Electronic Supplementary Material (ESI) for ChemComm.

Photoredox-Promoted Alkyl Radical Addition/Semipinacol Rearrangement Sequence of Alkenylcyclobutanols: Rapid Access to Cyclic Ketones

Sheng Yao,[a] Kai Zhang,[a] Quan-Quan Zhou,[a] Yu Zhao,[a] De-Qing Shi,*[a] and Wen-Jing Xiao[ab]

[a] CCNU-uOttawa Joint Research Centre on Synthesis and Catalysis, Key Laboratory of Pesticides & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei 430079, China

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, China

*Email : chshidq@mail.ccnu.edu.cn

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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.[1] Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). HRMS was recorded on Agilent technologies 6224 TOF LC/MS instrument or Bruker ultrafleXtreme MALDI-TOF/TOF mass spectrometer. All 1-(1-Arylvinyl)cyclobutanol derivatives **1** were prepared in accordance with the reported method.[2] Substrates **2** and **4** were synthesized according to the known literatures,[3,4] respectively.

References

[1] Perrin, D. D.; Armarego, W. L. F. W. L. F. *Purification of Laboratory Chemicals, 4th ed.*; Pergamon Press: Oxford,1997.

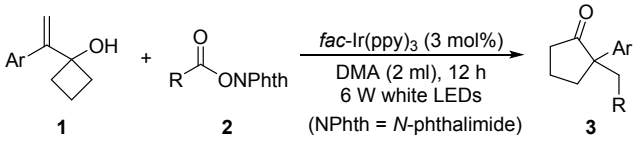
[2] Sahoo, B.; Li, J.-L.; Glorius, F.; *Angew. Chem. Int. Ed.* **2015**, *54*, 11577-11580.

[3] Zhao, Y.; Chen, J.-R.; Xiao, W.-J.; *Org. Lett.* **2018**, *20*, 224-227.

[4] Yu, X.-Y.; Chen, J.-R.; Wang, P.-Z.; Yang, M.-N.; Liang, D.; Xiao, W.-J.; *Angew. Chem. Int. Ed.* **2018**, *57*, 738-743.

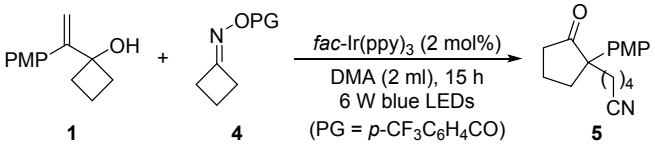
2. General Procedure

2.1 General procedure for the synthesis of 3a-s



Procedure: To a dried Schlenk tube was treated with **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), and *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%). Subsequently, DMA (2 ml) was added. This mixture solution was degassed for 3 times via 'freeze-pump-thaw' procedure. After that, this resulting solution was stirred at a distance of ~2 cm under irradiation by 6 W white LEDs at room temperature for 12 h. The mixture was extracted with ethyl acetate for three times. The organic layer was dried over anhydrous Na_2SO_4, concentrated in vacuum and purified by chromatography on silica gel using petroleum ether/diethyl ether (80:1 to 60:1) as the eluent, furnishing the desired product **3a**.

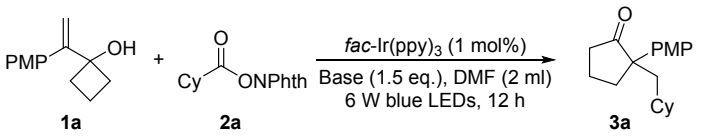
2.2 General procedure for the synthesis of 5a-k



Procedure: To a dried Schlenk tube was treated with **1** (0.2 mmol, 1.0 equiv), **4** (0.3 mmol, 1.5 equiv), and *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol%). Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via 'freeze-pump-thaw' procedure. After that, this resulting solution was stirred at a distance of ~2 cm under irradiation by 6 W blue LEDs at room temperature for 15 h. The mixture was extracted with ethyl acetate for three times. The organic layer was dried over anhydrous Na_2SO_4, concentrated in vacuum and purified by chromatography on silica gel using petroleum ether/diethyl ether (5:1 to 4:1) as the eluent, affording the desired product **5a.**

3. Optimization of the Reaction Conditions

3.1 The effect of bases on the reaction[a]



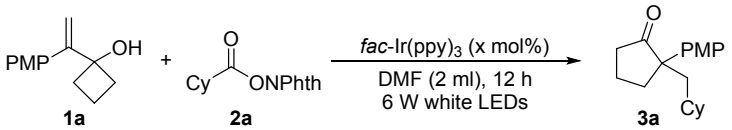
1a **2a** **3a**

PMP = 4-MeO-C_6H_4; NPhth = *N*-phthalimide

Entry	Base	Yield/%[b]
1	no	40
2	Na_2CO_3	36
3	Na_2HPO_4	33
4	NaOAc	14
5	Et_3N	trace
6	pyridine	34
7	$^{i}Pr_2NEt$	complex

[a] **1a** (0.2 mmol), **2a** (0.22 mmol), and *fac*-Ir(ppy)$_3$ (1 mol%) in 2 ml of DMF at rt under the irradiation of 6 W blue LEDs for 12 h. [b] Isolated yields. DMF: *N,N*-dimethylformamide; Et_3N: triethylamine; $^{i}Pr_2NEt$: *N,N*-Diisopropylethylamine.

3.2 The effect of the loading of photocatalyst[a]



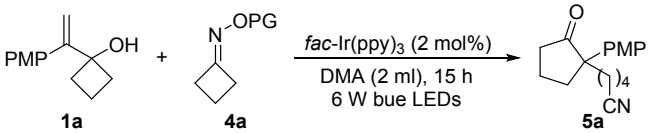
1a **2a** **3a**

PMP = 4-MeO-C_6H_4; NPhth = *N*-phthalimide

Entry	PC (x mol%)	Yield/%[b]
1	1	40
2	2	42
3	3	48
4	4	33
5	5	22

[a] **1a** (0.2 mmol), **2a** (0.22 mmol), and *fac*-Ir(ppy)$_3$ (x mol%) in 2 ml of DMF at rt under the irradiation of 6 W blue LEDs for 12 h. [b] Isolated yields. DMF: *N,N*-dimethylformamide.

3.3 Screen other parameters for the reaction[a]



1a **4a** **5a**

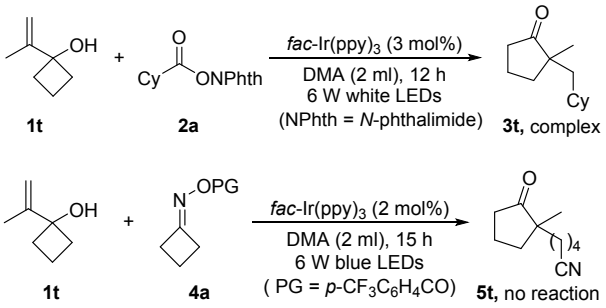
PMP = 4-MeO-C_6H_4; PG = *p*-$CF_3C_6H_4CO$

Entry	PC	Solvent	Yield/%[b]
1	*fac*-Ir(ppy)$_3$	CH_3CN	no

2	*fac*-Ir(ppy)$_3$	DMF	62
3	*fac*-Ir(ppy)$_3$	DMSO	85
4	***fac*-Ir(ppy)$_3$**	**DMA**	**92**
5[c]	Eosin Y	DMA	72
6[c]	Rose Bengal	DMA	76
7	Ru(bpy)$_3$Cl$_2$·H$_2$O	DMA	no
8	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	DMA	45

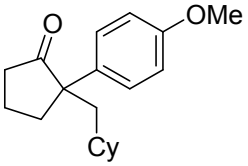
[a] **1a** (0.2 mmol), **4a** (0.3 mmol), and *fac*-Ir(ppy)$_3$ (2 mol%), in 2 ml of solvent at rt under the irradiation of 6 W blue LEDs for 15 h. [b] Isolated yields. [c] Reaction time is 24 h. DMF: *N,N*-dimethylformamide; DMSO: Dimethyl sulfoxide; DMA: *N,*N-Dimethylacetamide.

3.4 Unsuccessful substrate



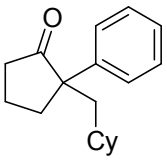
4. Spectral data of the products

2-(Cyclohexylmethyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3a)



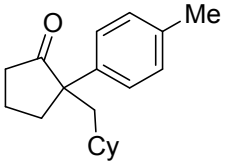
Yield of **3a** : 70% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 6.90 – 6.81 (m, 2H), 3.79 (s, 3H), 2.87 – 2.58 (m, 1H), 2.38 – 2.12 (m, 2H), 2.07 – 1.72 (m, 4H), 1.69 – 1.56 (m, 2H), 1.54 – 1.40 (m, 3H), 1.27 (d, *J* = 12.9 Hz, 1H), 1.17 – 0.96 (m, 4H), 0.96 – 0.67 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.9, 158.2, 131.1, 128.1, 113.8, 56.0, 55.1, 46.3, 36.7, 34.7, 34.4, 33.9, 26.3, 26.2, 18.6. **IR** (in KBr): 2923, 1734, 1510, 1251 cm^{-1}. **HRMS (ESI)** for $C_{19}H_{26}O_2$ $[M+K]^+$: calcd 325.1564, found: 325.1560.

2-(cyclohexylmethyl)-2-phenylcyclopentan-1-one (3b)



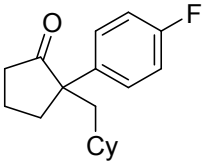
Yield of **3b** : 69% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 2.84 – 2.65 (m, 1H), 2.32 – 2.15 (m, 2H), 2.08 – 1.86 (m, 3H), 1.86 – 1.73 (m, 1H), 1.64-1.56 (m, 5H), 1.31 – 1.20 (m, 1H), 1.17 – 0.96 (m, 4H), 0.97 – 0.66 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.2, 139.5, 128.4, 126.9, 126.6, 56.6, 46.3, 36.9, 36.8, 34.7, 34.4, 33.8, 26.2, 18.6. **IR** (in KBr): 2923, 1736, 1402 cm^{-1}. **HRMS (ESI)** for $C_{18}H_{24}O$ $[M+K]^+$: calcd 295.1459, found: 295.1480.

2-(cyclohexylmethyl)-2-(p-tolyl)cyclopentan-1-one (3c)



Yield of **3c** : 70% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.72 – 2.69 (m, 1H), 2.31 (s, 3H), 2.28 – 2.14 (m, 2H), 2.07 – 1.73 (m, 4H), 1.69 – 1.43 (m, 5H), 1.28 (d, *J* = 13.9 Hz, 1H), 1.19 – 0.98 (m, 4H), 0.96 – 0.69 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.8, 136.3, 136.2, 129.1, 126.8, 56.4, 46.3, 36.8, 34.7, 34.4, 34.3, 33.9, 26.3, 26.2, 26.1, 20.9, 18.6. **IR** (in KBr): 2923, 1736, 1402 cm^{-1}. **HRMS (ESI)** for $C_{19}H_{26}O$ $[M+K]^+$: calcd 309.1615, found: 309.1603.

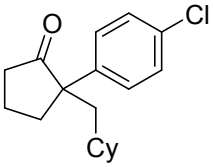
2-(cyclohexylmethyl)-2-(4-fluorophenyl)cyclopentan-1-one (3d)



Yield of **3d** : 68% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.30 (m, 2H), 7.09 – 6.91 (m, 2H), 2.70 – 2.65 (m, 1H), 2.31 – 2.19 (m, 2H), 2.11 – 1.71 (m, 4H), 1.68 – 1.41 (m, 5H), 1.24 (d, *J* = 13.3 Hz, 1H), 1.14 – 1.01 (m, 4H), 0.95 – 0.65 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.5, 161.6 (d, *J* =

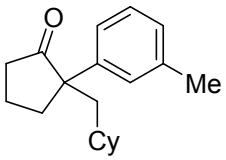
254.1 Hz), 135.1 (d, *J* = 2.1 Hz), 128.6 (d, *J* = 7.8 Hz), 115.2 (d, *J* = 20.0 Hz), 56.0, 46.3, 36.8, 34.7, 34.4, 34.0, 26.2 (d, *J* = 4.6 Hz), 26.1, 18.6. **IR** (in KBr): 2923, 1736, 1508 , 1232 cm^{-1}. **HRMS (ESI)** for $C_{18}H_{23}FO$ $[M+Na]^+$: calcd 297.1625, found: 297.1621.

2-(4-chlorophenyl)-2-(cyclohexylmethyl)cyclopentan-1-one (3e)



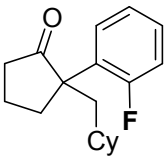
Yield of **3e** : 75% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 2H), 2.69 – 2.63 (m, 1H), 2.30 – 2.22 (m, 2H), 2.13 – 1.72 (m, 4H), 1.69 – 1.39 (m, 5H), 1.34 – 1.21 (m, 1H), 1.18 – 0.97 (m, 4H), 0.95 – 0.68 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.3, 138.0, 132.5, 128.5, 128.4, 56.2, 46.2, 36.8, 34.7, 34.4, 33.8, 26.2, 26.1, 18.6. **IR** (in KBr): 2943, 1736, 1400 cm^{-1}. **HRMS (ESI)** for $C_{18}H_{23}ClO$ $[M+Na]^+$: calcd 313.1330, found: 313.1323.

2-(cyclohexylmethyl)-2-(m-tolyl)cyclopentan-1-one (3f)



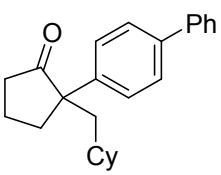
Yield of **3f** : 80% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 3.4 Hz, 3H), 7.03 (t, *J* = 4.5 Hz, 1H), 2.71 (dd, *J* = 12.2, 6.1 Hz, 1H), 2.33 (s, 3H), 2.29 – 2.15 (m, 2H), 2.03 – 1.75 (m, 4H), 1.60 (d, *J* = 11.6 Hz, 2H), 1.57 – 1.47 (m, 3H), 1.29 (d, *J* = 13.3 Hz, 1H), 1.19 – 0.99 (m, 4H), 0.96 – 0.69 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.9, 139.4, 137.9, 128.2, 127.6, 127.4, 123.8, 56.7, 46.3, 36.9, 34.7, 34.5, 34.4, 33.8, 26.3, 26.2, 26.1, 21.6, 18.6. **IR** (in KBr): 2923, 1735, 1401 cm^{-1}. **HRMS (ESI)** for $C_{19}H_{26}O$ $[M+Na]^+$: calcd 293.1876, found: 293.1874.

2-(cyclohexylmethyl)-2-(2-fluorophenyl)cyclopentan-1-one (3g)



Yield of **3g** : 55% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 –7.19 (m, 2H), 7.12 – 6.92 (m, 2H), 2.54 – 2.33 (m, 1H), 2.42 – 2.33 (m, 2H), 2.16 – 2.06 (m, 1H), 2.01 – 1.92 (m, 1H), 1.99 – 1.77 (m, 3H), 1.58 (t, *J* = 12.3 Hz, 6H), 1.19 – 1.06 (m, 3H), 0.90 (d, *J* = 12.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.6, 161.2 (d, *J* = 246.0 Hz), 129.6 (d, *J* = 12.3 Hz), 128.7 (d, *J* = 3.7 Hz), 128.5 (d, *J* = 8.8 Hz), 123.8 (d, *J* = 3.3 Hz), 116.5 (d, *J* = 23.5 Hz), 55.1 (d, *J* = 2.7 Hz), 42.3, 37.4, 36.2, 36.1, 35.1, 34.7, 34.3, 26.3 (d, *J* = 4.1 Hz), 26.2, 18.9. **IR** (in KBr): 2924, 1739, 1401, 1218 cm^{-1}. **HRMS (ESI)** for $C_{18}H_{23}FO$ $[M+Na]^+$: calcd 297.1625, found: 297.1622.

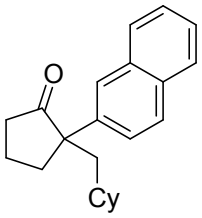
2-([1,1'-biphenyl]-4-yl)-2-(cyclohexylmethyl)cyclopentan-1-one (3h)



Yield of **3h** : 58% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 16.3, 8.2 Hz, 4H), 7.44 (dd, *J* = 25.6, 7.8 Hz, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 2.82 – 2.69 (m, 1H), 2.36 – 2.16 (m, 2H), 1.19 –1.06 (m, 3H), 1.88 –

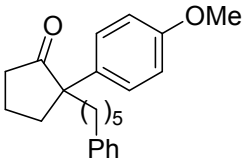
1.80 (m, 1H), 1.69 – 1.46 (m, 5H), 1.30 (t, *J* = 15.1 Hz, 1H), 1.21 – 1.00 (m, 4H), 0.97 – 0.71 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.7, 140.5, 139.3, 138.5, 128.7, 127.3, 127.2, 127.0, 126.9, 56.5, 46.3, 36.9, 34.7, 34.4, 34.3, 33.7, 26.3, 26.2, 26.1, 18.7. **IR** (in KBr): 2923, 1734, 1402 cm^{-1}. **HRMS (ESI)** for $C_{24}H_{28}O$ $[M+K]^+$: calcd 371.1772, found: 371.1748.

2-(cyclohexylmethyl)-2-(naphthalen-2-yl)cyclopentan-1-one (3i)



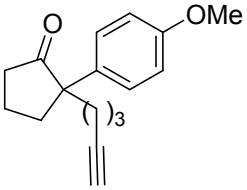
Yield of **3i** : 53% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 4H), 7.59 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.51 – 7.38 (m, 2H), 2.90 – 2.85 (m, 1H), 2.43 – 2.18 (m, 2H), 2.18 – 1.94 (m, 3H), 1.88 (dd, *J* = 11.5, 7.0 Hz, 1H), 1.60 (d, *J* = 8.8 Hz, 4H), 1.48 (s, 1H), 1.29 (d, *J* = 13.8 Hz, 1H), 1.21 – 0.97 (m, 4H), 0.92 (d, *J* = 2.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.7, 136.8, 133.2, 132.1, 128.1, 128.0, 127.4, 126.0, 125.8, 125.6, 125.2, 56.9, 46.2, 36.9, 34.7, 34.4, 34.3, 34.0, 26.3, 26.2, 26.1, 18.7. **IR** (in KBr): 2923, 1736 cm^{-1}. **HRMS (ESI)** for $C_{22}H_{26}O$ $[M+Na]^+$: calcd 329.1876, found: 329.1857.

2-(4-methoxyphenyl)-2-(5-phenylpentyl)cyclopentan-1-one (3j)



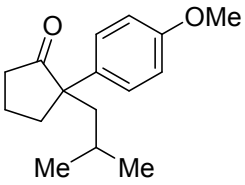
Yield of **3j** : 50% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.06 (m, 3H), 6.90 – 6.81 (m, 2H), 3.76 (s, 3H), 2.58 – 2.48 (m, 3H), 2.36 – 2.09 (m, 2H), 2.02 – 1.66 (m, 4H), 1.66 – 1.39 (m, 3H), 1.34 – 0.88 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.9, 158.2, 142.6, 131.2, 128.3, 128.1, 127.8, 125.5, 113.7, 56.0, 55.1, 38.7, 37.3, 35.7, 33.7, 31.1, 29.5, 24.3, 18.6. **IR** (in KBr): 2933, 1733, 1511, 1251 cm^{-1}. **HRMS (ESI)** for $C_{23}H_{28}O_2$ $[M+Na]^+$: calcd 359.1982, found: 359.1965.

2-(4-methoxyphenyl)-2-(pent-4-yn-1-yl)cyclopentan-1-one (3k)



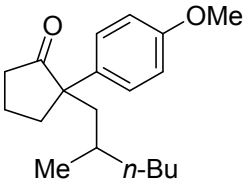
Yield of **3k** : 40% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.03 – 6.73 (m, 2H), 3.78 (s, 3H), 2.67 – 2.54 (m, 1H), 2.37 – 2.15 (m, 2H), 2.09 – 2.05 (m, 2H), 2.01 – 1.87 (m, 4H), 1.88 – 1.75 (m, 1H), 1.72 – 1.64 (m, 1H), 1.30 (dd, *J* = 12.0, 6.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.5, 158.3, 130.6, 127.9, 113.8, 84.0, 68.4, 55.7, 55.1, 38.0, 37.2, 33.8, 23.8, 18.7, 18.5. **IR** (in KBr): 2953, 1732, 1511, 1252 cm^{-1}. **HRMS (ESI)** for $C_{17}H_{20}O_2$ $[M+Na]^+$: calcd 279.1356, found: 279.1367.

2-isobutyl-2-(4-methoxyphenyl)cyclopentan-1-one (3l)



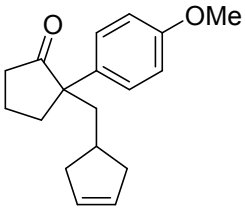
Yield of 3**l** : 70% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 6.83 – 6.73 (m, 2H), 3.71 (d, *J* = 1.6 Hz, 3H), 2.82 – 2.51 (m, 1H), 2.33 – 1.99 (m, 2H), 1.97 – 1.80 (m, 3H), 1.80 – 1.66 (m, 1H), 1.39 – 1.26 (m, 2H), 0.82 – 0.63 (m, 3H), 0.68 – 0.49 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.7, 158.2, 130.6, 128.1, 113.7, 56.0, 55.1, 47.5, 36.6, 33.9, 24.9, 24.4, 23.7, 18.6. **IR** (in KBr): 2956, 1734, 1511, 1252 cm^{-1}. **HRMS (ESI)** for $C_{16}H_{22}O_2$ $[M+Na]^+$: calcd 269.1512, found: 269.1508.

2-(4-methoxyphenyl)-2-(2-methylhexyl)cyclopentan-1-one (3m)



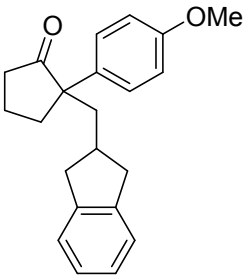
Yield of **3m** : 66% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 2.77 – 2.67 (m, 1H), 2.35 – 2.14 (m, 2H), 2.09 (dd, J = 14.1, 3.7 Hz, 1H, major), 2.02 – 1.89 (m, 2H), 1.87 – 1.77 (m, 1H), 1.56 (dd, J = 14.2, 4.9 Hz, 1H, monir), 1.32 (dd, J = 14.1, 8.3 Hz, 1H), 1.28 – 1.15 (m, 3H), 1.13 – 0.98 (m, 4H), 0.86 (t, J = 6.7 Hz, 2H), 0.78 (dd, J = 10.1, 6.6 Hz, 3H), 0.51 (d, J = 6.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.9, 219.7, 158.2, 130.9, 130.6, 128.2, 128.1, 113.7, 113.7, 56.1, 56.0, 55.1, 45.8, 45.7, 38.1, 37.7, 36.8, 36.6, 34.2, 33.7, 29.7, 29.3, 29.0, 28.8, 22.9, 22.7, 21.2, 21.0, 18.6, 18.5, 14.1, 14.0. **IR** (in KBr): 2958, 1734, 1511, 1252 cm^{-1}. **HRMS (ESI)**: for $C_{19}H_{28}O_2$ $[M+Na]^+$: calcd 311.1982, found: 311.1987.

2-(cyclopent-3-en-1-ylmethyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3n)



Yield of **3n** : 48% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.7, 1.7 Hz, 2H), 6.91 – 6.77 (m, 2H), 5.70 – 5.46 (m, 2H), 3.79 (d, *J* = 1.6 Hz, 3H), 2.85 – 2.62 (m, 1H), 2.44 – 2.14 (m, 4H), 2.05 (s, 1H), 2.01 – 1.92 (m, 4H), 1.88 – 1.77 (m, 1H), 1.73 – 1.64 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.7, 158.3, 130.4, 130.2, 129.8, 128.1, 113.8, 56.3, 55.2, 45.1, 39.9, 39.7, 36.7, 35.1, 34.0, 18.5. **IR** (in KBr): 2927, 1733, 1609, 1511, 1251 cm^{-1}. **HRMS (ESI)** for $C_{18}H_{22}O_2$ $[M+Na]^+$: calcd 293.1512, found: 293.1514.

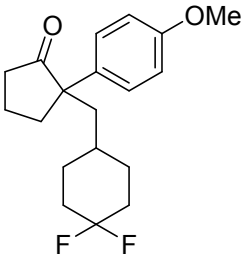
2-((2,3-dihydro-1H-inden-2-yl)methyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3o)



Yield of **3o** : 50% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 2H), 7.10 (d, *J* = 5.1 Hz, 1H), 7.07 – 7.00 (m, 3H), 6.90 – 6.82 (m, 2H), 3.78 (s, 3H), 2.89 (dd, *J* = 15.3, 7.6 Hz, 1H), 2.77 (dd, *J* = 11.5, 5.8 Hz, 1H), 2.62 – 2.51 (m, 2H), 2.43 – 2.12 (m, 5H), 1.98 (d, *J* =

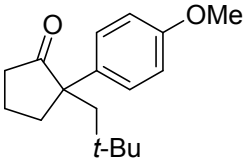
8.5 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.4, 158.4, 143.3, 143.2, 130.2, 128.0, 126.0, 125.9, 124.0, 124.0, 113.9, 56.1, 55.2, 44.5, 40.3, 40.1, 37.5, 36.6, 34.1, 18.5. **IR** (in KBr): 2934, 1732, 1510, 1251 cm^{-1}. **HRMS (ESI)** for $C_{22}H_{24}O_2$ $[M+Na]^+$: calcd 343.1669, found: 343.1642.

2-((4,4-difluorocyclohexyl)methyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3p)



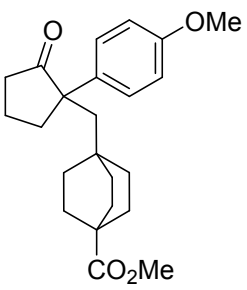
Yield of **3p** : 70% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 2H), 6.92 – 6.79 (m, 2H), 3.79 (d, *J* = 2.0 Hz, 3H), 2.76 – 2.69 (m, 1H), 2.22 (s, 2H), 2.09 – 1.75 (m, 6H), 1.72 – 1.39 (m, 4H), 1.41 – 0.97 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.2, 158.4, 130.2, 127.9, 123.3 (dd, J = 241.6, 239.5 Hz), 113.9, 55.7, 55.1, 44.4 (d, *J* = 2.0 Hz), 36.5, 33.5, 33.3 (d, *J* = 2.8 Hz), 33.0, 32.4, 30.2 (d, *J* = 9.2 Hz), 29.8 (d, *J* = 8.2 Hz), 18.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.80 (dd, *J* = 235.0, 167.6 Hz, 1F), -101.97 (dd, *J* = 234.8, 124.4 Hz, 1F). **IR** (in KBr): 2938, 1733, 1511, 1251, 1114 cm^{-1}. **HRMS (ESI)** for $C_{19}H_{24}F_2O_2$ $[M+Na]^+$: calcd 345.1637 found: 345.1604.

2-(4-methoxyphenyl)-2-neopentylcyclopentan-1-one (3q)



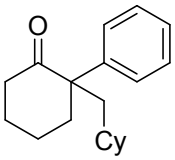
Yield of **3q** : 71% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.30 (m, 2H), 6.94 – 6.76 (m, 2H), 3.79 (s, 3H), 3.14 – 2.83 (m, 1H), 2.30 – 2.06 (m, 3H), 2.05 – 1.90 (m, 2H), 1.88 – 1.75 (m, 1H), 1.44 (d, *J* = 14.7 Hz, 1H), 0.69 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.3, 158.4, 129.3, 128.8, 113.7, 56.0, 55.2, 51.6, 35.6, 34.6, 31.9, 31.3, 18.5. **IR** (in KBr): 2957, 1732, 1400, 1252 cm^{-1}. **HRMS (ESI)** for $C_{17}H_{24}O_2$ $[M+Na]^+$: calcd 283.1669, found: 283.1672.

