

Supporting Information

Palladium-catalyzed and Norbornene-mediated C-H Amination and C-O Alkenylation of Aryl Triflates

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Table of contents

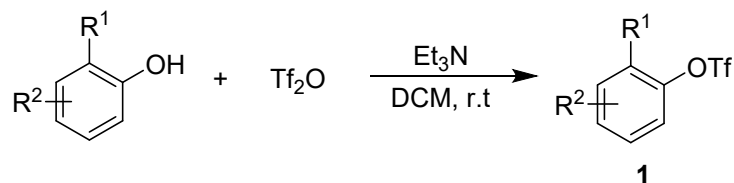
1. General Information	(S1)
2. General procedure for the preparation of compound 1, 2, NBEs, 4 and 4a	(S1-S5)
3. <i>E/Z</i> structure ratio calculation (4ad)	(S6-S9)
4. Characterization data for the compound 1, 2, NBEs and 4	(S10-S41)
5. ¹H, ¹³C NMR spectra for the compound 1, 2, NBEs and 4; HRMS of 4, GC of 4a, entry 31 and GC-MS of 4 (S42-S128)	

1. General Information

General experimental methods: The reactions were carried out in Schlenk tubes of 10 mL under N₂ atmosphere. For reactions that require heating, heating mantle was used as the heat source. All solvents were purified according to standard operation procedures. All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar, and Aladdin. Column chromatography was performed using Silica Gel 60 (300-400 mesh). The reactions were monitored by GC and GC-MS, GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2014. The ¹H, ¹³C NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz, 100 MHz respectively, and chemical shifts were reported in parts per million (ppm). The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI.

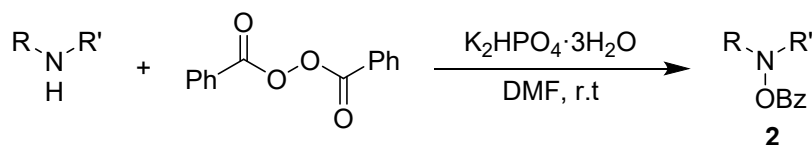
2. General procedure for the preparation of compound 1, 2, NBEs and 4

2.1 General procedure for the preparation of compound 1 according the literature [1]:



To a stirred solution of phenols (10 mmol) and Et₃N (2.0 equiv., 2.8 mL) in DCM (50 mL) was slowly added Trifluoromethanesulfonyl anhydride (Tf₂O) (1.5 equiv., 2.5 mL) at 0 °C. Then the mixture was warmed up to room temperature and stirred for overnight. The reaction was monitored by TLC. The reaction mixture was quenched with water and extracted with EtOAc (25 mL x 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc.

2.2 General procedure for the preparation of compound 2 according the literature [2]:

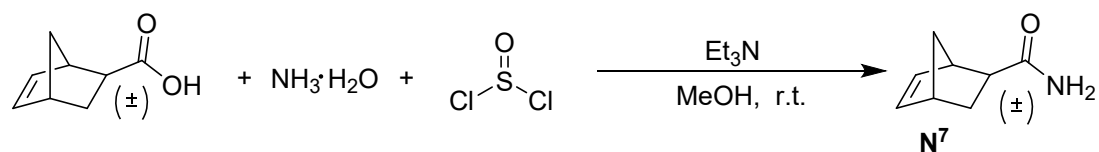


A 100 mL, one-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar

was charged with benzoyl peroxide (1.211 g, 5 mmol), $K_2HPO_4 \cdot 3H_2O$ (1.71 g, 7.5 mmol), and DMF (12.5 mL) under N_2 atmosphere. The suspension was stirred at 0 °C and the amine (5 mmol) was added via syringe in one portion. After then, the reaction mixture was warmed up to room temperature and stirred for the indicated reaction time according to TLC. Water (25 mL) was added and the contents were stirred vigorously for several minutes until all solids dissolved. The reaction mixture was transferred to a 100 mL separator funnel and extracted with EtOAc (25 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc, to afford the desired product **2** and stored it in fridge for further usage.

2.3 General procedure for the preparation of compound NBEs

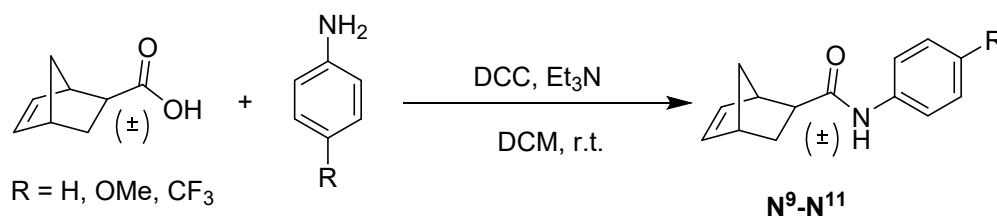
N¹, **N**², **N**³, **N**⁴, **N**⁵, **N**⁶ were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd.



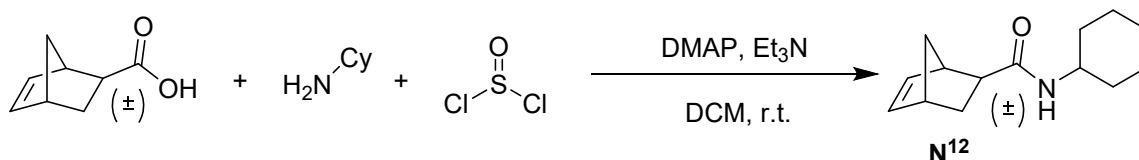
A 100 mL, one-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar was charged with 5-Norbornene-2-carboxaldehyde (0.69 g/0.61 mL, 5 mmol), Ammonium hydroxide (0.51 mL, 7.5 mmol), triethylamine (1.01 g/1.39 mL, 10 mmol) and MeOH (50.0 mL). The suspension was stirred at 0 °C and the thionyl chloride (1.19 g/0.73 mL, 10 mmol) was added via syringe in one portion. After then, the reaction mixture was warmed up to room temperature and stirred for the indicated reaction time according to TLC. Water (25 mL) was added and the contents were stirred vigorously for several minutes until all solids dissolved. The reaction mixture was transferred to a 100 mL separator funnel and extracted with EtOAc (25 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4 , filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc, to afford the desired product **N**⁷.



A 100 mL, one-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar was charged with 5-Norbornene-2-carboxaldehyde (0.69 g/0.61 mL, 5 mmol), methylamine hydrochloride (0.71 g, 10.5 mmol), DMAP (0.31 g, 2.5 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (1.44 g, 7.5 mmol) and DCM (50.0 mL). After then, the reaction mixture was warmed up to room temperature and stirred for the indicated reaction time according to TLC. Water (25 mL) was added and the contents were stirred vigorously for several minutes until all solids dissolved. The reaction mixture was transferred to a 100 mL separator funnel and extracted with EtOAc (25 mL x 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc, to afford the desired product N⁸ [17].

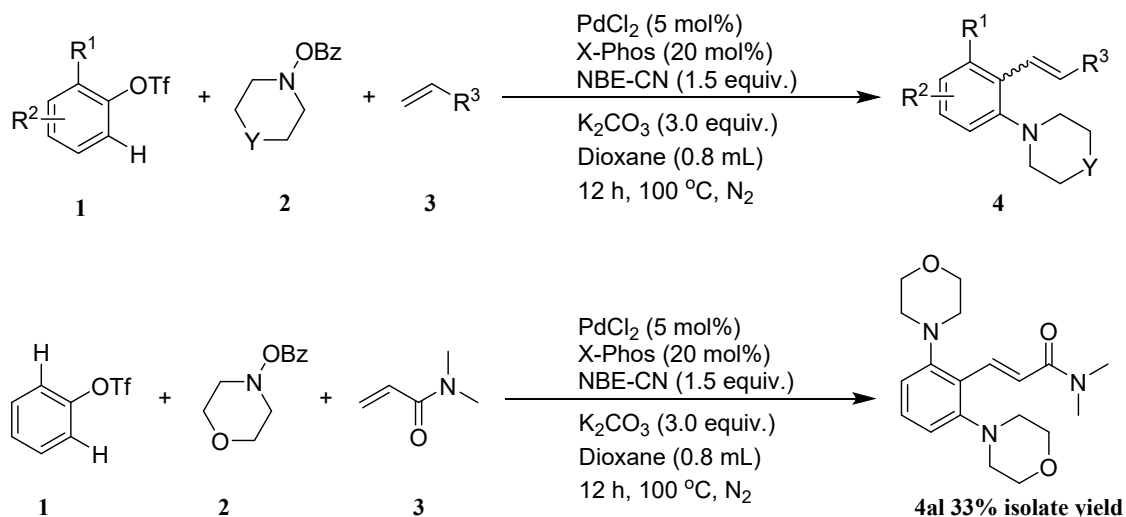


A 100 mL, one-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar was charged with 5-Norbornene-2-carboxaldehyde (0.69 g/0.61 mL, 5 mmol), amine (7.5 mmol), triethylamine (1.01 g/1.39 mL, 10 mmol), DCC (1.24g, 2.5 mmol) and DCM (50.0 mL). After then, the reaction mixture was warmed up to room temperature and stirred for the indicated reaction time according to TLC. Water (25 mL) was added and the contents were stirred vigorously for several minutes until all solids dissolved. The reaction mixture was transferred to a 100 mL separator funnel and extracted with EtOAc (25 mL x 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc, to afford the desired product N⁹-N¹¹



A 100 mL, one-necked, round-bottomed flask equipped with a Teflon-coated magnetic stir bar was charged with 5-Norbornene-2-carboxaldehyde (0.69 g/0.61 mL, 5 mmol), amine (7.5 mmol), triethylamine (1.01 g/1.39 mL, 10 mmol), DMAP (0.31g, 2.5 mmol) and DCM (50.0 mL). The suspension was stirred at 0 °C and the thionyl chloride (1.19 g/0.73 mL, 10 mmol) was added via syringe in one portion. After then, the reaction mixture was warmed up to room temperature and stirred for the indicated reaction time according to TLC. Water (25 mL) was added and the contents were stirred vigorously for several minutes until all solids dissolved. The reaction mixture was transferred to a 100 mL separator funnel and extracted with EtOAc (25 mL x 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc, to afford the desired product **N¹²**.

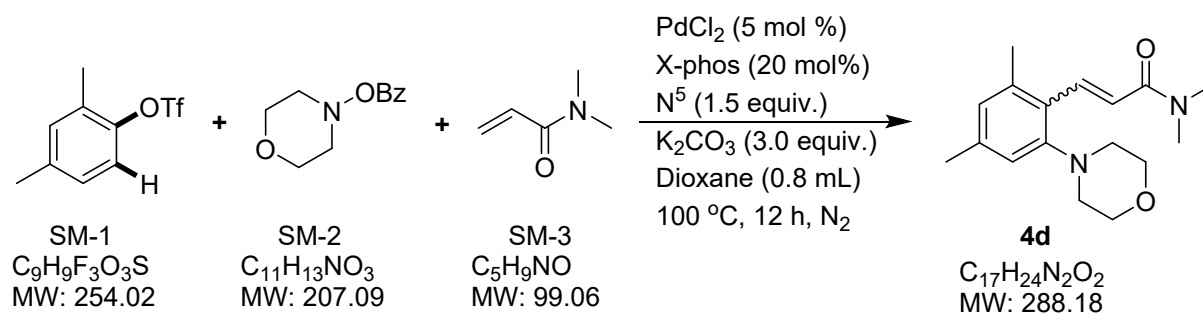
2.4 General procedure for the preparation of compound 4 and 4a1



In an oven dried 10 mL Schlenk tube charged with **1** (0.2 mmol), **2** (0.28 mmol), terminal alkene **3** (0.28 mmol), PdCl₂ (1.8 mg, 0.01 mmol), X-Phos (19.1 mg, 0.04 mmol), K₂CO₃ (82.9 mg, 0.6 mmol), NBE-CN (36.0 μL, 0.3 mmol), and dioxane (0.8 mL) under N₂. The suspension was stirred at room temperature for 10 min, and then heated to 100 °C for 12 h. The reaction was

monitored by GC-MS. After being cooled to room temperature, the reaction mixture was quenched with water (5 mL) and transferred to a 50 mL of separator funnel and then extracted with EtOAc (10 mL x 3). The organic layer was collected and combined and then washed with brine, dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc, to afford the desired product **4 and 4a**.

3. *E/Z* structure ratio calculation (4d)



Material:

Compound	MW	mmol	Amount	Eq.
SM-1	254.02	0.20	50.8 mg/40 μL	1.0
SM-2	207.09	0.28	57.9 mg	1.4
SM-3	99.06 (0.96 g/mL)	0.28	27.7 mg/29.00 μ L	1.4
K_2CO_3	138.21	0.60	82.9 mg	3.0
N^5	119.16 (0.99 g/mL)	0.30	35.8 mg/36.00 μ L	1.5
$PdCl_2$	177.33	0.01	1.8 mg	0.05
X-phos	476.72	0.04	19.1 mg	0.2
Solvent	Dioxane		0.8 mL	

$c = 0.25$ mmol/mL

In an oven dried 10 mL Schlenk tube charged with **SM-1** (50.08 mg, 0.2 mmol), **SM-2** (57.9 mg, 0.28 mmol), terminal alkene **SM-3** (29.0 μ L, 0.28 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol), X-Phos (19.1 mg, 0.04 mmol), K_2CO_3 (82.9 mg, 0.6 mmol), NBE-CN (36.00 μ L, 0.3 mmol), and dioxane (0.8 mL) under N_2 . The suspension was stirred at room temperature for 10 min, and then heated to 100 °C for 12 h. After the reaction was completed and cooled to room temperature, add internal standard dodecane (30 μ L) into the reaction solution, and then determine the *Z/E* ratio of the product by GC. The reaction mixture was quenched with water (5 mL) and transferred to a 50 mL of separator funnel and then extracted with EtOAc (10 mL x 3). The organic layer was collected and combined and then washed with brine, dried over Na_2SO_4 , filtered and concentrated under vacuum. The crude product was purified by silica gel on column chromatography, eluting with petroleum ether/EtOAc, to afford the desired product **4d**.

The proportion of *Z* and *E* components in the target product **4d mixture was analyzed by gas chromatography with internal standard method:**

This experiment uses dodecane as the internal standard, the target product **4d** was the tested sample. Assume the mass of **4d** in the test sample was m_i and peak area is A_i , the total amount of substance in the test sample is $N(0.2$ mmol), the mass of dodecane added was m_s and peak area

was A_s . The calculation formula of the correction factor f_i :

$$f_i = \frac{n_i A_s}{n_s A_i}$$

Calculate the GC yield formula of product **4d**: GC yield = $\frac{A_i n_s}{A_s N} \cdot f_i$

Compound	MW	Amount	Area (GC)
4d	288.18	$m_i=15.2$ mg	$A_i=21.231$
dodecane	170.34	$m_s=22.60$ mg/30.00 μ L	$A_s=78.769$

The correction factor can be obtained according to the above table:

$$f_i = \frac{n_i A_s}{n_s A_i} = \frac{0.0527(\text{mmol}) \cdot 78.769}{0.1326(\text{mmol}) \cdot 21.231} = 1.47$$

Compound	MW	Area (GC)
4d(E)	288.18	$A_E=26.094$
4d(Z)	288.18	$A_Z=0.480$
dodecane	170.34	$A_s=73.426$

$$\text{GC yield of } \mathbf{4d(E)} = \frac{A_i n_s}{A_s N} \cdot f_i \times 100\% = \frac{26.094 \cdot 0.133(\text{mmol})}{73.426 \cdot 0.2(\text{mmol})} \cdot 1.47 \times 100\% = 34.74\%$$

$$\text{GC yield of } \mathbf{4d(Z)} = \frac{A_i n_s}{A_s N} \cdot f_i \times 100\% = \frac{0.480 \cdot 0.133(\text{mmol})}{73.426 \cdot 0.2(\text{mmol})} \cdot 1.47 \times 100\% = 0.63\%$$

$$\mathbf{4d(E):4d(Z)} = \left(\frac{55.14}{56.14} : \frac{1}{56.14} \right) \bullet 100\% \approx 98.2 : 1.8$$

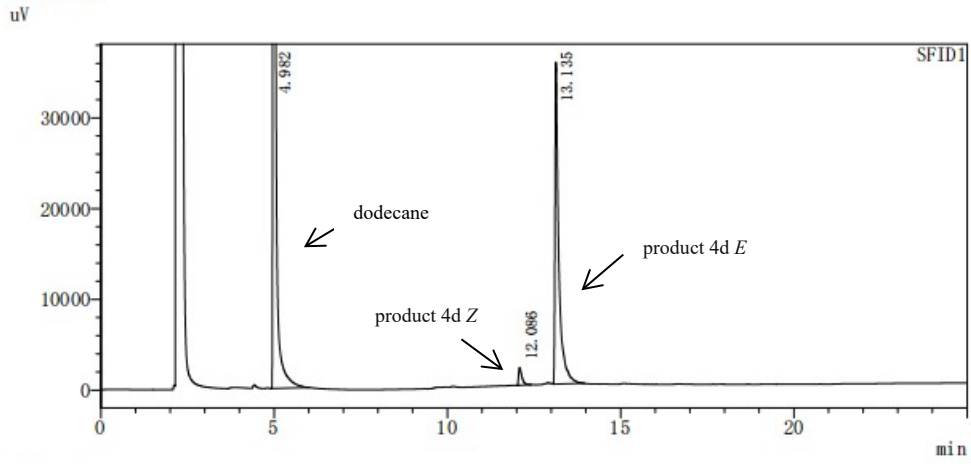
Product 4d GC diagram

SHIMADZU LabSolutions 分析报告

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 样品ID :
 数据文件名 : JIAJI校正因子.gcd
 方法文件名 : 高温方法-280度-25min.gcm
 批处理文件名 : 20230307.gcb
 样品瓶号 : 1
 进样体积 : 1 uL
 分析日期 : 2023/3/7 11:39:09
 处理日期 : 2023/3/7 12:04:16
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

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<峰表>

SFID1

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.982	992554	263416	77.970			
2	12.086	12913	1970	1.014			
3	13.135	267521	35423	21.015			
总计		1272988	300810				

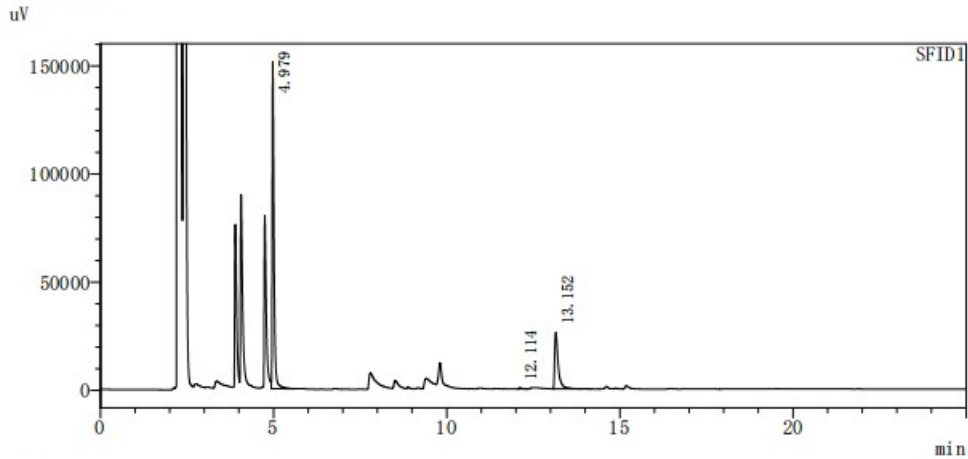
Reaction GC diagram

SHIMADZU LabSolutions 分析报告

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 样品ID :
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 方法文件名 : 高温方法-280度-25min. gcm
 批处理文件名 : 2023. 3. 4. gcb
 样品瓶号 : 1
 进样体积 : 1 uL
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 处理者 : System Administrator

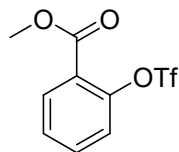
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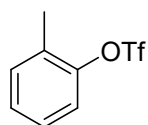
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1	4.979	532012	150121	73.426			
2	12.114	3480	606	0.480			
3	13.152	189062	26076	26.094		S	
总计		724554	176803	100.000			

4. Characterization data for the compound 1, 2, 4 and NBEs



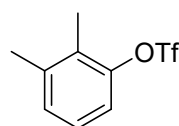
methyl 2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1a**^[3]

Yield 85%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.64-7.59 (m, 1H), 7.47-7.43 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.02, 148.23, 134.30, 132.58, 128.42, 124.26, 122.65, 118.70 (q, *J* = 318.4 Hz), 52.37.



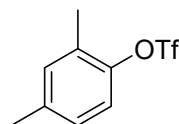
o-tolyl trifluoromethanesulfonate **1b**^[3]

Yield 84%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.23-7.14 (m, 4H), 2.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.64, 132.17, 130.90, 128.25, 127.61, 121.20, 118.84 (q, *J* = 317.7 Hz), 15.95.



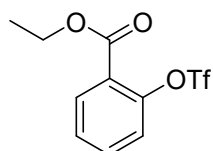
2,3-dimethylphenyl trifluoromethanesulfonate **1c**^[4]

Yield 84%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.05 (m, 3H), 2.29 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.62, 139.99, 129.60, 129.53, 126.71, 118.78, 118.76 (q, *J* = 318.0 Hz), 19.98, 12.76.



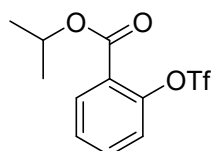
2,4-dimethylphenyl trifluoromethanesulfonate **1d**⁵¹

Yield 86%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.12-6.99 (m, 3H), 2.32 (s, 3H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.53, 138.30, 132.72, 130.44, 128.13, 120.92, 118.72 (q, *J* = 318.1 Hz), 20.72, 16.20.



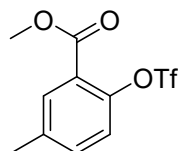
ethyl 2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1e**⁶¹

Yield 87%; colorless oil; purified by column silica gel on column chromatography with petroleum ether/EtOAc = 10:1(v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.08 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.64-7.59 (m, 1H), 7.49-7.45 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.76, 148.27, 134.12, 132.69, 128.41, 124.84, 122.65, 118.74 (q, *J* = 318.6 Hz), 62.13, 13.97.



isopropyl 2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1f**³¹

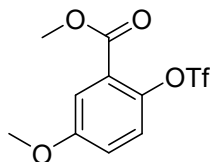
Yield 84%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.63-7.59 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 5.37-5.28 (m, 1H), 1.40 (d, *J* = 6.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 163.29, 148.24, 133.93, 132.65, 128.36, 125.30, 122.58, 118.75 (q, *J* = 318.8 Hz), 70.18, 21.58.



methyl 5-methyl-2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1g**⁷¹

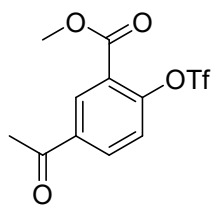
Yield 79%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* =

8.4, 2.0 Hz, 1H), 7.17 (d, $J = 8.4$ Hz, 1H), 3.94 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.21, 146.19, 138.82, 134.72, 132.90, 123.78, 122.36, 118.71 (q, $J = 318.4$ Hz), 52.34, 20.45.



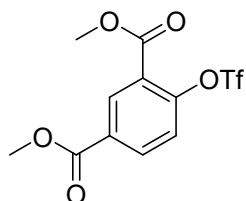
methyl 5-methoxy-2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1h**¹⁸¹

Yield 85%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 3.2$ Hz, 1H), 7.20 (d, $J = 9.2$ Hz, 1H), 7.09 (dd, $J = 9.2, 3.2$ Hz, 1H), 3.95 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.04, 158.72, 141.63, 125.08, 123.76, 119.61, 118.71 (q, $J = 318.6$ Hz), 116.66, 55.82, 52.57.



methyl 5-acetyl-2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1i**¹⁹¹

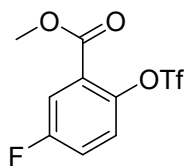
Yield 85%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.63 (d, $J = 2.0$ Hz, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 4.01-4.00 (m, 3H), 2.67 (d, $J = 1.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.34, 163.46, 150.90, 136.71, 133.80, 132.89, 124.71, 123.39, 118.65 (d, $J = 318.6$ Hz), 52.94, 26.64.



dimethyl 4-(((trifluoromethyl)sulfonyl)oxy)isophthalate **1j**¹⁰¹

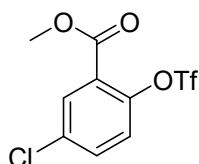
Yield 85%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.73 (d, $J = 2.4$ Hz, 1H), 8.29 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.40 (d, $J = 8.8$ Hz, 1H), 4.00 (s, 3H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.58, 163.29, 150.93, 135.22, 134.03, 130.45, 124.58, 123.12, 118.64 (q, $J = 318.6$ Hz), 52.83,

52.69.



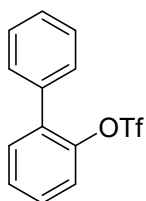
methyl 5-fluoro-2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1k**^[8]

Yield 87%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, DMSO) δ 7.85 (dd, J = 8.4, 3.2 Hz, 1H), 7.75-7.70 (m, 1H), 7.66 (dd, J = 8.8, 4.4 Hz, 1H), 3.94 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 162.97 (d, J = 1.7 Hz), 162.24, 159.77, 143.92 (d, J = 3.0 Hz), 125.89 (dd, J = 20.0, 8.5 Hz), 122.31 (d, J = 23.9 Hz), 119.26 (d, J = 26.0 Hz), 118.63 (q, J = 318.6 Hz), 53.22.



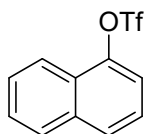
methyl 5-chloro-2-(((trifluoromethyl)sulfonyl)oxy)benzoate **1l**^[11]

Yield 87%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 2.8 Hz, 1H), 7.58 (dd, J = 8.8, 2.8 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 3.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.94, 146.59, 134.32, 134.08, 132.46, 125.67, 124.19, 118.66 (q, J = 318.6 Hz), 52.83.



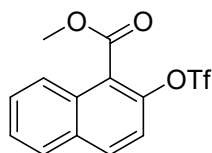
[1,1'-biphenyl]-2-yl trifluoromethanesulfonate **1m**^[12]

Yield 83%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.34 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 146.90, 135.66, 132.05, 129.45, 129.06, 128.61, 128.57, 128.38, 122.15, 118.45 (q, J = 318.4 Hz).



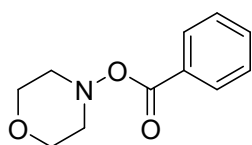
naphthalen-1-yl trifluoromethanesulfonate **1n**^[4]

Yield 88%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.54-7.44 (m, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 145.75, 134.99, 128.57, 128.11, 127.88, 127.40, 126.43, 125.09, 120.73, 119.014 (q, *J* = 318.0 Hz), 117.83.



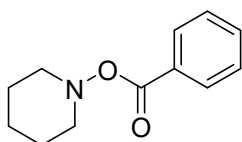
methyl 2-(((trifluoromethyl)sulfonyl)oxy)-1-naphthoate **1o**^[9]

Yield 86%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.61-7.52 (m, 2H), 7.36 (d, *J* = 9.2 Hz, 1H), 4.07 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.03, 144.63, 133.07, 132.28, 130.63, 128.73, 128.34, 127.56, 125.61, 123.57, 119.12, 118.63 (q, *J* = 318.2 Hz), 52.92.



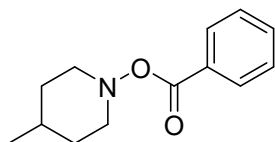
morpholino benzoate **2a**^[13]

Yield 86%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.02-8.00 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.42 (m, 2H), 3.98-3.83 (m, 4H), 3.44-3.41 (m, 2H), 3.04-3.00 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 164.53, 133.19, 129.42, 129.12, 128.44, 65.81, 56.97.



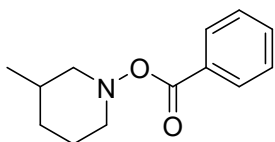
piperidin-1-yl benzoate **2b**^[13]

Yield 88%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.04-7.98 (m, 2H), 7.58-7.53 (m, 1H), 7.47-7.39 (m, 2H), 3.51 (s, 2H), 2.80-2.78 (m, 2H), 1.84-1.83 (m, 4H), 1.67 (s, 1H), 1.29 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.56, 132.83, 129.53, 129.26, 128.26, 57.39, 24.90, 23.22.



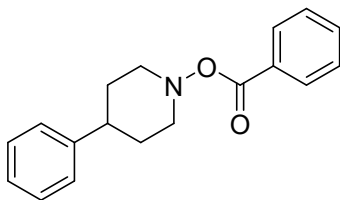
4-methylpiperidin-1-yl benzoate **2c**^[13]

Yield 80%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 3.53 (d, *J* = 9.2 Hz, 2H), 2.74 (t, *J* = 10.8 Hz, 2H), 1.93-1.76 (m, 2H), 1.65-1.55 (m, 2H), 1.50-1.42 (m, 1H), 0.95 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.81, 132.91, 129.62, 129.39, 128.35, 57.19, 33.52, 30.08, 21.20.



3-methylpiperidin-1-yl benzoate **2d**^[13]

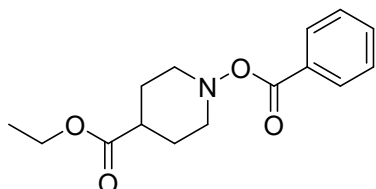
Yield 83%; colorless oil; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.03-7.98 (m, 2H), 7.55-7.51 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 3.51 (d, *J* = 10.4 Hz, 2H), 2.61 (t, *J* = 9.2 Hz, 1H), 2.36-2.29 (m, 1H), 2.00-1.67 (m, 4H), 0.94 (s, 2H), 0.92 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 164.66, 132.87, 129.30, 128.29, 77.66, 77.34, 77.02, 64.71, 56.97, 31.93, 31.35, 24.60, 19.47.



4-phenylpiperidin-1-yl benzoate **2e**^[14]

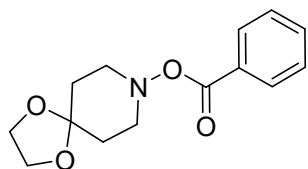
Yield 82%; white solid; purified by silica gel on column chromatography with petroleum

ether/EtOAc = 5:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.25-7.20 (m, 3H), 3.68 (d, $J = 10.4$ Hz, 2H), 2.91 (t, $J = 10.8$ Hz, 2H), 2.63 (t, $J = 12.0$ Hz, 1H), 2.21-2.12 (m, 2H), 2.04-1.80 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.87, 144.87, 133.08, 129.48, 128.62, 128.46, 126.85, 126.53, 57.46, 41.77, 32.80.



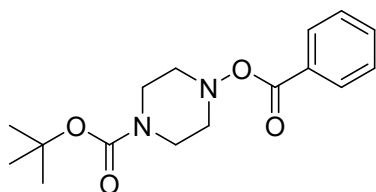
ethyl 1-(benzoyloxy)piperidine-4-carboxylate **2f**^[14]

Yield 87%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.4$ Hz, 2H), 7.58-7.53 (m, 1H), 7.45-7.41 (m, 2H), 4.16 (s, 2H), 3.60 (s, 1H), 3.27 (s, 1H), 2.78 (s, 1H), 2.61-1.97 (m, 5H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.95 (s), 164.59 (s), 133.03 (s), 129.36 (s), 128.37 (s), 60.51 (s), 56.11 (s), 40.33 (s), 27.57 (s), 14.18 (s).



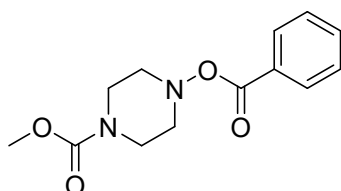
1,4-dioxa-8-azaspiro[4.5]decan-8-yl benzoate **2g**^[14]

Yield 79%; colorless oil; Yield 87%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.99 (m, 2H), 7.58-7.53 (m, 1H), 7.45-7.41 (m, 2H), 3.97 (d, $J = 1.6$ Hz, 4H), 3.44 (b, 2H), 3.27-3.25 (m, 2H), 1.96 (t, $J = 5.6$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.56, 133.00, 129.26, 129.20, 128.33, 105.78, 64.36, 64.24, 53.87, 32.51.



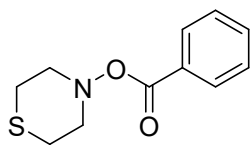
tert-butyl 4-(benzoyloxy)piperazine-1-carboxylate **2h**^[13]

Yield 85%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 7.6$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 4.04 (s, 2H), 3.44-3.32 (m, 4H), 2.92 (s, 2H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.58, 154.45, 133.26, 129.46, 129.08, 128.48, 80.25, 55.85, 42.36, 28.39.



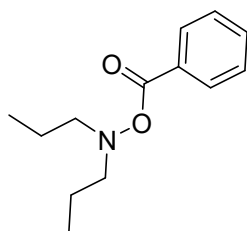
methyl 4-(benzoyloxy)piperazine-1-carboxylate **2i**^[15]

Yield 87%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.99 (m, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.45 (t, $J = 8.0$ Hz, 2H), 4.09 (s, 2H), 3.73 (s, 3H), 3.45-3.38 (m, 4H), 2.93 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.49, 155.63, 133.27, 129.42, 128.98, 128.47, 55.71, 52.84, 42.16.



thiomorpholino benzoate **2j**^[14]

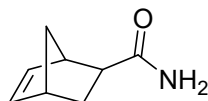
Yield 84%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.03-8.00 (m, 2H), 7.60-7.56 (m, 1H), 7.47-7.43 (m, 2H), 3.69-2.86 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.43, 133.27, 129.48, 129.16, 128.50, 57.74, 26.66.



O-benzoyl-*N,N*-dipropylhydroxylamine **2k**^[16]

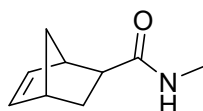
Yield 82%; white solid; purified by silica gel on column chromatography with petroleum

ether/EtOAc = 10:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 8.11-7.90 (m, 1H), 7.60-7.51 (m, 1H), 7.48-7.39 (m, 1H), 2.98-2.89 (m, 2H), 1.72-1.51 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.64, 132.94, 129.46, 129.32, 128.38, 77.46, 77.14, 76.82, 61.62, 20.17, 11.71.



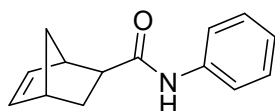
(1*R*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-carboxamide **N⁷**^[17]

Yield 56%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 6.26 (dd, $J = 5.6, 2.8$ Hz, 1H), 6.03 (dd, $J = 5.6, 2.8$ Hz, 1H), 5.35 (b, 2H), 3.15 (s, 1H), 2.96-2.88 (m, 2H), 1.96-1.94 (m, 1H), 1.47-1.35 (m, 1H), 1.36-1.30 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.00, 132.23, 50.14, 46.24, 44.48, 42.75, 29.98.



(1*R*,4*R*)-*N*-methylbicyclo[2.2.1]hept-5-ene-2-carboxamide **N⁸**^[17]

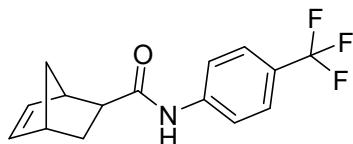
Yield 62%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 6.22 (dd, $J = 5.6, 3.2$ Hz, 1H), 5.97 (dd, $J = 5.2, 2.4$ Hz, 1H), 5.78 (b, 1H), 3.14 (s, 1H), 2.94 – 2.84 (m, 2H), 2.75 (d, $J = 4.8$ Hz, 3H), 1.93-1.92 (m, 1H), 1.48-1.41 (m, 1H), 1.37-1.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 175.06, 137.66, 132.32, 50.00, 46.16, 44.68, 42.71, 29.86, 26.27.



(1*R*,4*R*)-*N*-phenylbicyclo[2.2.1]hept-5-ene-2-carboxamide **N⁹**^[17]

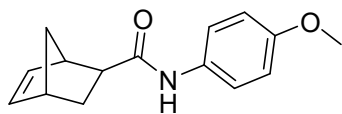
Yield 68%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.34-7.23 (m, 3H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.29 (dd, $J = 6.0, 3.2$ Hz, 1H), 6.04 (dd, $J = 5.6, 2.8$ Hz, 1H), 3.22 (s, 1H), 3.05-2.93 (m, 2H), 2.03-1.94 (m, 1H), 1.52-1.43 (m, 2H), 1.33 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR

(100 MHz, CDCl₃) δ 172.65, 138.11 (d, J = 5.1 Hz), 132.05, 128.95, 123.98, 119.72, 750.21, 46.59, 45.89, 42.89, 29.96.



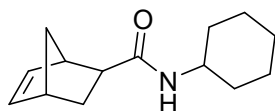
(1*R*,4*R*)-*N*-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide **N¹⁰**

Yield 56%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, J = 23.6, 8.8 Hz, 4H), 7.26 (s, 1H), 6.32 (dd, J = 5.6, 3.2 Hz, 1H), 6.04 (dd, J = 5.6, 2.8 Hz, 1H), 3.25 (s, 1H), 3.08-2.98 (m, 2H), 2.08-1.99 (m, 1H), 1.55-1.45 (m, 2H), 1.37 (d, J = 8.0 Hz, 1H). ¹³C NMR (100 MHz, DMSO) δ 173.03, 143.58, 137.82, 132.05, 126.36 (d, J = 3.6 Hz), 124.92 (dd, J = 270, 539 Hz), 123.18 (d, J = 31.7 Hz), 119.31, 50.07, 46.65, 44.91, 42.79, 28.71.



(1*R*,4*R*)-*N*-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carboxamide **N¹¹** ^[17]

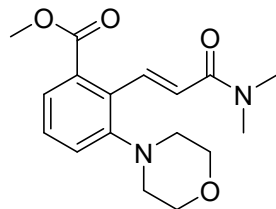
Yield 66%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, DMSO) δ 9.58 (s, 1H), 7.46 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.15 (dd, J = 5.6, 2.8 Hz, 1H), 5.85 (dd, J = 5.6, 2.8 Hz, 1H), 3.70 (s, 3H), 3.26 (s, 1H), 3.03-2.96 (m, 1H), 2.86 (s, 1H), 1.80-1.78 (m, 1H), 1.44-1.27 (m, 3H). ¹³C NMR (100 MHz, DMSO) δ 171.90, 155.32, 137.54, 133.24, 132.28, 121.18, 114.13, 55.59, 50.07, 46.60, 44.54, 42.76, 28.85.



(1*R*,4*R*)-*N*-cyclohexylbicyclo[2.2.1]hept-5-ene-2-carboxamide **N¹²** ^[18]

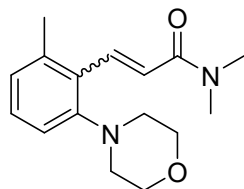
Yield 61%; white solid; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, DMSO) δ 7.69 (d, J = 7.6 Hz, 1H), 6.12 (s, 2H), 3.54-3.47 (m, 1H), 2.82 (s, 1H), 2.73 (s, 1H), 2.02-1.99 (m, J = 9.2, 4.1 Hz, 1H), 1.77-1.64 (m,

6H), 1.55 (d, $J = 12.4$ Hz, 1H), 1.29-1.18 (m, 2H), 1.16-1.06 (m, 5H). ^{13}C NMR (100 MHz, DMSO) δ 174.01, 138.15, 136.84, 47.90, 47.60, 46.05, 43.38, 41.47, 33.05, 32.98, 30.23, 25.76, 25.14.



methyl (*E*)-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4a**

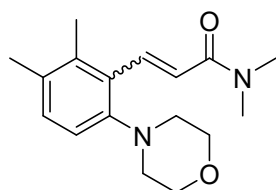
Yield 95%; yellow oil; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ^1H NMR (400 MHz, DMSO) δ 7.69 (d, $J = 16.0$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 2H), 6.80 (d, $J = 16.0$ Hz, 1H), 3.78 (s, 3H), 3.70 (t, $J = 4.4$ Hz, 4H), 3.06 (s, 3H), 2.93 (s, 3H), 2.87 (t, $J = 4.4$ Hz, 4H). ^{13}C NMR (100 MHz, DMSO) δ 169.36, 165.68, 152.28, 137.11, 133.67, 129.82, 128.68, 123.19, 122.62, 121.84, 66.81, 52.83, 52.50, 37.16, 35.69. HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 319.1652; Found 319.1652. GC-MS (EI, 70 eV) $m/z = 318([\text{M}-\text{CH}_3]^+, 0.85)$, 273(24), 246(51), 232(51), 214(35), 156(23), 129(21), 87(42), 72(100).



N,N-dimethyl-3-(2-methyl-6-morpholinophenyl)acrylamide **4b**

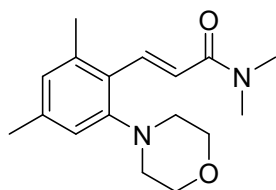
Yield 72%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 16.0$ Hz, 1H, *E*), 7.21-7.17(m, 1H, *E*), 6.98-6.87 (m, 3H, *E+Z*), 6.30 (d, $J = 12.0$ Hz, 1H, *Z*), 3.83 (t, $J = 4.4$ Hz, 4H, *E*), 3.79 (t, $J = 4.4$ Hz, 4H, *Z*), 3.15 (s, 3H, *E*), 3.09 (s, 3H, *E*), 2.99-2.93 (m, 5H, *E+Z*), 2.89 (s, 3H, *Z*), 2.42 (s, 3H, *E*), 2.18 (s, 3H, *Z*). ^{13}C NMR (100 MHz, CDCl_3) δ 167.24 (*E*), 152.31 (*E*), 139.31 (*E*), 137.86 (*E*), 136.38 (*Z*), 136.23 (*Z*), 129.18 (*E*), 128.93 (*E*), 128.16 (*Z*), 125.77 (*E*), 125.22 (*Z*), 123.43 (*Z*), 121.58 (*E*), 116.30 (*E*), 115.58 (*Z*), 67.31 (*Z*), 52.63 (*E*), 37.36 (*E*), 35.85 (*E*), 34.77 (*Z*), 21.69 (*E*), 20.07 (*Z*). HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 275.1754; Found

275.1754. GC-MS (EI, 70 eV) $m/z = 274([M]^+ , 46), 243(10), 229(9), 202(100), 188(39), 170(25), 158(47), 144(84), 115(40), 103(6).$



3-(2, 3-dimethyl-6-morpholinophenyl)-*N, N*-dimethylacrylamide **4c**

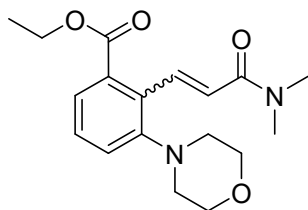
Yield 58%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (d, $J = 16.0$ Hz, 1H, *E*), 7.10 (d, $J = 8.4$ Hz, 1H, *E*), 7.05 (d, $J = 8.0$ Hz, 1H, *Z*), 6.91 (d, $J = 12.4$ Hz, 1H, *Z*), 6.85 (s, 1H, *E*), 6.82 (d, $J = 7.2$ Hz, 1H, *E*), 6.32 (d, $J = 12.4$ Hz, 1H, *Z*), 3.80 (t, $J = 4.4$ Hz, 4H, *E*), 3.77 (d, $J = 4.8$ Hz, 4H, *Z*), 3.14 (s, 3H, *E*), 3.08 (s, 3H, *E*), 2.98 (s, 3H, *Z*), 2.93 (d, $J = 4.4$ Hz, 4H, *Z*), 2.91-2.88 (m, 7H, *E+Z*), 2.31 (s, 3H, *E*), 2.26 (s, 3H, *E*), 2.22 (s, 3H, *Z*), 2.10 (s, 3H, *Z*). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.48 (*Z*), 167.05 (*E*), 150.07 (*E*), 148.97 (*Z*), 139.97 (*E*), 137.02 (*Z*), 135.93 (*E*), 134.55 (*Z*), 132.08 (*E*), 130.29 (*E*), 130.12 (*E*), 129.64 (*Z*), 123.45 (*Z*), 122.44 (*E*), 115.96 (*E*), 115.54 (*Z*), 67.35 (*E*), 52.65 (*E*), 37.35 (*E*), 35.82 (*E*), 34.76 (*Z*), 20.45 (*E*), 20.33 (*Z*), 17.31 (*E*), 16.42 (*Z*). HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_2$ $[M+H]^+$ 289.1911; Found 289.1911. GC-MS (EI, 70 eV) $m/z = 288([M]^+ , 9), 257(9), 243(14), 228(2), 216(100), 201(49), 184(26), 172(45), 158(74), 143(18), 129(13), 115(17), 103(3).$



(*E*)-3-(2, 4-dimethyl-6-morpholinophenyl)-*N, N*-dimethylacrylamide **4d**

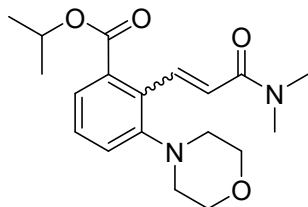
Yield 64%; white solid; mp = 128.7-128.8 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). $^1\text{H NMR}$ (400 MHz, DMSO) δ 7.69 (d, $J = 15.6$ Hz, 1H), 6.93 (d, $J = 16.0$ Hz, 1H), 6.78 (d, $J = 11.2$ Hz, 2H), 3.70 (t, $J = 4.4$ Hz, 4H), 3.11 (s, 3H), 2.94 (s, 3H), 2.83 (t, $J = 4.4$ Hz, 4H), 2.35 (s, 3H), 2.26 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.47, 152.45, 139.32, 139.08, 137.89, 126.66, 126.12, 120.74, 117.14, 67.35, 52.69,

37.37, 35.86, 21.69, 21.46. HRMS (ESI) Calcd for $C_{17}H_{24}N_2O_2$ $[M+H]^+$ 289.1911; Found 289.1911. GC-MS (EI, 70 eV) m/z = 288($[M]^+$, 7), 257(7), 243(8), 216(100), 201(33), 184(22), 172(37), 158(56), 143(13), 129(10), 115(13).



ethyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4e**

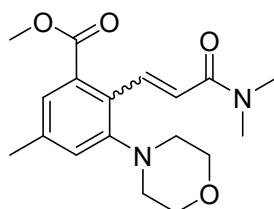
Yield 98%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 16.0 Hz, 1H, *E*), 7.56-7.51 (m, 2H, *Z*), 7.37-7.29 (m, 2H, *E*), 7.15 (dd, J = 7.6, 1.6 Hz, 1H, *E*), 7.08 (d, J = 12.4 Hz, 1H, *Z*), 6.81 (d, J = 16.0 Hz, 1H, *E*), 6.26 (d, J = 12.4 Hz, 1H, *Z*), 4.31 (q, J = 6.8 Hz, 2H, *E*), 3.83 (t, J = 4.4 Hz, 4H, *E*), 3.79 (t, J = 4.4 Hz, 4H, *Z*), 3.12 (s, 3H, *E*), 3.06 (s, 3H, *E*), 2.95 (t, J = 4.4 Hz, 4H, *E*), 2.90 (s, 3H, *Z*), 2.82 (s, 3H, *Z*), 1.34 (t, J = 7.2 Hz, 3H, *E*), 0.96 (t, J = 7.2 Hz, 3H, *Z*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.15 (*E*), 166.50 (*E*), 152.01 (*E*), 151.39 (*Z*), 138.29 (*E*), 135.23 (*Z*), 133.62 (*E*), 129.44 (*E*), 129.04 (*E*), 128.23 (*Z*), 124.55 (*Z*), 123.29 (*E*), 122.55 (*Z*), 122.07 (*E*), 121.08 (*E*), 67.12 (*E*), 67.03 (*Z*), 61.46 (*E*), 60.84 (*Z*), 52.40 (*Z*), 37.48 (*Z*), 37.26 (*E*), 35.76 (*E*), 34.69 (*Z*), 14.21 (*Z*), 14.12 (*E*). HRMS (ESI) Calcd for $C_{18}H_{24}N_2O_4$ $[M+H]^+$ 333.1809; Found 333.1808. GC-MS (EI, 70 eV) m/z = 332($[M]^+$, 1), 287(27), 260(36), 246(41), 230(21), 214(19), 200(24), 188(9), 174(15), 156(18), 144(10), 130(15), 117(7).



isopropyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4f**

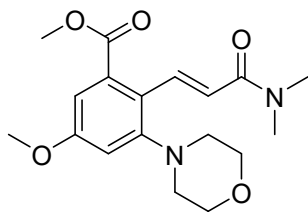
Yield 92%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). 1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 16.0 Hz, 1H, *E*), 7.55-7.50 (m, 1H, *Z*), 7.36-7.27 (m, 2H, *E*), 7.14 (dd, J = 8.0, 0.8 Hz, 1H, *E*), 7.07 (d, J = 12.4, Hz,

1H, Z), 6.82 (d, $J = 16.0$ Hz, 1H, *E*), 6.24 (d, $J = 12.4$ Hz, 1H, *Z*), 5.22-5.14 (m, 1H, *E*), 3.82 (t, $J = 4.4$, Hz, 4H, *E*), 3.79 (t, $J = 4.4$, Hz, 4H, *Z*), 3.12 (s, 3H, *E*), 3.06 (s, 3H, *E*), 2.96-2.92 (m, 8H, *E+Z*), 2.89 (s, 3H, *Z*), 2.81 (s, 3H, *Z*), 1.33 (s, 3H, *E*), 1.31 (s, 3H, *E*). ^{13}C NMR (100 MHz, CDCl_3) δ 168.72 (*E*), 166.43 (*E*), 151.99 (*E*), 138.39 (*E*), 135.42 (*Z*), 134.11 (*E*), 129.39 (*E*), 129.03 (*E*), 128.19 (*Z*), 124.58 (*Z*), 123.27 (*E*), 122.36 (*Z*), 122.06 (*E*), 121.81 (*Z*), 120.97 (*E*), 69.08 (*E*), 68.33 (*Z*), 67.15 (*E*), 67.01 (*Z*), 52.41 (*E*), 37.48 (*Z*), 37.26 (*E*), 35.78 (*E*), 34.73 (*Z*), 29.70 (*Z*), 21.72 (*E*). HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 347.1965; Found 347.1965. GC-MS (EI, 70 eV) $m/z = 346([\text{M}]^+, 1)$, 315(2), 301(25), 287(11), 274(26), 260(39), 242(10), 232(37), 218(31), 200(24), 188(19), 174(22), 156(16), 144(11), 130(15), 117(7).



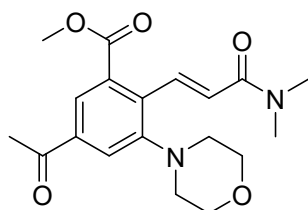
methyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-5-methyl-3-morpholinobenzoate **4g**

Yield 94%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1(v/v). ^1H NMR (400 MHz, DMSO) δ 7.68 (d, $J = 15.6$ Hz, 1H, *E*), 7.17 (s, 2H, *Z*), 7.09 (s, 2H, *E*), 6.88 (d, $J = 12.4$ Hz, 1H, *Z*), 6.80 (d, $J = 15.6$ Hz, 1H, *E*), 6.29 (d, $J = 12.4$ Hz, 1H, *Z*), 3.79 (s, 3H, *E*), 3.77 (t, $J = 4.4$ Hz, 4H, *E*), 3.67 (t, $J = 4.4$ Hz, 4H, *Z*), 3.06 (s, 3H, *E*), 2.93 (s, 3H, *E*), 2.89 - 2.86(m, 7H, *E+Z*), 2.70 (s, 3H, *Z*), 2.33 (s, 3H, *E*), 2.31 (s, 3H, *Z*). ^{13}C NMR (100 MHz, DMSO) δ 169.53 (*E*), 165.78 (*E*), 152.34 (*E*), 139.80 (*E*), 137.97 (*Z*), 137.11 (*E*), 134.54 (*Z*), 133.65 (*E*), 129.74 (*Z*), 129.04 (*Z*), 125.53 (*E*), 124.50 (*Z*), 123.67 (*E*), 122.91 (*Z*), 122.35 (*E*), 121.74 (*E*), 66.83 (*E*), 52.81 (*E*), 52.55 (*E*), 37.38 (*Z*), 37.14 (*E*), 35.70 (*E*), 34.51 (*Z*), 21.31 (*E*), 21.24 (*Z*). HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 333.1809; Found 333.1810. GC-MS (EI, 70 eV) $m/z = 332([\text{M}]^+, 2)$, 301(7), 287(28), 273(3), 260(66), 246(53), 228(42), 216(26), 202(32), 184(10), 170(22), 158(13), 143(21), 130(9), 115(20).



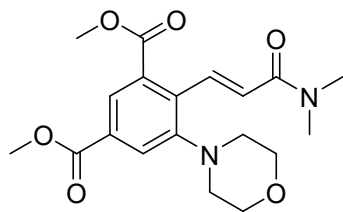
methyl (*E*)-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-5-methoxy-3-morpholinobenzoate **4h**

Yield 80%; yellow oil; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, DMSO) δ 7.63 (d, *J* = 15.6 Hz, 1H), 6.83-6.80 (m, 2H), 6.76 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.71 (t, *J* = 4.4 Hz, 4H), 3.06 (s, 3H), 2.92 (s, 3H), 2.88 (t, *J* = 4.4 Hz, 4H). ¹³C NMR (100 MHz, DMSO) δ 169.38, 165.93, 160.35, 154.09, 136.90, 135.20, 120.54, 108.02, 107.88, 66.78, 56.00, 52.94, 52.50, 37.14, 35.70. HRMS (ESI) Calcd for C₁₈H₂₄N₂O₅ [M+H]⁺ 349.1758; Found 349.1755. GC-MS (EI, 70 eV) *m/z* = 348([M]⁺, 3), 317(6), 303(30), 276(73), 261(50), 244(30), 230(27), 218(30), 202(10), 186(16), 174(8), 159(11), 144(11), 116(12).



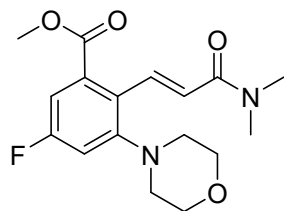
methyl (*E*)-5-acetyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4i**

Yield 86%; white solid; mp: 161.0-161.1 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, DMSO) δ 7.85 (d, *J* = 1.6 Hz, 1H), 7.70-7.66 (m, 2H), 6.90 (d, *J* = 15.6 Hz, 1H), 3.83 (s, 3H), 3.72 (t, *J* = 4.4 Hz, 4H), 3.07 (s, 3H), 2.95-2.94 (m, 7H), 2.62 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 197.51, 168.66, 165.36, 152.58, 137.41, 136.26, 133.94, 133.08, 123.98, 122.92, 120.44, 66.73, 53.12, 52.27, 37.18, 35.73, 27.34. HRMS (ESI) Calcd for C₁₉H₂₄N₂O₅ [M+H]⁺ 361.1758; Found 361.1758. GC-MS (EI, 70 eV) *m/z* = 360([M]⁺, 1), 329(7), 315(22), 288(60), 274(37), 256(25), 244(24), 230(22), 214(22), 200(15), 184(9), 170(8), 156(8), 144(7), 128(10), 101(5).



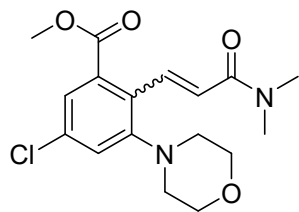
dimethyl (*E*)-4-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-5-morpholinoisophthalate **4j**

Yield 58%; yellow solid; mp: 224.6-224.8 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 1:1 (v/v). ¹H NMR (400 MHz, DMSO) δ 7.85 (d, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.67 (d, *J* = 15.6 Hz, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.71 (t, *J* = 4.0 Hz, 4H), 3.07 (s, 3H), 2.93-2.92(m, 7H). ¹³C NMR (100 MHz, DMSO) δ 168.26, 165.68, 165.36, 152.62, 136.13, 133.78, 133.61, 130.47, 124.20, 123.70, 121.66, 66.69, 53.15, 53.01, 52.21, 37.18, 35.73. HRMS (ESI) Calcd for C₁₉H₂₄N₂O₆ [M+H]⁺ 377.1707; Found 377.1708. GC-MS (EI, 70 eV) *m/z* = 376([M]⁺, 1), 345(10), 331(24), 317(4), 304(65), 290(38), 272(30), 260(25), 246(24), 228(12), 214(24), 187(9), 172(7), 156(10), 143(6), 128(11).



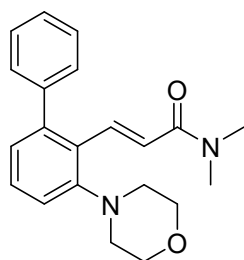
methyl (*E*)-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-5-fluoro-3-morpholinobenzoate **4k**

Yield 72%; yellow oil; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 16.0 Hz, 1H), 7.02 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.85 (dd, *J* = 10.0, 2.4 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 3.83 (t, *J* = 4.4 Hz, 4H), 3.12 (s, 3H), 3.06 (s, 3H), 2.95 (t, *J* = 4.4 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 168.37 (d, *J* = 3.0 Hz), 166.43, δ 162.51 (d, *J* = 248.6 Hz) 154.10 (d, *J* = 8.2 Hz), 137.40, 134.43 (d, *J* = 8.7 Hz), 125.51 (d, *J* = 3.3 Hz), 121.99, 110.07 (d, *J* = 23.7 Hz), 108.61 (d, *J* = 22.4 Hz), 66.92, 52.72, 52.22, 37.27, 35.77. HRMS (ESI) Calcd for C₁₇H₂₁N₂O₄F [M+H]⁺ 337.1558; Found 337.1559. GC-MS (EI, 70 eV) *m/z* = 336([M]⁺, 2), 305(7), 291(26), 264(64), 250(46), 232(38), 220(27), 206(29), 188(11), 174(19), 162(11), 147(17), 133(7), 120(7), 109(7).



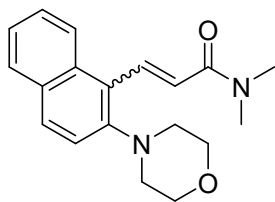
methyl-5-chloro-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4l**

Yield 86%; yellow oil; *E/Z* isomer 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 16.0 Hz, 1H, *E*), 7.49 (d, *J* = 2.0 Hz, 1H, *Z*), 7.30 (d, *J* = 2.0 Hz, 1H, *E*), 7.11 (d, *J* = 2.0 Hz, 1H, *Z*), 7.09 (d, *J* = 2.4 Hz, 1H, *E*), 7.00 (d, *J* = 12.4 Hz, 1H, *Z*), 6.78 (d, *J* = 16.0 Hz, 1H, *E*), 6.30 (d, *J* = 12.4 Hz, 1H, *Z*), 3.85 (s, 3H, *E*), 3.84-3.81 (m, 7H, *E+Z*), 3.78 (t, *J* = 4.4 Hz, 4H, *Z*), 3.11 (s, 3H, *E*), 3.06 (s, 3H, *E*), 2.97 – 2.93 (m, 7H, *E+Z*), 2.84 (s, 3H, *Z*). ¹³C NMR (101 MHz, CDCl₃) δ 168.26 (*E*), 166.91 (*Z*), 166.62 (*Z*), 166.32 (*E*), 153.17 (*E*), 152.52 (*Z*), 137.24 (*E*), 134.74 (*E*), 134.64 (*Z*), 134.19 (*E*), 133.86 (*Z*), 132.23 (*Z*), 131.38 (*Z*), 127.94 (*E*), 124.44 (*Z*), 123.15 (*E*), 122.95 (*Z*), 122.44 (*E*), 121.47 (*E*), 66.95 (*E*), 52.74 (*E*), 52.23 (*E*), 37.52 (*Z*), 37.29 (*E*), 35.80 (*E*), 34.76 (*Z*). HRMS (ESI) Calcd for C₁₇H₂₁N₂O₄Cl [M+H]⁺ 353.1263; Found 353.1262.



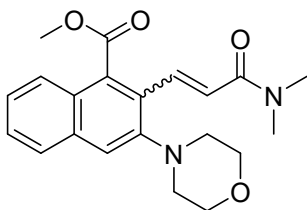
(*E*)-*N,N*-dimethyl-3-(3-morpholino-[1,1'-biphenyl]-2-yl)acrylamide **4m**

Yield 50%; white solid; mp: 166.2-166.4 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 1:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.39-7.26 (m, 6H), 7.08 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.99 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.09 (d, *J* = 16.0 Hz, 1H), 3.89 (t, *J* = 4.4 Hz, 4H), 2.99 (t, *J* = 4.4 Hz, 4H), 2.91 (s, 3H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.85, 152.43, 143.01, 142.42, 137.97, 129.59, 128.85, 128.31, 126.81, 125.76, 123.48, 117.93, 67.30, 52.88, 36.63, 35.61. HRMS (ESI) Calcd for C₂₁H₂₄N₂O₂ [M+H]⁺ 337.1911; Found 337.1911. GC-MS (EI, 70 eV) *m/z* = 336([M]⁺, 7), 307(5), 291(14), 264(100), 250(33), 232(24), 220(46), 206(47), 193(8), 178(18), 165(12), 152(7), 102(9).



N,N-dimethyl-3-(2-morpholinonaphthalen-1-yl)acrylamide **4n**

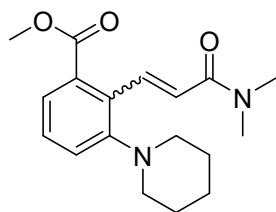
Yield 74%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 1:1(v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.25-8.20 (m, 2H, *E*), 7.82-7.78 (m, 2H, *E*), 7.49-7.45 (M, 1H, *E*), 7.41-7.37 (m, 1H, *E*), 7.33 (d, *J* = 8.8 Hz, 1H, *E*), 7.13 (d, *J* = 12.0 Hz, 1H, *Z*), 7.02 (d, *J* = 16.0 Hz, 1H, *E*), 6.49 (d, *J* = 12.0 Hz, 1H, *Z*), 3.87 (t, *J* = 4.4 Hz, 4H, *E*), 3.84 (t, *J* = 4.4 Hz, 4H, *Z*), 3.17 (s, 3H, *E*), 3.12 (s, 3H, *E*), 3.08 (t, *J* = 4.4 Hz, 4H, *Z*), 3.05 (t, *J* = 4.4 Hz, 4H, *E*), 2.91 (s, 3H, *Z*), 2.73 (s, 3H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 167.35 (*Z*), 166.91 (*E*), 149.23 (*E*), 147.92 (*Z*), 138.68 (*E*), 134.55 (*Z*), 131.97 (*E*), 131.44 (*Z*), 130.62 (*Z*), 130.43 (*E*), 129.91 (*E*), 129.29 (*Z*), 128.49 (*E*), 128.41 (*Z*), 126.96 (*Z*), 126.84 (*E*), 126.07 (*Z*), 125.44 (*E*), 124.80 (*Z*), 124.50 (*E*), 124.24 (*E*), 123.93 (*Z*), 123.01 (*E*), 118.66 (*E*), 118.47 (*Z*), 67.39 (*E*), 52.58 (*E*), 52.46 (*Z*), 37.54 (*Z*), 37.45 (*E*), 35.92 (*E*), 34.68 (*Z*). HRMS (ESI) Calcd for C₁₉H₂₂N₂O₂ [M+H]⁺ 311.1754; Found 311.1754. GC-MS (EI, 70 eV) *m/z* = 311([M + H]⁺, 3), 310([M]⁺, 11), 265(19), 238(100), 224(26), 206(27), 246(20), 194(38), 180(57), 152(29), 72(41).



methyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-morpholino-1-naphthoate **4o**

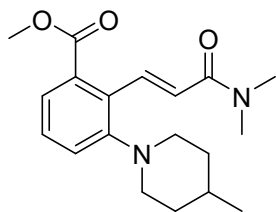
Yield 78%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 1:1(v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 15.6 Hz, 1H, *E*), 7.76 (d, *J* = 8.0 Hz, 1H, *E*), 7.66 (d, *J* = 8.0 Hz, 1H, *E*), 7.50-7.44 (m, 1H, *E*), 7.42-7.39(m, 2H, *E*), 7.37-7.34 (m, 2H, *Z*), 7.01 (d, *J* = 12.4 Hz, 1H, *Z*), 6.95 (d, *J* = 15.6 Hz, 1H, *E*), 6.33 (d, *J* = 12.0 Hz, 1H, *Z*), 3.95 (s, 3H, *E*), 3.94 (s, 3H, *Z*), 3.89 (t, *J* = 4.4 Hz, 4H, *E*), 3.84 (t, *J* = 4.4 Hz, 4H, *Z*), 3.15 (s, 3H, *E*), 3.11 (t, *J* = 4.4 Hz, 4H, *Z*), 3.08 (s, 3H, *E*), 3.04 (t, *J* = 4.4 Hz, 4H, *E*), 2.92 (s, 1H, *Z*), 2.86 (s, 1H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 170.05 (*E*), 169.28 (*Z*), 166.67 (*Z*), 166.23 (*E*),

148.90 (*E*), 148.53 (*Z*), 138.91 (*E*), 135.36 (*E*), 133.96 (*E*), 132.26 (*E*), 128.30 (*E*), 127.33 (*E*), 127.18 (*E*), 126.59 (*Z*), 126.28 (*E*), 125.92 (*E*), 125.51 (*Z*), 124.97 (*Z*), 124.83 (*E*), 122.48 (*E*), 116.80 (*Z*), 116.72 (*E*), 67.14 (*E*), 67.08 (*Z*), 52.90 (*E*), 52.79 (*E*), 52.69 (*Z*), 52.21 (*Z*), 37.56 (*Z*), 37.32 (*E*), 35.83 (*E*), 34.73 (*Z*). HRMS (ESI) Calcd for C₂₁H₂₄N₂O₄ [M+H]⁺ 369.1807; Found 369.1807.



methyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(piperidin-1-yl)benzoate **4p**

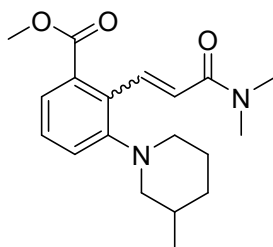
Yield 64%; yellow oil; *E/Z* isomer 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 160 Hz, 1H, *E*), 7.44 (d, *J* = 7.6 Hz, 1H, *Z*), 7.31-7.22 (m, 2H, *E*), 7.15-7.12 (m, 1H, *E*), 7.07 (d, *J* = 12.4 Hz, 1H, *Z*), 6.83 (d, *J* = 16.0 Hz, 1H, *E*), 6.23 (d, *J* = 12.4 Hz, 1H, *Z*), 3.84 (s, 3H, *E*), 3.81 (s, 3H, *Z*), 3.11 (s, 3H, *E*), 3.06 (s, 3H, *E*), 2.90-2.82 (m, 14H, *E+Z*), 1.73-1.67 (m, 4H, *E*), 1.65-1.61 (m, *J* = 4H, *Z*), 1.57-1.50 (m, 2H, *E*). ¹³C NMR (100 MHz, CDCl₃) δ 169.86 (*E*), 168.35 (*Z*), 167.03 (*Z*), 166.82 (*E*), 153.74 (*E*), 153.06 (*Z*), 138.56 (*E*), 135.43 (*Z*), 133.07 (*E*), 132.56 (*Z*), 131.15 (*Z*), 129.38 (*E*), 128.82 (*E*), 127.99 (*Z*), 123.74 (*Z*), 122.51 (*E*), 122.23 (*Z*), 121.94 (*Z*), 121.49 (*E*), 121.39 (*E*), 53.64 (*E*), 53.56 (*Z*), 52.41 (*E*), 51.88 (*Z*), 37.49 (*Z*), 37.27 (*E*), 35.75 (*E*), 34.67 (*Z*), 26.29 (*E*), 26.21 (*Z*), 24.23 (*Z*), 24.11 (*E*). HRMS (ESI) Calcd for C₁₈H₂₄N₂O₃ [M+H]⁺ 317.1860; Found 317.1860. GC-MS (EI, 70 eV) *m/z* = 316([M]⁺, 4), 271(45), 244(80), 228(100), 212(33), 198(29), 184(27), 156(20), 144(11), 128(20), 72(77).



methyl (*E*)-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(4-methylpiperidin-1-yl)benzoate **4q**

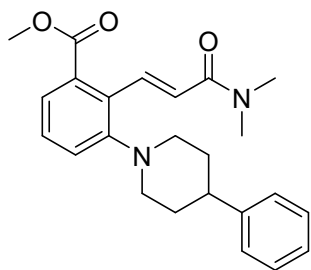
Yield 64%; yellow oil; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with

petroleum ether/EtOAc = 2:1 (v/v). ^1H NMR (400 MHz, DMSO) δ 7.68 (d, J = 15.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.24-7.19 (m, 2H), 6.81 (d, J = 16.0 Hz, 1H), 3.78 (s, 3H), 3.09 (s, 1H), 3.06 (s, 4H), 2.93 (s, 3H), 2.63-2.58 (m, 2H), 1.69-1.66 (m, 2H), 1.48-1.43 (m, 1H), 1.32-1.22 (m, 2H), 0.96 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 169.58, 165.76, 153.42, 137.31, 133.65, 129.69, 128.45, 122.57, 121.96, 121.91, 52.88, 52.82, 37.13, 35.72, 34.70, 30.40, 22.31. HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 331.2016; Found 331.2016. GC-MS (EI, 70 eV) m/z = 330($[\text{M}]^+$, 5), 315(3), 299(7), 285(38), 270(4), 258(78), 242(100), 226(30), 212(28), 198(19), 184(13), 156(22), 144(11), 129(17), 115(10), 102(8).



