

**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

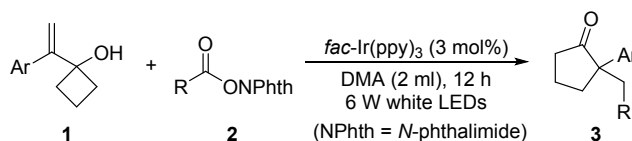
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.¹ Flash column chromatography was performed using 200-300 mesh silica gel. ¹H NMR spectra were recorded on 400 MHz spectrophotometers. 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. ¹³C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton decoupling spectrophotometers (CDCl₃: 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.

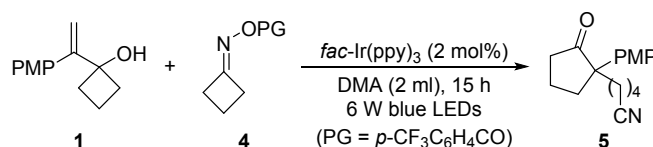
2. General Procedure

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 Na₂SO₄, 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**.

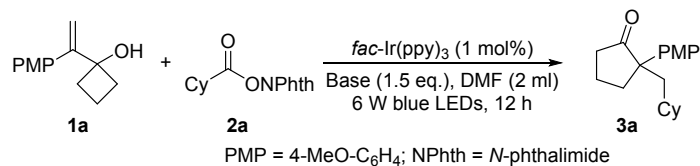
2.2 General procedure for the synthesis of 5a-k



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 Na₂SO₄, 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

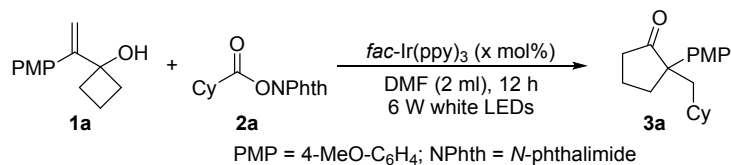
3.1 The effect of bases on the reaction^a



Entry	Base	Yield/% ^b
1	no	40
2	Na ₂ CO ₃	36
3	Na ₂ HPO ₄	33
4	NaOAc	14
5	Et ₃ N	trace
6	pyridine	34
7	^t Pr ₂ NEt	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; Et₃N: triethylamine; ^tPr₂NEt: *N,N*-Diisopropylethylamine.

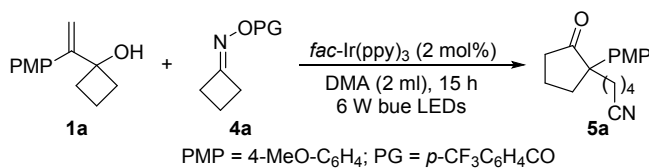
3.2 The effect of the loading of photocatalyst^a



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

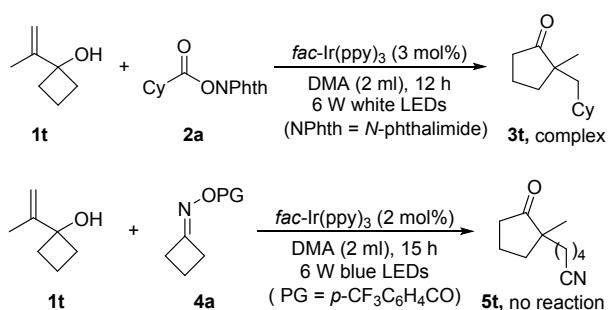


Entry	PC	Solvent	Yield/% ^b
1	<i>fac</i> -Ir(ppy) ₃	CH ₃ CN	no

2	<i>fac</i> -Ir(ppy) ₃	DMF	62
3	<i>fac</i> -Ir(ppy) ₃	DMSO	85
4	<i>fac</i>-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

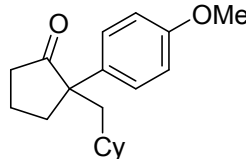
^a **1a** (0.2 mmol), **4a** (0.3 mmol), and *fac*-Ir(ppy)₃ (2 mol%), in 2 ml of solvent at rt under the irradiation of 6 W blue LEDs for 15 h. ^b Isolated yields. ^c Reaction time is 24 h. DMF: *N,N*-dimethylformamide; DMSO: Dimethyl sulfoxide; DMA: *N,N*-Dimethylacetamide.

3.4 Unsuccessful substrate



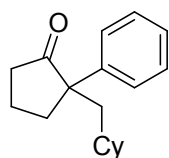
4. Spectral data of the products

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



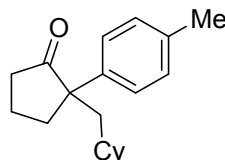
Yield of **3a** : 70% as a yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.29 (m, 2H), 6.90 – 6.81 (m, 2H), 3.79 (s, 3H), 2.87 – 2.58 (m, 1H), 2.38 – 2.12 (m, 2H), 2.07 – 1.72 (m, 4H), 1.69 – 1.56 (m, 2H), 1.54 – 1.40 (m, 3H), 1.27 (d, $J = 12.9$ Hz, 1H), 1.17 – 0.96 (m, 4H), 0.96 – 0.67 (m, 2H). $^{13}\text{C NMR}$ (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 $\text{C}_{19}\text{H}_{26}\text{O}_2$ $[\text{M}+\text{K}]^+$: calcd 325.1564, found: 325.1560.

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



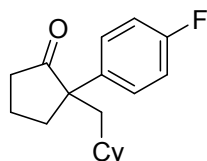
Yield of **3b** : 69% as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.8$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 2.84 – 2.65 (m, 1H), 2.32 – 2.15 (m, 2H), 2.08 – 1.86 (m, 3H), 1.86 – 1.73 (m, 1H), 1.64–1.56 (m, 5H), 1.31 – 1.20 (m, 1H), 1.17 – 0.96 (m, 4H), 0.97 – 0.66 (m, 2H). $^{13}\text{C NMR}$ (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 $\text{C}_{18}\text{H}_{24}\text{O}$ $[\text{M}+\text{K}]^+$: calcd 295.1459, found: 295.1480.

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



Yield of **3c** : 70% as a colorless oil. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{19}\text{H}_{26}\text{O}$ $[\text{M}+\text{K}]^+$: calcd 309.1615, found: 309.1603.

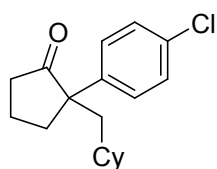
2-(cyclohexylmethyl)-2-(4-fluorophenyl)cyclopentan-1-one (3d)



Yield of **3d** : 68% as a colorless oil. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{18}\text{H}_{23}\text{FO}$ $[\text{M}+\text{Na}]^+$: calcd 297.1625, found: 297.1621.

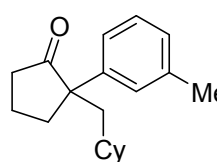
2-(4-chlorophenyl)-2-(cyclohexylmethyl)cyclopentan-1-one (3e)



Yield of **3e**: 75% as a colorless oil. **^1H 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 $\text{C}_{18}\text{H}_{23}\text{ClO}$ $[\text{M}+\text{Na}]^+$: calcd 313.1330, found: 313.1323.

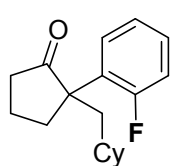
2-(cyclohexylmethyl)-2-(m-tolyl)cyclopentan-1-one (3f)



Yield of **3f**: 80% as a yellow oil. **^1H 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 $\text{C}_{19}\text{H}_{26}\text{O}$ $[\text{M}+\text{Na}]^+$: calcd 293.1876, found: 293.1874.

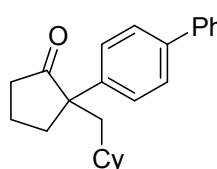
2-(cyclohexylmethyl)-2-(2-fluorophenyl)cyclopentan-1-one (3g)



Yield of **3g**: 55% as a colorless oil. **^1H 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 $\text{C}_{18}\text{H}_{23}\text{FO}$ $[\text{M}+\text{Na}]^+$: calcd 297.1625, found: 297.1622.

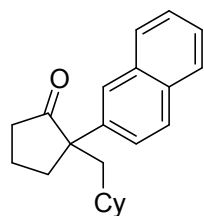
2-([1,1'-biphenyl]-4-yl)-2-(cyclohexylmethyl)cyclopentan-1-one (3h)



Yield of **3h**: 58% as a yellow oil. **^1H 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 $\text{C}_{24}\text{H}_{28}\text{O}$ $[\text{M}+\text{K}]^+$: calcd 371.1772, found: 371.1748.

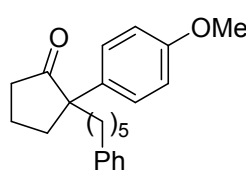
2-(cyclohexylmethyl)-2-(naphthalen-2-yl)cyclopentan-1-one (3i)



Yield of **3i** : 53% as a yellow oil. ^1H 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 $\text{C}_{22}\text{H}_{26}\text{O}$ $[\text{M}+\text{Na}]^+$: calcd 329.1876, found: 329.1857.

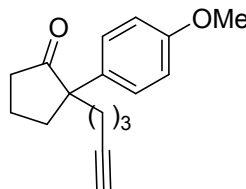
2-(4-methoxyphenyl)-2-(5-phenylpentyl)cyclopentan-1-one (3j)



Yield of **3j** : 50% as a colorless oil. ^1H 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 $\text{C}_{23}\text{H}_{28}\text{O}_2$ $[\text{M}+\text{Na}]^+$: calcd 359.1982, found: 359.1965.

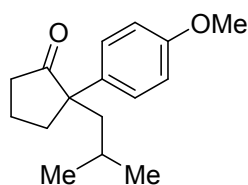
2-(4-methoxyphenyl)-2-(pent-4-yn-1-yl)cyclopentan-1-one (3k)



Yield of **3k** : 40% as a colorless oil. ^1H 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

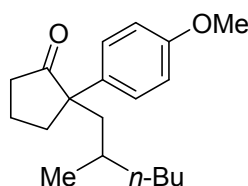
NMR (100 MHz, CDCl_3) δ 219.5, 158.3, 130.6, 127.9, 113.8, 84.0, 68.4, 55.7, 55.1, 38.0, 37.2, 33.8, 23.8, 18.7, 18.5. IR (in KBr): 2953, 1732, 1511, 1252 cm^{-1} . HRMS (ESI) for $\text{C}_{17}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{Na}]^+$: calcd 279.1356, found: 279.1367.

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



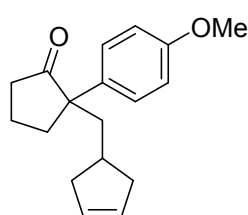
Yield of **3l** : 70% as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.30 – 7.22 (m, 2H), 6.83 – 6.73 (m, 2H), 3.71 (d, *J* = 1.6 Hz, 3H), 2.82 – 2.51 (m, 1H), 2.33 – 1.99 (m, 2H), 1.97 – 1.80 (m, 3H), 1.80 – 1.66 (m, 1H), 1.39 – 1.26 (m, 2H), 0.82 – 0.63 (m, 3H), 0.68 – 0.49 (m, 3H). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₆H₂₂O₂ [M+Na]⁺: calcd 269.1512, found: 269.1508.

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



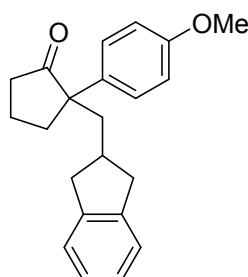
Yield of **3m** : 66% as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.77 – 2.67 (m, 1H), 2.35 – 2.14 (m, 2H), 2.09 (dd, *J* = 14.1, 3.7 Hz, 1H, major), 2.02 – 1.89 (m, 2H), 1.87 – 1.77 (m, 1H), 1.56 (dd, *J* = 14.2, 4.9 Hz, 1H, minor), 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). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₉H₂₈O₂ [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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₈H₂₂O₂ [M+Na]⁺: calcd 293.1512, found: 293.1514.

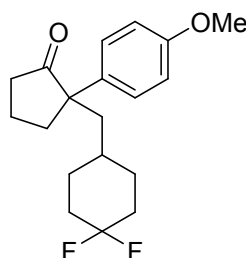
2-((2,3-dihydro-1H-inden-2-yl)methyl)-2-(4-methoxyphenyl)cyclopentan-1-one (**3o**)



Yield of **3o** : 50% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) 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* =

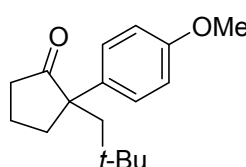
8.5 Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 219.4, 158.4, 143.3, 143.2, 130.2, 128.0, 126.0, 125.9, 124.0, 124.0, 113.9, 56.1, 55.2, 44.5, 40.3, 40.1, 37.5, 36.6, 34.1, 18.5. IR (in KBr): 2934, 1732, 1510, 1251 cm^{-1} . HRMS (ESI) for $\text{C}_{22}\text{H}_{24}\text{O}_2$ $[\text{M}+\text{Na}]^+$: calcd 343.1669, found: 343.1642.

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



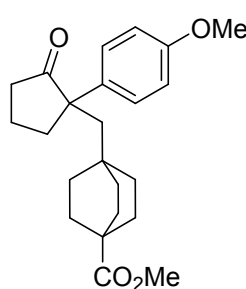
Yield of **3p**: 70% as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.27 (m, 2H), 6.92 – 6.79 (m, 2H), 3.79 (d, $J = 2.0$ Hz, 3H), 2.76 – 2.69 (m, 1H), 2.22 (s, 2H), 2.09 – 1.75 (m, 6H), 1.72 – 1.39 (m, 4H), 1.41 – 0.97 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 219.2, 158.4, 130.2, 127.9, 123.3 (dd, $J = 241.6, 239.5$ 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 $\text{C}_{19}\text{H}_{24}\text{F}_2\text{O}_2$ $[\text{M}+\text{Na}]^+$: calcd 345.1637 found: 345.1604.

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



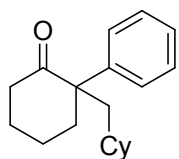
Yield of **3q**: 71% as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.30 (m, 2H), 6.94 – 6.76 (m, 2H), 3.79 (s, 3H), 3.14 – 2.83 (m, 1H), 2.30 – 2.06 (m, 3H), 2.05 – 1.90 (m, 2H), 1.88 – 1.75 (m, 1H), 1.44 (d, $J = 14.7$ Hz, 1H), 0.69 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 219.3, 158.4, 129.3, 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 $\text{C}_{17}\text{H}_{24}\text{O}_2$ $[\text{M}+\text{Na}]^+$: calcd 283.1669, found: 283.1672.

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



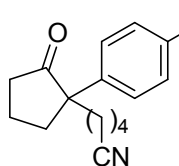
Yield of **3r**: 54% as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, $J = 8.5$ Hz, 2H), 6.77 (d, $J = 8.5$ Hz, 2H), 3.72 (s, 3H), 3.51 (s, 3H), 2.85 (dd, $J = 11.9, 5.5$ Hz, 1H), 2.11 (d, $J = 15.2$ Hz, 3H), 1.85 (dd, $J = 6.6, 3.0$ Hz, 3H), 1.52 (t, $J = 6.5$ Hz, 6H), 1.25 (d, $J = 14.9$ Hz, 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 $\text{C}_{23}\text{H}_{30}\text{O}_4$ $[\text{M}+\text{Na}]^+$: calcd 393.2036, found: 393.2046.

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



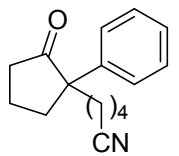
Yield of **3s** : 33% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 2.75 (dd, *J* = 13.7, 2.9 Hz, 1H), 2.36 – 2.22 (m, 2H), 1.96 – 1.89 (m, 1H), 1.86 – 1.62 (m, 5H), 1.62 – 1.42 (m, 5H), 1.17 – 0.81 (m, 6H), 0.67 (d, *J* = 11.3 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₉H₂₆O [M+K]⁺: calcd 309.1615, found: 309.1617.

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



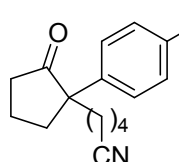
Yield of **5a** : 92% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 2.62 (dd, *J* = 11.2, 6.0 Hz, 1H), 2.35 – 2.18 (m, 4H), 1.98 – 1.76 (m, 4H), 1.61 – 1.51 (m, 3H), 1.38 – 1.07 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 219.6, 158.4, 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 C₁₇H₂₁NO₂ [M+Na]⁺: calcd 294.1465, found: 294.1439.

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



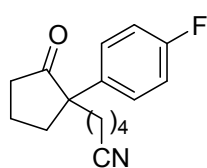
Yield of **5b** : 50% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.39 – 7.32 (m, 4H), 7.26 (d, *J* = 6.9 Hz, 1H), 2.66 (dd, *J* = 11.0, 6.3 Hz, 1H), 2.38 – 2.15 (m, 4H), 2.06 – 1.76 (m, 4H), 1.71 – 1.46 (m, 3H), 1.26 (s, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 219.5, 138.7, 128.7, 127.0, 126.7, 119.5, 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 C₁₆H₁₉NO [M+Na]⁺: calcd 264.1359, found: 264.1339.

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



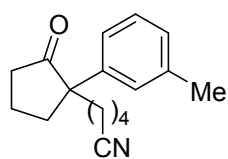
Yield of **5c** : 80% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 7.9, 5.0 Hz, 4H), 7.43 (dd, *J* = 11.5, 7.9 Hz, 4H), 7.35 (d, *J* = 7.3 Hz, 1H), 2.68 (s, 1H), 2.45 – 2.16 (m, 4H), 2.07 – 1.78 (m, 4H), 1.74 – 1.48 (m, 3H), 1.34 – 1.20 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 219.4, 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 C₂₂H₂₃NO [M+Na]⁺: calcd 340.1672, found: 340.1648.

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



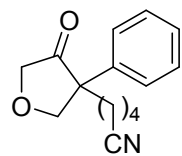
Yield of **5d** : 54% as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 – 7.32 (m, 2H), 7.06 – 7.00 (m, 2H), 2.70 – 2.51 (m, 1H), 2.41 – 2.16 (m, 4H), 2.08 – 1.75 (m, 4H), 1.66 – 1.45 (m, 3H), 1.36 – 1.06 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 219.1, 161.7 (d, $J = 244.8$ Hz), 134.5, 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 $\text{C}_{16}\text{H}_{18}\text{FNO}$ $[\text{M}+\text{Na}]^+$: calcd 282.1265, found: 282.1243.

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



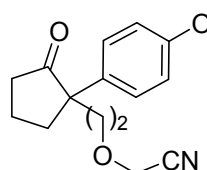
Yield of **5e** : 54% as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 – 7.19 (m, 1H), 7.16 (d, $J = 6.7$ Hz, 2H), 7.06 (d, $J = 7.3$ Hz, 1H), 2.75 – 2.58 (m, 1H), 2.34 (s, 3H), 2.31 – 2.15 (m, 4H), 2.04 – 1.70 (m, 4H), 1.68 – 1.47 (m, 3H), 1.38 – 1.12 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, 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 $\text{C}_{17}\text{H}_{21}\text{NO}$ $[\text{M}+\text{Na}]^+$: calcd 278.1515, found: 278.1513.

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



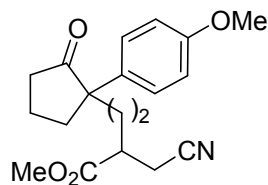
Yield of **5f** : 83% as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 – 7.33 (m, 3H), 7.33 – 7.23 (m, 2H), 4.95 (d, $J = 2.4$ Hz, 1H), 4.71 (dd, $J = 13.1$, 9.3 Hz, 1H), 4.27 (dd, $J = 30.6$, 9.1 Hz, 1H), 4.05 (s, 1H), 2.34 – 2.02 (m, 2H), 1.61 (d, $J = 15.3$ Hz, 4H), 1.28 (dd, $J = 13.7$, 6.4 Hz, 2H). $^{13}\text{C NMR}$ (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 $\text{C}_{15}\text{H}_{17}\text{NO}_2$ $[\text{M}+\text{Na}]^+$: calcd 266.1151, found: 266.1126.

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



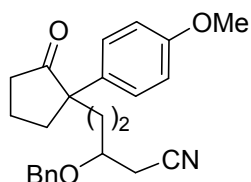
Yield of **5g** : 54% as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.3 – 7.2 (m, 2H), 6.9 (d, $J = 8.9$ Hz, 2H), 4.1 (d, $J = 8.7$ Hz, 2H), 3.8 (s, 3H), 3.4 (d, $J = 1.2$ Hz, 2H), 2.8 – 2.6 (m, 1H), 2.4 – 2.1 (m, 3H), 2.0 – 1.7 (m, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 218.8, 158.5, 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 $\text{C}_{16}\text{H}_{19}\text{NO}_3$ $[\text{M}+\text{Na}]^+$: calcd 296.1257, found: 296.1259.

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



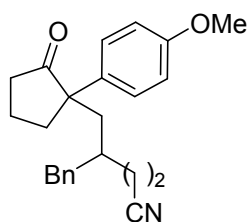
Yield of **5h** : 90% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.29 – 7.26 (m, 2H), 6.95 – 6.74 (m, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 2.64 – 2.59 (m, 2H), 2.60 – 2.42 (m, 4H, minor), 2.38 – 2.13 (m, 4H, major), 2.04 – 1.73 (m, 4H), 1.72 – 1.27 (m, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 219.0, 172.7, 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 C₁₉H₂₃NO₄ [M+Na]⁺: calcd 352.1519, found: 352.1513.

