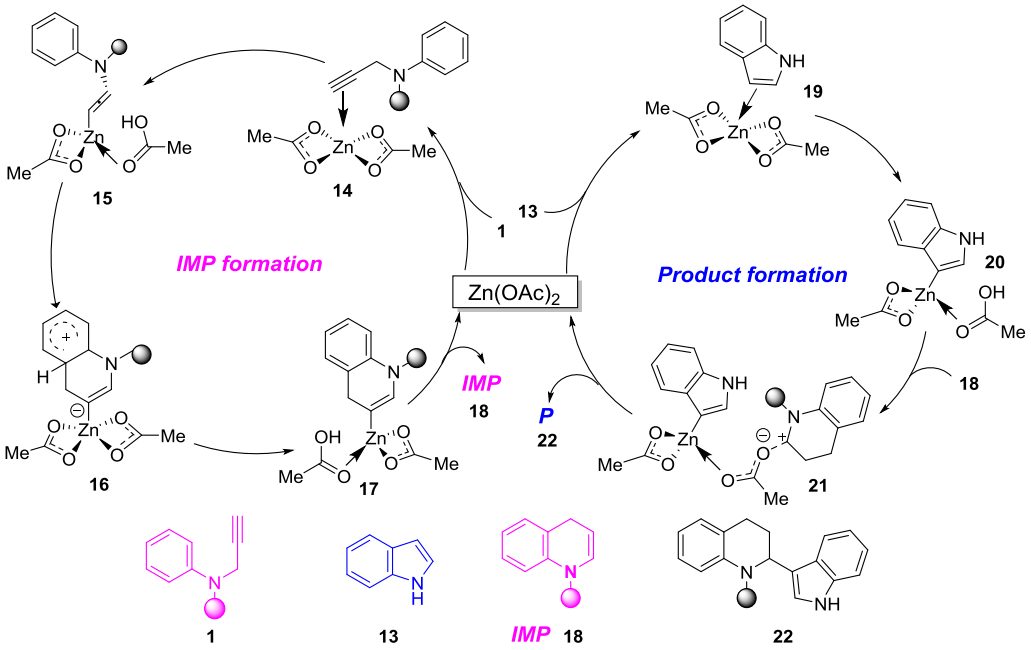
2.2 Optimization of the reaction conditions for phenylacetylene (Table S2)



Entry	Cat.	X	Y	Temp. [^{o}C]	**9aa**[a] (%)	Rec.**1a**[a] (%)
1	CuBr	20	3	120	75	N.D.
2	CuI	20	3	120	64	N.D.
3	$CuBr_2$	20	3	120	41	N.D.
4	CuCl	20	3	120	31	51
5	$Cu(AcO)_2$	20	3	120	43	15
6	$CuSO_4$	20	3	120	17	72
7	Cu(OTf)	20	3	120	16	9
8	$Cu(OTf)_2$	20	3	120	12	4
9	$ZnBr_2$	20	3	120	**78**	N.D.
10	$Zn(OAc)_2$	20	3	120	26	N.D.
11	ZnI_2	20	3	120	N.D.	N.D.
12	$Pd(AcO)_2$	20	3	120	N.D.	4
13	$Sc(OTf)_2$	20	3	120	48	11
14	$Yb(OTf)_3$	20	3	120	18	16
15	$RuCl_2$	20	3	120	N.D.	5
16	$FeCl_2$	20	3	120	N.D.	87
17	$FeCl_3$	20	3	120	N.D.	91
18	$Fe(OAc)_3$	20	3	120	N.D.	85
19	InI_3	20	3	120	N.D.	N.D.
20	Ph_3PAuCl	20	3	120	N.D.	N.D.
21	$In(OTf)_3$	20	3	120	N.D.	17
22	$ZnBr_2$	20	3	120	80(80) [b]	N.D.
23	$ZnBr_2$	15	3	120	38	N.D
24	$ZnBr_2$	10	3	120	35	N.D.
25	$ZnBr_2$	5	3	120	22	N.D.
26	$ZnBr_2$	20	1	120	39	N.D.
27	$ZnBr_2$	20	2	120	66	N.D
28	$ZnBr_2$	20	3	120	75	N.D.
29	$ZnBr_2$	20	4	120	76	N.D.
30	$ZnBr_2$	20	3	120	78	N.D.
31	$ZnBr_2$	20	3	80	N.D.	61
32	$ZnBr_2$	20	3	50	N.D.	84
33	$ZnBr_2$	20	3	r.t	N.D.	99

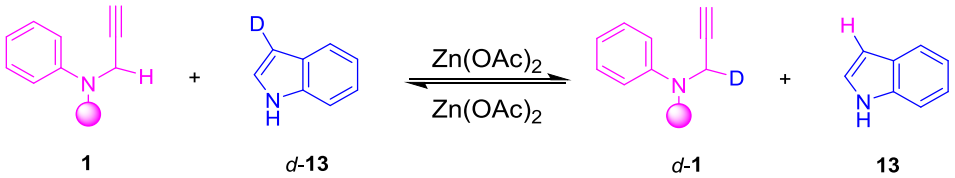
[a] ^{1}H-NMR yield; [b] Isolated yield

3. The DFT study reported by Zhang *et al.* (Scheme S1, Scheme S2, Scheme S3)



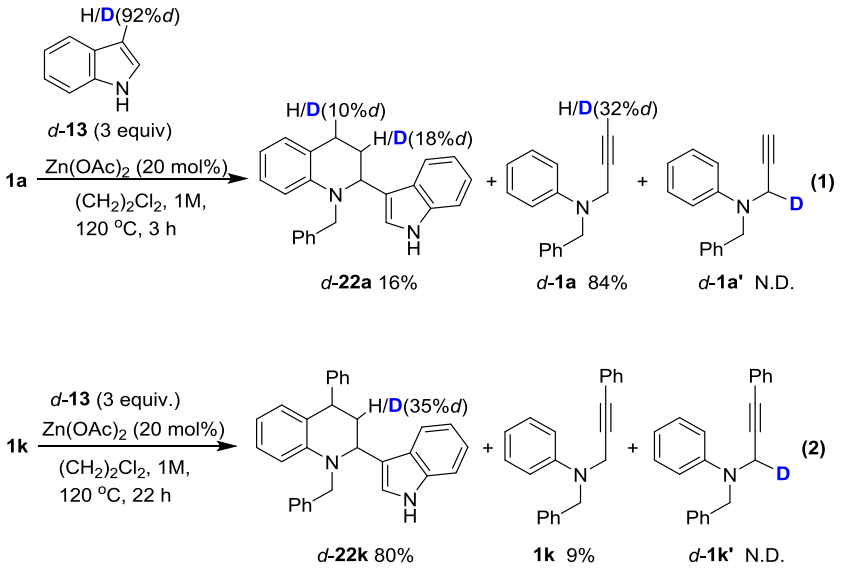
Scheme S1. Catalytic cycle proposed on the basis of calculations by Zhang *et al.*

The DFT study reported an alternative reaction mechanism via an allene intermediate by Zhang *et al.* was summarized in Scheme S1[1]. The proposed catalytic cycle consists of two discrete subcycles: transformation of **1** into **18** (**IMP**) and its further reaction with **2** to give the final product **22** (**P**). The generation of **IMP** occurs through sequential C(sp^3)-H activation (**14** → **15**), cyclization/phenyl C(sp^2)-H activation (**14** → **15** → **16**) and protonation (**17** → **IMP**) steps. The transformation from **IMP** into **P** is achieved by undergoing indole C(sp^2)-H activation (**19** → **20**), protonation of **IMP** (**20** → **21**), and nucleophilic addition (**21** → **P**) steps successively. All three C–H bonds are activated with the assistance of an acetate ligand.



Scheme S2. The **1** and *d*-**13** are in equilibrium with ***d*-1** and **13**

Zhang *et al.* suggested that the generation of the deuterated **1** (*d*-**1**) and **13** via the allene intermediate from the initial reactants **1** and *d*-**13** in equilibrium (Scheme S2).



Scheme S3. Deuterium labeling study for the reaction of *N*-propargylanilines and *d*-indoles.

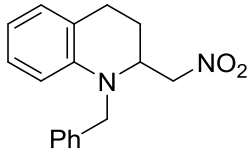
In order to verify the possibility of the allene intermediate, we conducted deuterium labeling experiments (Scheme S3). *N*-benzyl-*N*-(2-propynyl)aniline (**1a**) was treated with the deuterated indole ***d*-13** in the presence of $Zn(OAc)_2$ in 1,2-dichloroethane, and the reaction was quenched after 3 h (Scheme S3, eq 1). Although Zhang et al. suggested the deuterated **1a** (***d*-1a'**) was supposed to be generated via the allene intermediate (Scheme S1), however ***d*-1a'** was not detected in our reaction mixture. Interestingly, ***d*-1a**, in which the terminal alkyne hydrogen was deuterated, was detected in 84% yield, revealing that terminal alkyne hydrogens were readily exchanged with the indole hydrogen under the conditions. Which meant that under this catalytic condition, the hydrogen atom at the C3 position of indole exchange with the hydrogen atom at the terminal alkyne of **1a**, rather than themethylene hydrogen atom of **1a**. Similarly, the reaction of **1k** with indole ***d*-13** was carried out in the presence of $Zn(OAc)_2$ in 1,2-dichloroethane for 22 hours (Scheme S3, eq 2), and only 9% of **1k** was recovered without ***d*-1k′**. The above experimental results show that the redox CDC reaction is caused by the cyclization reaction, not the activation of methylene C(sp^3)-H bond via the allene intermediate.

4. Representative procedure

4.1 Reaction of *N*-propargylaniline 1 with nitromethane 2 (Table 2)

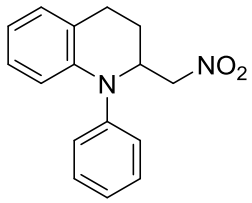
Reaction of *N*-benzyl-*N*-(2-propynyl)aniline 1a with nitromethane 2a

N-benzyl-*N*-(2-propynyl)aniline (**1a**), $ZnBr_2$ (5.6 mg, 0.025 mmol) in nitromethane (**2**) (0.5 ml) were stirred at 100 °C for 24 hours in a closed vial tube protected with N_2 (Table 1, entry 1). The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 30:1 (v/v)) to give *N*-benzyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline (**3a**, 45.8 mg, 65% yield) as yellow solid.



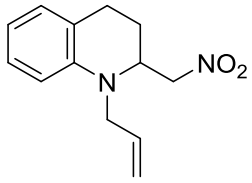
***N*-Benzyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3a**

Light yellow solid, 65% yield (45.8 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.3 Hz, 2H), 7.23 (dd, J = 14.1, 7.1 Hz, 3H), 7.04 (d, J = 7.4 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 6.67 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 8.3 Hz, 1H), 4.62 (ABq, J = 16.9 Hz, 2H), 4.54-4.39 (m, 2H), 4.20 (td, J = 8.2, 3.7 Hz, 1H), 2.98-2.74 (m, 2H), 2.13-1.94 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 142.9, 137.9, 129.4, 128.8, 127.5, 127.3, 126.4, 120.9, 117.5, 112.8, 76.2, 56.5, 54.4, 23.2, 22.9; HRMS (ESI) m/z Calcd for $C_{17}H_{19}N_2O_2$ $[M+H]^+$: 283.1446. Found: 283.1436.



***N*-Phenyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3b**

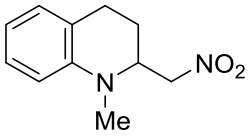
Light yellow oil; 61% yield (40.8 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 7.8 Hz, 2H), 7.20-7.14 (m, 3H), 7.09 (d, J = 7.5 Hz, 1H), 6.96 (t, J = 7.7 Hz, 1H), 6.79 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 8.2 Hz, 1H), 4.63-4.44 (m, 3H), 2.93-2.84 (m, 2H), 2.15 (ddd, J = 18.2, 10.1, 4.0 Hz, 1H), 1.99 (dt, J = 13.8, 2.8 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 147.1, 142.2, 129.5, 126.9, 125.9, 125.1, 123.2, 119.7, 118.4, 76.4, 57.7, 23.0, 22.9; HRMS (ESI) m/z Calcd for $C_{16}H_{17}N_2O_2$ $[M+H]^+$: 269.1290. Found: 269.1285.



***N*-Allyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3c**

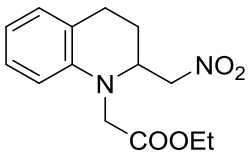
Light yellow oil; 55% yield (31.9 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.08 (t, J = 7.8 Hz, 1H), 7.03 (d, J = 7.3 Hz, 1H), 6.69 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 8.3 Hz, 1H), 5.85 (ddt, J = 15.6, 10.0, 4.9 Hz, 1H),

5.24-5.16 (m, 2H), 4.53 (dd, *J* = 11.5, 5.6 Hz, 1H), 4.43 (dd, *J* = 11.4, 8.6 Hz, 1H), 4.15 (dq, *J* = 8.7, 3.9 Hz, 1H), 4.04 (dd, *J* = 17.3, 4.9 Hz, 1H), 3.88 (dd, *J* = 17.2, 4.8 Hz, 1H), 2.82 (qt, *J* = 12.5, 6.7 Hz, 2H), 1.99 (dd, *J* = 8.7, 4.2 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 142.6, 133.4, 129.3, 127.4, 121.0, 117.3, 116.8, 112.5, 76.4, 56.2, 53.4, 23.0, 23.0; HRMS (ESI) m/z Calcd for $C_{13}H_{17}N_2O_2$ $[M+H]^+$: 233.1290. Found: 233.1279.



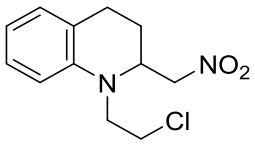
***N*-Methyl-2-nitromethyl -1,2,3,4-tetrahydroquinoline 3d**

Light yellow oil; 69% yield (35.5 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.12 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 4.54 (dd, *J* = 11.3, 5.8 Hz, 1H), 4.40 (dd, *J* = 11.3, 8.0 Hz, 1H), 4.12 (tt, 1H), 2.99 (s, 3H), 2.90-2.74 (m, 2H), 2.11-1.93 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.5, 129.1, 127.5, 120.9, 117.2, 111.5, 75.8, 57.8, 38.1, 23.3, 22.8; HRMS (ESI) m/z Calcd for $C_{11}H_{15}N_2O_2$ $[M+H]^+$: 207.1133. Found: 207.1125.



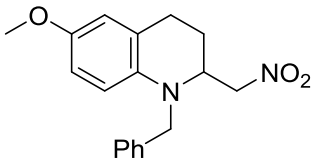
Ethyl 2-(2-(nitromethyl)-3,4-dihydroquinolin-1(2H)-yl)acetate 3e

Light yellow oil; 40% yield (27.8 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.09-7.02 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.39 (d, *J* = 8.2 Hz, 1H), 4.71 (dd, *J* = 12.3, 6.1 Hz, 1H), 4.46 (dd, *J* = 12.3, 7.9 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 3H), 4.10 (s, 2H), 2.91-2.75 (m, 2H), 2.10 (ddt, *J* = 13.1, 10.7, 5.0 Hz, 1H), 1.96 (ddt, *J* = 14.1, 5.8, 2.9 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.8, 142.0, 129.5, 127.5, 120.9, 117.9, 111.4, 76.7, 61.3, 57.4, 53.4, 23.0, 22.8; HRMS (ESI) m/z Calcd for $C_{14}H_{18}N_2O_4$ $[M+H]^+$: 279.1345. Found: 279.1342.



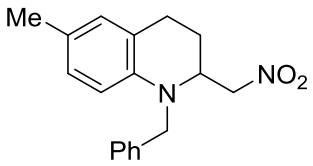
***N*-(2-chloroethyl)-2-(nitromethyl)-1,2,3,4-tetrahydroquinoline 3f**

Light yellow oil; 17% yield (10.8 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.15-7.00 (m, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 4.49 (dd, *J* = 11.6, 7.0 Hz, 1H), 4.39 (dd, *J* = 11.6, 7.1 Hz, 1H), 4.27 (tdd, *J* = 7.0, 4.2, 2.8 Hz, 1H), 3.90 (ddd, *J* = 15.2, 6.8, 4.1 Hz, 1H), 3.69 (dt, *J* = 10.9, 7.4 Hz, 1H), 3.59 (ddd, *J* = 11.0, 7.1, 4.1 Hz, 1H), 3.47 (dt, *J* = 15.2, 7.6 Hz, 1H), 2.80 (dd, *J* = 8.9, 3.5 Hz, 2H), 2.12-2.01 (m, 1H), 1.96 (ddd, *J* = 10.7, 5.8, 3.1 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 141.3, 130.0, 127.6, 121.1, 117.9, 112.2, 76.4, 57.0, 52.9, 40.8, 22.7; HRMS (ESI) m/z Calcd for $C_{12}H_{15}ClN_2O_2$ $[M+H]^+$: 255.0895. Found: 255.0900.



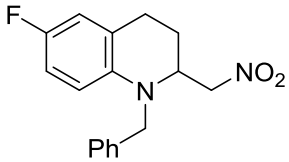
***N*-Benzyl-2-nitromethyl-6-methoxyl-1,2,3,4-tetrahydroquinoline 3g**

Light yellow oil; 47% yield (36.7 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.3 Hz, 2H), 7.24 (t, J = 7.4 Hz, 3H), 6.66-6.57 (td, 2H), 6.51 (d, J = 8.8 Hz, 1H), 4.53 (ABq, J = 16.6 Hz, 2H), 4.50-4.36 (m, 2H), 4.13 (tt, J = 7.3, 3.8 Hz, 1H), 3.71 (s, 3H), 2.93-2.73 (m, 2H), 2.12-2.00 (m, 1H), 1.99-1.89 (m, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.9, 138.2, 137.1, 128.7, 127.2, 126.6, 122.6, 114.8, 114.7, 113.0, 76.0, 56.3, 55.5, 23.2, 23.1; HRMS (ESI) m/z Calcd for $C_{18}H_{21}N_2O_3$ $[M+H]^+$: 313.1552. Found: 313.1543.



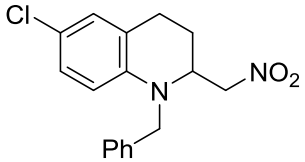
***N*-Benzyl-2-nitromethyl-6-methyl-1,2,3,4-tetrahydroquinoline 3h**

Light yellow oil; 52% yield (38.5 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.2 Hz, 2H), 7.28-7.20 (m, 4H), 6.89 (s, 1H), 6.83 (d, J = 8.3 Hz, 1H), 6.48 (d, J = 8.3 Hz, 1H), 4.60 (ABq, J = 16.8 Hz, 2H), 4.54- 4.42 (m, 2H), 4.19 (td, J = 8.1, 3.6 Hz, 1H), 2.89 (ddd, J = 18.2, 12.7, 5.9 Hz, 1H), 2.80 (ddd, J = 16.9, 5.6, 2.7 Hz, 1H), 2.22 (s, 3H), 2.14-1.95 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.5, 138.0, 130.0, 128.7, 128.0, 127.2, 126.8, 126.5, 121.0, 113.1, 76.0, 56.5, 54.7, 23.2, 22.8, 20.2; HRMS (ESI) m/z Calcd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$: 297.1603. Found: 297.1591.



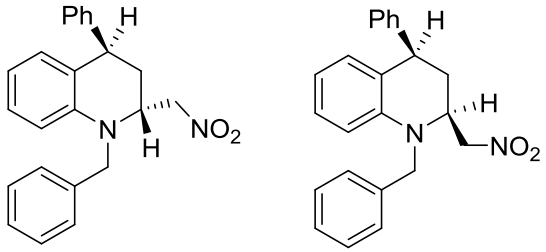
***N*-Benzyl-2-nitromethyl-6-fluoro-1,2,3,4-tetrahydroquinoline 3i**

Light yellow oil; 44% yield (33.0 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 7.2 Hz, 2H), 7.28-7.22 (m, 1H), 7.19 (d, J = 7.3 Hz, 2H), 6.77 (dd, J = 8.9, 2.9 Hz, 1H), 6.70 (td, J = 8.6, 3.0 Hz, 1H), 6.46 (dd, J = 9.0, 4.7 Hz, 1H), 4.56 (ABq, J = 16.8 Hz, 2H), 4.52-4.38 (m, 2H), 4.19 (td, J = 8.2, 3.7 Hz, 1H), 2.93-2.75 (m, 2H), 2.12-1.93 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 155.6 (d, $^{1}J_{C\text{-}F}$ = 236.8 Hz), 139.2 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 137.8, 128.9, 127.4, 126.5, 122.7 (d, $^{3}J_{C\text{-}F}$ = 6.8 Hz), 115.7 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 114.2 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 114.0 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 76.1, 56.4, 55.3, 23.2, 23.0; HRMS (ESI) m/z Calcd for $C_{17}H_{18}FN_2O_2$ $[M+H]^+$: 301.1352. Found: 301.1343.



***N*-Benzyl-2-nitromethyl-6-chloro-1,2,3,4-tetrahydroquinoline 3j**

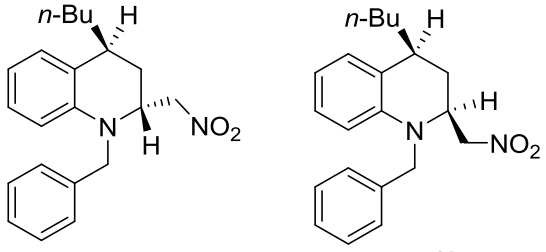
Light yellow oil; 70% yield (55.3 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.2 Hz, 2H), 7.28-7.23 (m, 1H), 7.18 (d, J = 7.4 Hz, 2H), 7.02 (d, J = 2.4 Hz, 1H), 6.93 (dd, J = 8.8, 2.5 Hz, 1H), 6.45 (d, J = 8.8 Hz, 1H), 4.60 (ABq, J = 17.0 Hz, 2H), 4.55-4.39 (m, 2H), 4.22 (td, J = 8.2, 3.6 Hz, 1H), 2.93-2.75 (m, 2H), 2.03 (ttd, J = 14.0, 7.1, 6.2, 3.8 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 141.4, 137.3, 128.9, 128.8, 127.4, 127.3, 126.3, 122.5, 122.2, 114.0, 76.0, 56.4, 54.5, 23.0, 22.8; HRMS (ESI) m/z Calcd for $C_{17}H_{18}ClN_2O_2$ $[M+H]^+$: 317.1057. Found: 317.1048.



***trans*-3k** ***cis*-3k**

_N_-Benzyl-2-nitromethyl-4-phenyl-1,2,3,4-tetrahydroquinoline 3k

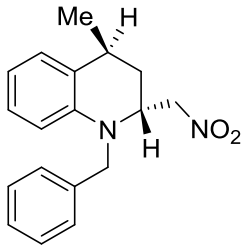
The configurations were assigned by the coupling constant of 2-H and 4-H according to our previous reports.[4] *Trans/cis* isomer total yield: 15% (total weight: 13.4 mg), a mixture of *trans*-isomer and *cis*-isomer (*trans*/*cis* = 9:1) observed in the ^{1}H-NMR spectra. *trans*-isomer: light yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 4H), 7.30-7.23 (m, 5H), 7.22-7.17 (m, 2H), 7.06-6.99 (m, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.67-6.57 (m, 2H), 4.69 (ABq, J = 16.7 Hz, 2H), 4.65-4.48 (m, 2H), 4.22 (tt, J = 7.5, 4.0 Hz, 1H), 4.14 (dd, J = 12.1, 5.8 Hz, 1H), 2.29 (ddd, J = 13.6, 12.3, 4.4 Hz, 1H), 2.19 (ddd, J = 13.8, 5.8, 3.4 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 144.6, 143.3, 137.9, 130.0, 128.8, 128.7, 128.6, 127.8, 127.4, 126.8, 126.6, 125.0, 117.8, 113.4, 56.3, 55.0, 39.8, 33.4; HRMS (ESI) m/z Calcd for $C_{23}H_{23}N_2O_2$ $[M+H]^+$: 359.1760. Found: 359.1744.



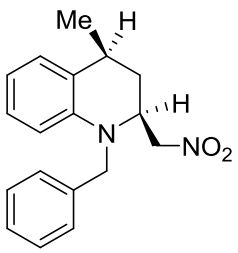
***trans*-3l** ***cis*-3l**

_N_-Benzyl-2-nitromethyl-4-*n*-Butyl-1,2,3,4-tetrahydroquinoline 3l

The configurations were assigned by the coupling constant of 2-H and 4-H according to our previous reports.[4] *Trans/cis* isomer total yield: 22% (total weight: 18.6 mg), a mixture of *trans*-isomer and *cis*-isomer (*trans*/*cis* = 12:1) observed in the ^{1}H-NMR spectra. *trans*-isomer: Light yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33 (t, J = 7.2 Hz, 2H), 7.25 (t, J = 10.1 Hz, 4H), 7.18 (d, J = 7.5 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 8.2 Hz, 1H), 4.62 (ABq, J = 16.9 Hz, 2H), 4.56-4.39 (m, 2H), 4.15 (dq, J = 9.7, 4.9 Hz, 1H), 2.86 (tt, J = 10.0, 5.1 Hz, 1H), 2.06 (dt, J = 13.6, 5.0 Hz, 1H), 1.91 (dtt, J = 14.4, 10.6, 4.8 Hz, 2H), 1.34 (ddt, J = 23.5, 17.5, 8.6 Hz, 4H), 0.93 (t, J = 6.6 Hz, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.5, 138.1, 128.8, 127.3, 127.3, 126.7, 126.6, 126.4, 117.9, 113.6, 77.1, 56.0, 55.1, 34.5, 32.0, 30.2, 28.6, 22.9, 14.1; HRMS (ESI) m/z Calcd for $C_{21}H_{27}N_2O_2$ $[M+H]^+$: 339.2068. Found: 339.1994.



***trans*-3m**



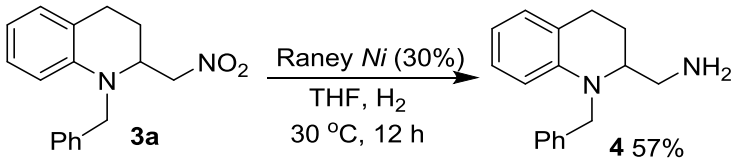
***cis*-3m**

_N_-Benzyl-2-nitromethyl-4-methyl-1,2,3,4-tetrahydroquinoline 3m

The configurations were assigned by the coupling constant of 2-H and 4-H according to our previous reports.[4] *Trans/cis* isomer total yield: 41% (total weight: 30.2 mg), a mixture of *trans*-isomer and *cis*-isomer (*trans*/*cis* = 11:1) observed in the ^{1}H-NMR spectra. *trans*-isomer: light yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.1 Hz, 2H), 7.28-7.19 (m, 4H), 7.01 (t, J = 7.7 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 6.55 (d, J = 8.2 Hz, 1H), 4.63 (ABq, J = 17.0 Hz, 2H), 4.57-4.45 (m, 2H), 4.21-4.14 (m, 1H), 2.96-3.05 (m, 1H), 2.01 (dt, J = 14.6, 3.3 Hz, 1H), 1.86 (td, J = 13.8, 13.3, 4.1 Hz, 1H), 1.40 (d, J = 6.6 Hz, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ 142.7, 137.8, 128.8, 127.4, 127.3, 127.0, 126.5, 126.4, 117.7, 112.9, 76.8, 56.5, 32.7, 26.4, 20.6; HRMS (ESI) m/z Calcd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$: 296.1603. Found: 297.1597.

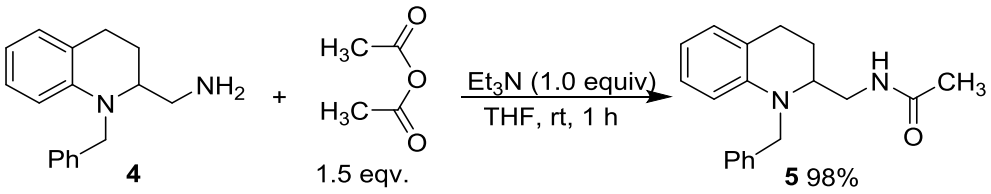
4.2 Synthesis of important intermediates (Scheme 2)

Synthesis of compound 4



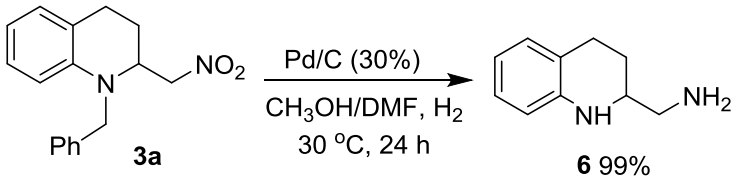
3a (60.0 mg, 0.21 mmol) and Raney nickel (18.0 mg, 30%) in THF (15.0 ml) were stirred at 30 ° C for 12 h in a two-necked flask protected by hydrogen ballon. The reaction solution was filtered into a flask (using celite) and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (methanol/dichloromethane = 1:10 (v/v)) to give (1-benzyl-1,2,3,4-tetrahydroquinolin-2-yl)methanamine **4** (30.7 mg, 57% yield) as colorless oily liquid. ^{1}H-NMR (400 MHz, Methanol-d_4): δ 7.35-7.19 (m, 5H), 7.01-6.90 (m, 2H), 6.63-6.55 (m, 2H), 4.70 (d, J = 16.9 Hz, 1H), 4.51 (d, J = 16.9 Hz, 1H), 3.54 (dq, J = 8.3, 5.1 Hz, 1H), 2.95-2.79 (m, 3H), 2.74 (dt, J = 16.3, 4.2 Hz, 1H), 2.07 (ddt, J = 12.1, 5.8, 3.3 Hz, 1H), 1.93 (ddt, J = 18.1, 11.6, 4.9 Hz, 1H); ^{13}C-NMR (101 MHz, Methanol-d_4): δ 143.9, 139.0, 128.6, 128.2, 126.7, 126.6, 126.5, 116.5, 113.2, 57.5, 54.7, 48.2, 48.0, 47.8, 47.6, 47.4, 47.2, 47.0, 41.3, 22.9, 22.0; HRMS (ESI) m/z Calcd for $C_{17}H_{20}N_2$ $[M+H]^+$: 253.1705. Found: 279.1699.

Synthesis of compound 5



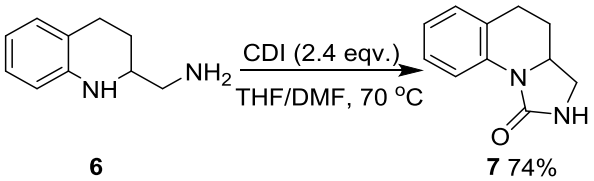
Et_3N (35 µl) and Acetic anhydride (0.29 mmol, 27 µl) were added to a cold solution of compound **4** (0.2 mmol, 52.8 mg) in THF (1.5 mL), then the resulting mixture was stirred at room temperature for 1 h. The resulting mixture was concentrated under reduced pressure.The residue was dissolved in EtOAc, washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried (Na_2SO_4) , then concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (EtOAc) to give *N*-((1-benzyl-1,2,3,4-tetrahydroquinolin-2-yl)methyl)acetamide **5** (54.8 mg, 98% yield) as greyish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 5H), 7.01 (t, J = 7.4 Hz, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 8.3 Hz, 1H), 5.62 (s, 1H), 4.62 (d, J = 17.0 Hz, 1H), 4.52 (d, J = 17.0 Hz, 1H), 3.51 (p, J = 6.2 Hz, 1H), 3.31 (q, J = 6.1 Hz, 2H), 2.91-2.81 (m, 1H), 2.75 (dt, J = 16.5, 4.5 Hz, 1H), 1.98-1.92 (m, 2H), 1.78 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.3, 144.6, 139.4, 129.1, 128.8, 127.3, 127.0, 126.7, 122.0, 116.8, 113.1, 57.4, 55.8, 41.6, 23.9, 23.3, 23.2. Spectral data are in accordance with the reported data.[2]

Synthesis of compound 6



3a (0.38 mmol, 105.0 mg) and Pd/C (5% loading, 31.5 mg, 30%) in a mixed solvent of methanol/tetrahydrofuran (22 ml, v:v=10:1) were stirred at 30 ° C for 24 h in a 100 ml reaction flask protected by hydrogen ballon. The resulting mixture was filtered into a flask (using celite) and concentrated under reduced pressure to give a crude product. The residure was purified by silica gel column chromatography (methanol: methylene chloride = 1:10 (v/v)) to give (1,2,3,4-tetrahydroquinolin-2-yl)methanamine **6** (60.5 mg, yield 99%) as white solid product. ^{1}H-NMR (400 MHz, Methanol-d_4): δ 6.94 (t, J = 7.5 Hz, 2H), 6.61 (d, J = 7.6 Hz, 2H), 3.61 (dq, J = 8.7, 5.4 Hz, 1H), 3.06 (d, J = 5.7 Hz, 2H), 2.82 (dtt, J = 27.9, 10.6, 5.7 Hz, 2H), 1.99 (dtd, J = 15.1, 5.7, 3.7 Hz, 1H), 1.85-1.74 (m, 1H). Spectral data are in accordance with the reported data.[2]

Synthesis of compound 7



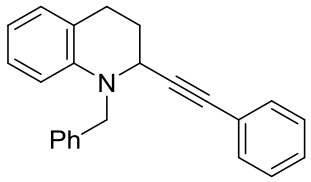
compound **6** (0.33 mmol, 54.3 mg) and CDI (1,1-Carbonyldiimidazole) (0.8 mmol, 2.4 equiv, 101.7 mg) in a mixed solution of THF/DMF (1.2 ml, v:v = 1:3) were stirred at 70 °C overnight in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 1:1 (v/v)) to give 3,3a,4,5-tetrahydroimidazo[1,5-a]quinolin-1(2H)-one **7** (45.9 mg, 74% yield) as white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.3 Hz, 1H), 7.18 (t, J = 7.9 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 4.78 (s, 1H), 4.09 (dtd, J = 11.1, 8.2, 2.7 Hz, 1H), 3.68 (t, J = 8.4 Hz, 1H), 3.22 (t, J = 8.1 Hz, 1H), 3.02-2.83 (m, 2H), 2.11 (ddd, J = 10.6, 5.8, 2.9 Hz, 1H), 1.89 (tt, J = 12.7, 6.3 Hz, 1H);

^{13}C-NMR (101 MHz, $CDCl_3$): δ 159.3, 136.7, 129.0, 126.7, 124.4, 122.1, 118.6, 54.6, 44.0, 27.3, 27.0; HRMS (ESI) m/z Calcd for $C_{11}H_{12}N_2O$ $[M+H]^+$: 189.1022. Found: 189.1030.

4.3 Reaction of *N*-propargylaniline 1 with phenylacetylene 8 (Table 4)

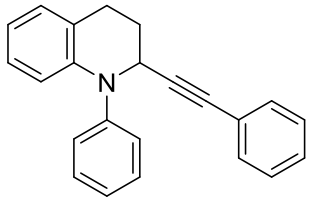
Reaction of *N*-Benzyl-*N*-(2-propynyl)aniline 1a with phenylacetylene 8

N-benzyl-*N*-(2-propynyl)aniline (**1a**), $ZnBr_2$ (11.3 mg, 0.05 mmol) and phenylacetylene (**8a**) (0.75 mmol, 81 µl) in 1,2-dichloroethane (0.25 ml) were stirred at 120 °C for 24 hours in a closed vial tube protected with N_2 (Table 2, entry 1). The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : eluent ethyl acetate= 30:1 (v/v)) to give *N*-benzyl-2-ethynylbenzene-1,2,3,4 tetrahydroquinoline **9aa** (64.7 mg, 80% yield) as light yellow oil.



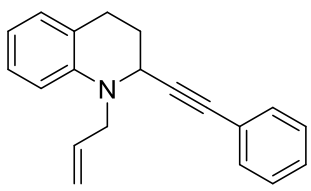
***N*-Benzyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9aa**

Light yellow oil; 80% yield (64.7 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 6.8 Hz, 6H), 7.29-7.21 (m, 4H), 7.01 (dd, J = 18.4, 7.7 Hz, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 8.2 Hz, 1H), 4.71-4.60 (ABq, J = 17.0 Hz, 2H), 4.47 (t, J = 3.5 Hz, 1H), 3.26 (dt, J = 16.6, 8.7 Hz, 1H), 2.78 (d, J = 15.9 Hz, 1H), 2.41-2.08 (m, 2H); ^{13}C-NMR(101 MHz, $CDCl_3$): δ 144.2, 138.7, 131.7, 128.8, 128.6, 128.2, 128.0, 127.2, 126.8, 126.7, 123.0, 122.2, 116.7, 111.8, 89.2, 83.3, 53.8, 27.8, 24.9; HRMS (ESI) m/z Calcd for $C_{24}H_{21}N$ $[M+H]^+$: 324.1754. Found: 324.1740.



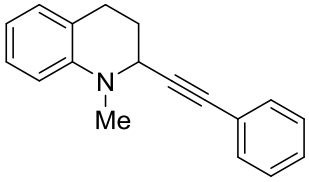
***N*-Phenyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9ba**

Light yellow oil; 51% yield (39.4 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.44-7.38 (m, 4H), 7.33 (dd, J = 6.7, 3.1 Hz, 2H), 7.28-7.23 (m, 4H), 7.08 (d, J = 7.5 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8.3 Hz, 1H), 4.74 (t, J = 3.7 Hz, 1H), 3.33 (ddd, J = 17.2, 12.2, 5.9 Hz, 1H), 2.84 (dt, J = 16.3, 3.6 Hz, 1H), 2.28 (tddt, J = 12.8, 9.4, 6.3, 3.6 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 146.8, 143.1, 131.6, 129.5, 129.3, 128.1, 128.0, 126.5, 125.2, 123.0, 122.7, 118.1, 115.2, 89.4, 83.9, 52.1, 27.7, 24.5; HRMS (ESI) m/z Calcd for $C_{24}H_{21}N$ $[M+H]^+$: 310.1597. Found: 310.1586.



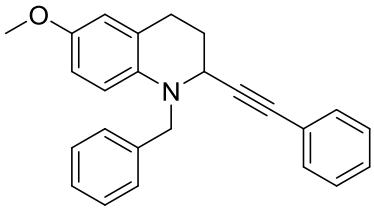
***N*-Allyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9ca**

Light yellow oil; 58% yield (39.6 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37 (dq, J = 8.1, 4.3, 3.9 Hz, 2H), 7.26 (dt, J = 6.3, 2.9 Hz, 3H), 7.06 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.66-6.59 (m, 2H), 5.94 (ddt, J = 17.1, 10.0, 4.9 Hz, 1H), 5.33-5.15 (m, 2H), 4.44 (t, J = 3.8 Hz, 1H), 4.12-3.99 (m, 2H), 3.20 (ddd, J = 16.4, 12.0, 5.2 Hz, 1H), 2.74 (dt, J = 15.9, 3.8 Hz, 1H), 2.17 (tddt, J = 17.1, 12.7, 8.9, 4.2 Hz, 2H); ^{13}C-NMR(101 MHz, $CDCl_3$): δ 143.8, 134.0, 131.7, 128.8, 128.2, 128.0, 127.1, 123.1, 122.2, 116.5, 116.0, 111.7, 89.5, 83.1, 52.5, 49.8, 27.8, 24.9; HRMS (ESI) m/z Calcd for $C_{20}H_{19}N$ $[M+H]^+$: 274.1596. Found: 274.1591.



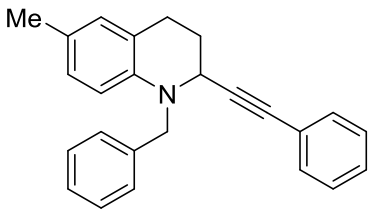
***N*-Methyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9da**

Light yellow oil; 70% yield (43.2 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39-7.33 (m, 2H), 7.28-7.22 (m, 3H), 7.10 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.68 (t, J = 8.0 Hz, 2H), 4.35 (t, J = 3.8 Hz, 1H), 3.19 (ddd, J = 16.8, 11.6, 6.1 Hz, 1H), 3.01 (s, 3H), 2.74 (d, J = 16.1 Hz, 1H), 2.21 (qt, J = 12.9, 6.8 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 144.9, 131.7, 128.7, 128.2, 128.0, 127.1, 123.0, 122.7, 117.3, 112.0, 88.4, 83.7, 51.9, 37.9, 27.7, 24.7; HRMS (ESI) m/z Calcd for $C_{18}H_{17}N$ $[M+H]^+$: 248.1439. Found: 248.1439.



***N*-Benzyl-2-ethynylbenzene-6-Methoxy-1,2,3,4-tetrahydroquinoline 9ga**

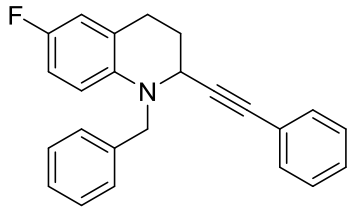
Light yellow oil; 58% yield (51.2 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39-7.30 (m, 6H), 7.25 (dd, J = 5.5, 2.1 Hz, 4H), 6.66 (d, J = 2.8 Hz, 1H), 6.59 (dd, J = 8.9, 2.8 Hz, 1H), 6.49 (d, J = 8.9 Hz, 1H), 4.64-4.51 (ABq, J = 16.5 Hz, 2H), 4.40 (t, J = 3.8 Hz, 1H), 3.72 (s, 3H), 3.48 (s, 2H), 3.24 (ddd, J = 16.5, 11.1, 6.1 Hz, 1H), 2.81-2.71 (m, 1H), 2.22 (qt, J = 9.0, 5.3 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.5, 139.2, 138.8, 131.8, 128.6, 128.2, 128.1, 127.0, 126.9, 123.8, 123.1, 115.0, 113.2, 112.4, 89.2, 83.5, 55.7, 54.6, 50.4, 28.1, 25.3; HRMS (ESI) m/z Calcd for $C_{25}H_{23}NO$ $[M+H]^+$: 354.1858. Found: 354.1846.



***N*-Benzyl-2-ethynylbenzene-6-Methyl-1,2,3,4-tetrahydroquinoline 9ha**

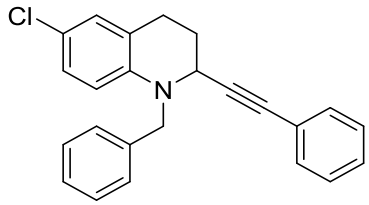
Light yellow oil; 52% yield (43.8 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38-7.19 (m, 10H), 6.86 (s, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.46 (d, J = 8.3 Hz, 1H), 4.68-4.56 (ABq, J = 16.8 Hz, 2H), 4.43 (t, J = 3.9 Hz,

1H), 3.23 (dt, *J* = 16.6, 8.6 Hz, 1H), 2.75 (dt, *J* = 16.1, 4.0 Hz, 1H), 2.22 (d, *J* = 7.7 Hz, 5H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 142.1 139.0, 131.7, 129.6, 128.5, 128.2, 128.0, 127.6, 126.8, 125.9, 123.1, 122.3, 112.0, 89.3, 83.4, 54.0, 50.3, 28.0, 24.9, 20.2; HRMS (ESI) m/z Calcd for $C_{25}H_{23}N$ $[M+H]^+$: 338.1909. Found: 338.1901.



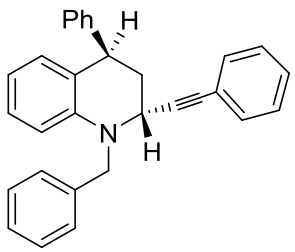
***N*-Benzyl-2-ethynylbenzene-6-fluoro-1,2,3,4-tetrahydroquinoline 9ia**

Light yellow oil; 61% yield (52.0 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.22 (m, 11H), 6.77 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.68 (td, *J* = 8.6, 3.0 Hz, 1H), 6.44 (dd, *J* = 9.0, 4.7 Hz, 1H), 4.64-4.54 (ABq, *J* = 16.7 Hz, 2H), 4.42 (t, *J* = 3.9 Hz, 1H), 3.24 (dt, *J* = 16.8, 8.9 Hz, 1H), 2.76 (dt, *J* = 16.3, 4.1 Hz, 1H), 2.26-2.18 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3 (d, $^1J_{C\text{-}F}$ = 235.5 Hz), 140.7 (d, $^4J_{C\text{-}F}$ = 1.7 Hz), 138.6, 131.7, 128.6, 128.2, 128.1, 127.0, 126.8, 123.9 (d, $^3J_{C\text{-}F}$ = 6.8 Hz), 122.9, 115.3 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 113.2 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 112.8 (d, $^3J_{C\text{-}F}$ = 7.3 Hz), 88.8, 83.7, 54.5, 50.3, 27.8, 25.1; HRMS (ESI) m/z Calcd for $C_{24}H_{20}FN$ $[M+H]^+$: 342.1658. Found: 342.1646.

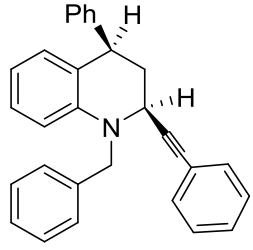


***N*-Benzyl-2-ethynylbenzene-6-chloro-1,2,3,4-tetrahydroquinoline 9ja**

Light yellow oil; 56% yield (50.0 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38-7.23 (m, 11H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.44 (d, *J* = 8.8 Hz, 1H), 4.66-4.58 (ABq, *J* = 16.9 Hz, 2H), 4.45 (t, *J* = 3.6 Hz, 1H), 3.23 (ddd, *J* = 16.9, 10.9, 6.4 Hz, 1H), 2.75 (dt, *J* = 16.1, 3.8 Hz, 1H), 2.26-2.17 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 135.8, 131.2, 124.7, 121.7, 121.5, 121.2, 120.0, 119.8, 119.6, 116.9, 115.8, 114.5, 106.1, 81.7, 70.3, 70.0, 69.7, 47.0, 43.3, 20.6, 17.8; HRMS (ESI) m/z Calcd for $C_{24}H_{20}ClN$ $[M+H]^+$: 358.1363. Found: 358.1357.



***trans*-9ka**

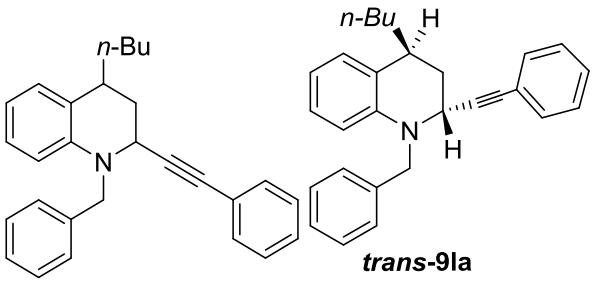


***cis*-9ka**

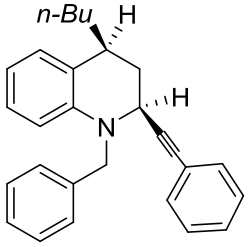
***N*-Benzyl-2-ethynylbenzene-4-phenyl-1,2,3,4-tetrahydroquinoline 9ka**

The configurations were assigned by the coupling constant of 2-H and 4-H according to our previous reports.[4] *Trans/cis* isomer total yield: 59% (total weight: 58.9 mg), a mixture of *trans*-isomer and *cis*-isomer (*trans*/*cis* = 8:1) observed in the ^{1}H-NMR spectra. *trans*-isomer: light yellow oil; ^{1}H-NMR (400

MHz, $CDCl_3$): δ 7.42-7.31 (m, 8H), 7.26 (ddd, J = 11.4, 6.0, 1.8 Hz, 7H), 7.05-6.99 (m, 1H), 6.69 (dt, J = 7.5, 1.2 Hz, 1H), 6.63 (d, J = 8.3 Hz, 1H), 6.57 (td, J = 7.5, 0.8 Hz, 1H), 4.79-4.64 (ABq, J = 16.8 Hz, 2H), 4.47 (dt, J = 9.1, 5.0 Hz, 2H), 2.52-2.39 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 145.0, 144.5, 138.7, 131.7, 129.4, 128.9, 128.6, 128.5, 128.2, 128.1, 127.5, 126.9, 126.9, 126.5, 125.4, 122.9, 116.9, 112.1, 89.1, 83.9, 54.0, 49.5, 41.3, 36.8; HRMS (ESI) m/z Calcd for $C_{30}H_{26}N$ $[M+Na]^+$:422.1885. Found: 422.1879.



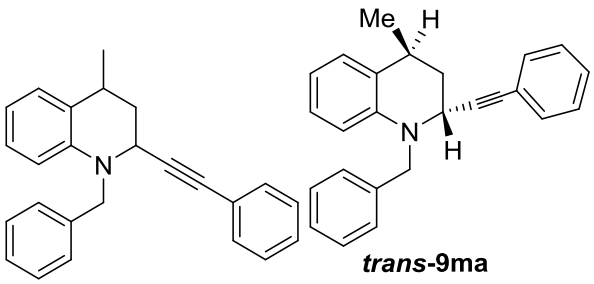
***trans*-9la**



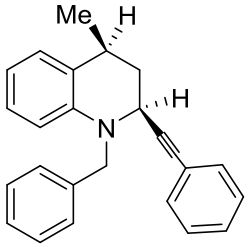
***cis*-9la**

***N*-Benzyl-2-ethynylbenzene-4-*n*-buthyl-1,2,3,4-tetrahydroquinoline 9la**

The configurations were assigned by the coupling constant of 2-H and 4-H according to our previous reports.[4] *Trans/cis* isomer total yield: 67% (total weight: 63.5 mg), a mixture of *trans*-isomer and *cis*-isomer (*trans*/*cis* = 5:1) observed in the ^{1}H-NMR spectra. *trans*-isomer: light yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.13 (m, 10H), 7.06 (d, J = 7.5 Hz, 1H), 6.96-6.89 (m, 1H), 6.64-6.57 (m, 1H), 6.50 (dd, J = 7.6, 4.4 Hz, 1H), 4.72-4.50 (ABq, J = 16.8 Hz, 2H), 4.45-4.35 (m, 1H), 3.00 (tt, J = 8.8, 4.9 Hz, 1H), 2.32-2.12 (m, 1H), 2.01 (ddd, J = 12.9, 8.3, 4.4 Hz, 1H), 1.81 (ddt, J = 15.3, 10.2, 5.2 Hz, 1H), 1.52 (dtt, J = 13.2, 8.6, 3.5 Hz, 1H), 1.43-1.26 (m, 4H), 0.90-0.82 (m, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 144.25, 138.93, 131.61, 128.48, 128.16, 127.99, 127.50, 127.17, 127.02, 126.87, 126.76, 126.58, 123.03, 116.80, 112.36, 89.58, 83.57, 53.85, 48.82, 36.27, 34.32, 33.93, 33.61, 28.86, 22.92, 14.08; HRMS (ESI) m/z Calcd for $C_{28}H_{30}N$ $[M+H]^+$: 380.2378. Found: 380.2371.



***trans*-9ma**

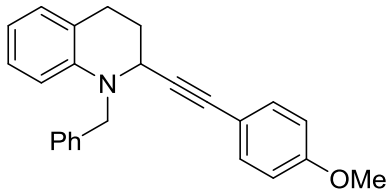


***cis*-9ma**

***N*-Benzyl-2-ethynylbenzene-4-methyl-1,2,3,4-tetrahydroquinoline 9ma**

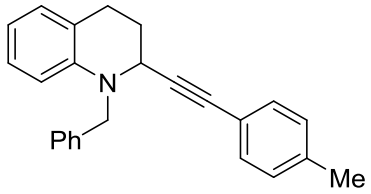
The configurations were assigned by the coupling constant of 2-H and 4-H according to our previous reports.[4] *Trans/cis* isomer total yield: 51% (total weight: 43.0 mg),a mixture of *trans*-isomer and *cis*-isomer (*trans*/*cis* = 5:1) observed in the ^{1}H-NMR spectra. *trans*-isomer: light yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33-7.22 (m, 5H), 7.18 (dt, J = 9.2, 3.9 Hz, 5H), 7.10 (dt, J = 7.6, 1.2 Hz, 1H), 6.96-6.89 (m, 1H), 6.63 (dtd, J = 11.5, 7.4, 1.0 Hz, 1H), 6.48-6.44 (m, 5H), 4.67-4.53 (ABq, J = 17.0 Hz, 5H), 4.44-4.36 (m, 1H), 3.23 (dq, J = 11.6, 6.8, 5.8 Hz, 1H), 2.16 (dt, J = 12.9, 4.5 Hz, 1H), 2.03-1.88 (m, 1H), 1.34 (d, J = 6.8 Hz, 14H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ143.90, 138.77, 131.70, 128.58, 128.18, 128.06, 127.33, 127.10, 126.83, 126.73, 126.53, 123.03, 117.37, 116.83, 112.80, 111.86, 89.65, 83.49,

53.89, 49.58, 36.60, 28.14, 20.37; HRMS (ESI) m/z Calcd for $C_{25}H_{24}N$ $[M+H]^+$: 338.1909. Found: 338.1906.



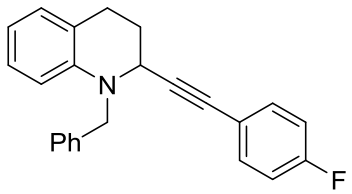
***N*-Benzyl-2-(4-methoxyphenylethynyl)-1,2,3,4-tetrahydroquinoline 9ab**

Light yellow oil; 58% yield (51.2mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.28 (m, 5H), 7.27-7.21 (m, 2H), 7.04-6.95 (m, 2H), 6.80-6.76 (m, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 8.2 Hz, 1H), 4.70-4.60 (ABq, J = 17.0 Hz, 2H), 4.45 (t, J = 3.7 Hz, 1H), 3.77 (s, 3H), 3.25 (dt, J = 16.5, 9.0 Hz, 1H), 2.77 (dt, J = 15.9, 3.9 Hz, 1H), 2.24-2.18 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 159.4, 144.3, 138.8, 133.1, 128.8, 128.5, 127.2, 126.8, 126.7, 122.3, 116.6, 115.1, 113.8, 111.8, 87.8, 83.2, 55.2, 53.8, 50.4, 25.0; HRMS (ESI) m/z Calcd for $C_{25}H_{24}NO$ $[M+H]^+$: 354.1858. Found: 354.1855.



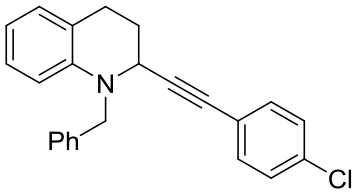
***N*-Benzyl-2-(4-methylphenylethynyl)-1,2,3,4-tetrahydroquinoline 9ac**

Light yellow oil; 75% yield (63.2 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32 (q, J = 7.6 Hz, 4H), 7.23 (d, J = 6.7 Hz, 3H), 7.10-6.95 (m, 4H), 6.64 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 8.2 Hz, 1H), 4.70 -4.60 (ABq, J = 16.9 Hz, 2H), 4.45 (t, J = 3.8 Hz, 1H), 3.25 (dt, J = 16.5, 8.8 Hz, 1H), 2.77 (dt, J = 16.1, 3.6 Hz, 1H), 2.31 (s, 3H), 2.22 (dq, J = 7.0, 3.8 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 144.3, 138.9, 138.1, 131.6, 128.9, 128.9, 128.6, 127.2, 126.8, 126.7, 122.3, 120.0, 116.7, 111.9, 88.6, 83.5, 53.8, 50.4, 27.9, 25.0, 21.4; HRMS (ESI) m/z Calcd for $C_{25}H_{24}N$ $[M+H]^+$: 338.1909. Found: 338.1905.



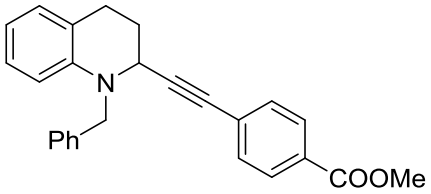
***N*-Benzyl-2-(4-fluorophenylethynyl)-1,2,3,4-tetrahydroquinoline 9ad**

Light yellow oil; 73% yield (62.2 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 6H), 6.98 (dt, J = 28.0, 8.2 Hz, 4H), 6.65 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 8.2 Hz, 1H), 4.70-4.59 (ABq, J = 16.9 Hz, 2H), 4.45 (t, J = 3.9 Hz, 1H), 3.24 (dt, J = 16.6, 8.6 Hz, 1H), 2.79 (dt, J = 16.1, 3.7 Hz, 1H), 2.22 (dt, J = 8.3, 4.0 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 162.3 (d, $^1J_{C\text{-}F}$ = 249.3 Hz), 144.2, 138.7, 133.6 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.9, 128.6, 127.2, 126.9, 126.7, 122.2, 119.1 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 116.8, 115.4 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 111.9, 89.0, 82.4, 53.9, 50.3, 27.8, 25.0; HRMS (ESI) m/z Calcd for $C_{24}H_{21}FN$ $[M+H]^+$: 342.1658. Found: 342.1643.



***N*-Benzyl-2-(4-chlorophenylethynyl)-1,2,3,4-tetrahydroquinoline 9ae**

Light yellow oil; 60% yield (53.6 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.28 (m, 5H), 7.27-7.21 (m, 7H), 7.01 (dd, *J* = 16.8, 7.7 Hz, 3H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 4.70-4.58 (ABq, *J* = 16.9 Hz, 2H), 4.45 (t, *J* = 4.1 Hz, 1H), 3.23 (dt, *J* = 16.6, 8.6 Hz, 1H), 2.84-2.73 (m, 2H), 2.22 (dt, *J* = 8.4, 4.1 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 144.1, 138.6, 134.0, 132.9, 128.9, 128.6, 128.5, 127.2, 126.9, 126.7, 122.1, 121.5, 116.9, 111.9, 90.3, 82.3, 53.9, 50.3, 27.7, 24.9; HRMS (ESI) m/z Calcd for $C_{24}H_{21}ClN$ $[M+H]^+$: 358.1363. Found: 358.1357.

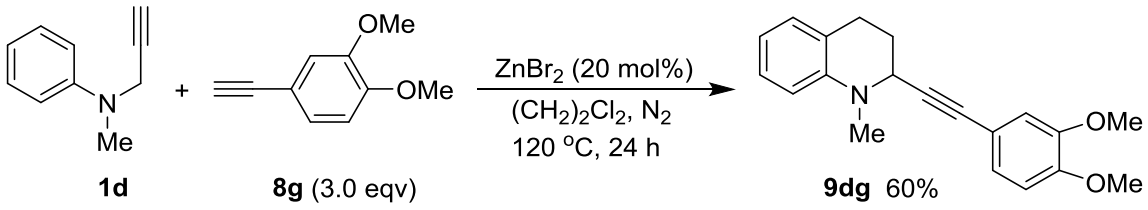


***N*-Benzyl-2-(4-methylformatephenylethynyl)-1,2,3,4-tetrahydroquinoline 9af**

Light yellow oil; 78% yield (74.3 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.35-7.33 (m, 3H), 7.26 (s, 3H), 7.02 (dd, *J* = 16.9, 7.7 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 4.72-4.60 (ABq, *J* = 16.9 Hz, 2H), 4.49 (t, *J* = 3.8 Hz, 1H), 3.90 (s, 3H), 3.25 (dt, *J* = 16.6, 8.6 Hz, 1H), 2.80 (dt, *J* = 16.1, 3.8 Hz, 1H), 2.25 (dt, *J* = 8.4, 4.1 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.5, 144.1, 138.6, 131.6, 129.4, 129.3, 128.9, 128.6, 127.7, 127.3, 126.9, 126.7, 122.1, 117.0, 111.9, 92.5, 82.8, 53.9, 52.2 50.4, 27.7, 25.0; HRMS (ESI) m/z Calcd for $C_{26}H_{24}NO_2$$[M+H]^+$: 382.1807. Found: 382.1797.

