Supporting Information

Transition Metal-Free Functionalized Hydration of Alkynes: One-Pot Synthesis of fluorinated *β*-keto-imidates using Selectfluor

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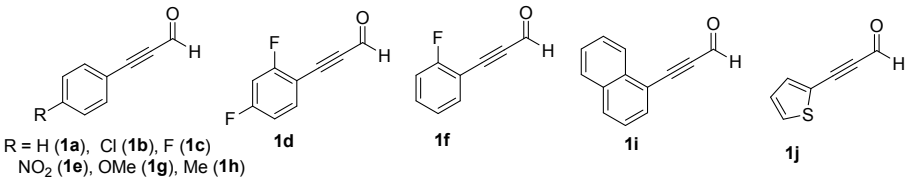
1.0 General Considerations

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under nitrogen atmosphere. Chloroform-*d* purchased from Cambridge Isotope Laboratories, Inc. was degassed and used as a solvent without additional purification for optimization and mechanistic studies. All other reagents were directly used as purchased without further purification unless otherwise stated. All experiments were monitored by analytical thin layer chromatography (TLC) on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (60-120 mesh) using a proper eluent. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak ($CHCl_3$ in $CDCl_3$: 7.26 ppm). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). $^{13}C\{^1H\}$ NMR was recorded on Agilent Technologies DD2 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of $CDCl_3$. ^{19}F-NMR was recorded on Agilent Technologies DD2 (100 MHz). High resolution mass spectra were HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Infrared (IR) spectra were recorded using FT-IR Spectrometer from Agient Co., Ltd. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance peaks are reported. X-ray data for the compound KA456 was collected on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The compound **3a'**[S1] and **4**[S2] are reported and corresponding reference are cited 3-arylpropiolaldehyde and *N*-Arylhydroxylamine are prepared according to the literature procedure whereas all analytical and spectral data are given for newly synthesized products.

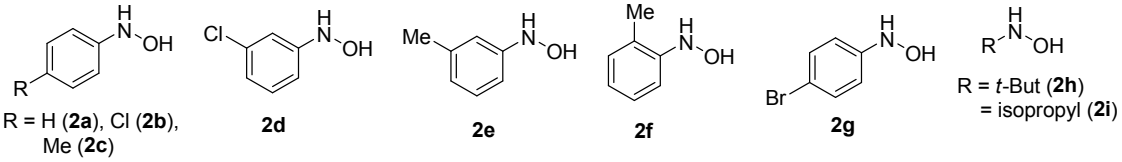
2.0 Preparation of starting materials

3-arylpropiolaldehyde **1**[S1] and *N*-Arylhydroxylamine compounds **2**[S3] were synthesized according to the reported procedures.

List of Aldehydes:



List of *N*-Arylhydroxylamine compounds:



3.0 General Experimental Procedure for Optimization Study (Table S1)

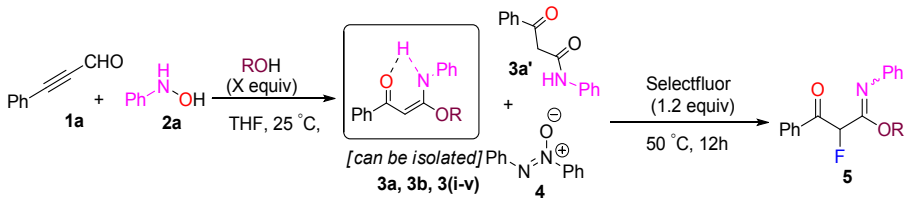
a) For Three-component Reaction:

The perfectly dried THF (2 ml) was added in to the oven dried 25 mL R.B.F containing compound **2a** (59.95 mg, 0.55 mmol), 4Å molecular sieves under nitrogen atmosphere. Then, THF (1 mL) solution of compound **1a** (65.00 mg, 0.5 mmol) followed by ROH (0–2 mmol) was added. The reaction mixture was stirred at 25 °C for 6 h, the solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 2% EA/Hexane) to get the compound. The reaction was repeated twice and product is isolated to determine the yield (by average of two run).

b) For Four-component one-pot reaction (entries 10 and 11, Table S1):

The perfectly dried THF (2 ml) was added in to the oven dried a 25 mL R.B.F containing compound **2a** (59.95 mg, 0.55 mmol), 4Å molecular sieves under nitrogen atmosphere. Then, THF (1 mL) solution of compound **1a** (65.00 mg, 0.5 mmol) followed by MeOH (64.01 mg, 2 mmol) was added and reaction mixture was stirred at 25 °C (~ 6 h). After the complete consumption of starting material (Indicated by TLC), Selectflour (212.33 mg, 0.6 mmol) was added the parent THF solution and continue starring at 50 °C for 12 h. The solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 1.5% EA/Hexane) to get the compound. The reaction was repeated twice and product is isolated to determine the yield (by average of two run).

***Table S1*. Optimization of reaction condition**[a]



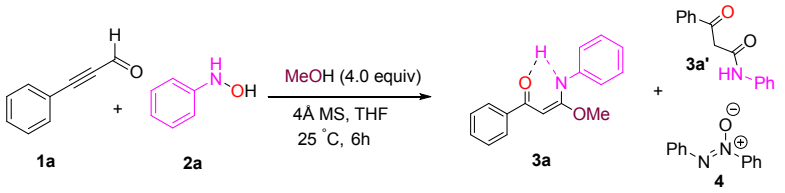
Entry	ROH (equiv)	Solvent	time (*h*)	Compounds[b]	
				3(%) / **3a'**(%)	**5a** (%)
1	ROH = none	Wet toluene	24	**3a**(0) / **3a'**(67)	—

2	MeOH (4)	Wet toluene	15	**3a** (41) / **3a'**(26)	—
3	MeOH (4)	toluene	15	**3a** (56) / **3a'**(trace)	—
4	MeOH (4)	THF	6	**3a** (91) / **3a'**(trace)	—
5	MeOH (4)	1,4-dioxane	16	**3a** (55) / **3a'**(15)	—
6	MeOH (4)	Dichloromethane	10	**3a** (31) / **3a'**(10)	—
7	MeOH (4)	Acetonitrile	10	Messy	—
8	MeOH (3)	THF	10	**3a** (76) / **3a'**(10)	—
9	MeOH (2)	THF	18	**3a** (58) / **3a'**(31)	—
10[c]	**MeOH (4)**	**THF**	**6**	**3a (~95) / 3a'(trace)**	**81**
11[c]	MeOH (3)	THF	10	**3a** (~81) / **3a'**(14)	72
12[d]	ROH = EtOH (4)	THF	10	**3b**(58)/**3a'**(21)	**5b**(44)
13	*t*-BuOH (4)	THF	15	**3i** (trace) / **3a'**(38)	—
14	*n*-BuOH (4)	THF	18	**3ii** (trace) / **3a'**(41)	—
15	*i*-PrOH (4)	THF	18	**3iii** (5-10) / **3a'**(21)	—
16	PhOH (4)	THF	18	**3iv** (trace) / **3a'**(30)	—
17	BnOH (4)	THF	12	**3v**(10)/**3a'**(18)	–

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), ROH (0–4 equiv), molecular sieves (4Å) in THF (3 mL) at 25 °C then (in case of entries 10 and 11) Selectfluor (1.2 equiv) at 50 °C. [b]yields are reported after purification form silica column (average of two run). [c] In these cases, **3a**/**3a'** are not isolated and their approx. TLC conversion is shown. [d]yields corresponds to Selectfluor addition to the purified **3b**.

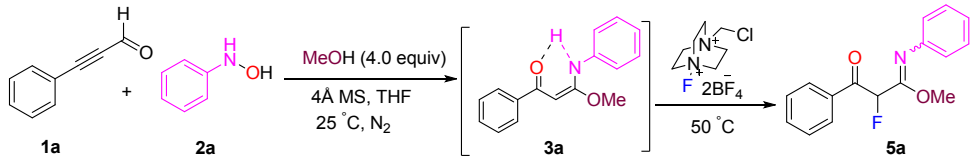
4.0 Experimental Procedure

a) For three component synthesis of 3-amino-2- en 1-ones:



The perfectly dried THF (2 ml) was added in to the oven dried 25 mL R.B.F containing compound **2a** (59.95 mg, 0.55 mmol), 4Å molecular sieves under nitrogen atmosphere. Then, THF (1 mL) solution of compound (65.00 mg, 0.5 mmol) followed by MeOH (64.01 mg, 2 mmol) was added. The reaction mixture was stirred at 25 °C for 6 h, the solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 2% EA/Hexane) to get the compound (*E*)-3-methoxy-1-phenyl-3-(phenylamino)prop-2-en-1-one (**3a**) (115.16 mg, 91%). as a yellowish solid and side product 3-oxo-*N*,3-diphenylpropanamide **3a'** as a off-white solid.

b) For four-component one-pot synthesis of 3-imino-2-fluoro 1-ones:



The perfectly dried THF (2 ml) was added in to the oven dried a 25 mL R.B.F containing compound **2a** (59.95 mg, 0.55 mmol), 4Å molecular sieves under nitrogen atmosphere. Then, THF (1 mL) solution of compound 1a (65.00 mg, 0.5 mmol) followed by MeOH (64.01 mg, 2 mmol) was added and reaction mixture was stirred at 25 °C (~ 6 h). After the complete consumption of starting material (Indicated by TLC), Selectfluor (212.33 mg, 0.6 mmol) was added the parent THF solution and continue starring at 50 °C for 12 h. The solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 1.5% EA/Hexane) to get the compound. The reaction was repeated twice and product is isolated to determine the yield (by average of two run).

5.0 Representative procedure of gram scale reaction

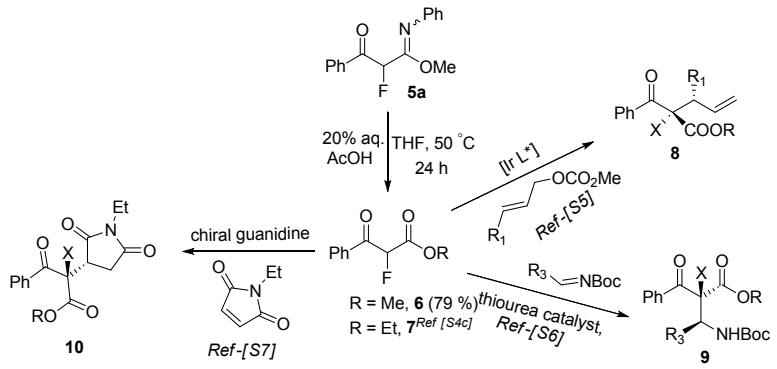
To a flame dried 50 mL round bottom flask were added compound **2a** (0.92 g, 8.44 mmol)), 4Å molecular sieves and THF (10 mL) under nitrogen atmosphere. Then, THF (5 mL) solution of compound **1a** (1.0 g, 7.68 mmol) followed by MeOH (0.98 g, 30.72 mmol) was added and reaction mixture was stirred at 25 °C for around 7 h. After the complete consumption of starting material (Indicated by TLC), Selectfluor (3.26 g, 9.21 mmol) was added the parent THF solution and continue starring at 50 °C for 12 h. The solvent was evaporated by rotary evaporator and crude compound was purified by column chromatography (eluent: 1.5% EA/Hexane) to get the compound **5a** (1.62 g, 78 %) as a yellow solid.

6.0 Synthesis and Application of Fluorinated *β*-keto esters 6

6.1) Representative procedure of imine hydrolysis: Preparation of fluorinated *β*-keto methylester 6[S4]

To a RBF with magnetic stir bar was added compound (**5a**) (35.4 mg, 0.1 mmol) followed by THF (10 mL). The mixture of 20% aq. solution of AcOH (2.0 mL) was then added and reaction mixture was further stirred under heating at 50 °C for 24 h. After the completion of the reaction, a pinch of $MgSO_4$ was added to adsorb the traces of water and reaction mass was filtered through cellite pad and washed with dichloromethane, filtrate was evaporated by rotary evaporator and crude compound is purified by column chromatography (eluent: 2% EA/Hexane) to get fluorinated *β*-keto methylester **6** (18.6 mg,79 %).

6.2) Application of fluorinated *β*-keto methylester 6: The application of analogous compound[S4c] **7** (ethyl ester of **6**) in organic synthesis is depicted in (Scheme 1). For example; Soltz *et al*.[S5] reported iridium catalyzed asymmetric allylic alkylation of **7** leads to the highly functionalized fluoro-building block **8**. Lu *et al.* reported, asymmetric Mannich reaction of **7** with a bifunctional thiourea catalyst furnish **9** [S6] Importantly, guanidine-catalyzed Michael addition of **7** gives access to **10** in good yield and selectivity.[S7]



Scheme 1: Importance of **5** as a valuable precursor

7.0 Studies with EGFR Kinase: Schematic diagram

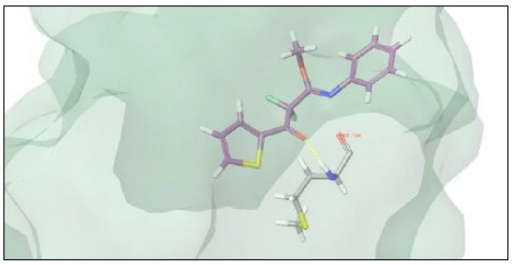
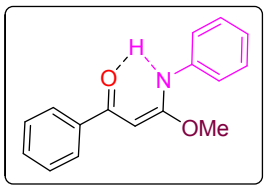


Figure 1: Interaction of **5k** with EGFR kinase. Compound **5k** was docked in EGFR kinase (PDB ID: 1M17)

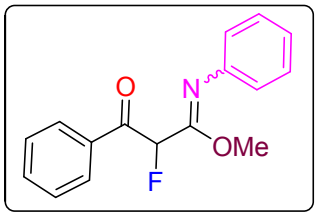
8.0 Spectroscopic Data of Obtained Fluorinated Products:

(*E*)-3-methoxy-1-phenyl-3-(phenylamino)prop-2-en-1-one (3a)



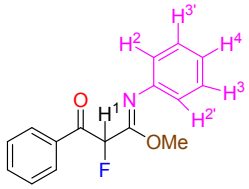
Yellow solid; m.p. 131–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.08 (s, 1H), 7.91 –7.89 (m, 2H), 7.74 –7.76 (m, 3H), 7.36 – 7.31 (m, 4H), 7.12 – 7.10 (m, 1H), 5. 58 (s, 1H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 167.0, 141.4, 137.3, 131.8, 129.0, 128.2, 126.8, 124.2, 122.0, 121.9, 55.8; IR (cm^1): 3420 (bs), 3010, 1739, 1600, 1021; HRMS (ESI) calcd. for $C_{16}H_{15}NO_2$ $[M]^+$: 253.1103; found 253.1106

Methyl 2-fluoro-3-oxo-*N*,3-diphenylpropanimidate (5a)

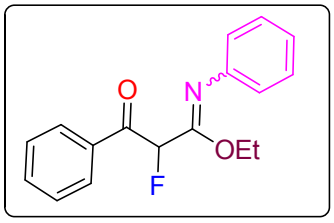


Yellow solid; m.p. 141 – 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 4.0 Hz, 1H), 7.44 (t, J = 4.0 Hz, 2H), 7.36 (t, J = 4.0 Hz, 2H), 7.14 (t, J = 4.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 5.97 (d, J = 32.0 Hz, 1H,) 3.83 (s, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -188.71 (d, J_{C-F} = 48.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J_{C-F} = 13.0 Hz), 155.0 (d, J_{C-F} = 12.0 Hz), 146.1, 134.1, 133.7, 129.3, 128.7, 128.6, 124.3, 121.2, 86.4 (d, J_{C-F} = 128.0 Hz, 54.4); IR (cm^{-1}): 1741, 1690, 1654, 1250, 1050; HRMS (ESI) calcd. for $C_{16}H_{14}FNO_2$ $[M]^+$: 271.1009; found 271.1013.

^{1}H-NOE spectral data of 5a.

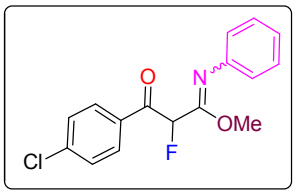
Structure of **5a**	Irradiation	Intensity Increase (%)
	OMe (δ 3.83)	H^1 (δ 6.02 ~ 5.94, 0.0 %), H^2 $H^{2'}$ (δ 7.37 ~ 7.34, 0.0 %), H^3 $H^{3'}$ (δ 7.13 ~ 6.95, 0.0 %)
	H^1 (δ 6.02 ~ 5.94)	H^2 $H^{2'}$(δ 7.37 ~ 7.34, 0.0 %), OMe (δ 3.83, 0.0 %)
	H^2 $H^{2'}$ (δ 7.37 ~ 7.34)	OMe (δ 3.83, 0.0 %), H^1 (δ 6.02 ~ 5.94, 0.0 %), H^3 $H^{3'}$ (δ 7.13 ~ 6.95, 1.39 %)
	H^3 $H^{3'}$ (δ 7.13 ~ 6.95)	OMe (δ 3.83, 0.0 %), H^2 $H^{2'}$(δ 7.37 ~ 7.34, 1.13 %)

Ethyl 2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanimidate (5b)



Red semi solid; m.p. 159 – 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (d, J = 8.0 Hz, 2H), 7.61 – 7.57 (t, J = 8 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.13 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 4.0 Hz, 2H), 6.95 (d, J = 48.0 Hz, 1H), 4.25(q, J = 8.0 Hz, 2H), 1.23 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (d, J = 20.0 Hz), 154.5 (d, J = 18.0 Hz), 146.2, 134.0, 133.8, 129.3, 128.6, 128.53, 128.5, 124.2, 121.2, 86.5(d, J = 191.0 Hz), 63.0, 13.7; IR (cm^{-1}): 1774, 1677, 1626, 1170, 1151, 1062, 988; HRMS (ESI) calcd for $C_{24}H_{21}FNO_5$ $[M]^+$: 285.1165; found $[M+H]^+$: 286.1231.

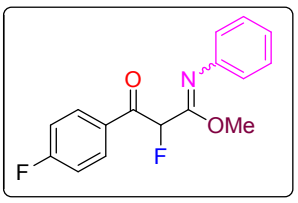
Methyl 3-(4-chlorophenyl)-2-fluoro-3-oxo-*N*-phenylpropanimidate (5c)



Yellow solid; m.p. 148 – 149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 7.33 (d, J = 8.0 Hz,

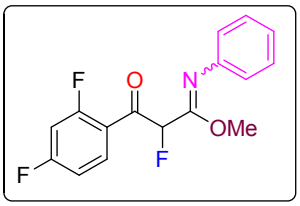
2H), 7.14 (t , J = 8.0 Hz, 1H), 6.94 (d, J = 8 Hz, 2H), 5.99 – 5.87 (d, J = 48 Hz, 1H), 3.83 (s, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -188.21 (d, J_{C-F} = 48.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7 (d, J = 20 Hz), 154.7 (d, J = 18 Hz), 145.9, 140.7, 132.0, 130.2, 130.1, 129.3, 129.0, 124.4, 121.1, 87.5 (d, J = 192 Hz), 54.4; IR (cm^{-1}): 1749, 1693, 1659, 1150, 1108, 801; HRMS (ESI) calcd. for $C_{16}H_{13}ClFNO_2$ $[M]^+$: 305.0619; found $[M+H]^+$: 306.0688.

Methyl 2-fluoro-3-(4-fluorophenyl)-3-oxo-*N*-phenylpropanimidate (5d)



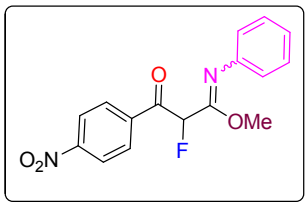
Pale yellow semi solid; m.p. 150 – 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, J = 8.0 Hz, 2H), 7.35 (t, J = 8 Hz, 2H), 7.15 – 7.09 (m, 3H), 6.94 (d, J = 8 Hz, 2H), 5.93 (d, J = 48 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3 (d, J_{C-F} = 21 Hz), 166.2 (d, J_{C-F} = 256 Hz), 154.8 (d, J_{C-F} = 18 Hz), 146.0, 131.6 (d, J_{C-F} = 4.0 Hz), 131.5 (d, J_{C-F} = 5.0 Hz), 129.3, 124.3, 121.1, 116.0, 115.8, 86.6 (d, J = 192 Hz), 54.4; IR (cm^{-1}): 1769, 1673, 1629, 1180, 1128, 1008; HRMS (ESI) calcd. for $C_{16}H_{13}F_2NO_2$ $[M]^+$: 289.0914.

Methyl 3-(2,4-difluorophenyl)-2-fluoro-3-oxo-*N*-phenylpropanimidate (5e)



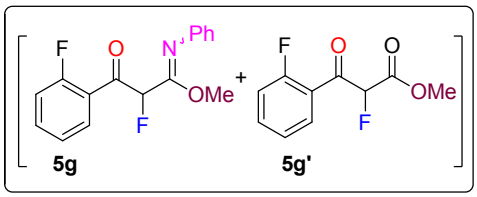
Pale yellow solid; m.p. 146 – 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.89(q, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0Hz, 2H), 7.11(t, J = 8.0 Hz, 1H), 7.02 – 6.97 (m, 1H), 6.90 ~ 6.82(m, 3H), 5.85 (d, J = 48 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3 (d, J = 21Hz), 166.9 (dd, J_{C-F} =158.0 and 13.0Hz), 172.3 *(dd,* J_{C-F} = 256 and 12 Hz), 154.1 (d, J_{C-F} = 18Hz), 146.9, 133.2, 132.8 (d, J_{C-F} = 9.0 Hz), 129.0, 124.1, 121.1, 112.7(d, J_{C-F} = 21.0 Hz), 104.6 (t, J_{C-F} = 21 Hz), 88.5(d, J_{C-F} =18.0 Hz), 54.3, 29.6 (grease); IR (cm^{-1}): 1769, 1673, 1629, 1180, 1128, 1008; HRMS (ESI) calcd. for $C_{16}H_{12}F_3NO_2$ $[M]^+$: 307.0820; found $[M+H]^+$: 308.0890.