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



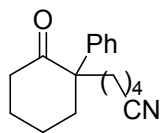
Yield of **5i** : 43% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.26 (m, 7H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.61 – 4.28 (m, 2H), 3.78 (s, 3H), 3.58 – 3.50 (m, 1H), 2.64 – 2.56 (m, 1H), 2.51 – 2.16 (m, 4H), 1.96 – 1.86 (m, 3H), 1.82 (d, *J* = 9.0 Hz, 2H, major), 1.71 (d, *J* = 4.6 Hz, 2H, minor), 1.46 (dd, *J* = 7.8, 4.9 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₄H₂₇NO₃ [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. **¹H NMR** (400 MHz, CDCl₃) 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). **¹³C NMR** (100 MHz, CDCl₃) 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 C₂₄H₂₇NO₂ [M+Na]⁺: calcd 384.1934, found: 384.1904.

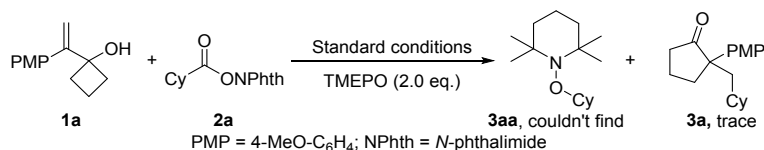
5-(2-oxo-1-phenylcyclohexyl)pentanenitrile (**5k**)



Yield of **5k** : 69% as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) 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). **¹³C NMR** (100 MHz, CDCl₃) 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 C₁₇H₂₁NO [M+Na]⁺: calcd 278.1515, found: 278.1503.

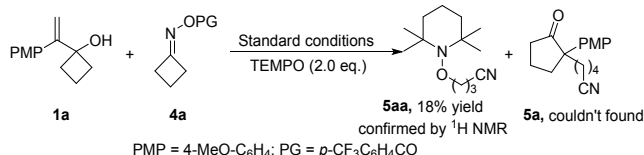
5. Mechanism Investigation and the Proposed Mechanism

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



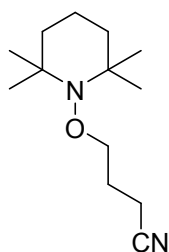
Procedure: To a dried Schlenk tube was treated with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), *fac*-Ir(ppy)₃ (0.006 mmol, 3 mol%) and TEMPO (62.50 mg, 0.4 mmol) . Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via 'freeze-pump-thaw' procedure. 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)



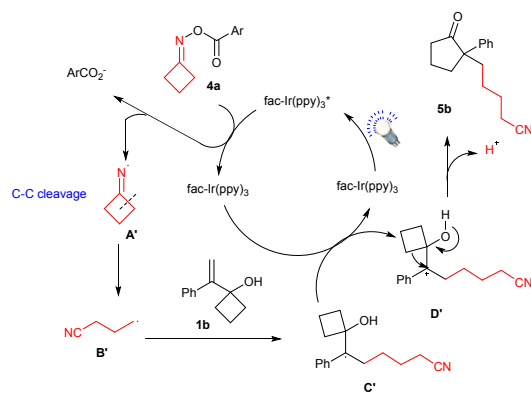
Procedure: To a dried Schlenk tube was treated with **1a** (0.2 mmol, 1.0 equiv), **4a** (0.3 mmol, 1.5 equiv), *fac*-Ir(ppy)₃ (0.004 mmol, 2 mol%) and TEMPO (62.50 mg, 0.4 mmol) . Subsequently, DMA (2 ml) was added. And then this mixture solution was degassed for 3 times via 'freeze-pump-thaw' procedure. 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 ¹H NMR.

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

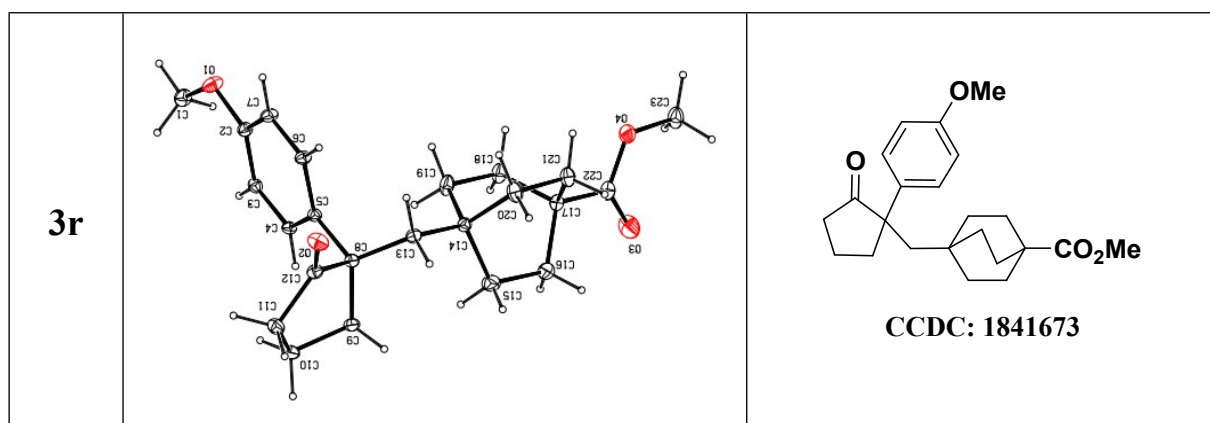


Yield of **5aa**: 18% yield of a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 3.84 (t, *J* = 5.8 Hz, 1H), 2.49 (t, *J* = 7.2 Hz, 1H), 2.00 – 1.76 (m, 1H), 1.57 (s, 2H), 1.45 (dd, *J* = 7.7, 4.2 Hz, 2H), 1.37 – 1.28 (m, 1H), 1.12 (d, *J* = 23.3 Hz, 6H). the ¹H NMR data are consistent with the reported literature (*Angew. Chem. Int. Ed.* **2018**, *57*, 738-743.).

5.3 A plausible mechanism involved 4a

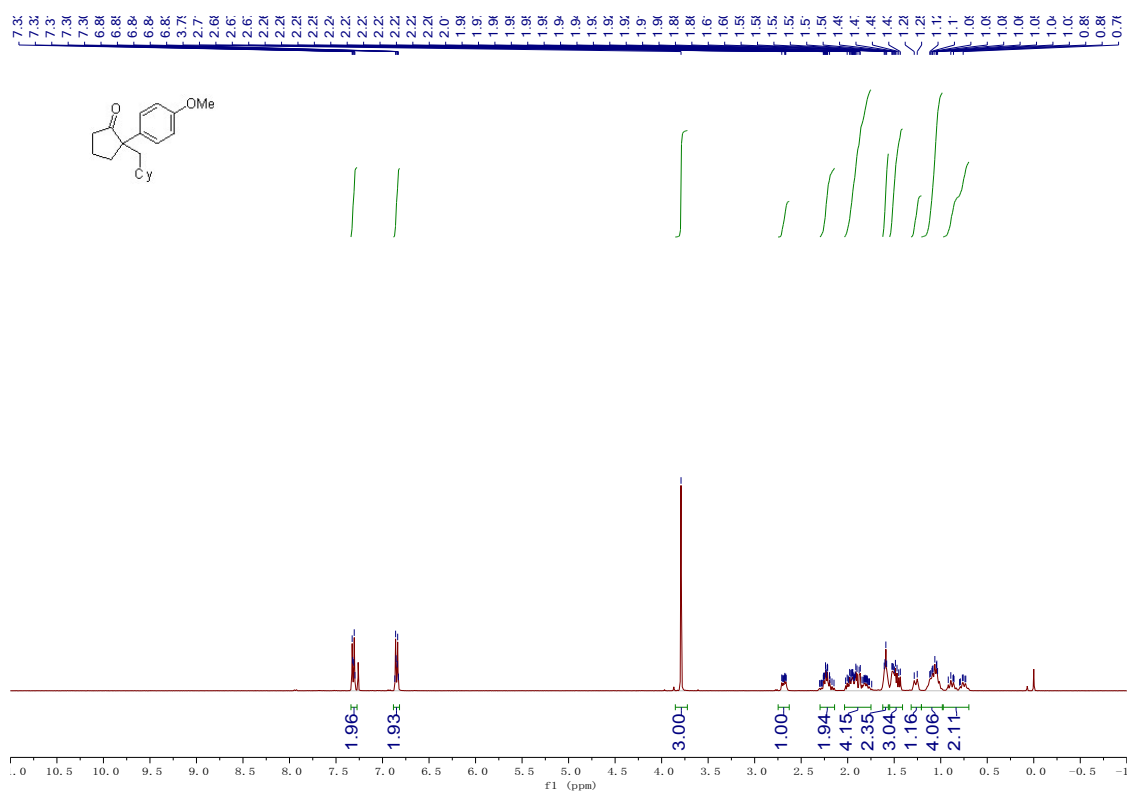


6. X-Ray Crystal Structure Determination of 3r

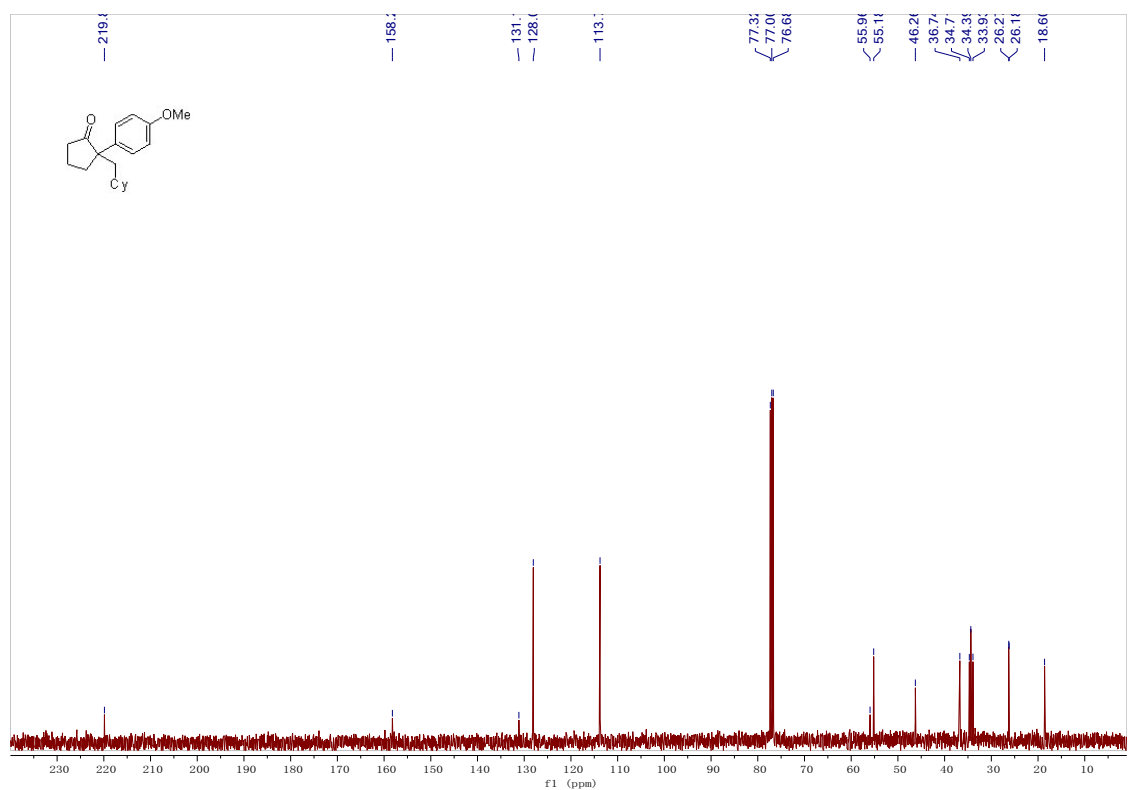


7. Copies of ^1H , ^{13}C and ^{19}F NMR Spectra

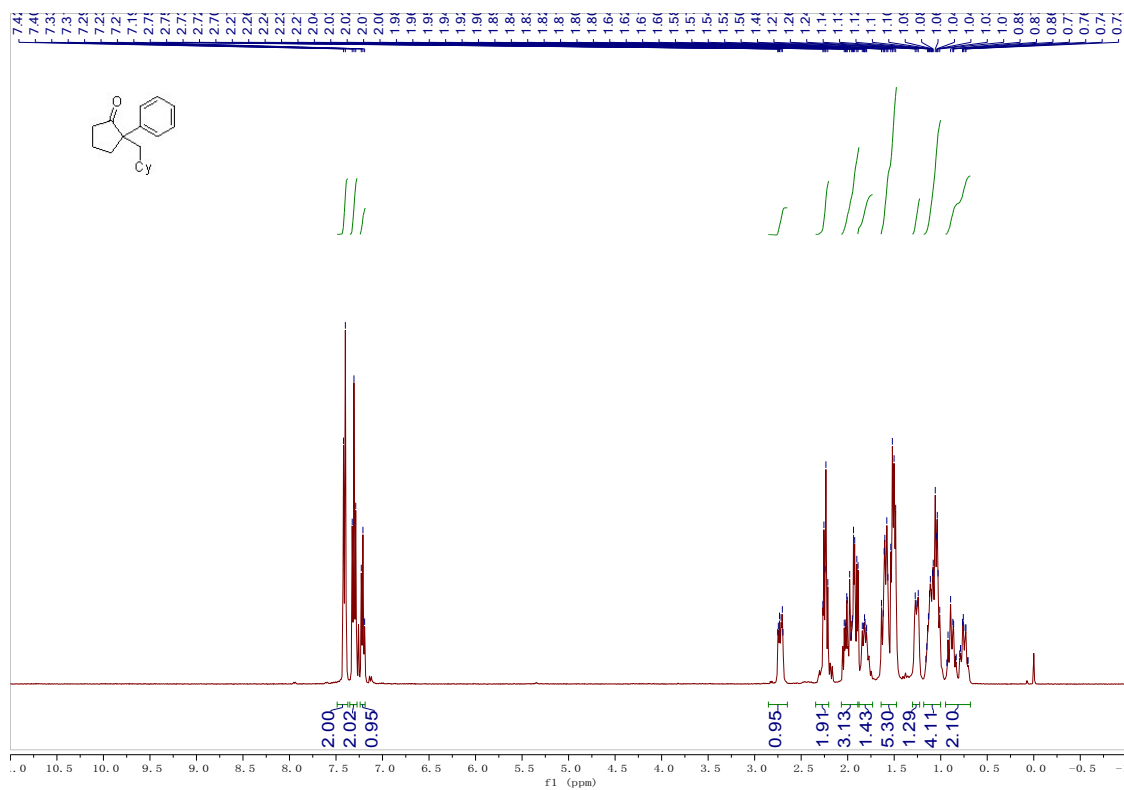
^1H NMR Spectrum of **3a**



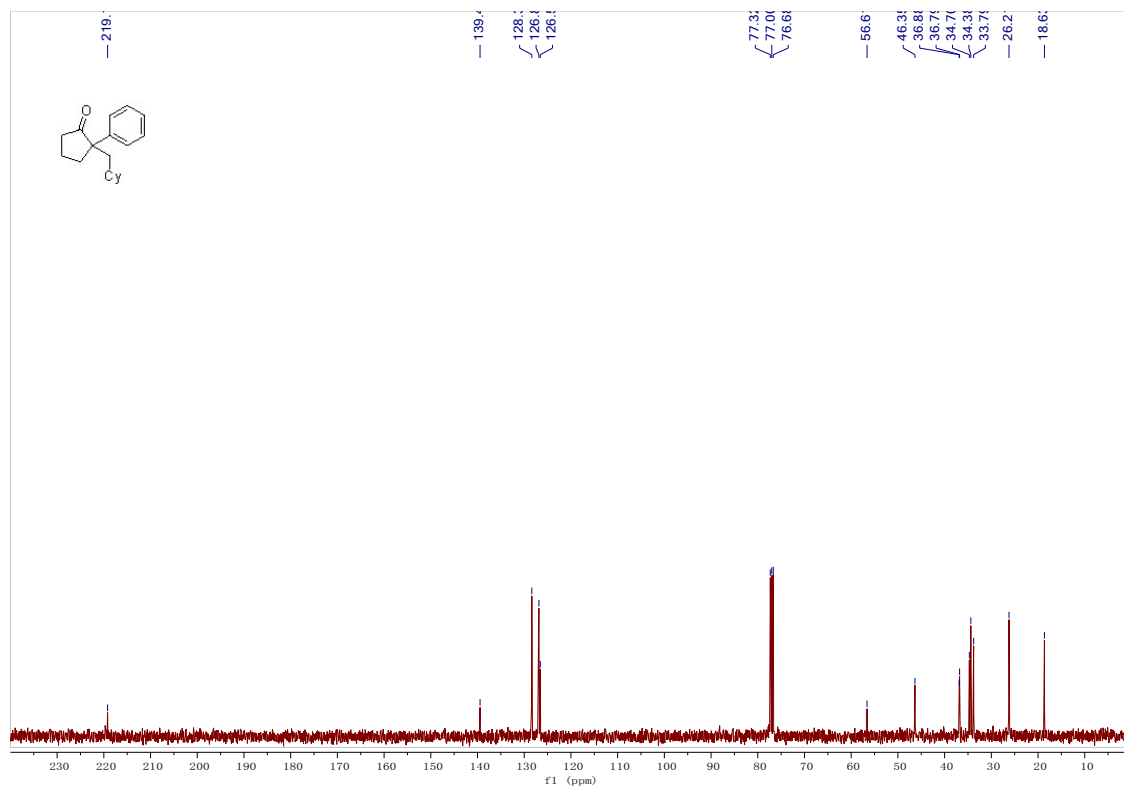
^{13}C NMR Spectrum of **3a**



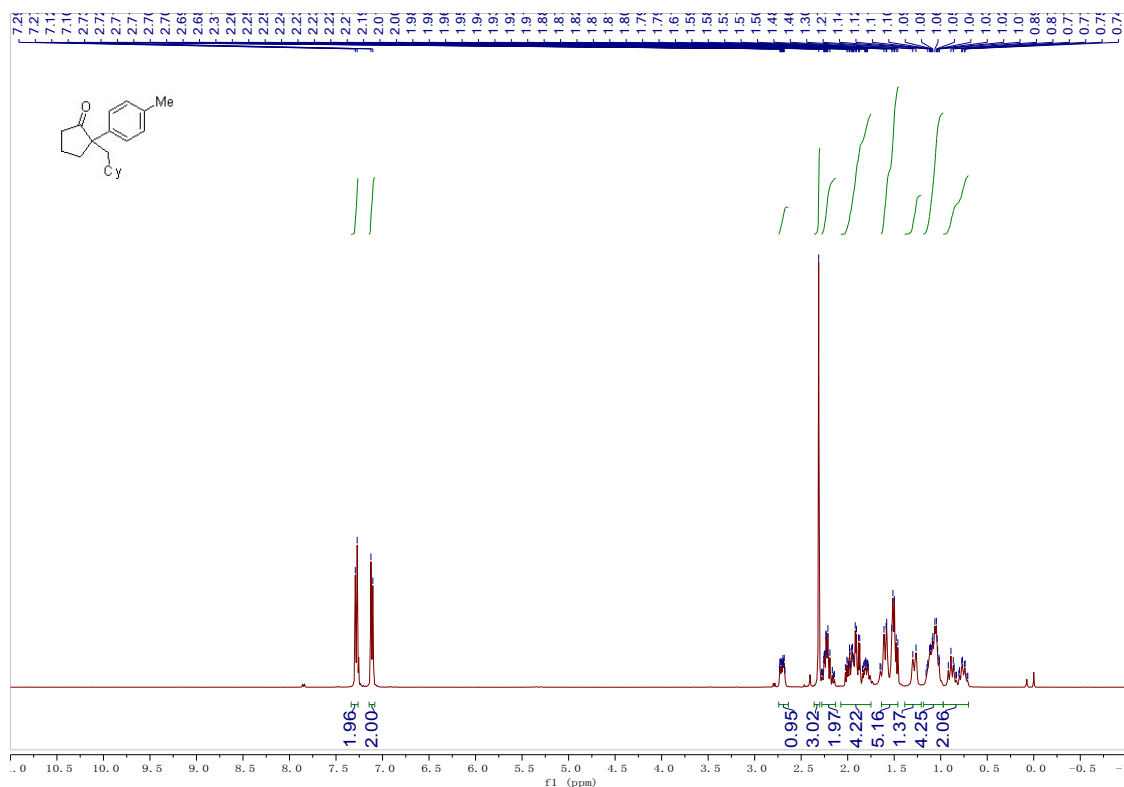
¹H NMR Spectrum of **3b**



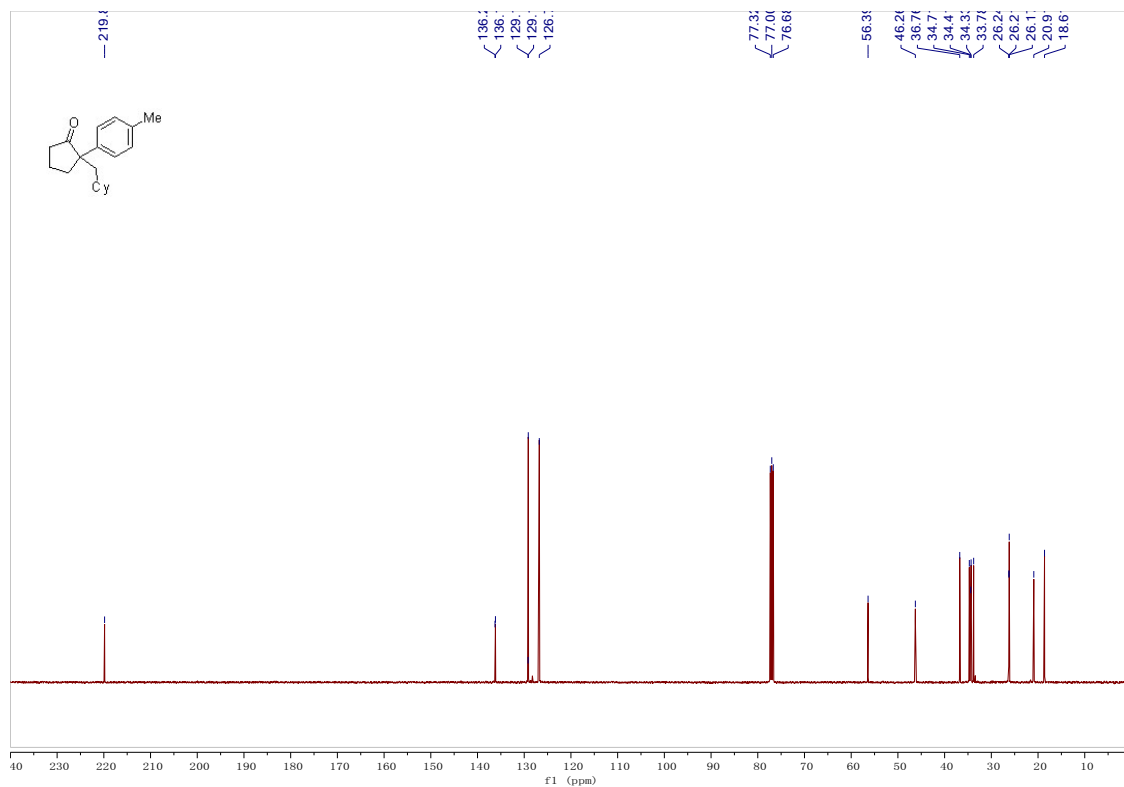
¹³C NMR Spectrum of **3b**



¹H NMR Spectrum of **3c**



¹³C NMR Spectrum of **3c**



Chemical structure: 1-(cyclopentylmethyl)-4-fluorobenzene

C1CCC(CC1)Cc2ccc(F)cc2

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (7.0-7.4 ppm) and aliphatic region (1.0-2.5 ppm). Integration values are provided below the peaks.