Methyl-4-((1-(4-methoxyphenyl)-2-oxocyclopentyl)methyl)bicyclo[2.2.2]octane-1-carboxylate (3r)



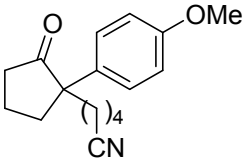
Yield of **3r** : 54% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 3.51 (s, 3H), 2.85 (dd, *J* = 11.9, 5.5 Hz, 1H), 2.11 (d, *J* = 15.2 Hz, 3H), 1.85 (dd, *J* = 6.6, 3.0 Hz, 3H), 1.52 (t, *J* = 6.5 Hz, 6H), 1.25 (d, *J* = 14.9 Hz, 1H), 1.22 – 1.00 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.1, 178.5, 158.4, 129.2, 128.6, 113.7, 55.4, 55.1, 51.5, 49.8, 38.3, 35.5, 34.8, 31.8, 31.4, 28.4, 18.4. **IR** (in KBr): 2950, 1728, 1510, 1251, 1185 cm^{-1}. **HRMS (ESI)** for $C_{23}H_{30}O_4$ $[M+Na]^+$: calcd 393.2036, found: 393.2046.

2-(cyclohexylmethyl)-2-phenylcyclohexan-1-one (3s)



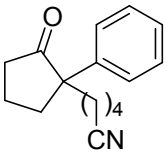
Yield of **3s** : 33% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 2.75 (dd, *J* = 13.7, 2.9 Hz, 1H), 2.36 – 2.22 (m, 2H), 1.96 – 1.89 (m, 1H), 1.86 – 1.62 (m, 5H), 1.62 – 1.42 (m, 5H), 1.17 – 0.81 (m, 6H), 0.67 (d, *J* = 11.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.7, 141.3, 128.7, 126.9, 126.5, 57.6, 47.5, 40.1, 35.5, 35.2, 35.1, 33.3, 28.2, 26.5, 26.4, 26.2, 21.6. **IR** (in KBr): 2925, 1708, 1447 cm^{-1}. **HRMS (ESI)** for $C_{19}H_{26}O$ $[M+K]^+$: calcd 309.1615, found: 309.1617.

5-(1-(4-methoxyphenyl)-2-oxocyclopentyl)pentanenitrile (5a)



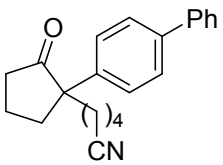
Yield of **5a** : 92% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 2.62 (dd, *J* = 11.2, 6.0 Hz, 1H), 2.35 – 2.18 (m, 4H), 1.98 – 1.76 (m, 4H), 1.61 – 1.51 (m, 3H), 1.38 – 1.07 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.6, 158.4, 130.2, 127.8, 119.5, 113.9, 55.8, 55.2, 38.0, 37.1, 33.6, 25.6, 23.8, 18.5, 16.9. **IR** (in KBr): 2944, 2245, 1731, 1511, 1251 cm^{-1}. **HRMS (ESI)** for $C_{17}H_{21}NO_2$ $[M+Na]^+$: calcd 294.1465, found: 294.1439.

5-(2-oxo-1-phenylcyclopentyl)pentanenitrile (5b)



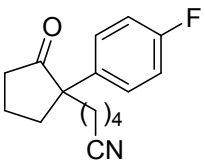
Yield of **5b** : 50% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.26 (d, *J* = 6.9 Hz, 1H), 2.66 (dd, *J* = 11.0, 6.3 Hz, 1H), 2.38 – 2.15 (m, 4H), 2.06 – 1.76 (m, 4H), 1.71 – 1.46 (m, 3H), 1.26 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.5, 138.7, 128.7, 127.0, 126.7, 119.5, 56.5, 38.1, 37.3, 33.6, 25.6, 23.7, 18.6, 16.9. **IR** (in KBr): 2945, 2245, 1731, 1401 1155 cm^{-1}. **HRMS (ESI)** for $C_{16}H_{19}NO$ $[M+Na]^+$: calcd 264.1359, found: 264.1339.

5-(1-([1,1'-biphenyl]-4-yl)-2-oxocyclopentyl)pentanenitrile (5c)



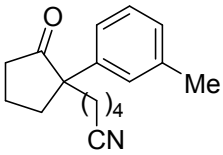
Yield of **5c** : 80% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 5.0 Hz, 4H), 7.43 (dd, *J* = 11.5, 7.9 Hz, 4H), 7.35 (d, *J* = 7.3 Hz, 1H), 2.68 (s, 1H), 2.45 – 2.16 (m, 4H), 2.07 – 1.78 (m, 4H), 1.74 – 1.48 (m, 3H), 1.34 – 1.20 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.4, 140.4, 139.8, 137.8, 130.5, 128.7, 127.3, 127.1, 126.9, 119.5, 56.4, 38.0, 37.3, 33.6, 25.6, 23.9, 18.6, 16.9. **IR** (in KBr): 2944, 2245, 1732, 1402, 1154 cm^{-1}. **HRMS (ESI)** for $C_{22}H_{23}NO$ $[M+Na]^+$: calcd 340.1672, found: 340.1648.

5-(1-(4-fluorophenyl)-2-oxocyclopentyl)pentanenitrile (5d)



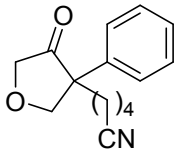
Yield of **5d** : 54% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.06 – 7.00 (m, 2H), 2.70 – 2.51 (m, 1H), 2.41 – 2.16 (m, 4H), 2.08 – 1.75 (m, 4H), 1.66 – 1.45 (m, 3H), 1.36 – 1.06 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.1, 161.7 (d, J = 244.8 Hz), 134.5, 128.4 (d, J = 7.8 Hz), 119.4, 115.4 (d, J = 21.0 Hz), 55.9, 38.1, 37.3, 33.8, 25.5, 23.8, 18.5, 16.9. **IR** (in KBr): 2947, 2246, 1733, 1508, 1402, 1229 cm^{-1}. **HRMS (ESI)** for $C_{16}H_{18}FNO$ $[M+Na]^+$: calcd 282.1265, found: 282.1243.

5-(2-oxo-1-(m-tolyl)cyclopentyl)pentanenitrile (5e)



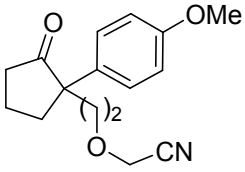
Yield of **5e** : 54% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 1H), 7.16 (d, J = 6.7 Hz, 2H), 7.06 (d, J = 7.3 Hz, 1H), 2.75 – 2.58 (m, 1H), 2.34 (s, 3H), 2.31 – 2.15 (m, 4H), 2.04 – 1.70 (m, 4H), 1.68 – 1.47 (m, 3H), 1.38 – 1.12 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.5, 138.7, 138.2, 128.4, 127.6, 127.3, 123.6, 119.5, 56.4, 38.0, 37.2, 33.7, 25.6, 23.8, 21.5, 18.5, 16.8. **IR** (in KBr): 2949, 2246, 1733, 1402 cm^{-1}. **HRMS (ESI)** for $C_{17}H_{21}NO$ $[M+Na]^+$: calcd 278.1515, found: 278.1513.

5-(4-oxo-3-phenyltetrahydrofuran-3-yl)pentanenitrile (5f)



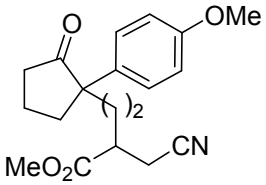
Yield of **5f** : 83% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 3H), 7.33 – 7.23 (m, 2H), 4.95 (d, J = 2.4 Hz, 1H), 4.71 (dd, J = 13.1, 9.3 Hz, 1H), 4.27 (dd, J = 30.6, 9.1 Hz, 1H), 4.05 (s, 1H), 2.34 – 2.02 (m, 2H), 1.61 (d, J = 15.3 Hz, 4H), 1.28 (dd, J = 13.7, 6.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.6, 136.9, 128.9, 127.5, 126.6, 119.2, 76.3, 71.0, 54.9, 35.0, 25.6, 23.7, 16.9. **IR** (in KBr): 3132, 2945, 2246, 1756, 1400, 1066 cm^{-1}. **HRMS (ESI)** for $C_{15}H_{17}NO_2$ $[M+Na]^+$: calcd 266.1151, found: 266.1126.

2-(2-(1-(4-methoxyphenyl)-2-oxocyclopentyl)ethoxy)acetonitrile (5g)



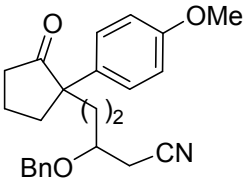
Yield of **5g** : 54% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.3 – 7.2 (m, 2H), 6.9 (d, J = 8.9 Hz, 2H), 4.1 (d, J = 8.7 Hz, 2H), 3.8 (s, 3H), 3.4 (d, J = 1.2 Hz, 2H), 2.8 – 2.6 (m, 1H), 2.4 – 2.1 (m, 3H), 2.0 – 1.7 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 218.8, 158.5, 129.6, 127.8, 115.9, 114.1, 68.6, 55.9, 55.1, 54.5, 37.5, 36.5, 34.3, 18.5. **IR** (in KBr): 3138, 2361, 1637, 1400 cm^{-1}. **HRMS (ESI)** for $C_{16}H_{19}NO_3$ $[M+Na]^+$: calcd 296.1257, found: 296.1259.

Methyl 2-(cyanomethyl)-4-(1-(4-methoxyphenyl)-2-oxocyclopentyl)butanoate (5h)



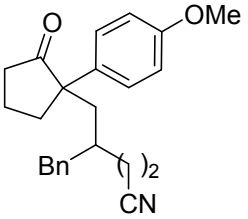
Yield of **5h** : 90% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 6.95 – 6.74 (m, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 2.64 – 2.59 (m, 2H), 2.60 – 2.42 (m, 4H, minor), 2.38 – 2.13 (m, 4H, major), 2.04 – 1.73 (m, 4H), 1.72 – 1.27 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.0, 172.7, 172.6, 158.5, 129.7, 129.6, 127.8, 127.7, 117.5, 117.4, 114.0, 113.9, 55.5, 55.4, 55.1, 52.2, 52.1, 41.3, 41.2, 36.9, 36.8, 35.3, 35.2, 33.6, 26.3, 19.1, 19.0, 18.4. **IR** (in KBr): 2957, 2250, 1734, 1512, 1252, 1186 cm^{-1}. **HRMS (ESI)** for $C_{19}H_{23}NO_4$ $[M+Na]^+$: calcd 352.1519, found: 352.1513.

3-(benzyloxy)-5-(1-(4-methoxyphenyl)-2-oxocyclopentyl)pentanenitrile (5i)



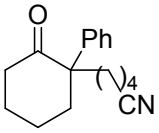
Yield of **5i** : 43% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 7H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.61 – 4.28 (m, 2H), 3.78 (s, 3H), 3.58 – 3.50 (m, 1H), 2.64 – 2.56 (m, 1H), 2.51 – 2.16 (m, 4H), 1.96 – 1.86 (m, 3H), 1.82 (d, *J* = 9.0 Hz, 2H, major), 1.71 (d, *J* = 4.6 Hz, 2H, minor), 1.46 (dd, *J* = 7.8, 4.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.4, 158.5, 137.4, 130.3, 130.1, 128.0, 127.9, 127.8, 127.7, 117.4, 117.3, 114.0, 74.4, 71.8, 71.6, 55.6, 55.4, 55.2, 37.2, 37.1, 33.8, 33.7, 29.1, 29.0, 22.8, 22.7, 18.5. **IR** (in KBr): 2955, 2249, 1731, 1511, 1251 cm^{-1}. **HRMS (ESI)** for $C_{24}H_{27}NO_3$ $[M+Na]^+$: calcd 400.1883, found: 400.1883.

4-benzyl-5-(1-(4-methoxyphenyl)-2-oxocyclopentyl)pentanenitrile (5j)



Yield of **5j** : 65% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 1H), 7.27 – 7.24 (m, 2H), 7.22 – 7.14 (m, 2H), 7.08 – 6.98 (m, 1H), 6.93 – 6.89 (m, 2H), 6.86 – 6.79 (m, 1H), 3.79 (d, *J* = 9.8 Hz, 3H), 2.80 – 2.59 (m, 1H), 2.50 (dd, *J* = 13.6, 6.7 Hz, 1H, minor), 2.39 (dd, *J* = 13.6, 7.9 Hz, 1H, major), 2.29 – 2.15 (m, 3H), 2.10 – 1.56 (m, 6H), 1.56 – 1.43 (m, 2H), 1.26 (d, *J* = 3.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 219.0, 218.9, 158.7, 158.5, 139.7, 139.5, 129.6, 129.4, 129.0, 128.9, 128.4, 128.3, 128.1, 128.0, 126.2, 126.1, 119.7, 119.5, 114.2, 114.0, 55.8, 55.5, 55.2, 55.1, 41.8, 41.6, 41.2, 41.1, 36.6, 36.5, 35.8, 35.5, 34.0, 33.9, 29.8, 29.7, 18.4, 18.2, 14.5, 14.3. **IR** (in KBr): 2931, 2245, 1732, 1511, 1251 cm^{-1}. **HRMS (ESI)** for $C_{24}H_{27}NO_2$ $[M+Na]^+$: calcd 384.1934, found: 384.1904.

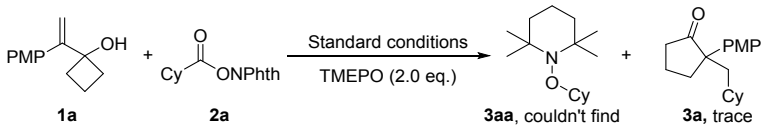
5-(2-oxo-1-phenylcyclohexyl)pentanenitrile (5k)



Yield of **5k** : 69% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 2.74 (dd, *J* = 13.9, 3.1 Hz, 1H), 2.39 – 2.16 (m, 4H), 2.06 – 1.90 (m, 1H), 1.82 – 1.62 (m, 6H), 1.57 – 1.46 (m, 2H), 1.34 – 1.16 (m, 1H), 1.13 – 0.95 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.6, 140.5, 128.9, 126.8, 119.7, 57.1, 40.1, 39.3, 35.0, 28.3, 25.8, 22.9, 21.6, 16.9. **IR** (in KBr): 2941, 2246, 1706, 1400 cm^{-1}. **HRMS (ESI)** for $C_{17}H_{21}NO$ $[M+Na]^+$: calcd 278.1515, found: 278.1503.

5. Mechanism Investigation and the Proposed Mechanism

5.1 Control Experiment with 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)

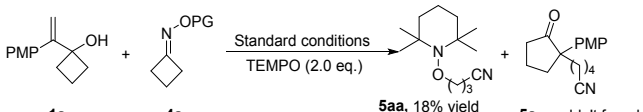


1a **2a** **3aa**, couldn't find **3a,** trace

PMP = 4-MeO-C_6H_4; NPhth = *N*-phthalimide

Procedure: To a dried Schlenk tube was treated with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), *fac*-Ir(ppy)$_3$ (0.006 mmol, 3 mol%) and TEMPO (62.50 mg, 0.4 mmol) . Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via 'freeze-pump-thaw' procedure. After that, this resulting solution was stirred at room temperature under irradiation by 6 W white LEDs (distance of ~2 cm) for 12 h. **3aa** can't be detected by TLC.

5.2 Control Experiment with 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO)

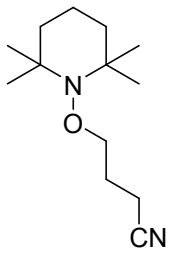


1a **4a** **5aa,** 18% yield confirmed by ^{1}H NMR **5a,** couldn't found

PMP = 4-MeO-C_6H_4; PG = *p*-$CF_3C_6H_4CO$

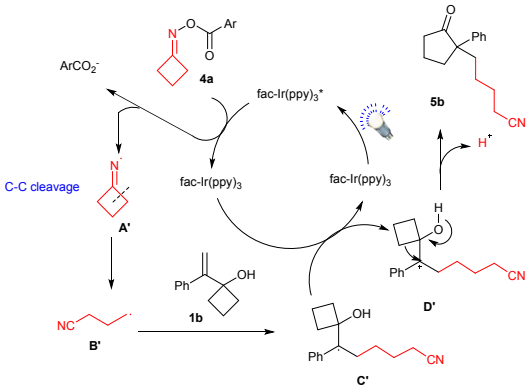
Procedure: To a dried Schlenk tube was treated with **1a** (0.2 mmol, 1.0 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol%) and TEMPO (62.50 mg, 0.4 mmol) . Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via 'freeze-pump-thaw' procedure. After that, this resulting solution was stirred at room temperature under irradiation by 6 W blue LEDs (distance of ~2 cm) for 15 h. Product **5a** was not be detected by TLC, but the radical could be captured by TEMPO, **5aa** was be characterized by ^{1}H NMR.

4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (5aa)

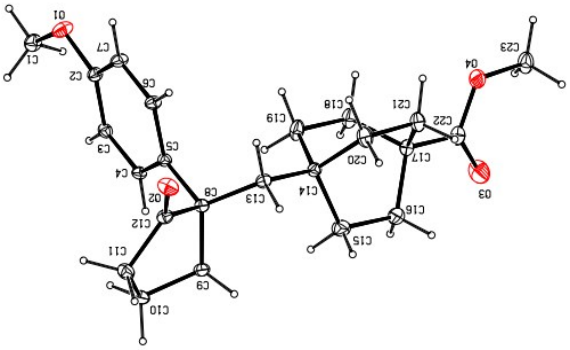
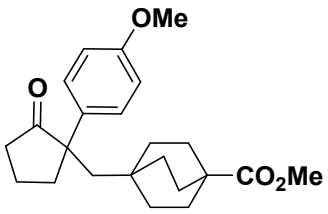


Yield of **5aa**: 18% yield of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (t, *J* = 5.8 Hz, 1H), 2.49 (t, *J* = 7.2 Hz, 1H), 2.00 – 1.76 (m, 1H), 1.57 (s, 2H), 1.45 (dd, *J* = 7.7, 4.2 Hz, 2H), 1.37 – 1.28 (m, 1H), 1.12 (d, *J* = 23.3 Hz, 6H). the ^{1}H NMR data are consistent with the reported literature (*Angew. Chem. Int. Ed.* **2018**, *57*, 738-743.).

