Supplementary Information

Radical-mediated [3+2+1] annulation of α-polyfluoromethyl-alkenes with arylisocyanates enabled by C(sp^3)-F activation

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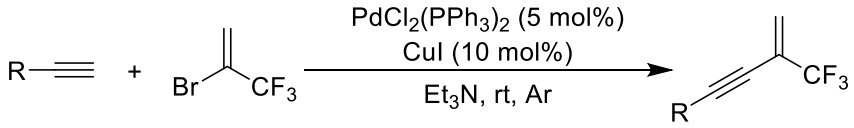
(A) Typical experimental procedure

(a) General

All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 MHz advance spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. Low-resolution mass spectra (LRMS) data were measured on GCMS-QP 2010 Ultra. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting point was recorded on Hanon MP100 Apparatus. All products were identified by ^{1}H, ^{19}F and ^{13}C NMR, LRMS and HRMS. Unless otherwise noted, all reactions were carried out using the standard Schlenk techniques, and all starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

(b) General procedure for the preparation of (3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzenes:[1]

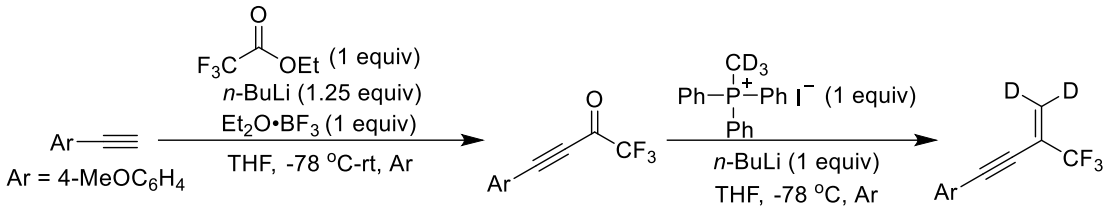


CuI (57.2 mg, 10 mol%) and $Pd(PPh_3)_2Cl_2$ (105.3 mg, 5 mol%) were dissolved in Et_3N (30 mL) under argon at room temperature. To the solution were added 2-bromo-3,3,3-trifluoroprop-1-ene (0.498 mL, 4.8 mmol, 1.6 equiv) and alkyne (3.0 mmol, 1.0 equiv). The reaction mixture was left to stir at room temperature for 16 h. The resultant mixture was diluted with saturated aqueous NH_4Cl (20 mL) followed by

extraction with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100 : 1) to give the desired enyne.

(c) General procedure for the preparation of 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl-4,4-*d*$_2$)benzene:[2]

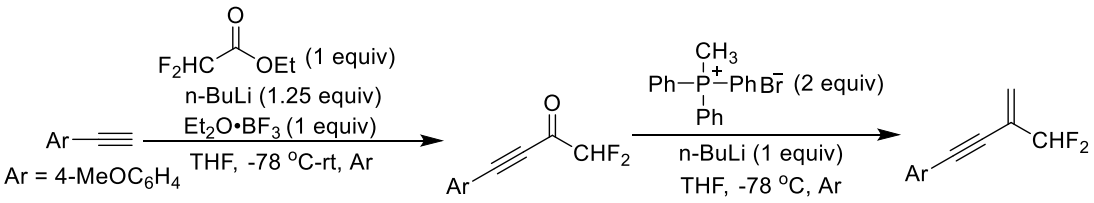
Synthesis of 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl-4,4-*d*$_2$)benzene.



1-Ethynyl-4-methoxybenzene (1.1 mL, 10 mmol) in THF (25 mL) was cooled to −78 °C and *n*-butyllithium (5 mL, 2.5 M, 12.5 mmol) was added dropwise. The solution was left to stir at this temperature for 30 minutes and ethyl trifluoroacetate (1.75 mL, 10 mmol) and $Et_2O \cdot BF_3$ (1.4 mL, 10 mmol) were added dropwise. The solution was left to stir for 1 h at -78 °C before warming to room temperature. The reaction mixture was washed with water (3 × 25 mL) and saturated aqueous ammonium chloride solution (2 × 20 mL) and the combined aqueous phases were extracted with Et_2O. The combined organic extracts were dried with magnesium sulphate and concentrated under reduced pressure. The product was purified by vacuum distillation (20 °C, 7.5 × 10-2 mbar) to give 1,1,1-trifluoro-4-phenylbut-3-yn-2-one as a yellow oil.

To a solution of methyl-d_3-triphenylphosphonium iodide (2.35 g, 5 mmol) in THF (20 mL) at -78 °C was added *n*-BuLi (3.2 mL, 1.6 M in THF) dropwise over 5 min. The solution was stirred at -78 °C for 15 min, and then warmed to room temperature. and stirred for 30 minutes. The reaction mixture was cooled back down to -78 °C and 1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-yn-2-one (1.14 g, 5 mmol) was added dropwise over 5 minutes. After 20 minutes, the solution was warmed to room temperature and stirred for 18 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (100% *n*-pentane) to afford the title compound **1a-*d*$_2$** (91%-D) as a colorless oil.

Synthesis of 1-(3-(difluoromethyl)but-3-en-1-yn-1-yl)-4-methoxybenzene:

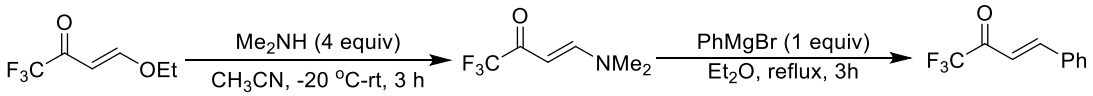


1-Ethynyl-4-methoxybenzene (1.1 mL, 10 mmol) in THF (25 mL) was cooled to -78 °C and *n*-butyllithium (5 mL, 2.5 M, 12.5 mmol) was added dropwise. The solution was left to stir at this temperature for 30 min and ethyl 3,3-difluoropropanoate (1.40 mL, 10 mmol) and $Et_2O \cdot BF_3$ (1.4 mL, 10 mmol) were added dropwise. The solution was left to stir for 1 h at -78 °C before warming to room temperature. The reaction mixture was washed with water (3 × 25 mL) and saturated aqueous ammonium chloride solution (2 × 20 mL) and the combined aqueous phases were extracted with Et_2O. The combined organic extracts were dried

with magnesium sulphate and concentrated under reduced pressure. The product was purified by vacuum distillation (20 °C, 7.5 × 10^{-2} mbar) to give 1,1-difluoro-4-(4-methoxyphenyl)but-3-yn-2-one as a yellow oil.

To a solution of methyltriphenylphosphonium bromide (3.60 g, 10 mmol) in THF (20 mL) at -78 °C was added *n*-BuLi (3.2 mL, 1.6 M in THF) dropwise over 5 min. The solution was stirred at -78 °C for 15 min, and then warmed to room temperature and stirred for 30 minutes. The reaction mixture was cooled back down to -78 °C and 1-(3-(difluoromethyl)but-3-en-1-yn-1-yl)-4-methoxybenzene (1.04 g, 5 mmol) was added dropwise over 5 minutes. After 20 min, the solution was warmed to r.t. and stirred for 18 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. The residue was purified by flash column chromatography (100% *n*-pentane) to afford the title compound **1y** as a colorless oil.

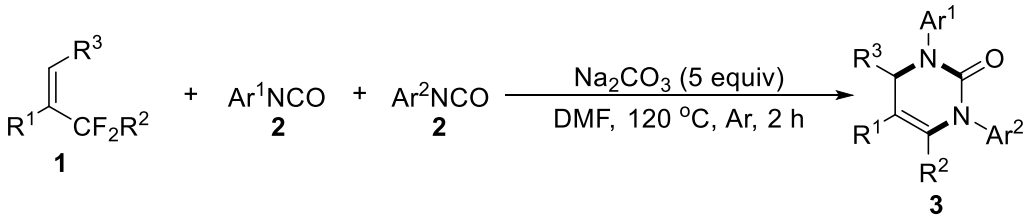
(d) General procedure for the preparation of (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one:[3]



To a stirred solution of (*E*)-4-ethoxy-1,1,1-trifluorobut-3-en-2-one (1.67 g; 10 mmol) and acetonitrile (10 mL) was slow dropped 33% Me_2NH in the water (10.0 mL; 40 mmol) at -20 °C. After the addition was complete, the solution was warmed up to room temperature and the mixture was stirred for 3 h at this temperature. After completion of the reaction, the solvent was evaporated in vacuum, the rest was extracted by dichloromethane. Then the organic phase was dried with magnesium sulfate and the solvent was evaporated in vacuum. Crystallization with toluene and n-hexane to afford (*E*)-4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one.

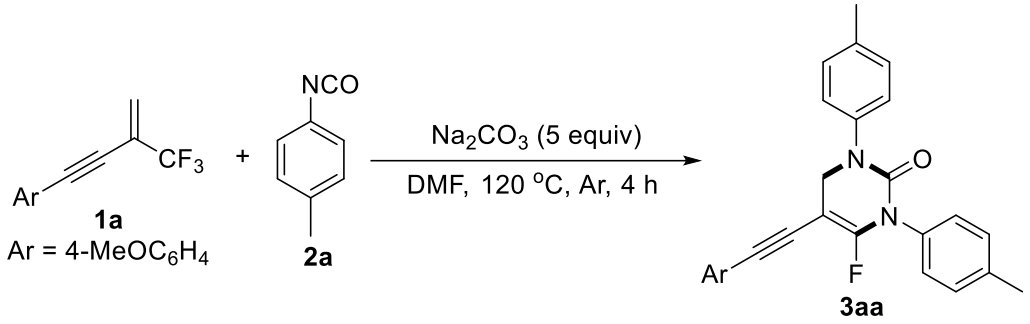
A solution of the phenyl magnesium bromide (10 mmol) was prepared by reported method. A solution of (*E*)-4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one (1.7 g; 10 mmol) in anhydrous ether (15.0 mL) was then added to the solution of the Grignard reagent at room temperature with stirring. The resulting mixture was heated under reflux for 3 h before the reaction mixture was poured into 2 M hydrochloric acid. The aqueous layer further extracted with ether. The combined ether phases were washed with water, dried over sodium sulfate and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (petrol ether) to afford (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**1x)**.

(e) Typical Experimental Procedure for Synthesis of 3,4-Dihydropyrimidin-2(1*H*)-ones 3：



To a Schlenk tube were added (3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzenes **1** (0.2 mmol), isocyanatobenzenes **2** (0.8 mmol; 4.0 equiv), Na_2CO_3 (106 mg; 1.0 mmol; 5 equiv) and DMF (0.1 M; 1 mL). Then the tube was charged with argon (1 atm), and was stirred at 120 ^oC for 2 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1) to afford the desired 3,4-dihydropyrimidin-2(1*H*)-one product **3**.

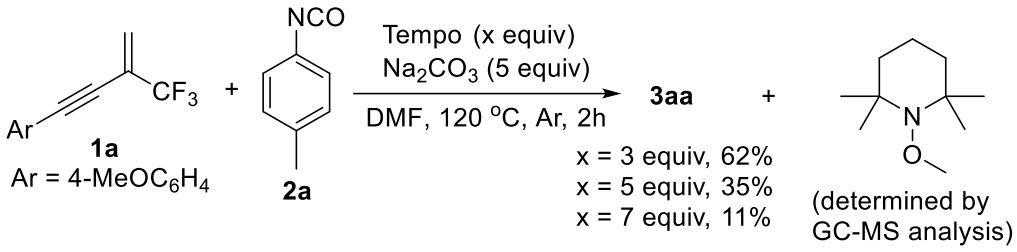
(f) Experimental Procedure for the Reaction at a 5 mmol Scale of 1-Methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene (1a):



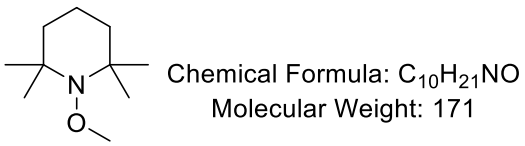
To a Schlenk tube were added 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene **1a** (1.14 g; 5 mmol), 1-isocyanato-4-methylbenzene **2a** (2.66 g; 20 mmol; 4.0 equiv), Na_2CO_3 (2.65 g; 25 mmol; 5 equiv) and DMF (0.1 M; 50 mL). Then the tube was charged with argon (1 atm), and was stirred at 120 °C for 4 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1) to afford the desired 6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one **3aa** (75%; 1.60 g).

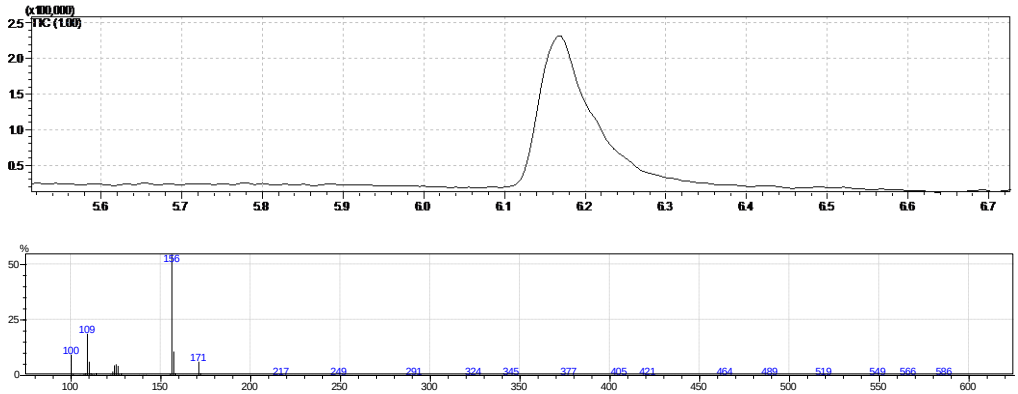
(g) Control Experiments:

(i) Control Experiments with Radical Inhibitors:



To a Schlenk tube were added 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene **1a** (45.6 mg; 0.2 mmol), 1-isocyanato-4-methylbenzene **2a** (106.4 mg; 0.8 mmol; 4.0 equiv), 2,2,6,6-tetramethyl-1-piperidinyloxy (156.3 mg; 1 mmol; 5 equiv), Na_2CO_3 (106.0 mg; 1.0 mmol; 5 equiv) and DMF (0.1 M; 1mL). Then the tube was charged with argon (1 atm), and was stirred at 120 °C for 2 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by GC-MS analysis to afford the desired 1-methoxy-2,2,6,6-tetramethylpiperidine.





[MS Spectrum]

# of Peaks494

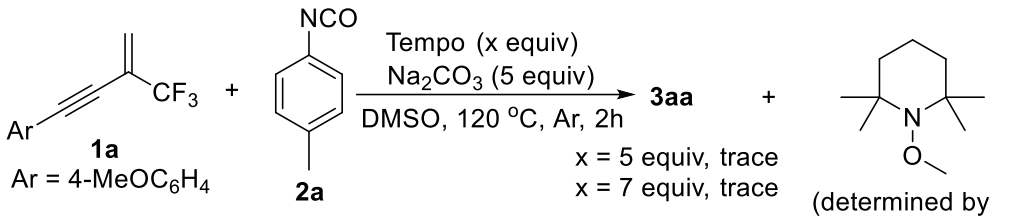
Raw Spectrum 6.165 (scan : 434)

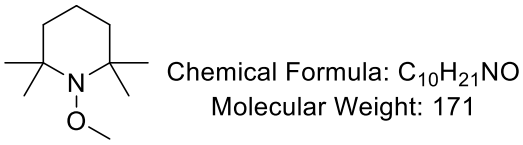
Background No Background Spectrum

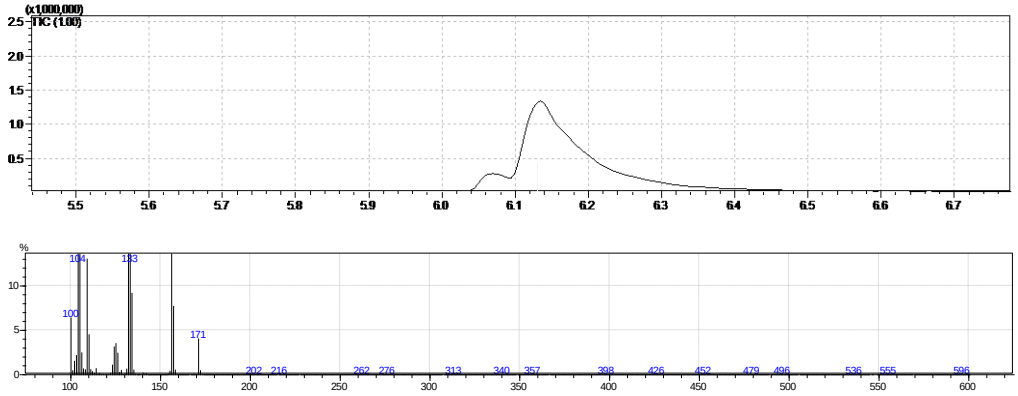
Base Peak m/z 156.20 (Inten : 110,068)

Event# 1

m/z	Absolute Intensity	Relative Intensity						
100.10	9554	8.68	110.15	6690	6.08	**156.20**	**110068**	**100.00**
101.15	811	0.74	111.20	841	0.76	157.20	11884	10.80
107.15	849	0.77	123.20	1689	1.53	**171.20**	**6447**	**5.86**
108.15	912	0.83	124.15	4808	4.37	172.20	820	0.74
109.15	**20080**	**18.24**	125.20	5447	4.95	173.20	73	0.07
			126.20	4054	3.68	174.20	50	0.05
			155.25	663	0.60			







[MS Spectrum]

# of Peaks 489

Raw Spectrum 6.130 (scan : 427)

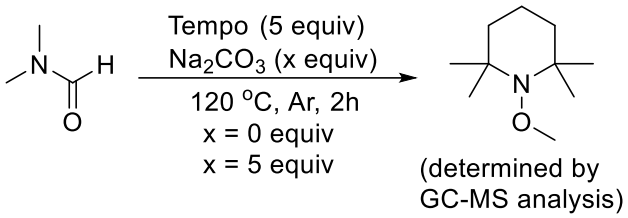
Background No Background Spectrum

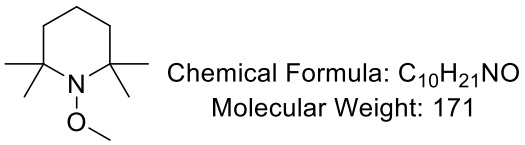
Base Peak m/z 133.10 (Inten : 346,345)

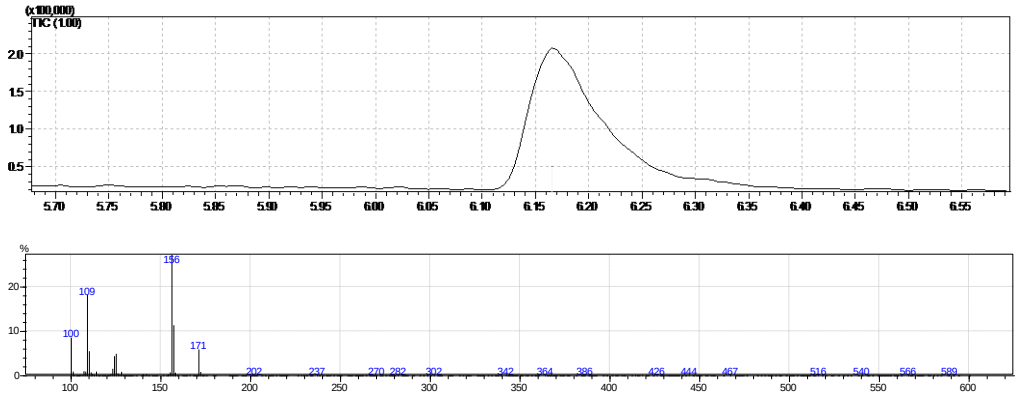
Event# 1

m/z	Absolute Intensity	Relative Intensity						
100.10	22162	6.40	105.10	84007	24.26	124.20	10879	3.14
102.10	5282	1.53	106.10	8614	2.49	125.20	12218	3.53
103.15	7537	2.18	**109.15**	**45116**	**13.03**	126.20	8492	2.45
104.10	201748	58.25	110.15	15610	4.51	132.10	177046	51.12

133.10	346345	100.00	**156.20**	**252658**	**72.95**	172.20	1615	0.47
134.10	31833	9.19	157.20	26706	7.71	173.20	129	0.04
155.25	1418	0.41	**171.20**	**14050**	**4.06**			







[MS Spectrum]

# of Peaks 314

Raw Spectrum 6.165 (scan : 434)

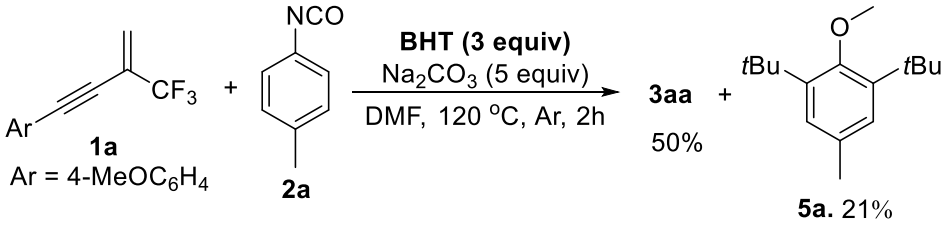
Background 6.125 -> 6.225 (scan : 426 -> 446)

Base Peak m/z 156.20 (Inten : 39,954)

Event# 1

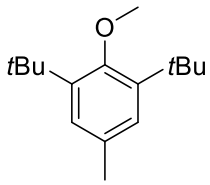
m/z Absolute Intensity Relative Intensity

100.10	3398	8.50	124.15	1740	4.36	172.20	313	0.78
101.15	350	0.88	125.20	1948	4.88	**173.20**	**5**	**0.01**
109.15	7249	18.14	**156.20**	**39954**	**100.00**	174.20	25	0.06
110.15	2185	5.47	157.20	4521	11.32			
123.20	602	1.51	**171.20**	**2348**	**5.88**			

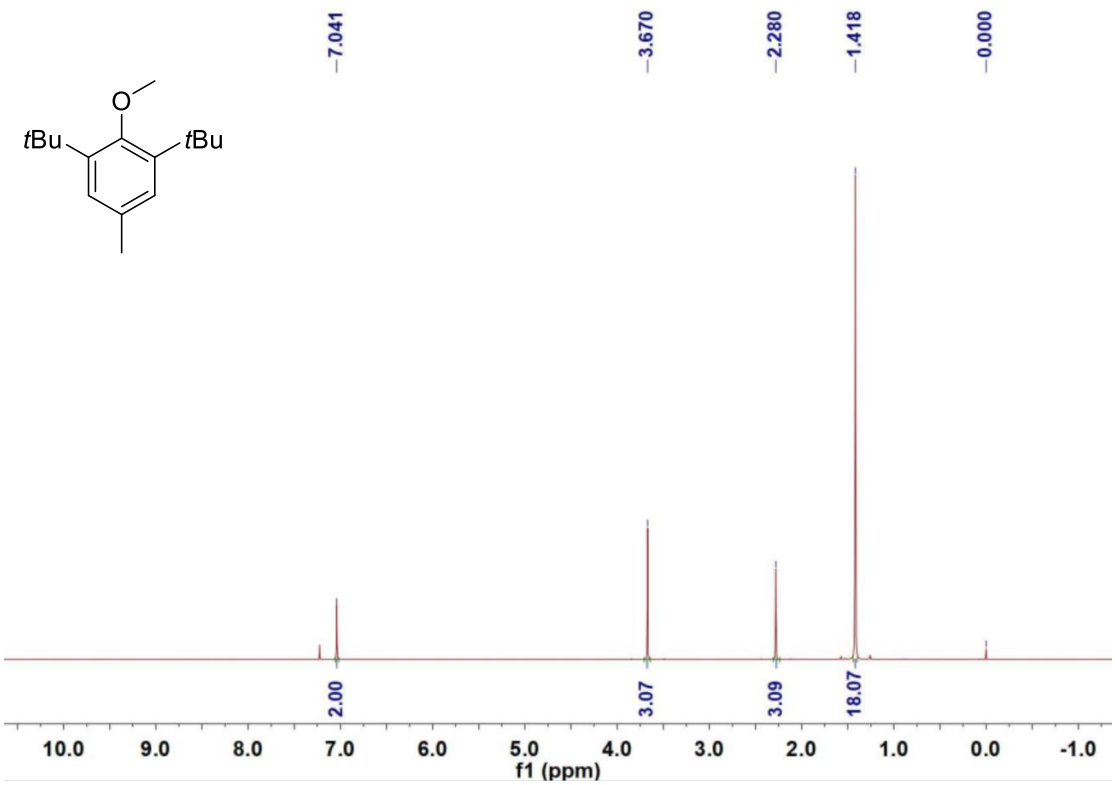


To a Schlenk tube were added 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene **1a** (45.6 mg; 0.2 mmol), 1-isocyanato-4-methylbenzene **2a** (106.4 mg; 0.8 mmol; 4.0 equiv), Butylated hydroxytoluene (132.0 mg; 0.6 mmol; 3 equiv), Na_2CO_3 (106.0 mg; 1.0 mmol; 5 equiv) and DMF (0.1 M; 1mL). Then the tube was charged with argon (1 atm), and was stirred at 120 °C for 2 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20 : 1) to afford the desired **3aa** (50%; 42.6 mg), 1,3-di-tert-butyl-2-methoxy-5-methylbenzene **5a** (21%; 9.8 mg).

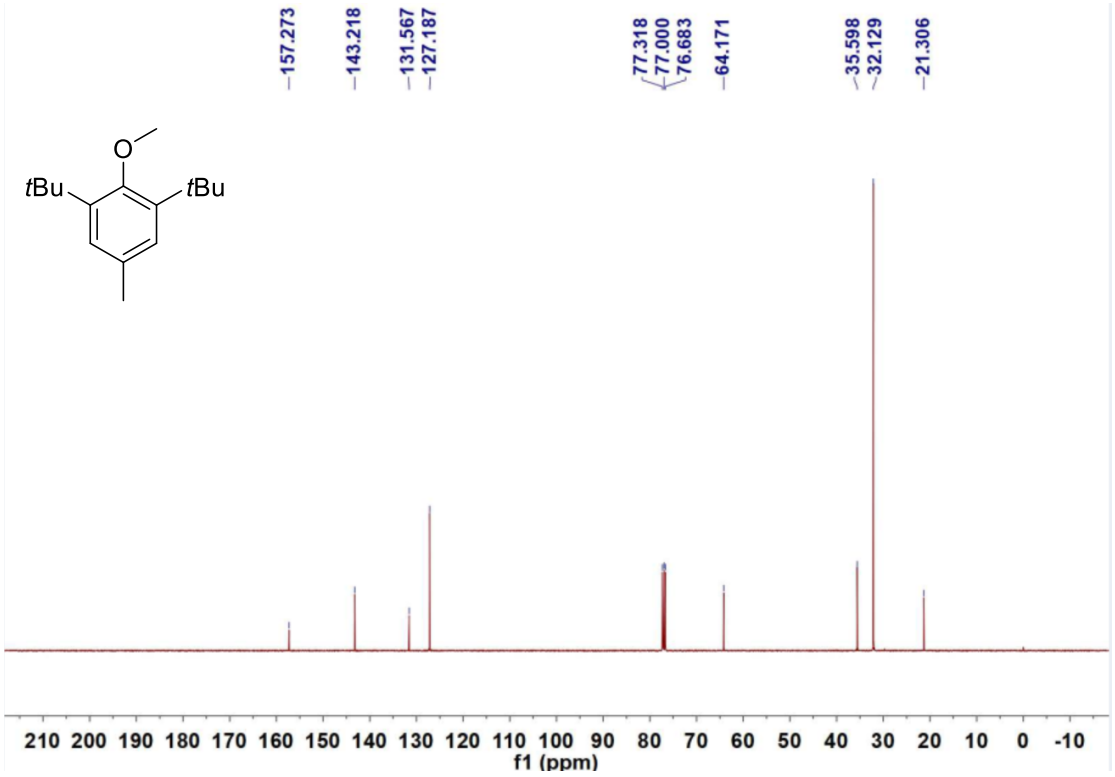
1,3-di-tert-butyl-2-methoxy-5-methylbenzene (5a):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20 : 1 (v/v)). 9.8 mg, 21%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.041 (s, 2H), 3.670 (s, 3H), 2.280 (s, 3H), 1.418 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3，143.2， 131.6， 127.2， 35.6， 32.1， 21.3; LRMS (EI, 70 eV) *m/z* (%): 234 (M^+, 64), 219 (100), 163 (19), 91 (11); HRMS *m/z* (ESI) calcd for $C_{16}H_{27}O$ ($[M+H]^+$) 235.2056, found 235.2056.

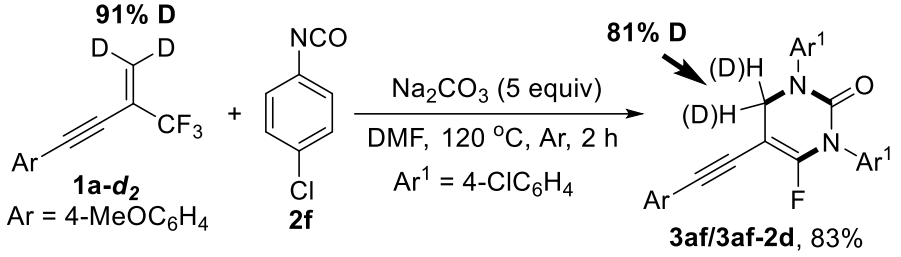


^{1}H NMR (400 MHz, $CDCl_3$)



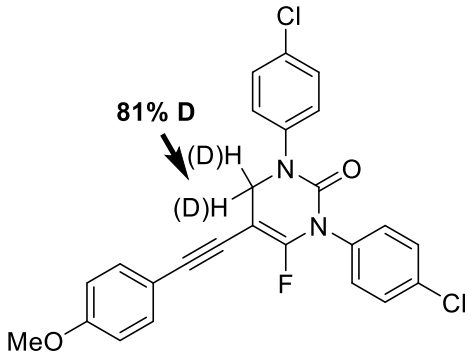
^{13}C NMR (100 MHz, $CDCl_3$)

(ii) Isotopic Labeling Experiments：



To a Schlenk tube were added 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl-4,4-d_2)benzene **1a-*d*$_2$** (46.0 mg; 0.2 mmol), 1-chloro-4-isocyanatobenzene **2f** (122.8 mg; 0.8 mmol; 4.0 equiv), Na_2CO_3 (106.0 mg; 1.0 mmol; 5 equiv) and DMF (0.1 M; 1 mL). Then the tube was charged with argon (1 atm), and was stirred at 120 °C for 2 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1) to afford the desired 1,3-bis(4-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4 dihydropyrimidin-2(1*H*)-one-4,4-d_2 products **3af/3af-2*d*** (78.0 mg, 83% yeild, 81% D).

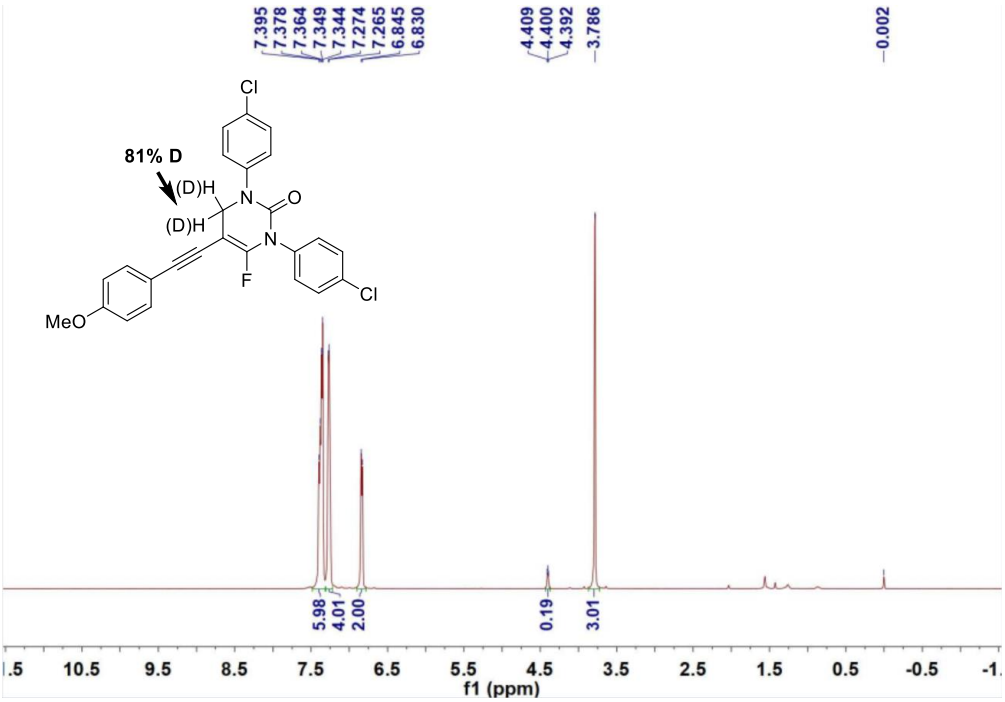
1,3-bis(4-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one-4,4-*d*$_2$ (3af/3af-2*d*):



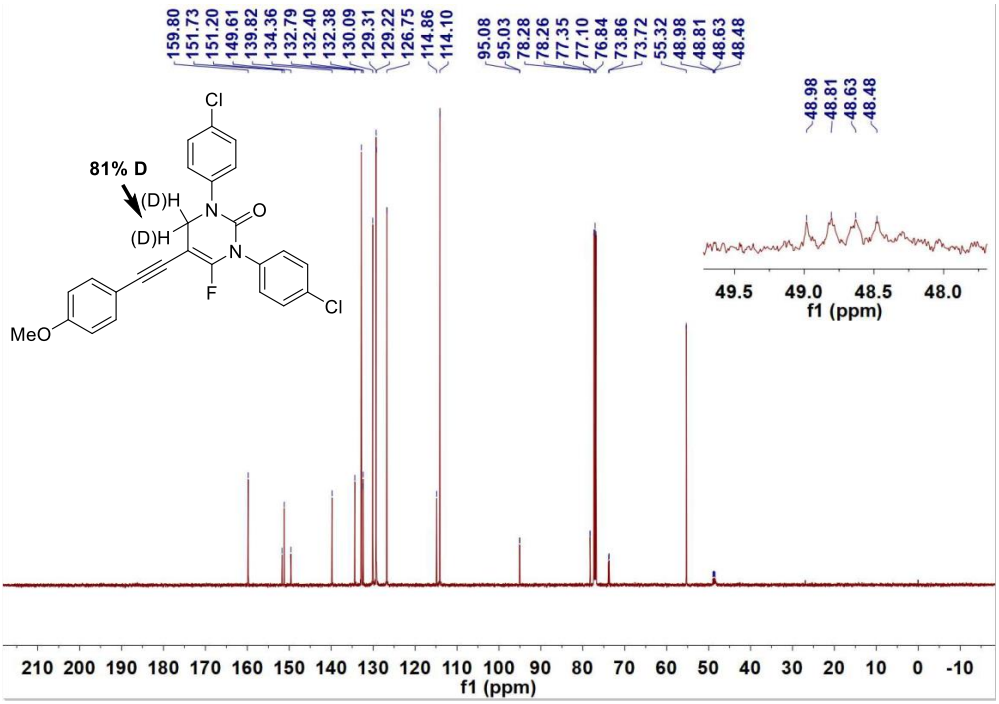
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 78.0 mg, 83%; Brown yellow solid, mp 123.6-125.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40-7.34 (m, 6H), 7.27 (d, *J* = 4.5 Hz, 4H), 6.84 (d, *J* = 7.5 Hz, 2H), 4.40 (t, *J* = 4.5 Hz, 0.19H/0.89D), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.8, 151.2, 150.7 (d, *J* = 263.75 Hz), 139.8, 134.4, 132.8, 132.4 (2C), 130.1, 129.3, 129.2, 126.8, 114.9, 114.1, 95.1 (d, *J* = 5.0 Hz), 78.3 (d, *J* = 1.25 Hz), 73.8 (d, *J* = 16.25 Hz), 55.3, 48.7 (q, *J* = 21.25 Hz); ^{19}F NMR

(471 MHz, $CDCl_3$) δ: -96.46 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{25}H_{16}D_2Cl_2FN_2O_2$ ($[M+H]^+$) 469.0849, found 469.0850.

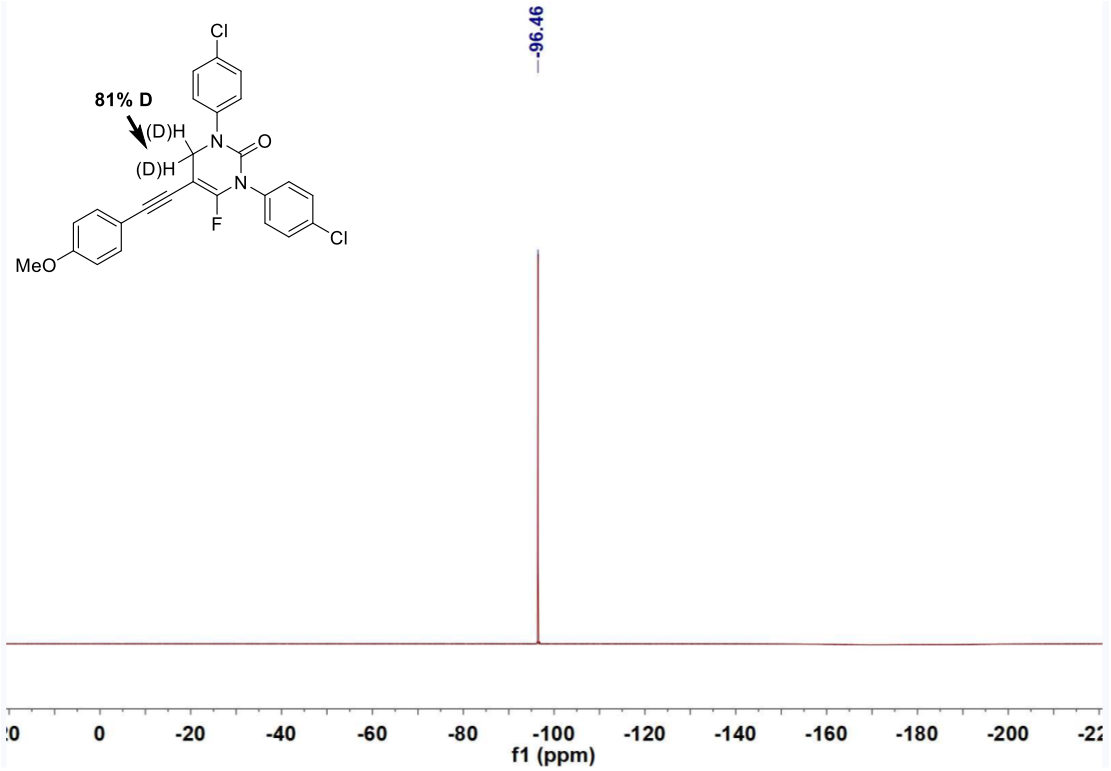
1,3-bis(4-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one-4,4-d_2 (3af/3af-2*d*)



^{1}H-NMR (500 MHz, $CDCl_3$)

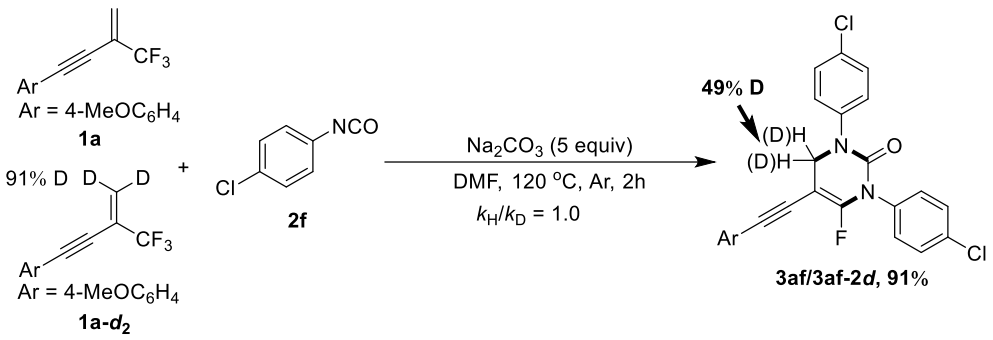


^{13}C-NMR (125 MHz, $CDCl_3$)

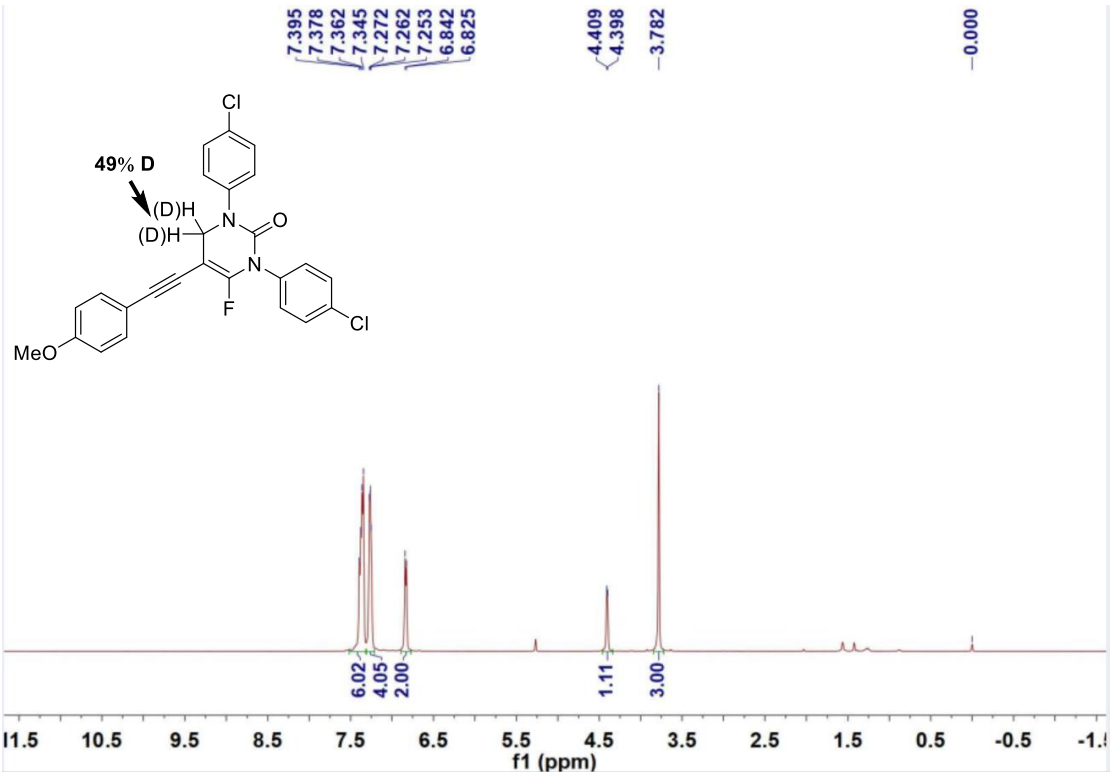


^{19}F-NMR (471 MHz, $CDCl_3$)

(iii) Intermolecular Kinetic Isotope Effect (KIE) Experiments：

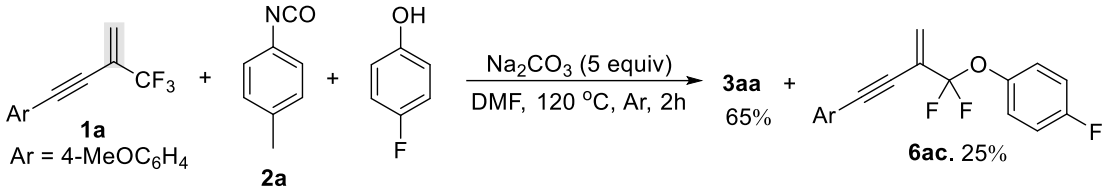


To a Schlenk tube were added 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene **1a** (45.6 mg; 0.2 mmol), 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl-4,4-d_2)benzene **1a-*d*$_2$** (46.0 mg; 0.2 mmol), 1-chloro-4-isocyanatobenzene **2f** (122.8 mg; 0.8 mmol; 4.0 equiv), Na_2CO_3 (106 mg; 1.0 mmol; 5 equiv) and DMF (0.1 M; 1 mL). Then the tube was charged with argon (1 atm), and was stirred at 120 °C for 2 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1) to afford the desired 1,3-bis(4-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4 dihydropyrimidin-2(1*H*)-one-4,4-d_2 products **3af/3af-2*d*** (86.0 mg, 91% yeild, 49% D).



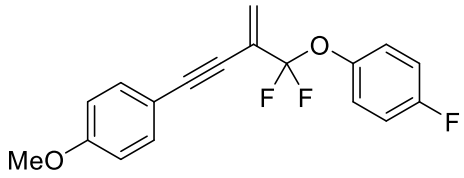
^{1}H-NMR (500 MHz, $CDCl_3$)

(iii) The Reaction in the Presence of Nucleophiles:

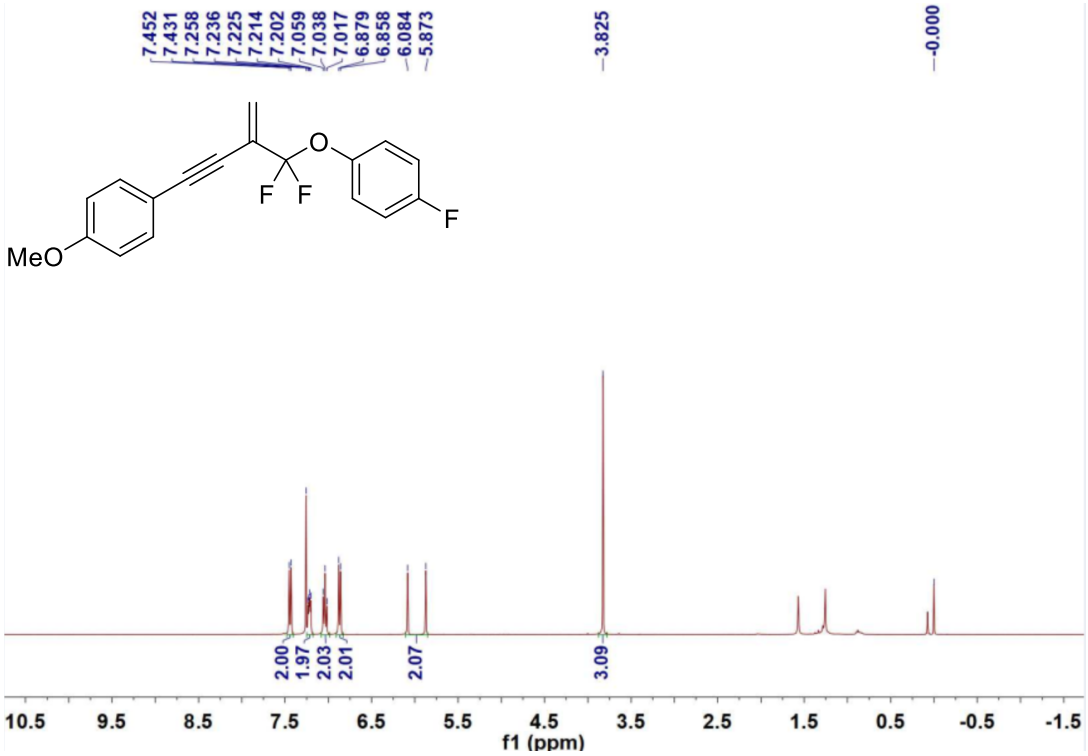


To a Schlenk tube were added 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene **1a** (45.6 mg; 0.2 mmol), 1-isocyanato-4-methylbenzene **2a** (106.4 mg; 0.8 mmol; 4.0 equiv), 4-fluorophenol (67.2 mg; 0.6 mmol; 3 equiv), Na_2CO_3 (106.0 mg; 1.0 mmol; 5 equiv) and DMF (0.1 M; 1mL). Then the tube was charged with argon (1 atm), and was stirred at 120 °C for 2 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1) to afford the desired **3aa** (65%; 55.4 mg) and 1-(3-(difluoro(4-fluorophenoxy)methyl)but-3-en-1-yn-1-yl)-4-methoxybenzene **6ac** (25%; 15.9 mg).

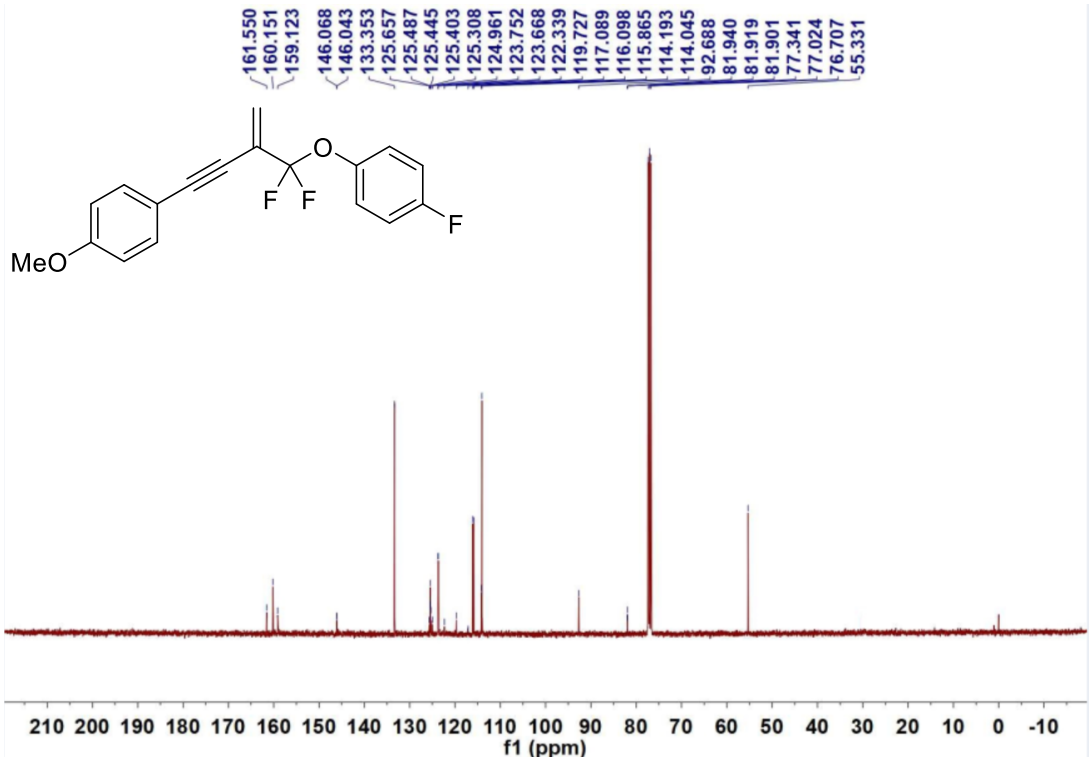
1-(3-(difluoro(4-fluorophenoxy)methyl)but-3-en-1-yn-1-yl)-4-methoxybenzene (6ac):



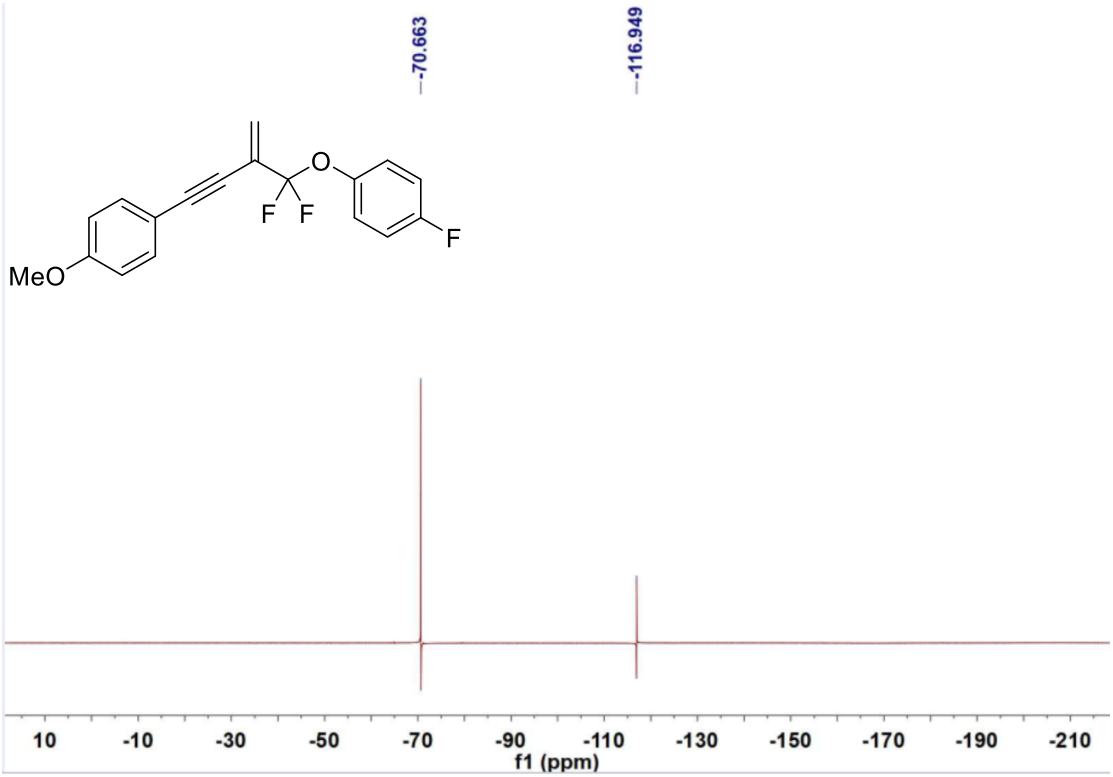
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30 : 1 (v/v)). 15.9 mg, 25%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 8.4 Hz, 2H), 7.24-7.20 (m, 4H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 84.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3 (d, *J* = 242.7 Hz), 160.2, 146.1 (d, *J* = 2.5 Hz), 133.4, 125.5 (d, *J* = 34.9 Hz), 125.4 (t, *J* = 4.2 Hz), 123.7 (d, *J* = 8.4 Hz), 121.0 (q, *J* = 262.2 Hz), 116.0 (d, *J* = 23.3 Hz), 114.2, 114.0, 92.7, 81.9 (t, *J* = 2.1 Hz), 55.3; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: -70.66 (s, 2F), -116.95 (s, 1F); LRMS (EI, 70 eV) *m/z* (%): 318 (M^+, 100), 207 (49), 157 (75); HRMS *m/z* (ESI) calcd for $C_{18}H_{14}F_3O_2$ ($[M+H]^+$) 319.0940, found 319.0940.



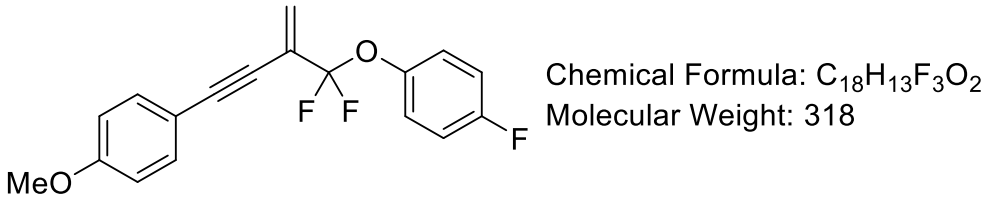
^{1}H-NMR (400 MHz, $CDCl_3$)

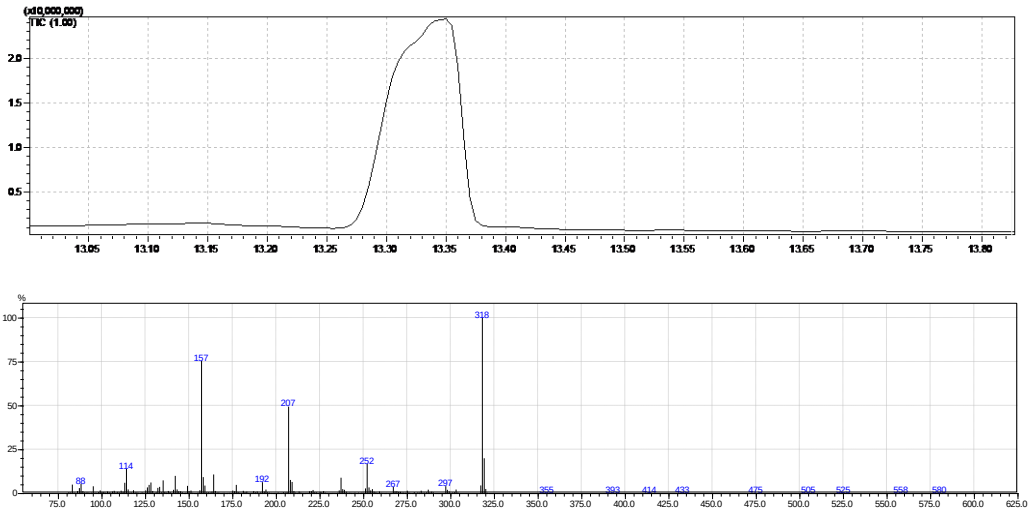


^{13}C-NMR (100 MHz, $CDCl_3$)



^{19}F-NMR (376.5 MHz, $CDCl_3$)





[MS Spectrum]

# of Peaks 521

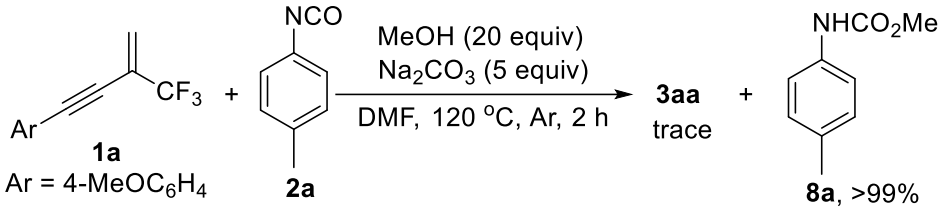
Raw Spectrum 13.345 (scan : 1870)

Background No Background Spectrum

Base Peak m/z 318.05 (Inten : 4,513,671)

Event# 1

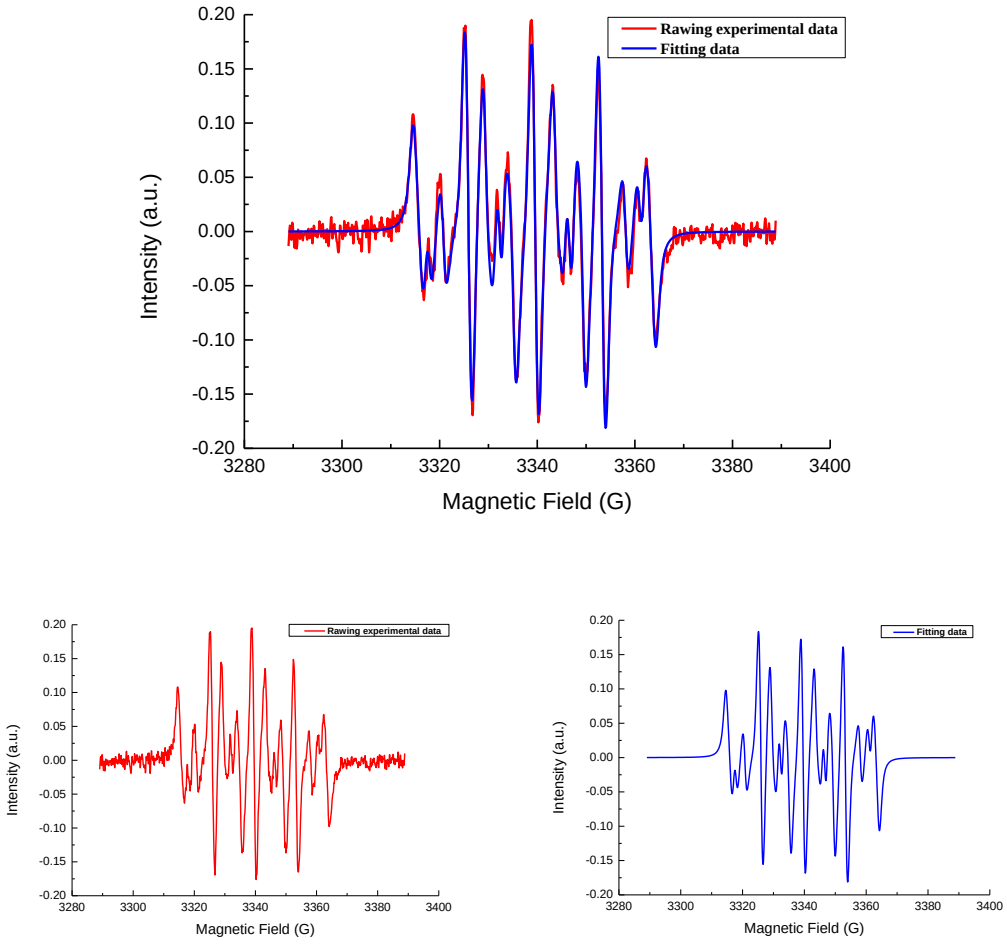
m/z	Absolute Intensity	Relative Intensity						
83.00	221964	4.92	145.05	50146	1.11	237.00	400254	8.87
86.00	54714	1.21	149.05	187506	4.15	238.00	104913	2.32
87.05	130894	2.90	149.95	55354	1.23	239.00	88508	1.96
88.05	242251	5.37	151.05	69344	1.54	251.05	123049	2.73
89.05	55913	1.24	156.15	77236	1.71	252.05	755052	16.73
95.05	177192	3.93	**157.05**	**3405389**	**75.45**	253.05	149131	3.30
99.00	71018	1.57	158.05	413171	9.15	254.00	72377	1.60
107.05	61803	1.37	159.05	197162	4.37	255.00	106809	2.37
111.00	65881	1.46	164.00	484170	10.73	267.05	159046	3.52
113.05	267196	5.92	165.00	57047	1.26	268.00	46516	1.03
114.05	625152	13.85	175.00	69614	1.54	269.00	49158	1.09
115.05	99106	2.20	176.00	50727	1.12	275.00	63903	1.42
118.05	76848	1.70	177.00	213858	4.74	283.00	64558	1.43
125.05	72717	1.61	181.00	60924	1.35	287.00	91666	2.03
126.05	150096	3.33	187.00	56060	1.24	297.05	183088	4.06
127.05	212643	4.71	192.00	281537	6.24	298.00	85351	1.89
128.05	275031	6.09	194.00	93938	2.08	299.00	48852	1.08
129.10	57457	1.27	**207.00**	**2226310**	**49.32**	303.00	93121	2.06
132.05	137286	3.04	208.00	341884	7.57	317.15	199012	4.41
133.05	164931	3.65	209.00	288329	6.39	**318.05**	**4513671**	**100.00**
135.05	331238	7.34	210.00	53438	1.18	319.05	898150	19.90
138.05	58036	1.29	219.00	52415	1.16	320.00	108446	2.40
141.05	88448	1.96	220.00	55826	1.24	320.95	99570.22	
142.05	447251	9.91	221.00	83143	1.84			
143.05	96667	2.14	227.00	53639	1.19			
144.05	51982	1.15	236.00	71201	1.58			



To a Schlenk tube were added 1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl)benzene **1a** (45.6 mg; 0.2 mmol), 1-isocyanato-4-methylbenzene **2a** (106.4 mg; 0.8 mmol; 4.0 equiv), MeOH (128 mg; 4 mmol; 20 equiv), Na_2CO_3 (106.0 mg; 1.0 mmol; 5 equiv) and DMF (0.1 M, 1mL). Then the tube was charged with argon (1 atm), and was stirred at 120 ^{o}C for 2 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was filtered by a crude column with ethyl acetate as eluent, and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1) to afford the desired methyl *p*-tolylcarbamate **8a** (99%; 130.7 mg).

(h) EPR Experiments:

The reaction between Na_2CO_3, α-polyfluoromethyl alkene **1a** and arylisocyanate **2a** in DMF were investigated by in situ EPR in the presence of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin trap to detect the short-lived radicals during the reaction. The EPR measurement of the reaction mixture shows three different EPR signals arising from the spin adducts. The first signal at g = 2.0057 with coupling constant A_N = 13.68 G, which is the N-radical generated by DMPO itself under high temperature condition. The second signal at g = 2.0057 with coupling constant A_N = 14.40 G and A_H = 18.16 G due to the formation of DMPO-C spin adduct. The third signal at g = 2.0057 with A_H = 14.54 G, $A_{N\alpha}$ = 14.3 G and $A_{N\beta}$ = 2.92 G due to the formation of DMPO-*N* spin adduct.

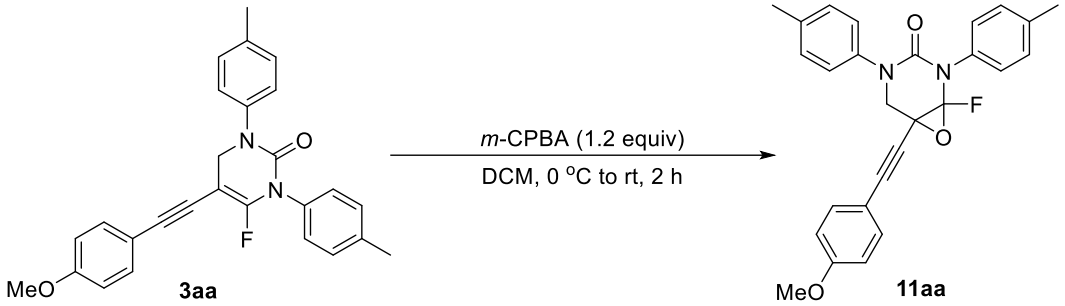


Rawing experimental data **Fitting data (blue line)**

Figure S1. EPR spectra. The reaction was conducted under the standard Conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), Na_2CO_3 (1.0 mmol; 5 equiv) in DMF (0.2 M; 1mL) was stirred at 120 °C under Ar for 0.5 h. Rawing experimental data (red line); Fitting data (blue line).

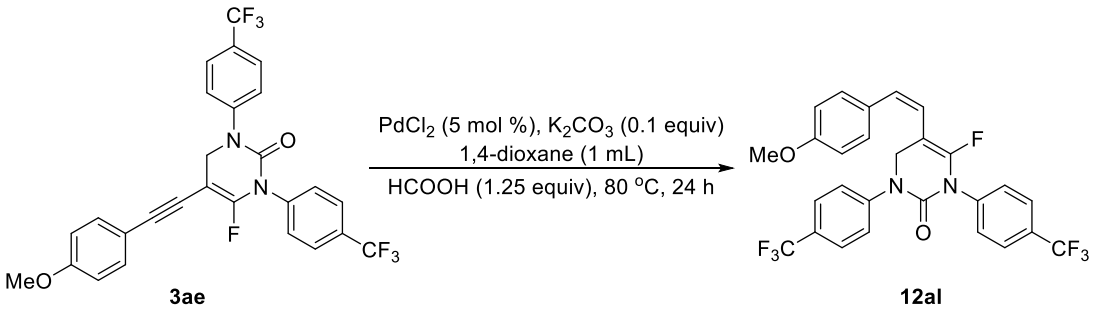
(i) Synthetic Ultizations：

Synthesis of 1-fluoro-6-((4-methoxyphenyl)ethynyl)-2,4-di-*p*-tolyl-7-oxa-2,4-diazabicyclo[4.1.0]heptan-3-one (11aa):[4]



To a Schlenk tube solution of **3aa** (42.6 mg, 0.1 mmol, 1.0 equiv) in DCM 1.0 mL, *m*-CPBA (20.7 mg, 0.12 mmol, 1.2 equiv). The reaction mixture was stirred at 0 °C to room temperature for 2 h. After the reaction was completed, which was determined by TLC analysis. The resulting crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3 : 1) to give compound **11aa** (23.9 mg, 54%) as a brown yellow solid.

Synthesis of (*Z*)-6-fluoro-5-(4-methoxystyryl)-1,3-bis(4-(trifluoromethyl)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (12al):[5]

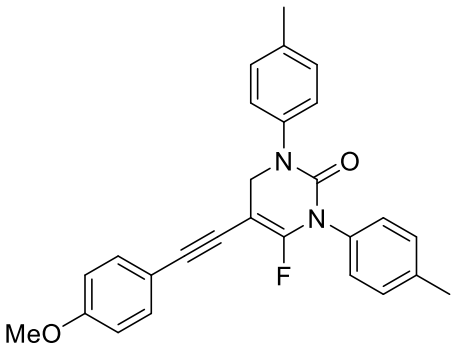


To an oven-dried 10 mL Schlenk tube equipped with a stir bar was added **3ae** (53.4 mg, 0.10 mmol, 1.0 equiv), $PdCl_2$ (5 mol %, 0.9 mg, 0.05 equiv), K_2CO_3 (2.8 mg, 0.010 mmol, 0.1 equiv), and 1,4-dioxane (1.0 mL) under argon atmosphere. Then, formic acid (5.8 mg, 0.125 mmol, 1.25 equiv) was added rapidly to this suspension. A black precipitate was formed and the suspension was stirred at 80 °C for 24 h. After the completion, insoluble materials were removed by filtration

through a pad of Celite and washes with CH_2Cl_2 (10 mL × 3). The solvent was concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5 : 1) to give compound **12al** (23.0 mg, 43%) as a brown yellow solid.

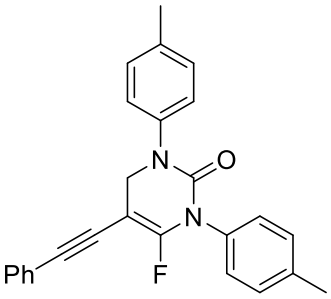
(B) Analytical Data

6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3aa):



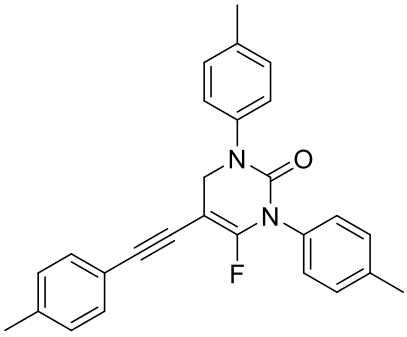
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 70.7 mg, 83%; Brown yellow solid, mp 122.3-124.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 8.0 Hz, 2H), 7.23-7.17 (m, 8H), 6.82 (d, *J* = 8.0 Hz, 2H), 4.42 (d, *J* = 5.5 Hz, 2H), 3.78 (s, 3H), 2.34 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.6, 151.4 (d, *J* = 263.75 Hz), 151.7, 139.1, 138.3, 136.6, 132.7, 131.4, 129.8, 129.6, 128.6, 125.4, 115.2, 114.0, 94.4 (d, *J* = 5.0 Hz), 78.9 (d, *J* = 1.25 Hz), 73.0 (d, *J* = 17.5 Hz), 55.3, 49.4 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.93 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}FN_2O_2$ ($[M+H]^+$) 427.1816, found 427.1817.

6-fluoro-5-(phenylethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ba):



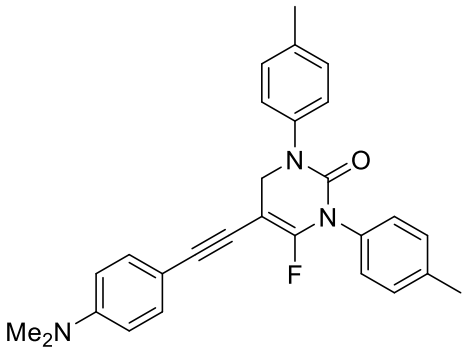
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 64.9 mg, 82%; Brown yellow solid, mp 118.5-120.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 4.5 Hz, 2H), 7.29 (d, *J* = 5.0 Hz, 2H), 7.24-7.18 (m, 8H), 4.44 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.8 (d, *J* = 265.0 Hz), 151.6, 139.0, 138.4, 136.7, 131.3, 131.2, 129.8, 129.6, 128.6, 128.4, 128.2, 125.5, 123.1, 94.5 (d, *J* = 5.0 Hz), 80.4 (d, *J* = 2.5 Hz), 72.7 (d, *J* = 17.5 Hz), 49.4 (d, *J* = 3.75 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.07 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{22}FN_2O$ ($[M+H]^+$) 397.1711, found 397.1712.

6-fluoro-1,3-di-*p*-tolyl-5-(*p*-tolylethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ca):



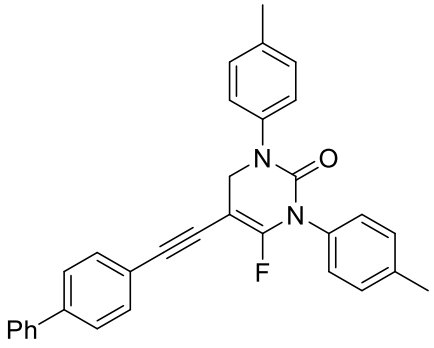
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 76.3 mg, 93%; Brown yellow solid, mp 123.4-125.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.299 (d, *J* = 8.0 Hz, 2H), 7.208 (t, *J* = 5.2 Hz, 8H), 7.103 (d, *J* = 8.0 Hz, 2H), 4.437 (d, *J* = 5.6 Hz, 2H), 2.349 (d, *J* = 11.2 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.7, 151.6 (d, *J* = 263.75 Hz), 139.0, 138.4, 138.3, 136.7, 131.4, 131.1, 129.8, 129.6, 129.1, 128.6, 125.5, 120.1, 94.6 (d, *J* = 5.0 Hz), 79.7 (d, *J* = 2.5 Hz), 72.9 (d, *J* = 17.5 Hz), 49.4 (d, *J* = 2.5 Hz), 21.5, 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.53 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}FN_2O$ ($[M+H]^+$) 411.1867, found 411.1867.

5-((4-(dimethylamino)phenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3da**):



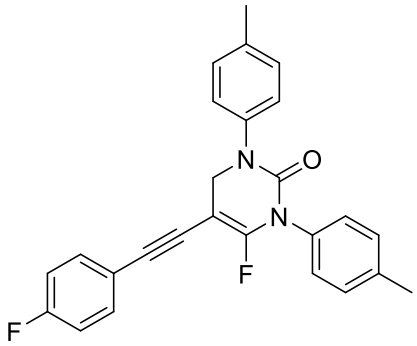
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 26.3 mg, 30%; Brown yellow solid, mp 176.3-178.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.282 (d, *J* = 8.8 Hz, 2H), 7.229-7.154 (m, 8H), 6.591 (d, *J* = 8.8 Hz, 2H), 4.410 (d, *J* = 5.6 Hz, 2H), 2.928 (s, 6H), 2.334 (d, *J* = 10.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.8, 150.8 (d, *J* = 263.75 Hz), 150.1, 139.1, 138.2, 136.5, 132.4, 131.6, 129.7, 129.5, 128.6, 125.4, 111.8, 109.8, 95.5 (d, *J* = 5.0 Hz), 77.9 (d, *J* = 2.5 Hz), 73.5 (d, *J* = 17.5 Hz), 49.6 (d, *J* = 3.75 Hz), 40.2, 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.93 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{28}H_{27}FN_3O$ ($[M+H]^+$) 440.2133, found 440.2128.

