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Selective Hydration of Asymmetric Internal Aryl Alkynes without Directing Groups to α-Aryl Ketones over Cu-based catalyst

Qingqing Mei, Huizhen Liu*, Minqiang Hou, Hangyu Liu, and Buxing Han*

Abstract: Hydration of internal aryl alkynes to provide aryl carbonyl compounds is a class of important reactions and has been widely investigated. However, the hydration of asymmetric internal aryl alkynes without directing groups usually gave aryl ketone or a mixture of aryl ketone and α-aryl ketone. High regioselectivity to α-aryl ketone is a great challenge and has not been reported. Herein, we found that CuBr and *p*-fluoro aniline had an excellent synergistic effect in catalyzing the hydration of internal aryl alkynes without directing groups to α-aryl ketones with regioselectivity up to more than 90%, which is much higher than those reported. The reaction mechanism was proposed and the reason for the high selectivity was clarified by combination of density functional theory (DFT) calculation, Condensed Dual Descriptor (CDD) study, and experimental results. It was demonstrated that the formations of α-aryl ketone and aryl ketone were promoted by different catalytic active species, CuBr and CuBr[*p*-fluoro aniline], respectively. CuBr enlarged the difference of electron population on the two trple-bond carbon atoms, resulting in α-aryl ketones as the main products.

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1. Experimental Procedures

1.1 General experimental details.

All the reagents were purchased from Beijing innoChem Science & Technology Co., Ltd. and used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) were recorded on a Bruker Avance III HD NMR Spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) at ambient temperature in $CDCl_3$ (d, 99.8% + 3% v/v TMS) or DMSO-d_6. The sample was analyzed by a gas chromatography (GC, HP 4890) equipped with a flame ionization detector (FID), and n-decane was used as the internal standard. The HRMS spectra were recorded on GTC Premier Spectrometer (WATERS) using EI ionization method. X-ray diffraction data were collected on a Rigaku Raxis Rapid IP diffractometer, using graphite monochromatized Mo-K α radiation (λ = 0.71073 Å).

1.2 General procedures for synthesis of the aryl-alkyl internal alkynes.

Substrates **1d-1g** were prepared via Sonogashira reaction: a dry teflon tube was charged with aryl iodide or aryl bromide (10 mmol), $Pd(Ph_3P)_2Cl_2$ (5 mol%), CuI (10 mol%). The mixture was vacuumed and flushed with N_2 for three times. Pentyne or cyclohexylacetylene (12 mmol), triethylamine (10 mL), and THF (40 mL) were then added. The mixture was stirred at 100°C for 4h, and then cooled down to room temperature. The obtained mixture was concentrated under vacuum to remove most of the THF and then diluted with diethyl ether, washed with water and saturated brines, and dried with anhydrous magnesium sulfate overnight. The desired product was purified by flash column chromatography on silica gel. The characterization of the product was shown in supporting information include ^{1}H NMR and ^{13}C NMR.

1.3 General procedures for hydration of internal alkynes.

A Teflon tube was charged with the desired amounts of catalyst, amines, alkynes and H_2O (1 mL) and placed in an autoclave. The autoclave was purged with N_2 to remove the air. The reaction mixture was stirred at the required temperature for the required time. After reaction the reactor was placed in ice water. The product was extracted with CH_2Cl_2 for five times, and then the organic phase was collected and dried with anhydrous magnesium sulfate overnight. The reaction mixture was purified by flash column chromatography on silica gel to afford the desired product. The characterization of the product was shown in supporting information include ^{1}H NMR, ^{13}C NMR and HRMS.

2. Computational details.

2.1 Transition states exploration.

All calculations were performed with Gaussian 09 package.[S17] Structure optimization and frequency analysis were conducted at M06-2x/TZVP level with Grimme's DFT-D3 dispersion correction[S22] at 393.15 K and 1 atm to obtain thermal correction to Gibbs Free Energy (G_{cor}). All minima (reactants, products, and intermediates) have no imaginary frequencies and all transition state structures have only one imaginary frequency, which vibrational mode corresponds to the motion along the reaction coordinate. More accurate single point energies (E_e) were calculated at M06-2x/def2-TZVP level with Grimme's DFT-D3 dispersion correction based on the optimized structures. Intrinsic

reaction coordinate (IRC) calculations were performed to confirm that a given transition state connects a particular couple of consecutive minima. Solvent effect was taken into account by SMD model[S23] at M05-2x/6-31g* level with water as the solvent. The solvation energy (E_{sol}) is the difference of the single point energy in liquid phase and gas phase. The total relative free energy (ΔG) of each transition state, reactants, products, or intermediate is the summation of E_e, G_{cor}, and E_{sol}.

2.2 CDD (Condensed Dual Descriptor) calculations.

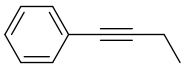
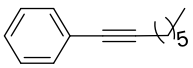
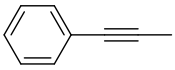
Stable structures of the alkynes and the alkyne-CuBr complexes were optimized at the B3LYP/6-311g* level using Gaussian 09 package.[S17] The structures are listed in section 2.4.3**.** Hirshfeld atomic charge was calculated based on the wave function of the optimum structures using the Multiwfn code.[S24] Then the CDDs[S25] were calculated manually based on the Hirshfeld atomic charges. The more detailed description is provided by other authors.[S19,S20]

3. Results and Discussion

3.1 Reported results

Table S1 summarized the results for the hydration of typical aryl-alkyl internal alkynes. Both aryl ketone or α-aryl ketone could be produced as major product. High yield of aryl ketone could be obtained, but high selectivity to α-aryl ketone has not been achieved. This work got high yield of α-aryl ketone as well as high selectivity (>90%).

Table S1. Typical results of the hydration of aryl-alkynes without directing group

Entry	Substrates	Catalytic Systems	Product Aryl	Product α-Aryl	Refs.
1	 **1b**	[(IPr)]AuOH, $HSbF_6$ MeOH/Water	50%	15%	S1
2		[(IPr)]AuOH, $AgSbF_6$ 1,4-Dioxane/water	66%	15%	S2
3		$PtCl_4$-CO THF/water	35%	55%	S3
4		$Ga(OTf)_3$ $HOAc/H_2O$		85%	S4
5		Ag_3STA H_2O		20%	S5
6		CuBr, *p*-F-aniline H_2O	**88%**		This work
7	 **1x**	$AuPPh_3NTf_2$ MeOH	15%	15%	S6
8		AuSPhosOTf MeOH	60%	40%	
9		$AuSPhosNTf_2$ MeOH	60%	40%	
10	 1a	Surfactant, HCl H_2O		60%	S7
11		Au-HS/SO_3H-PMO(Et) H_2O		95%	S8
12		$Cu(OTf)_2$ EtOAc		94%	S9
13		$AgOSO_2C_8F_{17}\cdot H_2O$, PFOS H_2O		74%	S10
14		CuBr, *p*-F-aniline H_2O	**92%**		This work

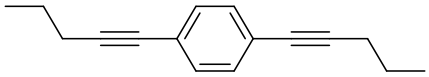
3.2 Effect of the amount of *p*-fluoroaniline

Table S2. Effect of the amount of *p*-fluoroaniline

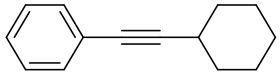
Entry	Amount of *p*-fluoroaniline (mmol)	Yields	Selectivity
1	0.1	n.r.	-
2	0.2	6%	95%
3	0.5	74%	94%
4	1.0	99%	93%

Reaction conditions: **1a** (1 mmol), CuBr (0.1 mmol), *p*-fluoroaniline, H_2O (1 mL), 120°C, 12 h

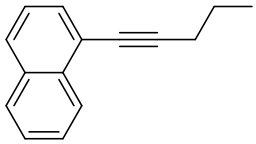
3.3 Synthesized substrates characterization



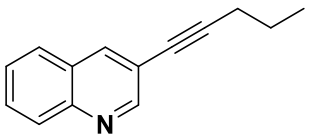
1,4-di(pent-1-yn-1-yl)benzene (1d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 2.37 (t, *J* = 7.0 Hz, 4H), 1.61 (h, *J* = 7.3 Hz, 4H), 1.03 (d, *J* = 14.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.33, 123.22, 91.68, 80.57, 22.19, 21.46, 13.52.



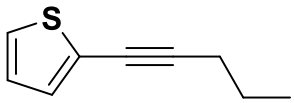
(Cyclohexylethynyl)benzene (1e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.33 – 7.15 (m, 3H), 2.58 (tt, *J* = 9.0, 3.7 Hz, 1H), 1.90 – 1.24 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.58, 128.13, 127.38, 124.22, 94.44, 80.60, 32.77, 29.71, 25.99, 24.93.



1-(pent-1-yn-1-yl)naphthalene (1f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.3 Hz, 1H), 7.77 (dd, *J* = 22.8, 8.1 Hz, 2H), 7.67 – 7.29 (m, 4H), 2.53 (t, *J* = 7.0 Hz, 2H), 1.83 – 1.61 (m, 2H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.58, 133.27, 130.03, 128.21, 127.89, 126.48, 126.35, 126.22, 125.25, 121.88, 95.38, 78.82, 22.45, 21.79, 13.71.

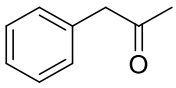


3-(pent-1-yn-1-yl)quinolone (1g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 2.0 Hz, 1H), 8.21 – 7.99 (m, 2H), 7.77 – 7.61 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 2.45 (s, 2H), 1.68 (s, 2H), 1.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.50, 146.54, 137.83, 129.53, 129.31, 127.36, 127.33, 127.02, 118.23, 93.88, 78.11, 22.08, 21.52, 13.56.

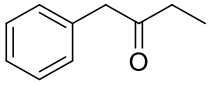


2-(pent-1-yn-1-yl)thiophene (1h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 2.37 (t, *J* = 7.0 Hz, 4H), 1.61 (h, *J* = 7.3 Hz, 4H), 1.03 (d, *J* = 14.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.33, 123.22, 91.68, 80.57, 22.19, 21.46, 13.52.

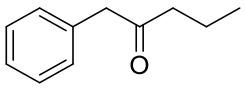
3.4 Products characterization



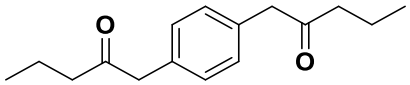
1-phenylpropan-2-one (2a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.12 (m, 5H), 3.69 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 134.3, 129.4, 128.8, 127.0, 51.1, 29.2. In consistence with literature.[S11]



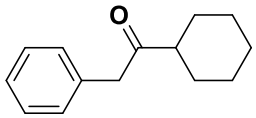
1-phenylbutan-2-one (2b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.20 (m, 5H), 3.68 (s, 2H), 2.47 (q, J = 7.3 Hz, 2H), 1.03 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 134.5, 129.4, 128.7, 126.9, 49.8, 35.2, 7.8. In consistence with literature.[S12]



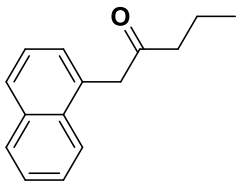
1-phenylpentan-2-one (2c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.12 (m, 5H), 3.66 (s, 2H), 2.41 (t, J = 7.3 Hz, 2H), 1.57 (h, J = 7.4Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 134.41, 129.4, 128.7, 126.9, 50.2, 43.9, 17.2, 13.6. In consistence with literature.[S13]



1,1'-(1,4phenylene)bis(pentan-2-one) (2d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 3.66 (s, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 1.58 (q, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.25, 133.04, 129.69, 49.66, 43.94, 17.16, 13.60. HRMS (MALDI): calculate for $C_{16}H_{22}O_2$ $[M+Na]^+$ *m/z* 269.151201, found 269.151274.

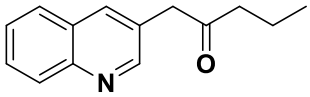


1-cyclohexyl-2-phenylethan-1-one (2e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.09 (m, 5H), 3.71 (s, 2H), 2.45 (tt, *J* = 11.4, 3.4 Hz, 1H), 1.84 – 1.15 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.13, 134.47, 129.36, 128.54, 126.80, 50.12, 47.85, 28.57, 25.84, 25.63. In consistence with literature.[S14]

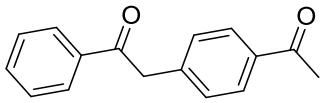


1-(naphthalene-1-yl)pentan-2-one (2f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.72 (m, 3H), 7.57 – 7.29 (m, 4H), 4.07 (s, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 1.54 (h, *J* = 7.4 Hz, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.77,

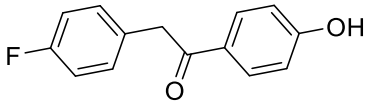
133.95, 132.30, 131.24, 128.78, 128.23, 127.97, 126.48, 125.88, 125.57, 123.95, 48.47, 43.43, 17.19, 13.63. HRMS (EI): calculated for $C_{15}H_{16}O$ (M^+), 212.1201; found 212.1203.



1-(quinolin-3-yl)pentan-2-one (2g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.70 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 3.89 (s, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 1.65 (p, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.04, 151.73, 147.22, 136.02, 129.29, 129.24, 127.56, 126.87, 46.86, 44.56, 17.20, 13.65. HRMS (MALDI): calculate for $C_{14}H_{15}NO$ $[M+H]^+$ *m/z* 214.122641, found 214.122668.

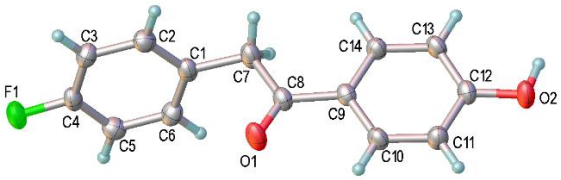


1-phenylethan-2-(4-acetylphenyl)-1-one (2j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 4.34 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 196.7, 140.1, 136.4, 135.9, 133.4, 129.8, 128.8, 128.7, 128.5, 45.3, 26.6. HRMS (EI): calculated for $C_{16}H_{14}O_2$ (M^+), 238.0994; found 238.0997. In consistence with literature.[S15]

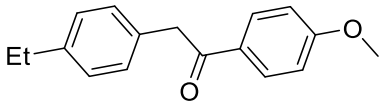


1-(4-hydroxyphenyl)ethan-2-(4-fluorophenyl)-1-one (2k). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 7.97-7.89 (m, 2H), 7.32-7.24 (m, 2H), 7.15-7.09 (m, 2H), 6.90-6.82 (m, 2H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.1, 162.7, 160.3, 132.2, 132.2, 132.0, 131.9, 131.4, 128.3, 115.7, 115.5, 115.3, 43.7. CCDC 1438782.

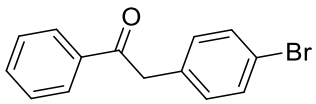
Crystallographic analysis



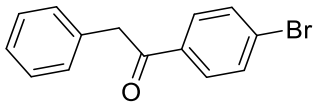
Selected crystal data: Crystal System; monoclinic, Space Group; $P2_1/n$ (No. 14), a = 7.940(2) Å, b = 16.998(5) Å, c = 8.091(2) Å, β = 90.287(5)°, V = 1092.0(5) Å^3, Z = 4, R_1 = 0.0503, wR_2 = 0.1178.



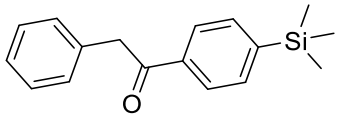
1-(4-methoxyphenyl)ethan-2-(4-ethylphenyl)-1-one (2l). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 2H), 7.16 (q, J = 8.1 Hz, 4H), 6.91 (d, J = 8.9 Hz, 2H), 4.18 (s, 2H), 3.84 (s, 3H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.41, 163.49, 142.68, 132.13, 130.95, 129.76, 129.28, 128.15, 113.78, 55.44, 44.9, 28.46, 15.48. HRMS (EI): calculated for $C_{17}H_{18}O_2$ (M^+), 254.1307; found, 254.1311. In consistence with literature.[S21]



1-phenylethan-2-(4-bromophenyl)-1-one (2m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.48-7.43 (m, J = 10.9, 8.2 Hz, 4H), 7.17-7.06 (m, 2H), 4.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.95, 136.43, 133.47, 133.36, 131.74, 131.27, 128.73, 128.51, 120.97, 44.76. HRMS (EI): calculated for $C_{14}H_{11}O^{79}Br$ (M^+), 273.9993; found, 273.9995; calculated for $C_{14}H_{11}O^{81}Br$ (M^+), 275.9973; found, 275.9968. In consistence with literature.[S16]



1-(4-bromophenyl)-2-phenylethan-1-one (2m'). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.34-7.31 (m, 2H), 7.27-7.23 (m, 3H), 4.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.57, 135.30, 134.16, 131.96, 130.15, 129.37, 128.77, 128.36, 127.05, 45.54. HRMS (EI): calculated for $C_{14}H_{11}O^{79}Br$ (M^+), 273.9993; found, 273.9996; calculated for $C_{14}H_{11}O^{81}Br$ (M^+), 275.9973; found, 275.9970. In consistence with literature.[S16]



2-phenyl-1-(4-(trimethylsilyl)phenyl)ethan-1-one (**2n**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.26 (m, 5H), 4.25 (s, 2H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.10, 148.67, 138.02, 135.97, 134.91, 130.78, 130.00, 128.88, 128.19, 46.88, 0.00. HRMS (EI): calculated for $C_{17}H_{18}O_2$ (M^+), 268.1283; found, 268.1280.

3.5 Reaction free energy profiles

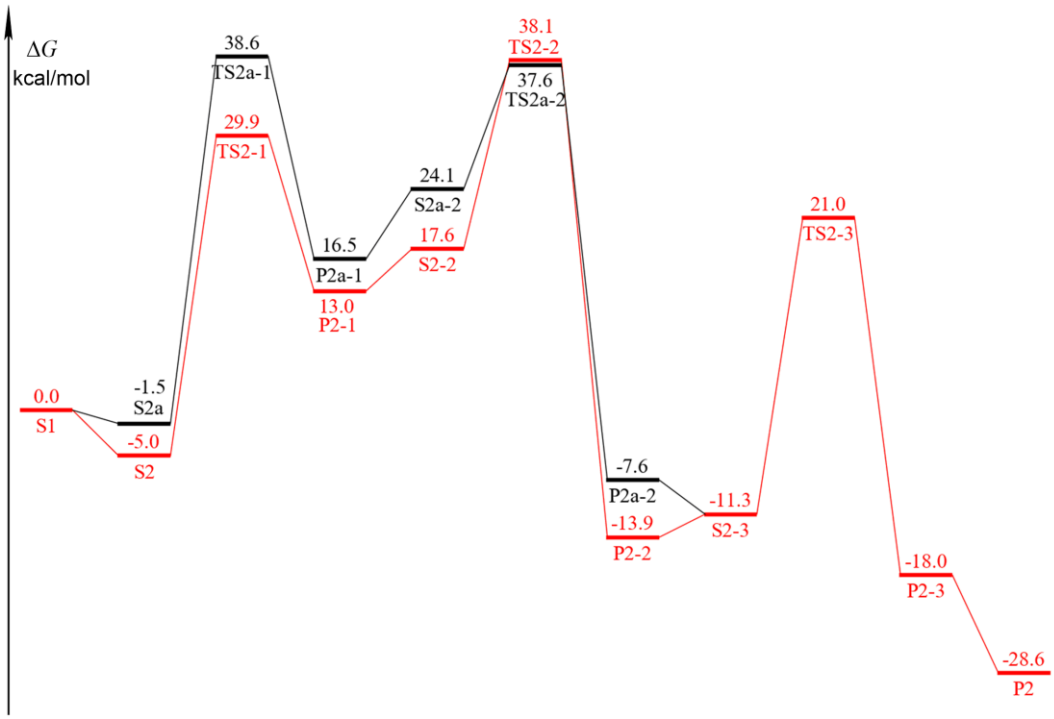


Figure S1. Computed reaction free energy profiles to produce α-aryl ketone over CuBr catalyst (red) and CuBr[*p*-fluoro aniline] catalyst (black).

