Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of cyclopent-1-enecarbonitriles via a tandem Giese/HWE reaction initiated by visible light

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Contents

1. General Methods

NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for ^{1}H and 176 MHz for ^{13}C, respectively and on JEOL JNM-ECZL 376 MHz for ^{19}F . Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for 1H NMR, 77.16 ppm for ^{13}C NMR). Mass spectra were recorded on a Bruker Maxis Impact spectrometer using electrospray (ES+) ionization (referenced to the mass of the charged species). Analytical thin layer chromatography (TLC) was performed using precoated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka). Blue LED (50 W, λ = 456 nm), were purchased from commercial supplier Kessil LED photoreactor lightning. Fluorescence measurements were performed using Varian Cary Eclipse spectrofluorometer equipped with thermos stated cell holder. *N*-(Acyloxy)phthalimides **1** were prepared from the corresponding starting materials following the literature procedure. [1] Phosphonates **2** were synthetized according to the literature procedure.[2] Figure 1 shows the 50W 456nm photochemical reaction setup. The reaction vials in front of the 50W 456 nm bulb at approximatively 4.5 cm distance. To maintain a stable reaction temperature two fans were placed in close proximity to the reaction vials (23±2 °C).

[1] A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers, V. K. Aggarwal, *Science*, **2017**, *357*, 283.

[2] R. Chowdhury, S. K. Ghosh, *Eur. J. Org. Chem.* **2008**, 3868-3874.

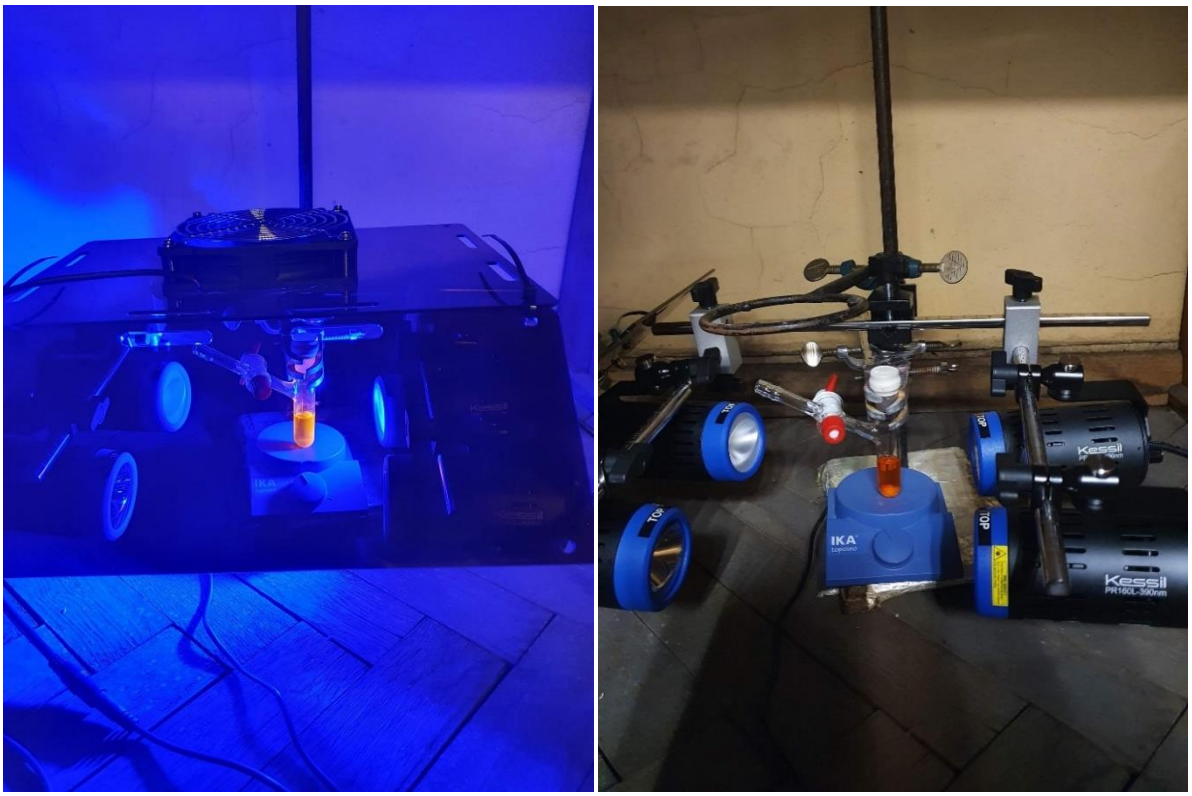


Fig. S1. Photochemical reaction setup using 50W 456nm Kessil LED.

2. Cyclic voltammetry

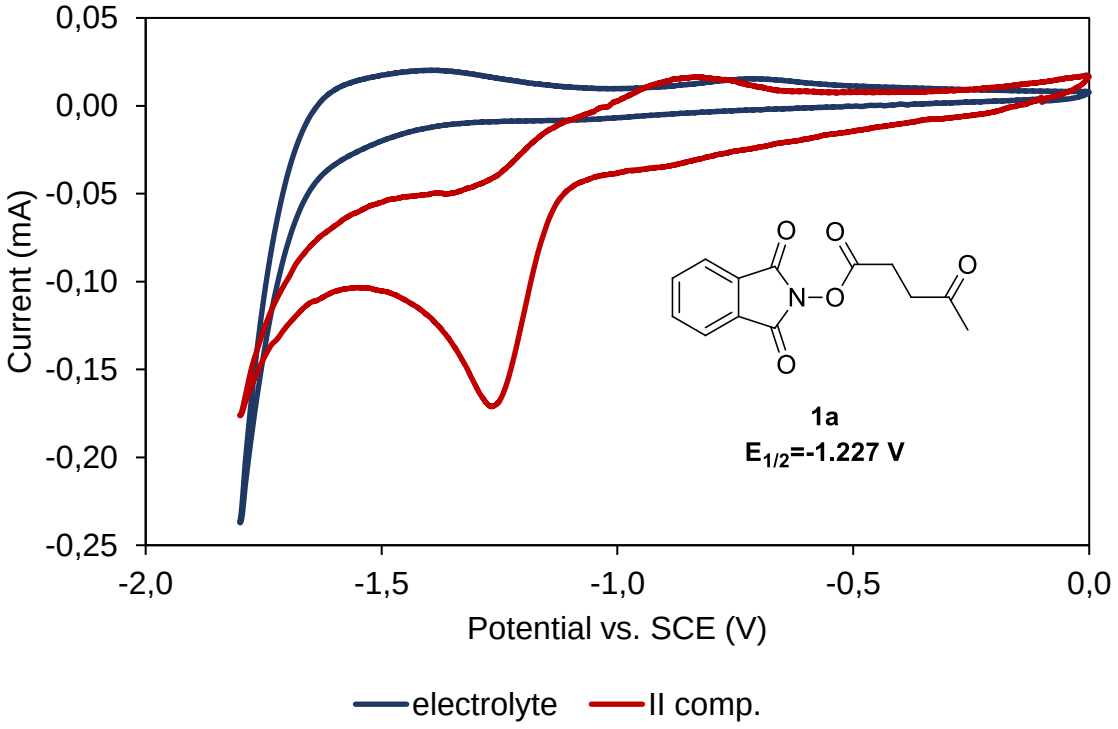


Fig. 1. Cyclic voltammograms recorded in a solution of **1a** (electroreduction) and in the supporting electrolyte (0.1 M TBAP) in CH_3CN at the scan rate of 0.1 V/s.

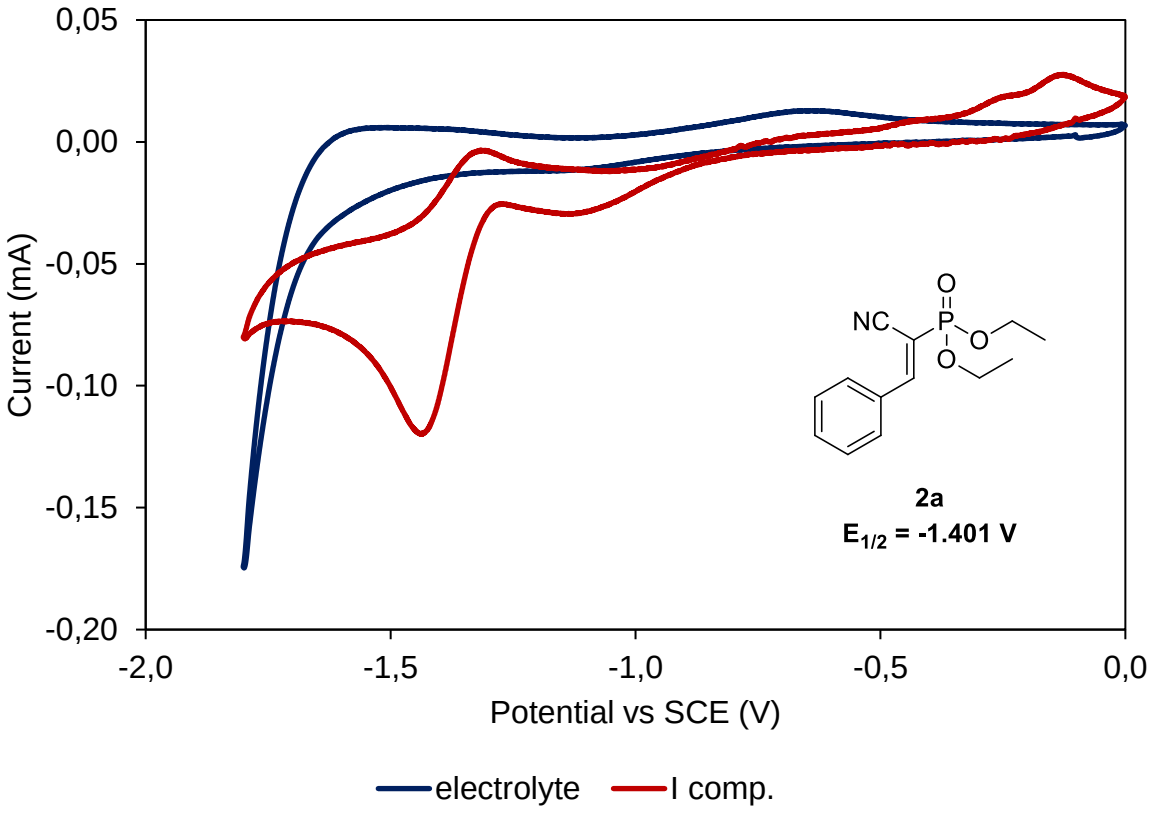


Fig. 2. Cyclic voltammograms recorded in a solution of **2a** compound (electroreduction) and in the supporting electrolyte (0.1 M TBAP) in CH_3CN at the scan rate of 0.1 V/s.

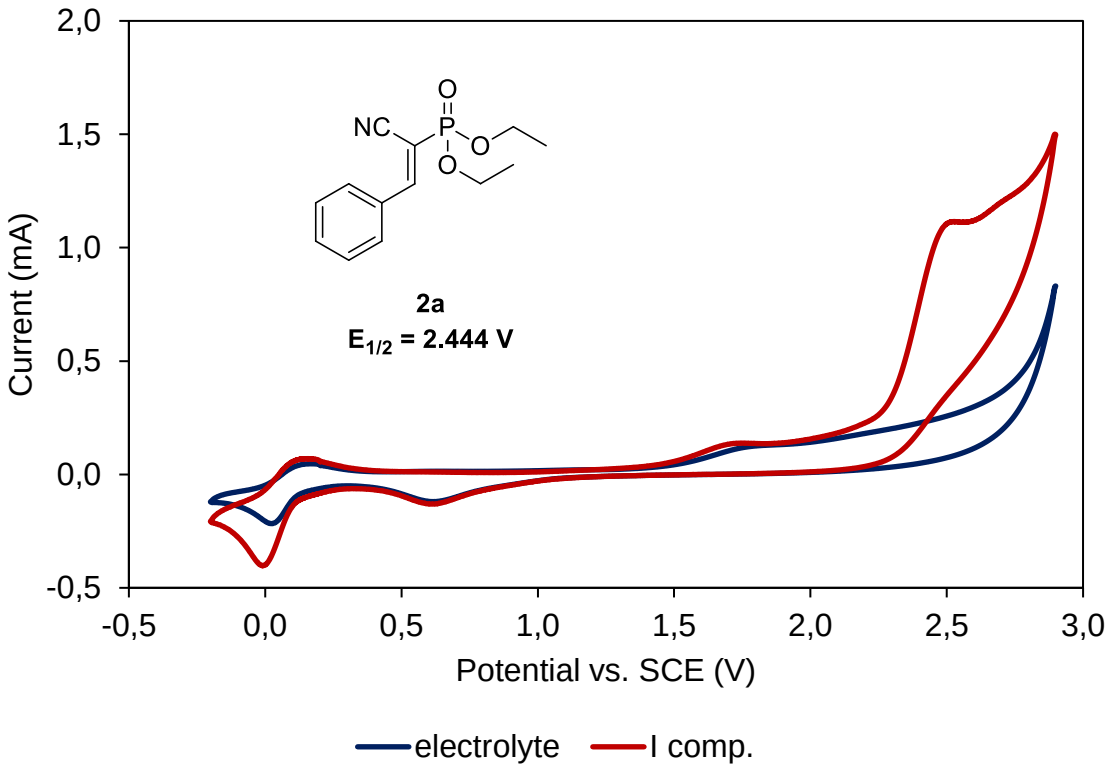


Fig. 3. Cyclic voltammograms recorded in the solution of **2a** (electrooxidation) and in the supporting electrolyte (0.1 M TBAP) in CH_3CN at the scan rate of 0.1 V/s.

$E_{1/2}$ value determined for **1a** vs. SCE – electroreduction

1a – **$E_{1/2}$ = -1.227 V**

$E_{1/2}$ value determined for **2a** vs. SCE – electroreduction

2a – $E_{1/2}$ = -1.401 V

$E_{1/2}$ value determined for **2a**· vs. SCE – electrooxidation

2a – **$E_{1/2}$ = 2.444 V**

3. Fluorescence Quenching

All $Ir(ppy)_3$ solution were irradiated at 382 nm and approximately and the emission intensity from 450 nm to 700 nm was recorded by PMT-780 Spectrophotometer ($\lambda_{\max emission} = 518\, nm$). A 2 mL solution of $Ir(ppy)_3$ in DMSO (1μM) was added **1a** or **2a** (0 μM, 100 μM, 300 μM, 500 μM 900 μM in turn), emission spectra was collected instantly after each addition.

