Supporting Information

Iridium-Catalysed Reductive Beta-alkyltion of (Iso)quinoline Derivatives by an In-situ Enone-trapping Strategy

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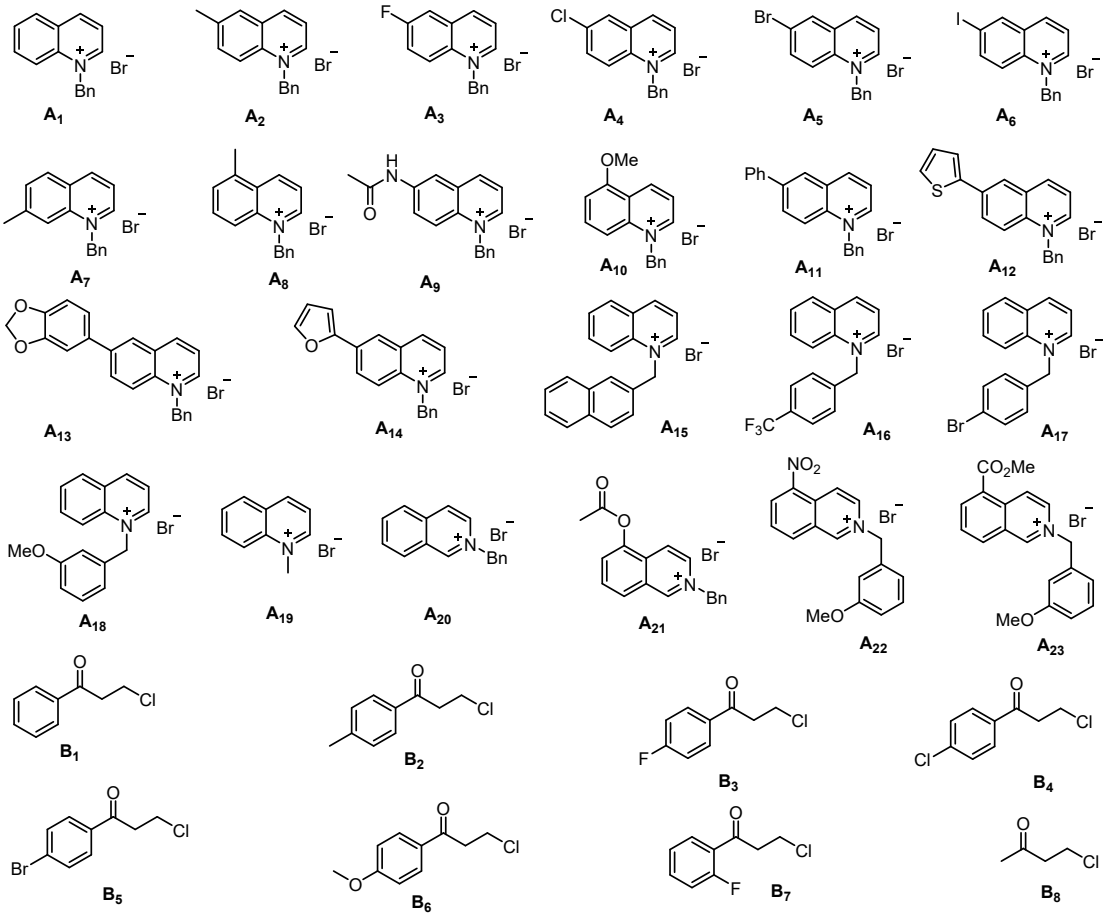
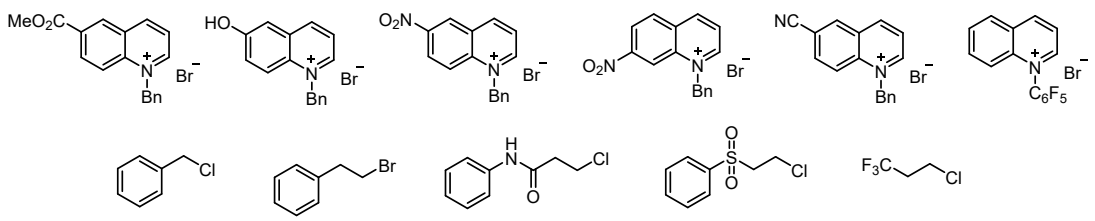
General information

All the obtained products were characterized by melting points (m.p.), ^{1}H NMR, ^{13}C NMR and mass spectra (MS). Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 or Bruker-500 and referenced to 7.26 ppm for chloroform solvent or 2.54 ppm for dimethyl sulfoxide solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 600 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Unless otherwise stated, all the reagents were purchased from commercial sources, used without further purification. Moreover, the N-heteroareniums are named as $\mathbf{A_x}$ (Synthesised according to literature)[1], the chloralkane are named as $\mathbf{B_x}$, and the obtained final products are named as $\mathbf{C_x}$.

successful substrates:



unsuccessful substrates:

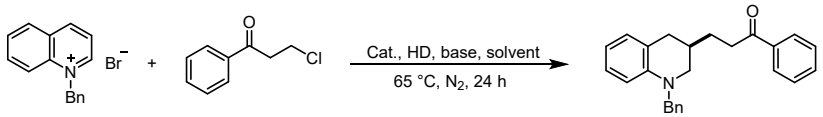


Scheme S1. Substrates employed for the reaction

Typical procedure for the synthesis of C

(Iso)quinolinium salts (0.2mmol), chloroalkyl ketone (0.28 mmol), $[IrCp^*Cl_2]_2$ (0.002 mmol), $Mg(OMe)_2$ (1.5 eq), $(CH_2O)_n$ (3 eq) and KI (2 eq) were added to a 50 mL Schlenk tube. After charging N_2 for three times, 1mL methanol was added and the tube was then closed. The resulting mixture which was stirred at 65 ℃ for 24 h. After cooling down to room temperature, the reaction mixture was concentrated under vacuum, and nitromethane (0.2 mmol) was added as the internal standard to calculate ^1H NMR yield. (Some products were isolated by preparative TLC on silica)

Table S1. Optimization of reaction conditions[a]



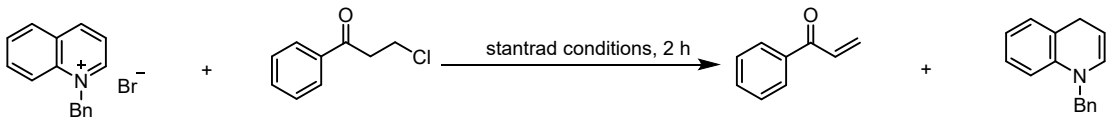
A_1 B_1 C_1

Entry	catalyst	base	solvent	Yield(%)[b]
1	$[IrCp^*Cl_2]_2$	$Mg(OMe)_2$	MeOH	56%
2	$[Ir(cod)Cl_2]_2$	$Mg(OMe)_2$	MeOH	trace
3	$Ru(p\text{-}cymene)_2Cl_2$	$Mg(OMe)_2$	MeOH	43%
4	$RuCl_3 \cdot H_2O$	$Mg(OMe)_2$	MeOH	trace
5	$RuCl_2PPh_3$	$Mg(OMe)_2$	MeOH	trace
6	RuCp*(cod)Cl	$Mg(OMe)_2$	MeOH	trace
5	$[RhCp^*Cl_2]_2$	$Mg(OMe)_2$	MeOH	39%
7	$[IrCp^*Cl_2]_2$	NaOMe	MeOH	trace
8	$[IrCp^*Cl_2]_2$	Cs_2CO_3	MeOH	trace
9	$[IrCp^*Cl_2]_2$	$Mg(EtO)_2$	MeOH	20%
10	$[IrCp^*Cl_2]_2$	K_3PO_4	MeOH	trace
11	$[IrCp^*Cl_2]_2$	LiOMe	MeOH	trace
12	$[IrCp^*Cl_2]_2$	$Mg(OMe)_2$	EtOH	30%
13	$[IrCp^*Cl_2]_2$	$Mg(OMe)_2$	^{i}PrOH	trace
14	$[Ir(cod)Cl_2]_2$	$Mg(OMe)_2$	MeOH	(65, 64)[c]
15	$[Ir(cod)Cl_2]_2$	$Mg(OMe)_2$	MeOH	73[d]
16	$[Ir(cod)Cl_2]_2$	$Mg(OMe)_2$	MeOH	46[e]

[a] Conditions: unless otherwise stated, all the reactions were performed with $\mathbf{A_1}$ (0.20 mmol), $\mathbf{B_1}$ (0.24 mmol), catalyst (1 mol %), $(HCHO)_n$ (2.0 equiv), base (1.5 equiv), KI (2.0 equiv), MeOH (1.0 mL) at 65 °C for 24 h under N_2 protection. [b] NMR yield using nitromethane as an internal standard. [c] Yield obtained with 3.0 and 4.0 equiv. $(HCHO)_n$ respectively. [d] Yield obtained with 3.0 equiv. $(HCHO)_n$ and 0.28 mmol $\mathbf{B_1}$. [e] Yield obtained with the absence of KI.

Control experiments

Intermediate capture



A_1 B_1 mass detected A_1'

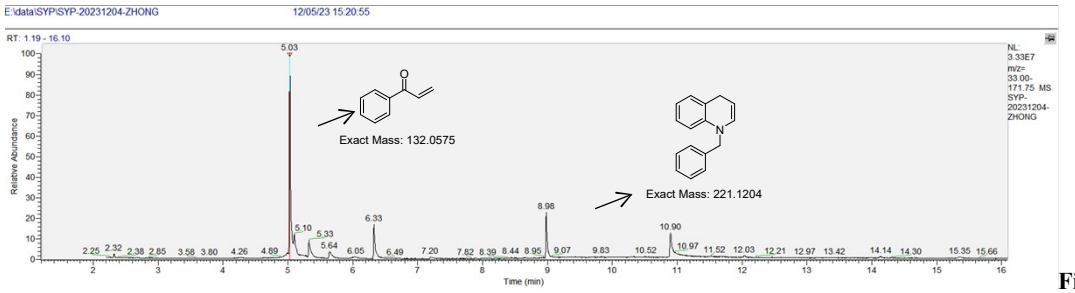
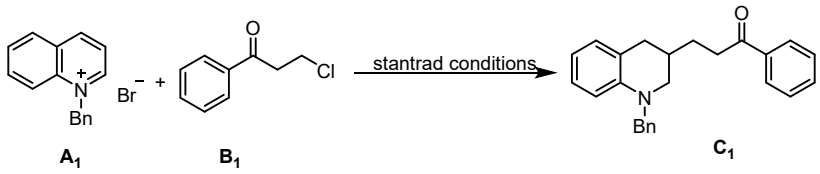


Figure S2 GC-MS of the product $\mathbf{C_1}$ generated by interruption test of the model reaction at 2 h

Deuterium-labelling studies



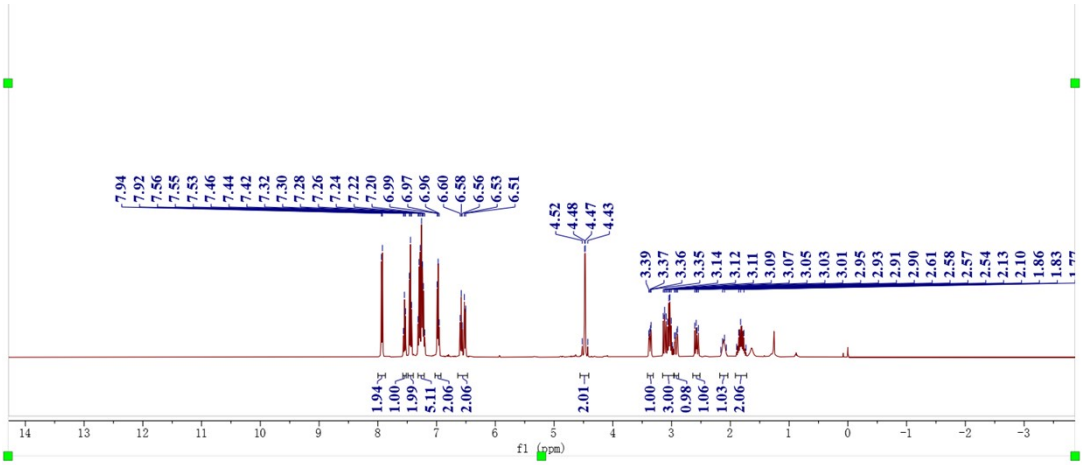
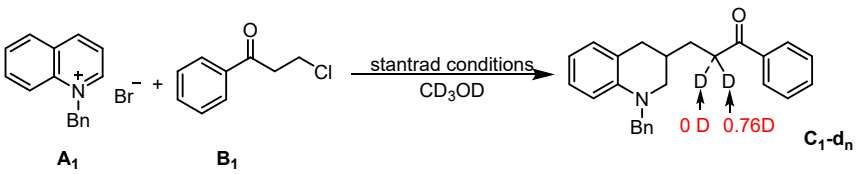


Figure S3 ^{1}H-NMR spectrum of C_1



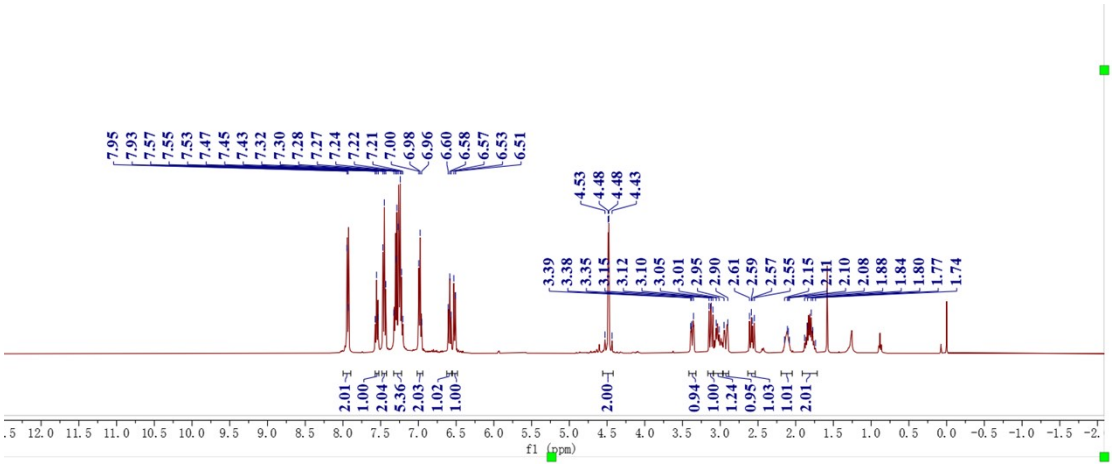


Figure S4 ^{1}H-NMR spectrum of C_1 with CD_3OD as solvent

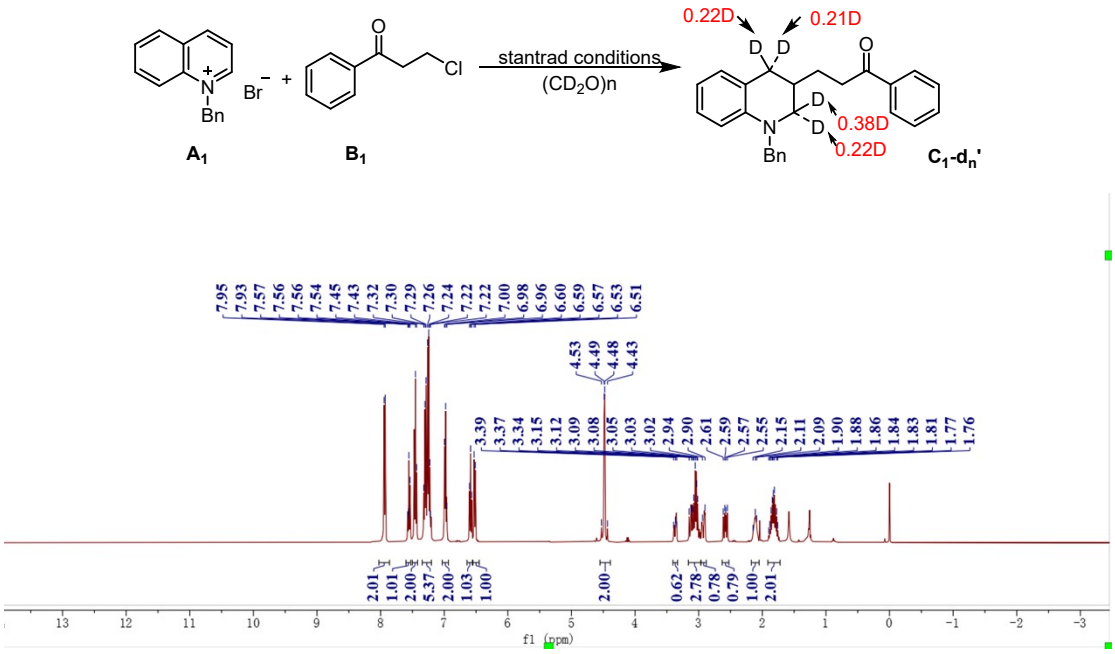
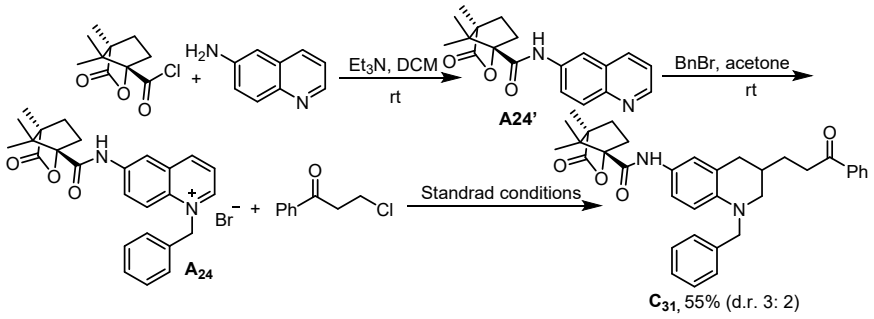


Figure S5 ^{1}H-NMR spectrum of C_1 with $(CD_2O)_n$

The Synthetic Utility

Synthesis of camphor analogue C_{31}

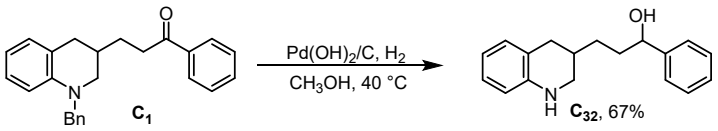


Scheme S2. Synthesis of compound C_{31}

To a solution of 6-aminoquinoline (10 mmol, 1.44 g) in anhydrous CH_2Cl_2 was added triethylamine (12 mmol, 1.21 g) and (-)-(1S,4R)-Camphanoyl chloride (11 mmol, 2.38 g) at 0 ℃. The reaction mixture was stirred at room temperature until the reaction was completed (monitored by TLC). Water (50 mL) was added to the mixture and extracted with CH_2Cl_2 (30 mL). The organic phase was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **A_{24}'**. **A_{24}'** (3 mmol), benzyl bromide (6 mmol) and acetone (5 mL) were introduced in a flask (50 mL). And it was stirred at room temperature for 24 h. Then, the solvent was removed. The reaction mixture was washed with small amount of diethyl ether and finally dried under vacuum to get **A_{24}** (The product is a known compound, consistent with the literature reports)[2].

A_{24} (0.2mmol), chloroalkyl ketone (0.28 mmol), $[IrCp^*Cl_2]_2$ (0.002 mmol), $Mg(OMe)_2$ (1.5 eq), $(CH_2O)_n$ (3 eq) and KI (2 eq) were added to a 50 mL Schlenk tube. After charging N_2 for three times, 1mL methanol was added and the tube was then closed, which was stirred at 65 ℃ for 24 h. After cooling down to the room temperature, the reaction mixture was concentrated under vacuum and purified by preparative TLC on silica to obtain product **C_{31}** (55% isolated yield).

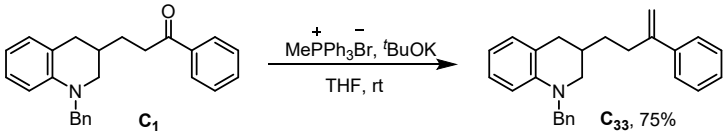
The transformation of C_1
Debenzylation and reduction



Scheme S3. Synthesis of compound **C_{32}**

Under N_2 atmosphere, $Pd(OH)_2/C$ (10 mol%), C_1 (0.2 mmol), HCOOH (0.6 mmol) were added to a 50 mL Schlenk tube. The tube was closed and stirred at 40 ℃ for 24 h. After cooling down to the room temperature, the mixture was filtered through a funnel with filter paper and concentrated filtrate. Finally, the residue was purified by preparative TLC on silica to give **C_{32}** as liquid (65% isolated yield).

Wittig Reaction

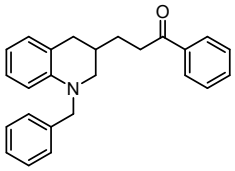


Scheme S4. Synthesis of compound **C_{33}**

Methyltriphenylphosphonium bromide (0.3 mmol) was introduced into a dry Schlenk tube. Then, the tube was charged with N_2 for three times, and ^{t}BuOK in THF (1M) and THF (0.5 mL) were added to the tube. The reaction mixture was stirred at 0 °C, and C_1 in 0.5 Ml THF was added dropwise. The resulting mixture was warmed to room temperature and stirred overnight. Upon completion, the reaction mixture was filtered through a funnel with filter paper and concentrated filtrate. Finally, the residue was purified by preparative TLC on silica to give **C_{33}** as liquid (75% yield).

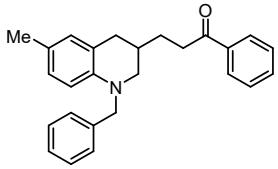
Analytic data of the obtained compounds

(1) 3-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_1**)



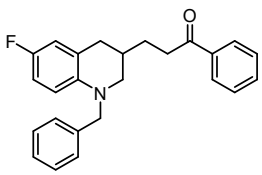
Brown solid; M.p. 124-126 ºC, (73% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.97 (t, *J* = 7.0 Hz, 2H), 6.64 – 6.47 (m, 2H), 4.52-4.43 (m, 2H), 3.39-3.35 (m, 1H), 3.15 – 2.96 (m, 3H), 2.95-2.90 (m, 1H), 2.57 (dd, *J* = 16.0, 12.0 Hz, 1H), 2.16 – 2.07 (m, 1H), 1.89 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 145.2, 138.8, 136.8, 133.0, 129.2, 128.6, 128.6, 128.0, 127.2, 126.8, 126.6, 121.2, 116.1, 110.9, 55.2, 54.9, 35.8, 34.3, 32.0, 27.8. HRMS (ESI): Calcd. for $C_{25}H_{26}NO^+$ $[M+H]^+$: 356.2009; found: 356.2004.

(2) 3-(1-benzyl-6-methyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_2**)



Yellow solid; M.p. 78-82 ºC, (57% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.20 (m, 5H), 6.81-6.77 (m, 2H), 6.44(d, *J* = 8.0 Hz, 1H), 4.49 – 4.39 (m, 2H), 3.36 – 3.31 (m, 1H), 3.10 – 3.00 (m, 3H), 2.91-2.86 (m, 1H), 2.58 – 2.52 (m, 1H), 2.19 (s, 3H), 2.41 – 2.05 (m, 1H), 1.89 – 1.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 143.1, 139.1, 136.9, 133.0, 130.0, 128.6, 128.5, 128.0, 127.6, 126.7, 126.6, 125.2, 121.2, 111.0, 55.4, 54.9, 35.9, 34.3, 32.2, 27.8, 20.2. HRMS (ESI): Calcd. for $C_{26}H_{28}NO^+$ $[M+H]^+$: 370.2165; found: 370.2161.

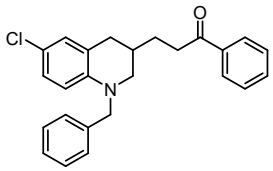
(3) 3-(1-benzyl-6-fluoro-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_3**)



Brown oily liquid, (65% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95-7.92 (m, 2H),

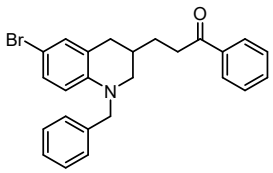
7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.322 – 7.21 (m, 5H), 6.72 – 6.65 (m, 2H), 6.40 (dd, *J* = 9.0, 4.6 Hz, 1H), 4.48 – 4.38 (m, 2H), 3.36 – 3.32 (m, 1H), 3.11 – 2.86 (m, 3H), 2.92 – 2.86 (m, 1H), 2.59 – 2.52 (m, 1H), 2.14 – 2.06 (m, 1H), 1.89 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 156.0, 153.6, 141.7 (d, *J* = 2.0 Hz), 138.7, 136.8, 133.0, 128.6, 128.0, 126.9, 126.6, 122.7 (d, *J* = 6.1 Hz), 115.6 (d, *J* = 22.2 Hz), 113.2 (d, *J* = 21.2 Hz), 111.6 (d, *J* = 8.1 Hz), 55.7, 54.9, 35.8, 34.4, 32.0, 27.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -129.74. HRMS (ESI): Calcd. for $C_{25}H_{25}NOF^+$ $[M+H]^+$: 374.1915; found: 374.1912.

(4) 3-(4-benzyl-7-chloro-1,2,3,4-tetrahydronaphthalen-2-yl)-1-phenylpropan-1-one (**C$_4$**)



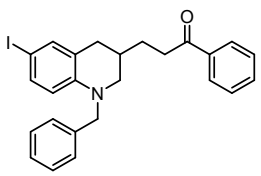
Brown oily liquid, (48% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.93 (d, *J* = 2.6 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.40 (d, *J* = 8.8 Hz, 1H), 4.50 – 4.39 (m, 2H), 3.39 – 3.34 (m, 1H), 3.14 – 2.96 (m, 3H), 2.90 – 2.85 (m, 1H), 2.57 – 2.50 (m, 1H), 2.13 – 2.05 (m, 1H), 1.89 – 1.73 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.7, 143.7, 138.2, 136.6, 133.1, 128.8, 128.6, 128.6, 128.0, 126.9, 126.8, 126.5, 122.8, 120.4, 111.9, 55.2, 54.8, 35.7, 34.1, 31.7, 27.5. HRMS (ESI): Calcd. for $C_{25}H_{25}NOCl^+$ $[M+H]^+$: 390.1619; found: 390.1615.

(5) 3-(1-benzyl-6-bromo-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C$_5$**)



Red oily liquid, (31% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24 – 7.20 (m, 3H), 7.07 – 7.01 (m, 2H), 6.36 (d, *J* = 8.6 Hz, 1H), 4.50 – 4.39 (m, 2H), 3.39 – 3.35 (m, 1H), 3.14 – 3.00(m, 3H), 2.91 – 2.85 (m, 1H), 2.57 – 2.51 (m, 1H), 2.13 – 2.05 (m, 1H), 1.89 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.7, 144.2, 138.1, 136.7, 133.1, 131.5, 129.7, 128.7, 128.6, 128.0, 126.9, 126.5, 123.3, 112.4, 107.5, 55.1, 54.8, 35.7, 34.0, 31.7, 27.5. HRMS (ESI): Calcd. for $C_{25}H_{25}NOBr^+$ $[M+H]^+$: 434.1114; found: 434.1109.

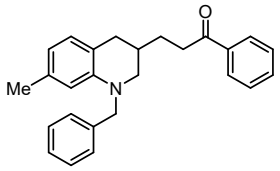
(6) 3-(1-benzyl-6-iodo-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C$_6$**)



Yellow oily liquid, (20% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.19 (m, 7H), 6.27 (d, *J* = 8.6 Hz, 1H), 4.50 –

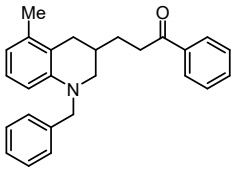
4.40 (m, 2H), 3.40 – 3.36 (m, 1H), 3.15 – 2.96 (m, 3H), 2.90 – 2.84 (m, 1H), 2.56 – 2.50 (m, 1H), 2.14 – 2.04 (m, 1H), 1.89 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.7, 144.8, 138.1, 137.3, 136.8, 135.7, 133.1, 128.7, 128.6, 128.0, 127.0, 126.4, 123.9, 113.0, 54.9, 54.8, 35.7, 33.9, 31.6, 27.5. HRMS (ESI): Calcd. for $C_{25}H_{25}NOI^+$ $[M+H]^+$: 482.0975; found: 482.0971.

(7) 3-(1-benzyl-7-methyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C$_7$**)



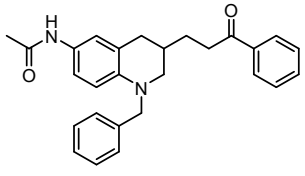
Yellow solid; M.p. 104-107 ºC, (71% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.90 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.19 (m, 5H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 4.50 – 4.41 (m, 2H), 3.34 – 3.30 (m, 1H), 3.09 – 2.93 (m, 3H), 2.91 – 2.85 (m, 1H), 2.55-2.49 (m, 1H), 2.17 (s, 3H), 2.10 – 2.04 (m, 1H), 1.87 – 1.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 145.2, 138.9, 136.9, 136.8, 132.9, 129.1, 128.5, 128.0, 126.7, 126.7, 118.3, 116.9, 111.5, 55.1, 54.7, 35.8, 34.0, 32.1, 27.7, 21.5. HRMS (ESI): Calcd. for $C_{26}H_{28}NO^+$ $[M+H]^+$: 370.2165; found: 370.2163.

(8) 3-(1-benzyl-5-methyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C$_8$**)



Off-white solid; M.p. 117-119 ºC, (60% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.20 (m, 5H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 8.2 Hz, 1H), 4.52 – 4.42 (m, 2H), 3.36 – 3.31 (m, 1H), 3.12 – 2.99 (m, 3H), 2.91 – 2.85 (m, 1H), 2.41 – 2.34 (m, 1H), 2.21 (s, 3H), 2.16 – 2.08 (m, 1H), 1.84 (q, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 145.5, 139.0, 136.9, 136.6, 133.0, 128.6, 128.5, 128.0, 126.7, 126.6, 126.4, 119.9, 118.3, 109.4, 55.9, 54.5, 35.9, 32.0, 31.4, 28.2, 19.9. HRMS (ESI): Calcd. for $C_{26}H_{28}NO^+$ $[M+H]^+$: 370.2165; found: 370.2160

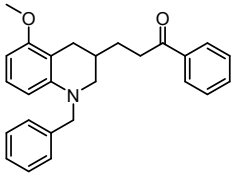
(9) (R)-N-(1-benzyl-3-(3-oxo-3-phenylpropyl)-1,2,3,4-tetrahydroquinolin-6-yl)acetamide (**C$_9$**)



Red oily liquid, (59% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 3H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.19 (m, 6H), 6.97 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.40 (d, *J* = 8.8 Hz, 1H), 4.44 – 4.34 (m, 2H), 3.30 – 3.27 (m, 1H), 3.06 – 2.95 (m, 3H), 2.84 – 2.79 (m, 1H), 2.50 – 2.44 (m, 1H), 2.04 (s, 3H), 2.06 – 2.00 (m, 1H), 1.83 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 168.4, 142.3, 138.6, 136.6, 132.9, 128.5, 128.4, 127.8, 127.1, 126.7, 126.5, 122.4,

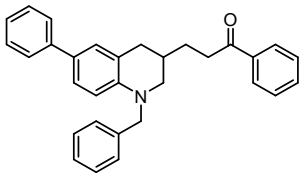
121.3, 120.1, 110.7, 55.1, 54.7, 35.8, 34.2, 31.9, 27.5, 23.9. HRMS (ESI): Calcd. for $C_{27}H_{29}N_2O_2^+$ $[M+H]^+$: 413.2224; found: 413.2219.