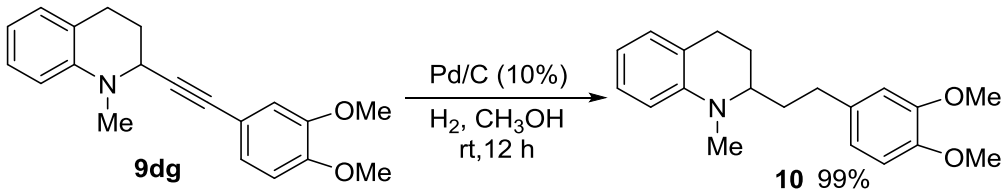
4.4 Synthesis of natural alkaloids and important intermediates (Scheme 3)

Synthesis of 9dh and (±) galipinine 10 (Scheme 3, entry 1)



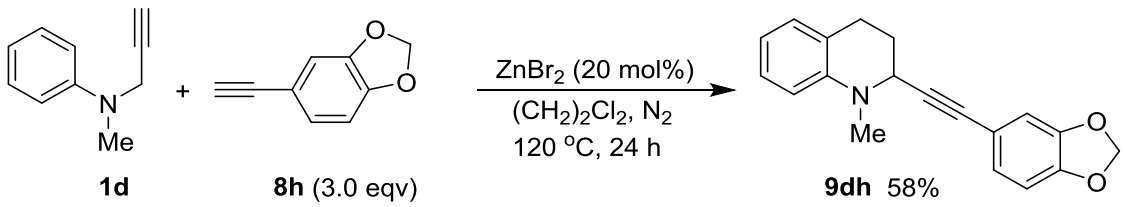
N-Methyl-*N*-(2-propynyl)aniline (**1d**), $ZnBr_2$ (11.3 mg, 0.05 mmol) and 4-ethynyl-1,2-dimethoxybenzene (**8g**) (0.75 mmol, 81 µl) in 1,2-dichloroethane (0.25 ml) were stirred at 120 °C for 24 hours in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate= 30:1 (v/v)) to give *N*-benzyl-2-ethynylbenzene-1,2,3,4 tetrahydroquinoline **9dg** (64.7 mg, 80% yield) as light yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (m, 1H), 7.03-6.99 (m, 1H), 6.96

(dd, *J* = 8.3, 1.9 Hz, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 2H), 4.35 (t, *J* = 3.8 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.18 (ddd, *J* = 16.2, 11.2, 6.3 Hz, 1H), 3.01 (s, 3H), 2.74 (dt, *J* = 16.0, 4.1 Hz, 1H), 2.27-2.13 (m, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 149.2, 148.5, 145.0, 128.7, 127.1, 125.0, 122.6, 117.0, 115.2, 114.4, 111.8, 110.8, 87.0, 83.5, 55.9, 55.8, 51.8, 37.8, 27.8, 24.7; HRMS (ESI) m/z Calcd for $C_{20}H_{22}NO_2$ $[M+H]^+$: 308.1651. Found: 308.1644.

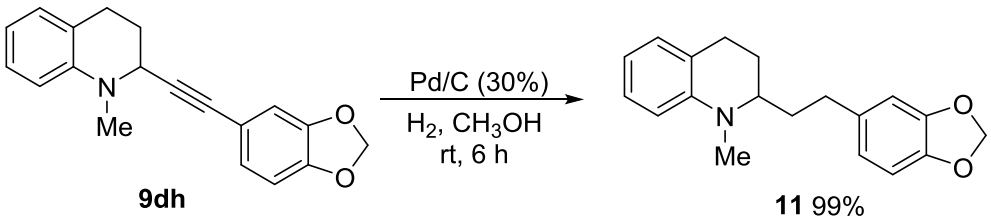


Compound **9dg** (42.6 mg, 0.14 mmol) and Pd/C (5% loading, 12.8 mg, 30%) in methanol (10 ml) were stirred at room temperature overnight protected by a hydrogen balloon. The resulting mixture was concentrated under reduced pressure to give **(±) galipinine 10** (43.1 mg, 99%) as a white solid without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.08 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 10.0 Hz, 2H), 6.59 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 3.86 (d, *J* = 5.7 Hz, 6H), 3.29 (dq, *J* = 8.4, 4.1 Hz, 1H), 2.92 (s, 3H), 2.85 (ddd, *J* = 17.7, 11.9, 6.4 Hz, 1H), 2.68 (ddd, *J* = 18.8, 9.5, 4.8 Hz, 2H), 2.53 (ddd, *J* = 13.9, 10.1, 6.5 Hz, 1H), 2.00-1.86 (m, 3H), 1.73 (dtd, *J* = 13.9, 9.5, 5.5 Hz, 1H); MS (ESI) m/z Calcd for $C_{20}H_{26}NO_2[M+H]^+$: 312.20. Found : 312.27. Spectral data are in accordance with the reported data.[3]

Synthesis of 9di and (±) cuspareine 11 (Scheme 3, entry 1)

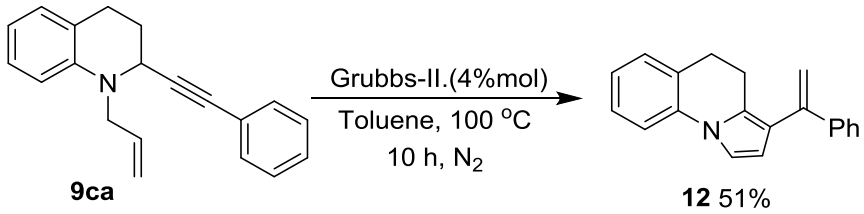


N-benzyl-*N*-(2-propynyl)aniline (**1d**), $ZnBr_2$ (11.3 mg, 0.05 mmol) and 4-ethynyl-1,2-ylidenedioxybenzene (**8h**) (0.75 mmol, 81 µl) in 1,2-dichloroethane (0.25 ml) were stirred at 120 °C for 24 h in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : eluent ethyl acetate= 30:1 (v/v)) to give *N*-benzyl-2-ethynylbenzene-1,2,3,4 tetrahydroquinoline **9dh** (64.7 mg, 80% yield) as light yellow oil.White solid; 58% yield (42.2 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.10 (td, *J* = 8.1, 1.4 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.80 (d, *J* = 1.5 Hz, 1H), 6.70-6.63 (m, 2H), 5.93 (s, 2H), 4.33-4.30 (m, 1H), 3.21-3.11 (m, 1H), 2.99 (s, 3H), 2.73 (dt, *J* = 16.1, 4.2 Hz, 1H), 2.18 (ddtt, *J* = 9.9, 7.8, 6.1, 4.2 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 147.7, 147.3, 145.1, 128.8, 127.1, 126.3, 122.7, 117.1, 116.4, 111.9, 111.8, 108.3, 101.2, 86.9, 83.5, 51.9, 37.9, 27.9, 24.8; HRMS (ESI) m/z Calcd for $C_{19}H_{18}NO_2[M+H]^+$: 292.1338. Found: 292.1330.



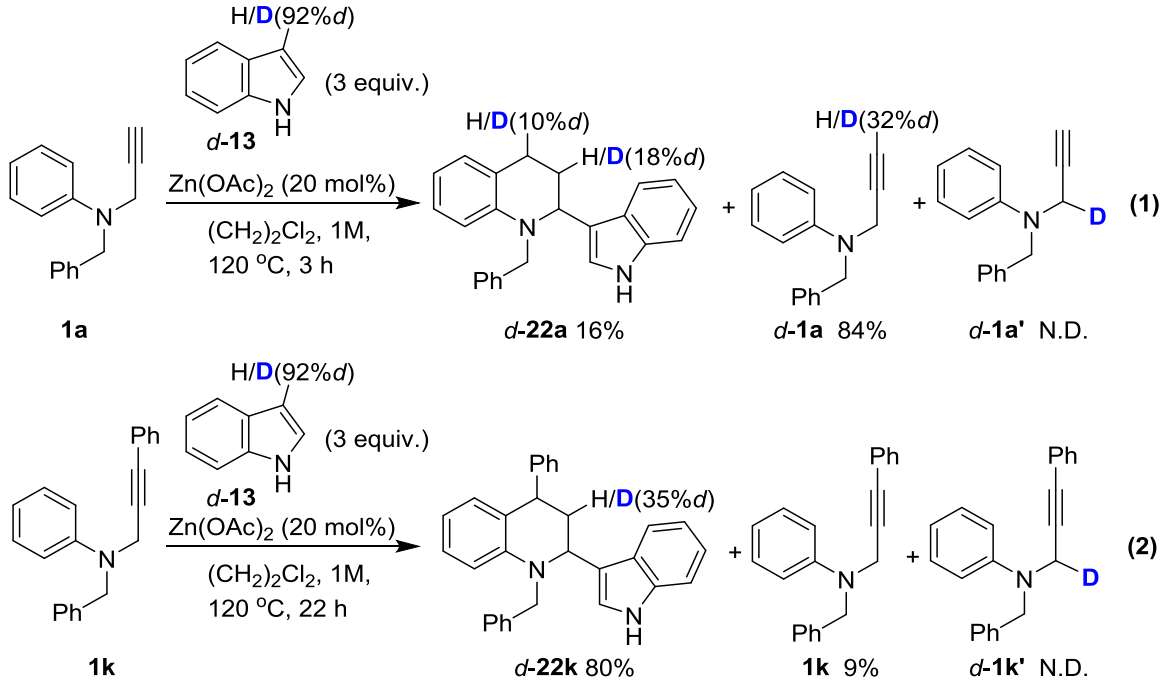
Compound **9dh** (55.6 mg, 0.19 mmol) and Pd/C (5% loading, 16.7 mg, 30%) in methanol (10 ml) were stirred at room temperature in a hydrogen autoclave (0.6 Mpa) for 6 hours protected by a hydrogen balloon. The resulting mixture was concentrated under reduced pressure to give 2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-1-methyl-1,2,3,4-tetrahydroquinoline **11** (56.1 mg, 99%) as a white solid without further purification. ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* 7.07 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.74-6.67 (m, 2H), 6.65-6.56 (m, 2H), 6.52 (d, *J* = 8.2 Hz, 1H), 5.91 (s, 2H), 3.26 (dq, *J* = 8.5, 4.1 Hz, 1H), 2.90 (s, 3H), 2.83 (ddd, *J* = 17.6, 11.5, 6.7 Hz, 1H), 2.65 (ddt, *J* = 23.9, 15.4, 4.9 Hz, 2H), 2.50 (ddd, *J* = 13.9, 9.9, 6.6 Hz, 1H), 1.95-1.83 (m, 3H), 1.70 (dtd, *J* = 14.2, 9.5, 5.5 Hz, 1H); MS (ESI-TOF) m/z Calcd for $C_{19}H_{22}NO_2[M+H]^+$: 295.17. Found: 296.22. Spectral data are in accordance with the reported data.[3]

Synthesis of compound 12 (Scheme 3, entry 2)



Compound **9ca** (0.25 mmol, 68.2 mg) and Grubbs-II catalyst (0.01 mmol, 8.5 mg) in toluene (1.5 ml), were stirred at 110 ° C for 40 hours. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (dichloromethane: petroleum ether = 1:4 (V:V)) to give 3-(1-phenylvinyl)-4,5-dihydropyrrolo[1,2-a]quinoline **12** (24.0 mg, 51% yield) as white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, J = 7.8, 1.6 Hz, 2H), 7.36-7.27 (m, 5H), 7.21 (d, J = 7.1 Hz, 1H), 7.17 (d, J = 3.1 Hz, 1H), 7.06 (td, J = 7.4, 1.1 Hz, 1H), 6.27 (d, J = 3.0 Hz, 1H), 5.39 (d, J = 1.6 Hz, 1H), 5.22 (d, J = 1.6 Hz, 1H), 2.81-2.76 (m, 2H), 2.64 (dd, J = 8.2, 5.7 Hz, 2H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.9, 142.3, 136.6, 128.8, 128.0, 128.0, 127.8, 127.6, 127.4, 127.4, 123.9, 120.9, 115.2, 114.2, 112.5, 111.2, 26.7, 21.6; HRMS (ESI) m/z Calcd for $C_{24}H_{20}ClN$ $[M+H]^+$: 272.1439. Found: 272.1425.

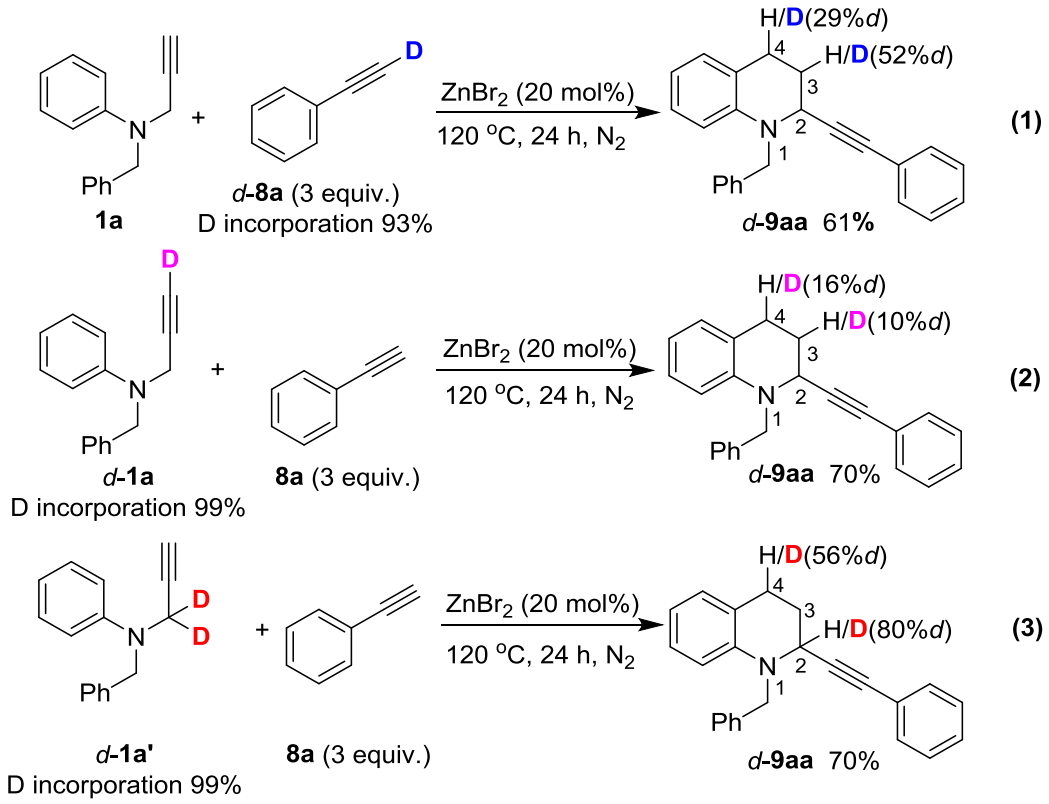
4.5 Isotopic labeling experiments (Scheme 4, Scheme 5)



Eq 1: **1a** (0.25 mmol, 55.3 mg), $ZnBr_2$ (0.025 mmol, 11.3 mg) and *d*-**13** (0.75 mmol, 87.9 mg) in 1,2-dichloroethane (250 μl) were stirred at 120 ° C for 3 hours in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : eluent ethyl acetate = 30:1 (v/v)) to give the final product *d*-**22a** (13.0 mg, yield: 16%; *d*-incorporation: C3: 18%, C4: 10%), *d*-**1a** (47.2 mg, yield: 84%; *d*-incorporation:

32%), no *d*-**1a′** was detected or isolated. They were characterized by ^{1}H-NMR. The deuterium atom at the C2-position (92% *d*) of *d*-**13** might have been not only transferred to C3-position (18% *d*) and C4-position (10% *d*) of *d*-**22a**, but also transferred to terminal alkyne (32%*d*) of *d*-**1a**.

Eq 2: **1k** (0.25 mmol, 74.3 mg), $ZnBr_2$ (0.025 mmol, 11.3 mg) and *d*-**13** (0.75 mmol, 87.9 mg) in 1,2-dichloroethane(250 µl) were stirred at 120 °C for 24 hours in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : eluent ethyl acetate = 30:1 (v/v)) to give the *d*-**22k** (83.0 mg, yield: 80%; *d*-incorporation: C3: 35%), **1k** (6.8 mg, yield: 9%), and no *d*-**1k′** was detected or isolated. They were characterized by ^{1}H-NMR. The deuterium atom at the C2-position (92%*d*) of *d*-**13** can be transferred to C3-position (35%*d*) of *d*-**22k**, but cannot be transferred to **1k′** (with no active terminal alkyne).



Eq 1: **1a** (0.25 mmol, 55.3 mg), $ZnBr_2$ (0.025 mmol, 11.3 mg) and *d*-**8a** (0.75 mmol, 81 µl) in 1,2-dichloroethane(250 µl) were stirred at 120 °C for 24 hours in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : eluent ethyl acetate = 30:1 (v/v)) to give the final product *d*-**9aa**, characterized by ^{1}H-NMR. The deuterium atom at the terminal alkyne (93% *d*) of *d*-**8a** might have been transferred to C3-position (52% *d*) and C4-position (29% *d*) of *d*-**9aa** according to the ^{1}H-NMR spectrum of *d*-**9aa** .

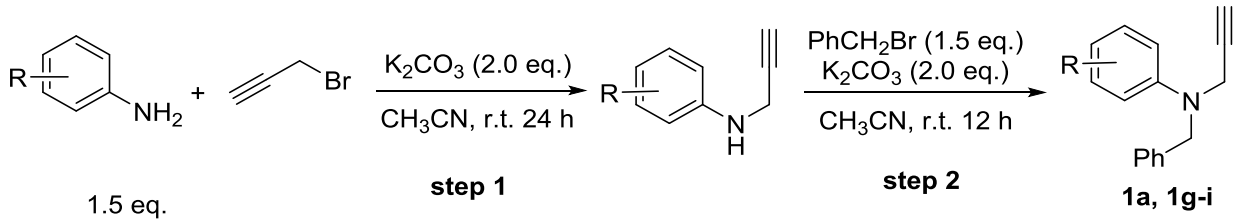
Eq 2: *d*-**1a** (0.25 mmol, 55.9 mg), $ZnBr_2$ (0.025 mmol, 11.3 mg) and phenylacetylene (**8a**) (0.75 mmol, 81 µl) in 1,2-dichloroethane(250 µl) were stirred at 120 °C for 24 hours in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by

silica gel column chromatography (petroleum ether : eluent ethyl acetate = 30:1 (v/v)) to give the final product *d*-**9aa**, and characterized by ^{1}H-NMR. The deuterium atom at the terminal alkyne (93% *d*) of *d*-**8a** might have been transferred to C3-position (10% *d*) and C4-position (16% *d*) of *d*-**9aa** according to the ^{1}H-NMR spectrum of *d*-**9aa** .

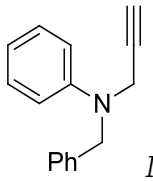
Eq 3: *d*-**1a'** (0.25 mmol, 55.8 mg), $ZnBr_2$ (0.025 mmol, 11.3 mg) and phenylacetylene (**8a**) (0.75 mmol, 81 μl) in 1,2-dichloroethane(250 μl) were stirred at 120 °C for 24 hours in a closed vial tube protected with N_2. The resulting mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether : eluent ethyl acetate = 30:1 (v/v)) to give the final product *d*-**9aa**, and characterized by ^{1}H-NMR. The deuterium atom at the C2 position of *d*-**1a'** (99% d) might have been transferred to C4-position (56% *d*) of *d*-**9aa** according to the ^{1}H-NMR spectrum of *d*-**9aa**.

5. Synthesis of starting materials

Synthesis of *N*-benzyl-*N*-(2-propynyl)anilines 1a,1g-i [4]

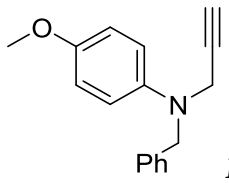


To a solution of anilines (15 mmol) in acetonitrile (40 mL) was added potassium carbonate (2.76 g, 20 mmol) followed by propargyl bromide (0.75 mL, 10 mmol) and the resultant mixture was stirred for 24 h at room temperature. The reaction mixture was filtered and concentrated to afford the crude residue, which was purified by silica gel column chromatography to afford *N*-(prop-2-ynyl)anilines. To a solution of *N*-(2-propynyl)anilines (5 mmol) in acetonitrile (10 mL) was added potassium carbonate (1.38 g, 10 mmol) followed by benzyl bromide (0.9 mL, 7.5 mmol) and the resultant mixture was stirred 12 h at room temperature. The reaction mixture was filtered and concentrated to afford the crude residue, which was purified by silica gel column chromatography (hexane : ethyl acetate = 30 : 1 (v:v)) to afford *N*-benzyl-*N*-(2-propynyl)anilines.



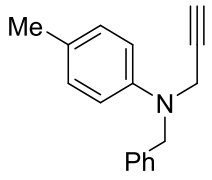
***N*-Benzyl-*N*-(2-propynyl)aniline 1a**

Yellow oil; 88% yield (0.97 g); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 4.7 Hz, 4H), 7.30-7.22 (m, 3H), 6.91 (d, J = 8.1 Hz, 2H), 6.82 (t, J = 7.3 Hz, 1H), 4.56 (s, 2H), 4.03 (d, J = 2.2 Hz, 2H), 2.22 (t, J = 2.3 Hz, 1H). Spectral data are in accordance with the reported data.[4]



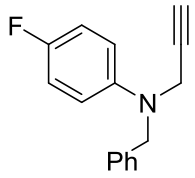
***N*-Benzyl-*N*-(2-propynyl)-4-methoxyaniline 1g**

White solid; 81% yield (1.01 g); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 5H), 6.92 (d, J = 9.0 Hz, 2H), 6.83 (d, 2H), 4.43 (s, 2H), 3.91 (d, J = 2.2 Hz, 2H), 3.76 (s, 3H), 2.22 (t, J = 2.1 Hz, 1H). Spectral data are in accordance with the reported data.[4]



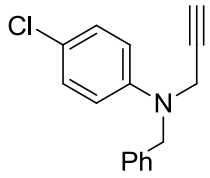
***N*-Benzyl-*N*-(2-propynyl)-4-methylaniline 1h**

Yellow oil; 80% yield (0.94 g); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42-7.16 (m, 5H), 7.07 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.4 Hz, 1H), 4.50 (s, 2H), 3.98 (d, J = 1.9 Hz, 1H), 2.26 (s, 3H), 2.20 (t, J = 2.0 Hz, 1H). Spectral data are in accordance with the reported data.[4]



***N*-Benzyl-*N*-(2-propynyl)-4-fluoroaniline 1i**

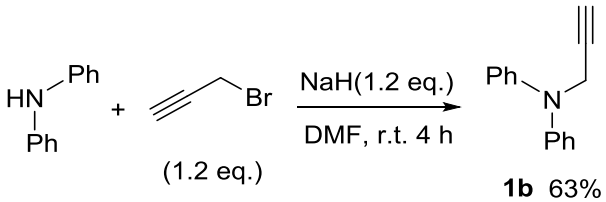
Yellow oil; 80% yield (0.96 g); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38-7.23 (m, 6H), 6.95 (t, J = 8.6 Hz, 2H), 6.86 (dd, J = 9.0, 4.4 Hz, 2H), 4.47 (s, 2H), 3.95 (d, J = 1.6 Hz, 2H), 2.23 (t, J = 2.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.6 (d, $^1J_{C\text{-}F}$ = 237.5 Hz), 145.5 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 138.2, 128.6, 127.4, 127.3, 116.4 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 79.4, 72.4, 55.8, 40.6; HRMS (ESI) m/z Calcd for $C_{16}H_{15}FN$ $[M+H]^+$: 240.1189. Found: 240.1181.



***N*-Benzyl-*N*-(2-propynyl)-4-chloroaniline 1j**

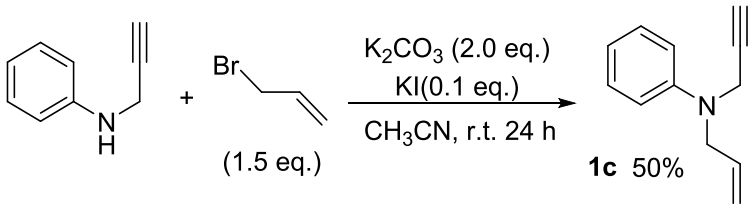
Yellow oil; 81% yield (1.04 g); ^{1}H-NMR (400 MHz, $CDCl_3$) : δ 7.31 (dt, J = 14.3, 6.6 Hz, 5H), 7.17 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 7.8 Hz, 2H), 4.51 (s, 2H), 3.99 (d, J = 2.3 Hz ,2H), 2.25-2.20 (t, J = 2.3 Hz ,1H). Spectral data are in accordance with the reported data.[4]

Synthesis of *N, N*-diphenyl-*N*-(2-propynyl)amine 1b[4]



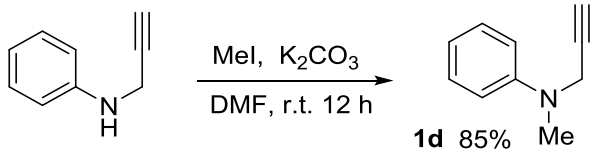
To a dry dimethylformamide solution (30 mL) of diphenylamine (3.38 g, 20 mmol) was added 60% NaH (0.96 g, 24 mmol) at 0 °C under N_2, and the mixture was stirred for 30 min at room temperature. Then propargyl bromide (1.80 ml, 24 mmol) was added to the reaction media and let stirring continue for 4 h. The reaction was quenched by saturated NH_4Cl aqueous solution and the mixture was extracted three times with ethyl acetate. The combined organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 30 : 1 (v:v)) give to **1b** (2.60 g, 63% yield) as light yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30 (td, J = 7.4, 2.0 Hz, 4H), 7.12-7.04 (m, 4H), 7.05-6.96 (m, 2H), 4.41 (d, J = 2.3 Hz, 2H), 2.22 (t, J = 2.4 Hz, 1H). Spectral data are in accordance with the reported data.[4]

Synthesis of *N*-allyl-*N*-(2-propynyl)aniline 1c[4]



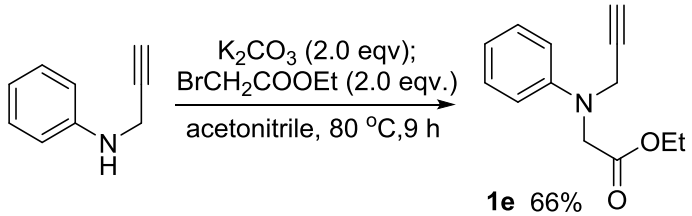
To a solution of the *N*-propargyl aniline (655.9 mg, 5.0 mmol) in acetonitrile (8.0 mL) at room temperature was added potassium bicarbonate (1.5g, 10 mmol) and potassium iodide (0.5 mmol, 83.0 mg) , followed by adding allyl bromide (907.3 mg, 648.0 μl, 7.5 mmol), and tthe reaction solution was stirred for 12 hours. Filtered the inorganic salt and then the solvent was evaporated and the oily residue was purified with silica gel column chromatography (petroleum ether : ethyl acetate = 30 : 1 (v:v)) to give **1c** (427.5 mg, 50% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 2H), 6.87 (d, J = 8.2 Hz, 2H), 6.80 (t, J = 7.3 Hz, 1H), 5.90 (ddt, J = 17.0, 10.3, 5.2 Hz, 1H), 5.31-5.17 (m, 3H), 4.02 (d, J = 2.3 Hz, 2H), 3.97 (d, J = 5.2 Hz, 2H), 2.19 (t, J = 2.3 Hz, 1H). Spectral data are in accordance with the reported data.[4]

Synthesis of *N*-methyl-*N*-(2-propynyl)anilines 1d[4]



To a solution of *N*-(2-propynyl)aniline (1.31 g, 10 mmol) in dimethylformamide (40 mL) was added potassium carbonate (2.07 g, 15 mmol) followed by iodomethane (0.93 mL, 15 mmol) at 0 °C and the resultant mixture was stirred over night at room temperature. The reaction was quenched by water and the mixture was extracted three times with ethyl acetate. The combined organic layer was washed with saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane : ethyl acetate = 30 : 1 (V:V)) to give **1d** (1.23 g, 85 % yield) as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 3H), 6.88 (d, J = 7.9 Hz, 2H), 6.83 (t, J = 7.2 Hz, 1H), 4.06 (d, J = 2.3 Hz, 2H), 2.98 (s, 3H), 2.18 (t, J = 2.3 Hz, 1H). Spectral data are in accordance with the reported data.[4]

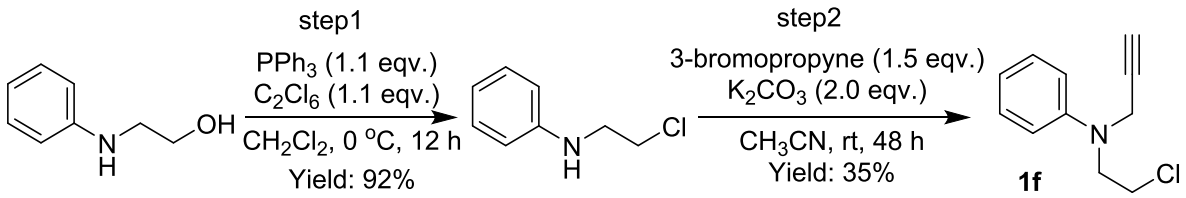
Synthesis of Ethyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)glycinate 1e [5]



A solution of *N*-phenylpropargylamine (656 mg, 5.0 mmol), K_2CO_3 (1.50 g, 10 mmol) and ethyl bromoacetate (947 μL, 10 mmol) in acetonitrile (10 mL) was heated to 80 °C overnight. The suspension is filtered and washed with EtOAc (20 mL). The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 20 : 1 (v:v)) to give **1e** (0.71 g, 66 % yield) as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.25 (tt, J = 7.4, 2.2 Hz, 2H), 6.84-6.76 (m, 3H), 4.19 (q, J

= 7.1 Hz, 2H), 4.15 (d, *J* = 2.4 Hz, 2H), 4.12 (s, 2H), 2.27 (t, *J* = 2.4 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.2, 144.1, 125.5, 115.1, 110.0, 75.8, 57.4, 48.8, 37.4, 10.5; HRMS (ESI) m/z Calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$: 218.1181. Found: 218.1172.

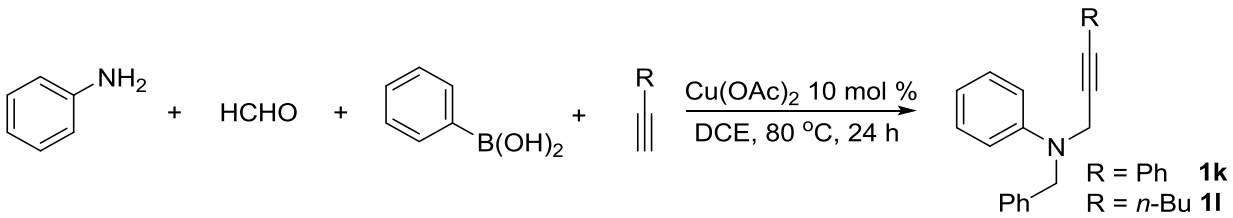
Synthesis of *N*-(2-chloroethyl)-*N*-(prop-2-yn-1-yl)aniline 1f [6]



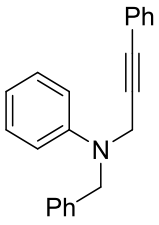
(1) *N*-(2 hydroxyethyl)aniline (1.03g, 7.5 mmol) was added to a 300 mL round-bottom flask followed by CH_2Cl_2 (80 mL). The resulting solution was cooled in an ice bath before addition of C_2Cl_6 (2.0 g, 8.3 mmol). To this system, PPh_3 (2.2 g, 8.3 mmol) was slowly added in portions using a powder funnel. After complete addition of PPh_3, the funnel was washed with CH_2Cl_2 (20 mL). The reaction was subsequently left to warm to room temperature overnight. The resulting white precipitate was collected, added to H_2O (15 mL), and quenched with 3 equiv of saturated $NaHCO_3$ aq. The product was extracted with CH_2Cl_2 (3×30mL) and dried with Na_2SO_4. After solvent removal on a rotary evaporator, the very pale yellow oil was further dried over Na_2SO_4 (1.07 g, 92% yield).

(2) *N*-chloroethylaniline (1.0 g, 6.9 mmol) in anhydrous acetonitrile (20 ml) , adding potassium carbonate (1.9 g, 13.8 mmol), then 3-bromopropyne (1.2 g, 10.4 mmol), were stirred at room temperature for 48 h. The crude product was washed with ethyl acetate into a flask, and concentrated under reduced pressure to give a crude product. Finally, the crude product is purified by silica gel column chromatography(petroleum ether: methylene chloride = 3:1 (v/v)), to give product (461.7 mg, 35% yield) as pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): *δ* 7.31-7.24 (m, 2H), 6.83 (dd, *J* = 13.8, 7.7 Hz, 3H), 4.09 (d, *J* = 2.3 Hz, 2H), 3.76-3.67 (m, 4H), 2.23 (t, *J* = 2.3 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$): *δ* 147.0, 129.4, 118.6, 113.6, 79.7, 72.4, 53.3, 40.7, 40.6; HRMS (ESI) m/z Calcd for $C_{11}H_{13}ClN$ $[M+H]^+$: 194.0737, Found: 194.0726.

Synthesis of *N*-benzyl-*N*-(2-propynyl)anilines 1k, 1l

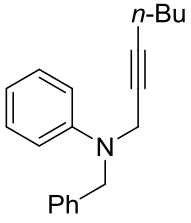


A mixture of aniline (0.47 g, 0.46 mL, 5.0 mmol), formaldehyde (40% aqueous solution) (0.83 g, 0.76 mL, 11.0 mmol), phenylboronic acid (0.64 g, 5.25 mmol), alkyne (6.0 mmol), Copper(II) acetate (0.09 g, 10 mol%) and 1, 2-dichloroethane (15 mL) was stirred in a sealed glass tube at 80 °C for 24 hours. After completion of the reaction, the reaction solution was filtered. After evaporating the solvents in vacuum, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 30 : 1 (v:v)) to give the pure products.



***N*-Benzyl-*N*-(3-phenyl-2-propynyl)aniline 1k**

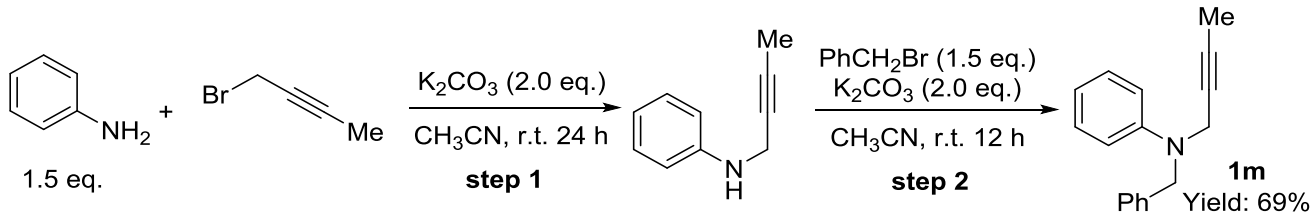
Yellow oil; 75% yield (1.12 g); ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.35-7.31 (m, 6H), 7.27-7.24 (m,6H), 6.94 (d, J = 8.0 Hz, 2H), 6.80 (t, J = 7.5 Hz, 1H), 4.62 (s, 2H), 4.24 (s, 2H). Spectral data are in accordance with the reported data.[4]



***N*-Benzyl-*N*-(2-heptynyl)aniline 1l**

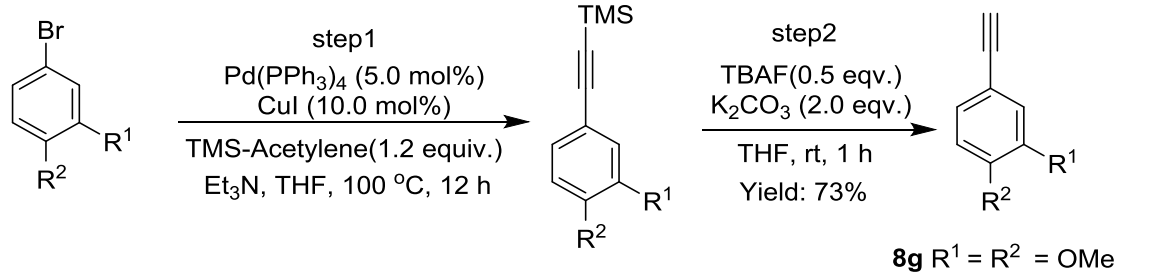
Yellow oil; 70% yield (0.97 g); ^{1}H-NMR (500 MHz; $CDCl_3$): δ 7.31-7.29 (m, 4H), 7.24-7.19 (m, 3H), 6.87 (d, J = 8.0 Hz, 2H), 6.76 (t, J = 7.5 Hz, 1H), 4.54 (s, 2H), 3.99 (t, J = 2.0 Hz, 2H), 2.17-2.13 (m, 2H), 1.47-1.42 (m, 2H), 1.41-1.32 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H). Spectral data are in accordance with the reported data.[4]

Synthesis of *N*-benzyl-*N*-(2-propynyl)anilines 1m [7]



To a solution of anilines (7.5 mmol) in acetonitrile (20 mL) was added potassium carbonate (1.4 g, 10 mmol) followed by 1-bromo-2-butyne (455 µl, 5 mmol) and the resultant mixture was stirred at room temperature for 12 h. The reaction mixture was filtered and concentrated to afford the crude residue, which was purified by silica gel column chromatography to afford *N*-(3-methyl-2-butyne)anilines. To a solution of *N*-(3-methyl-2-butyne)anilines (2.6 mmol) in acetonitrile (10 mL) was added potassium carbonate (0.7 g, 5.2 mmol) followed by benzyl bromide (463 µl, 3.9 mmol) and the resultant mixture was stirred at room temperature for12 h. The reaction mixture was filtered and concentrated to afford the crude residue, which was purified by silica gel column chromatography (hexane : ethyl acetate = 30 : 1 (v:v)) to give *N*-Benzyl-*N*-(3-methyl-2-butyne)anilines (420.8 mg, 69% yield) as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.29 (m, 4H), 7.23 (t, J = 7.0 Hz, 3H), 6.87 (d, J = 7.6 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 4.55 (s, 2H), 3.98 (s, 2H), 1.80 (d, J = 2.0 Hz, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$): δ 149.0, 138.9, 129.2, 128.6, 127.1, 127.0, 117.9, 114.0, 79.8, 75.0, 55.1, 40.2, 3.7. Spectral data are in accordance with the reported data.[7]

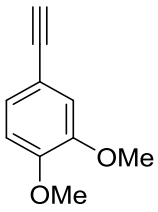
Synthesis of Acetylene substrate [8]



8g $R^1 = R^2$ = OMe
8h $R^1 = R^2$ = OCH_2O

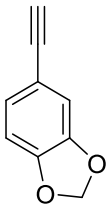
(1) [$Pd(PPh_3)_4$] (288.9 mg, 0.25, 5.0 mol%), CuI (95.2mg, 0.05 mmol, 10.0mol%), 4-bromo aromatic ether (5.0 mmol, 1.0 equiv.) and triethylamine (2.0 mL) were dissolved in dry THF (2.5 mL). Then trimethylsilylacetylene (850 µl, 6.0 mmol, 1.2 equiv) was added to the reaction mixture slowly. The resulting mixture was stirred at 50 °C for 24 h in a closed vial protected by N_2. The mixture was cooled to room temperature and passed through a short pad of celite using ethyl acetate, then concentrated under reduced pressure. The residue was used for the next step without any further purification.

(2) The crude silylated product was dissloved in THF (10 mL), and TBAF (0.65 g, 0.5 equiv) was added portion wise into the flask under N_2 atmosphere at 0 °C. The resulting mixture was stirred at room temperature for 1 h. The mixture was extracted with ethyl acetate (100 mL) and washed with water (100 mL). After drying over with Na_2SO_4, the solvent was concentrated under reduced pressure and purified by silica gel chromatographic (hexane as eluent).



4-Ethynyl-1,2-dimethoxybenzene (8g)

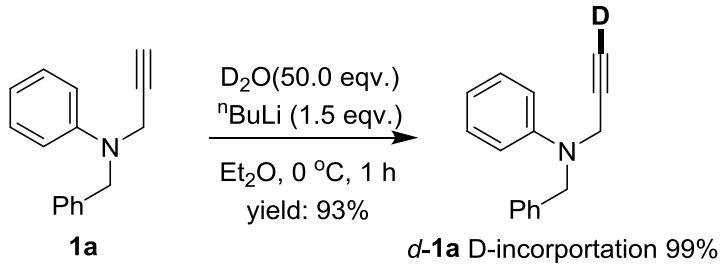
Brown solid; 73% yield (591.0 mg); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.11 (dd, J = 8.3, 1.5 Hz, 1H), 6.99 (d, J = 1.4 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 3.88 (d, J = 4.8 Hz, 6H), 3.00 (s, 1H). Spectral data are in accordance with the reported data. [8]



4-Ethynyl-1,2-ylidenedioxybenzene(8g)

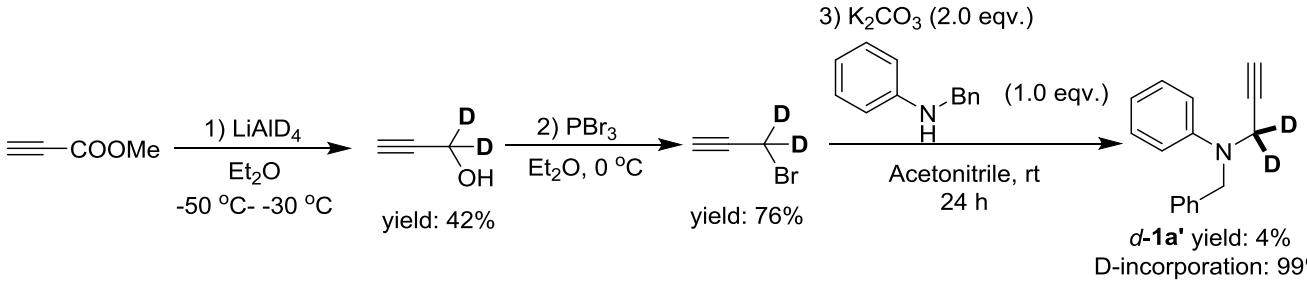
Brown solid; 64%yield (521.7.0 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.02 (d, J = 8.0 Hz, 1H), 6.93 (s, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.97 (s, 2H), 2.97 (s, 1H). Spectral data are in accordance with the reported data.[8]

Synthesis of *d*-1a [9]



Propargyl aniline **1a** (0.95 mmol, 210.0 mg) was dissolved in Et_2O (20 ml), then added *n*-BuLi (in hexane , 1.6 M, 846 µl, 1.35 mmol) drop wise at 0 ℃. The mixture was allowed to warm to room temperature and was stirred for 1 h. After the quench by D_2O (1 ml), the mixture was dried over with $MgSO_4$ and decanted. The residure was concentrated in vacuo to give *d*-**1a** (197.0 mg, 93% yield) as colorless liquid. The ^{1}H-NMR peak at 2.21 ppm completely disappeared compared to 1a indication more than 99% incorporation.

Synthesis of *d*-1a′ [10]



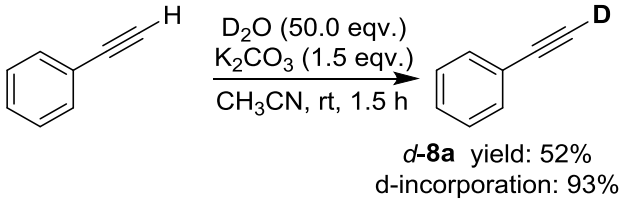
(1) A suspension of lithium aluminum deuteride ($LiAlD_4$) (2.4 g, 57.7 mmol) in ether (150 mL) was cooled to -50 ^{o}C under nitrogen in a two neck round-bottomed flask. A solution of Methyl propiolate (5.1 g, 61.22 mmol) in ether (50 mL) was added drop wise over a period of 60 min with continuous stirring. The reaction mixture was stirred for another 90 min at -30 ^{o}C, and was allowed to cool to room temperature slowly over a period of 3 h and the stirred overnight. The reaction mixture was quenched by successive drop-wise addition of H_2O (3 mL), NaOH (0.22 g in 1.5 mL H_2O) and H_2O (2 mL). The solid was allowed to settle and decanted. The residual solid was washed with ether (2 X 50 mL) and the washings were collected. The combined liquid was dried over $MgSO_4$ and the ether was evaporated under vaccum. The residual liquid was subjected to distillation under reduced pressure at 650 mbar. The fraction between 60 and 90 ^{o}C was collected to give the desired product. The final product was obtained as colorless oil (1.4 g, 42%) without further purification.

(2) To the stirred solution of Deuterated propynol (1.2 g, 20.66 mmol) in dichloromethane (15 mL) at -5 ^{o}C under nitrogen, phosphorus tribromide (PBr_3) (6.0 g, 22.38 mmol) was added drop wise. The solution was stirred at that temperature for 1 h, heated up to room temperature and stirred for three more hours. The reaction mixture was quenched at 0 ^{o}C with H_2O (15.0 mL). The organic layer was washed successively with saturated $NaHCO_3$ (25.0 mL) and H_2O (25.0 mL) and dried over $MgSO_4$. The solvent was evaporated carefully and the final product was obtained as colorless oil (1.8 g, 15.0 mmol, 72.6%)

and was analyzed by NMR. The product was considered pure enough for the next step without further purification.

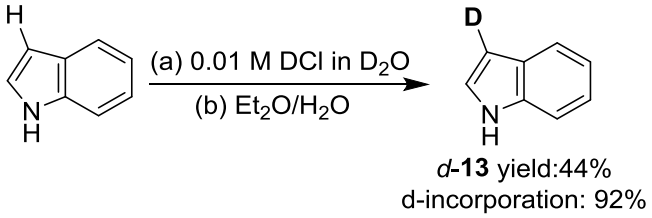
(3) *N*-benzylaniline was dissolved (2.5 mmol, 460.0 mg) in anhydrous acetonitrile (10.0 ml), adding anhydrous potassium carbonate (690.0 mg) and *d*-bromopropyne (5.0 mmol, 610.0 mg) and stired at room temperature for 24 h. The reaction mixture was filtered and concentrated to afford the crude residue, which was purified by silica gel column chromatography (hexane : ethyl acetate = 30 : 1) to give *d*-**1a′** (21.3 mg, 4% yield) as colorless liquid. The ^{1}H-NMR double peak at 4.03 ppm completely disappeared compared to **1a** indicating more than 99% incorporation.

Synthesis of *d*-8a



The phenylacetylene **8a** (5.0 mmol, 550 μl) was dissolved in acetonitrile (12.0 ml), stirred at room temperature for 0.5 hours. Deutirium oxide (2.26 ml) was added and stirred for 1 h. Finally, it was dried over by anhydrous $MgSO_4$, and filtered to give a acetonitrile solution, and concentrated under reduced pressure to give *d*-**8a** (270.1 mg, yield 52%, *d* incorpotation 93%) as light yellow liquid. The ^{1}H-NMR peak at 3.07 ppm almost disappeared compared to **8a**.

Synthesis of *d*-13 [4]



Indole (2.0 g, 17 mmol) was stirred in a 0.01 M solution of DCl in D_2O (20 mL) at 60°C for 4 h under N_2. The reaction was cooled and extracted three times with dry Et_2O (20 mL). The organic layers were combined, dried over $MgSO_4$ and filtered and reduced under vacuum. The resulting oil was triturated in pentane to afford a colorless solid. The solid ([1,3- ^{2}H]Indole) was dissolved in a mixture of Et_2O (20 mL) and H_2O (10 mL) and stirred for 2 h at room temperature. The layers were separated and the aqueous layer extracted twice with Et_2O (20 mL). The organic layers were combined, dried over $MgSO_4$ and filtered and reduced under vacuum to give [3- ^{2}H]Indole (*d*-**13**, 0.88 g, 44% yield) as colorless solid. The ^{1}H-NMR peak at 6.55 ppm completely disappeared compared to indole indication more than 92% incorporation.

6. References

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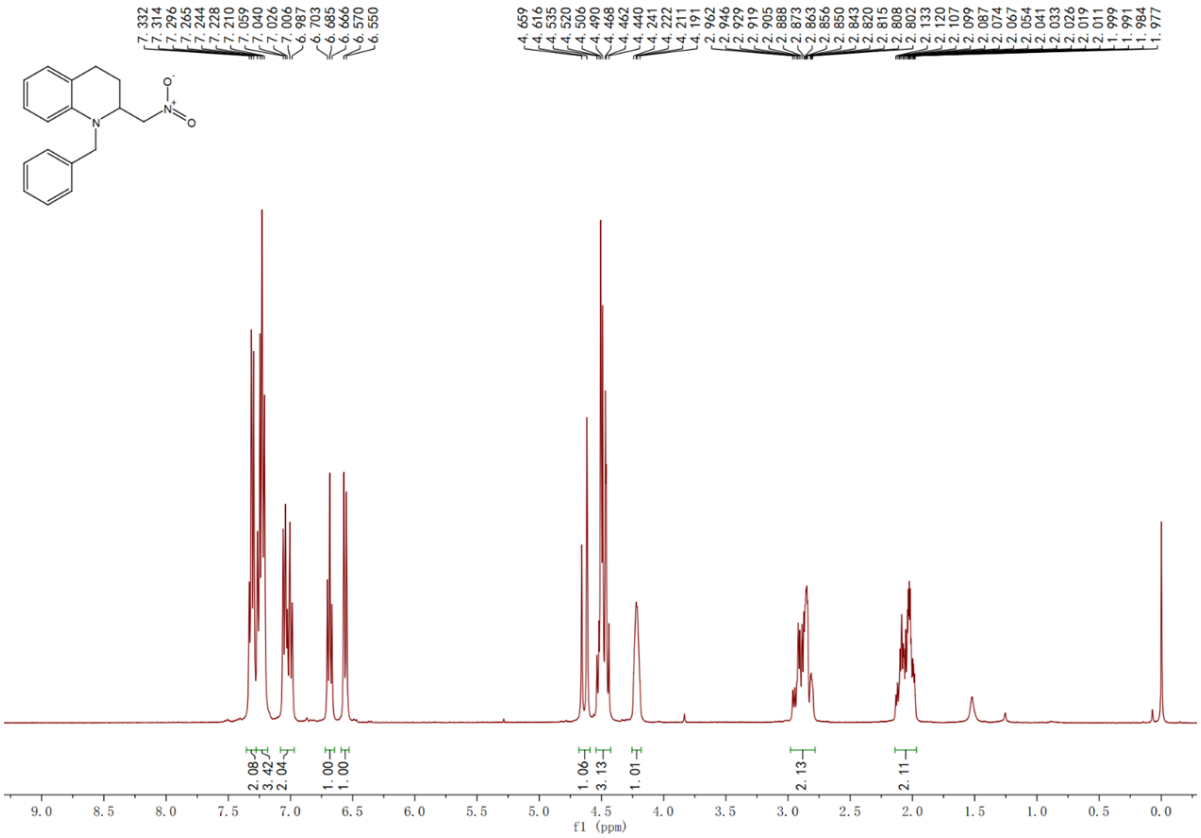
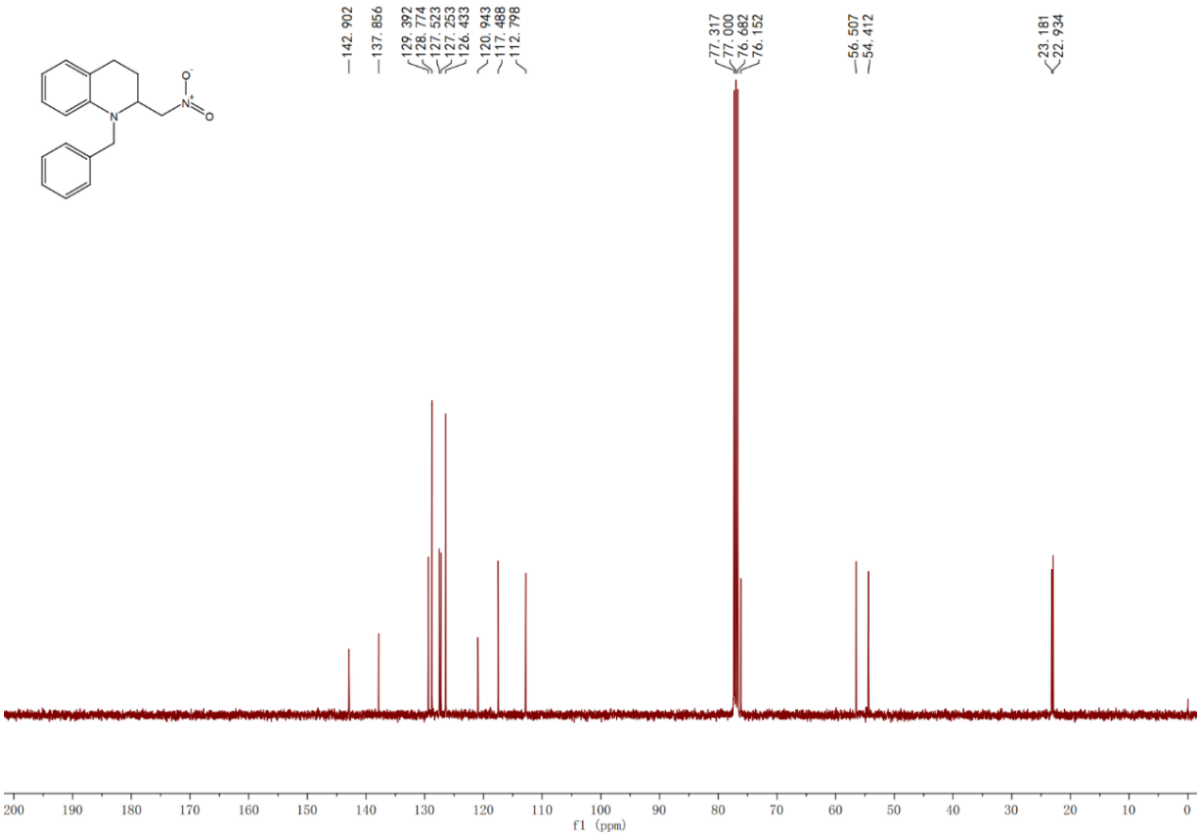
7. Copies of ^{1}H-NMR, ^{13}C-NMR spectra

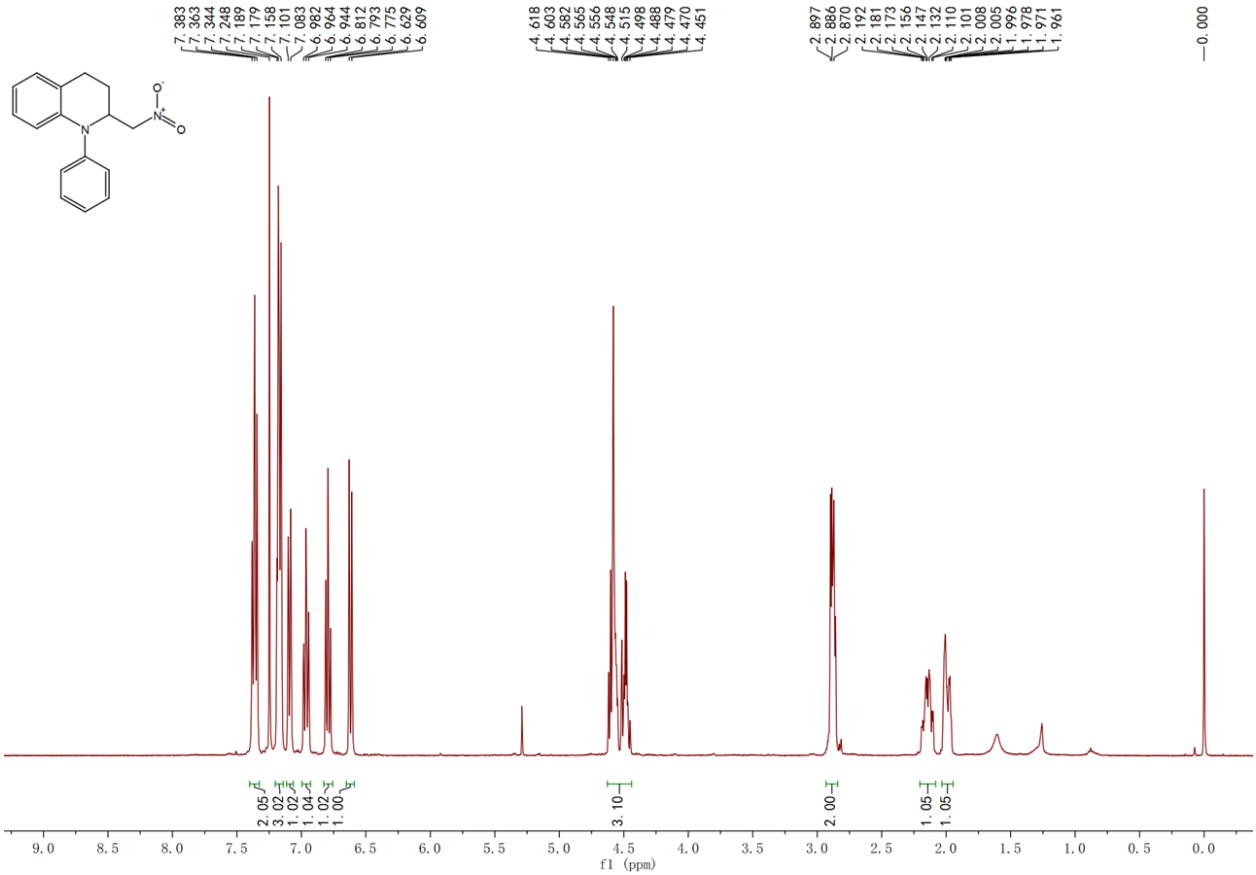
***N*-Benzyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3a (^{1}H-NMR)**



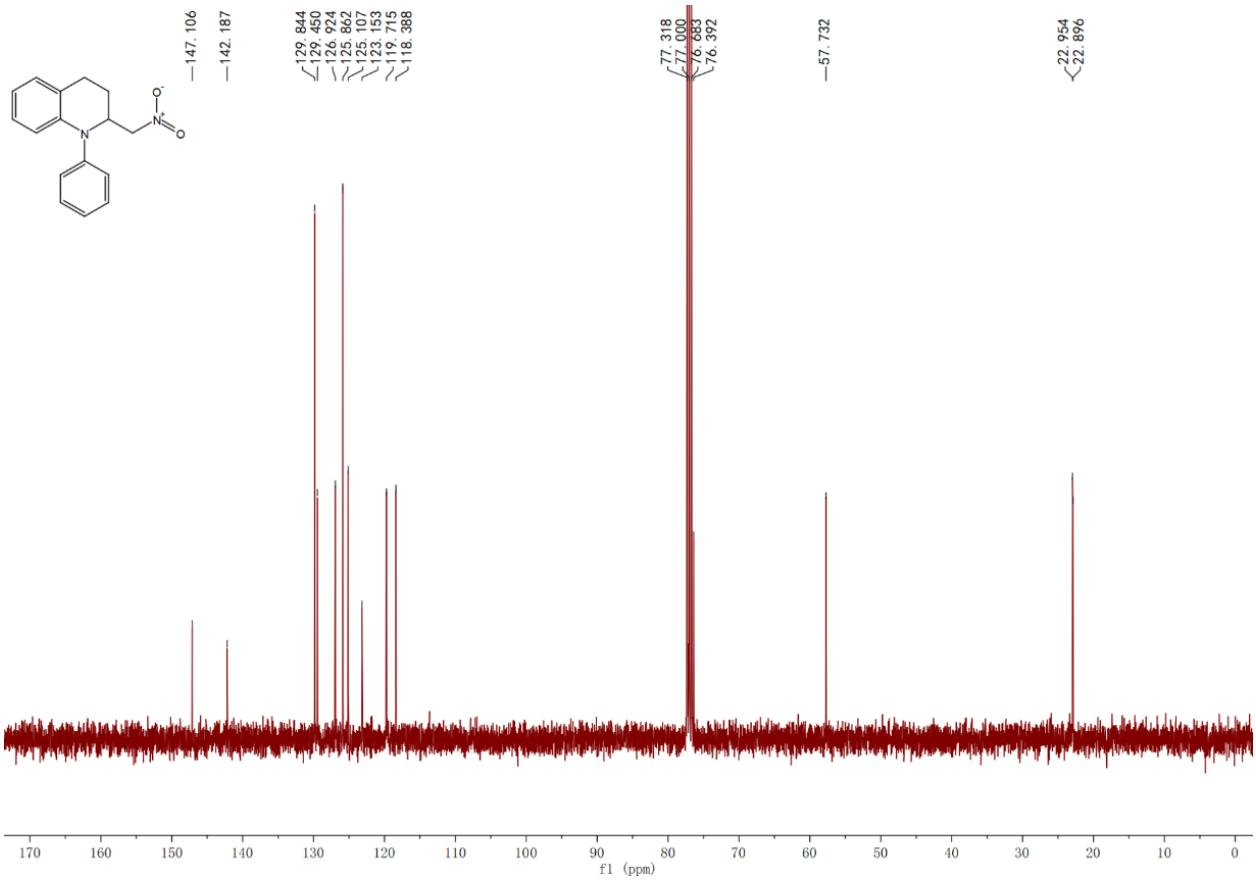
***N*-Benzyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3a (^{13}C-NMR)**