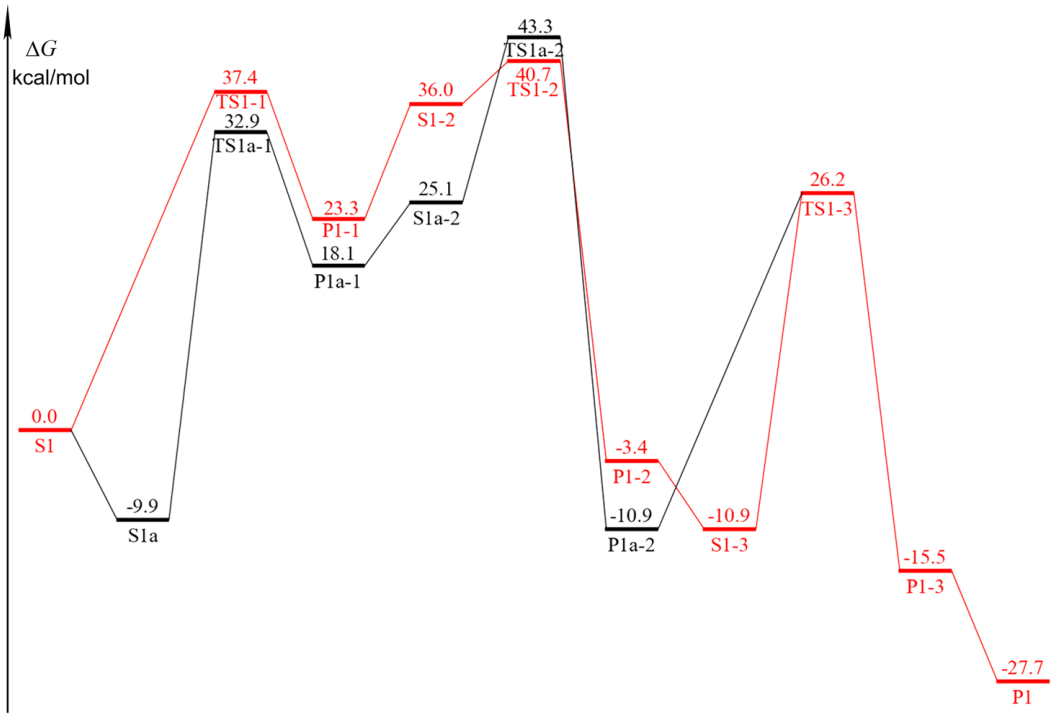


Figure S2. Computed reaction free energy profiles to produce aryl ketone over CuBr catalyst (black) and CuBr[*p*-fluoro aniline] catalyst (red).

3.6 CDD analysis

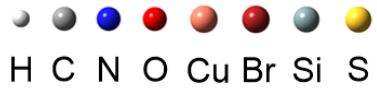
3.6.1 CDD values

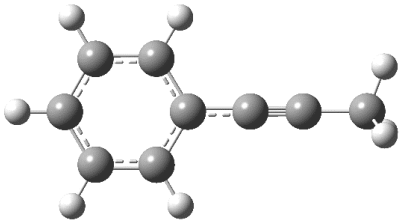
Table S3. The values and differences of condensed dual descriptor (CDD) of the triple bond carbons of the substrates

sites	CDD		CDD(C2)-CDD(C1)	
	Alkyne	Alkyne + CuBr	Alkyne	Alkyne + CuBr
1a-C1 **1a**-C2	-0.045 -0.037	0.005 0.032	0.008	0.027
1b-C1 **1b**-C2	-0.046 -0.043	0.004 0.032	0.003	0.028
1c-C1 **1c**-C2	-0.047 -0.038	0.003 0.033	0.009	0.030
1d-C1 **1d**-C2	-0.025 -0.017	0.003 0.033	0.008	0.030
1e-C1 **1e**-C2	-0.049 -0.029	0.003 0.032	0.02	0.029
1f-C1 **1f**-C2	-0.025 -0.021	-0.004 0.012	-0.004	0.016
1g-C1 **1g**-C2	-0.051 -0.036	-0.015 0.012	0.015	0.027
1h-C1 **1h**-C2	-0.033 -0.032	0.003 0.025	0.001	0.022
1i-C1 **1i**-C2	-0.017 -0.023	0.019 0.027	-0.006	0.008
1j-C1 **1j**-C2	-0.051 -0.016	-0.013 0.011	0.008	0.030
1k-C1 **1k**-C2	-0.024 -0.001	0.004 0.022	0.023	0.018
1l-C1 **1l**-C2	-0.023 -0.002	0.004 0.021	0.021	0.017
1m-C1 **1m**-C2	-0.02 -0.016	0.01 0.011	0.004	0.010
1n-C1 **1n**-C2	-0.022 -0.023	0.007 0.008	-0.001	0.001
1o-C1 **1o**-C2	-0.168 -0.177	0.047 0.048	-0.009	0.001

From the table, it is easy to see that most of the CDD value turns positive, when the substrates coordinate with CuBr, which makes the sites more easily be attacked by the nucleophile, *p*-fluoro aniline. Moreover, for most of the substrates, the CDD difference (CDD(C2)-CDD(C1)) are enlarged with CuBr, which is proportional related to the selectivity in Table 2.

3.6.2 Structures for CDD modeling





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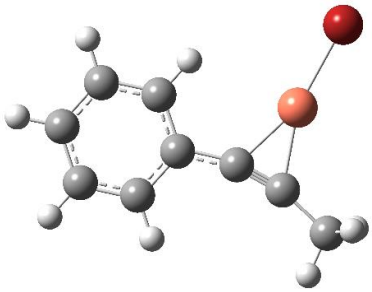

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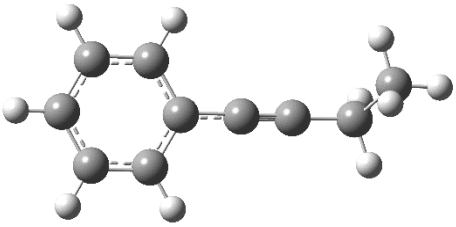

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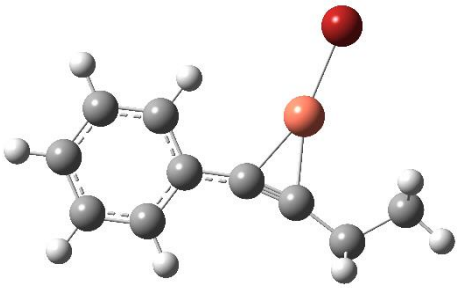

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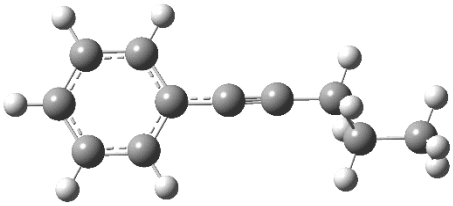

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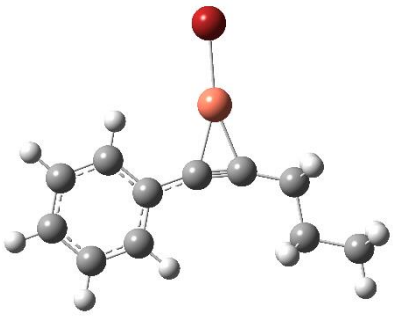

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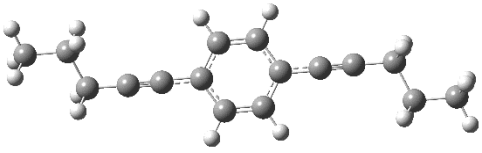

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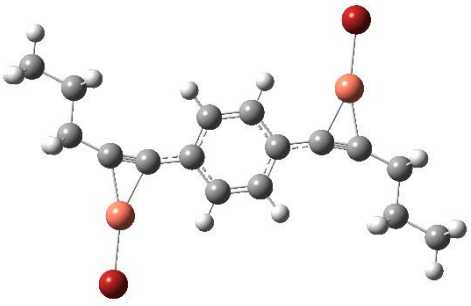

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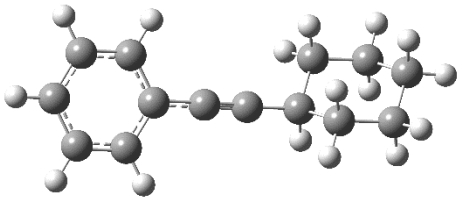

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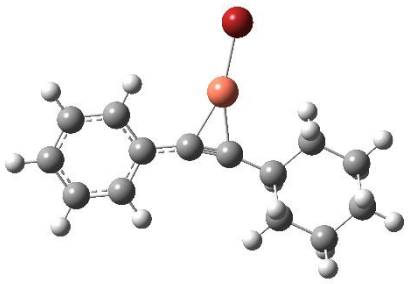

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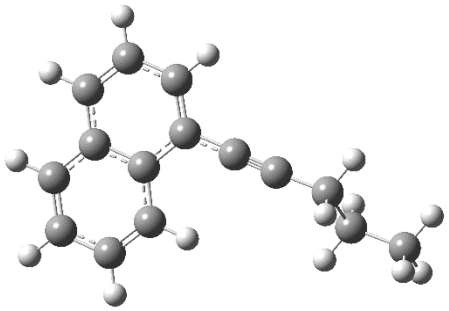

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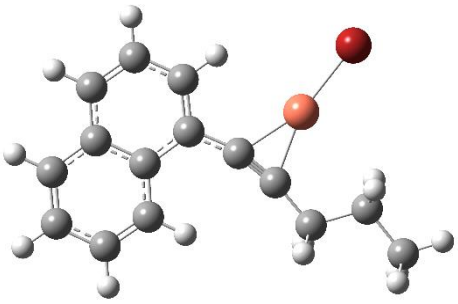

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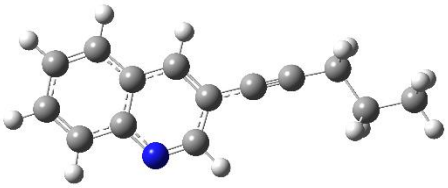

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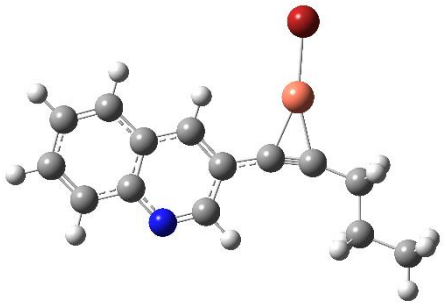

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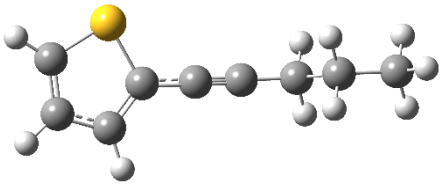

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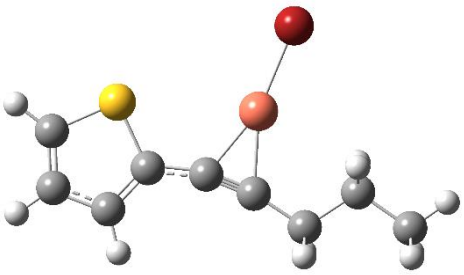

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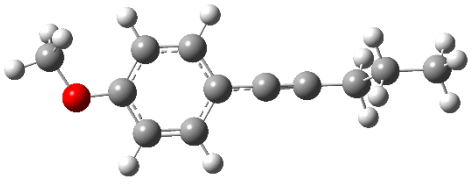

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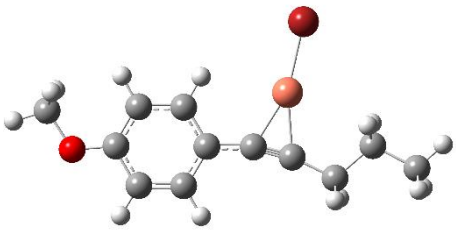

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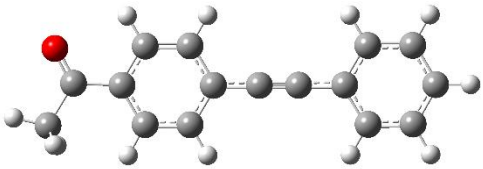

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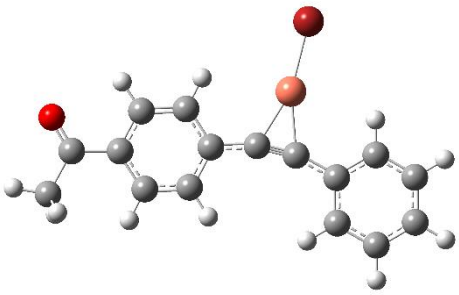

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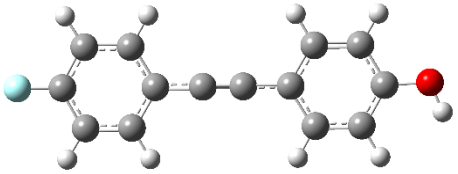

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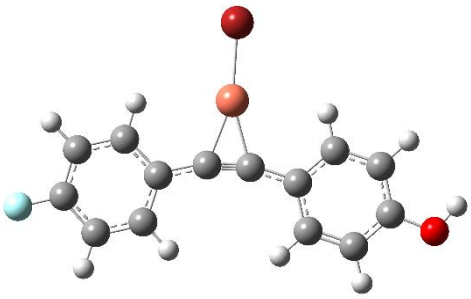

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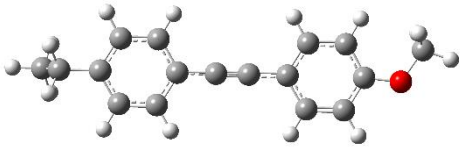

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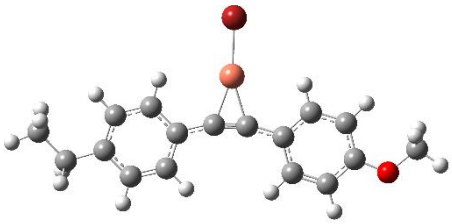

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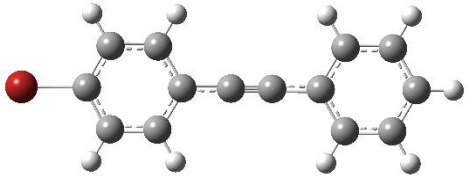

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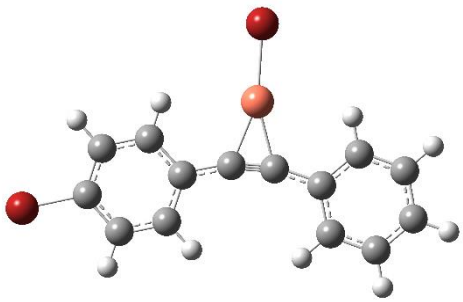

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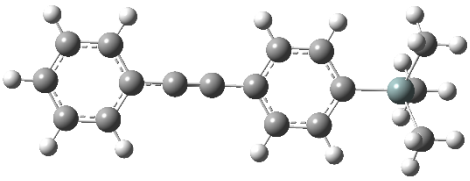

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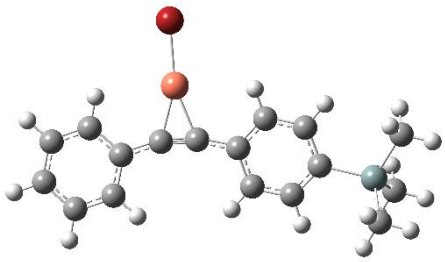

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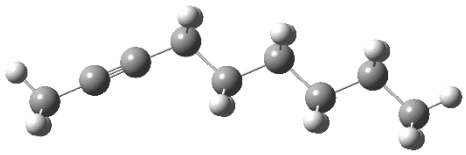

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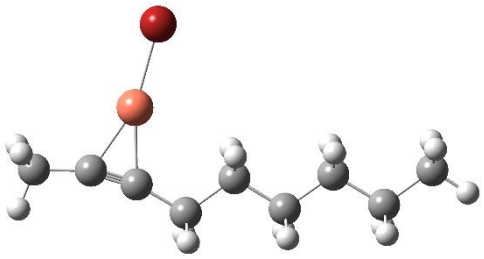

1o-CuBr

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5. NMR Spectra

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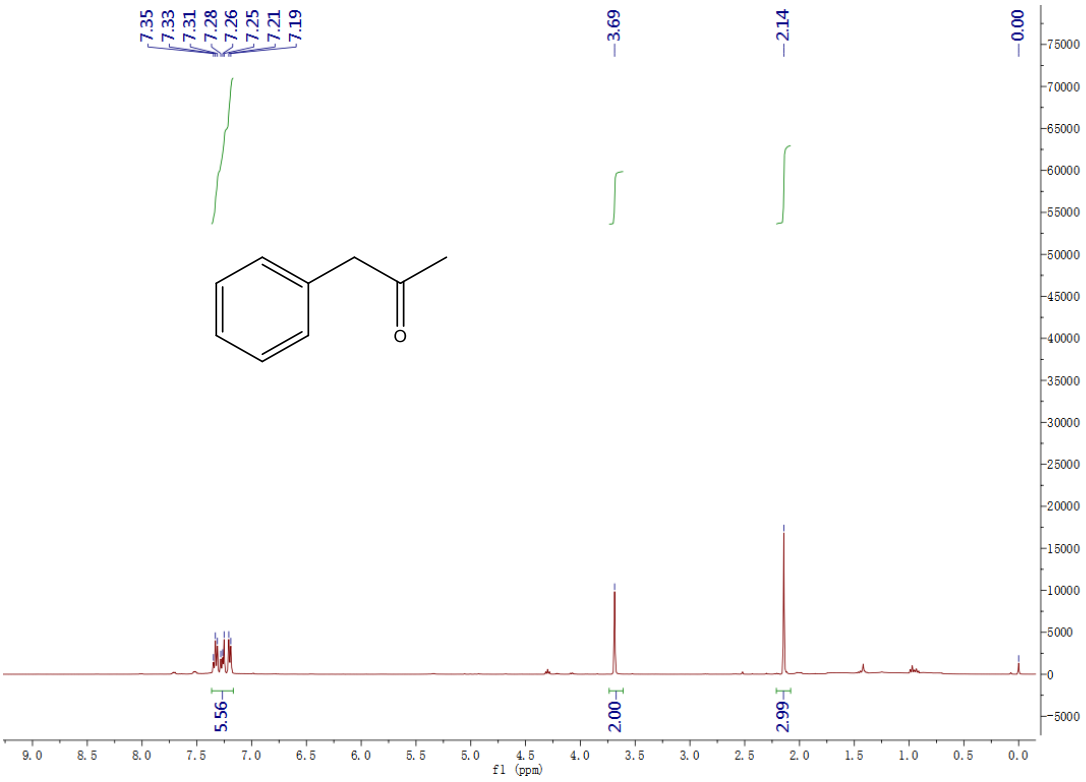
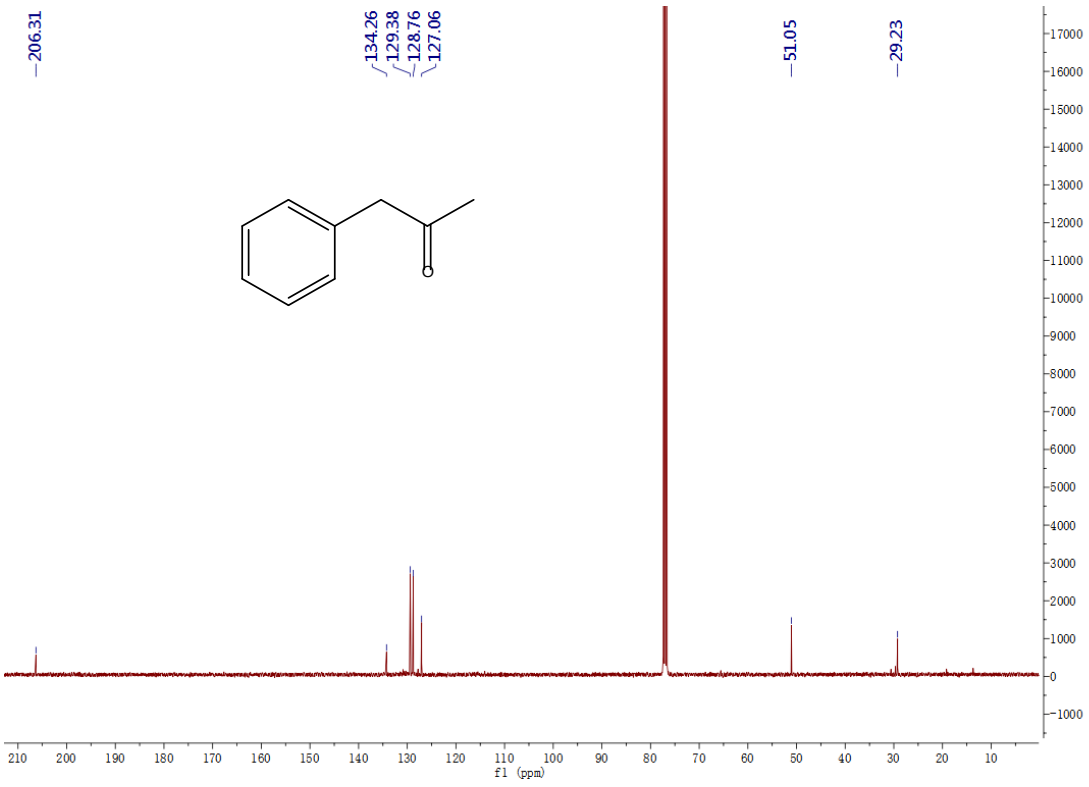
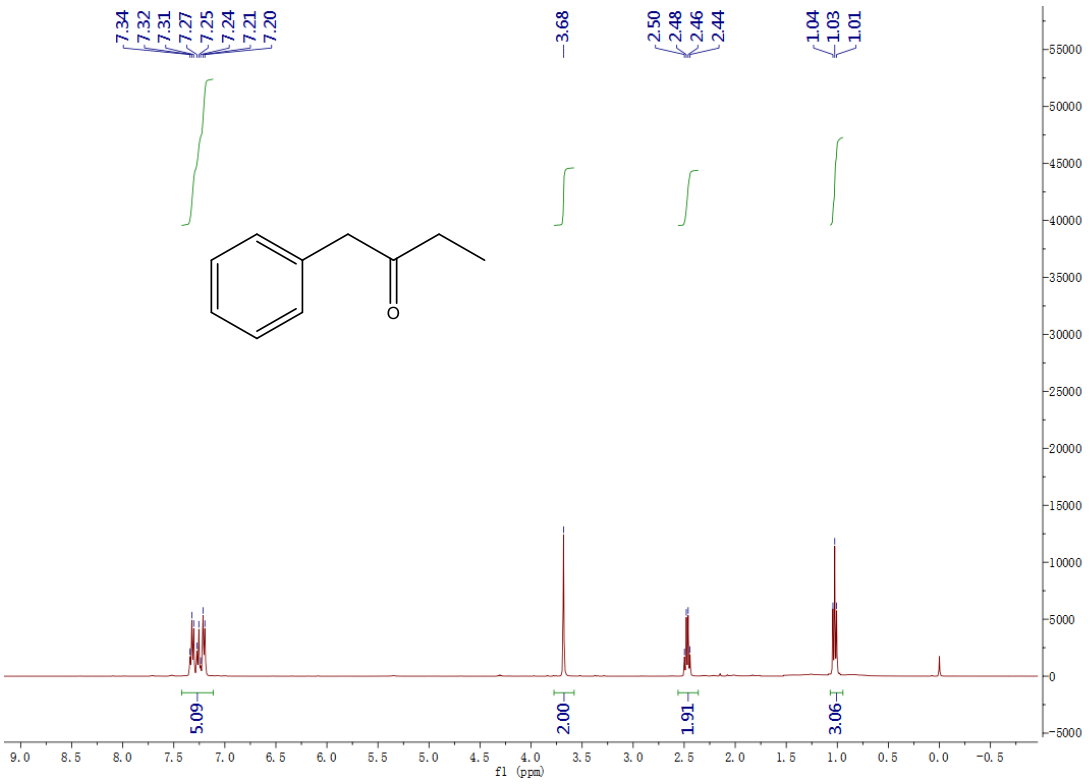


