5-*Endo* Trig Oxidative Radical Cyclizations of Ugi-3CR Products Towards 1,4-Imidazolidinones.

Kevin Schofield†, Christopher Foley†§, Christopher Hulme†§*

*E-mail: Hulme@pharmacy.arizona.edu

†Department of Chemistry and Biochemistry, College of Science, The University of Arizona, Tucson, AZ, 85721, USA.

§ Department of Pharmacology and Toxicology, College of Pharmacy, The University of Arizona, Tucson, AZ, 85721, USA

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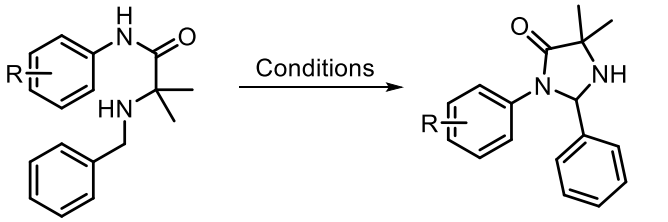
1. General Information

All reagents and solvents were acquired from commercially available suppliers and used without further purification. 18-Crown-6 and KBr were obtained from Alfa Aesar, while PIDA and acetonitrile (dried on molecular sieves-Acroseal) were obtained from Acros. Phenylphosphinic acid was obtained from Strem, while aniline was obtained from Sigma Aldrich. The products were purified using a Teledyne CombiFlash Rf automated flash chromatography apparatus with a cartridge utilizing the compounds dry loaded using a Teledyne Isco silica column (12g). High resolution mass spectra were obtained using an Orbitrap^{TM} for all the compounds, obtained in an Ion Cyclotron Resonance (ICR) spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker NMR spectrometer at 400 and 100 MHz respectively. The data is reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublets, t = triplet, q=quartet, p= pentet, m = multiplet). Coupling constant are reported in Hertz (Hz) and were automatically generated using known NMR analyzer software (MestReNova), these were then subsequently curated. The reactions were always carried out in vacuum-oven dried 2-5 mL (20mL in some cases) Biotage microwave vials (MWV), sealed with Blue-Biotage-Teflon septum without the use of inert conditions. Single crystals of **2h**, **2i**, and **9a** were submitted for structure determination. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimization.

2. Optimization of Reaction Conditions



R = 4-MeO (**1a**)
3,4-DiMe (**1b**)
3,4-DiMeO (**1c**)

R = 4-MeO (**2a**)
3,4-DiMe (**2b**)
3,4-DiMeO (**2c**)

Table S1. Preliminary Reaction Optimization

Entry	SM	T (°C)	Time	Oxidant	Additive	Solvent	Yield (brsm)[a]
1	1a	100	16 h	IBX (1eq)	-	DMSO (0.5M)	23%[b]
2	1a	60	16 h	IBX (1 eq)	TFA (2 eq)	DCM (0.2M)	0%
3	1a	100	18 h	IBX (2 eq)	-	DMSO (0.37M)	26% (84%)[b]
4	1c	100	18 h	IBX (3 eq)	-	DMSO (0.5M)	30% (66%)[b]
5	1c	130	18 h	IBX (3 eq)	-	DMSO (0.5M)	0%
6	1c	rt	16 h	IBX (1.2 eq)	NaBr (1 eq)	DCM (0.14M)	34% (73%)[b]
7	1c	rt	24 h	PIDA (2 eq)	-	HFIP (0.14M)	31%[b]
8	1c	rt	24h	PIDA (3 eq)	-	HFIP (0.63 M)	34%[b]
9	1b	rt	27 h	PIDA (2 eq)	-	HFIP (0.83M)	73%[b]
10	1c	rt	46 h	PIDA (2 eq)	O2	HFIP (0.83M)	9%[b]
11	1a	rt	24 h	PIDA (2 eq)	-	DCM (0.83M)	36%[b]
12	1a	rt	24 h	PIFA (2 eq)	-	HFIP (0.87M)	0%
13	1a	rt	24 h	DMP (2 eq)	-	HFIP (0.87M)	0%
14	1a	rt	24 h	PIDA (2 eq)	-	HFIP (0.87M)	40%[b]
15	1a	rt	24 h	PIDA (1.5 eq)	-	HFIP (0.87M)	55% (70%)[b]
16	1a	rt	24 h	PIDA (1 eq)	-	HFIP (0.87M)	59% (84%)[b]
17	1a	50	24 h	PIDA (1 eq)	-	HFIP (0.87M)	33% (49%)[b]
18	**1a**	**rt**	**24 h**	**PIDA (1.5 eq)**	**-**	**HFIP (0.87M)**	**13%[c]**
19	1b	70	2 h	TBHP (2 eq)	CuBr (10 mol%)	PhMe (0.17M)	28% (50%)[c]
20	1b	rt	24 h	Iodosobenzene	TBAI (0.5 eq)	THF (0.30M)	53%[c]
21	1b	rt	24 h	PIDA (2 eq)	NaBr (1 eq)	DCM (0.1M)	31%[c]
22	1b	rt	24 h	PIDA (1.5 eq)	-	HFIP (0.87M)	52%[c]
23	1b	rt	24 h	PIDA (2 eq)	-	HFIP (0.87M)	14%[c]
24	**1b**	**rt**	**24 h**	**PIDA (1.2 eq)**	**KBr (1 eq)**	**DCM (0.1M)**	**48%[c]**
25	1b	rt	24 h	PIDA (1.5 eq)	KBr (1 eq)	ACN (0.1M)	32% (42%)[c]

26	1b	rt	24 h	PIDA (1.2 eq)	KBr (1 eq) 4A MS	DCM (0.1M)	15% (58%)[c]

[a]Yield based on recovered starting material. [b]NMR Yield (the rest are isolated yields), [c]Purification with an alumina column gave pure product.

Table S2. Solvent screen

Entry	Solvent	Yield (brsm)[a]
1	DCM (0.1M)	48%
2	**ACN (0.1M)**	**47% (74%)**
3	DCE (0.1 M)	24% (53%)
4	DCM:ACN (1:1, 0.1M)	31% (46%)
5	ACN (0.2M)	45% (68%)
6	ACN (0.05M)	54% (65%)
7	THF (0.1M)	32% (38%)
8	Dioxane (0.1M)	40% (67%)
9	DME (0.1M)	49%

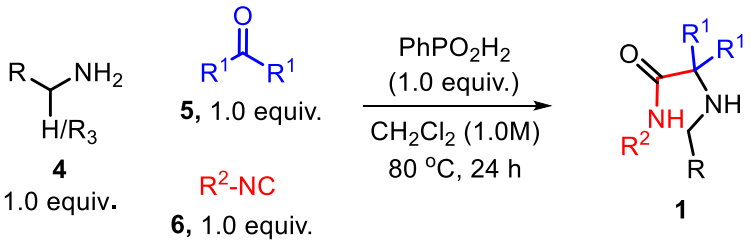
[a]Yield based on recovered starting material. Conditions: PIDA (1.2 equiv.), KBr (1 equiv.), 24 hours at room temperature using starting material **1b**.

Table S3. Exploration of 18-crown-6 as an additive.

ID	Oxidant	Additive	Additive #2	Yield
1	PIDA (1.2 eq)	KBr (1 eq)	18-Crown-6 (0.17 eq)	63%
2	PIDA (1.2 eq)	KBr (1 eq)	18-Crown-6 (0.5 eq)	63%
3	**PIDA (1.2 eq)**	**KBr (1 eq)**	**18-Crown-6 (1.2 eq)**	**84%**
4	PIDA (1.2 eq)	KBr (1 eq)	18-Crown-6 (2 eq)	78%
5	PIDA (2 eq)	KBr (1 eq)	18-Crown-6 (1.2 eq)	23%
6	PIDA (1.2 eq)	KBr (2 eq)	18-Crown-6 (1.2 eq)	70%

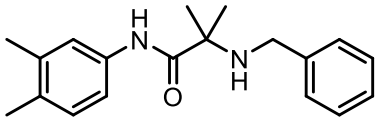
Conditions: MeCN (0.1M) and 24 hours at room temperature using starting material **1b**.

3. General Ugi 3-component reaction Procedure 1: Preparation of Ugi 3-component reaction products 1.



Amine (1.0 equiv., 1.0 mmol), ketone (1.1 equiv., 1.1 mmol) and DCM (0.7 ml., 1.1 M) were added simultaneously to a sealed 5 ml microwave vial (MWV) containing isocyanide (1.0 equiv., 1.0 mmol) and phenylphosphinic acid (1.0 equiv., 1.0 mmol). The resulting mixture was stirred at 80 °C in an oil bath for 24 h. The reaction vessel was cooled, diluted with DCM and saturated sodium bicarbonate and the aqueous layer was extracted further with DCM (3 x 15 ml). The combined organic layers were washed with saturated sodium bicarbonate and brine. The organic layers were recombined, dried over sodium sulfate, and concentrated under reduced pressure. The resulting residue was purified by automated flash column chromatography (gradient 0 – 30% EtOAc/Hexanes typically). For a representative example, see **1b**.

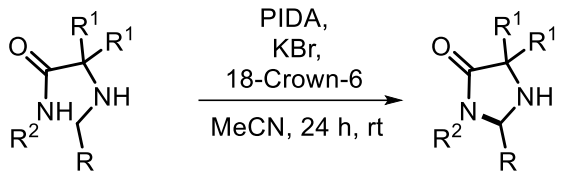
N-(3,4-dimethylphenyl)-2-methyl-2-((4-methylbenzyl)amino)propenamide (1b)



1b

Prepared by general procedure 1 by adding benzylamine (0.39 ml, 3.60 mmol), acetone (0.26 ml, 3.60 mmol) and DCM (2.60 ml, 1.1 M) simultaneously to a sealed 5 ml MWV equipped with a stir bar containing PPA (511 mg, 3.60 mmol) and 4-isocyano-1,2-dimethylbenzene (472 mg, 3.60 mmol). The crude residue was purified by using a Teledyne ISCO™ to afford title compound **1b** (721 mg, 2.43 mmol, 67% yield, eluting at 12% EtOAc in hexanes), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.52 (s, 1H), 7.43 – 7.28 (m, 6H), 7.28 – 7.23 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 3.75 (s, 2H), 2.26 (s, 3H), 2.23 (s, 3H), 1.49 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 140.1, 137.4, 136.1, 132.2, 130.1, 128.9, 128.1, 127.5, 120.6, 116.7, 59.8, 48.4, 25.9, 20.0, 19.3. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{25}N_2O$ 297.1961; found 297.1953.

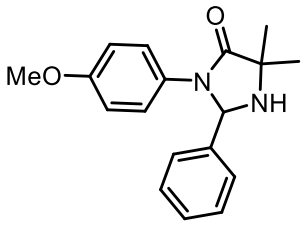
4. General Hypervalent Iodine Oxidative Cyclization Procedure 2: Preparation of 1,4-imidazolidionones.



1 **2**

Acetonitrile (2.00 ml, 0.10 M) was added to a 5 ml MWV equipped with a stir bar containing Ugi product **1a** (1.0 equiv, 0.20 mmol), PIDA (1.2 equiv., 0.24 mmol), KBr (1.0 equiv., 0.20 mmol), 18-Crown-6 (1.2 equiv., 0.24 mmol). The reaction vessel was covered in aluminum foil and the reaction was stirred for 24 h at room temperature. The reaction mixture was then diluted with DCM and concentrated under reduced pressure. The resulting crude residue was diluted with DCM/saturated sodium bicarbonate and extracted with DCM (3 x 10 ml) and washed further with saturated sodium bicarbonate and brine. The organic layers were recombined, dried with sodium sulfate, then and concentrated under reduced pressure. The resulting crude solid was purified by automated flash column chromatography (gradient 0 – 30% EtOAc,/Hexanes typically). For a representative example, see **2a**.

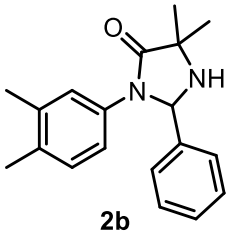
3-(4-methoxyphenyl)-5,5-dimethyl-2-phenylimidazolidin-4-one (2a)



2a

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1a** (1 equiv., 63 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2a** (54 mg, 0.18 mmol, 87%, eluting at 42% EtOAc in hexanes), a yellow semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.24 (m, 5H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 9.3 Hz, 2H), 5.88 (s, 1H), 3.70 (s, 3H), 2.01 (bs, 1H), 1.49 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.9, 157.1, 138.8, 130.4, 129.3, 129.1, 127.1, 124.1, 114.2, 75.5, 60.2, 55.4, 25.9, 24.5. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{18}H_{21}N_2O_2$ 297.1598; found 297.1602.

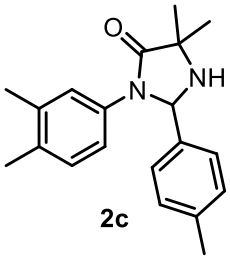
3-(3,4-dimethylphenyl)-5,5-dimethyl-2-phenylimidazolidin-4-one (2b)



2b

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1b** (1.0 equiv., 64 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol), and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by automated flash chromatography using a Teledyne ISCO^{TM} (0 – 20 % EtOAc/Hexane) to afford title compound **2b** (52 mg, 0.18 mmol, 84%, eluting at 12% EtOAc in hexanes), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 5H), 7.20 (d, *J* = 2.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.92 (dd, *J* = 8.2, 2.3 Hz, 1H), 5.92 (s, 1H), 2.17 (s, 3H), 2.14 (s, 3H), 1.94 (bs, 1H), 1.49 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 139.0, 137.2, 135.1, 133.9, 129.9, 129.2, 129.2, 127.0, 123.8, 119.7, 75.3, 60.3, 25.8, 24.5, 20.1, 19.3. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{23}N_2O$ 295.1805; found 295.1804.

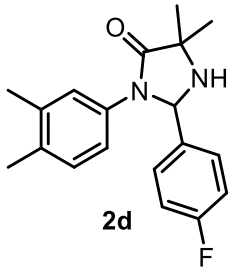
3-(3,4-dimethylphenyl)-5,5-dimethyl-2-(p-tolyl)imidazolidin-4-one (2c)



2c

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a 5 ml dry MWV equipped with a magnetic stir bar containing **1c** (1.0 equiv., 65 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2c** (33 mg, 0.11 mmol, 52%, eluting at 18% EtOAc in hexanes), a clear semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.97 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.94 (s, 1H), 2.35 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 1.96 (bs, 1H), 1.54 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.0, 139.0, 137.1, 136.0, 135.2, 133.8, 129.8, 129.8, 126.9, 123.8, 119.7, 75.1, 60.3, 25.8, 24.40, 21.3, 20.0, 19.3. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{20}H_{25}N_2O$ 309.1961; found 309.1960.

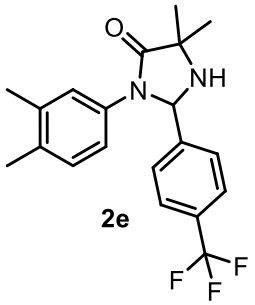
3-(3,4-dimethylphenyl)-2-(4-fluorophenyl)-5,5-dimethylimidazolidin-4-one (2d)



2d

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a 5 ml dry 5 ml MWV equipped with a magnetic stir bar containing **1d** (1.0 equiv., 66 mg, 0.21 mmol) PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude solid was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2d** (35 mg, 0.11 mmol, 53%, eluting at 16% EtOAc in hexanes), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 2H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.06 – 6.94 (m, 3H), 6.89 (dd, *J* = 8.1, 2.4 Hz, 1H), 5.91 (s, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 1.92 (bs, 1H), 1.48 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.8, 163.0 (d, *J* = 248.1 Hz), 137.3, 134.9, 134.8 (d, *J* = 3.2 Hz), 134.1, 129.9, 128.9 (d, *J* = 8.4 Hz), 123.9, 119.8, 116.2 (d, *J* = 21.8 Hz), 74.5, 60.3, 25.9, 24.4, 20.0, 19.3. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{22}FN_2O$ 313.1711; found 313.1709.

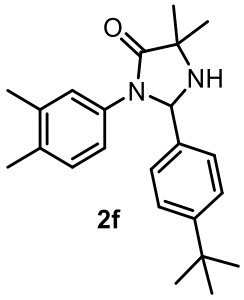
3-(3,4-dimethylphenyl)-5,5-dimethyl-2-(4-(trifluoromethyl)phenyl)imidazolidin-4-one (2e)



2e

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5ml MWV equipped with a magnetic stir bar containing **1e** (1.0 equiv., 77 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2e** (47 mg, 0.13 mmol, 68%, eluting at 16% EtOAc in hexanes), a clear semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 2.3 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.91 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.00 (s, 1H), 2.19 (s, 3H), 2.16 (s, 3H), 1.98 (bs, 1H), 1.47 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.8, 143.2, 137.5, 134.8, 134.2, 131.3 (q, *J* = 32.6 Hz), 130.0, 127.5, 126.2 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.3 Hz), 123.7, 119.5, 74.4, 60.4, 25.9, 24.6, 20.4, 19.3. **^{19}F NMR** (376 MHz, CDCl3) δ -62.7. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{20}H_{22}F_3N_2O$ 363.1679; found 363.1677.

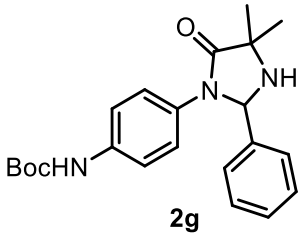
2-(4-(tert-butyl)phenyl)-3-(3,4-dimethylphenyl)-5,5-dimethylimidazolidin-4-one (2f)



2f

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1f** (1.0 equiv., 74 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to yield **2f** (49 mg, 0.14 mmol, 67%, eluting at 12% EtOAc in hexanes), a yellow solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.01 – 6.88 (m, 2H), 5.89 (s, 1H), 2.17 (s, 3H), 2.14 (s, 3H), 1.90 (bs, 1H), 1.46 (s, 3H), 1.37 (s, 3H), 1.26 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.2, 152.2, 137.1, 136.0, 135.3, 133.7, 129.8, 126.6, 126.1, 123.8, 119.7, 75.0, 60.3, 34.8, 31.4, 25.8, 24.5, 20.1, 19.4. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{23}H_{31}N_2O$ 351.2431; found 351.2427.

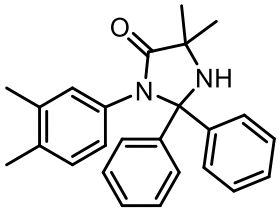
tert-butyl (4-(4,4-dimethyl-5-oxo-2-phenylimidazolidin-1-yl)phenyl)carbamate (2g)



2g

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1g** (1.0 equiv., 81 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.4 equiv., 76 mg, 0.29 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to yield **2g** (50 mg, 0.13 mmol, 62%, eluting at 50% EtOAc in hexanes), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 5H), 7.22 (s, 4H), 6.45 (s, 1H), 5.90 (s, 1H), 1.96 (bs, 1H), 1.49 (s, 3H), 1.47 (s, 9H), 1.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.0, 152.8, 138.7, 135.7, 132.5, 129.4, 129.2, 127.0, 123.1, 118.9, 80.7, 75.3, 60.3, 28.4, 25.9, 24.5. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{22}H_{28}N_3O_3$ 382.2125; found 382.2126.

3-(3,4-dimethylphenyl)-5,5-dimethyl-2,2-diphenylimidazolidin-4-one (2h)



2h

Preparation according to general procedure 2 (reaction time: 48 h) where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1h** (1.0 equiv., 78 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude solid was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2h** (48 mg, 0.13 mmol, 62%, eluting at 19% EtOAc in hexanes), a yellow solid. About 15 mg of **2h** was added to a 20 ml dram vial with 2 ml of ethyl acetate. The vial was loosely fitted with a cap and was evaporated over a few days. Single crystals were afforded and were suitable for x-ray crystallography (**table S4**). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 4H), 7.32 – 7.27 (m, 6H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.63 (dd, *J* = 8.1, 2.3 Hz, 1H), 2.33 (bs, 1H), 2.14 (s, 3H), 2.05 (s, 3H), 1.44 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.0, 143.6, 136.8, 135.4, 134.8, 129.7, 128.0, 128.8, 128.3, 128.0, 125.0, 114.4, 85.5, 59.1, 27.6, 19.9, 19.4. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{27}N_2O$ 371.2118; found 371.2123.

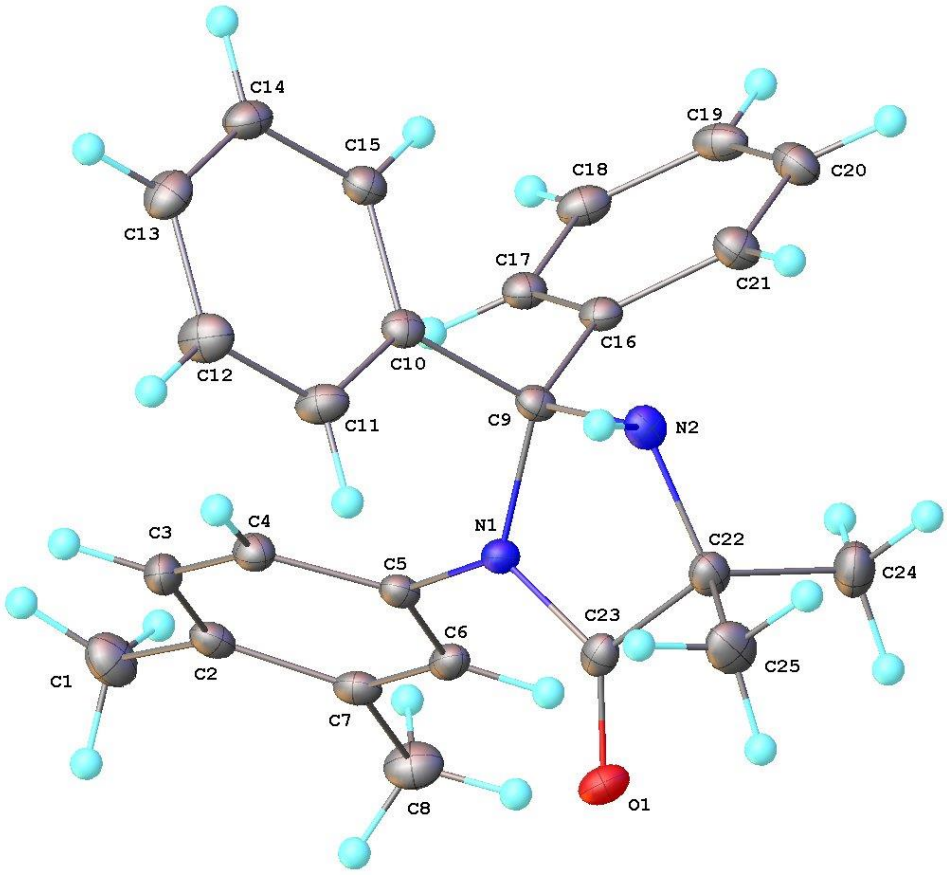
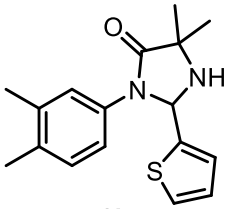


Table S4. Crystal data and structure refinement for compound **2h**. The displacement ellipsoids are at 50% probability level; the hydrogen atoms at carbons are at predicted positions. Unlike the related structure (**2i**) this one shows a well-defined hydrogen at N2 (without a distribution over two positions).

Deposition Number	1991579
Empirical moiety formula	$C_{25}H_{26}N_2O$
Formula weight [g/mol]	370.48
Temperature [K]	100.0
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.877 Å α=73.180(15)°
	b= 10.334 Å β=70.815(15)°
	c=11.272 Å γ=64.357(13)°
Volume [$Å^3$]	964.9(9)
Z	2
ρ_{calc} g/cm^3	1.275
μ[mm^{-1}]	0.078
Crystal size/mm^3	0.35 x 0.34 x 0.24
Radiation	MoKα (λ = 0.71073)
Θ range	3.884 – 53.364
Index ranges	$-12 \leq h \leq 12$, $-13 \leq k \leq 12$, $-13 \leq l \leq 14$
Refl. collected	18931
Independent reflections	4042 [R_{int} = 0.0199, R_{sigma} = 0.0137]
Data/restraints/parameters	4042/0/261
GooF on F2	1.057
Final R indices [I>2σ(I)]	R_1 = 0.0350, wR_2 = 0.0880
R indices (all data)	R_1 = 0.0377, wR_2 = 0.0901
$\Delta\rho_{max}$, $\Delta\rho_{min}$, [e·Å-3]	0.38/-0.22

3-(3,4-dimethylphenyl)-5,5-dimethyl-2-(thiophen-2-yl)imidazolidin-4-one (2i)



2i

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a stir bar containing **1i** (1.0 equiv., 64 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2i** (36 mg, 0.12 mmol, 57%, eluting at 20% EtOAc in hexanes), a white solid. Roughly 15 mg of **2i** was added to a 20 ml dram vial with 2 ml of ethyl acetate. The vial was loosely fitted with a cap and was evaporated over a few days. Single were afforded and were suitable for x-ray crystallography (**table S5**). **^{1}H NMR** ^{1}H NMR ($CDCl_3$) δ: 7.26 – 7.21 (m, 1H), 7.15 (d, J = 2.3 Hz, 1H), 7.06 – 7.00 (m, 2H), 6.99 – 6.92 (m, 1H), 6.91 – 6.84 (m, 1H), 6.19 (s, 1H), 2.20 (s, 4H), 2.18 (s, 3H), 1.50 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.2, 143.6, 137.3, 134.7, 134.6, 130.0, 127.1, 127.0, 126.4, 124.8, 120.7, 71.2, 60.1, 26.1, 24.8, 20.0, 19.4. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{21}N_2OS$ 301.1369; found 301.1369.