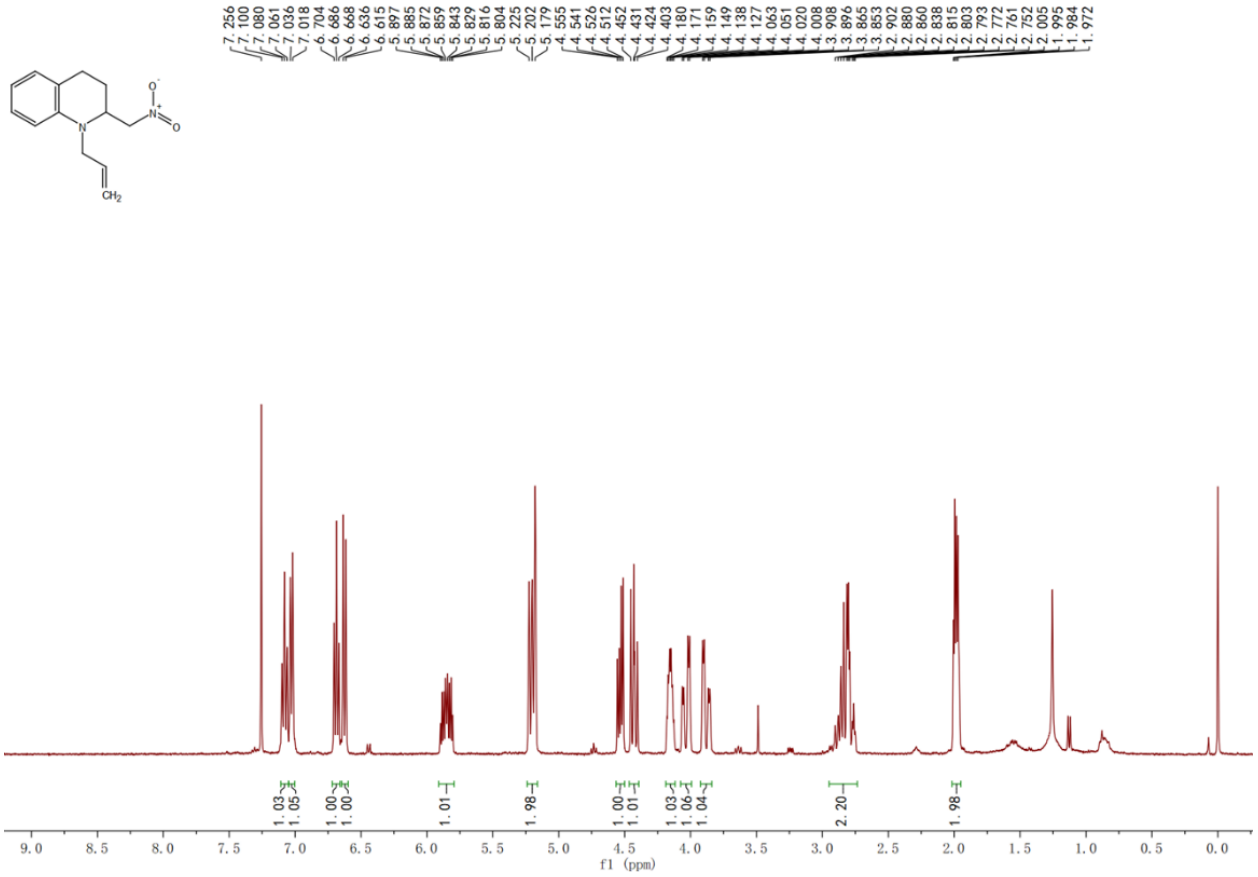
_N_-Phenyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3b (^{1}H-NMR)



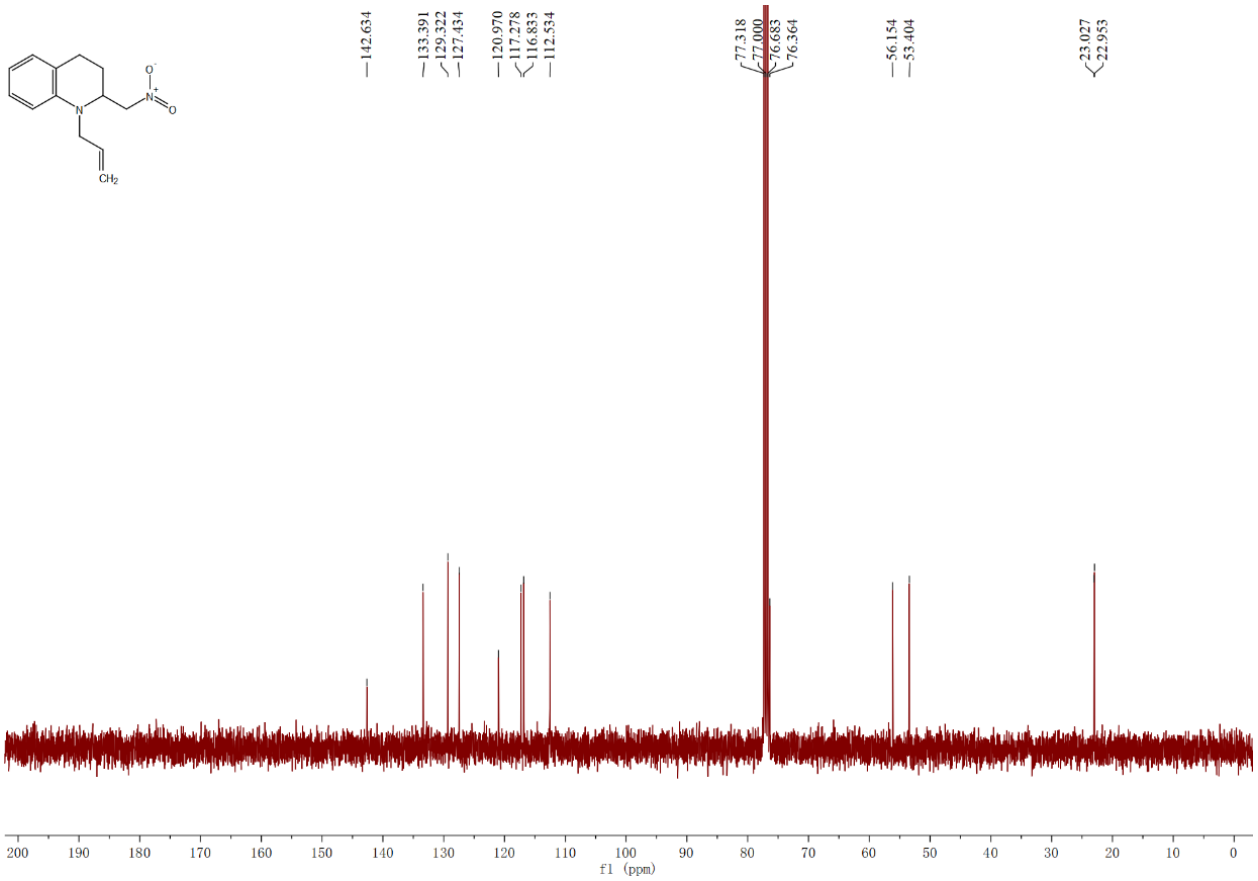
_N_-Phenyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3b (^{13}C-NMR)



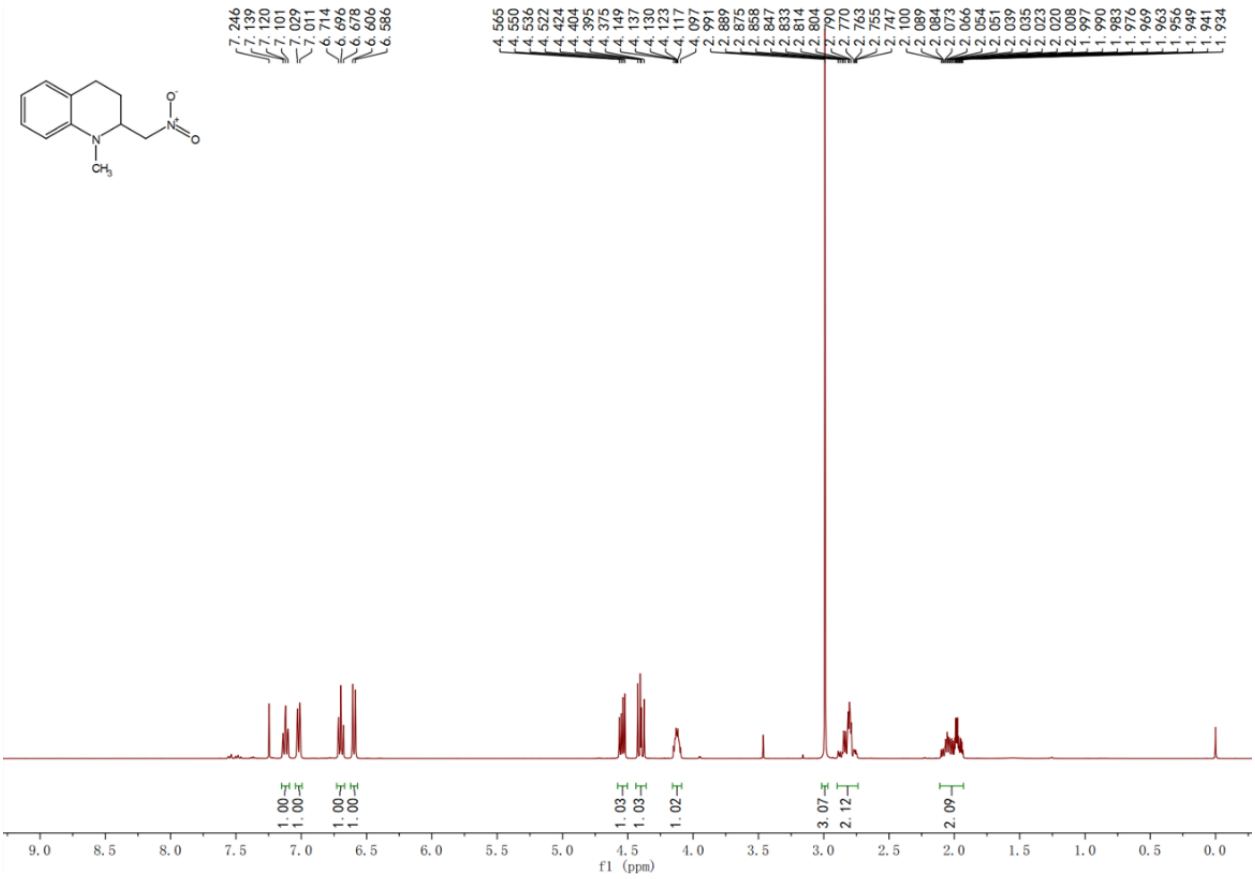
N-Allyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3c (^{1}H-NMR)



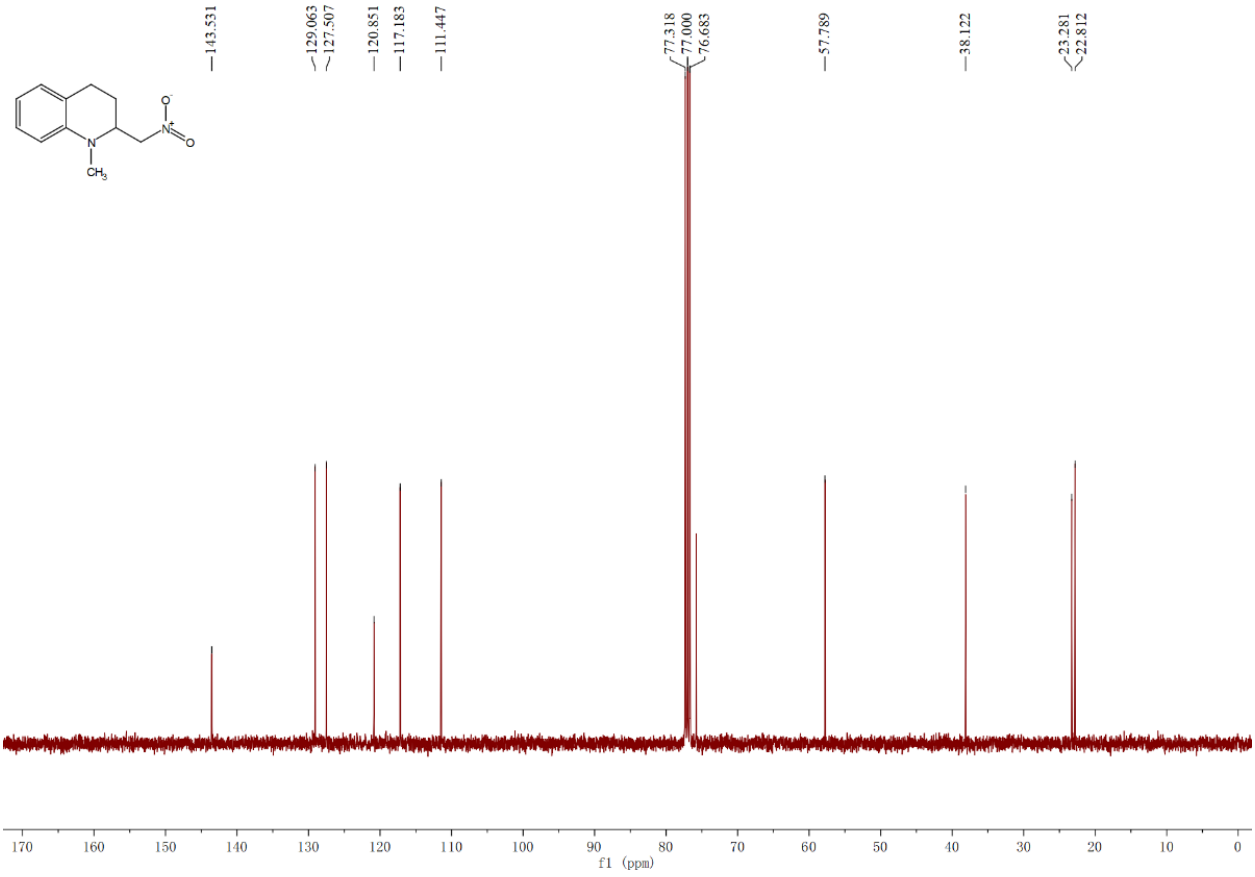
N-Allyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3c (^{13}C-NMR)



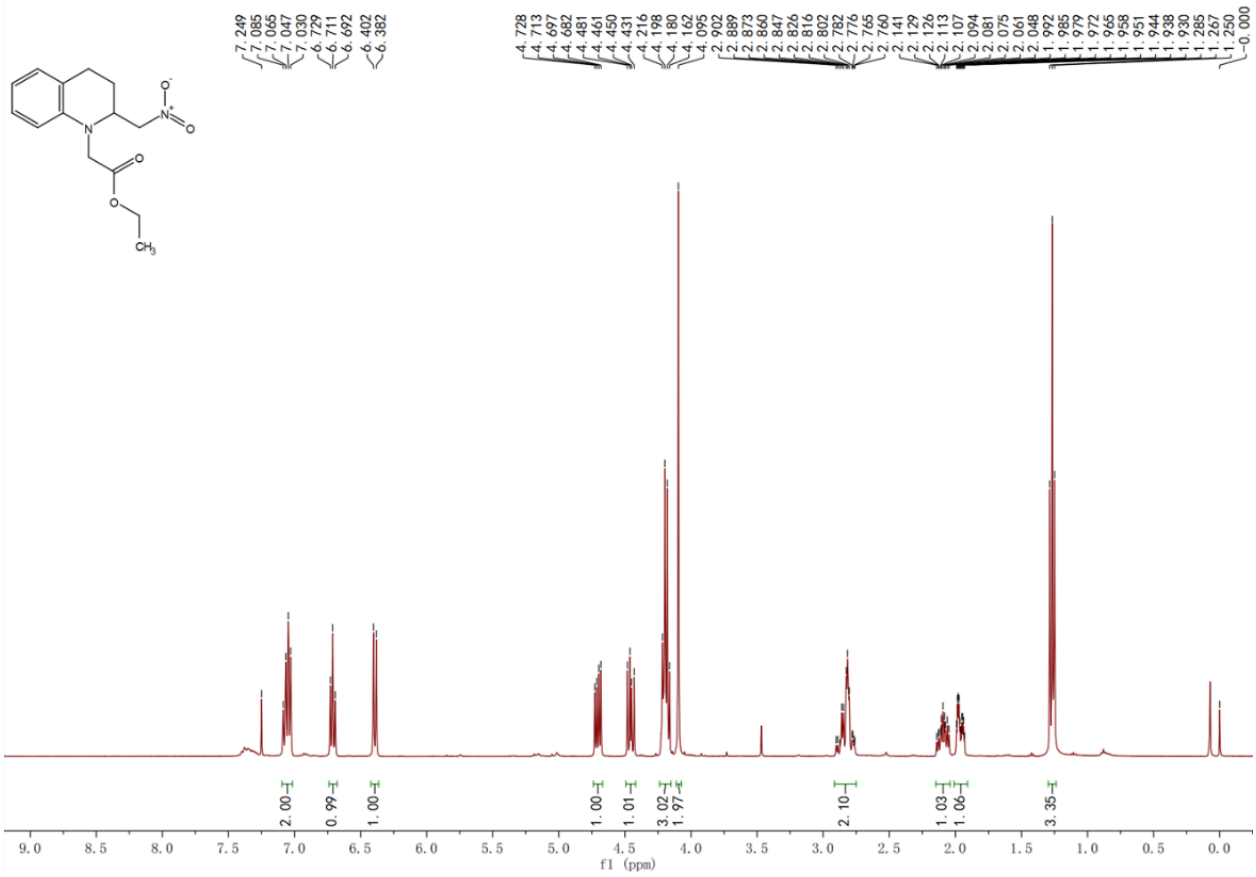
_N_-Methyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3d (^{1}H-NMR)



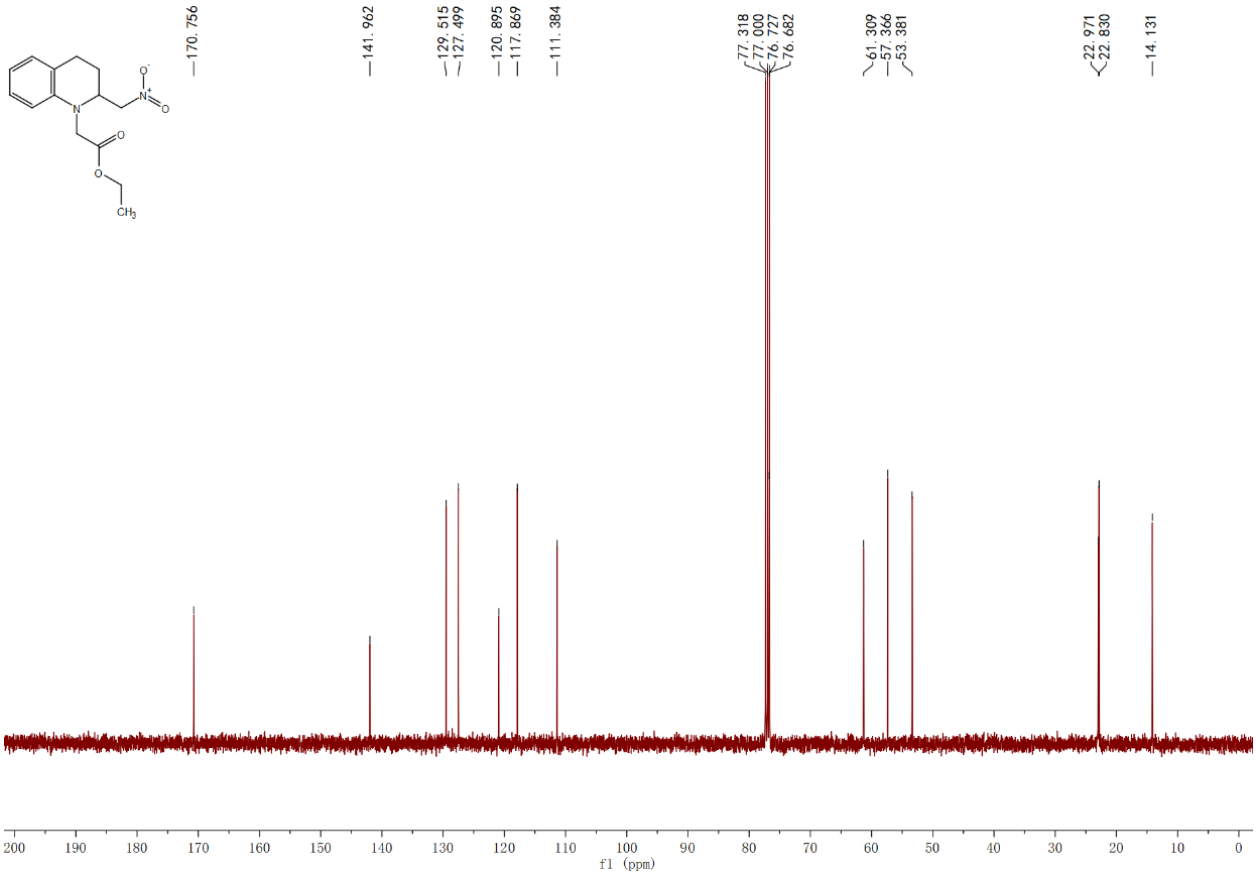
_N_-Methyl-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3d (^{13}C-NMR)



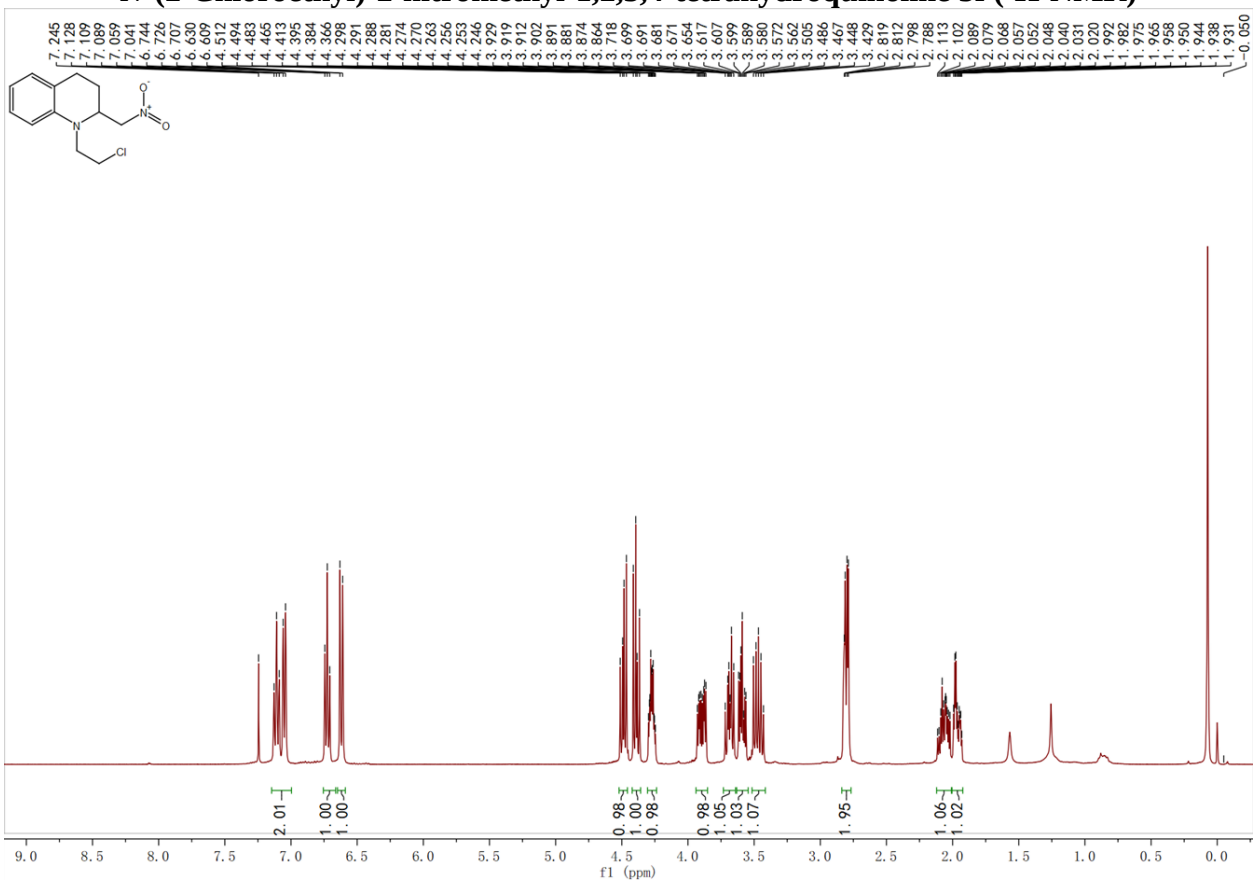
Ethyl 2-(2-(nitromethyl)-3,4-dihydroquinolin-1(2H)-yl)acetate 3e (^{1}H-NMR)



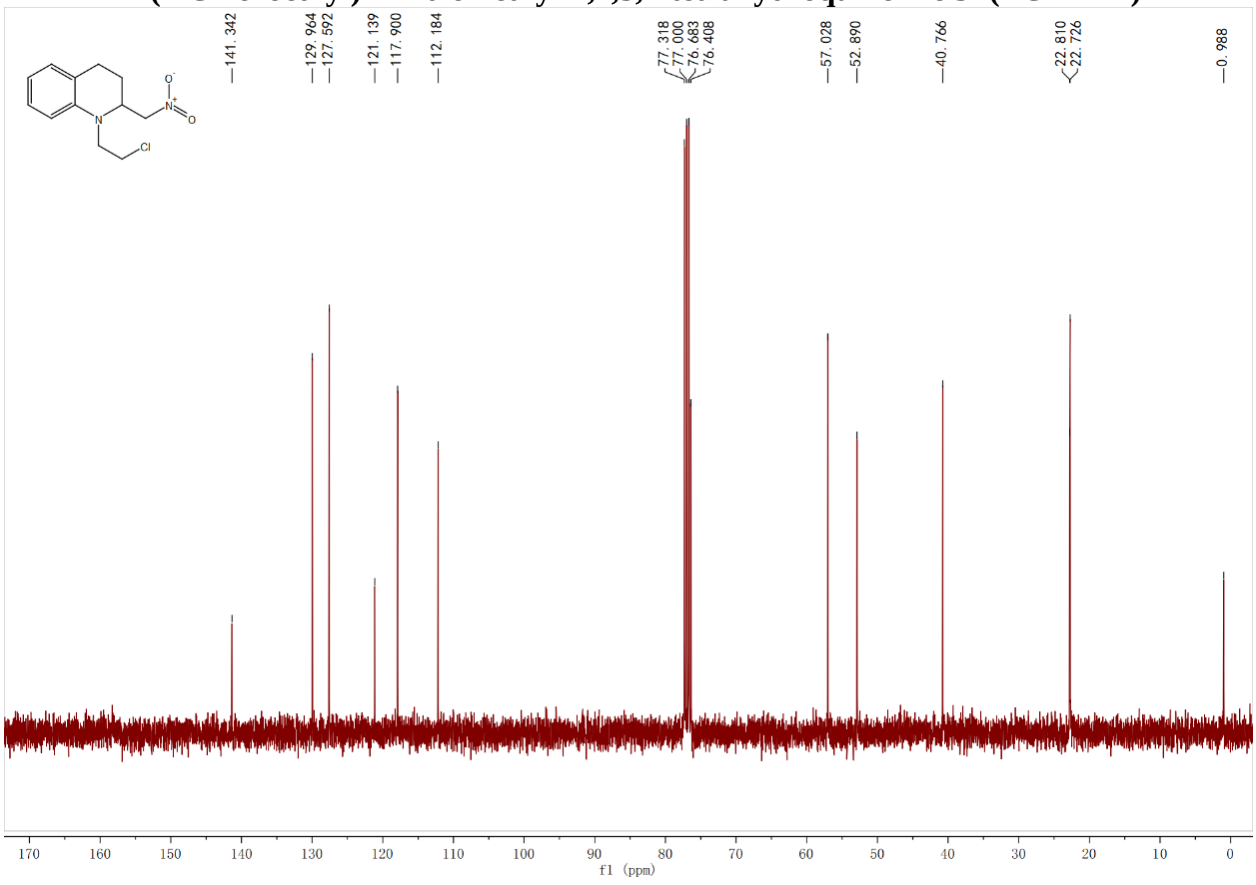
Ethyl 2-(2-(nitromethyl)-3,4-dihydroquinolin-1(2H)-yl)acetate 3e (^{13}C-NMR)



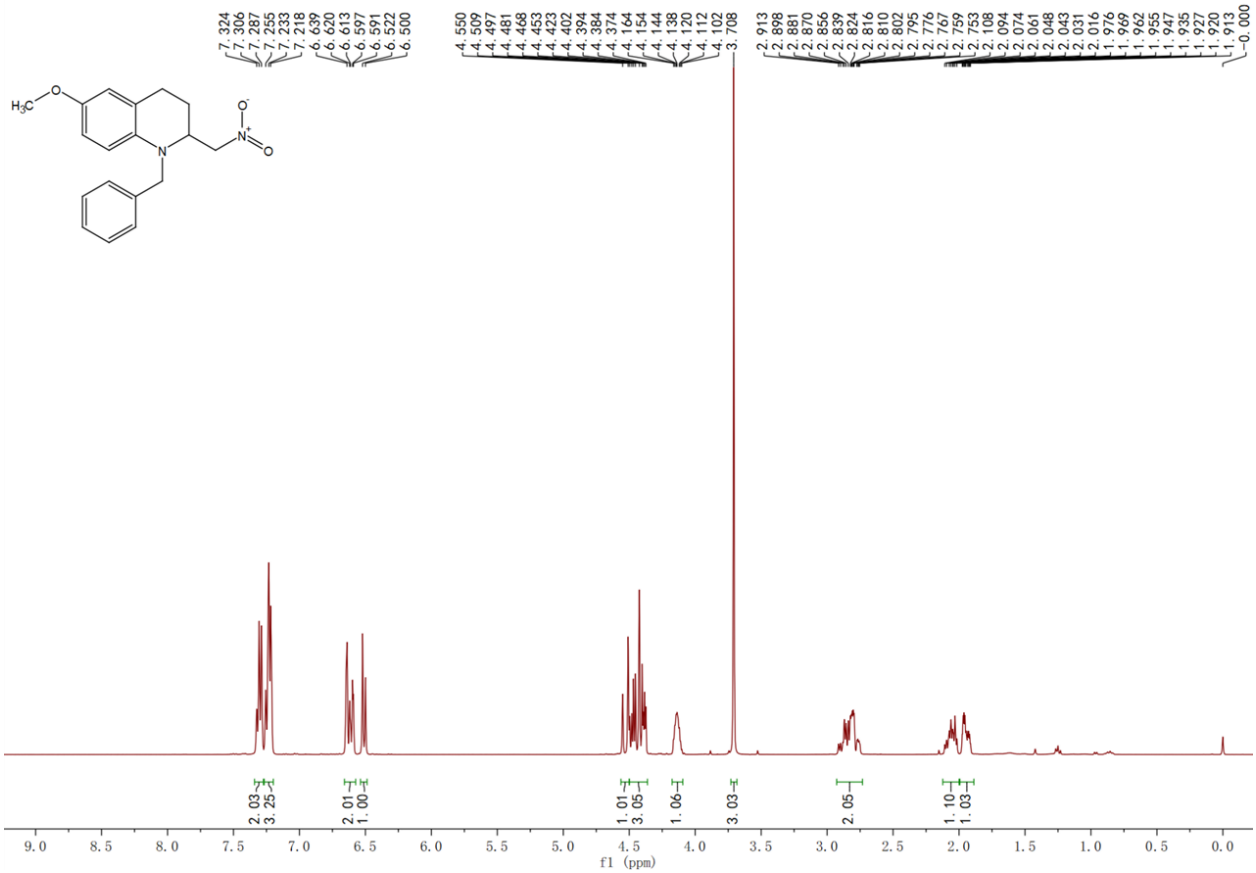
_N_-(2-Chloroethyl)-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3f (^{1}H-NMR)



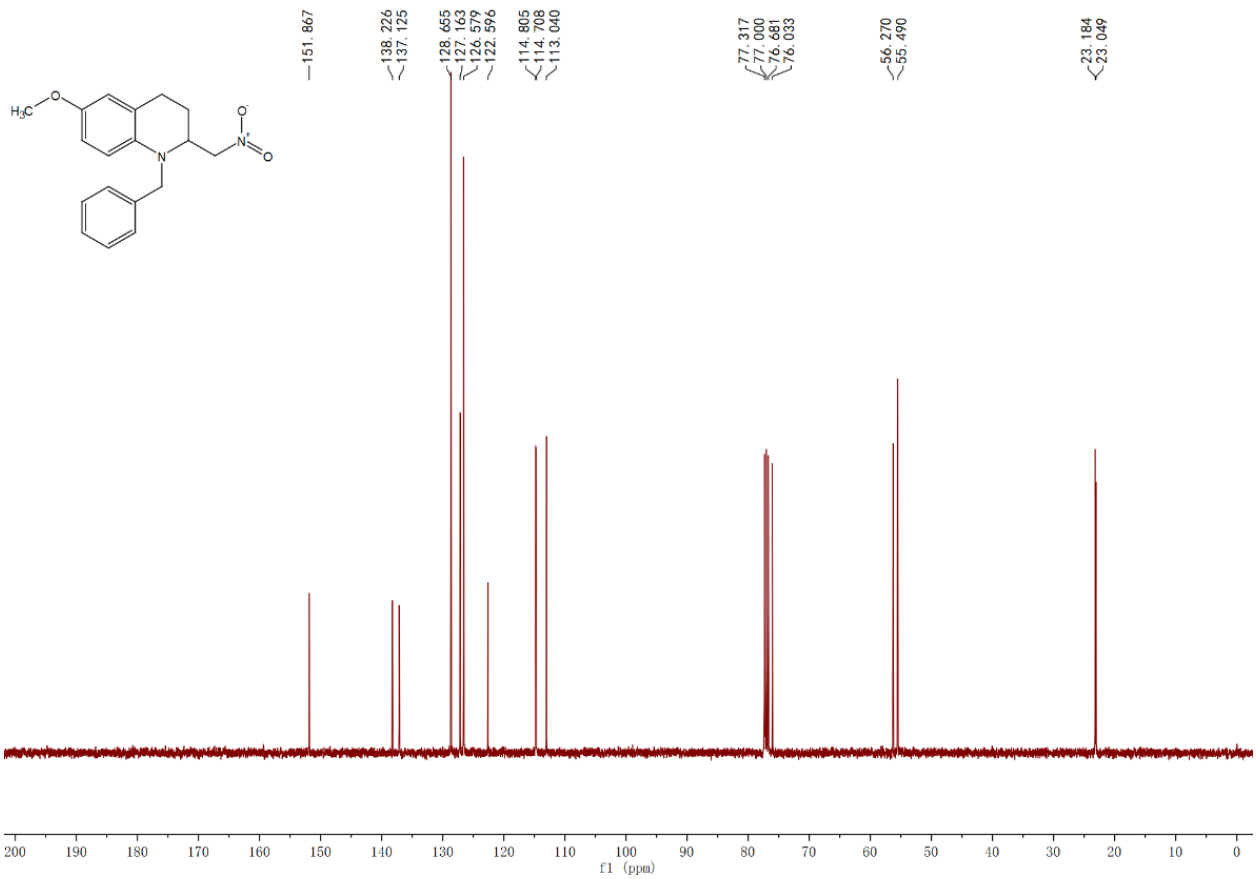
_N_-(2-Chloroethyl)-2-nitromethyl-1,2,3,4-tetrahydroquinoline 3f (^{13}C-NMR)



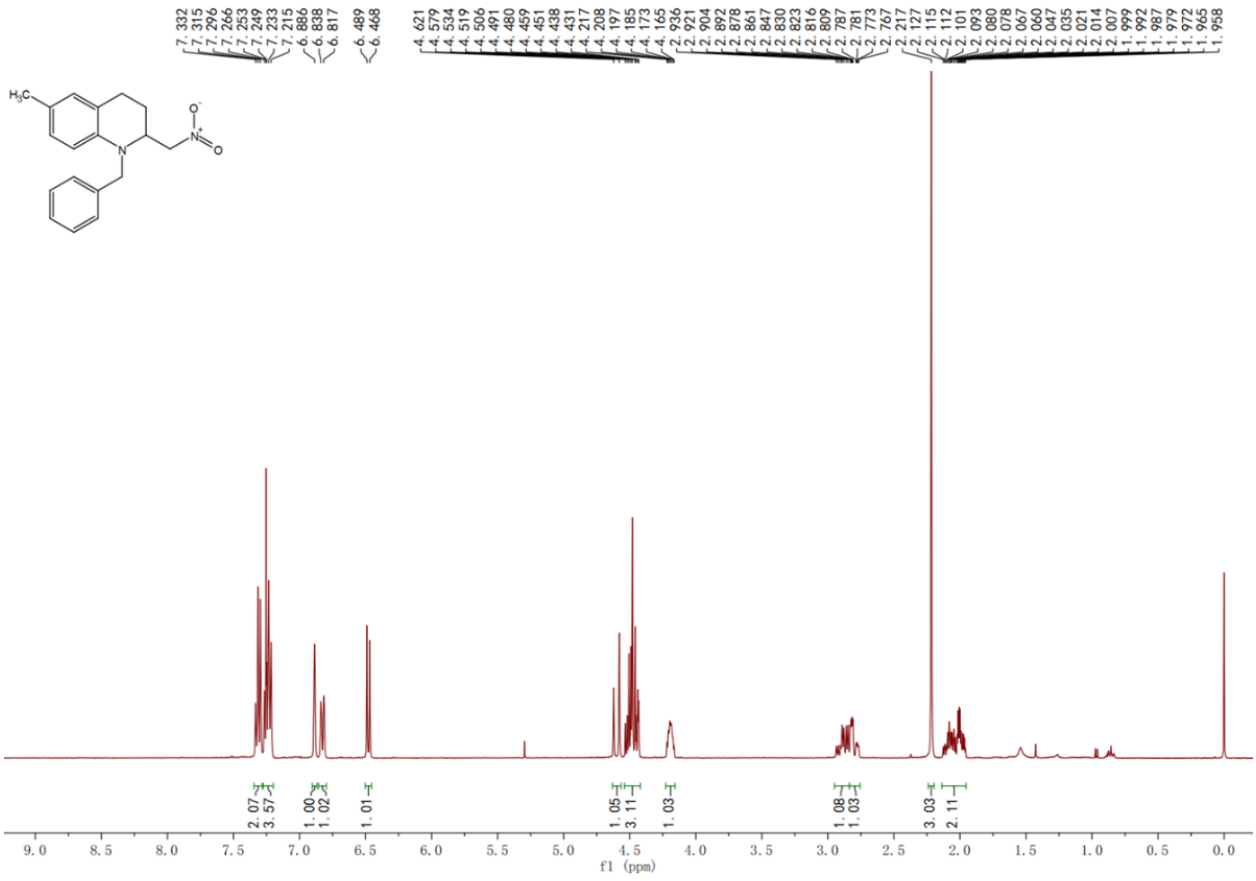
_N_-Benzyl-2-nitromethyl-6-methoxyl-1,2,3,4-tetrahydroquinoline 3g (^{1}H-NMR)



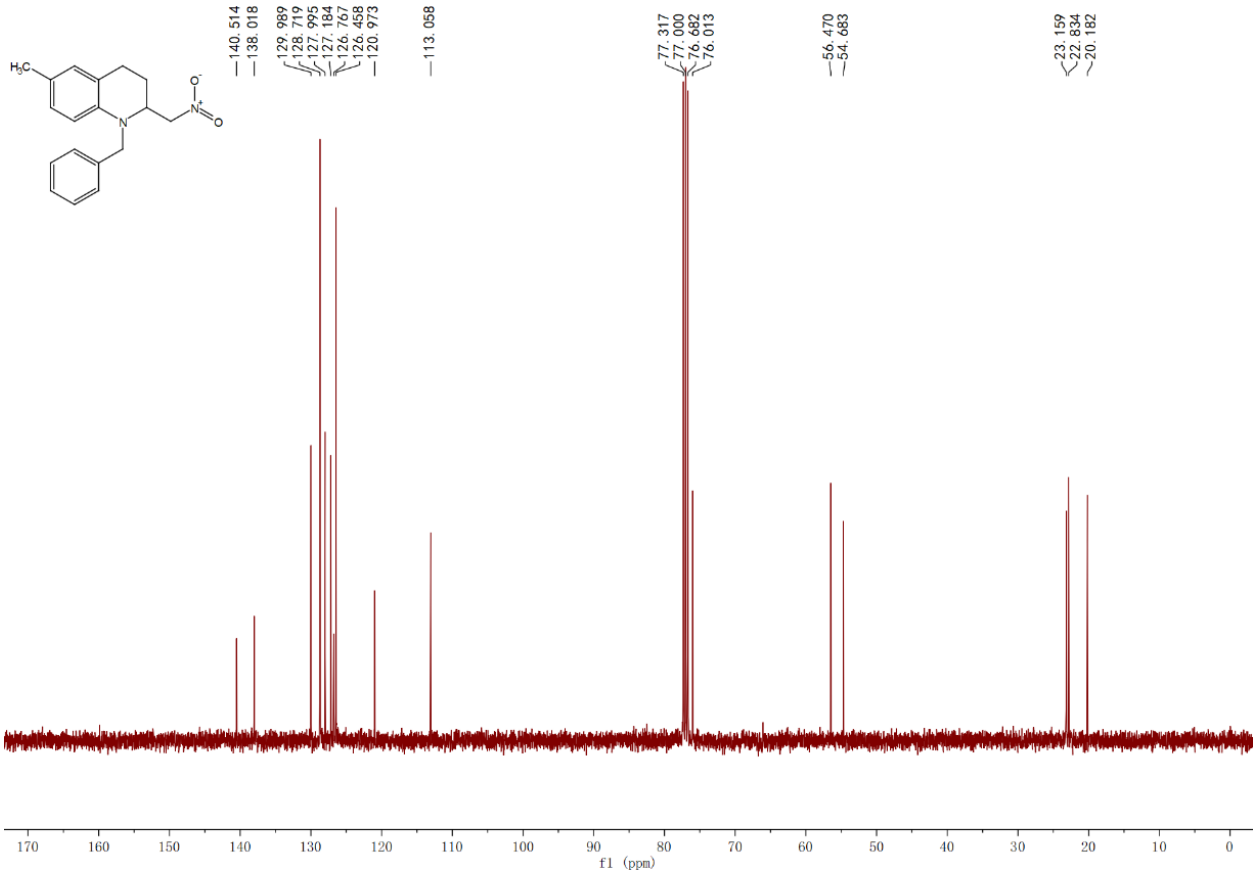
_N_-Benzyl-2-nitromethyl-6-methoxyl-1,2,3,4-tetrahydroquinoline 3g (^{13}C-NMR)



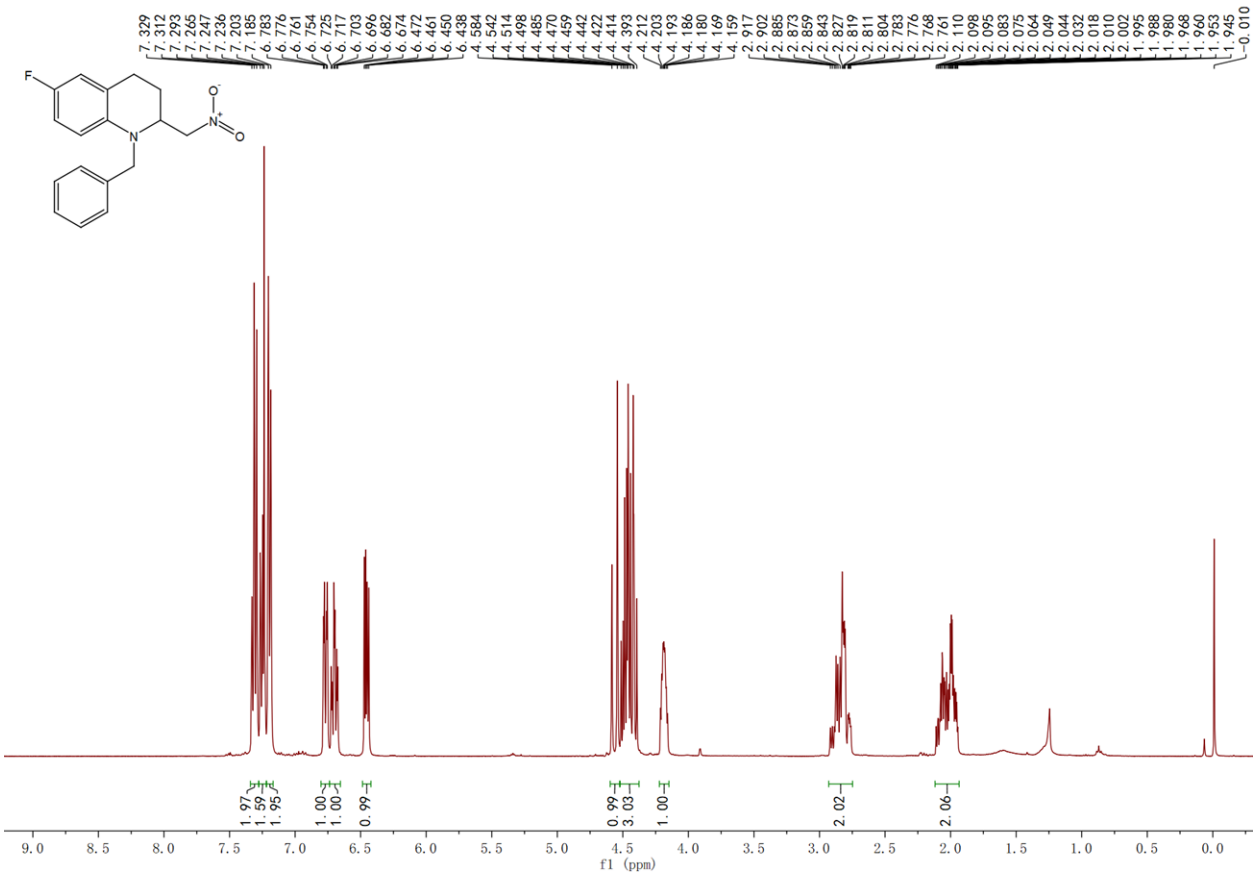
_N_-Benzyl-2-nitromethyl-6-methyl-1,2,3,4-tetrahydroquinoline 3h (^{1}H-NMR)



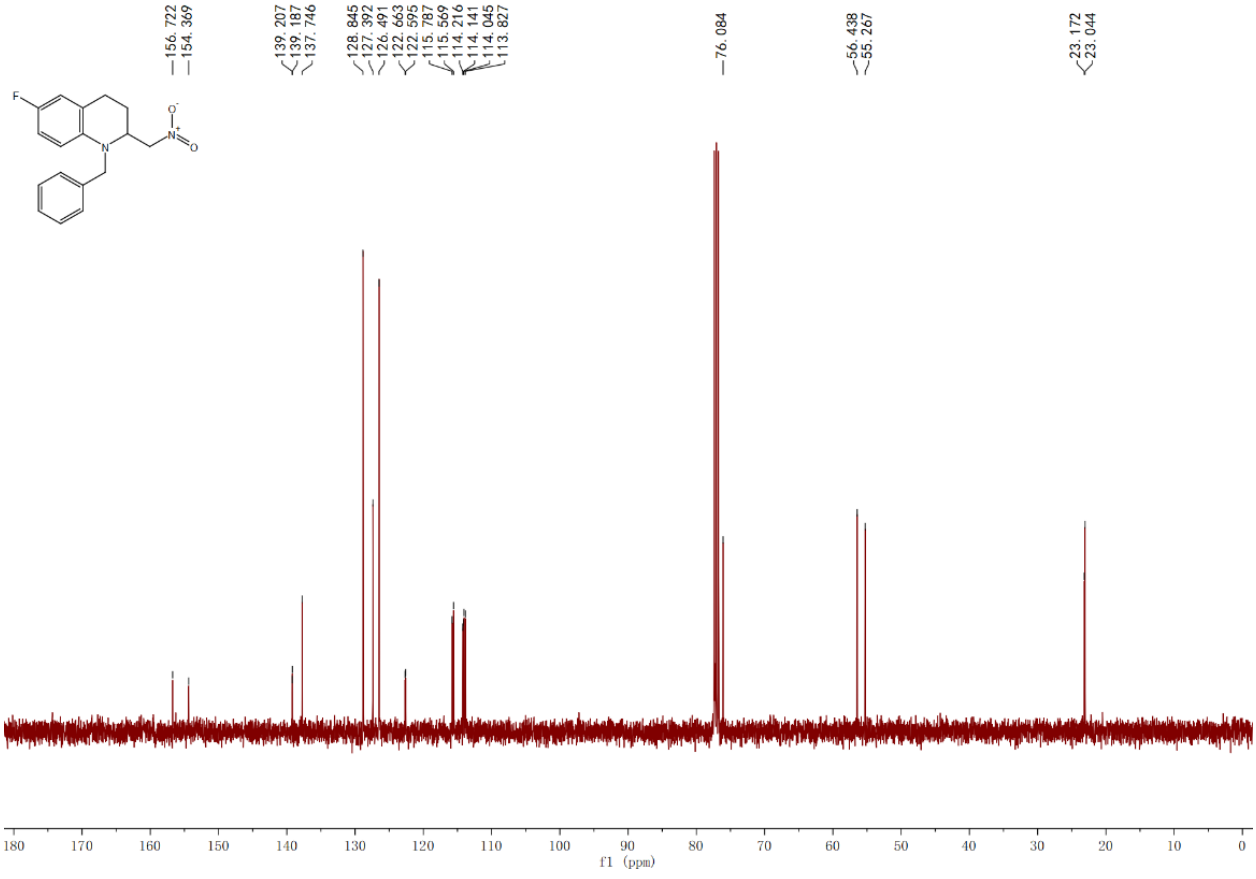
_N_-Benzyl-2-nitromethyl-6-methyl-1,2,3,4-tetrahydroquinoline 3h (^{13}C-NMR)



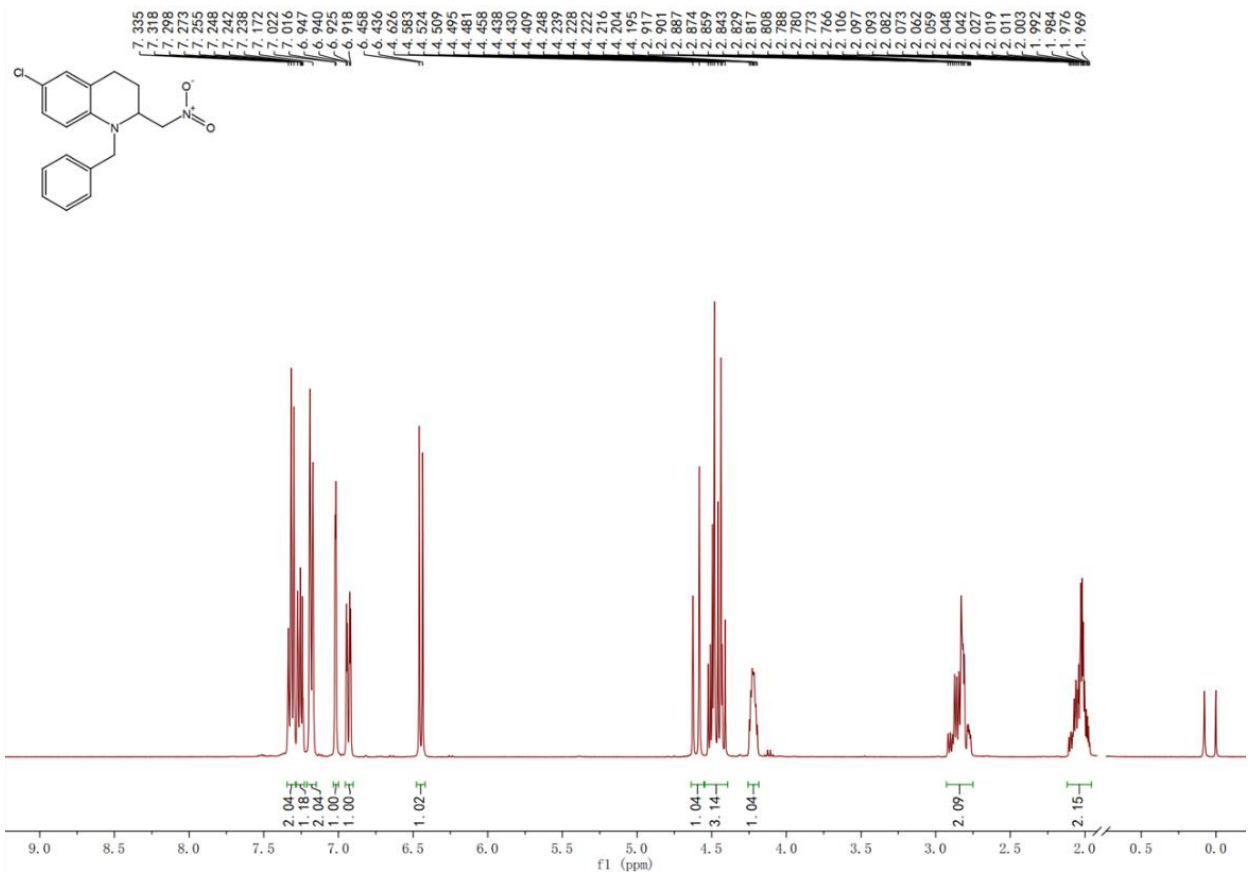
_N_-Benzyl-2-nitromethyl-6-fluoro-1,2,3,4-tetrahydroquinoline 3i (^{1}H-NMR)



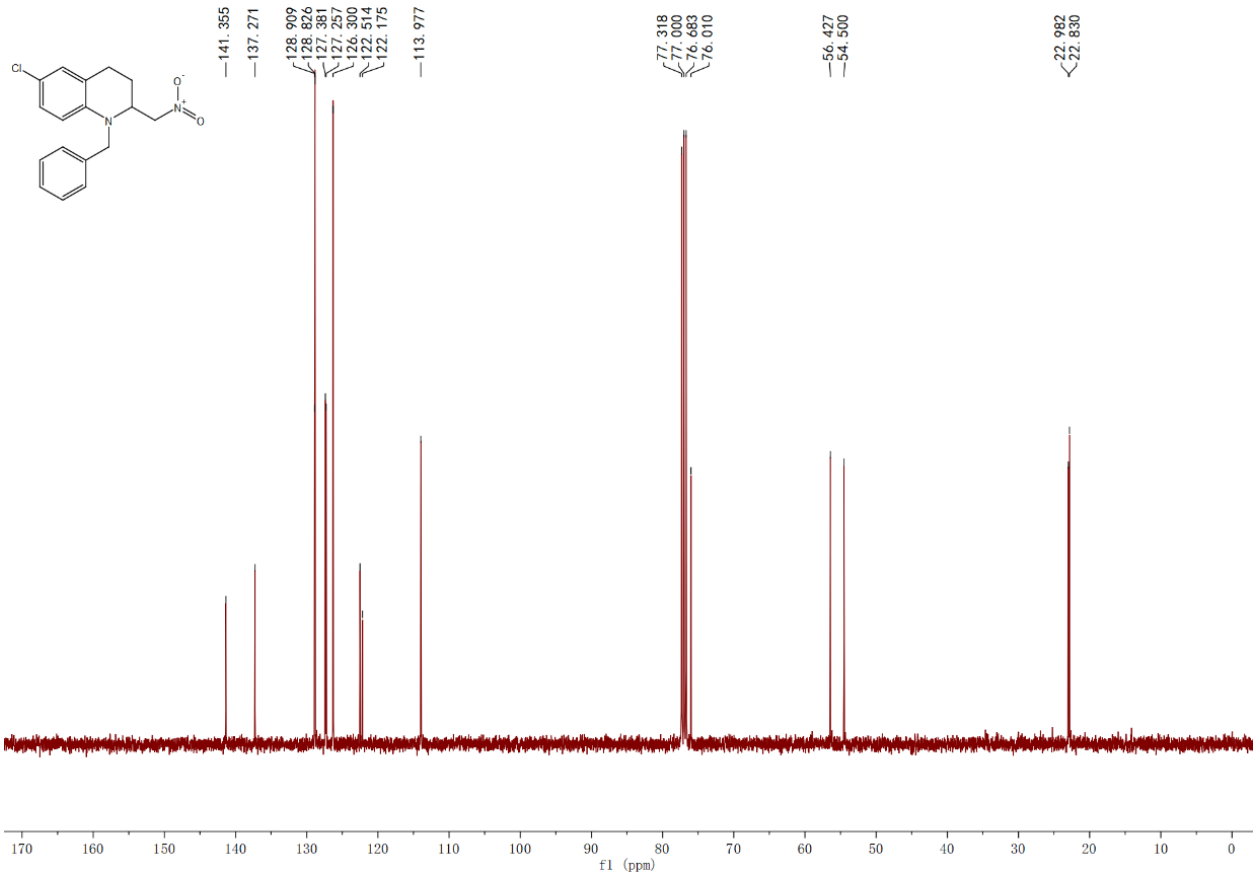
_N_-Benzyl-2-nitromethyl-6-fluoro-1,2,3,4-tetrahydroquinoline 3i (^{13}C-NMR)



