Supplementary Information

Carbene and Photocatalyst-Catalyzed Decarboxylative Radical Coupling of Carboxylic Acids and Acyl Imidazoles to Form Ketones

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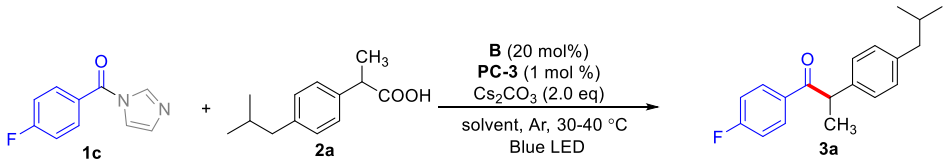
1. General information

All reactions and manipulations involving air-sensitive compounds were carried out using standard Schlenk techniques. Anhydrous toluene, hexane, Et_2O and THF were distilled from sodium benzophenone ketyl. Anhydrous CH_2Cl_2 and $CHCl_3$ were distilled from CaH_2 under an atmosphere of nitrogen. Anhydrous MeCN were purchased from Sigma-Aldrich Co., Inc. All reactions were monitored by TLC. TLC analysis was performed by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the stationary phase. ^1H NMR spectra were recorded on a Bruker Avance (500 MHz) or Bruker BBFO (400 MHz) instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker BBFO (100 MHz) or Bruker Avance (125 MHz) instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.0 ppm). ^{19}F NMR spectra were recorded on a Bruker BBFO (376 MHz) instrument. High resolution mass spectra (HRMS) (EI^+) were recorded on an a Finnigan MAT 95 XP mass spectrometer. Melting points are uncorrected and were recorded on an MPA 100 OptiMelt Automated Melting Point System. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Commercially available reagents were purchased from Energy Chemical, J& K Scientific, Adamas-beta and Sigma-Aldrich Co., Inc.

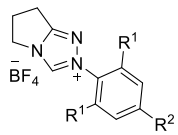
2. Condition optimizations

Supplementary Table S1. Influence of solvent[a]

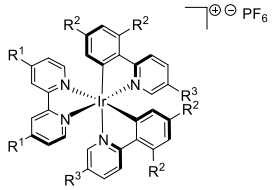


entry	solvent	yield/ %
1	MeCN	82 (78)[b]
2	THF	52
3	DCE	46
4	DMSO	42
5	DCE/H_2O (v:v = 1:1)	15

[a] Reaction conditions: **1c** (0.15 mmol), **2a** (0.1 mmol), **B** (20 mol %), **PC-3** (1 mol %) and Cs_2CO_3 (2.0 equiv) in solvent (2.0 mL), blue LED (Kessil PR160 series, λ_{max}= 427 nm), Ar atmosphere, 30-40 °C, 24 h. [b] Isolated yield.

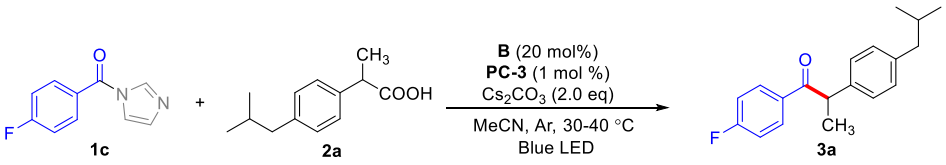


B: $R^1 = R^2 = CH_3$



PC-3: R^1 = H, R^2 = F, $R^3 = CF_3$

Supplementary Table S2. Influence of light source[a]



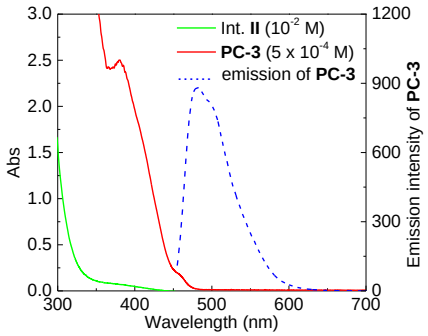
entry	light source	yield/ %
1	Blue LED (λ_{max} = 427 nm)	82 (78)[b]
2	Blue LED (λ_{max} = 440 nm)	76
3	Blue LED (λ_{max} = 467 nm)	62
4	23 W CFL	36

[a] Reaction conditions: **1c** (0.15 mmol), **2** (0.10 mmol), **B** (20 mol %) **PC-3** (1 mol %) and Cs_2CO_3 (2.0 equiv) in MeCN (2.0 mL), light source, Ar atmosphere, 30-40 °C, 24 h. [b] Isolated yield.

3. Mechanistic studies

3.1 UV-Vis absorption spectrum and emission spectra

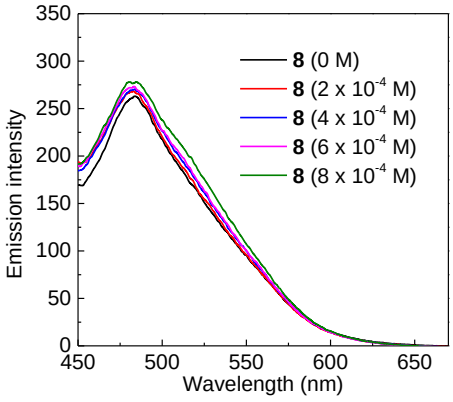
The UV-Vis absorption spectra of pre-formed acyl azolium intermediate **II** (Int. **II**) and **PC-3** were measured on a SHIMADZU UV-3600 UV/Vis spectrometer under reaction concentration in anhydrous DMSO. The emission spectrum of **PC-3** (10^{-5} M in DMSO) upon excitation at 420 nm was recorded (Supplementary Figure 1, blue dashed line).



Supplementary Figure 1. UV-Vis absorption spectra and emission spectra

3.2 Stern-Volmer quenching experiments of Int. II

The emission spectrum of acyl azolium intermediate **II** (Int. **II**, 10^{-3} M in DMSO) upon excitation at 420 nm was recorded (Figure S2, black line). Stern-Volmer quenching experiment between Int. **II** and sodium 2-(4-isobutylphenyl)propanoate (**8**) were conducted (Supplementary Figure 2). The results revealed that sodium 2-(4-isobutylphenyl)propanoate (**8**) can not quench the excited Int. **II**. This suggests the excitation of acyl azolium intermediate **II** do not responsible to the oxidative decarboxylation process.



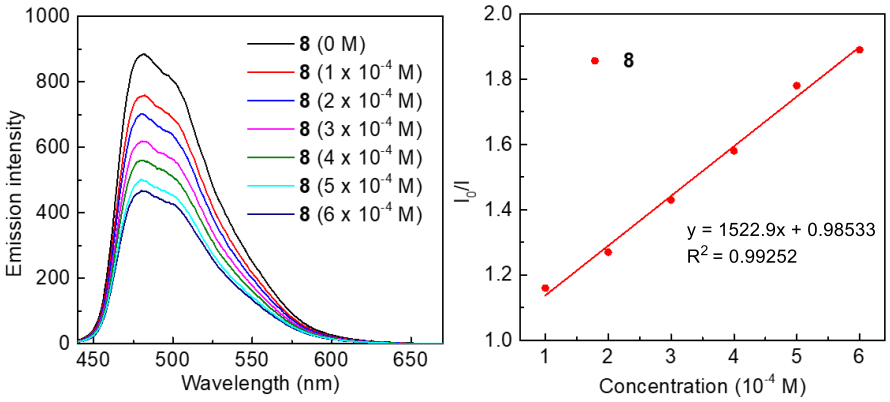
Supplementary Figure 2. Stern-Volmer quenching experiments between Int. **II** and **8**

Experimental protocol: The emission spectra of freshly prepared solution of Int. **II** (1 x

10^{-3} M in DMSO, 0.5 mL) was recorded. Then, a solution of sodium 2-(4-isobutylphenyl)propanoate (**8**) in DMSO (2 x 10^{-2} M, 5 μL) was added to the solution, and another emission spectra was recorded. The addition of **8** and the recordation were repeated 4 consecutive times.

3.3 Stern-Volmer quenching experiments of PC-3

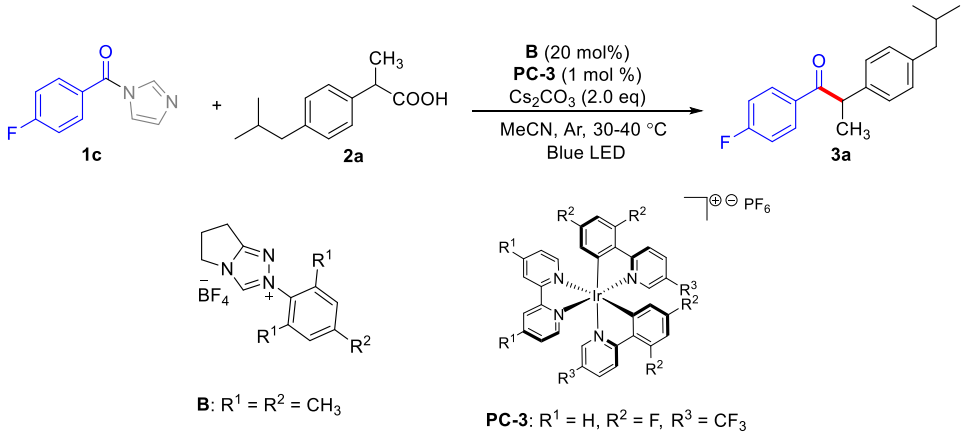
To support the proposed reductive quenching of photocatalyst (**PC-3**) by carboxylic acid anion, we conducted Stern-Volmer quenching experiments by using sodium 2-(4-isobutylphenyl)propanoate (**8**) as quenching agent (Supplementary Figure 3). It was found that sodium 2-(4-isobutylphenyl)propanoate (**8**) could effectively quench the emission of **PC-3**. The quenching rate constant (k_q = 6.68 x 10^8 $M^{-1}s^{-1}$) was calculated by using the reported[1] lifetime of **PC-3** (2280 ns).



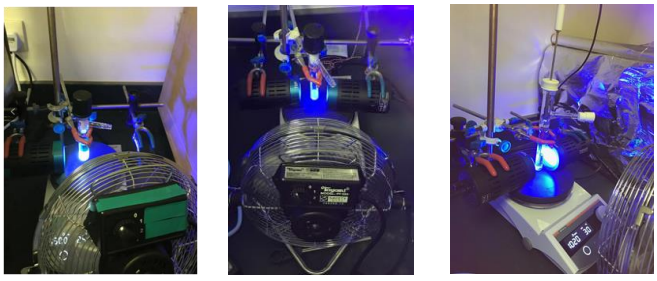
Supplementary Figure 3. Stern-Volmer quenching experiments

Experimental protocol: The emission spectra of a solution of **PC-3** (10^{-5} M in DMSO, 0.5 mL) was recorded. Then, a solution of sodium 2-(4-isobutylphenyl)propanoate (**8**) in DMSO (1 x 10^{-2} M, 5 μL) was added to the solution, and another emission spectra was recorded. The addition of **8** and the recordation were repeated 5 consecutive times.

4. General procedure for coupling of carboxylic acids and acyl imidazoles



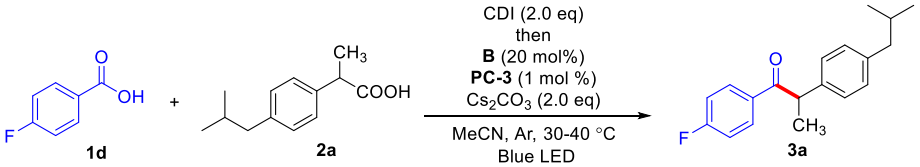
General procedure A: To a 10 mL Schlenk tube equipped with a stir bar was added (4-fluorophenyl)(1H-imidazol-1-yl)methanone **1c** (28.5 mg, 0.15 mmol), 2-(4-isobutylphenyl)propanoic acid **2a** (20.6 mg, 0.10 mmol), NHC pre-catalyst **B** (6.3 mg, 0.02 mmol), photocatalyst **PC-3** (1.0 mg, 0.001 mmol) and dry Cs_2CO_3 (65.0 mg, 0.20 mmol). The Schlenk tube was sealed and placed under argon before 2 mL of dry MeCN was added. The reaction was stirred and irradiated with one/two blue LED Kessil lamp (λ_{max} = 427 nm, intensity = 100%, 3 cm away from the Schlenk tube, with cooling fan to keep the reaction temperature at 30-40 °C. Reaction set-up see Supplementary Picture 1) for 24 hours. Then the reaction mixture was filtered through a pad of celite and washed with ethyl acetate. The filtrate was concentrated in vacuum to afford the crude material which was purified by column chromatography (silica gel, EtOAc/hexanes) to give product **3a** in 78% isolated yield (22.1 mg) as colorless liquid. **Note**: For reactions which used aliphatic carboxylic acyl imidazoles as substrates, Cs_2CO_3 (1.2 equiv) and two 440 nm blue LEDs were used.



reaction setup with one blue LED | reaction setup with two blue LEDs | temperature measurement

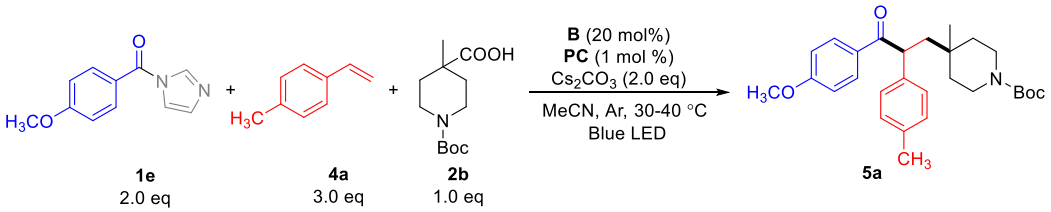
Supplementary Picture 1: Picture of reaction set-up and temperature measurement.

5. General procedure for formally coupling of two carboxylic acids



General procedure B: In gloves box, to a 4 mL vial equipped with a stir bar was added 4-flurobenzoic acid **1d** (30.4 mg, 0.2 mmol) and CDI (32.4 mg, 0.2 mmol). MeCN (2 mL) was added as solvent. The reaction mixture was stirred for 2.5 hours in gloves box at room temperature until the solution become homogenous. The resulting reaction mixture was mixed with 2-(4-isobutylphenyl)propanoic acid **2a** (20.6 mg, 0.10 mmol), NHC pre-catalyst **B** (6.3 mg, 0.02 mmol), photocatalyst **PC-3** (1.0 mg, 0.001 mmol) and dry Cs_2CO_3 (65.0 mg, 0.20 mmol). The resulting mixture was sealed and take out from the gloves box. Then the reaction was stirred and irradiated with one blue LED Kessil lamp (λ_{max} = 427 nm, intensity = 100%, 3 cm away from the Schlenk tube, with cooling fan to keep the reaction temperature at 30-40 ℃. Reaction set-up see Supplementary Picture 1) for 12-24 hours. The reaction mixture was filtered through a pad of celite and washed with ethyl acetate. The filtrate was concentrated in vacuum to afford the crude material which was purified by column chromatography (silica gel, EtOAc/hexanes) to give product **3a** in 68% isolated yield (19.3 mg) as colorless liquid. **Note**: For nalidixic acid (**3b**, **7g**, **7h**), dehydrocholic acid (**3d**) and adapalene (**7j**) which cannot dissolve in MeCN, DMSO was used as solvent. For synthesis of **3b**, **7g**, **7h**, and **7j**, the corresponding mixtures of acid and CDI were stirred for 10 hours.

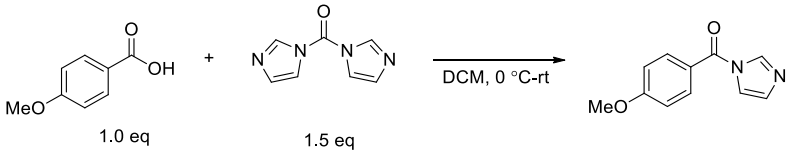
6. General procedure for three-component radical relay coupling



General procedure C: To a 10 mL Schlenk tube equipped with a stir bar was added (1H-imidazol-1-yl)(4-methoxyphenyl)methanone **1e** (40.4 mg, 0.2 mmol),1-methyl-4-vinylbenzene **4a** (35.5 mg, 0.3 mmol) 1-(tert-butoxycarbonyl)-4-methylpiperidine-4-carboxylic acid **2b** (24.3 mg, 0.10 mmol), NHC pre-catalyst **B** (6.3 mg, 0.02 mmol), photocatalyst **PC-3** (1.0 mg, 0.001 mmol) and dryCs_2CO_3 (65.0 mg, 0.20 mmol). The Schlenk tube was sealed and placed under argon before 2-3 mL of dry MeCN was added. The reaction was stirred and irradiated with two blue LED Kessil lamp (λ_{max} = 427 nm, intensity = 75%, 3 cm away from the Schlenk tube, with cooling fan to keep the reaction temperature at 30-40 ℃. Reaction set-up see Supplementary Picture 1) for 24 hours. Then the reaction mixture was filtered through a pad of celite and washed with ethyl acetate. The filtrate was concentrated in vacuum to afford the crude material which was purified by column chromatography (silica gel, EtOAc/hexanes) to give product **5a** in 90% yield (40.6 mg) as colorless oil.

7. General procedure for preparation of starting materials

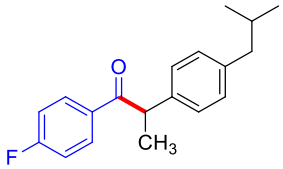
All the carboxylic acids are commercially available, and the acyl imidazoles were prepared according to the following procedure.[2]



General procedure E: Acyl imidazoles were prepared according to slightly modefied literature procedure[1]. To an oven-dried 100 mL round bottom flask equipped with a stir bar was added 4-methoxybenzoic acid (1.52 g, 10 mmol, 1.0 eq) and dry DCM (30 mL). CDI (2.43g, 15 mmol, 1.5 eq) was added slowly under 0 ºC. The reaction mixture was allowed warm to room temperature and stirred over night. Then the reaction mixture was washed vigorously 3 times with water and one time with brine. The organic layer was then dried over $MgSO_4$ and concentration under vacuum. The resulting product (0.98 g) was used directly without further purification.

8. Characterizations of new compounds

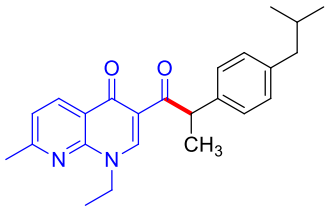
1-(4-fluorophenyl)-2-(4-isobutylphenyl)propan-1-one (3a)



According to the general procedure **A** (0.1 mmol scale), product **3a** was isolated in 78% yield (22.1 mg) as colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.94 (1H, m), 7.18-7.13 (2H, m), 7.10-6.99 (4H, m), 4.60 (1H,q, *J* = 6.8 Hz), 2.41 (2H,d, *J* = 7.2 Hz), 1.88-1.74 (1H, m), 1.51 (3H,d, *J* = 6.8 Hz), 0.87 (6H,t, *J* = 6.5 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.9, 165.4 (d, *J* = 253.0 Hz), 140.4, 138.5, 132.9 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 9.2 Hz), 129.7, 127.3, 115.5 (d, *J*= 21.7 Hz), 47.6, 45.0, 30.1, 22.35, 22.33, 19.5; **^{19}F NMR** (376MHz, $CDCl_3$) δ -105.8 (m); **HRMS (ESI)**: Found: *m/z* 307.1474. Calcd for $C_{19}H_{21}OFNa$ $(M+Na)^+$ 307.1474.

Note: 3a could also be obtained via one-pot operation according to general procedure B in 68% yield.

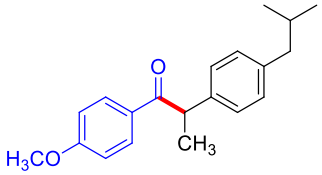
1-ethyl-3-(2-(4-isobutylphenyl)propanoyl)-7-methyl-1,8-naphthyridin-4(1H)-one (3b)



According to the general procedure **A** (0.1 mmol scale), product **3b** was isolated in 78% yield (29.3 mg) as white solid; mp: 140-141 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (1H, d, *J* = 8.3 Hz), 8.55 (1H, s), 7.34-7.27 (2H,m), 7.22 (1H, d, *J* = 8.1 Hz), 7.07-6.99 (2H, m), 5.56 (1H, q, *J* =7.2 Hz), 4.51-4.35 (2H, m), 2.63 (3H, s), 2.38 (2H,d, *J* = 7.0 Hz), 1.85-1.74 (1H, m), 1.50 (3H, d, *J* = 6.9 Hz), 1.44 (3H, t, *J* = 7.0 Hz), 0.85 (6H, d, *J* = 6.7 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 200.7, 175.5, 162.6, 148.6, 148.5, 139.8, 138.7, 136.8, 129.0, 128.2, 121.9, 121.0, 118.8, 48.6, 46.6, 45.1, 30.1, 25.0, 22.4, 18.5, 15.1; **HRMS (ESI)**: Found: *m/z* 399.2039.Calcd for $C_{24}H_{28}N_2O_2Na$ $(M+Na)^+$ 399.2048.

Note: 3b could also be obtained via one-pot operation according to general procedure B in 70% yield.

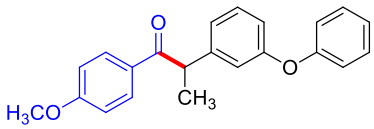
2-(4-isobutylphenyl)-1-(4-methoxyphenyl)propan-1-one (3c)



According to the general procedure **A** (0.2 mmol scale), product **3c** was isolated in 71% yield (42.1 mg) as yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.92 (2H, m),7.23-7.15 (2H, m), 7.10-7.03 (2H, m), 6.90-6.82 (2H, m), 4.62 (1H, q, *J* = 6.8 Hz), 3.81 (3H, s), 2.41 (2H, d, *J* = 7.3 Hz), 1.88-1.75 (1H, m), 1.51 (3H, d, *J* = 6.9 Hz), 0.87 (6H, d, *J* = 6.7 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.1, 163.1, 140.1, 139.0, 131.0, 129.6, 129.5, 127.3, 113.6, 55.3, 47.0, 44.9, 30.1, 22.35, 22.33, 19.5; **HRMS (ESI)**: Found: *m/z* 297.1853. Calcd for $C_{20}H_{25}O_2$ $(M+H)^+$ 297.1855.

Note: 3c could also be obtained via one-pot operation according to general procedure B in 60% yield.

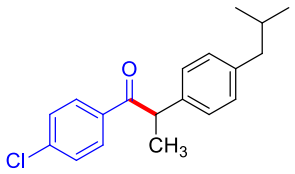
1-(4-methoxyphenyl)-2-(3-phenoxyphenyl)propan-1-one (3d)



According to the general procedure **B** (0.1 mmol scale), product **3d** was isolated in 75% yield (22.2 mg) as yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (2H, d, *J* = 8.8 Hz), 7.31 (2H, t, *J* = 7.8 Hz), 7.24 (1H, t, *J* = 8.0 Hz, 1H), 7.09 (1H, t, *J* = 7.3 Hz), 7.04- 6.97 (2H,m), 6.95 (2H, d, *J* = 8.1 Hz), 6.87 (2H, d, *J* = 8.8 Hz), 6.82 (1H, dd, *J* = 8.1, 1.7 Hz), 4.66-4.56 (1H, *J* = 6.9 Hz), 3.83 (3H, s), 1.52 (3H, d, *J* = 6.8 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.4, 163.2, 157.5, 157.1, 143.8, 131.0, 130.1, 129.7, 129.3, 123.2, 122.5, 118.7, 118.5, 117.0, 113.6, 55.4, 47.3, 19.3; **HRMS (ESI)**: Found: *m/z* 355.1318. Calcd for $C_{22}H_{20}O_3Na$ $(M+Na)^+$ 355.1310.

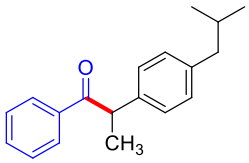
Note: 3d could also be obtained via one-pot operation according to general procedure B in 67% yield.

1-(4-chlorophenyl)-2-(4-isobutylphenyl)propan-1-one (3e)



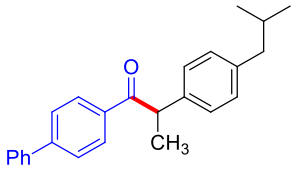
According to the general procedure **A** (0.1 mmol scale), product **3e** was isolated in 58% yield (17.6 mg) as colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91-7.85 (2H,m), 7.38-7.31 (2H,m), 7.18-7.13 (2H, m), 7.09-7.04 (2H, m), 4.58 (1H, q, *J* = 6.8 Hz), 2.41 (2H, d, *J* = 7.2 Hz), 1.91-1.75 (1H, m), 1.51 (3H, d, *J* = 6.8 Hz), 0.87 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.2, 140.5, 139.1, 138.3, 134.8, 130.2, 129.8, 128.7, 127.3, 47.7, 44.9, 30.1, 22.35, 22.34, 19.4; **HRMS (ESI)**: Found: *m/z* 301.1349. Calcd for $C_{19}H_{22}OCl$ $(M+H)^+$ 301.1359.

2-(4-isobutylphenyl)-1-phenylpropan-1-one (3f)



According to the general procedure **A** (0.2 mmol scale), product **3f** was isolated in 62% yield (33.1 mg) as yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.94 (2H,m), 7.50-7.44 (1H,m), 7.41-7.34 (2H, m), 7.22-7.16 (2H, m), 7.10-7.04 (2H, m), 4.67 (1H, q, *J* = 6.7 Hz), 2.41 (2H, d, *J* = 7.3 Hz), 1.89-1.74 (1H, m), 1.53 (3H, d, *J* = 6.8 Hz), 0.87 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 200.5, 140.3, 138.6, 136.6, 132.7, 129.6, 128.8, 128.4, 127.4, 47.4, 44.9, 30.1, 22.4, 22.3, 19.5; **HRMS (ESI)**: Found: *m/z* 289.1558. Calcd for $C_{19}H_{22}ONa$ $(M+Na)^+$ 3289.1568.

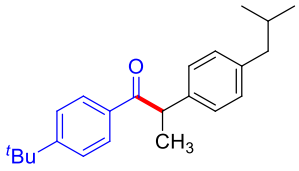
1-([1,1'-biphenyl]-4-yl)-2-(4-isobutylphenyl)propan-1-one (3g)



According to the general procedure **A** (0.1 mmol scale), product **3g** was isolated in 64% yield (22.0 mg) as white solid; mp: 88-89 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07-8.01 (2H,m),7.64-7.55 (4H,m), 7.47-7.41 (2H, m), 7.41-7.35 (1H, m), 7.25-7.20 (2H, m),

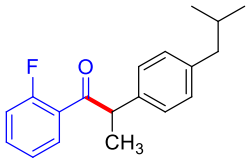
7.11-7.06 (2H, m), 4.70 (1H, q, *J* = 6.7 Hz), 2.42 (2H, d, *J* = 7.3 Hz), 1.88-1.78 (1H, m), 1.56 (3H, d, *J* = 6.8 Hz), 0.88 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.1, 145.3, 140.3, 139.9, 138.7, 135.2, 129.7, 129.4, 128.7, 128.1, 127.4, 127.2, 127.1, 47.5, 44.9, 30.1, 22.4, 22.35, 19.5; **HRMS (ESI)**: Found: *m/z* 343.2067. Calcd for $C_{25}H_{27}O$ $(M+H)^+$ 343.2062.

1-(4-(tert-butyl)phenyl)-2-(4-isobutylphenyl)propan-1-one (3h)



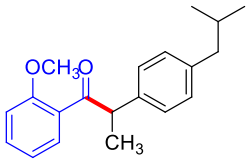
According to the general procedure **A** (0.1 mmol scale), product **3h** was isolated in 69% yield (22.1 mg) as yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95-7.89 (2H, m), 7.43-7.38 (2H, m), 7.23-7.18 (2H, m), 7.09-7.05 (2H, m), 4.67 (1H, q, *J* = 6.9 Hz), 2.42 (2H, d, *J* = 7.2 Hz), 1.87-1.77 (1H, m), 1.52 (3H, d, *J* = 6.9 Hz), 1.30 (9H, s), 0.88 (6H, d, *J* = 6.7 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.1, 156.3, 140.2, 138.8, 134.0, 129.6, 128.7, 127.4, 125.4, 47.3, 45.0, 35.0, 31.0, 30.1, 22.4, 22.35, 19.6; **HRMS (ESI)**: Found: *m/z* 345.2202. Calcd for $C_{23}H_{30}ONa$ $(M+Na)^+$ 345.2194.

1-(2-fluorophenyl)-2-(4-isobutylphenyl)propan-1-one (3i)



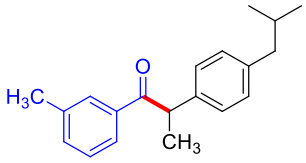
According to the general procedure **A** (0.1 mmol scale), product **3i** was isolated in 75% yield (21.4 mg) as yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (1H,td, *J* = 7.6, 1.8 Hz), 7.44-7.36 (1H,m), 7.16-7.10 (3H, m), 7.06-6.98 (3H, m), 4.58 (1H, q, *J* = 6.9 Hz), 2.39 (2H, d, *J* = 7.3 Hz), 1.86-1.74 (1H, m), 1.53 (3H, d, *J* = 6.9 Hz), 0.86 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0 (d, *J* = 4.3 Hz), 160.9 (d, *J* = 252.1 Hz), 140.3, 137.6, 133.9 (d, *J* = 8.9 Hz), 131.0 (d, *J* = 2.9 Hz), 129.4, 127.8, 126.3 (d, *J* = 13.1 Hz), 124.3 (d, *J* = 3.3 Hz), 116.4 (d, *J* = 23.6 Hz), 51.5 (d, *J* = 6.3 Hz), 45.0, 30.1, 22.3, 18.8; **^{19}F NMR** (376MHz, $CDCl_3$) δ -110.1 (m); **HRMS (ESI)**: Found: *m/z* 285.1650. Calcd for $C_{19}H_{22}OF$ $(M+H)^+$ 285.1655.

2-(4-isobutylphenyl)-1-(2-methoxyphenyl)propan-1-one (3j)



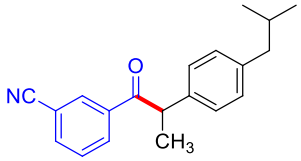
According to the general procedure **A** (0.1 mmol scale), product **3j** was isolated in 58% yield (17.1 mg) as colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (1H,dd, *J* = 7.6, 1.8 Hz), 7.38-7.31 (1H,m), 7.14-7.09 (2H, m), 7.04-6.98 (2H, m), 6.93-6.83 (2H, m), 4.67 (1H, q, *J* =7.0 Hz), 3.83 (3H, s), 2.40 (2H, d, *J* = 7.2 Hz), 1.86-1.74 (1H, m), 1.50 (3H, d, *J* =7.0 Hz), 0.86 (6H, d, *J* = 6.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.4, 157.5, 139.9, 138.4, 132.5, 130.3, 129.1, 129.0, 127.8, 120.5, 111.3, 55.4, 51.4, 45.9, 30.1, 22.34, 22.32,18.6; **HRMS (ESI)**: Found: *m/z* 319.1669.Calcd for $C_{20}H_{24}O_2Na$ $(M+Na)^+$ 319.1674.

2-(4-isobutylphenyl)-1-(m-tolyl)propan-1-one (3k)



According to the general procedure **A** (0.1 mmol scale), product **3k** was isolated in 75% yield (20.9 mg) as colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.79 (1H,m), 7.79-7.74 (1H, m), 7.34-7.27 (2H, m), 7.23-7.18 (2H, m), 7.11-7.06 (2H, m), 4.68 (1H, q, *J* =6.9 Hz), 2.43 (3H, d, *J* = 7.1 Hz), 2.38 (3H,s), 1.89-1.77 (1H, m), 1.54 (3H, d, *J* =6.9 Hz), 0.89 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.8, 140.2, 138.7, 138.2, 136.6, 133.5, 129.6, 129.3, 128.3, 127.4, 126.0, 47.4, 45.0, 30.1, 22.36, 22.33, 21.3,19.5; **HRMS (ESI)**: Found: *m/z* 303.1717. Calcd for $C_{20}H_{24}ONa$ $(M+Na)^+$ 303.1725.

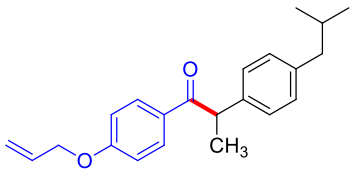
3-(2-(4-isobutylphenyl)propanoyl)benzonitrile (3l)



According to the general procedure **A** (0.1 mmol scale, 440 nm blue LED was used as light source), product **3l** was isolated in 36% yield (10.6 mg) as yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (1H,s), 8.14 (1H,d, *J* =8.0 Hz), 7.73 (1H, d, d, *J* = 8.0 Hz),

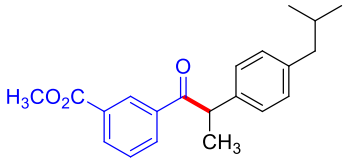
7.50 (1H, t, *J* = 8.0 Hz), 7.16-7.11 (2H, m), 7.10-7.05 (2H, m), 4.57 (1H, q, *J* =6.8 Hz), 2.43 (3H, d, *J* = 7.3 Hz), 1.87-1.75 (1H, m), 1.52 (3H, d, *J* =6.8 Hz), 0.86 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.3, 140.9, 137.6, 137.3, 135.5, 132.7, 132.4, 130.0, 129.4, 127.4, 118.0, 112.9, 48.0, 44.9, 30.1, 22.33, 22.32, 19.3; **HRMS (ESI)**: Found: *m/z* 292.1693. Calcd for $C_{20}H_{22}NO$ $(M+H)^+$ 292.1701.

1-(4-(allyloxy)phenyl)-2-(4-isobutylphenyl)propan-1-one (3m)



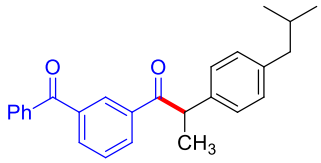
According to the general procedure **A** (0.1 mmol scale), product **3m** was isolated in 83% yield (26.7 mg) as yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.91 (2H,m), 7.22-7.13 (2H, m), 7.10-7.03 (2H, m), 6.90-6.83 (2H, m), 6.08-5.94 (1H, m), 5.39 (1H, dd, *J* = 17.3, 1.2 Hz), 5.29 (1H, dd, *J* = 10.5, 1.2 Hz), 4.62 (1H, q, *J* =6.8 Hz), 4.57-4.51 (2H, m), 2.40 (2H, d, *J* = 7.3 Hz), 1.87-1.75 (1H, m), 1.50 (3H, d, *J* =6.9 Hz), 0.87 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 162.1, 140.1, 139.0, 132.5, 131.0, 129.16, 129.59, 127.3, 118.1, 114.3, 68.8, 47.1, 45.0, 30.1, 22.36, 22.34, 19.5; **HRMS (ESI)**: Found: *m/z* 323.2010. Calcd for $C_{22}H_{27}O_2$ $(M+H)^+$ 323.2011.

methyl 3-(2-(4-isobutylphenyl)propanoyl)benzoate (3n)



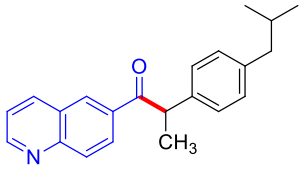
According to the general procedure **A** (0.1 mmol scale), product **3n** was isolated in 62% yield (20.2 mg) as colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (1H,s), 8.12 (2H,t, *J* =7.0 Hz), 7.46 (1H,t, *J* = 7.7 Hz), 7.22-7.14 (2H, m), 7.10-7.02 (2H, m), 4.68 (1H, q, *J* =6.7 Hz), 3.92 (3H, s), 2.39 (2H, d, *J* = 7.1 Hz), 1.87-1.74 (1H, m), 1.54 (3H, d, *J* =6.9 Hz), 0.85 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.7, 166.3, 140.5, 138.1, 136.8, 132.4, 132.9, 130.5, 129.9, 129.7, 128.7, 127.5,52.3, 47.6, 45.0, 30.1, 22.33, 22.31, 19.3; **HRMS (ESI)**: Found: *m/z* 325.1806.Calcd for $C_{21}H_{25}O_3$ $(M+H)^+$ 325.1804.

1-(3-benzoylphenyl)-2-(4-isobutylphenyl)propan-1-one (3o)



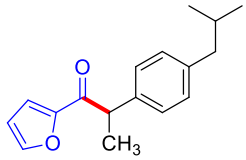
According to the general procedure **A** (0.1 mmol scale, two 440nm LEDs were used as light source), product **3o** was isolated in 55% yield (20.4 mg) as yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (1H,s), 8.18 (1H,d, *J* = 7.8 Hz), 7.94 (1H,d, *J* = 7.4 Hz), 7.75-7.67 (2H, m), 7.62 (1H,t, *J* = 7.4 Hz), 7.56-7.44 (3H, m), 7.17-7.10 (2H, m), 7.09-7.01 (2H, m), 4.64 (1H, q, *J* =6.6 Hz), 2.41 (2H, d, *J* = 7.2 Hz), 1.88-1.74 (1H, m), 1.52 (3H, d, *J* =6.8 Hz), 0.87 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.6, 195.7, 140.5, 138.1, 137.7, 137.0, 136.5, 133.8, 132.7, 132.4, 130.3, 130.0, 129.8, 128.8, 128.4, 127.5, 47.8, 45.0, 30.1, 22.35, 19.3; **HRMS (ESI)**: Found: *m/z* 371.2020. Calcd for $C_{26}H_{27}O_2$ $(M+H)^+$ 371.2011.

2-(4-isobutylphenyl)-1-(quinolin-6-yl)propan-1-one (3p)



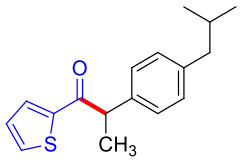
According to the general procedure **A** (0.1 mmol scale, two 427 nm blue LEDs were used), product **3p** was isolated in 54% yield (17.4 mg) as yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.96 (1H,dd, *J* =4.2, 1.7 Hz), 8.45 (1H,d,*J* =1.8 Hz), 8.24 (1H,dd, *J* =8.9, 1.9 Hz), 8.21 (1H,d, *J* = 8.4 Hz), 8.07 (1H,d, *J* = 8.9 Hz), 7.43 (1H,dd, *J* = 8.4, 4.3 Hz), 7.25-7.20 (2H, m), 7.10-7.04 (2H, m), 4.79 (1H, q, *J* =6.9 Hz), 2.39 (2H, d, *J* = 7.2 Hz), 1.85-1.74 (1H, m), 1.58 (3H, d, *J* =6.8 Hz), 0.85 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 152.4, 149.8, 140.5, 138.4, 137.6, 134.4, 130.1, 129.82, 129.80, 128.4, 127.4, 121.8, 47.8, 45.0, 30.1, 22.34, 22.32, 19.5; **HRMS (ESI)**: Found: *m/z* 318.1862. Calcd for $C_{22}H_{24}NO$ $(M+H)^+$ 318.1858.

1-(furan-2-yl)-2-(4-isobutylphenyl)propan-1-one (3q)



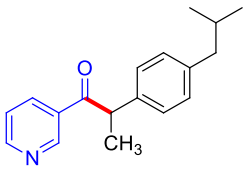
According to the general procedure **A** (0.2 mmol scale, two 427 nm blue LEDs were used), product **3q** was isolated in 59% yield (30.0 mg) as colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.50 (1H, m), 7.25-7.20 (2H,m), 7.15-7.11 (1H,m), 7.10-7.04 (2H,m), 6.45 (1H,d, *J* = 3.5, 1.7 Hz), 4.46 (1H, q, *J* =7.0 Hz), 2.41 (2H, d, *J* = 7.2 Hz), 1.88-1.75 (1H, m), 1.51 (3H, d, *J* =7.0 Hz), 0.88 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6, 152.2, 146.2, 140.4, 137.9, 129.4, 127.5, 117.8, 112.1, 47.5, 45.0, 30.1, 22.3, 18.3; **HRMS (ESI)**: Found: *m/z* 279.1354. Calcd for $C_{17}H_{20}O_2Na$ $(M+H)^+$ 279.1361.

2-(4-isobutylphenyl)-1-(thiophen-2-yl)propan-1-one (3r)



According to the general procedure **A** (0.2 mmol scale, two 427 nm blue LEDs were used), product **3r** was isolated in 78% yield (42.6 mg) as yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (1H, dd, *J* = 1.0, 3.8 Hz), 7.55 (1H, dd, *J* =5.0, 1.0 Hz), 7.26-7.20 (2H,m), 7.10-7.06 (2H,m), 7.04 (1H,dd, *J* =4.9, 3.9 Hz), 4.48 (1H, q, *J* =6.9 Hz), 2.42 (2H, d, *J* = 7.1 Hz), 1.88-1.76 (1H, m), 1.54 (3H, d, *J* =6.9 Hz), 0.88 (6H, d, *J* = 6.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.5, 143.8, 140.5, 138.4, 133.4, 132.3, 129.6, 128.0, 127.4, 48.9, 45.0, 30.1, 22.35, 22.34, 19.1; **HRMS (ESI)**: Found: *m/z* 295.1134. Calcd for $C_{17}H_{20}ONaS$ $(M+Na)^+$ 295.1133.

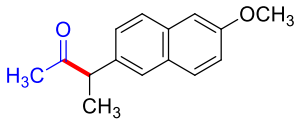
2-(4-isobutylphenyl)-1-(pyridin-3-yl)propan-1-one (3s)



According to the general procedure **A** (0.1 mmol scale, two 427 nm blue LEDs were used), product **3s** was isolated in 49% yield (13.2 mg) as yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.14 (1H, d, *J* = 1.8 Hz),8.67 (1H, dd, *J* =4.8, 1.7 Hz), 8.20 (1H, dt, *J* = 8.1, 2.0 Hz), 7.32 (1H, ddd, *J* = 8.1, 5.0, 0.7 Hz), 7.18-7.13 (2H,m), 7.09-7.04 (2H,m), 4.59 (1H, q, *J* =6.8Hz), 2.40 (2H, d, *J* = 7.18 Hz), 1.86-1.75 (1H, m), 1.53 (3H, d, *J*

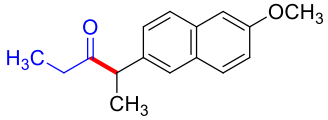
=6.8 Hz), 0.86 (6H, d, *J* = 6.6 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.2, 153.0, 150.2, 140.7, 137.7, 136.1, 131.8, 129.9, 127.5, 123.5, 48.2, 45.0, 30.1, 22.3, 19.1; **HRMS (ESI)**: Found: *m/z* 268.1700. Calcd for $C_{18}H_{22}NO$ $(M+H)^+$ 268.1701.

3-(6-methoxynaphthalen-2-yl)butan-2-one (3t)



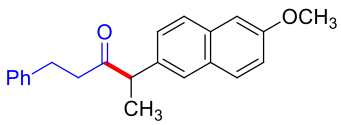
According to the general procedure **A** (0.2 mmol scale, 1.2 equiv Cs_2CO_3 was used; two 440 nm blue LEDs was used as light source), product **3t** was isolated in 76% yield (34.6 mg) as white solid; mp: 69-70 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (1H, d, *J* =5.6 Hz), 7.71 (1H, d, *J* = 5.9 Hz), 7.61 (1H, s), 7.29 (1H, dd, *J* = 8.5, 1.6 Hz), 7.17 (1H, dd, *J* = 8.9, 2.5 Hz), 7.13 (1H,d, *J* = 2.3 Hz), 3.92 (3H,s), 3.88 (1H, q, *J* =7.2Hz), 2.07 (3H,s), 1.47 (3H, d, *J* = 7.0 Hz); **^{13}C NMR** (125MHz, $CDCl_3$) δ 209.0, 157.7, 135.7, 133.7, 129.1, 129.08, 127.5, 126.4, 126.3, 119.1, 105.6, 55.3, 53.6, 28.4, 17.2; **HRMS (ESI)**: Found: *m/z* 229.1217. Calcd for $C_{15}H_{17}O_2$ $(M+H)^+$ 229.1229.

2-(6-methoxynaphthalen-2-yl)pentan-3-one (3u)



According to the general procedure **A** (0.2 mmol scale, 1.2 equiv Cs_2CO_3 was used; two 440 nm blue LEDs was used as light source), product **3u** was isolated in 64% yield (31.1 mg) as pink liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (1H, s), 7.69 (1H, s), 7.60 (1H, s), 7.29 (1H, dd, *J* = 8.6, 1.8 Hz), 7.16 (1H, dd, *J* = 8.9, 2.5 Hz), 7.12 (1H,d, *J* = 2.3 Hz), 3.92 (3H,s), 3.89 (1H, q, *J* =7.1Hz), 2.49-2.31 (2H,m), 1.47 (3H, d, *J* = 7.0 Hz), 0.97 (3H, t, *J* =7.3 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 211.7, 157.7, 136.0, 133.6, 129.1, 129.06, 127.4, 126.4, 126.3, 119.1, 105.6, 55.3, 52.6, 34.2, 17.5, 8.0; **HRMS (ESI)**: Found: *m/z* 243.1379. Calcd for $C_{16}H_{19}O_2$ $(M+H)^+$ 243.1385.

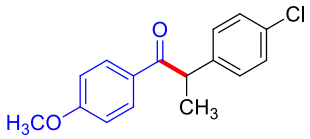
4-(6-methoxynaphthalen-2-yl)-1-phenylpentan-3-one (3v)



According to the general procedure **A** (0.1 mmol scale, 1.2 equiv Cs_2CO_3 was used; two 440 nm blue LEDs was used as light source), product **3v** was isolated in 74% yield

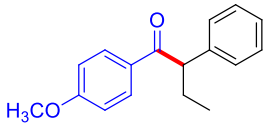
(23.4 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (1H, d, *J* = 6.4 Hz), 7.68 (1H, d, *J* = 6.8 Hz), 7.55 (1H, s), 7.26-7.10 (6H, m), 7.09-7.01 (2H, m), 3.93 (3H,s), 3.85 (1H, q, *J* =7.1 Hz), 2.91-2.64 (4H,m), 1.46 (3H, d, *J* =6.9 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 210.0, 157.7, 141.0, 135.5, 133.6, 129.2, 129.0, 128.3, 128.2, 127.5, 126.4, 126.3, 125.9, 119.1, 105.6, 55.3, 53.0, 42.5, 29.9, 17.3; **HRMS (ESI)**: Found: *m/z* 319.1702. Calcd for $C_{22}H_{23}O_2$ $(M+H)^+$ 319.1968.

2-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-1-one (3w)



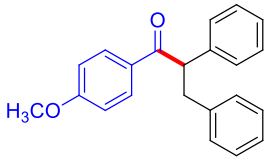
According to the general procedure **A** (0.2 mmol scale), product **3w** was isolated in 52% yield (28.6 mg) as yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.87 (2H, m), 7.26-7.18 (4H, m), 6.90-6.83 (2H, m), 4.63 (1H, q, *J* = 6.8 Hz), 3.82 (3H, s), 1.50 (3H, d, *J* = 6.9 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.4, 163.4, 140.3, 132.6, 131.0, 129.2, 129.1, 129.0, 113.7, 55.4, 46.7, 19.4; **HRMS (ESI)**: Found: *m/z* 297.0647. Calcd for $C_{16}H_{15}ONaCl$ $(M+Na)^+$ 297.0658.

1-(4-methoxyphenyl)-2-phenylbutan-1-one (3x)



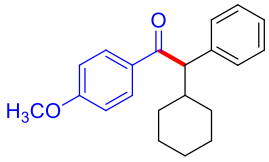
According to the general procedure **A** (0.2 mmol scale), product **3x** was isolated in 77% yield (39.2 mg) as white solid; mp: 45-46 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.92 (2H, m), 7.33-7.24 (4H, m), 7.21-7.15 (1H, m), 6.89-6.81 (2H, m), 4.40 (1H, t, *J* = 7.2 Hz), 3.80 (3H, s), 2.25-2.12 (1H, m), 1.91-1.77 (1H, m), 0.89 (3H, t, *J* = 7.4 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.6, 163.2, 140.1, 130.9, 130.0, 128.7, 128.1, 126.8, 113.6, 55.3, 55.0, 27.1, 12.3; **HRMS (ESI)**: Found: *m/z* 277.1209. Calcd for $C_{17}H_{18}ONa$ $(M+Na)^+$ 277.1204.

1-(4-methoxyphenyl)-2,3-diphenylpropan-1-one (3y)



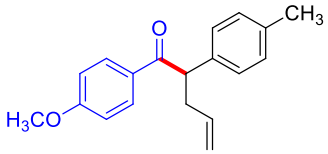
According to the general procedure **A** (0.1 mmol scale), product **3y** was isolated in 74% yield (23.4 mg) as white solid; mp: 100-101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.87 (2H, m), 7.29-7.23 (4H, m), 7.22-7.11 (4H, m), 7.11-7.06 (2H, m), 6.86-6.79 (2H, m), 4.78 (1H, t, *J* = 7.3 Hz), 3.80 (3H, s), 3.58 (1H, dd, *J* = 13.8, 7.5 Hz), 3.07 (1H, dd, *J* = 13.7, 7.0 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 163.2, 139.9, 139.5, 131.0, 129.7, 129.1, 128.8, 128.19, 128.16, 127.0, 126.0, 113.6, 55.5, 55.3, 40.1; **HRMS (ESI)**: Found: *m/z* 317.1548.Calcd for $C_{22}H_{21}O_2$ $(M+H)^+$ 317.1542.

2-cyclohexyl-1-(4-methoxyphenyl)-2-phenylethanone (3z)



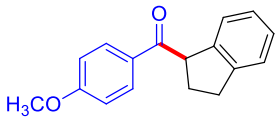
According to the general procedure **A** (0.1 mmol scale), product **3z** was isolated in 64% yield (19.8 mg) as white solid; mp: 96-97 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02-7.94 (2H, m), 7.37-7.31 (2H, m), 7.27-7.24 (2H, m), 7.21-7.15 (1H, m), 6.92-6.84 (2H, m), 4.26 (1H, d, *J* =10.3 Hz), 3.82 (3H, s), 2.36-2.21(1H, m), 1.88-1.77 (1H, m), 1.70-1.54(4H, m), 1.38-1.24 (2H, m), 1.23-1.07 (2H, m), 1.02-0.9 (1H, m), 0.9-0.76 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.2, 163.3, 138.4, 130.8, 130.78, 130.75, 128.8, 128.6, 126.8, 113.7, 59.6, 55.4, 41.1, 32.6, 30.8, 26.5, 26.2, 26.1; **HRMS (ESI)**: Found: *m/z* 309.1856. Calcd for $C_{21}H_{25}O_2$ $(M+H)^+$ 309.1855.

1-(4-methoxyphenyl)-2-(p-tolyl)pent-4-en-1-one (3aa)



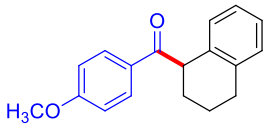
According to the general procedure **A** (0.2 mmol scale), product **3aa** was isolated in 77% yield (44.3 mg) as yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.92 (2H, m), 7.23-7.16 (2H, m), 7.14-7.06 (2H, m), 6.89-6.81 (2H, m), 5.84-5.67 (1H, m), 5.04 (1H, d, *J* = 17.3 Hz), 4.97 (1H, d, *J* = 10.3 Hz), 4.56 (1H, t, *J* = 7.3 Hz), 3.81 (3H, s), 2.99-2.87 (1H, m), 2.60-2.49 (1H, m), 2.28 (3H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 163.2, 136.5, 136.4, 136.2, 130.9, 129.6, 129.5, 127.9, 116.3, 113.6, 55.3, 52.7, 38.1, 20.9; **HRMS (ESI)**: Found: *m/z* 289.1210. Calcd for $C_{18}H_{18}O_2Na$ $(M+Na)^+$ 289.1204.

(2,3-dihydro-1H-inden-1-yl)(4-methoxyphenyl)methanone (3ab)



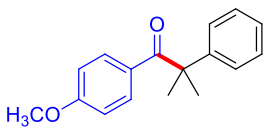
According to the general procedure **A** (0.2 mmol scale, two 427 nm blue LEDs were used), product **3ab** was isolated in 41% yield (20.9 mg) as white solid, mp: 65-66 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10-8.03 (2H, m), 7.30-7.26 (1H, m), 7.19 (1H, t, *J* = 6.9 Hz), 7.10 (1H, t, *J* = 6.9 Hz), 7.06 (1H, d, *J* = 7.4 Hz), 7.03-6.97 (2H, m), 5.01 (1H, t, *J* = 7.7 Hz), 3.90 (3H, s), 3.22-3.11 (1H, m), 3.06-2.95 (1H, m), 2.56-2.36 (2H, m); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.0, 163.6, 144.6, 141.9, 131.2, 130.0, 127.2, 126.2, 124.9, 124.8, 113.9, 55.5, 52.1, 32.0, 29.6; **HRMS (ESI)**: Found: *m/z* 253.1228. Calcd for $C_{17}H_{17}O_2$ $(M+H)^+$ 253.1229.

(4-methoxyphenyl)(1,2,3,4-tetrahydronaphthalen-1-yl)methanone (3ac)



According to the general procedure **A** (0.2 mmol scale), product **3ac** was isolated in 66% yield (26.6 mg) as colorless oil; **^{1}H NMR** (400MHz, $CDCl_3$) δ 8.05-7.96 (2H, m), 7.19-7.12 (2H, m), 7.11-7.04 (1H, m), 7.00-6.94 (2H, m), 6.93-6.86 (1H, m), 4.79 (1H, t, *J* = 6.9 Hz), 3.89 (3H, s), 2.97-2.87 (1H, m), 2.87-2.76 (1H, m), 2.23-2.13 (1H, m), 2.12-2.02 (1H, m), 2.02-1.91 (1H, m), 1.84-1.73 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.2, 163.4, 137.6, 135.1, 131.1, 129.5, 129.4, 129.3, 126.5, 125.8, 113.8, 55.5, 47.1, 29.3, 27.8, 20.8; **HRMS (ESI)**: Found: *m/z* 289.1201. Calcd for $C_{18}H_{18}O_2Na$ $(M+Na)^+$ 289.1204.

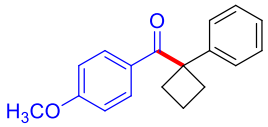
1-(4-methoxyphenyl)-2-methyl-2-phenylpropan-1-one (3ad)



According to the general procedure **A** (0.2 mmol scale, two 427 nm blue LEDs were used), product **3ad** was isolated in 50% yield (25.4 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.50 (2H, m), 7.37-7.20 (5H, m), 6.74-6.66 (2H, m), 3.75 (3H, s), 1.59 (6H, s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 162.2, 146.0, 132.3, 128.9, 128.5,

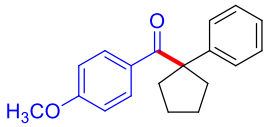
126.6.0, 125.6, 113.1, 55.3, 51.2, 28.1; **HRMS (ESI)**: Found: *m/z* 277.1204. Calcd for $C_{17}H_{18}O_2Na$ $(M+Na)^+$ 277.1204.

(4-methoxyphenyl)(1-phenylcyclobutyl)methanone (3ae)



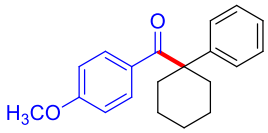
According to the general procedure **A** (0.2 mmol scale, two 427 nm blue LEDs were used), product **3ae** was isolated in 81% yield (43.1 mg) as white solid; **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.77-7.68 (2H, m), 7.45-7.38 (2H, m), 7.37-7.30 (2H, m), 7.20 (1H, t, *J* = 7.3 Hz), 6.80-6.73 (2H, m), 3.77 (3H, s), 2.99-2.87 (2H, m), 2.60-2.50 (2H, m), 2.14-2.00 (1H, m), 1.97-1.84 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.8, 162.6, 143.6, 132.0, 128.9, 127.0, 126.4, 125.5, 113.3, 56.9, 55.3, 32.3, 16.0; **HRMS (ESI)**: Found: *m/z* 289.1195. Calcd for $C_{18}H_{18}O_2Na$ $(M+Na)^+$ 289.1204.

(4-methoxyphenyl)(1-phenylcyclopentyl)methanone (3af)



According to the general procedure **A** (0.2 mmol scale, two 440 nm blue LEDs were used), product **3af** was isolated in 48% yield (23.0 mg) as white solid, mp: 85-86 °C; **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.69-7.63 (2H, m), 7.33-7.25 (4H, m), 7.23-7.17 (1H, m), 6.76-6.69 (2H, m), 3.77 (3H, s), 2.57-2.45 (2H, m), 2.14-2.03 (2H, m), 1.80-1.63 (4H, m); **^{13}C NMR** (100MHz, $CDCl_3$) δ 200.4, 162.3, 145.2, 132.3, 128.8, 128.6, 126.3, 125.9, 113.1, 63.1, 55.3, 37.7, 24.8; **HRMS (ESI)**: Found: *m/z* 303.1364. Calcd for $C_{19}H_{20}O_2Na$ $(M+Na)^+$ 303.1361.

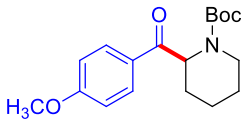
(4-methoxyphenyl)(1-phenylcyclohexyl)methanone (3ag)



According to the general procedure **A** (0.1 mmol scale, two 427 nm blue LEDs were used), product **3ag** was isolated in 65% yield (19.1 mg) as white solid, mp: 88-89 °C; **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.44-7.33 (6H, m), 7.28-7.23 (1H, m), 6.76-6.66 (2H,

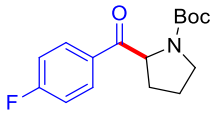
m), 3.76 (3H, s), 2.52 (2H, d, J = 13.3 Hz), 1.85-1.73 (2H, m), 1.69-1.58 (3H, m), 1.53-1.39 (2H, m), 1.34-1.26 (1H, m); **^{13}C NMR** (100MHz, $CDCl_3$) δ 203.0, 161.8, 144.9, 131.2, 130.5, 129.0, 126.7, 126.1, 113.0, 55.3, 55.2, 36.4, 25.9, 23.3; **HRMS (ESI)**: Found: *m/z* 295.1696. Calcd for $C_{20}H_{23}O_2$ $(M+H)^+$ 295.1698.

tert-butyl 2-(4-methoxybenzoyl)piperidine-1-carboxylate (3ah)



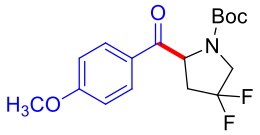
According to the general procedure **A** (0.1 mmol scale), product **3ah** was isolated in 55% yield (17.4 mg) as white solid, mp: 85-86 °C; The spectra data of **3ah** were consistent with the previous reported literature[3].

tert-butyl 2-(4-fluorobenzoyl)pyrrolidine-1-carboxylate (3ai)



According to the general procedure **A** (0.1 mmol scale), product **3ai** was isolated in 50% yield (14.6 mg) as yellow liquid; Mixture of rotamers (ratio: 45/55); **^{1}H NMR**(500 MHz, $CDCl_3$) δ 8.05-7.95 (2H, m), 7.18-7.08 (2H, m), 5.31-5.25 (0.43H, m), 5.17-5.10 (0.55H, m),3.71-3.64 (0.55H, m), 3.64-3.59 (0.43H, m), 3.58-3.51 (0.55H, m), 3.51-3.43 (0.43H, m), 2.38-2.21 (1H, m), 2.02-1.82 (3H, m), 1.46 (3.87H, s), 1.25 (4.95H, s); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.4, 197.0, 165.8 (d, J = 255.9 Hz), 154.5, 153.7, 131.6 (d, J = 3.0 Hz), 131.5 (d, J = 3.0 Hz), 131.2 (d, J = 9.2 Hz), 130.8 (d, J = 9.2 Hz), 115.9 (d, J = 21.5 Hz), 115.7 (d, J = 21.5 Hz), 79.8, 79.7, 61.2, 60.9, 46.8, 46.6, 30.8, 29.8, 28.4, 28.1, 24.2, 23.6; **^{19}F NMR** (376MHz, $CDCl_3$) δ -104.7 (m), -104.9 (m); **HRMS (ESI)**: Found: *m/z* 316.1237. Calcd for $C_{16}H_{20}NO_3NaF$ $(M+Na)^+$ 316.1325.

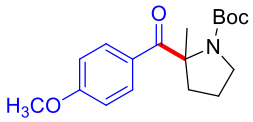
tert-butyl 4,4-difluoro-2-(4-methoxybenzoyl)pyrrolidine-1-carboxylate (3aj)



According to the general procedure **A** (0.1 mmol scale, two 427 nm blue LEDs were used), product **3aj** was isolated in 63% yield (21.5 mg) as yellow oil; Mixture of rotamers (ratio: 48/52); **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.93 (2H, dd, J = 8.4, 6.4 Hz),

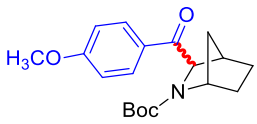
6.95 (2H, dd, *J* = 10.7, 9.0 Hz), 5.46 (0.48H, dd, *J* = 9.4, 5.7 Hz), 5.35 (0.52H, dd, *J* = 8.8, 7.0 Hz), 4.06-3.76 (5H, m), 2.88-2.69 (1H, m), 2.46-2.26 (1H, m), 1.46 (4.32H, s), 1.26 (4.68H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 194.9, 194.4, 164.1, 164.0, 153.8, 153.2, 130.9, 130.6, 127.4, 127.3, 126.8 (t, *J* = 249.6 Hz), 125.9 (t, *J* = 249.5 Hz), 114.1, 114.0, 81.0, 58.5, 58.4, 55.5, 53.9 (t, *J* = 32.5 Hz), 53.3 (t, *J* = 32.9 Hz), 39.1 (t, *J* = 26.1 Hz), 53.3 (t, *J* = 25.5 Hz), 28.3, 28.0; **^{19}F NMR** (376MHz, $CDCl_3$) δ -95.5 (m), -96.2 (m), -96.3 (m), -99.2 (m), -99.8 (m), -101.6 (m), -102.3 (m); **HRMS (ESI)**: Found: *m/z* 342.1515. Calcd for $C_{17}H_{22}NO_4F_2$ $(M+H)^+$ 342.1517.

tert-butyl 2-(4-methoxybenzoyl)-2-methylpyrrolidine-1-carboxylate (3ak)



According to the general procedure **A** (0.1 mmol scale, two 427 nm blue LEDs were used), product **3ak** was isolated in 56% yield (17.8 mg) as yellow solid, mp: 87-88 °C; Mixture of rotamers (ratio: 1/5); **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.91-7.78 (2H, m), 6.95-6.80 (2H, m), 3.84 (3H, s), 3.79-3.60 (2H, m), 2.50-2.35 (1H, m), 2.13-2.07 (1H, m), 1.95-1.85 (1H, m), 1.78-1.64 (1H, m), 1.54 (2.5H, s), 1.43 (0.5H, s), 1.26 (1.5H, s), 1.07 (7.5H, s); **^{13}C NMR**(100 MHz, $CDCl_3$) δ 198.9, 162.6, 153.1, 130.7, 130.4, 127.5, 113.5, 113.1, 80.3, 79.5, 69.5, 55.4, 47.1, 46.9, 38.6, 37.7, 28.4, 28.3, 27.7, 22.8, 22.6; **HRMS (ESI)**: Found: *m/z* 320.1864. Calcd for $C_{18}H_{26}NO_4$ $(M+H)^+$ 320.1862.