5-([1,1'-biphenyl]-4-ylethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3ea**):



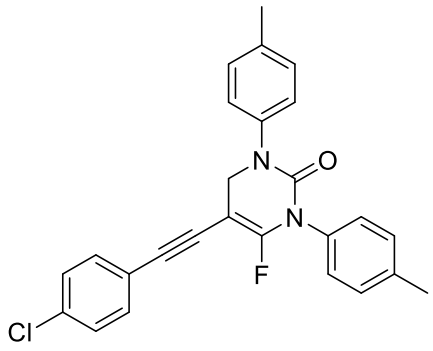
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 53.8 mg, 57%; Brown yellow solid, mp 211.5-213.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58-7.53 (m, 4H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.25-7.18 (m, 8H), 4.46 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.8 (d, *J* = 263.75 Hz), 151.7, 140.9, 140.3, 139.0, 138.4, 136.7, 131.6, 131.3, 129.8, 129.6, 128.9, 128.6, 127.7, 127.0 (2C), 125.5, 122.0, 94.4 (d, *J* = 5.0 Hz), 81.1 (d, *J* = 2.5 Hz), 72.8 (d, *J* = 16.25 Hz), 49.4 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -94.92 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{32}H_{26}FN_2O$ ($[M+H]^+$) 473.2024, found 473.2026.

6-fluoro-5-((4-fluorophenyl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3fa) :



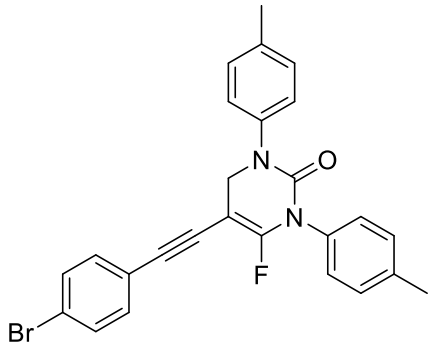
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 65.4 mg, 79%; Brown yellow solid, mp 142.0-144.2 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (t, *J* = 6.5 Hz, 2H), 7.24-7.18 (m, 8H), 6.99 (t, *J* = 8.5 Hz, 2H), 4.43 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4 (d, *J* = 248.75 Hz), 151.6, 151.9 (d, *J* = 265.0 Hz), 139.0, 138.4, 136.7, 133.1 (d, *J* = 7.5 Hz), 131.3, 129.8 129.6, 128.6, 125.4, 119.2 (d, *J* = 3.75 Hz), 115.7 (d, *J* = 22.5 Hz), 93.3 (d, *J* = 5.0 Hz), 80.1 (d, *J* = 1.25 Hz), 72.5 (d, *J* = 16.25 Hz), 49.3 (d, *J* = 3.75 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -94.99 (t, *J* = 4.71 Hz, 1F), -110.9--111.0 (q, *J* = 9.42 Hz, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}F_2N_2O$ ($[M+H]^+$) 415.1616, found 415.1617.

5-((4-chlorophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ga):



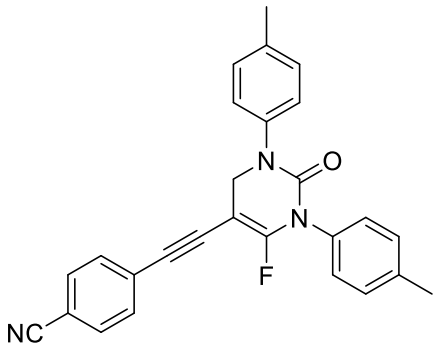
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 73.9 mg, 77%; Brown yellow solid, mp 201.5-203.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.24-7.18 (m, 8H), 4.43 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.6, 151.1 (d, *J* = 263.75 Hz), 139.0, 138.5, 136.8, 134.2, 132.4, 131.3, 129.8, 129.7, 128.8, 128.7, 125.5, 121.7, 93.4 (d, *J* = 5.0 Hz), 81.6 (d, *J* = 2.5 Hz), 72.5 (d, *J* = 16.25 Hz), 49.2 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -94.45 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}ClFN_2O$ ($[M+H]^+$) 431.1321, found 431.1319.

5-((4-bromophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ha):



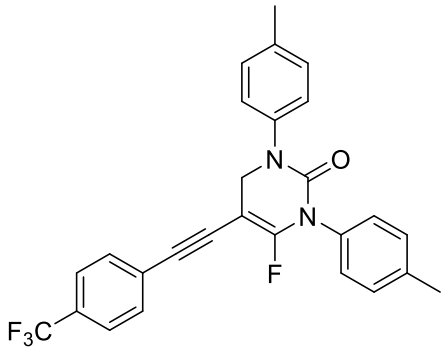
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 80.6 mg, 85%; Brown yellow solid, mp 189.5-190.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 8.0 Hz, 2H), 7.26-7.18 (m, 10H), 4.43 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.1 (d, *J* = 265.0 Hz), 151.6, 138.9, 138.5, 136.8, 132.6, 131.6, 131.2, 129.8, 129.6, 128.6, 125.4, 122.3, 122.1, 93.4 (d, *J* = 6.25 Hz), 81.7 (d, *J* = 2.5 Hz), 72.4 (d, *J* = 17.5 Hz), 49.2 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -94.38 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}BrFN_2O$ ($[M+H]^+$) 475.0816, found 475.0819.

4-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)benzonitrile (3ia):



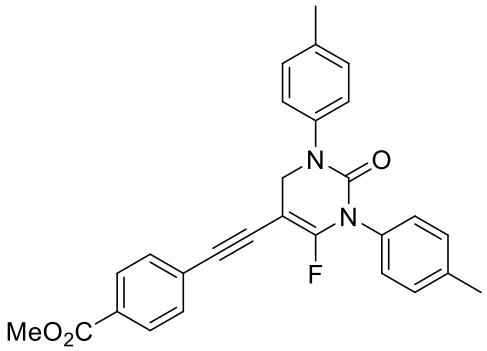
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 50.5 mg, 60%; Brown yellow solid, mp 240.5-243.3 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.24-7.18 (m, 8H), 4.45 (d, *J* = 5.6 Hz, 2H), 2.35 (d, *J* = 10.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.9 (d, *J* = 266.25 Hz), 151.4, 138.8, 138.7, 136.9, 132.1, 131.4, 131.0, 129.8, 129.7, 128.6, 128.1, 125.4, 118.6, 111.1, 93.1 (d, *J* = 5.0 Hz), 85.4 (d, *J* = 2.5 Hz), 71.9 (d, *J* = 16.25 Hz), 49.0 (d, *J* = 3.75 Hz), 21.2, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -92.54 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{21}FN_3O$ ($[M+H]^+$) 422.1663, found 422.1663.

6-fluoro-1,3-di-*p*-tolyl-5-((4-(trifluoromethyl)phenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ja**):



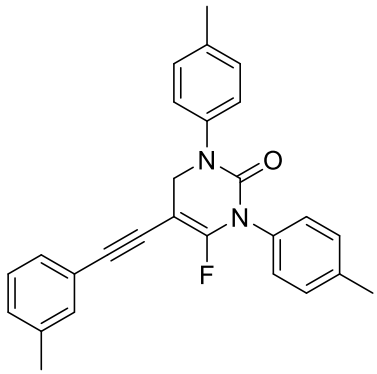
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 63.1 mg, 68%; Brown yellow solid, mp 245.3-247.2 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.25-7.19 (m, 8H), 4.46 (d, *J* = 5.5 Hz, 2H), 2.36 (d, *J* = 14.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:153.6, 151.5, 138.9, 138.6, 136.9, 131.3, 131.1, 129.8, 129.7, 128.6, 127.0, 125.4, 125.3 (d, *J* = 3.75 Hz), 125.0, 122.9, 93.2 (d, *J* = 5.0 Hz), 83.2, 72.1 (d, *J* = 17.5 Hz), 49.1 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -62.78 (s, 3F), -93.50 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{21}F_4N_2O$ ($[M+H]^+$) 465.1585, found 465.1582.

methyl 4-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)benzoate (**3ka**):



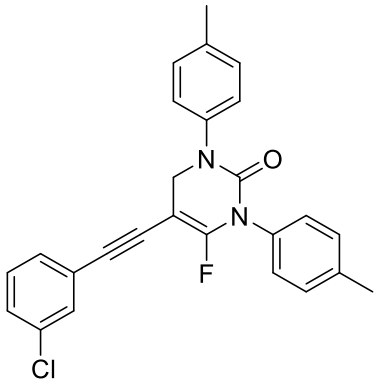
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 61.7 mg, 68%; Brown yellow solid, mp >250 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.966 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.24-7.18 (m, 8H), 4.45 (d, *J* = 5.5 Hz, 2H), 3.89 (s, 3H), 2.35 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:166.5, 152.4 (d, *J* = 266.25 Hz), 151.5, 138.9, 138.5, 136.8, 131.1, 130.9, 129.8, 129.7, 129.5, 129.2, 128.6, 127.8, 125.4, 93.9 (d, *J* = 5.0 Hz), 83.8 (d, *J* = 1.25 Hz), 72.2 (d, *J* = 16.25 Hz), 52.3, 49.1 (d, *J* = 3.75 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.53 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{28}H_{24}FN_2O_3$ ($[M+H]^+$) 455.1765, found 455.1763.

6-fluoro-1,3-di-*p*-tolyl-5-(*m*-tolylethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3la**):



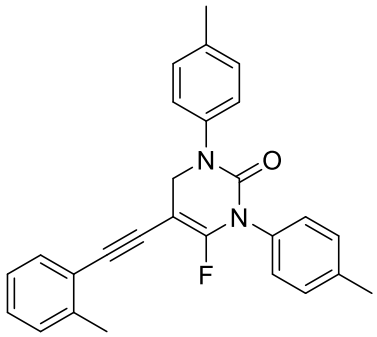
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 54.9 mg, 67%; Brown yellow solid, mp 124.9-126.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25-7.18 (m, 11H), 7.10 (d, *J* = 7.5 Hz, 1H), 4.44 (d, *J* = 5.5 Hz, 2H), 2.34 (t, *J* = 13.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:151.7, 151.6 (d, *J* = 263.75 Hz), 139.0, 138.4, 138.0, 136.7, 131.8, 131.3, 129.8, 129.6, 129.1, 128.6, 128.3, 128.2, 125.5, 122.9, 94.7 (d, *J* = 5.0 Hz), 80.0 (d, *J* = 2.5 Hz), 72.8 (d, *J* = 17.5 Hz), 49.4 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (; MHz, $CDCl_3$) δ: -95.29 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}FN_2O$ ($[M+H]^+$) 411.1867, found 411.1872.

5-((3-chlorophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3ma**):



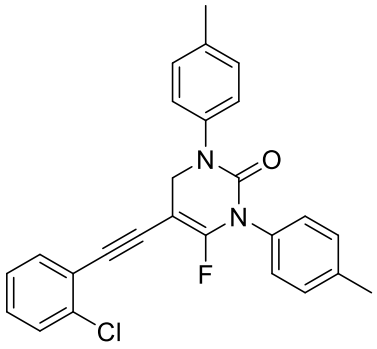
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 47.3 mg, 55%; Brown yellow solid, mp 223.6-225.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (s, 1H), 7.28-7.18 (m, 11H), 4.44 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 13.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.3 (d, *J* = 265.0 Hz), 151.5, 138.9, 138.5, 136.8, 134.2, 131.2, 130.9, 129.8, 129.7, 129.6, 129.3, 128.6, 128.4, 125.4, 124.9, 93.1 (d, *J* = 5.0 Hz), 81.8 (d, *J* = 2.5 Hz), 72.3 (d, *J* = 17.5 Hz), 49.2 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -94.08 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}ClFN_2O$ ($[M+H]^+$) 431.1321, found 431.1319.

6-fluoro-1,3-di-*p*-tolyl-5-(*o*-tolylethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3na**):



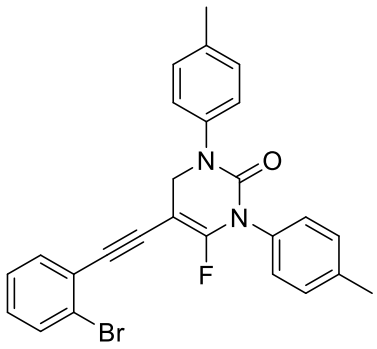
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 63.1 mg, 77%; Brown yellow solid, mp 131.6-133.2 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36 (d, *J* = 7.5 Hz, 1H), 7.25-7.19 (m, 10H), 7.13-7.11 (m, 1H), 4.46 (d, *J* = 5.5 Hz, 2H), 2.37 (t, *J* = 15.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:151.7, 151.6 (d, *J* = 263.75 Hz), 139.7, 139.0, 138.4, 136.8, 131.4, 131.3, 129.8, 129.6, 129.5, 128.7, 128.2, 125.6, 125.5, 122.9, 93.5 (d, *J* = 5.0 Hz), 84.3 (d, *J* = 2.5 Hz), 72.9 (d, *J* = 17.5 Hz), 49.4 (d, *J* = 3.75 Hz), 21.2, 21.1, 20.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.35 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}FN_2O$ ($[M+H]^+$) 411.1867, found 411.1866.

5-((2-chlorophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3oa**):



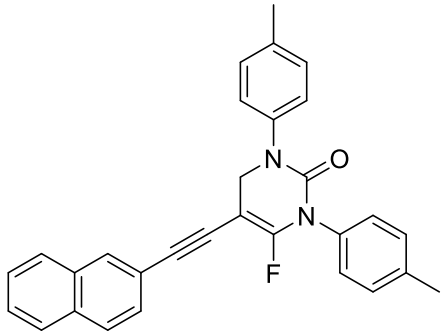
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 74.8 mg, 87%; Brown yellow solid, mp 232.3-236.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 7.0 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.25-7.18 (m, 10H), 4.47 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 12.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.3 (d, *J* = 265.0 Hz), 151.6, 139.0, 138.5, 136.8, 135.3, 132.7, 131.2, 129.8, 129.7, 129.3, 129.1, 128.7, 126.5, 125.5, 123.1, 91.4 (d, *J* = 5.0 Hz), 85.8 (d, *J* = 2.5 Hz), 72.4 (d, *J* = 16.25 Hz), 49.2 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -93.72 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}ClFN_2O$ ($[M+H]^+$) 431.1321, found 431.1317.

5-((2-bromophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3pa**):



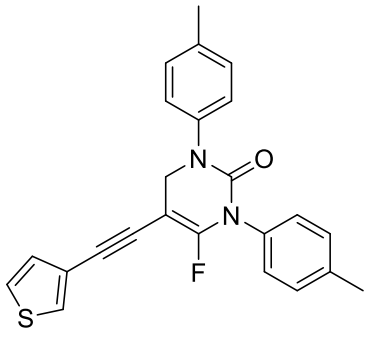
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 70.2 mg, 74%; Brown yellow solid, mp 243.6-244.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.553 (d, *J* = 8.0 Hz, 1H), 7.417 (d, *J* = 7.5 Hz, 1H), 7.25-7.18 (m, 9H), 7.11 (t, *J* = 8.0 Hz, 1H), 4.48 (d, *J* = 5.5 Hz, 2H), 2.35 (d, *J* = 12.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 152.3 (d, *J* = 266.25 Hz), 151.5, 139.0, 138.5, 136.8, 132.7, 132.4, 131.2, 129.8, 129.7, 129.2, 128.7, 127.1, 125.5, 125.3, 125.0, 93.2 (d, *J* = 5.0 Hz), 85.3 (d, *J* = 2.5 Hz), 72.4 (d, *J* = 17.5 Hz), 49.1 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -93.59 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}BrFN_2O$ ([M+H]+) 475.0816, found 475.0813.

6-fluoro-5-(naphthalen-2-ylethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3qa**):



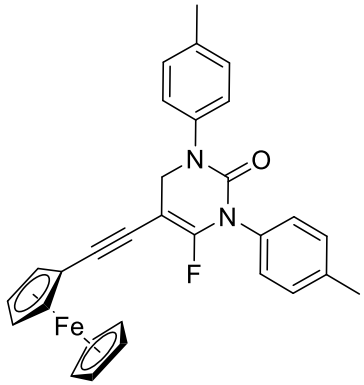
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 62.4 mg, 70%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (s, 1H), 7.79-7.74 (m, 2H), 7.58-7.41 (m, 4H), 7.25-7.18 (m, 8H), 4.48 (d, *J* = 5.0 Hz, 2H), 2.35 (d, *J* = 15.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:151.9 (d, *J* = 263.75 Hz), 151.7, 139.0, 138.4, 136.7, 133.0, 132.7, 131.6, 131.4, 130.9, 129.8, 129.6, 128.9, 128.6, 128.1, 127.8 (d, *J* = 5.0 Hz), 127.0 (d, *J* = 5.0 Hz), 126.6 (d, *J* = 5.0 Hz), 125.5, 120.4, 95.0 (d, *J* = 6.25 Hz), 80.9 (d, *J* = 1.25 Hz), 72.8 (d, *J* = 17.5 Hz), 49.4 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -94.81 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{30}H_{24}FN_2O$ ($[M+H]^+$) 447.1867, found 447.1867.

6-fluoro-5-(naphthalen-2-ylethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3ra**):



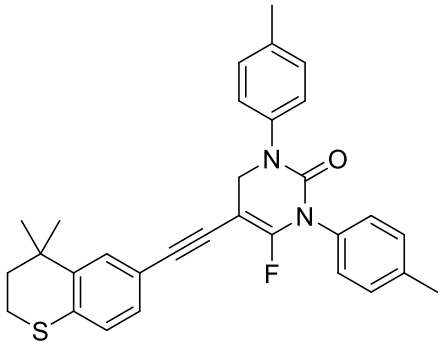
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 41.0 mg, 51%; Brown yellow solid, mp 222.9-225.1 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (s, 1H), 7.26-7.18 (m, 9H), 7.09 (d, *J* = 5.0 Hz, 1H), 4.43 (d, *J* = 5.0 Hz, 2H), 2.36 (d, *J* = 15.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:151.8 (d, *J* = 263.75 Hz), 151.6, 139.0, 138.4, 136.7, 131.3, 129.8, 129.7, 129.6, 128.6, 128.3, 125.4, 122.1, 89.5 (d, *J* = 6.25 Hz), 79.8 (d, *J* = 2.5 Hz), 72.6 (d, *J* = 17.5 Hz), 49.3 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.17 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{24}H_{20}FN_2OS$ ($[M+H]^+$) 403.1275, found 403.1274.

6-fluoro-5-(ferrocenylethynyl)-1,3-di-p-tolyl-3,4-dihydropyrimidin-2(1H)-one (3sa):



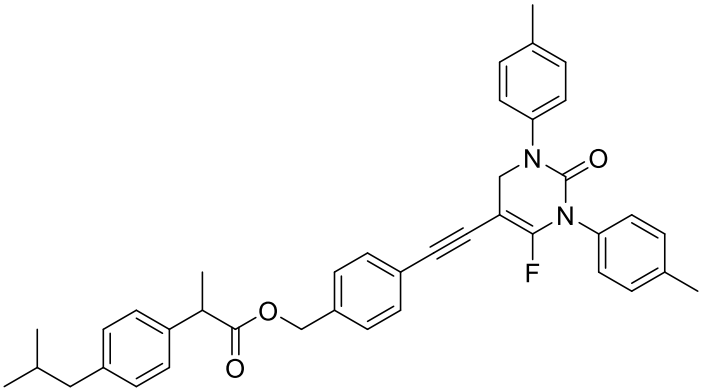
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 95.8 mg, 95%; Brownish red solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25-7.18 (m, 8H), 4.41 (s, 4H), 4.19 (d, *J* = 3.5 Hz, 7H), 2.36 (d, *J* = 15.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:151.7, 151.4 (d, *J* = 262.5 Hz), 139.0, 138.3, 136.7, 131.4, 129.8, 129.6, 128.6, 125.4, 92.2 (d, *J* = 5.0 Hz), 76.1 (d, *J* = 2.5 Hz), 73.2 (d, *J* = 17.5 Hz), 71.4, 70.1, 68.9, 64.9, 49.4 (d, *J* = 2.5 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.24 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{30}H_{26}FFeN_2O$ ($[M+H]^+$) 505.1073, found 505.1074.

5-((4,4-dimethylthiochroman-6-yl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3ta**):



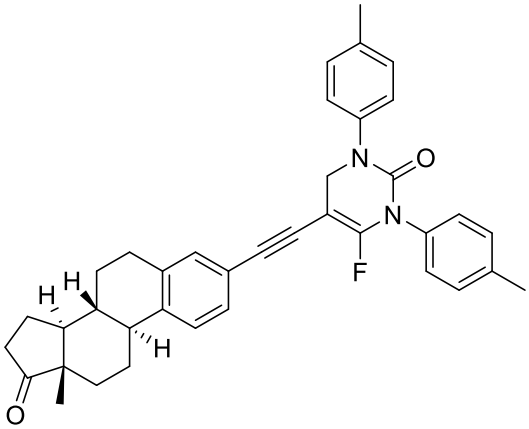
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 39.7 mg, 40%; Brown yellow solid, mp 216.3-217.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.39 (s, 1H), 7.25-7.18 (m, 8H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 3.03-3.01 (m, 2H), 2.36 (d, *J* = 14.0 Hz, 6H), 1.92 (d, *J* = 5.0 Hz, 2H), 1.30 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.7, 151.5 (d, *J* = 263.75 Hz), 142.0, 139.0, 138.3, 136.7, 133.0, 131.4, 129.8, 129.6, 129.3, 128.6, 126.5, 125.4, 118.3, 94.8 (d, *J* = 5.0 Hz), 79.5 (d, *J* = 1.25 Hz), 72.9 (d, *J* = 17.5 Hz), 49.4 (d, *J* = 2.5 Hz), 37.2, 32.9, 30.0, 23.2, 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.53 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{31}H_{30}FN_2OS$ ($[M+H]^+$) 497.2057, found 497.2055.

4-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)benzyl 2-(4-isobutylphenyl)propanoate (**3ua**):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 79.8 mg, 65%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (d, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 10H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 5.07 (s, 2H), 4.44 (d, *J* = 5.5 Hz, 2H), 3.76-3.71 (m, 2H), 2.44 (d, *J* = 7.0 Hz, 2H), 2.35 (d, *J* = 13.0 Hz, 6H), 1.88-1.80 (m, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:174.4, 151.9 (d, *J* = 265 Hz), 151.6, 140.7, 139.0, 138.4, 137.5, 136.7, 136.1, 131.3, 131.2, 129.8, 129.6, 129.4, 128.6, 127.7, 127.2, 125.4, 122.8, 94.2 (d, *J* = 5.0 Hz), 80.8 (d, *J* = 2.5 Hz), 72.6 (d, *J* = 16.25 Hz), 65.8, 49.3 (d, *J* = 3.75 Hz), 45.1 (2C), 30.2, 22.4, 21.2, 21.1, 18.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -94.83 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{40}H_{40}FN_2O_3$ ($[M+H]^+$) 615.3017, found 615.3020.

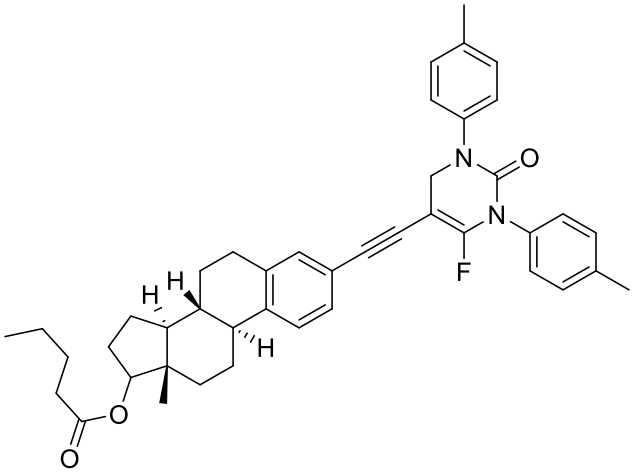
6-fluoro-5-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3va**):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 93.8 mg, 82%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24-7.16 (m, 11H), 4.43 (d, *J* = 5.5 Hz, 2H), 2.86 (t, *J* = 4.5 Hz, 2H), 2.52-2.46 (m, 1H), 2.35 (d, *J* = 13.5 Hz, 6H), 2.16-2.09 (m, 1H), 2.07-1.94 (m, 3H), 1.66-1.40 (m, 7H), 0.90 (s, 3H); ^{13}C NMR (125

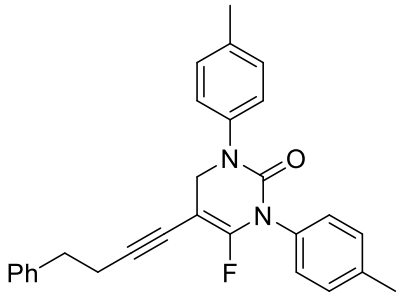
MHz, $CDCl_3$) δ: 220.7, 151.7, 151.6 (d, *J* = 263.75 Hz), 140.3, 139.0, 138.4, 136.7 (2C), 131.6, 131.4, 129.8, 129.6, 128.6, 128.5, 125.4, 120.4, 120.1, 94.6 (d, *J* = 5.0 Hz), 79.7 (d, *J* = 1.25 Hz), 72.9 (d, *J* = 16.25 Hz), 50.5, 49.4 (d, *J* = 3.75 Hz), 47.9, 44.5, 38.0, 35.8, 31.6, 29.1, 26.3, 25.6, 21.6, 21.2, 21.1, 13.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.47 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{38}H_{38}FN_2O_2$ ($[M+H]^+$) 573.2912, found 573.2910.

(8R,9S,13S,14S)-3-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl pentanoate (**3wa**):



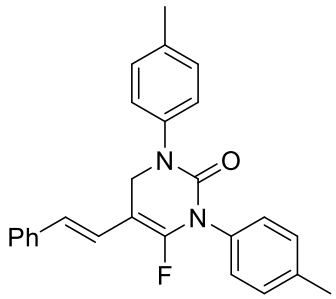
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 110.5 mg, 84%; Brown yellow solid, mp >250 °C (uncorrected); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.26-7.18 (m, 10H), 7.14 (s, 1H), 4.713-4.43 (m, 3H), 2.82 (t, *J* = 4.5 Hz, 2H), 2.37-2.21 (m, 11H), 1.89-1.71 (m, 4H), 1.55-1.26 (m, 10H), 0.92 (s, 4H), 0.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.0, 151.7, 151.5 (d, *J* = 263.75 Hz), 140.8, 139.0, 138.3, 136.8, 136.7, 131.6, 131.4, 129.7, 129.6, 128.6, 128.4, 125.4, 120.2, 94.7 (d, *J* = 5.0 Hz), 82.3, 79.5 (d, *J* = 1.25 Hz), 72.9 (d, *J* = 16.25 Hz), 49.9, 49.4 (d, *J* = 2.5 Hz), 44.3, 42.9, 38.2, 36.9, 34.3, 29.2, 27.6, 27.2, 27.0, 25.9, 23.3, 22.3, 21.2, 21.0, 13.8, 12.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.47 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{43}H_{48}FN_2O_3$ ($[M+H]^+$) 659.3643, found 659.3645.

6-fluoro-5-(4-phenylbut-1-yn-1-yl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3xa**):



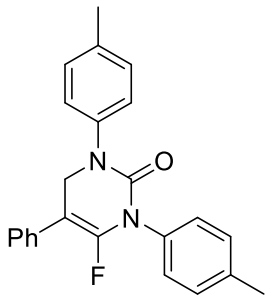
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 46.4 mg, 55%; Brown yellow solid, mp 111.3-112.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.26 (d, *J* = 7.5 Hz, 2H), 7.23-7.16 (m, 11H), 4.28 (d, *J* = 5.5 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.63 (t, *J* = 8.0 Hz, 2H), 2.34 (d *J* = 11.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.7, 151.4 (d, *J* = 261.25 Hz), 140.5, 19.1, 138.2, 136.6, 131.5, 129.7, 129.6, 128.6, 128.5, 128.4, 126.4, 125.4, 94.7 (d, *J* = 5.0 Hz), 72.9 (d, *J* = 17.5 Hz), 72.1 (d, *J* = 2.5 Hz), 49.6 (d, *J* = 3.75 Hz), 35.14, 22.0, 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -97.74 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{28}H_{26}FN_2O$ ($[M+H]^+$) 425.2024, found 425.2025.

(*E*)-6-fluoro-5-styryl-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ya):



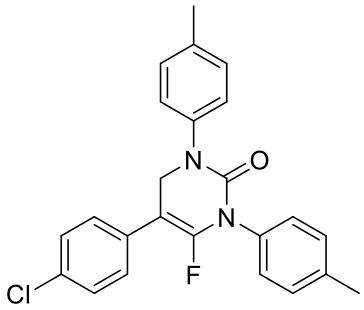
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 35.0 mg, 44%; Brown yellow solid, mp 119.3-120.6 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 4H), 7.24-7.20 (m, 7H), 7.06 (d, *J* = 16.5 Hz, 1H), 6.11 (d, *J* = 16.5 Hz, 1H), 4.55 (s, 2H), 2.370 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 151.6, 146.2 (d, *J* = 262.5 Hz), 139.6, 138.1, 137.4, 136.9, 131.7, 129.9, 129.5, 128.7, 128.6, 127.2, 125.9 (2C), 124.4 (d, *J* = 3.75 Hz), 118.5, 88.2 (d, *J* = 13.75 Hz), 47.9 (d, *J* = 3.75 Hz), 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -106.71 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{24}FN_2O$ ($[M+H]^+$) 399.1867, found 399.1866.

6-fluoro-5-phenyl-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3za):



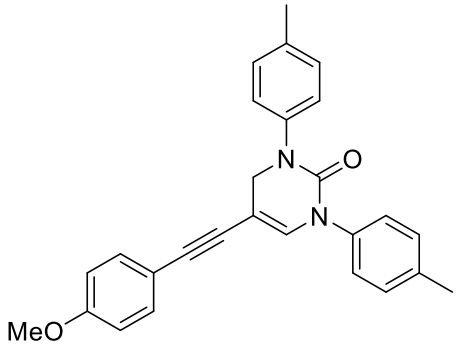
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 38.7 mg, 52%; Brown yellow solid, mp 121.6-123.1 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.31 (m, 4H), 7.28-7.25 (m, 4H), 7.20 (t, *J* = 10.4 Hz, 5H), 4.65 (d, *J* = 6.0 Hz, 2H), 2.36 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 145.5 (d, *J* = 261.2 Hz), 139.5, 137.9, 136.5, 133.0 (d, *J* = 4.6 Hz), 132.0 (d, *J* = 1.2 Hz), 129.7, 129.5, 128.7 (d, *J* = 1.2 Hz), 128.6, 126.6 (d, *J* = 1.3 Hz), 126.3 (d, *J* = 6.0 Hz), 125.5, 88.0 (d, *J* = 13.2 Hz), 49.9 (d, *J* = 4.9 Hz), 21.2, 21.0; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: -105.26 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{24}H_{22}FN_2O$ ($[M+H]^+$) 373.1711, found 373.1712.

5-(4-chlorophenyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3aaa):



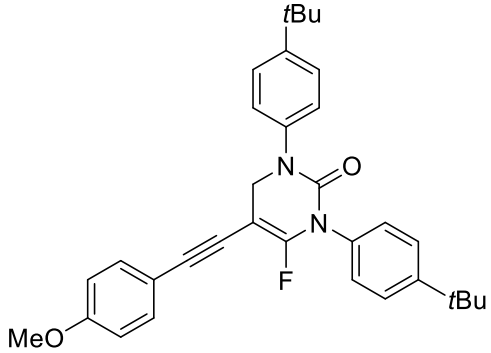
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 46.7 mg, 55%; Brown yellow solid, mp 135.9-137.2^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28-7.22 (m, 8H), 7.21-7.16 (m, 4H), 4.58 (d, *J* = 5.6 Hz, 2H), 2.33 (d, *J* = 9.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.1, 145.9 (d, *J* = 261.3 Hz), 139.4, 138.2, 136.6, 132.2 (d, *J* = 2.1 Hz), 131.9, 131.5 (d, *J* = 4.8 Hz), 129.7 (d, *J* = 17.9 Hz), 128.8, 127.5 (d, *J* = 6.3 Hz), 125.5, 87.0 (d, *J* = 12.9 Hz), 49.7 (d, *J* = 4.9 Hz), 21.2, 21.1; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: -106.05 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{24}H_{21}ClFN_2O$ ($[M+H]^+$) 407.1321, found 407.1322.

5-((4-methoxyphenyl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3aca):



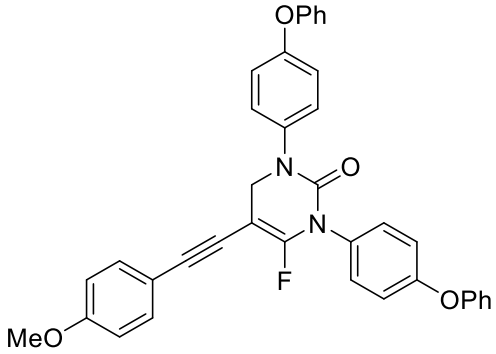
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 66.9 mg, 82%; Brown yellow solid, mp 109.2-110.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 4H), 7.18 (t, *J* = 6.5 Hz, 4H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 4.51 (s, 2H), 3.80 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.5, 151.8, 139.7, 138.2, 136.8, 136.3, 134.8, 132.7, 129.6, 129.5, 126.4, 125.5, 115.2, 114.0, 94.4, 91.2, 83.6, 55.3, 52.6, 21.0; HRMS *m/z* (ESI) calcd for $C_{27}H_{25}N_2O_2$ ($[M+H]^+$) 409.1911, found 409.1913.

1,3-bis(4-(tert-butyl)phenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ab**):



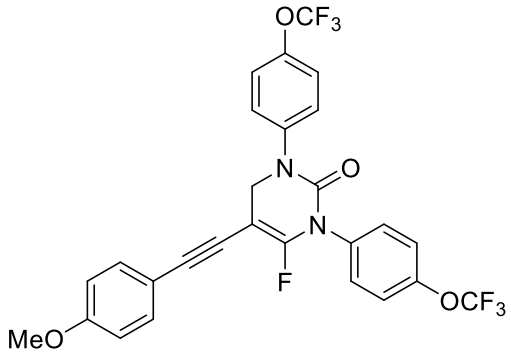
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 71.4 mg, 70%; Brown yellow solid, mp 236.5-238.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (t, *J* = 8.5 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29-7.24 (m, 4H), 6.83 (t, *J* = 7.0 Hz, 2H), 4.46 (d, *J* = 4.0 Hz, 2H), 3.80 (s, 3H), 1.32 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:159.6, 151.4 (d, *J* = 263.75 Hz), 151.7, 151.2, 149.7, 138.9, 132.7, 128.2, 126.0, 125.9, 125.1, 115.2, 114.0, 94.4 (d, *J* = 5.0 Hz), 79.0 (d, *J* = 2.5 Hz), 73.2 (d, *J* = 16.25 Hz), 55.3, 49.4 (d, *J* = 2.5 Hz), 34.7, 34.6, 31.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.84 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{33}H_{36}FN_2O_2$ ($[M+H]^+$) 511.2755, found 511.2761.

6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-bis(4-phenoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (**3ac**):



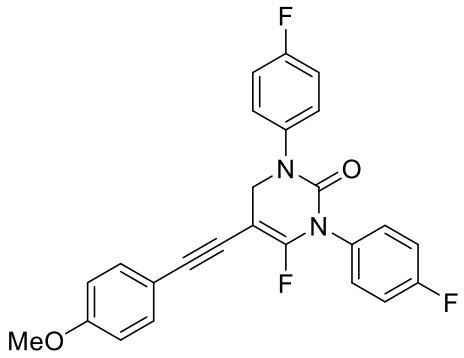
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 98.9 mg, 85%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37-7.31 (m, 7H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.15-7.09 (m, 2H), 7.04 (t, *J* = 9.5 Hz, 7H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.45 (d, *J* = 5.0 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.7, 157.4, 157.0, 156.6, 155.9, 151.8, 151.2 (d, *J* = 263.75 Hz), 136.5, 132.7, 130.2, 129.9, 129.8, 128.7, 127.3, 123.8, 123.6, 119.4, 119.3, 119.0, 118.7, 115.1, 114.1, 94.6 (d, *J* = 5.0 Hz), 78.7 (d, *J* = 1.25 Hz), 73.2 (d, *J* = 16.25 Hz), 55.3, 49.6 (d, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.02 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{37}H_{28}FN_2O_4$ ($[M+H]^+$) 583.2028, found 583.2029.

6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-bis(4-(trifluoromethoxy)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ad**):



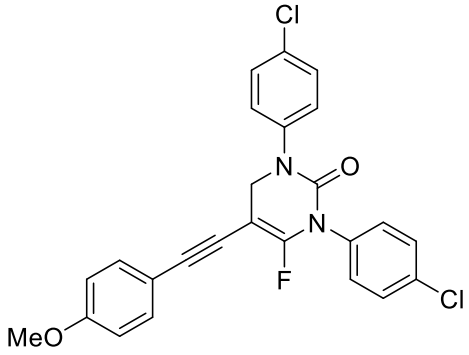
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 101.9 mg, 90%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40-7.35 (m, 6H), 7.27 (t, *J* = 10.0 Hz, 4H), 6.84 (d, *J* = 7.0 Hz, 2H), 4.46 (d, *J* = 4.0 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.8, 151.3, 150.6 (d, *J* = 265.0 Hz), 148.2 (d, *J* = 171.25 Hz), 139.7, 132.8, 132.2, 130.3, 130.2 (d, *J* = 37.5 Hz), 129.0 (d, *J* = 23.75 Hz), 127.0, 121, 8, 121.4, 119.4 (d, *J* = 3.75 Hz), 114.8, 114.1, 95.2 (d, *J* = 6.25 Hz), 78.1 (d, *J* = 2.5 Hz), 74.2 (d, *J* = 17.5 Hz), 55.3, 49.3 (d, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -57.95 (d, *J* = 47.1 Hz, 6F), -96.56 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{18}F_7N_2O_4$ ($[M+H]^+$) 567.1149, found 567.1139.

6-fluoro-1,3-bis(4-fluorophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ae**):



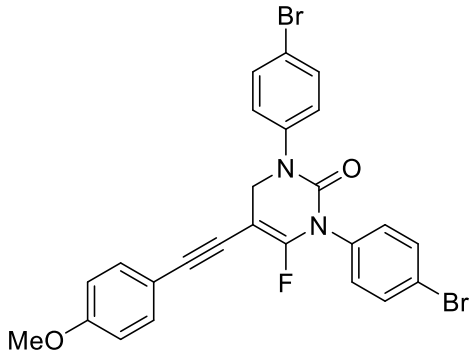
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 80.7 mg, 93%; Brown yellow solid, mp 143.5-145.2 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-7.30 (m, 6H), 7.12-7.06 (m, 4H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.42 (d, *J* = 5.5 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.3 (d, *J* = 246.25 Hz), 161.2 (d, *J* = 245.0 Hz), 159.8, 150.9 (d, *J* = 263.75 Hz), 151.6, 137.3 (d, *J* = 3.75 Hz), 132.8, 130.7 (d, *J* = 8.75 Hz), 130.3 (d, *J* = 8.75 Hz), 129.8 (d, *J* = 2.5 Hz), 127.6 (d, *J* = 8.75 Hz), 116.2, 116.1 (d, *J* = 3.75 Hz), 115.9, 114.9, 114.1, 94.9 (d, *J* = 5.0 Hz), 78.4 (d, *J* = 1.25 Hz), 73.5 (d, *J* = 16.25 Hz), 55.3, 49.6 (d, *J* = 3.75 Hz);^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.29 (s, 1F), -112.75 (d, *J* = 9.42 Hz, 1F), -114.36 (d, *J* = 4.71 Hz, 1F); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}F_3N_2O_2$ ($[M+H]^+$) 435.1315, found 435.1318.

1,3-bis(4-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3af**):



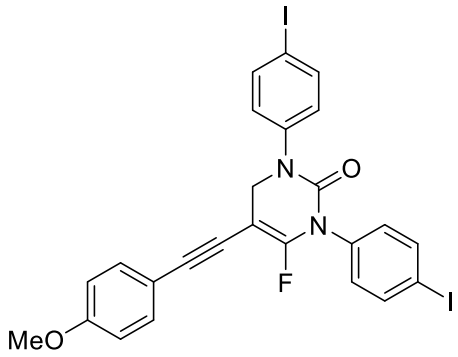
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 84.8 mg, 91%; Brown yellow solid, mp 209.1-211.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.32 (m, 7H), 7.26 (d, *J* = 5.5 Hz, 3H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.45 (d, *J* = 5.5 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:159.8, 151.2, 150.6 (d, *J* = 265 Hz), 148.1, 139.8, 135.6, 134.4, 132.8, 132.4 (d, *J* = 11.25 Hz), 131.8, 130.1, 129.7 (d, *J* = 1.25 Hz), 129.3, 129.2, 126.8, 114.8, 114.1, 95.1 (d, *J* = 6.25 Hz), 78.2 (d, *J* = 2.5 Hz), 74.0 (d, *J* = 16.25 Hz), 55.3, 49.2 (d, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.65 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}Cl_2FN_2O_2$ ($[M+H]^+$) 467.0724, found 467.0726.

1,3-bis(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ag**):



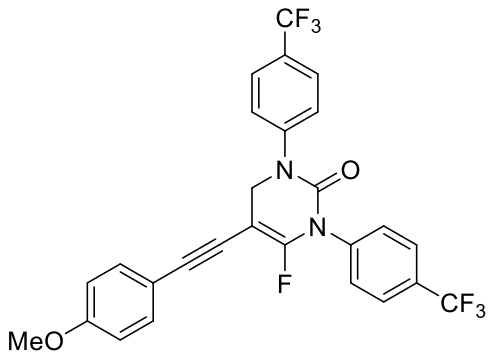
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 108.4 mg, 98%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56-7.50 (m, 4H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.21 (t, *J* = 8.5 Hz, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.42 (d, *J* = 5.5 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.8, 151.1, 150.6 (d, *J* = 265.0 Hz), 148.0, 140.3, 132.9, 132.8, 132.7, 132.3 (d, *J* = 11.25 Hz), 130.4, 130.0, 127.1, 122.4, 120.3, 114.8, 114.1, 95.1 (d, *J* = 5.0 Hz), 78.3 (d, *J* = 2.5 Hz), 74.1 (d, *J* = 17.5 Hz), 55.3, 49.1 (d, *J* = 3.75 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.52 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}Br_2FN_2O_2$ ($[M+H]^+$) 554.9714, found 554.9717.

6-fluoro-1,3-bis(4-iodophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ah**):



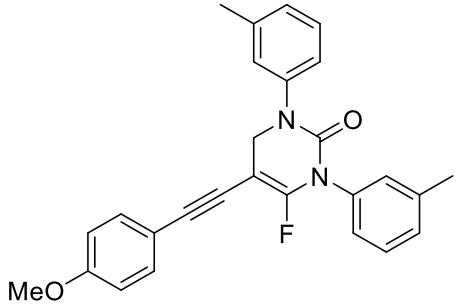
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 107.0 mg, 82%; Brown yellow solid, mp 243.3-244.6 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75-7.69 (m, 4H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.08 (t, *J* = 9.5 Hz, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.40 (d, *J* = 5.5 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.8, 151.0, 150.5 (d, *J* = 265.0 Hz), 141.1, 138.2 (d, *J* = 6.25 Hz), 133.7, 132.8, 130.6, 127.2, 114.8, 114.1, 95.1 (d, *J* = 5.0 Hz), 94.0, 91.5, 78.3 (d, *J* = 2.5 Hz), 74.1 (d, *J* = 16.25 Hz), 55.4, 48.9 (d, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.50 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}I_2FN_2O_2$ ($[M+H]^+$) 650.9436, found 650.9437.

6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-bis(4-(trifluoromethyl)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ai**):



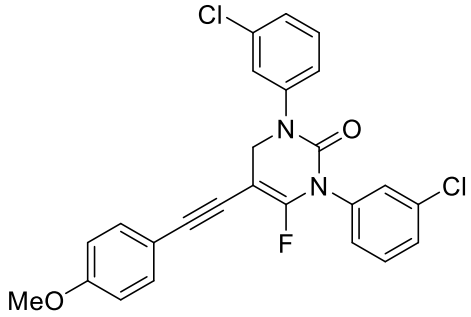
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 72.6 mg, 68%; Brown yellow solid, mp >250 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.717-7.658 (m, 4H), 7.489 (d, *J* = 7.6 Hz, 4H), 7.369 (d, *J* = 8.4 Hz, 2H), 6.848 (d, *J* = 8.4 Hz, 2H), 4.505 (d, *J* = 5.6 Hz, 2H), 3.800 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.9, 151.0, 150.3 (d, *J* = 266.25 Hz), 144.3, 137.0, 132.8, 130.5 (d, *J* = 32.5 Hz), 129.1, 128.7 (d, *J* = 32.5 Hz), 126.3 (q, *J* = 3.75 Hz), 126.1 (q, *J* = 3.75 Hz), 125.3, 124.8 (d, *J* = 10.0 Hz), 122.7 (d, *J* = 11.25 Hz), 114.7, 114.1, 95.5 (d, *J* = 5.0 Hz), 77.9 (d, *J* = 2.5 Hz), 74.9 (d, *J* = 17.5 Hz), 55.3, 48.8 (d, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -62.56 (d, *J* = 70.65 Hz, 6F), -96.89 (d, *J* = 4.71 Hz, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{18}F_7N_2O_2$ ($[M+H]^+$) 535.1251, found 535.1244.

6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-di-m-tolyl-3,4-dihydropyrimidin-2(1H)-one (**3aj**):



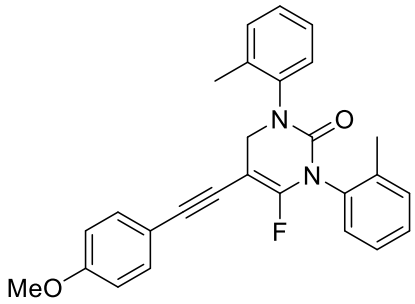
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 57.9 mg, 68%; Brown yellow solid, mp 120.8-122.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 10.5 Hz, 2H), 7.18-7.13 (m, 5H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.45 (d, *J* = 5.5 Hz, 2H), 3.78 (s, 3H), 2.35 (d, *J* = 8.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.6, 151.7, 151.3 (d, *J* = 263.75 Hz), 141.5, 139.1, 138.9, 133.9, 132.7, 129.5, 129.2, 129.0, 128.7, 127.7, 126.4, 125.9, 122.6, 115.2, 114.0, 94.5 (d, *J* = 5.0 Hz), 78.8 (d, *J* = 1.25 Hz), 73.2 (d, *J* = 16.25 Hz), 55.3, 49.4 (d, *J* = 2.5 Hz), 21.4, 21.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.00 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}FN_2O_2$ ($[M+H]^+$) 427.1816, found 427.1816.

1,3-bis(3-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ak**):



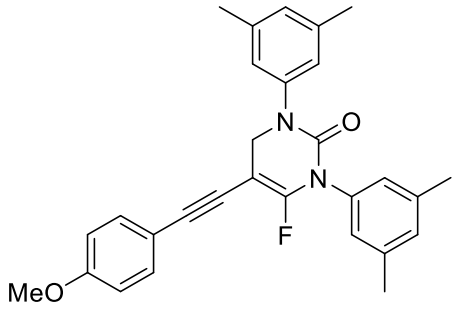
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 62.4 mg, 67%; Brown yellow solid, mp 229.3-230.4 ^{o}C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.369-7.280 (m, 7H), 7.225 (d, *J* = 7.6 Hz, 3H), 6.831 (d, *J* = 8.8 Hz, 2H), 4.411 (d, *J* = 5.6 Hz, 2H), 3.766 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:159.8, 151.1, 150.5 (d, *J* = 265.0 Hz), 142.4, 134.9, 134.6, 134.5, 132.8, 130.1, 129.9, 129.2, 128.8, 127.1 (2C), 125.8, 123.7, 114.8, 114.1, 95.2 (d, *J* = 5.0 Hz), 78.2 (d, *J* = 1.25 Hz), 74.3 (d, *J* = 16.25 Hz), 55.3, 49.1 (d, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.65 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}Cl_2FN_2O_2$ ($[M+H]^+$) 467.0724, found 467.0721.

6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-di-*o*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (**3al**):



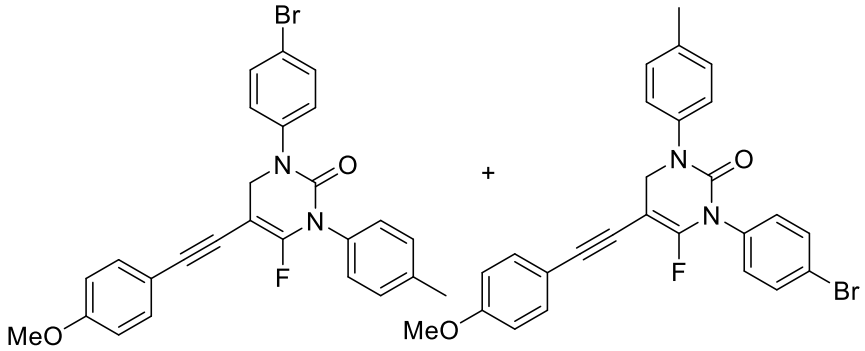
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 63.9 mg, 75%; Brown yellow solid, mp 1 oC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 8H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.51-4.46 (m, 1H), 4.26-4.22 (m, 1H), 3.78 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:159.6, 151.6 (d, *J* = 261.25 Hz), 150.5, 150.3, 140.0, 137.4, 137.1, 135.7 (d, *J* = 10.0 Hz), 133.0 (d, *J* = 7.5 Hz), 132.7, 131.3, 130.8 (d, *J* = 3.75 Hz), 129.8 (d, *J* = 10.0 Hz), 129.1 (d, *J* = 12.5 Hz), 128.2, 127.3, 127.2 (d, *J* = 8.75 Hz), 126.7, 115.2, 114.0, 94.4 (d, *J* = 5.0 Hz), 78.8 (d, *J* = 1.25 Hz), 72.0 (d, *J* = 17.5 Hz), 55.3, 49.5 (d, *J* = 3.75 Hz), 17.7, 17.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.93 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}FN_2O_2$ ($[M+H]^+$) 427.1816, found 427.1817.

1,3-bis(3,5-dimethylphenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3am**):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 72.6 mg, 80%; Brown yellow solid, mp 215.5-217.5 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 8.0 Hz, 2H), 6.9735 (t, *J* = 7.0 Hz, 5H), 6.89 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.44 (d, *J* = 4.5 Hz, 2H), 3.79 (s, 3H), 2.31 (d, *J* = 7.0 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.6, 151.7, 151.4 (d, *J* = 263.75 Hz), 148.9, 141.4, 139.1, 138.9, 138.6, 133.8, 133.4, 132.7, 131.0, 130.1, 128.6, 126.5, 125.9, 123.4, 115.3, 114.0, 94.3 (d, *J* = 6.25 Hz), 79.0 (d, *J* = 5.0 Hz), 73.0 (d, *J* = 16.25 Hz), 55.3, 49.5 (d, *J* = 3.75 Hz), 21.3, 21.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.95 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{29}H_{28}FN_2O_2$ ($[M+H]^+$) 455.2129, found 455.2134.

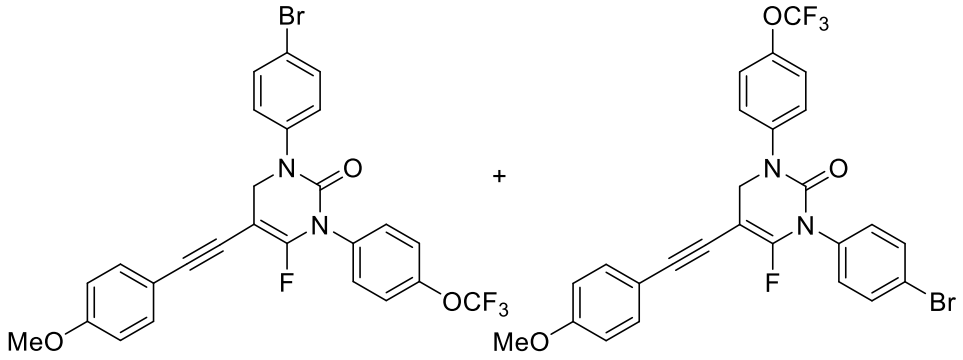
3-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-1-(*p*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3ag**) + **1-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3-(*p*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one** (**3aga**):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 65.7 mg, 67%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56-7.49 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 6H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.42 (d, *J* = 4.5 Hz, 2H), 3.79 (s, 3H), 2.35 (d, *J* = 12.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:159.7 (d, *J* = 11.25 Hz), 159.7 (d, *J* = 12.5 Hz), 152.4 (d, *J* = 23.75 Hz), 151.7 (d, *J* = 21.25 Hz), 151.6 (d, *J* = 22.5 Hz), 151.2 (d, *J* = 22.5 Hz), 151.3 (d, *J* = 23.75 Hz), 149.6 (d, *J* = 21.25 Hz), 148.2 (d, *J* = 42.5 Hz), 140.5 (d, *J* = 32.5 Hz), 138.9 (d, *J* = 32.5 Hz), 138.4 (d, *J* = 33.75 Hz),

136.8 (d, *J* = 38.75 Hz), 133.0 (d, *J* = 30.0 Hz), 132.8 (q, *J* = 5.0 Hz), 132.2 (d, *J* = 11.25 Hz), 132.1 (d, *J* = 10.0 Hz), 131.3 (d, *J* = 30.0 Hz), 130.4 (d, *J* = 7.5 Hz), 130.1, 129.8 (d, *J* = 10.0 Hz), 129.7 (d, *J* = 15.0 Hz), 128.6 (d, *J* = 7.5 Hz), 127.1 (d, *J* = 7.5 Hz), 125.5 (d, *J* = 3.75 Hz), 123.7, 122.3 (d, *J* = 32.5 Hz), 120.2 (d, *J* = 40.0 Hz), 115.1 (d, *J* = 20.0 Hz), 114.9 (d, *J* = 20.0 Hz), 114.1 (t, *J* = 3.75 Hz), 94.7 (q, *J* = 20.0 Hz), 78.6 (q, *J* = 26.25 Hz), 74.0 (q, *J* = 16.25 Hz), 73.1 (d, *J* = 17.5 Hz), 55.3, 49.5, 49.0, 21.2, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -95.92 (t, *J* = 4.71 Hz, 1F), -96.00 (t, *J* = 4.71 Hz, 1F), -96.47 (t, *J* = 4.71 Hz, 1F), -96.53 (t, *J* = 4.71 Hz, 1F); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}BrFN_2O_2$ ($[M+H]^+$) 491.0765, found 491.0767.

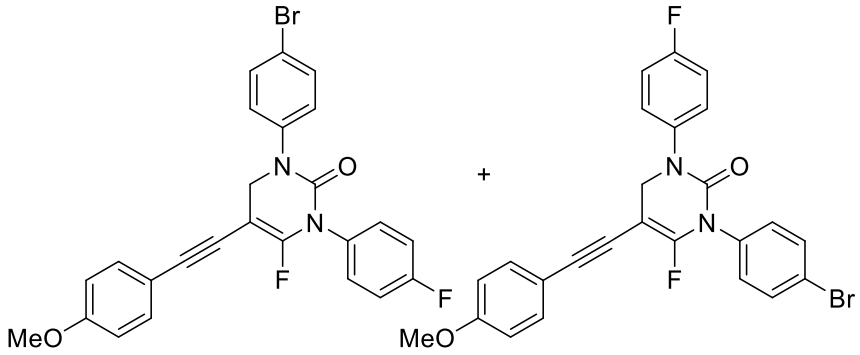
3-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-1-(4-(trifluoromethoxy)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3adg**) + **1-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3-(4-(trifluoromethoxy)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one** (**3agd**):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 71.7 mg, 64%; Brown yellow solid, mp >250 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.557-7.504 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.28-7.20 (m, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 4.46-4.41 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:159.8, 150.6 (d, *J* = 265.0 Hz), 151.3 (d, *J* = 11.25 Hz), 151.1 (d, *J* = 11.25 Hz), 148.8, 147.4, 144.1 (d, *J* = 2.5 Hz), 140.3 (d, *J* = 3.75 Hz), 139.8 (d, *J* = 3.75 Hz), 134.0 (d, *J* = 1.25 Hz), 133.2, 132.9 (d, *J* = 2.5 Hz), 132.8, 132.6 (d, *J* = 8.75 Hz), 132.5, 132.3 (d, *J* = 11.25 Hz), 130.3 (d, *J* = 12.5 Hz), 130.0 (d, *J* = 2.5 Hz), 128.0 (d, *J* = 13.75 Hz), 127.3 (d, *J* = 5.0 Hz), 127.1 (d, *J* = 3.75 Hz), 127.0 (d, *J* = 5.0 Hz), 122.4, 122.0 (d, *J* = 3.75 Hz), 121.8, 121.6, 121.5 (d, *J* = 3.75 Hz), 121.4, 120.4 (d, *J* = 6.25 Hz), 119.4 (d, *J* = 3.75 Hz), 114.8, 114.4, 114.1, 95.2 (q, *J* = 5.0 Hz), 78.2 (d, *J* = 2.5 Hz), 74.1 (m), 55.3,

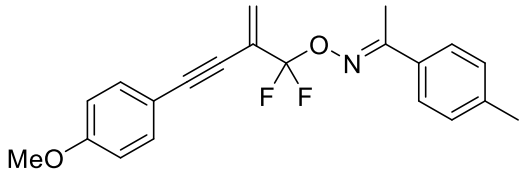
49.2 (d, *J* = 18.75 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -57.86 (s, 3F), -57.95 (s, 3F), -96.57 (s, 2F); HRMS *m/z* (ESI) calcd for $C_{26}H_{18}BrF_4N_2O_3$ ($[M+H]^+$) 561.0431, found 561.0432.

3-(4-bromophenyl)-6-fluoro-1-(4-fluorophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3aeg**) + **1-(4-bromophenyl)-6-fluoro-3-(4-fluorophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one** (**3age**):



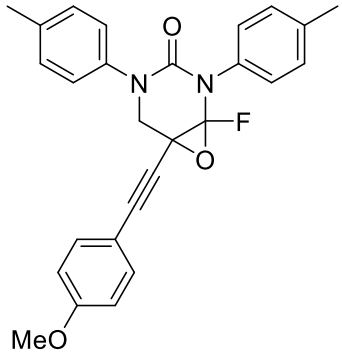
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 71.3 mg, 72%; Brown yellow solid, mp >250 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56-7.51 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.32-7.29 (m, 2H), 7.25-7.20 (m, 2H), 7.13-7.07 (m, 2H), 6.84 (t, *J* = 8.0 Hz, 2H), 4.43 (t, *J* = 4.5 Hz, 2H), 3.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:163.3 (d, *J* = 3.75 Hz), 162.2 (d, *J* = 3.75 Hz), 161.3 (d, *J* = 3.75 Hz), 160.2 (d, *J* = 3.75 Hz), 159.8 (t, *J* = 3.75 Hz), 151.9 (d, *J* = 11.25 Hz), 151.7, 151.6 (d, *J* = 5.0 Hz), 151.3 (d, *J* = 8.75 Hz), 151.1, 149.8 (d, *J* = 11.25 Hz), 149.5 (d, *J* = 11.25 Hz), 140.4 (d, *J* = 7.5 Hz), 137.3 (d, *J* = 2.5 Hz), 137.3 (d, *J* = 3.75 Hz), 132.9 (d, *J* = 8.75 Hz), 132.8, 132.3 (d, *J* = 3.75 Hz), 132.2 (d, *J* = 6.25 Hz), 130.6 (d, *J* = 8.75 Hz), 129.8 (d, *J* = 3.75 Hz), 129.7 (d, *J* = 3.75 Hz), 127.6 (d, *J* = 8.75 Hz), 127.1, 122.4 (d, *J* = 11.25 Hz), 120.3 (d, *J* = 8.75 Hz), 116.3 (d, *J* = 5.0 Hz), 116.1 (t, *J* = 6.25 Hz), 115.9 (d, *J* = 6.25 Hz), 114.9 (t, *J* = 6.25 Hz), 114.1, 95.1 (q, *J* = 5.0 Hz), 94.9 (q, *J* = 5.0 Hz), 78.4 (d, *J* = 3.75 Hz), 78.3 (t, *J* = 2.5 Hz), 78.2 (d, *J* = 2.5 Hz), 74.0 (q, *J* = 5.0 Hz), 73.6 (q, *J* = 5.0 Hz), 55.3, 49.6, 49.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -96.27 (t, *J* = 9.42 Hz, 1F), -96.40 (q, *J* = 4.71 Hz, 1F), -96.53 (t, *J* = 4.71 Hz, 1F), -112.62 (q, *J* = 4.71 Hz, 1F), -112.76 (t, *J* = 4.71 Hz, 1F), -114.27 (q, *J* = 9.42 Hz, 1F), -114.35 (d, *J* = 4.71 Hz, 1F). HRMS *m/z* (ESI) calcd for $C_{25}H_{18}BrF_2N_2O_2$ ($[M+H]^+$) 495.0514, found 495.0515.

1-(p-tolyl)ethan-1-one-*O*-(1,1-difluoro-4-(4-methoxyphenyl)-2-methylenebut-3-yn-1-yl) oxime (**7aa**):



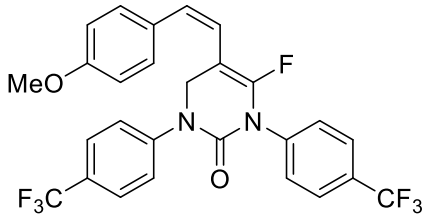
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 10.7 mg, 15%; Pale yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (t, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 8.5 Hz, 2H), 7.27-7.19 (m, 4H), 6.86 (t, *J* = 8.0 Hz, 2H), 6.10 (s, 1H), 5.90 (s, 1H), 3.82 (s, 3H), 2.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:161.0, 160.0, 140.5, 133.3, 132.2, 129.2, 126.7, 125.5, 125.2, 121.0 (t, *J* = 261.25 Hz), 114.5, 114.0, 92.2, 82.4, 55.3, 21.4, 13.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -75.54 (s, 2F); LRMS (EI, 70 eV) *m/z* (%): 355 (M^+, 18), 354 (78), 204 (94), 91 (100). HRMS *m/z* (ESI) calcd for $C_{21}H_{20}F_2NO_2$ ($[M+H]^+$) 356.1457, found 356.1458.

1-fluoro-6-((4-methoxyphenyl)ethynyl)-2,4-di-*p*-tolyl-7-oxa-2,4-diazabicyclo[4.1.0]heptan-3-one (**11aa**):



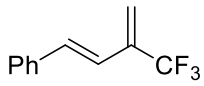
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3 : 1 (v/v)). 47.7 mg, 54%; Brown yellow solid, mp >250 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 10.0 Hz, 2H), 7.29-7.25 (m, 4H), 7.21 (d, *J* = 10.0 Hz, 2H), 7.14 (d, *J* = 10.0 Hz, 2H), 6.88 (d, *J* = 10.0 Hz, 2H), 4.37-4.32 (m, 1H), 4.22 (t, *J* = 10.0 Hz, 1H), 3.89 (s, 3H), 2.37 (d, *J* = 5.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.1 (d, *J* = 25 Hz), 161.0, 151.3, 138.8, 138.6, 137.4, 134.0 (d, *J* = 2.5 Hz), 133.6, 132.1, 129.9 (d, *J* = 3.75 Hz), 128.2, 125.6, 114.3, 112.1, 92.1 (d, *J* = 8.75 Hz), 82.8 (d, *J* = 186.25 Hz), 79.0 (d, *J* = 30.0 Hz), 55.4, 54.2, 53.9, 21.3, 21.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -152.99 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}FN_2O_3$ ($[M+H]^+$) 443.1765, found 443.1769.

(*Z*)-6-fluoro-5-(4-methoxystyryl)-1,3-bis(4-(trifluoromethyl)phenyl)-3,4-dihydropyrimidin-2(1H)-one (**12al**):



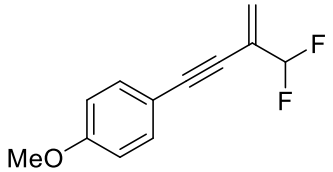
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 46.1 mg, 43%; Brown yellow solid, mp 143.6-145.9 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 5.0 Hz, 2H), 7.54 (t, *J* = 5.0 Hz, 2H), 7.26-7.18 (m, 4H), 6.82 (d, *J* = 5.0 Hz, 2H), 6.55 (d, *J* = 15.0 Hz, 1H), 6.26 (d, *J* = 10.0 Hz, 1H), 4.09 (d, *J* = 5.0 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:159.1, 151.9, 145.7 (d, *J* = 266.25 Hz), 144.4, 137.5, 130.2, 129.9, 129.8, 129.4 (d, *J* = 2.5 Hz), 128.7, 127.8 (d, *J* = 32.5 Hz), 126.0 (d, *J* = 3.75 Hz), 125.9 (d, *J* = 3.75 Hz), 124.9 (d, *J* = 8.75 Hz), 124.2, 122.7 (d, *J* = 7.5 Hz), 118.3, 113.6, 90.6 (d, *J* = 27.0 Hz), 55.3, 47.5 (d, *J* = 5.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -62.40 (s, 3F), -62.56 (s, 3F), -103.42 (s, 1F). HRMS *m/z* (ESI) calcd for $C_{27}H_{20}F_7N_2O_2$ ($[M+H]^+$) 537.1408, found 537.1409.

(*E*)-(3-(trifluoromethyl)buta-1,3-dien-1-yl)benzene (2y):[6]



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1 (v/v)). 0.90 g, 91%; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 80 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 16.5 Hz, 1H), 6.65 (d, *J* = 16.5 Hz, 1H), 5.69 (d, *J* = 59.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 136.5 (q, *J* = 16.25 Hz), 136.2, 132.9, 130.2, 128.8, 128.6, 126.8, 123.2 (d, *J* = 272.5 Hz), 121.6, 119.2 (q, *J* = 6.25 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -65.90 (s, 3F); LRMS (EI, 70 eV) *m/z* (%): 198 (M^+, 58), 177 (39), 129 (100).

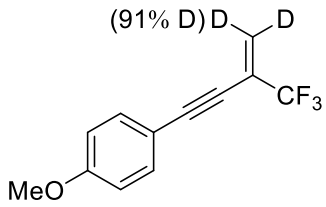
1-(3-(difluoromethyl)but-3-en-1-yn-1-yl)-4-methoxybenzene (2ac):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30 : 1 (v/v)). 0.68 g, 65%; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 6.0 Hz, 2H), 6.86 (d, *J* = 5.0 Hz, 2H), 6.11 (t, *J* = 56.0 Hz, 1H), 5.82 (d, *J* = 17.5 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (125

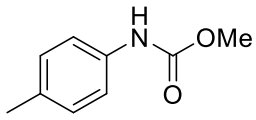
MHz, $CDCl_3$) δ: 160.1, 133.4, 129.9 (d, *J* = 260.0 Hz), 126.3 (t, *J* = 22.5 Hz), 124.8 (t, *J* = 7.5 Hz), 114.0, 113.6 (d, *J* = 155.0 Hz), 112.9 (d, *J* = 480.0 Hz), 93.1, 91.8 113.6 (t, *J* = 3.75 Hz), 55.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -115.31 (s, 2F); LRMS (EI, 70 eV) *m/z* (%): 208 (M^+, 100), 157 (93), 114 (46); HRMS *m/z* (ESI) calcd for $C_{12}H_{11}F_2O$ ($[M+H]^+$) 209.0772, found 209.0773.

1-methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl-4,4-*d*$_2$)benzene (1a-*d*$_2$):



The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1 (v/v)). 1.04 g, 91%; colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 6.0 Hz, 2H), 6.04 (s, 0.09H), 5.87 (s, 0.09H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:160.4, 133.4, 122.7 (q, *J* = 33.75 Hz), 121.5 (q, *J* = 272.5 Hz), 114.1, 113.7, 93.5, 80.3, 55.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -67.94 (s, 3F); LRMS (EI, 70 eV) *m/z* (%): 228 (M^+, 100), 185 (31), 135 (38); HRMS *m/z* (ESI) calcd for $C_{12}H_8D_2F_3O$ ($[M+H]^+$) 229.0804, found 229.0805.

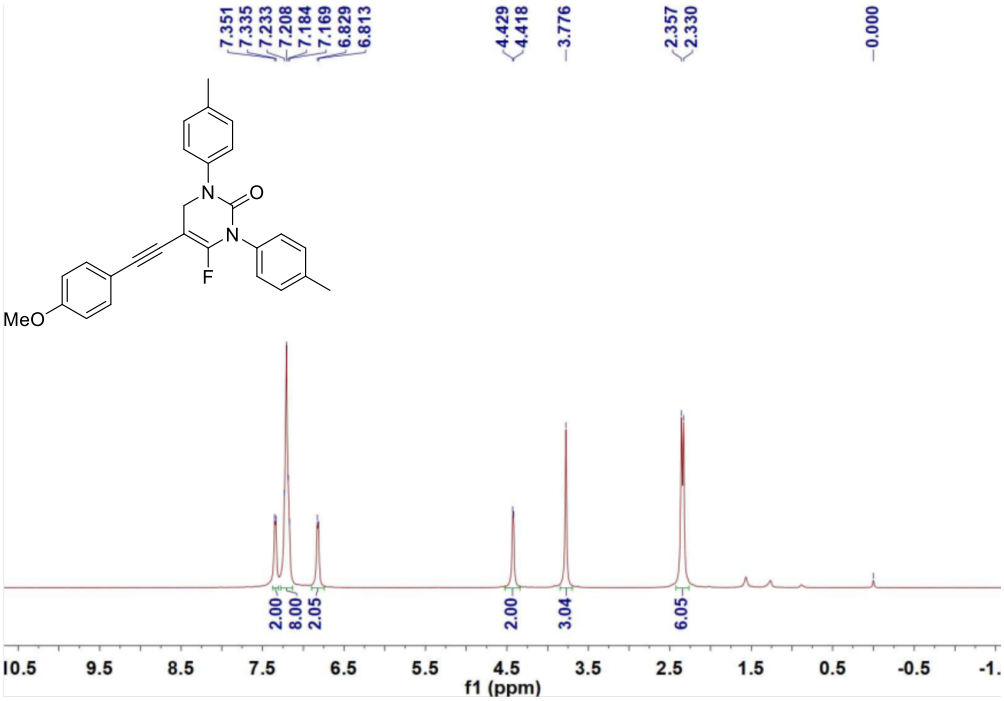
methyl *p*-tolylcarbamate (**8a**):[7]



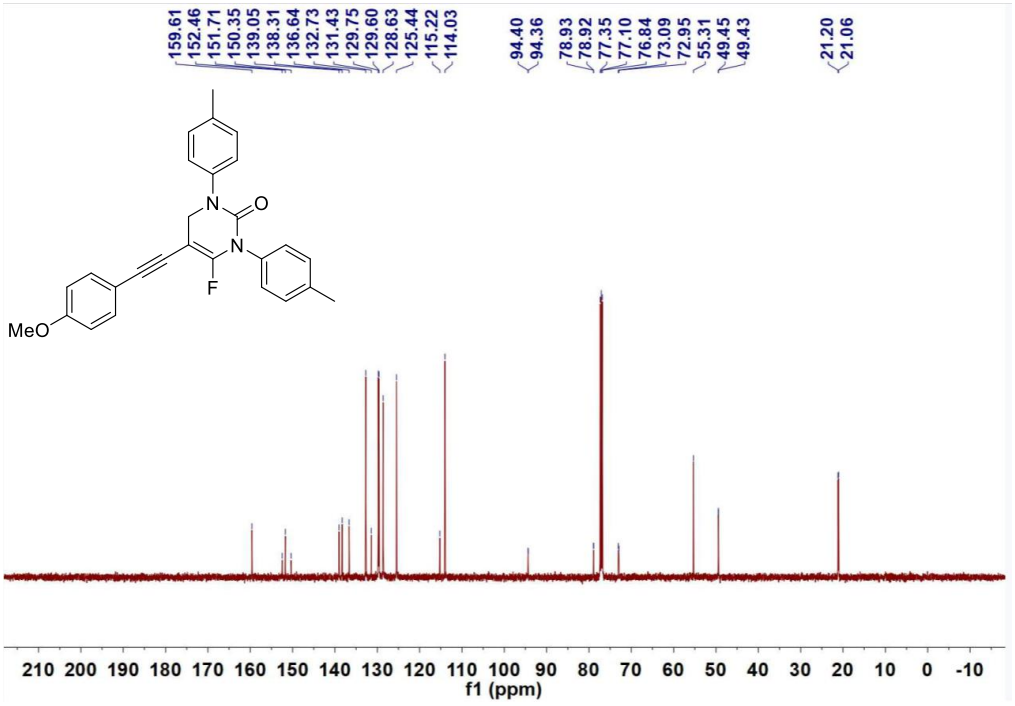
The product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5 : 1 (v/v)). 130.7 mg, >99%; Whiter solid; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.26 (d, *J* = 7.0 Hz, 2H), 7.08 (d, *J* = 10.0 Hz, 2H), 6.80 (brs, 1H), 3.74 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.3, 135.3, 133.0, 129.5, 118.9, 52.3, 20.8; LRMS (EI, 70 eV) *m/z* (%): 165 (M^+, 100), 133 (99), 106 (79).