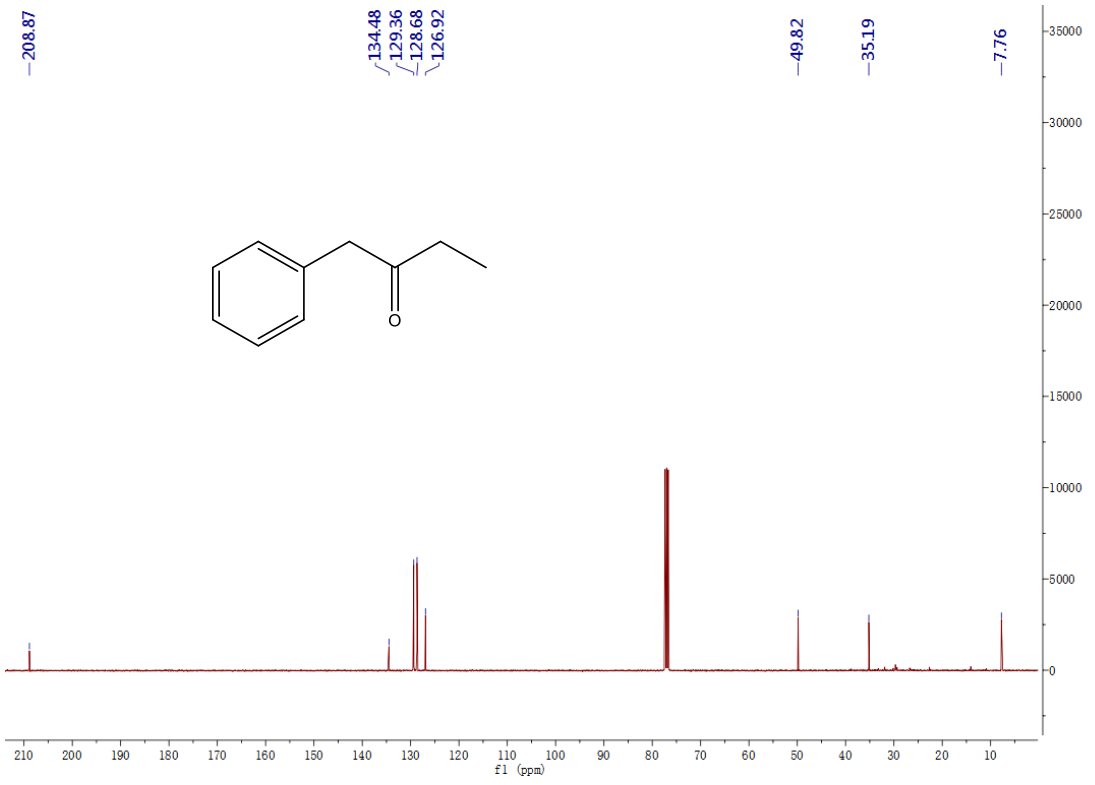
^{13}C NMR ($CDCl_3$)



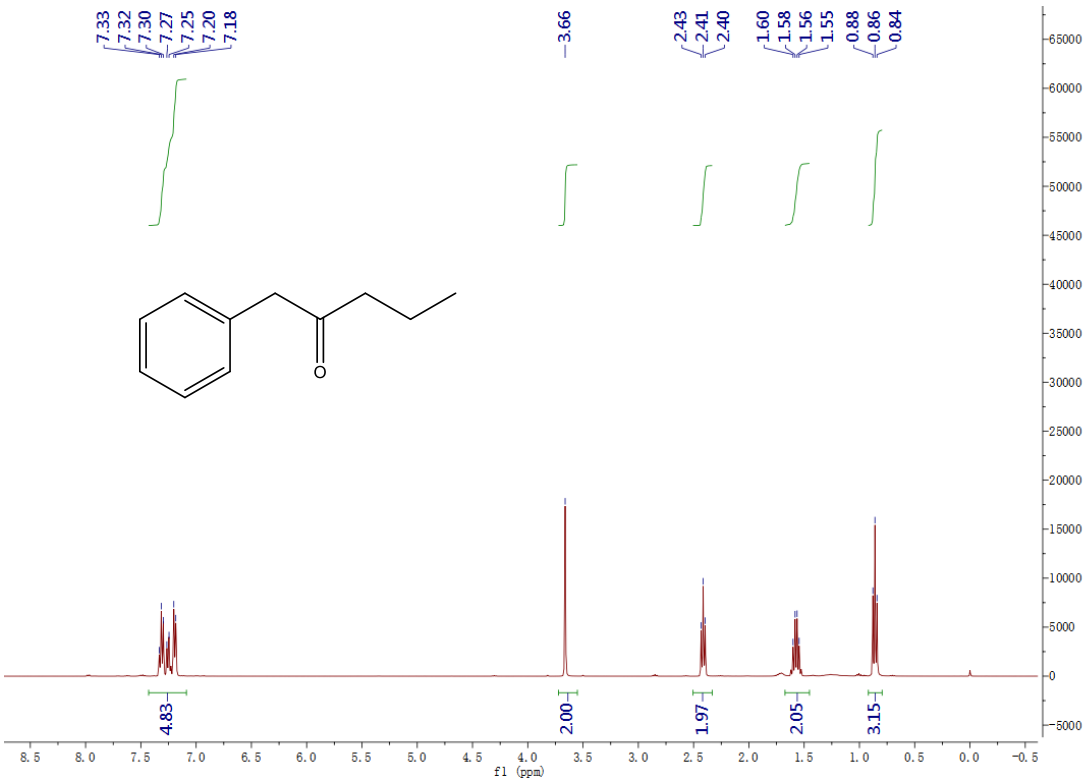
^{1}H NMR ($CDCl_3$)


7.34
7.32
7.31
7.27
7.25
7.24
7.21
7.20
3.68
2.50
2.48
2.46
2.44
1.04
1.03
1.01
O
5.09
2.00
1.91
3.06
f1 (ppm)

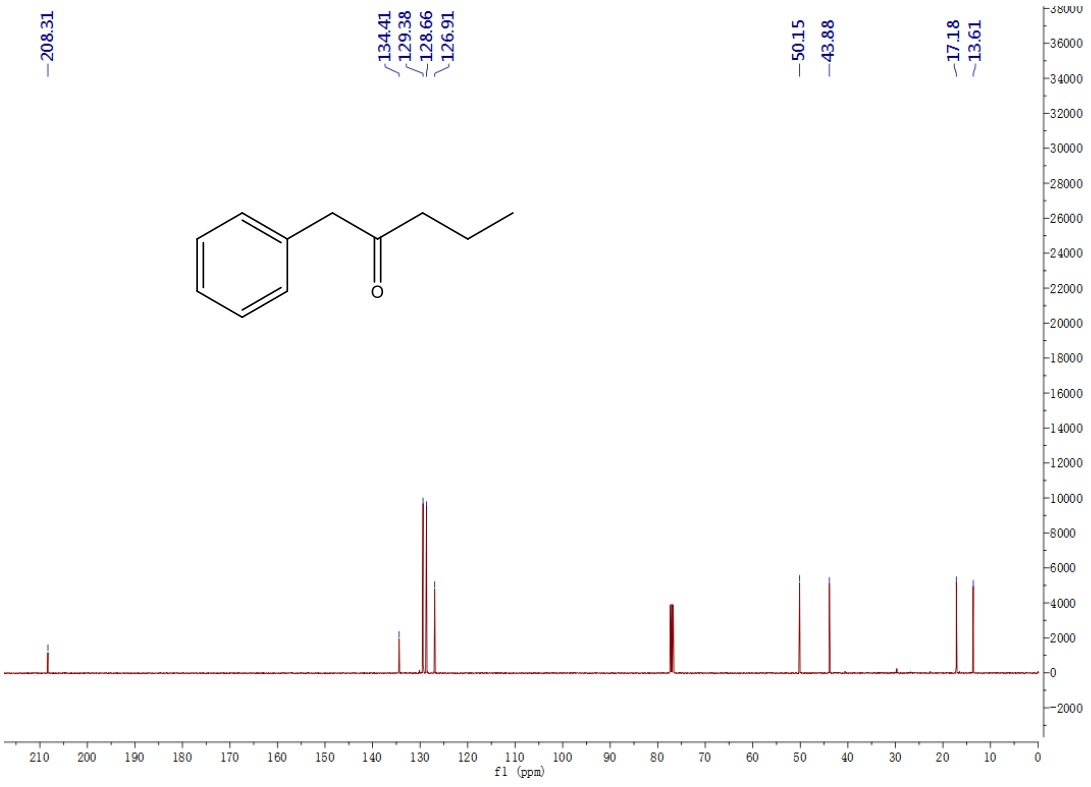
^{13}C NMR ($CDCl_3$)



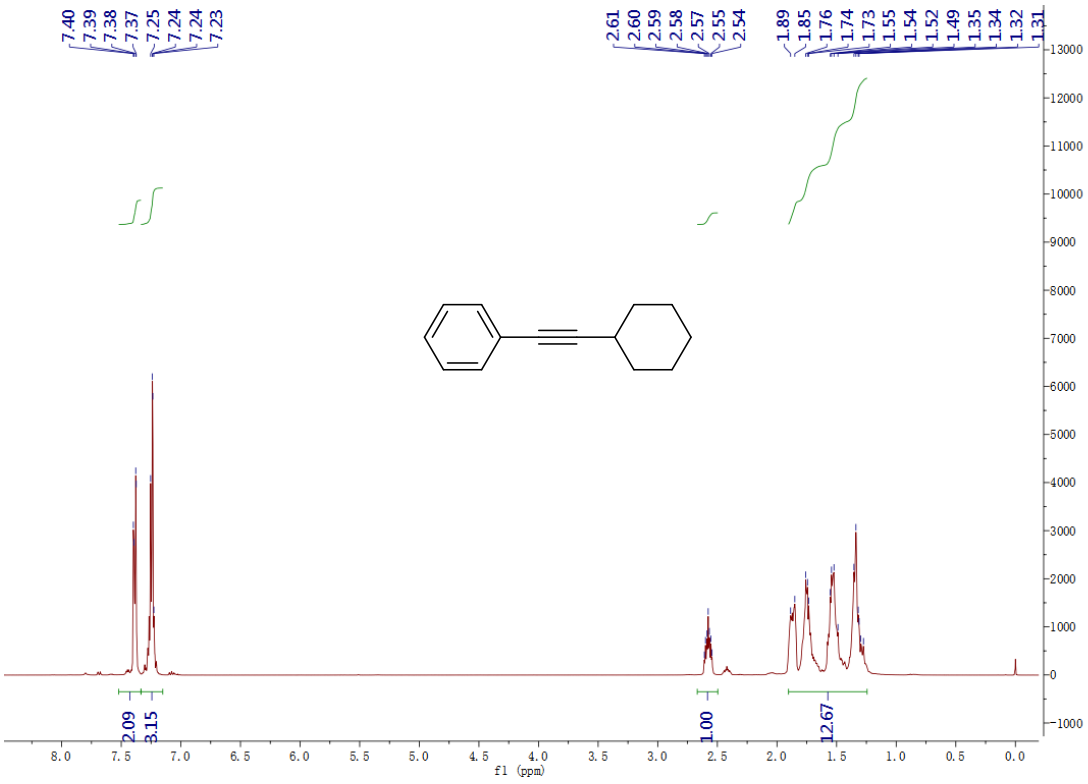
^{1}H NMR ($CDCl_3$)


7.33
7.32
7.30
7.27
7.25
7.20
7.18
3.66
2.43
2.41
2.40
1.60
1.58
1.56
1.55
0.88
0.86
0.84
O
4.83
2.00
1.97
2.05
3.15
f1 (ppm)

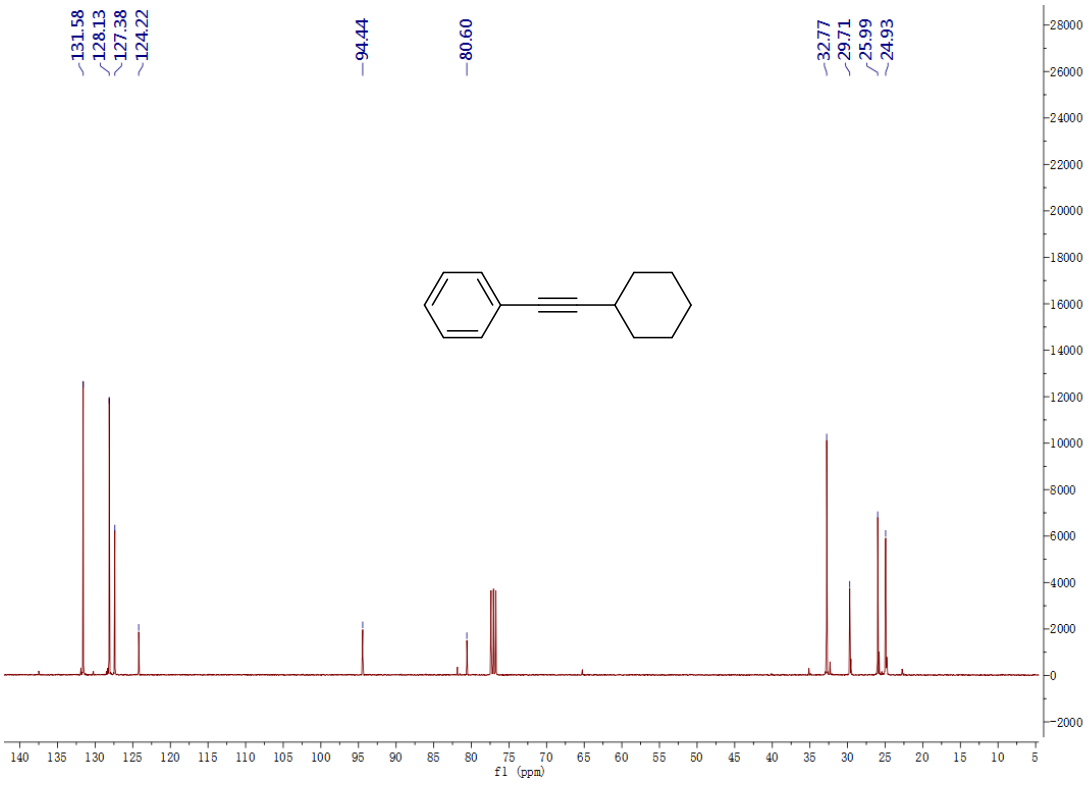
^{13}C NMR ($CDCl_3$)



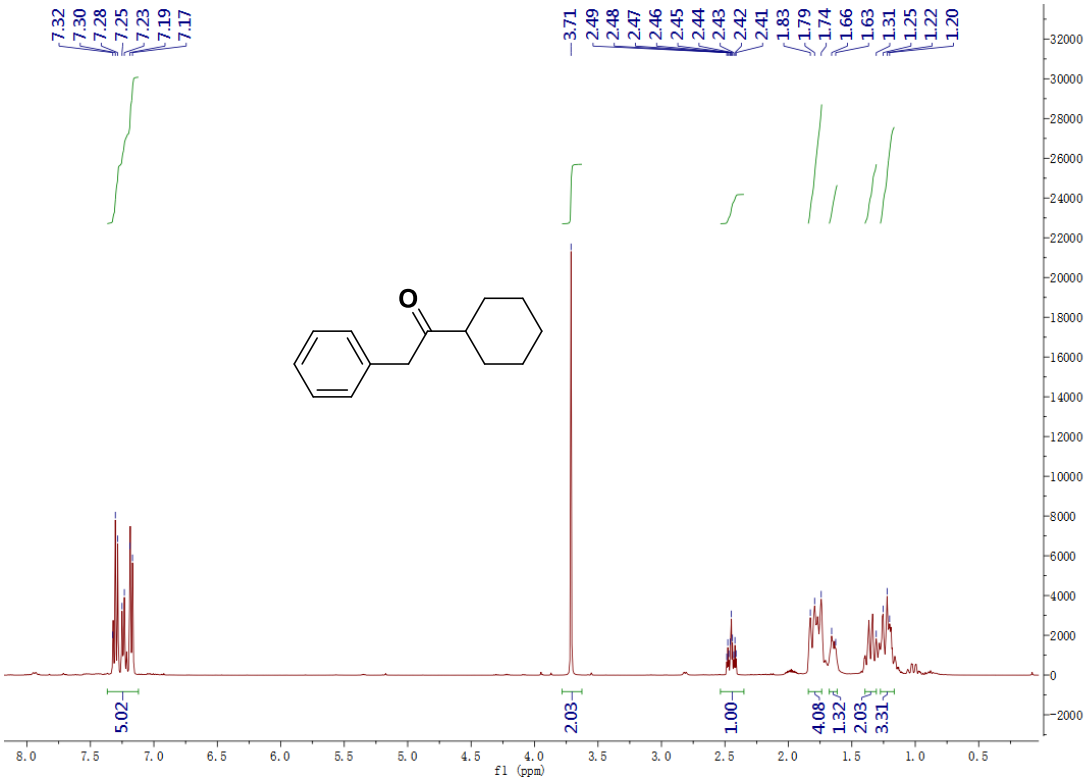
^{1}H NMR ($CDCl_3$)