Methyl 2-fluoro-3-(4-nitrophenyl)-3-oxo-*N*-phenylpropanimidate (5f)



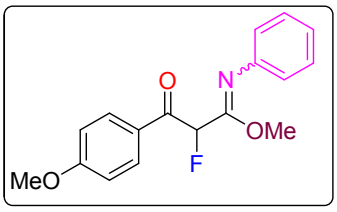
Yellow solid; m.p. 182−184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 5.93 (d, J = 48.0 Hz, 1H), 3.84 (s, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -187.60 (d, J_{C-F} = 48.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4 (d, J_{C-F} = 22.0 Hz), 154.1 (d, J_{C-F} = 18.0 Hz), 150.6, 145.7, 138.4, 130.0 (d, J_{C-F} = 4.0 Hz), 129.4, 124.5, 123.7, 121.1, 86.9 (d, J_{C-F} = 194.0 Hz), 54.5, 29.6 (grease); IR (cm^{-1}) 1769, 1673, 1629, 1573, 1383, 1128, 1008; HRMS (ESI) calcd. for $C_{16}H_{14}N_2O_4$ $[M]^+$:298.0954.

Methyl 2-fluoro-3-(2-fluorophenyl)-3-oxo-*N*-phenylpropanimidate + methyl 2-fluoro-3-(2-fluorophenyl)-3-oxopropanoate (5g +5g')



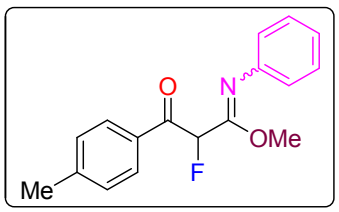
Brown oil; Characterization data of **5e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.84 ~ 7.80 (m, 1H), 7.59 ~ 7.51(m, 1H), 7.33 ~ 7.23 (m, 3H), 7.13 ~ 7.08 (m, 2H), 6.91 (d, J = 4.0 Hz, 2H), 5.89 (dd, J = 48.0 and J = 4Hz, 1H), 3.79 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8 (d, J_{C-F} = 22 Hz), 161.8 (d, J_{C-F} = 254.0 H), 153.3 (d, J_{C-F} = 18.0 Hz), 146.4, 136.6 (d, J_{C-F} = 9.0Hz), 135.4, (d, J_{C-F} = 9.0 Hz), 130.7, 129.0, 124.0,121.1, 116.0 (d, J_{C-F} = 23 Hz) 87.7 (dd, J_{C-F} = 48.0 and 8.0 Hz), 54.3; Characterization data of **5f'**: ^{1}H NMR (600 MHz, $CDCl_3$) major peaks: δ 7.96 ~ 7.92 (m, 1H), 7.73 ~ 7.61 (m, 2H), 5.95 (d, J = 48.0 Hz, 1H), 3.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) major peaks δ 167.6, 161.6 (d, J_{C-F} =257 Hz), 136.6, (d, J_{C-F} = 9.0 Hz), 128.8 (d, J_{C-F} = 6.0 Hz), 116.8 (d, J_{C-F} = 22 Hz) 53.8. IR (cm^{-1}): 1760, 1653, 1623, 1130, 1121, 1022; HRMS (ESI) calcd. for $C_{16}H_{13}F_2NO_2$ $[M]^+$: 289.0914; found $[M+H]^+$:290.0984.

Methyl 2-fluoro-3-(4-methoxyphenyl)-3-oxo-*N*-phenylpropanimidate (5h)



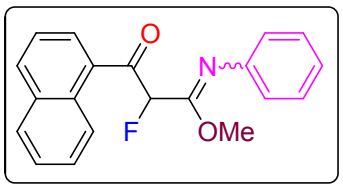
Yellow oil (82.5 mg; 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 2H), 6.94 (d, J = 4 Hz, 2H), 6.89 (d, J = 8 Hz, 2H), 5.94 (d, J_{C-F} = 48 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4 (d, J_{C-F} = 20.0 Hz), 158.9, 150.3 (d, J_{C-F} = 19.0 Hz), 140.8, 125.8 (d, J_{C-F} = 4.0 Hz), 123.9, 121.2, 118.9, 115.8, 108.6, 80.9 (d, J_{C-F} = 253.0 Hz), 50.2, 49.0; IR (cm^{-1}): 3456 (bs), 1770, 1683, 1630, 1187, 1178, 1009, 989; HRMS (ESI) calcd for $C_{17}H_{16}FNO_3$ $[M]^+$:301.1114; found $[M+H]^+$ 302.1183.

Methyl 2-fluoro-3-oxo-*N*-phenyl-3-(*p*-tolyl)propanimidate (5i)



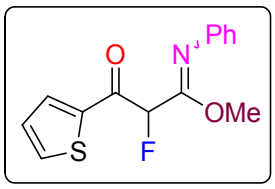
Yellow semi solid; mp 185−194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.23 (t, J = 6.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 5.96 (d, J = 44.0 Hz, 1H), 3.82 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8 (d, J_{C-F} = 20.0 Hz), 155.2 (d, J_{C-F} = 17.0 Hz), 146.1, 145.2, 131.2, 129.3, 129.2, 128.7, 128.6, 124.2, 121.2, 86.3 (d, J_{C-F} = 191.0 Hz), 54.3, 29.7 (grease), 21.7; IR (cm^{-1}) 1769, 1673, 1629, 1180, 1128, 1008; HRMS (ESI) calcd. for $C_{17}H_{17}FNO_2$ $[M]^+$: 285.1165.

Methyl 2-fluoro-3-(naphthalen-1-yl)-3-oxo-*N*-phenylpropanimidate (5j)



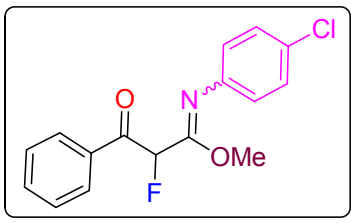
Yellow solid; m. p. 140 – 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.48 (d, J = 4.0 Hz, 1H), 7.44 – 7.40 (t, J = 8.0 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.13 (t, J = 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 2H), 6.14 – 6.02 (d, J = 48.0 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5 (d, J_{C-F} = 21.0 Hz), 154.9 (d, J_{C-F} = 18.0 Hz), 146.2, 133.8, 133.7, 131.4, 129.3, 128.5, 128.4, 128.0, 127.9, 126.8, 125.2, 124.2, 124.0, 121.1 86.1 (d, J_{C-F} = 194.0 Hz), 54.3; IR (cm^{-1}): 1760, 1683, 1639, 1605, 1122, 1121, 1012, 991; HRMS (ESI) calcd. for $C_{20}H_{16}FNO_2$ [M]$^+$: 364.1161.

Methyl 2-fluoro-3-oxo-*N*-phenyl-3-(thiophen-2-yl)propanimidate (5k)



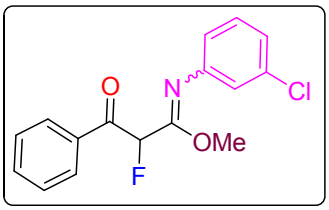
Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 1H), 7.74 (d, J = 4.0 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.16 – 7.09 (m, 2H), 6.98 – 6.94 (m, 2H), 5.80 (d, J = 48.0 Hz, 1H), 3.87 (s, 3H). ^{19}F NMR (400 MHz, $CDCl_3$) δ -194.02 (d, J_{C-F} = 4.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (d, J = 23.0 Hz), 155.4 (d, J = 18. Hz), 146.2, 140.0, 135.8, 134.7 (d, J =9.0 Hz), 132.5, 129.4, 128.6, 124.3, 121.4, 87.0 (d, J = 194.0 Hz), 54.5, 29.7 (grease); HRMS (ESI-MS): calcd. $C_{14}H_{13}NO_2SF$ [M]$^+$: 278.0651 found: 278.0652.

Methyl *N*-(4-chlorophenyl)-2-fluoro-3-oxo-3-phenylpropanimidate (5l)



Yellow semi solid; m. p. 180−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 2.0 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.44 (t, J = 8.0 Hz, 3H), 7.31 – 7.25 (m, 2H), 6.88 (d, J = 2.0 Hz, 2H), 5.99 (d, J_{C-F} = 48.0 Hz, 1H), 3.82 (s 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J_{C-F} = 21.0 Hz), 155.3 (d, J_{C-F} = 19.0 Hz), 144.6,134.1, 133.7, 129.6, 129.3, 128.8, 128.7, 122.4, 86.7 (d, J_{C-F} = 193.0 Hz), 54.5; IR (cm^{-1}): 1781, 1673, 1633, 1132, 1121, 1003, 981; HRMS (ESI) calcd. for $C_{26}H_{13}ClFNO_2$ [M]$^+$: 305.0619 found [M+H]$^+$: 306.0688.

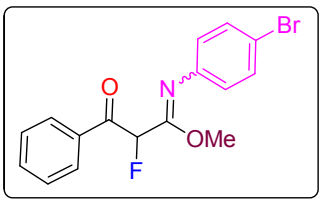
Methyl *N*-(3-chlorophenyl)-2-fluoro-3-oxo-3-phenylpropanimidate (5m)



Yellow solid; m.p.181 – 182°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.11 – 7.08 (m, 1H), 6.93 (t, J = 4.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.96 (d, J = 48.0 Hz, 1H), (s,

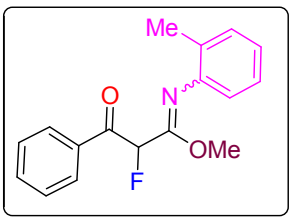
1H), 3.82 (s, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -194.02 (d, J_{C-F} = 4.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J = 21.0 Hz), 155.40 (d, J_{C-F} = 18.0 Hz), 147.3, 134.8, 134.2, 130.2, 128.7, 124.3, 121.4, 119.3, 86.7 (d, J_{C-F} = 193.0 Hz), 54.5; IR (cm^{-1}): 1779, 1671, 1630, 1189, 1123, 1011, 989,779; HRMS ((ESI) calcd for $C_{26}H_{13}ClFNO_2$ $[M]^+$: 305.0619 found $[M+H]^+$: 306.0691.

methyl *N*-(4-bromophenyl)-2-fluoro-3-oxo-3-phenylpropanimidate (5n)



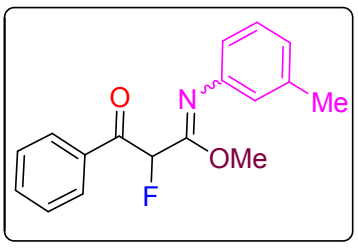
Brown solid; m.p.176 – 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 8.0 Hz, 1H), 7.44 -7.42 (m, 4H), 6.81 (d, J = 8.0 Hz, 2H), 5.92 (d, J = 48.0 Hz, 1H), 3.81 (s, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -188.10 (d, J_{C-F} = 52.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J = 20.0 Hz), 155.3 (d, J = 20.0 Hz), 145.1, 134.2, 133.6, 132.2, 128.7, 122.9, 117.3, 86.6 (d, J = 190.0 Hz), 54.5; IR (cm^{-1}): 1770, 1671, 1629, 1180, 1111, 1012, 632; HRMS (ESI) calcd for C $_{16}H_{13}BrFNO_2$ [M]+ : 349.0114, found $[(M+2)+H]^+$: 352.0168.

Methyl 2-fluoro-3-oxo-3-phenyl-*N*-(o-tolyl)propanimidate (5o)



Yellow semi solid; m.p. 145 – 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.43 (t, J = 6.0 Hz, 2H), 7.25 – 7.16 (m, 2H), 7.08 – 7.04 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 48.0 Hz, 1H), 3.85 (s, 3H), 2.17 (s, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -189.32 (d, J_{C-F} = 52.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7(d, J_{C-F} = 21.0 Hz), 154.2 (d, J_{C-F} = 18.0 Hz), 144.5, 134.1, 130.6, 129.7, 128.7, 128.6, 128.5, 126.7, 124.5, 120.3, 87.4 (d, J_{C-F} = 192.0 Hz), 54.3, 17.9; IR (cm^{-1}): 1770, 1671, 1629, 1180, 1111, 1012, 999; HRMS (ESI) calcd. for $C_{17}H_{17}FNO_2$ $[M]^+$: 285.1165; found $[M+H]^+$: 286.1231.

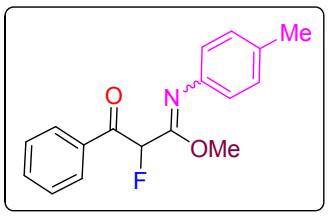
Methyl 2-fluoro-3-oxo-3-phenyl-*N*-(m-tolyl)propanimidate (5p)



Red semi solid; m.p. 189 – 190° °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H) 6.74 (d, J = 4.0 Hz, 1H), 6.05(d, J = 48.0 Hz, 1H), 3.80 (s, 3H), 2.34 (s, 3H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -188.88 (d, J_{C-F} = 52.0 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J_{C-F} = 20.0 Hz), 155.0, 146.0, 139.2, 134.0, 133.8, 129.1, 128.6, 125.0, 121.8, 118.1, 86.4 (d, J_{C-F} = 192.0 Hz), 54.3, 29.7 9 (grease), 21.4; IR (cm^{-1}): 1761, 1671, 1639, 1190, 1181, 1072,

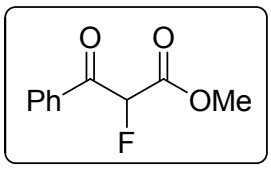
989; HRMS (ESI) calcd. for $C_{17}H_{17}FNO_2$ $[M]^+$: 285.1165; found $[M+H]^+$: 286.1230.

Methyl 2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanimidate (5q)



Red semi solid; m.p. 159 – 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.00 (d, *J* = 48.0 Hz, 1H), 3.80 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (d, *J* = 20.0 Hz), 155.1(d, *J* = 18.0 Hz), 143.5, 134.0, 133.8, 133.6, 129.9, 128.6, 128.6, 128.5, 121.0, 86.3 (d, *J* = 192.0 Hz), 54.3, 20.8; IR (cm^{-1}): 1770, 1671, 1629, 1180, 1111, 1012, 999; HRMS (ESI) calcd for $C_{17}H_{17}FNO_2$ $[M]^+$: 285.1165.

Methyl 2-fluoro-3-oxo-3-phenylpropanoate (6)



White solid; m.p.159 – 160 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 6.0 Hz, 2H), 5.95 – 5.83 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3(d, *J* = 20.0 Hz), 165.3 (d, *J* = 24.0 Hz), 134.5, 133.3, 129.51, 129.5, 128.8, 90.0 (d, *J* = 197.0 Hz), 29.7 (grease), 53.2; IR (cm^{-1}): 1790, 1691, 1690, 1189, 1191, 1092, 979; HRMS (ESI) m/z calcd for $C_{10}H_9FO_3Na$ $[M]^+$: 219.0433; found $[M+1]^+$: 219.0428.

9. References

[S1] a) R. K. Kawade, C. –C. Tseng; R. -S. Liu, *Chem. Eur. J.* 2014, **20**, 13927; b) C. K. Hazra, M. Oestreich, *Org. Lett.*, 2012, **14**, 4010.

[S2] a) Y. -F. Chen, J. Chen, L. –J. Lin, G. J. Chuang *J. Org. Chem.* 2017, **82**, 11626; b) C.-H Chen, Y.-C. Tsai, R.-S. Liu *Angew. Chem. Int. Ed.* 2013, **52**, 4599.

[S3] S. Ghorpade, R. -S. Liu *Angew Chem Int Ed* 2014, **53**, 12885.

[S4] a) T. C. Johnson, M. R. Chin, T. Han, J. P. Shen, T. Rana, D. Siegel, *J. Am. Chem. Soc.* 2016, **138**, 6068; b) T. C. Johnson,; Chin, M. R.; D. Siegel, *J. Org. Chem.* 2017, **82**, 4640; c) S. H. Kanga and D. Y. Kim, *Adv. Synth. Catal.* 2010, **352**, 2783.

[S5] W. -B. Liu, C. M. Reeves, B. M. Stoltz, *J. Am. Chem. Soc*. 2013, **135**, 17298.

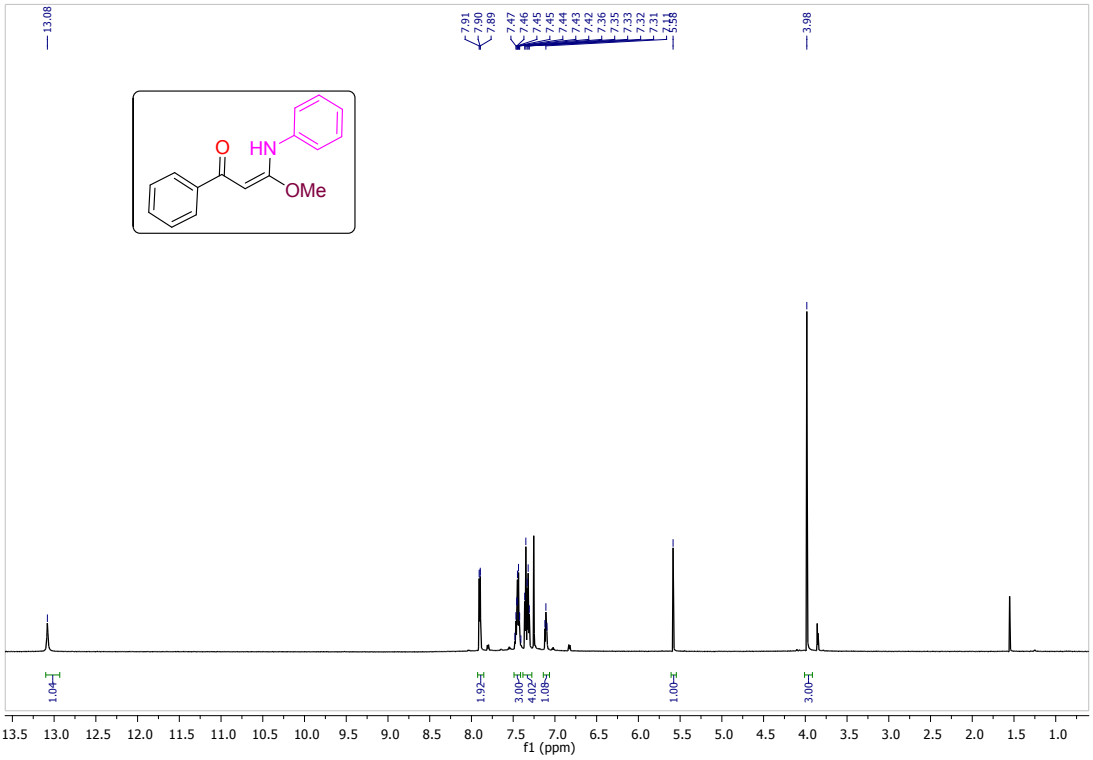
[S6] X. Han, J. Kwiatkowski, F. Xue, K. –W. Huang, Y. Lu, *Angew. Chem. Int. Ed.* 2009, **48**, 7604.

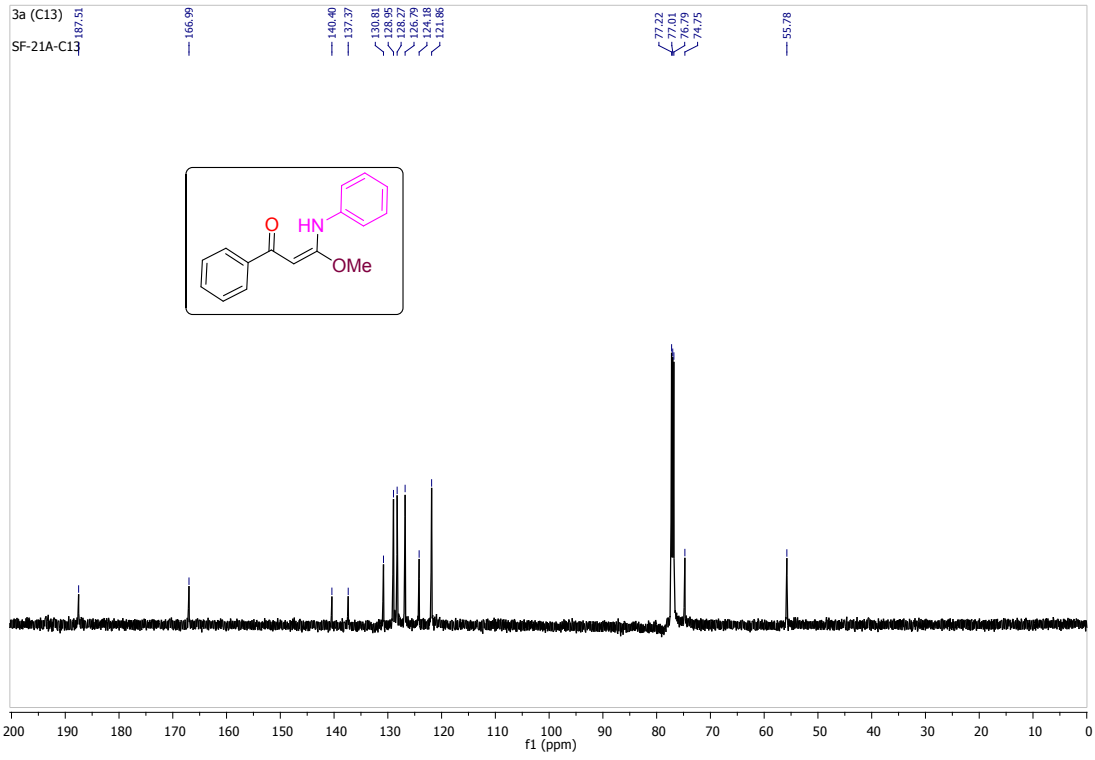
[S7] H. Xue, D. Jiang, H. Jiang, C. W. Kee, H. Hirao, T. Nishimura, M. W. Wong, C. –H. Tan, *J. Org. Chem.* 2015, **80**, 5745.