5.3 A plausible mechanism involved 4a

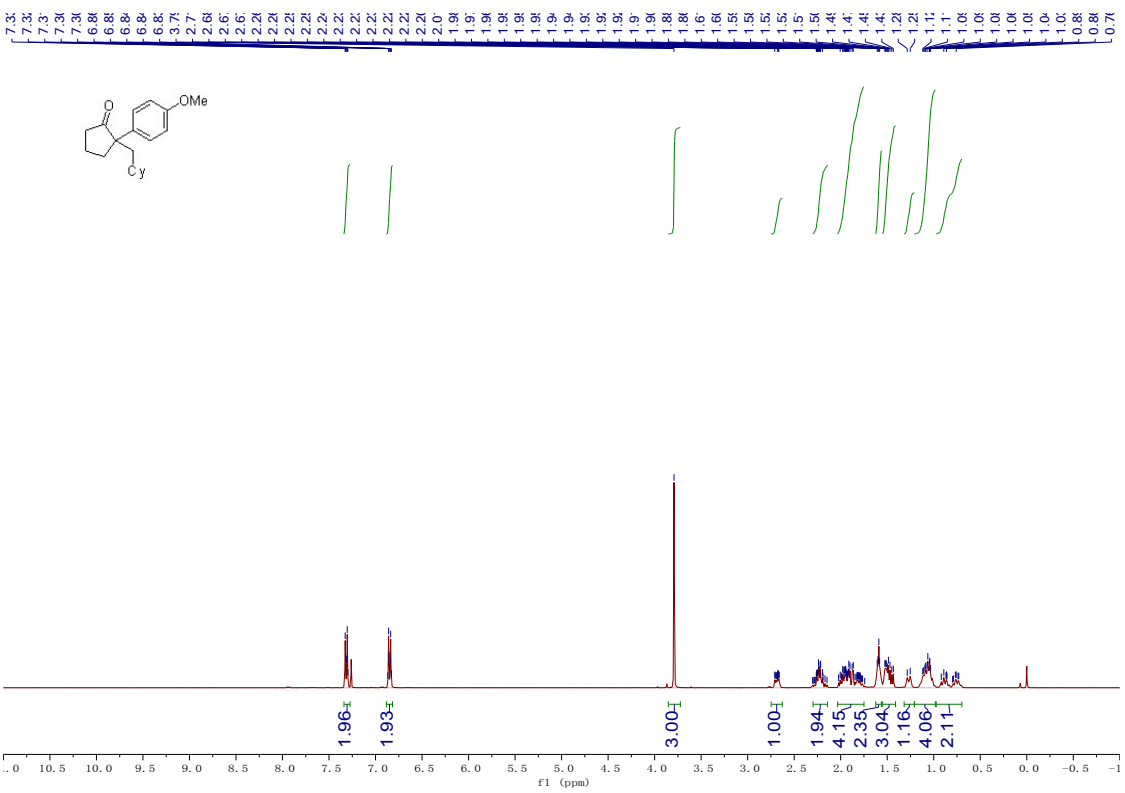


6. X-Ray Crystal Structure Determination of 3r

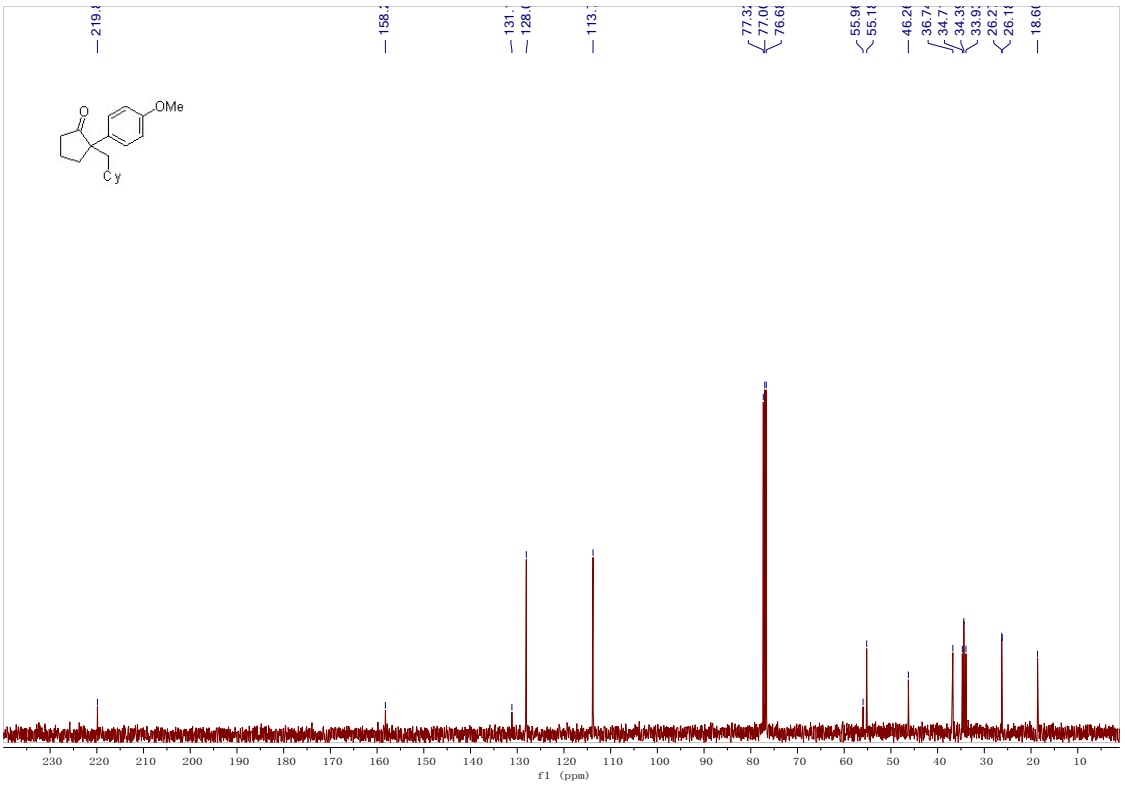
3r		 **CCDC: 1841673**

7. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

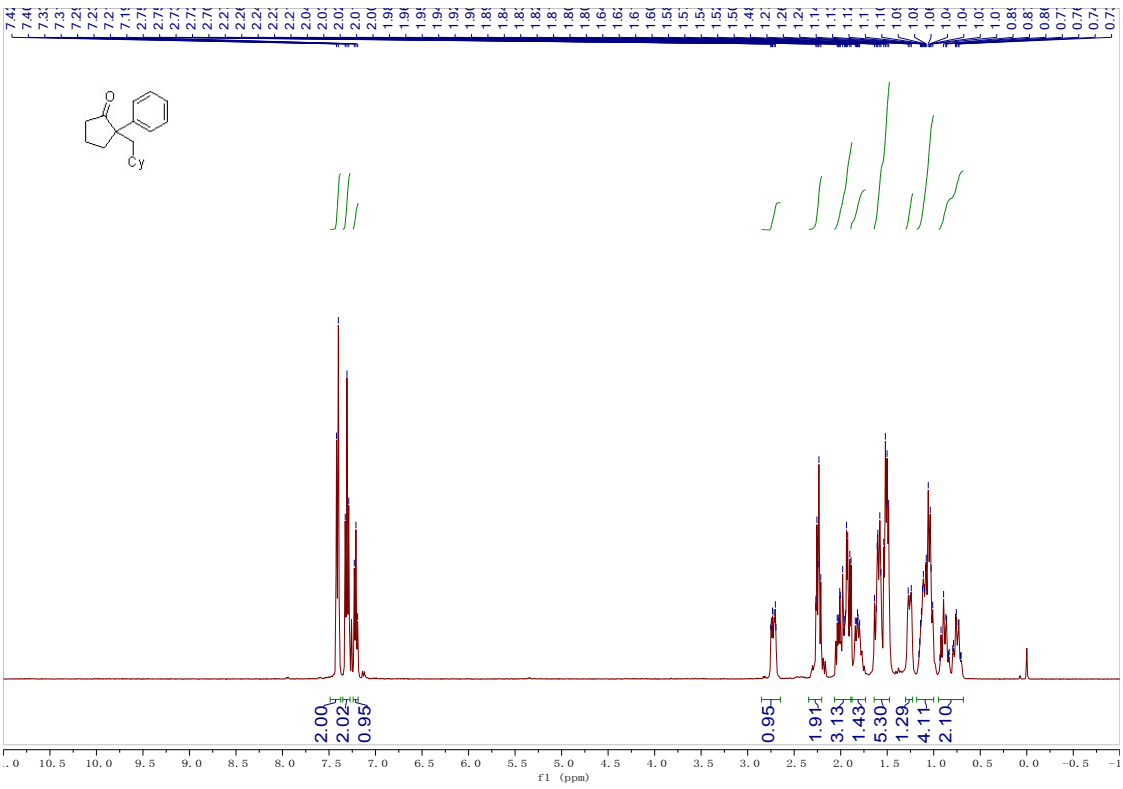
^{1}H NMR Spectrum of **3a**



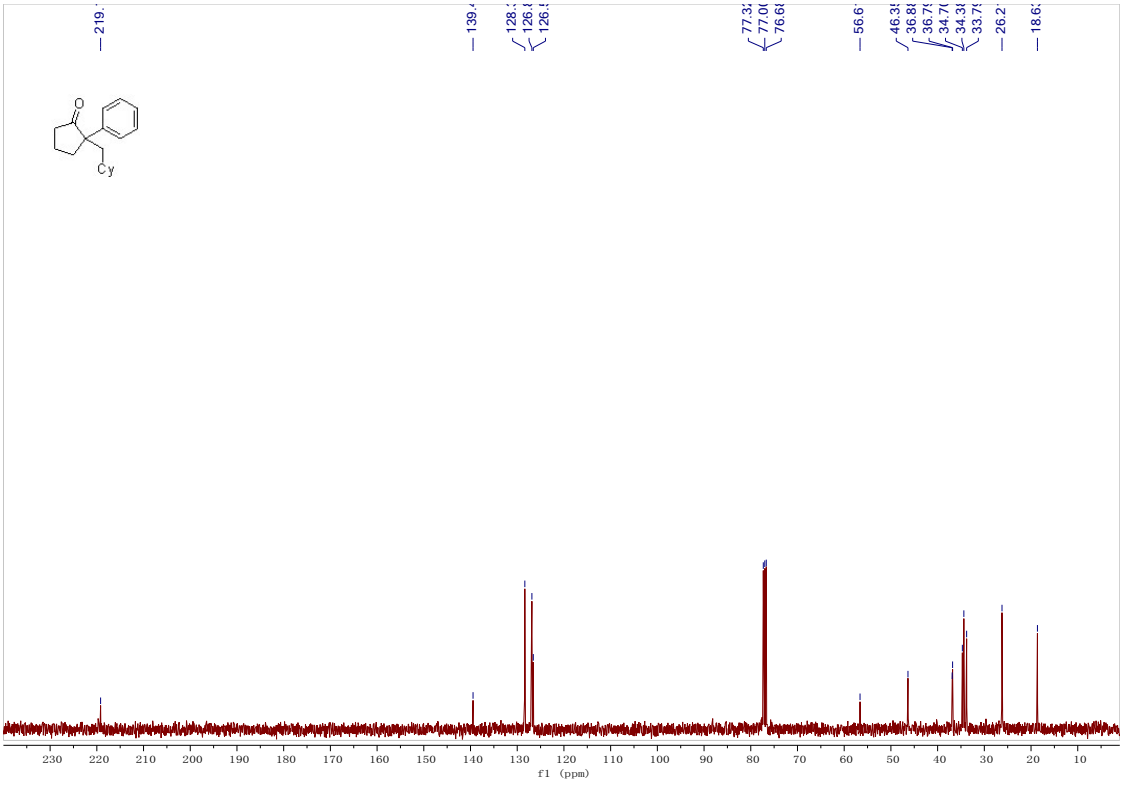
^{13}C NMR Spectrum of **3a**



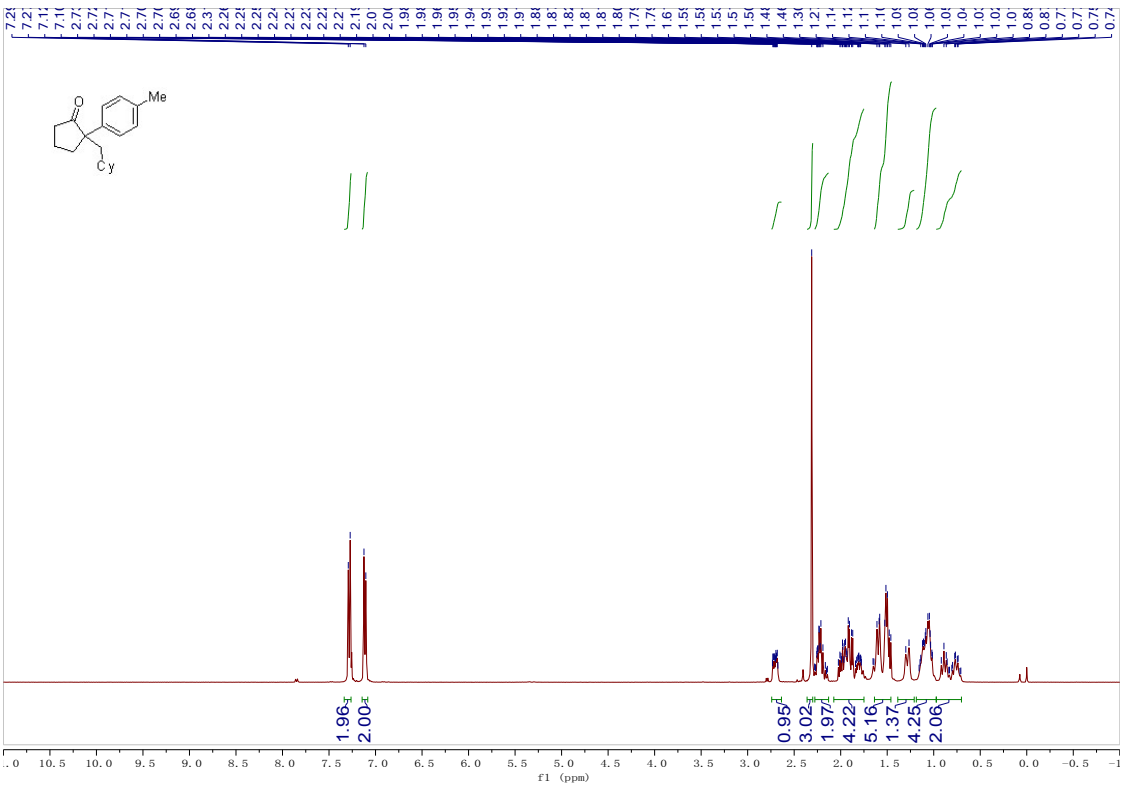
^{1}H NMR Spectrum of **3b**



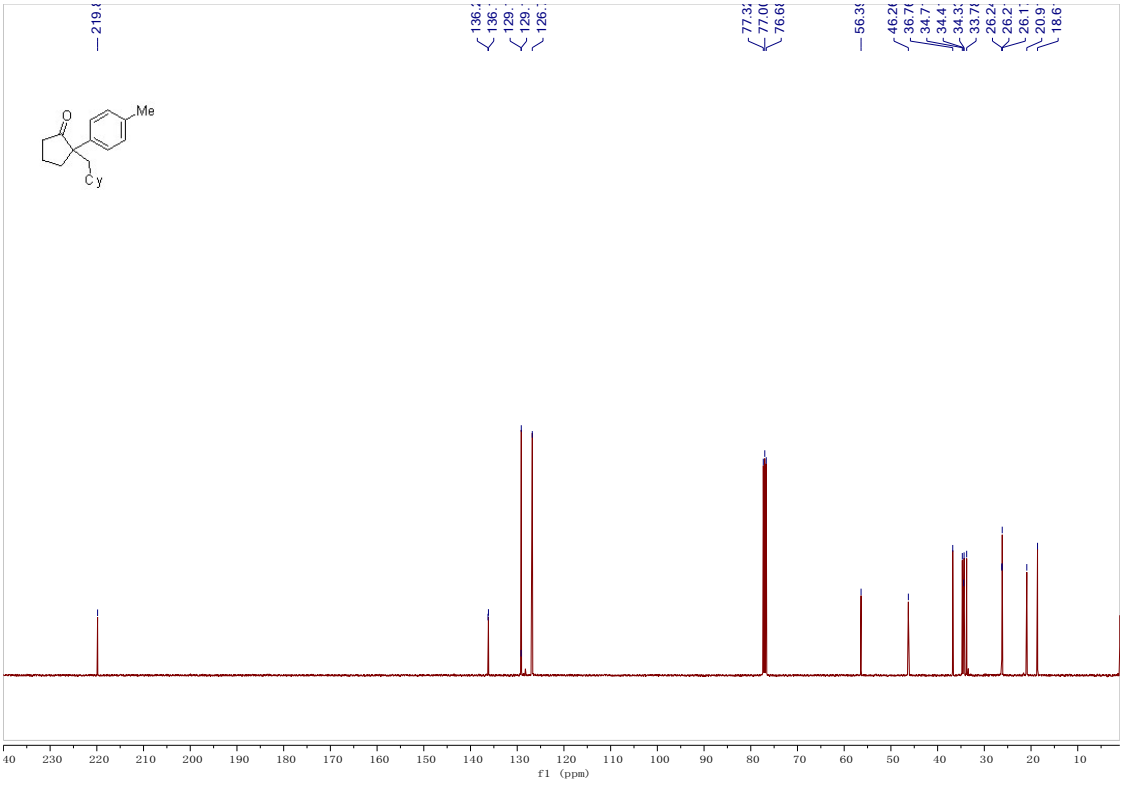
^{13}C NMR Spectrum of **3b**



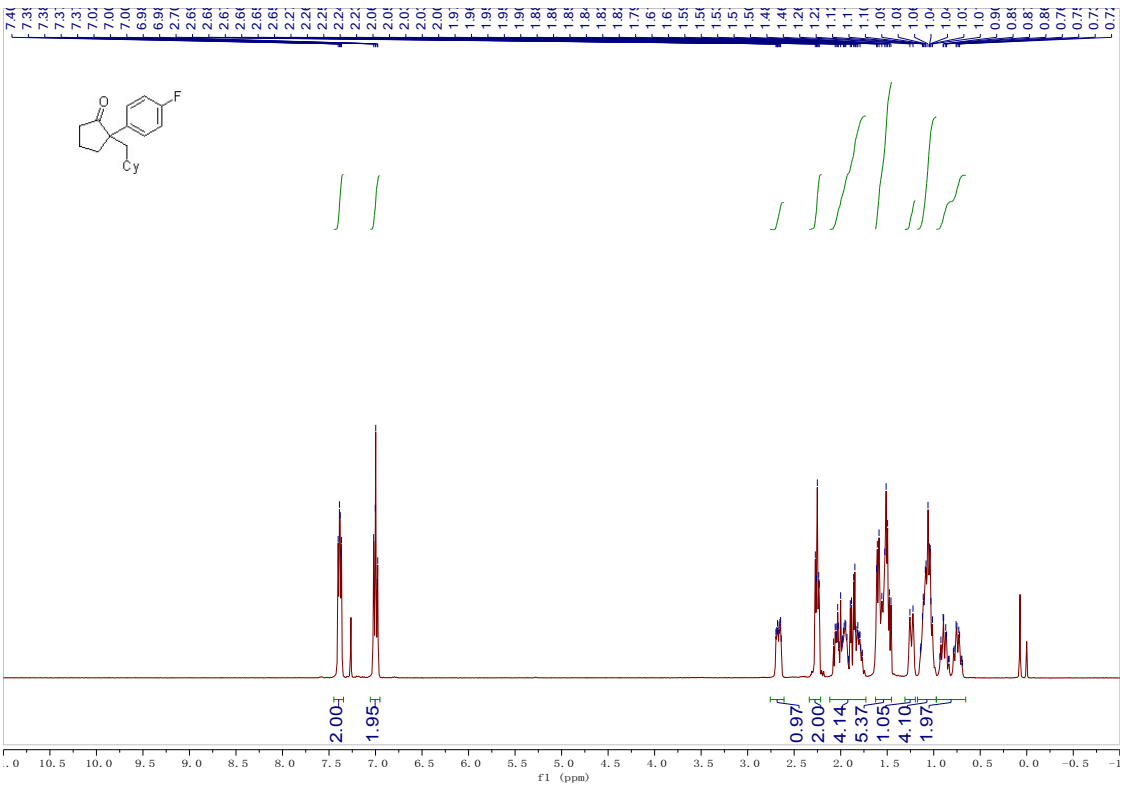
^{1}H NMR Spectrum of **3c**



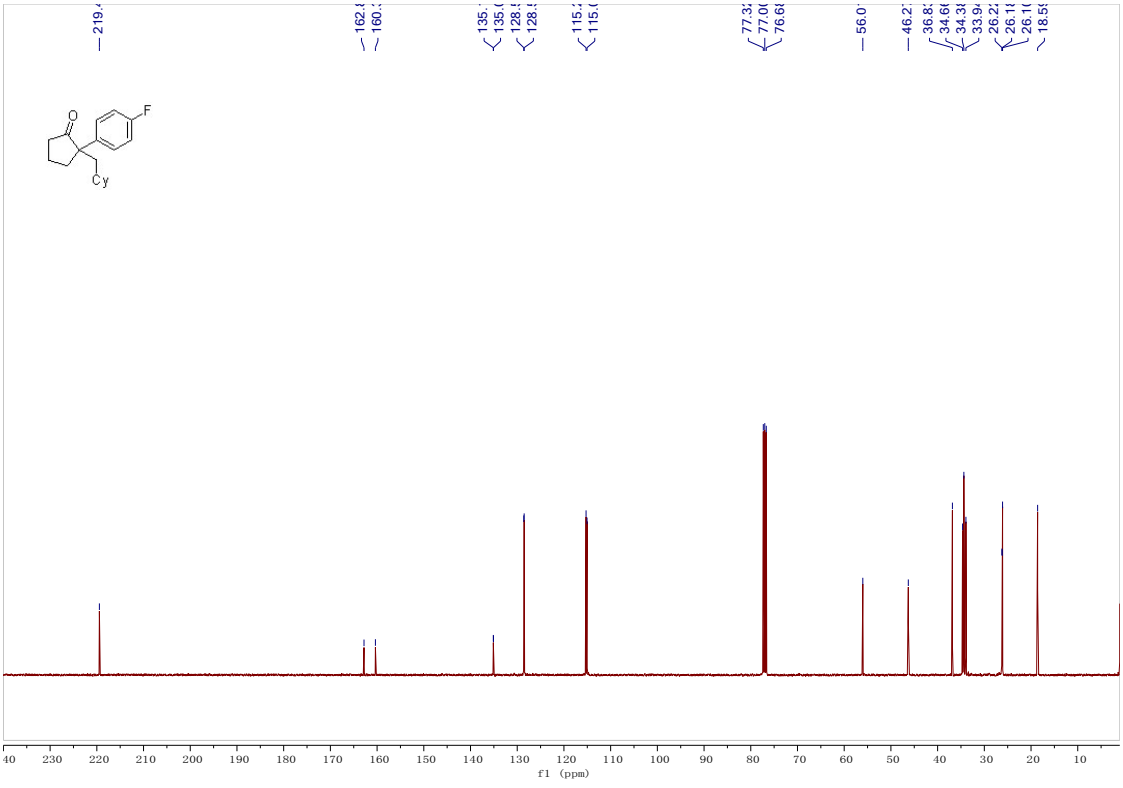
^{13}C NMR Spectrum of **3c**



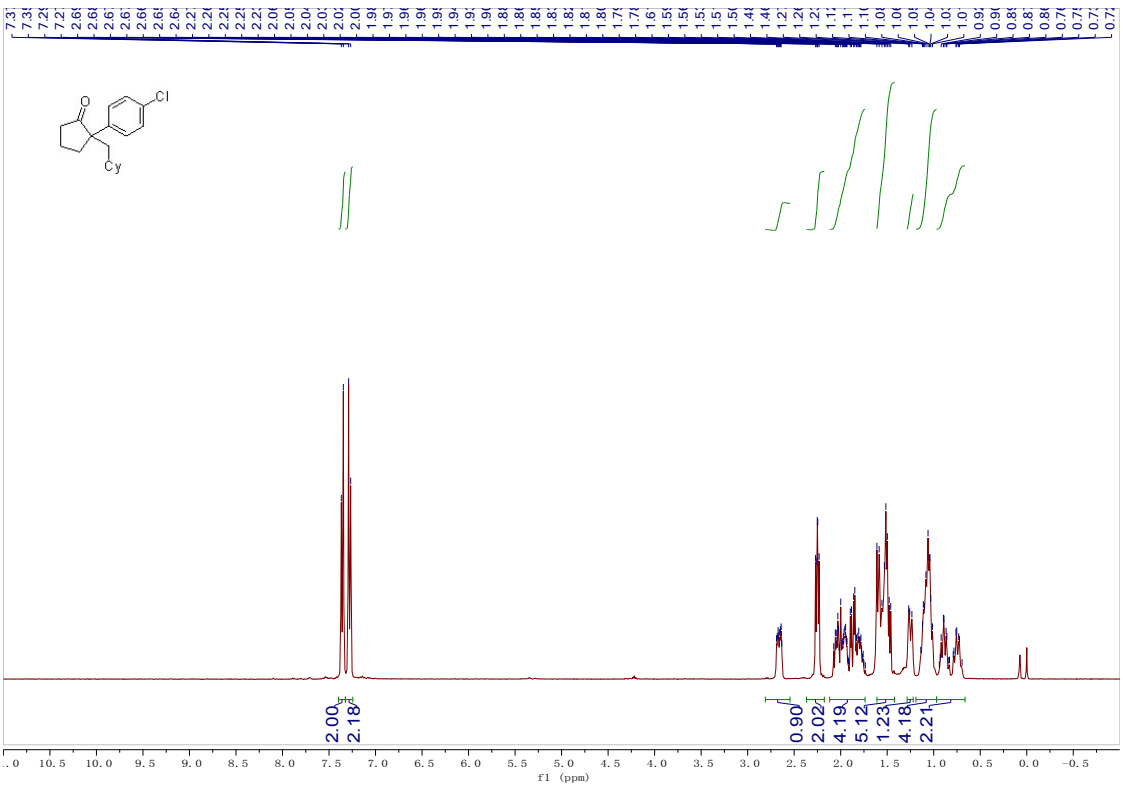
^{1}H NMR Spectrum of **3d**