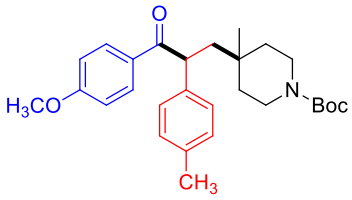
(1R,4S)-tert-butyl3-(4-methoxybenzoyl)-2-azabicyclo[2.2.1]heptane-2-carboxylate (3al)



According to the general procedure **A** (0.1 mmol scale, two 427 nm blue LEDs were used), product **3al** was isolated in 60% yield (19.7 mg) as yellow solid, mp: 172-173 °C; dr = 1/1; **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.99-7.95 (2H, m), 7.95-7.92 (2H, m), 6.97-6.93 (2H, m), 6.93-6.89 (2H, m), 4.73 (1H, s), 4.64 (1H, s), 4.43 (1H, s), 4.29 (1H, s), 3.90-3.80 (7H, m), 2.67-2.58 (2H, m), 1.95-1.88 (2H, m), 1.84-1.75 (2H, m), 1.72-1.63 (3H, m), 1.46 (9H, s), 1.27 (9H, s), 1.23-1.16 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.4, 194.0, 163.47, 163.45, 154.2, 153.0, 130.7, 130.3, 128.5, 128.2, 113.83 (s), 113.7,

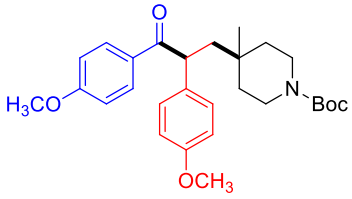
79.5, 79.5, 66.6, 66.4, 57.2, 56.0, 55.4, 55.4, 42.9, 42.3, 34.8, 34.1, 30.6, 30.6, 28.5, 28.3, 28.2, 28.1; **HRMS (ESI)**: Found: *m/z* 332.1872. Calcd for $C_{19}H_{26}NO_4$ $(M+H)^+$ 332.1862.

t-butyl4-(3-(4-methoxyphenyl)-3-oxo-2-(p-tolyl)propyl)-4-methylpiperidine-1-carboxylate (5a)



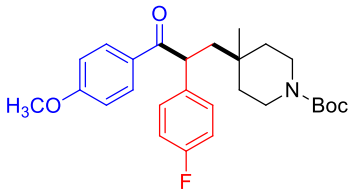
According to the general procedure **C** (0.1 mmol scale), product **5a** was isolated in 90% yield (40.6 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.95 (2H, m), 7.21-7.15 (2H, m), 7.10-7.04 (2H, m), 6.93-6.84 (2H, m), 4.70-4.60 (1H, m), 3.82 (3H, s), 3.62-3.46 (2H, m), 3.21-3.05 (2H, m), 2.65 (1H, dd, *J* = 14.1, 8.7 Hz), 2.26 (3H, s), 1.63-1.54 (1H, m), 1.42 (9H, s), 1.36-1.13 (4H, m), 0.92 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.1, 163.3, 154.9, 138.2, 136.4, 130.9, 129.6, 127.8, 113.8, 79.2, 55.4, 47.6, 45.5, 37.0, 32.2, 28.4, 23.7, 20.9; **HRMS (ESI)**: Found: *m/z* 452.2796. Calcd for $C_{28}H_{38}NO_4$ $(M+H)^+$ 452.2801.

t-butyl4-(2,3-bis(4-methoxyphenyl)-3-oxopropyl)-4-methylpiperidine-1-carboxylate (5b)



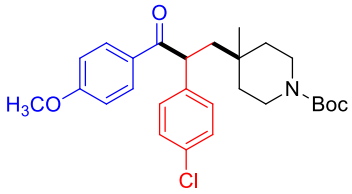
According to the general procedure **C** (0.1 mmol scale), product **5b** was isolated in 77% yield (36.1 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.92 (2H, m), 7.24-7.18 (2H, m), 6.93-6.85 (2H, m), 6.84-6.75 (2H, m), 4.69-4.60 (1H, m), 3.82 (3H, s), 3.73 (3H, s), 3.61-3.45 (2H, m), 3.20-3.06 (2H, m), 2.61 (1H, dd, *J* = 14.0, 8.5 Hz), 1.61 (1H, dd, *J* = 14.2, 2.9 Hz), 1.42 (9H,s), 1.36-1.14 (4H, m), 0.92 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.2, 163.3, 158.4, 154.9, 133.2, 130.8, 129.6, 129.0, 114.3, 113.8, 79.2, 55.4, 55.2, 47.1, 45.5, 37.0, 32.1, 28.4, 23.7; **HRMS (ESI)**: Found: *m/z* 468.2744. Calcd for $C_{28}H_{38}NO_5$ $(M+H)^+$ 468.2750.

***t*-butyl4-(2-(4-fluorophenyl)-3-(4-methoxyphenyl)-3-oxopropyl)-4-methylpiperidine-1-carboxylate (5c)**



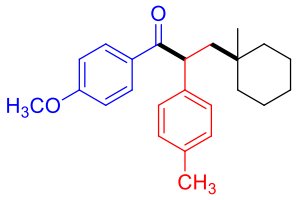
According to the general procedure **C** (0.1 mmol scale), product **5c** was isolated in 85% yield (38.8 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.93 (2H, m), 7.29-7.23 (2H, m), 6.98-6.92 (2H, m), 6.91-6.88 (2H, m), 4.69 (1H, dd, *J* = 8.5, 3.3 Hz), 3.82 (3H, s), 3.63-3.46 (2H, m), 3.17-3.04 (2H, m), 2.62 (1H, dd, *J* = 14.1, 8.6 Hz), 1.59 (1H, dd, *J* = 14.0, 3.2 Hz), 1.42 (9H, s), 1.37-1.13 (4H, m), 0.92 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.0, 163.5, 161.7 (d, *J* = 245.7 Hz), 154.9, 136.9 (d, *J* = 3.2 Hz), 130.8, 129.5 (d, *J* = 7.9 Hz), 129.4, 115.8 (d, *J* = 21.3 Hz), 113.9, 79.2, 55.4, 47.0, 45.7, 37.1, 32.2, 28.4, 23.6; **^{19}F NMR** (376MHz, $CDCl_3$) δ -115.8 (m); **HRMS (ESI)**: Found: *m/z* 456.2541. Calcd for $C_{27}H_{35}NO_4F$ $(M+H)^+$ 456.2550.

t-butyl4-(2-(4-chlorophenyl)-3-(4-methoxyphenyl)-3-oxopropyl)-4-methylpiperidine-1-carboxylate (5d)



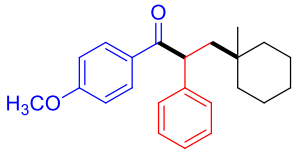
According to the general procedure **C** (0.1 mmol scale), product **5d** was isolated in 92% yield (43.2 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.92 (2H,m), 7.23 (4H,s), 6.92-6.86 (2H,m), 4.67 (1H, dd, *J* = 8.5, 3.4 Hz), 3.83 (3H, s), 3.63-3.46 (2H,m), 3.17-3.04 (2H,m), 2.63 (1H, dd, *J* = 14.1, 8.6 Hz), 1.58 (1H, dd, *J* = 14.2, 3.2 Hz), 1.42 (9H, s), 1.36-1.12 (4H, m), 0.92 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 197.7, 163.5, 154.9, 139.7, 132.7, 130.8, 129.3, 129.3, 129.1, 113.9, 79.2, 55.4, 47.2, 45.6, 37.0, 32.2, 28.4, 23.6; **HRMS (ESI)**: Found: *m/z* 472.2259. Calcd for $C_{27}H_{35}NO_4Cl$ $(M+H)^+$ 472.2255.

1-(4-methoxyphenyl)-3-(1-methylcyclohexyl)-2-(p-tolyl)propan-1-one (5e)



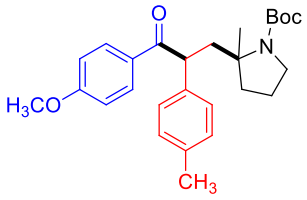
According to the general procedure **C** (0.1 mmol scale), product **5e** was isolated in 64% yield (21.8 mg) as yellow solid, 82-83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04-7.96 (2H, m), 7.23-7.18 (2H, m), 7.09-7.03 (2H, m), 6.92-6.85 (2H, m), 4.68 (1H, dd, *J* = 8.8, 3.0 Hz), 3.82 (3H,s), 2.62 (1H, dd, *J* = 14.1, 8.8 Hz), 2.27 (3H,s), 1.58 (1H, dd, *J* = 14.1, 3.0 Hz), 1.46-1.32 (5H, m), 1.29-1.15 (5H, m), 0.85 (3H,s); **^{13}C NMR** (125MHz, $CDCl_3$) δ 198.6, 163.2, 138.8, 136.1, 130.8, 129.9, 129.5, 127.9, 113.7, 55.4, 47.7, 46.4, 38.09, 38.06, 33.6, 26.4, 21.95, 21.94, 20.9; **HRMS (ESI)**: Found: *m/z* 373.2130. Calcd for $C_{24}H_{30}O_2Na$ $(M+Na)^+$ 373.2143.

1-(4-methoxyphenyl)-3-(1-methylcyclohexyl)-2-phenylpropan-1-one (5f)



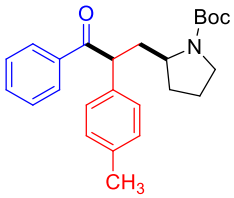
According to the general procedure **C** (0.1 mmol scale), product **5f** was isolated in 89% yield (29.9 mg) as colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04-7.96 (2H, m), 7.35-7.29 (2H, m), 7.28-7.22 (2H, m), 7.15 (1H, t, *J* = 7.2 Hz), 6.92-6.84 (2H, m), 4.71 (1H, dd, *J* = 8.7, 2.9 Hz), 3.82 (3H, s), 2.62 (1H, dd, *J* = 14.1, 8.8 Hz), 1.60 (1H, dd, *J* = 14.1, 2.9 Hz), 1.52-1.08 (11H, m), 0.85 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.5, 163.2, 141.8, 130.8, 129.9, 128.8, 128.0, 126.5, 113.7, 55.4, 48.1, 46.4, 38.1, 38.0, 33.6, 26.3, 24.9, 21.94, 21.93; **HRMS (ESI)**: Found: *m/z* 359.1996. Calcd for $C_{23}H_{28}O_2Na$ $(M+Na)^+$ 359.1987.

tert-butyl2-(3-(4-methoxyphenyl)-3-oxo-2-(p-tolyl)propyl)-2-methylpyrrolidine-1-carboxylate (5g)



According to the general procedure **C** (0.1 mmol scale), product **5g** was isolated in 80% yield (34.9 mg) as yellow oil; Mixture of diasteromers and rotamers (the ratio of the isomers cannot be identified from ^{1}H NMR). **^{1}H NMR** (500 MHz, $CDCl_3$)δ 8.02-7.91 (2H, m), 7.25-7.18 (1H, m), 7.17-7.11 (1H, m), 7.09-6.99 (2H, m), 6.90-6.80 (2H, m), 4.82-4.46 (1H, m), 3.80 (3H, s), 3.64-3.13 (2H, m), 3.07-2.72 (1H, m), 2.25 (3H, s), 1.84-1.72 (1H, m), 1.70-1.59 (2H, m), 1.56-1.31 (12H, m), 1.30-1.22 (2H, m); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.7, 198.5, 198.4, 163.4, 163.3, 163.2, 163.1, 154.6, 154.4, 153.7, 153.5, 138.2, 137.8, 137.7, 136.5, 136.3, 136.1, 131.0, 130.9, 129.9, 129.6, 129.6, 129.5, 128.5, 128.3, 128.0, 113.8, 113.7, 113.6, 79.6, 79.6, 78.5, 78.5, 62.9, 62.6, 55.4, 49.0, 48.7, 48.6, 48.5, 48.4, 48.3, 42.4, 42.1, 39.5, 39.4, 39.2, 28.6, 28.5, 28.5, 26.7, 26.6, 25.5, 25.0, 21.8, 21.7, 21.6, 21.4, 20.99, 20.9; **HRMS (ESI)**: Found: *m/z* 438.2645. Calcd for $C_{27}H_{36}NO_4$ $(M+H)^+$ 438.2644.

tert-butyl 2-(3-oxo-3-phenyl-2-(p-tolyl)propyl)pyrrolidine-1-carboxylate (5h)



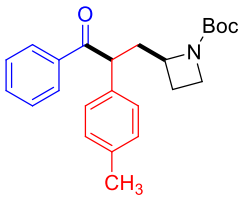
According to the general procedure **C** (2 mmol scale), product **5h** was isolated in 73% yield (537.7 mg), dr = 1.4/1.

Diasteromer1: Colorless oil; Mixture of rotamers (ratio; 40/60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.89 (2H, m), 7.49-7.29 (3H, m), 7.21 (2H,s,br), 7.12-7.02 (2H, m), 4.95 (0.6H,s,br), 4.60 (0.4 H, s, br), 4.07 (0.6H, s,br), 3.79 (0.4 H, s, br), 3.46-3.11 (2H, m), 2.83-2.55 (1H, m), 2.26 (3H, s), 2.04-1.66 (4H, m), 1.49 (4H, s, br), 1.27 (6H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.2, 155.0, 137.2, 137.1, 136.6, 136.4, 132.5, 129.6, 128.9, 128.3, 128.1, 79.5, 78.8, 56.1, 50.5, 46.0, 39.6, 39.2, 31.2, 28.5, 28.3, 23.6, 23.0, 21.0; **HRMS (ESI)**: Found: *m/z* 394.2386. Calcd for $C_{25}H_{32}NO_3$ $(M+H)^+$ 394.2382.

Diasteromer2: White solid, mp: 93-94 °C; Mixture of rotamers (ratio; 40/60); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03-7.89 (2H, m), 7.50-7.30 (3H, m), 7.20-7.12 (2H, m), 7.12-7.02 (2H, m), 4.70 (0.4H,s,br), 4.51 (0.6H,s,br), 3.92 (0.4H, s, br), 3.68 (0.6H, s, br), 3.54-3.17 (2H, m), 2.26 (3H, s), 2.13-1.62 (6H, m), 1.49-1.16 (9H, m); **^{13}C NMR**

(100MHz, $CDCl_3$) δ 199.4, 199.0, 154.8, 137.0, 136.7, 136.5, 136.0, 132.8, 132.4, 129.7, 128.8, 128.4, 128.1, 79.4, 78.8, 55.6, 50.5, 46.3, 45.7, 39.1, 37.8, 30.7, 28.4, 23.7, 22.8, 21.0; **HRMS (ESI)**: Found: *m/z* 394.2377. Calcd for $C_{25}H_{32}NO_3$ $(M+H)^+$ 394.2382.

tert-butyl 2-(3-oxo-3-phenyl-2-(p-tolyl)propyl)azetidine-1-carboxylate (5i)

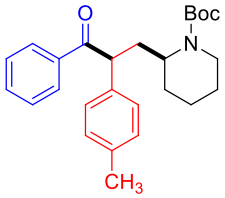


According to the general procedure **C** (0.3 mmol scale), product **5i** was isolated in 50% yield (56.9 mg), dr = 1.4/1;

Diasteromer 1: Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01-7.92 (2H, m), 7.45 (1H, t, *J* = 7.3 Hz), 7.41-7.33 (2H, m), 7.31-7.22 (2H, m), 7.12-7.05 (2H, m), 4.89 (1H, s, br), 4.29-4.18 (1H, m), 3.79-3.68 (2H, m), 2.77 (1H, s, br), 2.27 (3H, s), 2.19-1.97 (2H, m), 1.69-1.58 (1H, m), 1.44 (9H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.6, 156.8, 136.6, 136.5, 136.4, 132.7, 129.6, 128.8, 128.4, 128.3, 79.2, 60.4, 49.5, 46.6, 40.2, 28.4, 22.5, 21.0; **HRMS (ESI)**: Found: *m/z* 380.2231. Calcd for $C_{24}H_{30}NO_3$ $(M+H)^+$ 380.2226.

Diasteromer2: Colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$)δ 7.99-7.92 (2H, m), 7.45 (1H, t, *J* = 7.3 Hz), 7.39-7.33 (2H, m), 7.19-7.14 (2H, m), 7.11-7.05 (2H, m), 4.71 (1H, s, br), 4.10 (1H, s, br), 3.78 (2H, t, *J* = 7.6 Hz), 2.55-2.32 (2H, m), 2.31-2.21 (4H, m), 1.90-1.80 (1H, m), 1.38 (9H, s); **^{13}C NMR** (125MHz, $CDCl_3$) δ 199.3, 156.8, 136.7, 136.4, 132.7, 129.7, 128.8, 128.4, 128.0, 79.2, 60.6, 49.5, 46.4, 39.9, 28.3, 22.4, 21.0; **HRMS (ESI)**: Found: *m/z* 380.2231. Calcd for $C_{24}H_{30}NO_3$ $(M+H)^+$ 380.2226.

tert-butyl 2-(3-oxo-3-phenyl-2-(p-tolyl)propyl)piperidine-1-carboxylate (5j)

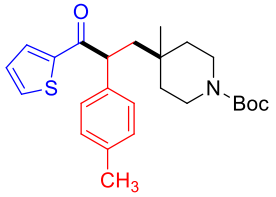


According to the general procedure **C** (0.3 mmol scale), product **5j** was isolated in 64% yield (77.8 mg), dr = 1.9/1;

Diasteromer 1: Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.89 (2H, m), 7.44 (1H, t, *J* = 7.3 Hz), 7.39-7.32 (2H, m), 7.25-7.19 (2H, m), 7.11-7.04 (2H, m), 4.62(1H, s, br), 4.37 (1H, s, br), 3.83 (1H, s, br), 3.16-2.64 (2H, m), 2.26 (3H, s), 1.72-1.51 (5H, m), 1.47-1.15 (11H, m); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.2, 155.2, 136.7, 136.6, 132.6, 129.6, 128.8, 128.4, 128.1, 79.1, 50.6, 49.8, 39.2, 34.8, 29.7, 28.2, 25.6, 21.0, 19.4; **HRMS (ESI)**: Found: *m/z* 408.2544. Calcd for $C_{26}H_{34}NO_3$ $(M+H)^+$ 408.2539.

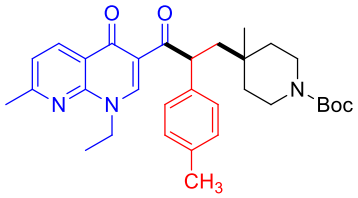
Diasteromer 2: Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02-7.90 (2H, m), 7.49-7.39 (1H, m), 7.38-7.29 (2H, m), 7.18-7.03 (4H, m), 4.46 (1H, dd, *J* = 10.3, 2.9 Hz), 4.28 (1H, s, br), 4.13 (1H, s, br), 2.78 (1H, t, *J* = 12.7 Hz), 2.44-2.30 (1H, m), 2.26 (3H, s), 2.14-2.02 (1H, m), 1.66-1.50 (5H, m), 1.44-0.95 (10H, m); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.5, 155.1, 137.2, 136.6, 132.7, 129.8, 128.9, 128.3, 127.8, 79.3, 49.5, 38.1, 34.0, 29.4, 28.0, 25.6, 20.9, 19.0; **HRMS (ESI)**: Found: *m/z* 408.2538. Calcd for $C_{26}H_{34}NO_3$ $(M+H)^+$ 408.2539.

tert-butyl4-methyl-4-(3-oxo-3-(thiophen-2-yl)-2-(p-tolyl)propyl)piperidine-1-carboxylate (5k)



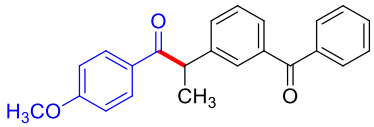
According to the general procedure **C** (0.1 mmol scale), product **5k** was isolated in 67% yield (28.5 mg) as white solid, mp:158-159 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (1H, dd, *J* = 3.8, 0.9 Hz), 7.57 (1H, dd, *J* = 4.9, 1.0 Hz), 7.24-7.19 (2H, m), 7.11-7.06 (3H, m), 4.49 (1H, dd, *J* = 8.5, 3.5 Hz), 3.63-3.46 (2H,m), 3.18-3.07 (2H,m), 2.61 (1H, dd, *J* = 14.2, 8.6 Hz), 2.28 (3H,s), 1.63 (1H, dd, *J* = 14.2, 3.4 Hz), 1.43 (9H, s), 1.36-1.29 (2H, m), 1.28-1.17 (2H,m), 0.94 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 192.5, 154.9, 143.8, 137.8, 136.7, 133.7, 132.0, 129.6, 128.2, 127.9, 79.2, 49.9, 45.2, 37.0, 32.2, 28.4, 23.6, 21.0; **HRMS (ESI)**: Found: *m/z* 428.2264. Calcd for $C_{25}H_{34}NO_3S$ $(M+H)^+$ 428.2259.

tert-butyl4-(3-(1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridin-3-yl)-3-oxo-2-(p-tolyl)propyl)-4-methylpiperidine-1-carboxylate (5l)



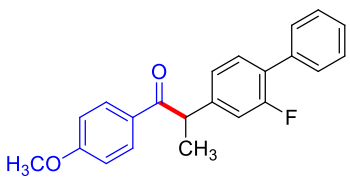
According to the general procedure **C** (0.1 mmol scale), product **5l** was isolated in 86% yield (45.8 mg) as yellowoil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (1H, d, *J* = 8.1 Hz), 8.52 (1H, s), 7.29 (2H, d, *J* = 7.9 Hz), 7.23 (1H, d, *J* = 8.1 Hz), 7.03 (2H, d, *J* = 7.9 Hz), 5.92 (1H, dd, *J* = 8.9, 2.9 Hz), 4.49-4.32 (2H, m), 3.61-3.46 (2H, m), 3.21-3.08 (2H, m), 2.73-2.60 (4H, m), 2.24 (3H, s), 1.59 (1H, dd, *J* = 13.9, 2.9 Hz), 1.47-1.38 (14H, m), 1.32-1.21 (2H, m), 0.99 (3H, s); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.8, 175.7, 162.7, 154.9, 149.0, 148.6, 138.6, 136.8, 136.2, 129.2, 128.5, 122.0, 121.1, 118.2, 79.0, 49.2, 46.7, 45.1, 37.1, 37.1, 32.3, 28.4, 25.0, 23.7, 21.0, 15.1; **HRMS (ESI)**: Found: *m/z* 532.3171. Calcd for $C_{32}H_{42}N_3O_4$ $(M+H)^+$ 532.3175.

2-(3-benzoylphenyl)-1-(4-methoxyphenyl)propan-1-one (6a)



According to the general procedure **B** (0.1 mmol scale), product **6a** was isolated in 62% yield (21.3 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.91 (2H,m), 7.78-7.69 (3H,m), 7.64-7.55 (2H,m), 7.54-7.50 (1H,m), 7.45 (2H, t, *J* = 7.7 Hz), 7.40 (1H, t, *J* = 7.7 Hz), 6.92-6.85 (2H,m), 4.74 (1H, q, *J* = 6.9 Hz), 3.83 (3H, s), 1.55 (3H, d, *J* = 6.9 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.4, 196.5, 163.4, 142.1, 138.1, 137.4, 132.5, 131.6, 131.05 (s), 130.0, 129.5, 129.1, 128.8, 128.7, 128.3, 113.8, 55.4), 47.1, 19.4; **HRMS (ESI)**: Found: *m/z* 367.1320. Calcd for $C_{23}H_{20}O_3Na$ $(M+Na)^+$ 367.1310.

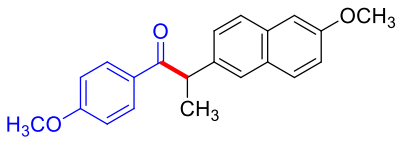
2-(2-fluoro-[1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)propan-1-one (6b)



According to the general procedure **B** (0.1 mmol scale), product **6b** was isolated in 56%

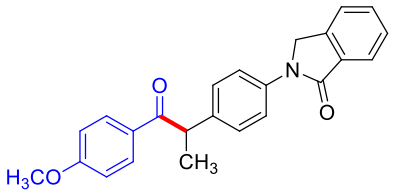
yield (18.7 mg) as colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ8.02-7.94 (2H,m), 7.54-7.47 (2H,m), 7.44-7.39 (2H,m), 7.38-7.32 (2H,m), 7.17-7.08 (2H,m), 6.94-6.87 (2H,m), 4.70 (1H, q, *J* = 6.9 Hz), 3.84 (3H,s), 1.56 (3H, d, *J* = 6.9 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.2, 163.4, 159.9 (d, *J* =247.1 Hz), 143.2 (d, *J* = 7.5 Hz), 135.4 (d, *J* = 1.1 Hz), 131.1, 131.0, 129.2, 128.9 (d, *J* = 2.8 Hz), 128.4, 127.6, 127.5 (d, *J* = 13.5 Hz), 123.7 (d, *J* = 3.3 Hz), 115.4 (d, *J* = 23.3 Hz), 113.8, 55.4, 46.7, 19.4; **^{19}F NMR** (376MHz, $CDCl_3$) δ -117.2 (m); **HRMS (ESI)**: Found: *m/z* 357.1263. Calcd for $C_{22}H_{19}O_2FNa$ $(M+Na)^+$ 357.1267.

2-(6-methoxynaphthalen-2-yl)-1-(4-methoxyphenyl)propan-1-one (6c)



According to the general procedure **B** (0.1 mmol scale), product **6c** was isolated in 94% yield (30.2 mg) as colorless oil; **^{1}H NMR** (400MHz, $CDCl_3$) δ 8.03-7.95 (2H,m), 7.72-7.61 (3H,m), 7.43-7.36 (1H,m), 7.12 (1H, dd, *J* = 9.0, 2.4 Hz), 7.08 (1H, d, *J* = 2.1 Hz), 6.88-6.80 (2H, m), 4.77 (1H, q, *J* = 6.8 Hz), 3.88 (3H, s), 3.78 (3H, s), 1.59 (3H, d, *J* = 6.8 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 198.9, 163.1, 157.5, 137.1, 133.4, 131.0, 129.5, 129.2, 127.5, 126.4, 126.1, 118.9, 113.6, 105.5, 55.3, 55.3, 47.5, 19.5; **HRMS (ESI)**: Found: *m/z* 321.1501.Calcd for $C_{21}H_{21}O_3$ $(M+H)^+$ 321.1491.

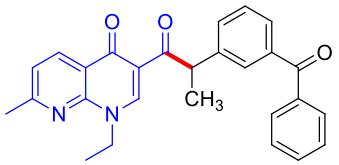
2-(4-(1-(4-methoxyphenyl)-1-oxopropan-2-yl)phenyl)isoindolin-1-one (6d)



According to the general procedure **B** (0.1 mmol scale), product **6d** was isolated in 54% yield (19.9 mg) as yellow solid, mp: 164-165 °C; **^{1}H NMR**(400MHz, $CDCl_3$) δ 7.99-7.93 (2H,m), 7.91-7.87 (1H,m), 7.82-7.75 (2H,m), 7.61-7.54 (1H,m), 7.52-7.44 (2H,m), 7.37-7.30 (2H,m), 6.89-6.82 (2H, m), 4.79 (2H, s), 4.66 (1H, q, *J* = 6.8 Hz), 3.81 (3H, s), 1.52 (3H, d, *J* = 6.8 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.7, 167.4, 163.2, 140.0, 138.1, 137.9, 133.1, 132.0, 131.0, 129.3, 128.4, 128.3, 124.1, 122.6, 119.9, 113.7, 55.4,

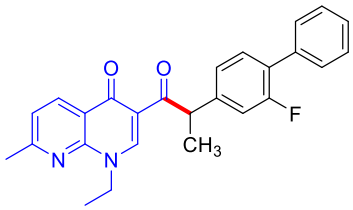
50.6, 46.8, 19.4; **HRMS (ESI)**: Found: *m/z* 394.1410. Calcd for $C_{24}H_{21}NO_3Na$ $(M+Na)^+$ 394.1419.

3-(2-(3-benzoylphenyl)propanoyl)-1-ethyl-7-methyl-1,8-naphthyridin-4(1H)-one (6e)



According to the general procedure **A** (0.1 mmol scale), product **6e** was isolated in 78% yield (33.2 mg) as white solid; mp: 133-134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63-8.56 (2H, m), 7.81 (1H, s), 7.79-7.73 (2H, m), 7.65 (1H, d, *J* = 7.7 Hz), 7.61 (1H, d, *J* = 7.7 Hz), 7.55 (1H, t, *J* = 7.4 Hz), 7.43 (2H, t, *J* = 7.6 Hz), 7.38 (1H, t, *J* = 7.7 Hz), 7.23 (1H, d, *J* = 8.1 Hz), 5.61 (1H, q, *J* = 7.0 Hz), 4.54-4.34 (2H, m), 2.64 (3H, s), 1.53 (3H, d, *J* = 7.0 Hz), 1.45 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.8, 196.7, 175.4, 162.8, 148.7, 148.6, 141.8, 137.6, 137.5, 136.7, 132.9, 132.3, 130.2, 130.1, 128.3, 128.2, 128.1, 121.9, 121.2, 118.4, 49.3, 46.7, 25.0, 18.5, 15.1; **HRMS (ESI)**: Found: *m/z* 447.1691.Calcd for $C_{27}H_{24}N_2O_3Na$ $(M+Na)^+$ 447.1685.

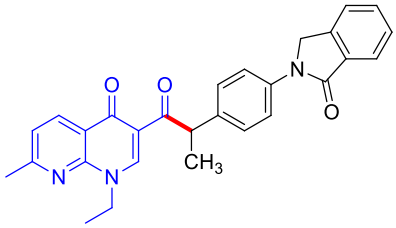
1-ethyl-3-(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoyl)-7-methyl-1,8-naphthyridin-4(1H)-one (6f)



According to the general procedure **B** (0.1 mmol scale), product **6f** was isolated in 52% yield (21.5 mg) as yellow solid; mp: 127-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ8.67-8.59 (2H, m), 7.53-7.45 (2H, m), 7.42-7.36 (2H, m), 7.36-7.30 (2H, m), 7.30-7.19 (3H, m), 5.65 (1H, q, *J* = 7.0 Hz), 4.56-4.37 (2H, m), 2.65 (3H, s), 1.55 (3H, d, *J* = 7.0 Hz), 1.47 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.8, 175.6, 162.8, 159.6 (d, *J* = 247.6 Hz), 148.8, 148.6, 143.1 (d, *J* = 7.7 Hz), 136.8, 135.8, 130.4 (d, *J* = 3.9 Hz), 128.9 (d, *J* = 3.0 Hz), 128.3, 127.3, 127.0 (d, *J* = 13.5 Hz), 124.6 (d, *J* = 3.2 Hz), 121.9, 121.2, 118.4, 116.0 (d, *J* = 23.3 Hz), 48.8, 46.8, 25.0, 18.4, 15.1; **^{19}F NMR** (376MHz,

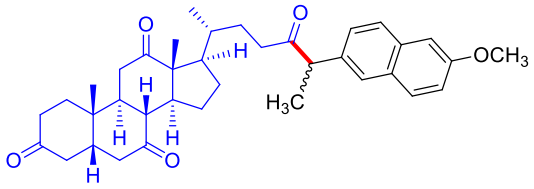
$CDCl_3$) δ -118.3 (m); **HRMS (ESI)**: Found: *m/z* 415.1808. Calcd for $C_{26}H_{24}N_2O_2F$ $(M+H)^+$ 415.1822.

1-ethyl-7-methyl-3-(2-(4-(1-oxoisoindolin-2-yl)phenyl)propanoyl)-1,8-naphthyridin-4(1H)-one (6g)



According to the general procedure **B** (0.1 mmol scale), product **6g** was isolated in 65% yield (29.6 mg) as white solid; mp: 178-179 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (1H, d, *J* = 8.1 Hz), 8.56 (1H, s), 7.90-7.84 (1H, m), 7.77-7.70 (2H, m), 7.58-7.52 (1H, m), 7.50-7.42 (4H, m), 7.21 (1H, d, *J* = 8.1 Hz), 5.59 (1H, q, *J* = 6.9 Hz), 4.78 (2H, s), 4.51-4.36 (2H, m), 2.62 (3H, s), 1.52 (3H,d, *J* = 7.0 Hz), 1.45 (3H,t, *J* = 7.2 Hz); **^{13}C NMR** (125MHz, $CDCl_3$) δ 200.2, 175.5, 167.3, 162.7, 148.6, 140.1, 137.9, 137.8, 136.7, 133.2, 131.9, 129.3, 128.3, 124.0, 122.5, 121.9, 121.1, 119.6, 118.7, 50.7, 48.8, 46.7, 25.0, 18.4, 15.1; **HRMS (ESI)**: Found: *m/z* 452.1979. Calcd for $C_{28}H_{26}N_3O_3$ $(M+H)^+$ 452.1974.

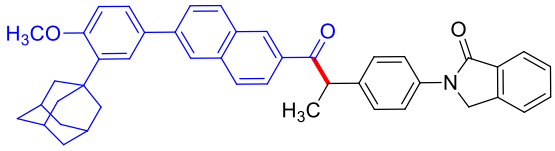
(5S,8R,9S,10S,13R,14S,17R)-17-((R)-6-(6-methoxynaphthalen-2-yl)-5-oxoheptan-2-yl)-10,13-dimethyldecahydro-1H-cyclopenta[a]phenanthrene-3,7,12(2H,4H,8H)-trione (6h)



According to the general procedure **B** (0.1 mmol scale, DMSO was used as solvent; 1.2 equiv Cs_2CO_3 was used; two 440 nm blue LEDs was used as light source), product **6h** was isolated in 65% yield (41.1 mg) as yellow solid, dr = 1.2:1, mp:188-189 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72-7.65 (2H, m), 7.59 (1H, d, *J* = 5.6 Hz), 7.30-7.26 (1H, m), 7.16-7.07 (2H, m), 3.93-3.83 (4H, m), 2.94-2.71 (3H, m), 2.50-2.16 (7H, m), 2.14-2.03 (2H, m), 2.00 (1H, d, *J* = 13.2 Hz), 1.95-1.88 (2H, m), 1.88-1.65 (4H, m), 1.59 (1H, td, *J* = 14.2, 5.1 Hz), 1.45 (1.46 H, d, *J* = 2.8 Hz), 1.44 (1.46 H, d, *J* = 2.8 Hz),1.36 (3H, s), 1.28-1.11 (4H, m), 0.97 (1.46 H, s), 0.93 (1.54 H, s), 0.69 (1.46 H, d, *J* = 6.3

Hz), 0.56 (1.56 H, d, *J* = 6.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.9, 211.9, 211.5, 211.3, 209.0, 208.7, 208.6, 157.6, 135.8, 135.7, 133.62, 133.61, 129.14, 129.12, 129.1, 127.44, 127.42, 126.43, 126.41, 126.3, 119.0, 105.6, 105.6, 56.8, 56.7, 55.3, 53.1, 52.9, 51.7, 51.6, 48.9, 48.89, 46.8, 45.6, 45.5, 45.4, 45.3, 44.9, 42.7, 38.5, 38.2, 37.8, 36.4, 35.9, 35.2, 35.2, 35.1, 29.4, 29.2, 27.5, 27.4, 25.0, 24.99, 21.8, 18.7, 18.5, 17.44, 17.42, 11.7, 11.69; **HRMS (ESI)**: Found: *m/z* 571.3431. Calcd for $C_{37}H_{47}O_5$ $(M+H)^+$ 571.3423.

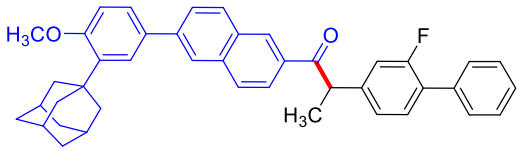
2-(4-(1-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-1-oxopropan-2-yl)phenyl)isoindolin-1-one (6i)



According to the general procedure **B** (0.05 mmol scale), product **6i** was isolated in 41% yield (12.9 mg) as yellow sold, mp: 226-227 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (1H, s), 8.04 (1H, dd, *J* = 8.6, 1.3 Hz), 7.98-7.93 (2H,m), 7.92-7.84 (2H,m), 7.84-7.79 (2H,m), 7.76 (1H, dd, *J* = 8.6, 1.4 Hz), 7.59-7.54 (2H,m), 7.53-7.45 (3H,m), 7.45-7.38 (2H,m), 6.98 (1H, d, *J* = 8.5 Hz), 4.89 (1H, q, *J* = 6.8 Hz), 4.79 (2H,s), 3.89 (3H,s), 2.17 (6H, s, br), 2.10 (3H, s, br), 1.80 (6H, s, br), 1.62 (3H, d, *J* = 6.8 Hz); **^{13}C NMR**(100MHz, $CDCl_3$) δ 200.1, 167.4, 158.9, 141.6, 140.0, 139.0, 138.3, 137.7, 135.8, 133.3, 133.1, 132.4, 132.0, 131.2, 130.2, 130.0, 128.5, 128.4, 128.4, 126.5, 125.9, 125.7, 124.9, 124.6, 124.1, 122.6, 120.0, 112.1, 55.1, 50.6, 47.2, 40.6, 37.2, 37.1, 29.1, 19.5; **HRMS (ESI)**: Found: *m/z* 632.3138. Calcd for $C_{44}H_{42}NO_3$ $(M+H)^+$ 632.3165.

6i could also be obtained according to general procedure **A** in 56% yield when acyl imidazole was used as starting material.

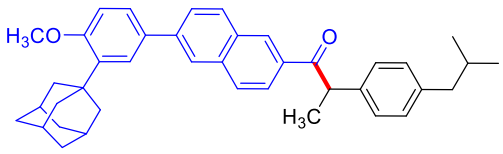
1-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propan-1-one (6j)



According to the general procedure **A** (0.05 mmol scale), product **6j** was isolated in 53% yield (15.7 mg) as white solid, mp:192-193 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (1H, s), 8.06 (1H, d, *J* = 8.6 Hz), 8.02-7.94 (2H,m), 7.90 (1H, d, *J* = 8.7 Hz), 7.79 (1H,

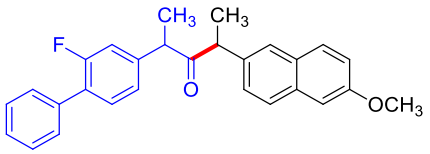
d, J = 9.6 Hz), 7.59 (1H, d, J = 2.0 Hz), 7.57-7.47 (3H, m), 7.45-7.30 (4H, m), 7.24-7.15 (2H, m), 6.99 (1H, d, J = 8.4 Hz), 4.92 (1H, q, J = 6.8 Hz), 3.90 (3H, s), 2.18 (6H, s, br), 2.11 (3H, s, br), 1.81 (6H, s, br), 1.65 (3H, d, J = 6.8 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 199.6, 159.9 (d, J = 250.0 Hz), 159.0, 142.9 (d, J = 8.0 Hz), 141.74, 139.0, 136.0, 135.4, 133.2, 132.4, 131.17, 131.13, 130.2, 130.0, 128.9 (d, J = 2.8 Hz), 128.6, 128.4, 127.6 (d, J = 13.5 Hz), 127.59, 126.6, 125.9, 125.7, 124.8, 124.6, 123.8 (d, J = 3.2 Hz), 115.5 (d, J = 23.3 Hz), 112.1, 55.2, 47.1, 40.6, 37.2, 37.1, 29.1, 19.4; **^{19}F NMR** (376MHz, $CDCl_3$) δ -117.1 (m); **HRMS (ESI)**: Found: *m/z* 595.3004. Calcd for $C_{42}H_{40}O_2F$ $(M+H)^+$ 595.3012.

1-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-2-(4-isobutylphenyl)propan-1-one (6k)



According to the general procedure **A** (0.05 mmol scale), product **6k** was isolated in 51% yield (14.1 mg) as yellow solid, mp: 137-138 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (1H, s), 8.04 (1H, dd, J = 8.7, 1.6 Hz), 7.97-7.92 (2H,m), 7.86 (1H, d, J = 8.7 Hz), 7.77 (1H, dd, J = 8.6, 1.6 Hz), 7.58 (1H, d, J = 2.2 Hz), 7.53 (1H, dd, J = 8.4, 2.2 Hz), 7.26-7.24 (2H, m), 7.11-7.05 (2H, m), 6.99 (1H, d, J = 8.5 Hz), 4.85 (1H, q, J =6.8 Hz), 3.90 (3H, s), 2.41 (2H, d, J = 7.1 Hz), 2.21-2.16 (6H, m), 2.13-2.08 (3H, m), 1.84-1.77 (7H, m), 1.60 (3H, d, J = 6.9 Hz), 0.86 (6H, d, J = 6.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.4, 158.9, 141.5, 140.3, 139.0, 138.8, 135.8, 133.5, 132.5, 131.2, 130.2, 130.0, 129.7, 128.3, 127.5, 126.4, 125.9, 125.7, 125.0, 124.6, 112.1, 55.1, 47.4, 45.0, 40.6, 37.2, 37.1, 30.1, 29.1, 22.37, 22.35, 19.6; **HRMS (ESI)**: Found: *m/z* 579.3235. Calcd for $C_{40}H_{44}O_2Na$ $(M+Na)^+$ 579.3239.

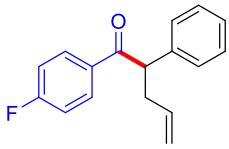
2-(2-fluoro-[1,1'-biphenyl]-4-yl)-4-(6-methoxynaphthalen-2-yl)pentan-3-one (6l)



According to the general procedure **B** (0.1 mmol scale), product **6l** was isolated in 65%

yield (24.9 mg) as colorless oil, dr =1.5/1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.54 (2H, m), 7.44-7.30 (6H, m), 7.14-7.03 (4H, m), 6.76 (1H, dd, *J* = 11.8, 1.4 Hz), 6.70 (1H, dd, *J* = 7.9,1.4 Hz), 4.04 (1H, q, *J* = 7.0 Hz), 3.93 (1H, q, *J* =7.0 Hz),3.91 (3H, s), 1.47 (3H, d, *J* = 7.0 Hz), 1.42 (3H, d, *J* = 7.1 Hz); **^{13}C NMR** (100MHz, $CDCl_3$) δ 210.8, 159.4 (d, *J* = 248.3 Hz), 157.6, 141.7 (d, *J* = 7.7 Hz), 135.5, 135.0, 133.6, 130.3 (d, *J* = 4.0 Hz), 129.1, 128.88, 128.86, 128.3, 127.5, 127.3 (d, *J* = 13.5 Hz), 127.2, 126.9, 126.5, 123.9 (d, *J* = 3.3 Hz), 119.0, 115.6 (d, *J* = 23.5 Hz), 105.6, 55.3, 52.2, 50.9, 18.4, 18.2. **^{19}F NMR** (376MHz, $CDCl_3$) δ -118.1 (m); **HRMS (ESI)**: Found: *m/z* 413.1911. Calcd for $C_{28}H_{26}O_2F$ $(M+H)^+$ 413.1917.

1-(4-fluorophenyl)-2-phenylpent-4-en-1-one (7)



According to the general procedure **A** (0.1 mmol scale), product **7** was isolated in 19% yield (4.8 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02-7.93 (2H, m), 7.33-7.27 (4H, m), 7.24-7.17 (1H, m), 7.09-6.99 (2H, m), 5.74 (1H, ddt, *J* = 17.1, 10.2, 6.9 Hz), 5.03 (1H, d, *J* = 17.1 Hz), 4.97 (1H, d, *J* = 10.2 Hz), 4.56 (1H, t, *J* = 7.3 Hz), 2.99-2.87 (1H, m), 2.61-2.50 (1H, m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 165.5 (d, *J* = 254.9 Hz), 138.9, 135.9, 133.1 (d, *J* = 3.1 Hz), 131.3 (d, *J* = 9.3 Hz), 129.0, 128.1, 127.2, 116.7, 115.6 (d, *J* = 21.8 Hz), 53.7, 38.1; **^{19}F NMR** (376MHz, $CDCl_3$) δ -105.4. **HRMS (ESI)**: Found: *m/z* 255.1186. Calcd for $C_{17}H_{16}OF$ $(M+H)^+$ 255.1185.

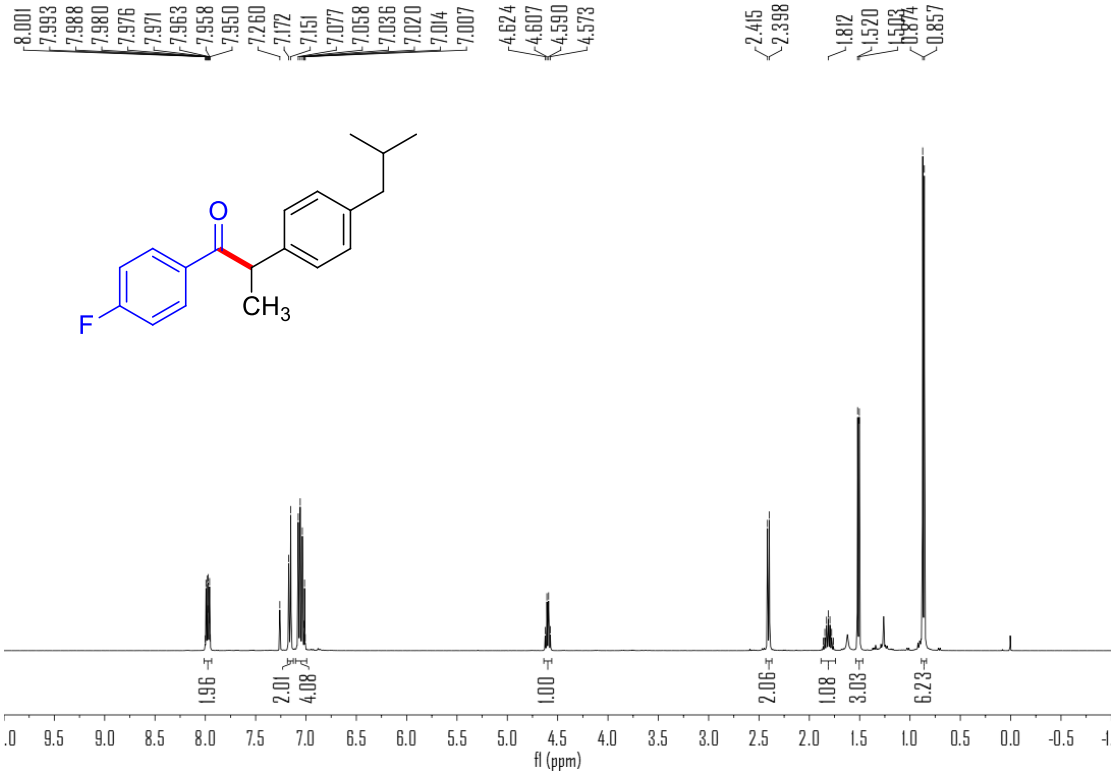
9. Supplementary references

1. Bryden, M. A., Zysman-Colman, E. Organic thermally activated delayed fluorescence (TADF) compounds used in photocatalysis. *Chem. Soc. Rev*. **50**, 7587–7680 (2021).

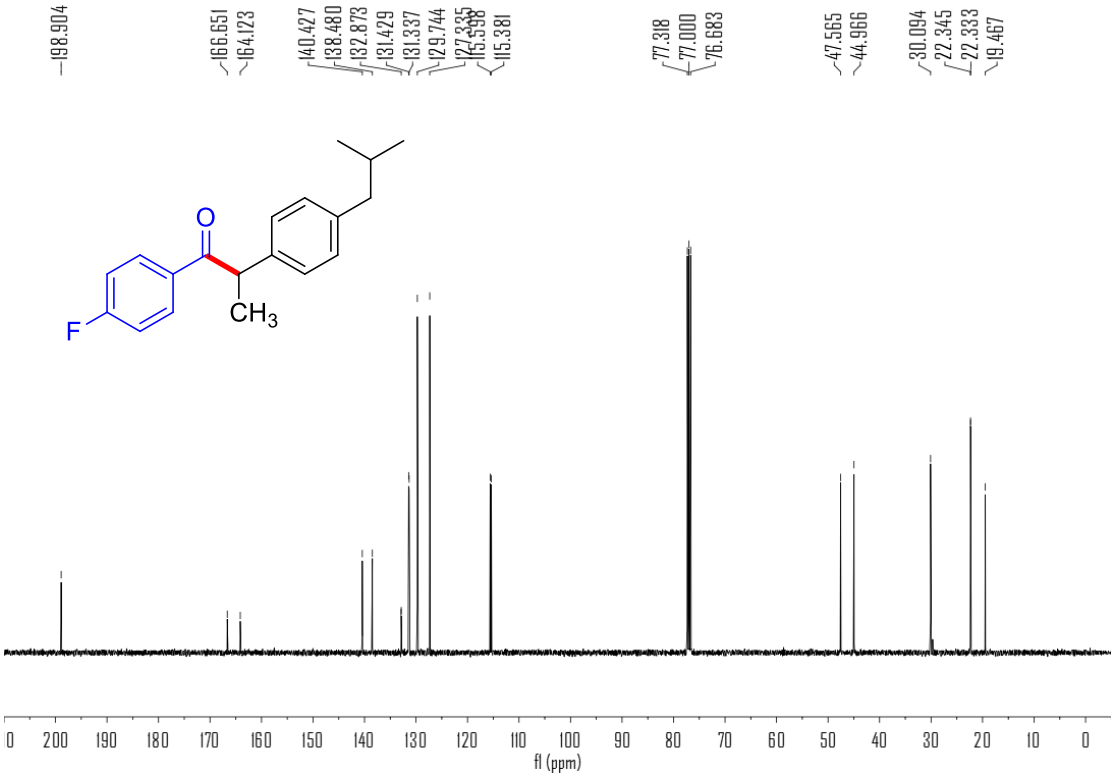
2. Lee, A., Scheidt, K. A. *N*-Heterocyclic carbene-catalyzed enantioselective annulations: a dual activation strategy for a formal [4+2] addition for dihydrocoumarins. *Chem. Commun.* **51**, 3407-3410 (2015).

3. Thai, D. L., Sapko, M. T., Reiter, C. T., Bierer, D. E., Perel, J. M. Asymmetric Synthesis and Pharmacology of Methylphenidate and Its Para-Substituted Derivatives. *J. Med. Chem.* **41**, 591-601 (1998).

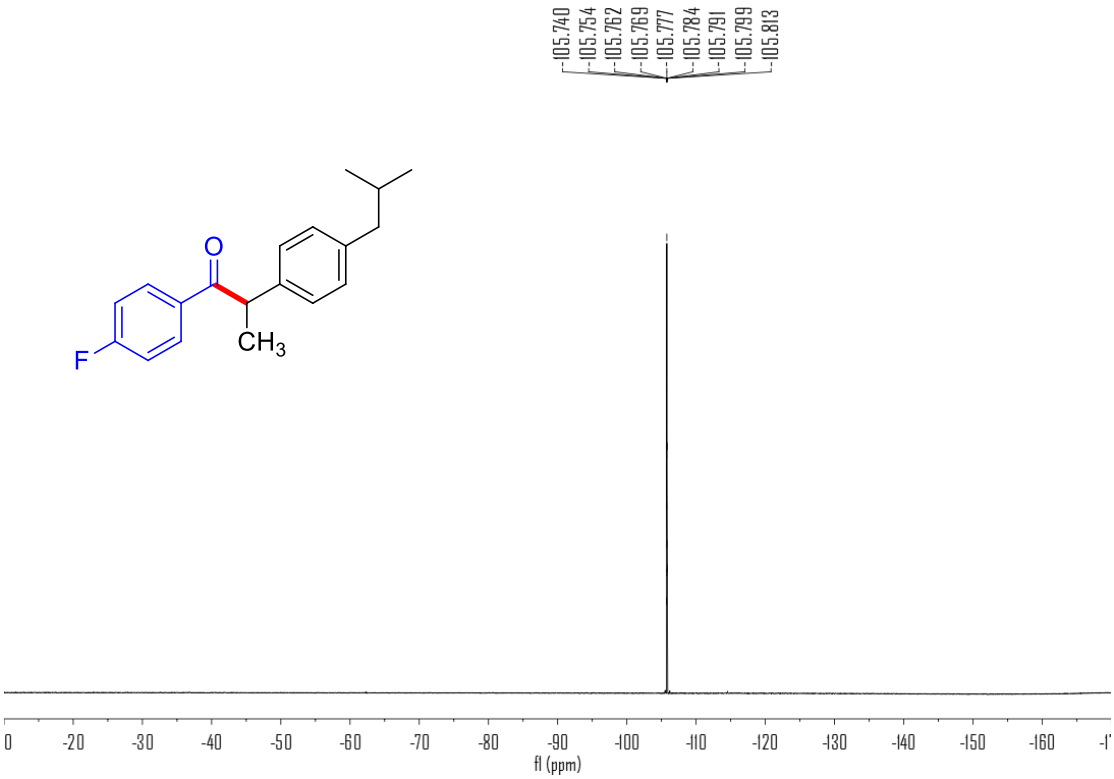
Appendix: ^{1}H, ^{13}C, and ^{19}F NMR spectra for new compounds



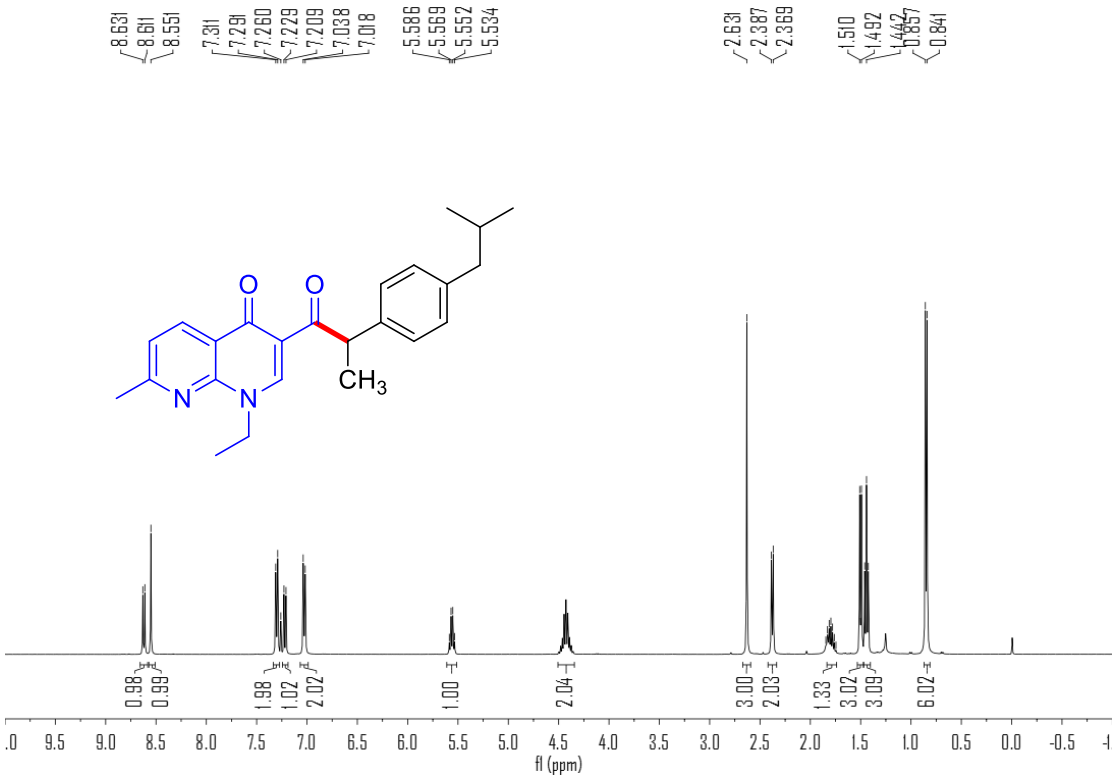
Supplementary Figure 4. ^{1}H **NMR** spectrum of **3a**



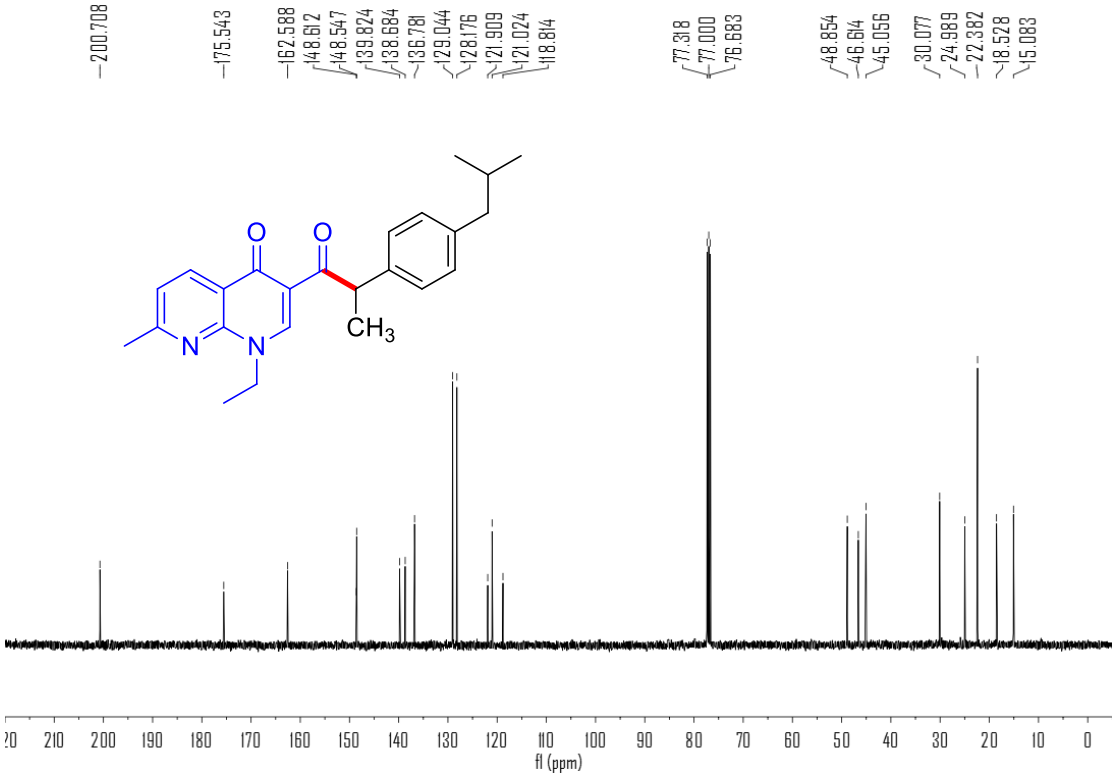
Supplementary Figure 5. ^{13}C **NMR** spectrum of **3a**



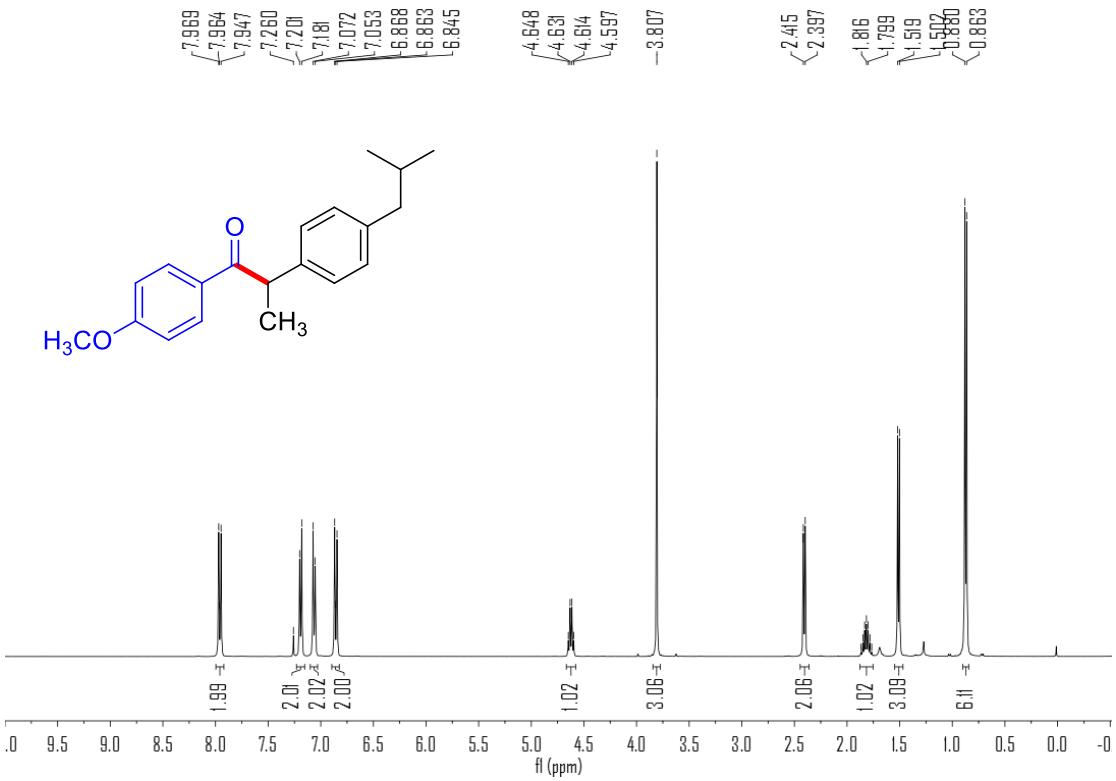
Supplementary Figure 6. ^{19}**F NMR** spectrum of **3a**