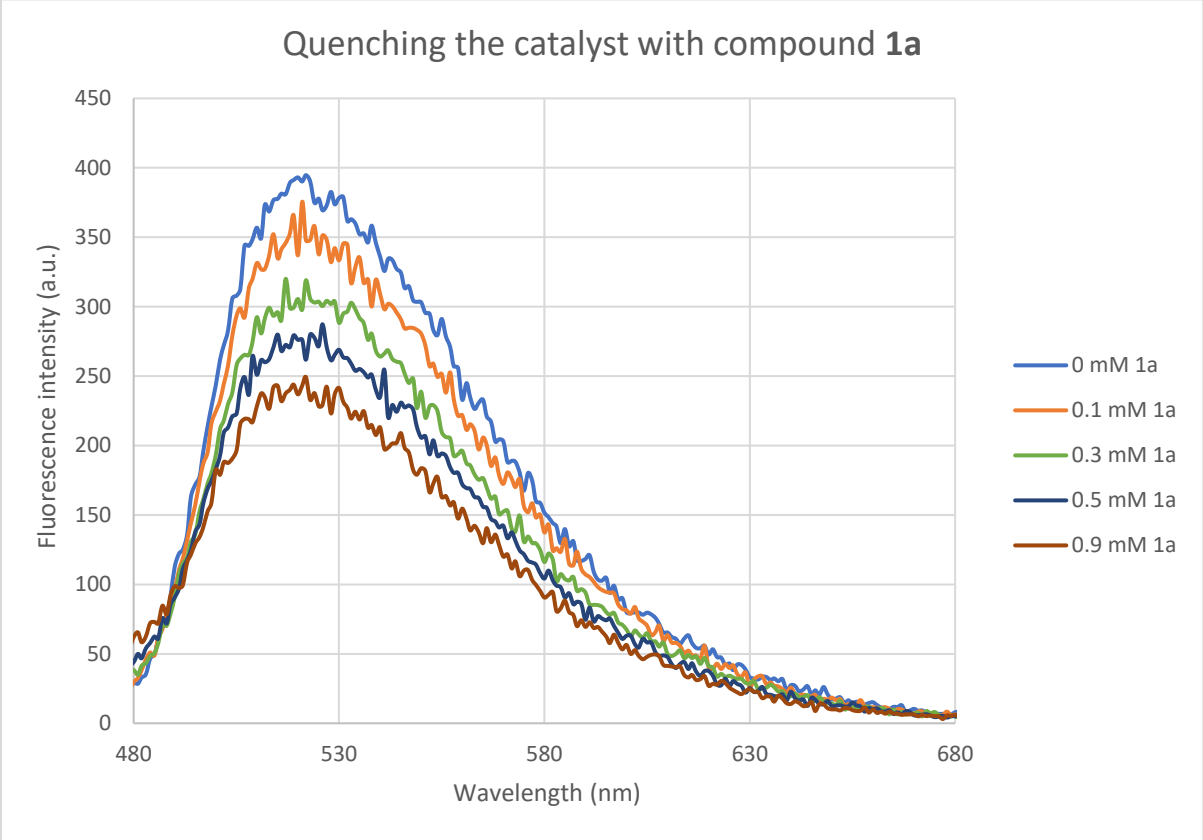


Fig.1 Fluorescent quenching of $Ir(ppy)_3$ by **1a**

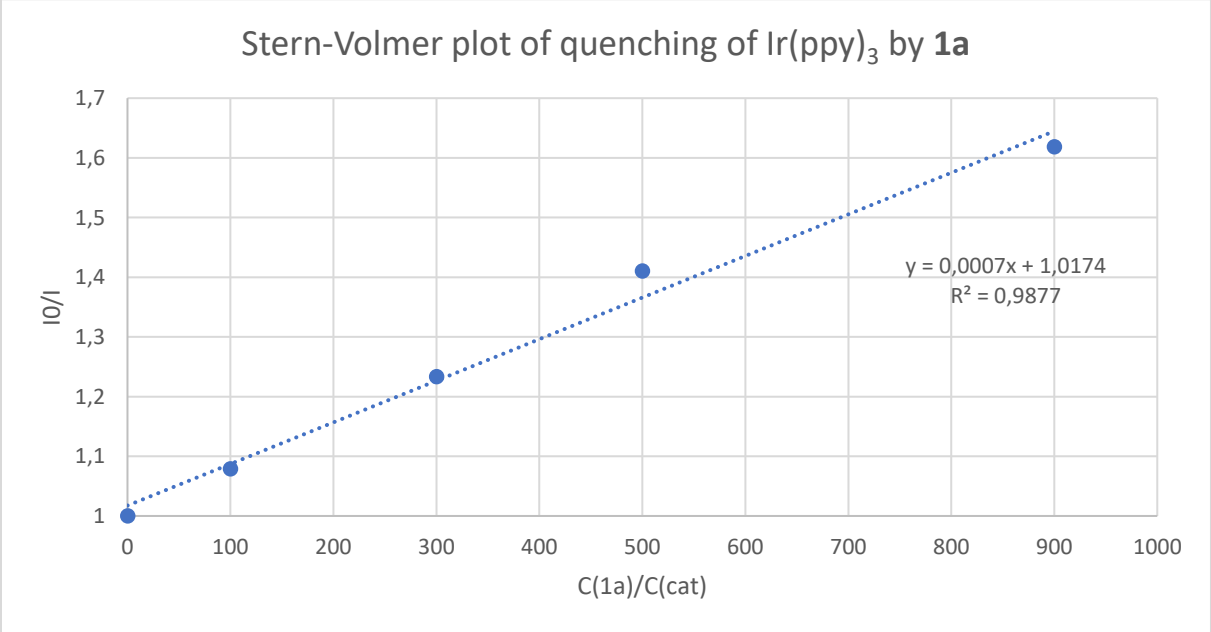


Fig. 2 Stern-Volmer plot of quenching of $Ir(ppy)_3$ by **1a**

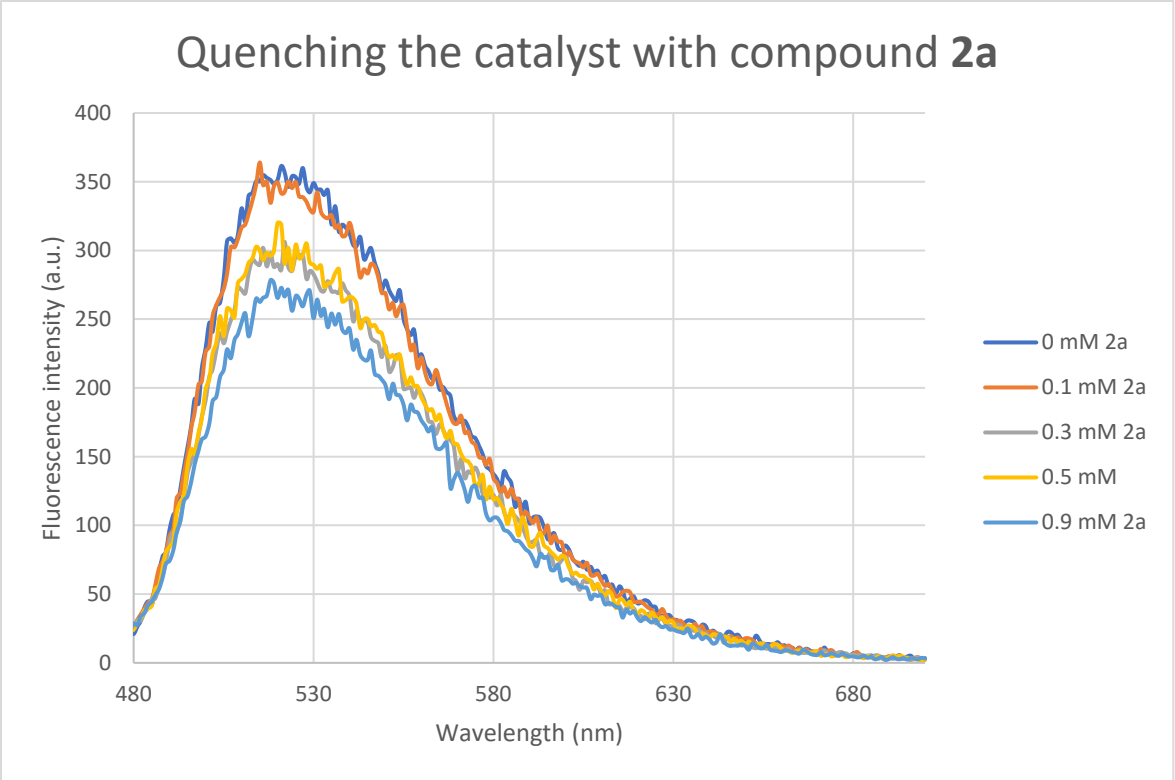


Fig.3 Fluorescent quenching of $Ir(ppy)_3$ by **2a**

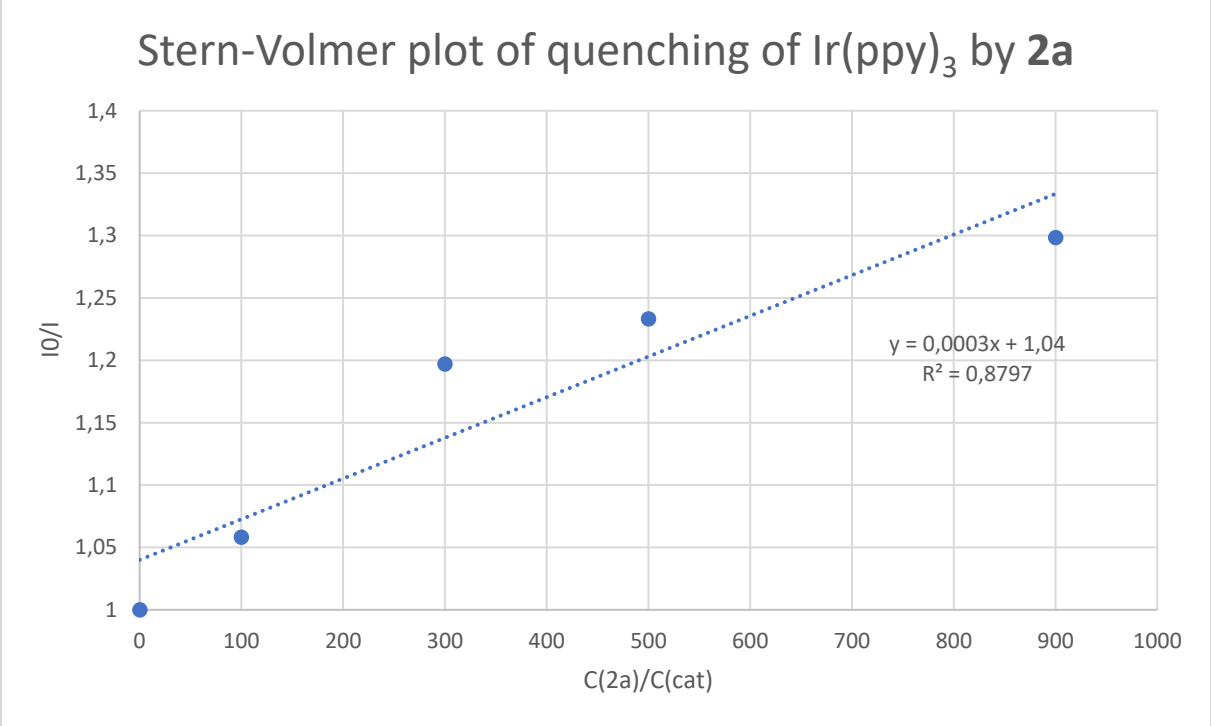
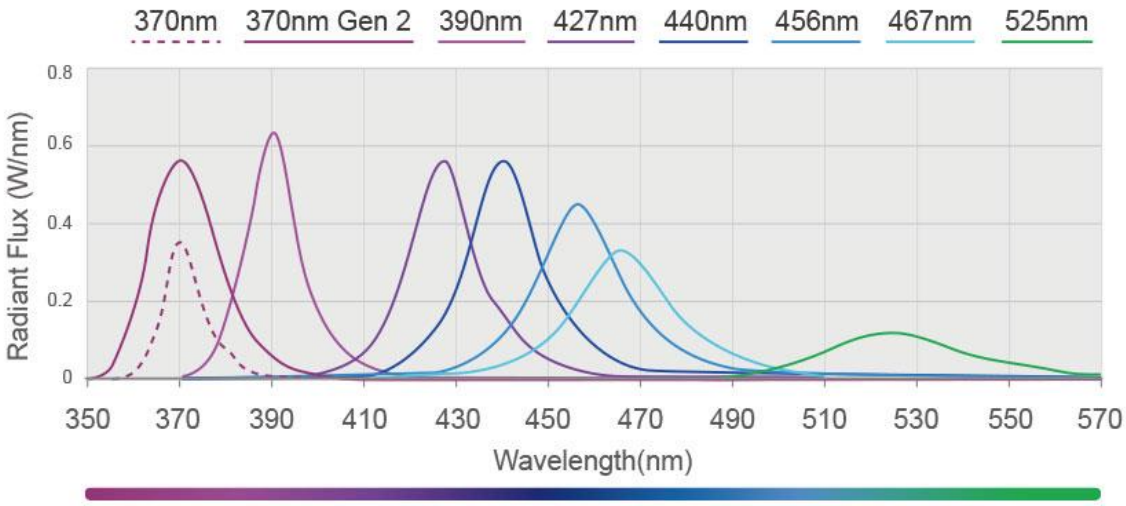


Fig. 4 Stern-Volmer plot of quenching of $Ir(ppy)_3$ by **2a**

4. Light sources emission spectra



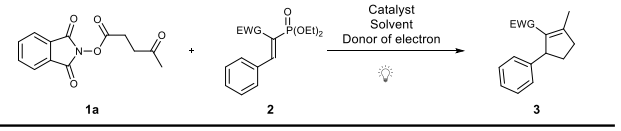
TECHNICAL SPECIFICATIONS

Power Consumption (AC)	370nm Gen 2 (max 44W), 370nm (max 43W), 390nm (max 52W), 427nm & 440nm (max 45W), 456nm (max 50W), 467nm (max 44W), 525nm (max 44W)
Input Voltage	100-240 VAC
Operating Temperature	0 - 40°C / 32 - 104°F
Beam Angle	56°
Wavelength Options	370nm, 390nm, 427nm, 440nm, 456nm, 467nm, 525nm
Average Intensity of PR160 series	399mW/cm2 (measured from 1 cm distance)
Dimensions (H x D)	4.49" x 2.48" / 11.4cm x 6.3cm

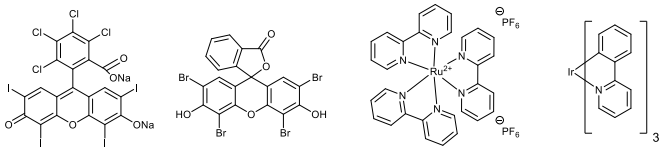
Figure : Kessil lights emission spectra used in project. The image downloaded from Kessil website: kessil.com/products/science_PR160L.php

5. Tandem Giese/HWE reaction initiated by visible light– optimization studies

Table 1. Tandem Giese/HWE reaction initiated by visible light– optimization studies[a]



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



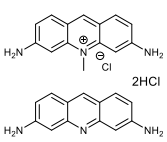
4a Rose Bengal

4b Eosin Y

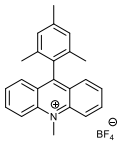
4c $Ru(bpy_3)_2(PF_6)_2$

4d $Ir(ppy)_3$

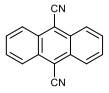
4e Chloranil



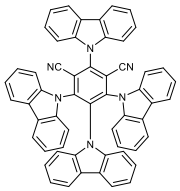
4f Akryflavin



4g 9-Mesityl-10-methylacridinium tetrafluoroborate



4h 9,10-Antracenedicarbonitrile



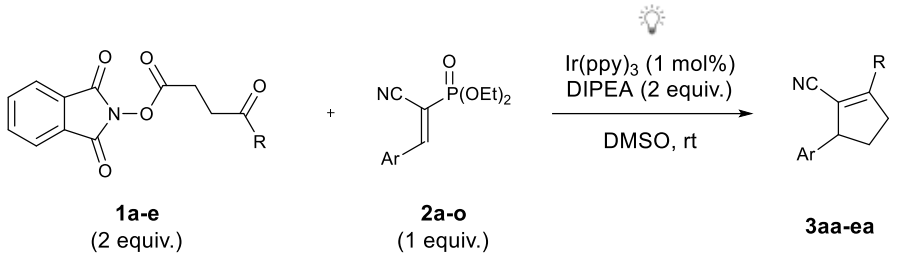
4i 4CzIPN

Entry	EWG	Cat.	Sol-vent	Donor of electron [equiv.]	**1a:2a**	Yield [%]
1[b]	CO_2Et	**4a**	CH_2Cl_2	DIPEA [2]	1.5:1	-
2[b]	CO_2tBu	**4a**	CH_2Cl_2	DIPEA [2]	1.5:1	-
3[b]	C(O)Ph	**4a**	CH_2Cl_2	DIPEA [2]	1.5:1	-
4[b]	CN	**4a**	CH_2Cl_2	DIPEA [2]	1.5:1	35
5[b]	CN	**4b**	CH_2Cl_2	DIPEA [2]	1.5:1	41
6[b]	CN	**4c**	CH_2Cl_2	DIPEA [2]	1.5:1	45
7[c]	CN	**4d**	CH_2Cl_2	DIPEA [2]	1.5:1	55
8[c]	CN	**4e**	CH_2Cl_2	DIPEA [2]	1.5:1	-
9[c]	CN	**4f**	CH_2Cl_2	DIPEA [2]	1.5:1	51
10[c]	CN	**4g**	CH_2Cl_2	DIPEA [2]	1.5:1	-
11[c]	CN	**4h**	CH_2Cl_2	DIPEA [2]	1.5:1	55
12[c]	CN	**4i**	CH_2Cl_2	DIPEA [2]	1.5:1	26
13[c]	CN	**4d**	Acetone	DIPEA [2]	1.5:1	56
14[c]	CN	**4d**	DMF	DIPEA [2]	1.5:1	54
15[c]	CN	**4d**	MeCN	DIPEA [2]	1.5:1	52
16[c]	CN	**4d**	DMSO	DIPEA [2]	1.5:1	65
17[c]	CN	**4d**	Toluene	DIPEA [2]	1.5:1	29
18[c]	CN	**4d**	AcOEt	DIPEA [2]	1.5:1	38
19[c]	CN	**4d**	MeOH	DIPEA [2]	1.5:1	-
20[c]	CN	**4d**	DMSO	Vit. C [2]	1.5:1	-
21[c]	CN	**4d**	DMSO	TEA [2]	1.5:1	-
22[c]	CN	**4d**	DMSO	DIPEA [1]	1.5:1	50
23[c]	CN	**4d**	DMSO	DIPEA [0.2]	1.5:1	-
24[c]	CN	**4d**	DMSO	DIPEA [2]	2:1	78
25[c, d]	CN	**4d**	DMSO	DIPEA [2]	2:1	76

26[c,e]	CN	**4d**	DMSO	DIPEA [2]	2:1	72
27[c,e]	CN	**-**	DMSO	DIPEA [2]	2:1	-
28[c,e]	CN	**4d**	DMSO	-	2:1	-
29[e,f]	CN	**4d**	DMSO	DIPEA [2]	2:1	-

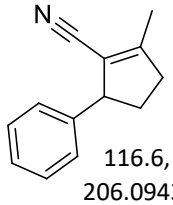
[a] All reactions were performed in a 0.20 mmol scale using **1a** (1.2 equiv.) and **2a** (1.0 equiv.) in the presence of the corresponding photoredox catalyst **4** (10 mol%) and the corresponding base (2 equiv.) in the solvent (3 mL). [b]Reaction performed under irradiation with the green light. [c]Reaction performed under irradiation with the blue light. [d] Reaction performed using 5 mol% of catalyst. [e] Reaction performed using 1 mol% of catalyst. [f] Reaction performed in the dark.

6. General procedure for the synthesis of cyclopent-1-enecarbonitriles



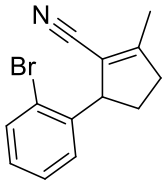
In a 10 mL Schlenk flask equipped with a magnetic stirring bar, *N*-acyloxyphthalimide **1** (0.4 mmol, 2 equiv.), phosphonate **2** (0.2 mmol, 1 equiv.), $Ir(ppy)_3$ (0.002 mmol, 0.01 equiv.) and DIPEA (0.4 mmol, 2 equiv.) were placed and dissolved in DMSO (2 mL). Then the reaction mixture was degassed three times and filled the atmosphere with argon. The flask was placed about 5 cm away from the blue LED lamp and was irradiated for 24 hours. Then reaction mixture was quenched with saturated solution of Na_2CO_3 and washed the aqueous phase with CH_2Cl_2 three times (3 x 10 mL). The organic phase was washed with brine (1 x 20 mL) and dry organic residue with $MgSO_4$, then evaporated it under reduced pressure. The crude product was purified by column chromatography (petroleum ether : ethyl acetate 9:1) to obtain desire product.

2-methyl-5-phenylcyclopent-1-enecarbonitrile (3aa)



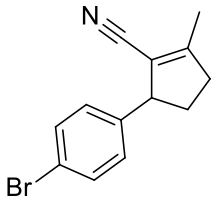
The product (26.4 mg, 72%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as an yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.26-7.23 (m, 1H), 7.19-7.16 (m, 2H), 4.09-4.05 (m, 1H), 2.67-2.60 (m, 1H) 2.58-2.47 (m, 2H), 2.11-2.09 (m, 3H), 1.95-1.88 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 161.9, 142.8, 129.0 (2C), 127.3 (2C), 127.2, 116.6, 113.0, 53.0, 37.8, 33.6, 17.0 HRMS calculated for $C_{13}H_{13}N$ [M+Na]+ m/z: 206.0940, found: 206.0943

5-(2-bromophenyl)-2-methylcyclopent-1-enecarbonitrile (3ab)



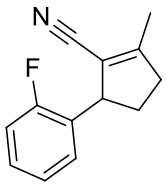
The product (32.9 mg, 63%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a green oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.57 (dd *J* = 7.9, 1.3 Hz, 1H), 7.30 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 (dd *J* = 7.9, 1.8 Hz, 1H) 7.11 (td *J* = 7.5, 1.8 Hz, 1H) 4.59-4.54 (m, 1H) 2.66-2.50 (m, 3H), 2.15-2.12 (m, 3H), 1.78-1.72 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 163.6, 141.8, 133.3, 128.7, 128.1, 127.8, 124.3, 116.4, 111.4, 52.0, 37.4, 32.5, 17.1 HRMS calculated for $C_{13}H_{12}BrN$ [M+Na]+ m/z: 284.0046, found: 284.0048

5-(4-bromophenyl)-2-methylcyclopent-1-enecarbonitrile (3ac)



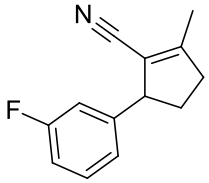
The product (35.5 mg, 68%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a brown oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz 2H), 7.06 (d, *J* = 8.4 Hz 2H), 4.05-4.01 (m, 1H), 2.66-2.59 (m, 1H), 2.57-2.47 (m, 2H) 2.12-2.09 (m, 3H), 1.89-1.82 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 162.4, 141.8, 132.1, 129.0, 121.1, 116.3, 112.5, 52.4, 37.8, 33..6, 17.0 HRMS calculated for $C_{13}H_{12}BrN$ [M+Na]+ m/z: 284.0046, found: 284.0042

5-(2-fluorophenyl)-2-methylcyclopent-1-enecarbonitrile (3ad)



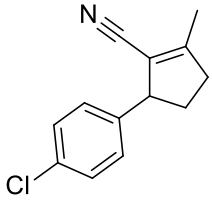
The product (31.0 mg, 77%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a green oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.19-7.15 (m, 1H), 7.09 (td, *J* = 7.6, 1.9 Hz, 1H) 7.05 (td, *J* = 7.4, 1.2 Hz, 1H), 6.98 (dd *J* = 10.4, 8.2, 1.2 Hz, 1H), 4.35-4.30 (m, 1H), 2.61-2.54 (m, 1H), 2.52-2.43 (m, 2H), 2.07-2.03 (m, 3H), 1.87-1.79 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 162.7, 160.8 (d, *J* = 246.2 Hz), 129.5 (d, *J* = 13.9 Hz), 128.8 (d, *J* = 8.3 Hz) 128.4 (d, *J* = 4.3 Hz), 124.5 (d, *J* = 3.6 Hz), 116.4, 115.8 (d, 22.0 Hz,) 111.3, 46.0, 37.7, 32.3, 17.0 ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.6 (dt, *J* = 11.4, 6.1 Hz) HRMS calculated for $C_{13}H_{13}FN$ [M+Na]+ m/z: 224.0846, found: 224.0843

5-(3-fluorophenyl)-2-methylcyclopent-1-enecarbonitrile (3ae)



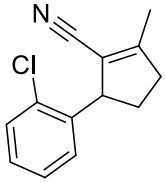
The product (30.2 mg, 75%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as an yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.31-7.28 (m, 1H), 6.99-6.96 (m, 1H), 6.96-6.93 (m, 1H), 6.89-6.87 (m, 1H), 4.09-4.04 (m, 1H), 2.67-2.60 (m, 1H), 2.57-2.48 (m, 2H), 2.12-2.09 (m, 3H), 1.94-1.85 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 163.3 (d, *J* = 246.3 Hz), 162.5, 145.4 (d, *J* = 6.7 Hz), 130.4 (d, *J* = 6.7 Hz), 123.0 (d, *J* = 2.8 Hz), 116.3, 114.2 (d, *J* = 9.9 Hz), 114.1 (d, *J* = 10.2 Hz), 112.4, 52.6, 37.7, 33.4, 16.9 ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6 (ddd *J* = 10.0, 8.7, 5.9) HRMS calculated for $C_{13}H_{13}FN$ [M+Na]+ m/z: 224.0846, found: 224.0845

5-(4-chlorophenyl)-2-methylcyclopent-1-enecarbonitrile (3af)



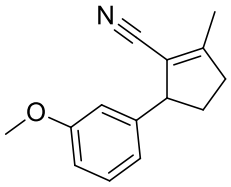
The product (33.9 mg, 78%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a brown oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.13-7.10 (m, 2H), 4.06-4.02 (m, 1H), 2.66-2.59 (m, 1H), 2.58-2.46 (m ,2H), 2.11-2.08 (m, 3H), 1.89-1.82 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 162.4, 141.3, 133.0, 129.1 (2C), 128.6 (2C), 116.3, 112.6, 52.3, 37.7, 33.6, 17.0 HRMS calculated for $C_{13}H_{12}ClN$ [M+Na]+ m/z: 240.0551, found: 240.0555

5-(2-chlorophenyl)-2-methylcyclopent-1-enecarbonitrile (3ag)