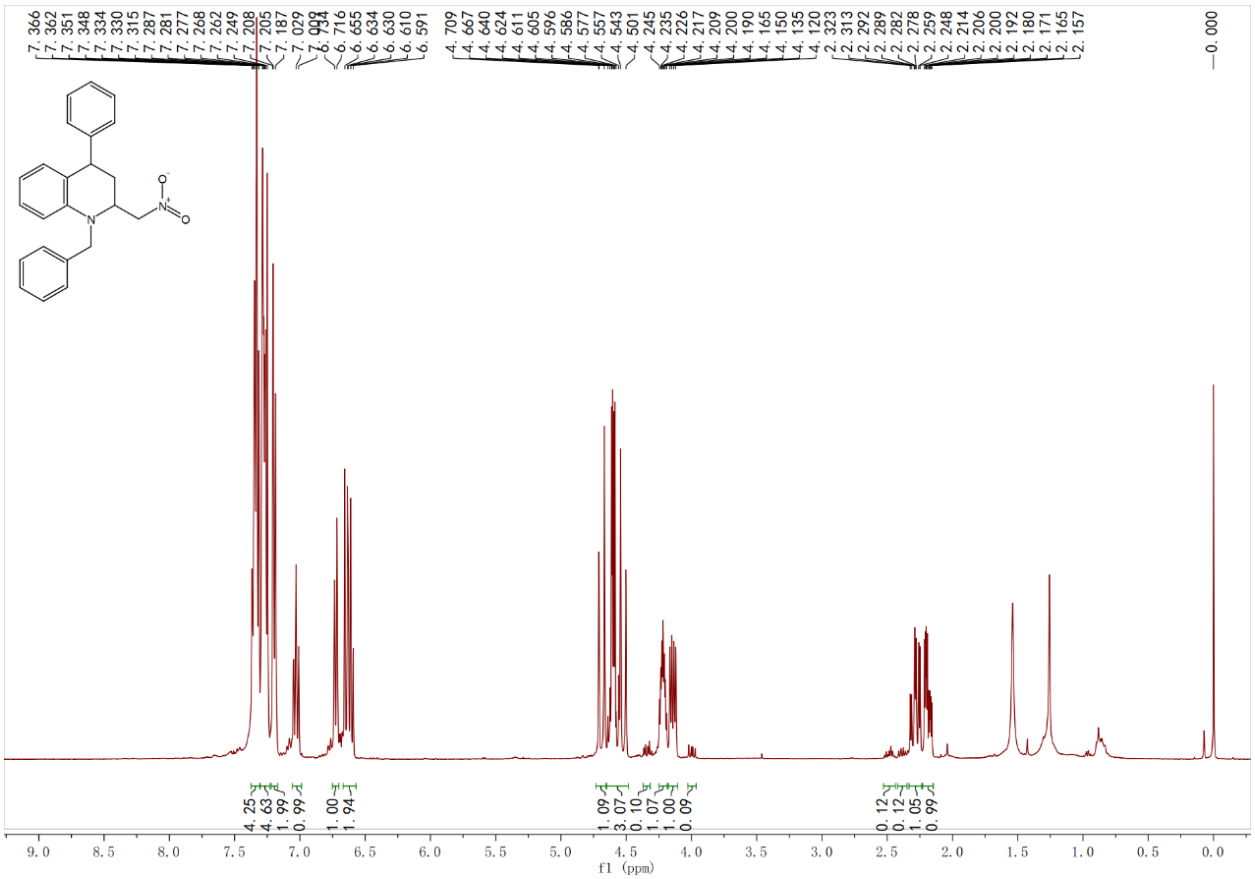
_N_-Benzyl-2-nitromethyl-6-chloro-1,2,3,4-tetrahydroquinoline 3j (^{1}H-NMR)



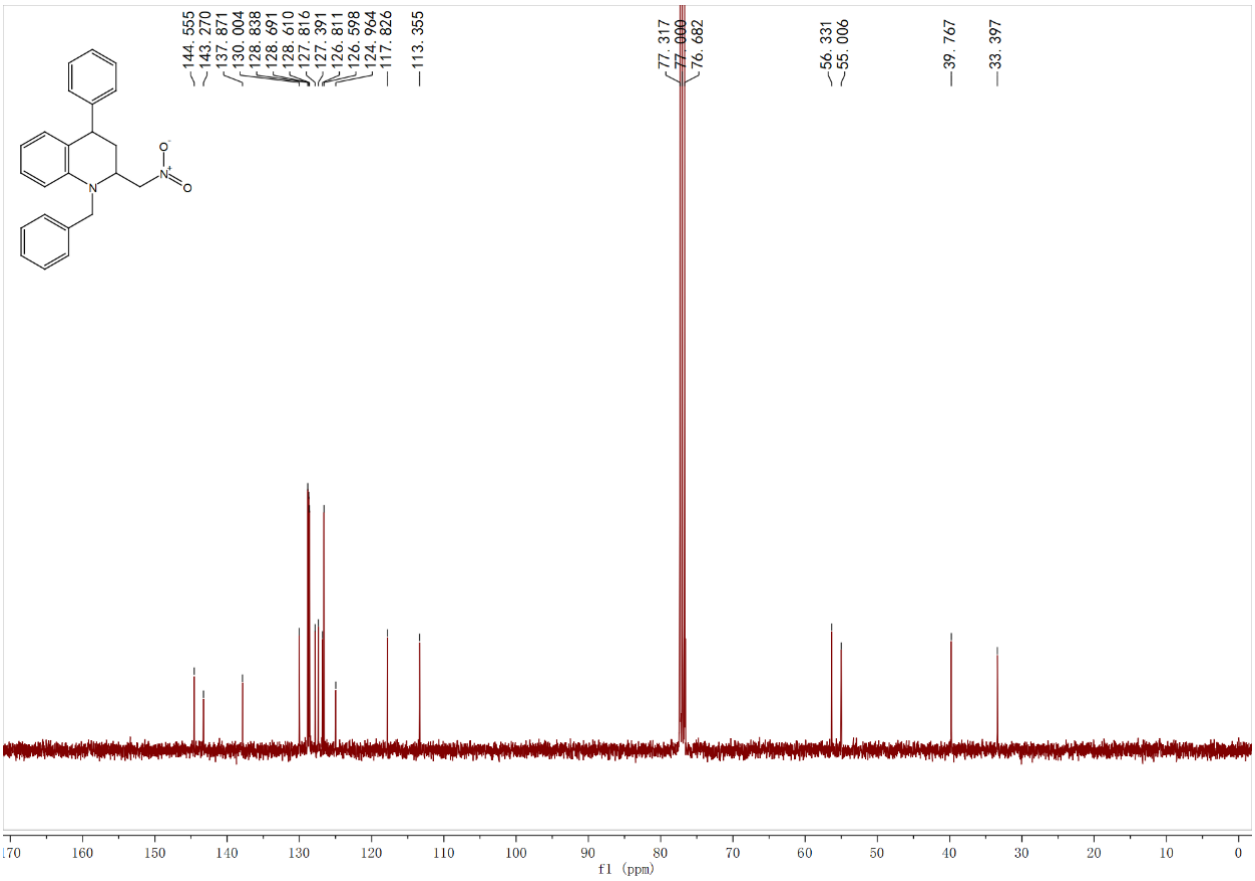
_N_-Benzyl-2-nitromethyl-6-chloro-1,2,3,4-tetrahydroquinoline 3j (^{13}C-NMR)



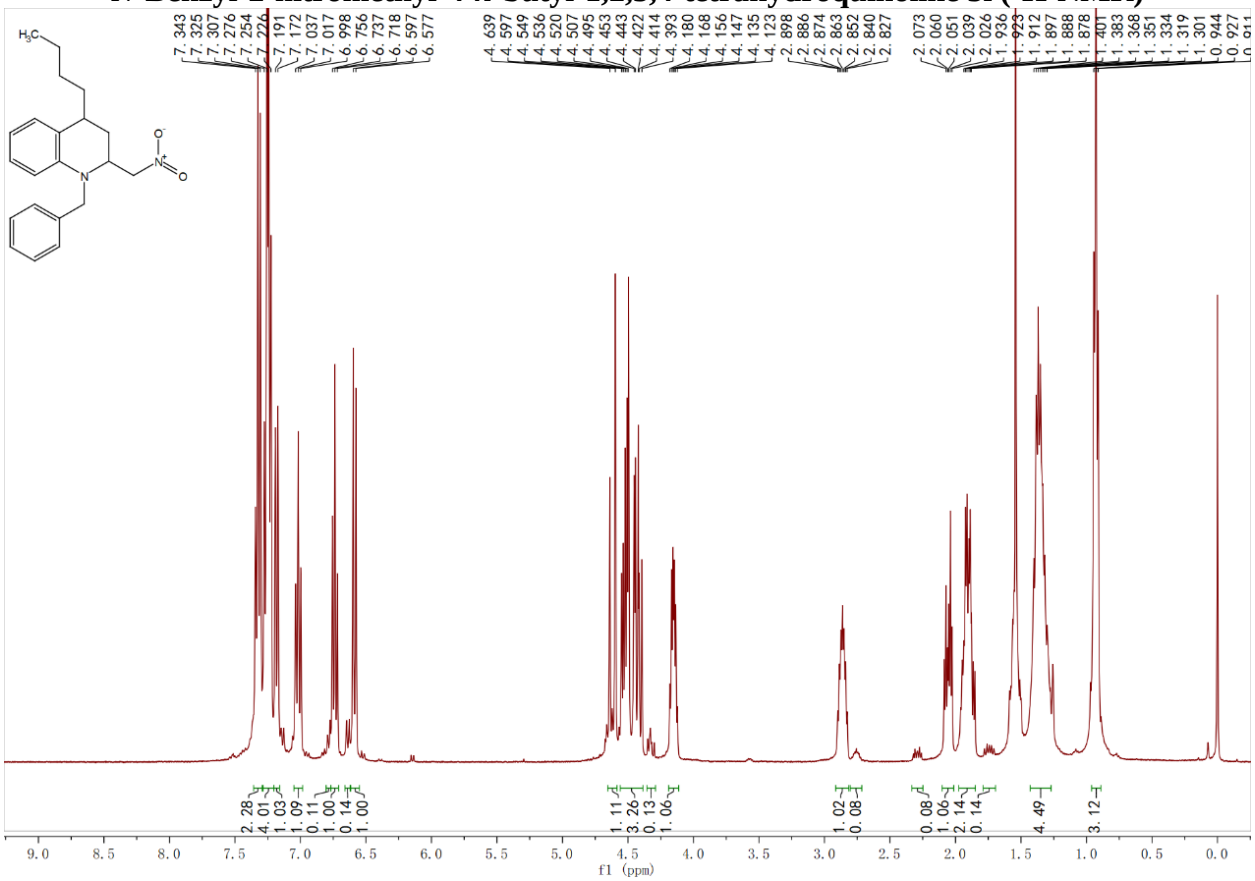
_N_-Benzyl-2-nitromethyl-4-phenyl-1,2,3,4-tetrahydroquinoline 3k (^{1}H-NMR)



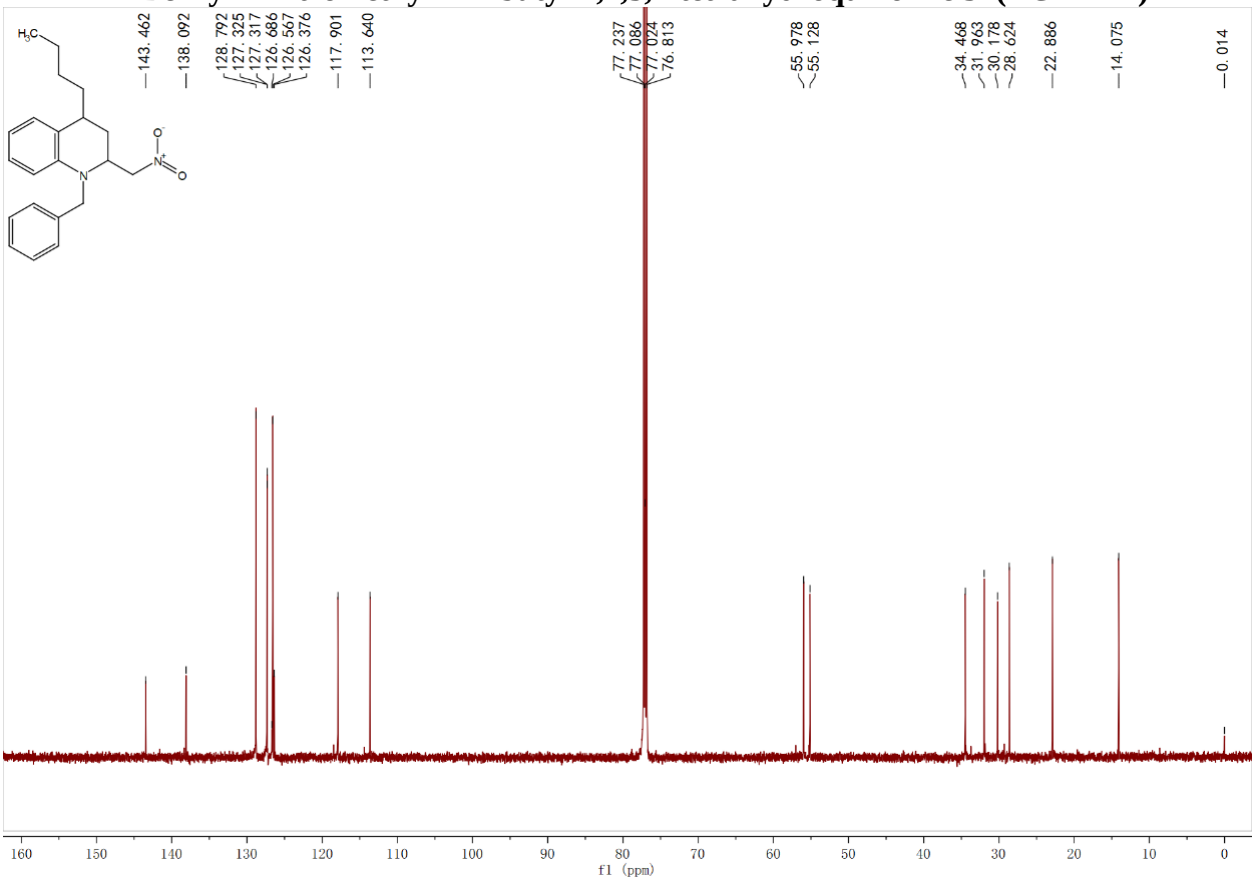
_N_-Benzyl-2-nitromethyl-4-phenyl-1,2,3,4-tetrahydroquinoline 3k (^{13}C-NMR)



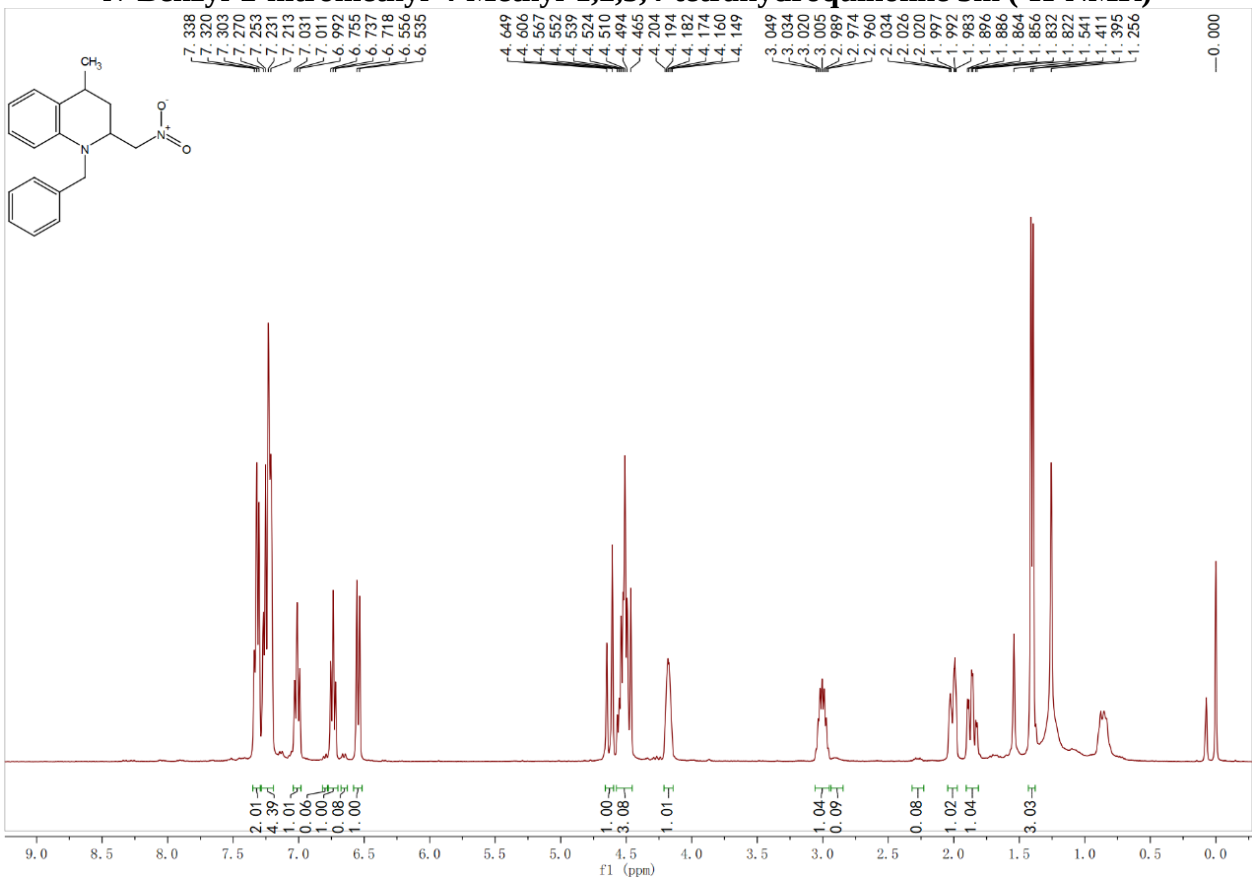
_N_-Benzyl-2-nitromethyl-4-_n_-butyl-1,2,3,4-tetrahydroquinoline 3l (^{1}H-NMR)



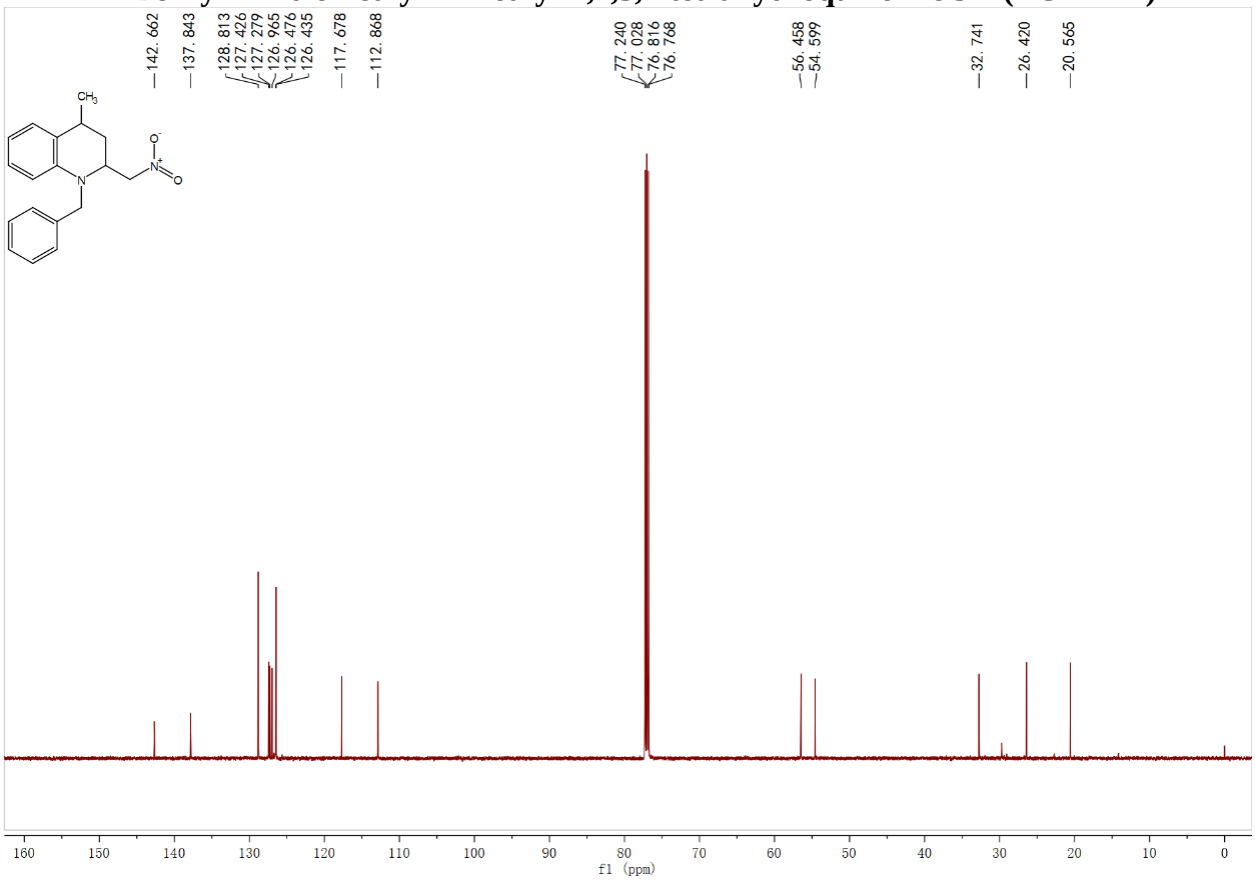
_N_-Benzyl-2-nitromethyl-4-_n_-butyl-1,2,3,4-tetrahydroquinoline 3l (^{13}C-NMR)



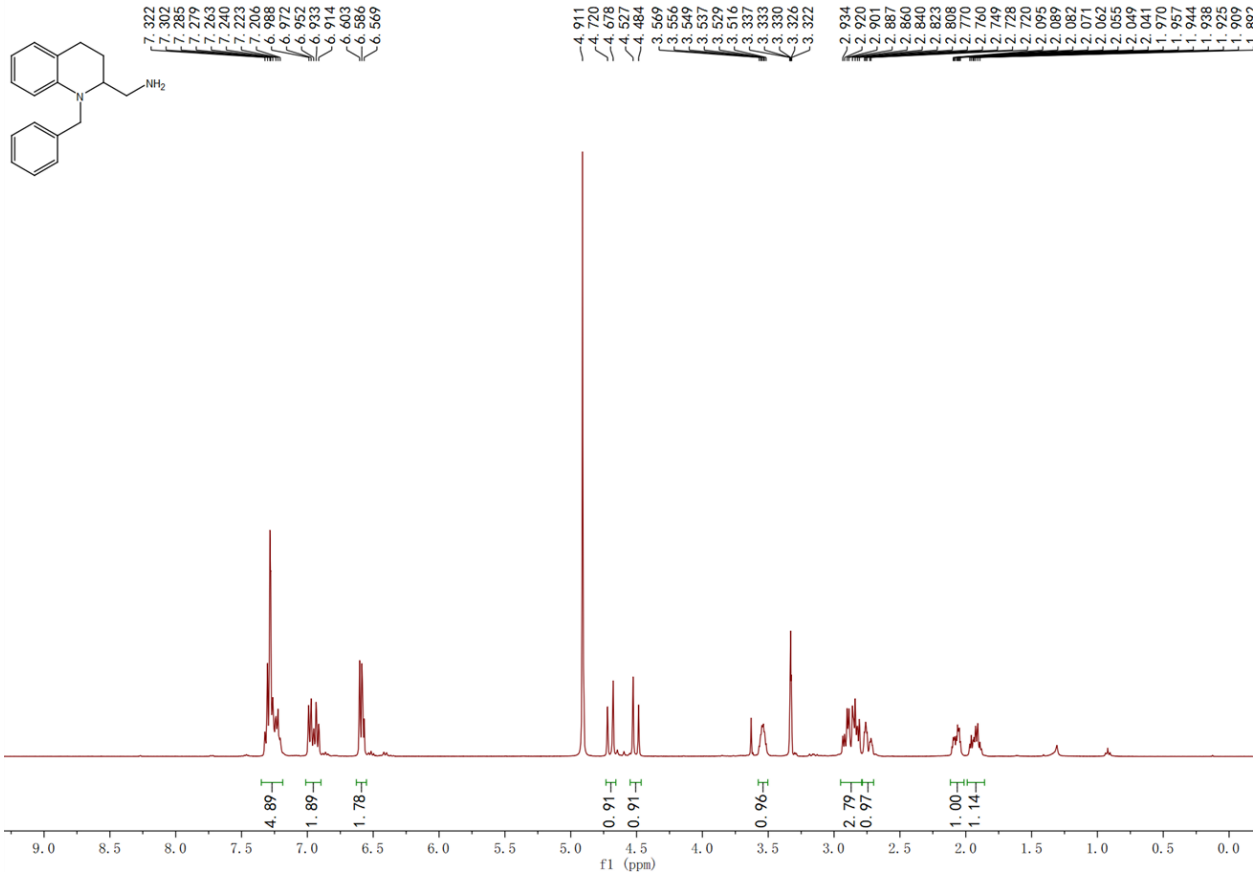
_N_-Benzyl-2-nitromethyl-4-Methyl-1,2,3,4-tetrahydroquinoline 3m (^{1}H-NMR)



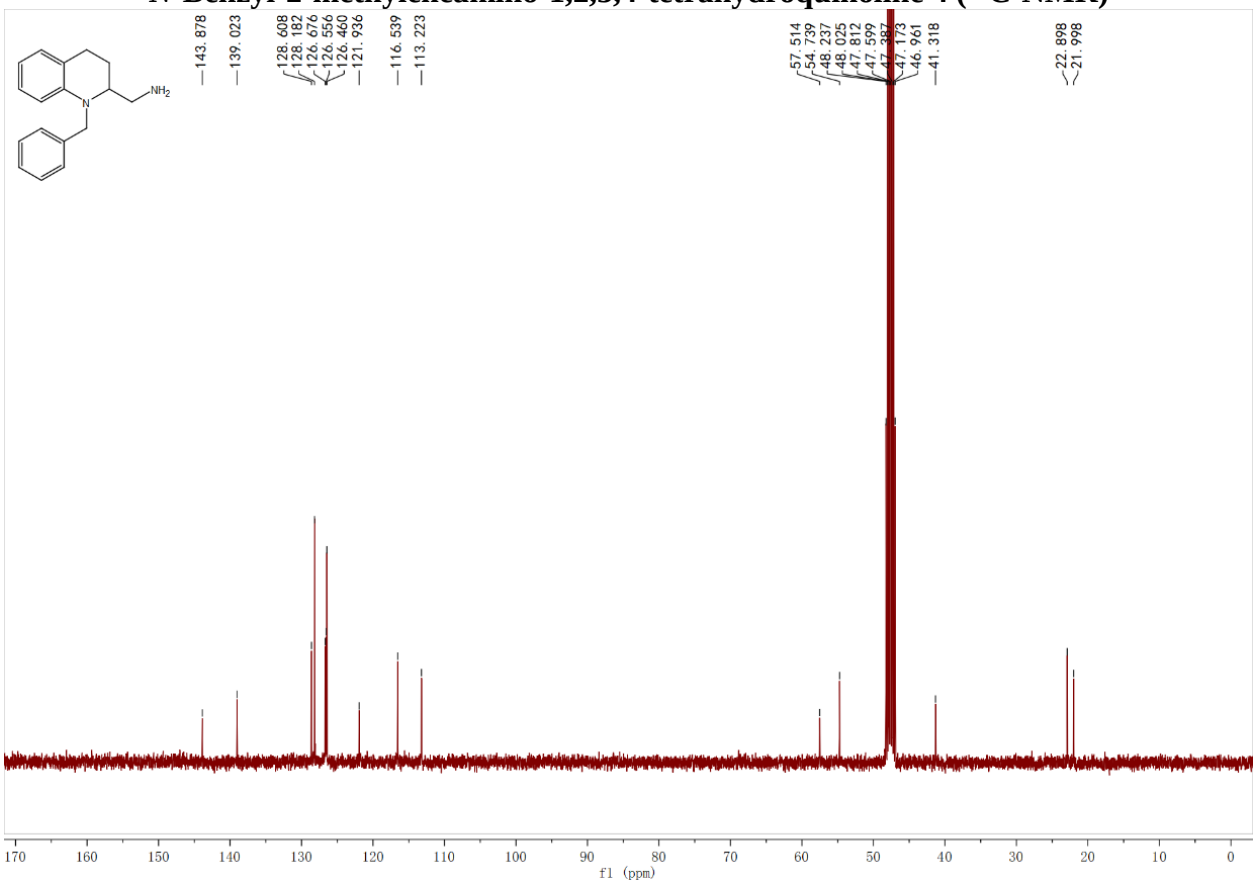
_N_-Benzyl-2-nitromethyl-4-Methyl-1,2,3,4-tetrahydroquinoline 3m (^{13}C-NMR)



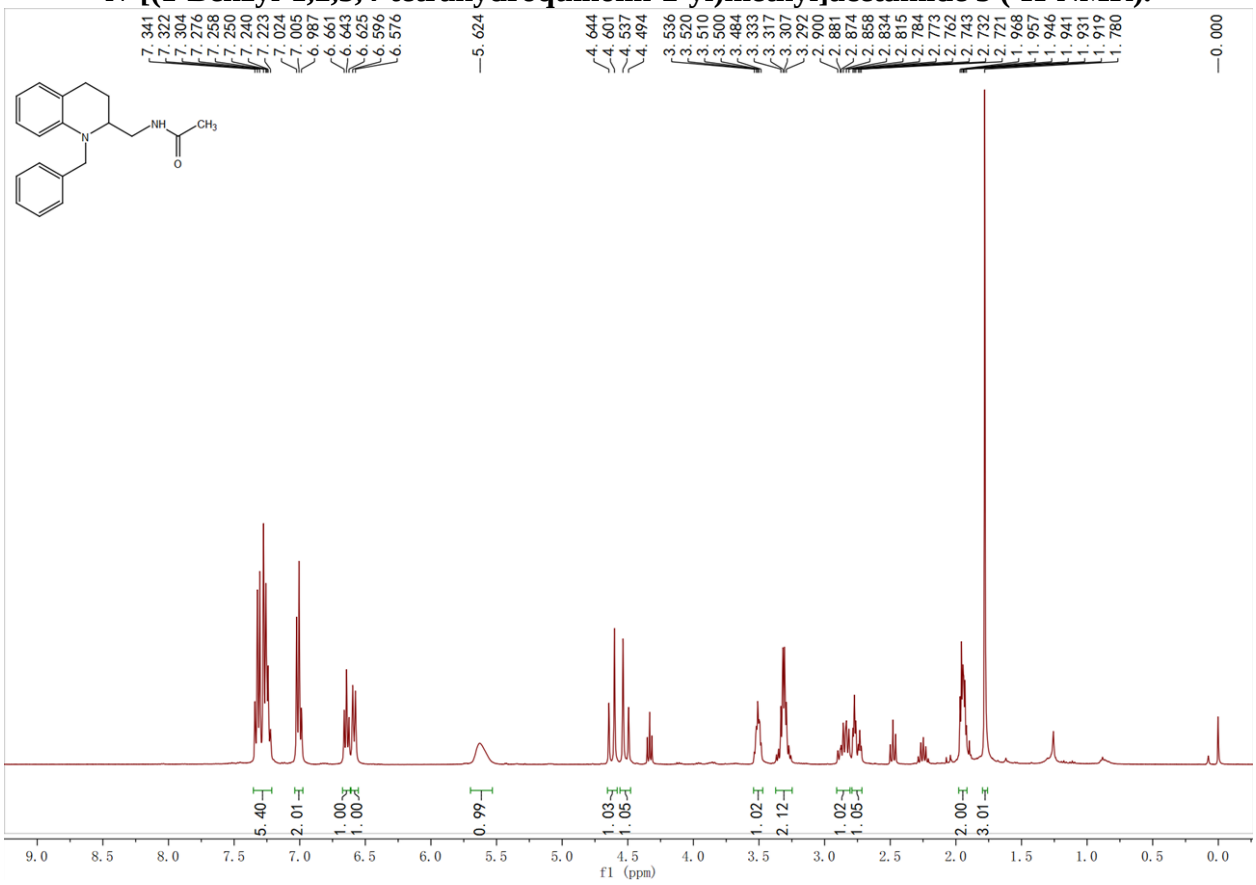
_N_-Benzyl-2-methyleneamino-1,2,3,4-tetrahydroquinoline 4 (^{1}H-NMR)



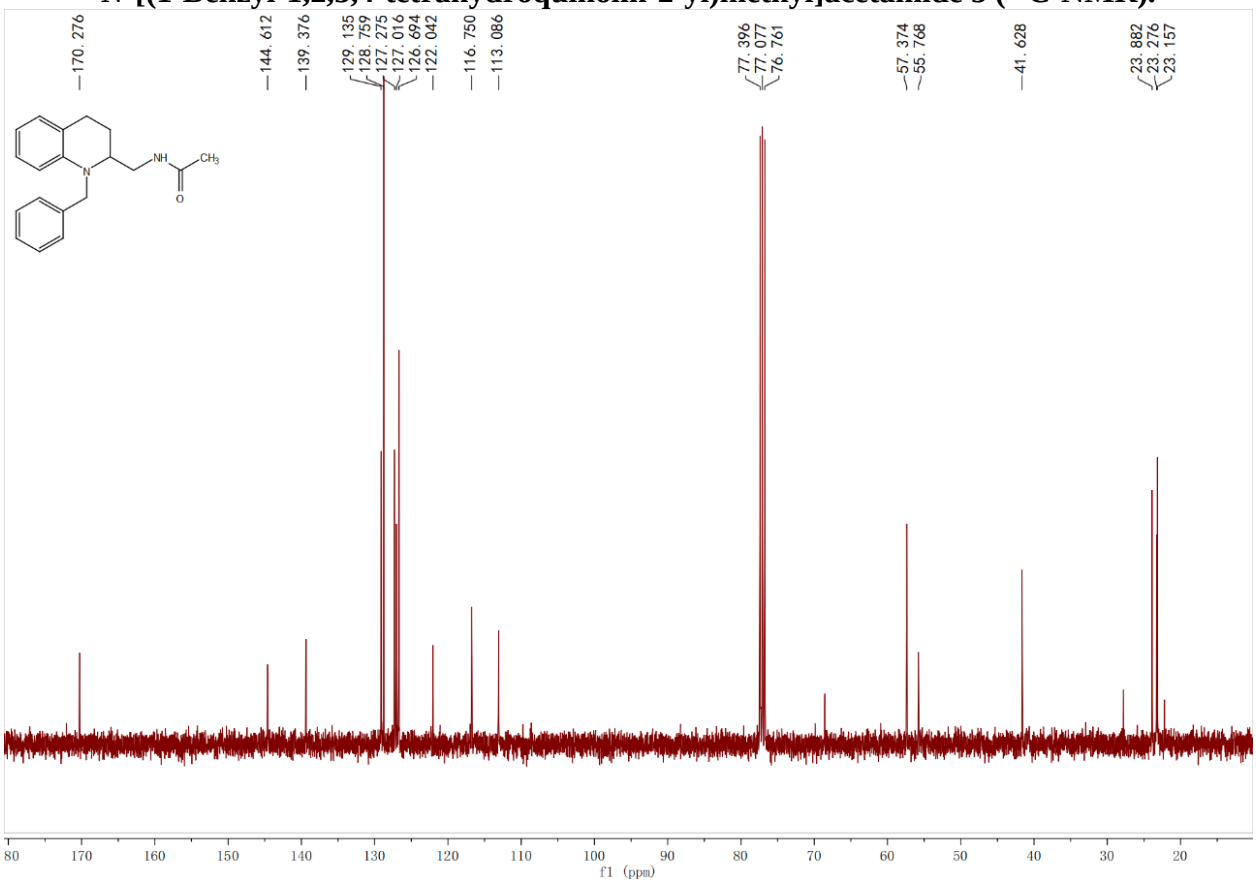
_N_-Benzyl-2-methyleneamino-1,2,3,4-tetrahydroquinoline 4 (^{13}C-NMR)



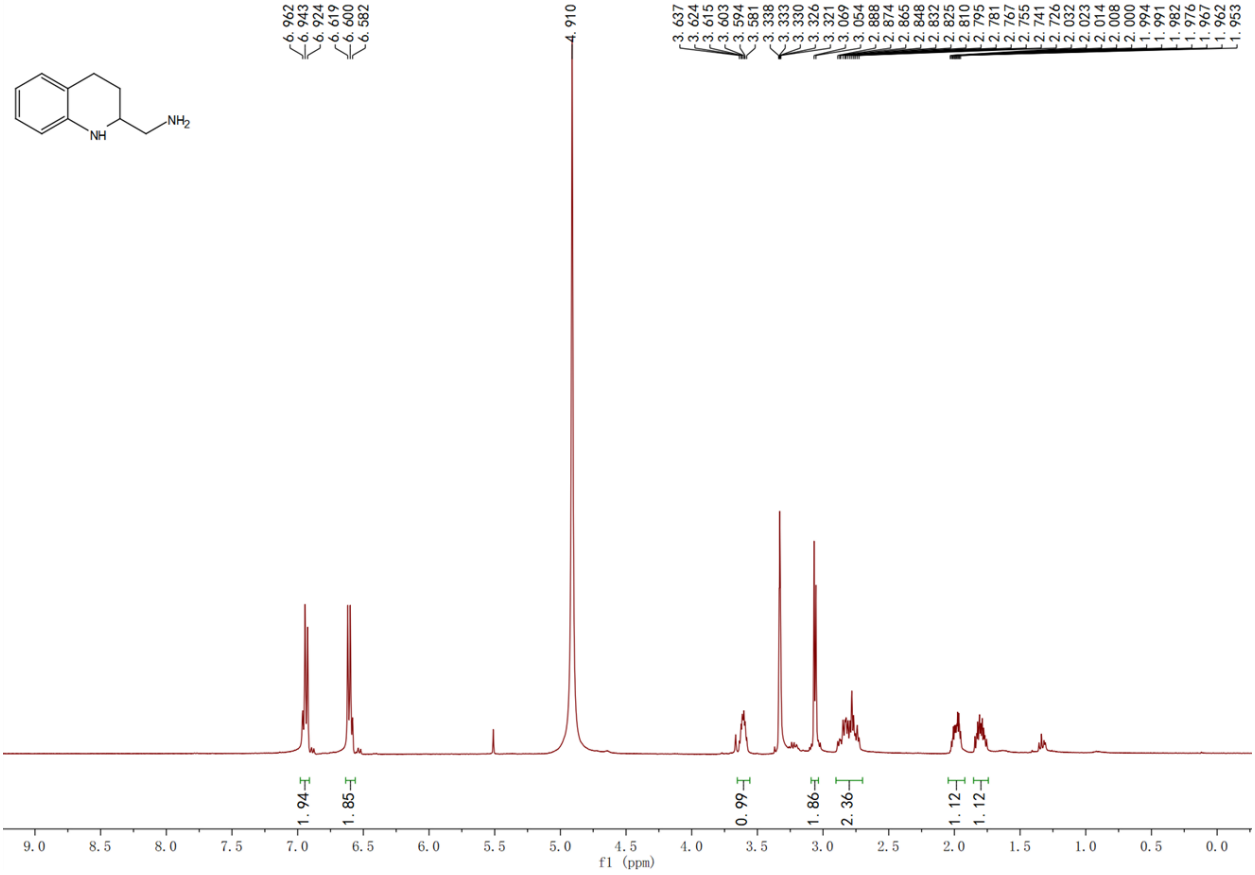
***N*-[(1-Benzyl-1,2,3,4-tetrahydroquinolin-2-yl)methyl]acetamide 5 (^{1}H-NMR).**



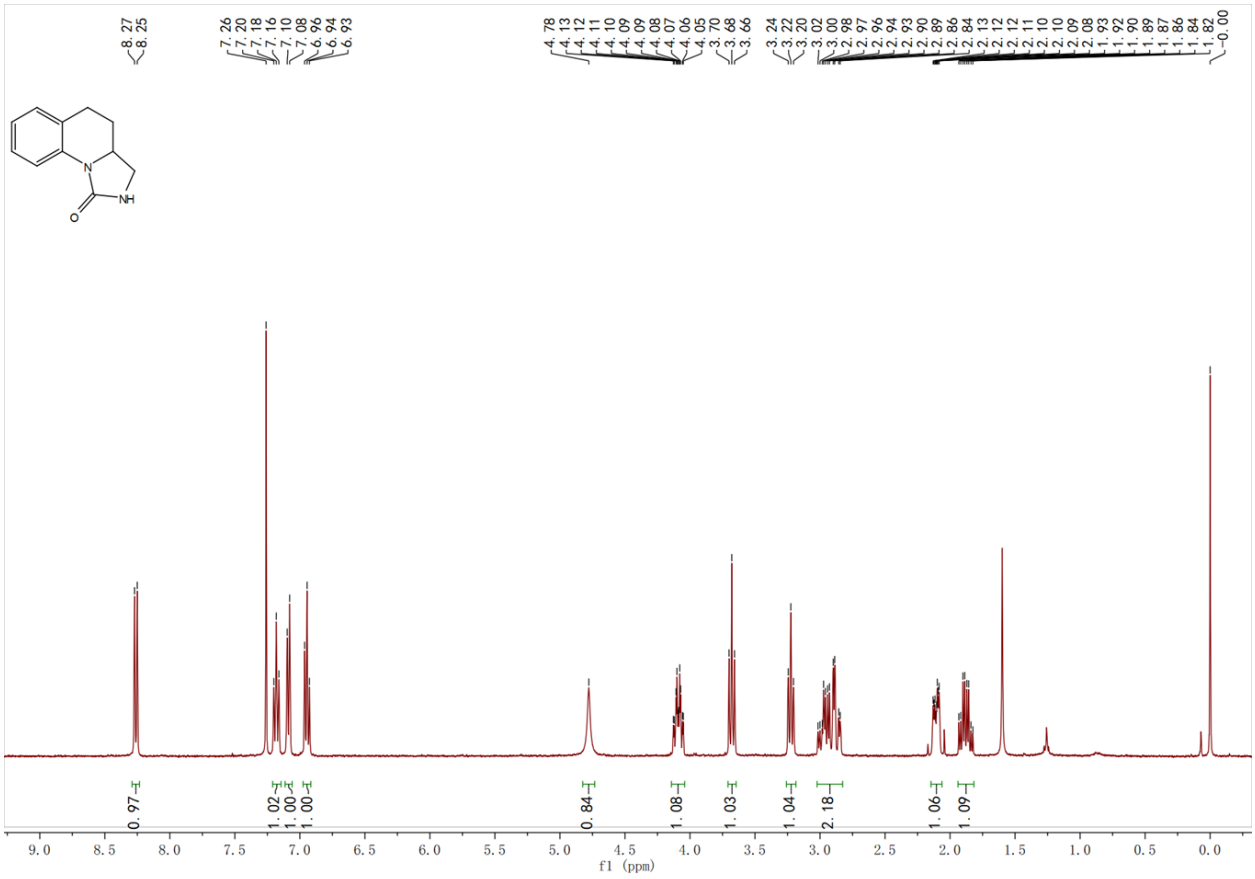
***N*-[(1-Benzyl-1,2,3,4-tetrahydroquinolin-2-yl)methyl]acetamide 5 (^{13}C-NMR).**



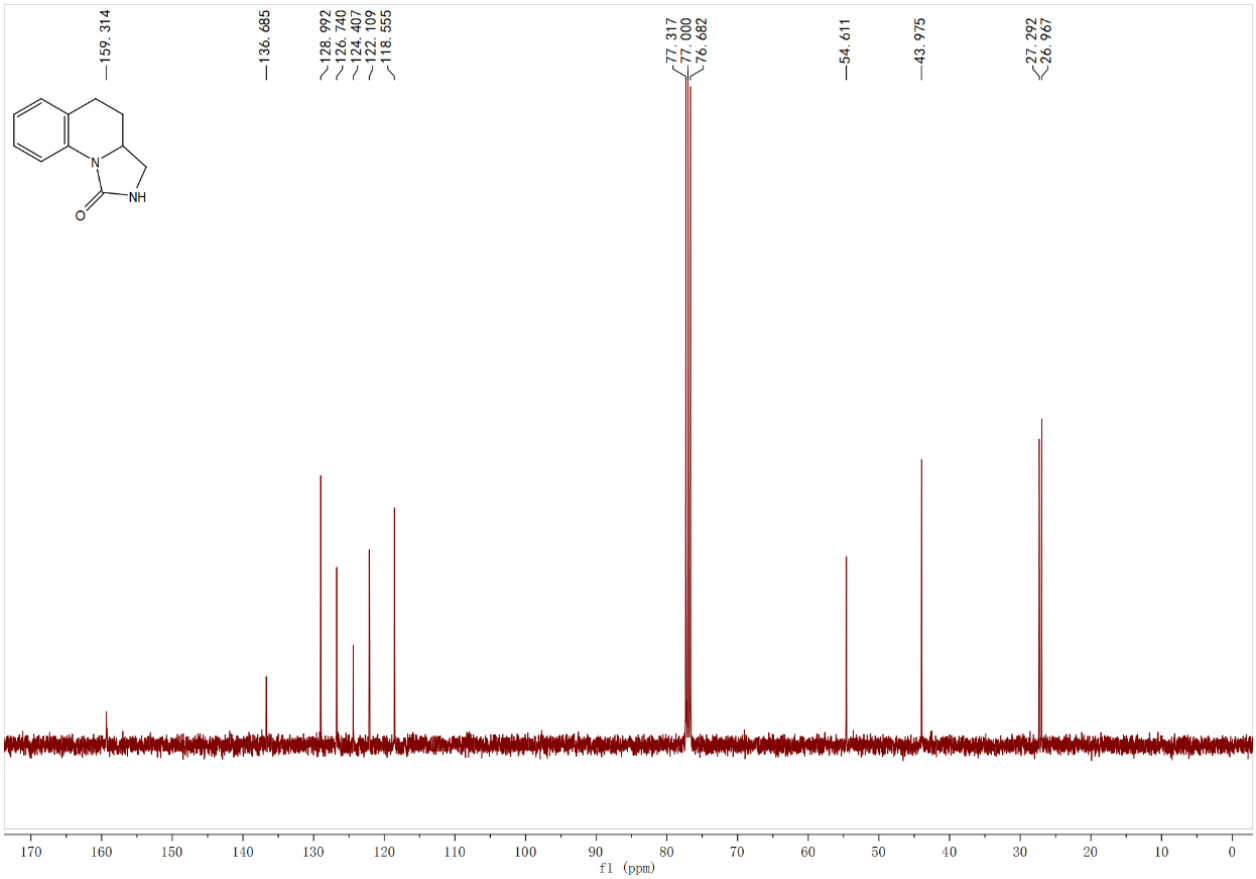
2-Methyleneamino-1,2,3,4-tetrahydroquinoline 6 (^{1}H-NMR)



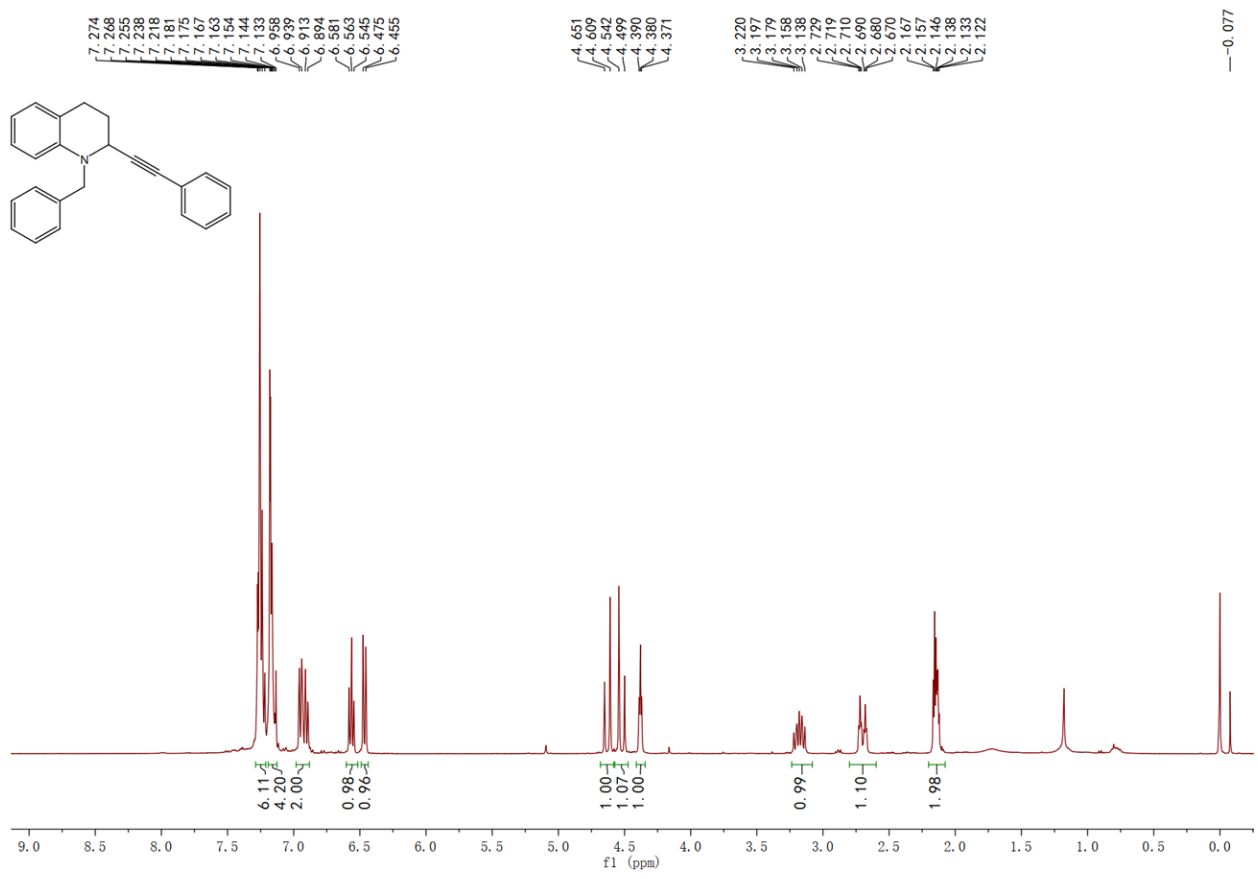
3,3a,4,5-tetrahydroimidazo[1,5-a]quinolin-1(2H)-one 7 (^{1}H-NMR)



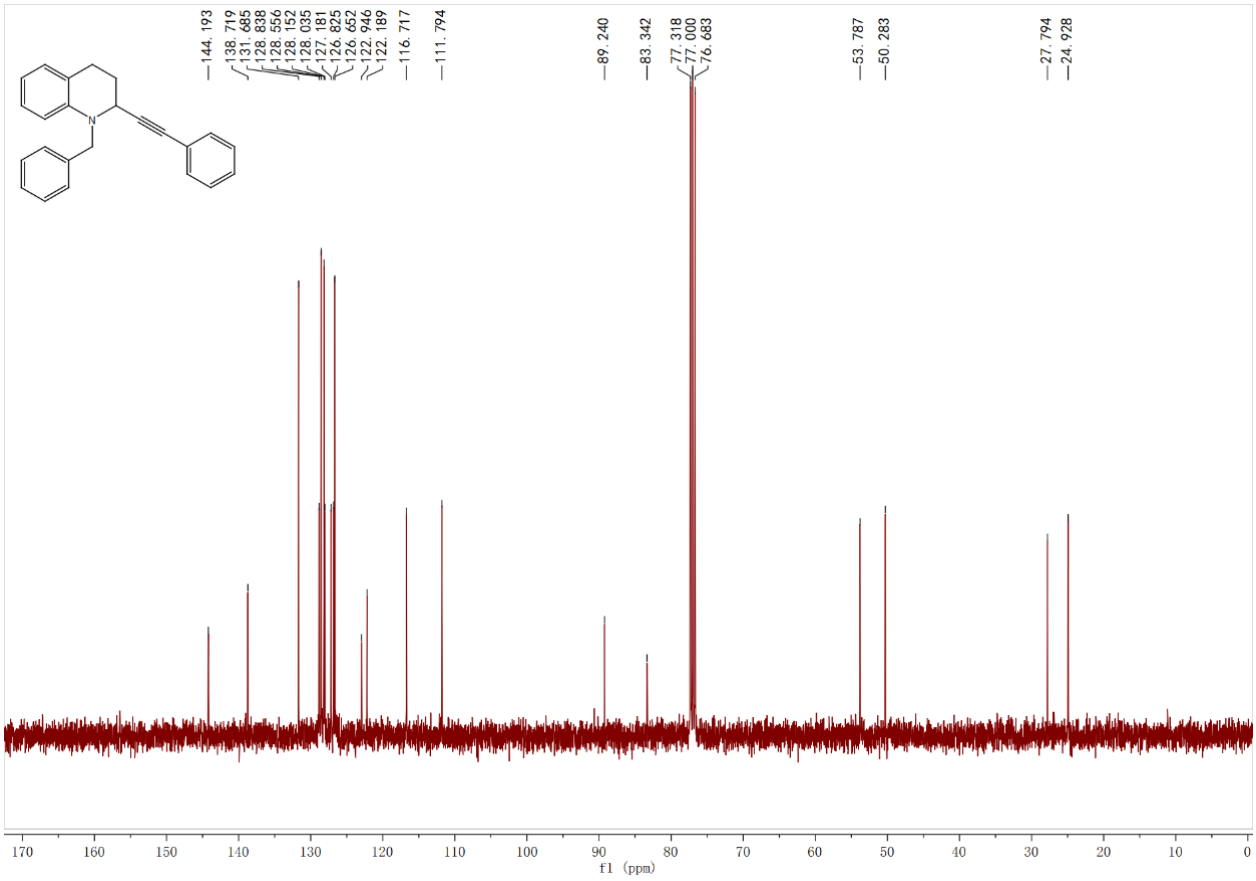
3,3a,4,5-tetrahydroimidazo[1,5-a]quinolin-1(2H)-one 7 (^{13}C-NMR)



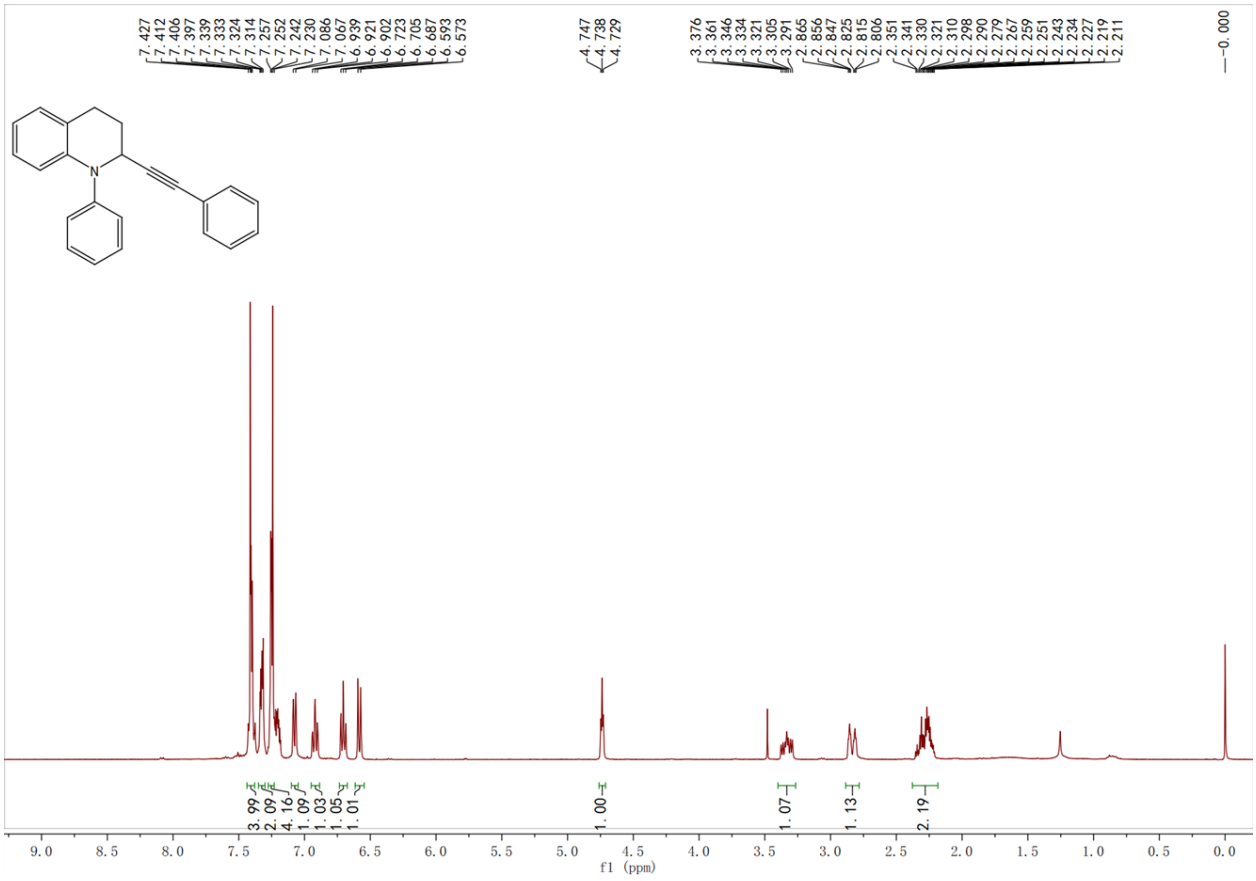
***N*-Benzyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9aa (^{1}H-NMR)**



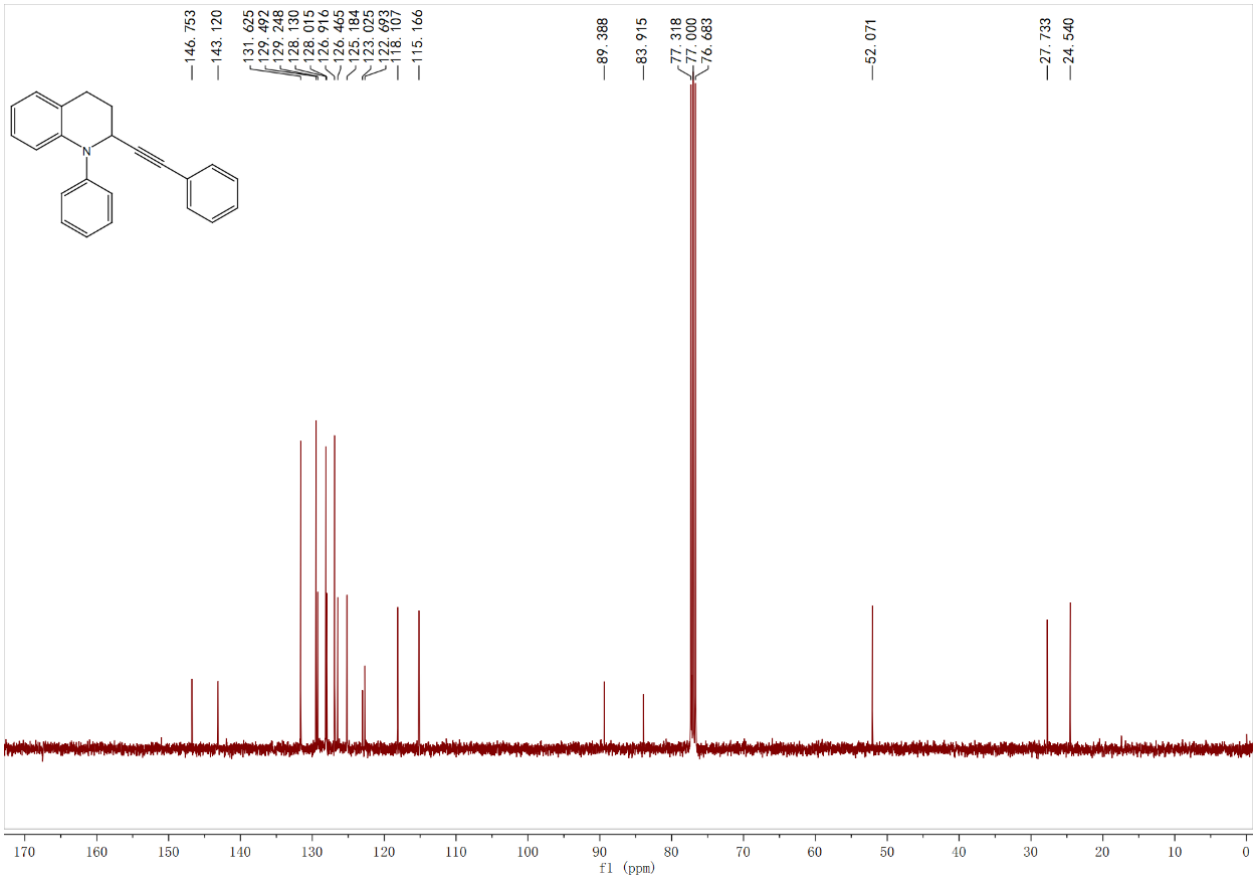
_N_-Benzyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9aa (^{13}C-NMR)