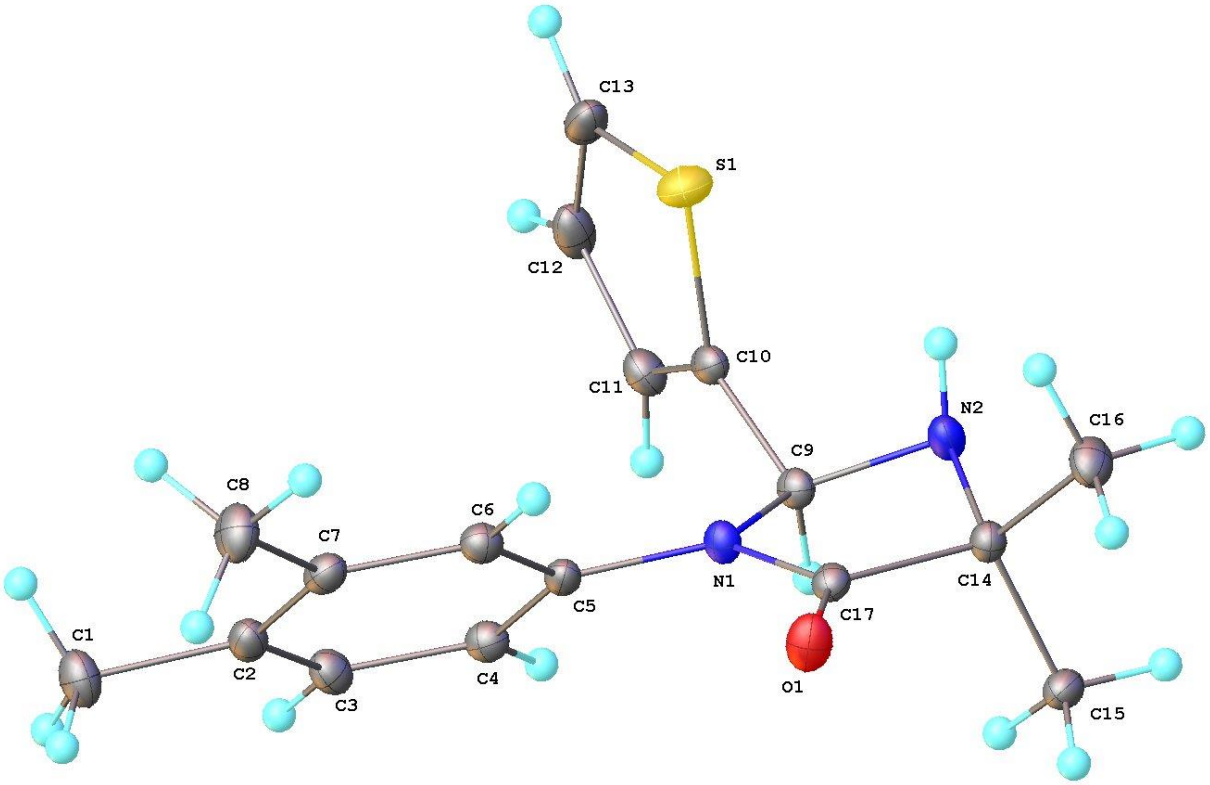
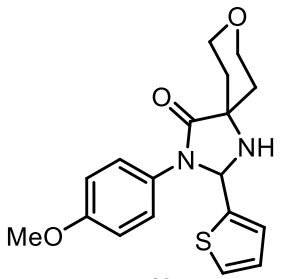


Table S5. Crystal data and structure refinement for compound **2i**. The molecule has a chirality at C9, and the structure is a racemic mix of enantiomers. There are 4 molecules per unit cell and 1 molecule per asymmetric unit. The displacement ellipsoids are at 50% probability level; the hydrogen atoms and carbons are at predicted positions. The hydrogen atom at N2 is distributed with 50% probability over 2 positions symmetric with respect to C9-N2-C14 plane. Only one of these hydrogens (H2B) is shown in the figure, while the other one (H2A) is omitted for clarity.

Deposition Number	1991583
Empirical moiety formula	$C_{17}H_{20}N_2OS$
Formula weight [g/mol]	300.41
Temperature [K]	100.0
Wavelength [Å]	
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	A = 15.895(6) Å α = 90°
	b = 7.869(3) Å β = 105.020°
	c = 12.418(5) Å γ = 90°
Volume [$Å^3$]	1500.3(10)
Z	4
$\rho_{calc}g/cm^3$	1.330
$\mu[mm^{-1}]$	0.216
Crystal size/mm^3	0.35 x 0.34 x 0.12
Radiation	MoKα (λ = 0.71073)
Θ range	2.652 – 52.192°
Index ranges	$-19 \leq h \leq 19$, $-9 \leq k \leq 9$, $-10 \leq l \leq 15$
Refl. collected	26837
Independent reflections	2968 [R_{int} = 0.0264, R_{sigma} = 0.0136]
Data/restraints/parameters	2968/0/202
GooF on F2	1.039
Final R indices [I>2σ(I)]	R_1 = 0.0318, wWr_2 = 0.0825

R indices (all data)	R_1 = 0.0341, wWr_2 = 0.0843
$\Delta\rho_{max}$, $\Delta\rho_{min}$, [e·Å-3]	0.39/-0.30

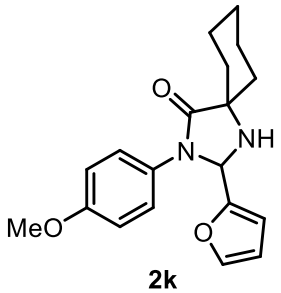
3-(4-methoxyphenyl)-2-(thiophen-2-yl)-8-oxa-1,3-diazaspiro[4.5]decan-4-one (2j)



2j

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1j** (1.0 equiv., 73 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2j** (39 mg, 0.11 mmol, 54%, eluting at 47% EtOAc), a white solid. **^{1}H NMR** ^{1}H NMR ($CDCl_3$) δ: 7.29 – 7.23 (m, 1H), 7.18 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 3.5 Hz, 1H), 6.88 (dd, J = 5.1, 3.5 Hz, 1H), 6.81 (d, J = 9.0 Hz, 2H), 6.18 (s, 1H), 4.06 – 3.93 (m, 2H), 3.81 (t, J = 11.3 Hz, 1H), 3.75 (s, 3H), 3.69 (t, J = 11.3 Hz, 1H), 2.41 – 2.28 (m, 1H), 2.28 (s, 1H), 2.13 – 2.01 (m, 1H), 1.67 – 1.54 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.4, 157.8, 143.6, 129.5, 127.4, 127.0, 126.7, 125.2, 114.3, 71.7, 63.8, 63.7, 60.0, 55.5, 35.0, 32.8. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{18}H_{21}N_2O_3S$ 345.1267; found 345.1264.

2-(furan-2-yl)-3-(4-methoxyphenyl)-1,3-diazaspiro[4.5]decan-4-one (2k)

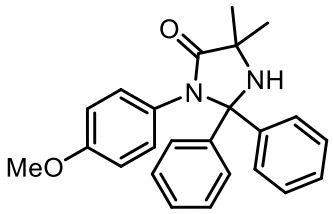


2k

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1k** (1.0 equiv., 69 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2k** (10 mg, 0.03 mmol, 15%, eluting at 26% EtOAc in hexanes), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 9.1 Hz, 2H), 6.31 – 6.27 (m, 2H), 5.81 (s, 1H), 3.75 (s, 3H), 2.32 (bs,

1H), 2.10 – 1.99 (m, 1H), 1.83 – 1.31 (m, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.2, 157.9, 150.7, 143.3, 129.6, 125.7, 114.3, 110.7, 110.7, 70.3, 62.4, 55.5, 34.4, 31.9, 25.4, 21.9, 21.7. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{23}N_2O_3$ 327.1703; found 327.1704.

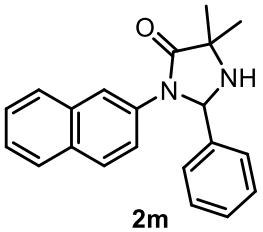
3-(4-methoxyphenyl)-5,5-dimethyl-2,2-diphenylimidazolidin-4-one (2l)



2l

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry MWV containing **1l** (1.0 equiv., 79 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2l** (59 mg, 0.16 mmol, 75%, eluting at 22% EtOAc), a yellow solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 4H), 7.32 – 7.27 (m, 6H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 3.72 (s, 3H), 2.28 (bs, 1H), 1.46 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.1, 158.4, 143.5, 130.0, 129.4, 128.7, 128.3, 128.0, 114.0, 85.6, 59.0, 55.4, 27.8. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{25}N_2O_2$ 373.1911; found 373.1918.

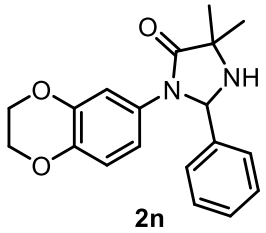
5,5-dimethyl-3-(naphthalen-2-yl)-2-phenylimidazolidin-4-one (2m)



2m

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1m** (1.0 equiv., 67 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2m** (14 mg, 0.04 mmol, 21%, eluting at 80% EtOAc in hexanes), a brown semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 2.1 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.48 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.44 – 7.33 (m, 4H), 7.33 – 7.20 (m, 3H), 6.10 (s, 1H), 2.03 (bs, 1H), 1.52 (s, 3H), 1.44 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.2, 138.7, 135.1, 133.5, 131.0, 129.4, 129.3, 128.7, 127.9, 127.6, 127.0, 126.4, 125.6, 121.1, 120.1, 75.3, 60.5, 25.8, 24.5. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{21}H_{21}N_2O$ 317.1648; found 317.1638.

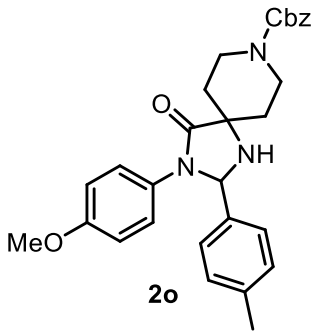
3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5,5-dimethyl-2-phenylimidazolidin-4-one (2n)



2n

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry MWV equipped with a magnetic stir bar containing **1n** (1.0 equiv., 69 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2n** (41 mg, 0.13 mmol, 60%, eluting at 88% EtOAc in hexanes), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.77 – 6.66 (m, 2H), 5.84 (s, 1H), 4.17 (s, 4H), 1.95 (bs, 1H), 1.48 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.0, 143.5, 141.4, 138.9, 131.0, 129.3, 129.2, 127.1, 117.2, 116.1, 112.3, 75.5, 64.4, 64.3, 60.3, 25.8, 24.5. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{21}N_2O_3$ 325.1547; found 325.1535.

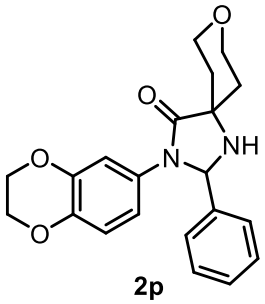
phenyl 3-(4-methoxyphenyl)-5,5-dimethyl-4-oxo-2-(p-tolyl)imidazolidine-1-carboxylate (2o)



2o

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1o** (1.0 equiv., 100 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2o** (65 mg, 0.13 mmol, 65%, eluting at 58% EtOAc in hexanes), a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.26 (m, 5H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 9.1 Hz, 2H), 5.85 (s, 1H), 5.14 (s, 2H), 4.09 (bs, 2H), 3.72 (s, 3H), 3.47 – 3.33 (m, 1H), 3.22 – 3.07 (m, 1H), 2.31 (s, 3H), 2.29 (bs, 1H), 1.96 – 1.79 (m, 2H), 1.59 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.3, 157.3, 155.3, 139.5, 136.9, 135.7, 130.1, 130.0, 128.6, 128.1, 128.1, 127.0, 124.2, 114.2, 75.8, 67.3, 64.9, 60.9, 55.5, 40.1, 21.4. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{29}H_{32}N_3O_4$ 486.2387; found 486.2374.

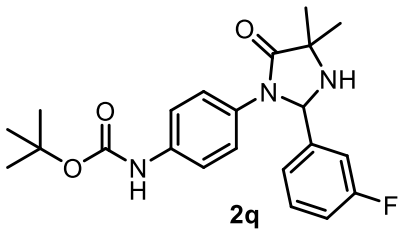
3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-phenyl-8-oxa-1,3-diazaspiro[4.5]decan-4-one (2p)



2p

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1p** (1.0 equiv., 77 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2p** (34 mg, 0.09 mmol, 44%, eluting at 70% EtOAc in hexanes), a yellow solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 5H), 6.87 (d, *J* = 1.9 Hz, 1H), 6.76 – 6.66 (m, 2H), 5.85 (s, 1H), 4.16 (s, 4H), 3.97 (ddt, *J* = 15.9, 11.5, 4.1 Hz, 2H), 3.84 (td, *J* = 11.0, 2.8 Hz, 1H), 3.62 (td, *J* = 11.4, 2.8 Hz, 1H), 2.39 (ddd, *J* = 13.8, 11.2, 4.7 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.90 (bs, 1H), 1.63 (dq, *J* = 13.5, 2.9 Hz, 1H), 1.53 (dq, *J* = 13.7, 2.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.3, 143.5, 141.5, 138.8, 130.6, 129.4, 129.2, 127.1, 117.2, 116.1, 112.3, 75.8, 64.4, 64.3, 63.8, 63.6, 60.3, 34.8, 32.2. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{21}H_{23}N_2O_4$ 367.1652; found 367.1638.

tert-butyl (4-(2-(3-fluorophenyl)-4,4-dimethyl-5-oxoimidazolidin-1-yl)phenyl)carbamate (2q)



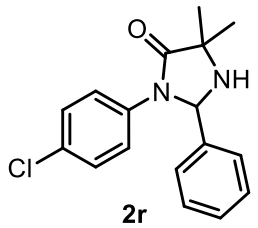
2q

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1q** (1.0 equiv., 67 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2q** (39 mg, 0.10 mmol, 59%, eluting at 44% EtOAc in hexanes), a red semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.19 (m, 5H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.09 – 6.95 (m, 2H), 6.54 (s, 1H), 5.92 (s, 1H), 2.01 (bs, 1H), 1.50 (s, 12H), 1.42 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.8, 162.8 (d, *J* = 247.6 Hz), 152.78, 141.44 (d, *J* = 6.7 Hz), 135.93, 132.14, 130.89 (d, *J* = 8.2 Hz), 123.07, 122.81 (d, *J* = 3.1 Hz), 119.0, 116.4 (d, *J* = 21.2 Hz), 114.1 (d, *J* = 22.2 Hz), 80.7, 74.6 (d, *J* = 1.9 Hz), 60.3, 28.4, 25.9, 24.5. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{22}H_{27}N_3O_3$ 400.2031; found 400.2024.

Gram-scale transformation

Preparation according to general procedure 2 where dry acetonitrile (29.75 ml, 0.1M) was added to a dry round bottom flask equipped with a magnetic stir bar containing **1q** (1.0 equiv., 1.20 g, 2.99 mmol), PIDA (1.2 equiv., 1.15 g, 3.59 mmol), KBr (1.0 equiv., 355 mg, 2.99 mmol), and 18-crown-6 (1.2 equiv., 984 mg, 3.59 mmol). The residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2q** (494 mg, 1.24 mmol, 41%, eluting at 75% ethyl acetate in hexanes), a brown solid.

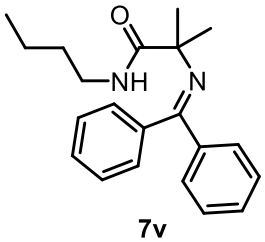
3-(4-chlorophenyl)-5,5-dimethyl-2-phenylimidazolidin-4-one (2r)



2r

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1r** (1.0 equiv., 64 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21 mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2r** (50 mg, 0.16 mmol, 79%, eluting at 50% EtOAc in hexanes), a brown semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 (s, 5H), 7.30 – 7.25 (m, 2H), 7.20 (d, *J* = 9.0 Hz, 2H), 5.93 (s, 1H), 1.97 (bs, 1H), 1.49 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.0, 138.3, 136.1, 130.5, 129.5, 129.4, 129.0, 126.9, 123.1, 75.1, 60.4, 25.8, 24.4. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{18}ClN_2O$ 301.1102; found 301.1097.

N-butyl-2-((diphenylmethylene)amino)-2-methylpropanamide (7v)

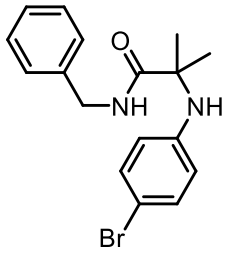


7v

Preparation according to general procedure 2 where dry acetonitrile (1.30ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1v** (1.0 equiv., 42 mg, 0.13 mmol), PIDA (1.2 equiv., 50 mg, 0.16 mmol), KBr (1.0 equiv., 15 mg, 0.13 mmol) and 18-crown-6 (1.2 equiv., 41 mg, 0.16 mmol). The crude residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **7v** (29 mg, 0.09 mmol, 69%, eluting at 14% EtOAc in hexanes), a clear oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.55 – 7.48 (m, 2H), 7.46 – 7.40 (m, 3H), 7.37 – 7.31 (m, 3H), 7.24 – 7.15 (m, 2H), 3.37 (td, *J* = 7.1, 5.8 Hz, 2H), 1.60 (p, *J* = 7.6, 6.8 Hz, 2H), 1.45 (p, *J* = 7.3 Hz, 2H), 1.25 (s, 6H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.4, 166.4, 141.32, 138.5, 130.3, 128.6, 128.3, 128.3, 128.1,

128.1, 64.4, 39.3, 32.0, 26.1, 20.4, 14.0. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{21}H_{27}N_2O$ 323.2118; found 323.2108. Note: Reaction was stirred in an oil bath at 50 C.

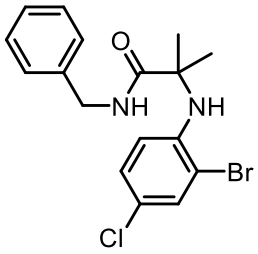
N-benzyl-2-((4-bromophenyl)amino)-2-methylpropanamide (7w)



7w

Preparation according to general procedure 2 where dry acetonitrile (2.05 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1w** (1.0 equiv., 56 mg, 0.21 mmol), PIDA (1.2 equiv., 81 mg, 0.25 mmol), KBr (1.0 equiv., 25 mg, 0.21mmol) and 18-crown-6 (1.2 equiv., 67 mg, 0.25 mmol). The crude residue was purified by automated silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **7w** (56 mg, 0.16 mmol, 77%), a tan semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.19 (m, 7H), 6.42 (d, *J* = 8.7 Hz, 2H), 4.46 (d, *J* = 5.9 Hz, 2H), 3.87 (s, 1H), 1.54 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.3, 143.7, 138.3, 131.9, 128.7, 127.9, 127.6, 117.6, 111.2, 58.3, 43.8, 26.1. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{20}BrN_2O$ 347.0754; found 347.0753.

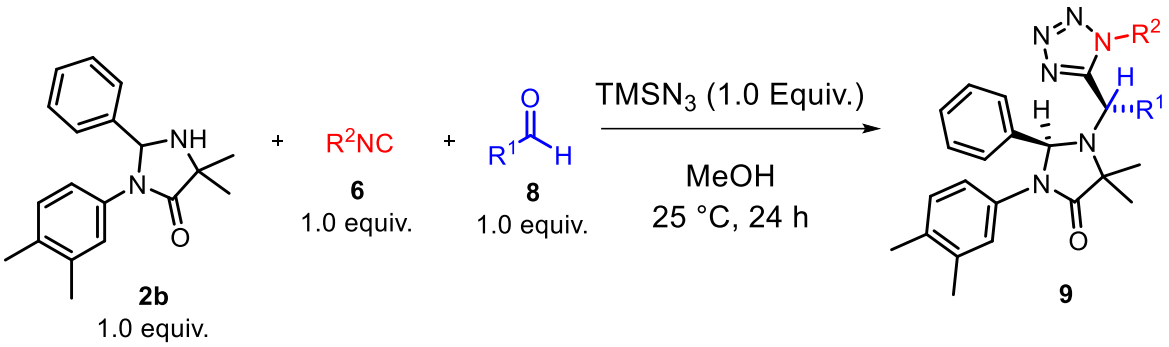
N-benzyl-2-((2-bromo-4-chlorophenyl)amino)-2-methylpropanamide (7x)



7x

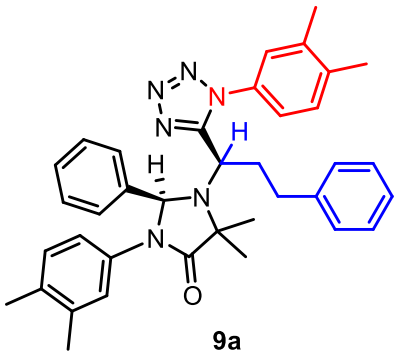
Preparation according to general procedure 2 where dry acetonitrile (1.32 ml, 0.1M) was added to a dry 5 ml MWV equipped with a magnetic stir bar containing **1x** (1.0 equiv., 40 mg, 0.13 mmol), PIDA (1.2 equiv., 51 mg, 0.16 mmol), KBr (1.0 equiv., 16 mg, 0.13 mmol) and 18-crown-6 (1.2 equiv., 42 mg, 0.16 mmol). The crude solid was purified by automated silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **7x** (43 mg, 0.11 mmol, 85%), a yellow solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 2.4 Hz, 1H), 7.34 – 7.23 (m, 3H), 7.21 – 7.17 (m, 2H), 7.07 (t, *J* = 5.8 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.40 (d, *J* = 8.8 Hz, 1H), 4.50 (s, 1H), 4.43 (d, *J* = 6.0 Hz, 2H), 1.55 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.9, 140.6, 138.2, 132.2, 128.8, 128.1, 127.9, 127.7, 123.9, 116.1, 111.6, 58.6, 43.8, 26.1. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{19}BrClN_2O$ 381.0364; found 381.0372.

5. General Ugi-Azide Reaction of 2b Procedure 3: Preparation of functionalized 1,4-imidazolidinones.



Aldehyde (1.0 equiv., 0.15 mmol), $TMSN_3$ (1.0 equiv., 0.15 mmol), and methanol (0.15 ml, 1.0M), were added simultaneously to a sealed and dry 5 ml microwave vial equipped with a magnetic stir bar containing **2b** (1.0 equiv., 0.15 mmol), and isocyanide (1.0 equiv., 0.15 mmol). The reaction was stirred for 24 h at room temperature and was then diluted with DCM and concentrated under reduced pressure. The crude residue was purified by automated flash column chromatography using a Teledyne ISCO^{TM} (gradient 0 – 30% EtOAc/Hexanes typically) to give an inseparable mixture of diastereomers. For a representative example, see **9a**. The diastereomeric ratios were determined by integrating signals belonging to each diastereomer and taking their ratio. The attached NMRs for **9a** contain these integrations.