Appendix

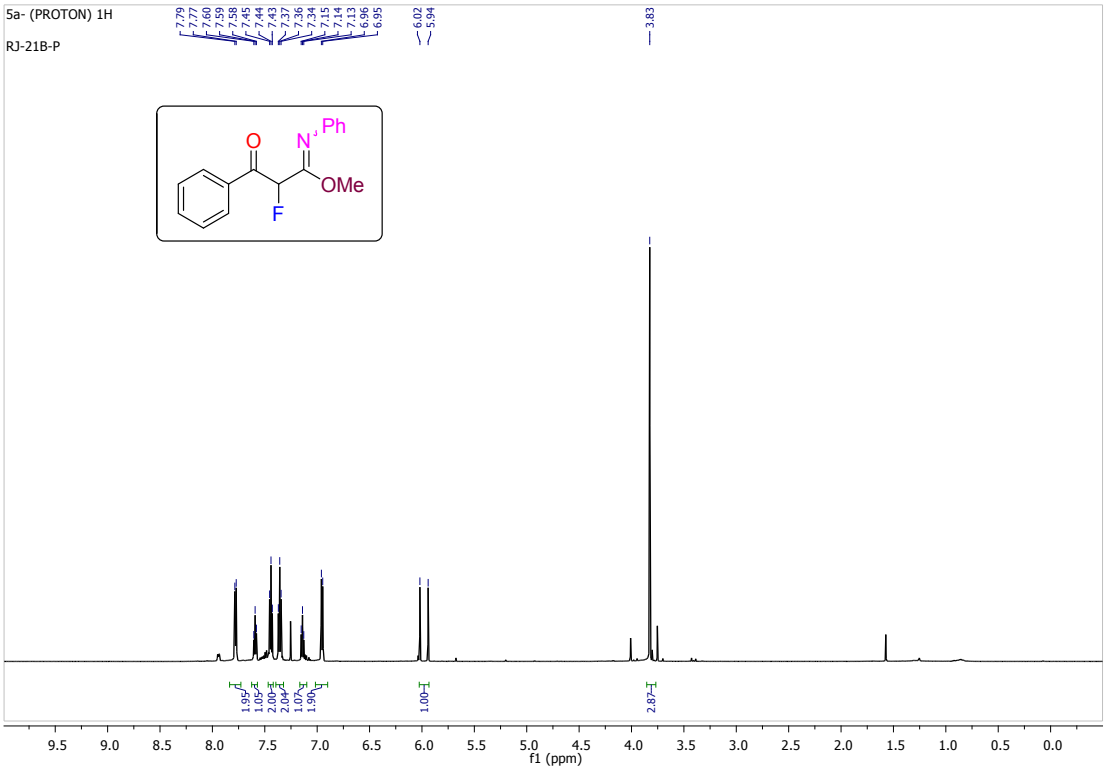
Spectral Copies of ^{1}H, ^{13}C and ^{19}F NMR of Compounds Obtained in This Study

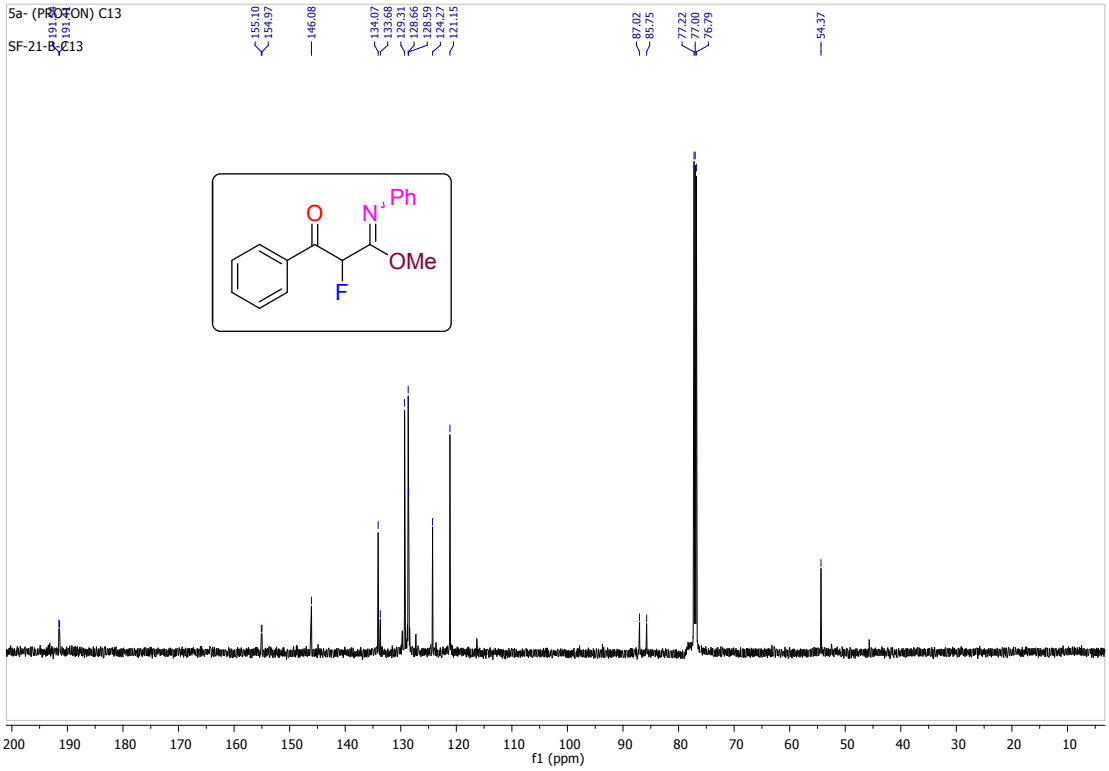
(*E*)-3-methoxy-1-phenyl-3-(phenylamino)prop-2-en-1-one (3a)

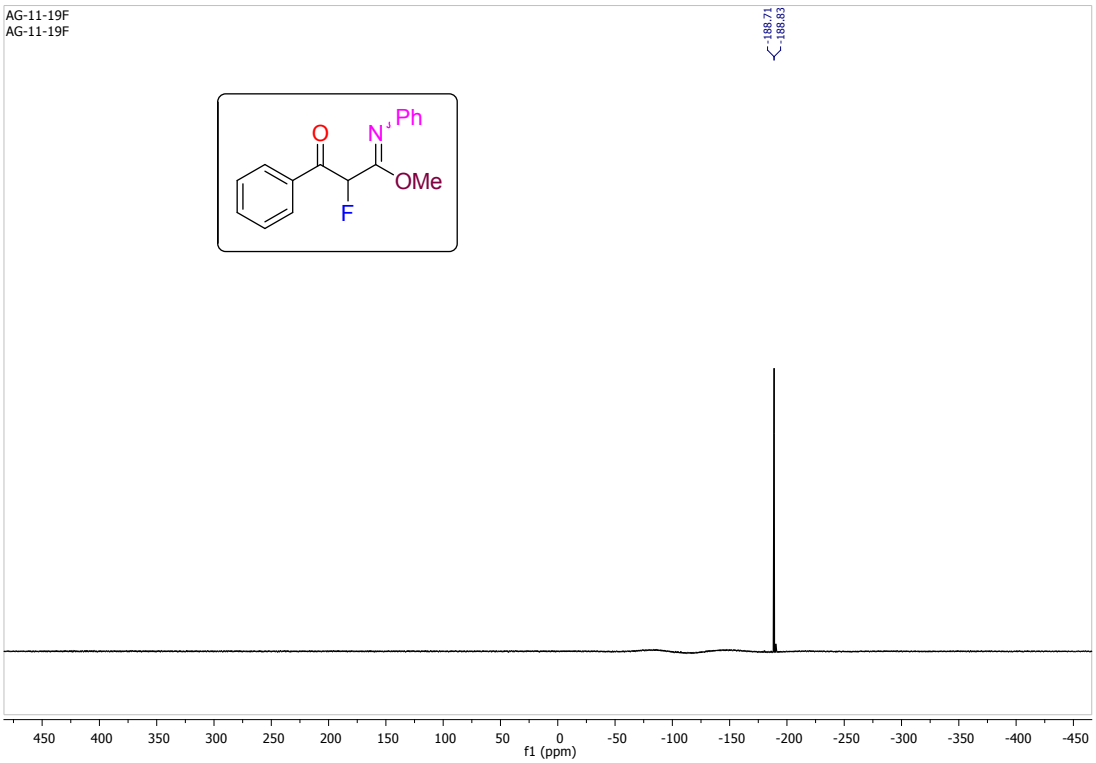


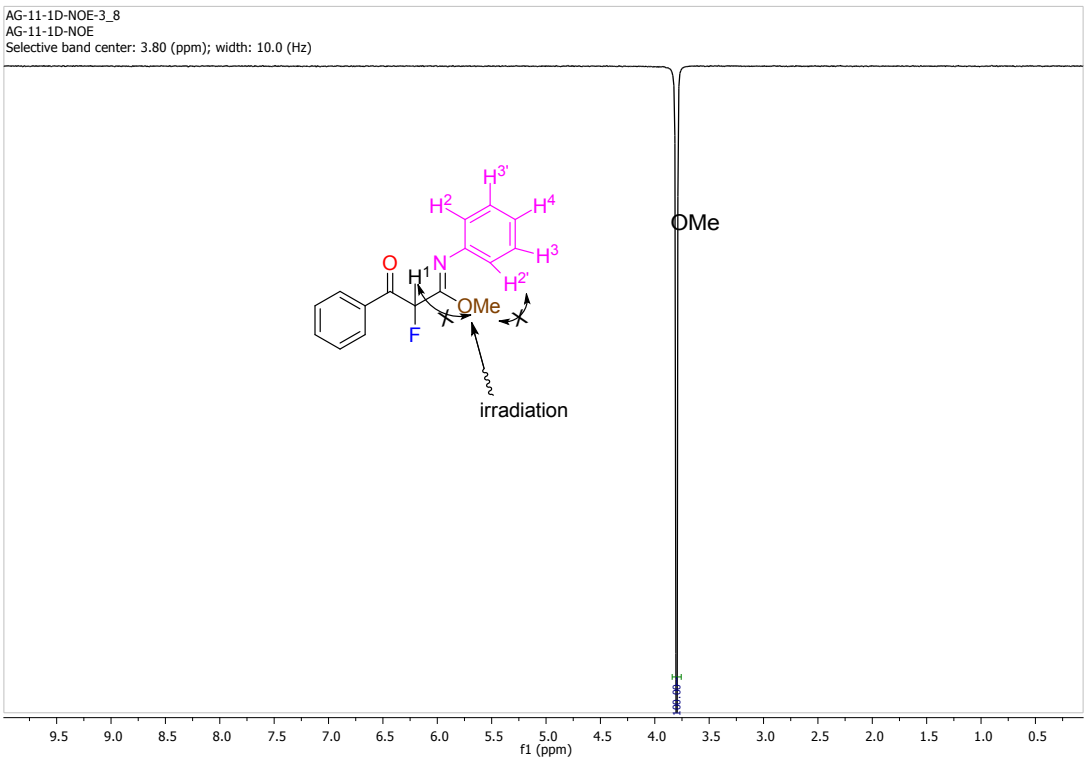


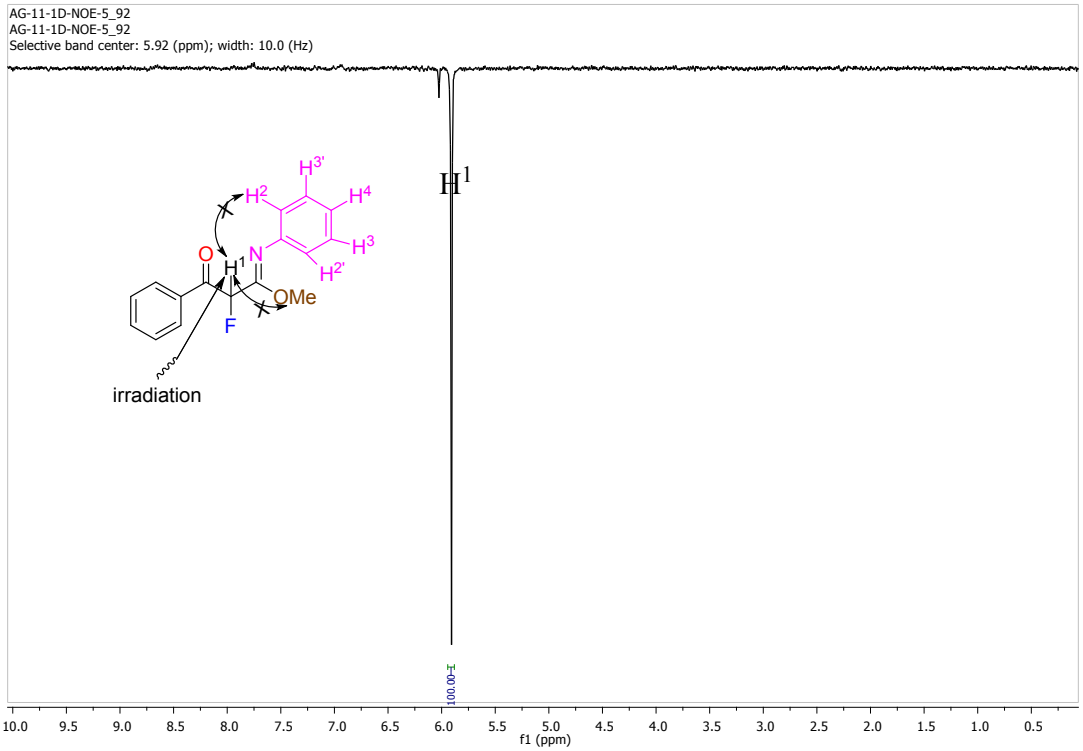
Methyl 2-fluoro-3-oxo-*N*,3-diphenylpropanimidate (5a)

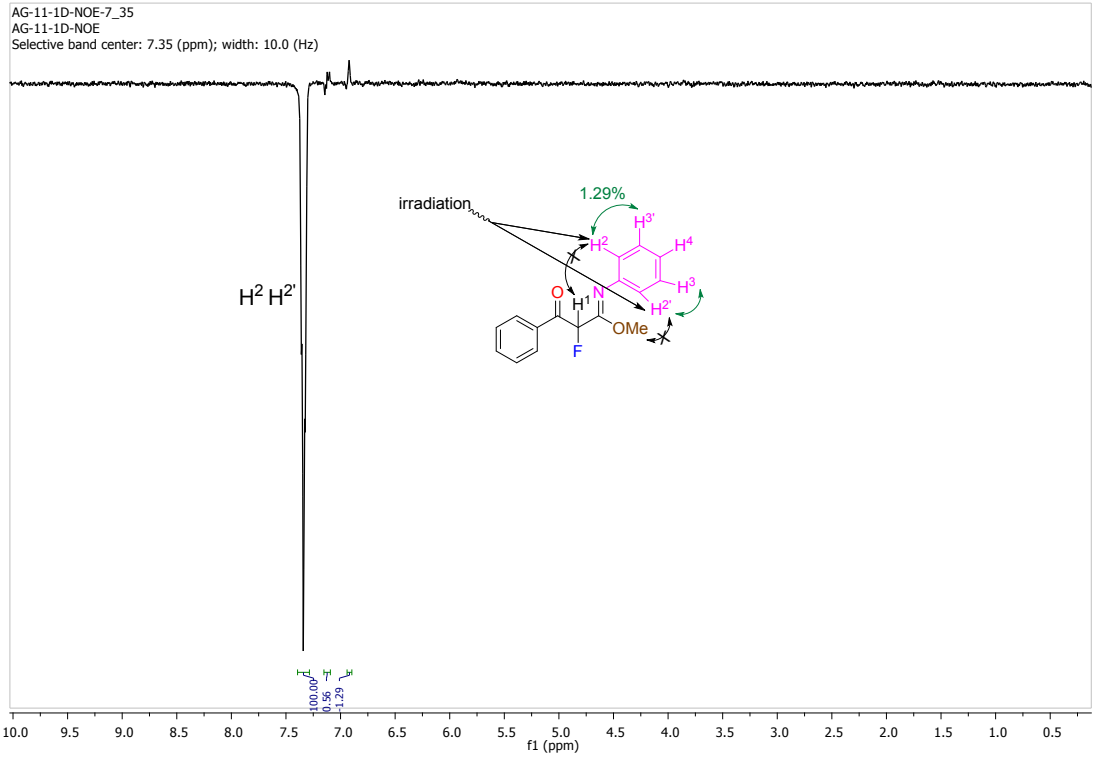


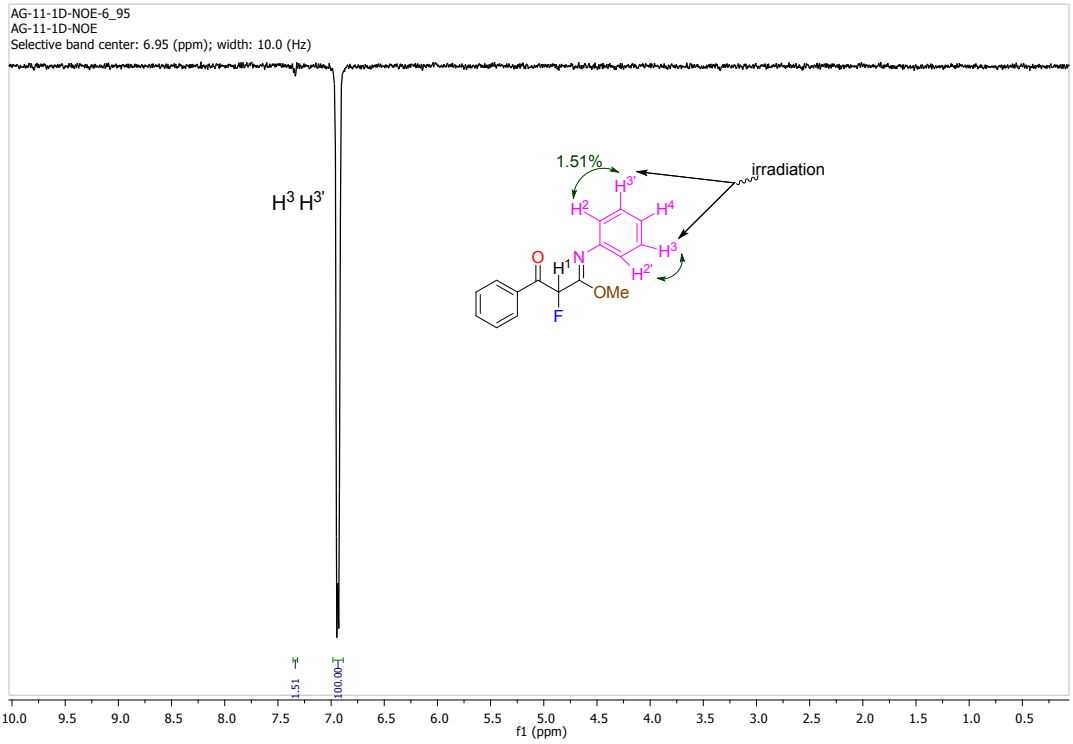



AG-11-19F
AG-11-19F
-188.71
-188.83
O
N
Ph
OMe
F
450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 -450
f1 (ppm)

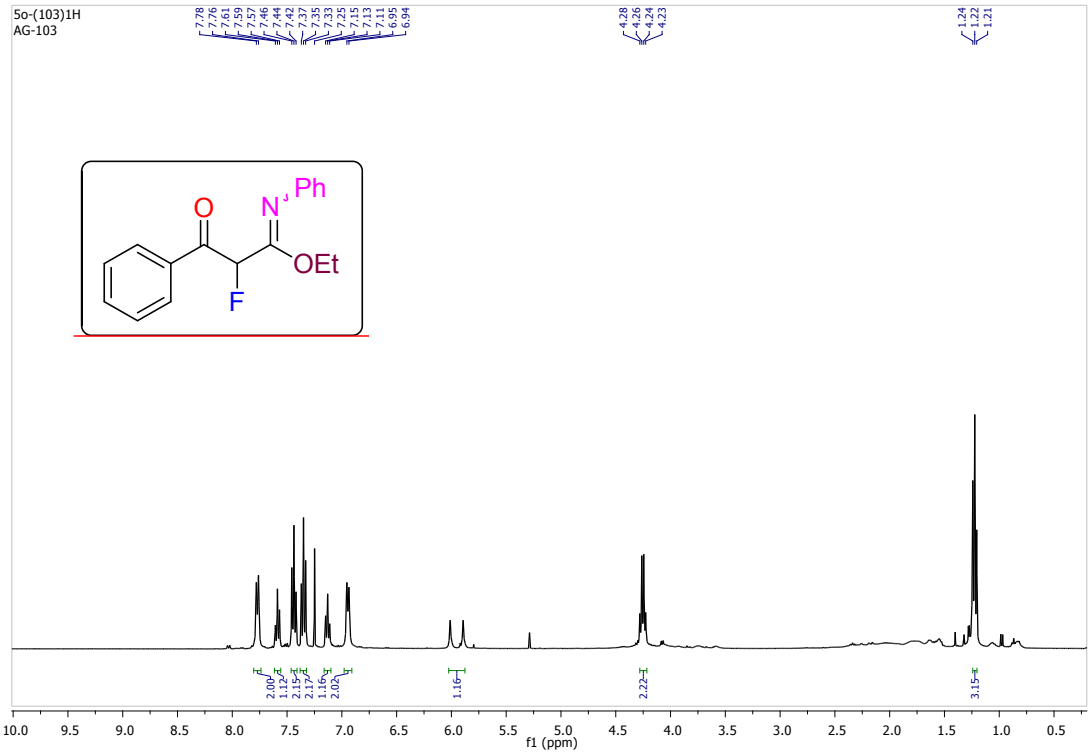

AG-11-1D-NOE-3_8
AG-11-1D-NOE
Selective band center: 3.80 (ppm); width: 10.0 (Hz)
H3'
H2
H4
H3
H2'
N
O
H1
OMe
F
irradiation
OMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