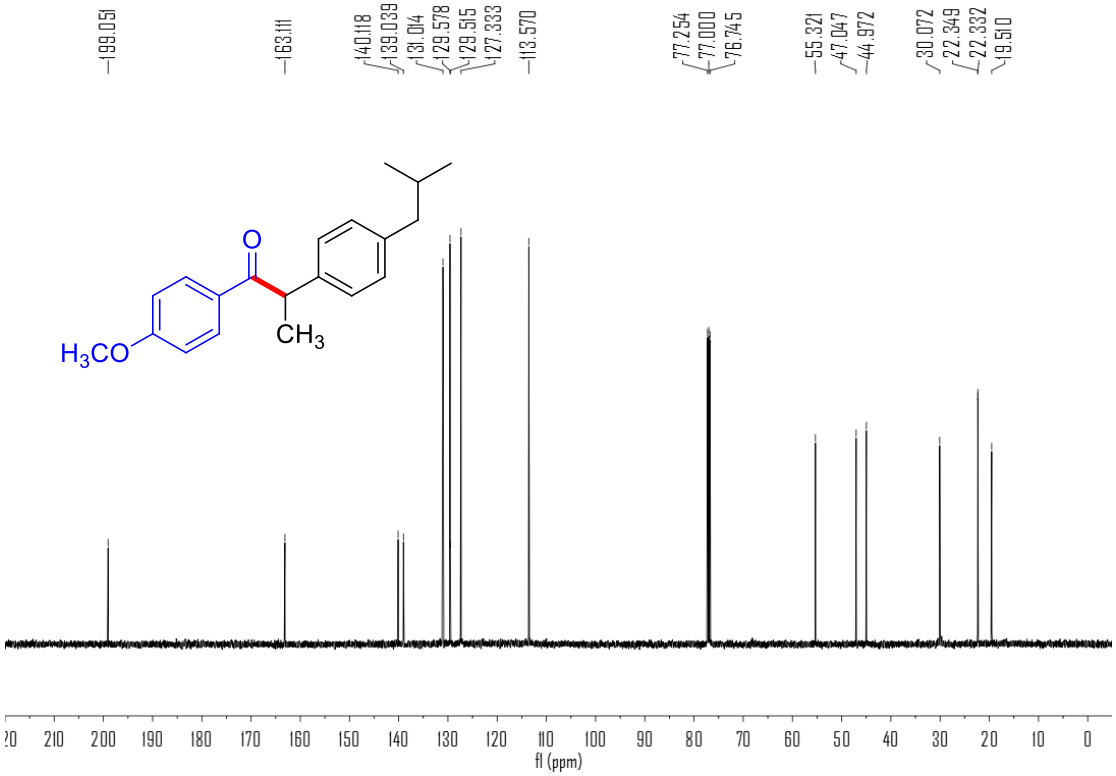
Supplementary Figure 7. ^{1}**H NMR** spectrum of **3b**



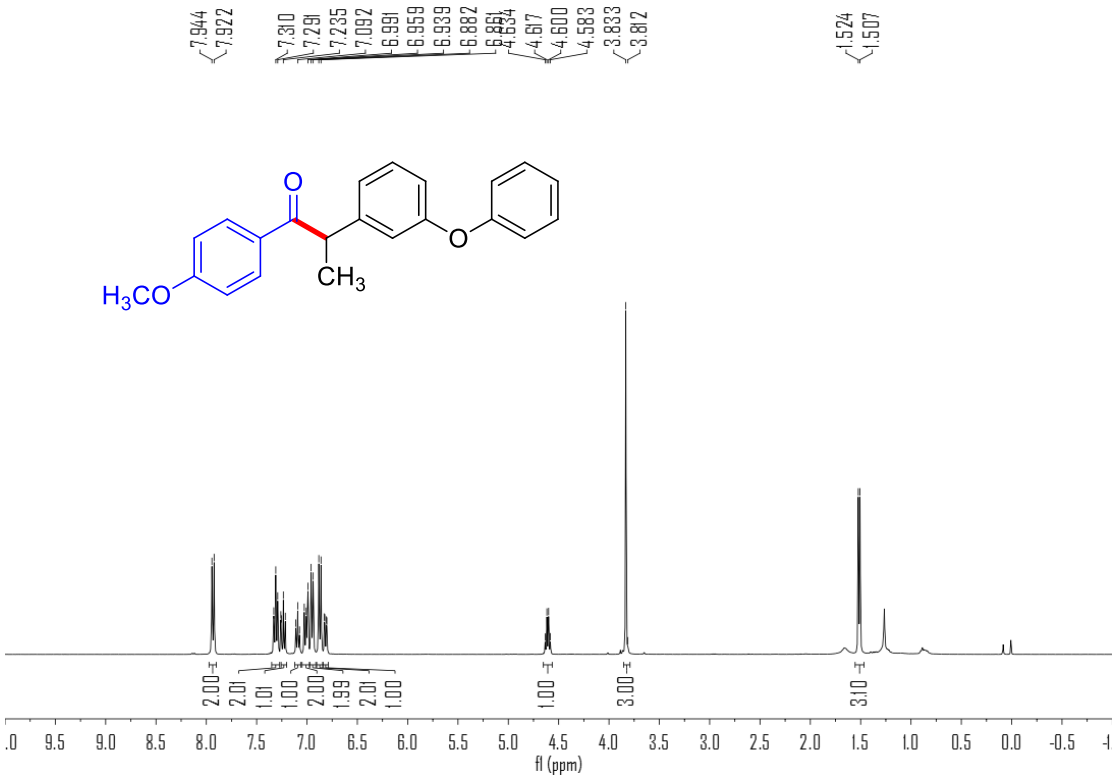
Supplementary Figure 8. ^{13}**C NMR** spectrum of **3b**



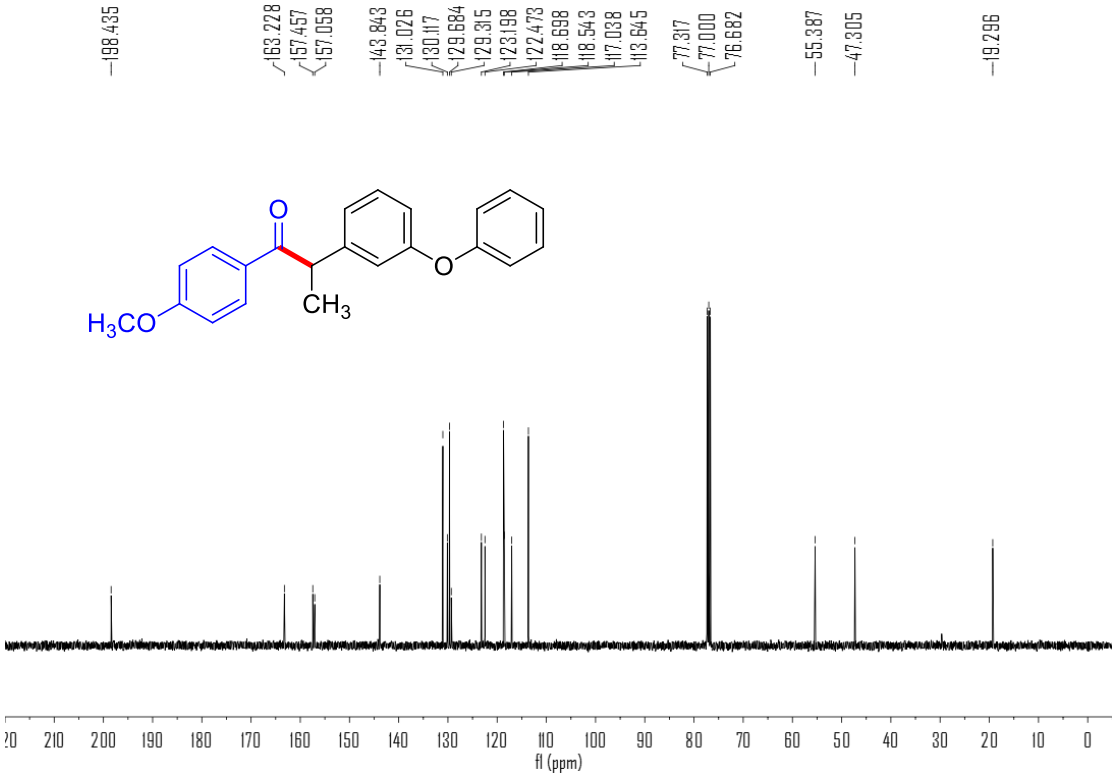
Supplementary Figure 9. ^{1}**H NMR** spectrum of **3c**



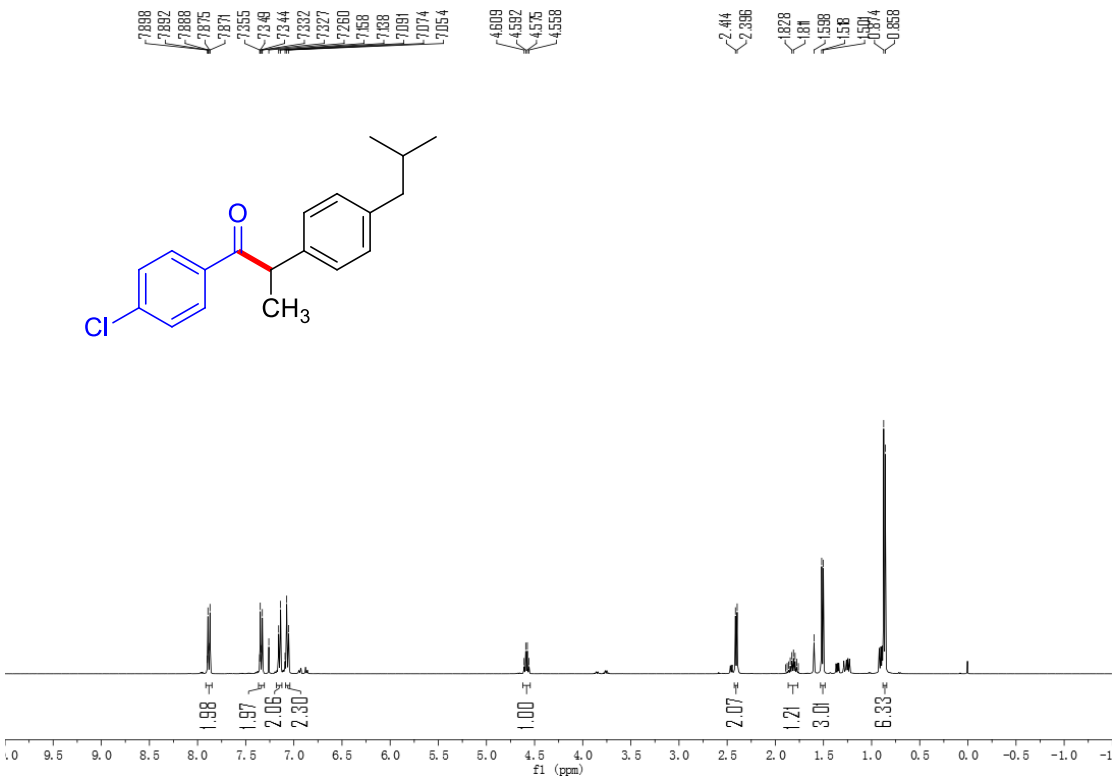
Supplementary Figure 10. ^{13}**C NMR** spectrum of **3c**



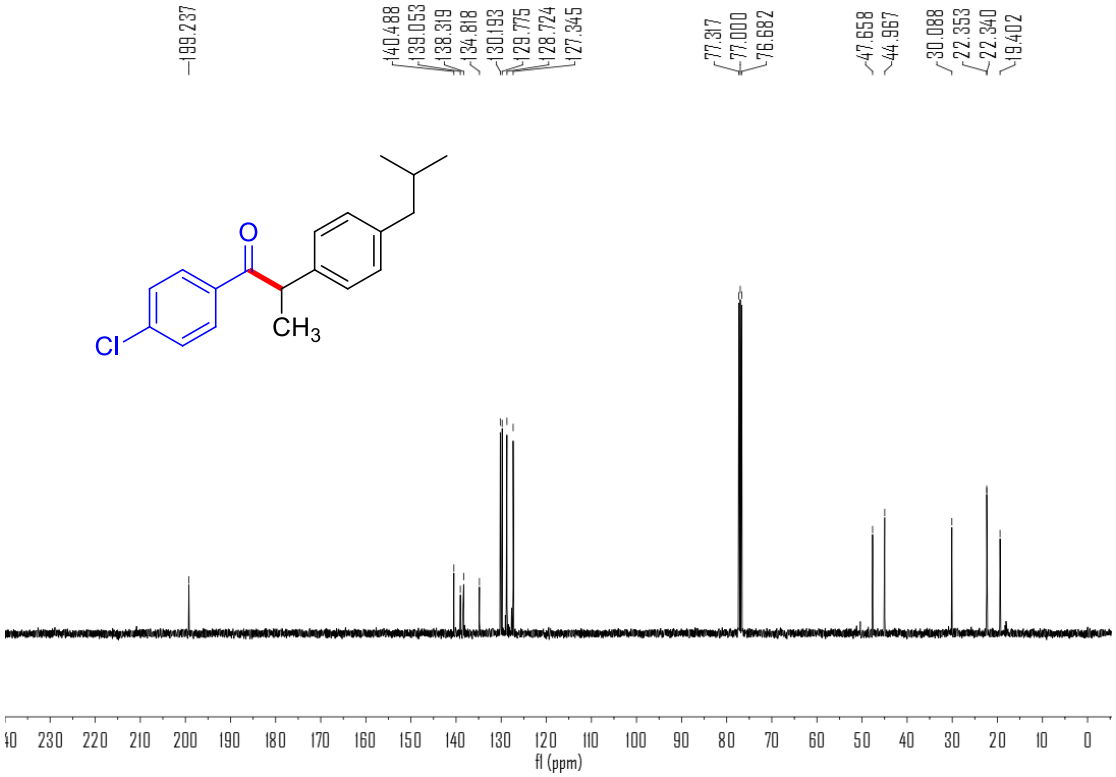
Supplementary Figure 11. ^{1}**H NMR** spectrum of **3d**



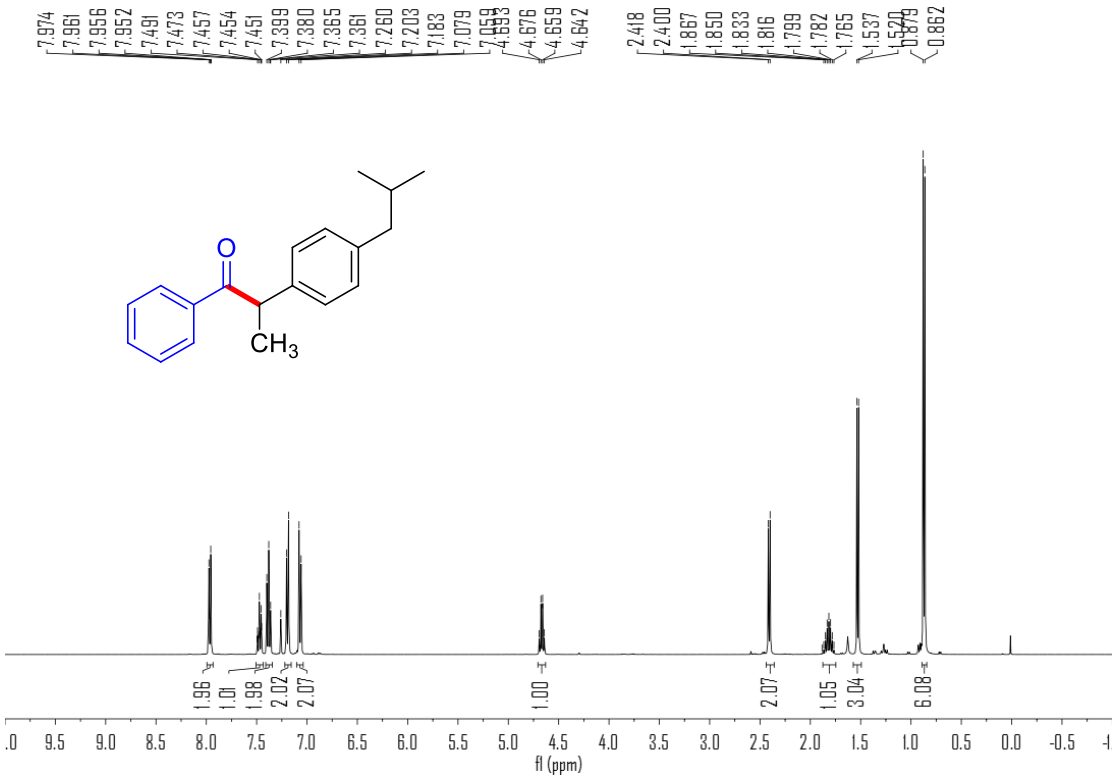
Supplementary Figure 12. ^{13}**C NMR** spectrum of **3d**



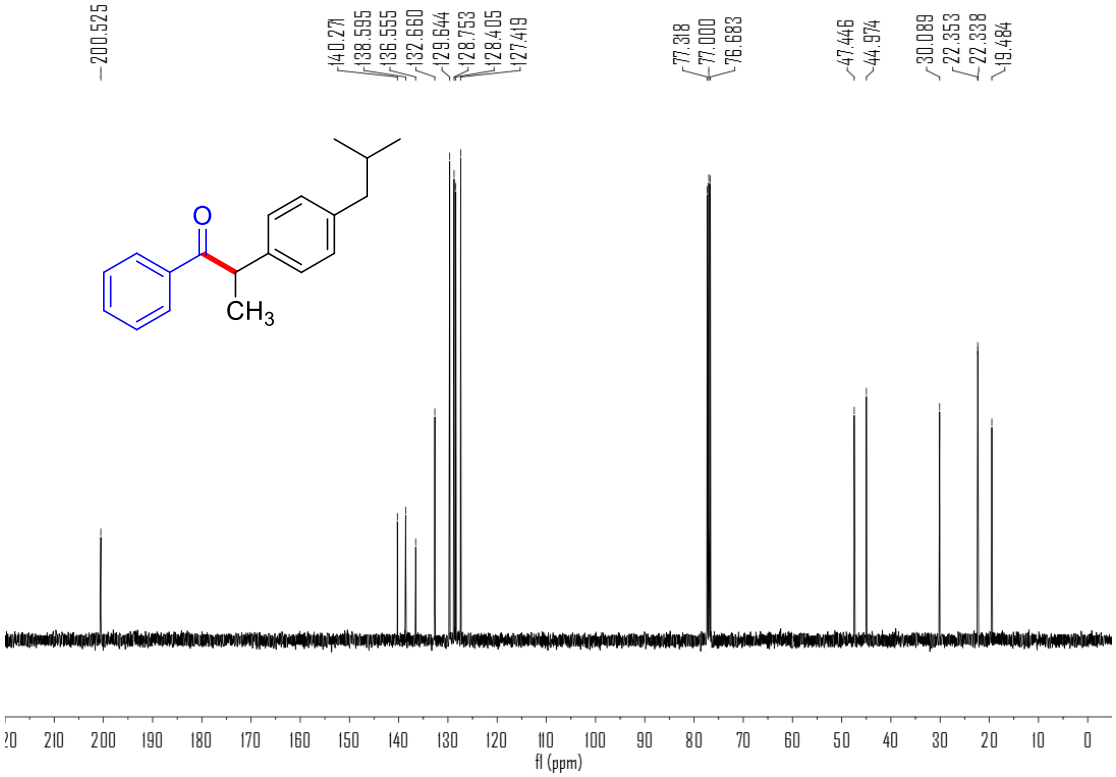
Supplementary Figure 13. ^{1}**H NMR** spectrum of **3e**



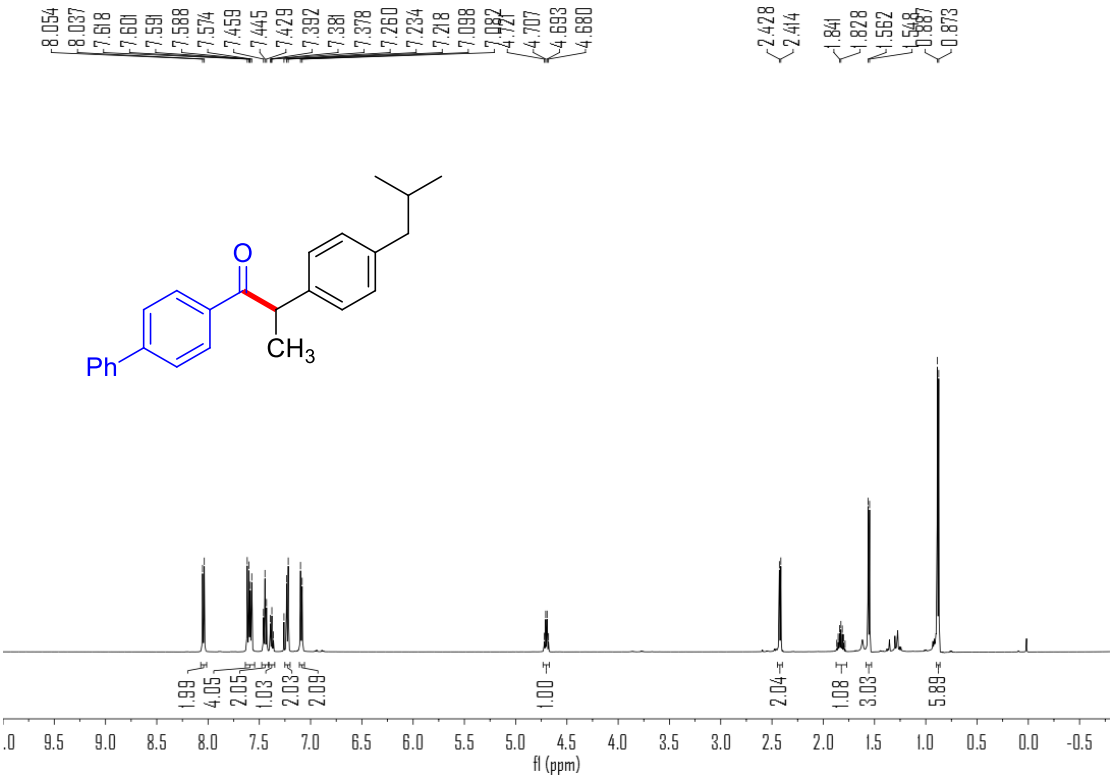
Supplementary Figure 14. ^{13}**C NMR** spectrum of **3e**



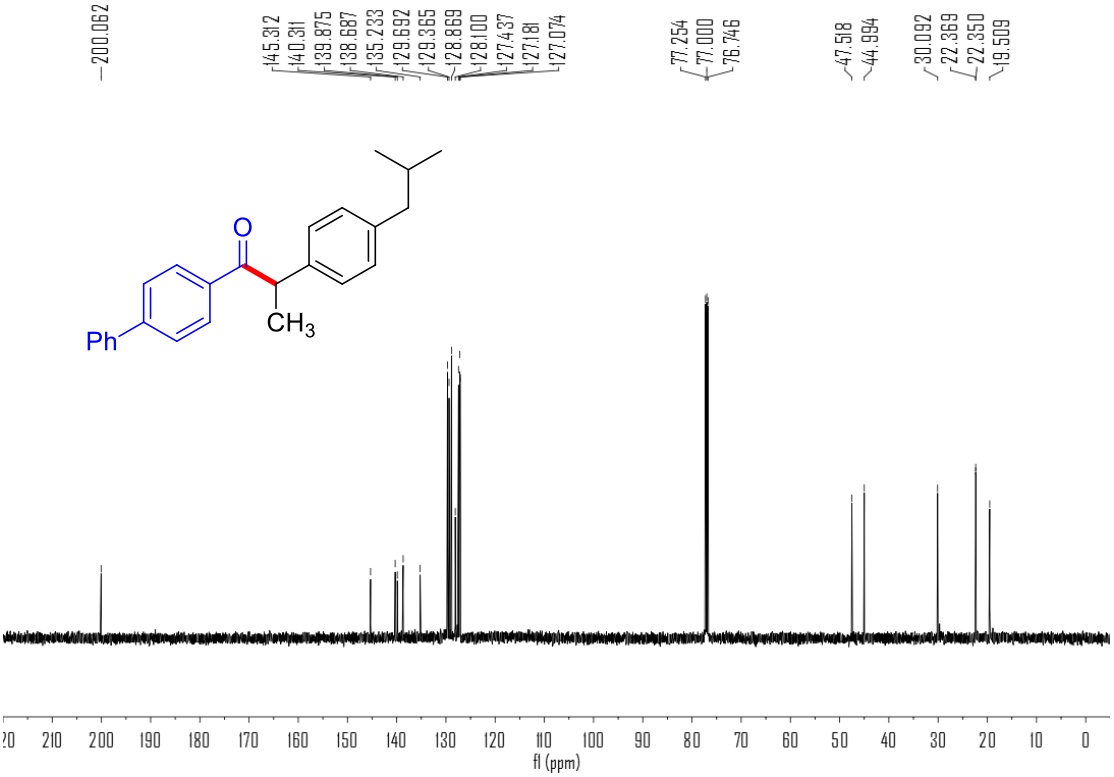
Supplementary Figure 15. ^{1}H NMR spectrum of **3f**



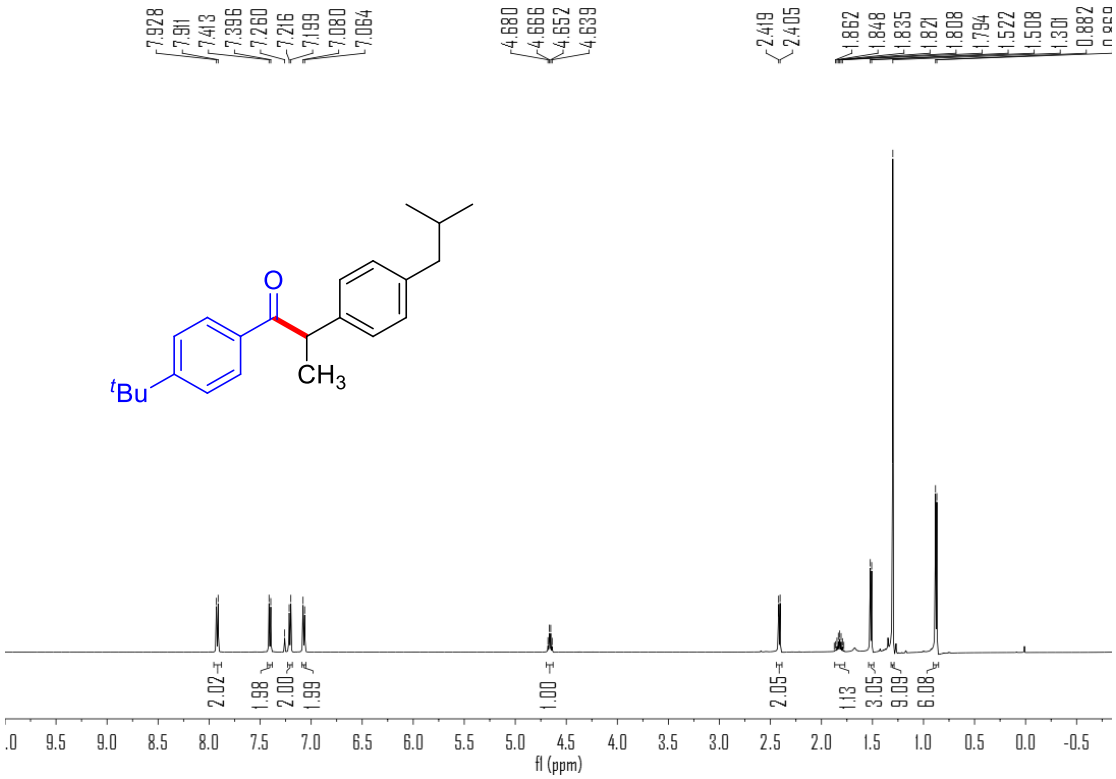
Supplementary Figure 16. ^{13}C NMR spectrum of **3f**



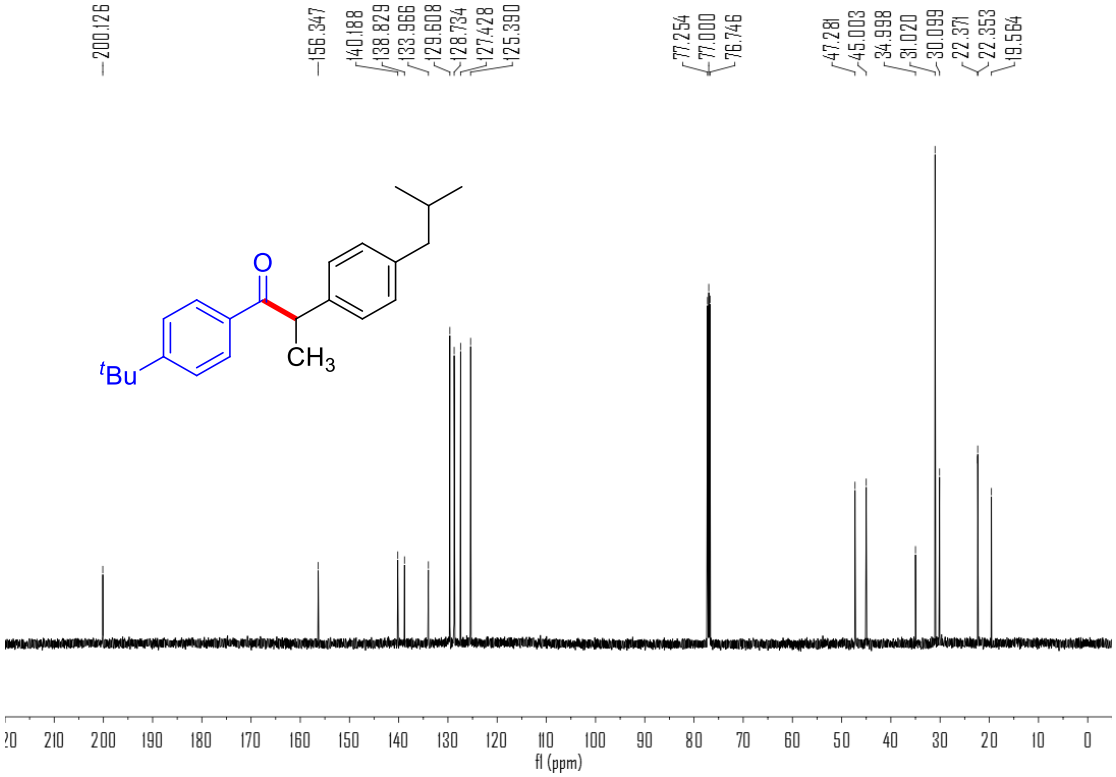
Supplementary Figure 17. ^{1}H NMR spectrum of **3g**



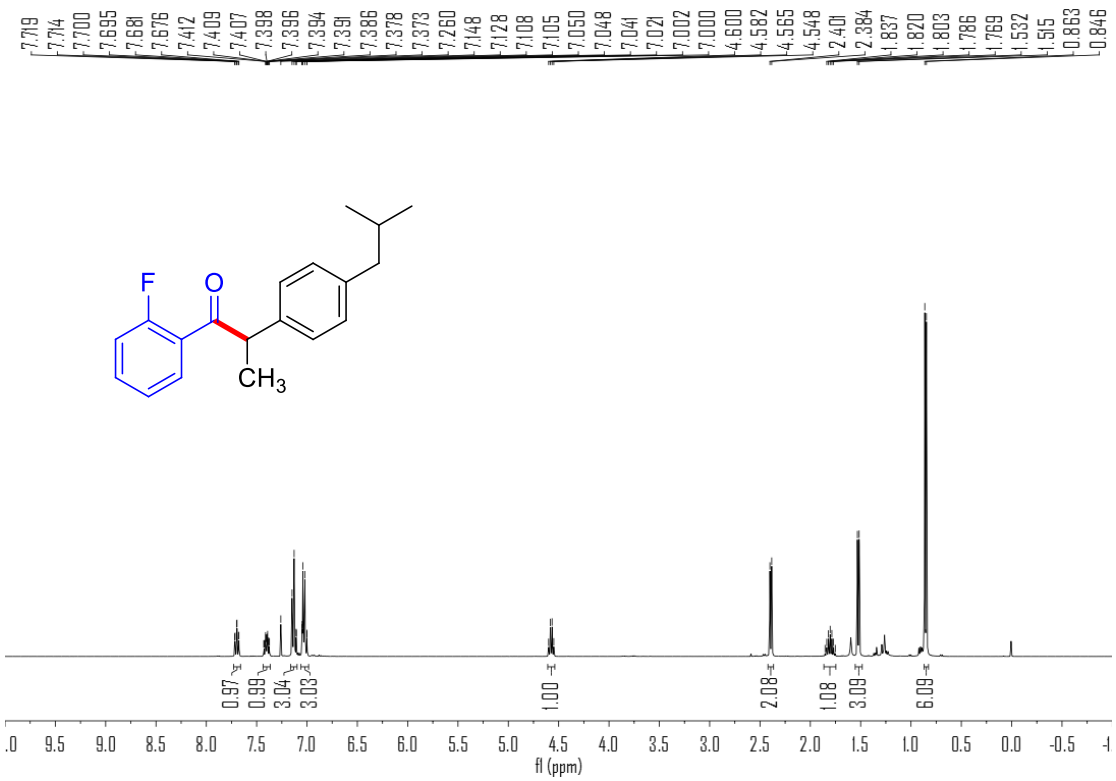
Supplementary Figure 18. ^{13}C NMR spectrum of **3g**



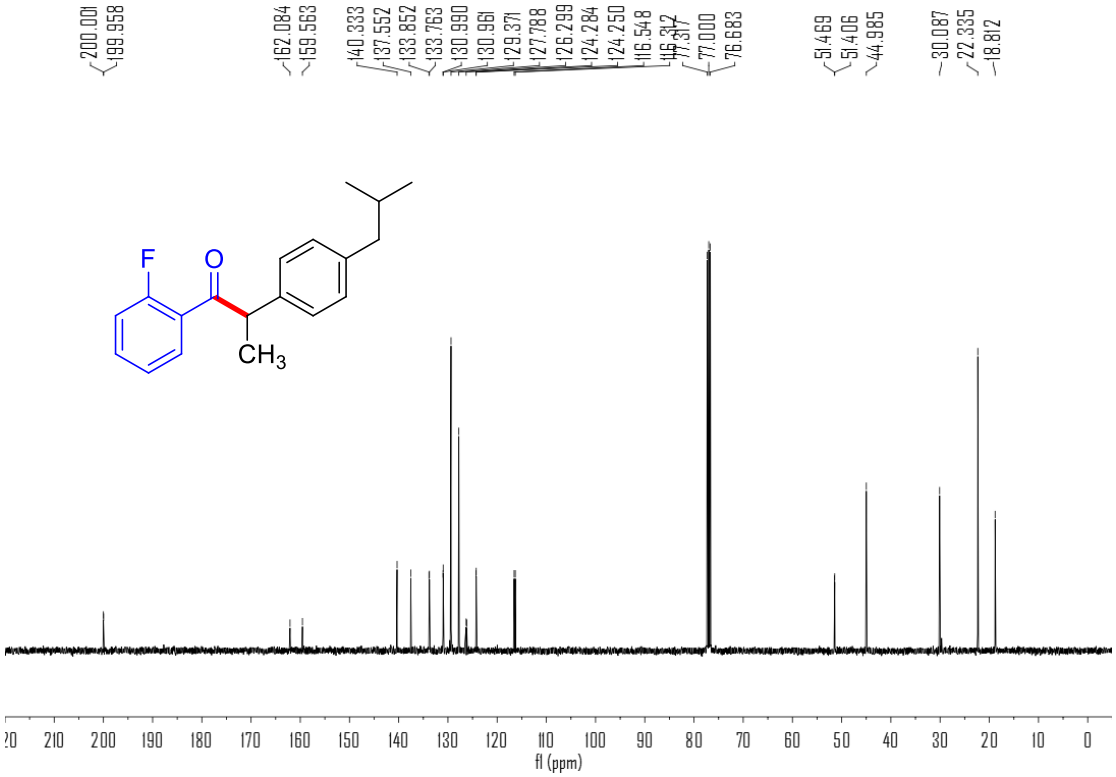
Supplementary Figure 19. ^{1}H NMR spectrum of **3h**



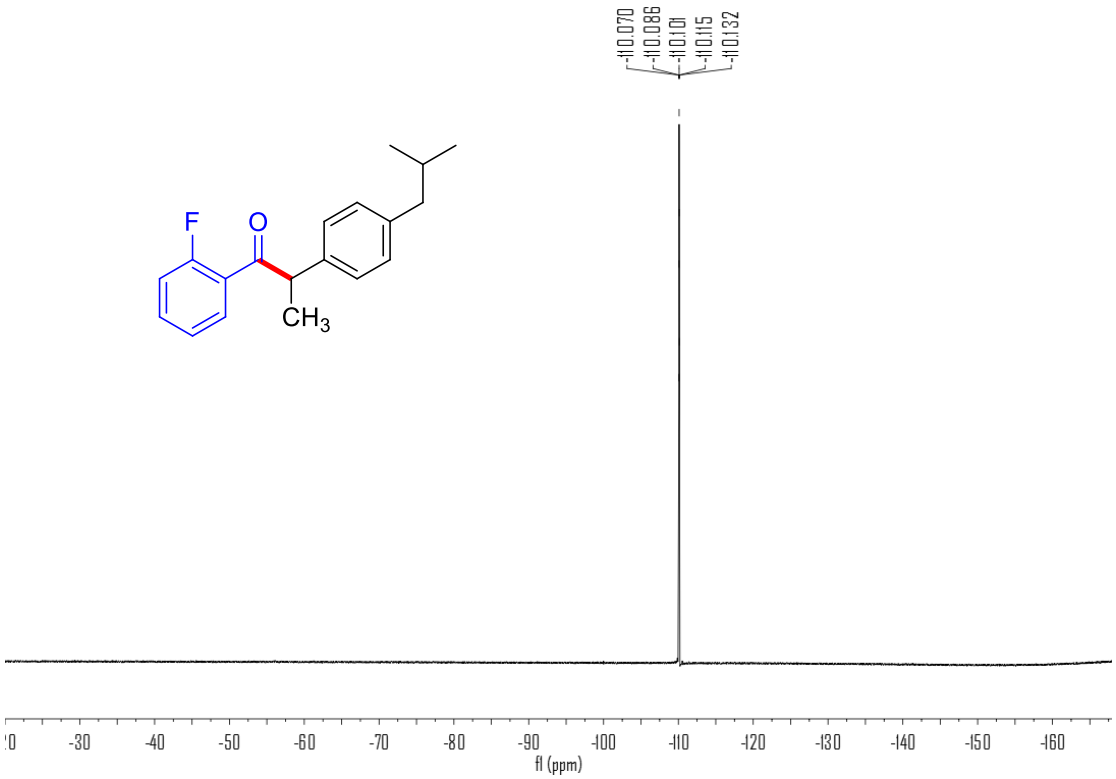
Supplementary Figure 20. ^{13}C NMR spectrum of **3h**



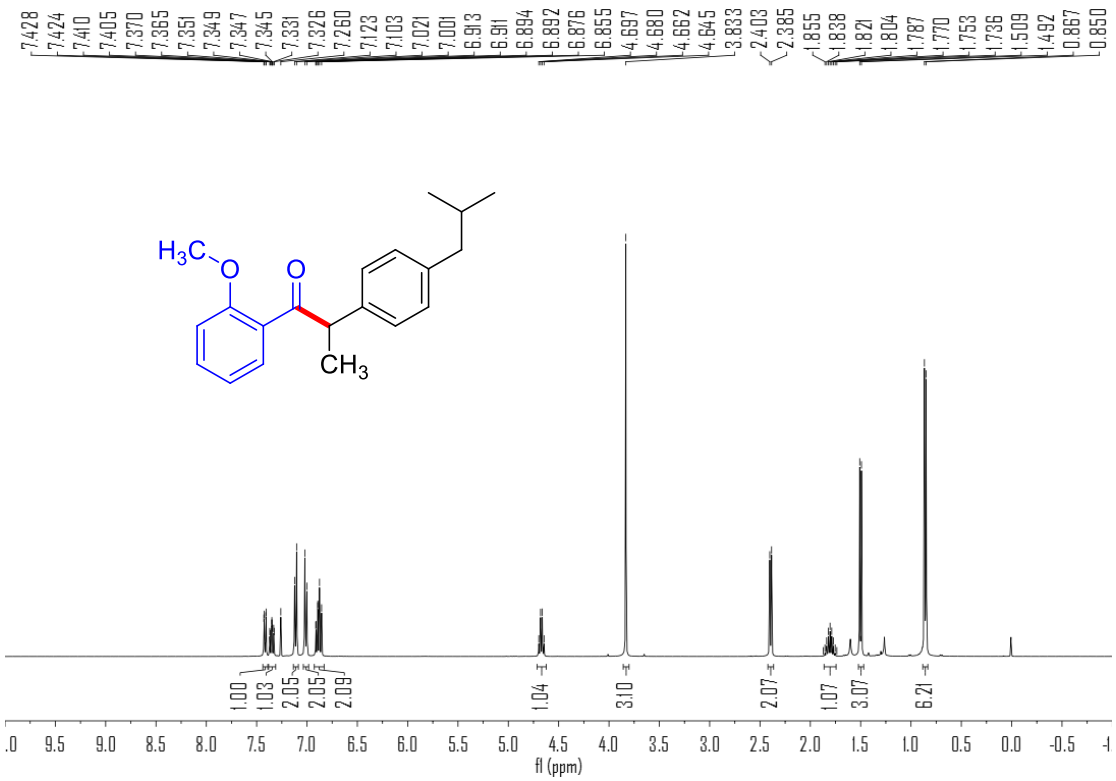
Supplementary Figure 21. ^{1}**H NMR** spectrum of **3i**



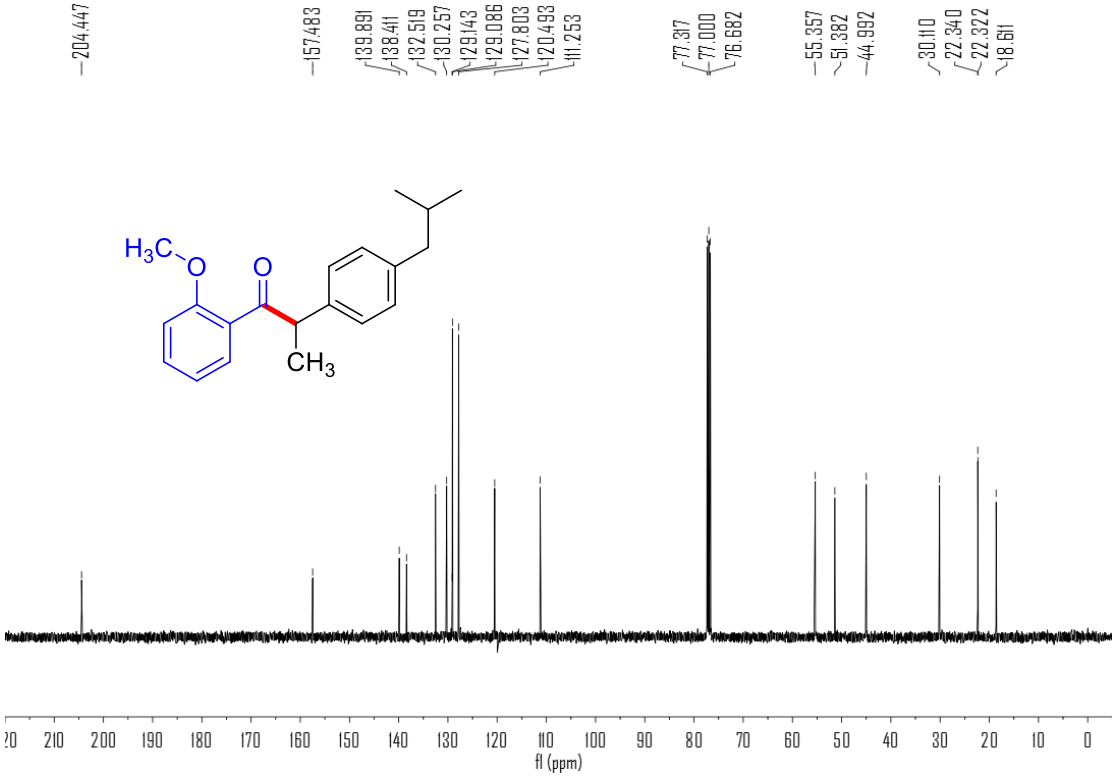
Supplementary Figure 22. ^{13}**C NMR** spectrum of **3i**



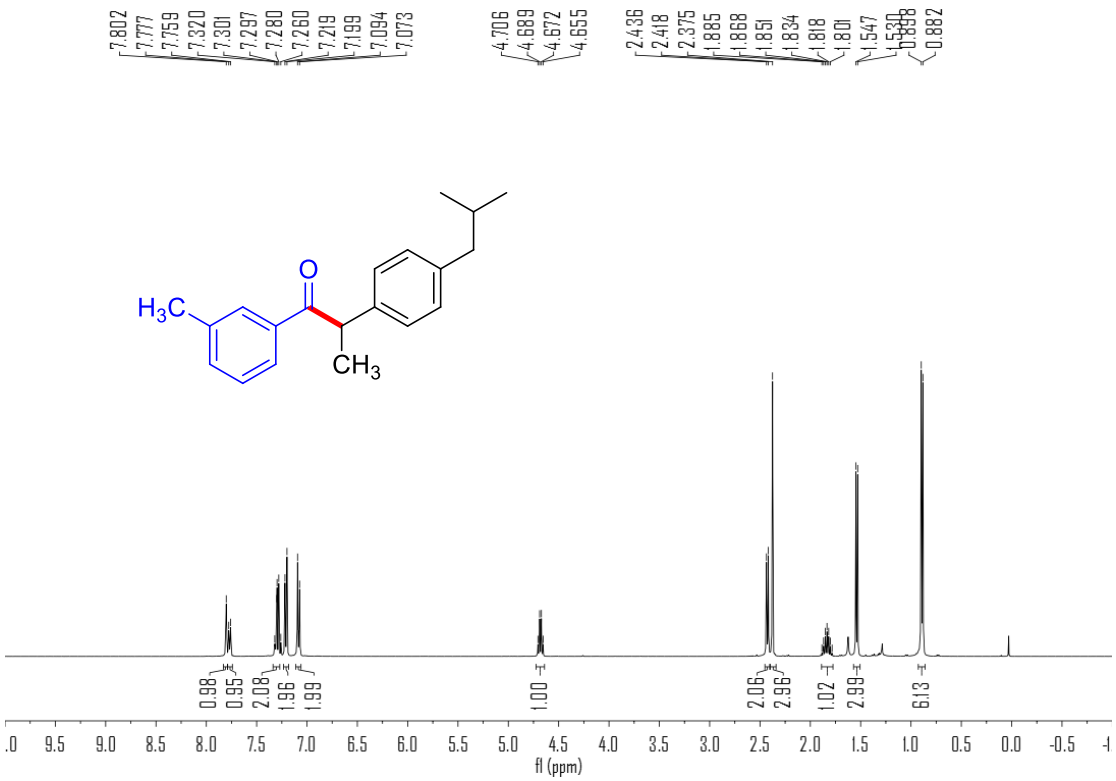
Supplementary Figure 23. ^{19}**F NMR** spectrum of **3i**



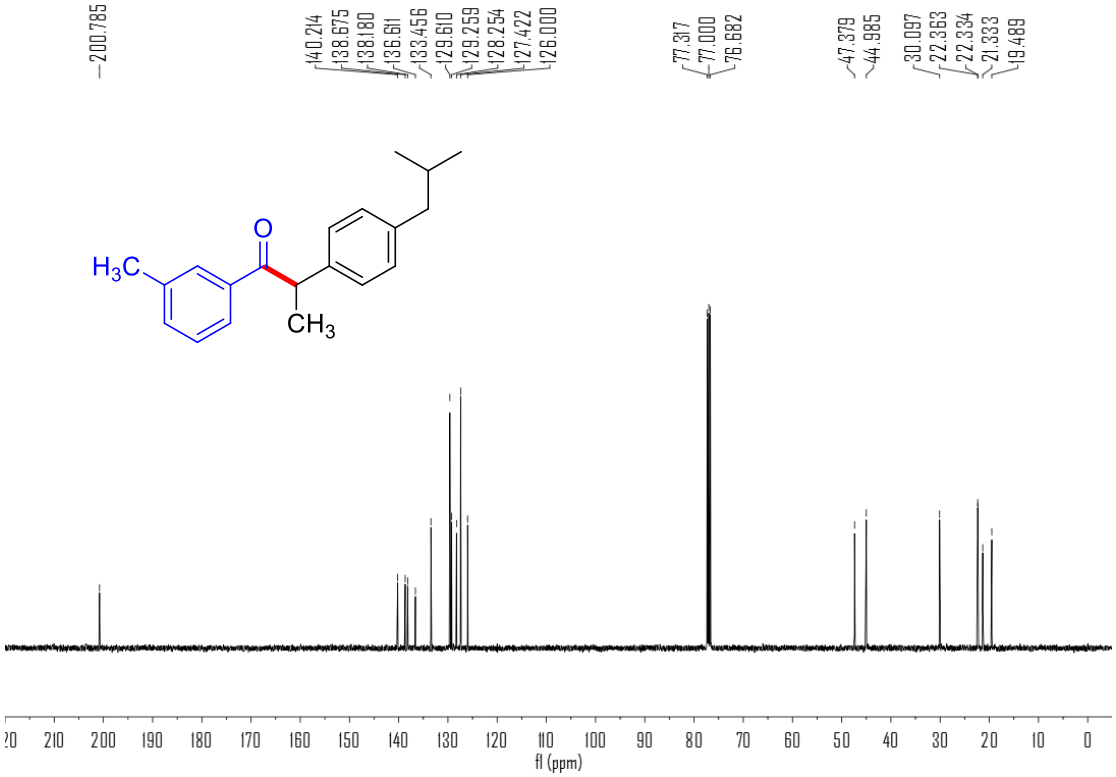
Supplementary Figure 24. ^{1}**H NMR** spectrum of **3j**



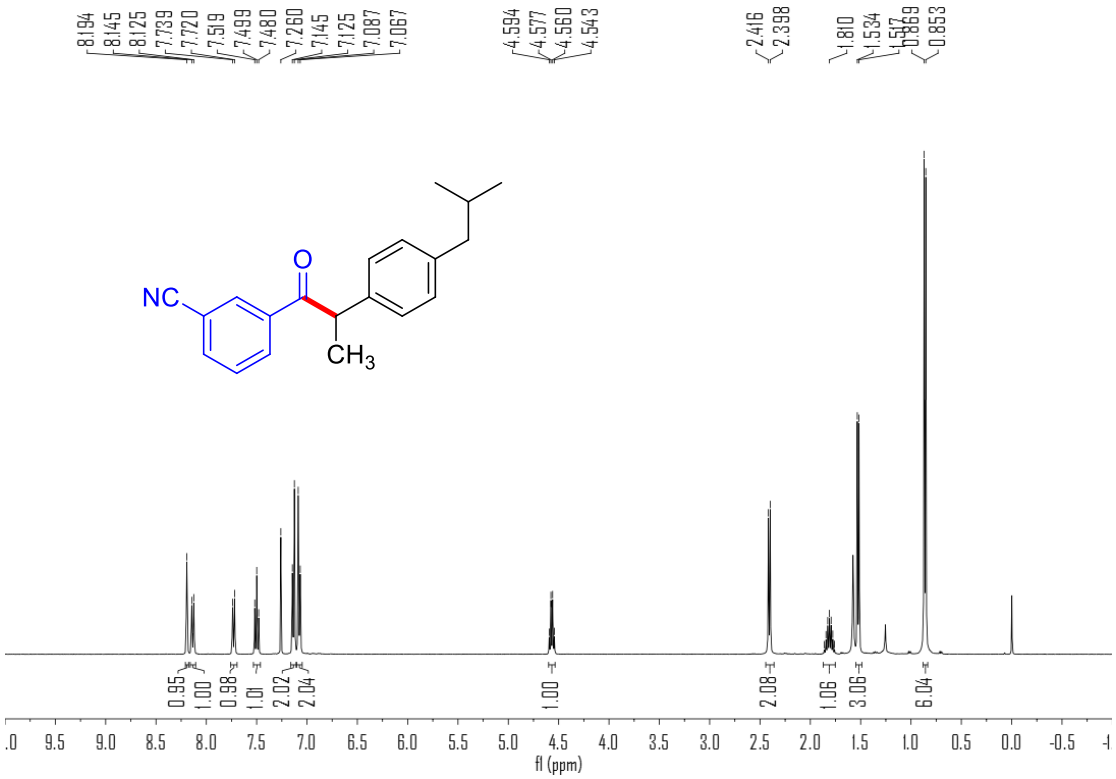
Supplementary Figure 25. ^{13}**C NMR** spectrum of **3j**



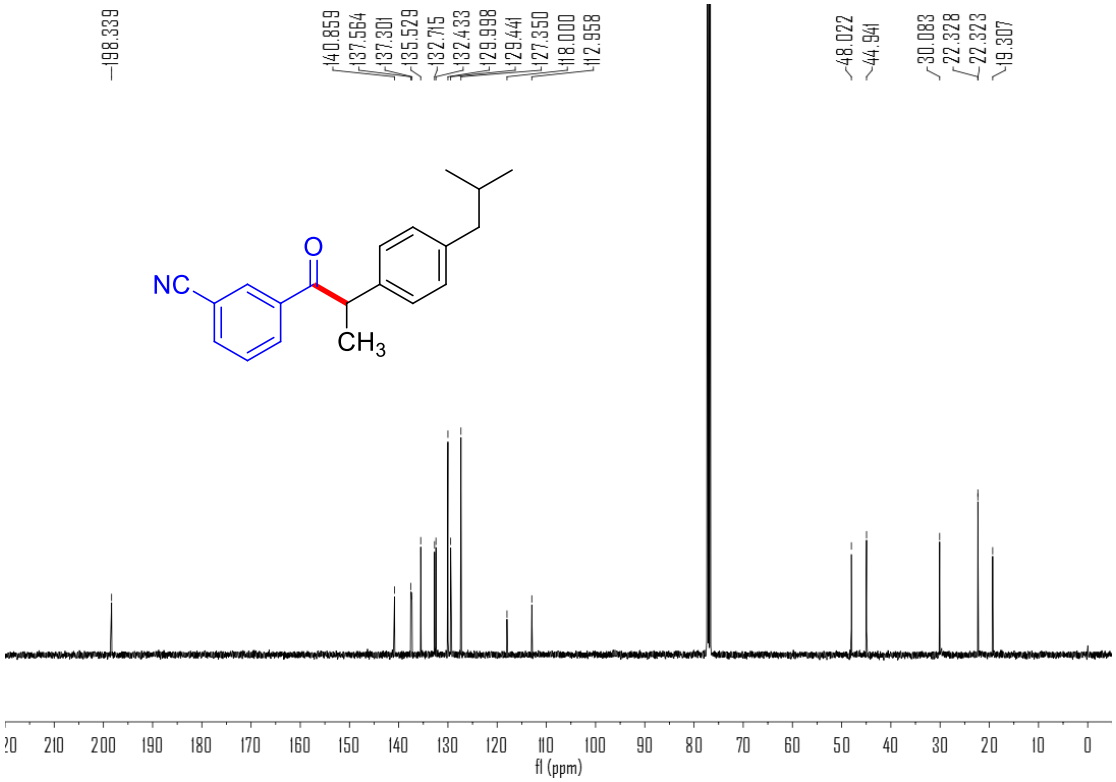
Supplementary Figure 26. ^{1}H NMR spectrum of **3k**



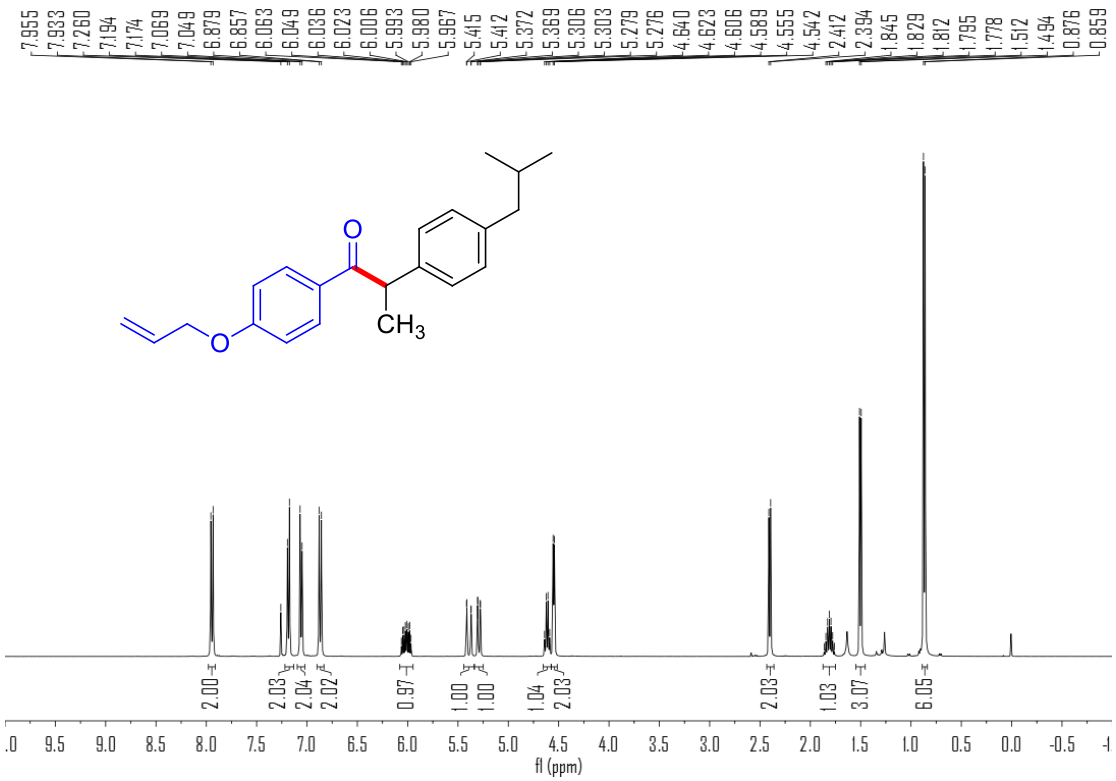
Supplementary Figure 27. ^{13}C NMR spectrum of **3k**



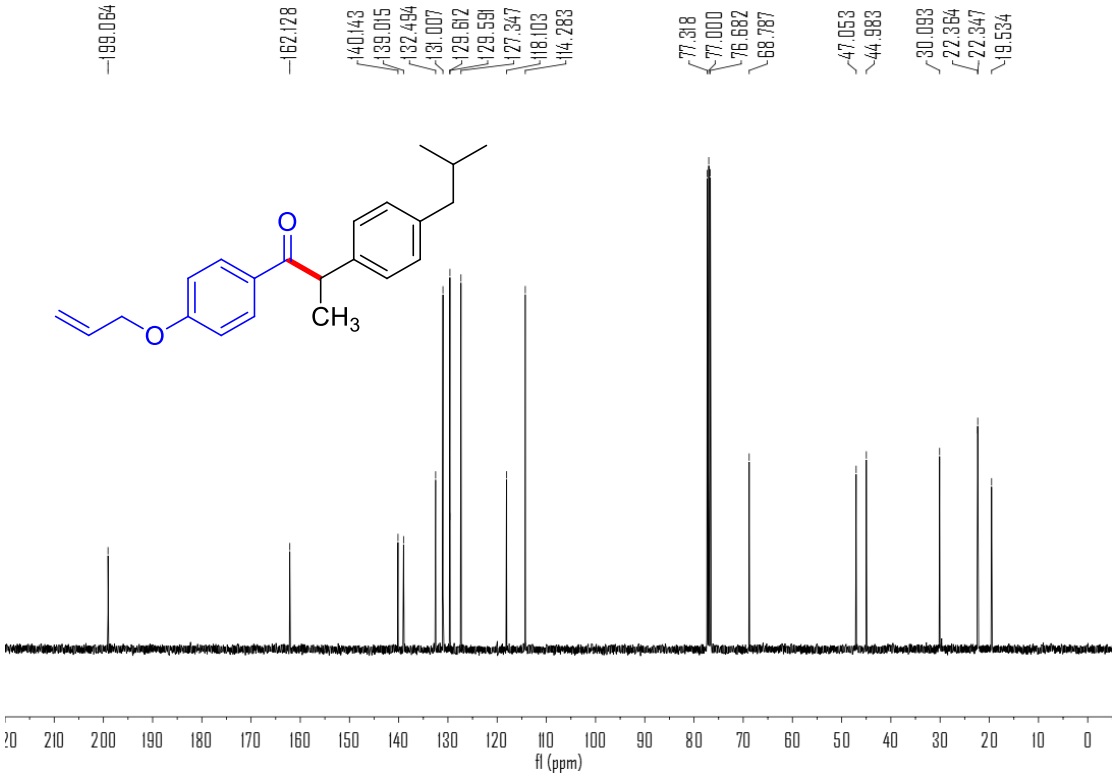
Supplementary Figure 28. ^{1}H NMR spectrum of **3l**