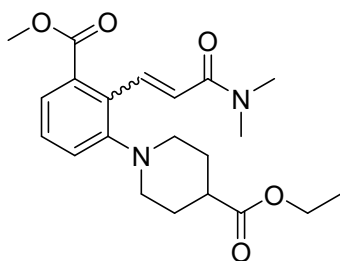
methyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(3-methylpiperidin-1-yl)benzoate **4r**

Yield 62%; yellow oil; *E/Z* isomer 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 15.6 Hz, 1H, *E*), 7.45 (dd, J = 7.6, 0.8 Hz, 1H, *Z*), 7.31-7.22 (m, 2H, *E+Z*), 7.13 (dd, J = 7.6, 1.2 Hz, 1H, *E*), 7.07 (d, J = 12.4 Hz, 1H, *Z*), 6.82 (d, J = 15.6 Hz, 1H, *E*), 6.21 (d, J = 12.4 Hz, 1H, *Z*), 3.84 (s, 3H, *E*), 3.81 (s, 3H, *Z*), 3.11-2.81(m, 10H, *E*), 2.56-2.26(m, 10H, *Z*), 1.87-1.61 (m, 5H, *E*), 1.05-0.93 (m, 5H, *Z*), 0.90 (d, J = 6.4 Hz, 3H, *E*). ^{13}C NMR (100 MHz, CDCl_3) δ 169.88 (*E*), 167.02(*Z*), 166.80 (*E*), 153.49 (*E*), 152.82 (*Z*), 138.58 (*E*), 135.33 (*Z*), 133.12 (*E*), 132.54 (*Z*), 131.16(*Z*), 129.45 (*E*), 128.83 (*E*), 128.01 (*Z*), 123.75 (*Z*), 122.54 (*E*), 122.36(*Z*), 121.96 (*Z*), 121.59 (*E*), 121.46(*E*), 60.46 (*E*), 53.42 (*E*), 53.22 (*Z*), 52.43 (*E*), 51.92 (*Z*), 37.51 (*Z*), 37.30 (*E*), 35.77 (*E*), 34.68 (*Z*), 32.86 (*Z*), 32.71 (*E*), 31.43 (*E*), 31.29 (*Z*), 25.77 (*E*), 25.70 (*Z*), 19.61 (*Z*), 19.48 (*E*). HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 331.2016; Found 331.2016.



methyl (*E*)-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(4-phenylpiperidin-1-yl)benzoate **4s**

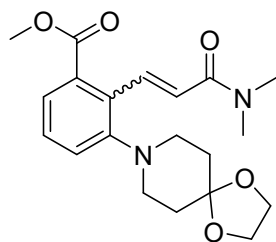
Yield 45%; white solid; mp: 146.7-146.8 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 1:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 15.6 Hz, 1H), 7.34-7.24 (m, 6H), 7.23-7.17 (m, 2H), 6.84 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 3.32 (d, *J* = 12.0 Hz, 2H), 3.12 (s, 3H), 3.05 (s, 3H), 2.82-2.73 (m, 2H), 2.66-2.58 (m, 1H), 1.96-1.90 (m, 4H). ¹³C NMR (100 MHz, DMSO) δ 169.91, 166.70, 153.21, 145.95, 138.47, 133.28, 129.46, 128.93, 128.45, 126.94, 126.24, 122.80, 121.70, 121.52, 53.42, 52.48, 42.33, 37.34, 35.81, 33.70. HRMS (ESI) Calcd for C₂₄H₂₈N₂O₃ [M+H]⁺ 393.2173; Found 393.2173. GC-MS (EI, 70 eV) *m/z* = 392([M]⁺, 5), 347(34), 320(49), 304(67), 288(17), 274(18), 260(9), 216(23), 201(38), 188(17), 156(30), 143(14), 129(30), 115(25).



ethyl-1-(2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(methoxycarbonyl)phenyl)piperidine-4-carboxylate **4t**

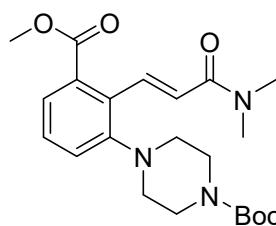
Yield 62%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 15.6 Hz, 1H, *E*), 7.48 (dd, *J* = 7.6, 0.8 Hz, 1H, *Z*), 7.31-7.26 (m, 2H, *E*), 7.14 (dd, *J* = 6.8, 2.4 Hz, 1H, *E*), 7.07 (d, *J* = 12.4 Hz, 1H, *Z*), 6.85 (d, *J* = 15.6 Hz, 1H, *E*), 6.27 (d, *J* = 12.4 Hz, 1H, *Z*), 4.18-4.12 (m, 4H, *E+Z*), 3.85 (s, 3H, *E*), 3.81 (s, 1H, *Z*), 3.23-3.19 (m, 2H, *E*), 3.12 (s, 3H, *E*), 3.06 (s, 3H, *E*), 2.97 (s, 3H, *Z*), 2.84 (s, 3H, *Z*), 2.71-2.65 (m, 2H, *E*), 2.44-2.36 (m, 1H, *Z*), 2.02-2.01 (m, 2H, *E*), 1.95 - 1.86 (m, 2H, *E*), 1.28 (d, *J* = 7.2 Hz, 3H, *E*). ¹³C NMR (100 MHz, CDCl₃) δ 175.27 (*Z*), 174.85

(*E*), 169.61 (*E*), 168.21 (*Z*), 166.82 (*Z*), 166.66 (*E*), 152.85 (*E*), 152.13 (*Z*), 138.25 (*E*), 135.69 (*Z*), 133.13 (*E*), 132.93 (*Z*), 131.12 (*Z*), 129.60 (*E*), 128.86 (*E*), 127.99 (*E*), 124.24 (*Z*), 123.09 (*E*), 122.31 (*Z*), 122.00 (*Z*), 121.79 (*E*), 121.59 (*E*), 60.43 (*E*), 60.38 (*Z*), 52.44 (*E*), 52.02 (*E*), 51.93 (*Z*), 51.89 (*Z*), 40.96 (*Z*), 40.78 (*E*), 37.50 (*Z*), 37.30 (*E*), 35.78 (*E*), 34.71 (*Z*), 28.62 (*Z*), 28.54 (*E*), 14.25 (*E*). HRMS (ESI) Calcd for C₂₁H₂₈N₂O₅ [M+H]⁺ 389.2071; Found 389.2071.



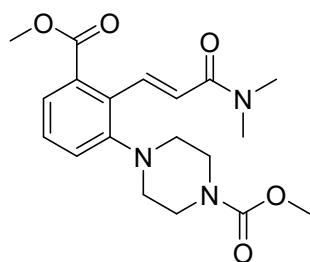
methyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(1,4-dioxo-8-azaspiro[4.5]decan-8-yl)benzoate **4u**

Yield 78%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 16.0 Hz, 1H, *E*), 7.49-7.47 (m, 2H, *Z*), 7.31-7.28 (m, 2H, *E*), 7.27-7.24 (m, 1H, *Z*), 7.20-7.16 (m, 1H, *E*), 6.85 (d, *J* = 15.6 Hz, 1H, *E*), 6.26 (d, *J* = 12.0 Hz, 1H, *Z*), 3.97 (s, 4H, *E*), 3.85 (s, 3H, *E*), 3.81 (s, 3H, *Z*), 3.11 (s, 3H, *E*), 3.05 (s, 3H, *E*), 3.03 (t, *J* = 5.2 Hz, 4H, *E*), 2.94 (s, 3H, *Z*), 2.83 (s, 3H, *Z*), 1.85 (t, *J* = 5.4 Hz, 4H, *E*), 1.81 (t, *J* = 5.4 Hz, 4H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 169.50 (*E*), 168.20 (*Z*), 166.90 (*Z*), 166.68 (*E*), 152.57 (*E*), 151.94 (*Z*), 138.31 (*E*), 135.51 (*Z*), 132.93 (*E*), 132.80 (*Z*), 131.04 (*Z*), 129.64 (*E*), 128.83 (*E*), 128.03 (*Z*), 124.25 (*Z*), 123.11 (*E*), 122.54 (*Z*), 122.04 (*Z*), 121.80 (*E*), 121.72 (*E*), 107.03 (*Z*), 106.86 (*E*), 64.28 (*E*), 52.43 (*E*), 51.91 (*Z*), 50.43 (*E*), 50.37 (*Z*), 37.48 (*Z*), 37.30 (*E*), 35.48 (*Z*), 35.76 (*E*), 35.30 (*E*), 34.68 (*Z*). HRMS (ESI) Calcd for C₂₀H₂₆N₂O₅ [M+H]⁺ 375.1914; Found 375.1913.



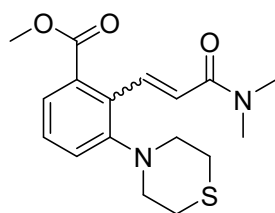
tert-butyl-(*E*)-4-(2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(methoxycarbonyl)phenyl)piperazine-1-carboxylate **4v**

Yield 61%; white solid; mp: 132.4-132.6 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.35-7.29 (m, 2H), 7.13 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 3H), 3.57 (t, *J* = 4.4 Hz, 4H), 3.11 (s, 3H), 3.06 (s, 3H), 2.89 (b, 4H), 1.47 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 169.57, 166.51, 154.86, 152.09, 138.11, 133.11, 129.72, 129.02, 123.42, 122.28, 121.46, 79.79, 52.47, 51.66, 44.41, 43.44, 37.29, 35.75, 28.43. HRMS (ESI) Calcd for C₂₂H₃₁N₃O₅ [M+H]⁺ 418.2336; Found 418.2336.



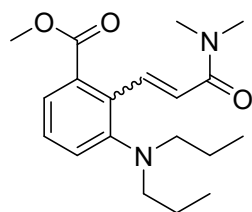
methyl-4-(2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(methoxycarbonyl)phenyl)piperazine-1-carboxylate **4w**

Yield 81%; yellow oil; *E/Z* isomer 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 15.6 Hz, 1H, *E*), 7.52 (d, *J* = 7.6 Hz, 1H, *Z*), 7.36-7.30 (m, 2H, *E*), 7.13 (dd, *J* = 6.4, 2.6 Hz, 1H, *E*), 7.07 (d, *J* = 12.4 Hz, 1H, *Z*), 6.75 (d, *J* = 16.0 Hz, 1H, *E*), 6.26 (d, *J* = 12.0 Hz, 1H, *Z*), 3.84 (s, 3H, *E*), 3.82 (s, 3H, *Z*), 3.71 (s, 3H, *E*), 3.62 (s, 4H, *E*), 3.11 (s, 3H, *E*), 3.06 (s, 3H, *E*), 2.95-2.87 (m, 7H, *E+Z*), 2.82 (s, 3H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 169.47 (*E*), 167.97 (*Z*), 166.95 (*Z*), 166.43 (*E*), 155.97 (*E*), 151.92 (*E*), 151.31 (*Z*), 138.05 (*E*), 134.95 (*Z*), 133.08 (*E*), 132.92 (*Z*), 131.14 (*Z*), 129.80 (*E*), 129.03 (*E*), 128.23 (*Z*), 124.76 (*Z*), 123.57 (*E*), 122.75 (*Z*), 122.34 (*E*), 121.52 (*E*), 52.65 (*E*), 52.46 (*E*), 51.96 (*E*), 51.84 (*E*), 44.05 (*E*), 37.49 (*Z*), 37.27 (*E*), 35.73 (*E*), 34.66 (*Z*). HRMS (ESI) Calcd for C₁₉H₂₅N₃O₅ [M+H]⁺ 376.1867; Found 376.1867.



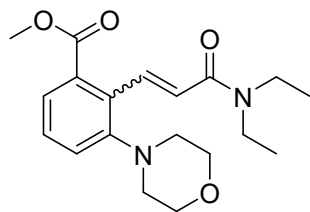
methyl-2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-thiomorpholinobenzoate **4x**

Yield 40%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 16.0 Hz, 1H, *E*), 7.50 (d, *J* = 7.6 Hz, 1H, *Z*), 7.35-7.31 (m, 2H, *E*), 7.30-7.27(m, 2H, *Z*), 7.15 (dd, *J* = 7.2, 2.1 Hz, 1H, *E*), 7.04 (d, *J* = 12.0 Hz, 1H, *Z*), 6.71 (d, *J* = 16.0 Hz, 1H, *E*), 6.28 (d, *J* = 12.4 Hz, 1H, *Z*), 3.84 (s, 3H, *E*), 3.81 (s, 3H, *Z*), 3.20-3.15 (m, 8H, *E+Z*), 3.12 (s, 3H, *E*), 3.06 (s, 3H, *E*), 2.94 (s, 3H, *Z*), 2.83 (s, 3H, *Z*), 2.78 (t, *J* = 4.8 Hz, 4H, *E*), 2.74 (t, *J* = 4.8 Hz, 4H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 169.58 (*E*), 168.09 (*Z*), 166.89 (*Z*), 166.49 (*E*), 153.31 (*E*), 152.62(*Z*), 138.18 (*E*), 135.54 (*Z*), 133.22 (*Z*), 133.01 (*E*), 131.16 (*Z*), 130.16 (*E*), 129.00 (*E*), 128.17 (*Z*), 124.69 (*Z*), 123.52 (*E*), 123.10 (*Z*), 122.36 (*E*), 122.29 (*E*), 54.66 (*E*), 54.49 (*Z*), 52.48 (*E*), 51.94 (*Z*), 37.49 (*Z*), 37.30 (*E*), 35.78 (*E*), 34.73 (*Z*), 28.16 (*E*), 28.12 (*Z*). HRMS (ESI) Calcd for C₁₇H₂₂N₂O₃S [M+H]⁺ 335.1424; Found 335.1424.



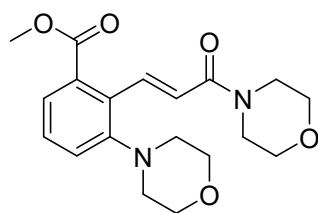
methyl 2-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)-3-(dipropylamino)benzoate **4y**

Yield≈10%; yellow oil, *E/Z* isomer 10:1.1(By the ¹H spectrum integral ratio), purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 16.0 Hz, 1H, *E*), 7.42 (d, *J* = 7.2 Hz, 1H, *Z*), 7.23 (m, 6H, *E+Z*), 7.09 (d, *J* = 12.0 Hz, 1H, *Z*), 6.69 (d, *J* = 16.0 Hz, 1H, *E*), 6.25 (d, *J* = 12.4 Hz, 1H, *Z*), 3.84 (s, 3H, *E*), 3.80 (s, 3H, *Z*), [3.07 (d, *J* = 13.9 Hz), 2.90 (s), 2.83 (s), 12H, *E+Z*] 2.95 (t, *J* = 7.6 Hz, 8H, *E+Z*), 1.49 – 1.39 (m, 8H, *E+Z*), 0.81 (t, *J* = 7.2 Hz, 12H, *E+Z*). ¹³C NMR (100 MHz, CDCl₃) δ 170.12 (*E*), 168.61 (*Z*), 166.75 (*E*), 151.37 (*E*), 150.59 (*Z*), 139.33 (*E*), 136.64 (*Z*), 133.49 (*E*), 132.06 (*Z*), 130.78 (*E*), 128.23 (*E*), 127.36 (*Z*), 124.51 (*Z*), 124.09 (*E*), 123.83 (*Z*), 122.52 (*E*), 121.84 (*Z*), 121.28 (*E*), 55.22 (*E*), 55.10 (*Z*), 52.43 (*E*), 51.87 (*Z*), 37.43 (*Z*), 37.26 (*E*) 35.77 (*E*), 34.75 (*Z*), 29.72 (*Z*), 20.17 (*Z*), 20.04 (*E*), 11.68 (*E*). HRMS (ESI) Calcd for C₁₉H₂₈N₂O₃ [M+H]⁺ 333.2173; Found 333.2182. GC-MS (EI, 70 eV) m/z = 332 ([M]⁺, 3), 303(11), 287(11), 258(15), 246(25), 230(31), 216(10), 200(23), 188(8), 72(100).



methyl-2-(3-(diethylamino)-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4z**

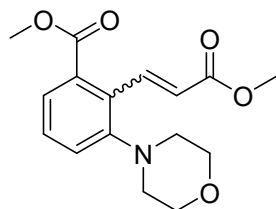
Yield 94%; yellow oil; *E/Z* isomer 97:3; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 15.6 Hz, 1H, *E*), 7.37-7.29 (m, 2H, *E*), 7.16 (dd, *J* = 7.6, 2.0 Hz, 1H, *E*), 7.11 (d, *J* = 12.0 Hz, 1H, *Z*), 6.70 (d, *J* = 16.0 Hz, 1H, *E*), 6.26 (d, *J* = 12.0 Hz, 1H, *Z*), 3.86-3.82 (m, 7H, *E*), 3.80 (s, 3H, *Z*), 3.78 (t, *J* = 4.4 Hz, 4H, *Z*), 3.49 (q, *J* = 7.2 Hz, 2H, *E*), 3.41 (q, *J* = 6.8 Hz, 2H, *E*), 2.96 (t, *J* = 4.4 Hz, 4H, *E*), 1.25-1.17 (m, 6H, *E*), 1.04-0.94 (m, 6H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 169.54 (*E*), 165.63 (*E*), 152.09 (*E*), 138.13 (*E*), 136.58 (*Z*), 133.68 (*Z*), 133.15 (*E*), 129.92 (*Z*), 129.78 (*E*), 128.95 (*E*), 128.27 (*Z*), 128.03 (*Z*), 124.80 (*Z*), 123.36 (*E*), 122.66 (*E*), 122.27 (*Z*), 121.20 (*E*), 67.33 (*Z*), 67.13 (*E*), 52.44 (*E*), 52.41 (*E*), 51.93 (*Z*), 42.03 (*E*), 40.80 (*E*), 39.46 (*Z*), 15.06 (*E*), 14.26 (*Z*), 13.22 (*E*), 12.84 (*Z*). HRMS (ESI) Calcd for C₁₉H₂₆N₂O₄ [M+H]⁺ 347.1965; Found 347.1965. GC-MS (EI, 70 eV) *m/z* = 346([M]⁺, 1), 315(5), 273(17), 256(6), 246(69), 232(76), 214(39), 200(22), 188(26), 170(12), 156(25), 144(15), 129(22), 115(85), 100(100).



methyl (*E*)-3-morpholino-2-(3-morpholino-3-oxoprop-1-en-1-yl)benzoate **4aa**

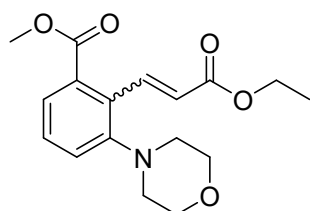
Yield 82%; white solid; mp: 153.5-153.6 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 15.6 Hz, 1H), 7.38-7.31 (m, 2H), 7.17 (dd, *J* = 6.8, 1.6 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 3.84-3.82 (m, 7H), 3.73 (b, 6H), 3.61 (b, 2H), 2.96 (t, *J* = 4.4 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 169.43, 165.50, 152.04, 138.85, 133.02, 129.44, 129.18, 123.45, 121.43, 121.33, 67.12, 66.86, 52.48, 52.41, 46.16, 42.42. HRMS (ESI) Calcd for C₁₉H₂₄N₂O₅ [M+H]⁺ 361.1758; Found 361.1759. GC-MS (EI, 70 eV) *m/z* = 360([M]⁺, 2), 329(11), 317(2), 301(4), 285(3), 273(48),

246(97), 232(100), 214(60), 202(35), 188(40), 170(15), 156(35), 144(17), 129(47), 114(45), 102(12).



methyl-2-(3-methoxy-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4ab**

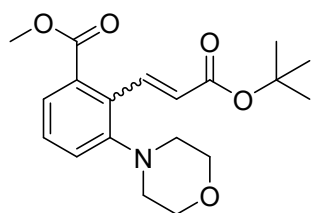
Yield 86%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1(v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 16.4 Hz, 1H, *E*), 7.62 (d, *J* = 7.6 Hz, 1H, *Z*), 7.37 (s, 1H, *E*), 7.36 (d, *J* = 1.6 Hz, 1H, *E*), 7.34 (s, 1H, *Z*), 7.32 (d, *J* = 3.6 Hz, 1H, *Z*), 7.20-7.17 (m, 1H, *E*), 6.33 (d, *J* = 16.4 Hz, 1H, *E*), 6.04 (d, *J* = 12.4 Hz, 1H, *Z*), 3.86 (s, 3H, *E*), 3.83-3.81 (m, 7H, *E*), 3.74 (t, *J* = 4.4 Hz, 4H, *Z*), 3.54 (s, 3H, *Z*), 2.93 (t, *J* = 4.4 Hz, 4H, *E*), 2.89 (t, *J* = 4.4 Hz, 4H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 168.94 (*E*), 167.71 (*Z*), 167.18 (*E*), 166.40 (*Z*), 152.20 (*E*), 151.29 (*Z*), 141.29 (*E*), 141.07 (*Z*), 133.09 (*E*), 132.55 (*Z*), 130.67 (*Z*), 129.64 (*E*), 128.71 (*E*), 128.56 (*Z*), 124.78 (*Z*), 123.85 (*E*), 122.53 (*Z*), 122.07 (*E*), 121.69 (*E*), 120.21 (*Z*), 67.10 (*Z*), 66.99 (*E*), 52.52 (*E*), 52.33 (*Z*), 52.05 (*Z*), 51.75 (*E*), 51.07 (*Z*). HRMS (ESI) Calcd for C₁₆H₁₉NO₅ [M+H]⁺ 306.1336; Found 306.1336. GC-MS (EI, 70 eV) *m/z* = 306([M + H]⁺, 8), 305([M]⁺, 41), 274(37), 246(50), 231(21), 214(37), 202(26), 188(100), 170(22), 156(52), 144(23), 129(24), 115(10).



methyl-2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4ac**

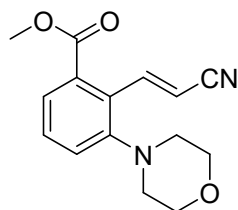
Yield 80%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 16.4 Hz, 1H, *E*), 7.61 (d, *J* = 8.0 Hz, 2H, *Z*), 7.36 (d, *J* = 4.4 Hz, 2H, *E*), 7.18 (t, *J* = 4.4 Hz, 1H, *E*), 6.30 (d, *J* = 16.4 Hz, 1H, *E*), 6.02 (d, *J* = 12.0 Hz, 1H, *Z*), 4.26 (q, *J* = 6.8 Hz, 2H, *E*), 3.97 (q, *J* = 7.2 Hz, 2H,

Z), 3.86 (s, 3H, *E*), 3.82 (s, 7H, *E*+*Z*), 3.74 (d, *J* = 3.2 Hz, 4H, *Z*), 2.93 (s, 4H, *E*), 2.89 (s, 4H, *Z*), 1.33 (t, *J* = 7.2 Hz, 3H, *E*), 1.06 (t, *J* = 6.8 Hz, 3H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 168.99 (*E*), 166.67 (*Z*), 166.67 (*E*), 165.96 (*Z*), 152.14 (*E*), 151.21 (*Z*), 140.92 (*E*), 133.11 (*E*), 132.84 (*Z*), 130.69 (*Z*), 129.57 (*E*), 128.63 (*E*), 128.40 (*Z*), 124.67 (*Z*), 123.74 (*E*), 122.48 (*E*), 121.57 (*E*), 120.65 (*Z*), 67.08 (*Z*), 66.96 (*E*), 60.45 (*E*), 59.86 (*Z*), 52.49 (*E*), 52.45 (*E*), 52.30 (*Z*), 51.99 (*Z*), 14.31 (*E*), 13.88 (*Z*). HRMS (ESI) Calcd for C₁₇H₂₁NO₅ [M+H]⁺ 320.1492; Found 320.1491. GC-MS (EI, 70 eV) *m/z* = 320([M + H]⁺, 8), 319([M]⁺, 39), 304(5), 288(29), 274(14), 260(8), 246(59), 231(28), 214(50), 202(40), 188(100), 170(32), 156(58), 144(26), 129(30), 115(12).



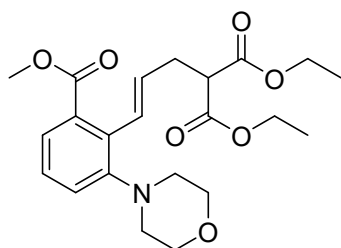
methyl-2-(3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-3-morpholinobenzoate **4ad**

Yield 75%; yellow oil; *E/Z* isomer 97:3; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 16.4 Hz, 1H, *E*), 7.35-7.32 (m, 2H, *E*), 7.16 (dd, *J* = 6.4, 2.8 Hz, 1H, *E*), 6.20 (d, *J* = 16.4 Hz, 1H, *E*), 5.93 (d, *J* = 12.4 Hz, 1H, *Z*), 3.86 (s, 3H, *E*), 3.84-3.81 (m, 7H, *E*+*Z*), 2.94 (t, *J* = 4.4 Hz, 4H, *E*), 1.53 (s, 9H, *E*), 1.22 (s, 9H, *Z*). ¹³C NMR (100 MHz, CDCl₃) δ 169.22 (*E*), 167.78 (*Z*), 165.99 (*E*), 165.21 (*Z*), 152.07 (*E*), 150.99 (*Z*), 140.32 (*Z*), 139.71 (*E*), 133.45 (*Z*), 133.19 (*E*), 129.41 (*E*), 128.78 (*E*), 128.19 (*Z*), 124.69 (*Z*), 124.41 (*E*), 123.67 (*E*), 122.71 (*Z*), 122.36 (*Z*), 121.45 (*E*), 80.45 (*E*), 80.00 (*Z*), 67.23 (*Z*), 67.03 (*Z*), 52.49 (*E*), 52.42 (*E*), 52.32 (*Z*), 51.96 (*Z*), 28.24 (*E*), 27.77 (*Z*). HRMS (ESI) Calcd for C₁₉H₂₅NO₅ [M+H]⁺ 348.1805; Found 348.1805. GC-MS (EI, 70 eV) *m/z* = 348([M + H]⁺, 6), 347([M]⁺, 25), 291(37), 274(20), 260(13), 246(100), 232(37), 214(47), 202(37), 188(85), 170(14), 156(37), 144(19), 129(28).



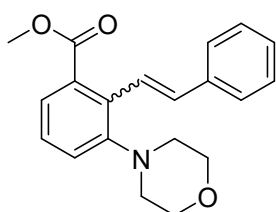
methyl (*E*)-2-(2-cyanovinyl)-3-morpholinobenzoate **4ae**

Yield 68%; white solid; mp: 105.3-105.4 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.67 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 5.61 (d, *J* = 11.6 Hz, 1H), 3.89 (s, 3H), 3.81 (t, *J* = 4.4 Hz, 4H), 2.94 (t, *J* = 4.4 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 167.03, 151.99, 147.59, 130.50, 129.96, 125.46, 123.84, 122.99, 116.63, 100.21, 67.08, 52.42, 52.14. HRMS (ESI) Calcd for C₁₅H₁₆N₂O₃ [M+H]⁺ 273.1234; Found 273.1234. GC-MS (EI, 70 eV) *m/z* = 273([M + H]⁺, 17), 272([M]⁺, 100), 241(44), 213(33), 200(72), 187(88), 182(33), 154(57), 128(33), 101(25), 91(11).



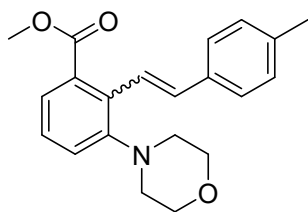
diethyl (*E*)-2-(3-(2-(methoxycarbonyl)-6-morpholinophenyl)allyl)malonate **4af**

Yield 65%; white solid; mp: 94.1-94.3 °C; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 1:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.20 (m, 2H), 7.09 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.78 (d, *J* = 16.0 Hz, 1H), 5.91-5.83 (m, 1H), 4.26-4.15 (m, 4H), 3.84 (s, 3H), 3.81 (t, *J* = 4.4 Hz, 4H), 3.44 (t, *J* = 7.6 Hz, 1H), 2.92 (t, *J* = 4.4 Hz, 4H), 2.82-2.78 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.17, 168.82, 151.21, 133.29, 131.02, 129.93, 128.52, 127.76, 123.22, 120.90, 67.25, 61.53, 52.22, 52.14, 51.75, 32.76, 14.09. HRMS (ESI) Calcd for C₂₂H₂₉NO₇ [M+H]⁺ 420.2017; Found 420.2017. GC-MS (EI, 70 eV) *m/z* = 421([M + H]⁺, 3), 420([M]⁺, 17), 419(67), 404(7), 388(14), 374(21), 362(16), 346(18), 328(9), 268(23), 260(17), 246(54), 228(100), 214(45), 202(98), 188(100), 169(55), 156(41), 144(29), 128(38).



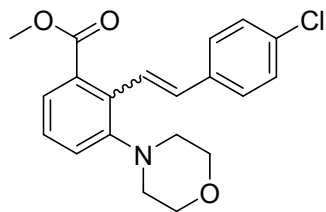
methyl-3-morpholino-2-styrylbenzoate **4ag**

Yield 62%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.42 (m, 3H, *E*), 7.36 (t, *J* = 7.2 Hz, 2H, *E*), 7.33-7.25 (m, 3H, *E*), 7.14 (dd, *J* = 7.6, 2.0 Hz, 1H, *E*), 6.88 (d, *J* = 16.8 Hz, 1H, *E*), 6.58 (d, *J* = 12.4 Hz, 1H, *Z*), 3.83-3.79 (m, 7H, *E*), 3.65 (s, 3H, *Z*), 2.98 (t, *J* = 4.4 Hz, 4H, *E*). ¹³C NMR (100 MHz, CDCl₃) δ 170.31 (*E*), 151.54 (*E*), 137.67 (*E*), 132.98 (*E*), 132.76 (*E*), 132.31 (*Z*), 131.33 (*E*), 129.96 (*Z*), 128.82 (*E*), 128.17 (*Z*), 127.99 (*Z*), 127.90 (*E*), 127.81 (*E*), 127.05 (*Z*), 126.39 (*E*), 124.59 (*E*), 124.28 (*Z*), 123.57 (*E*), 122.23 (*Z*), 121.06 (*E*), 67.31 (*E*), 67.02 (*Z*), 52.37 (*E*), 52.30 (*E*), 52.00 (*Z*), 51.93 (*Z*). HRMS (ESI) Calcd for C₂₀H₂₁NO₃ [M+H]⁺ 324.1594; Found 324.1593. GC-MS (EI, 70 eV) m/z = 324([M + H]⁺, 22), 323([M]⁺, 100), 308(10), 292(50), 264(58), 250(17), 232(51), 204(34), 188(14), 178(11), 146(9), 117(20), 102(22).



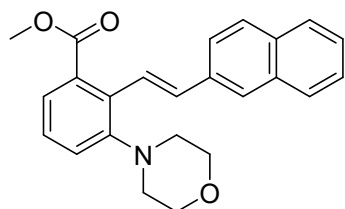
methyl-2-(4-methylstyryl)-3-morpholinobenzoate **4ah**

Yield 68%; yellow oil; *E/Z* isomer 2:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.28 (m, 4H, *E+Z*), 7.24-7.15 (m, 7H, *E+Z*), 7.10-6.99 (m, 5H, *E+Z*), 6.77 (d, *J* = 16.8 Hz, 2H, *E+Z*), 3.73-3.71 (m, 14H, *E+Z*), 2.90-2.87 (m, 8H, *E+Z*), 2.28 (d, *J* = 8.0 Hz, 6H, *E+Z*). ¹³C NMR (100 MHz, CDCl₃, *E+Z*) δ 170.41, 170.33, 151.52, 151.48, 138.37, 137.74, 137.64, 134.93, 133.00, 132.98, 132.90, 132.69, 131.43, 131.39, 129.52, 128.71, 128.64, 127.83, 127.73, 127.24, 126.32, 124.37, 123.57, 123.53, 123.51, 123.43, 121.00, 120.96, 67.31, 52.36, 52.33, 52.28, 52.27, 21.51, 21.29. HRMS (ESI) Calcd for C₂₁H₂₃NO₃ [M+H]⁺ 338.1751; Found 338.1751. GC-MS (EI, 70 eV) m/z = 338([M + H]⁺, 24), 337([M]⁺, 100), 322(8), 306(42), 278(54), 264(26), 246(32), 219(26), 200(27), 188(12), 115(10), 105(33).



methyl (*E*)-2-(4-chlorostyryl)-3-morpholinobenzoate **4ai**

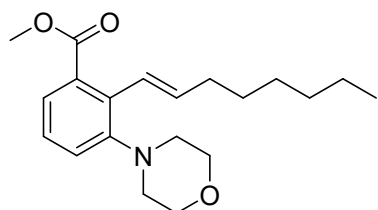
Yield 73%; yellow oil; *E/Z* isomer 98:2; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (dd, *J* = 7.6, 0.8 Hz, 1H, *Z*), 7.44-7.40 (m, 3H, *E*), 7.35-7.25 (m, 4H, *E*), 7.15 (dd, *J* = 8.0, 1.2 Hz, 1H, *E*), 7.10-7.05 (m, 4H, *Z*), 6.88-6.83 (m, 1H, *E*), 6.52 (d, *J* = 12.0 Hz, 1H, *Z*), 3.82-3.77 (m, 7H, *E*), 3.70 (s, 3H, *Z*), 2.97 (t, *J* = 4.4 Hz, 4H, *E*). ¹³C NMR (100 MHz, CDCl₃) δ 170.02 (*E*), 168.11 (*Z*), 151.60 (*E*), 151.51 (*Z*), 136.23 (*Z*), 136.18 (*E*), 133.40 (*E*), 132.83 (*E*), 132.57 (*Z*), 132.47 (*Z*), 131.41 (*E*), 131.16 (*E*), 129.39 (*Z*), 128.99 (*E*), 128.49 (*Z*), 128.24 (*Z*), 128.07 (*E*), 127.53 (*E*), 127.18 (*Z*), 125.30 (*E*), 124.44 (*Z*), 123.73 (*E*), 122.39 (*Z*), 121.24 (*E*), 67.27 (*E*), 67.00 (*Z*), 52.36 (*E*), 52.31 (*E*), 52.07 (*Z*), 51.94(*Z*). HRMS (ESI) Calcd for C₂₀H₂₀ClNO₃ [M+H]⁺ 358.1204; Found 358.1204. GC-MS (EI, 70 eV) *m/z* = 358([M + H]⁺, 24), 357([M]⁺, 100), 342(11), 326(56), 298(63), 284(22), 266(48), 239(41), 232(18), 200(57), 188(24), 176(28), 127(23), 125(60), 102(42).



methyl (*E*)-3-morpholino-2-(2-(naphthalen-2-yl)vinyl)benzoate **4aj**

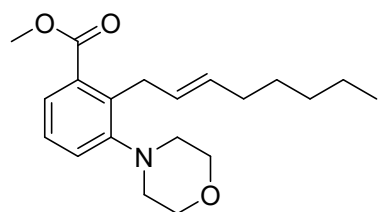
Yield 78%; yellow oil; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 5:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.74 (m, 5H), 7.57 (d, *J* = 16.8 Hz, 1H), 7.50-7.42 (m, 2H), 7.36-7.27 (m, 2H), 7.15 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 3.84-3.80 (m, 7H), 3.00 (t, *J* = 4.4 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.38, 151.61, 135.18, 133.74, 133.16, 132.99, 132.89, 131.39, 128.55, 128.09, 127.97, 127.78, 126.67, 126.48, 126.09, 125.01, 123.66, 123.20, 121.13, 67.35, 52.44, 52.34. HRMS (ESI) Calcd for C₂₄H₂₃NO₃ [M+H]⁺ 374.1751; Found 374.1751. GC-MS (EI, 70 eV) *m/z* = 374([M + H]⁺, 27), 373([M]⁺, 100), 358(11), 342(36), 328(7), 314(50), 300(17), 282(39), 254(51), 226(19), 200(46),

188(16), 141(61), 127(45), 113(21).



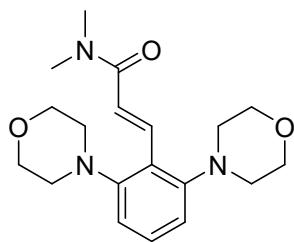
methyl (*E*)-3-morpholino-2-(oct-1-en-1-yl)benzoate **4ak**

Yield 58%; colorless oil; *E/Z* isomer > 99:1; purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.19-7.11 (m, 2H), 7.00 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.58-6.54 (m, 1H), 5.85-5.78 (m, 1H), 3.75-3.72 (m, 7H), 2.87 (t, *J* = 4.4 Hz, 4H), 2.15-2.09 (m, 2H), 1.38-1.33 (m, 2H), 1.28-1.20 (m, 6H), 0.84-0.80 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.62, 149.94, 134.36, 132.28, 130.84, 126.24, 124.48, 122.03, 119.64, 66.20, 51.07, 51.03, 32.66, 30.76, 28.30, 27.98, 21.64, 13.09. HRMS (ESI) Calcd for C₂₀H₂₉NO₃ [M+H]⁺ 332.2220; Found 332.2220. GC-MS (EI, 70 eV) *m/z* = 332 ([M + H]⁺, 16), 331 ([M]⁺, 56), 316 ([M - CH₃]⁺, 9), 300(41), 286(11), 274(8), 246(20), 216(28), 200(30), 188(100), 170(11), 144(27), 115(14).



methyl (*E*)-3-morpholino-2-(oct-2-en-1-yl)benzoate **4ak**

purified by silica gel on column chromatography with petroleum ether/EtOAc = 10:1 (v/v). ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.50 (m, 1H), 7.37-7.12 (m, 2H), 5.70-5.33 (m, 2H), 3.85-3.83 (m, 9H), 2.88-2.86 (m, 4H), 1.36-1.20 (m, 6H), 0.89 – 0.84 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 168.94, 152.28, 137.47, 132.62, 131.21, 129.16, 126.65, 126.07, 124.24, 77.37, 77.05, 76.74, 67.44, 53.38, 52.02, 32.60, 31.43, 30.49, 29.28, 22.54, 14.07. HRMS (ESI) Calcd for C₂₀H₂₉NO₃ [M+H]⁺ 332.2220; Found 332.2221. GC-MS (EI, 70 eV) *m/z* = 332 ([M + H]⁺, 14), 331 ([M]⁺, 58), 316 ([M - CH₃]⁺, 6), 300(37), 274(33), 246(37), 216(32), 203(46), 188(100), 175(29), 144(50), 130(24), 115(19).

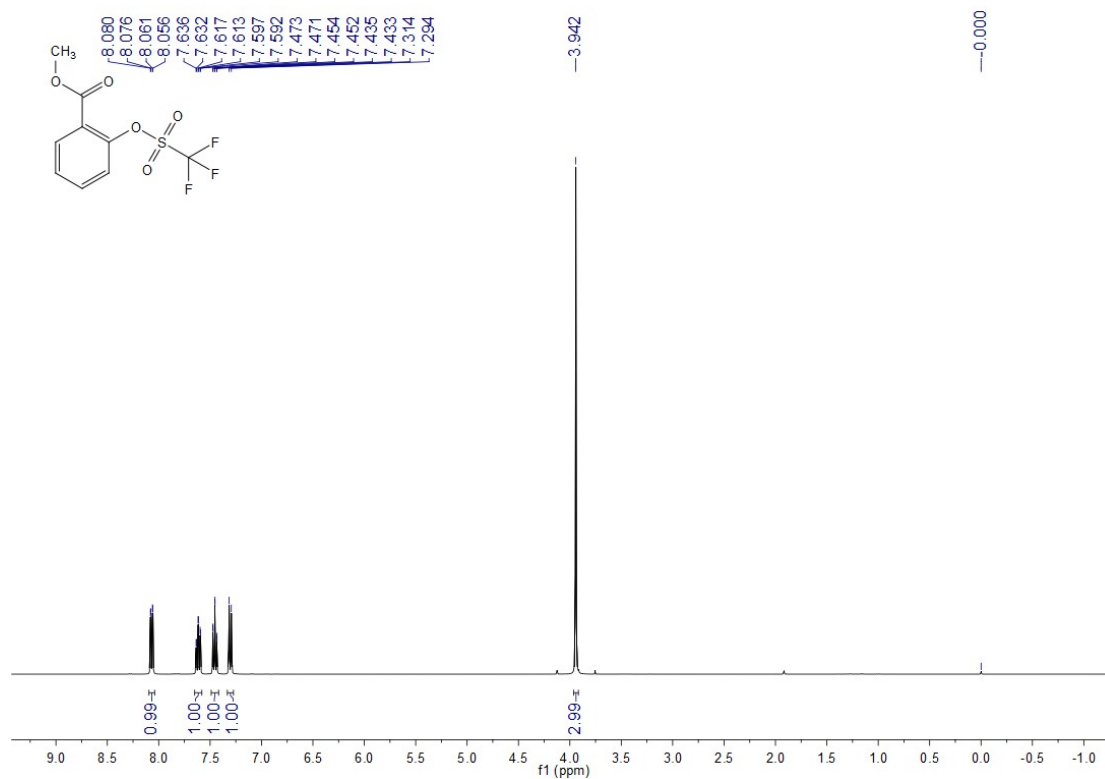


(E)-3-(2,6-dimorpholinophenyl)-*N,N*-dimethylacrylamide **4al**

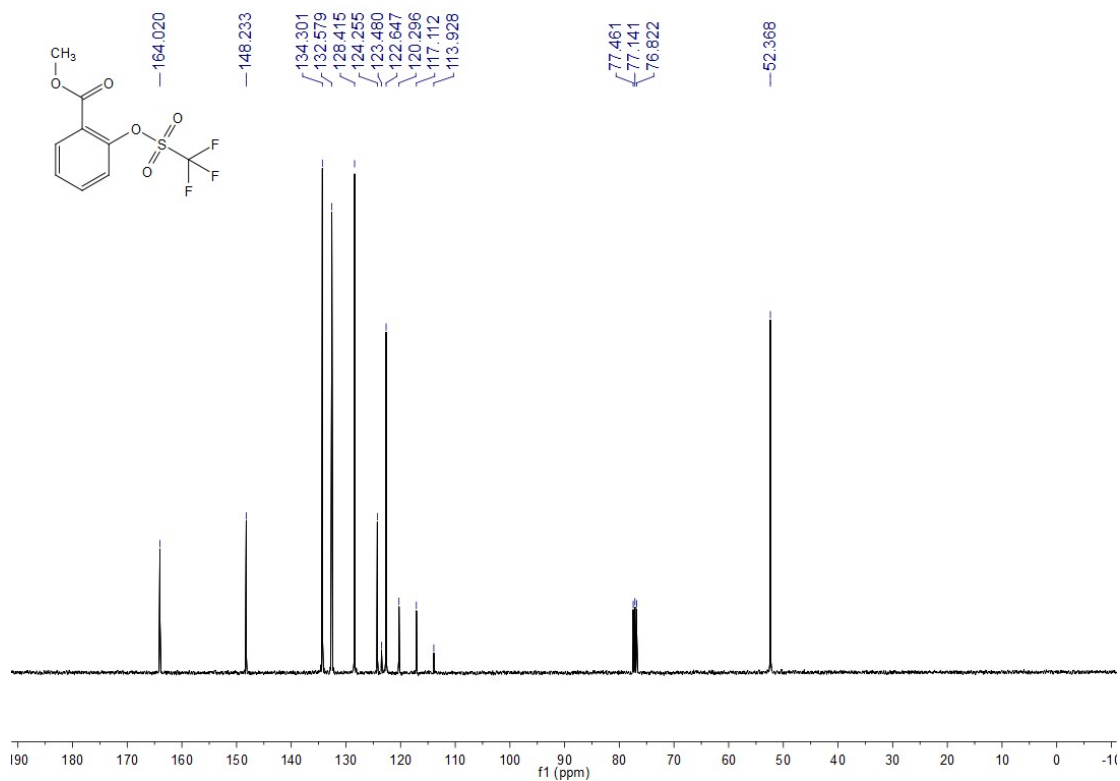
Yield 33%; yellow solid; mp: 173.3-173.5 °C; purified by silica gel on column chromatography with petroleum ether/EtOAc = 2:1 (v/v). ¹H NMR (400 MHz, DMSO) δ 7.88 (d, *J* = 15.6 Hz, 1H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.75-3.68 (m, 8H), 3.16 (s, 3H), 2.95 (s, 3H), 2.86-2.80 (m, 8H). ¹³C NMR (100 MHz, DMSO) δ 166.94, 153.81, 136.73, 130.60, 122.94, 119.78, 115.10, 66.96, 52.99, 37.37, 35.84. HRMS (ESI) Calcd for C₁₉H₂₇N₃O₃ [M+H]⁺ 346.2125; Found 346.2112.