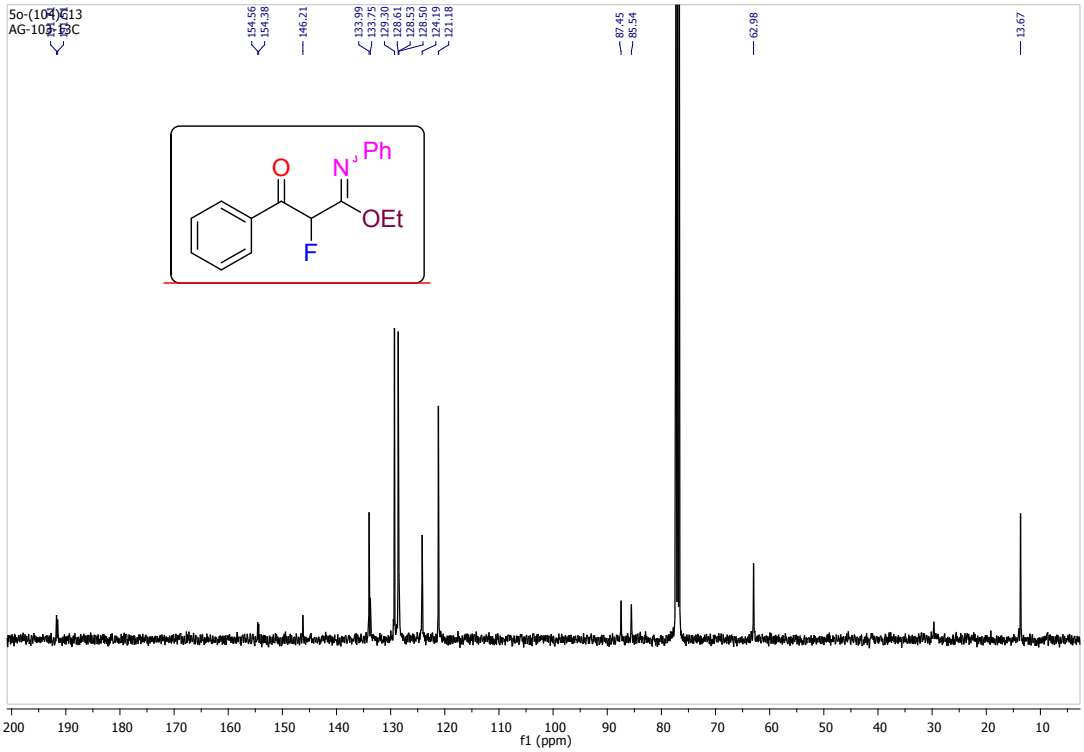

AG-11-1D-NOE-5_92
AG-11-1D-NOE-5_92
Selective band center: 5.92 (ppm); width: 10.0 (Hz)
H1
H3'
H2
H4
H3
H2'
O
N
H1
OMe
F
irradiation
100.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


AG-11-1D-NOE-7_35
AG-11-1D-NOE
Selective band center: 7.35 (ppm); width: 10.0 (Hz)
H2 H2'
irradiation
1.29%
H3'
H2
H4
H3
H2'
O
N
H1
OMe
F
100.00
0.56
1.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

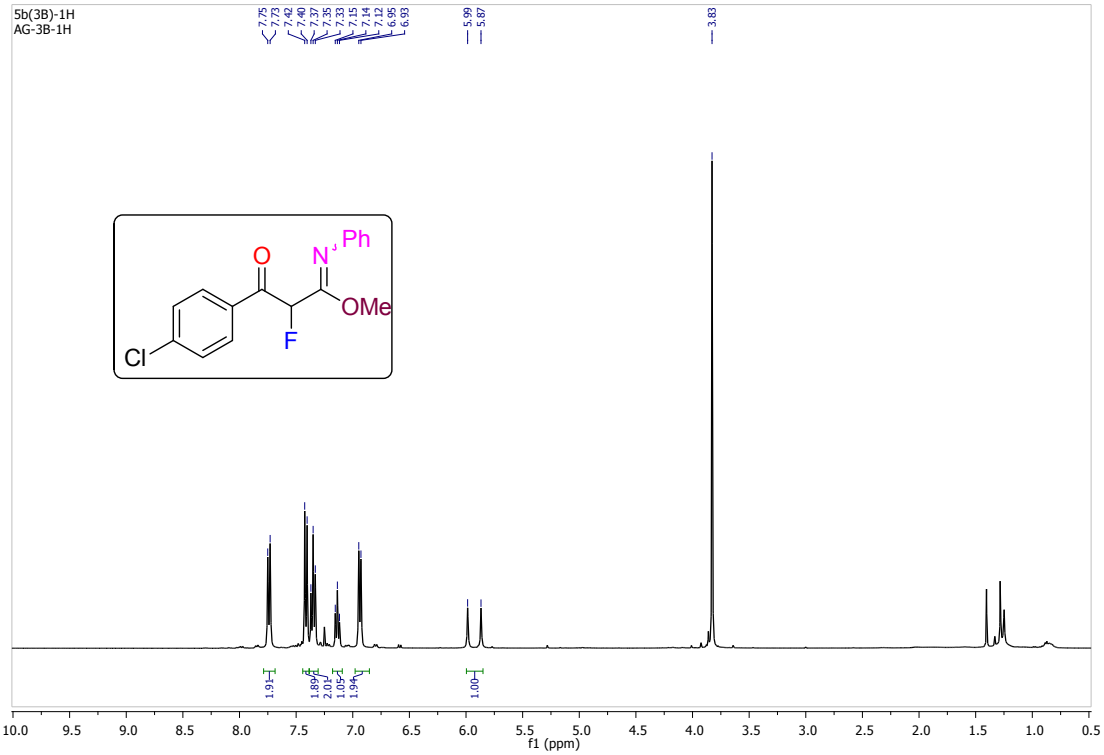


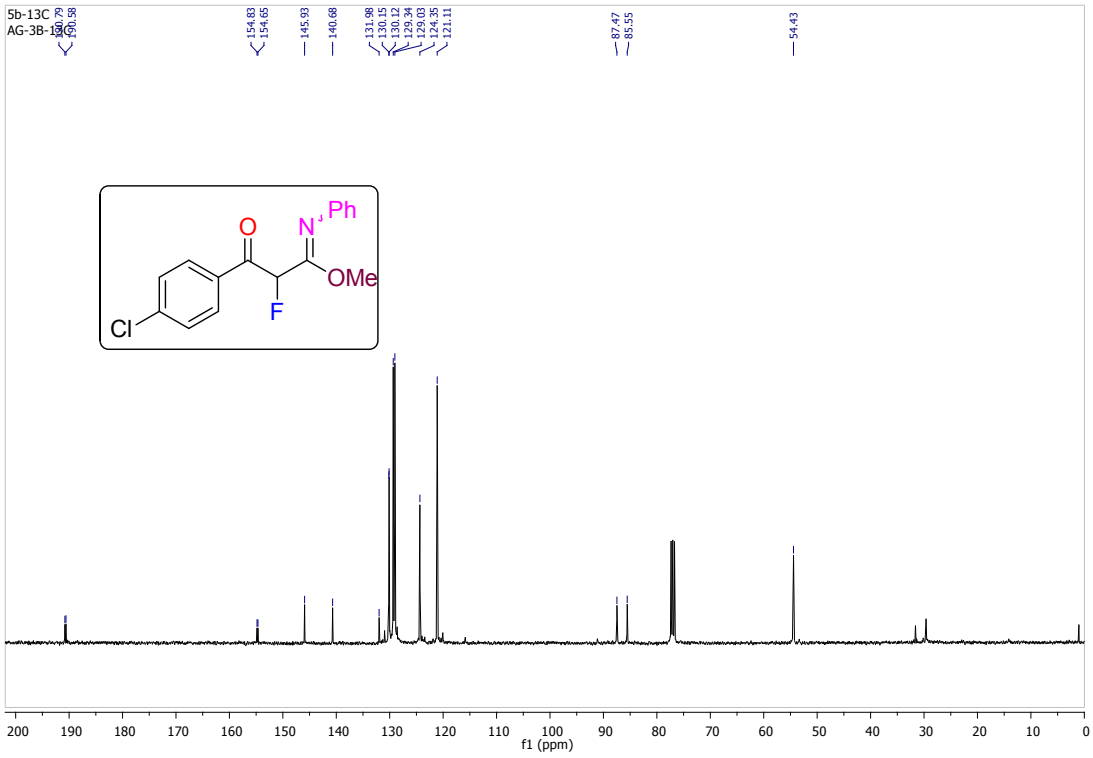
Ethyl 2-fluoro-3-oxo-*N*,3-diphenylpropanimidate (5b)

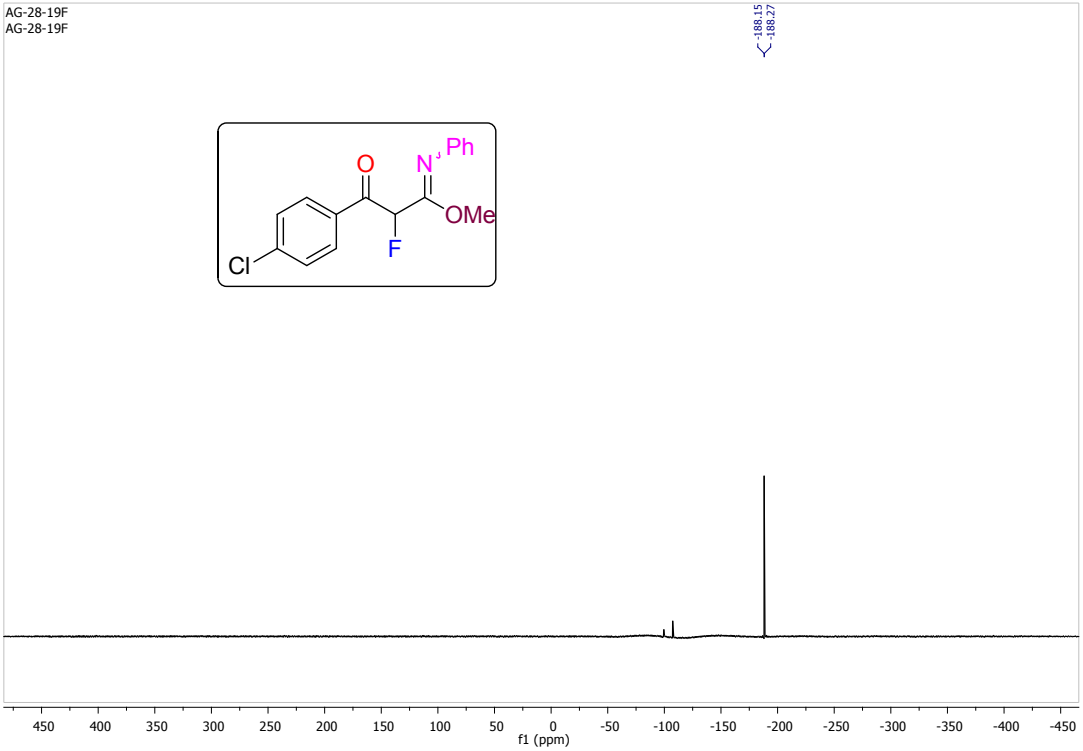




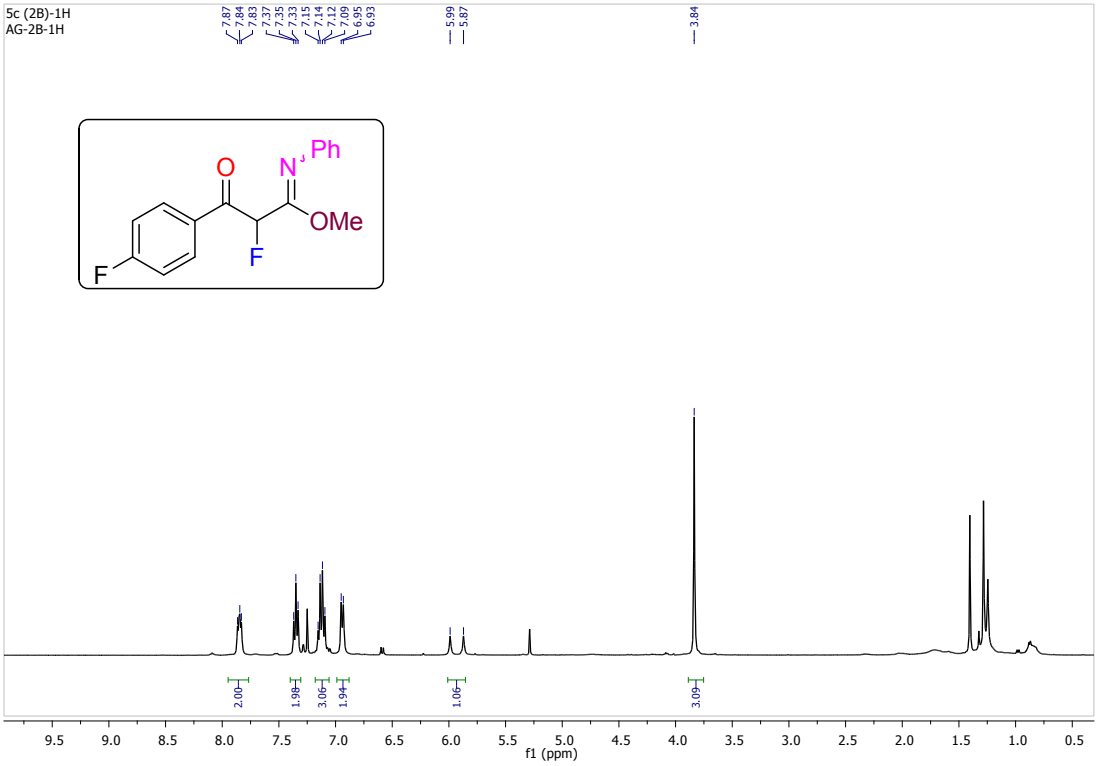
Methyl 3-(4-chlorophenyl)-2-fluoro-3-oxo-*N*-phenylpropanimidate (5c)

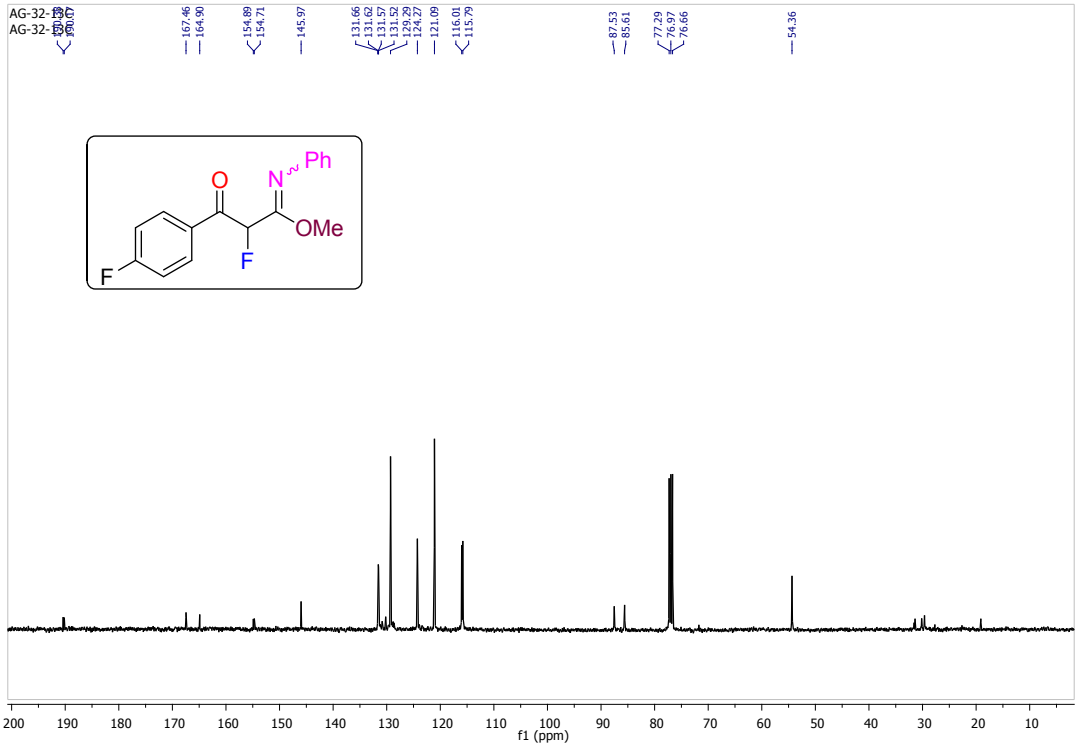



5b-13C
AG-3B-13C
190.79
190.58
154.83
154.65
145.93
140.68
131.98
130.15
130.12
129.34
129.03
124.35
121.11
87.47
85.55
54.43
O
N
Ph
OMe
F
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

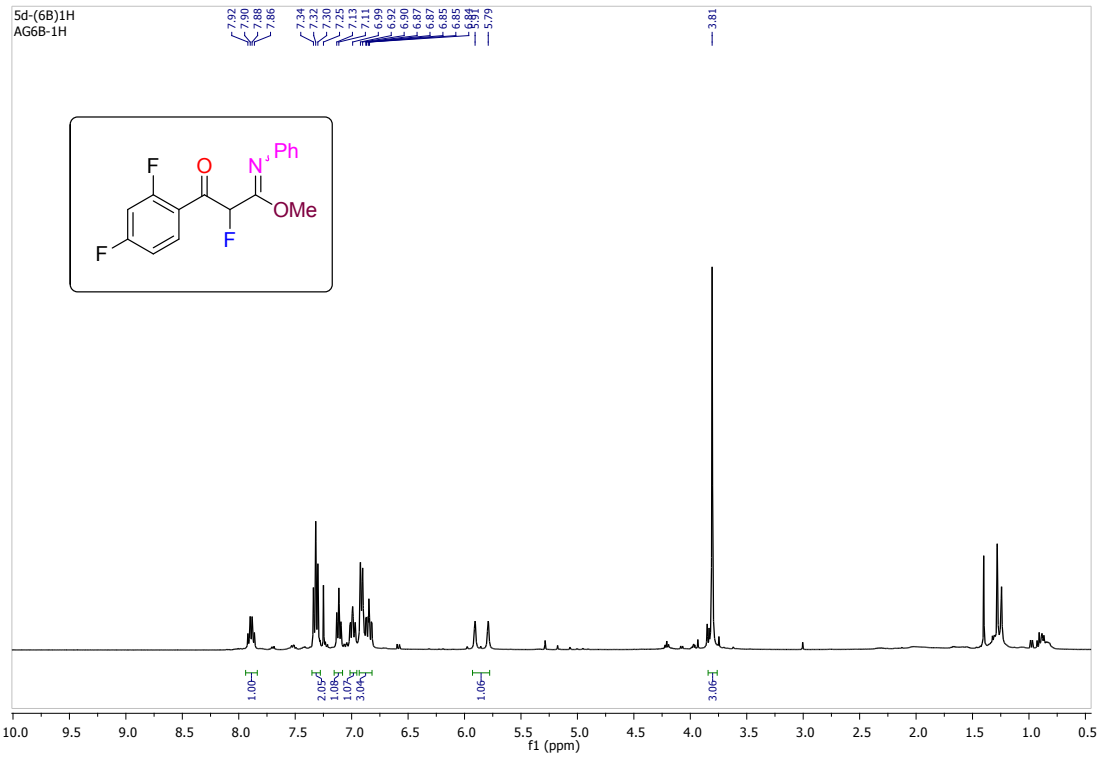

AG-28-19F
AG-28-19F
-188.15
-188.27
O
N
Ph
OMe
F
Cl
450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 -450
f1 (ppm)

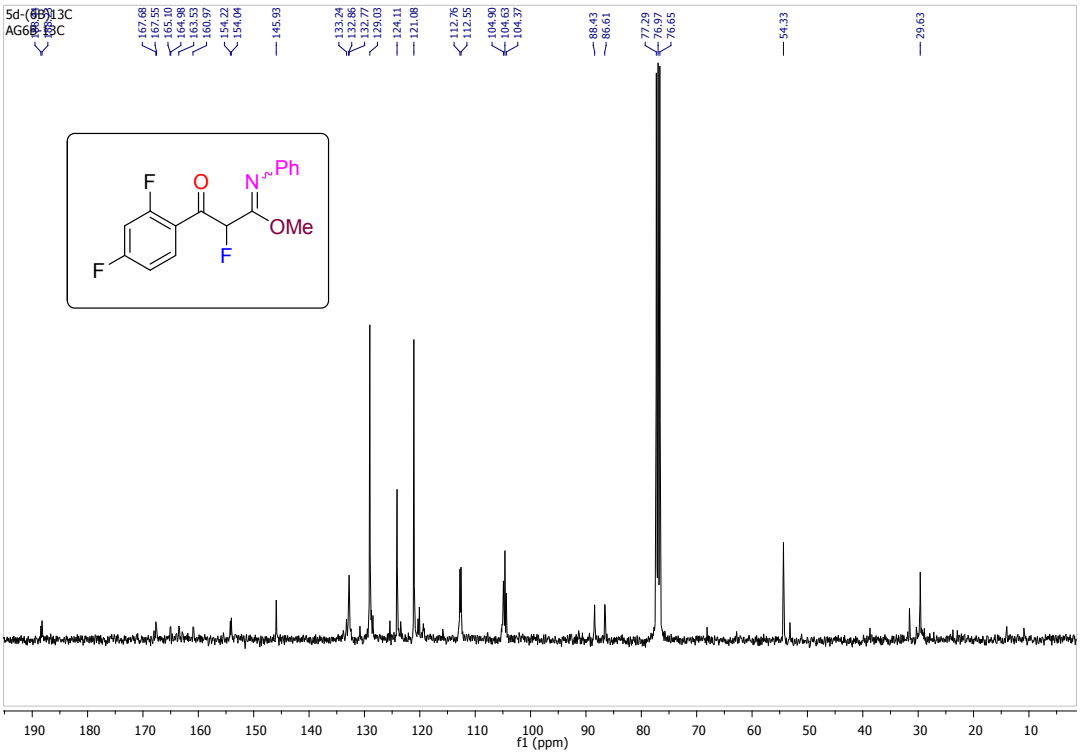
Methyl 2-fluoro-3-(4-fluorophenyl)-3-oxo-*N*-phenylpropanimidate (5d)