(10) 3-(1-benzyl-5-methoxy-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{10}**)



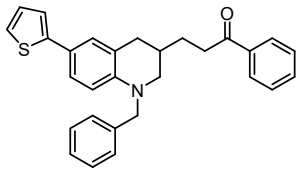
White solid; M.p. 78-80 ºC, (52% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.92 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.19 (m, 5H), 6.94 (t, *J* = 8.2 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 2H), 4.52 – 4.42 (m, 2H), 3.79 (s, 3H), 3.32 – 3.28 (m, 1H), 3.14 – 2.97 (m, 4H), 2.34 – 2.28 (m, 1H), 2.07 – 2.02 (m, 1H), 1.90 – 1.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.0, 157.4, 146.3, 139.0, 136.7, 132.9, 128.5, 128.5, 128.0, 126.9, 126.7, 126.6, 109.1, 104.7, 98.7, 55.6, 55.3, 54.6, 35.9, 31.5, 28.1, 27.4. HRMS (ESI): Calcd. for $C_{26}H_{28}NO_2^+$ $[M+H]^+$: 386.2115; found: 386.2109.

(11) 3-(1-benzyl-6-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{11}**)



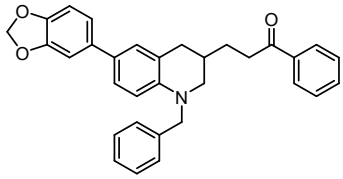
Yellow solid; M.p. 86-88 ºC, (63% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.19 (m, 10H), 6.59 (d, *J* = 8.4 Hz, 1H), 4.56 – 4.46 (m, 2H), 3.42 – 3.38 (m, 1H), 3.18 – 2.97 (m, 4H), 2.67 – 2.60 (m, 1H), 2.18 – 2.10 (m, 1H), 1.92 – 1.76 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 144.7, 141.2, 138.6, 136.8, 133.0, 128.8, 128.6, 128.4, 128.5, 128.0, 127.8, 126.7, 126.6, 126.1, 125.8, 125.8, 121.4, 111.1, 55.1, 55.0, 35.8, 34.4, 32.0, 27.7. HRMS (ESI): Calcd. for $C_{31}H_{30}NO^+$ $[M+H]^+$: 432.2322; found: 432.2319.

(12) 3-(1-benzyl-6-(thiophen-2-yl)-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{12}**)



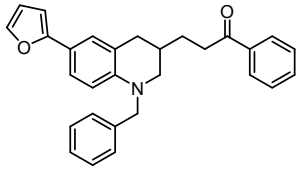
Yellow solid; M.p. 100-102 ºC, (44% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.22 (m, 7H), 7.11 – 7.08 (m, 2H), 7.00 – 6.98 (m, 1H), 6.51 (d, *J* = 8.6 Hz, 1H), 4.5 – 4.46 (m, 2H), 3.42 – 3.38 (m, 1H), 3.18 – 2.94 (m, 4H), 2.64 – 2.57 (m, 1H), 2.17 – 2.09 (m, 1H), 1.92 – 1,75 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 145.3, 144.8, 138.4, 136.8, 133.1, 128.7, 128.6, 128.0, 127.7, 127.0, 126.9, 126.6, 125.1, 122.6, 122.5, 121.4, 120.6, 111.0, 55.1, 55.0, 35.8, 34.3, 31.9, 27.7. HRMS (ESI): Calcd. for $C_{29}H_{28}NOS^+$ $[M+H]^+$: 438.1886; found: 438.1881.

(13)3-(6-(benzo[d][1,3]dioxol-5-yl)-1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{13}**)



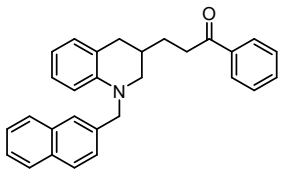
Brown oily liquid, (32% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.24 (m, 5H), 7.17 – 7.14 (s, 2H), 7.00 – 6.95 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 5.95 (s, 2H), 4.56 – 4.47 (m, 2H), 3.43 – 3.88 (m,1H), 3.19 – 2.995 (m, 4H), 2.66 – 2.60 (m, 1H), 2.23 – 2.15 (m, 1H), 1.93 – 1.77 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 147.9, 145.9, 144.5, 138.7, 136.8, 135.8, 133.1, 128.8, 128.6, 128.6, 128.0, 127.7, 126.9, 126.6, 125.6, 121.4, 119.4, 111.1, 108.4, 106.9, 100.9, 55.2, 56.0, 35.9, 34.5, 32.06, 27.7. HRMS (ESI): Calcd. for $C_{32}H_{30}NO_3^+$ $[M+H]^+$: 476.2220; found: 476.2217.

(14) 3-(1-benzyl-6-(furan-2-yl)-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{14}**)



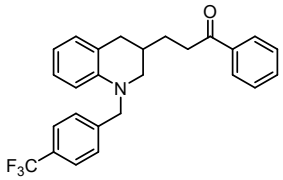
Red oily liquid, (46% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.28 (m, 5H), 7.26 – 7.22 (s, 3H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.41 – 6.37 (m, 2H), 4.57 – 4.47 (m, 2H), 3.43 – 3.39 (m, 1H), 3.19 – 2.94 (m, 4H), 2.64 – 2.58 (m, 1H), 2.18 – 2.09 (m,1H), 1.92 – 1.77 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 154.9, 144.7, 140.5, 138.5, 136.7, 133.1, 128.7, 128.6, 128.0, 126.9, 126.6, 125.1, 123.3, 121.2, 119.48, 111.4, 110.9, 101.7, 55.0, 55.0, 35.8, 34.3, 32.0, 27.6. HRMS (ESI): Calcd. for $C_{29}H_{28}NO_2^+$ $[M+H]^+$: 422.2115; found: 422.2109.

(15) 3-(1-(naphthalen-2-ylmethyl)-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{15}**)



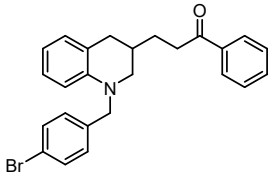
Red solid; M.p. 94-96 ºC, (62% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.88 (m, 2H), 7.81 – 7.74 (m, 3H), 7.69 (s, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (m, 5H), 7.02 – 6.96 (m, 2H), 6.62 (t, *J* = 8.0 Hz, 2H), 4.67 – 4.57 (m, 2H), 3.44 – 3.39 (m, 1H), 3.18 – 2.94 (m, 4H), 2.64 – 2.58 (m, 1H), 2.20 – 2.11 (m, 1H), 1.91 – 1.76 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.9, 145.4, 136.9, 136.4, 133.5, 133.0, 132.6, 129.3, 128.6, 128.4, 128.0, 127.7, 127.7, 127.3, 126.1, 125.5, 125.1, 125.0, 121.3, 116.2, 111.0, 55.5, 54.8, 35.8, 34.4, 32.0, 27.7. HRMS (ESI): Calcd. for $C_{29}H_{28}NO^+$ $[M+H]^+$:406.2165; found: 4406.2162.

(16) 1-phenyl-3-(1-(4-(trifluoromethyl)benzyl)-1,2,3,4-tetrahydroquinolin-3-yl)propan-1-one (**C_{16}**)



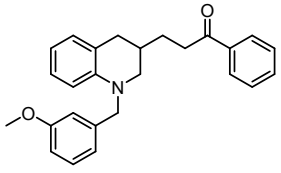
Yellow solid; M.p. 73-75 ºC, (61% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.93 (m, 2H), 7.58 – 7.54 (m, 3H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.95 (m, 2H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 8.2 Hz, 1H), 4.52 (s, 2H), 3.39 – 3.34 (m, 1H), 3.16– 2.99 (m, 3H), 2.97 – 2.92 (m, 1H), 2.62 – 2.56 (m, 1H), 2.19 – 2.08 (m, 1H), 1.92 – 1.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 144.9, 143.2 (d, *J* = 2.0 Hz), 136.8, 133.1, 129.4, 129.1 (q, *J* = 32.3 Hz), 128.6, 128.0, 127.3, 126.8, 125.5 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 272.7 Hz), 121.4, 116.6, 110.8, 55.3, 55.0, 35.8, 34.2, 32.0, 27.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28. HRMS (ESI): Calcd. for $C_{26}H_{25}F_3NO^+$ $[M+H]^+$: 424.1883; found: 424.1877.

(17) 3-(1-(4-bromobenzyl)-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{17}**)



Yellow solid; M.p. 86-88 ºC, (63% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 1H), 4.48 – 7.39 (m, 2H), 3.39 – 3.34 (m, 1H), 3.15 – 3.00 (m, 3H), 2.98 – 2.92 (m, 1H), 2.63 – 2.57 (m, 1H), 2.17 – 2.09 (m, 1H), 1.92 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 144.9, 137.6, 136.8, 133.0, 131.6 129.3, 128.6, 128.3, 127.9, 127.2, 121.3, 120.4, 116.3, 110.8, 55.0, 54.7, 35.7, 34.2, 31.9, 27.7. HRMS (ESI): Calcd. for $C_{25}H_{25}NOBr^+$ $[M+H]^+$:434.1114; found: 434.1109.

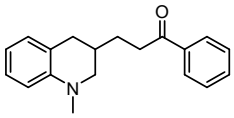
(18) 3-(1-(3-methoxybenzyl)-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{18}**)



Off-white solid; M.p. 70-72 ºC, (61% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.99 – 6.95 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 6.77 – 6.74 (m, 1H), 6.58 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 8.6 Hz, 1H), 4.48 – 4.39 (m, 2H), 3.74 (s, 3H), 3.38 – 3.35 (m, 1H), 3.14 – 2.96 (m, 3H), 2.94 – 2.89 (m, 1H), 2.60 – 2.54 (m, 1H), 2.16 – 2.07 (m, 1H), 1.89 – 1.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 159.9, 145.2, 140.6, 136.8, 133.0, 129.6, 129.2, 128.5, 128.0, 127.2, 121.1, 118.8, 116.1, 112.2, 112.0, 110.9, 55.2, 55.1, 54.9, 35.8, 34.3, 32.0, 27.7. HRMS (ESI): Calcd. for $C_{26}H_{28}NO_2^+$ $[M+H]^+$:

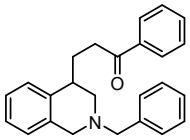
386.2114; found: 386.2109.

(19) 3-(1-methyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-phenylpropan-1-one (**C_{19}**)



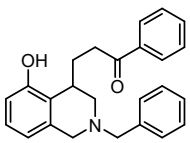
Brown oily liquid, (64% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.62 – 6.57 (m, 2H), 3.25 – 3.21 (m, 1H), 3.14 – 3.00 (m, 2H), 2.98 – 2.93 (m, 1H), 2.89 – 3.84 (m, 4H), 2.54 – 2.47 (m, 1H), 2.11 – 2.01 (m, 1H), 1.89 – 1.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 146.3, 136.8, 133.0, 128.9, 128.6, 128.0, 127.1, 121.8, 116.3, 110.7, 56.5, 39.0, 35.9, 34.1, 32.1, 28.0. HRMS (ESI): Calcd. for $C_{19}H_{22}NO^+$ $[M+H]^+$: 280.1696; found: 280.1692.

(20) 3-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-1-phenylpropan-1-one (**C_{20}**)



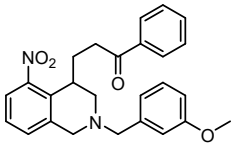
Brown oily liquid, (50% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.32 – 7.21 (m, 4H), 7.17 – 7.06 (m, 2H), 7.00 (d, *J* = 6.6 Hz, 1H), 3.84 – 7.72 (m, 2H), 3.58 – 3.44 (m, 2H), 2.98 – 2.799 (m, 4H), 2.58 (dd, *J* = 11.6, 4.2 Hz, 1H), 2.24 – 2.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 138.7, 138.3, 137.01, 135.0, 132.8, 129.1, 128.5, 128.3, 128.0, 127.1, 126.4, 126.2, 125.8, 62.8, 56.7, 54.0, 37.8, 35.9, 30.3. HRMS (ESI): Calcd. for $C_{25}H_{26}NO^+$ $[M+H]^+$: 356.2009; found: 356.2005.

(21) 3-(2-benzyl-5-hydroxy-1,2,3,4-tetrahydroisoquinolin-4-yl)-1-phenylpropan-1-one (**C_{21}**)



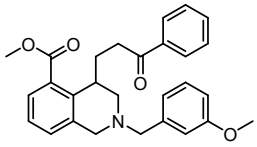
Yellow oily liquid, (14.9 mg, 20% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 7.99 – 7.97 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 3.90 (d, *J* = 13.6 Hz, 1H), 3.68 (dd, *J* = 80.6, 13.1 Hz, 2H), 3.35 (d, *J* = 14.9 Hz, 1H), 3.13 – 3.07 (m, 1H), 3.00 – 2.91 (m, 1H), 2.83 (d, *J* = 11.5 Hz, 1H), 2.74 – 2.70 (m, 1H), 2.322 – 2.24 (m, 2H), 1.99 (t, *J* = 13.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 155.2, 138.7, 136.3, 135.7, 133.8, 128.9, 128.7, 128.3, 127.1, 124.3, 117.6, 113.9, 62.7, 56.5, 52.4, 34.9, 33.2, 26.6. HRMS (ESI): Calcd. for $C_{25}H_{26}NO_2^+$ $[M+H]^+$: 372.1958; found: 372.1954.

(22) 3-(2-(3-methoxybenzyl)-5-nitro-1,2,3,4-tetrahydroisoquinolin-4-yl)-1-phenylpropan-1-one (**C_{22}**)



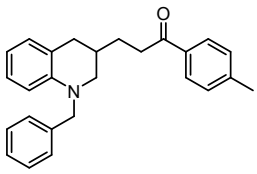
Brown oily liquid, (34.5 mg, 40% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.78 – 7.74 (m, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.96 – 6.93 (m, 2H), 6.74 – 6.71 (m, 1H), 4.04 (d, *J* = 15.4 Hz, 1H), 3.75 – 3.69 (m, 4H), 3.58 – 3.34 (m, 3H), 3.04 – 2.95 (m, 2H), 2.79 – 2.71 (m, 1H), 2.43 – 2.31 (m, 2H), 1.92 (t, *J* = 16.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.6, 159.7, 149.1, 139.7, 137.6, 136.8, 134.1, 132.8, 131.6, 129.3, 128.4, 128.0, 126.4, 123.2, 121.3, 114.4, 112.7, 62.3, 56.4, 55.0, 51.8, 36.9, 35.0, 29.7. HRMS (ESI): Calcd. for $C_{26}H_{27}N_2O_4^+$ $[M+H]^+$: 431.1965; found: 431.1958.

(23) 3-(2-(3-methoxybenzyl)-5-nitro-1,2,3,4-tetrahydroisoquinolin-4-yl)-1-phenylpropan-1-one (**C_{23}**)



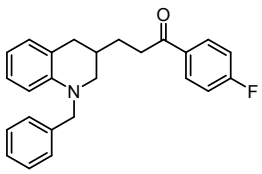
Yellow oily liquid, (30.4 mg, 35% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, 2H), 7.77 – 7.74 (m, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.13 (m, 3H), 6.89 – 6.95 (m, 2H), 6.74 – 6.72 (m, 1H), 4.04 – 3.95 (m, 1H), 3.83 (s, 3H), 3.78 – 3.71 (m, 2H), 3.69 (s, 3H), 3.52 – 3.41 (m, 2H), 3.05 – 2.97 (m, 2H), 2.81 – 2.73 (m, 1H), 2.41 – 2.38 (m, 1H), 2.34 – 2.24 (m, 1H), 1.93 – 1.89 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 167.9, 159.6, 140.9, 140.2, 137.0, 135.9, 132.6, 130.6, 129.2, 129.2, 129.0, 128.4, 128.1, 125.5, 121.3, 114.3, 112.6, 62.6, 57.0, 55.0, 52.3, 51.9, 37.2, 35.8, 30.8. HRMS (ESI): Calcd. for $C_{28}H_{30}NO_4^+$ $[M+H]^+$: 444.2169; found: 444.2163.

(24) 3-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-(p-tolyl)propan-1-one (**C_{24}**)



Yellow solid; M.p. 128-130 ºC, (40% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.20 (m, 7H), 6.97 (t, *J* = 7.1 Hz, 2H), 6.58 (t, *J* = 6.8 Hz, 1H), 6.51 (d, *J* = 8.2 Hz, 1H), 4.52 – 4.43 (m, 2H), 3.39 – 3.34 (m, 1H), 3.14 – 3.09 (m, 1H), 3.07 – 2.89 (m, 3H), 2.60 – 2.54 (m, 1H), 2.40 (s, 3H), 2.15 – 2.08 (m, 1H), 1.88 – 1.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 145.2, 143.8, 138.8, 134.4, 129.2, 129.2, 128.6, 128.1, 127.2, 126.8, 126.6, 121.2, 116.0, 110.8, 55.2, 55.0, 35.7, 34.4, 32.0, 27.9, 21.6. HRMS (ESI): Calcd. for $C_{26}H_{28}NO^+$ $[M+H]^+$: 370.2165; found: 370.2159.

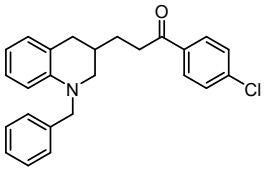
(25) 3-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-(4-fluorophenyl)propan-1-one (**C_{25}**)



Yellow solid; M.p. 140-142 ºC, (68% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 2H), 7.32 – 7.22 (m, 5H), 7.11 (t, *J* = 8.6 Hz, 2H), 6.99 – 6.96 (m, 2H), 6.58 (t, *J* = 7.3 Hz,

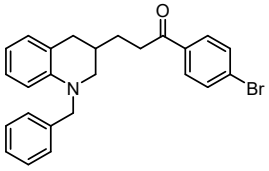
1H), 6.52 (d, *J* = 7.6 Hz, 1H), 4.52 – 4.42 (m, 2H), 3.38 – 3.34 (m, 1H), 3.14 – 3.09 (m, 1H), 3.03 – 2.89 (m, 3H), 2.60 – 2.54 (m, 1H), 2.14 – 2.05 (m, 1H), 1.89 – 1.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 158.7, 142.1, 141.0, 129.4 (d, *J* = 32.3 Hz), 129.0, 127.8, 127.2, 126.8, 126.6, 125.7 (d, *J* = 4.0 Hz), 124.1 (d, *J* = 272.0 Hz), 118.3, 111.2, 108.3, 84.6, 61.3, 52.1, 27.9, 27.3, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.27. HRMS (ESI): Calcd. for $C_{25}H_{25}NOF^+$ $[M+H]^+$: 3374.1915; found: 374.1912.

(26) 3-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-(4-chlorophenyl)propan-1-one (**C$_{26}$**)



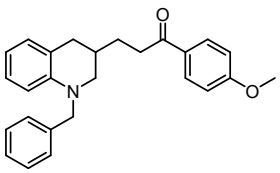
Yellow solid; M.p. 129-131 ºC, (44% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.00 – 6.97 (m, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 4.53 – 4.43 (m, 2H), 3.38 – 3.35 (m, 1H), 3.14 – 2.94 (m, 4H), 2.61 – 2.54 (m, 1H), 2.14 – 2.06 (m, 1H), 1.88 – 1.75 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 145.2, 139.5, 138.8, 135.1, 129.4, 129.2, 128.9, 128.6, 127.3, 126.8, 126.6, 121.1, 116.1, 110.7, 55.1, 54.8, 35.8, 34.3, 31.9, 27.6. HRMS (ESI): Calcd. for $C_{25}H_{25}ClNO^+$ $[M+H]^+$: 390.1619; found: 390.1614.

(27) 3-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-(4-bromophenyl)propan-1-one (**C$_{27}$**)



Yellow solid; M.p. 133-135 ºC, (41% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.22 (m, 5H), 6.70 – 6.96 (m, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 4.52 – 4.42 (m, 2H), 3.37 –3.33(m, 1H), 3.13 – 3.08 (m, 1H), 3.01 – 2.89 (m, 3H), 2.60 – 2.54 (m, 1H), 2.13 – 2.07 (m, 1H), 1.86 – 1.74 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 145.2, 138.8, 135.5, 131.7, 129.5, 129.2, 128.6, 128.1, 127.3, 126.8, 126.6, 121.0, 116.1, 110.8, 55.1, 54.8, 35.8, 34.3, 31.9, 27.6. HRMS (ESI): Calcd. for $C_{25}H_{25}NOBr^+$ $[M+H]^+$: 434.1114; found: 434.1110.

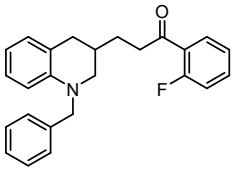
(28) 3-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-(4-methoxyphenyl)propan-1-one (**C$_{28}$**)



Off-white solid; M.p. 114-116 ºC, (39% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.91 (m, 2H), 7.32 – 7.22 (m, 5H), 6.99 – 6.91 (m, 4H), 6.58 (t, *J* = 6.8 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 4.53 – 4.43 (m, 2H), 3.86 (s, 3H), 3.39 – 3.35 (m, 1H), 3.14 – 3.09 (m, 1H), 3.02 – 2.89 (m, 3H), 2.61 – 2.54 (m, 1H), 2.13 – 2.07 (m, 1H), 1.87 – 1.76 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5,

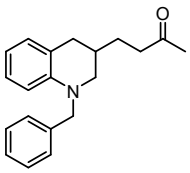
163.4, 145.3, 138.8, 130.3, 129.9, 129.2, 128.6, 127.2, 126.8, 126.6, 121.2, 116.0, 113.7, 110.8, 55.4, 55.2, 55.0, 35.5, 34.4, 32.0, 28.0. HRMS (ESI): Calcd. for $C_{26}H_{28}NO_2^+$ $[M+H]^+$: 386.2115; found: 386.2110.

(29) 3-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)-1-(2-fluorophenyl)propan-1-one (**C_{29}**)



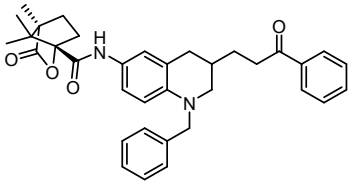
Yellow solid; M.p. 74-76 ºC, (64% ^{1}H NMR yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.81 (m, 1H), 7.53 – 7.47 (m, 1H), 7.32 – 7.20 (m, 6H), 7.14 – 7.10 (m, 1H), 6.97 (t, *J* = 7.3 Hz, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 4.52 – 4.43 (m, 2H), 3.38 – 3.34 (m, 1H), 3.14 – 3.05 (m, 3H), 2.94 – 2.88 (m, 1H), 2.60 – 2.53 (m, 1H), 2.13 – 2.05 (m, 1H), 1.88 – 1.73 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3 (d, *J* = 3.8 Hz), 161.8 (d, *J* = 254.5 Hz), 145.2, 138.8, 134.4 (d, *J* = 2.5 Hz), 130.6 (d, *J* = 2.5 Hz), 129.2, 128.6, 127.2, 126.8, 126.6, 125.7 (d, *J* = 12.6 Hz), 124.5 (d, *J* = 3.8 Hz), 121.2, 116.6 (d, *J* = 25.2 Hz), 116.0, 110.9, 55.2, 55.0, 40.9 (d, *J* = 7.6 Hz), 34.3, 31.6, 27.5 (d, *J* = 1.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.47. HRMS (ESI): Calcd. for $C_{25}H_{25}NOF^+$ $[M+H]^+$: 374.1915; found: 374.1910.

(30) 4-(1-benzyl-1,2,3,4-tetrahydroquinolin-3-yl)butan-2-one (**C_{30}**)



Brown oily liquid, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.23 (m, 5H), 6.99 – 6.96 (m, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 4.51 – 4.42 (m, 2H), 3.33 – 3.28 (m, 1H), 3.08 – 3.03 (m, 1H), 2.89 – 2.84 (m, 1H), 2.55 – 2.47 (m, 3H), 2.13 (s, 3H), 2.04 – 1.96 (m, 1H), 1.72 – 1.59 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.5, 145.2, 138.8, 129.2, 128.6, 127.2, 126.8, 126.6, 121.1, 116.1, 110.8, 55.1, 54.8, 41.0, 34.3, 31.9, 29.9, 27.2. HRMS (ESI): Calcd. for $C_{20}H_{25}NO^+$ $[M+H]^+$: 294.1852; found: 294.1848.

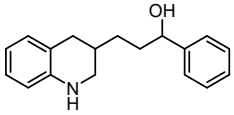
(31)(1S,4R)-N-(1-benzyl-3-(3-oxo-3-phenylpropyl)-1,2,3,4-tetrahydroquinolin-6-yl)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxamide (**C_{31}**)



Yellow oily liquid, (62.3 mg, 55% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 3H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.07 – 7.02 (m, 1H), 6.46 (d, *J* = 8.8 Hz, 1H), 4.52 – 4.42 (m, 2H), 3.38 – 3.35 (m, 1H), 3.15 – 3.10 (m, 1H), 3.08 – 3.01 (m, 2H), 2.95 – 2.91 (m, 1H), 2.63 – 2.54 (m, 2H), 2.10 (s, 1H), 2.00 – 1.94 (m, 2H), 1.88 – 1.67

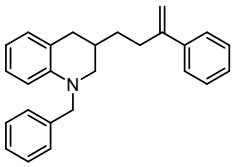
(m, 4H), 1.15 (s, 3H), 1.13 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 178.1, 164.4, 142.8, 138.4, 136.8, 133.0, 128.5, 127.9, 126.8, 126.5, 125.7, 121.8, 121.5, 119.6, 110.8, 92.4, 55.3, 55.1, 54.8, 54.1, 35.7, 34.3, 31.9, 30.3, 29.0, 27.5, 16.7, 16.5, 9.7. HRMS (ESI): Calcd. for $C_{35}H_{39}N_2O_4^+$ $[M+H]^+$: 551.2904; found: 551.2897.

(32) 1-phenyl-3-(1,2,3,4-tetrahydroquinolin-3-yl)propan-1-ol (**C$_{32}$**)



Yellow oily liquid, (35.8 mg, 67% yield, d.r. 3:2); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 4H), 7.29 – 7.25 (m, 1H), 6.96 – 6.90 (m, 2H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 9.1 Hz, 1H), 4.65 – 4.61 (m, 1H), 3.27 – 3.23 (m, 1H), 2.88 – 2.75 (m, 2.5H), 2.44 – 2.36 (m, 1H), 1.95 – 1.71 (m, 3H), 1.56 – 1.40 (m, 1H), 1.38 – 1.17 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 144.4, 129.6, 129.5, 128.5, 127.6, 126.7, 125.8, 120.8, 117.0, 113.9, 74.7, 74.6, 47.1, 47.0, 36.4, 36.3, 33.6, 33.5, 32.2, 32.1, 29.8, 29.7. HRMS (ESI): Calcd. for $C_{18}H_{22}NO^+$ $[M+H]^+$: 268.1696; found: 268.1690.

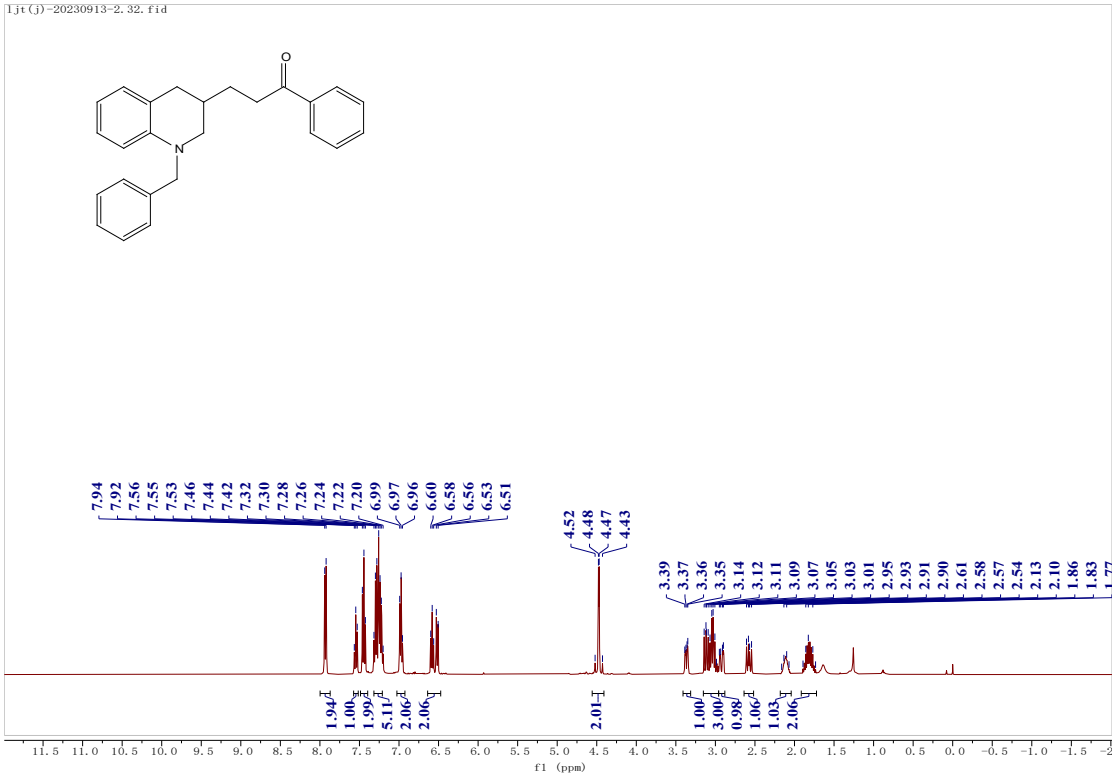
(33) 1-benzyl-3-(3-phenylbut-3-en-1-yl)-1,2,3,4-tetrahydroquinoline (**C$_{33}$**)



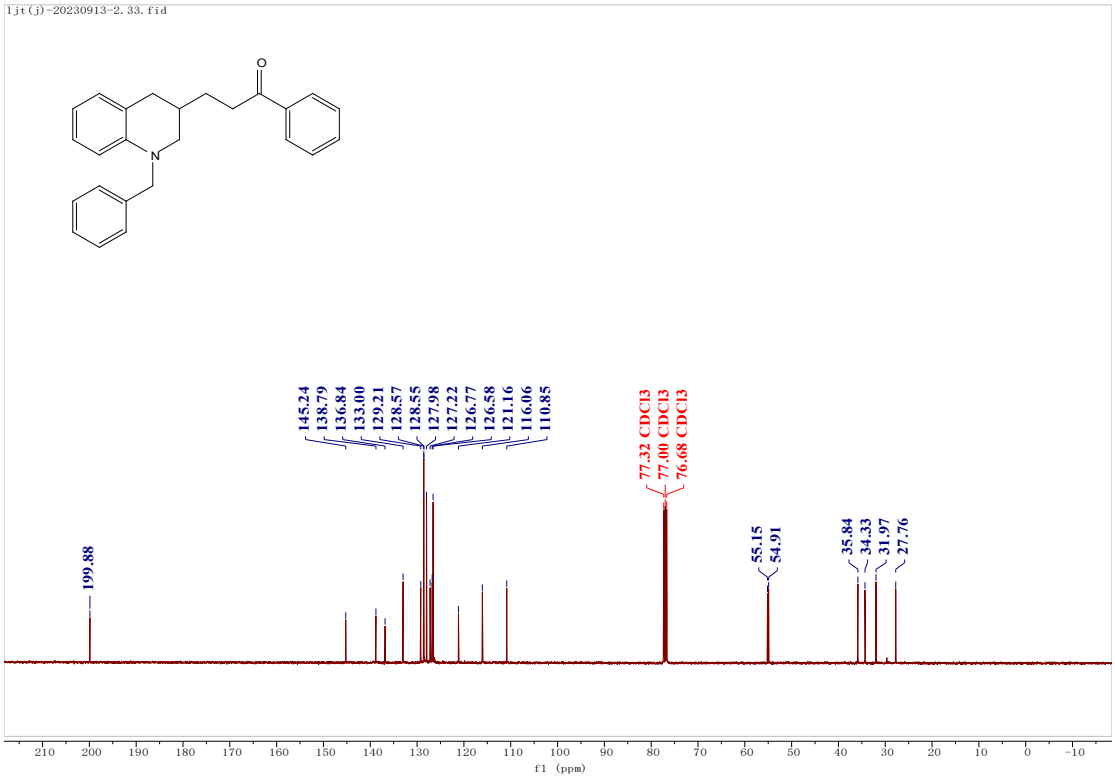
Yellow oily liqui, (53.0 mg, 75% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.36 (m, 2H), 7.32 – 7.19 (m, 8H), 6.97 – 6.94 (m, 2H), 6.57 (t, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 8.6 Hz, 1H), 5.25 (s, 1H), 5.04 (s, 1H), 4.44 (s, 2H), 3.32 – 3.28 (m, 1H), 3.06 – 3.01 (m, 1H), 2.90 – 2,84 (m, 5.6 Hz, 1H), 2.65 – 2.47 (m, 3H), 2.08 – 2.00 (m, 1H), 1.53 – 1.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 145.3, 141.1, 138.9, 129.2, 128.5, 128.3, 127.4, 127.1, 126.7, 126.5, 126.1, 121.5, 115.9, 112.5, 110.7, 55.1, 55.0, 34.5, 32.6, 32.1, 31.9. HRMS (ESI): Calcd. for $C_{26}H_{28}N^+$ $[M+H]^+$: 354.2216; found: 354.2213.