(C) Spectra

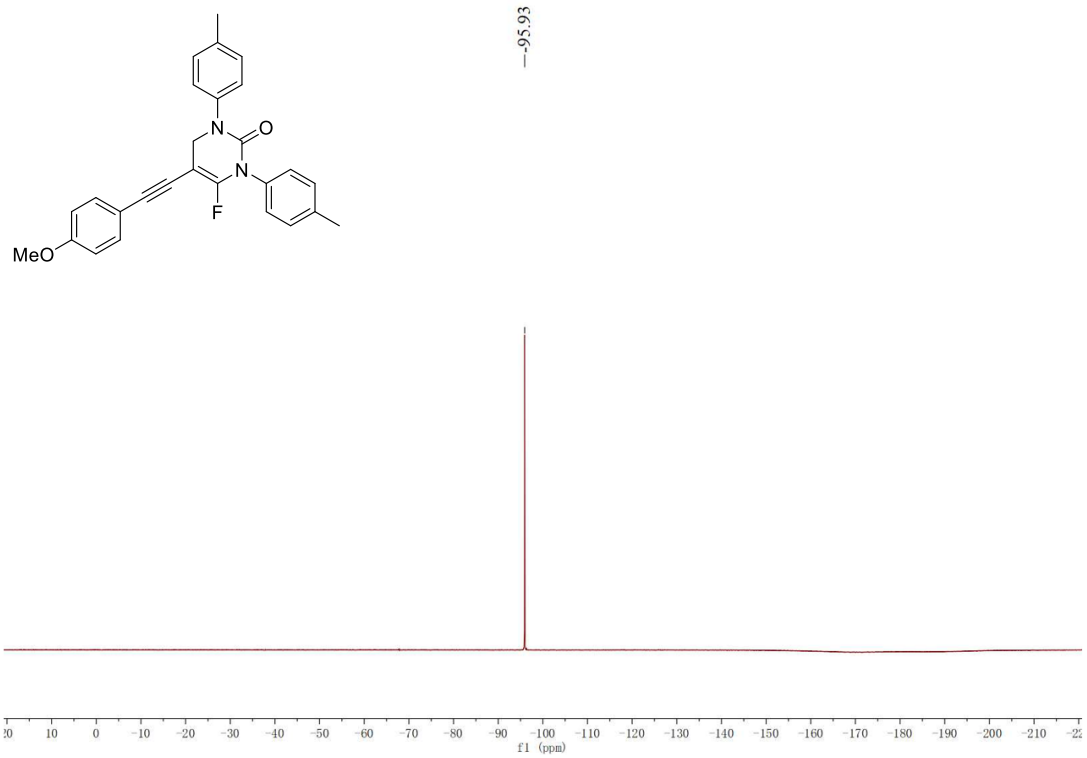
6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3aa)



^{1}H-NMR (500 MHz, $CDCl_3$)

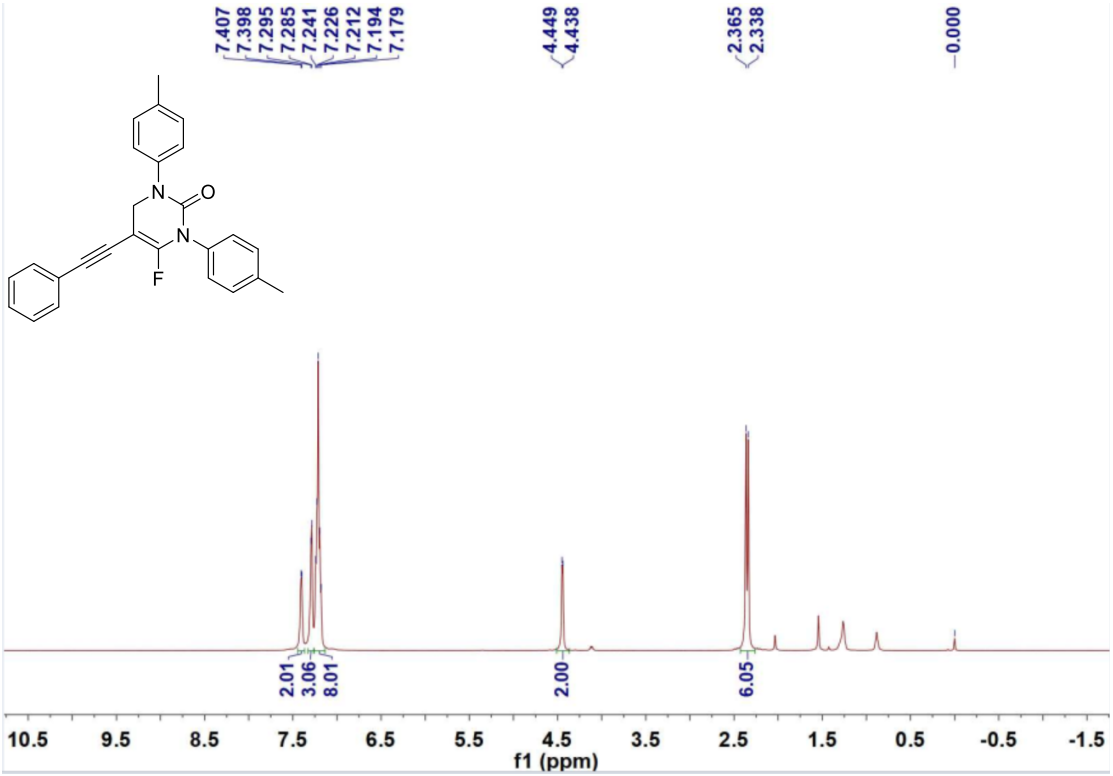


^{13}C-NMR (125 MHz, $CDCl_3$)

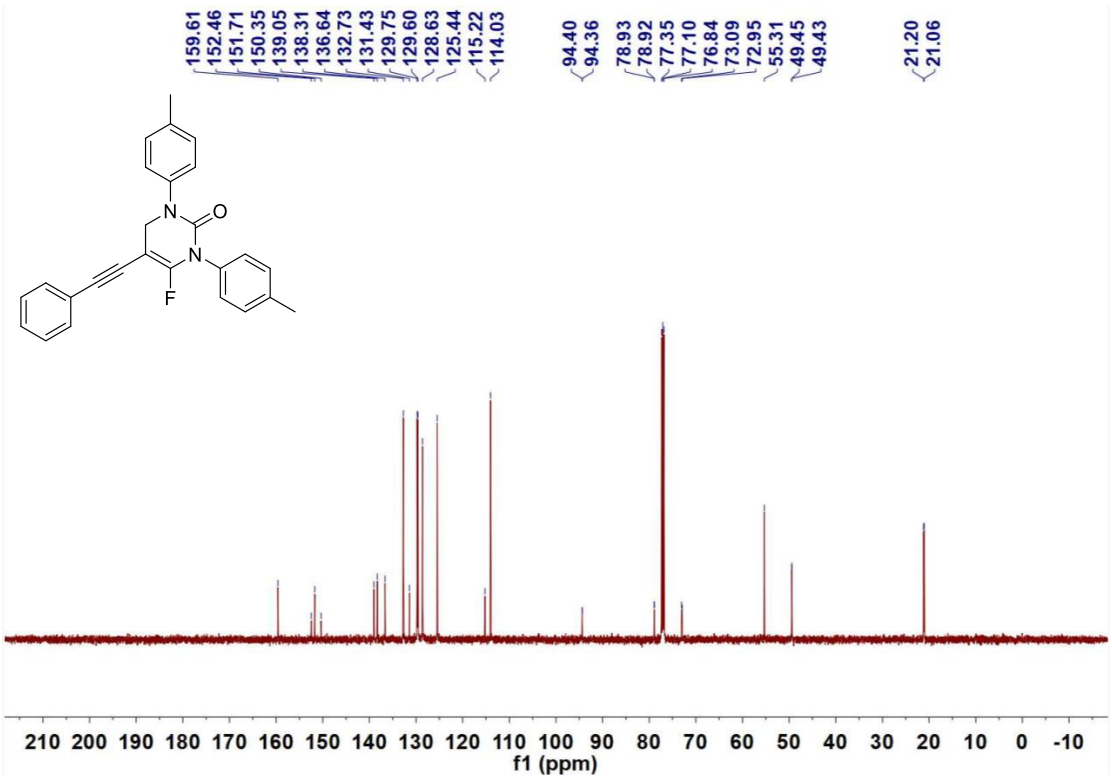


^{19}F-NMR (471 MHz, $CDCl_3$)

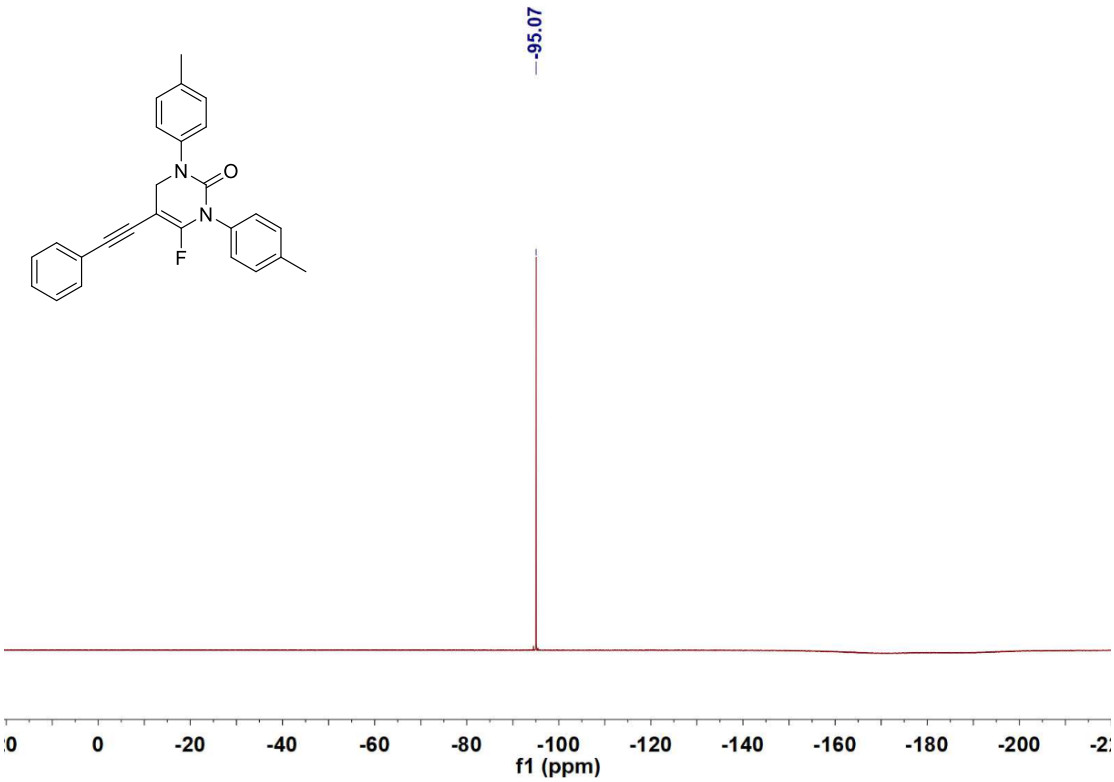
6-fluoro-5-(phenylethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ba)



^{1}H-NMR (500 MHz, $CDCl_3$)

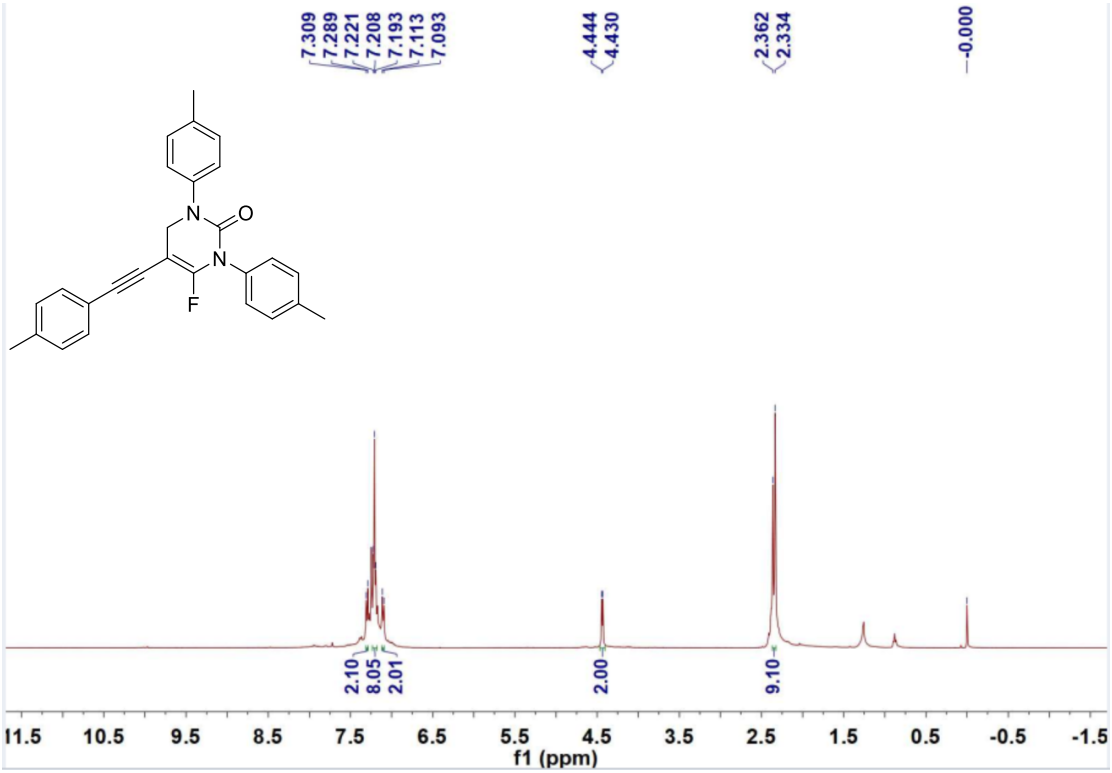


^{13}C-NMR (125 MHz, $CDCl_3$)

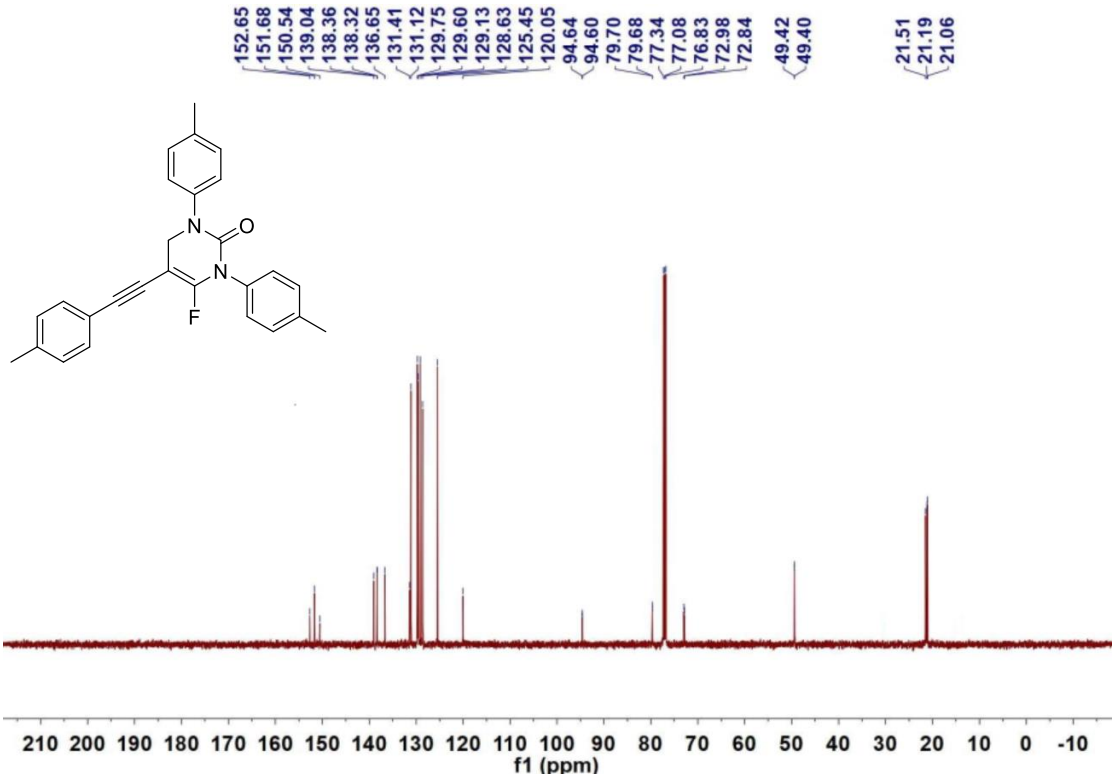


^{19}F-NMR (471 MHz, $CDCl_3$)

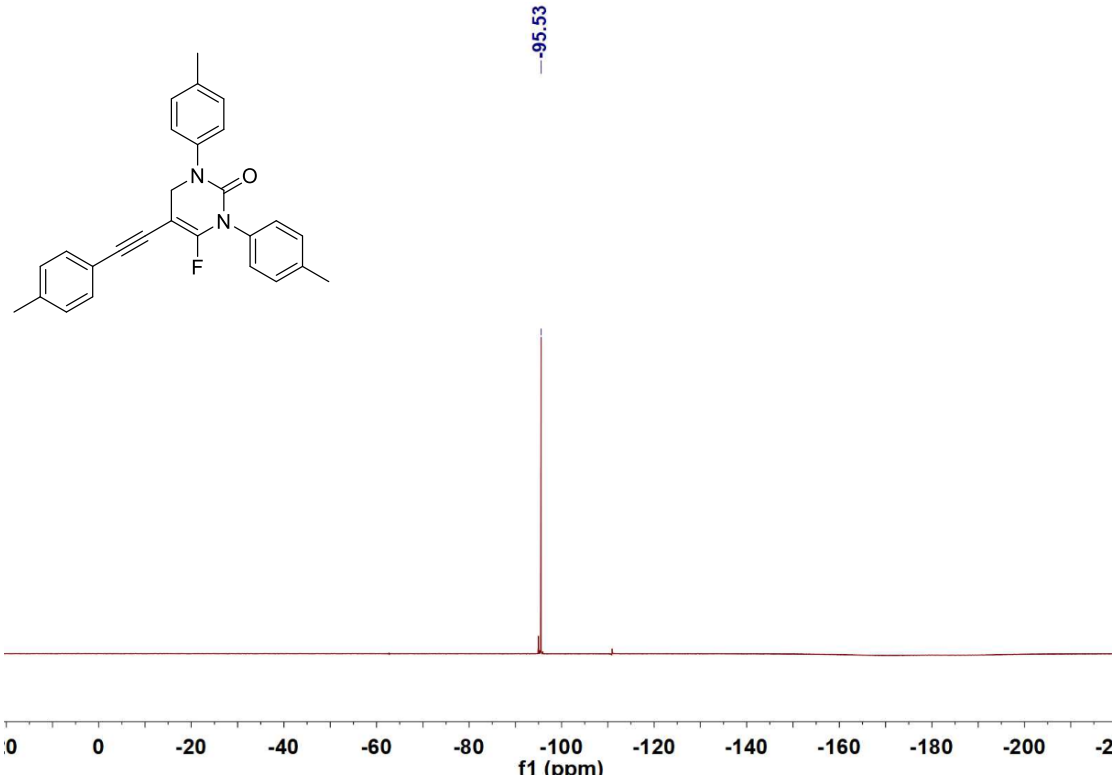
6-fluoro-1,3-di-*p*-tolyl-5-(*p*-tolylethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ca)



^{1}H-NMR (400 MHz, $CDCl_3$)

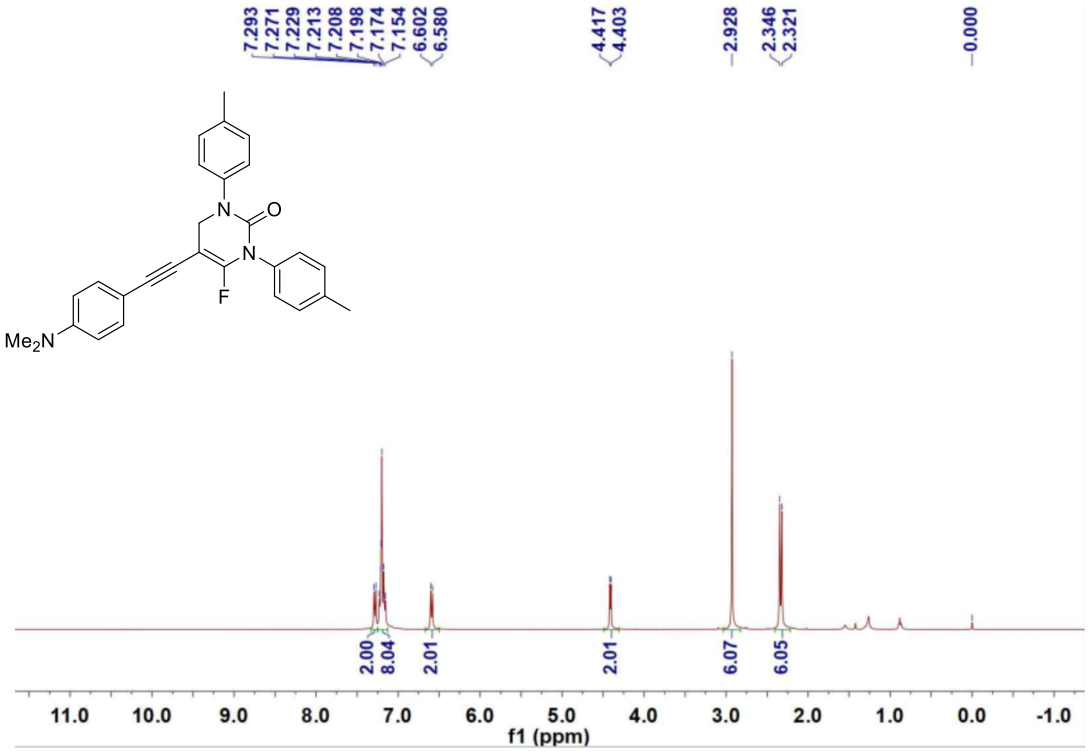


^{13}C-NMR (125 MHz, $CDCl_3$)

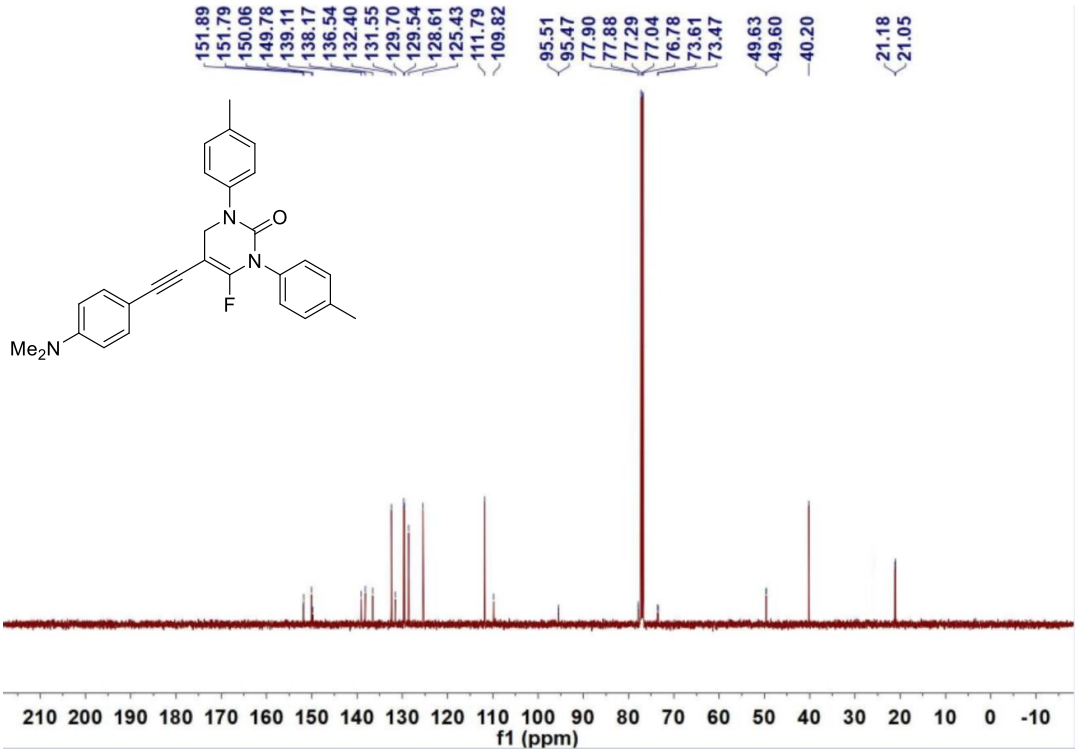


^{19}F-NMR (471 MHz, $CDCl_3$)

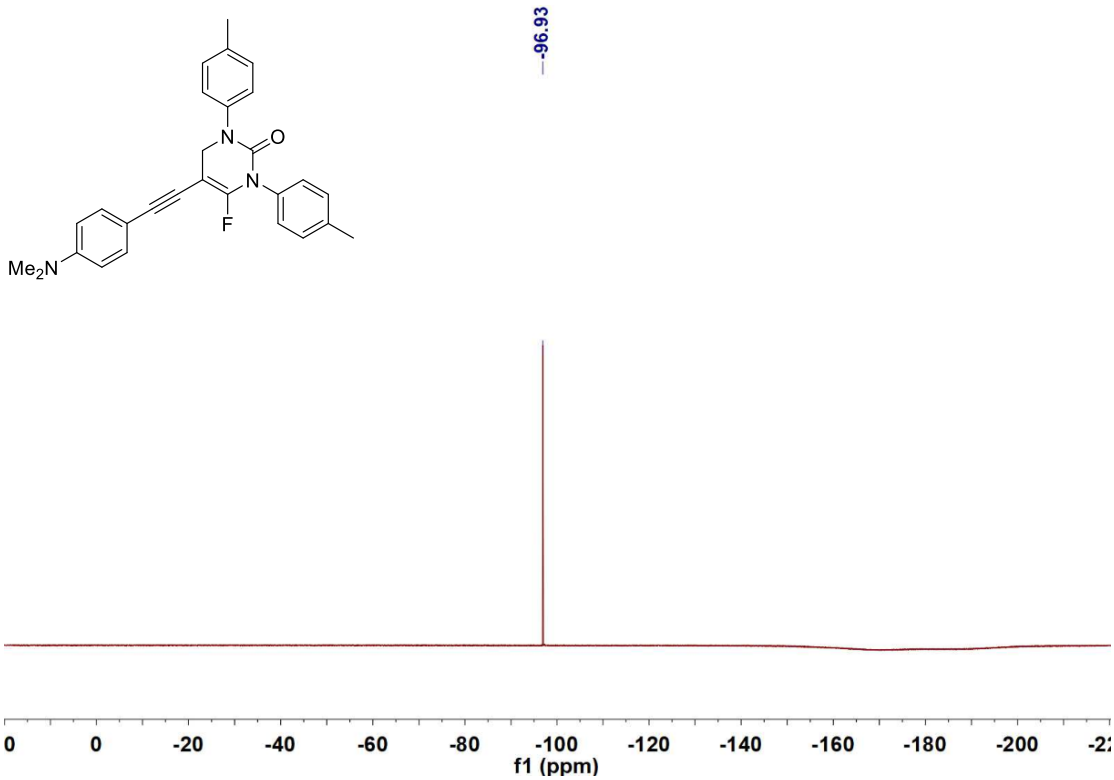
5-((4-(dimethylamino)phenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3da)



^{1}H-NMR (400 MHz, $CDCl_3$)

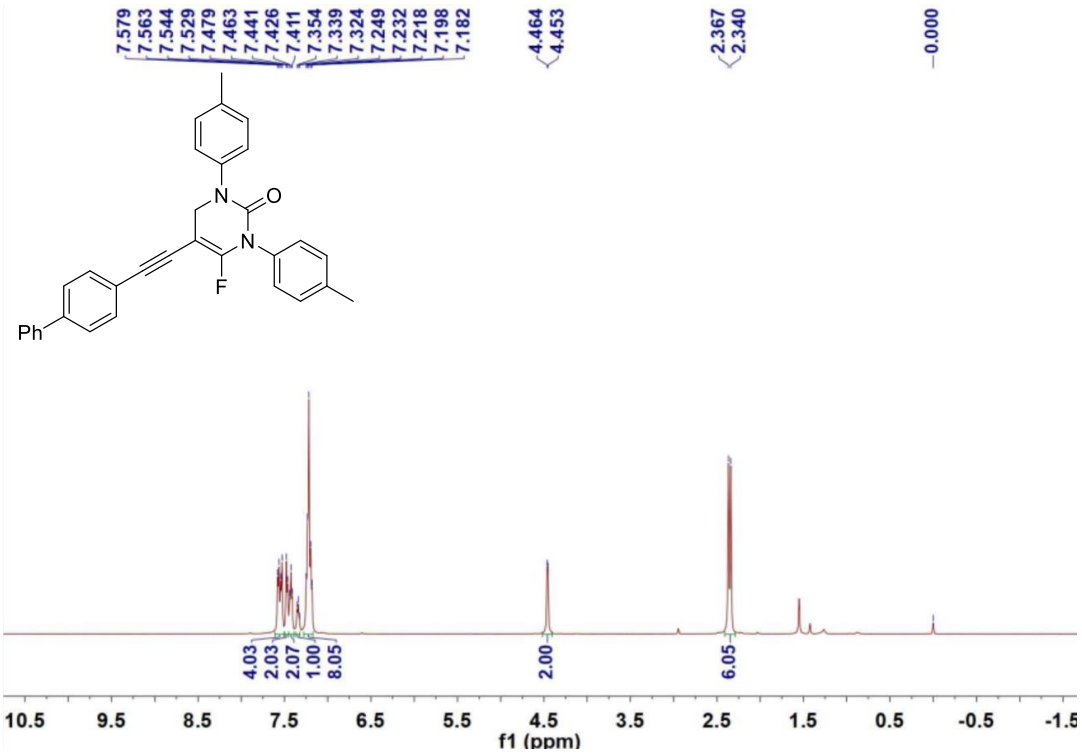


^{13}C-NMR (125 MHz, $CDCl_3$)

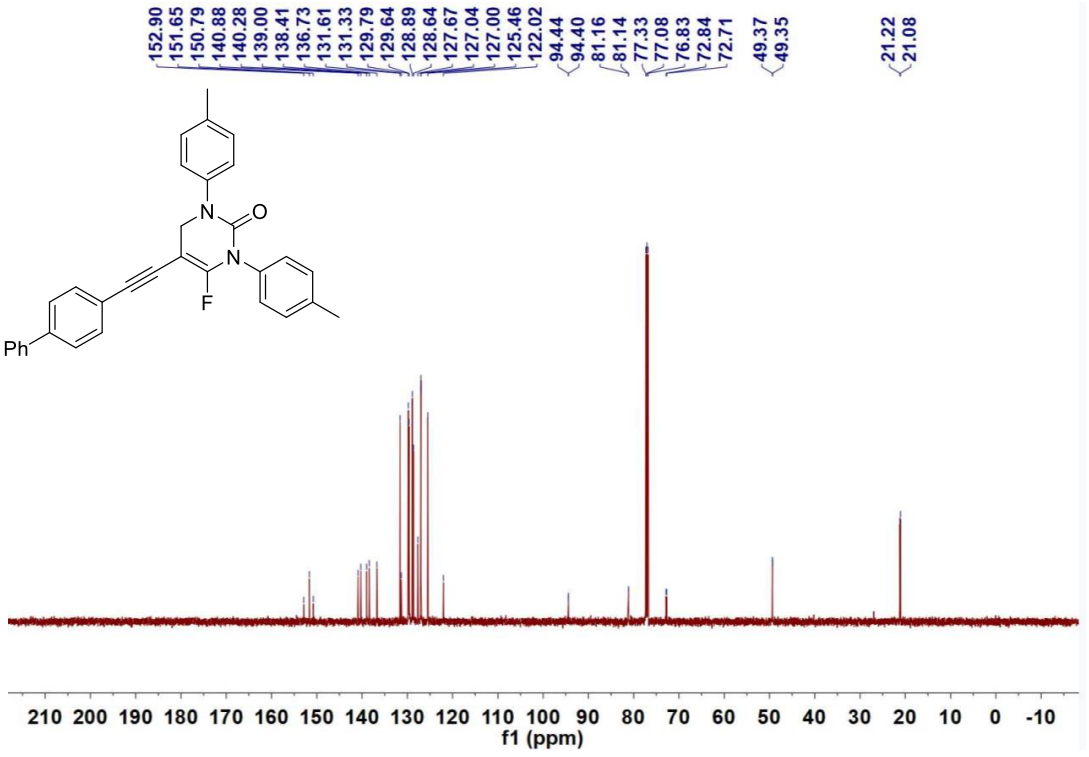


^{19}F-NMR (471 MHz, $CDCl_3$)

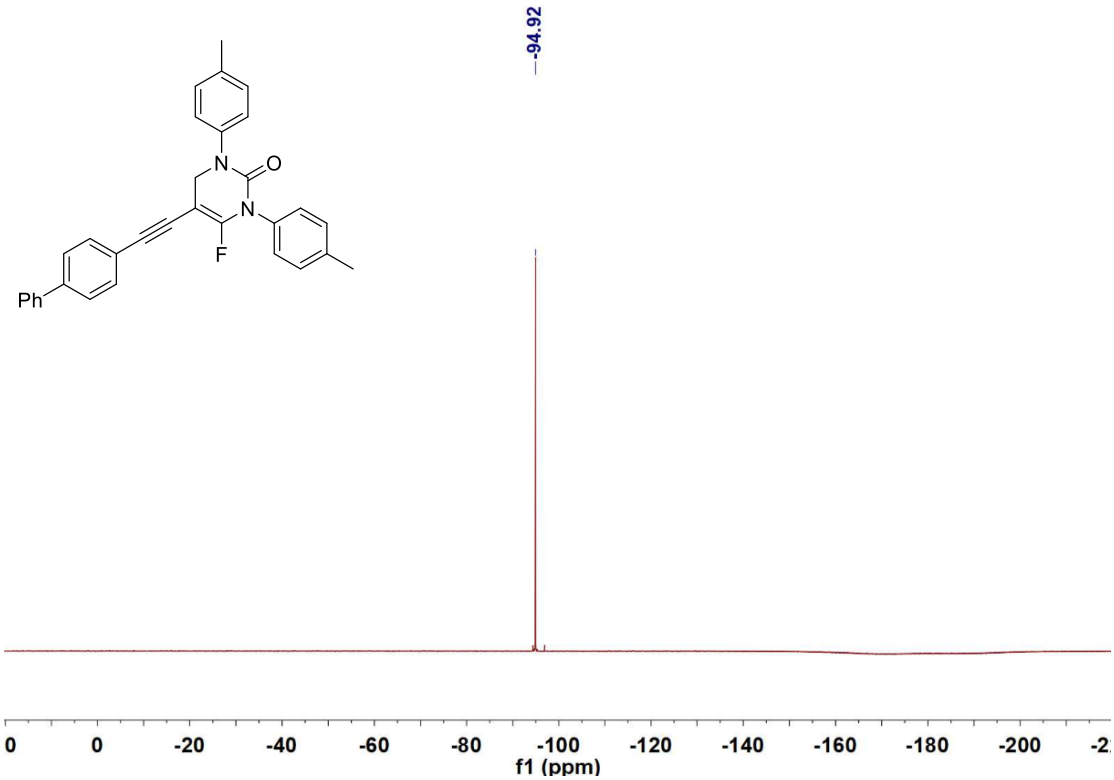
5-([1,1'-biphenyl]-4-ylethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ea)



^{1}H-NMR (500 MHz, $CDCl_3$)

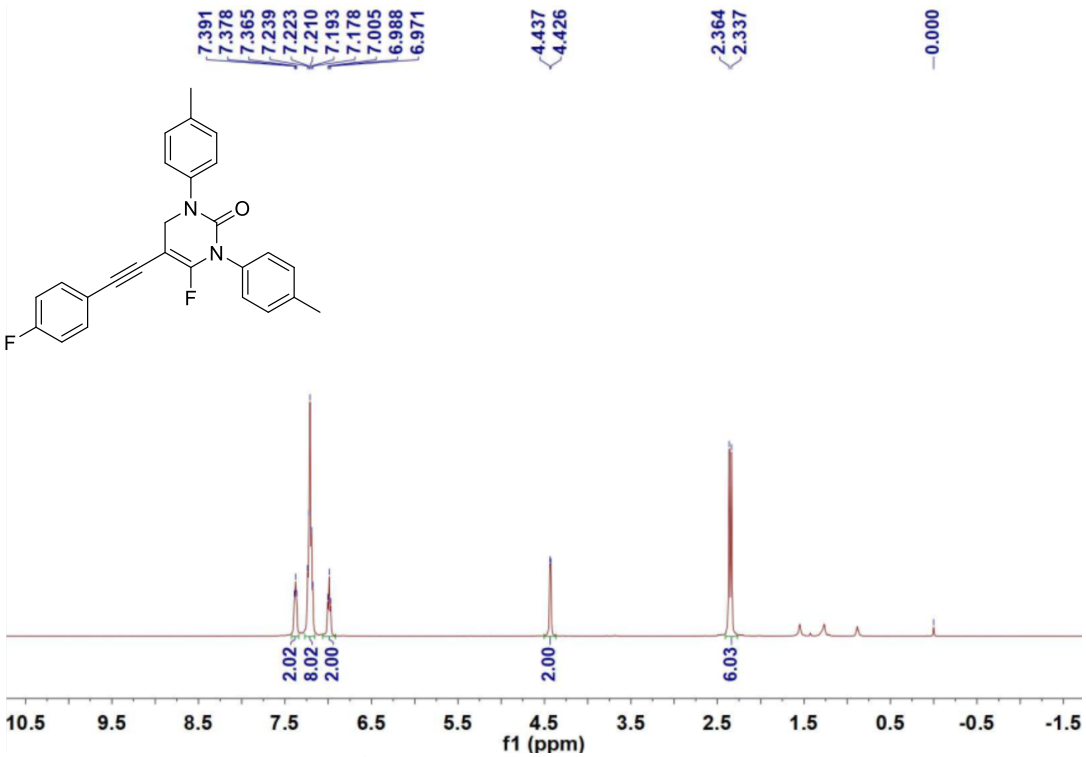


^{13}C-NMR (125 MHz, $CDCl_3$)

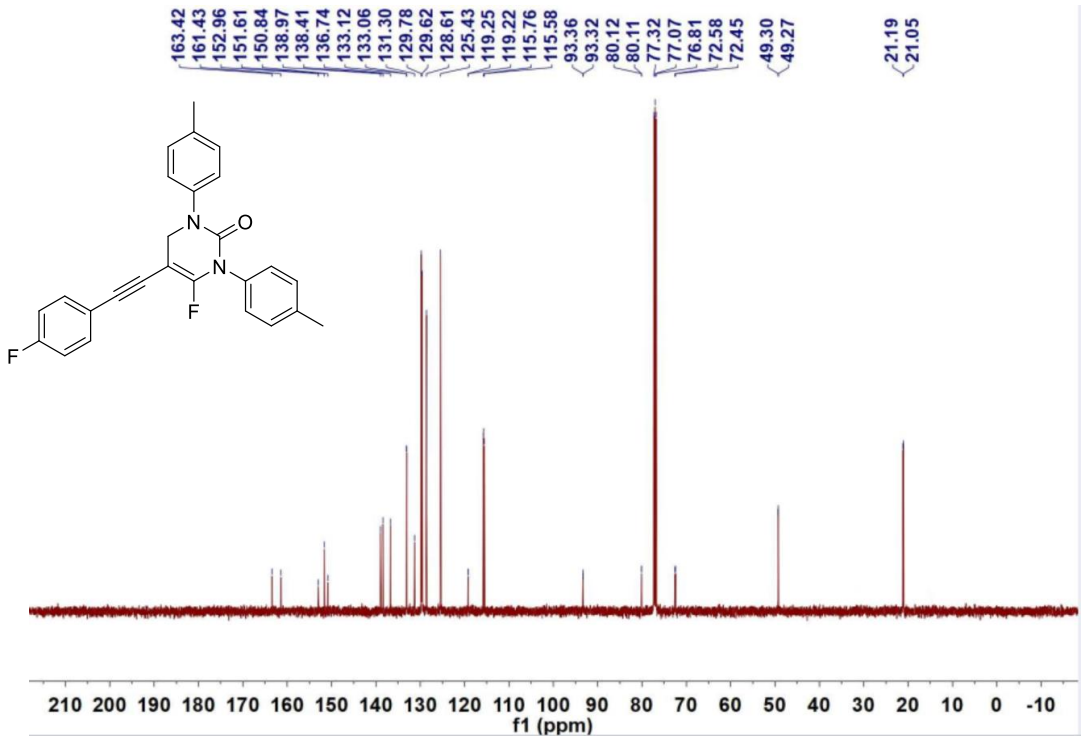


^{19}F-NMR (471 MHz, $CDCl_3$)

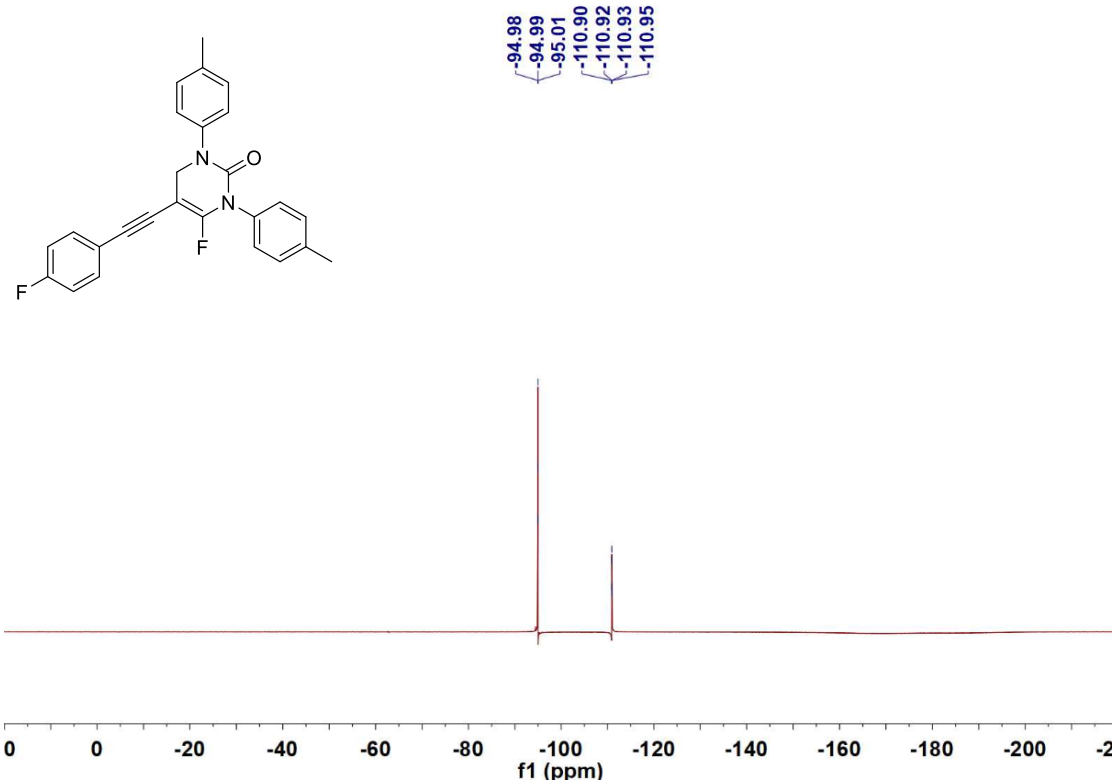
6-fluoro-5-((4-fluorophenyl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3fa)



^{1}H-NMR (500 MHz, $CDCl_3$)

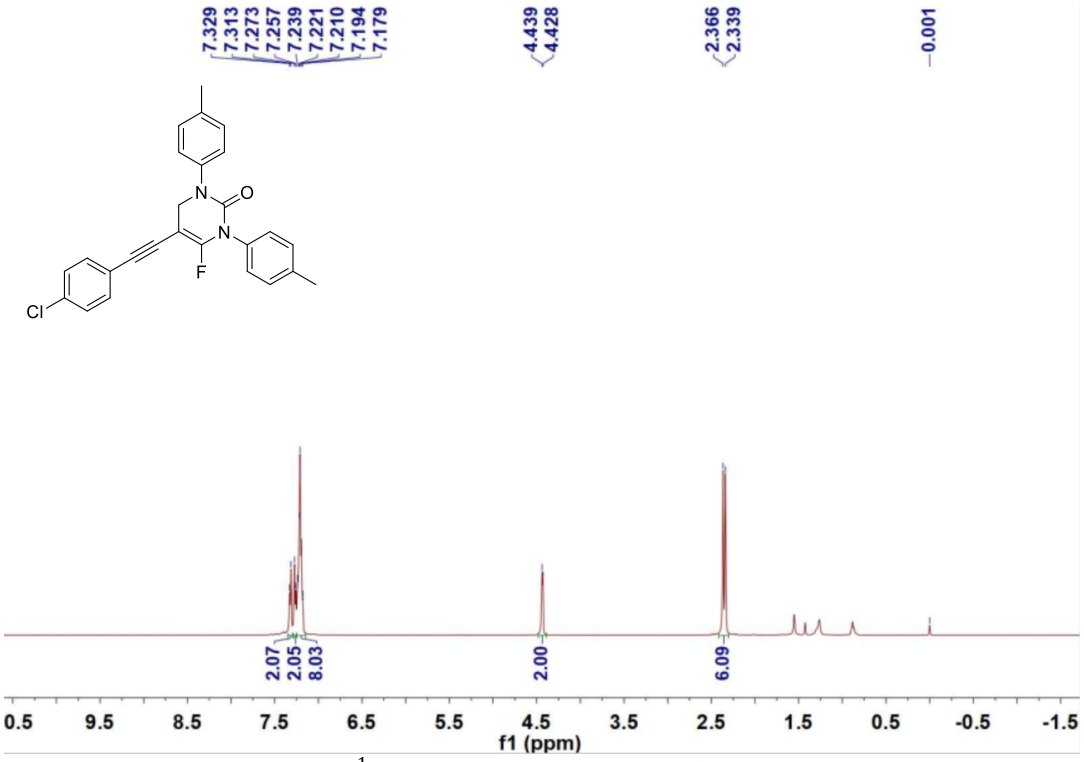


^{13}C-NMR (125 MHz, $CDCl_3$)

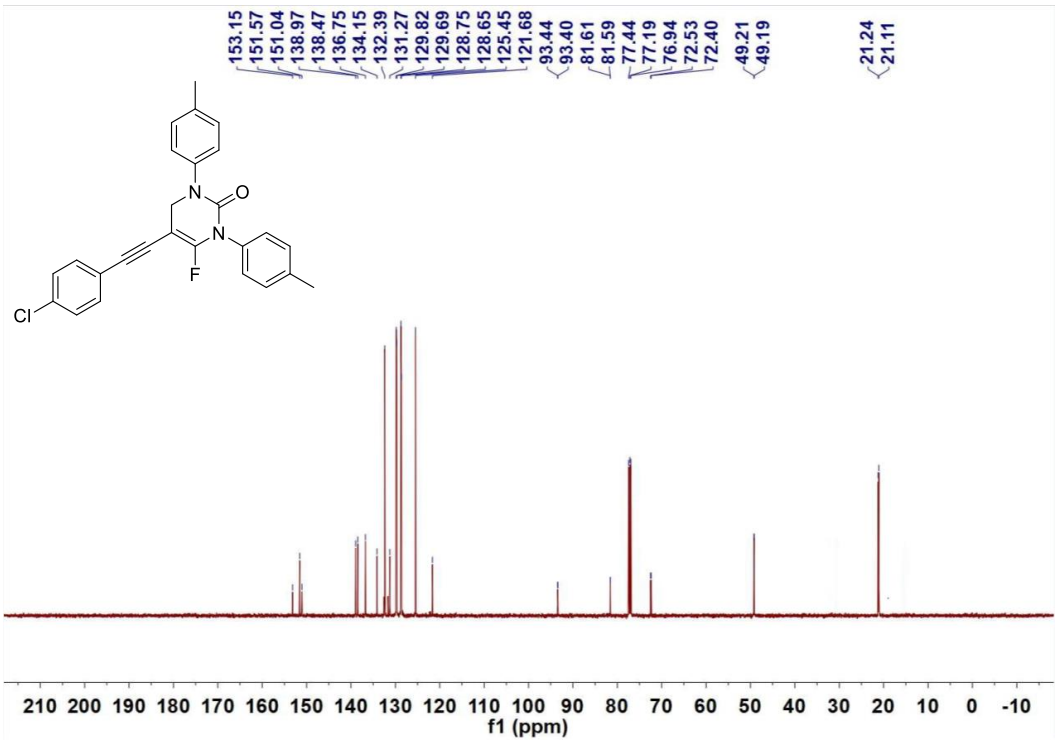


^{19}F-NMR (471 MHz, $CDCl_3$)

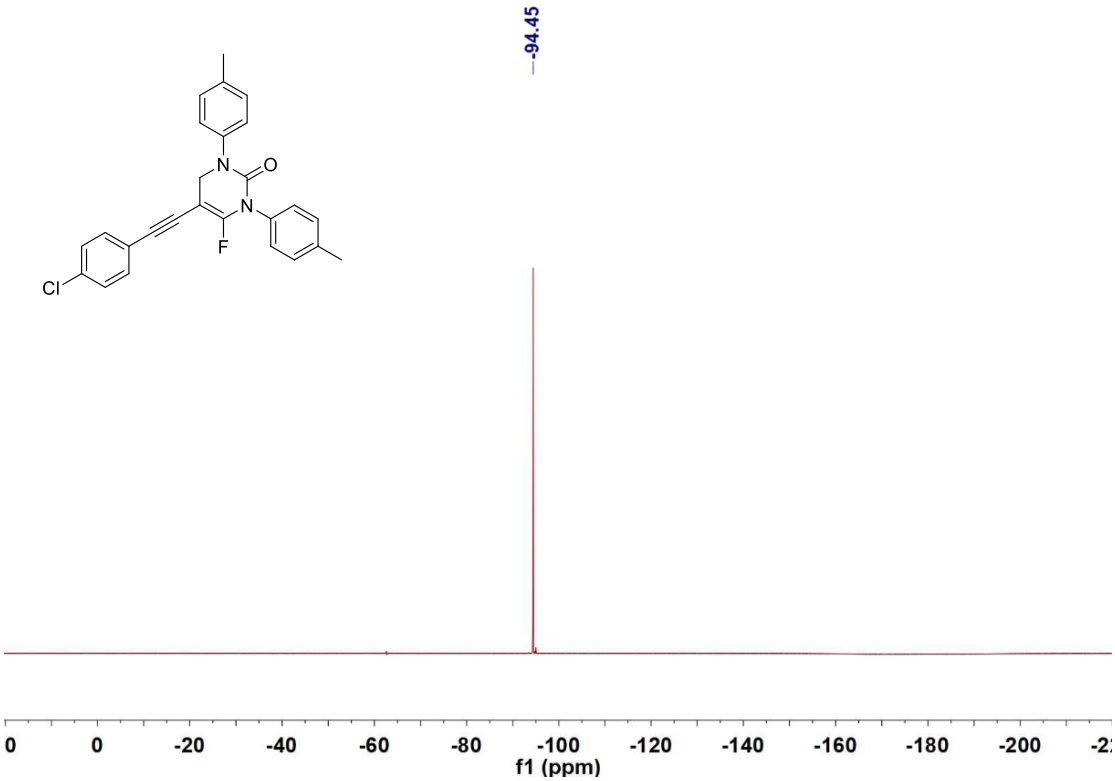
5-((4-chlorophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ga)



^{1}H-NMR (500 MHz, $CDCl_3$)

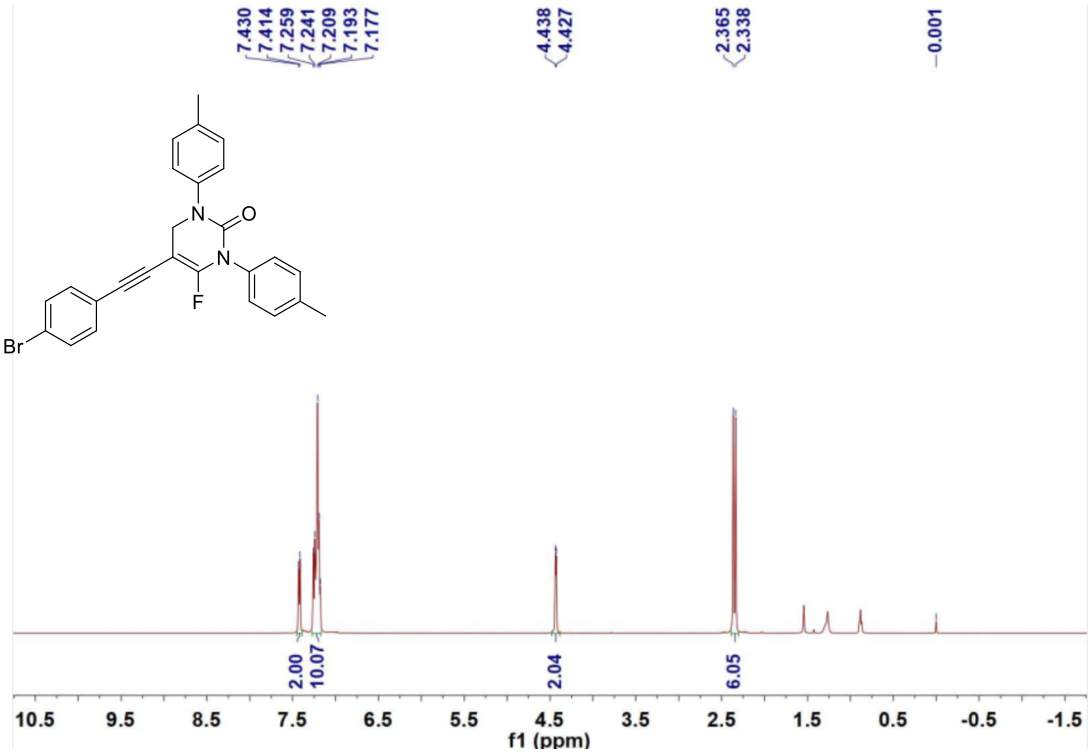


^{13}C-NMR (125 MHz, $CDCl_3$)

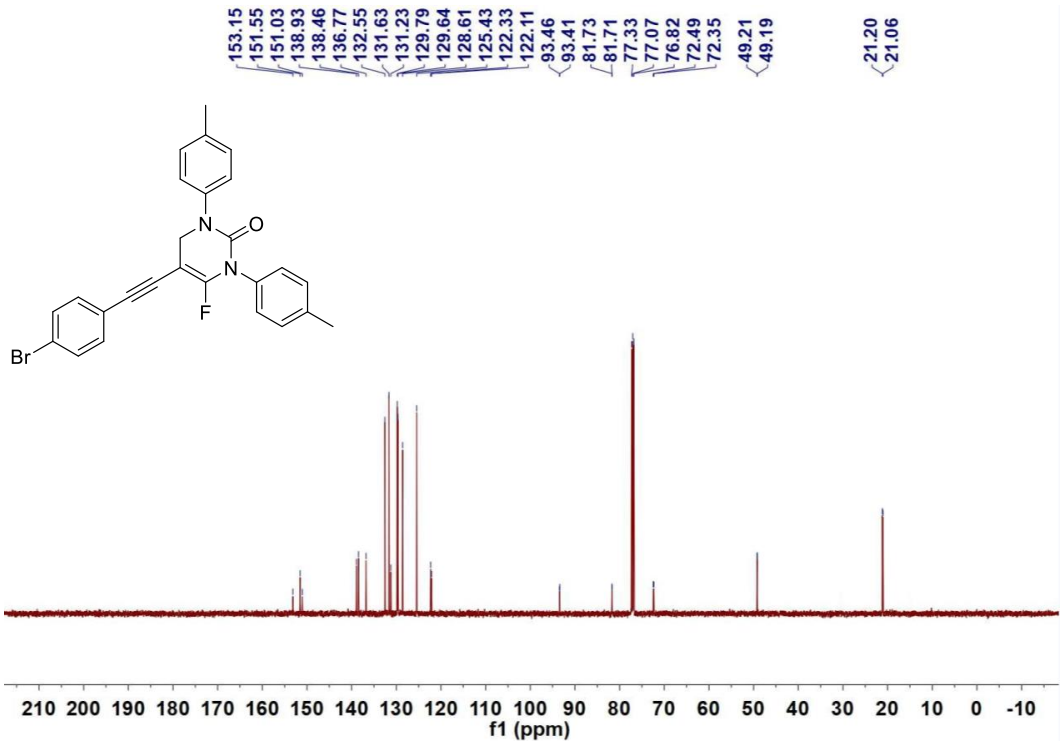


^{19}F-NMR (471 MHz, $CDCl_3$)

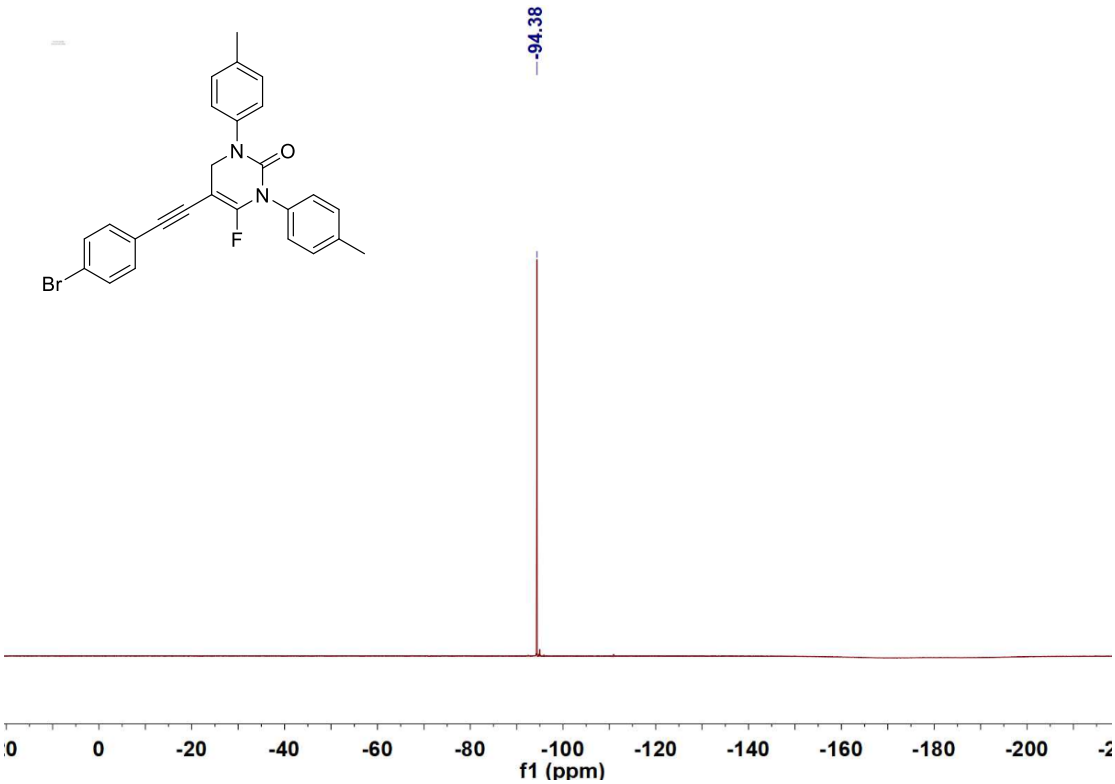
5-((4-bromophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ha)



^{1}H-NMR (500 MHz, $CDCl_3$)

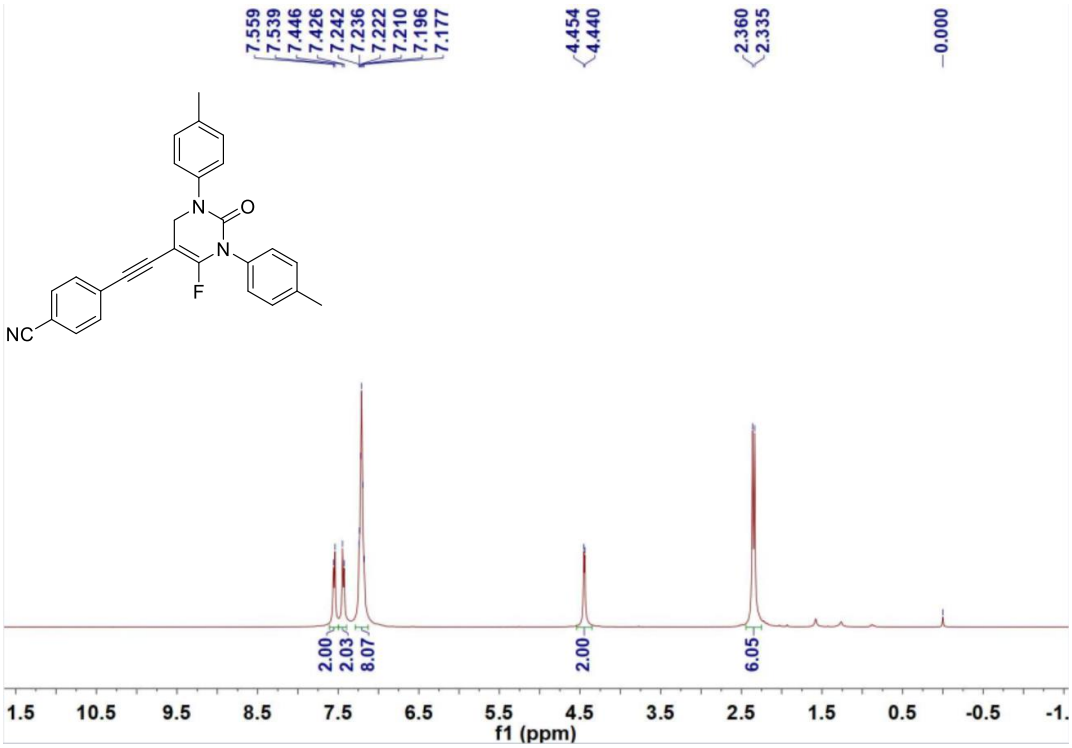


^{13}C-NMR (125 MHz, $CDCl_3$)

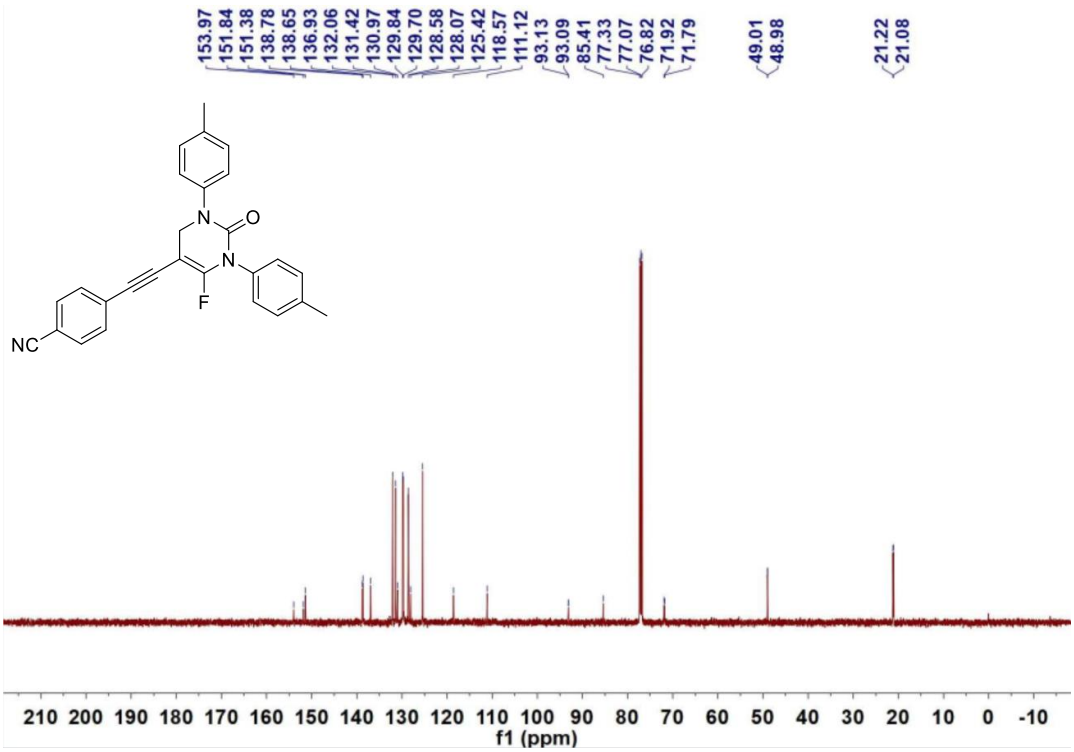


^{19}F-NMR (471 MHz, $CDCl_3$)

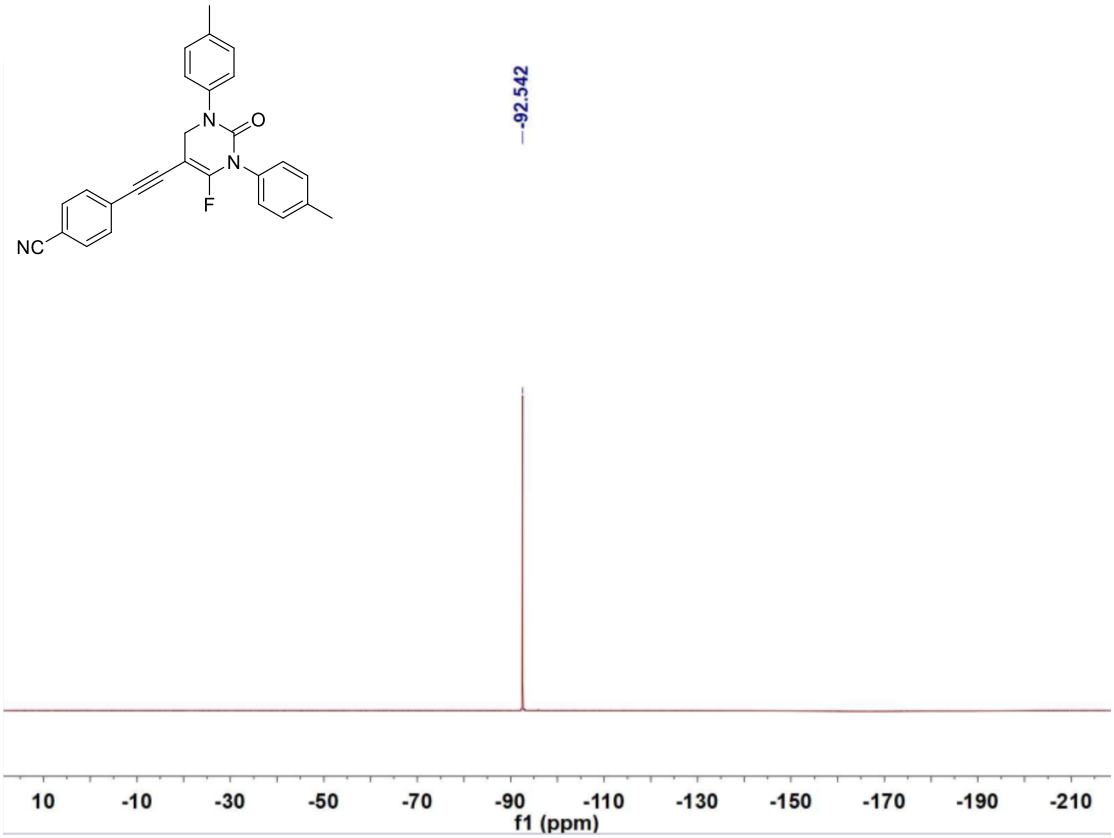
4-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)benzonitrile (3ia)



^{1}H-NMR (400 MHz, $CDCl_3$)

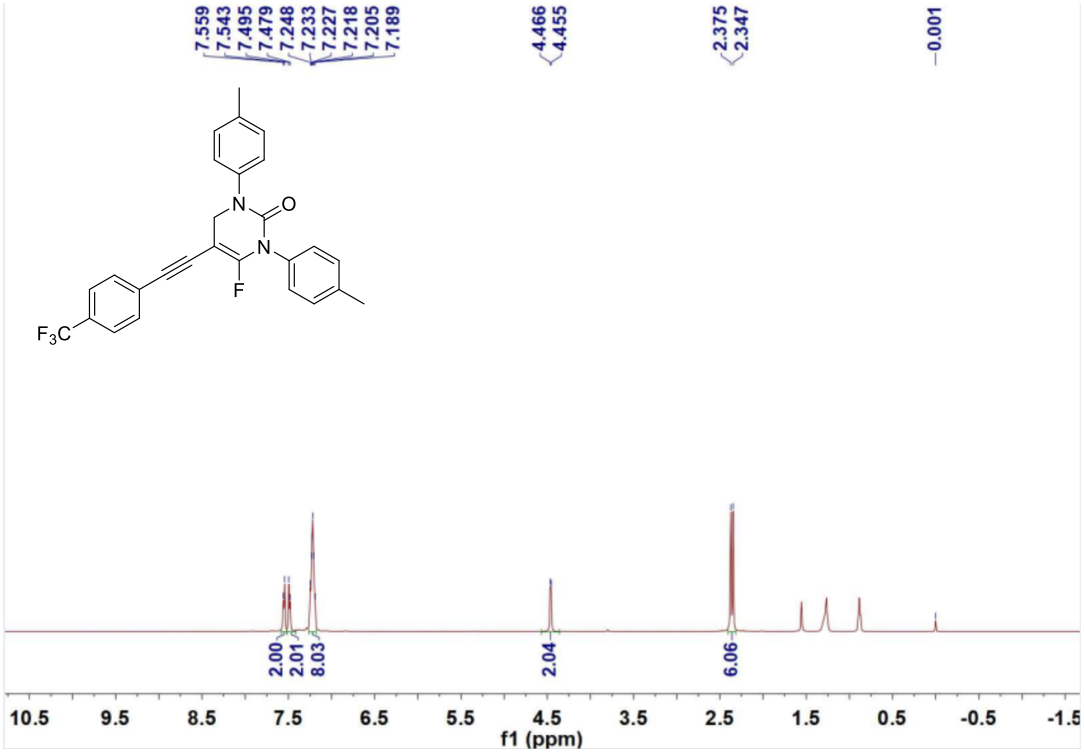


^{13}C-NMR (125 MHz, $CDCl_3$)

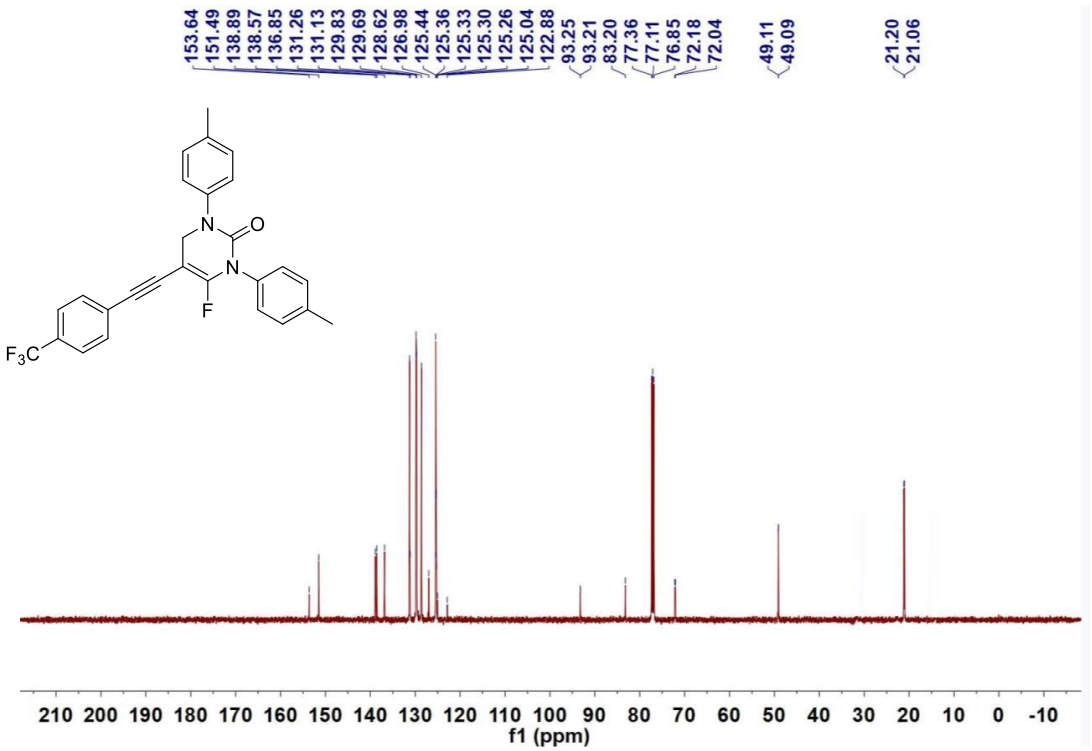


^{19}F-NMR (376 MHz, $CDCl_3$)

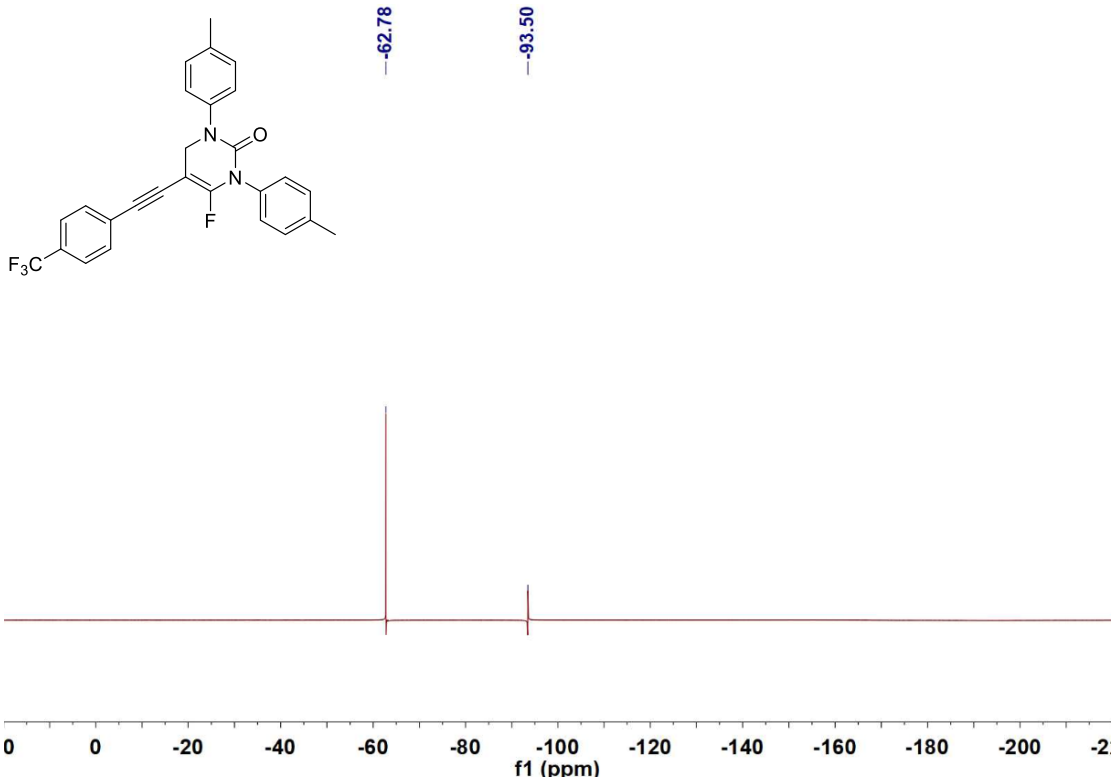
6-fluoro-1,3-di-*p*-tolyl-5-((4-(trifluoromethyl)phenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ja)



^{1}H-NMR (500 MHz, $CDCl_3$)