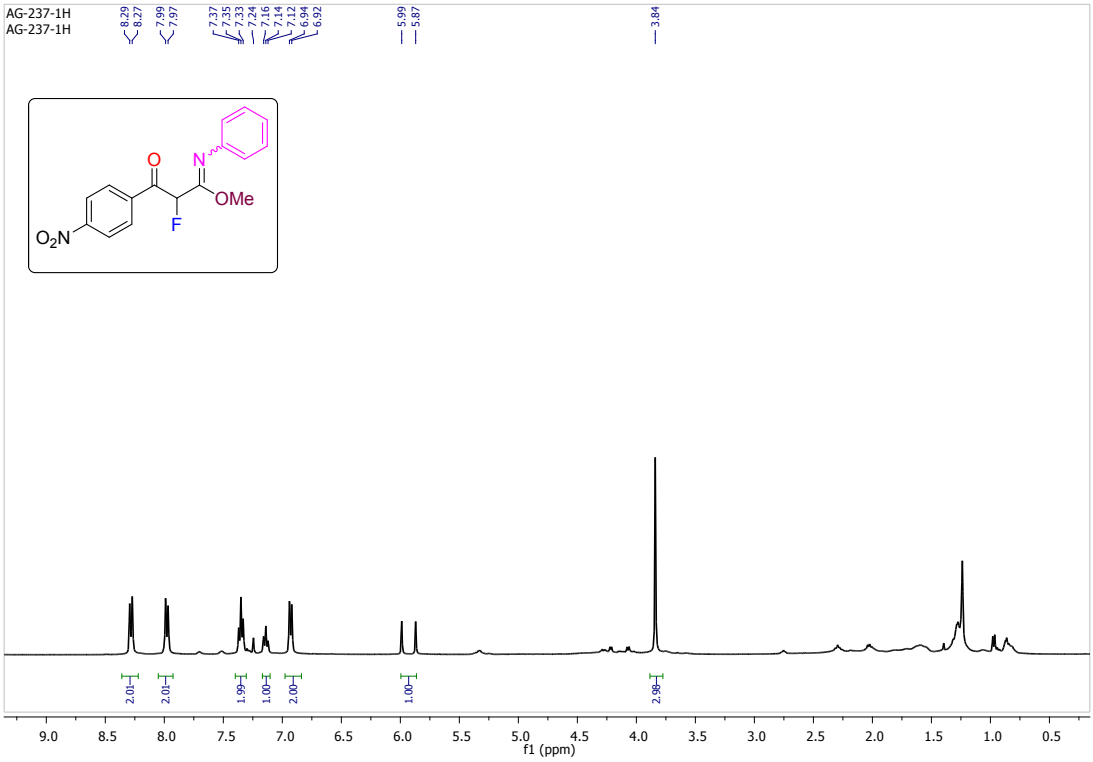


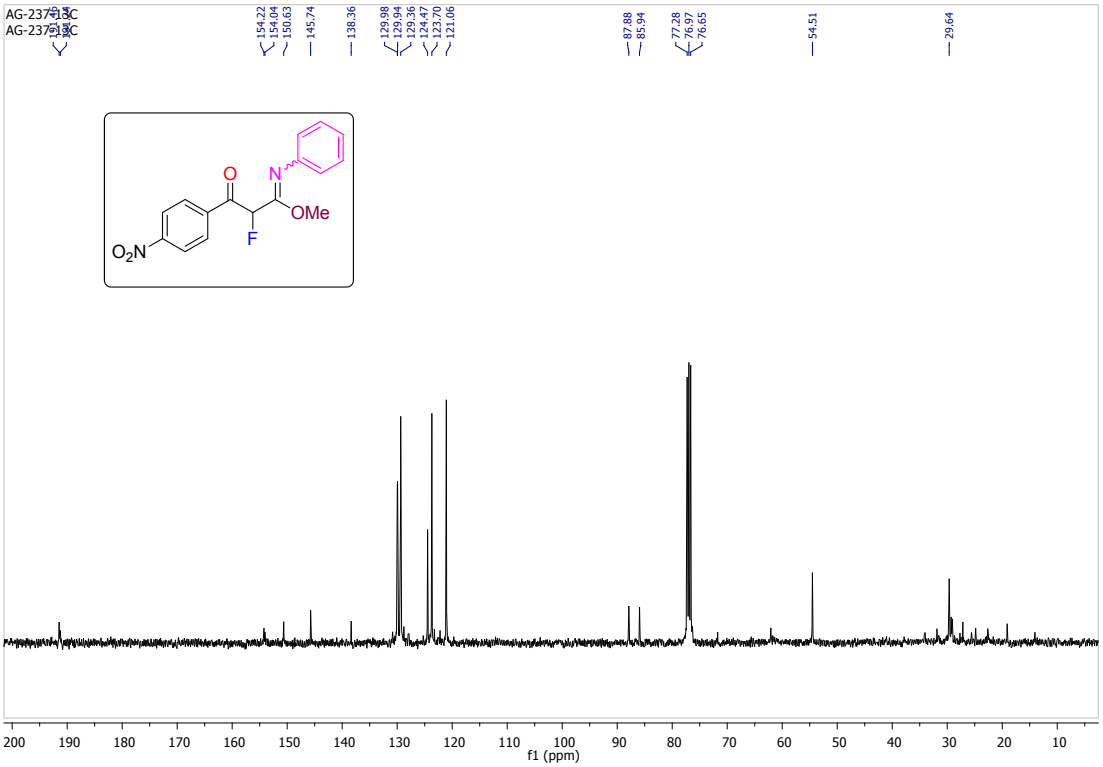
Methyl 3-(2,4-difluorophenyl)-2-fluoro-3-oxo-*N*-phenylpropanimidate (5e)

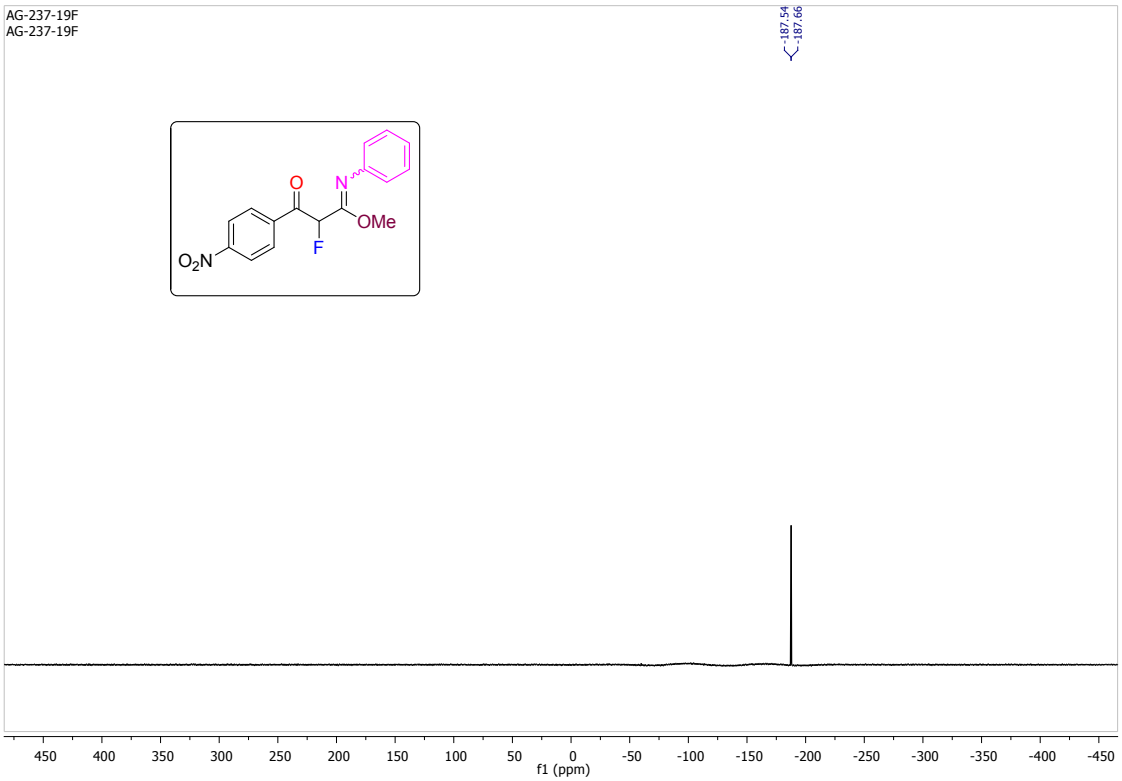




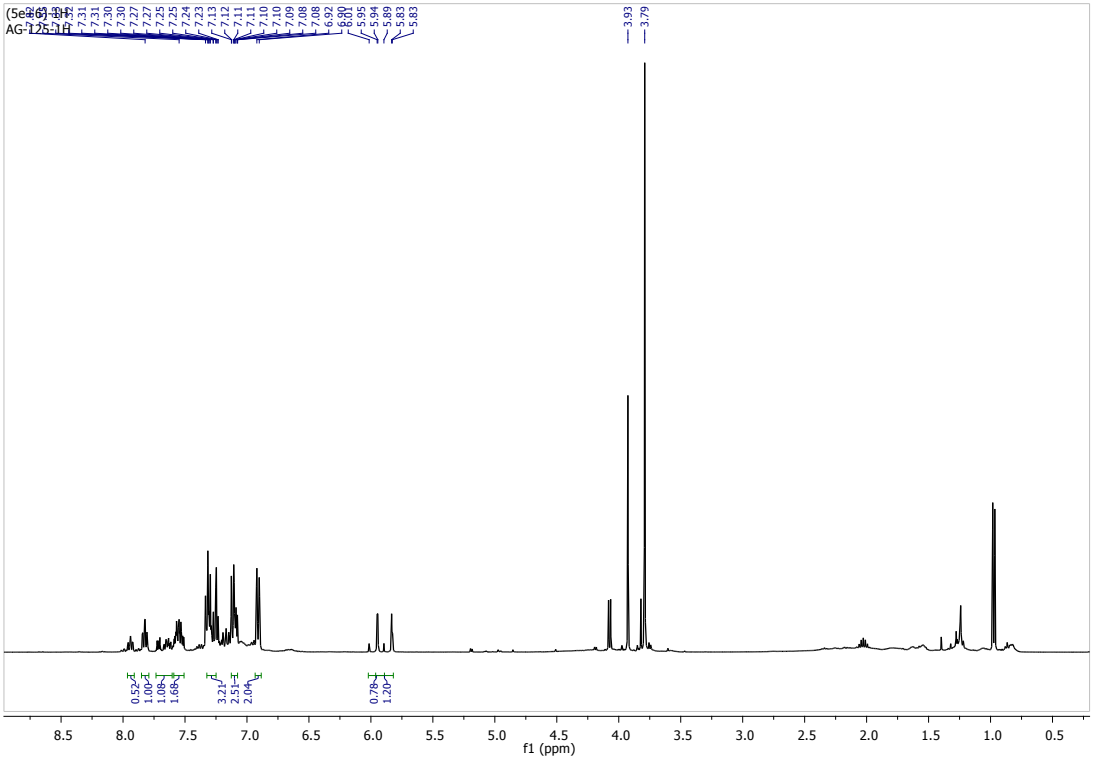
Methyl 2-fluoro-3-(4-nitrophenyl)-3-oxo-*N*-phenylpropanimidate (5f)

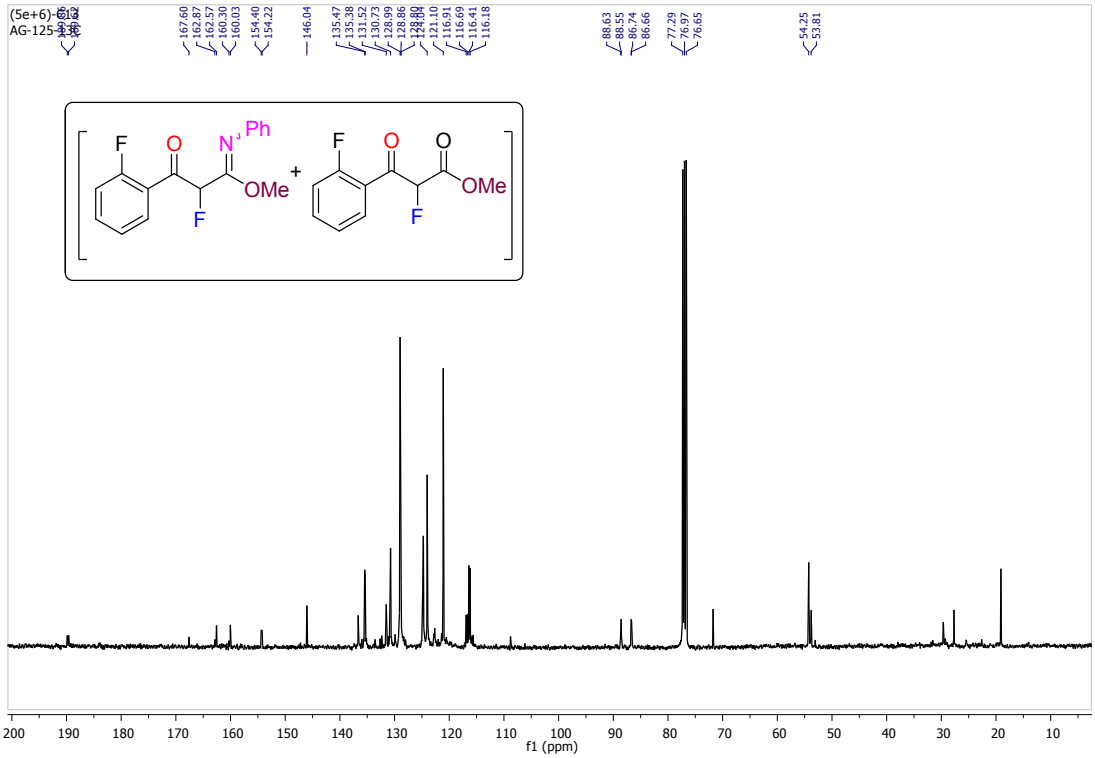




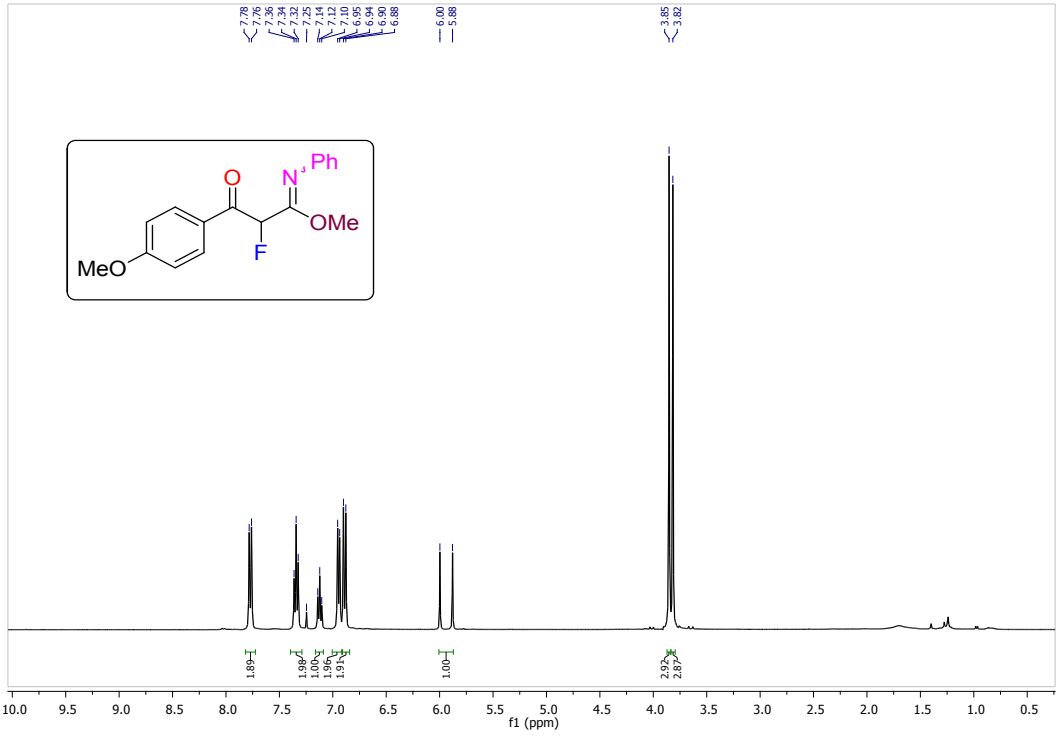


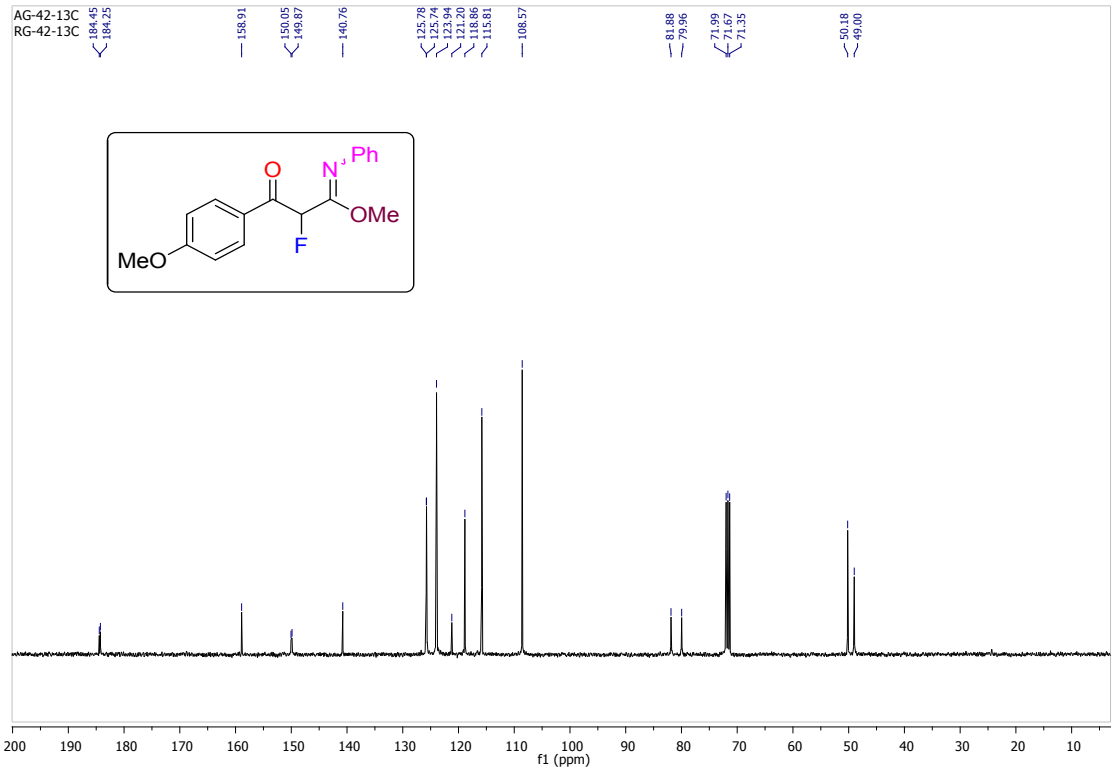
Methyl 2-fluoro-3-(2-fluorophenyl)-3-oxo-*N*-phenylpropanimidate + methyl 2-fluoro-3-(2-fluorophenyl)-3-oxopropanoate (5g + 5g')