NMR spectra of the obtained compounds

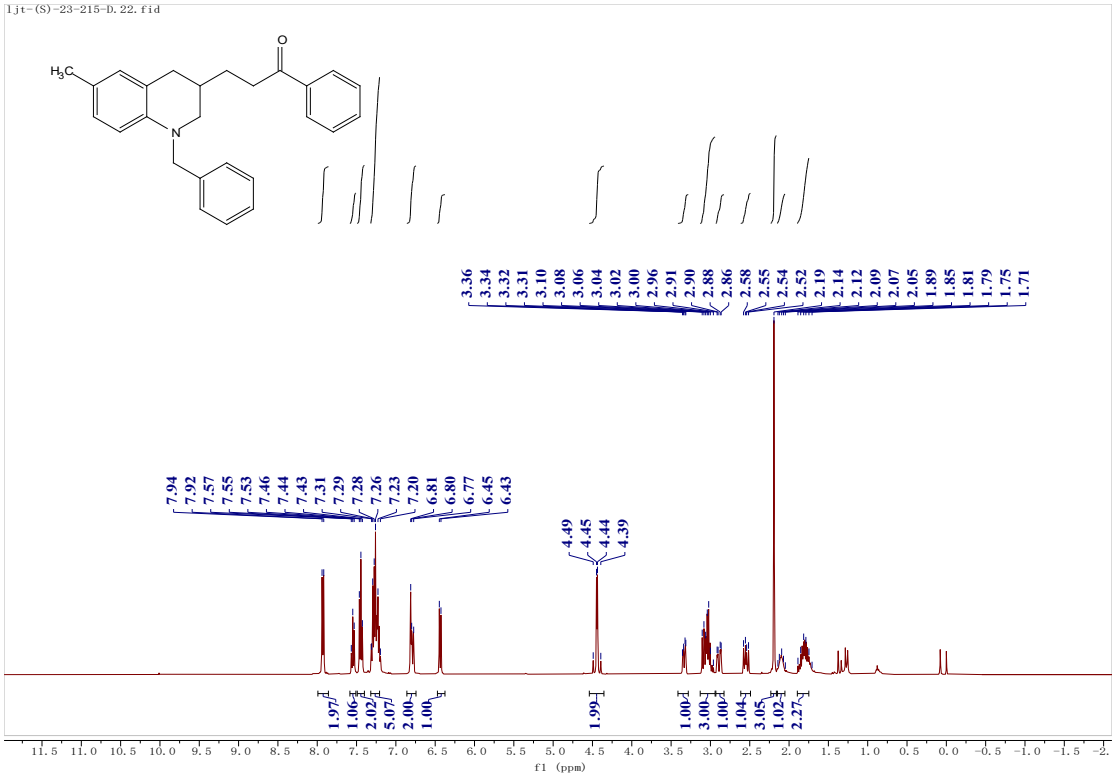
^{1}H-NMR spectrum of C_1



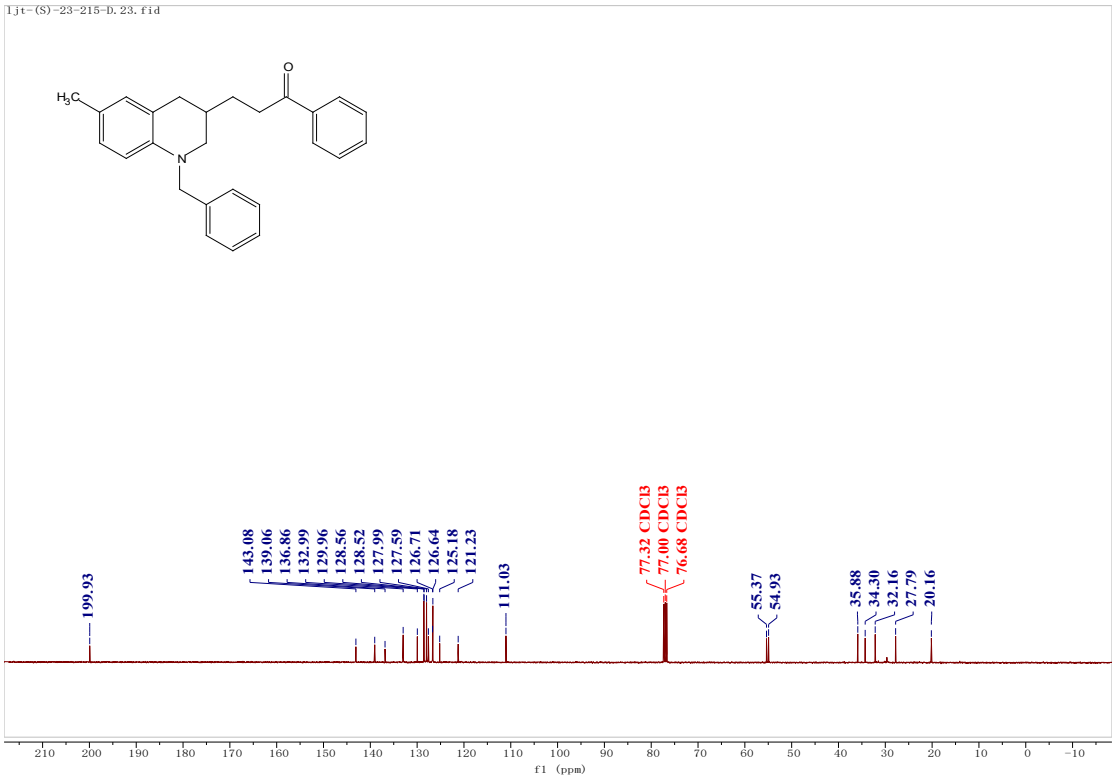
^{13}C-NMR spectrum of C_1



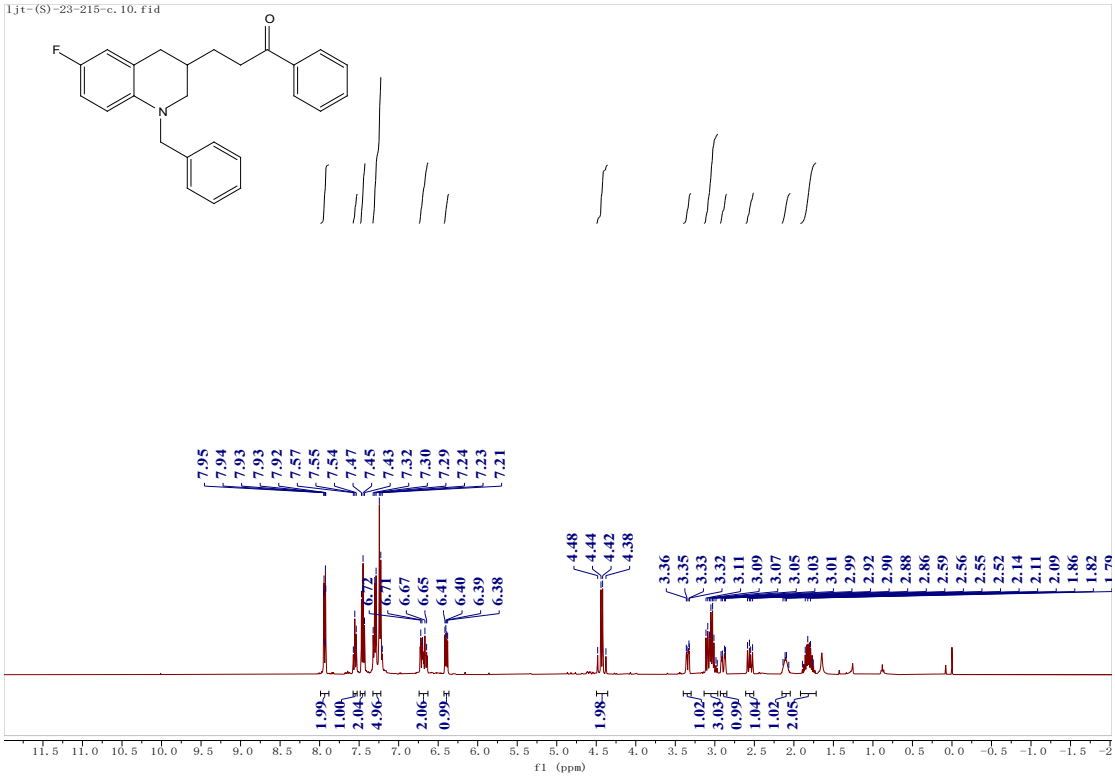
^{1}H-NMR spectrum of C_2



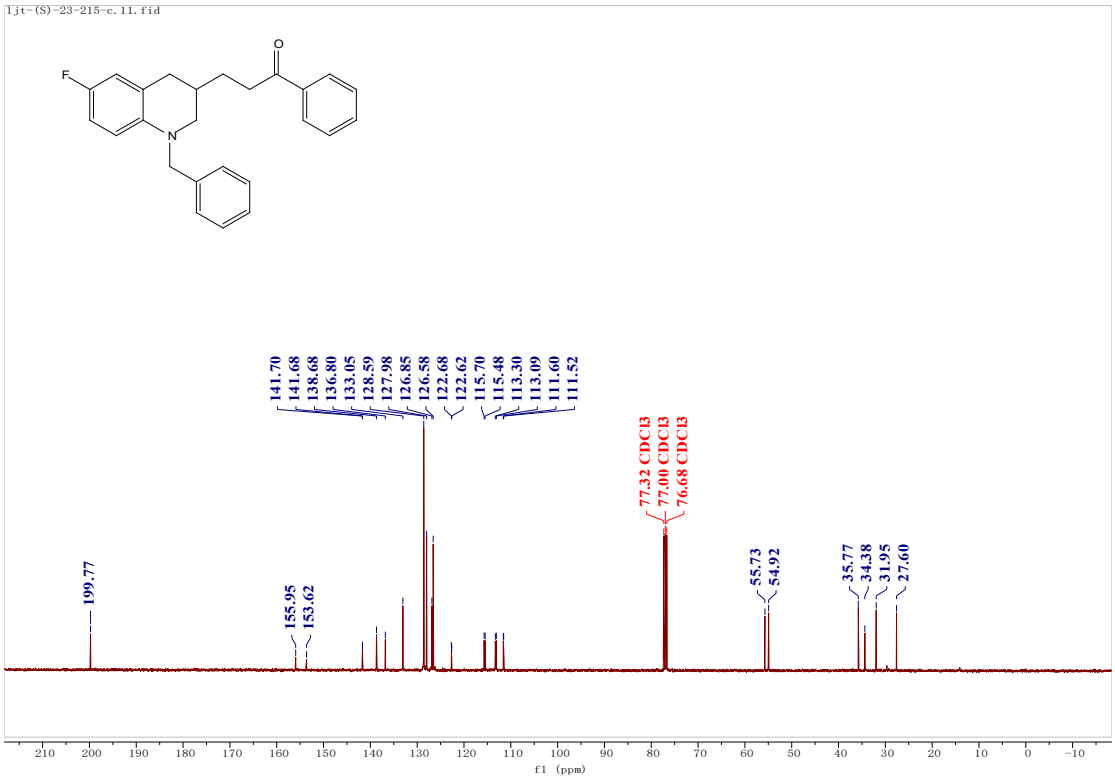
^{13}C-NMR spectrum of C_2



^{1}H-NMR spectrum of C_3

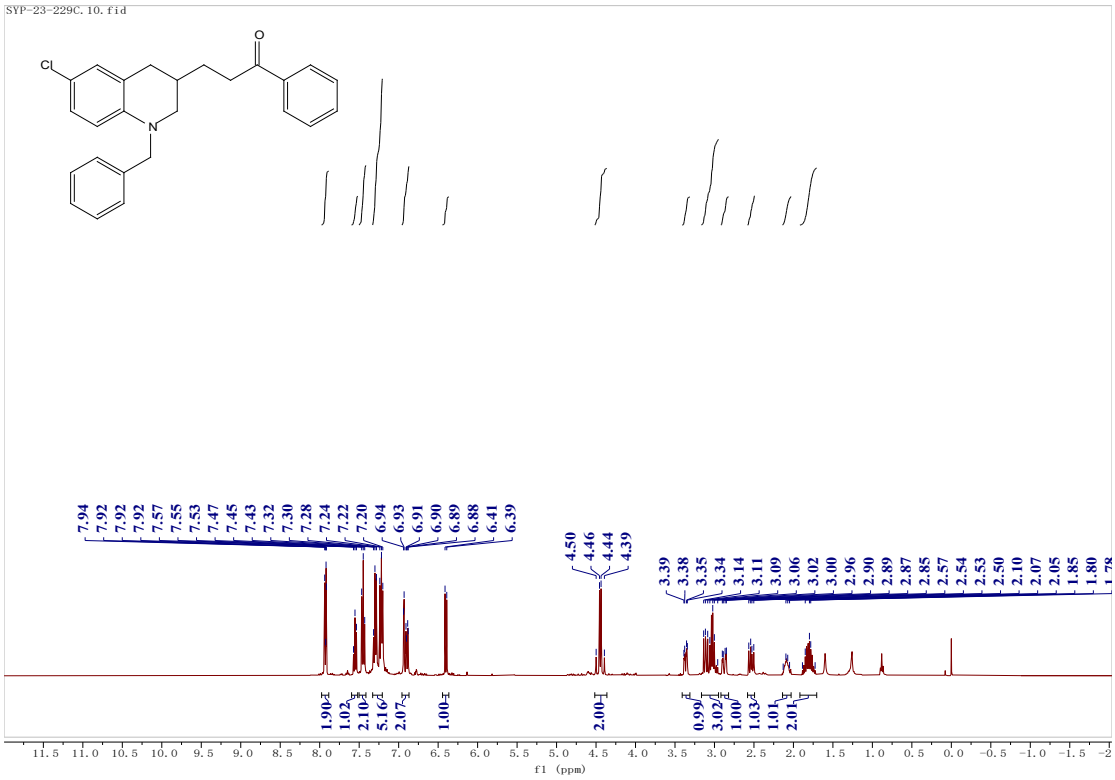


^{13}C-NMR spectrum of C_3

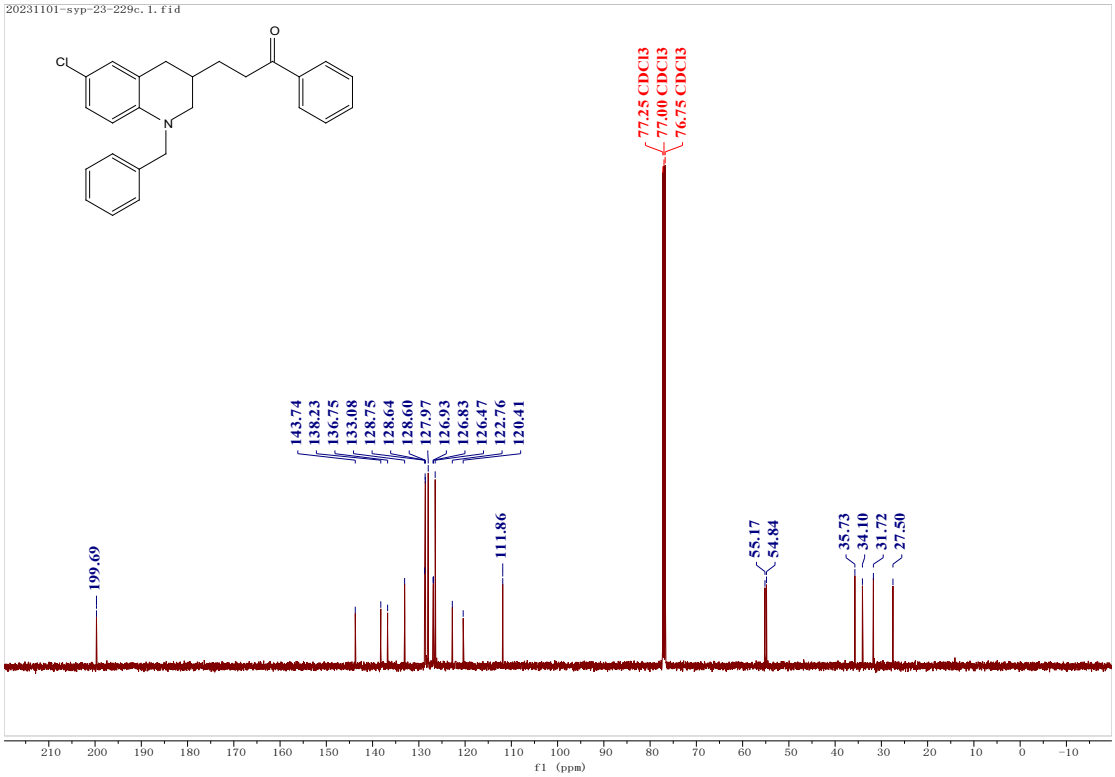


^{19}F-NMR spectrum of C_3

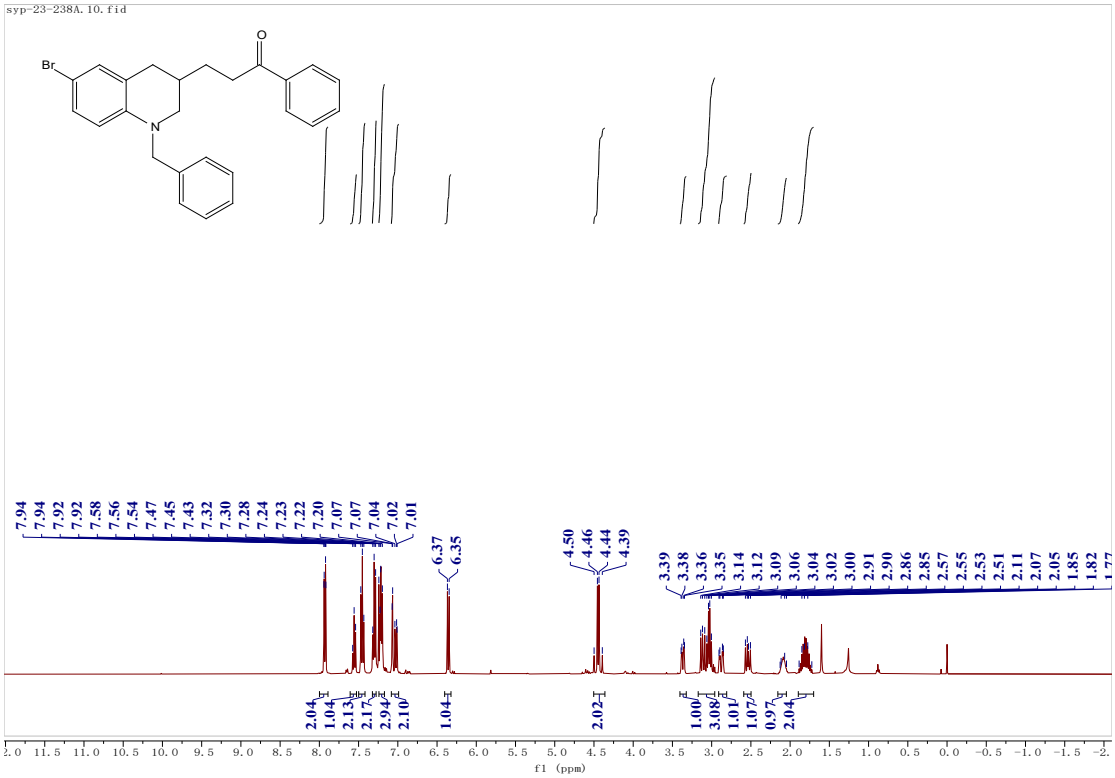
^{1}H-NMR spectrum of C_4



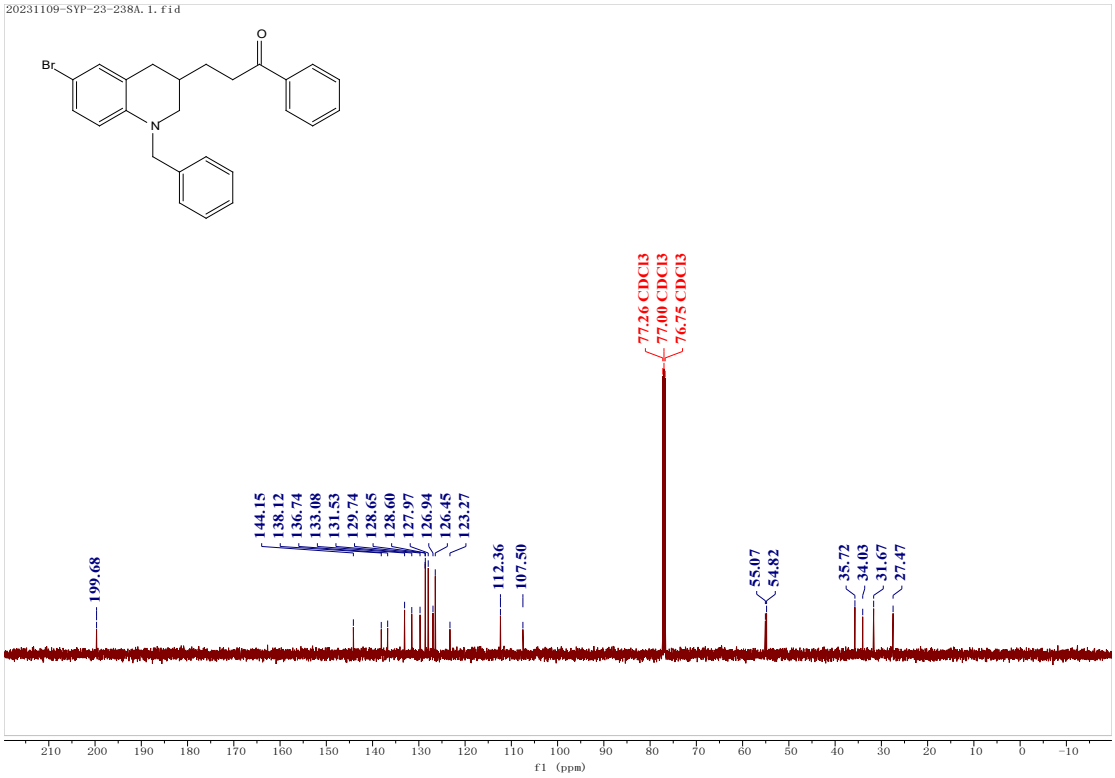
^{13}C-NMR spectrum of C_4



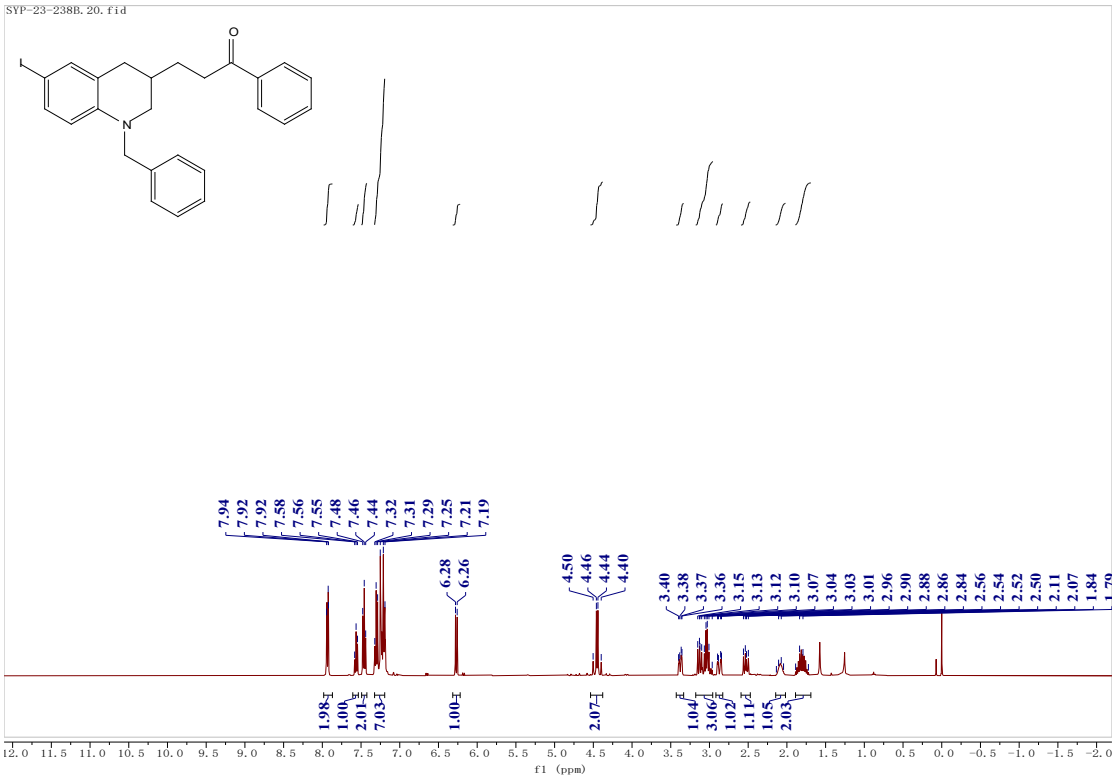
^{1}H-NMR spectrum of C_5



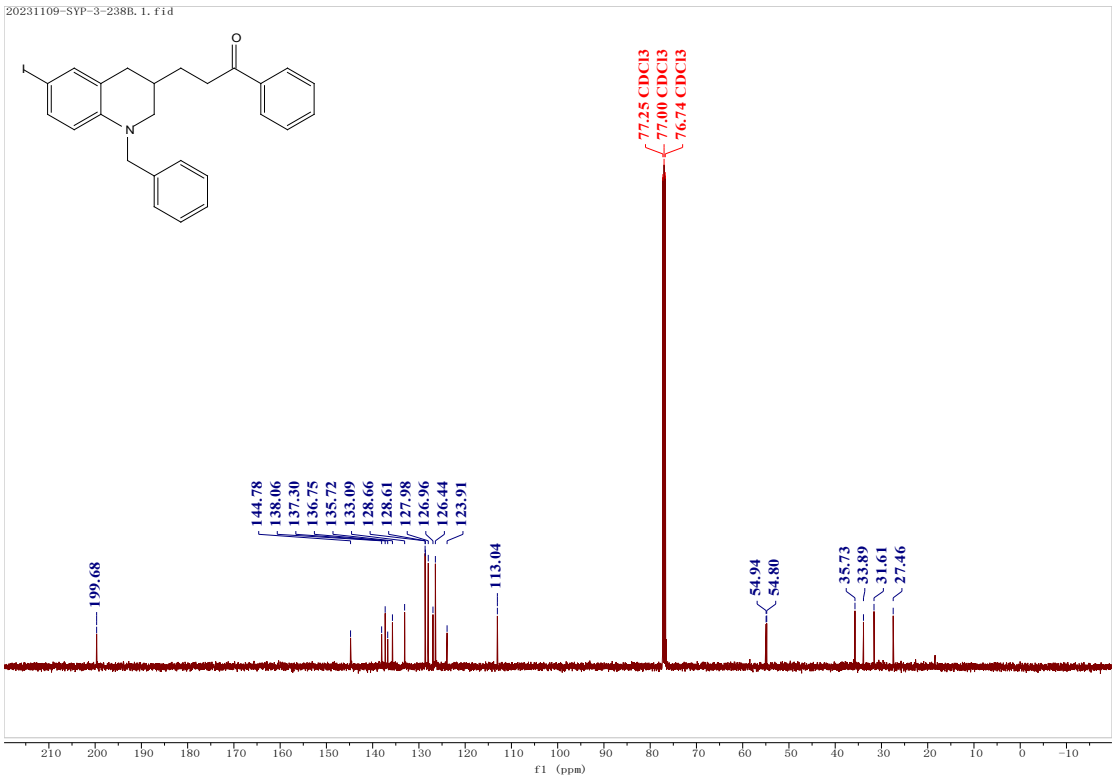
^{13}C-NMR spectrum of C_5



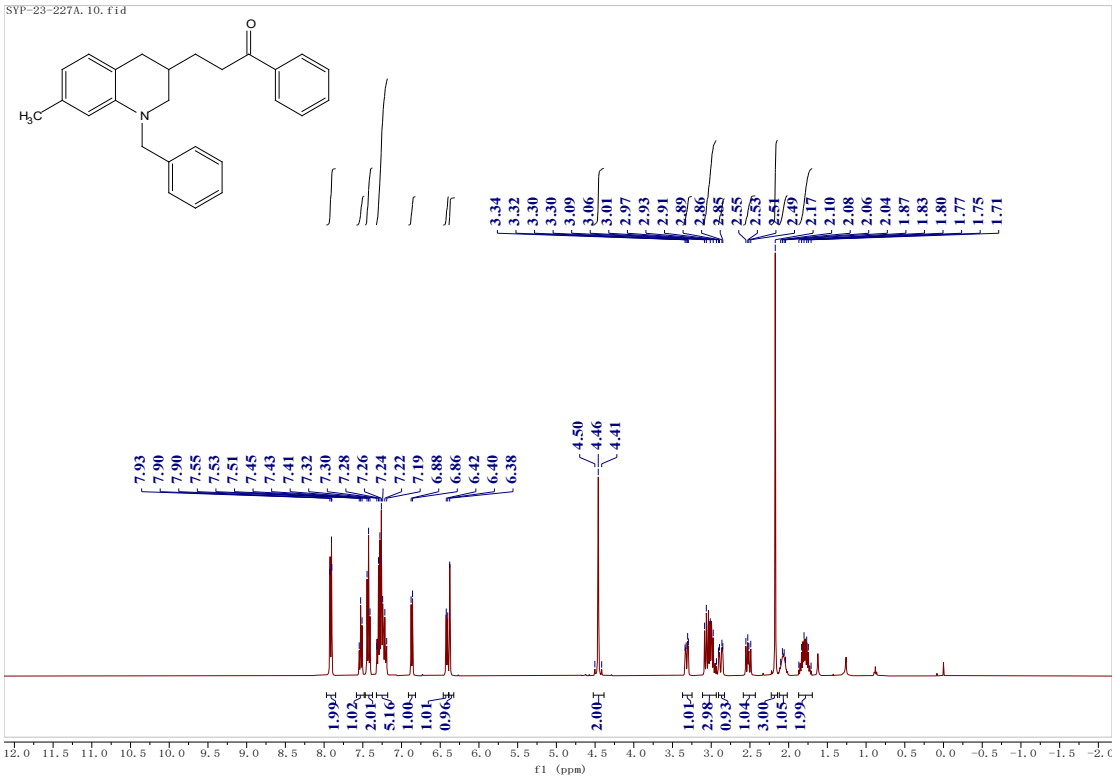
^{1}H-NMR spectrum of C_6



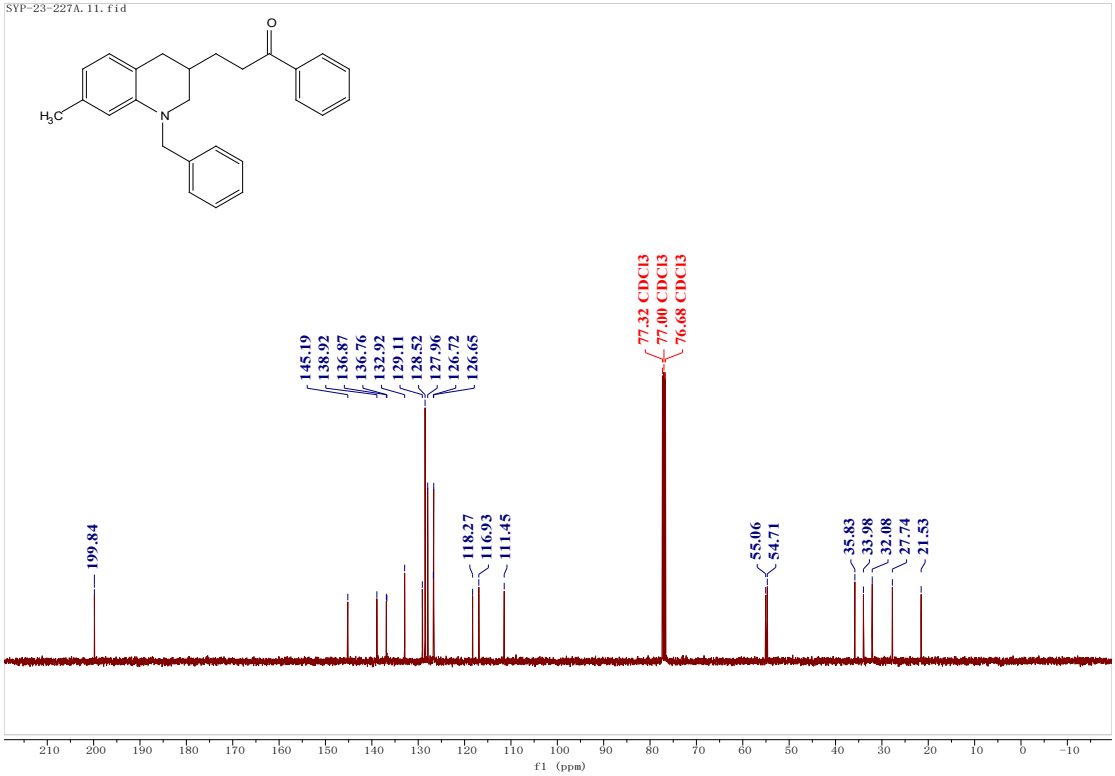
^{13}C-NMR spectrum of C_6