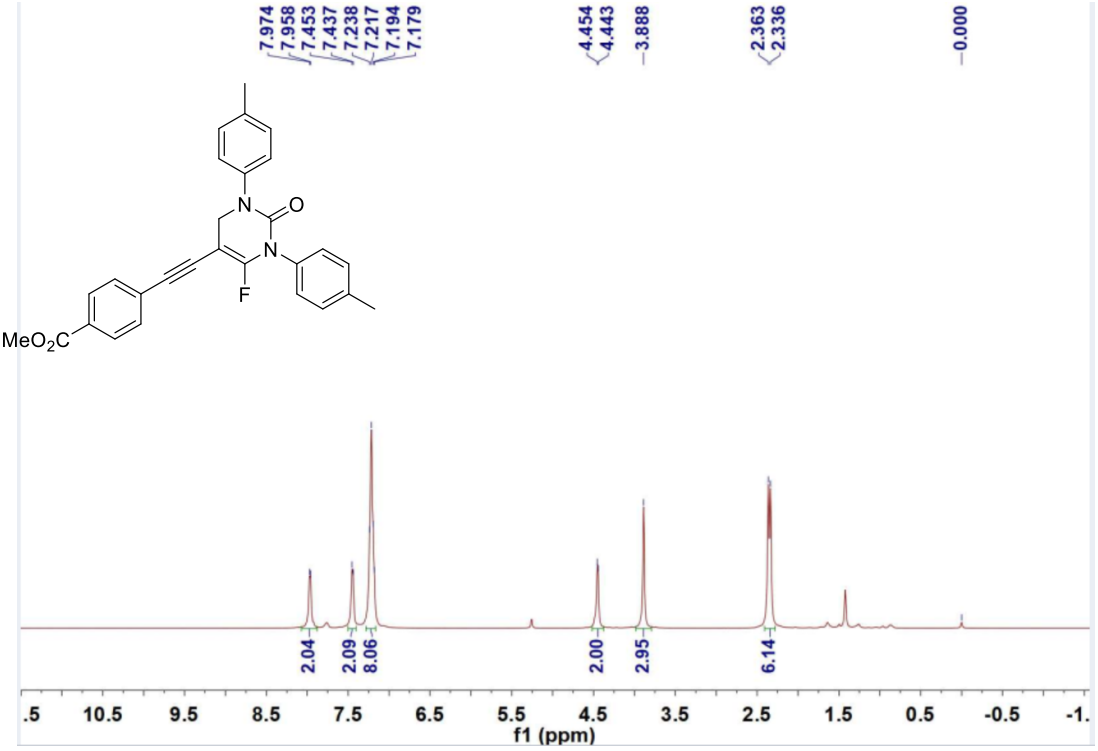


^{13}C-NMR (125 MHz, $CDCl_3$)

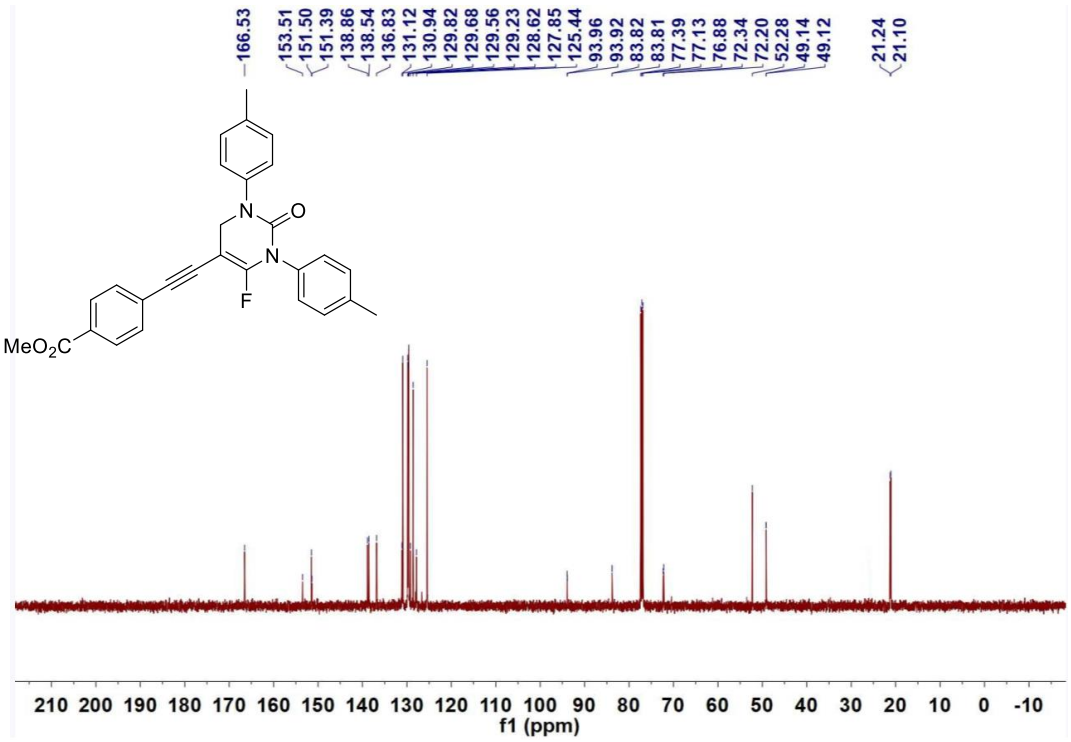


^{19}F-NMR (471 MHz, $CDCl_3$)

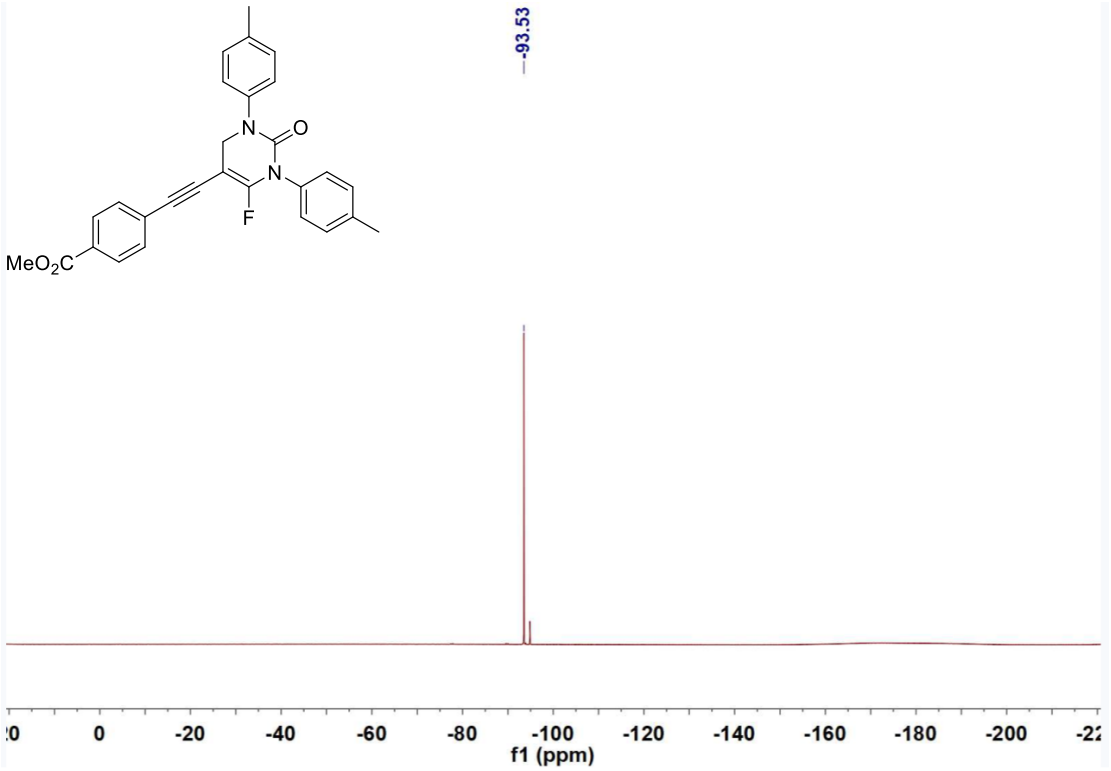
methyl 4-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)benzoate (3ka)



^{1}H-NMR (500 MHz, $CDCl_3$)

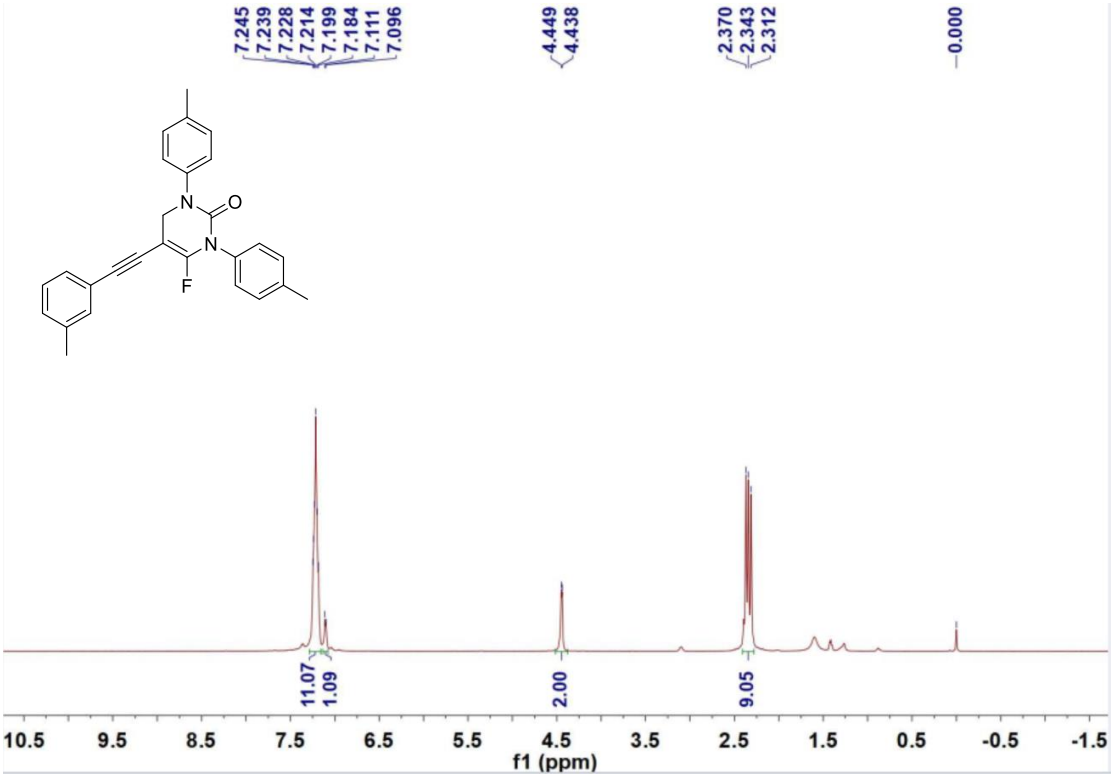


^{13}C-NMR (125 MHz, $CDCl_3$)

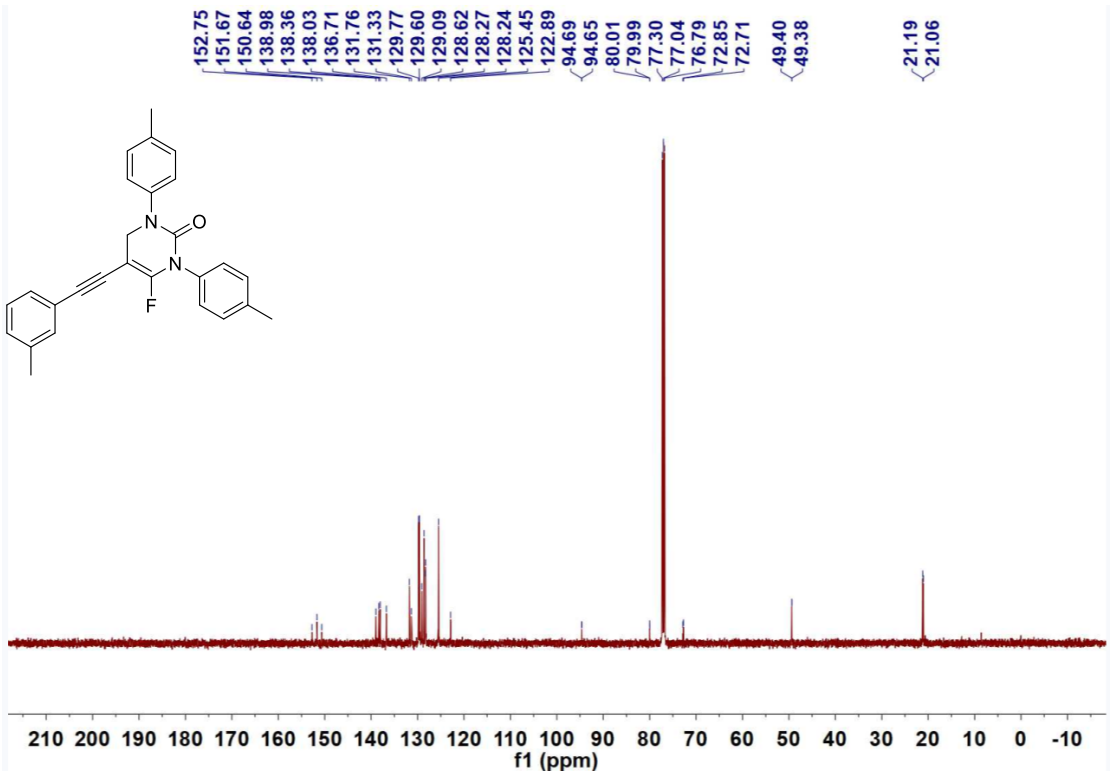


^{19}F-NMR (471 MHz, $CDCl_3$)

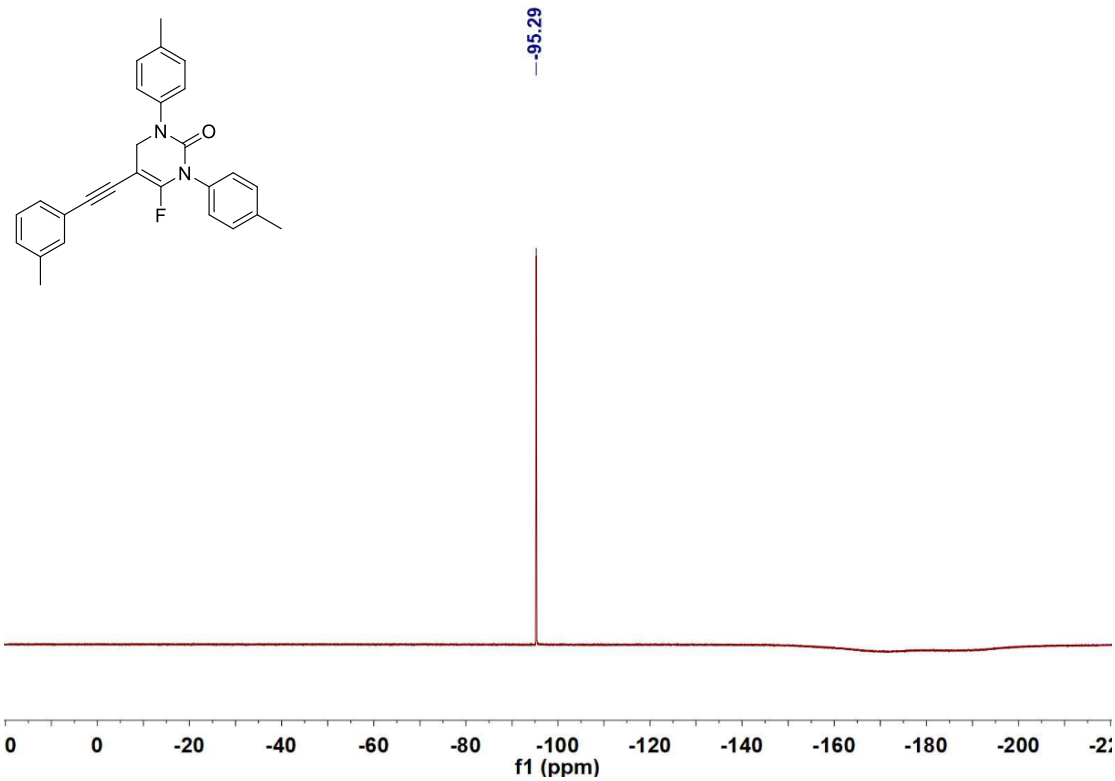
6-fluoro-1,3-di-p-tolyl-5-(*m*-tolylethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3la)



^{1}H-NMR (500 MHz, $CDCl_3$)

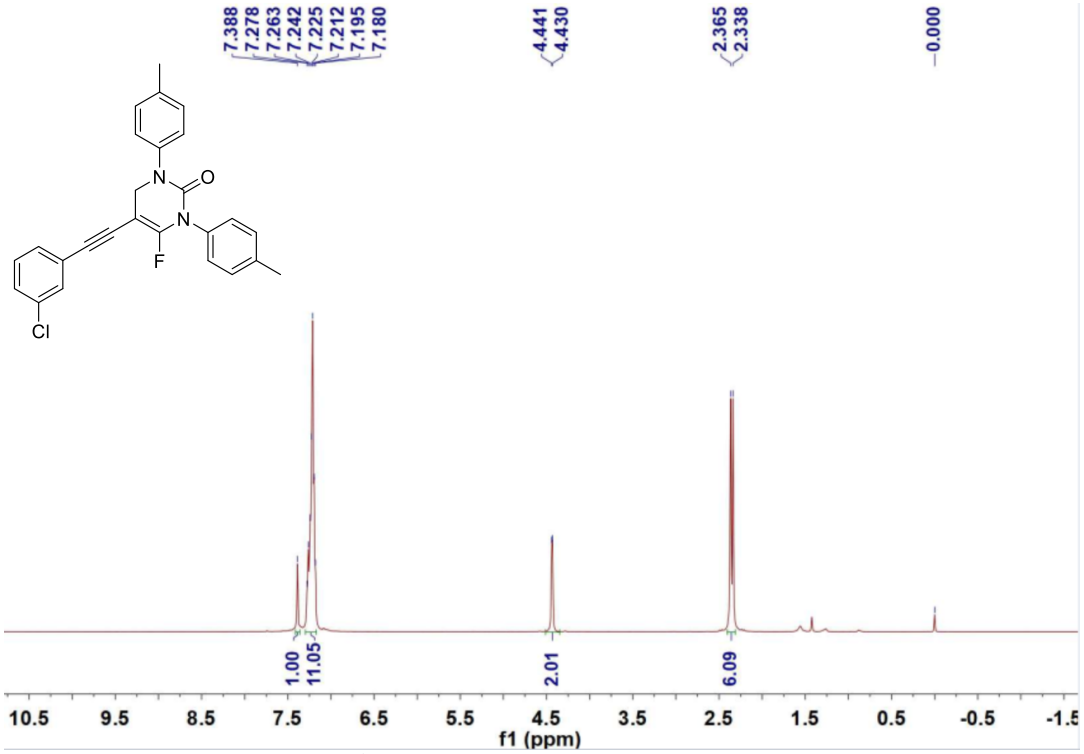


^{13}C-NMR (125 MHz, $CDCl_3$)

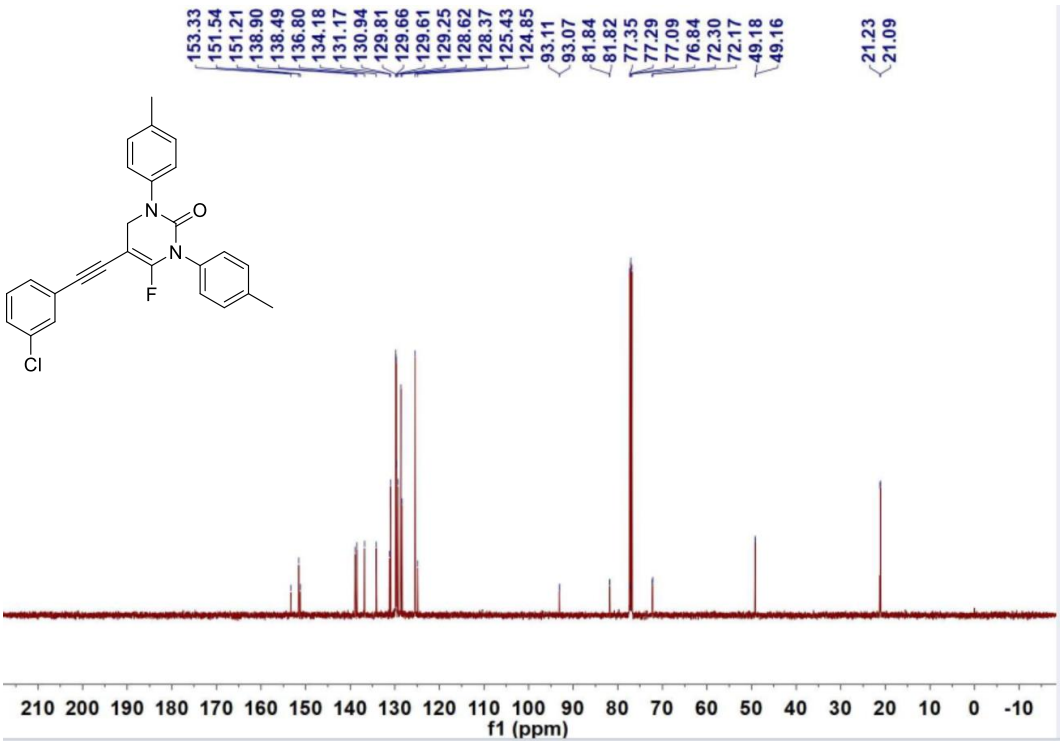


^{19}F-NMR (471 MHz, $CDCl_3$)

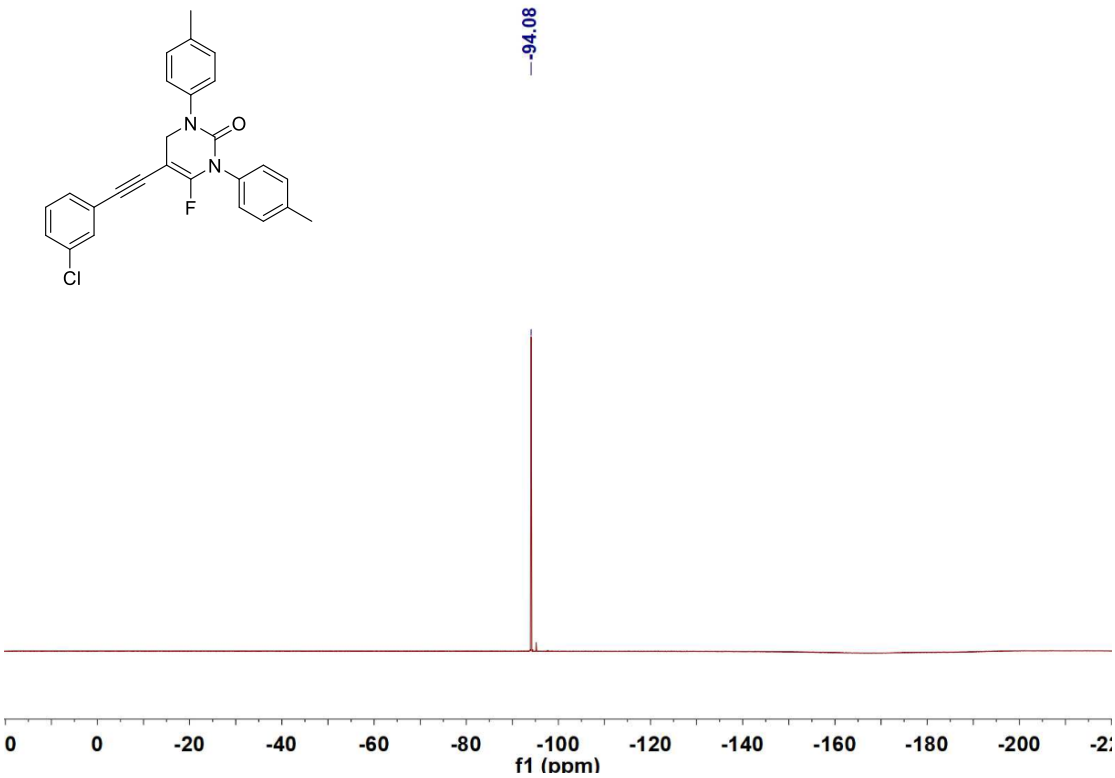
5-((3-chlorophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ma)



^{1}H-NMR (500 MHz, $CDCl_3$)

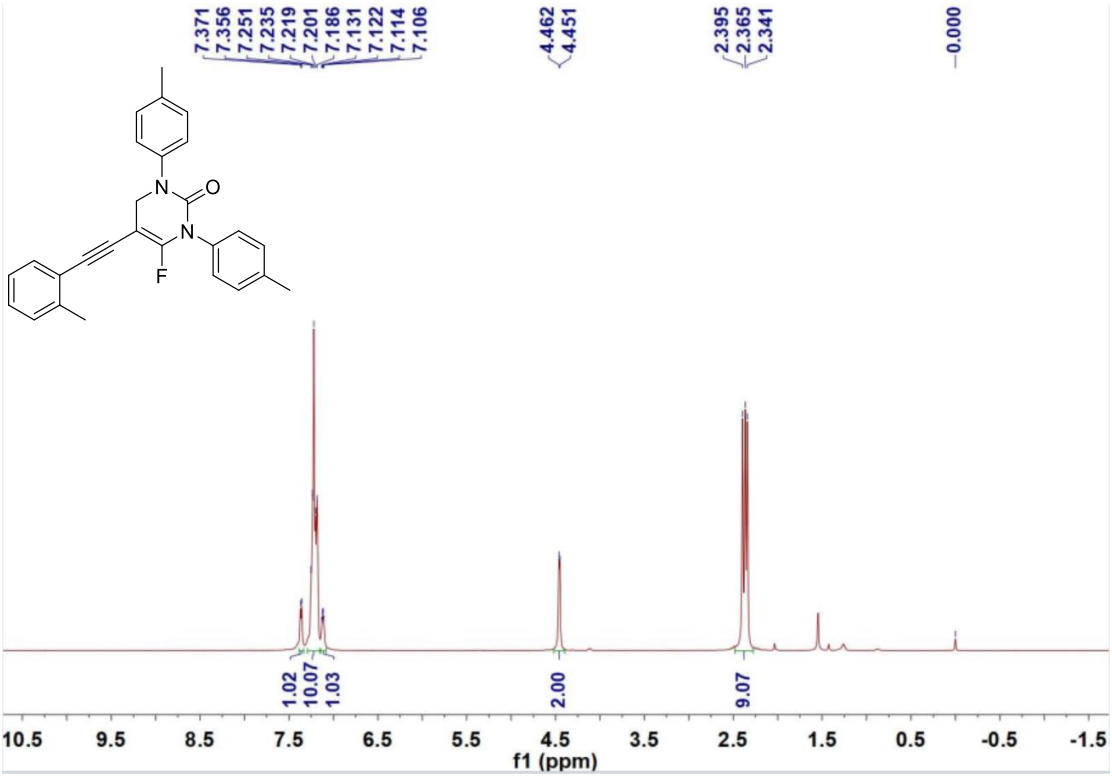


^{13}C-NMR (125 MHz, $CDCl_3$)

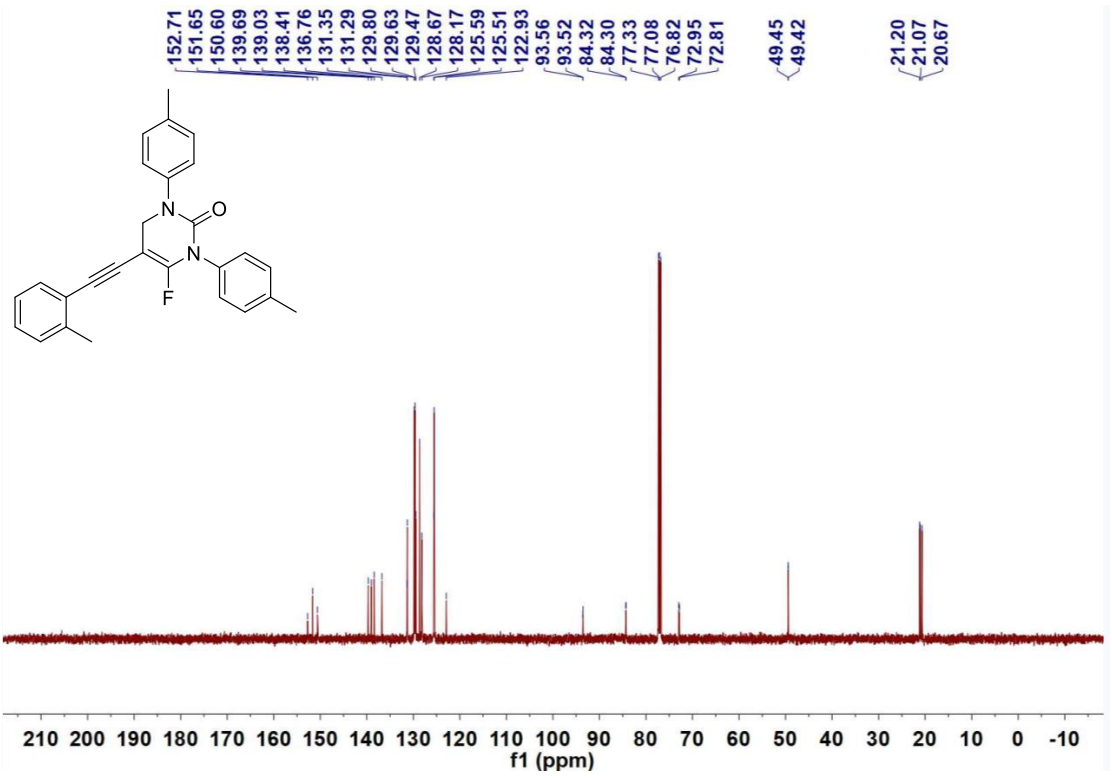


^{19}F-NMR (471 MHz, $CDCl_3$)

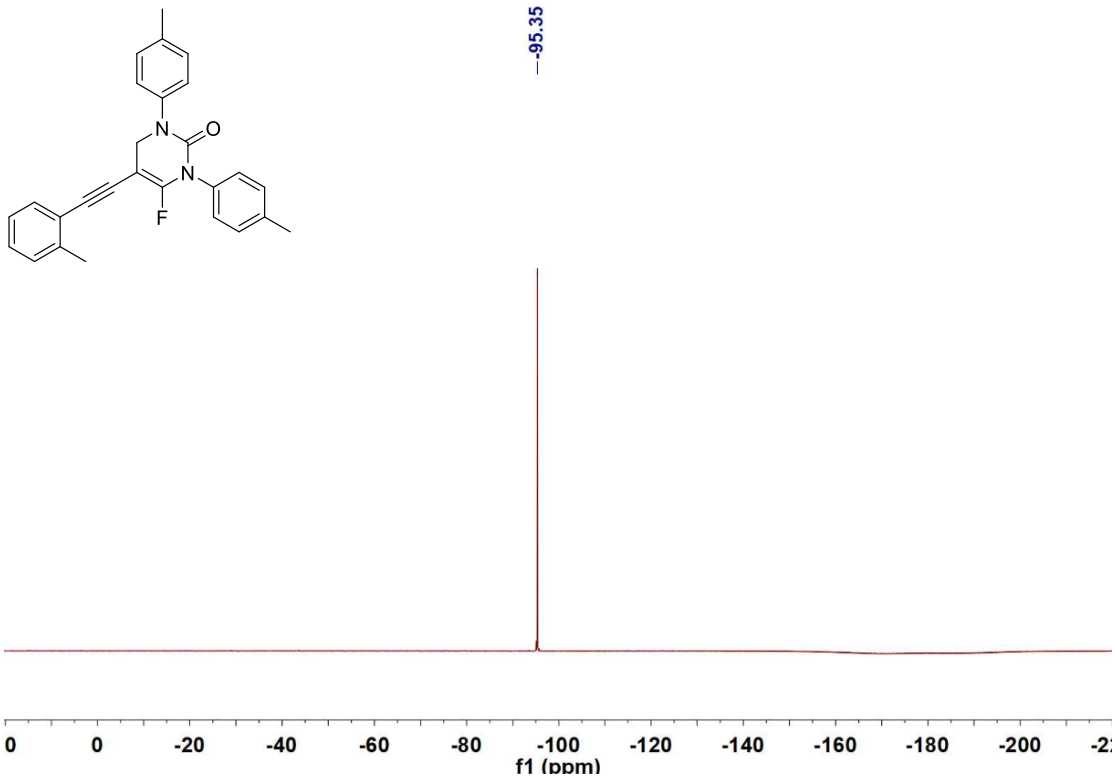
6-fluoro-1,3-di-p-tolyl-5-(*o*-tolylethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3na)



^{1}H-NMR (500 MHz, $CDCl_3$)

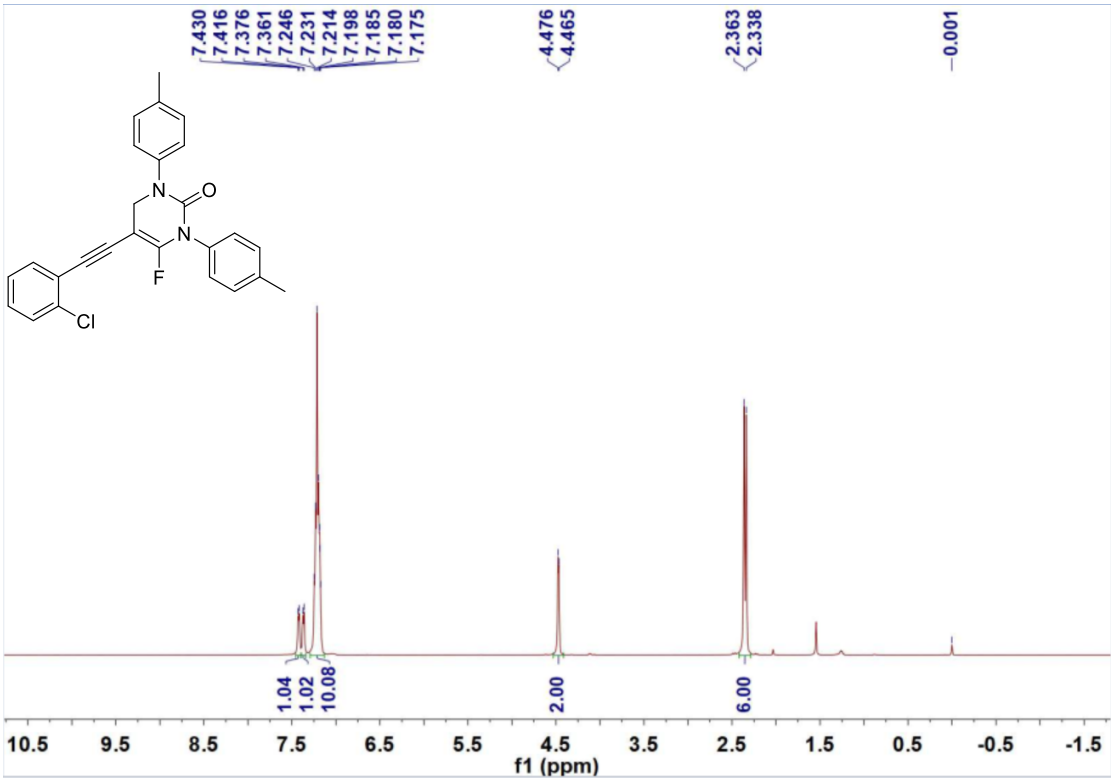


^{13}C-NMR (125 MHz, $CDCl_3$)

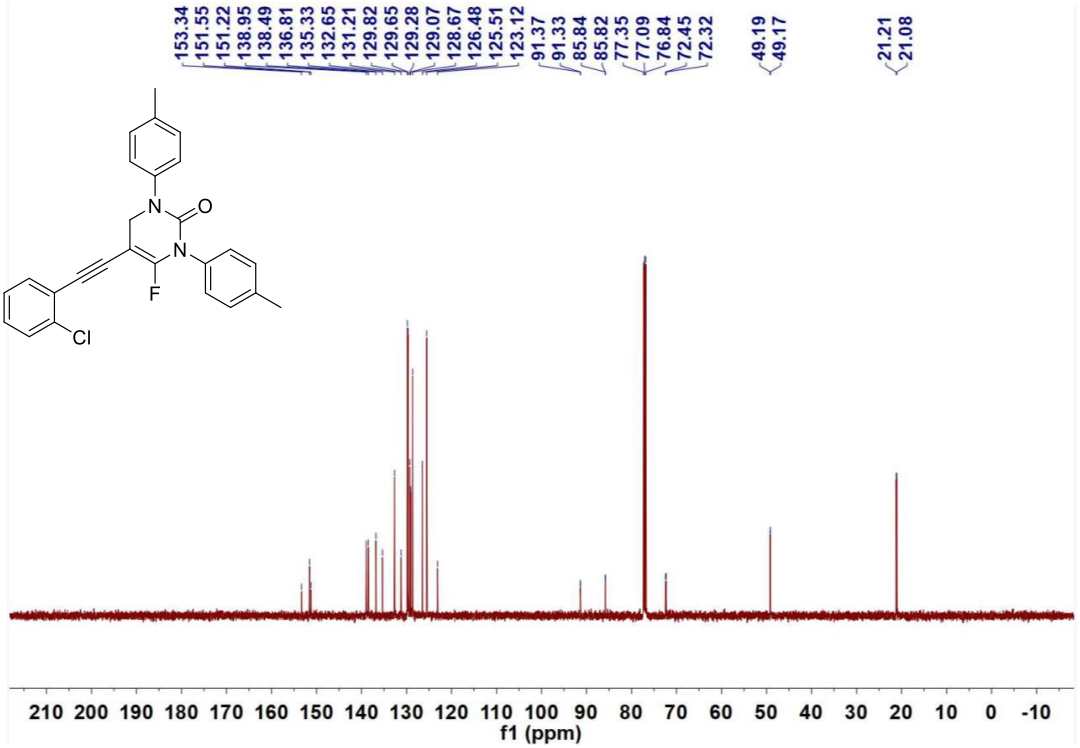


^{19}F-NMR (471 MHz, $CDCl_3$)

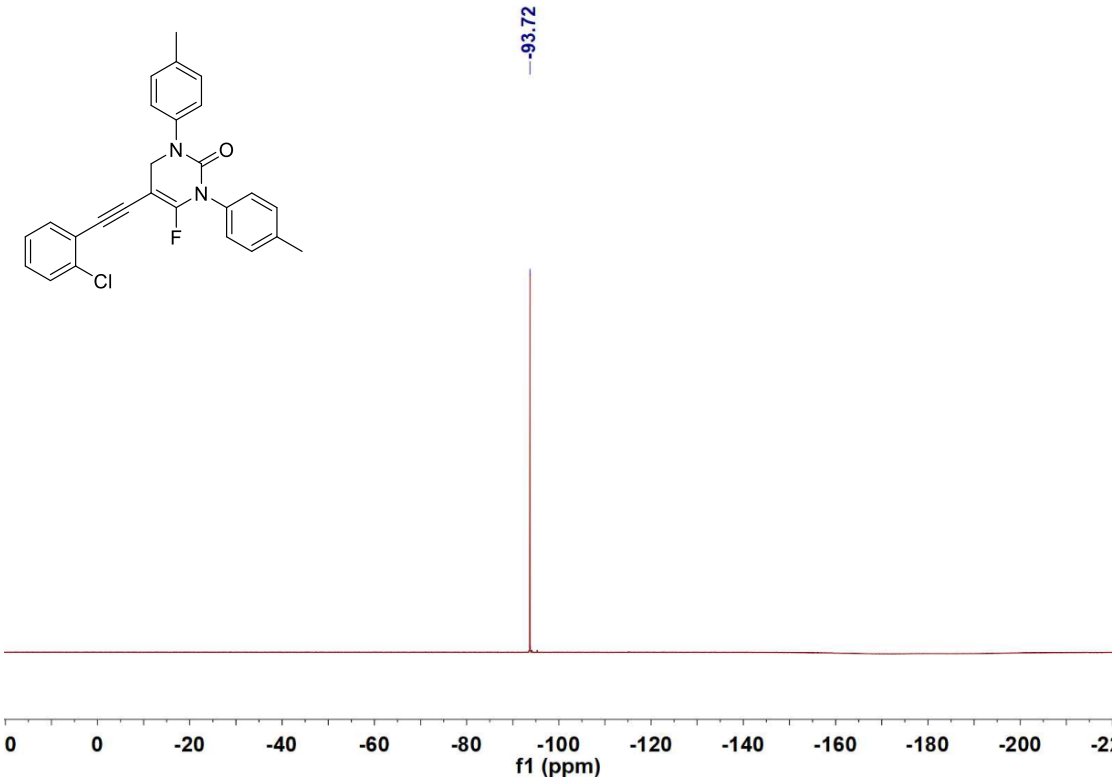
5-((2-chlorophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3oa)



^{1}H-NMR (500 MHz, $CDCl_3$)

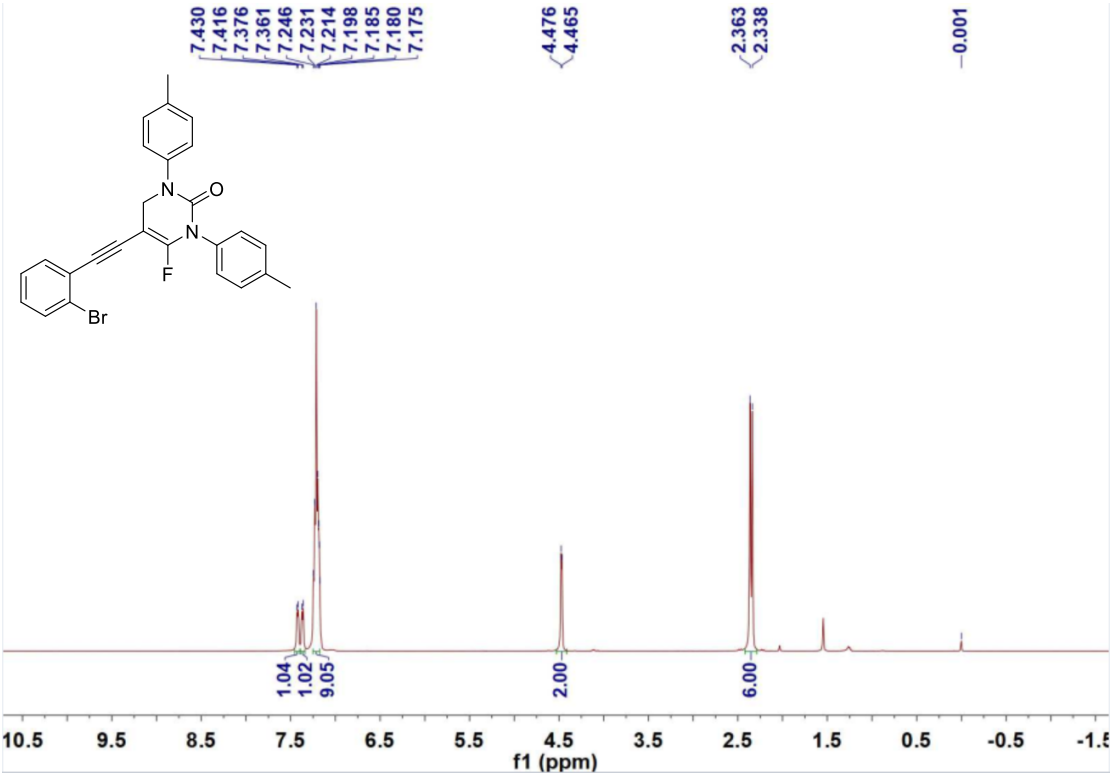


^{13}C-NMR (125 MHz, $CDCl_3$)

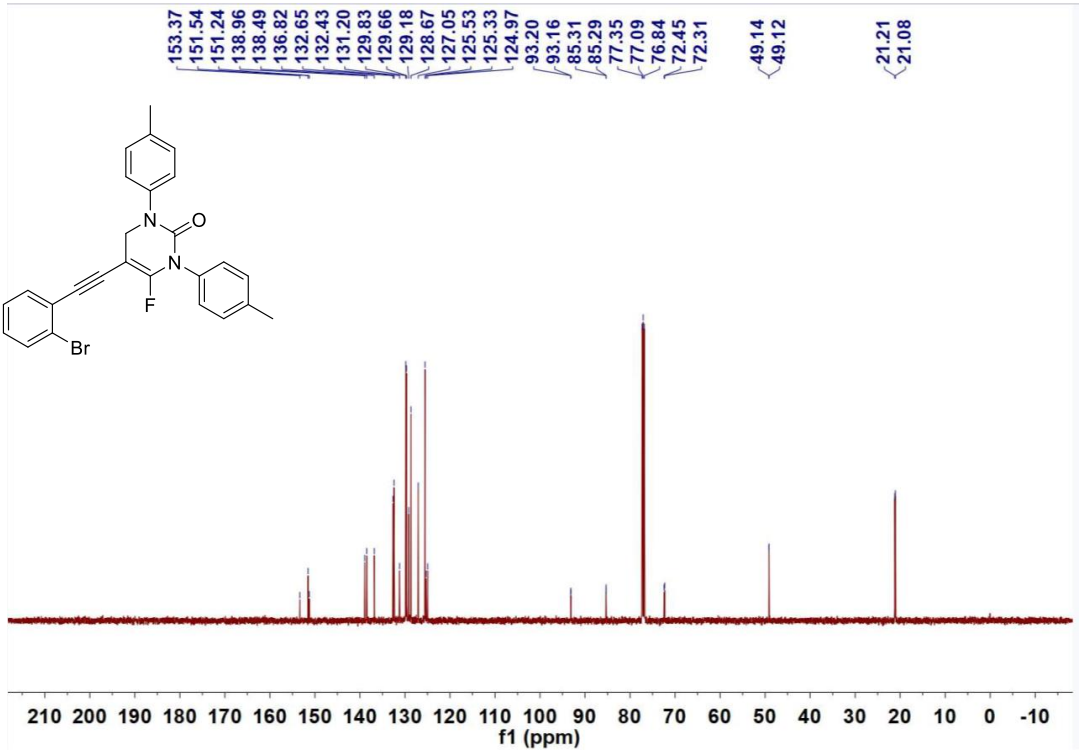


^{19}F-NMR (471 MHz, $CDCl_3$)

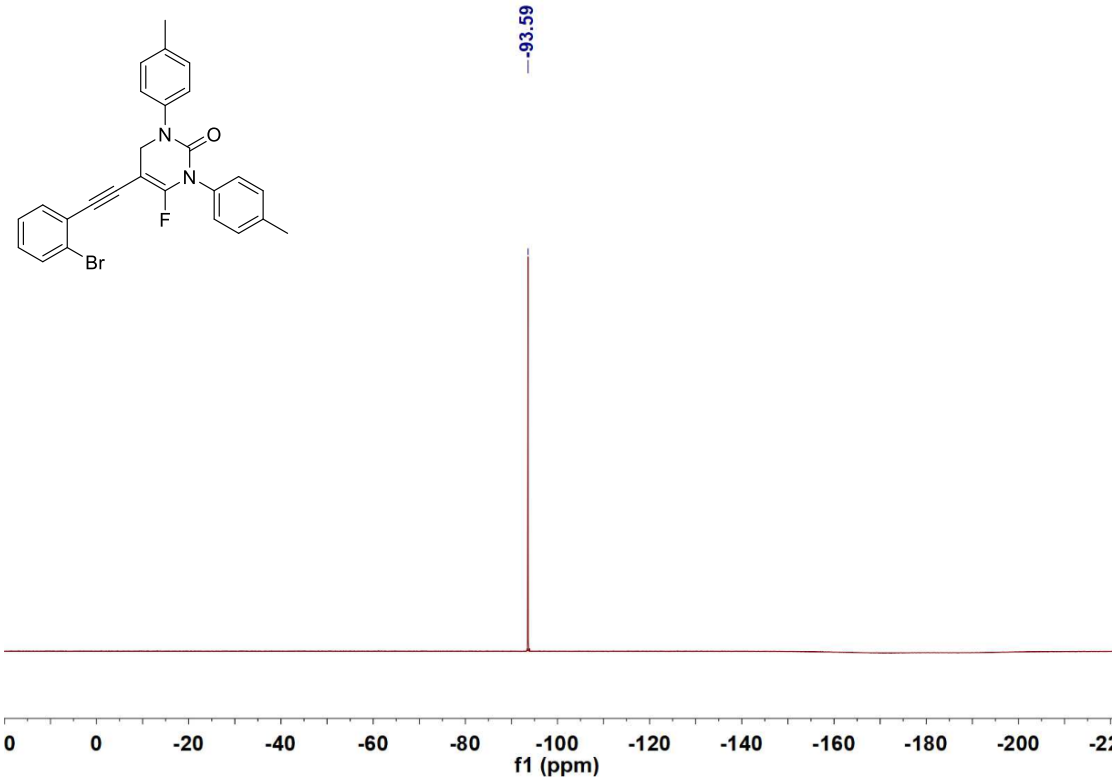
5-((2-bromophenyl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3pa)



^{1}H-NMR (500 MHz, $CDCl_3$)

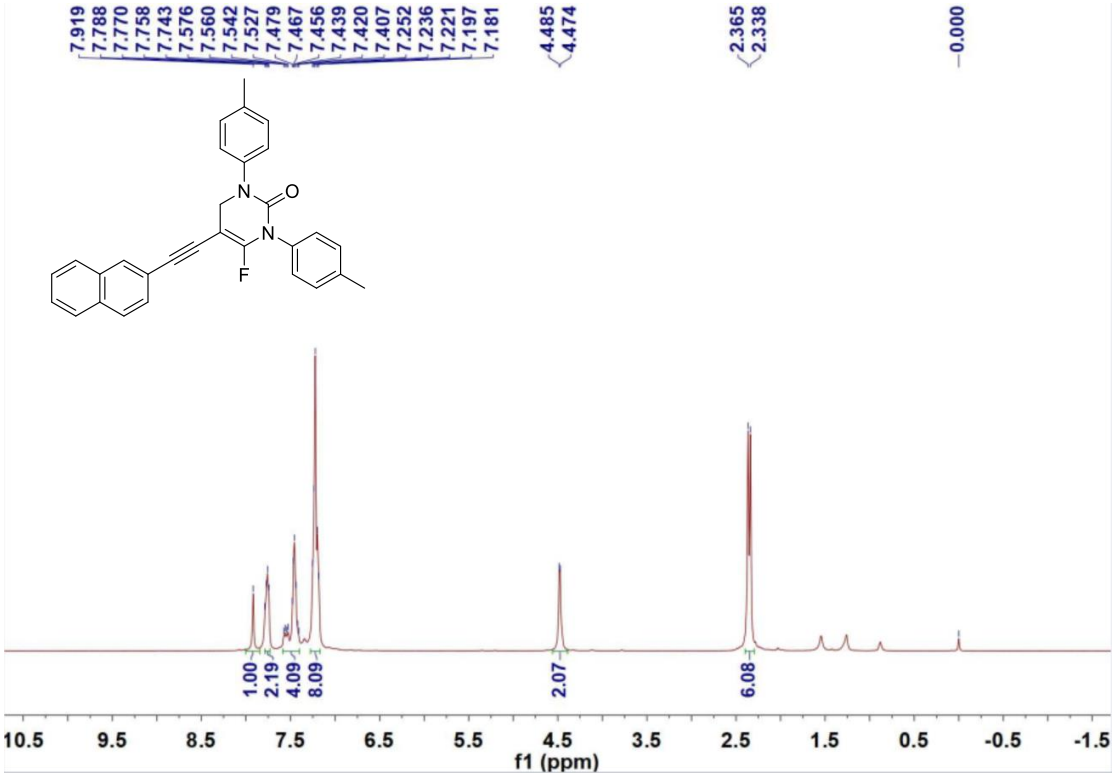


^{13}C-NMR (125 MHz, $CDCl_3$)

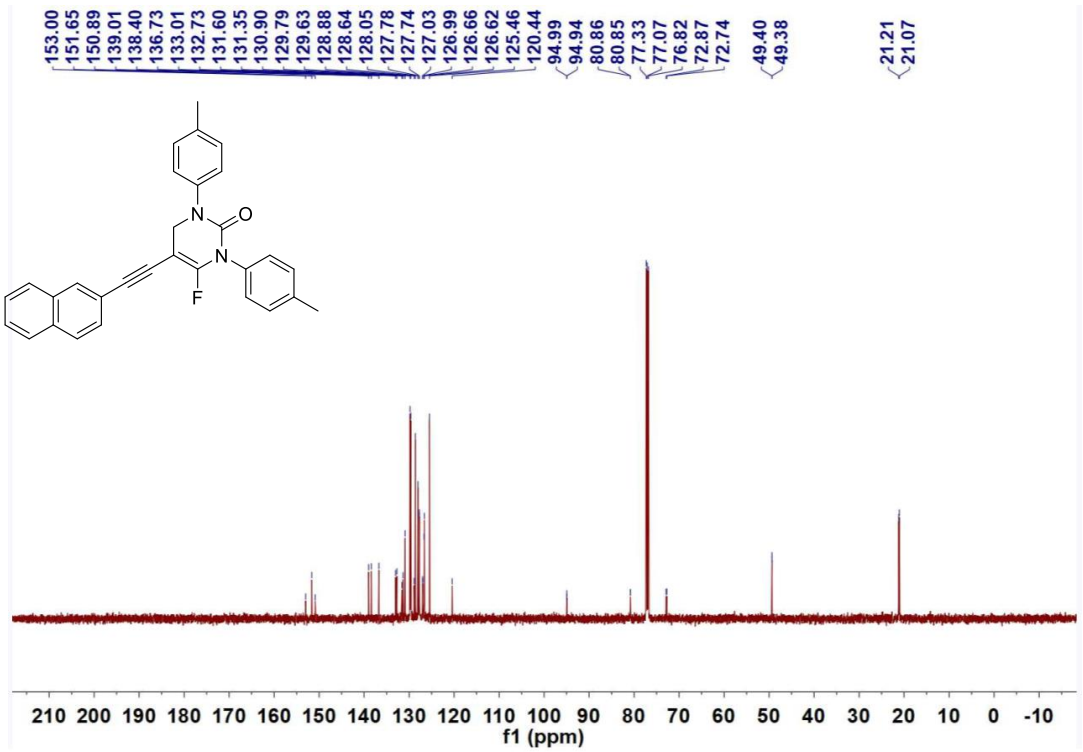


^{19}F-NMR (471 MHz, $CDCl_3$)

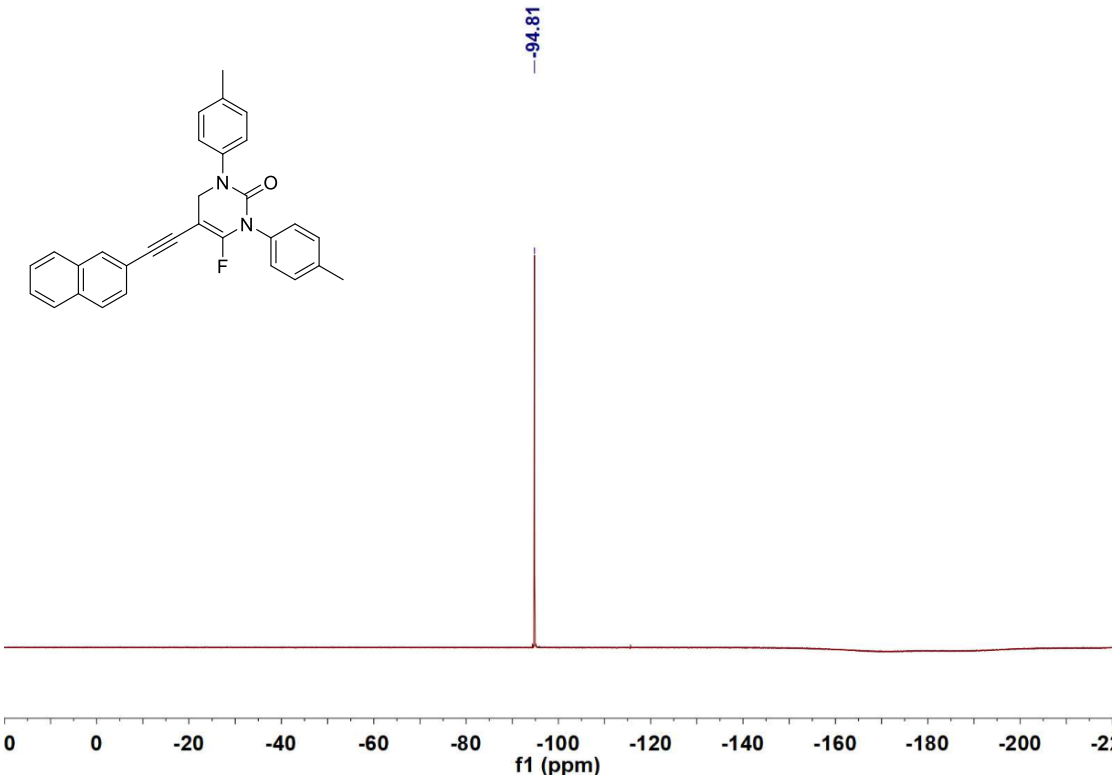
6-fluoro-5-(naphthalen-2-ylethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3qa)



^{1}H-NMR (500 MHz, $CDCl_3$)



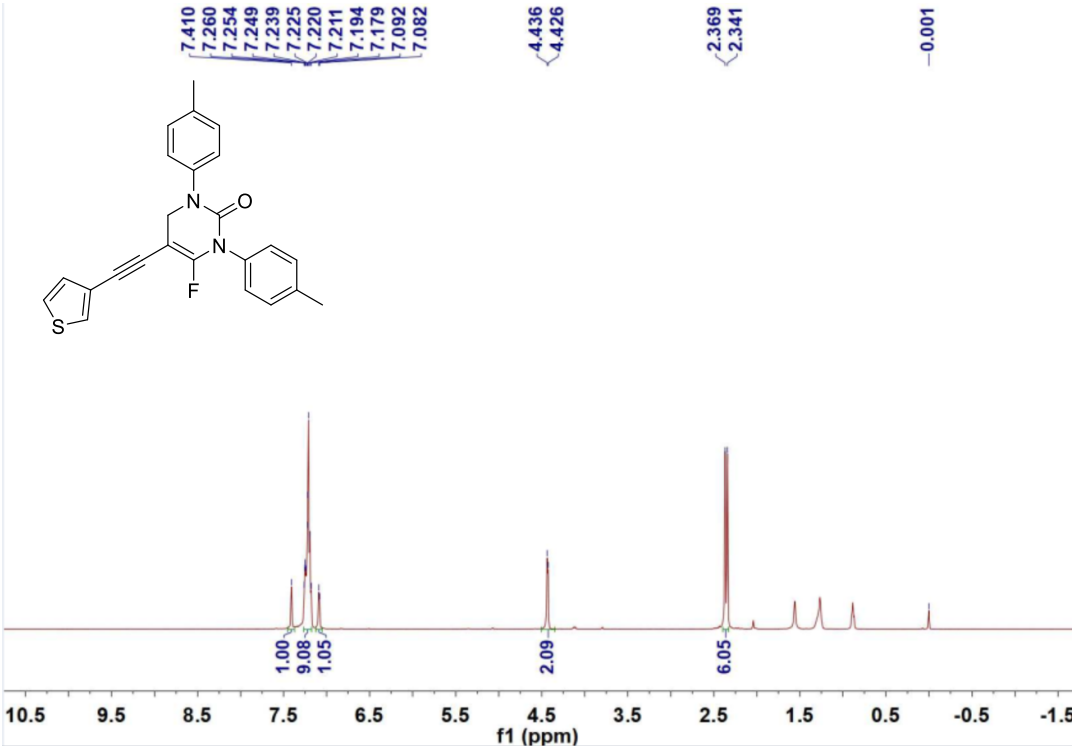
^{13}C-NMR (125 MHz, $CDCl_3$)



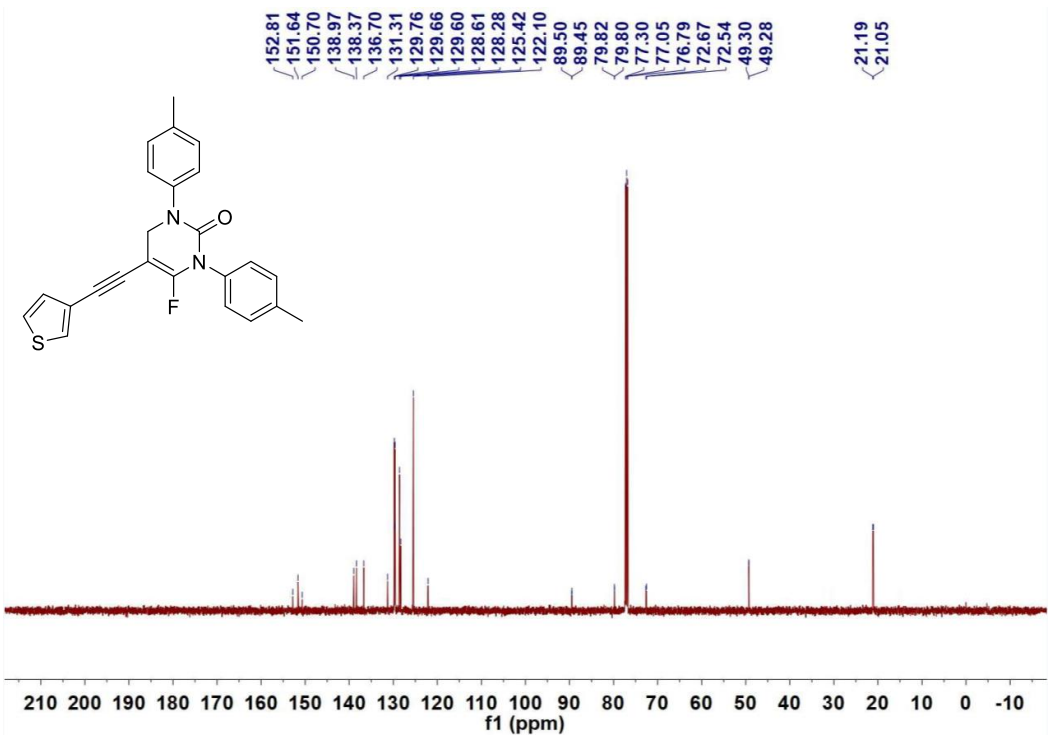
^{19}F-NMR (471 MHz, $CDCl_3$)

6-fluoro-5-(thiophen-3-ylethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one

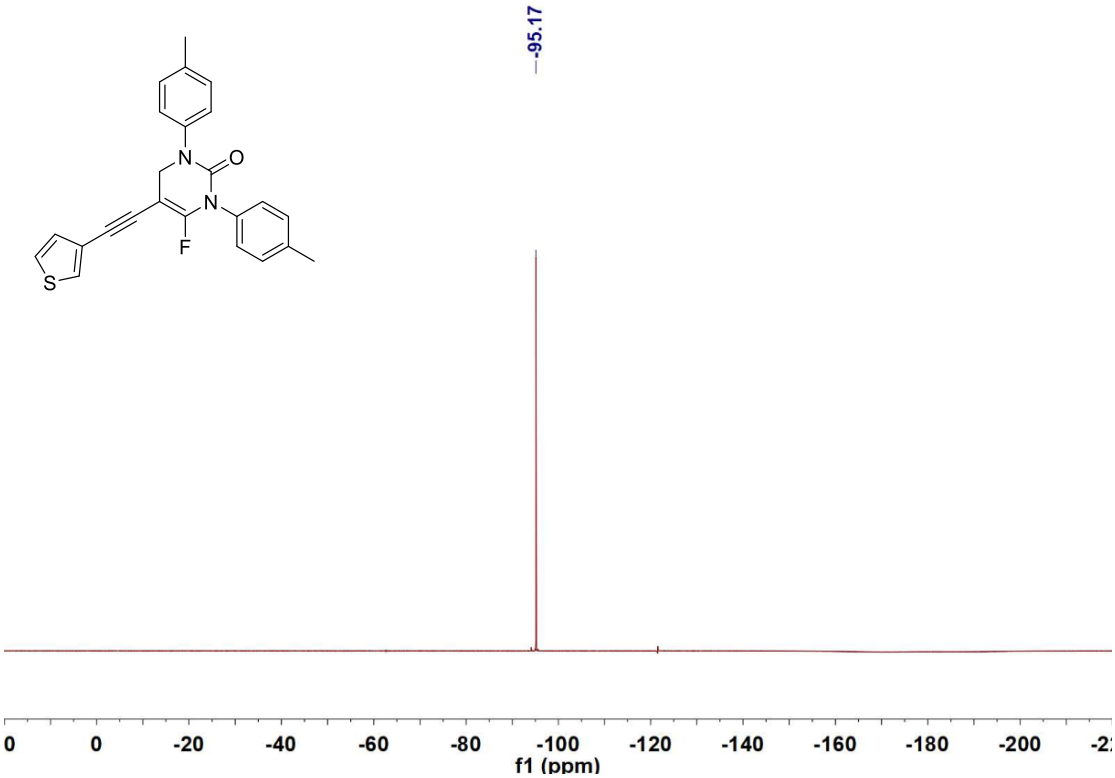
(3ra)



^{1}H-NMR (500 MHz, $CDCl_3$)

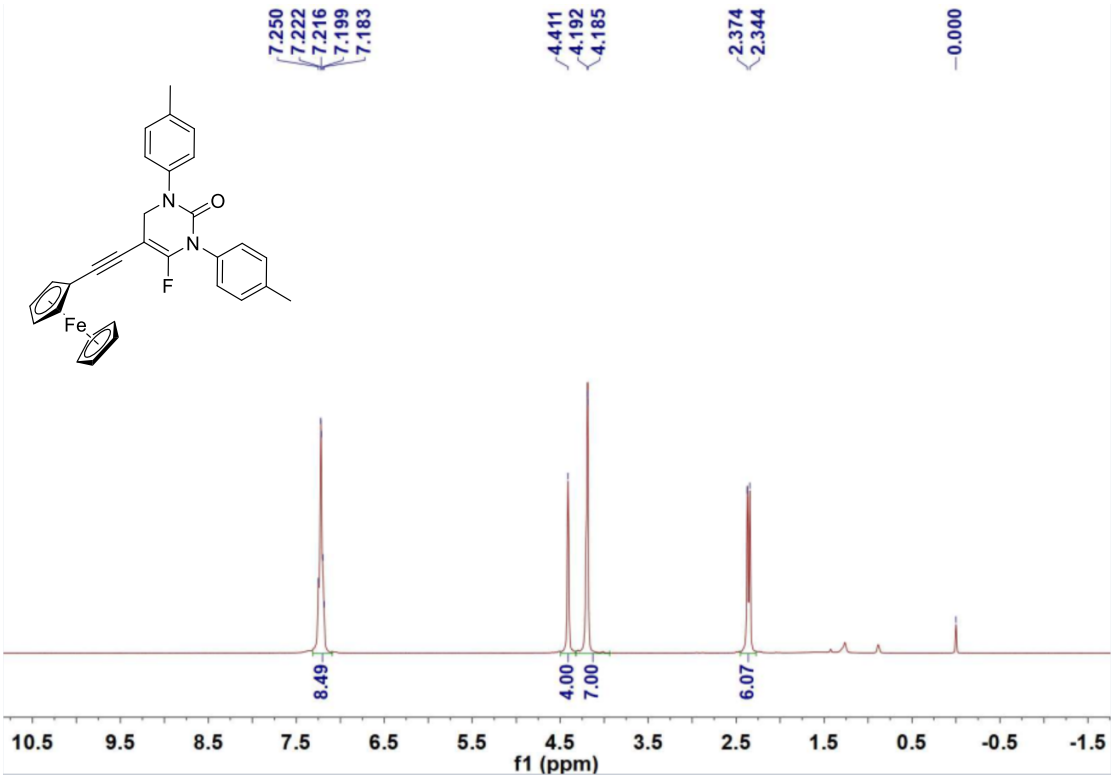


^{13}C-NMR (125 MHz, $CDCl_3$)

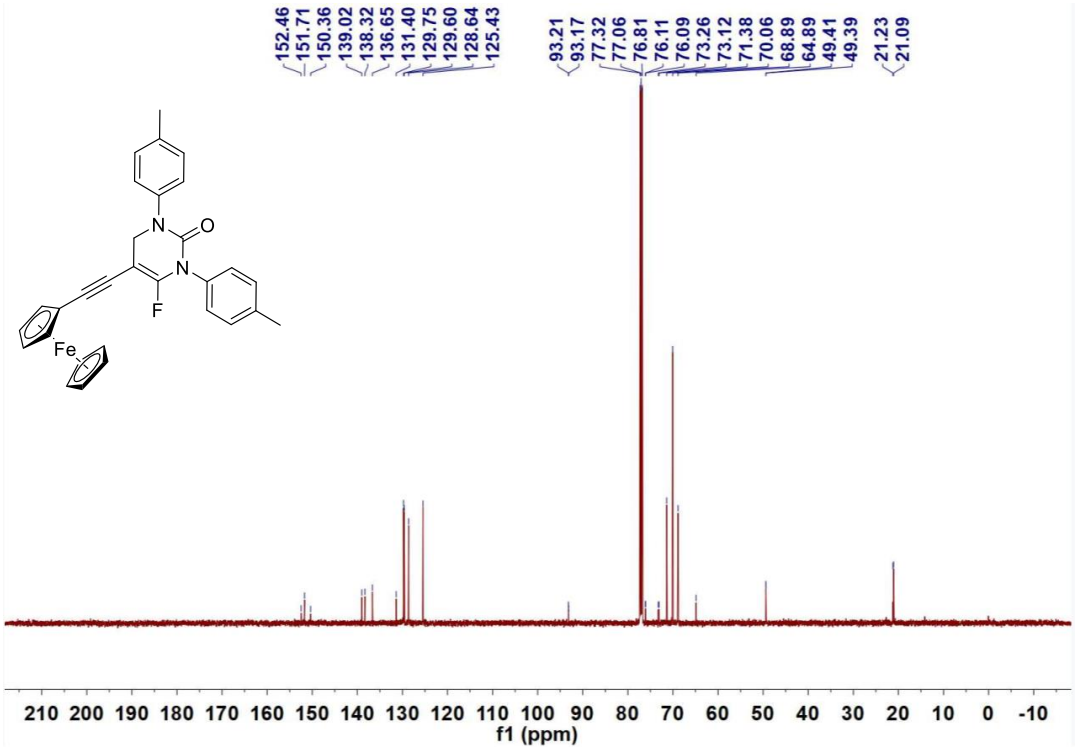


^{19}F-NMR (471 MHz, $CDCl_3$)

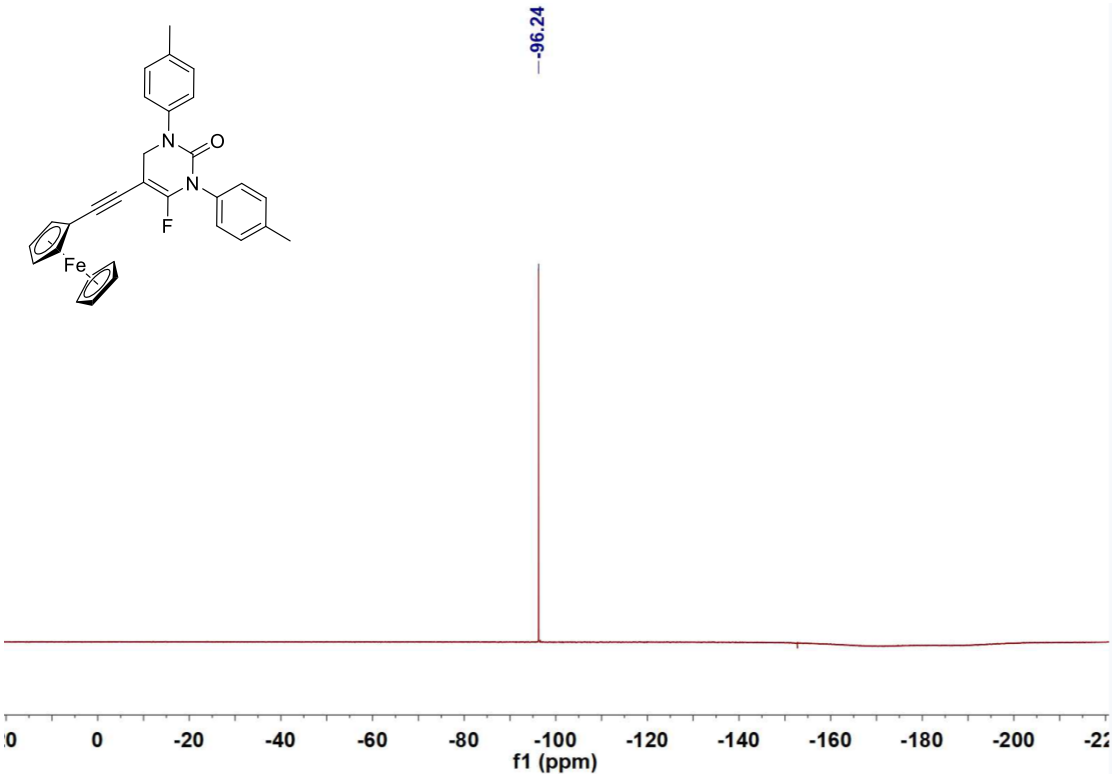
6-fluoro-5-(ferrocenylethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3sa)



^{1}H-NMR (500 MHz, $CDCl_3$)

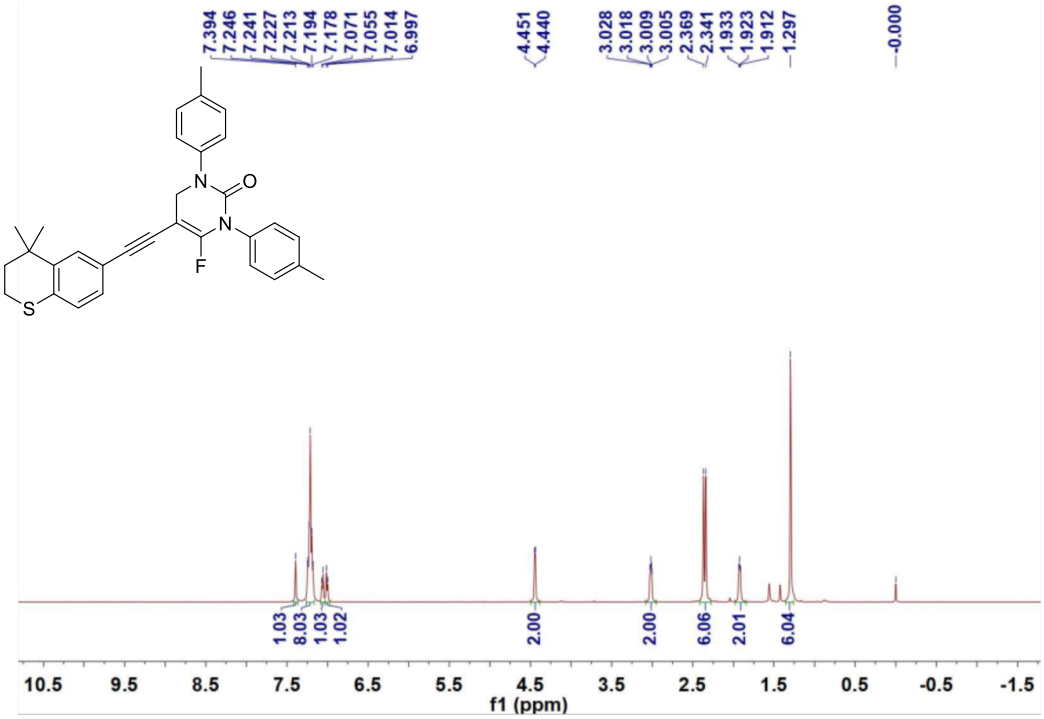


^{13}C-NMR (125 MHz, $CDCl_3$)