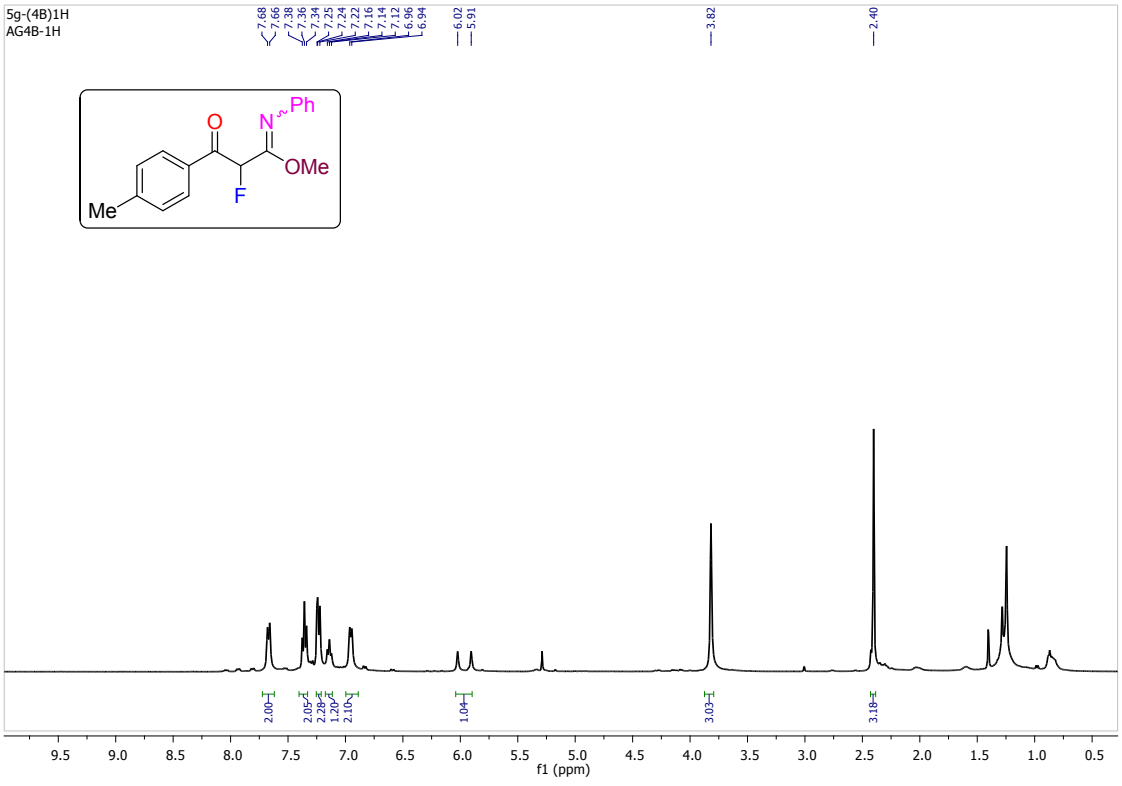


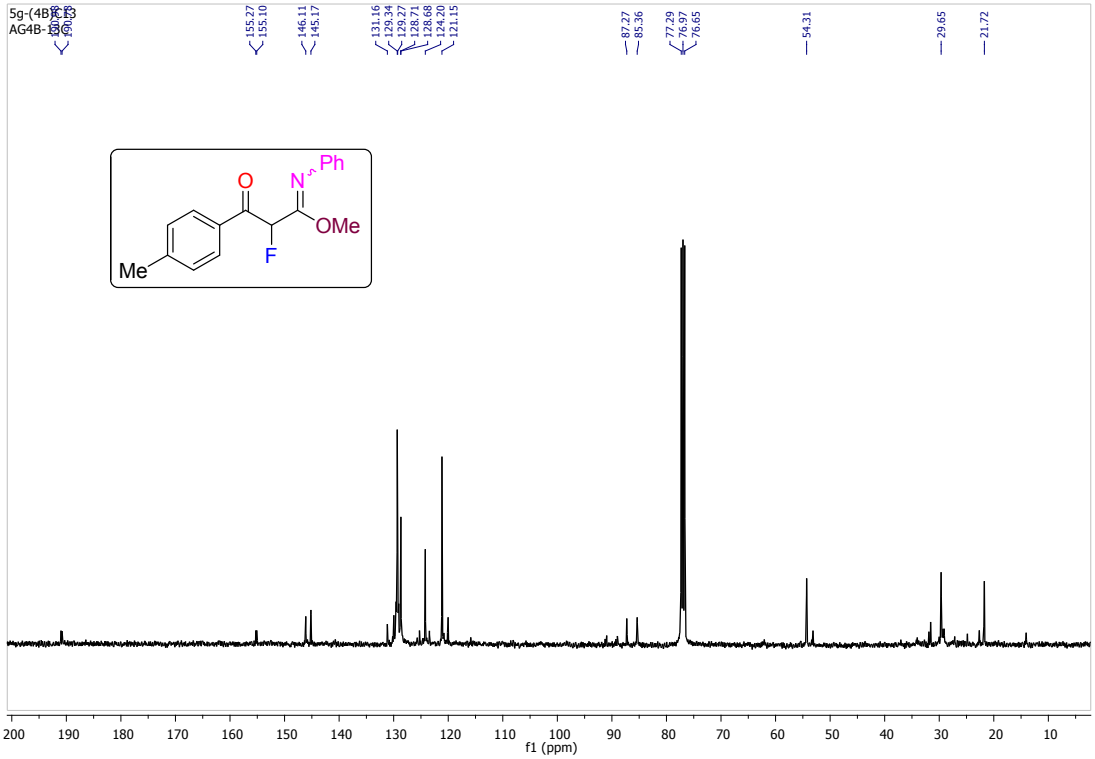
Methyl 2-fluoro-3-(4-methoxyphenyl)-3-oxo-*N*-phenylpropanimidate (5h)



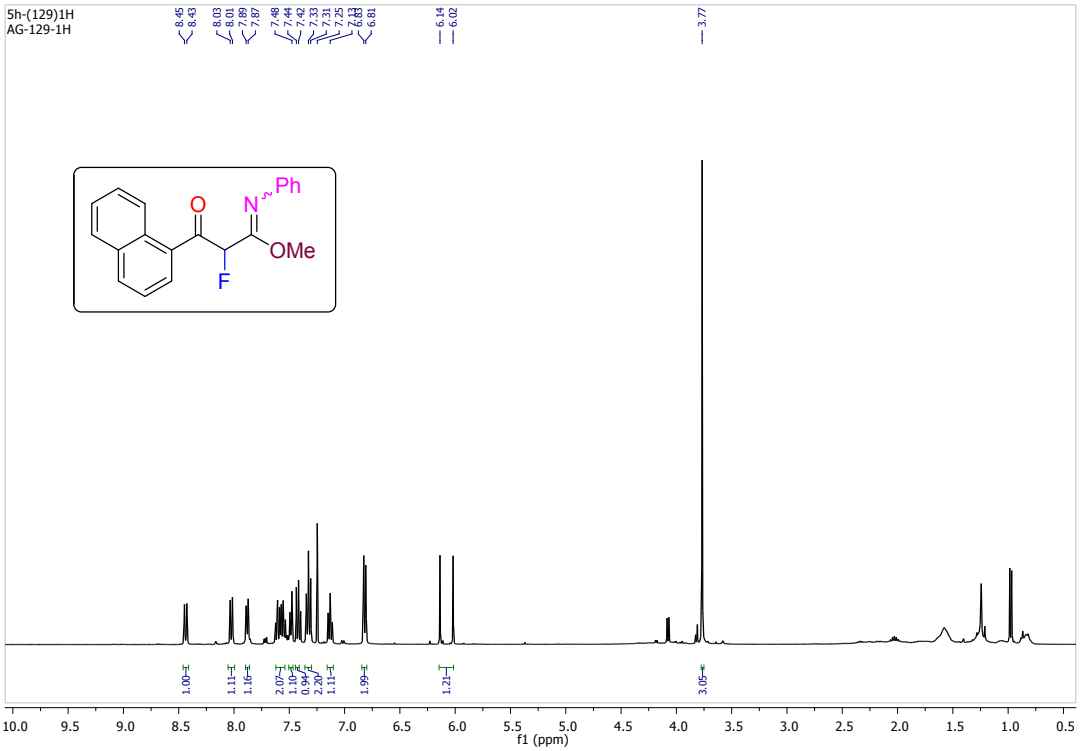


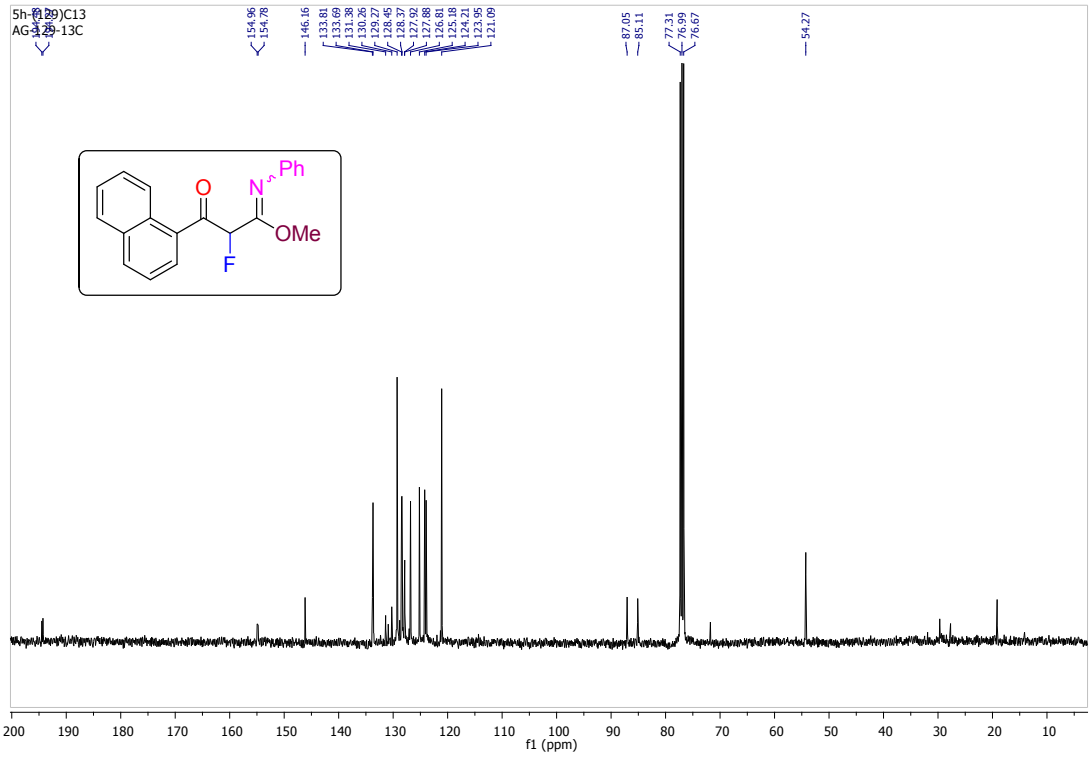
Methyl 2-fluoro-3-oxo-*N*-phenyl-3-(*p*-tolyl)propanimidate (5i)



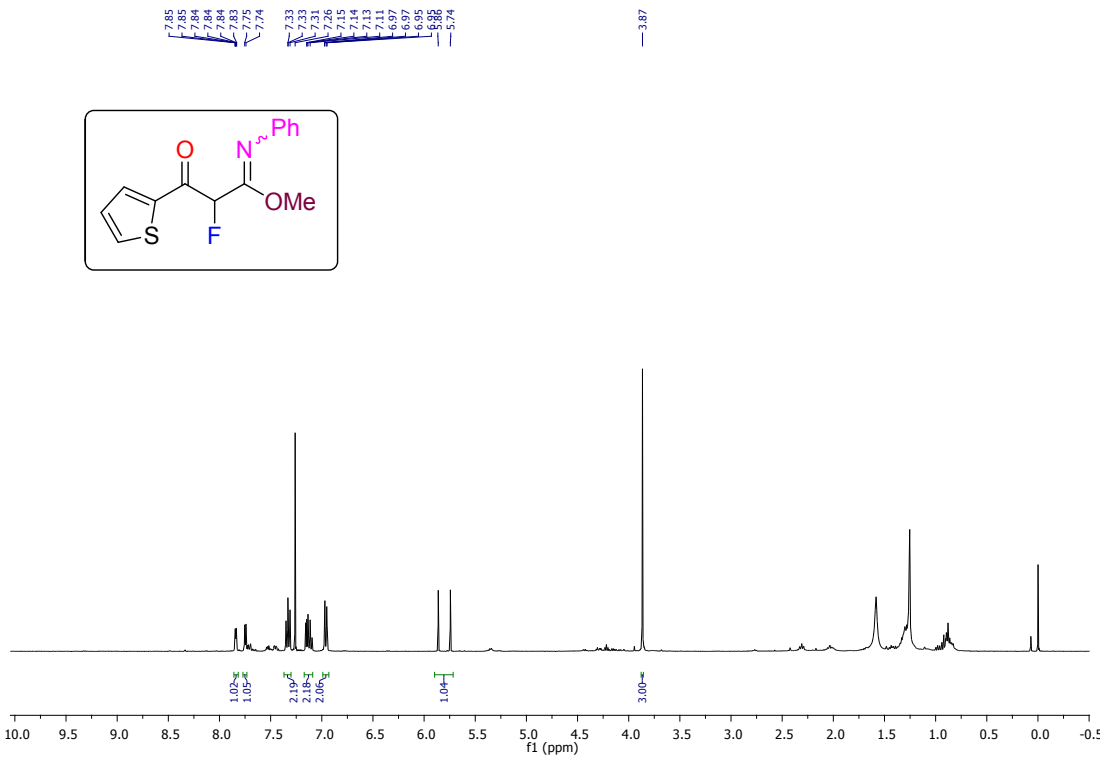


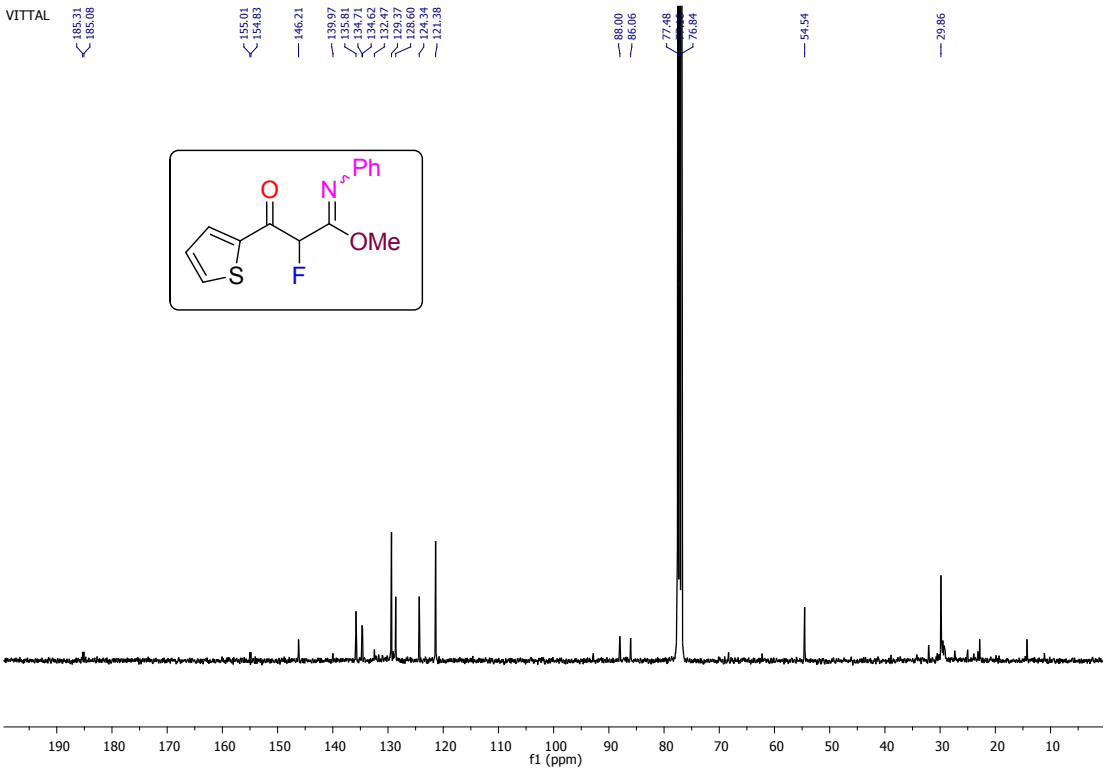
Methyl 2-fluoro-3-(naphthalen-1-yl)-3-oxo-*N*-phenylpropanimidate (5j)

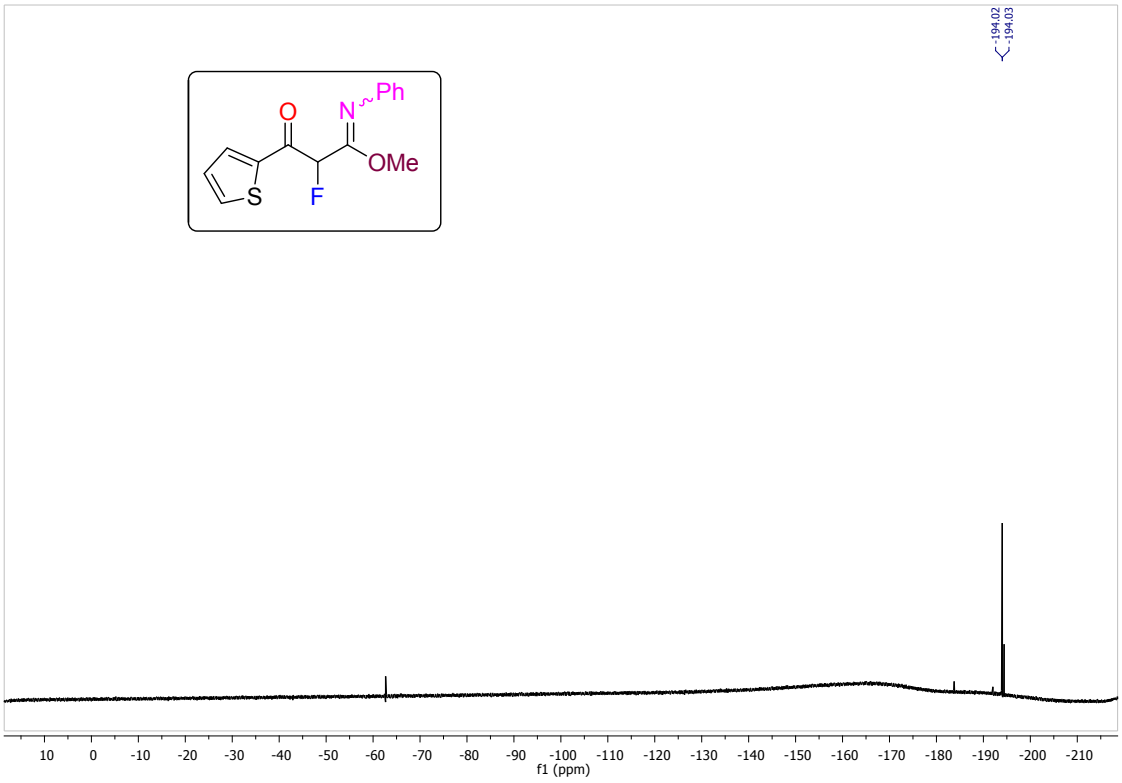




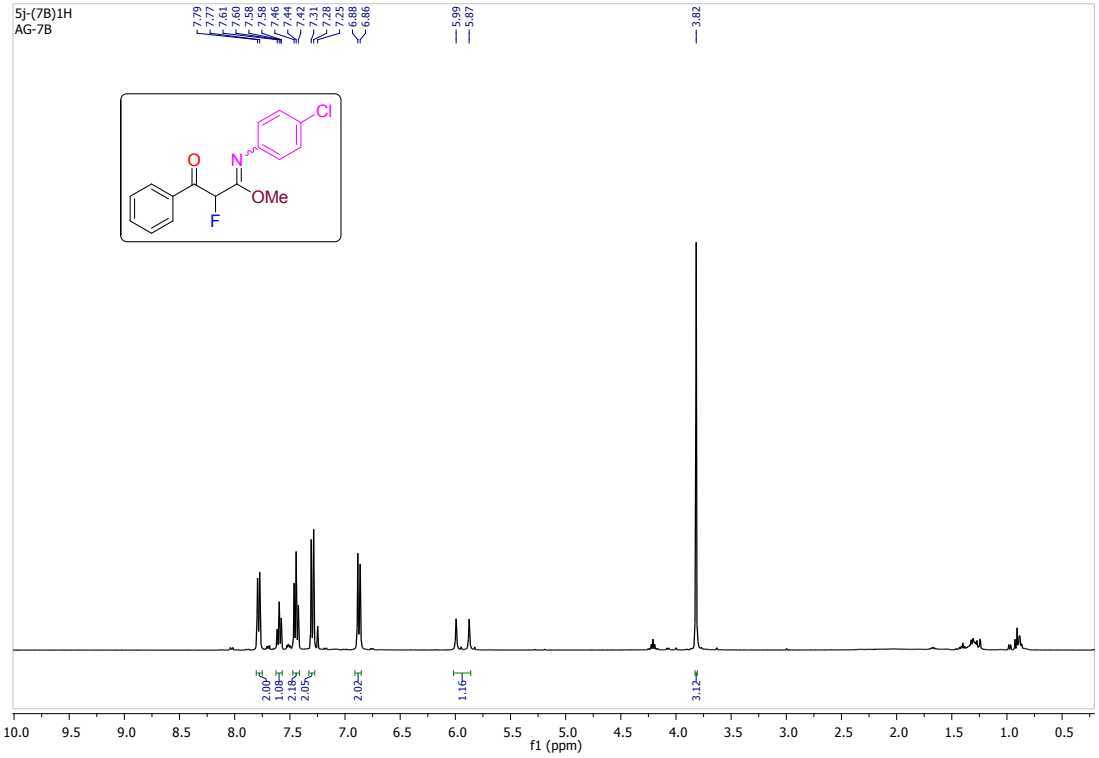
Methyl 2-fluoro-3-oxo-*N*-phenyl-3-(thiophen-2-yl)propanimidate (5k)

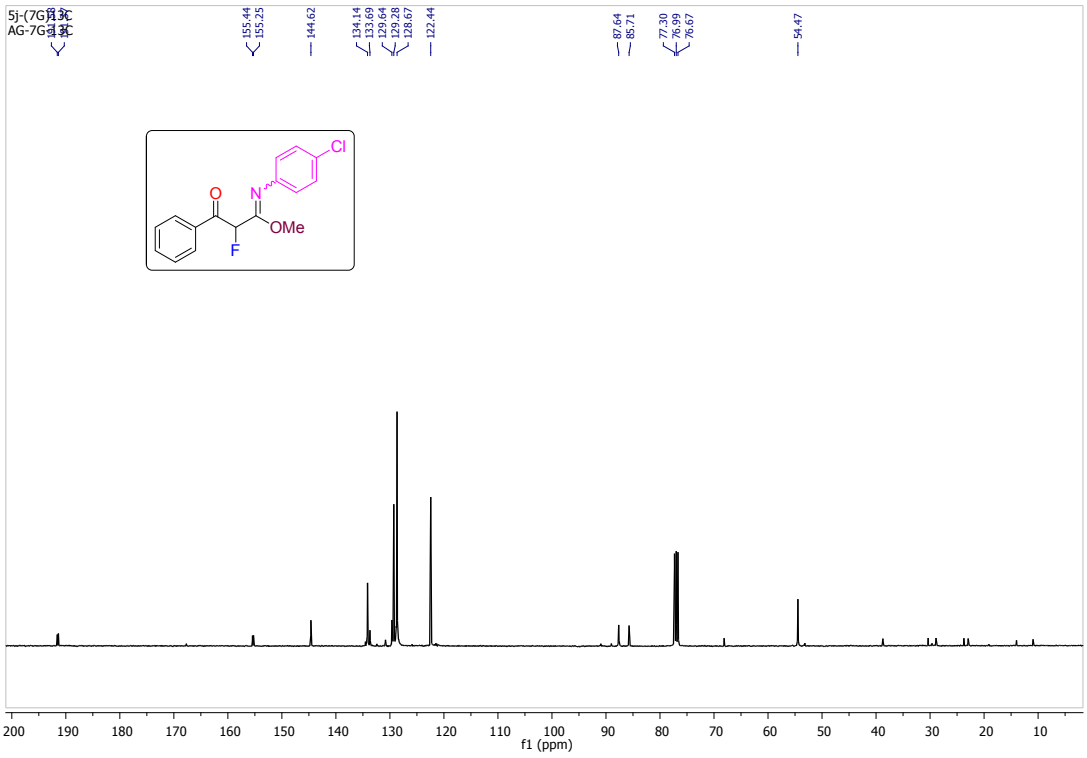



VITTAL
185.31
185.08
155.01
154.83
146.21
139.97
135.81
134.71
134.62
132.47
129.37
129.00
124.34
121.38
88.00
86.06
77.48
76.84
54.54
29.86
O
N
Ph
OMe
S
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