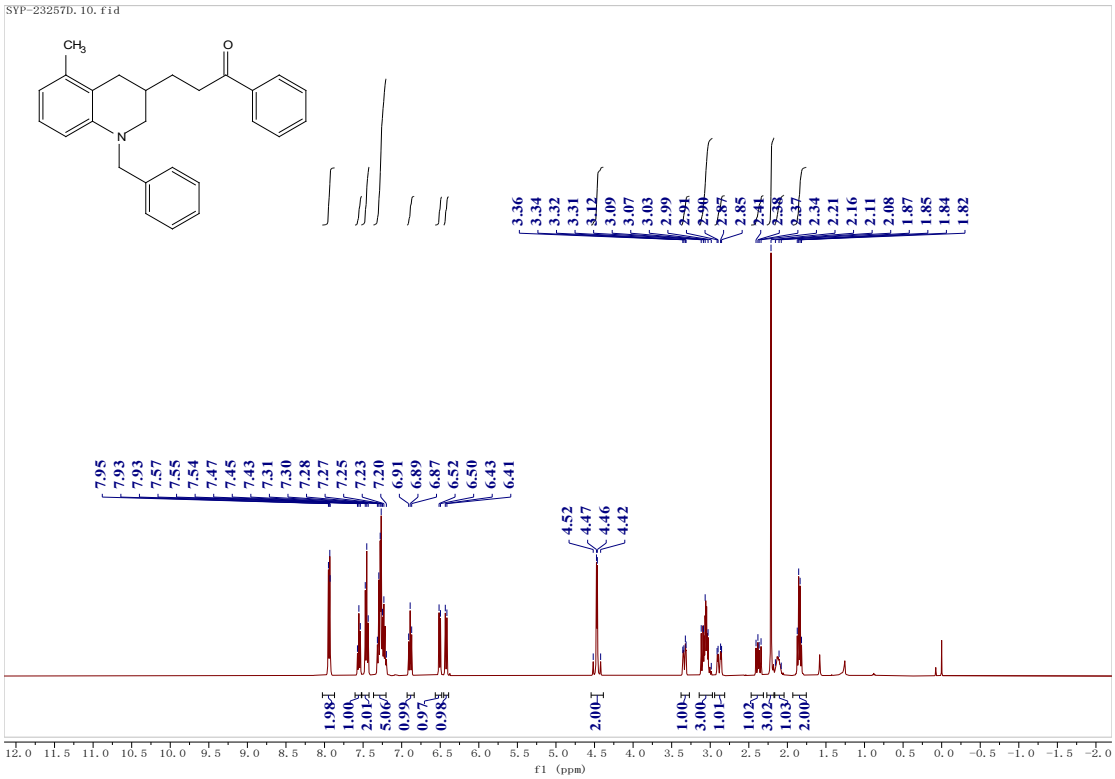
^{1}H-NMR spectrum of C_7



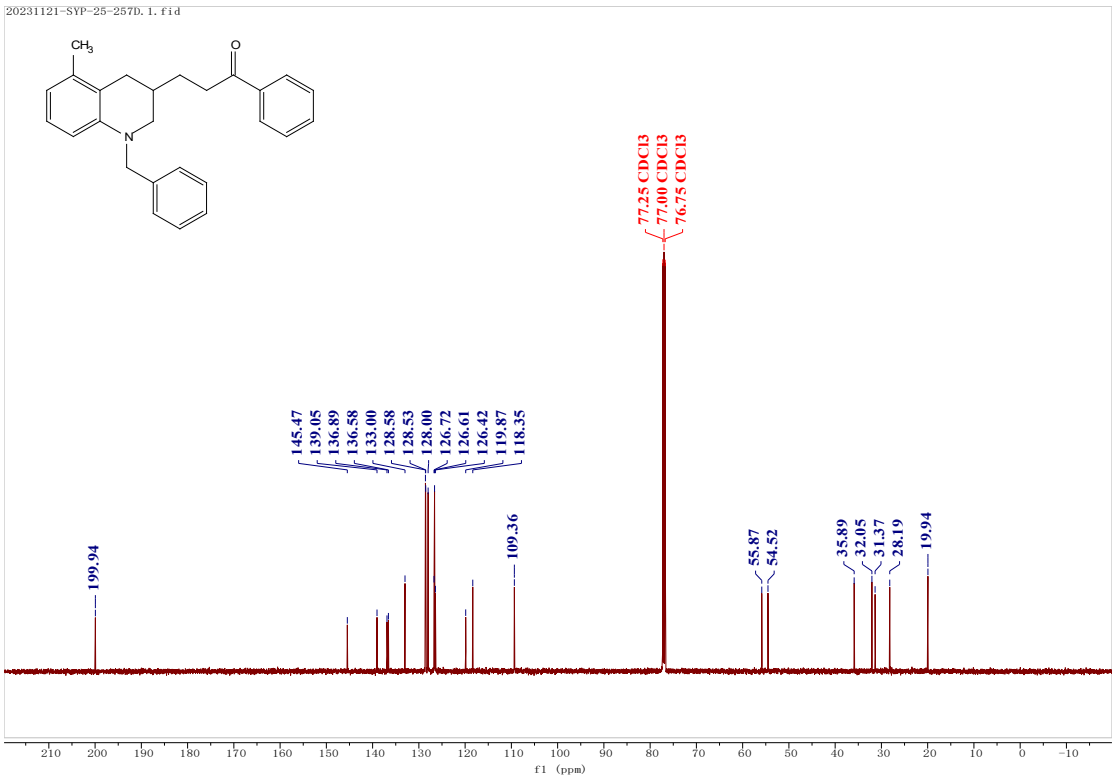
^{13}C-NMR spectrum of C_7



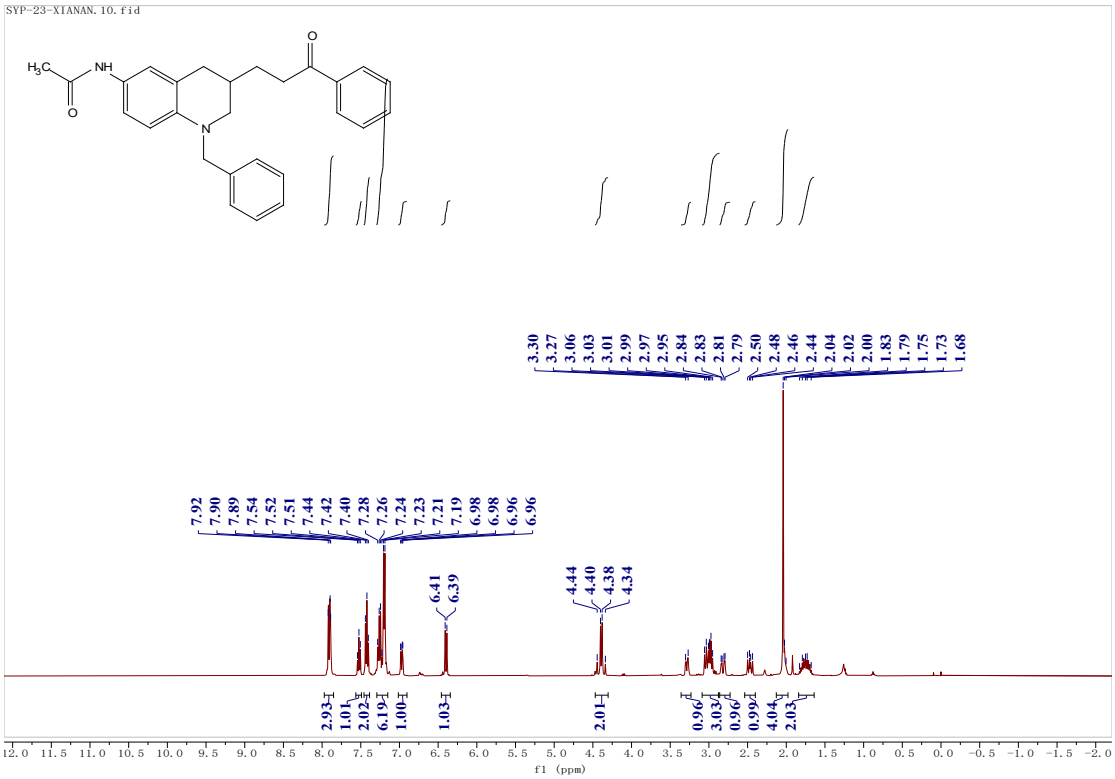
^{1}H-NMR spectrum of C_8



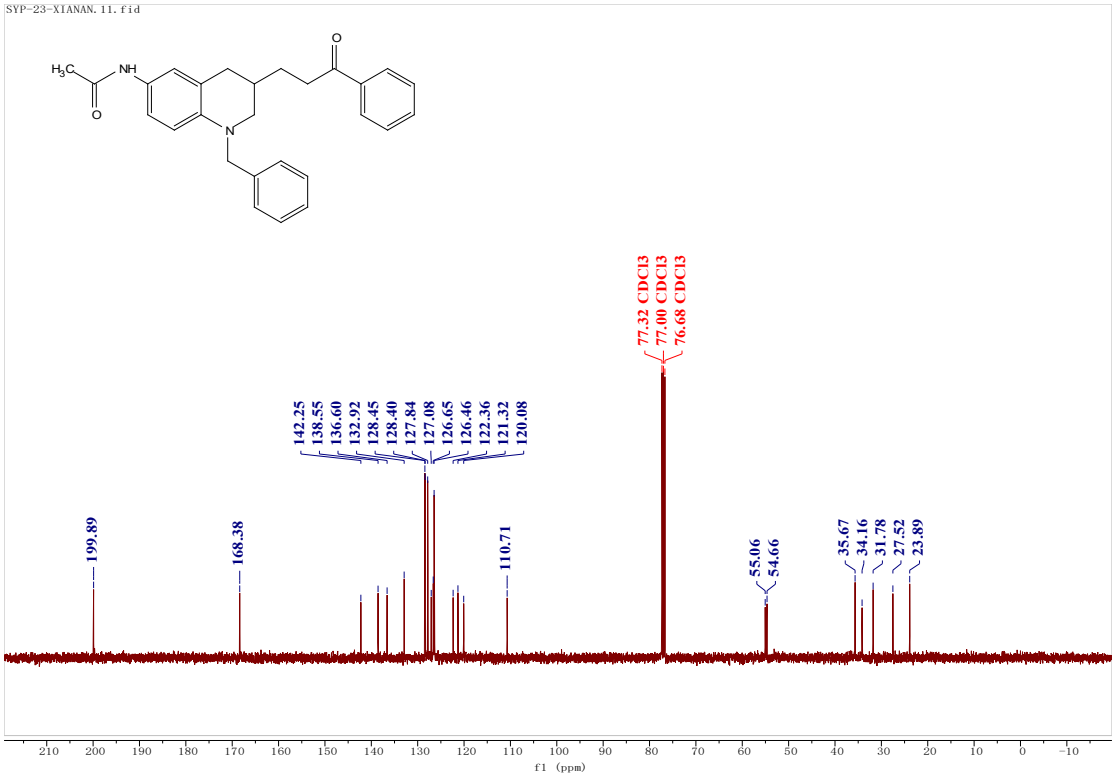
^{13}C-NMR spectrum of C_8



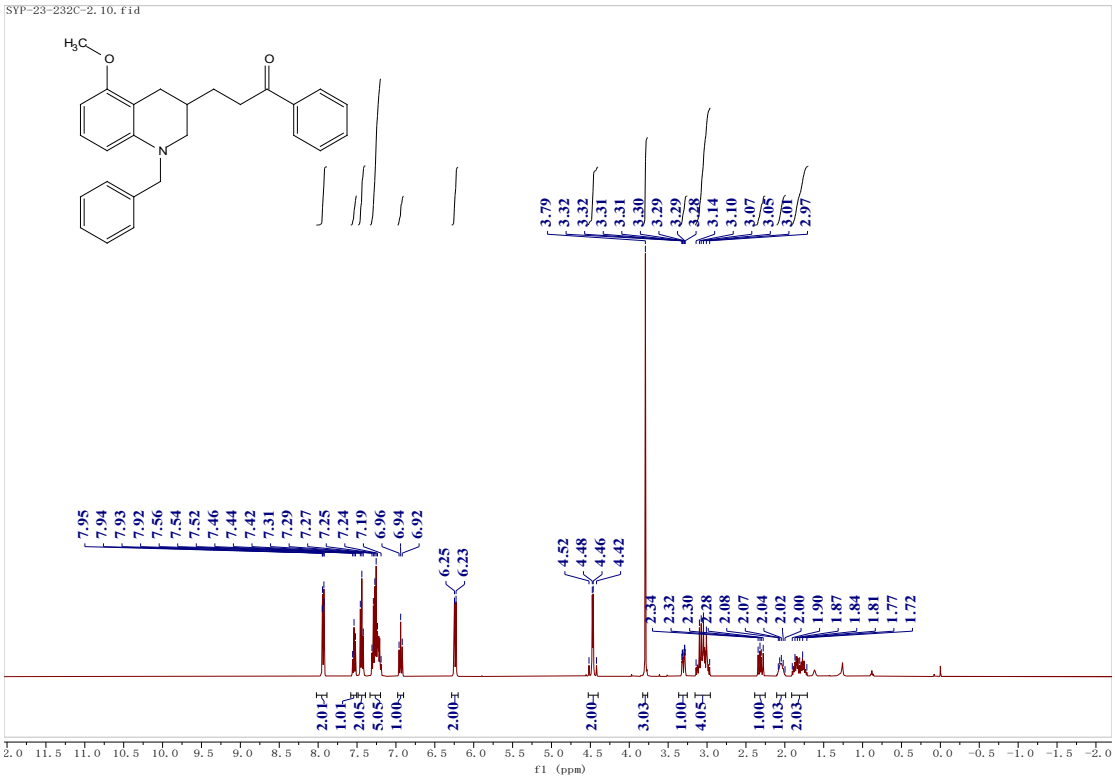
^{1}H-NMR spectrum of C_9



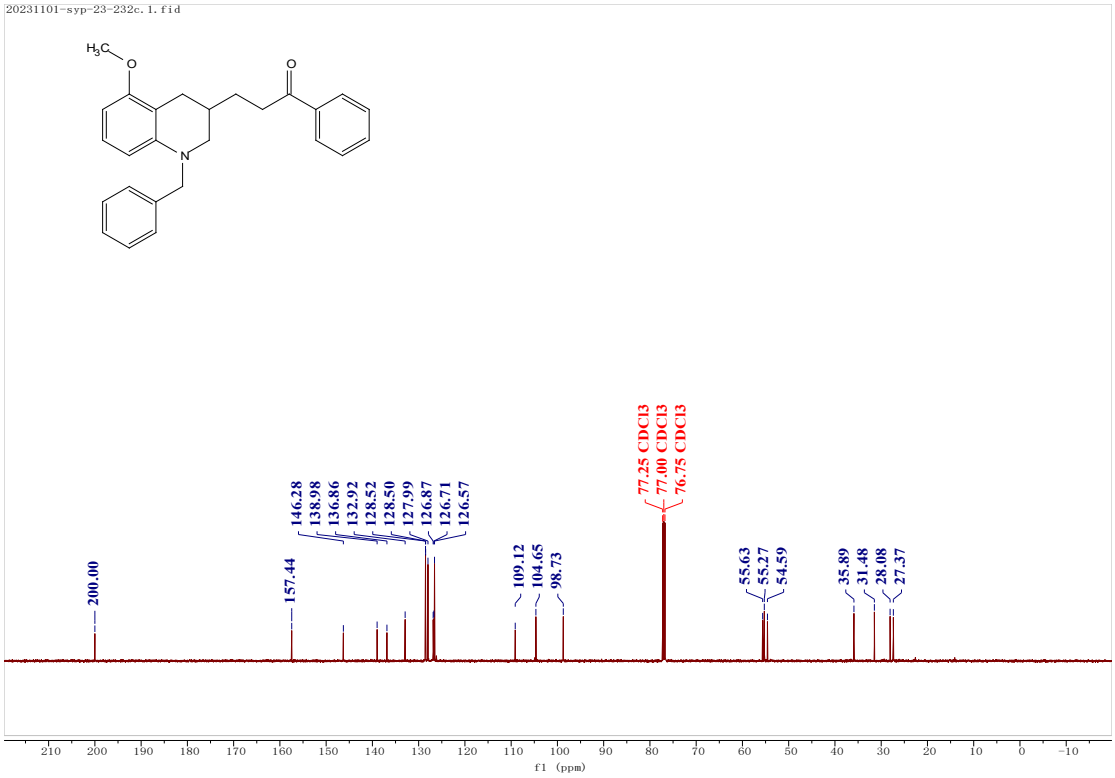
^{13}C-NMR spectrum of C_9



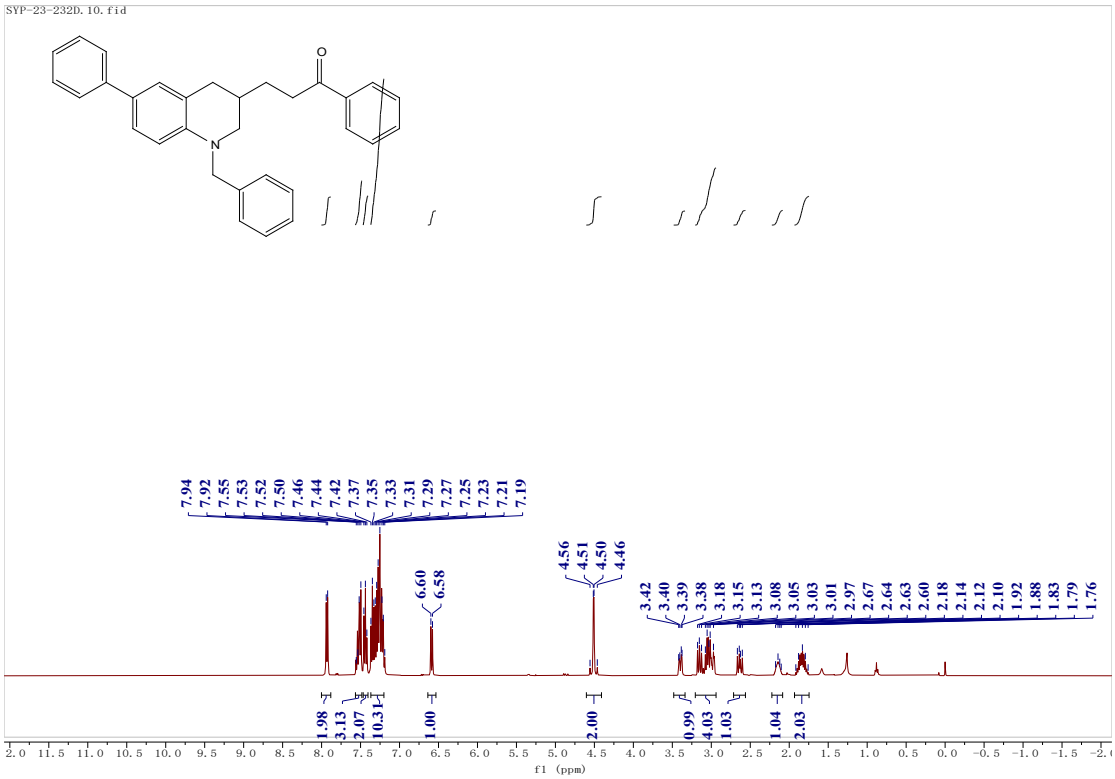
^{1}H-NMR spectrum of C_{10}



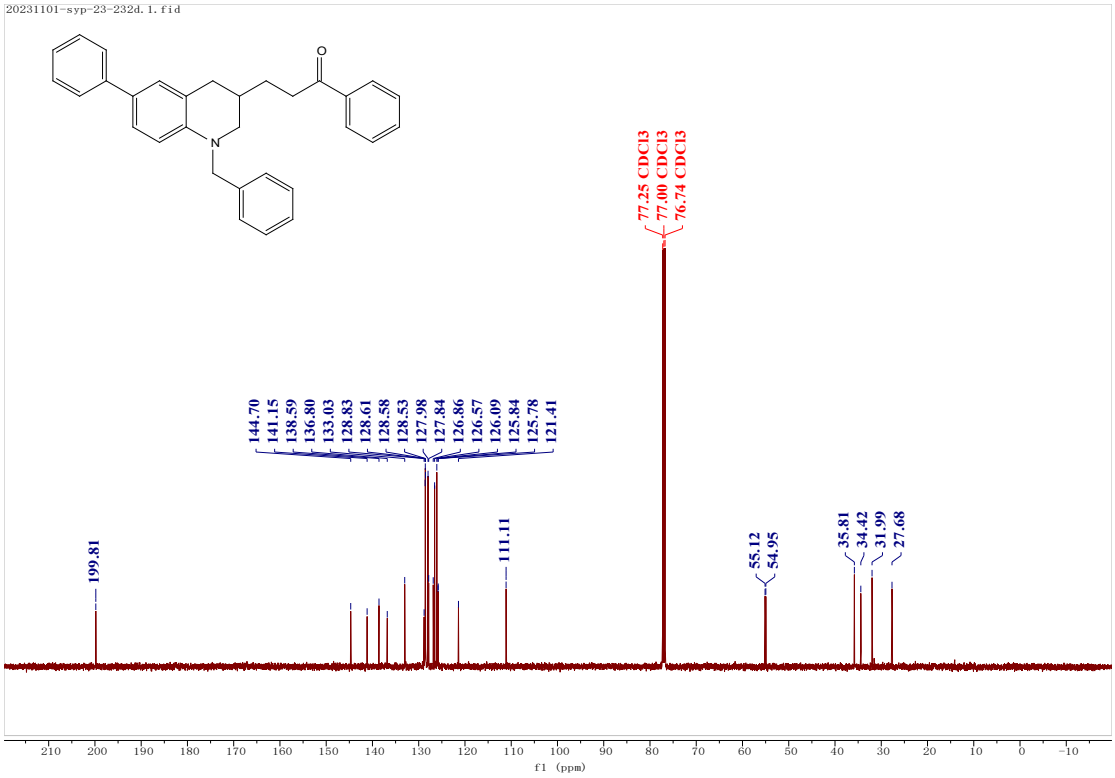
^{13}C-NMR spectrum of C_{10}



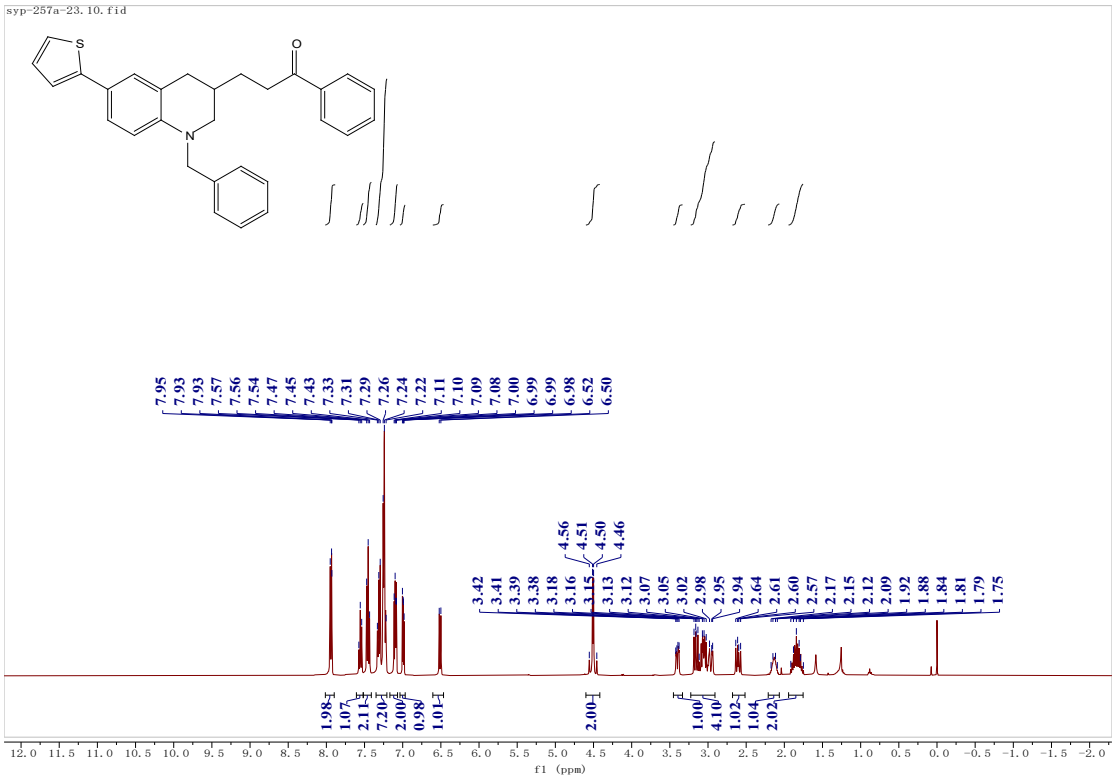
^{1}H-NMR spectrum of C_{11}



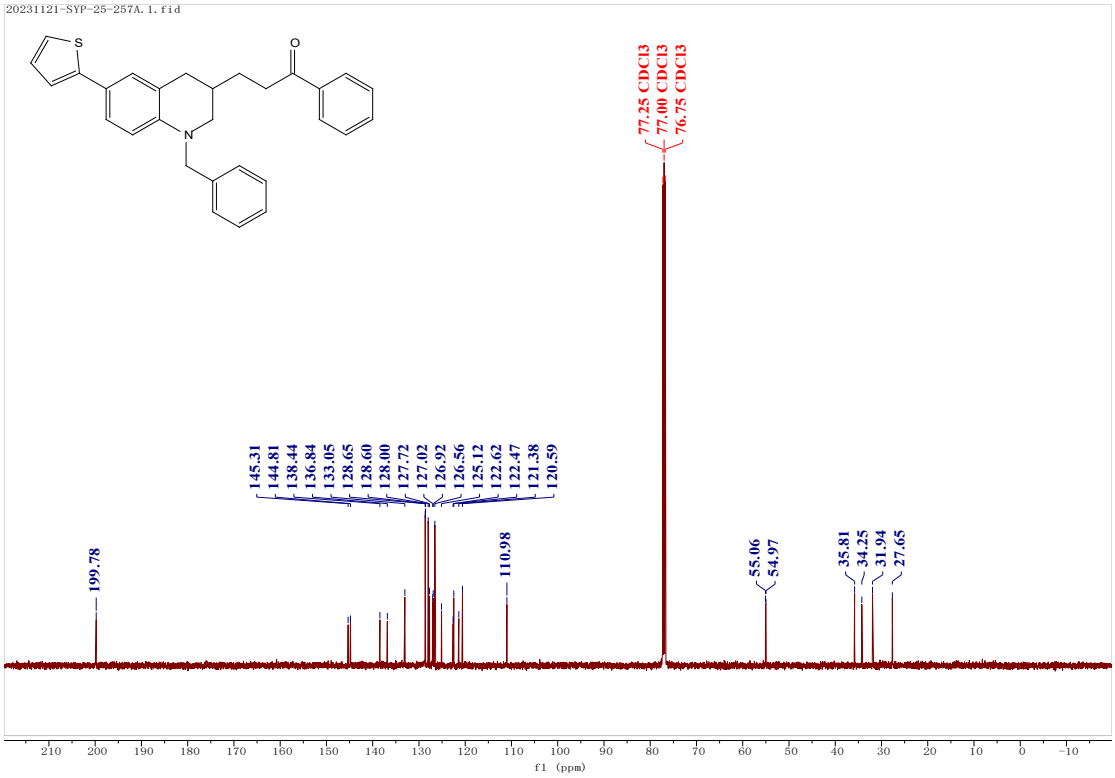
^{13}C-NMR spectrum of C_{11}



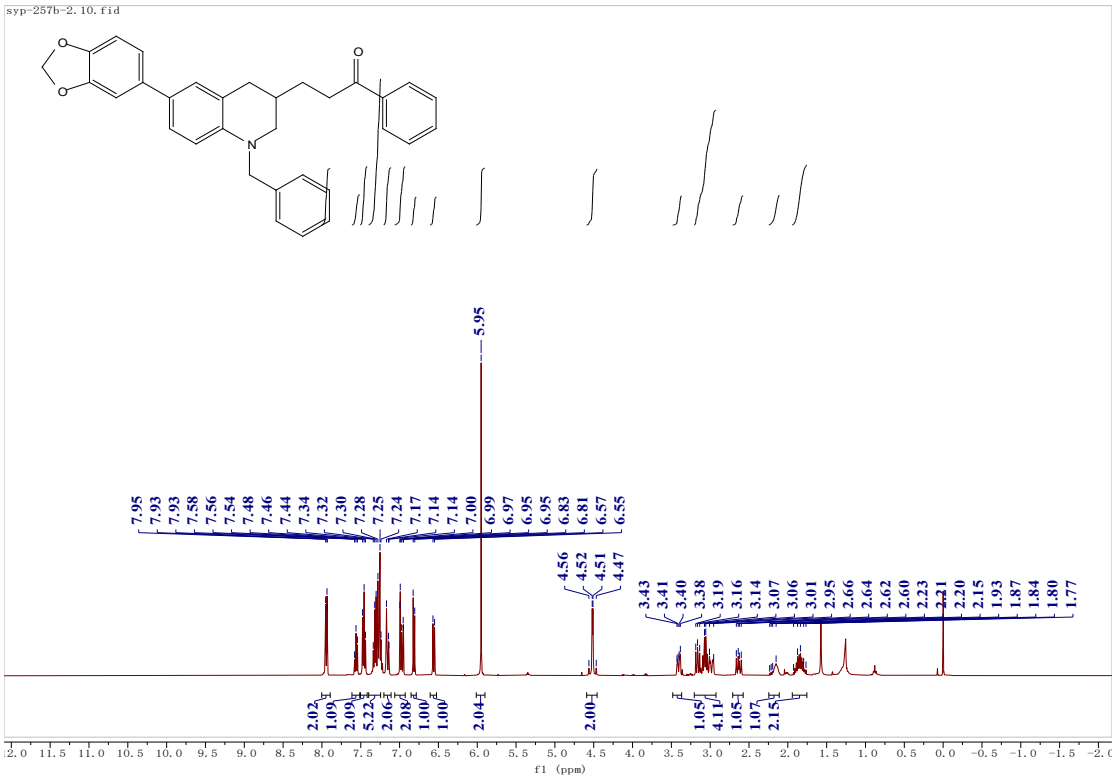
^{1}H-NMR spectrum of C_{12}



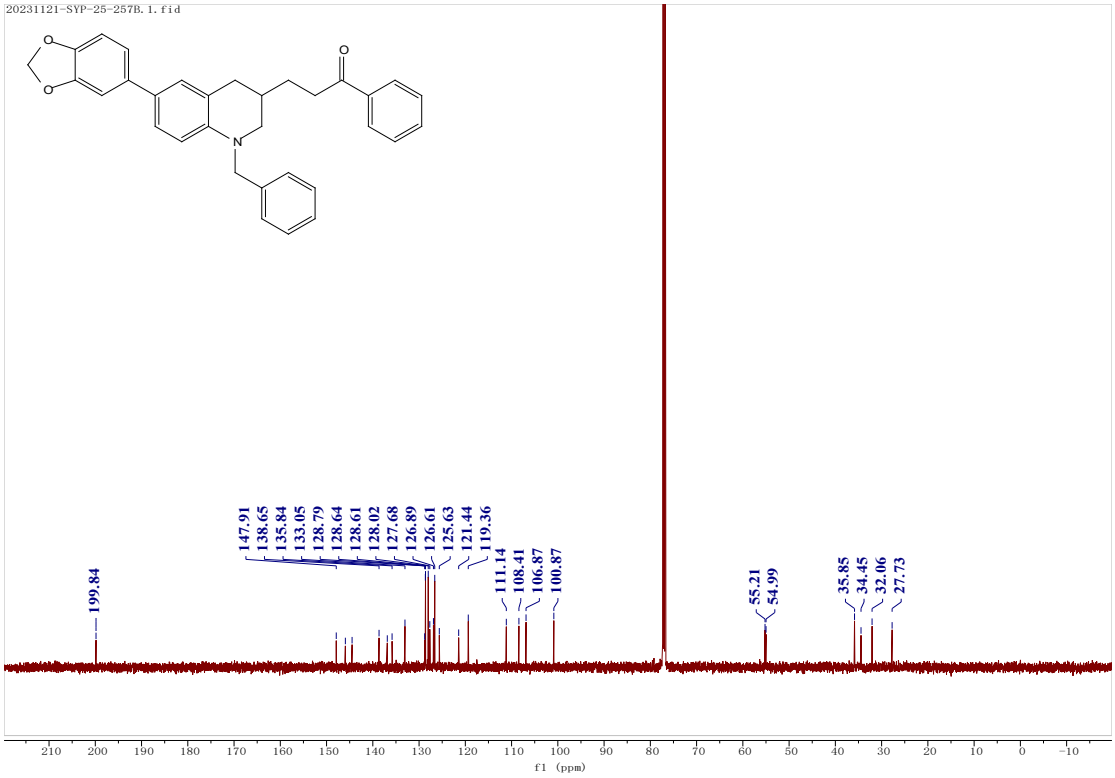
^{13}C-NMR spectrum of C_{12}



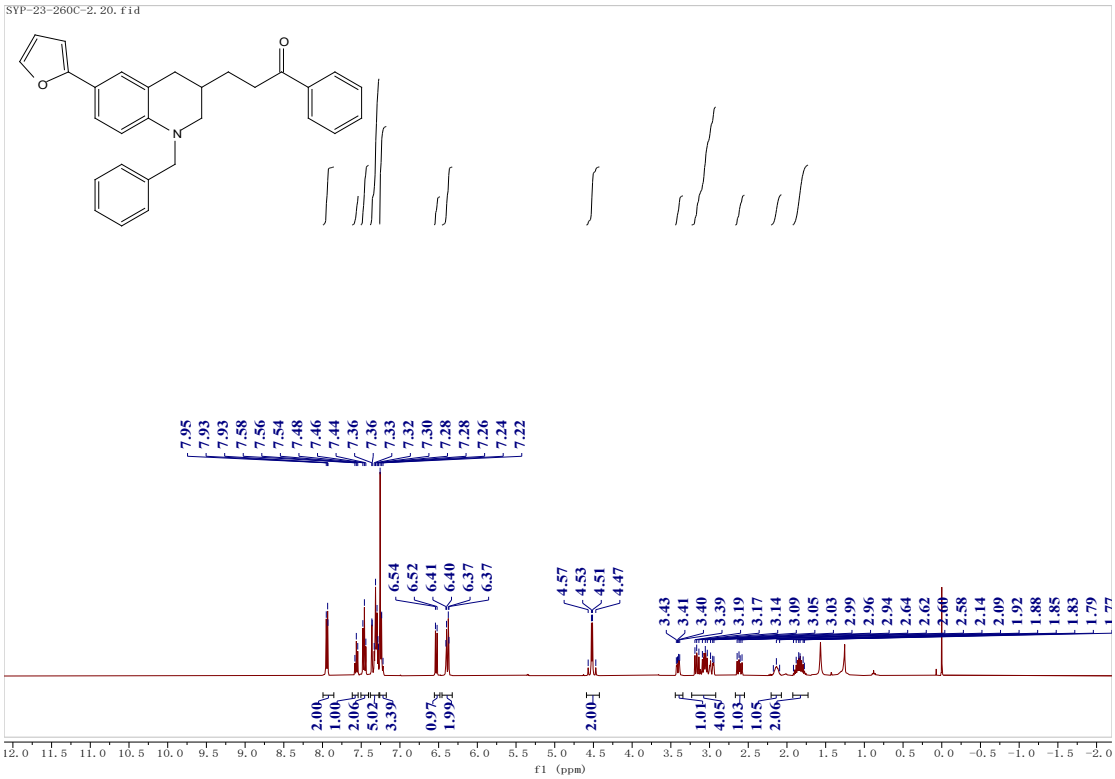