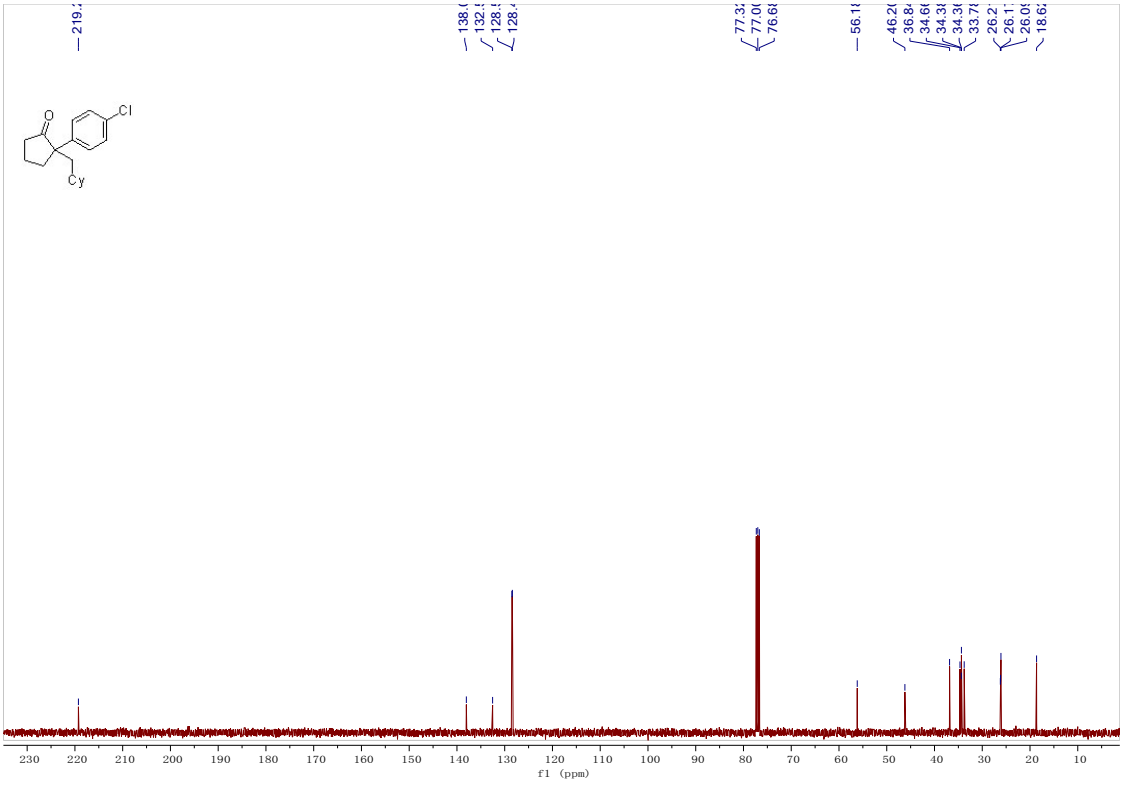
^{13}C NMR Spectrum of **3d**



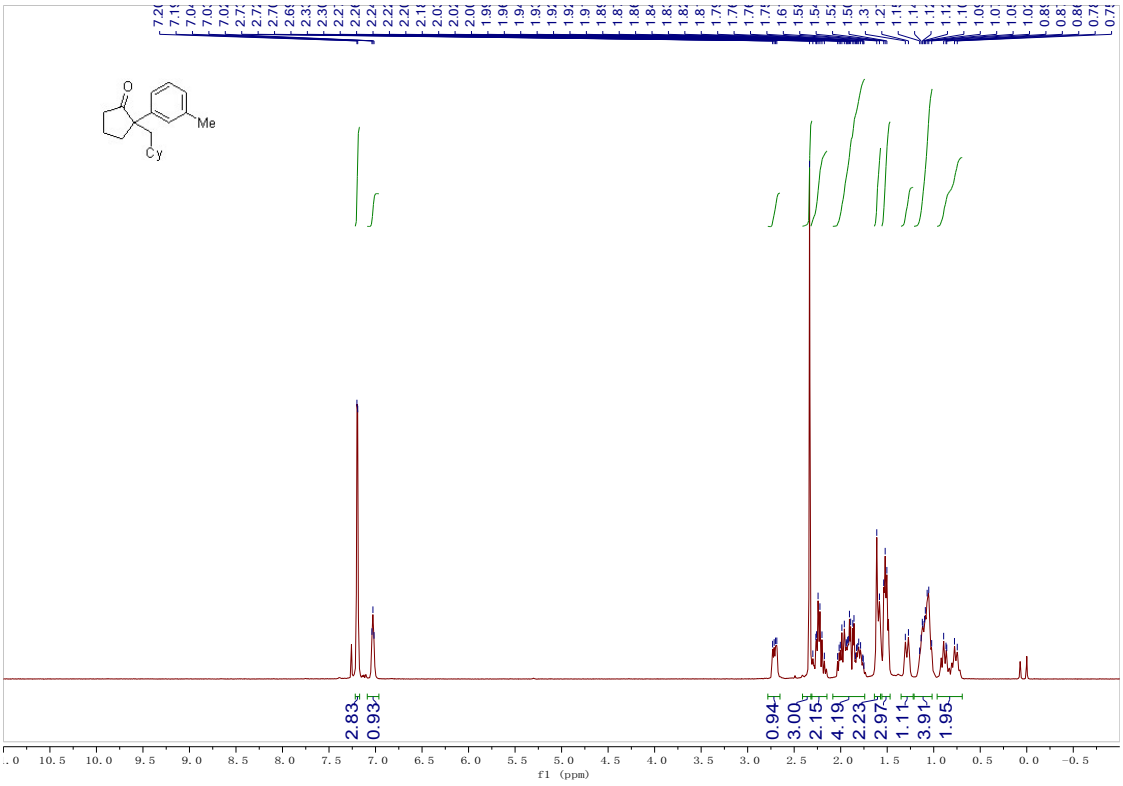
^{1}H NMR Spectrum of **3e**



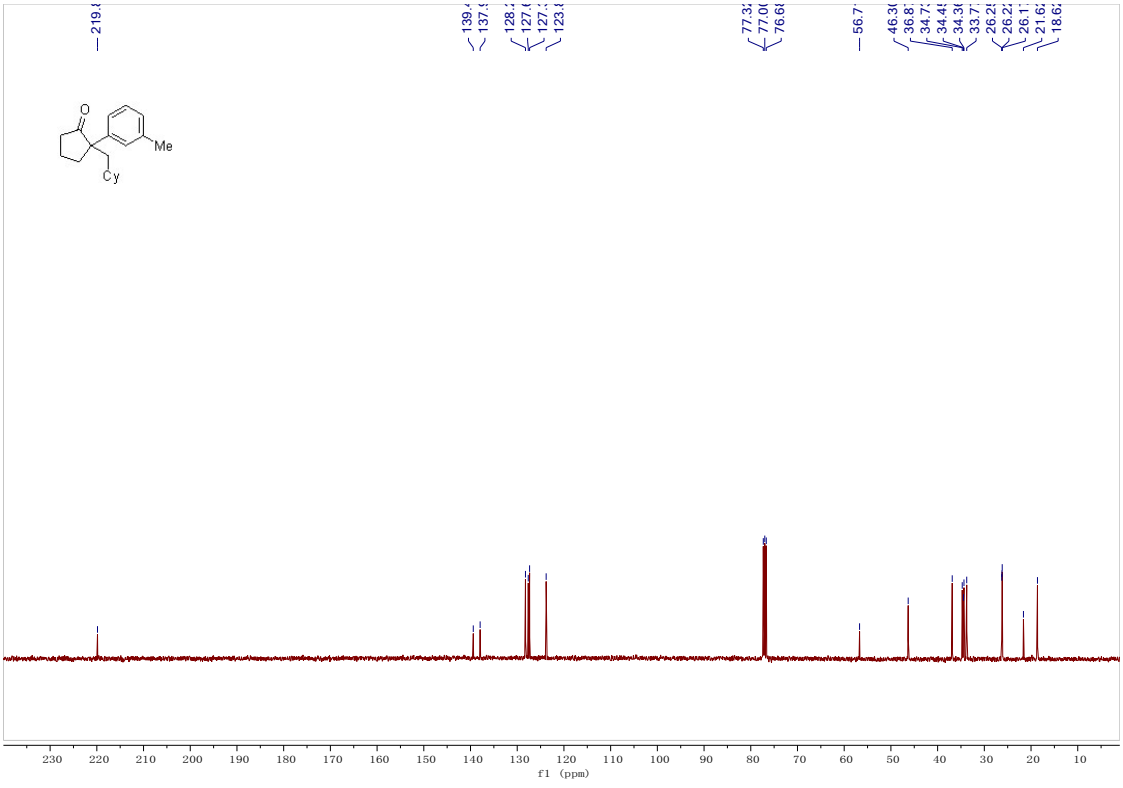
^{13}C NMR Spectrum of **3e**



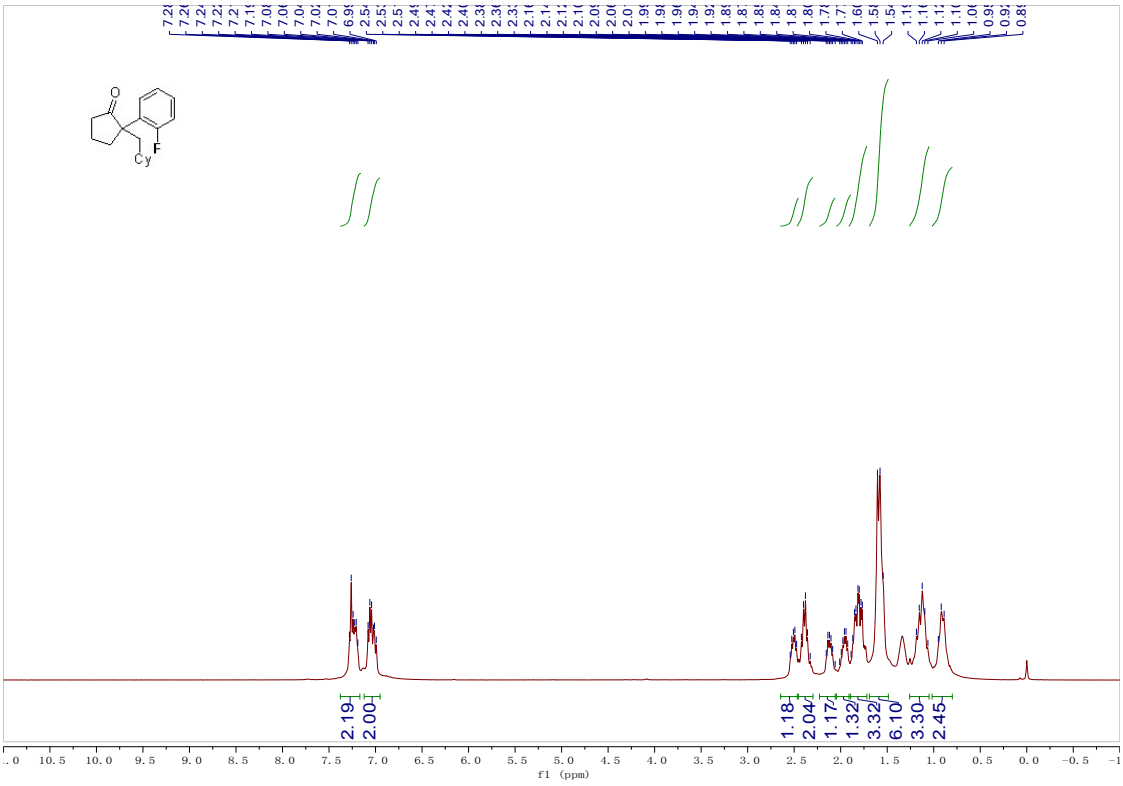
^{1}H NMR Spectrum of **3f**



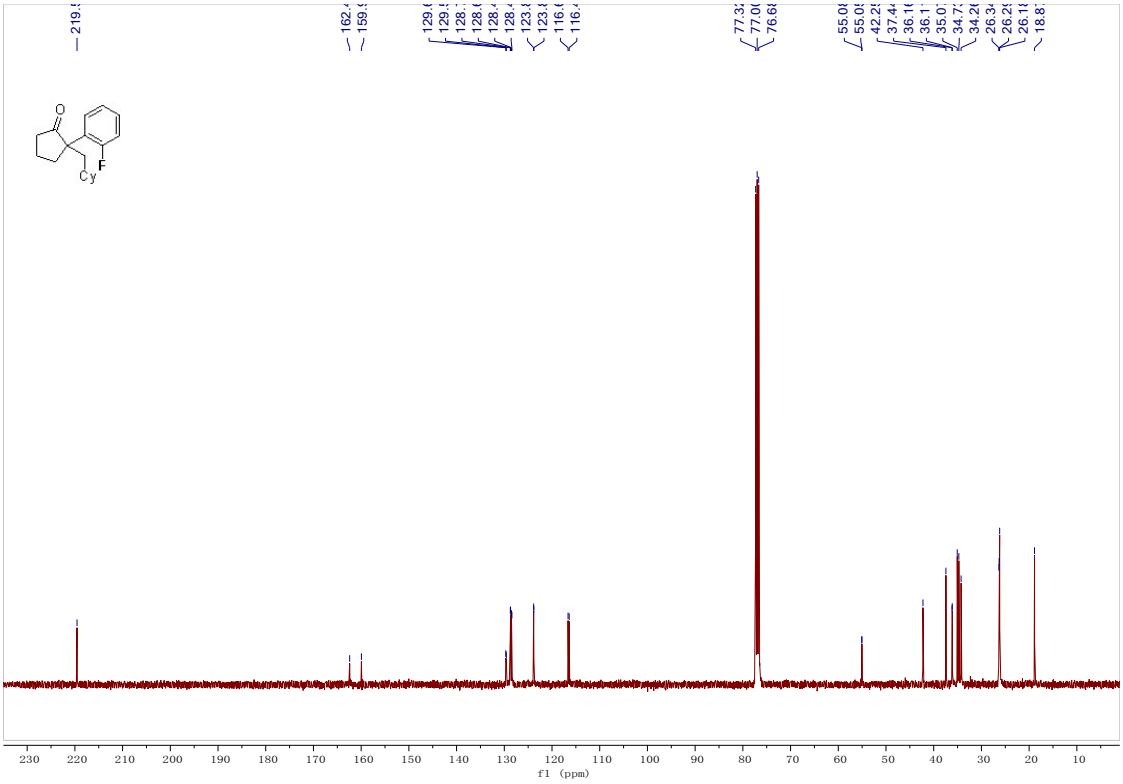
^{13}C NMR Spectrum of **3f**



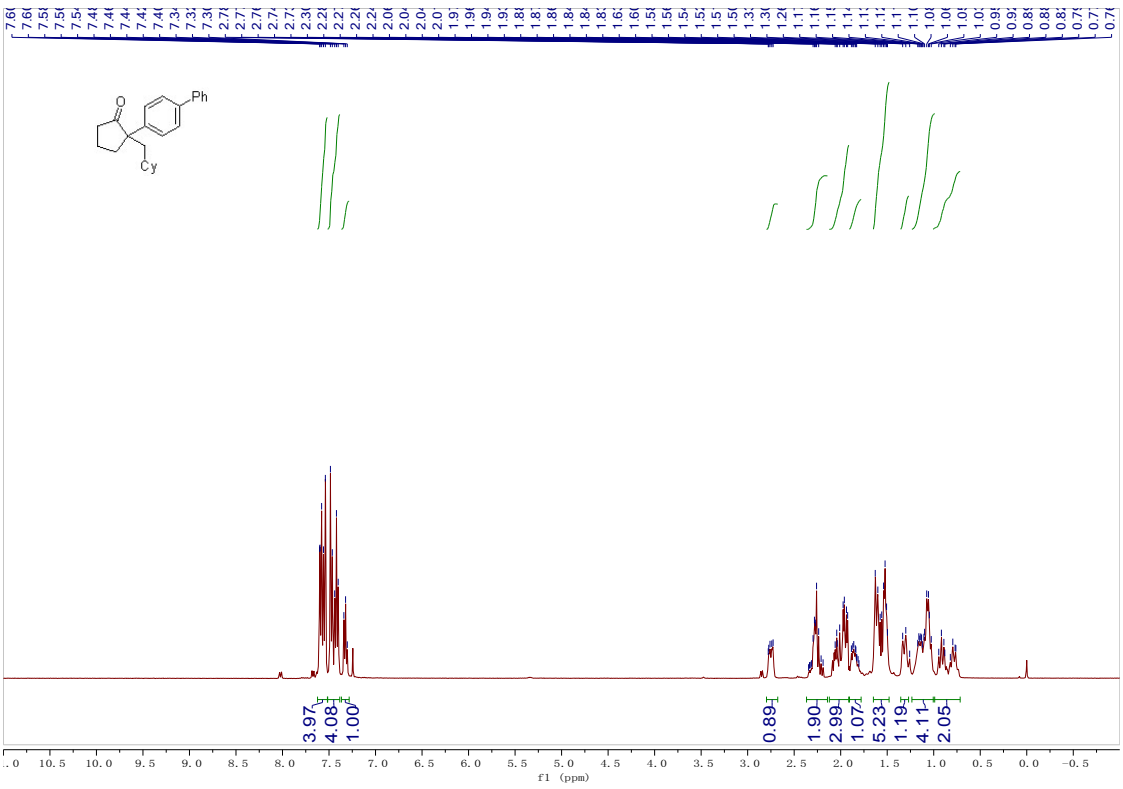
^{1}H NMR Spectrum of **3g**



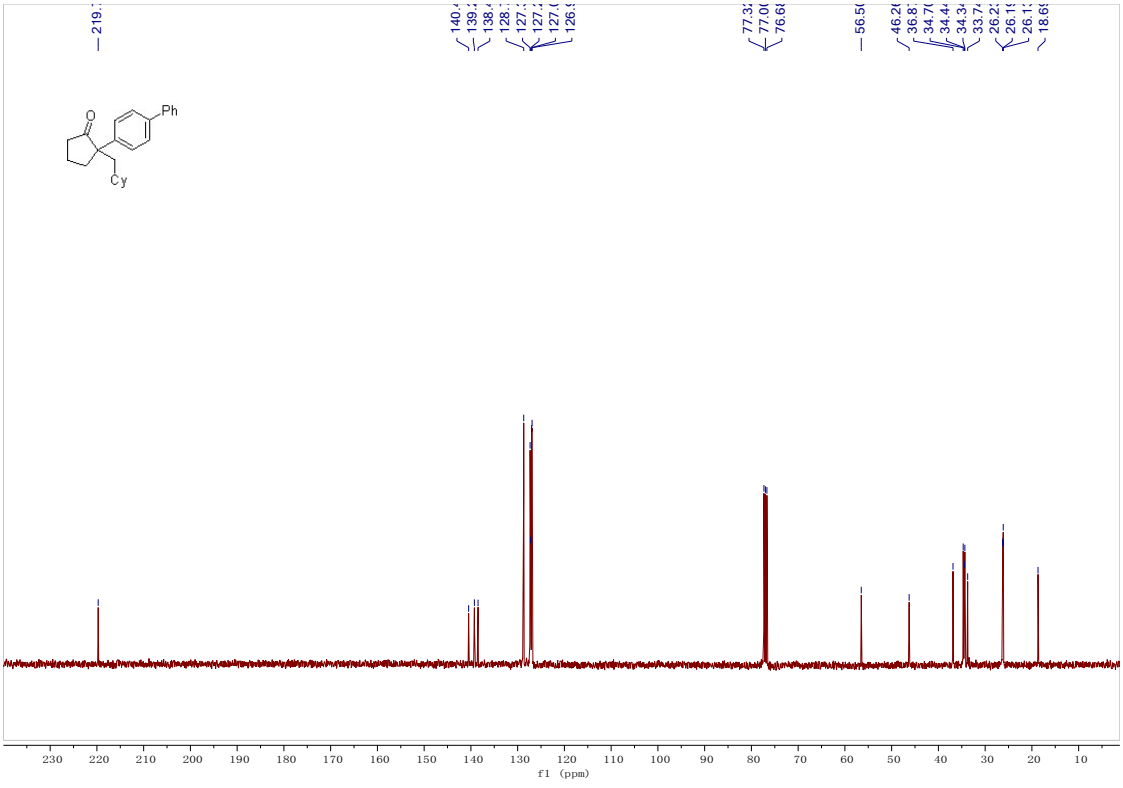
^{13}C NMR Spectrum of **3g**



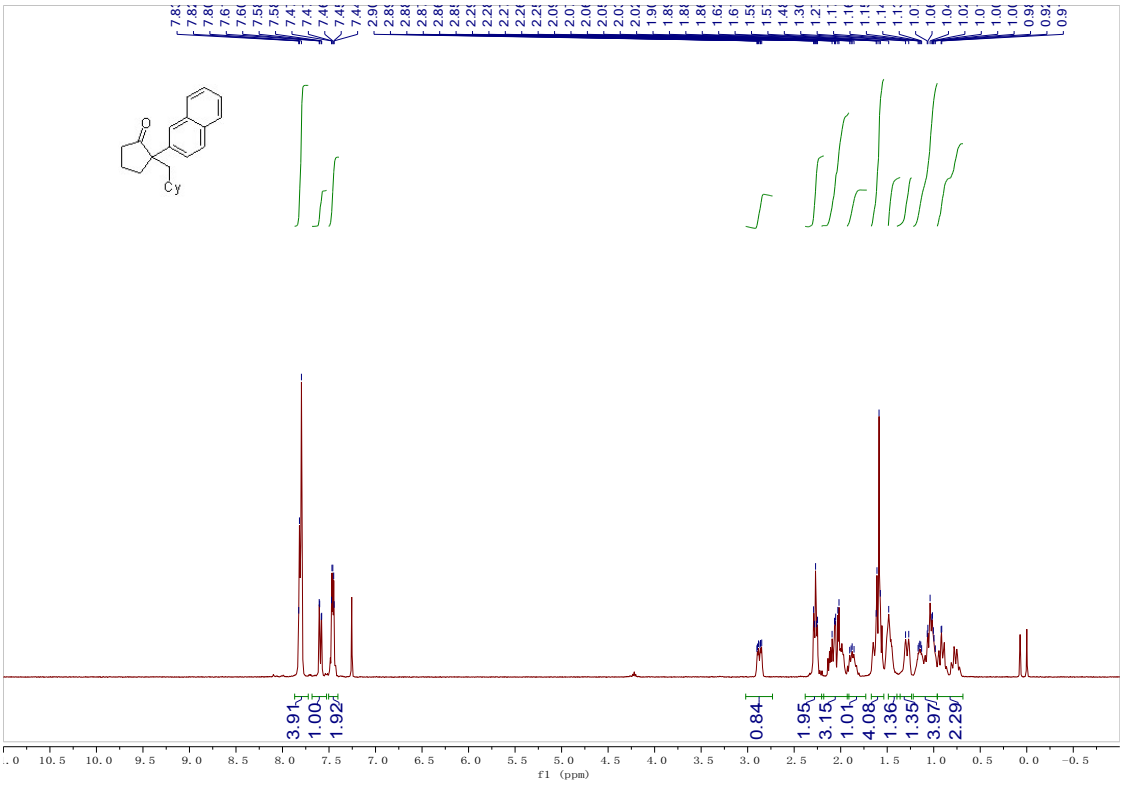
^{1}H NMR Spectrum of **3h**



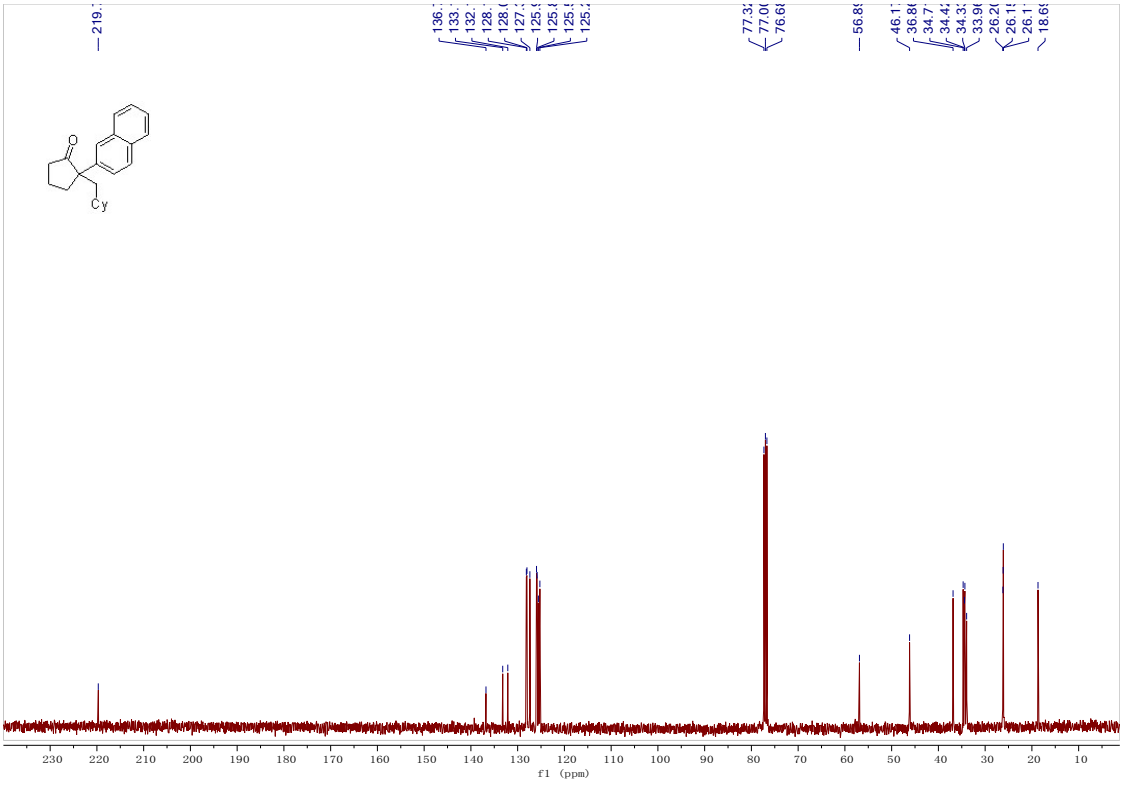
^{13}C NMR Spectrum of **3h**



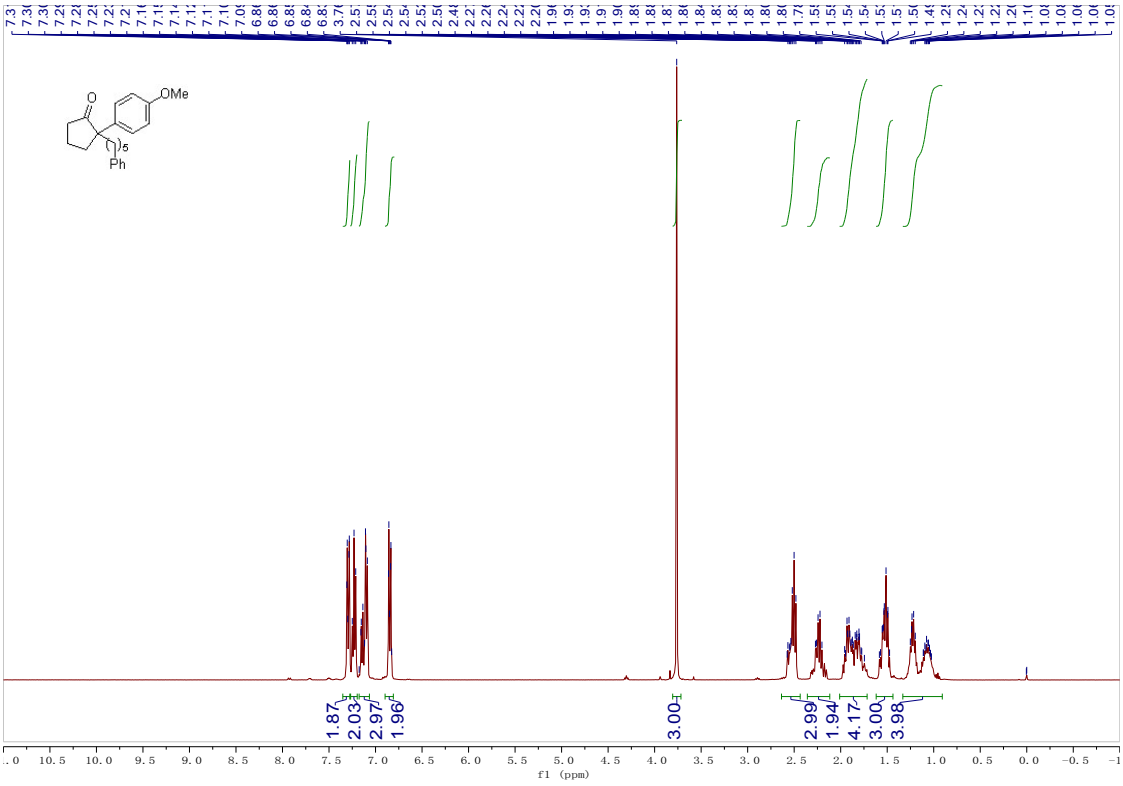
^{1}H NMR Spectrum of **3i**



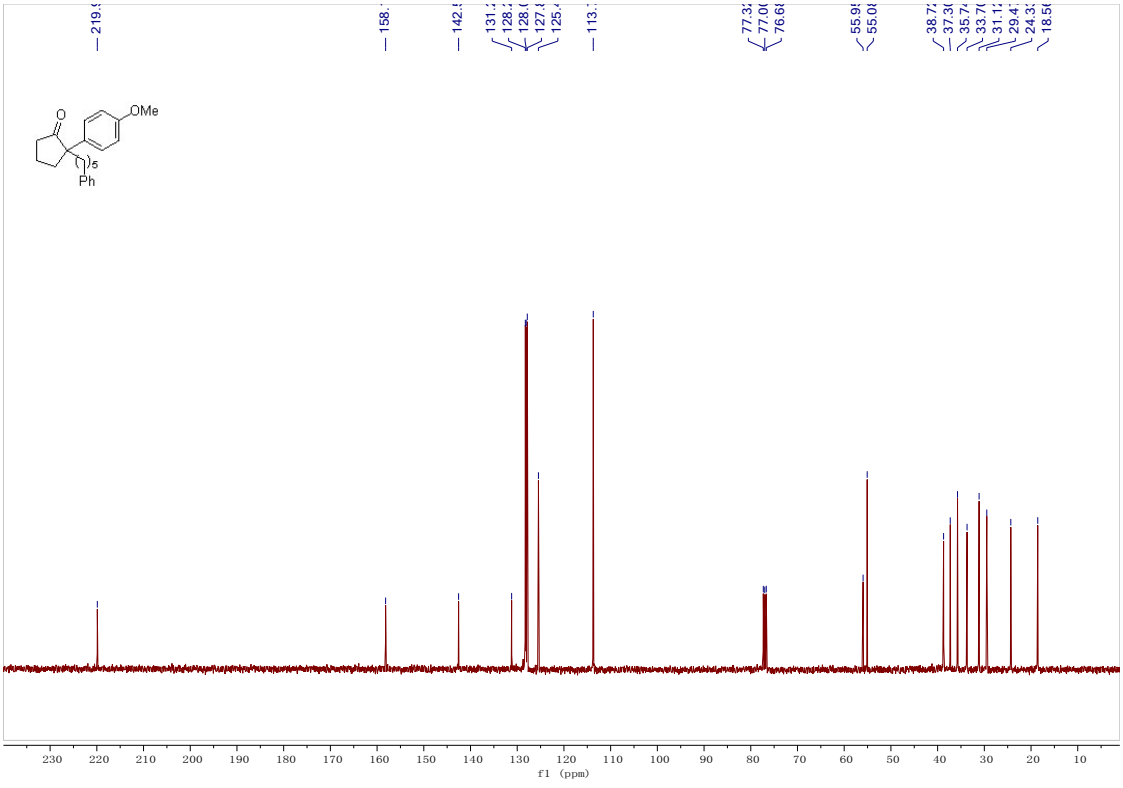