(±)-3-(3,4-dimethylphenyl)-1-(1-(1-(3,4-dimethylphenyl)-1*H*-tetrazol-5-yl)-3-phenylpropyl)-5,5-dimethyl-2-phenylimidazolidin-4-one (9a)



Preparation according to general procedure 3 where MeOH (0.15 ml, 1.0 M), $TMSN_3$ (1.0 equiv., 18 mg, 0.15 mmol), and 3-phenylpropanal (1.0 equiv., 21 mg, 0.15 mmol) were added to a dry 5 ml MWV equipped with a magnetic stir bar containing **2b** (1.0 equiv, 45 mg, 0.15 mmol) and 4-isocyano-1,2-dimethylbenzene (1.0 equiv., 20 mg, 0.15 mmol). The crude residue was purified by automated silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **9a** (61 mg, 0.10 mmol, 68% yield, 5:1 mixture of two diastereomers and its racemate), a white solid. 20 mg of **9a** was added to a 20 ml dram vial containing 2 ml of ethyl acetate. The vial was loosely fitted with a cap and was evaporated over a week. Single crystals were afforded and were suitable for x-ray diffraction. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 6.67 (m, 19H), 5.72 (s, 1H),

4.15 (dd, *J* = 11.8, 2.7 Hz, 1H), 3.27 – 3.14 (m, 1H), 2.90 (ddd, *J* = 13.8, 7.7, 4.3 Hz, 1H), 2.53 (ddd, *J* = 14.0, 9.9, 7.0 Hz, 1H), 2.41 – 2.35 (m, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 1.06 (s, 3H), 0.67 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*), *major diastereomer* δ 174.2, 154.3, 140.1, 139.8, 138.7, 137.9, 137.1, 134.7, 133.5, 131.7, 130.9, 129.9, 129.1, 128.9, 128.8, 128.2, 128.0, 126.7, 126.5, 125.2, 123.1, 121.3, 75.9, 63.4, 47.9, 32.6, 31.2, 25.2, 22.1, 19.9, 19.8, 19.8, 19.4. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{37}H_{41}N_6O$ 585.3336; found 585.3333. In the aliphatic region of the ^{1}H NMR, only the major diastereomer was integrated while in the aromatic region, both diastereomers were integrated together. This was because it was not possible to differentiate between the two in this particular region. The aromatic region was predicted to have 16 protons which corresponded to the major diastereomer. Because both diastereomers were integrated together, the integration came to be 19. This further matched the 5:1 diastereomeric ratio. Note: See ^{1}H NMR for the proper diastereomeric ratio determination.

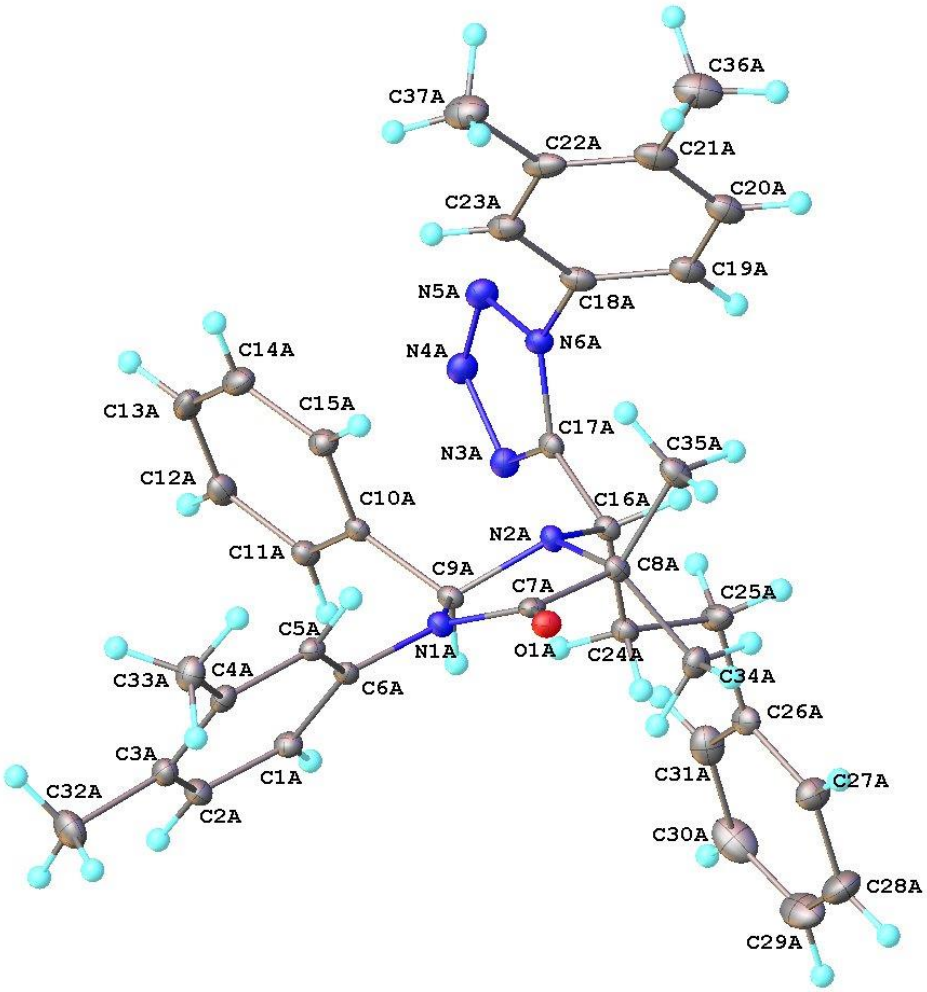
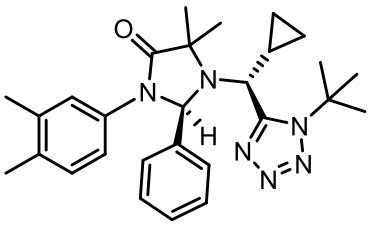


Table S6. Crystal data and structure refinement for compound **9a.** The displacement ellipsoids are at 50% probability level; the hydrogen atoms at carbons are at predicted positions.

Deposition Number	1992829

Empirical moiety formula	$C_{37}H_{40}N_6O$	
Formula weight [g/mol]	584.75	
Temperature [K]	100.0	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.5855(5) Å	α = 90°
	b = 22.6369(3) Å	β = 98.636(2)°
	c = 24.7598(11) Å	γ = 90°
Volume [$Å^3$]	6419.9 (5)	
Z	8	
ρ_{calc} g/cm^3	1.210	
μ[mm^{-1}]	0.075	
F(000)	2496.0	
Crystal size/mm^3	0.23 x 0.20 x 0.09	
Radiation	MoKα (λ = 0.71073)	
Θ range	3.328 – 51.458°	
Index ranges	$-14 \leq h \leq 14$, $-27 \leq k \leq 27$, $-30 \leq l \leq 30$	
Refl. collected	107736	
Independent reflections	12230 [R_{int} = 0.0494, R_{sigma} = 0.0319]	
Data/restraints/parameters	12230/2/805	
GooF on F2	1.020	
Final R indices [I>2σ(I)]	R_1 = 0.0420, wWr_2 = 0.1246	
R indices (all data)	R_1 = 0.0625, wWr_2 = 0.1434	
$\Delta\rho_{max}$, $\Delta\rho_{min}$, [e·Å-3]	0.52/-0.22	

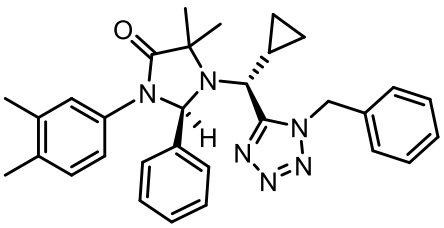
(±)-1-((1-(tert-butyl)-1H-tetrazol-5-yl)(cyclopropyl)methyl)-3-(3,4-dimethylphenyl)-5,5-dimethyl-2-phenylimidazolidin-4-one (9b)



9b

Preparation according to general procedure 3 where MeOH (0.15 ml), $TMSN_3$ (1.0 equiv., 16 mg, 0.14 mmol), tert-butylisocyanide (1.0 equiv., 16 mg, 0.14 mmol), and cyclopropanecarboxaldehyde (1.0 equiv., 10 mg, 0.14 mmol) were added simultaneously to an 8 ml MWV equipped with a stir bar containing **2b** (1.0 equiv, 40 mg, 0.14 mmol). The residue was purified by silica flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **9b** (54 mg, 0.13 mmol, 84% yield, eluting at 15-30% ethyl acetate in hexanes, 2.1:1 (RR:RS) mixture of two diastereomers and its racemate), a white solid. *Note:* purification yielded two fractions, one fraction with a 3.1:1 dr and the other with a 1.6:1 dr giving an overall 2.1:1 dr after taking into consideration the mass isolated in each fraction. The NMR represented in this section is the fraction containing the 3.1:1 dr. **^{1}H NMR** (400 MHz, Chloroform-*d*), *major diastereomer* δ 7.51 – 6.72 (m, 10H, RR & RS diastereomer), 6.55 (bs, 1H), 4.39 (d, *J* = 8.1 Hz, 1H), 2.19 (s, 3H), 2.17 (s, 3H), 1.72 (s, 9H), 1.64 (s, 3H), 1.15 (s, 3H), 0.80 – 0.65 (m, 1H), 0.57 (tt, *J* = 9.3, 5.2 Hz, 1H), 0.49 – 0.30 (m, 2H), 0.25 (dq, *J* = 10.5, 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*), *major diastereomer* δ 175.8, 155.2, 140.3, 137.4, 135.0, 134.8, 134.7, 134.0, 130.1, 128.1, 127.5, 122.2, 76.7, 64.4, 62.3, 62.1, 30.5, 27.4, 25.8, 20.1, 19.4, 12.7, 5.0. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{28}H_{37}N_6O$ 473.3023; found 473.3027. In aliphatic region of the ^{1}H NMR, only the major diastereomer was integrated while in the aromatic region, both diastereomers were integrated together. This was because it was not possible to differentiate between the two in this particular region. The aromatic region was predicted to have 8 protons which corresponded to the major diastereomer. Because both diastereomers were integrated together, the integration came to be 10. This further matched the 3.1:1 diastereomeric ratio (for this particular fraction). Note: See ^{1}H NMR for the proper diastereomeric ratio determination.

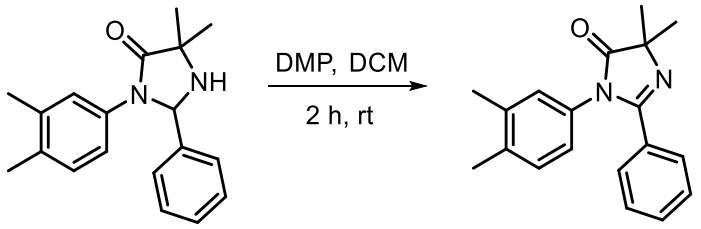
(±)-1-((1-benzyl-1H-tetrazol-5-yl)(cyclopropyl)methyl)-3-(3,4-dimethylphenyl)-5,5-dimethyl-2-phenylimidazolidin-4-one (9c)



9c

Preparation according to general procedure 3 where MeOH (0.15 ml), $TMSN_3$ (1.0 equiv., 16 mg, 0.14 mmol), and cyclopropanecarboxaldehyde (1.0 equiv., 10 mg, 0.14 mmol) were added to a dry 5 ml MWV equipped with a magnetic stir bar containing **2b** (1.0 equiv., 40 mg, 0.14 mmol) and 4-isocyano-1,2-dimethylbenzene (1 equiv., 16 mg, 0.14 mmol). The residue was purified by silica flash column chromatography using a Teledyne ISCO™ to afford title compound **9c** (67 mg, 0.13 mmol, 97% yield, 1.6:1 (RR:RS) mixture of the two diastereomers and its racemate), a clear semisolid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 6.67 (m, 21H, RR & RS diastereomer), 5.91 (s, 1H), 5.78 (d, *J* = 15.6 Hz, 1H), 5.65 (d, *J* = 15.7 Hz, 1H), 3.93 (d, *J* = 10.2 Hz, 1H), 3.36 (d, *J* = 9.8 Hz, 1H), 2.11 (s, 6H), 1.50 (s, 3H), 0.94 (s, 3H), 0.71 – 0.59 (m, 1H), 0.56 – 0.46 (m, 1H), 0.39 – 0.27 (m, 1H), -0.02 (dq, *J* = 10.7, 5.5 Hz, 1H), -0.12 – -0.22 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*), *major diastereomer* δ 173.9, 155.4, 141.1, 137.3, 135.6, 134.0, 133.4, 133.0, 129.9, 129.1, 129.1, 128.8, 128.5, 128.5, 126.8, 123.1, 78.3, 63.8, 59.1, 50.7, 25.4, 19.8, 19.4, 14.3, 11.7, 4.5. **HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{31}H_{35}N_6O$ 507.2867; found 507.2867. In aliphatic region of the ^{1}H NMR, only the major diastereomer was integrated with the exception of two cyclopropane C-H signals where the major and minor diastereomer overlapped (0.64 & 0.42 ppm). In the aromatic region, both diastereomers were integrated together because it was not possible to differentiate between the two in this particular region. The aromatic region was predicted to have 13 protons which corresponded to the major diastereomer. Because both diastereomers were integrated together, the integration came to be 21. This further matched the 1.6:1 diastereomeric ratio. Note: See ^{1}H NMR for the proper diastereomeric ratio determination.

3-(3,4-dimethylphenyl)-5,5-dimethyl-2-phenyl-3,5-dihydro-4H-imidazol-4-one (12)



2b **12**

DCM (1.18 ml, 0.1M) was added to a 5 ml microwave vial equipped with a magnetic stir bar containing **2b** (1.0 equiv., 35 mg, 0.12 mmol) and Dess Martin Periodinane (1.1 equiv., 55 mg, 0.13 mmol). The microwave vial was wrapped with aluminum foil and the reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was diluted with DI water and quenched with saturated sodium thiosulfate (2 ml). The heterogenous mixture was extracted with DCM (3 x 15 ml) and washed with saturated sodium bicarbonate and brine. The organic layers were recombined, dried over sodium sulfate, and concentrated under reduced pressure. The crude residue was purified by automated flash column chromatography using a Teledyne ISCO™ to afford title compound **12** (22 mg, 0.08 mmol, 63%, eluting at 16% ethyl acetate in hexanes), a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 3H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 6.74 (dd, *J* = 8.0, 2.2 Hz, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 1.54 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 185.9, 159.5, 137.9, 136.9, 132.2, 130.9,

130.4, 129.6, 128.8, 128.3, 128.0, 124.4, 67.8, 24.5, 19.9, 19.6. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{21}N_2O$ 293.1648; found 293.1640.

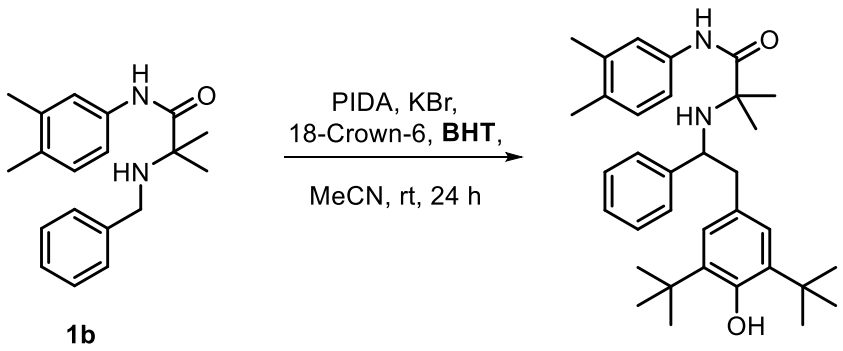
6. Radical Inhibition Studies

TEMPO and BHT as Radical Inhibitors

1b **2b**

Acetonitrile (1.35 ml) was added to a dry 5 ml microwave vial equipped with a magnetic stir bar containing **1b** (1.0 equiv, 40 mg, 0.13 mmol), PIDA (1.2 equiv.,52 mg, 0.16 mmol), KBr (1.0 equiv., 16 mg, 0.13 mmol), TEMPO (1.0 equiv., 21 mg, 0.13 mmol), and 18-Crown-6 (1.2 equiv., 43 mg, 0.16 mmol). The reaction vessel was covered in aluminum foil and the reaction was stirred for 24 h at room temperature. The reaction mixture was then diluted with DCM and concentrated under reduced pressure. The residue was extracted with DCM (3 x 10 ml) and washed with saturated sodium bicarbonate. The organic layers were recombined, dried over sodium sulfate, and concentrated under reduced pressure. The crude residue was purified by automated flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **2b** (36 mg, 0.12 mmol, 91%, eluting at 55% ethyl acetate in hexanes), a white solid.

2-((2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-phenylethyl)amino)-N-(3,4-dimethylphenyl)-2-methylpropanamide (13)



1b **13**

Acetonitrile (1.35 ml) was added to a dry 5 ml microwave vial equipped with a magnetic stir bar containing **1b** (1.0 equiv, 40 mg, 0.13 mmol), PIDA (1.2 equiv.,52 mg, 0.16 mmol), KBr (1.0 equiv., 16 mg, 0.13 mmol), BHT (5.0 equiv., 150 mg, 0.67 mmol), 18-Crown-6 (1.2 equiv., 43 mg, 0.16 mmol). The reaction vessel was covered in aluminum foil and the reaction was stirred

for 24 h at room temperature. The reaction mixture was then diluted with DCM and concentrated under reduced pressure. The residue was extracted with DCM (3 x 10 ml) and washed with saturated sodium bicarbonate. The organic layers were recombined, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by automated flash column chromatography using a Teledyne ISCO^{TM} to afford title compound **13** (69 mg, 0.07 mmol, 55%, eluting at 12% ethyl acetate in hexanes), a white semisolid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.46 (s, 1H), 7.48 – 7.15 (m, 7H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 2H), 5.08 (s, 1H), 3.75 (s, 2H), 3.72 (s, 2H), 2.29 (s, 3H), 2.27 (s, 3H), 1.42 (s, 18H), 1.39 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.6, 152.8, 143.4, 141.2, 137.3, 136.1, 135.8, 132.1, 130.8, 130.2, 128.4, 128.4, 126.9, 125.1, 120.5, 116.6, 66.9, 55.3, 54.9, 34.4, 30.5, 22.3, 20.0, 19.3. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{34}H_{47}N_2O_2$ 515.3632; found 515.3628.

7. NMR Spectra of Synthesized Compounds

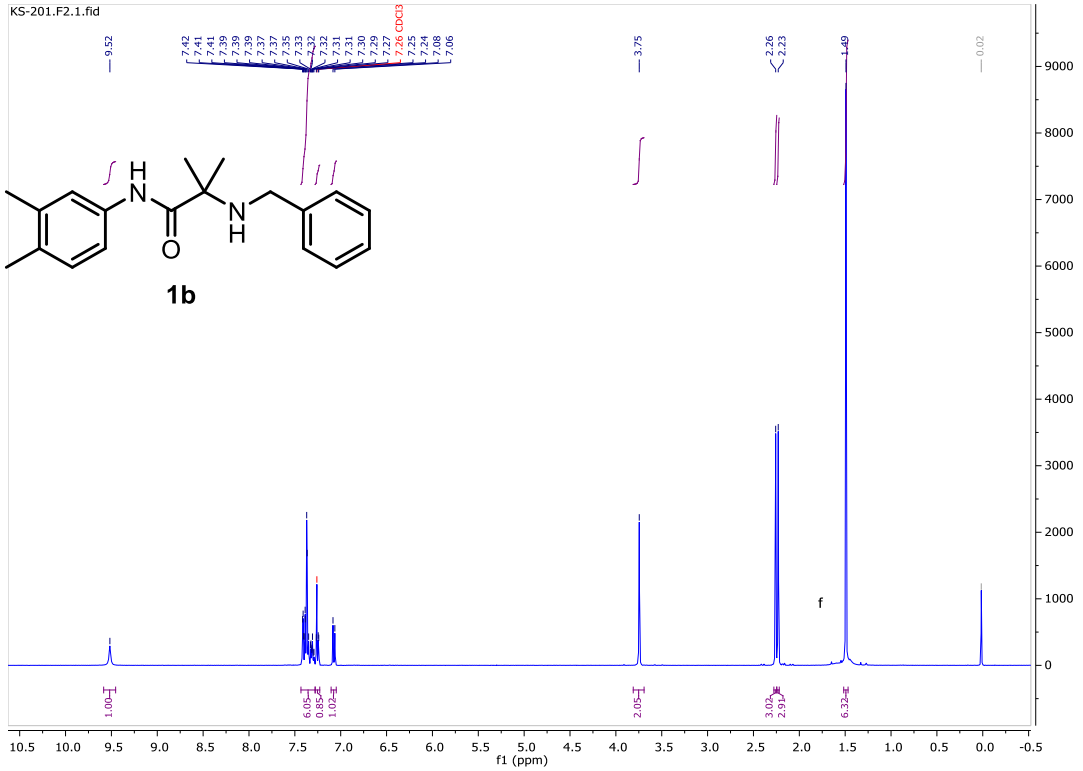


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b.**

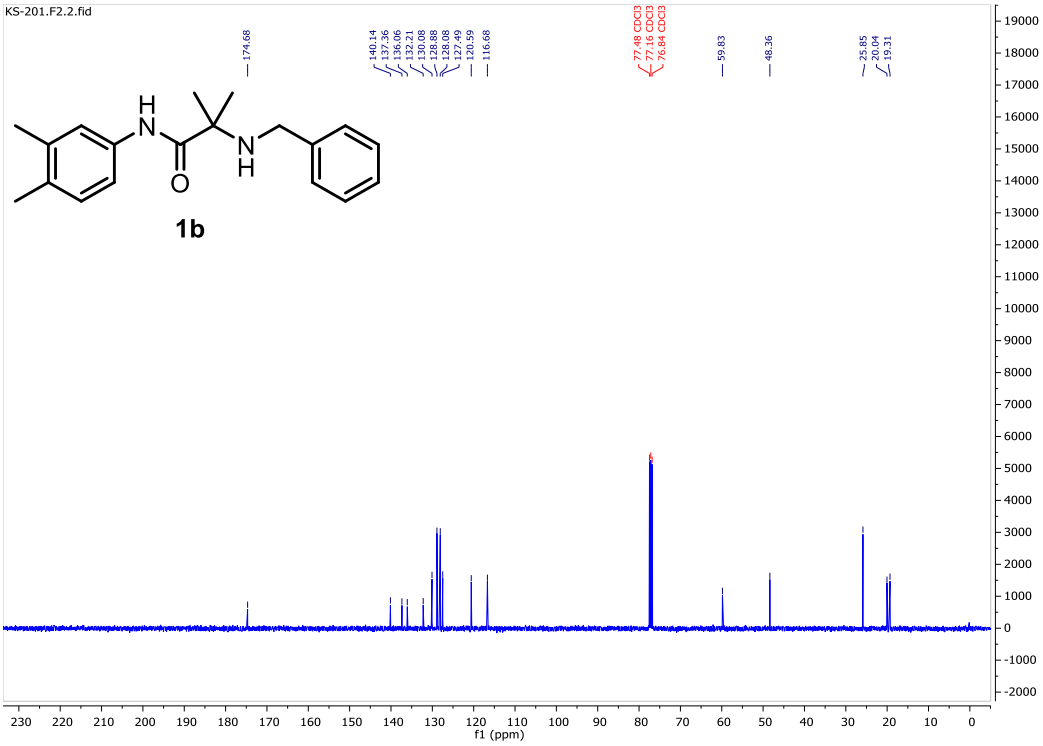


Figure S2. ^{13}C NMR (101 MHz $CDCl_3$) of **1b**.