^{1}H-NMR spectrum of C_{13}



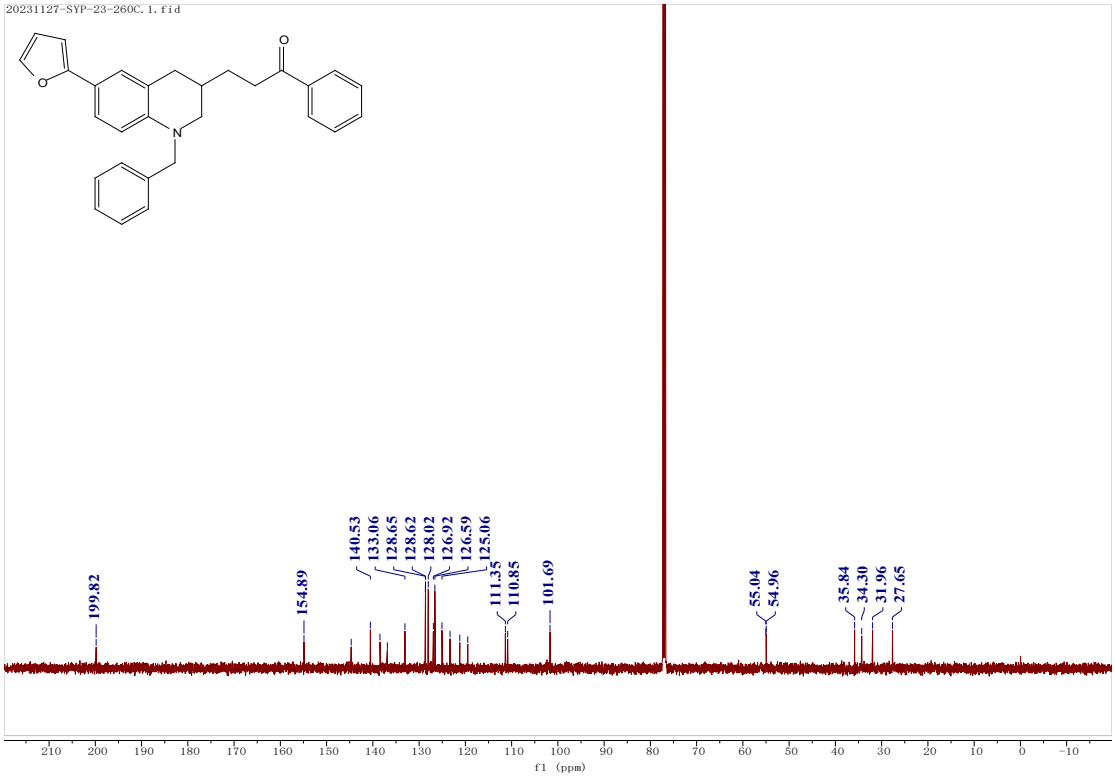
^{13}C-NMR spectrum of C_{13}



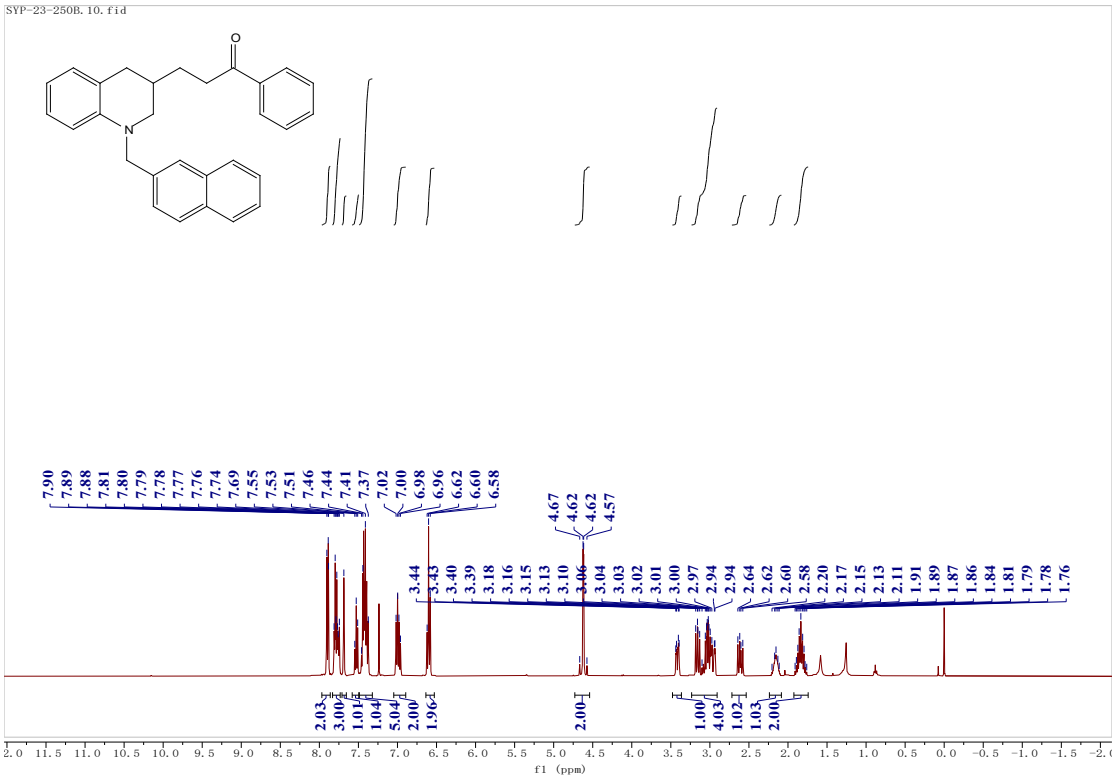
^{1}H-NMR spectrum of C_{14}



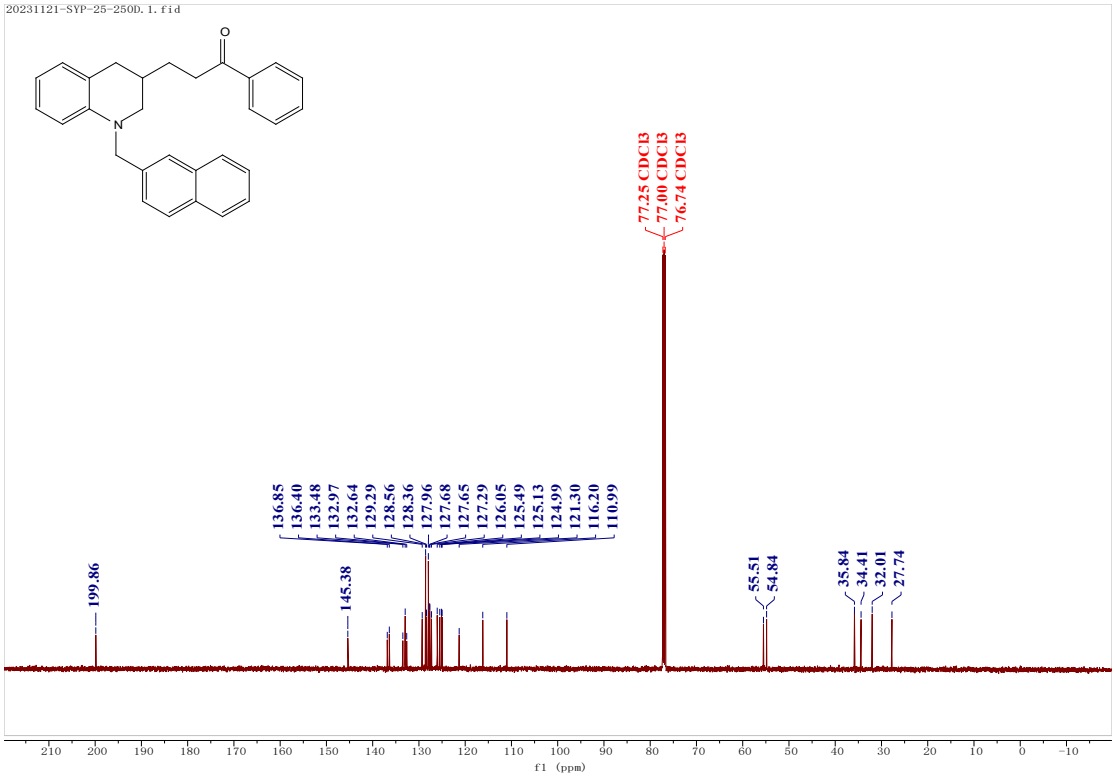
^{13}C-NMR spectrum of C_{14}



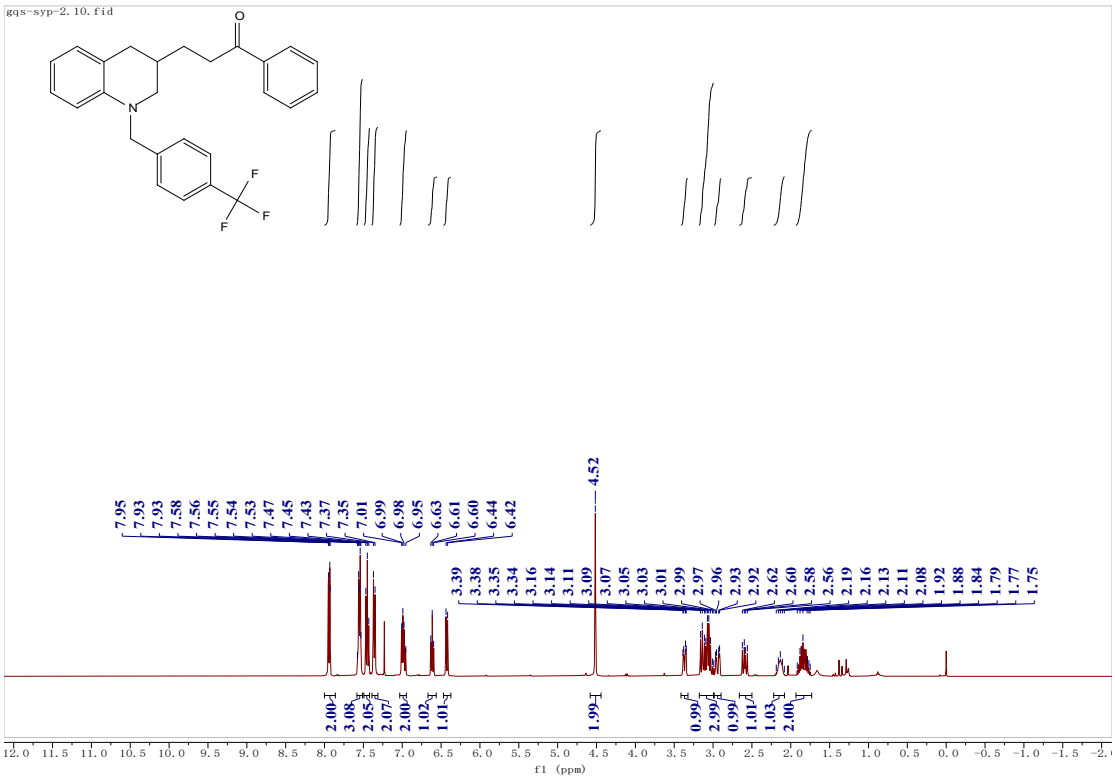
^{1}H-NMR spectrum of C_{15}



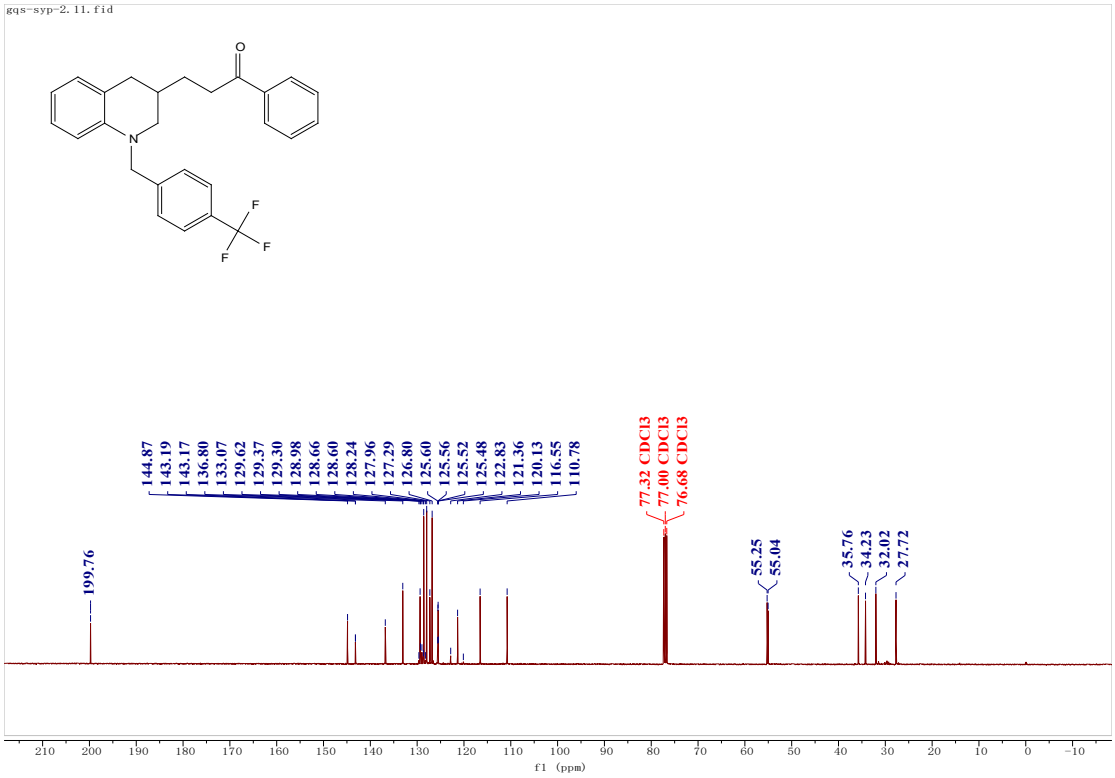
^{13}C-NMR spectrum of C_{15}



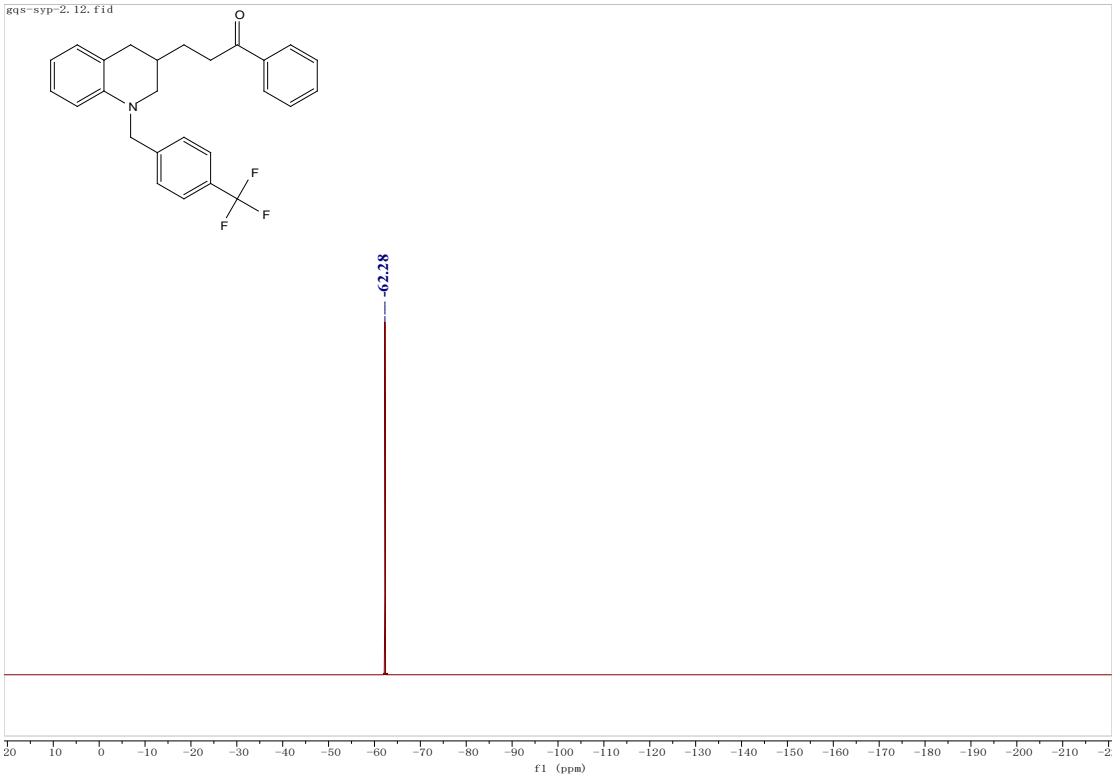
^{1}H-NMR spectrum of C_{16}



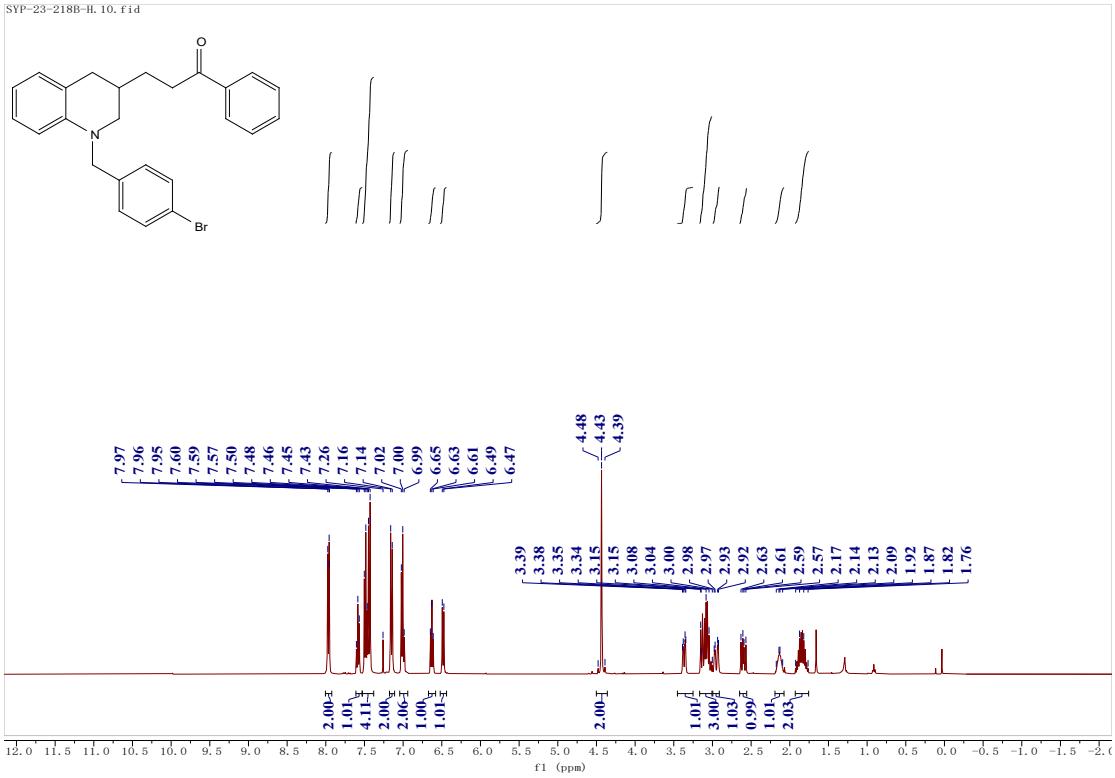
^{13}C-NMR spectrum of C_{16}



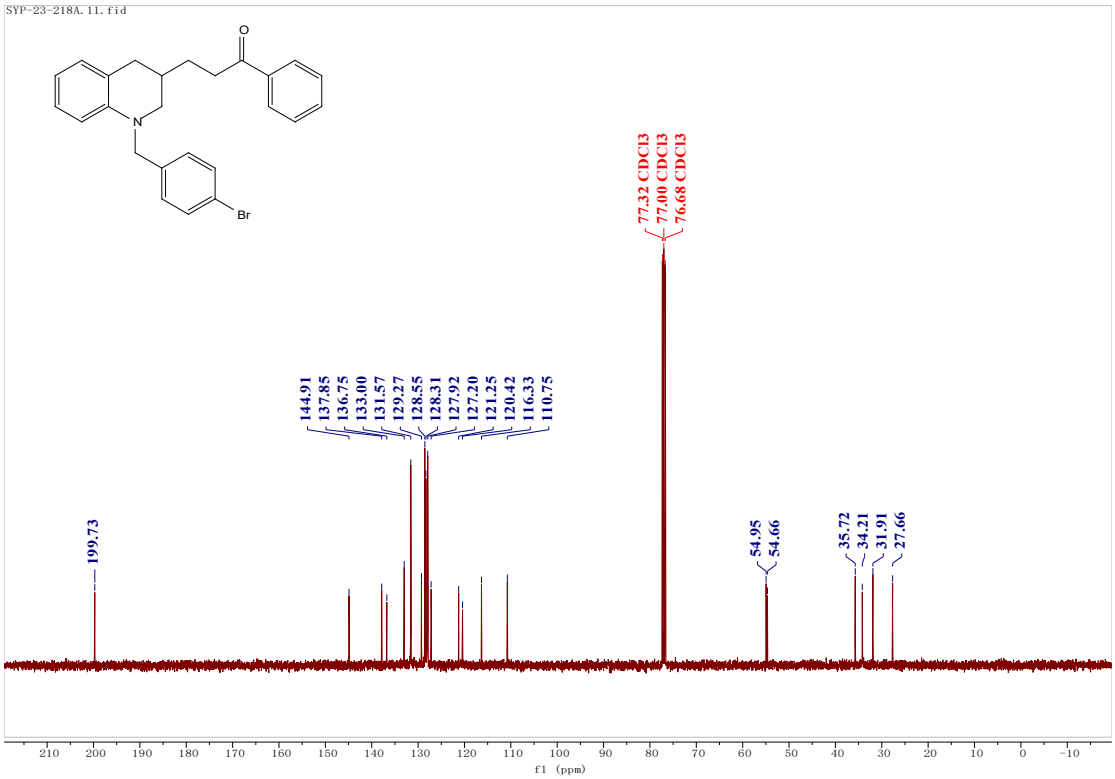
^{19}F-NMR spectrum of C_{17}



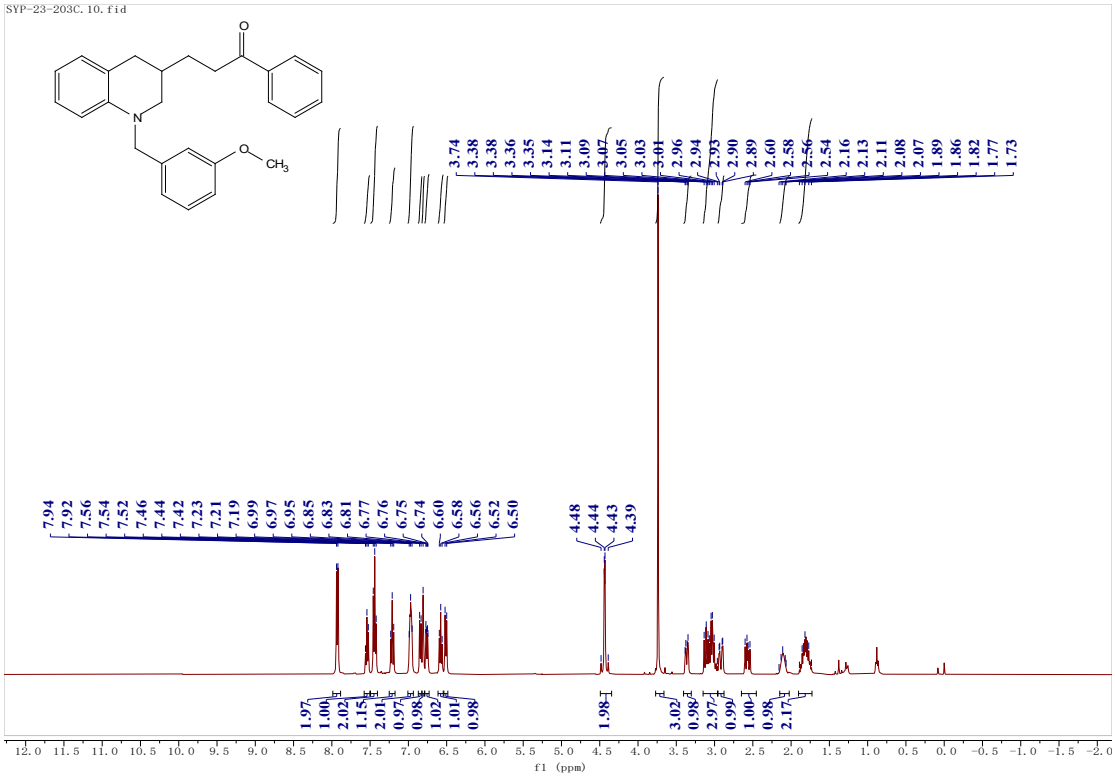
^{1}H-NMR spectrum of C_{17}



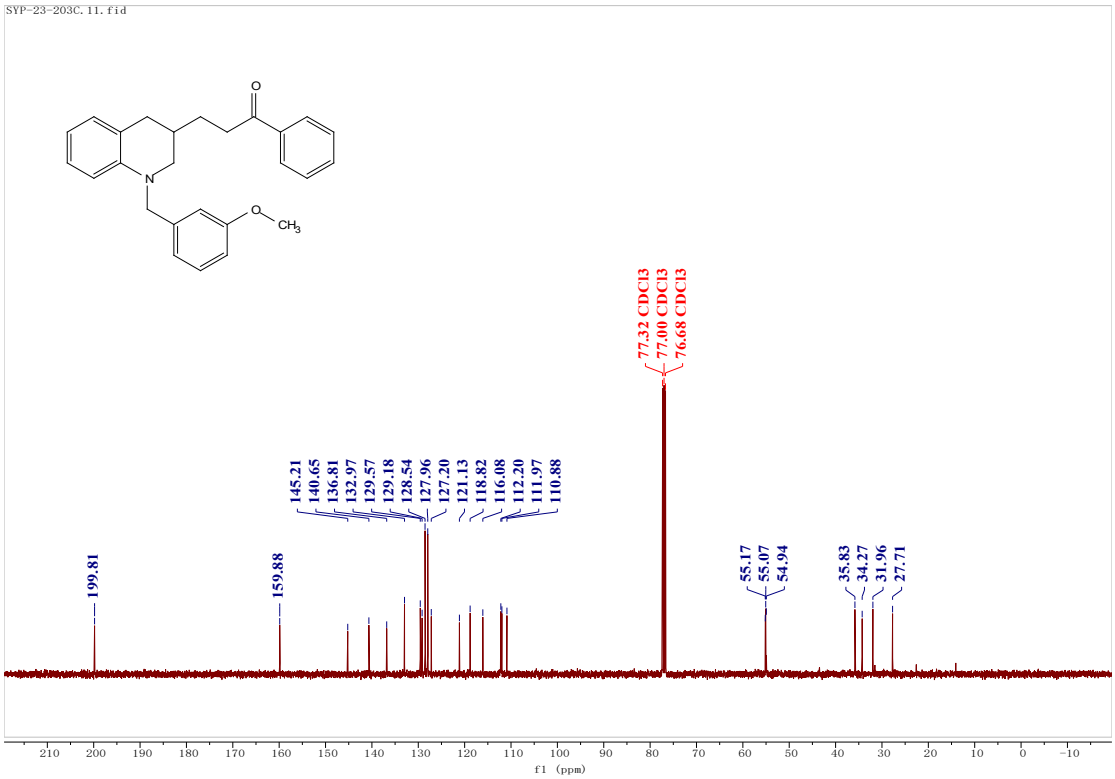
^{13}C-NMR spectrum of C_{17}



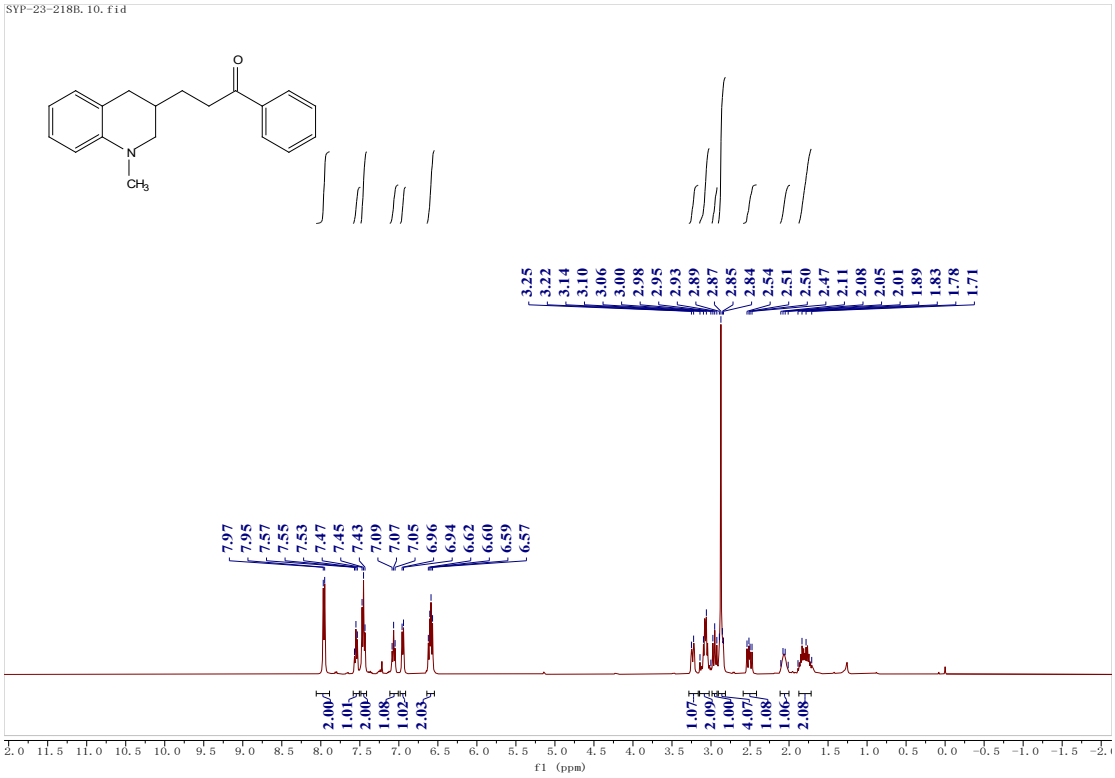
^{1}H-NMR spectrum of C_{18}



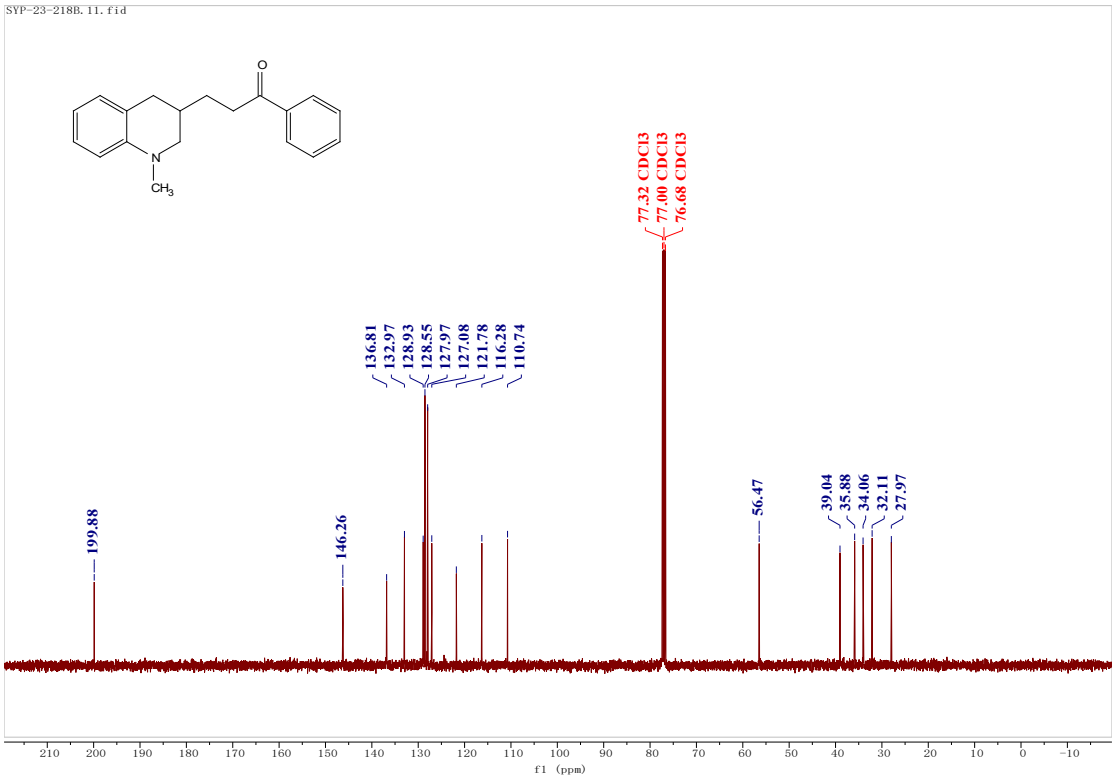
^{13}C-NMR spectrum of C_{18}