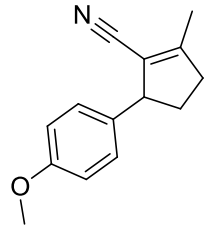
The product (30.4 mg, 70%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a brown oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.25 (td, *J* = 7.9, 1.3 Hz, 1H) 7.19 (td, *J* = 7.6, 1.7 Hz, 1H), 7.15 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.61-4.55 (m, 1H), 2.65-2.50 (m, 3H), 2.15-2.13 (m ,3H), 1.81-1.74 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 163.5, 140.1, 133.7, 129.9, 128.4, 127.7, 127.4, 116.4, 111.3, 49.4, 37.5, 32.3, 17.1 HRMS calculated for $C_{13}H_{12}ClN$ [M+Na]+ m/z: 240.0551, found: 240.0555

5-(3-methoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3ah)



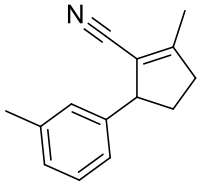
The product (26.4 mg, 62%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a colourless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz), 6.83-6.79 (m, 2H), 6.74 (dd, *J* = 2.6, 1.7 Hz, 1H), 4.08-4.04 (m, 1H), 3.83 (s, 3H), 2.69-2.60 (m, 1H), 2.58-2.48 (m, 2H), 2.14-2.10 (m, 3H), 1.97-1.90 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 162.0, 160.1, 144.4, 130.0, 119.6, 116.5, 113.3, 112.9, 112.3, 55.3, 52.9, 37.8, 33.5, 17.0 HRMS calculated for $C_{14}H_{15}NO$ [M+Na]+ m/z: 236.1046, found: 236.1042

5-(4-methoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3ai)



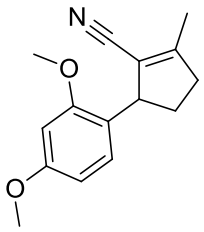
The product (30.6 mg, 72%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a colourless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.12-7.07 (m, 2H), 6.88-6.84 (m, 2H), 4.04-4.00 (m, 1H), 3.79 (s, 3H), 2.65-2.58 (m, 1H), 2.55-2.44 (m, 2H), 2.10-2.08 (m, 3H), 1.92-1.83 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 161.5, 158.8, 134.9, 128.3 (2C), 116.7, 114.3 (2C), 113.4, 55.4, 52.2, 37.8, 33.7, 17.0 HRMS calculated for $C_{14}H_{15}NO$ [M+Na]+ m/z: 236.1046, found: 236.1045

2-methyl-5-(m-tolyl)cyclopent-1-enecarbonitrile (3aj)



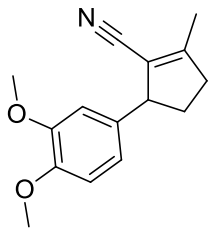
The product (30.0 mg, 76%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a brown oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.22 (td, *J* = 7.3, 1.3 Hz, 1H), 7.07-7.05 (m, 1H), 6.99-6.97 (m, 2H), 4.05-4.01 (m, 1H), 2.66-2.60 (m, 1H), 2.56-2.46 (m, 2H), 2.35 (s, 3H), 2.12-2.09 (m, 3H), 1.94-1.88 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 161.8, 142.7, 138.5, 128.8, 128.0 (2C), 124.3, 116.6, 113.1, 52.9, 37.8, 33.6, 21.6, 17.0 HRMS calculated for $C_{14}H_{15}N$ [M+Na]+ m/z: 220.1097, found: 220.1099

5-(2,4-dimethoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3ak)



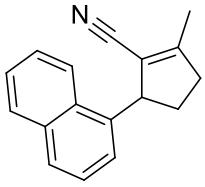
The product (27.7 mg, 57%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a colourless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.8 Hz, 1H), 6.73 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.65 (d, *J* = 3.0 Hz), 4.48-4.43 (m, 1H), 3,79 (s, 1H), 3.76 (s, 1H), 2.62-2.55 (m, 1H), 2.52-2.44 (m, 2H), 2.11-2.08 (m, 3H), 1.85-1.78 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 162.2, 153.9, 151.4, 132.2, 116.7, 114.2, 112.1, 111.9, 111.8, 56.3, 55.9, 46.2, 37.7, 32.2, 17.0 HRMS calculated for $C_{15}H_{17}NO_2$ [M+Na]+ m/z: 266.1151, found: 266.1153

5-(3,4-dimethoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3al)



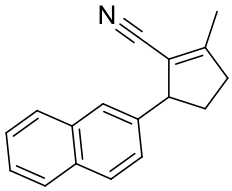
The product (28.7 mg, 59%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as an yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.83 (d, *J* = 8.2 Hz, 1H), 6.72 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.62 (d, *J* =2.1 Hz, 1H), 4.04-4.00 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.65-2.58 (m, 1H), 2.55-2.43 (m, 2H), 2.11-2.09 (m, 3H), 1.93-1.84 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 161.7, 149.4, 148.3, 135.3, 119.2, 116.6, 113.2, 111.6, 110.6, 56.1 (2C), 52.6, 37.8, 33.7, 17.0 HRMS calculated for $C_{15}H_{17}NO_2$ [M+Na]+ m/z: 266.1151, found: 266.1153

2-methyl-5-(naphthalen-1-yl)cyclopent-1-enecarbonitrile (3am)



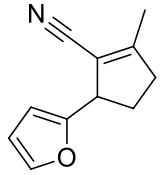
The product (26.1 mg, 56%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as an yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.54 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.45 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.28 (dd, *J* = 7.1, 1.2 Hz, 1H) 4.92-4.88 (m, 1H), 2.75-2.68 (m, 1H), 2.67-2.54 (m, 2H), 2.21-2.19 (m, 3H) 1.95-1.87 (m, 1H), ^{13}C (176 MHz, $CDCl_3$) δ 163.2, 138.5, 134.3, 131.5, 129.1, 127.7, 126.3, 125.8, 125.7, 123.3 (2C), 116.8, 111.7, 48.5, 37.5, 33.1, 17.1 HRMS calculated for $C_{17}H_{15}N$ [M+Na]+ m/z: 256.1097, found: 256.1098

2-methyl-5-(naphthalen-2-yl)cyclopent-1-enecarbonitrile (3an)



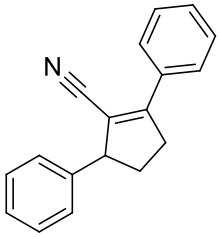
The product (28.4 mg, 61%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as an yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.85-7.79 (m, 3H), 7.64 (d, *J* = 1.8 Hz, 1H), 7.50-7.44 (m, 2H), 7.30 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.27-4.23 (m, 1H), 2.73-2.65 (m, 1H), 2.62-2.53 (m, 2H), 2.16-2.14 (m, 3H), 2.04-1.97 (m,1H) ^{13}C (176 MHz, $CDCl_3$) δ 162.2, 140.1, 133.7, 132.8, 128.9, 127.9, 127.8, 126.3, 125.8 (2C), 125.4, 116.6, 112.9, 53.1, 37.9, 33.5, 17.0 HRMS calculated for $C_{17}H_{15}N$ [M+Na]+ m/z: 256.1097, found: 256.1099

5-(furan-2-yl)-2-methylcyclopent-1-enecarbonitrile (3ao)



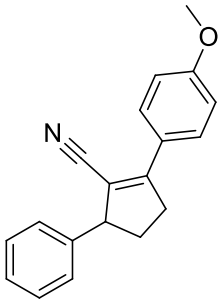
The product (13.8 mg, 40%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a colourless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.9, 09 Hz, 1H), 6.31 (dd, *J* = 3.2, 0.9, Hz, 1H), 6.14 (dd, *J* = 3.2, 1.9 Hz, 1H), 4.17-4.13 (m, 1H), 2.67-2.59 (m, 1H), 2.55-2.48 (m, 1H), 2.40-2.35 (m, 1H), 2.15-2.08 (m, 1H), 2.07-2.05 (m, 3H) ^{13}C (176 MHz, $CDCl_3$) δ 162.4, 154.9, 142.1, 116.3, 110.6, 110.4, 105.8, 46.0, 37.5, 29.8, 17.0 HRMS calculated for $C_{11}H_{11}NO$ [M+Na]+ m/z: 196.0733, found: 196.0735

2,5-diphenylcyclopent-1-enecarbonitrile (3ba)



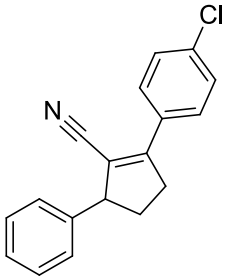
The product (18.1 mg, 37%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a green oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.84-780 (m, 2H), 7.47-7.41 (m, 3H), 7.38-7.34 (m, 2H), 7.30-7.24 (m, 2H), 4.28-4.24 (m, 1H), 3.15-3.08 (m, 1H), 3.07-2.99 (m, 1H), 2.66-2.59 (m, 1H), 2.10-2.02 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 158.7, 142.3, 133.5, 130.3, 129.1 (2C), 128.9 (2C), 127.6 (2C), 127.5 (2C), 127.4, 117.7, 110.9, 54.7, 35.7, 33.1 HRMS calculated for $C_{18}H_{15}N$ [M+Na]+ m/z: 268.1097, found: 268.1099

2-(4-methoxyphenyl)-5-phenylcyclopent-1-enecarbonitrile (3ca)



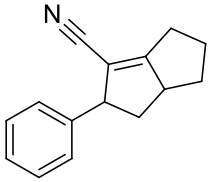
The product (22.0 mg, 40%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a colourless oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.38-7.32 (m, 2H), 7.28-7.24 (m, 3H), 6.97-6.94 (m, 2H), 4.26-4.22 (m, 1H), 3.86 (s, 3H), 3.12-3.06 (m, 1H), 3.02-2.93 (m, 1H), 2.62-2.57 (m, 1H), 2.06-1.99 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 161.2, 157.9, 142.7, 129.2 (2C), 129.0 (2C), 127.5 (2C), 127.4, 126.1, 118.3, 114.2 (2C), 108.4, 55.6, 54.6, 35.6, 33.1 HRMS calculated for $C_{19}H_{17}NO$ [M+Na]+ m/z: 298.1203, found: 298.1206

2-(4-chlorophenyl)-5-phenylcyclopent-1-enecarbonitrile (3da)



The product (17.9 mg, 32%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as an yellow oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.84-.7.81 (m, 2H), 7.47-7.41 (m, 3H), 7.38-735 (m, 2H), 7.30-7.26 (m, 2H), 4.28-4.24 (m, 1H), 3.16-3.10 (m, 1H), 3.07-2.99 (m, 1H), 2.67-2.58 (m, 1H), 2.09-2.03 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 158.7, 142.4, 133.5, 130.3, 129.0 (2C), 128.9 (2C), 127.6 (2C), 127.5 (2C), 127.4, 117.7, 110.9, 54.7, 35.7, 33.1 HRMS calculated for $C_{18}H_{14}ClN$ [M+Na]+ m/z: 302.0707, found: 302.0705

2-phenyl-2,3,3a,4,5,6-hexahydropentalene-1-carbonitrile (3ea)

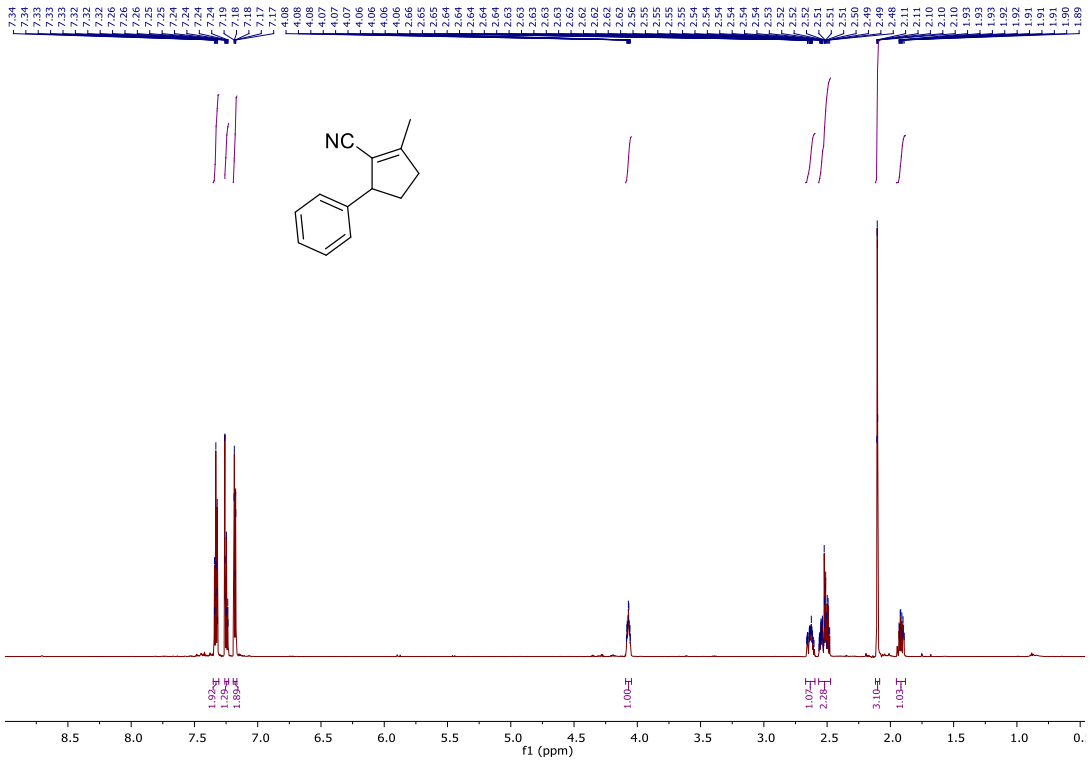


The product (dr 9:1, 18.8 mg, 45%) was purified with silica gel chromatography (petroleum ether : ethyl acetate 9:1) as a brown oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.28-7.25 (m, 1H), 7.24-7.22 (m, 2H), 4.40-4.33 (m, 1H), 3.14-3.07 (m, 1H), 2.65-2.60 (m, 1H), 2.60-2.44 (m, 2H), 2.27-1.98 (m, 3H), 1.59-1.51 (m, 1H), 1.32-1.21 (m, 1H) ^{13}C (176 MHz, $CDCl_3$) δ 176.6, 141.9, 128.3 (2C), 127.6 (2C), 127.4, 116.3, 106.1, 58.4, 53.4, 42.9, 31.6, 28.2, 25.0 HRMS calculated for $C_{15}H_{15}N$ [M+Na]+ m/z: 232.1097, found: 23.1094

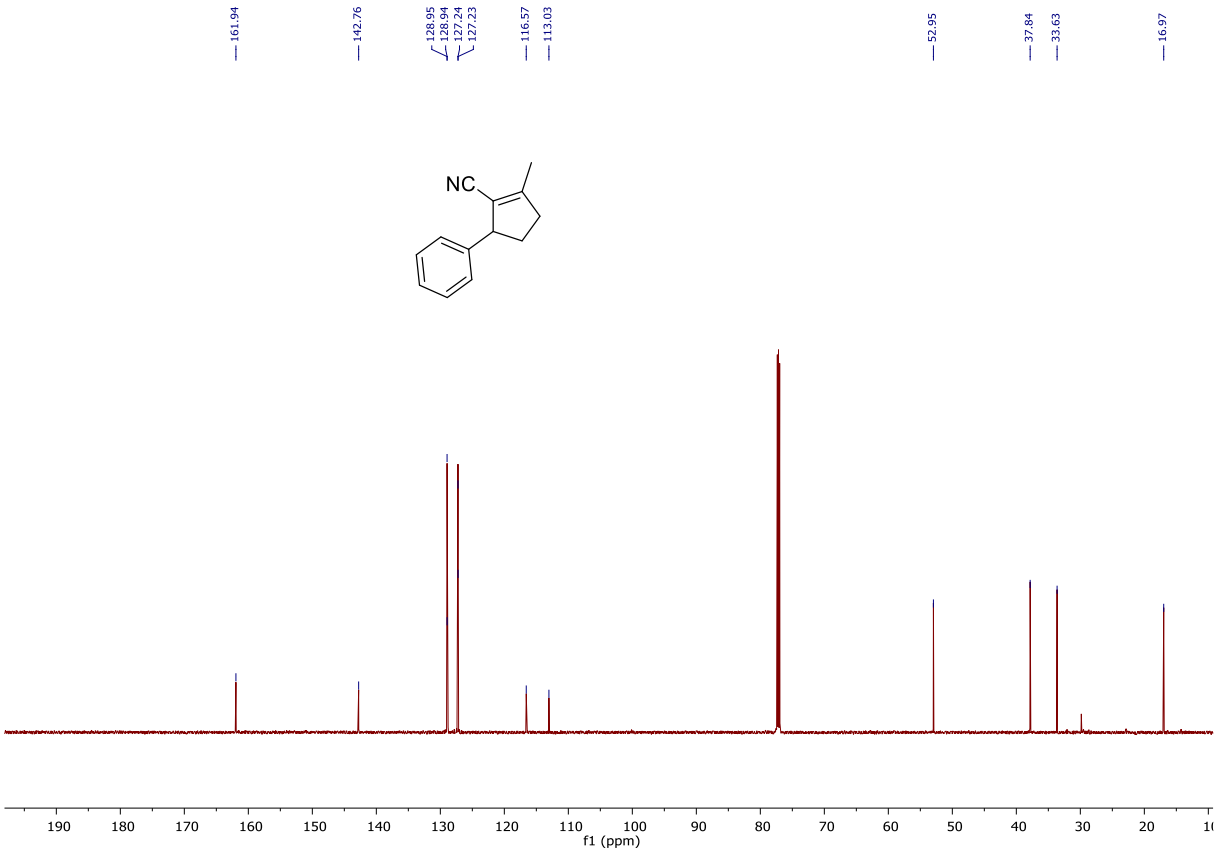
7. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR

2-methyl-5-phenylcyclopent-1-enecarbonitrile (3aa)

^{1}H NMR

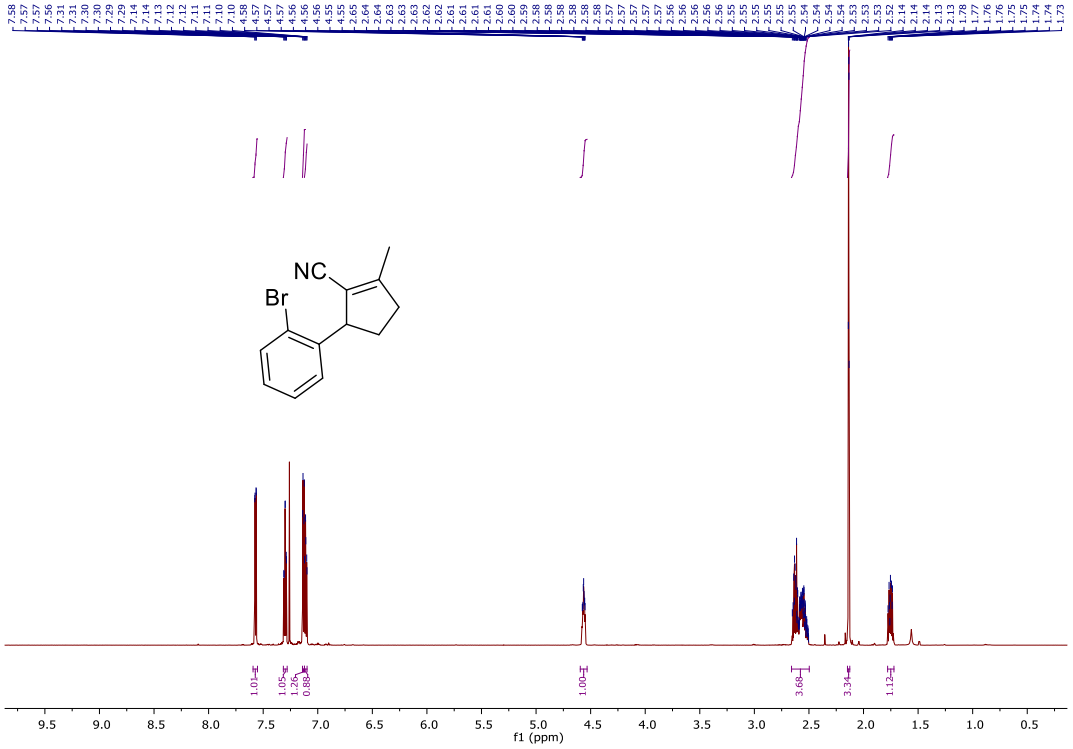


^{13}C NMR

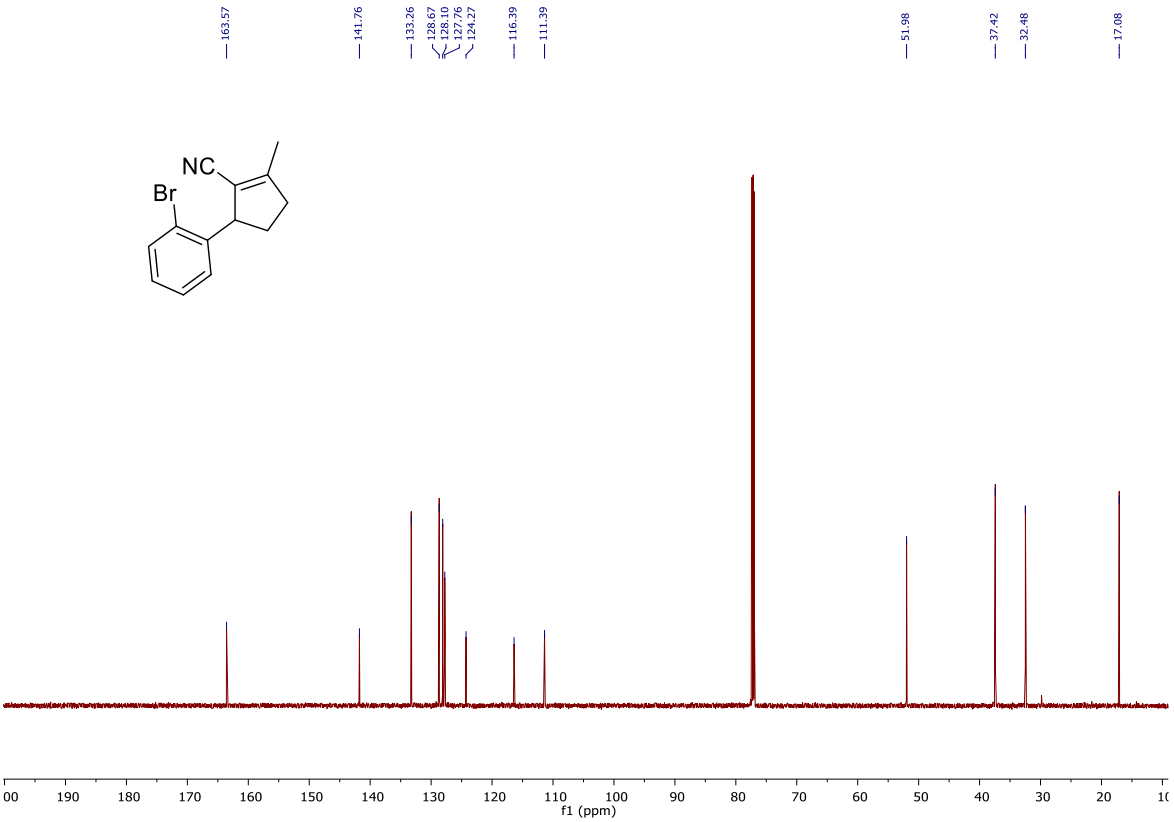


5-(2-bromophenyl)-2-methylcyclopent-1-enecarbonitrile (3ab)