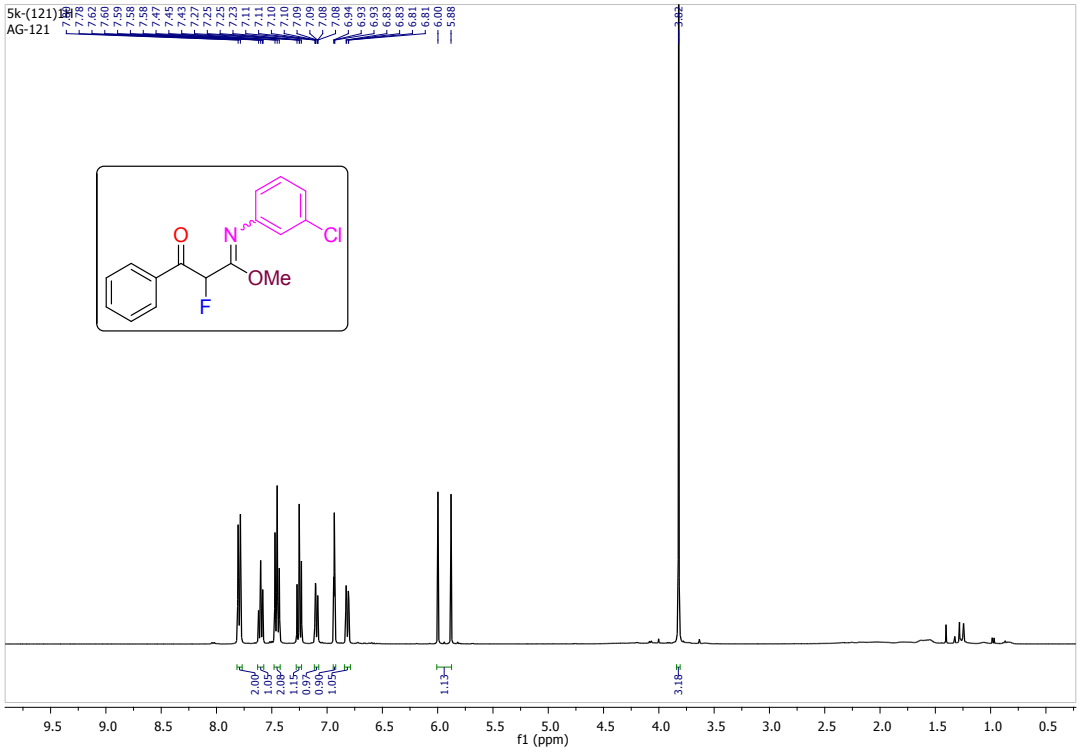

-194.02
-194.03
O
N
Ph
OMe
S
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

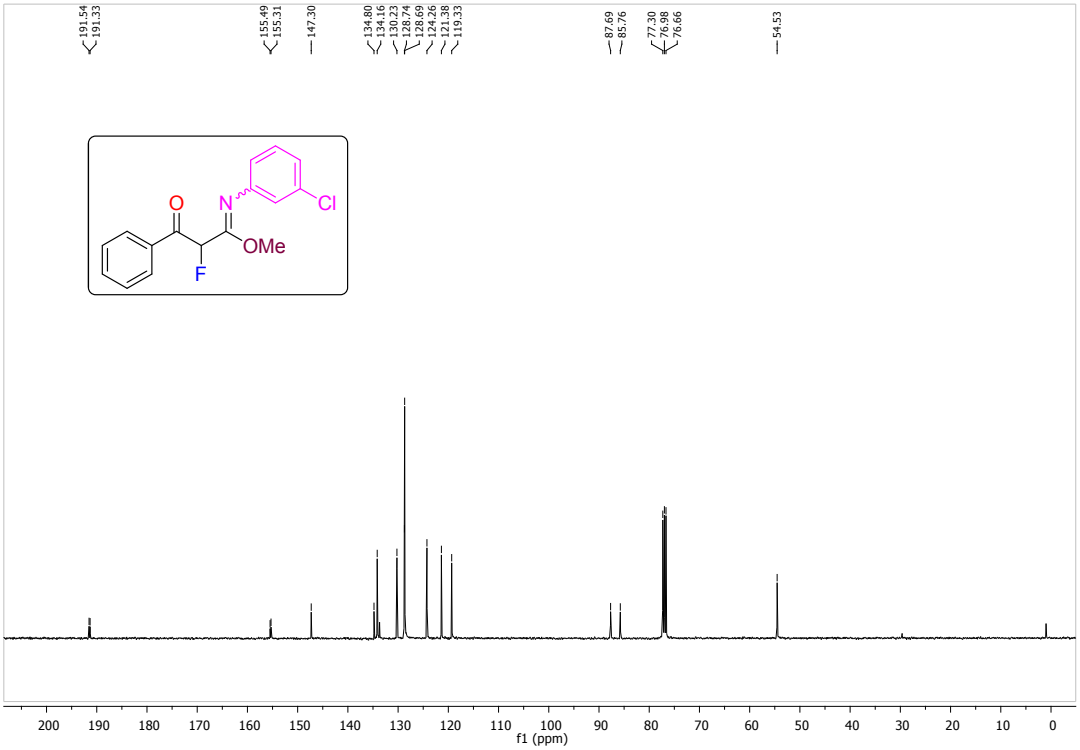
Methyl *N*-(4-chlorophenyl)-2-fluoro-3-oxo-3-phenylpropanimidate (5l)



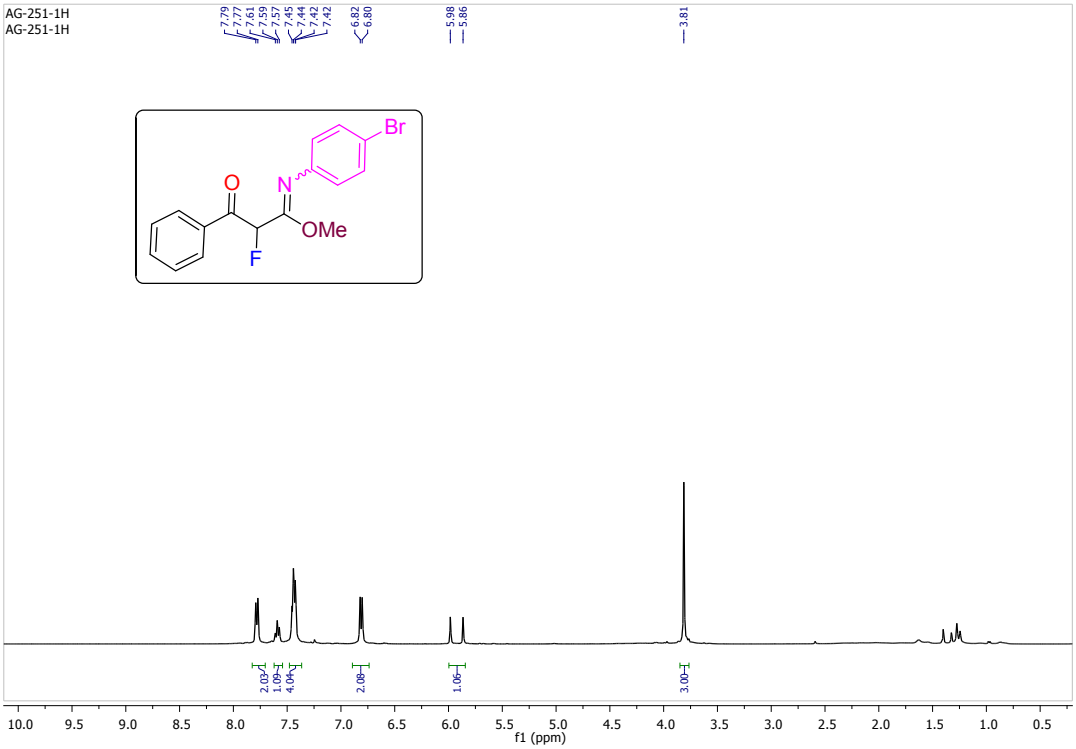


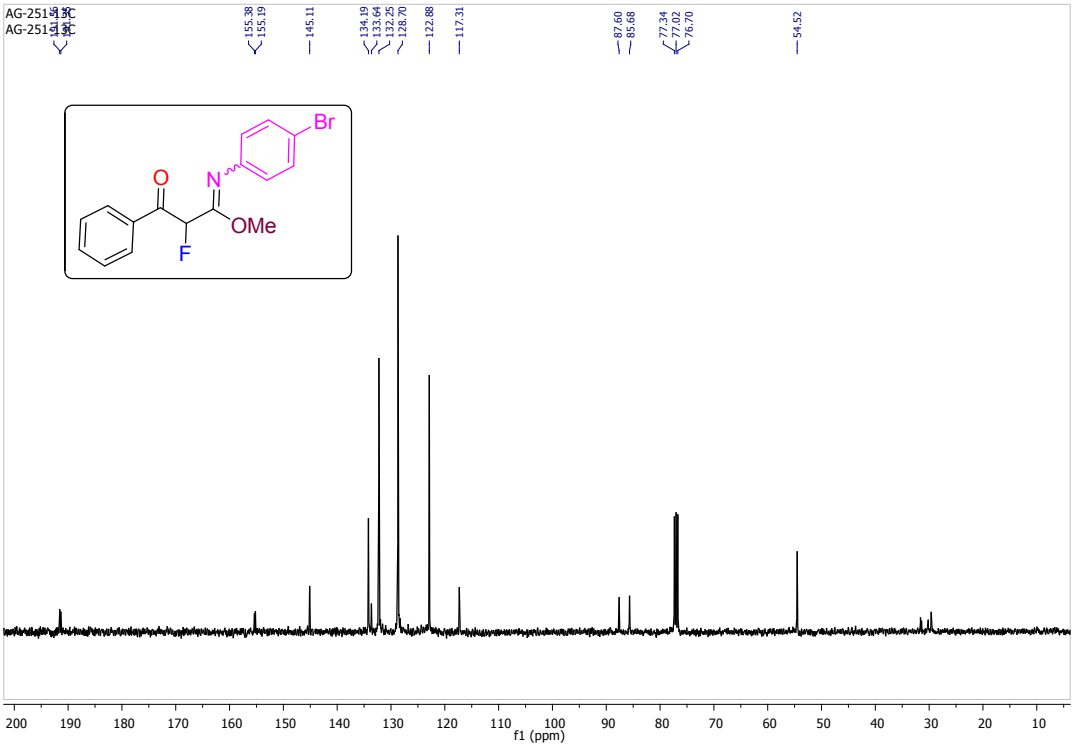
Methyl *N*-(3-chlorophenyl)-2-fluoro-3-oxo-3-phenylpropanimidate (5m)

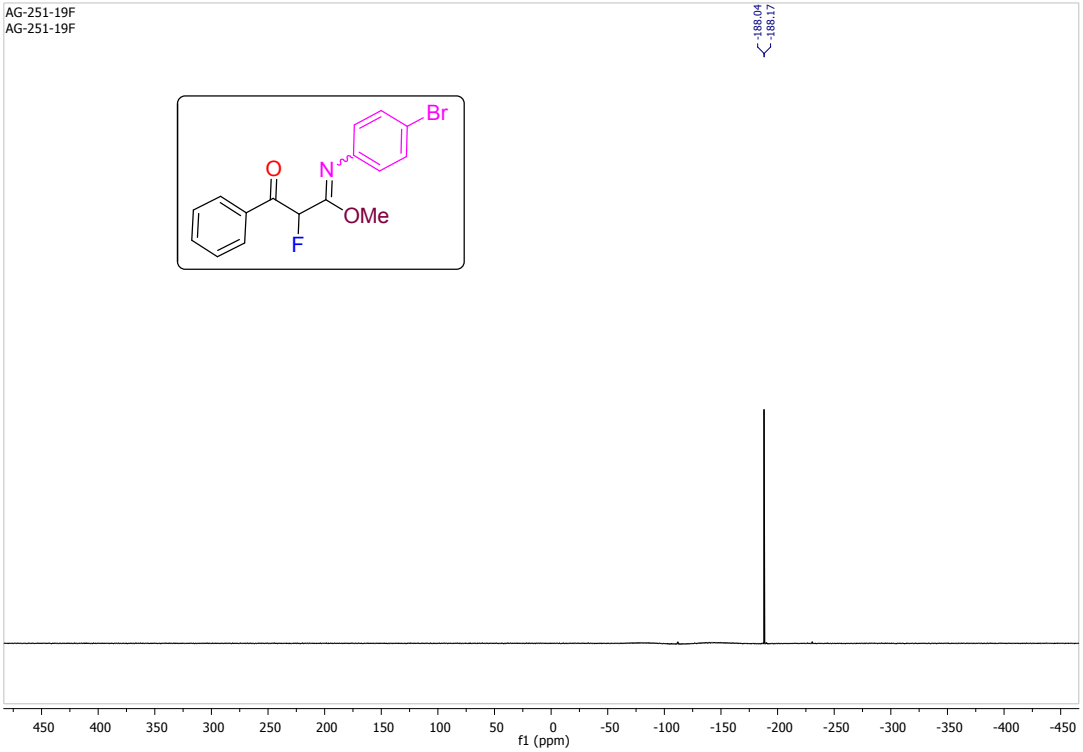




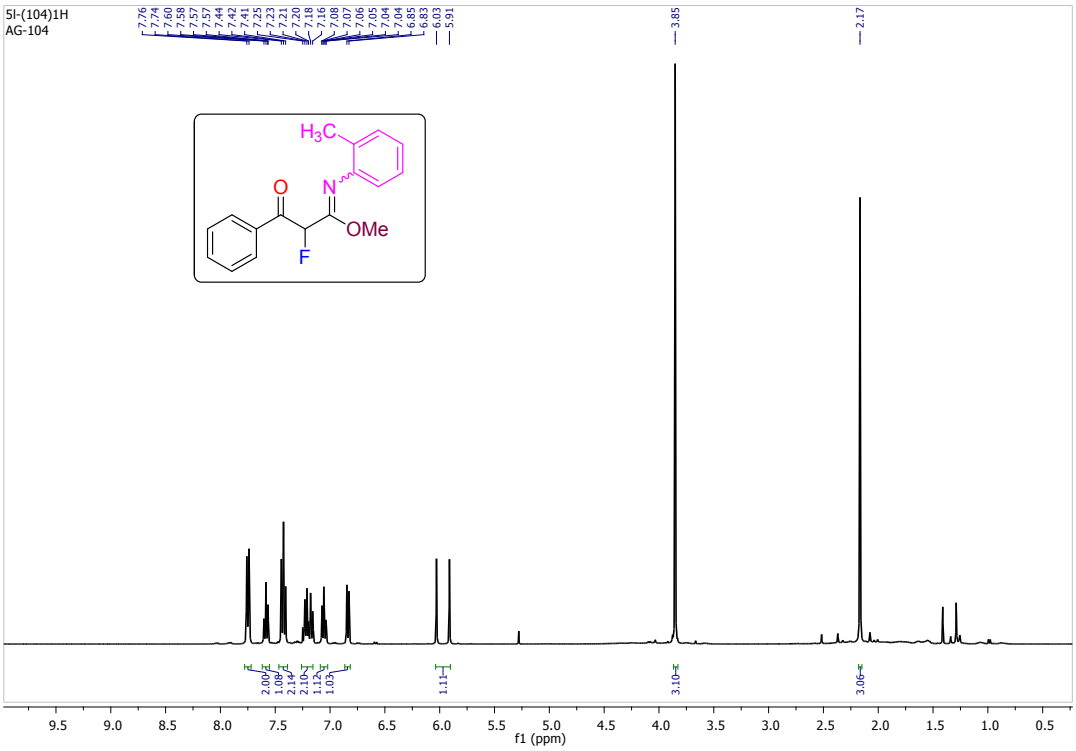
Methyl *N*-(4-bromophenyl)-2-fluoro-3-oxo-3-phenylpropanimidate (5n)

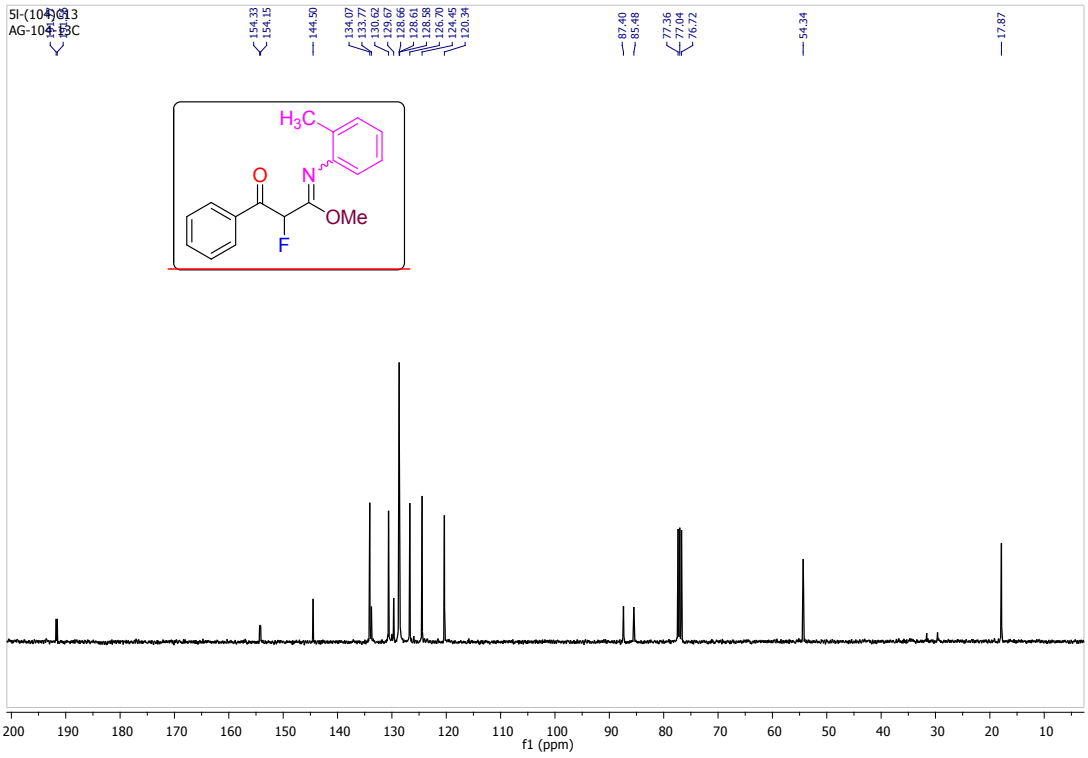


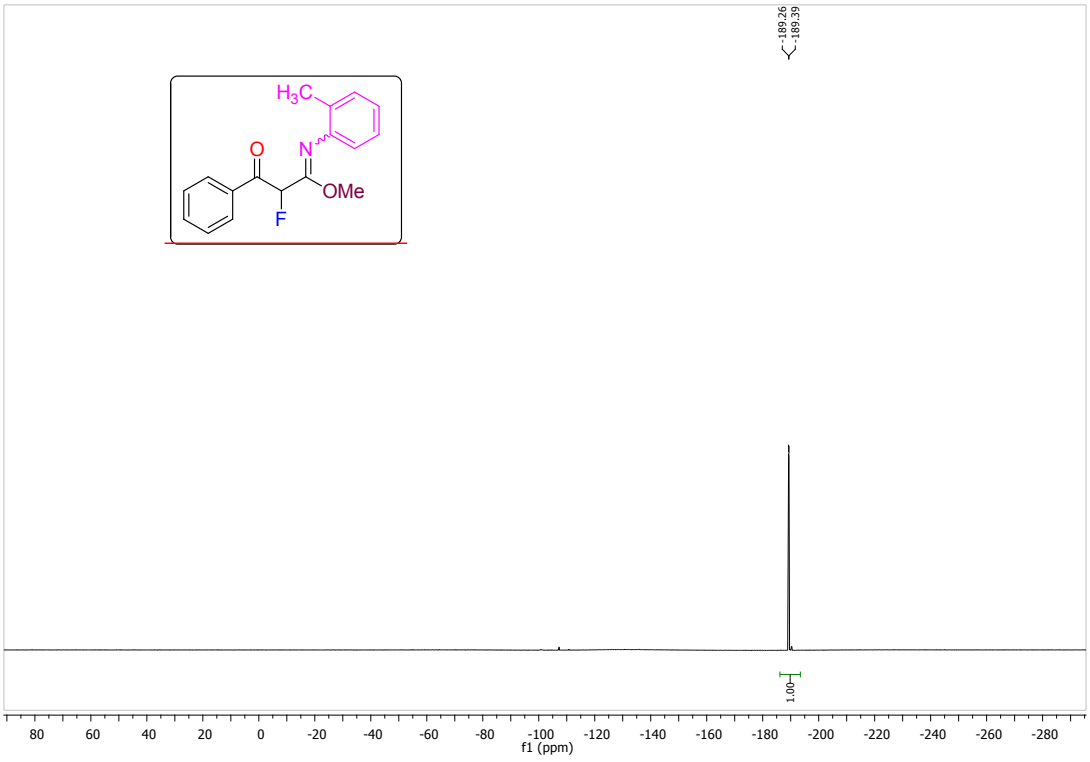




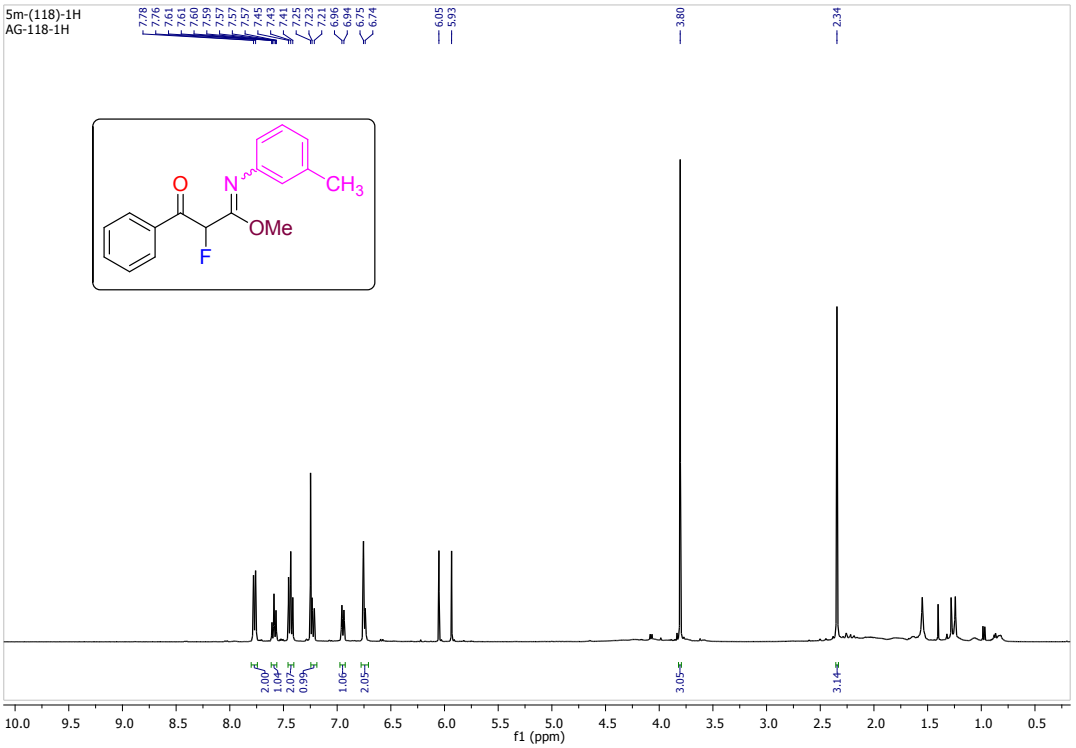
Methyl 2-fluoro-3-oxo-3-phenyl-*N*-(o-tolyl)propanimidate (5o)