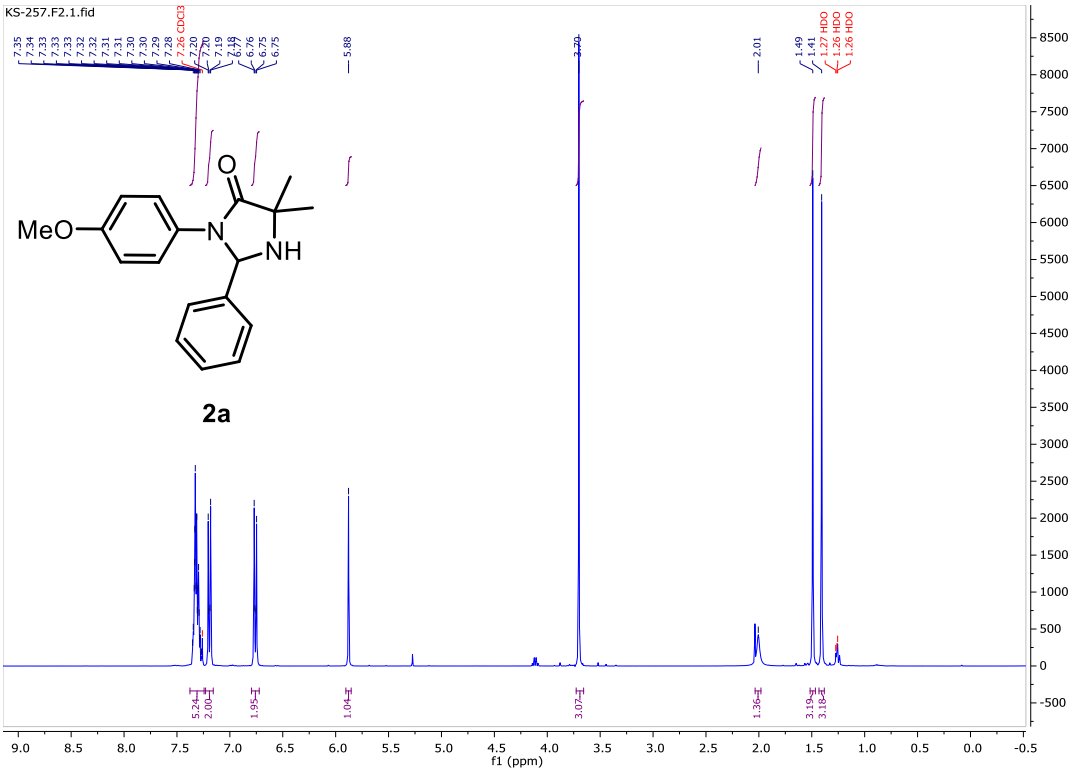


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a**

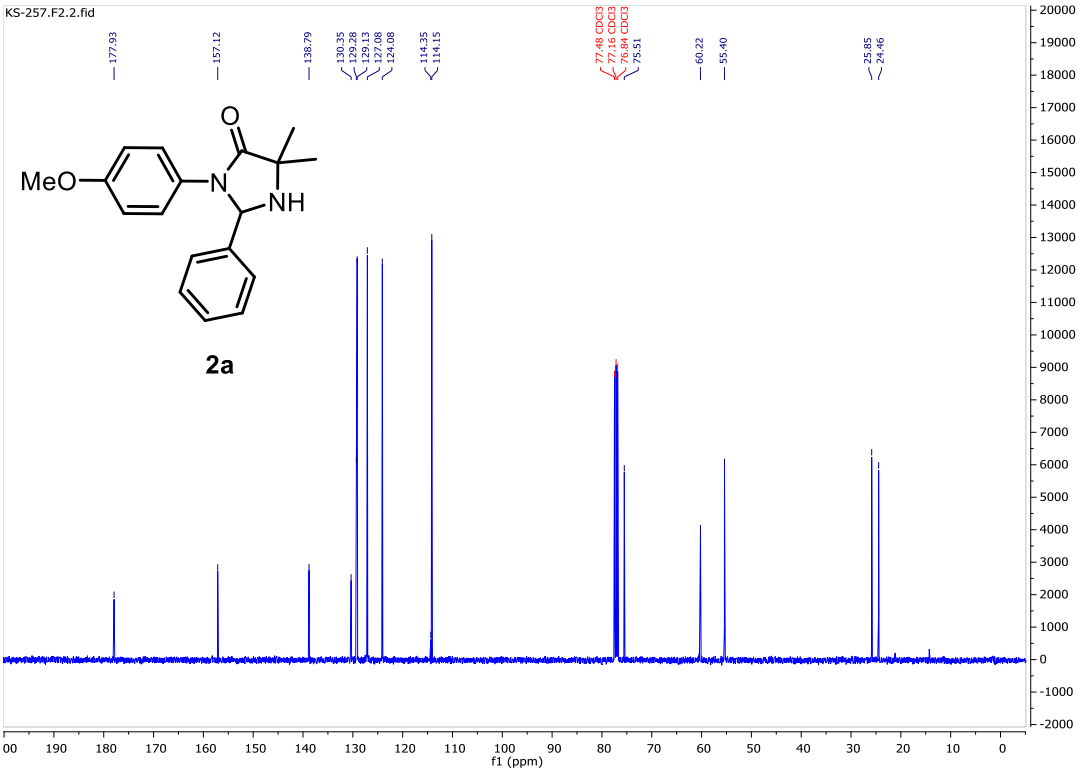


Figure S4. ^{13}C NMR (101 MHz $CDCl_3$) of **2a**.

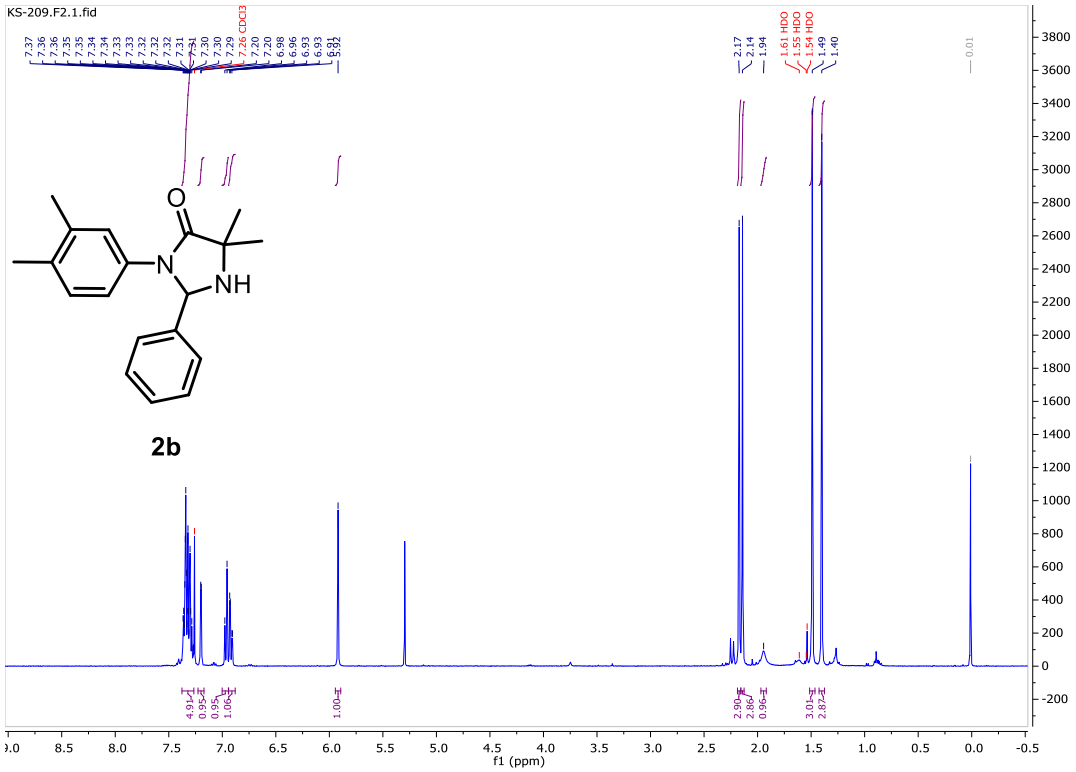


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b.**

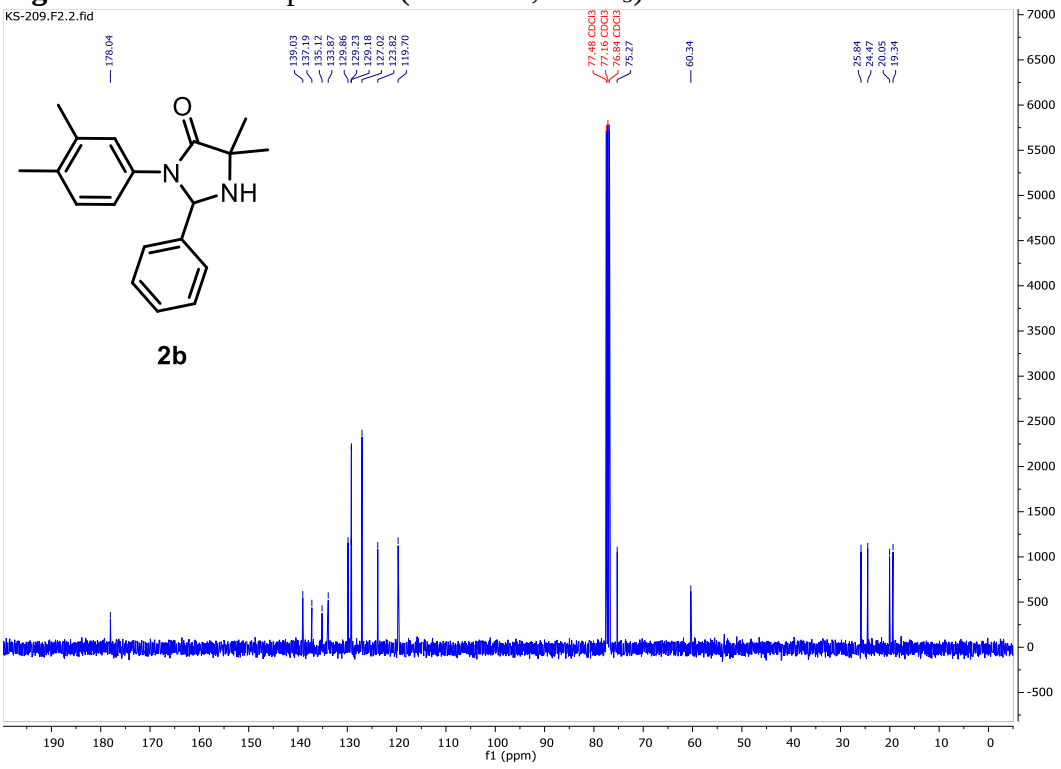


Figure S6. ^{13}C NMR (101 MHz $CDCl_3$) of **2b**.

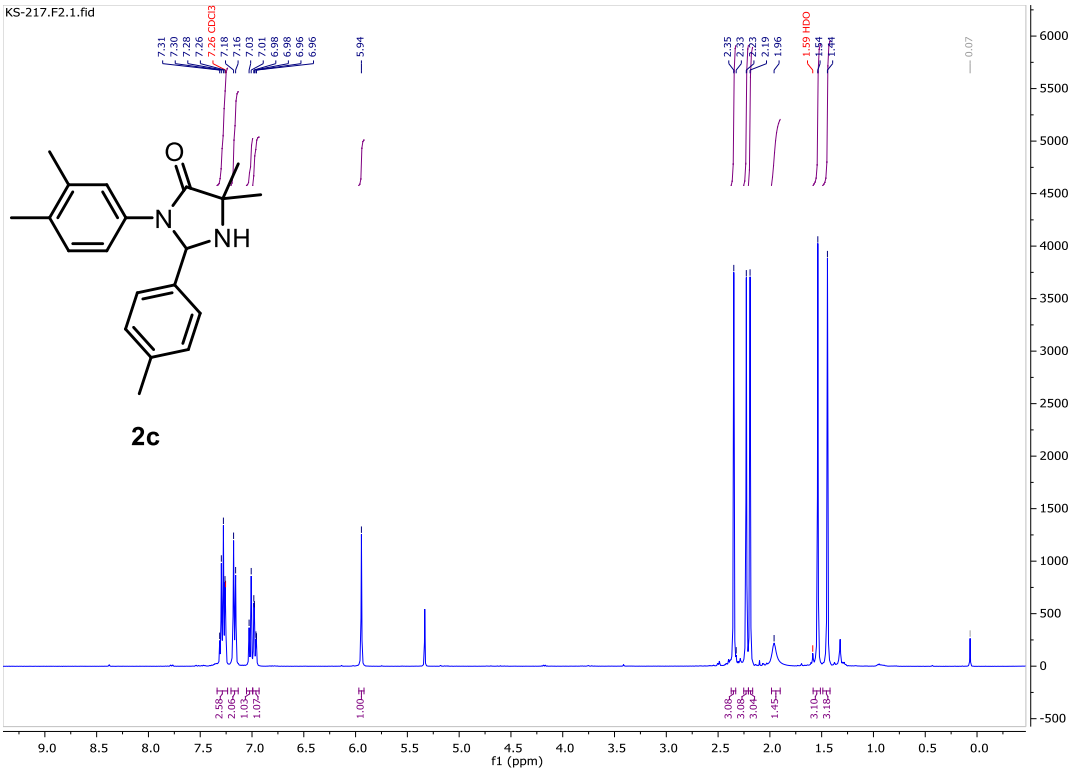


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**.

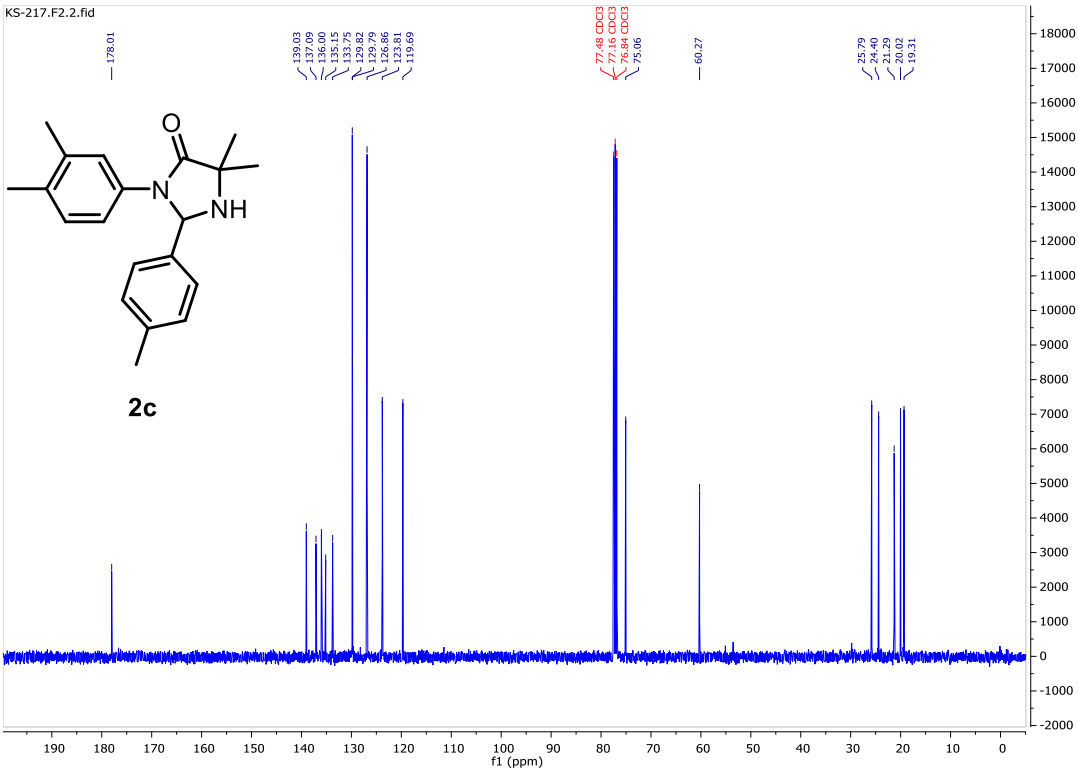


Figure S8. ^{13}C NMR (101 MHz $CDCl_3$) of **2c**.

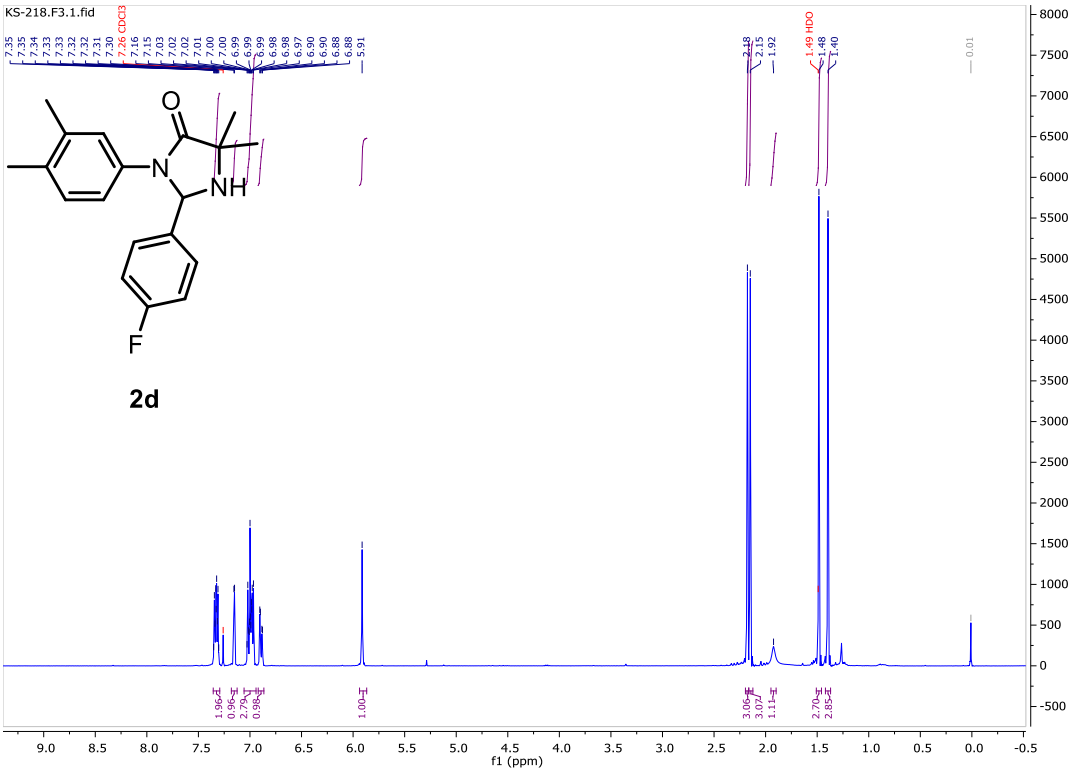


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2d**.

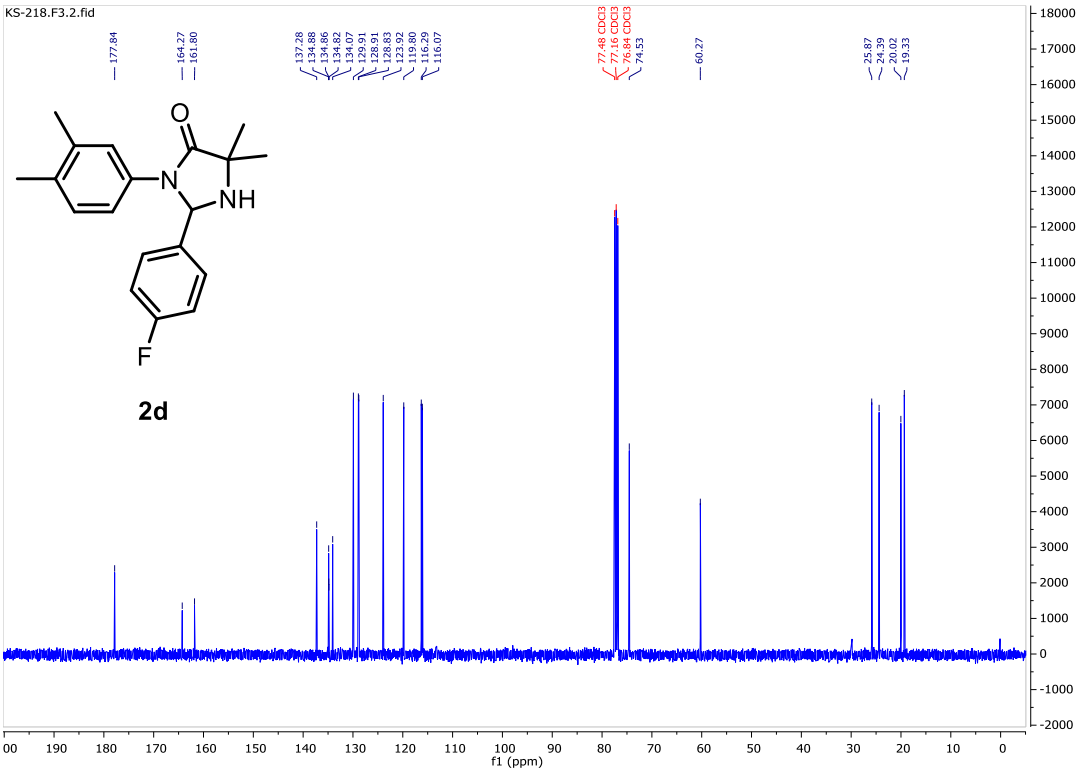


Figure S10. ^{13}C NMR (101 MHz $CDCl_3$) of **2d**.

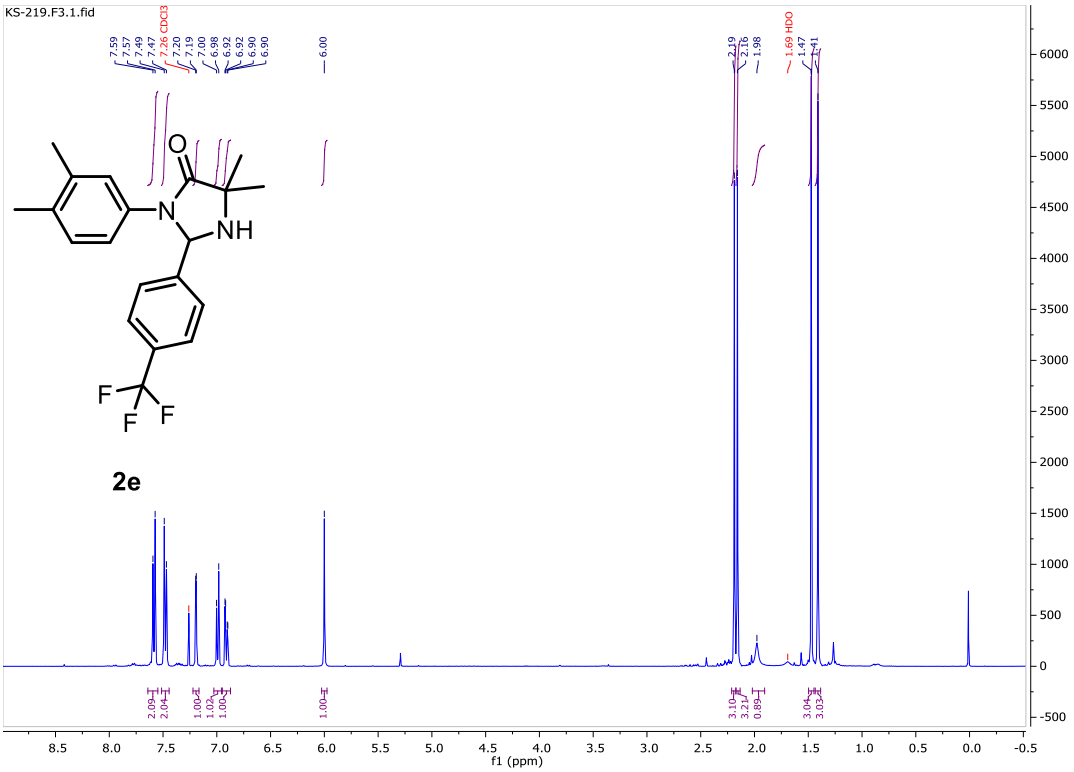


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2e**.

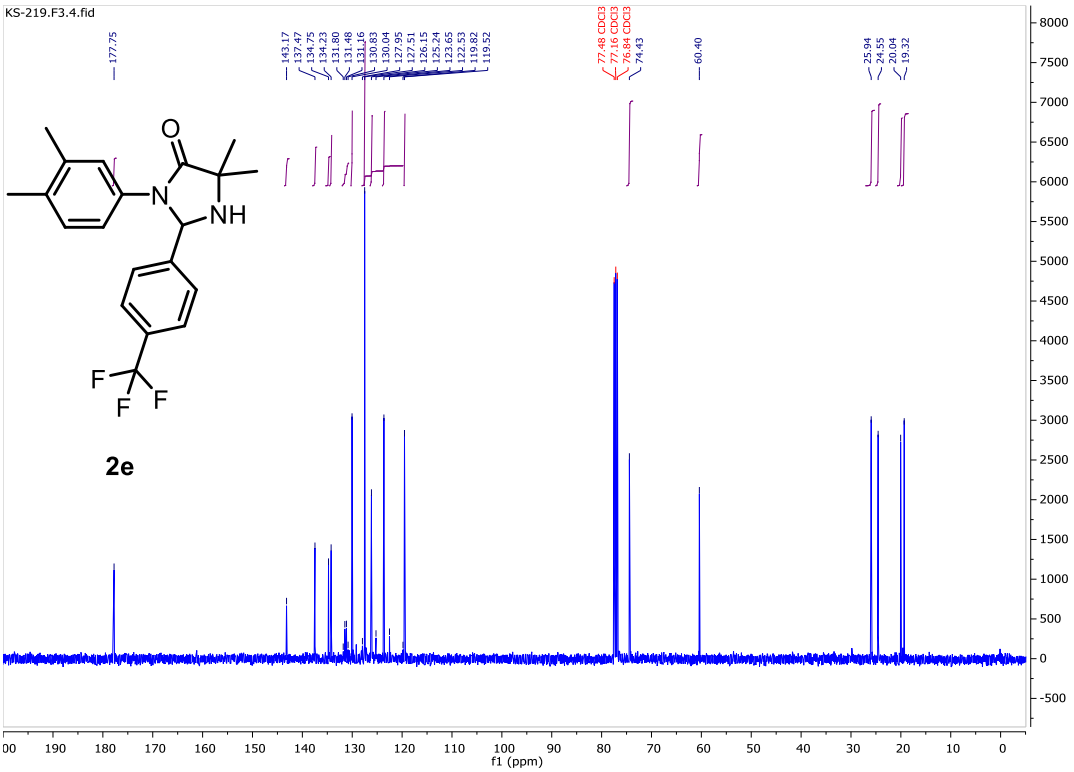


Figure S12. ^{13}C NMR (101 MHz $CDCl_3$) of **2e**.