^{1}H NMR

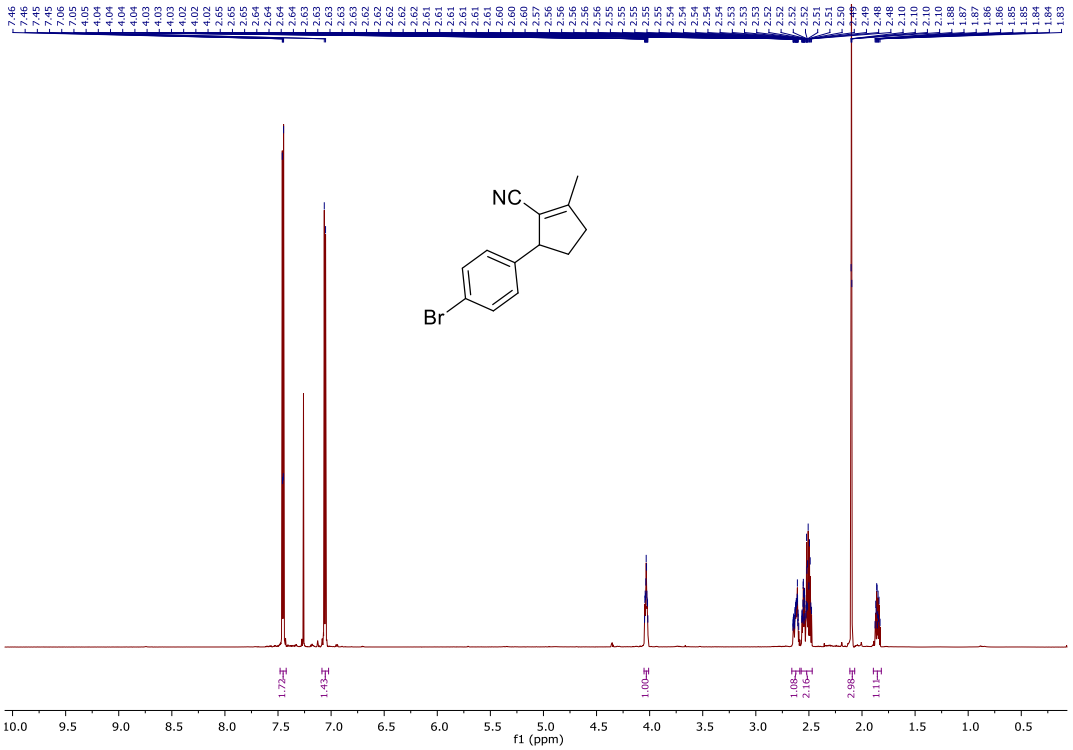


^{13}C NMR

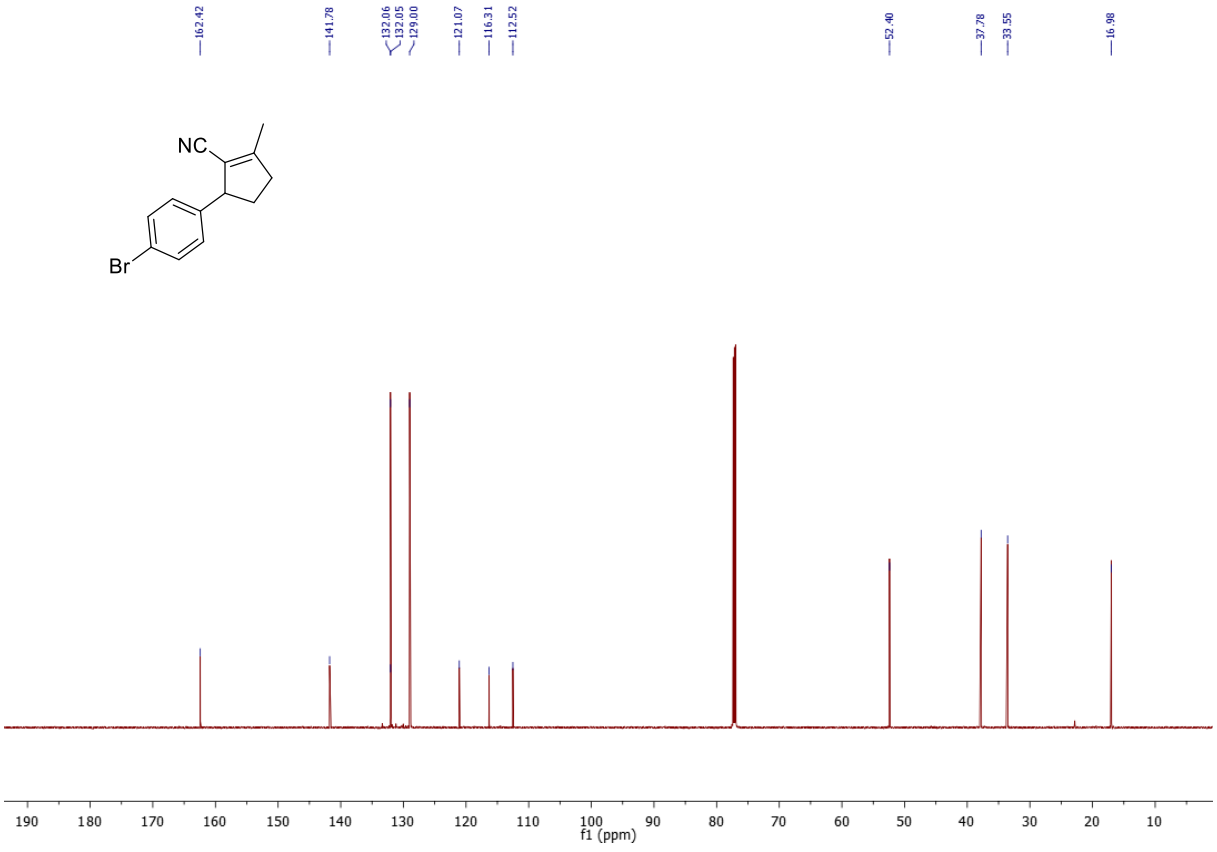


5-(4-bromophenyl)-2-methylcyclopent-1-enecarbonitrile (3ac)

^{1}H NMR

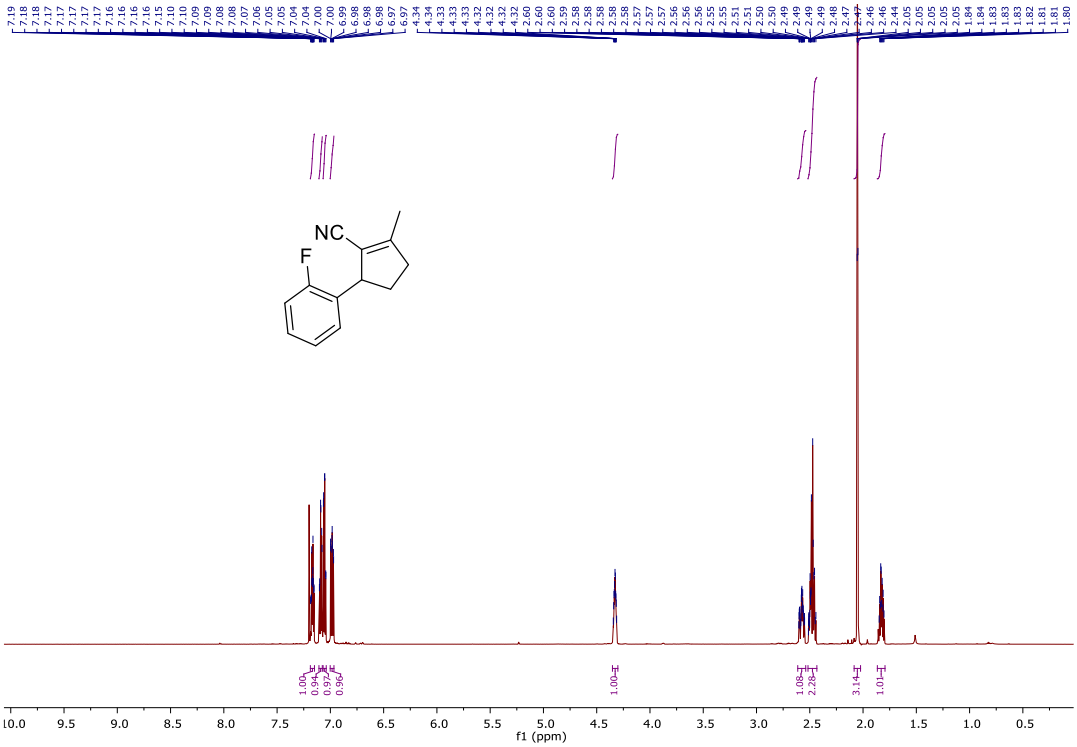


^{13}C NMR

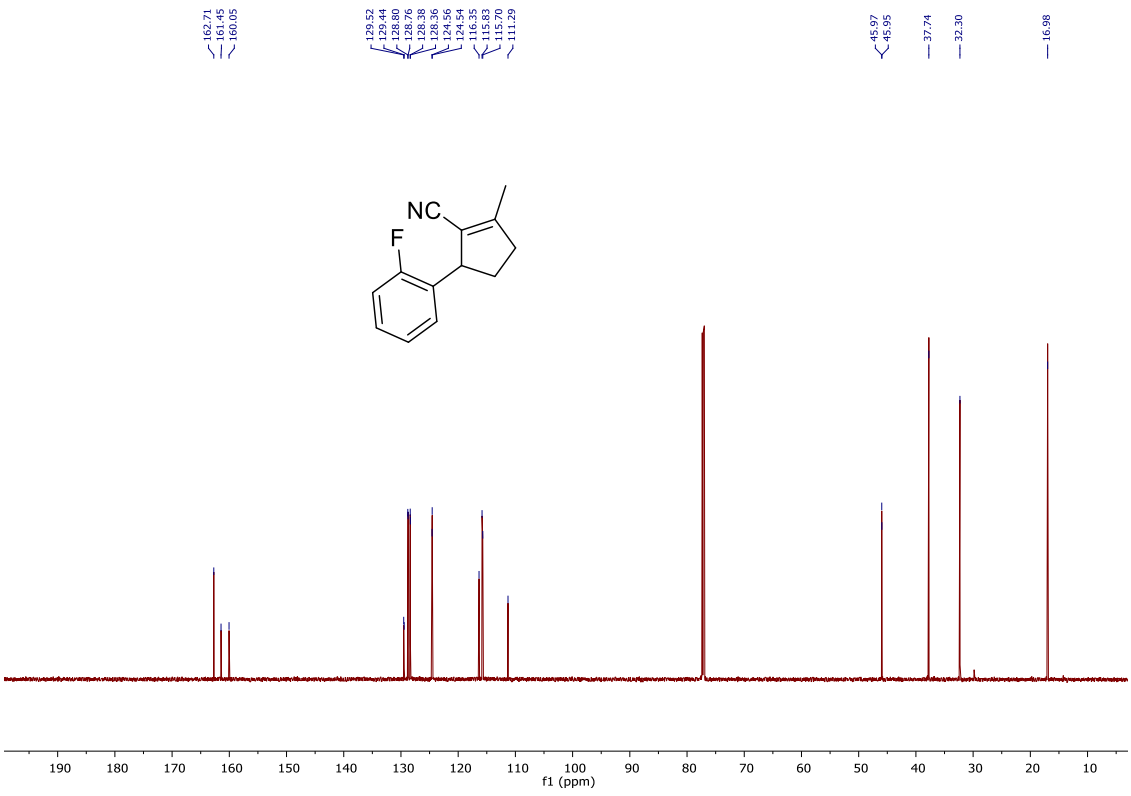


5-(2-fluorophenyl)-2-methylcyclopent-1-enecarbonitrile (3ad)

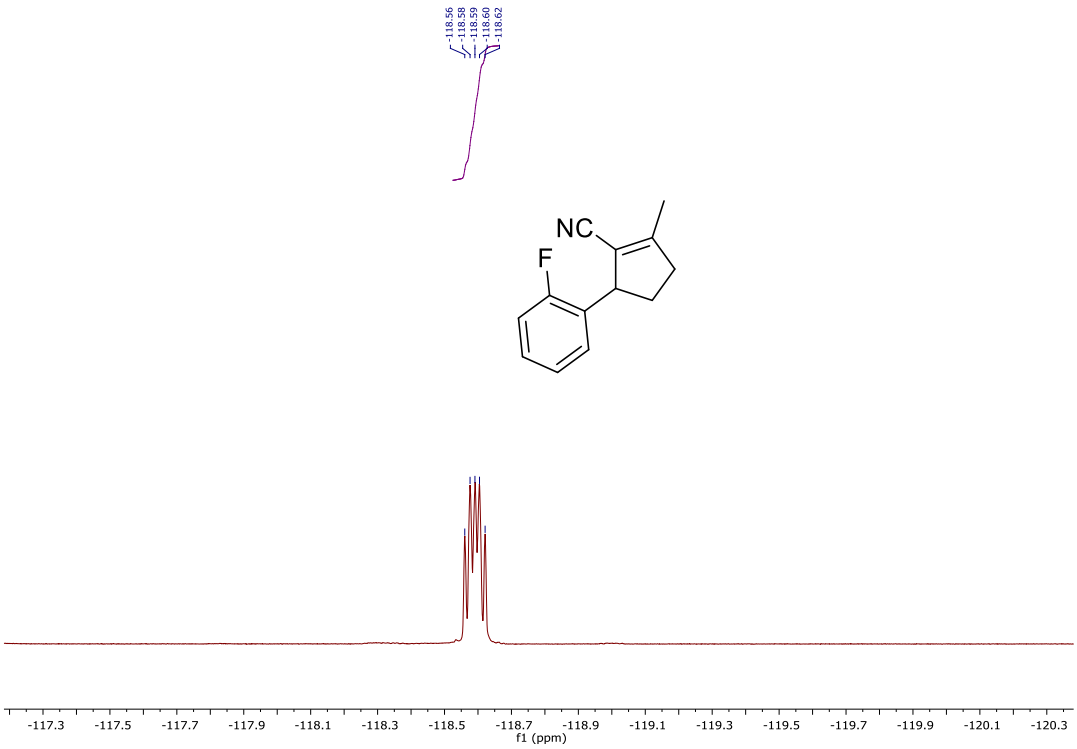
^{1}H NMR



^{13}C NMR

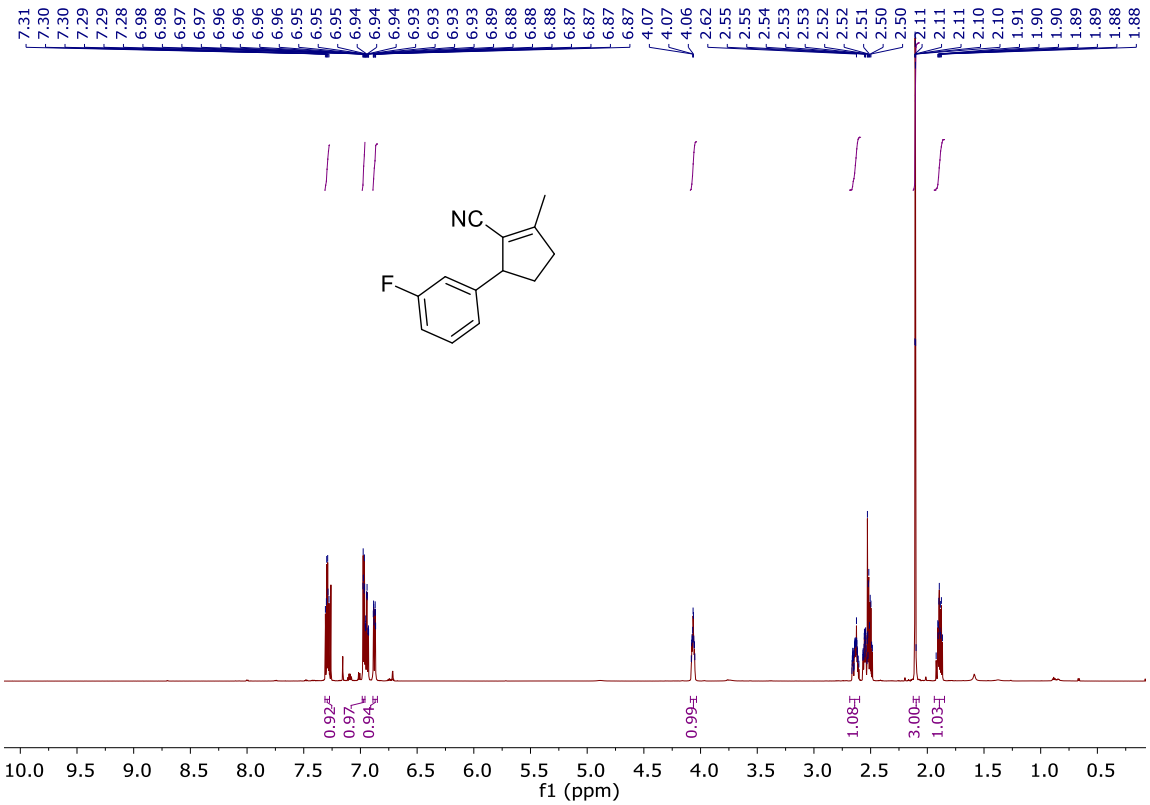


^{19}F NMR

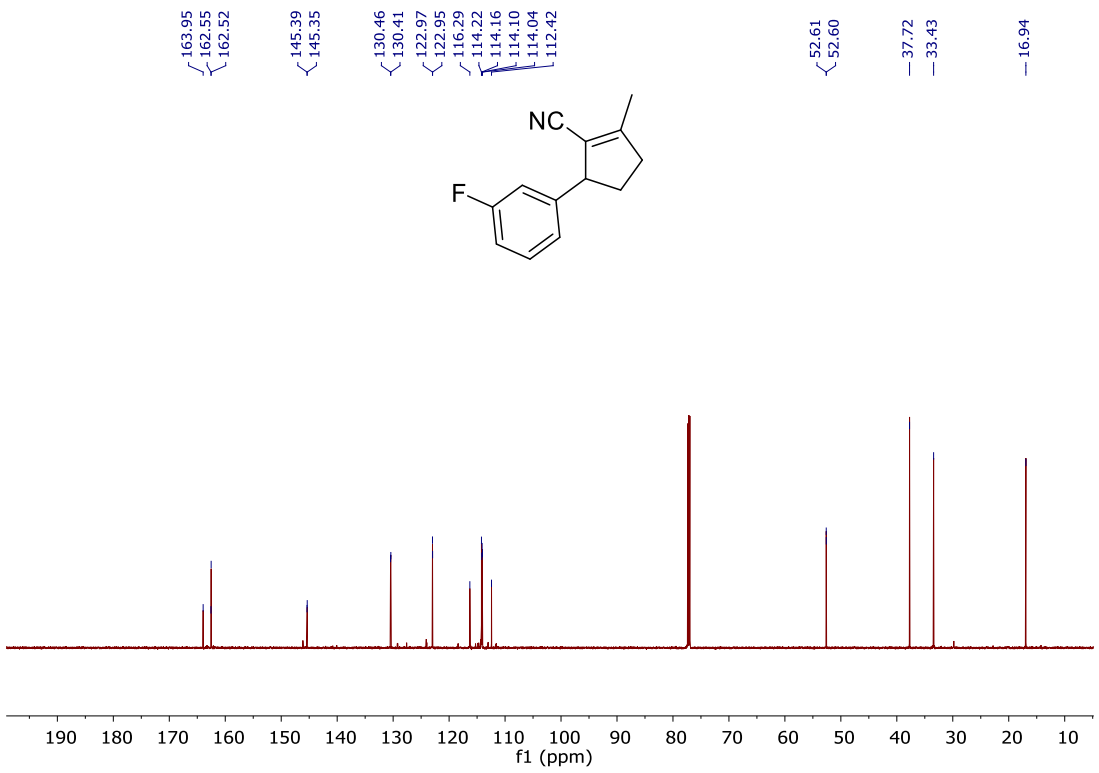

-118.56
-118.58
-118.59
-118.60
-118.62
NC
F
-117.3
-117.5
-117.7
-117.9
-118.1
-118.3
-118.5
-118.7
-118.9
-119.1
-119.3
-119.5
-119.7
-119.9
-120.1
-120.3
f1 (ppm)