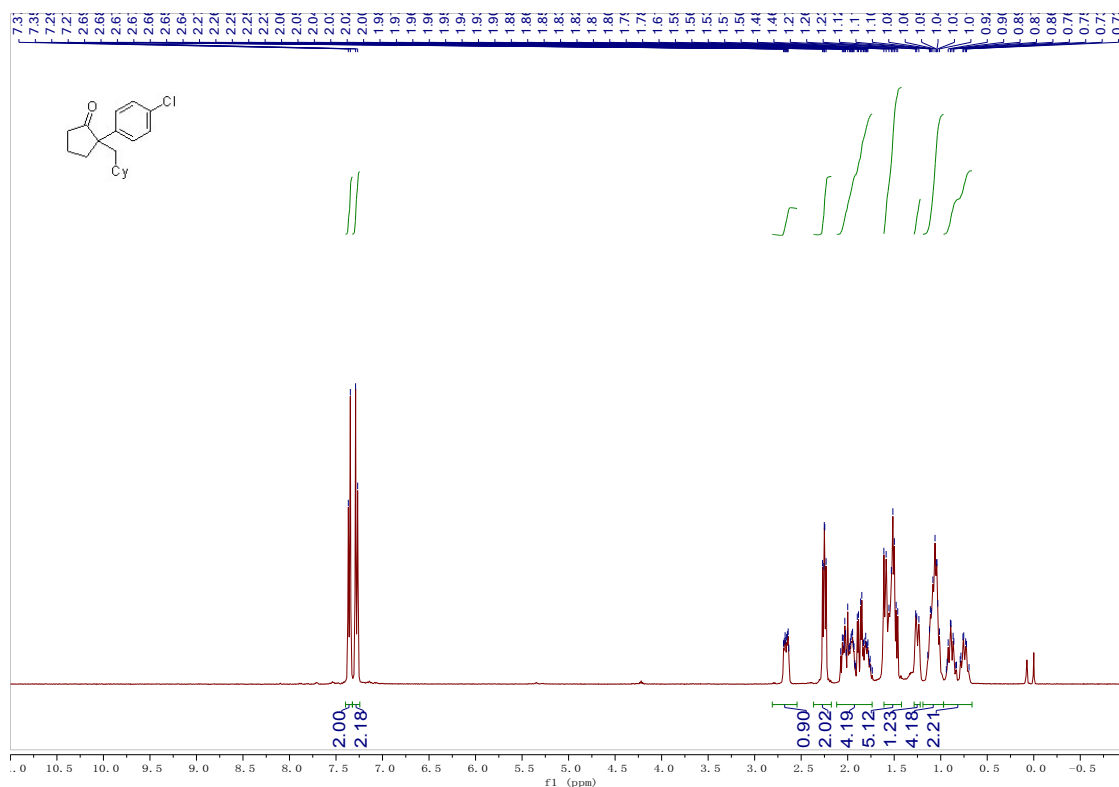
Chemical Shift (ppm)	Integration
7.33	2.00
7.23	1.95
7.13	0.97
7.03	2.00
7.00	4.14
6.99	5.37
6.97	1.05
6.95	4.10
6.93	1.97

Chemical structure: 1-(4-fluorophenyl)-2-methylcyclopentanone

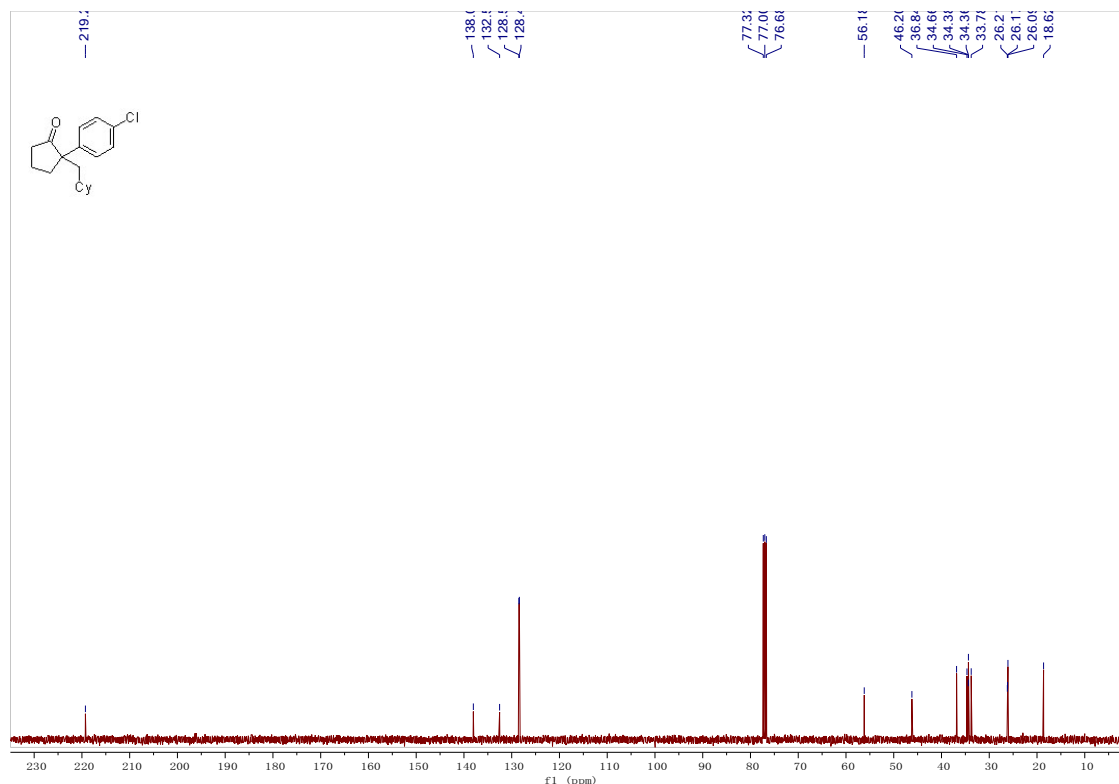
¹³C NMR spectrum (ppm):

- 219.4
- 162.1
- 160.1
- 135.1
- 135.1
- 128.1
- 128.1
- 115.1
- 115.1
- 77.3
- 77.0
- 76.8
- 56.0
- 46.2
- 36.8
- 34.6
- 34.3
- 33.9
- 26.2
- 26.1
- 26.1
- 18.5