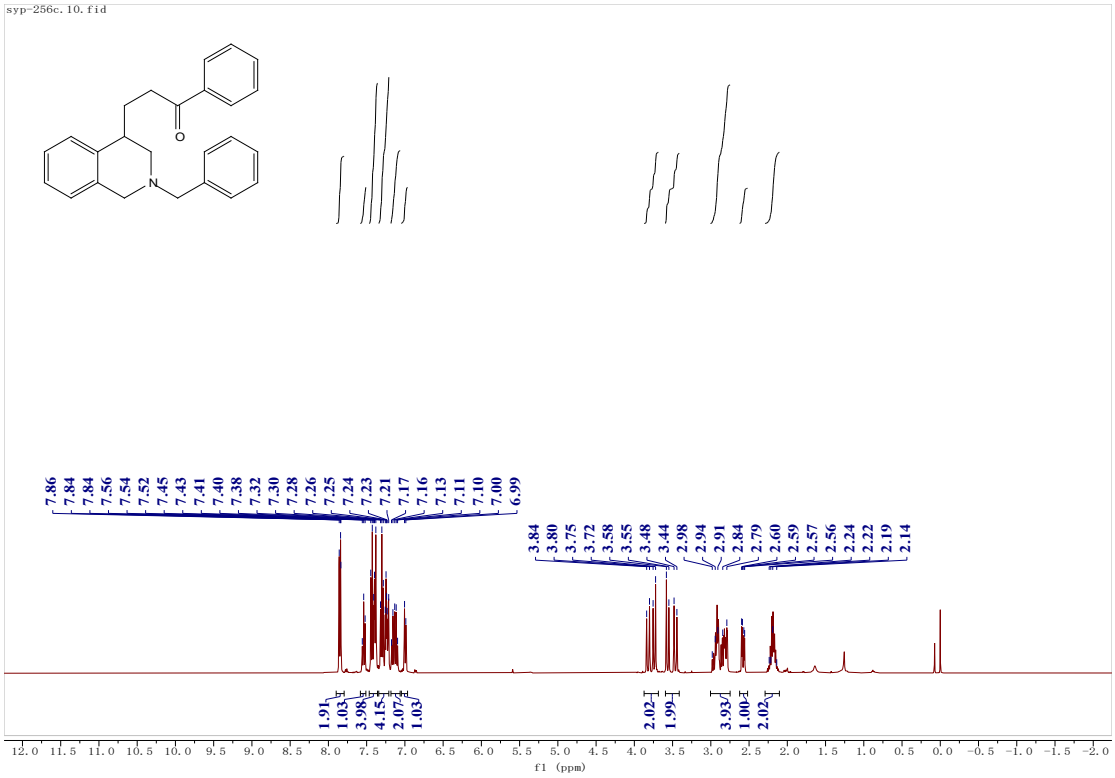
^{1}H-NMR spectrum of C_{19}



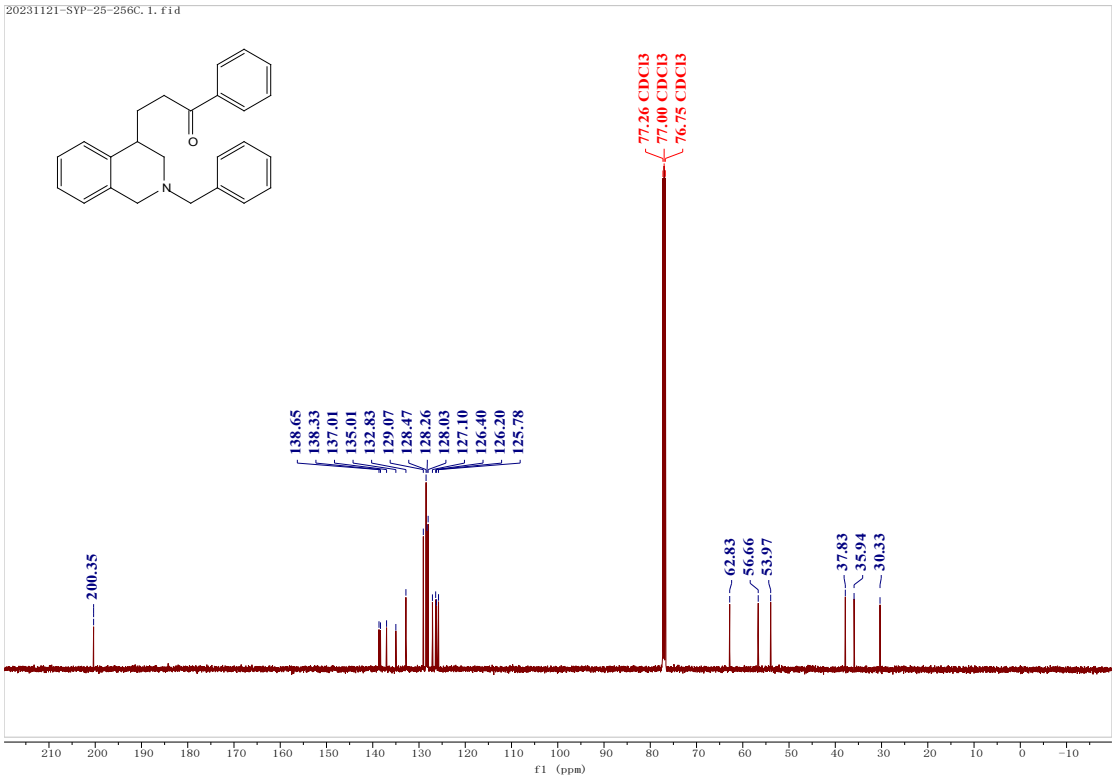
^{13}C-NMR spectrum of C_{19}



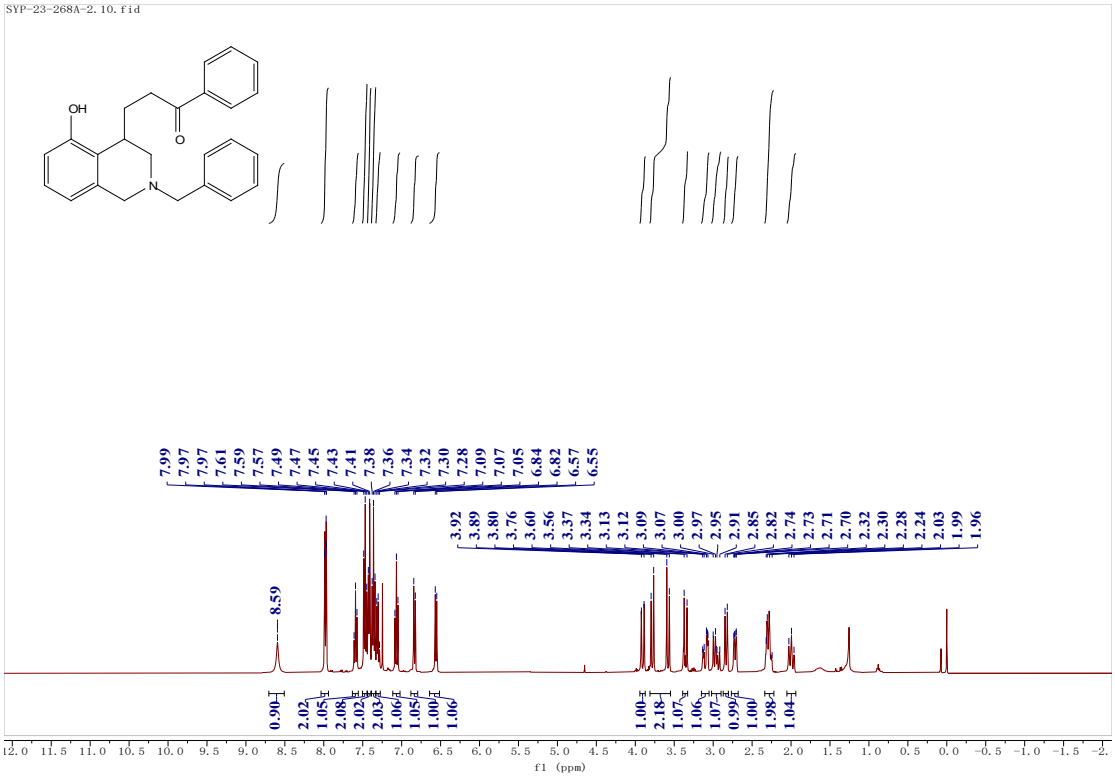
^{1}H-NMR spectrum of C_{20}



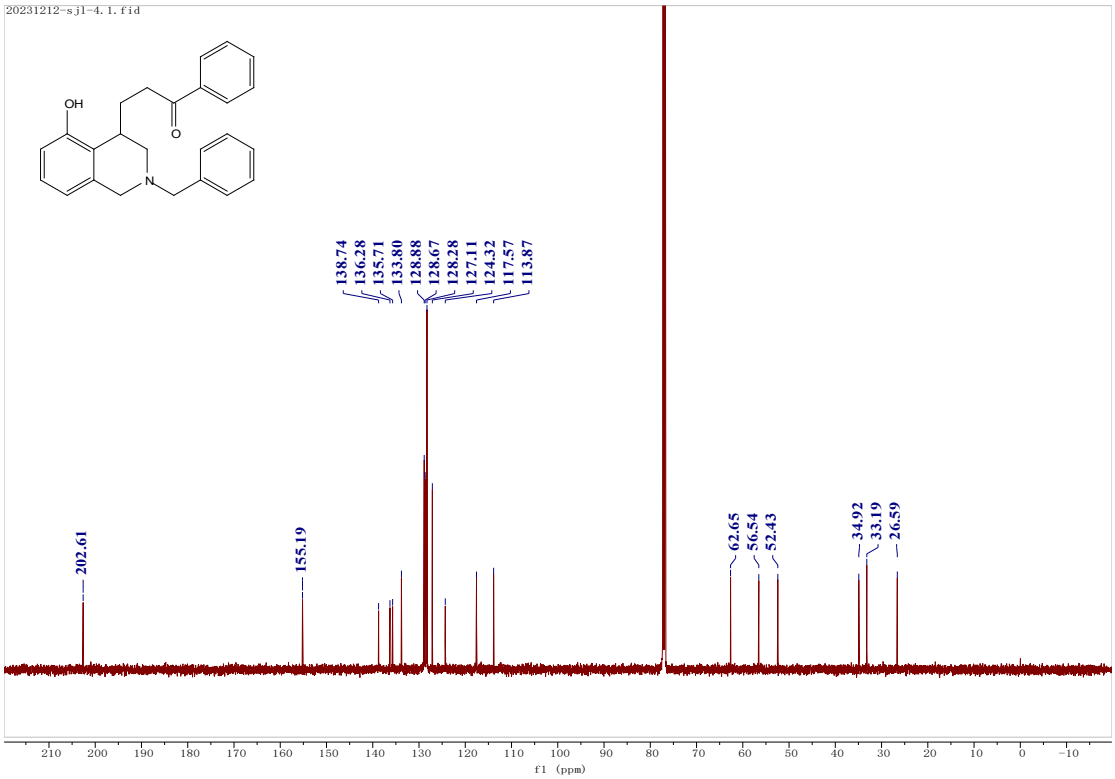
^{13}C-NMR spectrum of C_{20}



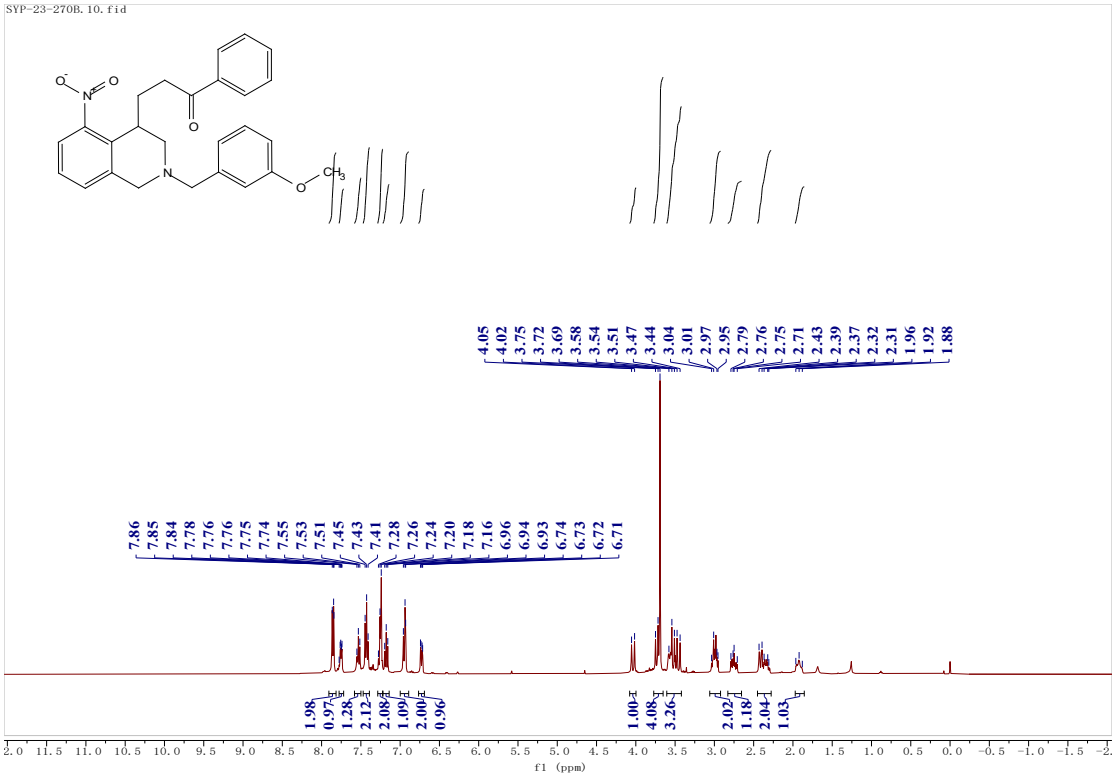
^{1}H-NMR spectrum of C_{21}



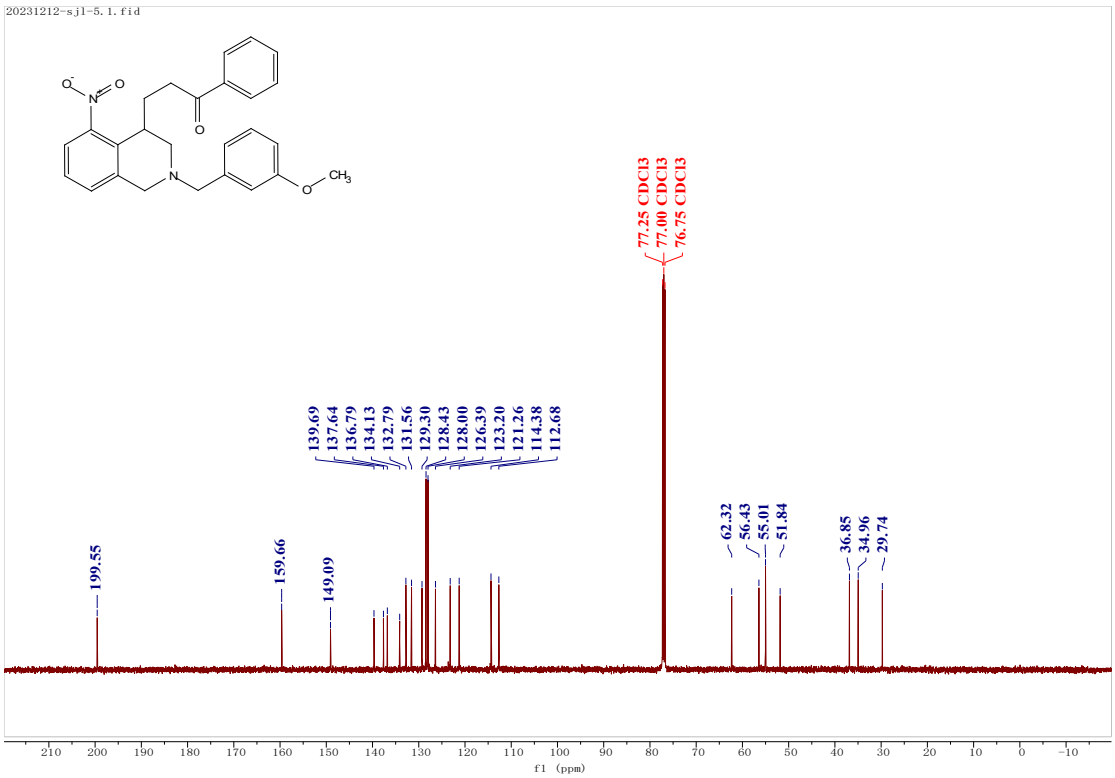
^{13}C-NMR spectrum of C_{21}



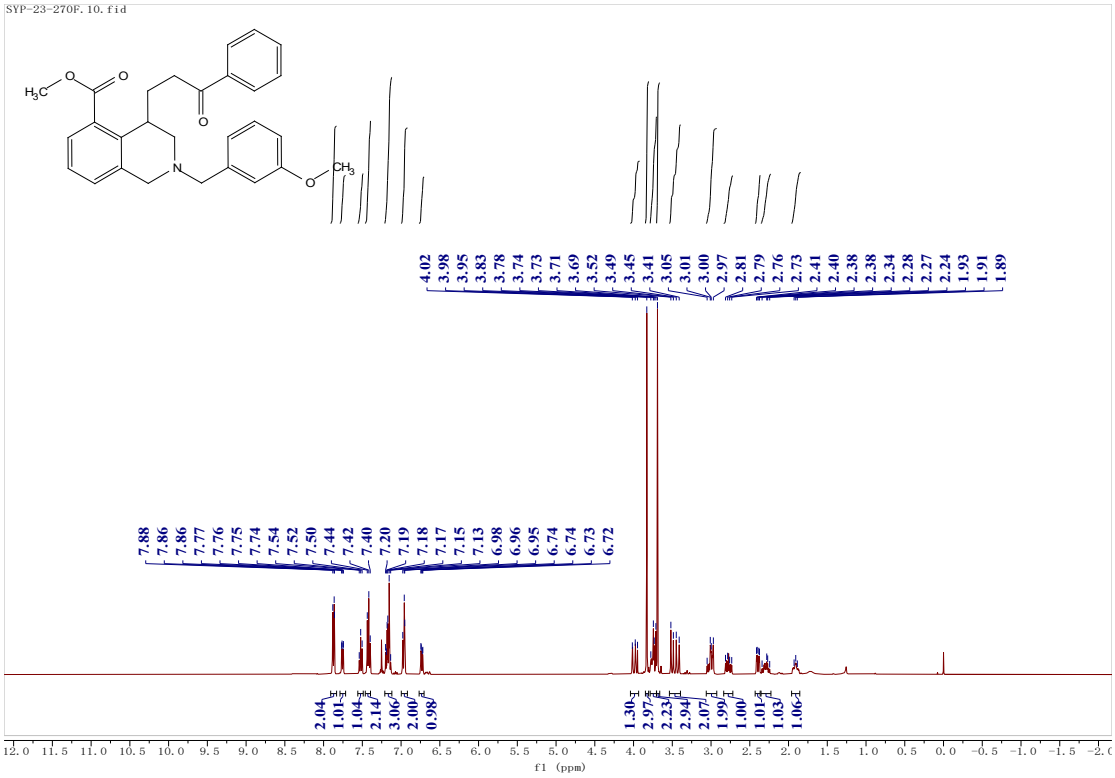
^{1}H-NMR spectrum of C_{22}



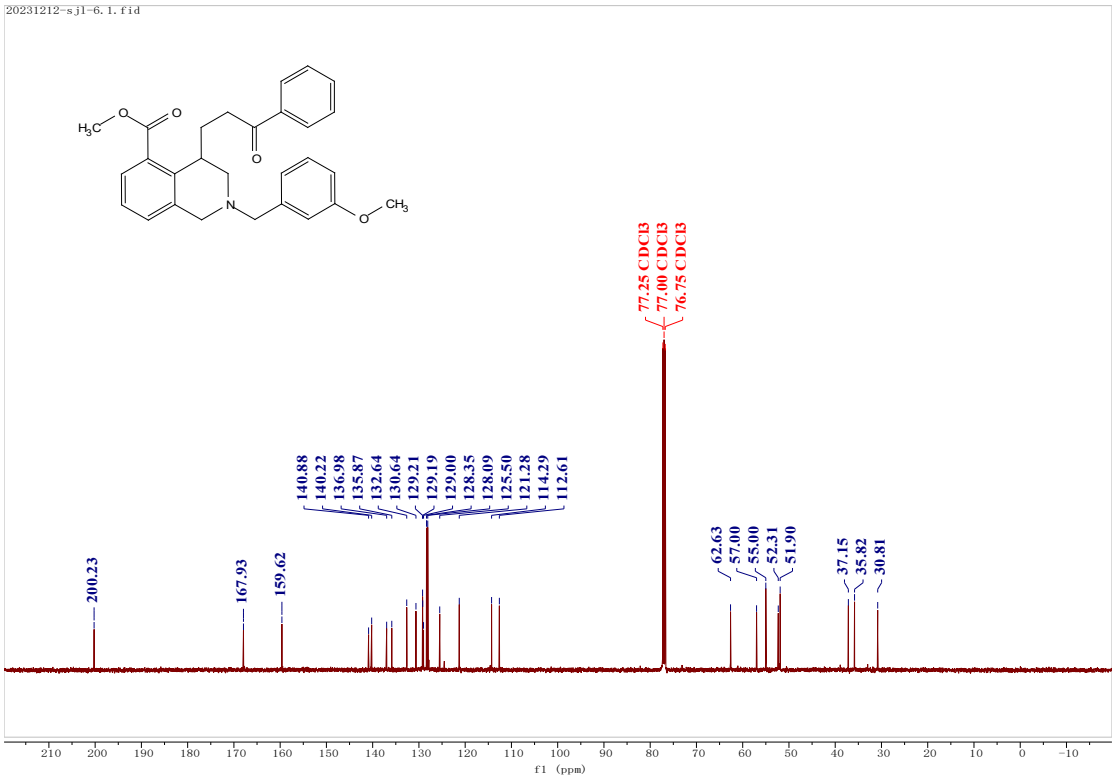
^{13}C-NMR spectrum of C_{22}



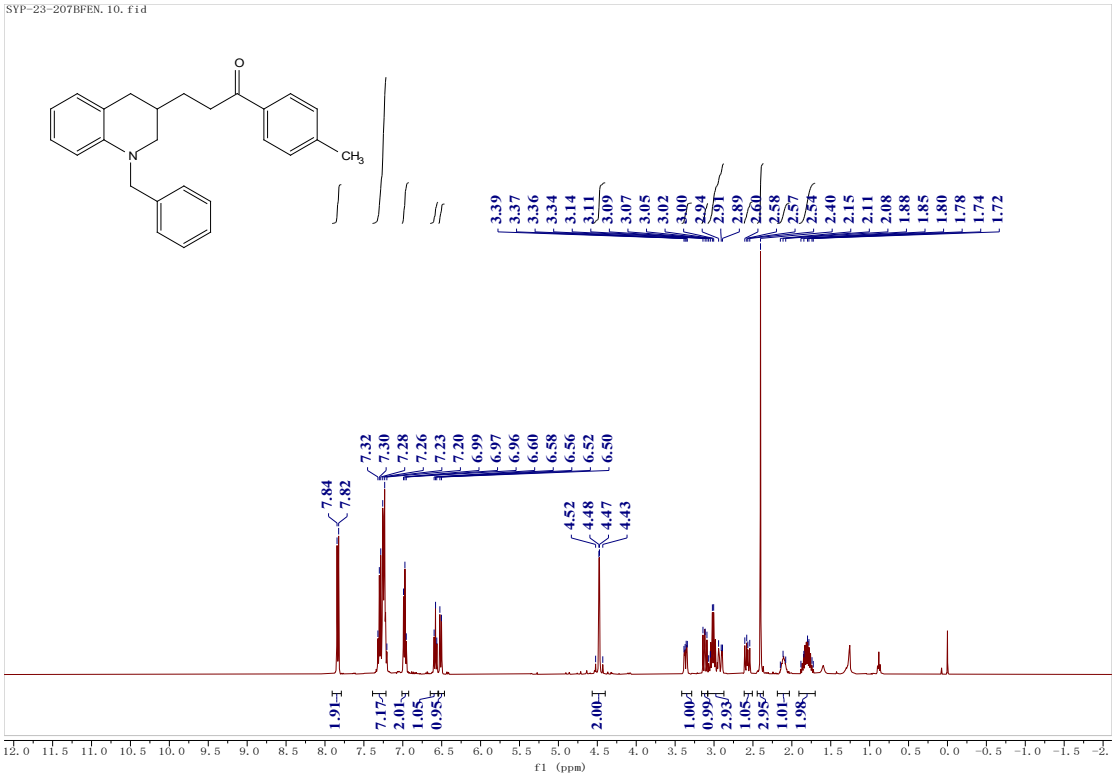
^{1}H-NMR spectrum of C_{23}



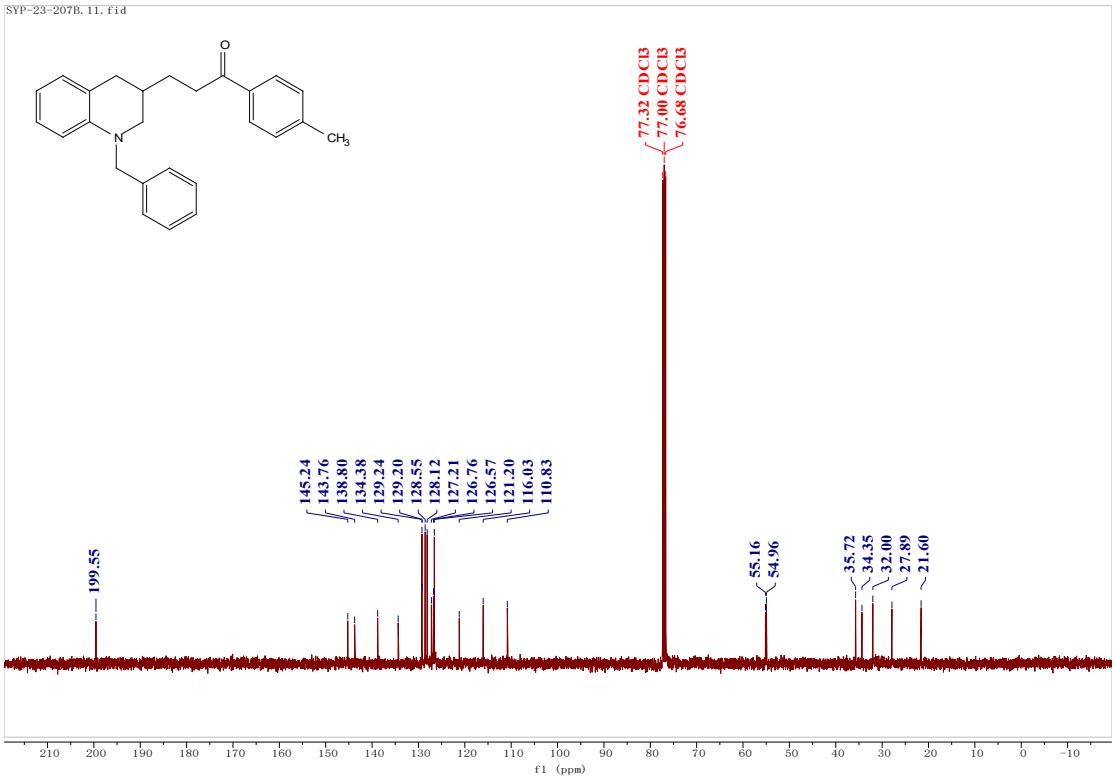
^{13}C-NMR spectrum of C_{23}



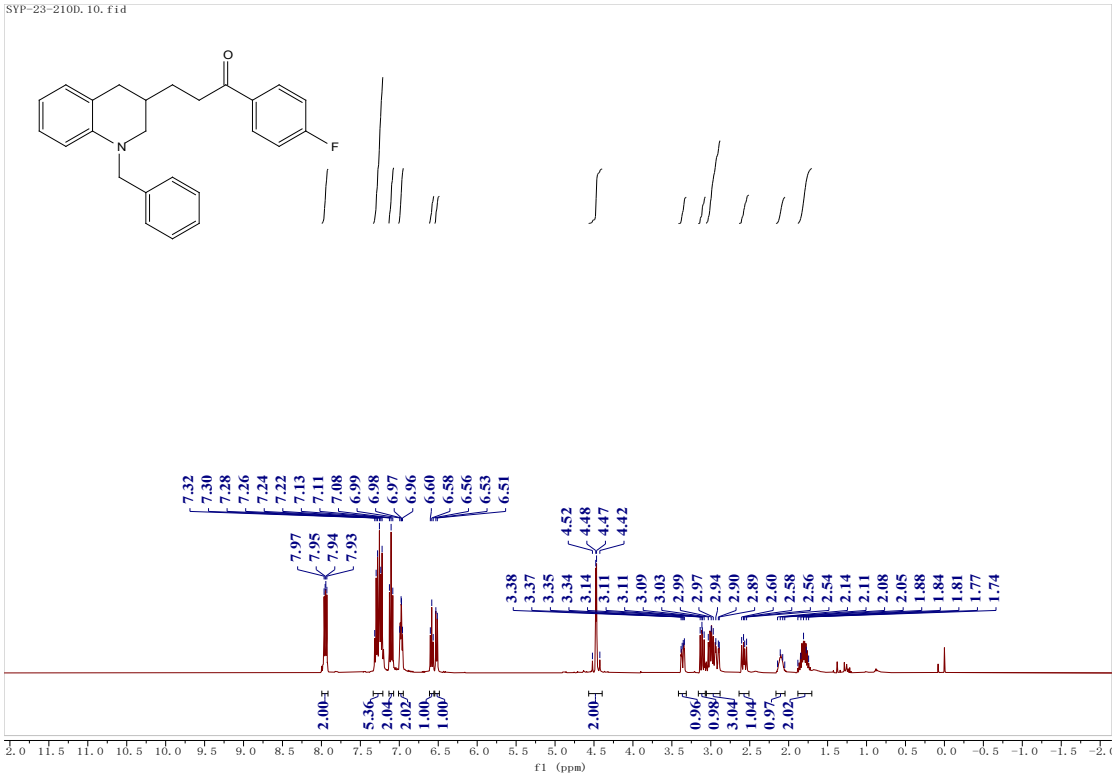
^{1}H-NMR spectrum of C_{24}



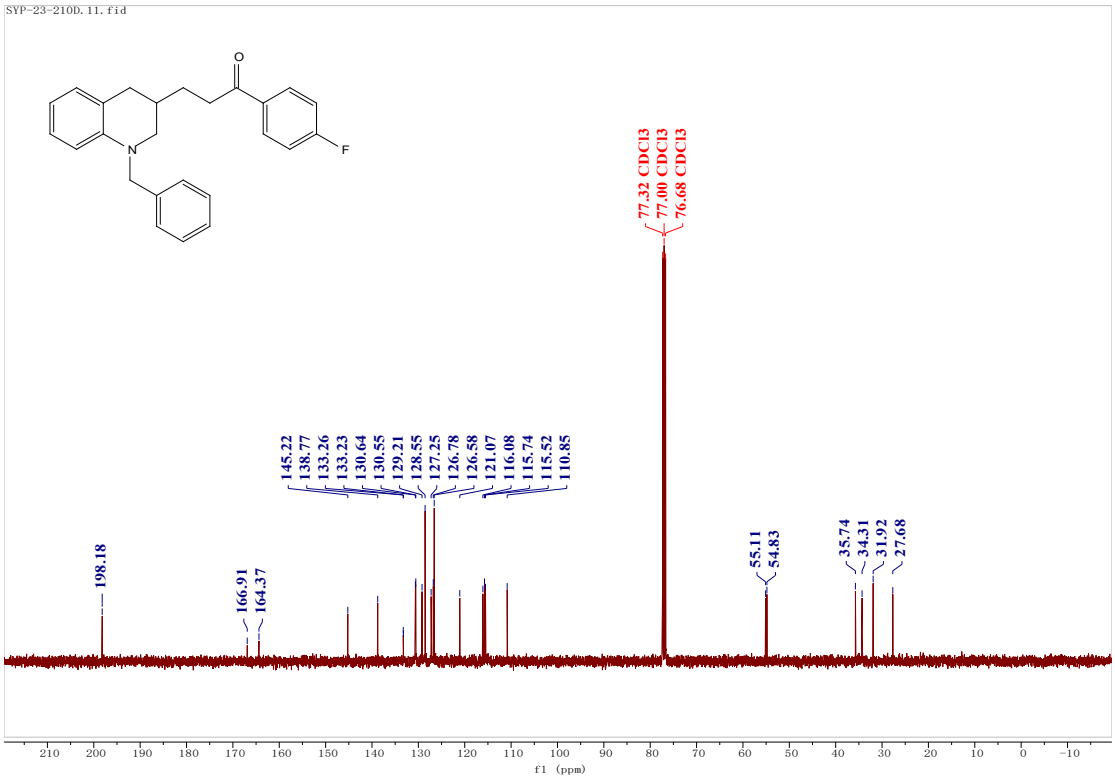
^{13}C-NMR spectrum of C_{24}



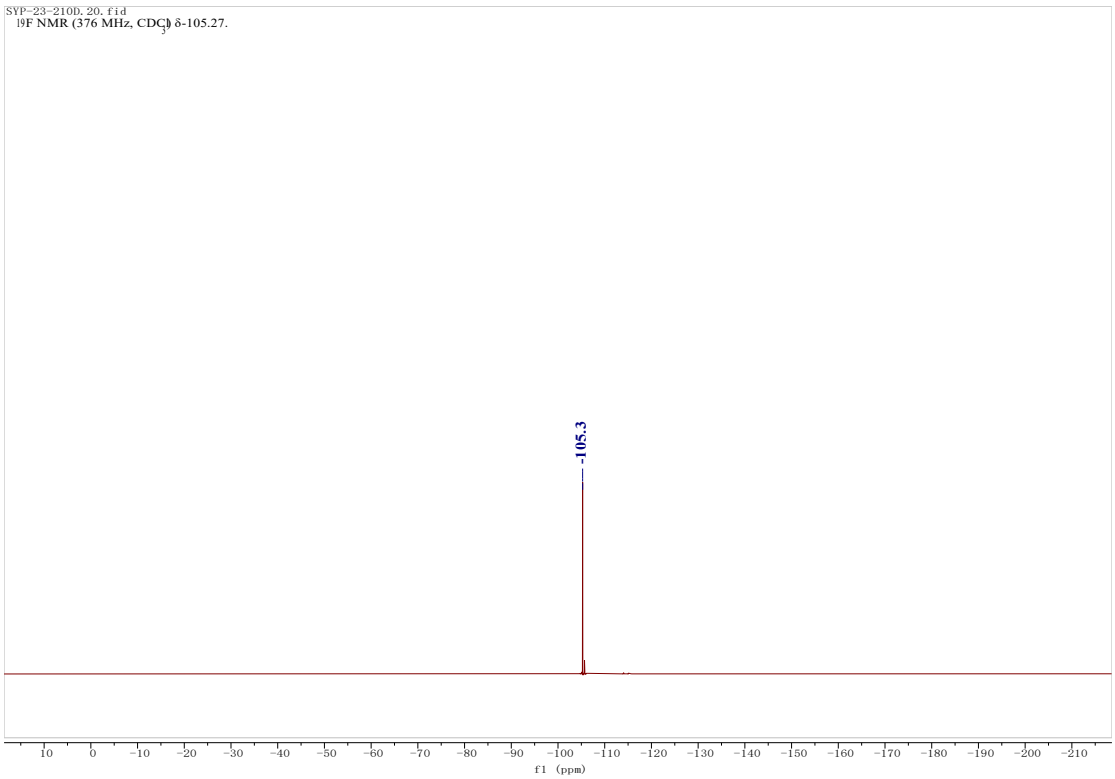