5. ^1H , ^{13}C NMR, GC, GC-MS and HRMS of 4y spectra

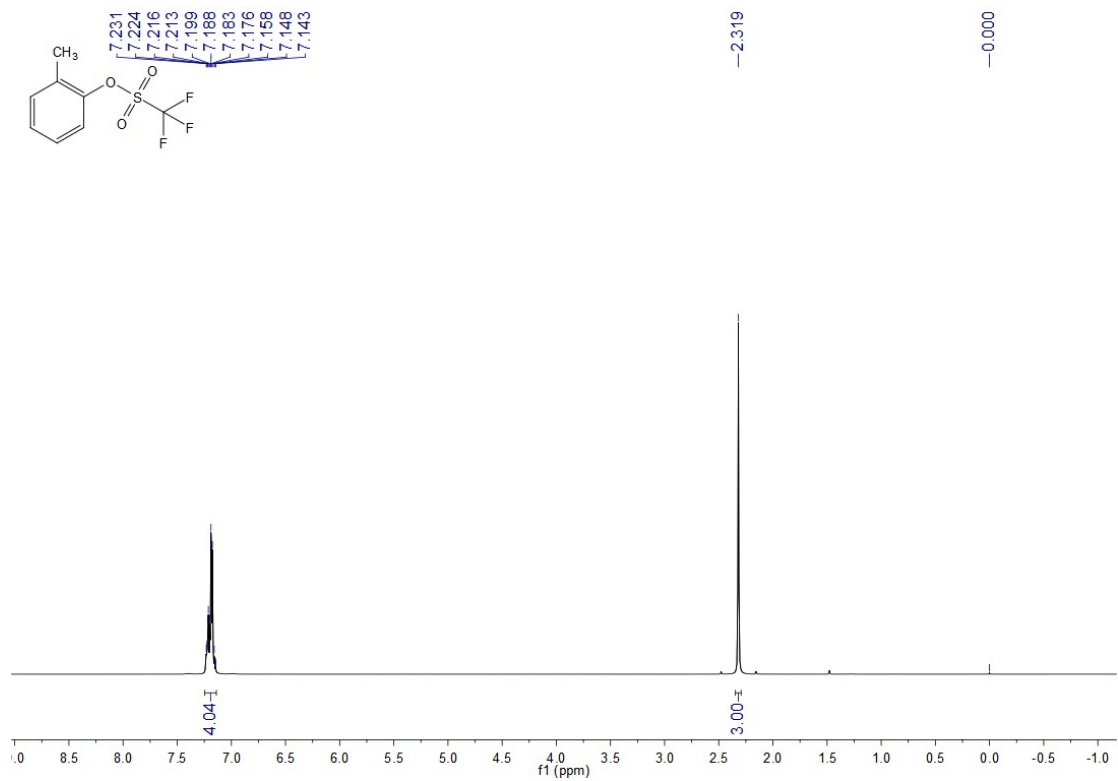
^1H NMR Spectrum of 1a



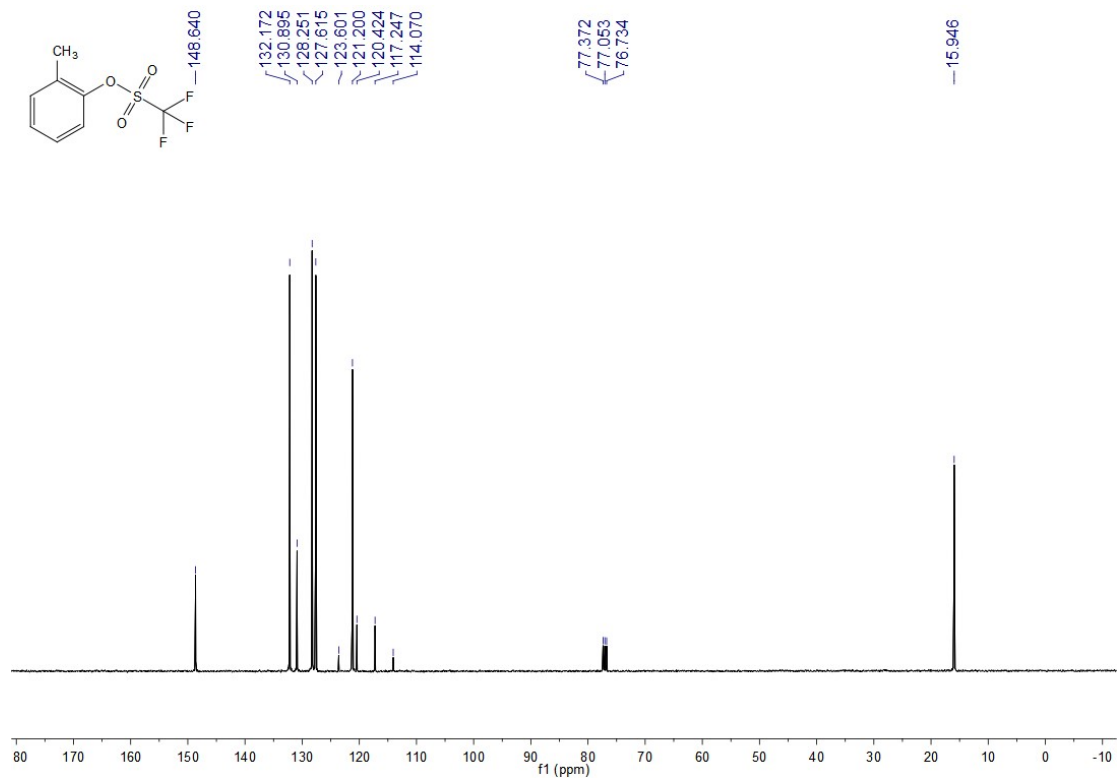
^{13}C NMR Spectrum of 1a



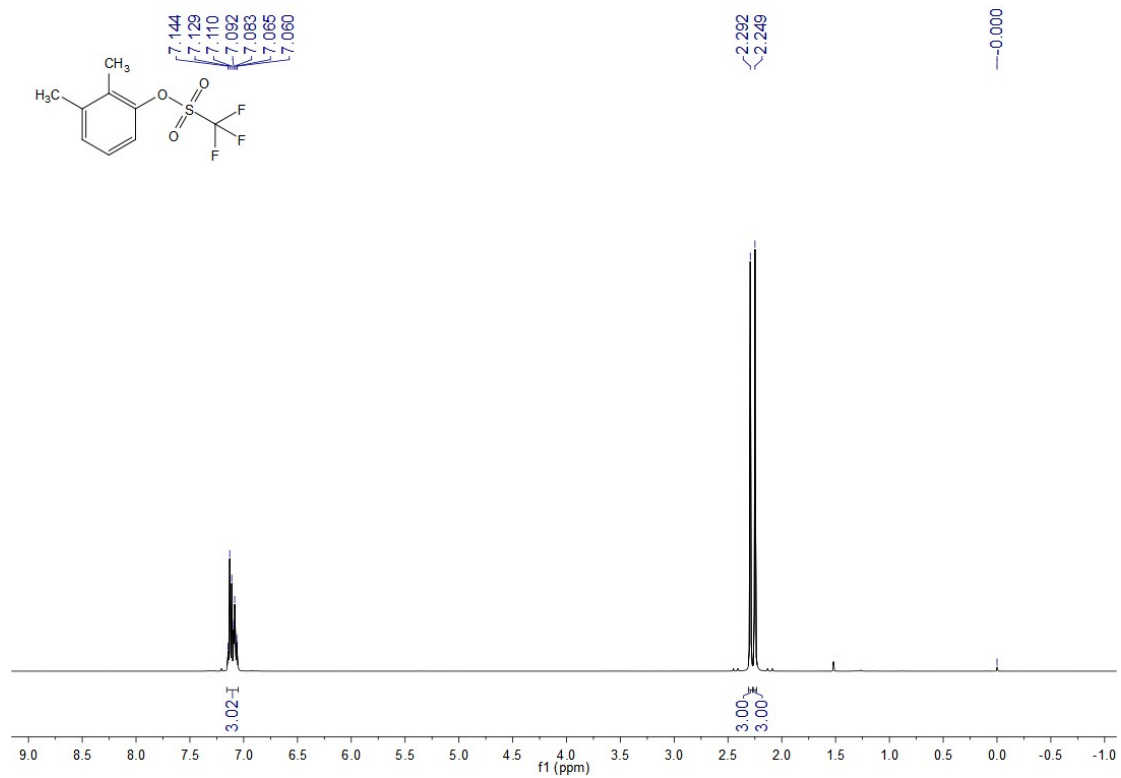
¹H NMR Spectrum of **1b**



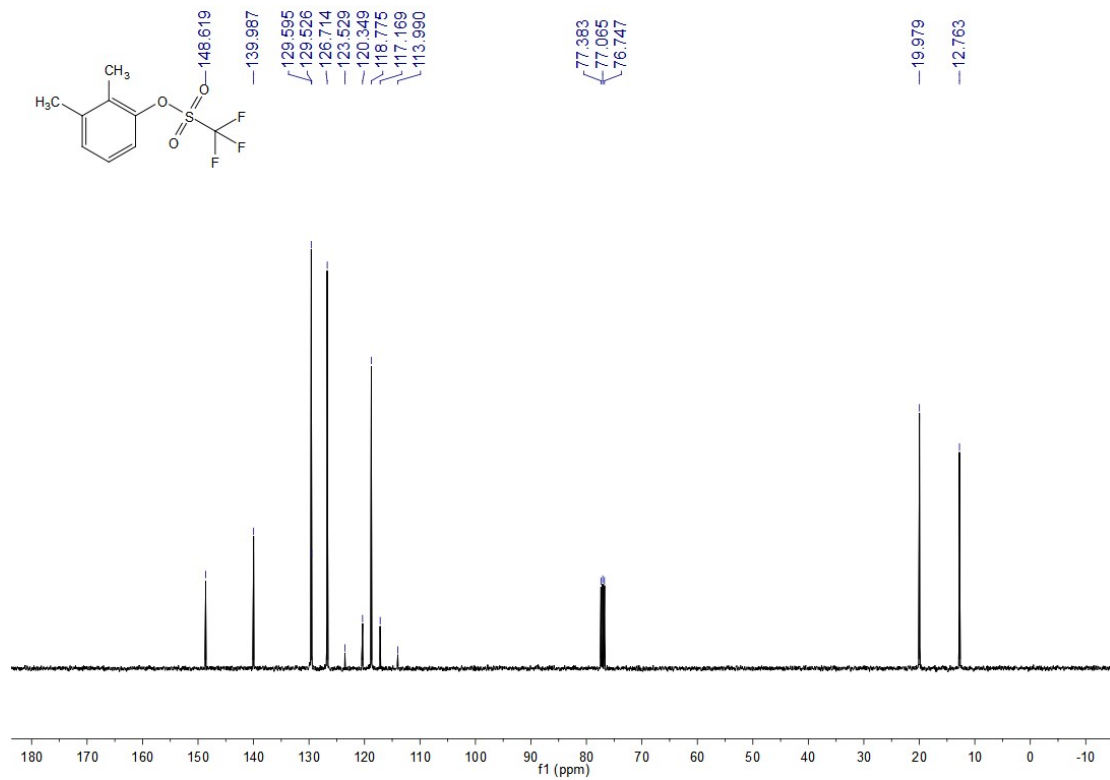
¹³C NMR Spectrum of **1b**



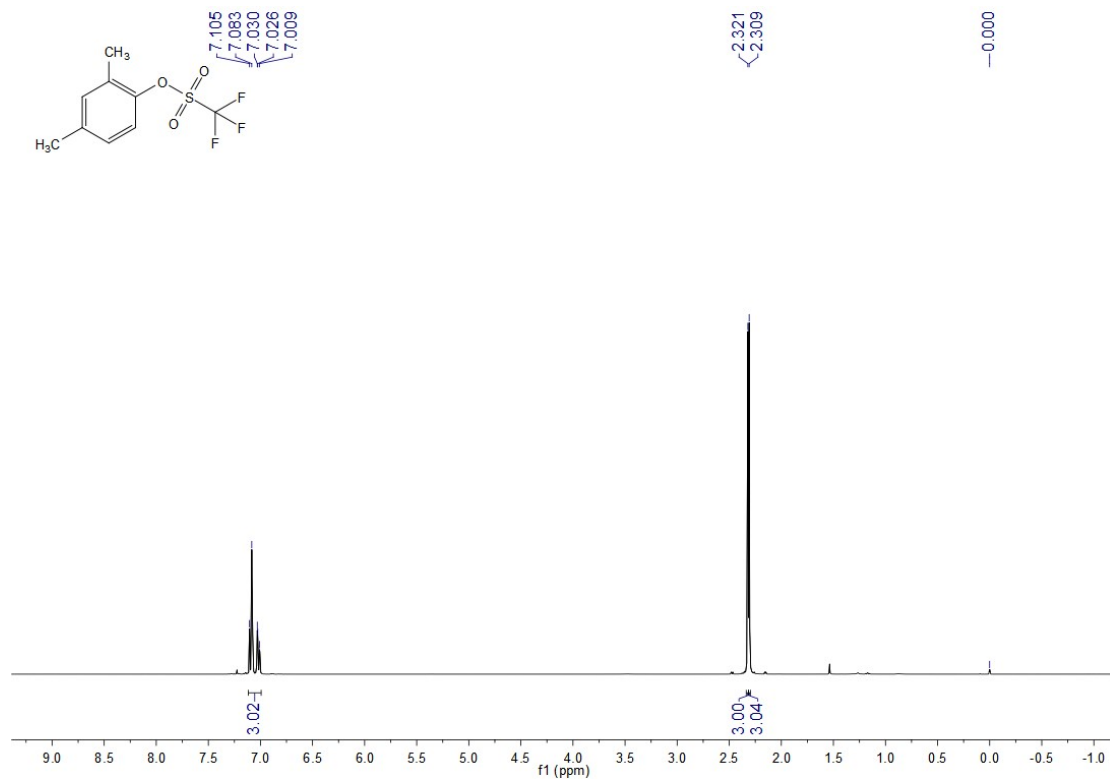
¹H NMR Spectrum of **1c**



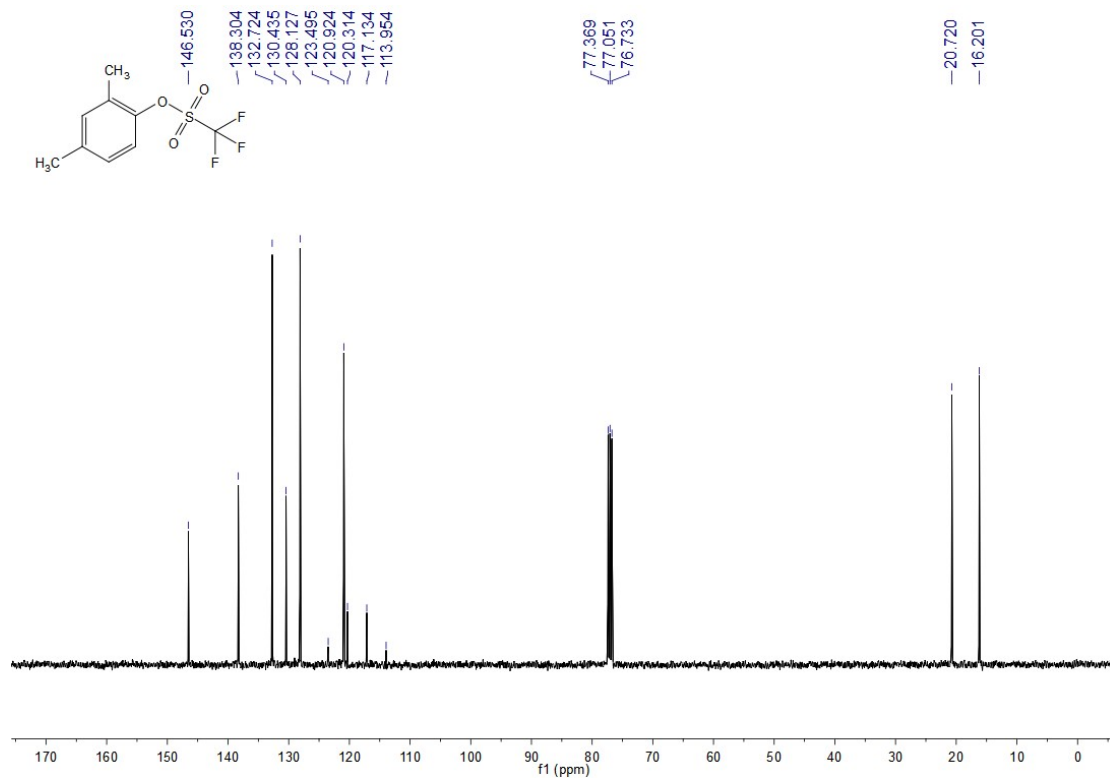
¹³C NMR Spectrum of **1c**



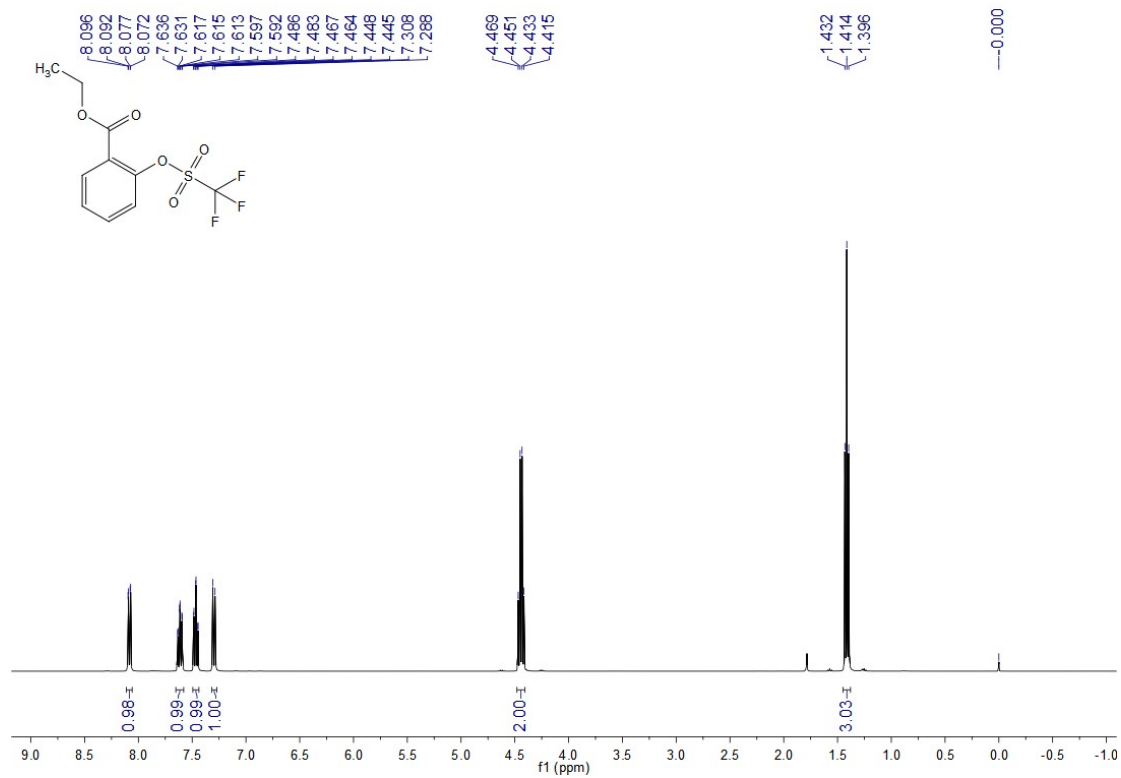
¹H NMR Spectrum of **1d**



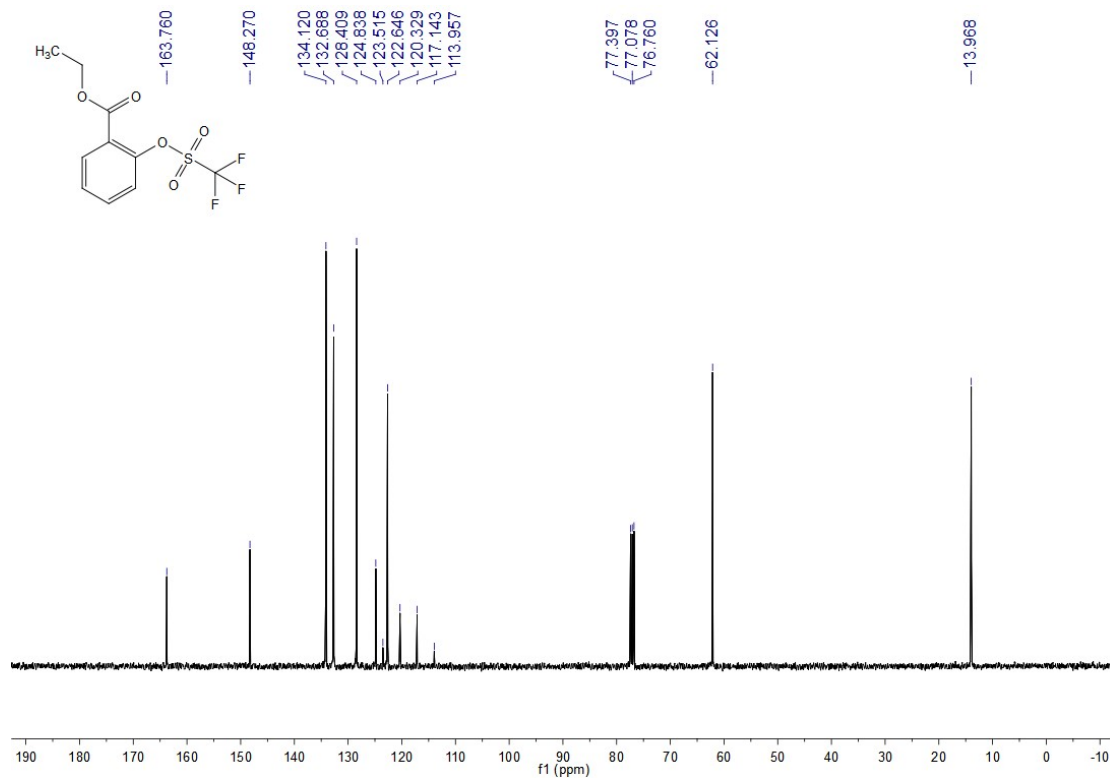
¹³C NMR Spectrum of **1d**



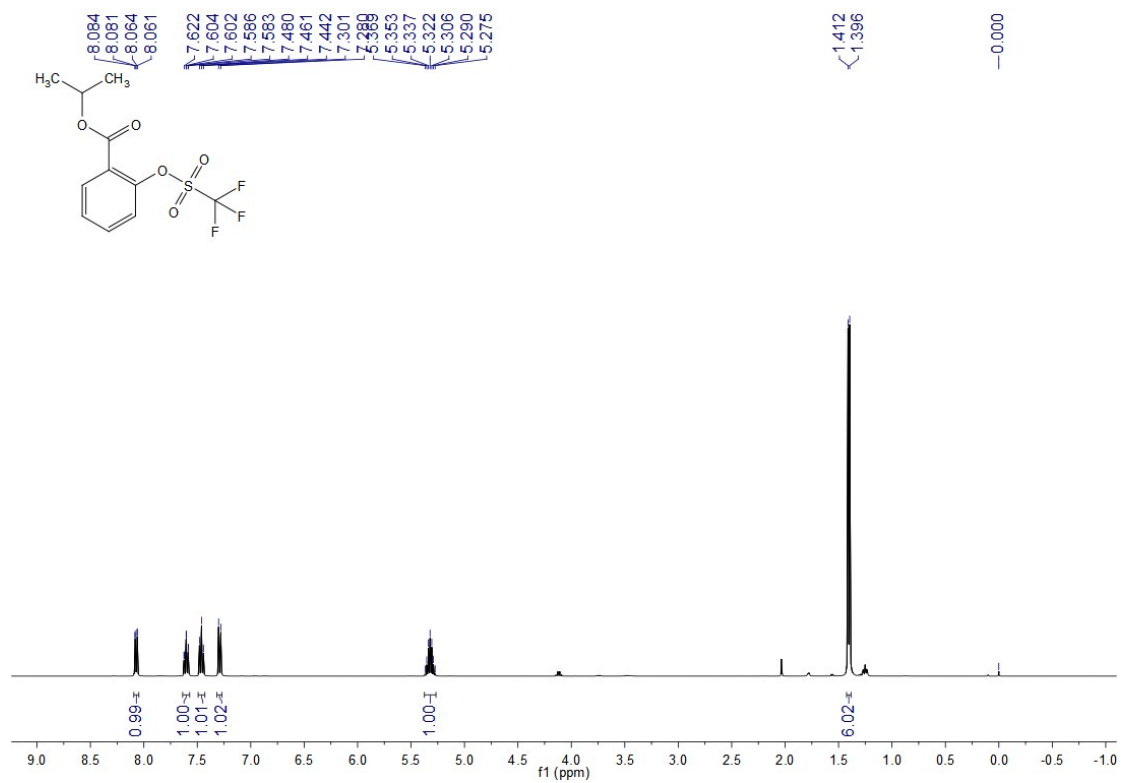
¹H NMR Spectrum of **1e**



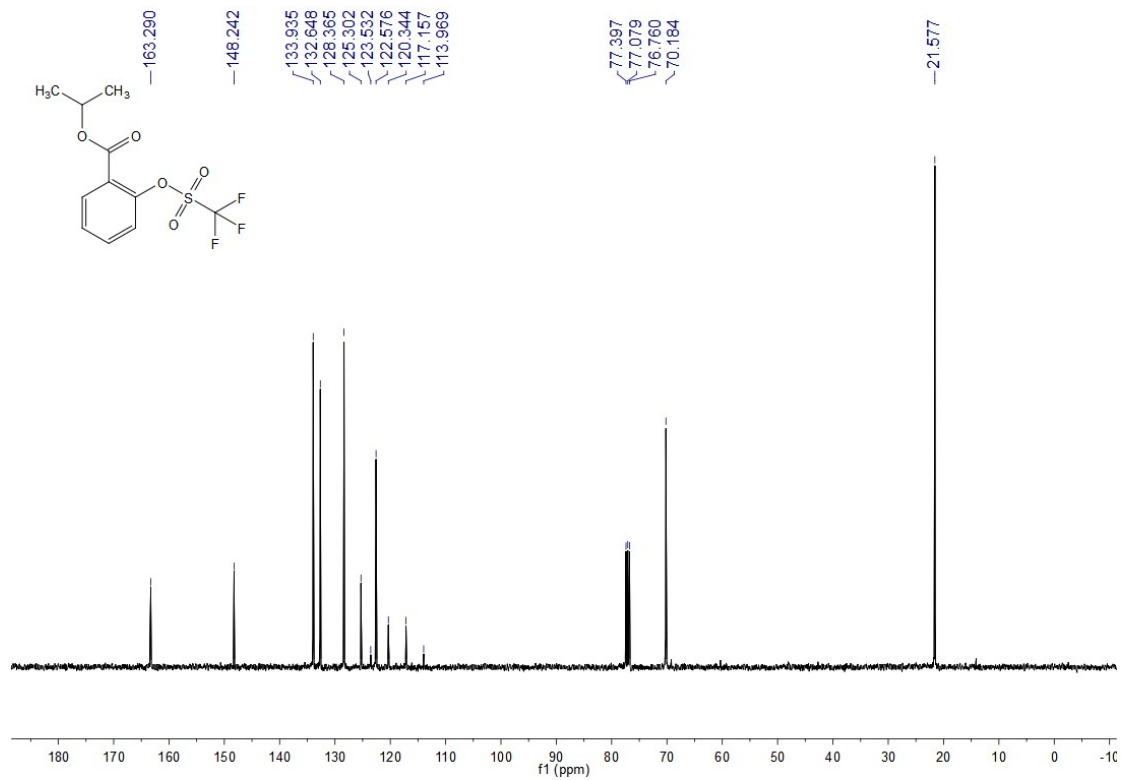
¹³C NMR Spectrum of **1e**



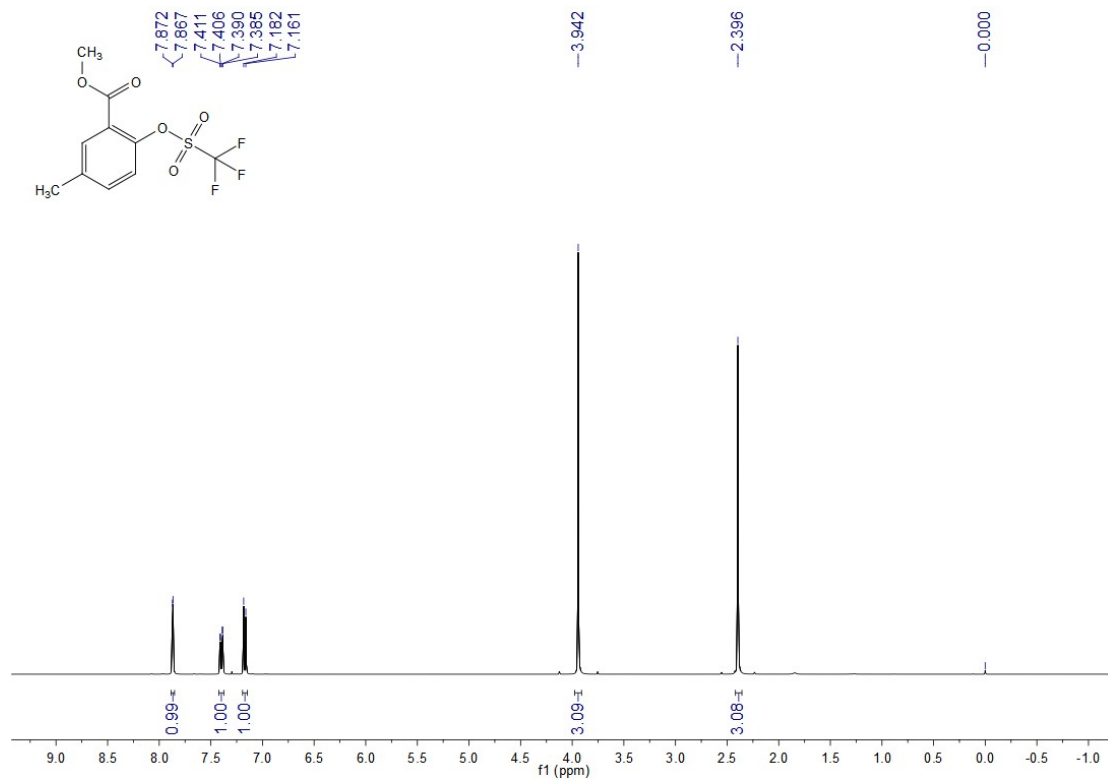
¹H NMR Spectrum of **1f**



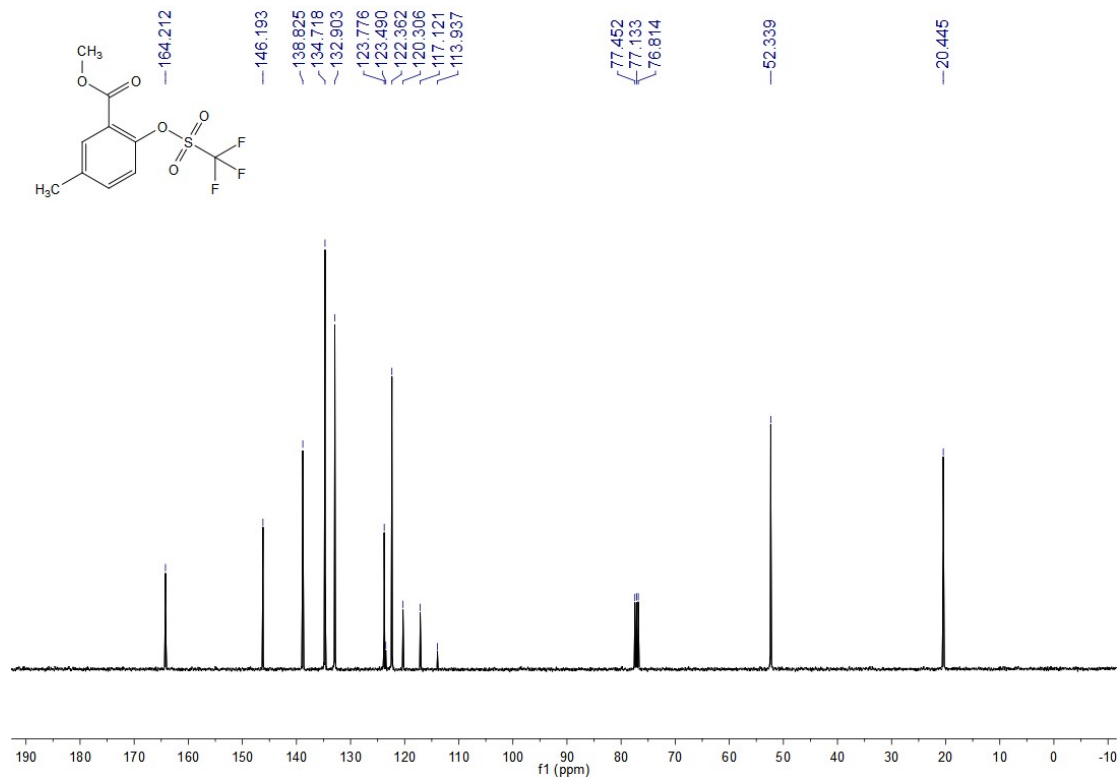
¹³C NMR Spectrum of **1f**



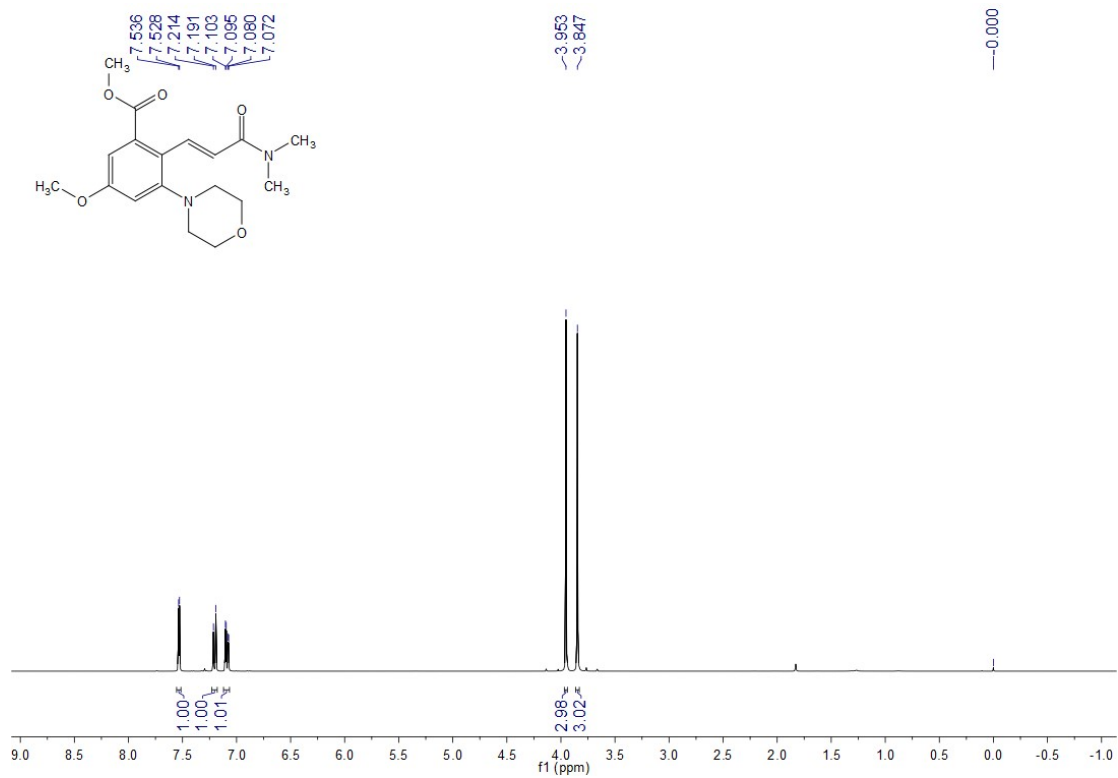
¹H NMR Spectrum of **1g**



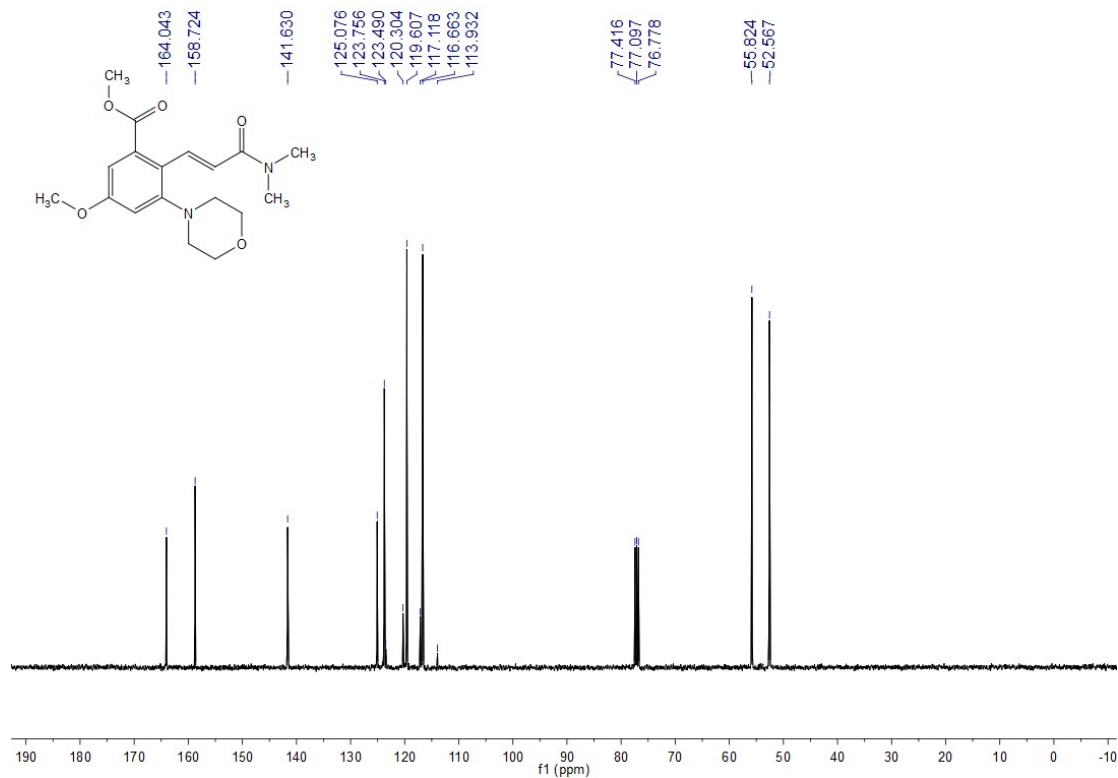
¹³C NMR Spectrum of **1g**



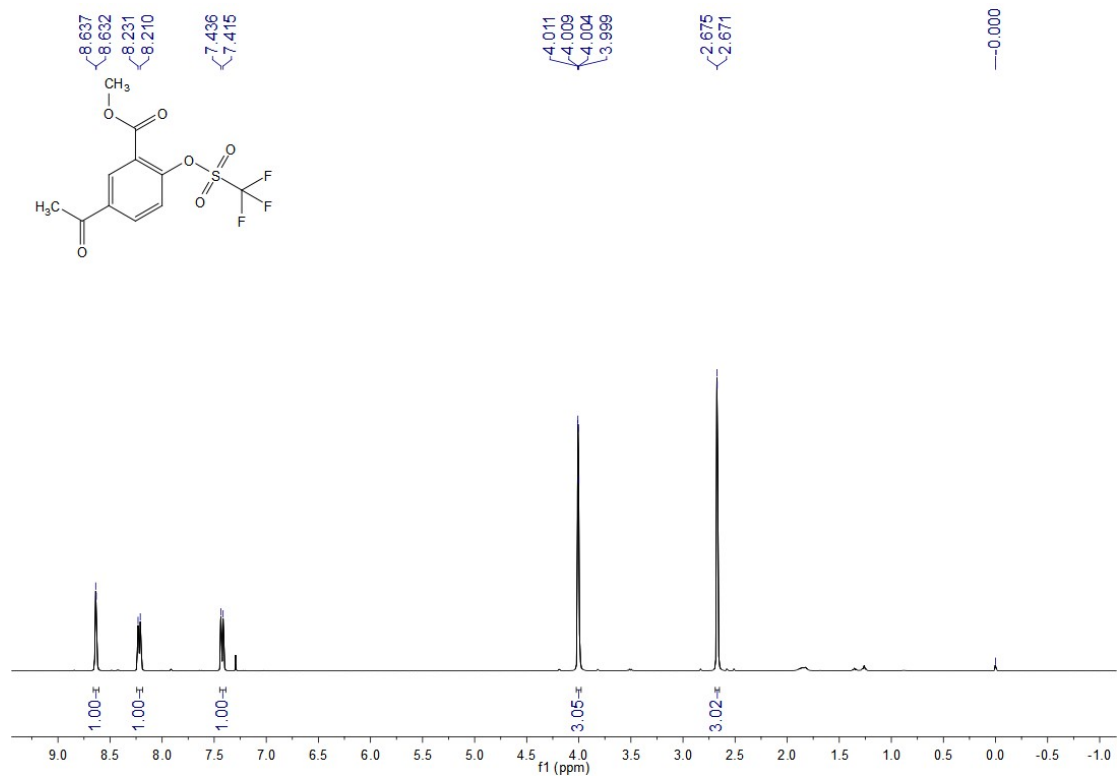
¹H NMR Spectrum of **1h**



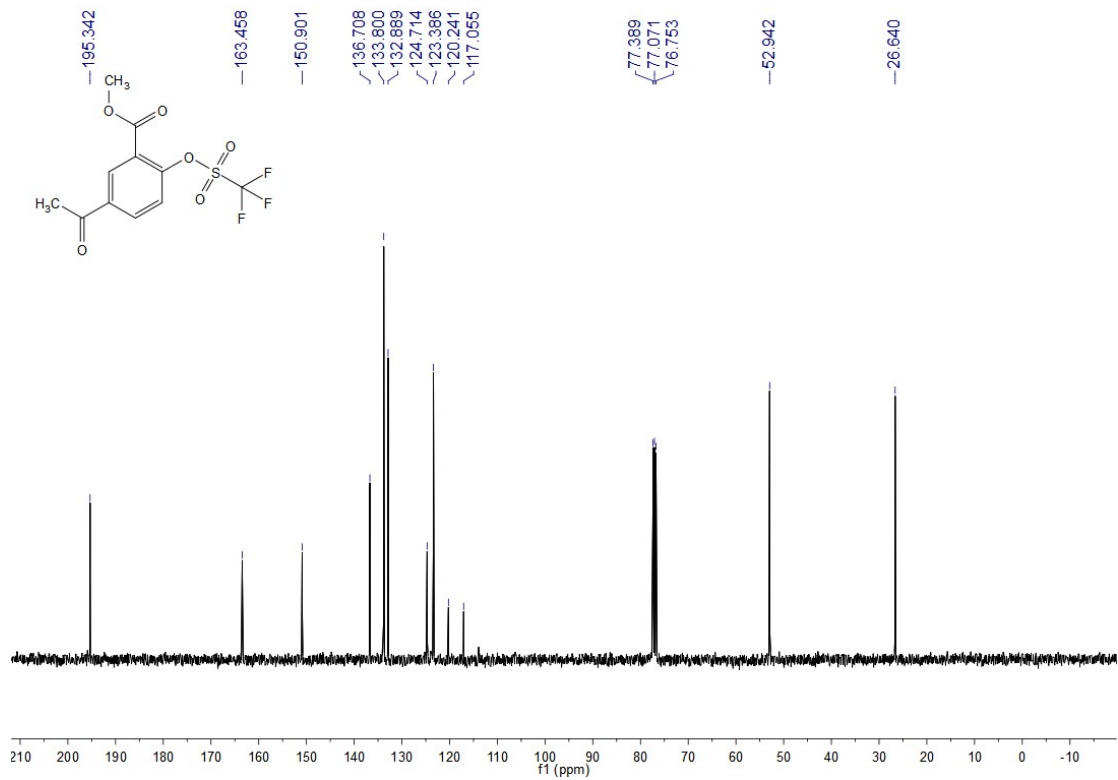
¹³C NMR Spectrum of **1h**



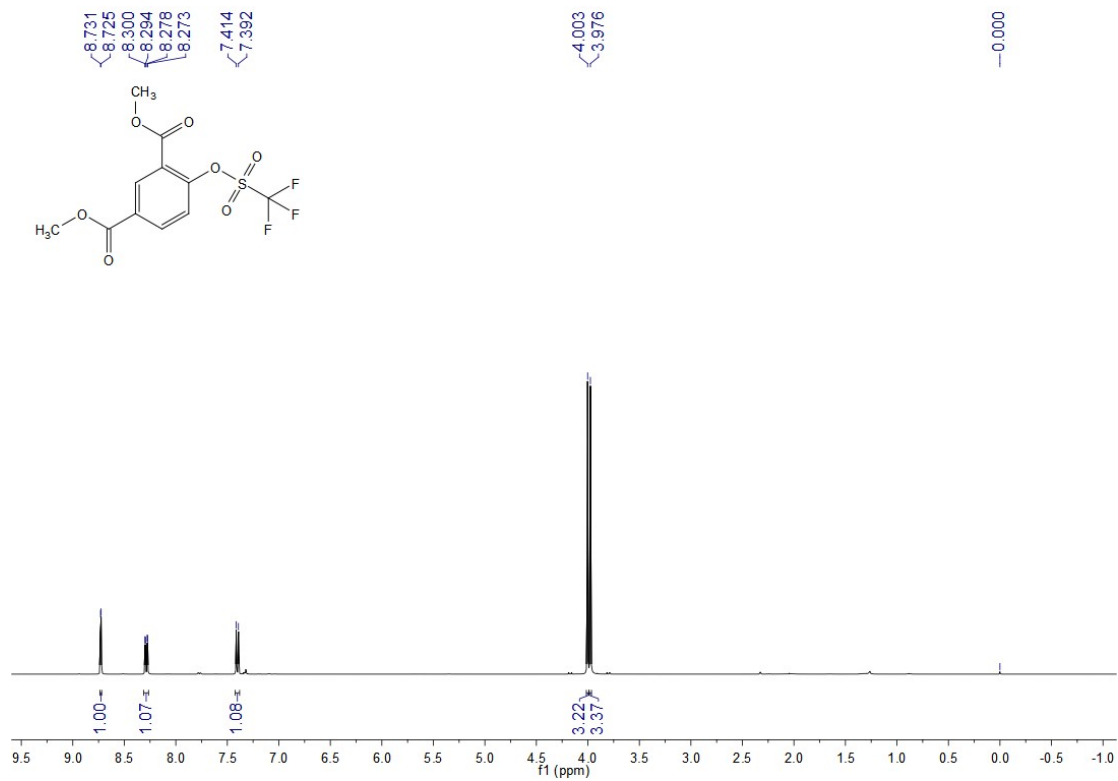
¹H NMR Spectrum of **1i**



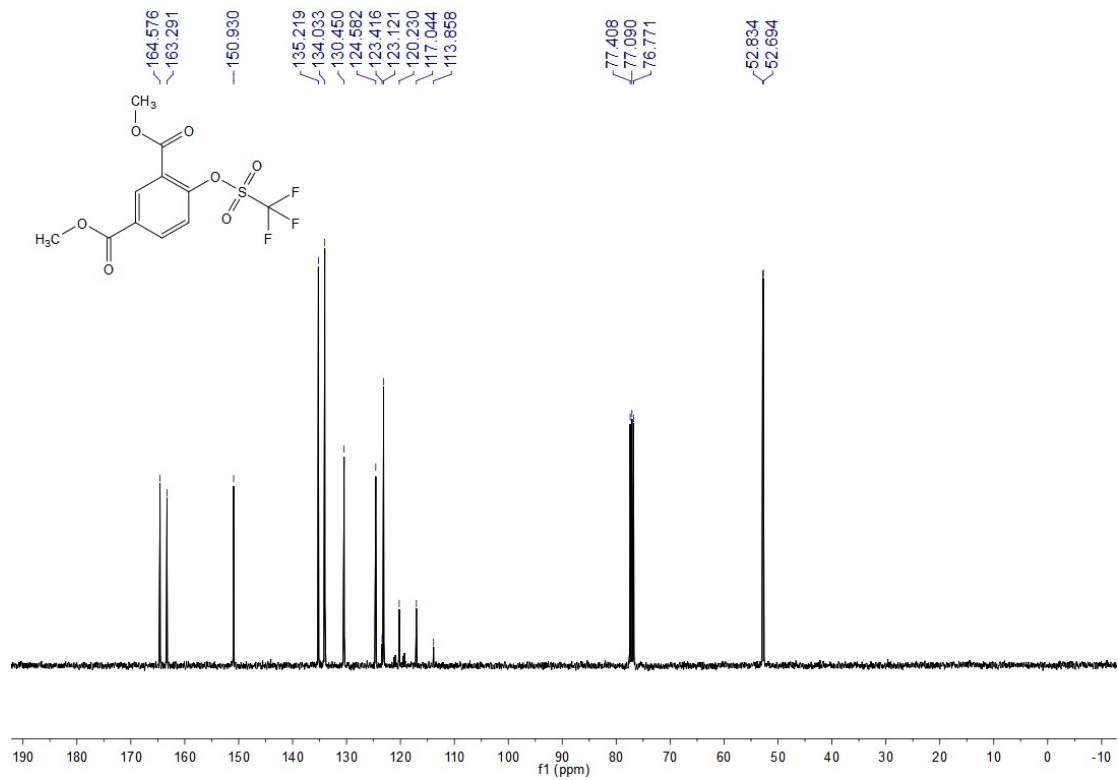
¹³C NMR Spectrum of **1i**



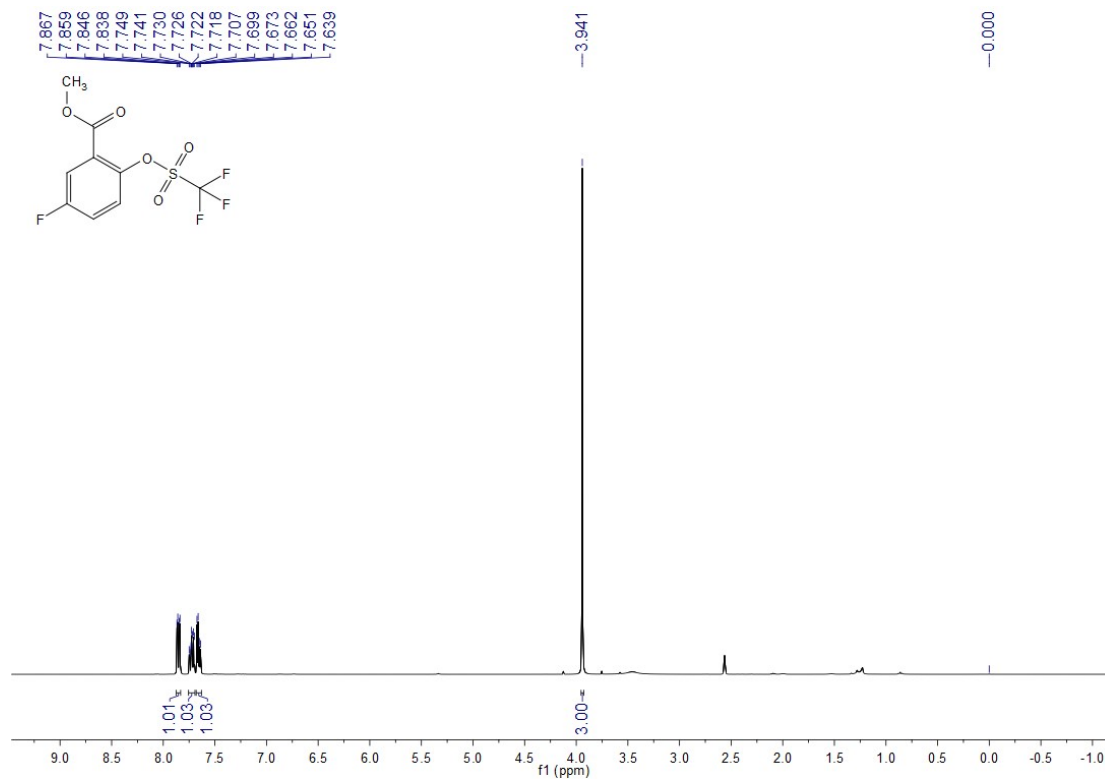
¹H NMR Spectrum of 1j



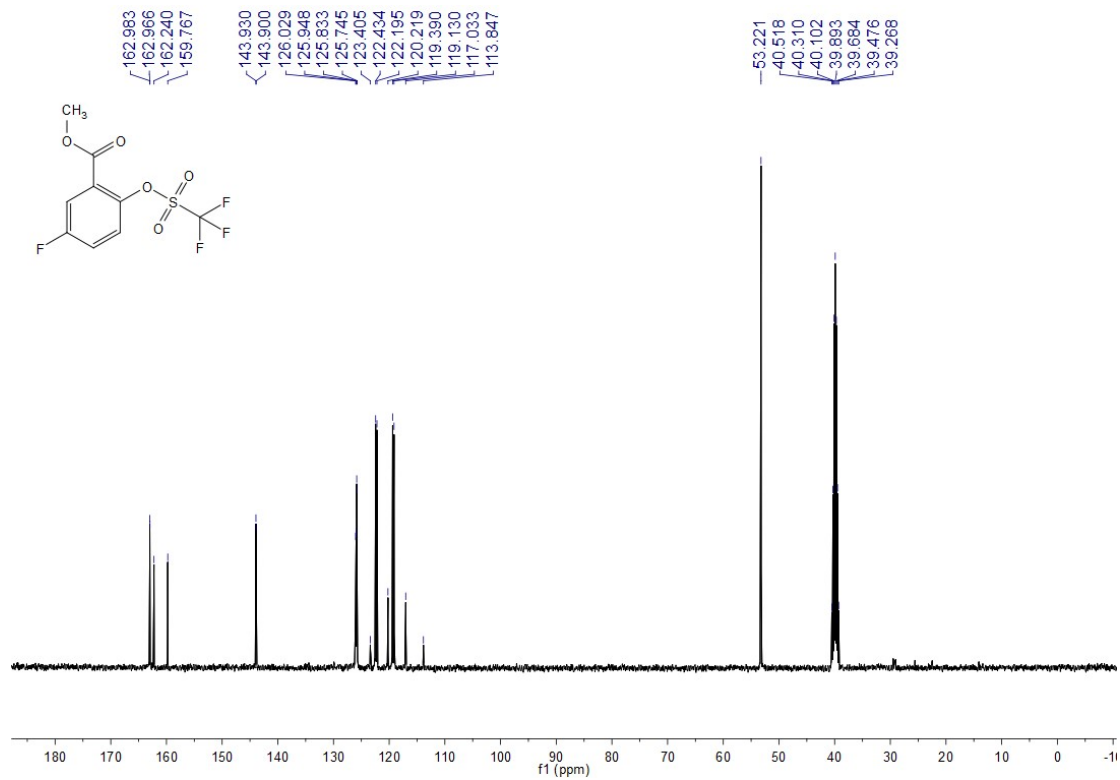
¹³C NMR Spectrum of 1j



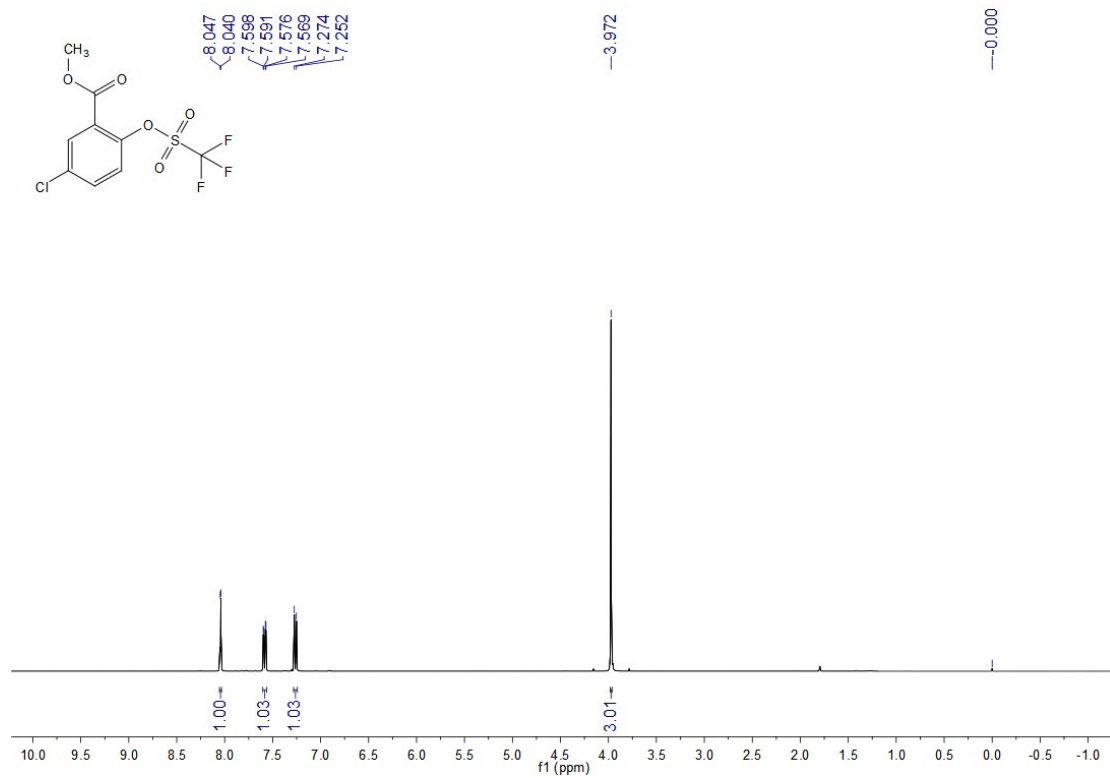
¹H NMR Spectrum of 1k



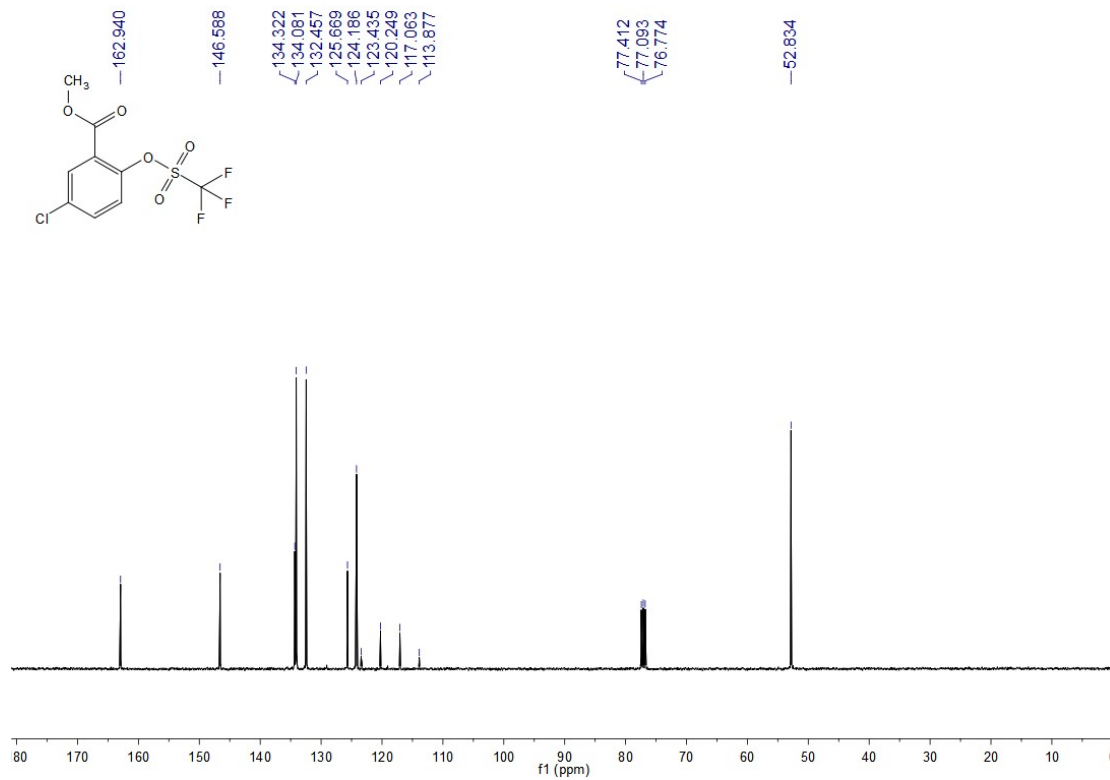
¹³C NMR Spectrum of 1k



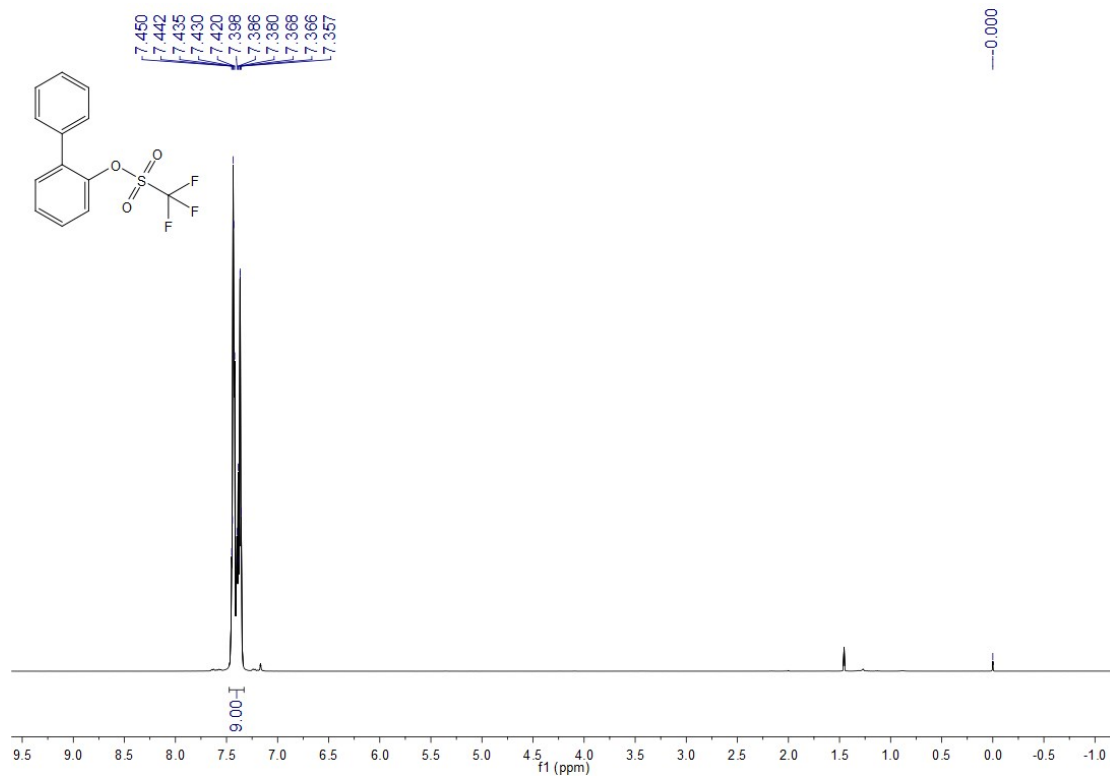
¹H NMR Spectrum of **11**



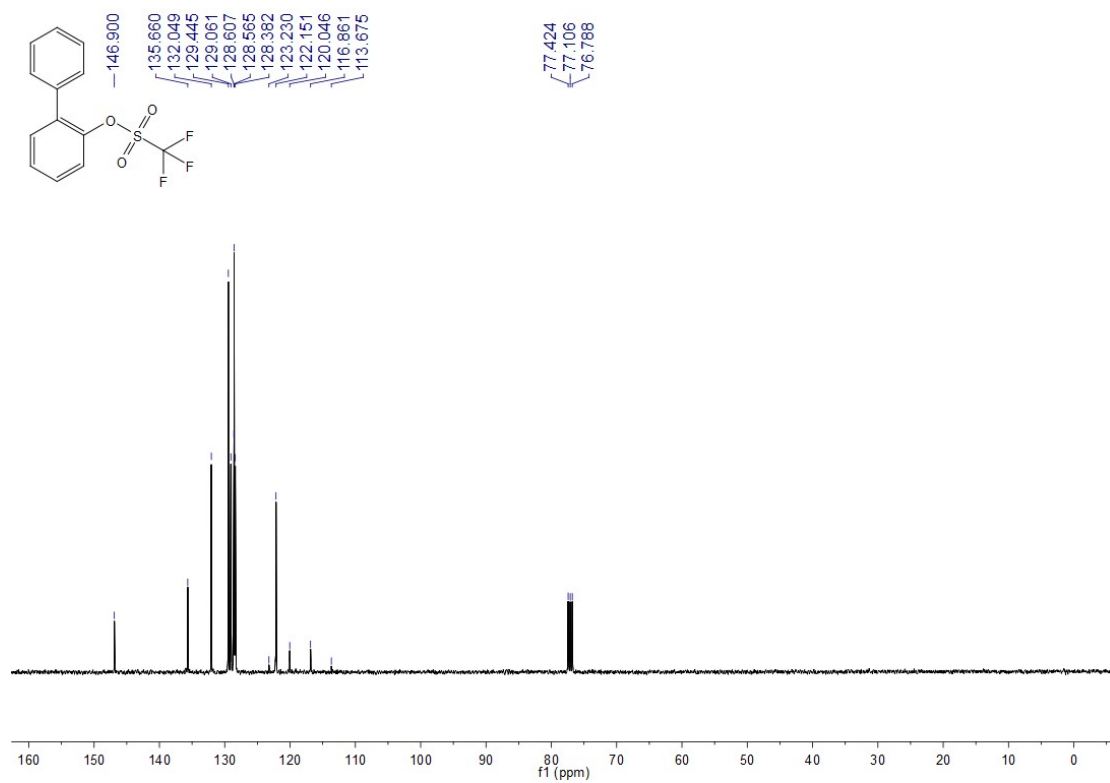
¹³C NMR Spectrum of **11**



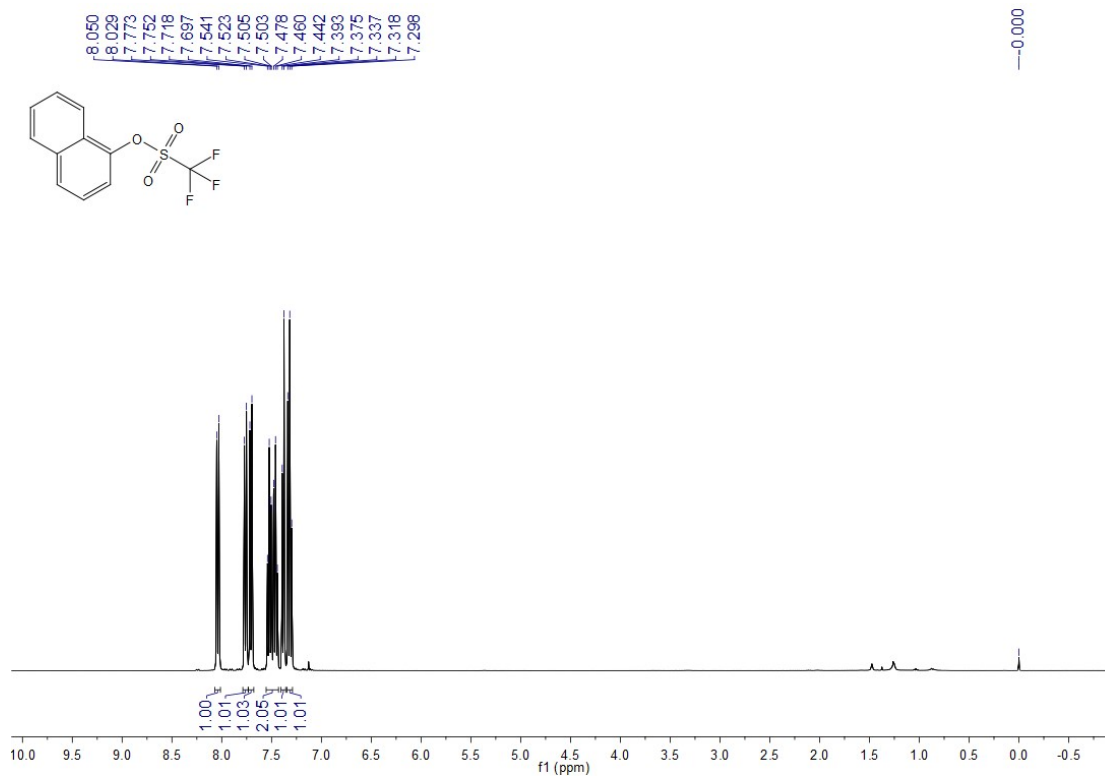
¹H NMR Spectrum of **1m**



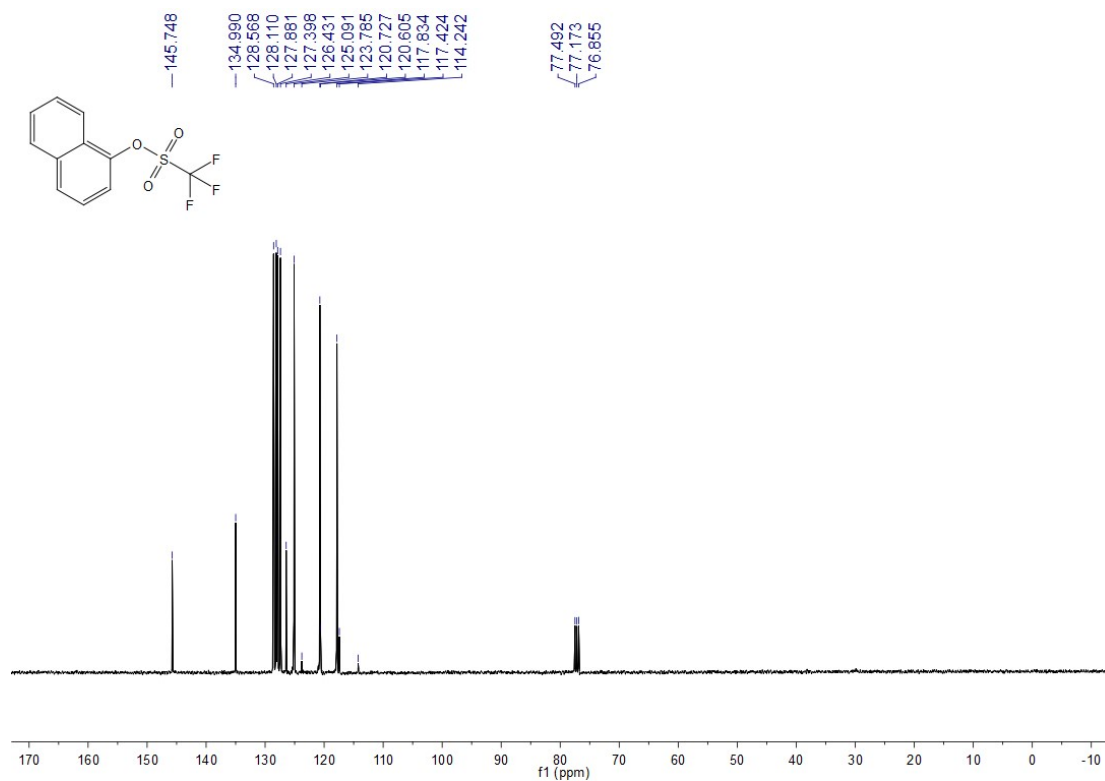
¹³C NMR Spectrum of **1m**



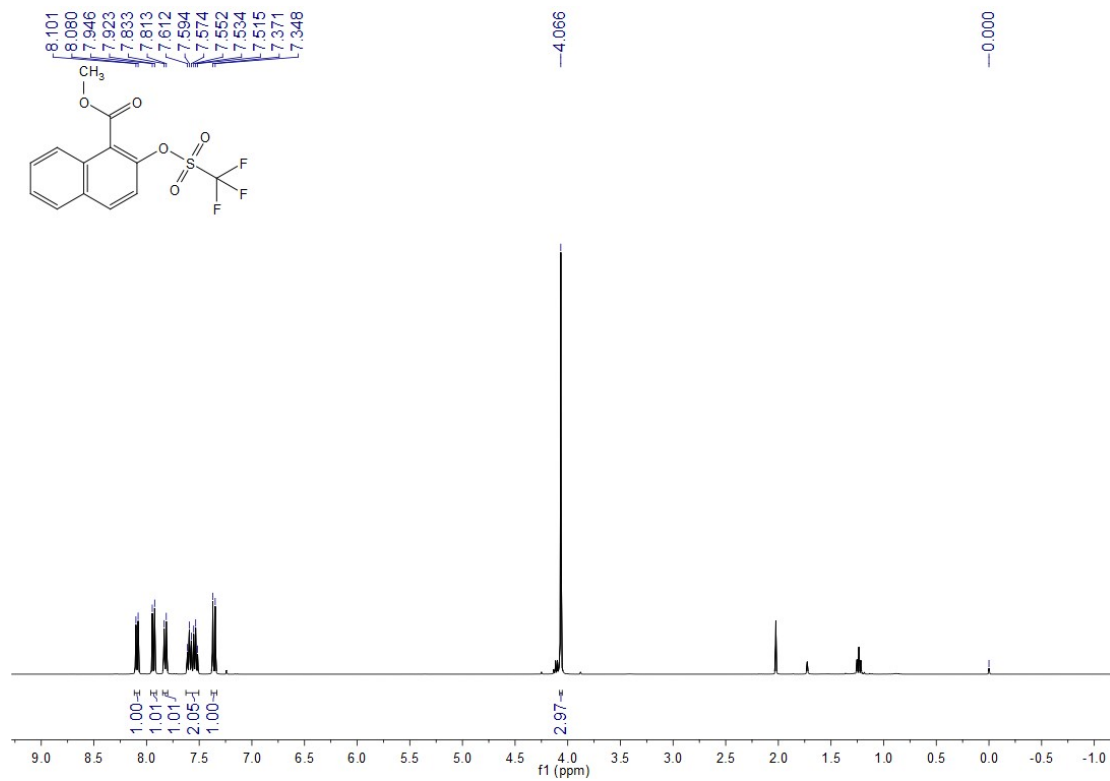
¹H NMR Spectrum of **1n**