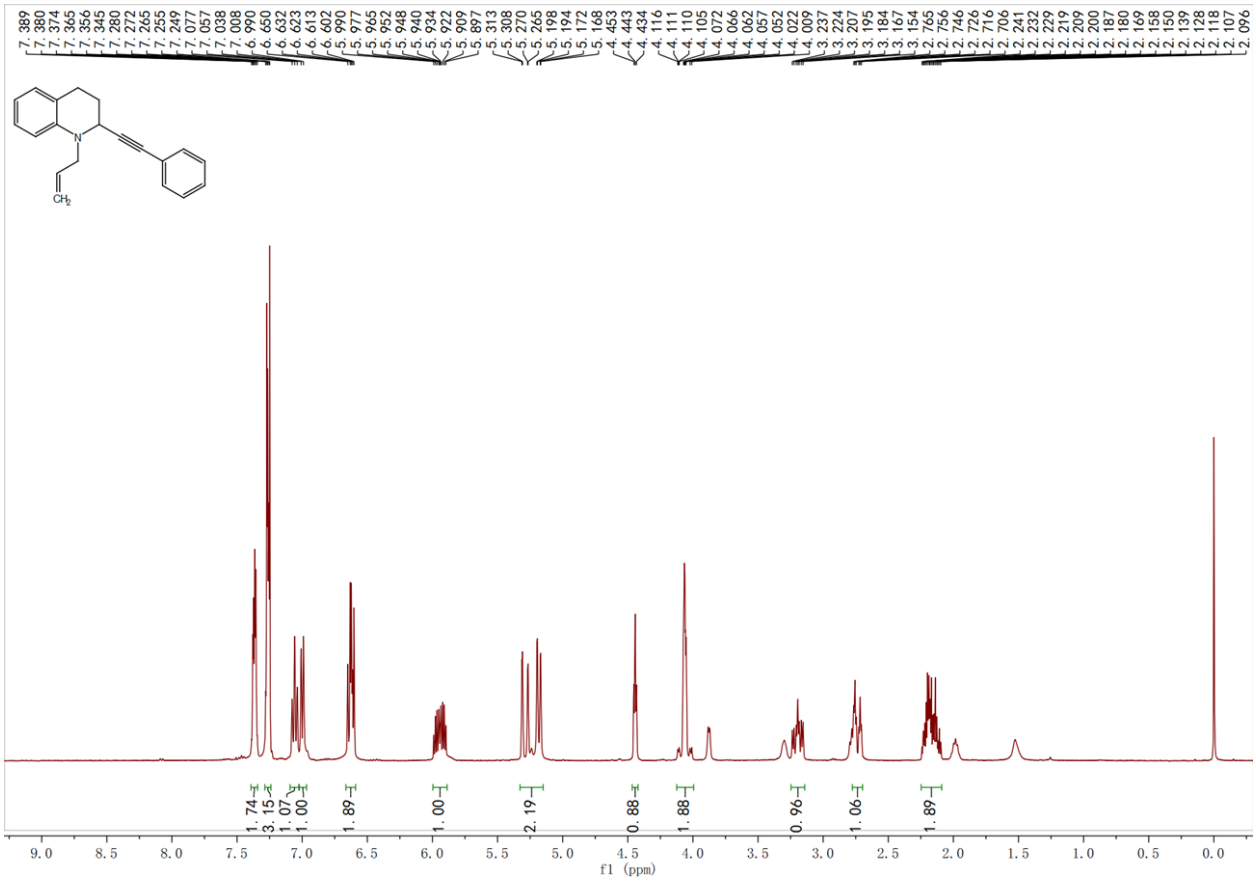
_N_-Phenyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9ba (^{1}H-NMR)



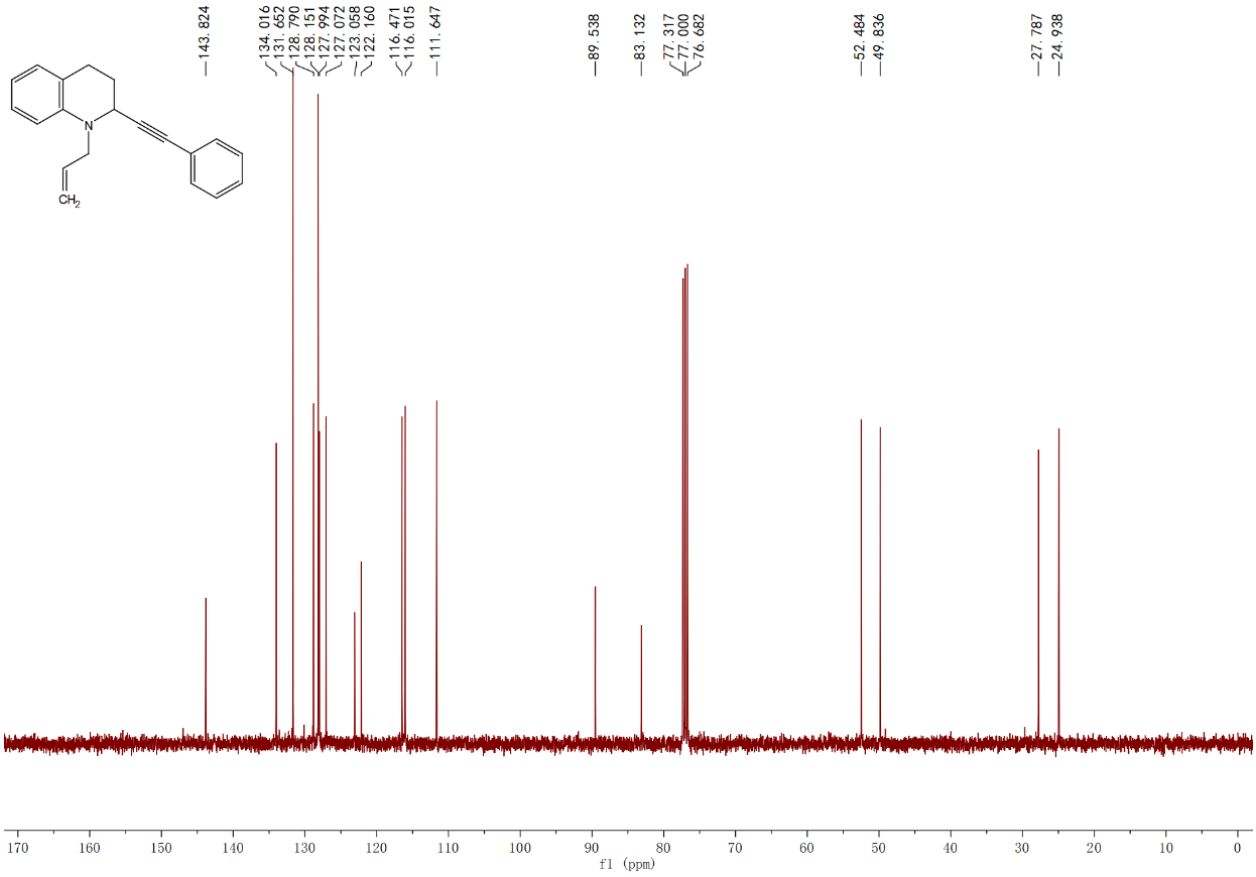
_N_-Phenyl -2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9ba (^{13}C-NMR)



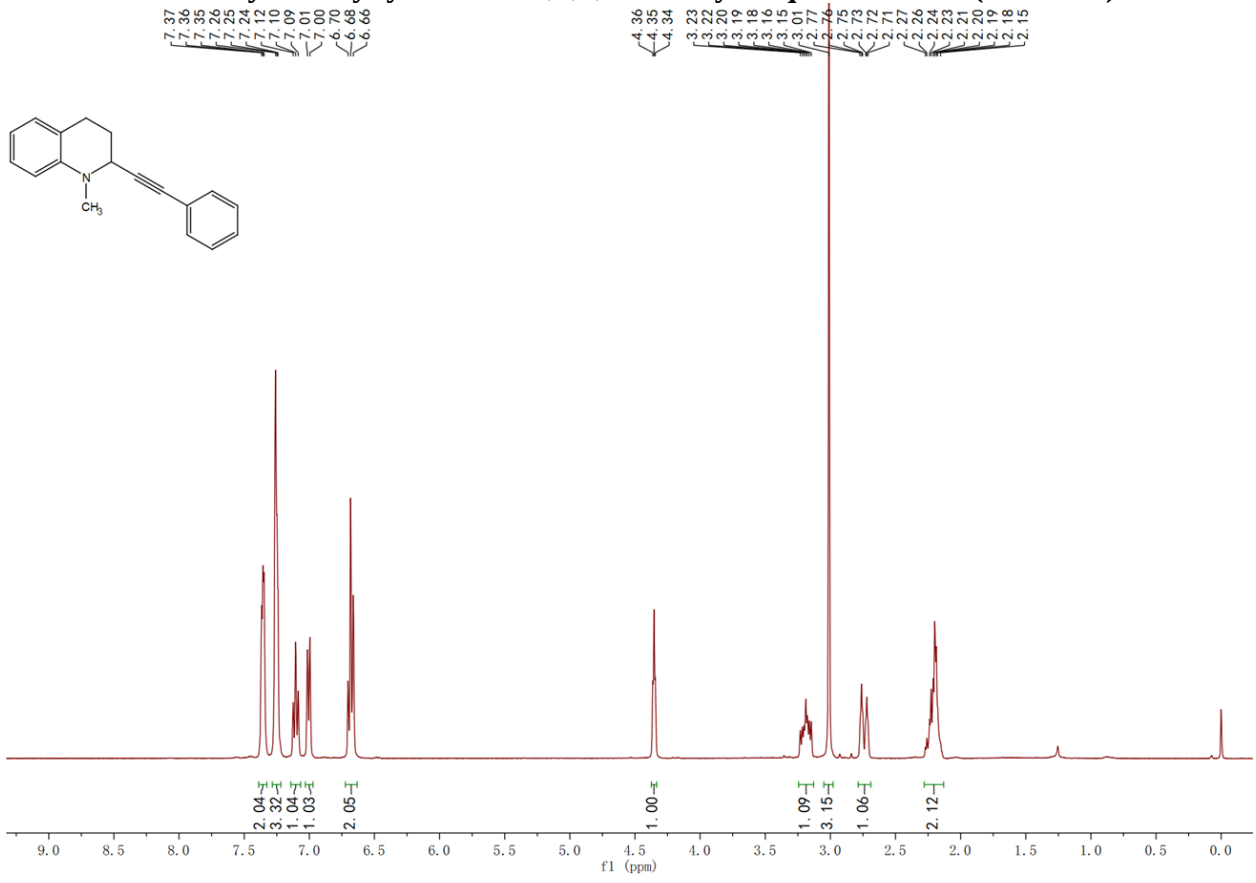
_N_-Allyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9ca (^{1}H-NMR)



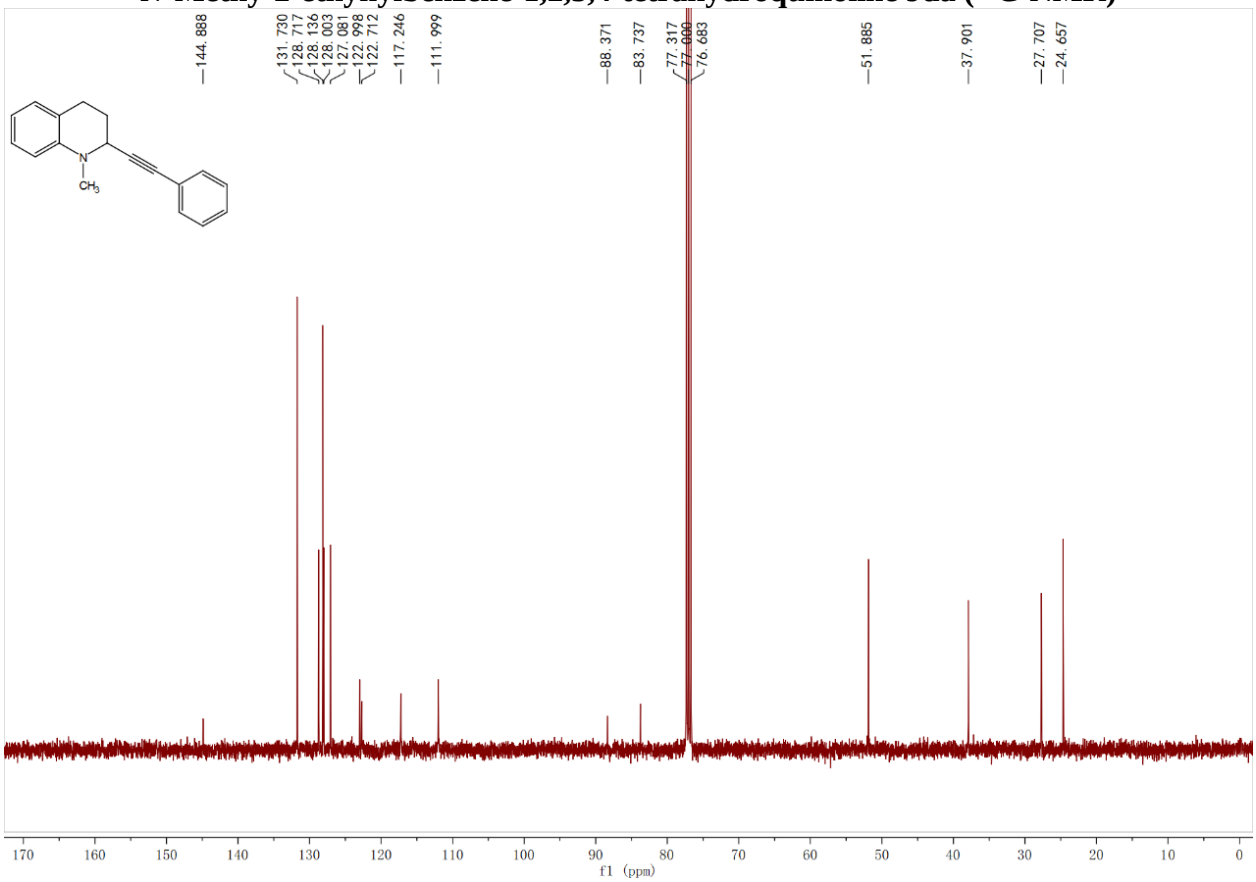
N-Allyl -2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9ca (^{13}C-NMR)



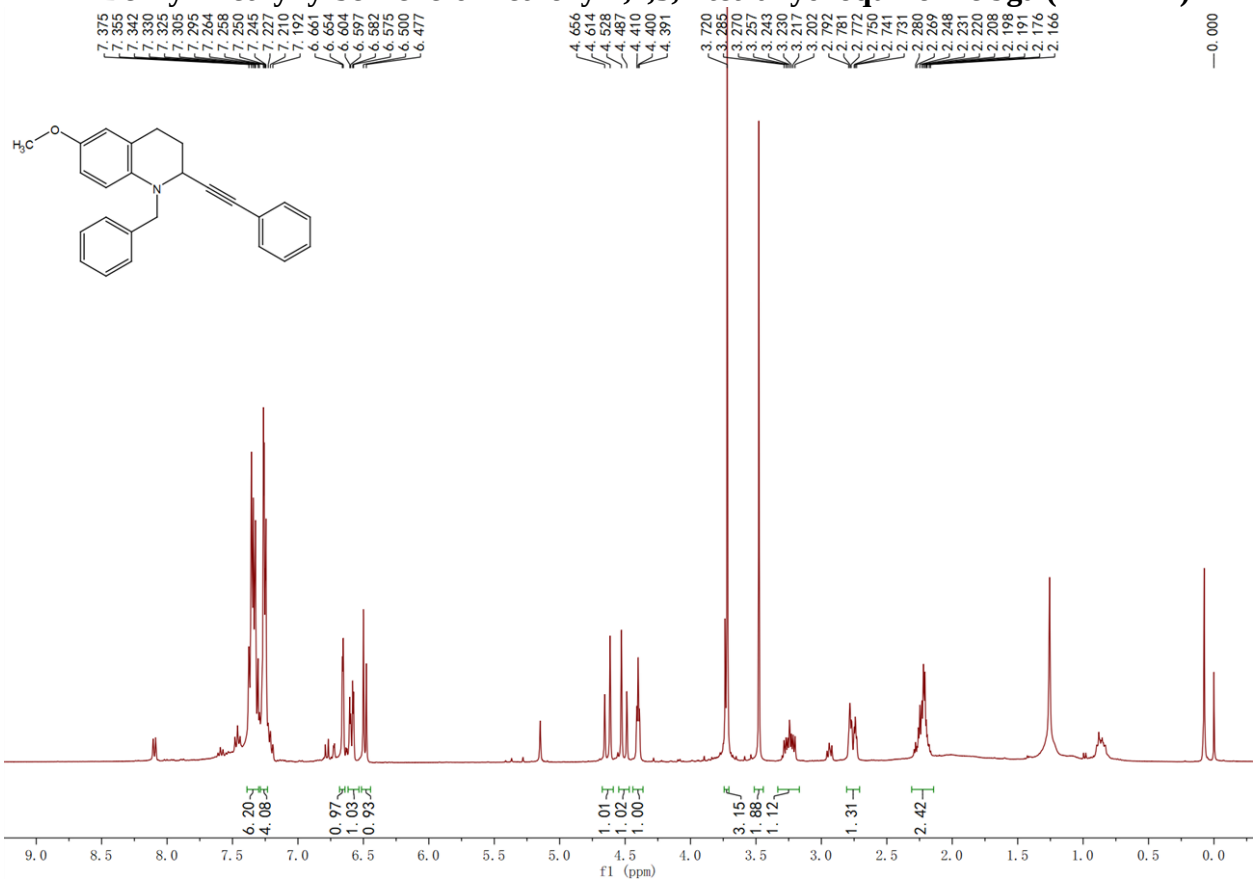
N-Methyl-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9da (^{1}H-NMR)



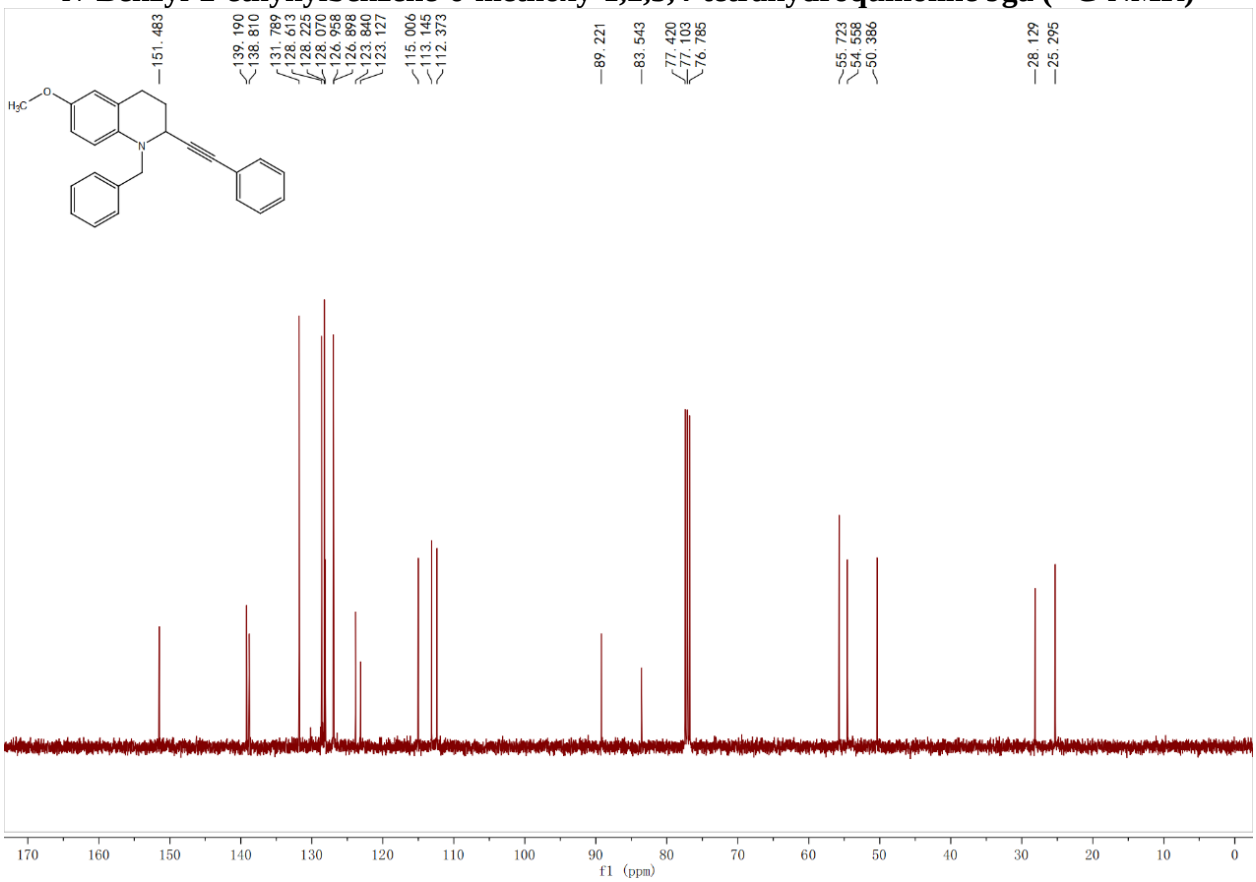
_N_-Methy-2-ethynylbenzene-1,2,3,4-tetrahydroquinoline 9da (^{13}C-NMR)



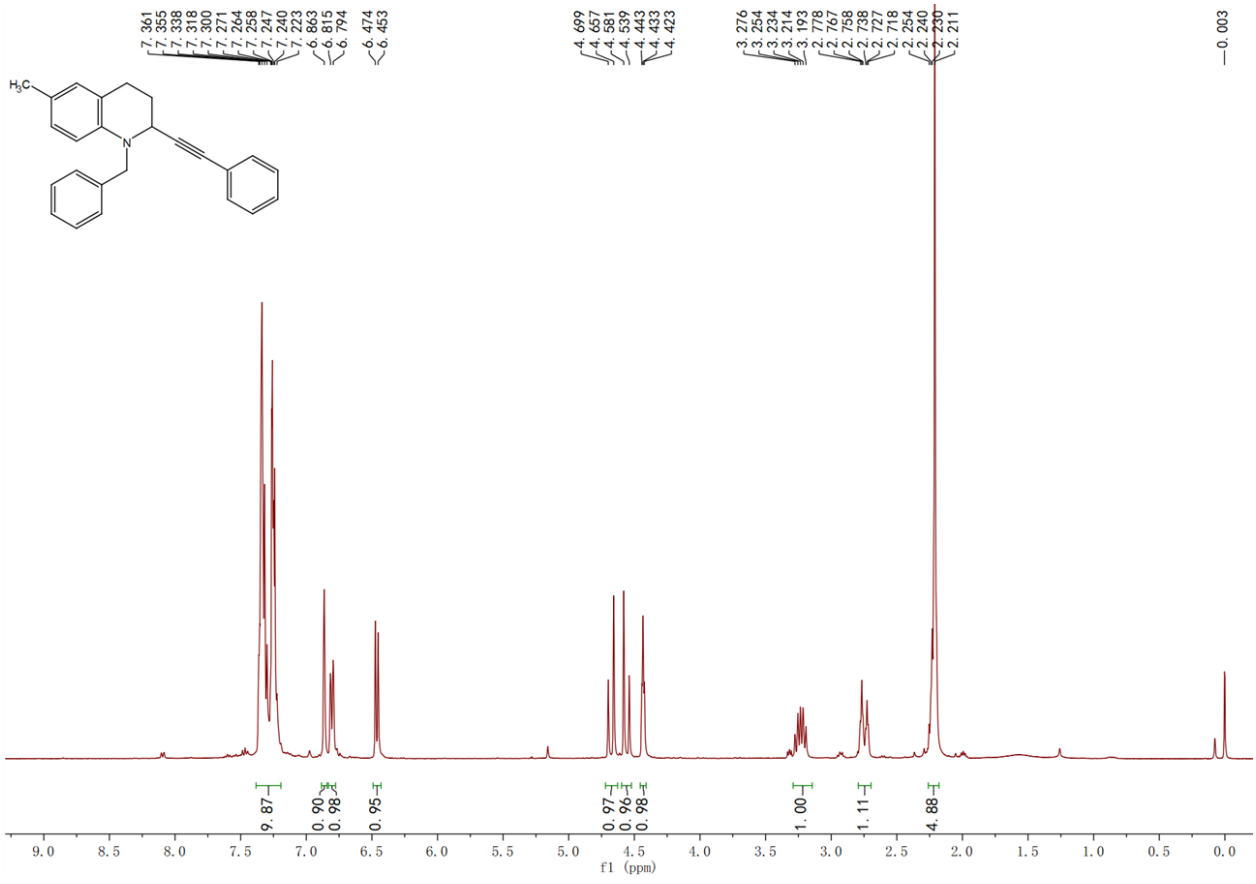
_N_-Benzyl-2-ethynylbenzene-6-methoxy-1,2,3,4-tetrahydroquinoline 9ga (^{1}H-NMR)



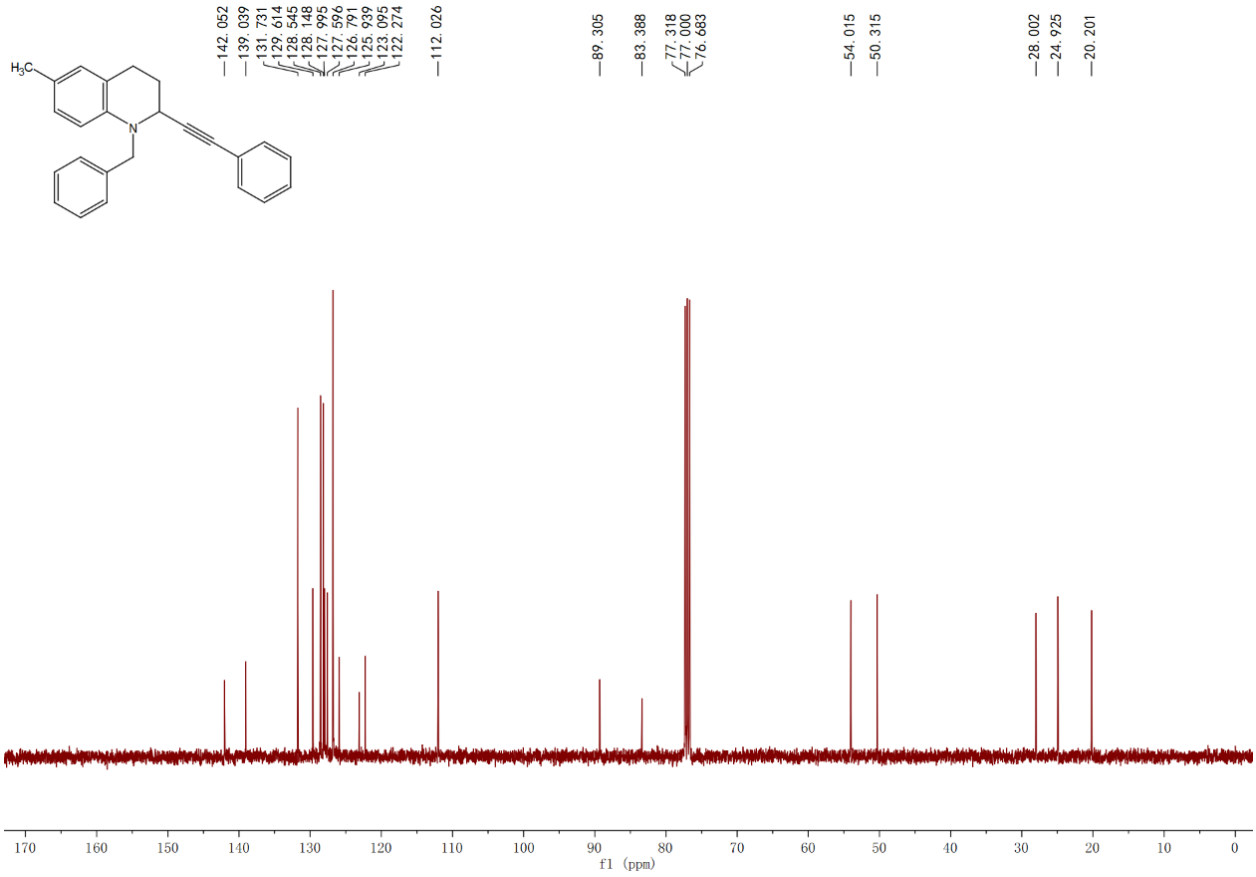
_N_-Benzyl-2-ethynylbenzene-6-methoxy-1,2,3,4-tetrahydroquinoline 9ga (^{13}C-NMR)



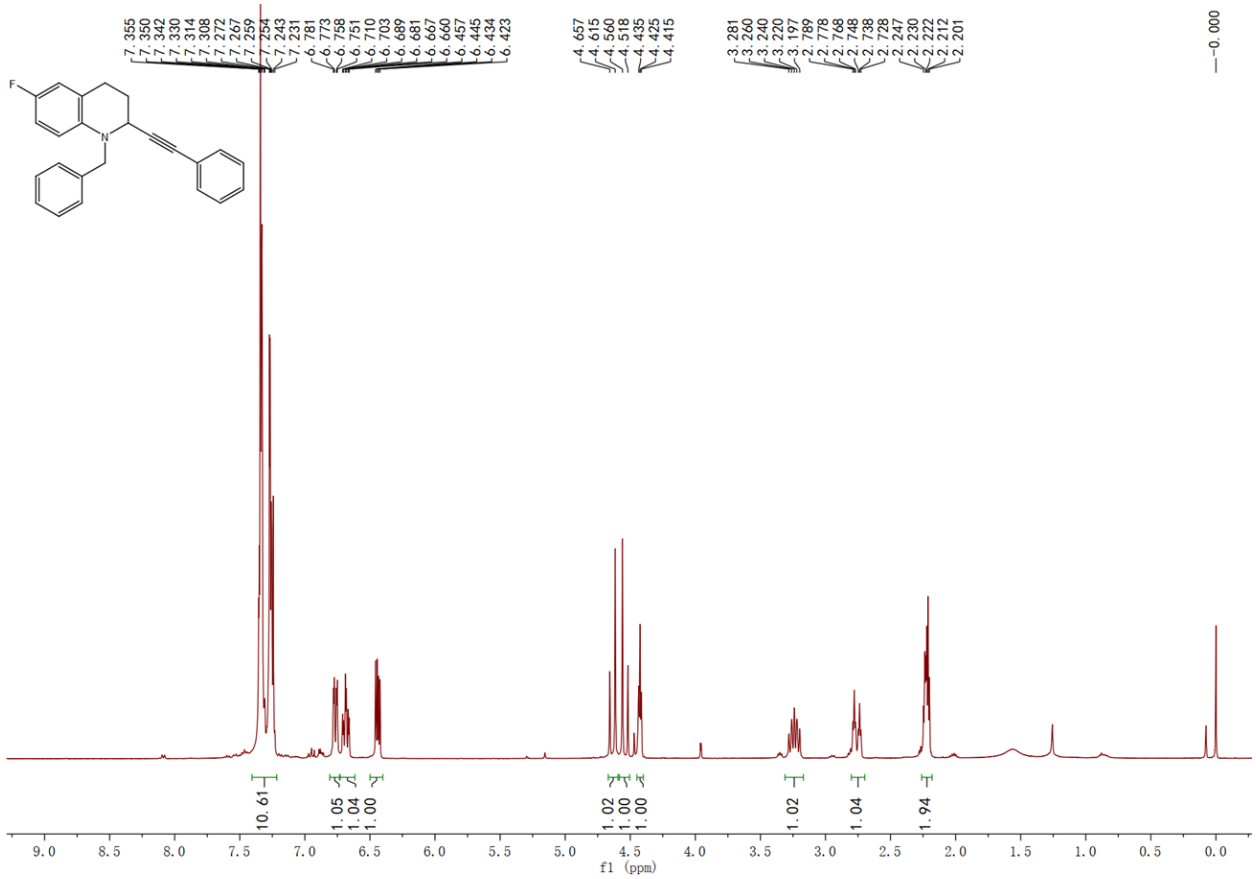
_N_-Benzyl-2-ethynylbenzene-6-methyl-1,2,3,4-tetrahydroquinoline 9ha (^{1}H-NMR)



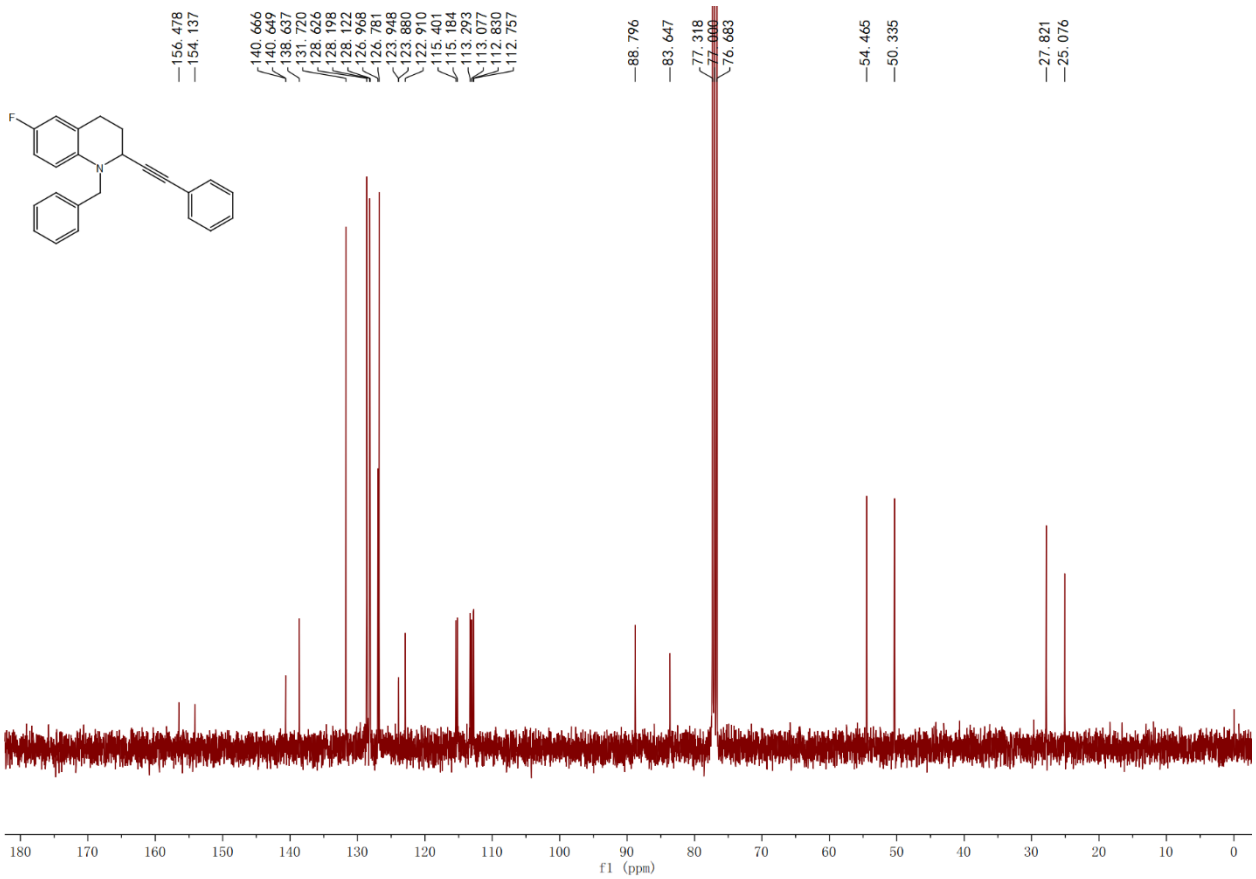
_N_-Benzyl-2-ethynylbenzene-6-methyl-1,2,3,4-tetrahydroquinoline 9ha (^{13}C-NMR)



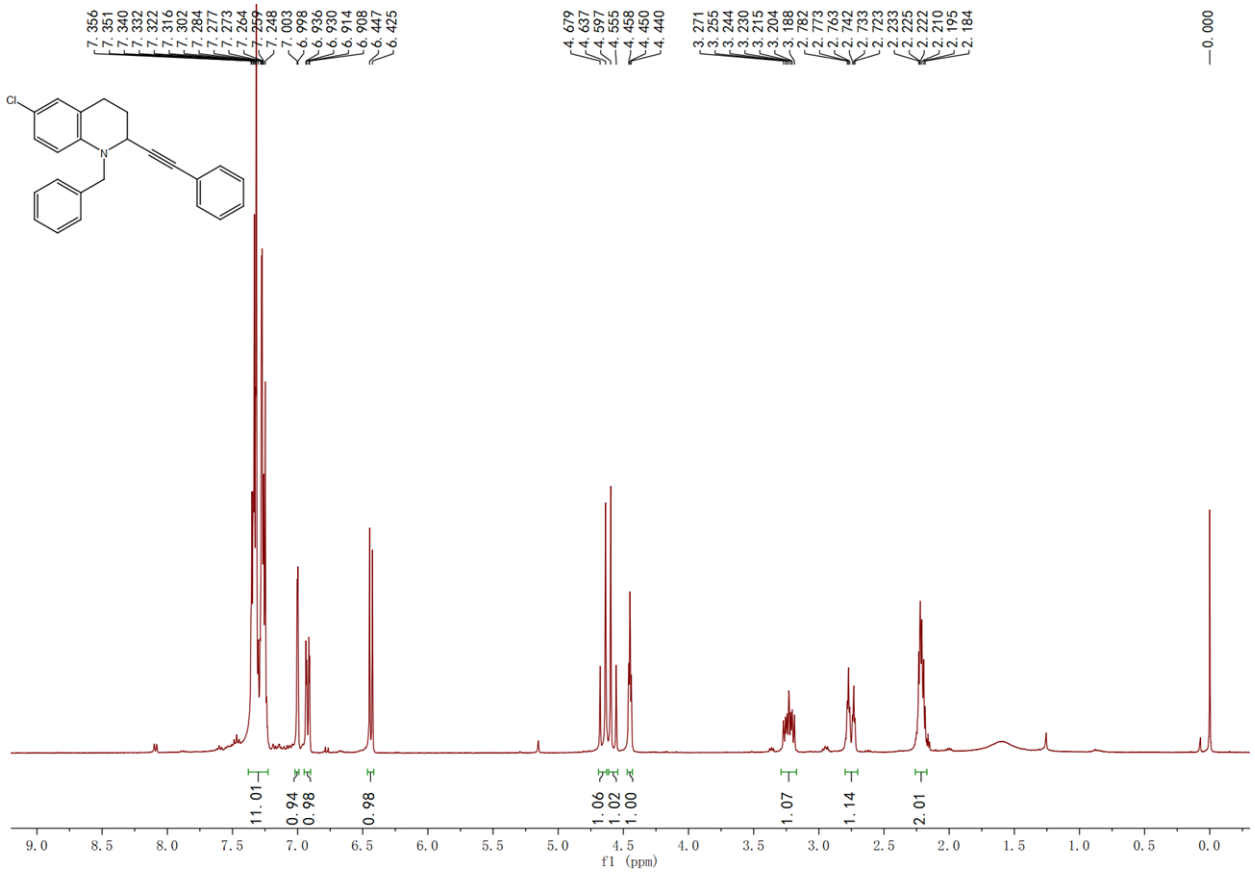
_N_-Benzyl-2-ethynylbenzene-6-fluoro-1,2,3,4-tetrahydroquinoline 9ia (^{1}H-NMR)



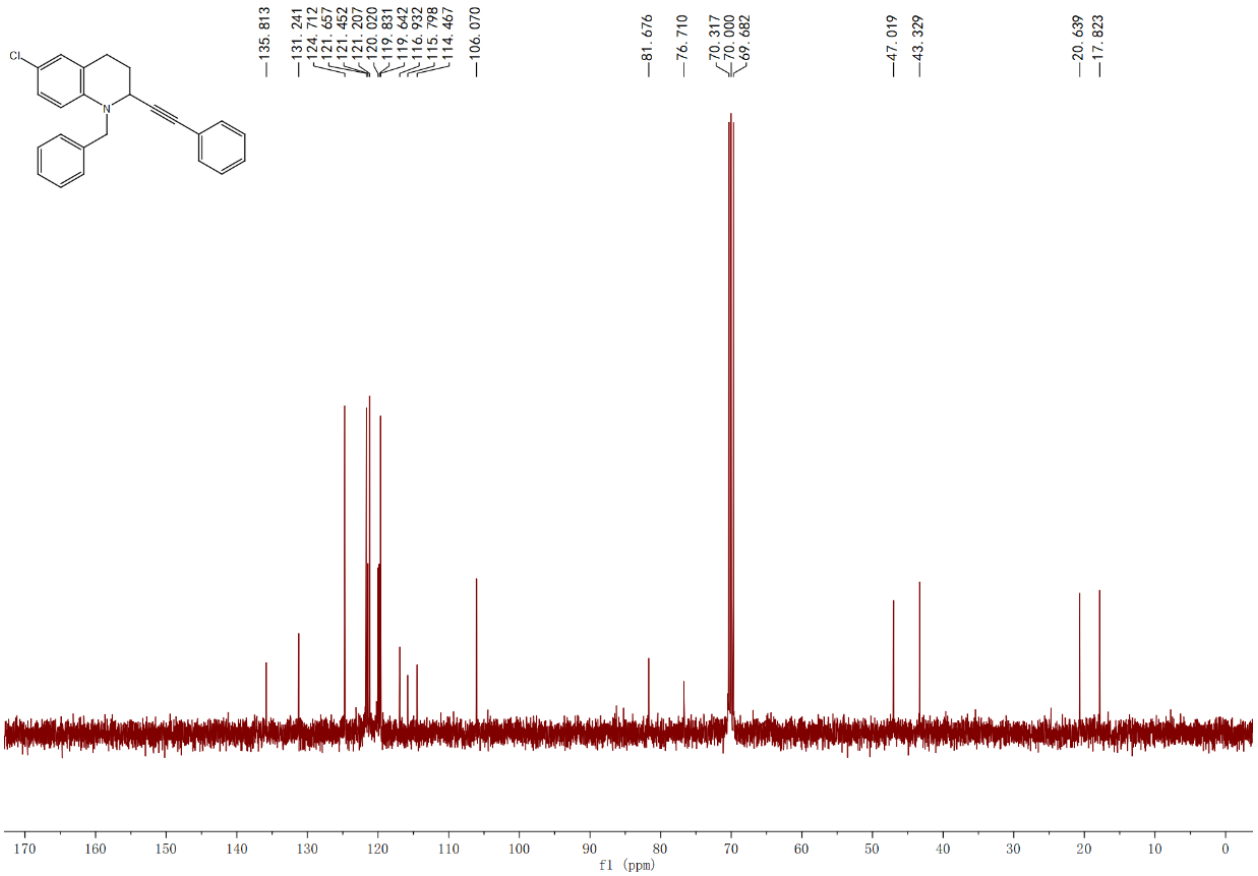
_N_-Benzyl-2-ethynylbenzene-6-fluoro-1,2,3,4-tetrahydroquinoline 9ia (^{13}C-NMR)



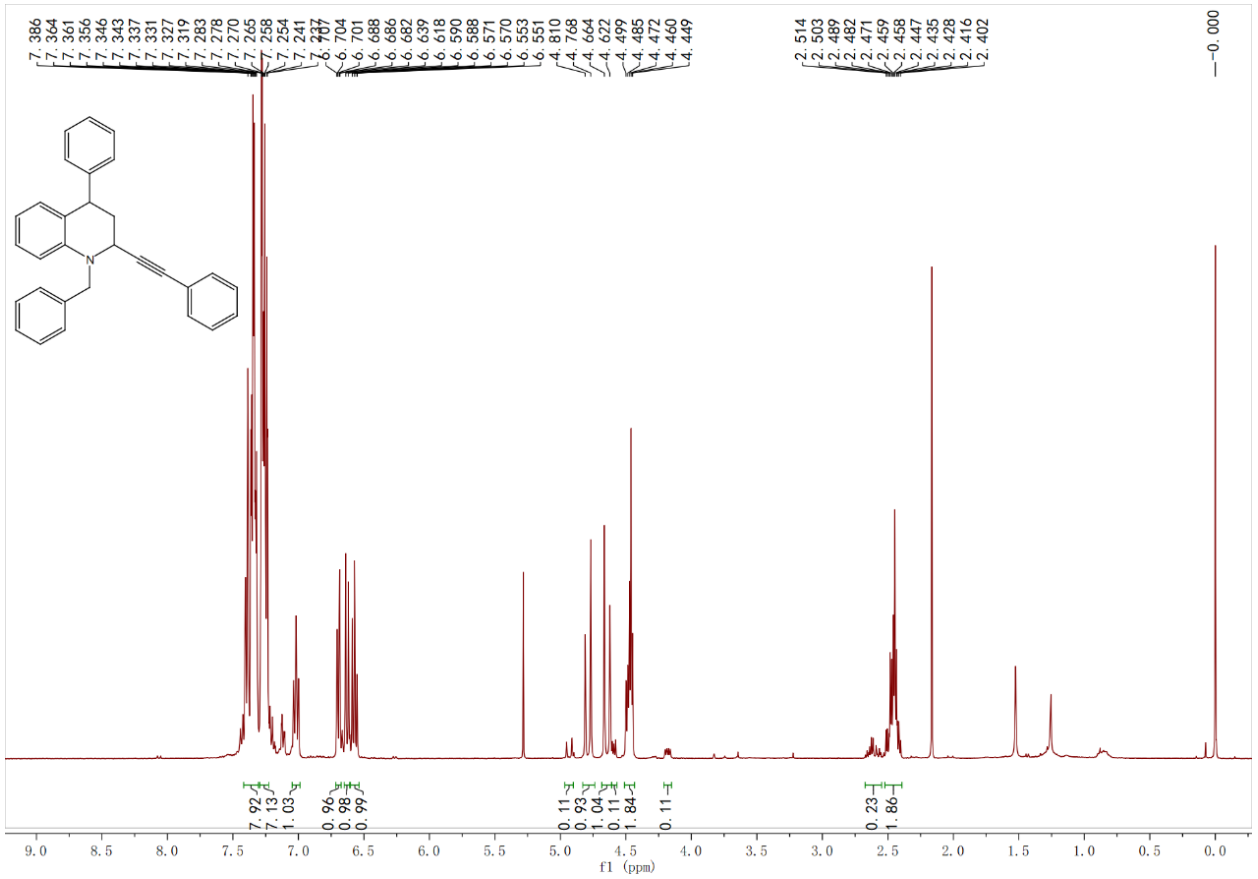
***N*-Benzyl-2-ethynylbenzene-6-chloro-1,2,3,4-tetrahydroquinoline 9ja (^{1}H-NMR)**



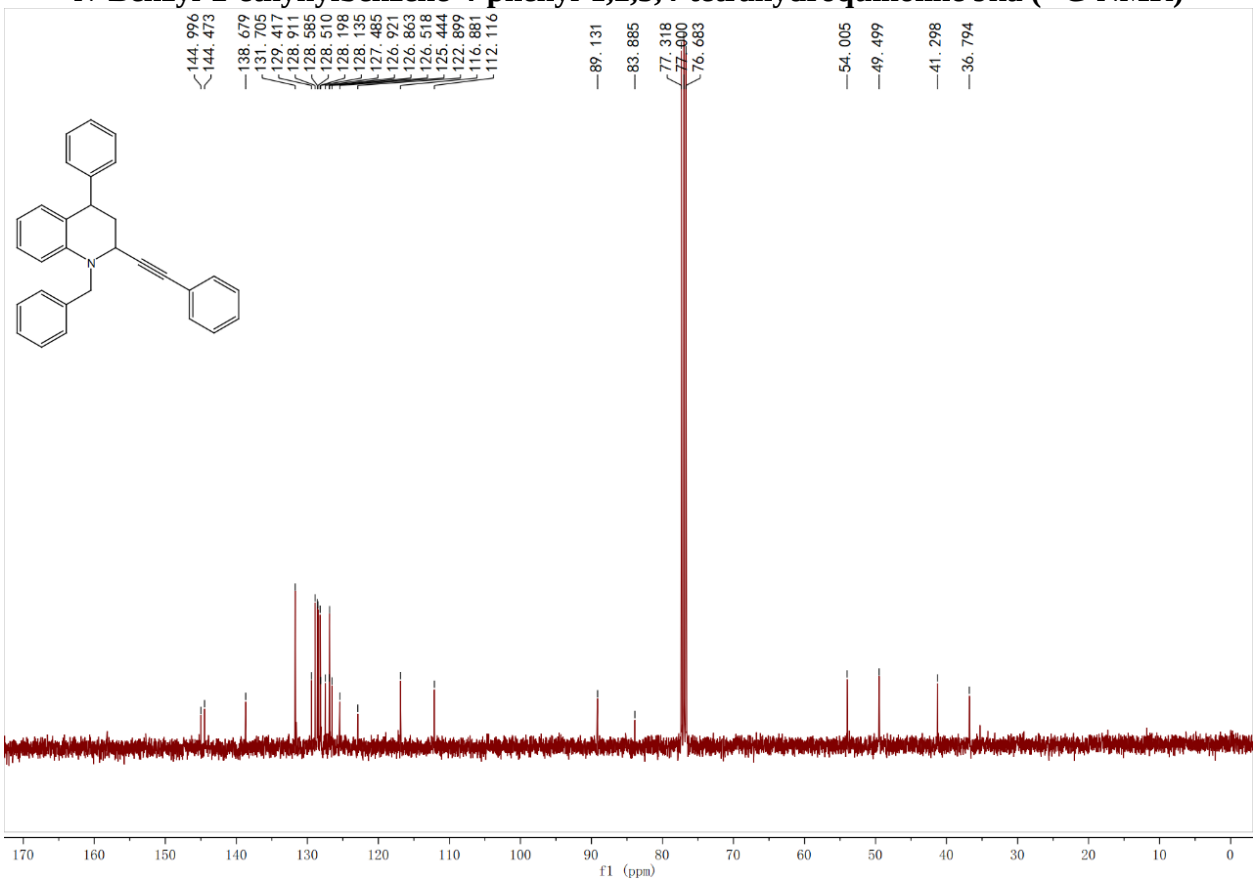
***N*-Benzyl-2-ethynylbenzene-6-chloro-1,2,3,4-tetrahydroquinoline 9ja (^{13}C-NMR)**



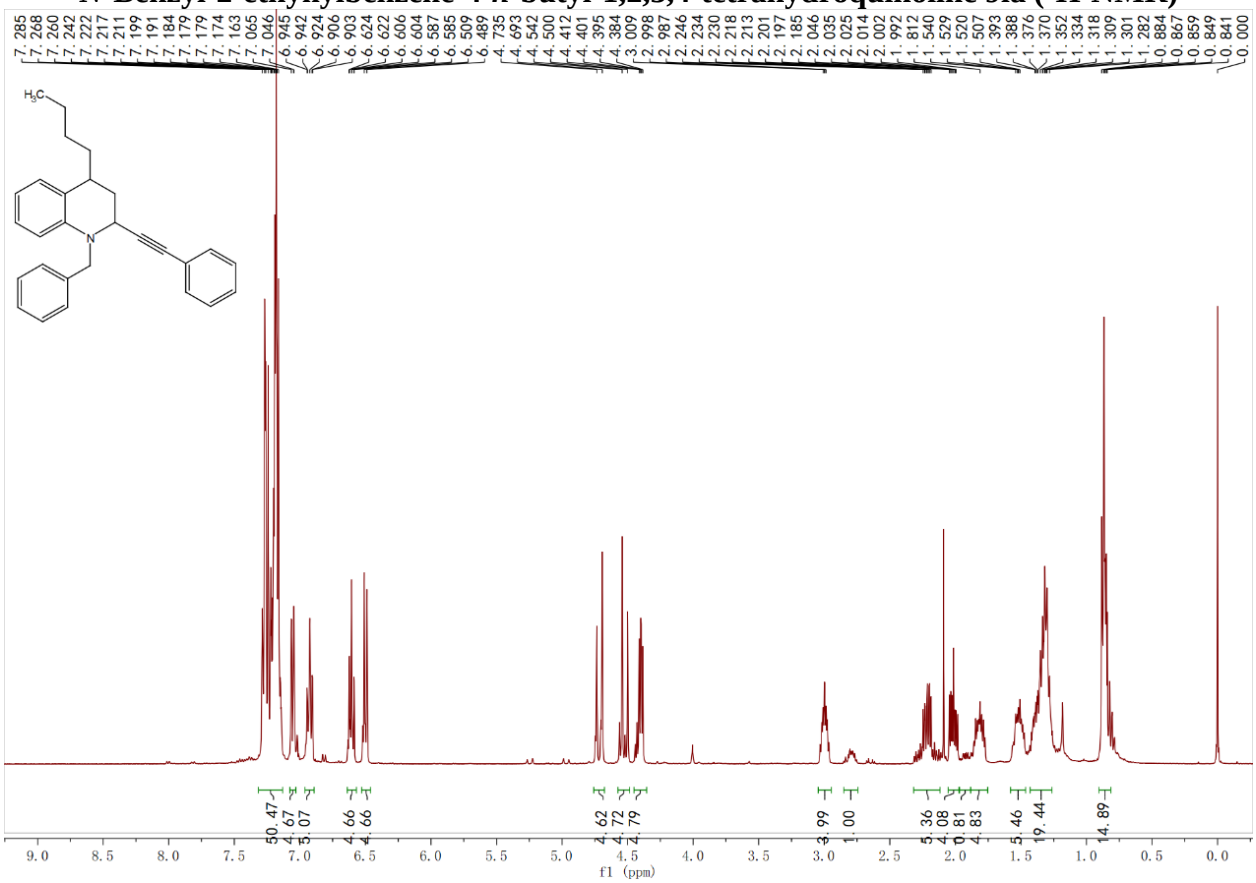
_N_-Benzyl-2-ethynylbenzene-4-phenyl-1,2,3,4-tetrahydroquinoline 9ka (^{1}H-NMR)



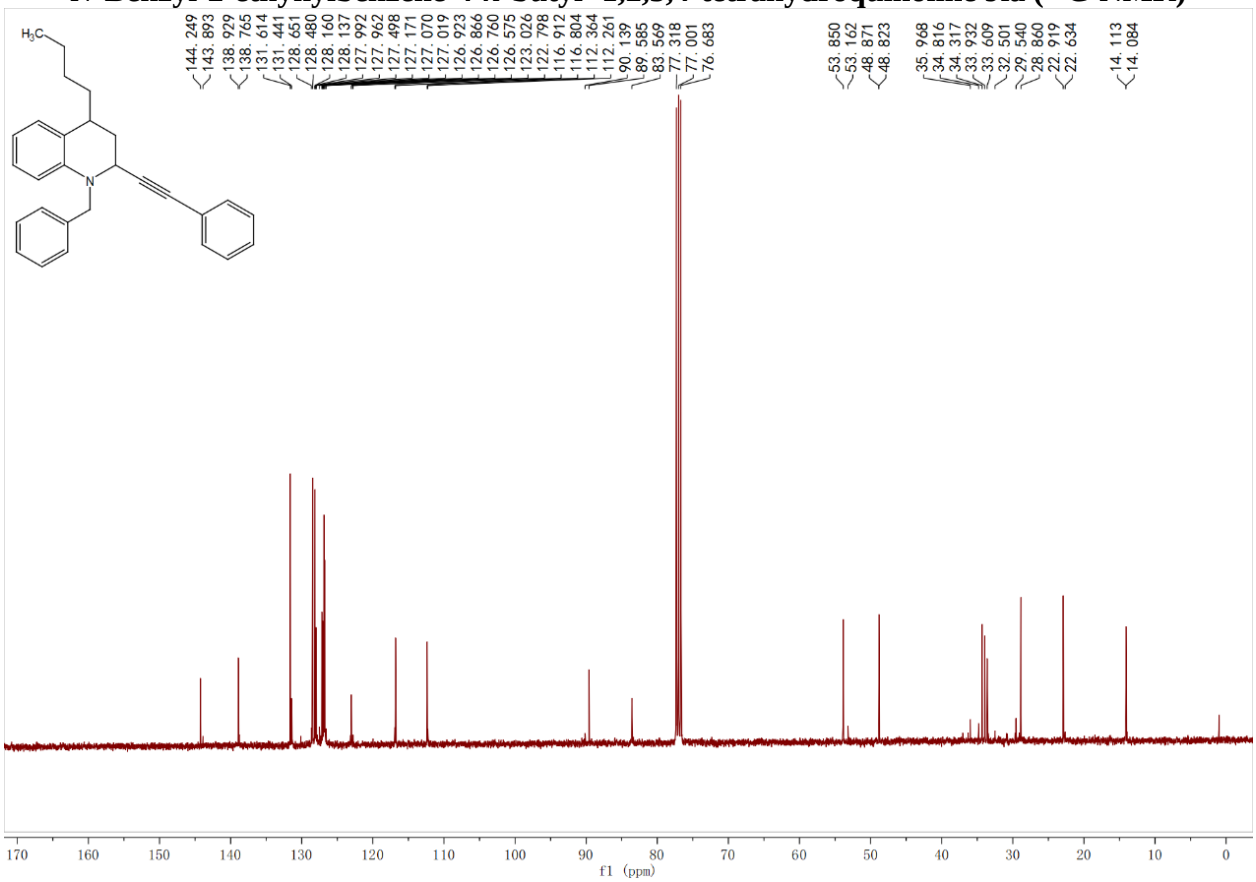
_N_-Benzyl-2-ethynylbenzene-4-phenyl-1,2,3,4-tetrahydroquinoline 9ka (^{13}C-NMR)