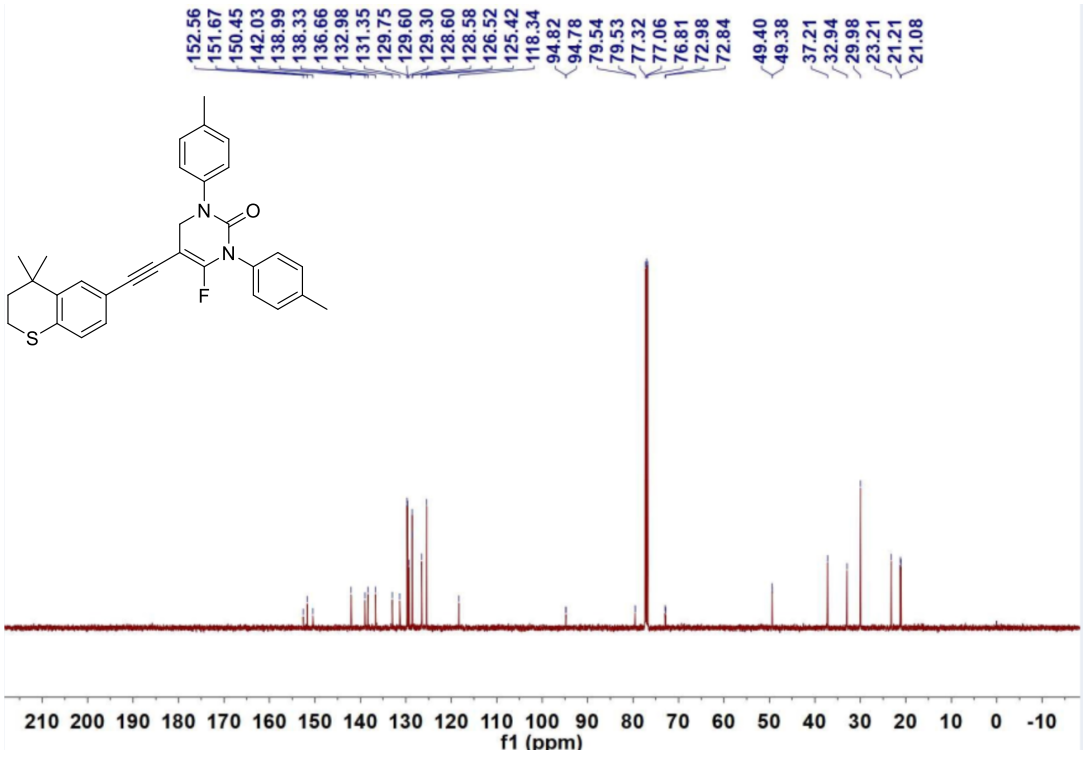


^{19}F-NMR (471 MHz, $CDCl_3$)

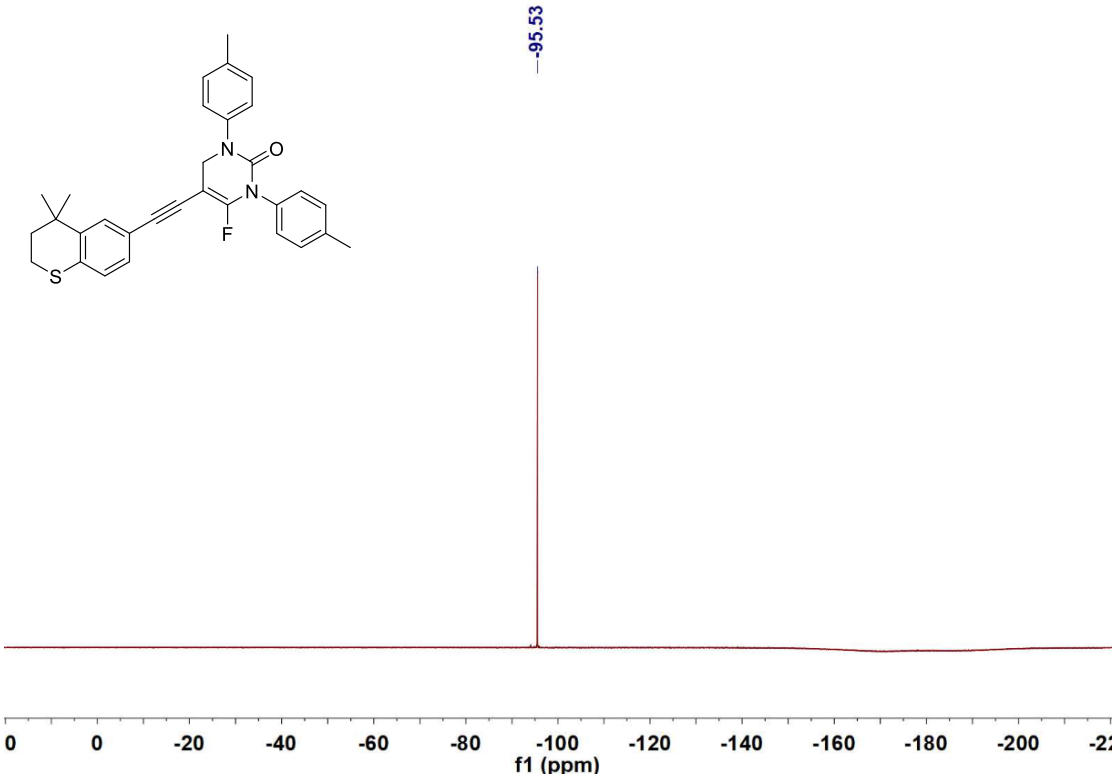
5-((4,4-dimethylthiochroman-6-yl)ethynyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ta)



^{1}H-NMR (500 MHz, $CDCl_3$)

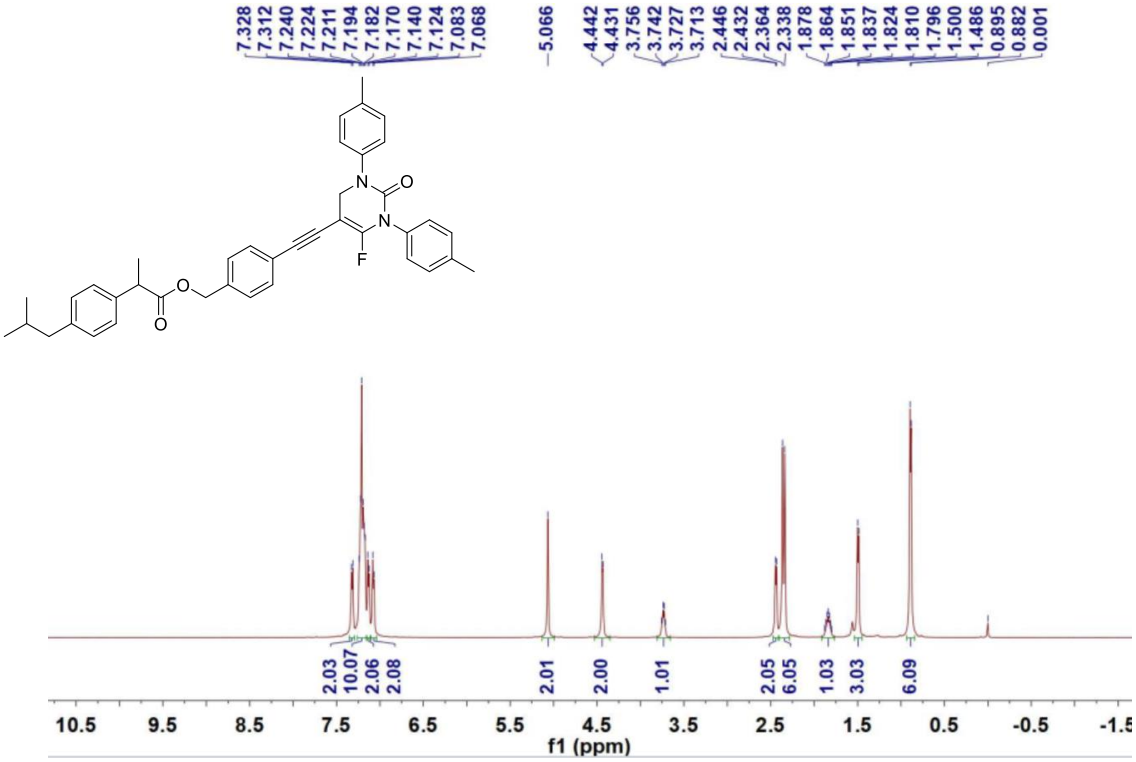


^{13}C-NMR (125 MHz, $CDCl_3$)

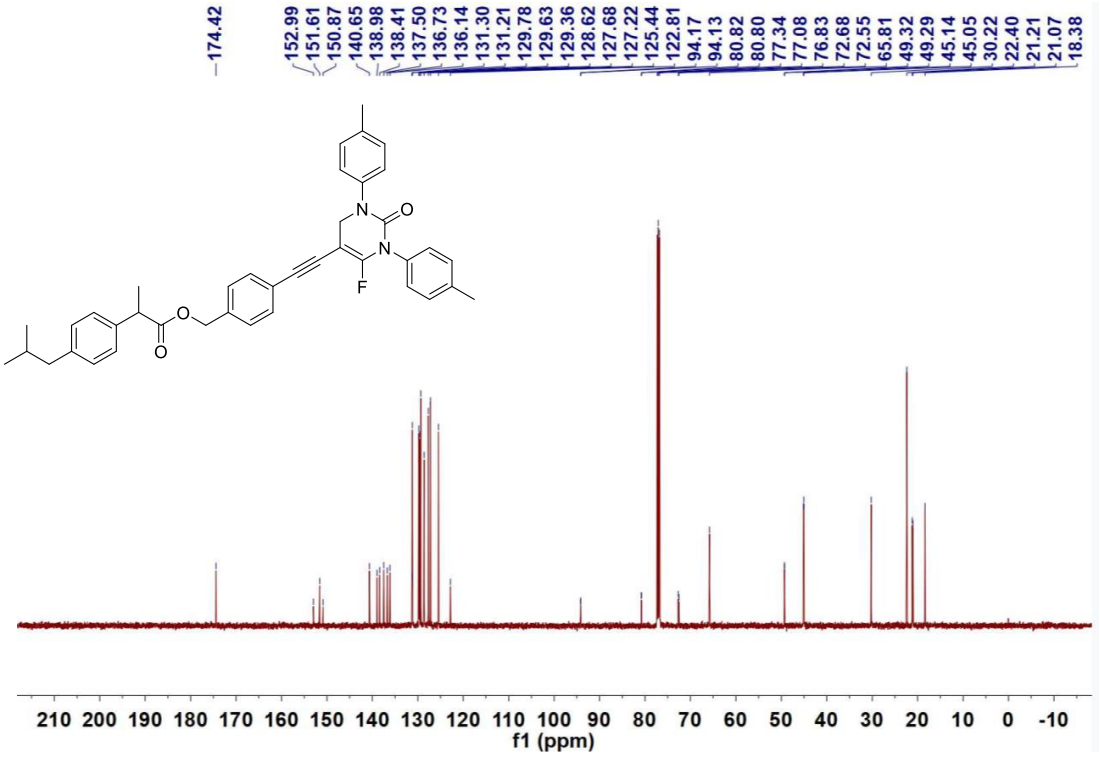


^{19}F-NMR (471 MHz, $CDCl_3$)

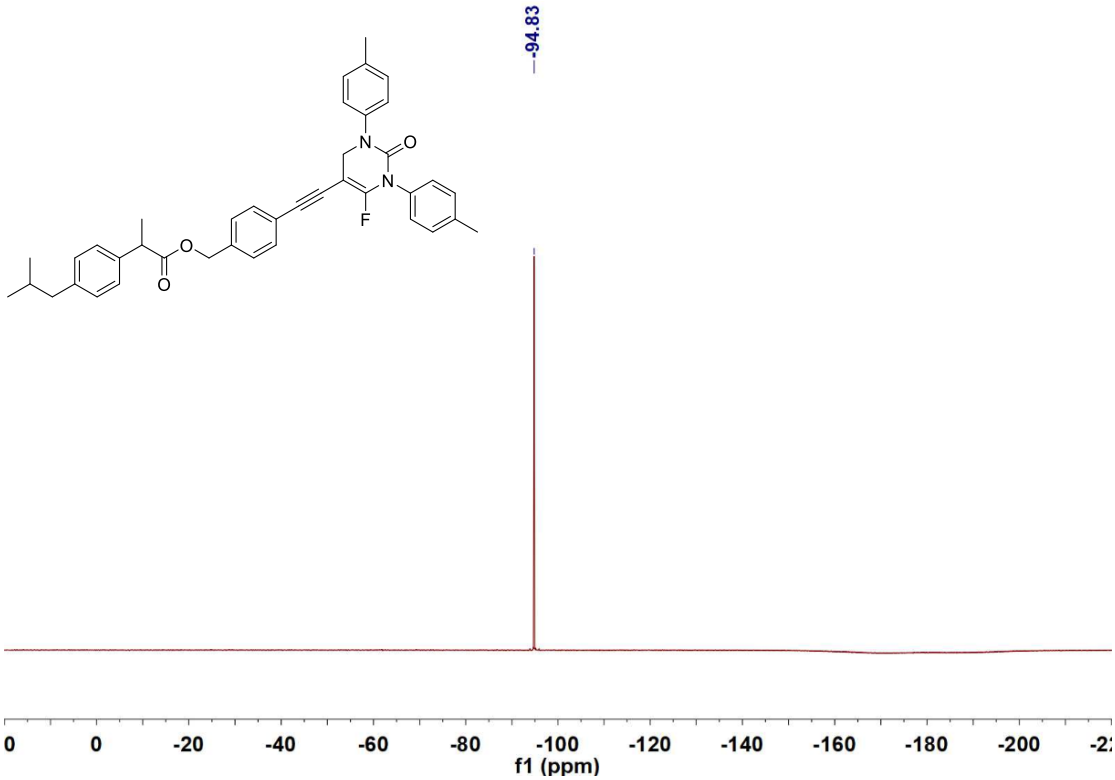
4-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)benzyl 2-(4-isobutylphenyl)propanoate (3ua)



^{1}H-NMR (500 MHz, $CDCl_3$)

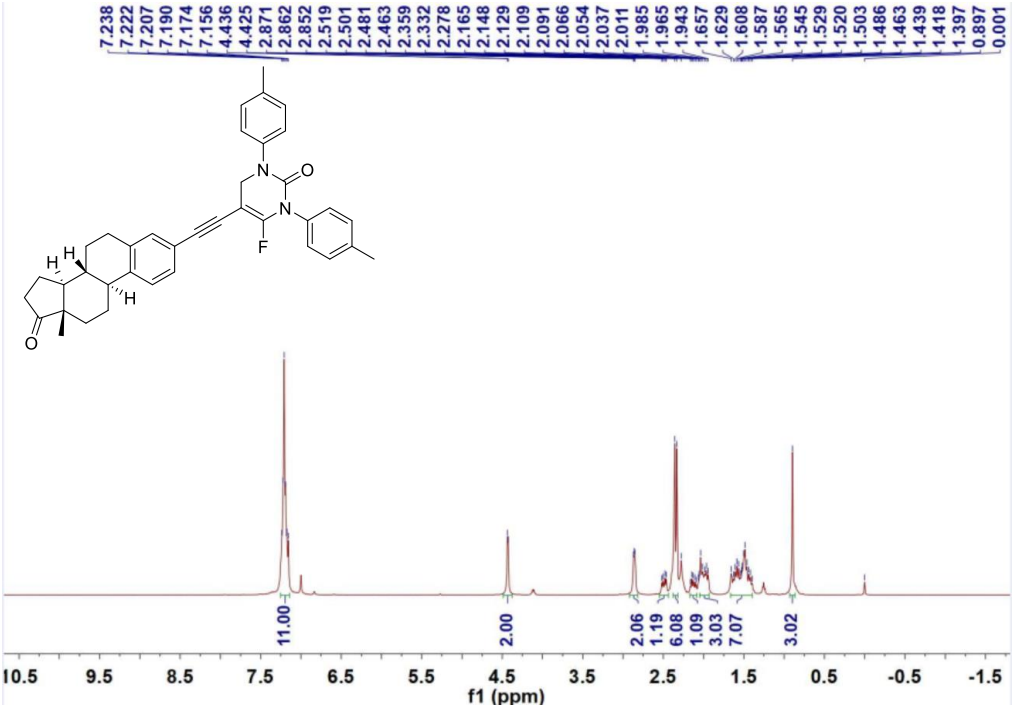


^{13}C-NMR (125 MHz, $CDCl_3$)

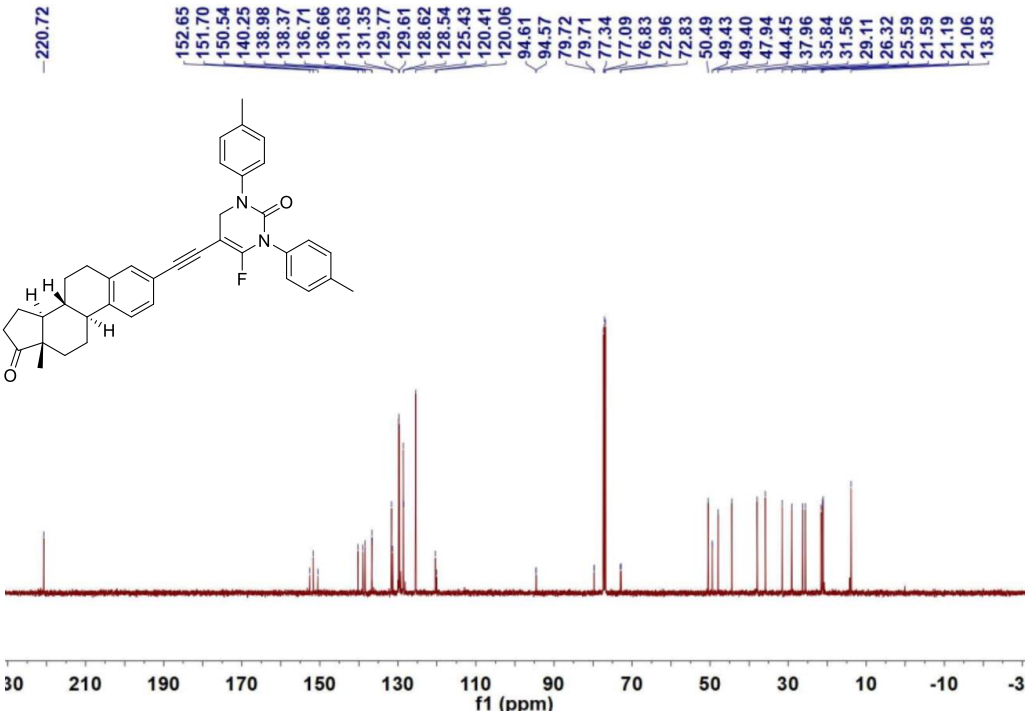


^{19}F-NMR (471 MHz, $CDCl_3$)

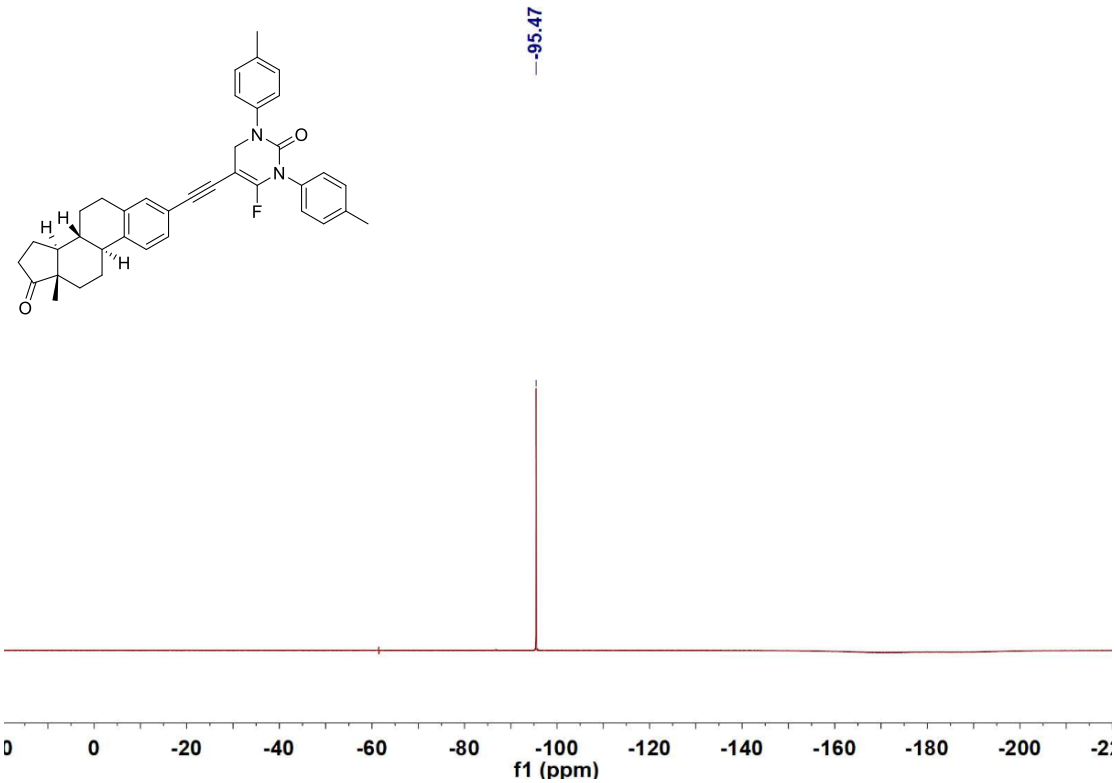
6-fluoro-5-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3va)



^{1}H-NMR (500 MHz, $CDCl_3$)

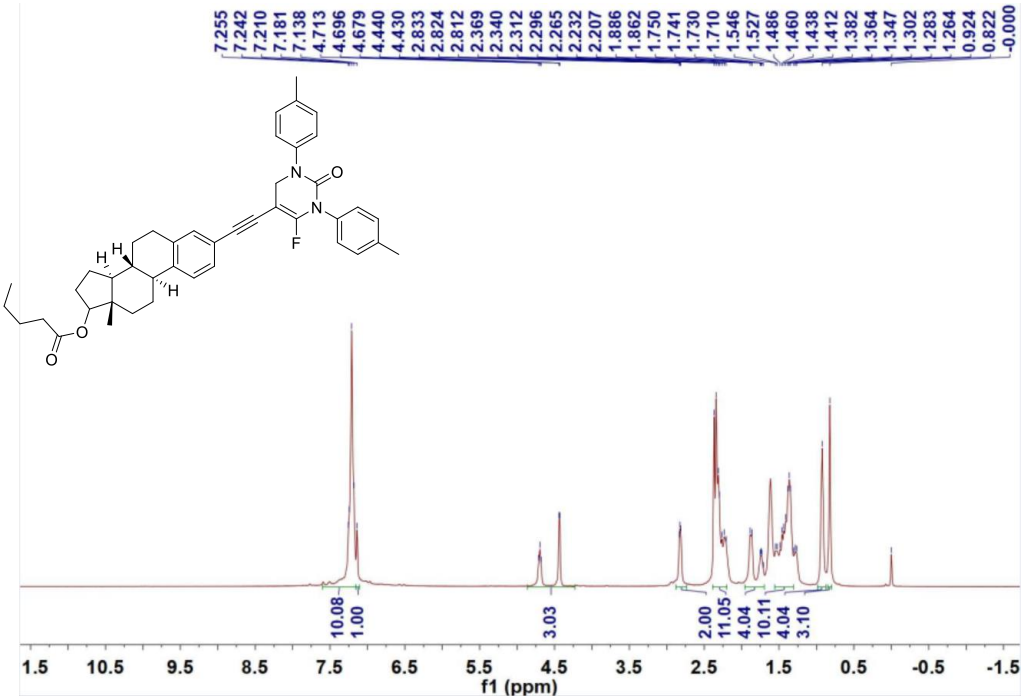


^{13}C-NMR (125 MHz, $CDCl_3$)

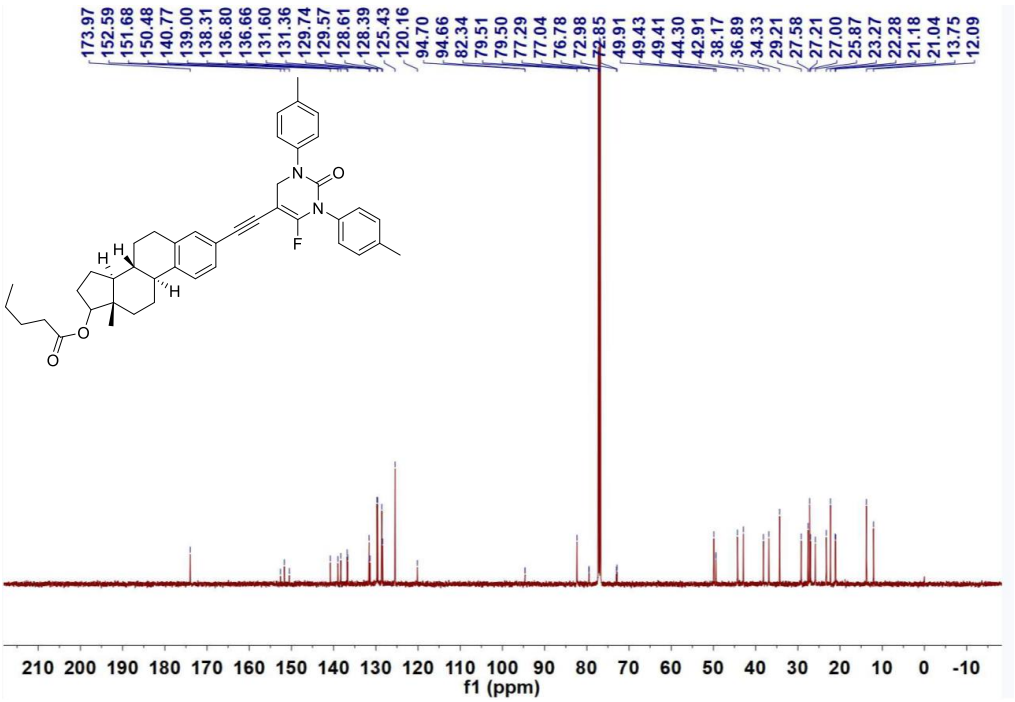


^{19}F-NMR (471 MHz, $CDCl_3$)

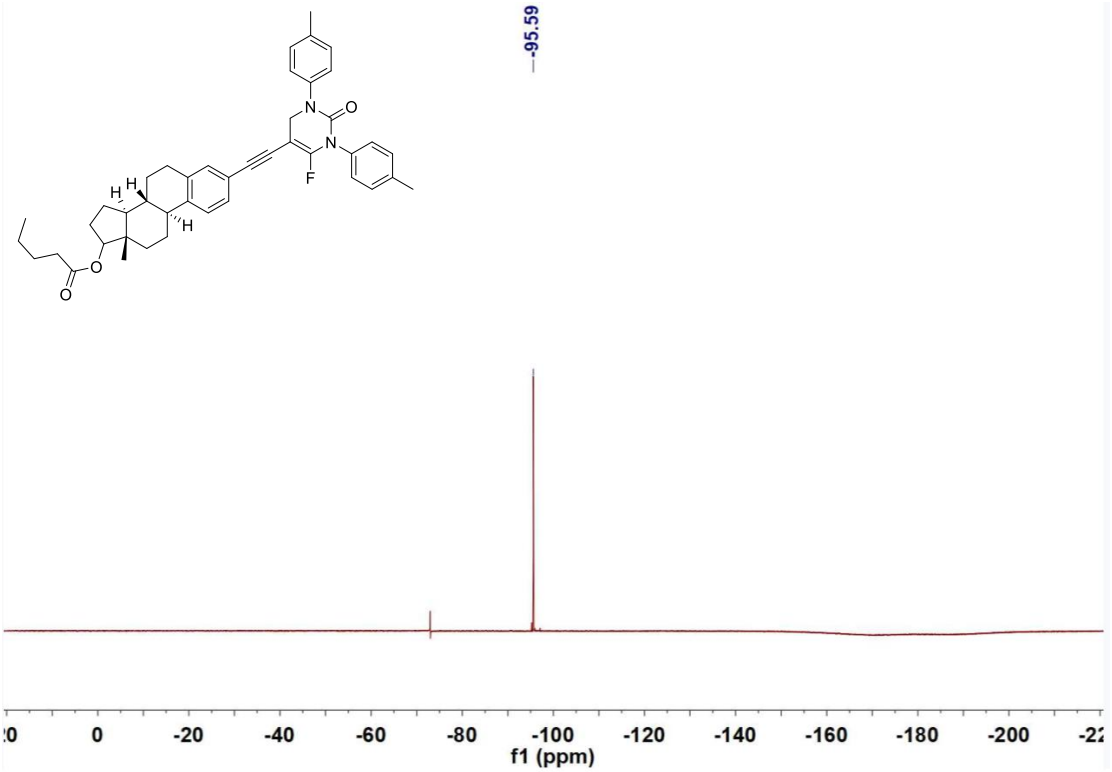
(8R,9S,13S,14S)-3-((6-fluoro-2-oxo-1,3-di-*p*-tolyl-1,2,3,4-tetrahydropyrimidin-5-yl)ethynyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl pentanoate (3wa)



^{1}H-NMR (500 MHz, $CDCl_3$)

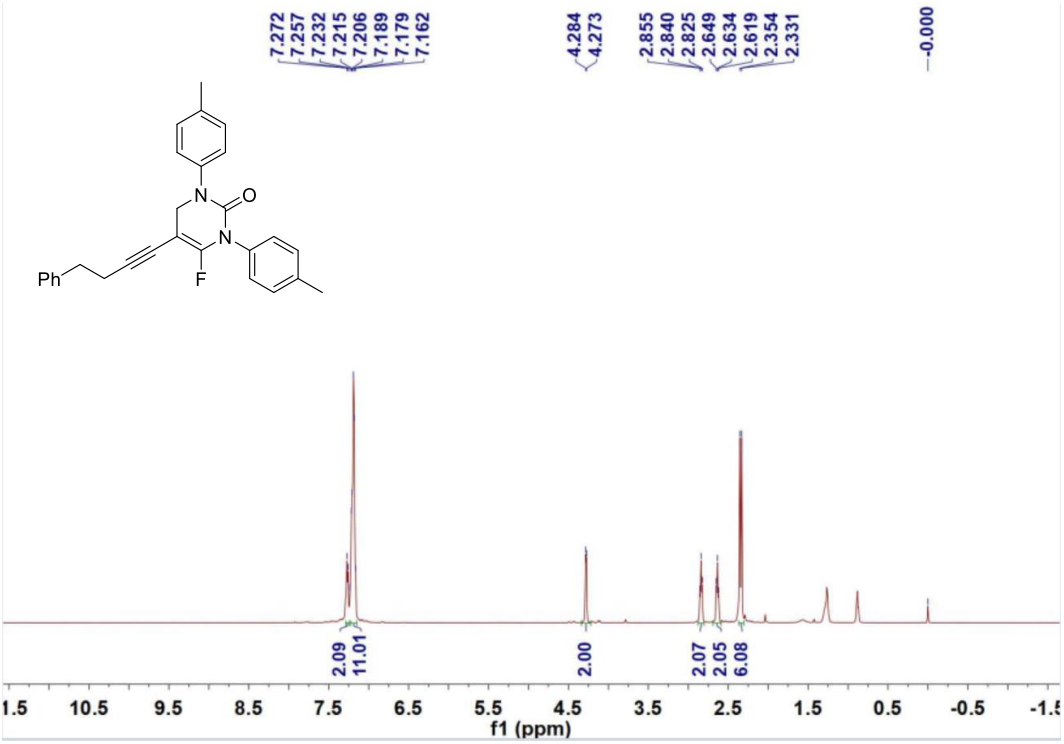


^{13}C-NMR (125 MHz, $CDCl_3$)

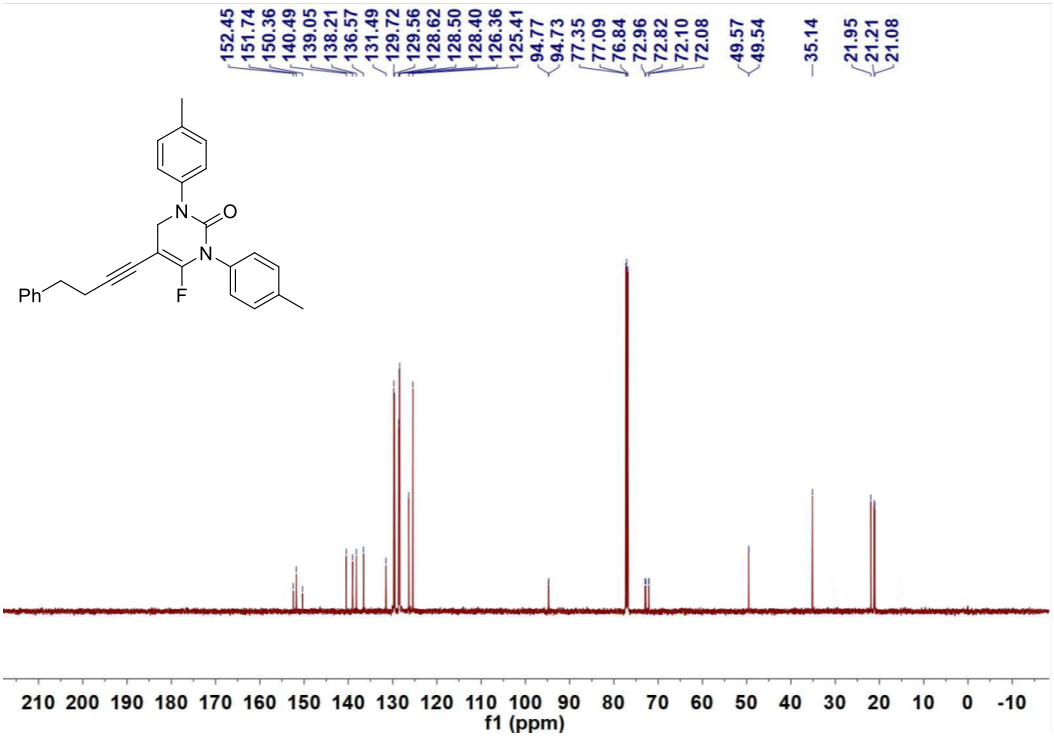


^{19}F-NMR (471 MHz, $CDCl_3$)

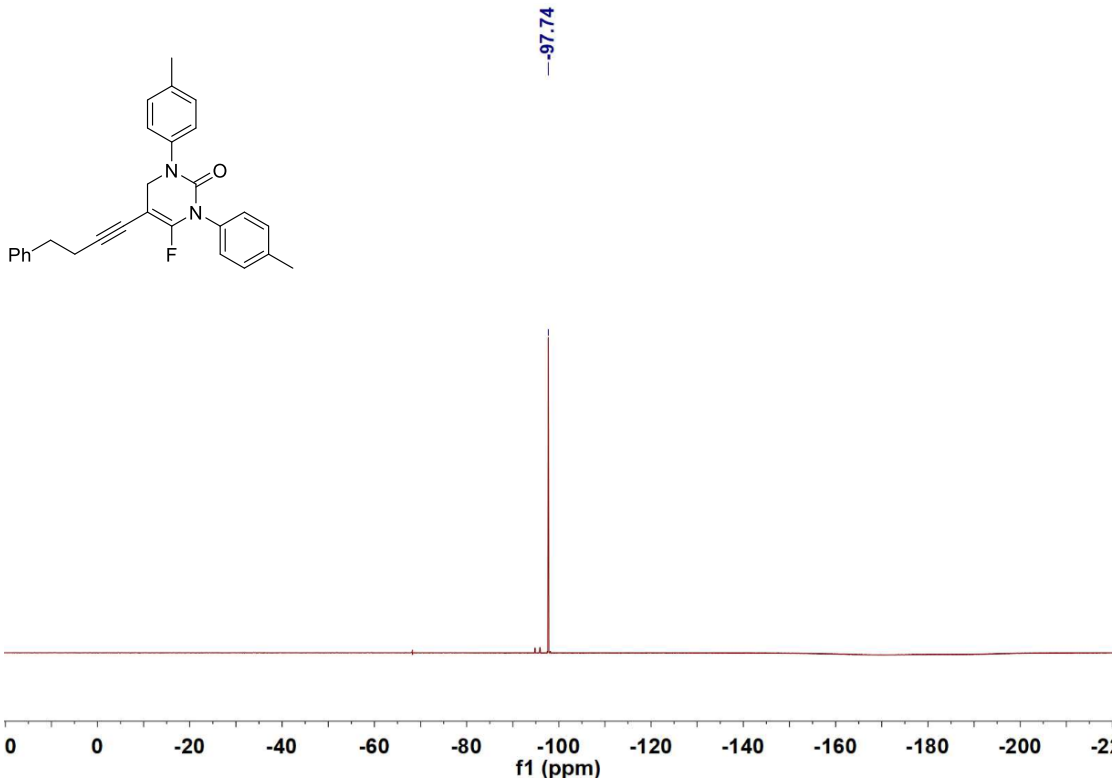
6-fluoro-5-(4-phenylbut-1-yn-1-yl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3xa)



^{1}H-NMR (500 MHz, $CDCl_3$)

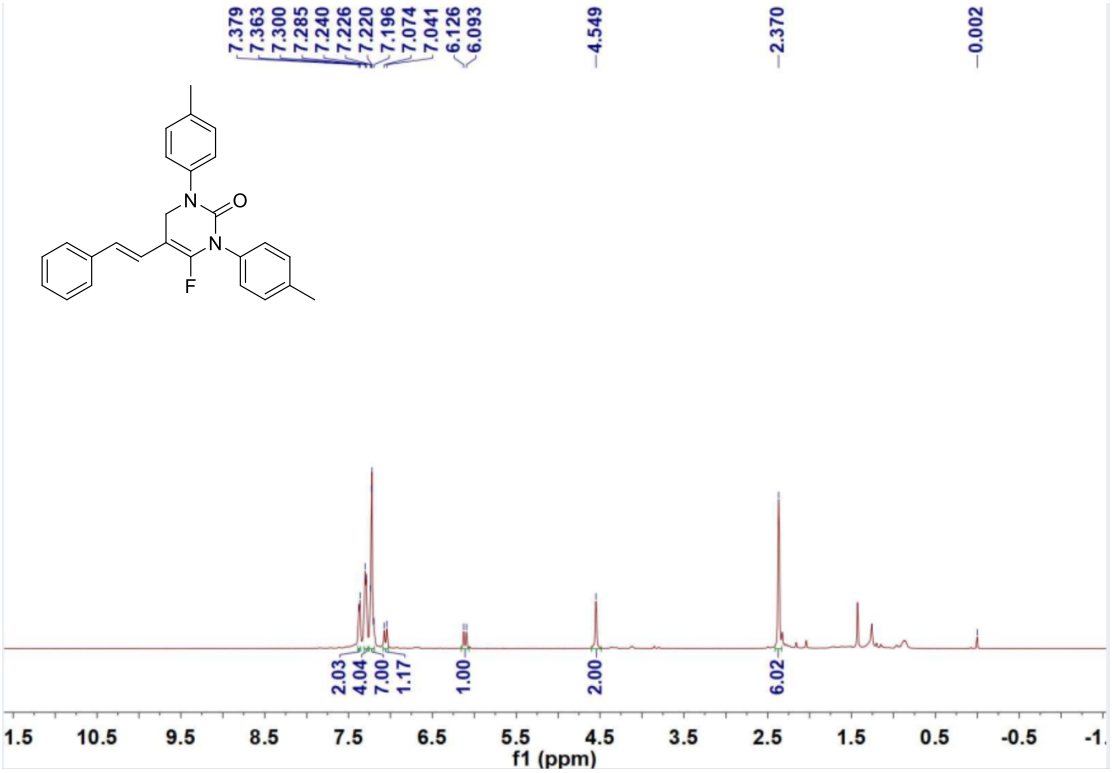


^{13}C-NMR (125 MHz, $CDCl_3$)

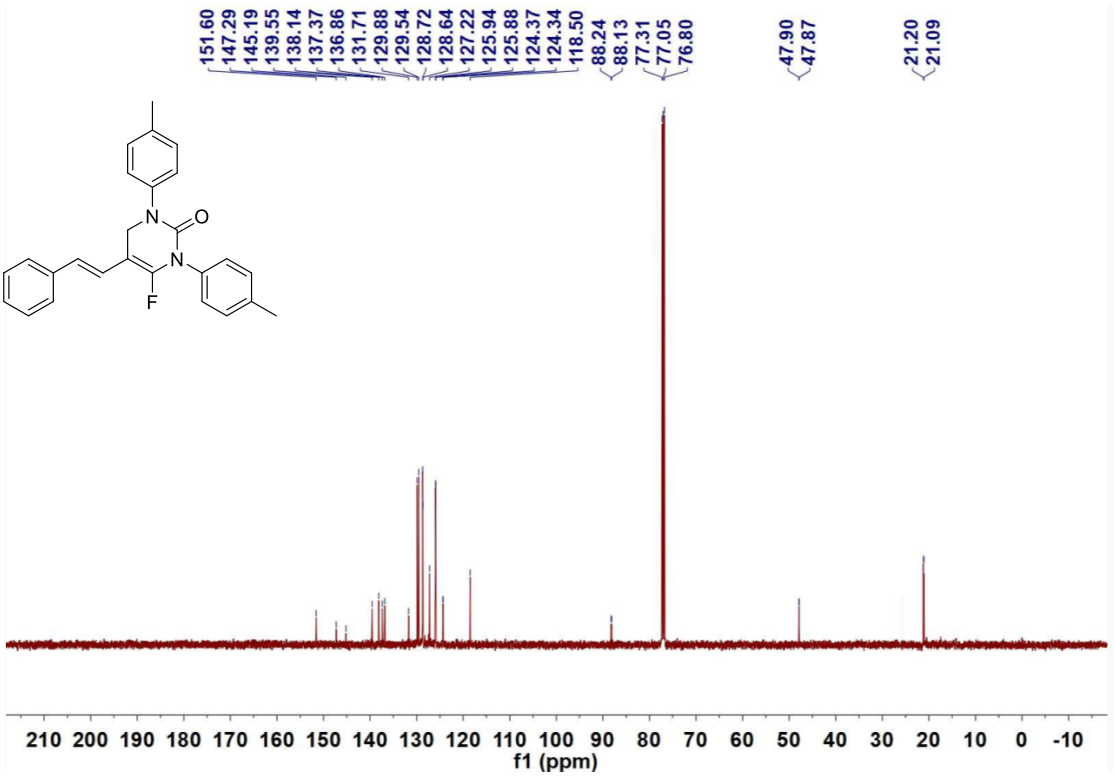


^{19}F-NMR (471 MHz, $CDCl_3$)

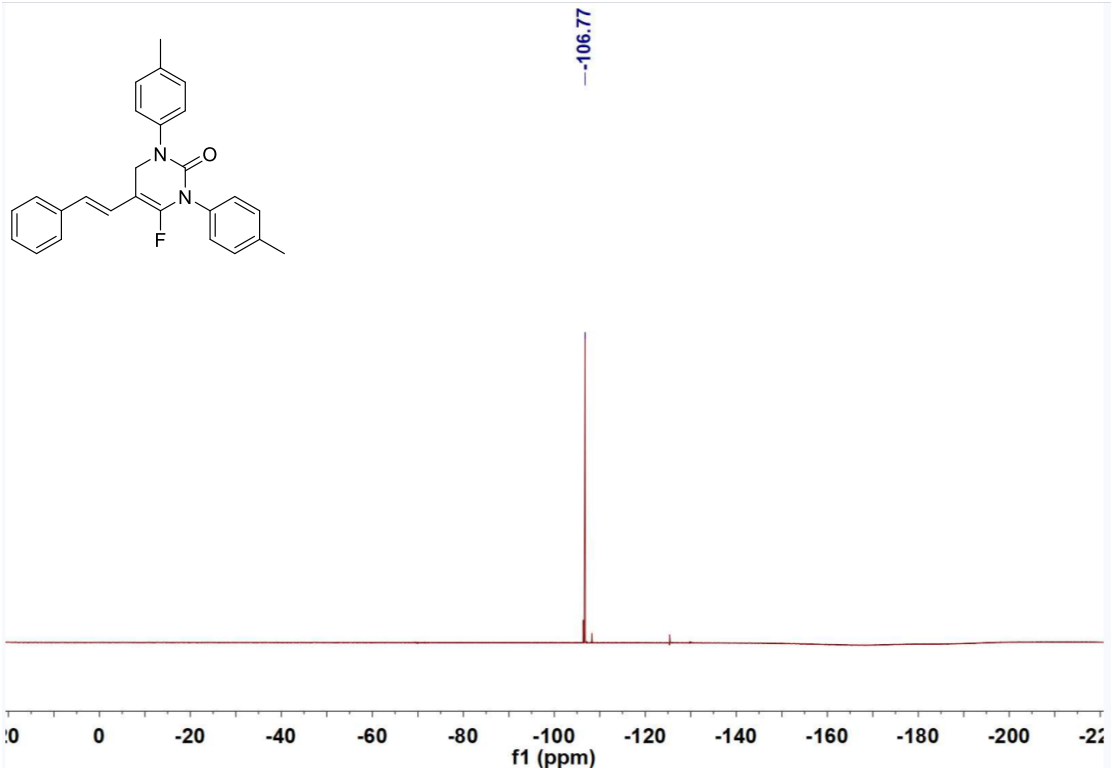
(*E*)-6-fluoro-5-styryl-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3ya)



^{1}H-NMR (500 MHz, $CDCl_3$)

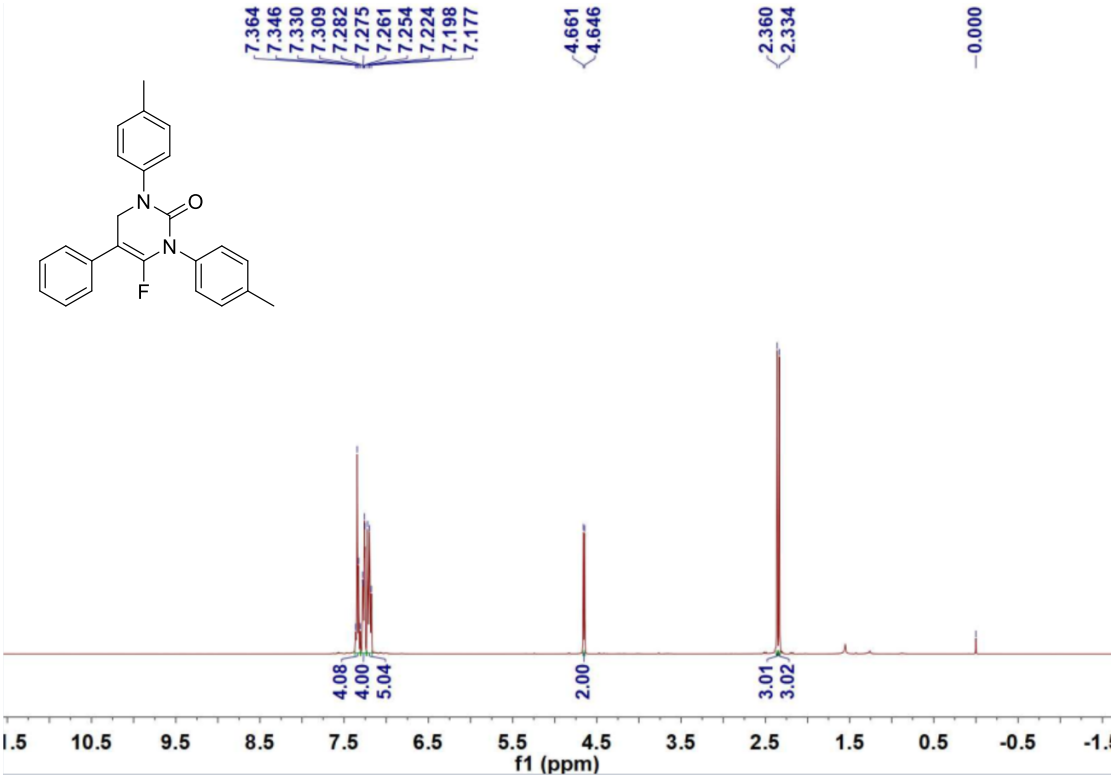


^{13}C-NMR (125 MHz, $CDCl_3$)

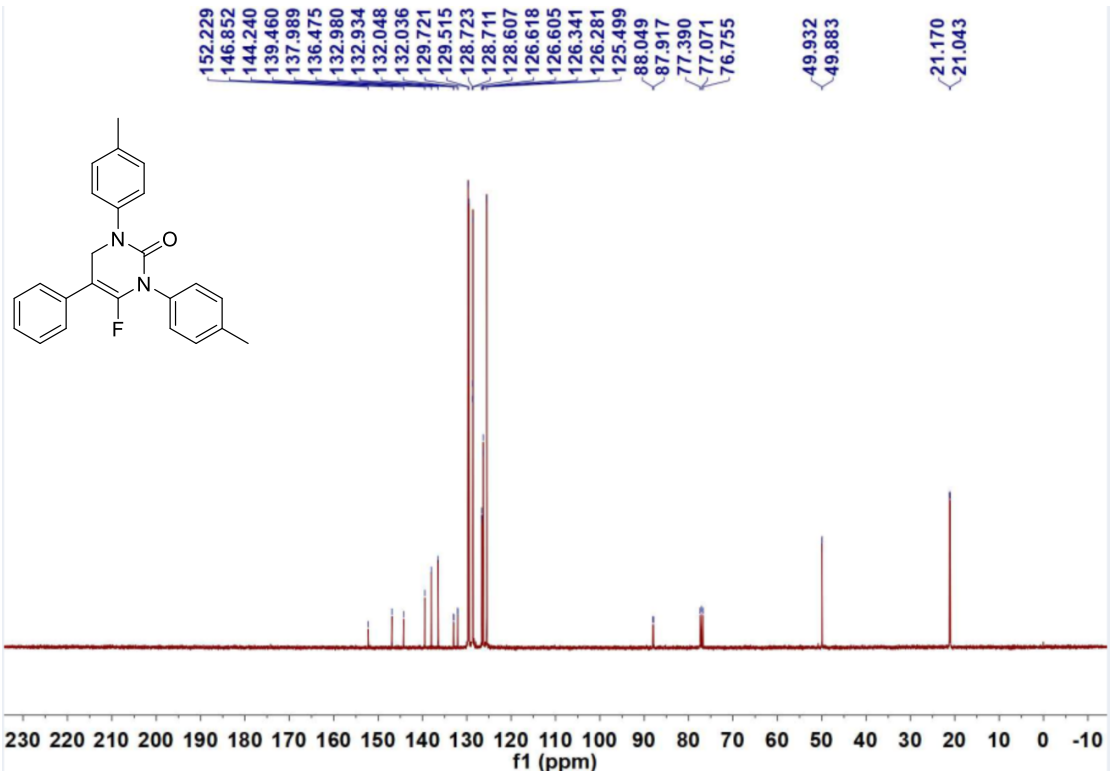


^{19}F-NMR (471 MHz, $CDCl_3$)

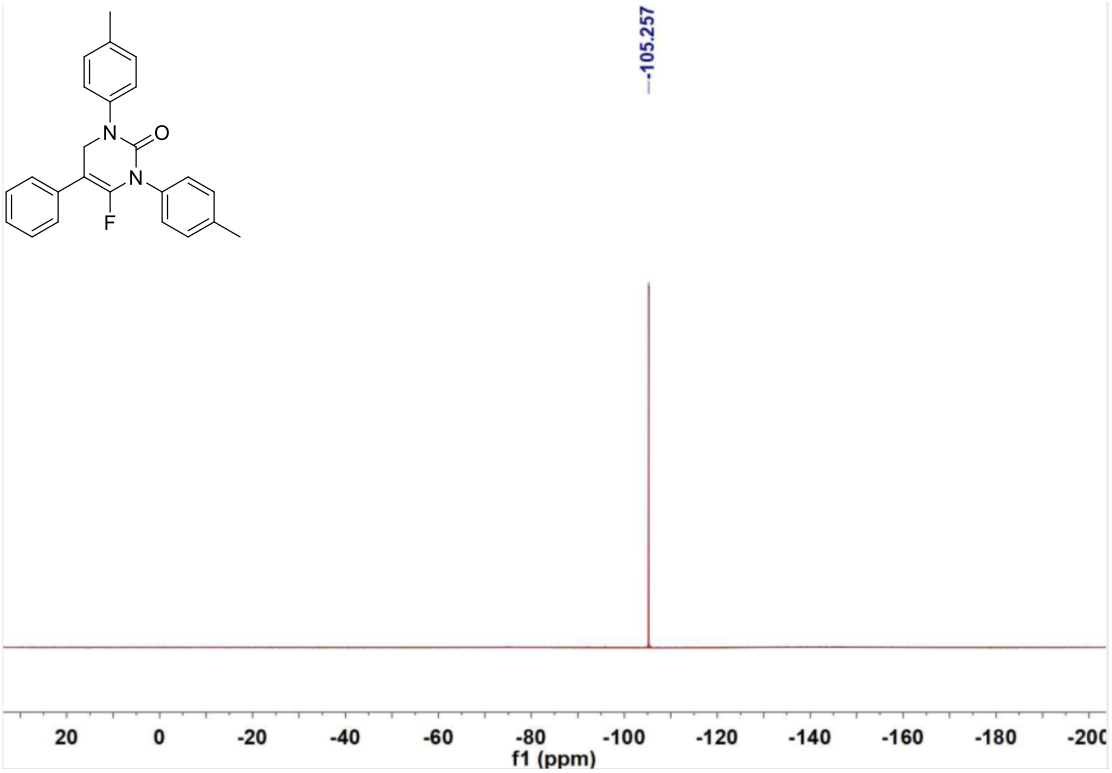
6-fluoro-5-phenyl-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3za)



^{1}H-NMR (400 MHz, $CDCl_3$)

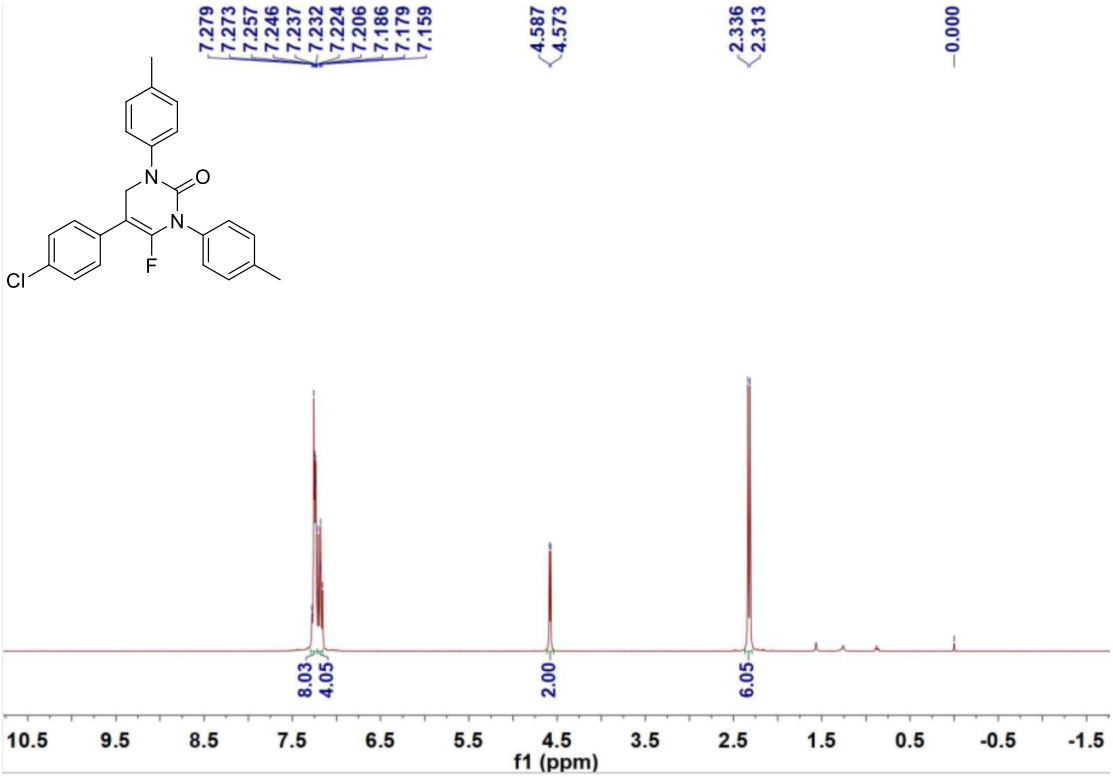


^{13}C-NMR (100 MHz, $CDCl_3$)

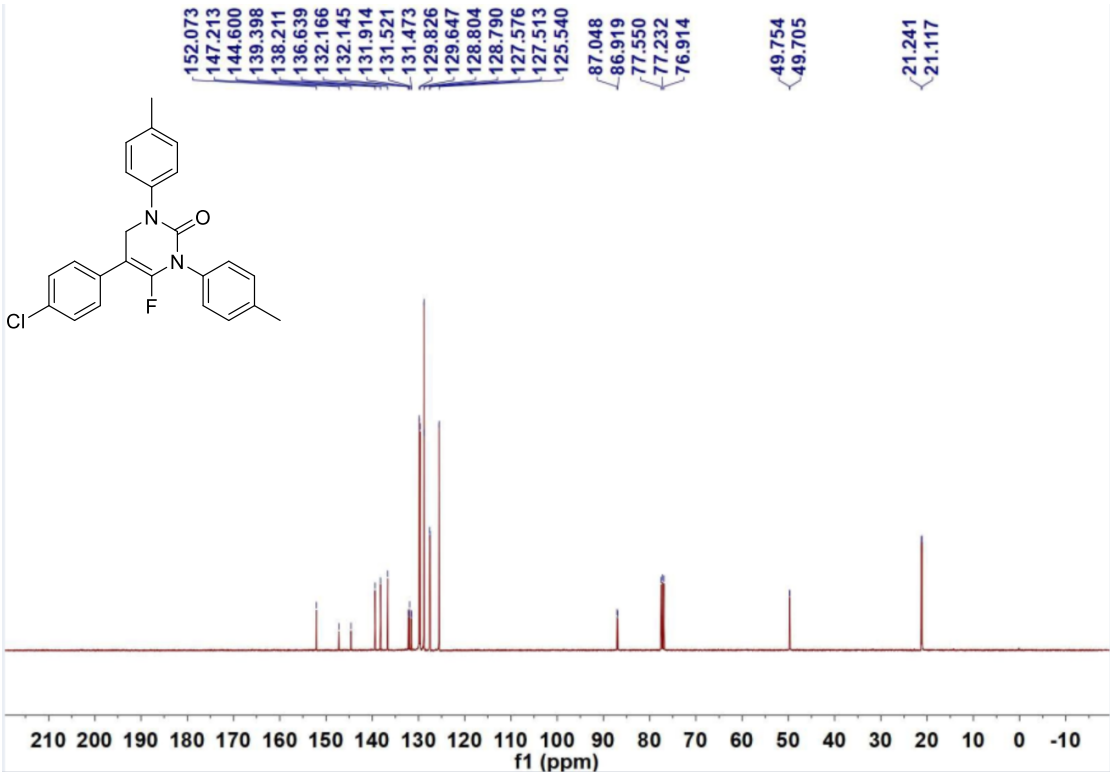


^{19}F-NMR (376.5 MHz, $CDCl_3$)

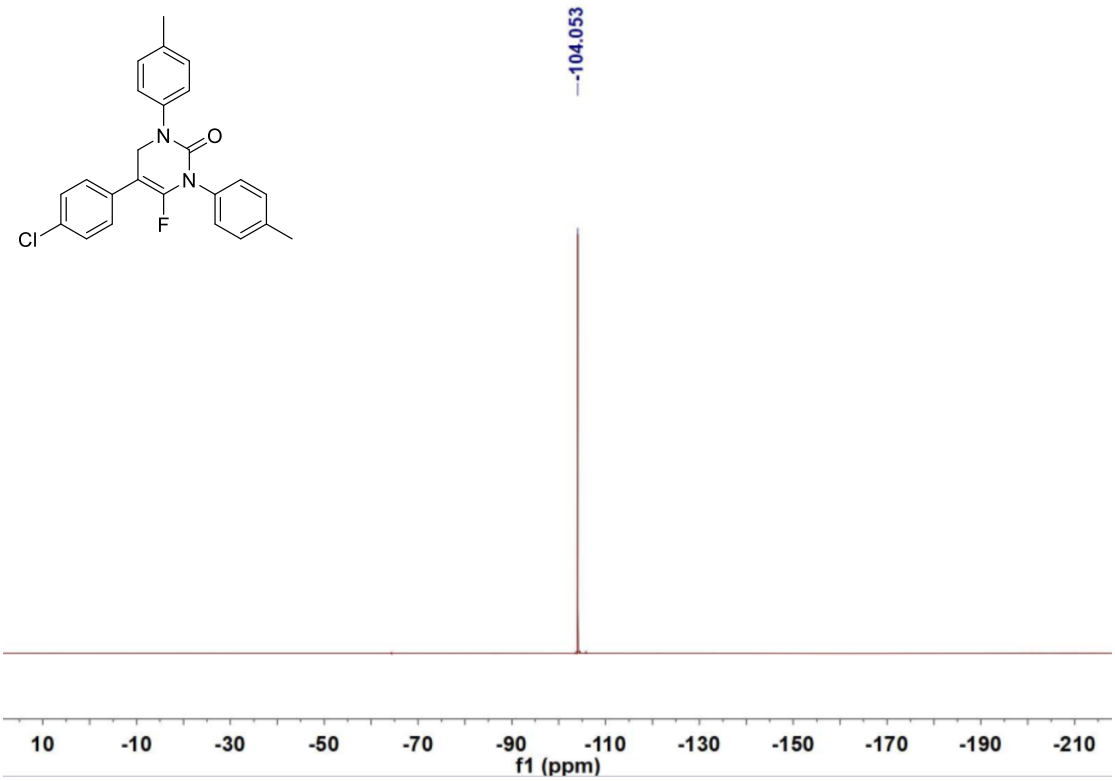
5-(4-chlorophenyl)-6-fluoro-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3aaa)



^{1}H-NMR (400 MHz, $CDCl_3$)



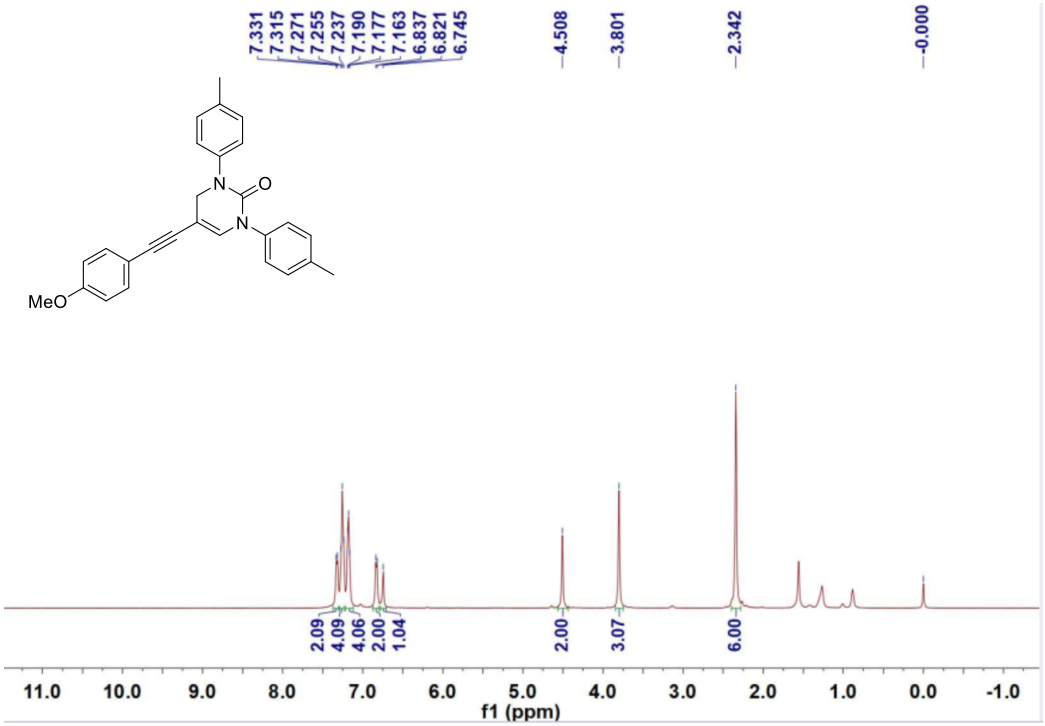
^{13}C-NMR (100 MHz, $CDCl_3$)



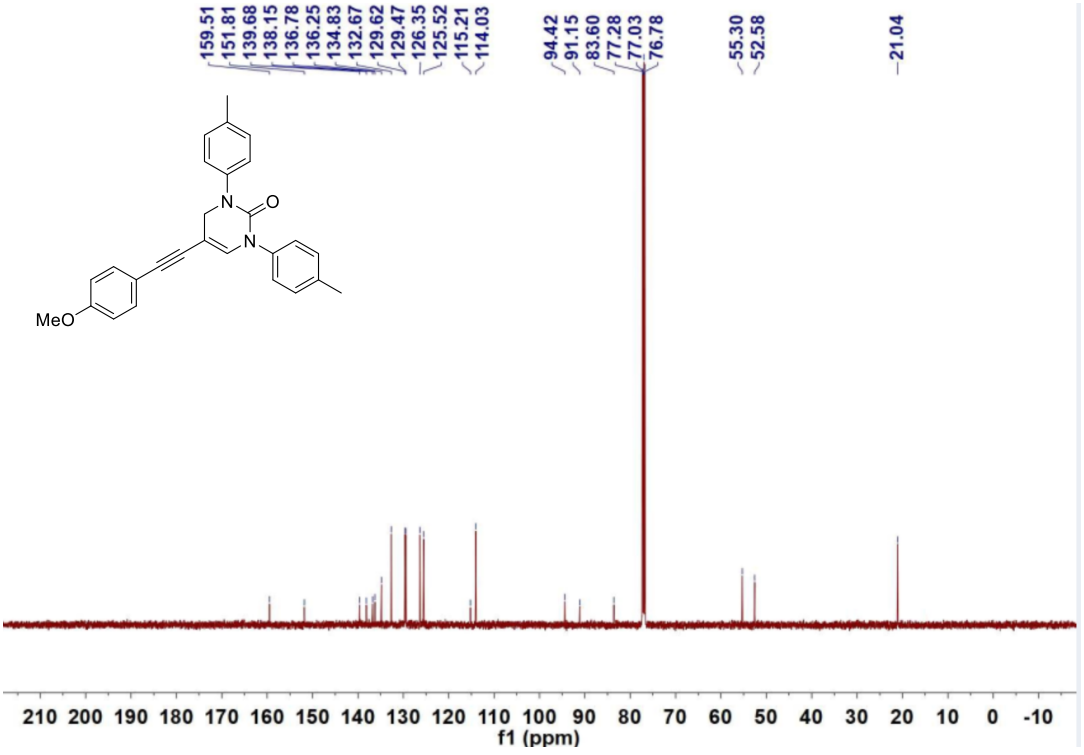
^{19}F-NMR (376.5 MHz, $CDCl_3$)

5-((4-methoxyphenyl)ethynyl)-1,3-di-*p*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one

(3aca)

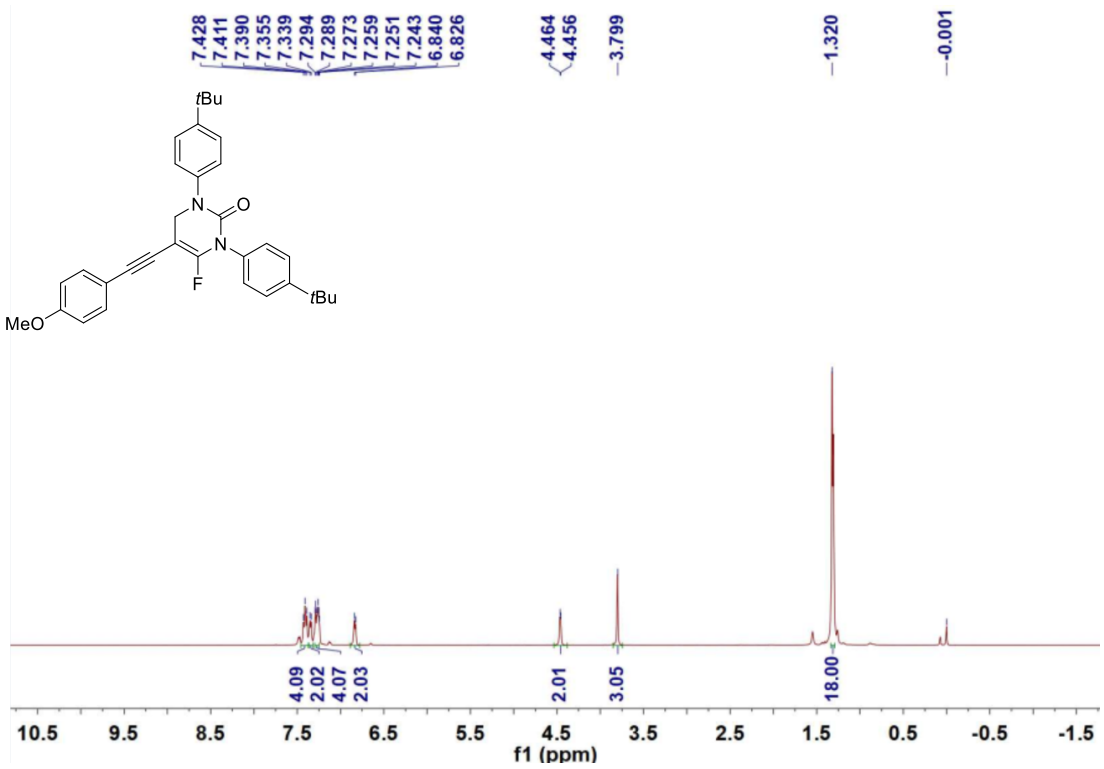


^{1}H-NMR (500 MHz, $CDCl_3$)

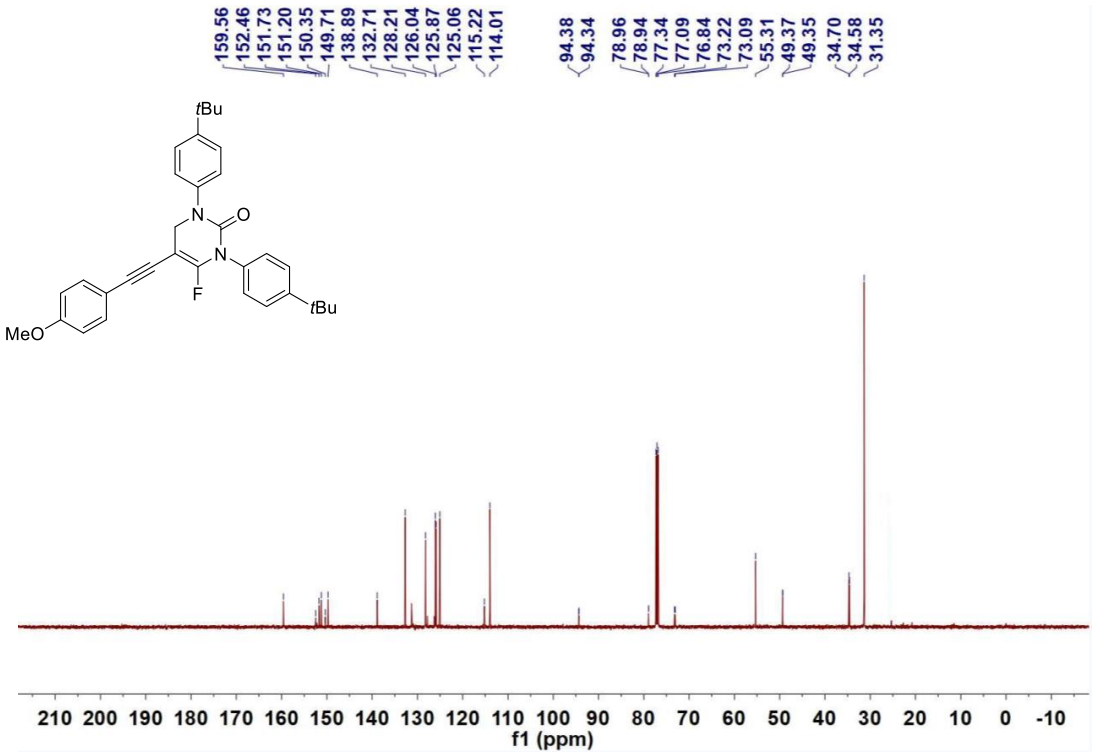


^{13}C-NMR (125 MHz, $CDCl_3$)