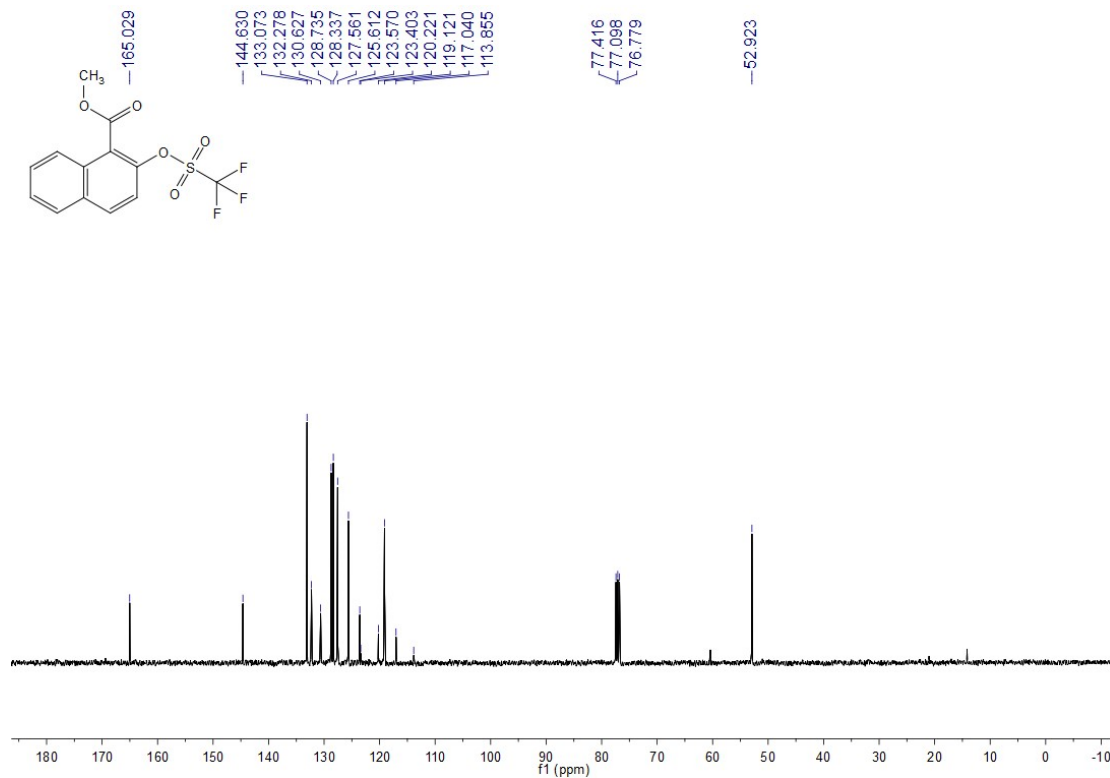
¹³C NMR Spectrum of **1n**



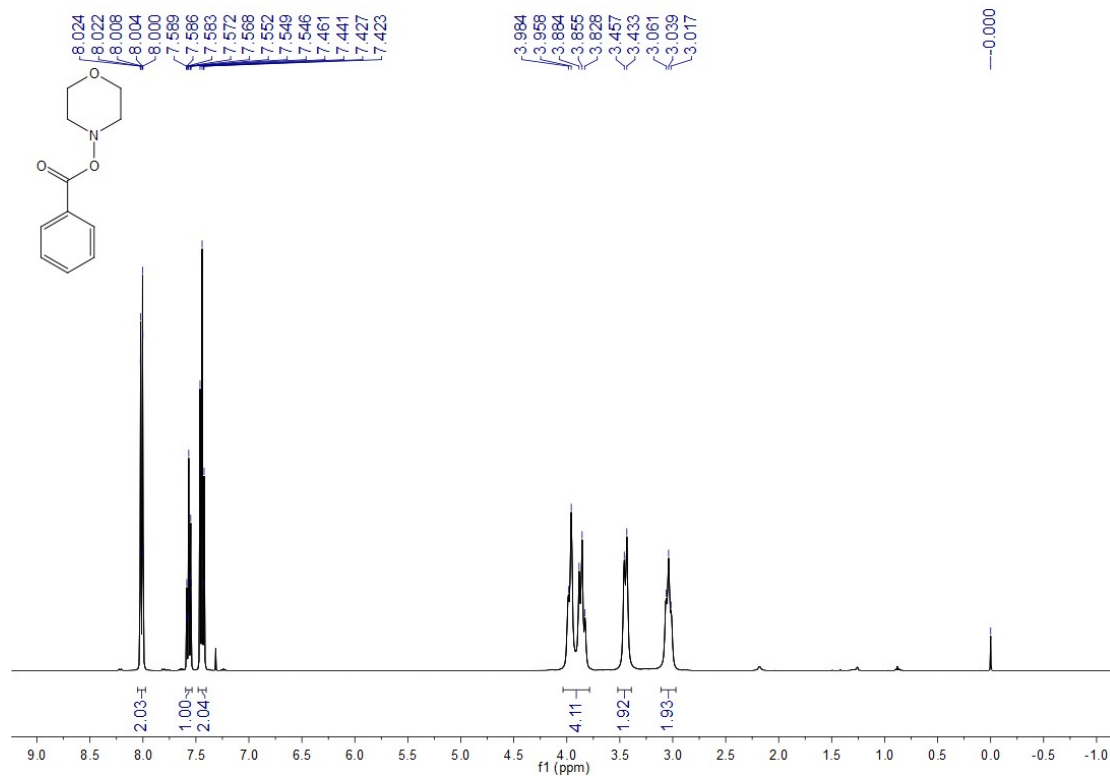
¹H NMR Spectrum of **1o**



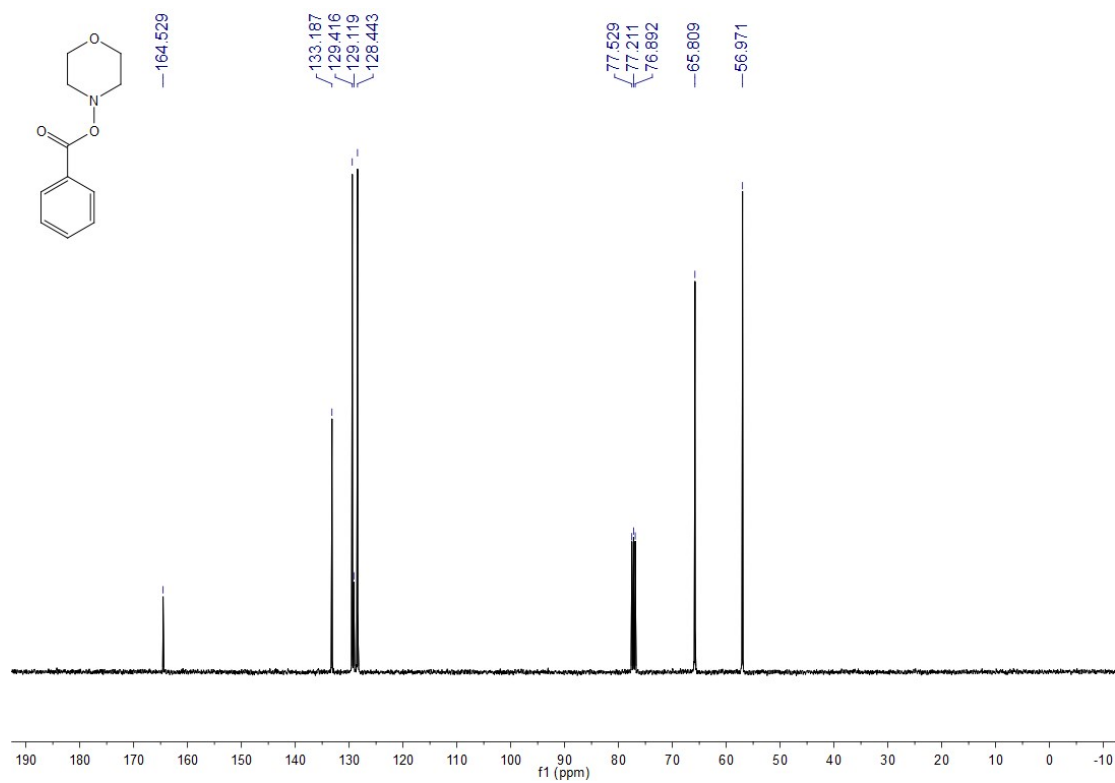
¹³C NMR Spectrum of **1o**



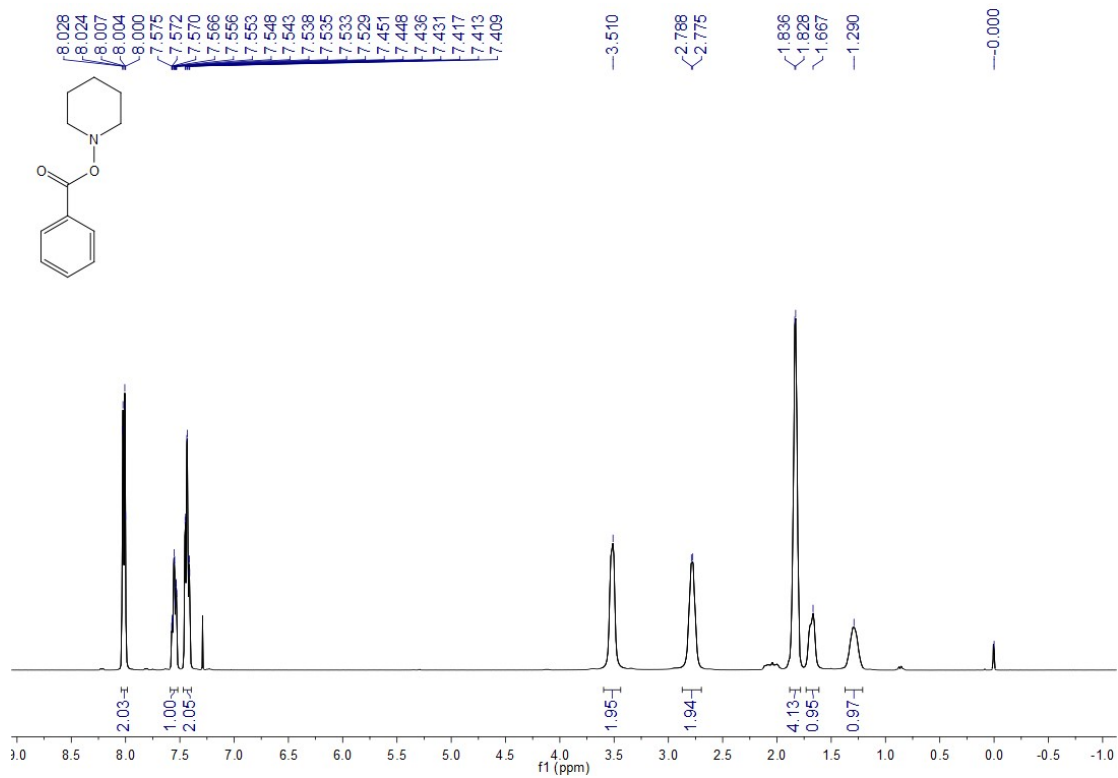
¹H NMR Spectrum of 2a



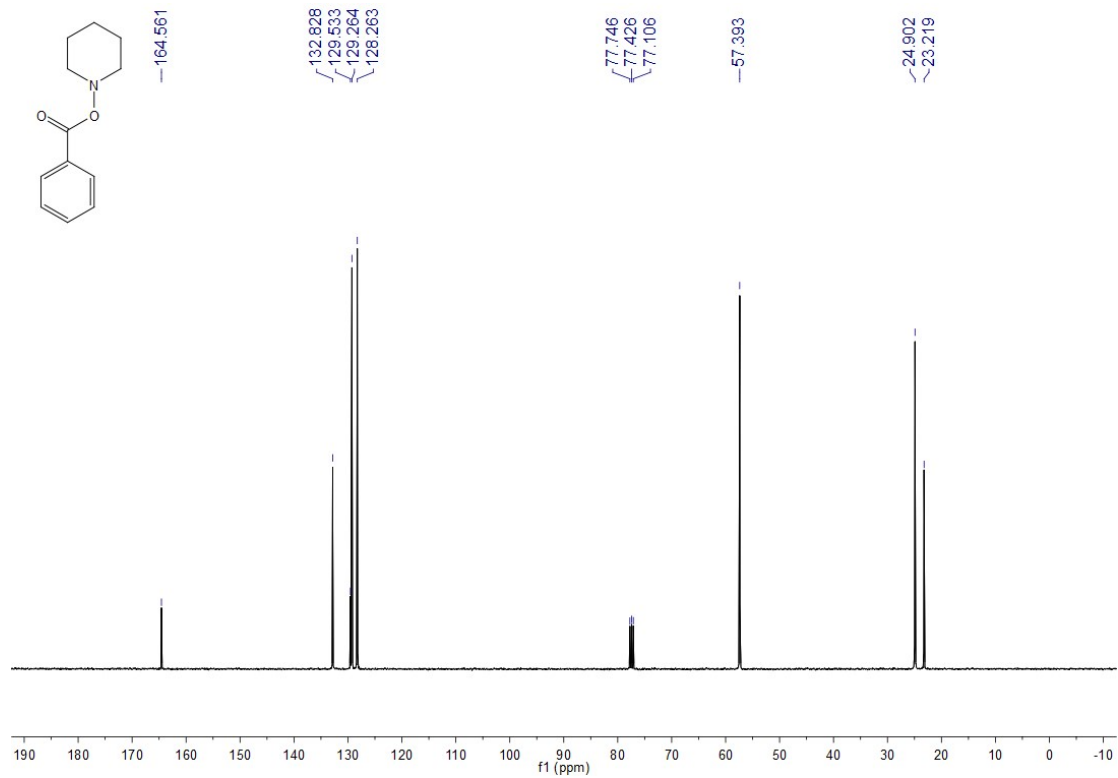
¹³C NMR Spectrum of 2a



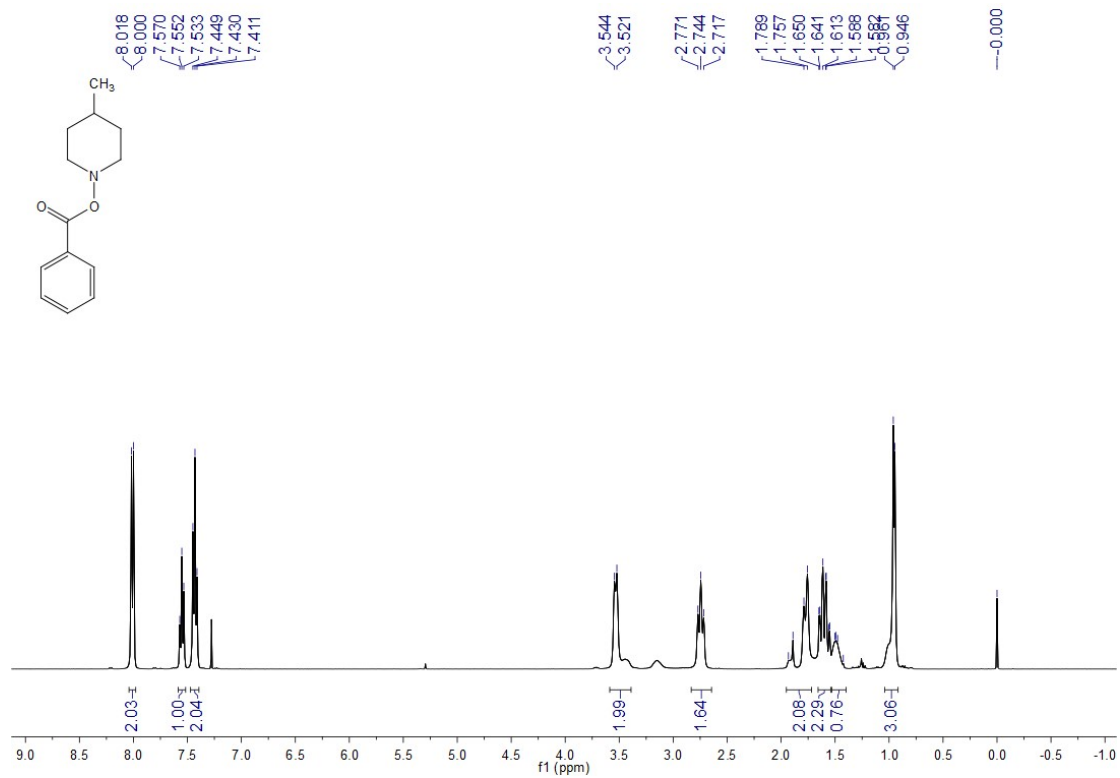
¹H NMR Spectrum of 2b



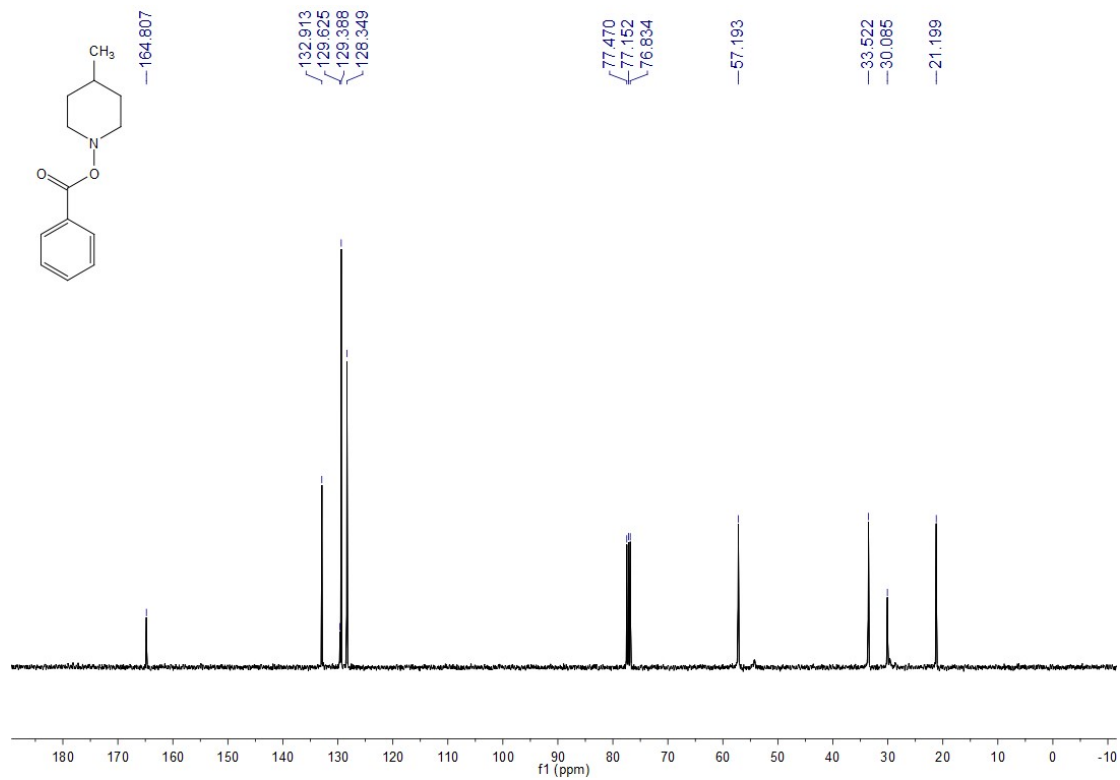
¹³C NMR Spectrum of 2b



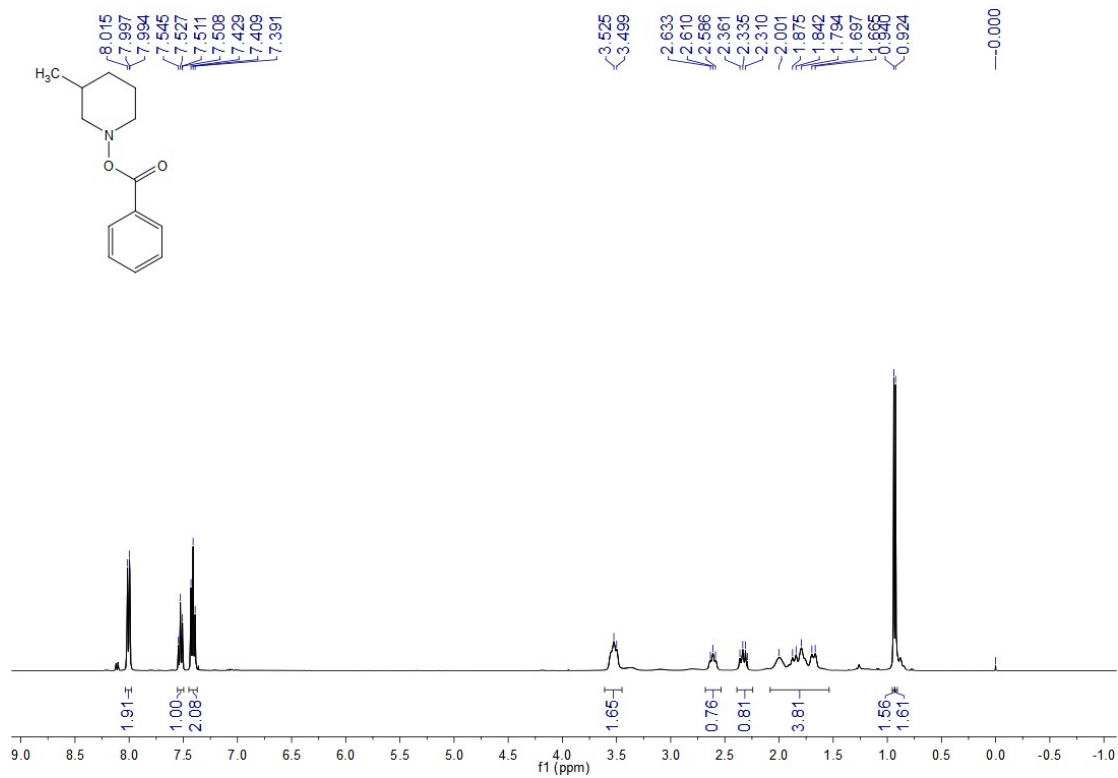
¹H NMR Spectrum of 2c



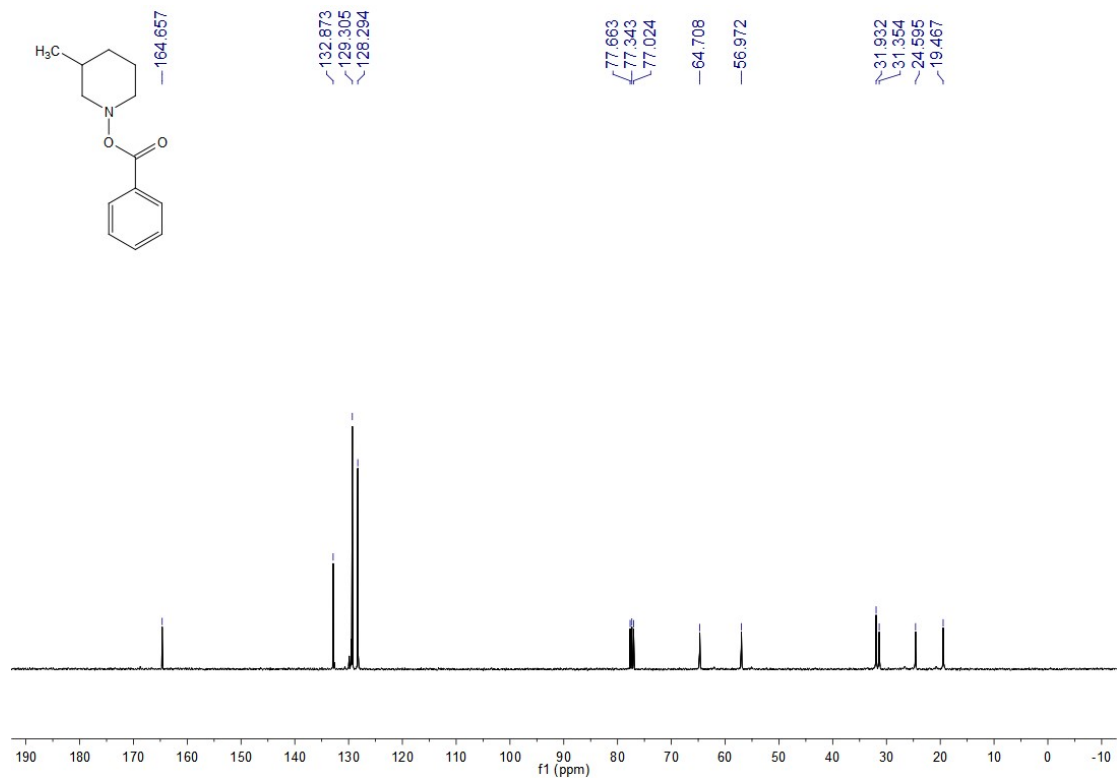
¹³C NMR Spectrum of 2c



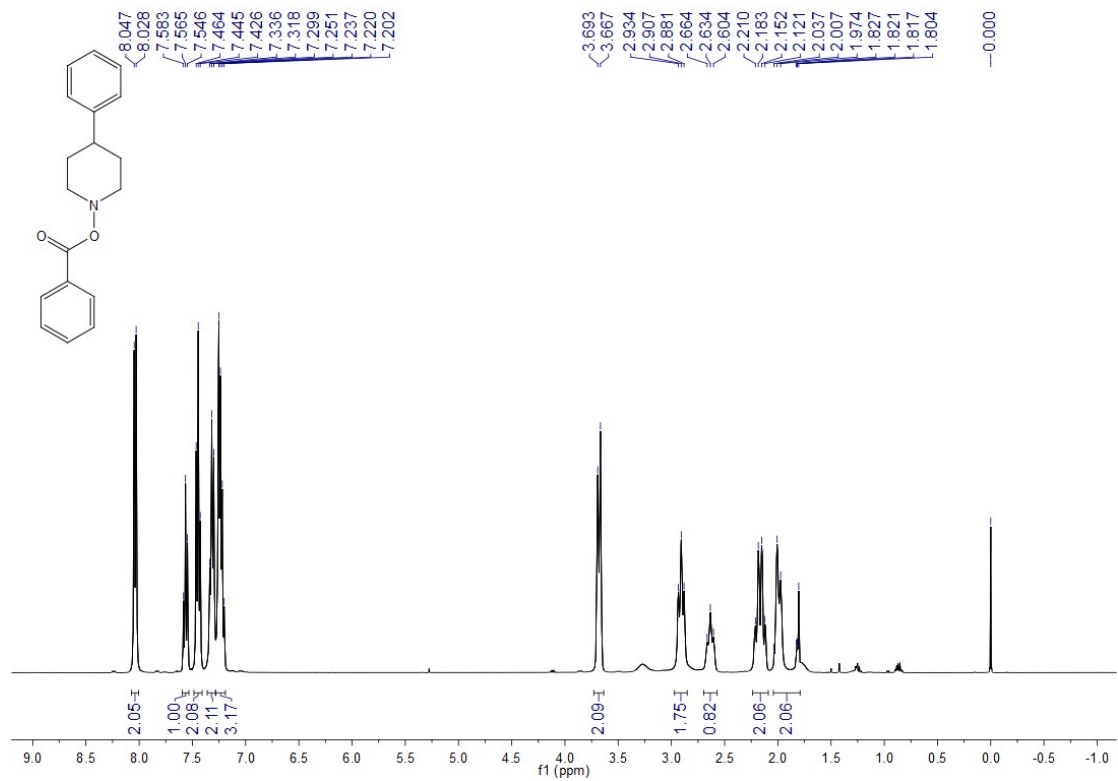
¹H NMR Spectrum of 2d



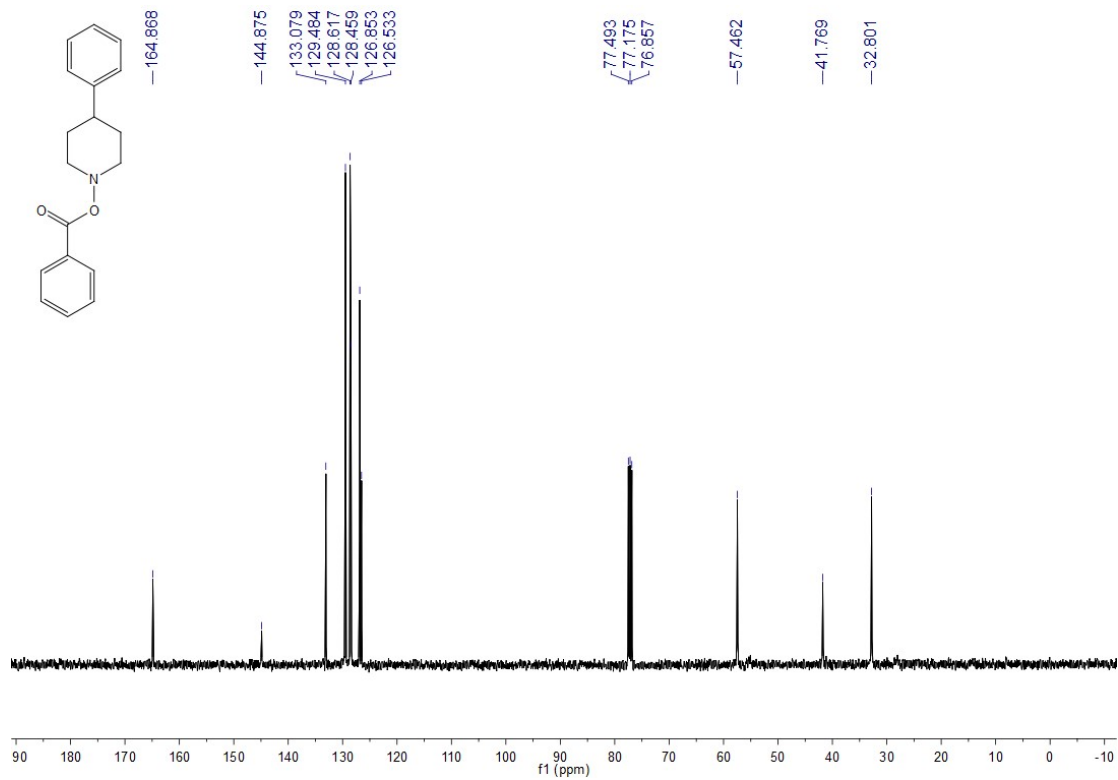
¹³C NMR Spectrum of 2d



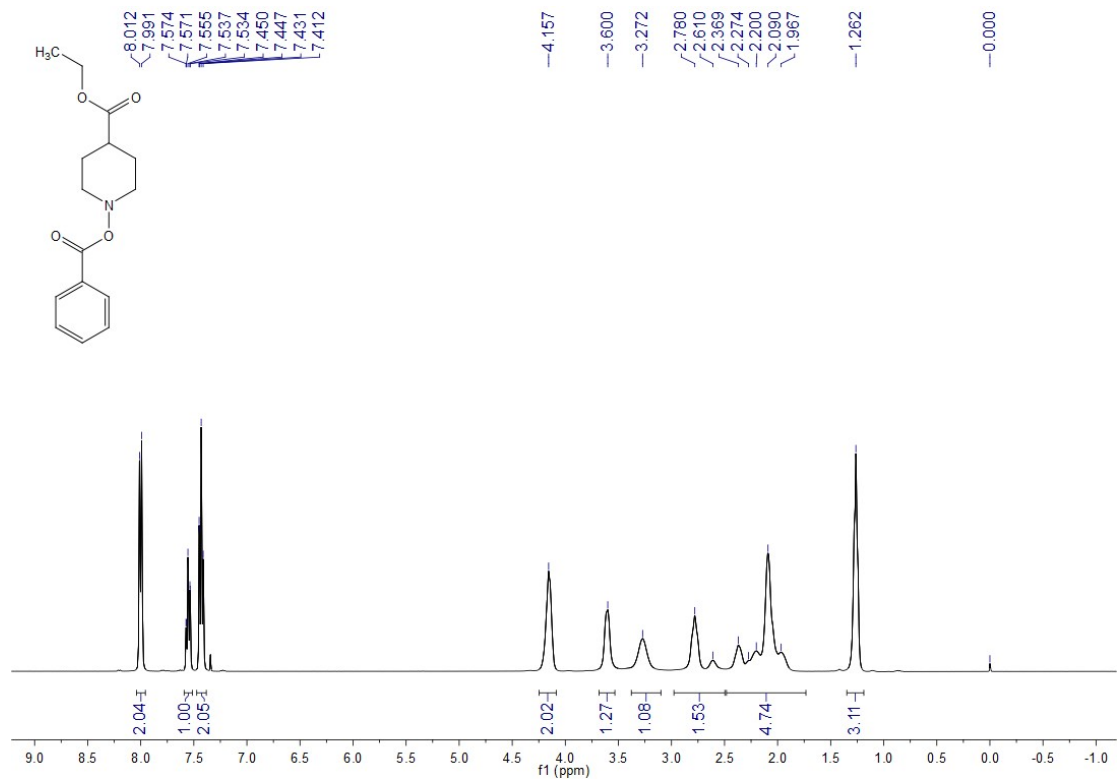
¹H NMR Spectrum of 2e



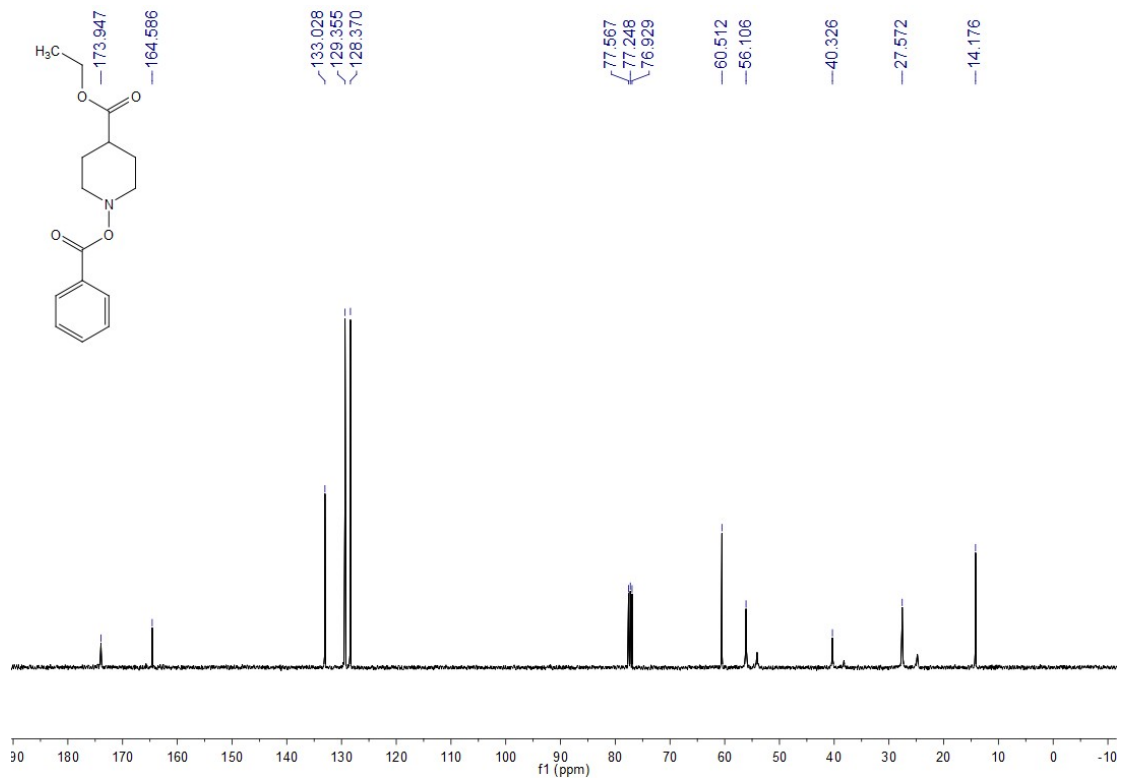
¹³C NMR Spectrum of 2e



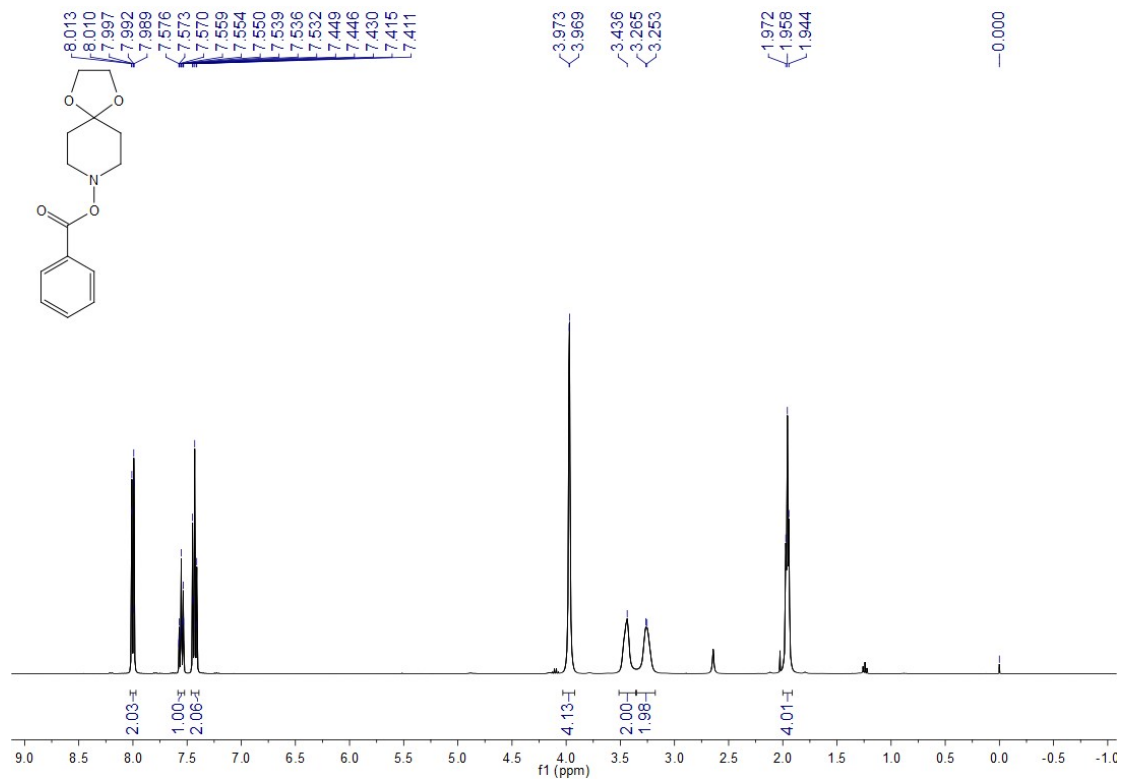
¹H NMR Spectrum of 2f



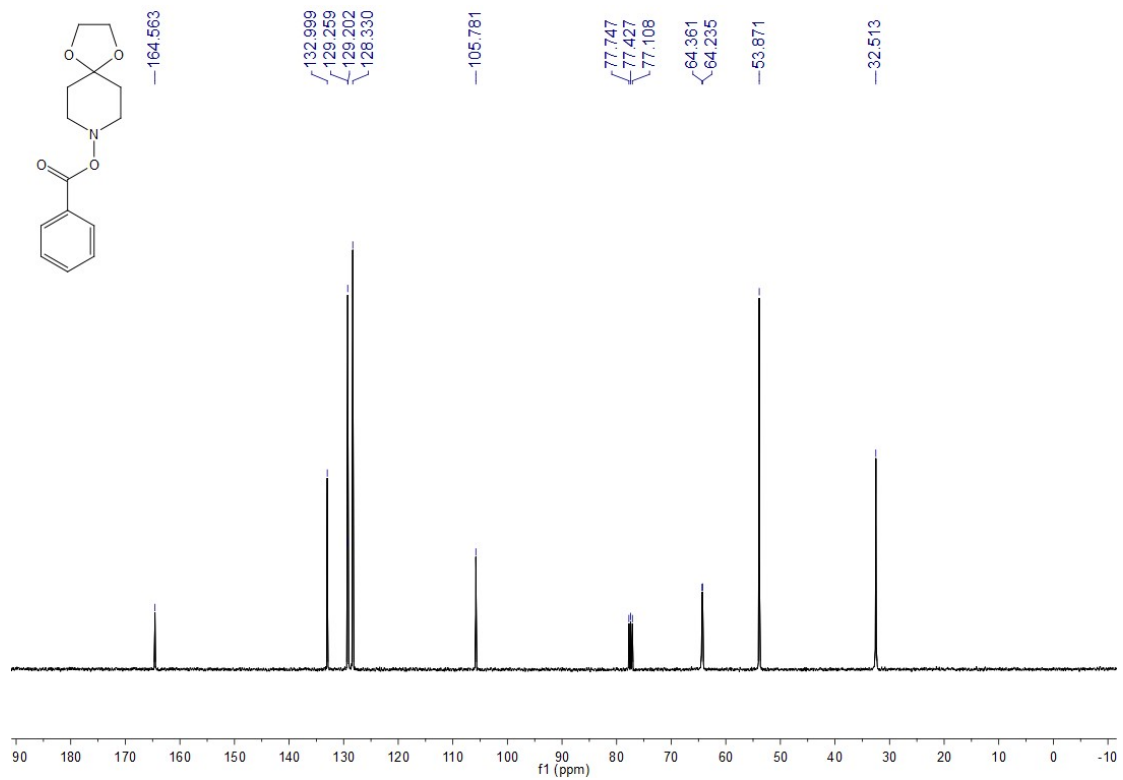
¹³C NMR Spectrum of 2f



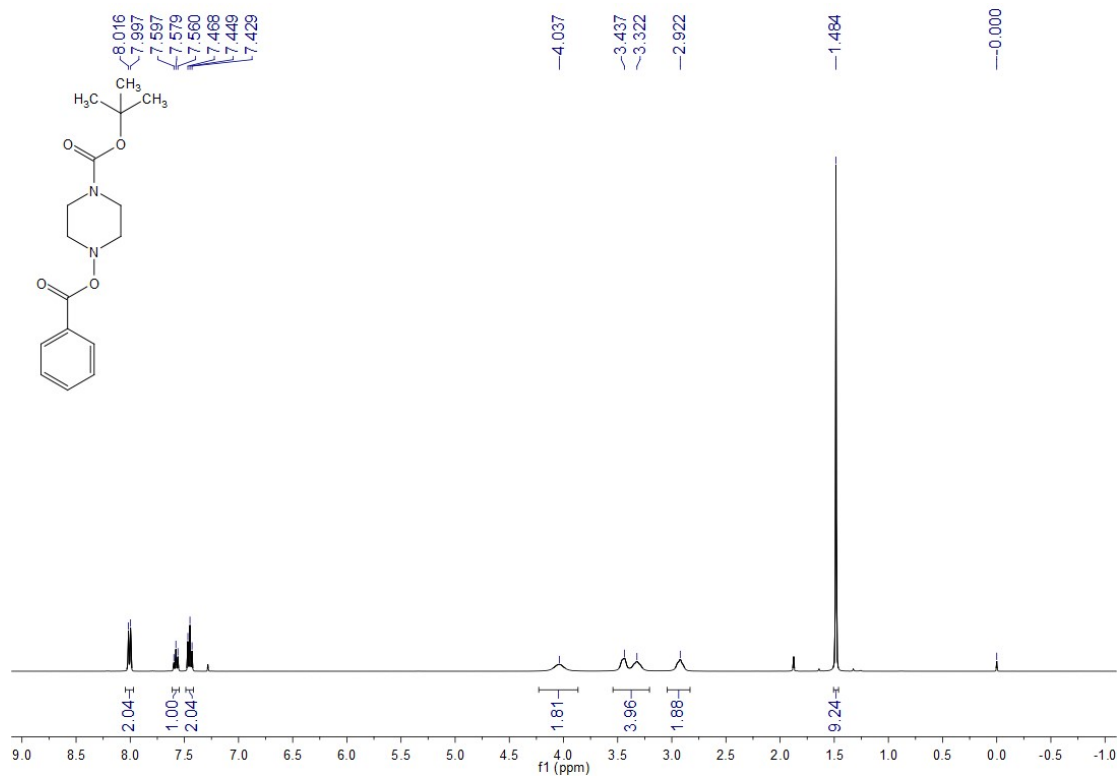
¹H NMR Spectrum of 2g



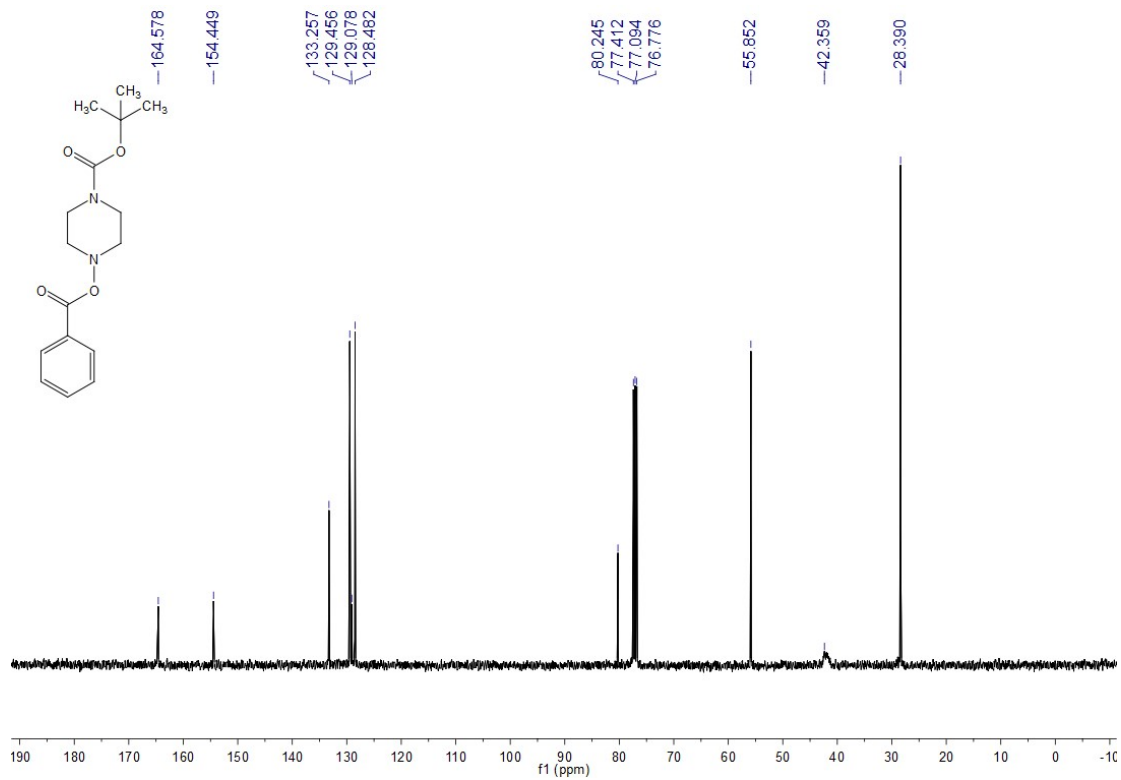
¹³C NMR Spectrum of 2g



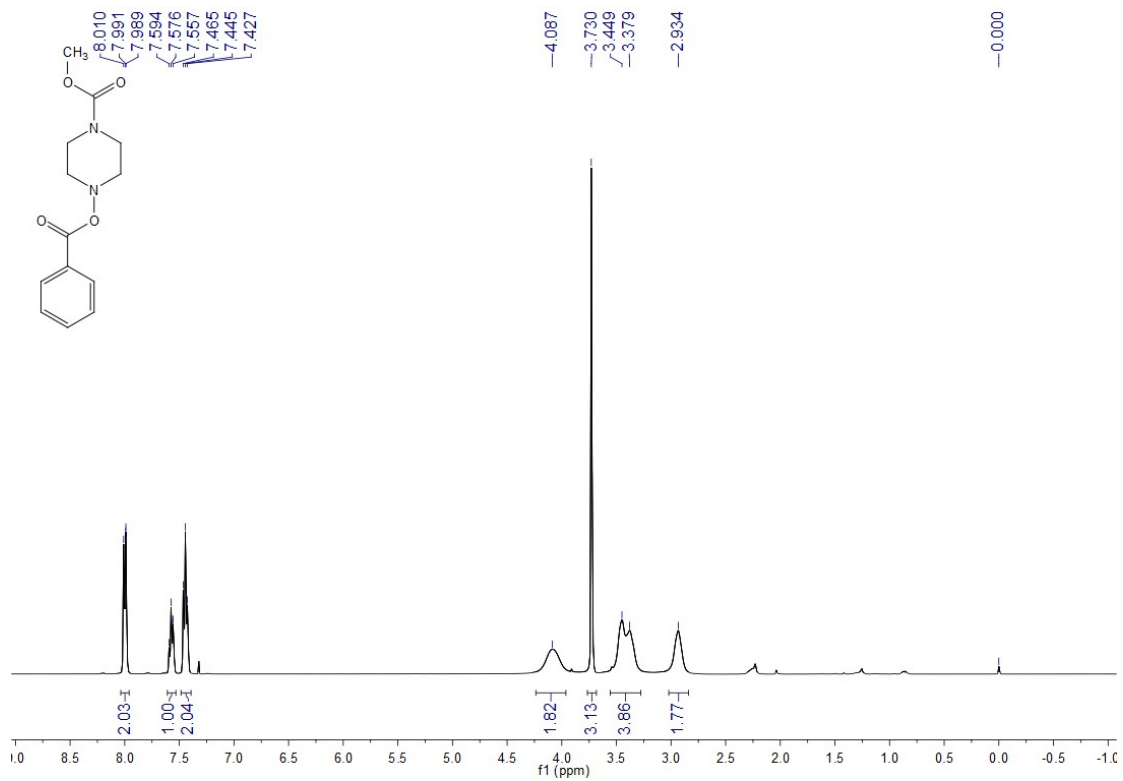
¹H NMR Spectrum of 2h



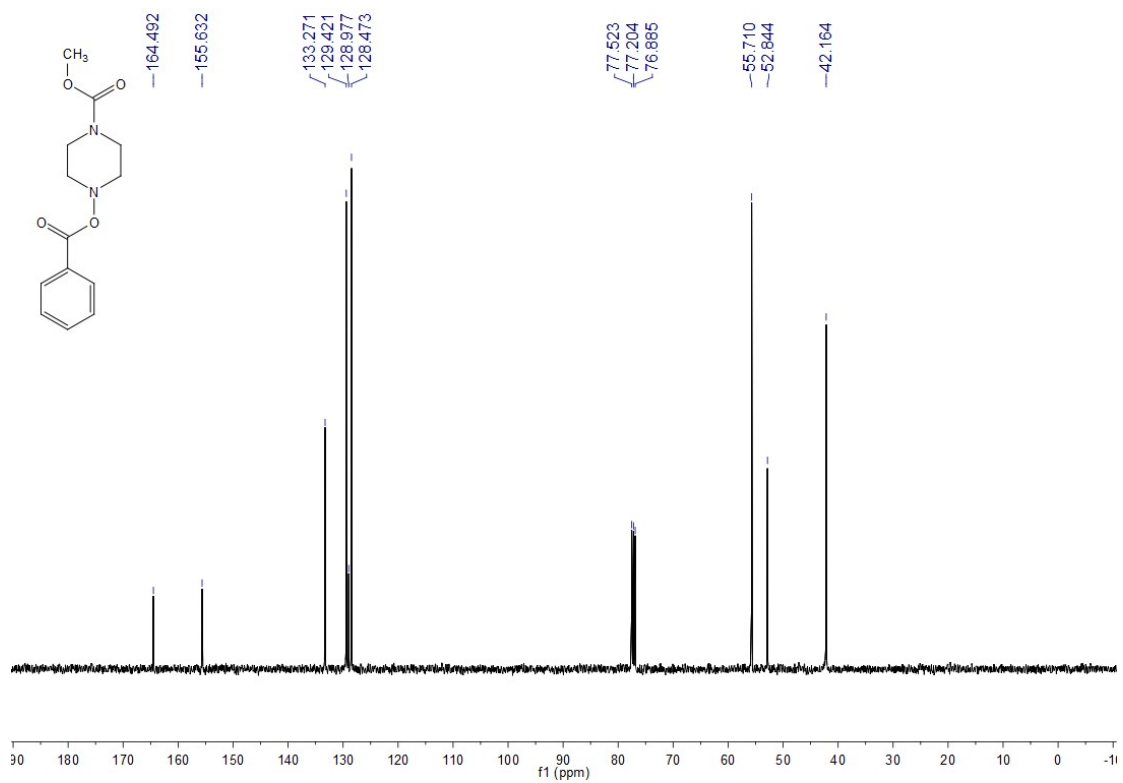
¹³C NMR Spectrum of 2h



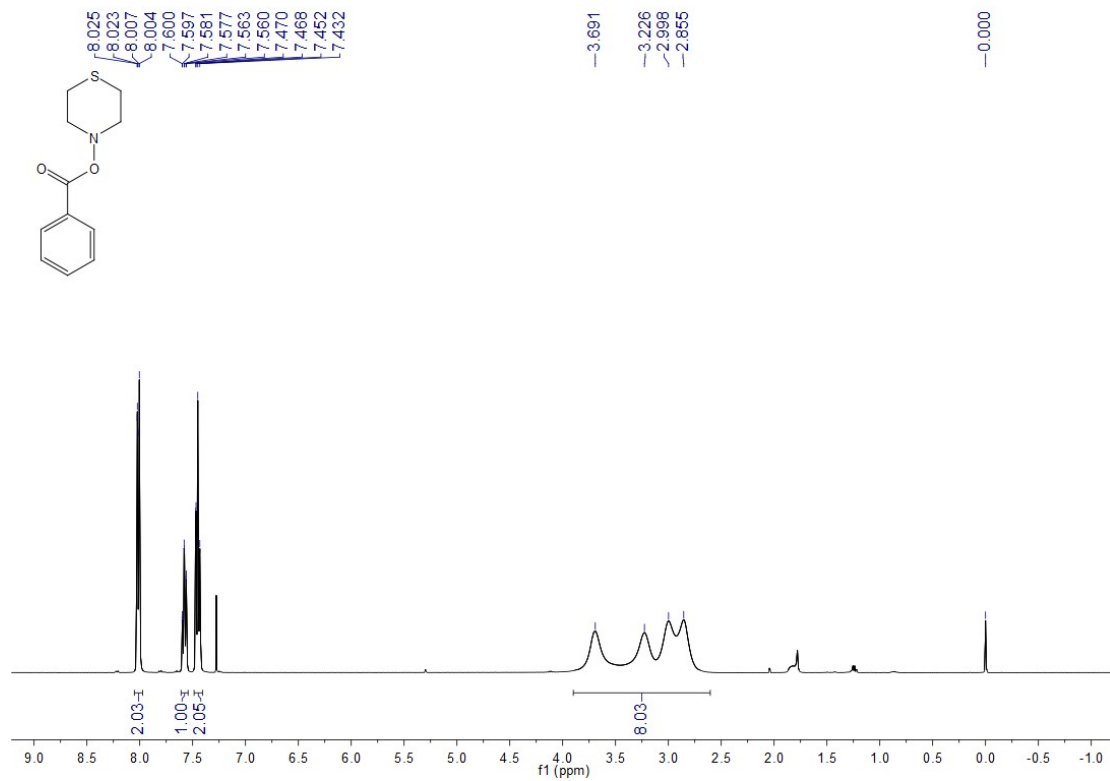
¹H NMR Spectrum of 2i



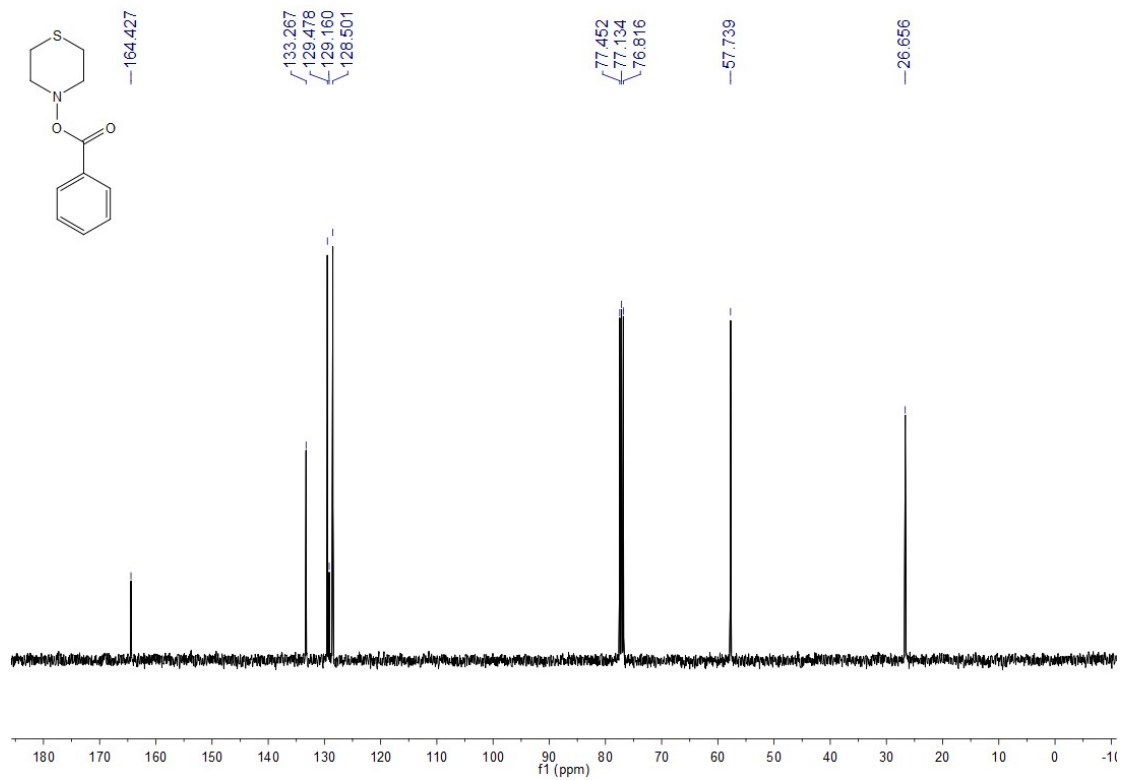
¹³C NMR Spectrum of 2i



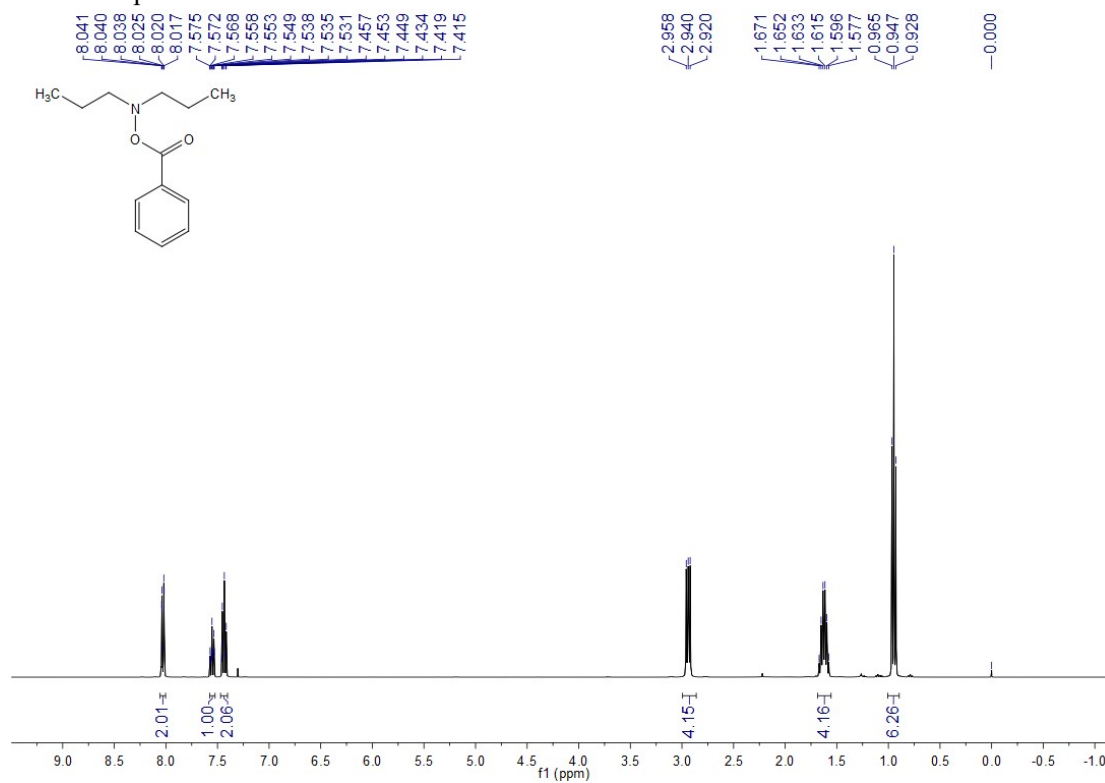
¹H NMR Spectrum of 2j



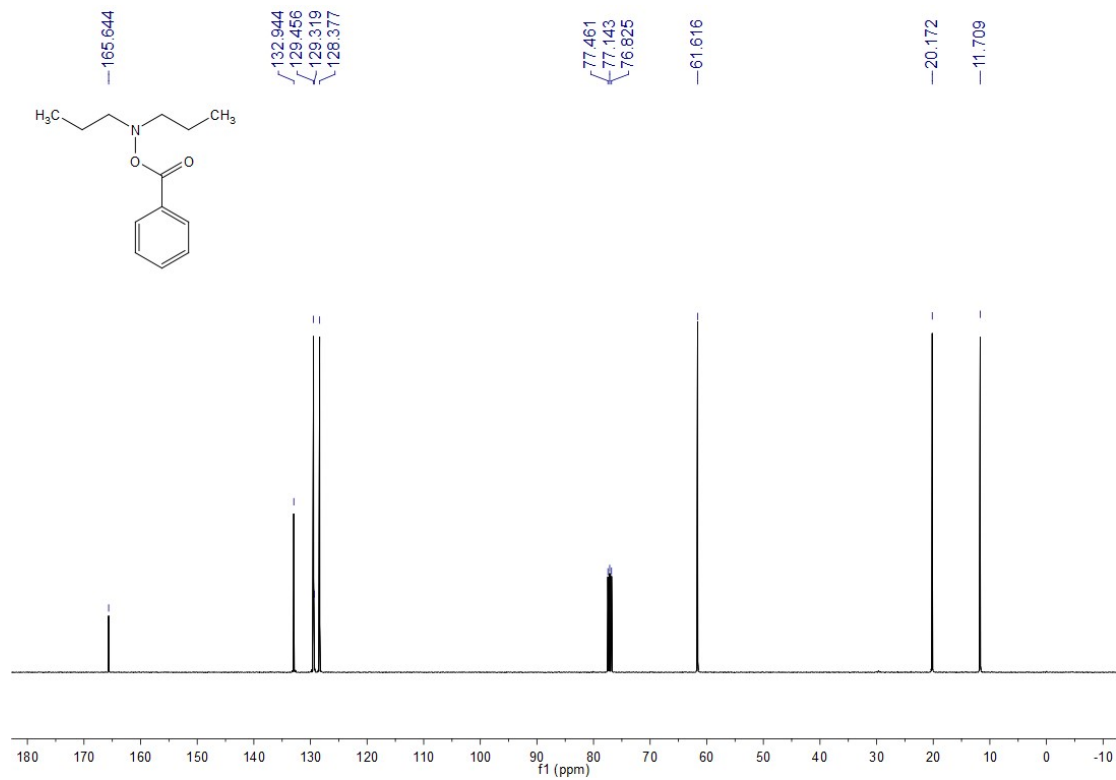
¹³C NMR Spectrum of 2j



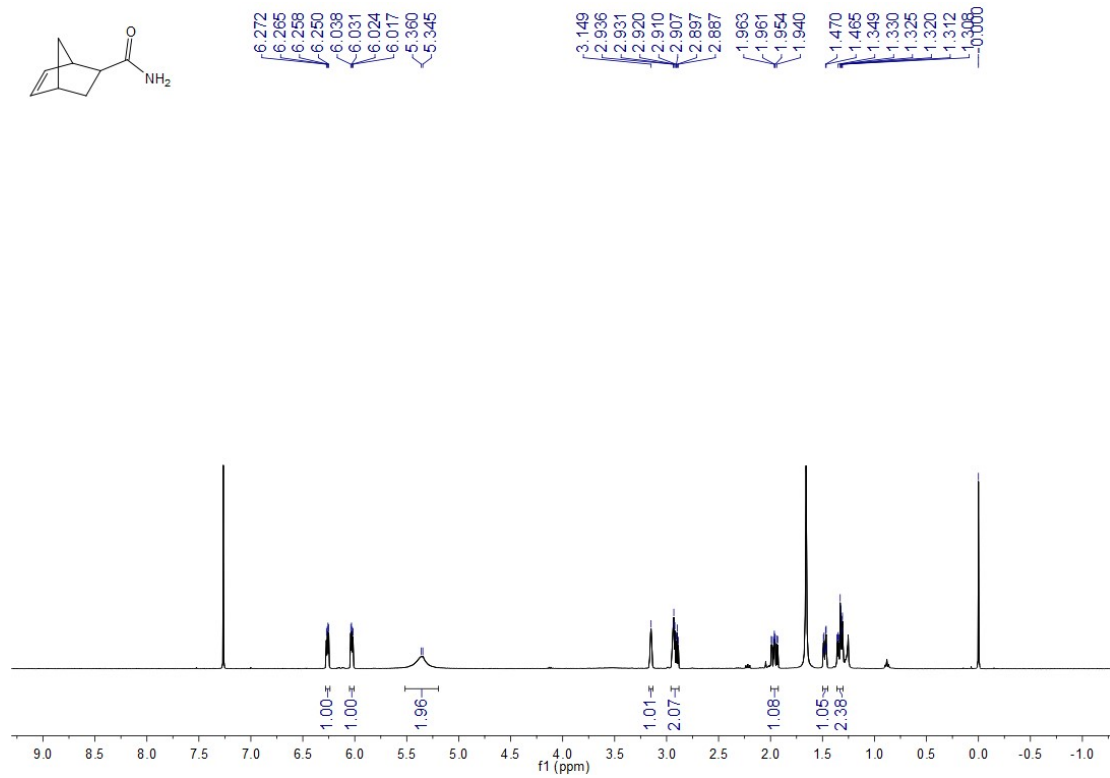
¹H NMR Spectrum of 2k



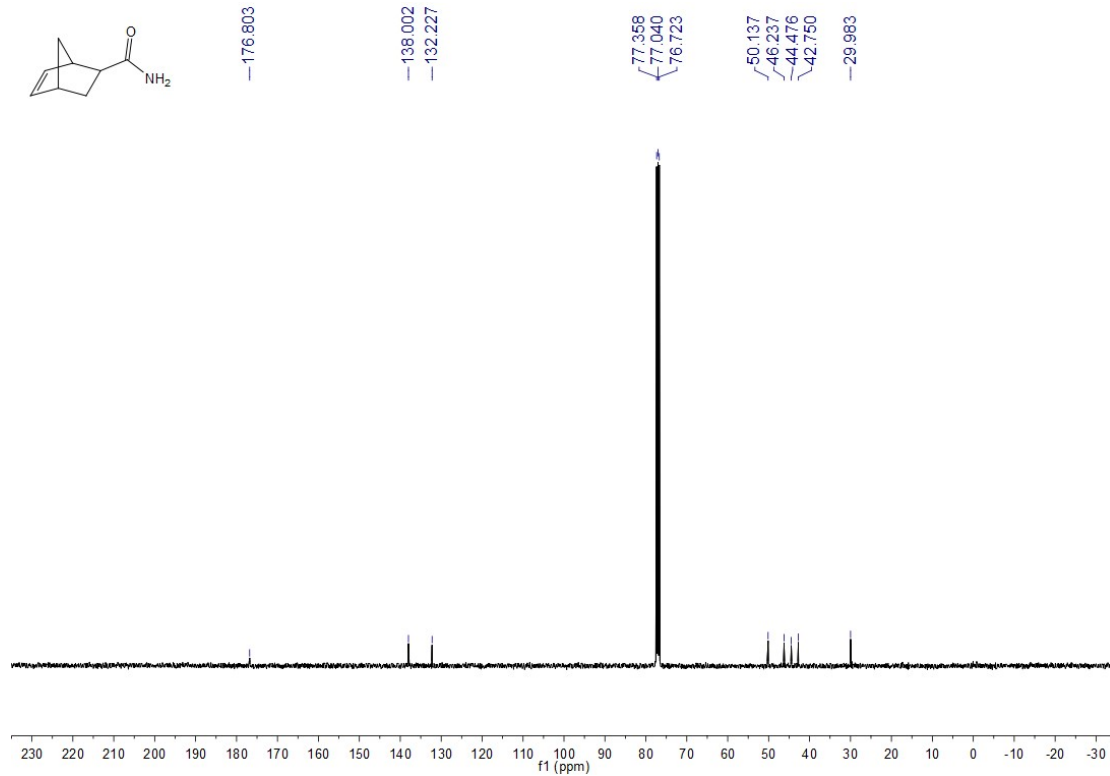
¹³C NMR Spectrum of 2k



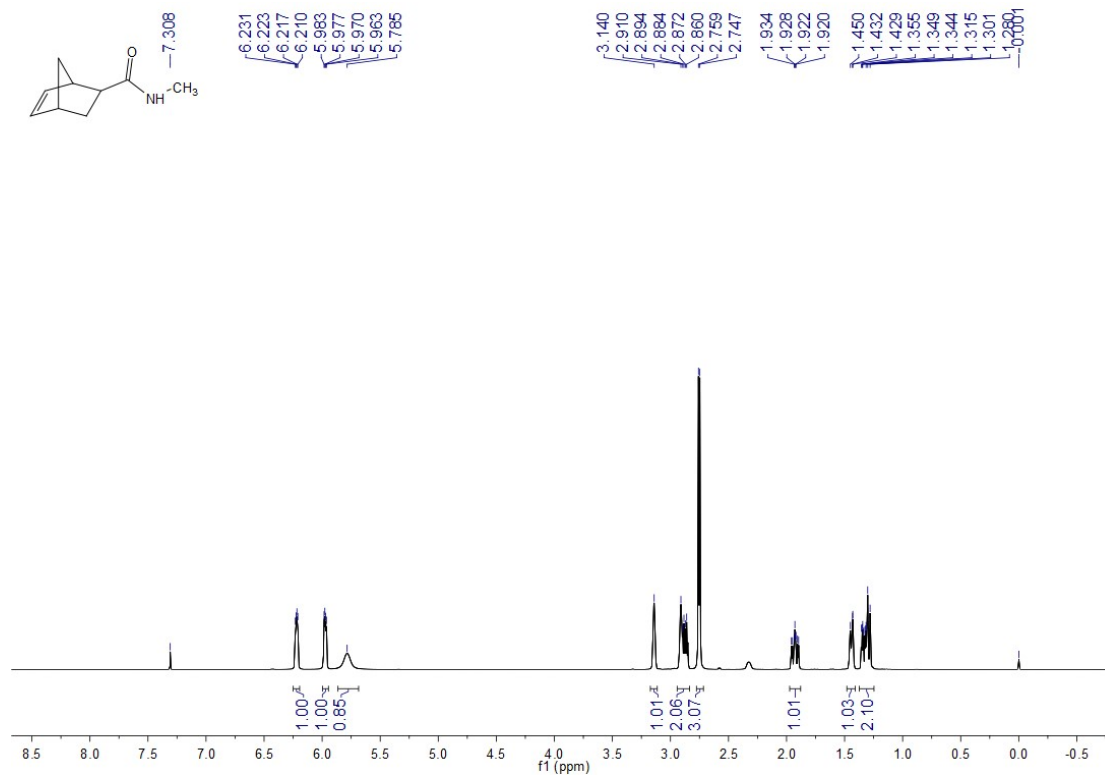
¹H NMR Spectrum of N⁷



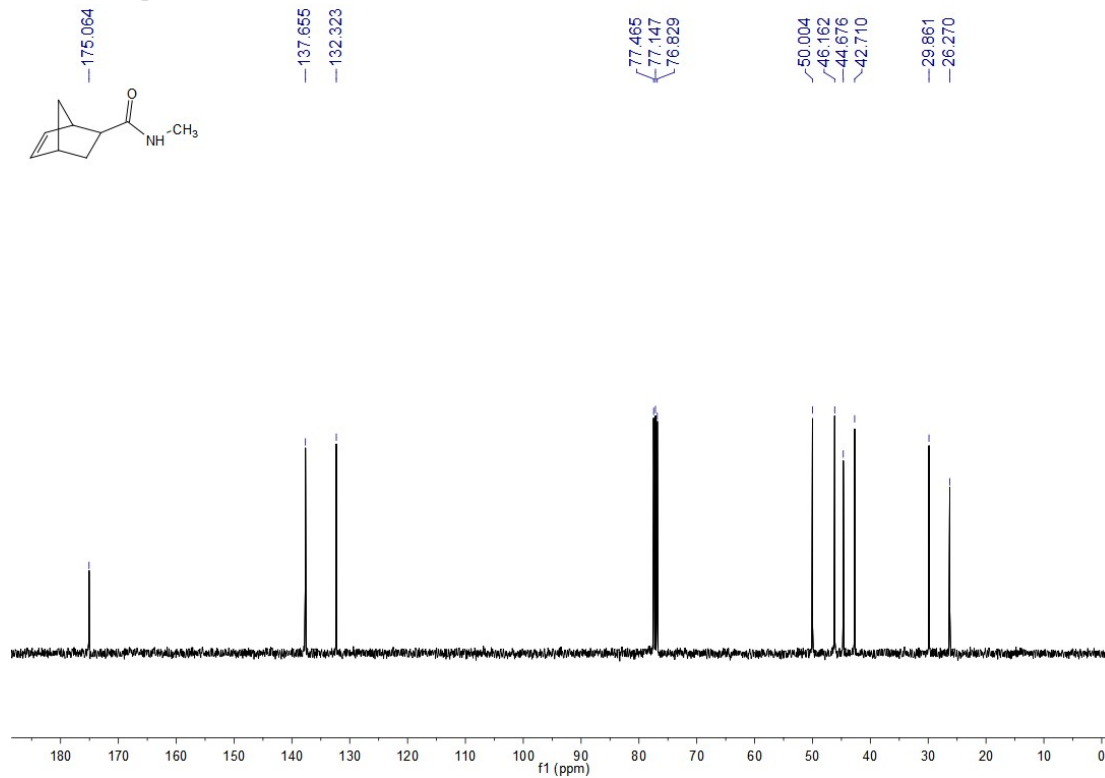
¹³C NMR Spectrum of N⁷



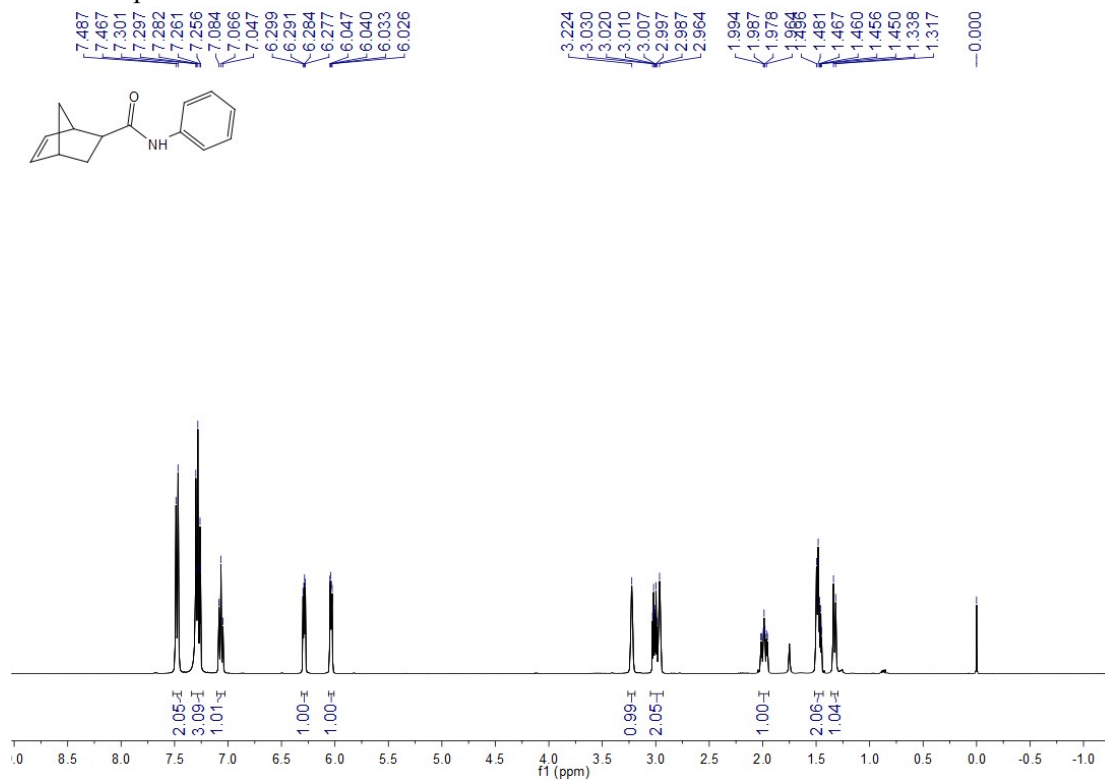
¹H NMR Spectrum of N⁸



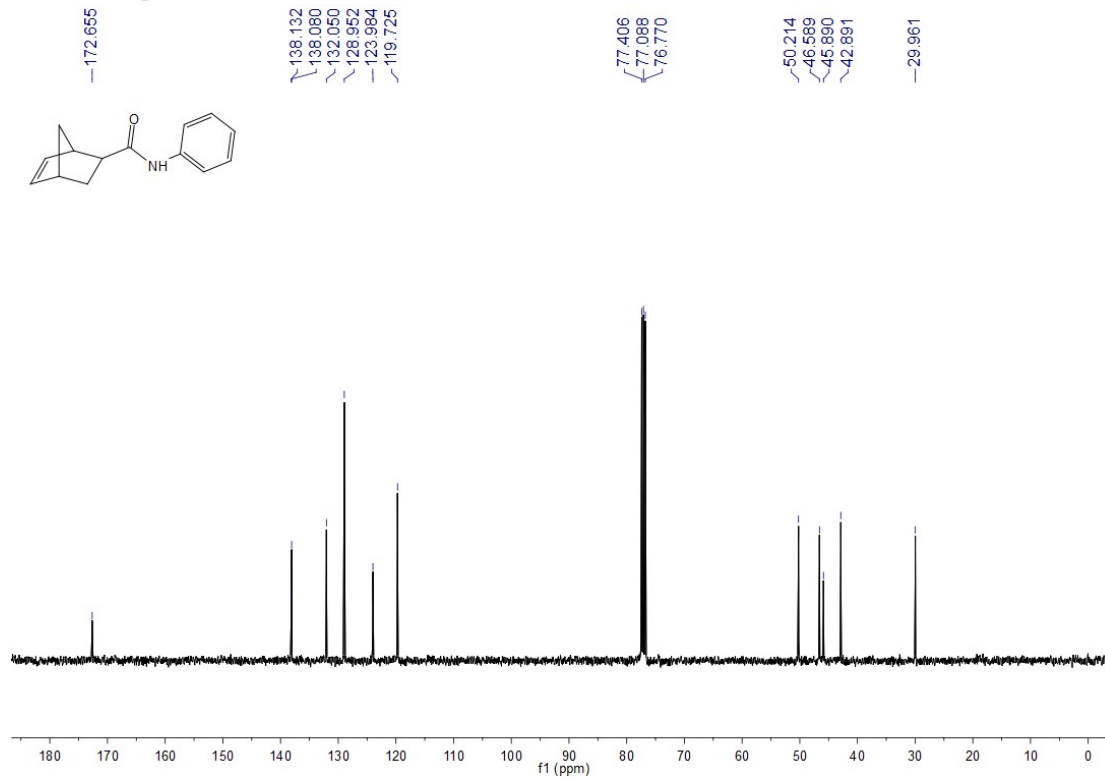
¹³C NMR Spectrum of N⁸