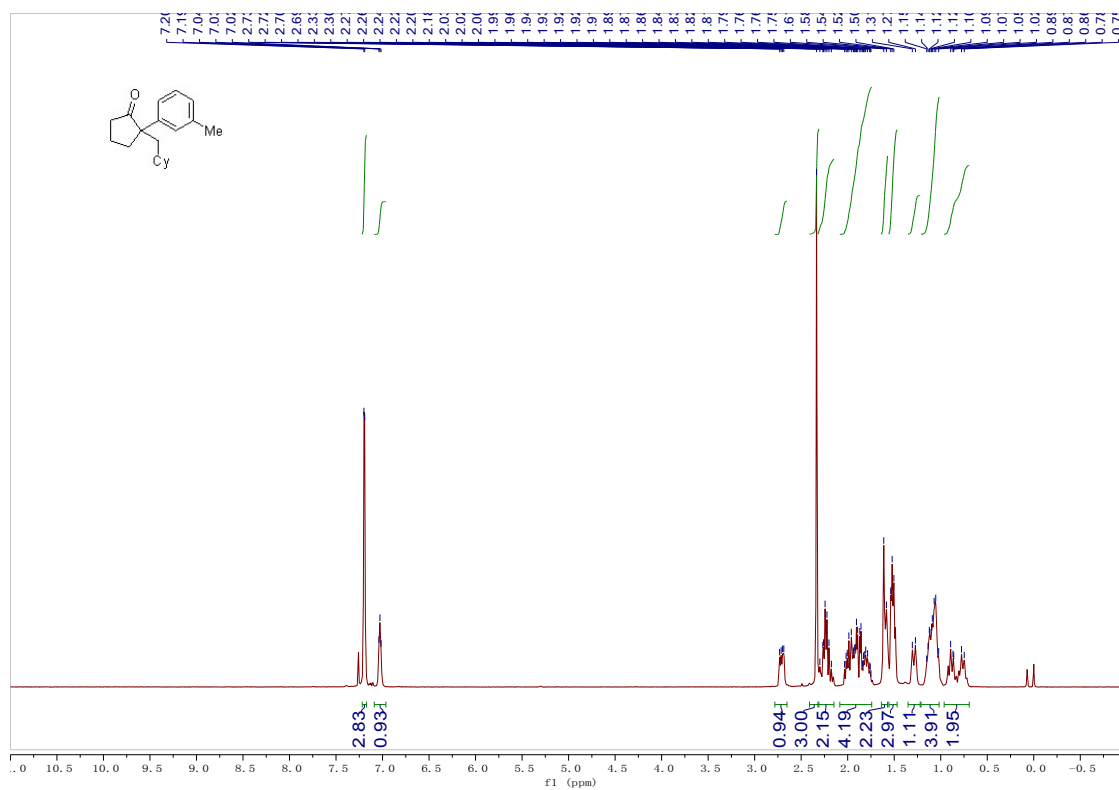
¹H NMR Spectrum of **3e**



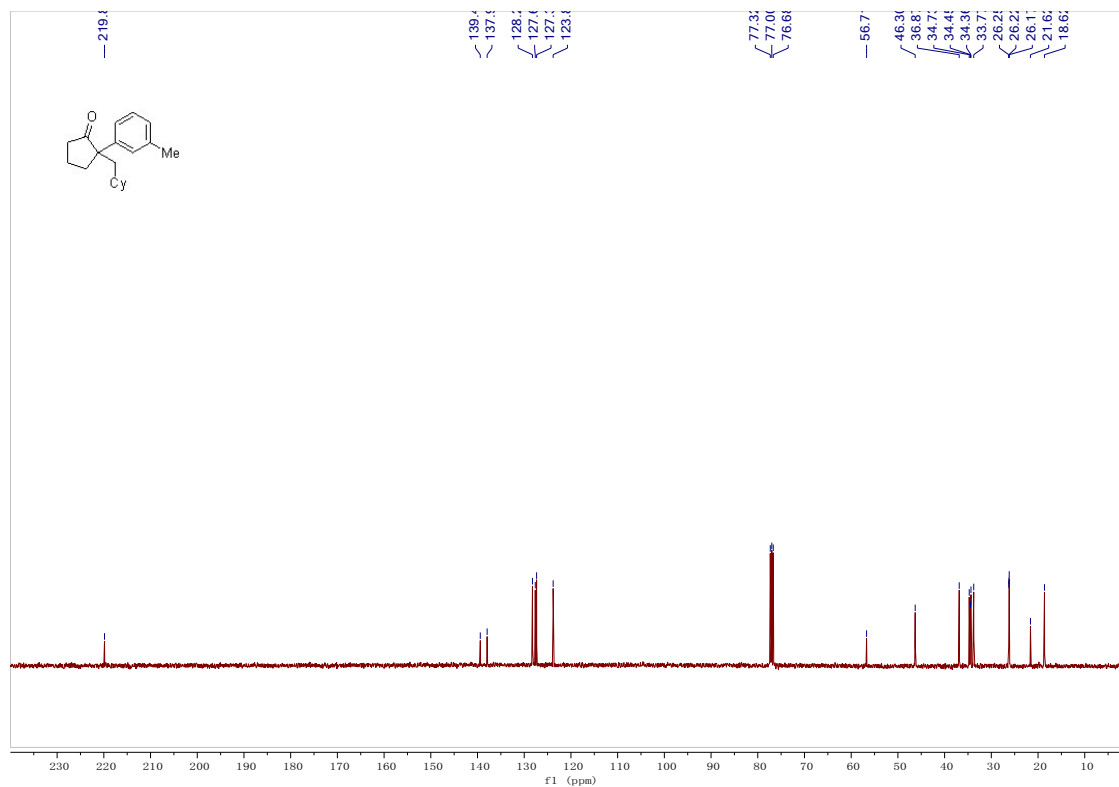
¹³C NMR Spectrum of **3e**



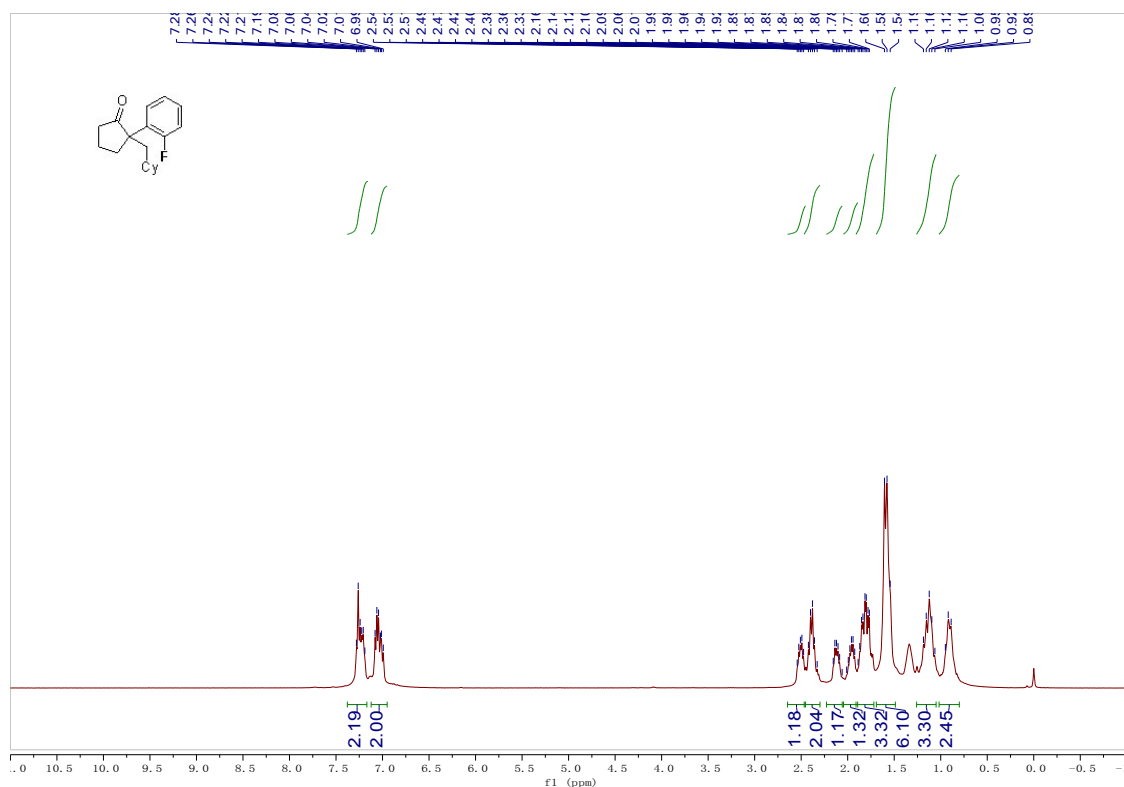
¹H NMR Spectrum of **3f**



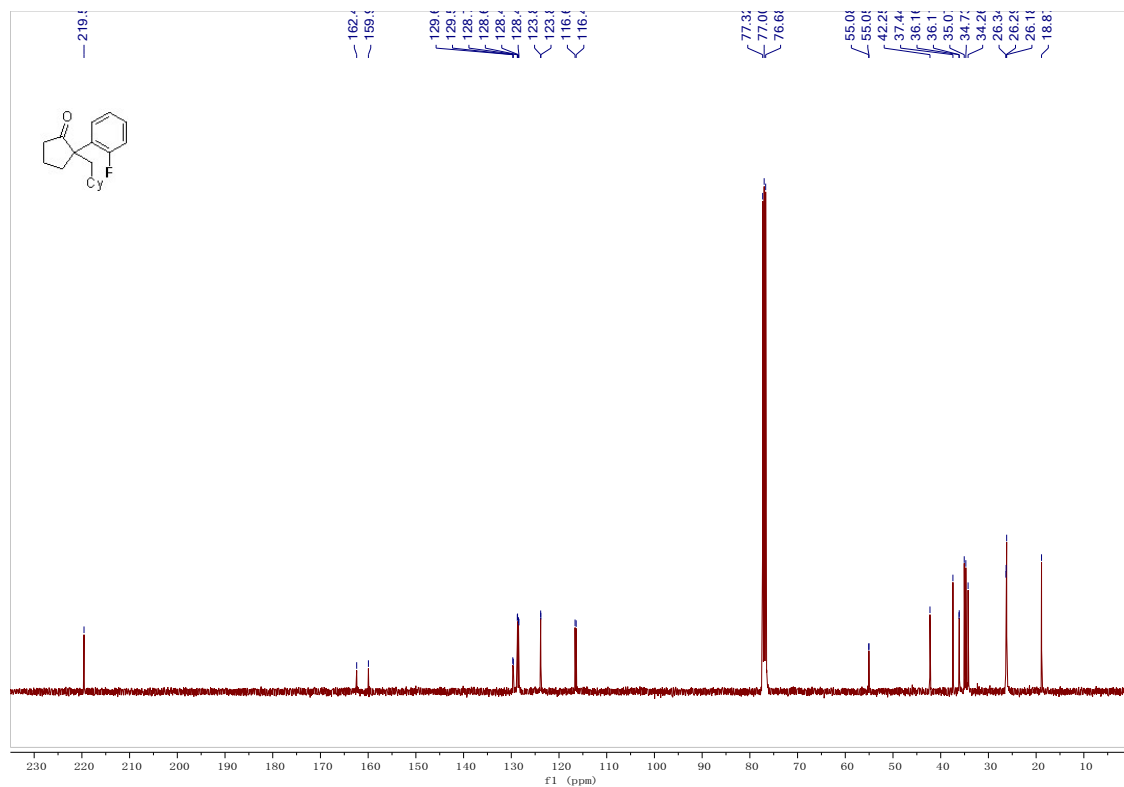
¹³C NMR Spectrum of **3f**



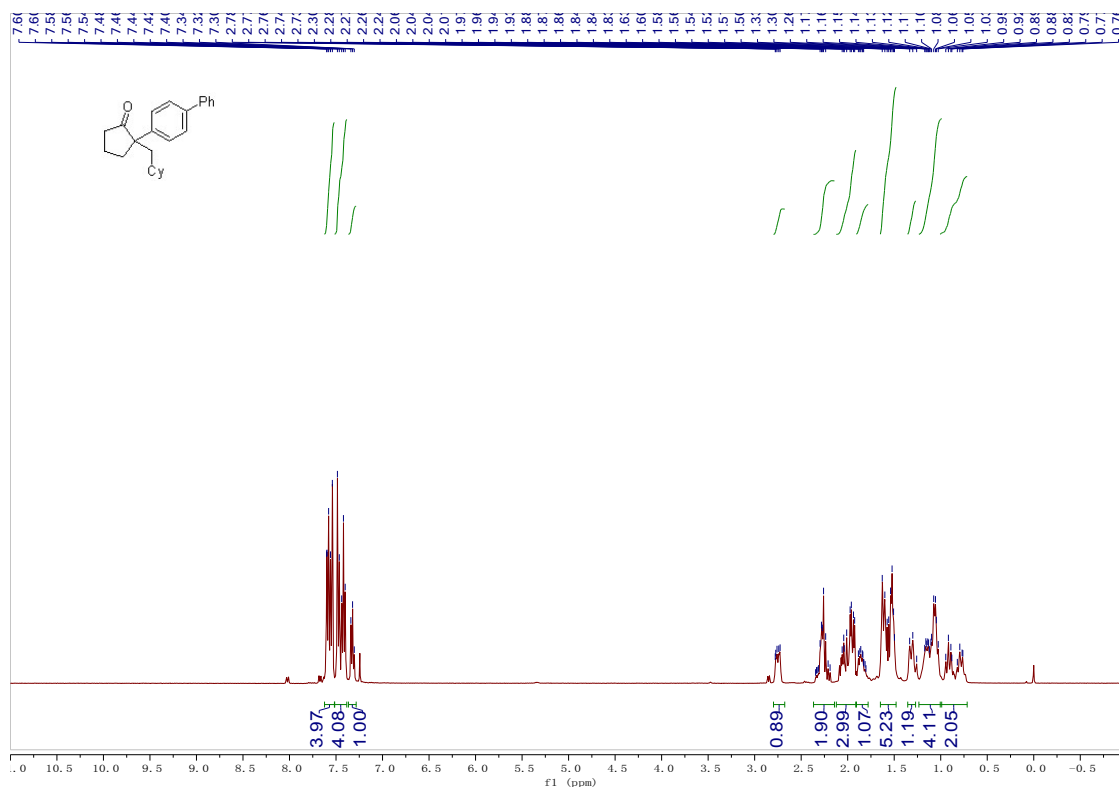
¹H NMR Spectrum of **3g**



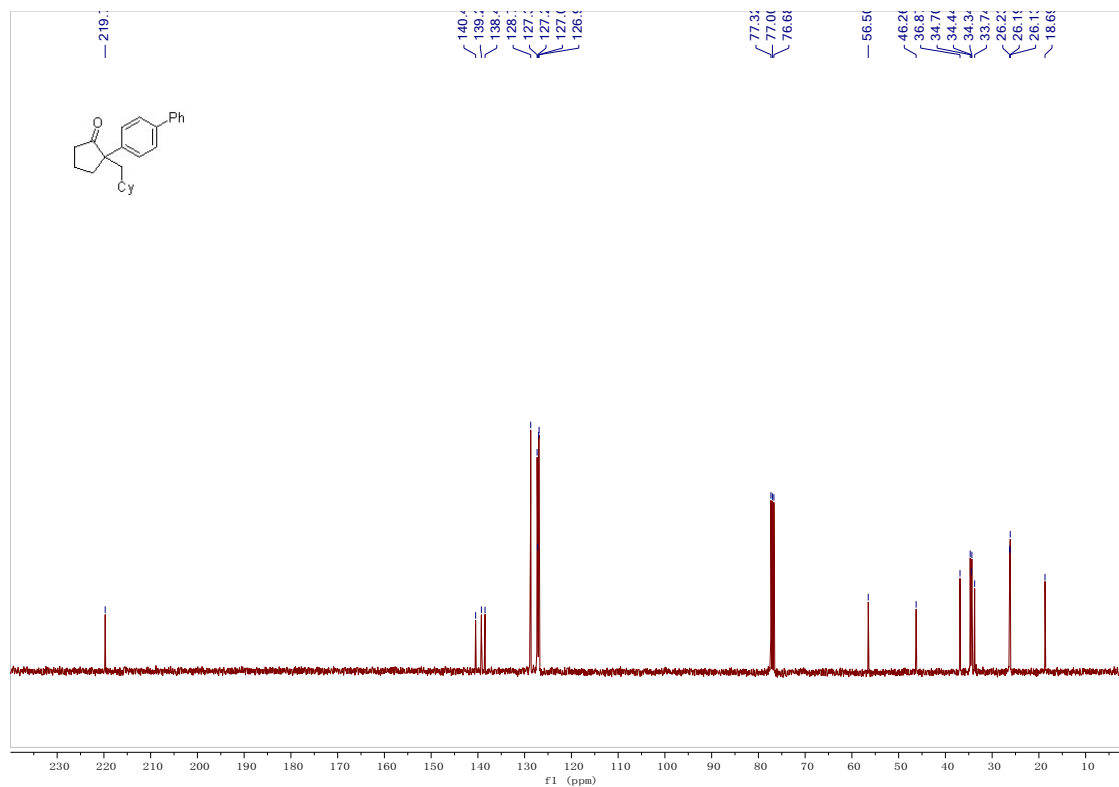
¹³C NMR Spectrum of **3g**



¹H NMR Spectrum of **3h**



¹³C NMR Spectrum of **3h**



C1=CC=C(C=C1)C2=CC=CC=C2C3CCCC3

Chemical structure: 1-(cyclopentylideneamino)benzene

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (7.2-7.9 ppm), a cyclopentylidene methine signal (4.6 ppm), and aliphatic signals (0.8-2.1 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.85	3.91
7.81	1.00
7.76	1.92
7.55	
7.45	
7.44	
7.43	
7.42	
2.91	
2.88	
2.87	
2.86	
2.85	
2.84	
2.83	
2.82	
2.81	
2.80	
2.79	
2.78	
2.77	
2.76	
2.75	
2.74	
2.73	
2.72	
2.71	
2.70	
2.69	
2.68	
2.67	
2.66	
2.65	
2.64	
2.63	
2.62	
2.61	
2.60	
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2.57	
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2.52	
2.51	
2.50	
2.49	
2.48	
2.47	
2.46	
2.45	
2.44	
2.43	
2.42	
2.41	
2.40	
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2.38	
2.37	
2.36	
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2.19	
2.18	
2.17	
2.16	
2.15	
2.14	
2.13	
2.12	
2.11	
2.10	
2.09	
2.08	
2.07	
2.06	
2.05	
2.04	
2.03	
2.02	
2.01	
2.00	
1.99	
1.98	
1.97	
1.96	
1.95	
1.94	
1.93	
1.92	
1.91	
1.90	
1.89	
1.88	
1.87	
1.86	
1.85	
1.84	
1.83	
1.82	
1.81	
1.80	
1.79	
1.78	
1.77	
1.76	
1.75	
1.74	
1.73	
1.72	
1.71	
1.70	
1.69	
1.68	
1.67	
1.66	
1.65	
1.64	
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1.61	
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1.57	
1.56	
1.55	
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1.53	
1.52	
1.51	
1.50	
1.49	
1.48	
1.47	
1.46	
1.45	
1.44	
1.43	
1.42	
1.41	
1.40	
1.39	
1.38	
1.37	
1.36	
1.35	
1.34	
1.33	
1.32	
1.31	
1.30	
1.29	
1.28	
1.27	
1.26	
1.25	
1.24	
1.23	
1.22	
1.21	
1.20	
1.19	
1.18	
1.17	
1.16	
1.15	
1.14	
1.13	
1.12	
1.11	
1.10	
1.09	
1.08	
1.07	
1.06	
1.05	
1.04	
1.03	
1.02	
1.01	
1.00	
0.99	
0.98	
0.97	
0.96	
0.95	
0.94	
0.93	
0.92	
0.91	
0.90	
0.89	
0.88	
0.87	
0.86	
0.85	
0.84	
0.83	
0.82	
0.81	
0.80	
0.79	
0.78	
0.77	
0.76	
0.75	
0.74	
0.73	
0.72	

Chemical structure: c1ccccc1C2CCCC2

¹³C NMR spectrum (CDCl₃) peaks (ppm):

- 221.9
- 136.1
- 133.1
- 132.1
- 128.1
- 127.1
- 125.1
- 123.1
- 77.3
- 77.0
- 76.6
- 56.8
- 46.1
- 36.8
- 34.7
- 34.4
- 34.3
- 33.9
- 26.2
- 26.1
- 18.6

Chemical structure of 1-(4-methoxyphenyl)-1-phenylcyclopentan-1-ol is shown. The ^1H NMR spectrum (400 MHz, CDCl_3) displays the following peaks and integrations:

Chemical Shift (ppm)	Integration
7.25, 7.23, 7.21, 7.19, 7.17, 7.15, 7.13, 7.11, 7.09, 7.07, 7.05, 7.03, 6.89, 6.87, 6.85, 6.83, 6.81, 6.79, 6.77, 6.75, 6.73, 6.71, 6.69, 6.67, 6.65, 6.63, 6.61, 6.59, 6.57, 6.55, 6.53, 6.51, 6.49, 6.47, 6.45, 6.43, 6.41, 6.39, 6.37, 6.35, 6.33, 6.31, 6.29, 6.27, 6.25, 6.23, 6.21, 6.19, 6.17, 6.15, 6.13, 6.11, 6.09, 6.07, 6.05, 6.03, 6.01, 5.99, 5.97, 5.95, 5.93, 5.91, 5.89, 5.87, 5.85, 5.83, 5.81, 5.79, 5.77, 5.75, 5.73, 5.71, 5.69, 5.67, 5.65, 5.63, 5.61, 5.59, 5.57, 5.55, 5.53, 5.51, 5.49, 5.47, 5.45, 5.43, 5.41, 5.39, 5.37, 5.35, 5.33, 5.31, 5.29, 5.27, 5.25, 5.23, 5.21, 5.19, 5.17, 5.15, 5.13, 5.11, 5.09, 5.07, 5.05, 5.03, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25, 1.24, 1.23, 1.22, 1.21, 1.20, 1.19, 1.18, 1.17, 1.16, 1.15, 1.14, 1.13, 1.12, 1.11, 1.10, 1.09, 1.08, 1.07, 1.06, 1.05, 1.04, 1.03, 1.02, 1.01, 1.00, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85, 0.84, 0.83, 0.82, 0.81, 0.80, 0.79, 0.78, 0.77, 0.76, 0.75, 0.74, 0.73, 0.72, 0.71, 0.70, 0.69, 0.68, 0.67, 0.66, 0.65, 0.64, 0.63, 0.62, 0.61, 0.60, 0.59, 0.58, 0.57, 0.56, 0.55, 0.54, 0.53, 0.52, 0.51, 0.50, 0.49, 0.48, 0.47, 0.46, 0.45, 0.44, 0.43, 0.42, 0.41, 0.40, 0.39, 0.38, 0.37, 0.36, 0.35, 0.34, 0.33, 0.32, 0.31, 0.30, 0.29, 0.28, 0.27, 0.26, 0.25, 0.24, 0.23, 0.22, 0.21, 0.20, 0.19, 0.18, 0.17, 0.16, 0.15, 0.14, 0.13, 0.12, 0.11, 0.10, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.00	1.87, 2.03, 2.97, 1.96, 3.00, 2.99, 1.94, 4.17, 3.00, 3.98

Chemical structure: COc1ccc(cc1)C2(=O)CCCC2c3ccccc3

¹³C NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)
219.5
158.1
142.1
131.2
128.1
127.1
125.4
113.1
77.31
77.01
76.61
55.91
55.01
38.71
37.31
35.71
33.71
31.11
29.41
24.31
18.51

Chemical structure: COc1ccc(cc1)C2(C)CCCC2=O

¹H NMR spectrum (ppm):

- 7.10 (d, 4H, integration 1.97)
- 3.80 (s, 3H, integration 3.00)
- 2.00-2.50 (m, 8H, integrations: 0.94, 2.06, 1.97, 4.15, 1.19, 1.00, 2.01)

Chemical structure: COc1ccc(cc1)C2(C#CC)C(=O)CCC2

¹³C NMR spectrum (ppm):

- 219.4
- 158.2
- 130.4
- 127.1
- 113.1
- 84.0
- 77.3
- 77.0
- 76.6
- 68.4
- 55.6
- 55.1
- 37.9
- 37.1
- 33.8
- 23.7
- 18.6
- 18.5

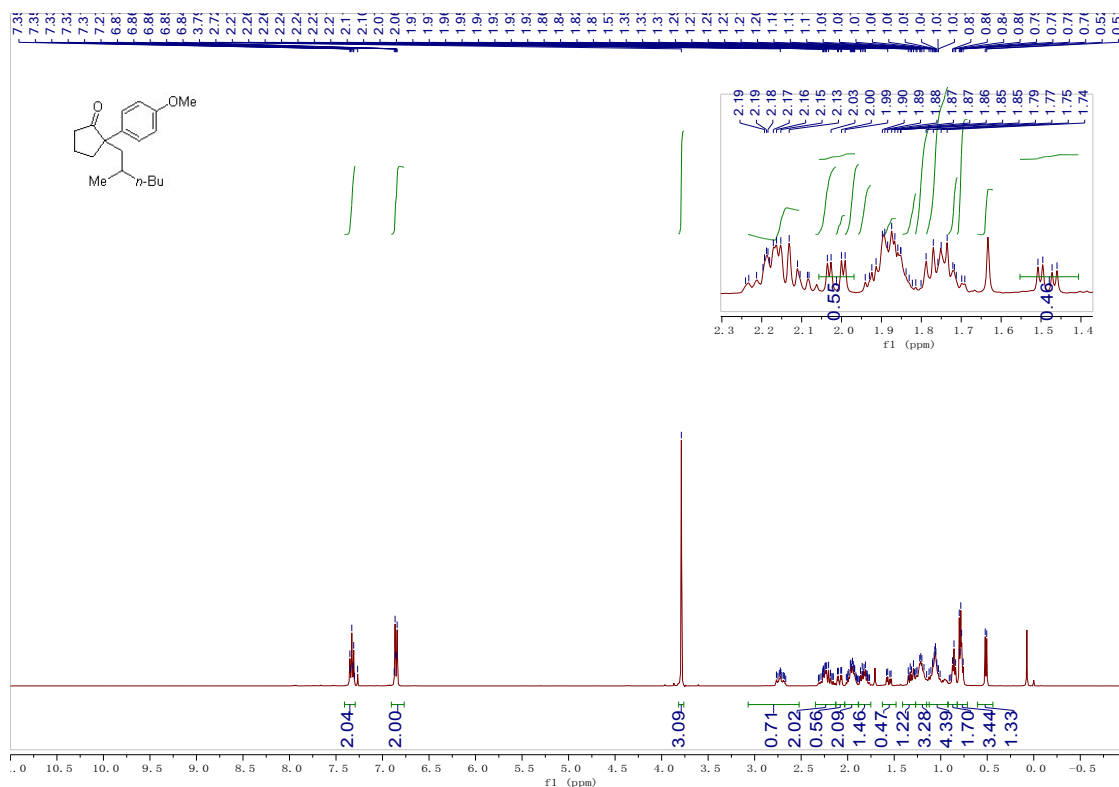
[illegible]

Chemical structure: COc1ccc(cc1)C2(CCCC2=O)C(C)C

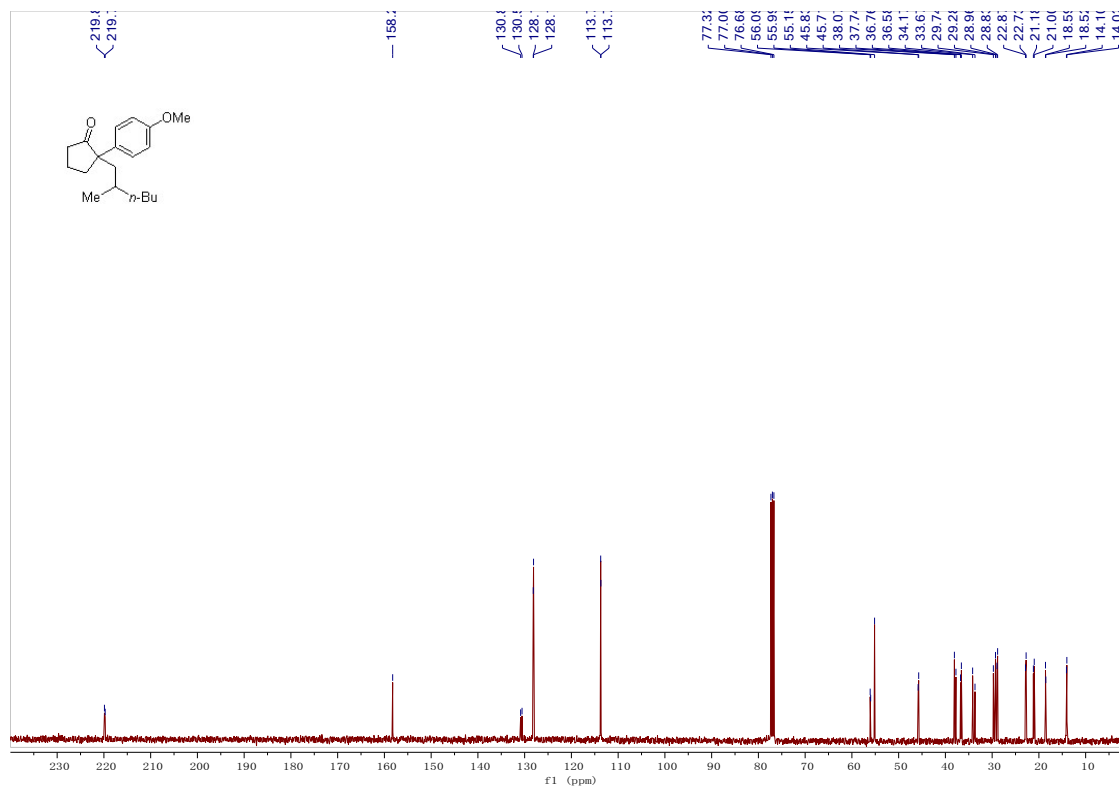
¹³C NMR spectrum (ppm):

- 219.1
- 158.1
- 130.1
- 128.1
- 113.1
- 77.31
- 77.01
- 76.61
- 56.01
- 55.11
- 47.51
- 36.51
- 33.91
- 24.91
- 24.31
- 23.61
- 18.51