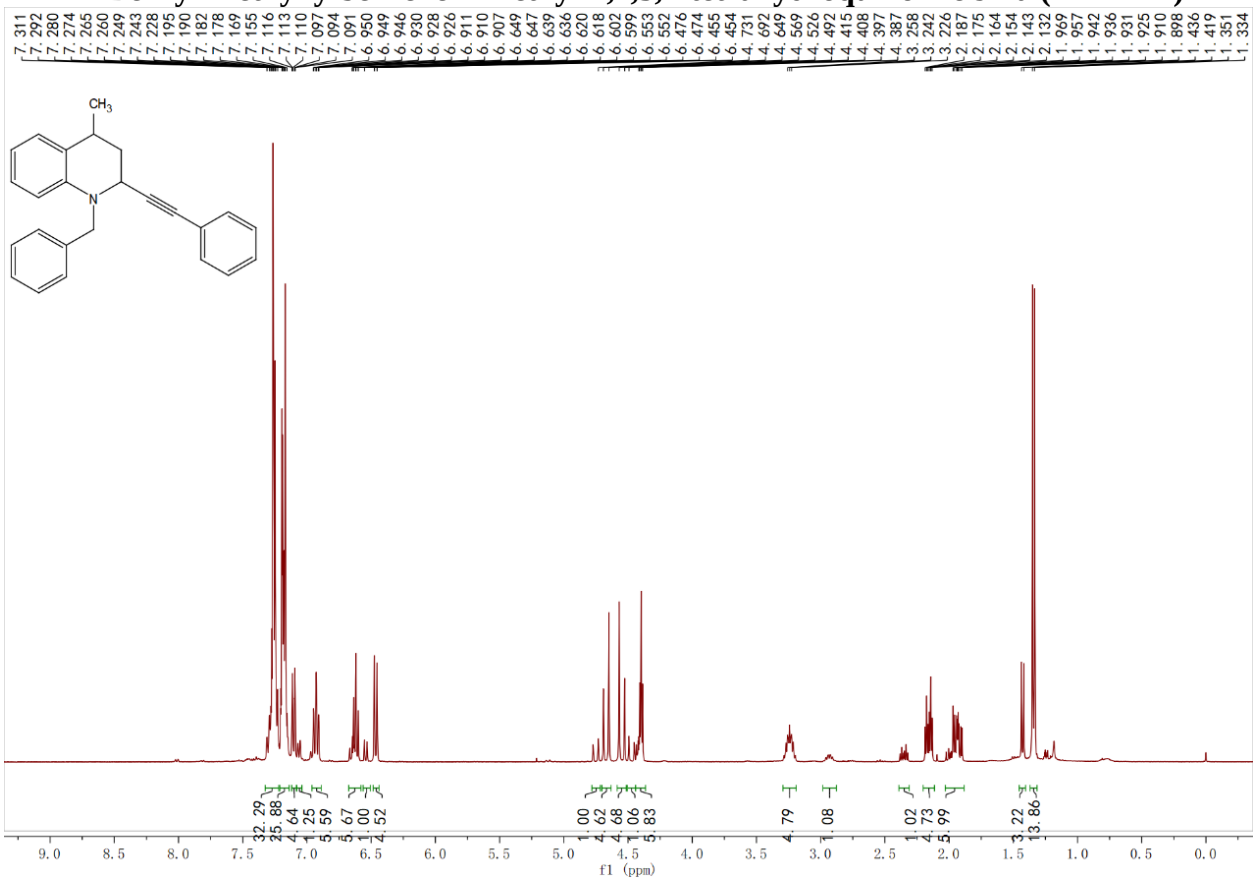
_N_-Benzyl-2-ethynylbenzene-4-_n_-butyl-1,2,3,4-tetrahydroquinoline 9la (^{1}H-NMR)



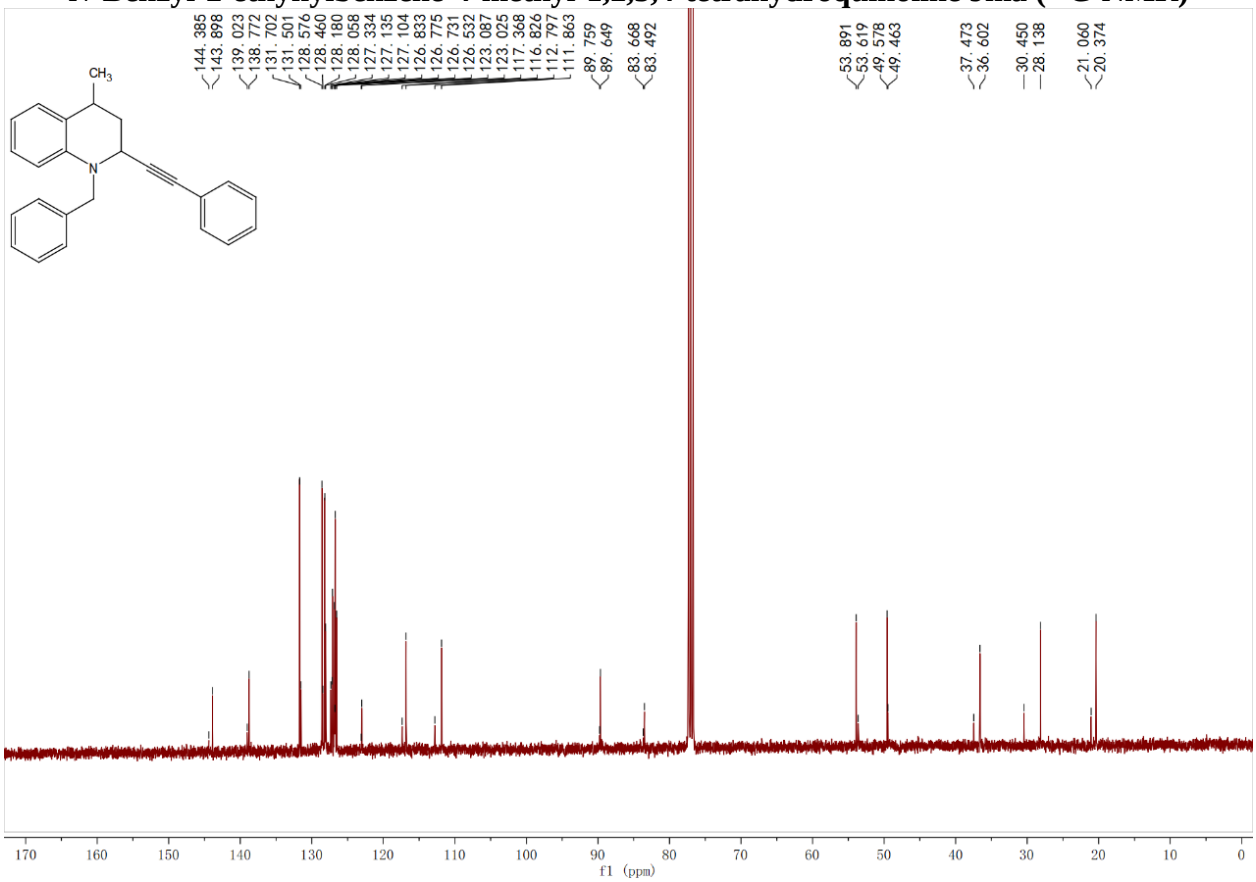
_N_-Benzyl-2-ethynylbenzene-4-_n_-butyl -1,2,3,4-tetrahydroquinoline 9la (^{13}C-NMR)



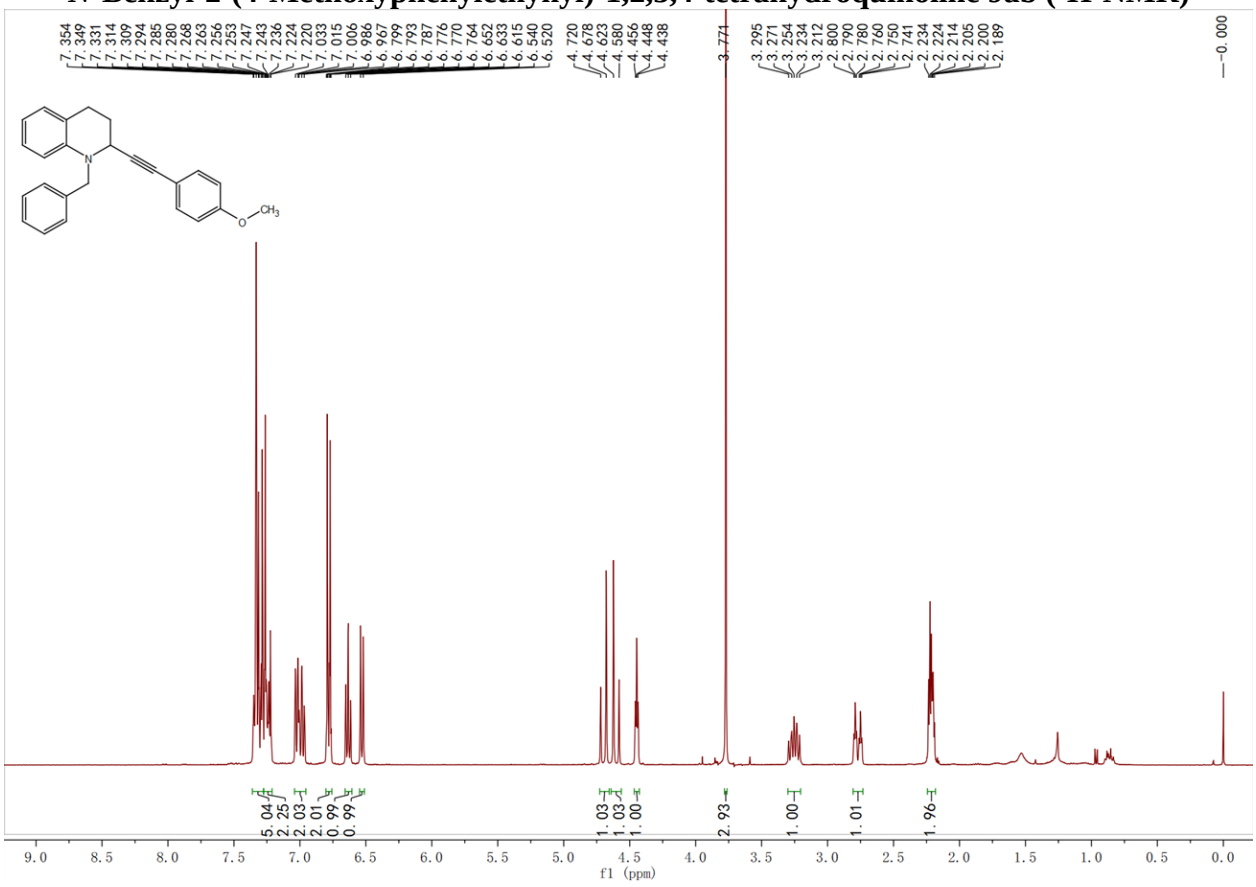
_N_-Benzyl-2-ethynylbenzene-4-methyl-1,2,3,4-tetrahydroquinoline 9ma (^{1}H-NMR)



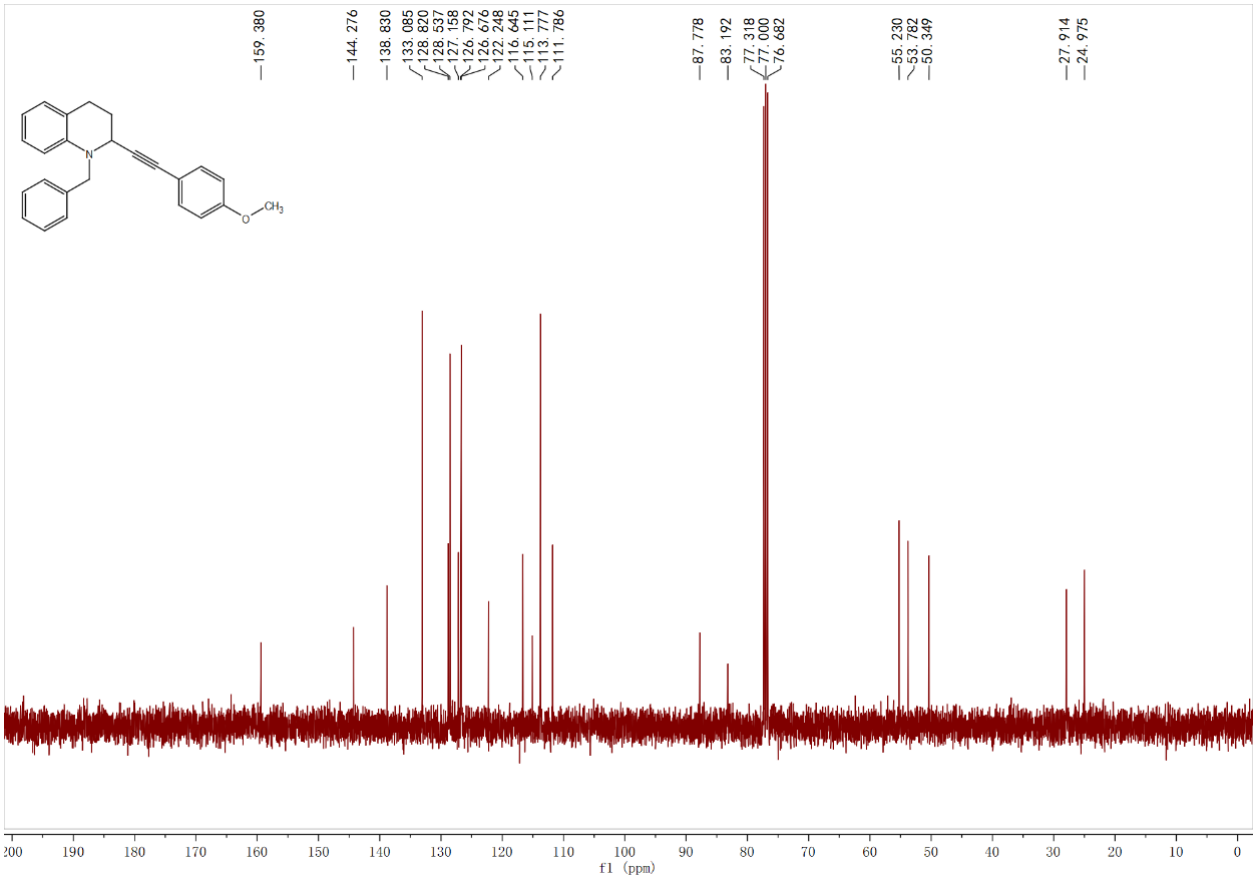
_N_-Benzyl-2-ethynylbenzene-4-methyl-1,2,3,4-tetrahydroquinoline 9ma (^{13}C-NMR)



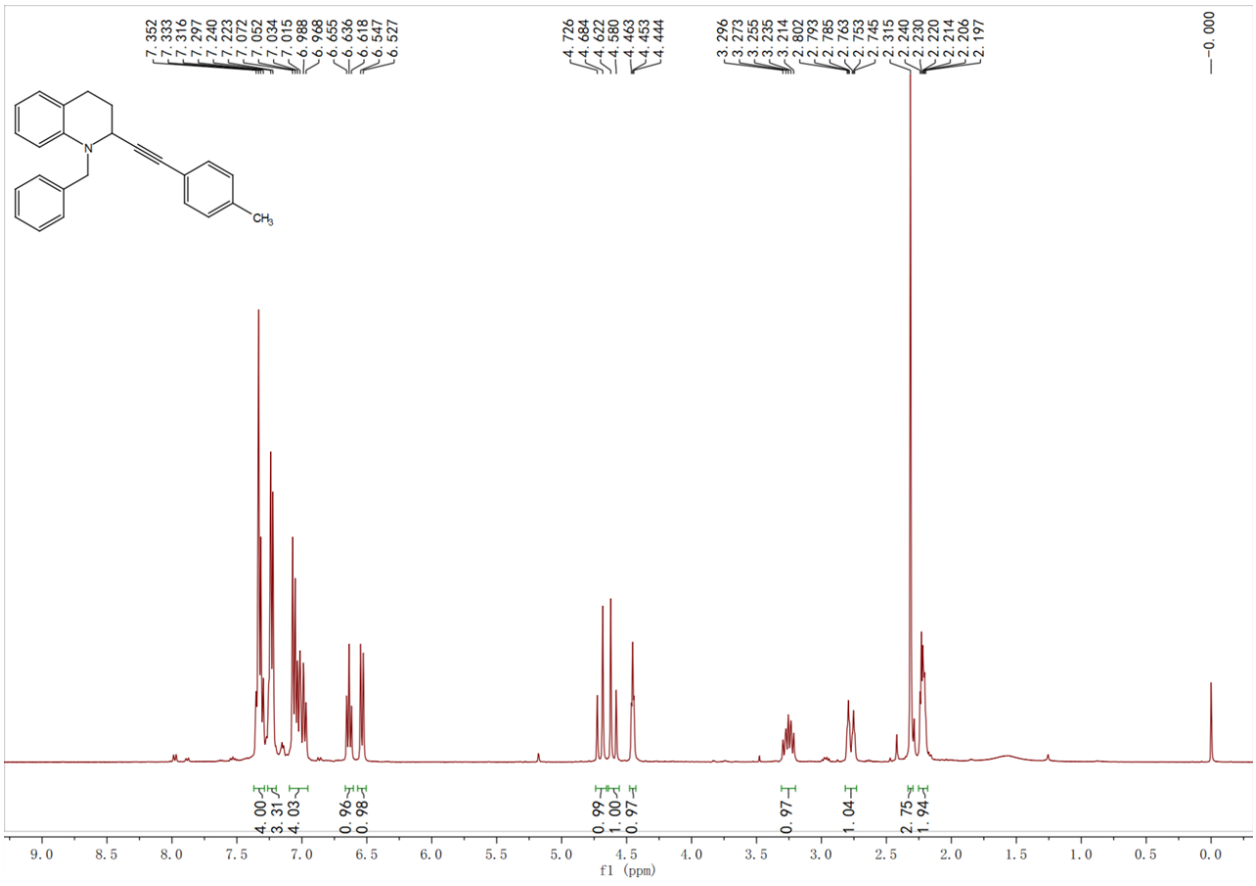
_N_-Benzyl-2-(4-Methoxyphenylethynyl)-1,2,3,4-tetrahydroquinoline 9ab (^{1}H-NMR)



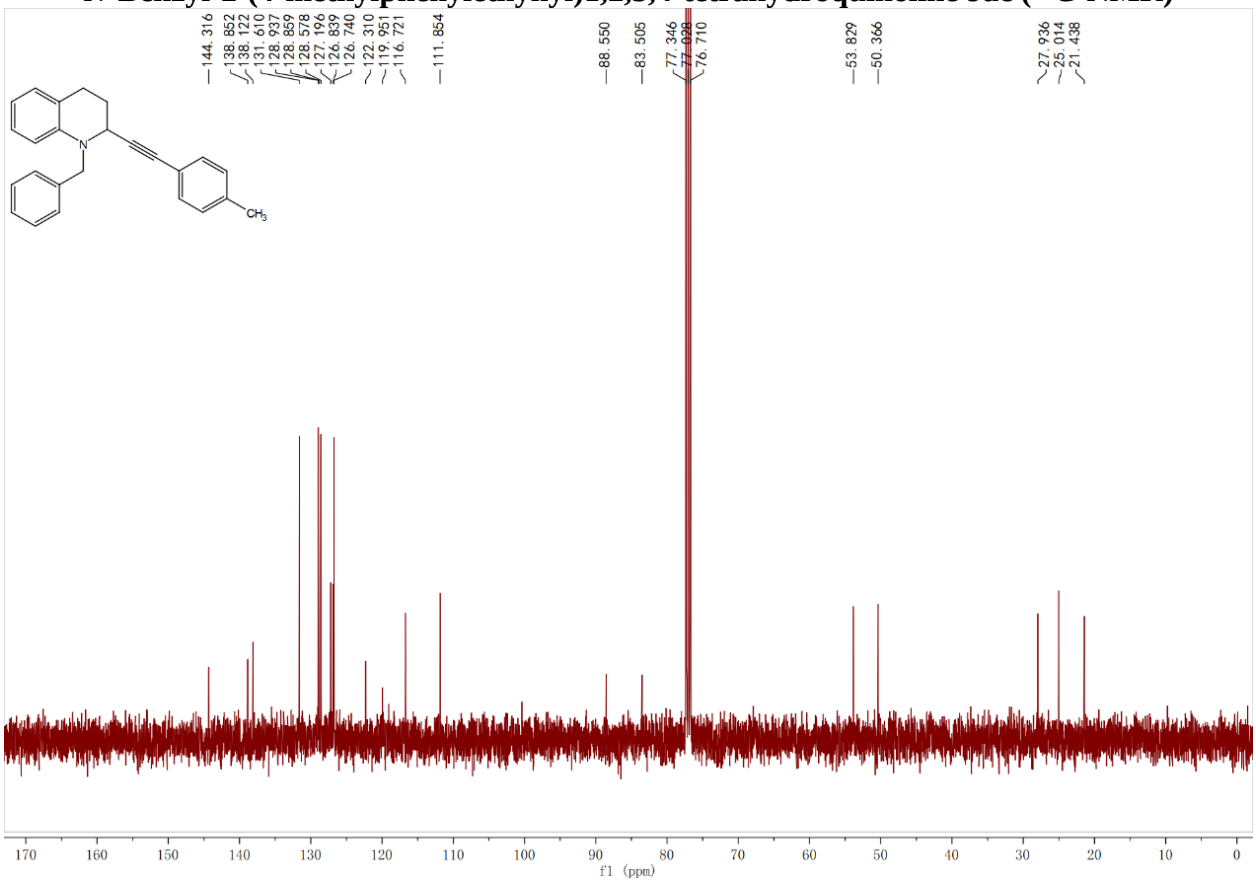
_N_-Benzyl-2-(4-Methoxyphenylethynyl)-1,2,3,4-tetrahydroquinoline 9ab (^{13}C-NMR)



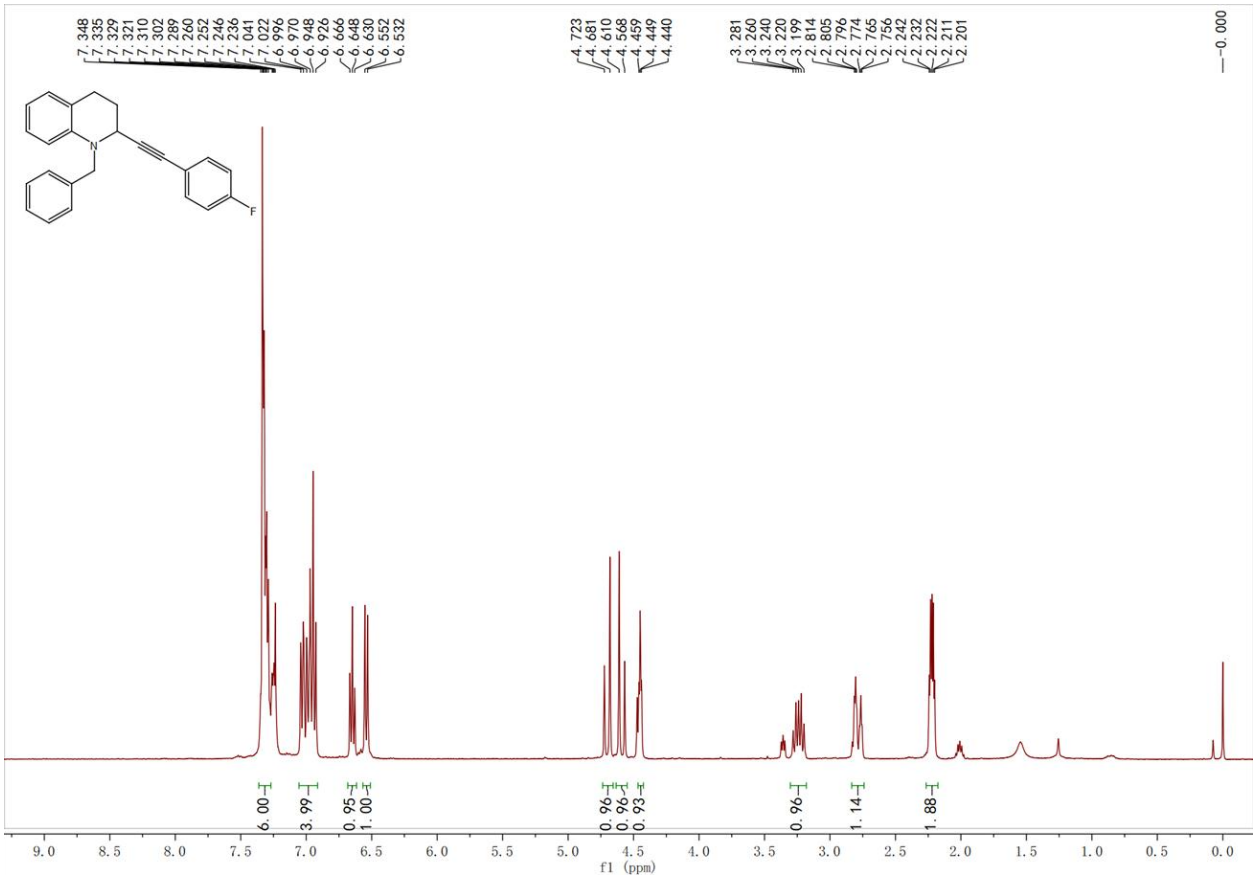
_N_-Benzyl-2-(4-methylphenylethynyl)-1,2,3,4-tetrahydroquinoline 9ac (^{1}H-NMR)



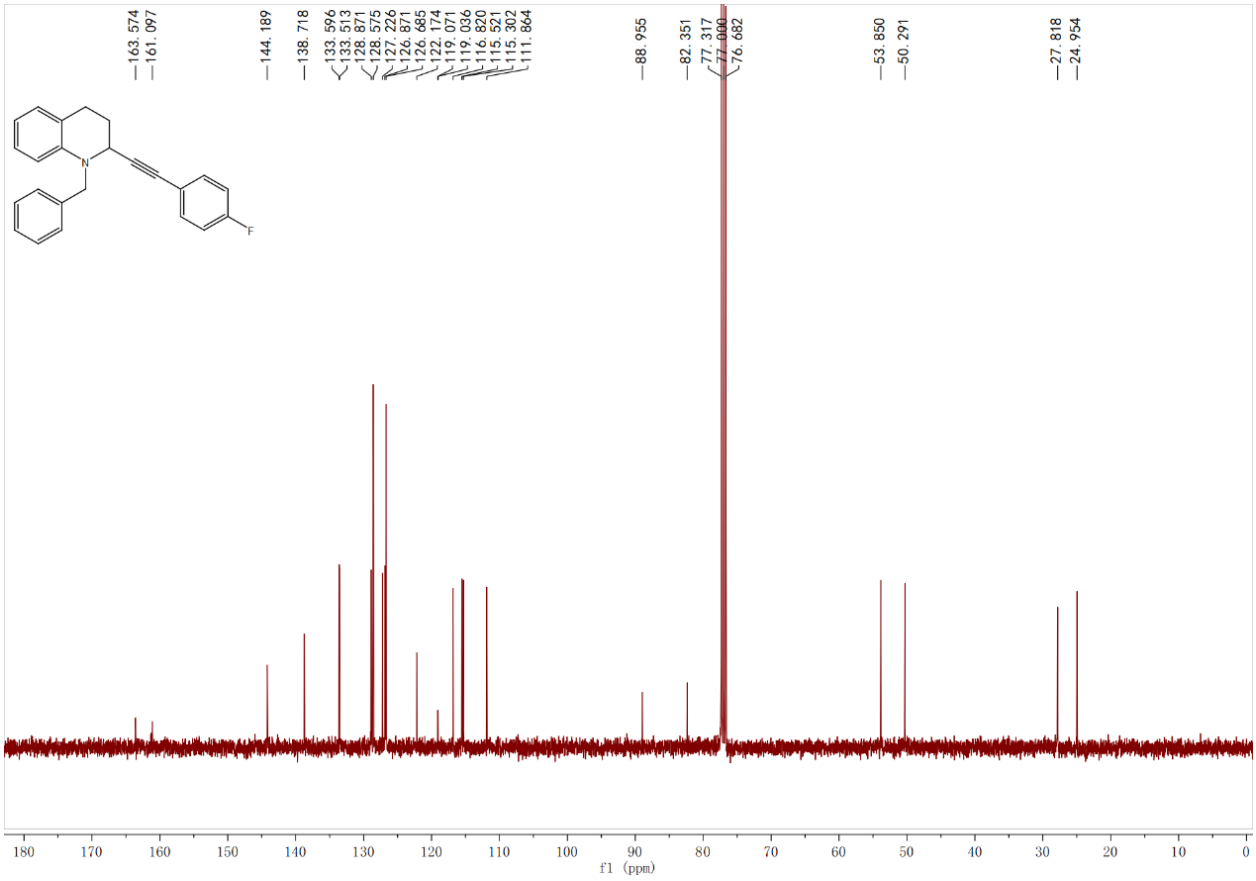
_N_-Benzyl-2-(4-methylphenylethynyl)1,2,3,4-tetrahydroquinoline 9ac (^{13}C-NMR)



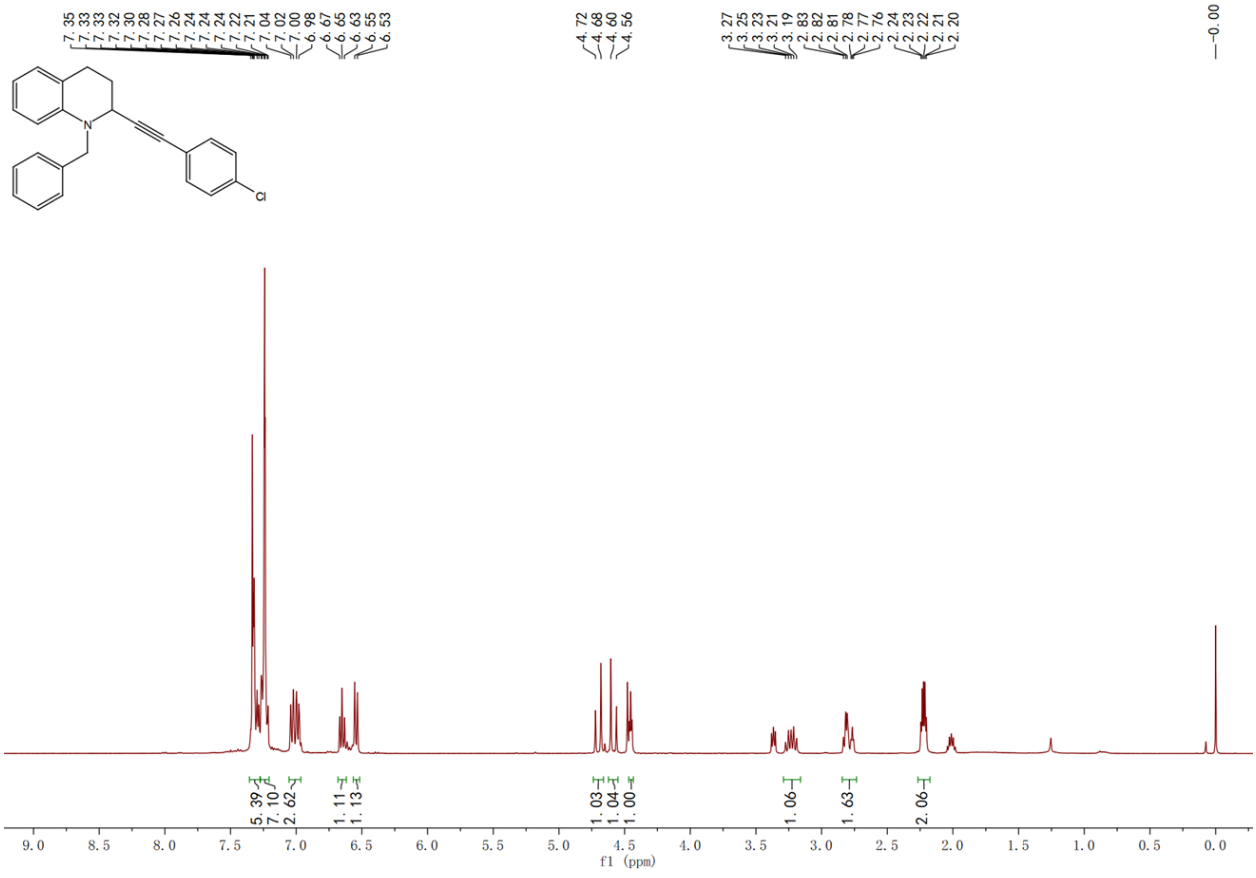
_N_-Benzyl-2-(4-fluorophenylethynyl)-1,2,3,4-tetrahydroquinoline 9ad (^{1}H-NMR)



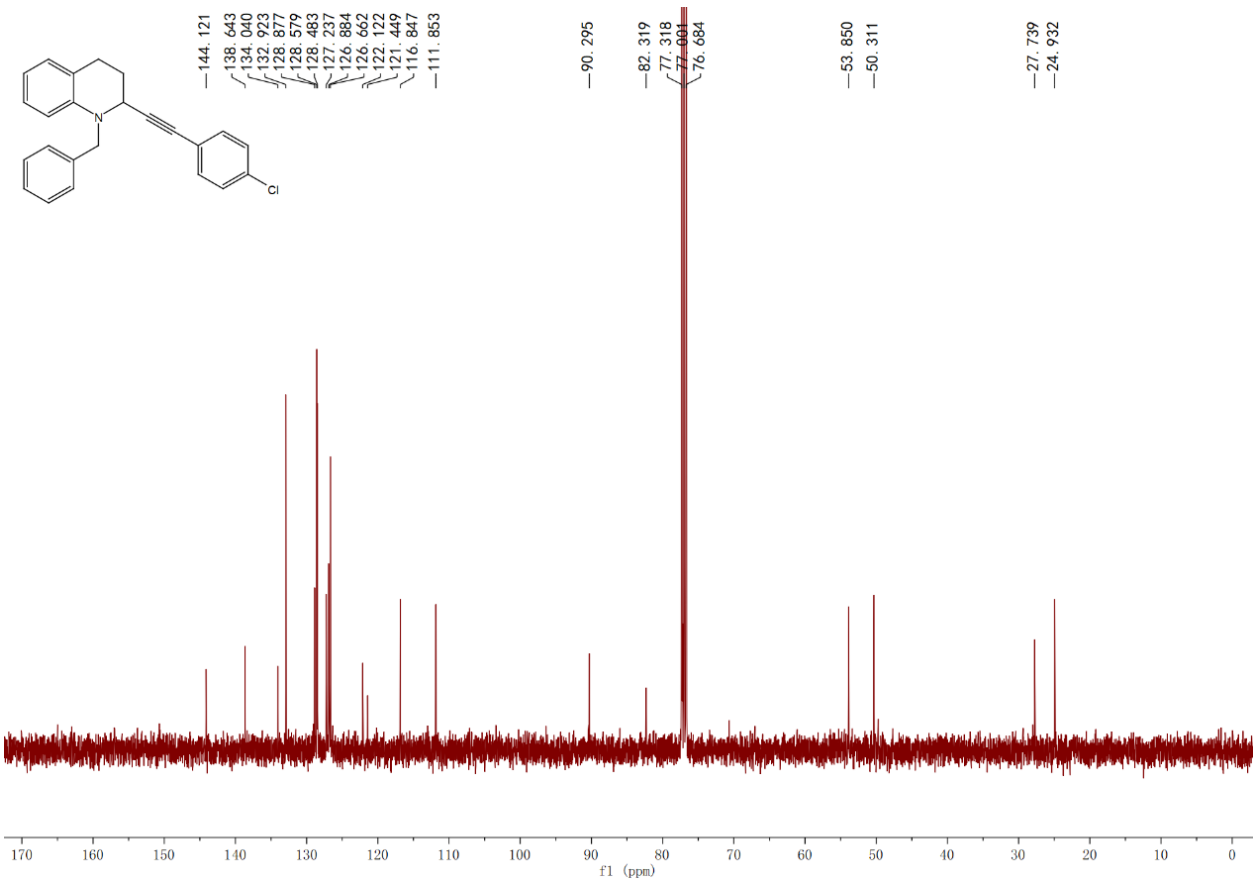
_N_-Benzyl-2-(4-fluorophenylethynyl)-1,2,3,4-tetrahydroquinoline 9ad (^{13}C-NMR)



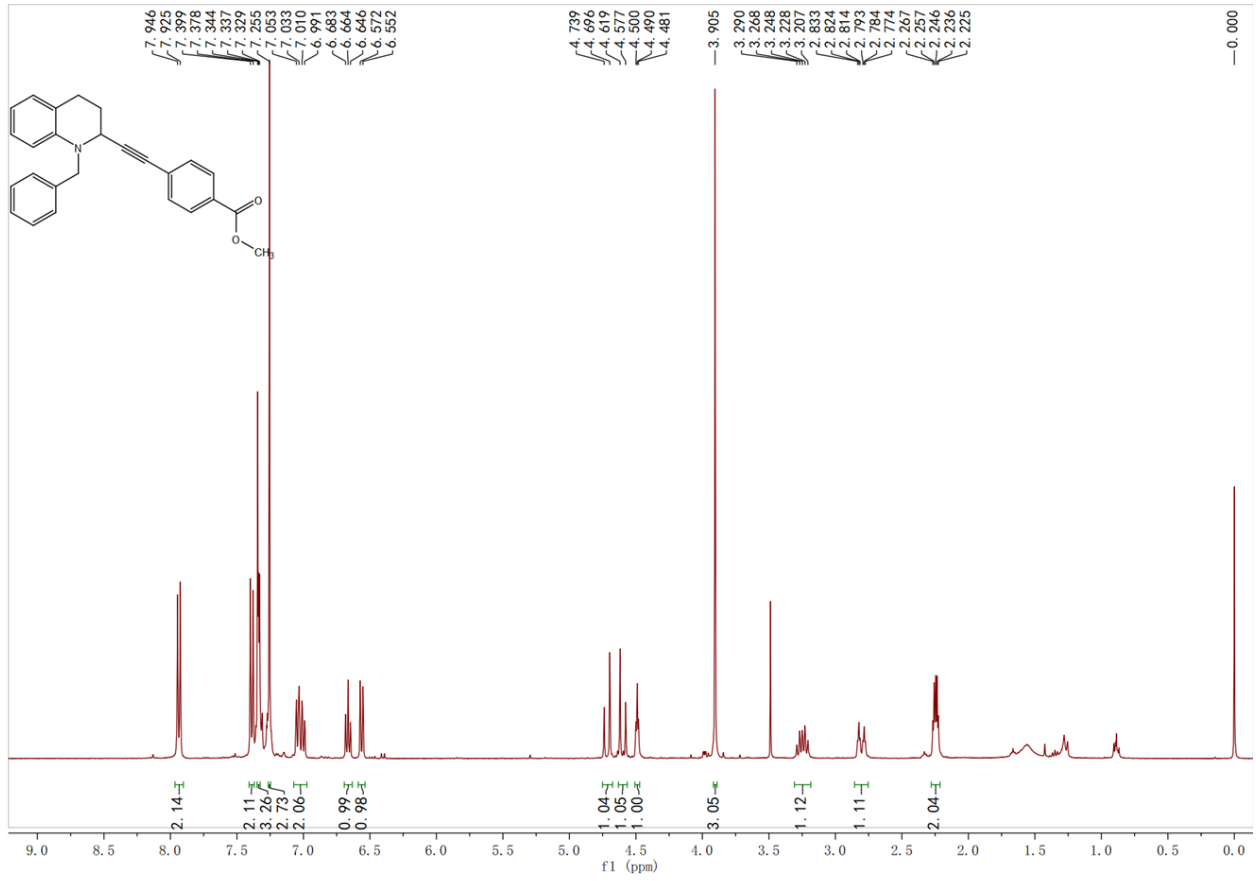
_N_-Benzyl-2-(4-chlorophenylethynyl)-1,2,3,4-tetrahydroquinoline 9ae (^{1}H-NMR)



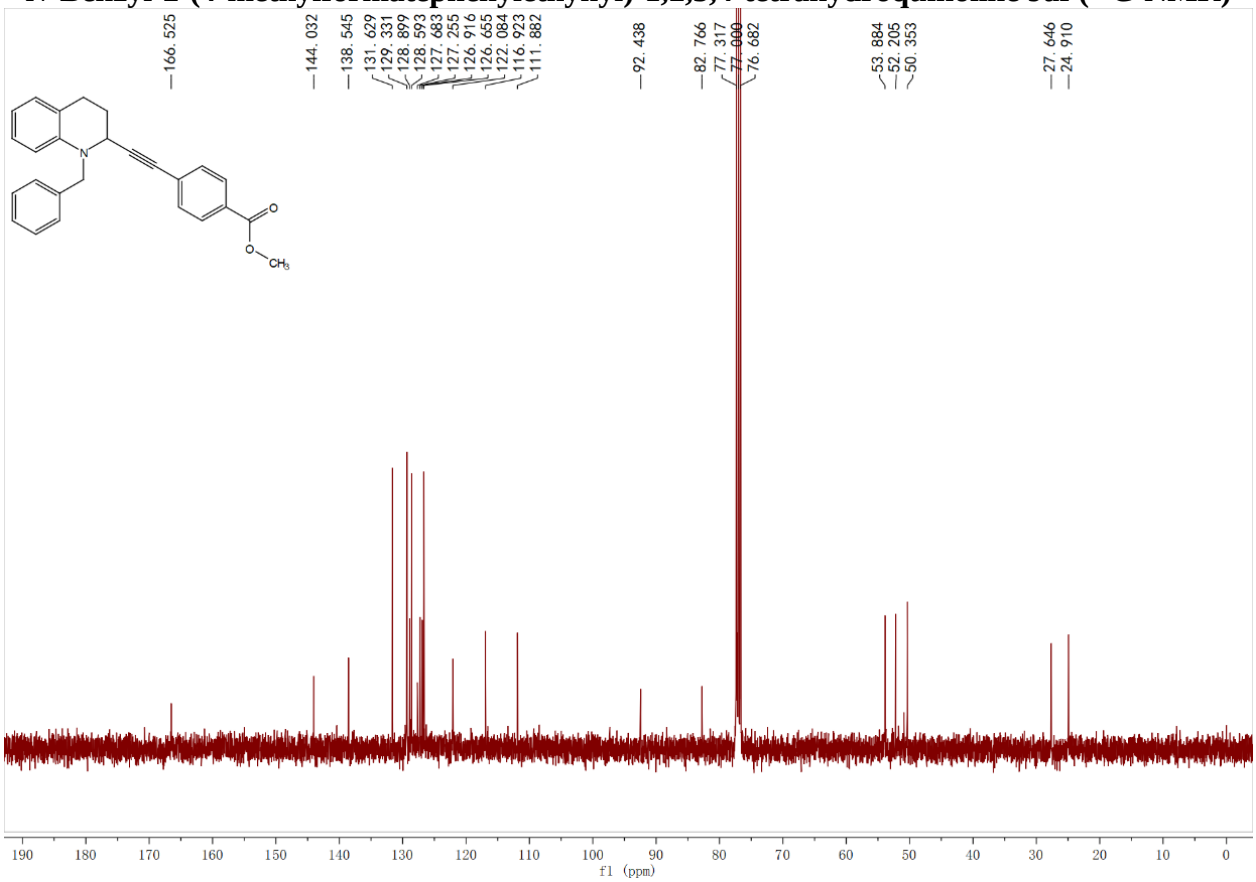
_N_-Benzyl-2-(4-chlorophenylethynyl)-1,2,3,4-tetrahydroquinoline 9ae (^{13}C-NMR)



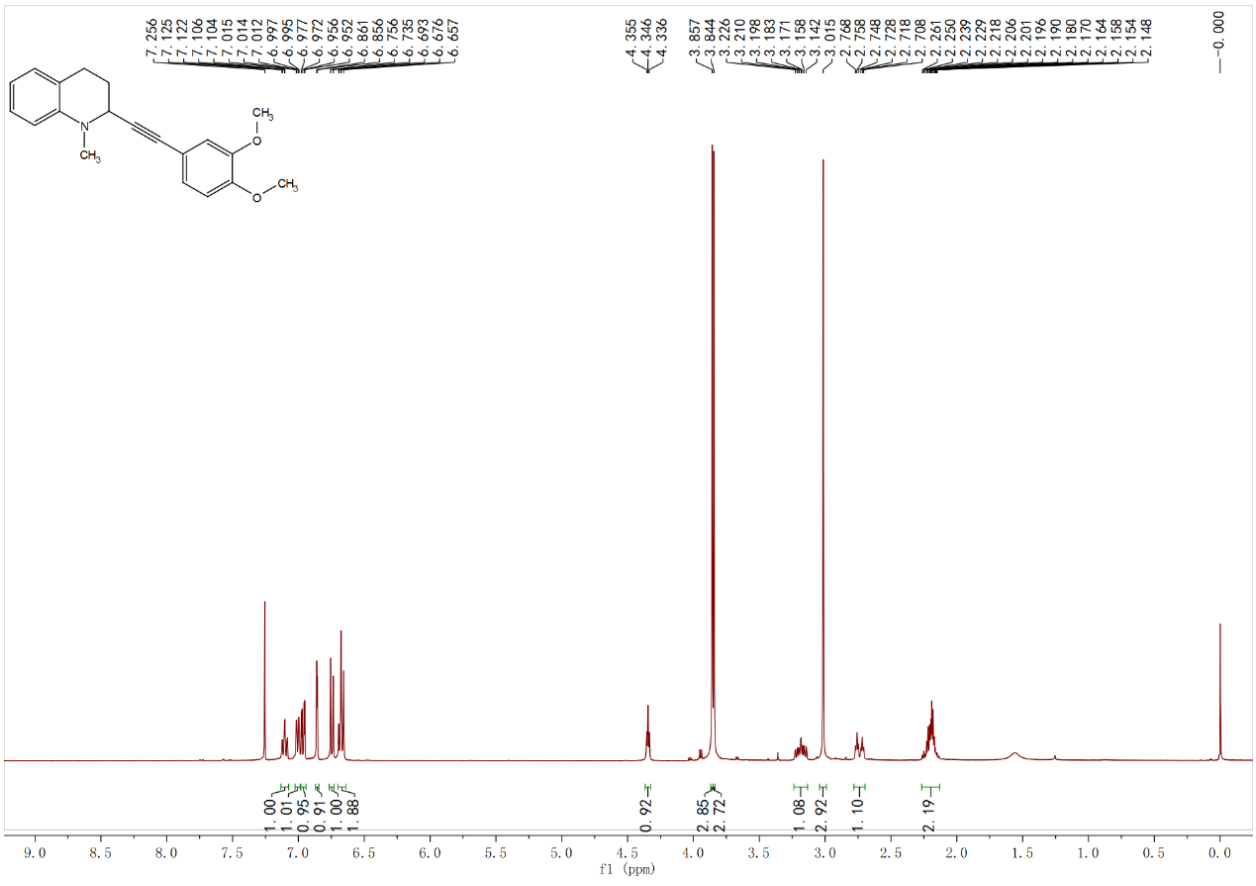
_N_-Benzyl-2-(4-methylformatephenylethynyl)-1,2,3,4-tetrahydroquinoline 9af (^{1}H-NMR)



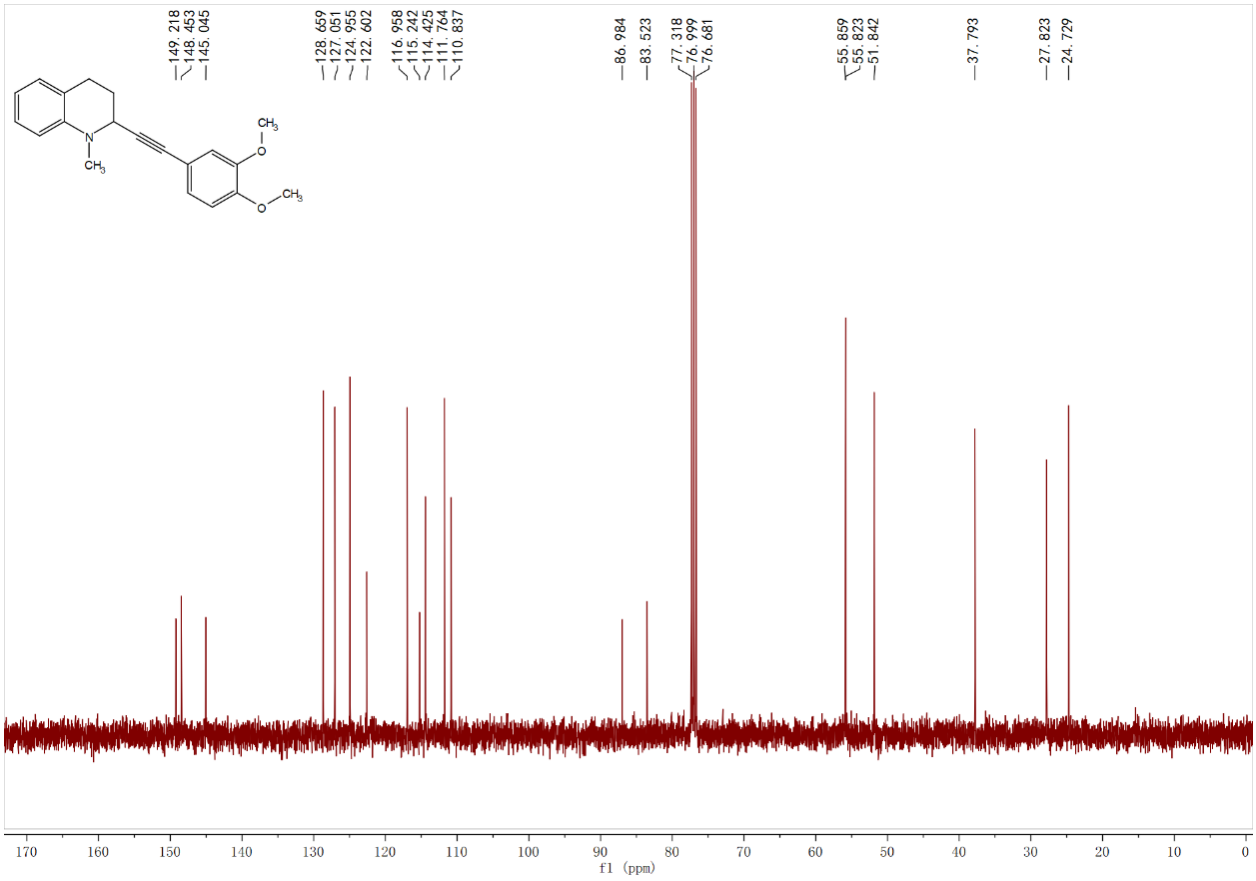
_N_-Benzyl-2-(4-methylformatephenylethynyl)-1,2,3,4-tetrahydroquinoline 9af (^{13}C-NMR)



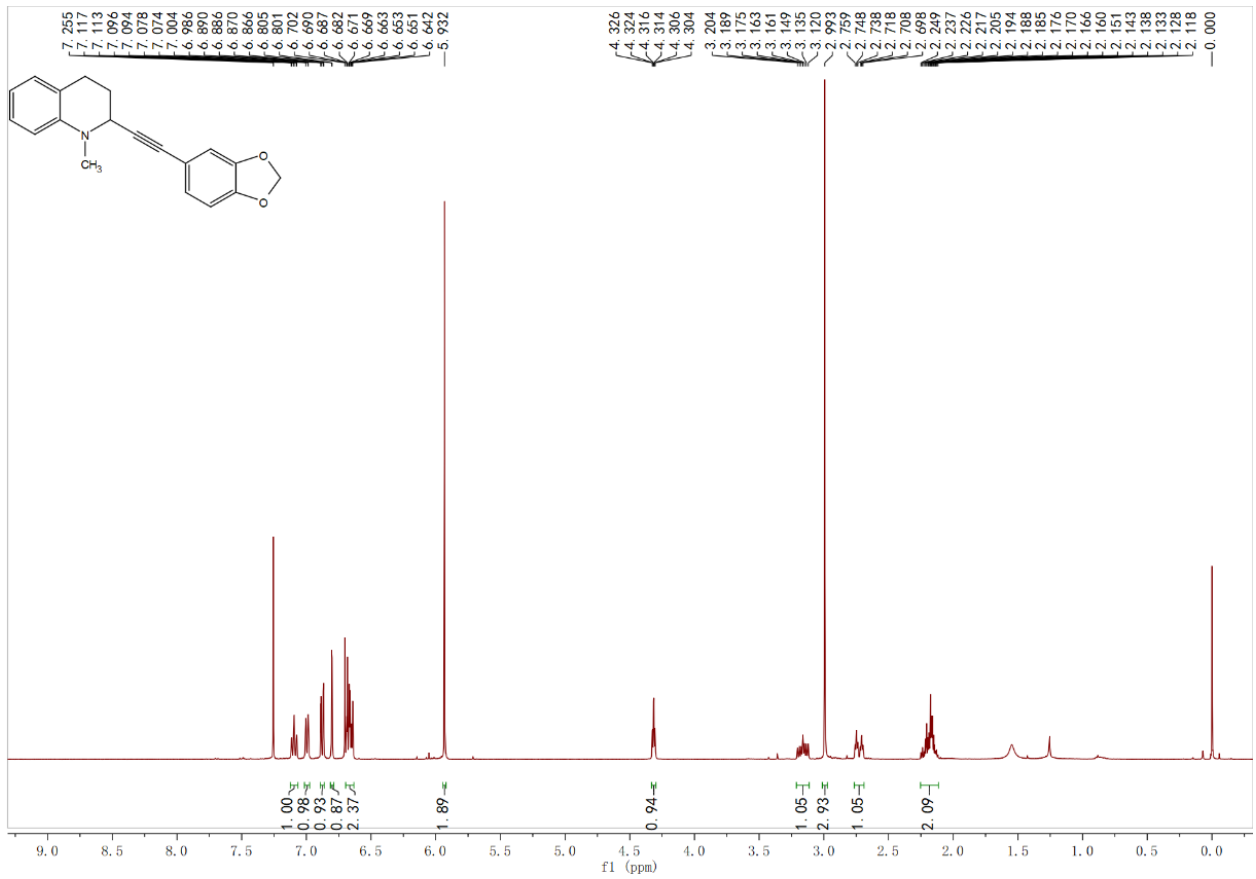
_N_-Benzyl-2-(3,4-dimethoxyphenylethynyl)-1,2,3,4-tetrahydroquinoline 9dg (^{1}H-NMR)



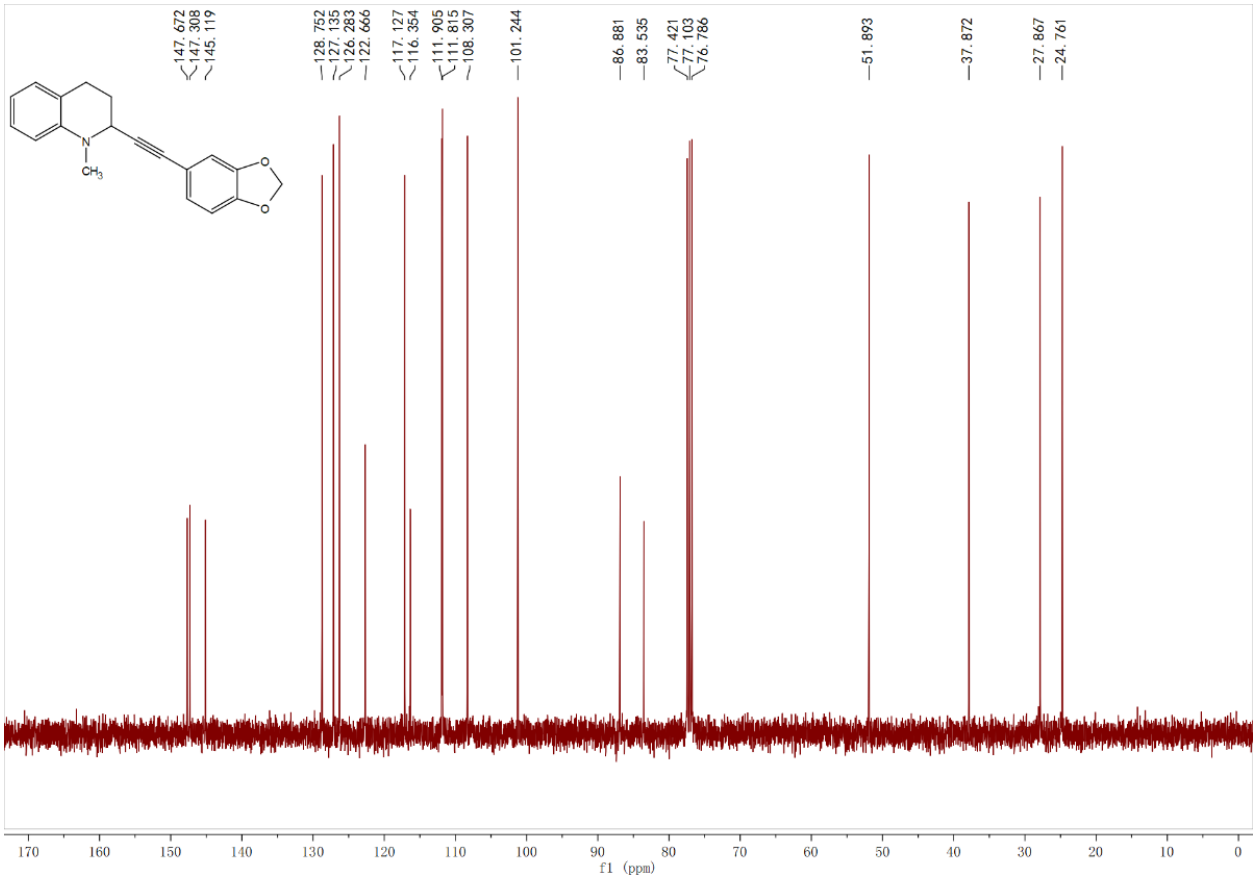
_N_-Benzyl-2-(3,4-dimethoxyphenylethynyl)-1,2,3,4-tetrahydroquinoline 9dg (^{13}C-NMR)



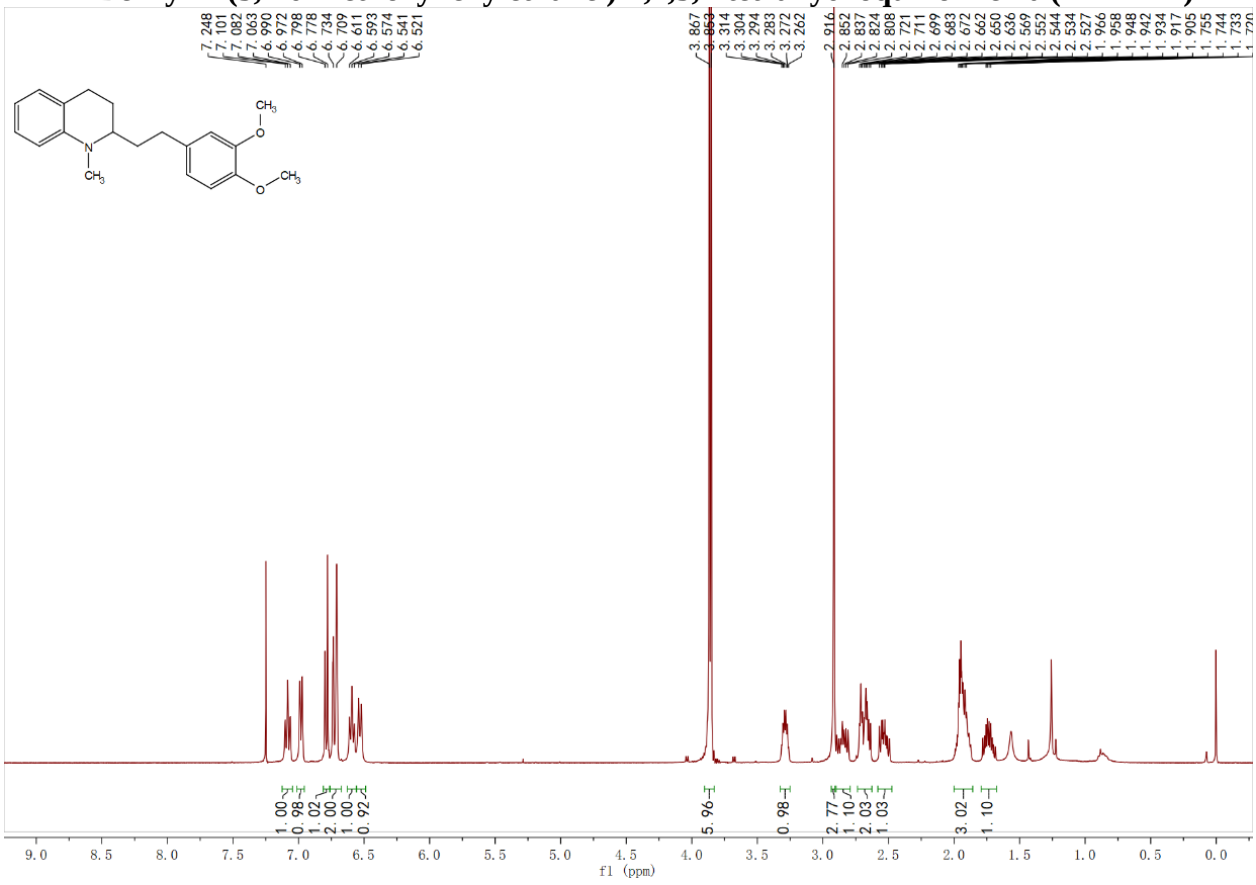
_N_-Benzyl-2-(3,4-dimethoxymethylenephenylethynyl)-1,2,3,4-tetrahydroquinoline 9dh (^{1}H-NMR)