^{1}H-NMR spectrum of C_{25}



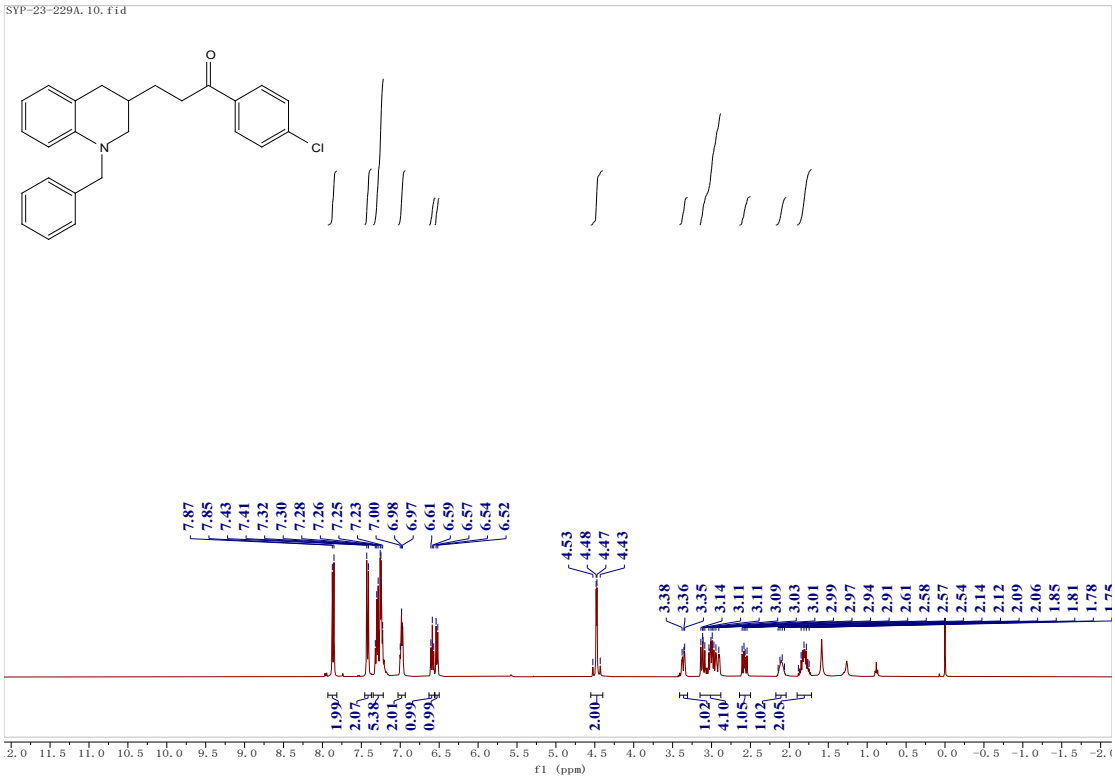
^{13}C-NMR spectrum of C_{25}



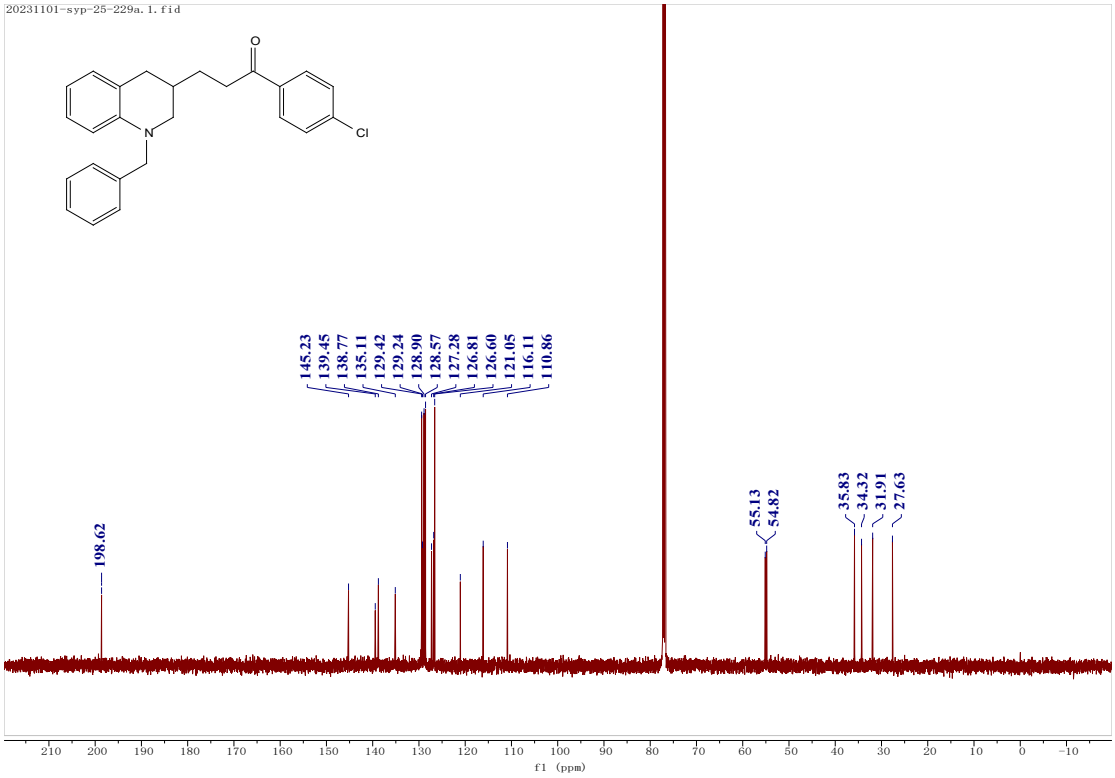
^{19}F-NMR spectrum of C_{25}



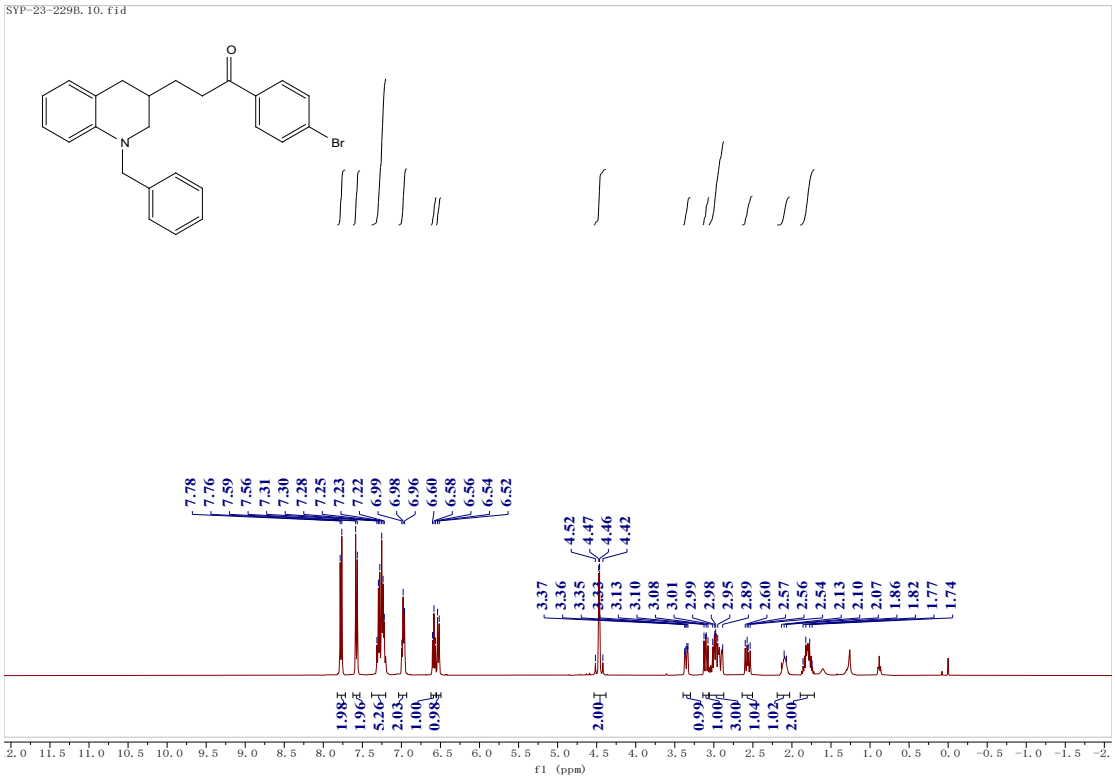
^{1}H-NMR spectrum of C_{26}



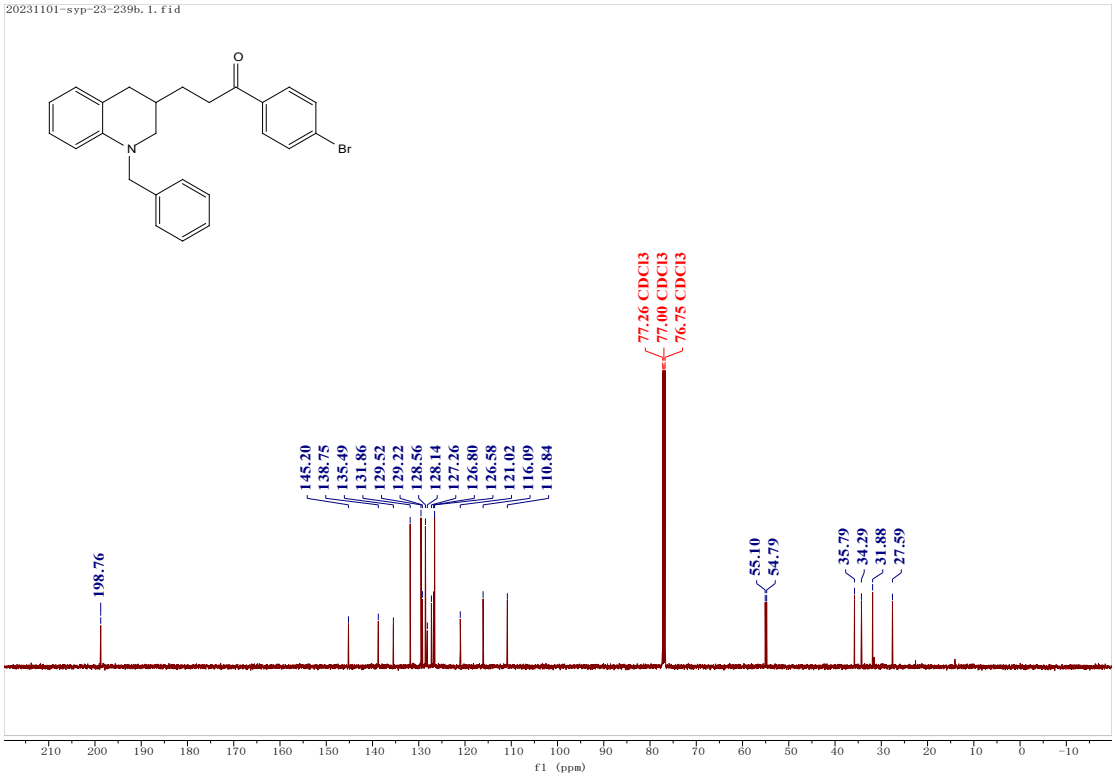
^{13}C-NMR spectrum of C_{26}



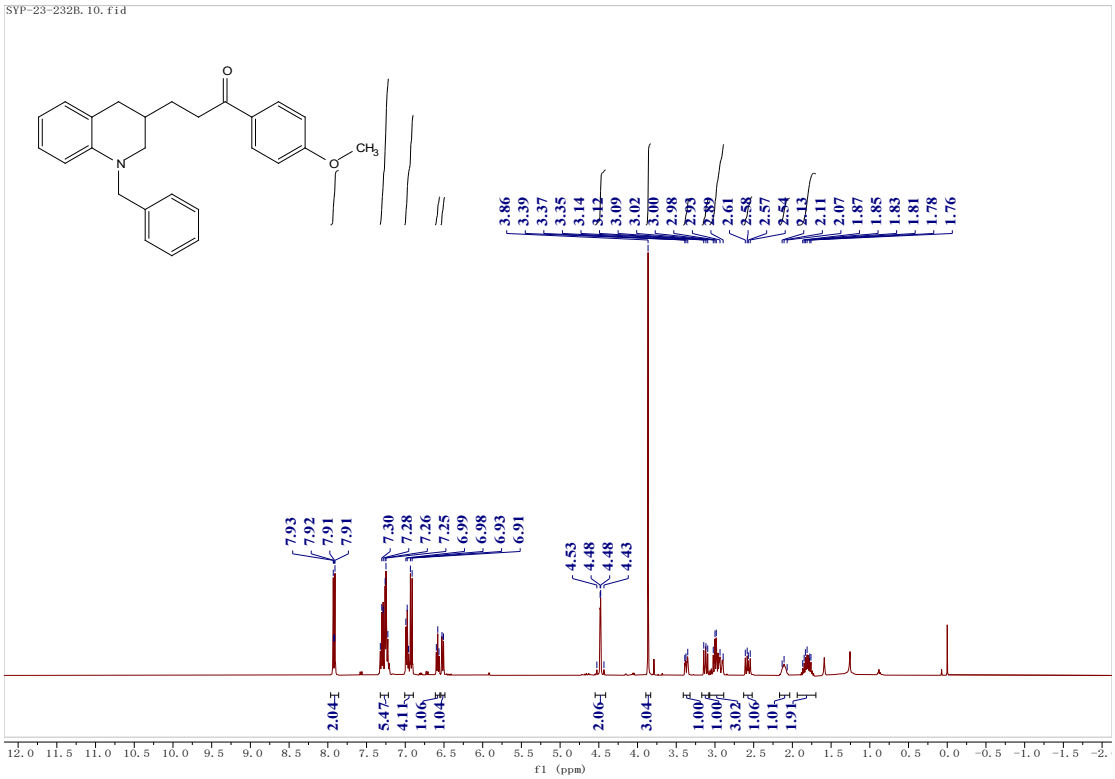
^{1}H-NMR spectrum of C_{27}



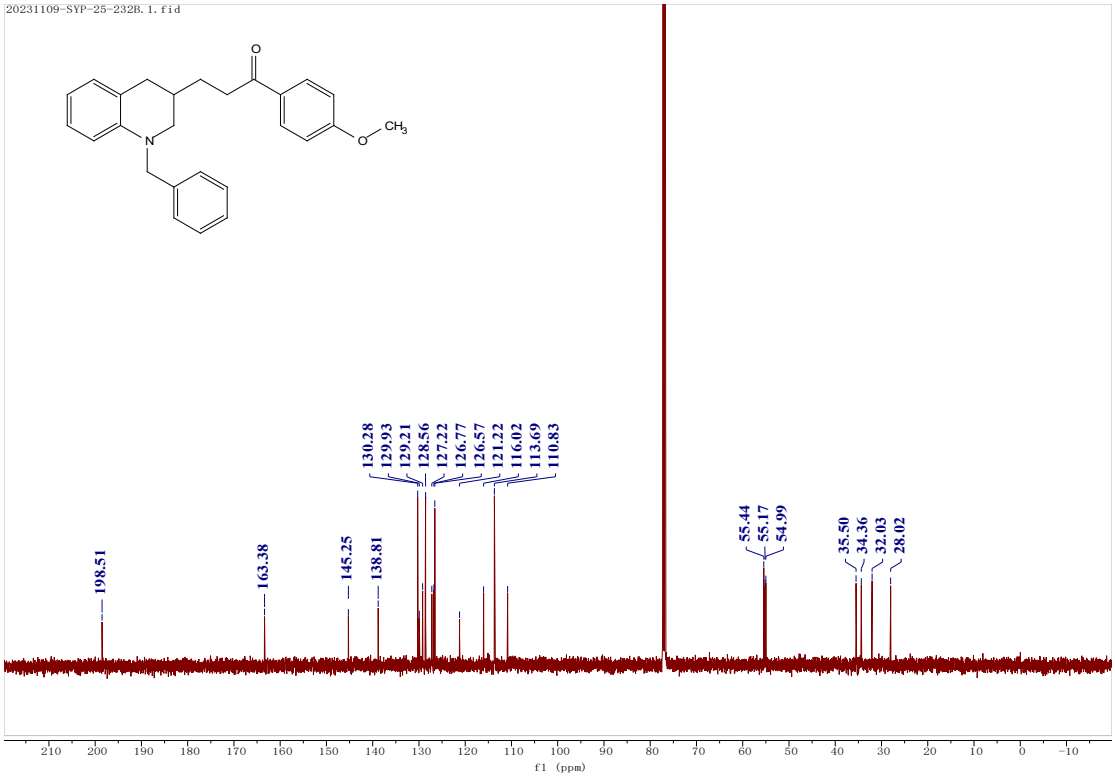
^{13}C-NMR spectrum of C_{27}



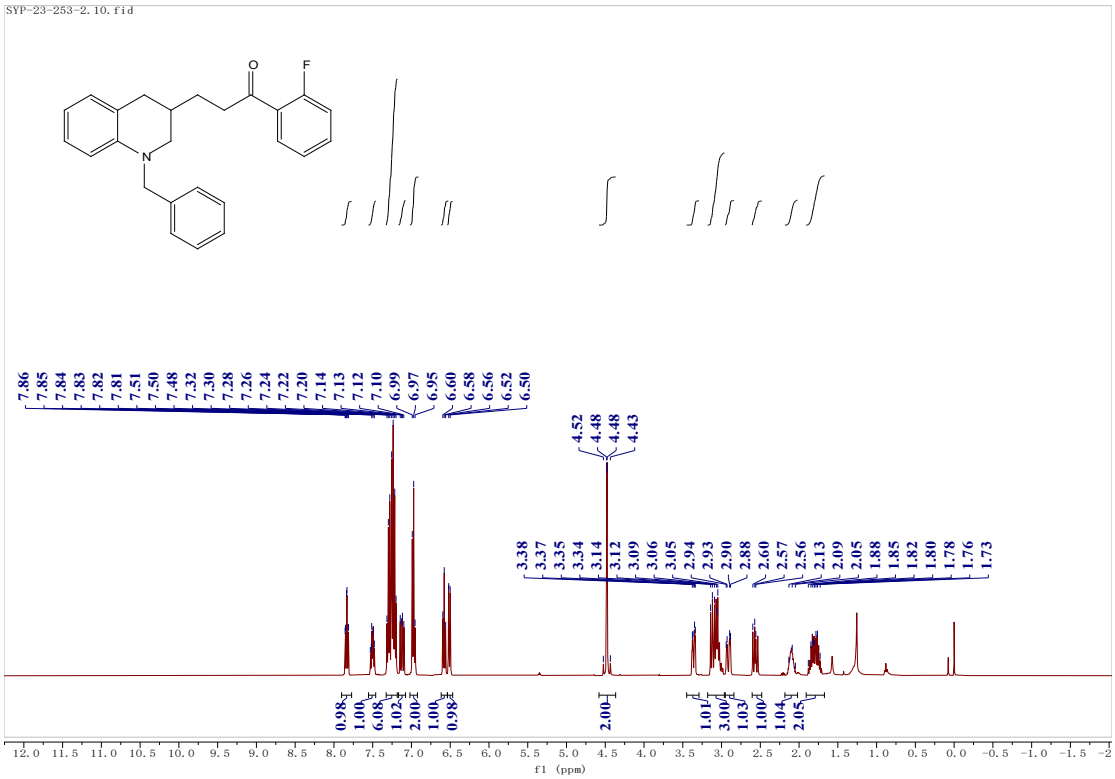
^{1}H-NMR spectrum of C_{28}



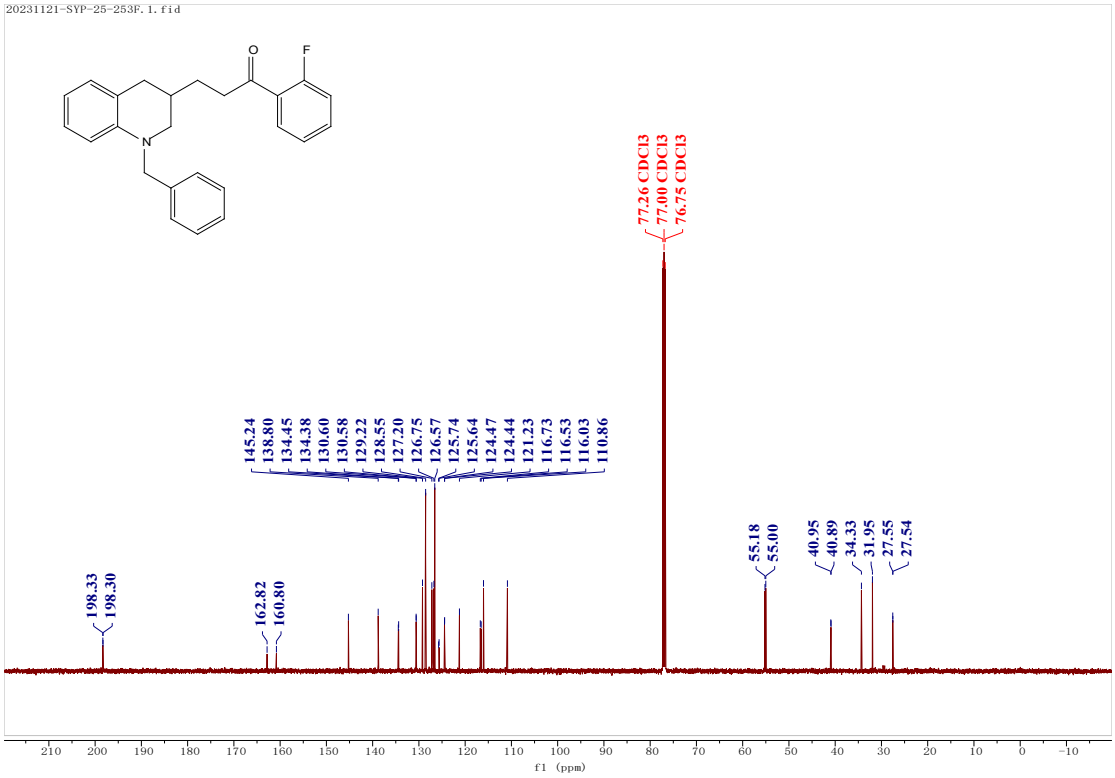
^{13}C-NMR spectrum of C_{28}



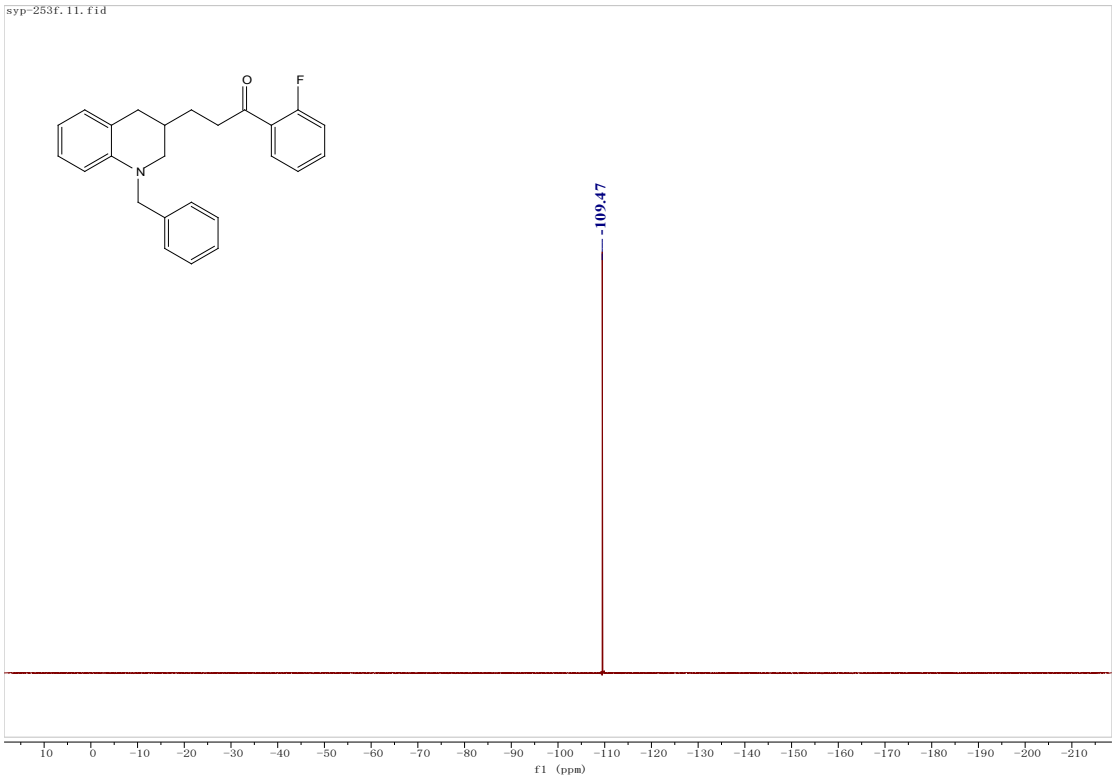
^{1}H-NMR spectrum of C_{29}



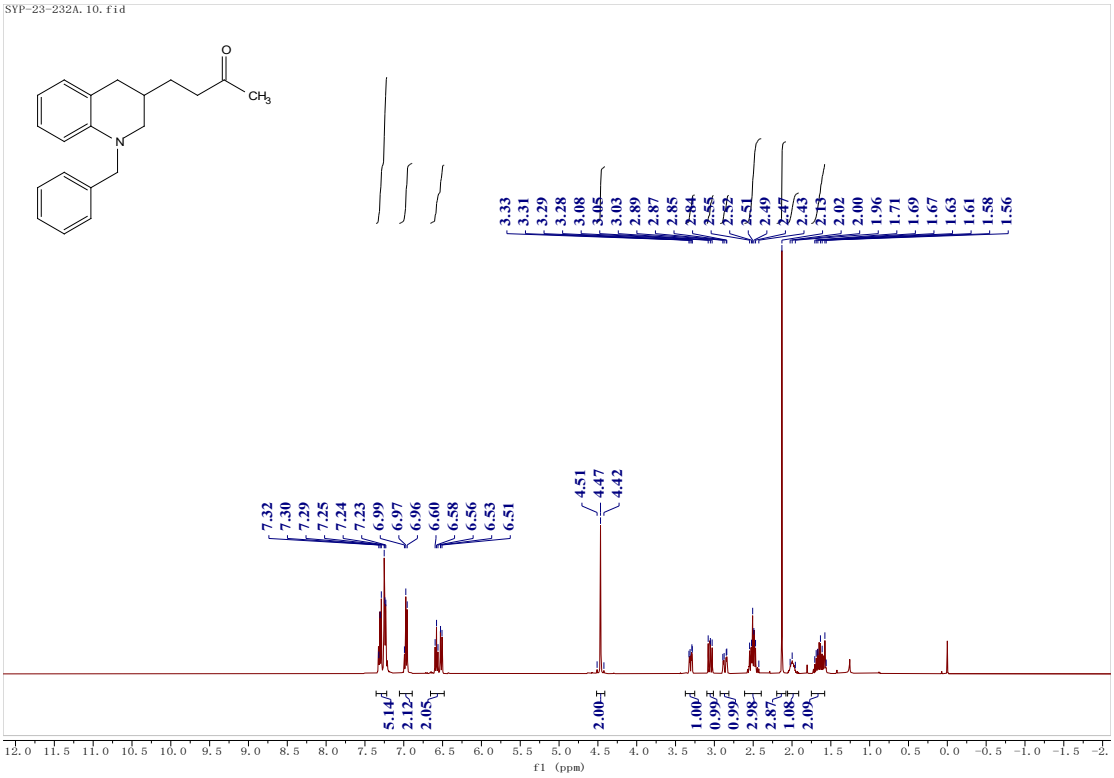
^{13}C-NMR spectrum of C_{29}



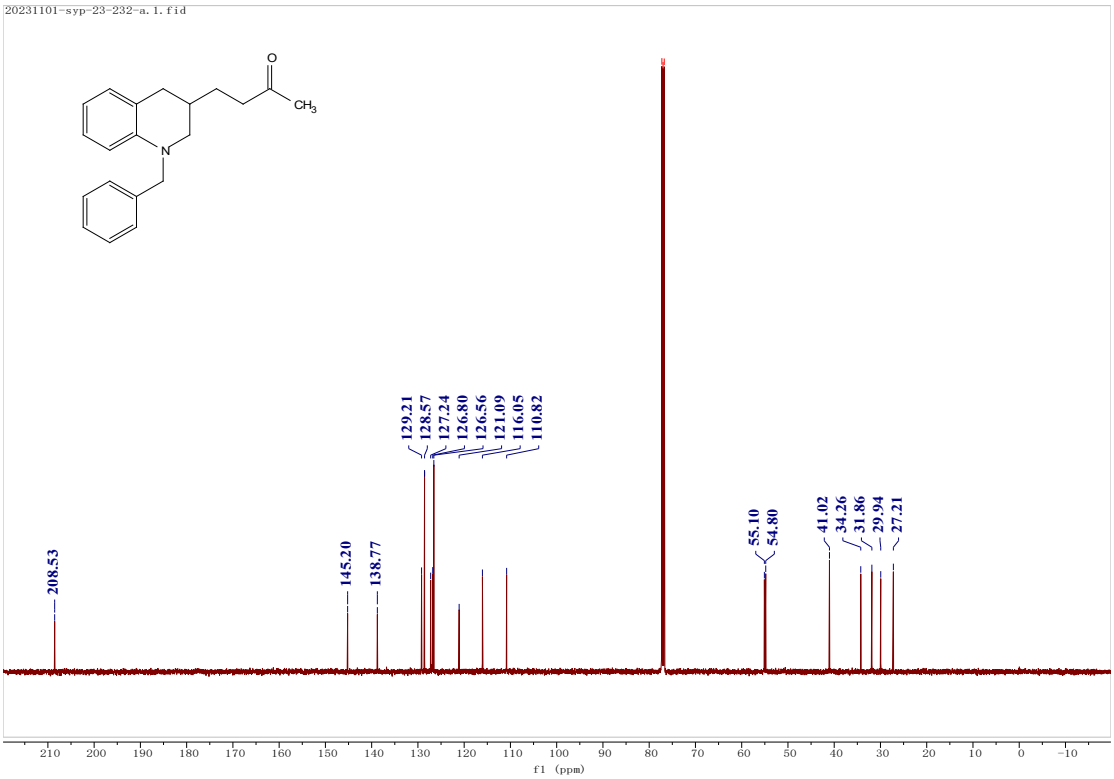
^{1}H-NMR spectrum of C_{29}



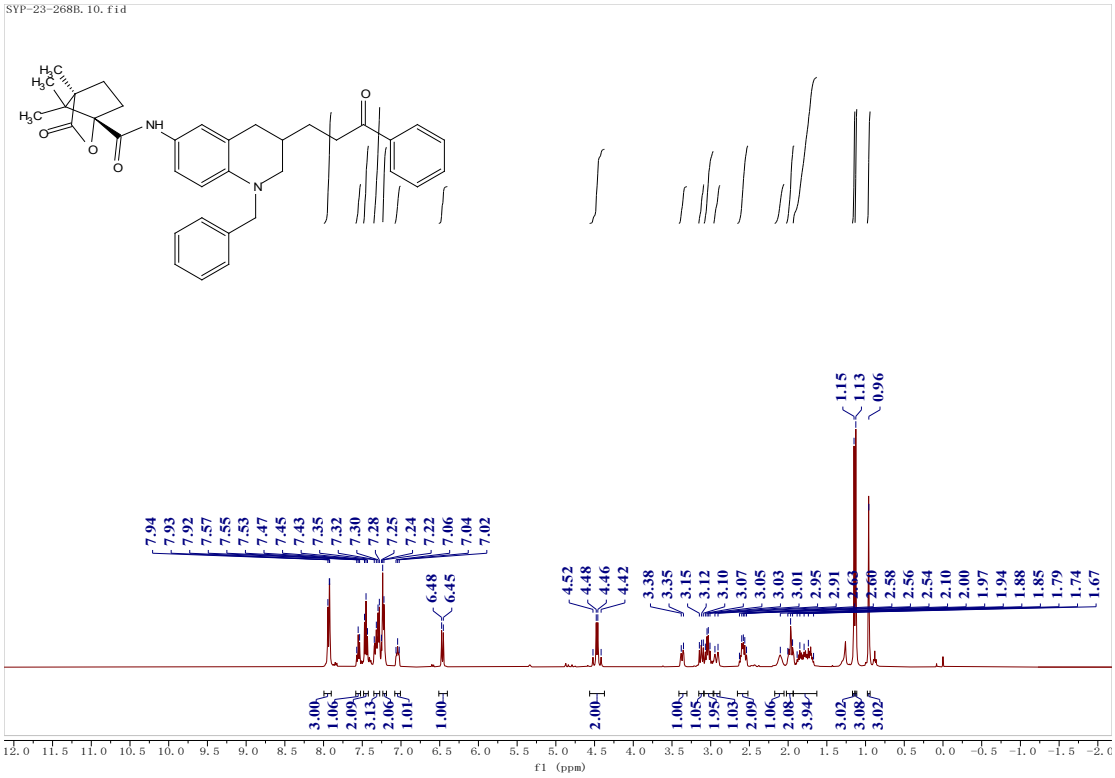
^{1}H-NMR spectrum of C_{30}