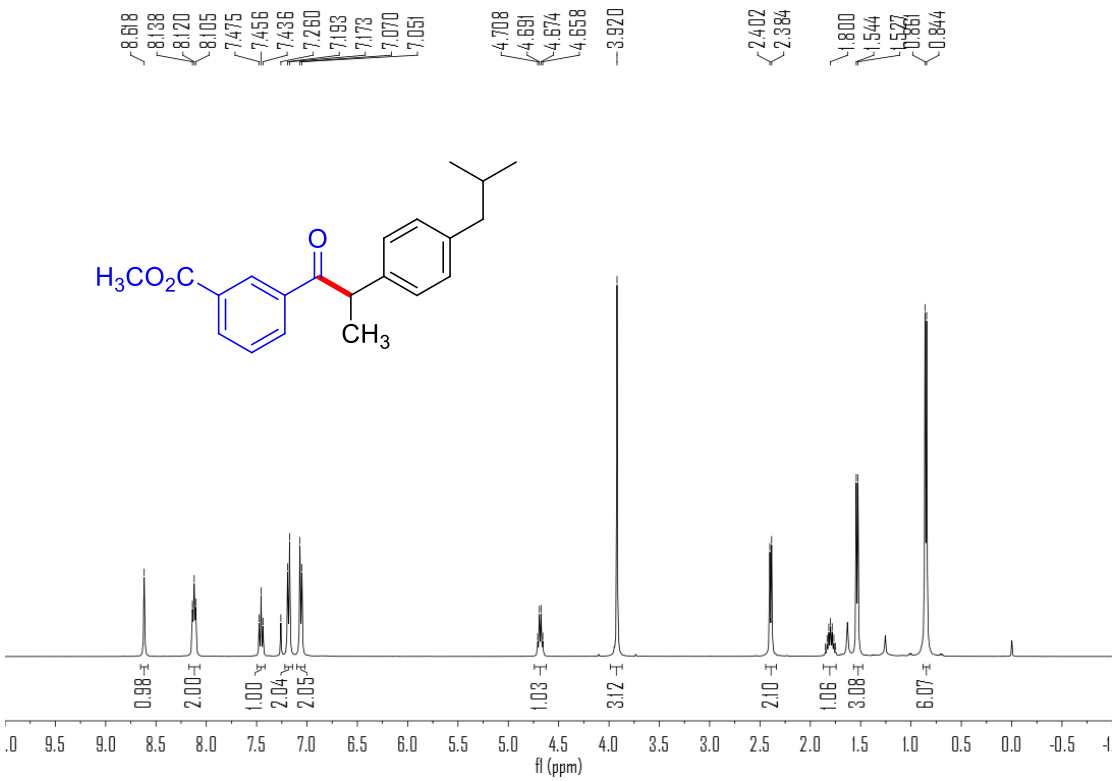
Supplementary Figure 29. ^{13}C NMR spectrum of **3l**



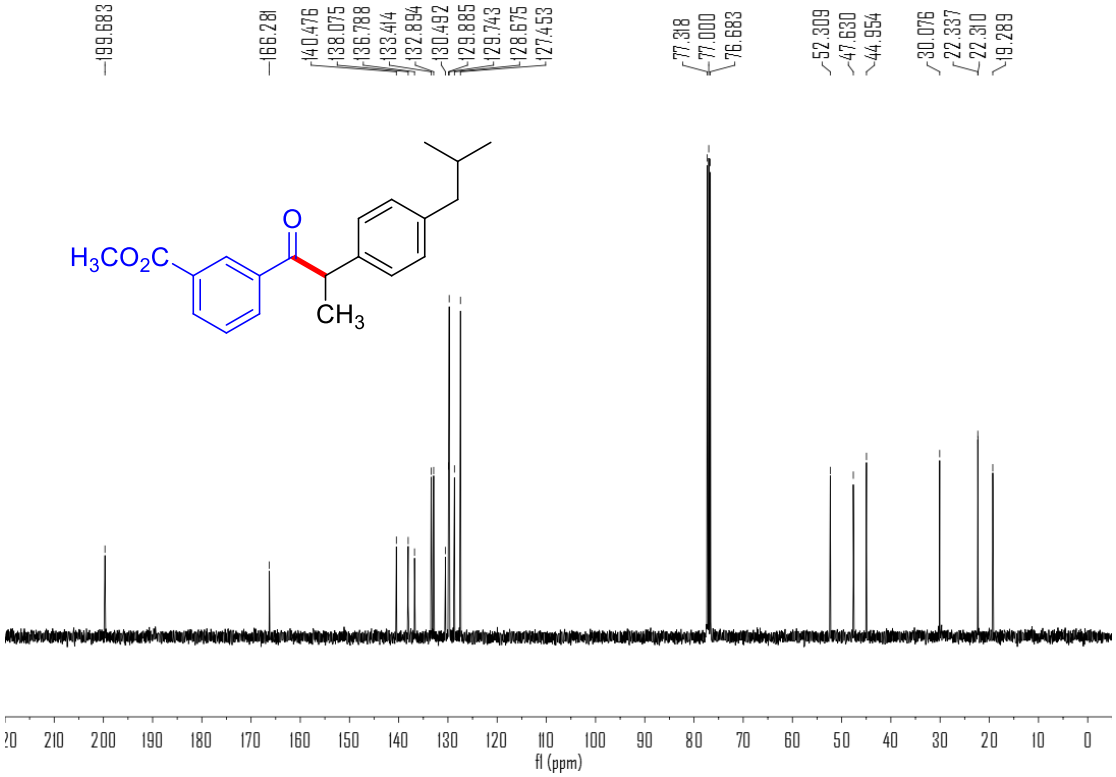
Supplementary Figure 30. ^{1}H NMR spectrum of **3m**



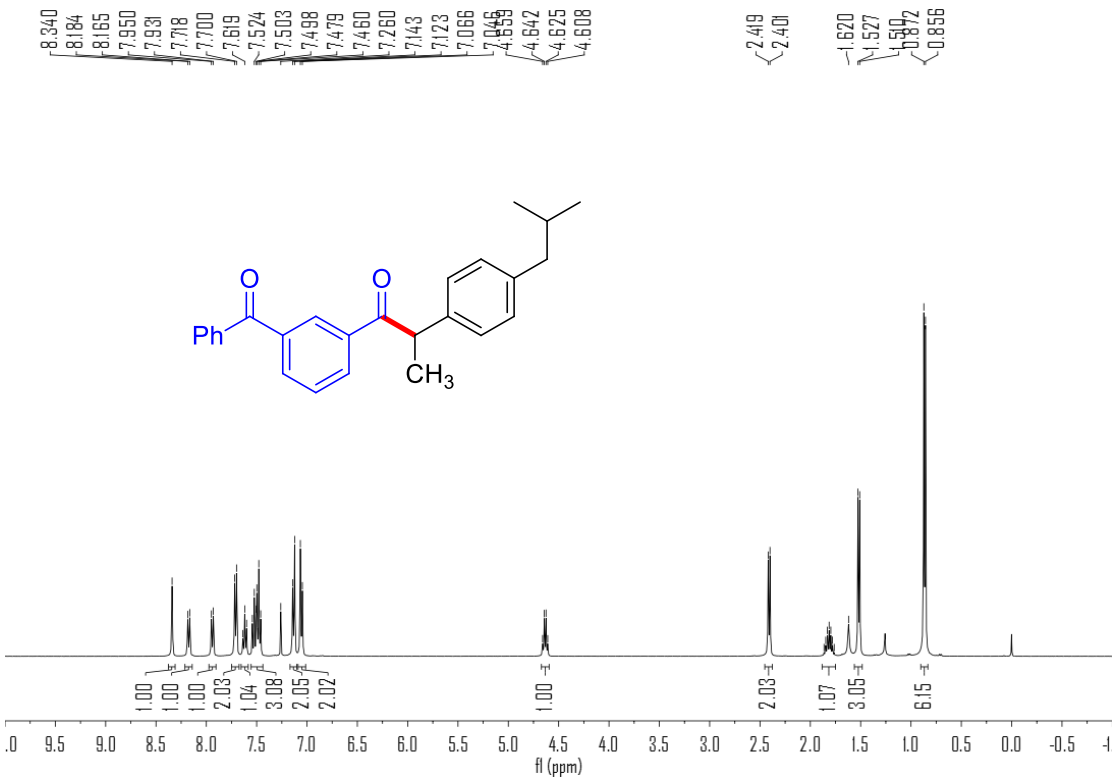
Supplementary Figure 31. ^{13}C NMR spectrum of **3m**



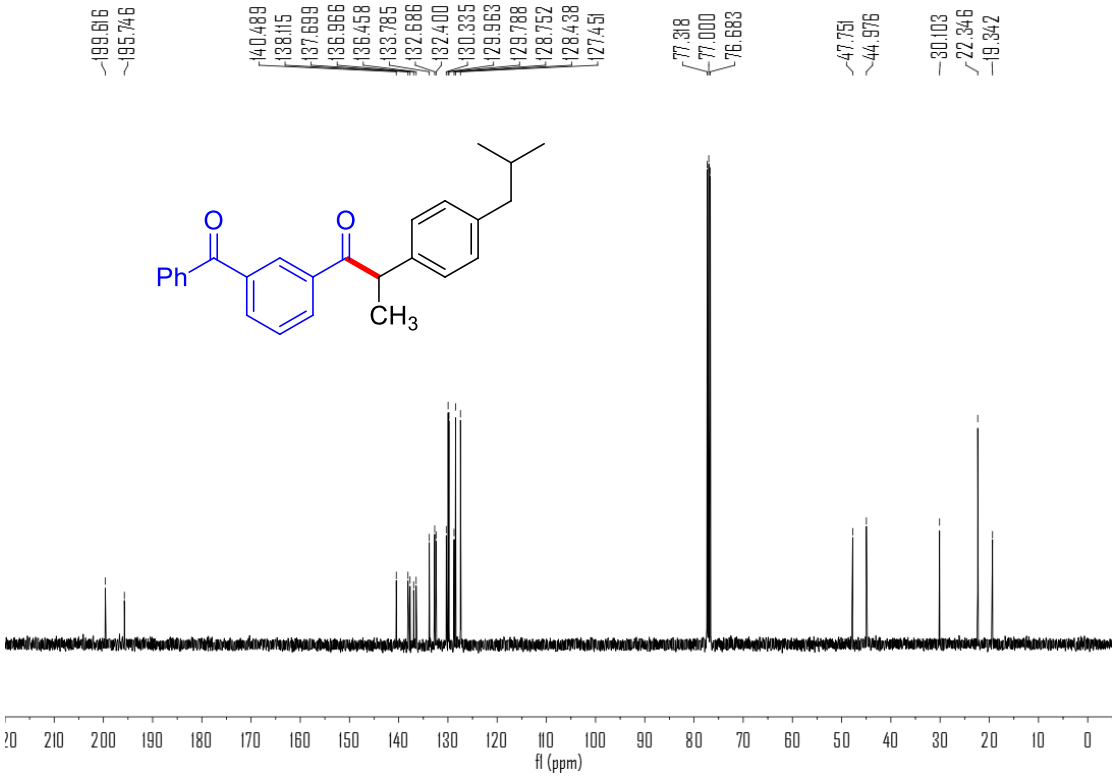
Supplementary Figure 32. ^{1}H NMR spectrum of **3n**



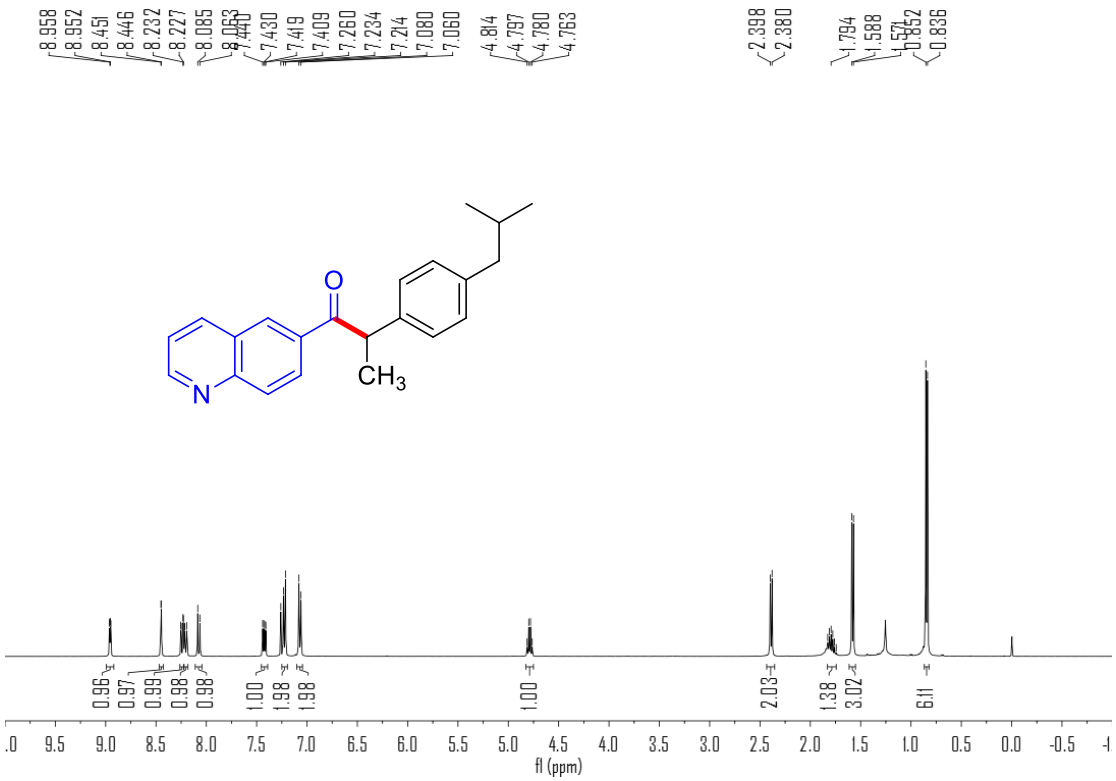
Supplementary Figure 33. ^{13}C NMR spectrum of **3n**



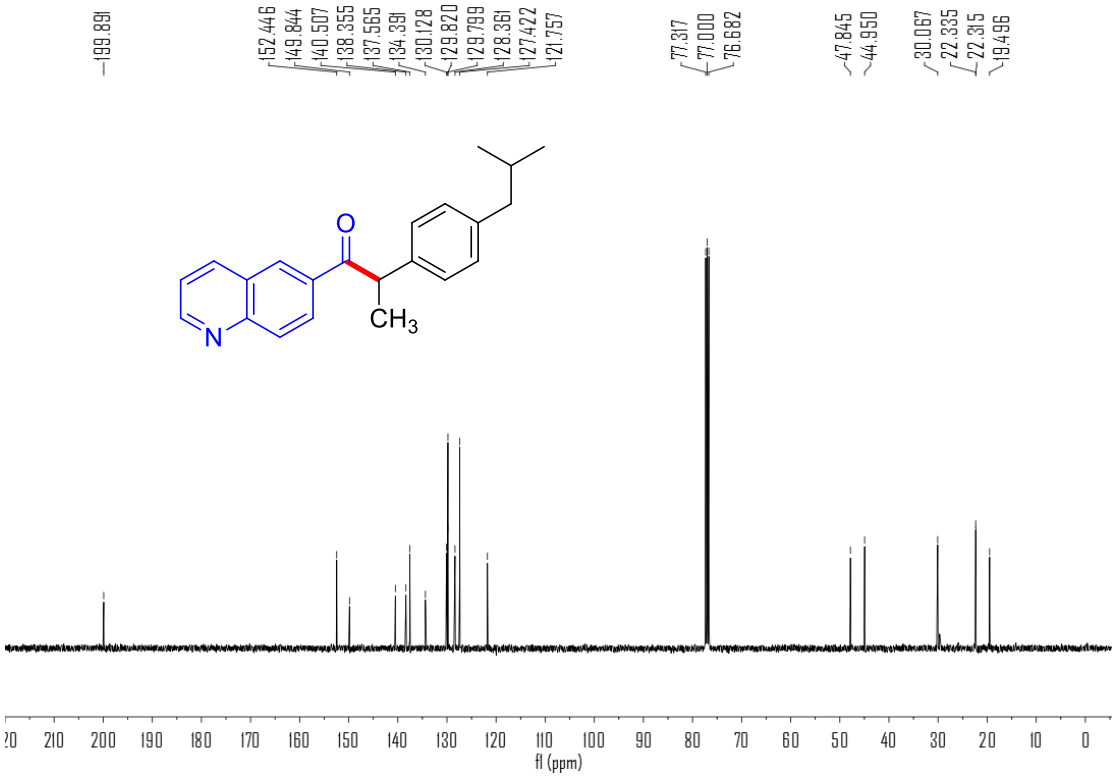
Supplementary Figure 34. ^{1}H NMR spectrum of **3o**



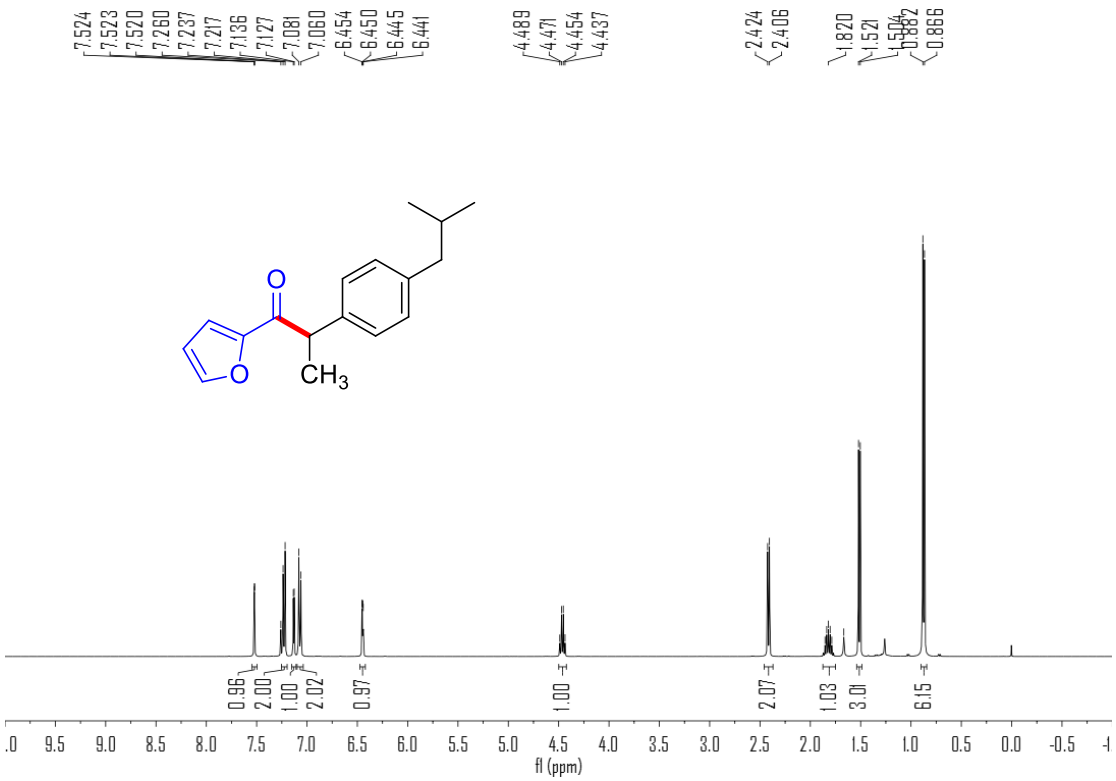
Supplementary Figure 35. ^{13}C NMR spectrum of **3o**



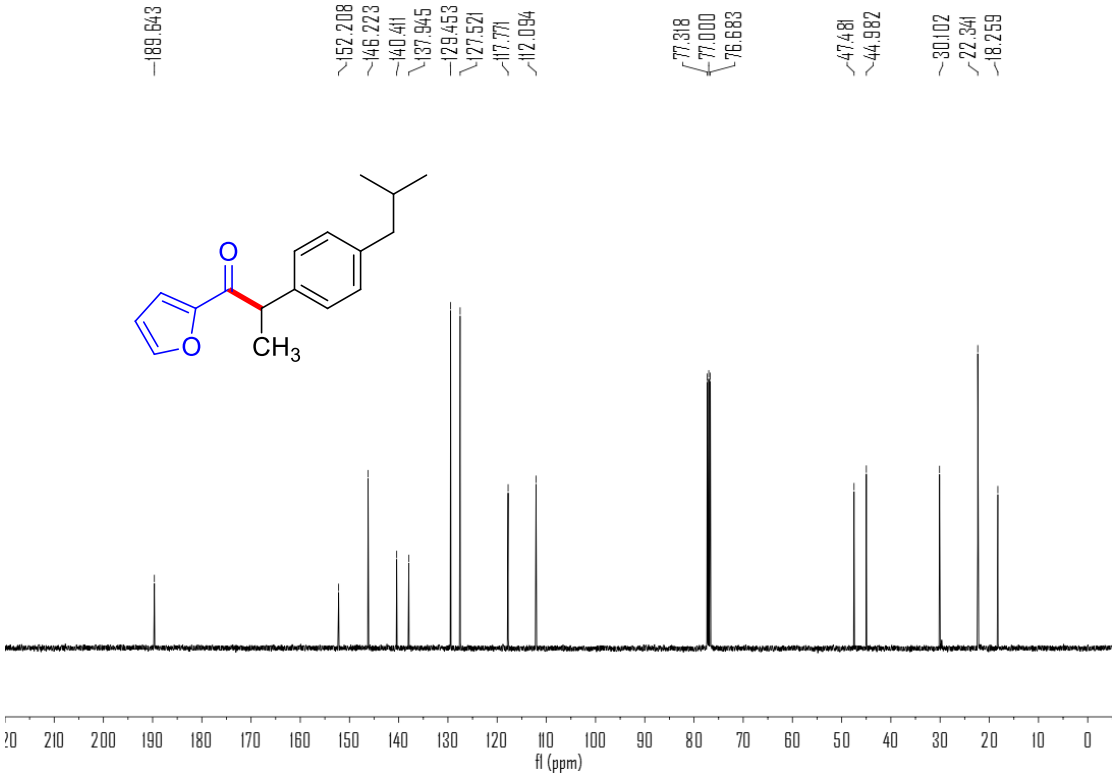
Supplementary Figure 36. ^{1}H NMR spectrum of **3p**



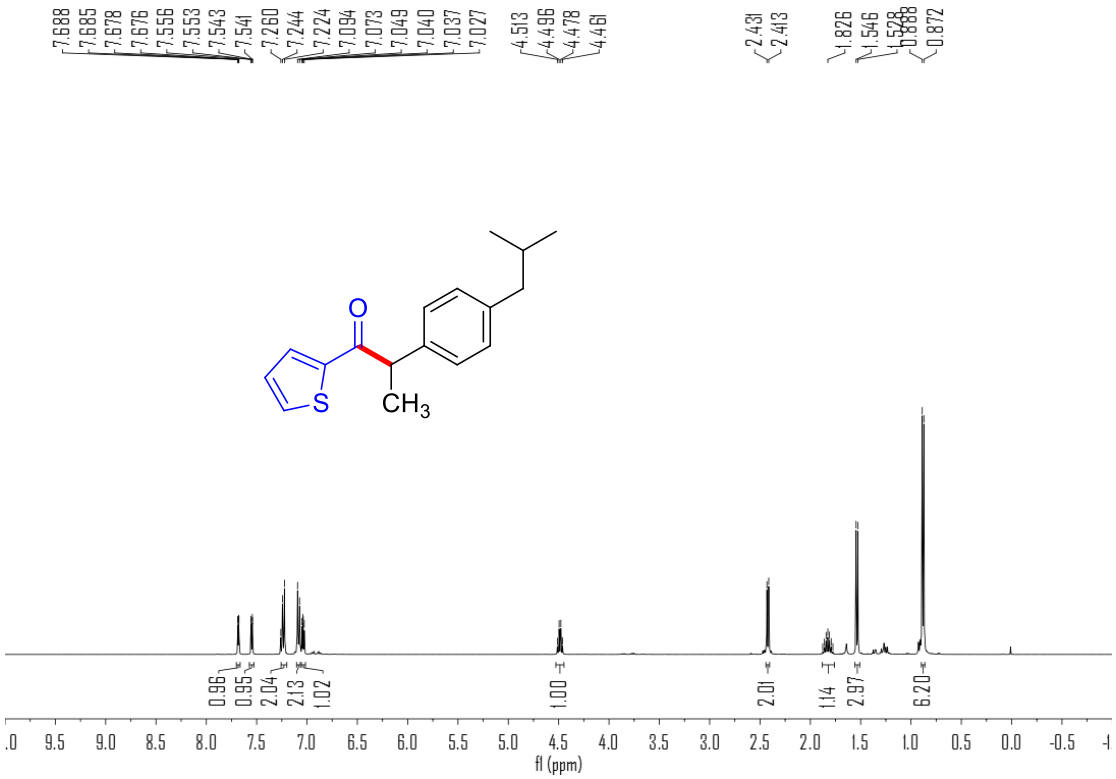
Supplementary Figure 37. ^{13}C NMR spectrum of **3p**



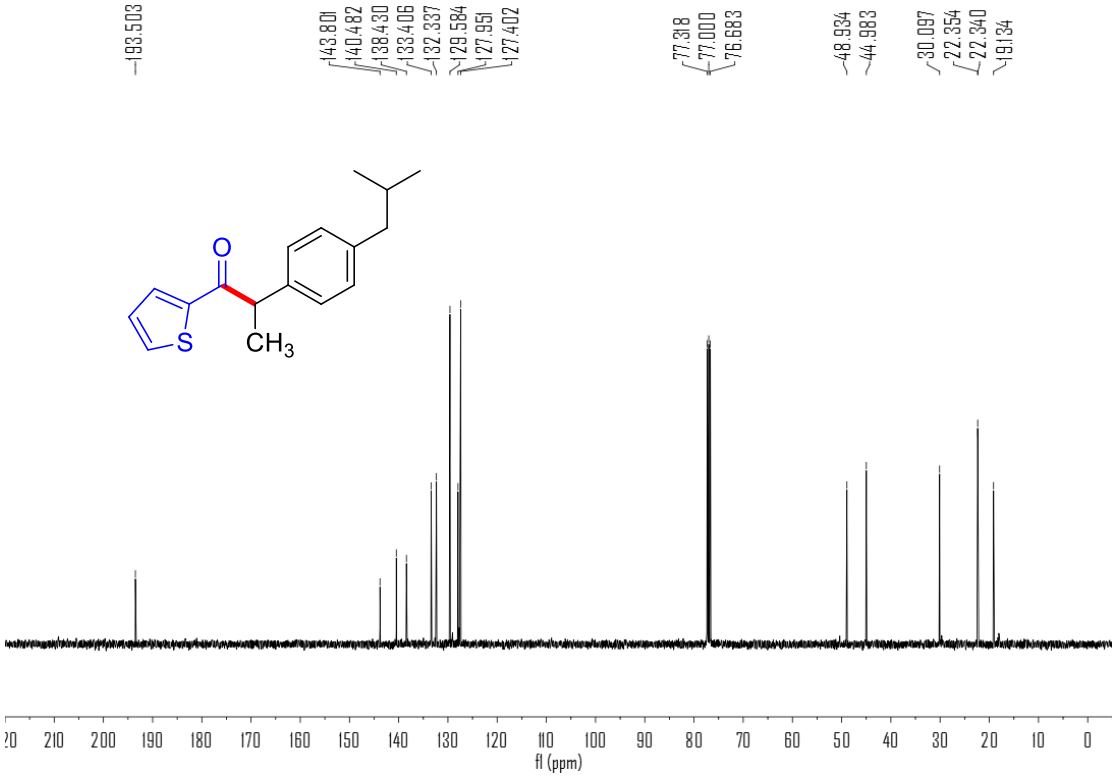
Supplementary Figure 38. ^{1}**H NMR** spectrum of **3q**



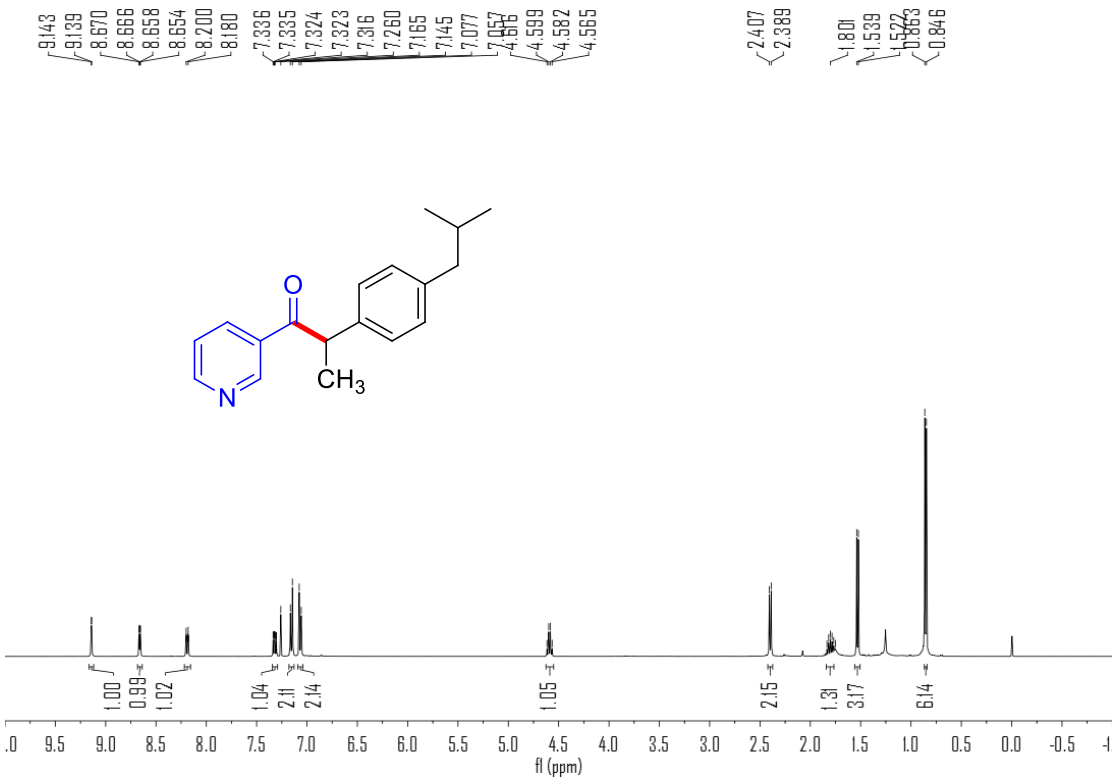
Supplementary Figure 39. ^{13}**C NMR** spectrum of **3q**



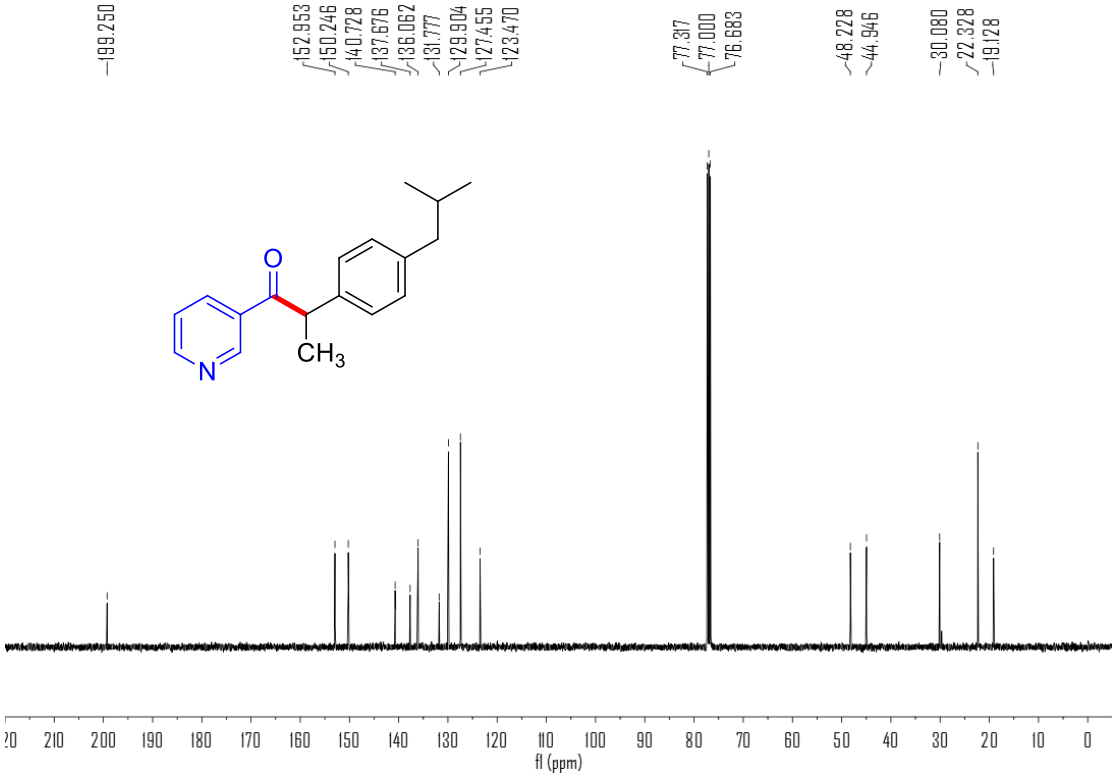
Supplementary Figure 40. ^{1}H NMR spectrum of **3r**



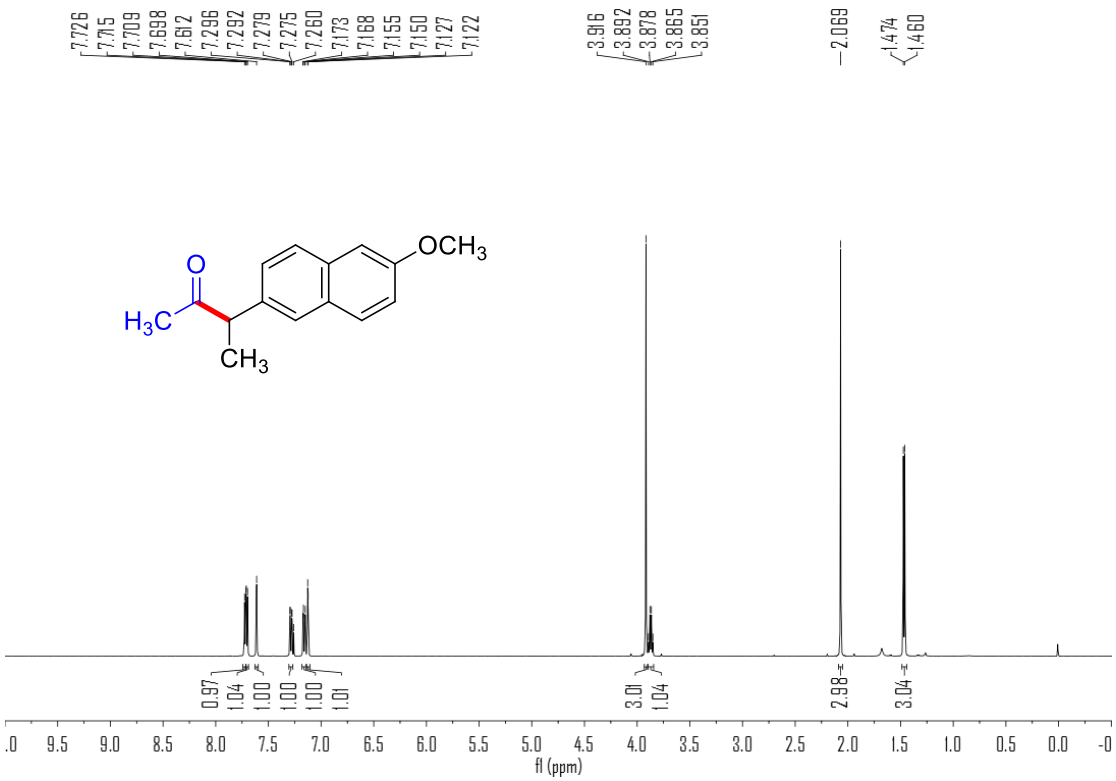
Supplementary Figure 41. ^{13}C NMR spectrum of **3r**



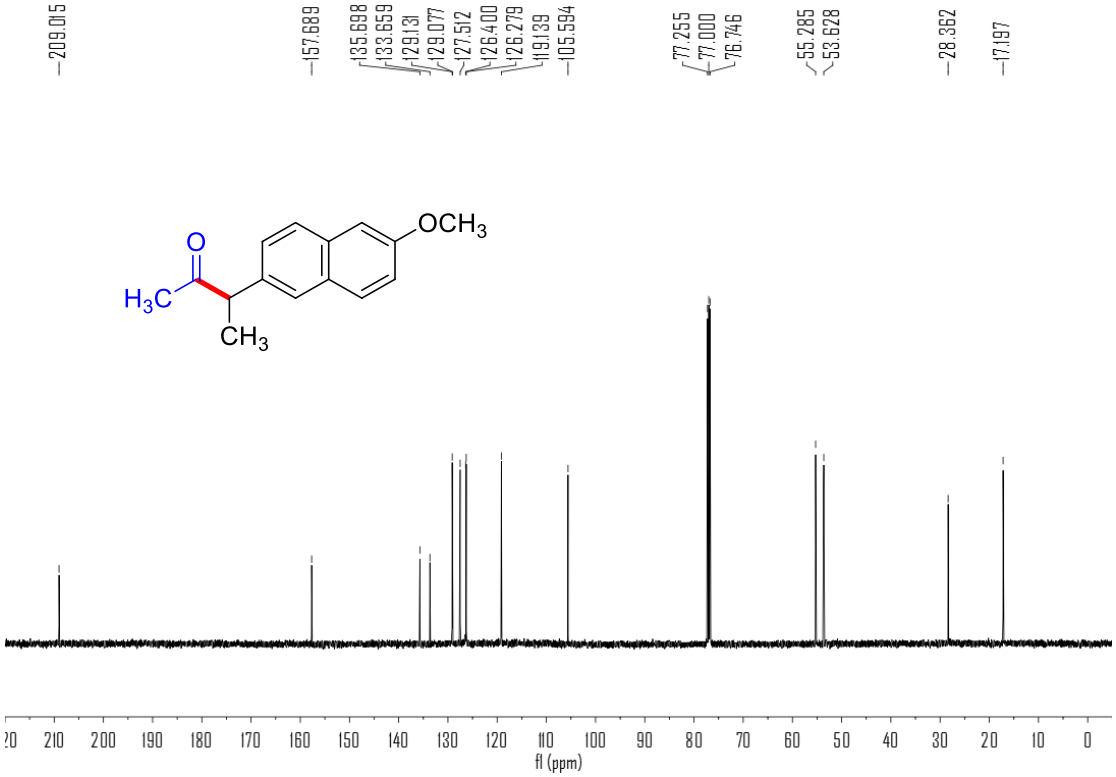
Supplementary Figure 42. ^{1}**H NMR** spectrum of **3s**



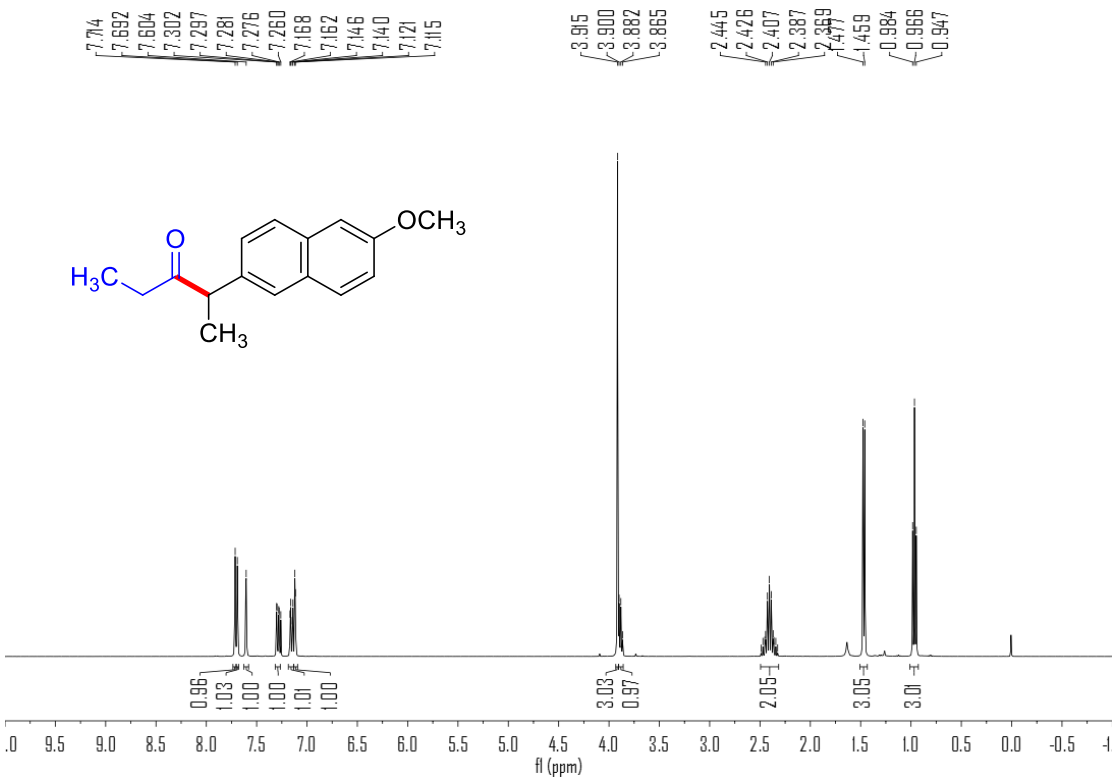
Supplementary Figure 43. ^{13}**C NMR** spectrum of **3s**



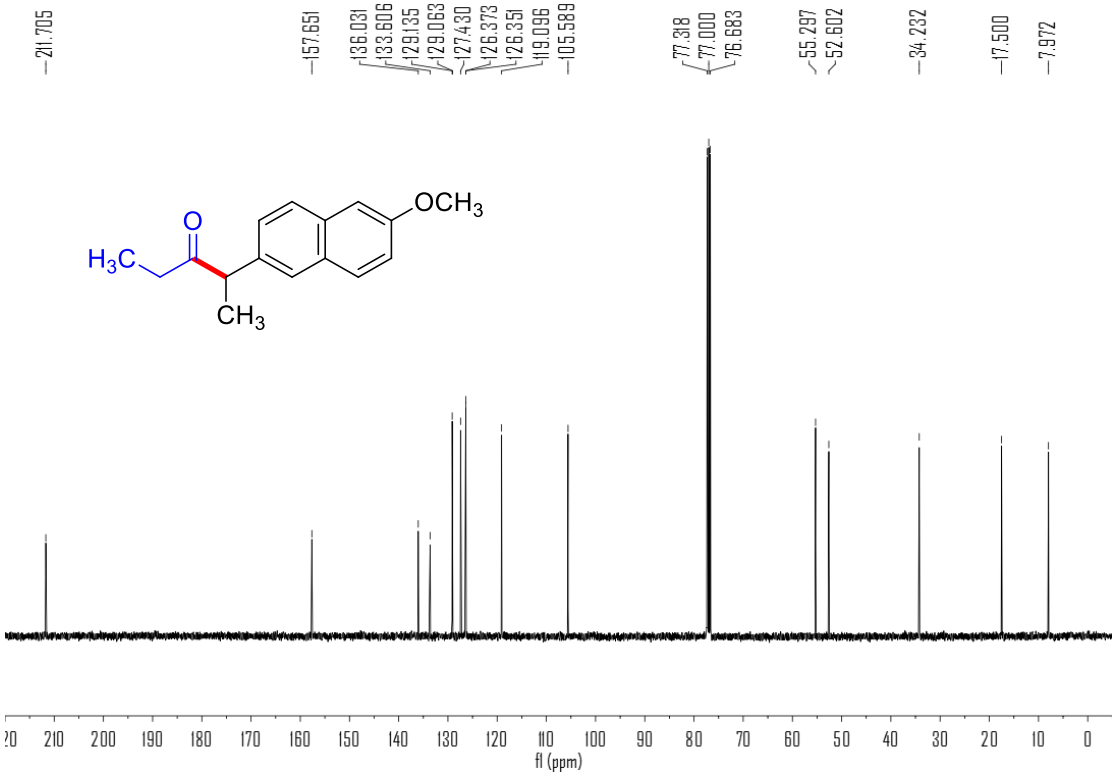
Supplementary Figure 44. ^{1}H NMR spectrum of **3t**



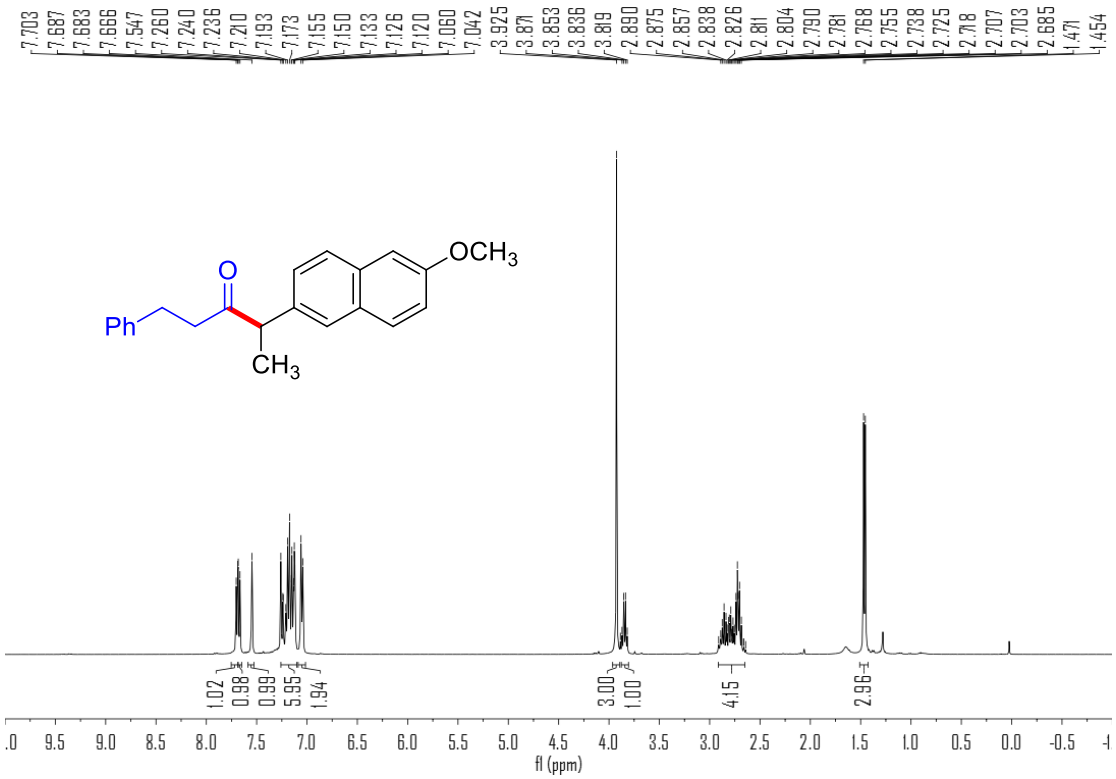
Supplementary Figure 45. ^{13}C NMR spectrum of **3t**



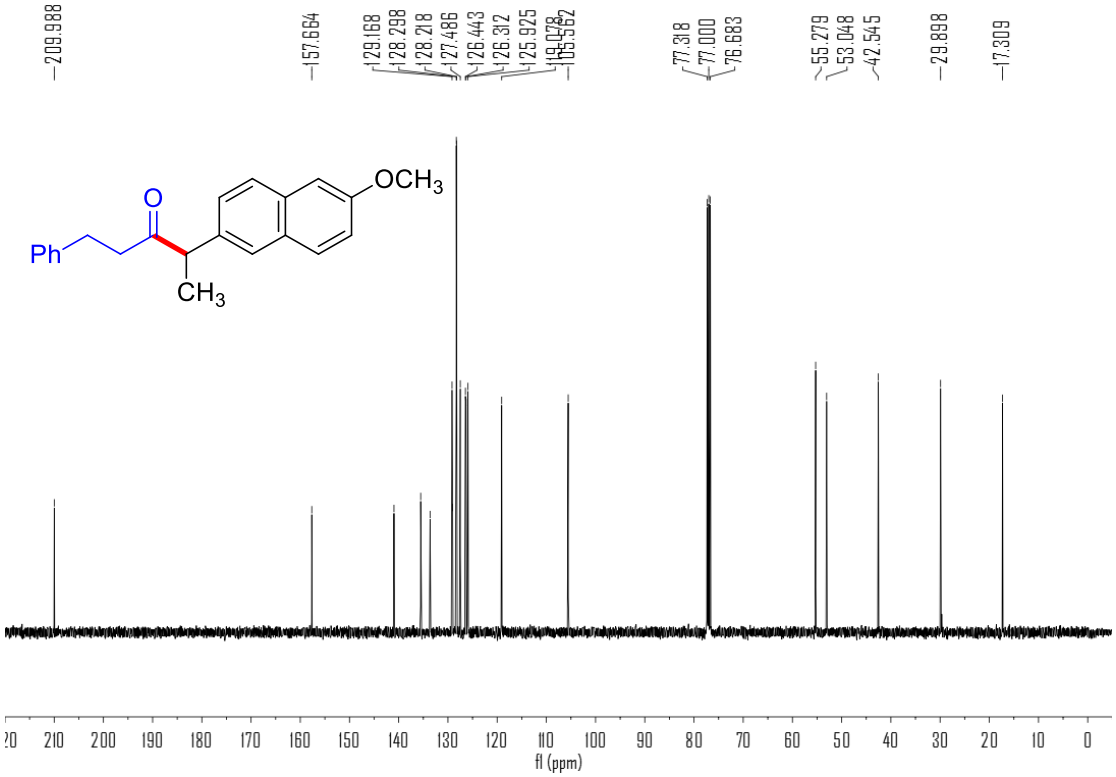
Supplementary Figure 46. ^{1}H NMR spectrum of **3u**



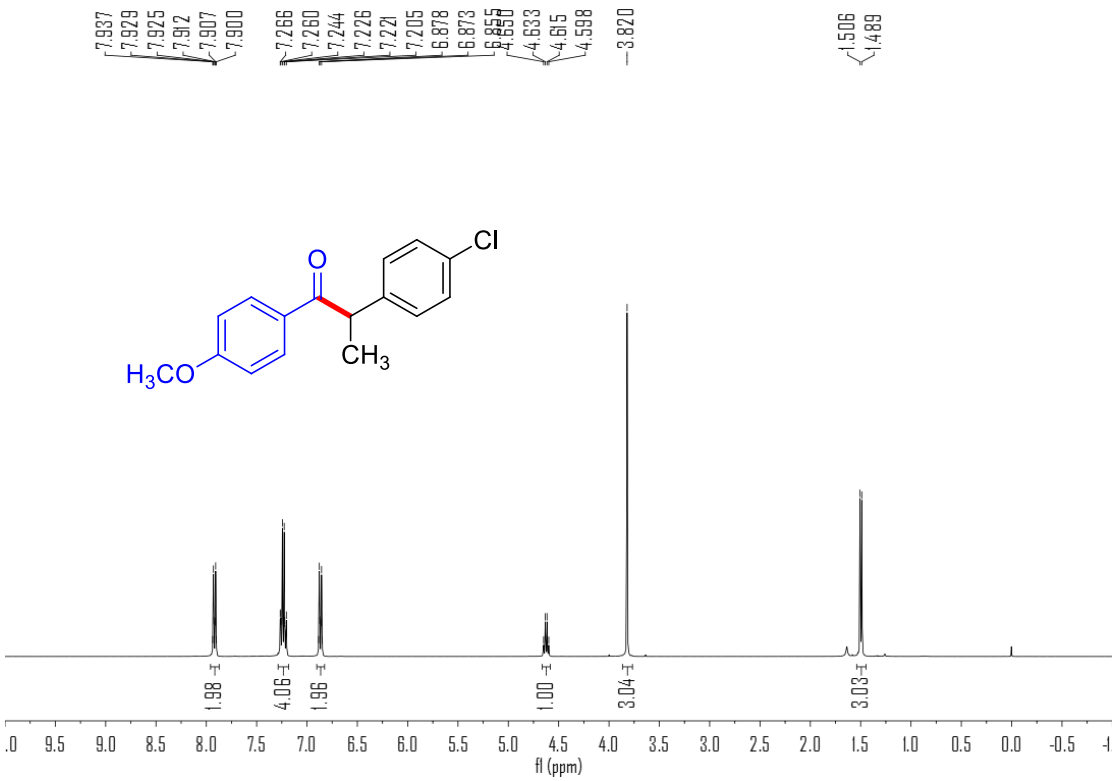
Supplementary Figure 47. ^{13}C NMR spectrum of **3u**



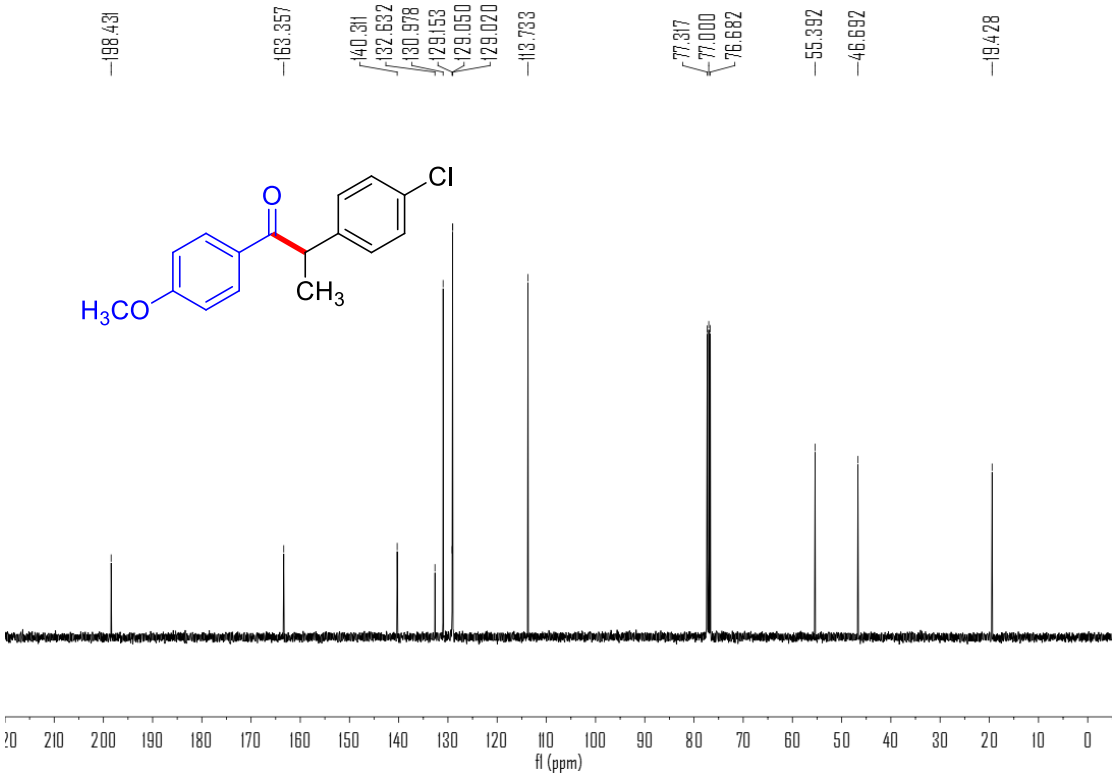
Supplementary Figure 48. ^{1}H NMR spectrum of **3v**



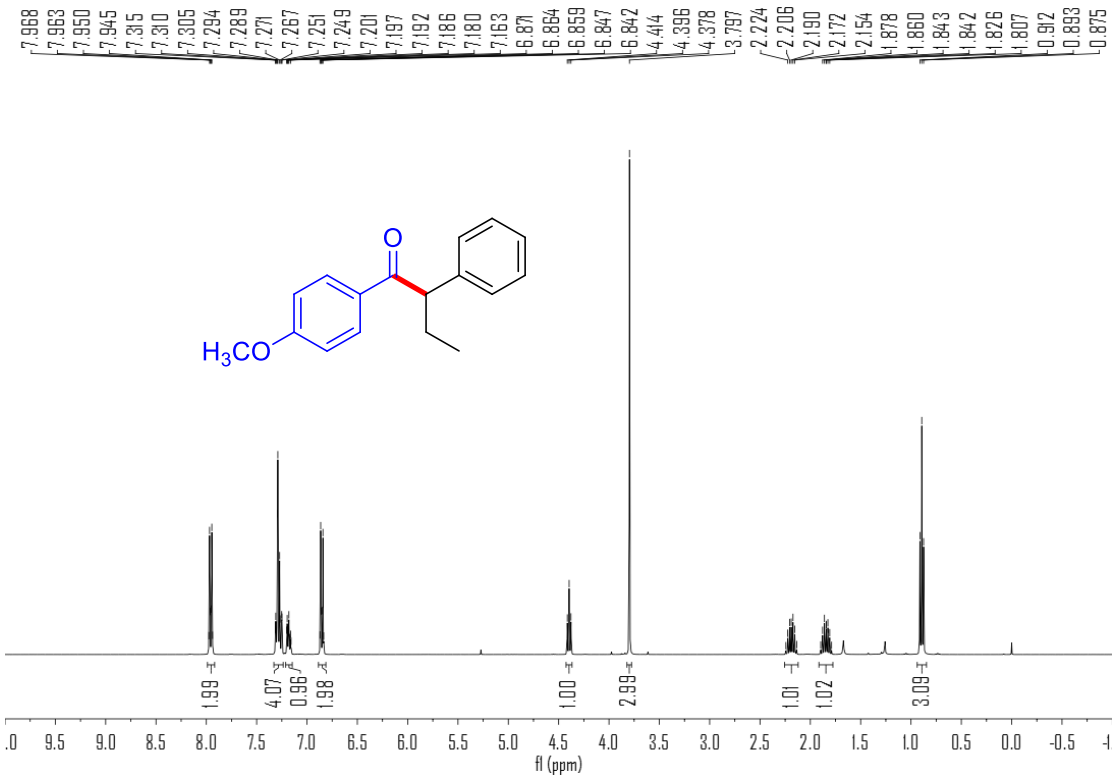
Supplementary Figure 49. ^{13}C NMR spectrum of **3v**



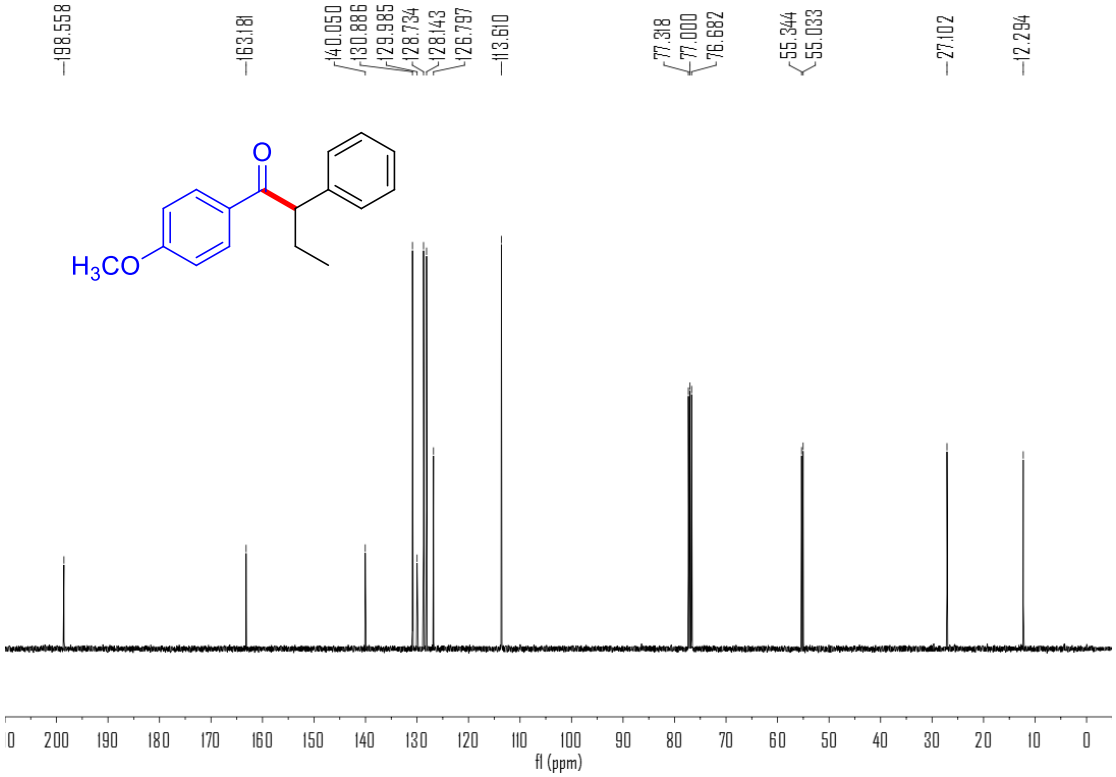
Supplementary Figure 50. ^{1}H NMR spectrum of **3w**



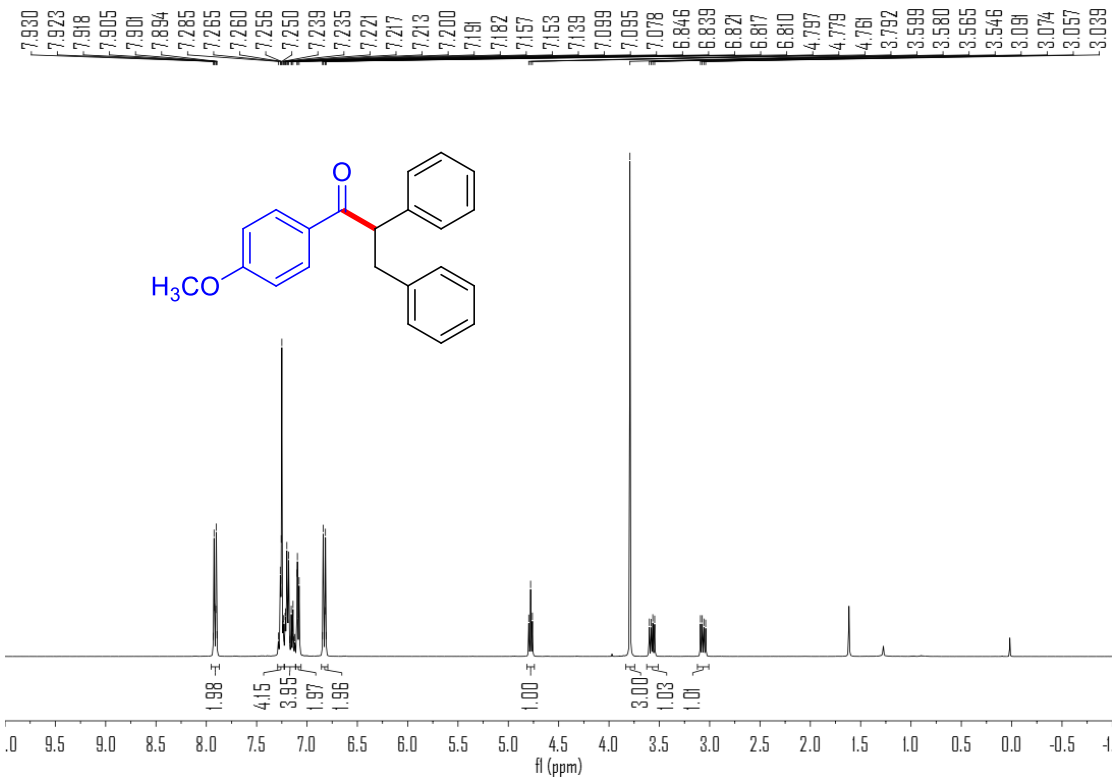
Supplementary Figure 51. ^{13}C NMR spectrum of **3w**