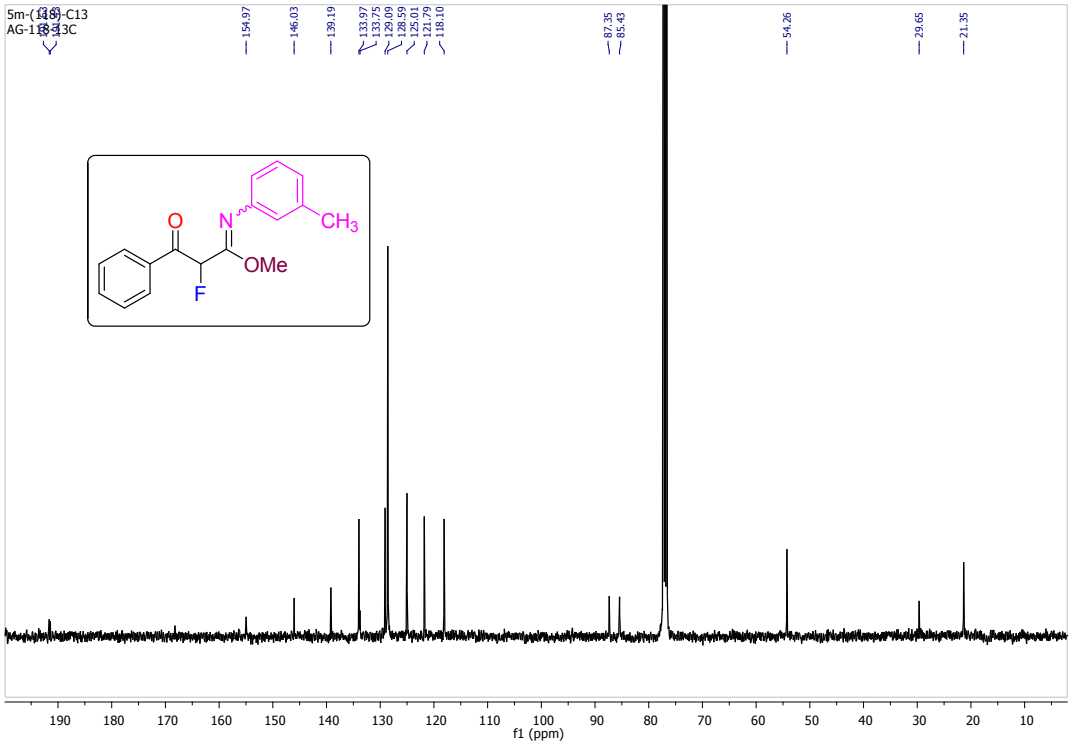


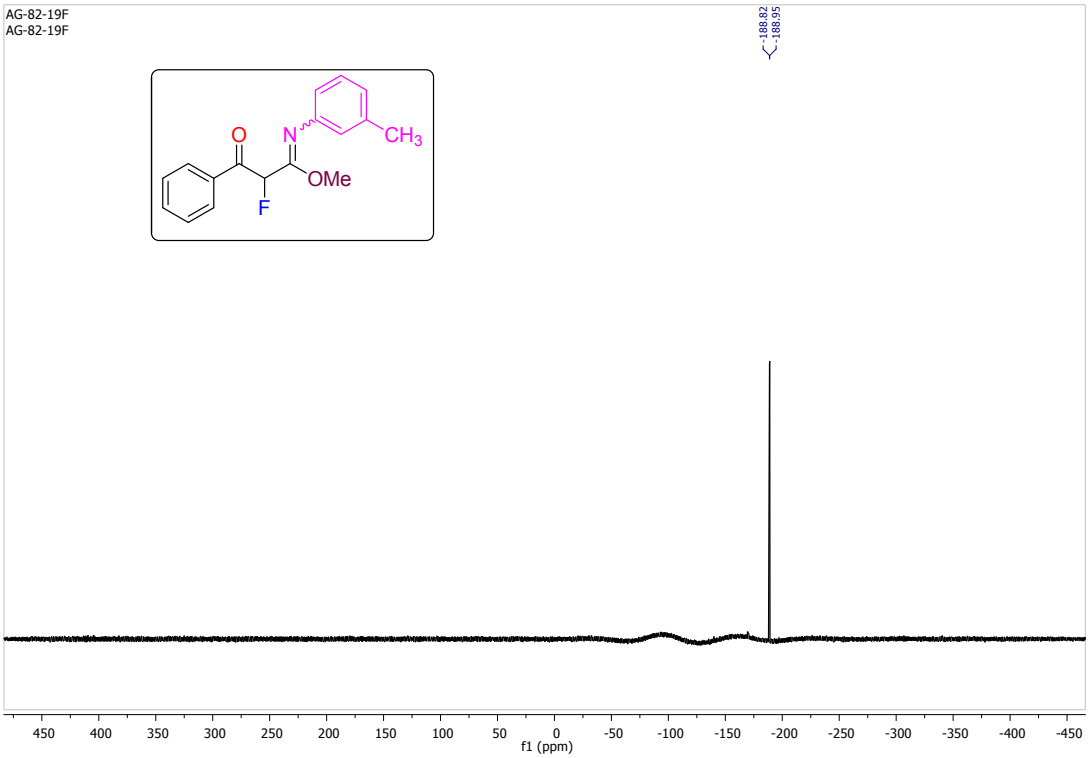

5l-(104)C13
AG-104-13C
154.33
154.15
144.50
134.07
133.77
130.62
129.67
128.66
128.61
128.58
126.70
124.45
120.34
87.40
85.48
77.36
77.04
76.72
54.34
17.87
H3C
O
N
OMe
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-189.26
-189.39
H3C
O
N
OMe
F
1.00
80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

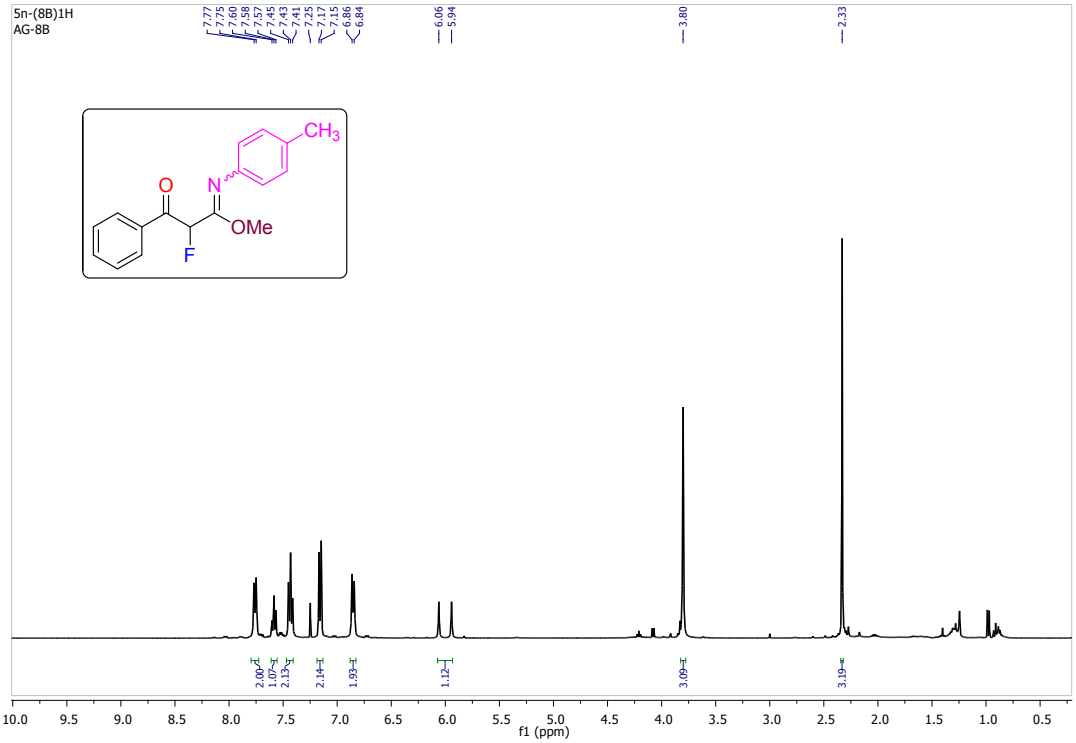
Methyl 2-fluoro-3-oxo-3-phenyl-*N*-(m-tolyl)propanimidate (5p)

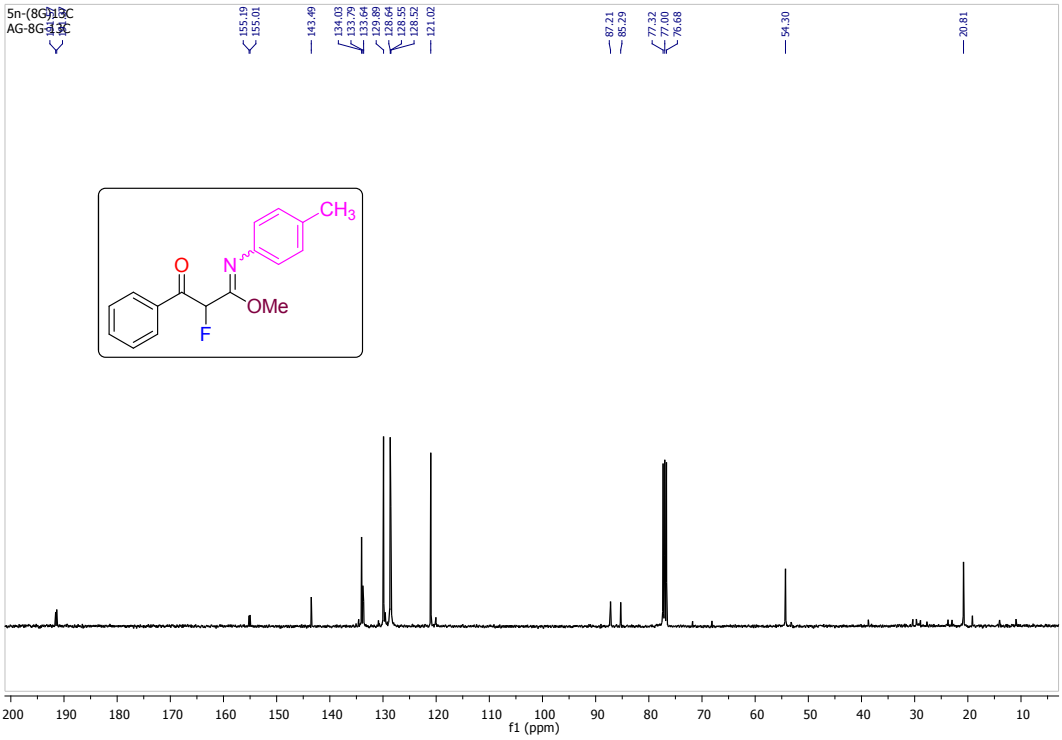




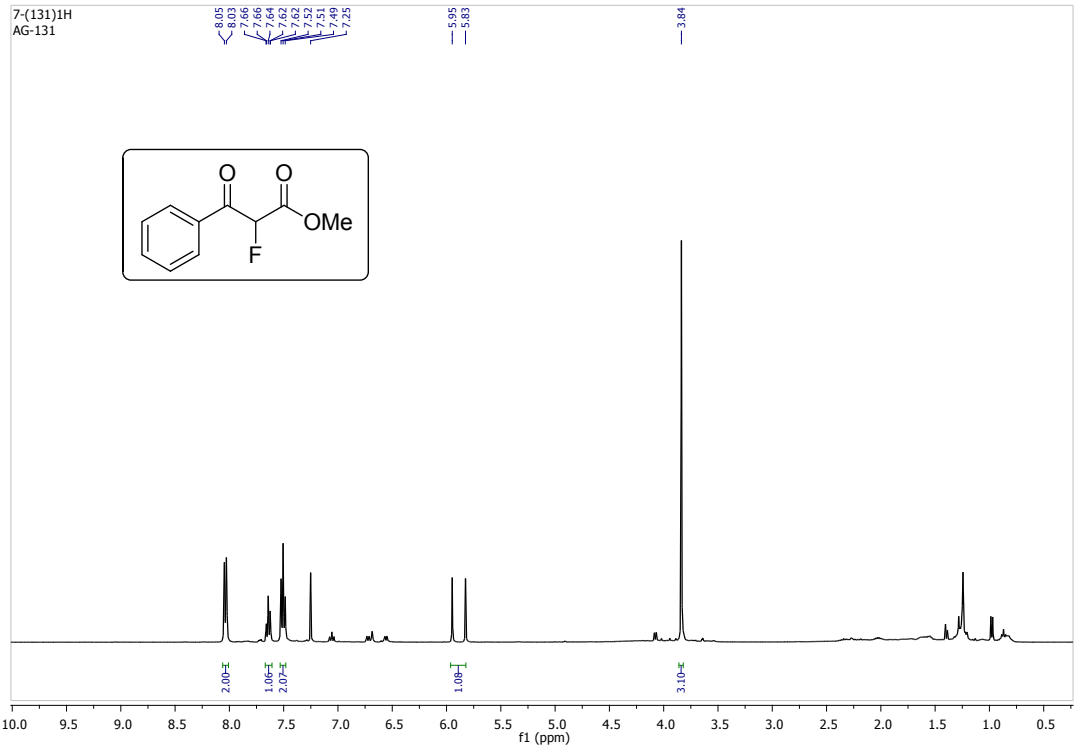


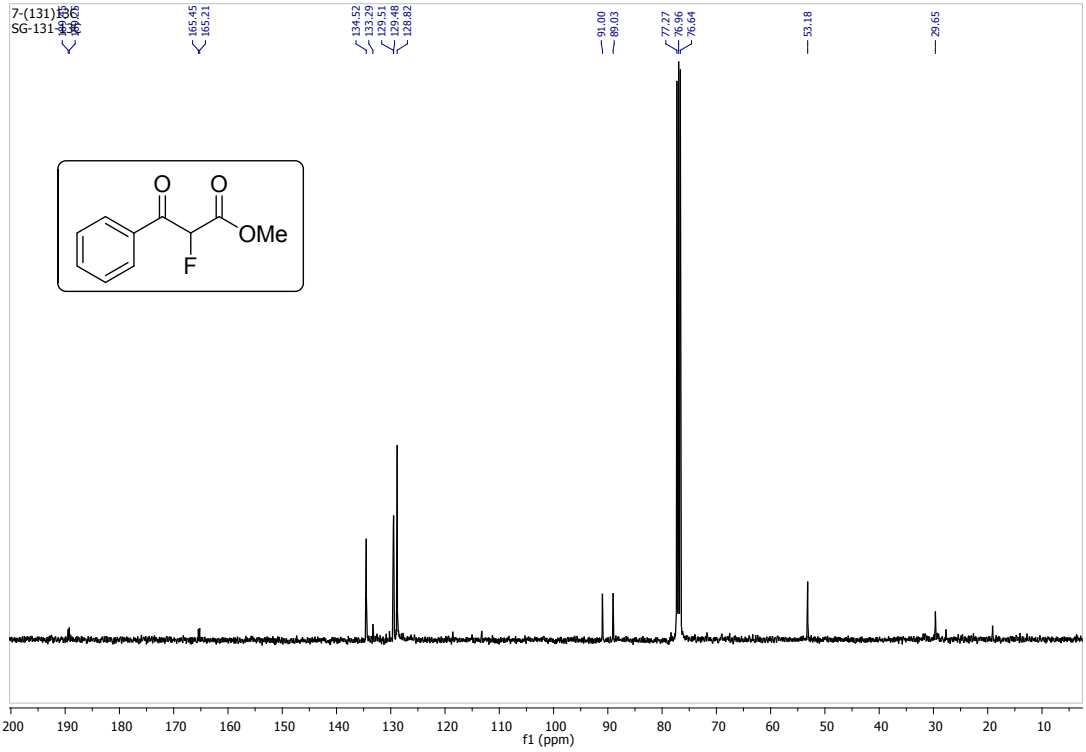
Methyl 2-fluoro-3-oxo-3-phenyl-*N*-(*p*-tolyl)propanimidate (5q)





3,3-Bis(methyloxycarbonyl)-2-phenyl-7-(4-toluensulfonylamide)-1- acetylindoline (6)




7-(131)-13C
SG-131-13C
165.45
165.21
134.52
133.29
130.51
129.48
128.82
91.00
89.03
77.27
76.96
76.64
53.18
29.65
O
O
OMe
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Crystallographic Data

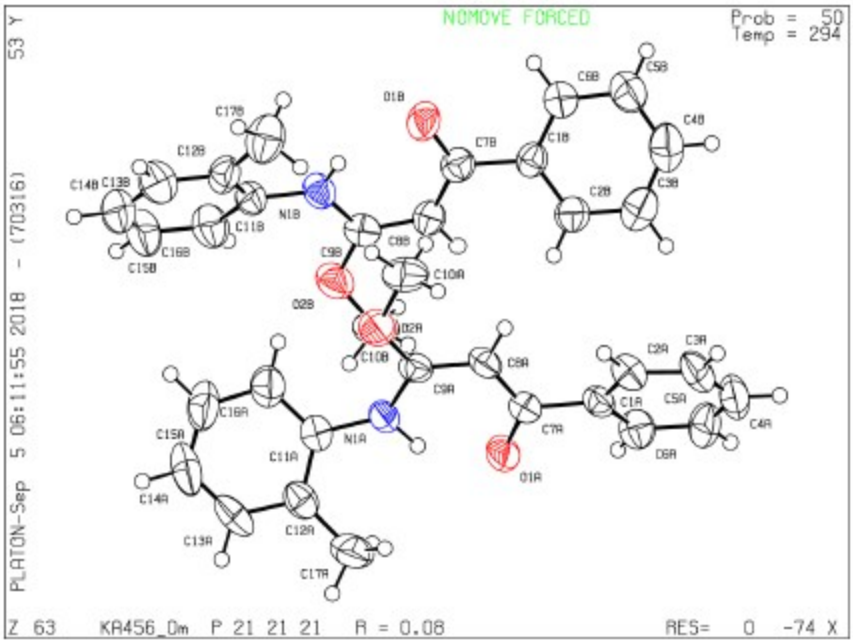


Figure S2. Crystal XRD image of **3o** (dimer: CCDC1865939)

X-ray data for the compound **3o** was collected on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs[1]. The structure was solved using intrinsic phasing method[2] and further refined with the SHELXL[2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The N-bound H atoms were located in difference Fourier maps, and their positions and isotropic displacement parameters were refined All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(C)$ for other H atoms].

Crystal Data for 3o: $C_{17}H_{17}NO_2$ (M =267.33 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.21212(9) Å, b = 15.4816(2) Å, c = 26.0416(3) Å, V = 2907.68(7) Å^3, Z = 8, T = 294.15 K, μ(Mo Kα) = 0.080 mm^{-1}, $Dcalc$ = 1.2213 g/cm^3,

38527 reflections measured (5.26° ≤ 2Θ ≤ 61.2°), 8955 unique (R_{int} = 0.0911, R_{sigma} = 0.0892) which were used in all calculations. The final R_1 was 0.0765 (I>2σ(I)) and wR_2 was 0.1416 (all data).

CCDC 1865939 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** *Acta Crystallography* C71: 3-8.

Figure Captions

Fig. S2. A view of **3o**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.