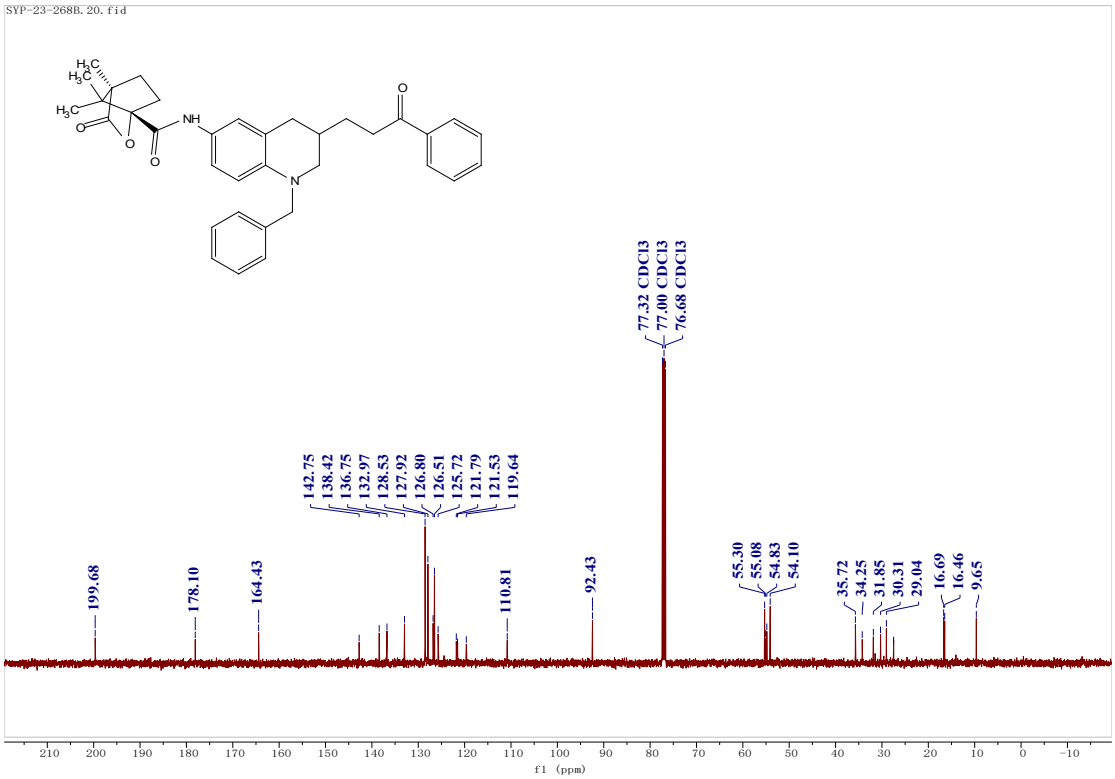
^{13}C-NMR spectrum of C_{30}



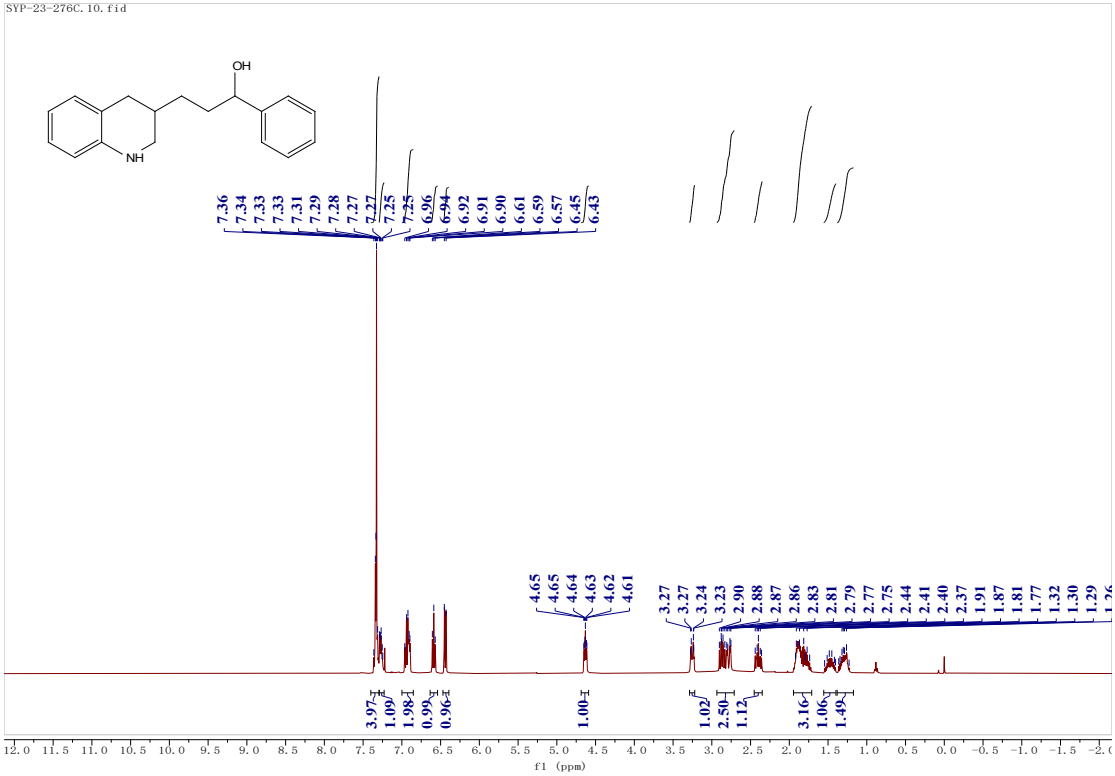
^{1}H-NMR spectrum of C_{31}



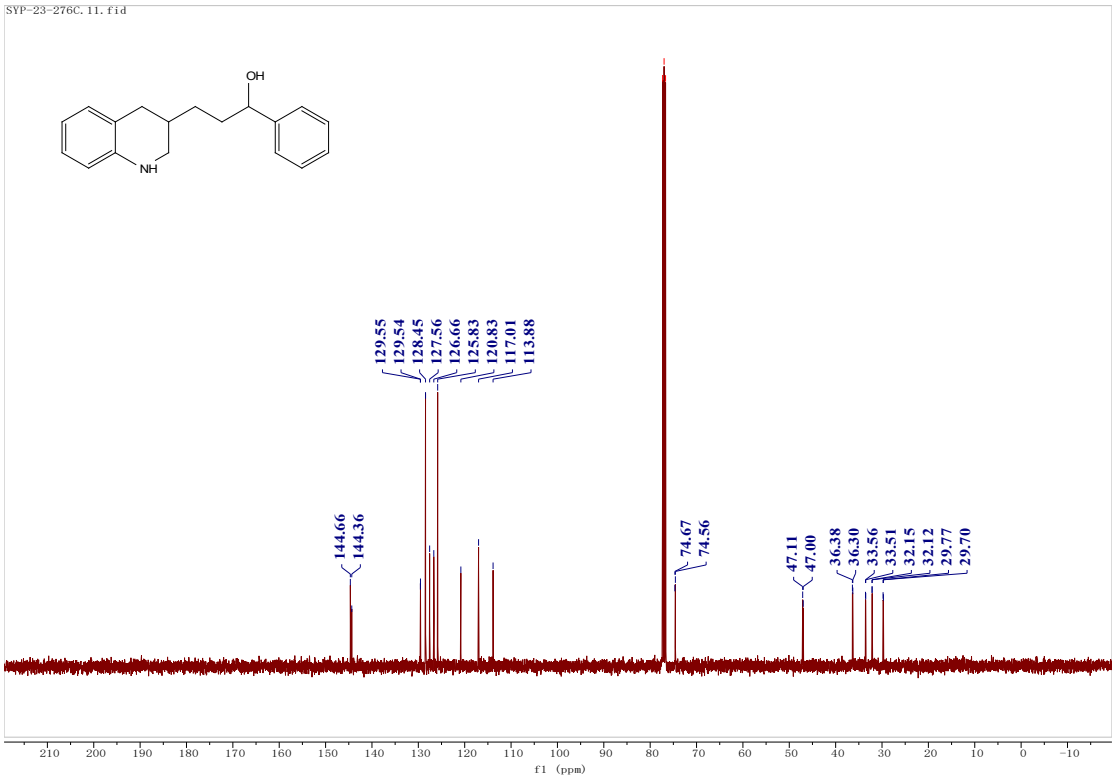
^{13}C-NMR spectrum of C_{31}



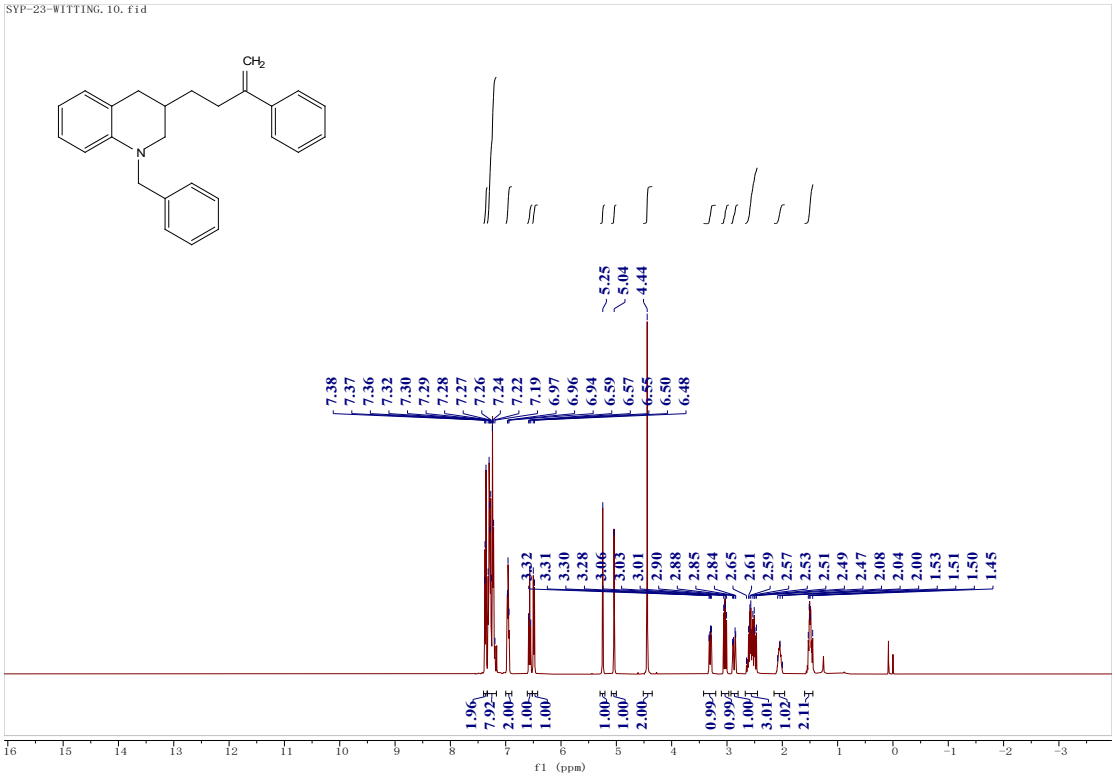
^{1}H-NMR spectrum of C_{32}



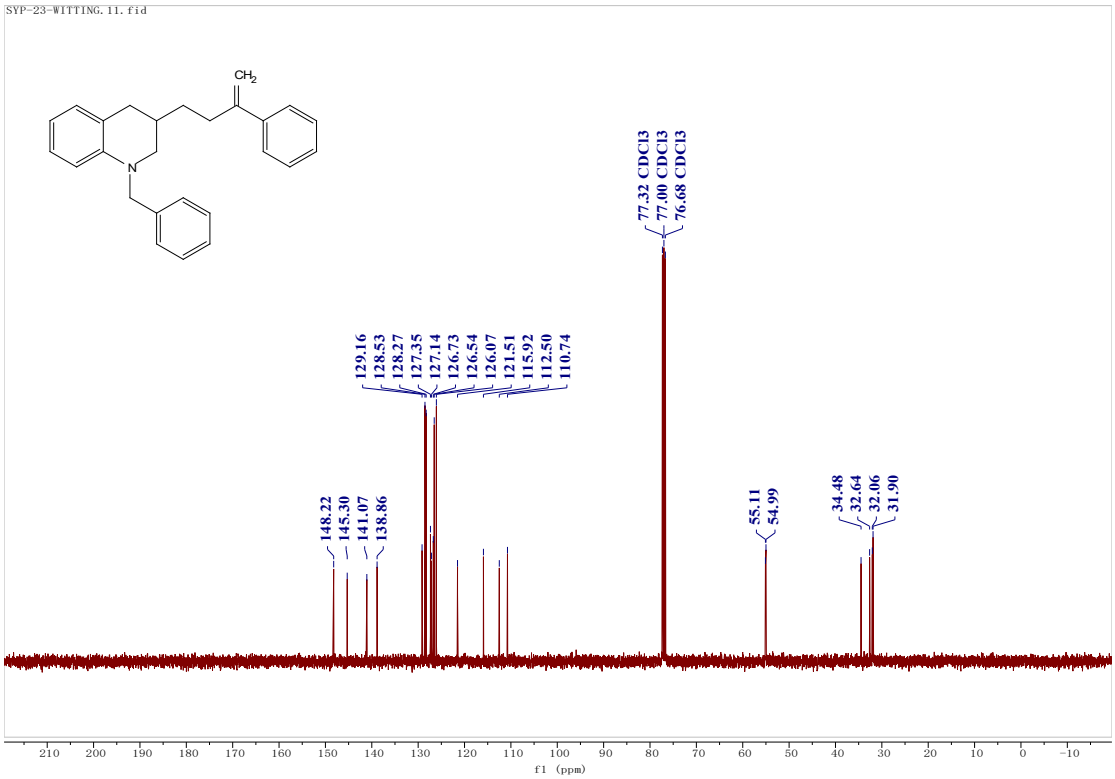
^{13}C-NMR spectrum of C_{32}



^{1}H-NMR spectrum of C_{33}



^{13}C-NMR spectrum of C_{33}



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(1) Wang, M.; Zhang, M. Diastereoselective Construction of Carbo-Bridged Polyheterocycles by a Three-component Tandem Annulation Reaction. *Org. Bio. Chem*. **2023**, *21*, 6342–6347.

(2) Yang, J.; Zhao, H.; Tan, Z.; Cao, L.; Jiang, H.; Ci, C.; Dixneuf, P. H.; Zhang, M. syn-Selective Construction of Fused Heterocycles by Catalytic Reductive Tandem Functionalization of *N*-Heteroarenes. *ACS Catal*. **2021**, *11*, 9271−9278.