5-(3-fluorophenyl)-2-methylcyclopent-1-enecarbonitrile (3ae)

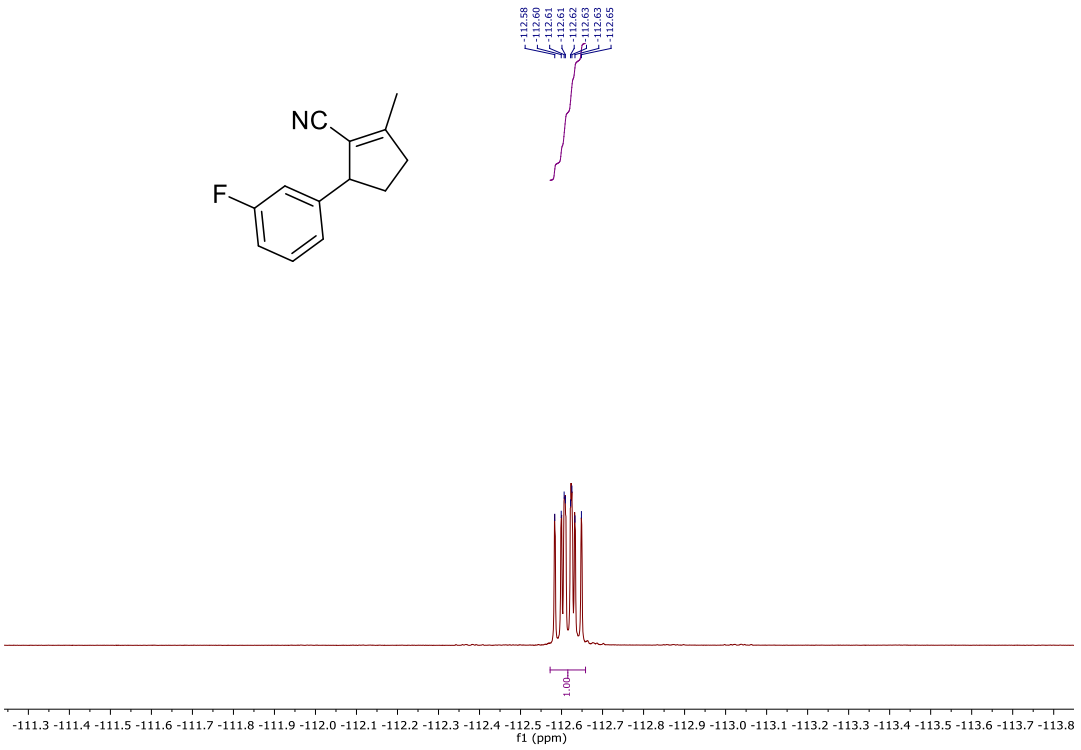
^{1}H NMR



^{13}C NMR

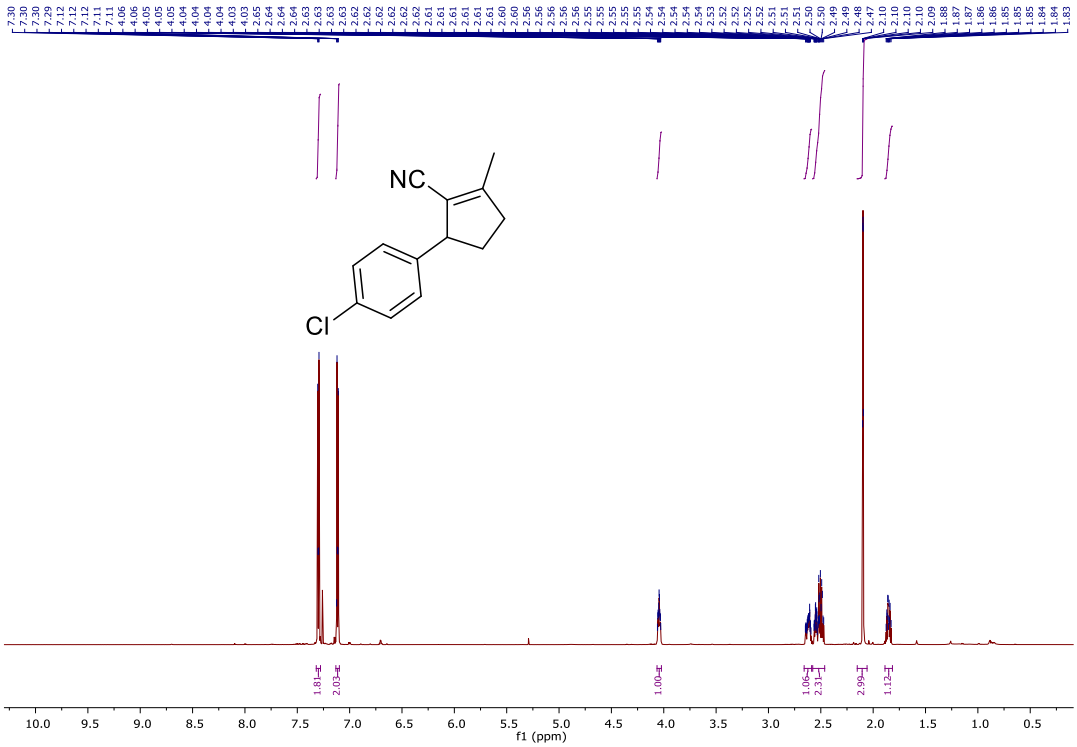


^{19}F NMR

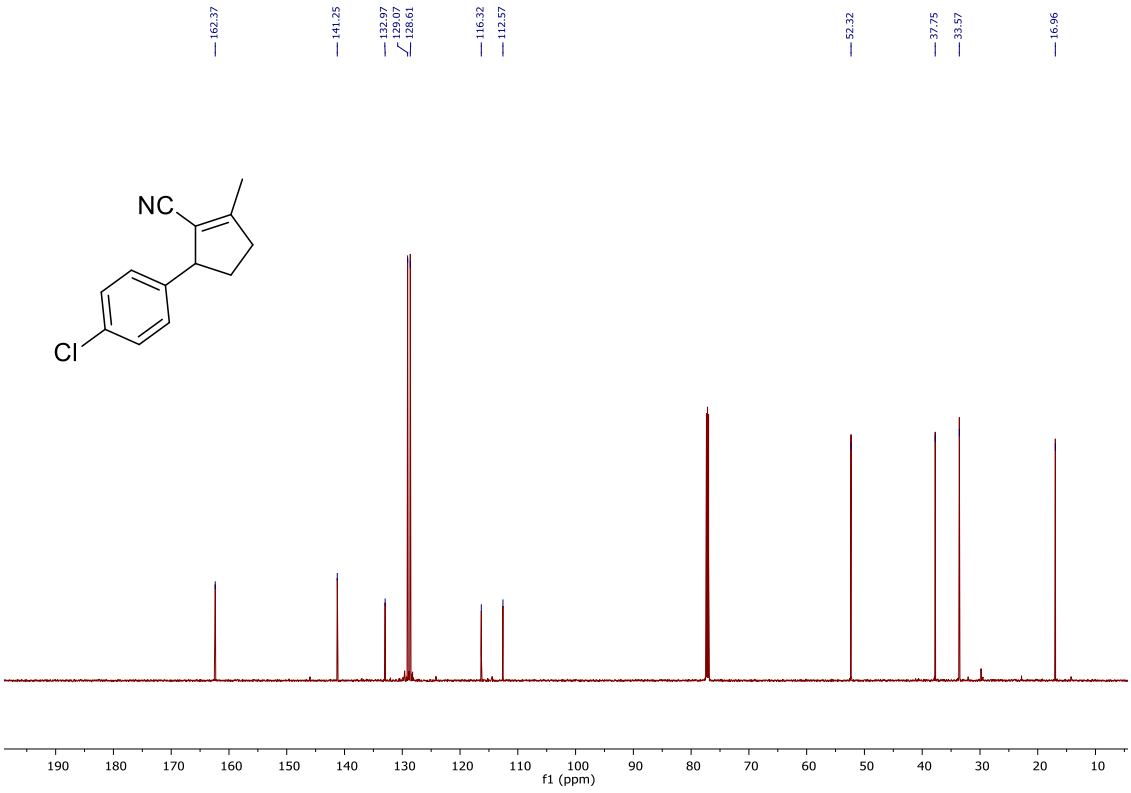

-112.58
-112.60
-112.61
-112.61
-112.62
-112.63
-112.63
-112.65
NC
F
1.00
-111.3 -111.4 -111.5 -111.6 -111.7 -111.8 -111.9 -112.0 -112.1 -112.2 -112.3 -112.4 -112.5 -112.6 -112.7 -112.8 -112.9 -113.0 -113.1 -113.2 -113.3 -113.4 -113.5 -113.6 -113.7 -113.8
f1 (ppm)

5-(4-chlorophenyl)-2-methylcyclopent-1-enecarbonitrile (3af)

^{1}H NMR

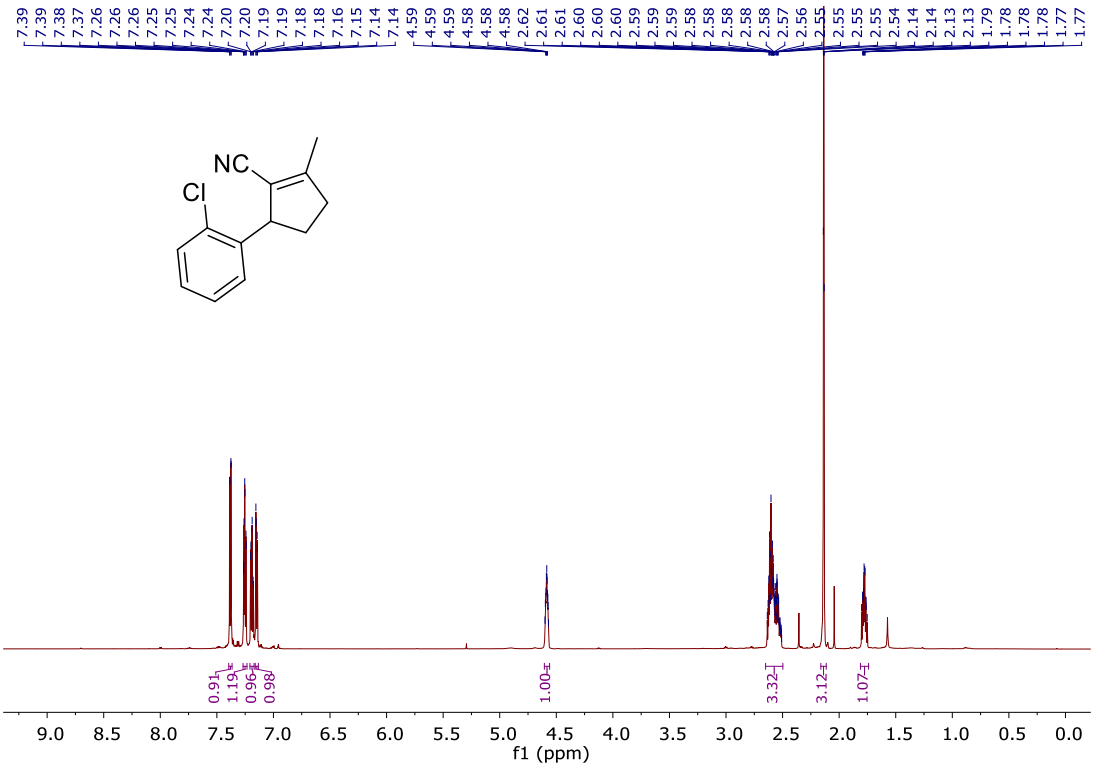


^{13}C NMR

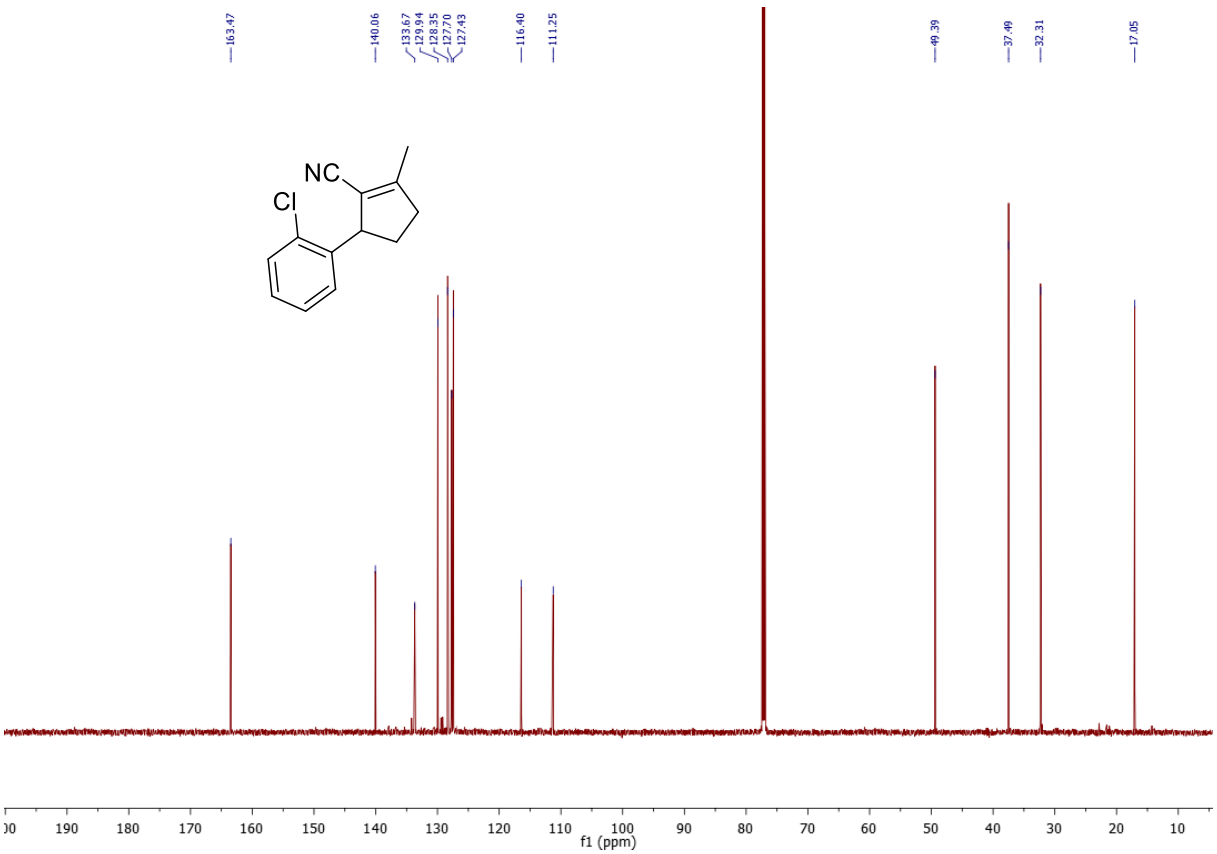


5-(2-chlorophenyl)-2-methylcyclopent-1-enecarbonitrile (3ag)

^{1}H NMR

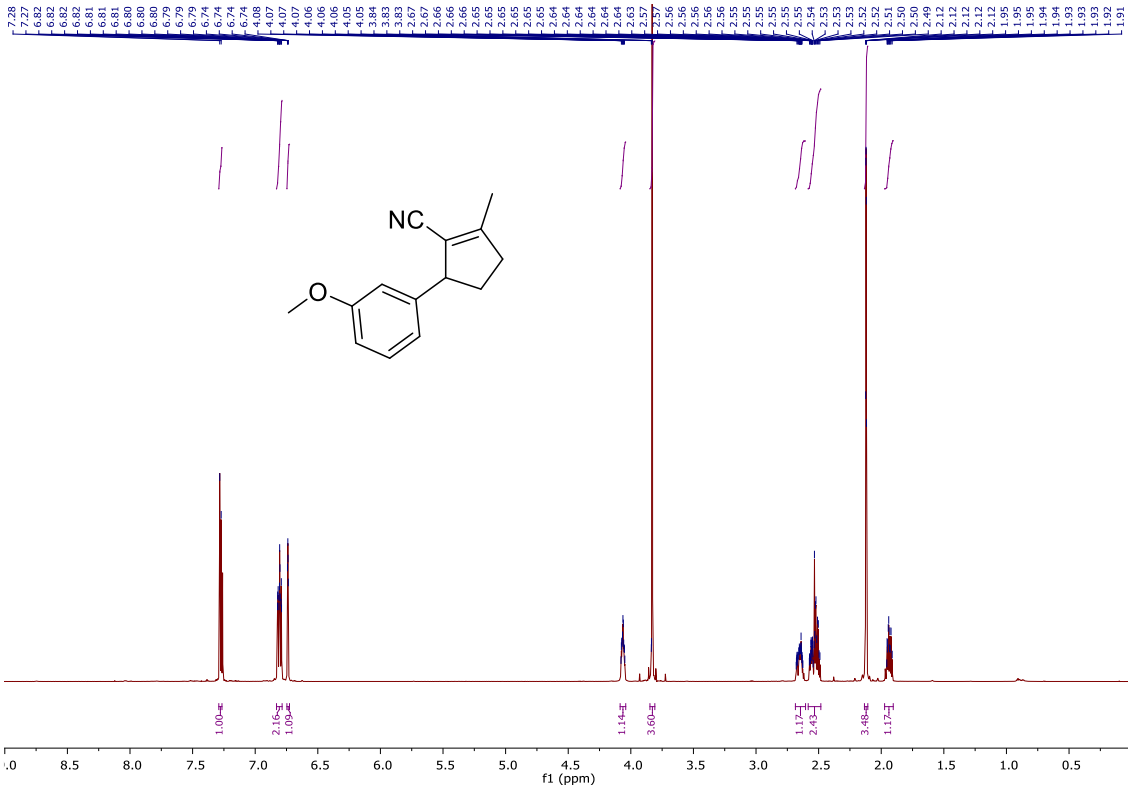


^{13}C NMR

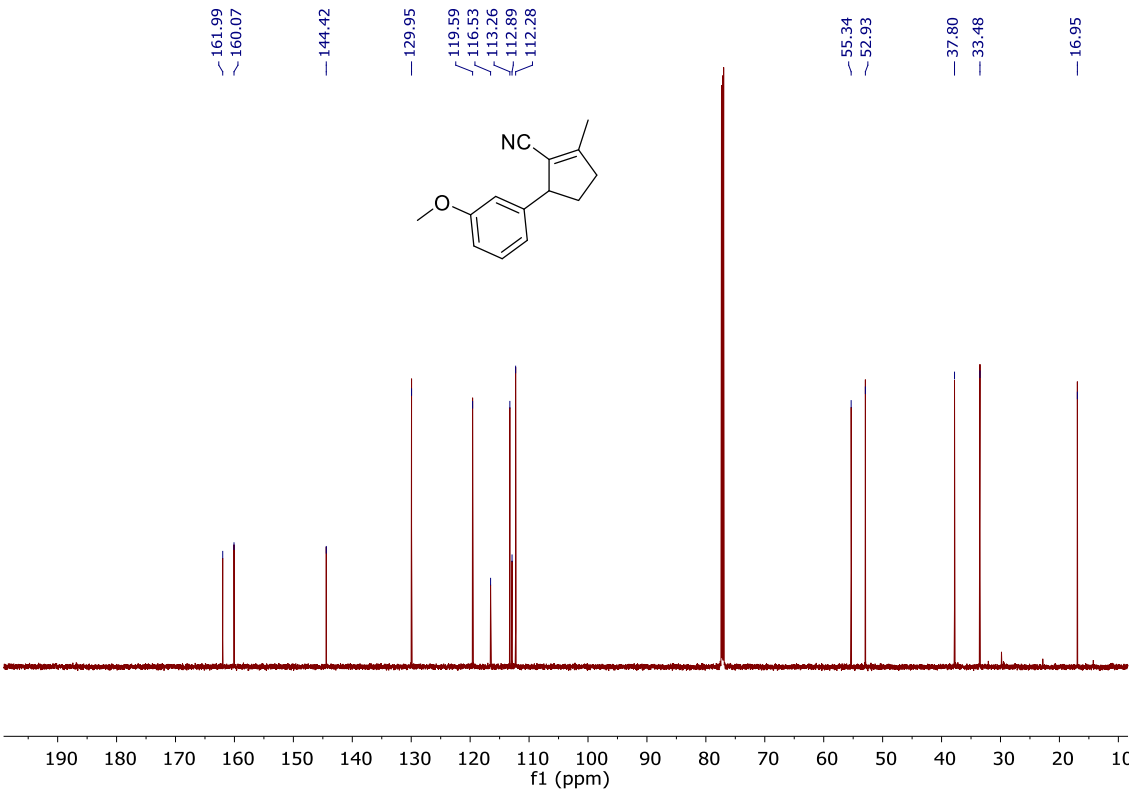


5-(3-methoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3ah)