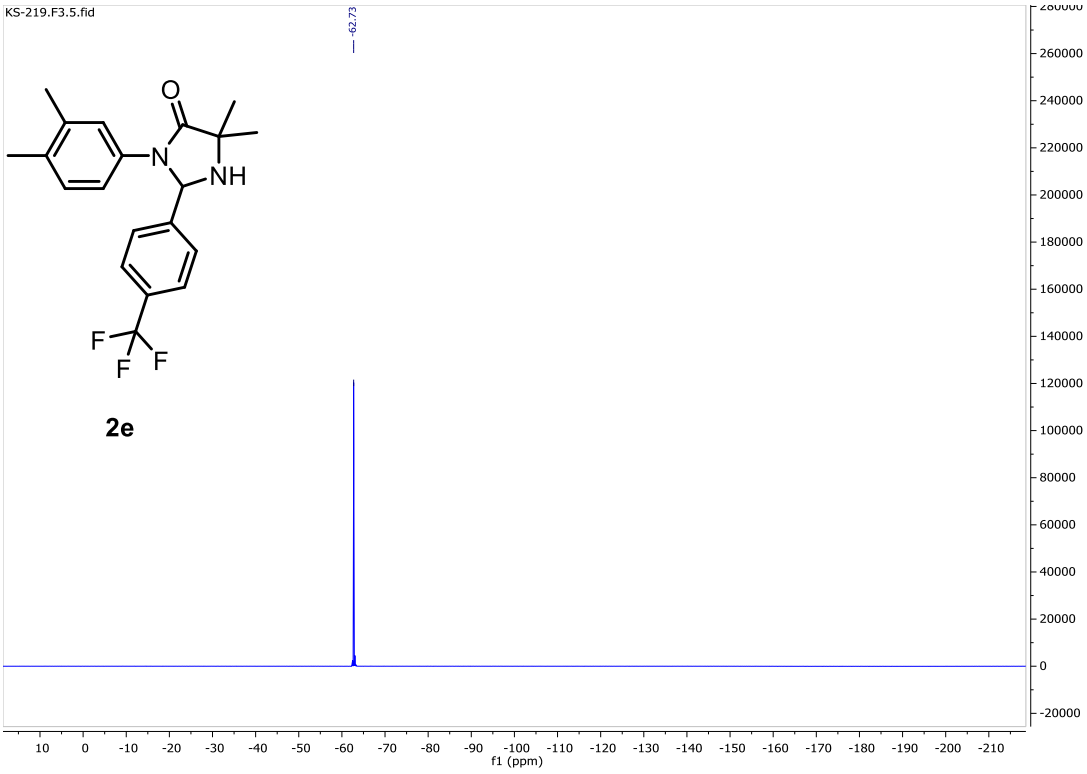


Figure S13. ^{19}F NMR (376 MHz $CDCl_3$) of **2e**.

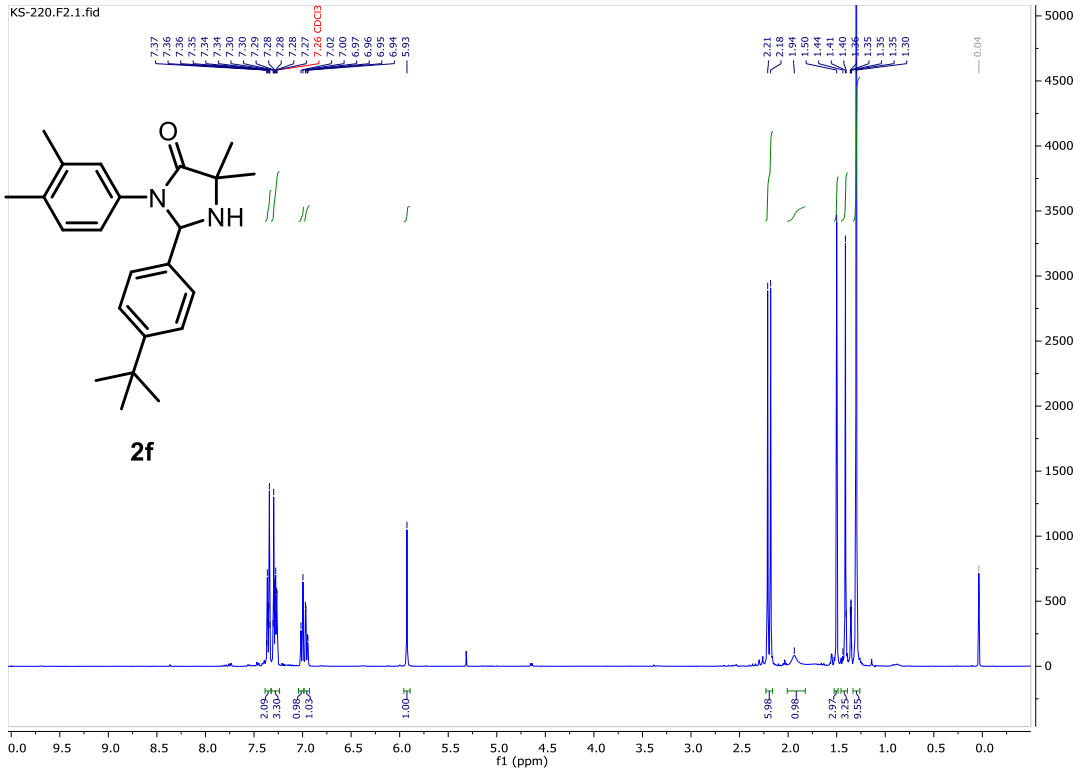


Figure S14. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2f**.

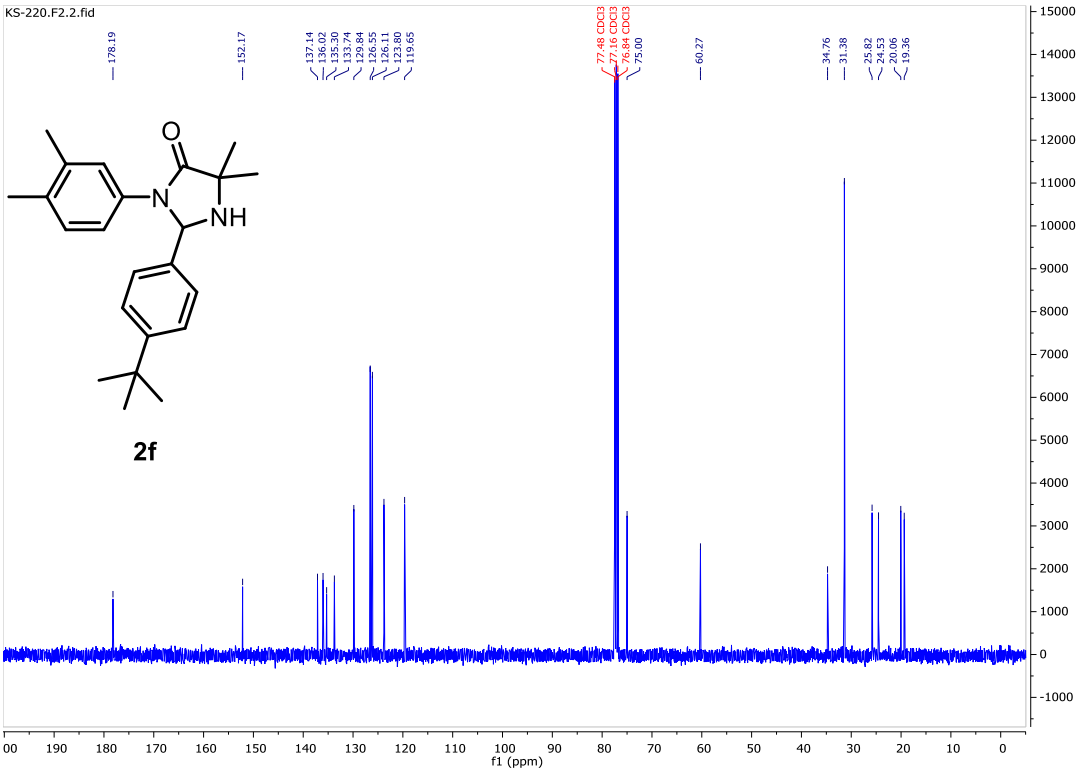


Figure S15. ^{13}C NMR (101 MHz $CDCl_3$) of **2f**.

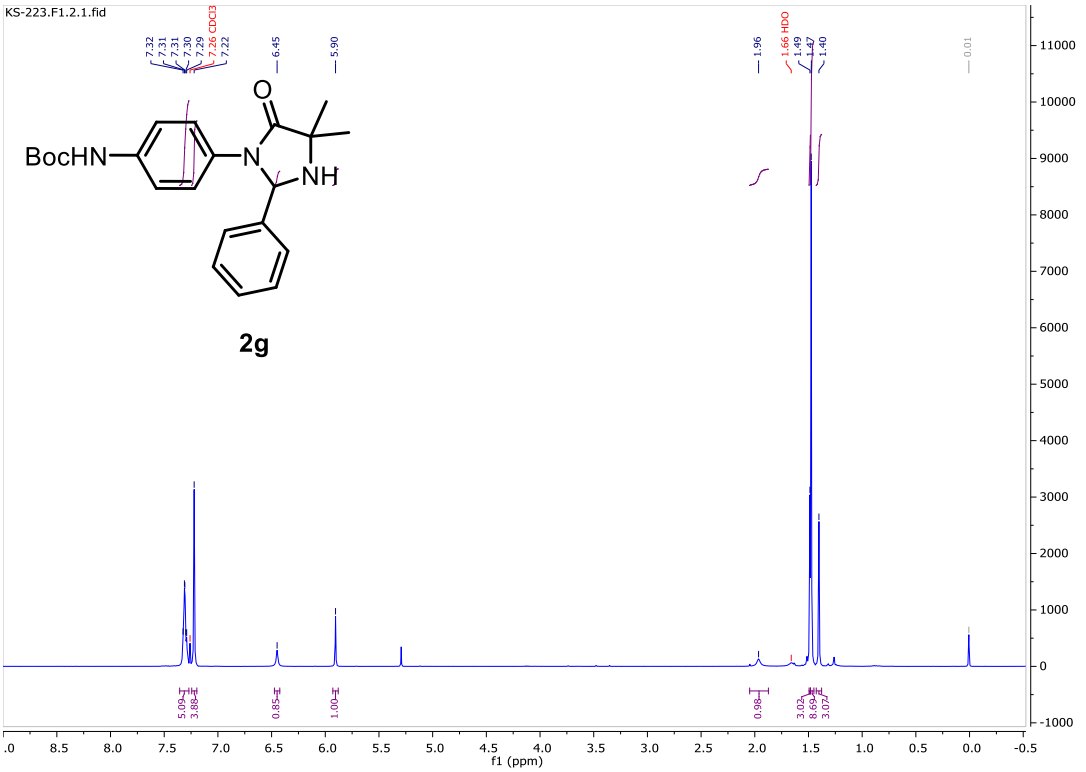


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2g**.

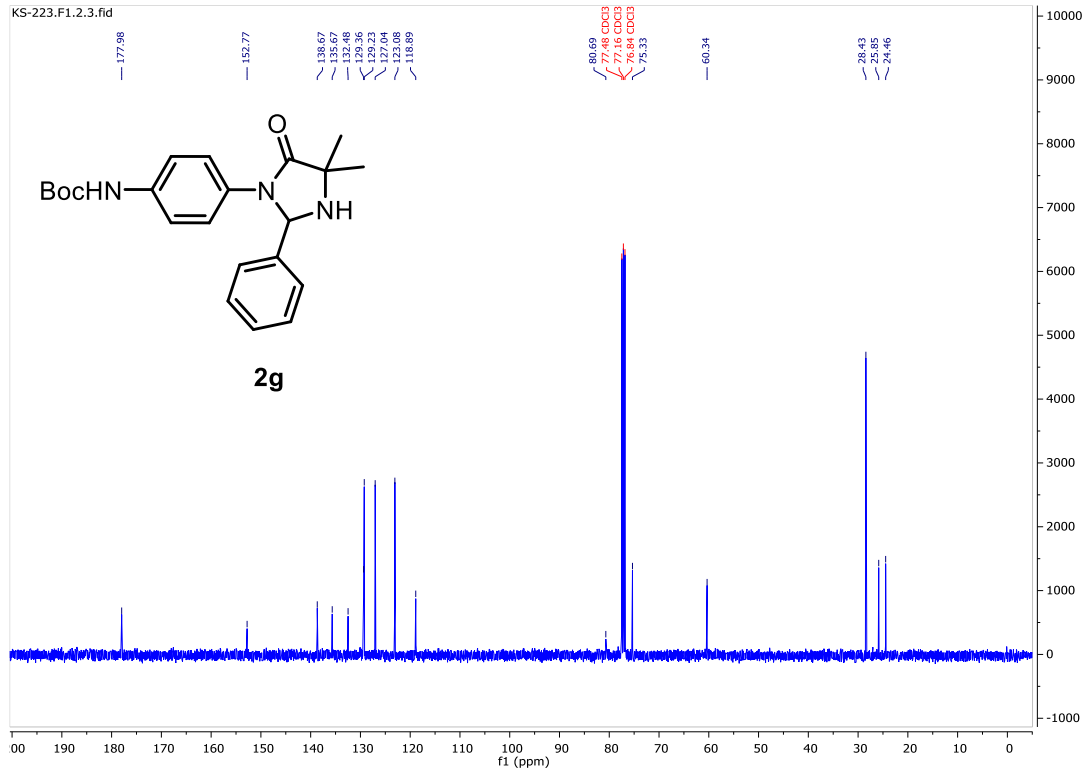


Figure S17. ^{13}C NMR (101 MHz $CDCl_3$) of **2g**.

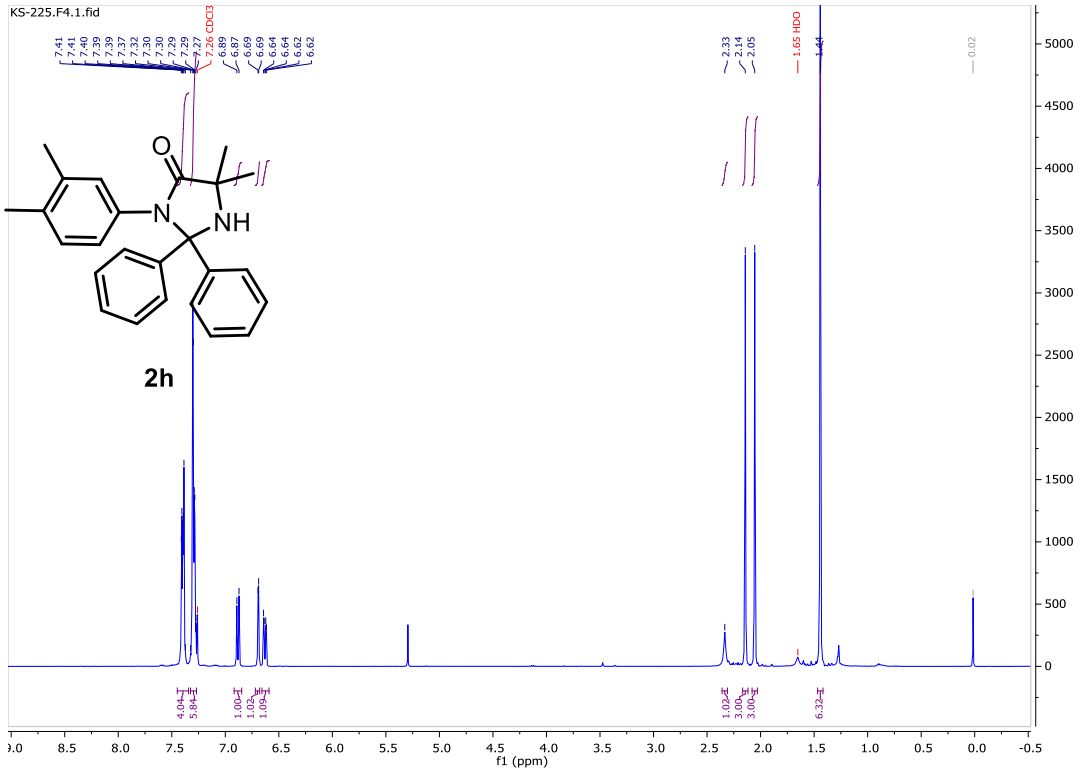


Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2h**.

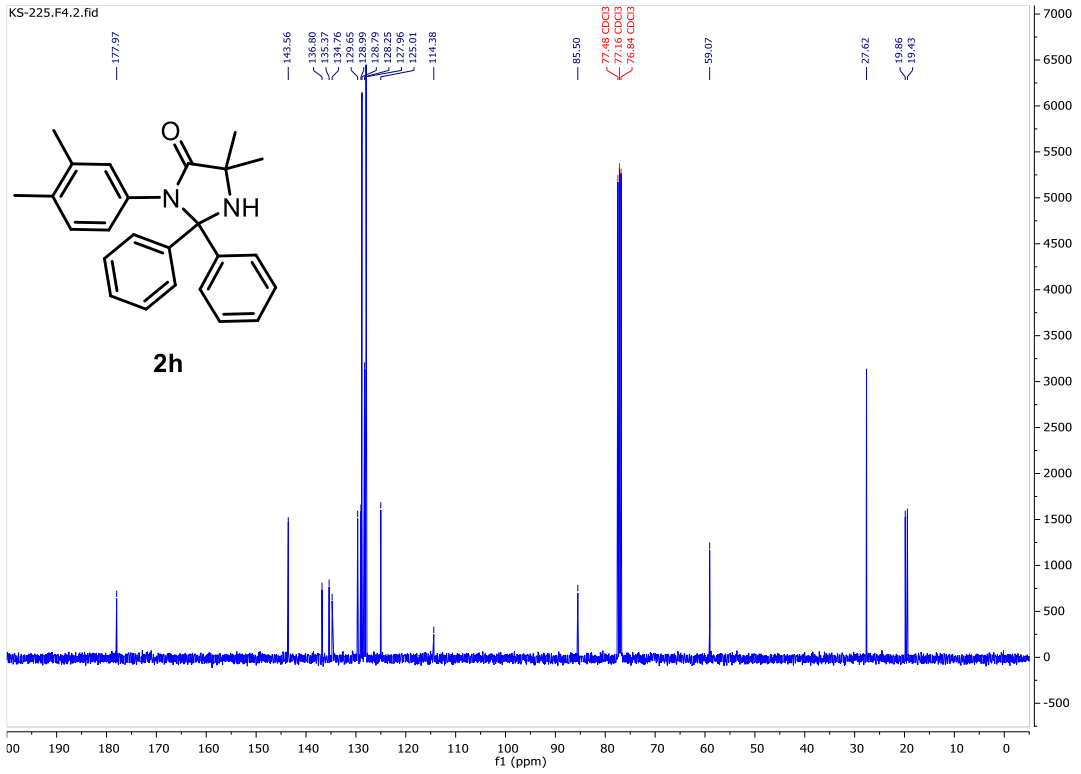


Figure S19. ^{13}C NMR (101 MHz $CDCl_3$) of **2h**.

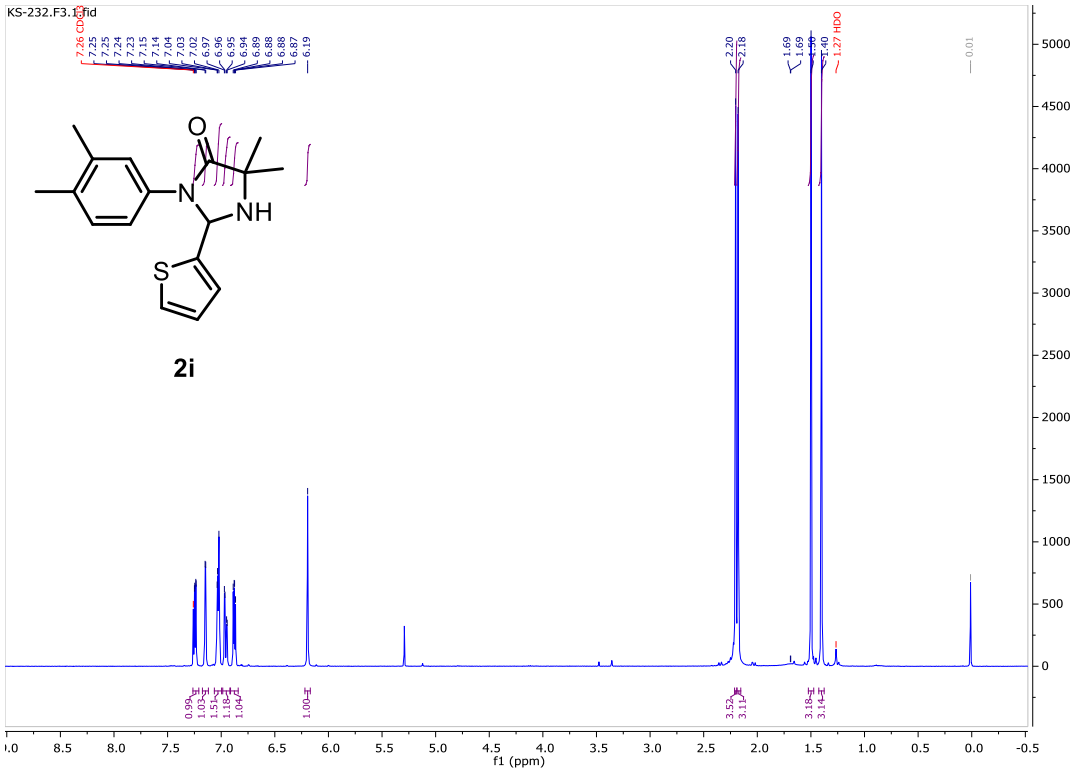


Figure S20. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2i**.

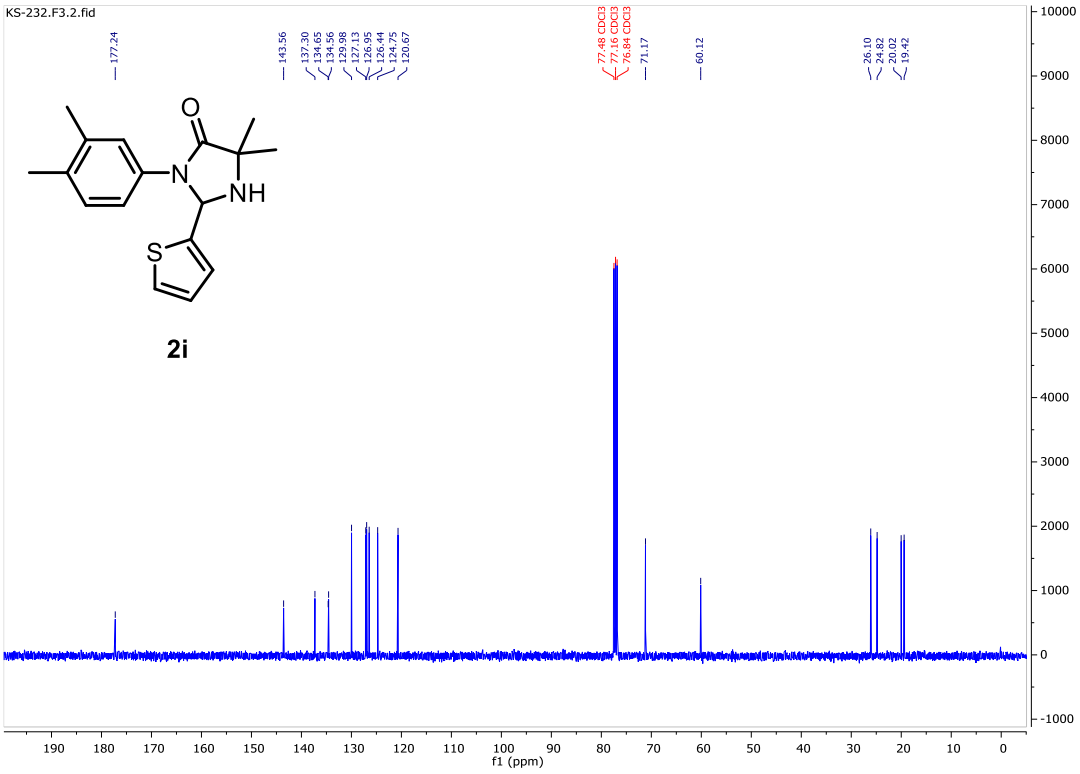


Figure S21. ^{13}C NMR (101 MHz $CDCl_3$) of **2i**.