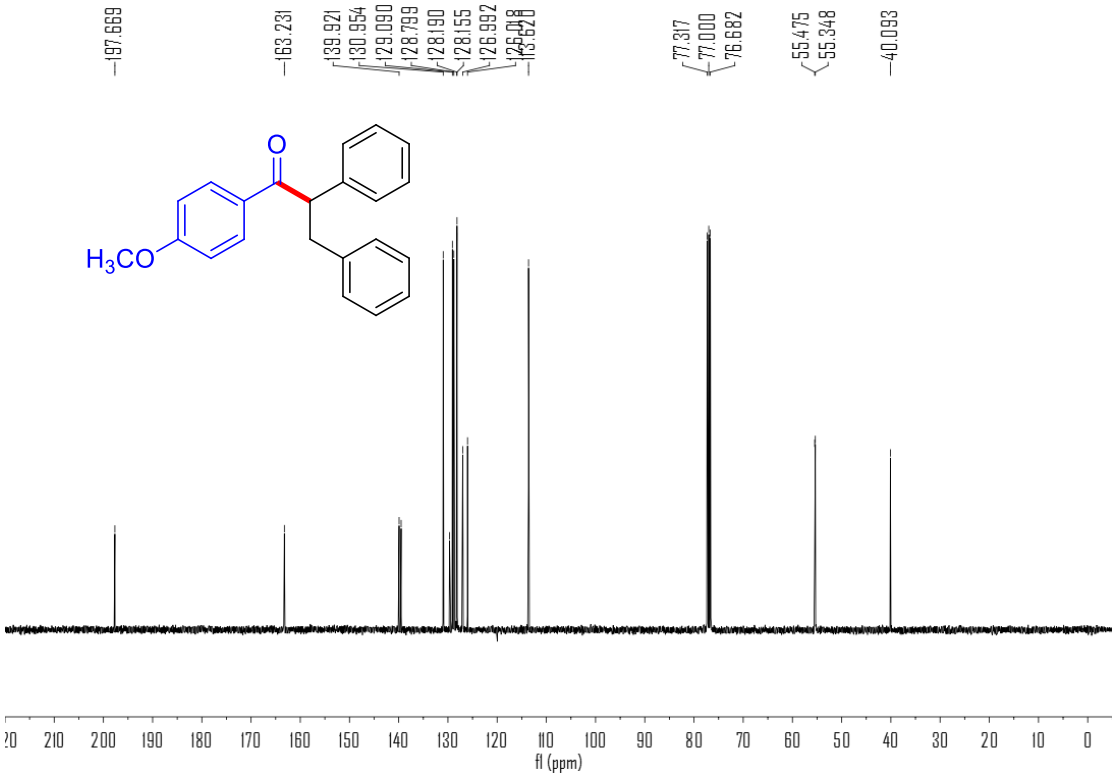
Supplementary Figure 52. ^{1}H NMR spectrum of **3x**



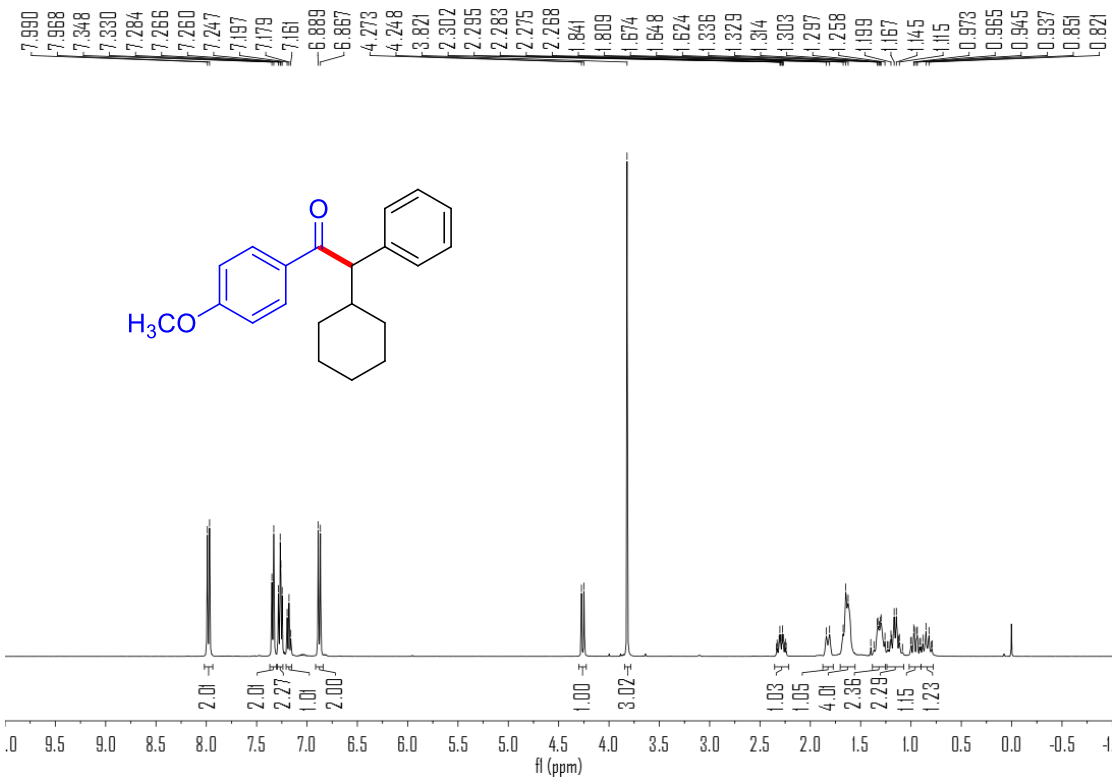
Supplementary Figure 53. ^{13}C NMR spectrum of **3x**



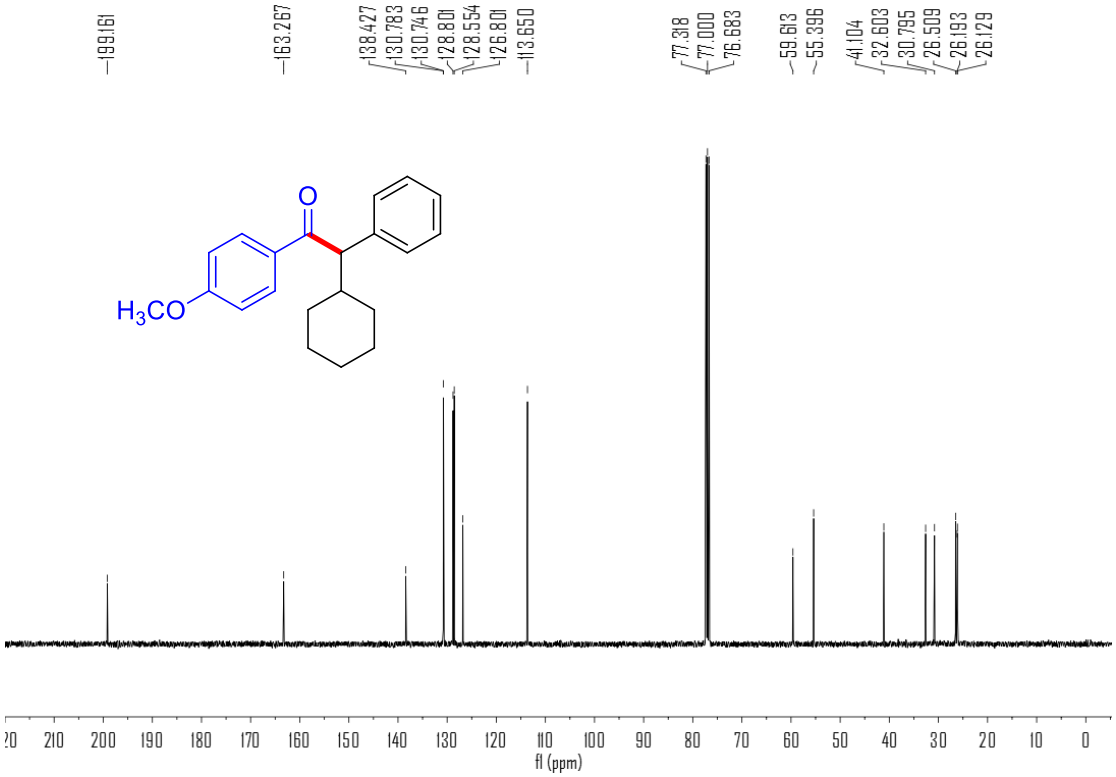
Supplementary Figure 54. ^{1}**H NMR** spectrum of **3y**



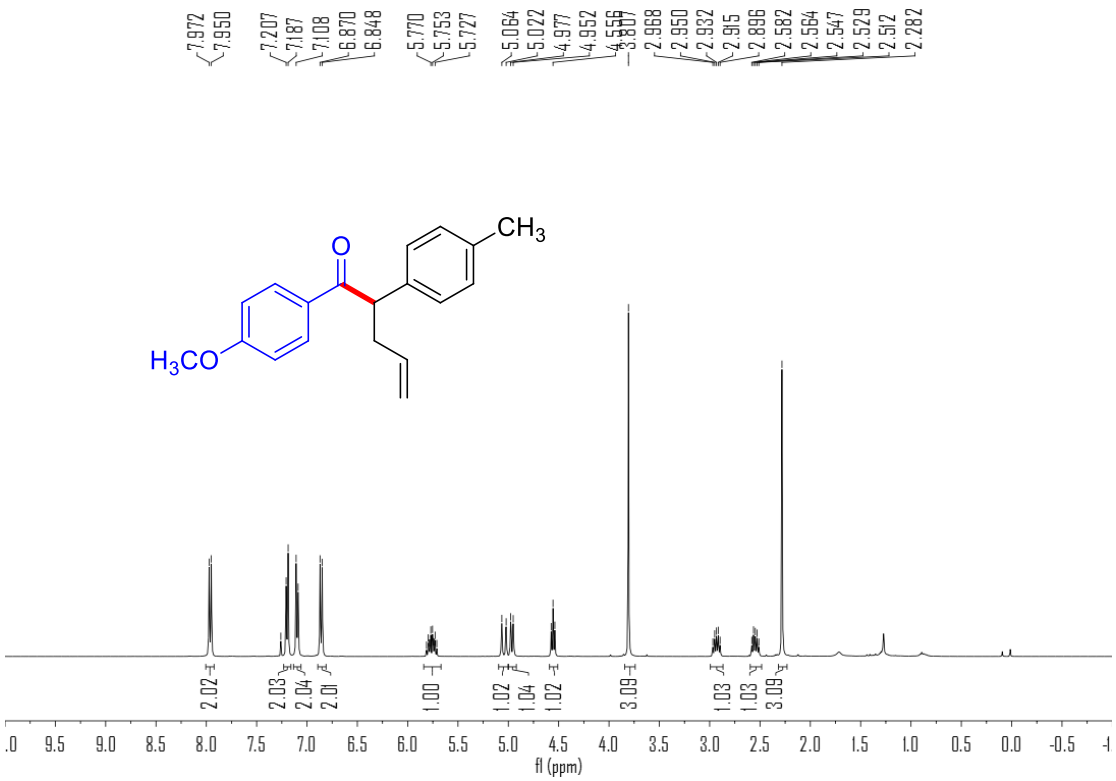
Supplementary Figure 55. ^{13}**C NMR** spectrum of **3y**



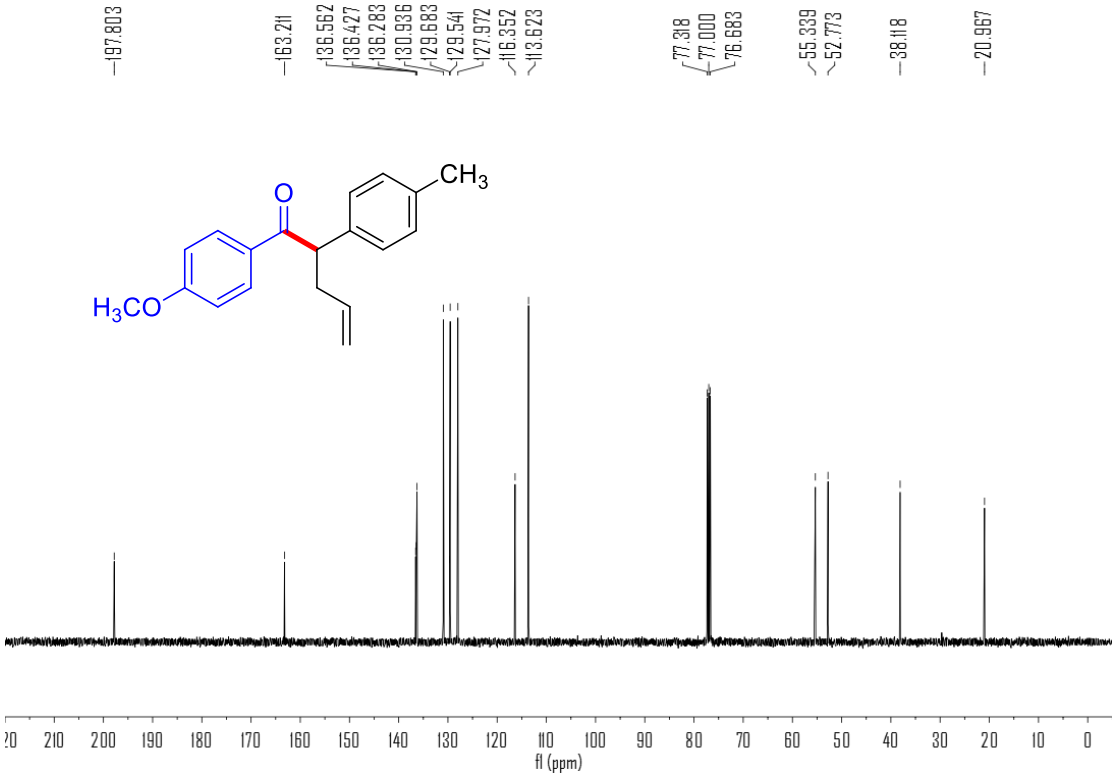
Supplementary Figure 56. ^{1}**H NMR** spectrum of **3z**



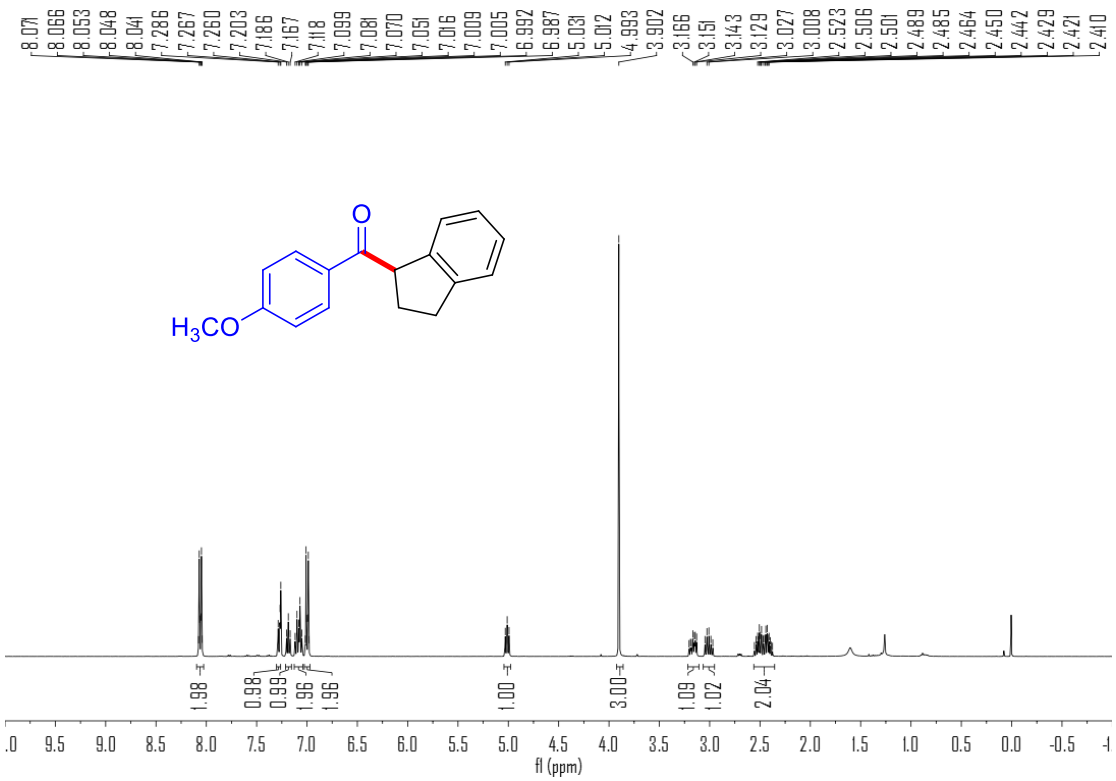
Supplementary Figure 57. ^{13}**C NMR** spectrum of **3z**



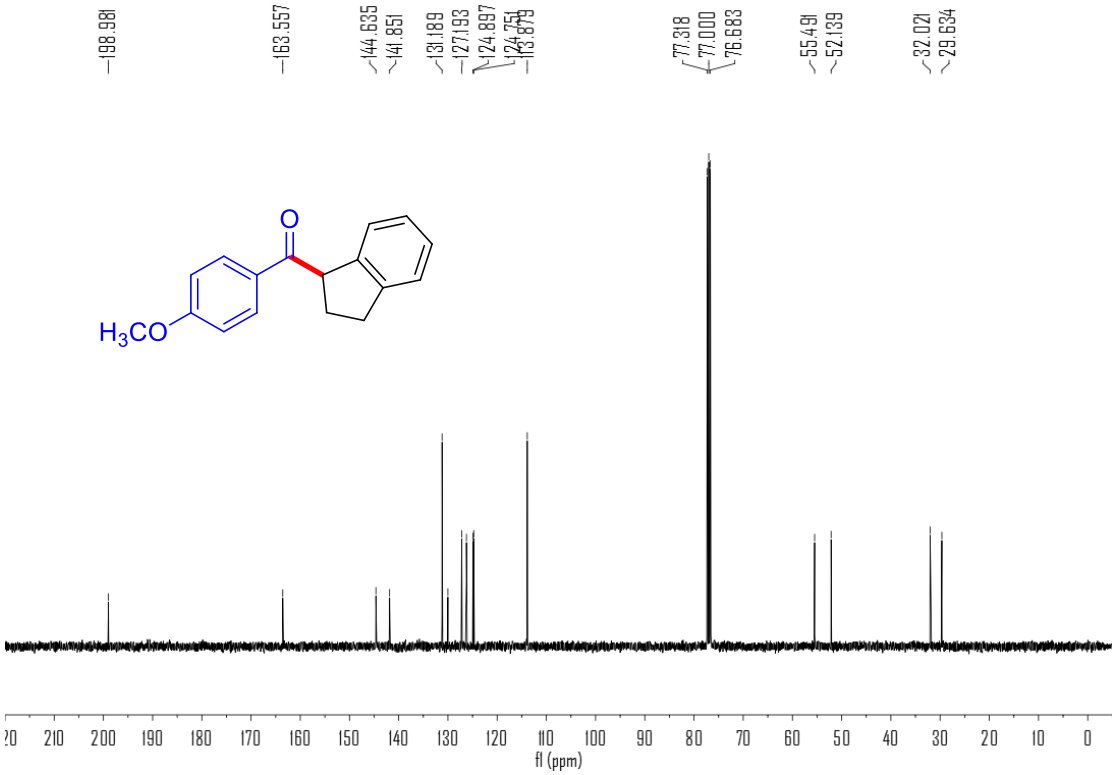
Supplementary Figure 58. ^{1}H NMR spectrum of **3aa**



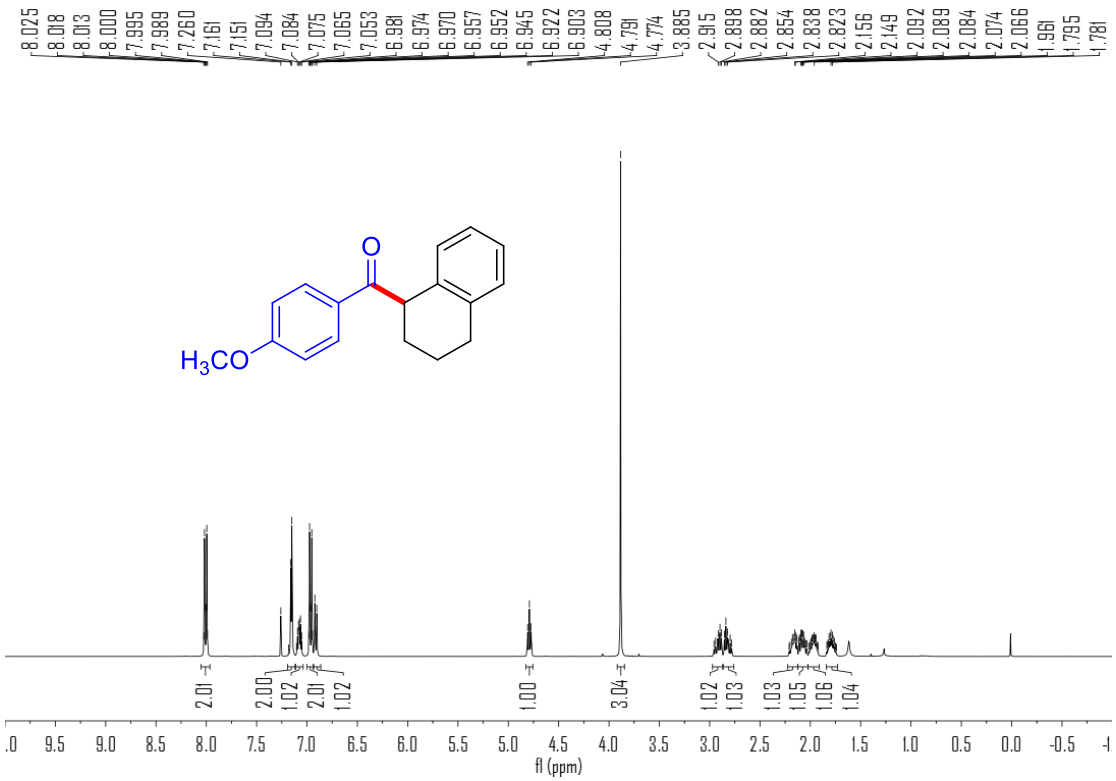
Supplementary Figure 59. ^{13}C NMR spectrum of **3aa**



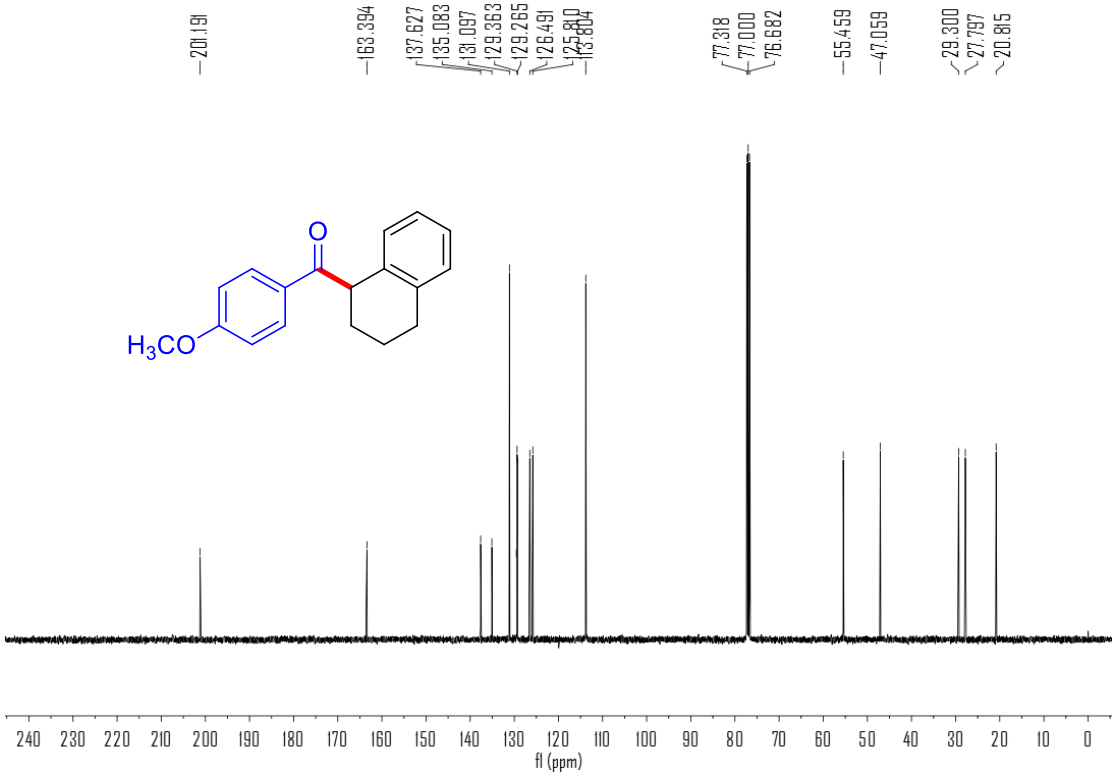
Supplementary Figure 60. ^{1}**H NMR** spectrum of **3ab**



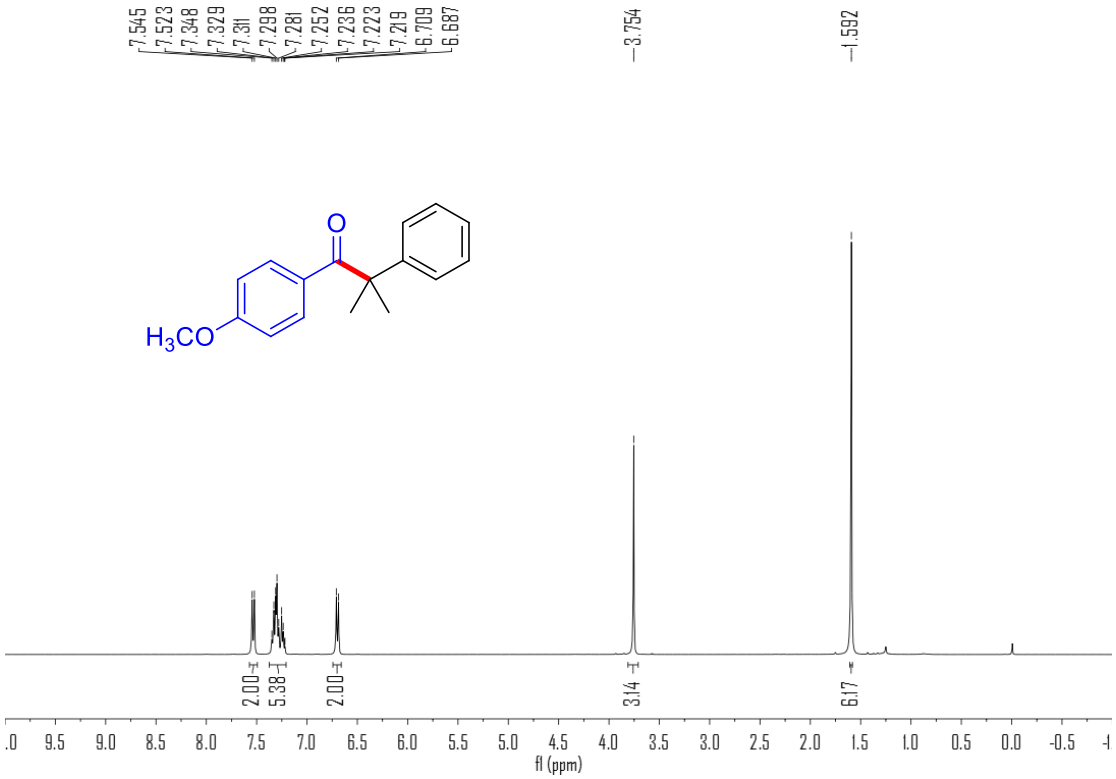
Supplementary Figure 61. ^{13}**C NMR** spectrum of **3ab**



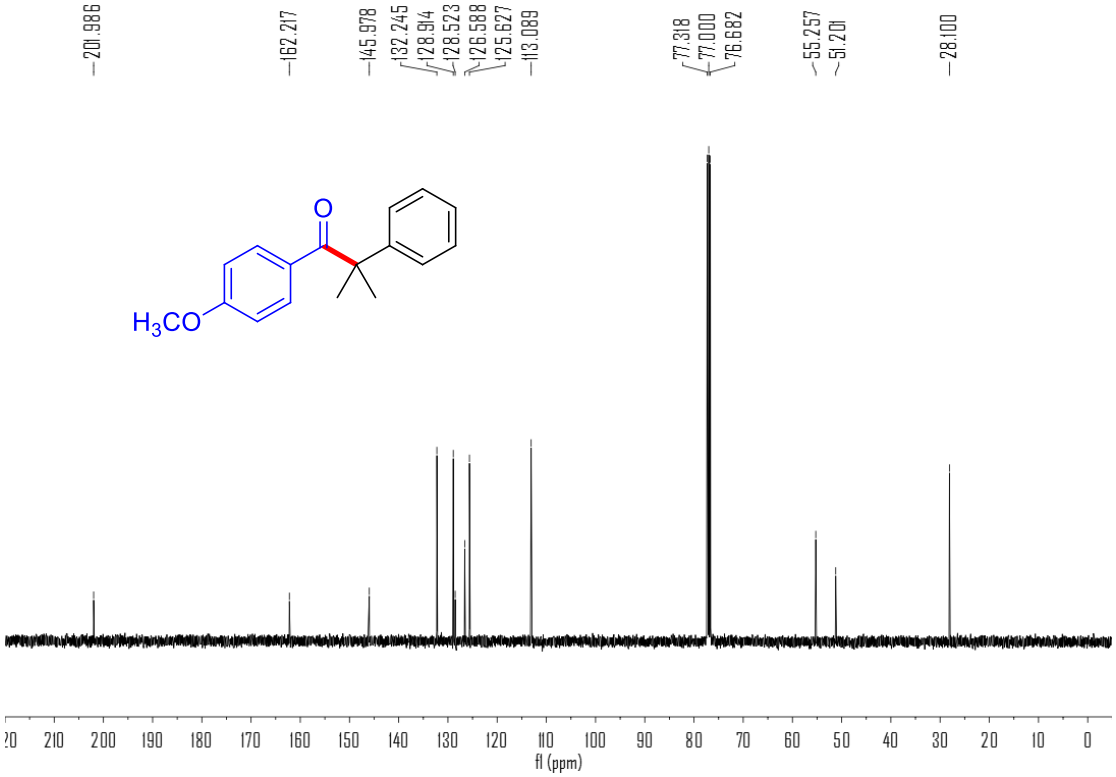
Supplementary Figure 62. ^{1}H NMR spectrum of **3ac**



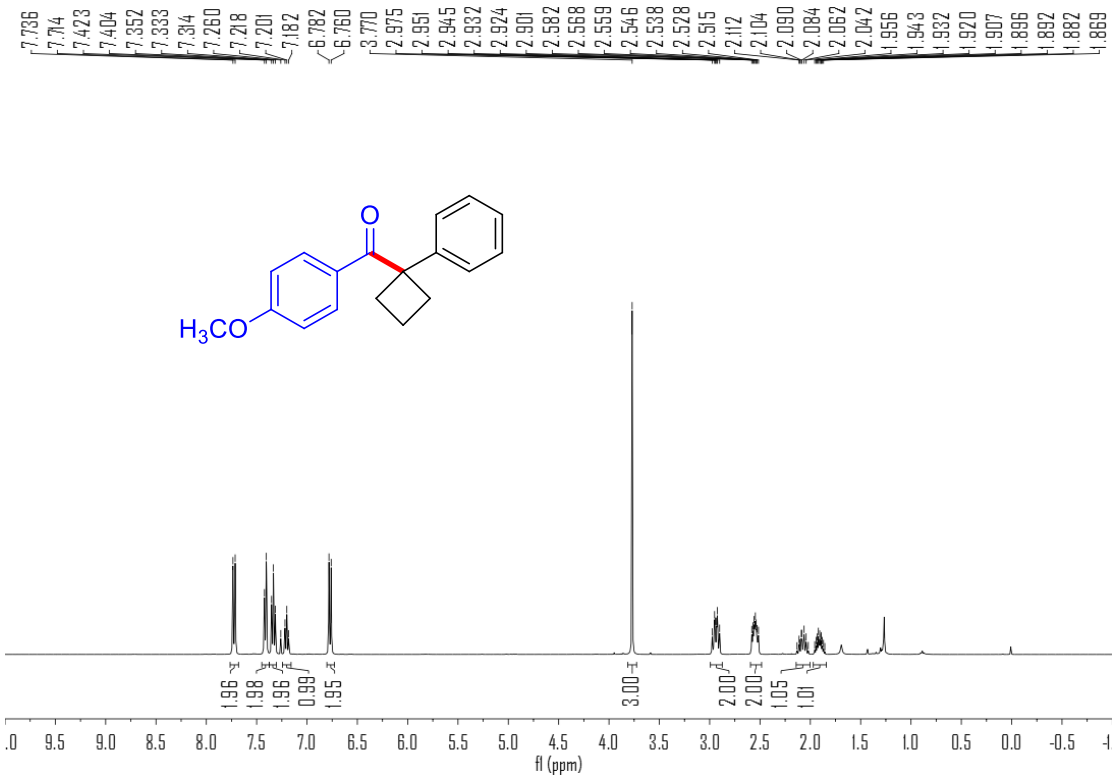
Supplementary Figure 63. ^{13}C NMR spectrum of **3ac**



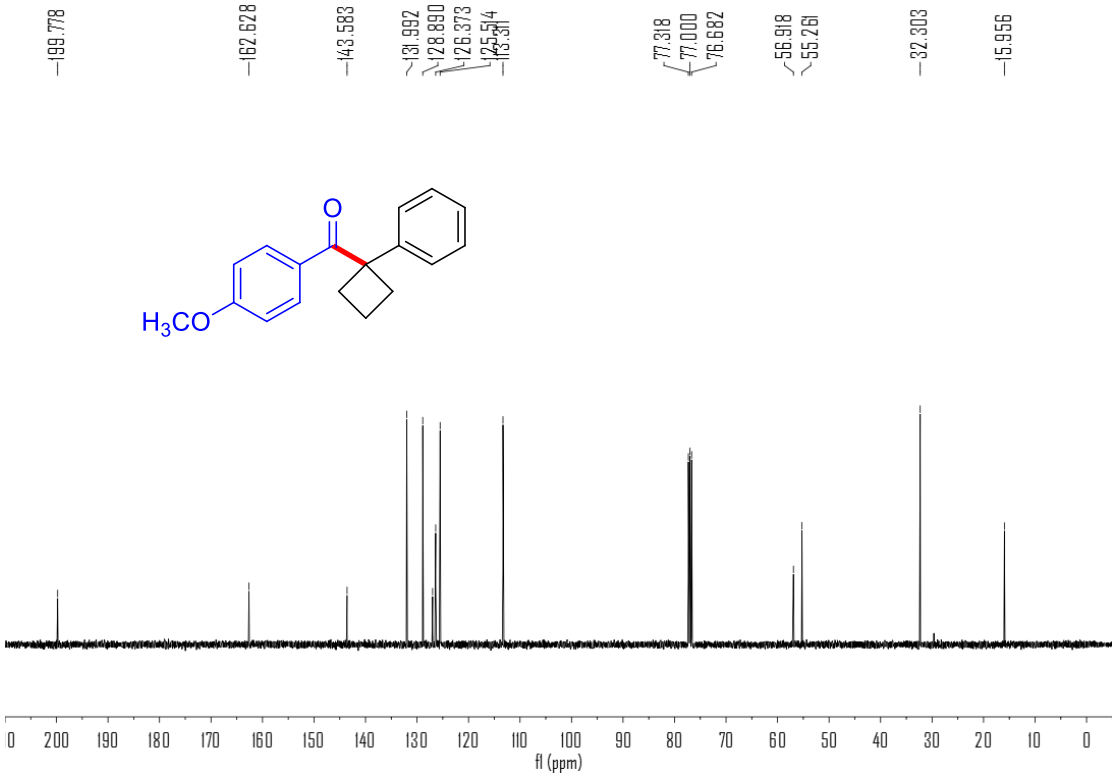
Supplementary Figure 64. ^{1}H NMR spectrum of **3ad**



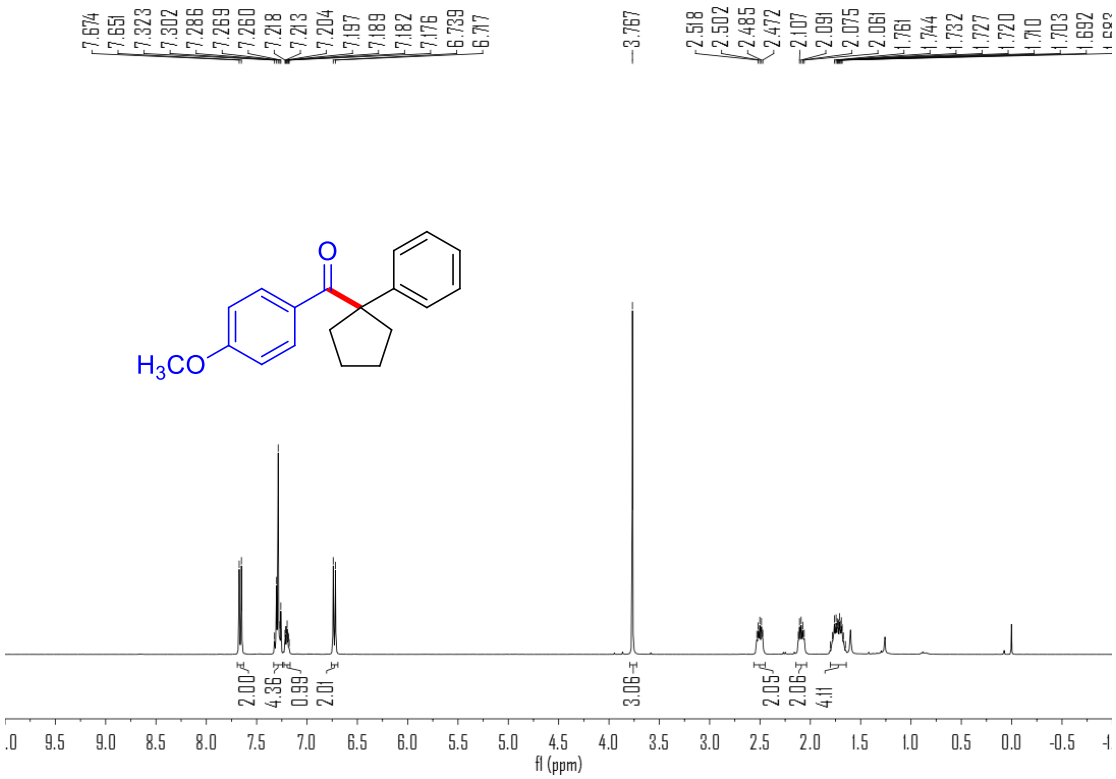
Supplementary Figure 65. ^{13}C NMR spectrum of **3ad**



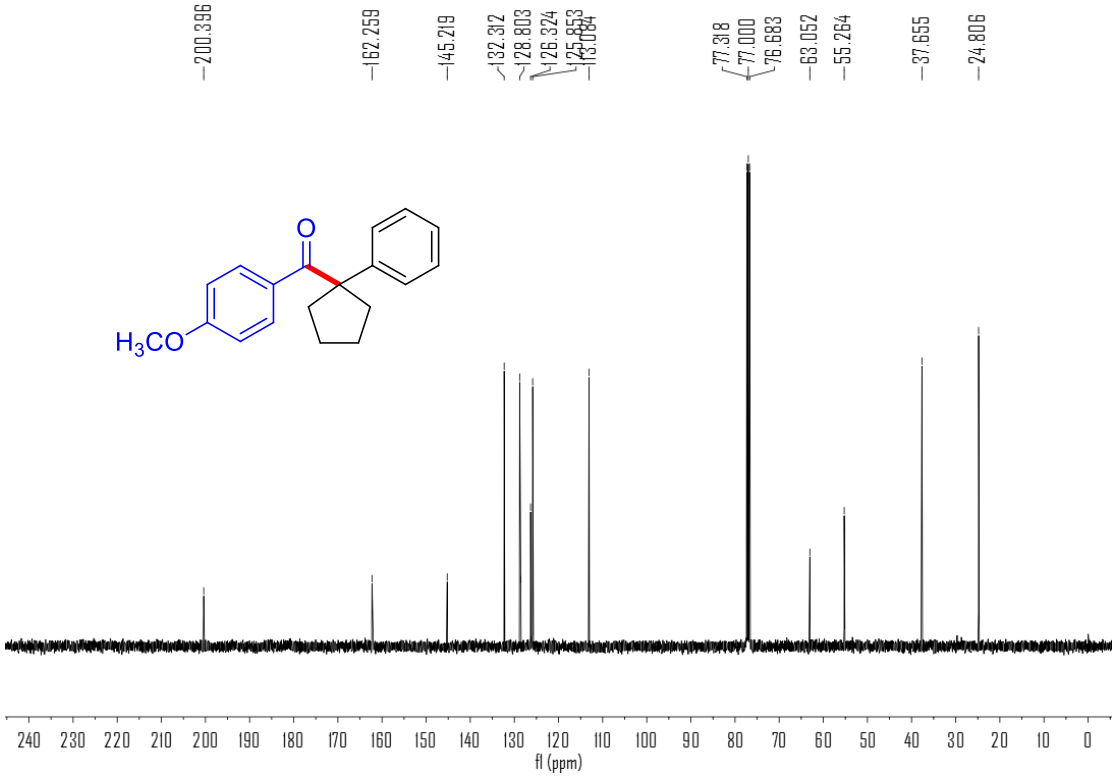
Supplementary Figure 66. ^{1}**H NMR** spectrum of **3ae**



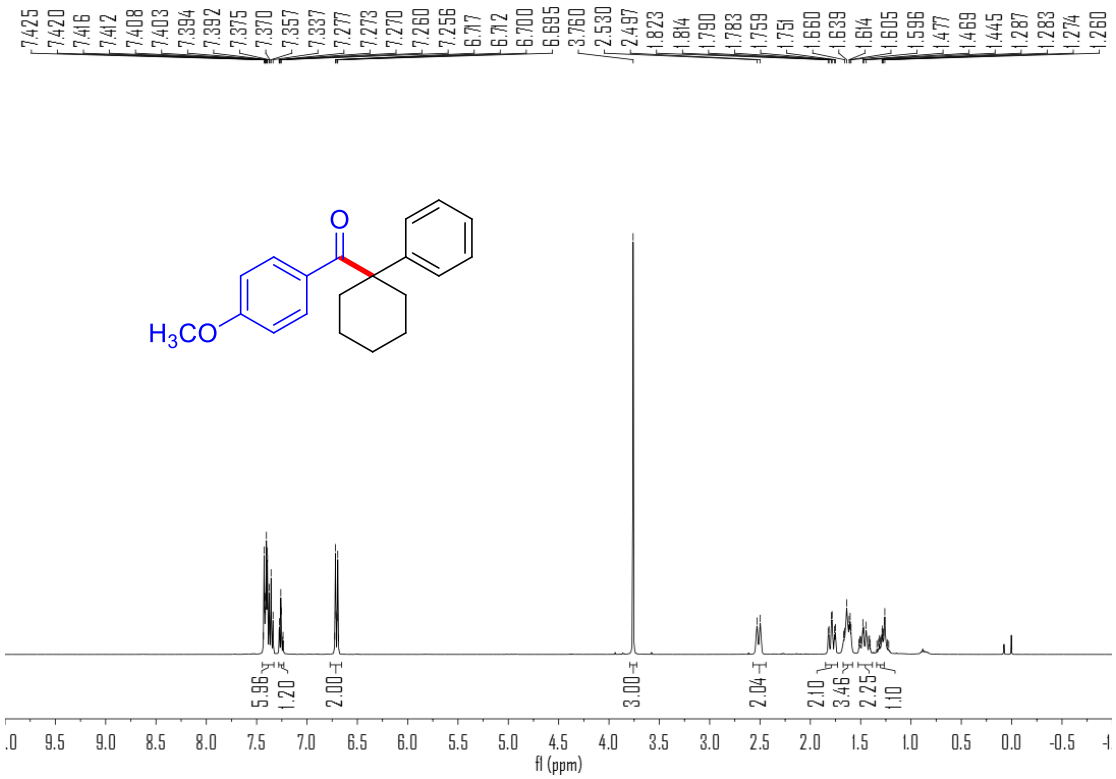
Supplementary Figure 67. ^{13}**C NMR** spectrum of **3ae**



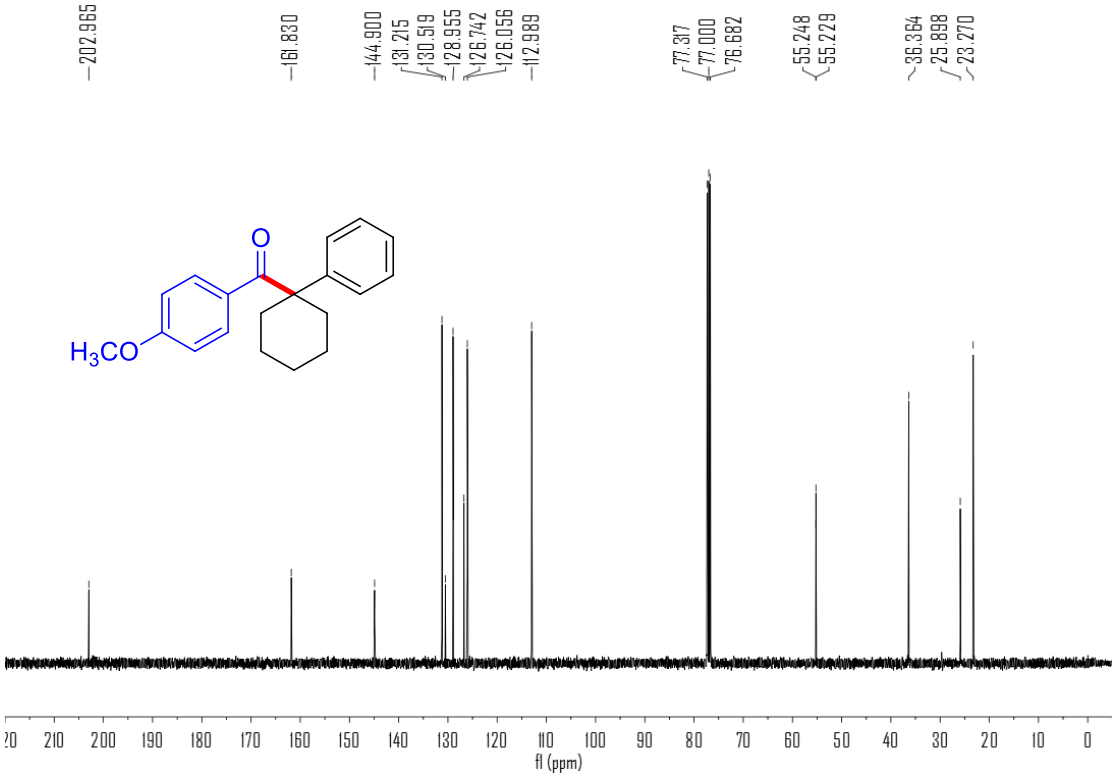
Supplementary Figure 68. ^{1}H NMR spectrum of **3af**



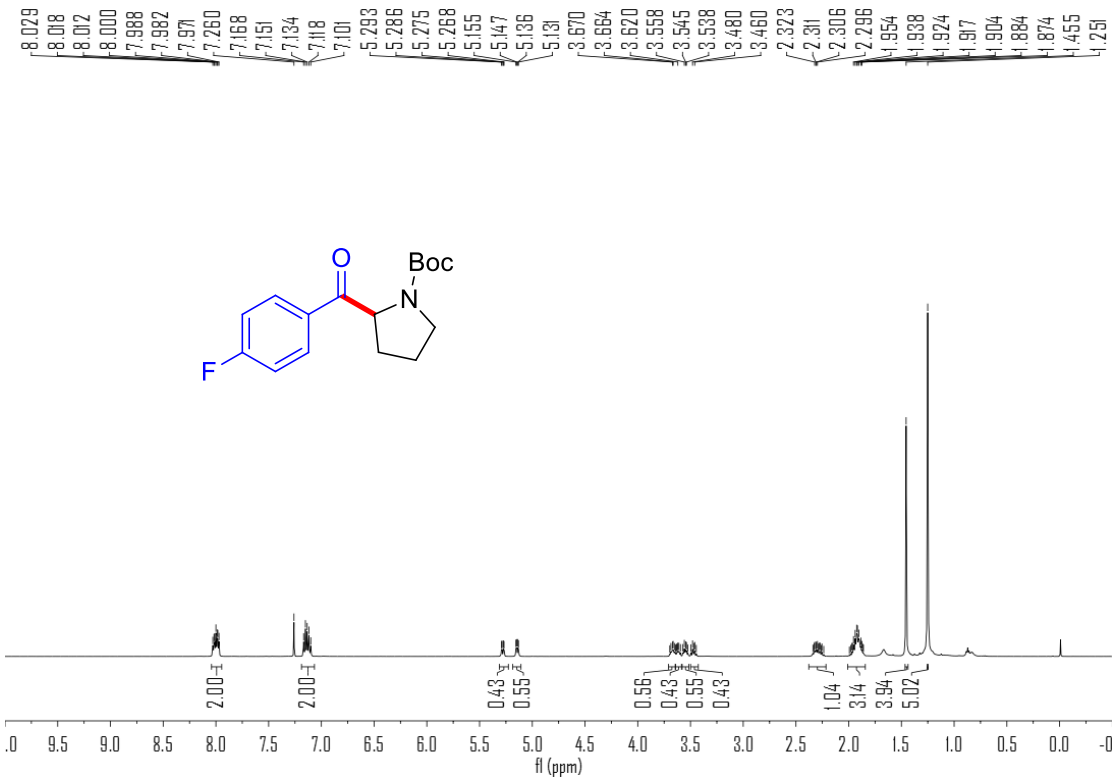
Supplementary Figure 69. ^{13}C NMR spectrum of **3af**



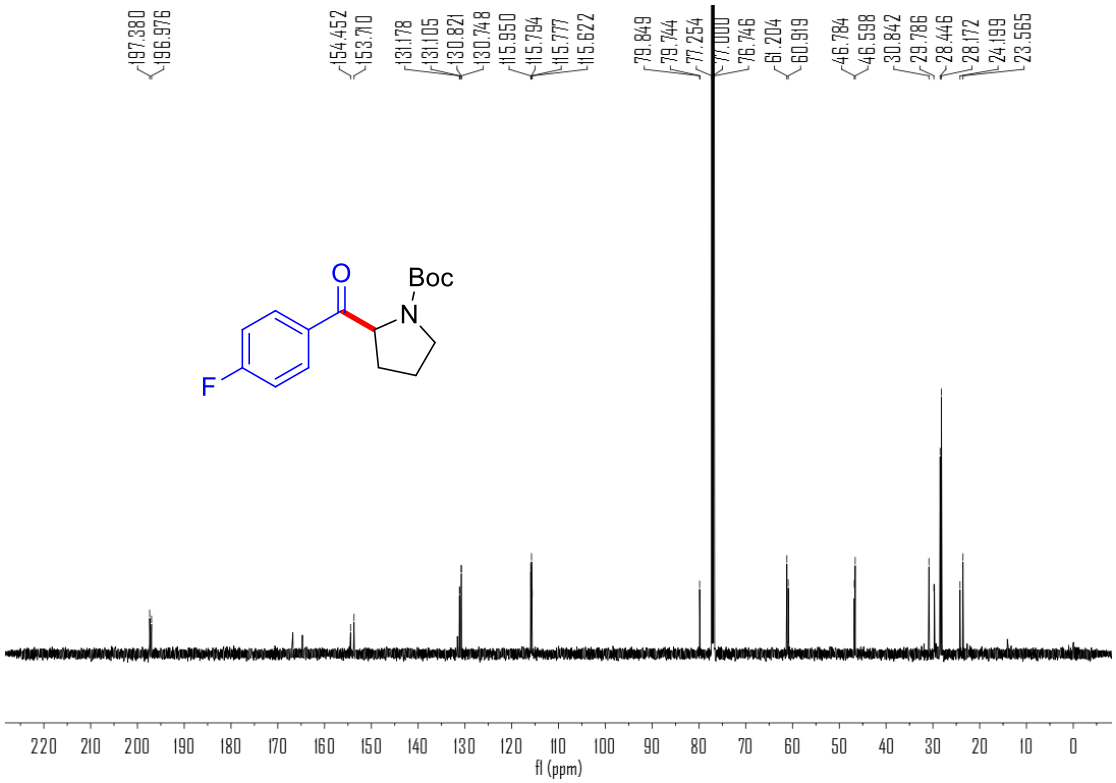
Supplementary Figure 70. ^{1}H NMR spectrum of **3ag**



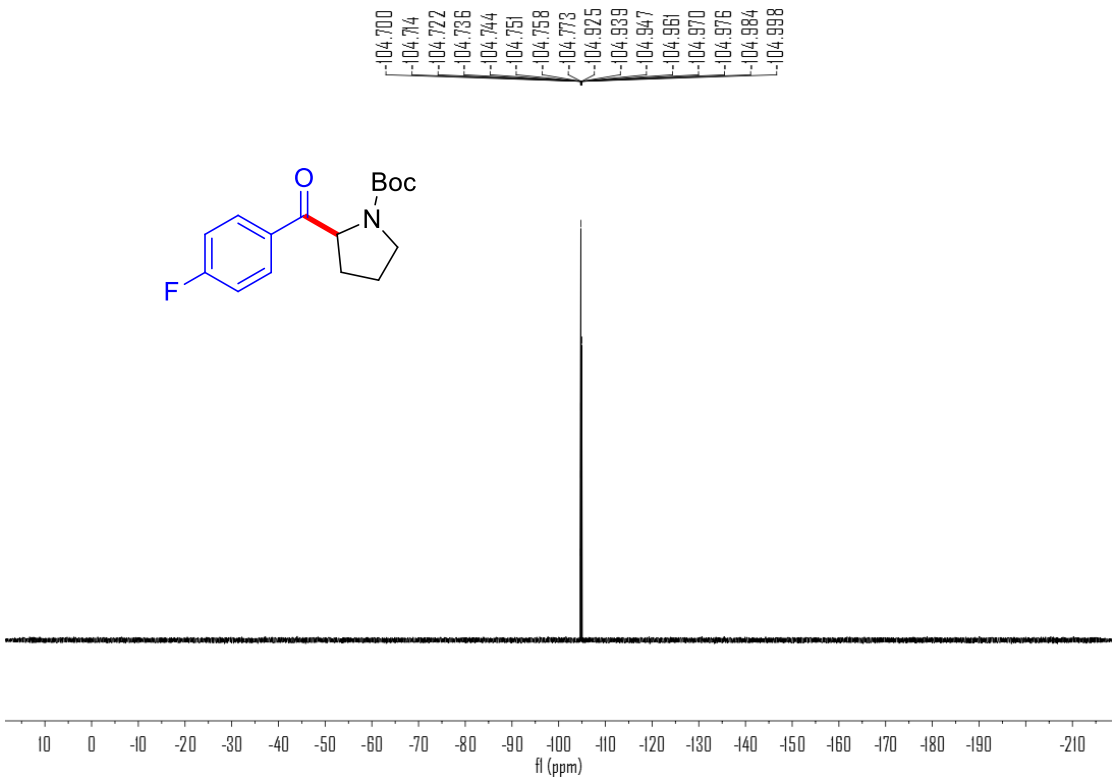
Supplementary Figure 71. ^{13}C NMR spectrum of **3ag**



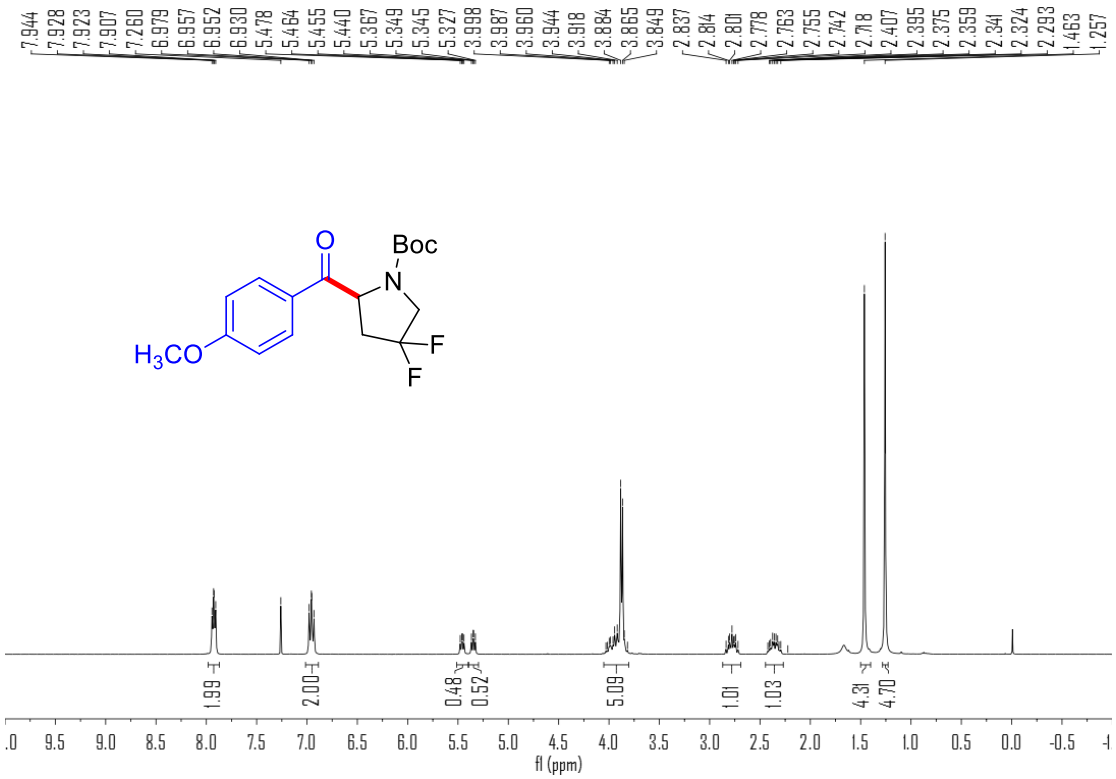
Supplementary Figure 72. ^{1}**H NMR** spectrum of **3ai**



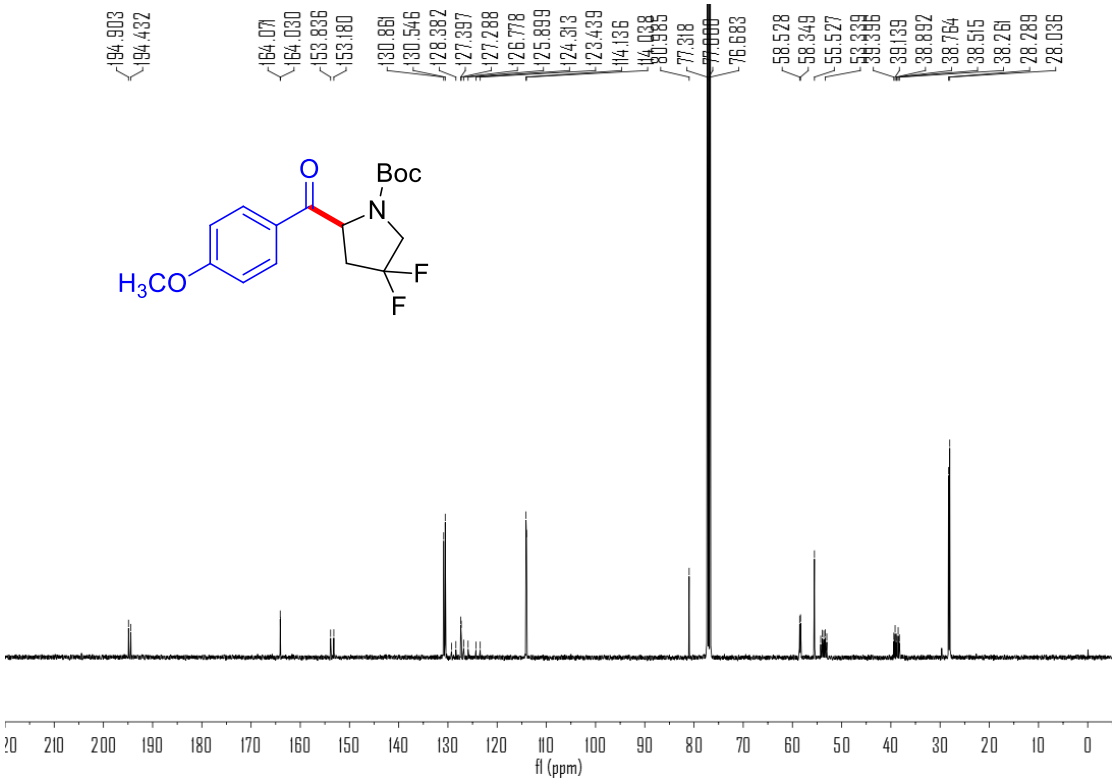
Supplementary Figure 73. ^{13}**C NMR** spectrum of **3ai**