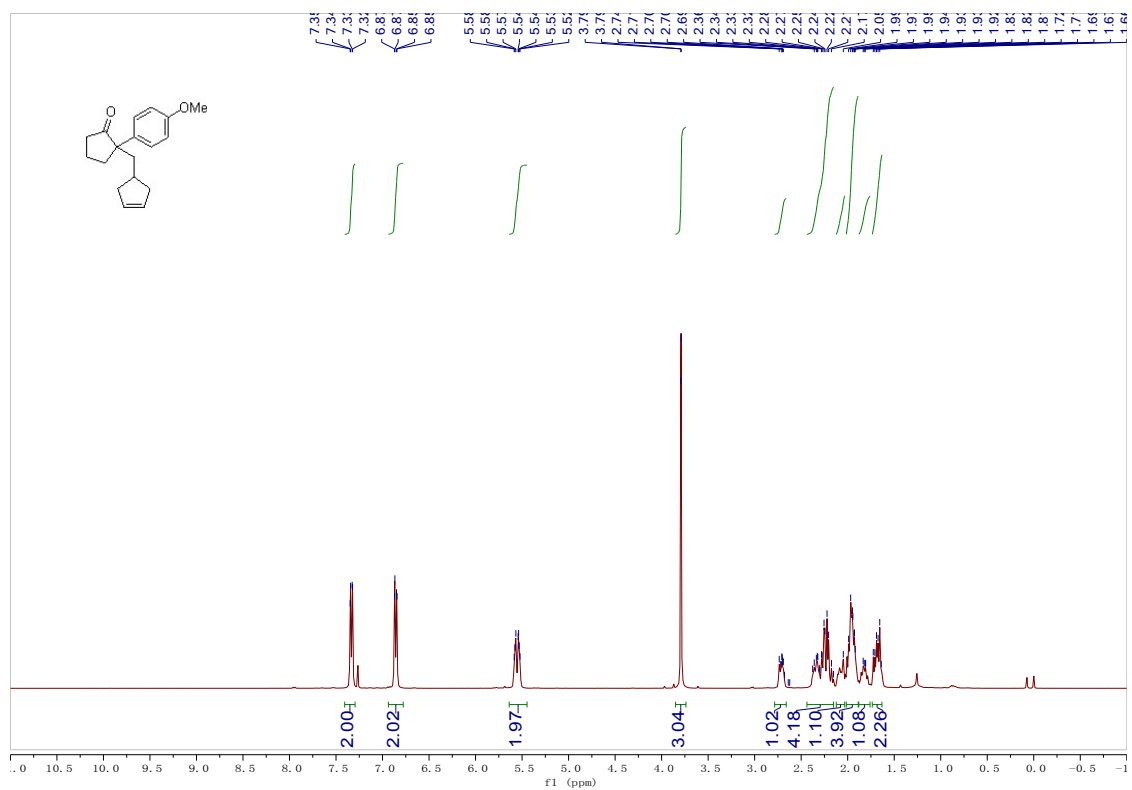
¹H NMR Spectrum of **3m**



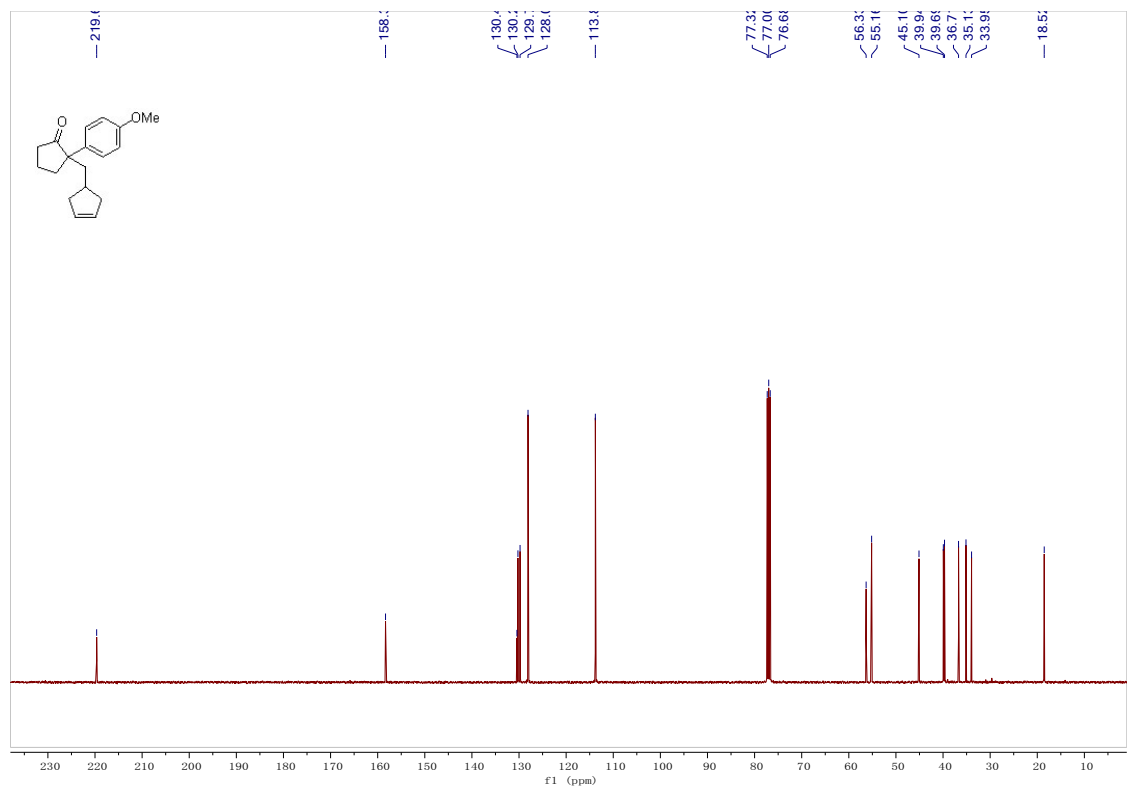
¹³C NMR Spectrum of **3m**



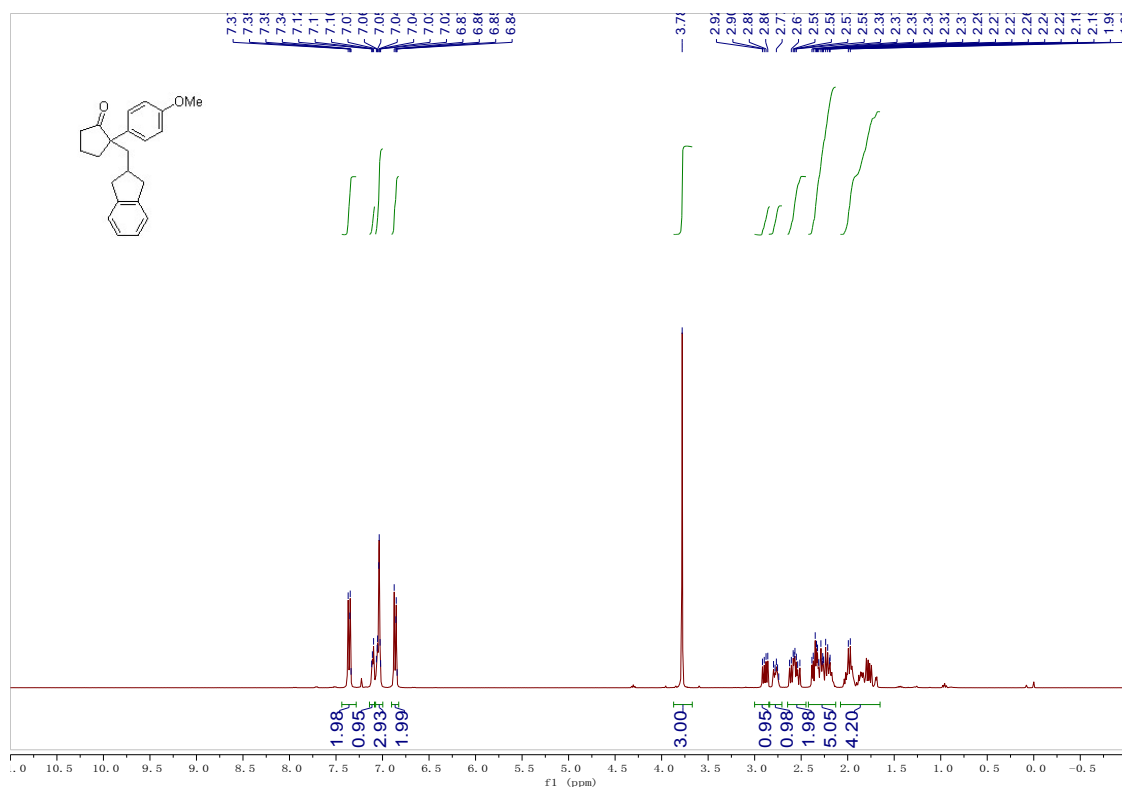
¹H NMR Spectrum of **3n**



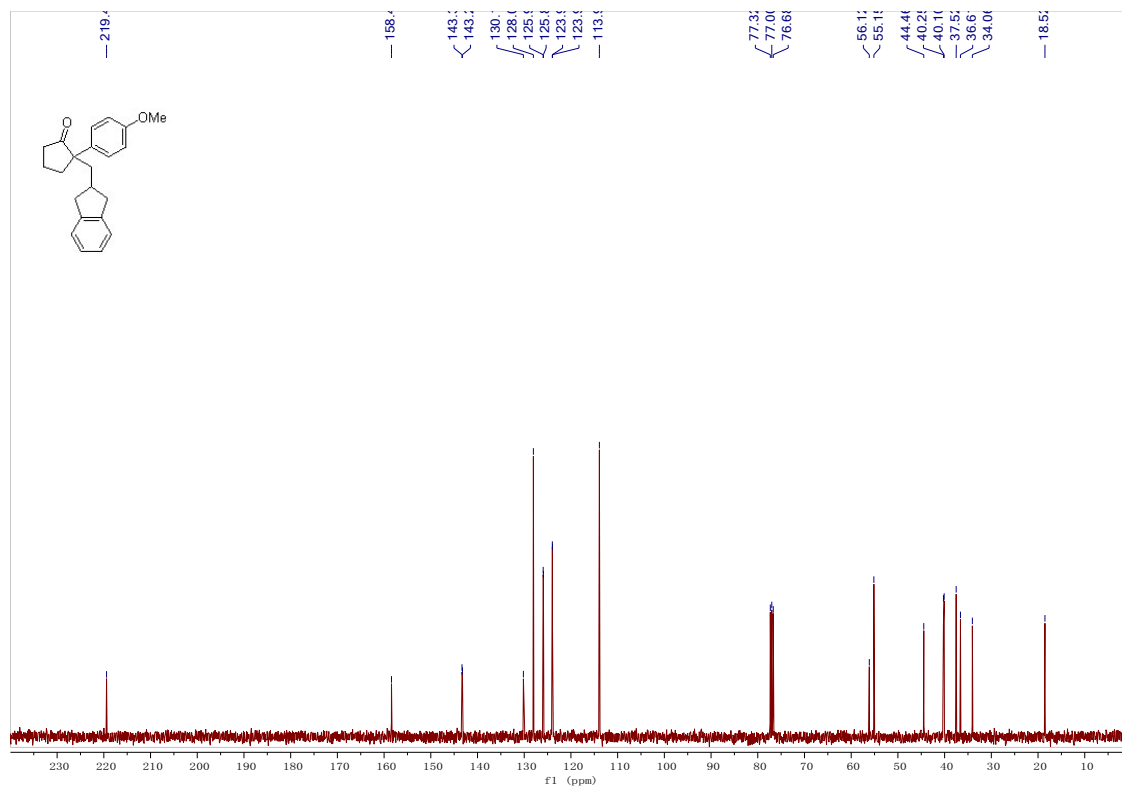
¹³C NMR Spectrum of **3n**



¹H NMR Spectrum of **3o**



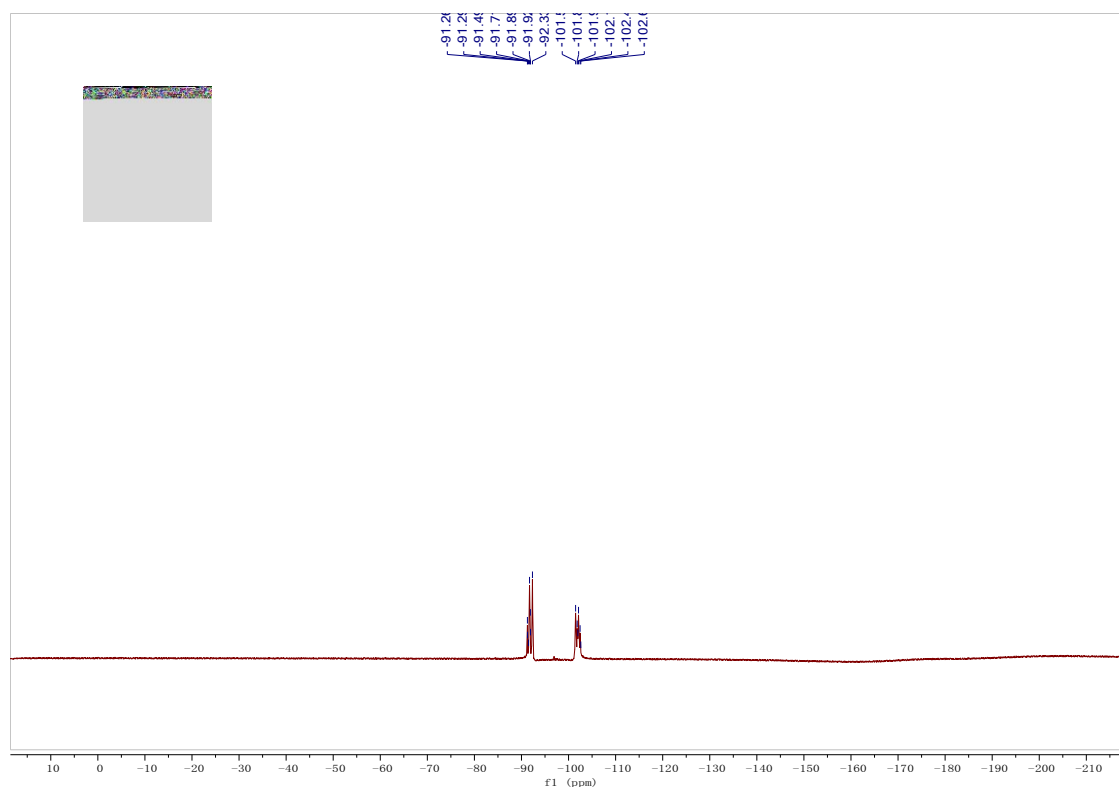
¹³C NMR Spectrum of **3o**



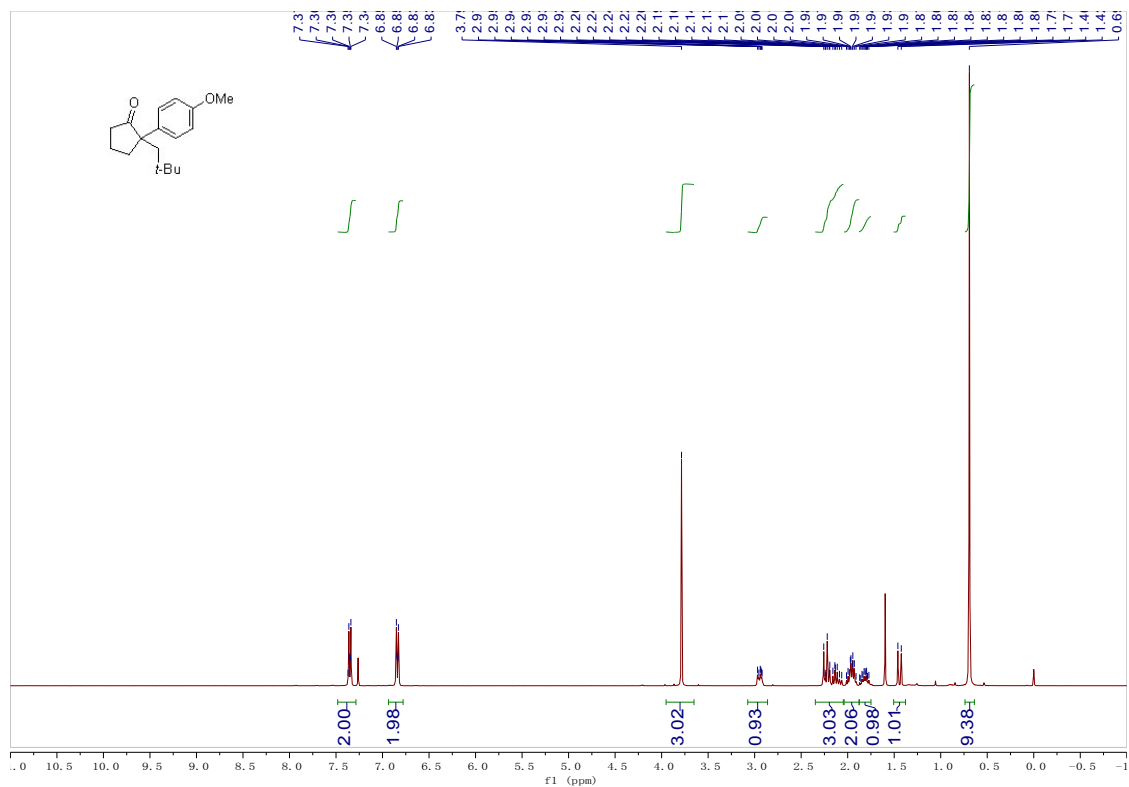
Chemical structure of the compound is shown above the spectrum. The spectrum displays peaks corresponding to the chemical structure, with the following chemical shifts (ppm) labeled on the right side:

219.7, 158.4, 130.2, 127.5, 125.6, 123.2, 123.1, 120.3, 113.5, 77.3, 77.0, 76.6, 55.6, 55.1, 44.4, 44.3, 36.5, 34.2, 33.2, 33.2, 33.0, 32.3, 30.2, 30.1, 29.8, 29.7, 19.2.