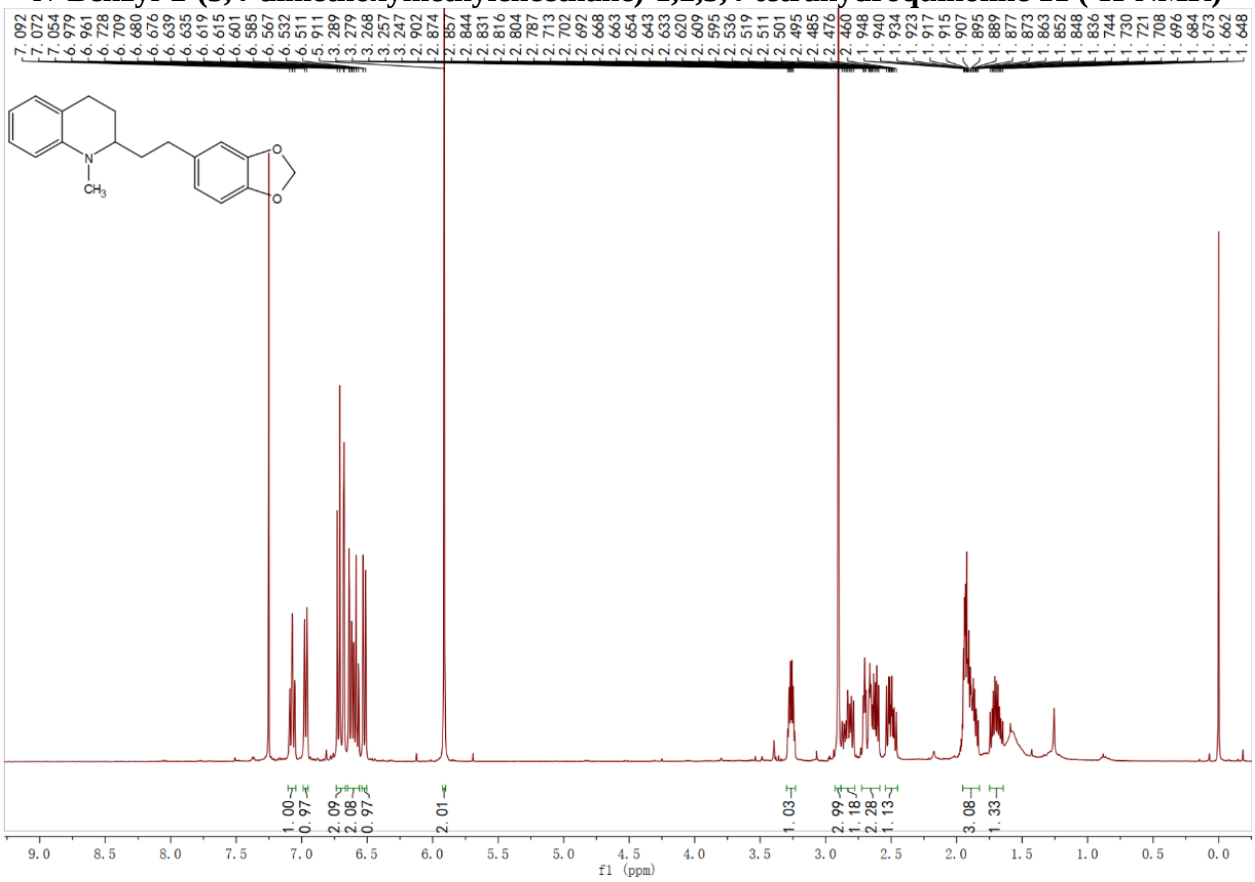
_N_-Benzyl-2-(3,4-dimethoxymethylenephenylethynyl)-1,2,3,4-tetrahydroquinoline 9dh (^{13}C-NMR)



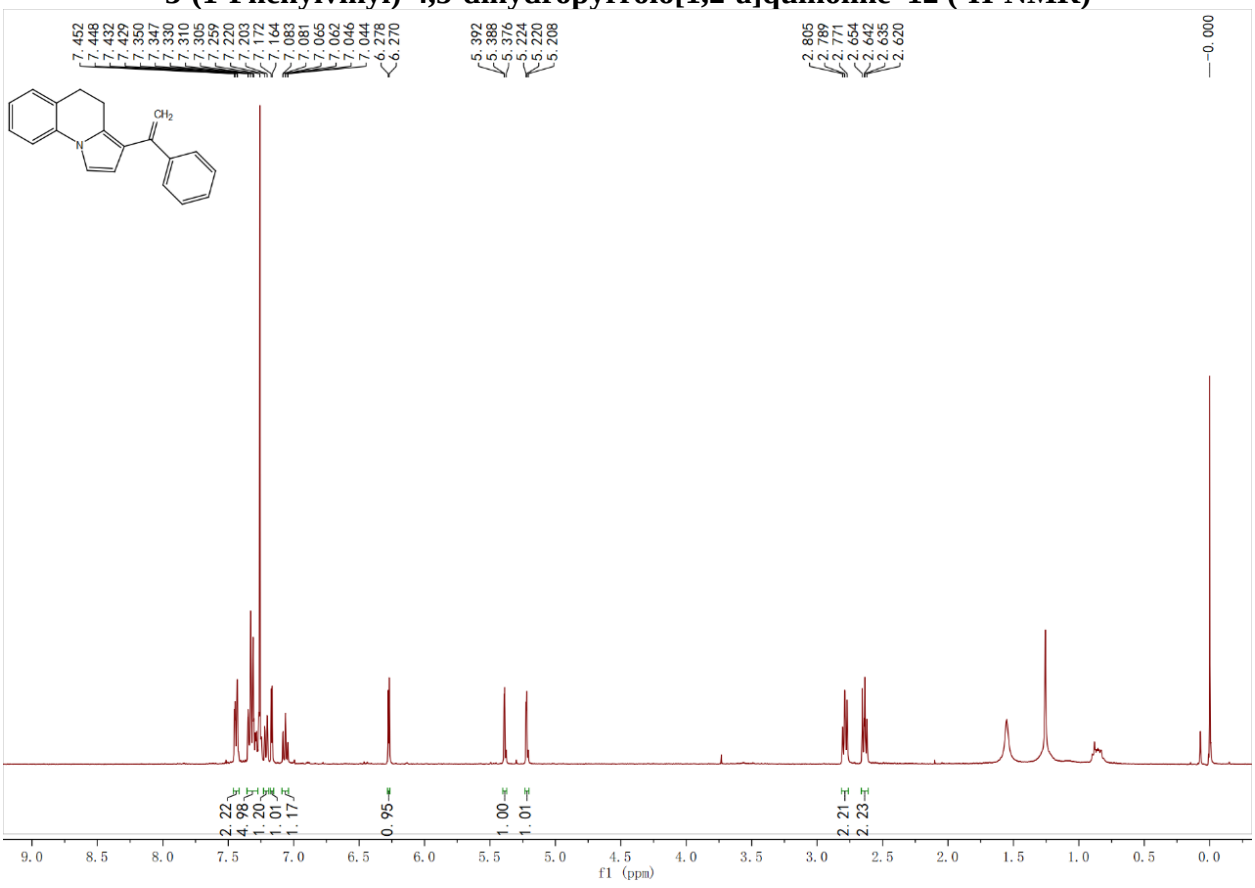
_N_-Benzyl-2-(3,4-dimethoxyhenylethane)-1,2,3,4-tetrahydroquinoline 10 (^{1}H-NMR)



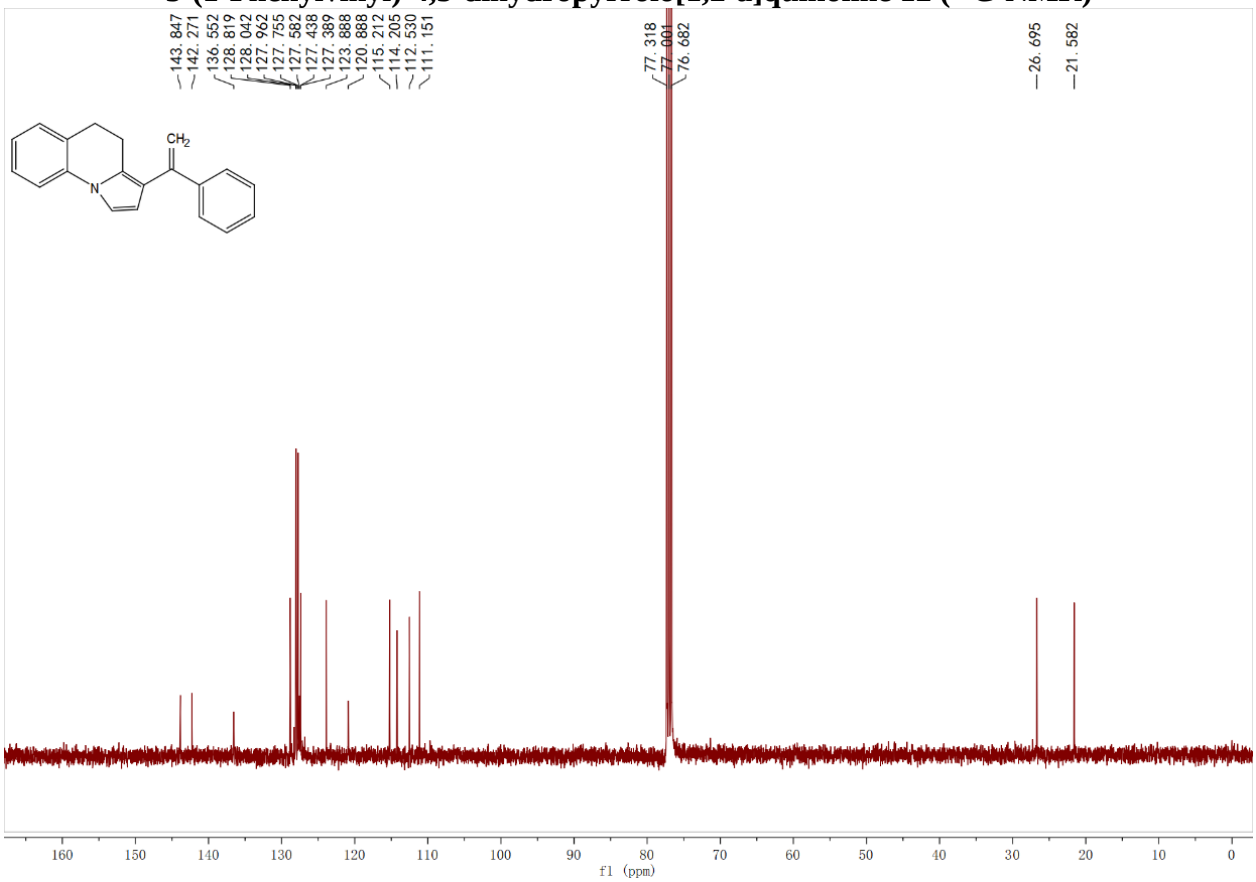
_N_-Benzyl-2-(3,4-dimethoxymethyleneethane)-1,2,3,4-tetrahydroquinoline 11 (^{1}H-NMR)



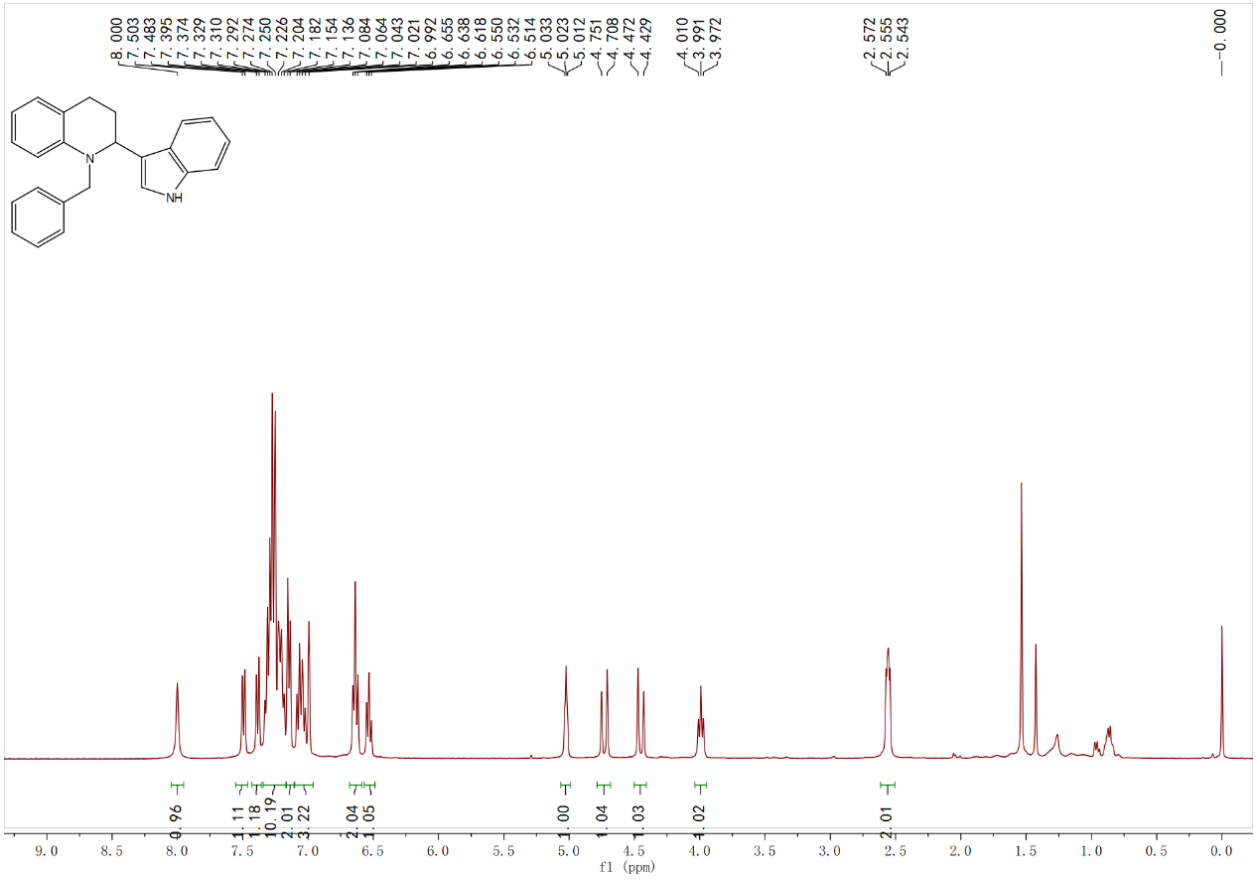
3-(1-Phenylvinyl)-4,5-dihydropyrrolo[1,2-a]quinoline 12 (^{1}H-NMR)



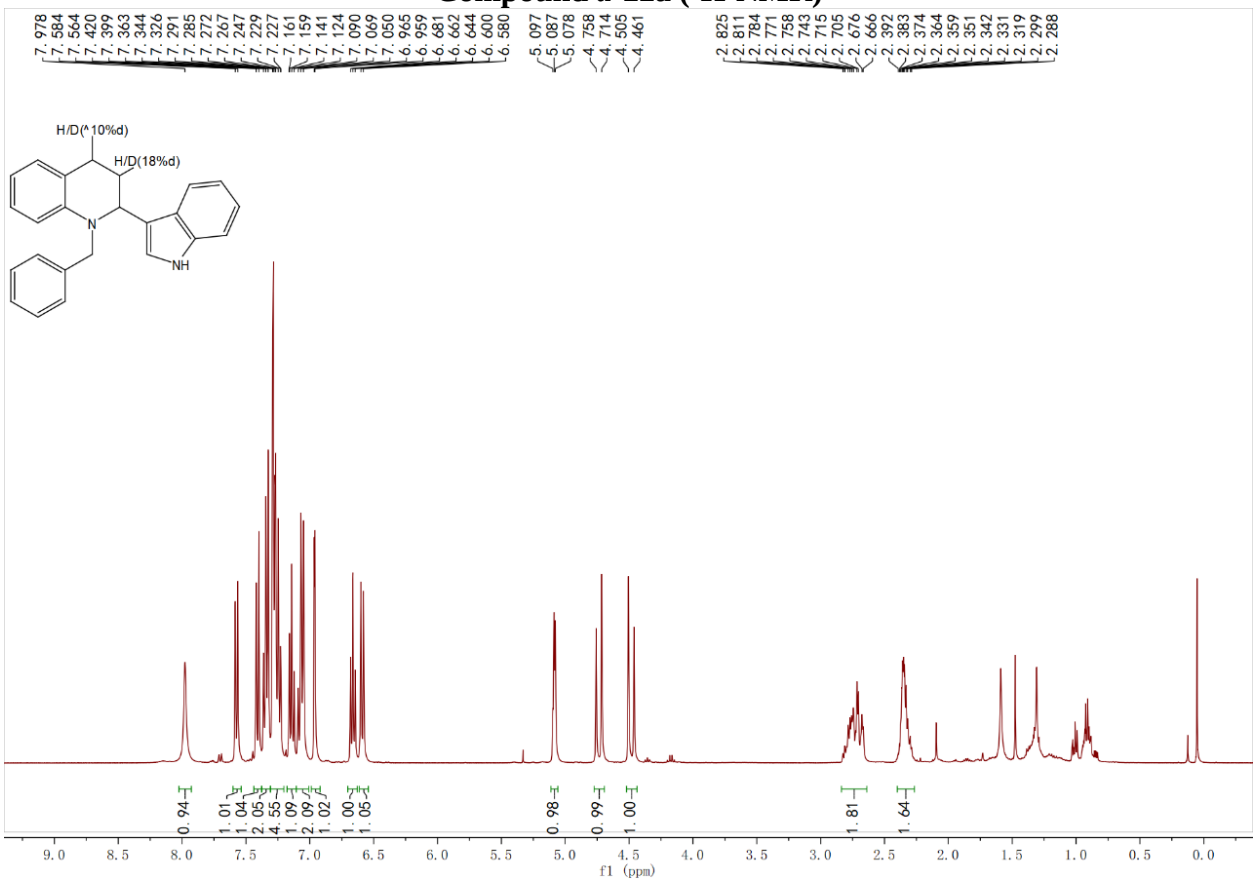
3-(1-Phenylvinyl)-4,5-dihydropyrrolo[1,2-a]quinoline 12 (^{13}C-NMR)



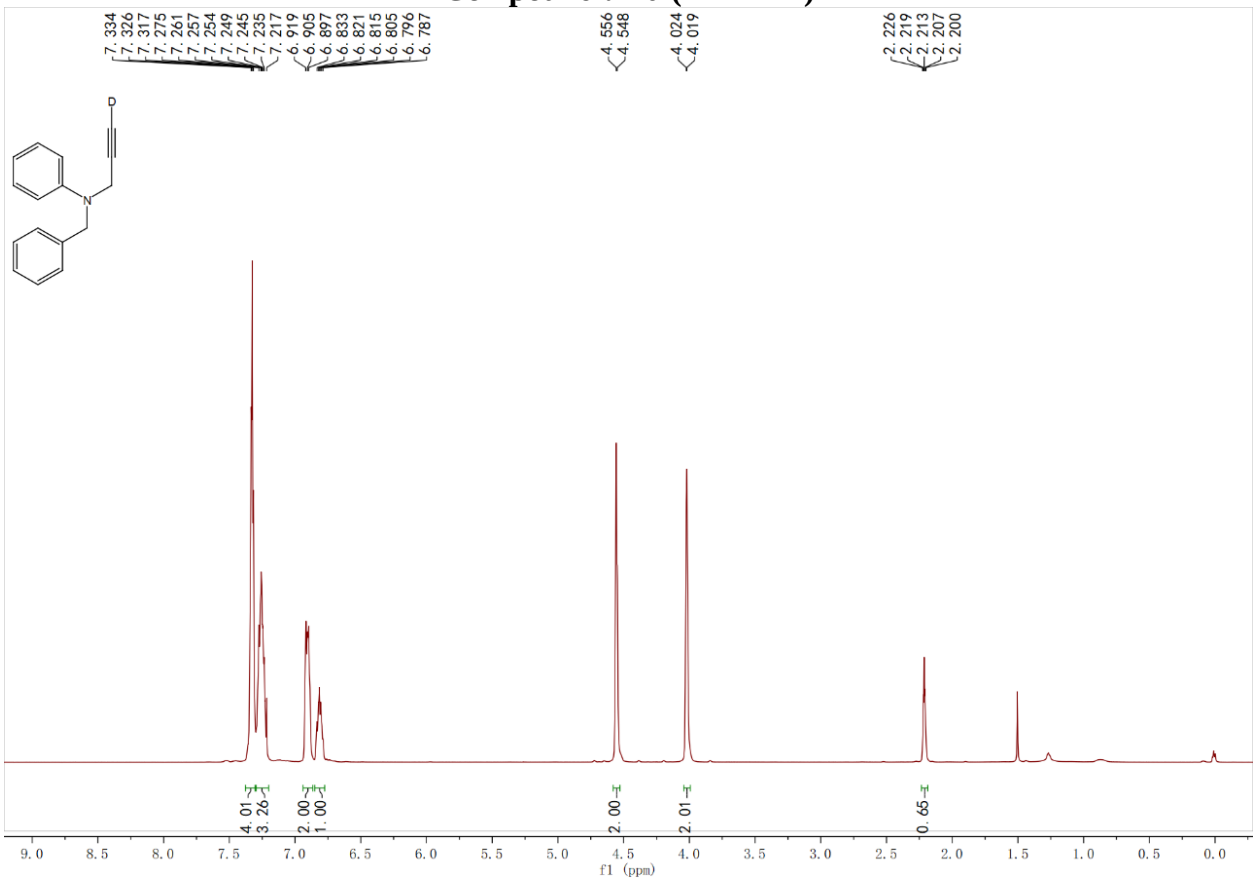
***N*-Benzyl-2-(3-indolyl)-1,2,3,4-tetrahydroquinoline 22a (^{1}H-NMR)**



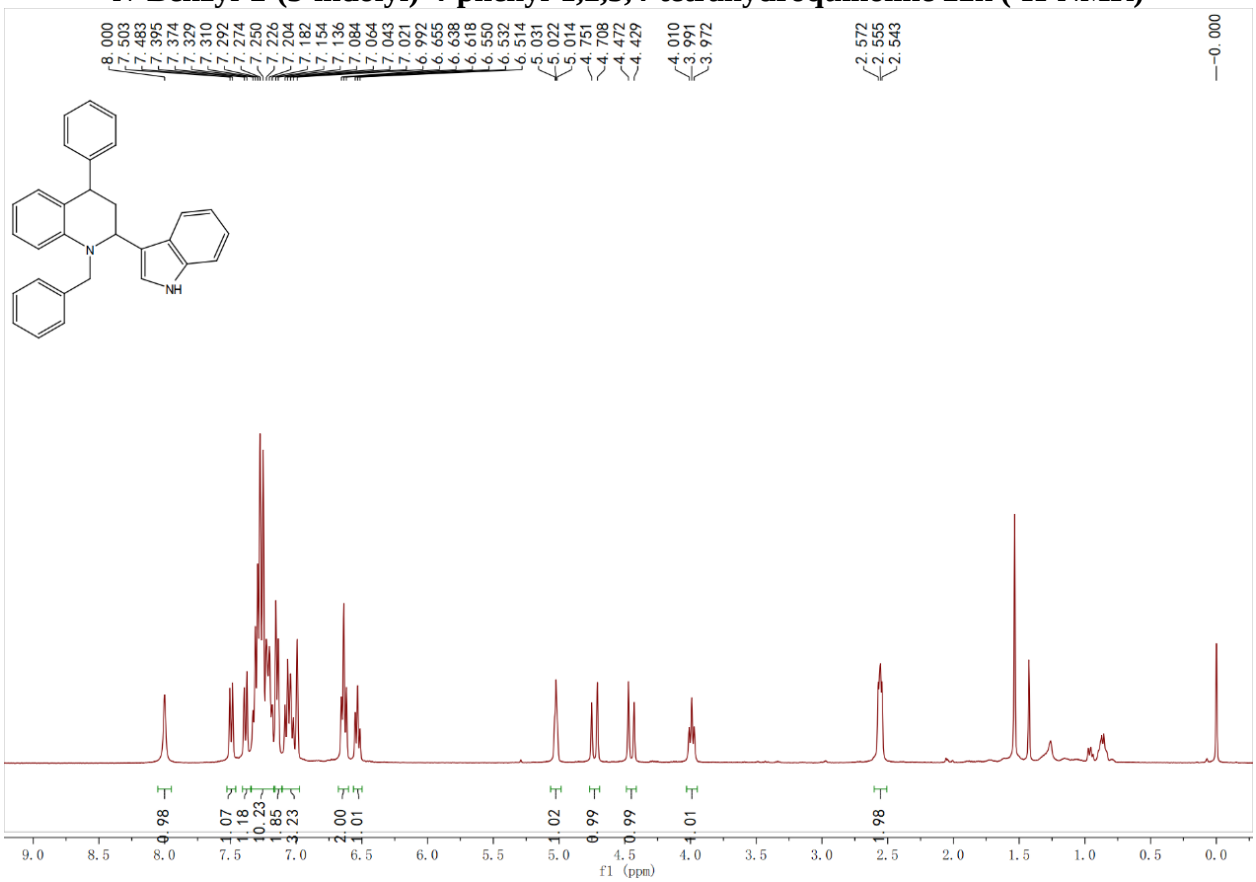
Compound *d*-22a (^{1}H-NMR)



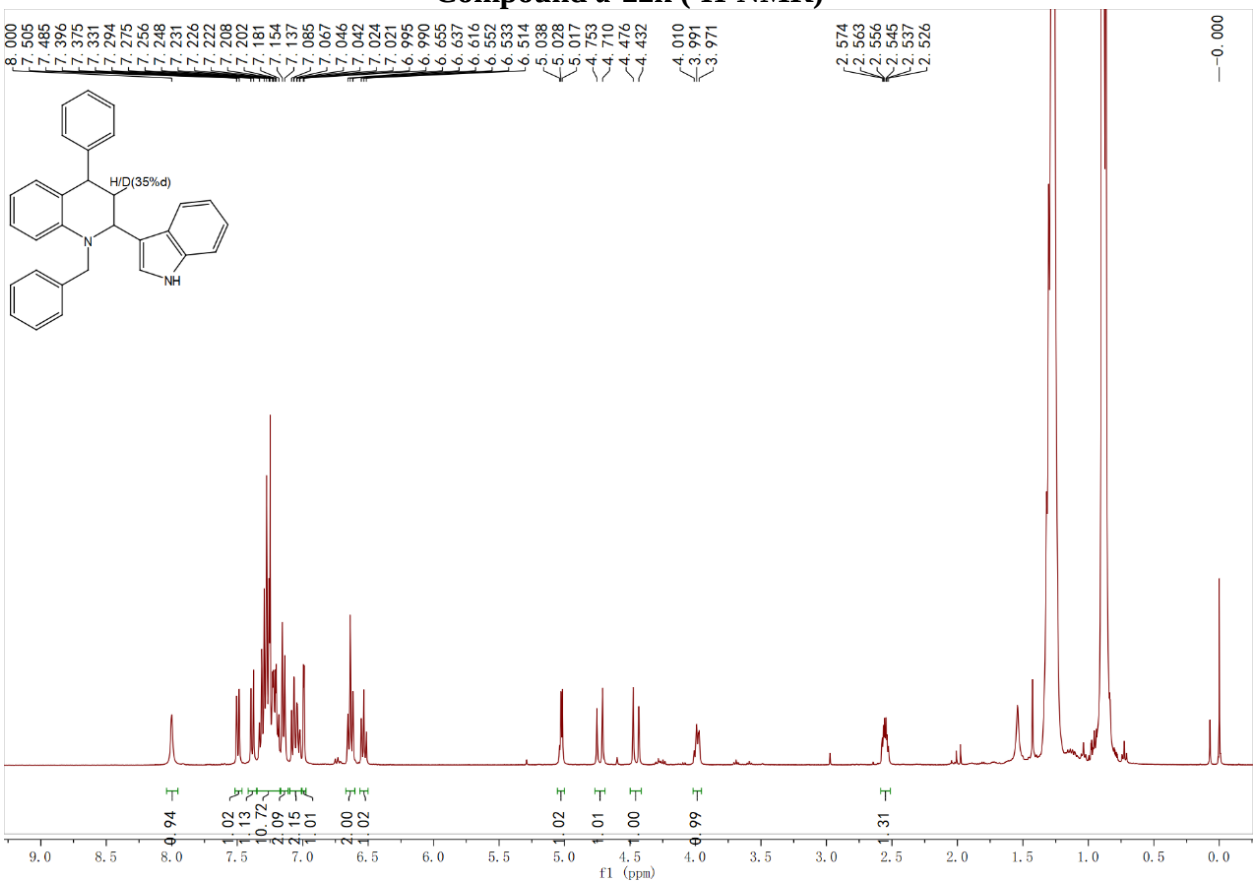
Compound *d*-1a (^{1}H-NMR)



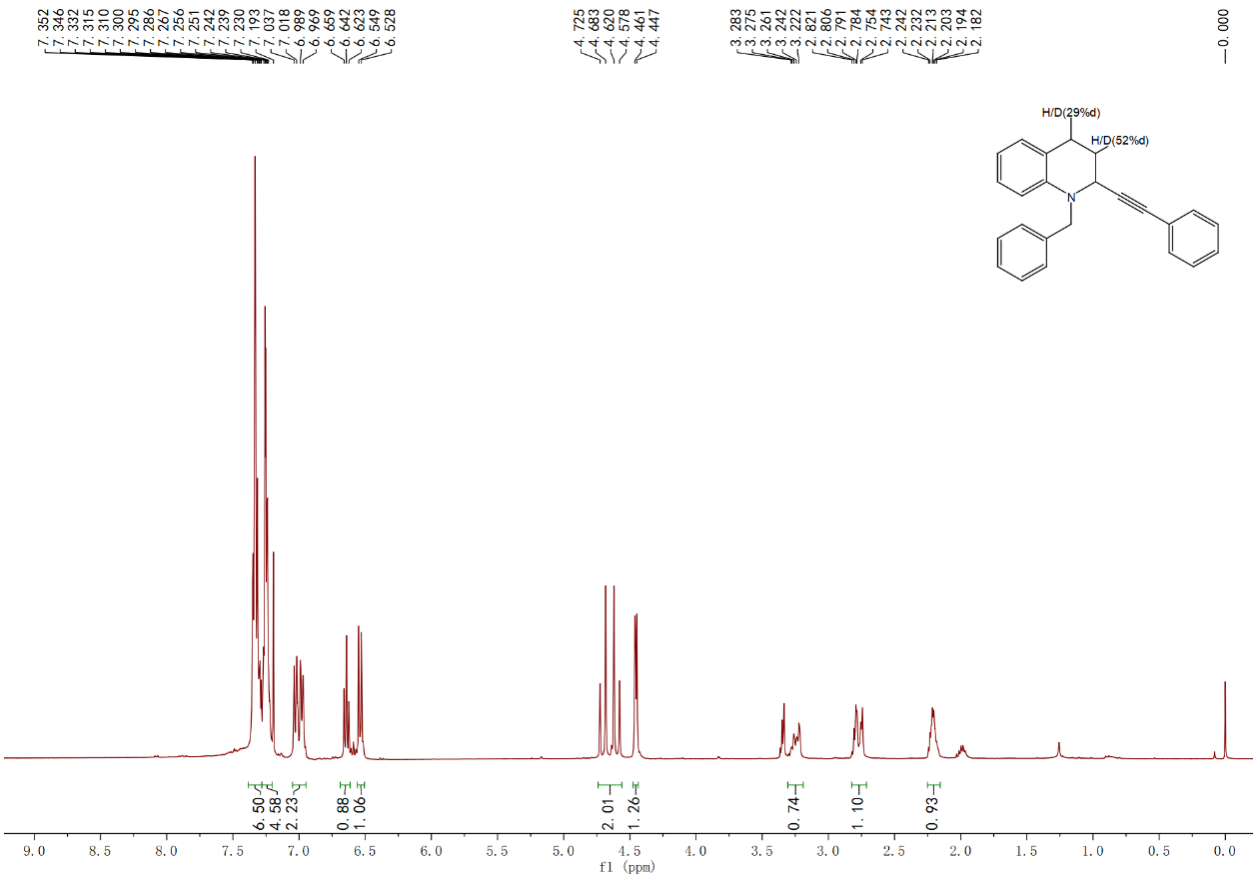
_N_-Benzyl-2-(3-indolyl)-4-phenyl-1,2,3,4-tetrahydroquinoline 22k (^{1}H-NMR)



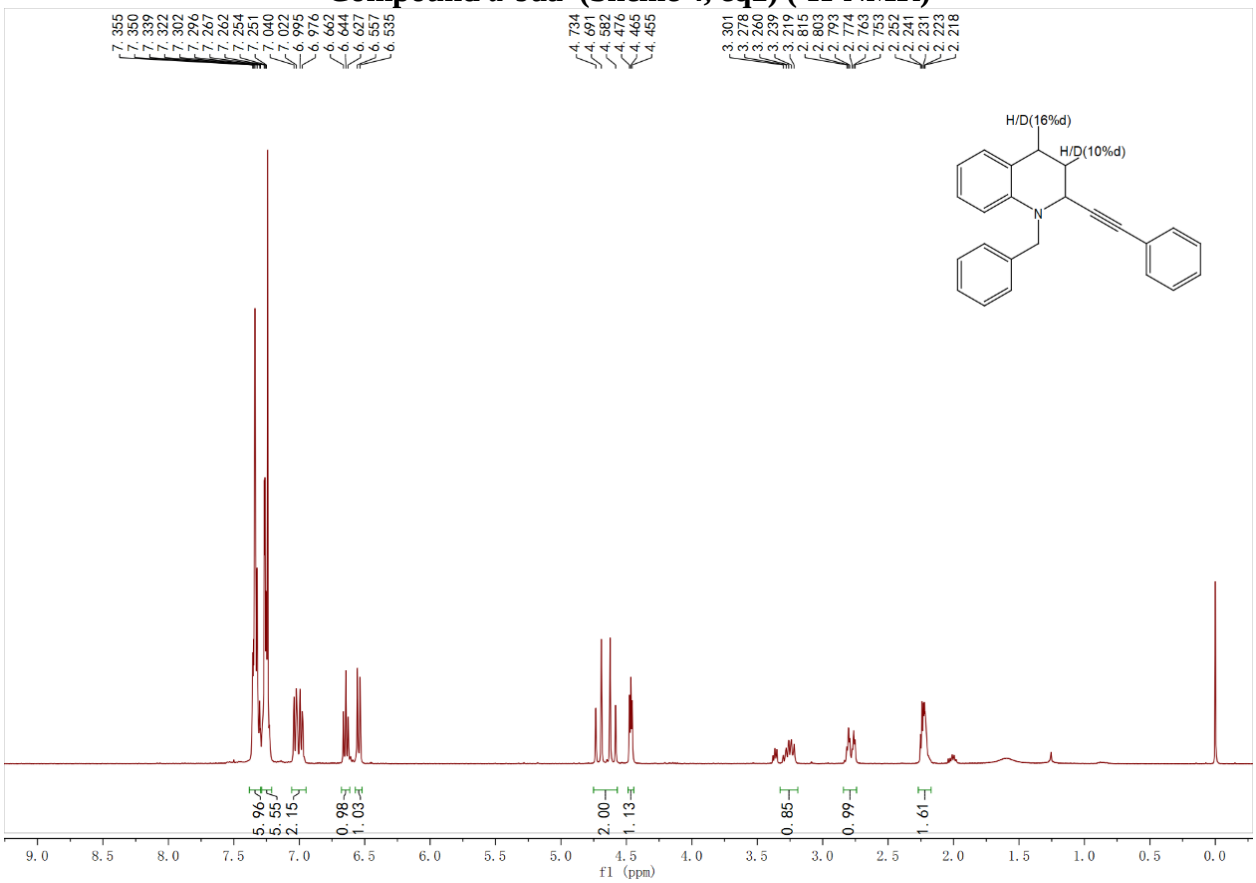
Compound _d_-22k (^{1}H-NMR)



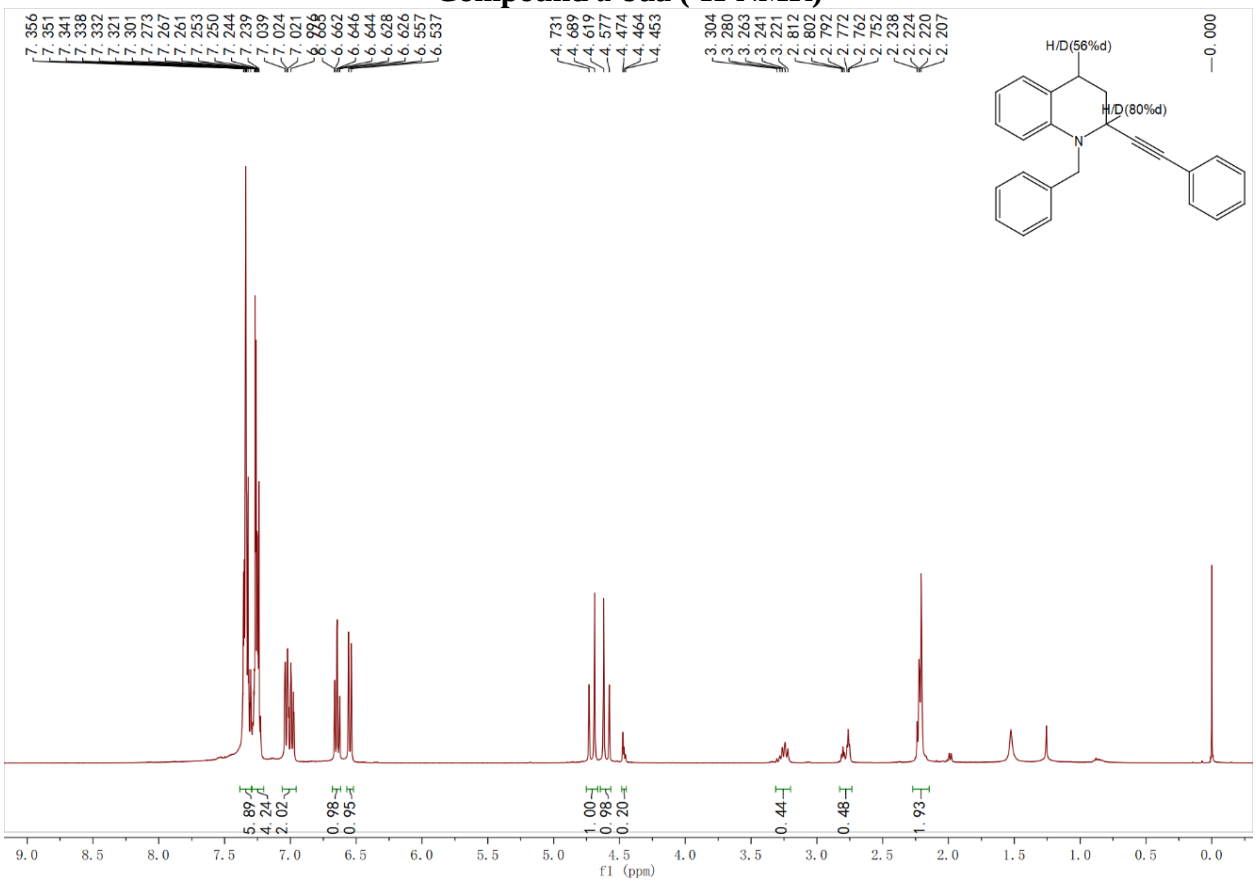
Compound _d_-9aa (^{1}H-NMR)



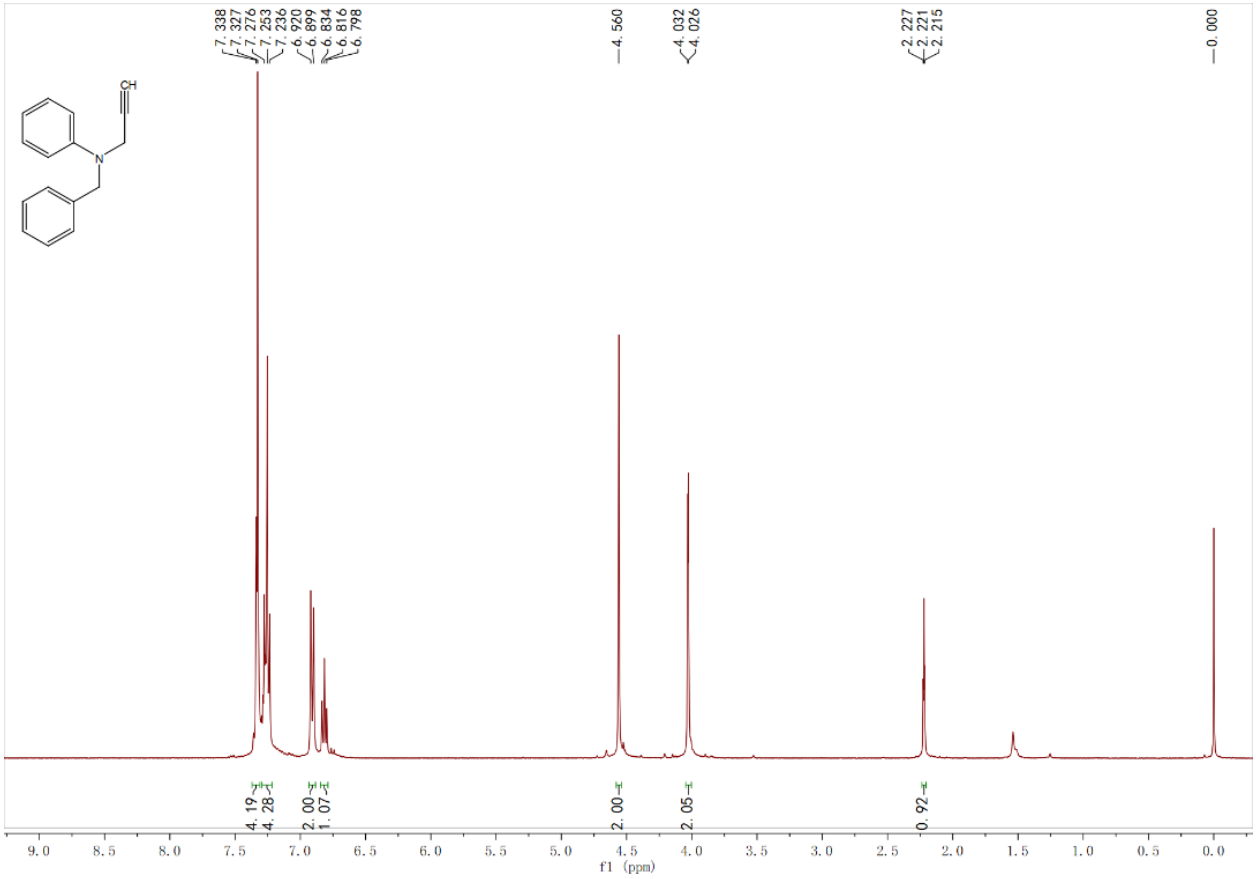
Compound *d*-9aa (Sheme 4, eq2) (^{1}H-NMR)



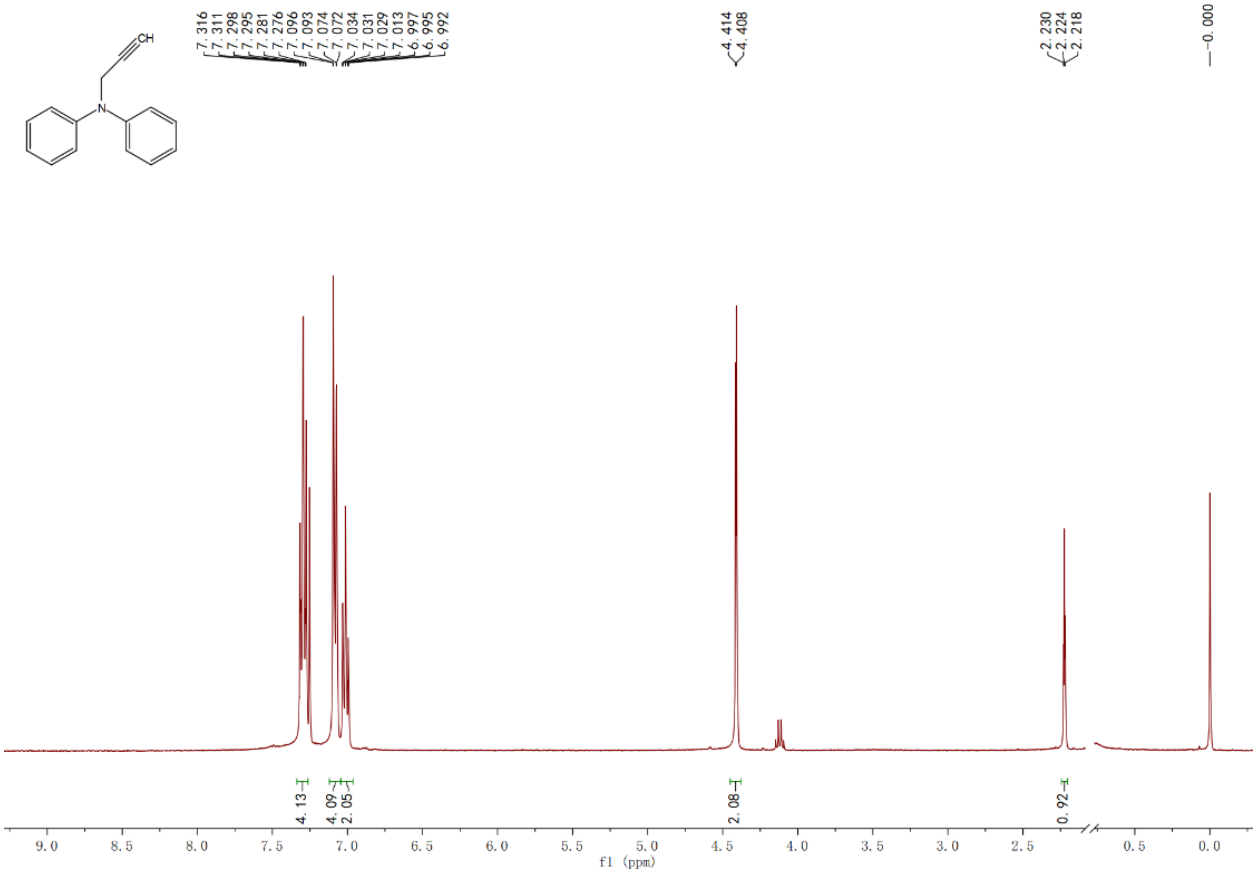
Compound *d*-9aa (^{1}H-NMR)



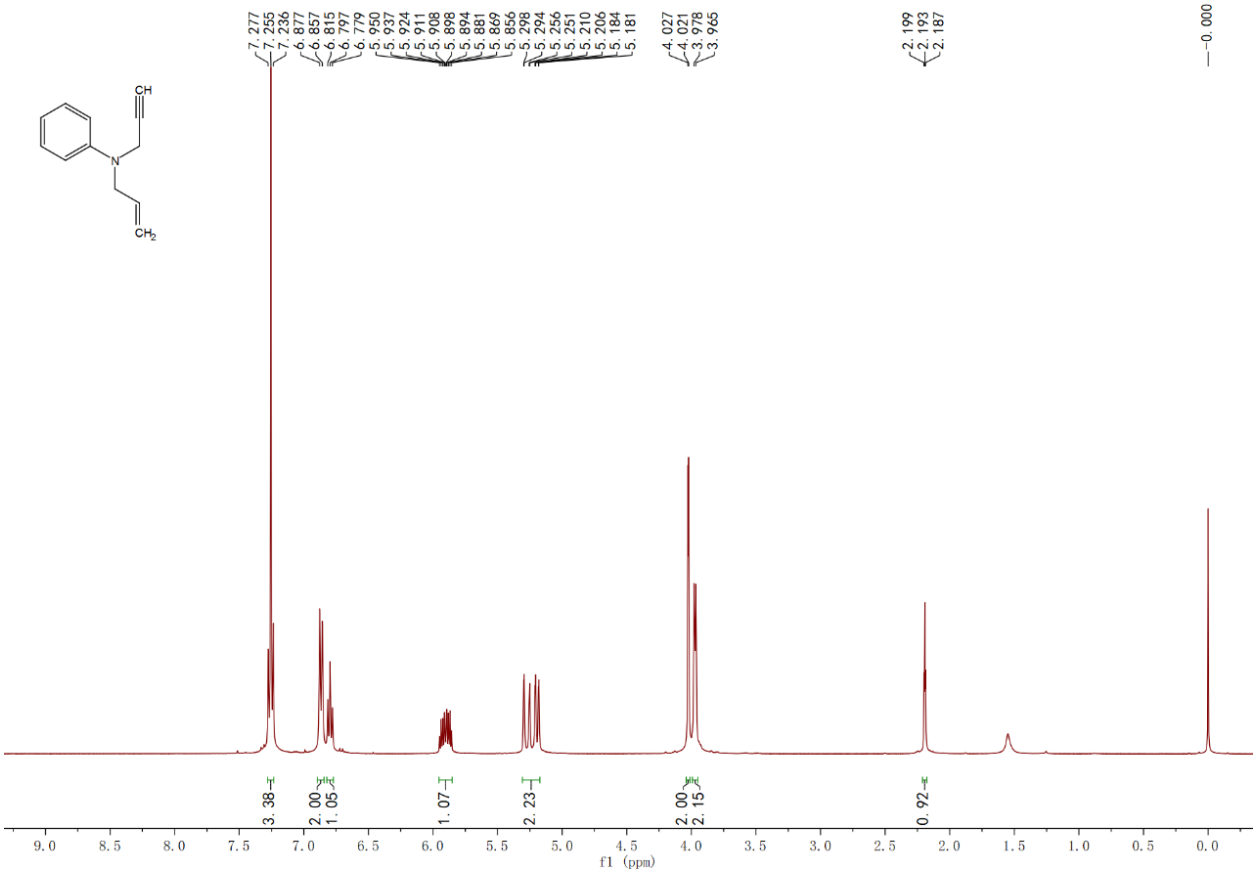
***N*-Benzyl-*N*-(2-propynyl)aniline 1a (^{1}H-NMR)**



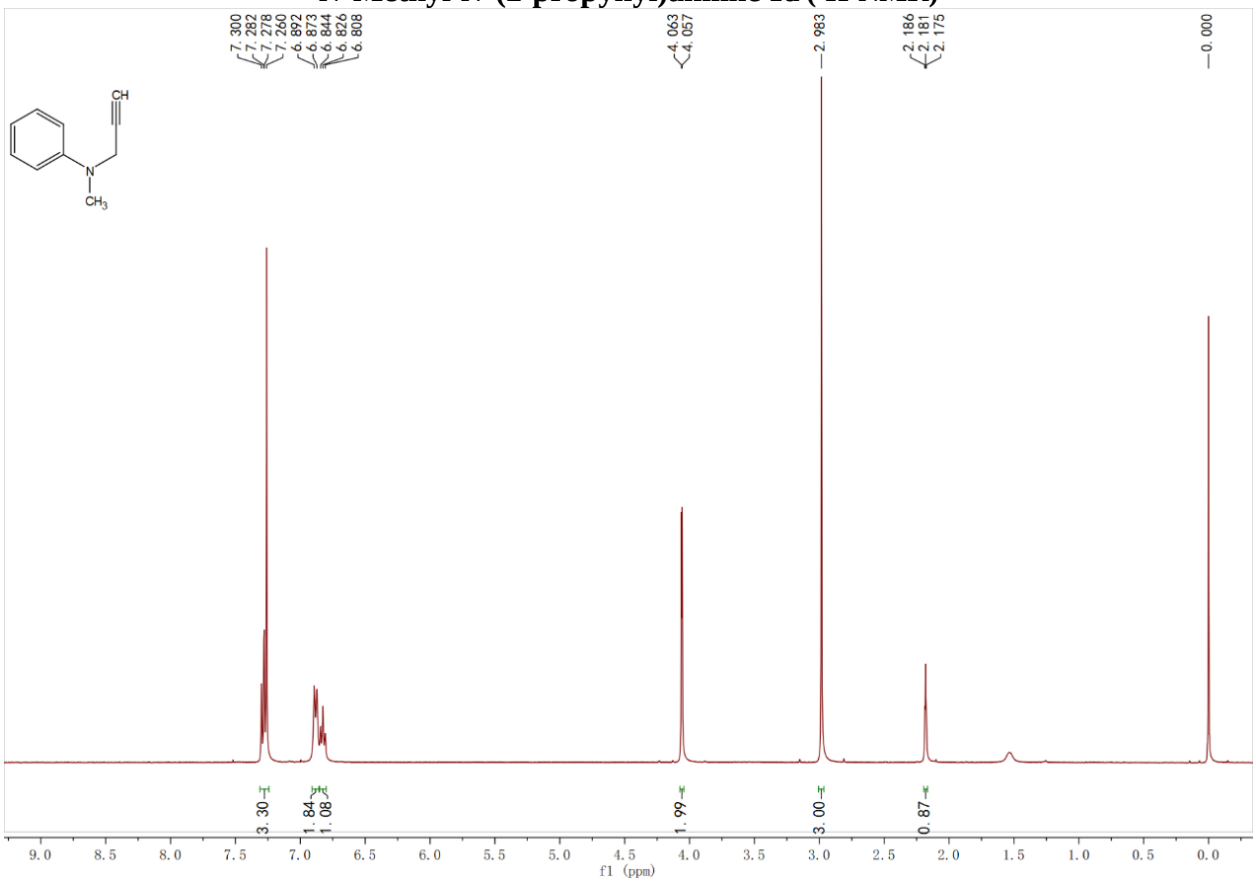
N-Phneyl-*N*-(2-propynyl)aniline 1b (^{1}H-NMR)



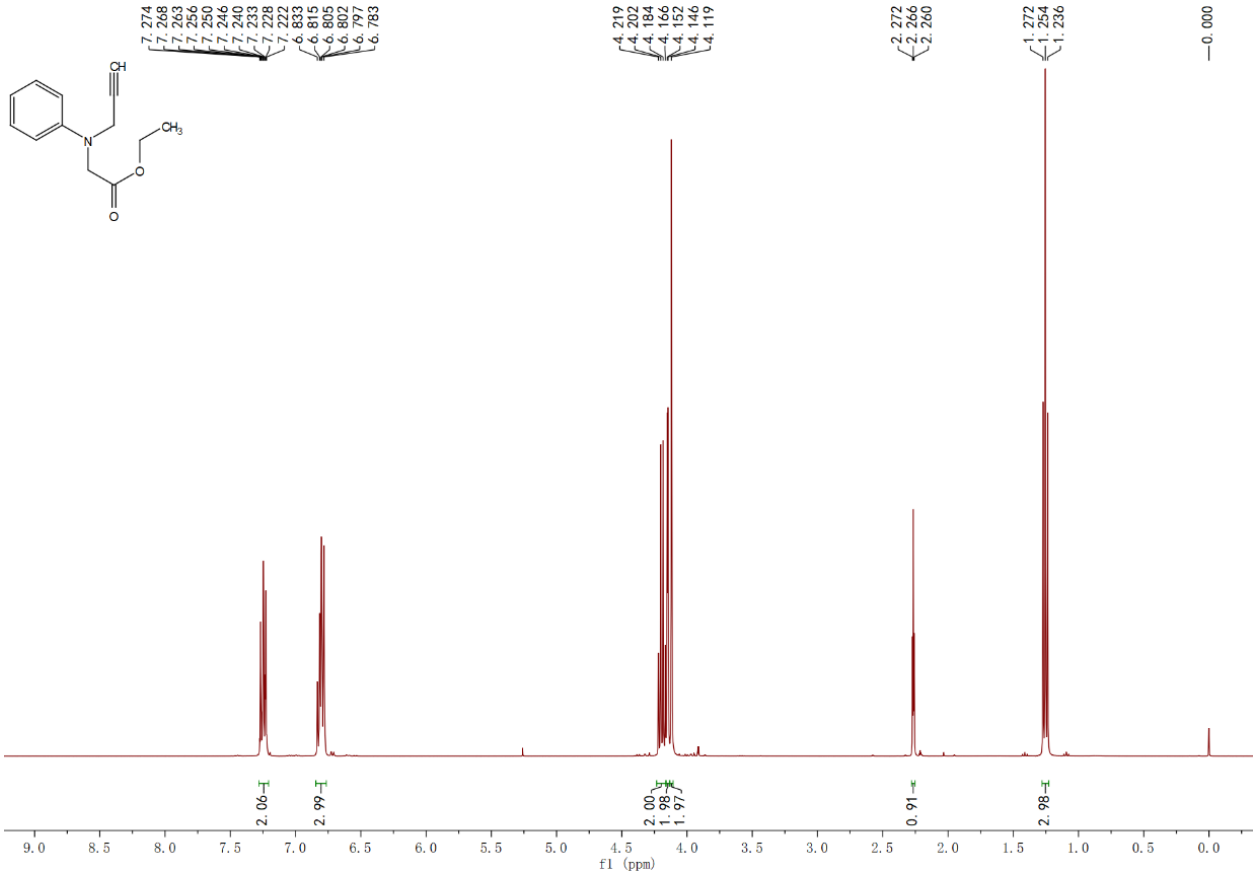
N-Allyl-*N*-(2-propynyl)aniline 1c (^{1}H-NMR)