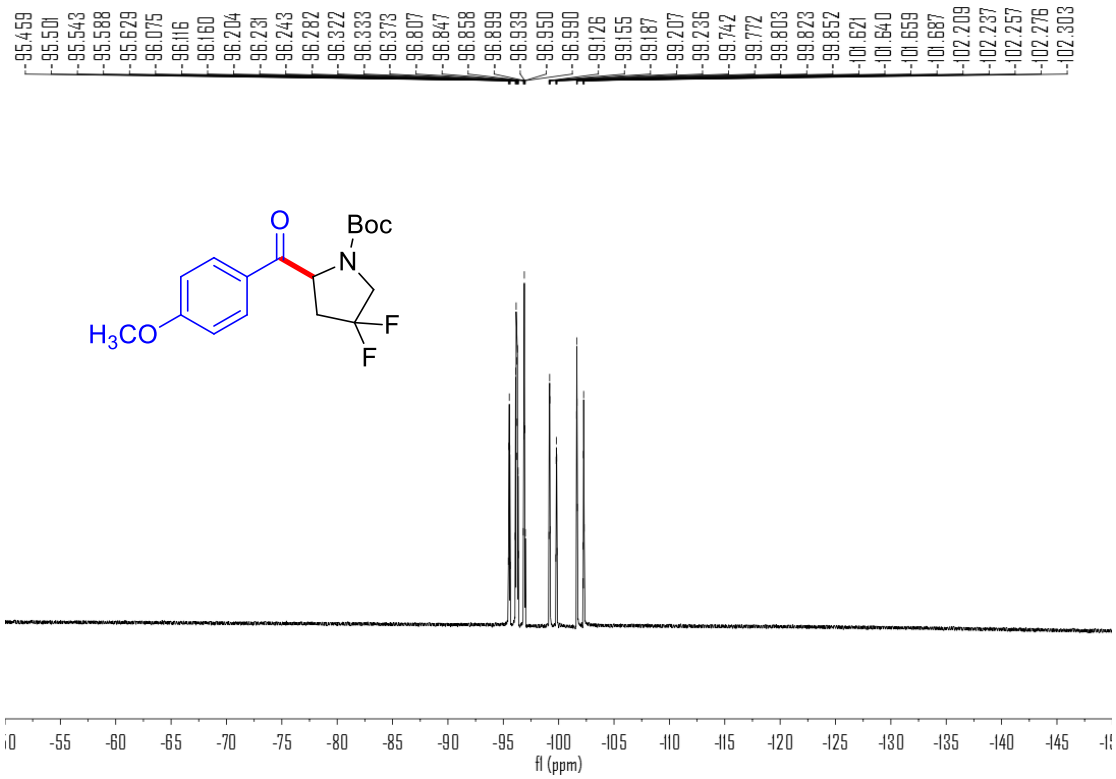
Supplementary Figure 74. ^{19}F NMR spectrum of **3ai**



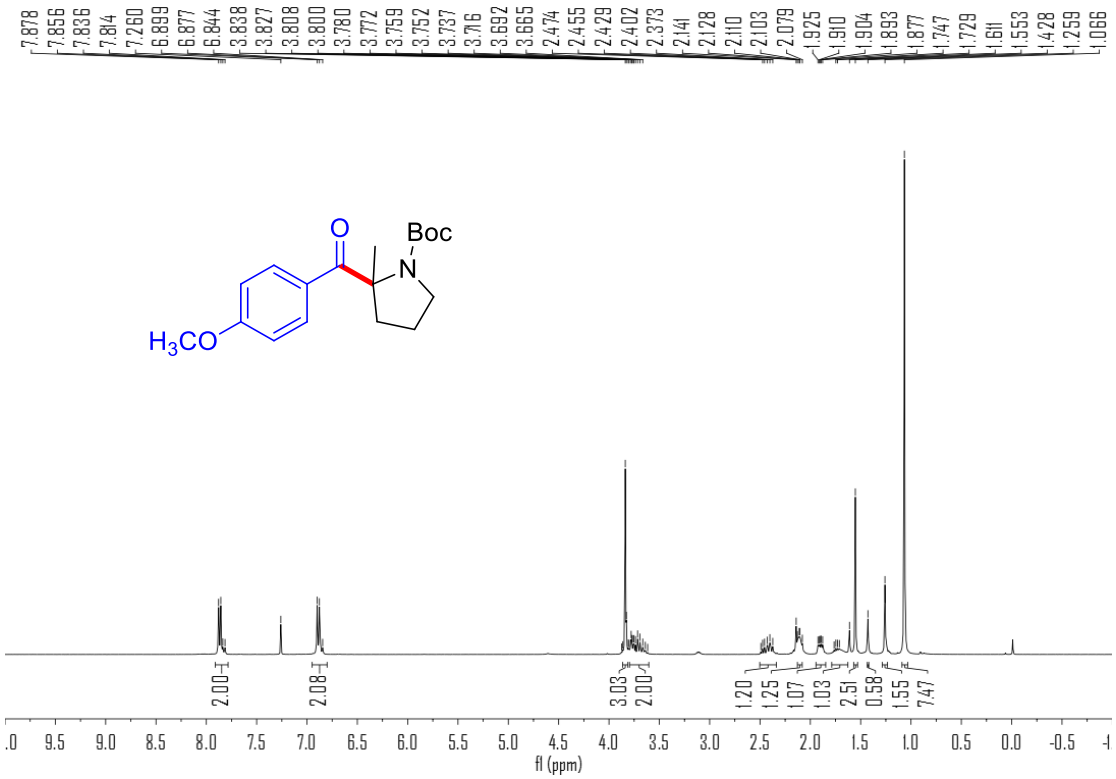
Supplementary Figure 75. ^{1}H NMR spectrum of **3aj**



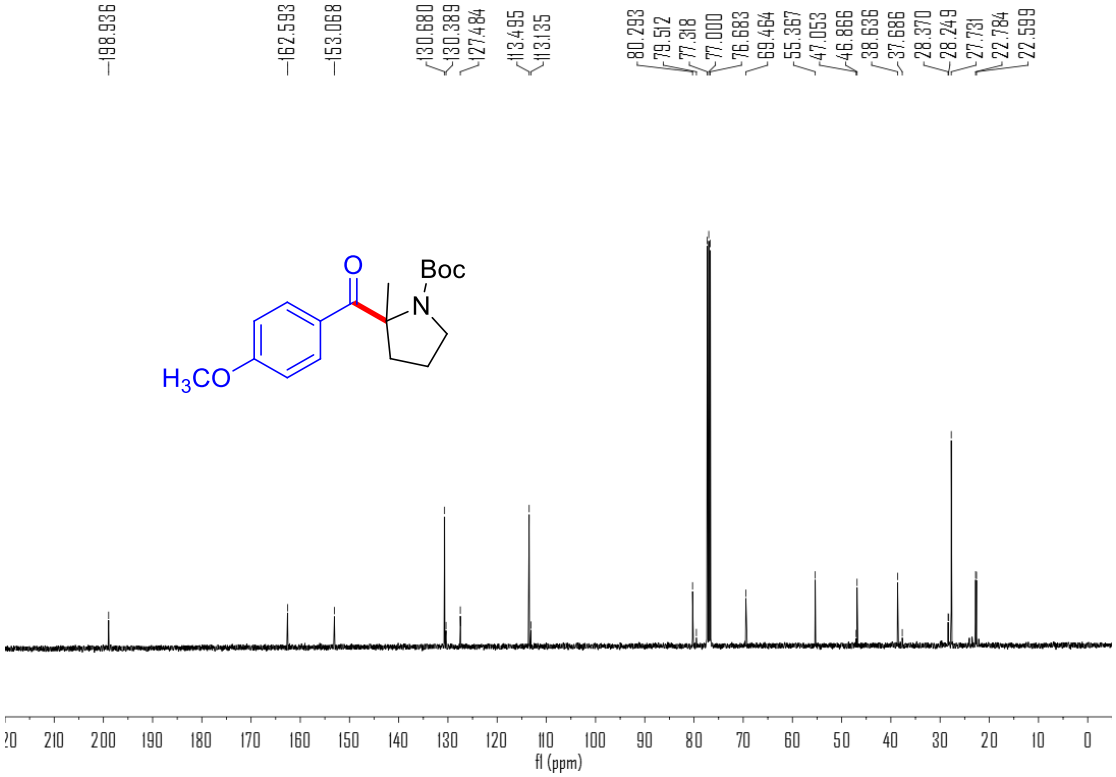
Supplementary Figure 76. ^{13}C NMR spectrum of **3aj**



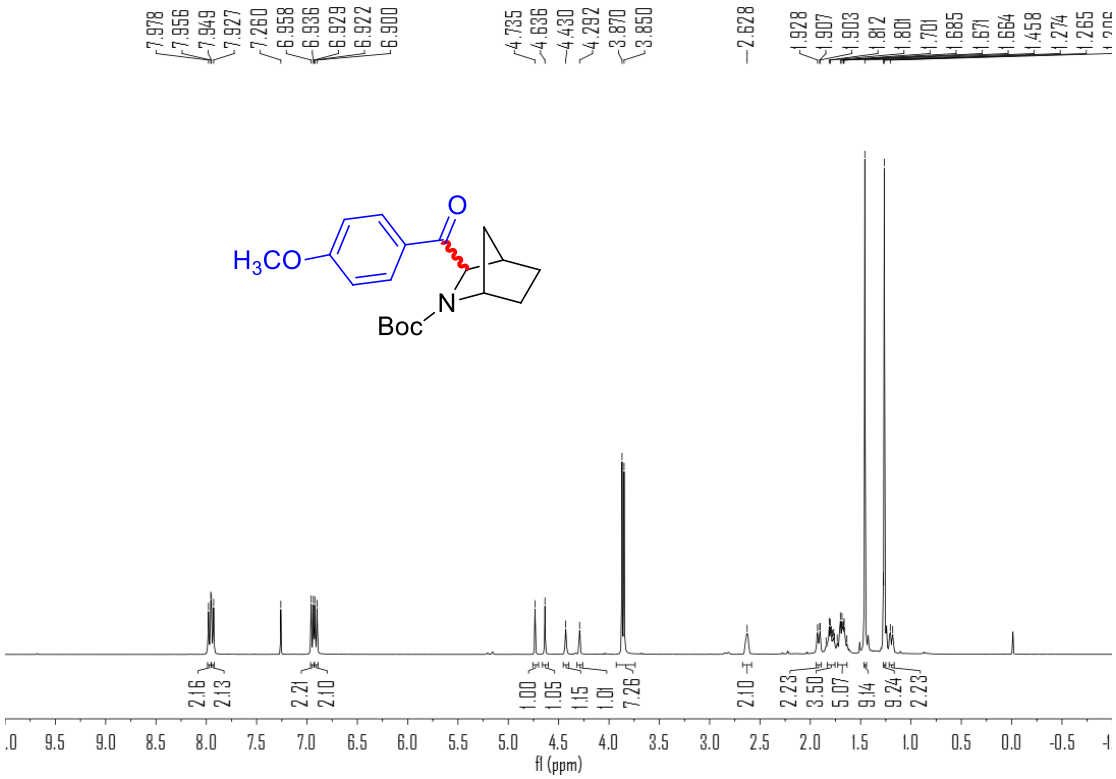
Supplementary Figure 77. ^{19}F NMR spectrum of **3aj**



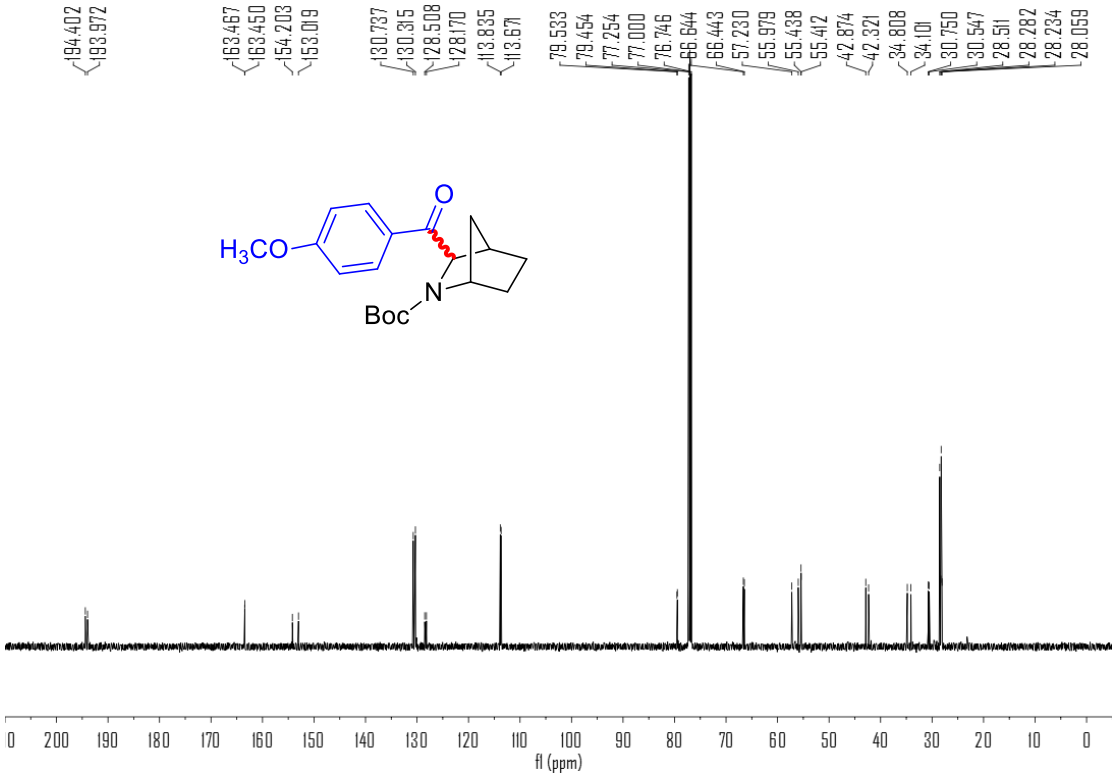
Supplementary Figure 78. ^{1}H NMR spectrum of **3ak**



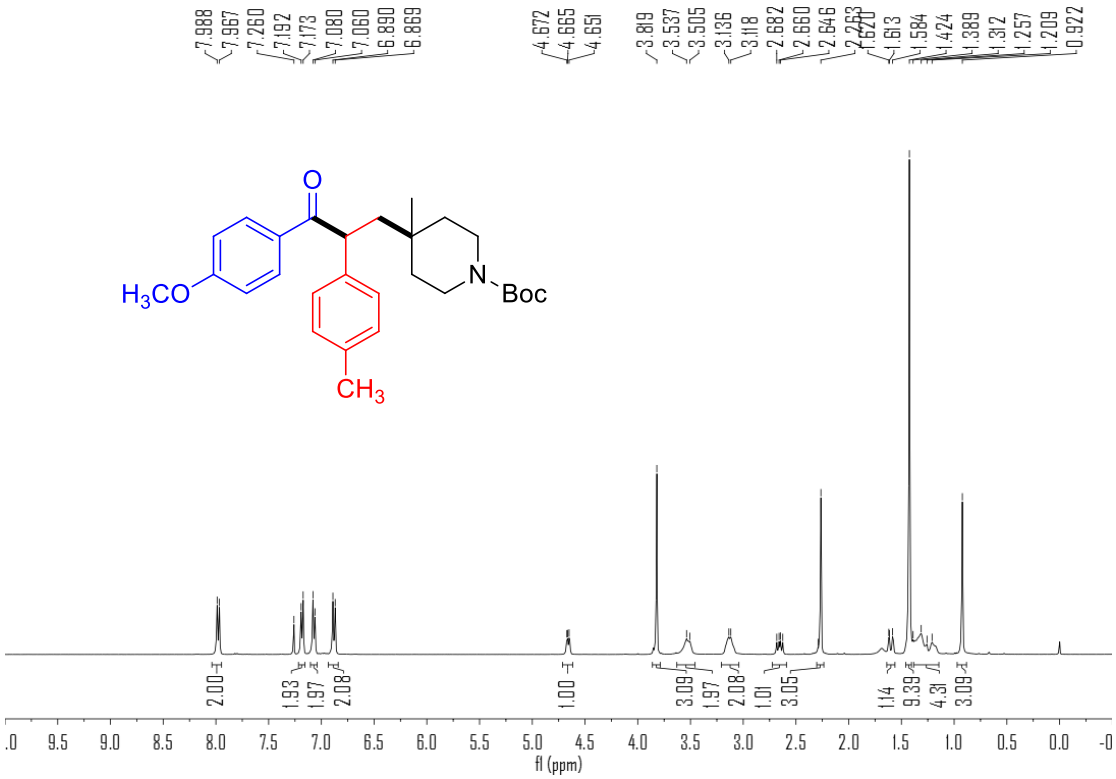
Supplementary Figure 79. ^{13}C NMR spectrum of **3ak**



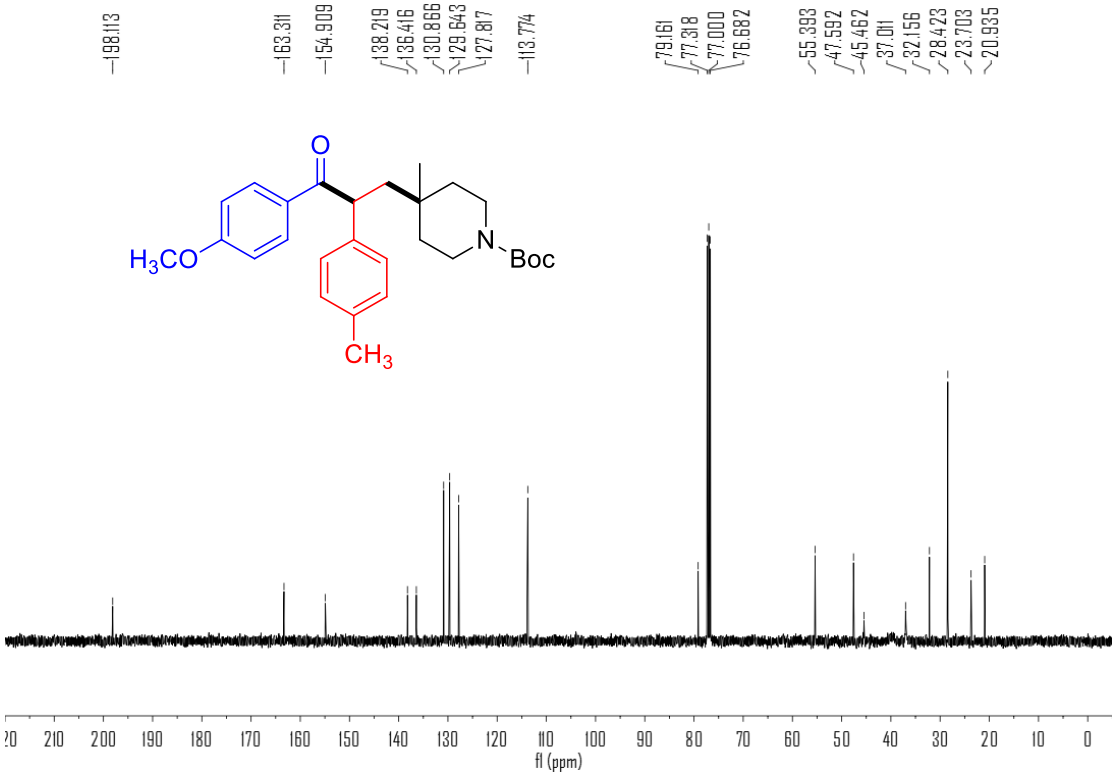
Supplementary Figure 80. ^{1}H NMR spectrum of **3al**



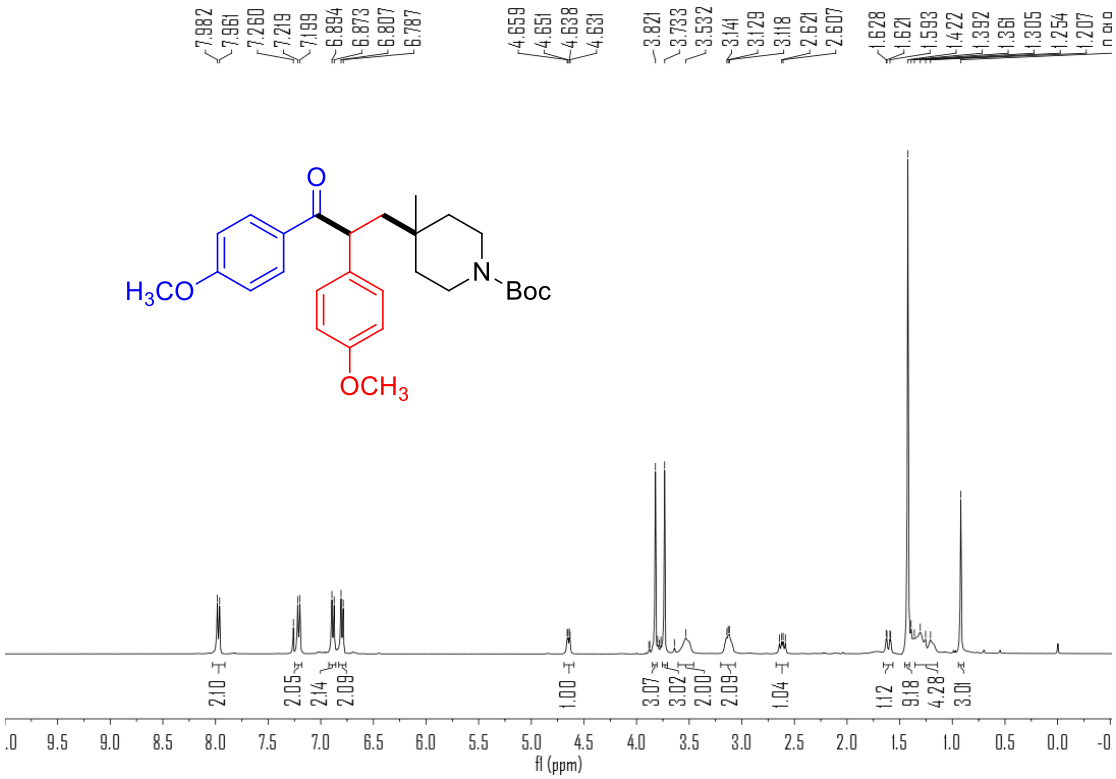
Supplementary Figure 81. ^{13}C NMR spectrum of **3al**



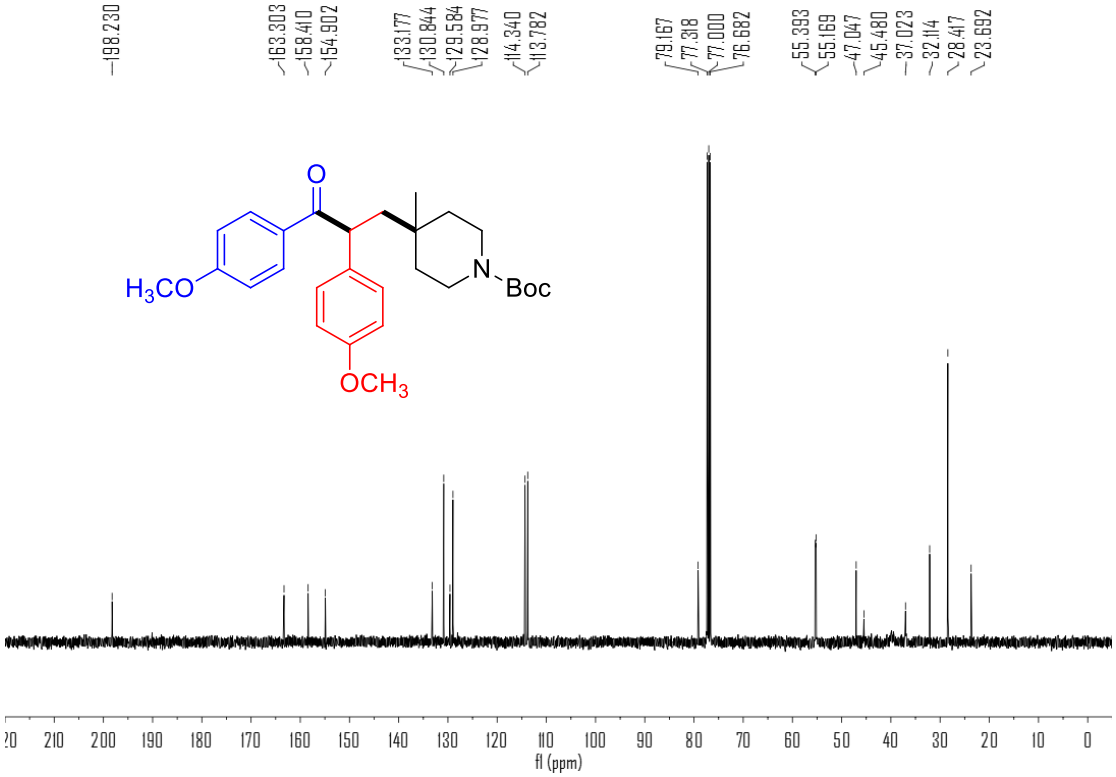
Supplementary Figure 82. ^{1}H NMR spectrum of **5a**



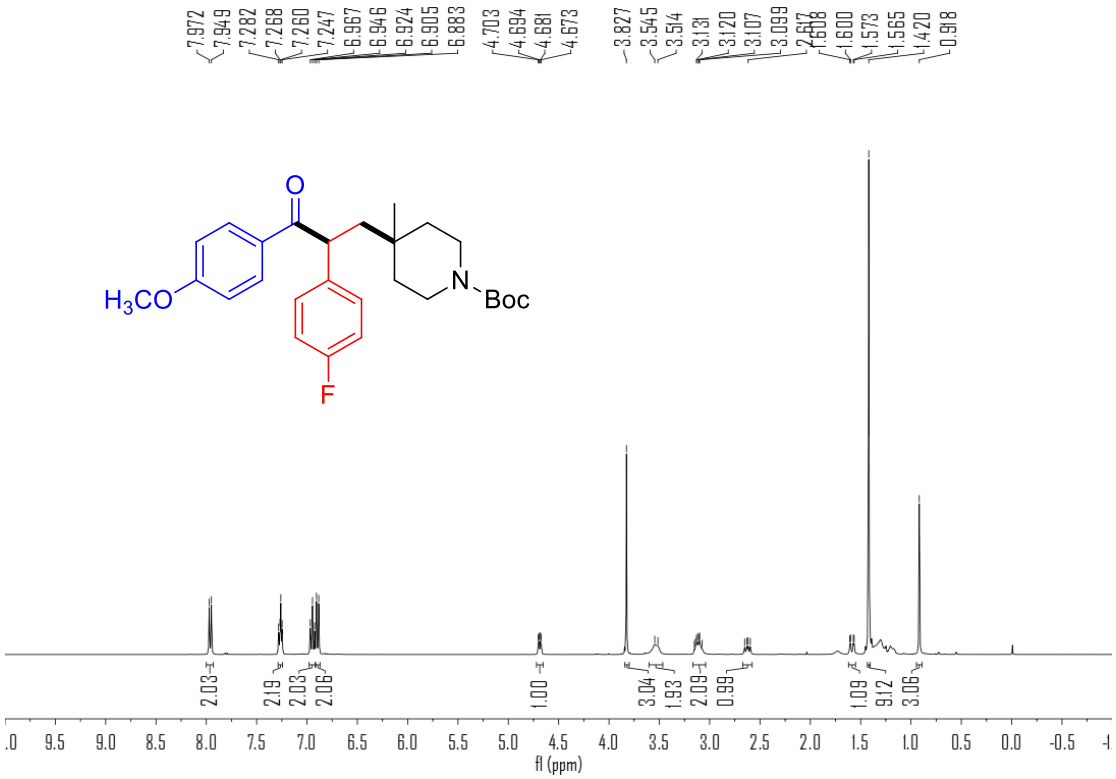
Supplementary Figure 83. ^{13}C NMR spectrum of **5a**



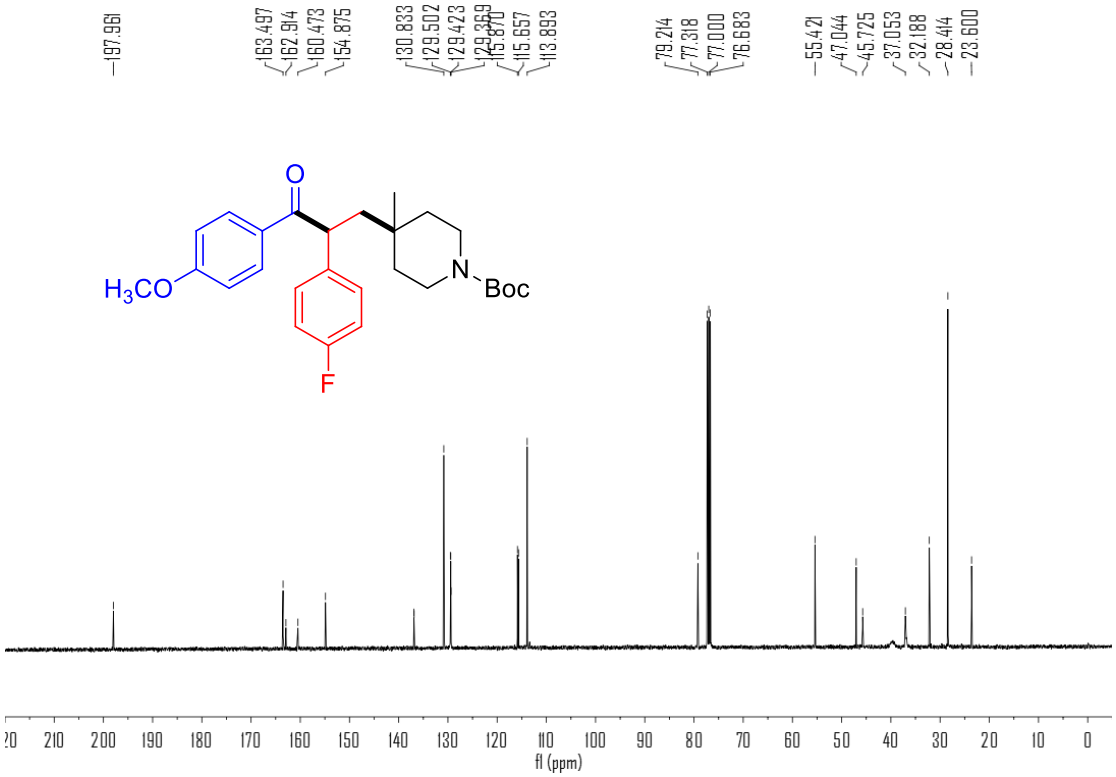
Supplementary Figure 84. ^{1}H NMR spectrum of **5b**



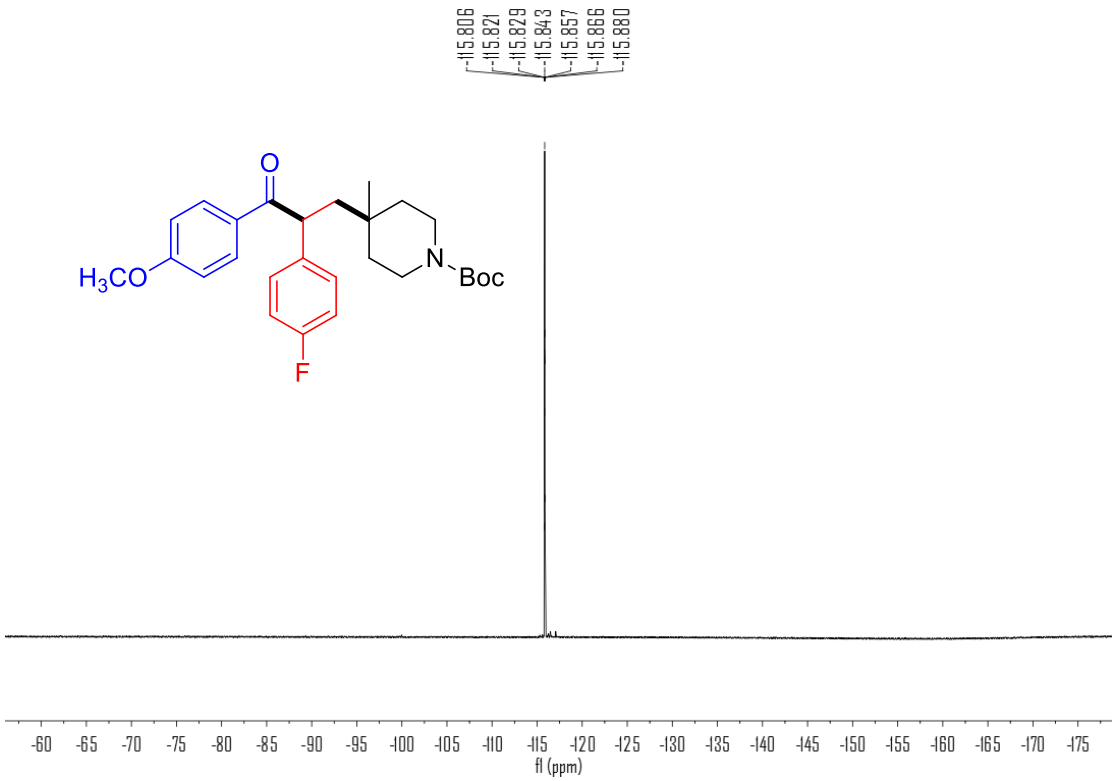
Supplementary Figure 85. ^{13}C NMR spectrum of **5b**



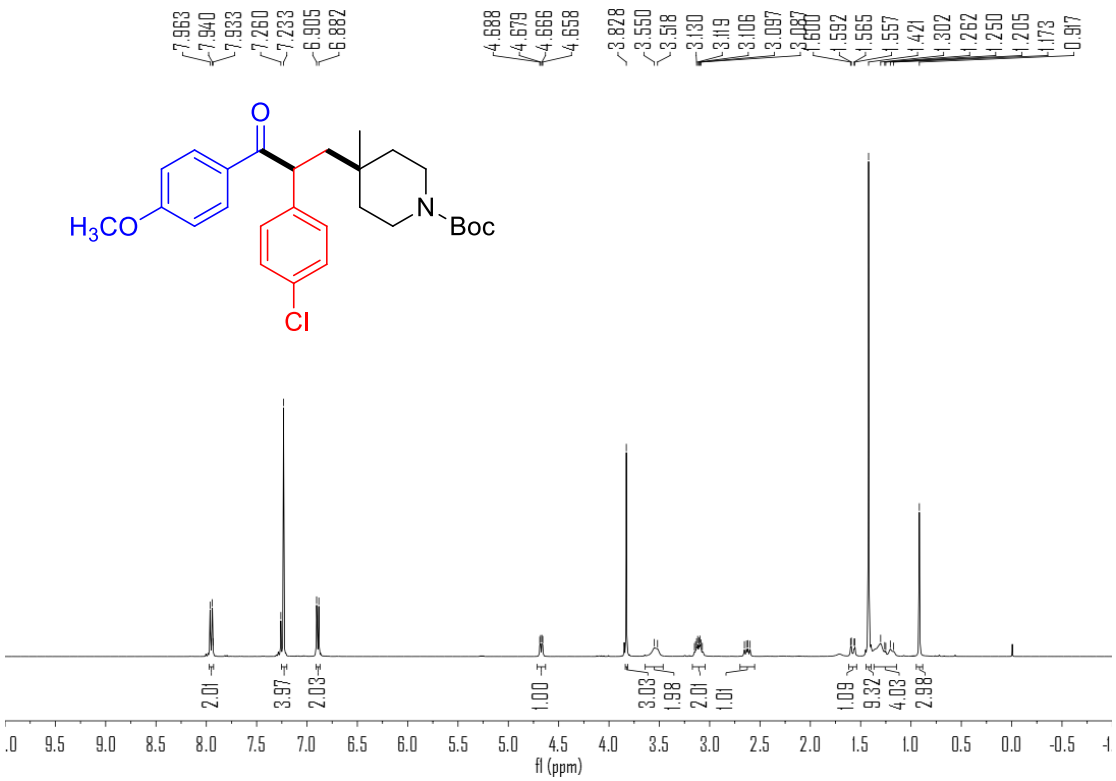
Supplementary Figure 86. ^{1}H NMR spectrum of **5c**



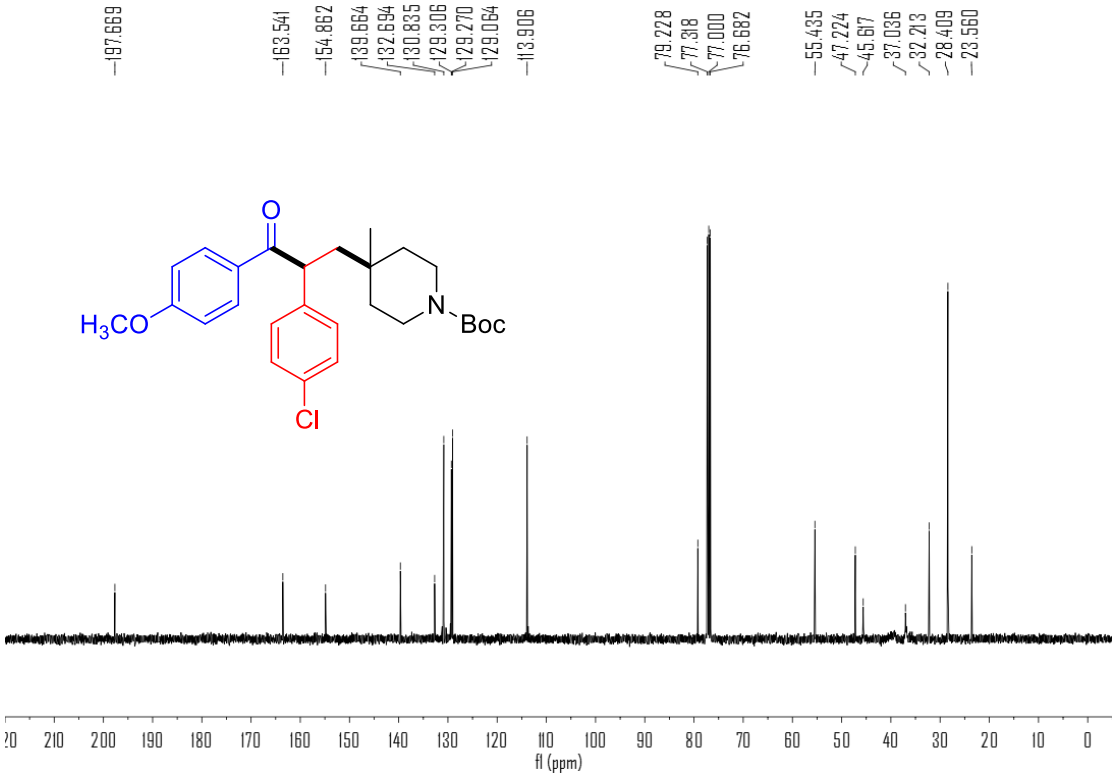
Supplementary Figure 87. ^{13}C NMR spectrum of **5c**



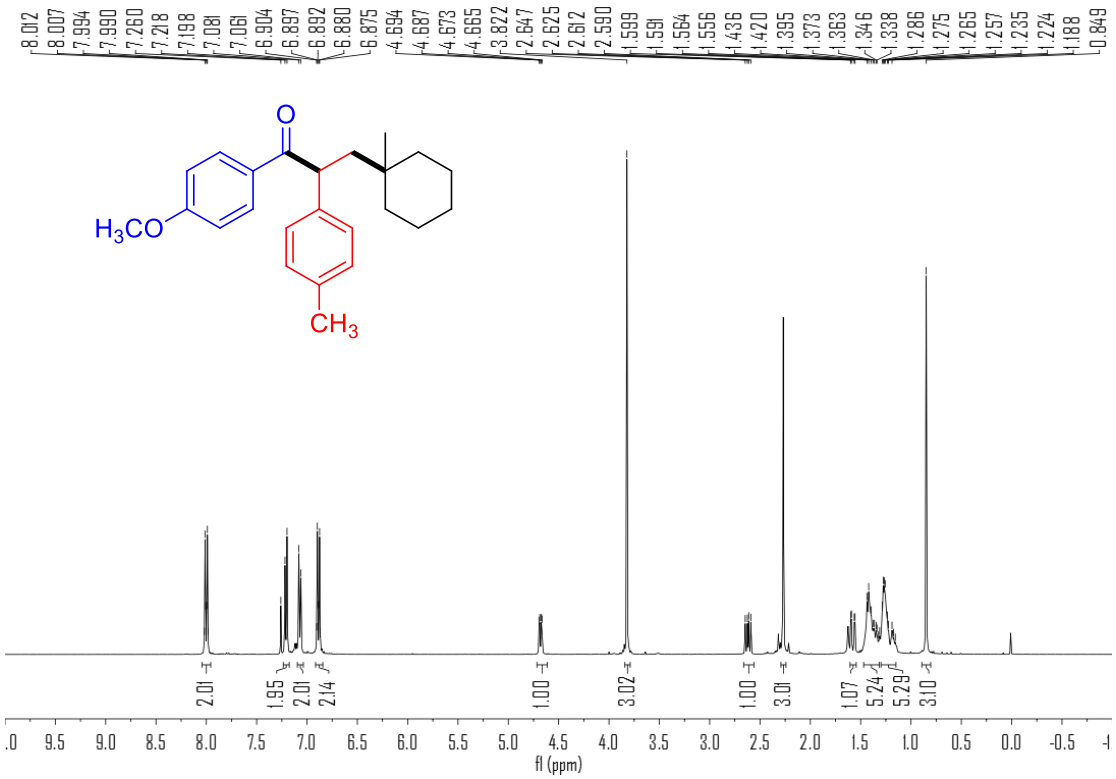
Supplementary Figure 88. ^{19}**F NMR** spectrum of **5c**



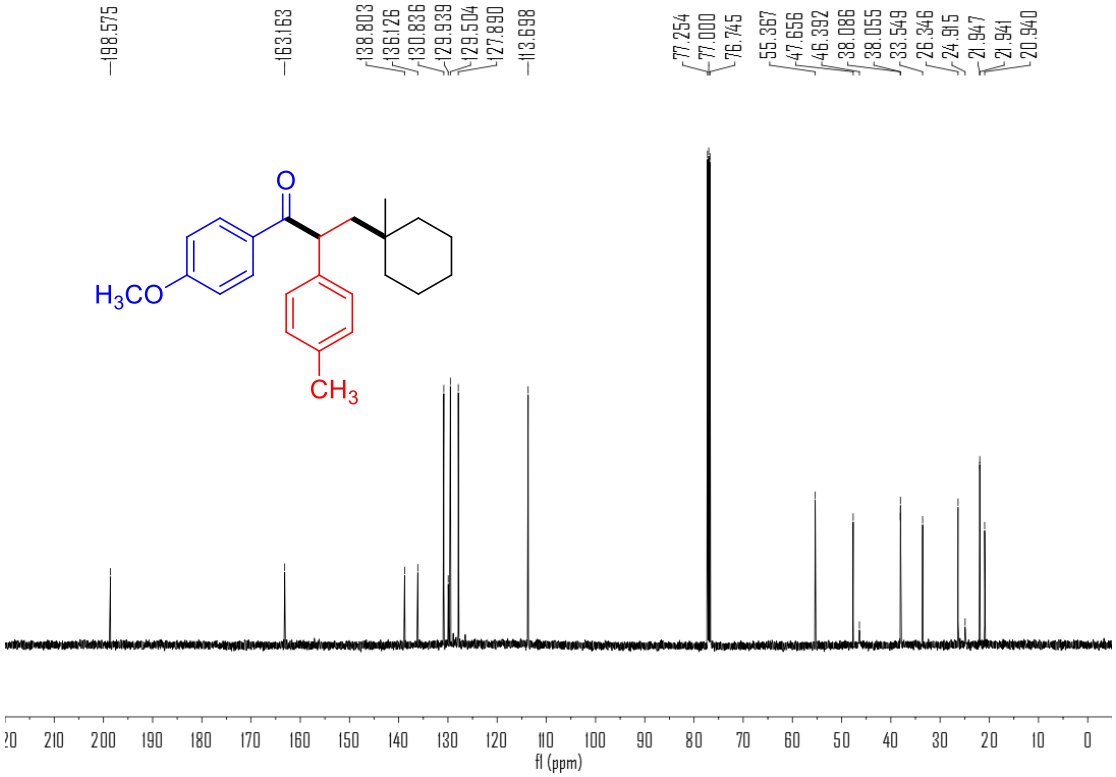
Supplementary Figure 89. ^{1}H NMR spectrum of **5d**



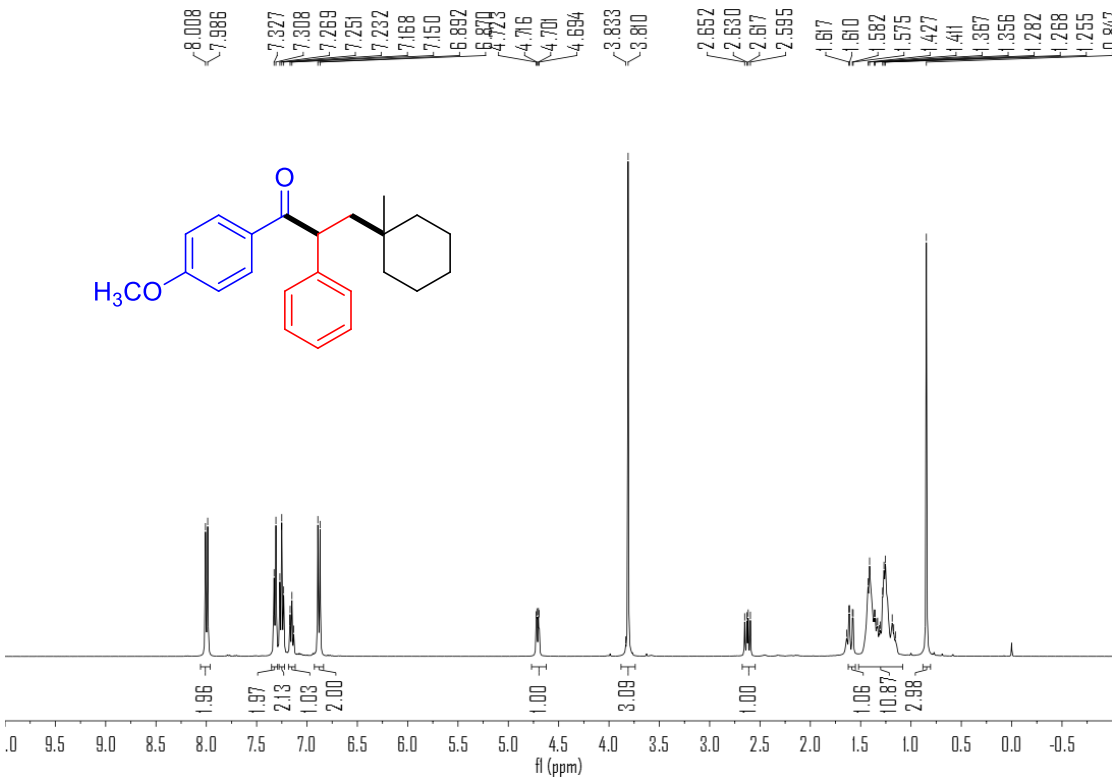
Supplementary Figure 90. ^{13}C NMR spectrum of **5d**



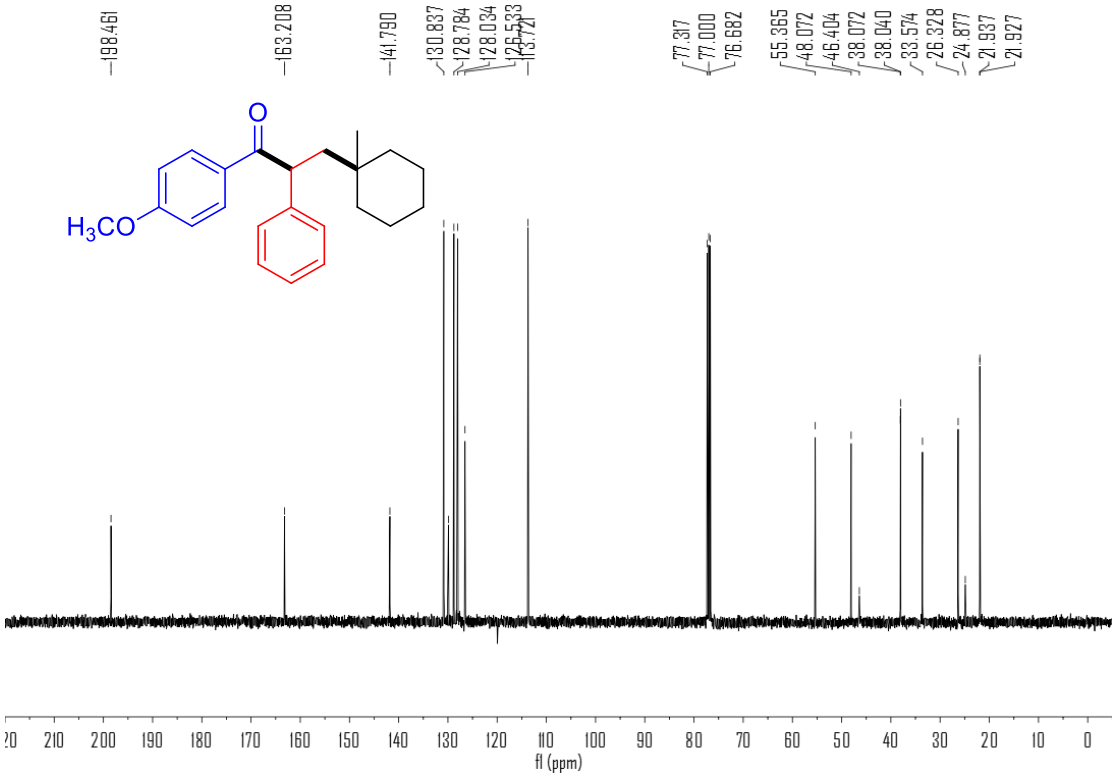
Supplementary Figure 91. ^{1}**H NMR** spectrum of **5e**



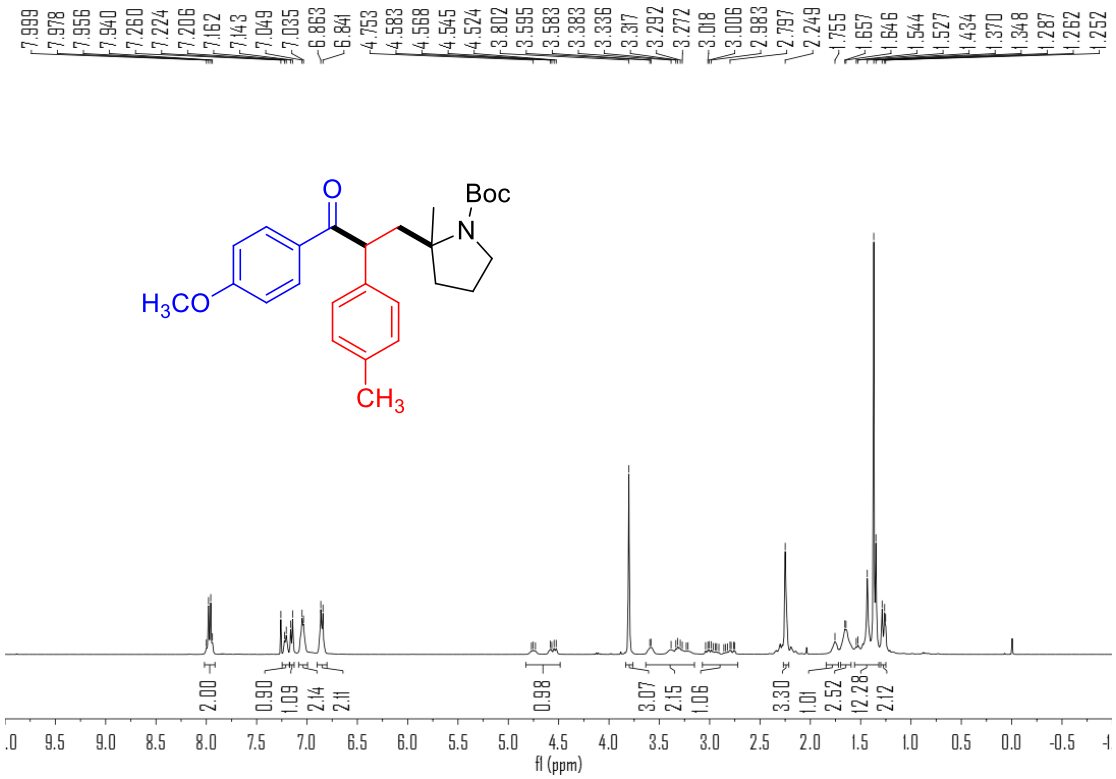
Supplementary Figure 92. ^{13}**C NMR** spectrum of **5e**



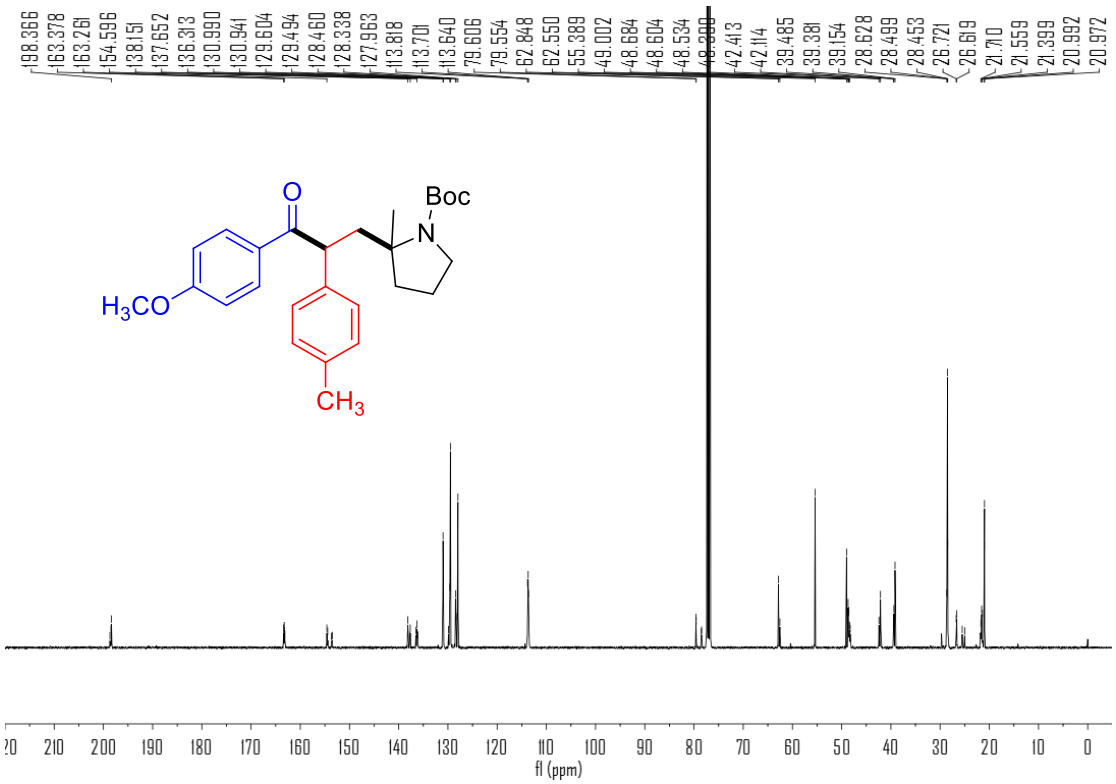
Supplementary Figure 93. ^{1}H NMR spectrum of **5f**



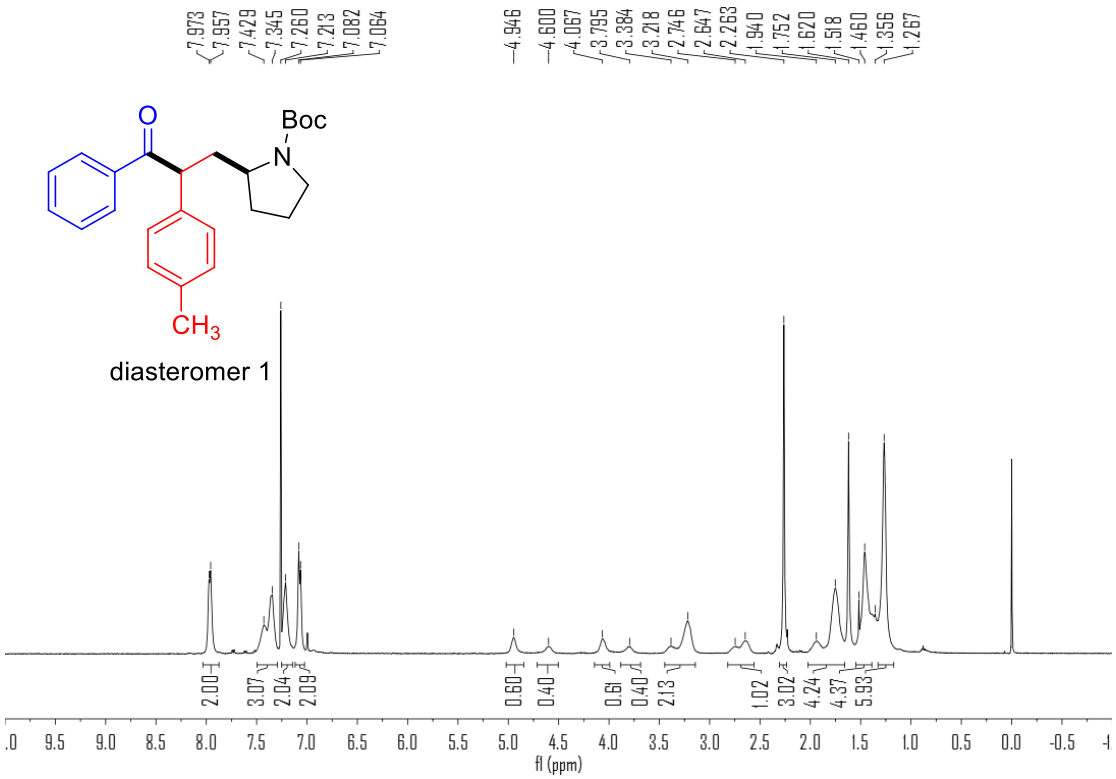
Supplementary Figure 94. ^{13}C NMR spectrum of **5f**



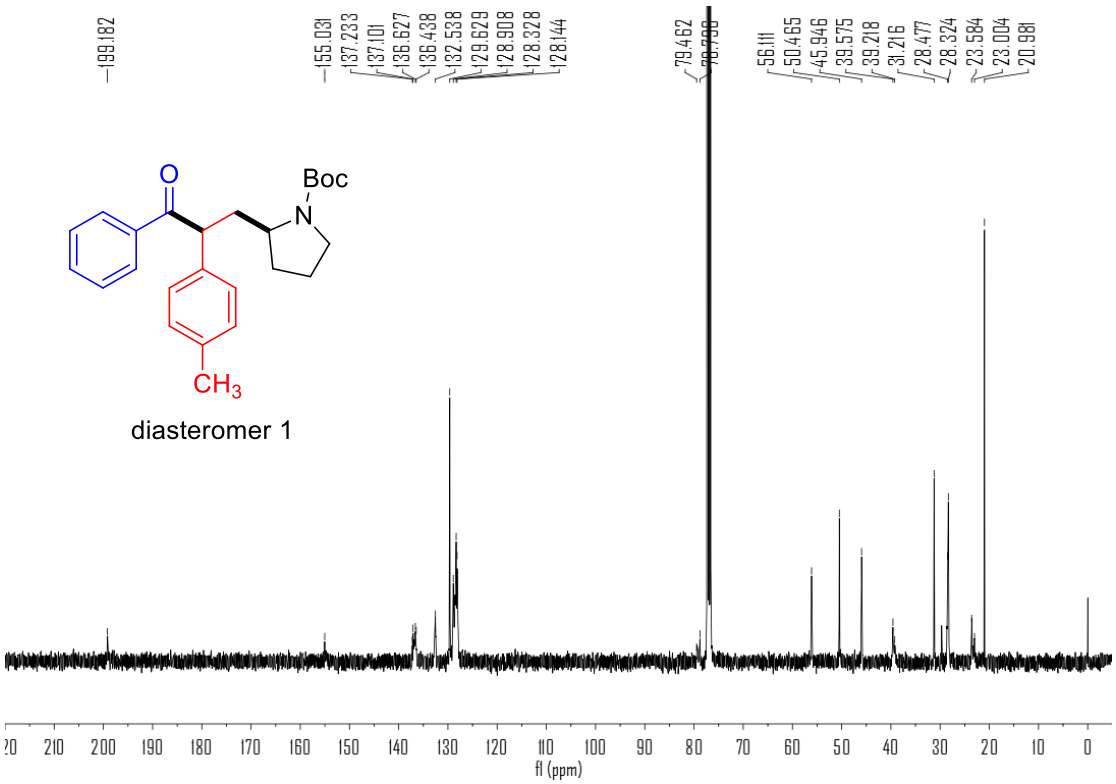
Supplementary Figure 95. ^{1}H NMR spectrum of **5g**