7.40
7.39
7.38
7.37
7.25
7.24
7.24
7.23
2.61
2.60
2.59
2.58
2.57
2.55
2.54
1.89
1.85
1.76
1.74
1.73
1.55
1.54
1.52
1.49
1.35
1.34
1.32
1.31
2.09
3.15
1.00
12.67
f1 (ppm)

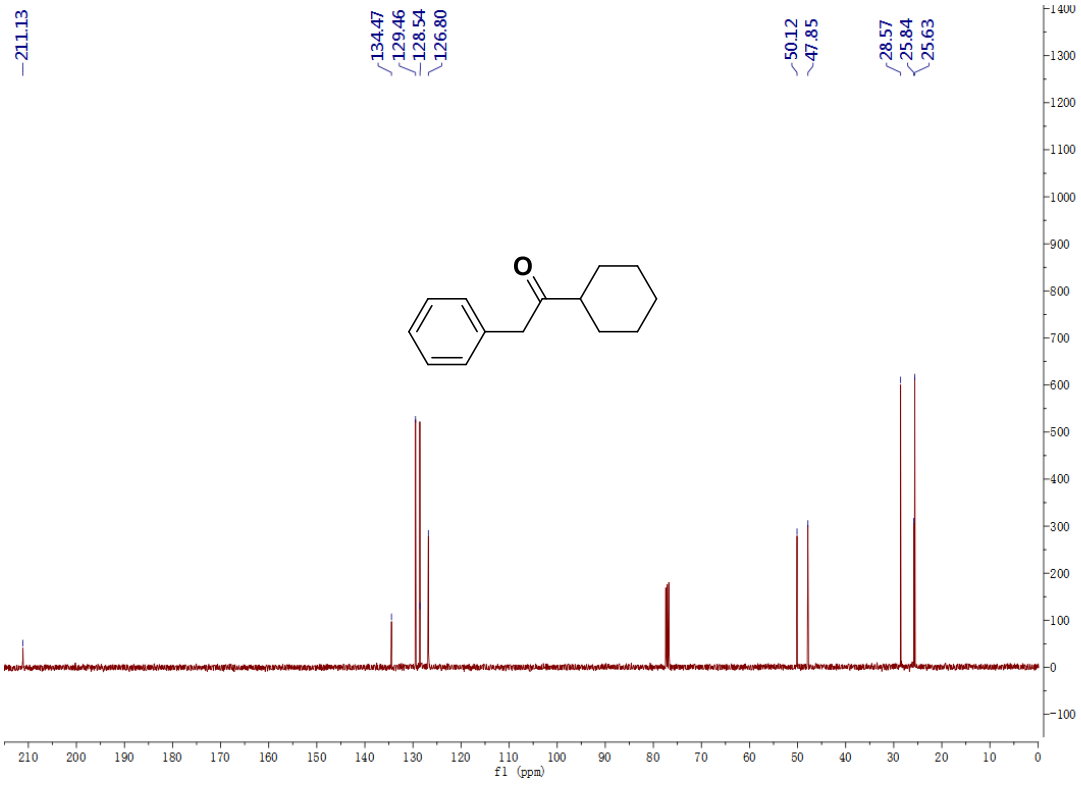
^{13}C NMR ($CDCl_3$)



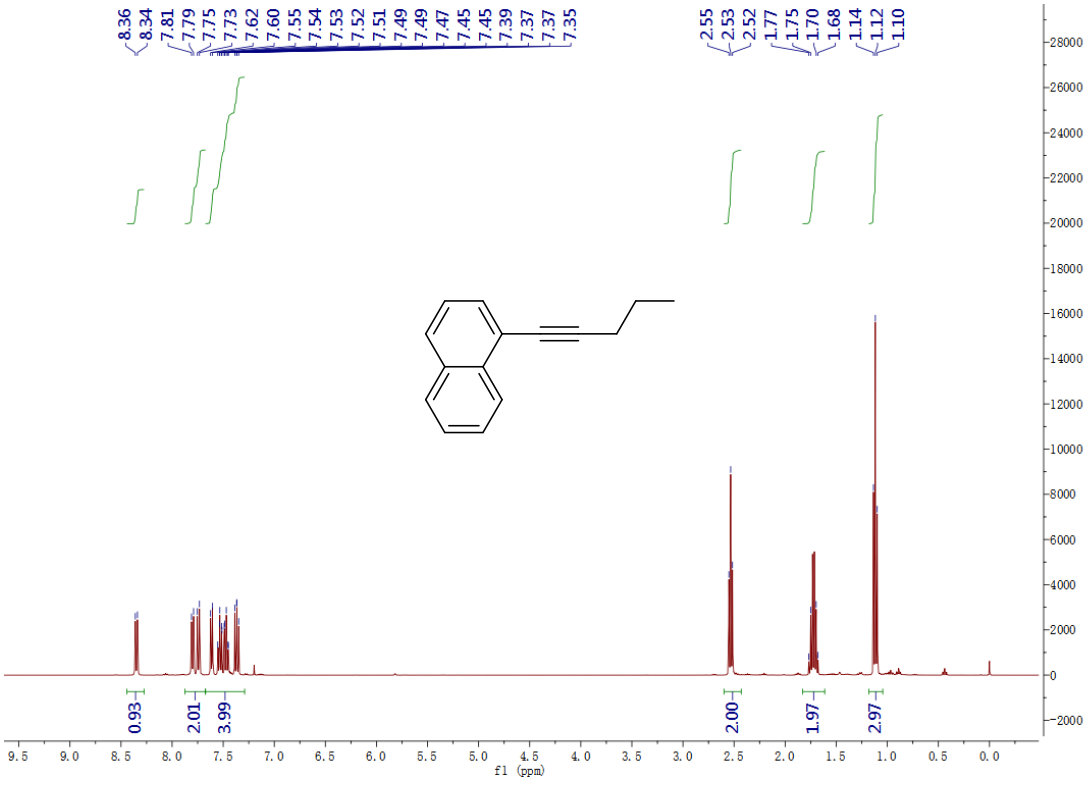
^{1}H NMR ($CDCl_3$)


7.32
7.30
7.28
7.25
7.23
7.19
7.17
3.71
2.49
2.48
2.47
2.46
2.45
2.44
2.43
2.42
2.41
1.83
1.79
1.74
1.66
1.63
1.31
1.25
1.22
1.20
O
5.02
2.03
1.00
4.08
1.32
2.03
3.31
f1 (ppm)

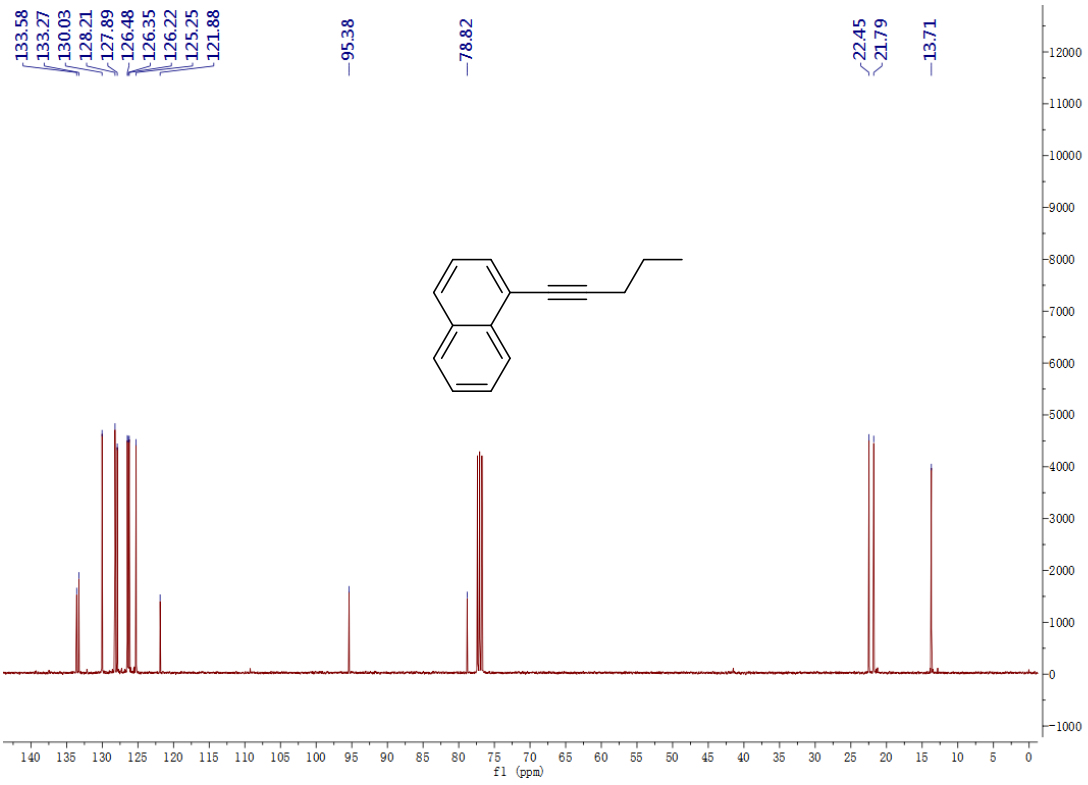
^{13}C NMR ($CDCl_3$)



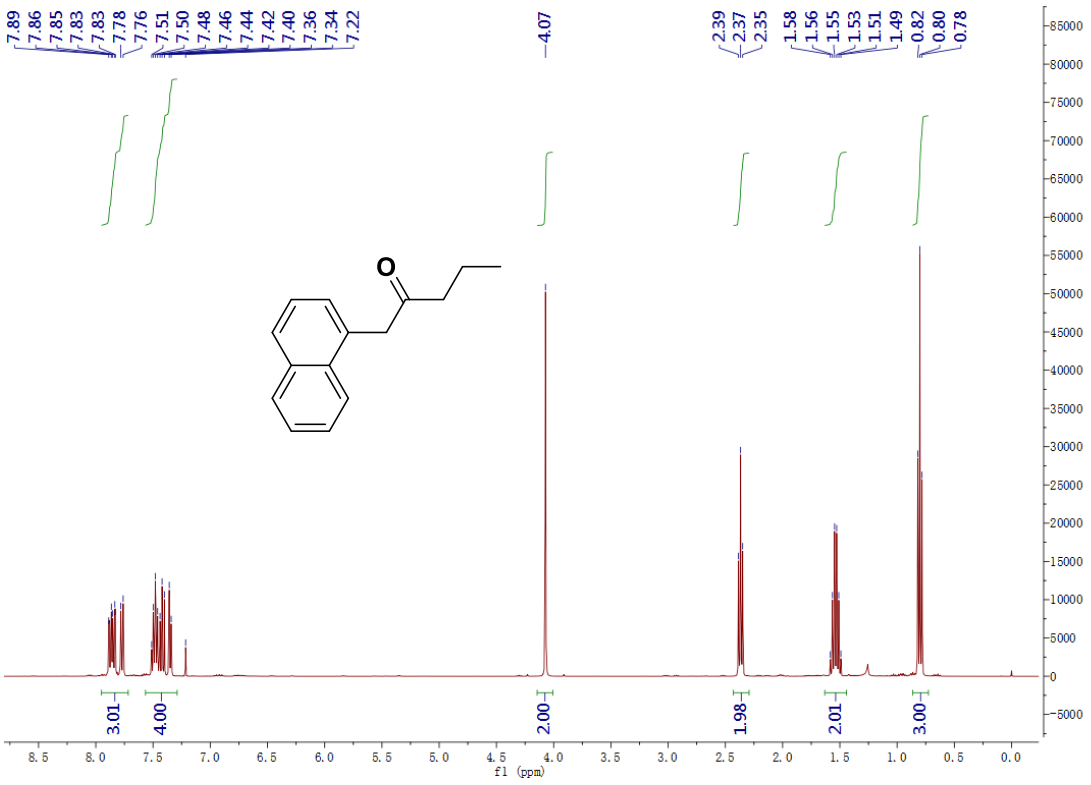
^{1}H NMR ($CDCl_3$)


8.36
8.34
7.81
7.79
7.75
7.73
7.62
7.60
7.55
7.54
7.53
7.52
7.51
7.49
7.49
7.47
7.45
7.45
7.39
7.37
7.37
7.35
2.55
2.53
2.52
1.77
1.75
1.70
1.68
1.14
1.12
1.10
0.93
2.01
3.99
2.00
1.97
2.97
f1 (ppm)

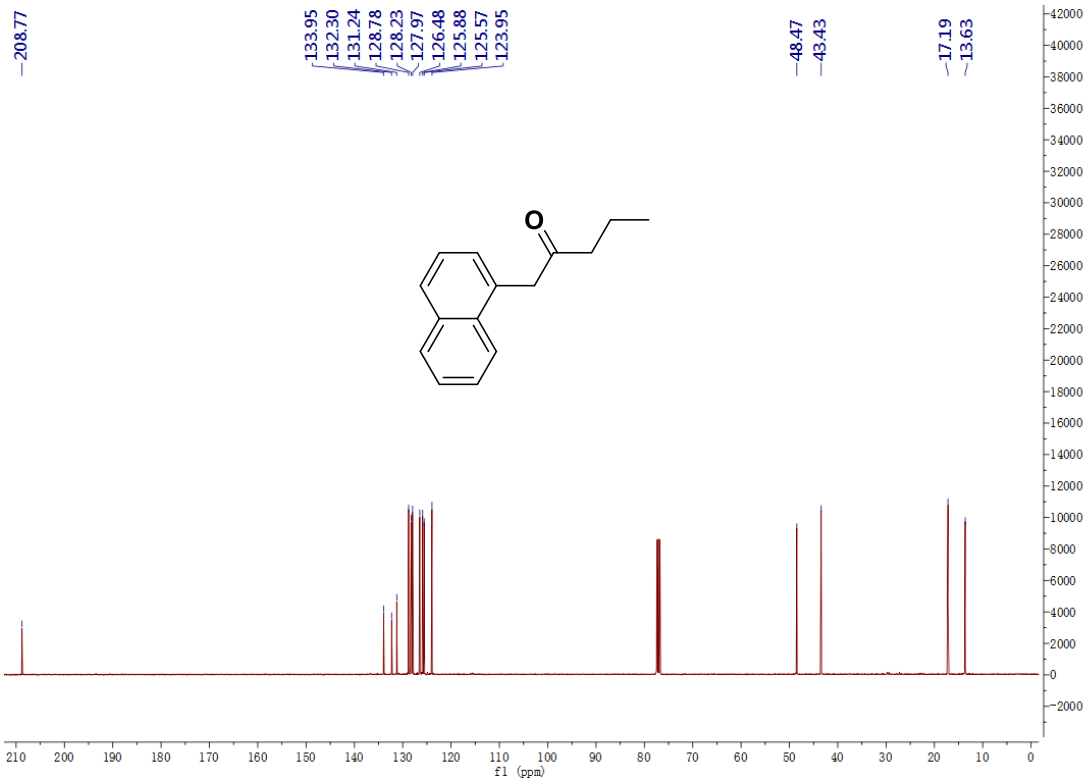
^{13}C NMR ($CDCl_3$)



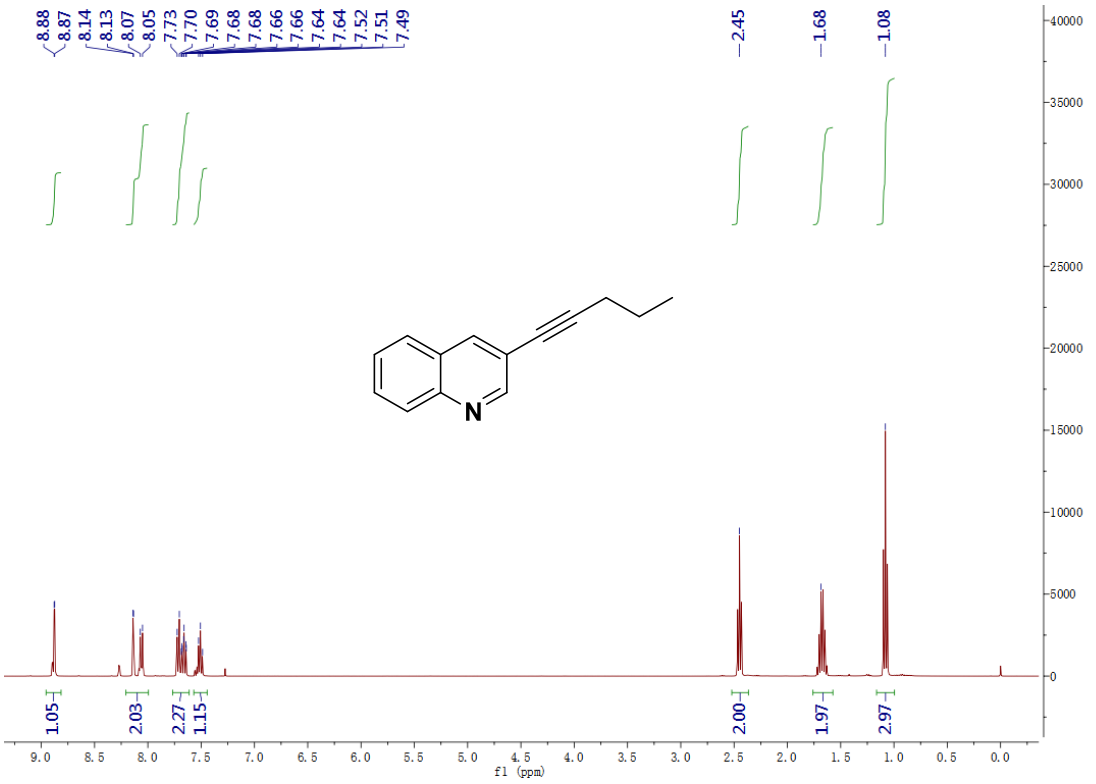
^{1}H NMR ($CDCl_3$)


7.89
7.86
7.85
7.83
7.83
7.78
7.76
7.51
7.50
7.48
7.46
7.44
7.42
7.40
7.36
7.34
7.22
4.07
2.39
2.37
2.35
1.58
1.56
1.55
1.53
1.51
1.49
0.82
0.80
0.78
O
3.01
4.00
2.00
1.98
2.01
3.00
f1 (ppm)

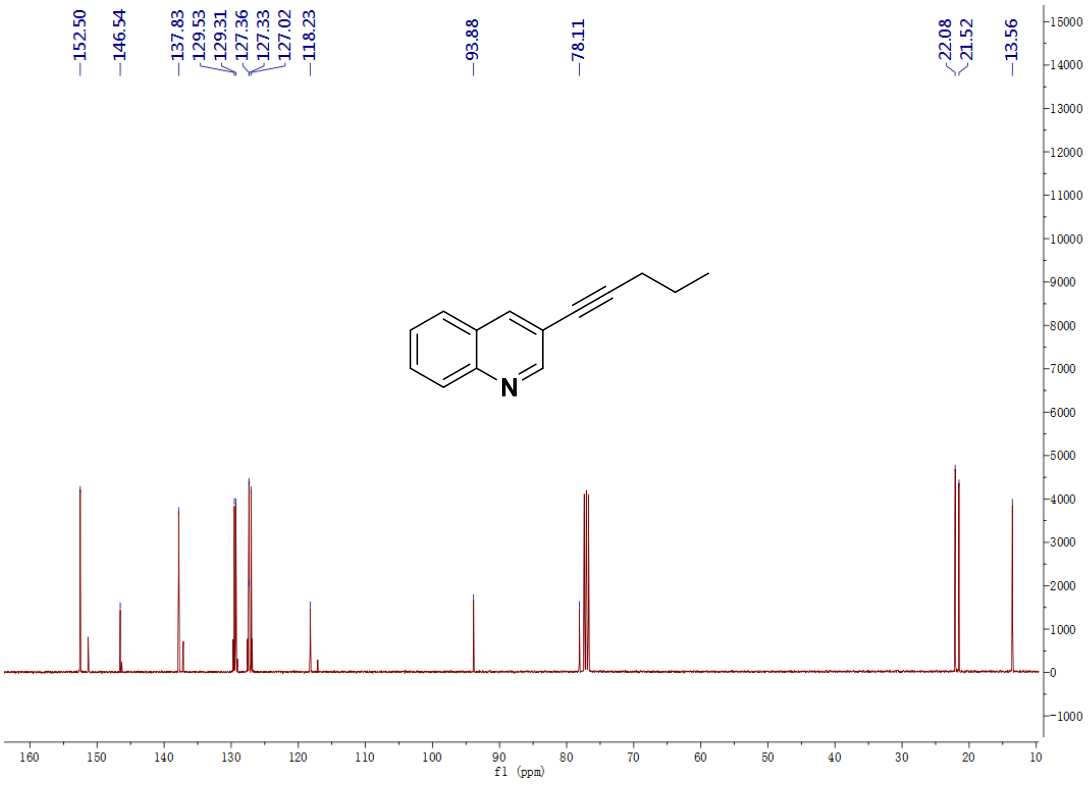
^{13}C NMR ($CDCl_3$)