^{1}H NMR

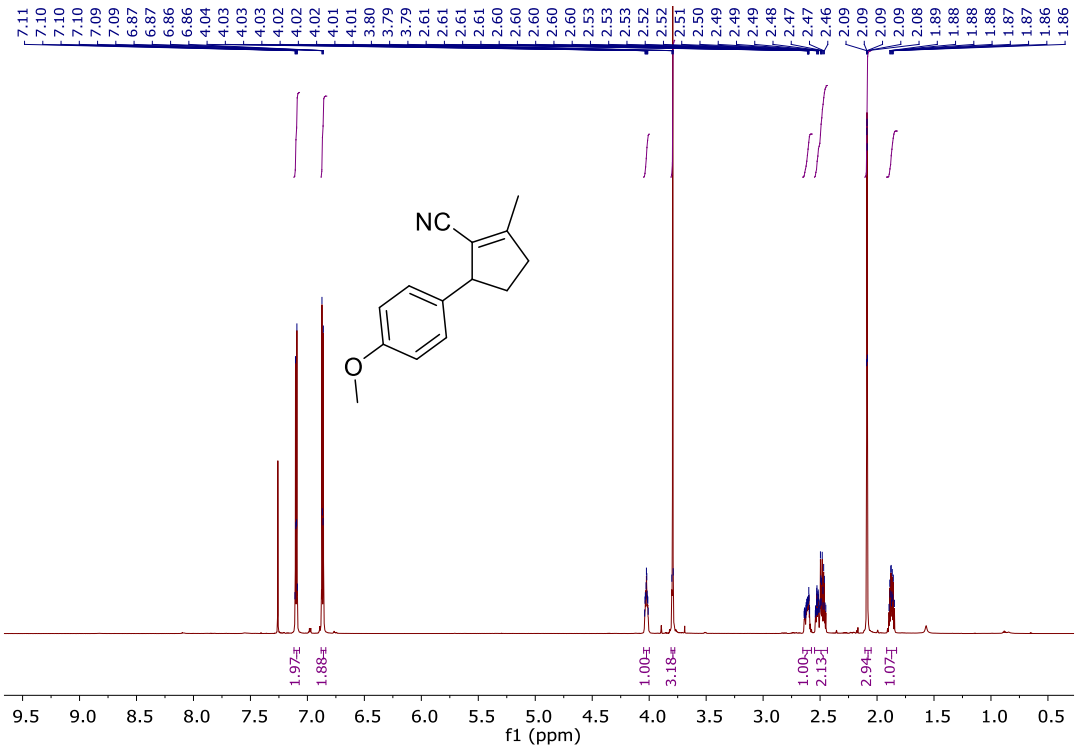


^{13}C NMR

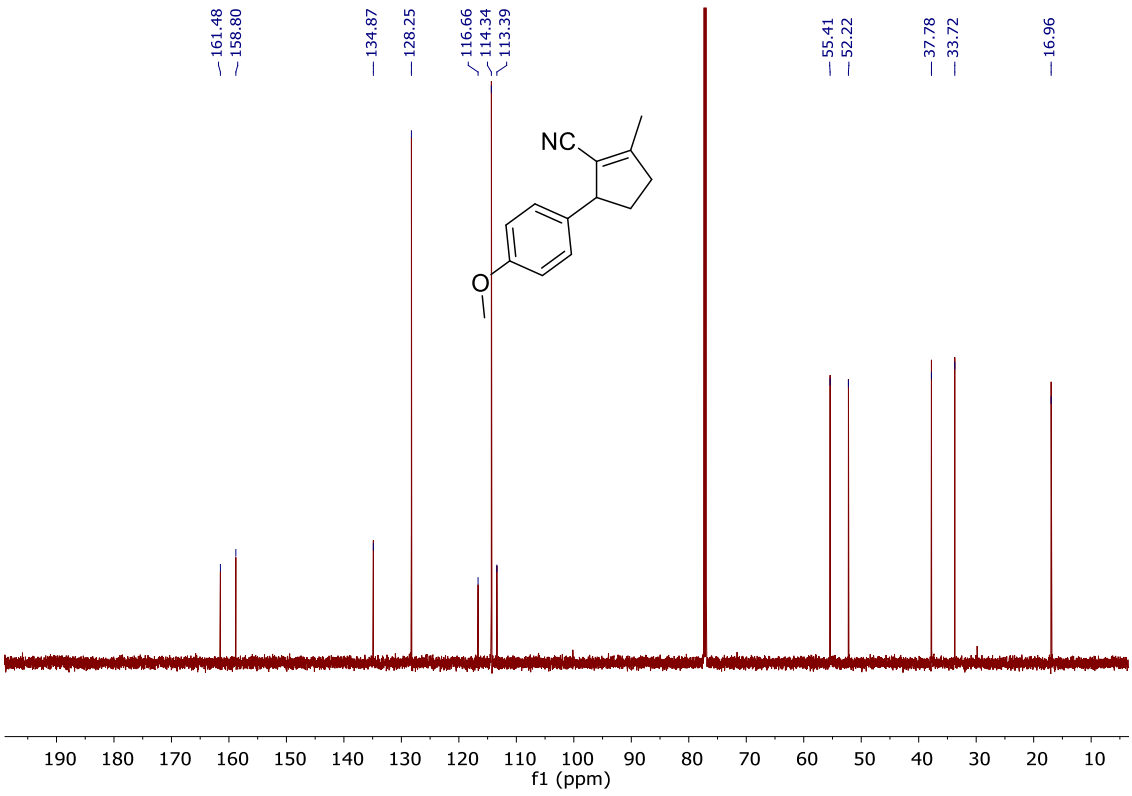


5-(4-methoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3ai)

^{1}H NMR

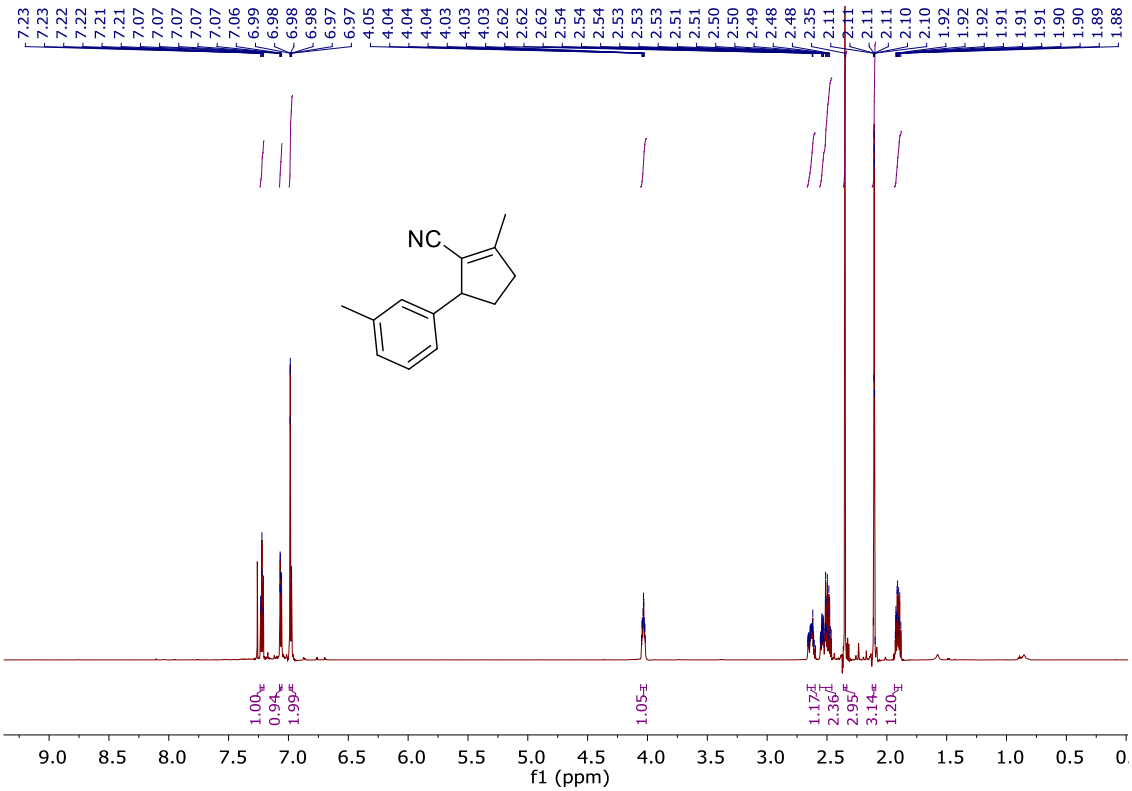


^{13}C NMR

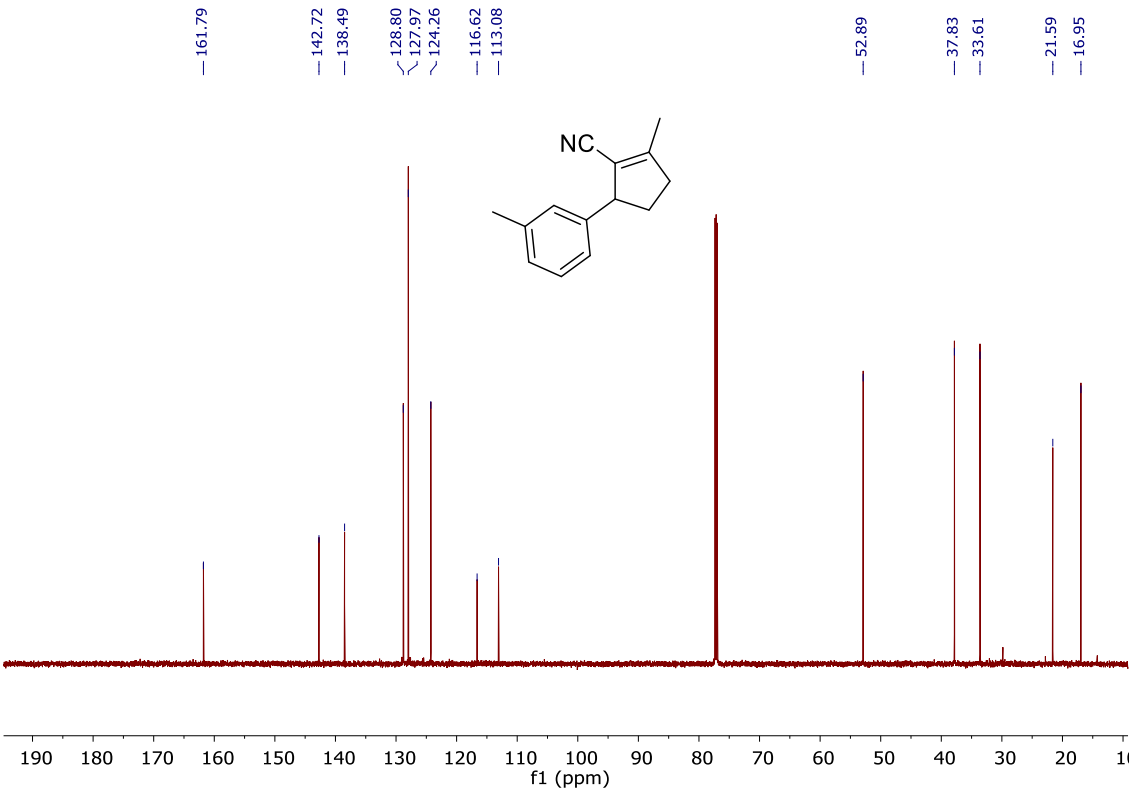


2-methyl-5-(m-tolyl)cyclopent-1-enecarbonitrile (3aj)

^{1}H NMR

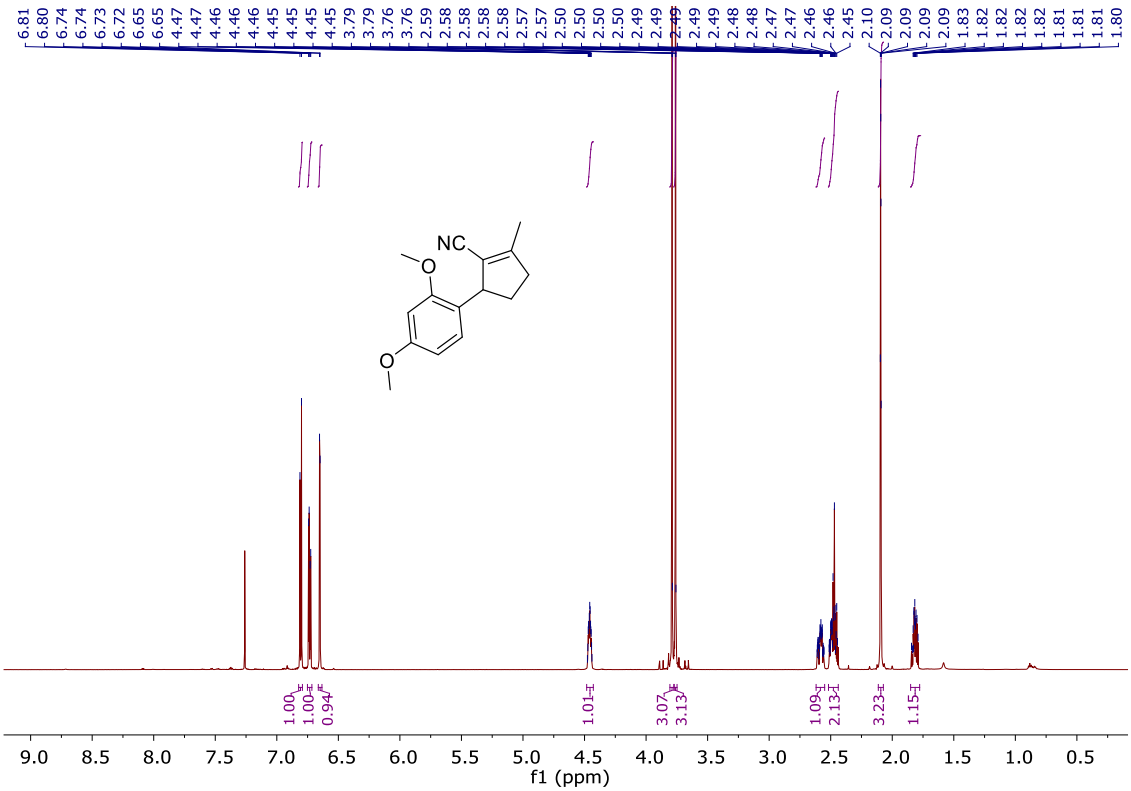


^{13}C NMR

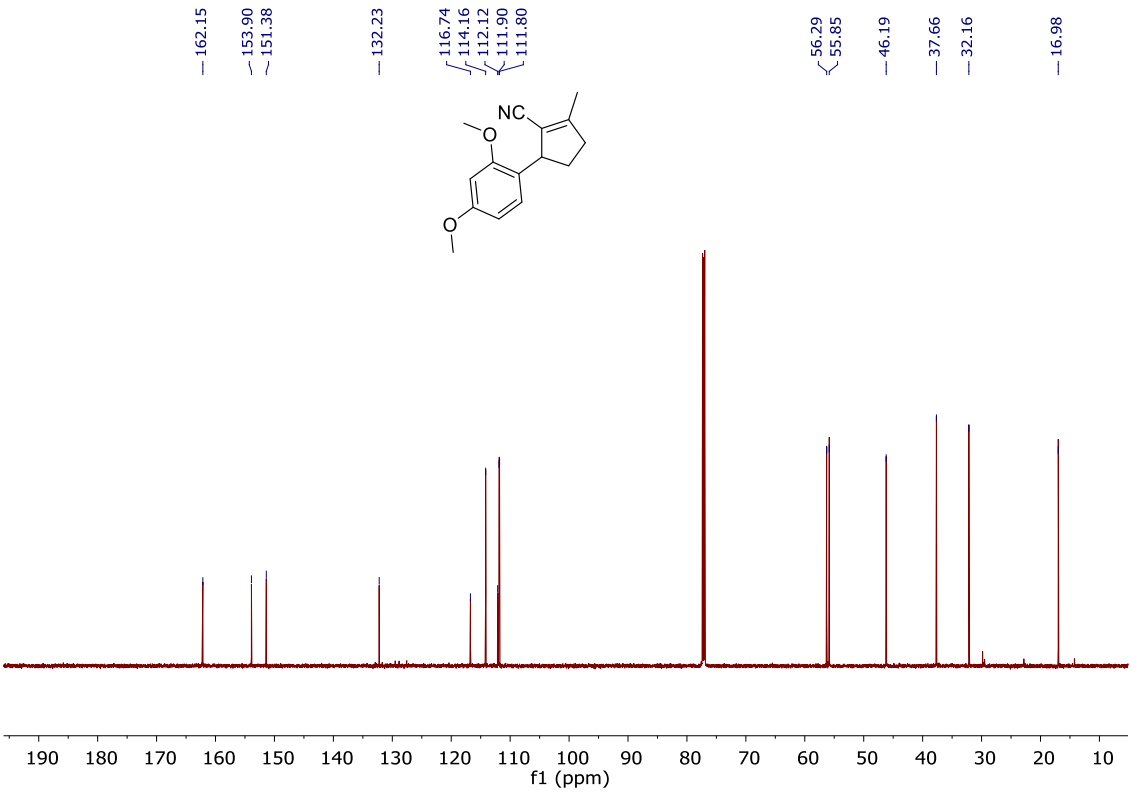


5-(2,4-dimethoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3ak)