^{13}C NMR Spectrum of **3i**



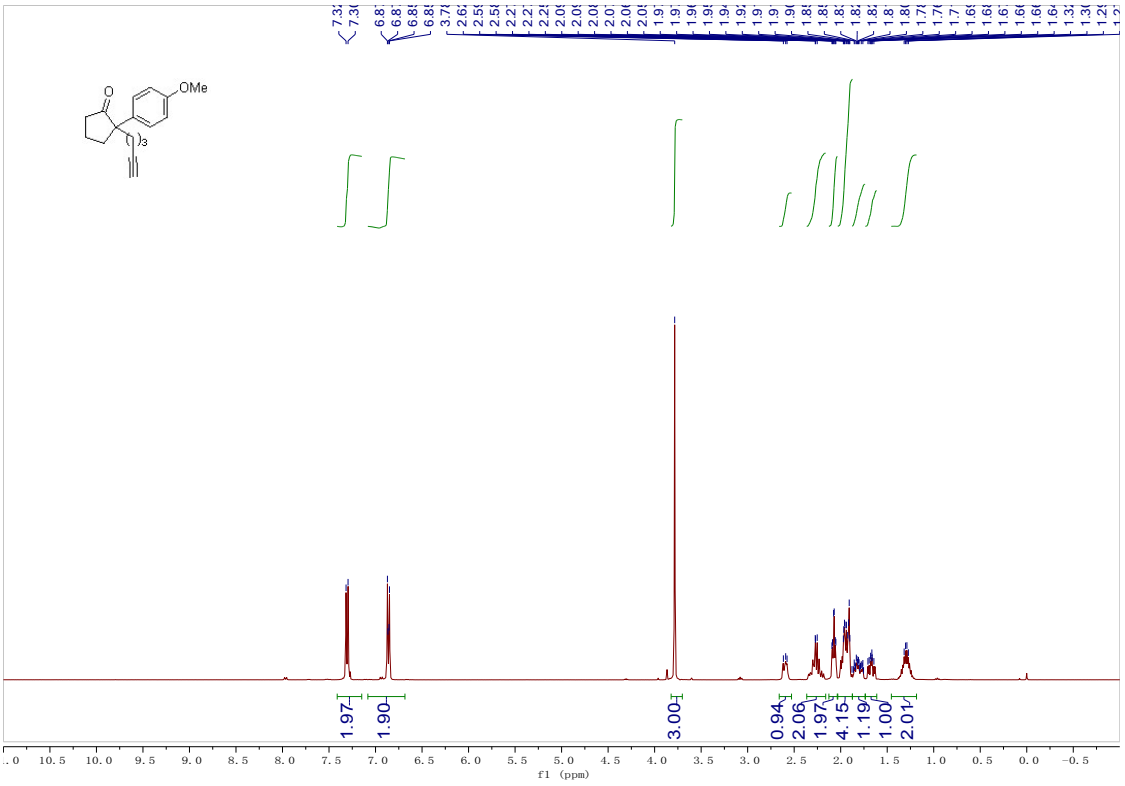
^{1}H NMR Spectrum of **3j**



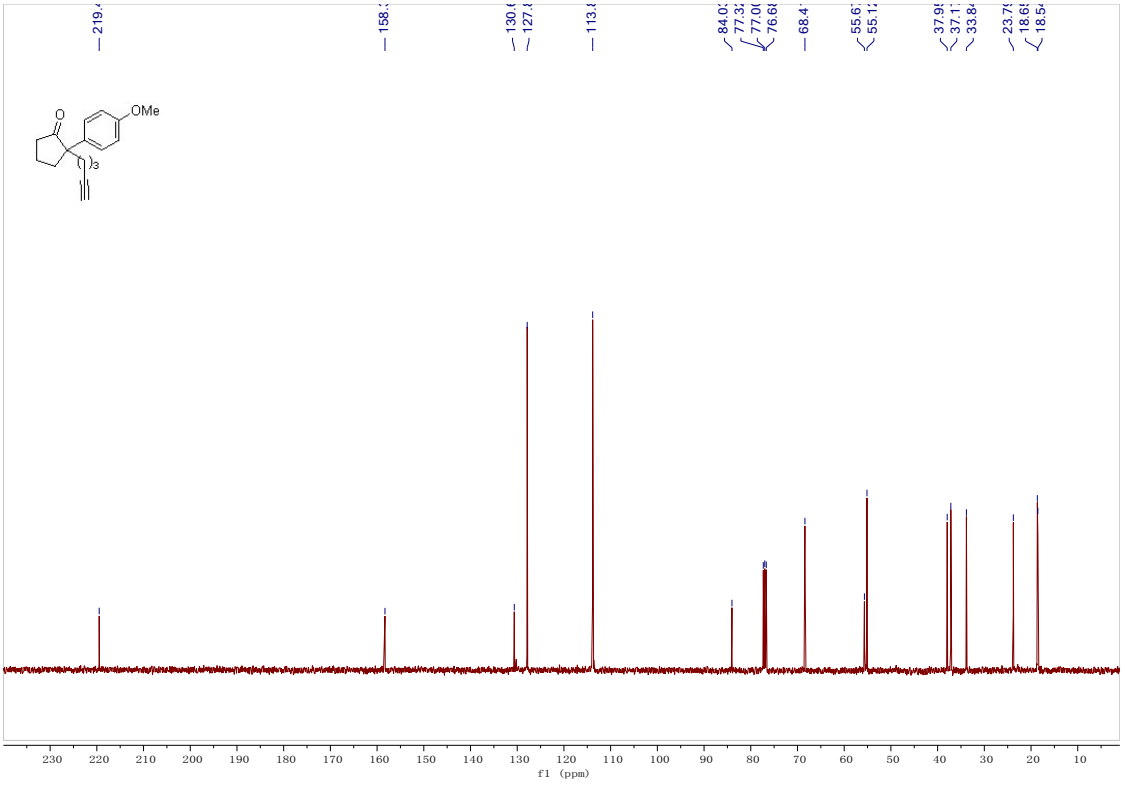
^{13}C NMR Spectrum of **3j**



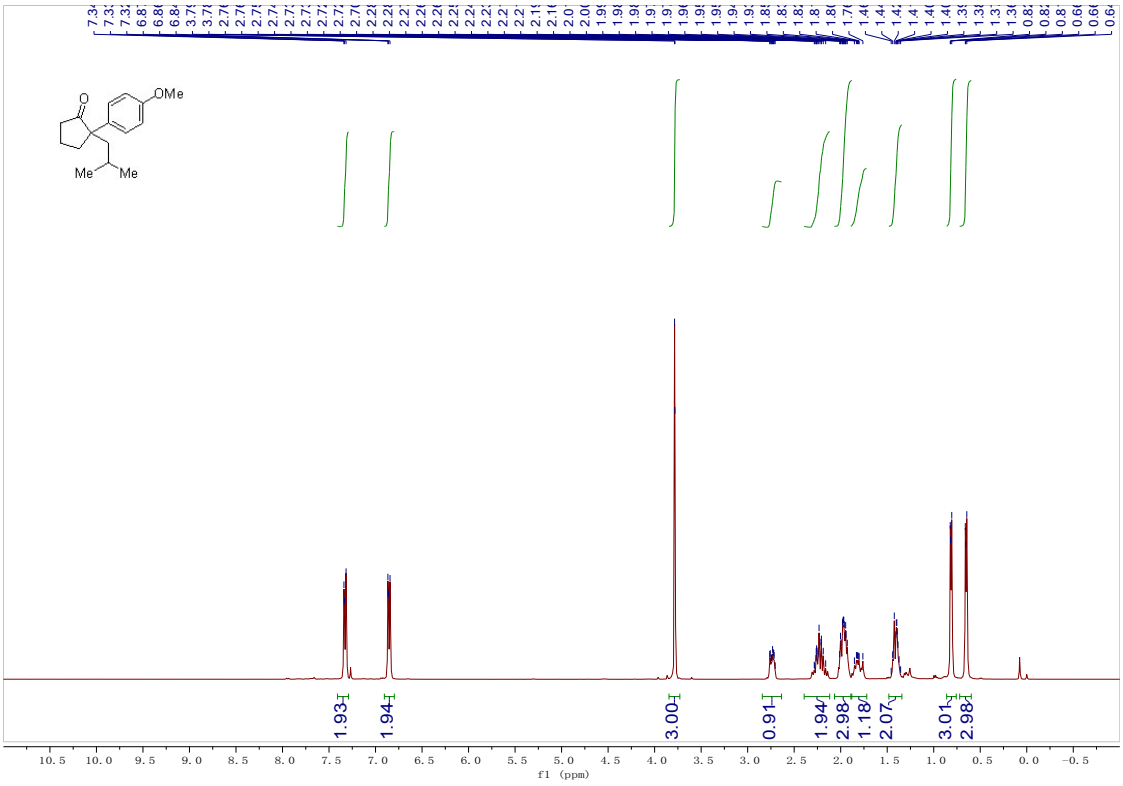
^{1}H NMR Spectrum of **3k**



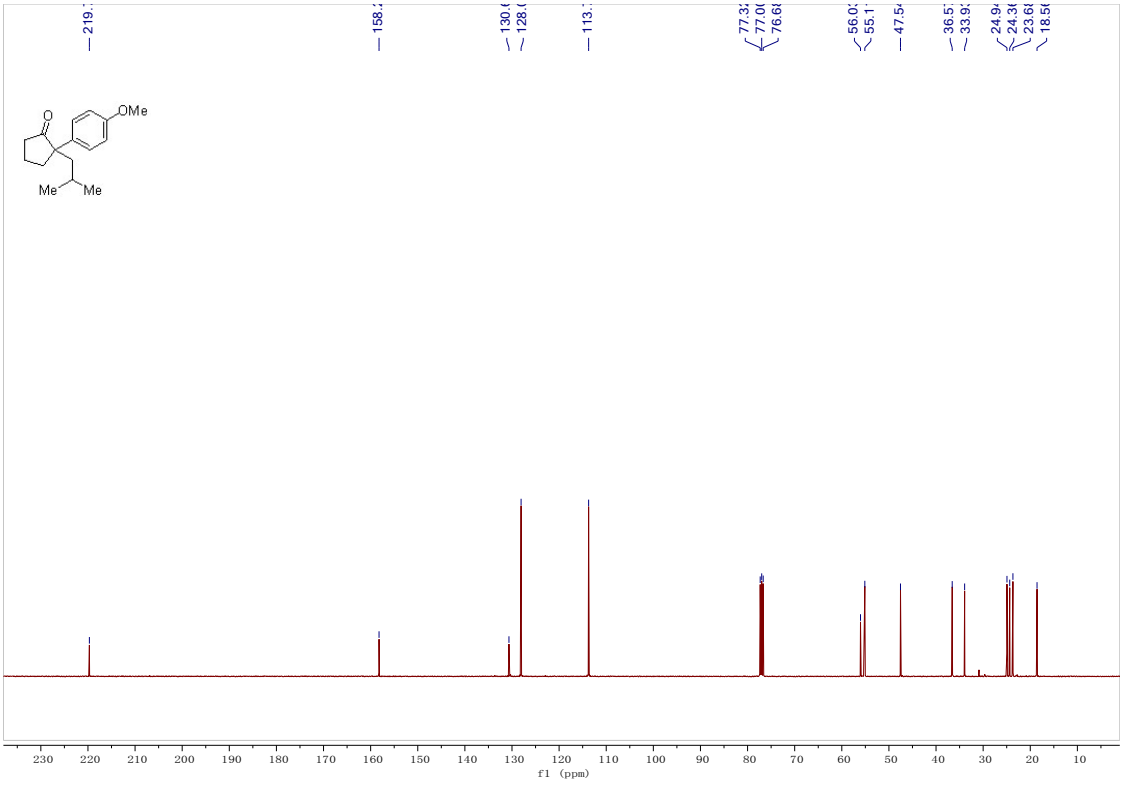
^{13}C NMR Spectrum of **3k**



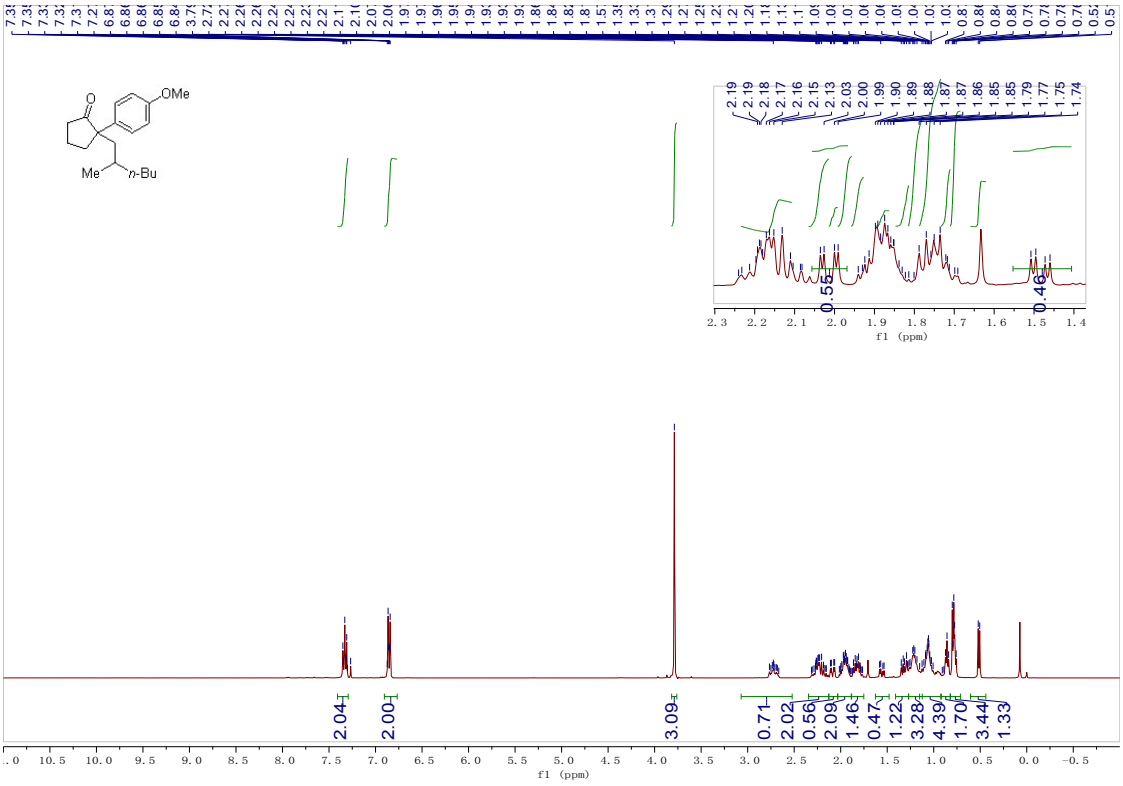
^{1}H NMR Spectrum of **3l**



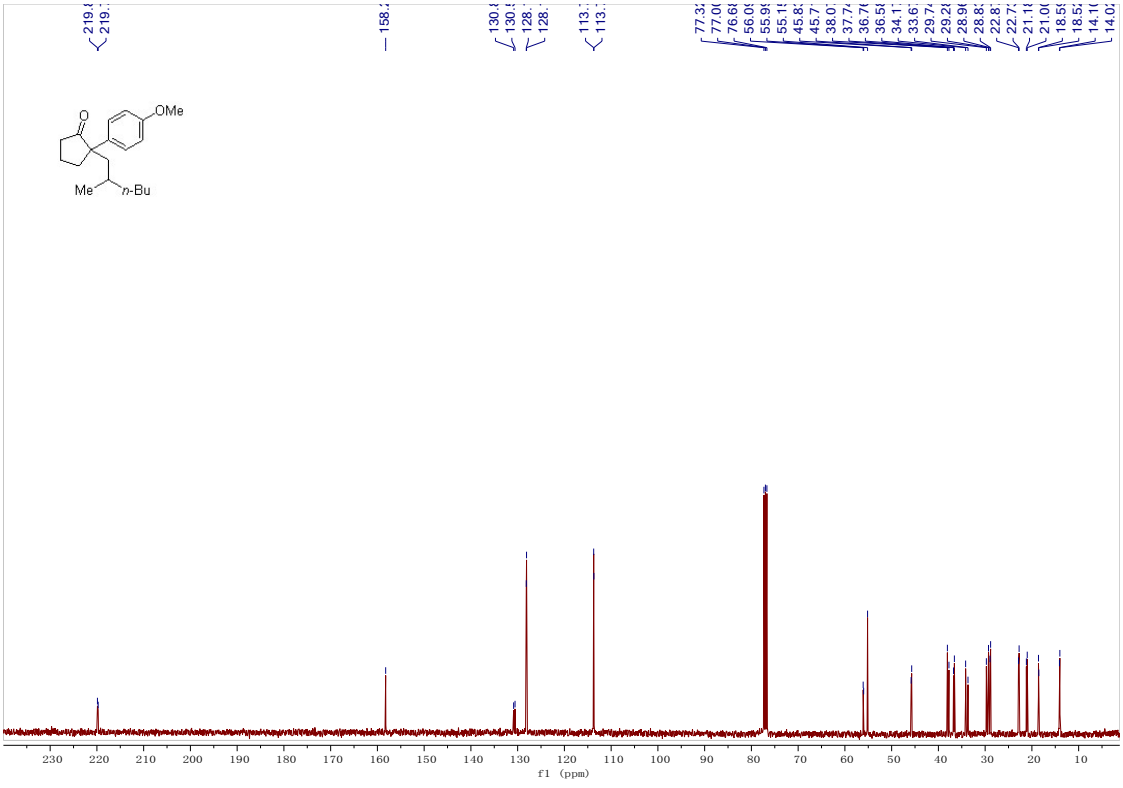
^{13}C NMR Spectrum of **3l**



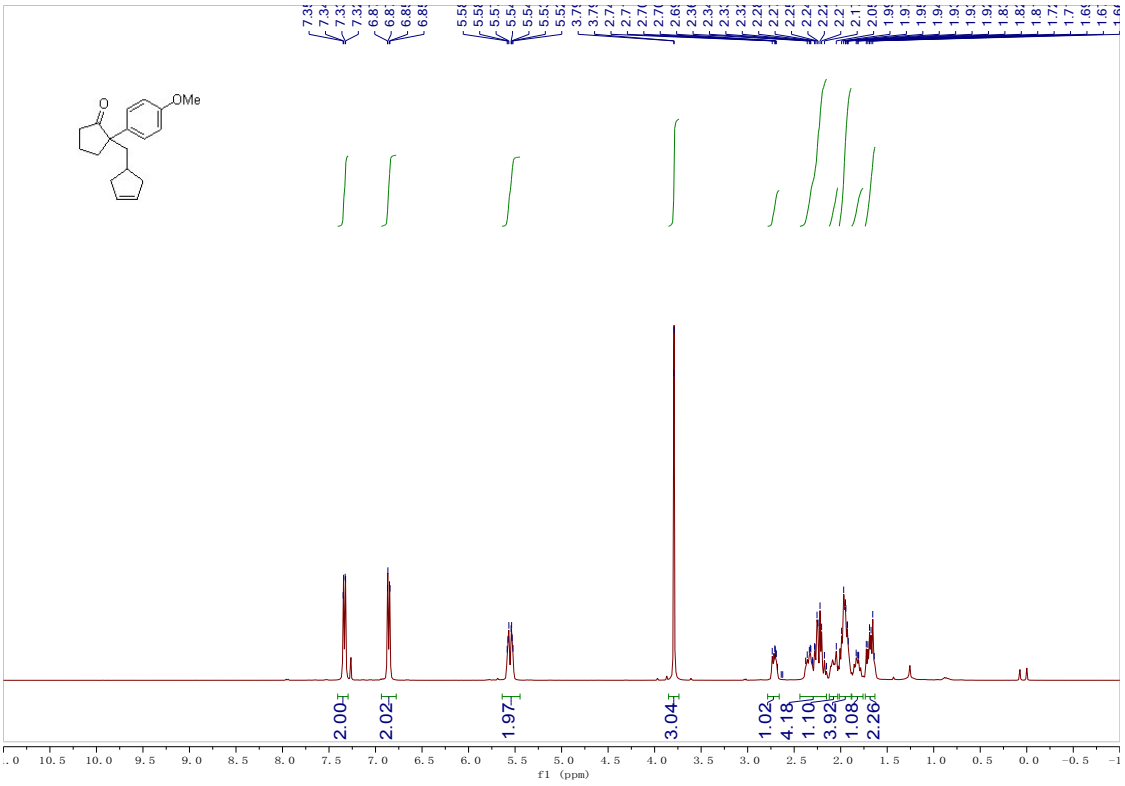
^{1}H NMR Spectrum of **3m**



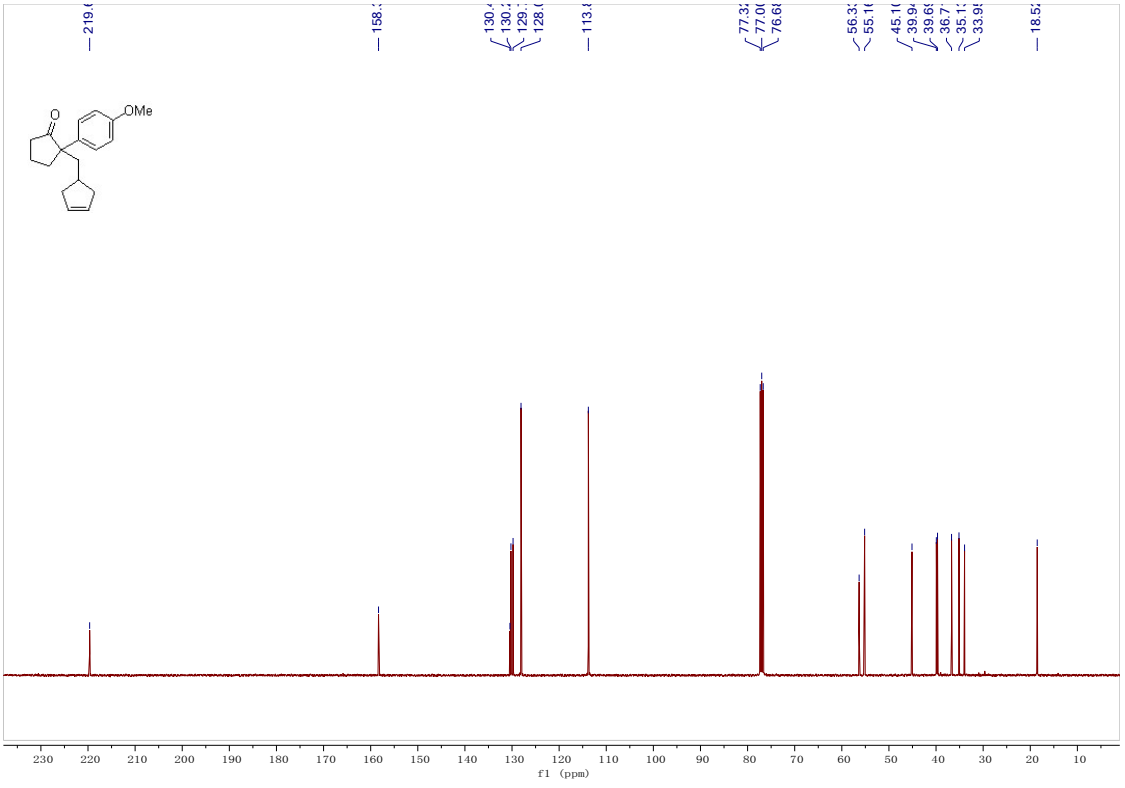
^{13}C NMR Spectrum of **3m**



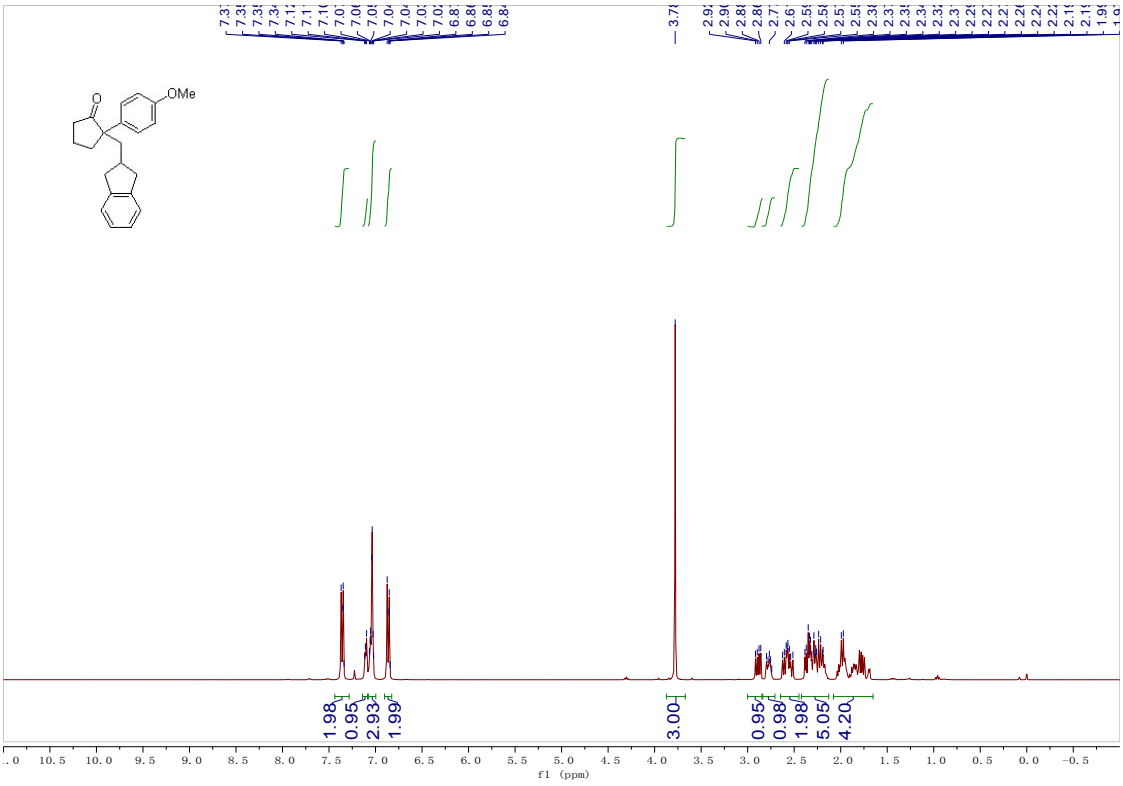
^{1}H NMR Spectrum of **3n**



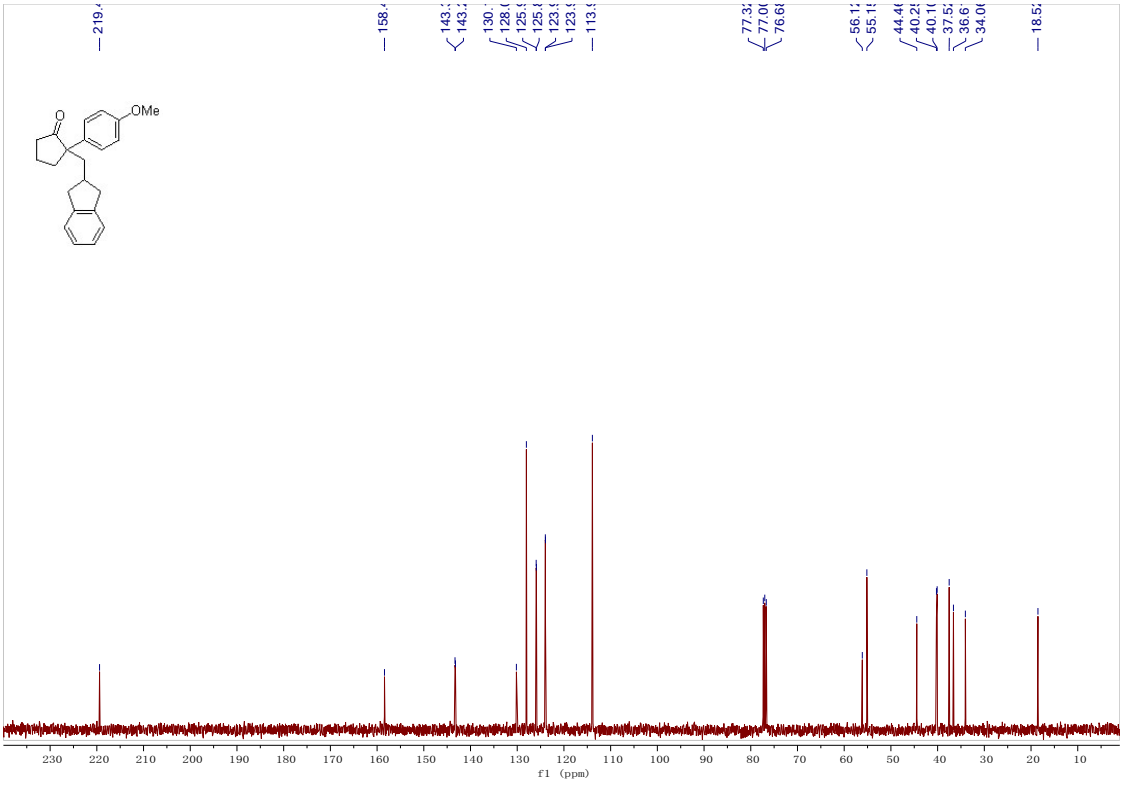
^{13}C NMR Spectrum of **3n**