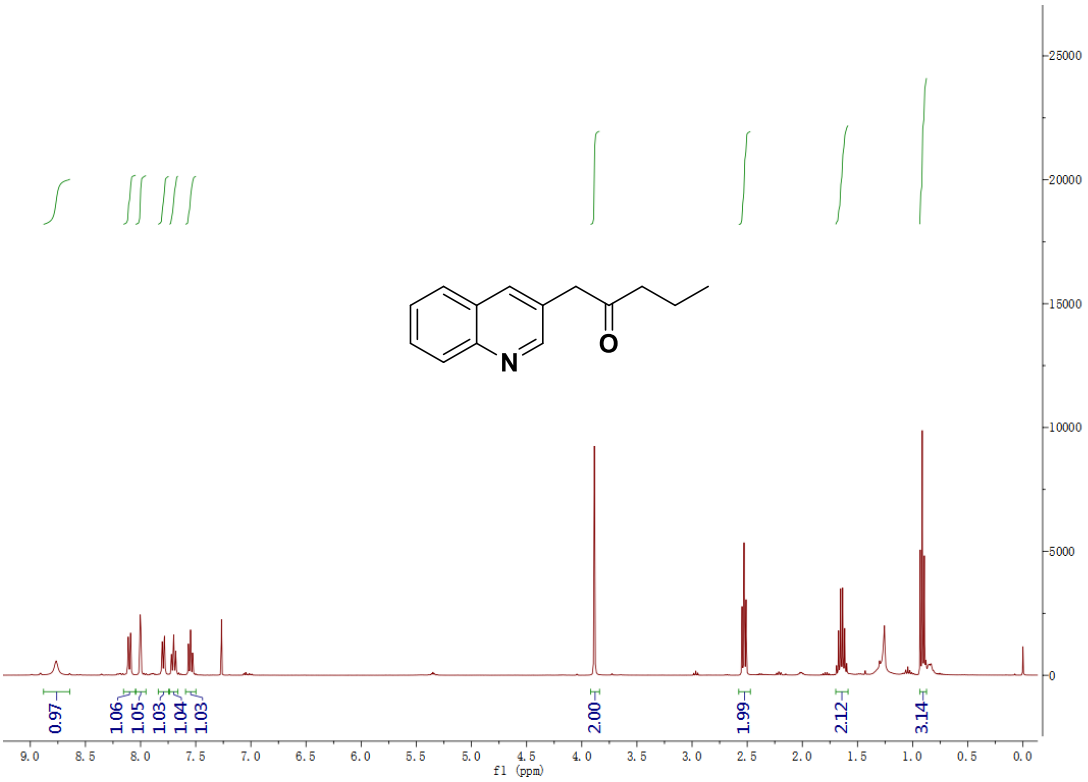
^{1}H NMR ($CDCl_3$)


8.88
8.87
8.14
8.13
8.07
8.05
7.73
7.70
7.69
7.68
7.68
7.66
7.66
7.64
7.64
7.52
7.51
7.49
2.45
1.68
1.08
N
1.05
2.03
2.27
1.15
2.00
1.97
2.97
f1 (ppm)

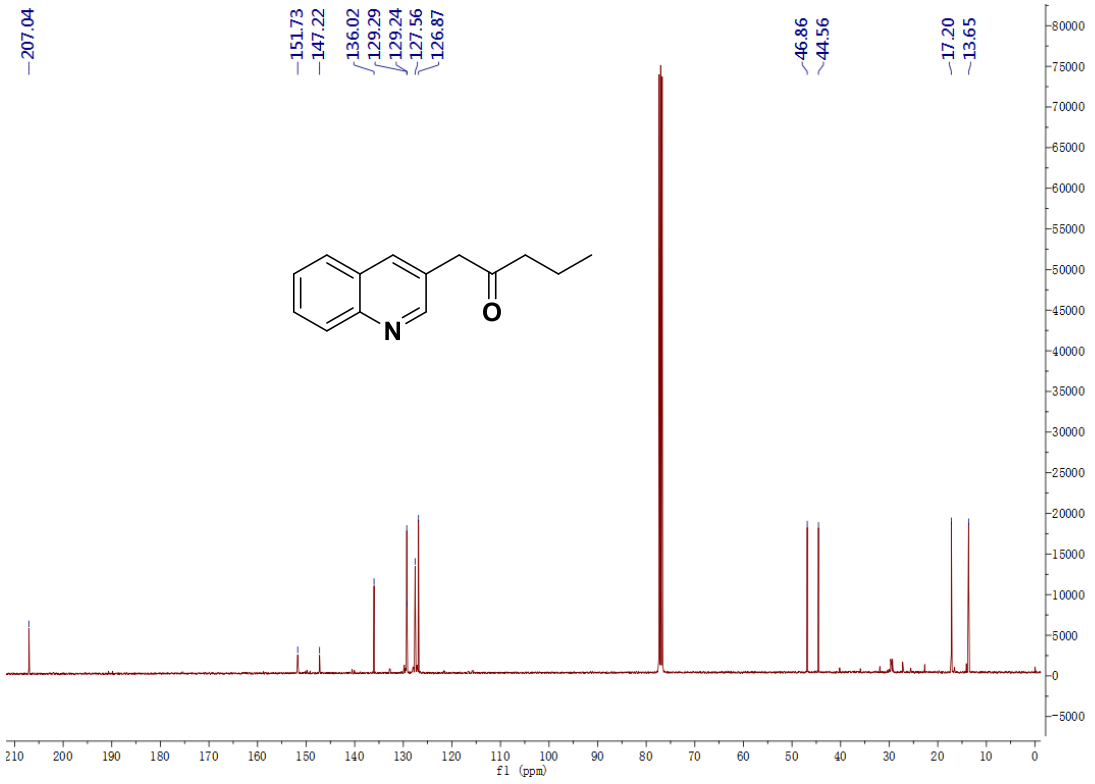
^{13}C NMR ($CDCl_3$)



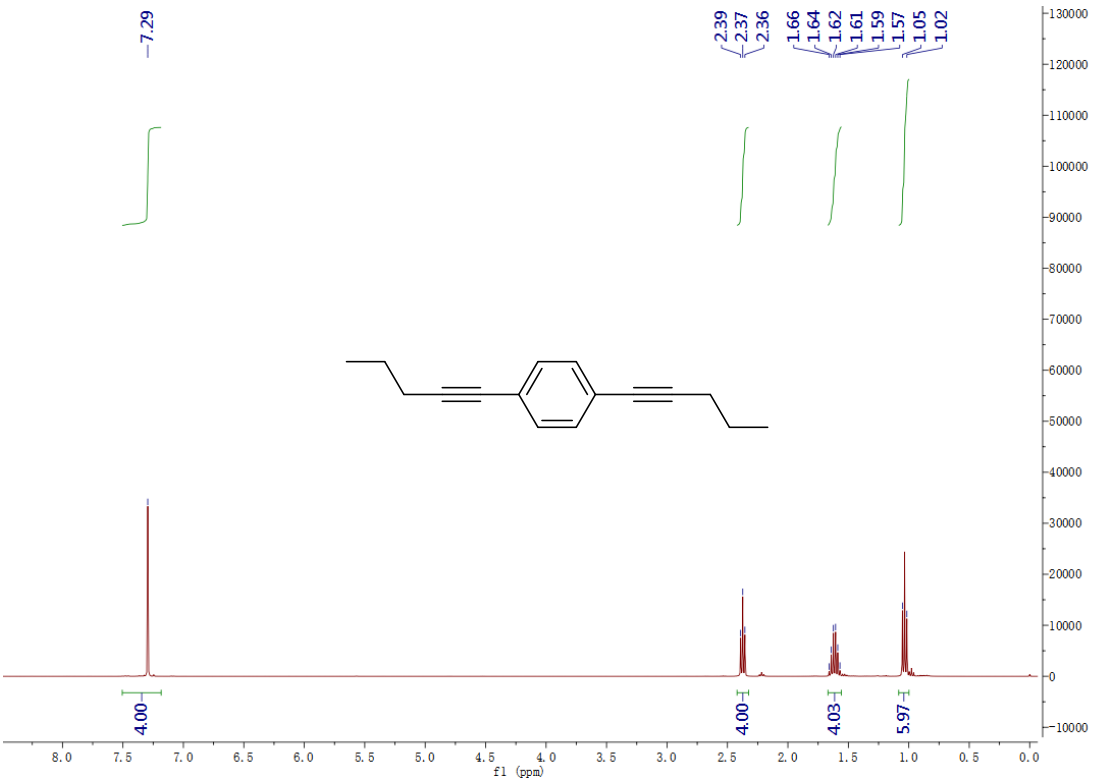
^{1}H NMR ($CDCl_3$)



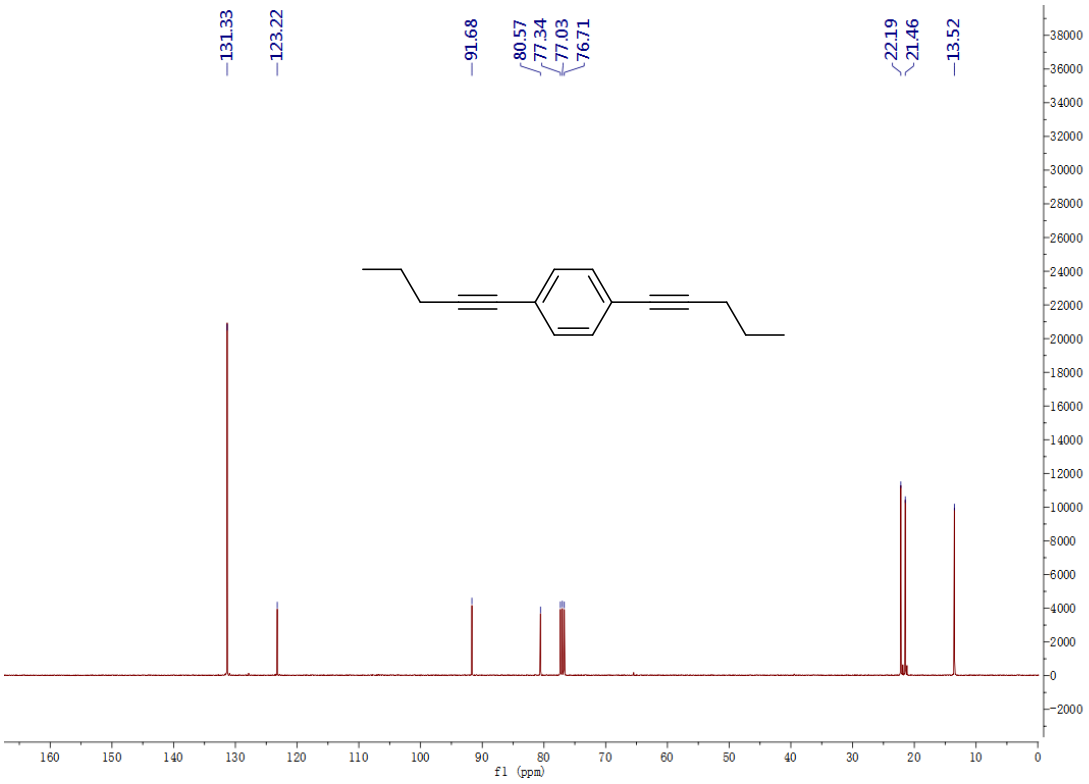
^{13}C NMR ($CDCl_3$)



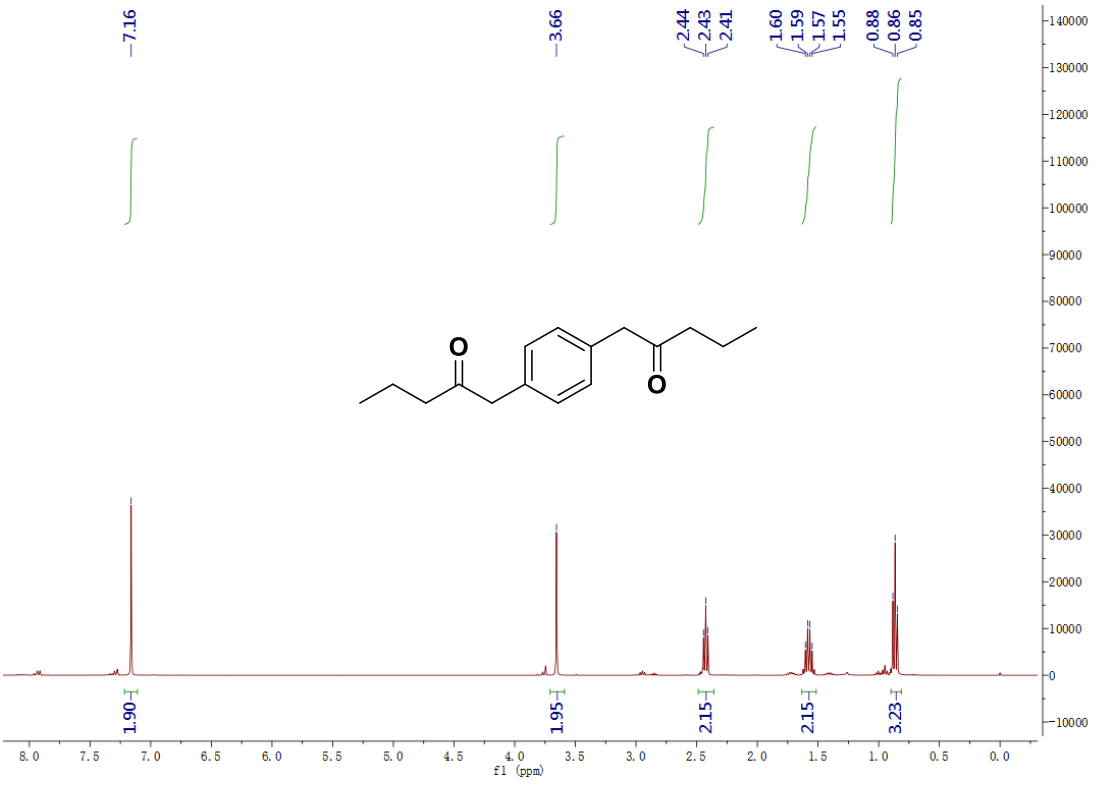
^{1}H NMR ($CDCl_3$)


7.29
2.39
2.37
2.36
1.66
1.64
1.62
1.61
1.59
1.57
1.05
1.02
4.00
4.00
4.03
5.97
f1 (ppm)

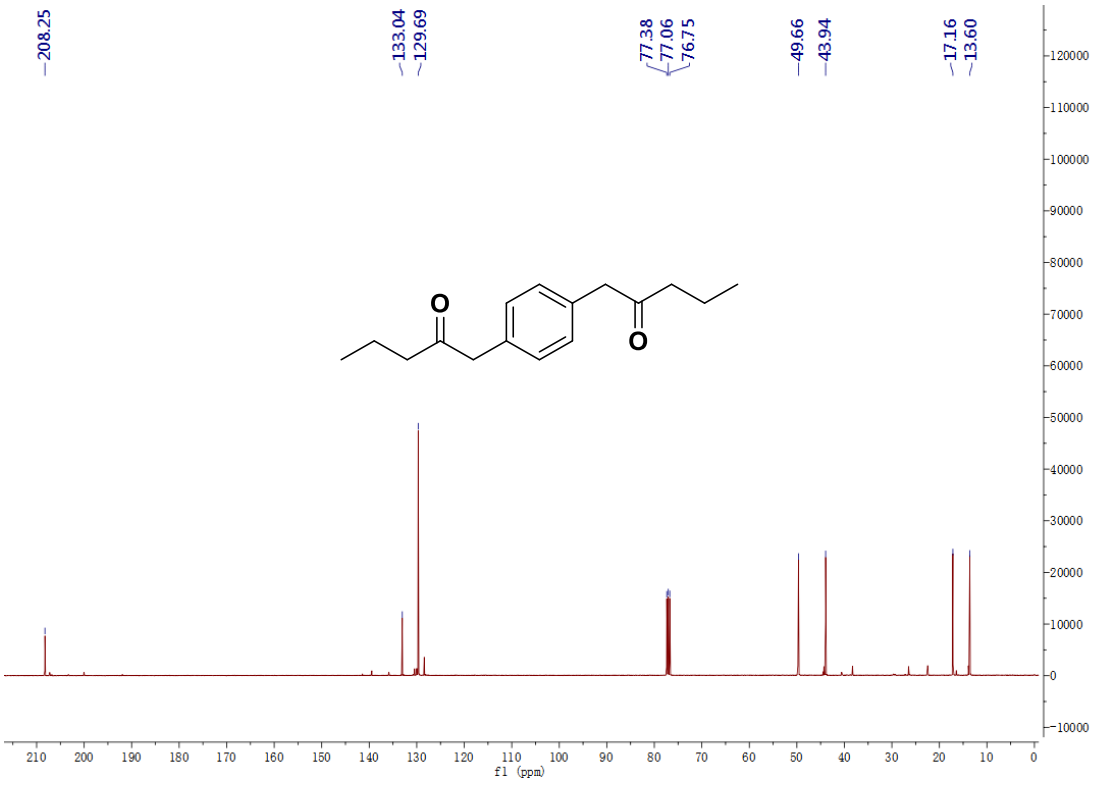
^{13}C NMR ($CDCl_3$)



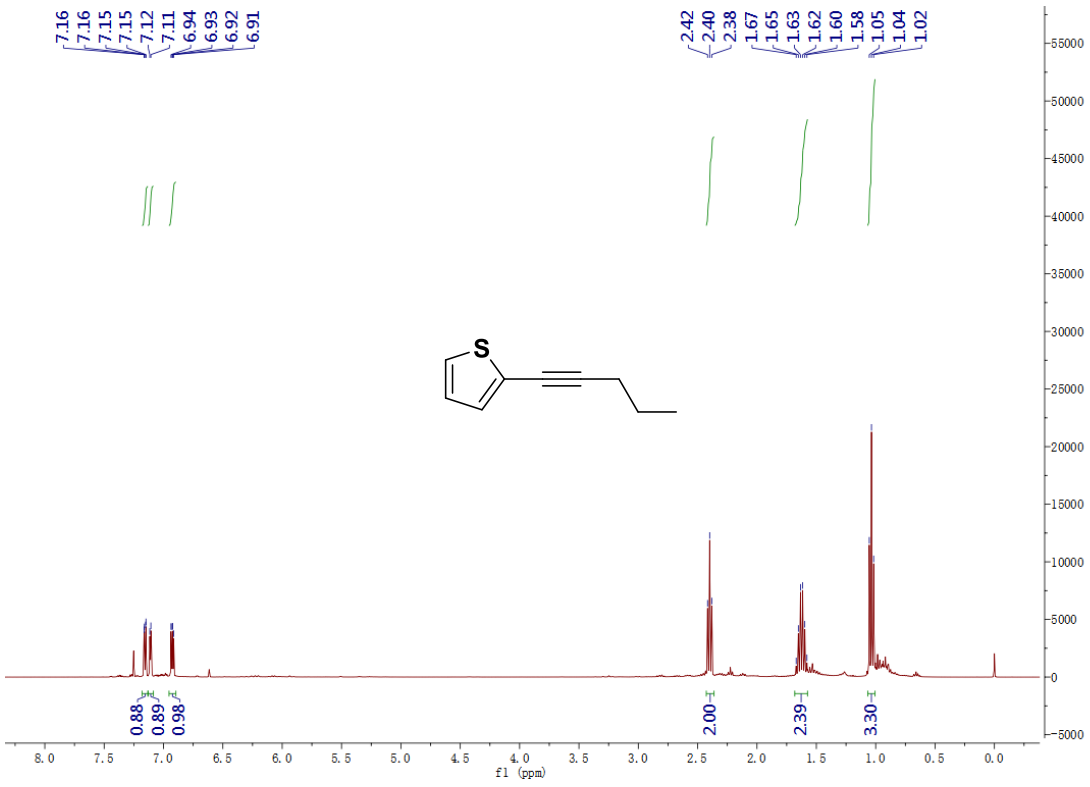
^{1}H NMR ($CDCl_3$)