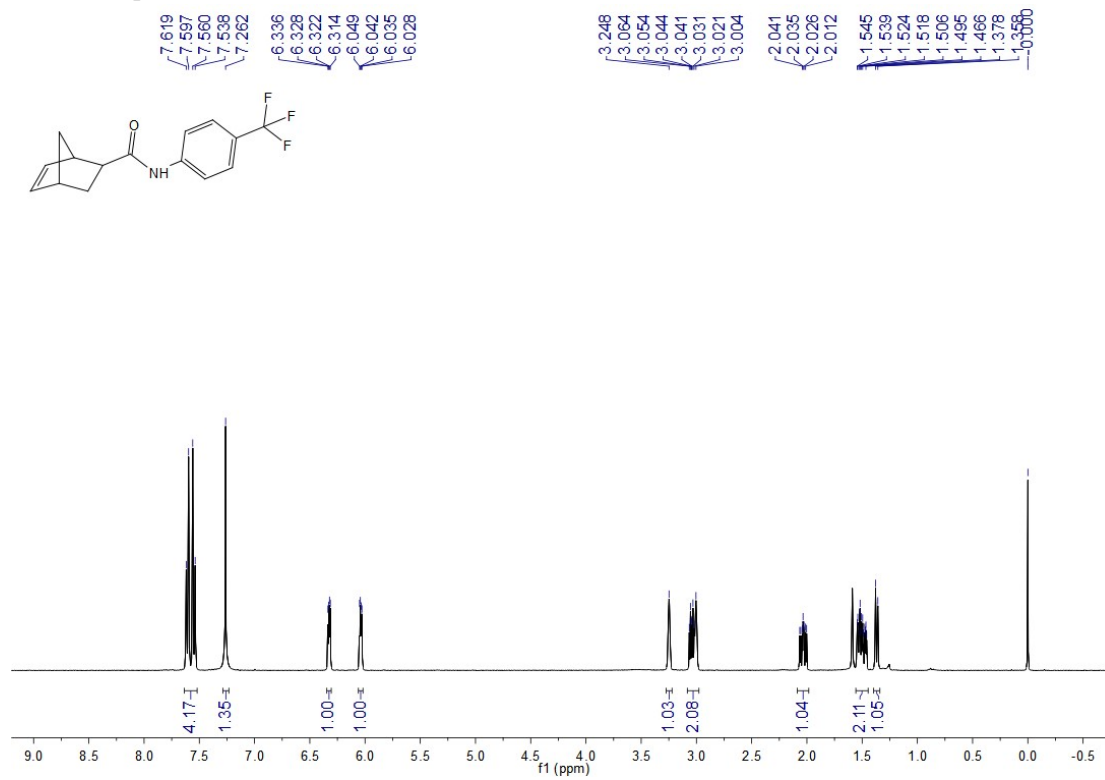
¹H NMR Spectrum of N⁹



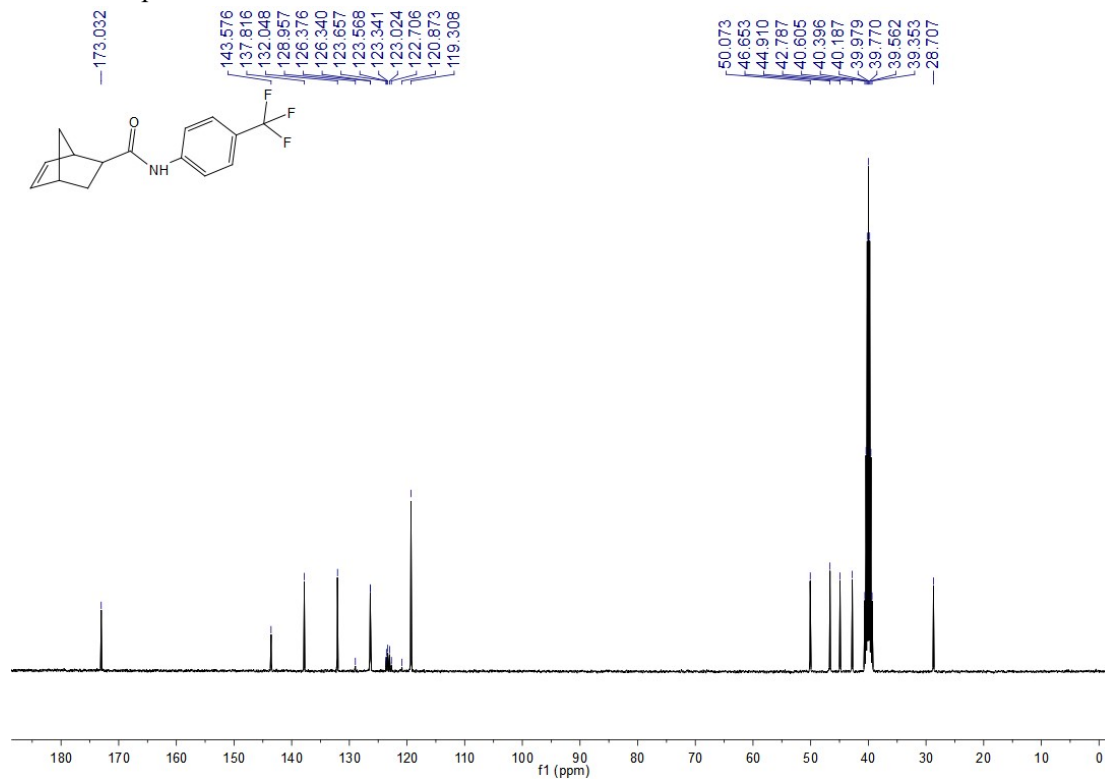
¹³C NMR Spectrum of N⁹



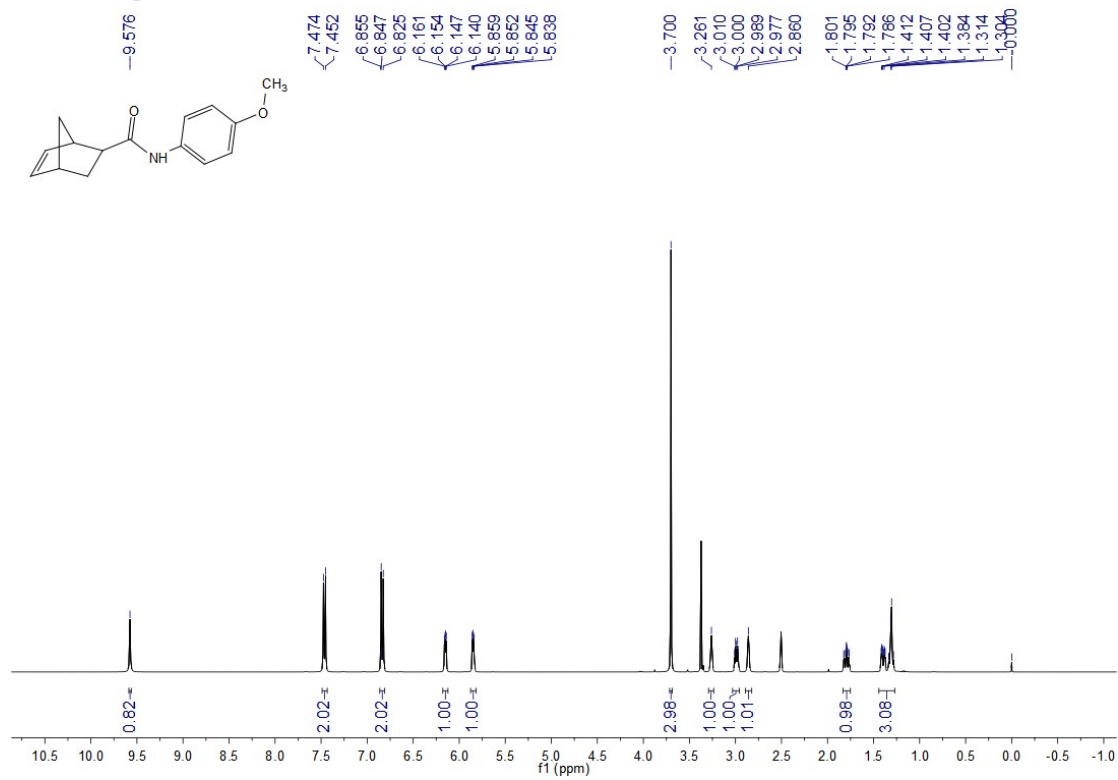
¹H NMR Spectrum of N¹⁰



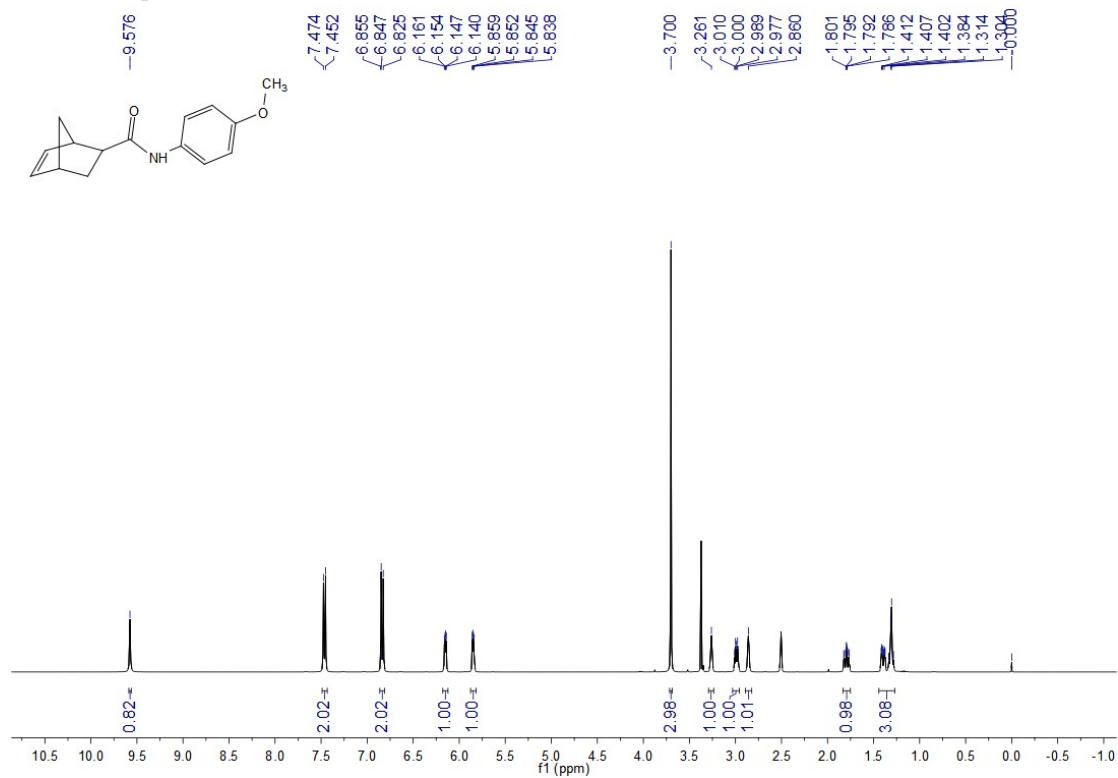
¹³C NMR Spectrum of N¹⁰



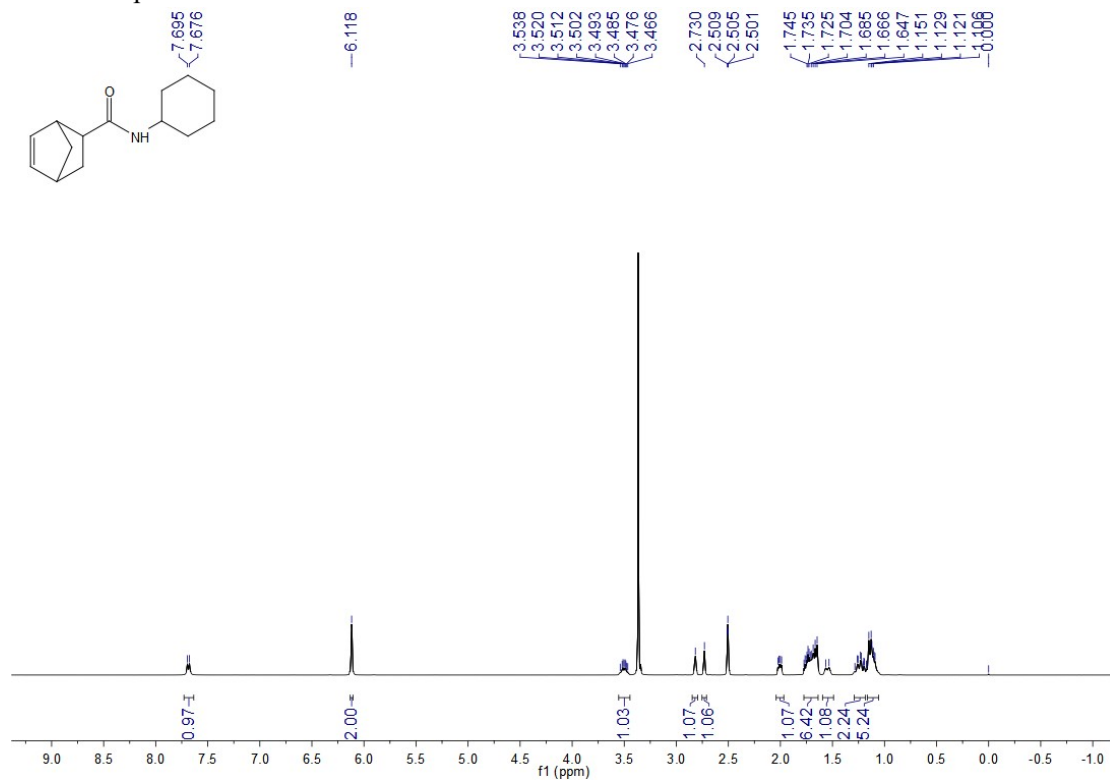
¹H NMR Spectrum of N¹¹



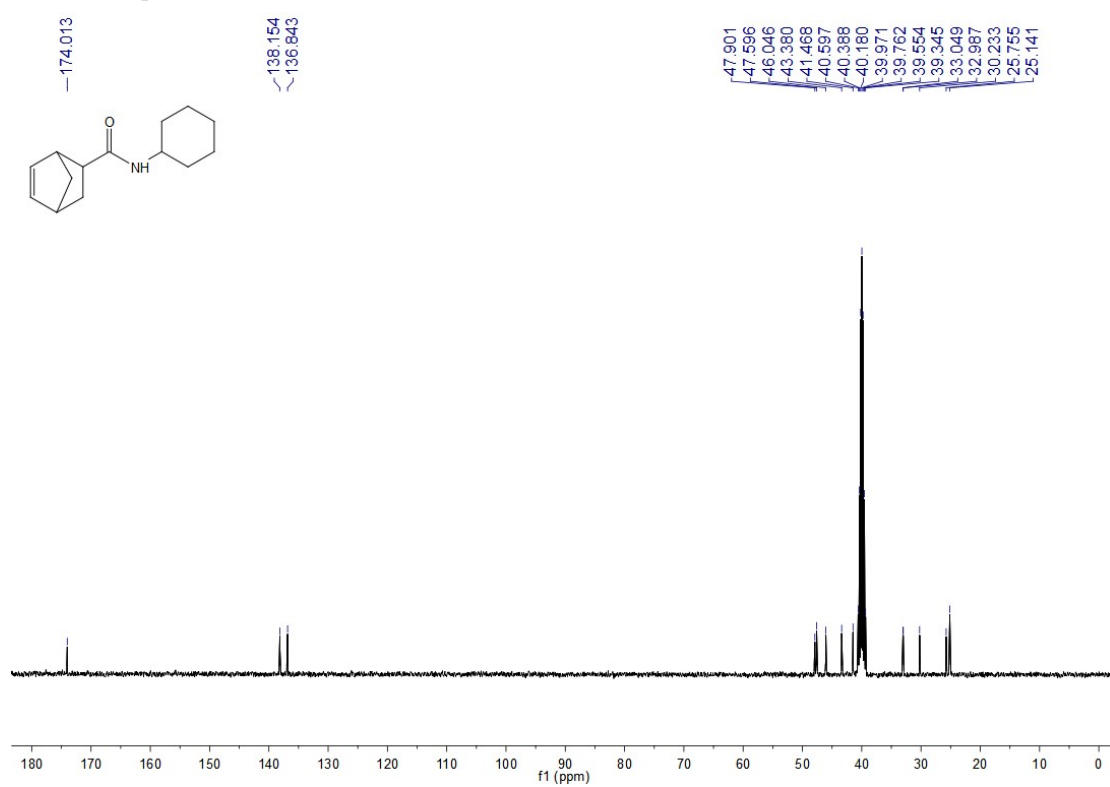
¹³C NMR Spectrum of N¹¹



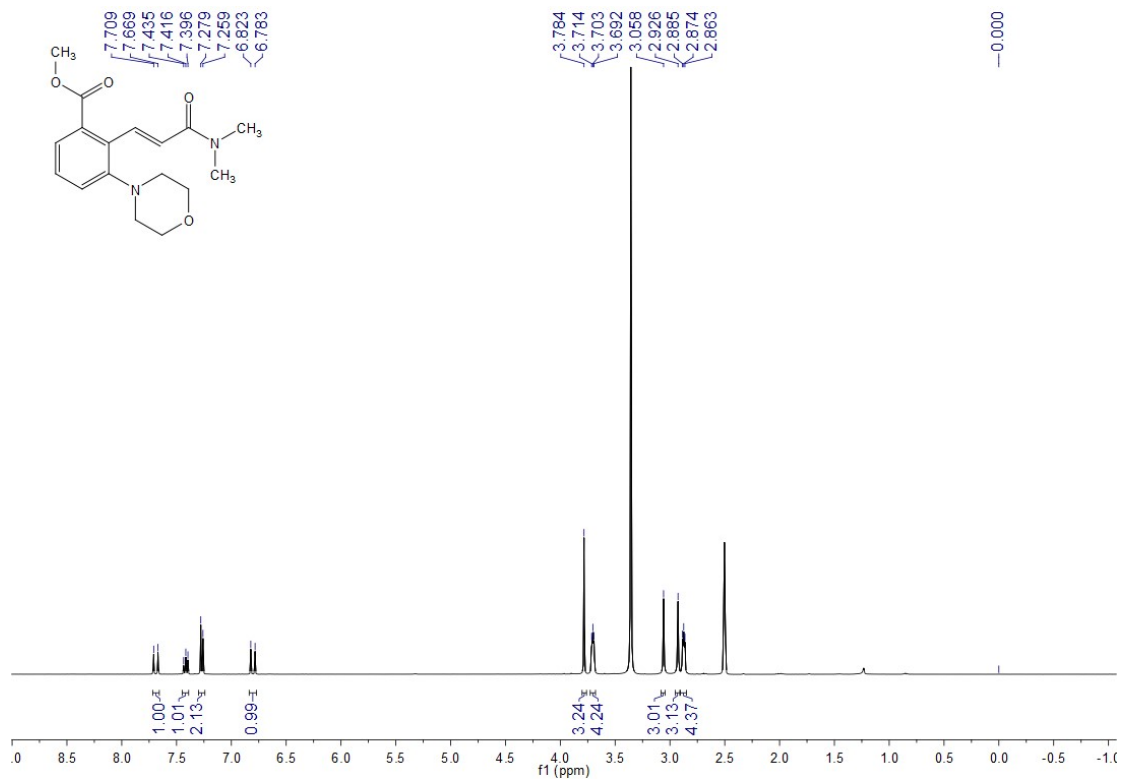
¹H NMR Spectrum of N¹²



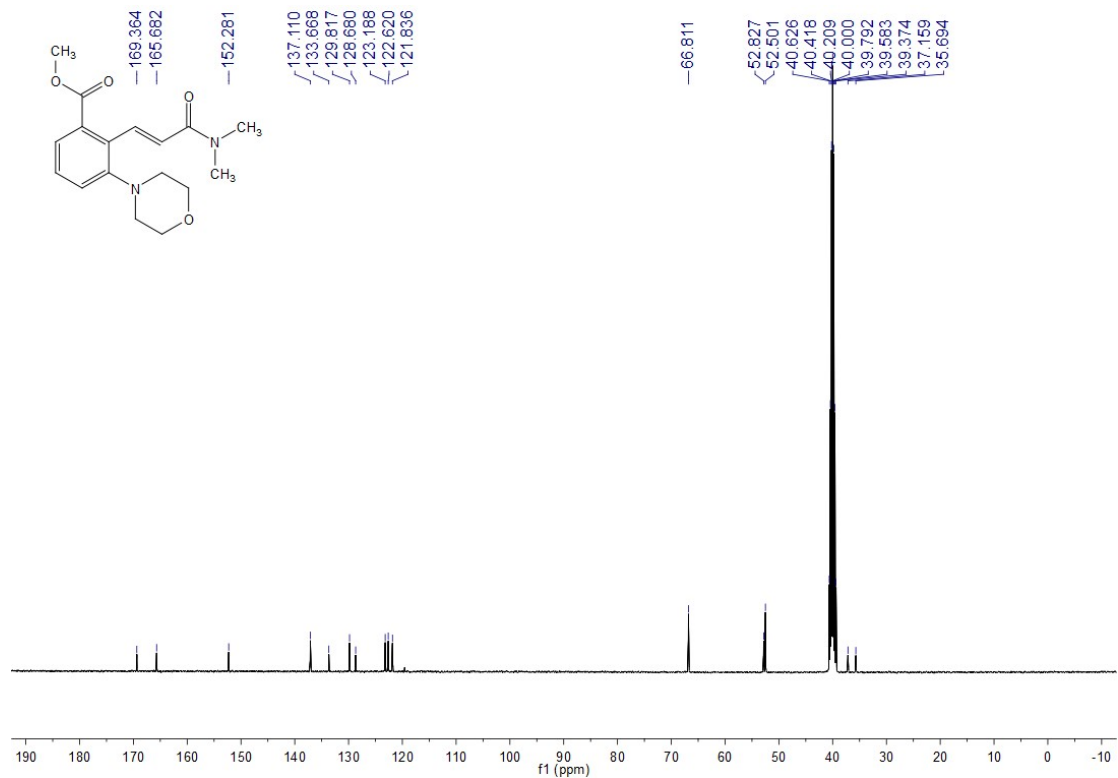
¹³C NMR Spectrum of N¹²



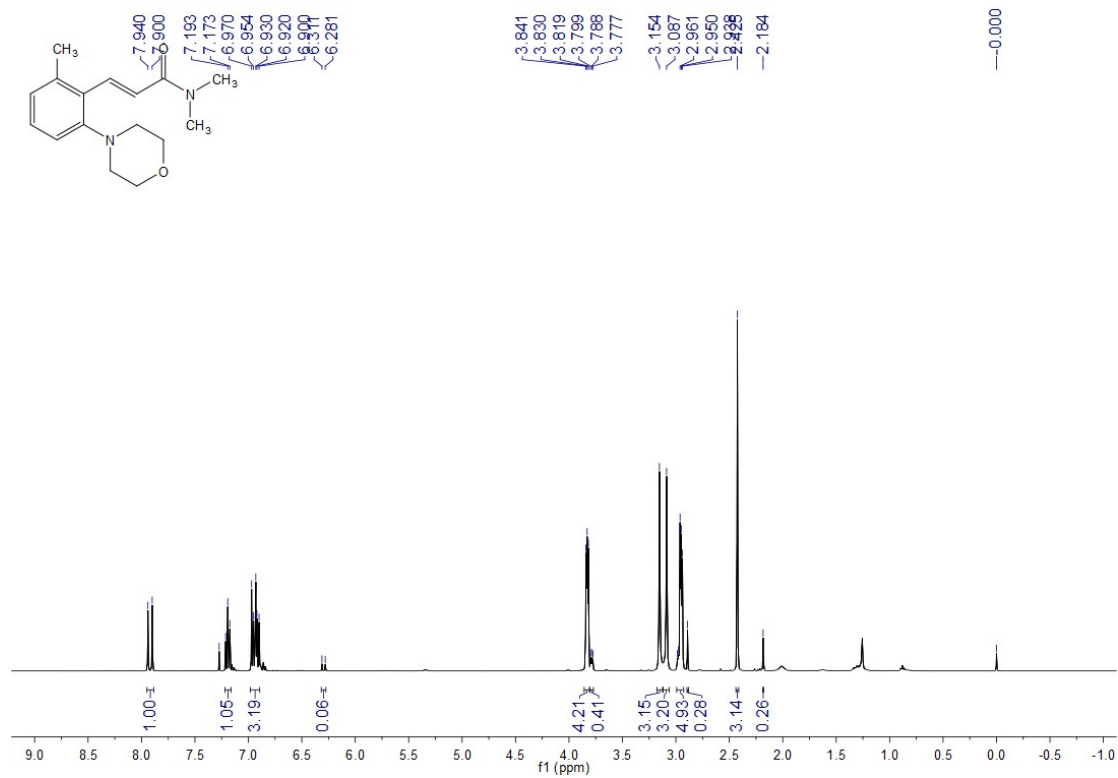
¹H NMR Spectrum of 4a



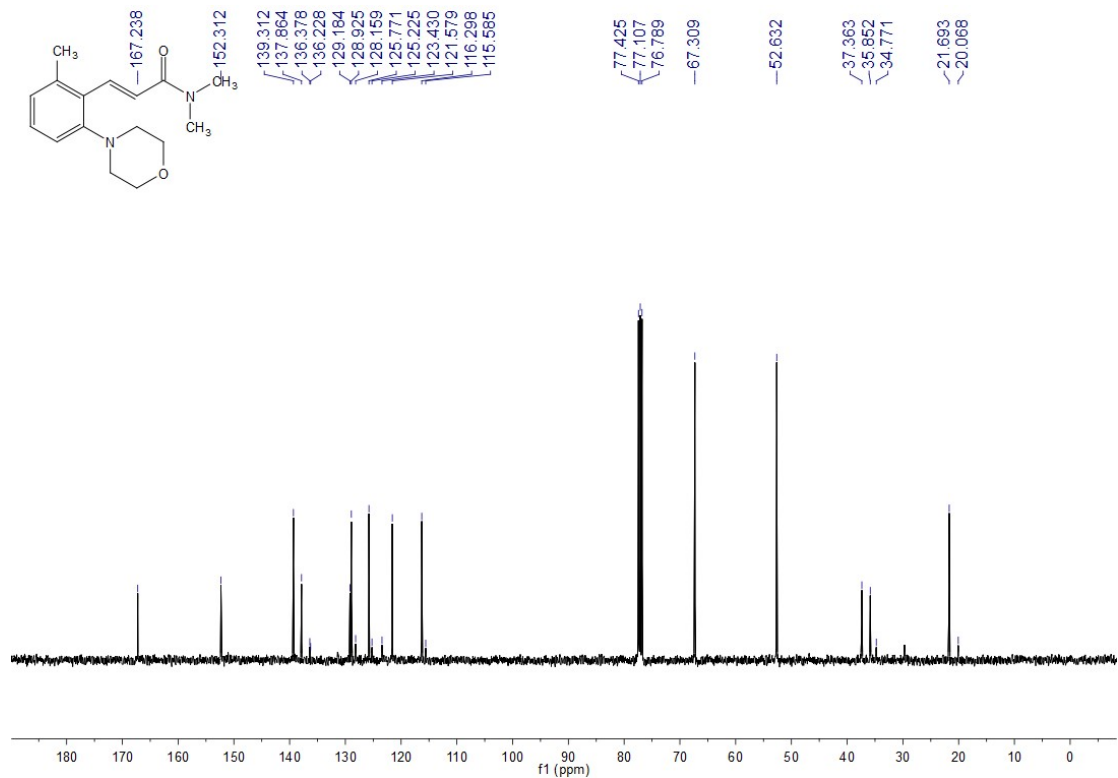
¹³C NMR Spectrum of 4a



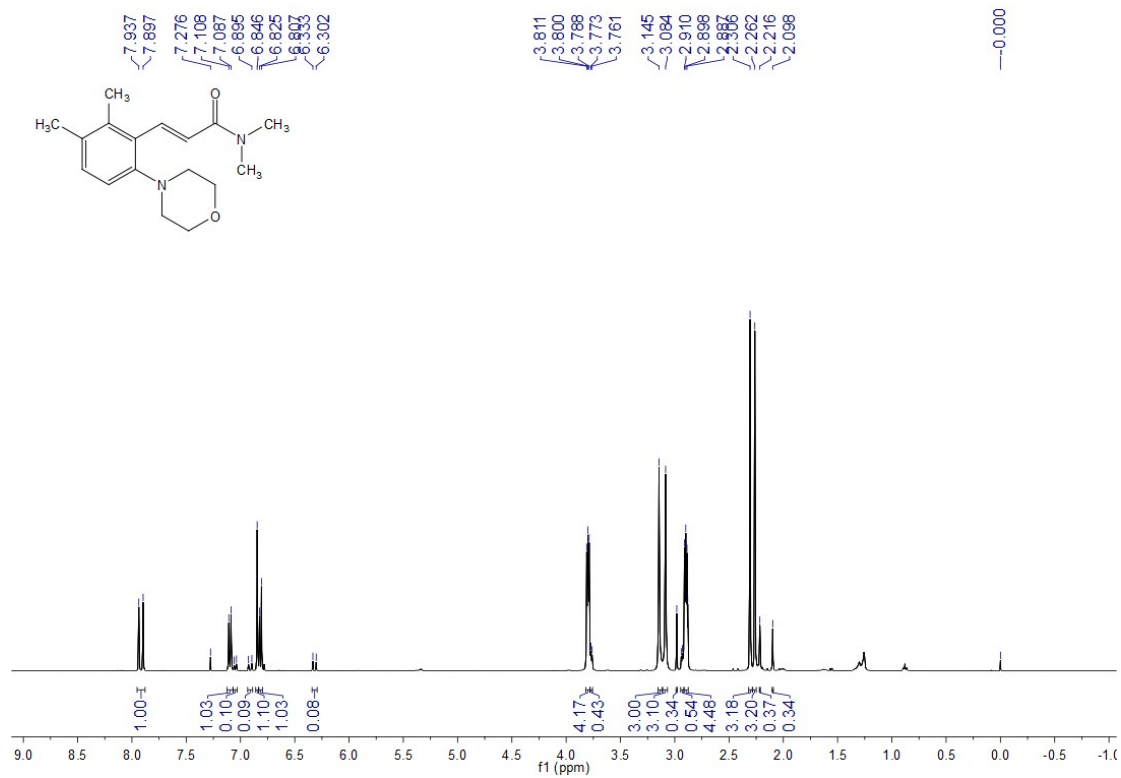
¹H NMR Spectrum of **4b**



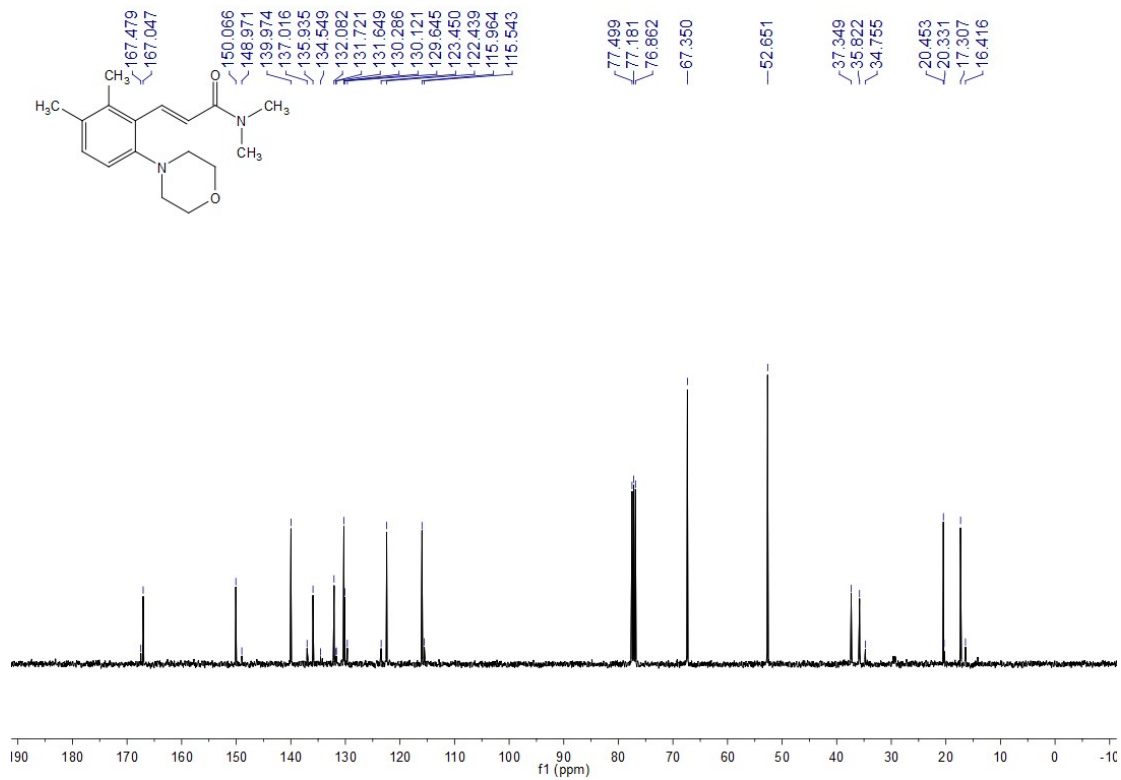
¹³C NMR Spectrum of **4b**



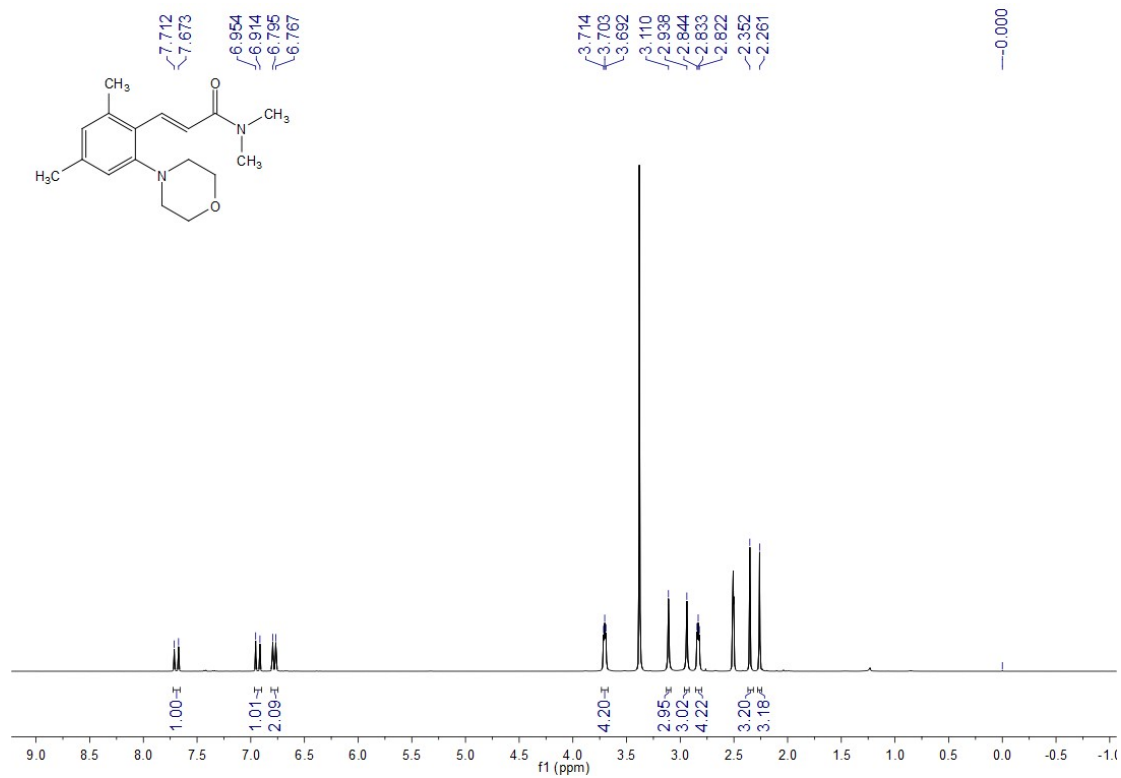
¹H NMR Spectrum of 4c



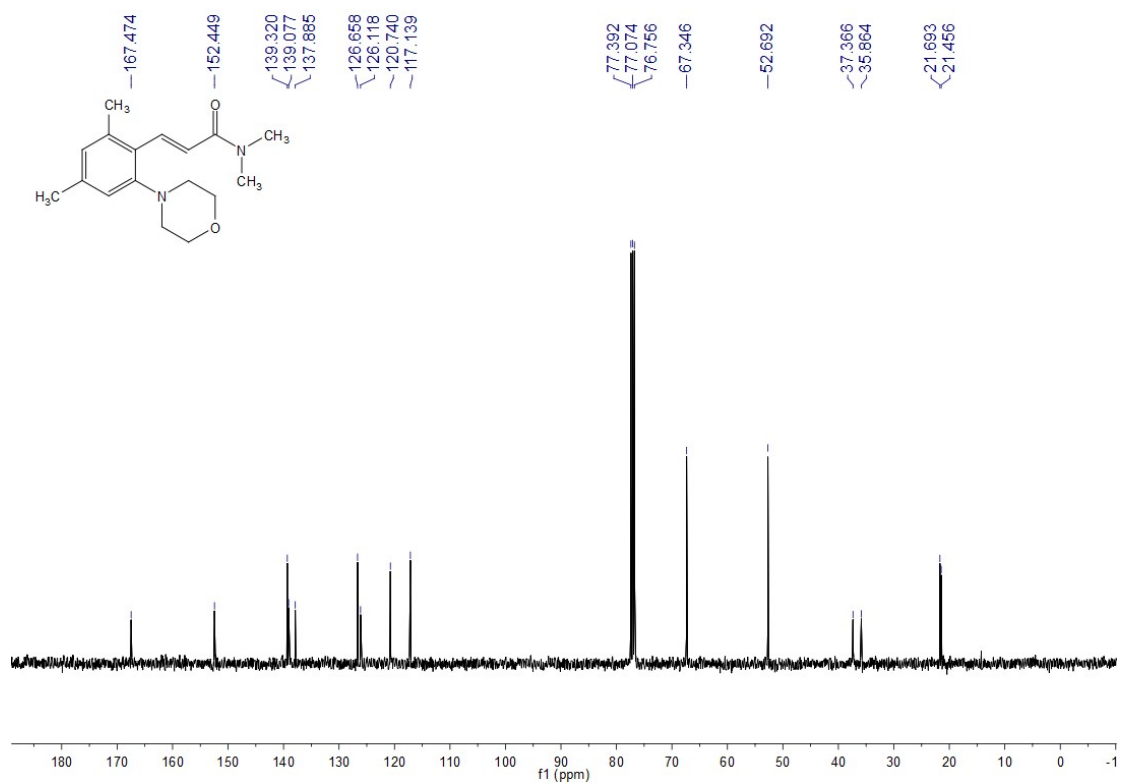
¹³C NMR Spectrum of 4c



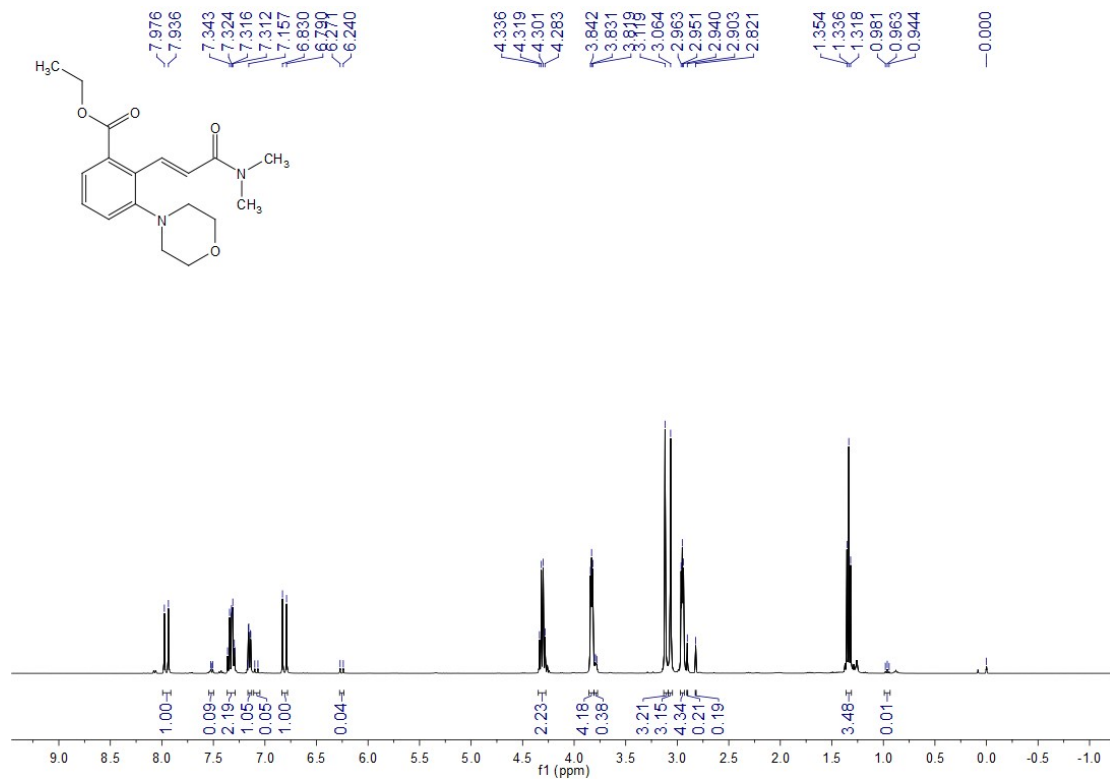
^1H NMR Spectrum of **4d**



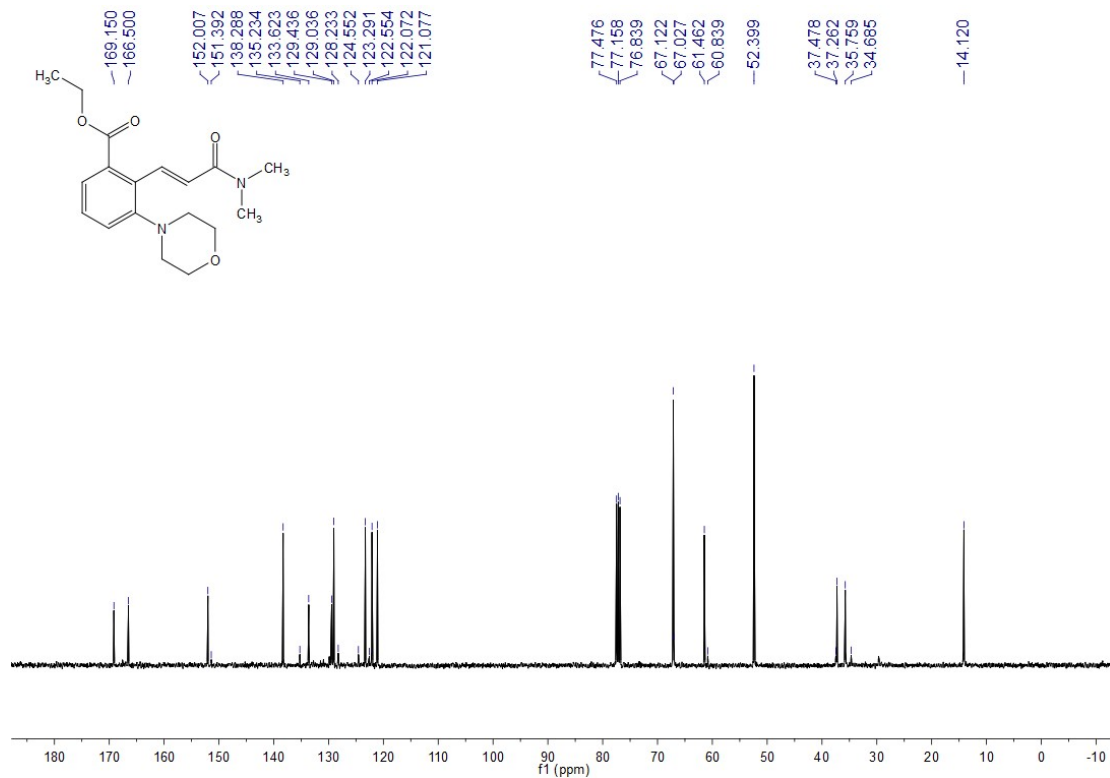
^{13}C NMR Spectrum of **4d**



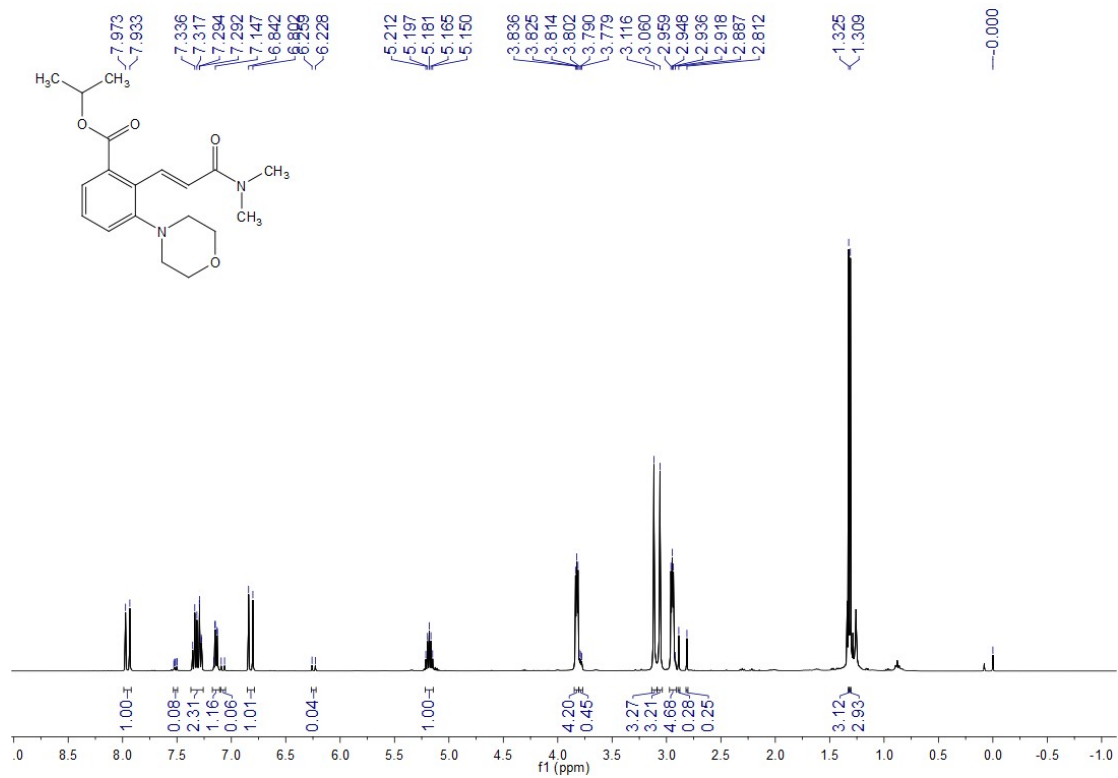
¹H NMR Spectrum of 4e



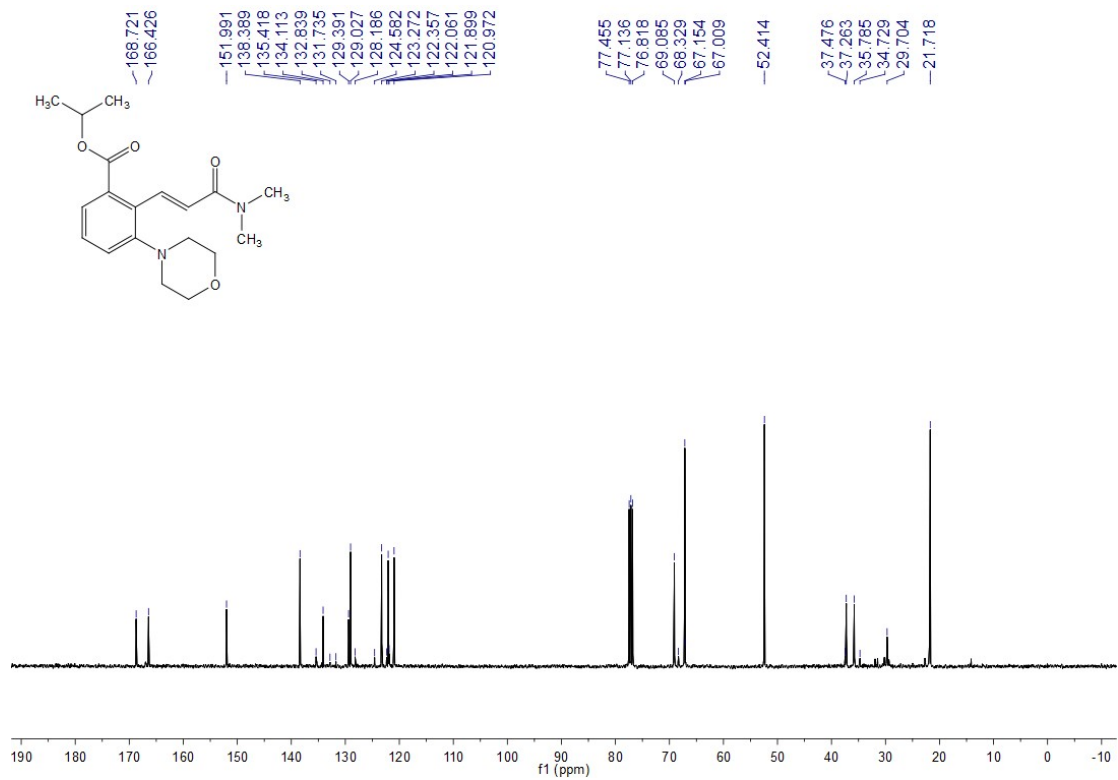
¹³C NMR Spectrum of 4e



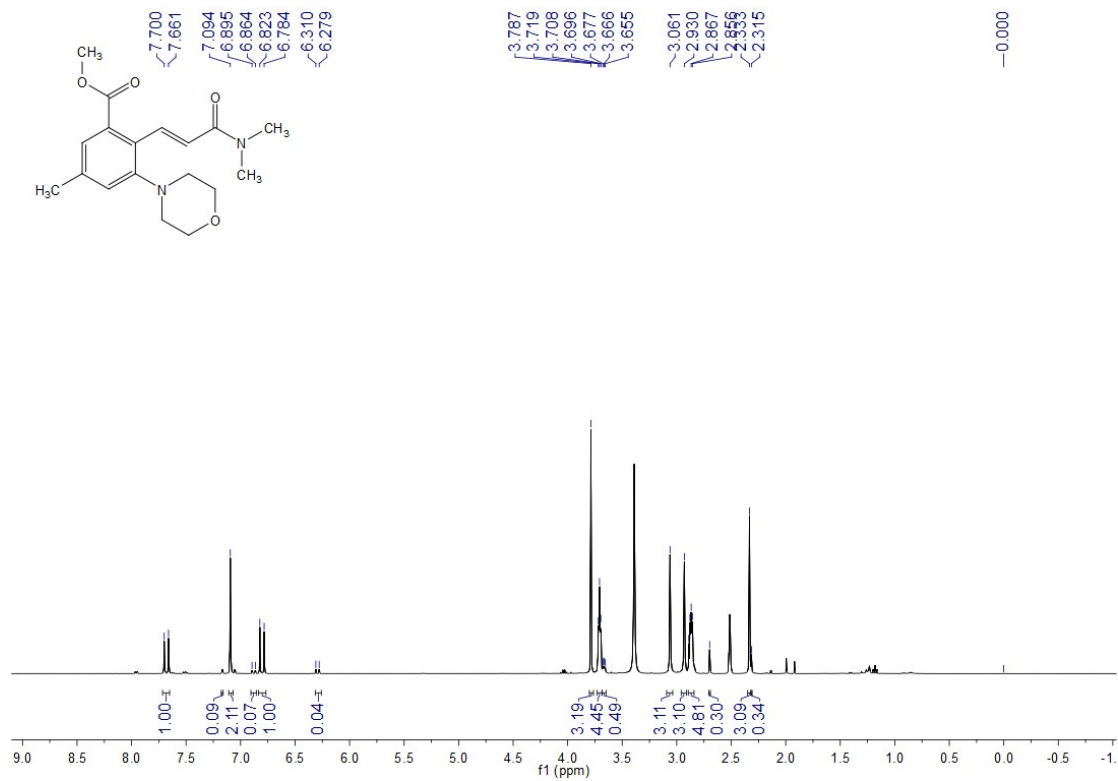
¹H NMR Spectrum of 4f



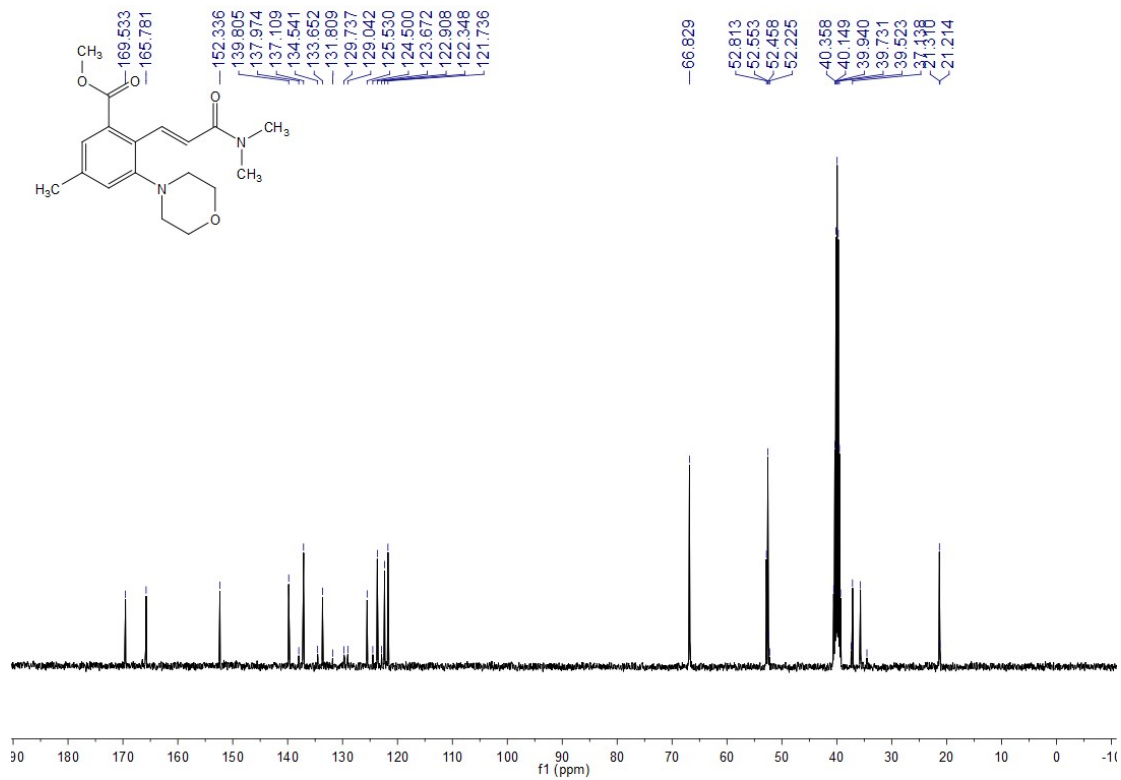
¹³C NMR Spectrum of 4f



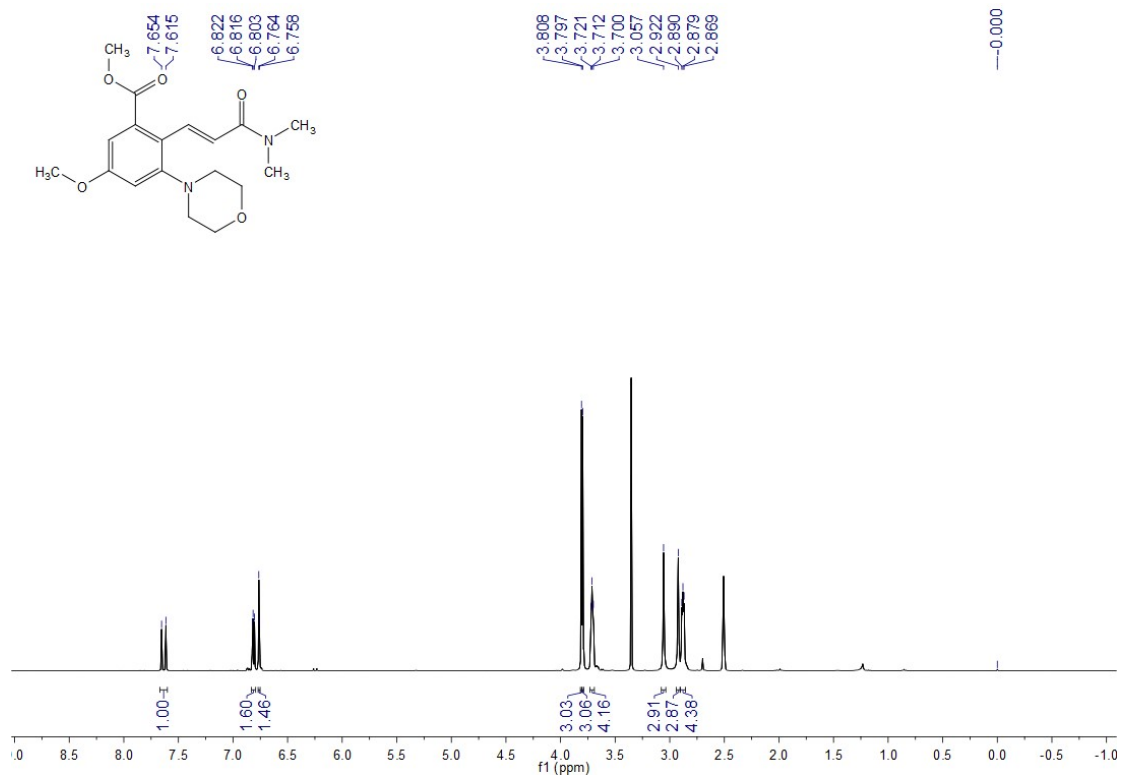
¹H NMR Spectrum of 4g



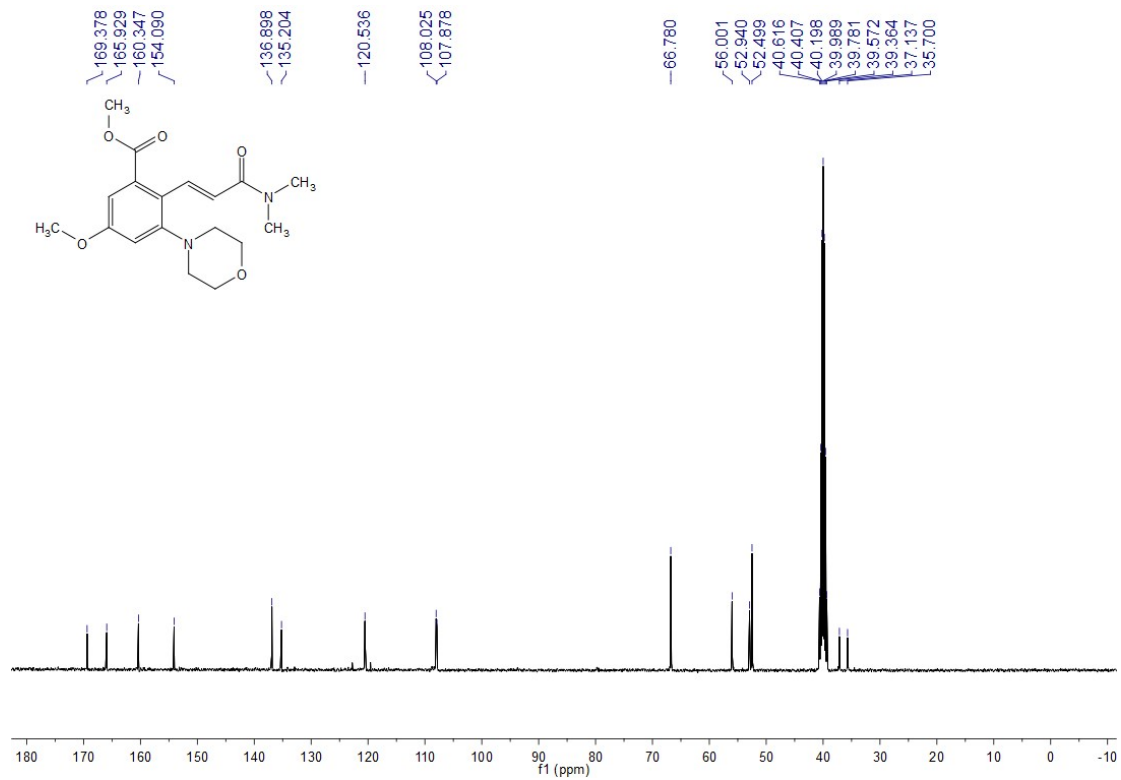
¹³C NMR Spectrum of 4g



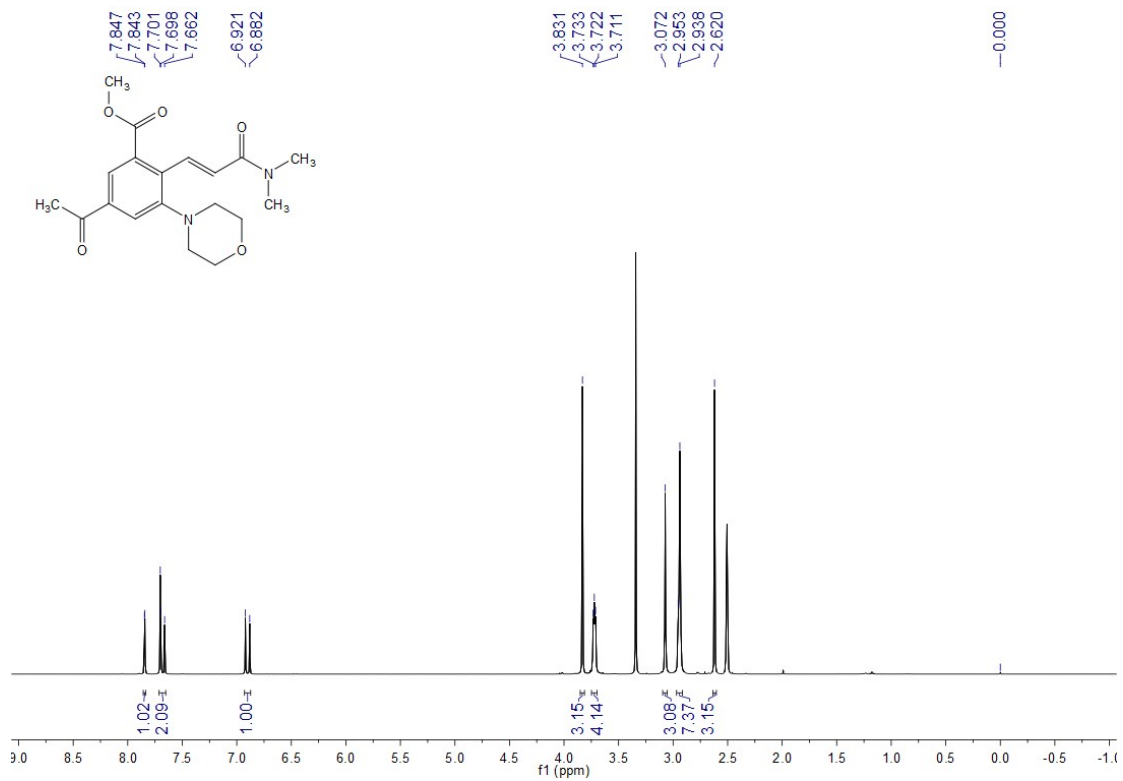
¹H NMR Spectrum of **4h**



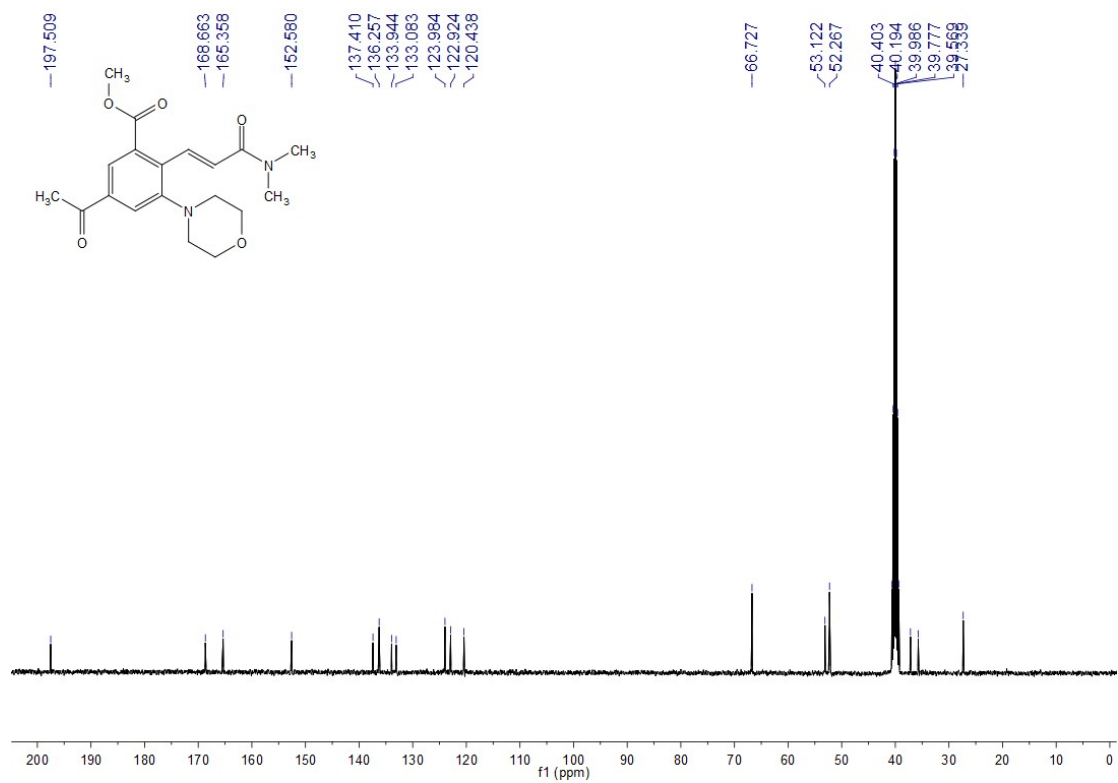
¹³C NMR Spectrum of **4h**



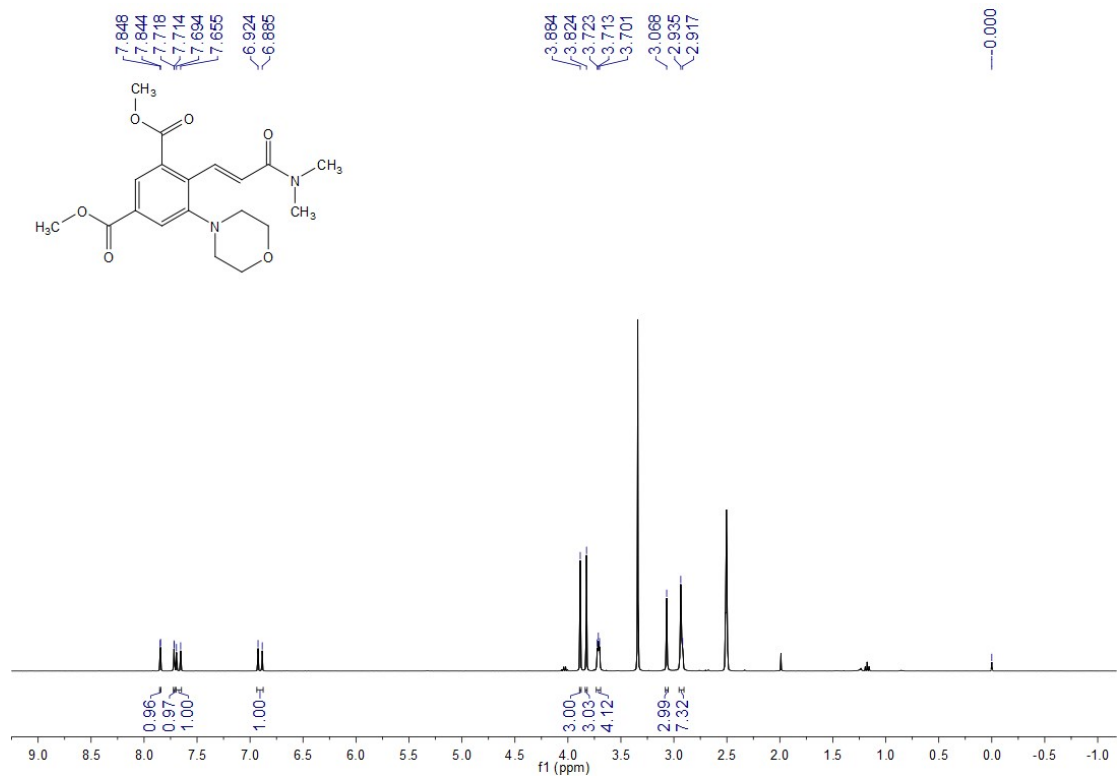
¹H NMR Spectrum of **4i**



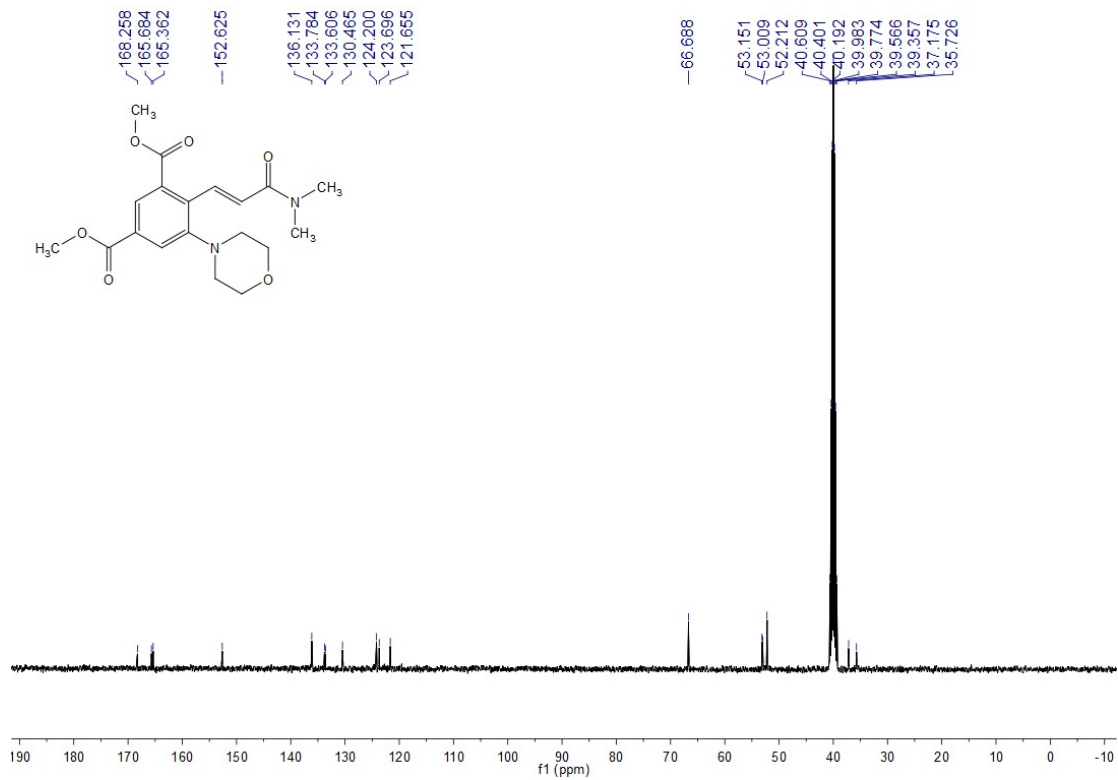
¹³C NMR Spectrum of **4i**



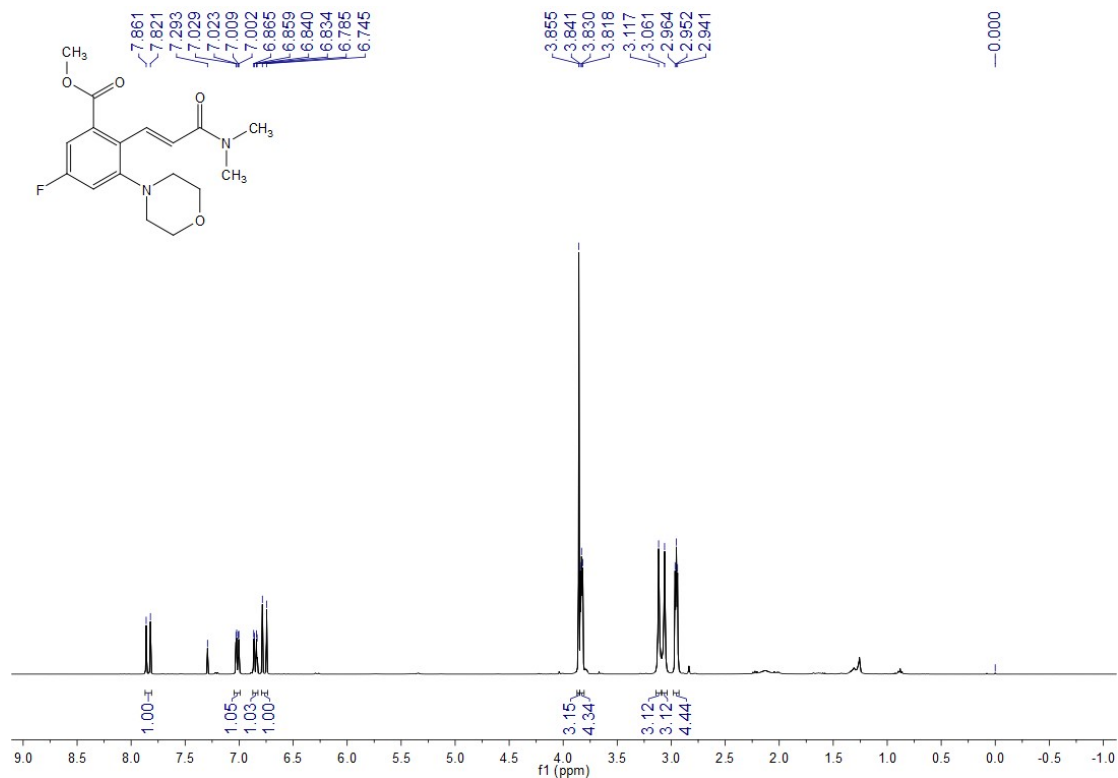
¹H NMR Spectrum of 4j



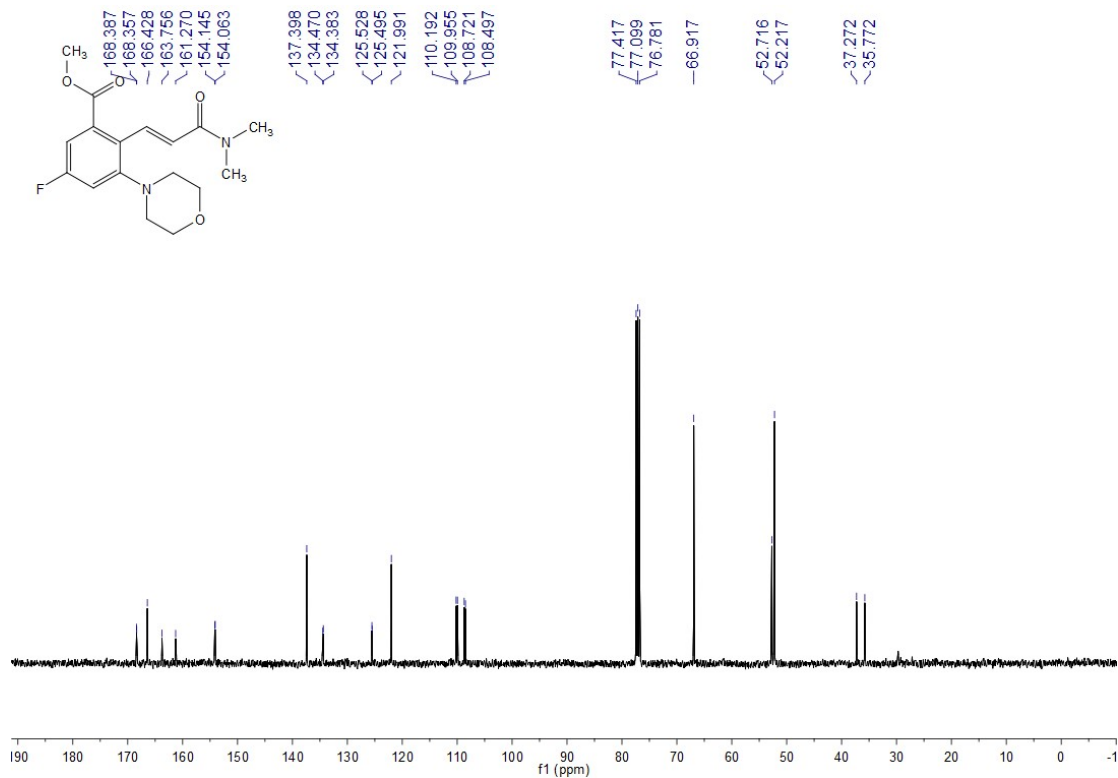
¹³C NMR Spectrum of 4j



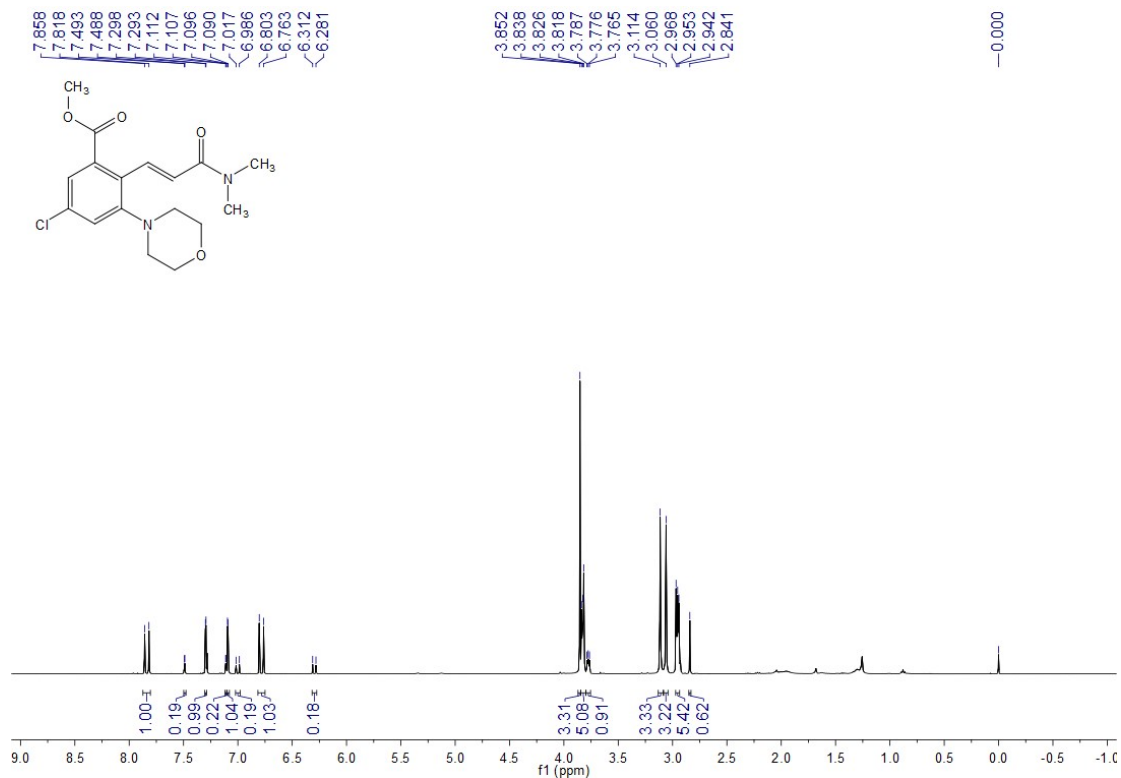