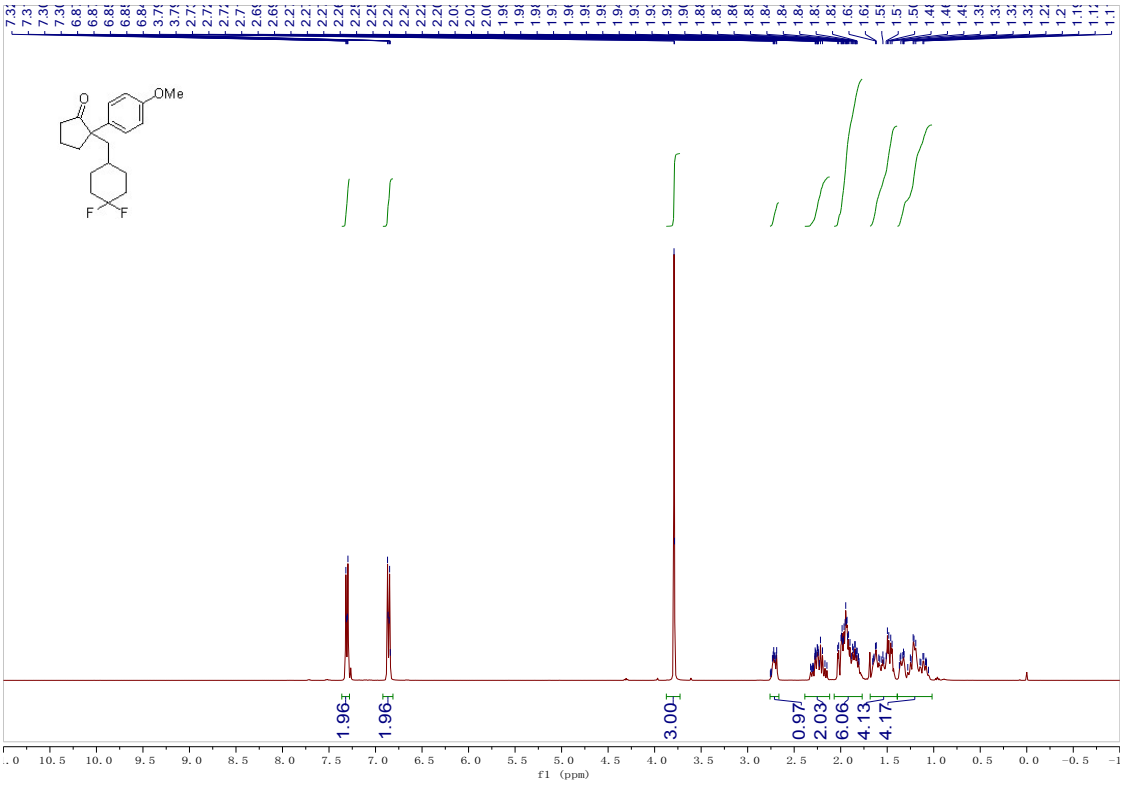
^{1}H NMR Spectrum of **3o**



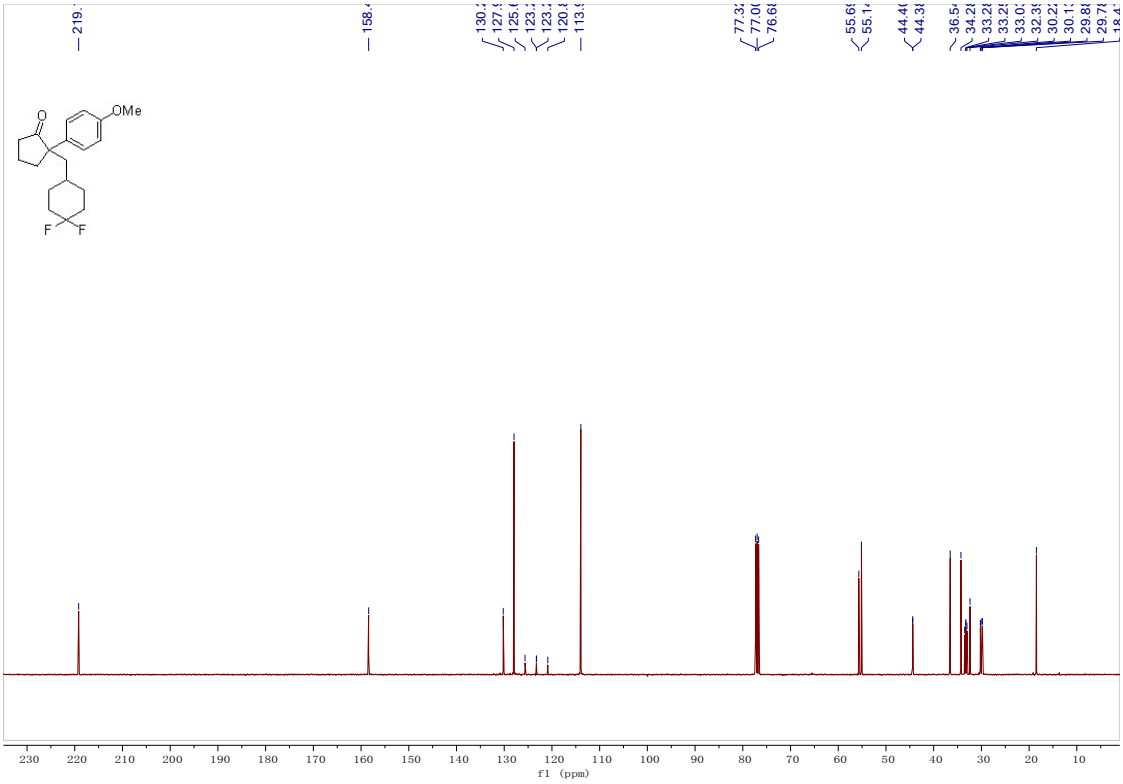
^{13}C NMR Spectrum of **3o**



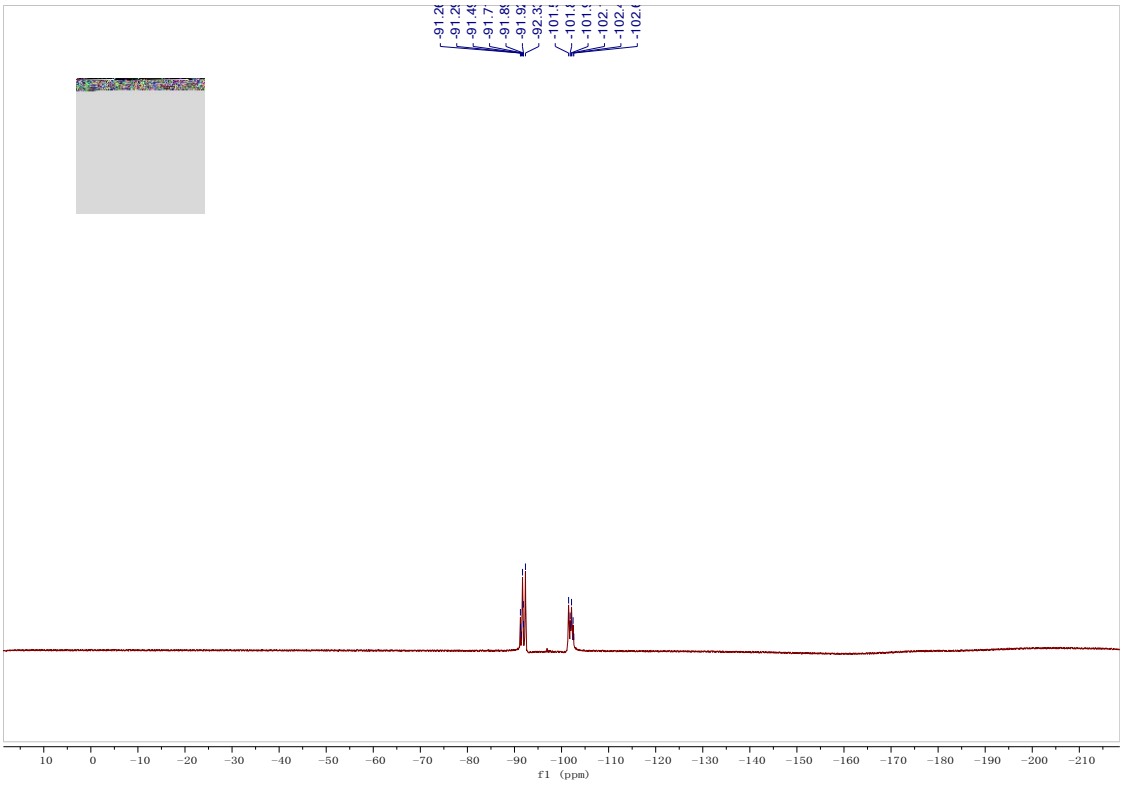
^{1}H NMR Spectrum of **3p**



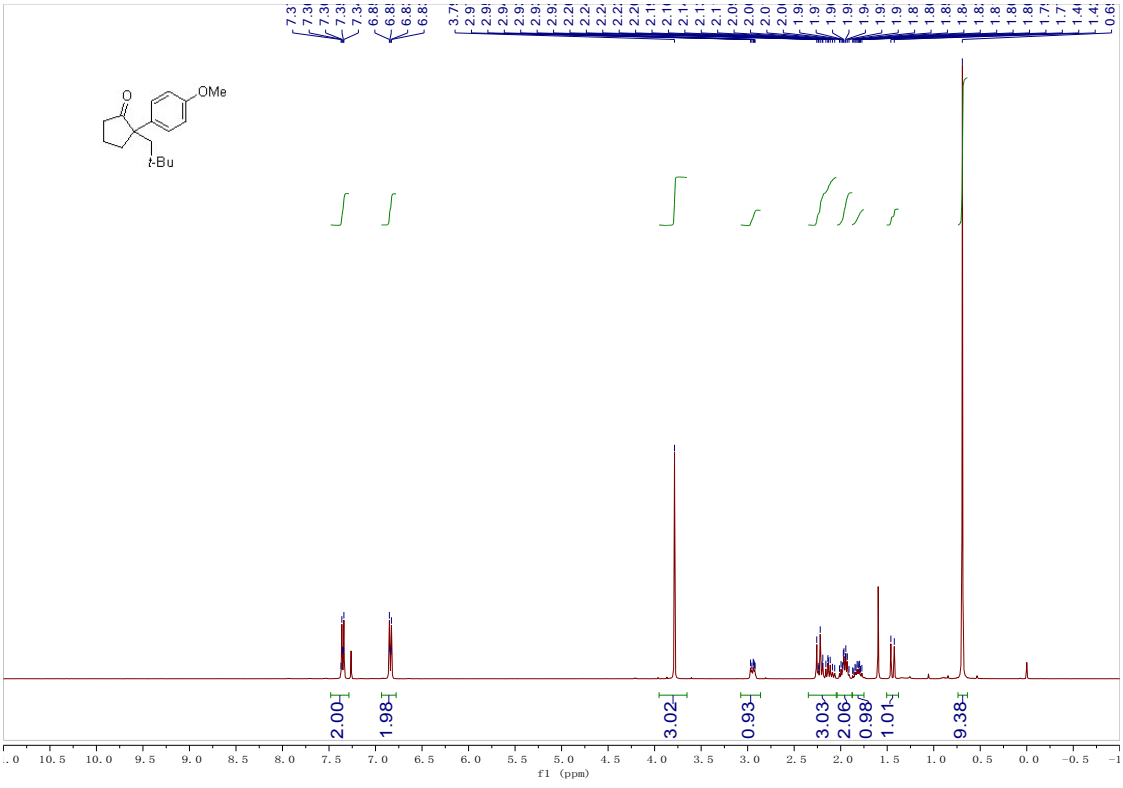
^{13}C NMR Spectrum of **3p**



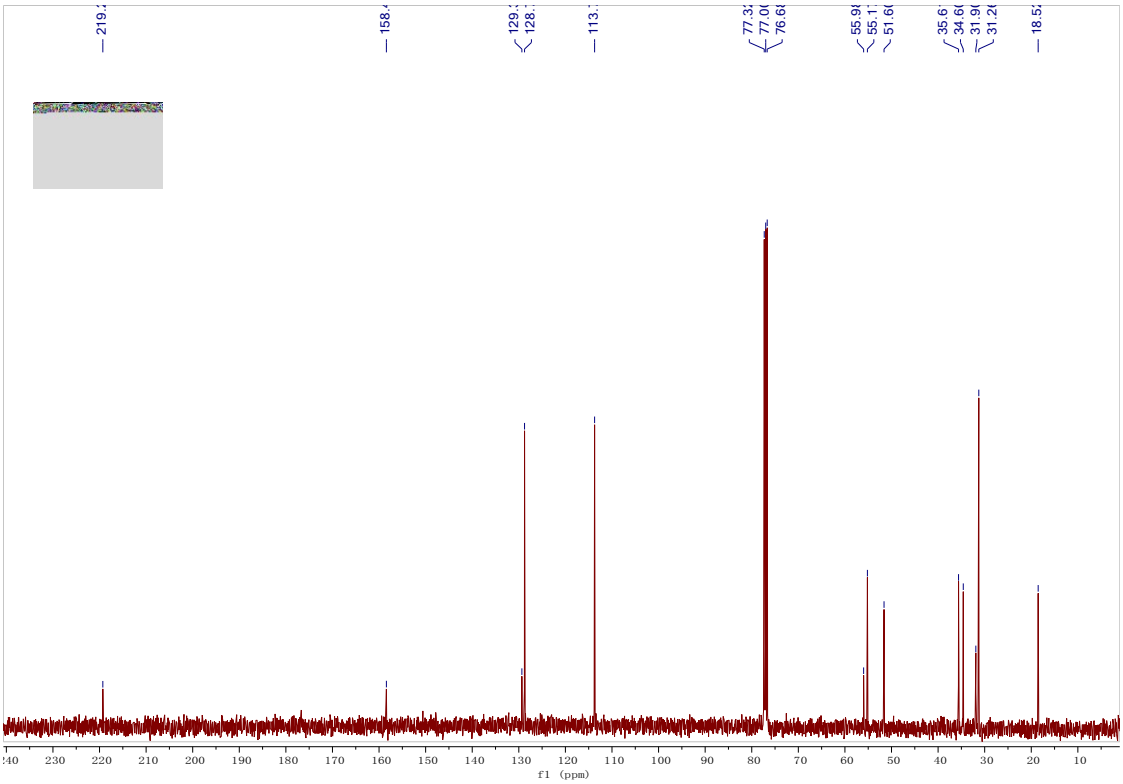
^{19}F NMR Spectrum of **3p**



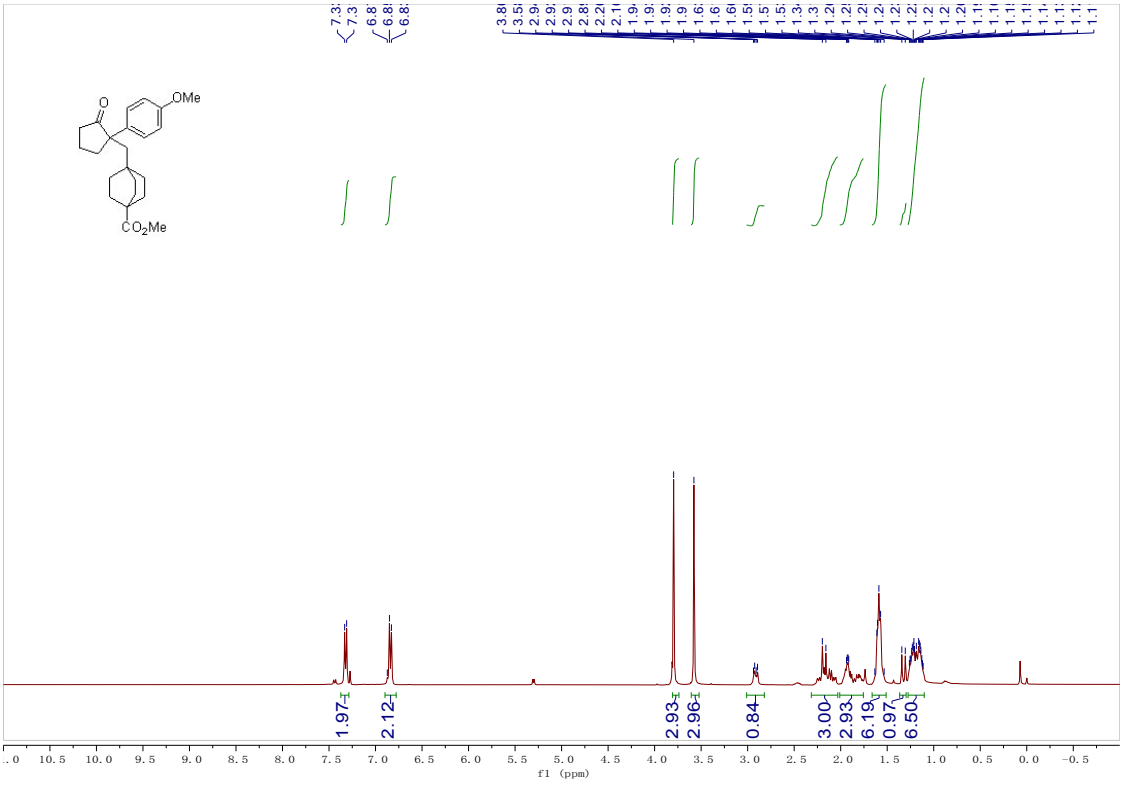
^{1}H NMR Spectrum of **3q**



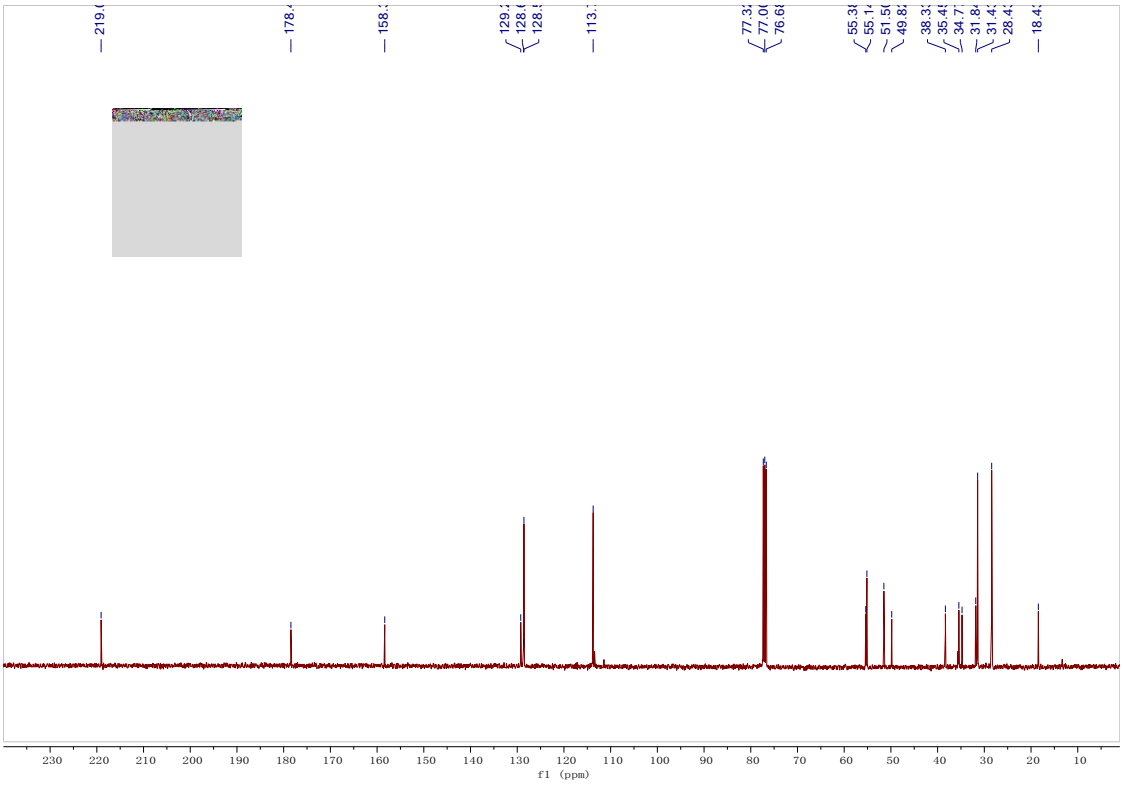
^{13}C NMR Spectrum of **3q**



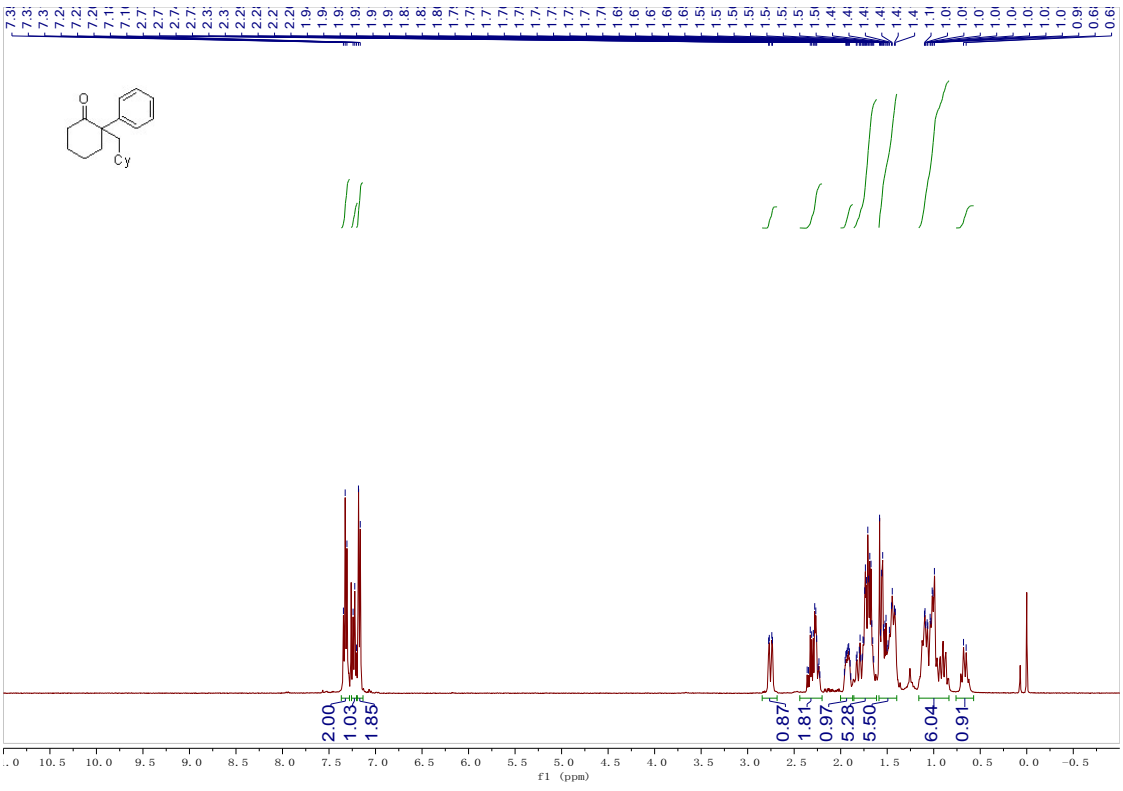
^{1}H NMR Spectrum of **3r**



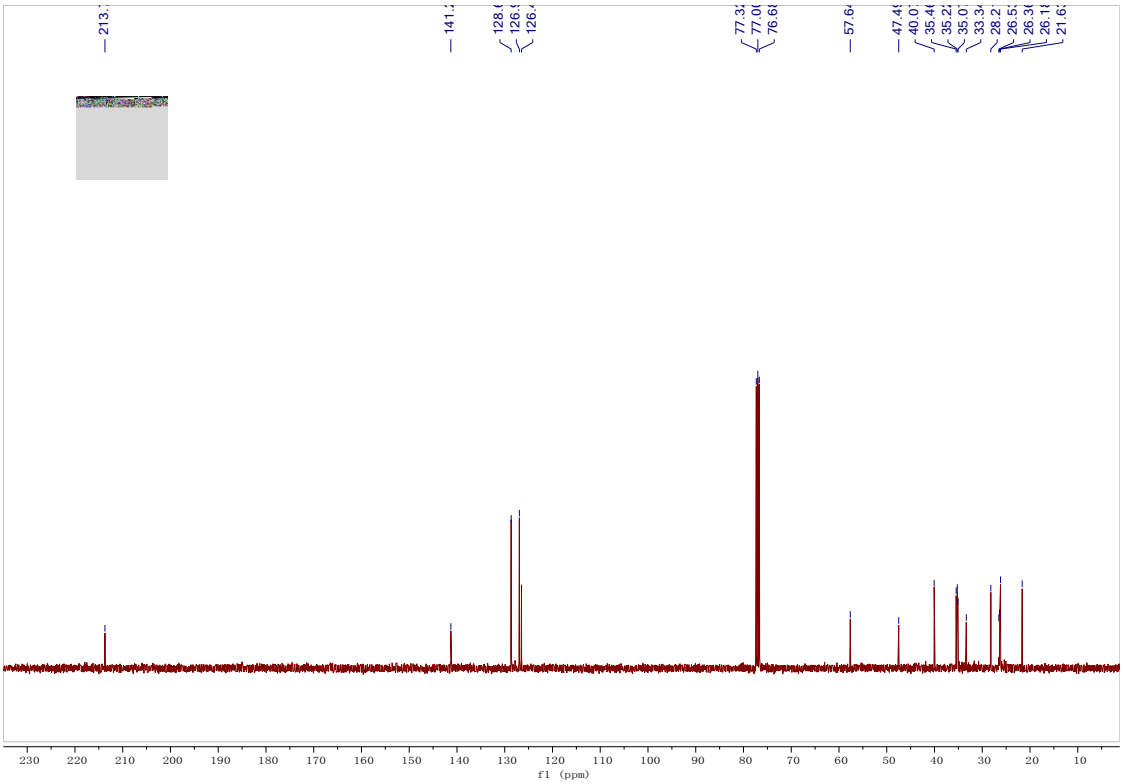
^{13}C NMR Spectrum of **3r**



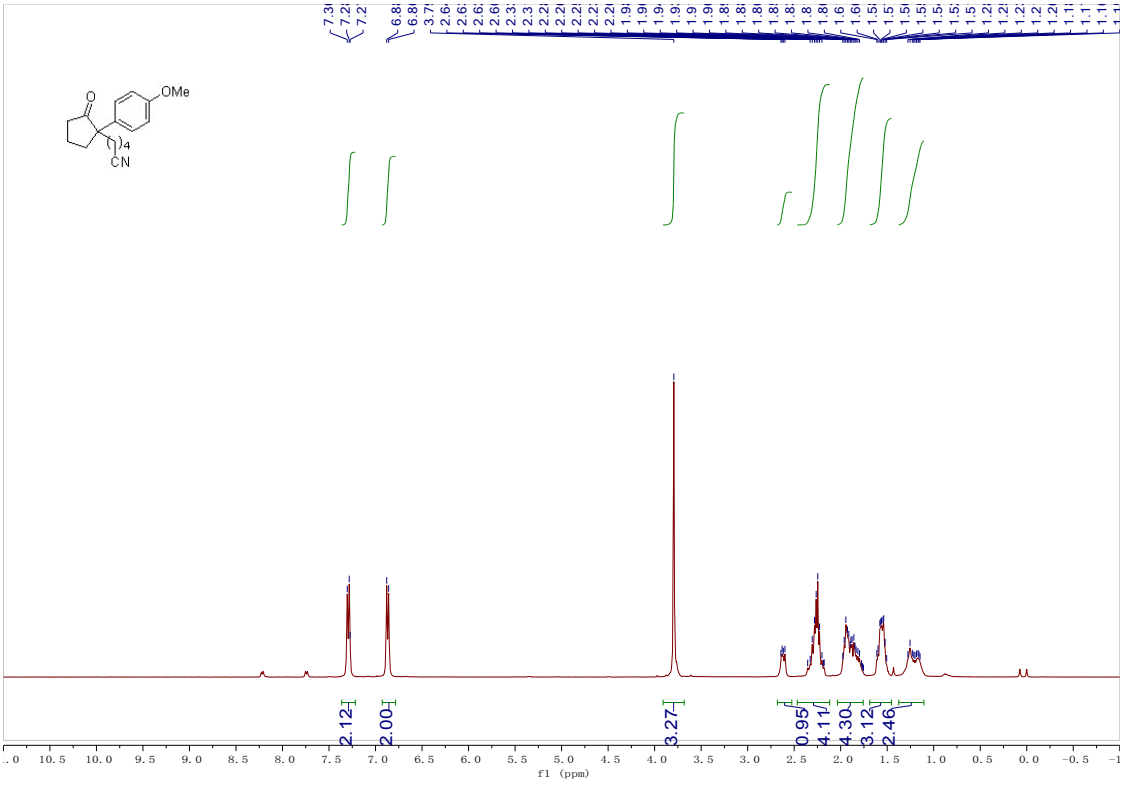
^{1}H NMR Spectrum of **3s**



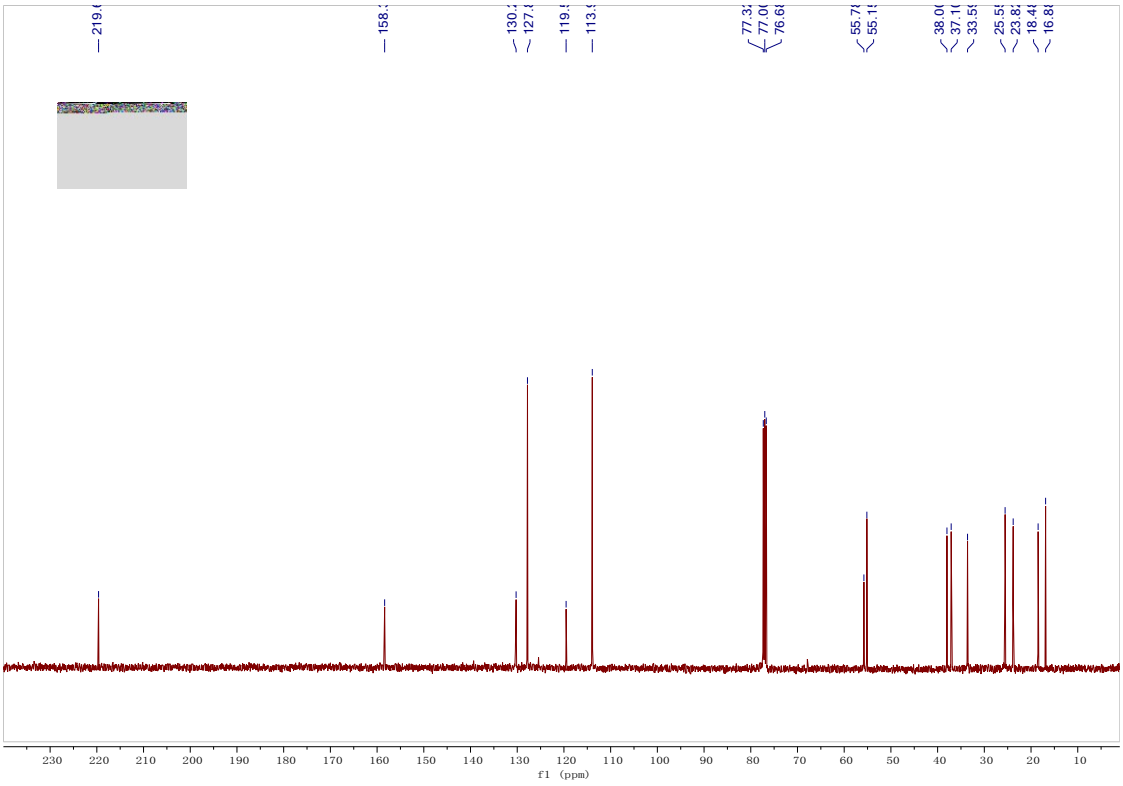