7.16
3.66
2.44
2.43
2.41
1.60
1.59
1.57
1.55
0.88
0.86
0.85
O
O
1.90
1.95
2.15
2.15
3.23
f1 (ppm)

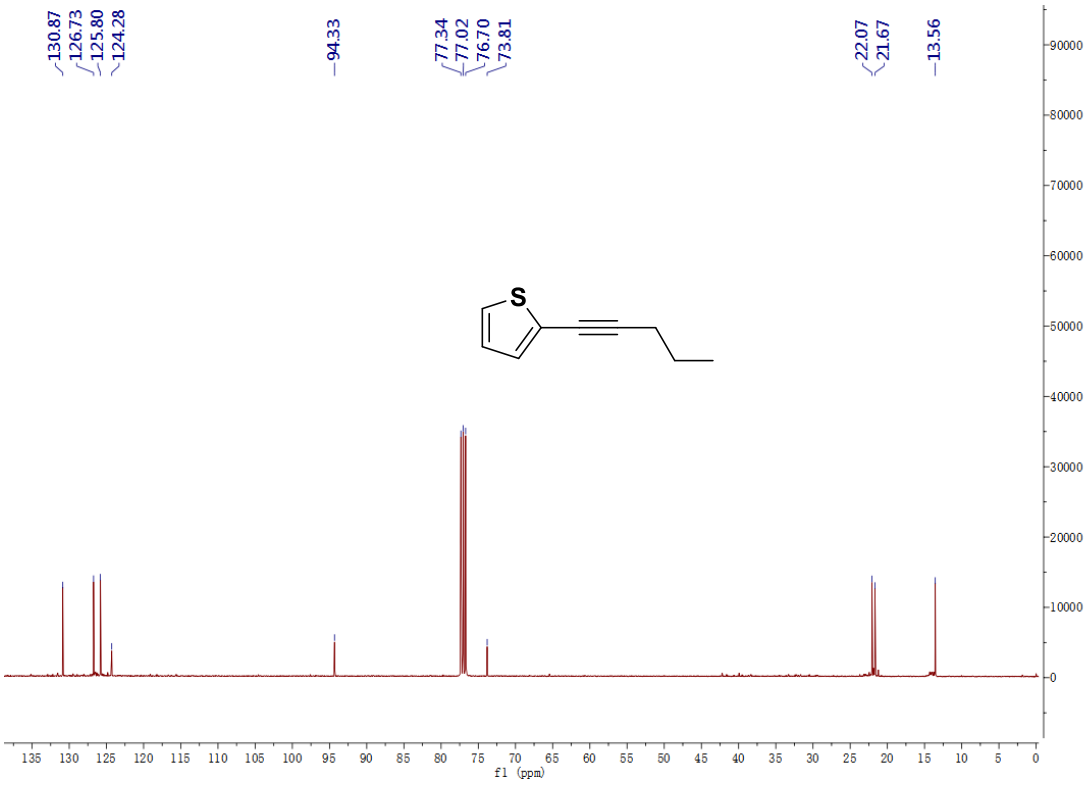
^{13}C NMR ($CDCl_3$)



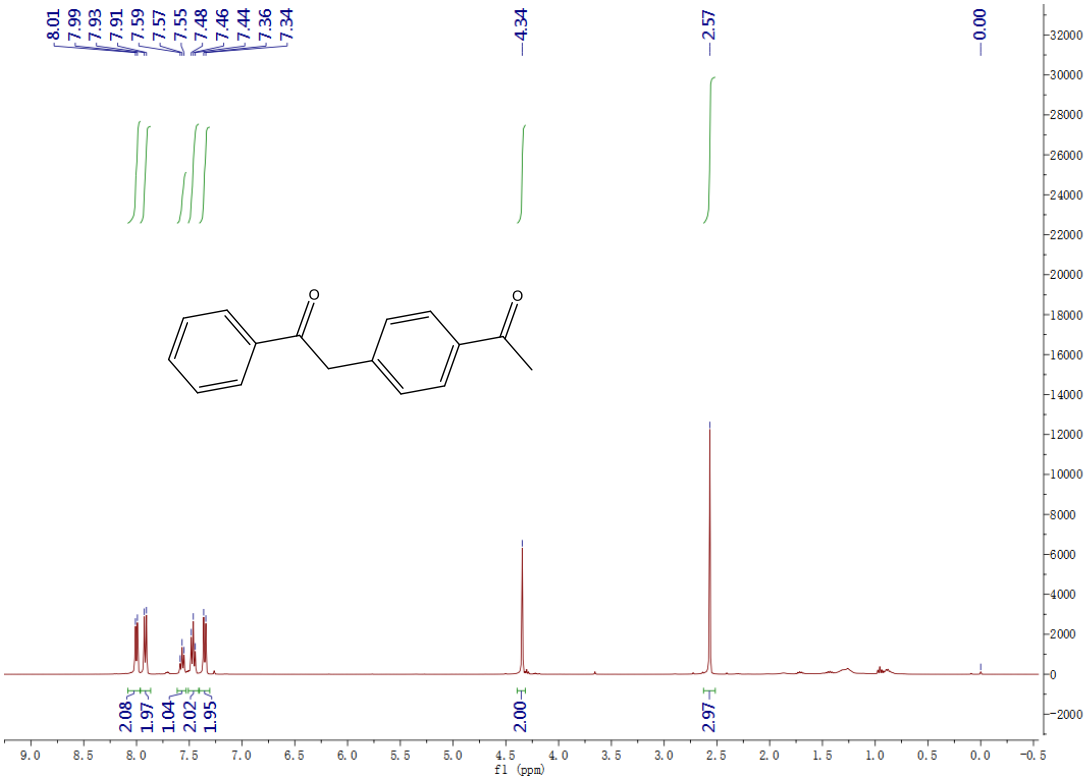
^{1}H NMR ($CDCl_3$)


7.16
7.16
7.15
7.15
7.12
7.11
6.94
6.93
6.92
6.91
2.42
2.40
2.38
1.67
1.65
1.63
1.62
1.60
1.58
1.05
1.04
1.02
S
0.88
0.89
0.98
2.00
2.39
3.30
f1 (ppm)

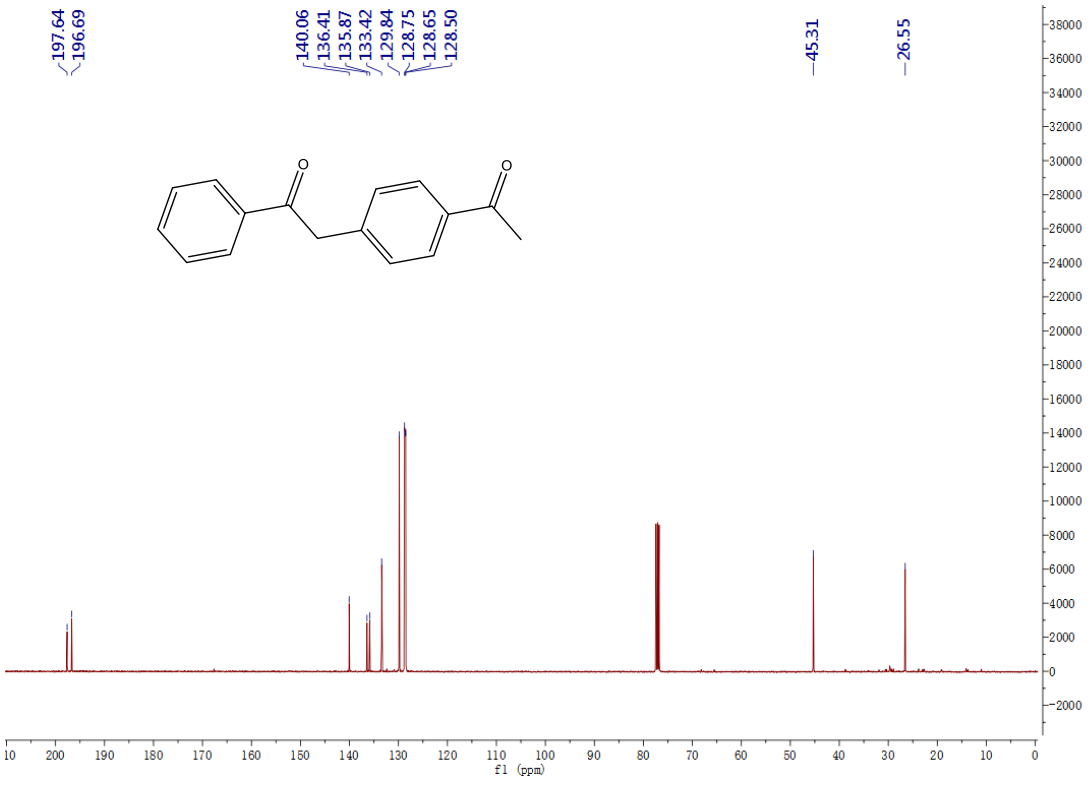
^{13}C NMR ($CDCl_3$)



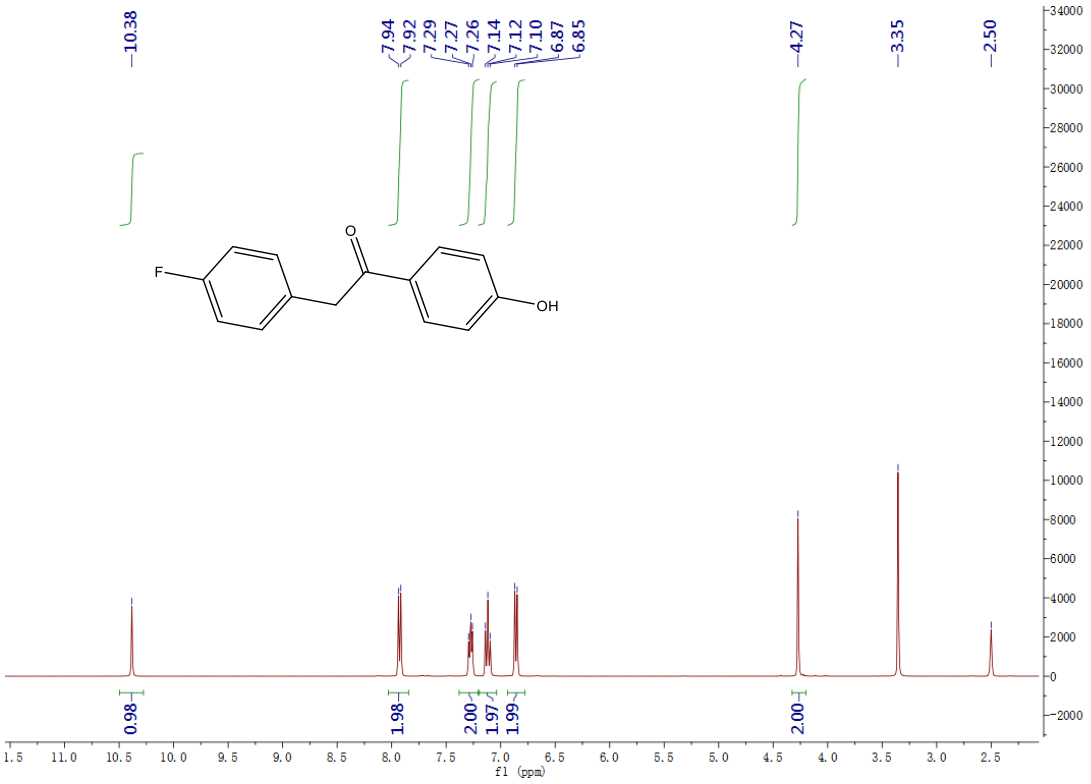
^{1}H NMR ($CDCl_3$)


8.01
7.99
7.93
7.91
7.59
7.57
7.55
7.48
7.46
7.44
7.36
7.34
4.34
2.57
0.00
O
O
2.08
1.97
1.04
2.02
1.95
2.00
2.97
f1 (ppm)

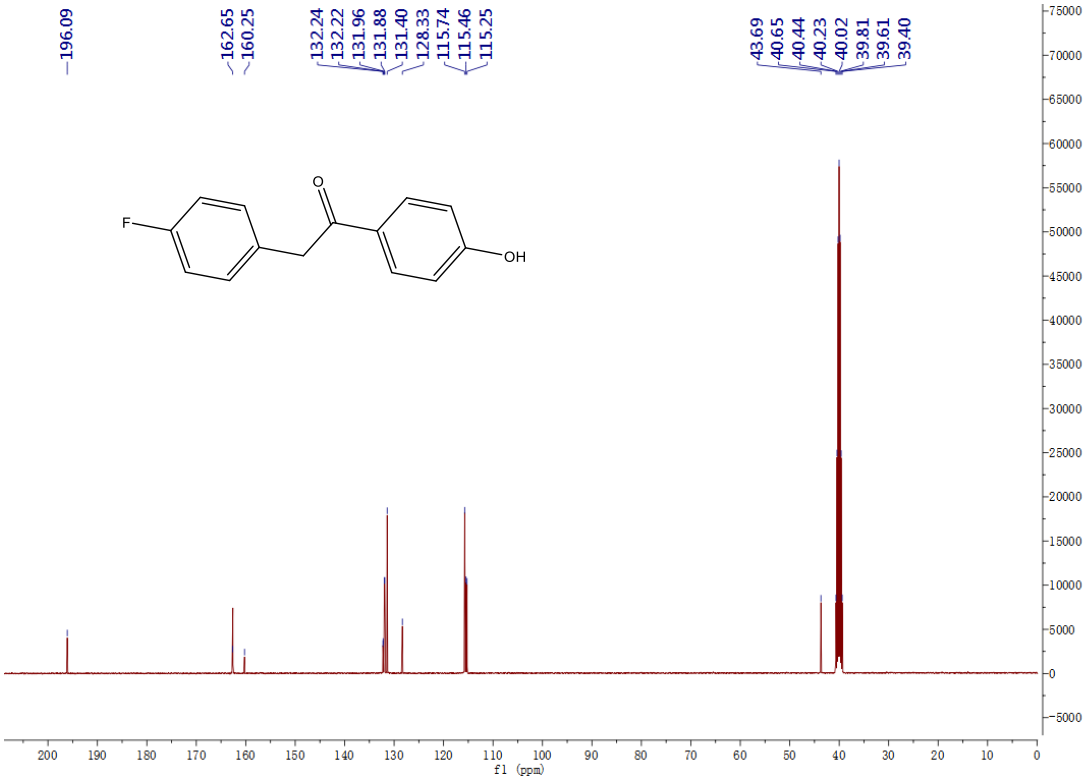
^{13}C NMR ($CDCl_3$)



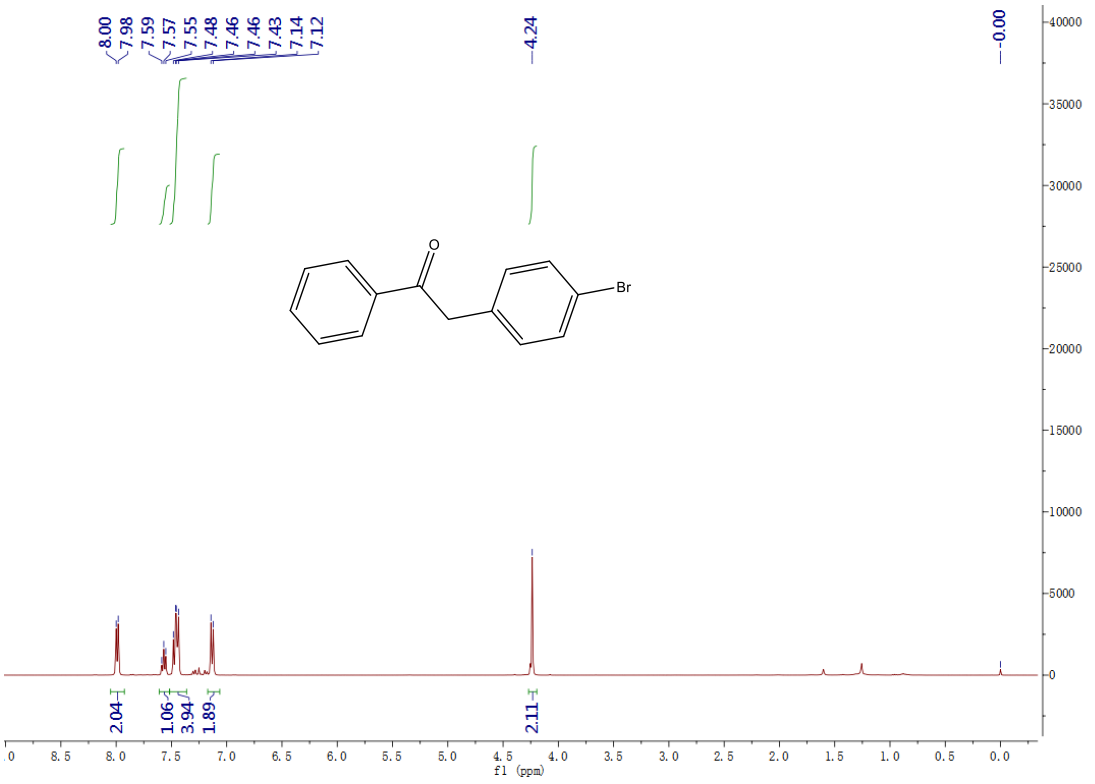
^{1}H NMR (DMSO)


10.38
7.94
7.92
7.29
7.27
7.26
7.14
7.12
7.10
6.87
6.85
4.27
3.35
2.50
O
F
OH
0.98
1.98
2.00
1.97
1.99
2.00
f1 (ppm)

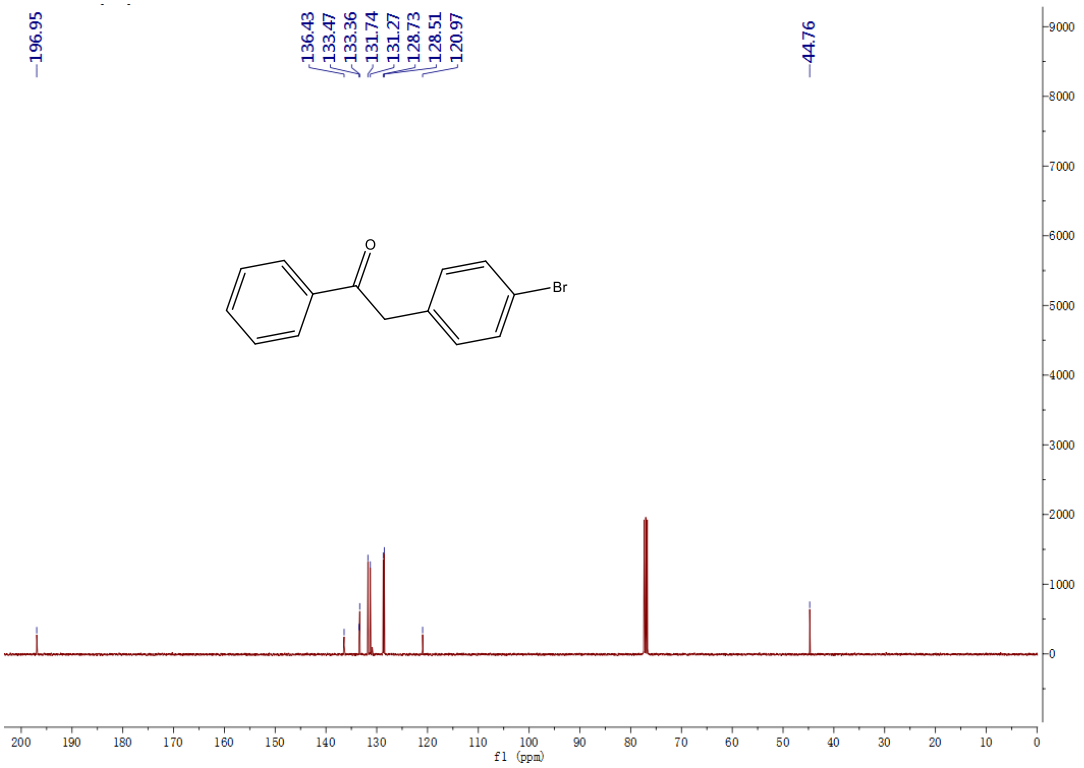
^{13}C NMR (DMSO)


196.09
162.65
160.25
132.24
132.22
131.96
131.88
131.40
128.33
115.74
115.46
115.25
43.69
40.65
40.44
40.23
40.02
39.81
39.61
39.40
F
O
OH
f1 (ppm)