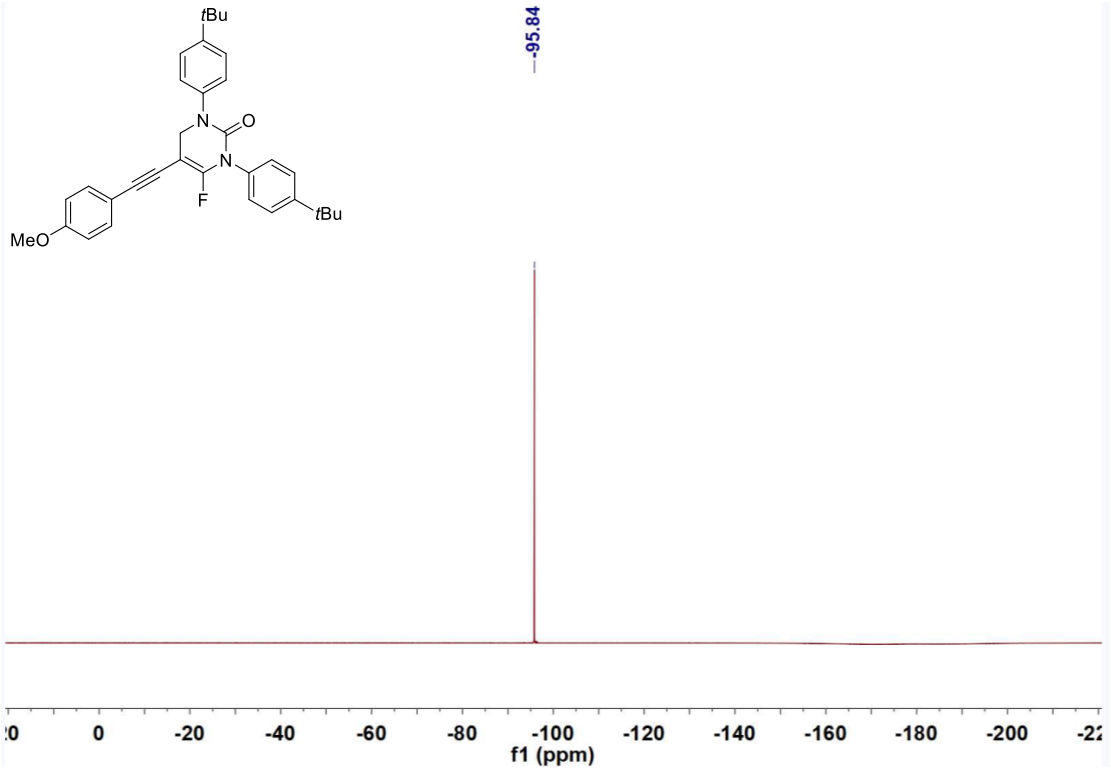
1,3-bis(4-(tert-butyl)phenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ab)



^{1}H-NMR (500 MHz, $CDCl_3$)

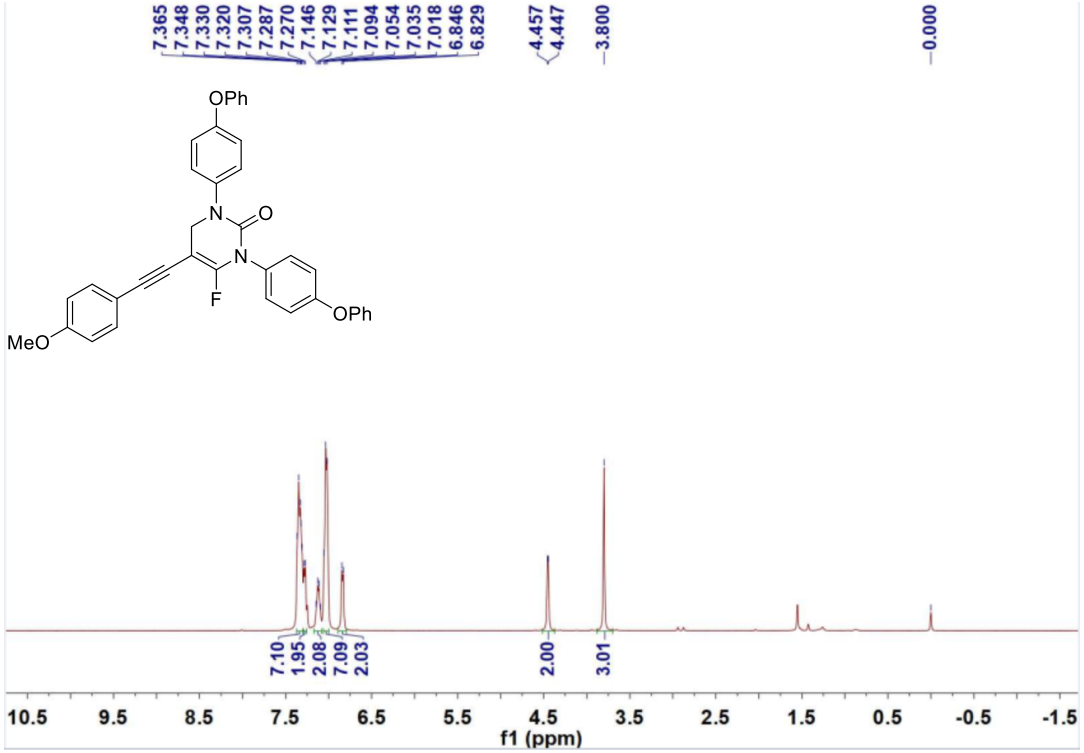


^{13}C-NMR (125 MHz, $CDCl_3$)

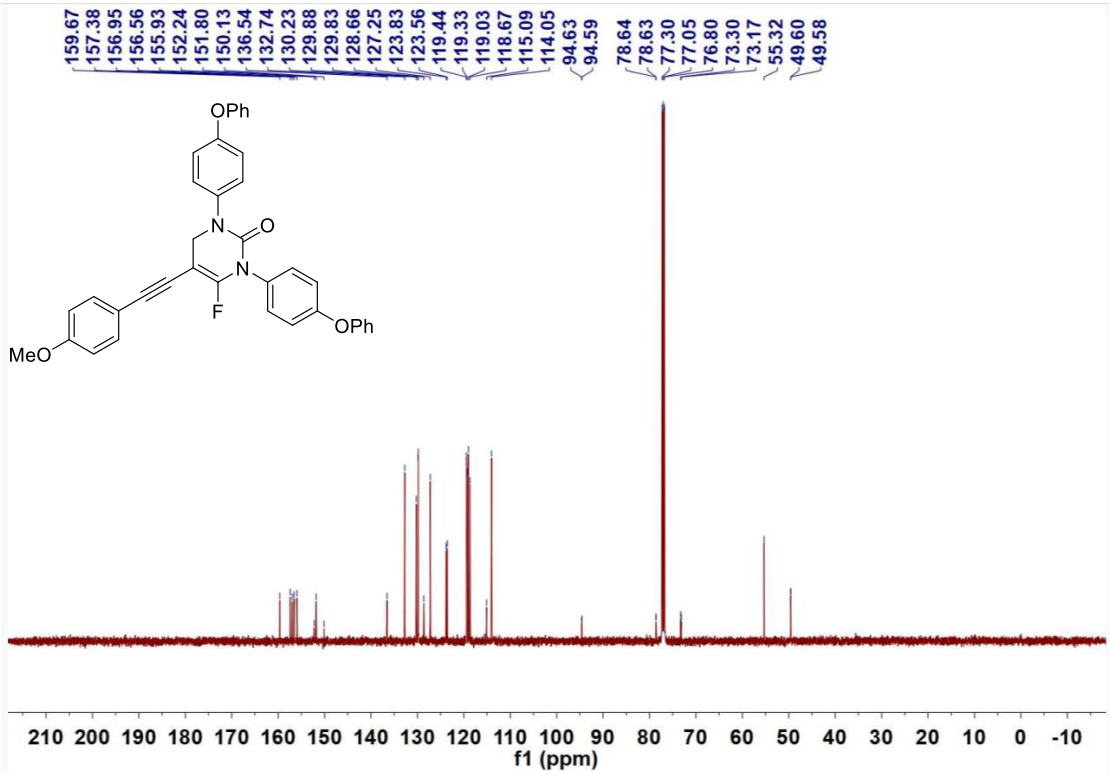


^{19}F-NMR (471 MHz, $CDCl_3$)

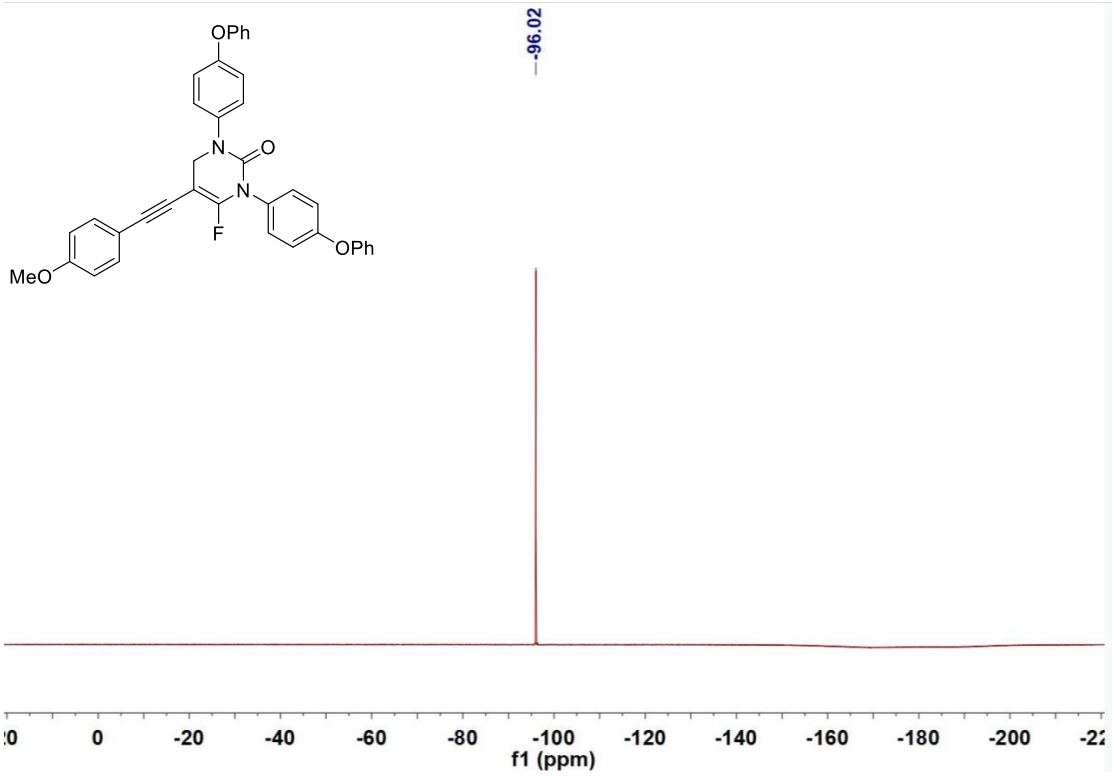
6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-bis(4-phenoxyphenyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ac)



^{1}H-NMR (500 MHz, $CDCl_3$)

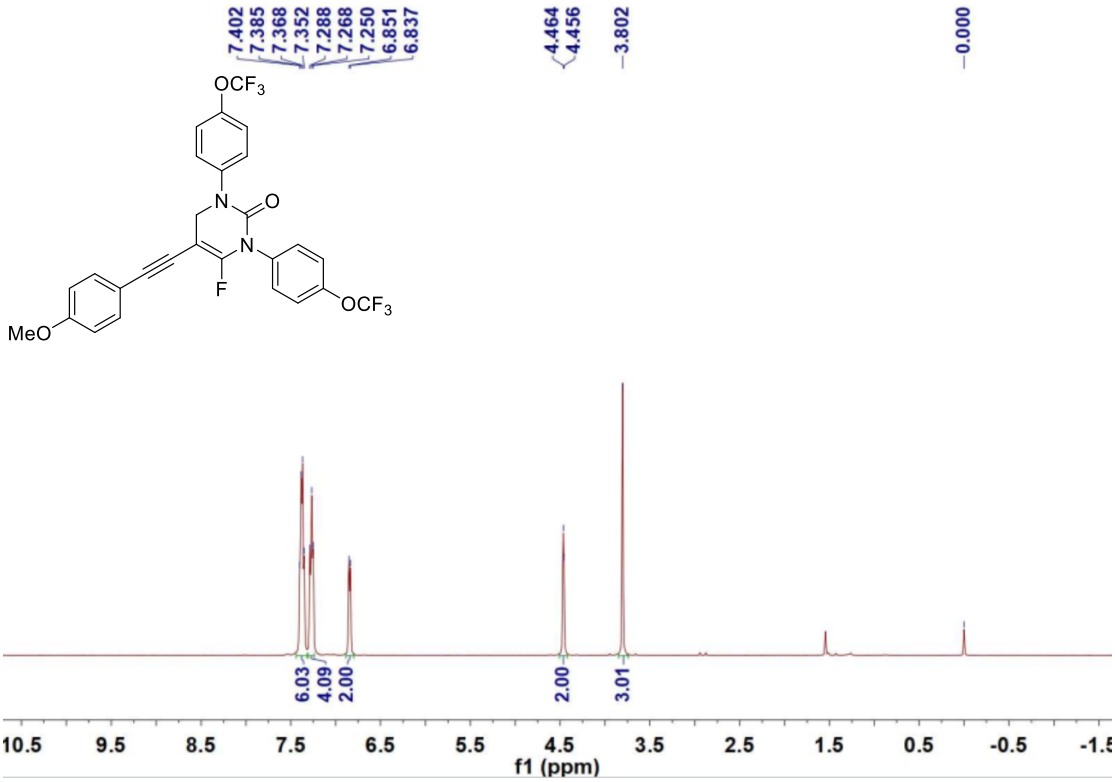


^{13}C-NMR (125 MHz, $CDCl_3$)

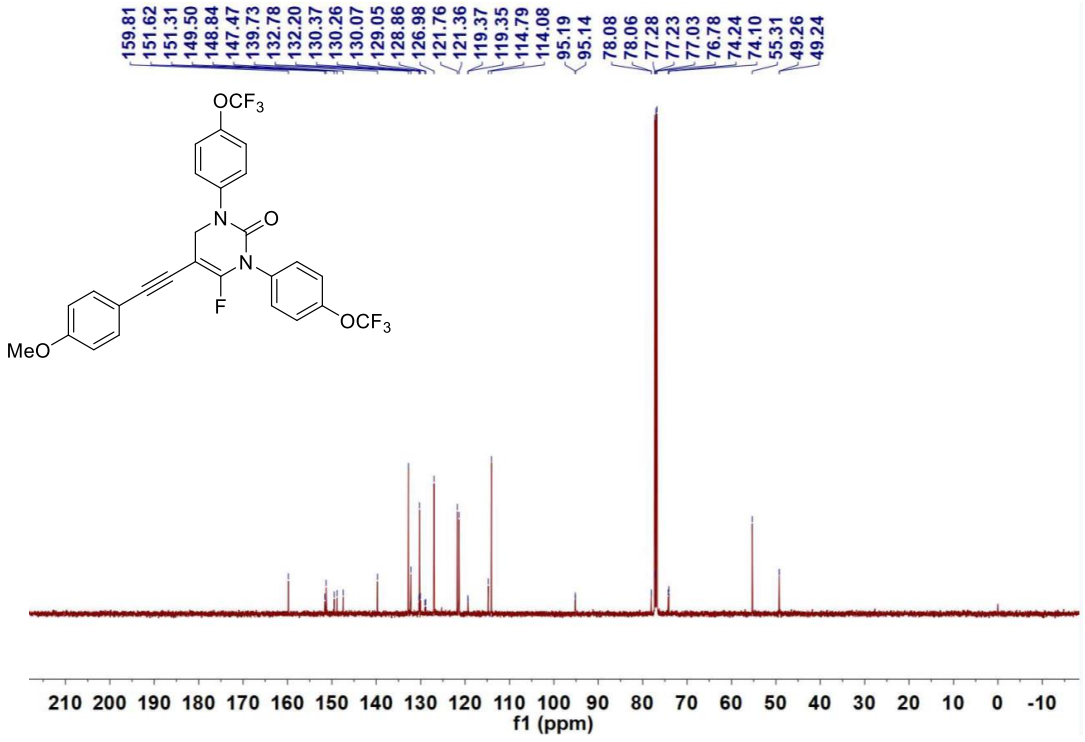


^{19}F-NMR (471 MHz, $CDCl_3$)

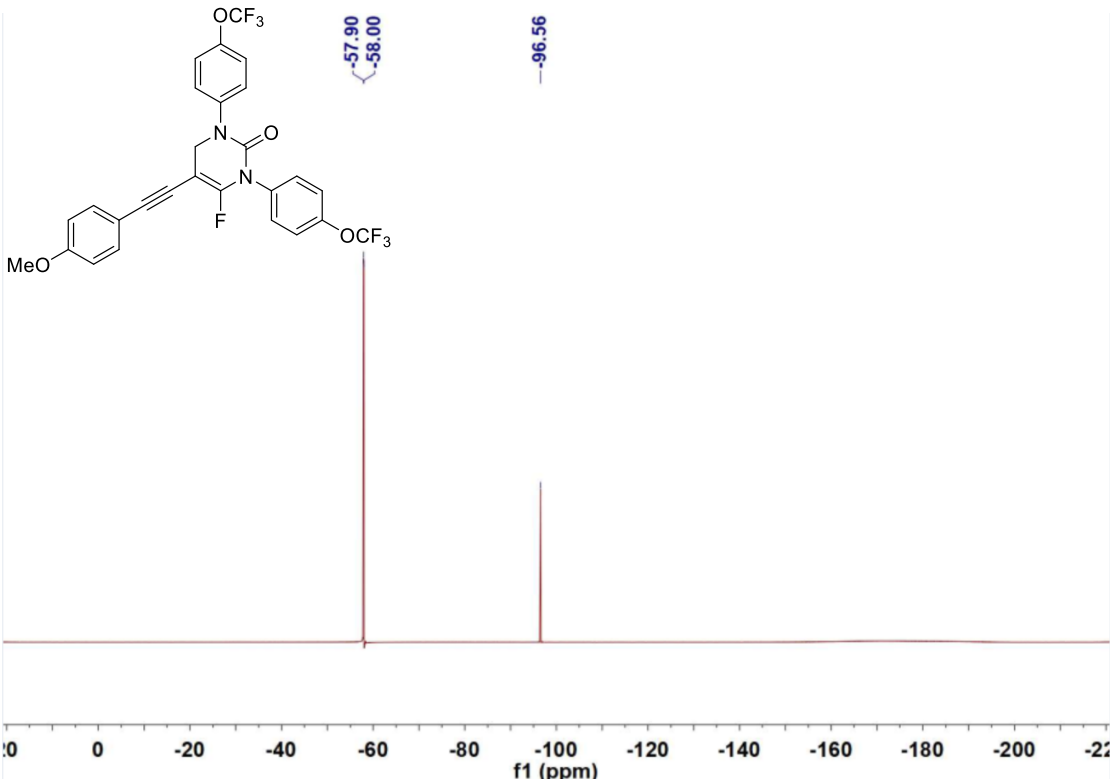
6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-bis(4-(trifluoromethoxy)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ad)



^{1}H-NMR (500 MHz, $CDCl_3$)

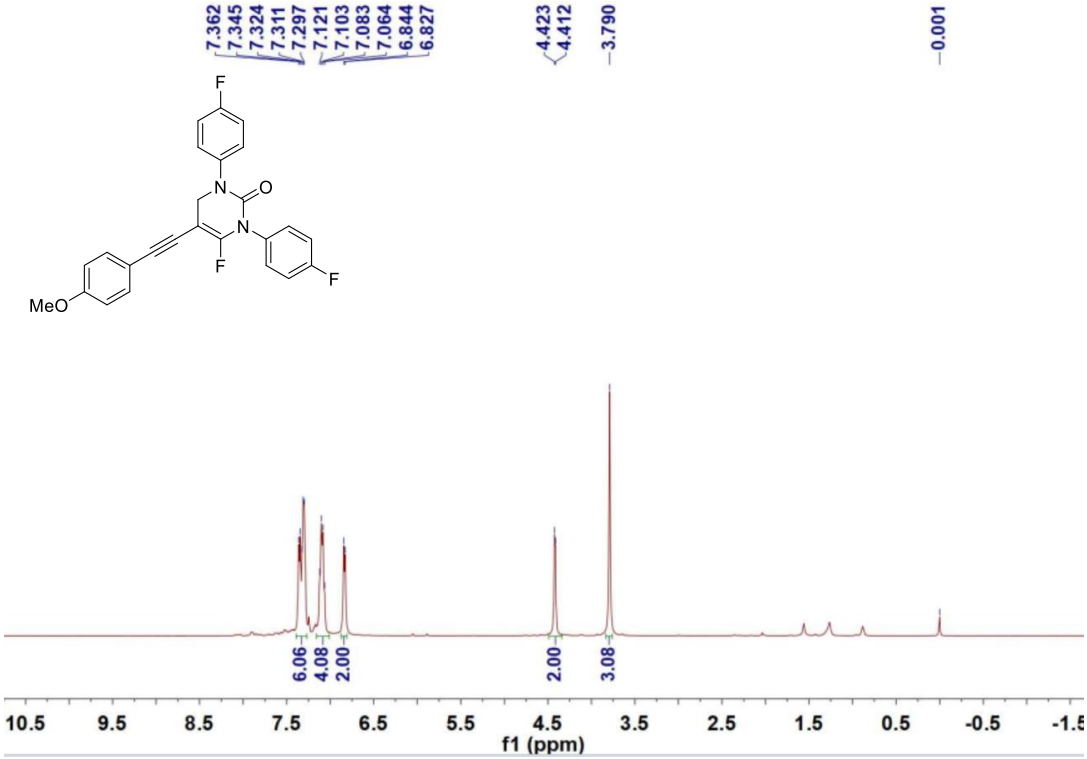


^{13}C-NMR (125 MHz, $CDCl_3$)

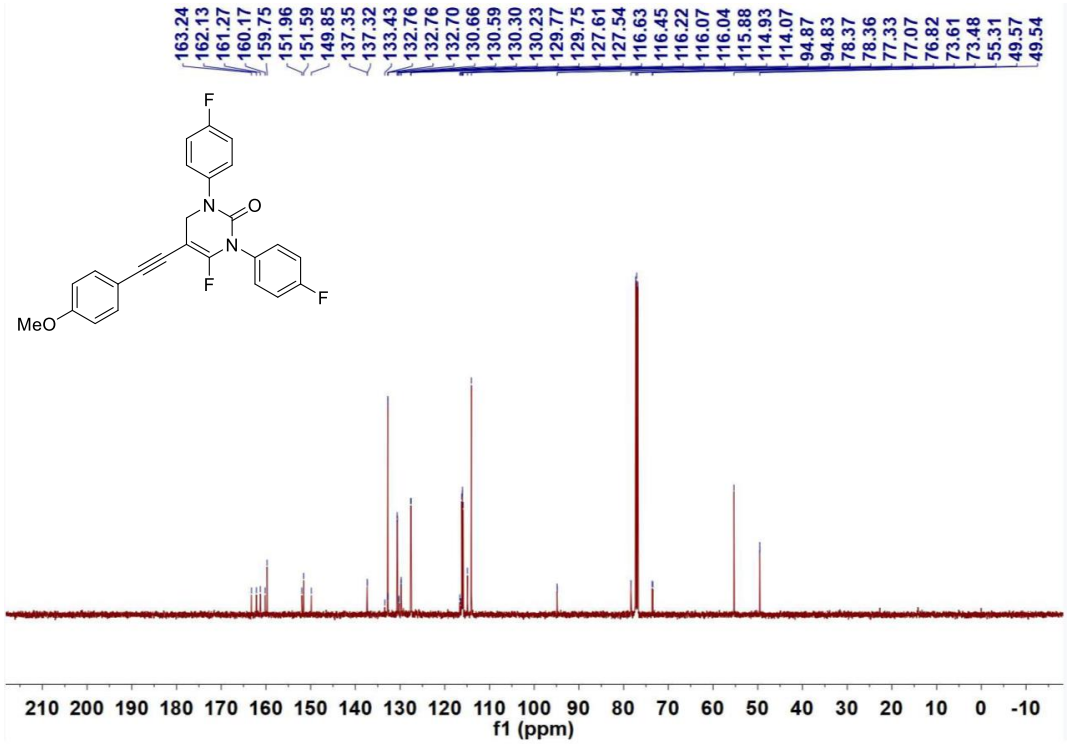


^{19}F-NMR (471 MHz, $CDCl_3$)

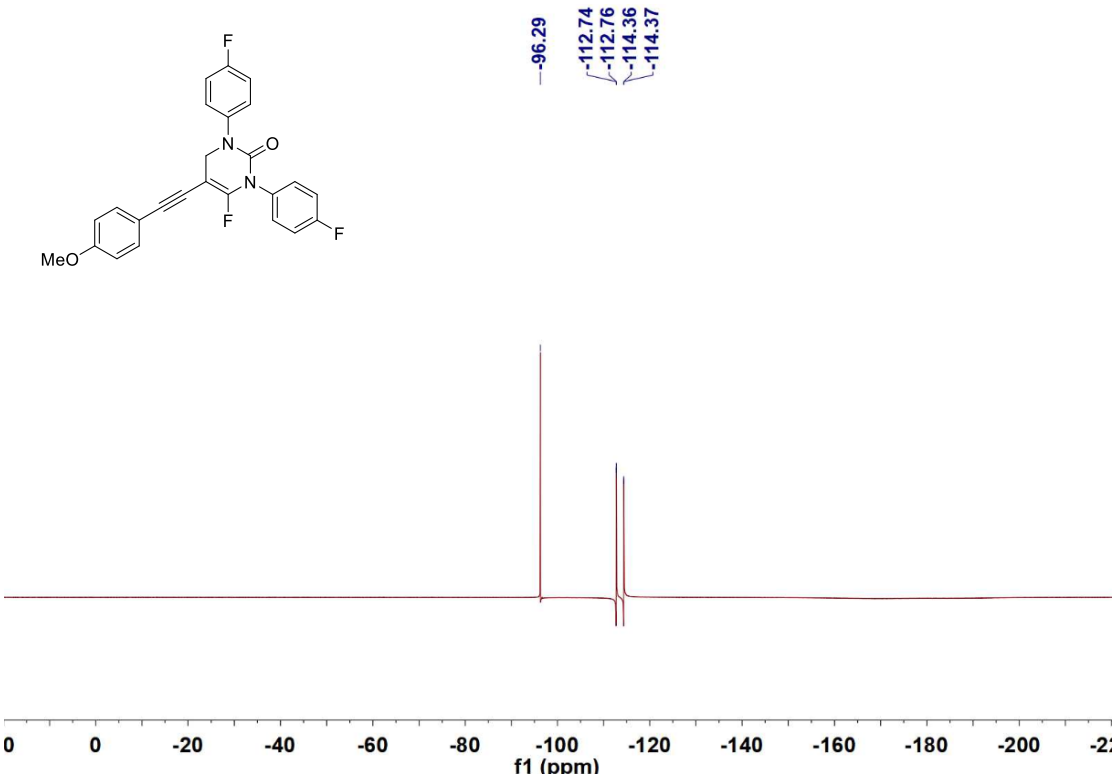
6-fluoro-1,3-bis(4-fluorophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ae)



^{1}H-NMR (500 MHz, $CDCl_3$)

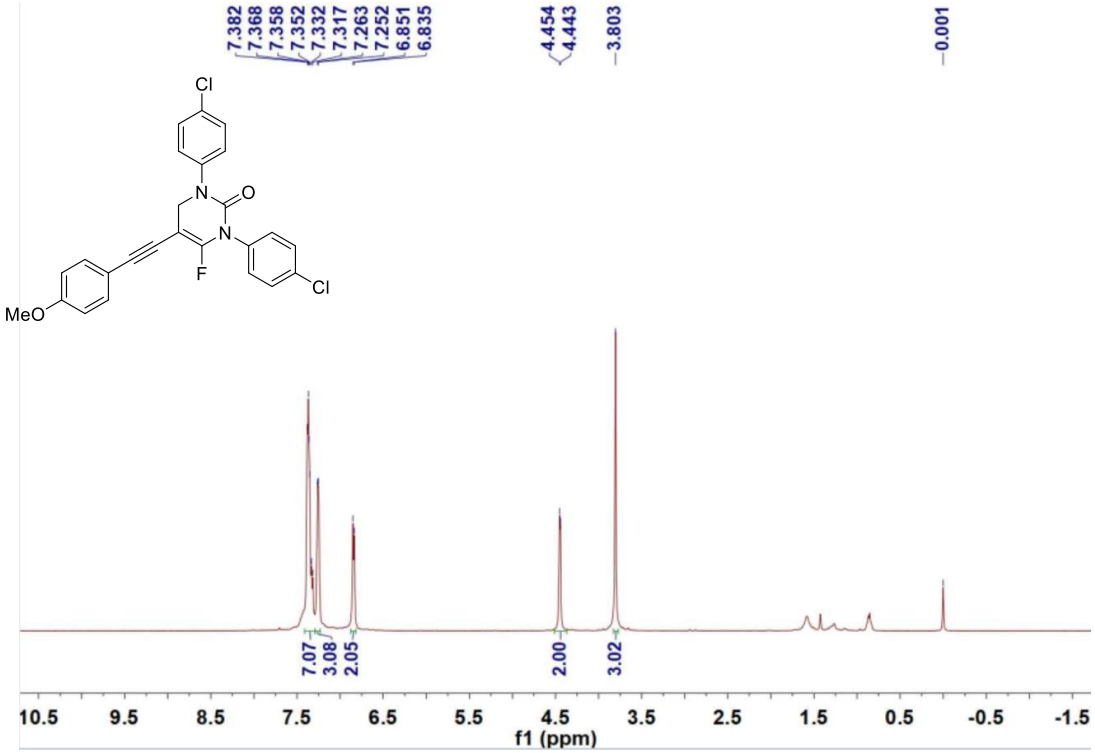


^{13}C-NMR (125 MHz, $CDCl_3$)

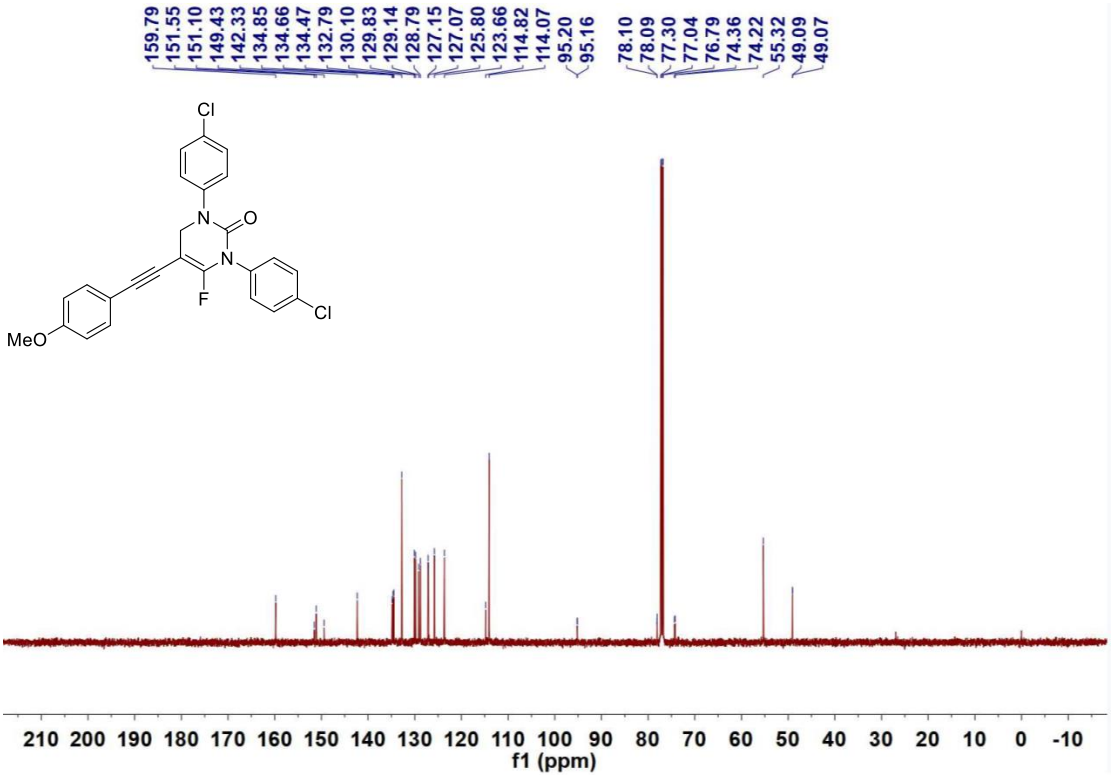


^{19}F-NMR (471 MHz, $CDCl_3$)

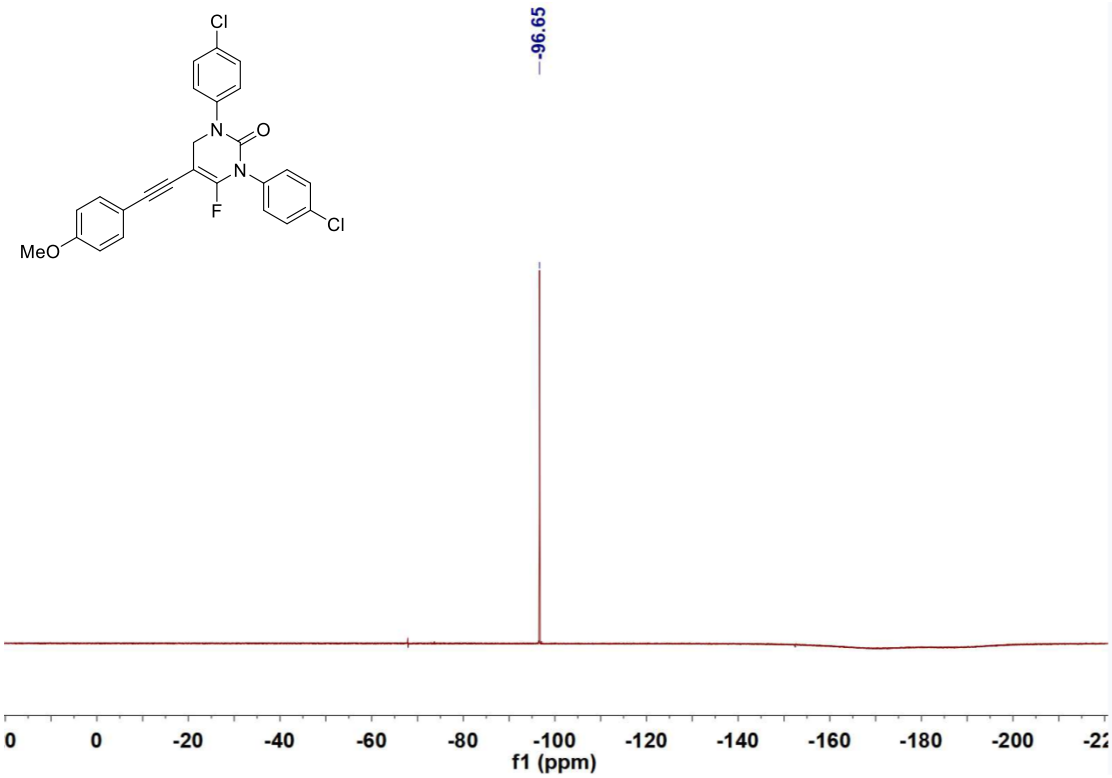
1,3-bis(4-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3af)



^{1}H-NMR (500 MHz, $CDCl_3$)

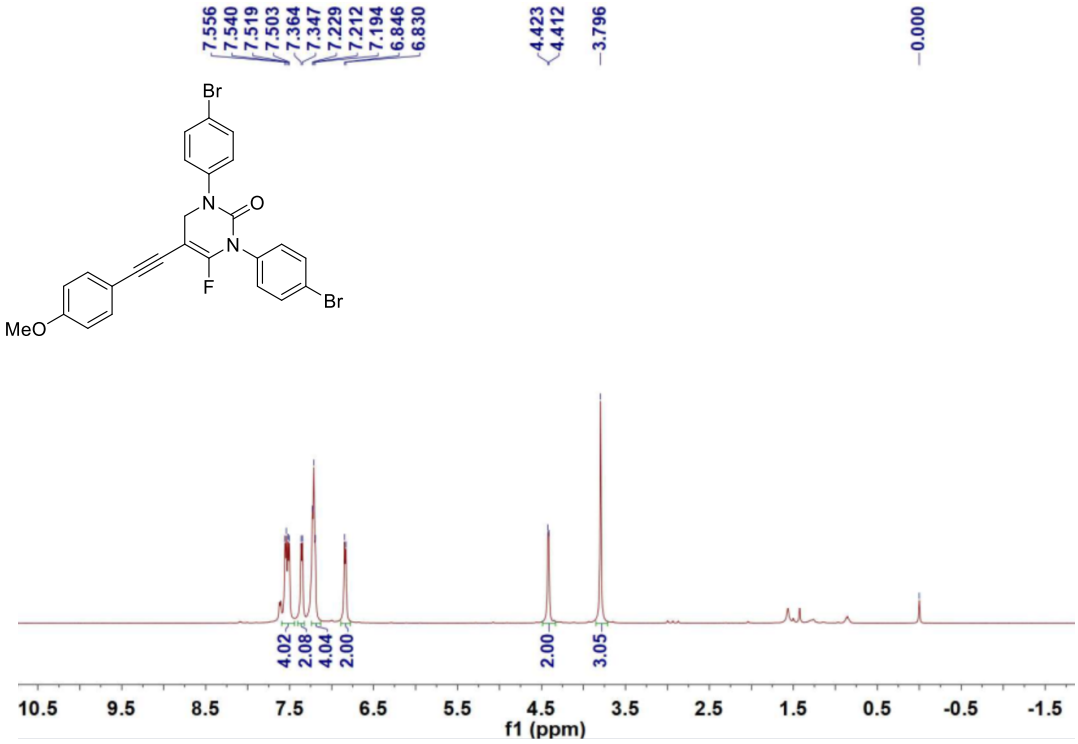


^{13}C-NMR (125 MHz, $CDCl_3$)

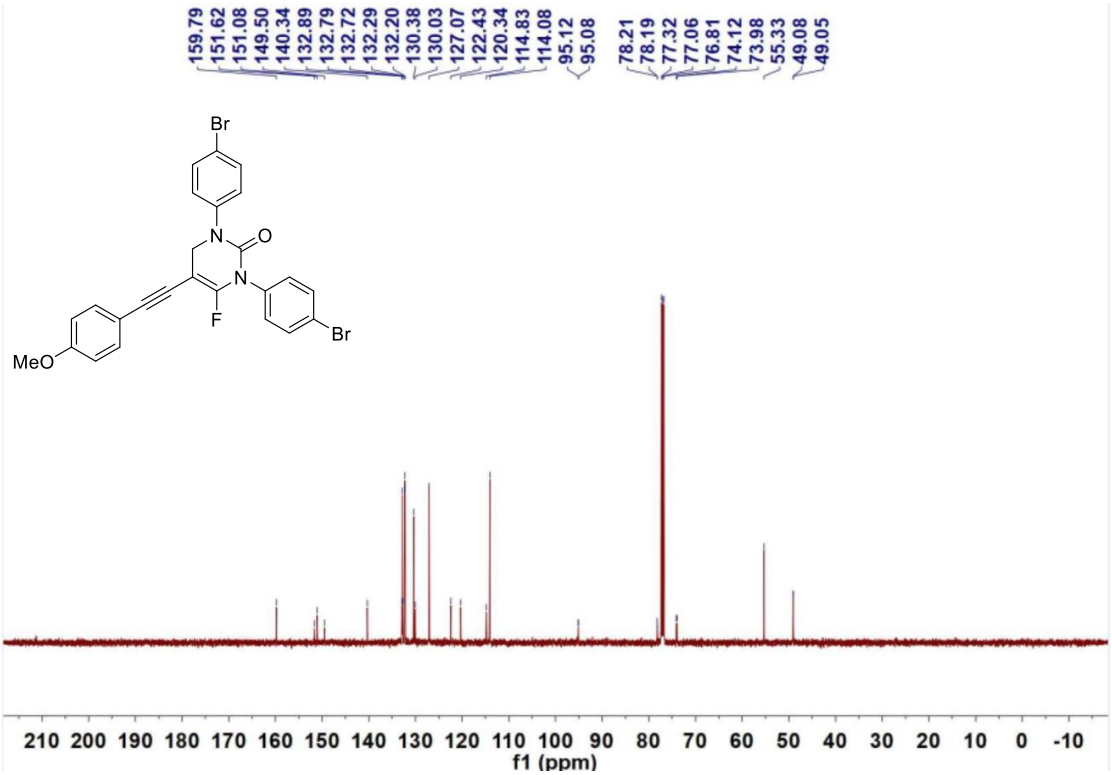


^{19}F-NMR (471 MHz, $CDCl_3$)

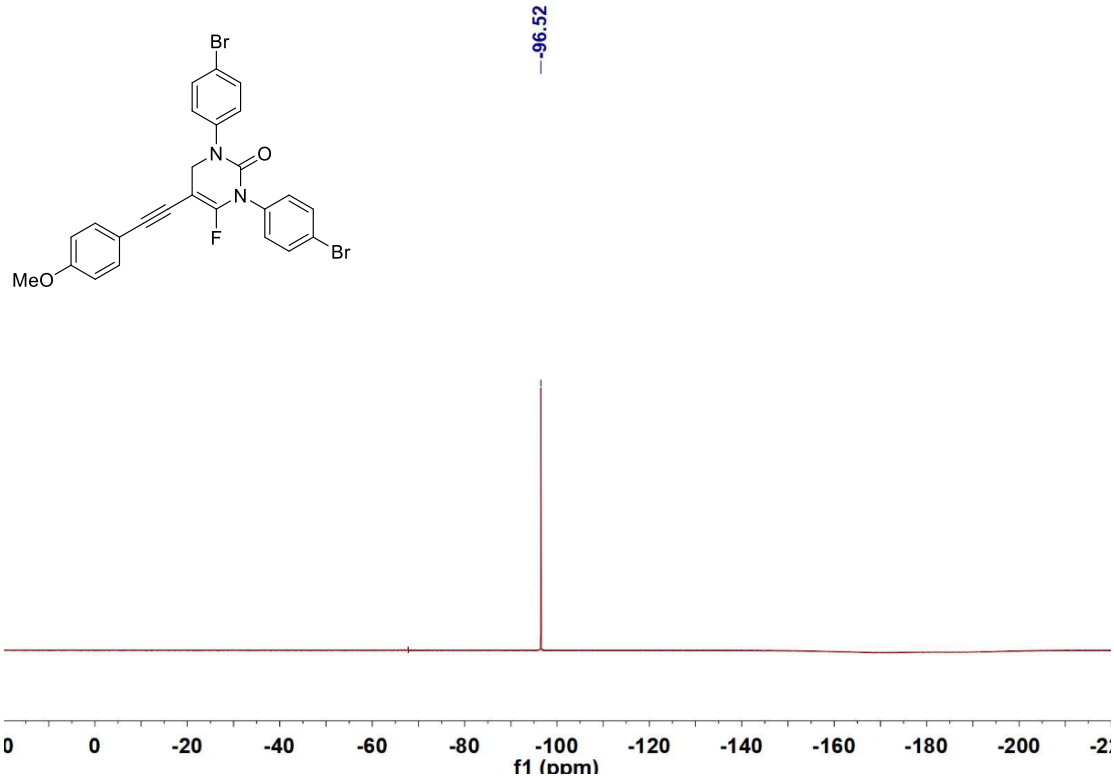
1,3-bis(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ag)



^{1}H-NMR (500 MHz, $CDCl_3$)

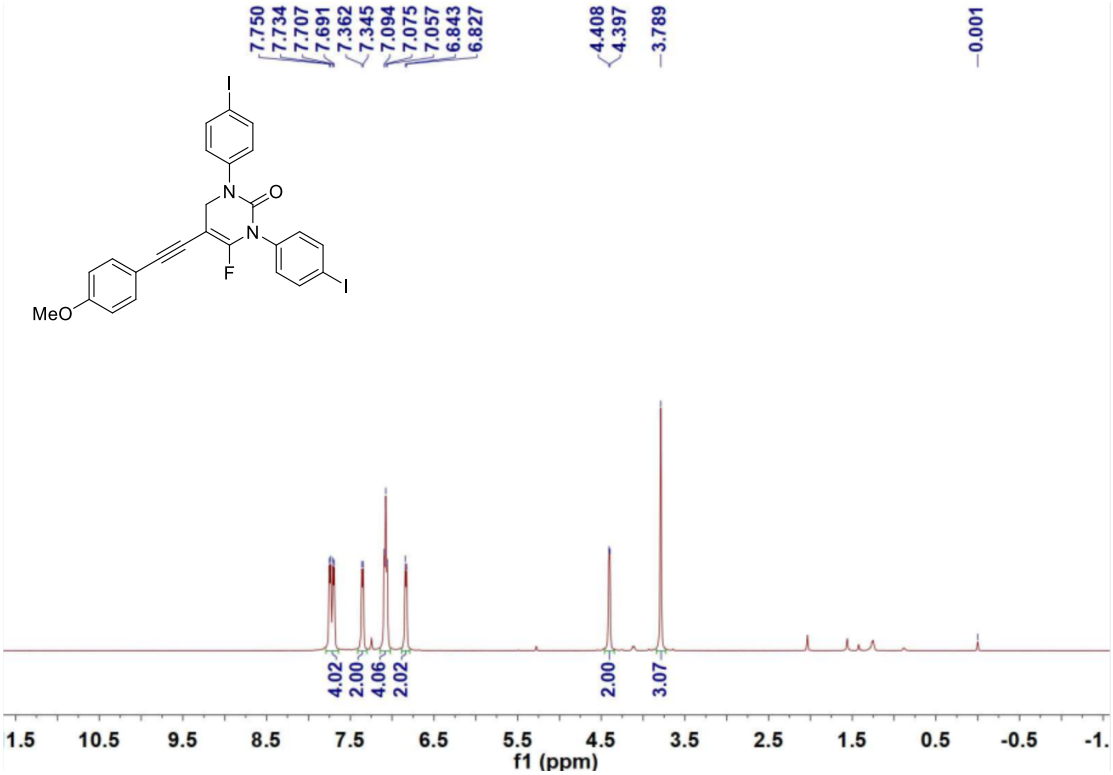


^{13}C-NMR (125 MHz, $CDCl_3$)

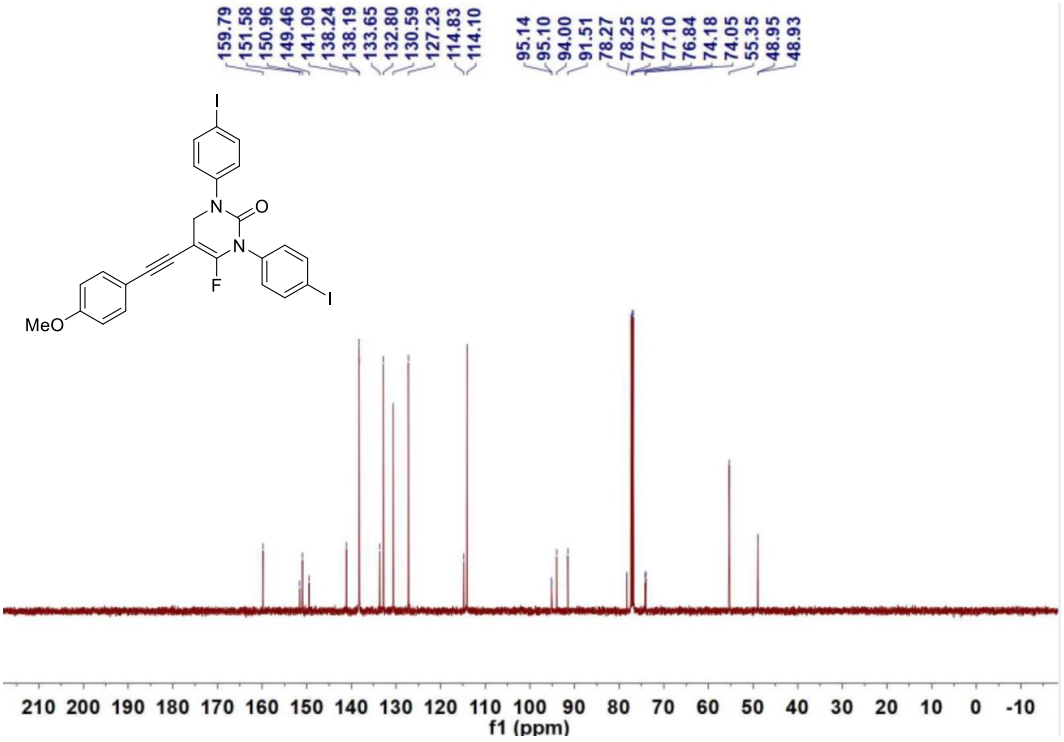


^{19}F-NMR (471 MHz, $CDCl_3$)

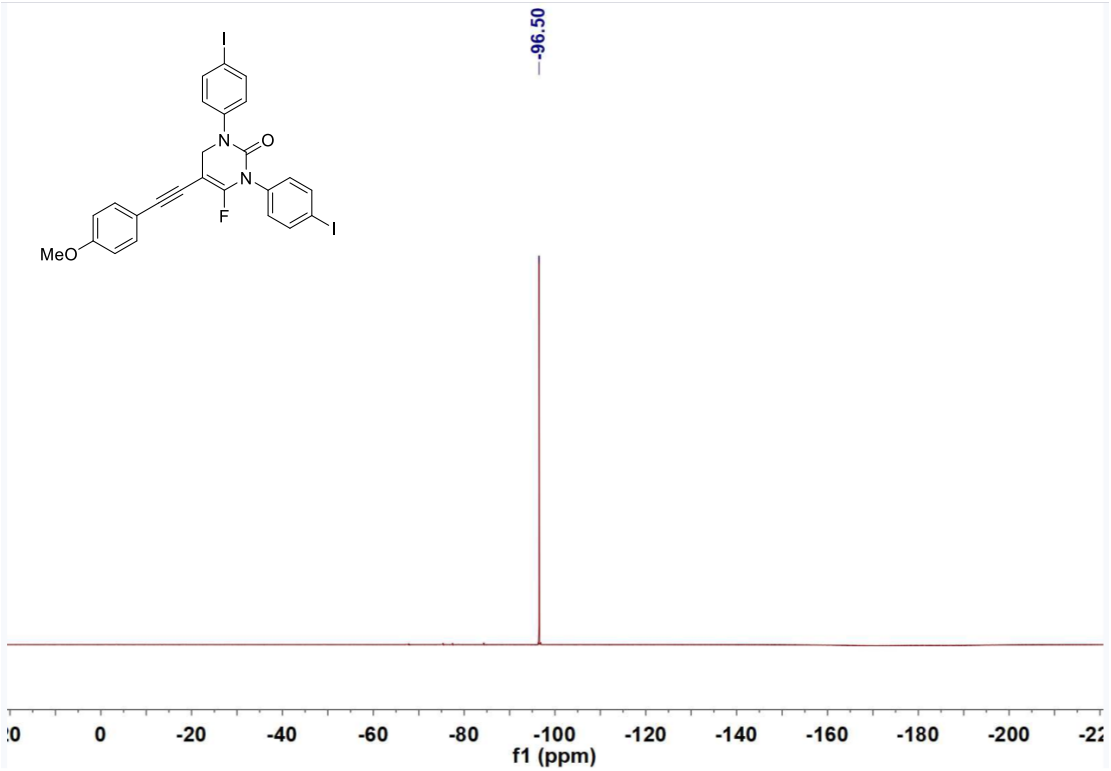
6-fluoro-1,3-bis(4-iodophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ah)



^{1}H-NMR (500 MHz, $CDCl_3$)

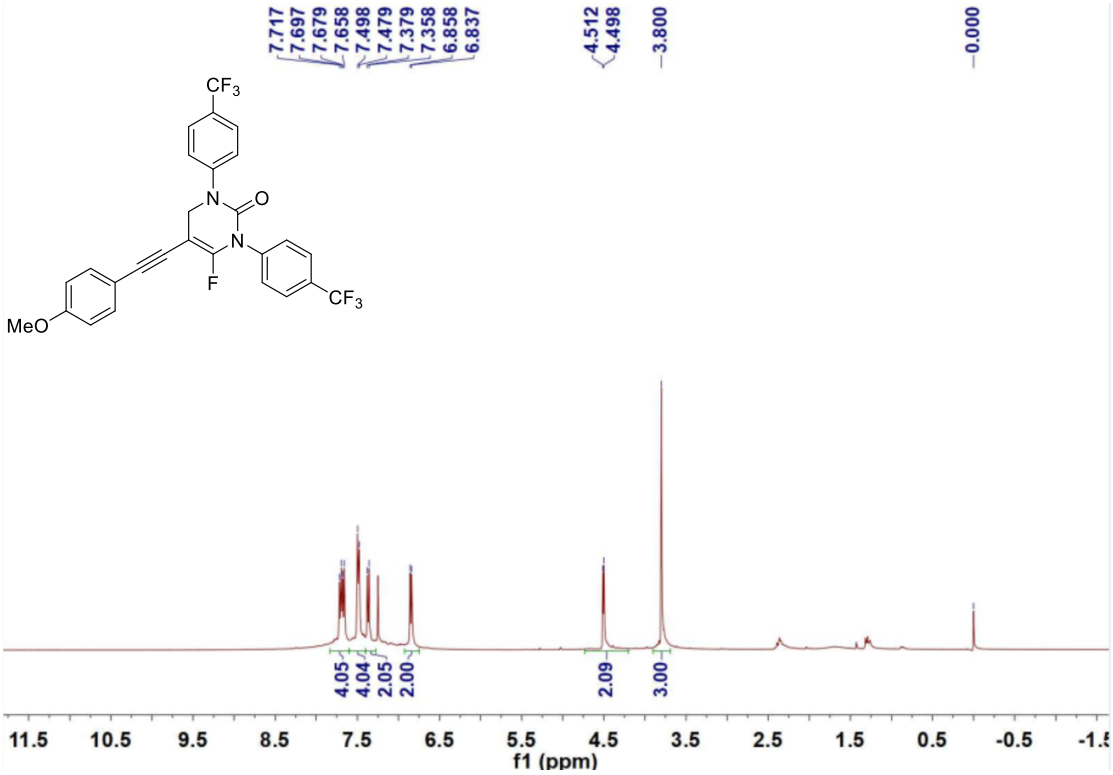


^{13}C-NMR (125 MHz, $CDCl_3$)

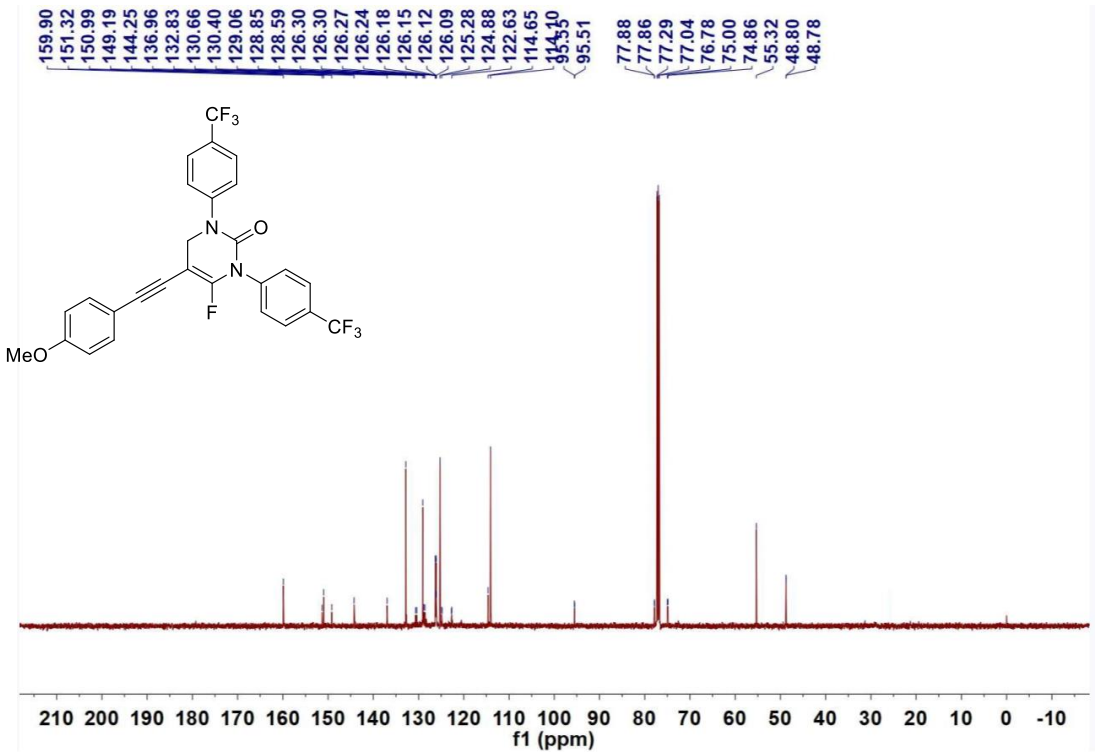


^{19}F-NMR (471 MHz, $CDCl_3$)

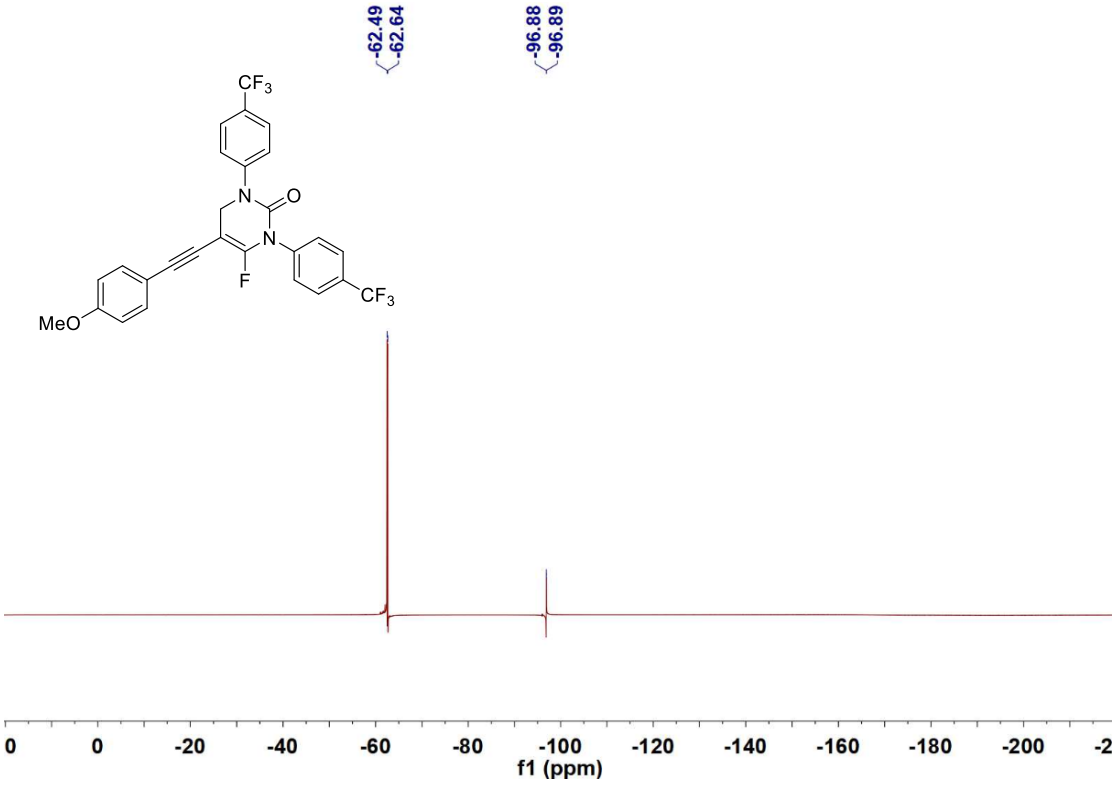
6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-bis(4-(trifluoromethyl)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ai)



^{1}H-NMR (400 MHz, $CDCl_3$)

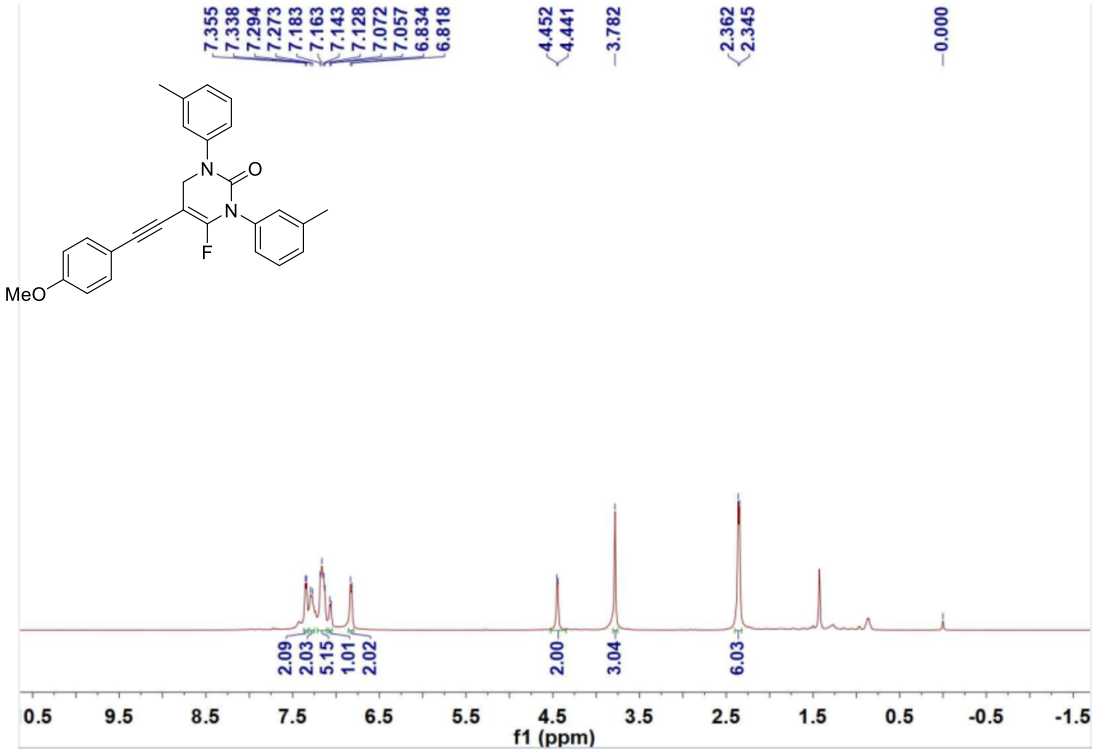


^{13}C-NMR (125 MHz, $CDCl_3$)

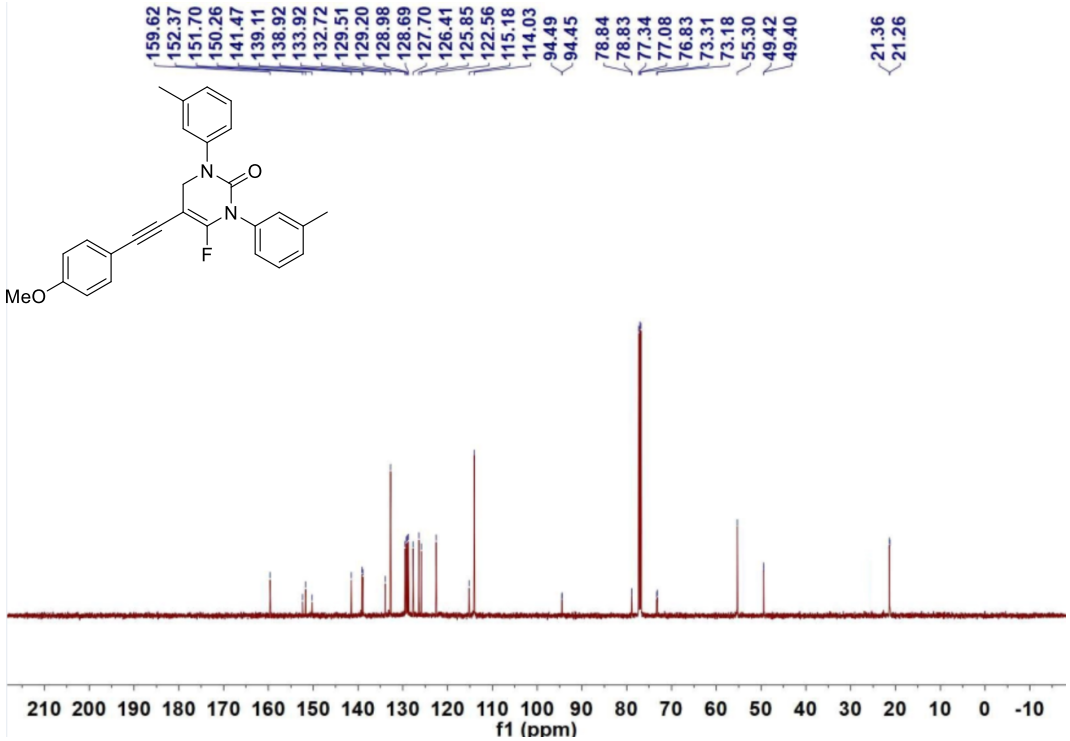


^{19}F-NMR (471 MHz, $CDCl_3$)

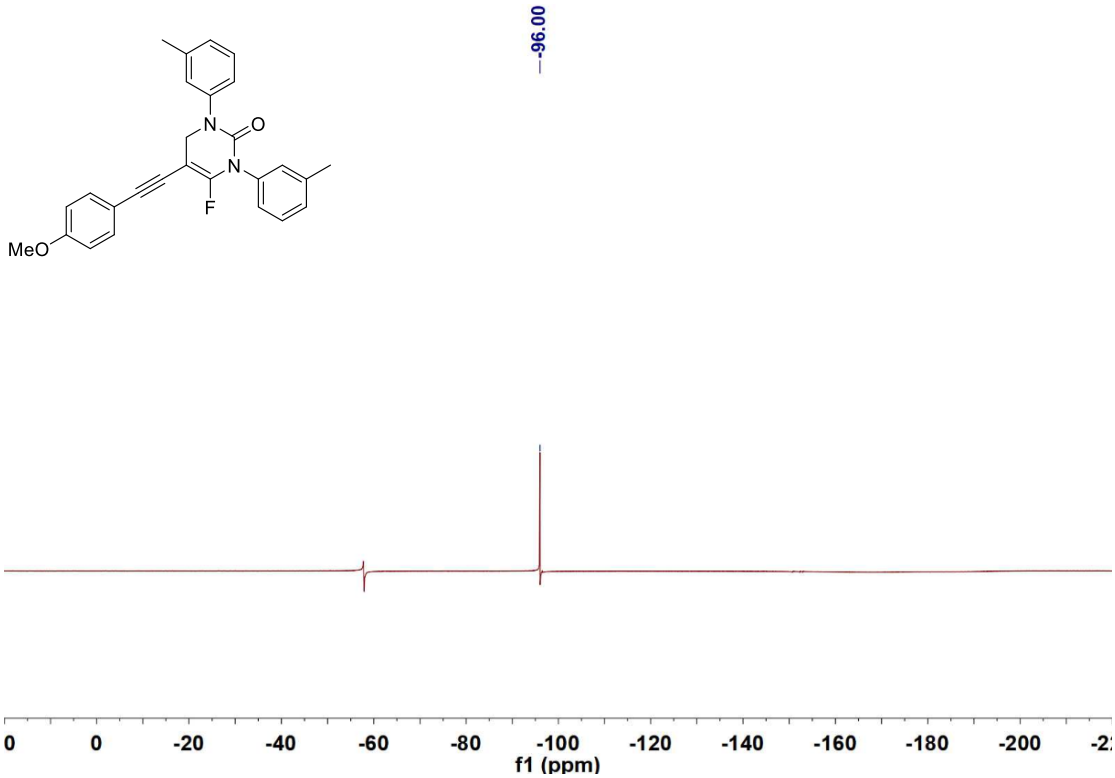
6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-di-*m*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3aj)



^{1}H-NMR (500 MHz, $CDCl_3$)

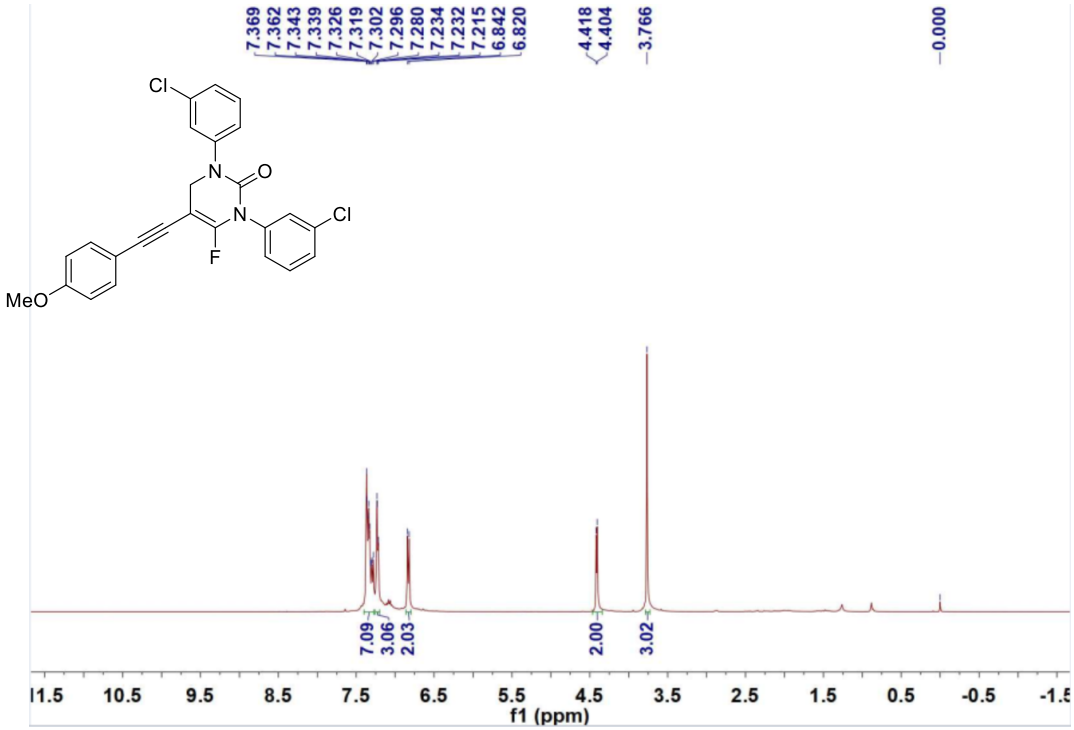


^{13}C-NMR (125 MHz, $CDCl_3$)

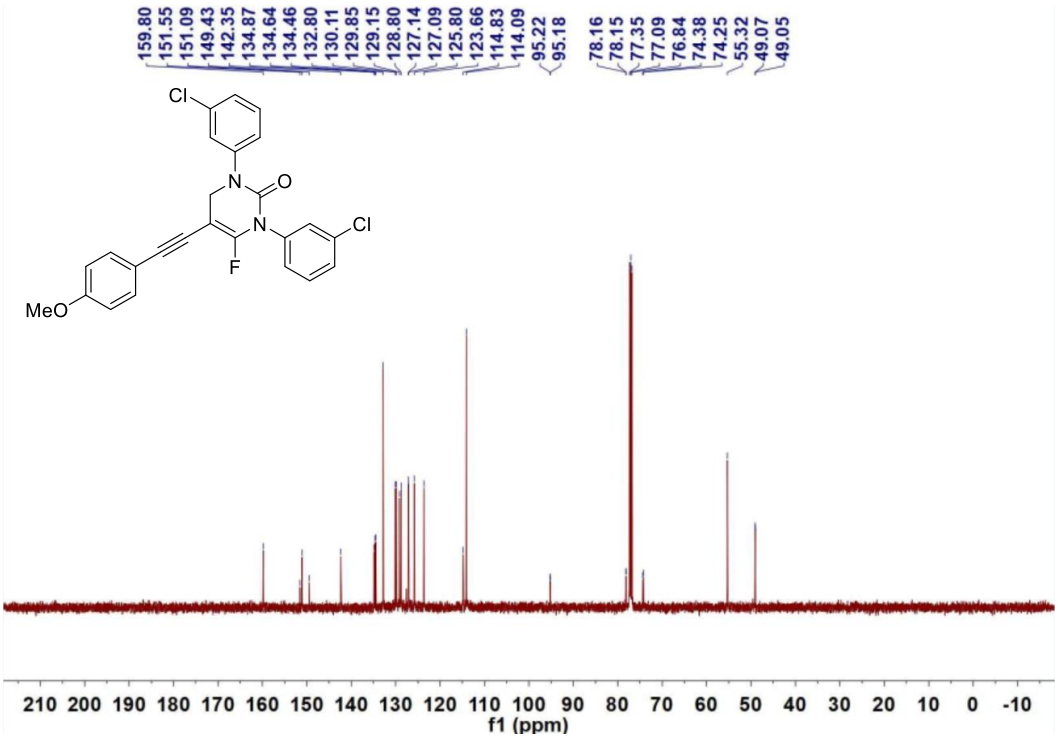


^{19}F-NMR (471 MHz, $CDCl_3$)

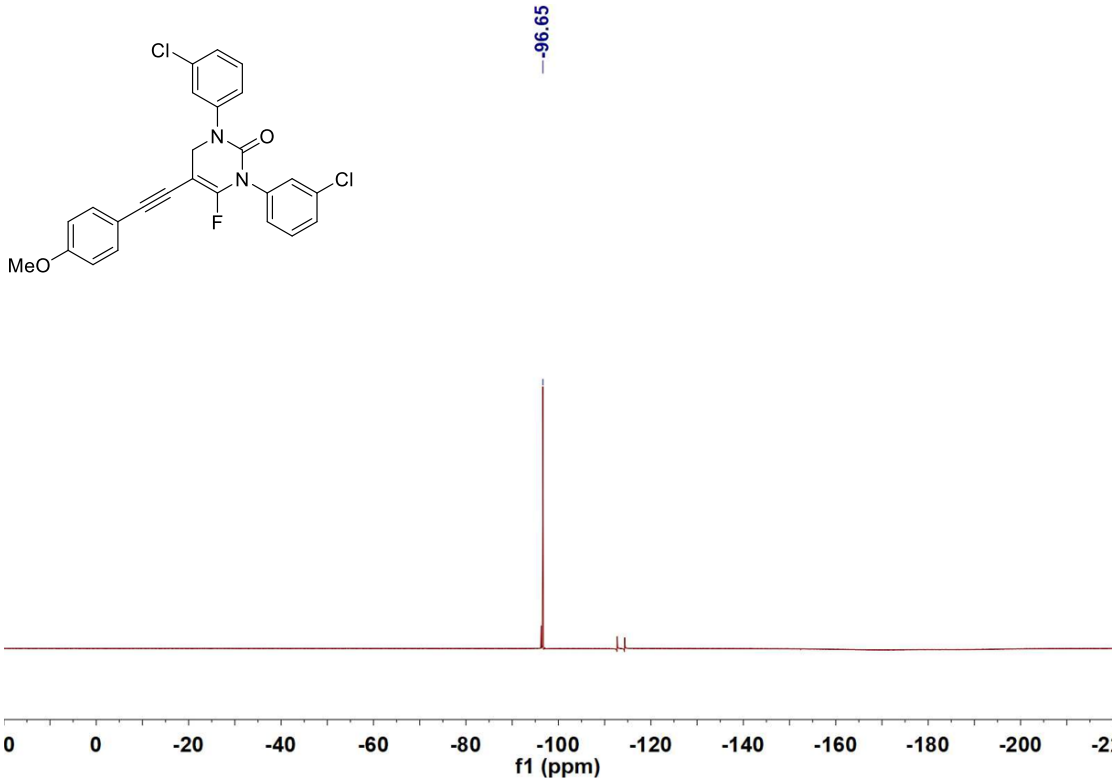
1,3-bis(3-chlorophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3ak)