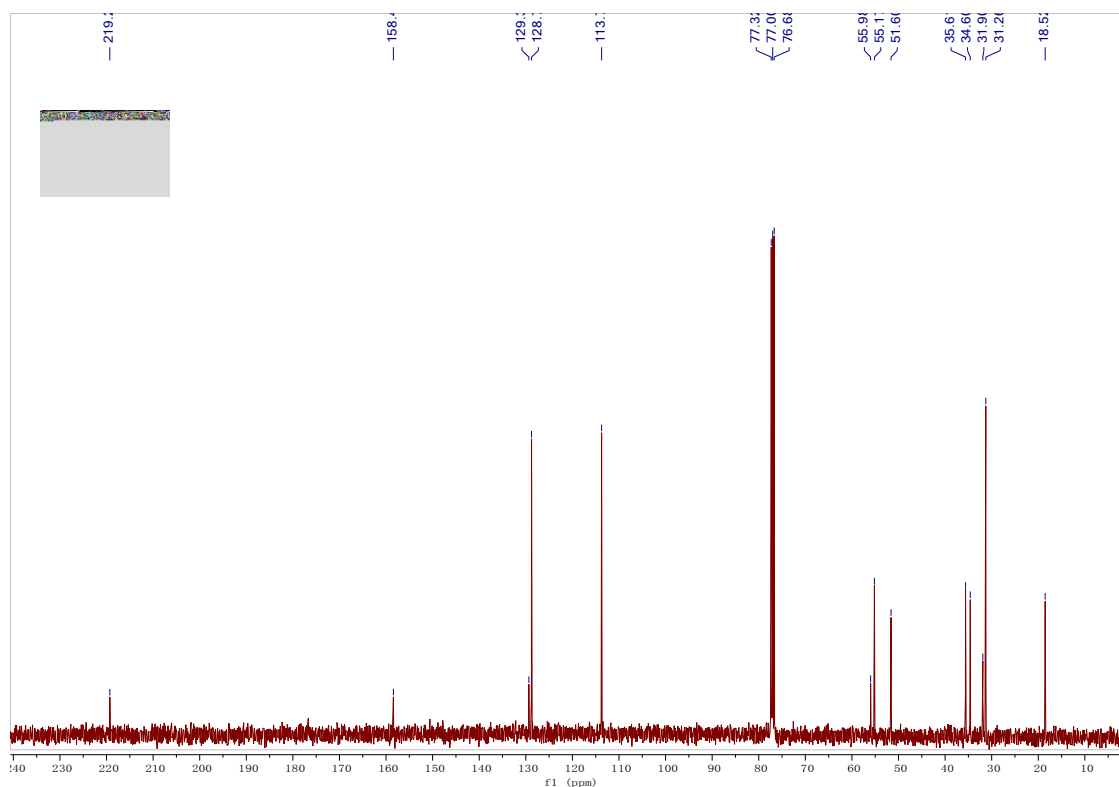
¹⁹F NMR Spectrum of **3p**



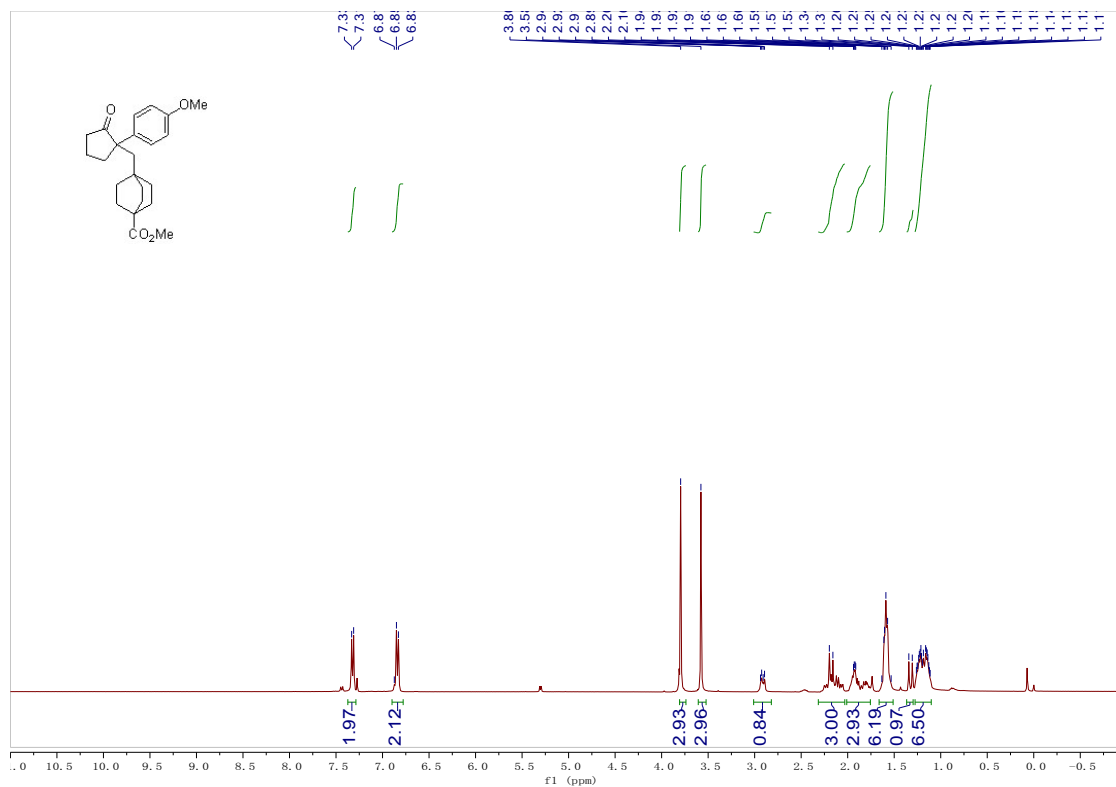
¹H NMR Spectrum of **3q**



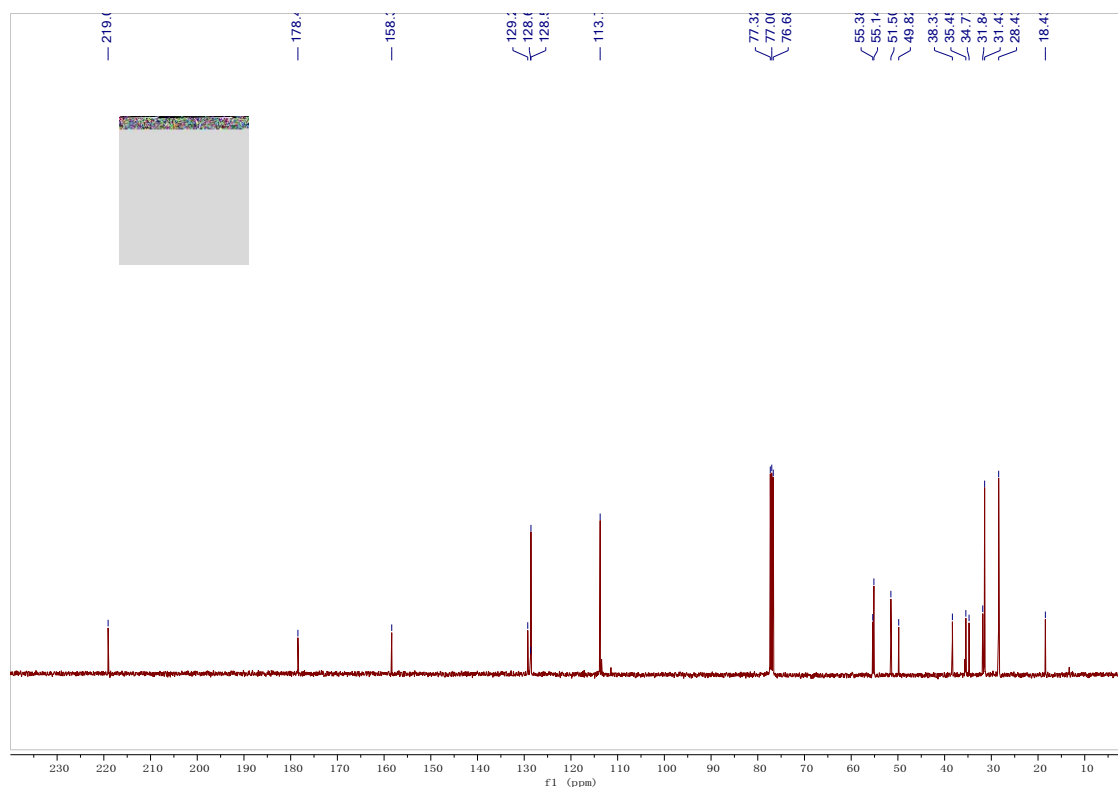
¹³C NMR Spectrum of **3q**



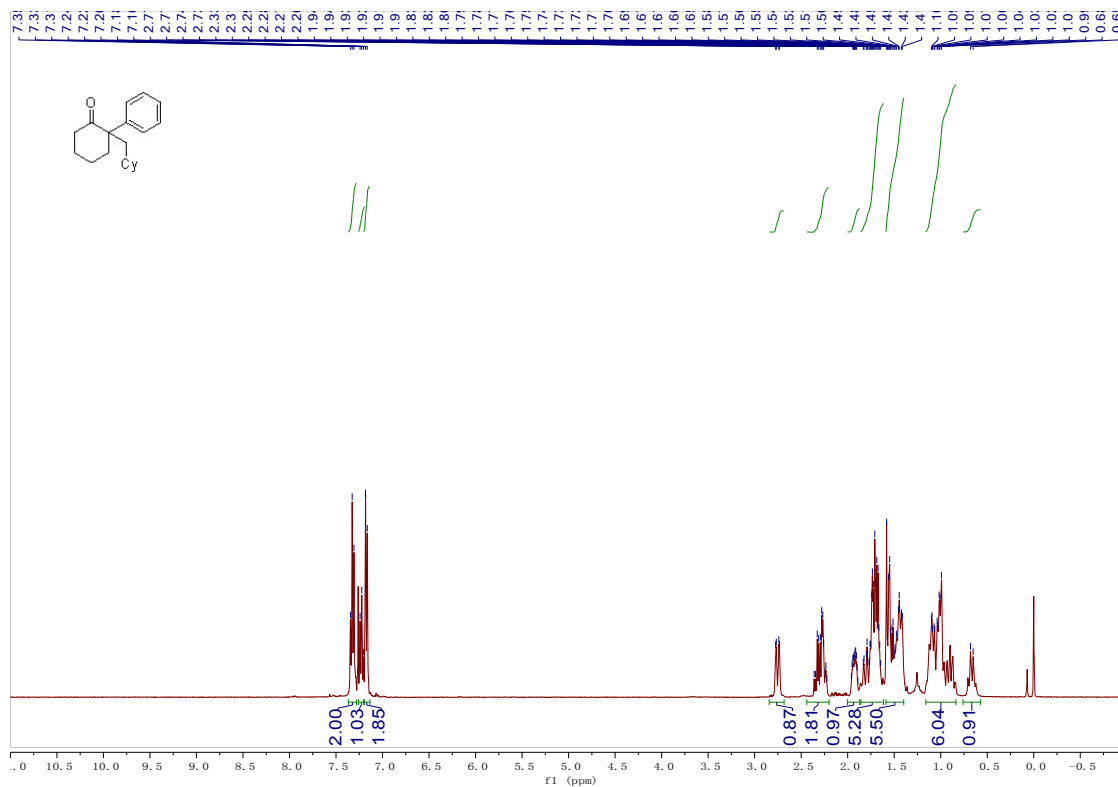
¹H NMR Spectrum of **3r**

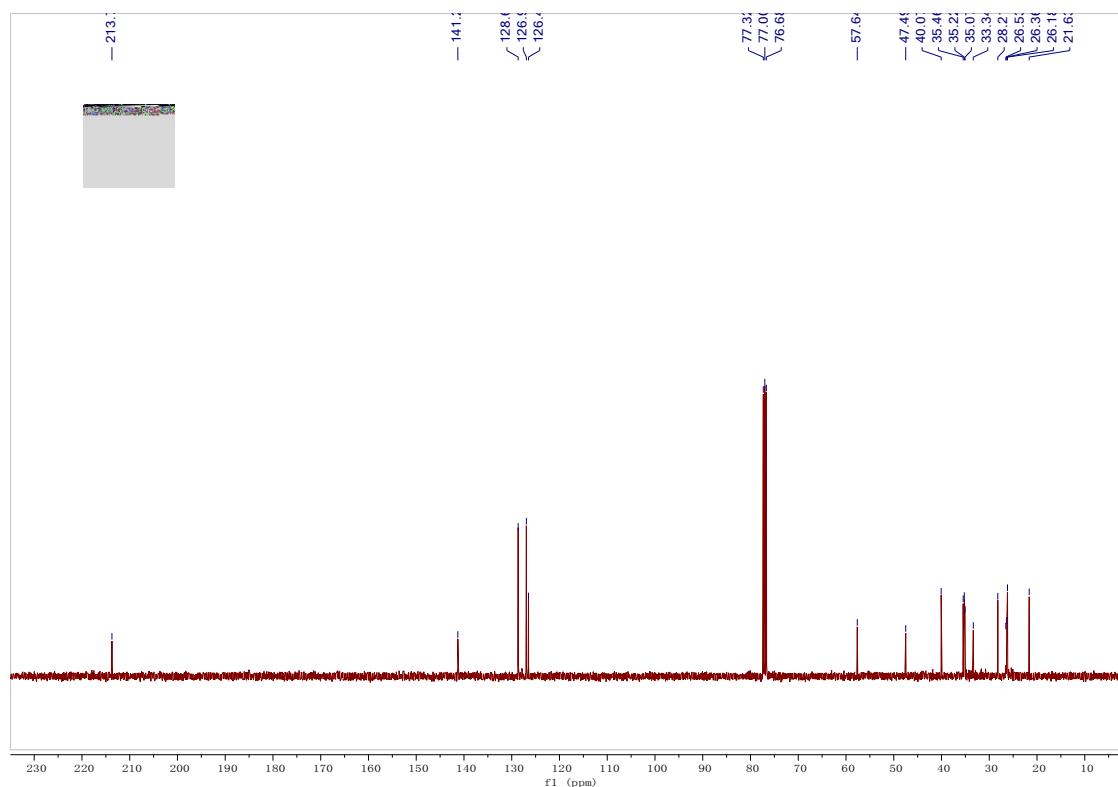


¹³C NMR Spectrum of **3r**

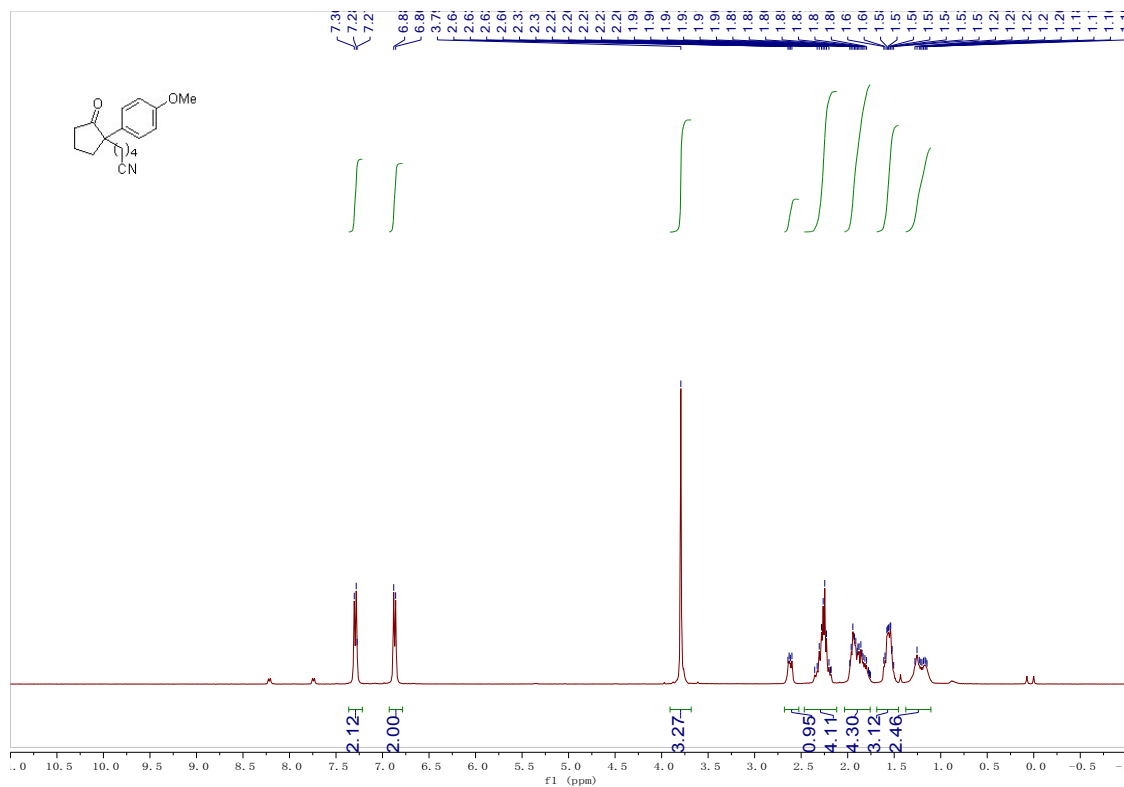


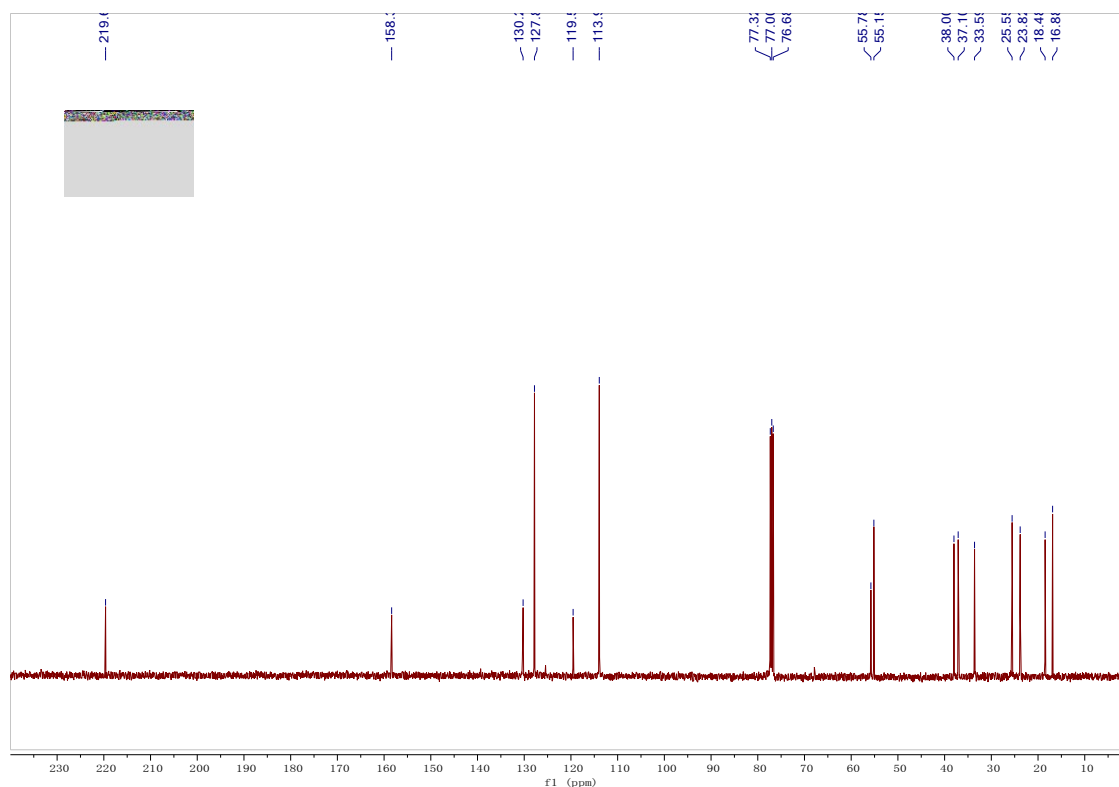
¹H NMR Spectrum of **3s**



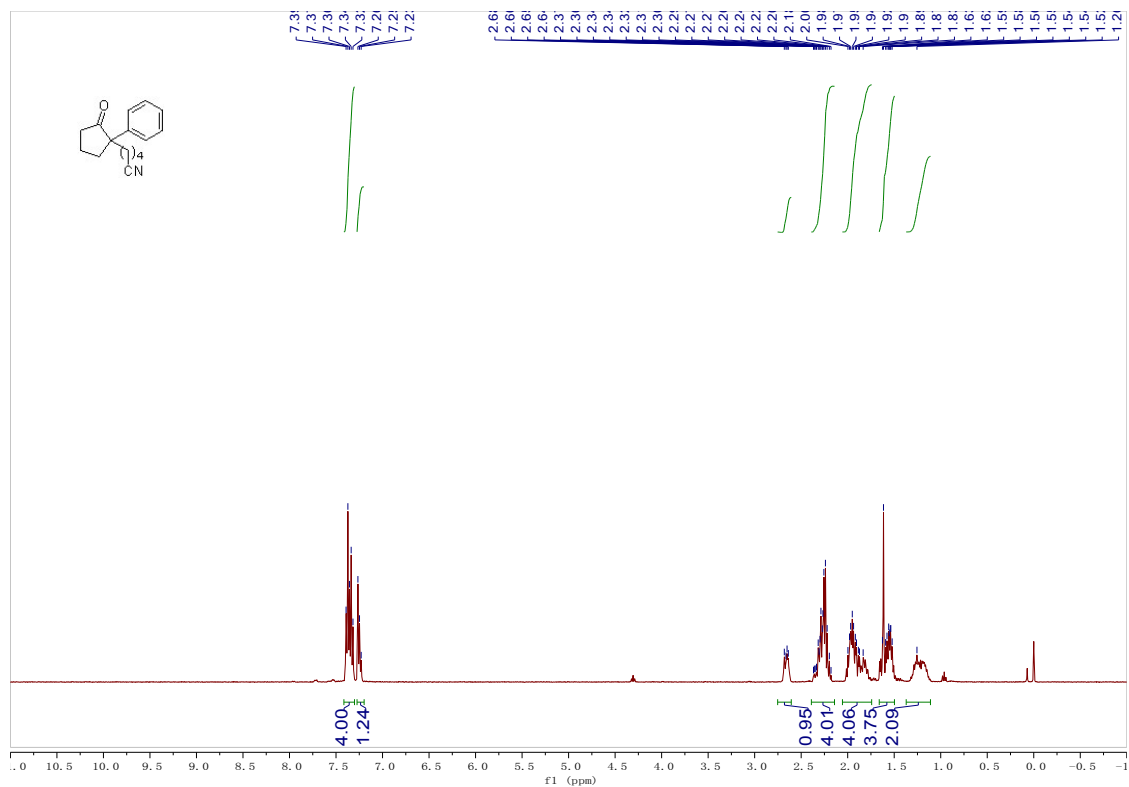
^{13}C NMR Spectrum of **3s**

¹H NMR Spectrum of **5a**

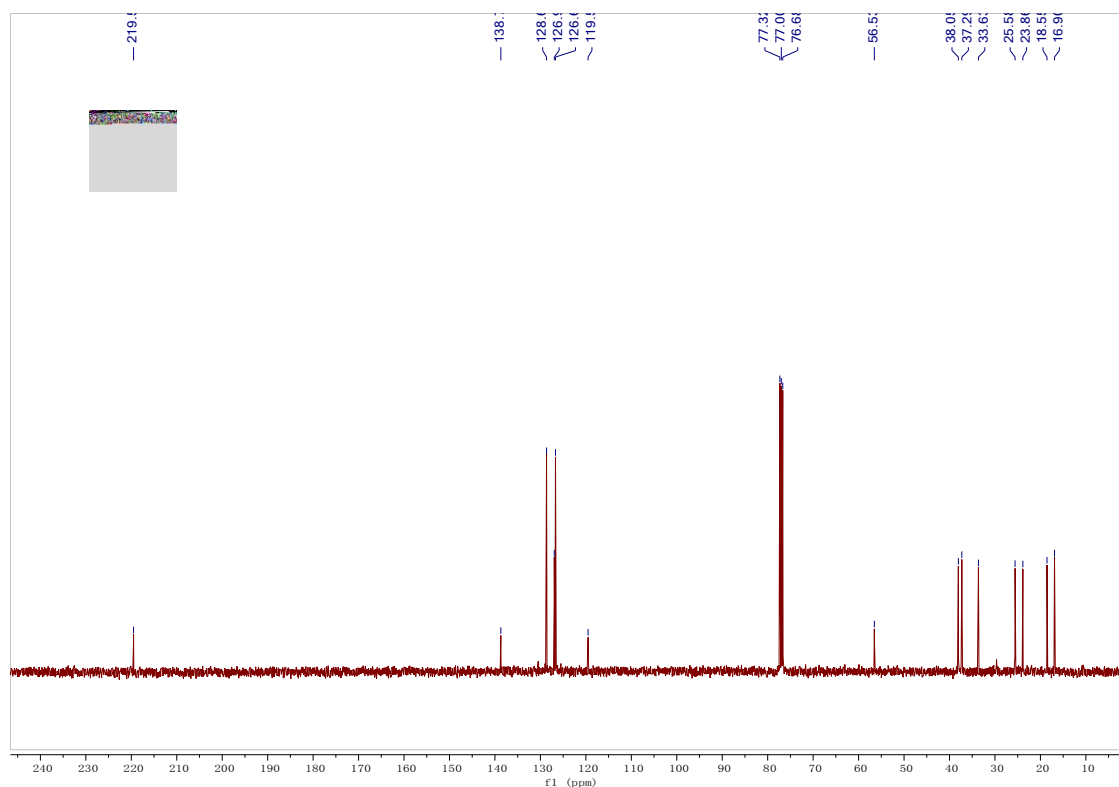


^{13}C NMR Spectrum of **5a**

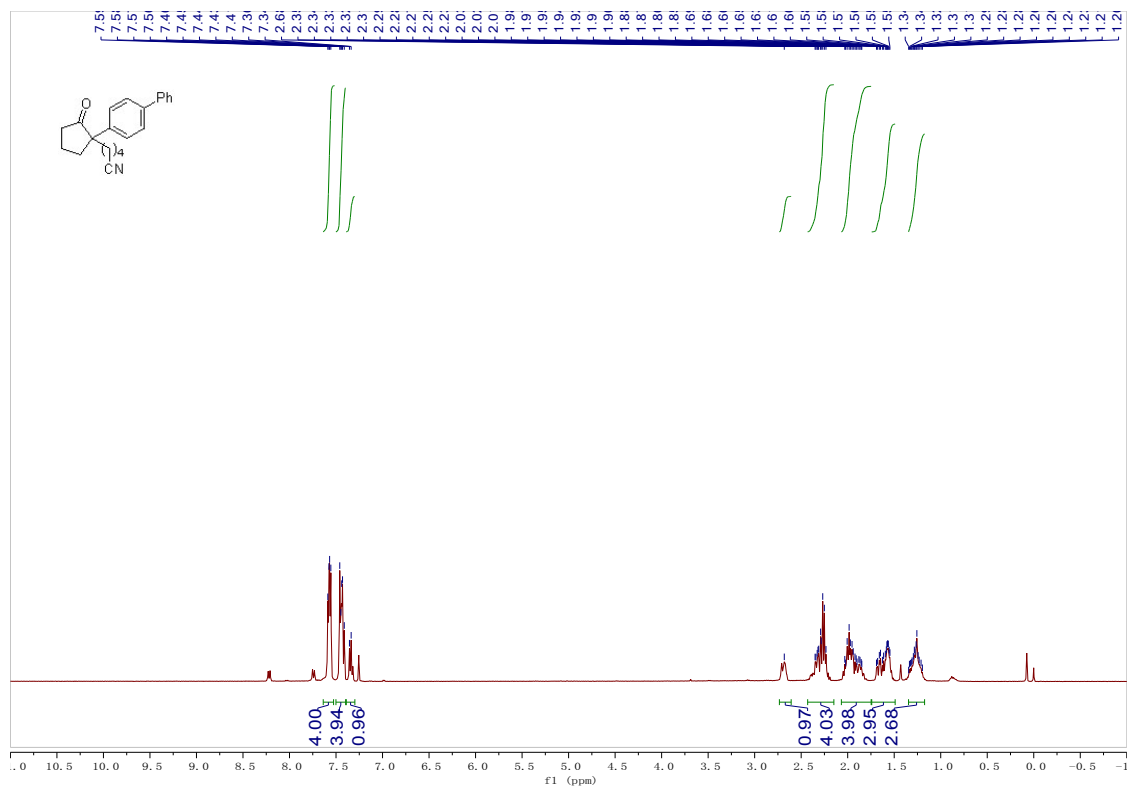
¹H NMR Spectrum of **5b**



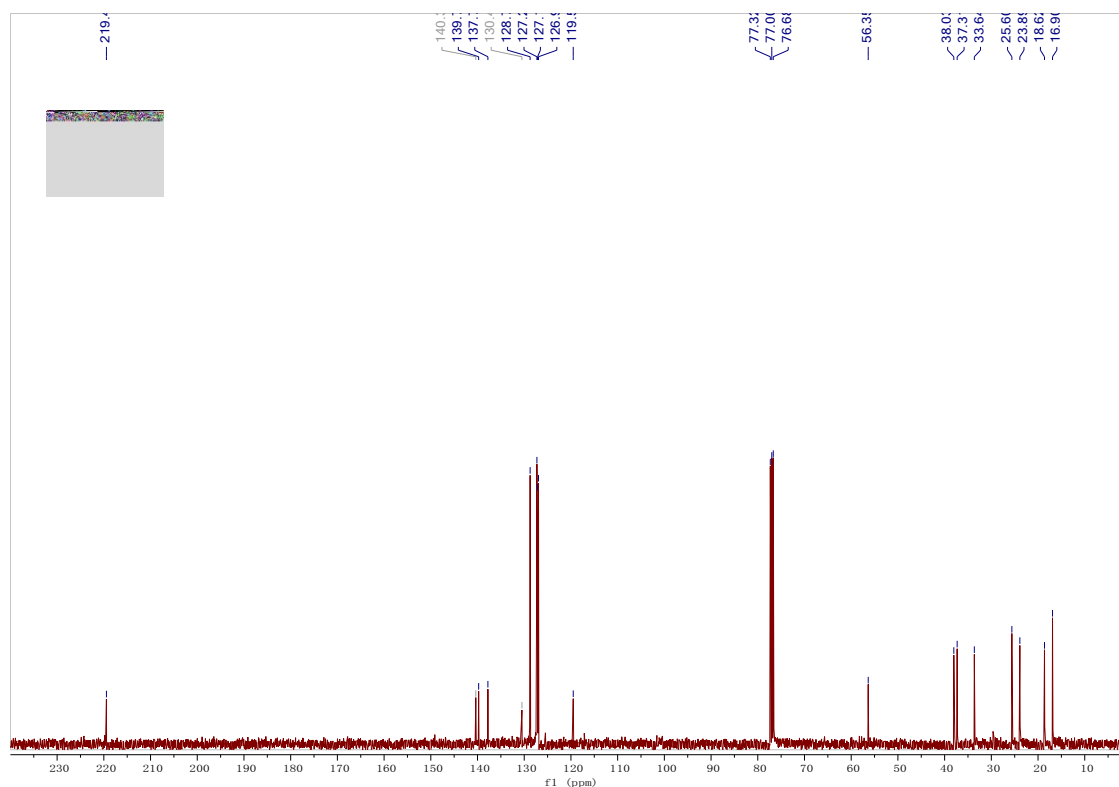
¹³C NMR Spectrum of **5b**



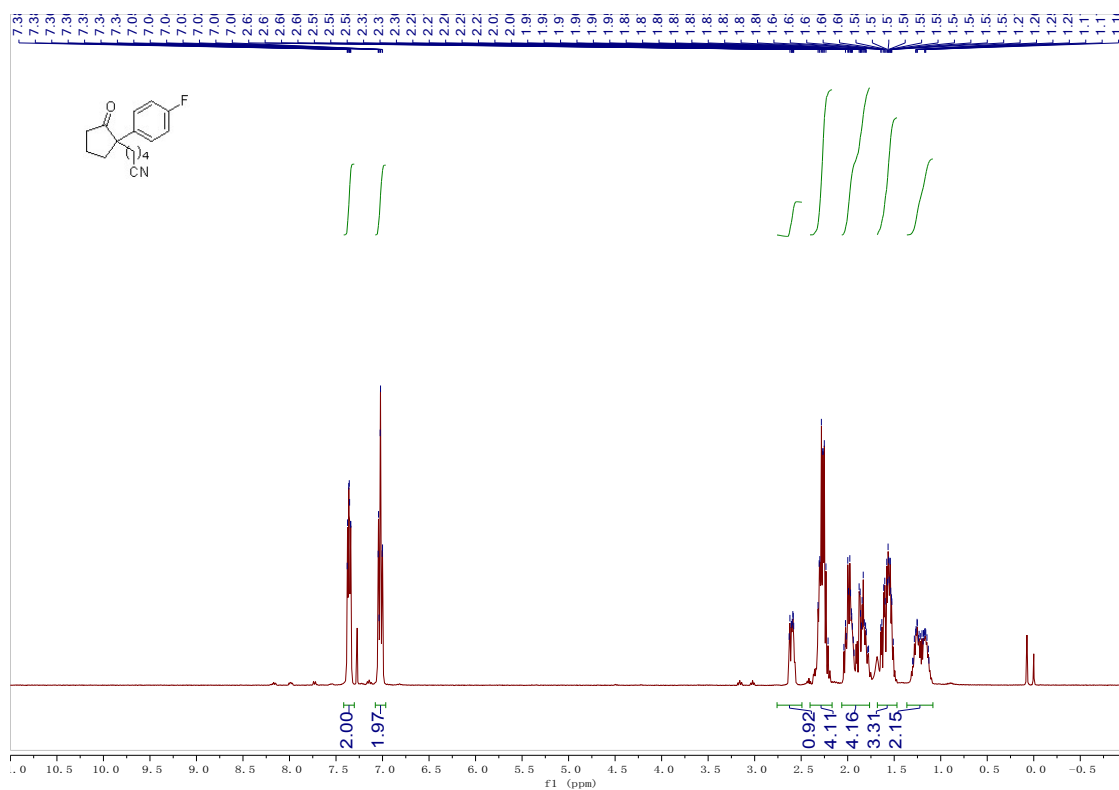
¹H NMR Spectrum of **5c**



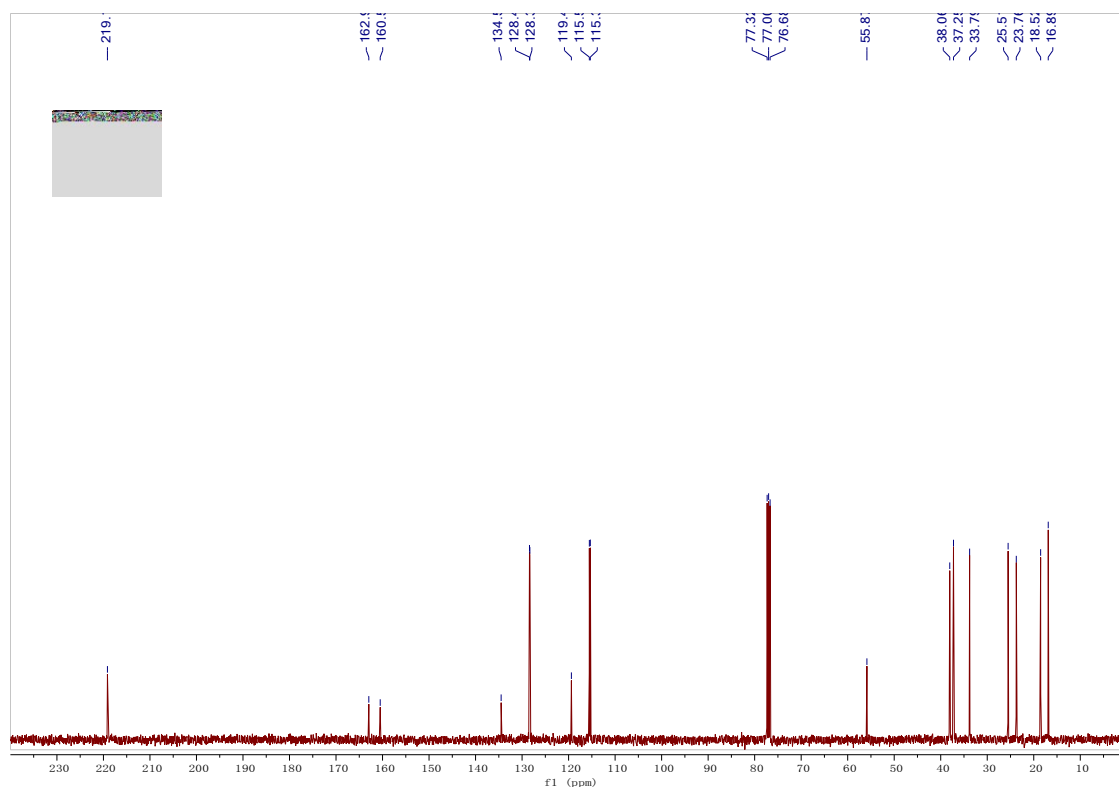
¹³C NMR Spectrum of **5c**



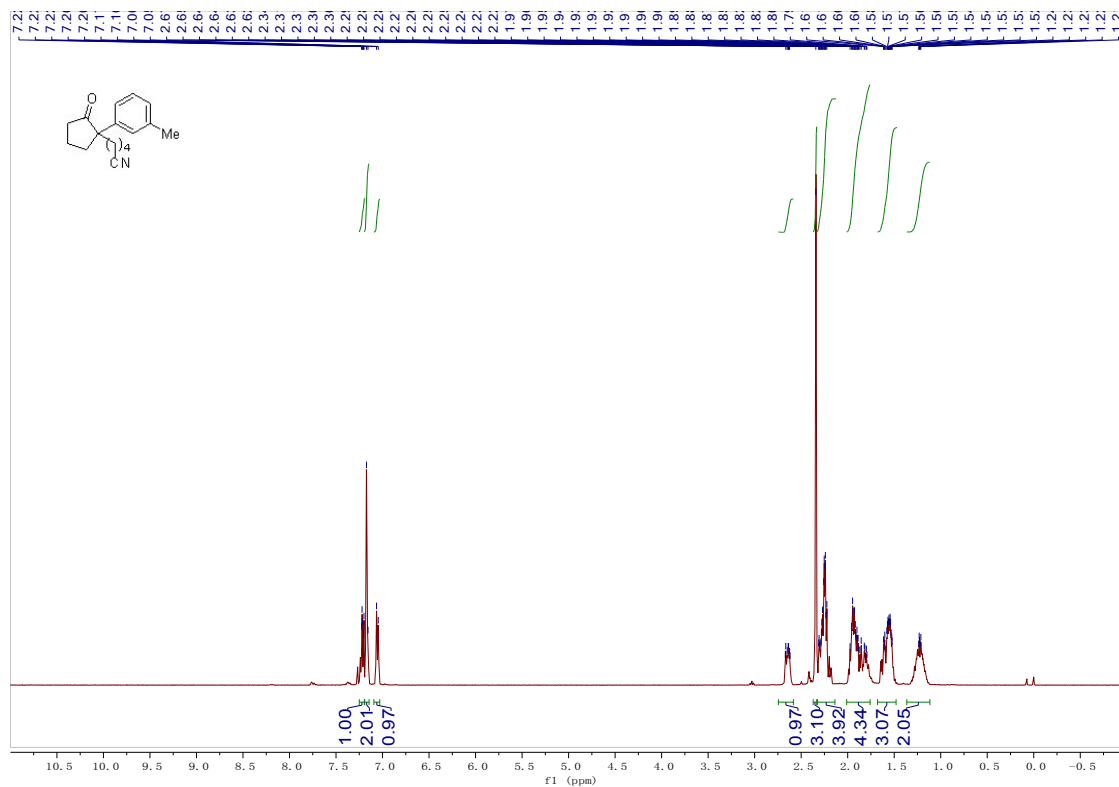
¹H NMR Spectrum of **5d**



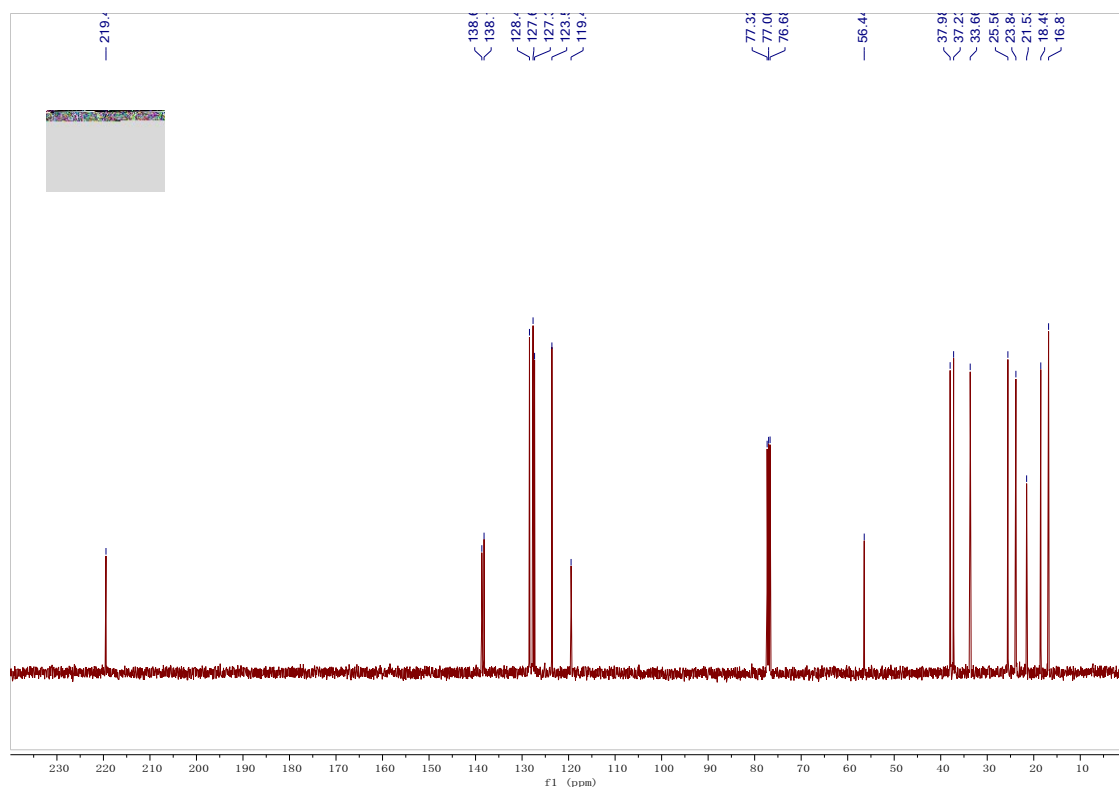
¹³C NMR Spectrum of **5d**



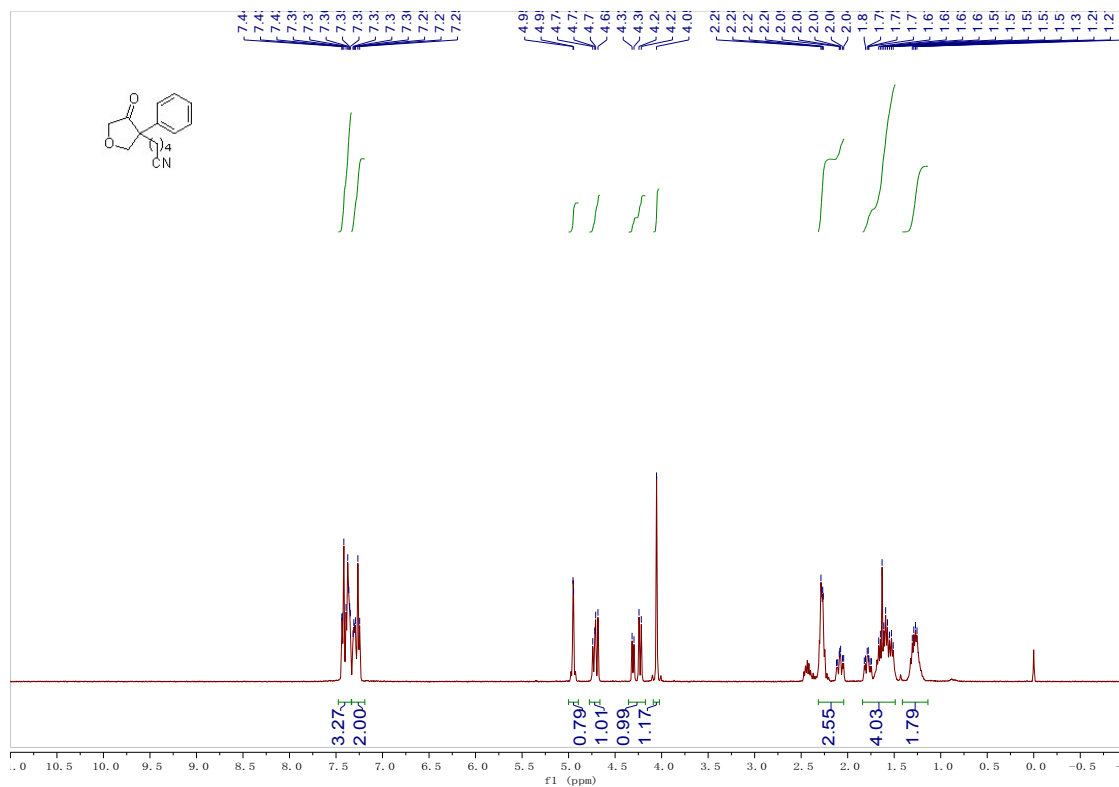
¹H NMR Spectrum of **5e**



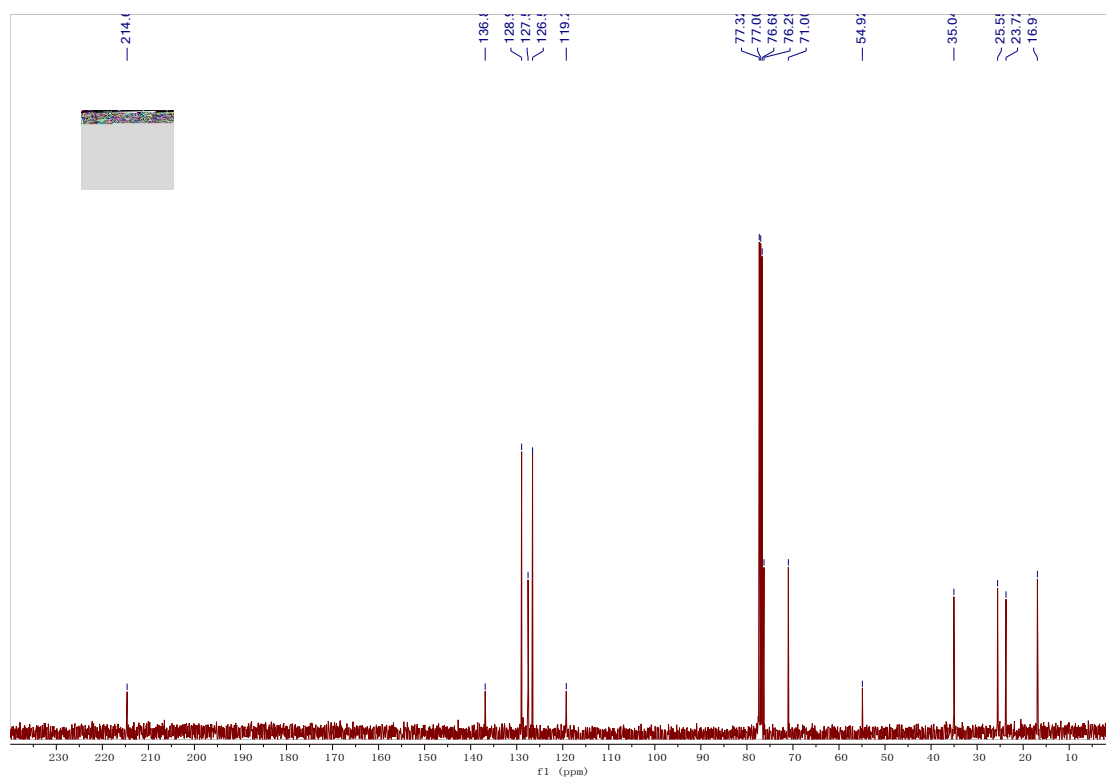
¹³C NMR Spectrum of **5e**



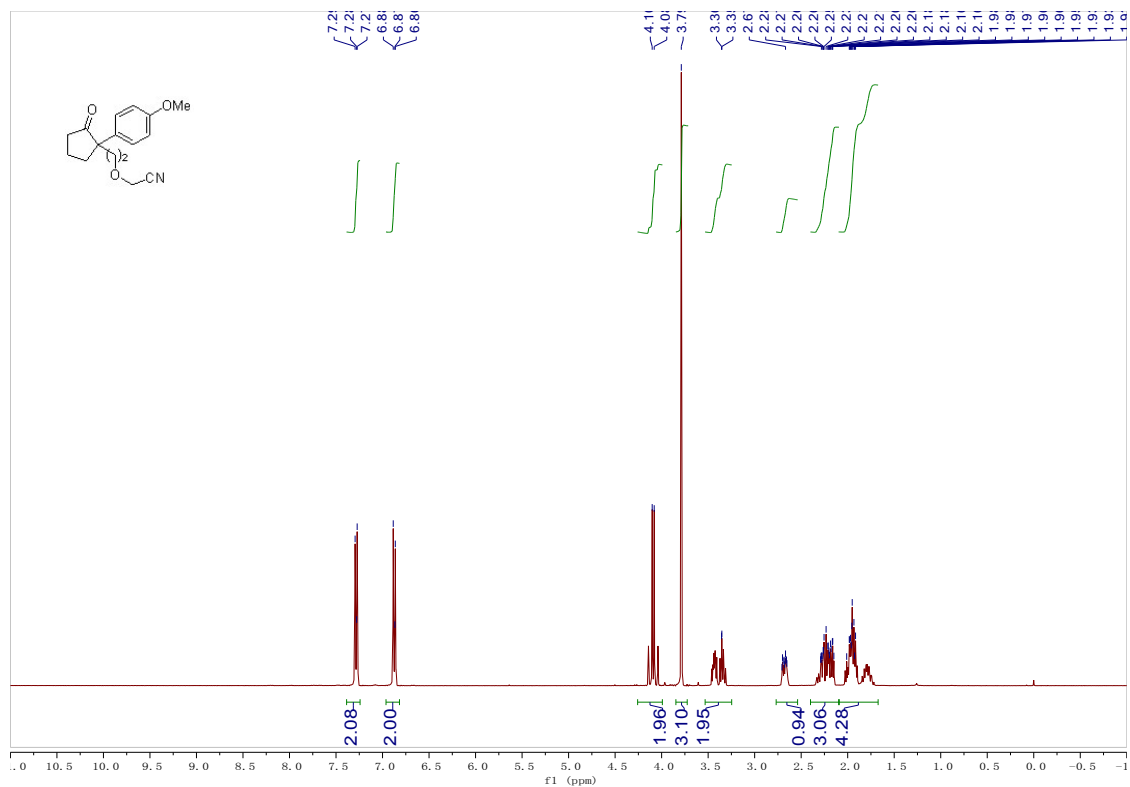