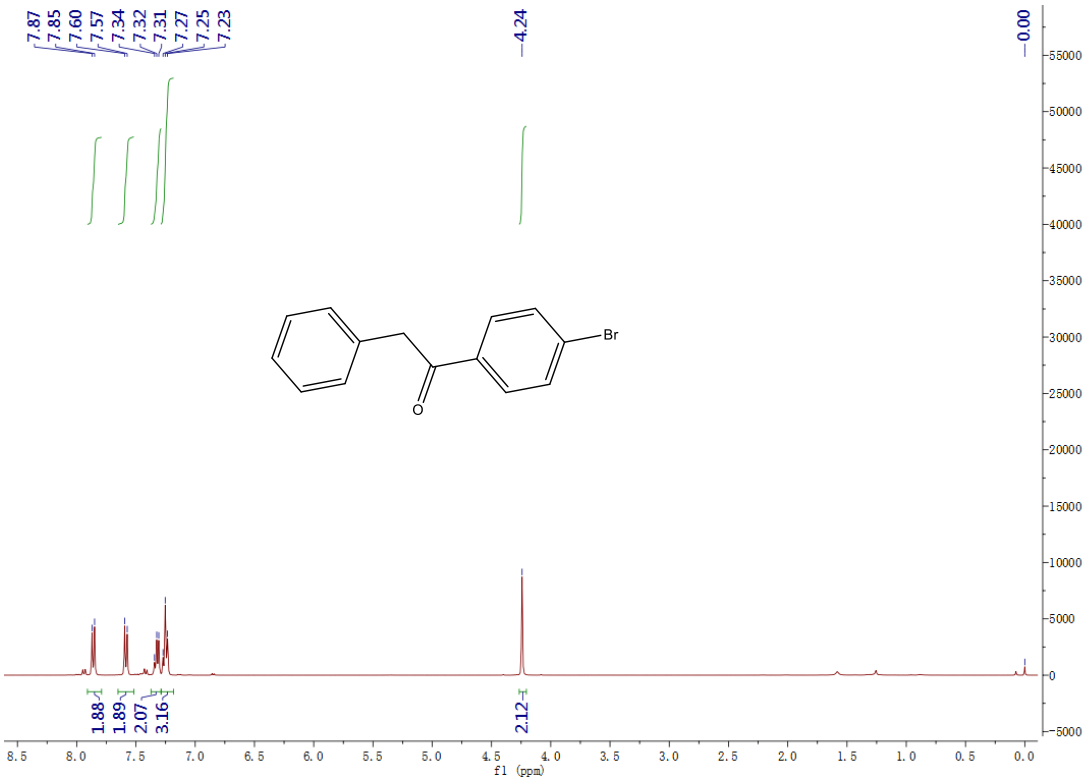
^{1}H NMR ($CDCl_3$)


8.00
7.98
7.59
7.57
7.55
7.48
7.46
7.46
7.43
7.14
7.12
4.24
0.00
O
Br
2.04
1.06
3.94
1.89
2.11
f1 (ppm)

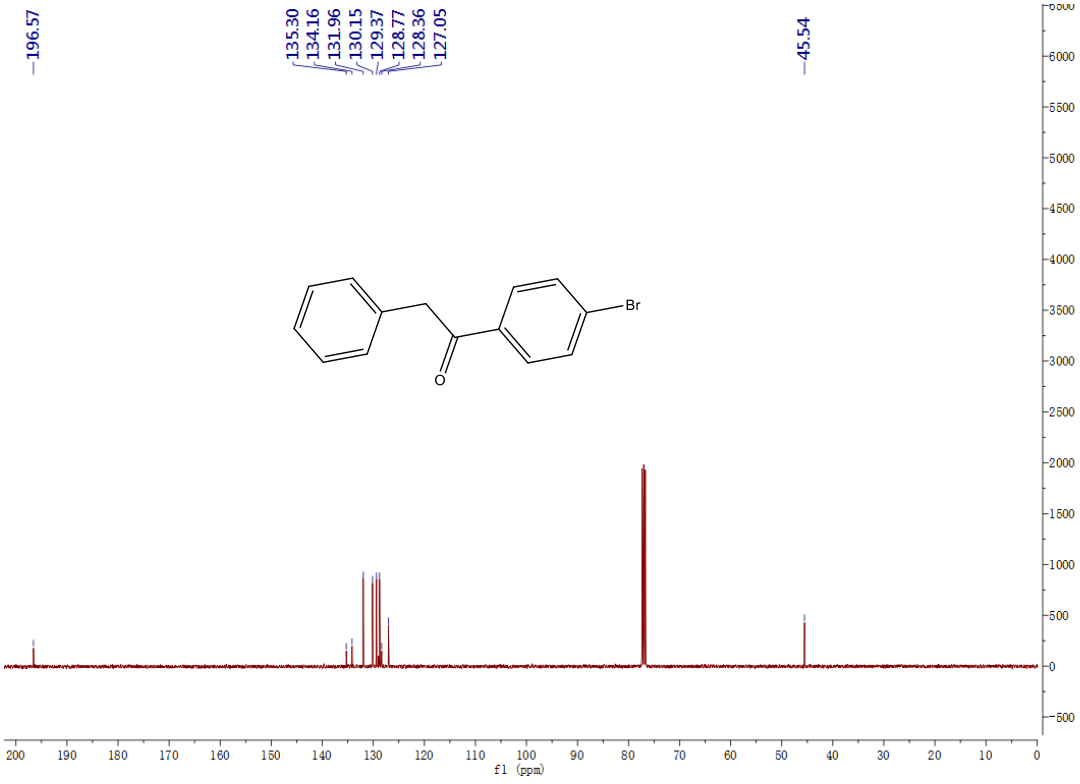
^{13}C NMR ($CDCl_3$)



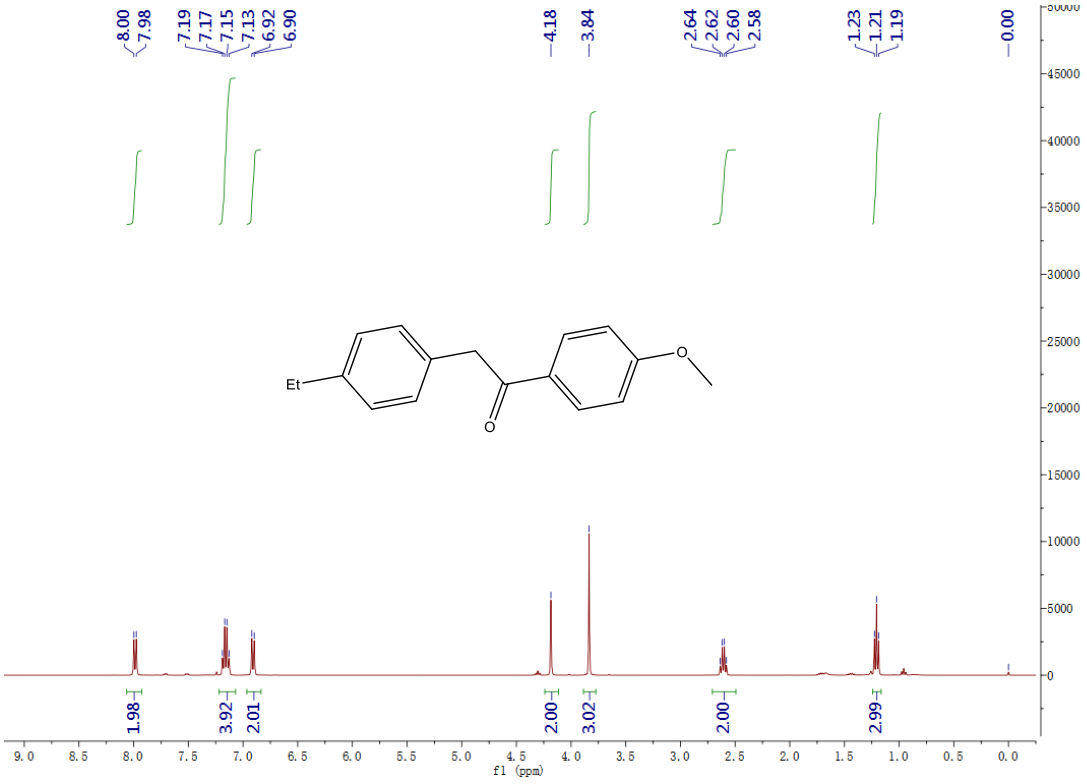
^{1}H NMR ($CDCl_3$)


7.87
7.85
7.60
7.57
7.34
7.32
7.31
7.27
7.25
7.23
4.24
0.00
Br
O
1.88
1.89
2.07
3.16
2.12
f1 (ppm)

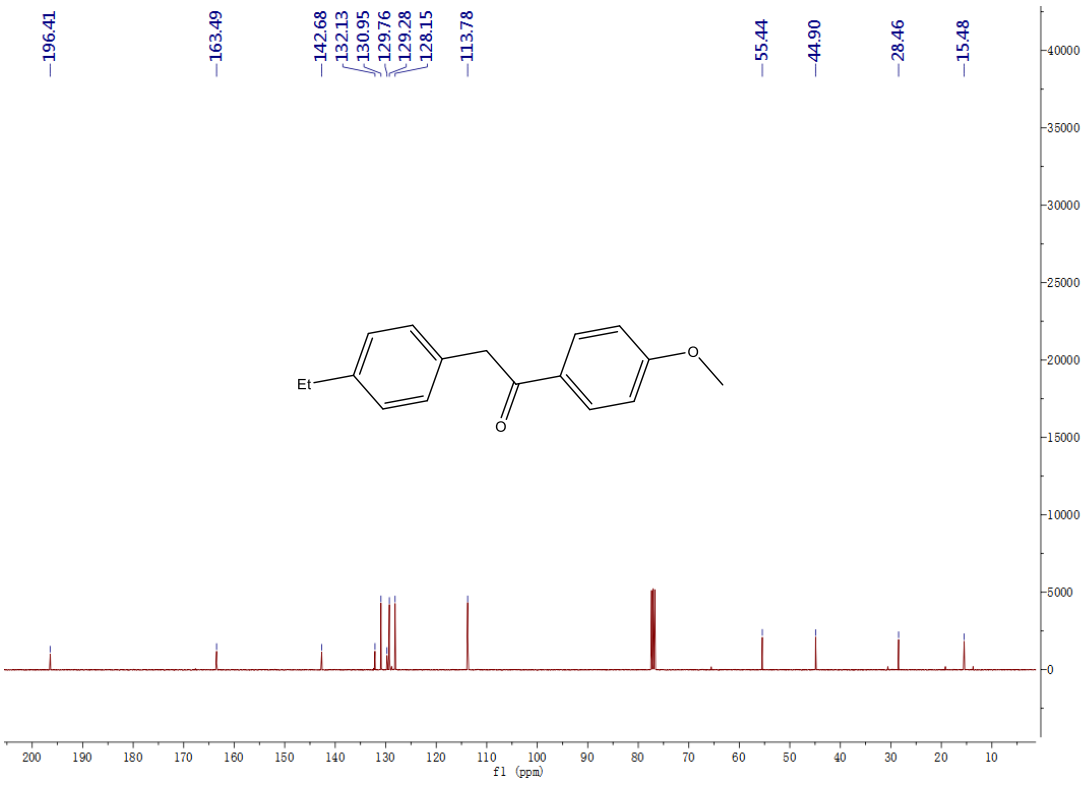
^{13}C NMR ($CDCl_3$)



^{1}H NMR ($CDCl_3$)


8.00
7.98
7.19
7.17
7.15
7.13
6.92
6.90
4.18
3.84
2.64
2.62
2.60
2.58
1.23
1.21
1.19
0.00
Et
O
O
1.98
3.92
2.01
2.00
3.02
2.00
2.99
f1 (ppm)

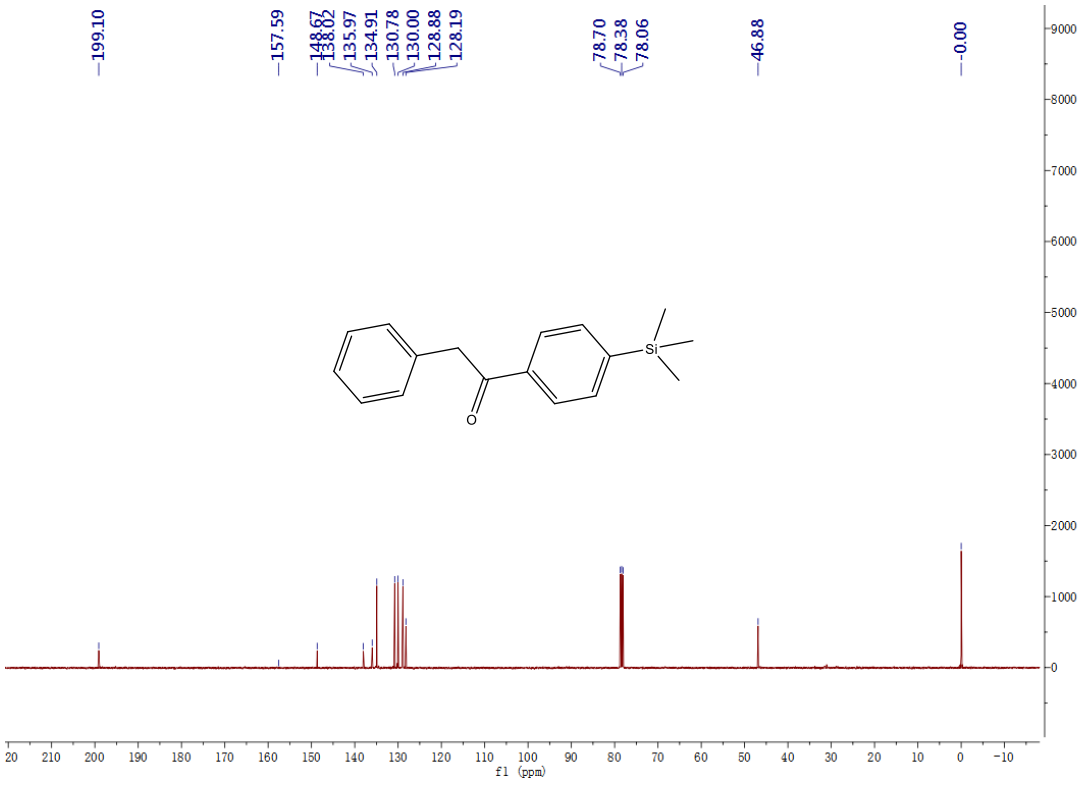
^{13}C NMR ($CDCl_3$)



^{1}H NMR ($CDCl_3$)


7.96
7.94
7.60
7.58
7.32
7.30
7.28
7.26
7.24
7.22
7.20
4.25
0.26
Si
O
2.04
1.99
4.70
2.00
9.01
f1 (ppm)

^{13}C NMR ($CDCl_3$)

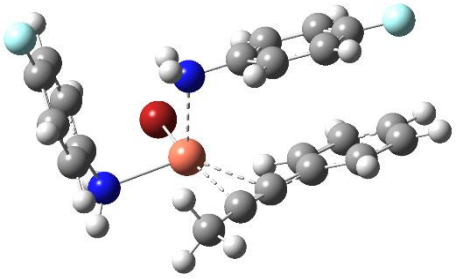


6. Coordinates

6.1 The starting tri- and tetra-coordinated complexes.

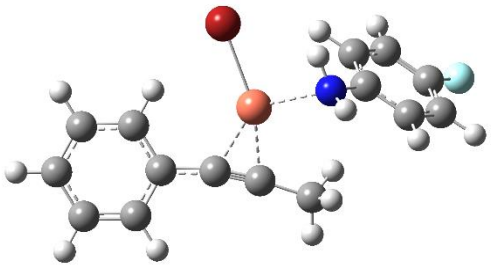
S1

Atom	X	Y	Z	Structure
C	-0.75140200	0.27900800	3.37944800	
C	0.36236800	-0.11574700	2.51715500	
C	1.36202800	-0.38622400	1.88575000	
Cu	-0.47195300	-0.96947400	0.56405200	
Br	-0.45575900	-2.50083400	-1.39077900	
C	0.95546400	2.61934300	-0.08305400	
C	2.24978700	3.11714100	-0.15610500	
C	3.16372400	2.47589700	-0.96736000	
C	2.82648000	1.36115000	-1.70950600	
C	1.53321800	0.86933100	-1.63164600	
C	0.58743200	1.50297800	-0.82659100	
H	0.22725800	3.10449400	0.55682500	
H	2.55399500	3.98575700	0.41247600	
H	3.57650400	0.87465300	-2.31833700	
H	1.25504800	-0.02774400	-2.17428100	
N	-0.71051800	0.94319800	-0.69369300	
H	-1.42308600	1.62541400	-0.46118700	
H	-0.99696900	0.42756900	-1.52087900	
F	4.42680800	2.94265700	-1.02194600	
C	-3.60842100	-0.37421900	-0.82661900	
C	-4.34155700	0.68050900	-1.34927200	
C	-4.90916600	1.59921100	-0.48517600	
C	-4.77607000	1.48697500	0.88434200	
C	-4.04094900	0.42810400	1.40192300	
C	-3.45448200	-0.50746100	0.55384800	
H	-3.14066000	-1.09965500	-1.48414500	
H	-4.47705900	0.79529000	-2.41657300	
H	-5.24536900	2.21745500	1.52952300	
H	-3.93385800	0.32441200	2.47570200	
N	-2.62621500	-1.53303600	1.07498400	
H	-2.90356600	-1.83095300	2.00183200	
H	-2.56028400	-2.33770300	0.45543000	
F	-5.61819300	2.62338800	-0.99093100	
C	2.63509200	-0.57870000	1.24383200	
C	3.66197300	0.33150100	1.50866700	
C	2.85328300	-1.63396900	0.35412700	
C	4.89284100	0.18827000	0.88757800	
H	3.48050700	1.15343700	2.18908300	
C	4.08780800	-1.76861400	-0.26063800	
H	2.04903200	-2.32266800	0.12500300	
C	5.10722100	-0.86028400	0.00181900	
H	5.67975800	0.90488800	1.08396900	
H	4.24866400	-2.58377600	-0.95433600	
H	6.06743000	-0.96670400	-0.48695400	
H	-1.47781400	0.87347000	2.82177600	
H	-1.25977300	-0.59838700	3.78106200	
H	-0.38198400	0.87395800	4.21547600	



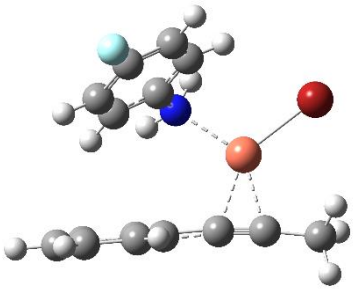
S2

Atom	X	Y	Z	Structure
C	5.18043800	-2.10470700	0.26149	
C	3.84689500	-2.26207000	-0.07663	
C	2.95247500	-1.19922000	0.090744	
C	3.40800200	0.01912100	0.597321	
C	4.74619300	0.16499500	0.931448	
C	5.63263100	-0.89059500	0.765933	
H	5.86886200	-2.92957400	0.130224	
H	3.48650400	-3.20377500	-0.47048	
H	2.71930000	0.84687300	0.718741	
H	5.09467400	1.11317800	1.320011	
H	6.67598600	-0.76845900	1.027663	
C	1.57023400	-1.41647500	-0.25869	
C	0.46644800	-1.83163700	-0.56307	
Cu	0.27609200	0.36530000	-0.59453	
Br	0.62564600	2.63717700	0.108501	
C	-3.69942700	-0.60666400	-1.19643	
C	-4.63616000	-1.19556300	-0.35669	
C	-4.60276200	-0.89455000	0.989984	
C	-3.67179400	-0.01976900	1.520299	
C	-2.73596800	0.55948200	0.67786	
C	-2.74914900	0.27065900	-0.68658	
H	-3.71723000	-0.82889300	-2.25753	
H	-5.38503900	-1.87802200	-0.73556	
H	-3.68257500	0.19547500	2.580376	
H	-1.98988200	1.24401500	1.06889	
N	-1.72406600	0.81010400	-1.51679	
H	-1.91179100	0.66696300	-2.5017	
H	-1.57147300	1.80376200	-1.3475	
C	-0.79331700	-2.51984200	-0.85516	
H	-1.54649300	-2.28773800	-0.10037	
H	-1.18760000	-2.22087400	-1.82676	
H	-0.62490600	-3.59734300	-0.86275	
F	-5.50584200	-1.46224300	1.807447	