¹H NMR Spectrum of 4k



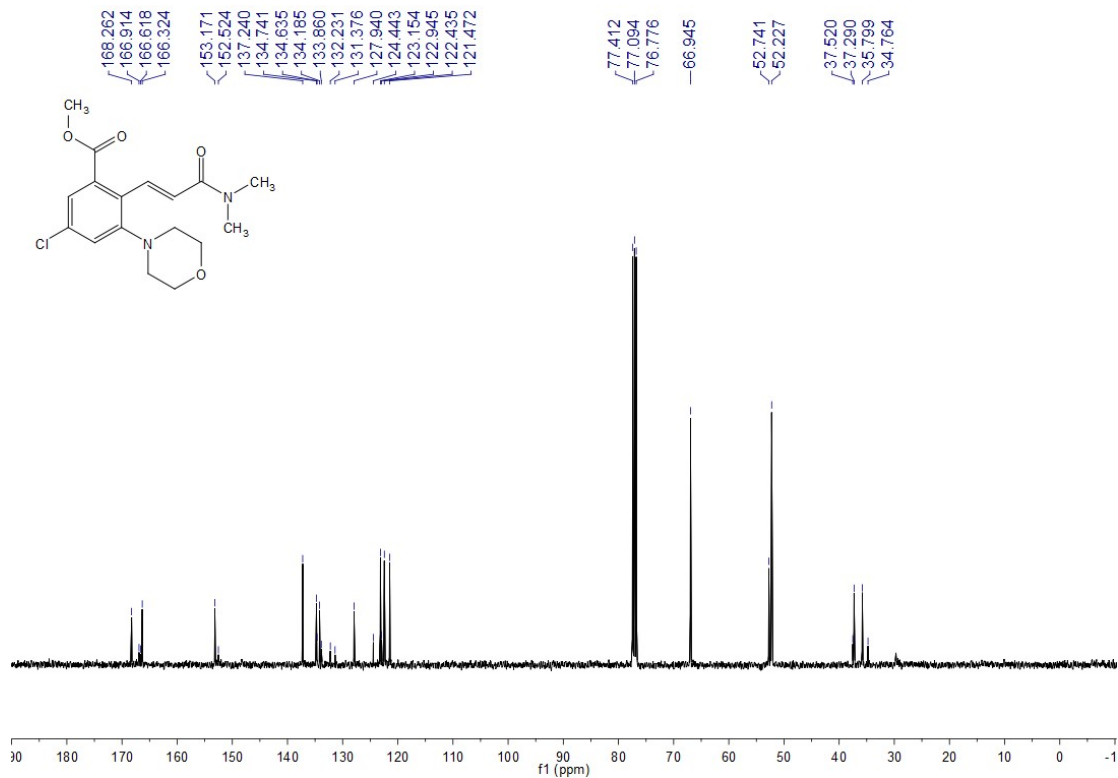
¹³C NMR Spectrum of 4k



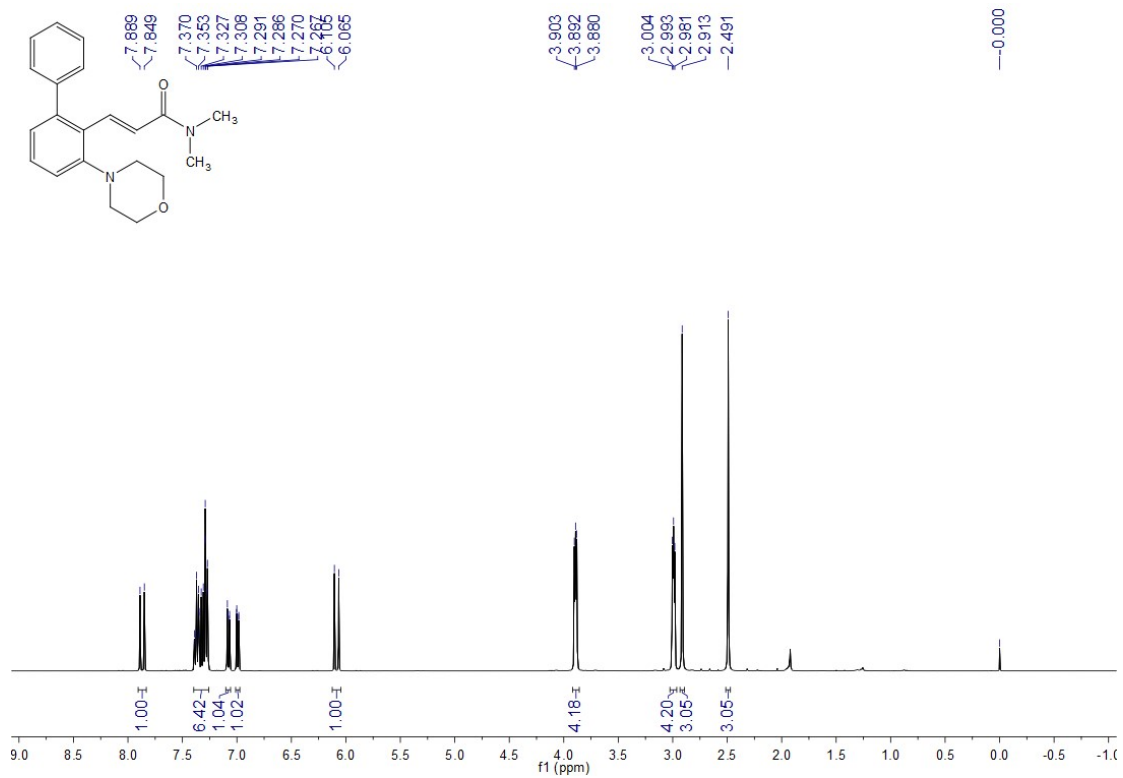
¹H NMR Spectrum of 4I



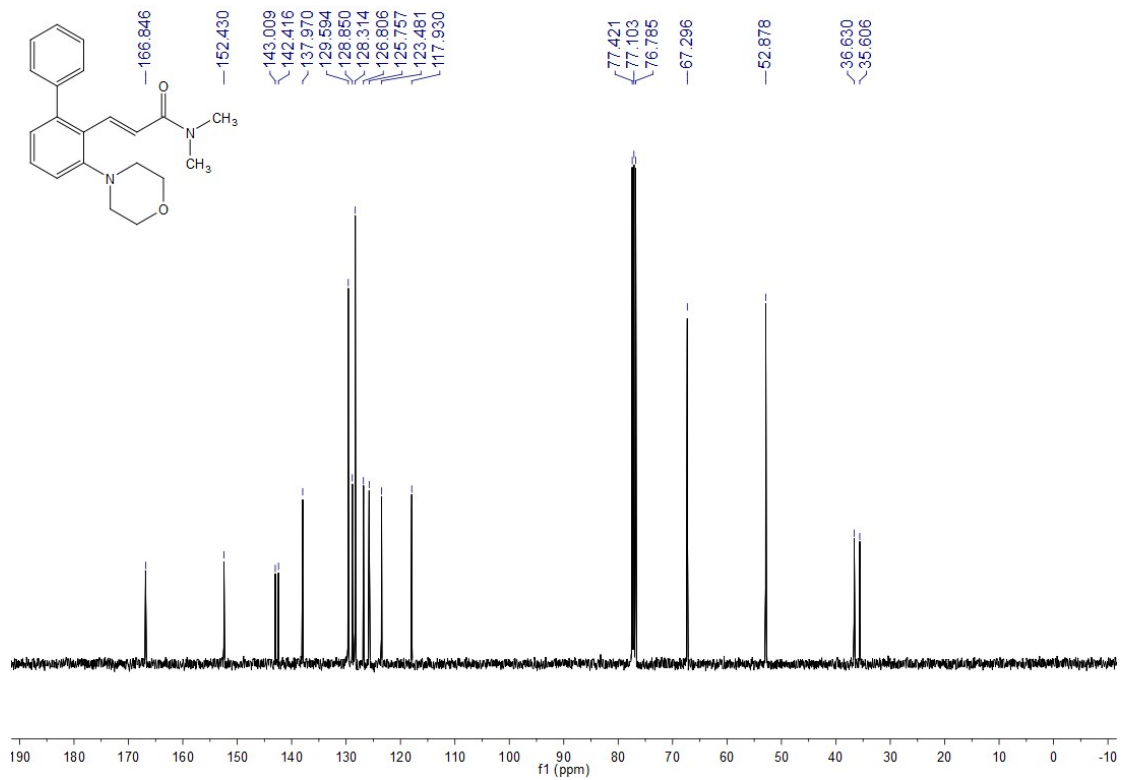
¹³C NMR Spectrum of 4I



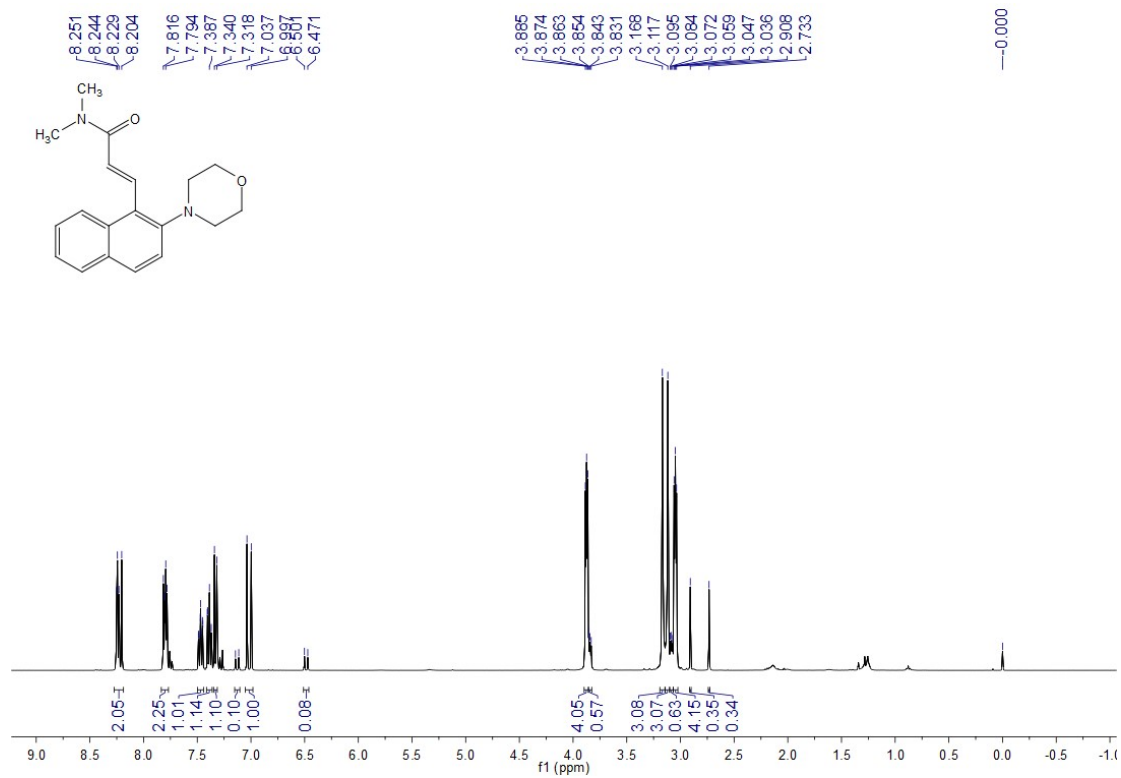
¹H NMR Spectrum of 4m



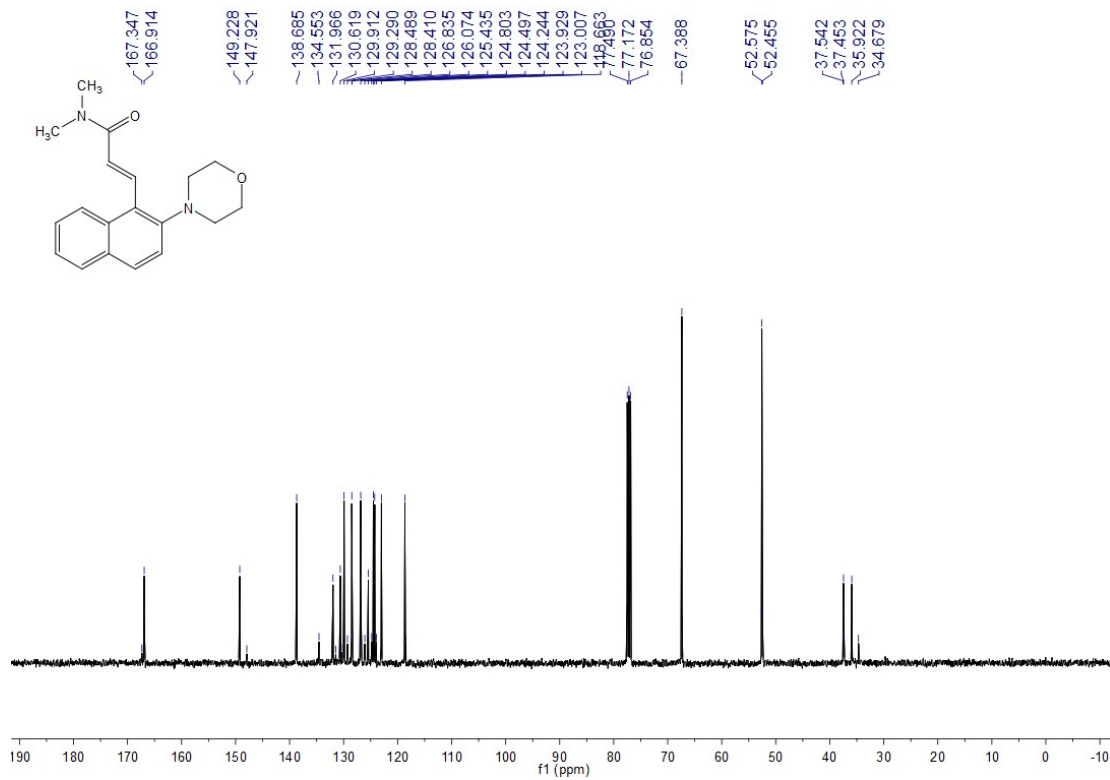
¹³C NMR Spectrum of 4m



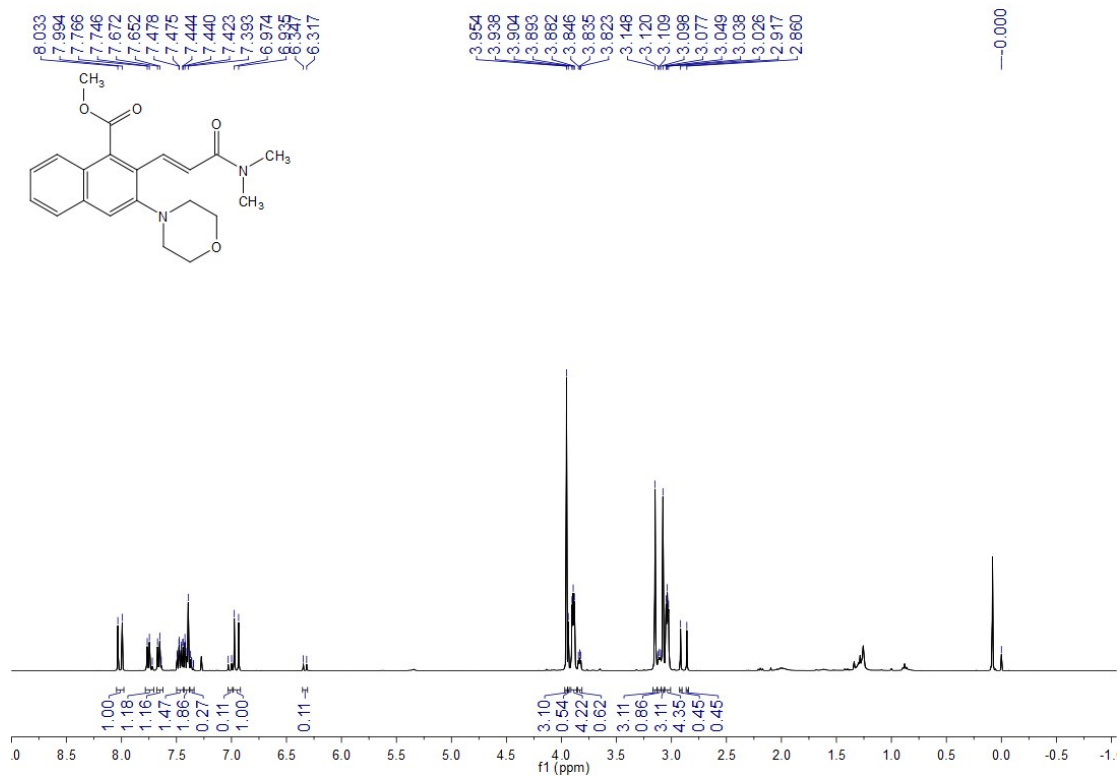
¹H NMR Spectrum of 4n



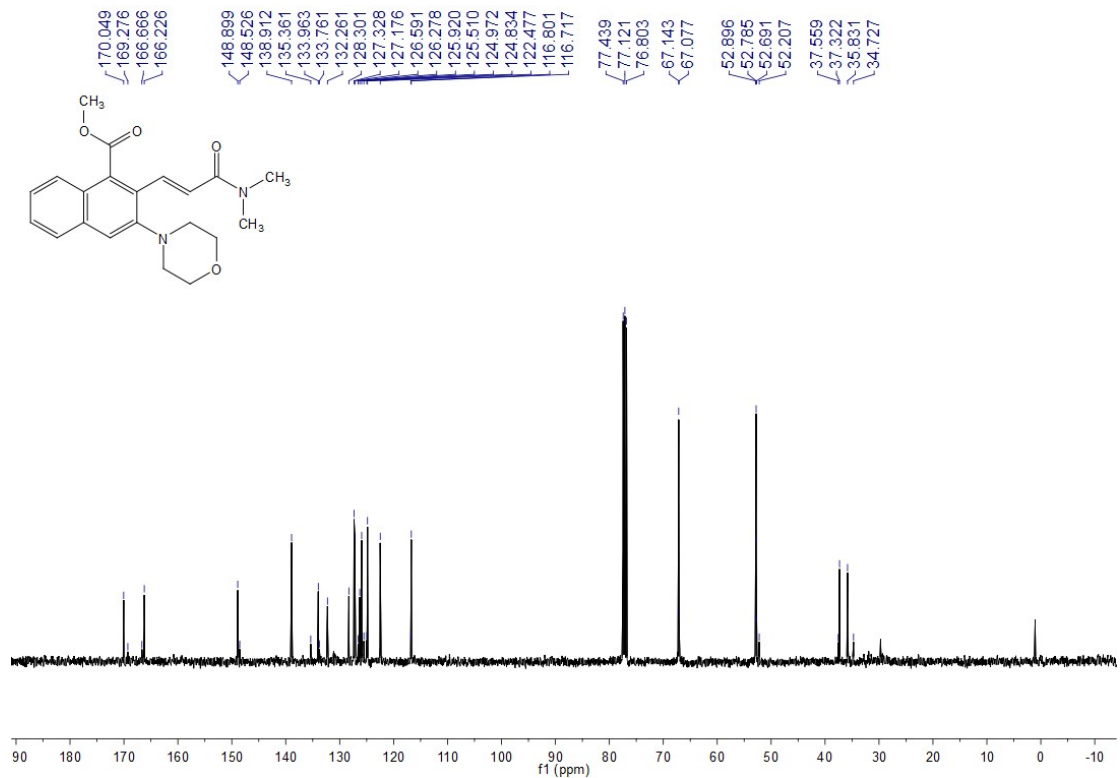
¹³C NMR Spectrum of 4n



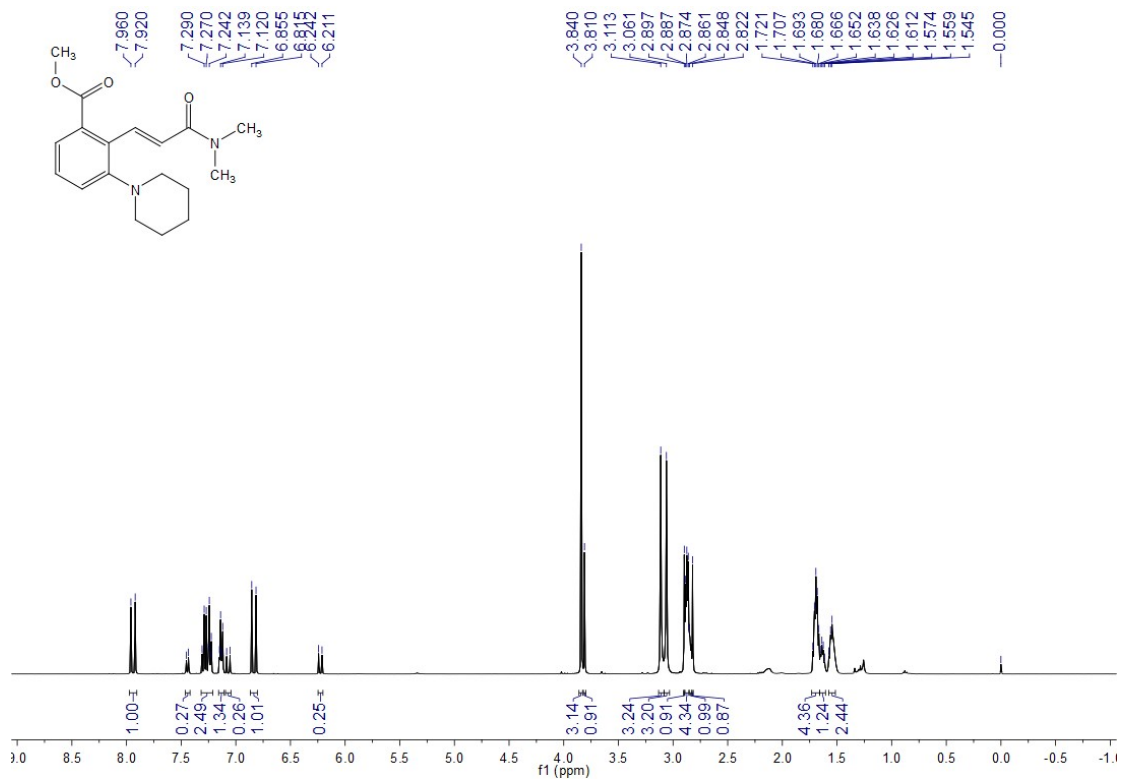
¹H NMR Spectrum of 4o



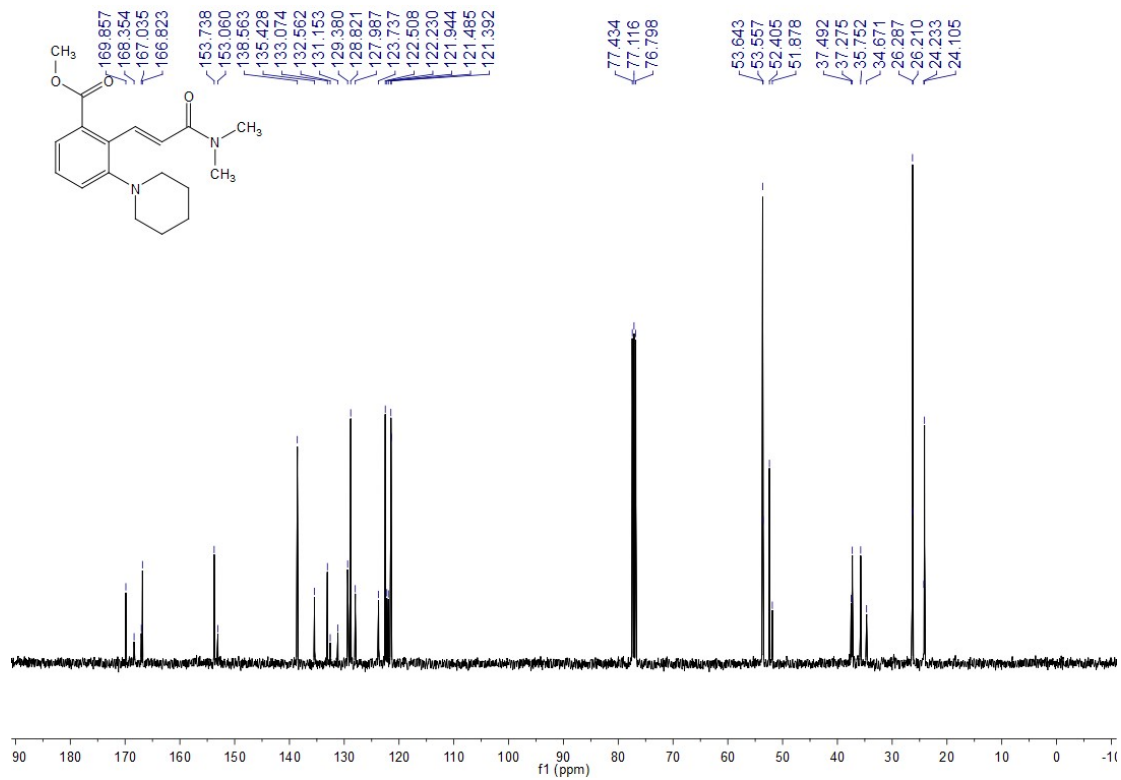
¹³C NMR Spectrum of 4o



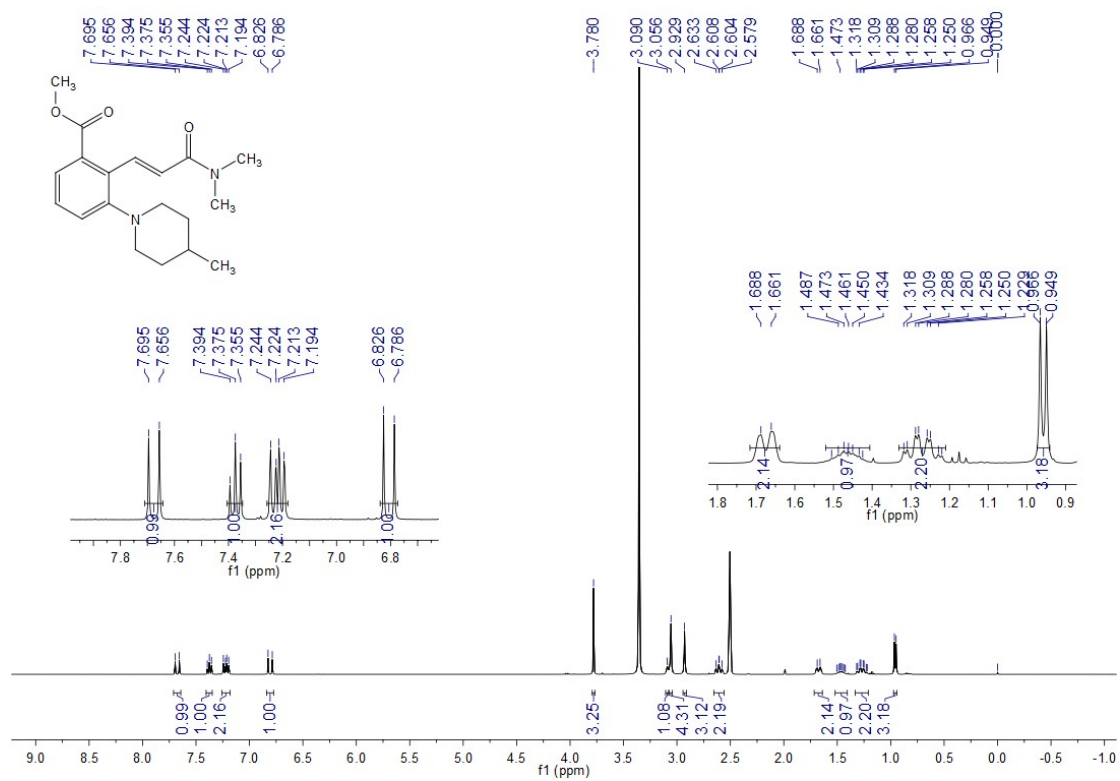
¹H NMR Spectrum of 4p



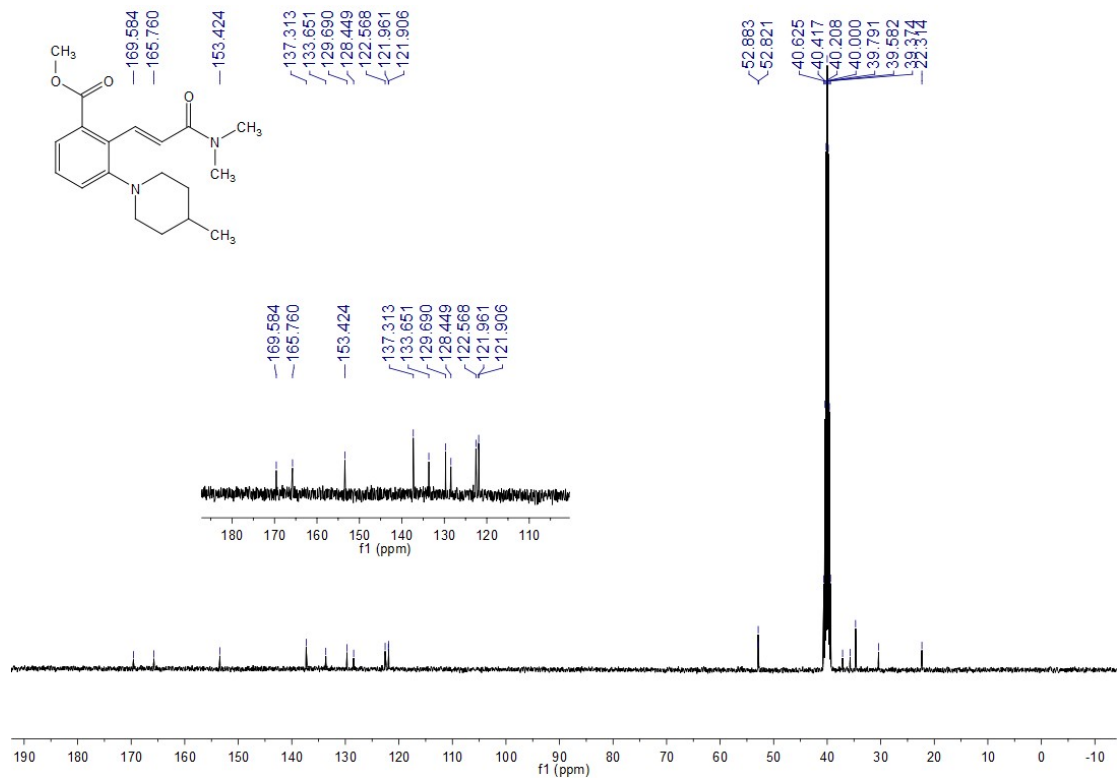
¹³C NMR Spectrum of 4p



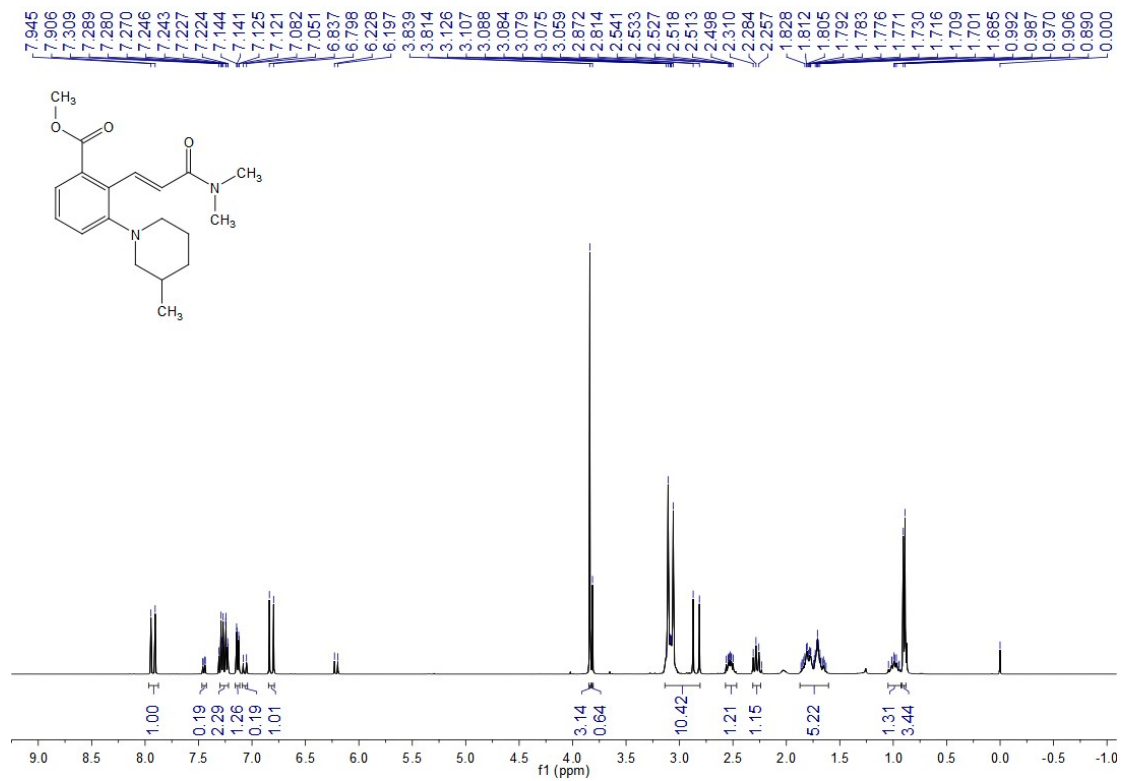
¹H NMR Spectrum of 4q



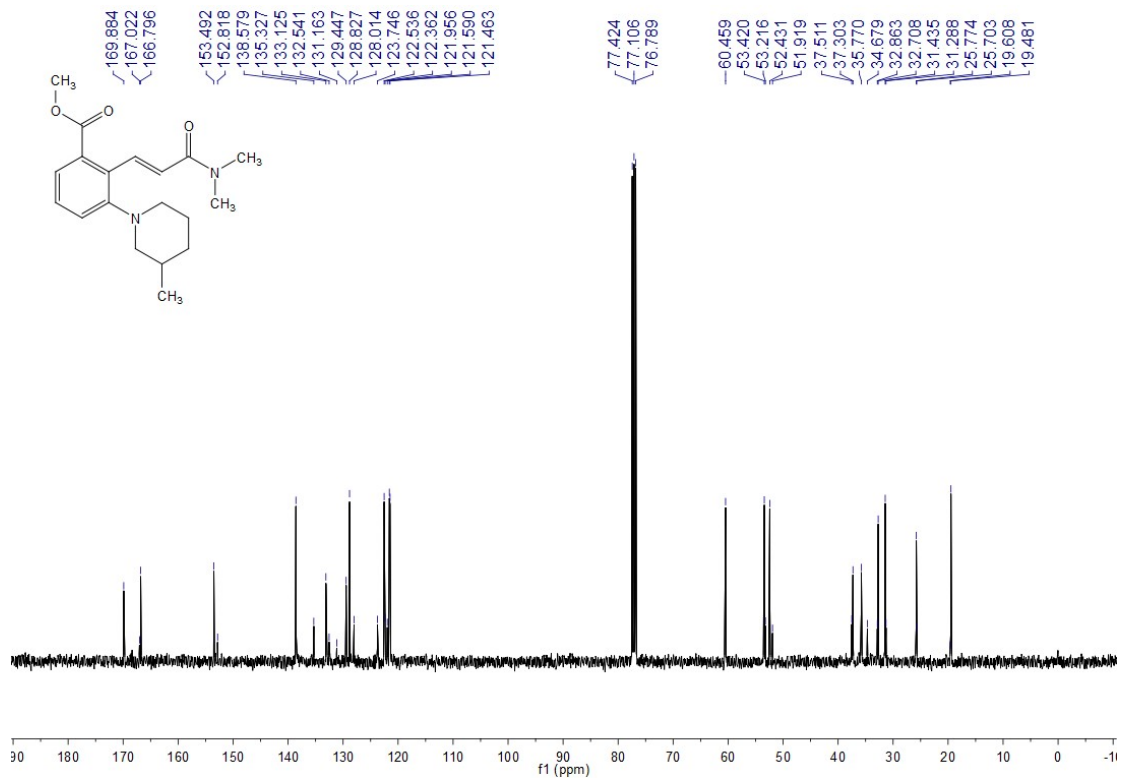
¹³C NMR Spectrum of 4q



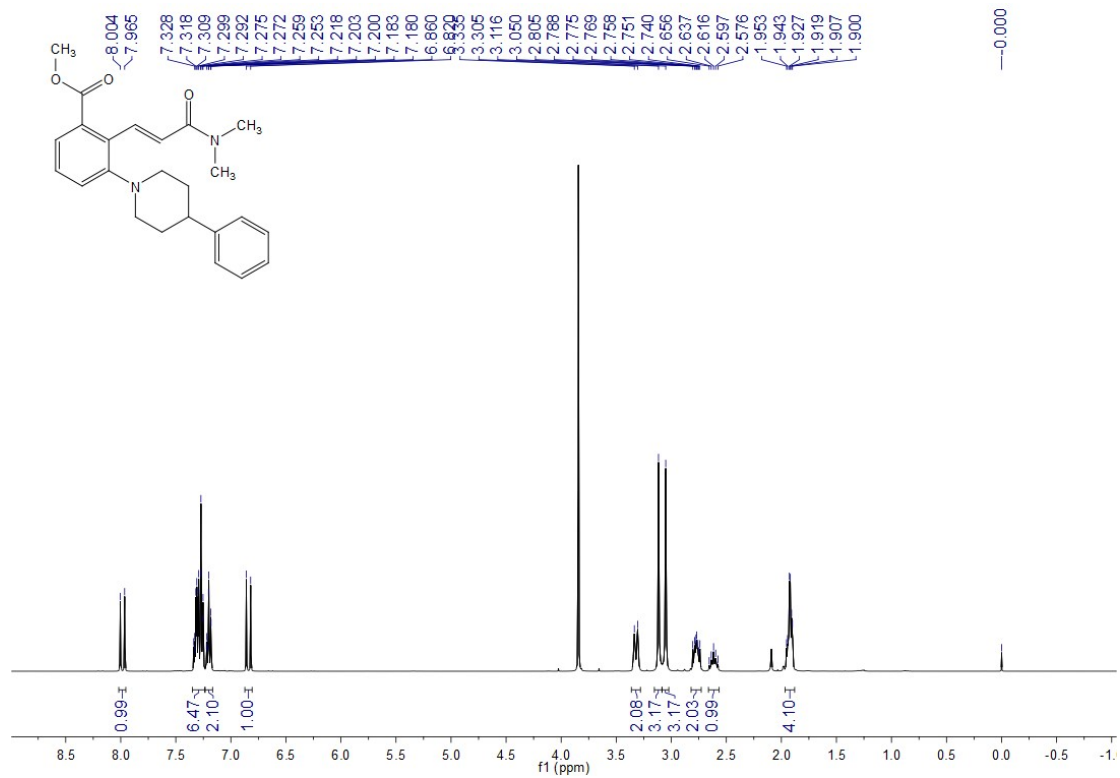
¹H NMR Spectrum of 4r



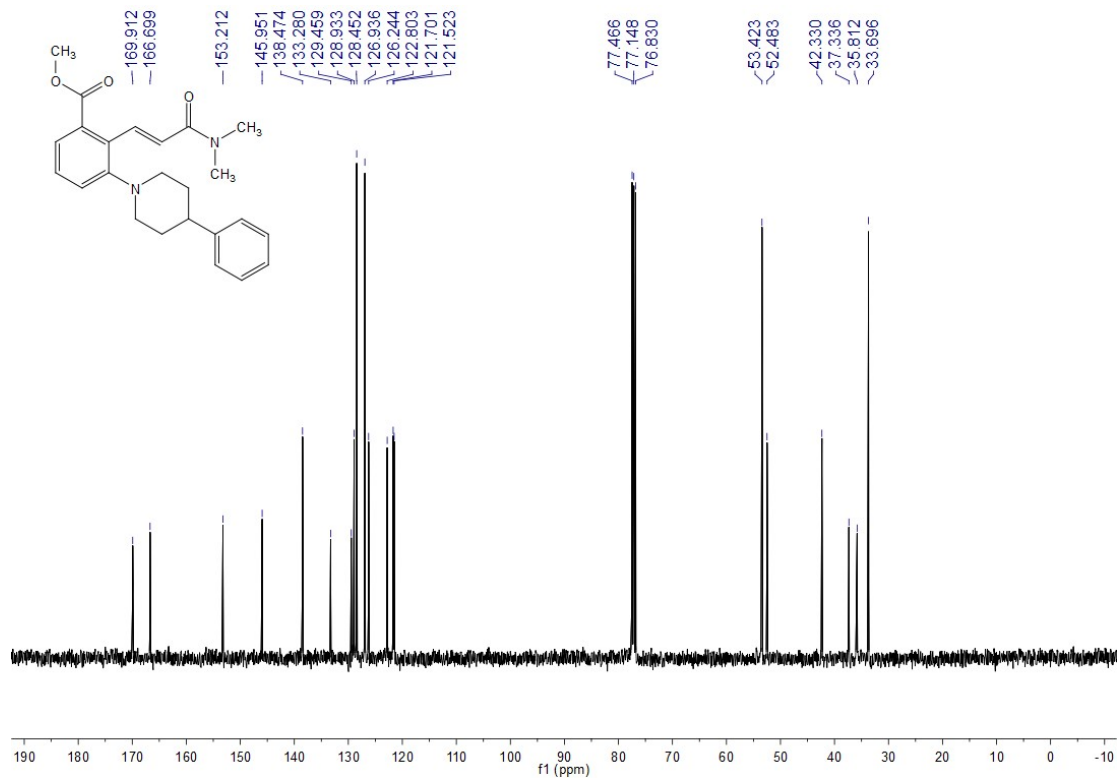
¹³C NMR Spectrum of 4r



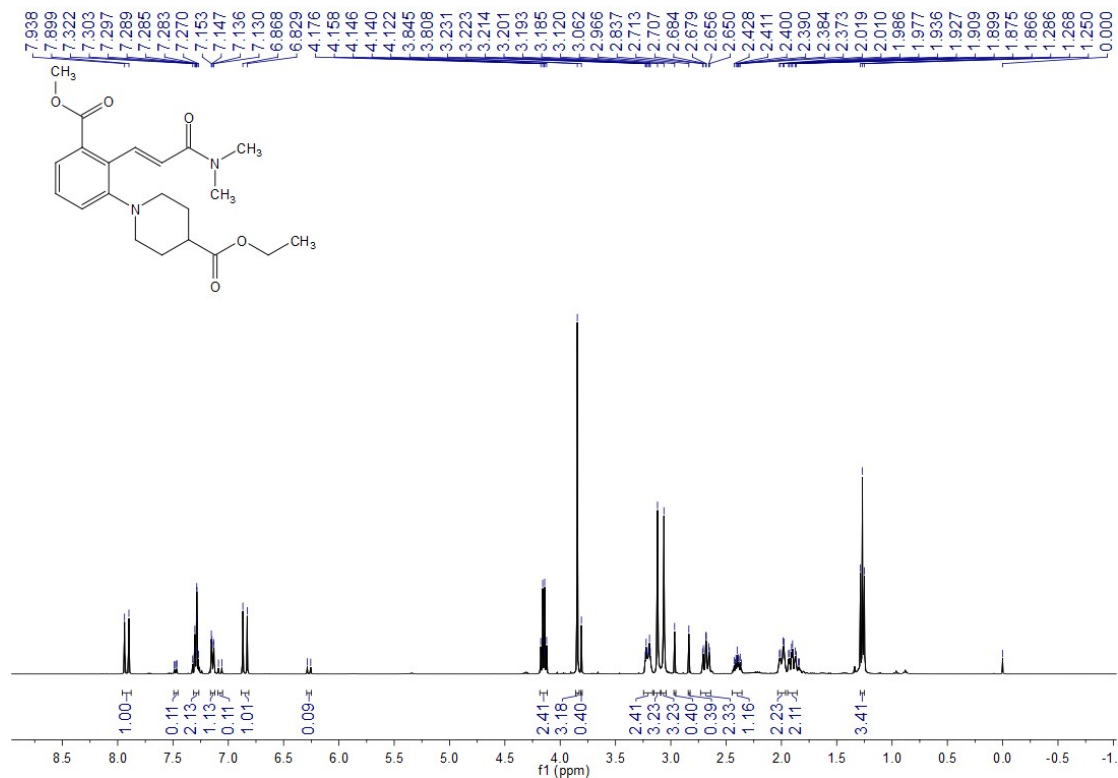
¹H NMR Spectrum of 4s



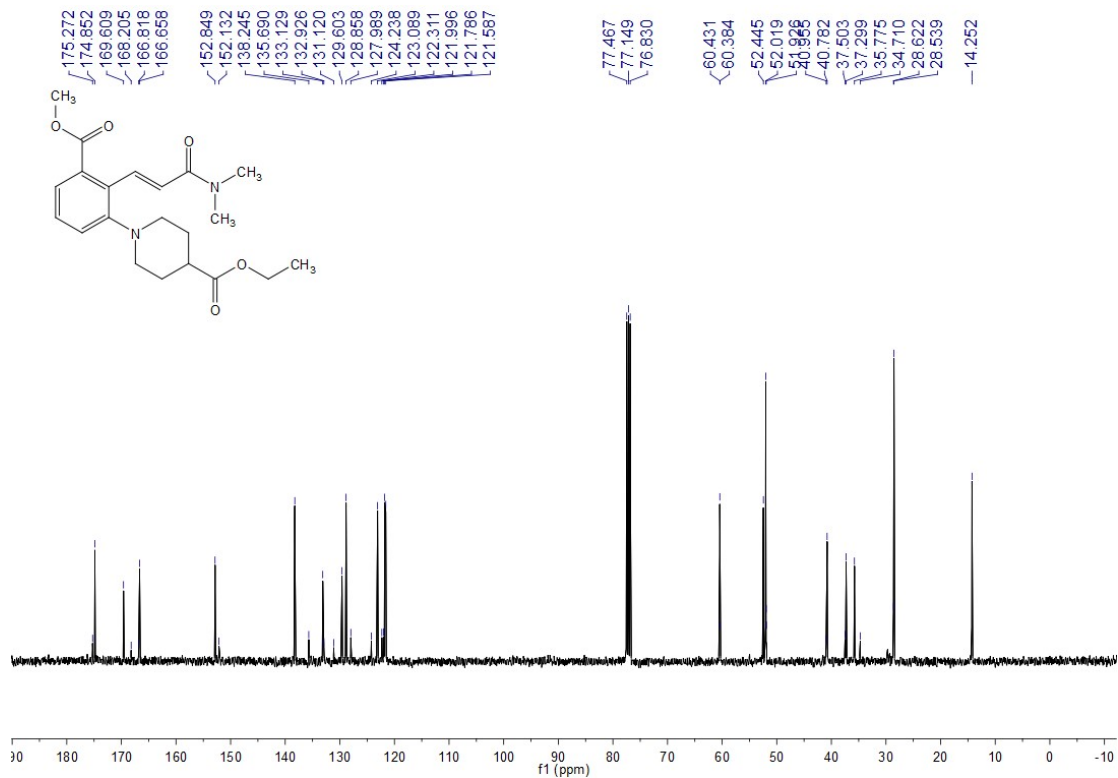
¹³C NMR Spectrum of 4s



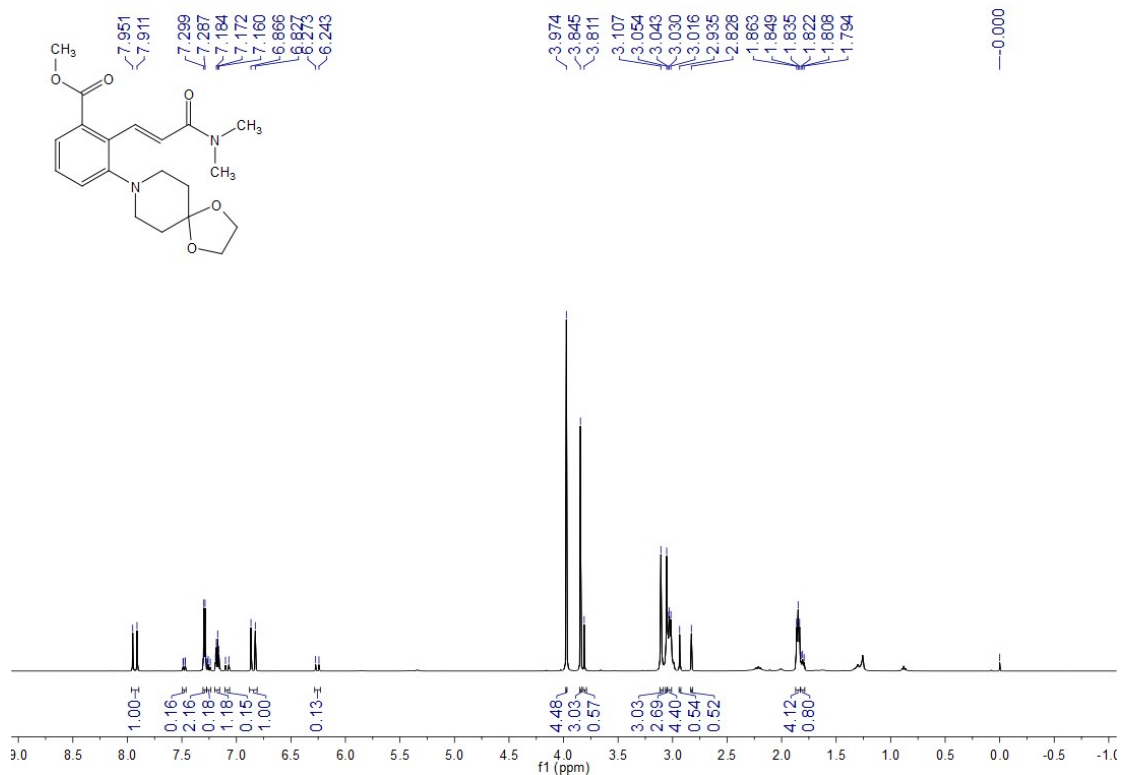
¹H NMR Spectrum of 4t



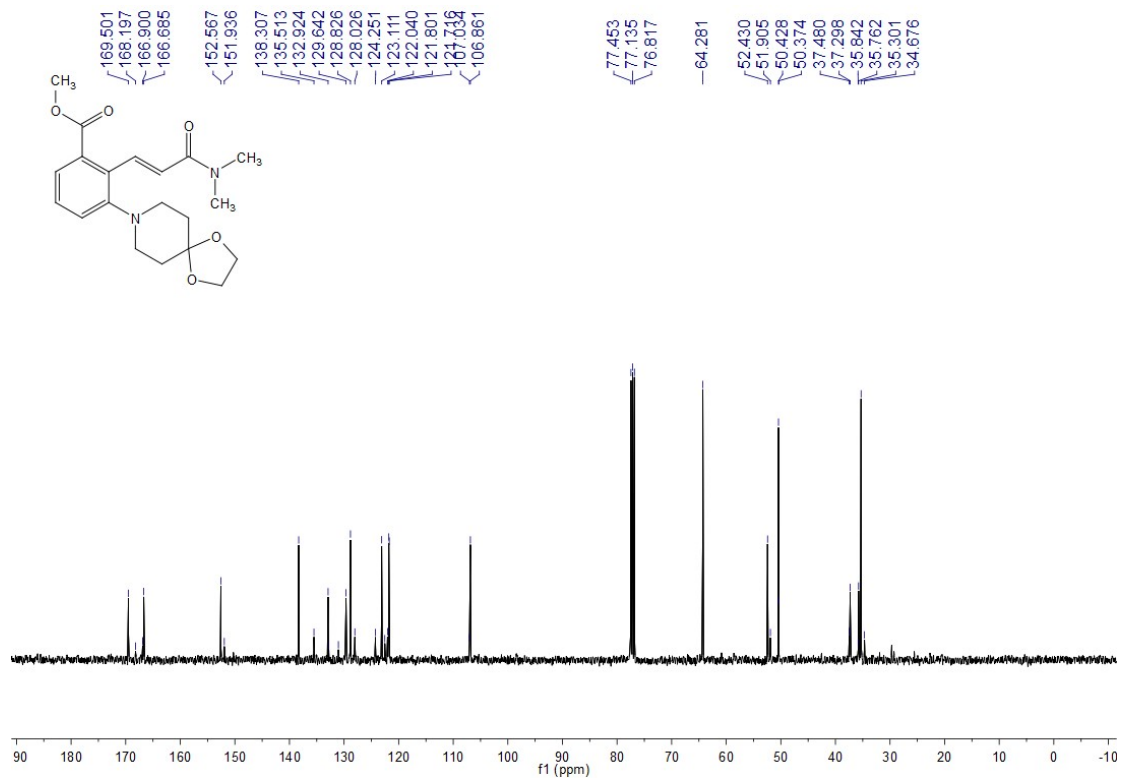
¹³C NMR Spectrum of 4t



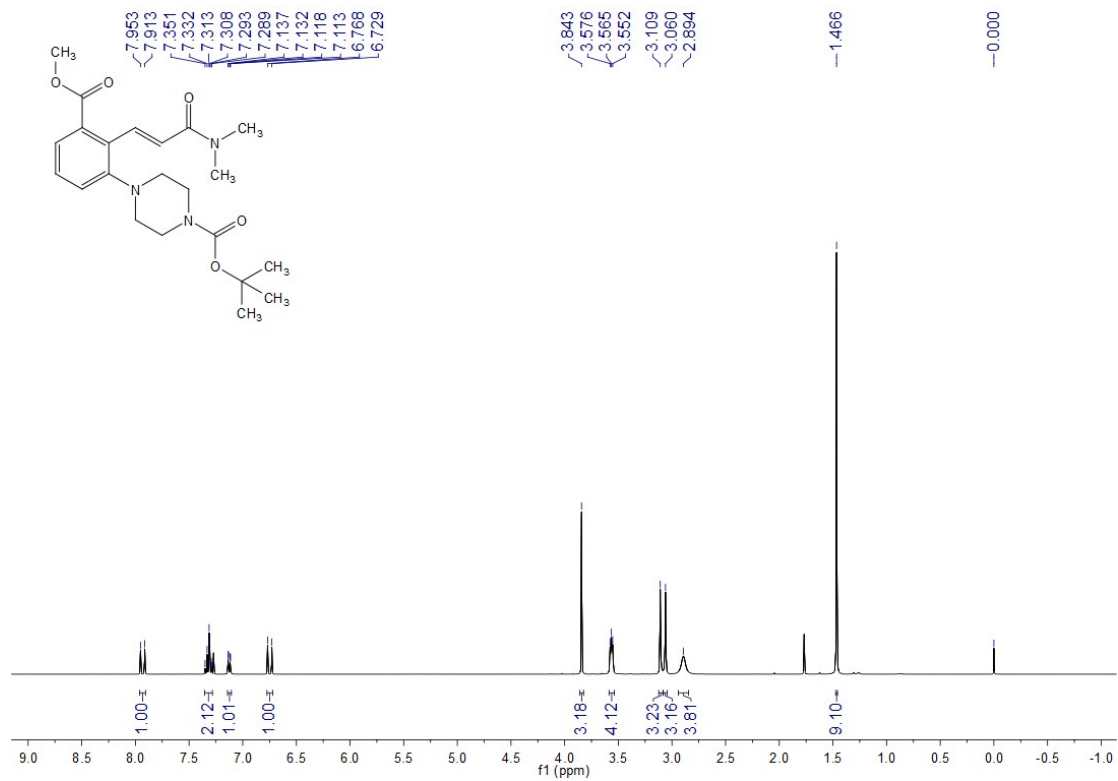
¹H NMR Spectrum of 4u



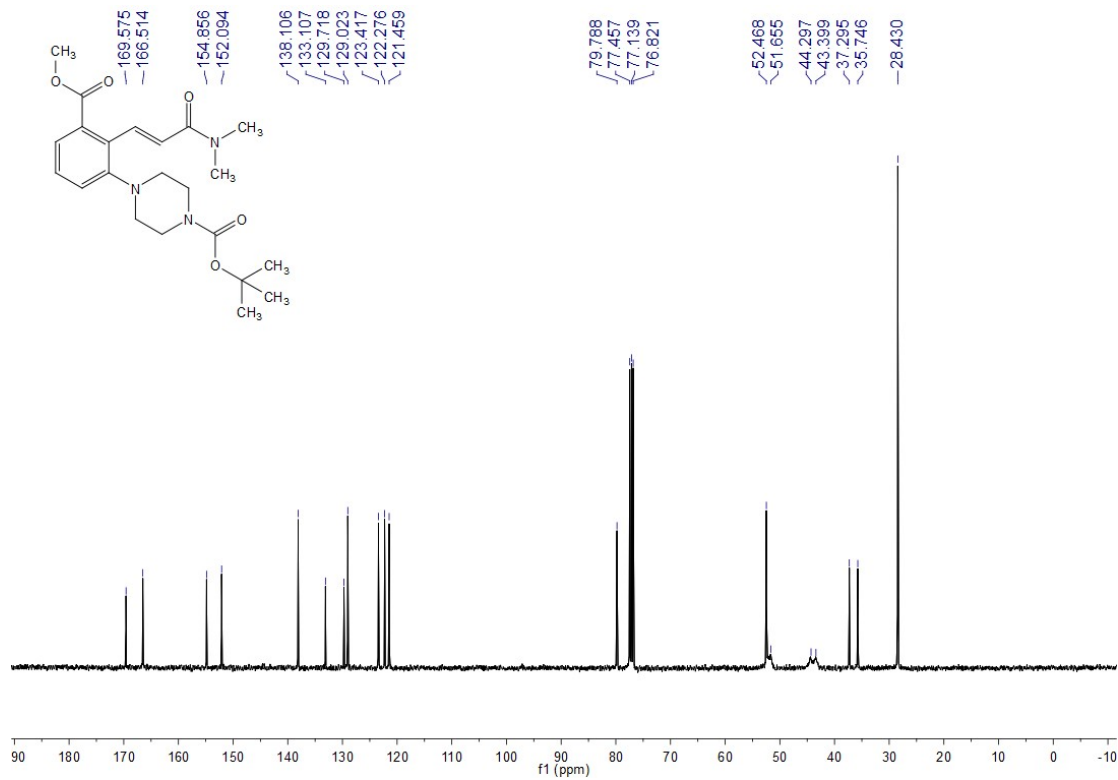
¹³C NMR Spectrum of 4u



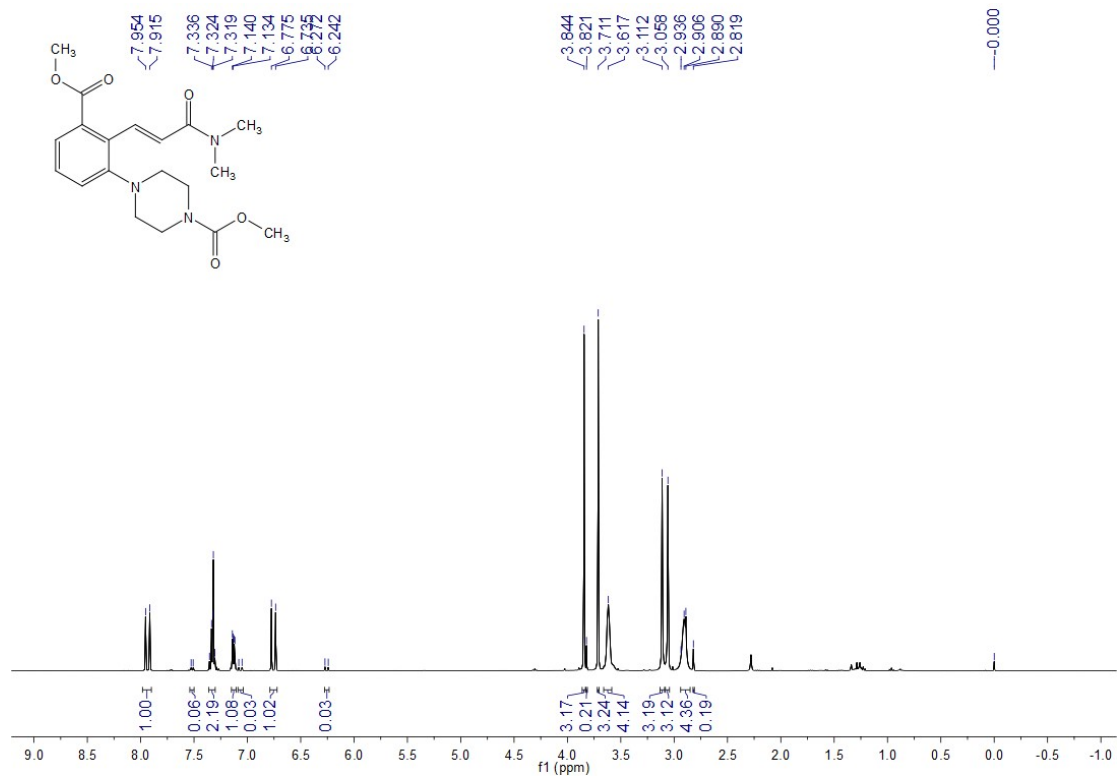
¹H NMR Spectrum of 4v



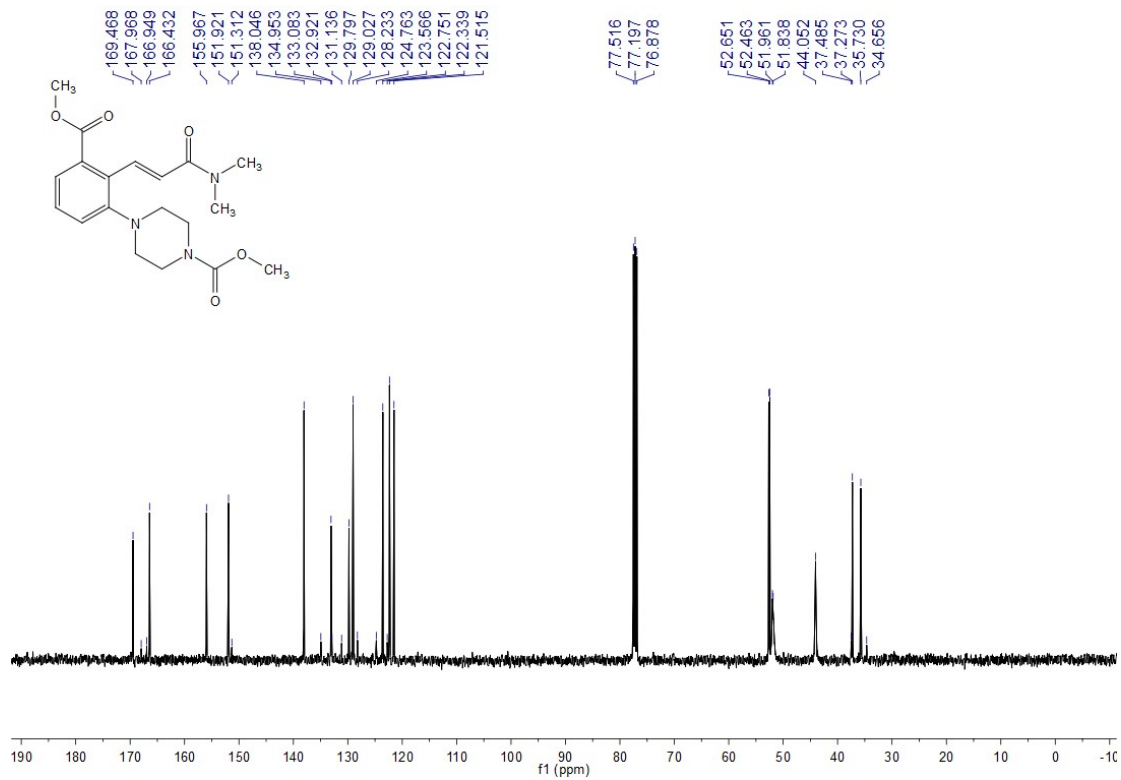
¹³C NMR Spectrum of 4v



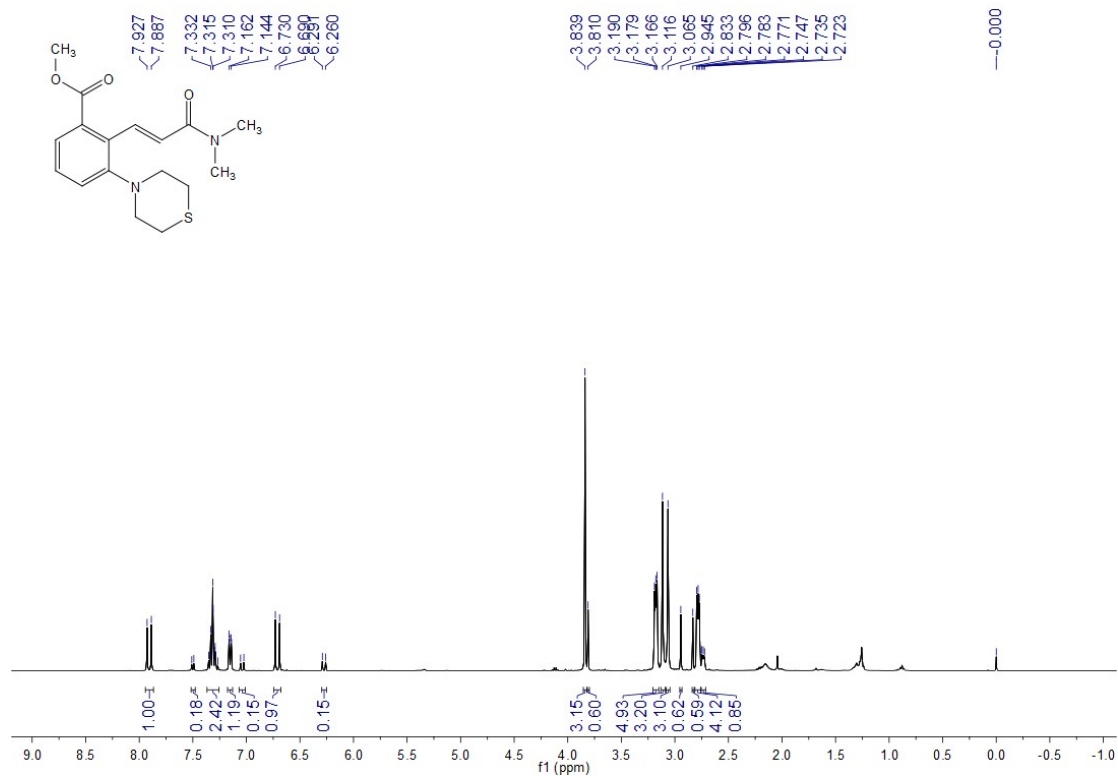
¹H NMR Spectrum of **4w**



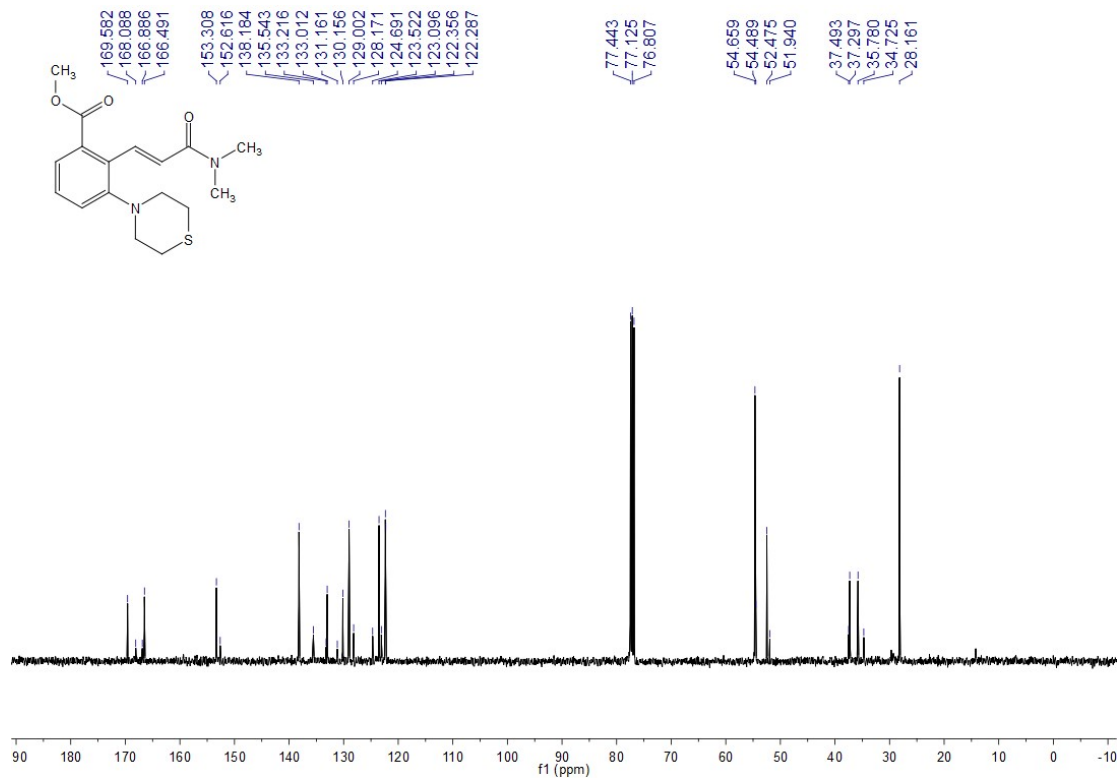
¹³C NMR Spectrum of **4w**



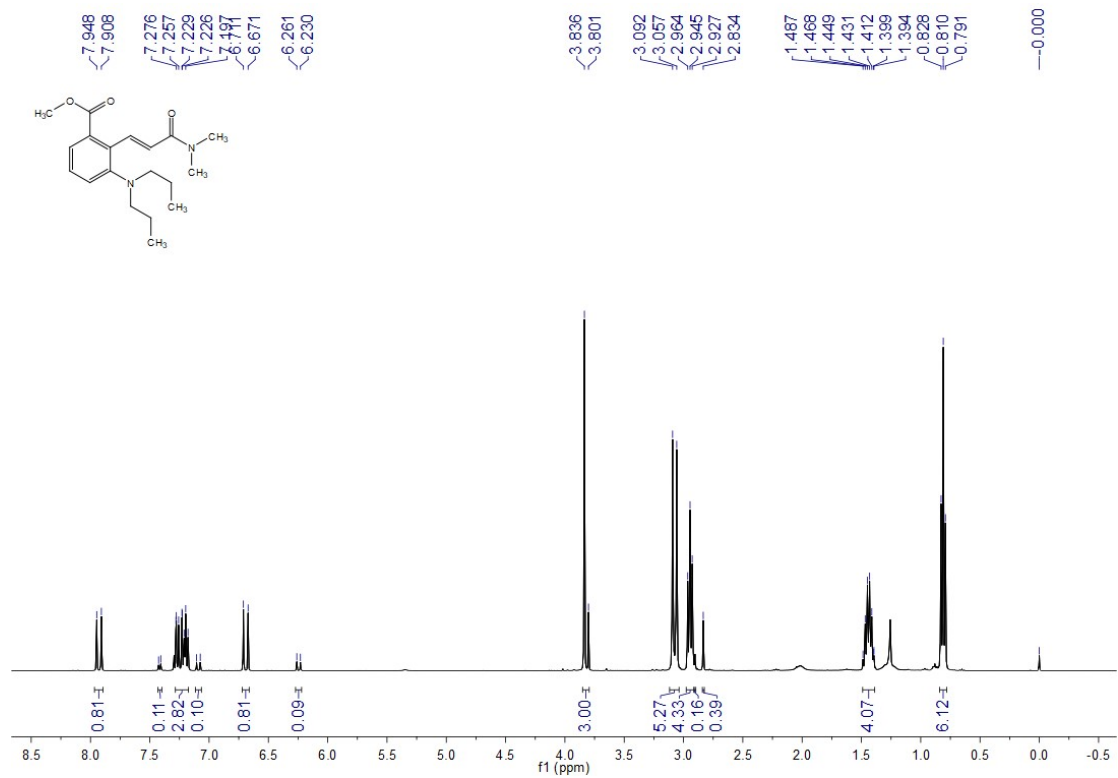
¹H NMR Spectrum of 4x



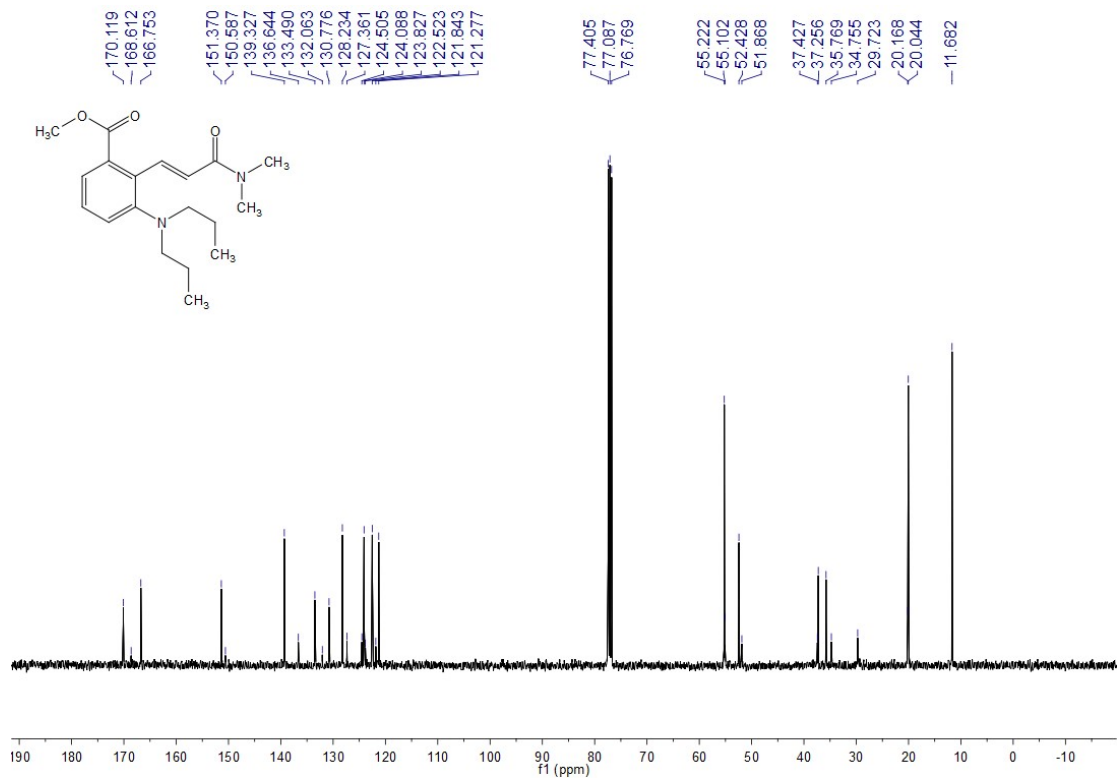
¹³C NMR Spectrum of 4x



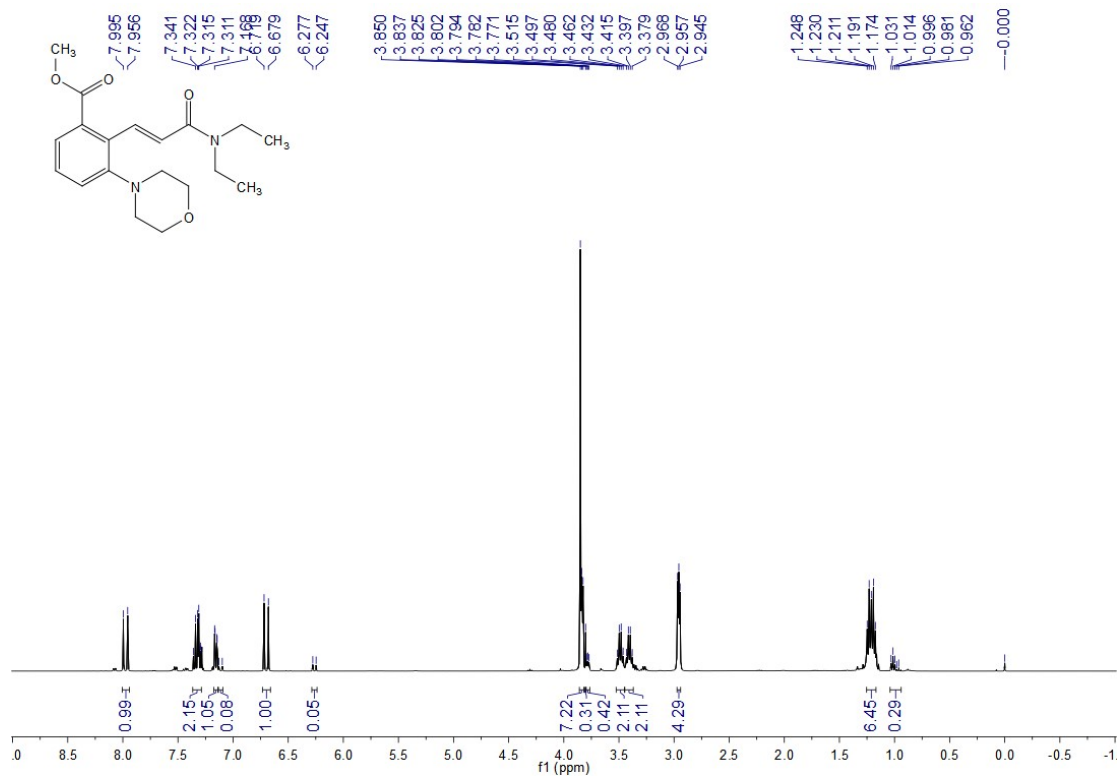
¹H NMR Spectrum of 4y



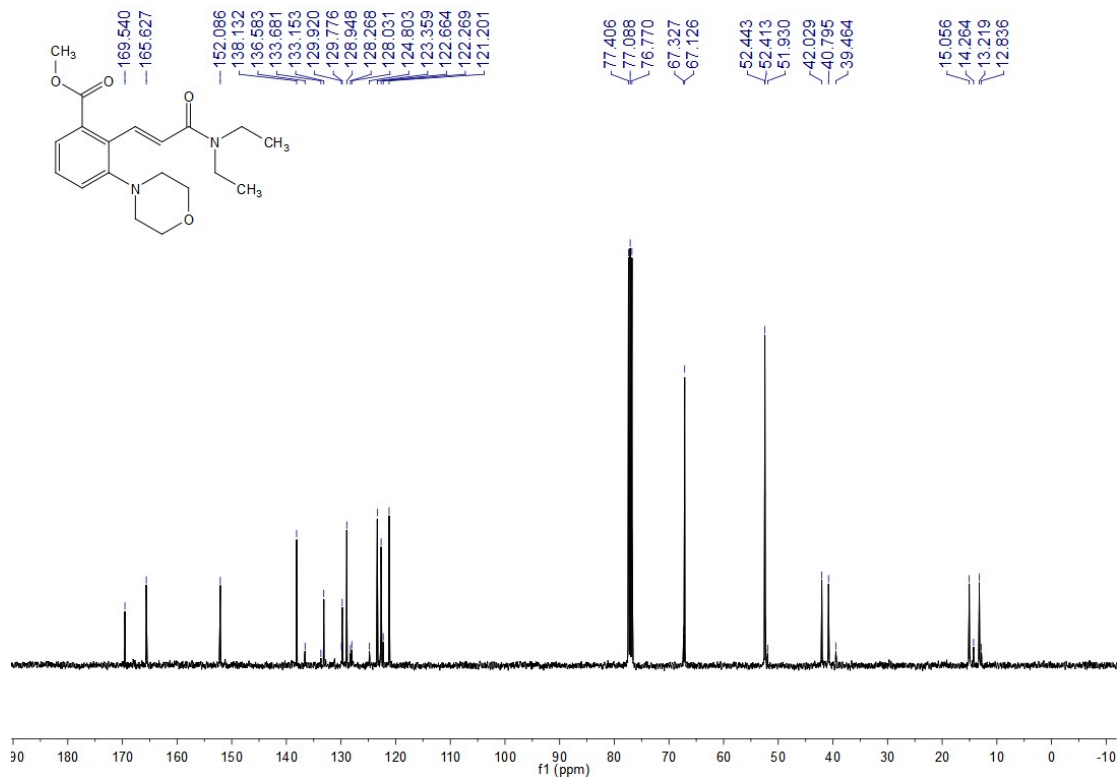