^{1}H NMR

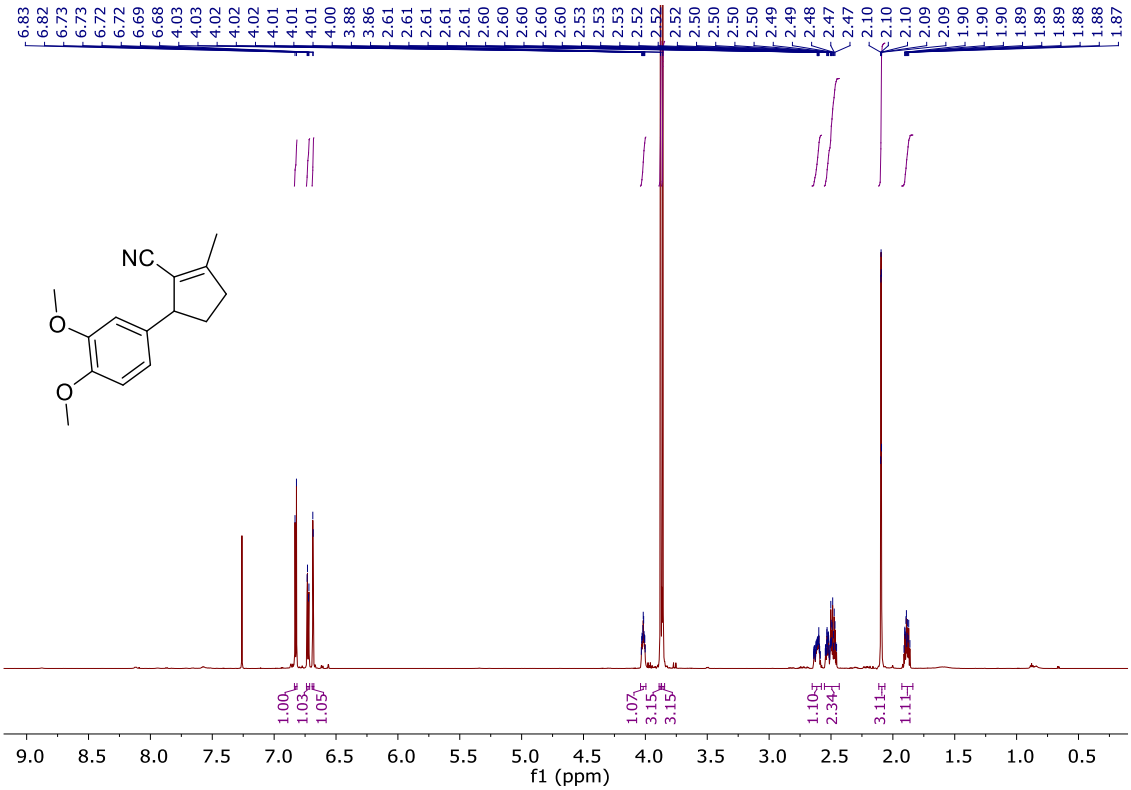


^{13}C NMR

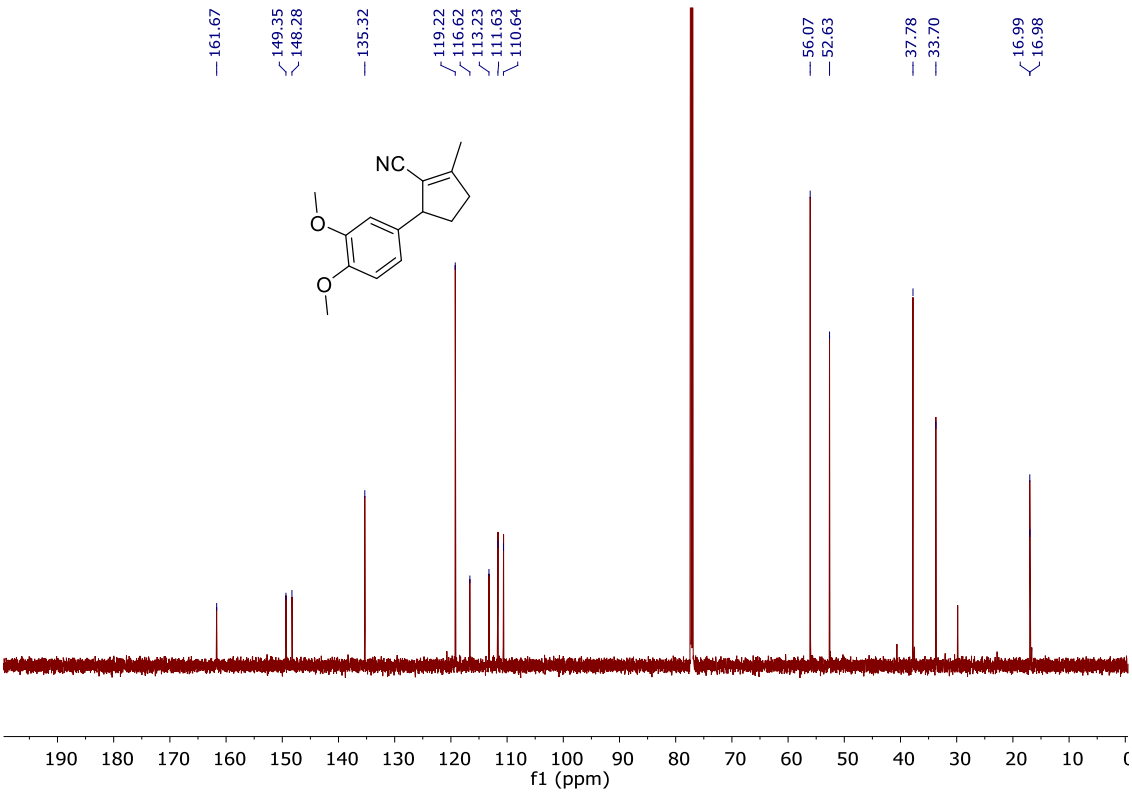


5-(3,4-dimethoxyphenyl)-2-methylcyclopent-1-enecarbonitrile (3al)

^{1}H NMR

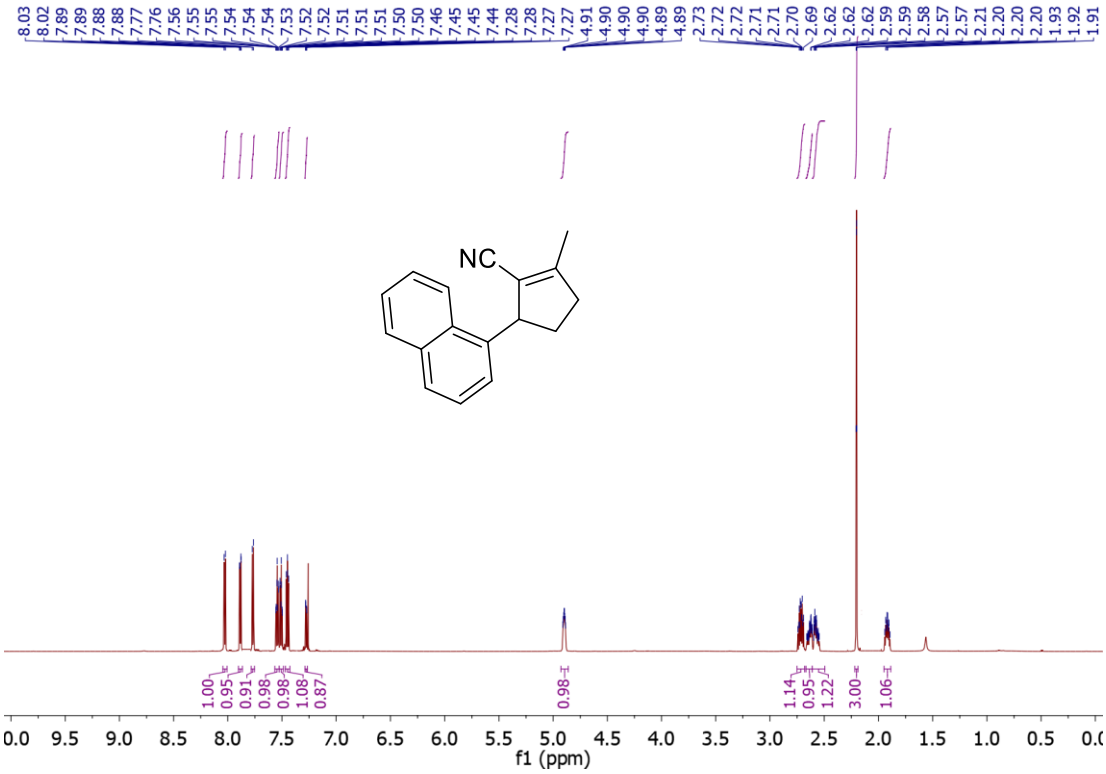


^{13}C NMR

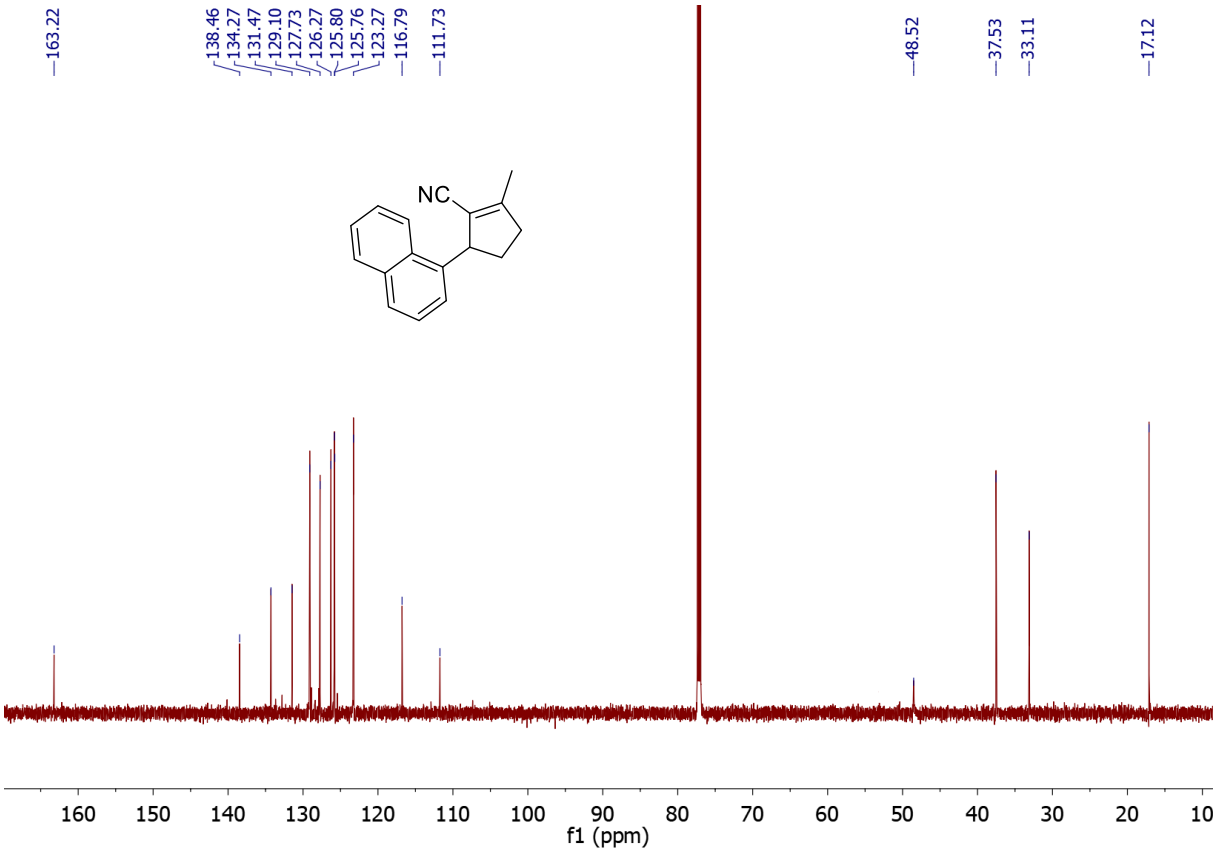


2-methyl-5-(naphthalen-1-yl)cyclopent-1-enecarbonitrile (3am)

^{1}H NMR

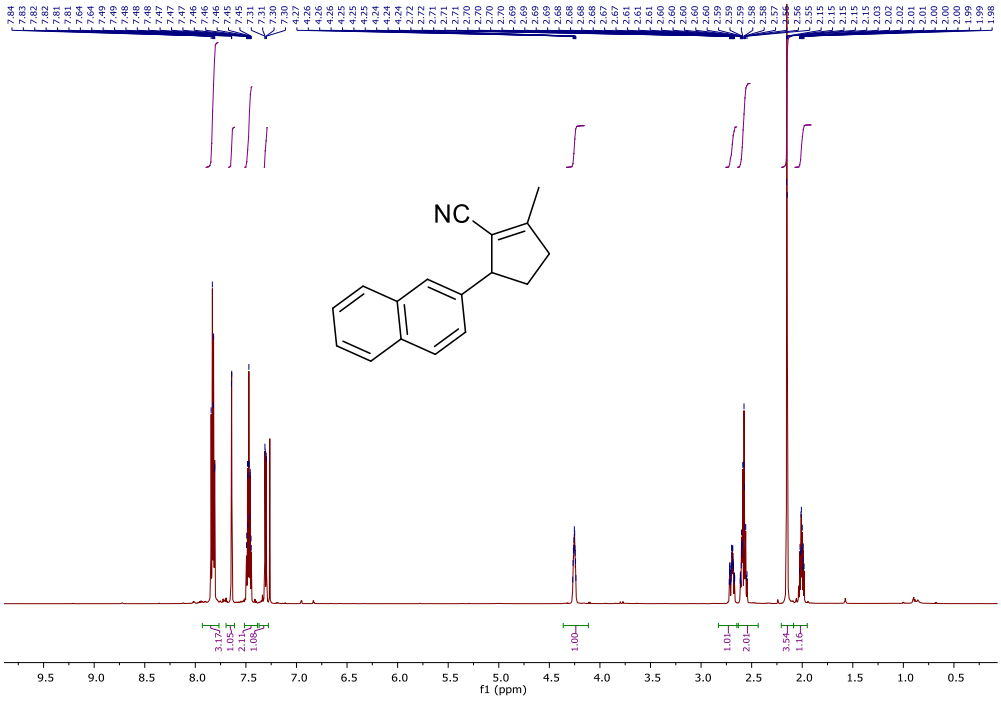


^{13}C NMR

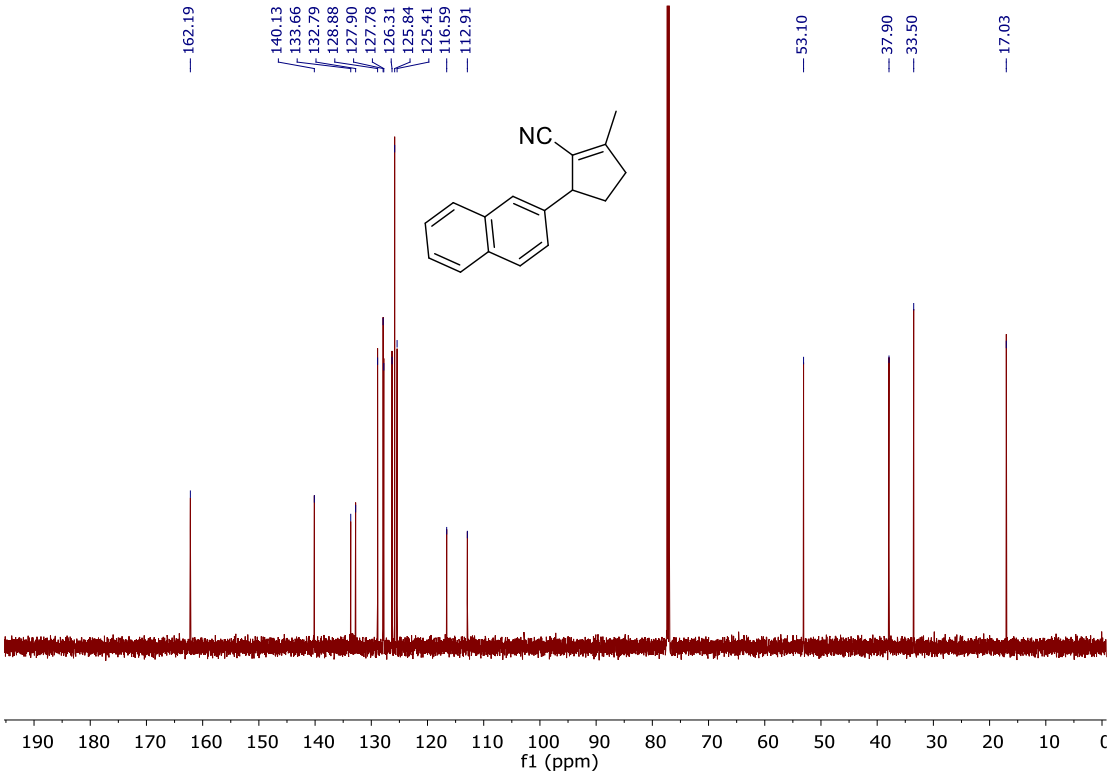


2-methyl-5-(naphthalen-2-yl)cyclopent-1-enecarbonitrile (3an)

^{1}H NMR

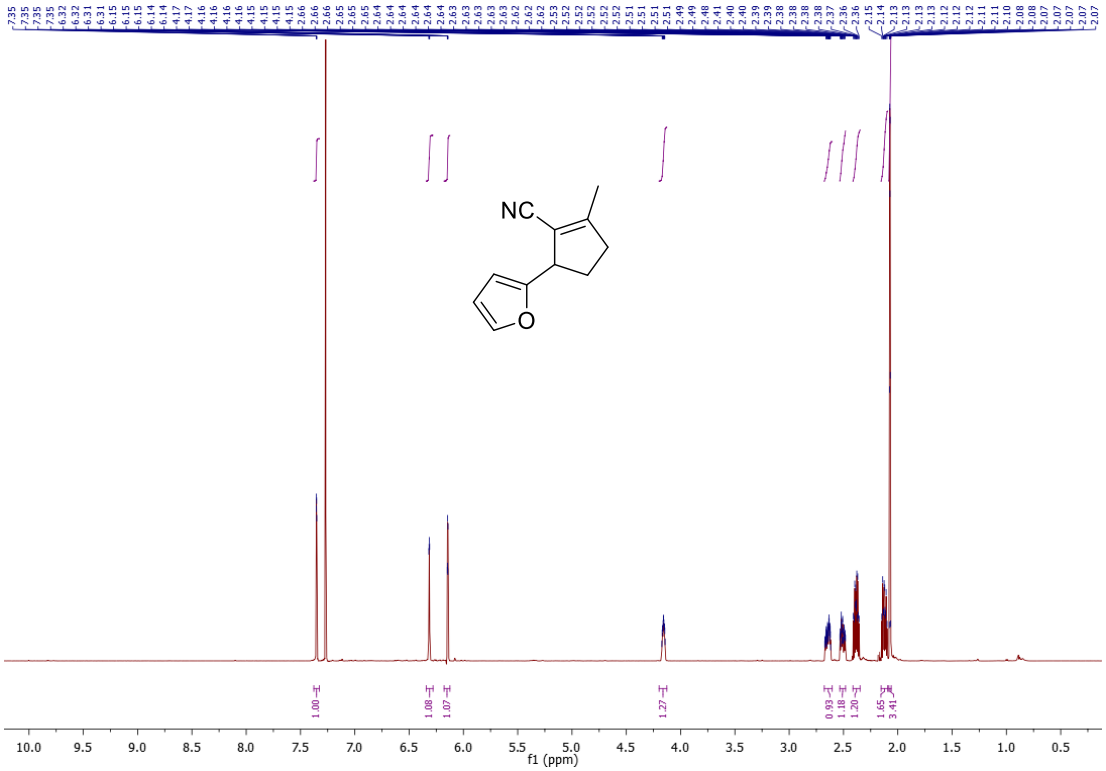


^{13}C NMR

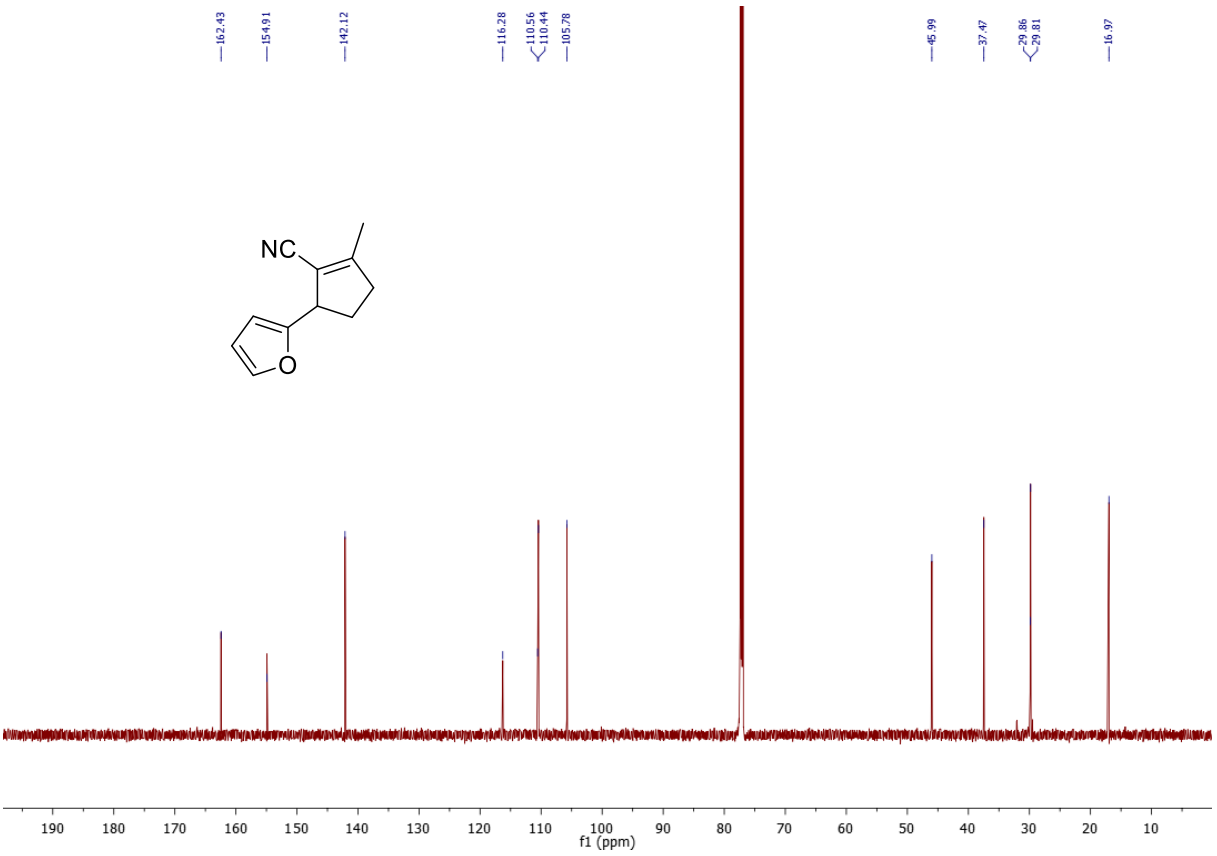


5-(furan-2-yl)-2-methylcyclopent-1-enecarbonitrile (3ao)