^{1}H-NMR (400 MHz, $CDCl_3$)

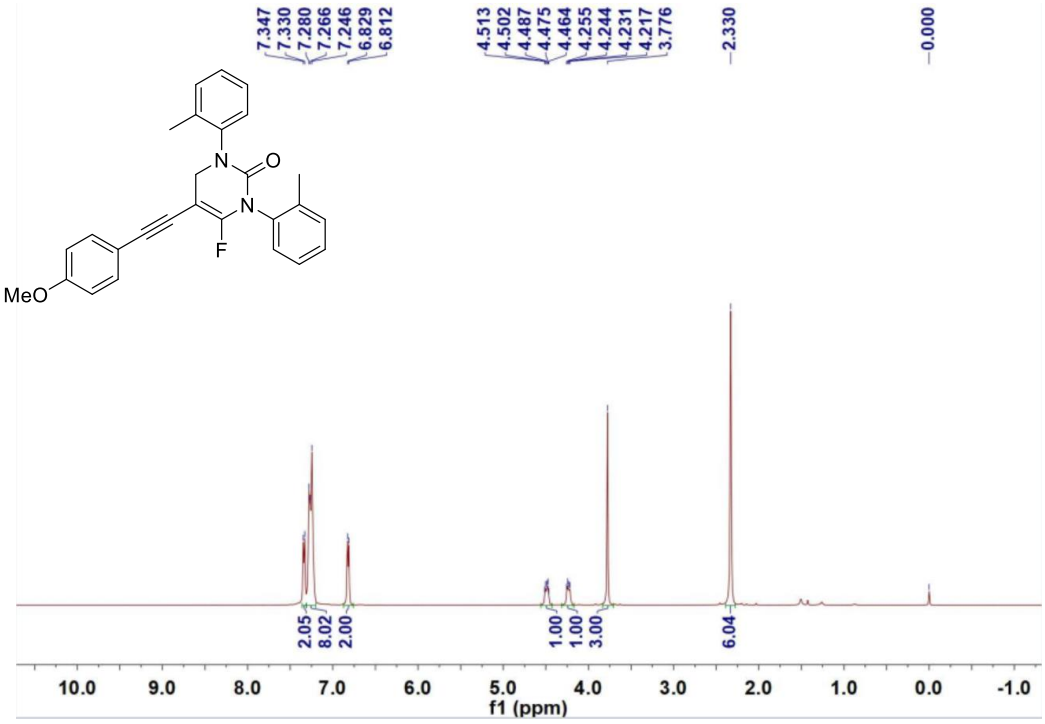


^{13}C-NMR (125 MHz, $CDCl_3$)

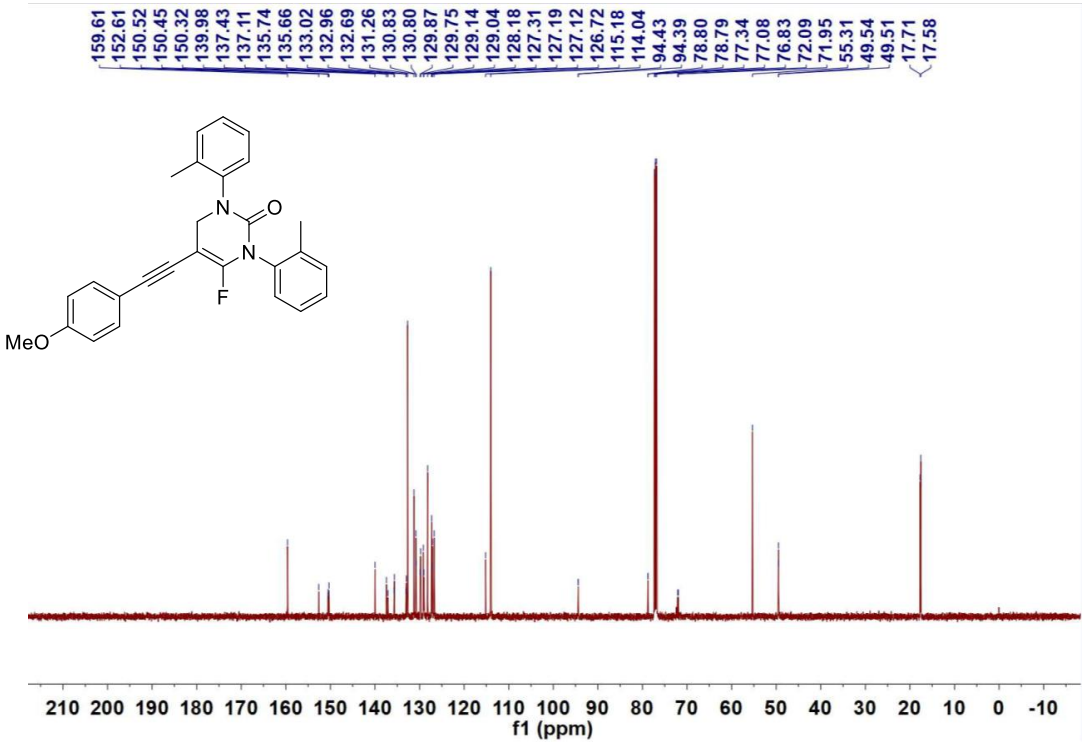


^{19}F-NMR (471 MHz, $CDCl_3$)

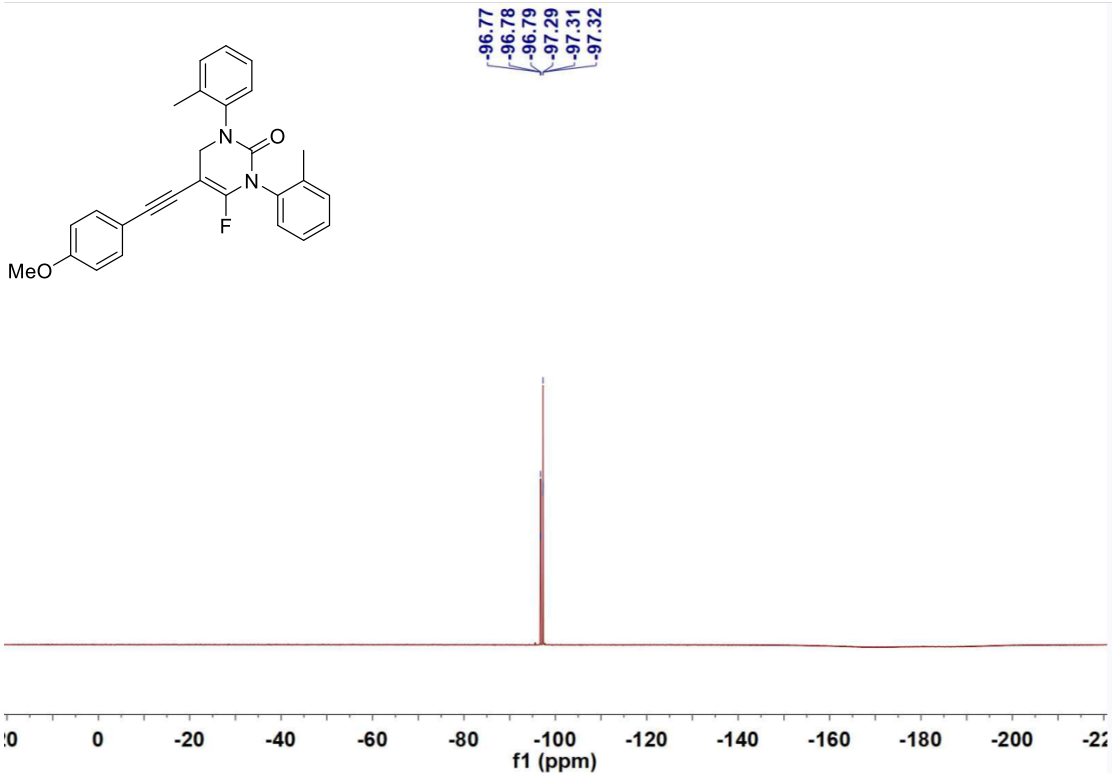
6-fluoro-5-((4-methoxyphenyl)ethynyl)-1,3-di-*o*-tolyl-3,4-dihydropyrimidin-2(1*H*)-one (3al)



^{1}H-NMR (500 MHz, $CDCl_3$)

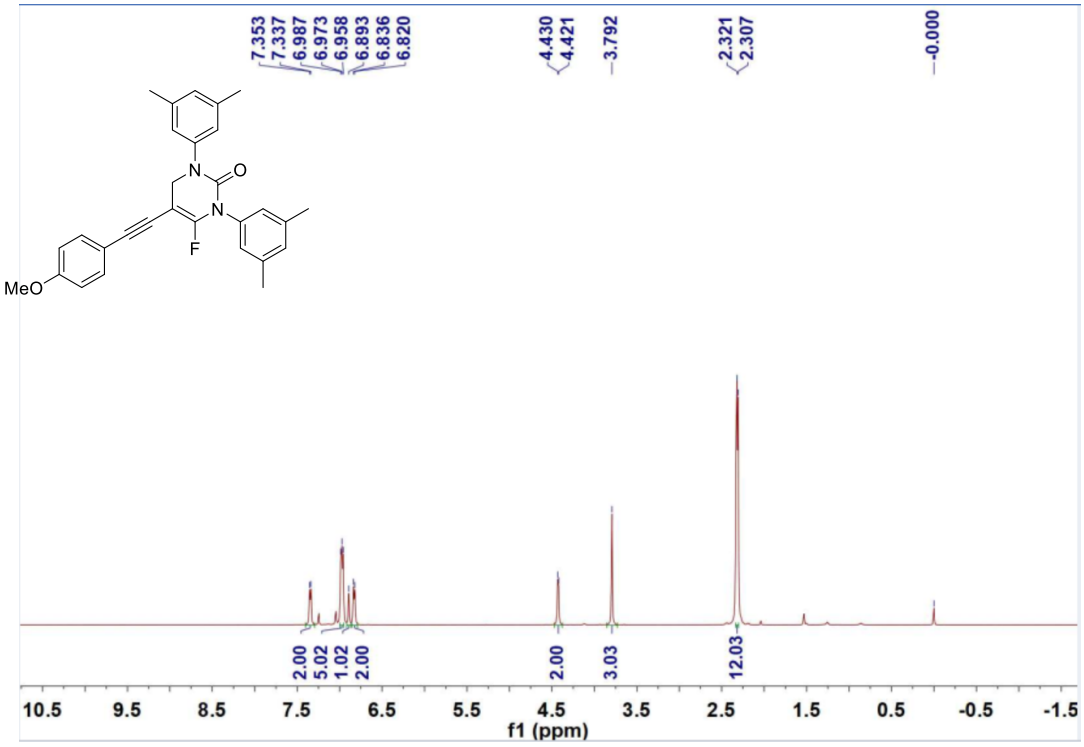


^{13}C-NMR (125 MHz, $CDCl_3$)

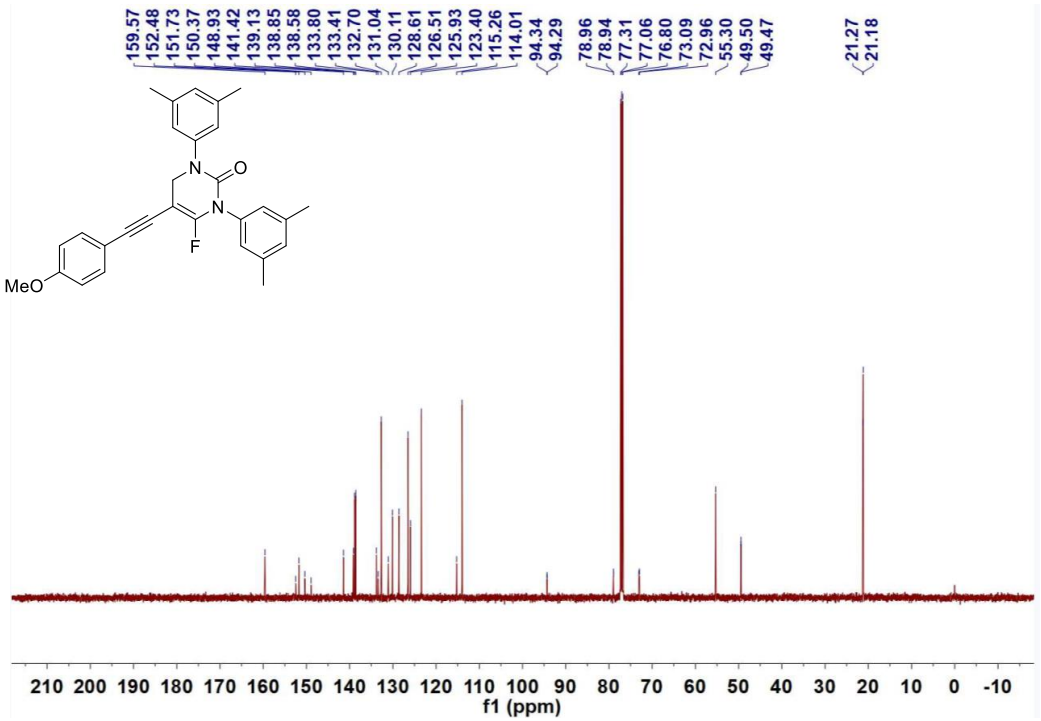


^{19}F-NMR (471 MHz, $CDCl_3$)

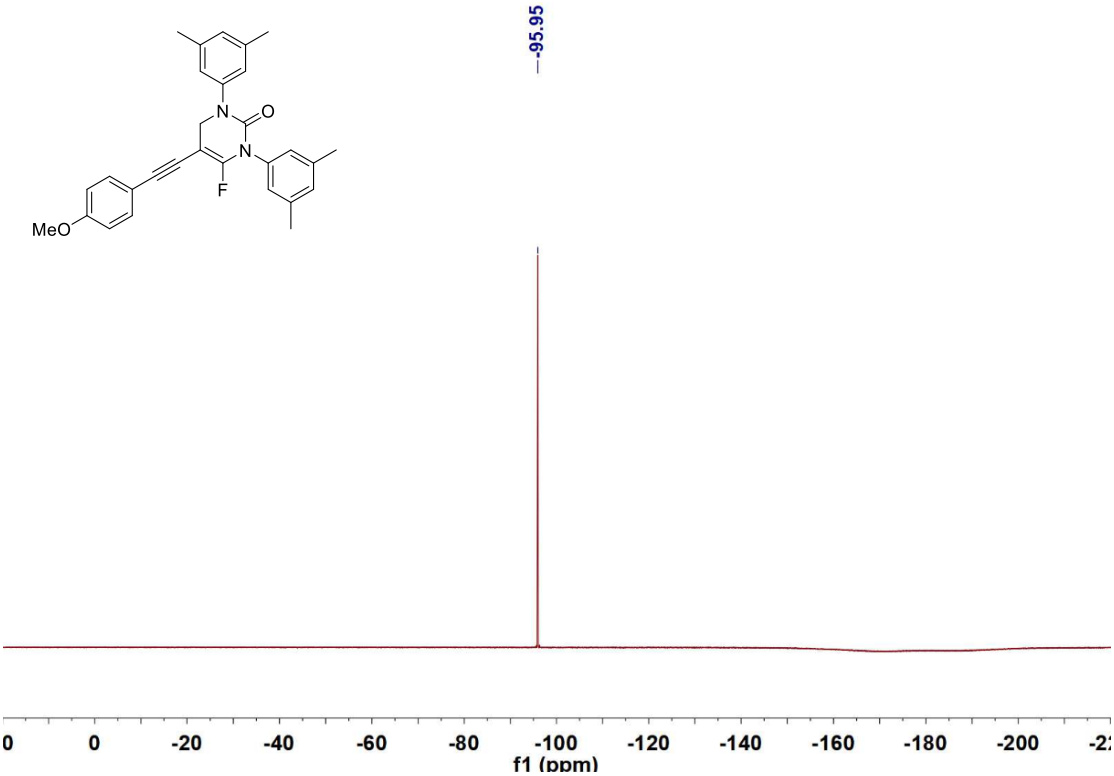
1,3-bis(3,5-dimethylphenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3am)



^{1}H-NMR (500 MHz, $CDCl_3$)

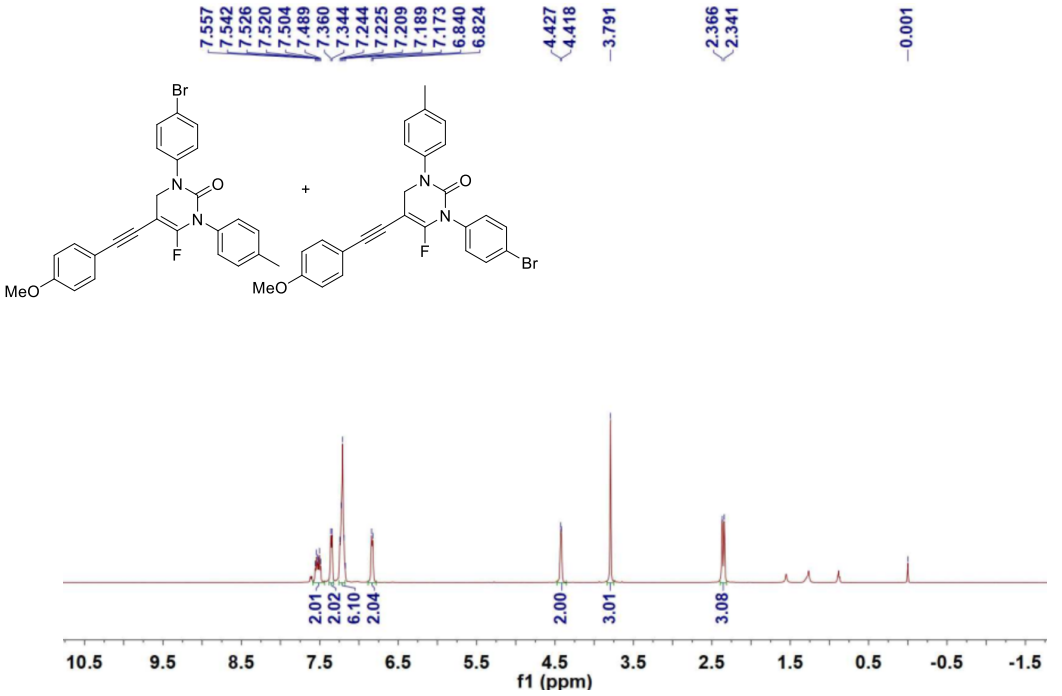


^{13}C-NMR (125 MHz, $CDCl_3$)

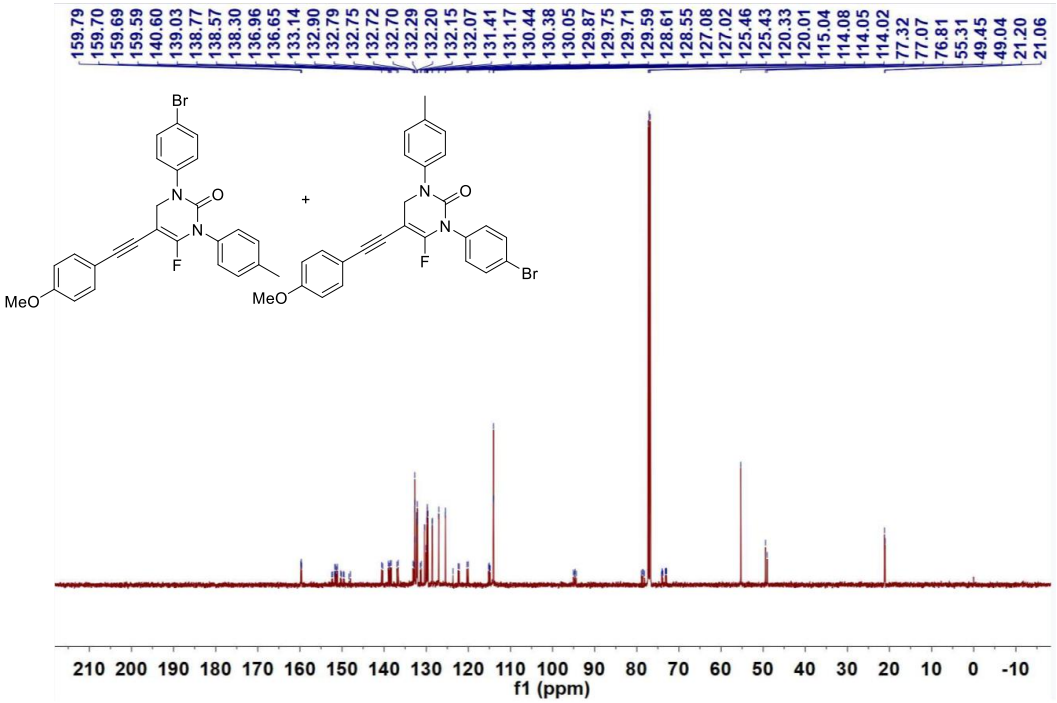


^{19}F-NMR (471 MHz, $CDCl_3$)

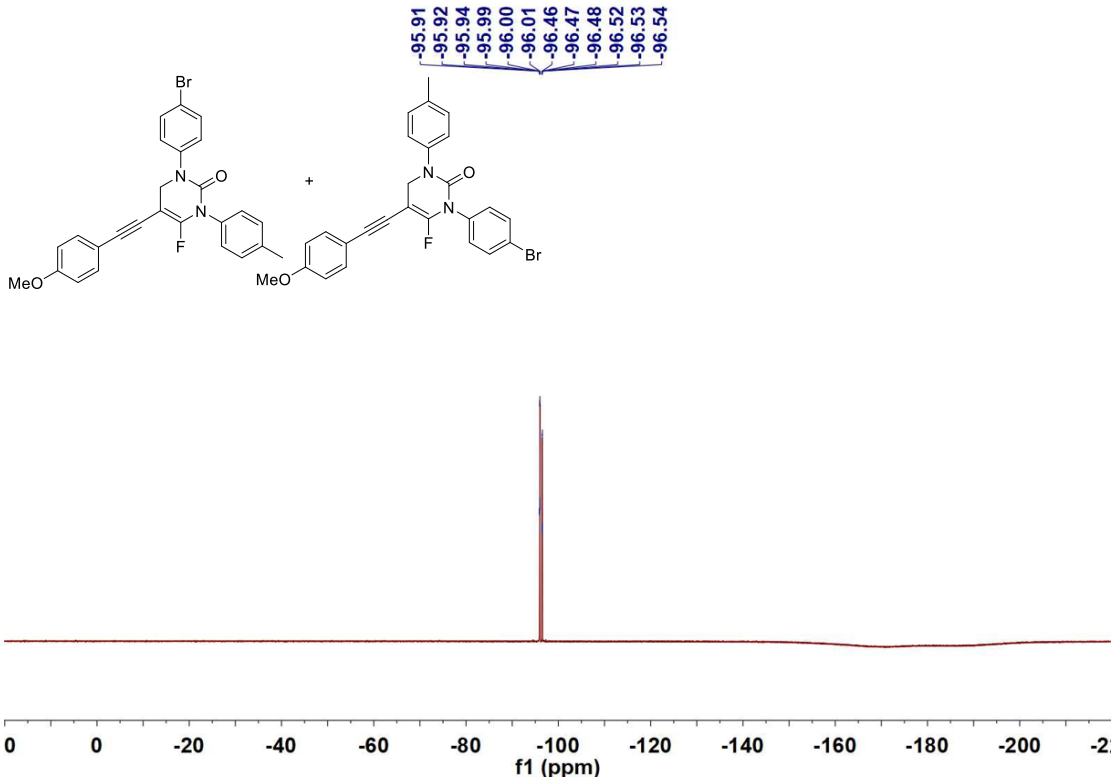
3-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-1-(*p*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one (3aag) + 1-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3-(*p*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one (3aga)



^{1}H-NMR (500 MHz, $CDCl_3$)

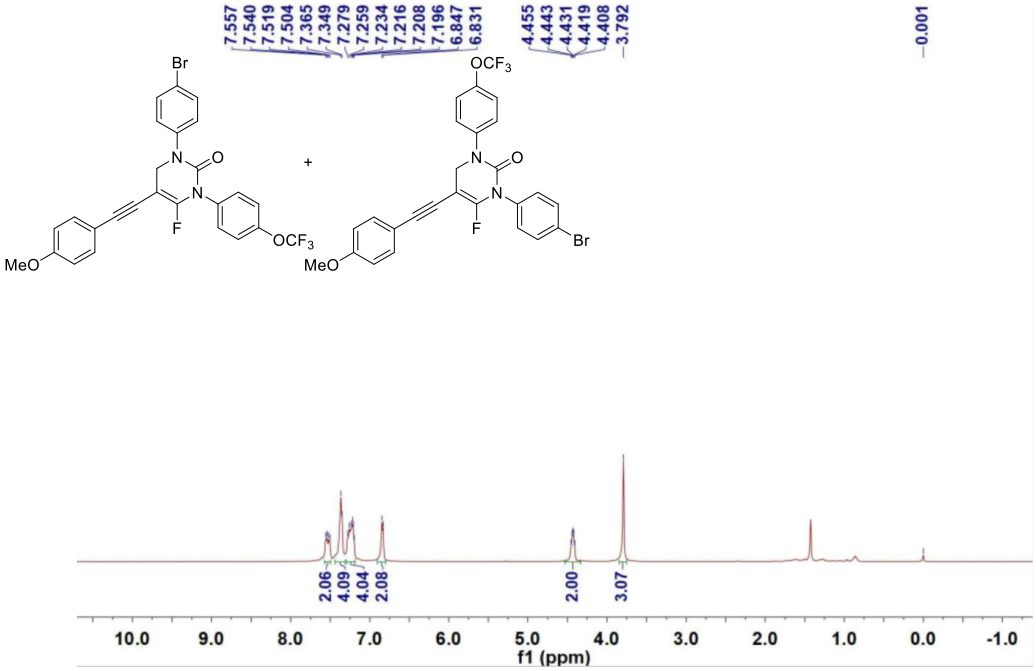


^{13}C-NMR (125 MHz, $CDCl_3$)

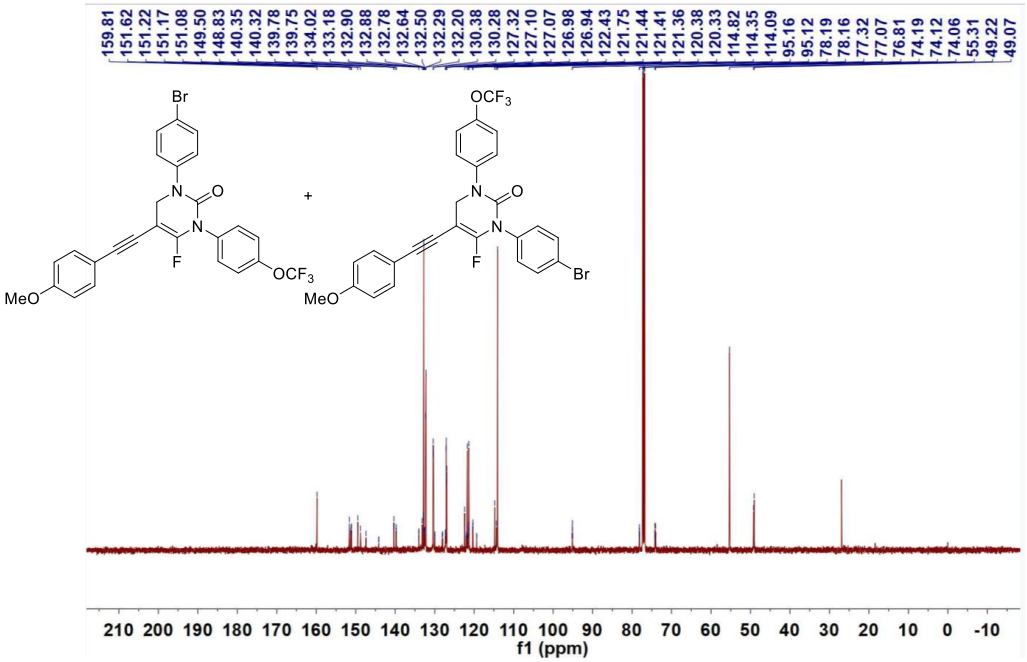


^{19}F-NMR (471 MHz, $CDCl_3$)

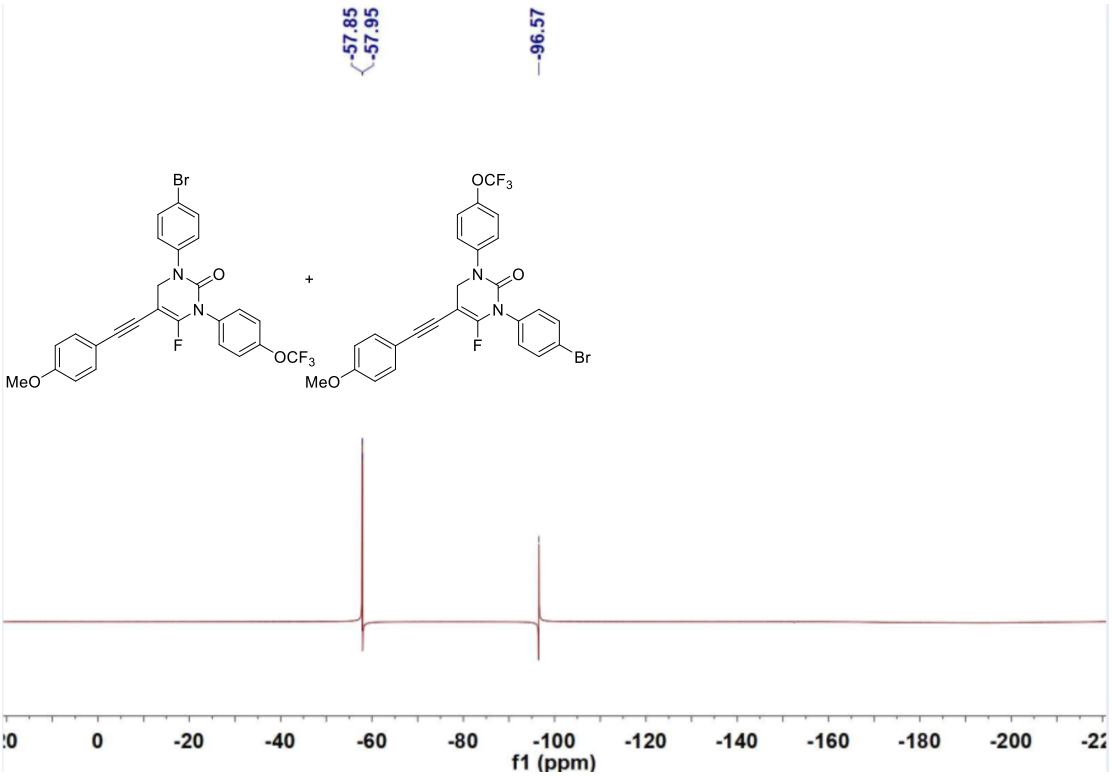
3-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-1-(4-(trifluoromethoxy)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (3adg) + 1-(4-bromophenyl)-6-fluoro-5-((4-methoxyphenyl)ethynyl)-3-(4-(trifluoromethoxy)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (3agd)



^{1}H-NMR (500 MHz, $CDCl_3$)

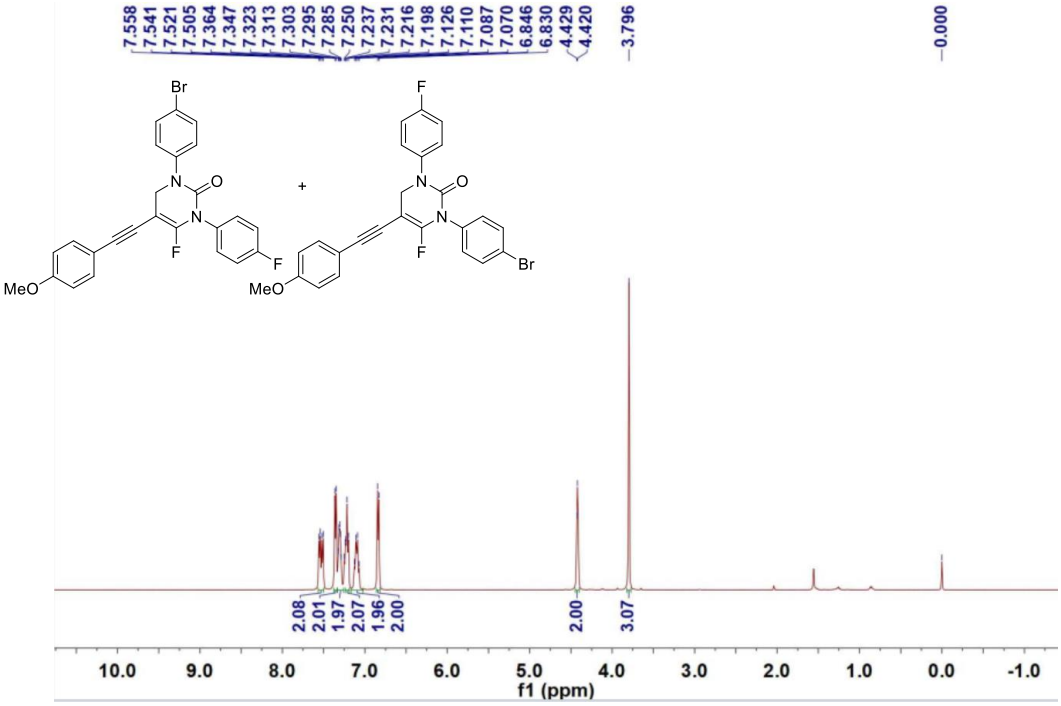


^{13}C-NMR (125 MHz, $CDCl_3$)

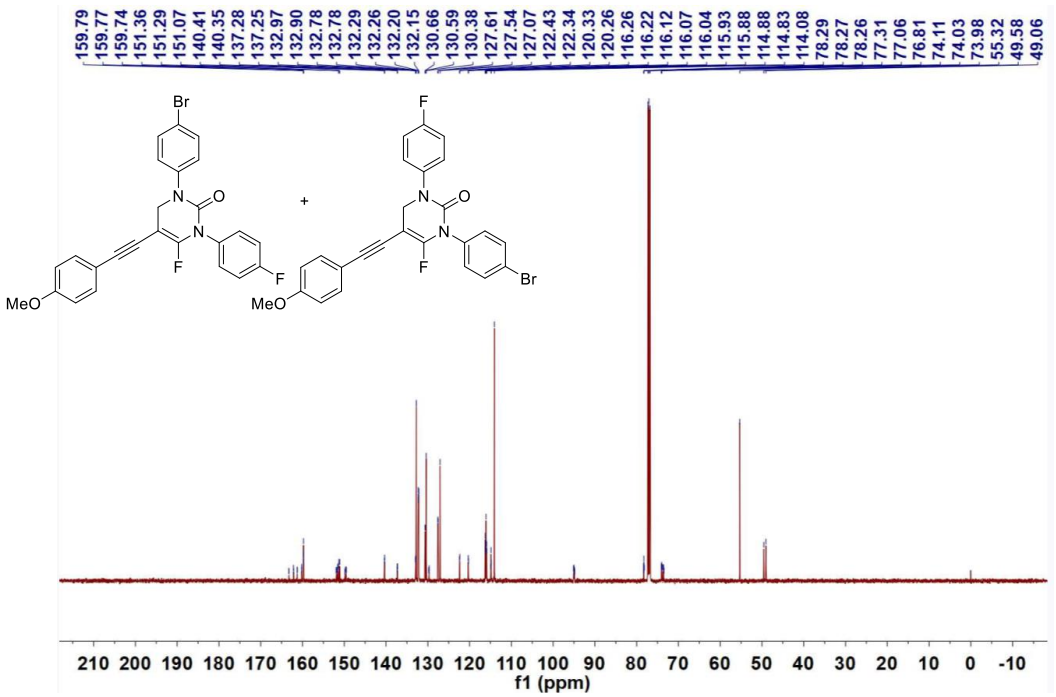


^{19}F-NMR (471 MHz, $CDCl_3$)

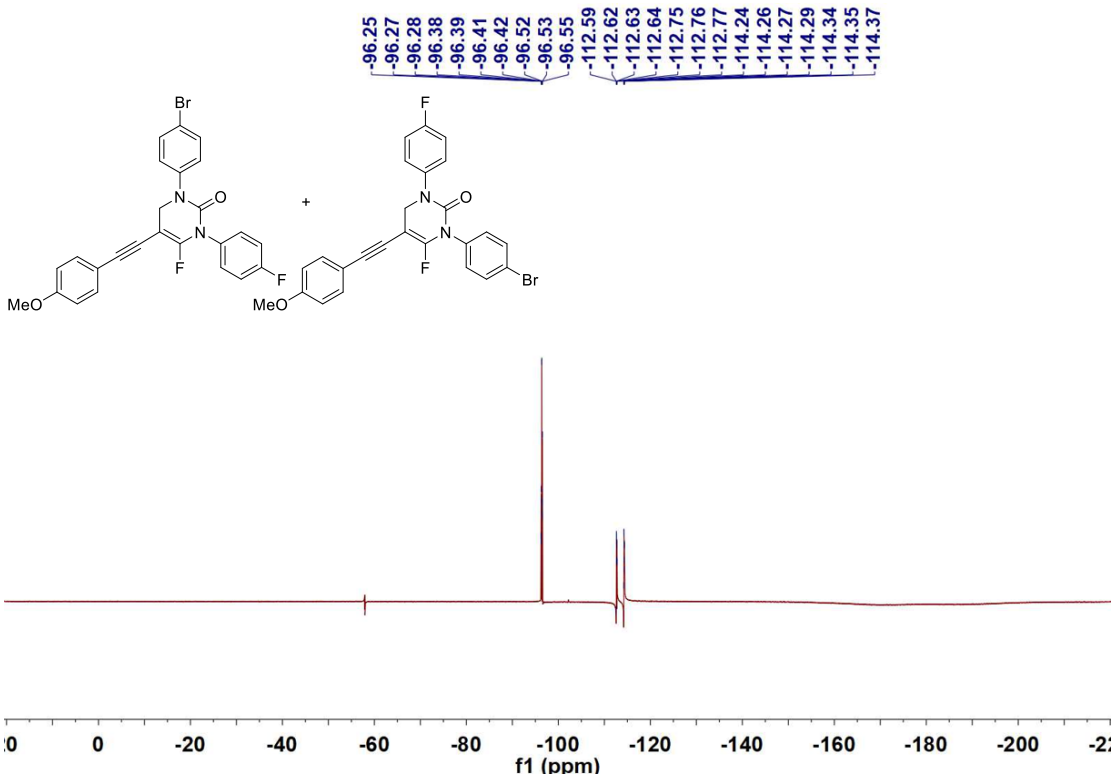
3-(4-bromophenyl)-6-fluoro-1-(4-fluorophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3aeg) + 1-(4-bromophenyl)-6-fluoro-3-(4-fluorophenyl)-5-((4-methoxyphenyl)ethynyl)-3,4-dihydropyrimidin-2(1*H*)-one (3age)



^{1}H-NMR (500 MHz, $CDCl_3$)

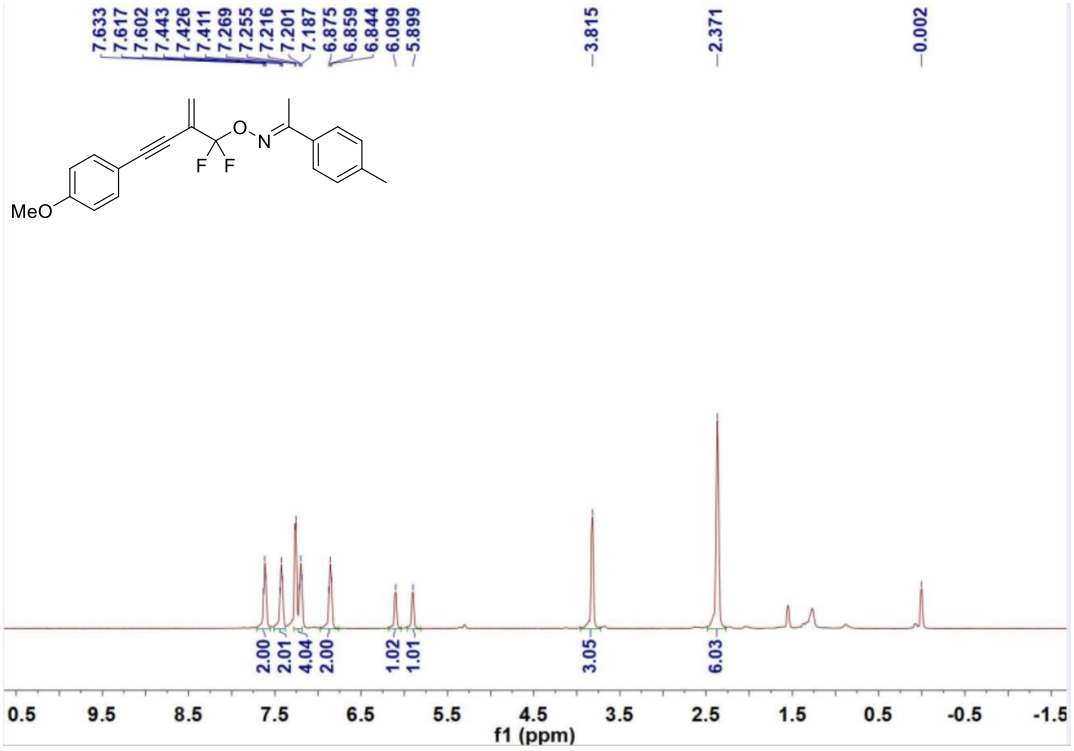


^{13}C-NMR (125 MHz, $CDCl_3$)

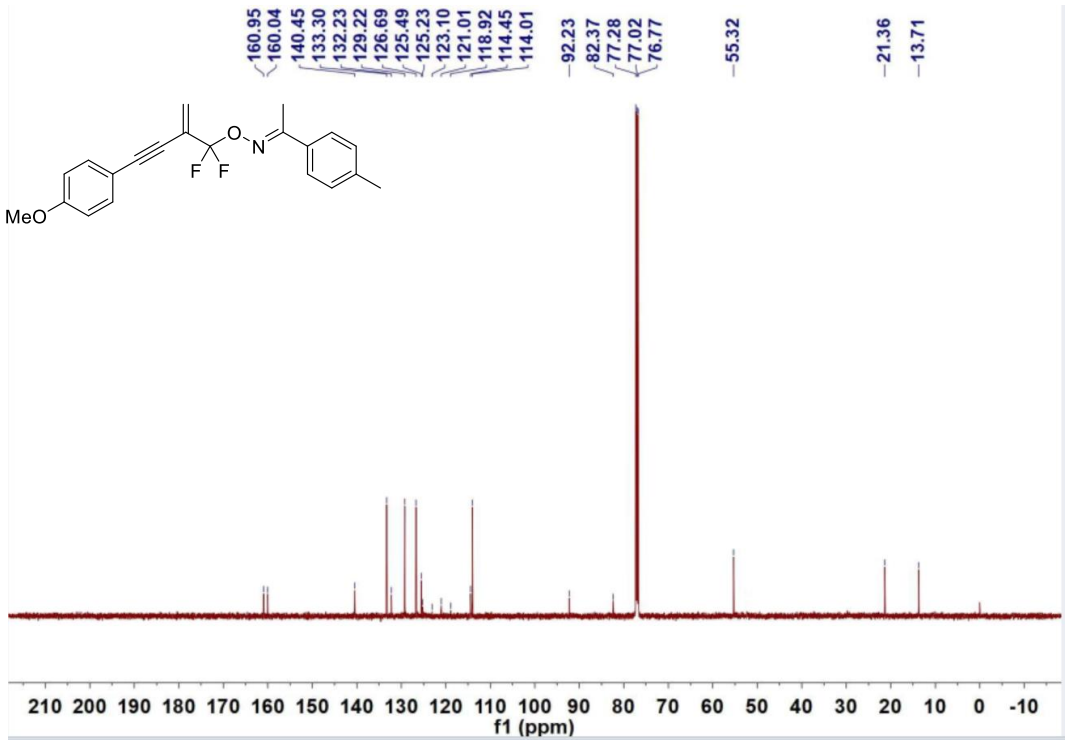


^{19}F-NMR (471 MHz, $CDCl_3$)

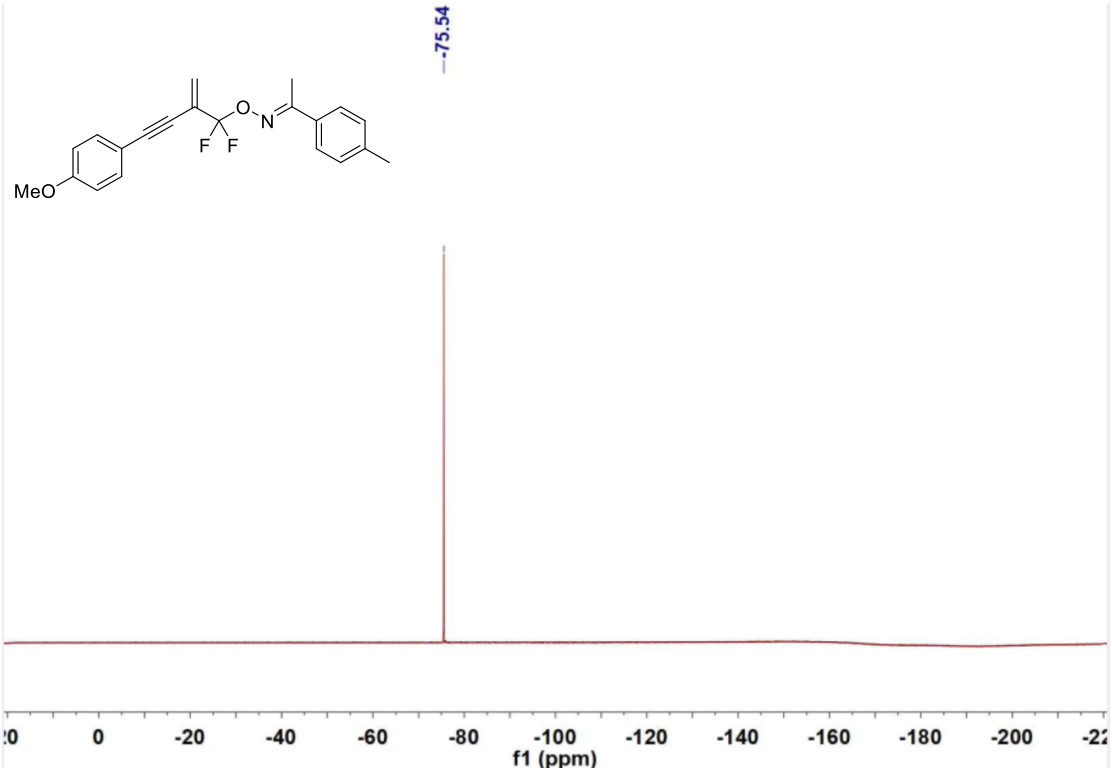
(*E*)-1-(*p*-tolyl)ethan-1-one *O*-(1,1-difluoro-4-(4-methoxyphenyl)-2-methylenebut-3-yn-1-yl) oxime (7aa)



^{1}H-NMR (500 MHz, $CDCl_3$)

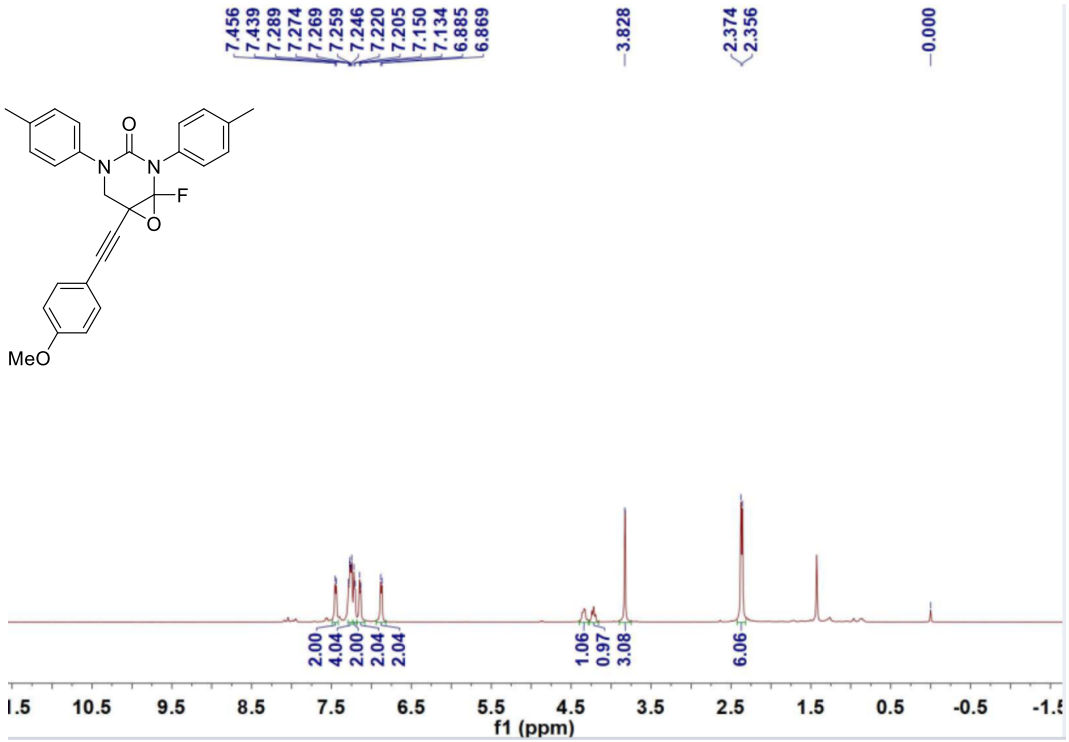


^{13}C-NMR (125 MHz, $CDCl_3$)

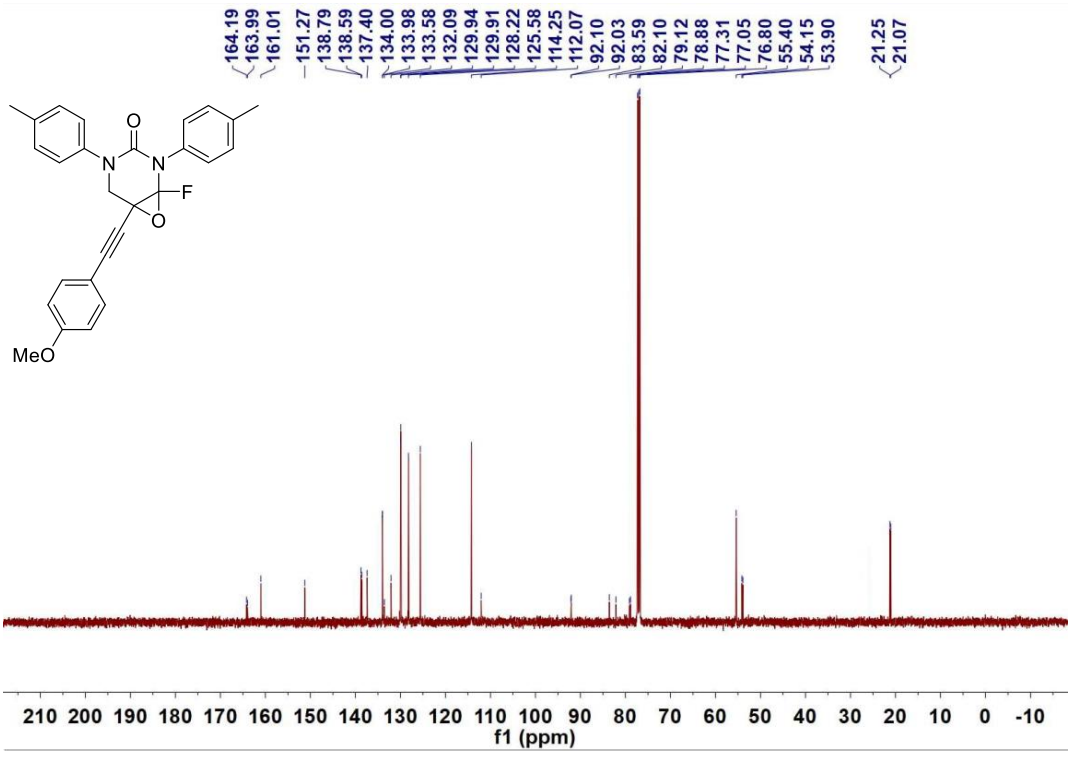


^{19}F-NMR (471 MHz, $CDCl_3$)

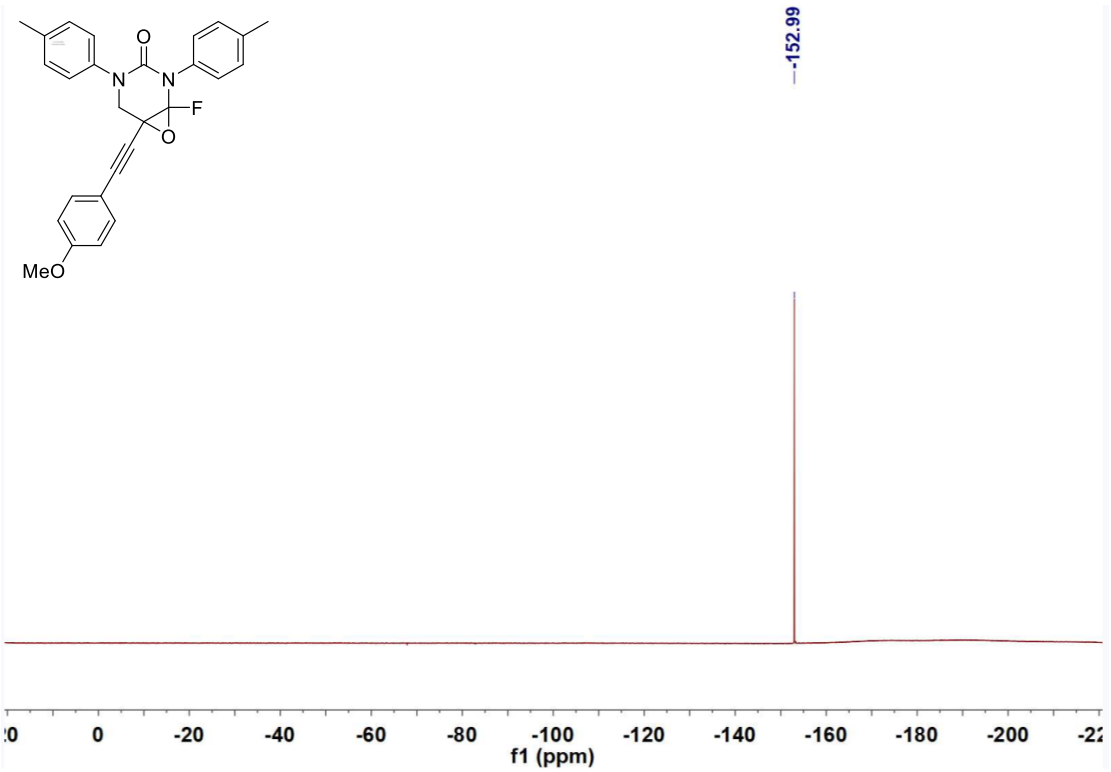
1-fluoro-6-((4-methoxyphenyl)ethynyl)-2,4-di-*p*-tolyl-7-oxa-2,4-diazabicyclo[4.1.0]heptan-3-one (11aa)



^{1}H-NMR (500 MHz, $CDCl_3$)

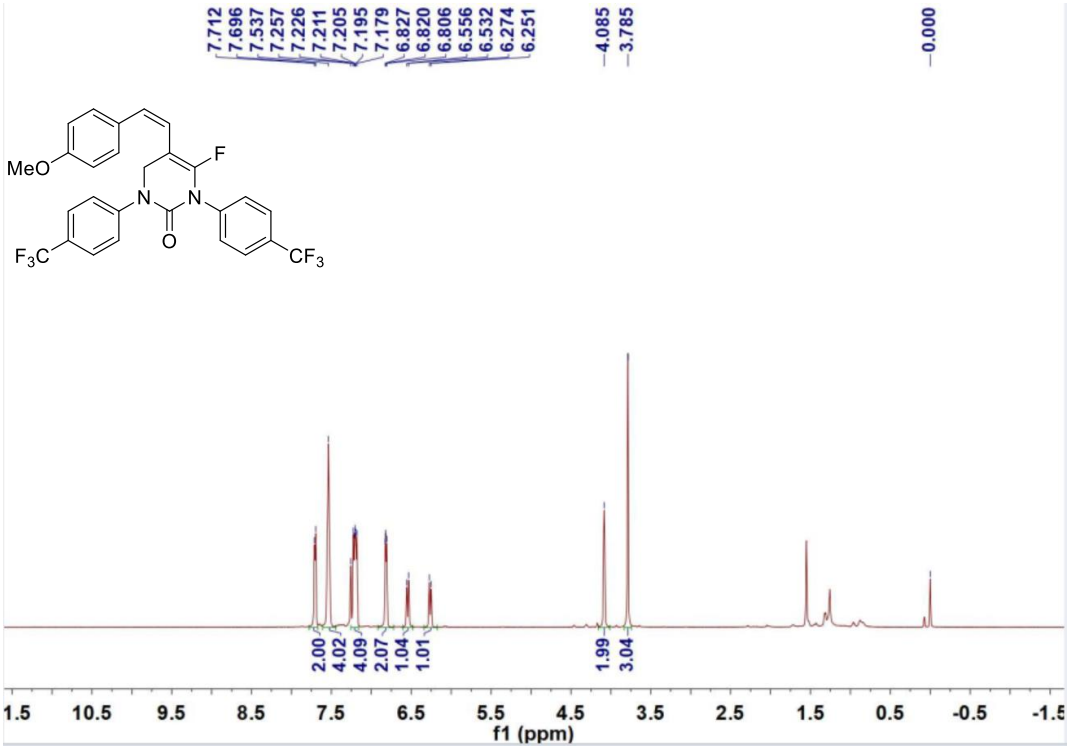


^{13}C-NMR (125 MHz, $CDCl_3$)

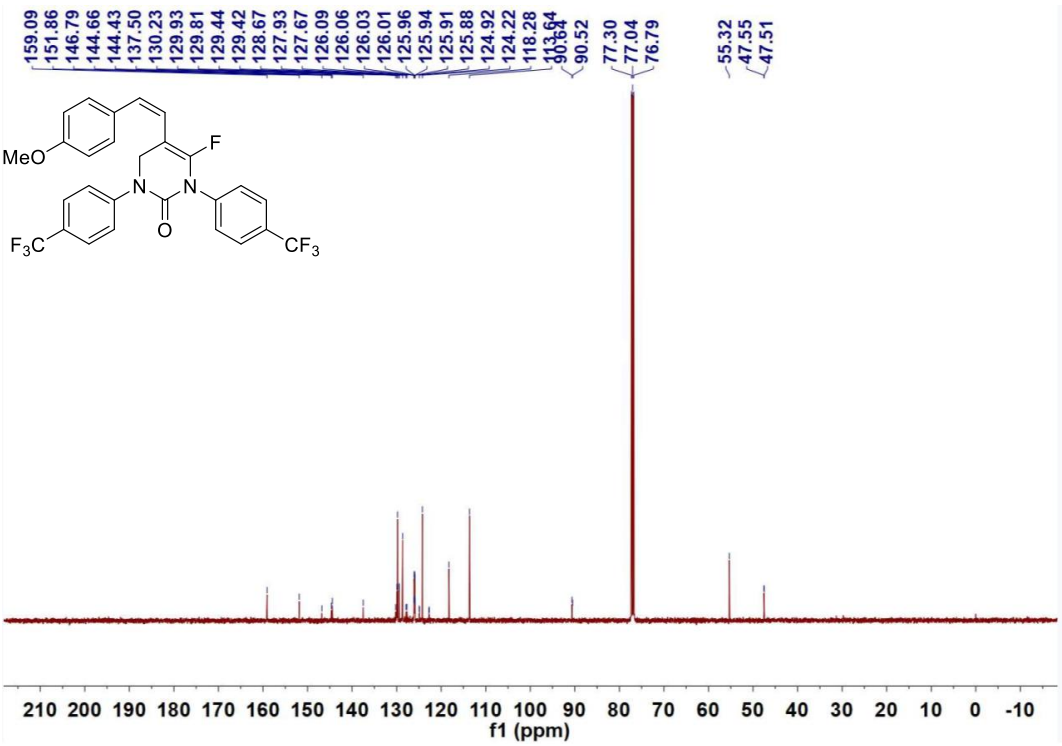


^{19}F-NMR (471 MHz, $CDCl_3$)

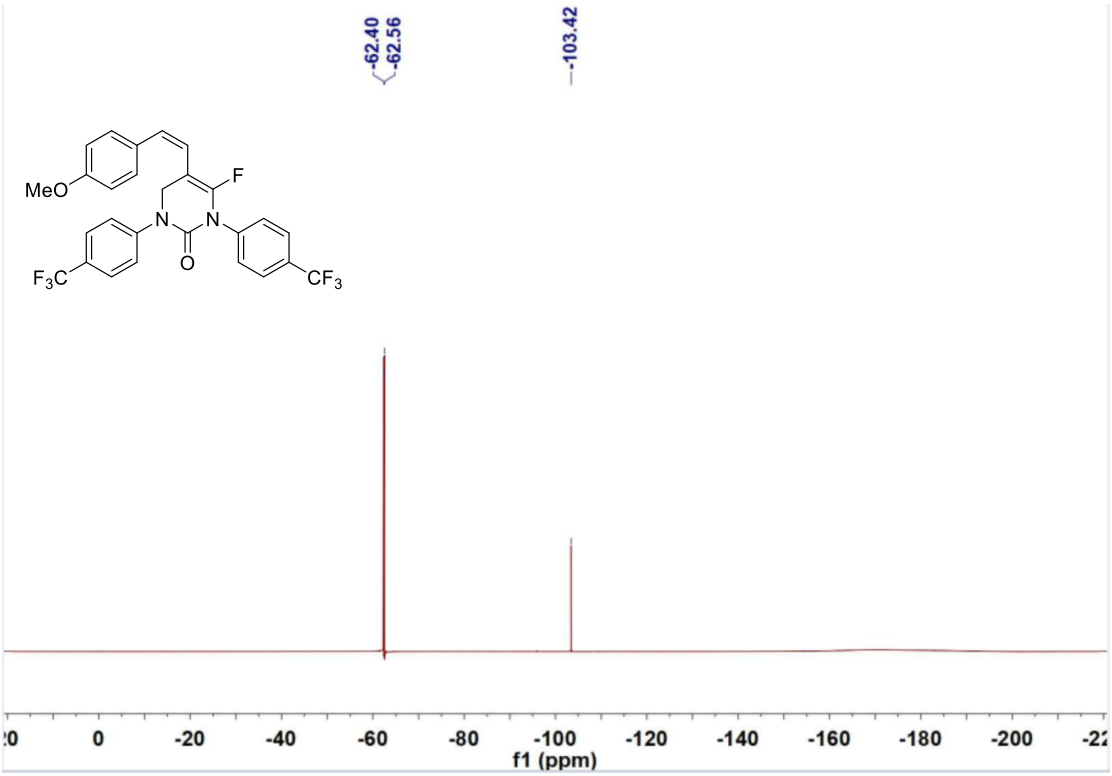
(*Z*)-6-fluoro-5-(4-methoxystyryl)-1,3-bis(4-(trifluoromethyl)phenyl)-3,4-dihydropyrimidin-2(1*H*)-one (12al)



^{1}H-NMR (500 MHz, $CDCl_3$)

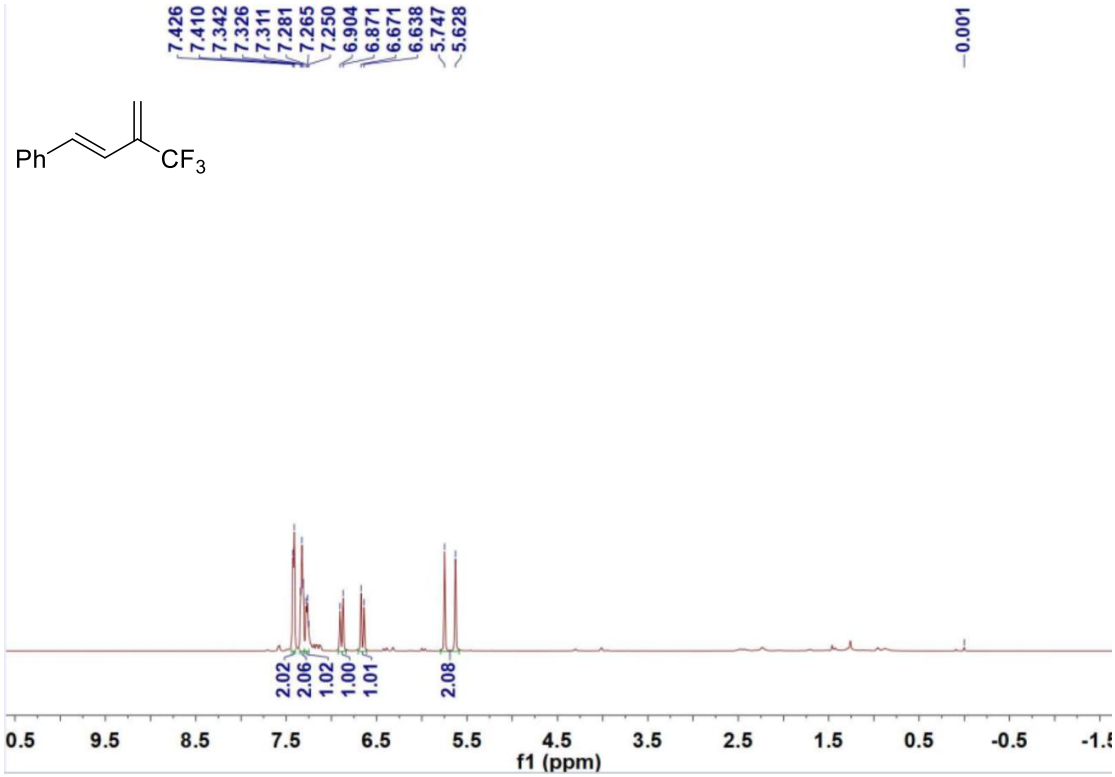


^{13}C-NMR (125 MHz, $CDCl_3$)

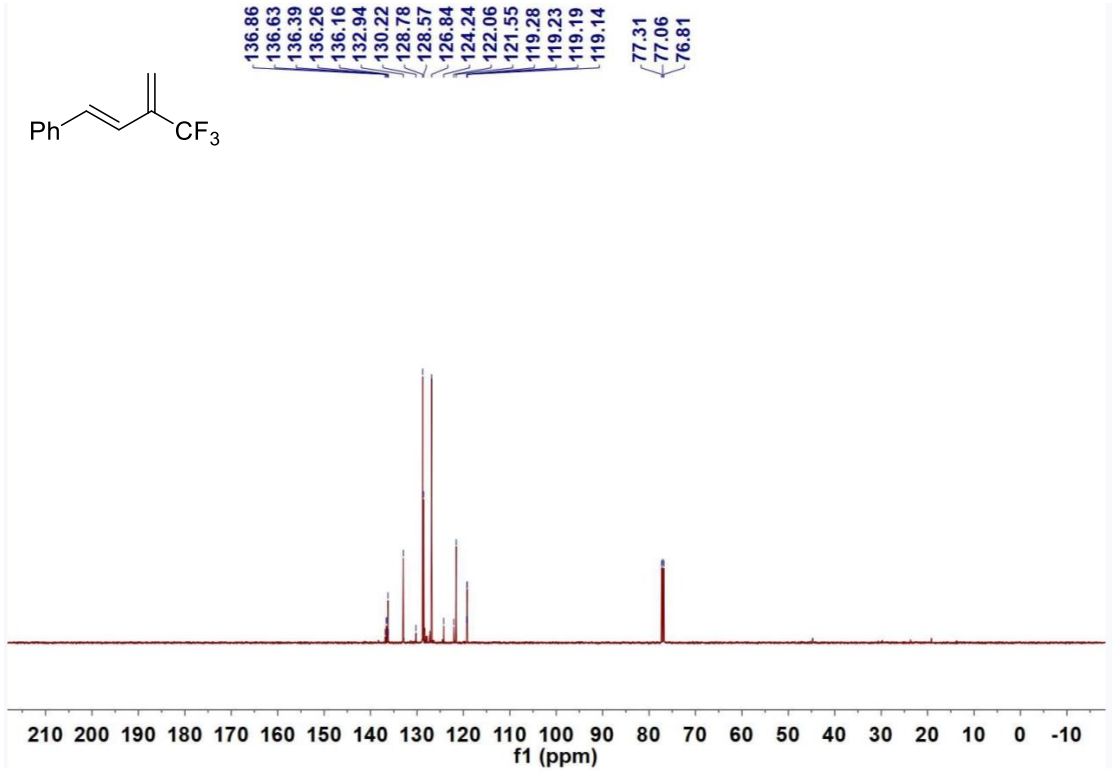


^{19}F-NMR (471 MHz, $CDCl_3$)

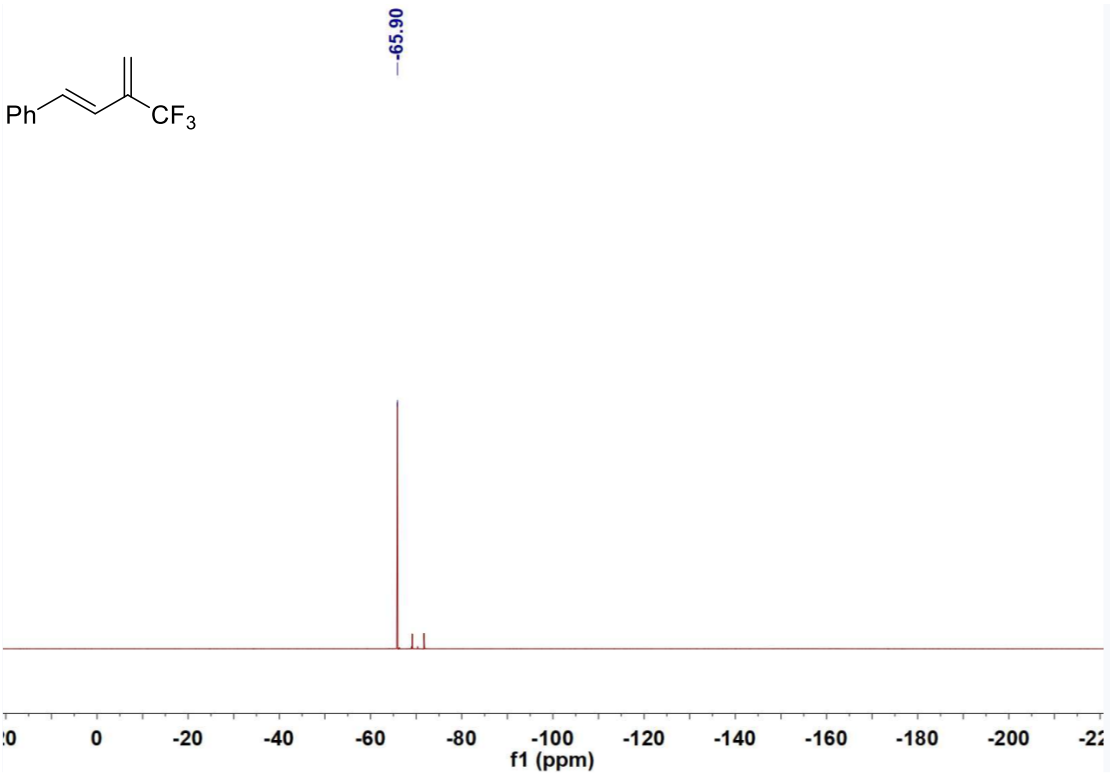
(*E*)-(3-(trifluoromethyl)buta-1,3-dien-1-yl)benzene (1y)



^{1}H-NMR (500 MHz, $CDCl_3$)

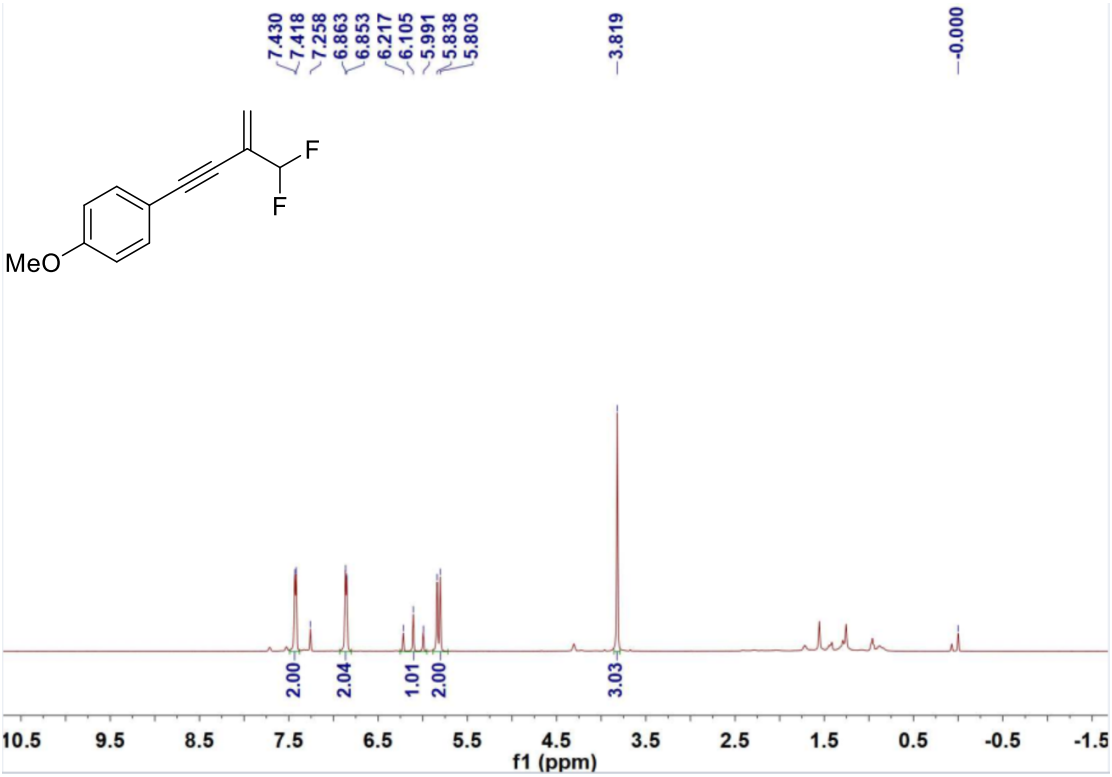


^{13}C-NMR (125 MHz, $CDCl_3$)