¹³C NMR Spectrum of 4y



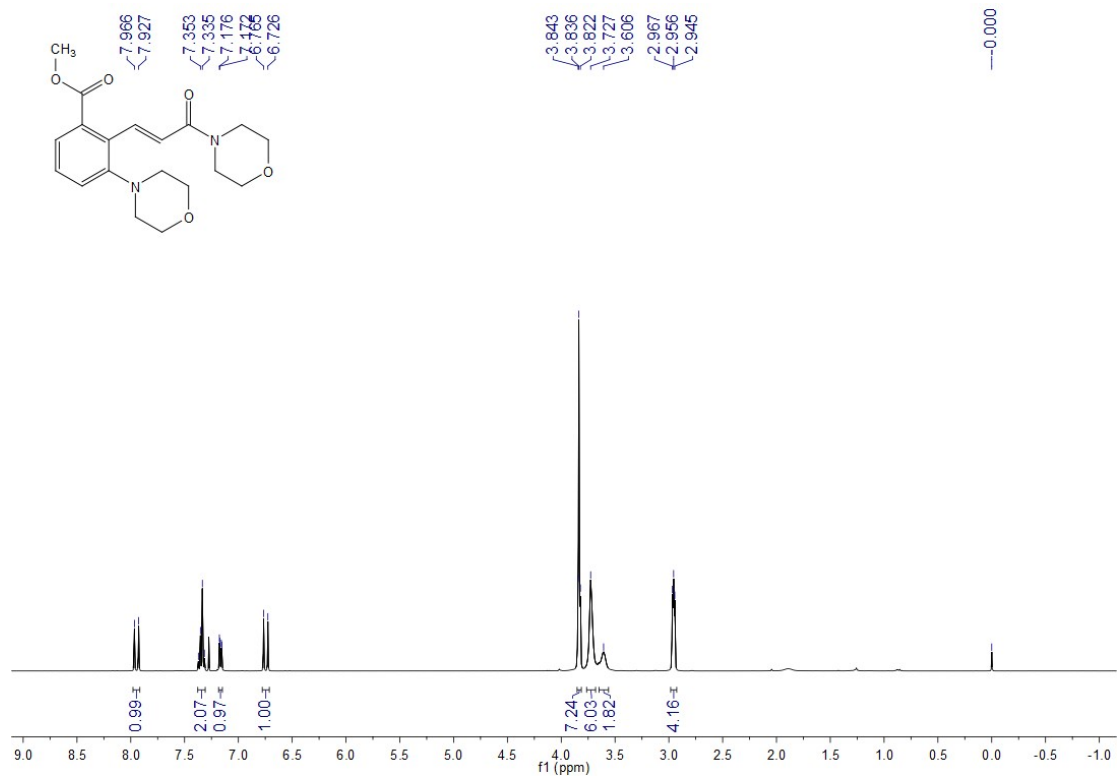
¹H NMR Spectrum of 4z



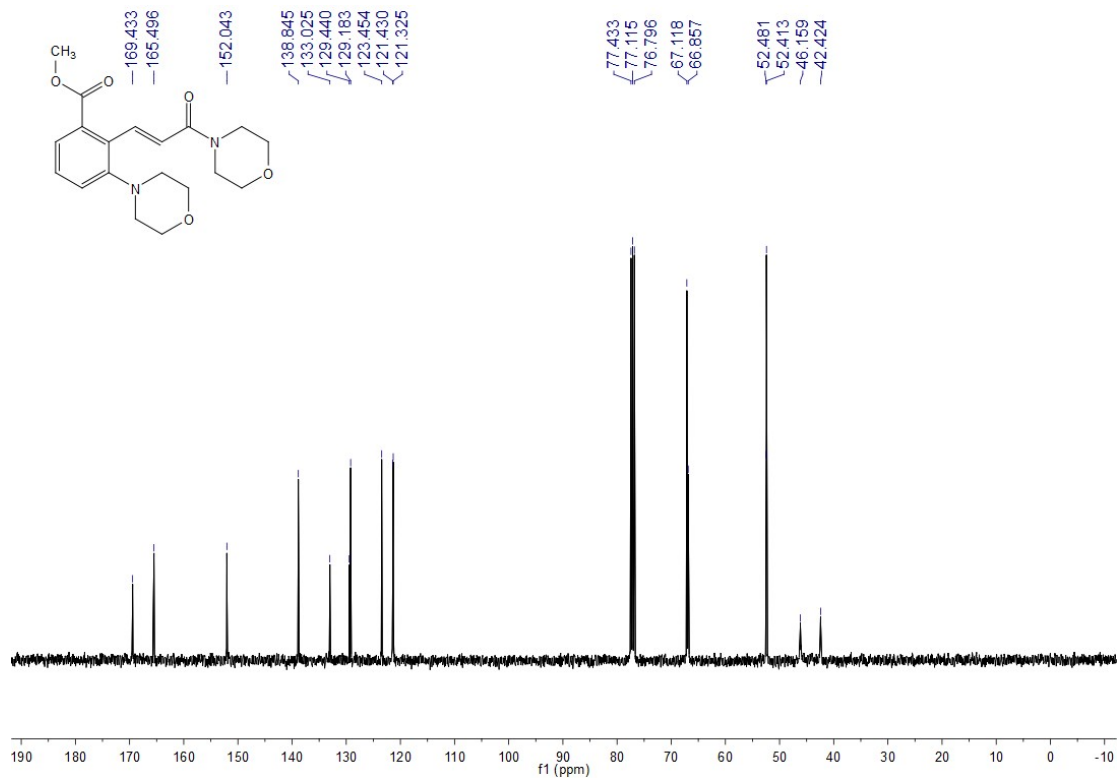
¹³C NMR Spectrum of 4z



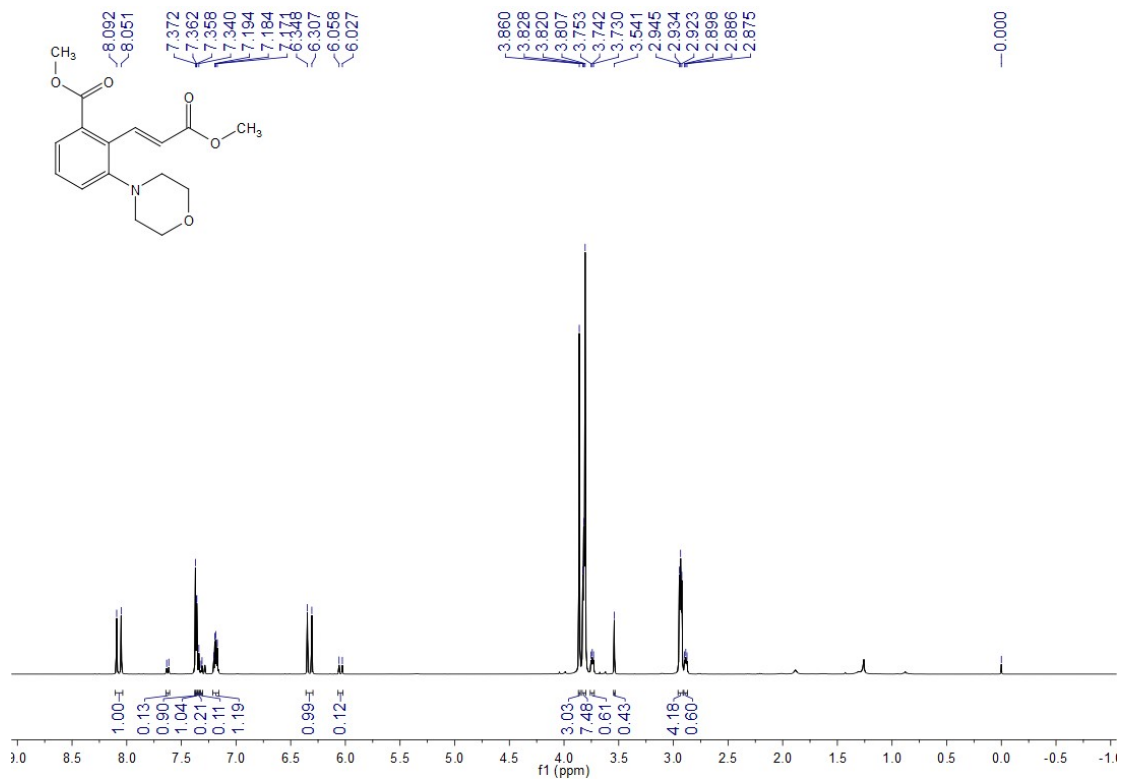
¹H NMR Spectrum of 4aa



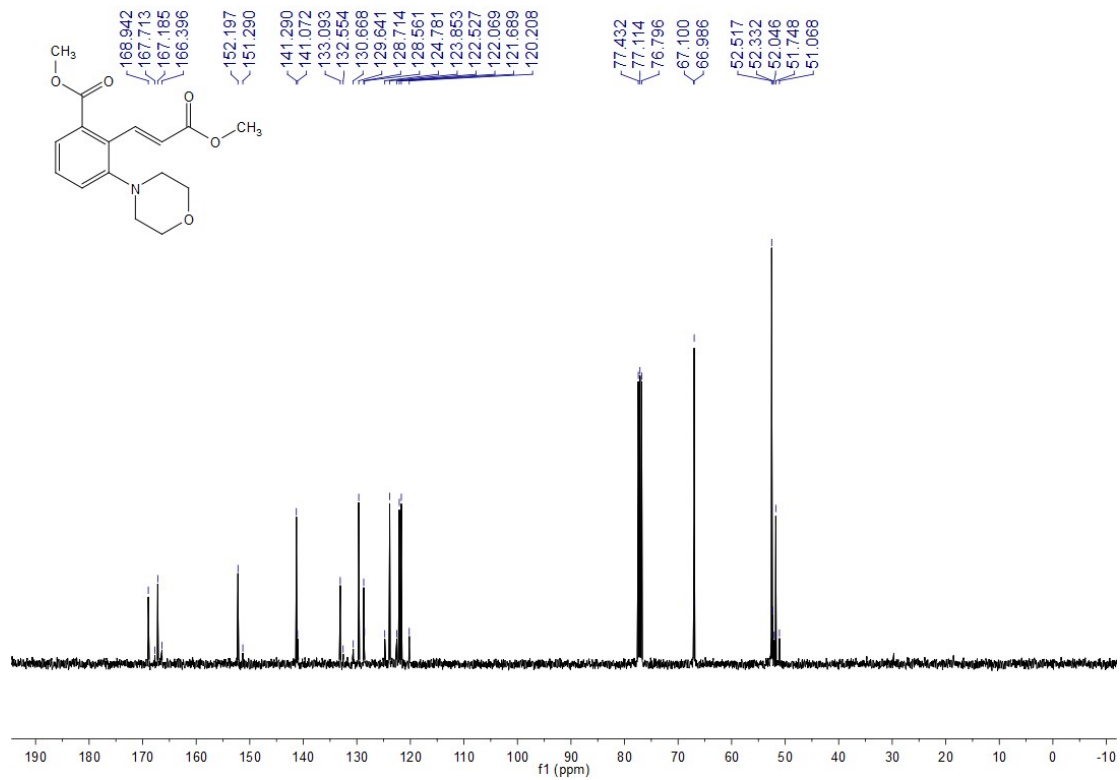
¹³C NMR Spectrum of 4aa



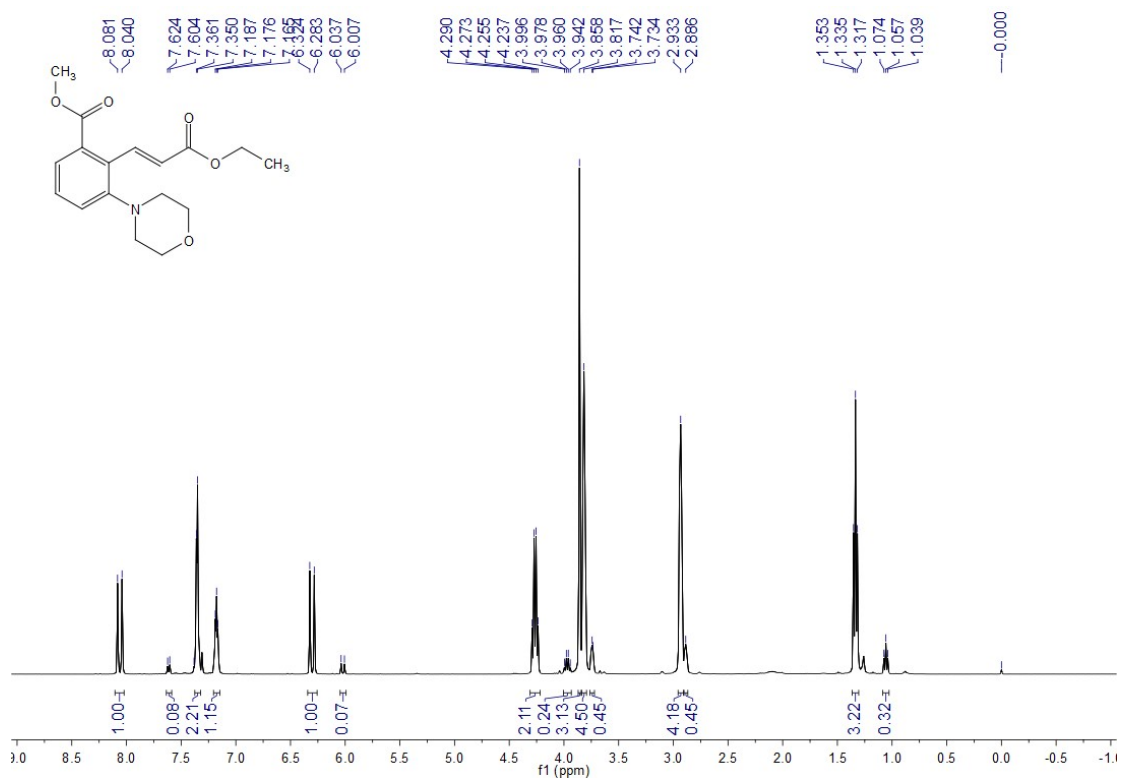
¹H NMR Spectrum of 4ab



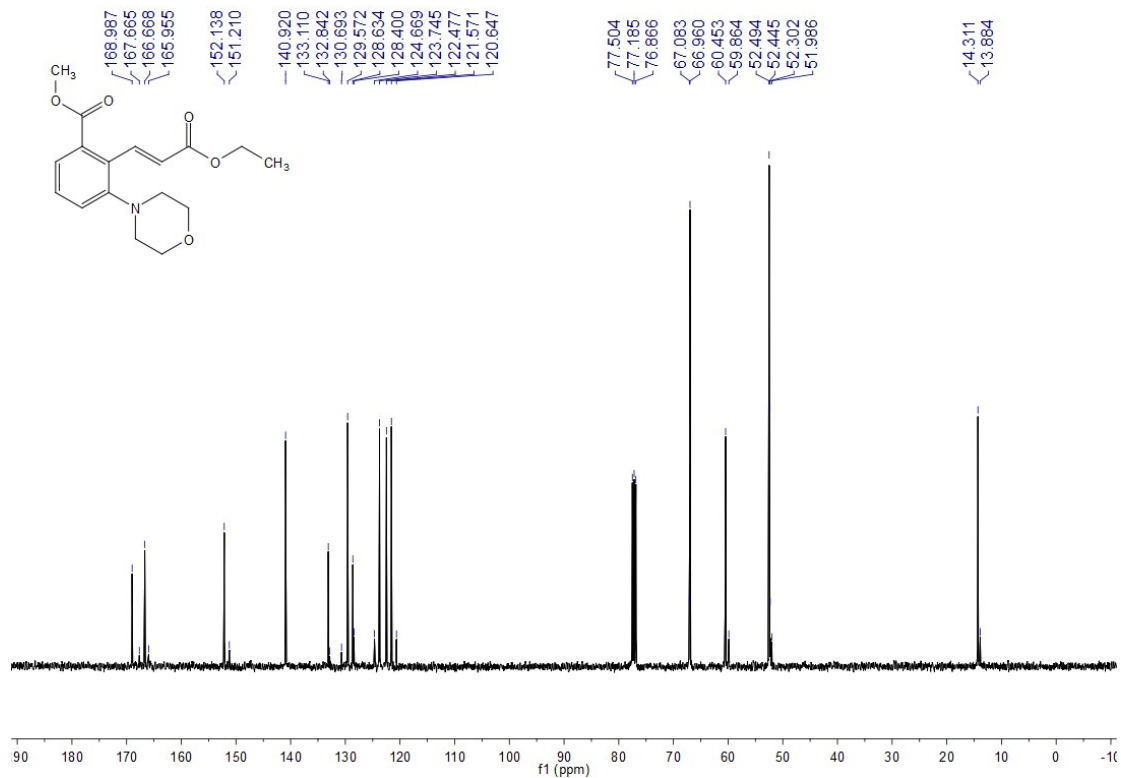
¹³C NMR Spectrum of 4ab



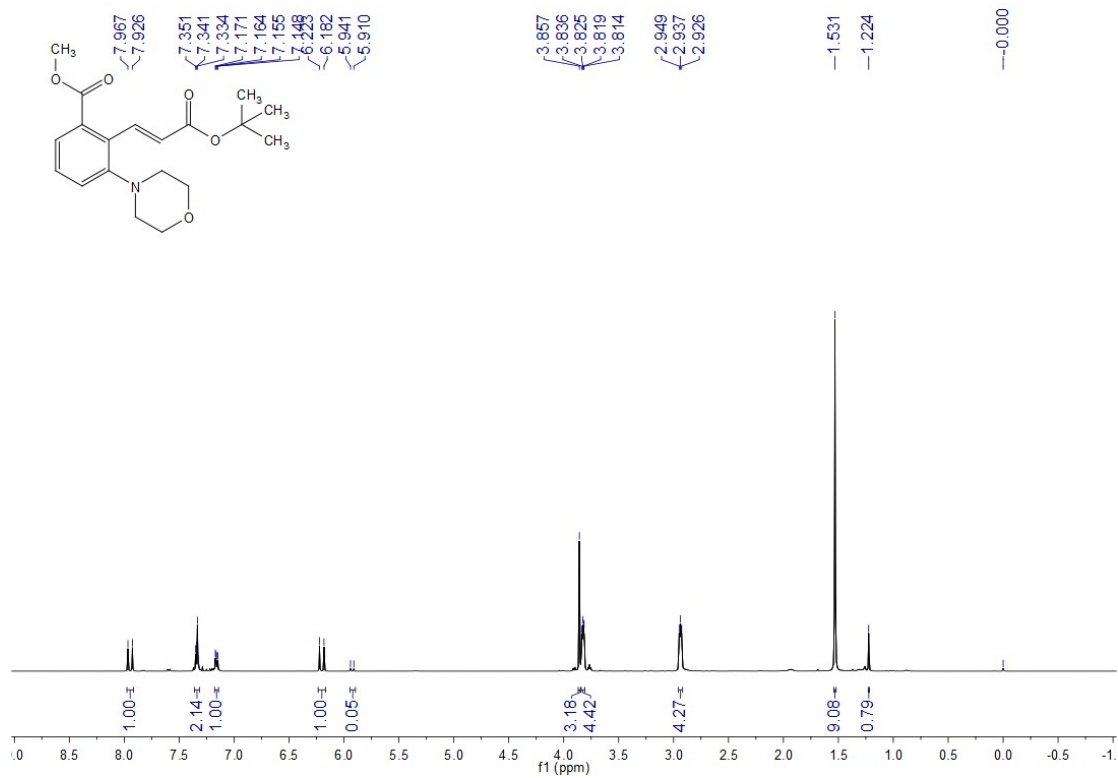
¹H NMR Spectrum of 4ac



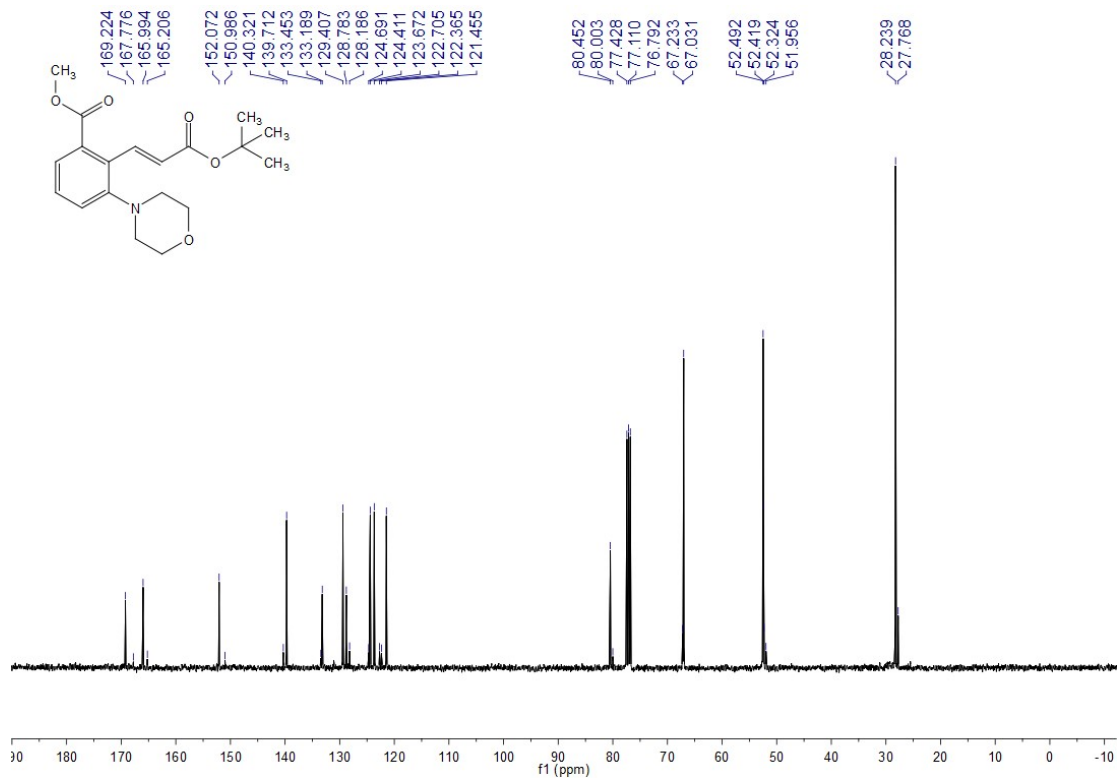
¹³C NMR Spectrum of 4ac



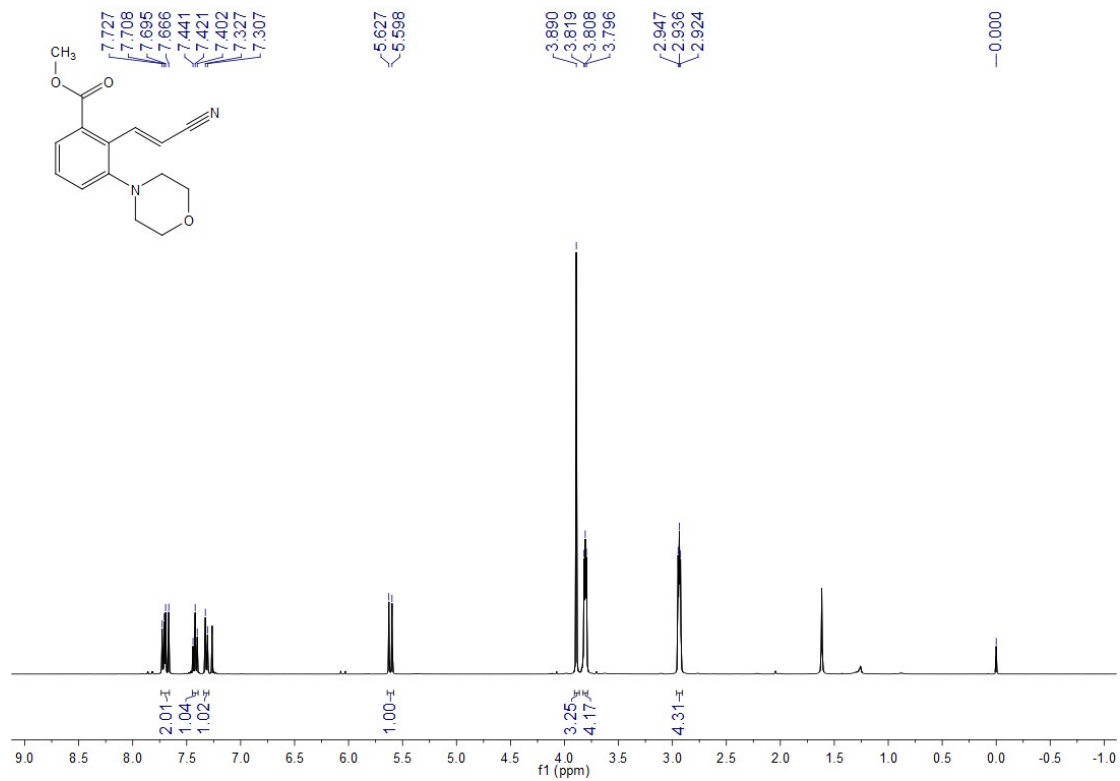
¹H NMR Spectrum of 4ad



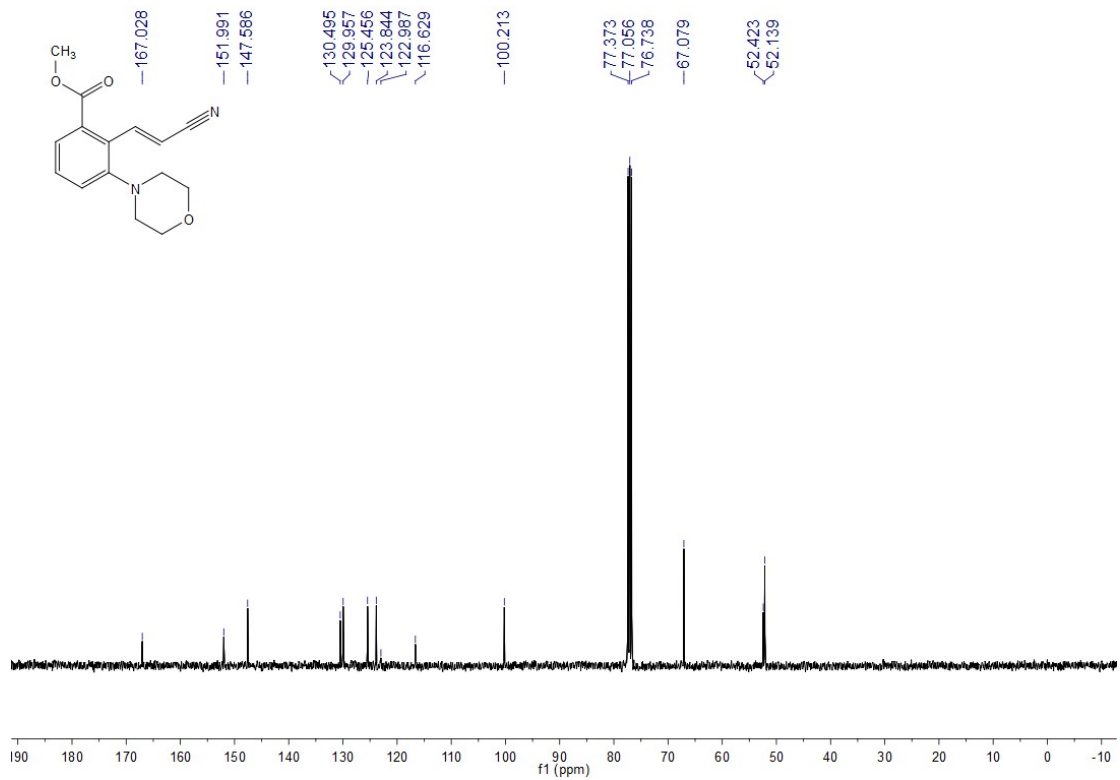
¹³C NMR Spectrum of 4ad



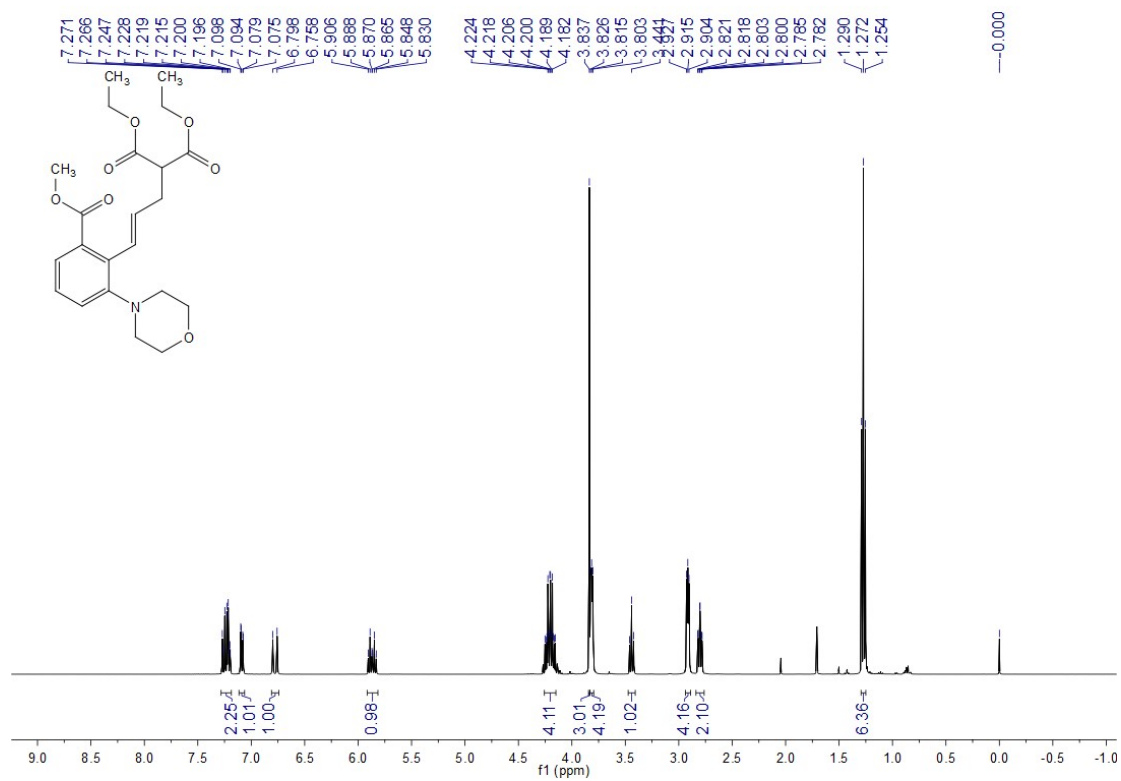
¹H NMR Spectrum of 4ae



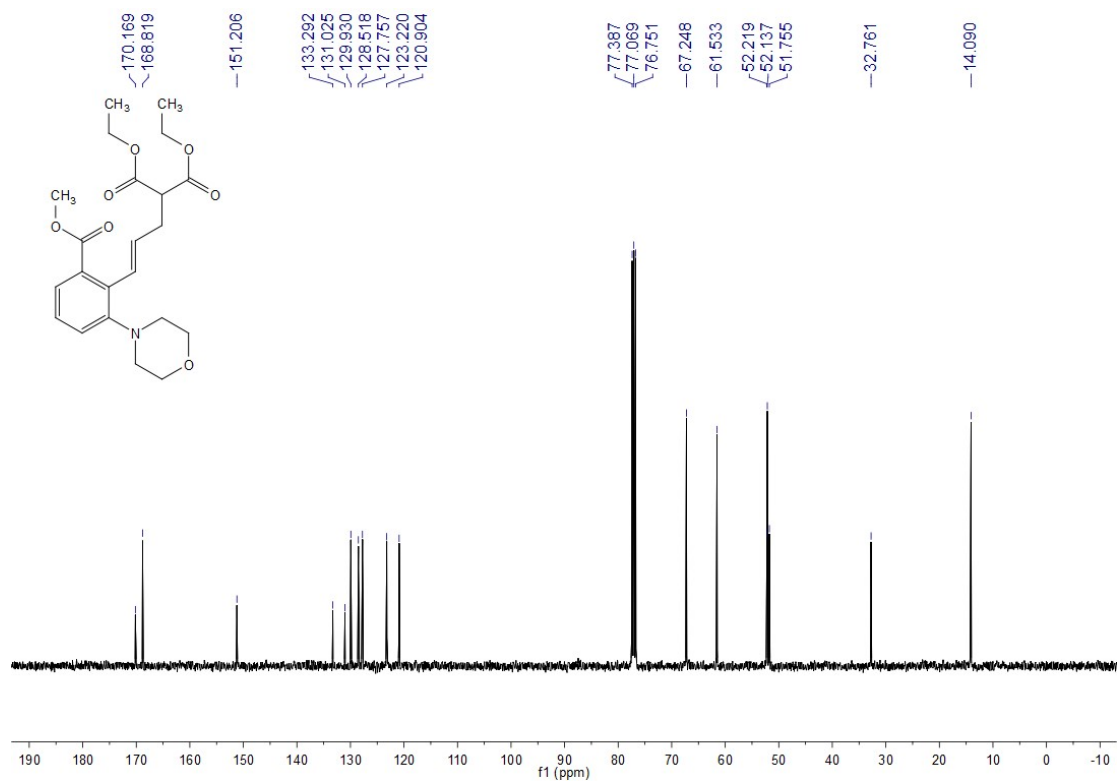
¹³C NMR Spectrum of 4ae



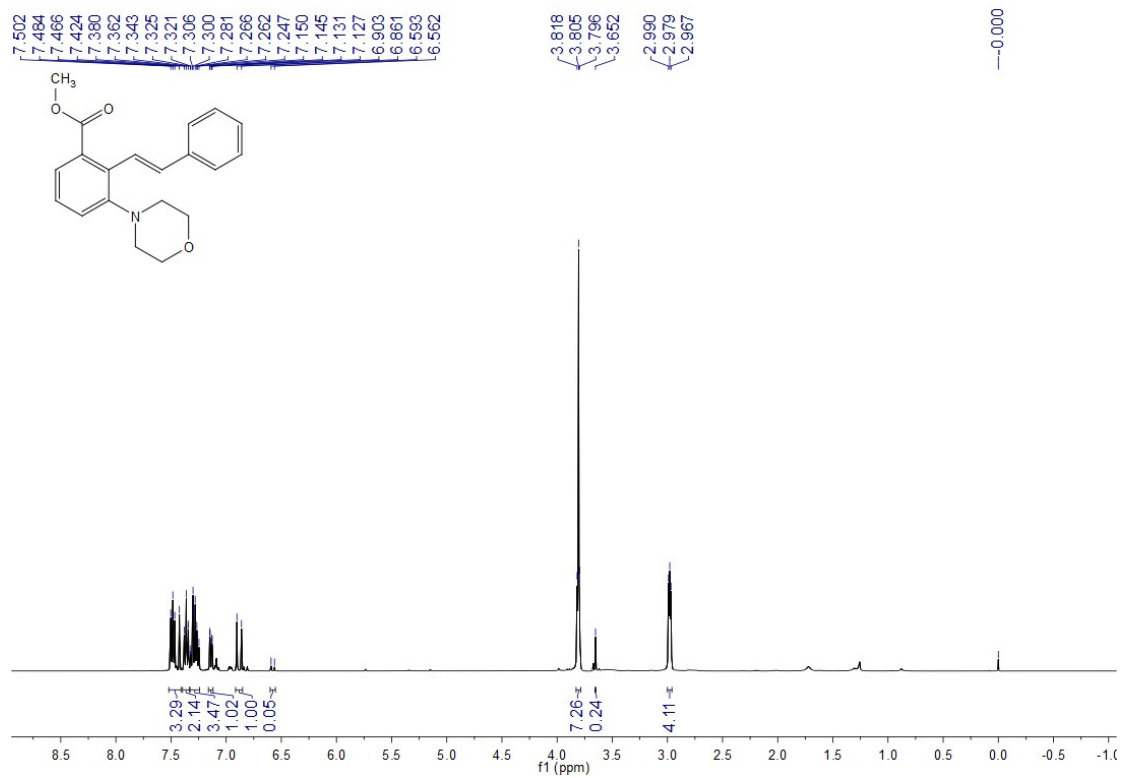
¹H NMR Spectrum of 4af



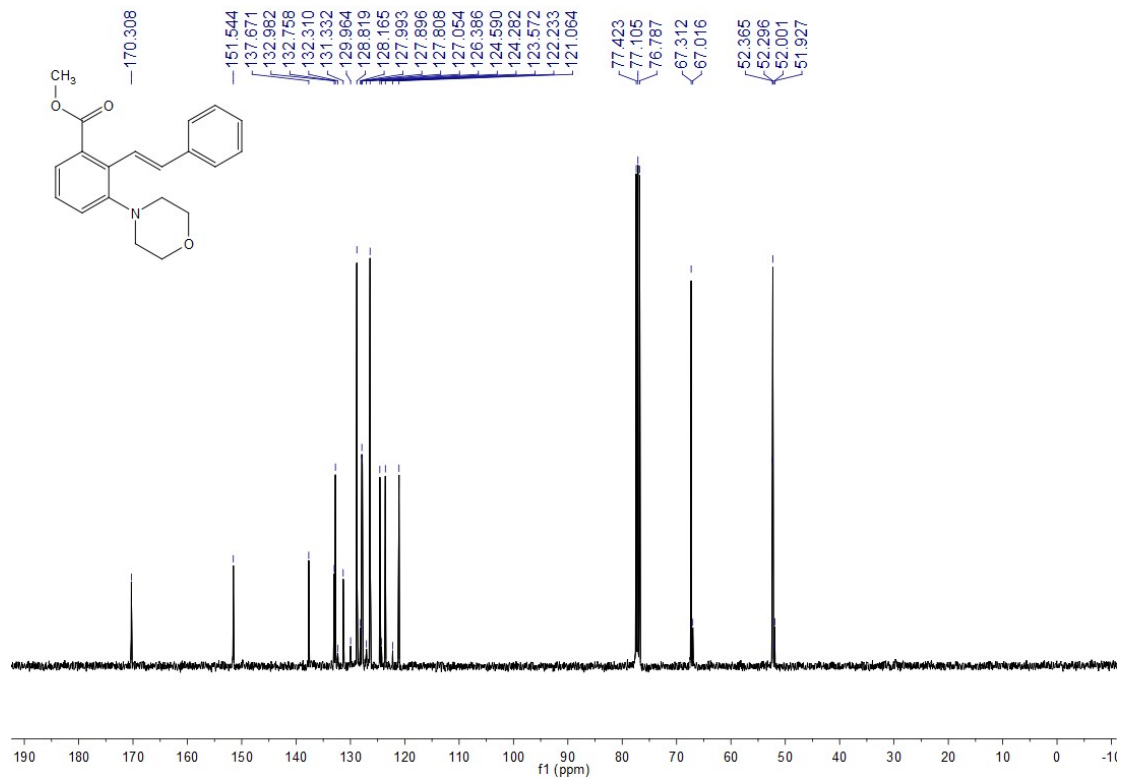
¹³C NMR Spectrum of 4af



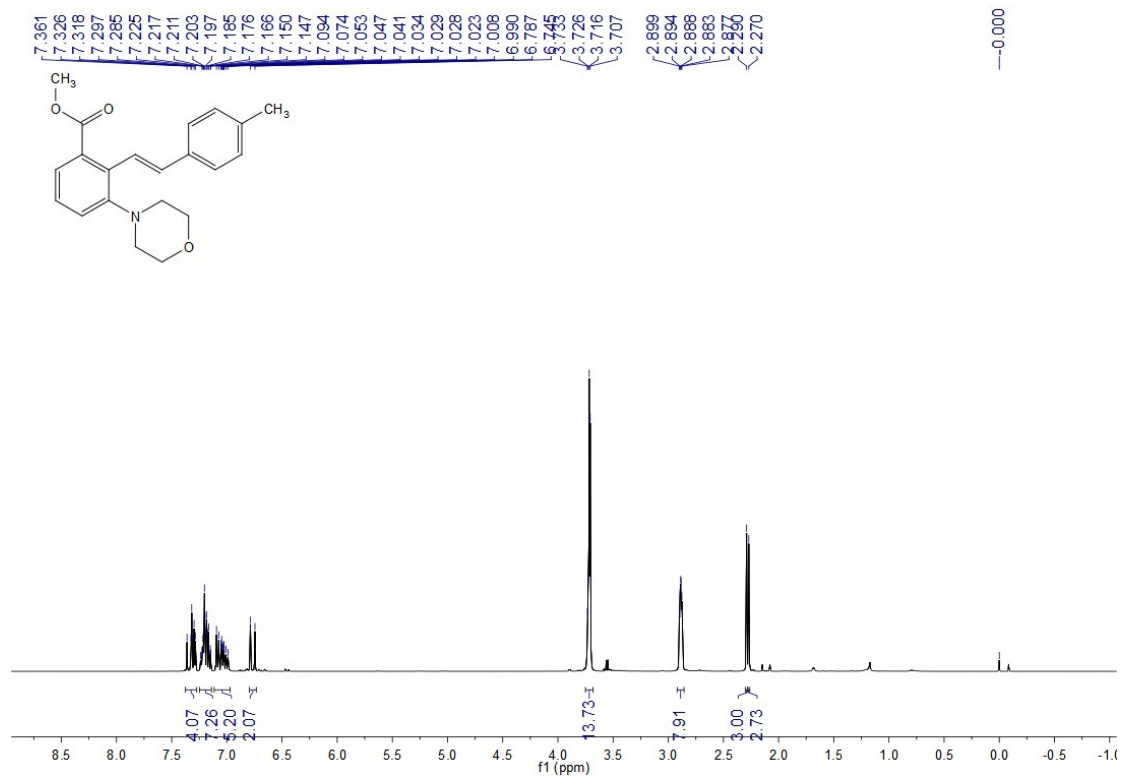
¹H NMR Spectrum of 4ag



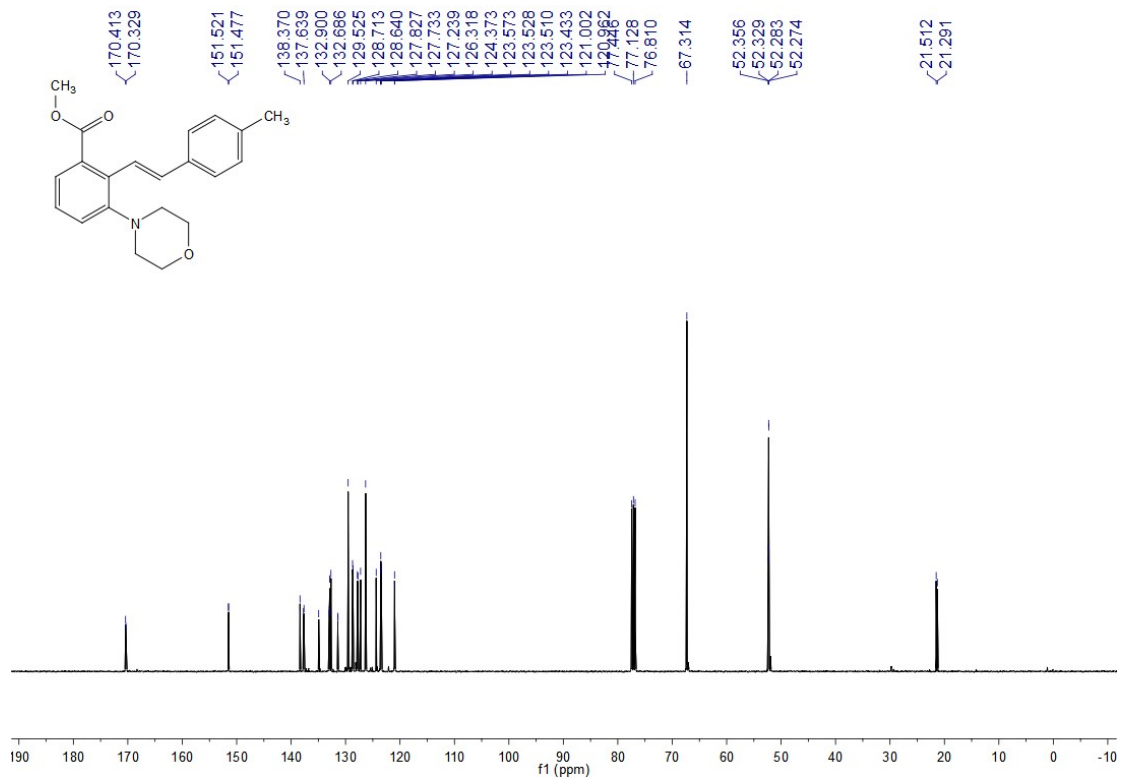
¹³C NMR Spectrum of 4ag



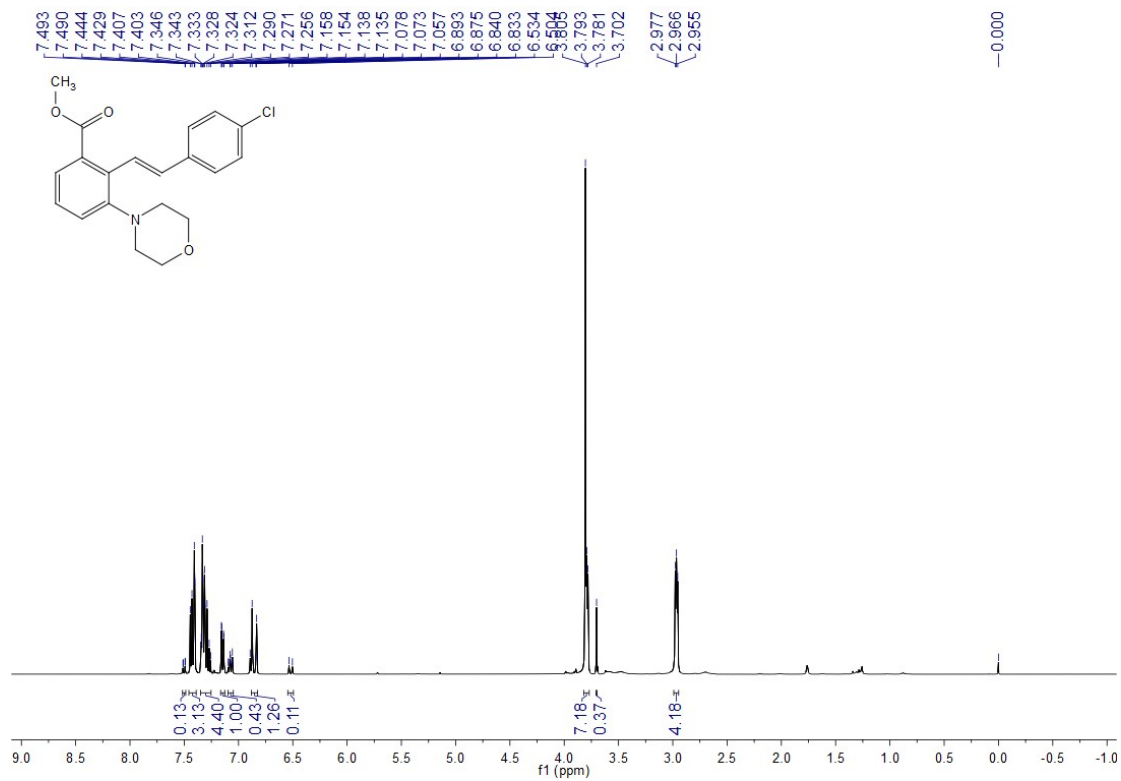
¹H NMR Spectrum of 4ah



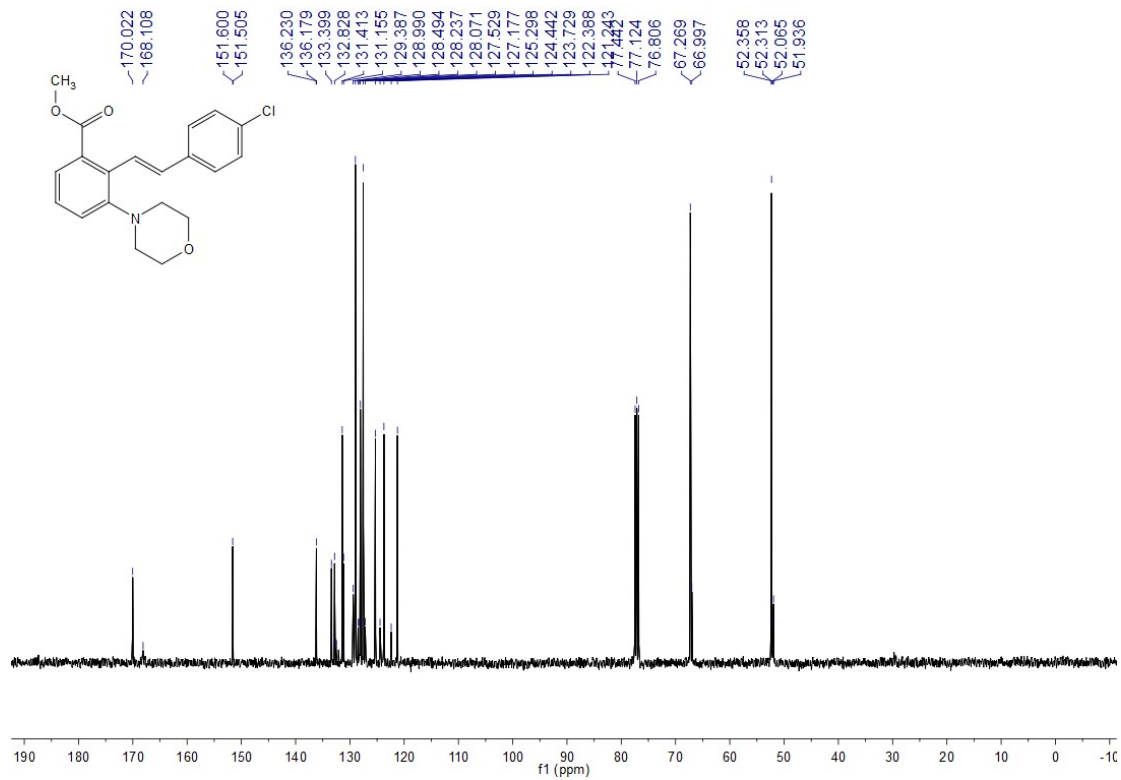
¹³C NMR Spectrum of 4ah



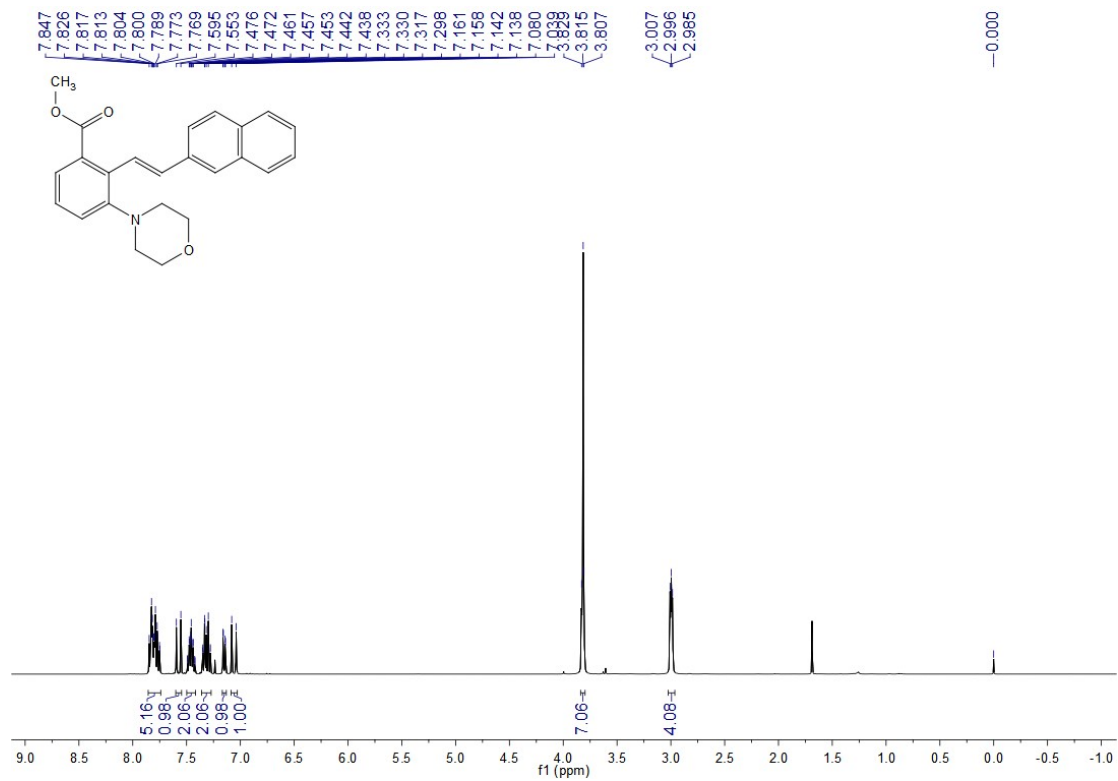
¹H NMR Spectrum of **4ai**



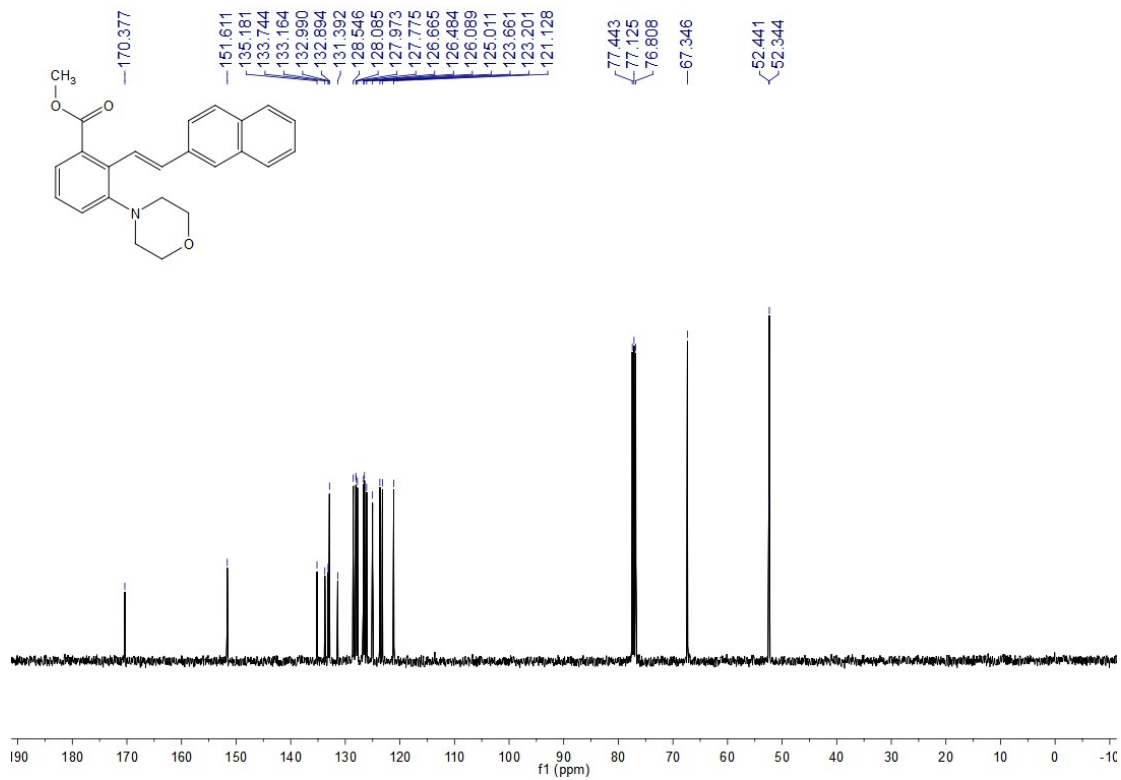
¹³C NMR Spectrum of **4ai**



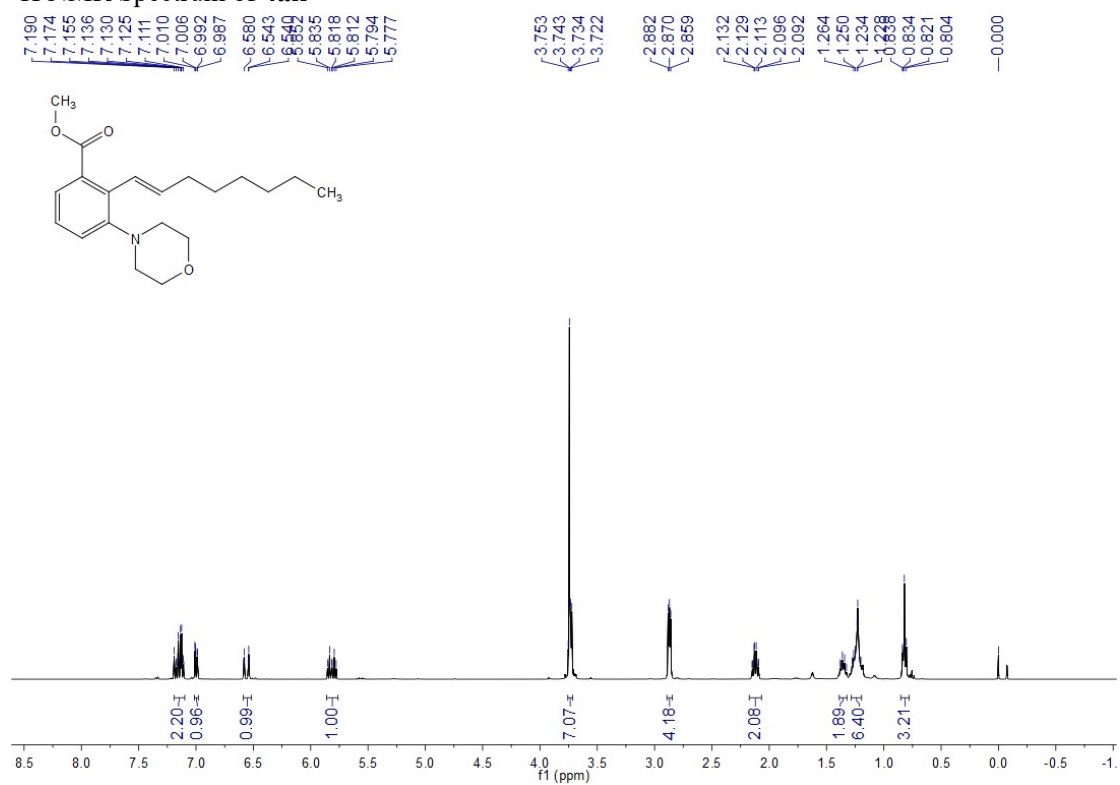
¹H NMR Spectrum of 4aj



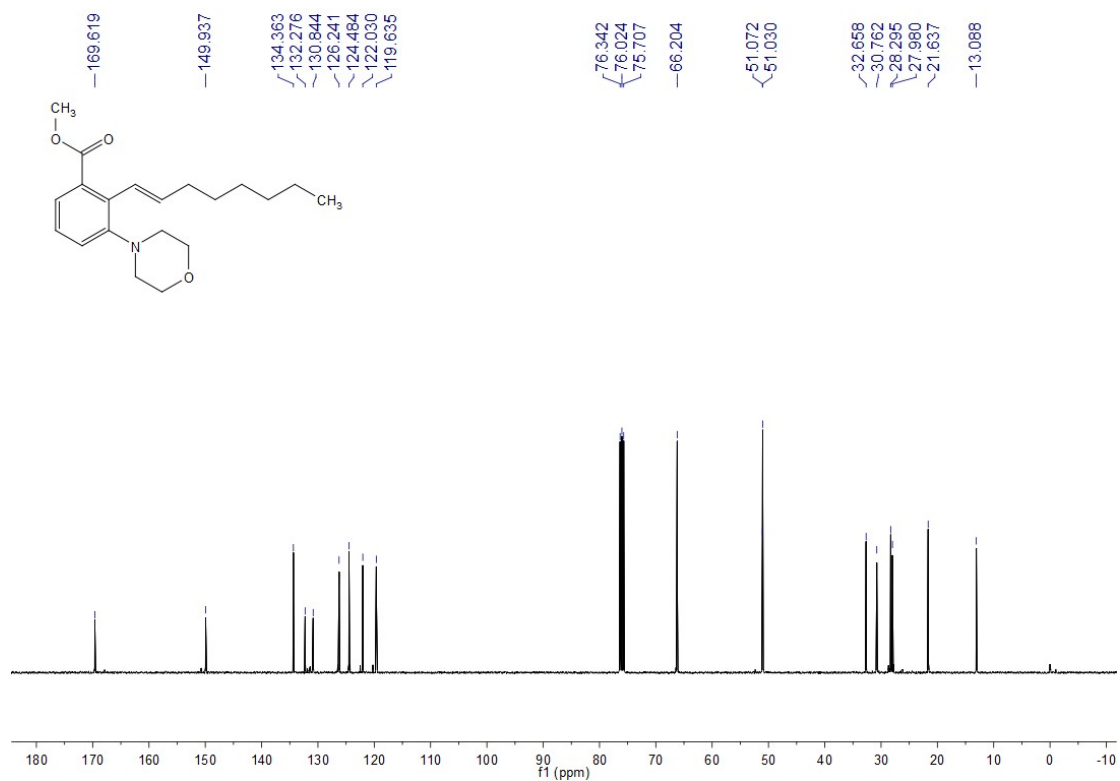
¹³C NMR Spectrum of 4aj



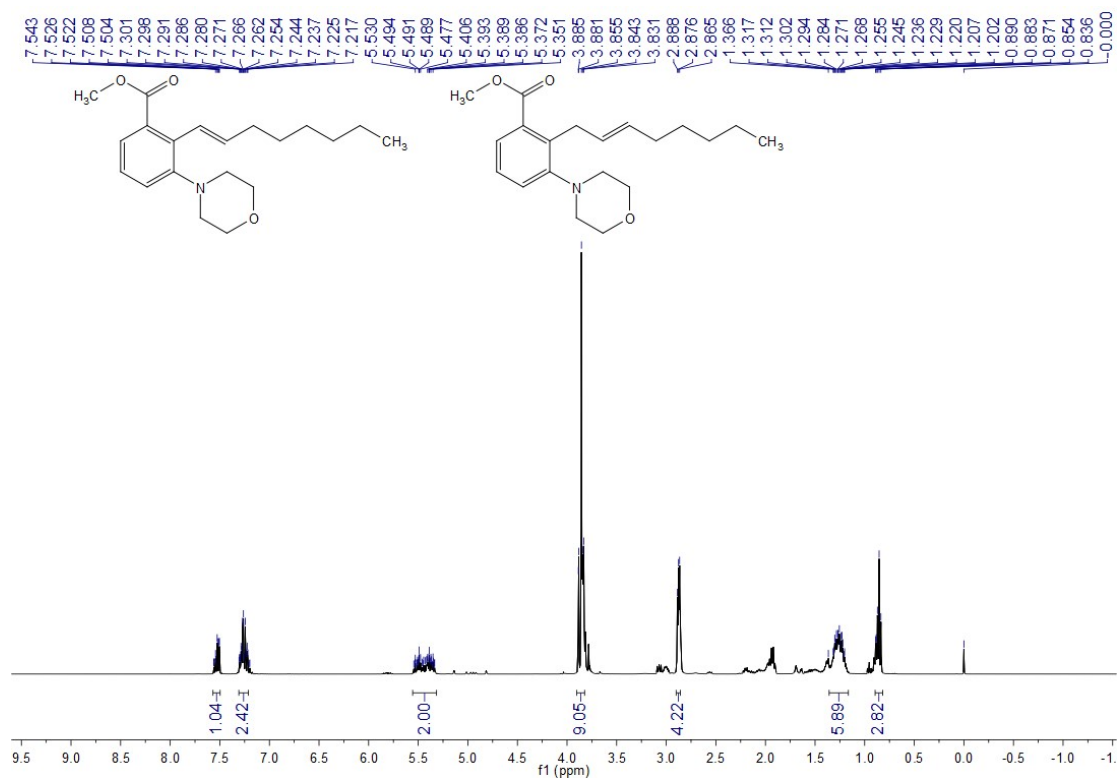
¹H NMR Spectrum of 4ak



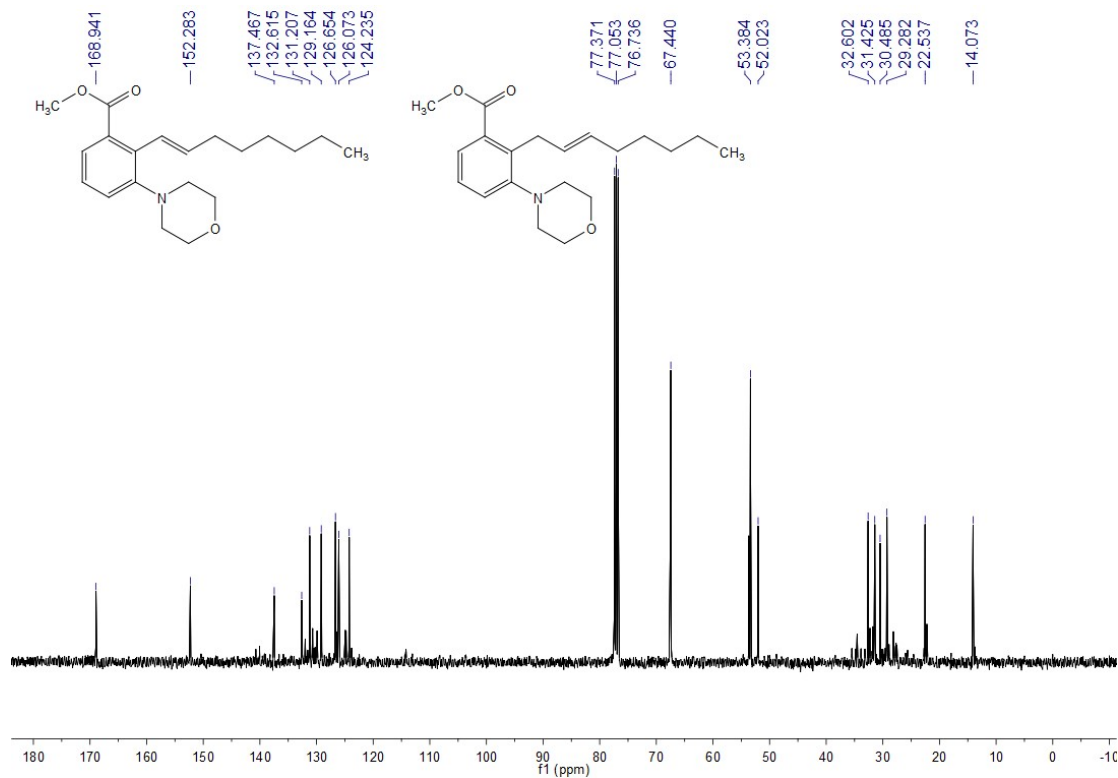
¹³C NMR Spectrum of 4ak



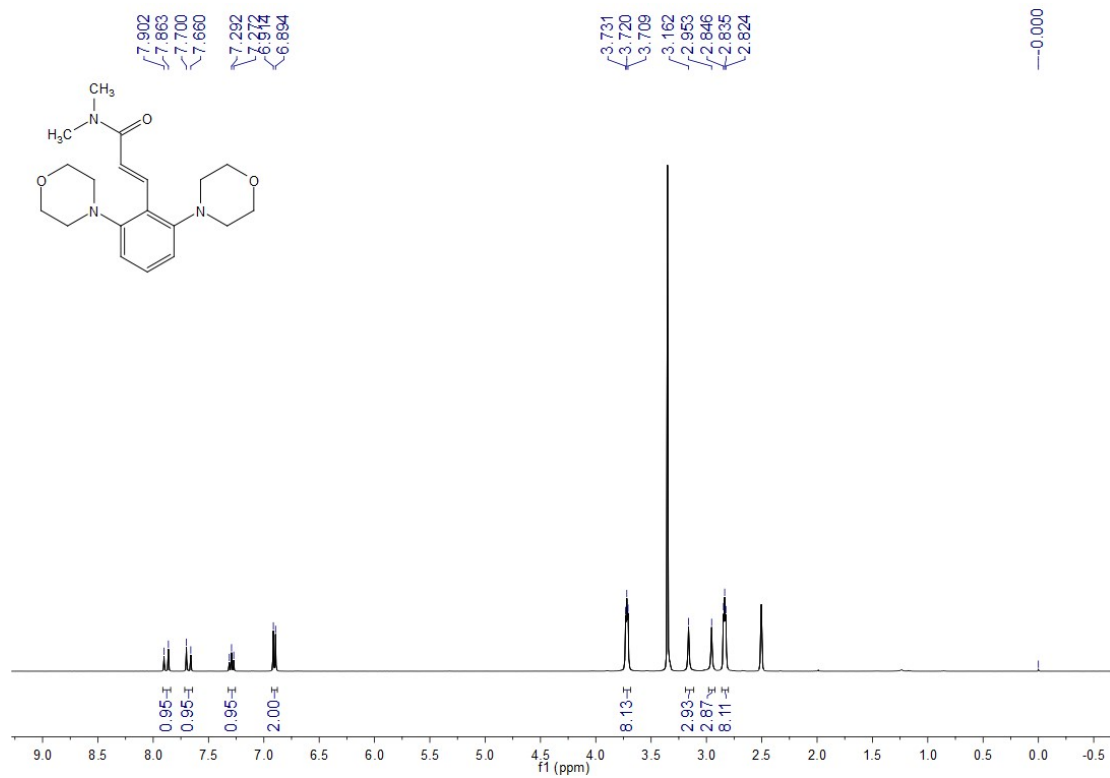
¹H NMR Spectrum of 4ak



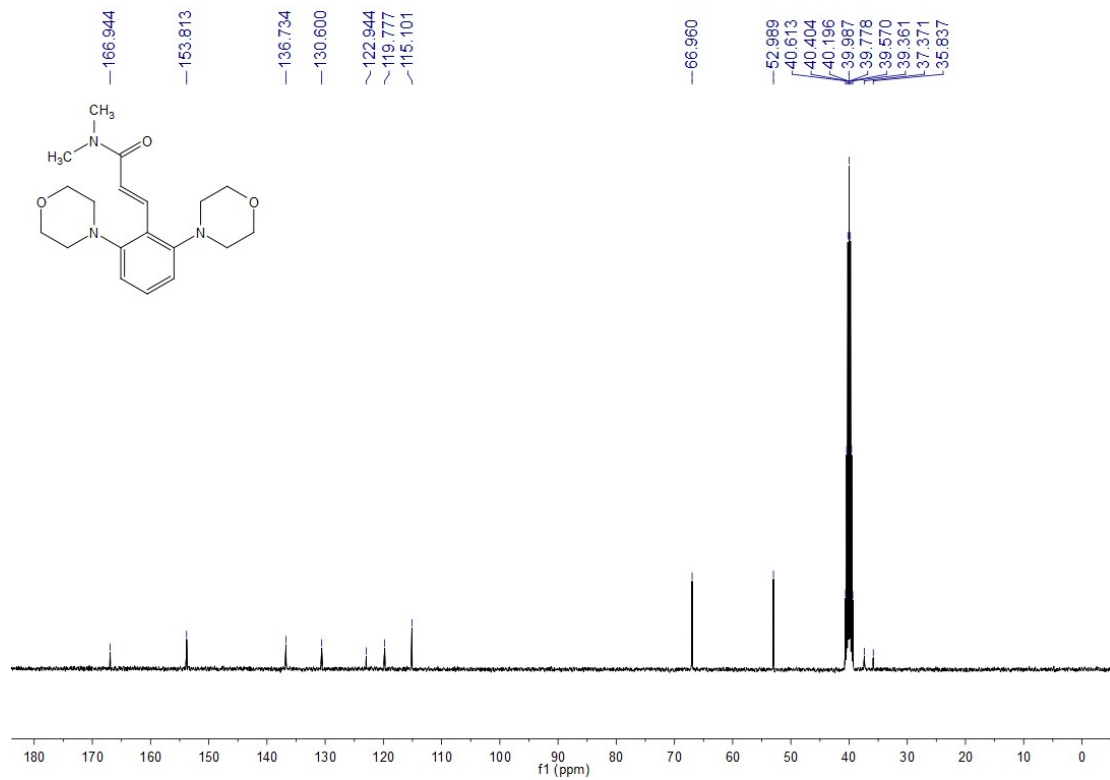
¹³C NMR Spectrum of 4ak



¹H NMR Spectrum of **4aI**



¹³C NMR Spectrum of **4aI**



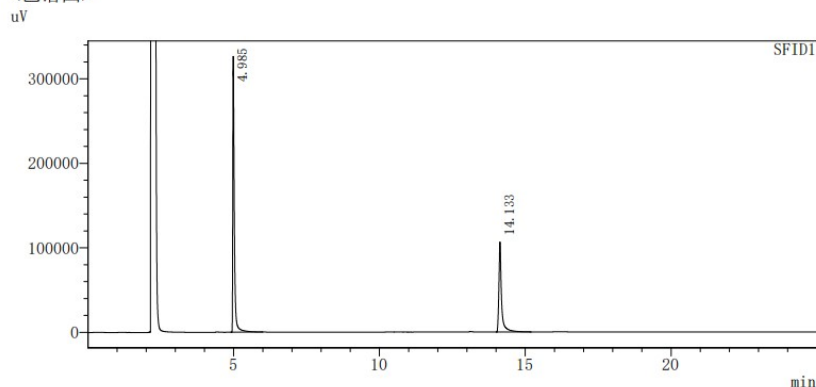
GC data diagram of 4a product, $f = 1.46$