^{1}H NMR

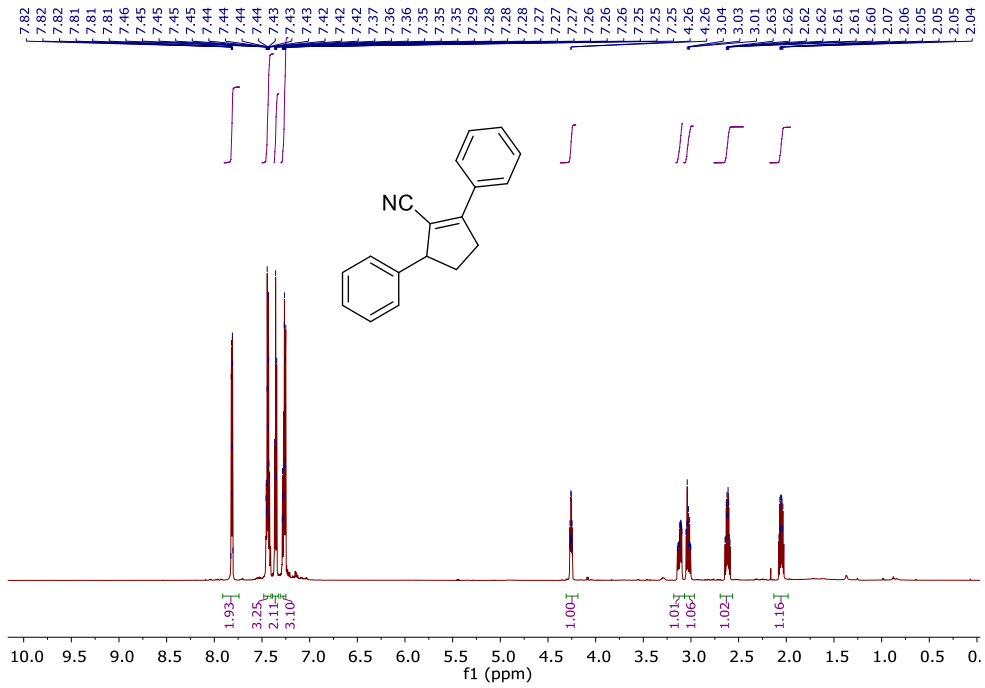


^{13}C NMR

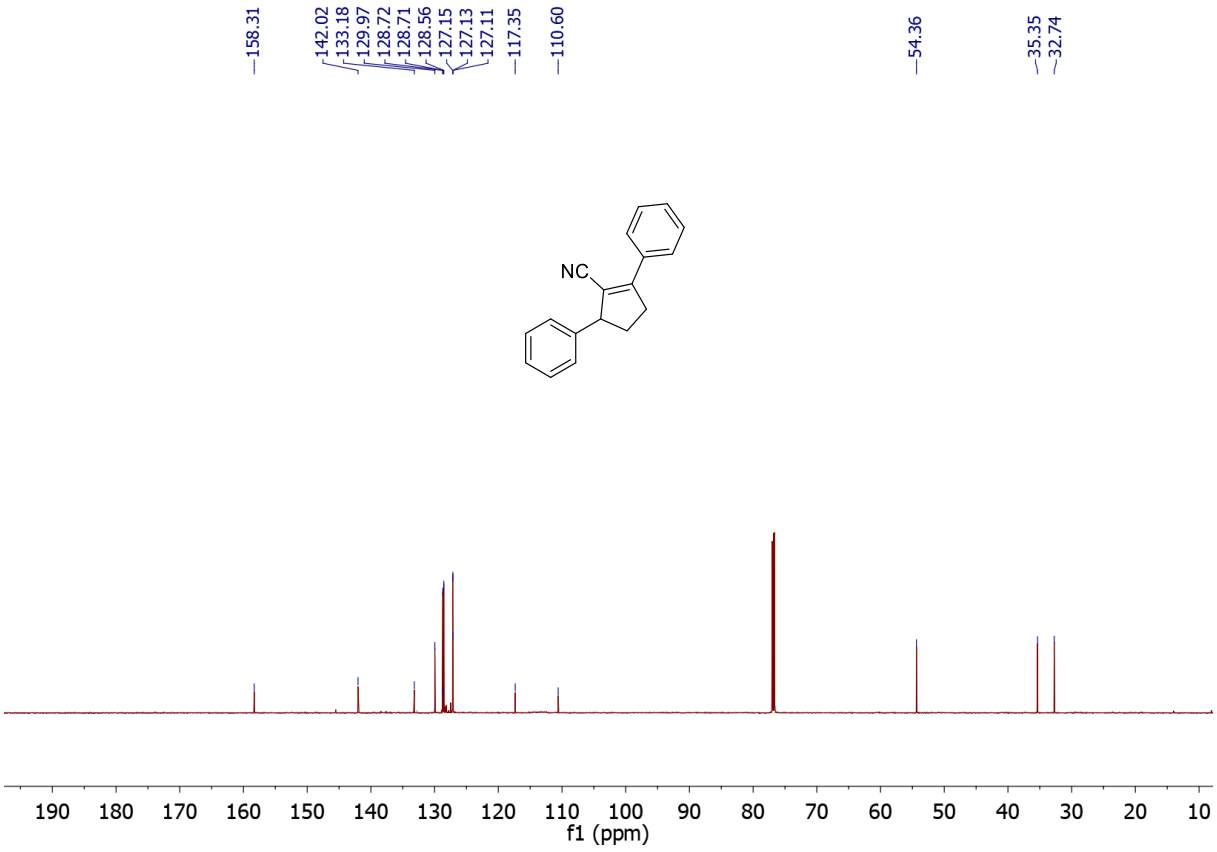


2,5-diphenylcyclopent-1-enecarbonitrile (3ba)

^{1}H NMR

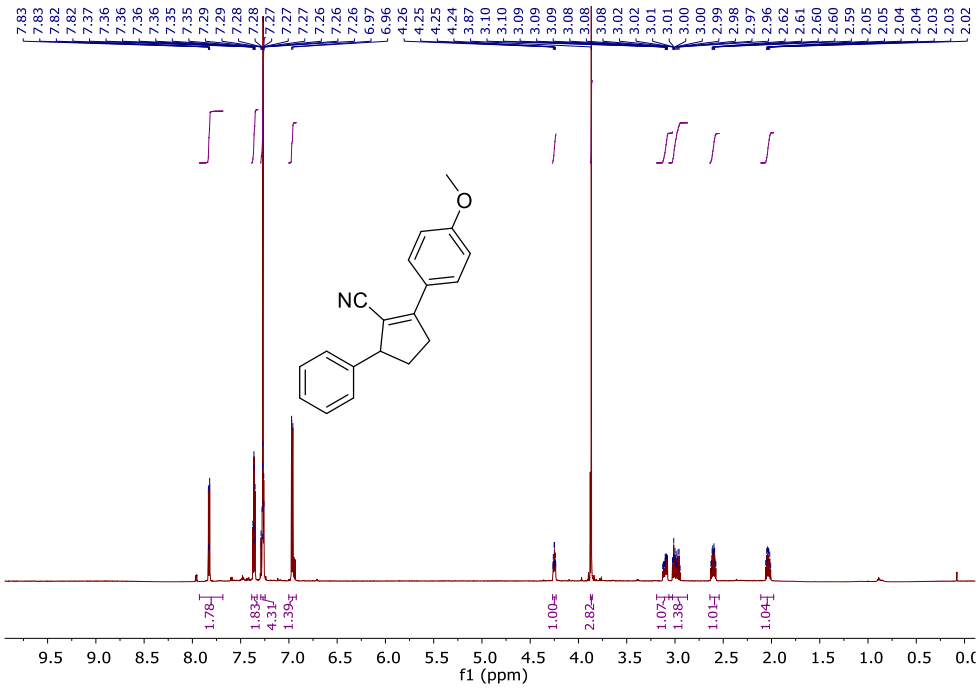


^{13}C NMR

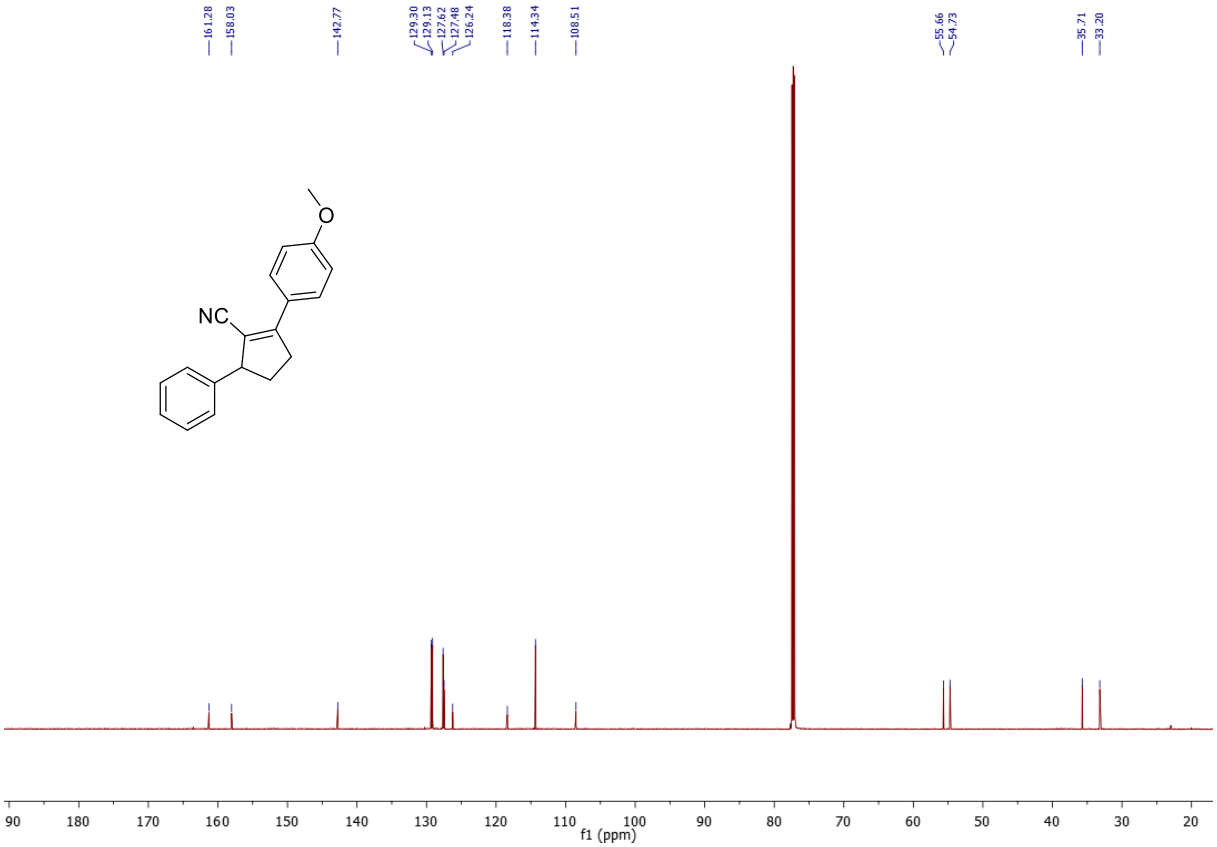


2-(4-methoxyphenyl)-5-phenylcyclopent-1-enecarbonitrile (3ca)

^{1}H NMR

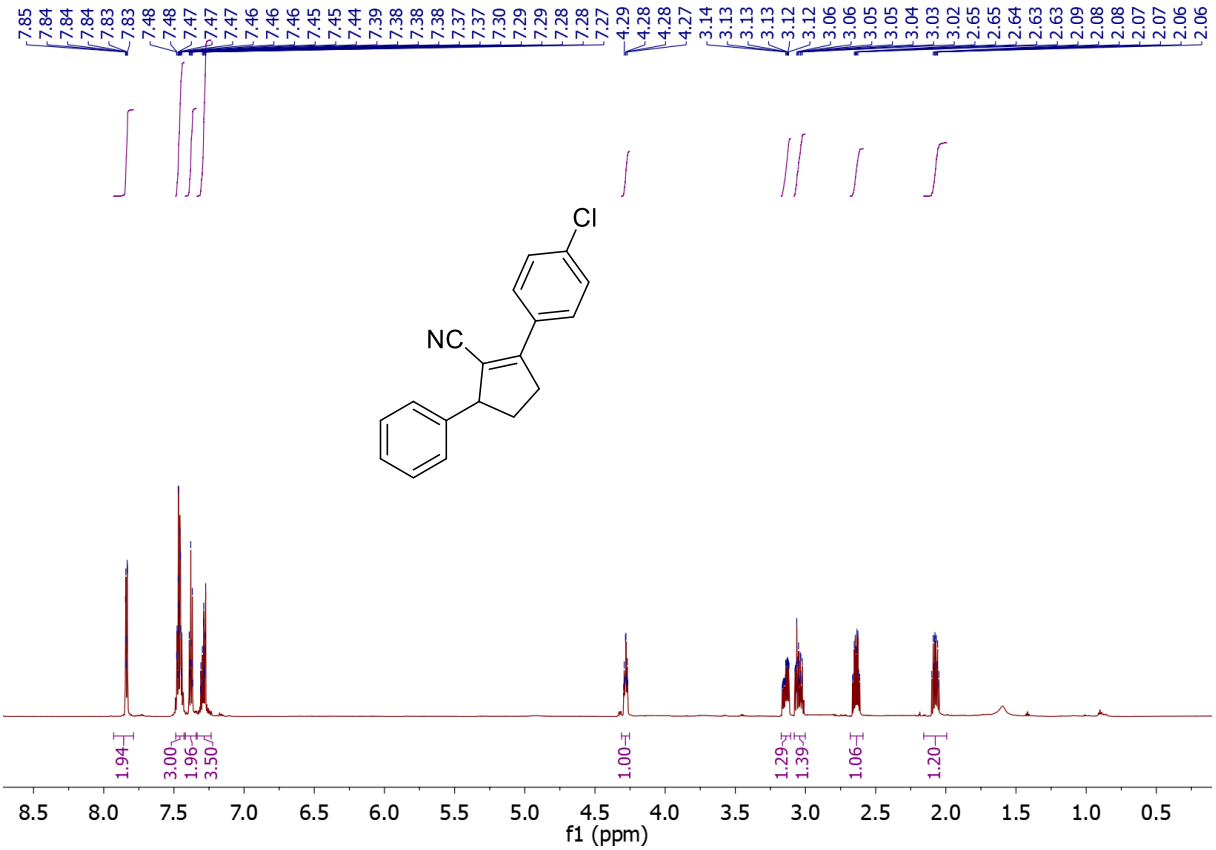


^{13}C NMR

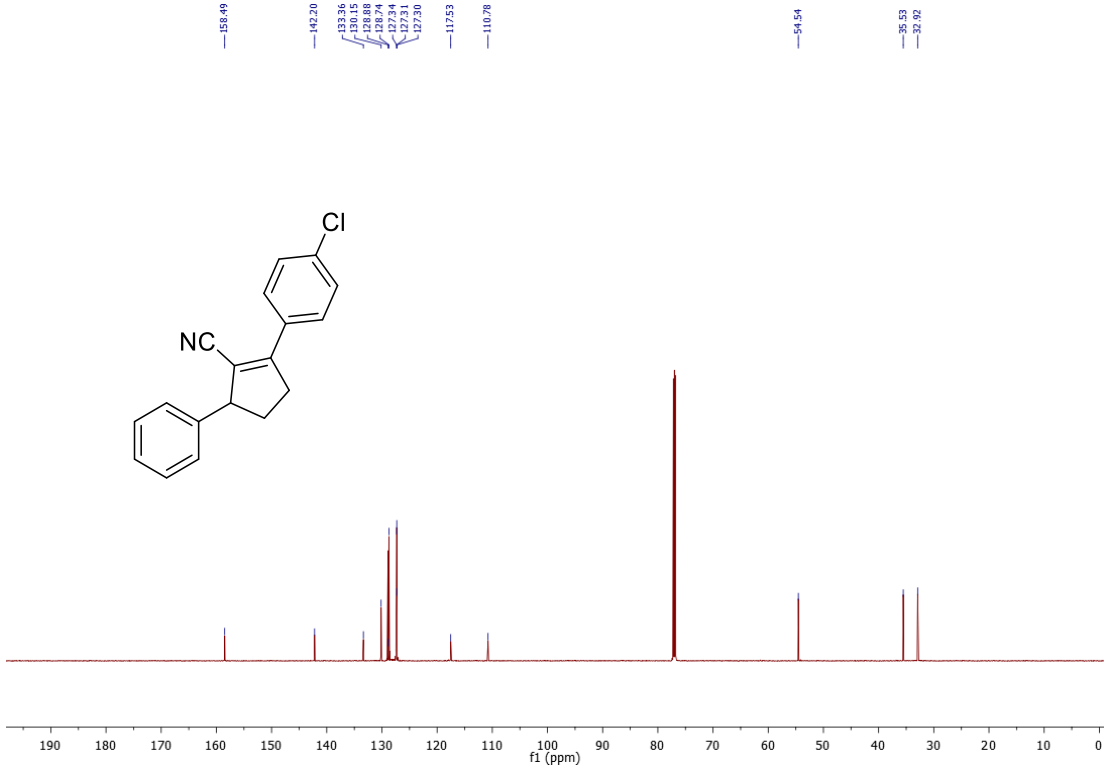


2-(4-chlorophenyl)-5-phenylcyclopent-1-enecarbonitrile (3da)

^{1}H NMR

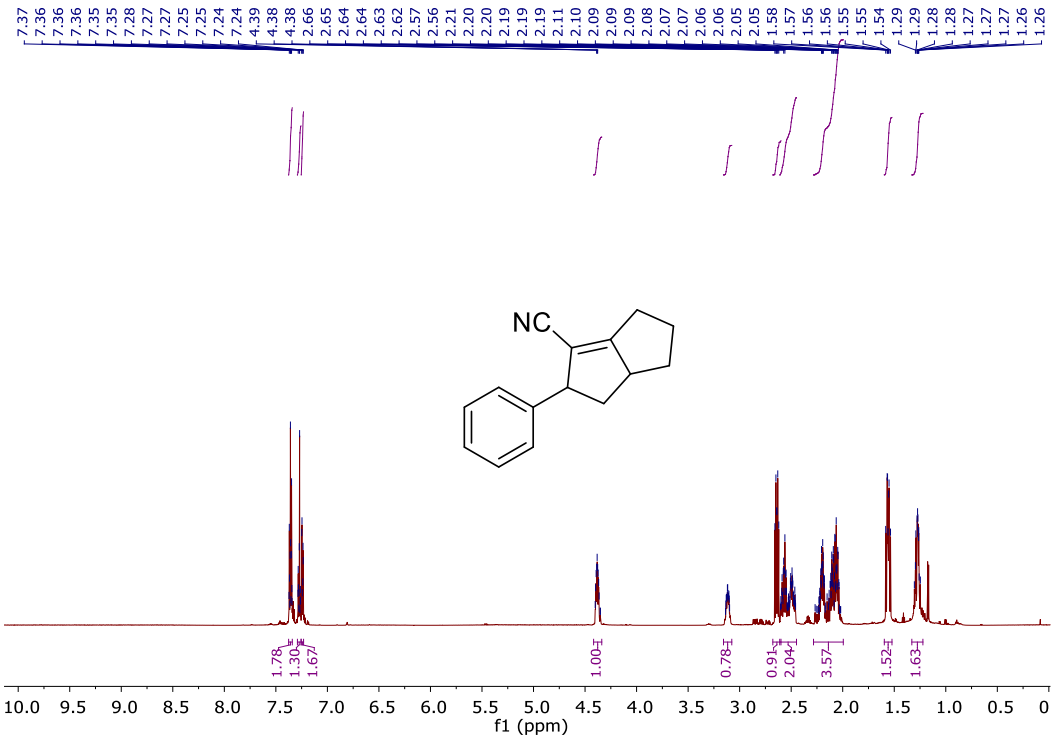


^{13}C NMR



2-phenyl-2,3,3a,4,5,6-hexahydropentalene-1-carbonitrile (3ea)

^{1}H NMR



^{13}C NMR