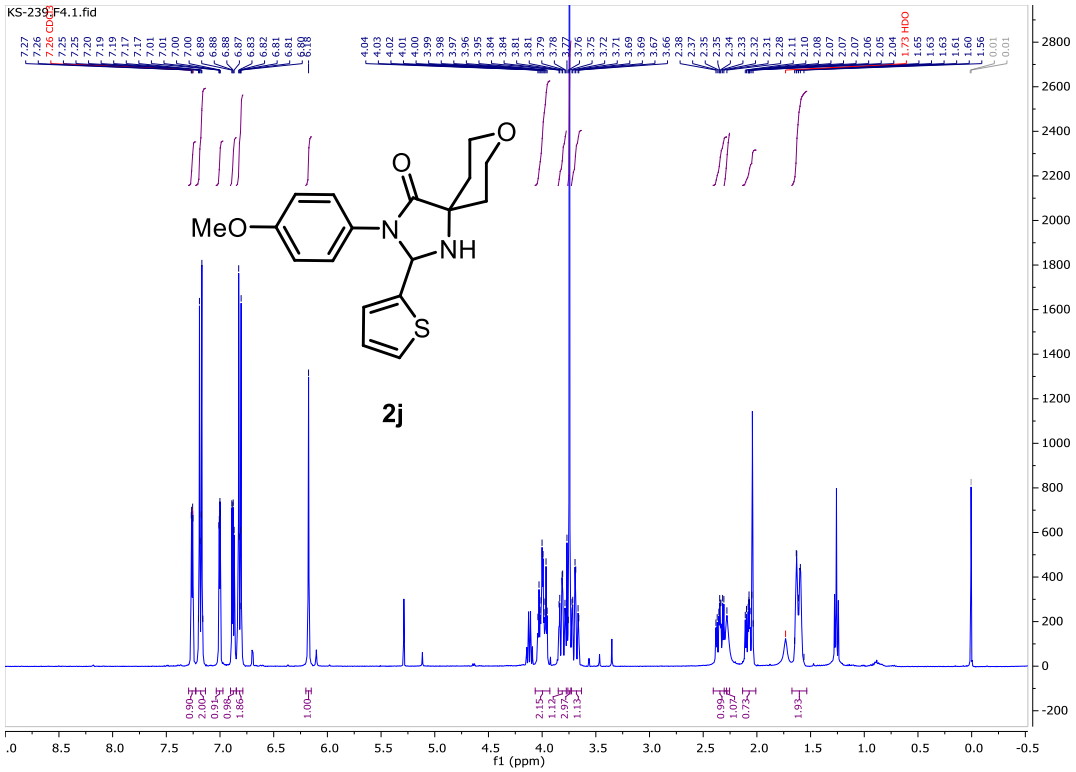


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2j**.

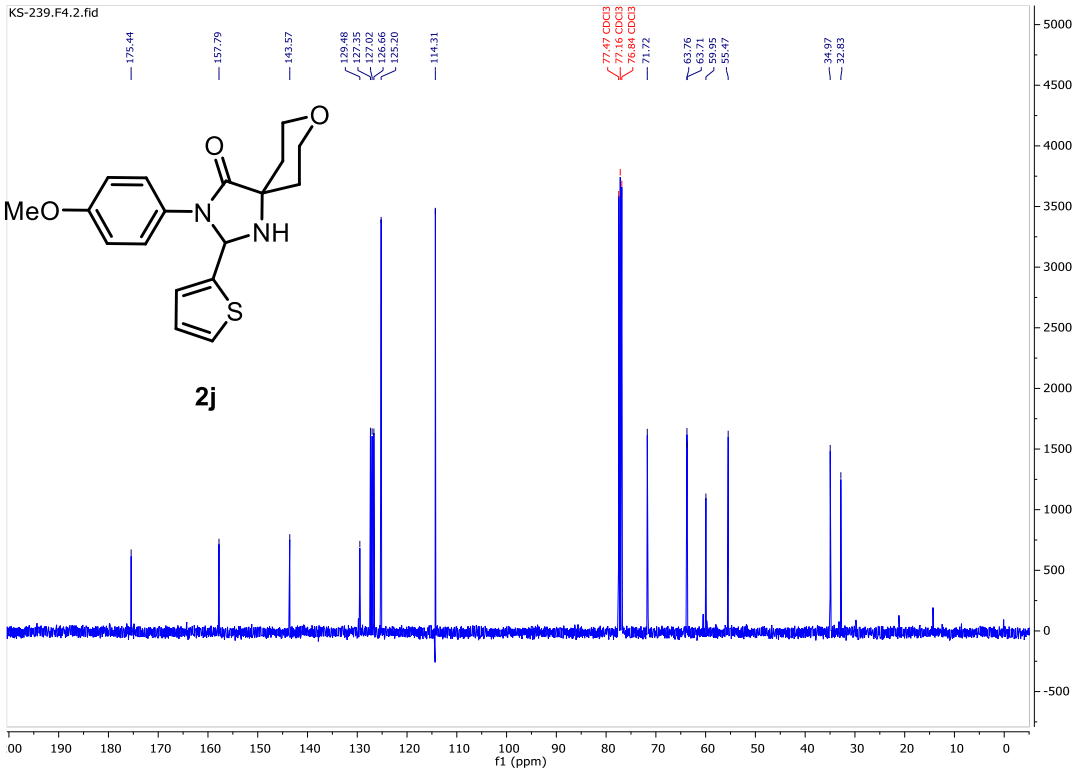


Figure S23. ^{13}C NMR (101 MHz $CDCl_3$) of **2j**.

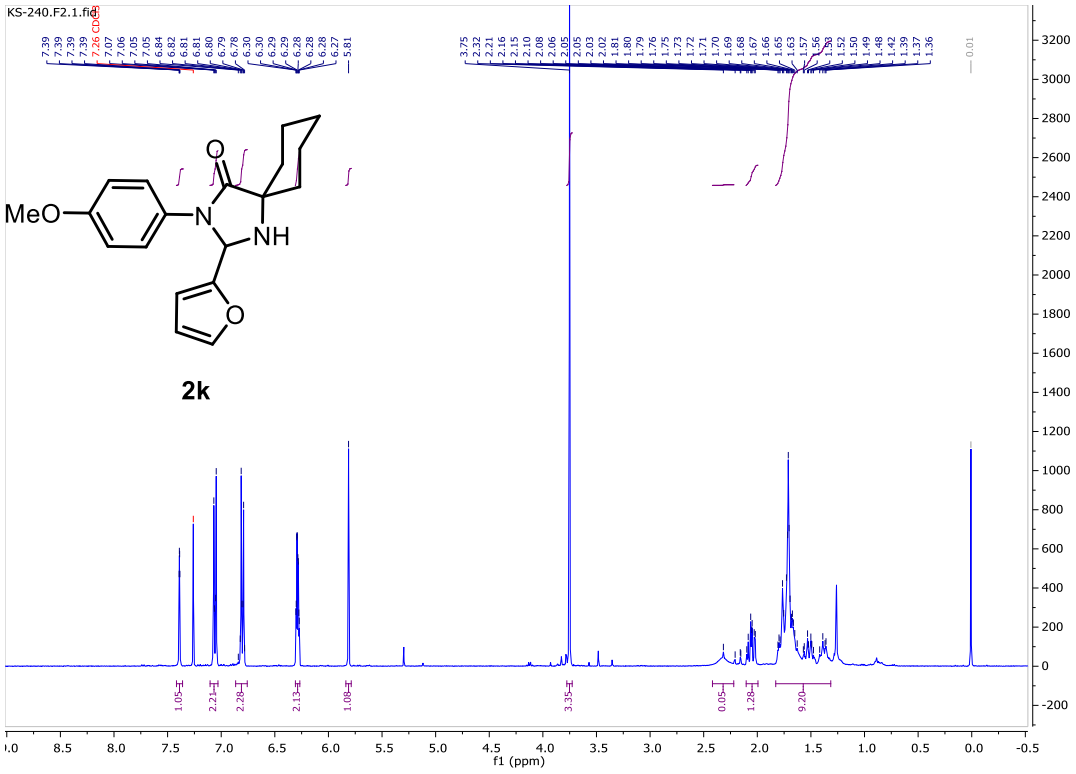


Figure S24. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2k**.

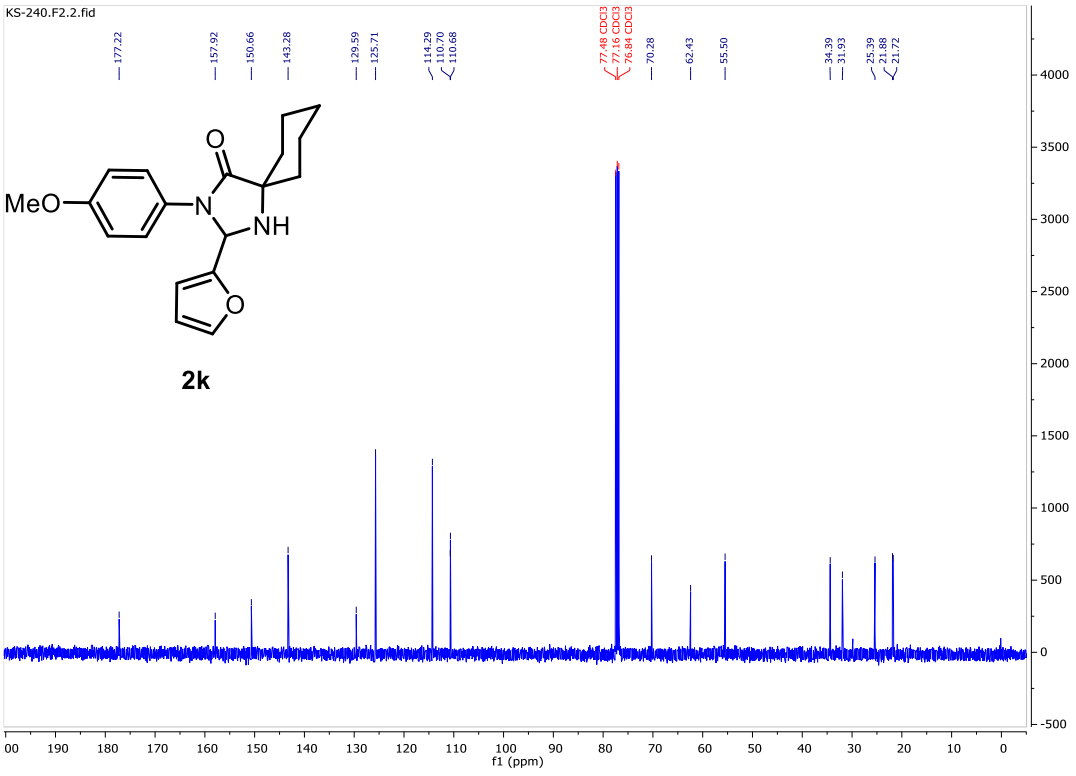


Figure S25. ^{13}C NMR (101 MHz $CDCl_3$) of **2k**.

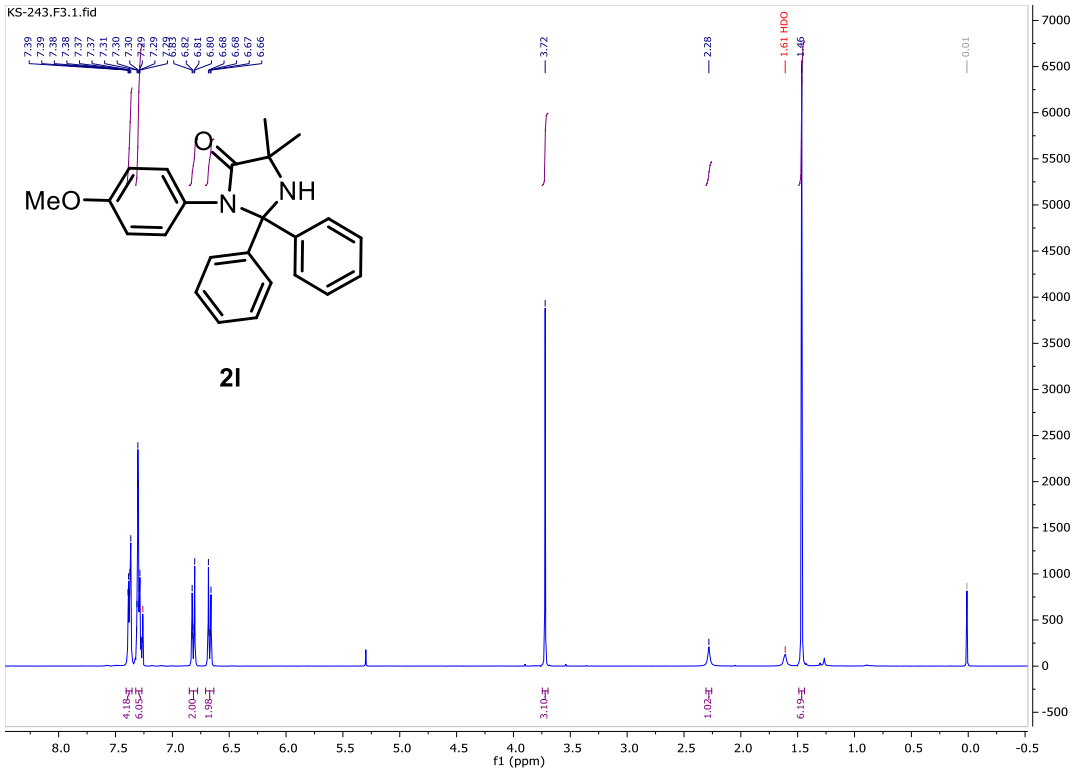


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2l**.

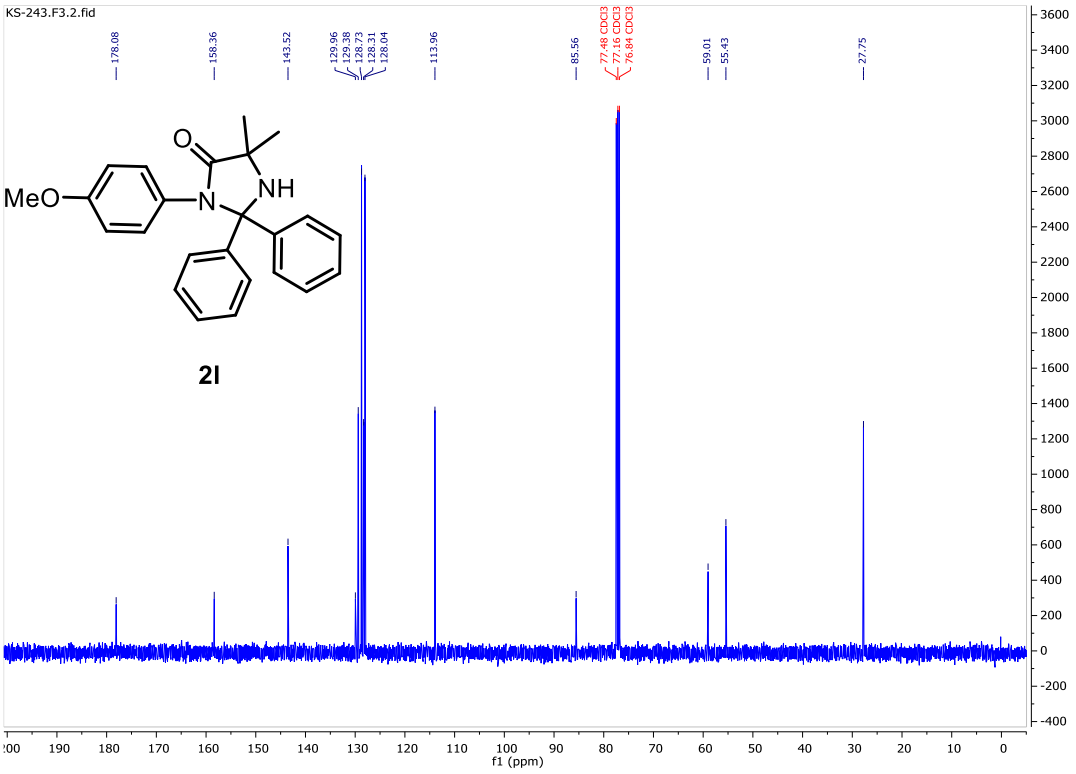


Figure S27. ^{13}C NMR (101 MHz $CDCl_3$) of **2l**.

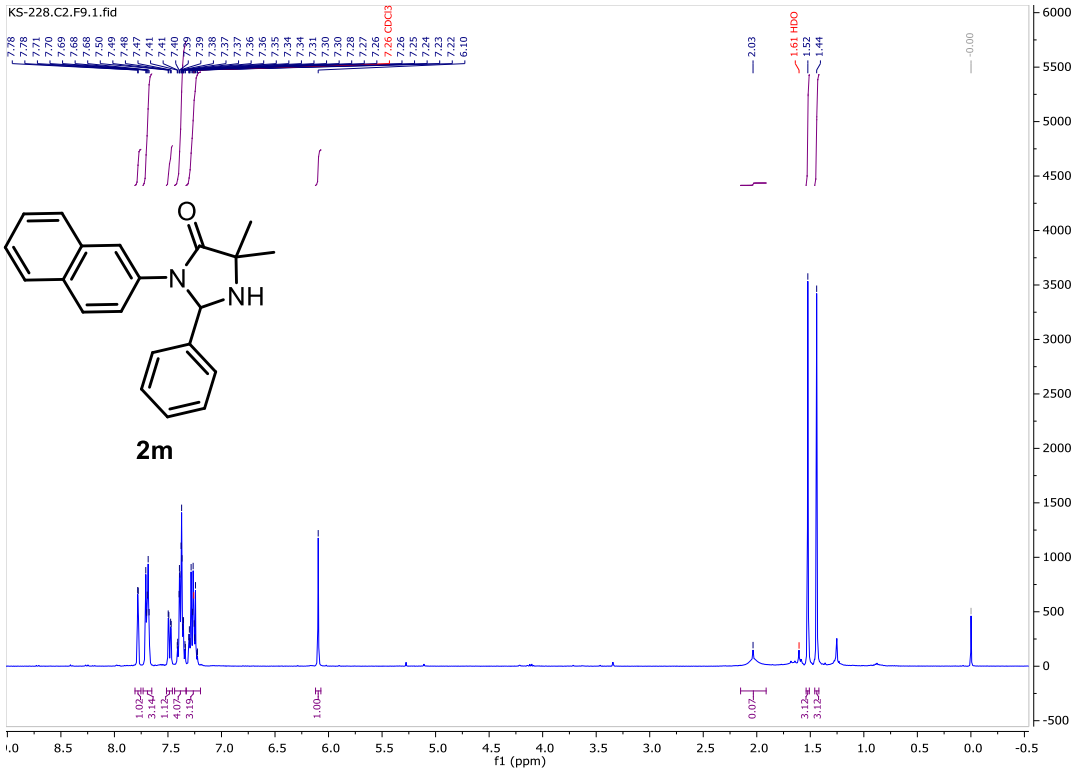


Figure S28. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2m**.

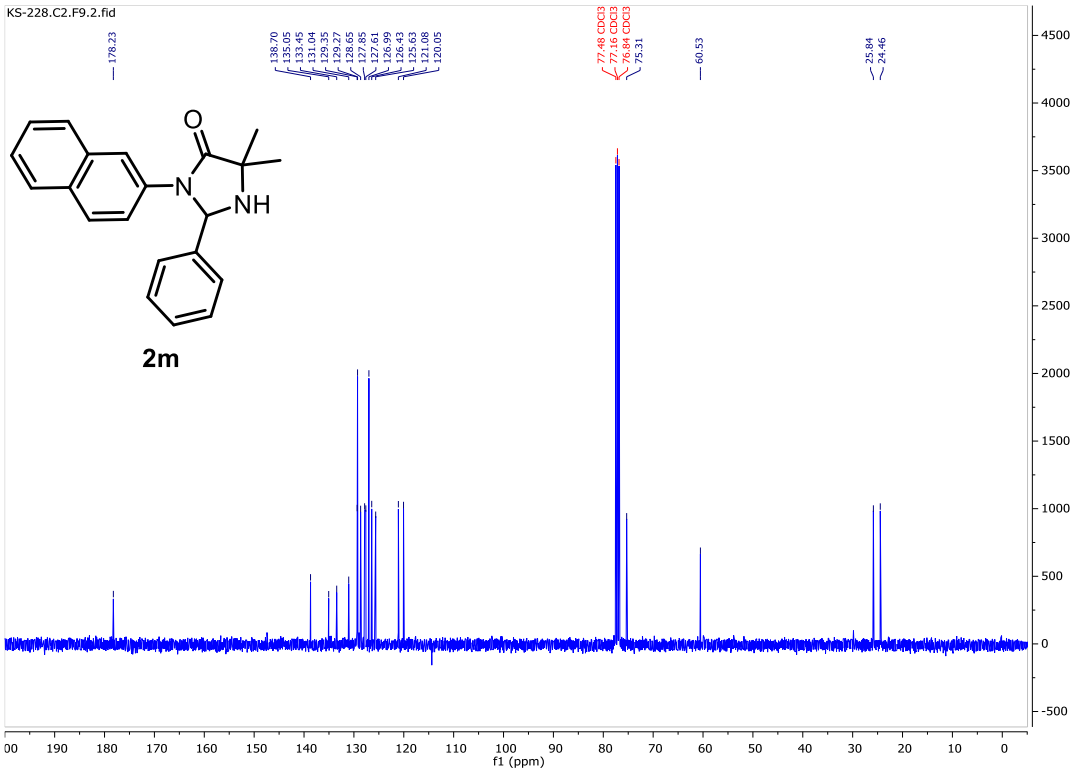


Figure S29. ^{13}C NMR (101 MHz $CDCl_3$) of **2m**.

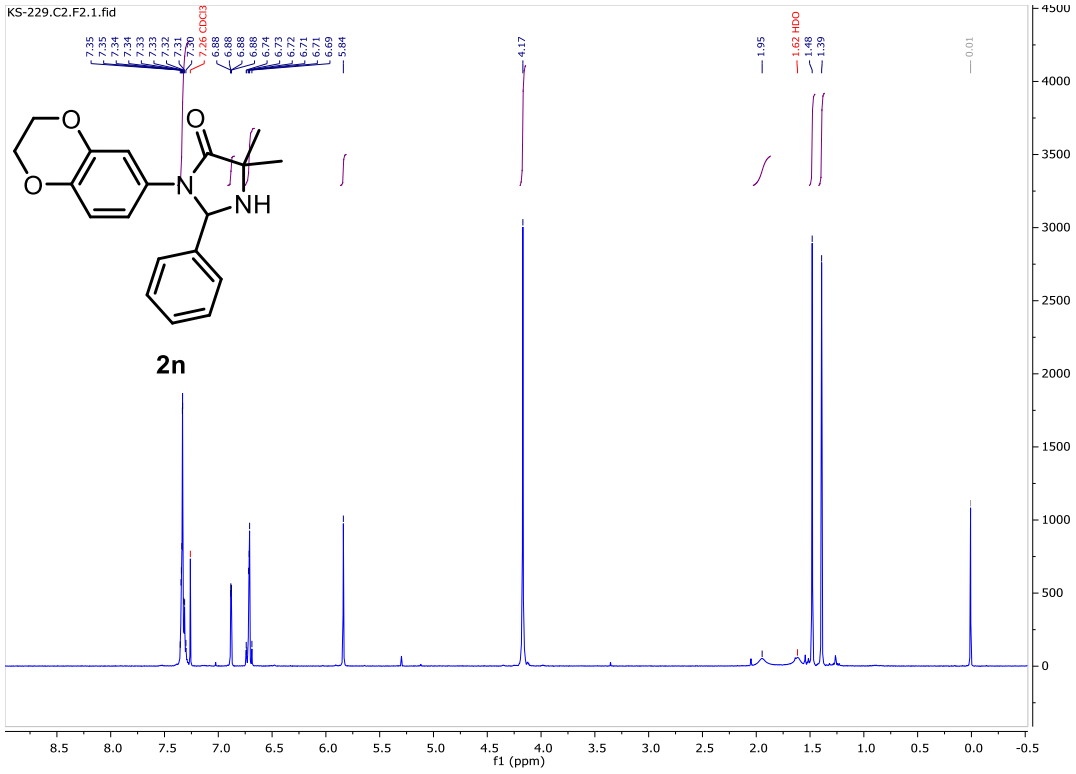


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2n**.