^{13}C NMR Spectrum of **3s**



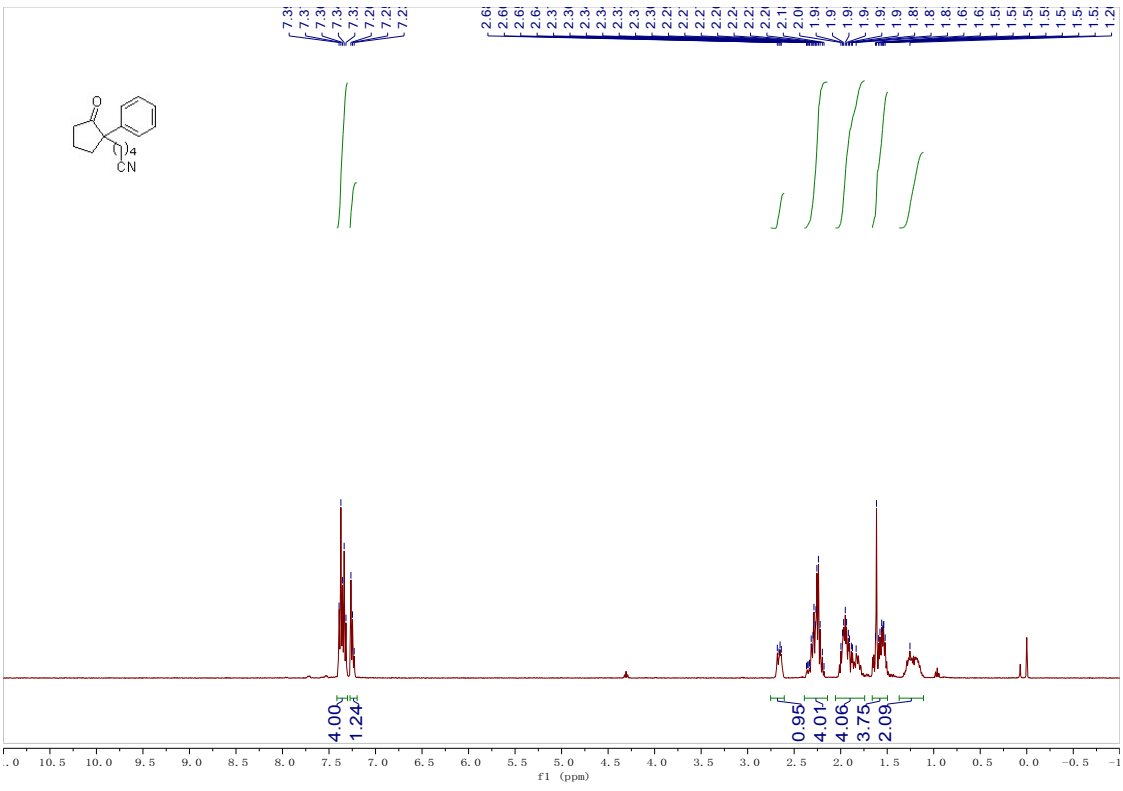
^{1}H NMR Spectrum of **5a**



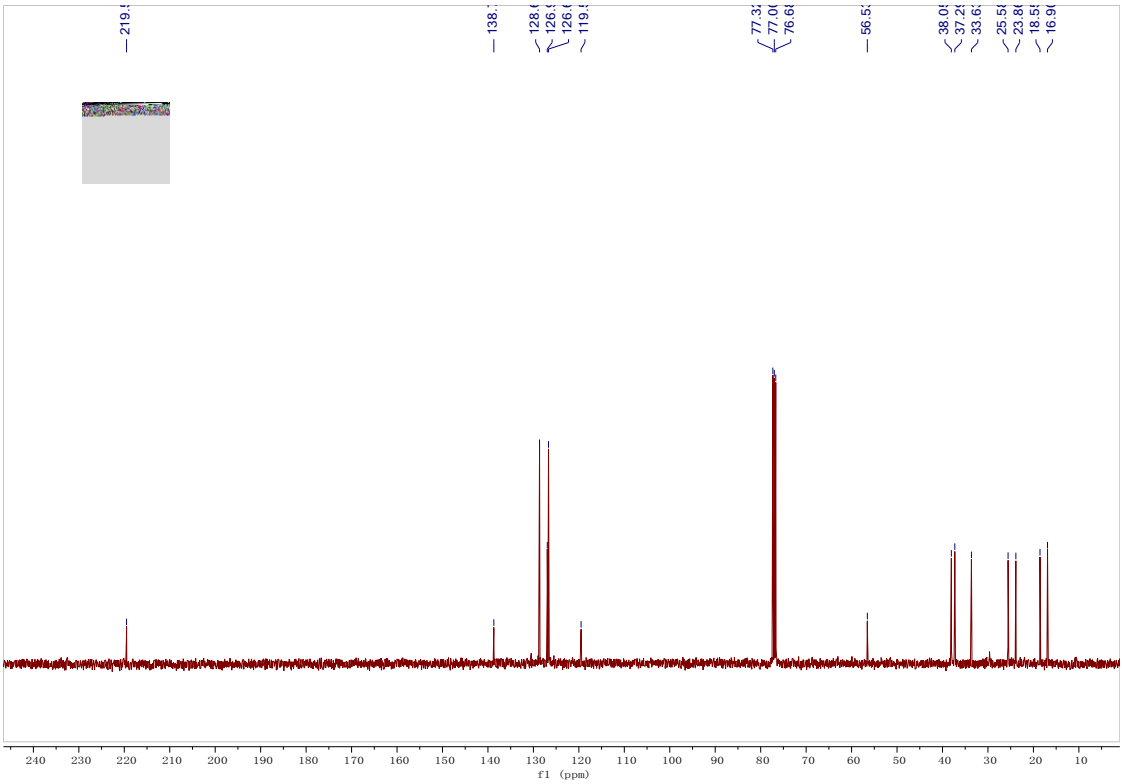
^{13}C NMR Spectrum of **5a**



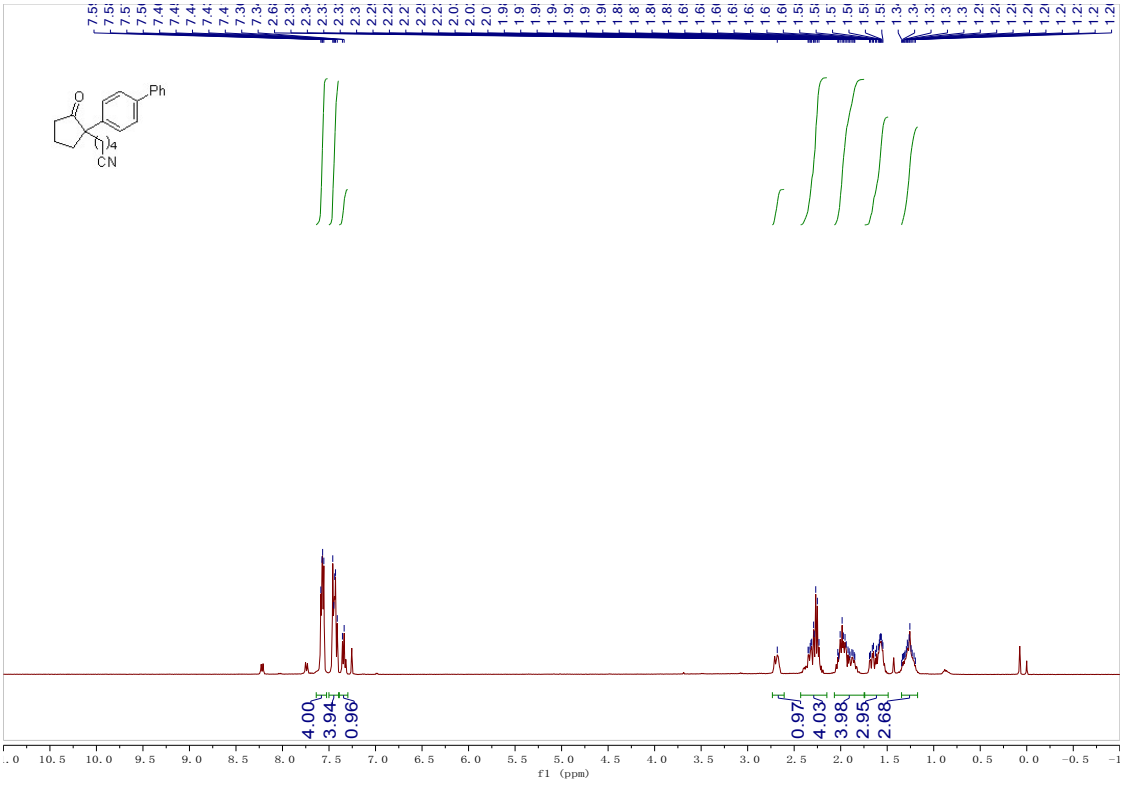
^{1}H NMR Spectrum of **5b**



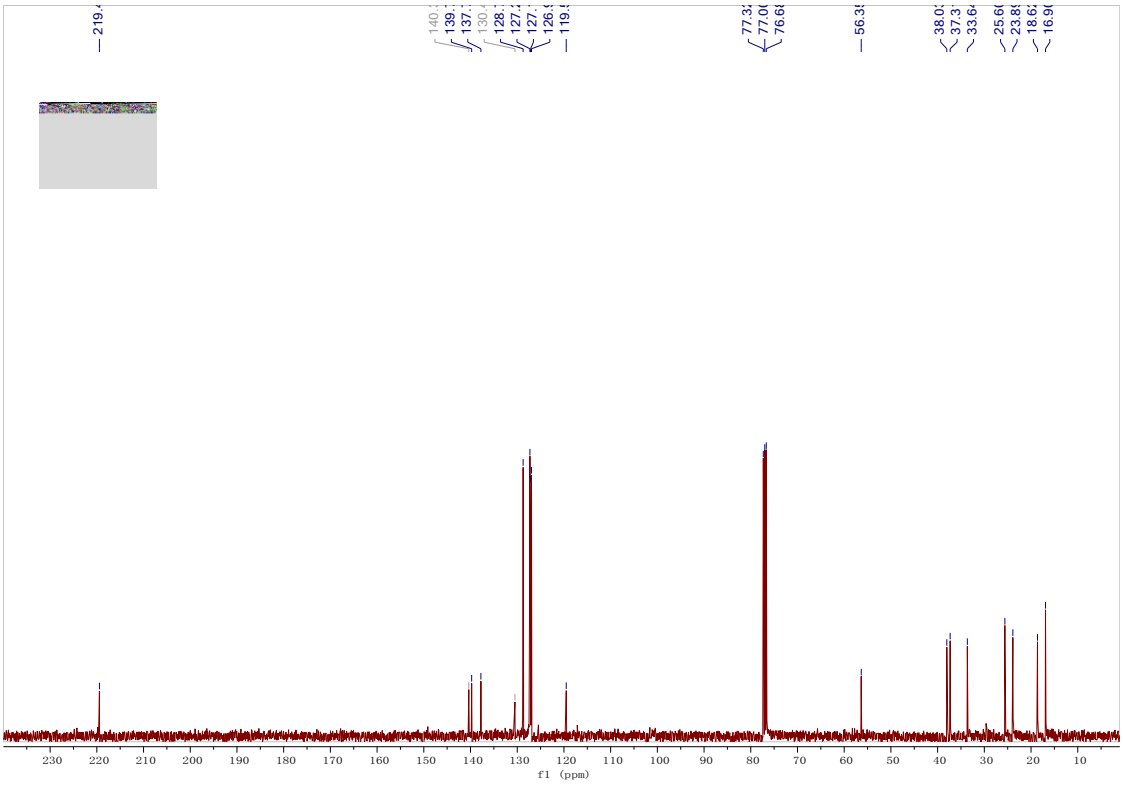
^{13}C NMR Spectrum of **5b**



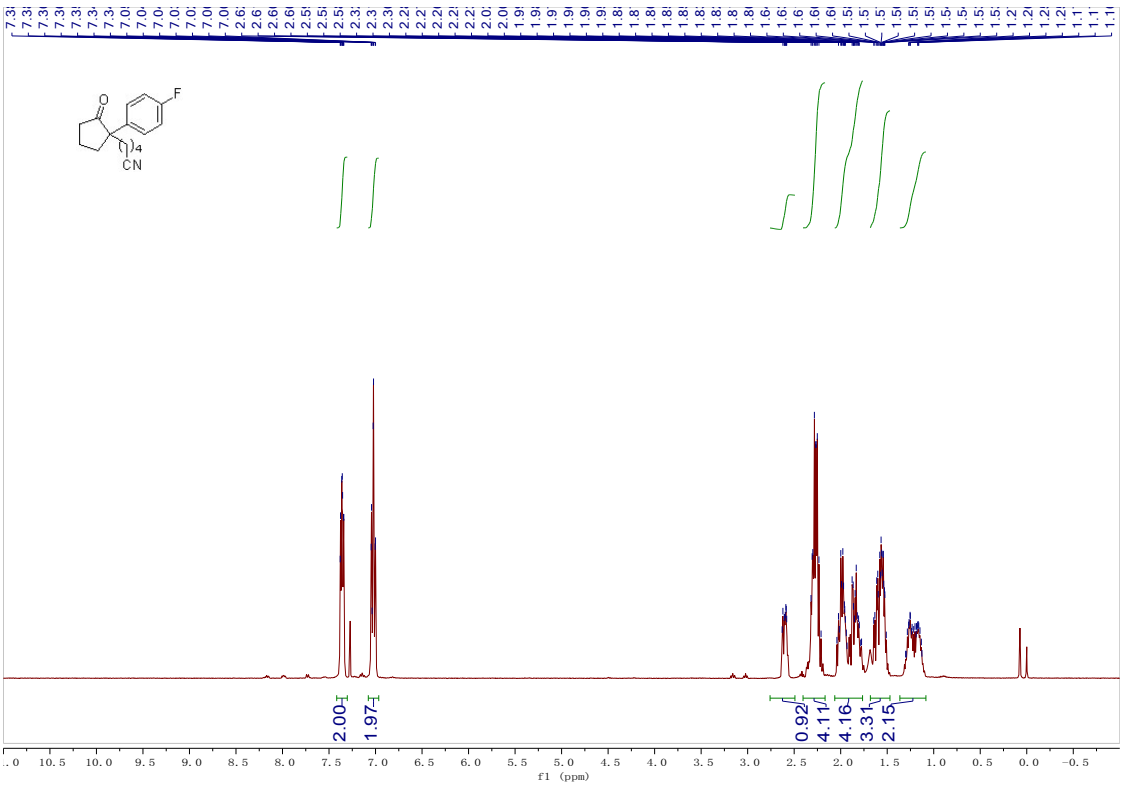
^{1}H NMR Spectrum of **5c**



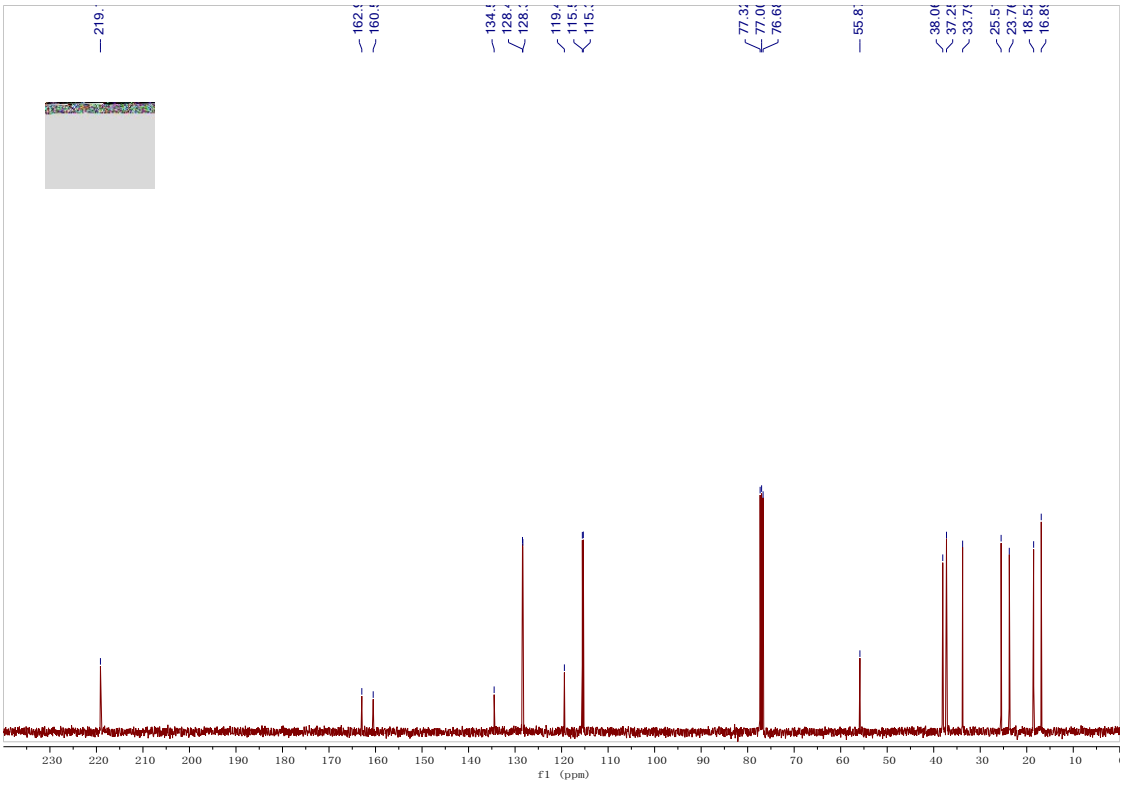
^{13}C NMR Spectrum of **5c**



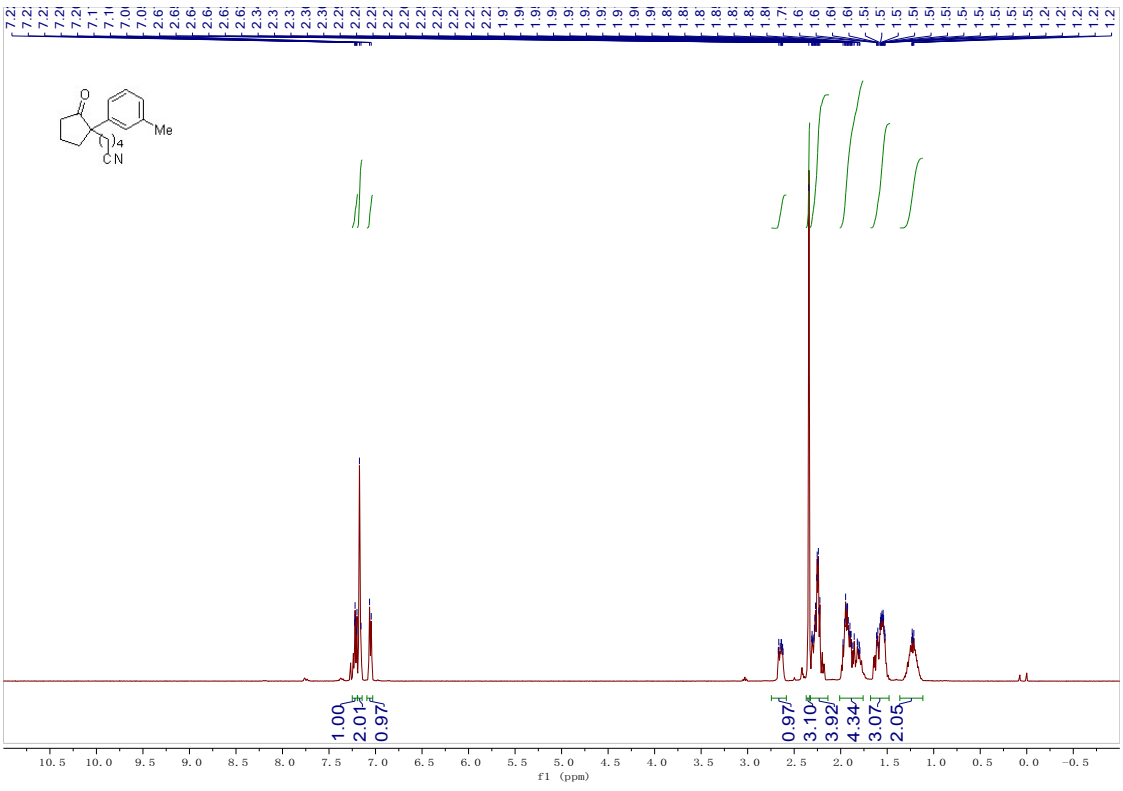
^{1}H NMR Spectrum of **5d**



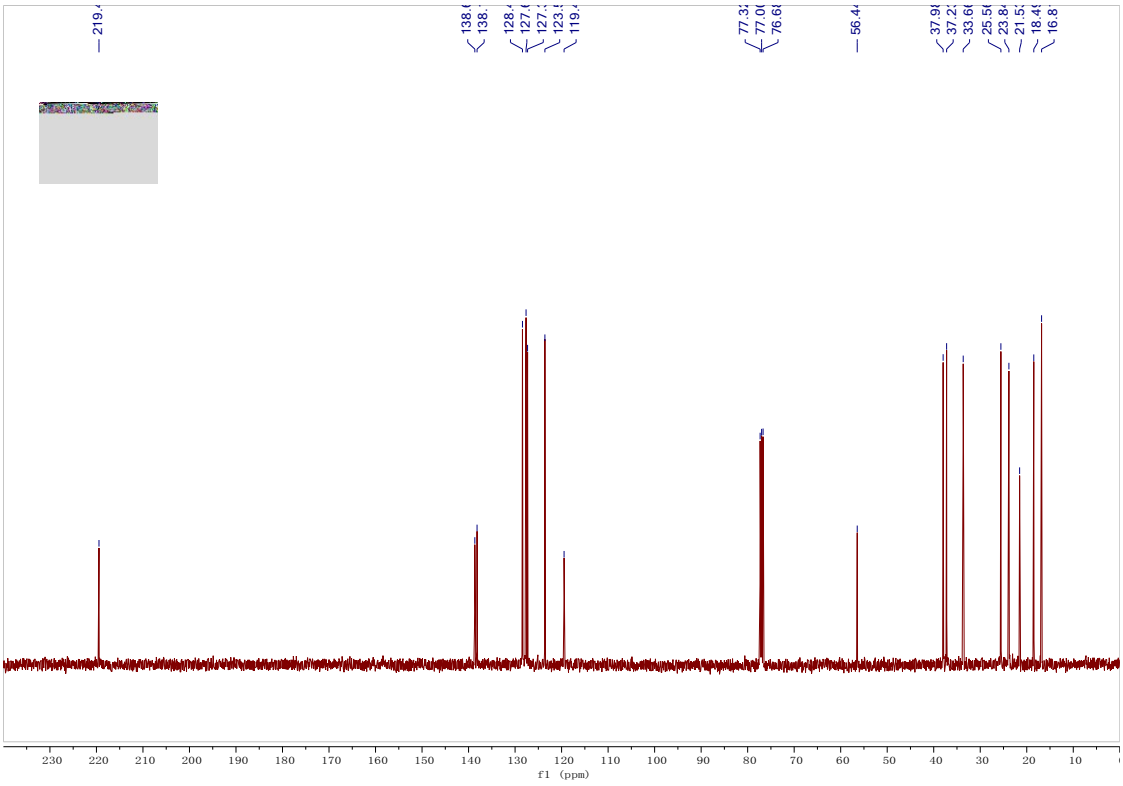
^{13}C NMR Spectrum of **5d**



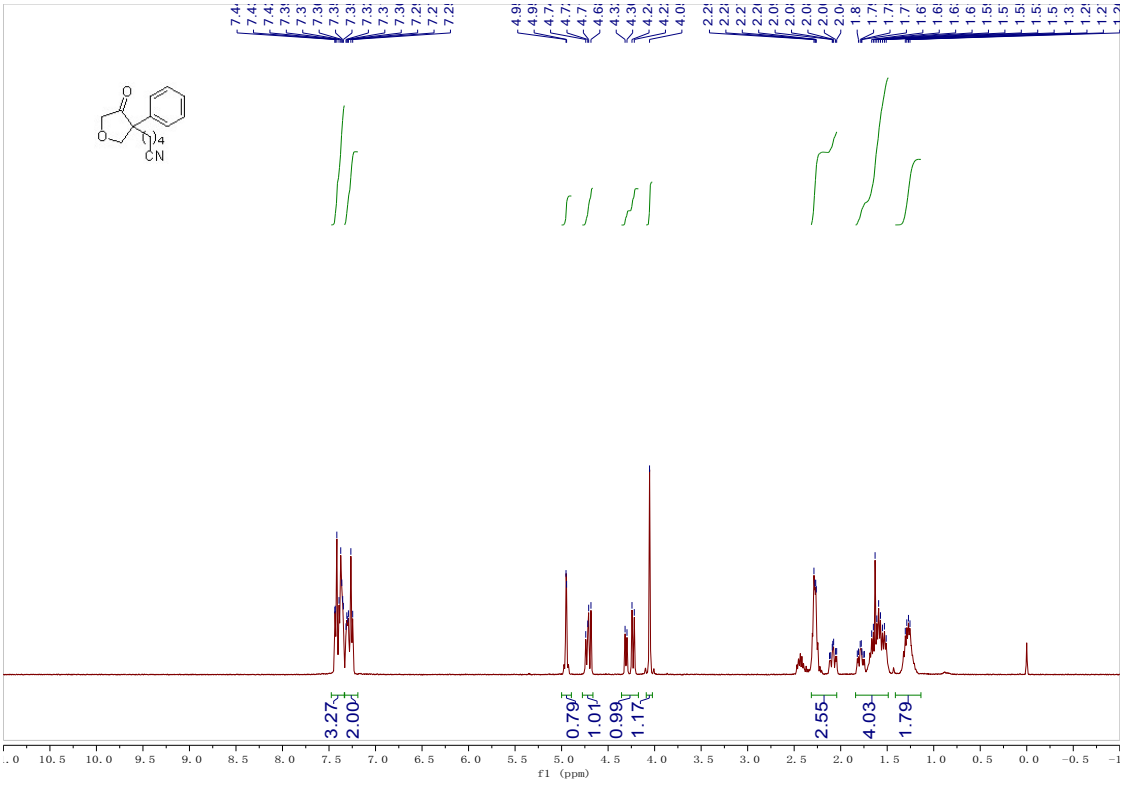
^{1}H NMR Spectrum of **5e**



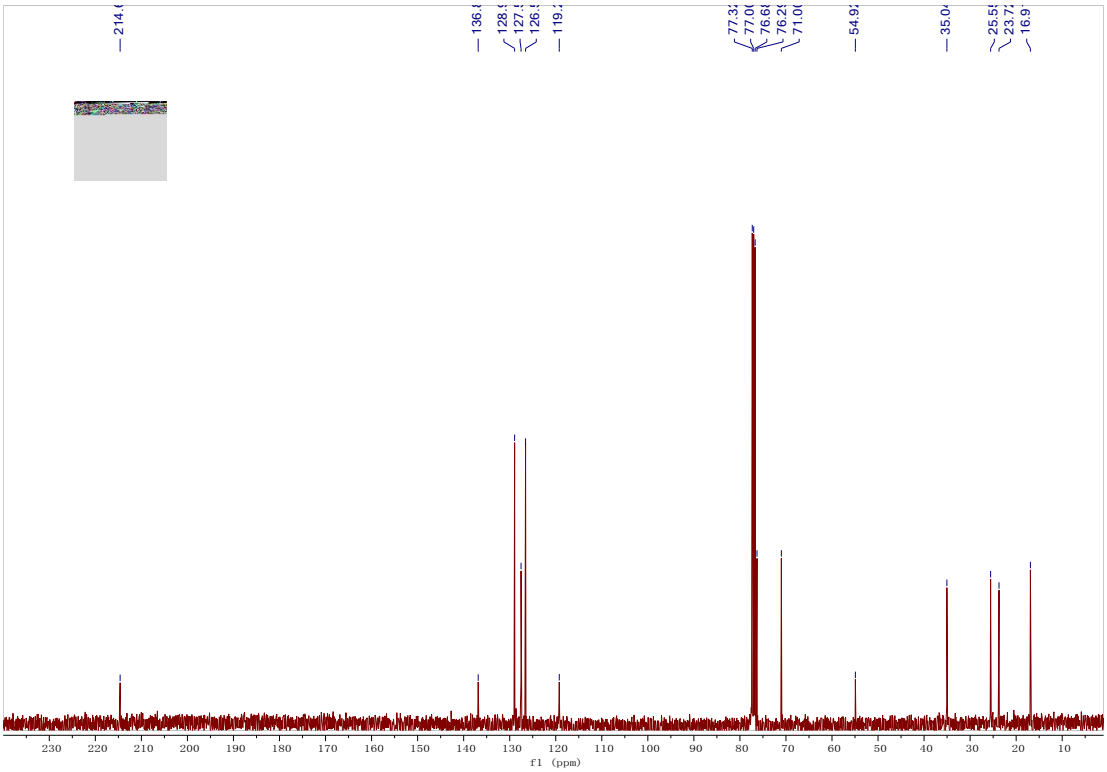
^{13}C NMR Spectrum of **5e**