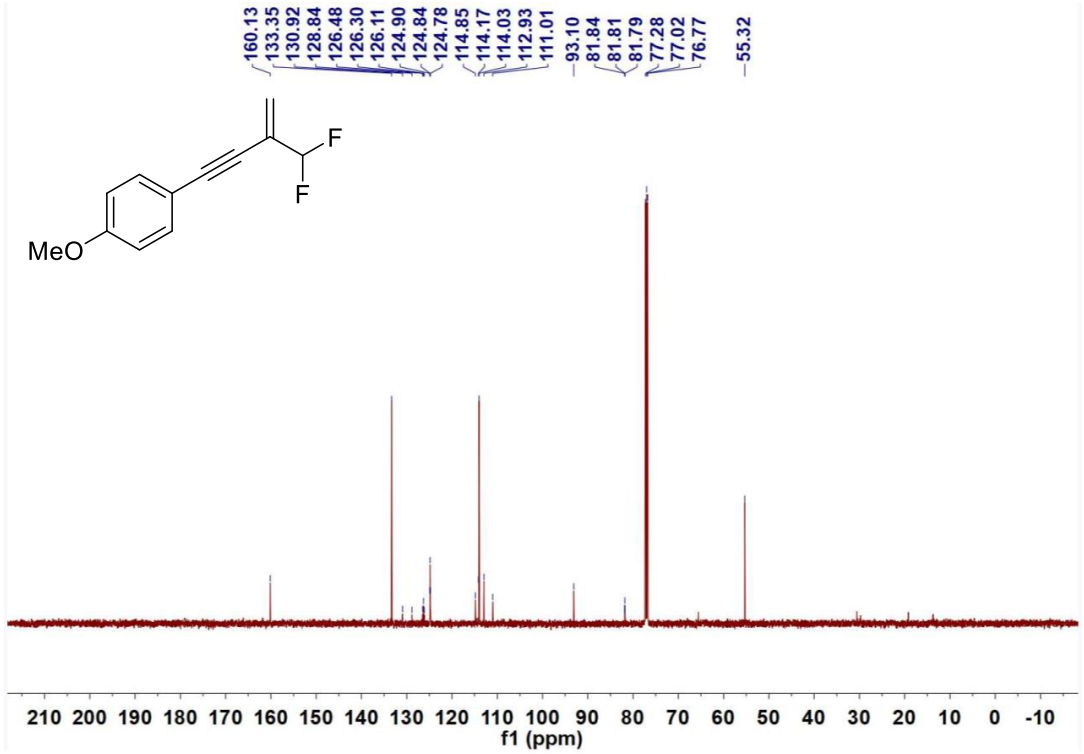


^{19}F-NMR (471 MHz, $CDCl_3$)

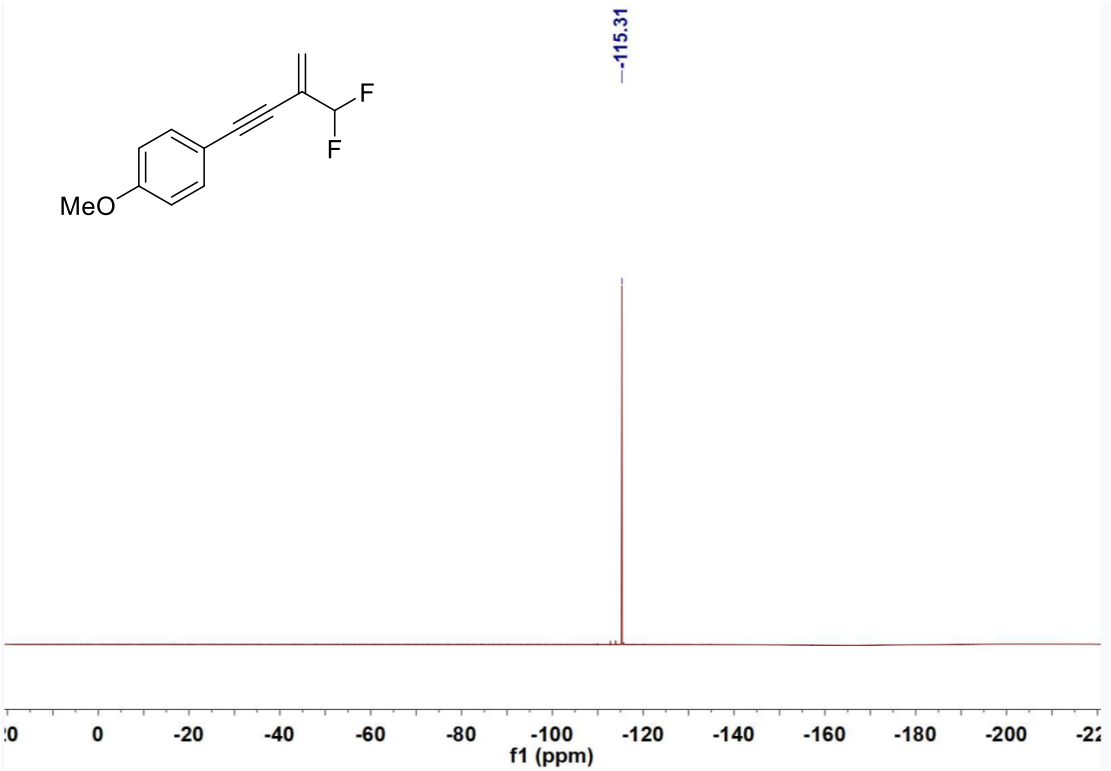
1-(3-(difluoromethyl)but-3-en-1-yn-1-yl)-4-methoxybenzene (1ac)



^{1}H-NMR (500 MHz, $CDCl_3$)

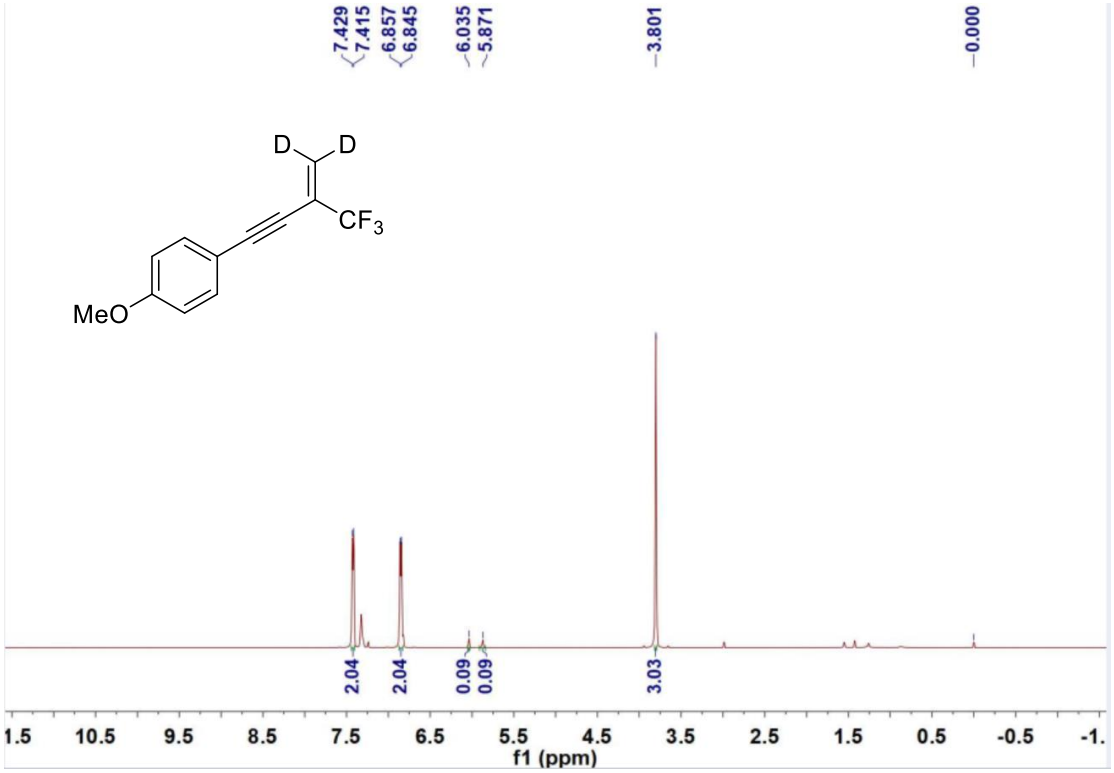


^{13}C-NMR (125 MHz, $CDCl_3$)

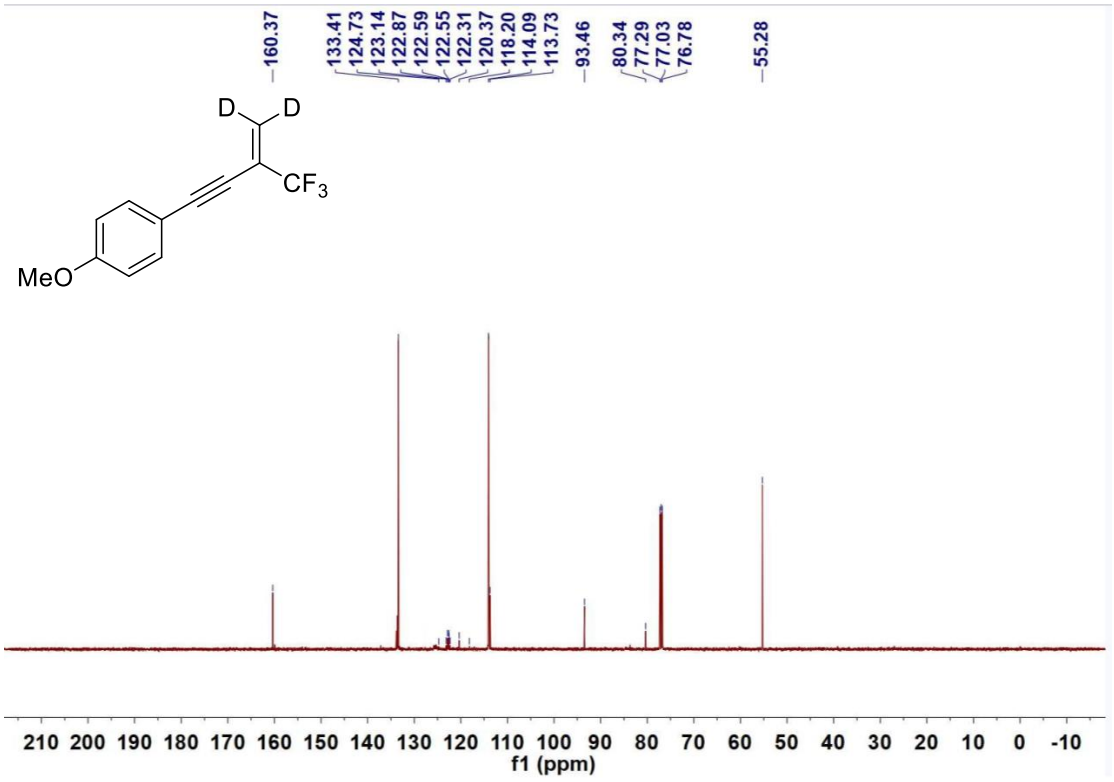


^{19}F-NMR (471 MHz, $CDCl_3$)

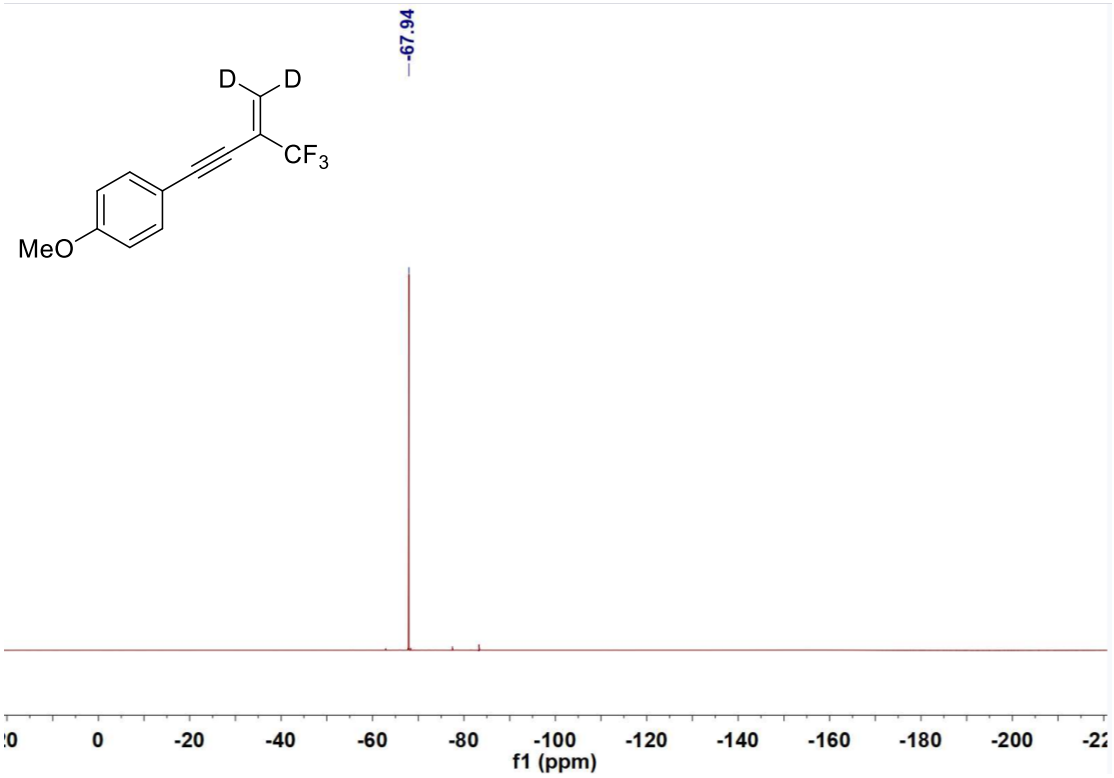
methoxy-4-(3-(trifluoromethyl)but-3-en-1-yn-1-yl-4,4-d_2)benzene (1a-d_2)



^{1}H-NMR (500 MHz, $CDCl_3$)

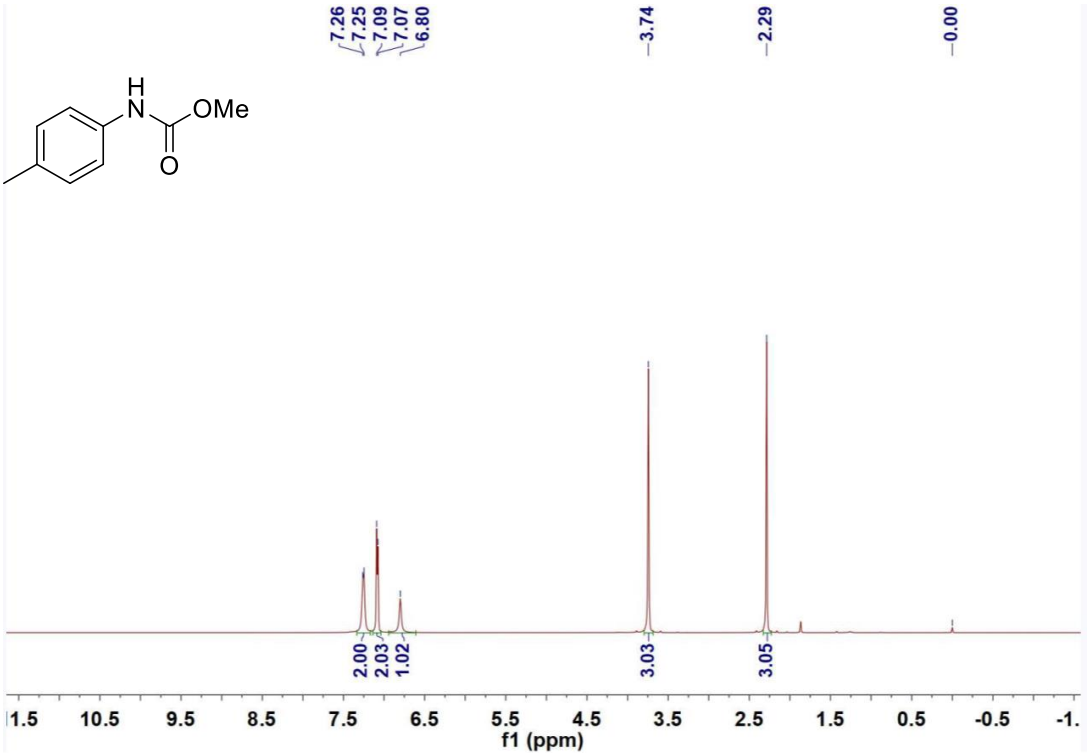


^{13}C-NMR (125 MHz, $CDCl_3$)

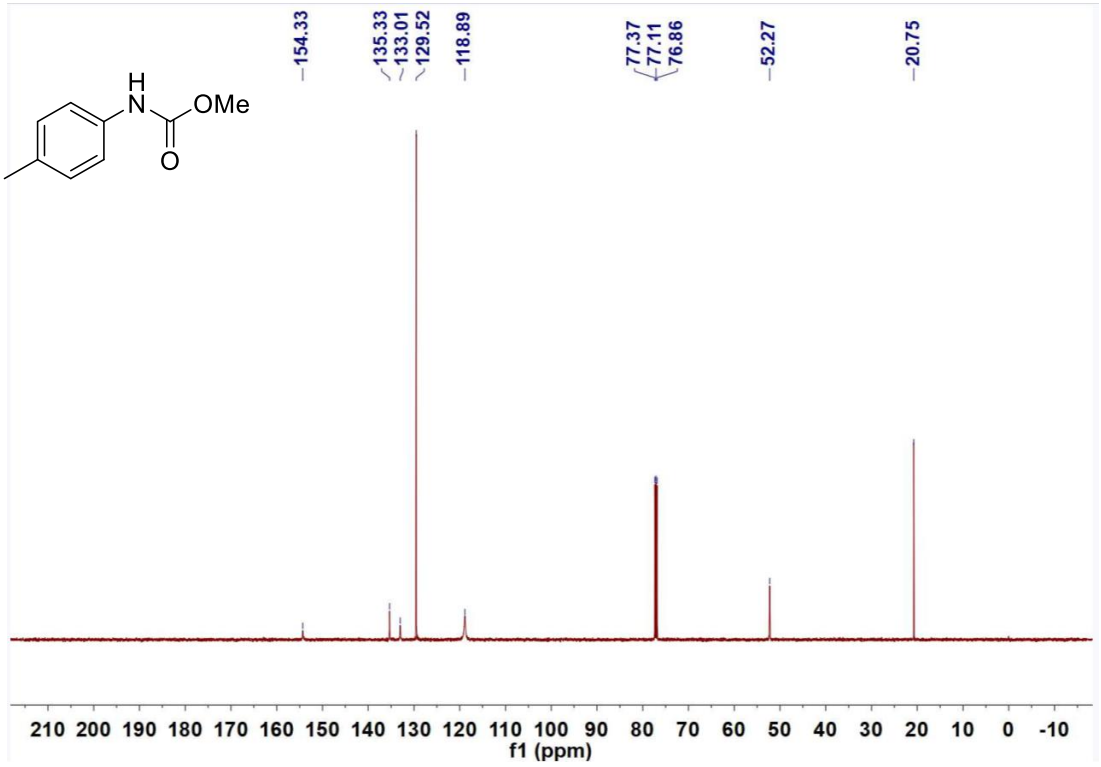


^{19}F-NMR (471 MHz, $CDCl_3$)

methyl *p*-tolylcarbamate (8a)



^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

(D) Computational Details

All calculations were carried out with the Gaussian 16 software program.[8] The geometries of all the species were fully optimized using the density functional theory (DFT) method with the M06-2X[9] functional. The 6-31G(d,p)[10,11] basis set was used for all atoms. Frequency calculations at the same level were performed to confirm each stationary point to be either a local minimum or a transition state (TS). The transition states were verified using intrinsic reaction coordinate (IRC)[12] calculations. The intermediates were characterized by all real frequencies. The SMD[13] solvation model with the DMF (n,n-dimethylformamide, ε = 37.219) solvent was used for all calculations. The energy unit of all structures was kcal/mol.

Cartesian Coordinates and Thermochemical Data (Energies in Hartree)

1a

Number of imaginary frequencies: 0

C	-0.38671000	0.40397300	0.00002100
C	1.02132500	0.15774800	0.00001500
C	1.51703600	-1.15924200	0.00000400
C	1.92959400	1.22334300	0.00001400
C	2.87873300	-1.39330700	0.00000000
H	0.82240300	-1.99303800	-0.00000100
C	3.30131900	0.99529400	0.00001000
H	1.55692900	2.24260500	0.00001400
C	3.78173600	-0.31897800	0.00000400
H	3.27313500	-2.40392500	-0.00000800
H	3.97937400	1.83996600	0.00000600
O	5.08981300	-0.65066400	0.00000500
C	6.03841900	0.40647900	-0.00002700
H	5.93650900	1.03088600	0.89412400
H	7.01935500	-0.06804800	-0.00001700
H	5.93650300	1.03084000	-0.89420900
C	-3.82395900	-0.40364500	-0.00000800

F	-5.13564700	-0.14590500	-0.00003400
F	-3.56393800	-1.16207900	1.07692300
F	-3.56389900	-1.16212000	-1.07689100
C	-1.57894200	0.62405200	0.00001000
C	-3.56635200	2.05496000	-0.00001300
H	-2.96291500	2.95563200	-0.00000300
H	-4.64549300	2.15625100	-0.00002500
C	-2.98935500	0.85017000	-0.00001200

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -837.0550406

Electronic Energy (0K) + ZPE = -836.870930

Enthalpy (298K) = -836.855522

Free Energy (298K) = -836.915185

2a

Number of imaginary frequencies: 0

O	4.11769800	-0.47625900	-0.00033100
C	3.03181500	-0.02923800	-0.00005800
N	1.98160000	0.55555000	0.00029700
C	0.60334700	0.30566700	0.00015600
C	-0.26846200	1.39180200	0.00003100
C	0.10008400	-0.99951300	0.00020500
C	-1.64313800	1.16973700	-0.00007100
H	0.13542000	2.39883000	0.00002300
C	-1.27312300	-1.20114300	0.00010200
H	0.78776400	-1.84004600	0.00032300
C	-2.16864500	-0.12375600	-0.00004200
H	-2.31848200	2.02082200	-0.00016000
H	-1.66046100	-2.21681100	0.00015300
C	-3.65430300	-0.36812300	-0.00017900

H	-3.95655400	-0.94267300	0.88111300
H	-4.20976300	0.57231500	-0.00088700
H	-3.95615800	-0.94381500	-0.88086500

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -438.8736949

Electronic Energy (0K) + ZPE = -438.741121

Enthalpy (298K) = -438.731270

Free Energy (298K) = -438.776382

Na^+

Number of imaginary frequencies: 0

Na	0.00000000	0.00000000	0.00000000

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -162.1554956

Electronic Energy (0K) + ZPE = -162.155496

Enthalpy (298K) = -162.153135

Free Energy (298K) = -162.169924

NaF

Number of imaginary frequencies: 0

F	0.00000000	0.00000000	-1.06719700
Na	0.00000000	0.00000000	0.87316100

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -262.1140101

Electronic Energy (0K) + ZPE = -262.112874

Enthalpy (298K) = -262.109344

Free Energy (298K) = -262.134077

A

Number of imaginary frequencies: 0

N	-0.32741800	-0.05168100	-0.00001300
C	-0.32907900	1.38681800	0.00005100
C	-1.60065700	-0.70377100	0.00005100
H	0.72177800	1.69294300	0.00002400
H	-0.82962700	1.81229200	-0.88534600
H	-0.82956000	1.81221100	0.88552500
H	-2.21270500	-0.45654000	0.88451700
H	-2.21280800	-0.45651700	-0.88433800
H	-1.41592000	-1.78395400	0.00002600
C	0.88113100	-0.85111000	-0.00005800
O	1.92029900	-0.15628600	-0.00007200

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -247.8333601

Electronic Energy (0K) + ZPE = -247.745089

Enthalpy (298K) = -247.738051

Free Energy (298K) = -247.774516

B

Number of imaginary frequencies: 0

N	0.31497300	-0.04704800	0.00000300
C	0.42994200	1.40827300	0.00000100
C	1.54907300	-0.81211200	-0.00000700
H	-0.56989700	1.84130100	0.00017400
H	0.97330900	1.73946700	0.89025100
H	0.97301200	1.73950100	-0.89041800
H	2.14103100	-0.57418000	-0.88949500
H	2.14116000	-0.57399100	0.88934600
H	1.30761800	-1.87539000	0.00012200
C	-0.86478600	-0.65573100	0.00002200
O	-1.98205200	-0.20124300	-0.00001300

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -247.74727

Electronic Energy (0K) + ZPE = -247.656169

Enthalpy (298K) = -247.649167

Free Energy (298K) = -247.685918

C

Number of imaginary frequencies: 0

C	0.30733500	0.63832300	0.29147600
C	-1.09687100	0.36079300	0.28007000
C	-1.58844500	-0.82534900	0.86118800
C	-1.99289600	1.24841700	-0.33192900
C	-2.94022800	-1.10618900	0.82615600
H	-0.90058600	-1.51361500	1.34412700
C	-3.35302100	0.97238900	-0.36420800
H	-1.61755100	2.16147600	-0.78239900
C	-3.83271200	-0.20981900	0.21607500
H	-3.33529000	-2.01306800	1.27092200
H	-4.02592900	1.67515400	-0.83971900
O	-5.12836600	-0.56889000	0.23730100
C	-6.07126300	0.30651200	-0.36908700
H	-5.86499100	0.42959600	-1.43731200
H	-7.04467500	-0.16510300	-0.23925600
H	-6.07217000	1.28574200	0.12046800
C	3.67929000	-0.29781500	0.11387900
F	4.96992500	-0.14216400	-0.14181000
F	3.16759100	-1.07271300	-0.89882000
F	3.55253400	-1.02966800	1.22159700
C	1.50552500	0.84019900	0.26271500
C	3.56974700	2.17029900	0.19127400

H	3.02066700	3.10247100	0.25937400
H	4.65100900	2.20810200	0.12086500
C	2.92598600	1.00113900	0.19592300
Na	0.93921000	-1.18292100	-1.48958000

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -999.2318902

Electronic Energy (0K) + ZPE = -999.047145

Enthalpy (298K) = -999.029678

Free Energy (298K) = -999.094021

D

Number of imaginary frequencies: 0

C	0.71458800	0.28765000	-0.00017900
C	-0.70260900	0.08698200	-0.00012100
C	-1.23978900	-1.21333300	-0.00023400
C	-1.57805600	1.17916600	0.00000700
C	-2.60849400	-1.40555700	-0.00018200
H	-0.57148100	-2.06843400	-0.00034000
C	-2.95688900	0.99369800	0.00003300
H	-1.17478300	2.18680700	0.00006400
C	-3.47806200	-0.30457300	-0.00004600
H	-3.03350200	-2.40376800	-0.00025600
H	-3.60829900	1.85925300	0.00010900
O	-4.79673900	-0.59623800	-0.00008000
C	-5.71101200	0.49008100	0.00038500
H	-5.58965000	1.11154400	-0.89354400
H	-6.70675300	0.04728700	0.00055100
H	-5.58916700	1.11116600	0.89451200
C	4.13701000	-0.44077300	0.00007100
F	5.45062500	-0.38651700	0.00030400

F	3.69755300	-1.67950300	0.00015600
C	1.91474500	0.45180200	-0.00023100
C	3.86943300	1.96405800	-0.00011200
H	3.21235400	2.82260700	-0.00049400
H	4.94070700	2.11695700	0.00007800
C	3.33261600	0.67424300	-0.00008800

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -737.1747127

Electronic Energy (0K) + ZPE = -736.997252

Enthalpy (298K) = -736.982240

Free Energy (298K) = -737.040782

TS_1

Number of imaginary frequencies: 1

C	1.17891300	-0.60698300	0.94369900
C	2.50727700	-0.25159500	0.55170300
C	2.97582800	-0.58188200	-0.73355300
C	3.35930000	0.42975900	1.42858500
C	4.25654500	-0.23726800	-1.12118400
H	2.32152700	-1.10811700	-1.42131600
C	4.65016500	0.77895900	1.04564900
H	3.00739300	0.68906400	2.42194200
C	5.10380000	0.44575600	-0.23521300
H	4.62860100	-0.48552600	-2.10959900
H	5.28724700	1.30494200	1.74621300
O	6.33449800	0.73892200	-0.70598800
C	7.22106300	1.43558300	0.15725500
H	7.43177800	0.85534700	1.06210500
H	8.14357900	1.57482100	-0.40590300
H	6.81480100	2.41343900	0.43761600

C	-1.92970000	-2.10857600	0.54710000
F	-3.14342000	-2.57669900	0.83074100
F	-1.18848500	-3.07869200	0.01267900
C	0.04907500	-0.90802100	1.26415800
C	-2.00064900	-0.79781900	2.61454300
H	-1.54509300	-0.10510100	3.31197800
H	-3.02840600	-1.10047200	2.77953600
C	-1.30002100	-1.28025800	1.56652800
O	-0.75758000	-2.04132100	-2.73613700
C	-1.46851500	-1.38452900	-2.05485200
N	-2.12298400	-1.05837000	-1.04087700
C	-2.71033800	0.21237400	-0.77437000
C	-3.93264200	0.26175500	-0.11218900
C	-2.04020000	1.38915800	-1.11271200
C	-4.49082000	1.50027300	0.19858500
H	-4.44422800	-0.65832800	0.14870900
C	-2.61639900	2.61429400	-0.80558800
H	-1.07691800	1.33252000	-1.61169200
C	-3.84848600	2.69157300	-0.14337900
H	-5.44695000	1.53728000	0.71296500
H	-2.09696500	3.53003400	-1.07576200
C	-4.45427900	4.03065000	0.18259100
H	-4.67082900	4.59377300	-0.73085100
H	-5.38591300	3.91745300	0.74130600
H	-3.76645300	4.63595400	0.78096800

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1176.0283095

Electronic Energy (0K) + ZPE = -1175.717198

Enthalpy (298K) = -1175.692536

Free Energy (298K) = -1175.776478

E

Number of imaginary frequencies: 0

C	1.01139300	-0.75928000	0.92953700
C	2.33399000	-0.38123600	0.54310900
C	2.70279800	-0.41925700	-0.81484200
C	3.27542100	0.03616400	1.49101200
C	3.97575500	-0.04934500	-1.20367500
H	1.97806700	-0.74402000	-1.55516800
C	4.55902300	0.40897300	1.10668800
H	2.99953400	0.06944500	2.54006100
C	4.91396700	0.36683700	-0.24632500
H	4.27274700	-0.07425800	-2.24676700
H	5.26739300	0.72807700	1.86138200
O	6.12941300	0.70632700	-0.72395100
C	7.11253800	1.12420000	0.21193900
H	7.33536200	0.33086400	0.93353400
H	8.00705200	1.34671300	-0.36930700
H	6.79338800	2.02495400	0.74702500
C	-2.16336800	-1.96661600	0.21373200
F	-3.46067700	-2.26511400	0.46503200
F	-1.57759200	-3.11020900	-0.18449000
C	-0.11827500	-1.07614400	1.23708000
C	-2.13129300	-1.34234600	2.62298800
H	-1.62807300	-0.97210600	3.50923000
H	-3.17397200	-1.62792900	2.70164800
C	-1.48033800	-1.44294600	1.46161500
O	-0.93099500	-2.21996700	-2.50547200
C	-1.45265200	-1.24614200	-2.05189100
N	-2.09596200	-1.00954500	-0.88487100

C	-2.50730400	0.34310500	-0.61088600
C	-3.78743100	0.60806400	-0.13427400
C	-1.60057200	1.38251600	-0.81902400
C	-4.15421200	1.92497000	0.13484900
H	-4.49442500	-0.20013800	0.01360100
C	-1.98957400	2.69141900	-0.56515200
H	-0.59985600	1.15685600	-1.17681700
C	-3.26892900	2.98372700	-0.07739600
H	-5.15412300	2.13113000	0.50600700
H	-1.28433900	3.50049000	-0.73534900
C	-3.66517000	4.40549100	0.21835200
H	-3.45305000	5.05690200	-0.63445900
H	-4.72941200	4.47872400	0.45264100
H	-3.10206800	4.79520500	1.07272000

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1176.0698748

Electronic Energy (0K) + ZPE = -1175.754994

Enthalpy (298K) = -1175.730919

Free Energy (298K) = -1175.812378

TS_2

Number of imaginary frequencies: 1

C	3.92625800	0.10983200	0.41338500
C	5.29447700	-0.10237100	0.05807400
C	5.67551600	-0.17633100	-1.29473600
C	6.27677100	-0.24033400	1.04630800
C	6.99803400	-0.38014600	-1.63895800
H	4.92203400	-0.07163200	-2.06876300
C	7.60968700	-0.44687400	0.70748400
H	5.99291100	-0.18524100	2.09238200

C	7.97556800	-0.51664000	-0.64130100
H	7.30378100	-0.43857400	-2.67826700
H	8.34746200	-0.55118200	1.49367300
O	9.23788800	-0.71161500	-1.07720600
C	10.25761600	-0.85674500	-0.09948500
H	10.34239800	0.04149100	0.52143100
H	11.18589100	-1.00423800	-0.65095500
H	10.07261300	-1.72618700	0.54052600
C	0.47920700	0.75308900	-0.13732400
F	0.57707400	2.04990000	-0.51114400
F	0.90650200	0.03108800	-1.20630800
C	2.76613100	0.28984200	0.71697900
C	0.93486500	0.56858500	2.30217200
H	1.60959800	0.44533300	3.14204500
H	-0.11560500	0.74687400	2.51084500
C	1.39282900	0.50355500	1.04812100
O	-0.51639400	-1.78213300	0.46034400
C	-1.24942100	-0.84318400	0.34667300
N	-0.91729000	0.46320100	0.10926400
C	-1.94280700	1.39675800	-0.27637800
C	-2.84114300	1.05726000	-1.28190800
C	-2.06432100	2.60669600	0.40573600
C	-3.87897600	1.93211900	-1.59683900
H	-2.73541200	0.10854400	-1.80098100
C	-3.09088600	3.47813500	0.06605900
H	-1.36293300	2.84950500	1.19811900
C	-4.01623000	3.15391900	-0.93501200
H	-4.58832300	1.66029300	-2.37339700
H	-3.18702200	4.42249400	0.59513200
C	-5.12286700	4.11232100	-1.28552400

H	-5.67781600	4.41318900	-0.39197400
H	-5.82443100	3.66498300	-1.99304900
H	-4.71814900	5.02332900	-1.73824700
O	-2.53651500	0.74996200	3.07528700
C	-2.94568200	-0.04386500	2.29741400
N	-2.87999800	-0.80819800	1.31339000
C	-3.93590100	-1.50309700	0.66025000
C	-5.21884200	-0.95526300	0.60846400
C	-3.65581700	-2.71169200	0.03149300
C	-6.22446100	-1.64140000	-0.05936900
H	-5.41400000	0.00199100	1.08367000
C	-4.67651400	-3.38072400	-0.64113800
H	-2.65426400	-3.12531900	0.07734000
C	-5.97210200	-2.86375500	-0.69519500
H	-7.22386000	-1.21589400	-0.09705600
H	-4.45823200	-4.32671800	-1.12864600
C	-7.07741700	-3.59277500	-1.41163600
H	-6.69808500	-4.48004000	-1.92329200
H	-7.55682000	-2.94670700	-2.15333700
H	-7.85416700	-3.91143500	-0.70898500

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1614.9227771

Electronic Energy (0K) + ZPE = -1614.475503

Enthalpy (298K) = -1614.441464

Free Energy (298K) = -1614.547452

F

Number of imaginary frequencies: 0

C	-3.66458800	-0.37445900	0.48190100
C	-4.99743200	-0.05354300	0.07755300

C	-5.31624200	0.07831600	-1.28686300
C	-6.00721000	0.13327600	1.02943400
C	-6.60541300	0.38572100	-1.67748100
H	-4.54099300	-0.06341700	-2.03294500
C	-7.30688600	0.44373800	0.64391100
H	-5.77124700	0.03418500	2.08415700
C	-7.61091700	0.57040000	-0.71601000
H	-6.86330000	0.48914800	-2.72621800
H	-8.06678700	0.58306200	1.40309500
O	-8.83687400	0.86657200	-1.19648400
C	-9.88374900	1.06010900	-0.25670000
H	-10.05719900	0.15534900	0.33566100
H	-10.77550600	1.28666200	-0.84066000
H	-9.66544400	1.89859200	0.41335200
C	-0.23791800	-1.29886100	0.09217100
F	-0.24174200	-2.63763000	-0.11548200
F	-0.66371400	-0.75226900	-1.07548800
C	-2.53539400	-0.64874400	0.82865500
C	-0.80330300	-1.08645000	2.49121600
H	-1.49725000	-0.92051100	3.30753100
H	0.22565200	-1.33931100	2.73096200
C	-1.20181300	-0.97286000	1.22018100
O	0.46421400	1.28383400	0.49504800
C	1.31649400	0.43729300	0.61351500
N	1.12537100	-0.90525300	0.35855600
C	2.19613400	-1.71890600	-0.16359900
C	2.90751500	-1.28720900	-1.27857300
C	2.51446700	-2.92557600	0.45711200
C	3.95803400	-2.06349300	-1.76401100
H	2.64465400	-0.34864800	-1.75989000

C	3.55002800	-3.69892300	-0.04984300
H	1.95356600	-3.24227500	1.33018100
C	4.29137400	-3.27849200	-1.16205400
H	4.51865300	-1.72199000	-2.62941200
H	3.79788800	-4.64164500	0.43058500
C	5.41829600	-4.12701900	-1.68704100
H	6.17573500	-4.28981100	-0.91400800
H	5.90092000	-3.65662600	-2.54636100
H	5.05301900	-5.11164300	-1.99523300
O	2.85445800	-0.89821100	2.68775300
C	3.24183200	0.03975000	2.05816500
N	2.64127700	0.75146800	1.07076500
C	3.34570000	1.87995400	0.51891400
C	4.63486400	1.66423600	0.03164900
C	2.77248000	3.14607800	0.47615200
C	5.35379700	2.72990600	-0.49399400
H	5.05934800	0.66468100	0.06673000
C	3.50171700	4.19892900	-0.07398100
H	1.77554200	3.30501100	0.86769400
C	4.79666900	4.01262800	-0.56158500
H	6.36017000	2.56292300	-0.86860600
H	3.05556100	5.18873700	-0.11061300
C	5.58293600	5.15367600	-1.14990700
H	5.02757200	6.09179800	-1.08451400
H	5.81243800	4.96564200	-2.20358000
H	6.53637200	5.28127300	-0.62828100

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1614.9684582

Electronic Energy (0K) + ZPE = -1614.517685

Enthalpy (298K) = -1614.484132

Free Energy (298K) = -1614.589244

TS_3

Number of imaginary frequencies: 1

C	-3.81833200	-0.03866900	-0.45545000
C	-5.18317600	0.06629800	-0.04240300
C	-5.50517000	0.33784700	1.30025300
C	-6.22206400	-0.10049100	-0.96618000
C	-6.82511500	0.43735700	1.69723700
H	-4.70837700	0.46866800	2.02532600
C	-7.55282900	-0.00241900	-0.57401800
H	-5.98466300	-0.31005400	-2.00426800
C	-7.85942100	0.26768800	0.76410600
H	-7.08467500	0.64623600	2.72972500
H	-8.33453300	-0.13609500	-1.31172700
O	-9.11427700	0.38257800	1.24833900
C	-10.19012800	0.20811100	0.33797900
H	-10.15932100	0.95645400	-0.46119600
H	-11.10218500	0.33795100	0.92003700
H	-10.17903300	-0.79518700	-0.10141400
C	-0.30185900	0.03240900	-0.09784000
F	-0.41741800	1.33930900	0.24999000
F	-0.66144700	-0.67240400	1.00602600
C	-2.66446900	-0.13180700	-0.81668900
C	-0.91137900	-0.48771800	-2.46809100
H	-1.64743500	-0.62994000	-3.25169600
H	0.13659000	-0.56036500	-2.73542200
C	-1.29445500	-0.23725300	-1.21400700
O	0.66580000	-2.46362200	-0.55867800
C	1.47275700	-1.55741000	-0.49046300

N	1.09025300	-0.22218700	-0.37807200
C	1.98675500	0.86932800	-0.65919400
C	2.34803700	1.75721200	0.35512400
C	2.54612600	0.99231700	-1.92665600
C	3.27036700	2.76117900	0.09243200
H	1.91787900	1.64338600	1.34480800
C	3.48009100	1.99610000	-2.17463200
H	2.27231100	0.29141600	-2.70940400
C	3.85735500	2.89236800	-1.17294300
H	3.55200500	3.44880600	0.88557300
H	3.92057700	2.08235900	-3.16387600
C	4.88038600	3.96611900	-1.42932100
H	5.79798100	3.76789500	-0.86547800
H	4.50979300	4.94521700	-1.11192400
H	5.13928000	4.02152500	-2.48892100
O	3.23038400	-4.01555400	-1.88379000
C	3.02602400	-3.60102300	-0.83399600
N	2.86005600	-1.74520800	-0.61240700
C	3.72127900	-1.25401300	0.36843900
C	5.04085600	-0.96959900	-0.01258300
C	3.32389600	-1.04754400	1.70140600
C	5.93553500	-0.45718400	0.91587700
H	5.33562500	-1.14069000	-1.04374300
C	4.22816300	-0.53496600	2.61654200
H	2.30483300	-1.27683200	2.00315100
C	5.54448800	-0.22544500	2.24051500
H	6.95342300	-0.22835200	0.61332600
H	3.91680400	-0.37040900	3.64450000
C	6.50169500	0.36270600	3.23892700
H	6.30516400	1.43247100	3.37196400

H	7.53700900	0.25143300	2.90936400
H	6.39084500	-0.11248000	4.21730000

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1614.9344512

Electronic Energy (0K) + ZPE = -1614.487650

Enthalpy (298K) = -1614.453570

Free Energy (298K) = -1614.560917

CO

Number of imaginary frequencies: 0

O	0.00000000	0.00000000	0.48474700
C	0.00000000	0.00000000	-0.64633000

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -113.2644906

Electronic Energy (0K) + ZPE = -113.256930

Enthalpy (298K) = -113.255985

Free Energy (298K) = -113.278417

G

Number of imaginary frequencies: 0

C	3.27456900	-1.88310200	-1.42057600
C	2.46434500	-0.77465400	-1.73058100
H	2.93767700	0.15061200	-2.04945000
C	1.09549700	-0.82797300	-1.59596200
H	0.49035200	0.04462700	-1.81698200
C	0.45791600	-2.02838700	-1.14222600
C	1.28940200	-3.16066700	-0.86526500
H	0.80501600	-4.06884300	-0.51979000
C	2.65466100	-3.07899800	-0.99535400
H	3.27535200	-3.93867000	-0.75802900

C	-1.68014300	-1.06309900	-1.10546200
C	-2.30864600	-1.18345600	1.31308100
C	-0.95494200	-1.64340200	1.81915200
C	-0.81011500	-2.84426200	2.38876000
H	-1.63697100	-3.54305200	2.43577500
H	0.14446100	-3.14371500	2.80704600
C	-3.41304000	0.37046400	-0.21464600
C	-4.68510500	-0.07664900	-0.55244300
H	-4.87302000	-1.14180500	-0.64790300
C	-5.70291400	0.85111800	-0.76471600
H	-6.69784600	0.50377300	-1.02895300
C	-5.46413900	2.22216300	-0.64327000
C	-4.17531200	2.64831000	-0.29770300
H	-3.97491200	3.71162700	-0.19489900
C	-3.15344300	1.73187000	-0.08161000
H	-2.15387500	2.05658500	0.19271900
C	0.11135900	-0.70073800	1.70170300
C	1.05281500	0.03738800	1.50095800
C	2.19220500	0.84057600	1.18728100
C	2.04040700	2.10574600	0.59263800
H	1.04467300	2.51096000	0.44196400
C	3.14945300	2.82582400	0.18841900
H	3.04587700	3.80139900	-0.27482800
C	4.43805100	2.29779800	0.36271100
C	4.60245300	1.04132200	0.95765300
H	5.58766400	0.61465400	1.10250900
C	3.48178000	0.32388500	1.36276900
H	3.60681300	-0.65898700	1.80696000
C	6.77303300	2.55756800	0.05846400
H	6.89181500	1.62170000	-0.49883600

H	7.43537100	3.31472100	-0.36053400
H	7.03054100	2.39094300	1.10984900
N	-0.84176500	-2.14529200	-0.86022300
N	-2.34962300	-0.57479000	0.01686900
O	-1.88382400	-0.59270700	-2.20982000
O	5.45526100	3.06997400	-0.07384100
F	-2.77549900	-0.25617800	2.19516700
C	4.76761100	-1.79951000	-1.51360100
C	-6.55772900	3.22908200	-0.88322300
H	5.15134600	-2.53091800	-2.23330100
H	5.22537700	-2.03417600	-0.54629600
H	5.09391400	-0.80385600	-1.82134800
H	-7.52067500	2.73818000	-1.04024600
H	-6.33834500	3.83767400	-1.76649700
H	-6.65352700	3.91277400	-0.03441600
F	-3.20106000	-2.21416300	1.37222600

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1501.693625

Electronic Energy (0K) + ZPE = -1501.253654

Enthalpy (298K) = -1501.222190

Free Energy (298K) = -1501.320202

TS_4

Number of imaginary frequencies: 1

C	-2.84514600	2.26445500	-1.14275400
C	-1.90987200	1.36322000	-1.67038900
H	-2.22334300	0.66493100	-2.44193600
C	-0.60716300	1.32245400	-1.20259000
H	0.09343000	0.59917000	-1.60951000
C	-0.18250000	2.21413700	-0.18781800

C	-1.12329000	3.13353500	0.33222000
H	-0.80209300	3.81407600	1.11529900
C	-2.42403800	3.14948500	-0.13562100
H	-3.13786200	3.85299400	0.28461300
C	2.06787800	1.44911600	-0.25280900
C	2.06446400	-0.41480600	1.45018700
C	0.79546200	0.18599800	1.97732600
C	0.90891700	1.46901000	2.42356400
H	1.88017300	1.87297300	2.68986400
H	0.03352800	2.02879500	2.73423700
C	3.88897100	-0.14926400	-0.11888500
C	5.10952600	0.17733100	0.45973900
H	5.13393200	0.85034400	1.31114100
C	6.28415900	-0.36282900	-0.06116900
H	7.23824300	-0.10715700	0.39115600
C	6.25255600	-1.22980300	-1.15509800
C	5.01029000	-1.54953700	-1.71961600
H	4.96991100	-2.22533300	-2.56998000
C	3.83349500	-1.01988300	-1.20685900
H	2.87127500	-1.27048600	-1.64261700
C	-0.44300200	-0.38208200	1.62451700
C	-1.54014900	-0.77880200	1.27467400
C	-2.82695200	-1.17025300	0.80927600
C	-3.03174700	-2.42144900	0.19569600
H	-2.20260800	-3.11594100	0.10749700
C	-4.27677800	-2.76299200	-0.29484300
H	-4.44691900	-3.72250700	-0.77173200
C	-5.35091300	-1.86447600	-0.18968800
C	-5.16283100	-0.61919400	0.42185100
H	-5.97853400	0.08732500	0.51584500

C	-3.90720900	-0.28079900	0.91276000
H	-3.75569800	0.68804600	1.37916300
C	-7.62924500	-1.39651600	-0.64059300
H	-7.42076800	-0.46676200	-1.18122700
H	-8.46122700	-1.91422200	-1.11708600
H	-7.89138500	-1.16444100	0.39714000
N	1.06011100	2.17713900	0.38821300
N	2.67666000	0.39275800	0.43976700
O	2.49144400	1.79150700	-1.34064000
O	-6.52342700	-2.28591700	-0.70537500
F	1.83736300	-1.66649800	0.96216100
C	-4.26150900	2.28988500	-1.64365200
C	7.51748800	-1.81368100	-1.72590800
H	-4.38080700	3.04926600	-2.42532800
H	-4.95937200	2.53795700	-0.83903100
H	-4.54703200	1.32544700	-2.07166800
H	8.39311400	-1.49579800	-1.15575200
H	7.65523600	-1.50212200	-2.76619100
H	7.48098000	-2.90745600	-1.71790300
F	2.97276300	-0.59201900	2.45507800

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1501.6766324

Electronic Energy (0K) + ZPE = -1501.236738

Enthalpy (298K) = -1501.206185

Free Energy (298K) = -1501.305108

H

Number of imaginary frequencies: 0

C	-2.47289300	5.49849500	-0.36239800
C	-2.63556700	4.53465800	-1.36618100

H	-2.98838900	4.84275400	-2.34736200
C	-2.34121000	3.19707600	-1.14248000
H	-2.46304800	2.46784800	-1.93449800
C	-1.88577700	2.78497500	0.11487600
C	-1.72087300	3.73032600	1.12607000
H	-1.37604300	3.42393600	2.10884600
C	-2.00722500	5.07286700	0.88084800
H	-1.87111200	5.79781500	1.67882700
C	-2.41560900	0.42346300	-0.00536800
C	-0.67044200	-1.28224800	0.58147900
C	0.24328100	-0.12321600	0.77139200
C	-0.42366600	1.12346200	1.25223700
H	-0.77998600	0.99678300	2.28505300
H	0.27546700	1.95865700	1.22734600
C	-2.93613500	-1.95246600	0.06556500
C	-3.58695100	-2.55548300	1.13488600
H	-3.40449500	-2.19645700	2.14269200
C	-4.46565200	-3.61171500	0.89819000
H	-4.97447800	-4.08288200	1.73443600
C	-4.70106500	-4.07349000	-0.39796600
C	-4.03031200	-3.45336100	-1.46097000
H	-4.20055200	-3.80417800	-2.47554500
C	-3.14898900	-2.40425700	-1.23632200
H	-2.62570400	-1.92812100	-2.05946800
C	1.58027000	-0.25569700	0.55210300
C	2.79200800	-0.36871400	0.35156600
C	4.17563600	-0.50293000	0.11805800
C	4.71113000	-1.72833700	-0.34194100
H	4.04629900	-2.56819000	-0.51484700
C	6.06425200	-1.85624600	-0.56939300

H	6.48783400	-2.79046000	-0.92234300
C	6.92734400	-0.76876400	-0.34611000
C	6.41224600	0.45282800	0.10940500
H	7.06127500	1.30153200	0.28672900
C	5.04993700	0.57811200	0.33723800
H	4.64859500	1.52247500	0.69017900
C	9.14239900	0.07473900	-0.38397900
H	8.90661700	0.92873000	-1.02740800
H	10.12663400	-0.31411300	-0.64299200
H	9.14018400	0.39289800	0.66367500
N	-1.54499200	1.42432900	0.35556000
N	-2.00737400	-0.88241400	0.31764400
O	-3.49075800	0.61622600	-0.54273100
O	8.22999300	-0.99470800	-0.59670900
F	-0.21709500	-2.10264000	-0.41301700
C	-2.79552200	6.94467900	-0.63022100
C	-5.65140400	-5.21100800	-0.66218600
H	-3.85834300	7.07325200	-0.85956300
H	-2.55748300	7.56906800	0.23397800
H	-2.23172900	7.32079800	-1.48965700
H	-6.07697100	-5.59592800	0.26710400
H	-6.47445100	-4.88895700	-1.30792500
H	-5.14226700	-6.03413200	-1.17313000
F	-0.66850900	-2.09349000	1.69174600

SMD-UM06-2X/6-31G(d,p)

Electronic Energy (0K) = -1501.7311821

Electronic Energy (0K) + ZPE = -1501.288068

Enthalpy (298K) = -1501.257187

Free Energy (298K) = -1501.355368

3aa

Number of imaginary frequencies: 0

C	-3.22486400	5.24486800	-0.24649300
C	-3.58584600	4.23115000	-1.14406000
H	-4.25006900	4.46511900	-1.97235700
C	-3.10267200	2.93777400	-1.01006200
H	-3.38625300	2.17165500	-1.72177400
C	-2.24517500	2.61835300	0.04949200
C	-1.87530100	3.61534900	0.95089000
H	-1.21414000	3.38864400	1.78077000
C	-2.36049200	4.91388700	0.79519200
H	-2.05973700	5.67902500	1.50575500
C	-2.55527500	0.22436300	0.07195000
C	-0.54549500	-1.13278600	0.06996500
C	0.27921000	-0.10868500	0.32156400
C	-0.37310700	1.17266200	0.77608400
H	-0.43188200	1.21185100	1.87242800
H	0.22272300	2.02323100	0.44070600
C	-2.74240000	-2.21438000	0.07594900
C	-3.46182500	-2.58995500	1.20805900
H	-3.39177700	-1.99154900	2.11101900
C	-4.26136700	-3.72522100	1.16362800
H	-4.82660500	-4.01730100	2.04474100
C	-4.34474100	-4.50500300	0.00329900
C	-3.60972000	-4.11140700	-1.11717800
H	-3.66281900	-4.70318500	-2.02660800
C	-2.81457200	-2.96789400	-1.08993100
H	-2.25330300	-2.66001600	-1.96666000
C	1.68723800	-0.21446500	0.20566000
C	2.89829000	-0.26298300	0.13169500

C	4.32359300	-0.33293900	0.03664900
C	4.96048300	-1.53874500	-0.31203500
H	4.36144000	-2.42150600	-0.51136000
C	6.33840700	-1.60421800	-0.40246800
H	6.83809600	-2.52919900	-0.67095500
C	7.12015300	-0.46811700	-0.14640100
C	6.50095100	0.73676400	0.20111500
H	7.08338100	1.62739800	0.40394300
C	5.11353800	0.79532200	0.28970100
H	4.63497800	1.73149400	0.55928700
C	9.28076600	0.49532300	-0.01252900
H	9.06261800	1.30788100	-0.71413700
H	10.30705800	0.15843300	-0.15729000
H	9.15949500	0.85884700	1.01376100
N	-1.70779700	1.30398000	0.17710900
N	-1.92162700	-1.03452300	0.12520500
O	-3.75839600	0.29843200	-0.08576800
O	8.45680700	-0.63348900	-0.25971800
F	-0.10307600	-2.33499800	-0.27884600
C	-3.76262500	6.64138400	-0.41237000
C	-5.20776900	-5.73837900	-0.02233200
H	-4.84921200	6.66075600	-0.27882900
H	-3.32009500	7.32458700	0.31616600
H	-3.55338300	7.02705900	-1.41498000
H	-6.24600700	-5.49335500	0.22176800
H	-5.18978700	-6.21386300	-1.00537600
H	-4.86466000	-6.46890900	0.71708900

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -1401.9359995

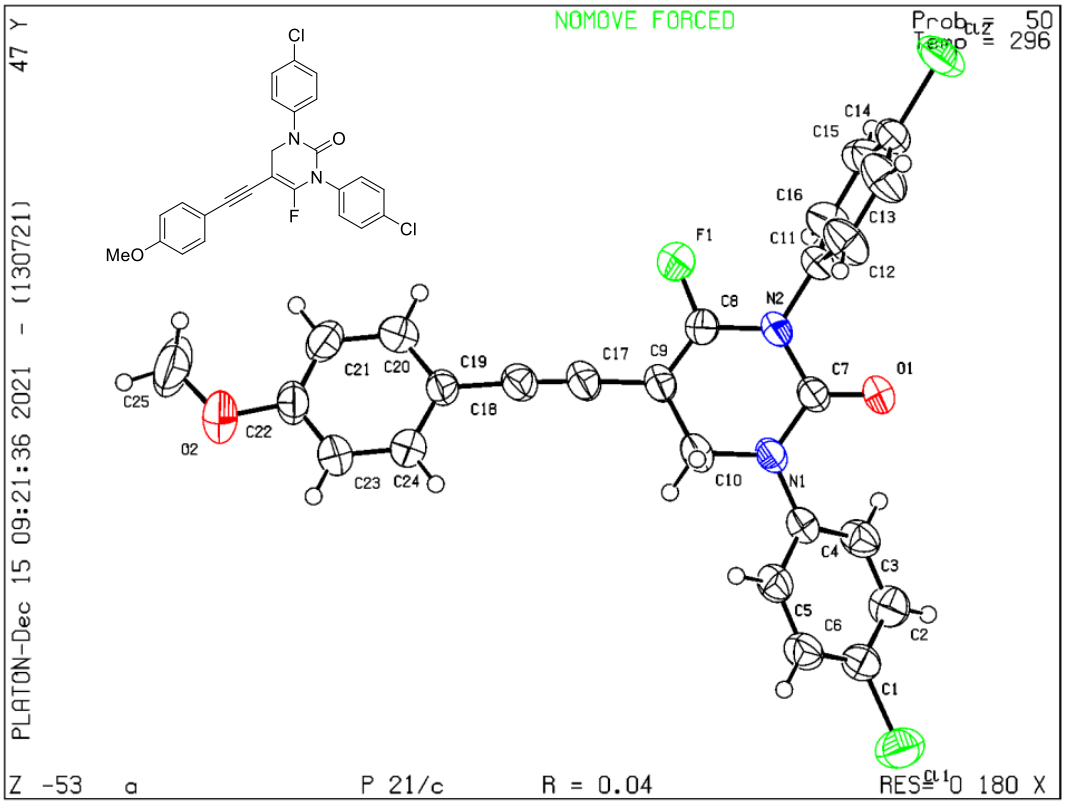
Electronic Energy (0K) + ZPE = -1401.494847

Enthalpy (298K) = -1401.464941

Free Energy (298K) = -1401.560355

(E) The X-ray Single-Crystal Diffraction Analysis of 3af (CCDC: 2128916)

Method for crystal growth: In a vial (25 mL) the product **3af** was dissolved in dichloromethane (0.2 mL), followed by addtion of petroleum ether (2 mL). Then, the big was covered with rubber cap (Don't seal it completely) and was set aside till the crystal formed. The crystal data for **3af** were integrated using the program SAINT and corrected for absorption effects using the program SADABS.9 The structures were solved by direct methods and refined on F_2 by full-matrix least squares using SHELXTL -2014 software.



The thermal ellipsoid plot of 3af with 30% displacement ellipsoids

Table S1. Crystal data and structure refinement for A.

Identification code	a
Empirical formula	$C_{25}H_{17}Cl_2FN_2O_2$
Formula weight	467.30
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 11.1466(16) A alpha = 90 deg.
	b = 23.276(3) A beta = 106.176(2) deg.
	c = 8.8545(12) A gamma = 90 deg.
Volume	2206.3(5) A^3
Z, Calculated density	4, 1.407 Mg/m^3
Absorption coefficient	0.328 mm^-1
F(000)	960
Crystal size	0.220 x 0.160 x 0.150 mm
Theta range for data collection	2.094 to 25.499 deg.
Limiting indices	-13<=h<=12, -28<=k<=18, -10<=l<=9
Reflections collected / unique	11525 / 4093 [R(int) = 0.0259]
Completeness to theta = 25.242	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4093 / 0 / 290
Goodness-of-fit on F^2	1.195
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1221
R indices (all data)	R1 = 0.0729, wR2 = 0.1356
Extinction coefficient	n/a
Largest diff. peak and hole	0.196 and -0.237 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for A.

U(eq) is defined as one third of the trace of the orthogonalized

Uij tensor.

	x	y	z	U(eq)
C(1)	8099(2)	10466(1)	502(3)	51(1)
C(2)	8662(2)	10376(1)	2079(3)	58(1)
C(3)	9256(2)	9865(1)	2571(3)	54(1)
C(4)	9311(2)	9438(1)	1502(2)	42(1)
C(5)	8718(2)	9538(1)	-77(2)	51(1)
C(6)	8112(2)	10047(1)	-572(3)	55(1)
C(7)	10987(2)	8877(1)	3226(2)	44(1)
C(8)	10789(2)	7843(1)	3009(2)	45(1)
C(9)	9857(2)	7848(1)	1703(2)	45(1)
C(10)	9521(2)	8415(1)	904(3)	54(1)
C(11)	12642(2)	8273(1)	4840(2)	44(1)
C(12)	13725(2)	8352(1)	4415(3)	68(1)
C(13)	14864(2)	8285(1)	5511(3)	75(1)
C(14)	14908(2)	8143(1)	7021(3)	59(1)
C(15)	13832(3)	8068(1)	7460(3)	66(1)
C(16)	12694(2)	8138(1)	6355(3)	57(1)
C(17)	9190(2)	7348(1)	1008(3)	50(1)
C(18)	8614(2)	6947(1)	338(3)	50(1)
C(19)	7865(2)	6482(1)	-475(3)	45(1)
C(20)	7838(2)	5947(1)	220(3)	57(1)
C(21)	7066(2)	5511(1)	-538(3)	61(1)
C(22)	6300(2)	5603(1)	-2037(3)	61(1)
C(23)	6333(2)	6125(1)	-2763(3)	62(1)

C(24)	7098(2)	6556(1)	-2008(3)	54(1)
C(25)	5393(3)	4667(1)	-2308(5)	114(1)
Cl(1)	7381(1)	11123(1)	-132(1)	78(1)
Cl(2)	16340(1)	8064(1)	8417(1)	104(1)
N(1)	9921(2)	8900(1)	1984(2)	43(1)
N(2)	11448(2)	8329(1)	3669(2)	47(1)
O(1)	11516(2)	9293(1)	3937(2)	59(1)
O(2)	5487(2)	5209(1)	-2939(3)	99(1)
F(1)	11191(1)	7365(1)	3815(1)	60(1)

Table S3. Bond lengths [A] and angles [deg] for A.

C(1)-C(6)	1.364(3)
C(1)-C(2)	1.378(3)
C(1)-Cl(1)	1.745(2)
C(2)-C(3)	1.372(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.386(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.390(3)
C(4)-N(1)	1.431(3)
C(5)-C(6)	1.374(3)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-O(1)	1.215(2)
C(7)-N(1)	1.377(3)
C(7)-N(2)	1.390(3)
C(8)-C(9)	1.322(3)
C(8)-F(1)	1.331(2)
C(8)-N(2)	1.386(3)
C(9)-C(17)	1.424(3)
C(9)-C(10)	1.496(3)
C(10)-N(1)	1.466(3)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(16)	1.364(3)
C(11)-C(12)	1.373(3)
C(11)-N(2)	1.447(3)
C(12)-C(13)	1.375(4)
C(12)-H(12)	0.9300

C(13)-C(14)	1.365(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.371(4)
C(14)-Cl(2)	1.736(2)
C(15)-C(16)	1.379(3)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(18)	1.193(3)
C(18)-C(19)	1.433(3)
C(19)-C(20)	1.393(3)
C(19)-C(24)	1.398(3)
C(20)-C(21)	1.378(3)
C(20)-H(20)	0.9300
C(21)-C(22)	1.380(3)
C(21)-H(21)	0.9300
C(22)-O(2)	1.377(3)
C(22)-C(23)	1.380(3)
C(23)-C(24)	1.364(3)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-O(2)	1.396(4)
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(6)-C(1)-C(2)	120.5(2)
C(6)-C(1)-Cl(1)	119.65(17)
C(2)-C(1)-Cl(1)	119.85(19)
C(3)-C(2)-C(1)	119.8(2)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1

C(2)-C(3)-C(4)	120.9(2)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	117.9(2)
C(3)-C(4)-N(1)	122.04(18)
C(5)-C(4)-N(1)	120.04(19)
C(6)-C(5)-C(4)	121.3(2)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(1)-C(6)-C(5)	119.6(2)
C(1)-C(6)-H(6)	120.2
C(5)-C(6)-H(6)	120.2
O(1)-C(7)-N(1)	124.6(2)
O(1)-C(7)-N(2)	119.85(18)
N(1)-C(7)-N(2)	115.52(18)
C(9)-C(8)-F(1)	122.8(2)
C(9)-C(8)-N(2)	123.9(2)
F(1)-C(8)-N(2)	113.32(17)
C(8)-C(9)-C(17)	124.1(2)
C(8)-C(9)-C(10)	116.9(2)
C(17)-C(9)-C(10)	119.02(19)
N(1)-C(10)-C(9)	112.41(18)
N(1)-C(10)-H(10A)	109.1
C(9)-C(10)-H(10A)	109.1
N(1)-C(10)-H(10B)	109.1
C(9)-C(10)-H(10B)	109.1
H(10A)-C(10)-H(10B)	107.9
C(16)-C(11)-C(12)	120.1(2)
C(16)-C(11)-N(2)	120.2(2)
C(12)-C(11)-N(2)	119.69(19)

C(11)-C(12)-C(13)	120.1(2)
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	119.5(2)
C(14)-C(13)-H(13)	120.3
C(12)-C(13)-H(13)	120.3
C(13)-C(14)-C(15)	120.9(2)
C(13)-C(14)-Cl(2)	119.9(2)
C(15)-C(14)-Cl(2)	119.2(2)
C(14)-C(15)-C(16)	119.2(2)
C(14)-C(15)-H(15)	120.4
C(16)-C(15)-H(15)	120.4
C(11)-C(16)-C(15)	120.2(2)
C(11)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(18)-C(17)-C(9)	175.9(3)
C(17)-C(18)-C(19)	177.1(2)
C(20)-C(19)-C(24)	117.1(2)
C(20)-C(19)-C(18)	122.3(2)
C(24)-C(19)-C(18)	120.6(2)
C(21)-C(20)-C(19)	122.0(2)
C(21)-C(20)-H(20)	119.0
C(19)-C(20)-H(20)	119.0
C(20)-C(21)-C(22)	119.3(2)
C(20)-C(21)-H(21)	120.4
C(22)-C(21)-H(21)	120.4
O(2)-C(22)-C(23)	114.5(2)
O(2)-C(22)-C(21)	125.8(2)
C(23)-C(22)-C(21)	119.7(2)
C(24)-C(23)-C(22)	120.8(2)

C(24)-C(23)-H(23)	119.6
C(22)-C(23)-H(23)	119.6
C(23)-C(24)-C(19)	121.0(2)
C(23)-C(24)-H(24)	119.5
C(19)-C(24)-H(24)	119.5
O(2)-C(25)-H(25A)	109.5
O(2)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(2)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(7)-N(1)-C(4)	120.39(17)
C(7)-N(1)-C(10)	121.87(18)
C(4)-N(1)-C(10)	116.45(16)
C(8)-N(2)-C(7)	121.21(17)
C(8)-N(2)-C(11)	120.15(18)
C(7)-N(2)-C(11)	118.63(17)
C(22)-O(2)-C(25)	118.7(3)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for A.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	43(1)	56(2)	53(1)	1(1)	13(1)	1(1)
C(2)	61(2)	63(2)	51(1)	-12(1)	16(1)	8(1)
C(3)	52(2)	64(2)	40(1)	-5(1)	7(1)	4(1)
C(4)	36(1)	49(1)	40(1)	-3(1)	7(1)	-6(1)
C(5)	54(2)	55(1)	39(1)	-6(1)	6(1)	-3(1)
C(6)	56(2)	62(2)	42(1)	5(1)	3(1)	-2(1)
C(7)	38(1)	48(1)	41(1)	-2(1)	4(1)	-6(1)
C(8)	43(1)	42(1)	49(1)	1(1)	12(1)	-4(1)
C(9)	38(1)	49(1)	47(1)	-8(1)	8(1)	-6(1)
C(10)	48(1)	56(2)	49(1)	-11(1)	-3(1)	-6(1)
C(11)	36(1)	47(1)	43(1)	-1(1)	2(1)	-3(1)
C(12)	46(2)	104(2)	51(1)	0(1)	12(1)	-15(1)
C(13)	40(2)	111(2)	71(2)	-13(2)	12(1)	-12(1)
C(14)	46(2)	52(2)	64(2)	-18(1)	-10(1)	10(1)
C(15)	70(2)	74(2)	45(1)	7(1)	4(1)	13(1)
C(16)	47(1)	74(2)	49(1)	8(1)	11(1)	1(1)
C(17)	40(1)	57(2)	52(1)	-10(1)	8(1)	-5(1)
C(18)	41(1)	54(1)	54(1)	-6(1)	9(1)	0(1)
C(19)	37(1)	42(1)	53(1)	-8(1)	9(1)	-1(1)
C(20)	52(2)	58(2)	55(1)	1(1)	6(1)	5(1)
C(21)	66(2)	39(1)	80(2)	0(1)	22(1)	-1(1)
C(22)	51(2)	48(2)	78(2)	-20(1)	9(1)	-7(1)

C(23)	62(2)	54(2)	60(2)	-9(1)	1(1)	-5(1)
C(24)	56(2)	46(1)	57(1)	-2(1)	9(1)	-1(1)
C(25)	97(3)	52(2)	191(4)	-22(2)	38(3)	-24(2)
Cl(1)	86(1)	66(1)	78(1)	6(1)	16(1)	20(1)
Cl(2)	65(1)	103(1)	107(1)	-32(1)	-38(1)	26(1)
N(1)	36(1)	48(1)	41(1)	-6(1)	2(1)	-4(1)
N(2)	37(1)	47(1)	48(1)	0(1)	-2(1)	-9(1)
O(1)	54(1)	50(1)	57(1)	-7(1)	-9(1)	-9(1)
O(2)	90(2)	61(1)	128(2)	-23(1)	-2(1)	-21(1)
F(1)	61(1)	51(1)	61(1)	4(1)	7(1)	-5(1)

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Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for A.

	x	y	z	U(eq)
H(2)	8640	10661	2807	70
H(3)	9628	9804	3637	64
H(5)	8731	9255	-814	61
H(6)	7714	10106	-1632	67
H(10A)	9909	8447	54	65
H(10B)	8624	8433	450	65
H(12)	13688	8452	3386	81
H(13)	15599	8337	5225	90
H(15)	13869	7971	8491	79
H(16)	11958	8093	6645	69
H(20)	8358	5882	1226	68
H(21)	7060	5159	-44	73
H(23)	5826	6184	-3779	74
H(24)	7110	6903	-2520	65
H(25A)	6204	4491	-1989	171
H(25B)	4839	4431	-3088	171
H(25C)	5072	4705	-1413	171

Table S6. Torsion angles [deg] for A.

C(6)-C(1)-C(2)-C(3)	0.9(4)
Cl(1)-C(1)-C(2)-C(3)	-178.21(19)
C(1)-C(2)-C(3)-C(4)	0.7(4)
C(2)-C(3)-C(4)-C(5)	-1.6(3)
C(2)-C(3)-C(4)-N(1)	-179.8(2)
C(3)-C(4)-C(5)-C(6)	1.0(3)
N(1)-C(4)-C(5)-C(6)	179.2(2)
C(2)-C(1)-C(6)-C(5)	-1.5(4)
Cl(1)-C(1)-C(6)-C(5)	177.60(18)
C(4)-C(5)-C(6)-C(1)	0.6(4)
F(1)-C(8)-C(9)-C(17)	-0.5(3)
N(2)-C(8)-C(9)-C(17)	179.0(2)
F(1)-C(8)-C(9)-C(10)	-178.82(19)
N(2)-C(8)-C(9)-C(10)	0.7(3)
C(8)-C(9)-C(10)-N(1)	-23.0(3)
C(17)-C(9)-C(10)-N(1)	158.6(2)
C(16)-C(11)-C(12)-C(13)	1.3(4)
N(2)-C(11)-C(12)-C(13)	-178.3(2)
C(11)-C(12)-C(13)-C(14)	-0.4(4)
C(12)-C(13)-C(14)-C(15)	-0.3(4)
C(12)-C(13)-C(14)-Cl(2)	-179.4(2)
C(13)-C(14)-C(15)-C(16)	0.1(4)
Cl(2)-C(14)-C(15)-C(16)	179.17(19)
C(12)-C(11)-C(16)-C(15)	-1.5(4)
N(2)-C(11)-C(16)-C(15)	178.1(2)
C(14)-C(15)-C(16)-C(11)	0.8(4)
C(24)-C(19)-C(20)-C(21)	-2.0(3)

C(18)-C(19)-C(20)-C(21)	176.4(2)
C(19)-C(20)-C(21)-C(22)	0.6(4)
C(20)-C(21)-C(22)-O(2)	179.6(2)
C(20)-C(21)-C(22)-C(23)	1.0(4)
O(2)-C(22)-C(23)-C(24)	-179.8(2)
C(21)-C(22)-C(23)-C(24)	-1.1(4)
C(22)-C(23)-C(24)-C(19)	-0.4(4)
C(20)-C(19)-C(24)-C(23)	1.9(3)
C(18)-C(19)-C(24)-C(23)	-176.6(2)
O(1)-C(7)-N(1)-C(4)	-3.8(3)
N(2)-C(7)-N(1)-C(4)	175.36(18)
O(1)-C(7)-N(1)-C(10)	162.7(2)
N(2)-C(7)-N(1)-C(10)	-18.1(3)
C(3)-C(4)-N(1)-C(7)	-35.8(3)
C(5)-C(4)-N(1)-C(7)	146.1(2)
C(3)-C(4)-N(1)-C(10)	157.0(2)
C(5)-C(4)-N(1)-C(10)	-21.2(3)
C(9)-C(10)-N(1)-C(7)	32.8(3)
C(9)-C(10)-N(1)-C(4)	-160.17(19)
C(9)-C(8)-N(2)-C(7)	16.1(3)
F(1)-C(8)-N(2)-C(7)	-164.40(18)
C(9)-C(8)-N(2)-C(11)	-163.7(2)
F(1)-C(8)-N(2)-C(11)	15.8(3)
O(1)-C(7)-N(2)-C(8)	172.3(2)
N(1)-C(7)-N(2)-C(8)	-6.9(3)
O(1)-C(7)-N(2)-C(11)	-7.9(3)
N(1)-C(7)-N(2)-C(11)	172.86(18)
C(16)-C(11)-N(2)-C(8)	-78.2(3)
C(12)-C(11)-N(2)-C(8)	101.5(3)
C(16)-C(11)-N(2)-C(7)	102.0(3)

C(12)-C(11)-N(2)-C(7)	-78.3(3)
C(23)-C(22)-O(2)-C(25)	179.7(3)
C(21)-C(22)-O(2)-C(25)	1.0(4)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for A [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(16)-H(16)...F(1)#2	0.93	2.54	3.309(3)	139.7
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(16)-H(16)...F(1)#2	0.93	2.54	3.309(3)	139.7
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5

C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5
C(10)-H(10B)...Cl(2)#4	0.97	2.81	3.707(2)	153.8
C(12)-H(12)...Cl(1)#3	0.93	2.96	3.846(3)	158.7
C(16)-H(16)...F(1)#2	0.93	2.54	3.309(3)	139.7
C(21)-H(21)...O(1)#1	0.93	2.58	3.361(3)	141.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+1/2 #2 x,-y+3/2,z+1/2 #3 -x+2,-y+2,-z

#4 x-1,y,z-1

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