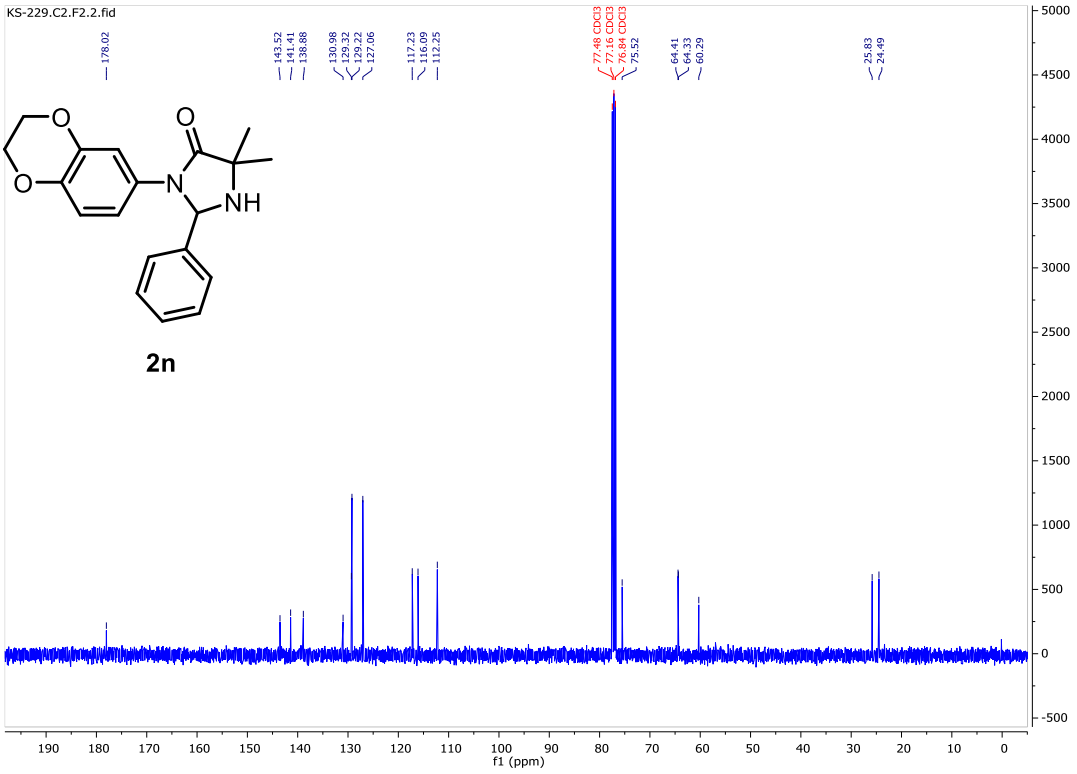


Figure S31. ^{13}C NMR (101 MHz $CDCl_3$) of **2n**.

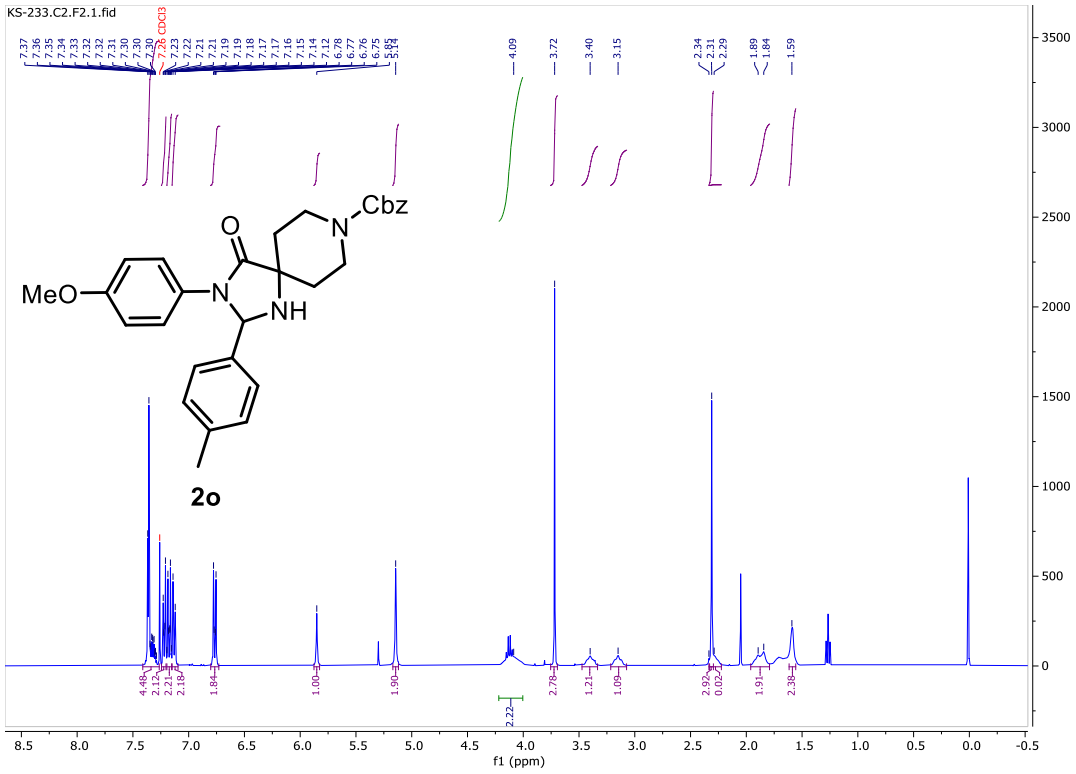


Figure S32. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2o**.

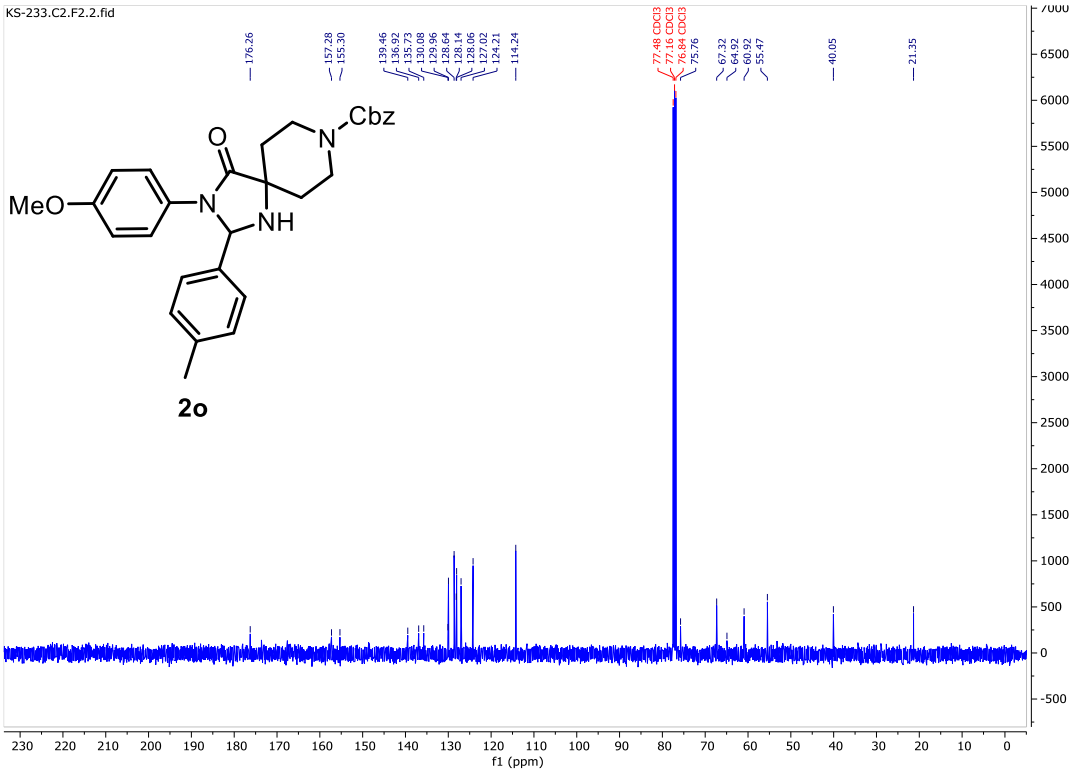


Figure S33. ^{13}C NMR (101 MHz $CDCl_3$) of **2o**.

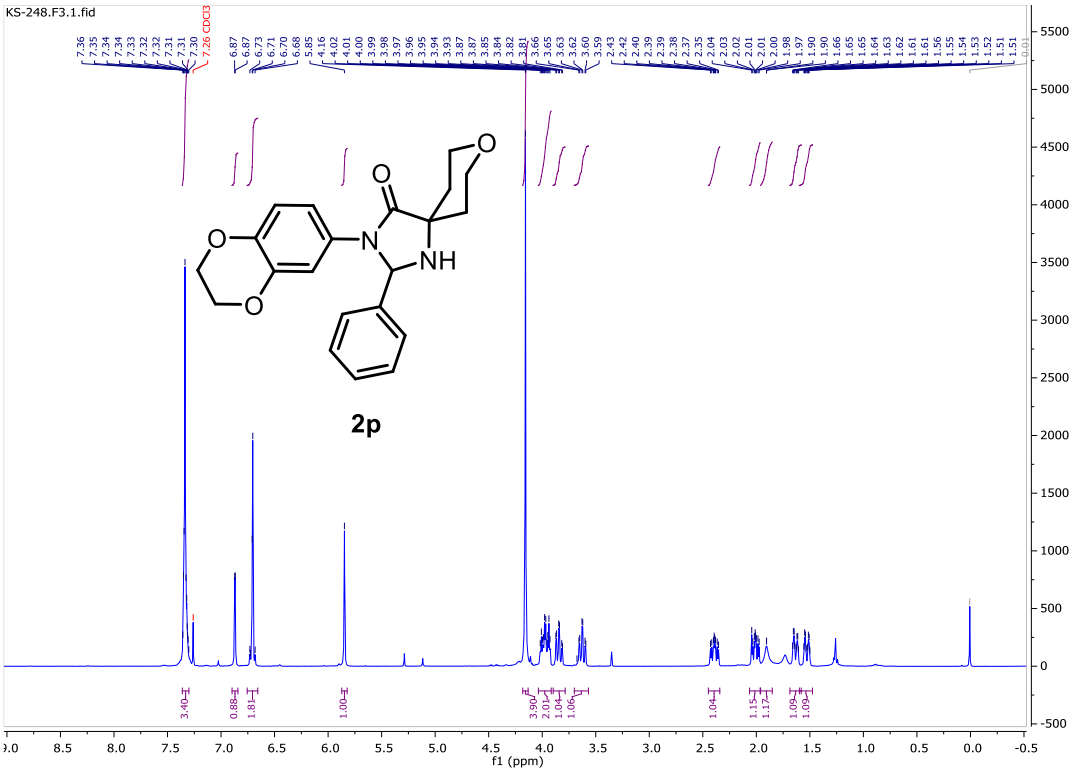


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2p**.

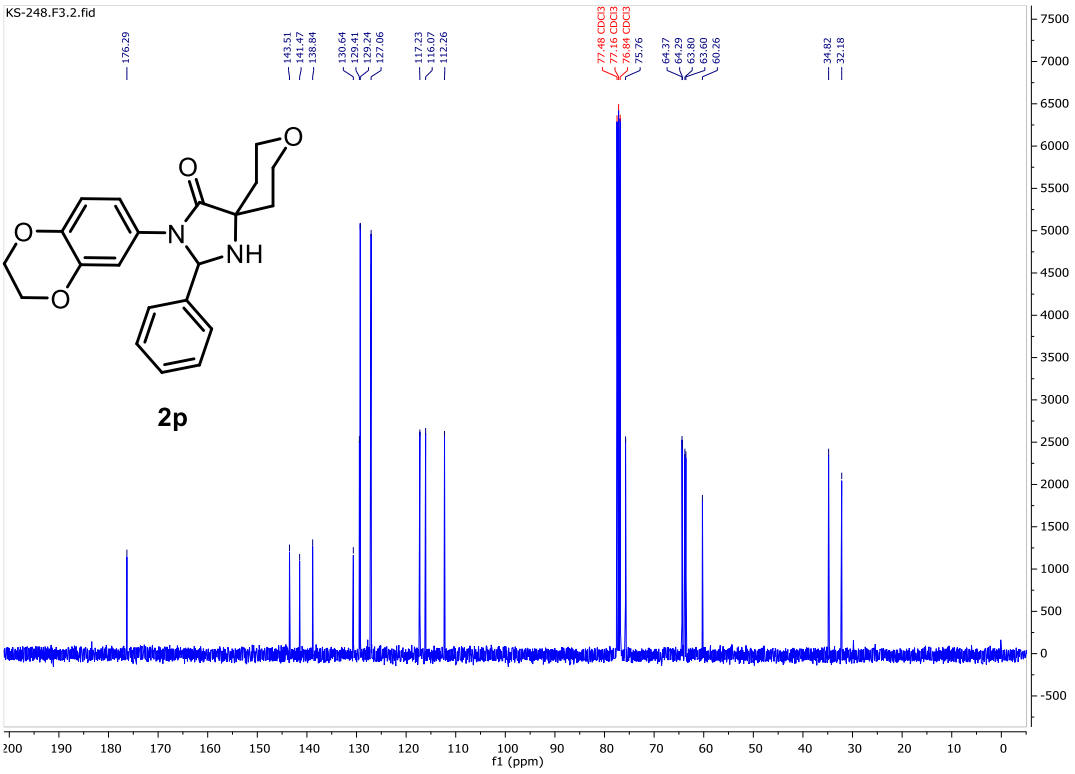


Figure S35. ^{13}C NMR (101 MHz $CDCl_3$) of **2p**.

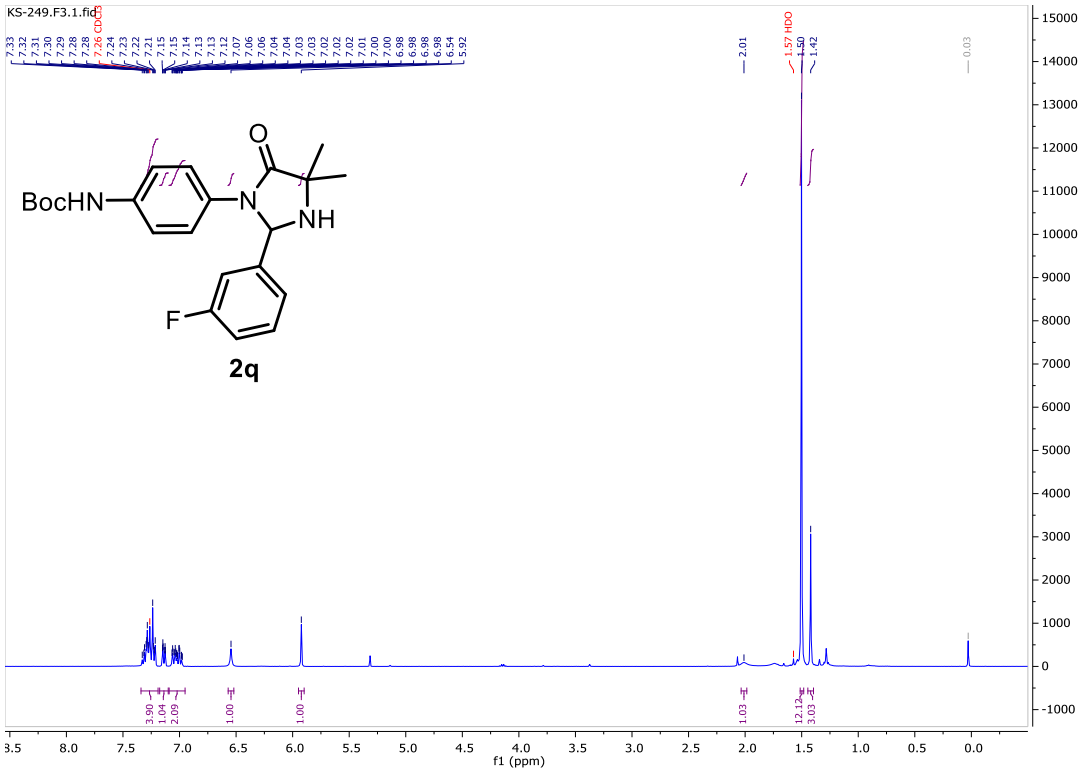


Figure S36. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2q**.

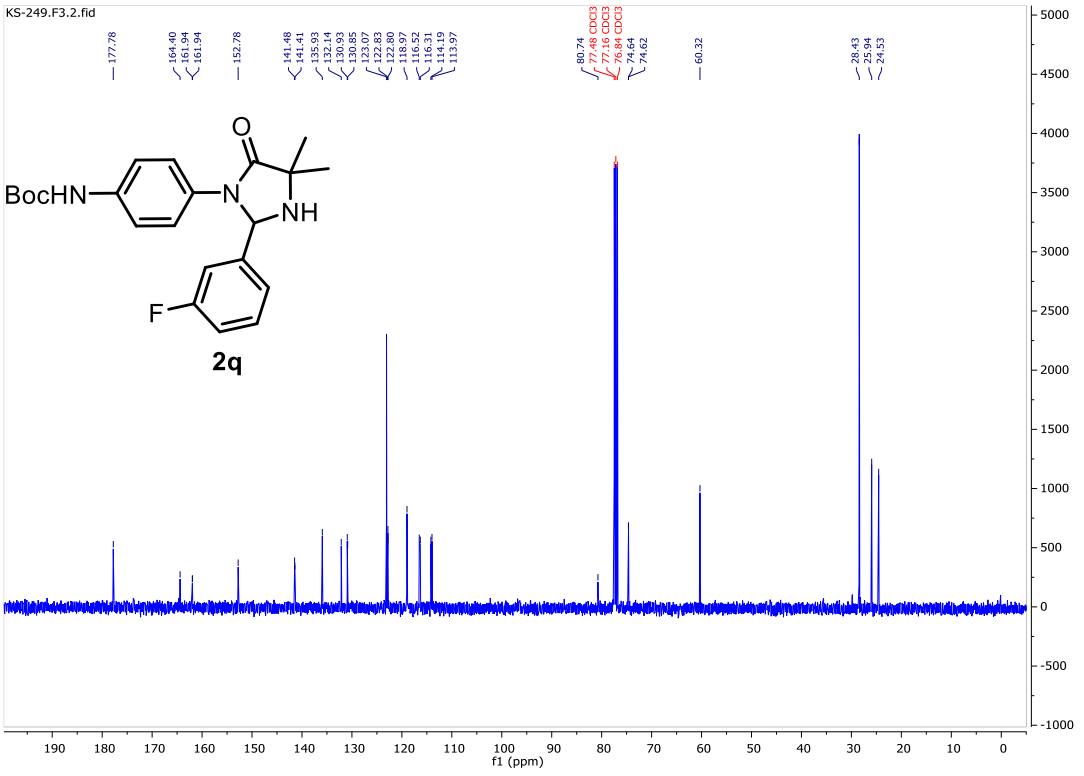


Figure S37. ^{13}C NMR (101 MHz $CDCl_3$) of **2q**.

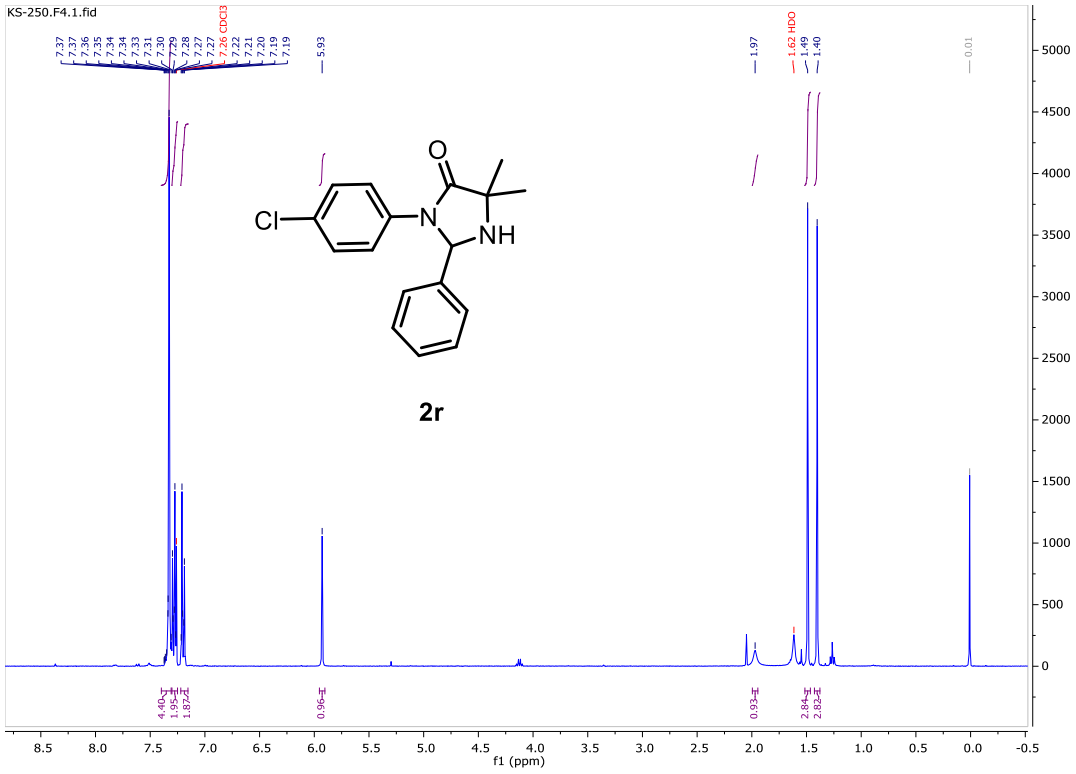


Figure S38. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2r**.

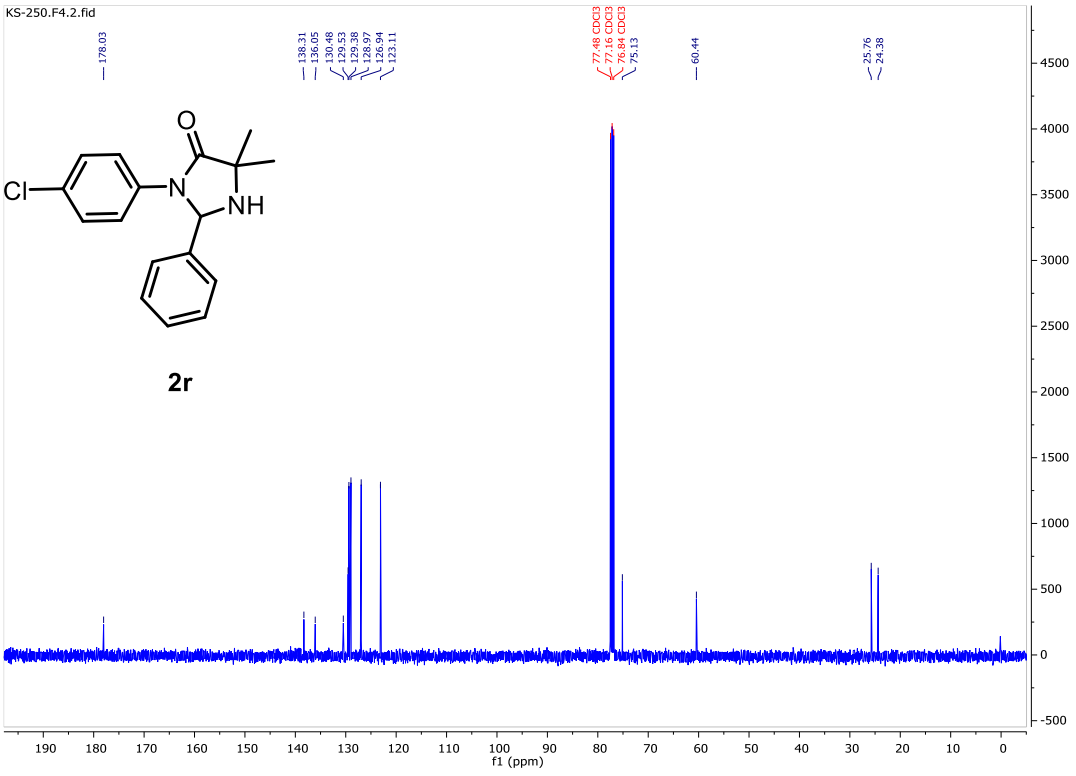


Figure S39. ^{13}C NMR (101 MHz $CDCl_3$) of **2r**.