SHIMADZU LabSolutions 分析报告

<样品信息>

样品名 :
 样品ID :
 数据文件名 : N, N-二甲基丙烯酰胺. gcb
 方法文件名 : 高温方法-280度-25min. gcm
 批处理文件名 : 20220321. gcb
 样品瓶号 : 3
 进样体积 : 1 uL
 分析日期 : 2022/3/21 23:43:12
 处理日期 : 2022/3/21 0:08:17
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

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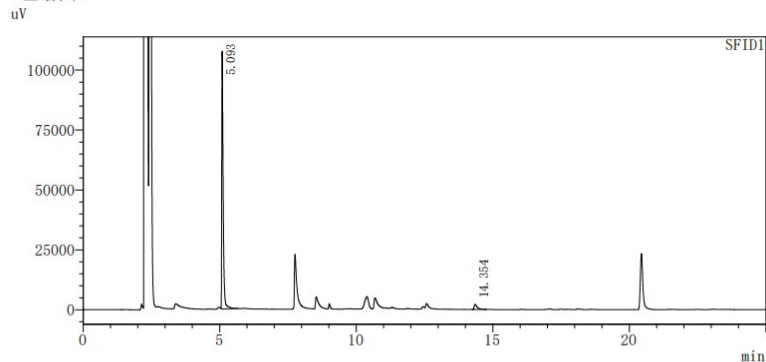
GC data diagram of entry 1

SHIMADZU LabSolutions 分析报告

<样品信息>

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 样品ID :
 数据文件名 : L-PP2. gcb
 方法文件名 : 高温方法-280度-25min. gcm
 批处理文件名 : 20220310. gcb
 样品瓶号 : 13
 进样体积 : 1 uL
 分析日期 : 2022/3/10 17:21:47
 处理日期 : 2022/3/10 17:46:50
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

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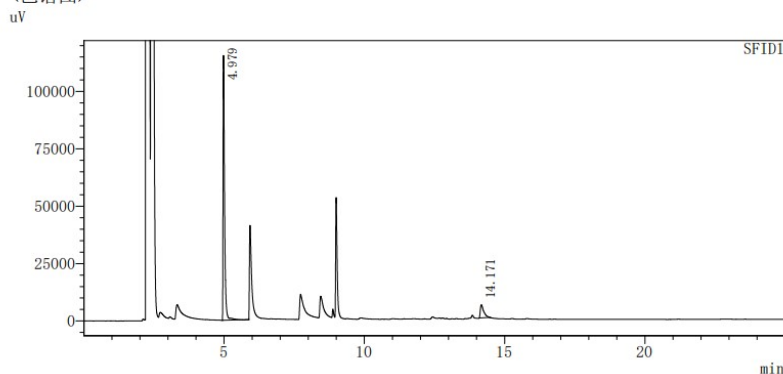
GC data diagram of entry 3

SHIMADZU LabSolutions 分析报告

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 样品ID :
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 方法文件名 : 高温方法-280度-25min.gcm
 批处理文件名 : 20220307.gcb
 样品瓶号 : 1
 进样体积 : 1 uL
 分析日期 : 2022/3/7 8:20:22
 处理日期 : 2022/3/7 8:45:28
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

<色谱图>



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2	14.171	48423	5724	10.167		M	
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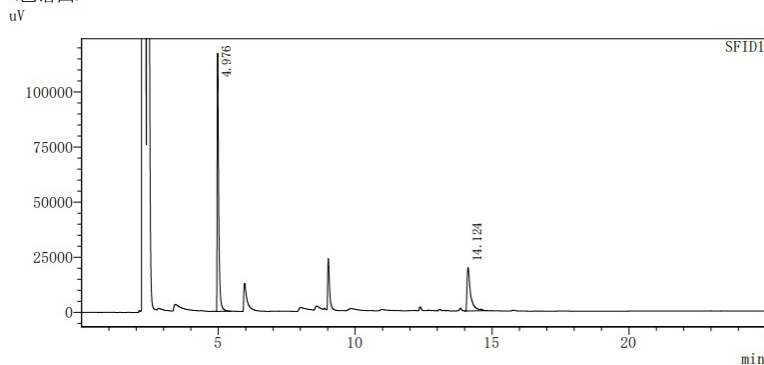
GC data diagram of entry 5

SHIMADZU LabSolutions 分析报告

<样品信息>

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 样品ID :
 数据文件名 : L-7.gcb
 方法文件名 : 高温方法-280度-25min.gcm
 批处理文件名 : 20220307.gcb
 样品瓶号 : 1
 进样体积 : 1 uL
 分析日期 : 2022/3/7 12:37:22
 处理日期 : 2022/3/7 13:02:26
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

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<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.976	448022	116256	71.375			
2	14.124	179677	19674	28.625			
总计		627699	135930				

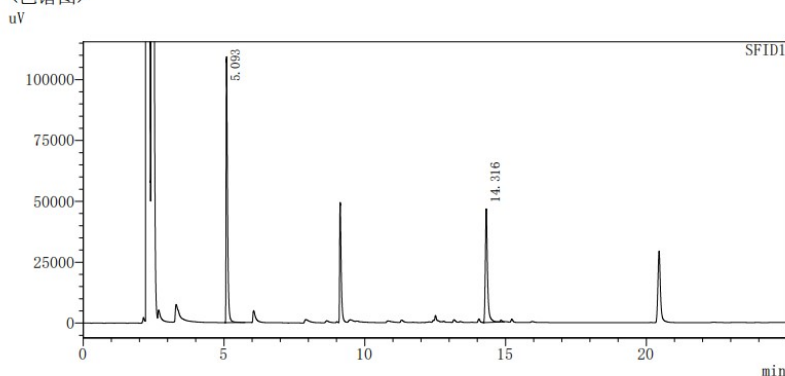
GC data diagram of entry 7

SHIMADZU LabSolutions 分析报告

<样品信息>

样品名 :
 样品ID :
 数据文件名 : L-9. gcb
 方法文件名 : 高温方法-280度-25min. gcm
 批处理文件名 : 20220309. gcb
 样品瓶号 : 11
 进样体积 : 1 uL
 分析日期 : 2022/3/9 16:15:29
 处理日期 : 2022/3/9 16:40:24
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

<色谱图>



<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.093	383976	108703	60.329			
2	14.316	252489	46562	39.671		S	
总计		636465	155264				

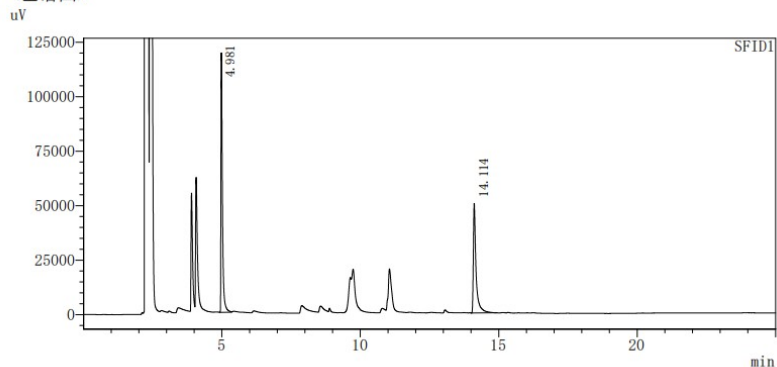
GC data diagram of entry 9

SHIMADZU LabSolutions 分析报告

<样品信息>

样品名 :
 样品ID :
 数据文件名 : L-10. gcb
 方法文件名 : 高温方法-280度-25min. gcm
 批处理文件名 : 20220311. gcb
 样品瓶号 : 25
 进样体积 : 1 uL
 分析日期 : 2022/3/11 1:13:23
 处理日期 : 2022/3/11 1:38:37
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

<色谱图>



<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.981	445335	118342	56.713			
2	14.114	339912	50163	43.287			
总计		785247	168504				

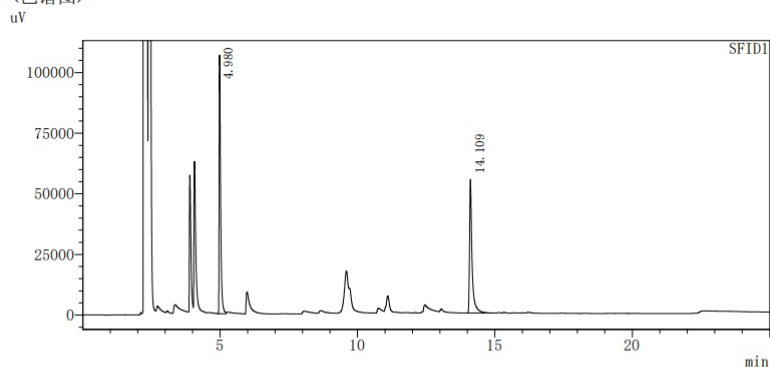
GC data diagram of entry 30

SHIMADZU LabSolutions 分析报告

<样品信息>

样品名 :
 样品ID :
 数据文件名 : wendu-3.gcd
 方法文件名 : 高温方法-280度-25min.gcm
 批处理文件名 : 20220417.gcb
 样品瓶号 : 5
 进样体积 : 1 uL
 分析日期 : 2022/4/17 11:20:40
 处理日期 : 2022/4/17 11:45:54
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

<色谱图>



<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.980	391792	105736	53.208			
2	14.109	344543	55040	46.792			
总计		736335	160775				

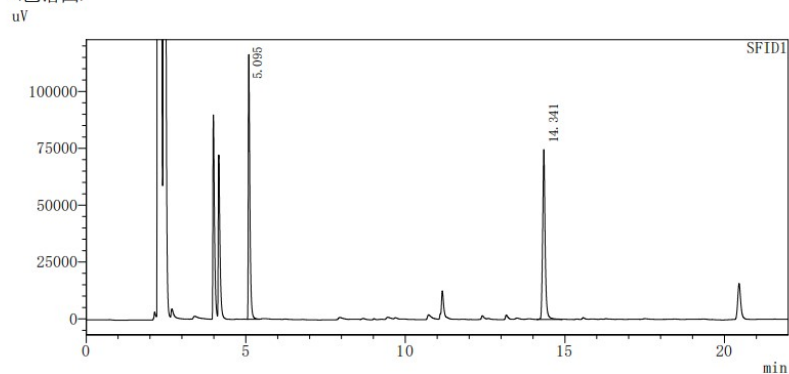
GC data diagram of entry 19

SHIMADZU LabSolutions 分析报告

<样品信息>

样品名 :
 样品ID :
 数据文件名 : 20220318-N-5.gcd
 方法文件名 : 高温方法-280度-22min.gcm
 批处理文件名 : 20220415.gcb
 样品瓶号 : 2
 进样体积 : 1 uL
 分析日期 : 2022/4/15 11:05:41
 处理日期 : 2022/4/15 11:27:43
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

<色谱图>



<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.095	393989	115912	49.642			
2	14.341	399675	74367	50.358		S	
总计		793663	190279				

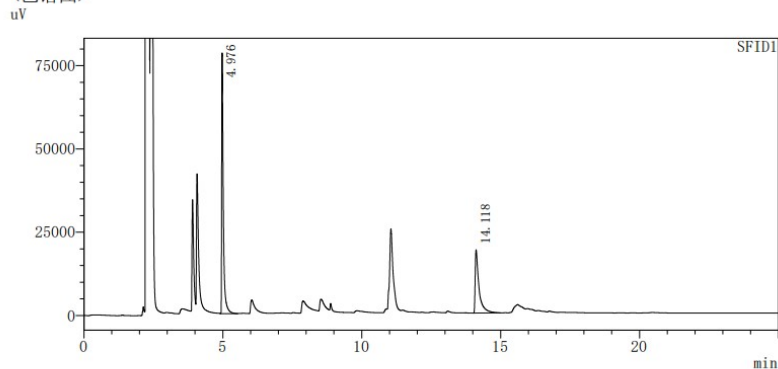
GC data diagram of entry 31

SHIMADZU LabSolutions 分析报告

<样品信息>

样品名 :
 样品ID :
 数据文件名 : 2023.3.14-1.gcd
 方法文件名 : 高温方法-280度-25min.gcm
 批处理文件名 : 20230314.gcb
 样品瓶号 : 1
 进样体积 : 1 uL
 分析日期 : 2023/3/14 22:50:59
 处理日期 : 2023/3/14 23:16:05
 样品类型 : 未知
 分析者 : System Administrator
 处理者 : System Administrator

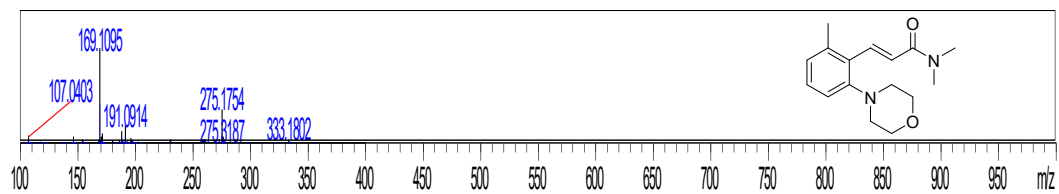
<色谱图>



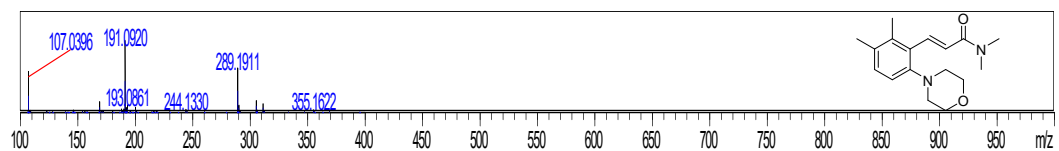
<峰表>

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	4.976	323576	77921	64.252			
2	14.118	180031	18982	35.748			
总计		503606	96903	100.000			

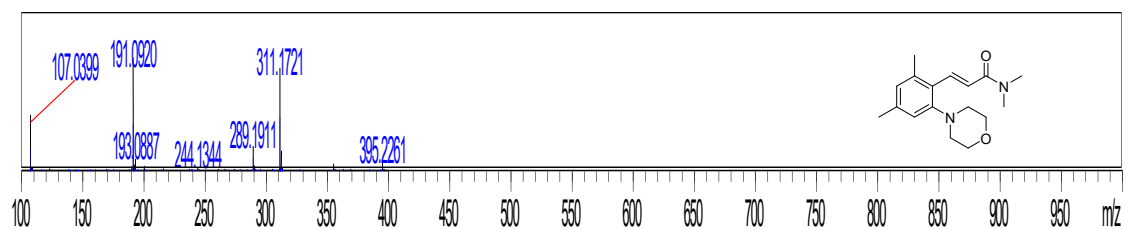
HRMS of 4b



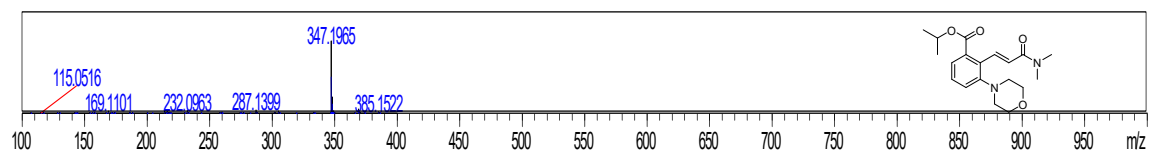
HRMS of 4c



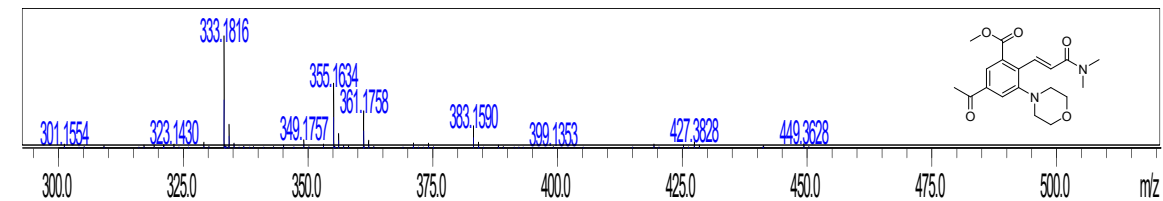
HRMS of 4d



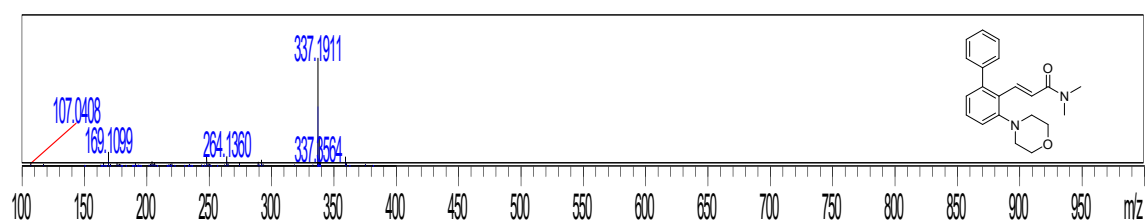
HRMS of 4f



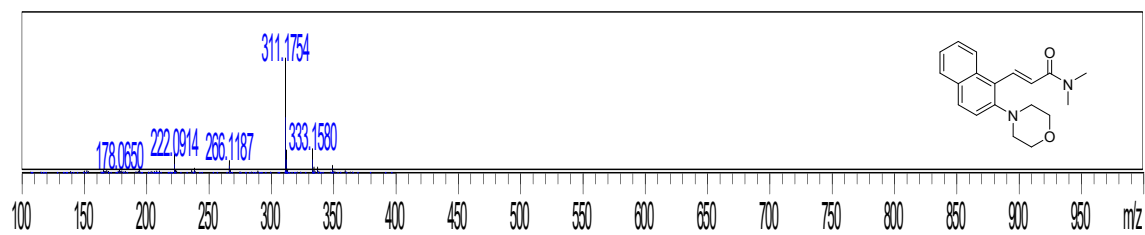
HRMS of 4i



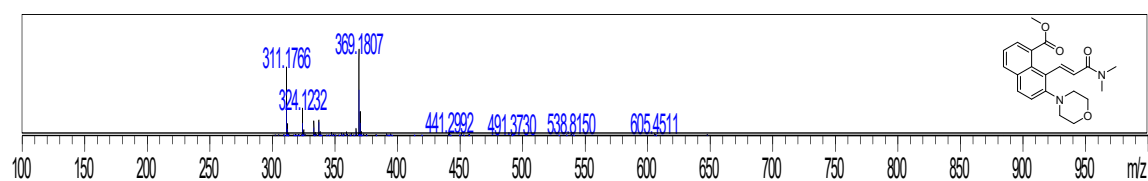
HRMS of 4m



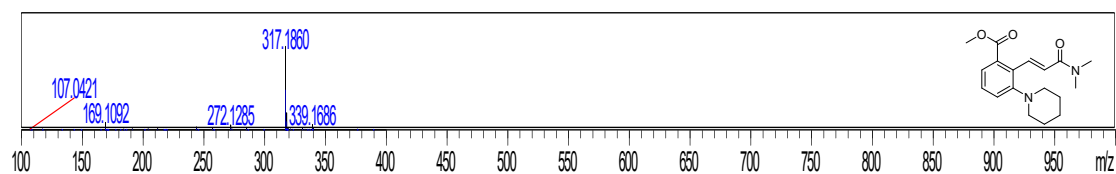
HRMS of 4n



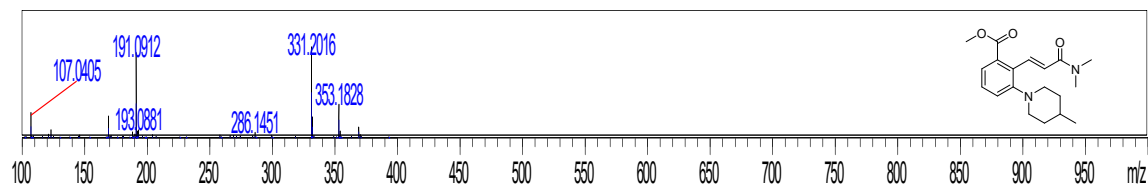
HRMS of 4o



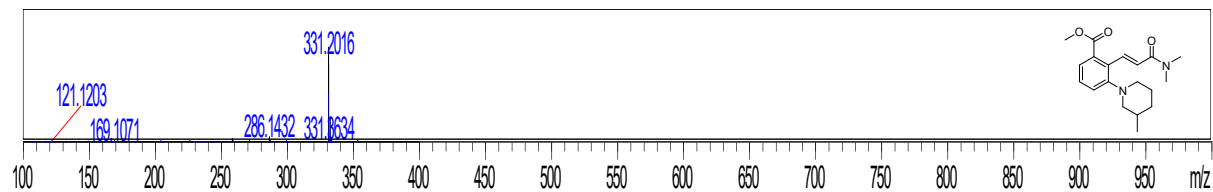
HRMS of 4p



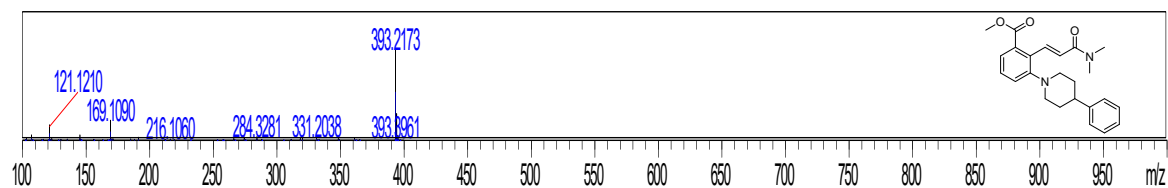
HRMS of 4q



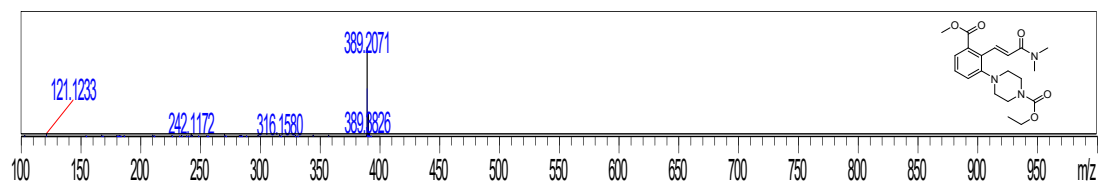
HRMS of 4r



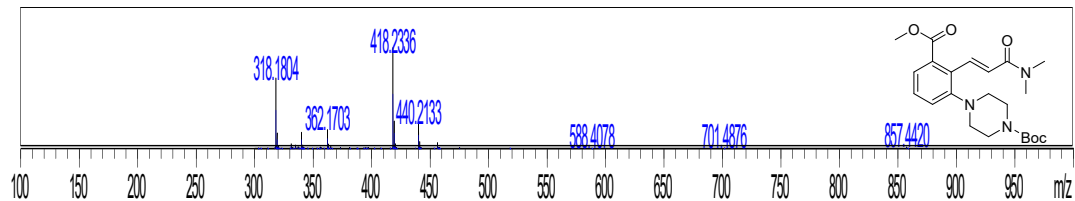
HRMS of 4s



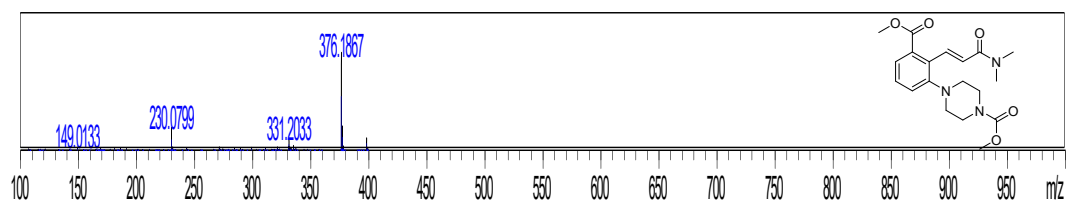
HRMS of 4t



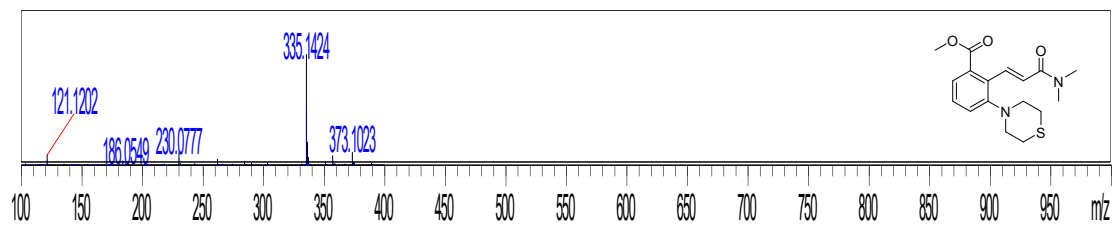
HRMS of 4v



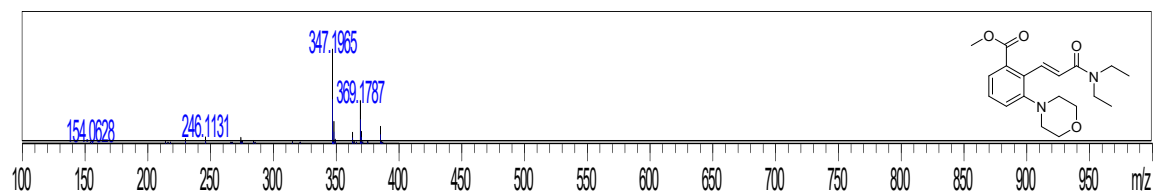
HRMS of 4w



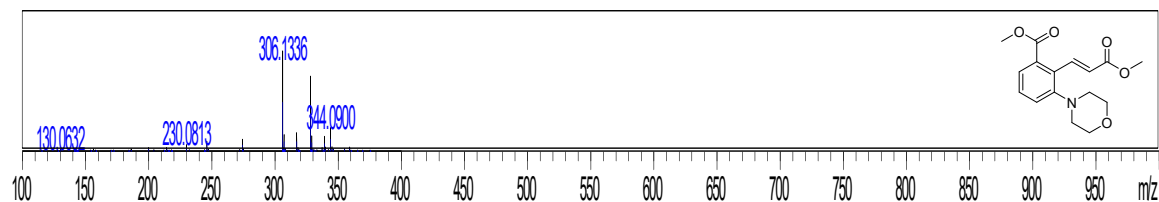
HRMS of 4x



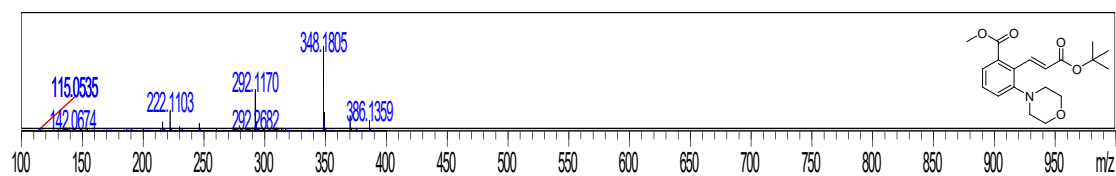
HRMS of 4z



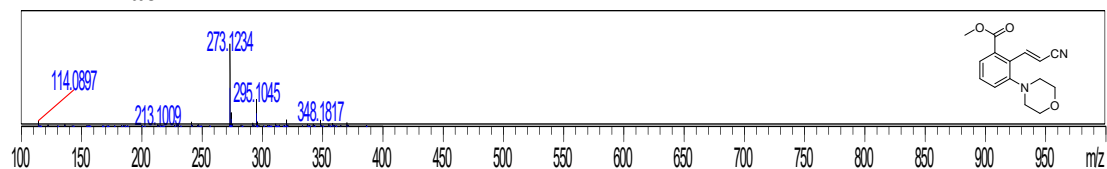
HRMS of 4ab



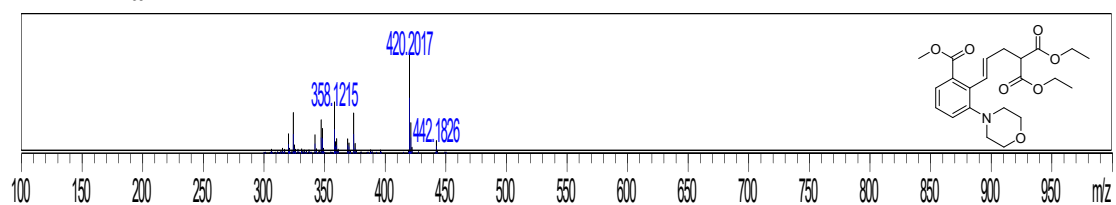
HRMS of 4ad



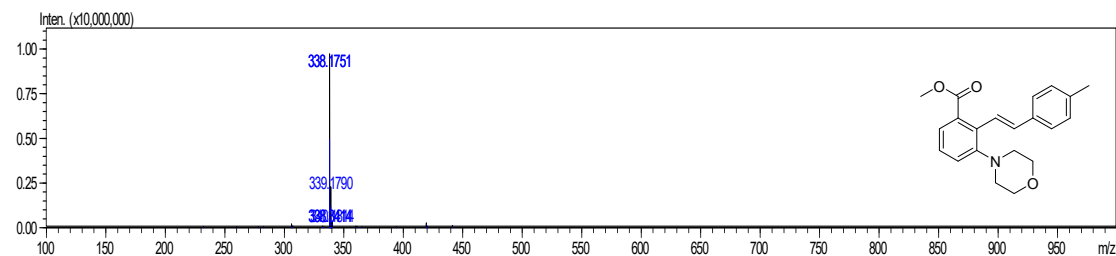
HRMS of 4ae



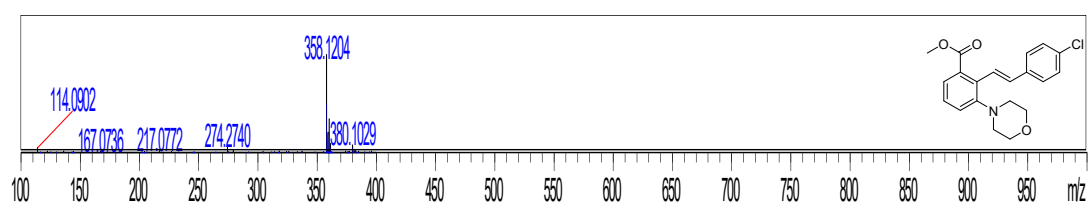
HRMS of 4af



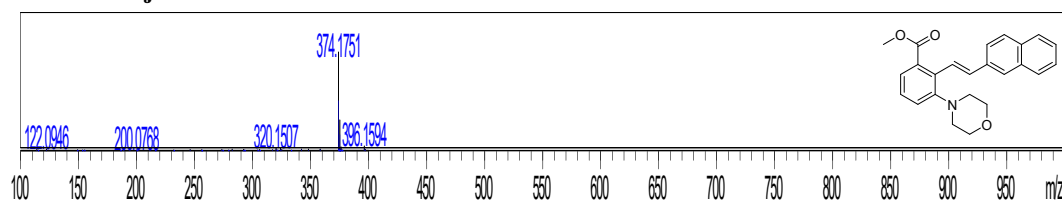
HRMS of 4ah



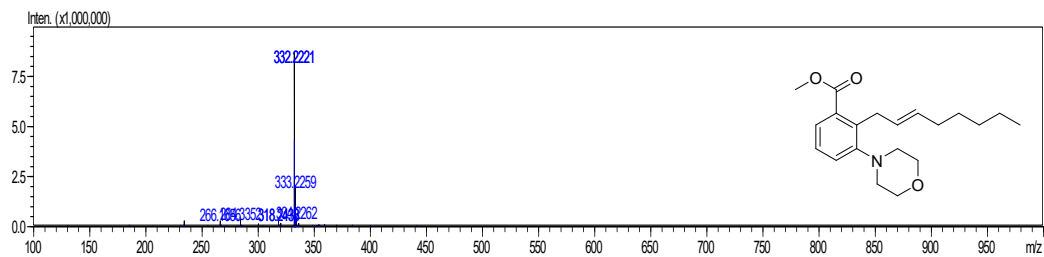
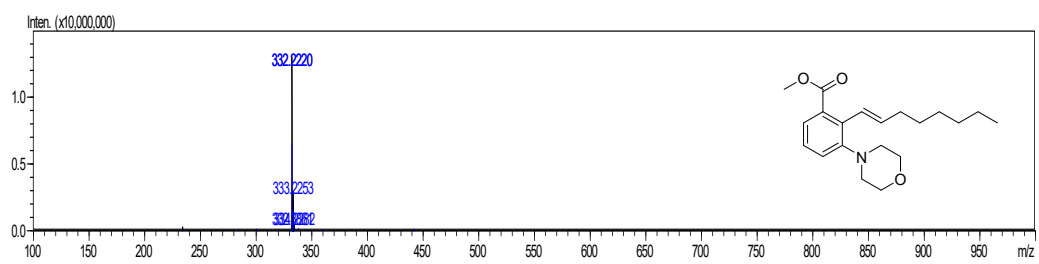
HRMS of 4ai



HRMS of 4aj



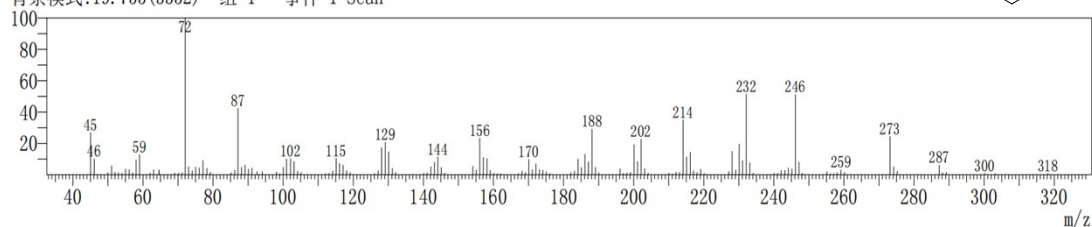
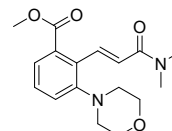
HRMS of 4ak



GC-MS of 4a

质谱

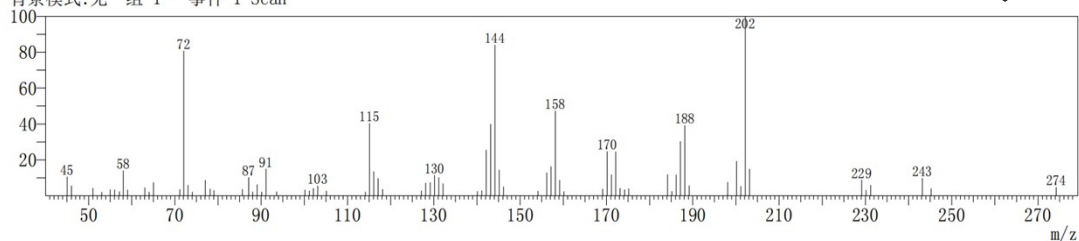
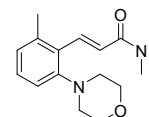
流路号:1 保留时间:19.555(扫描数:3312)
质量峰:146
原始模式:平均 18.785-19.780(3158-3357) 基峰:72(20652)
背景模式:19.755(3352) 组 1 - 事件 1 Scan



GC-MS of 4b

质谱

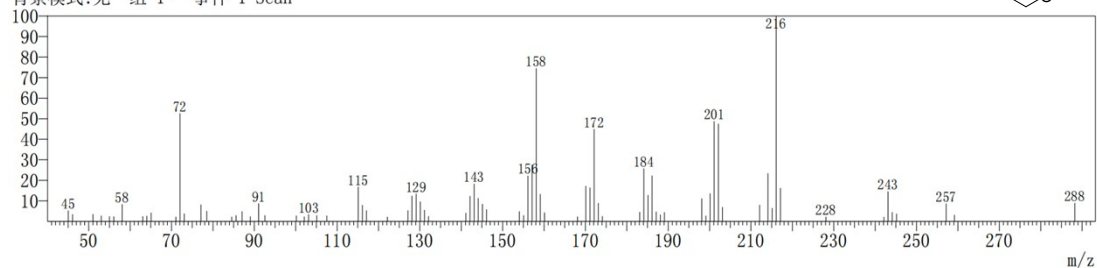
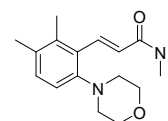
流路号:1 保留时间:16.345(扫描数:2670)
质量峰:79
原始模式:平均 16.290-16.375(2659-2676) 基峰:202(145074)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4c

质谱

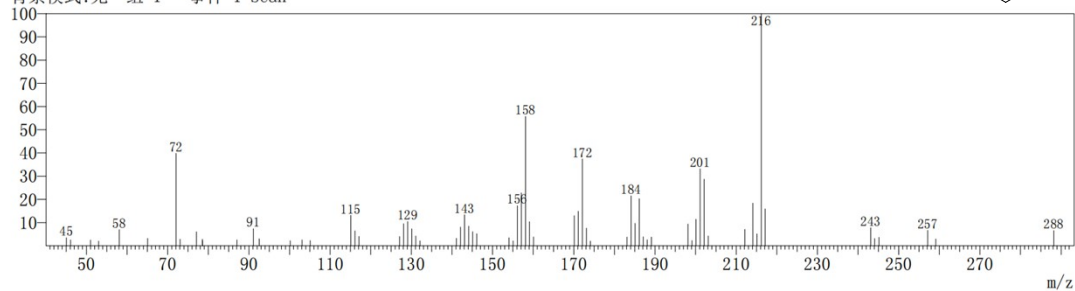
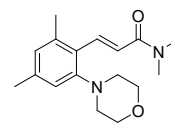
流路号:1 保留时间:17.925(扫描数:2986)
质量峰:81
原始模式:平均 17.040-18.895(2809-3180) 基峰:216(42719)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4d

质谱

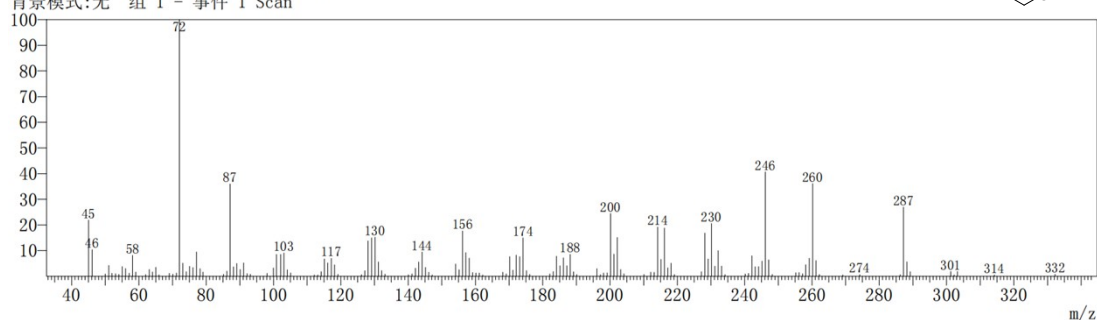
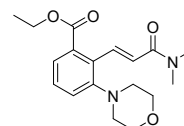
流路号:1 保留时间:17.505(扫描数:2902)
质量峰:68
原始模式:平均 16.850-17.900(2771-2981) 基峰:216(86826)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4e

质谱

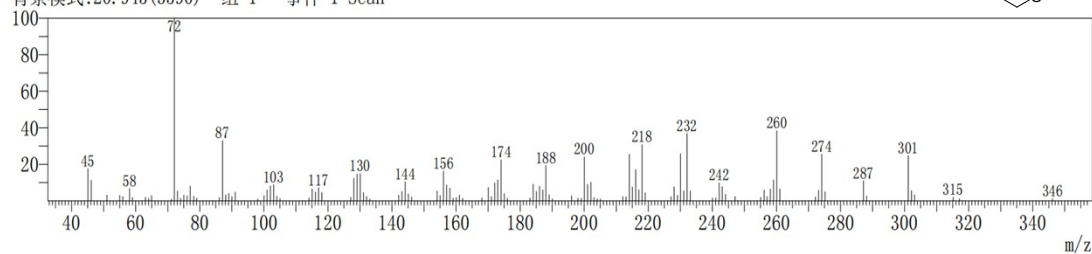
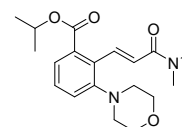
流路号:1 保留时间:20.475(扫描数:3496)
质量峰:149
原始模式:平均 20.350-20.495(3471-3500) 基峰:72(195973)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4f

质谱

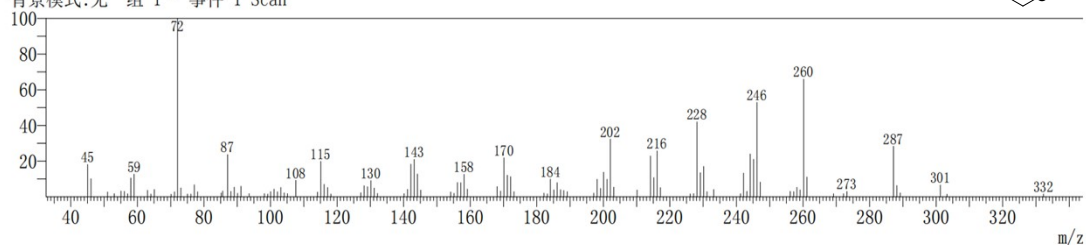
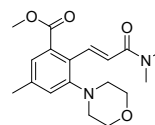
流路号:1 保留时间:20.620(扫描数:3525)
质量峰:123
原始模式:平均 20.270-20.770(3455-3555) 基峰:72(232661)
背景模式:20.945(3590) 组 1 - 事件 1 Scan



GC-MS of 4g

质谱

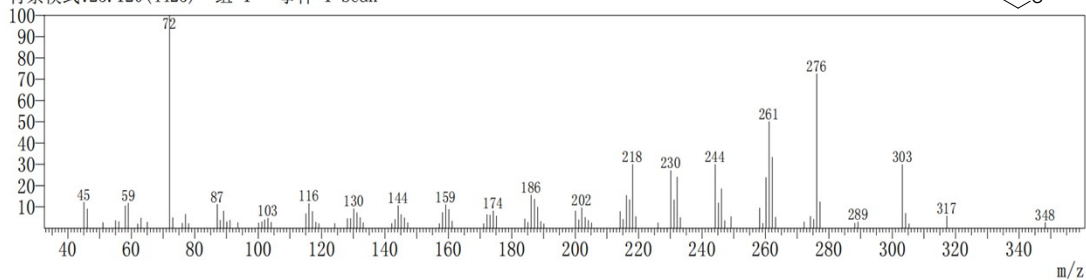
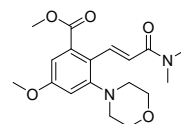
流路号:1 保留时间:21.425(扫描数:3686)
质量峰:115
原始模式:平均 21.315-21.455(3664-3692) 基峰:72(113459)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4h

质谱

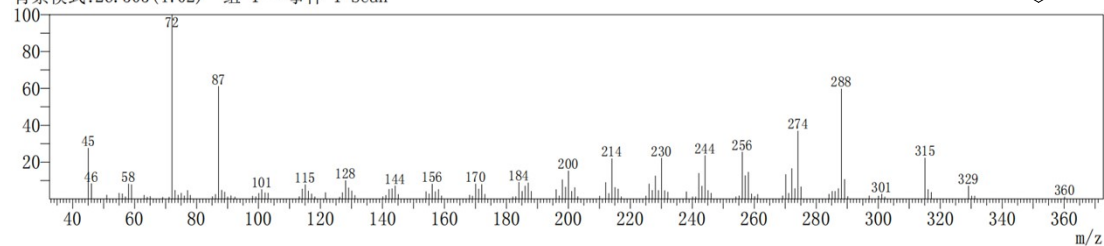
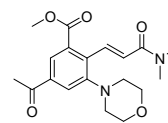
流路号:1 保留时间:24.880(扫描数:4377)
质量峰:101
原始模式:平均 24.600-25.015(4321-4404) 基峰:72(32525)
背景模式:25.120(4425) 组 1 - 事件 1 Scan



GC-MS of 4i

质谱

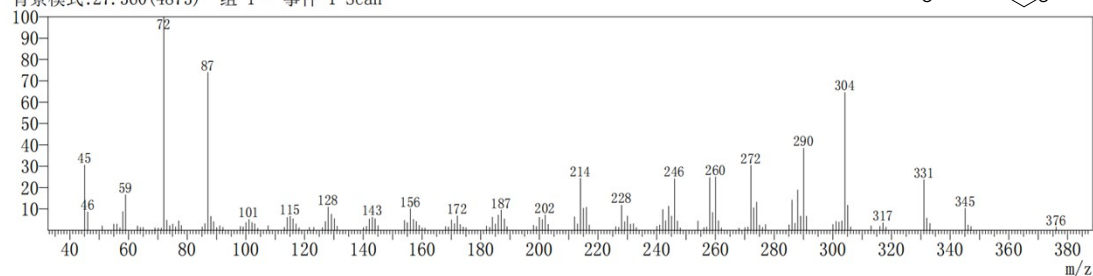
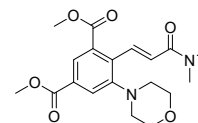
流路号:1 保留时间:26.720(扫描数:4745)
质量峰:136
原始模式:平均 26.510-26.775(4703-4756) 基峰:72(72181)
背景模式:26.505(4702) 组 1 - 事件 1 Scan



GC-MS of 4j

质谱

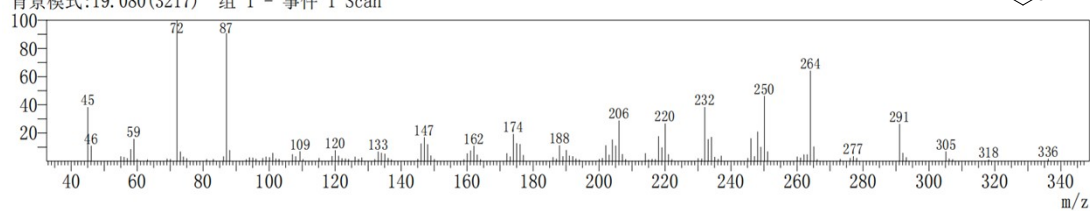
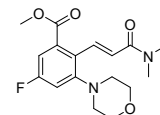
流路号:1 保留时间:27.545(扫描数:4910)
质量峰:152
原始模式:平均 27.425-27.590(4886-4919) 基峰:72(329836)
背景模式:27.360(4873) 组 1 - 事件 1 Scan



GC-MS of 4k

质谱

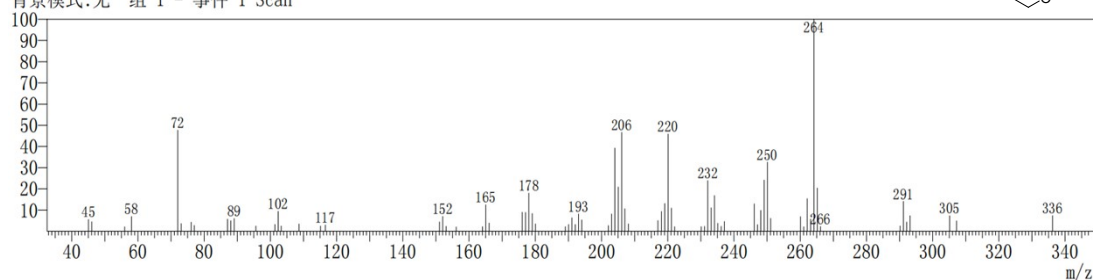
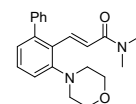
流路号:1 保留时间:18.520(扫描数:3105)
质量峰:129
原始模式:平均 18.220-18.895(3045-3180) 基峰:72(43510)
背景模式:19.080(3217) 组 1 - 事件 1 Scan



GC-MS of 4m

质谱

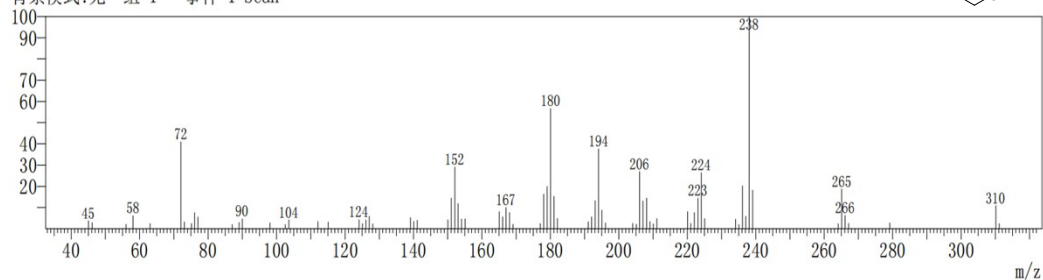
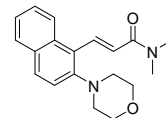
流路号:1 保留时间:25.210(扫描数:4443)
质量峰:77
原始模式:平均 25.055-25.365(4412-4474) 基峰:264(88780)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4n

质谱

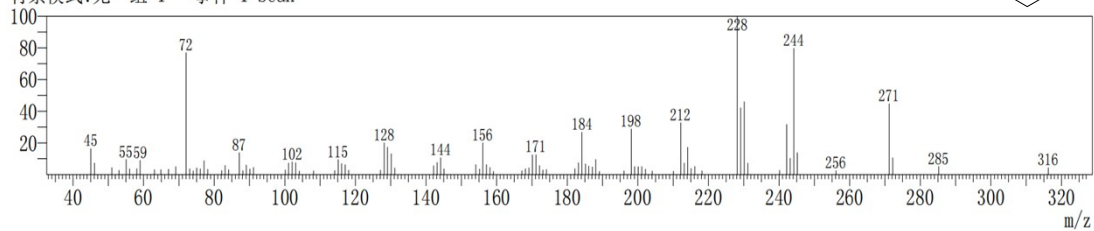
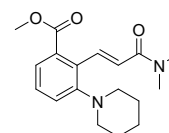
流路号:1 保留时间:25.755(扫描数:4552)
质量峰:76
原始模式:平均 24.970-26.345(4395-4670) 基峰:238(69847)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4p

质谱

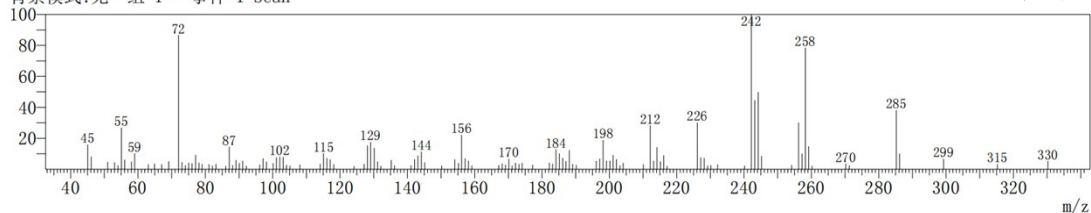
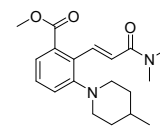
流路号:1 保留时间:19.140(扫描数:3229)
质量峰:97
原始模式:平均 18.250-19.565(3051-3314) 基峰:228(17451)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4q

质谱

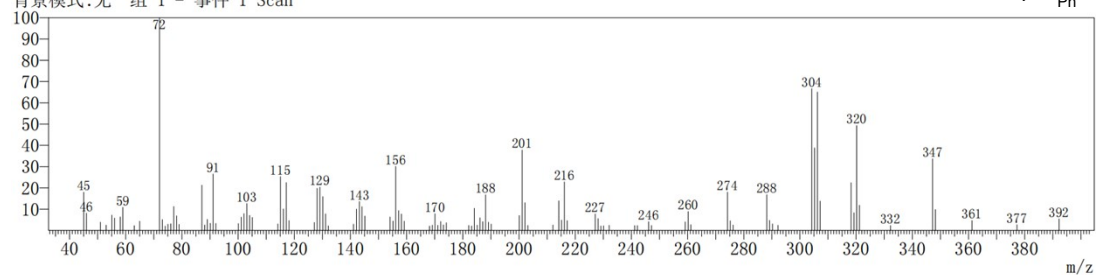
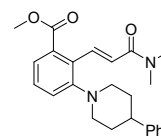
流路号:1 保留时间:19.800(扫描数:3361)
质量峰:125
原始模式:平均 19.405-21.205(3282-3642) 基峰:242(7603)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4s

质谱

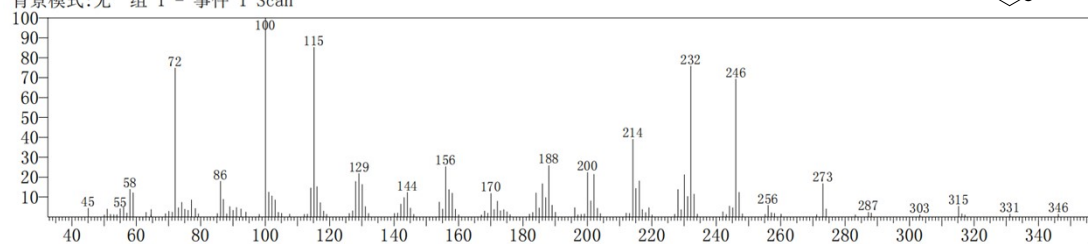
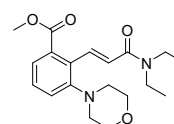
流路号:1 保留时间:34.540(扫描数:6309)
质量峰:110
原始模式:平均 33.930-34.950(6187-6391) 基峰:72(17521)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4z

质谱

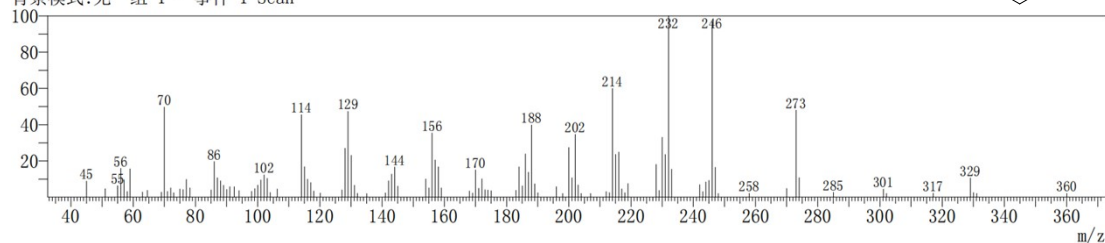
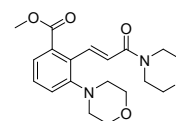
流路号:1 保留时间:21.090(扫描数:3619)
质量峰:140
原始模式:平均 19.940-22.175(3389-3836) 基峰:100(40137)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4aa

质谱

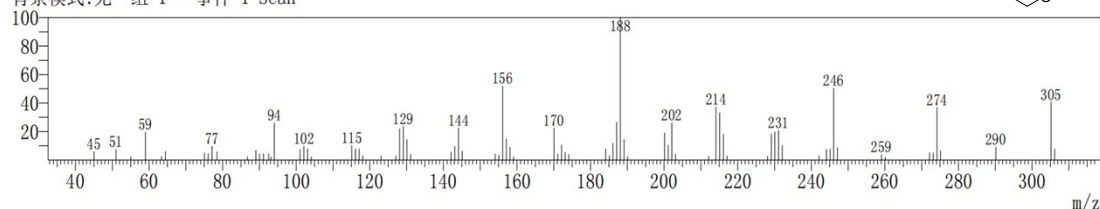
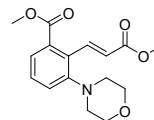
流路号:1 保留时间:26.695(扫描数:4740)
质量峰:116
原始模式:平均 26.455-26.710(4692-4743) 基峰:232(64929)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4ab

质谱

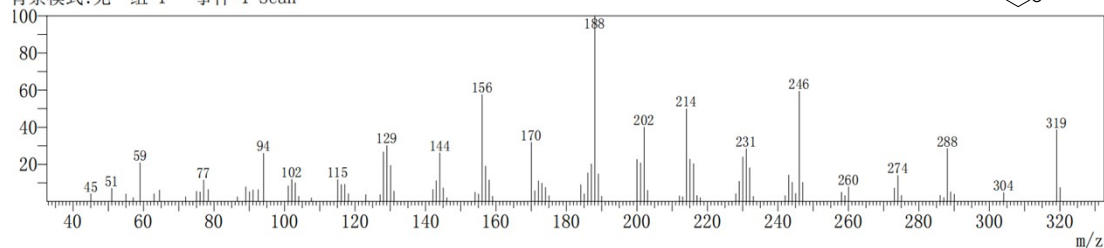
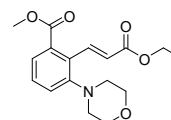
流路号:1 保留时间:15.490(扫描数:2499)
质量峰:81
原始模式:平均 15.045-15.960(2410-2593) 基峰:188(162205)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4ac

质谱

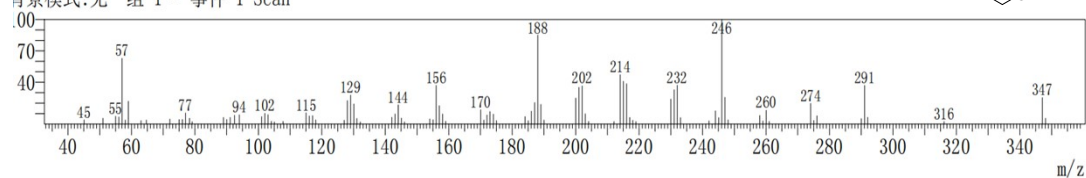
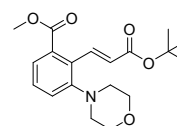
流路号:1 保留时间:16.055(扫描数:2612)
质量峰:94
原始模式:平均 15.975-16.260(2596-2653) 基峰:188(104140)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4ad

质谱

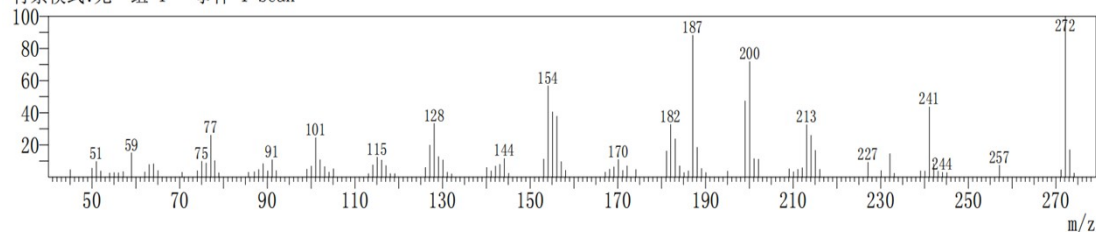
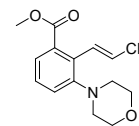
流路号:1 保留时间:16.595(扫描数:2720)
质量峰:95
原始模式:平均 16.310-17.040(2663-2809) 基峰:246(26780)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4ae

质谱

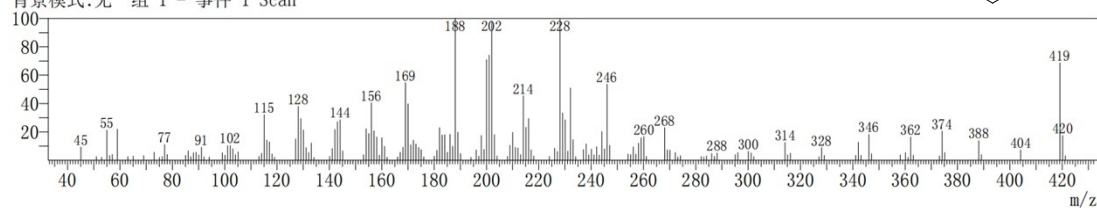
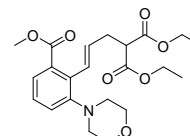
流路号:1 保留时间:14.995(扫描数:2400)
质量峰:106
原始模式:平均 14.780-15.560(2357-2513) 基峰:272(22317)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4af

质谱

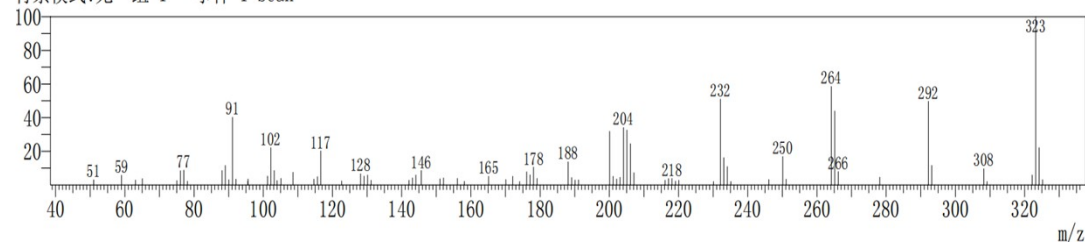
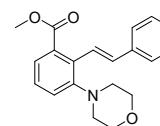
流路号:1 保留时间:24.645(扫描数:4330)
质量峰:176
原始模式:平均 24.460-24.810(4293-4363) 基峰:188(75436)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4ag

质谱

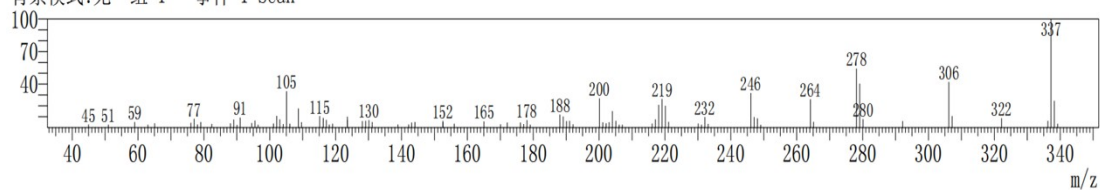
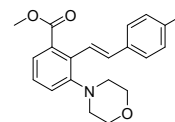
流路号:1 保留时间:19.830(扫描数:3367)
质量峰:82
原始模式:平均 19.245-20.290(3250-3459) 基峰:323(40539)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4ah

质谱

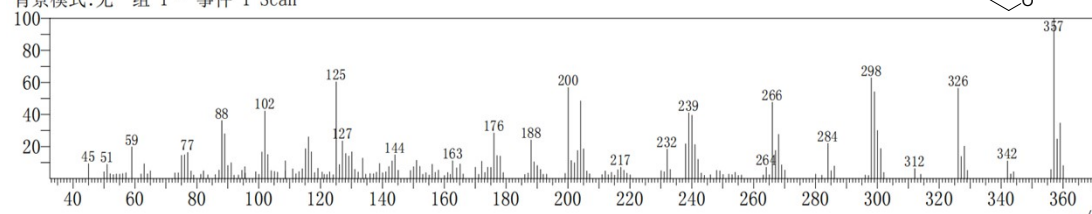
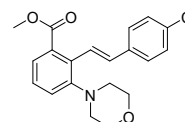
流路号:1 保留时间:21.060(扫描数:3613)
质量峰:90
原始模式:平均 20.830-21.285(3567-3658) 基峰:337(25817)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4ai

质谱

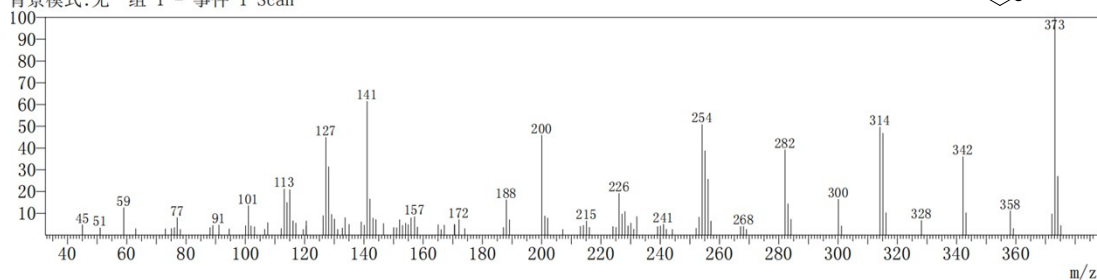
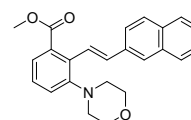
流路号:1 保留时间:24.150(扫描数:4231)
质量峰:187
原始模式:平均 23.495-24.405(4100-4282) 基峰:357(3344)
背景模式:无 组 1 - 事件 1 Scan



GC-MS of 4aj

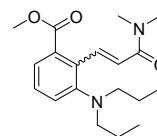
质谱

流路号:1 保留时间:32.830(扫描数:5967)
质量峰:111
原始模式:平均 32.555-33.200(5912-6041) 基峰:373(9809)
背景模式:无 组 1 - 事件 1 Scan

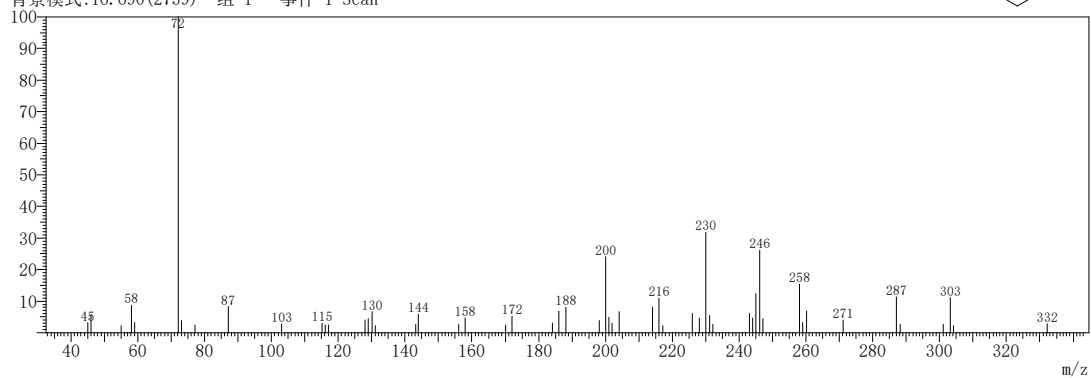


GC-MS of 4y

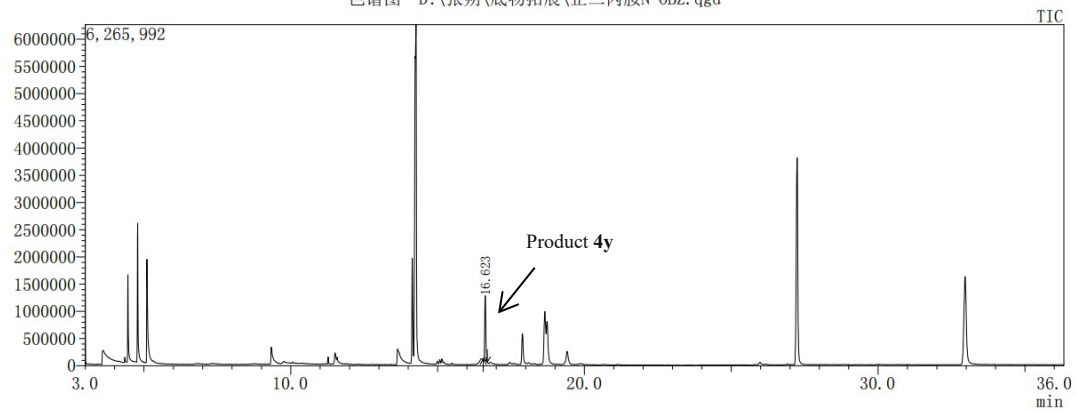
质谱



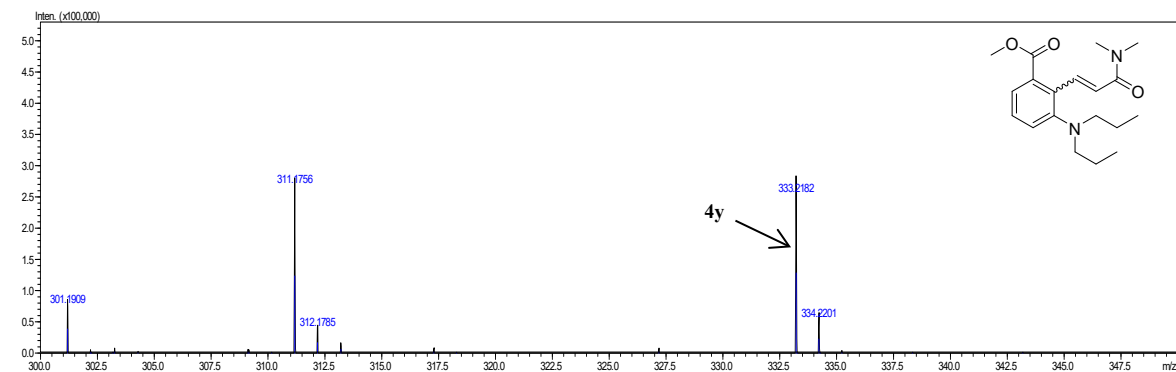
流路号:1 保留时间:16.625(扫描数:2726)
质量峰:54
原始模式:平均 16.545-16.660(2710-2733) 基峰:72(86014)
背景模式:16.690(2739) 组 1 - 事件 1 Scan



色谱图 D:\张翔\底物拓展\正二丙胺N-OBZ. qgd

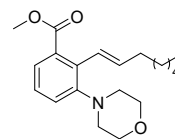


HRMS of 4y

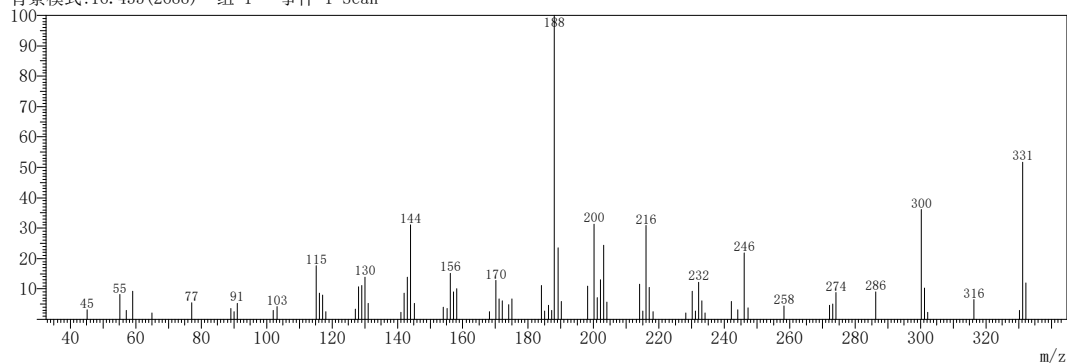


GC-MS of 4ak

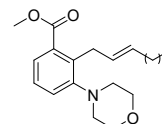
质谱



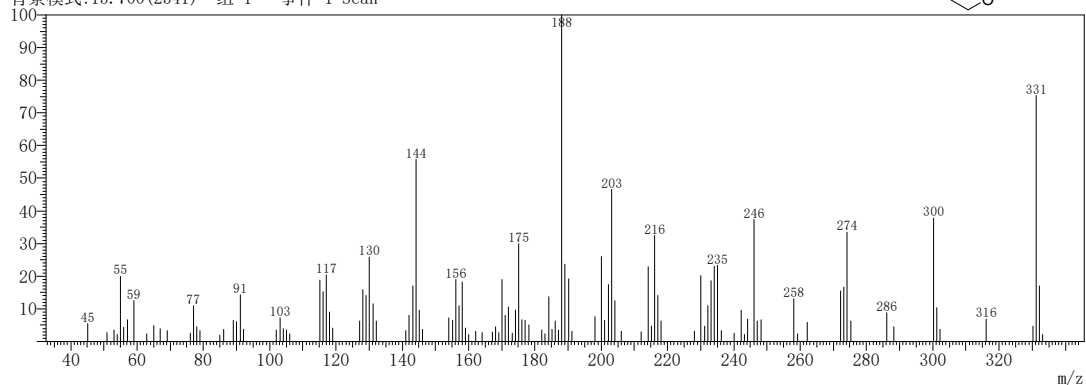
流路号:1 保留时间:16.525(扫描数:2706)
质量峰:76
原始模式:平均 16.320-16.680(2665-2737) 基峰:188(23413)
背景模式:16.435(2688) 组 1 - 事件 1 Scan



质谱



流路号:1 保留时间:15.775(扫描数:2556)
质量峰:120
原始模式:平均 15.735-15.820(2548-2565) 基峰:188(60828)
背景模式:15.700(2541) 组 1 - 事件 1 Scan



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