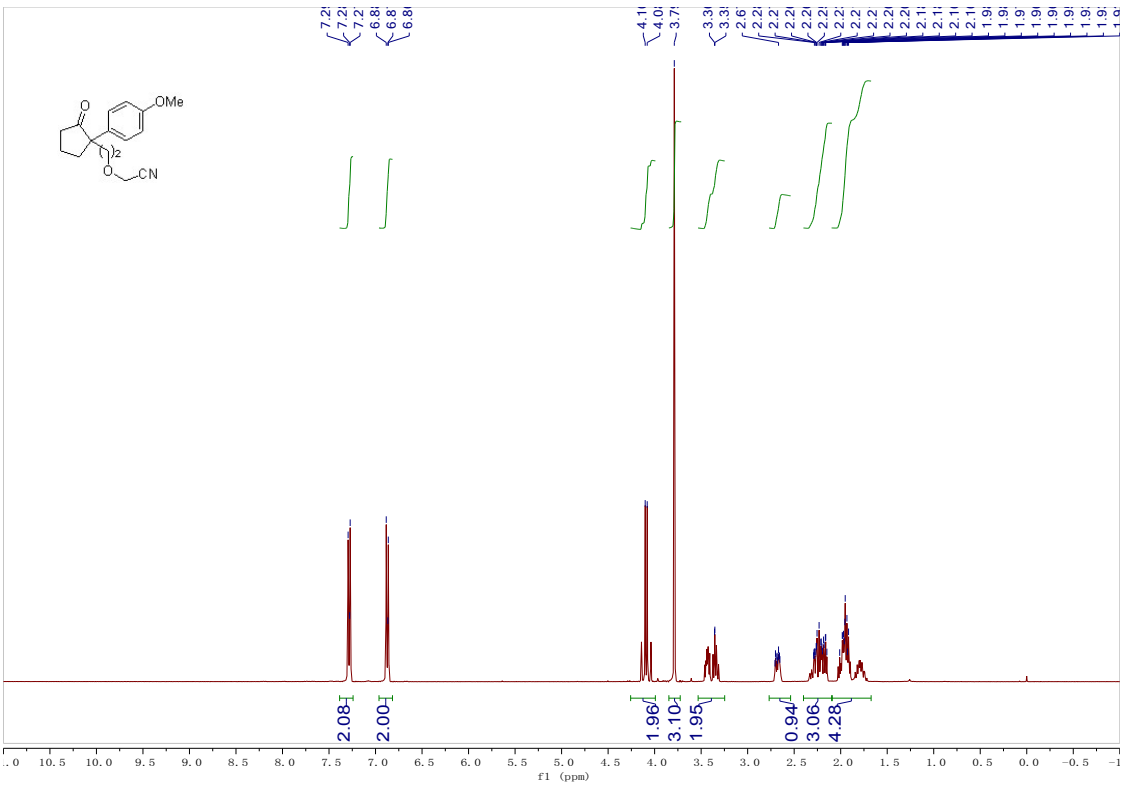
^{1}H NMR Spectrum of **5f**



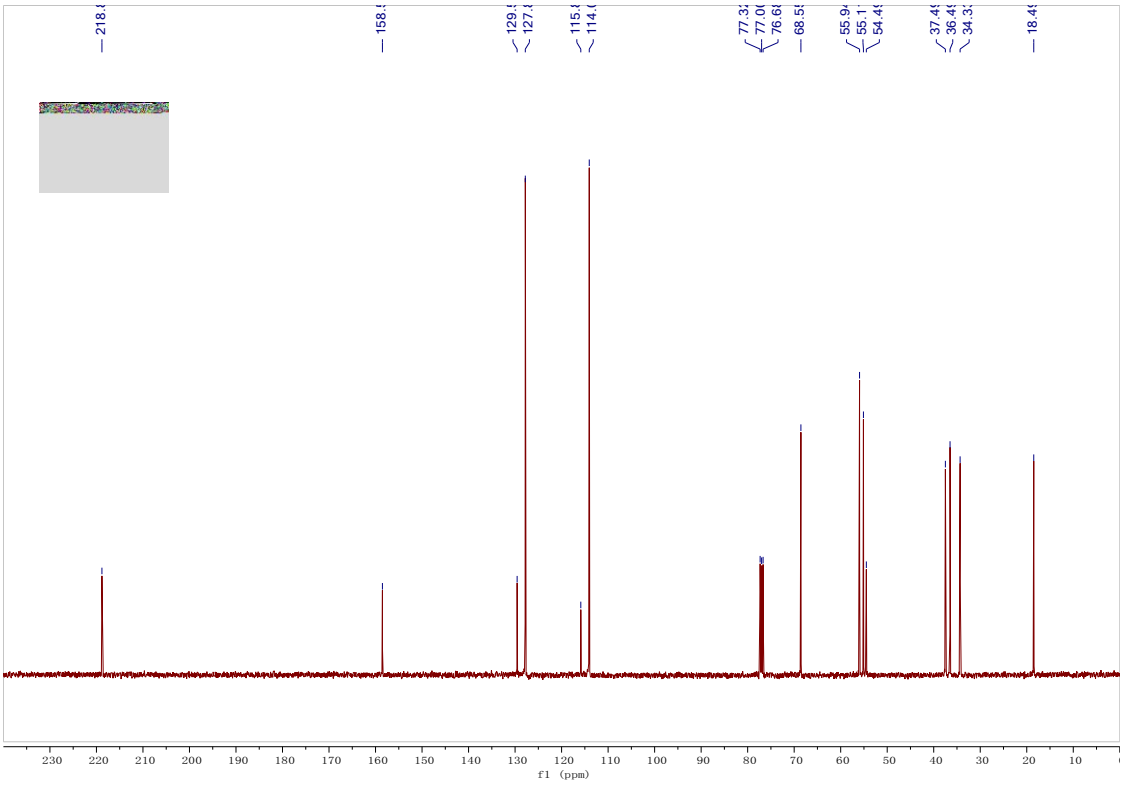
^{13}C NMR Spectrum of **5f**



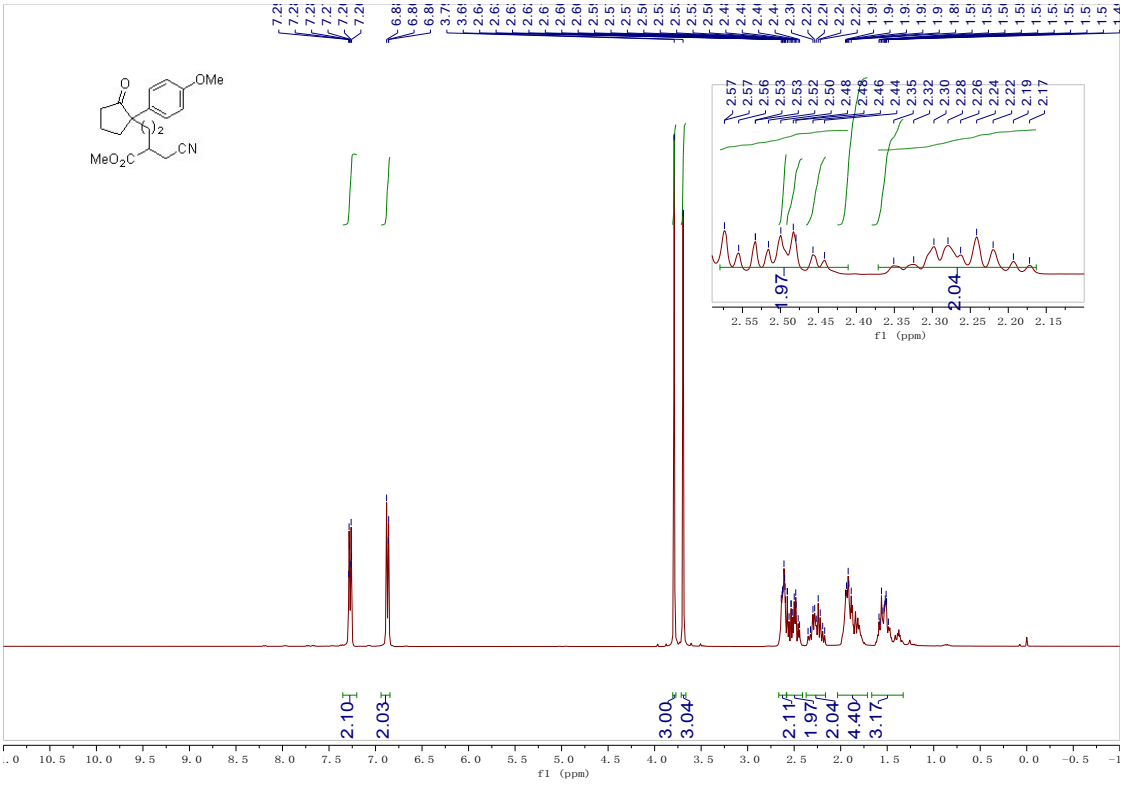
^{1}H NMR Spectrum of **5g**



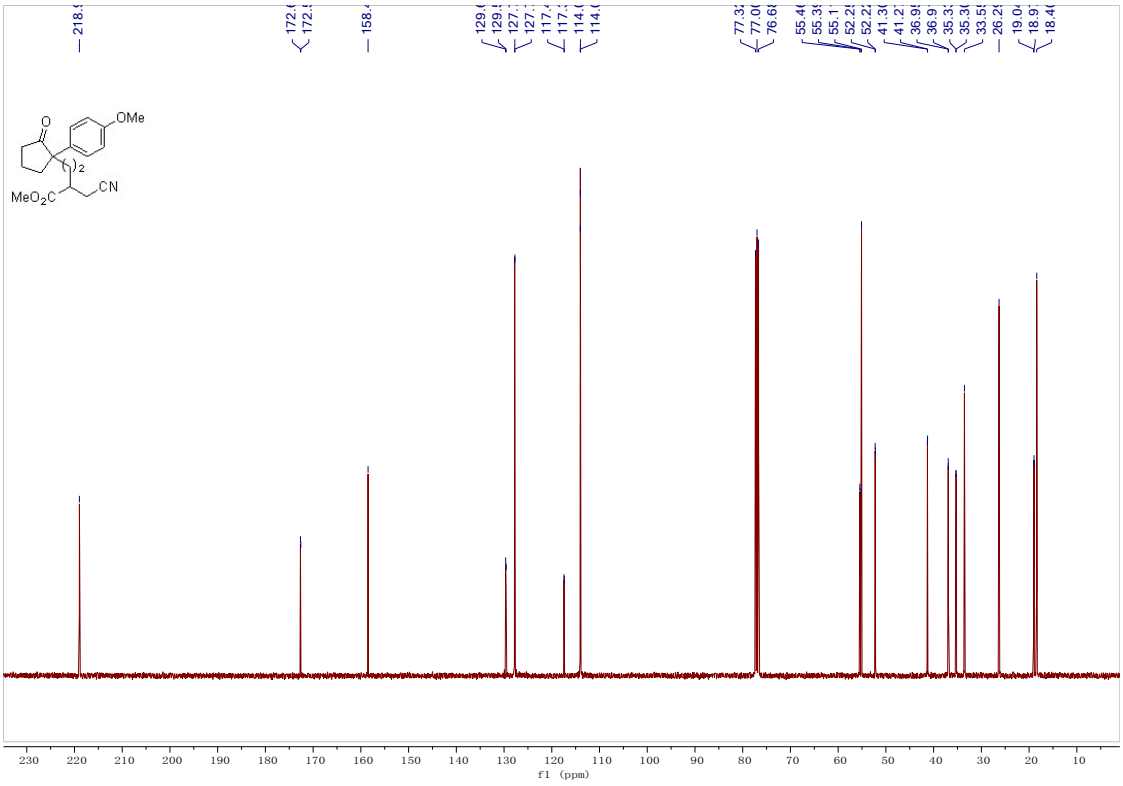
^{13}C NMR Spectrum of **5g**



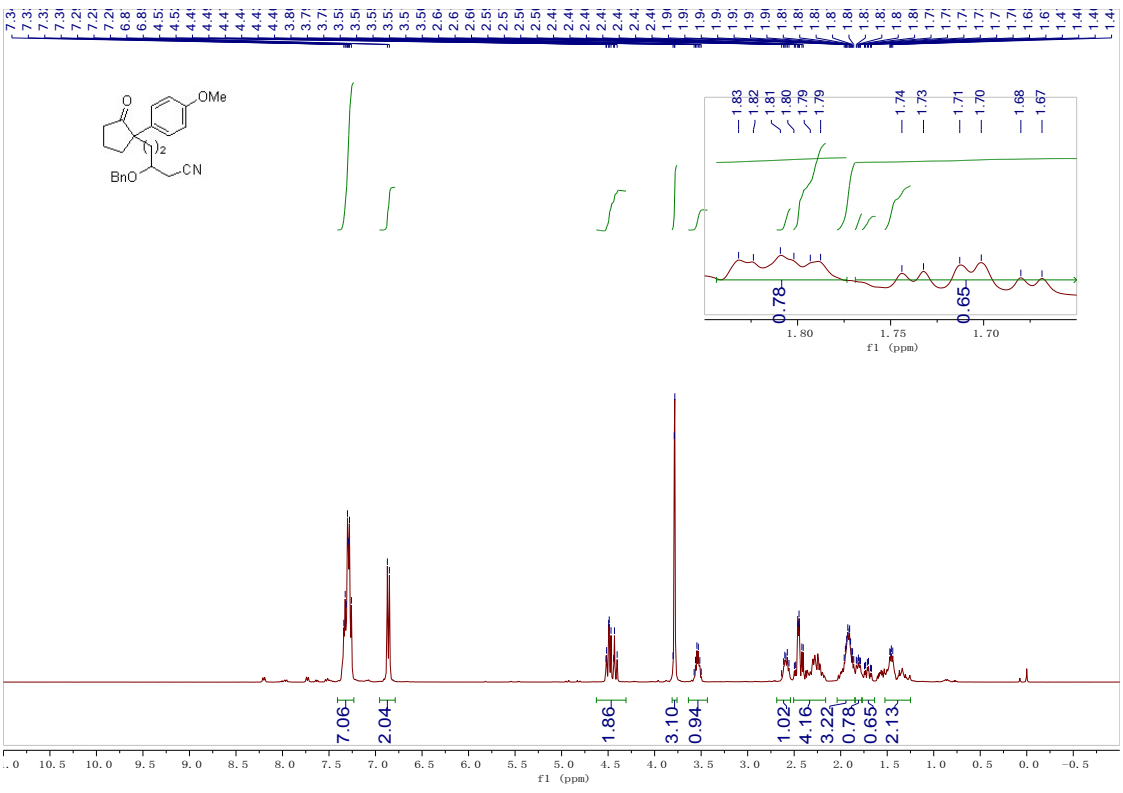
^{1}H NMR Spectrum of **5h**



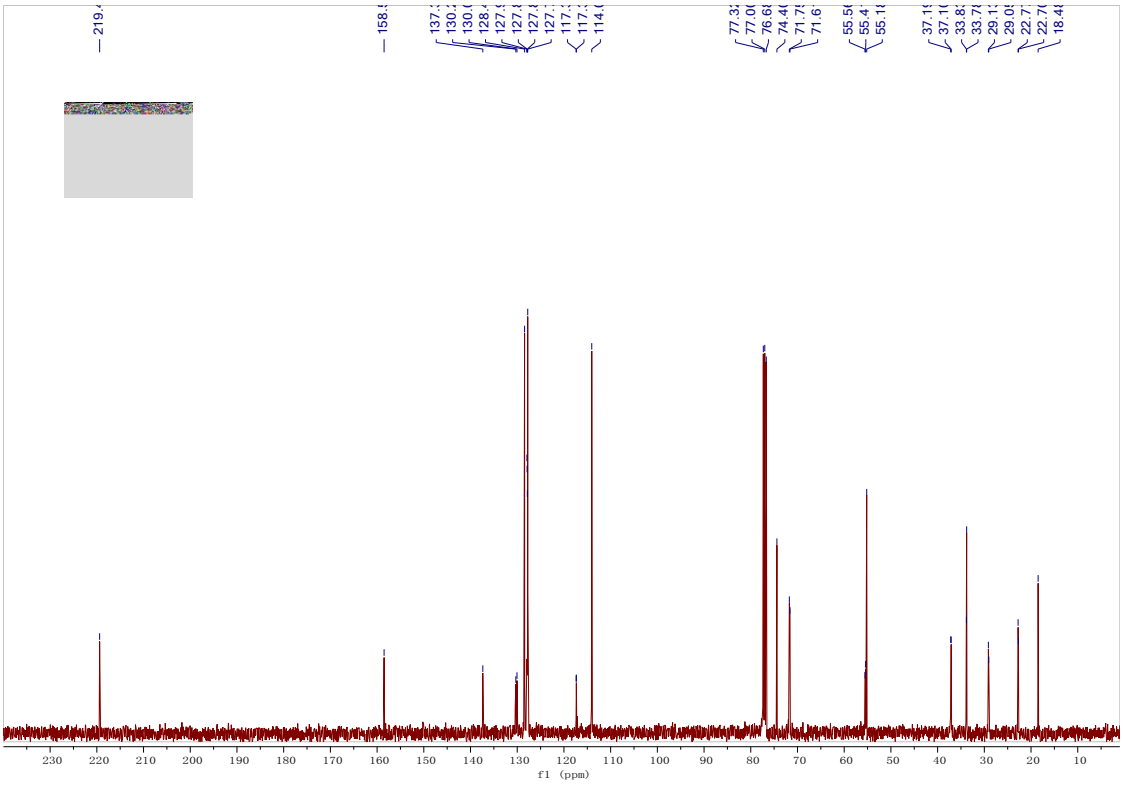
^{13}C NMR Spectrum of **5h**



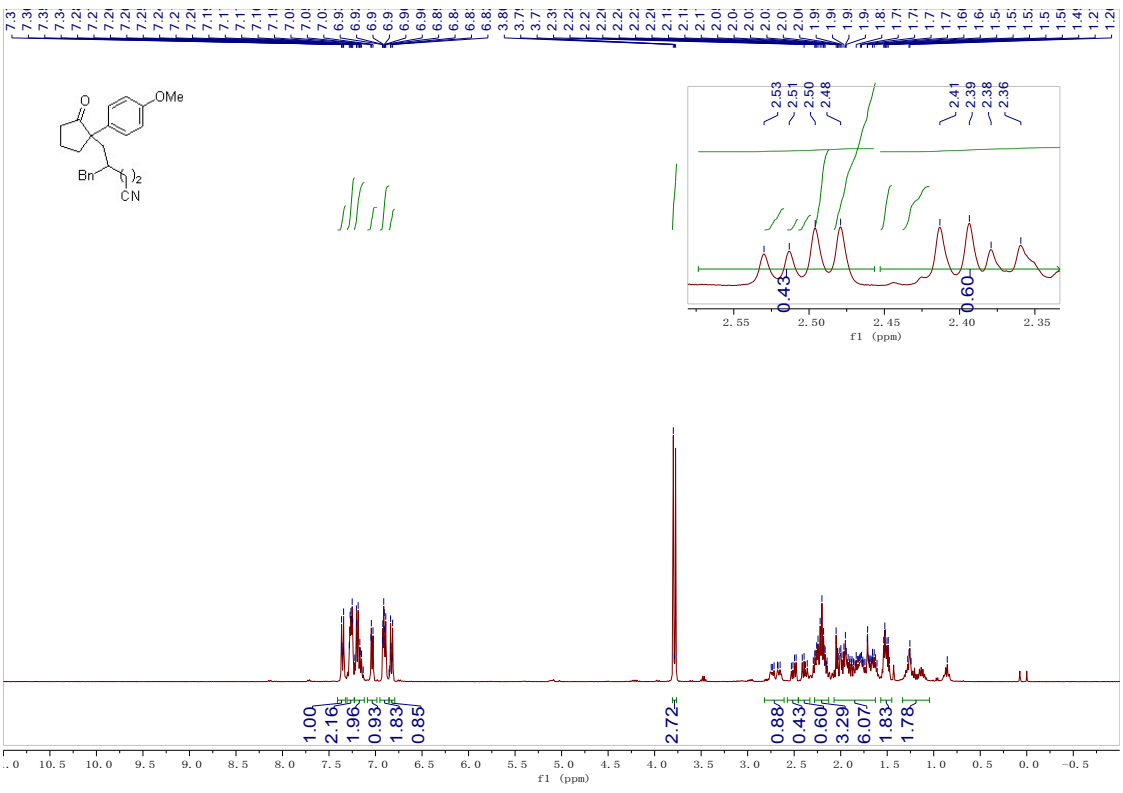
^{1}H NMR Spectrum of **5i**



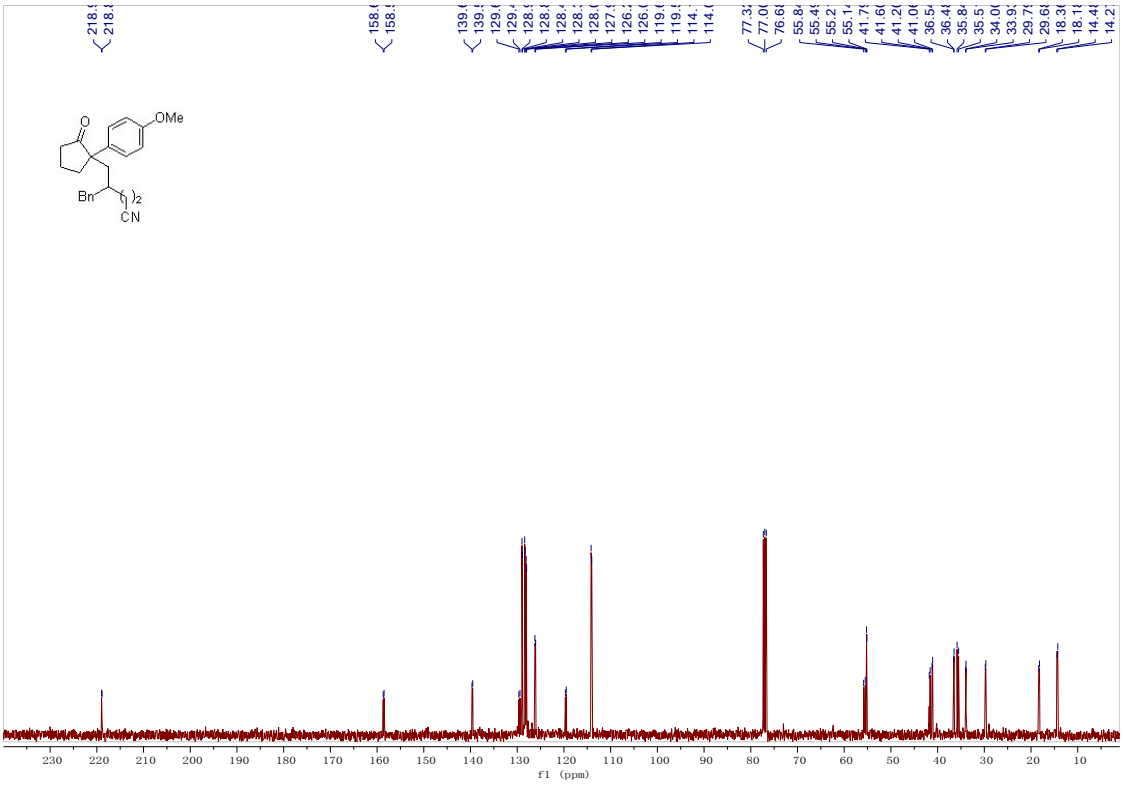
^{13}C NMR Spectrum of **5i**



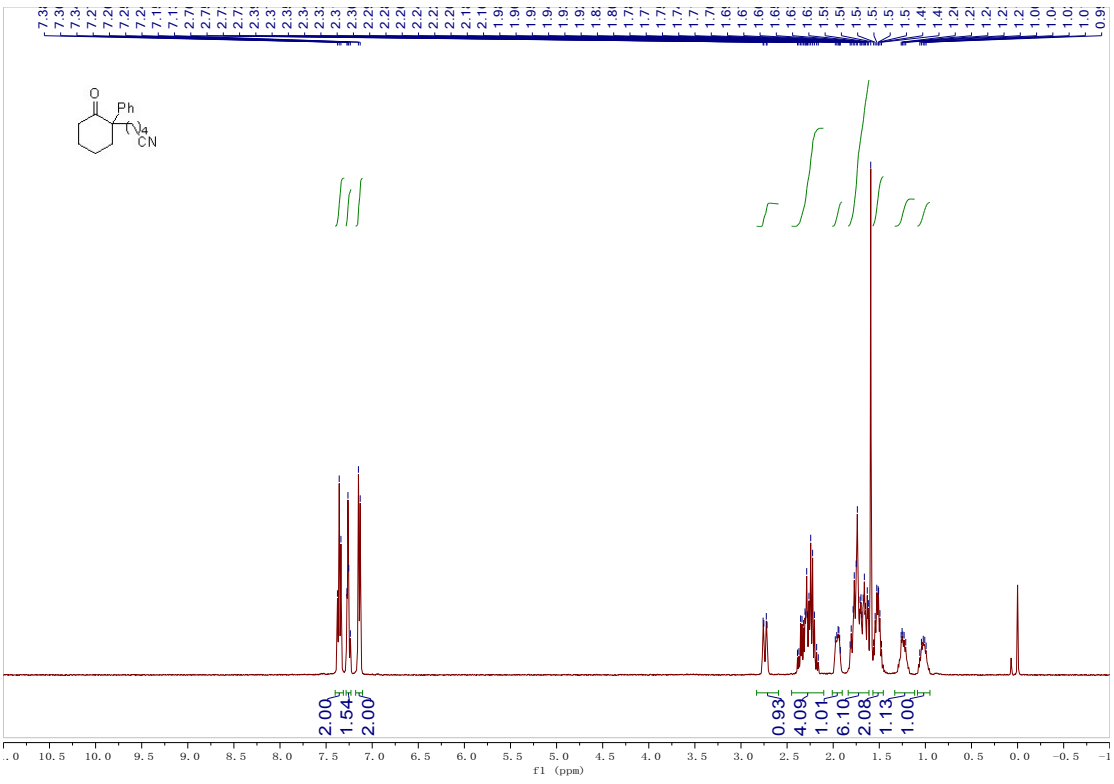
^{1}H NMR Spectrum of **5j**



^{13}C NMR Spectrum of **5j**



^{1}H NMR Spectrum of **5k**



^{13}C NMR Spectrum of **5k**