¹H NMR Spectrum of **5f**



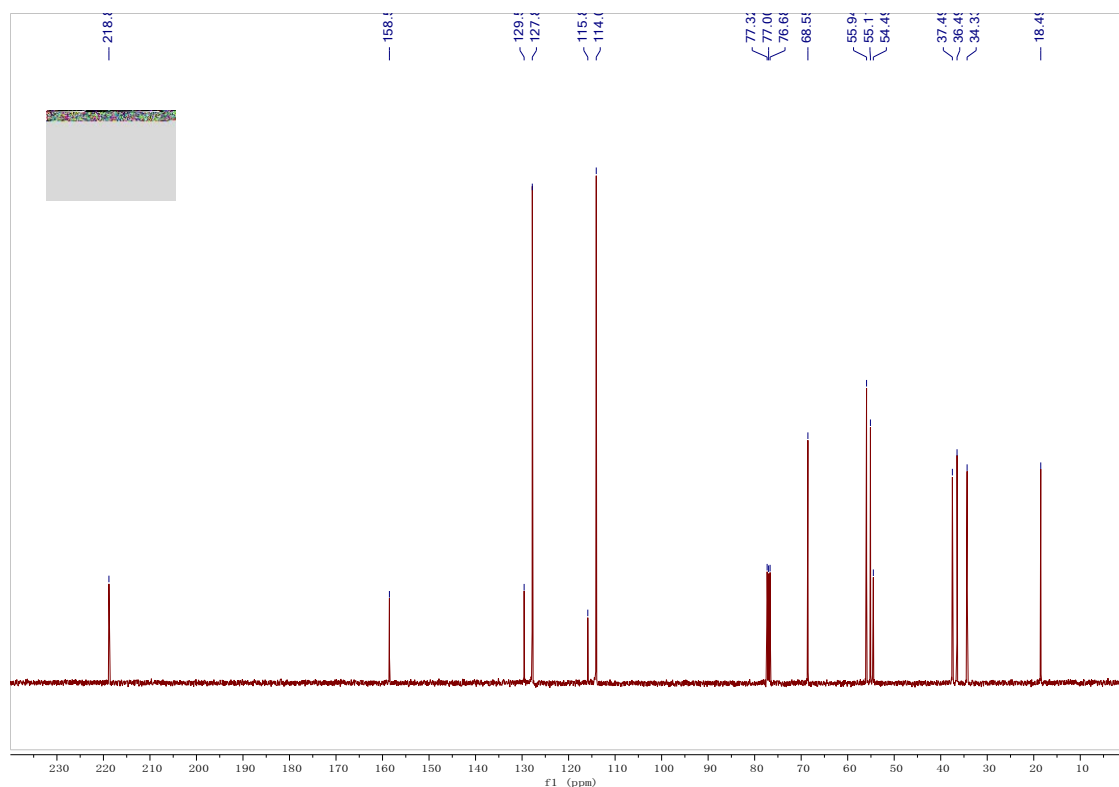
¹³C NMR Spectrum of **5f**



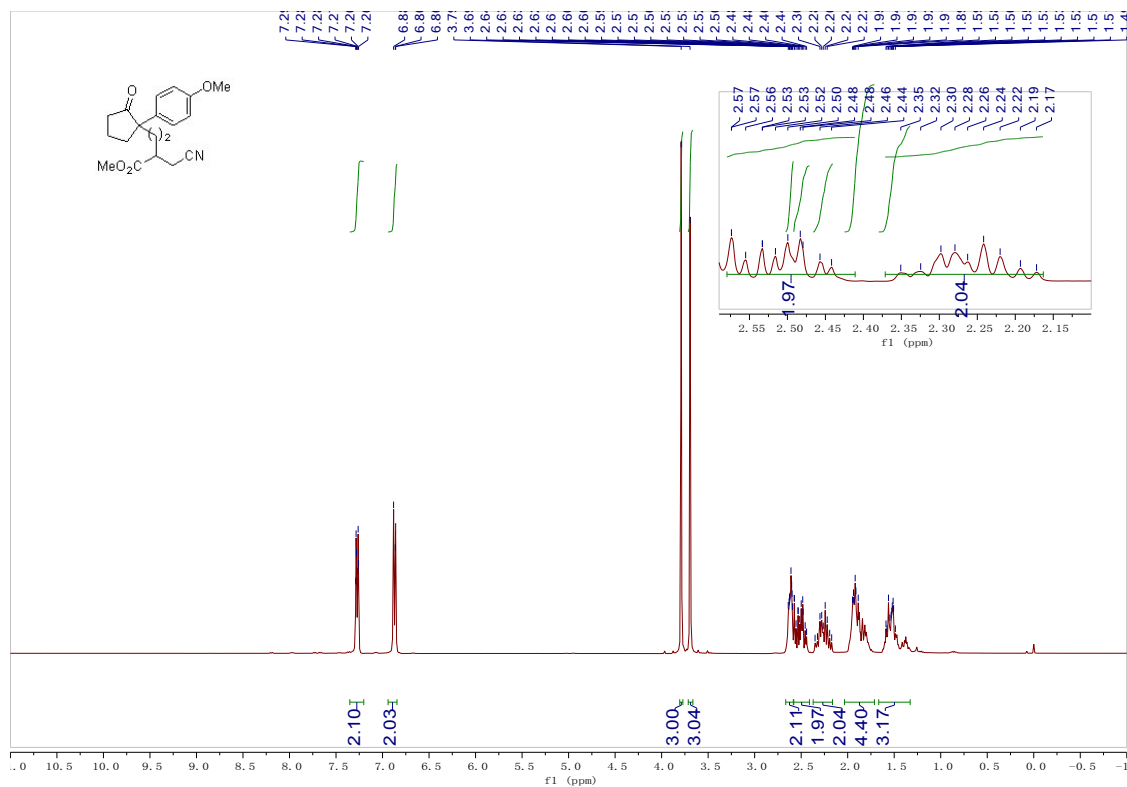
¹H NMR Spectrum of **5g**



¹³C NMR Spectrum of **5g**



¹H NMR Spectrum of **5h**



Chemical structure of the compound is shown above the spectrum. The structure is a cyclopentanone derivative with a 4-methoxyphenyl group and a 2-cyanoethyl group attached to the ring. The spectrum shows peaks corresponding to the structure, with the following chemical shifts (ppm) labeled above the peaks:

218.5, 172.1, 172.1, 158.4, 129.1, 129.1, 127.1, 127.1, 117.4, 117.4, 114.1, 114.1, 77.3, 77.0, 76.6, 55.4, 55.3, 55.1, 52.2, 52.2, 52.2, 41.3, 41.2, 36.9, 36.9, 35.3, 35.3, 33.5, 26.2, 19.0, 18.9, 18.4.

13C NMR spectrum (CDCl₃) of the compound. The x-axis represents the chemical shift in ppm, ranging from 10 to 230. The spectrum shows several peaks, with the following chemical shifts (ppm) labeled above the peaks:

218.5, 172.1, 172.1, 158.4, 129.1, 129.1, 127.1, 127.1, 117.4, 117.4, 114.1, 114.1, 77.3, 77.0, 76.6, 55.4, 55.3, 55.1, 52.2, 52.2, 52.2, 41.3, 41.2, 36.9, 36.9, 35.3, 35.3, 33.5, 26.2, 19.0, 18.9, 18.4.

Chemical structure of compound 10: COc1ccc(cc1)C2(CCN2)C(=O)C3CCCC3

¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm (f1), ranging from -0.5 to 7.5. The spectrum shows several peaks, with integration values provided below the baseline. An inset shows a zoomed-in view of the region from 1.65 to 1.85 ppm.

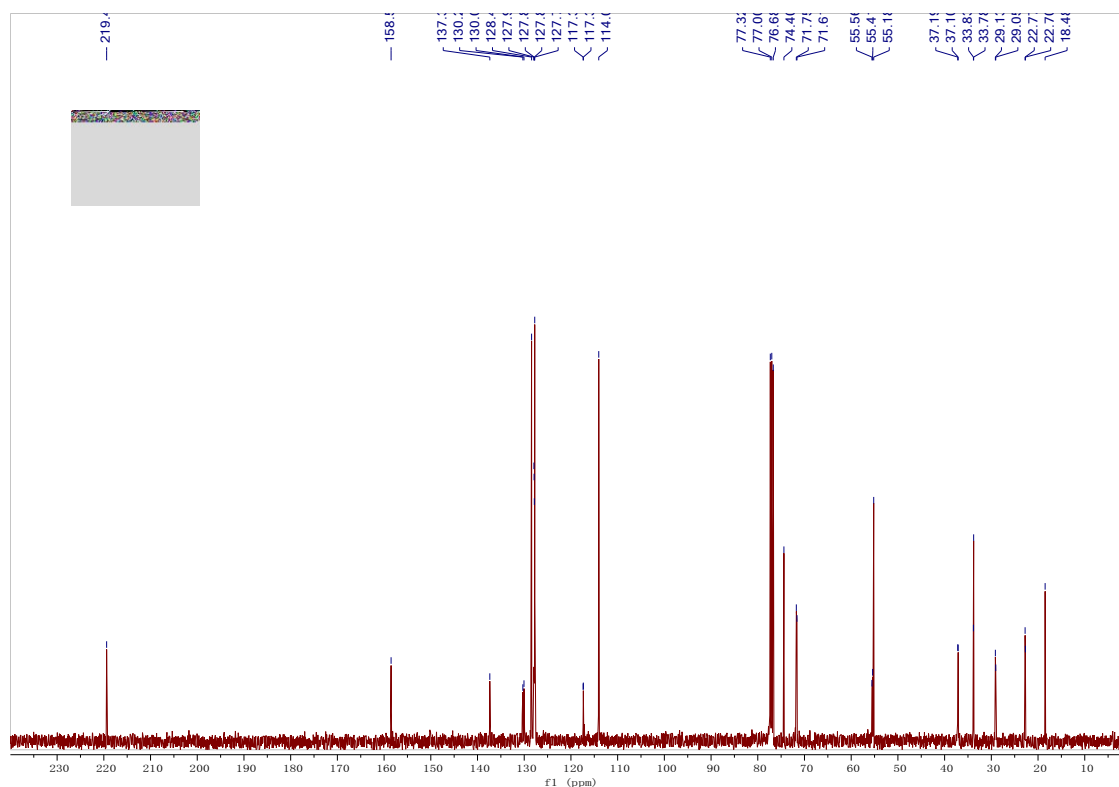
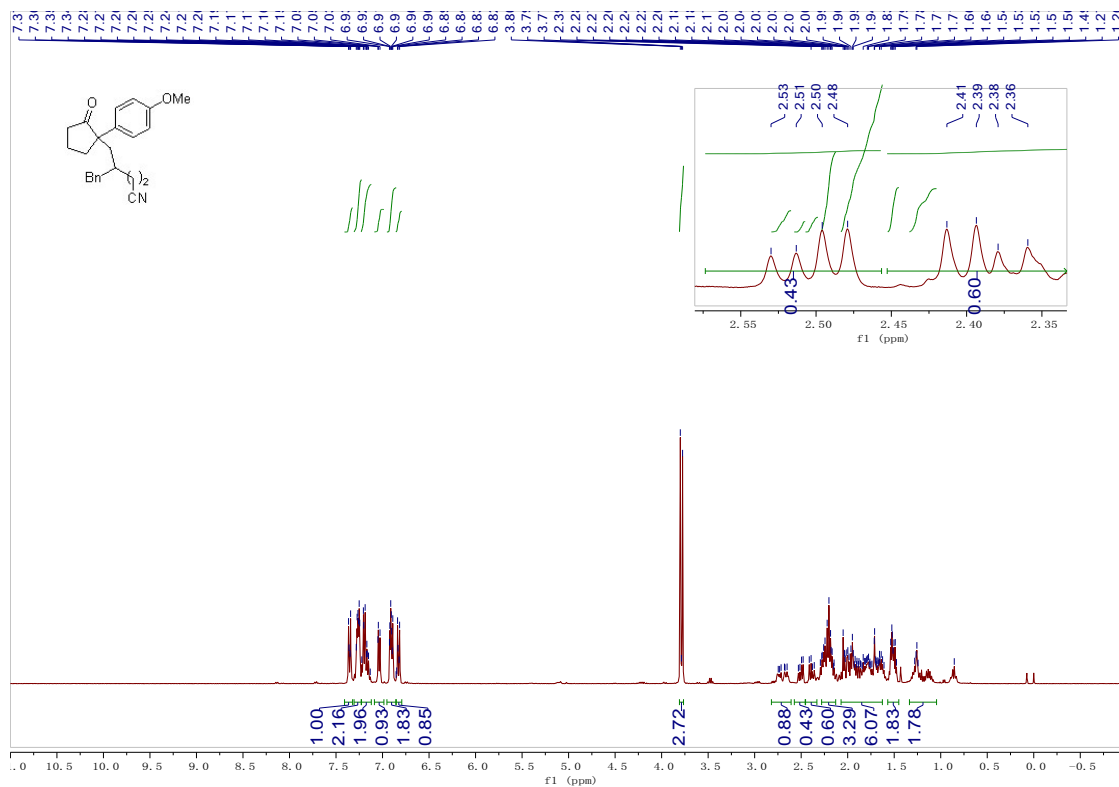
Integration values (from left to right): 7.06, 2.04, 1.86, 3.10, 0.94, 1.02, 4.16, 3.22, 0.78, 0.65, 2.13.

Chemical shift values (from left to right): 7.3, 7.3, 7.3, 7.2, 7.2, 7.2, 6.8, 6.8, 4.5, 4.5, 4.4, 4.4, 4.4, 4.4, 4.4, 3.8, 3.7, 3.7, 3.5, 3.5, 3.5, 2.6, 2.6, 2.6, 2.6, 2.5, 2.5, 2.5, 2.4, 2.4, 2.4, 2.4, 1.9, 1.9, 1.9, 1.9, 1.8, 1.8, 1.8, 1.8, 1.8, 1.8, 1.8, 1.7, 1.7, 1.7, 1.7, 1.7, 1.6, 1.6, 1.4, 1.4, 1.4, 1.4.

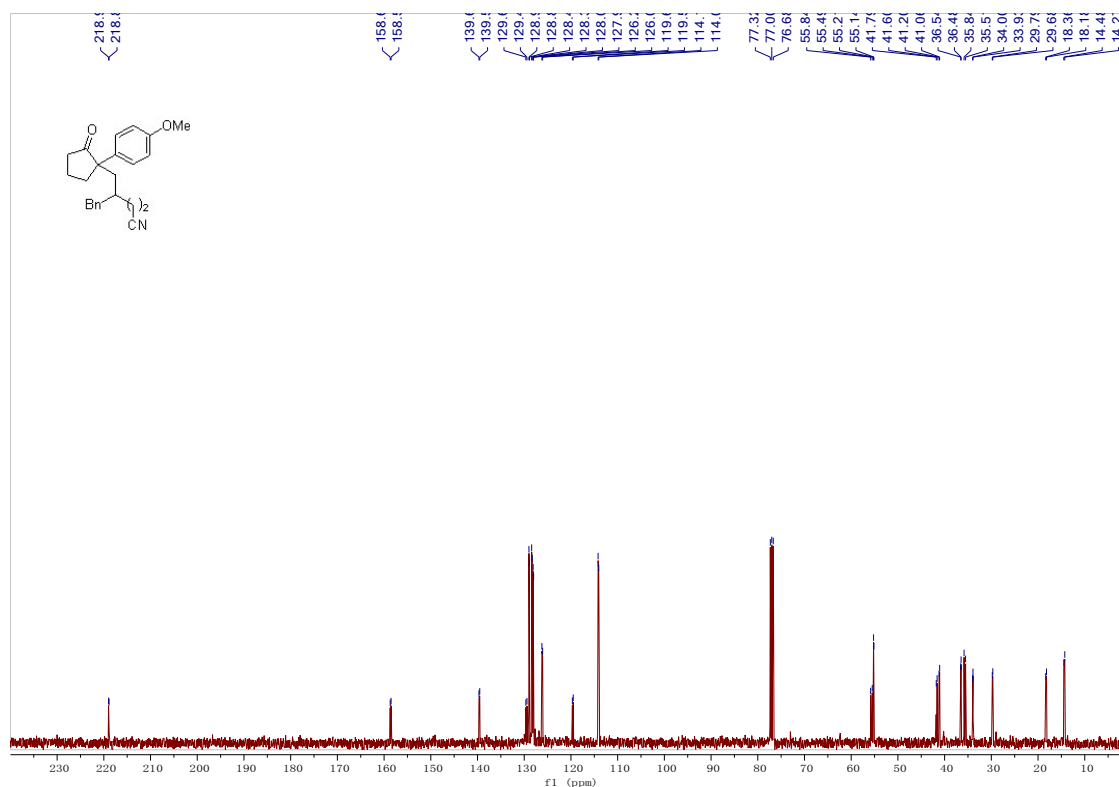
Inset x-axis (f1 (ppm)): 1.80, 1.75, 1.70.

Inset integration values (from left to right): 0.78, 0.65.

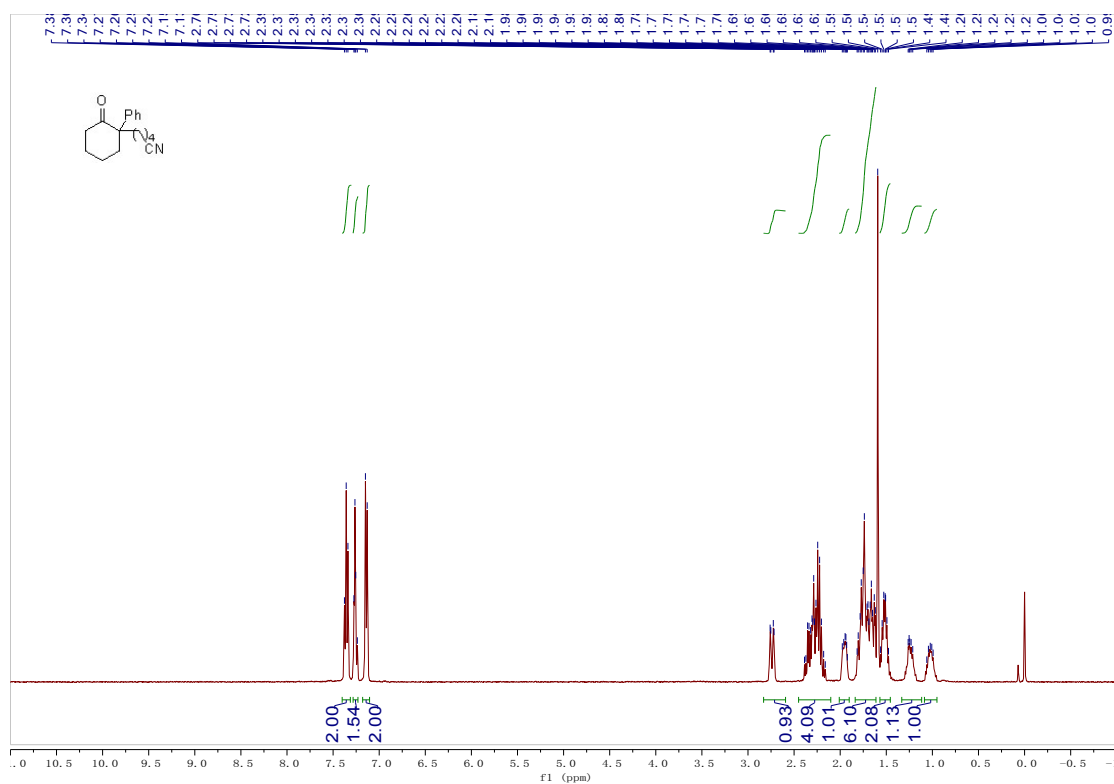
Inset chemical shift values (from left to right): 1.83, 1.82, 1.81, 1.80, 1.79, 1.79, 1.79, 1.74, 1.73, 1.71, 1.70, 1.68, 1.67.

^{13}C NMR Spectrum of **5i**¹H NMR Spectrum of **5j**

¹³C NMR Spectrum of **5j**



¹H NMR Spectrum of **5k**



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