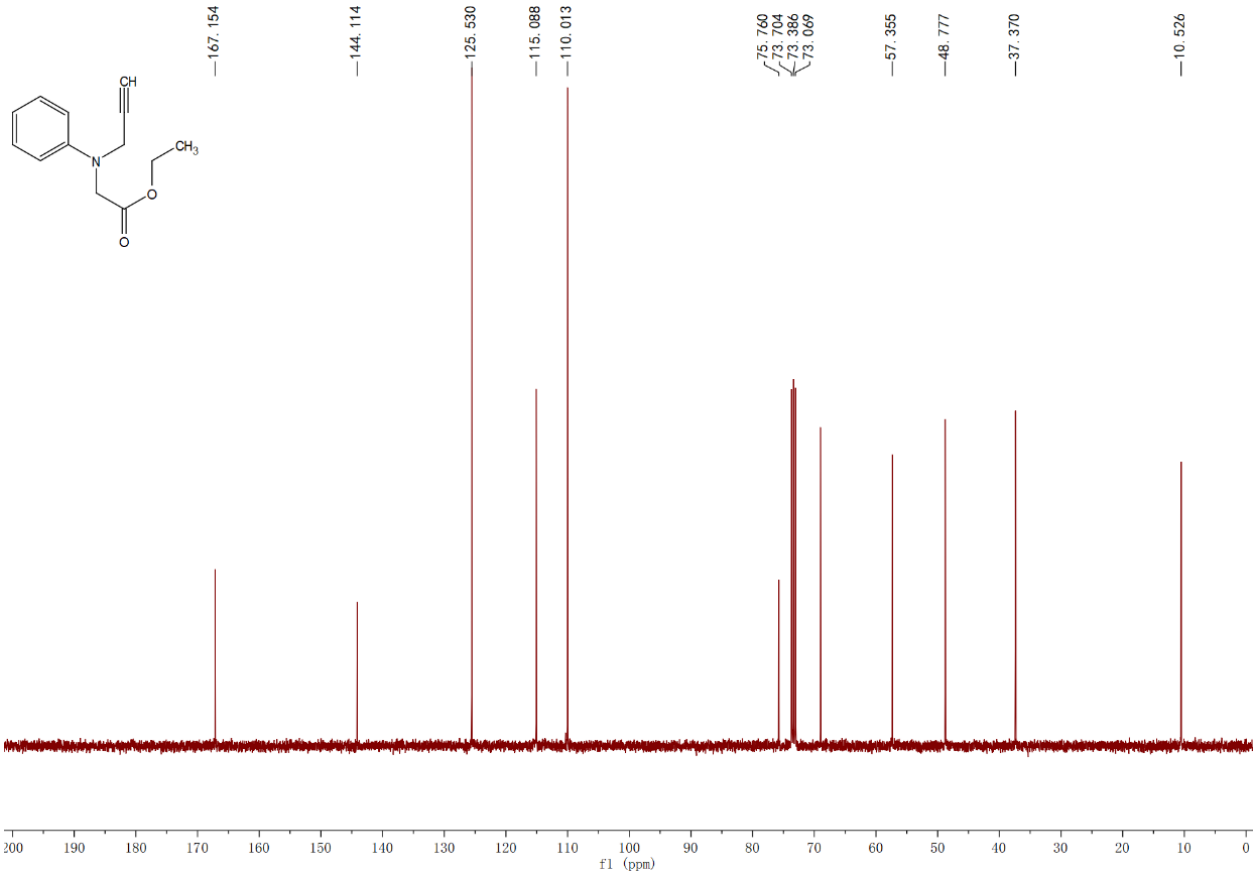
_N_-Methyl-_N_-(2-propynyl)aniline 1d (^{1}H-NMR)



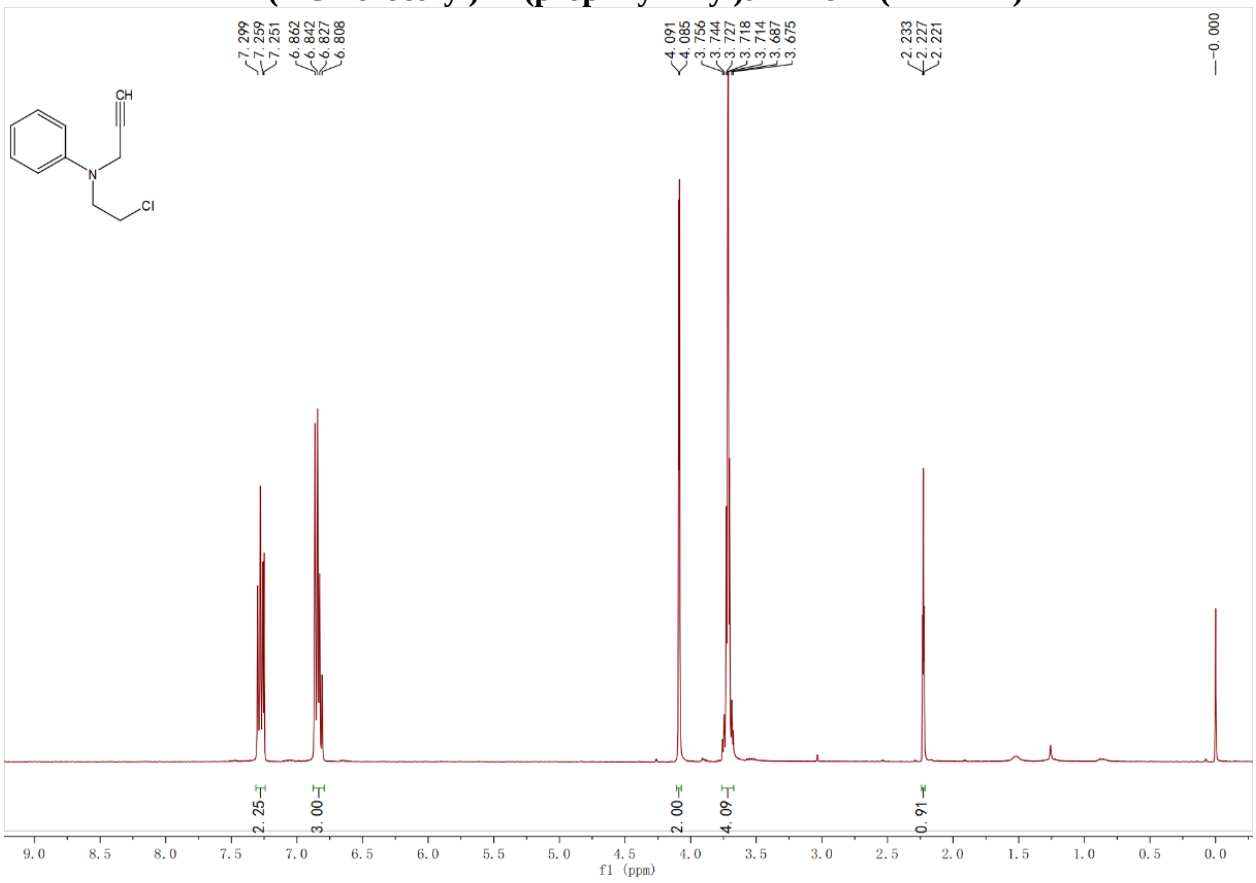
Ethyl-_N_-phenyl-_N_-(prop-2-yn-1-yl)glycinate 1e (^{1}H-NMR)



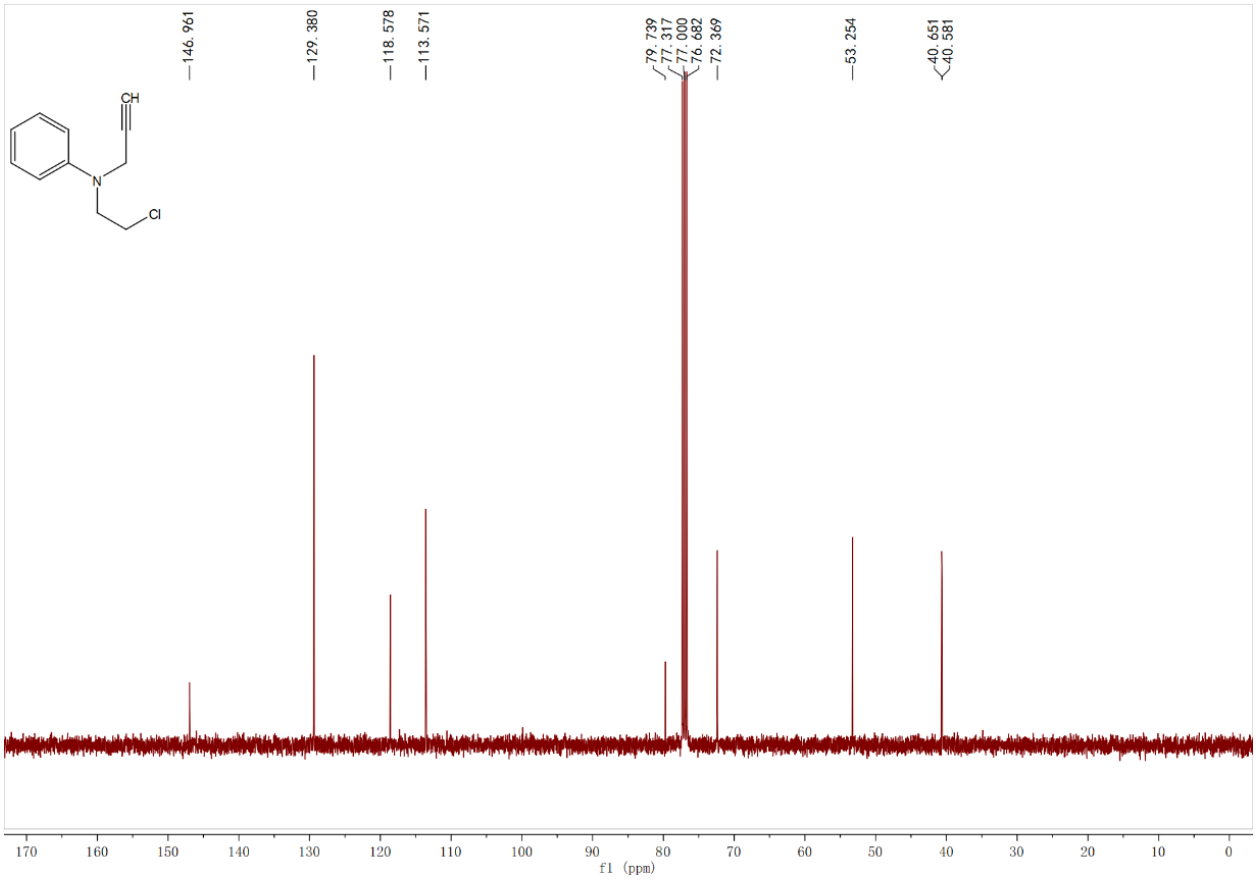
Ethyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)glycinate 1e (^{13}C-NMR)



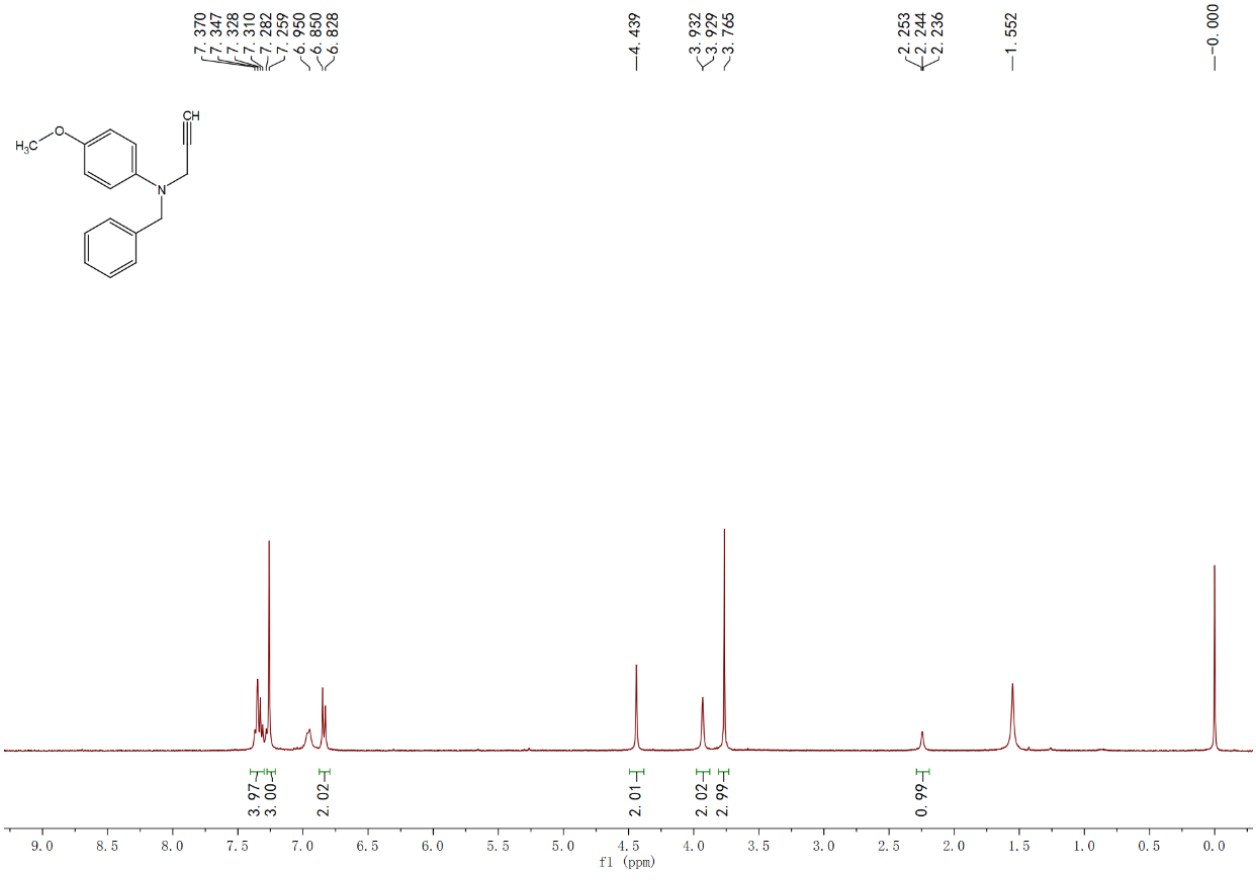
N-(2-Chloroethyl)-*N*-(prop-2-yn-1-yl)aniline 1f (^{1}H-NMR)



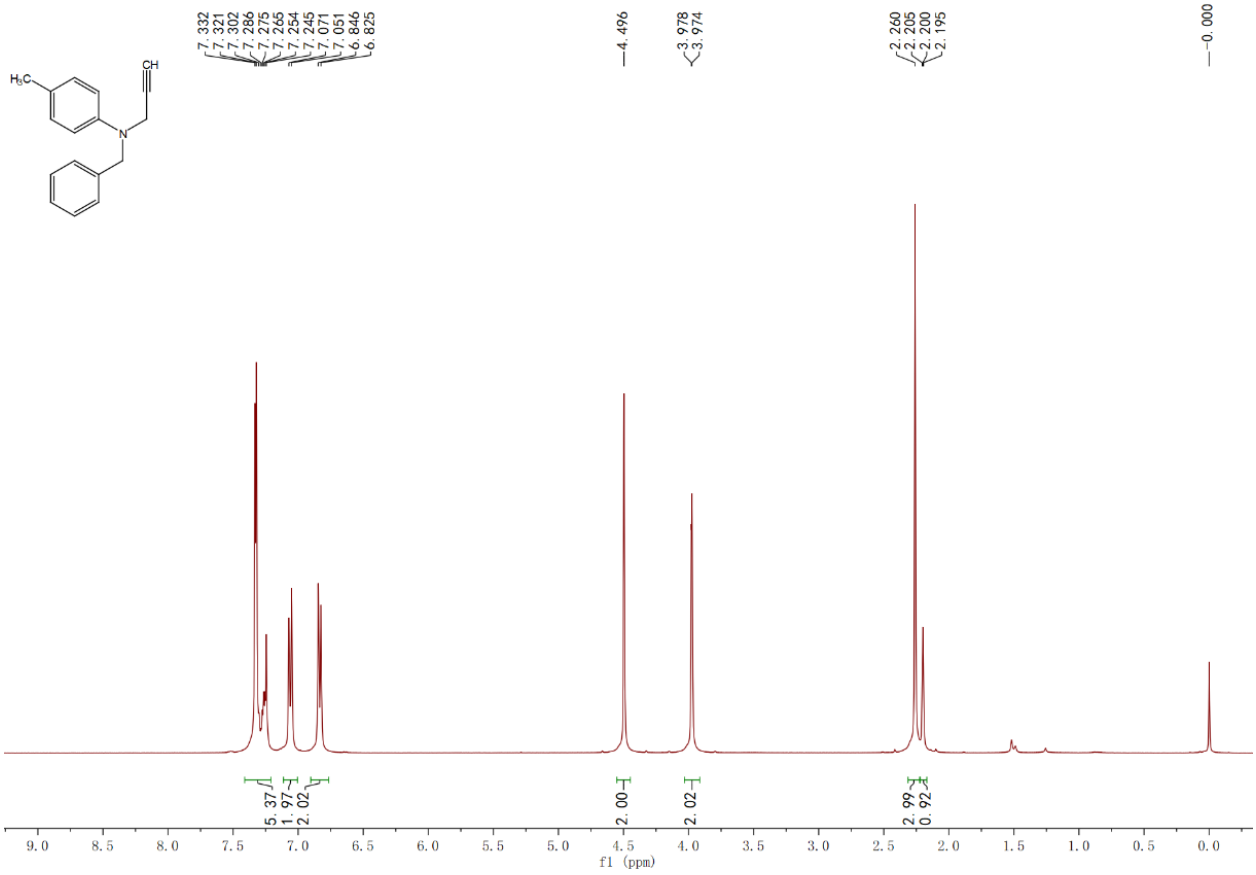
N-(2-Chloroethyl)-*N*-(prop-2-yn-1-yl)aniline 1f (^{13}C-NMR)



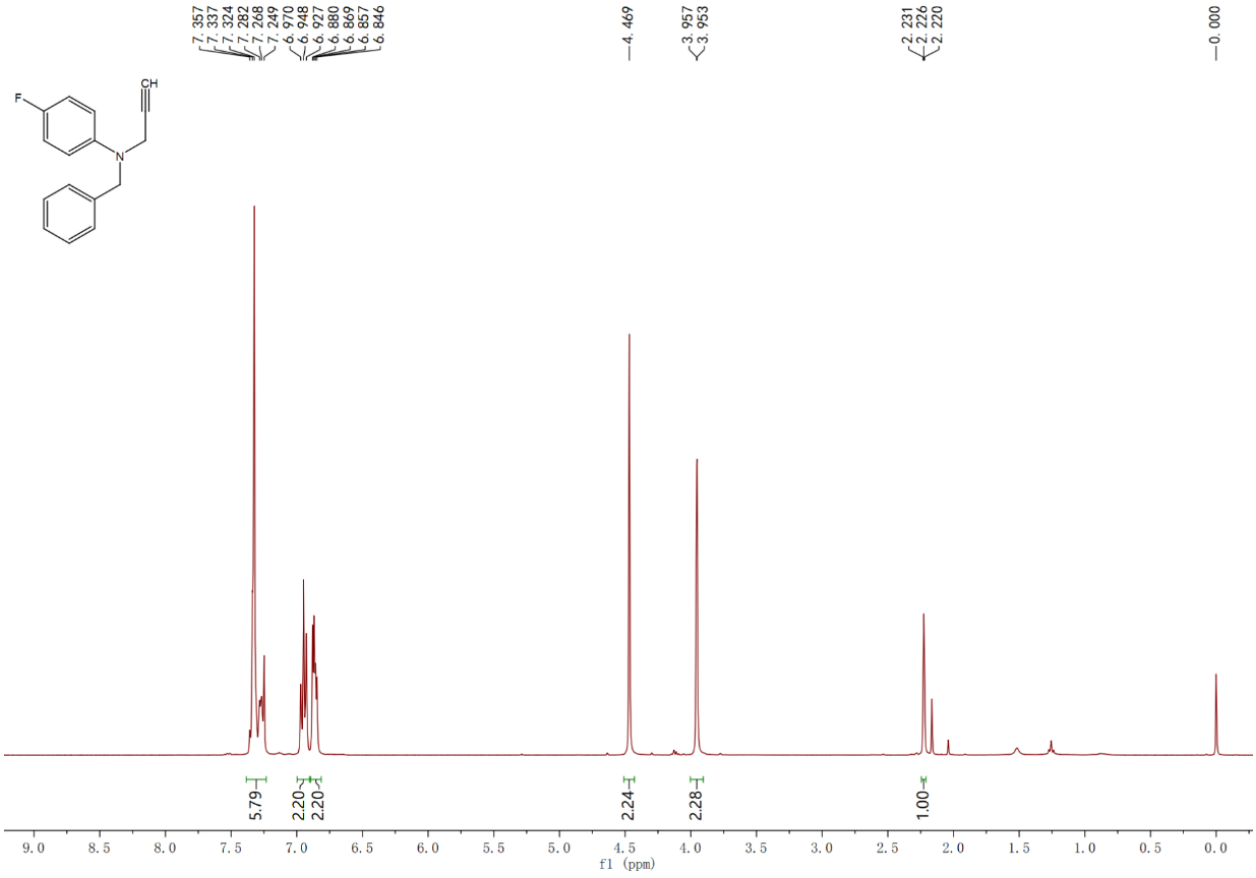
4-Methoxyl-*N*-benzyl-*N*-(2-propynyl)aniline 1g (^{1}H-NMR)



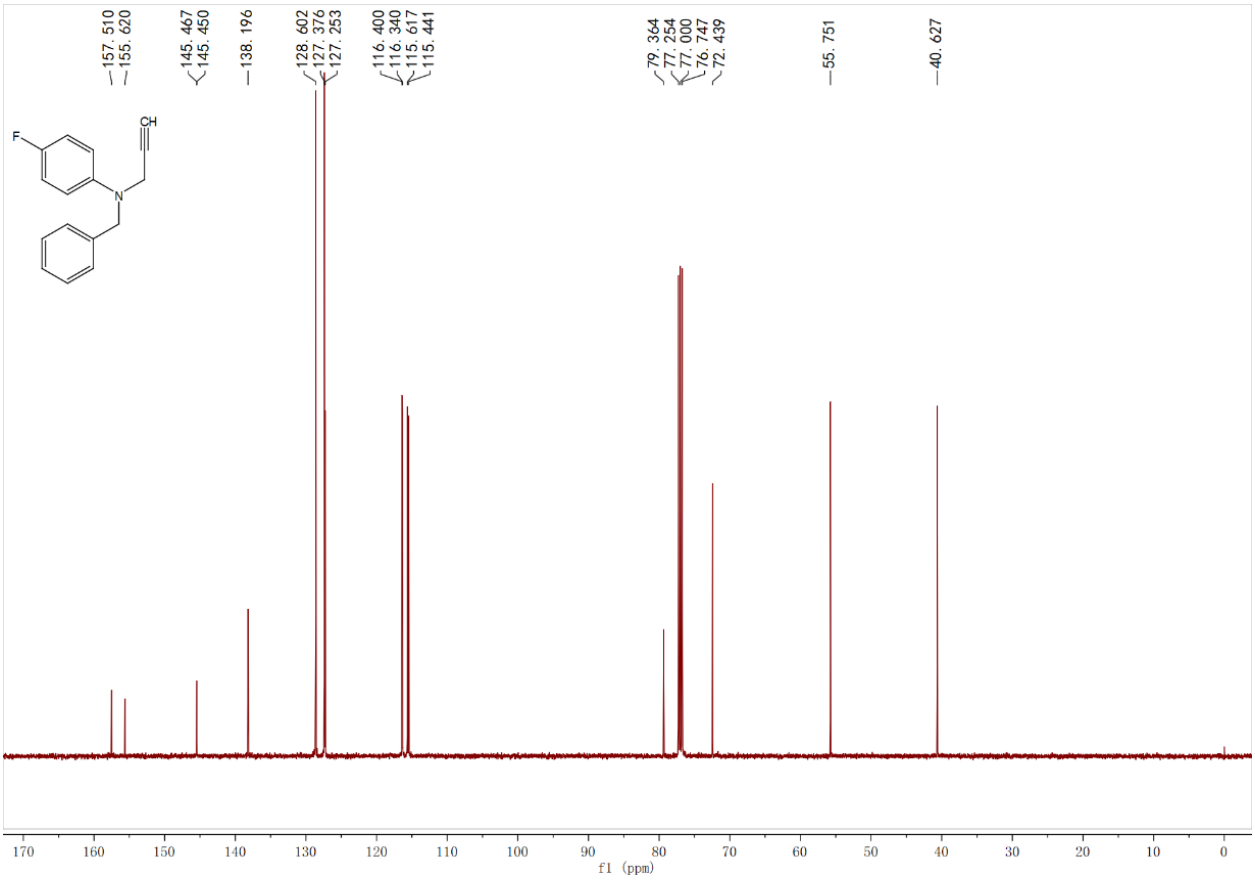
4-Methyl-*N*-benzyl-*N*-(2-propynyl)aniline 1h (^{1}H-NMR)



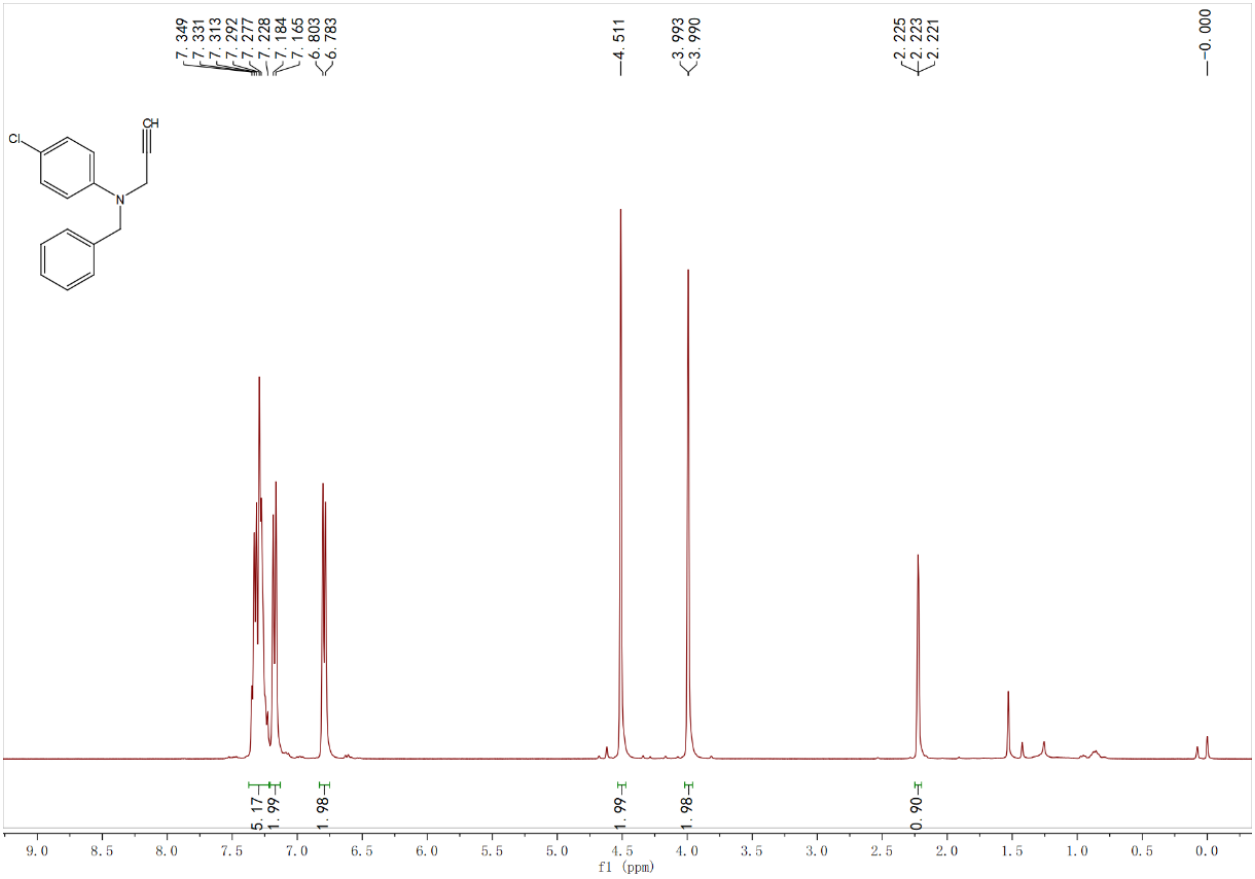
4-Fluoro-*N*-benzyl-*N*-(2-propynyl)aniline 1i (^{1}H-NMR)



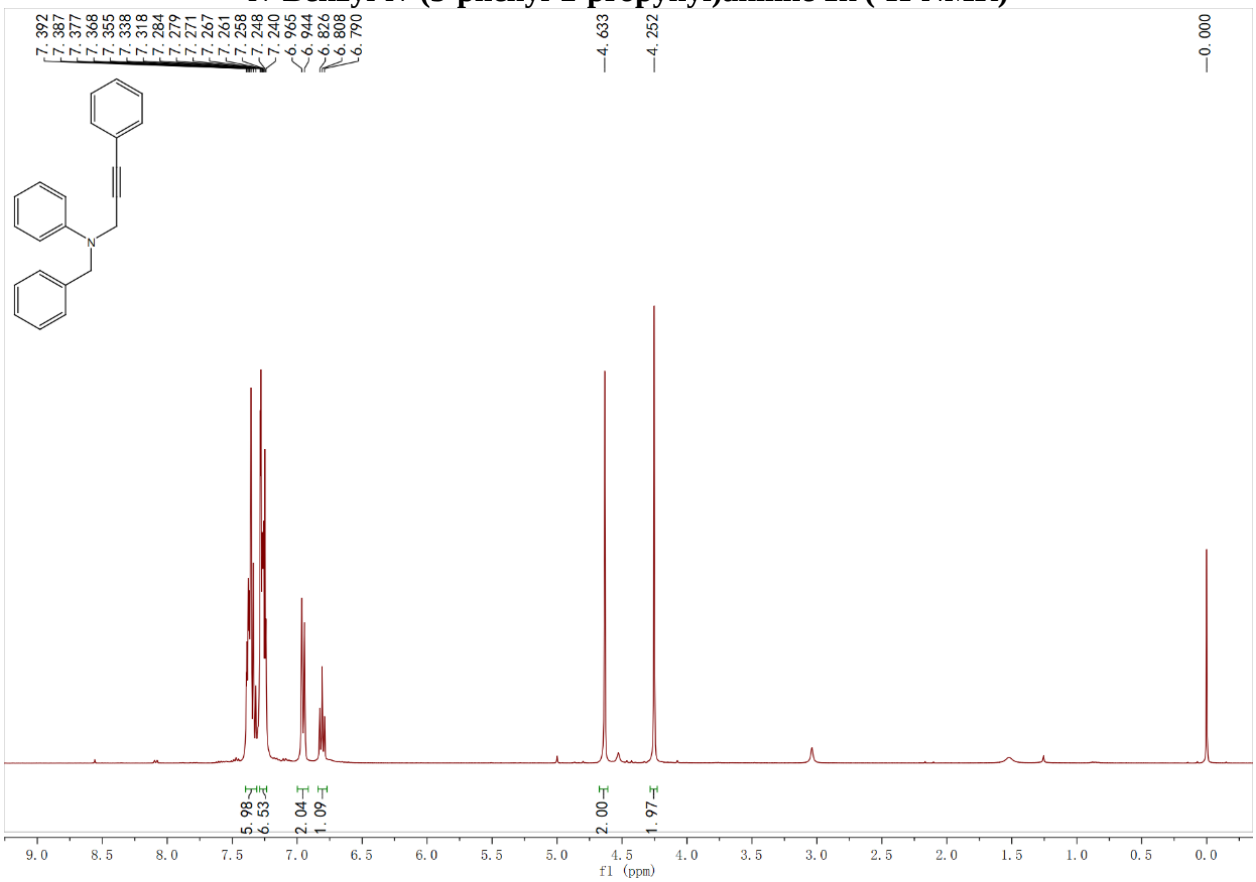
4-Fluoro-*N*-benzyl-*N*-(2-propynyl)aniline 1i (^{13}C-NMR)



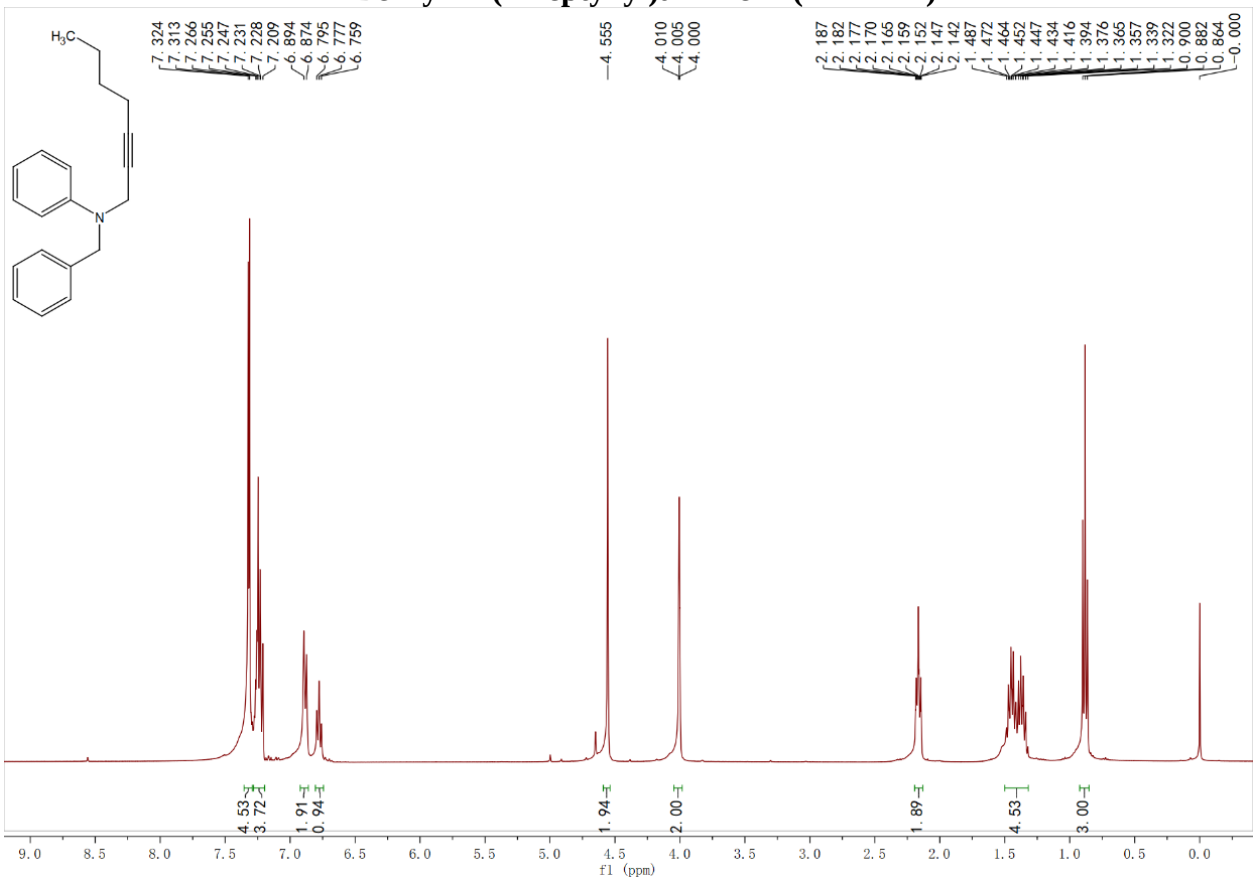
4-Chloro-*N*-benzyl-*N*-(2-propynyl)aniline 1j (^{1}H-NMR)



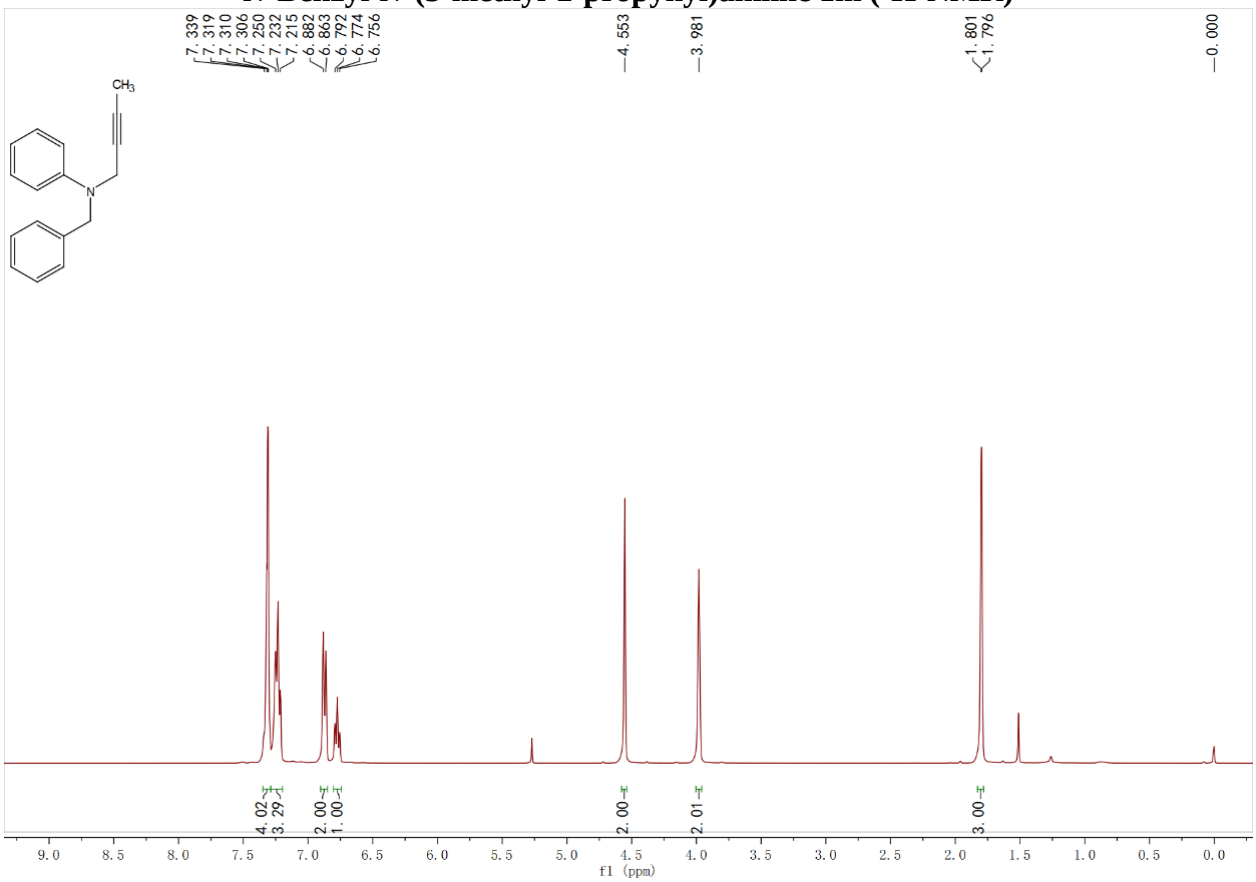
_N_-Benzyl-_N_-(3-phenyl-2-propynyl)aniline 1k (^{1}H-NMR)



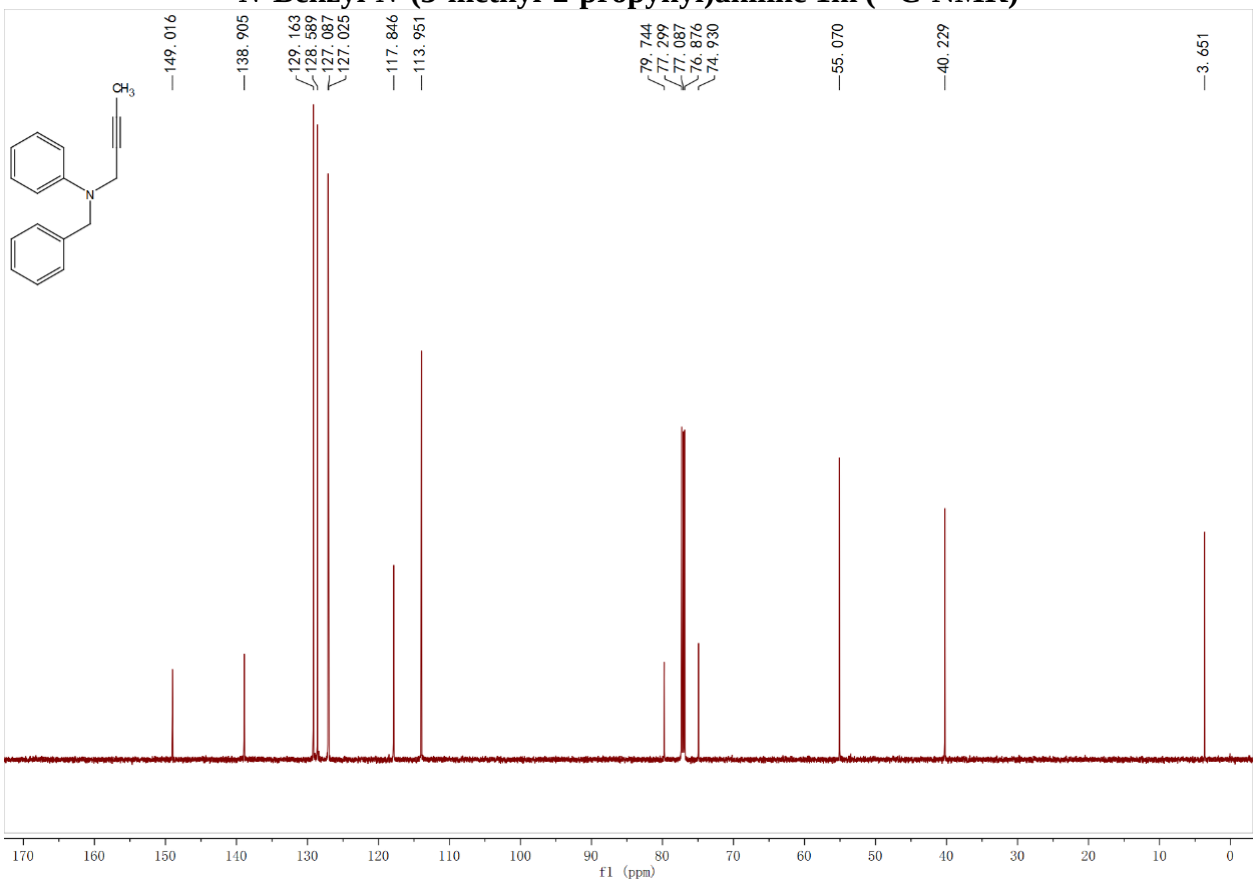
_N_-Benzyl-_N_-(2-heptynyl)aniline 1l (^{1}H-NMR)



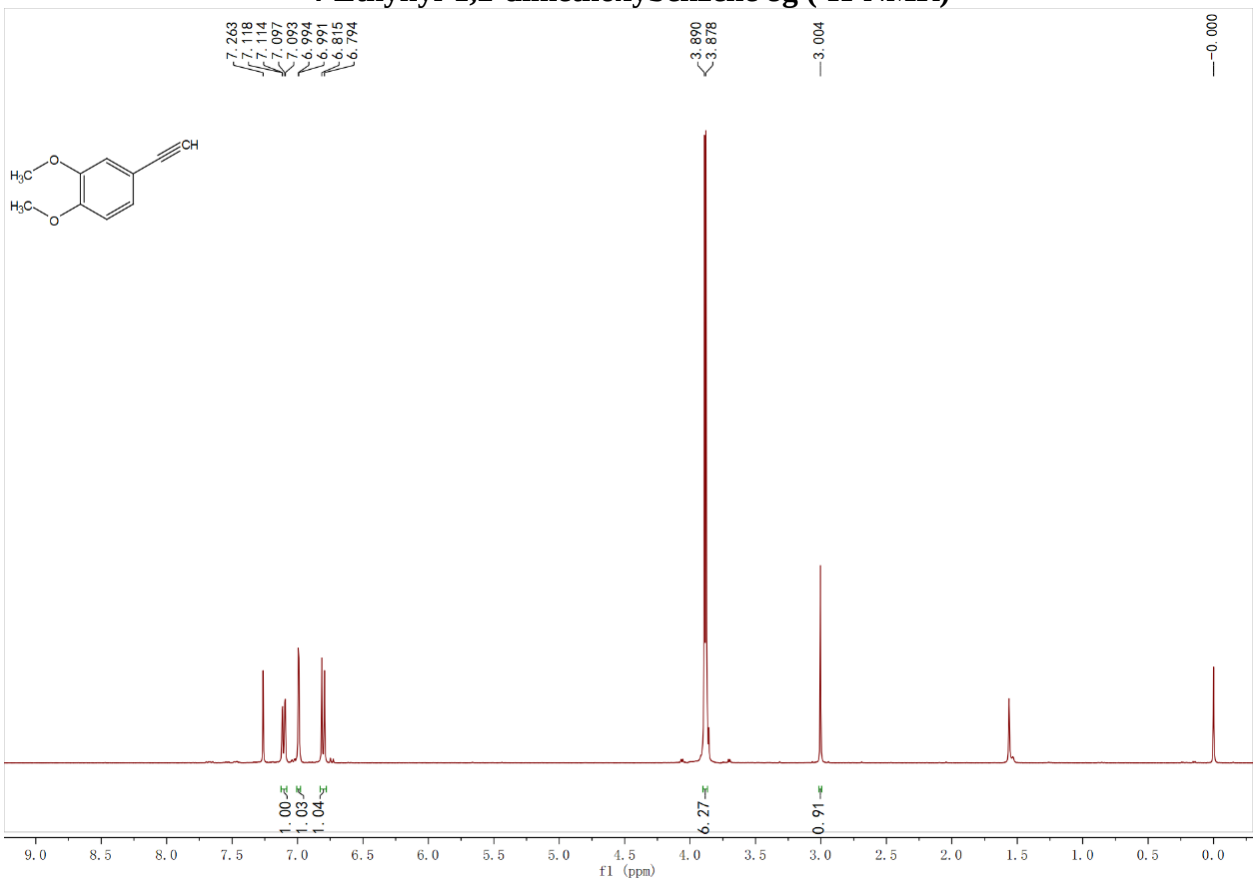
N-Benzyl-*N*-(3-methyl-2-propynyl)aniline 1m (^{1}H-NMR)



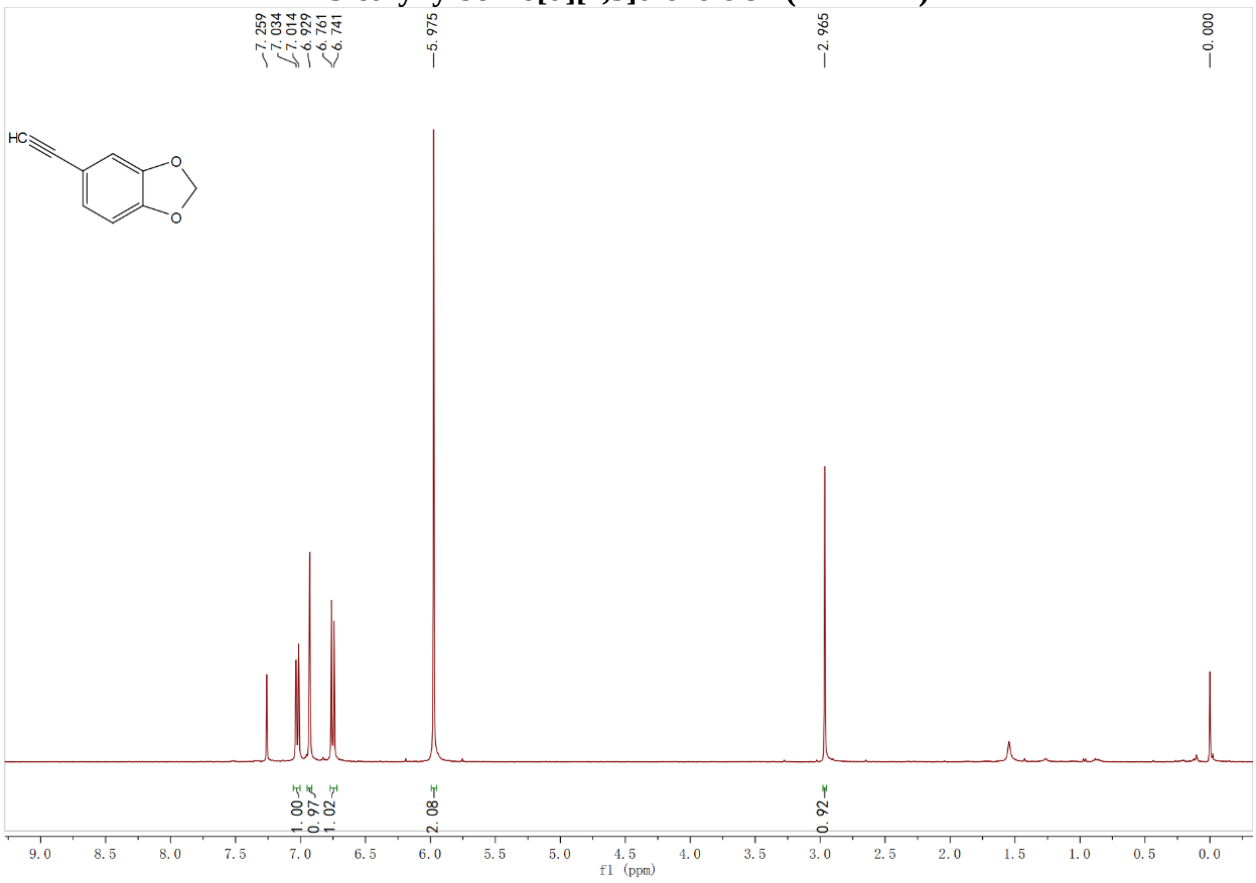
N-Benzyl-*N*-(3-methyl-2-propynyl)aniline 1m (^{13}C-NMR)



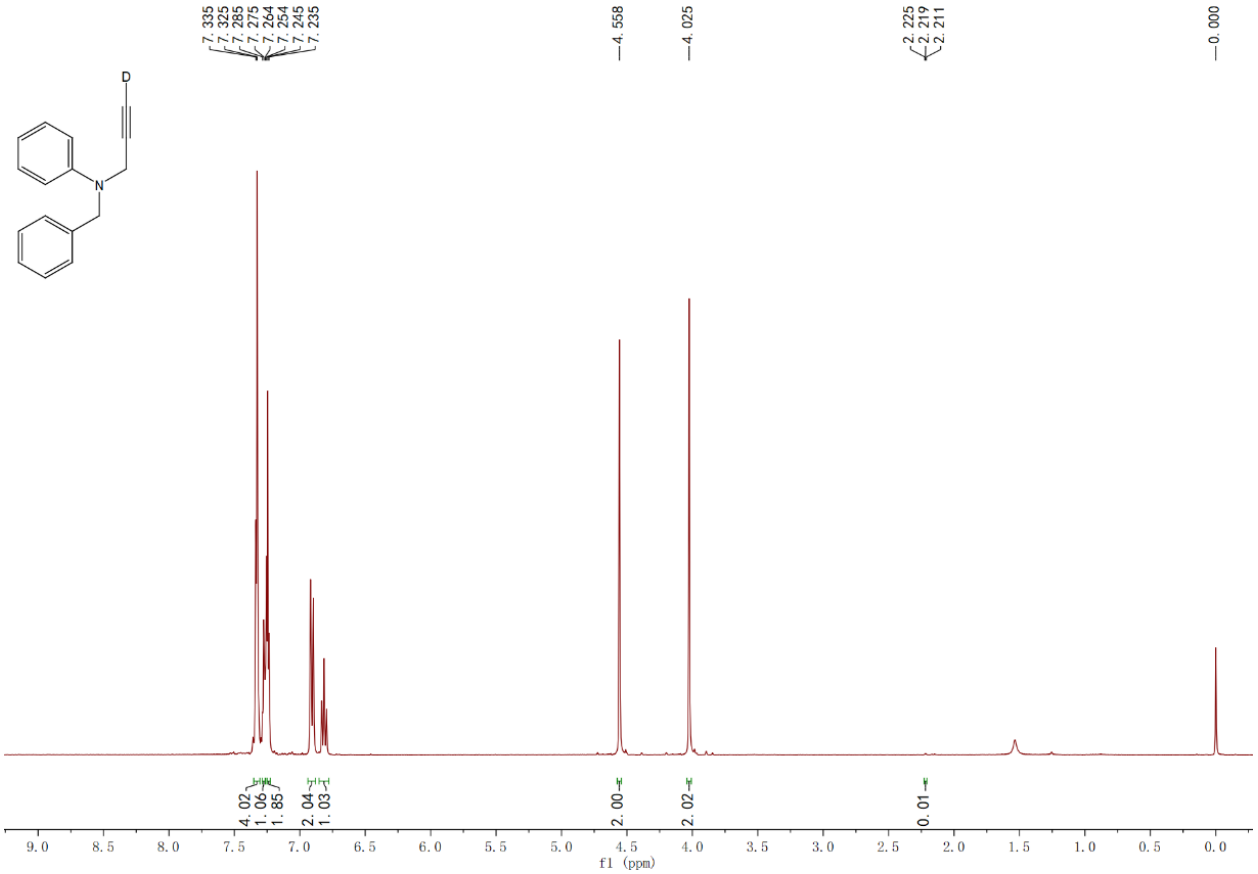
4-Ethynyl-1,2-dimethoxybenzene 8g (^{1}H-NMR)



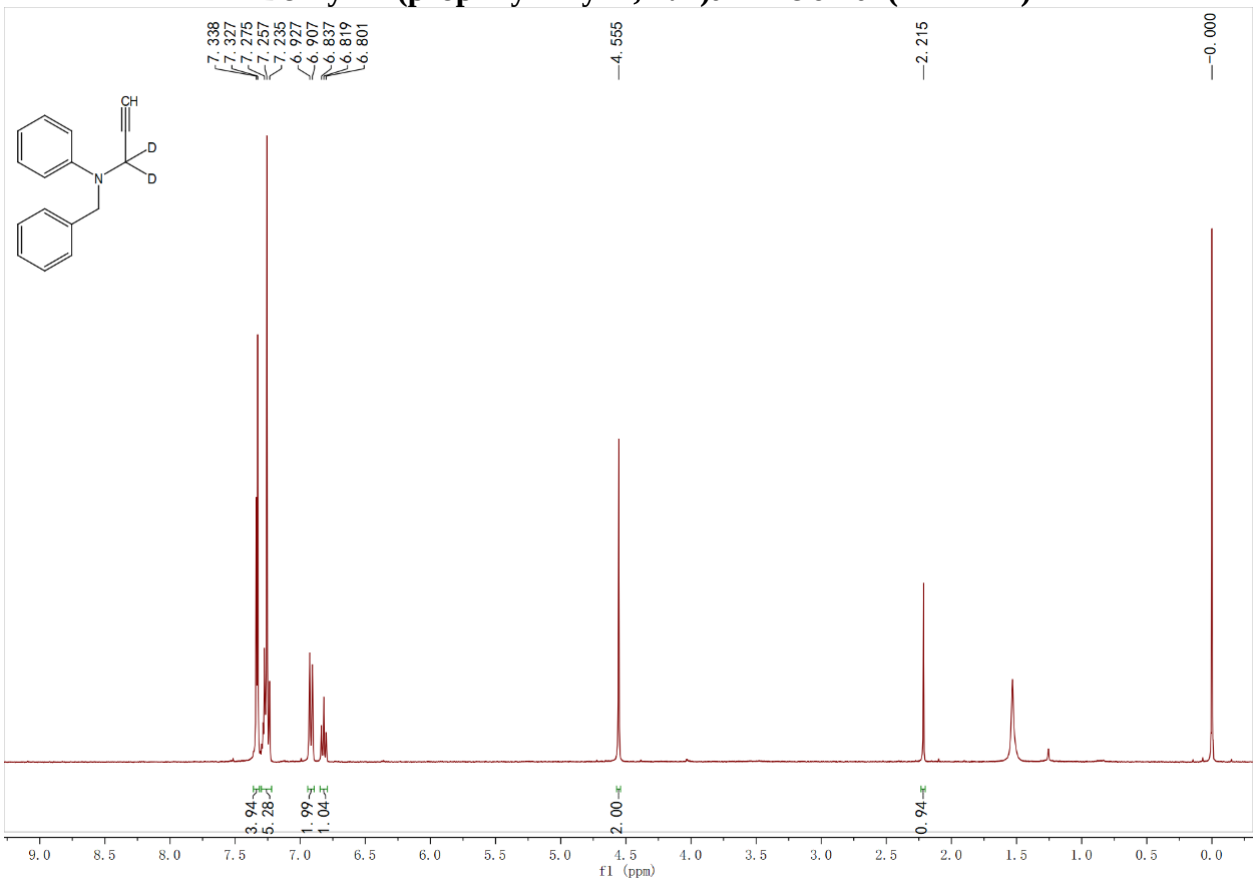
5-ethynylbenzo[d][1,3]dioxole 8h (^{1}H-NMR)



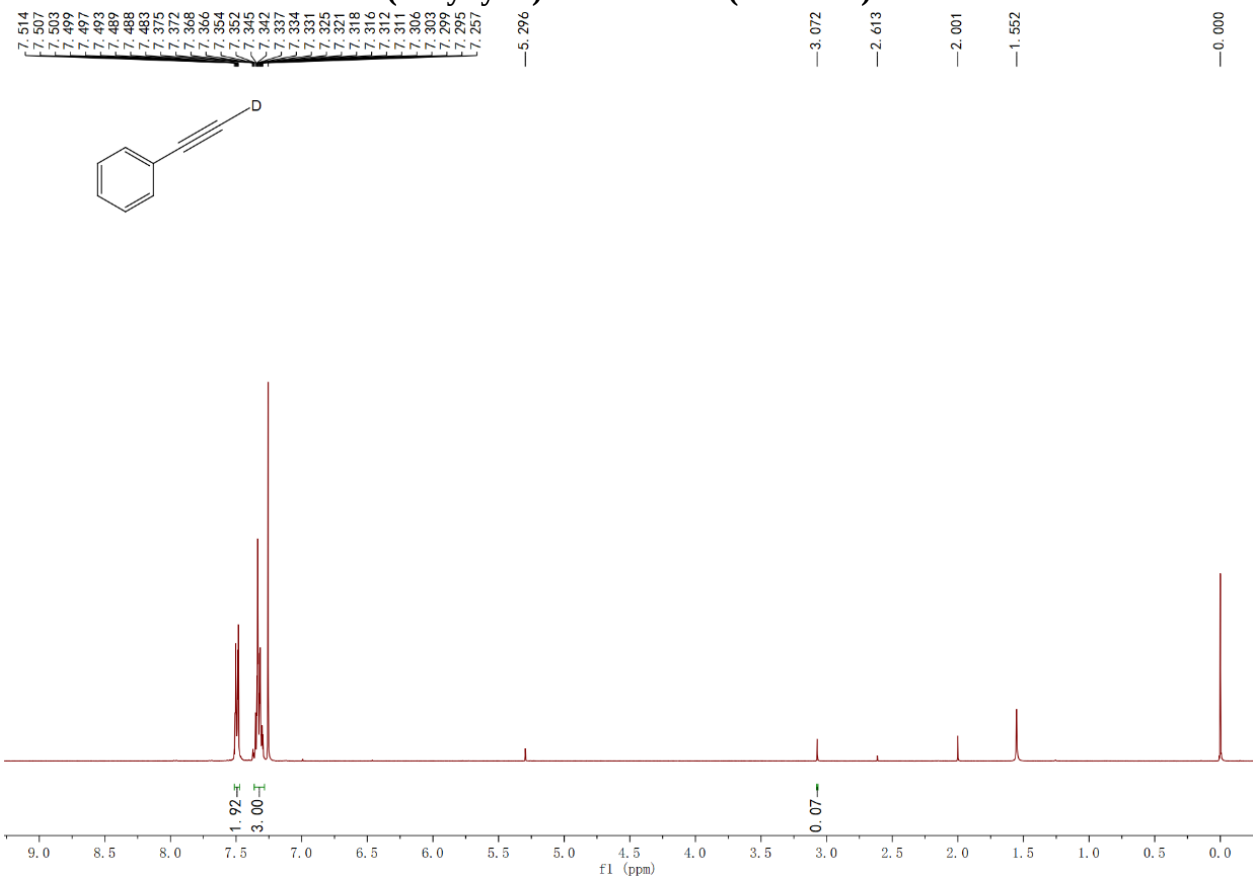
_N_-Benzyl-_N_-(prop-2-yn-1-yl-3-_d_)aniline _d_-1a (^{1}H-NMR)



_N_-Benzyl-_N_-(prop-2-yn-1-yl-1,1-_d2_)aniline d-1a′ (^{1}H-NMR)



(Ethynyl-*d*)benzene *d*-8a (^{1}H-NMR)



[3- ^{2}H] Indole *d*-13 (^{1}H-NMR)