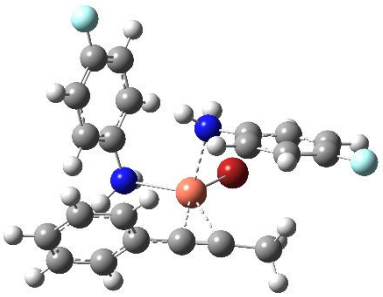
S1a

Atom	X	Y	Z	Structure
C	3.57135500	1.81213500	0.67671000	
C	2.27850700	1.71567400	1.17009900	
C	1.19734600	2.11799200	0.38269600	
C	1.42971600	2.60760400	-0.90680700	
C	2.72438600	2.69744200	-1.39431700	
C	3.79838200	2.30003800	-0.60373100	
H	4.40410000	1.50171700	1.29492000	
H	2.09507400	1.32382800	2.16193700	
H	0.58827200	2.92415400	-1.51156400	
H	2.89739100	3.08718100	-2.38954900	
H	4.80844900	2.37541500	-0.98557300	
C	-0.14410300	2.01218700	0.89391200	
C	-1.23815200	1.99310700	1.42536000	
Cu	-1.35203900	0.49666900	-0.21276500	
Br	-3.43501200	-0.66258200	-0.29921700	
C	2.09245900	-1.05670500	-0.77161900	
C	2.86227600	-1.90925700	0.00787600	
C	2.25992100	-3.00983000	0.58330200	
C	0.91602600	-3.28415700	0.40924500	
C	0.14951300	-2.42532500	-0.36302600	
C	0.74228800	-1.31831500	-0.96681500	
H	2.54786100	-0.18284500	-1.22546700	
H	3.91552200	-1.72486800	0.17240200	
H	0.47945200	-4.15205500	0.88460400	
H	-0.91454400	-2.59824900	-0.48649100	
N	-0.07047800	-0.40376500	-1.70899800	
H	0.49144100	0.20269900	-2.29571500	
H	-0.75933300	-0.88299900	-2.28170100	
C	-2.50163700	2.08047900	2.15794500	
H	-3.31061100	2.35498400	1.48176000	
H	-2.75396500	1.11061400	2.58657600	
H	-2.41894800	2.82368100	2.95207100	
F	3.00311300	-3.83870500	1.33806000	



S2a

Atom	X	Y	Z	Structure
C	3.53668200	2.94390900	-1.36132100	
C	2.23958600	2.57427600	-1.68309800	
C	1.25277800	2.53423400	-0.69217500	
C	1.58982100	2.87025500	0.62153900	
C	2.88888000	3.24208600	0.93625500	
C	3.86549200	3.27776900	-0.05111000	
H	4.29220700	2.98152000	-2.13603600	
H	1.97215300	2.32569800	-2.70323500	
H	0.82294900	2.84422200	1.38477900	
H	3.13817900	3.50605300	1.95630500	
H	4.87815100	3.56926300	0.19626900	
C	-0.09379600	2.14740500	-1.01378500	
C	-1.25713500	1.90005200	-1.25025700	
Cu	-0.16232800	-0.14442200	-1.17557500	
Br	-1.22638600	-2.12683600	-2.18913200	
C	-1.98793800	0.93943800	2.07586800	
C	-3.22911400	1.49710800	2.35095000	
C	-4.36225800	0.86796000	1.87312000	
C	-4.28999700	-0.29659300	1.13236400	
C	-3.04659800	-0.84647400	0.85836100	
C	-1.88723900	-0.23978900	1.34234100	
H	-1.08891400	1.42033300	2.44282300	
H	-3.32375900	2.40875800	2.92562600	
H	-5.19881400	-0.75744200	0.76878600	
H	-2.96639000	-1.73885100	0.24820900	
N	-0.61827400	-0.76697900	1.00450600	
H	0.09845100	-0.59807900	1.70131400	
H	-0.65122700	-1.75563800	0.77690900	
C	-2.68341700	1.72726400	-1.51864900	
H	-2.86248800	0.79748800	-2.06091700	
H	-3.22633500	1.68351500	-0.57278300	
H	-3.05716900	2.56731100	-2.10560700	
F	-5.56818000	1.40501400	2.13802300	
C	1.94612900	-2.54385900	0.20586300	
C	2.26448400	-2.97779200	1.48534900	
C	2.97687700	-2.13839500	2.32129300	
C	3.38422900	-0.88141600	1.91626500	
C	3.06477800	-0.45288000	0.63560900	
C	2.35211500	-1.28236900	-0.22609000	
H	1.36323500	-3.17338100	-0.45829000	
H	1.96314200	-3.95519100	1.83804300	
H	3.94442700	-0.25378600	2.59671800	
H	3.36472100	0.53529800	0.30393900	
N	1.93906500	-0.79512300	-1.49075100	
H	2.58589600	-0.12023700	-1.88149300	
H	1.73550200	-1.53207500	-2.15945800	
F	3.28544500	-2.55675800	3.56208200	

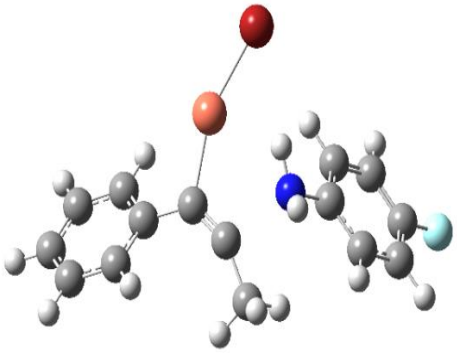


6.2 The transition states

The coordinate of the optimized structure of the transition states are listed in the following tables. The number marked under each of the structure is the imaginary vibrational frequency (cm^{-1})

TS2-1

Atom	X	Y	Z	Structure
C	-4.95654400	2.01461000	-0.29438200	
C	-3.68234000	1.68542700	-0.73174900	
C	-2.83488400	0.91652900	0.07063700	
C	-3.29930900	0.47054600	1.30934000	
C	-4.56719400	0.81852500	1.75096100	
C	-5.40119200	1.58948300	0.95110900	
H	-5.60386600	2.60735600	-0.92868700	
H	-3.33970000	2.01021300	-1.70665300	
H	-2.65506400	-0.14310400	1.92843900	
H	-4.90919800	0.47434600	2.71876100	
H	-6.39474300	1.84982300	1.29221400	
C	-1.47206700	0.58541100	-0.38509400	
C	-0.61133000	1.31050800	-0.94108000	
C	3.13580700	1.70532100	-1.11450500	
C	4.16998000	2.15297300	-0.30494300	
C	4.35547500	1.55299200	0.92510000	
C	3.55256400	0.51669900	1.36395600	
C	2.51977900	0.07528500	0.55294000	
C	2.31041100	0.66788500	-0.69103700	
H	2.98176600	2.15824000	-2.08776000	
H	4.82788300	2.95255100	-0.61708100	
H	3.74160900	0.06310800	2.32754500	
H	1.89703200	-0.75622700	0.86309800	
N	1.20335200	0.25686600	-1.48157400	
H	1.34618700	0.44094300	-2.46967600	
H	1.00876400	-0.73961300	-1.36205100	
C	-0.10734500	2.60772100	-1.38828100	
H	0.79044400	2.90280600	-0.84424600	
H	0.09423100	2.63244900	-2.46022200	
H	-0.89737200	3.33151700	-1.16541600	
F	5.35452900	1.98275600	1.71245900	
Cu	-0.89246300	-1.35196300	-0.06271500	
Br	0.50595300	-3.20685200	-0.14710000	



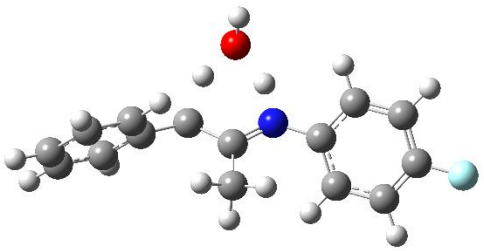
232.55***i***

TS2-2

Atom	X	Y	Z	Structure
C	-4.87292600	-1.09437100	-0.03264100	
C	-3.68657000	-0.70763700	0.57269500	
C	-2.45171300	-1.05831900	0.01844800	
C	-2.44442400	-1.77285500	-1.18488300	
C	-3.63242300	-2.14365400	-1.79926700	
C	-4.85158700	-1.81266500	-1.22229300	
H	-5.81874300	-0.82435100	0.42037200	
H	-3.70658400	-0.12966300	1.48955900	
H	-1.49357500	-2.02603500	-1.64136100	
H	-3.60519800	-2.69280500	-2.73228600	
H	-5.77796800	-2.10249400	-1.70114200	
C	-1.19354700	-0.61366100	0.66443500	
C	-0.27481500	-1.51180600	1.03937600	
C	3.00845400	-2.14915300	0.82265600	
C	4.11327000	-2.18297400	-0.01654800	
C	4.31526800	-1.12603500	-0.88262000	
C	3.46349700	-0.03822800	-0.92809600	
C	2.36935000	-0.00907200	-0.07698900	
C	2.13590100	-1.06806100	0.79182700	676.14***i***
H	2.82681000	-2.97163200	1.50545800	
H	4.80825500	-3.01147800	-0.00865400	
H	3.66602100	0.77859300	-1.60767600	
H	1.71773300	0.85755000	-0.08172600	
N	0.98321300	-1.03423900	1.66921700	
H	1.18039000	-1.64521100	2.45983800	
H	0.58747200	0.29583400	2.22458700	
C	-0.35132700	-3.00915000	0.97220500	
H	-1.33134600	-3.33967900	0.63701300	
H	0.40231900	-3.40155300	0.28320600	
H	-0.15396900	-3.44779100	1.95583100	
O	-0.13926900	1.06555200	2.44726000	
H	-0.84209000	0.58834800	1.71512000	
H	0.12361300	1.92194900	2.05120500	
F	5.37830900	-1.15348300	-1.69929800	
Cu	-0.88743400	1.22514900	-0.27976600	
Br	0.14574000	3.32867300	-0.20728300	

TS2-3

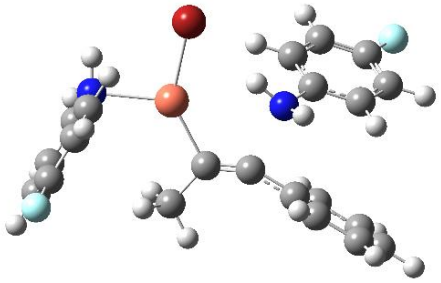
Atom	X	Y	Z
O	0.36664400	2.90125200	0.31269300
C	1.59191400	0.68146200	0.65011300
C	0.36992700	-0.00777300	0.27989000
C	-2.53363400	-0.92470700	0.76720200
C	-3.85329100	-1.30740600	0.57725600
C	-4.68334800	-0.48947800	-0.16444300
C	-4.24153300	0.69850900	-0.71640100
C	-2.92086900	1.06910600	-0.52581300
C	-2.05375000	0.25331800	0.19988000
H	-1.87827000	-1.53503400	1.37445600
H	-4.24649800	-2.21822300	1.00830000
H	-4.92804000	1.31524900	-1.28045500
H	-2.54883200	1.99841800	-0.93882300
N	-0.73055900	0.69897700	0.39168600
H	-0.46479800	1.83761800	0.40417900
C	0.35985300	-1.41202800	-0.24464700
H	-0.52306600	-1.62799600	-0.84320400
H	1.26177400	-1.59359500	-0.82383700
H	0.38843700	-2.10552300	0.60026100
F	-5.96242200	-0.85451600	-0.34572700
H	1.23139500	1.94116000	0.29500100
H	0.33452000	3.41843600	-0.49743600
H	1.55567200	0.95668100	1.70672100
C	2.90852700	0.14547400	0.22947000
C	3.88687000	-0.19467200	1.16556800
C	3.23014100	0.01628200	-1.12581000
C	5.13284600	-0.65967100	0.76625900
H	3.66472100	-0.09085900	2.22165500
C	4.46783500	-0.46277300	-1.52884300
H	2.49903700	0.31355100	-1.87099600
C	5.42732600	-0.80338000	-0.58295600
H	5.87535400	-0.91358900	1.51292400
H	4.69086400	-0.55461000	-2.58482400
H	6.39739900	-1.16747800	-0.89607800



1700.59***i***

TS1-1

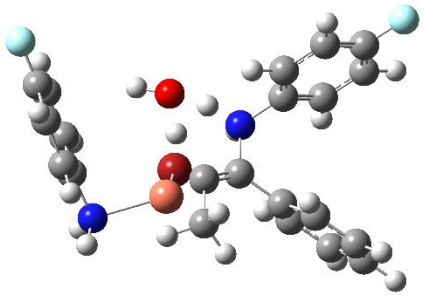
Atom	X	Y	Z	Structure
C	-0.98337600	-1.87261800	-1.85568700	
C	-0.20942500	-1.05216300	-0.85167700	
C	0.83658000	-1.37253700	-0.23200500	
C	3.94827900	0.13559200	0.91960200	
C	5.10907500	0.65532800	0.36565200	
C	5.00921700	1.73042600	-0.49509300	
C	3.79381300	2.30956200	-0.80977200	
C	2.63675700	1.78886400	-0.25241400	
C	2.71218800	0.70267300	0.61891100	
H	4.00262400	-0.71793300	1.58671100	
H	6.08000400	0.23460600	0.58933700	
H	3.76366100	3.16029300	-1.47699100	
H	1.67285300	2.23872300	-0.46014900	
N	1.52157200	0.12070300	1.10999200	
H	1.65405600	-0.35635100	1.99536700	
H	0.75498800	0.79484100	1.18823600	
F	6.13196200	2.23605400	-1.03677000	
C	-4.19479500	0.50086100	0.58132800	
C	-5.02311000	-0.41669700	1.20869000	
C	-5.63437500	-1.39777600	0.45115400	
C	-5.44920200	-1.48595400	-0.91379600	
C	-4.62334000	-0.56071700	-1.53798000	
C	-3.99997200	0.43881000	-0.79821900	
H	-3.68599900	1.26633000	1.15733600	
H	-5.19117500	-0.38239000	2.27664500	
H	-5.94663300	-2.26684200	-1.47298200	
H	-4.46721300	-0.61755300	-2.60915700	
N	-3.08950400	1.34025400	-1.41652700	
H	-3.22425100	1.40703000	-2.41729700	
H	-3.11563400	2.26881800	-1.00431600	
F	-6.43474700	-2.29122200	1.06015700	
C	1.94956600	-2.25591200	0.02296600	
C	1.98241900	-3.06490500	1.16424800	
C	3.00985600	-2.30388700	-0.88403200	
C	3.05817700	-3.90736700	1.38937200	
H	1.15413300	-3.02895700	1.86198700	
C	4.08232100	-3.15715500	-0.65825700	
H	2.98706300	-1.65983000	-1.75394900	
C	4.11029000	-3.95339000	0.47786100	
H	3.07678900	-4.53527500	2.27092900	
H	4.90172700	-3.18829000	-1.36475100	
H	4.94984100	-4.61319100	0.65618800	
H	-1.05665500	-1.32977300	-2.79901800	
H	-0.52735200	-2.84645900	-2.04604600	
H	-2.00303400	-2.02322800	-1.49754500	
Cu	-1.11318800	0.78808600	-0.50411400	
Br	-0.92921200	2.70984300	0.98311200	



270.20***i***

TS1-2

Atom	X	Y	Z	Structure
C	-0.13017100	-0.73739700	2.99339800	
C	-0.11769300	-0.04666000	1.65509400	
C	0.86399500	-0.31004900	0.76928000	
C	2.06935100	2.58612600	0.17509000	
C	3.19245400	3.39869400	0.15442000	
C	4.28821200	2.99865200	-0.58880500	
C	4.30534600	1.82313500	-1.31457100	
C	3.18040600	1.01099400	-1.28704000	
C	2.07558500	1.40269500	-0.54874300	
H	1.18059900	2.86626100	0.72886600	
H	3.22653800	4.33324200	0.69744300	
H	5.18631500	1.55385200	-1.88077500	
H	3.16558100	0.07557600	-1.83329300	
N	0.89762200	0.55326300	-0.47965400	
H	-0.00970300	1.19171400	-0.40035600	
H	0.80114300	-0.03787400	-1.31677800	
F	5.37527300	3.78466700	-0.60955100	
C	-3.95477300	0.03666500	-0.73809200	
C	-4.45269100	1.31719900	-0.93126000	
C	-4.71946200	2.10667800	0.17259900	
C	-4.50081000	1.65875100	1.46089100	
C	-4.00653900	0.37571000	1.64733200	
C	-3.75048800	-0.44187500	0.55325900	
H	-3.69517800	-0.58157500	-1.59022600	
H	-4.62151800	1.70984200	-1.92493800	
H	-4.70701900	2.31226000	2.29738900	
H	-3.81550500	0.01425800	2.65093700	
N	-3.16140100	-1.73411800	0.73836400	
H	-3.32902400	-2.09651700	1.66954400	
H	-3.50472300	-2.40603800	0.05938700	
F	-5.20442000	3.34446600	-0.01296500	
O	-1.07542900	1.92041200	0.31328800	
H	-1.98900600	1.95004800	0.00865200	
H	-0.89374800	1.08569000	1.10629200	
C	2.06018000	-1.19000400	0.87909400	
C	2.95915100	-1.02148100	1.93094700	
C	2.30832200	-2.17592200	-0.07780700	
C	4.08675100	-1.82628400	2.02721100	
H	2.77552700	-0.24535000	2.66468600	
C	3.43572600	-2.97875700	0.02070100	
H	1.60775600	-2.32210200	-0.89453600	
C	4.32751300	-2.80548600	1.07200900	
H	4.78213300	-1.68271100	2.84456800	
H	3.61351000	-3.74486600	-0.72357300	
H	5.20830300	-3.43085900	1.14570400	
H	-1.15153100	-0.97393200	3.30011600	
H	0.47148300	-1.65080500	3.04153000	
H	0.25560100	-0.04664800	3.74952600	
Cu	-1.12681900	-1.35528800	0.14897400	
Br	-0.85970800	-1.74051200	-2.24528800	

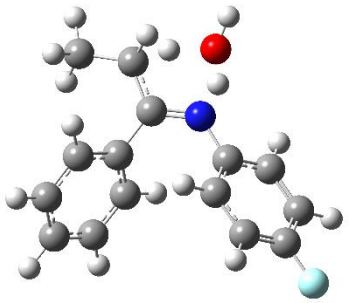


986.50***i***

TS1-3

Atom	X	Y	Z
C	-1.08182700	-2.43086700	-1.42539700
C	-0.89501800	-1.08963600	-1.12795800
C	-1.48484100	-0.53875000	0.00817300
C	-2.26316600	-1.33907900	0.84051200
C	-2.42684800	-2.68709700	0.55527800
C	-1.83969400	-3.23237700	-0.57964300
H	-0.63080800	-2.85320800	-2.31404800
H	-0.29209300	-0.46227300	-1.77377300
H	-2.72620600	-0.90245600	1.71728000
H	-3.01999600	-3.30993700	1.21264900
H	-1.97687600	-4.28177600	-0.80784500
C	-1.31038800	0.90306000	0.32232600
C	-2.42744400	1.79935800	0.43977600
C	2.12570900	1.38278600	-0.50721100
C	3.38374400	0.80692400	-0.58889100
C	3.63700200	-0.33950000	0.13982000
C	2.68107900	-0.91985800	0.95179700
C	1.42589700	-0.33694500	1.03142200
C	1.13638900	0.80523700	0.28727700
H	1.89062100	2.28034500	-1.06690200
H	4.16349600	1.23377900	-1.20508200
H	2.92837600	-1.80772900	1.51794800
H	0.66828600	-0.76989800	1.67137000
N	-0.11239300	1.45369700	0.34567100
H	-0.21658000	2.55976100	0.01717400
C	-3.82537300	1.32803100	0.09658200
H	-4.30612500	0.75553100	0.89411200
H	-4.46207000	2.18902800	-0.11116000
H	-3.82307600	0.70539500	-0.79919000
F	4.85506800	-0.90349500	0.06490800
H	-2.36806600	2.39793800	1.35040800
O	-0.86139400	3.54816700	-0.67862900
H	-1.87314400	2.77434100	-0.30195000
H	-0.98477500	4.39368900	-0.23901000

Structure



1759.72***i***