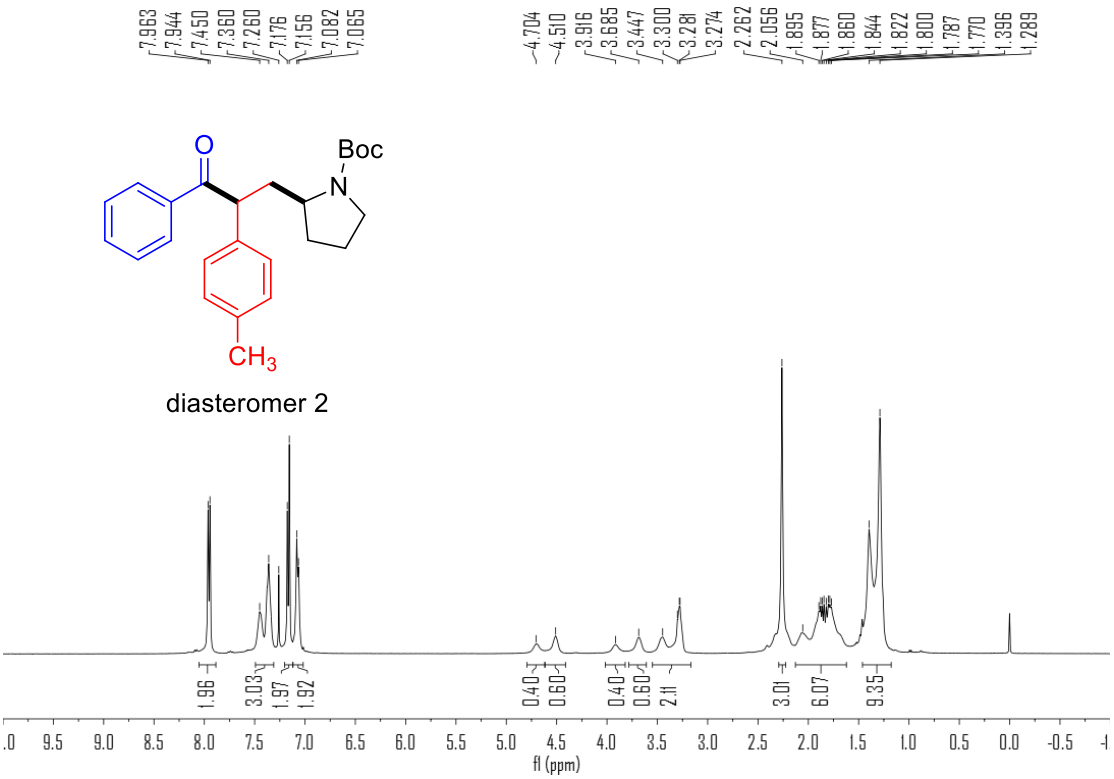
Supplementary Figure 96. ^{13}C NMR spectrum of **5g**



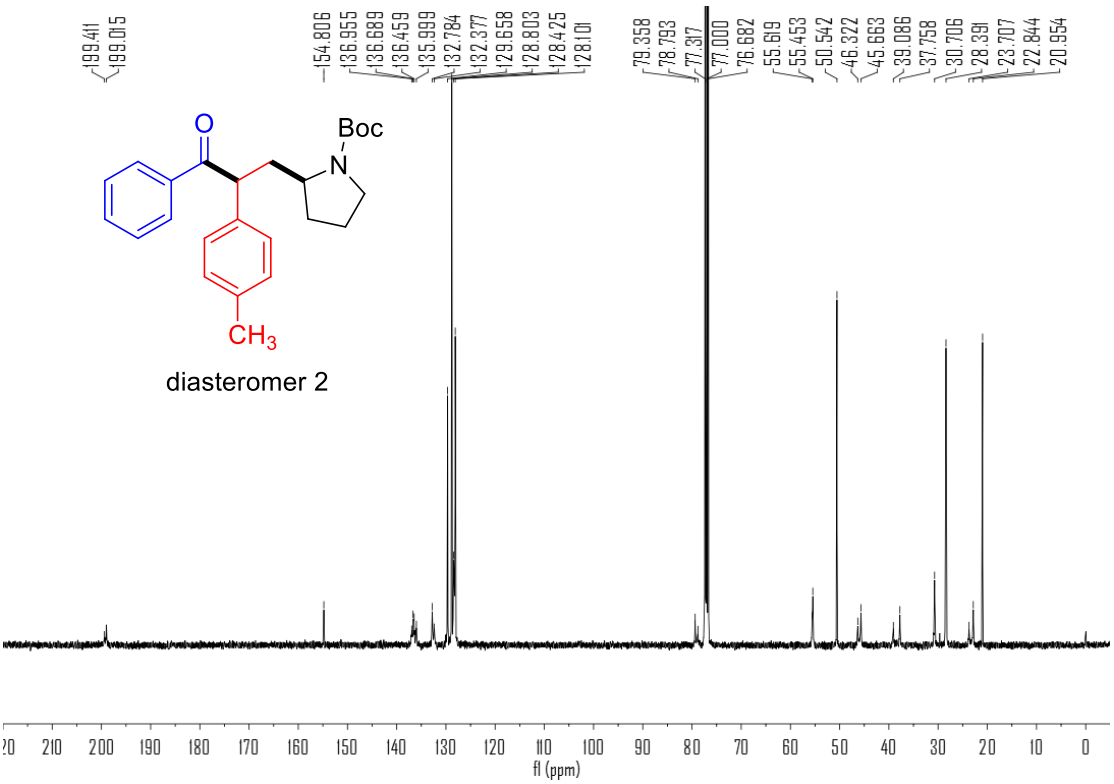
Supplementary Figure 97. ^{1}H NMR spectrum of **5h**



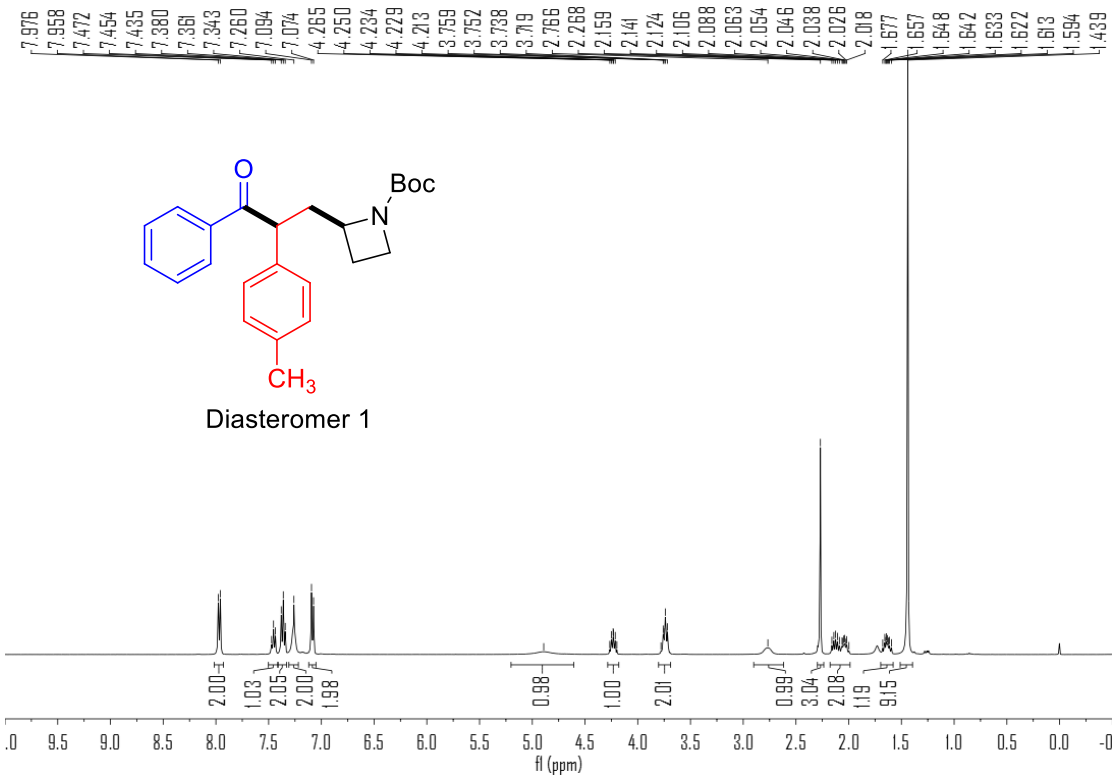
Supplementary Figure 98. ^{13}C NMR spectrum of **5h**



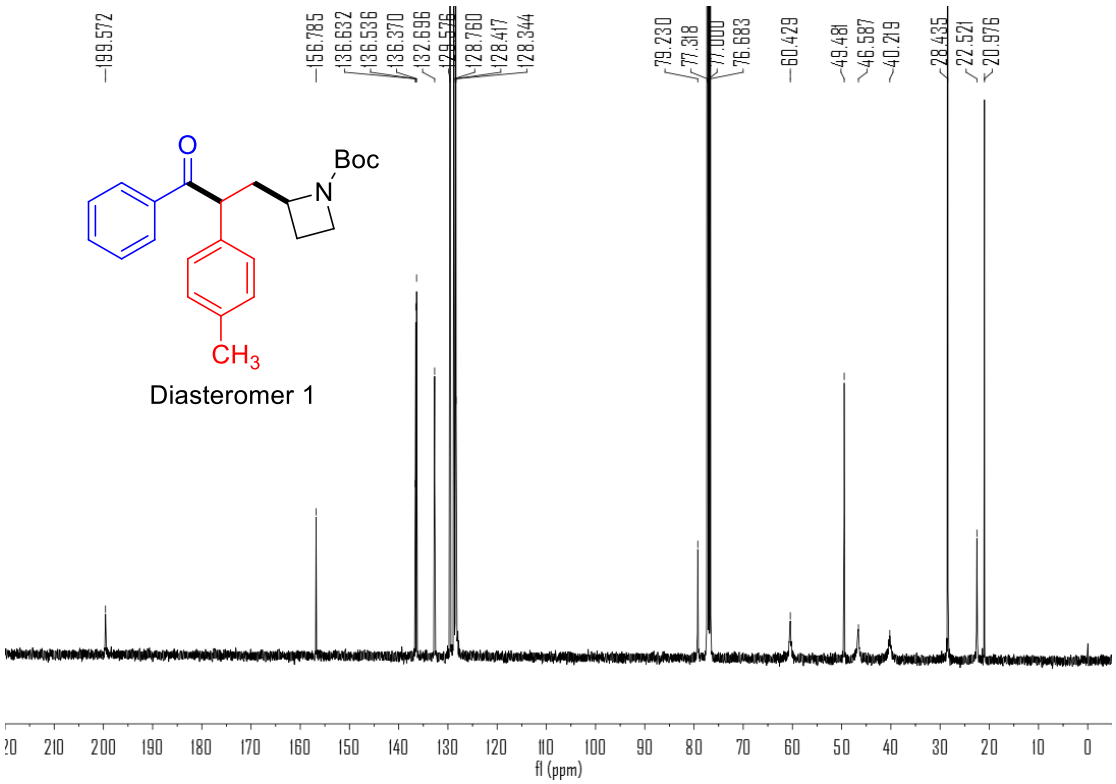
Supplementary Figure 99. ^{1}H NMR spectrum of **5h'**



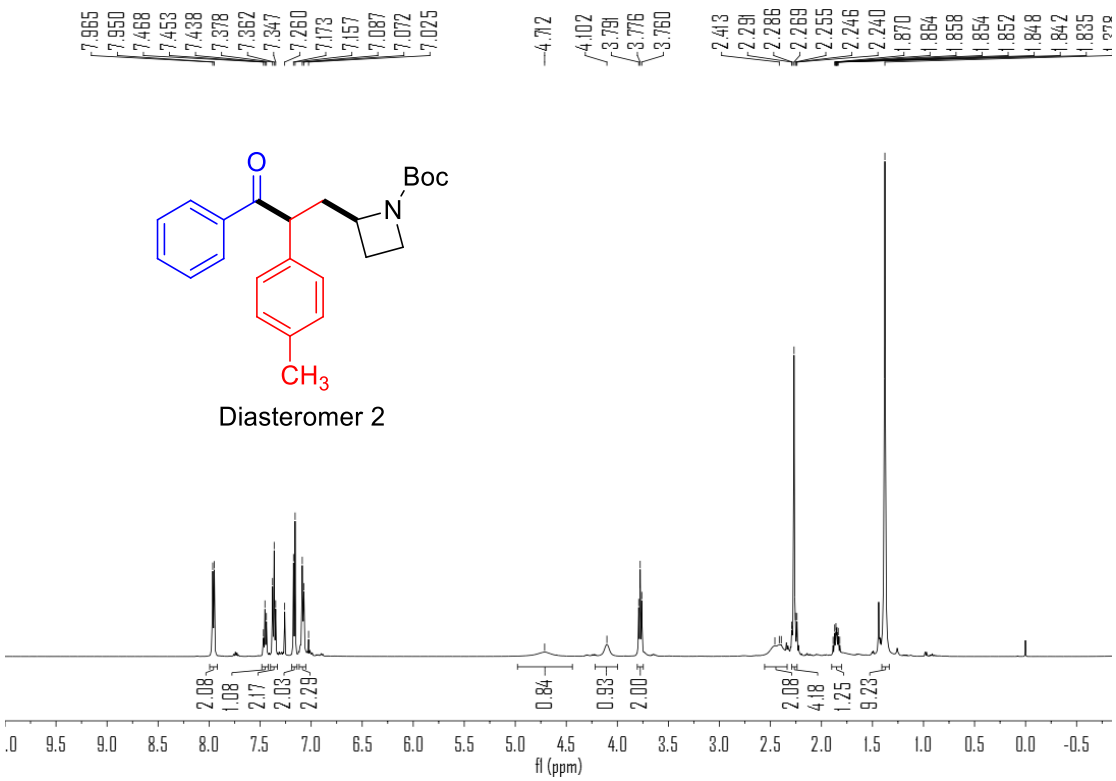
Supplementary Figure 100. ^{13}C NMR spectrum of **5 h'**



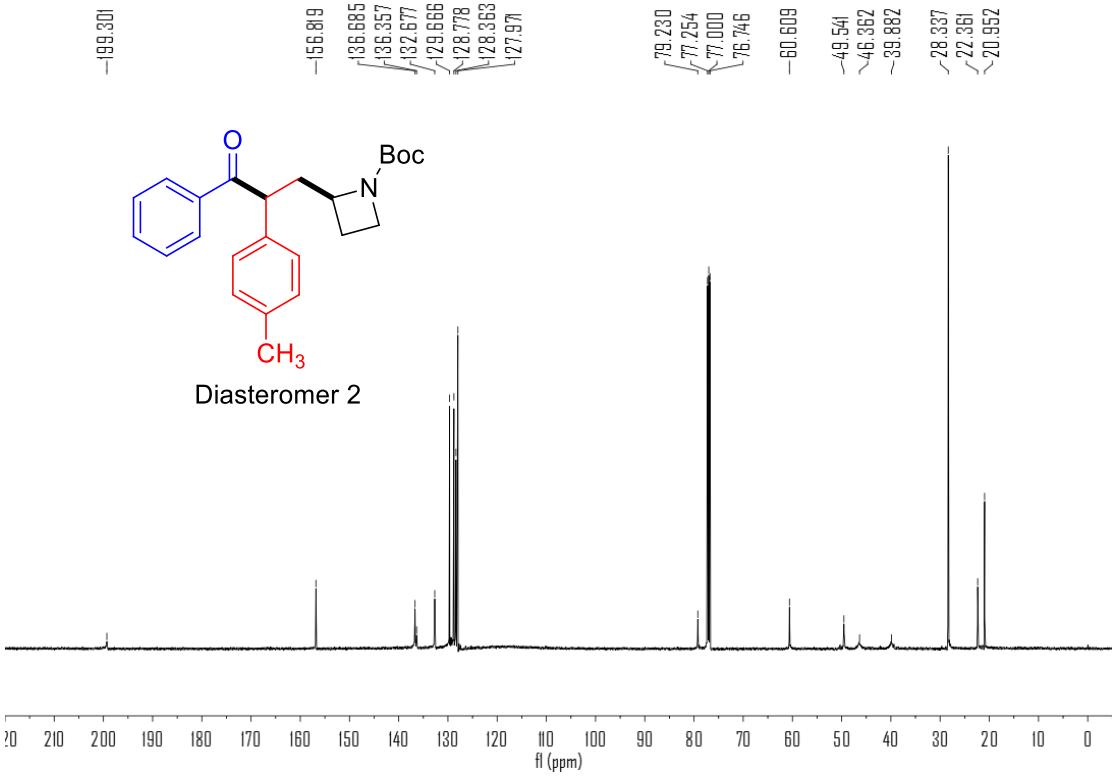
Supplementary Figure 101. ^{1}H NMR spectrum of **5i**



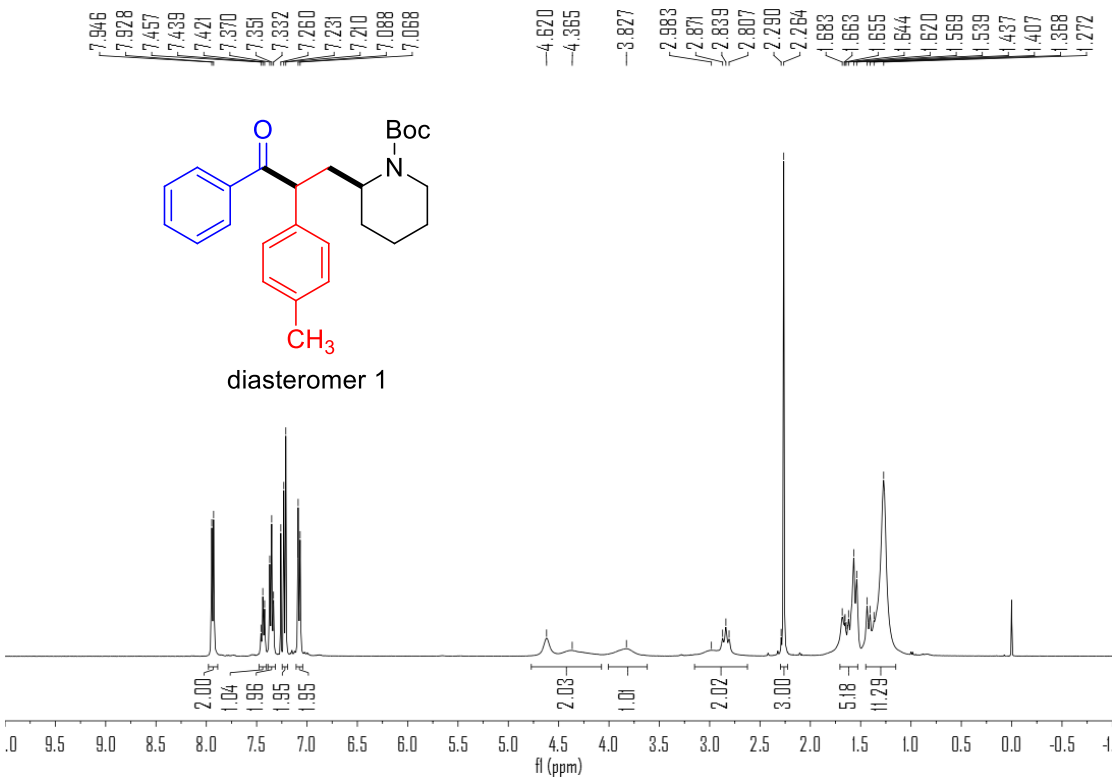
Supplementary Figure 102. ^{13}C NMR spectrum of **5 i**



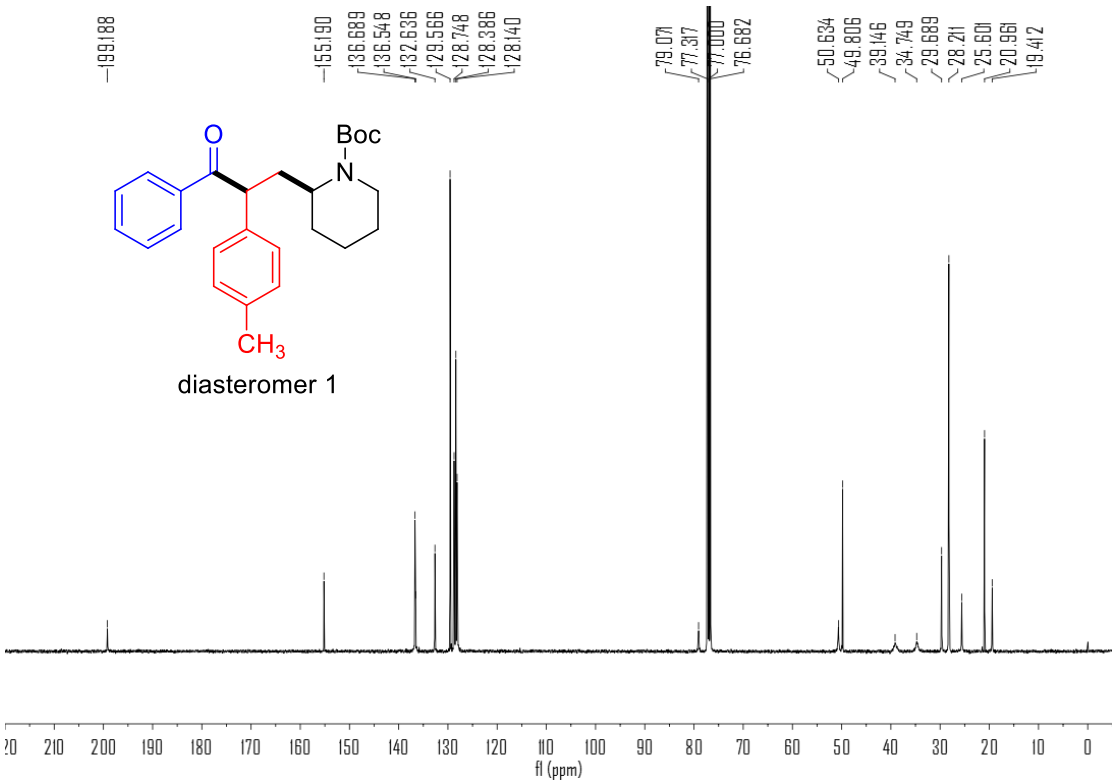
Supplementary Figure 103. ^{1}H NMR spectrum of **5i'**



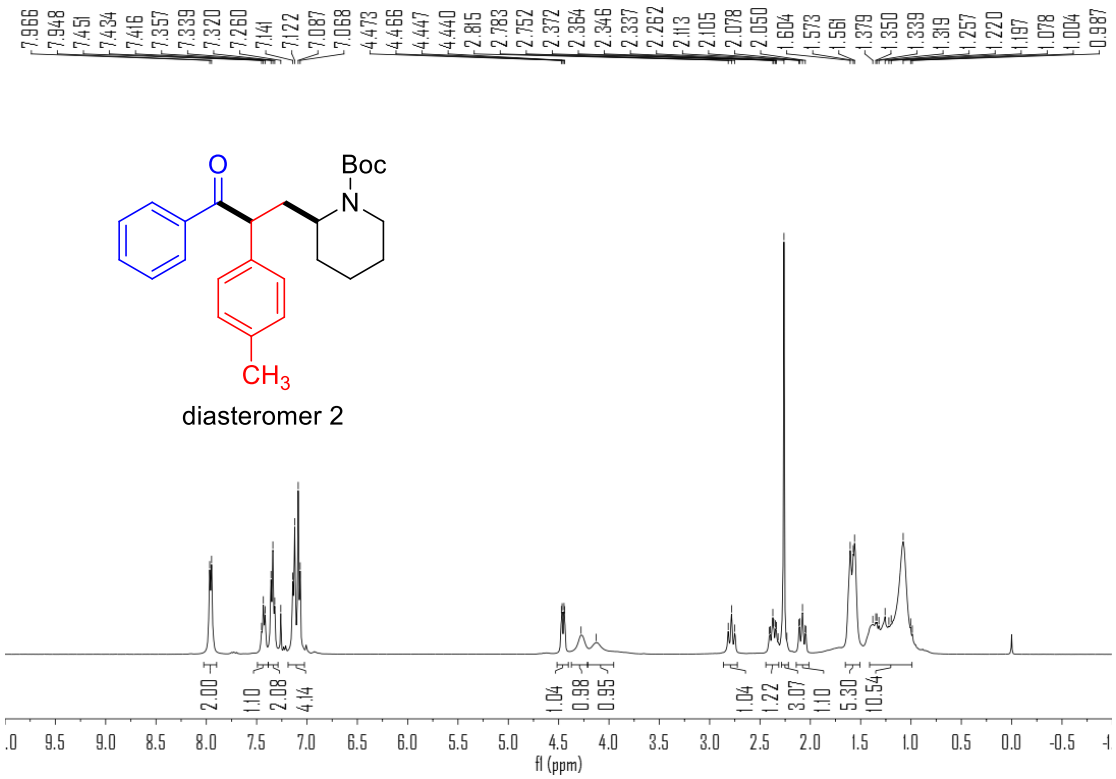
Supplementary Figure 104. ^{13}C NMR spectrum of **5 i'**



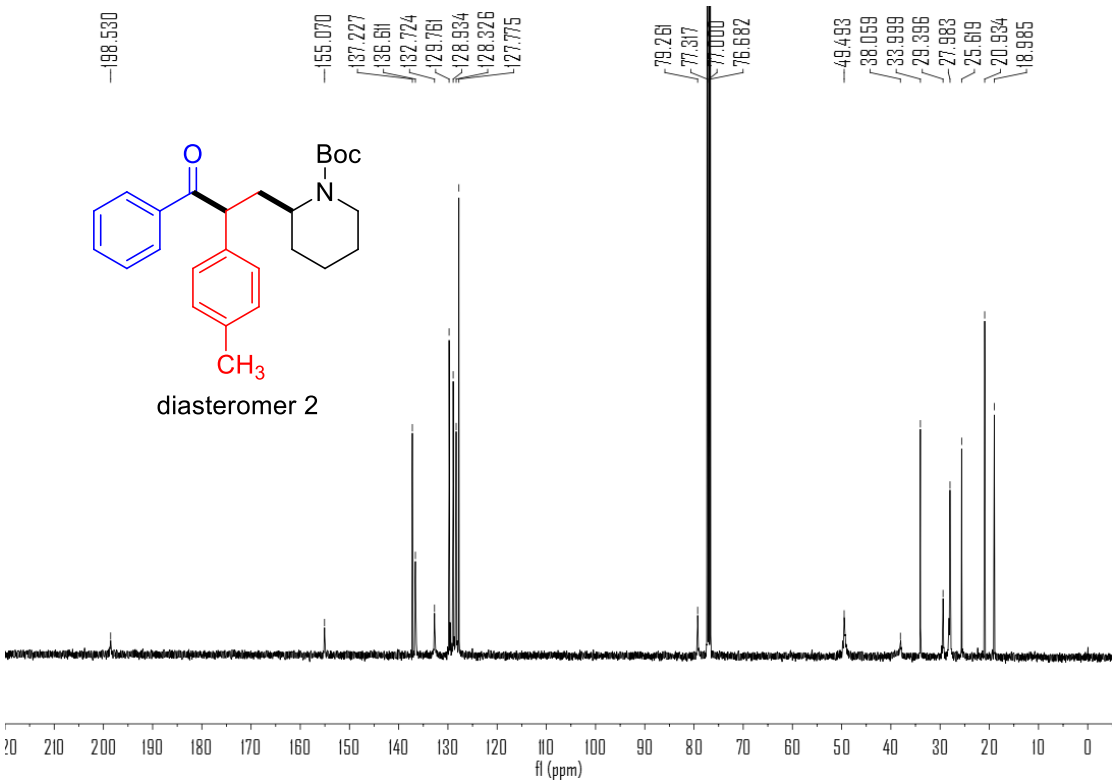
Supplementary Figure 105. ^{1}H NMR spectrum of **5j**



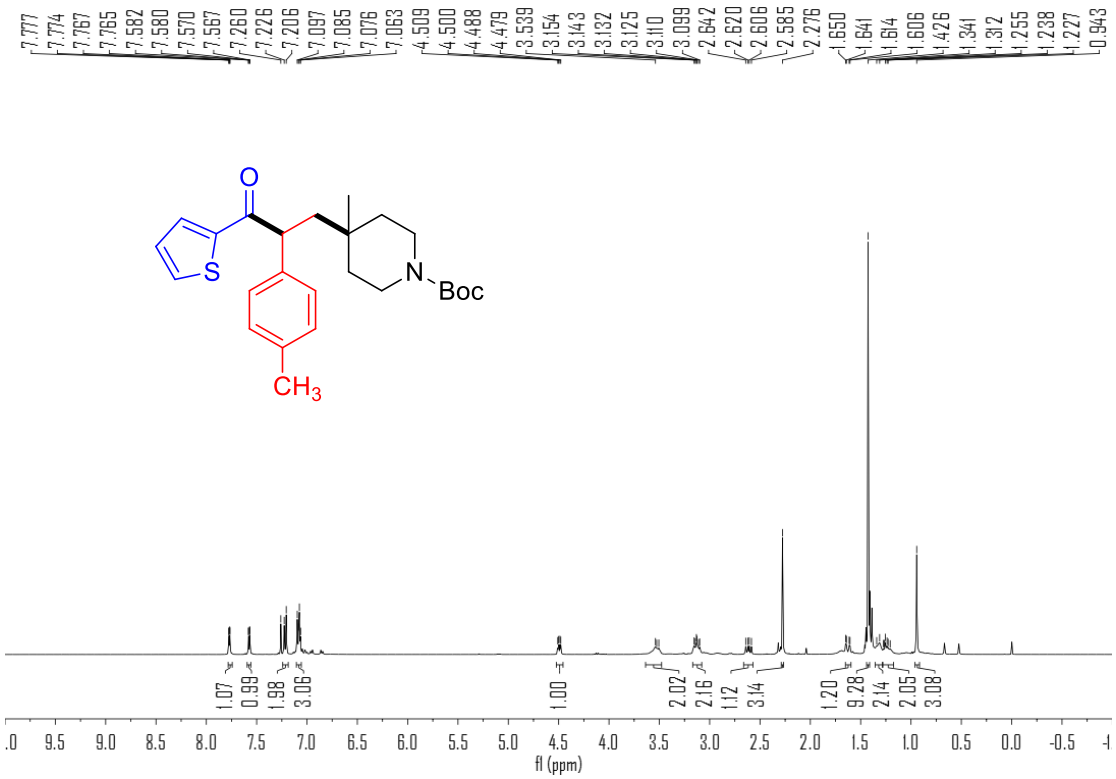
Supplementary Figure 106. ^{13}C NMR spectrum of **5 j**



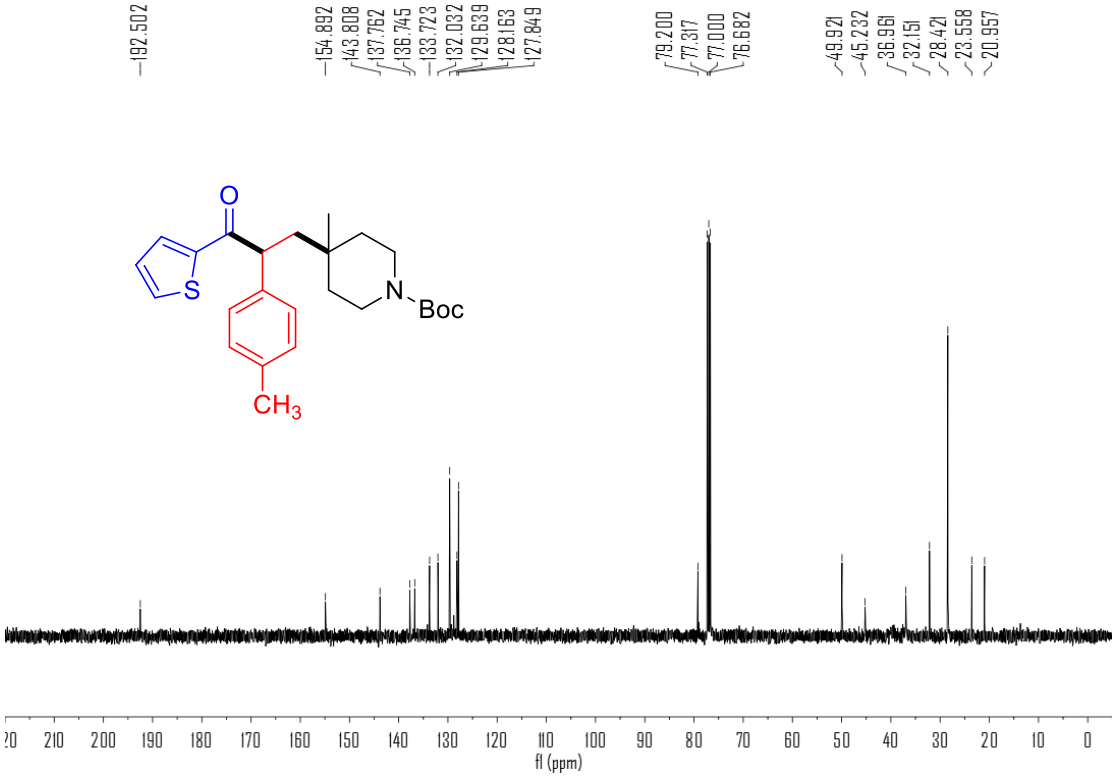
Supplementary Figure 107. ^{1}H NMR spectrum of **5j'**



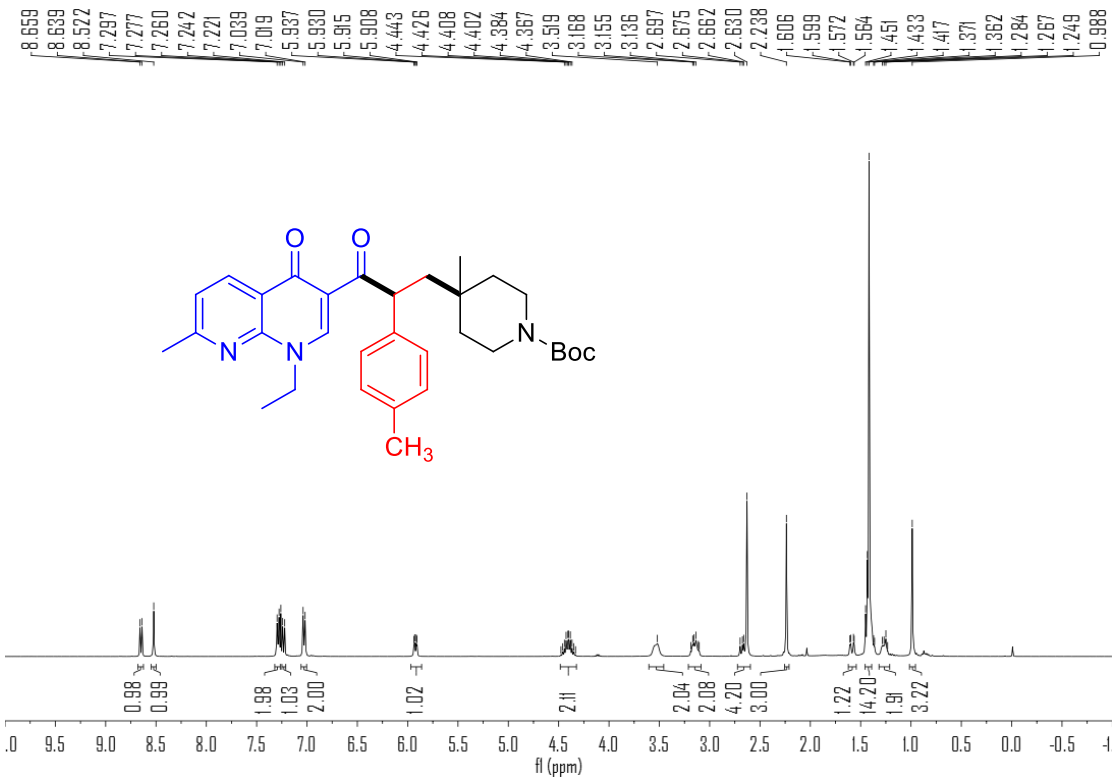
Supplementary Figure 108. ^{13}C NMR spectrum of **5 j'**



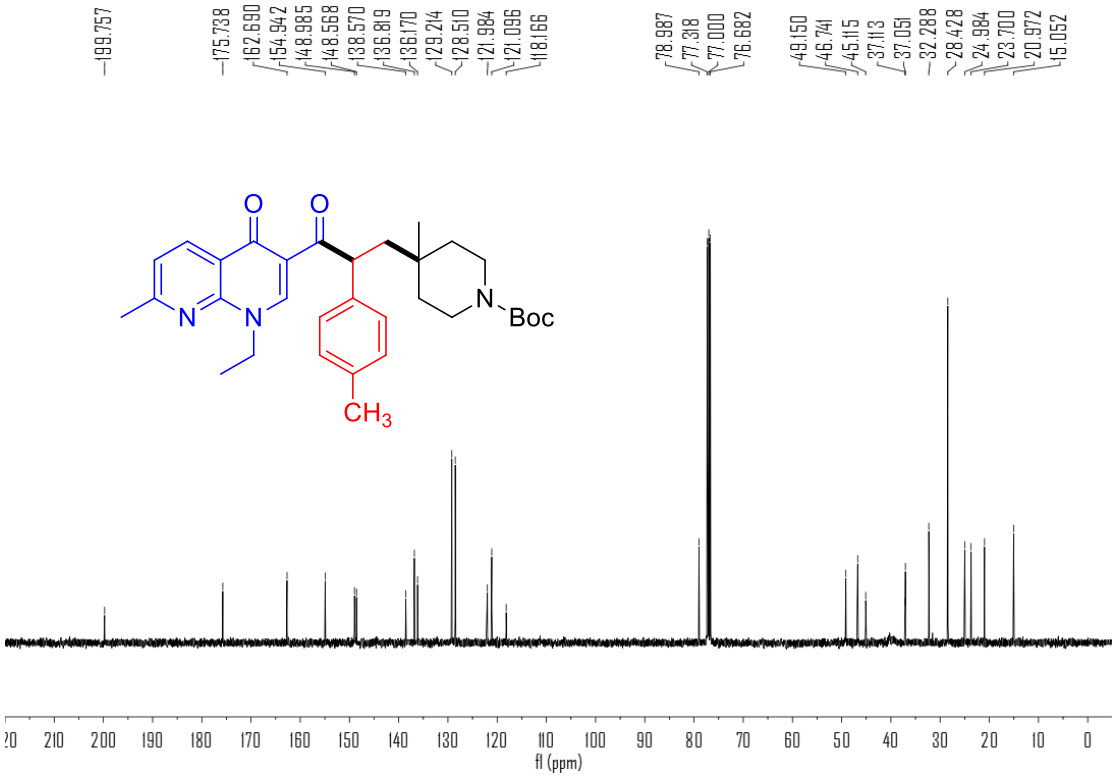
Supplementary Figure 109. ^{1}**H NMR** spectrum of **5k**



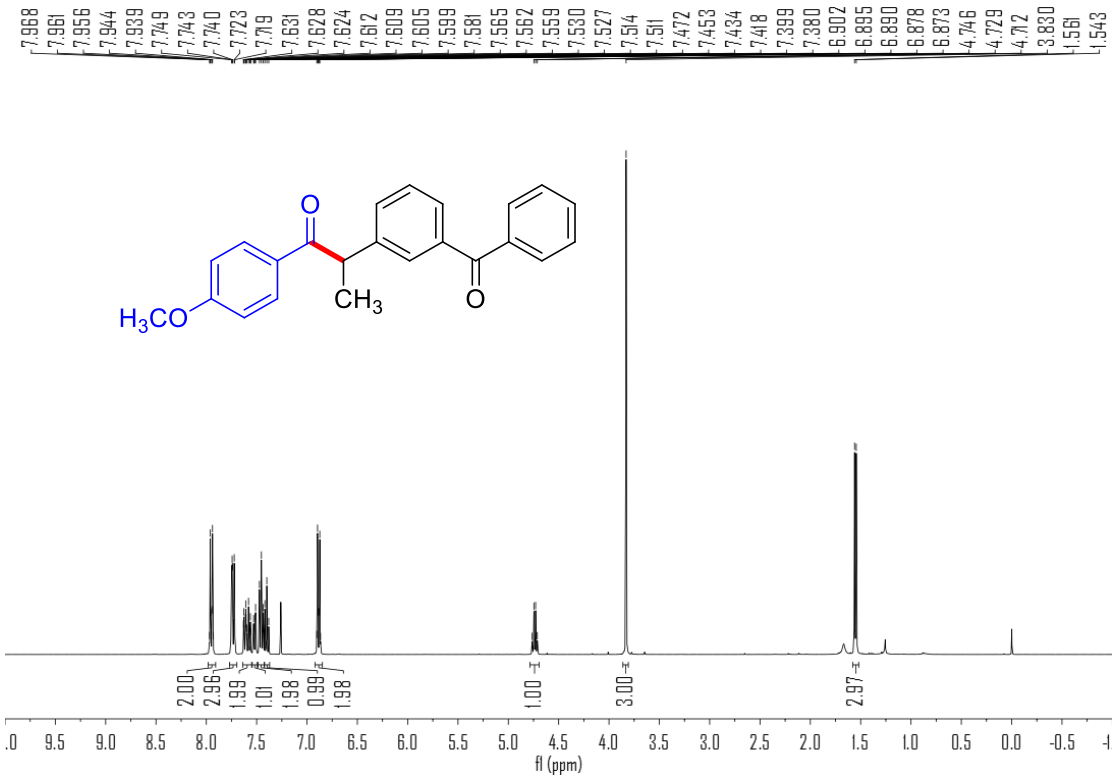
Supplementary Figure 110. ^{13}**C NMR** spectrum of **5 k**



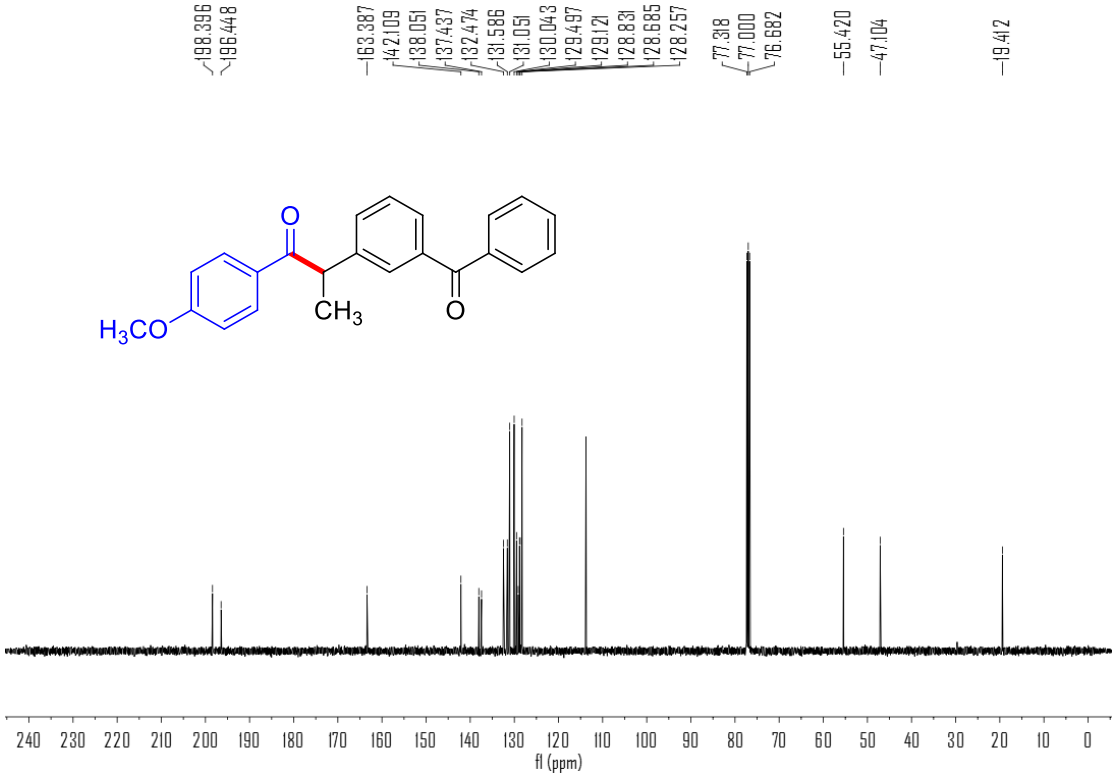
Supplementary Figure 111. ^{1}**H NMR** spectrum of **5l**



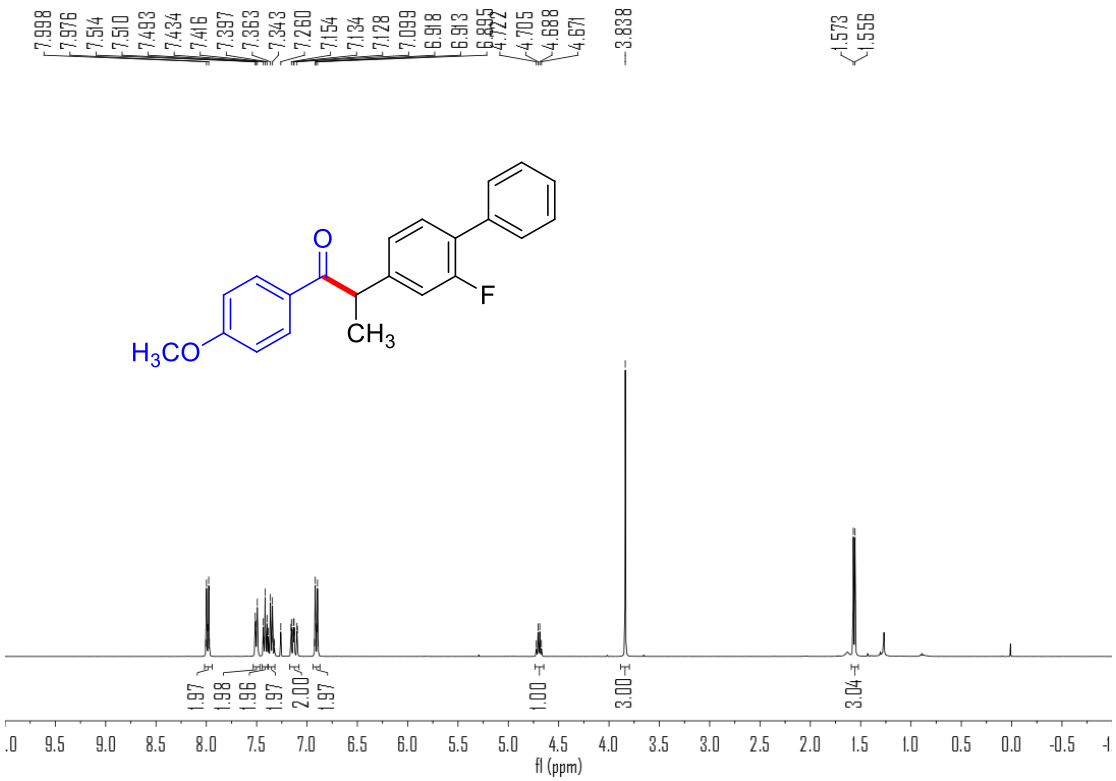
Supplementary Figure 112. ^{13}**C NMR** spectrum of **5l**



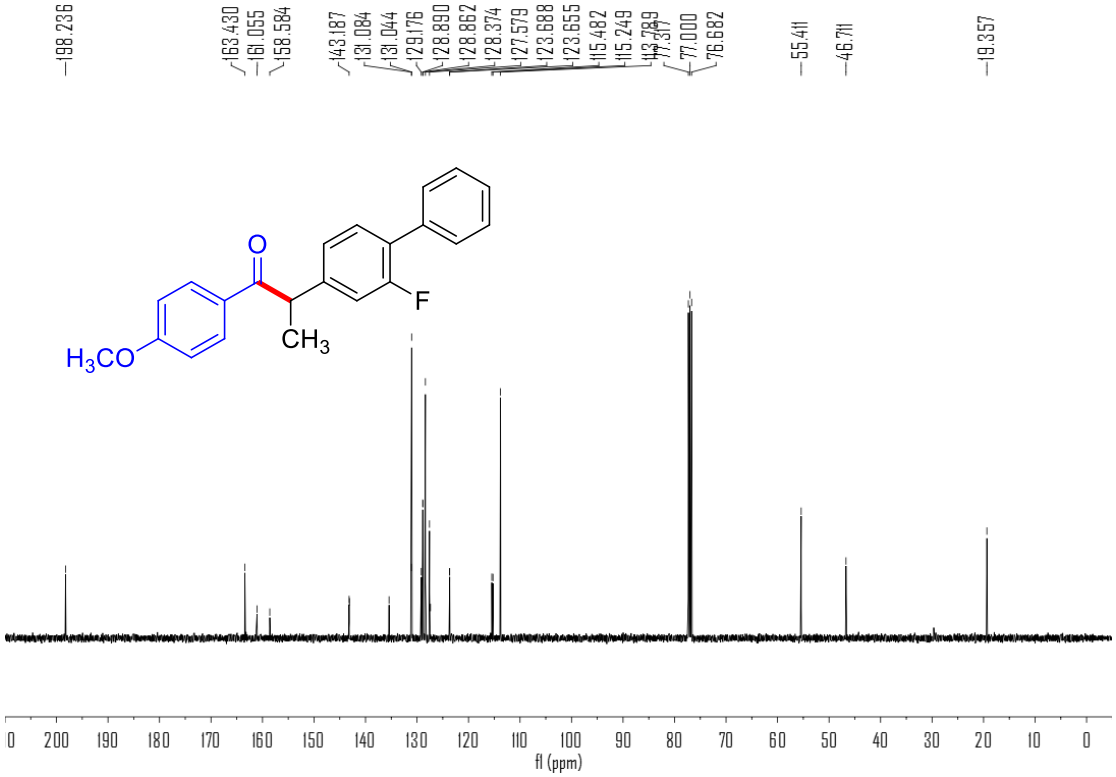
Supplementary Figure 113. ^{1}H NMR spectrum of **6a**



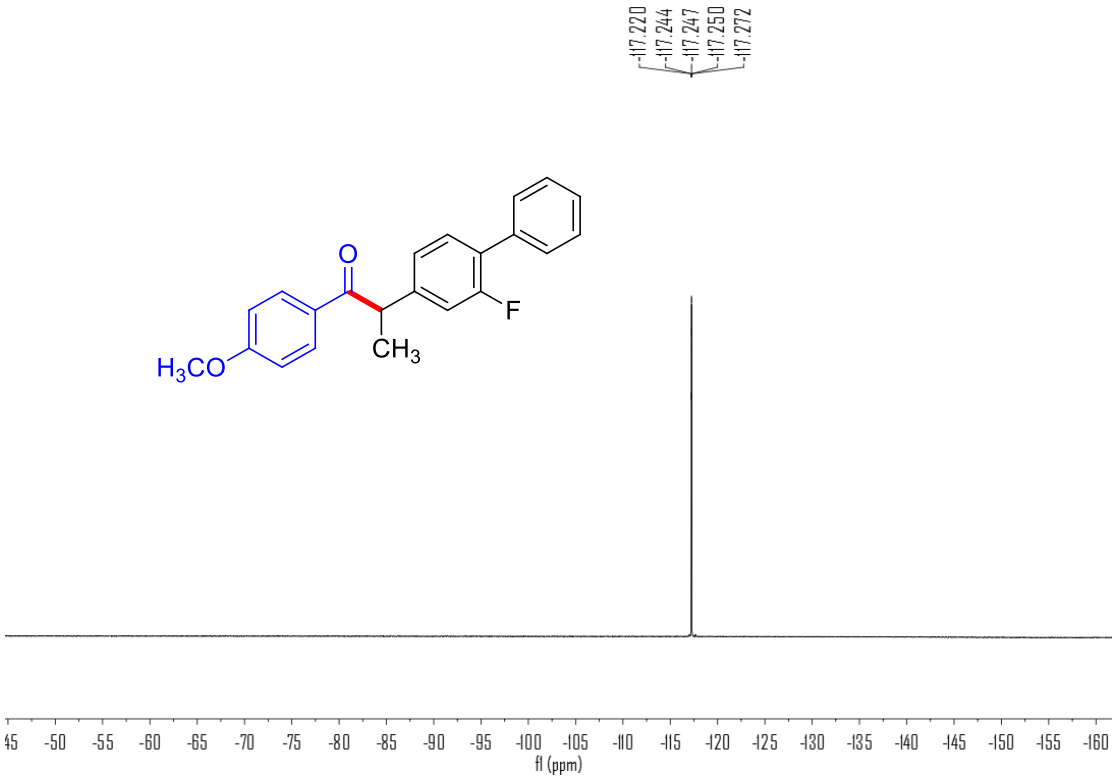
Supplementary Figure 114. ^{13}C NMR spectrum of **6a**



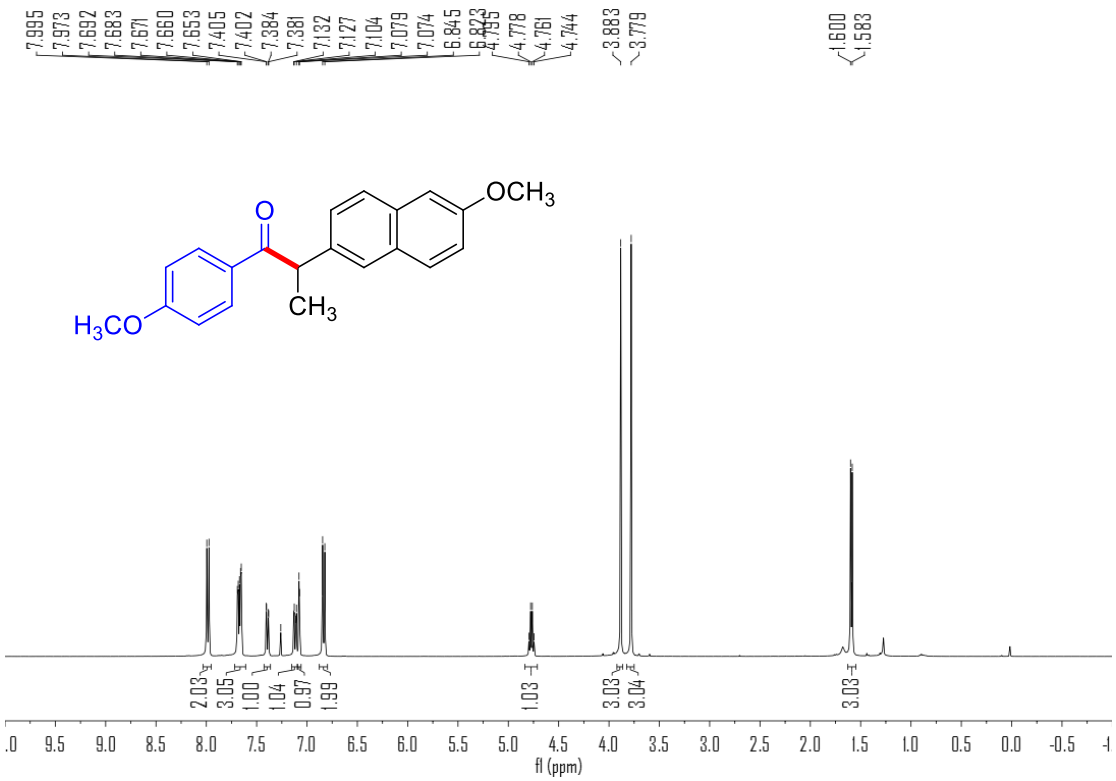
Supplementary Figure 115. ^{1}H NMR spectrum of **6b**



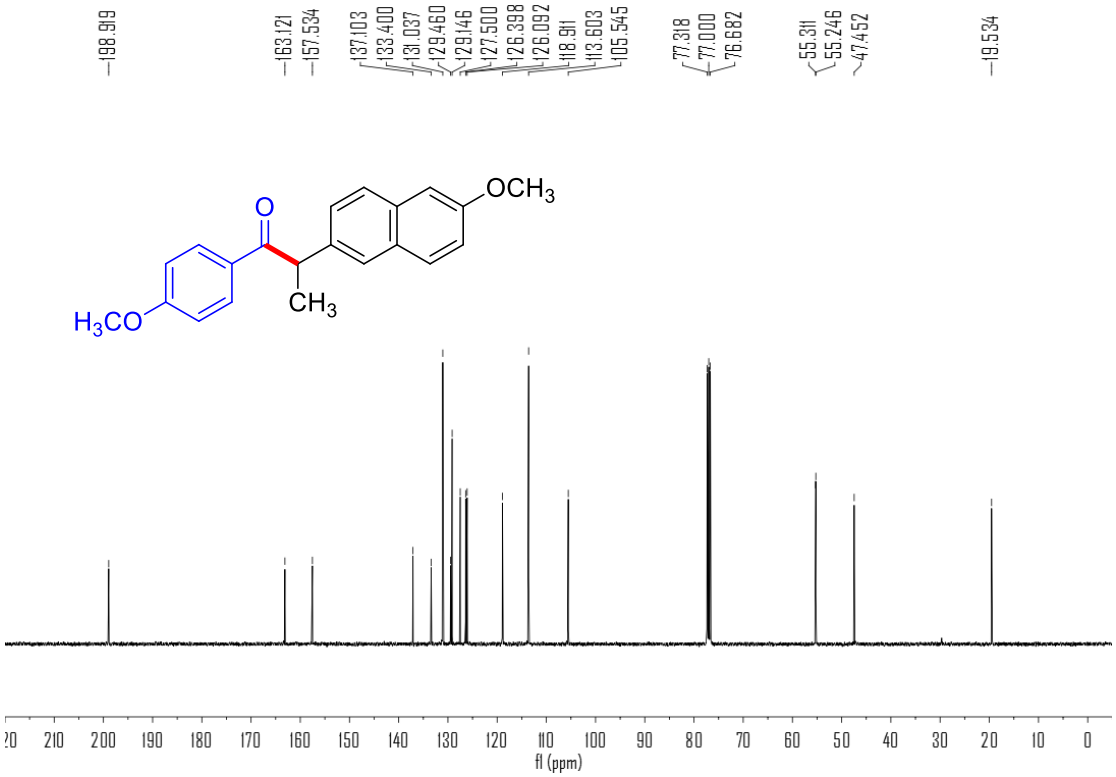
Supplementary Figure 116. ^{13}C NMR spectrum of **6b**



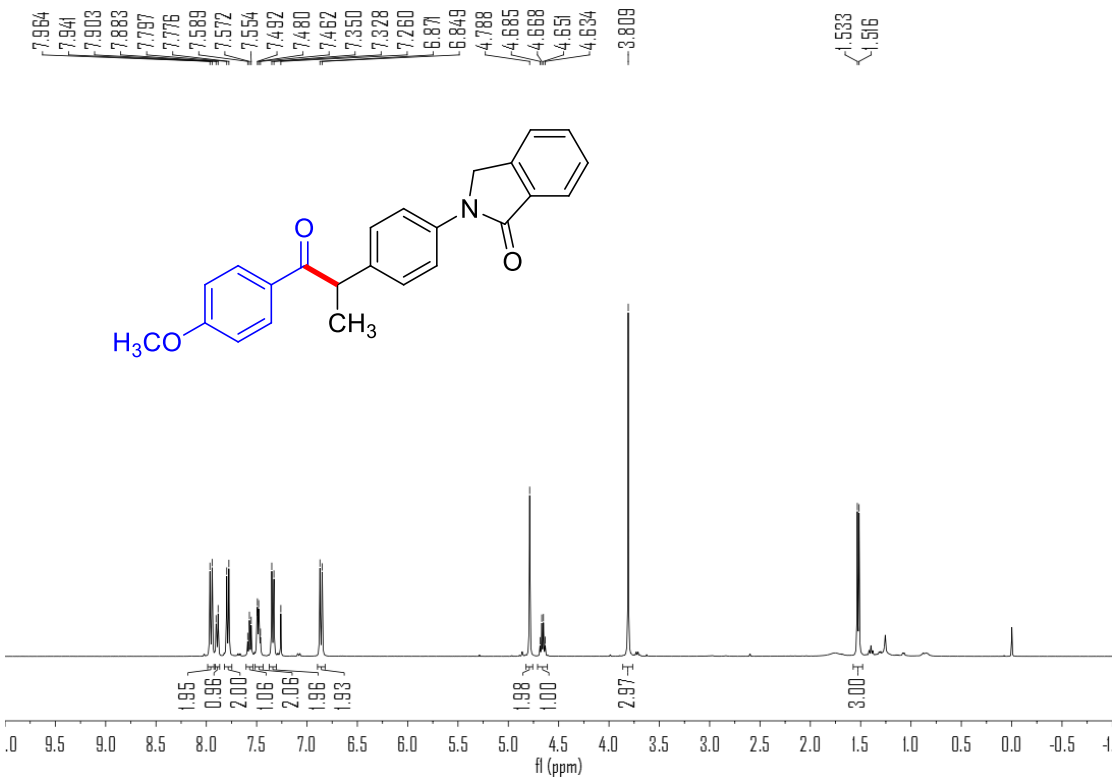
Supplementary Figure 117. ^{19}**F NMR** spectrum of **6b**



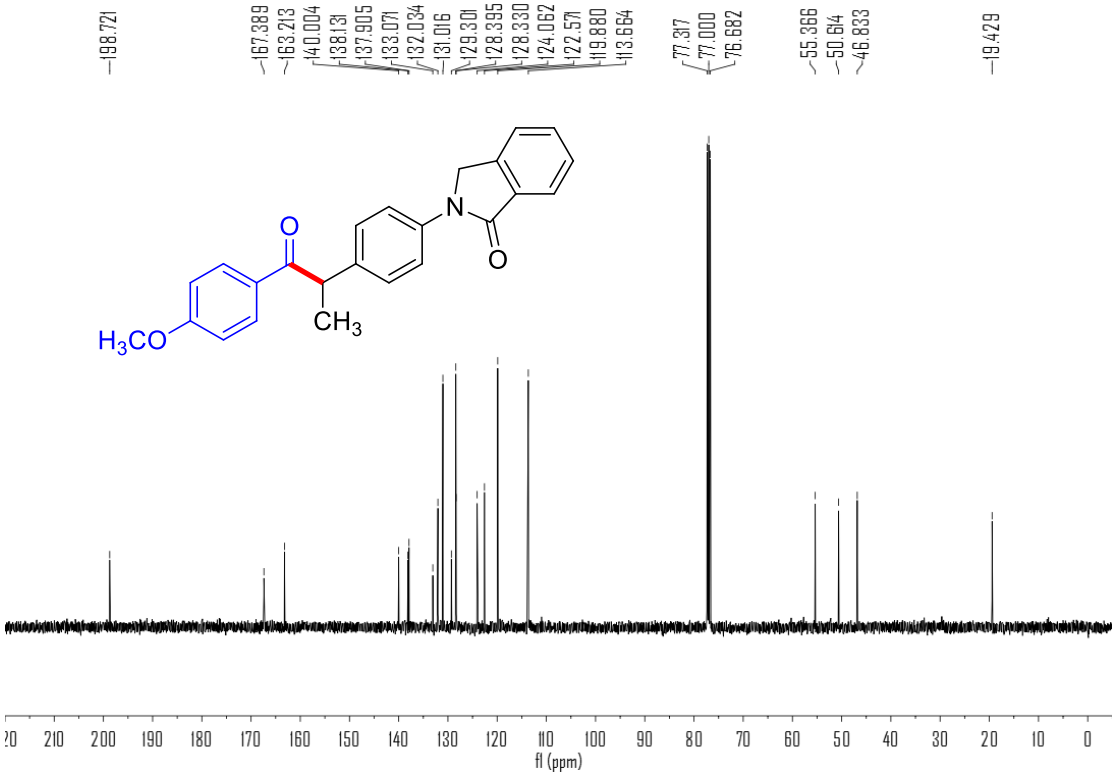
Supplementary Figure 118. ^{1}H NMR spectrum of **6c**



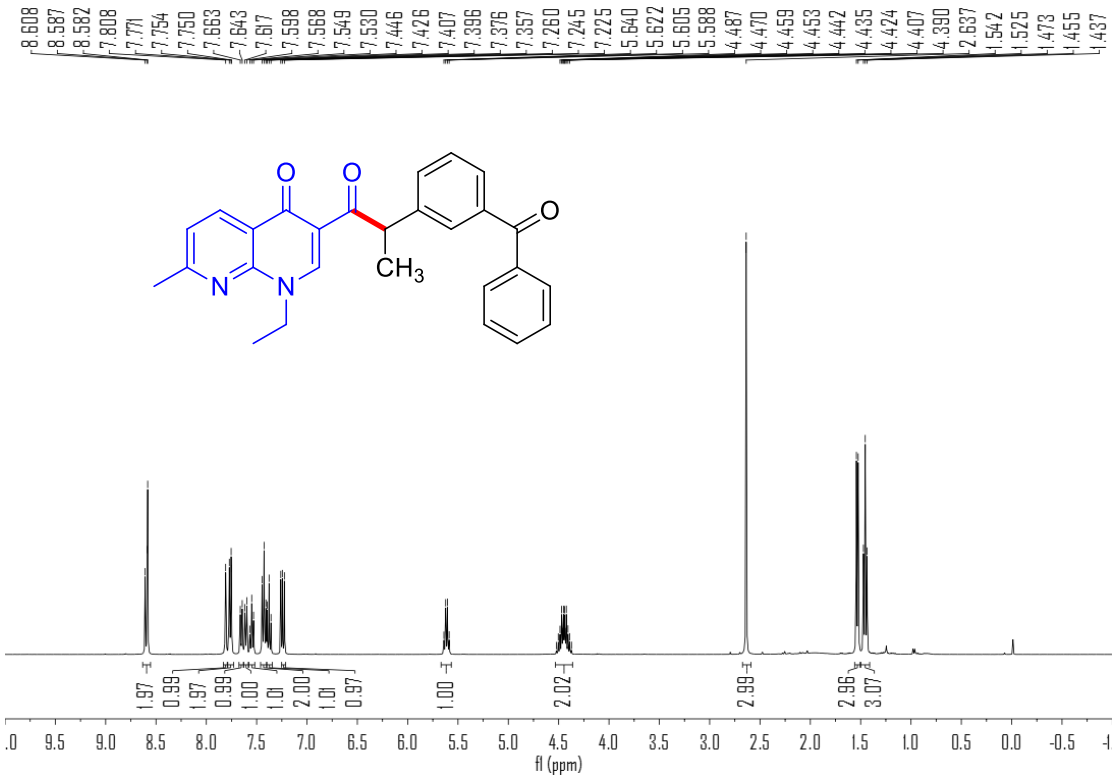
Supplementary Figure 119. ^{13}C NMR spectrum of **6c**



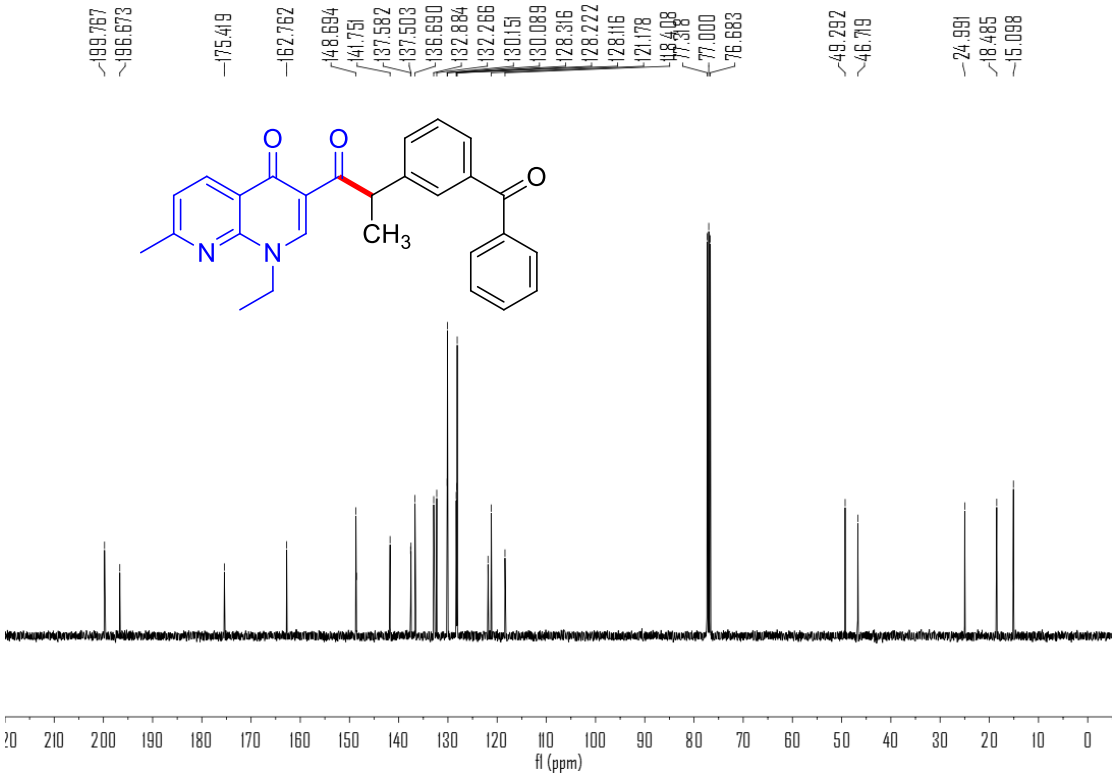
Supplementary Figure 120. ^{1}**H NMR** spectrum of **6d**



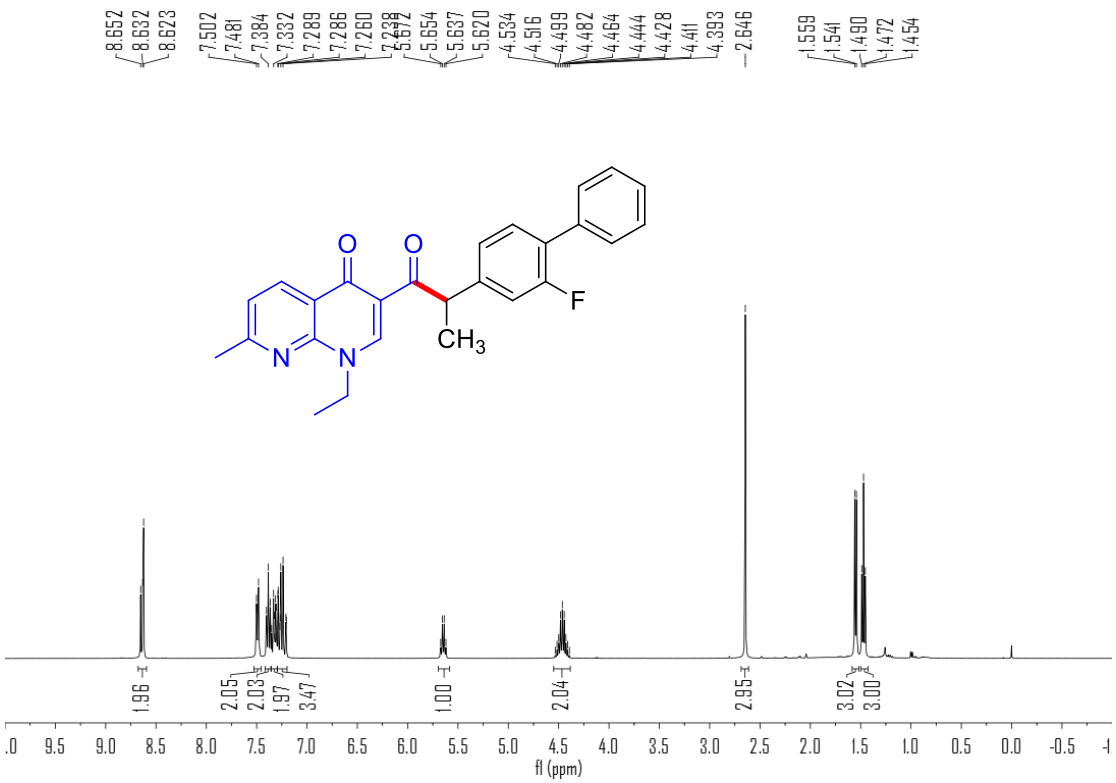
Supplementary Figure 121. ^{13}**C NMR** spectrum of **6d**



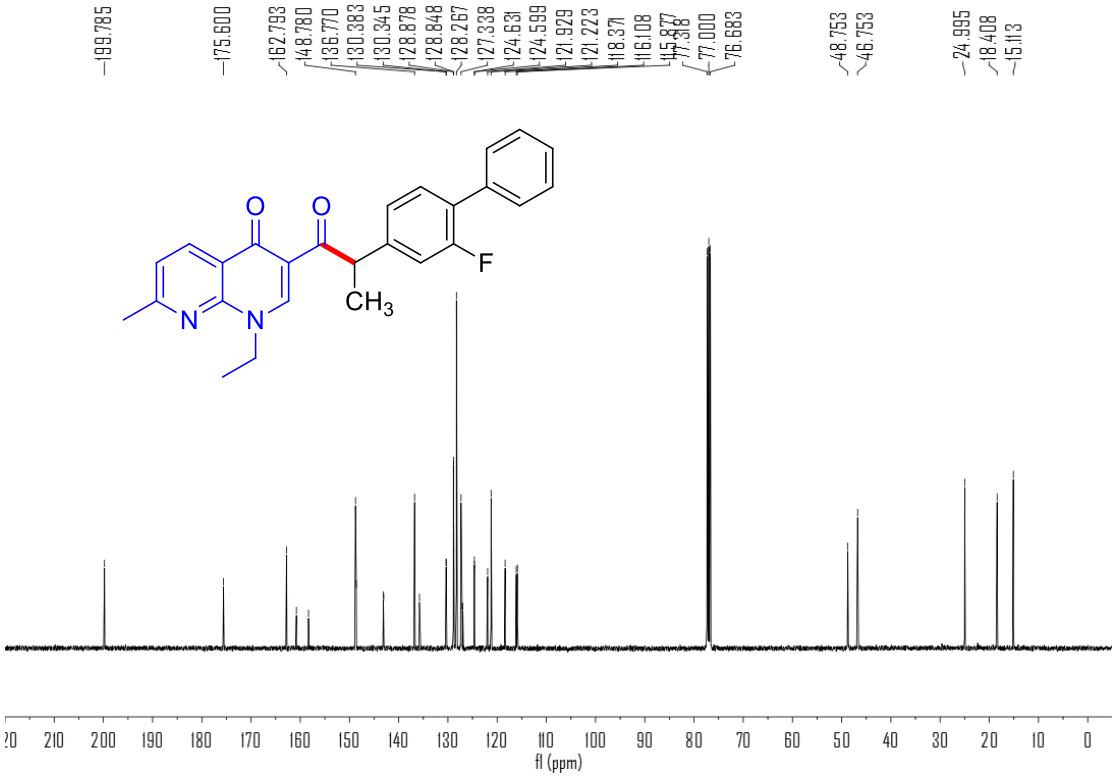
Supplementary Figure 122. ^{1}**H NMR** spectrum of **6e**



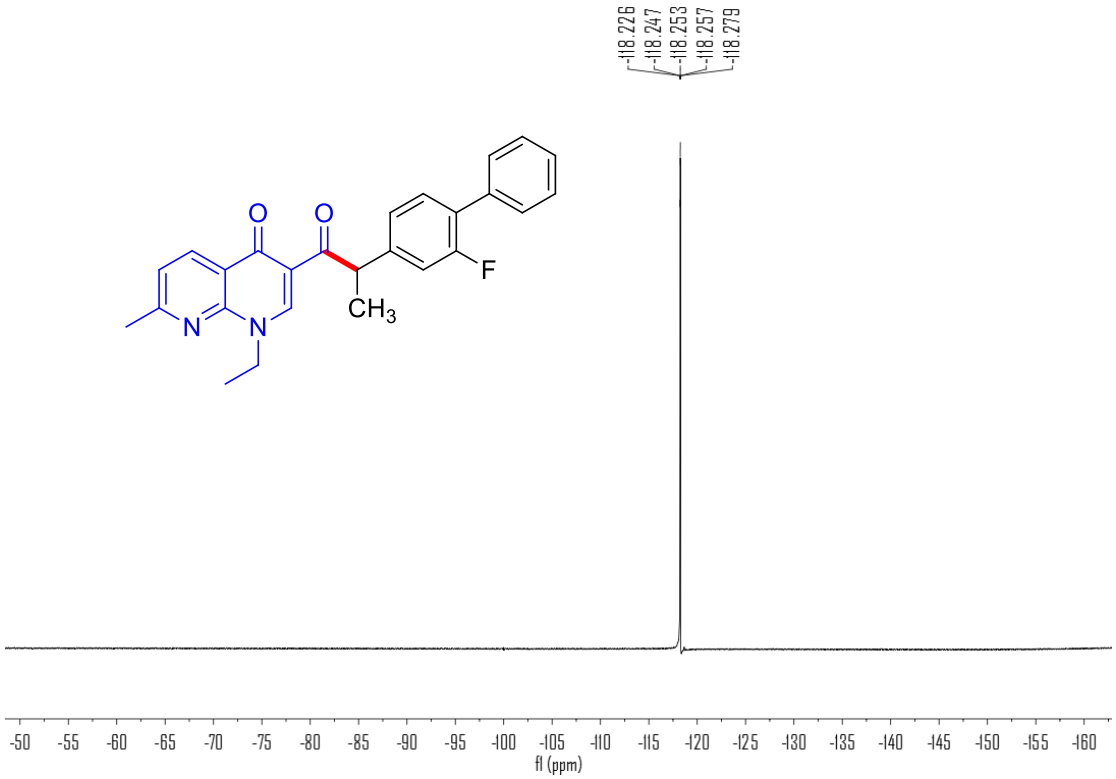
Supplementary Figure 123. ^{13}**C NMR** spectrum of **6e**



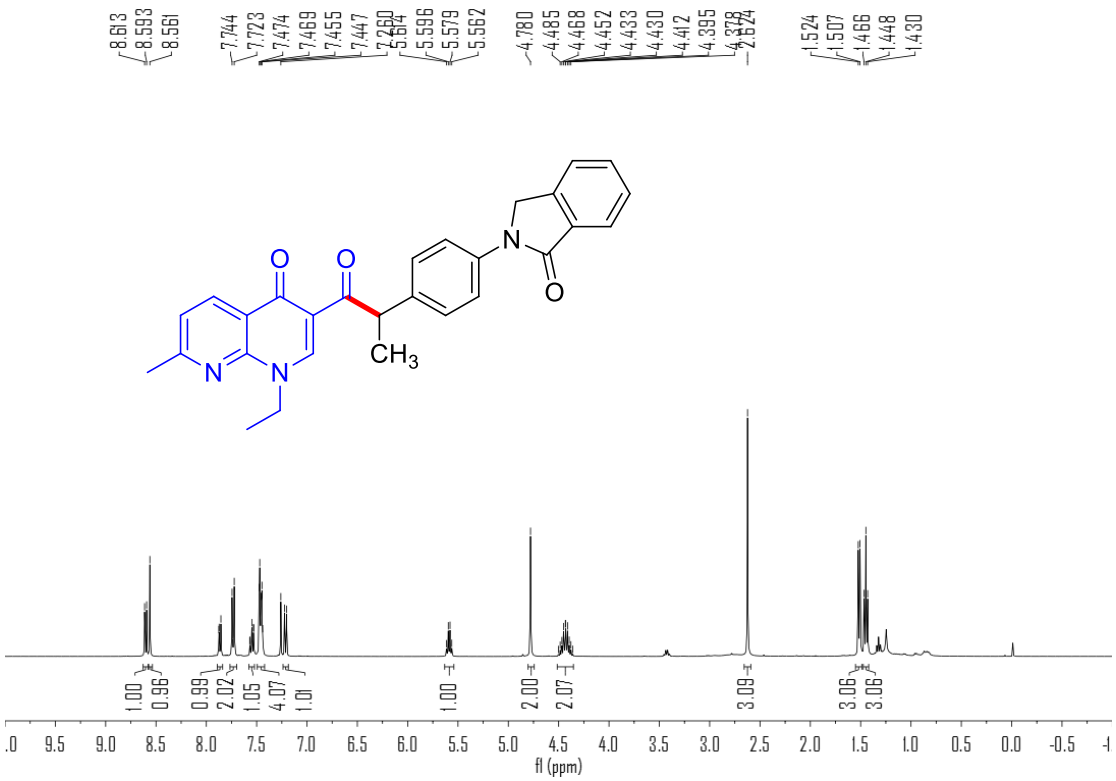
Supplementary Figure 124. ^{1}H NMR spectrum of **6f**



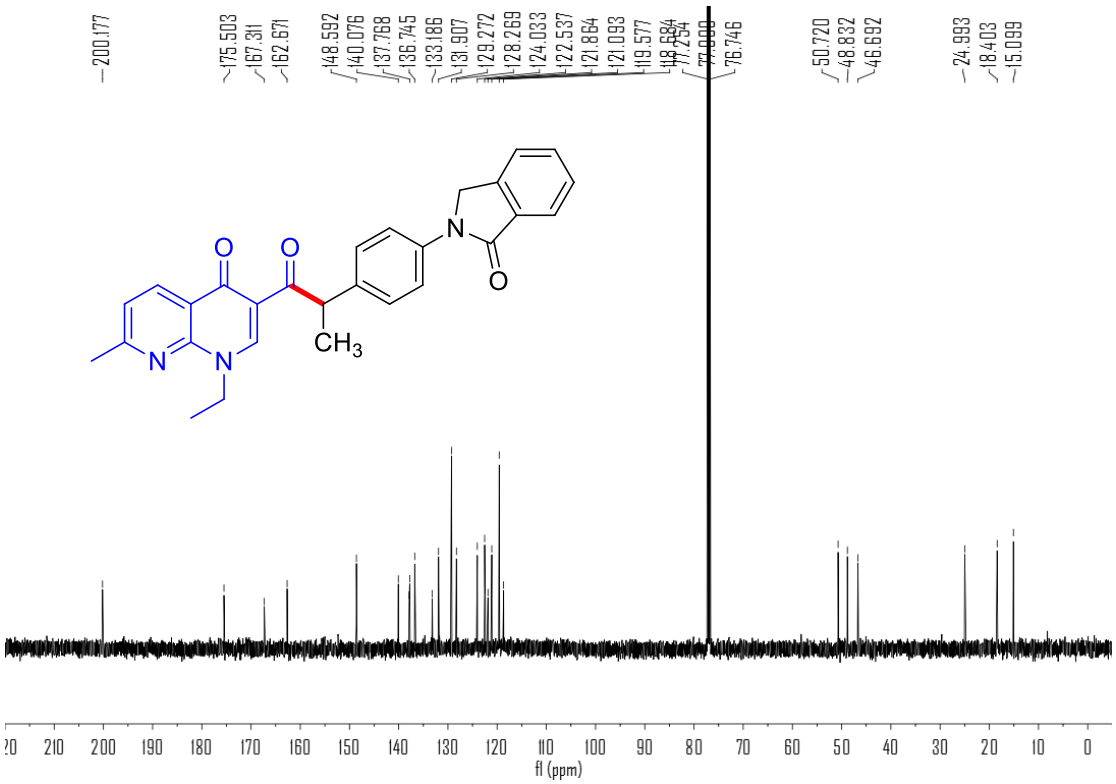
Supplementary Figure 125. ^{13}C NMR spectrum of **6f**



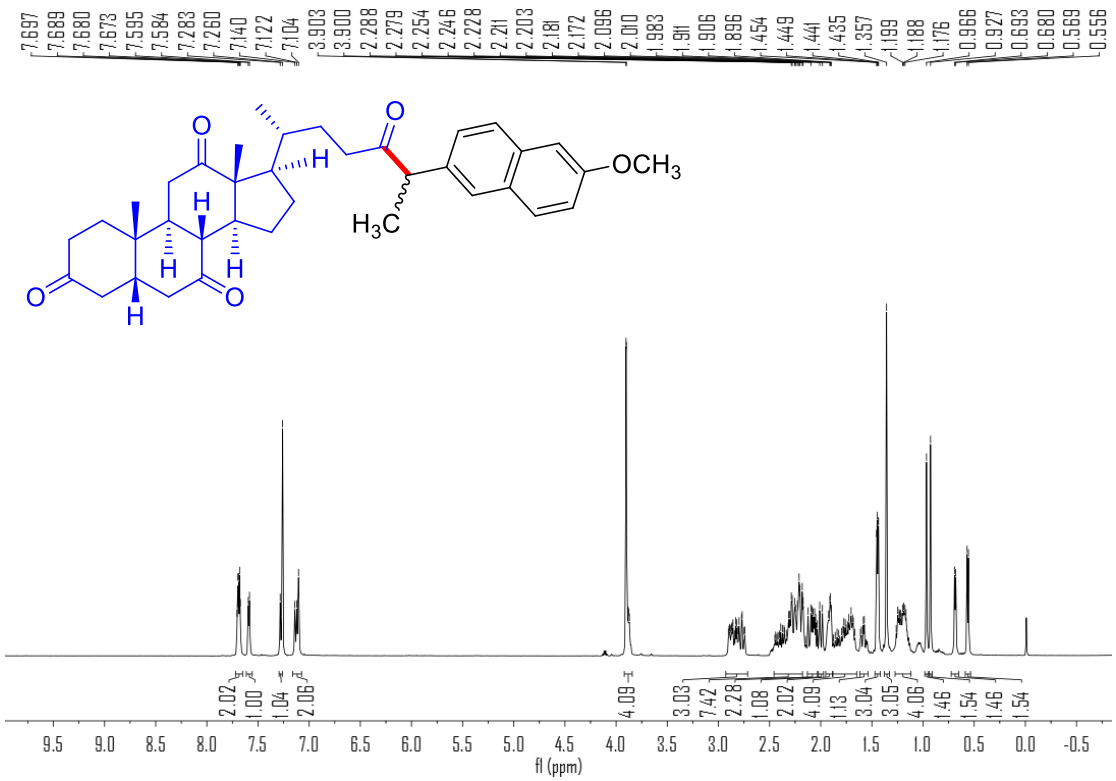
Supplementary Figure 126. ^{19}F NMR spectrum of **6f**



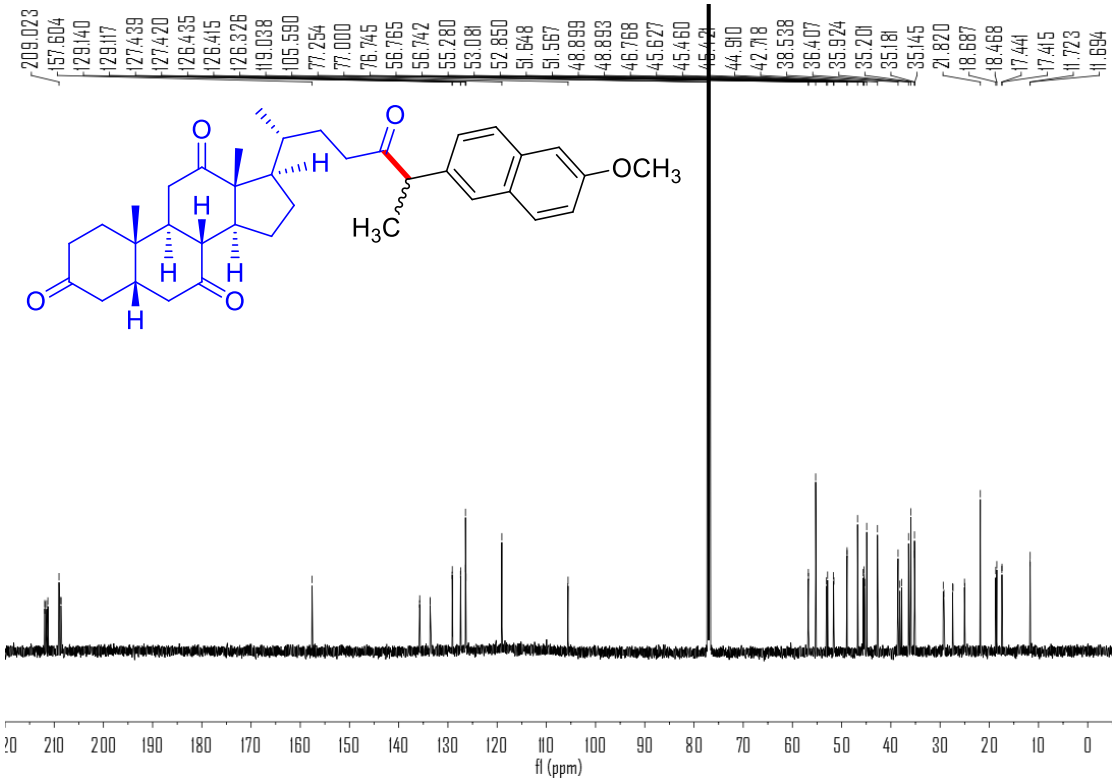
Supplementary Figure 127. ^{1}**H NMR** spectrum of **6g**



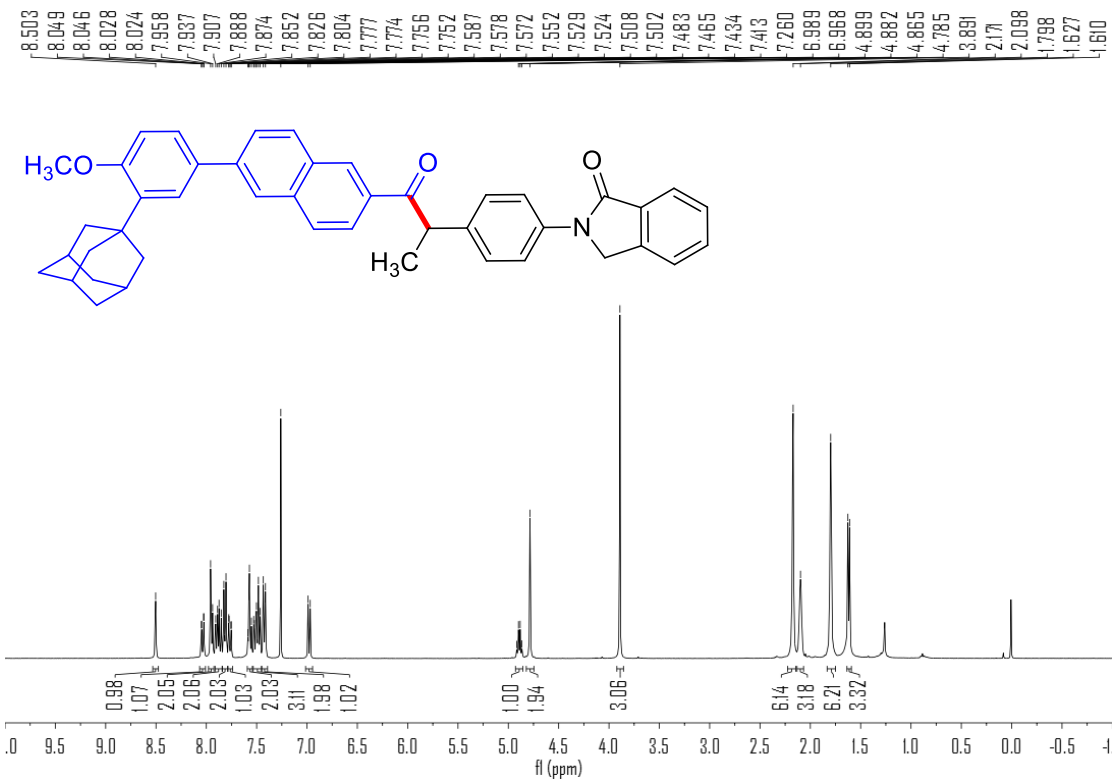
Supplementary Figure 128. ^{13}**C NMR** spectrum of **6g**



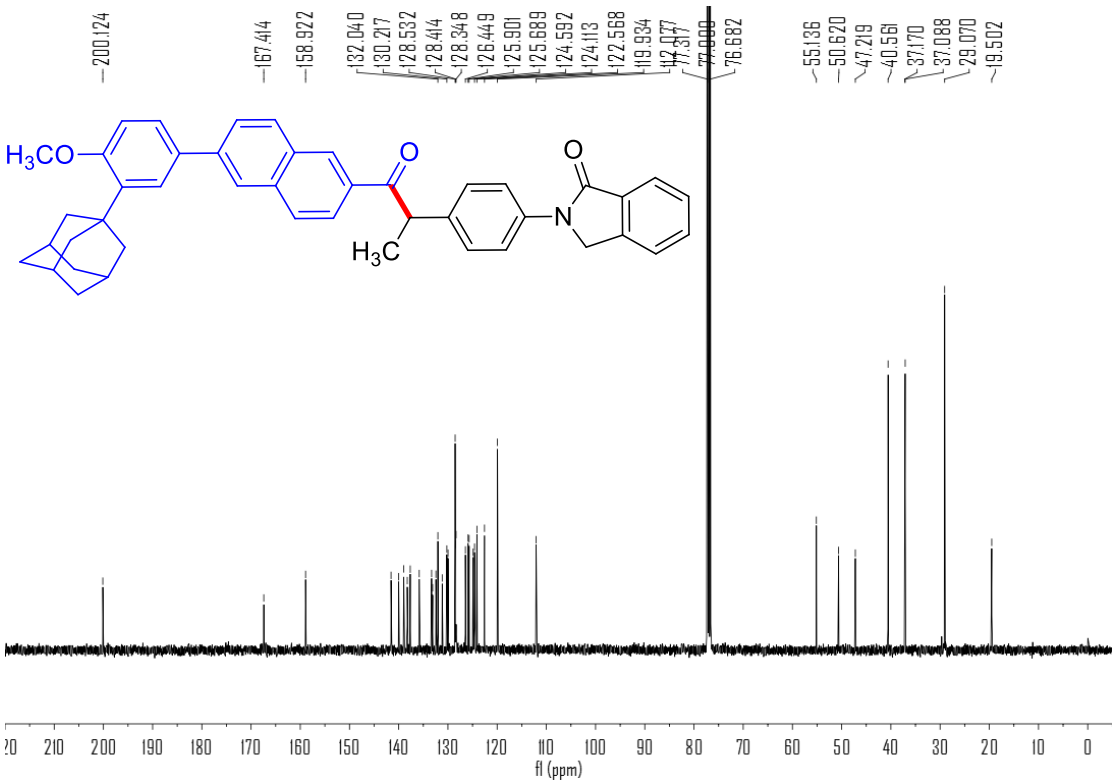
Supplementary Figure 129. ^{1}H NMR spectrum of **6h**



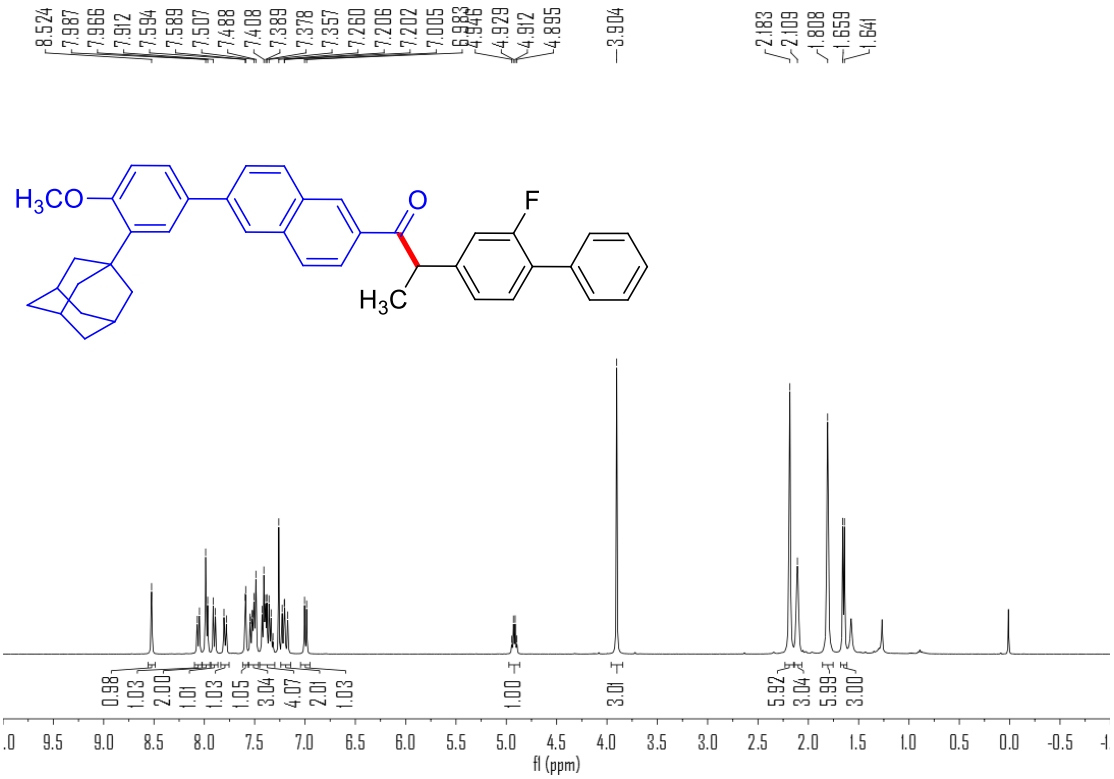
Supplementary Figure 130. ^{13}C NMR spectrum of **6h**



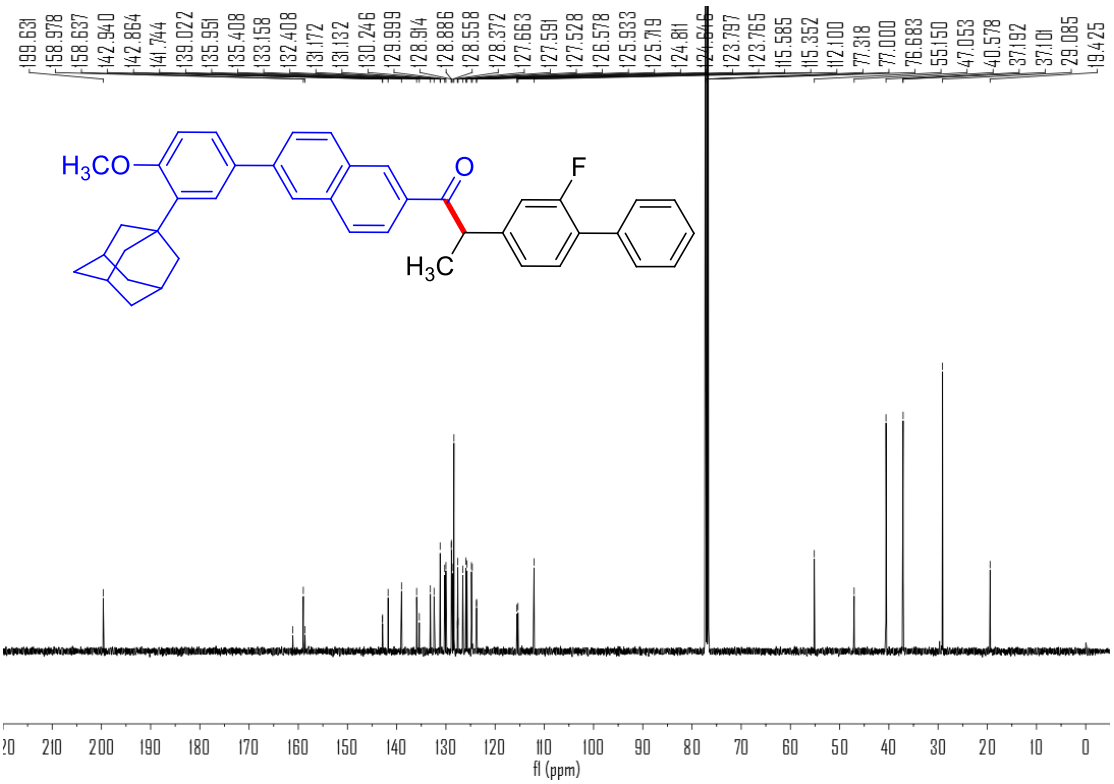
Supplementary Figure 131. ^{1}**H NMR** spectrum of **6i**



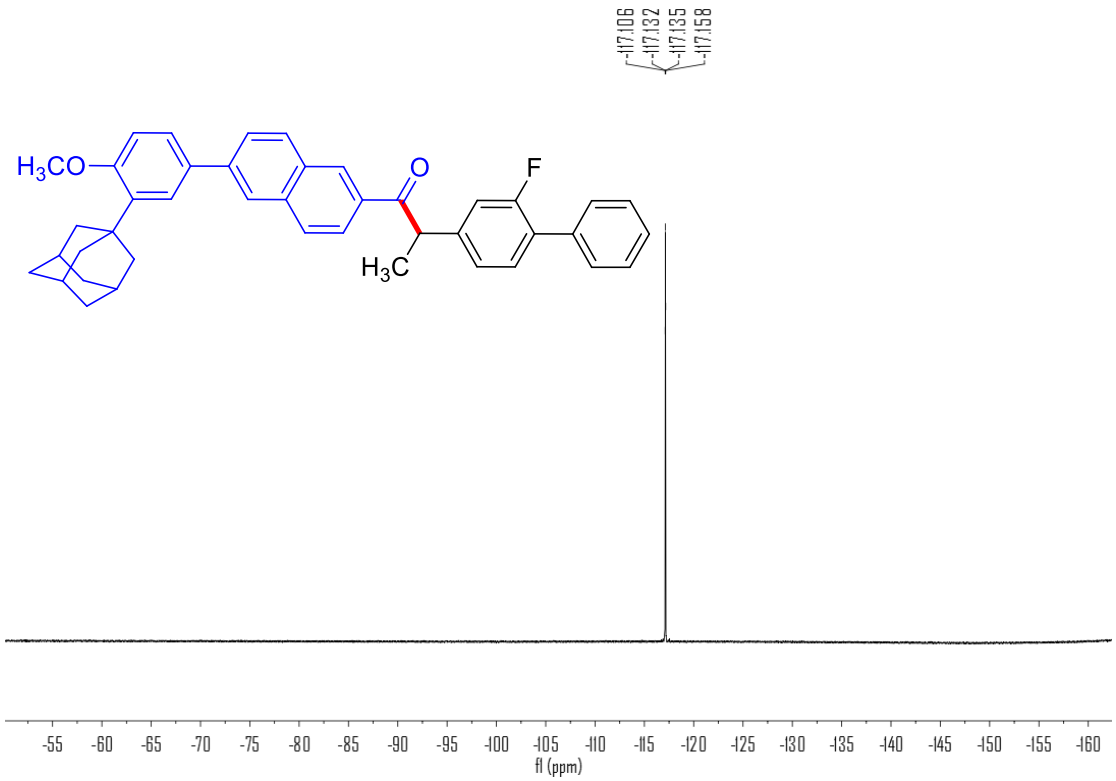
Supplementary Figure 132. ^{13}**C NMR** spectrum of **6i**



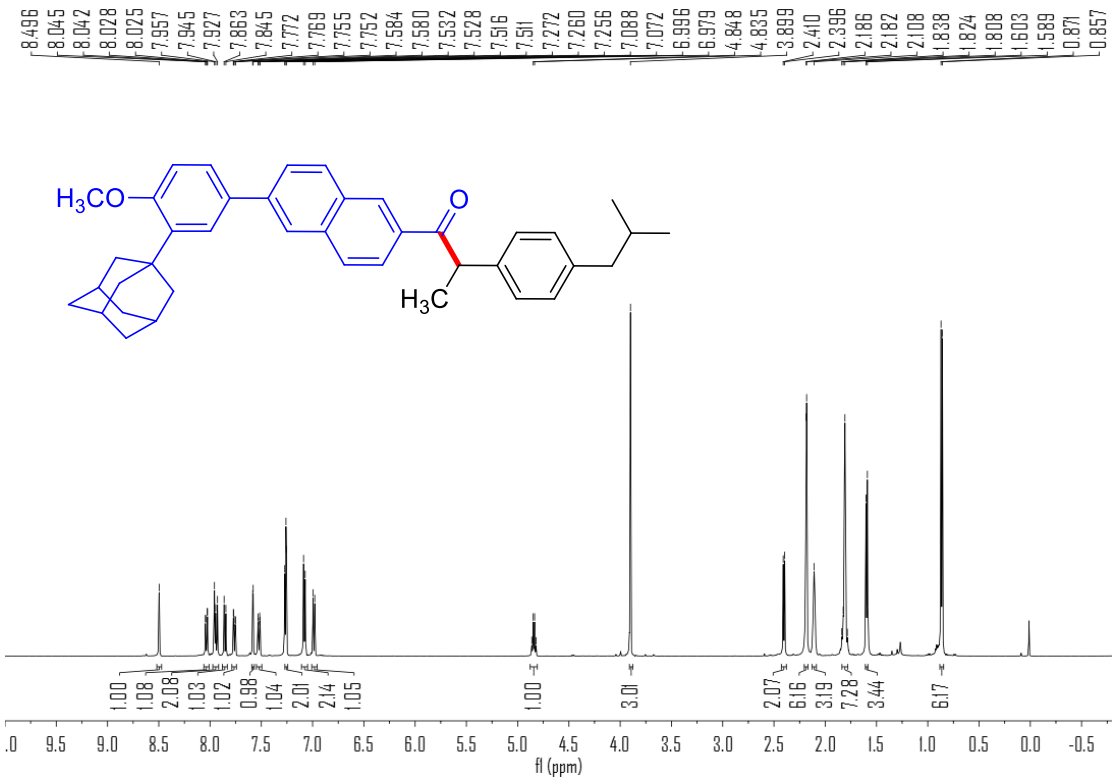
Supplementary Figure 133. ^{1}H NMR spectrum of **6j**



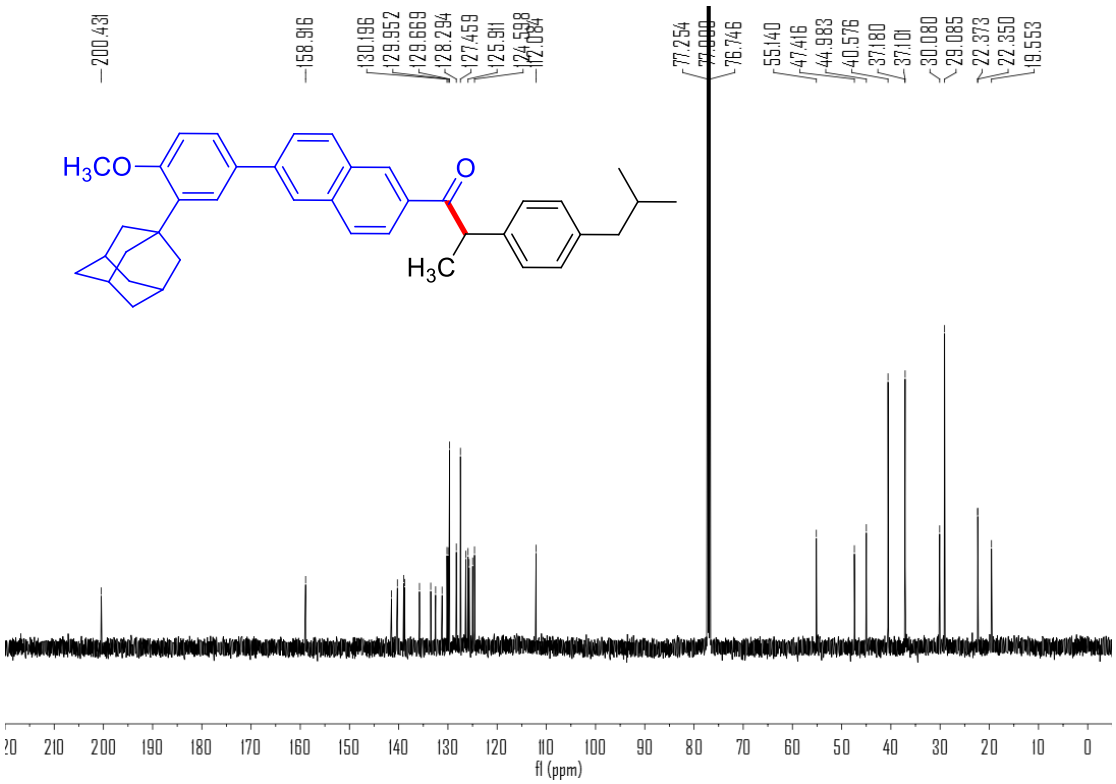
Supplementary Figure 134. ^{13}C NMR spectrum of **6j**



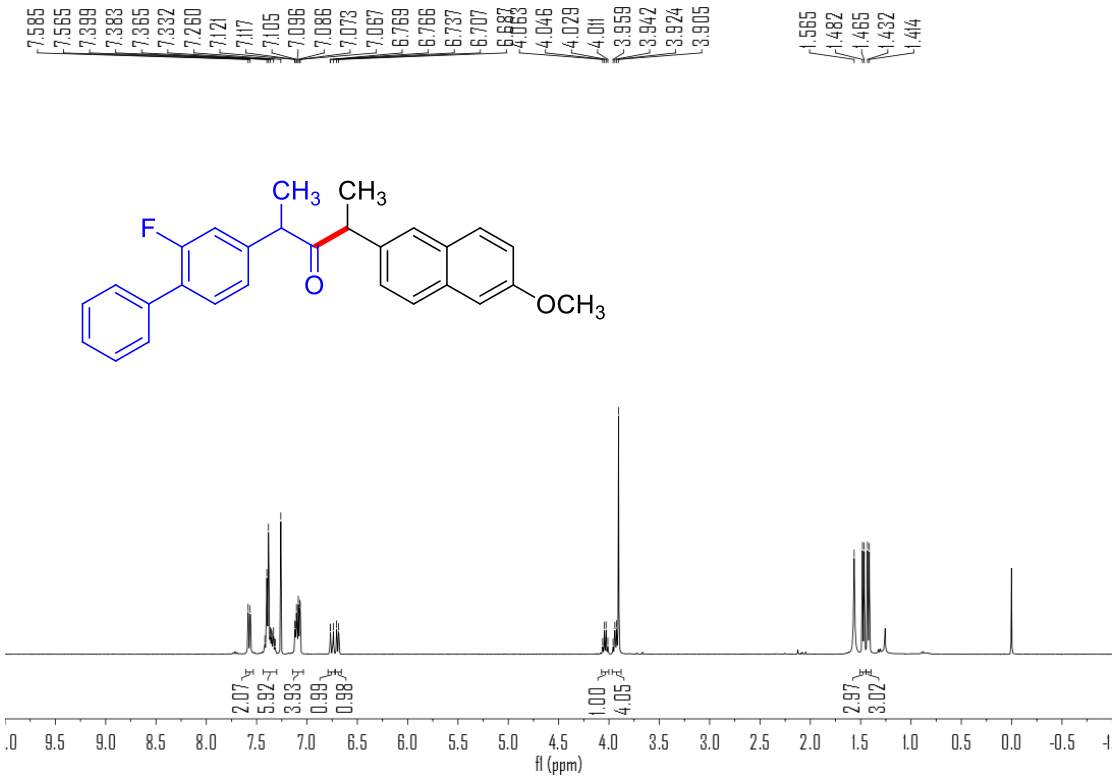
Supplementary Figure 135. ^{19}F NMR spectrum of **6j**



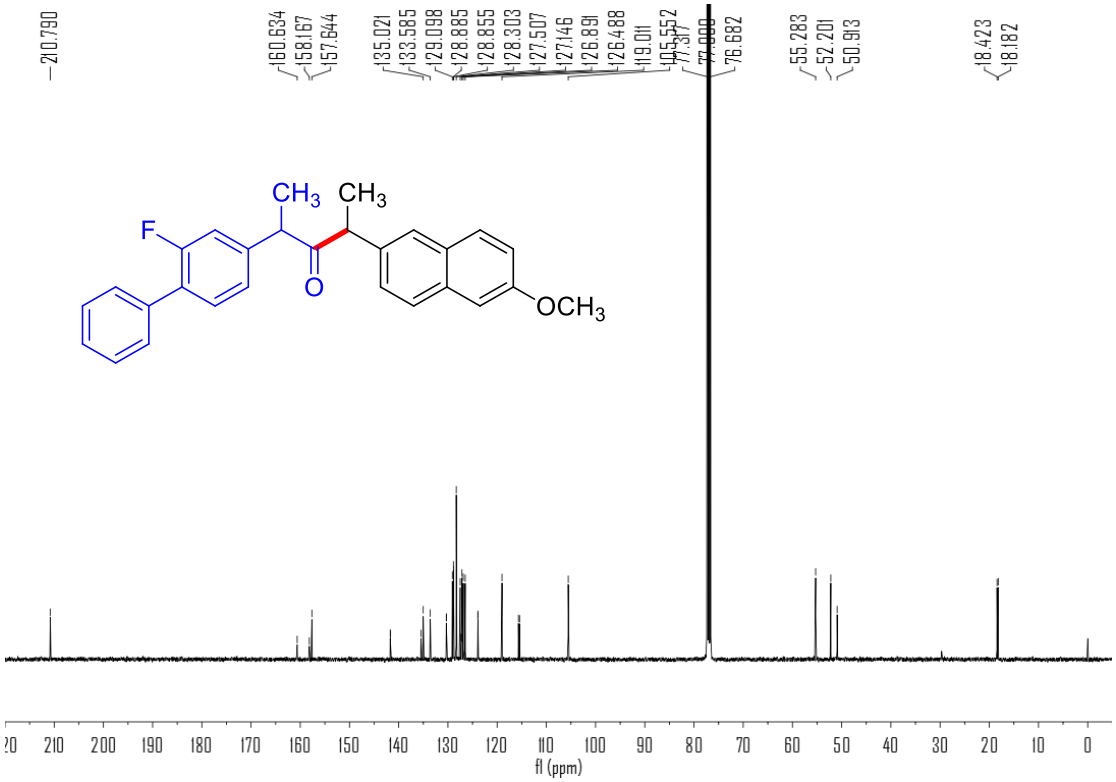
Supplementary Figure 136. ^{1}H NMR spectrum of **6k**



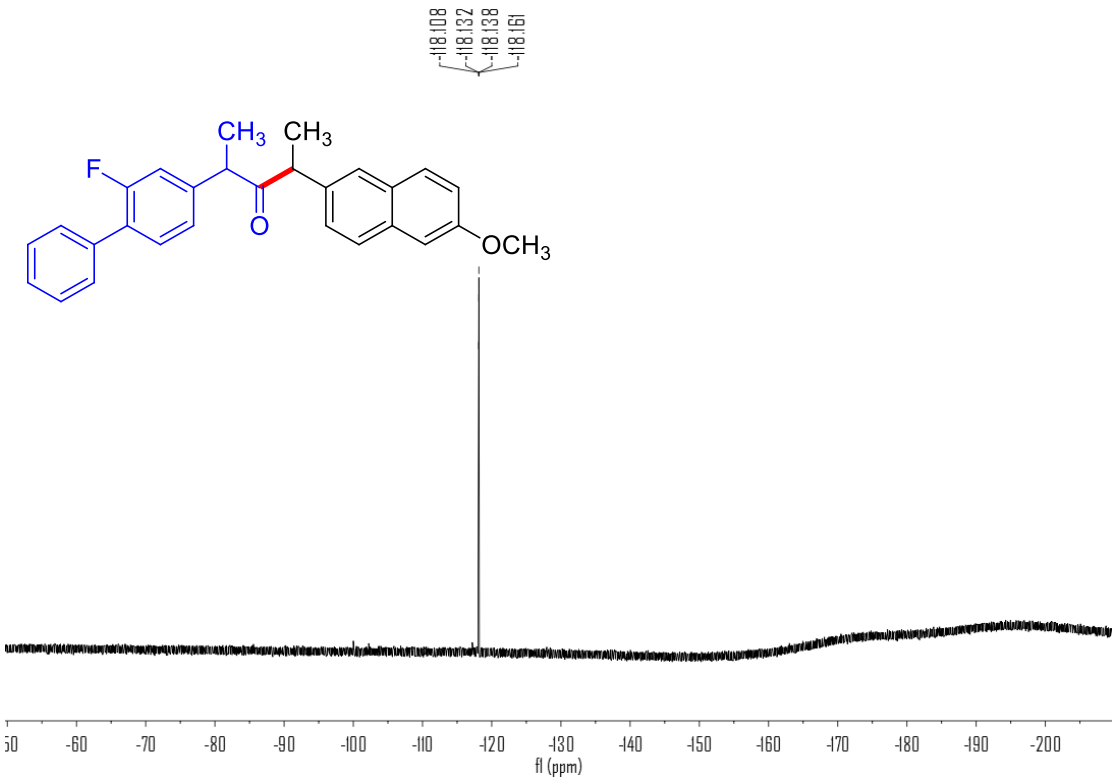
Supplementary Figure 137. ^{13}C NMR spectrum of **6k**



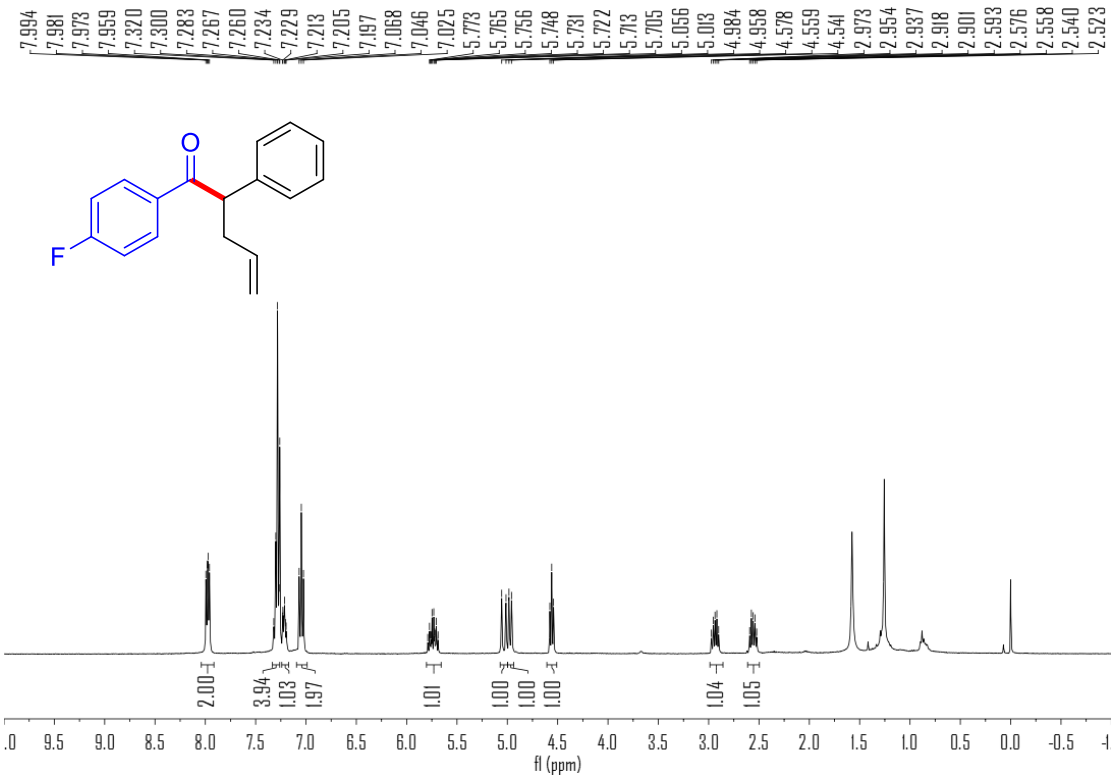
Supplementary Figure 138. ^{1}H NMR spectrum of **6l**



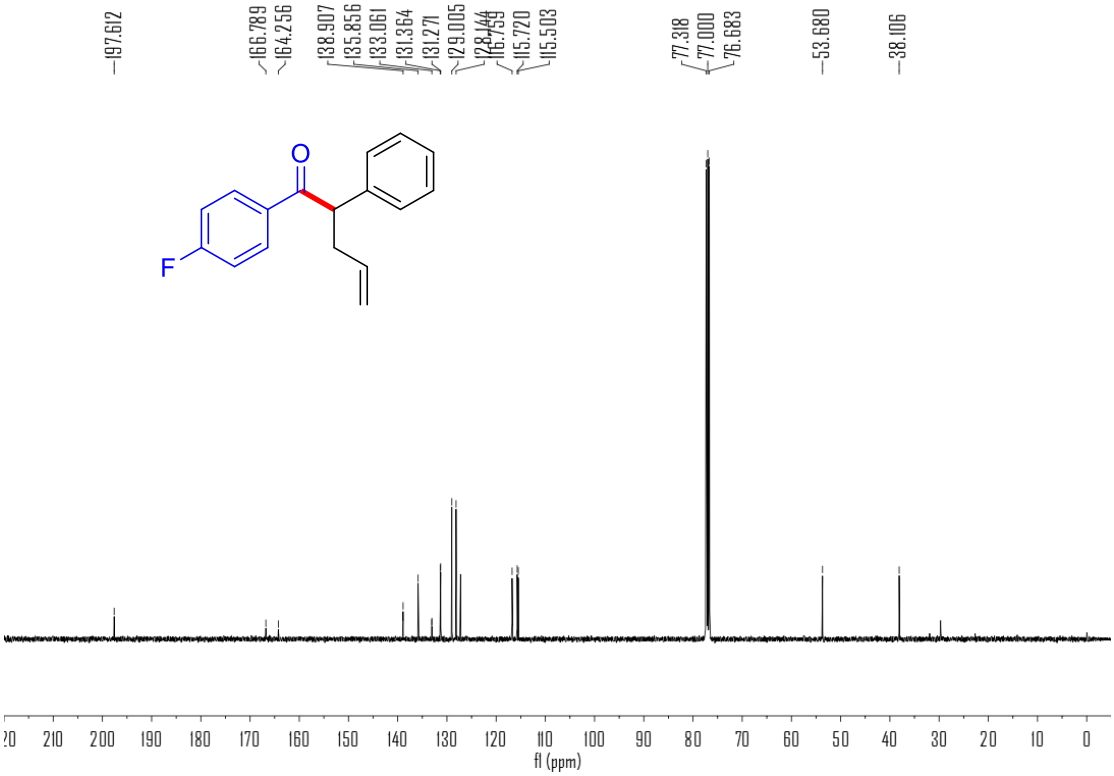
Supplementary Figure 139. ^{13}C NMR spectrum of **6l**



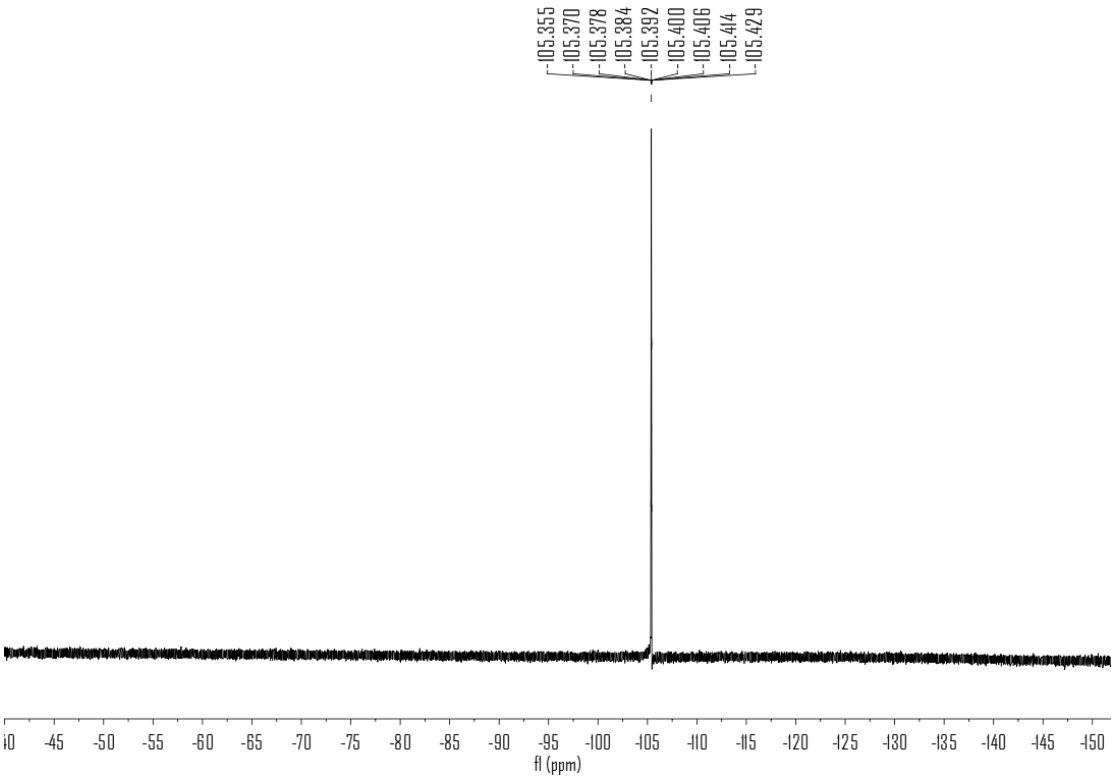
Supplementary Figure 140. ^{19}F NMR spectrum of **6l**



Supplementary Figure 141. ^{1}**H NMR** spectrum of **7**



Supplementary Figure 142. ^{13}**C NMR** spectrum of **7**



Supplementary Figure 143. ^{19}F NMR spectrum of **7**