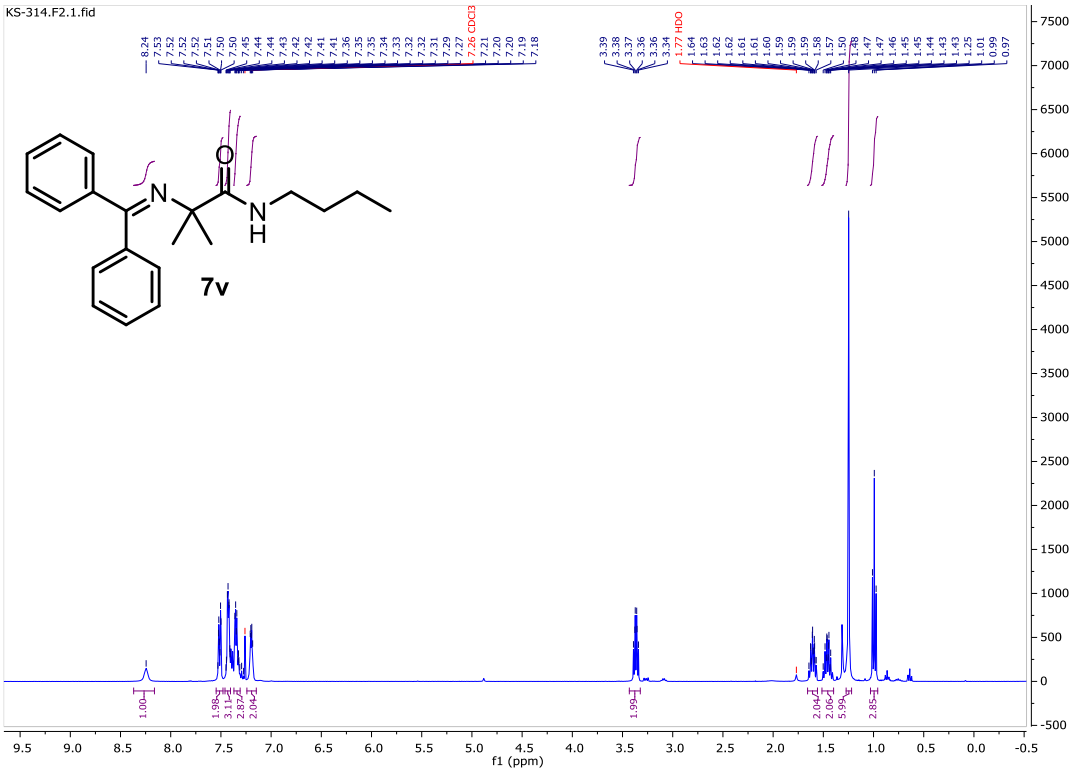


Figure S40. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7v**.

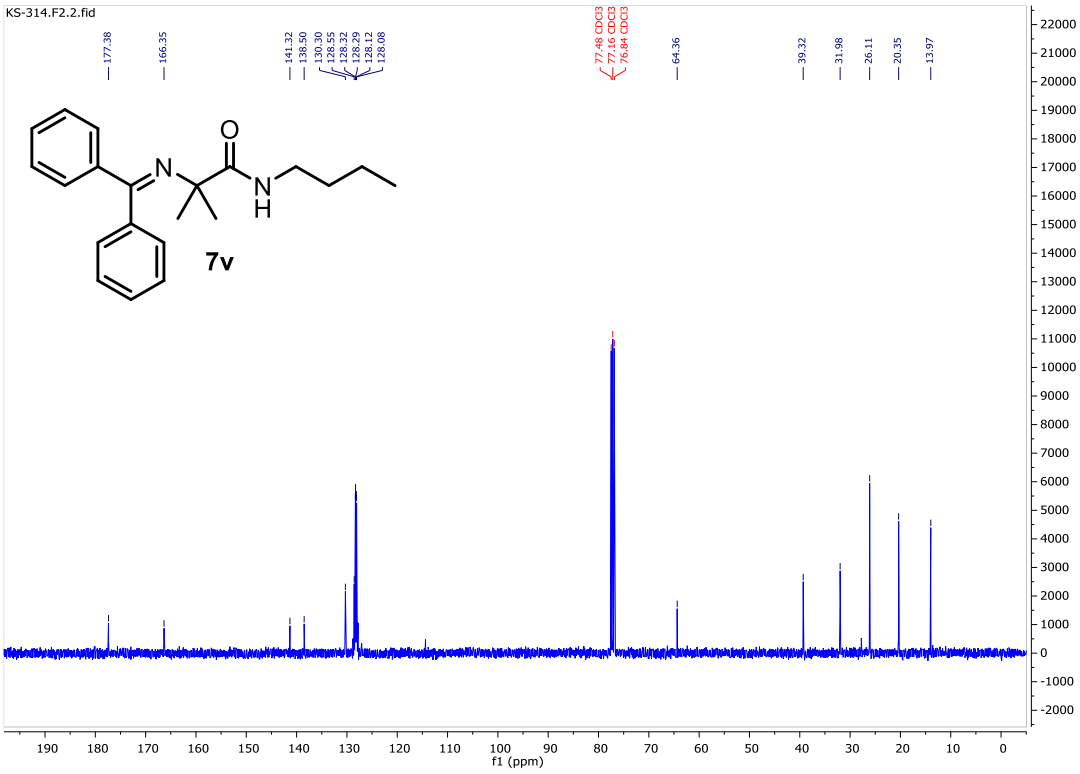


Figure S41. ^{13}C NMR (101 MHz $CDCl_3$) of **7v**.

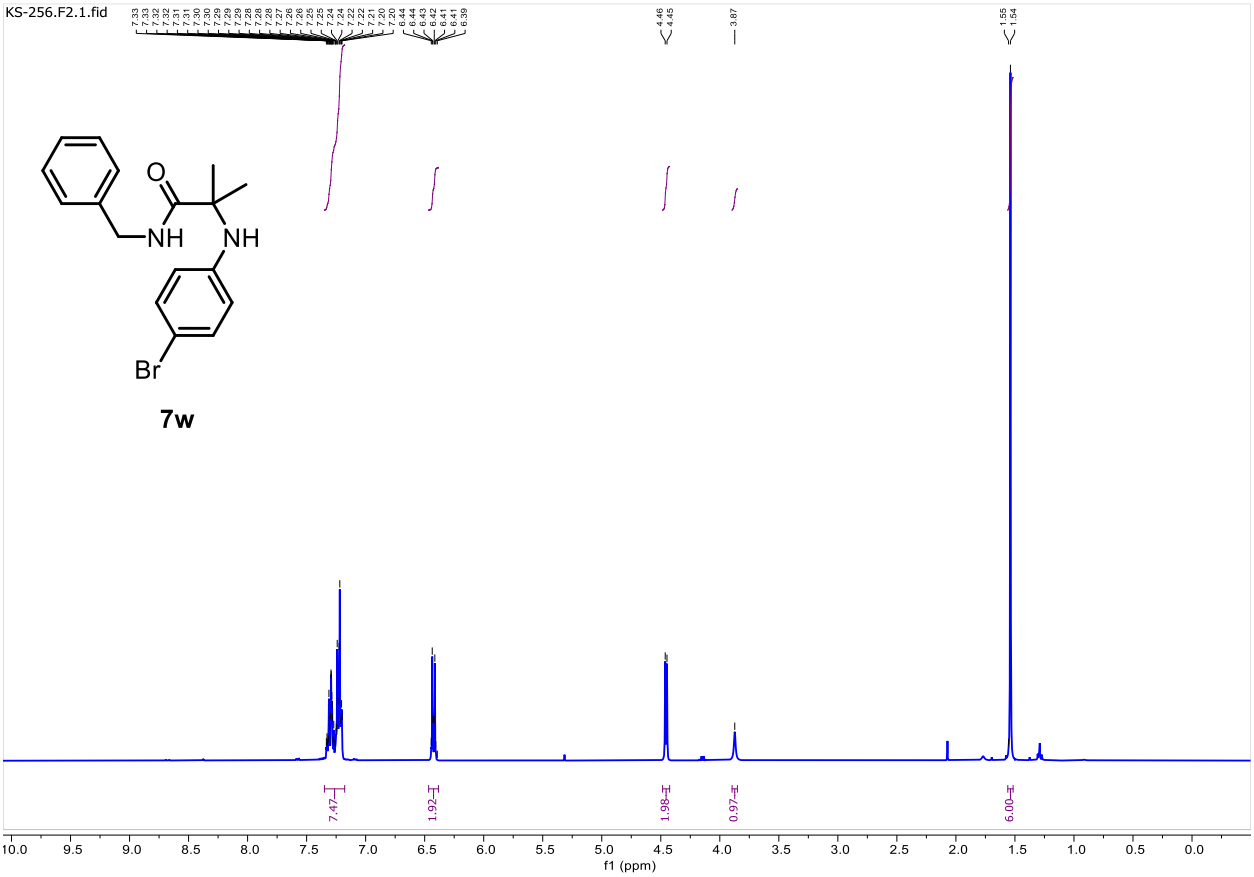


Figure S42. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7w**.

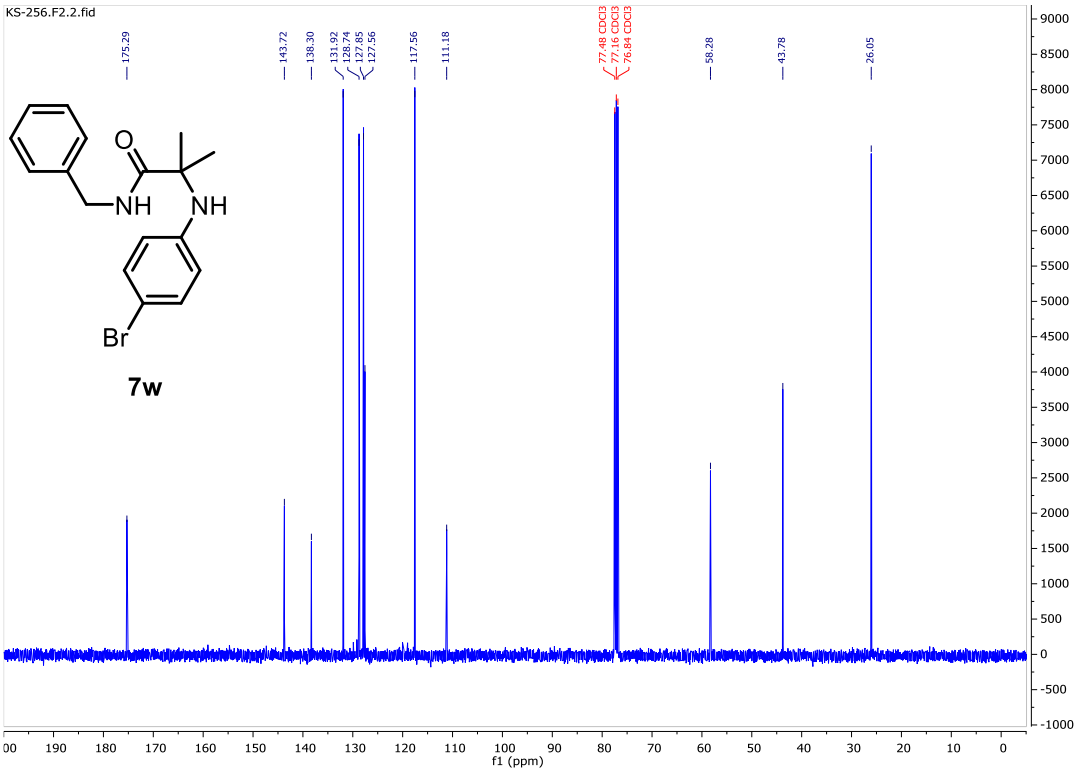


Figure S43. ^{13}C NMR (101 MHz $CDCl_3$) of **7w**.

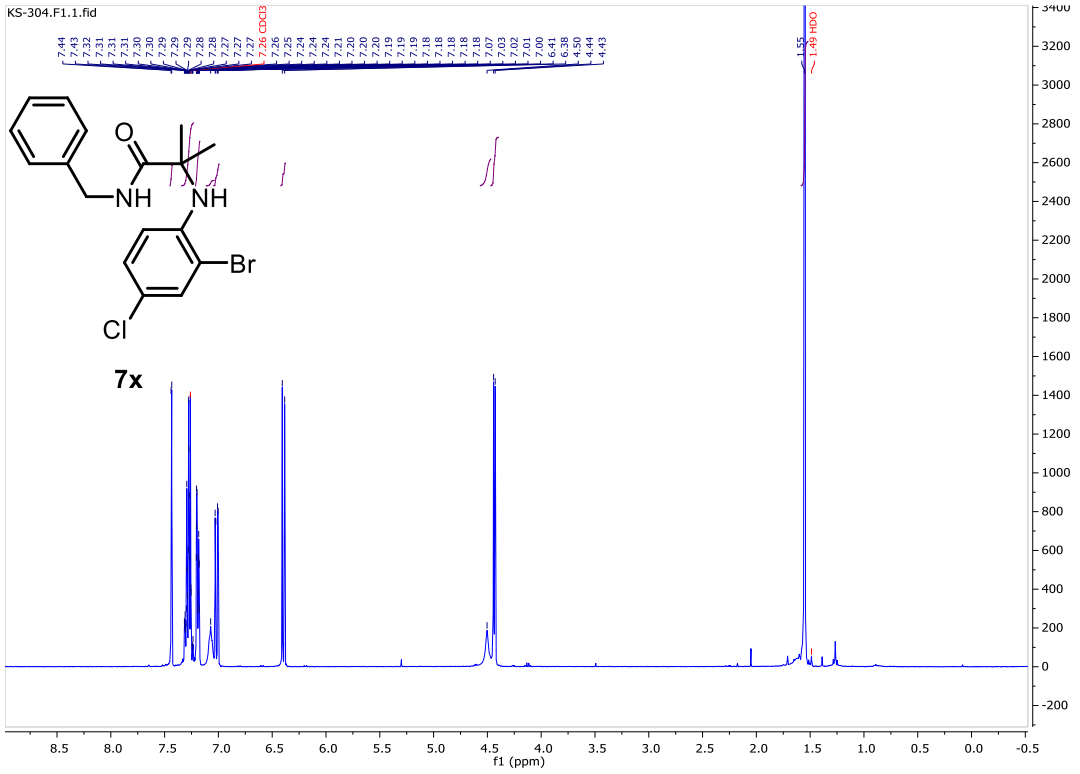


Figure S44. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7x**.

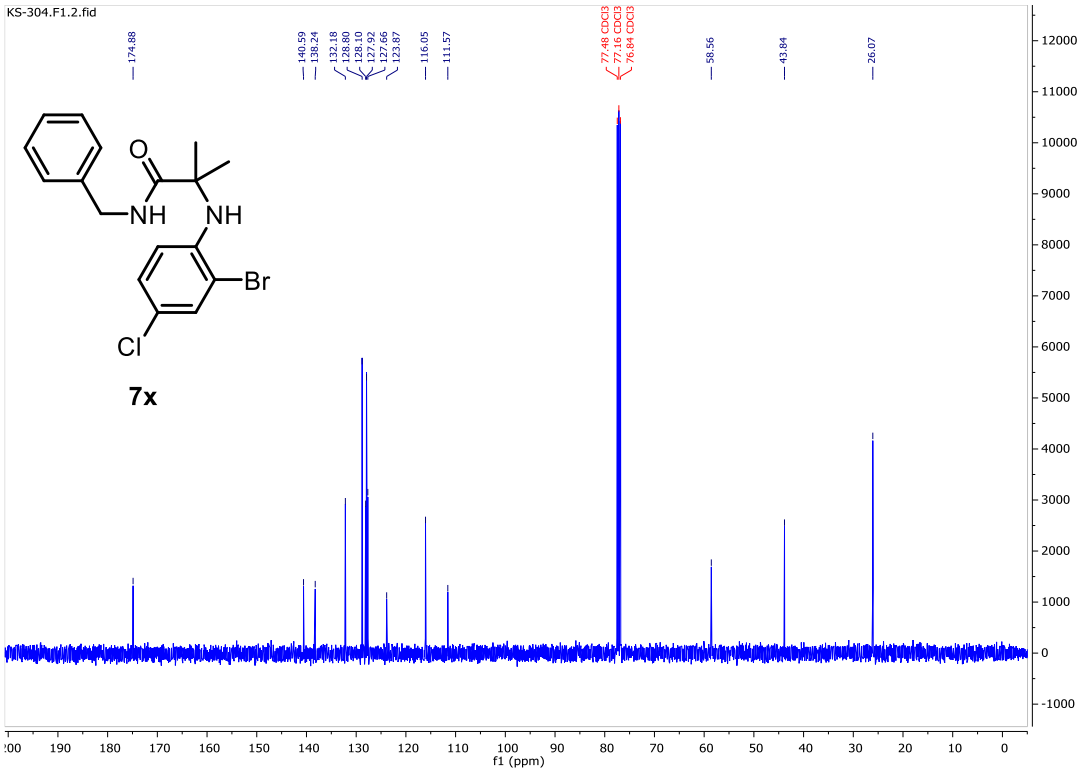


Figure S45. ^{13}C NMR (101 MHz $CDCl_3$) of **7x**.

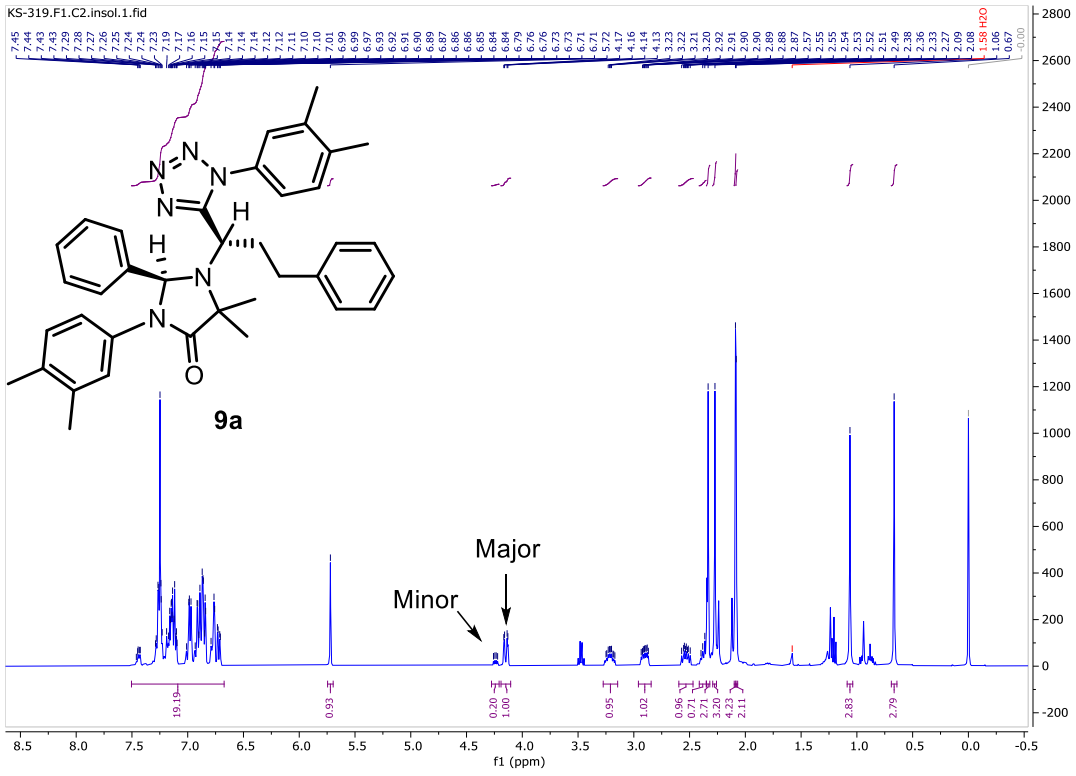


Figure S46. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9a**.

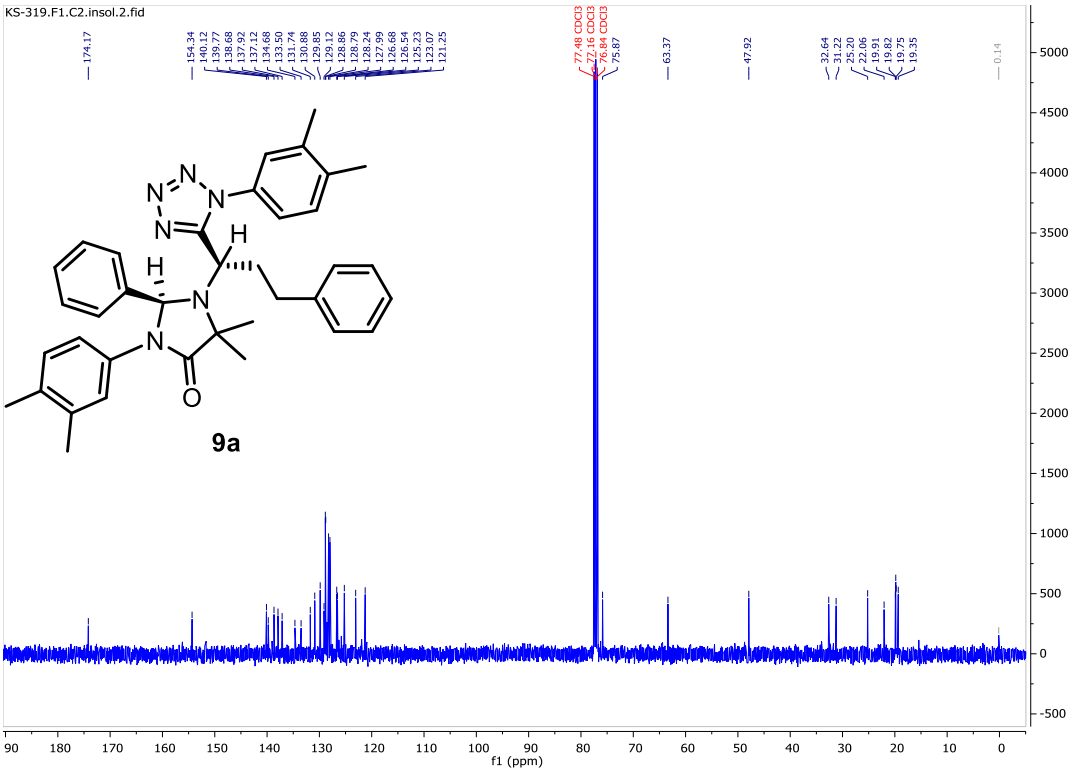


Figure S47. ^{13}C NMR (101 MHz $CDCl_3$) of **9a**.

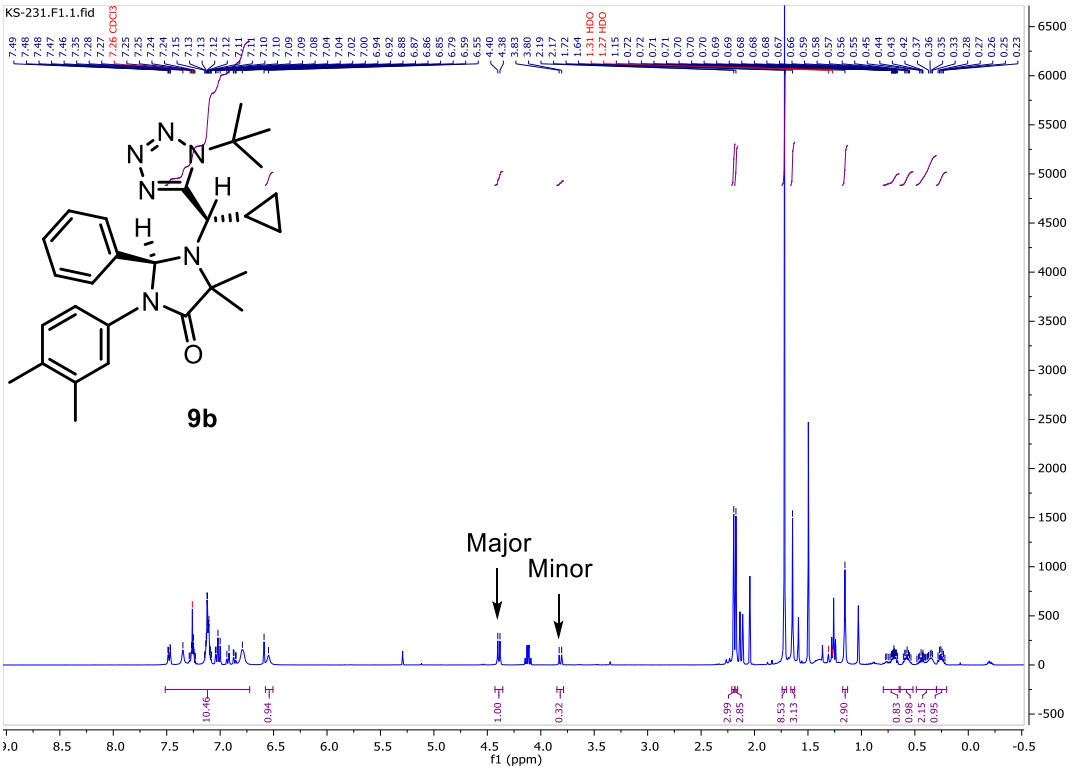


Figure S48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9b**.

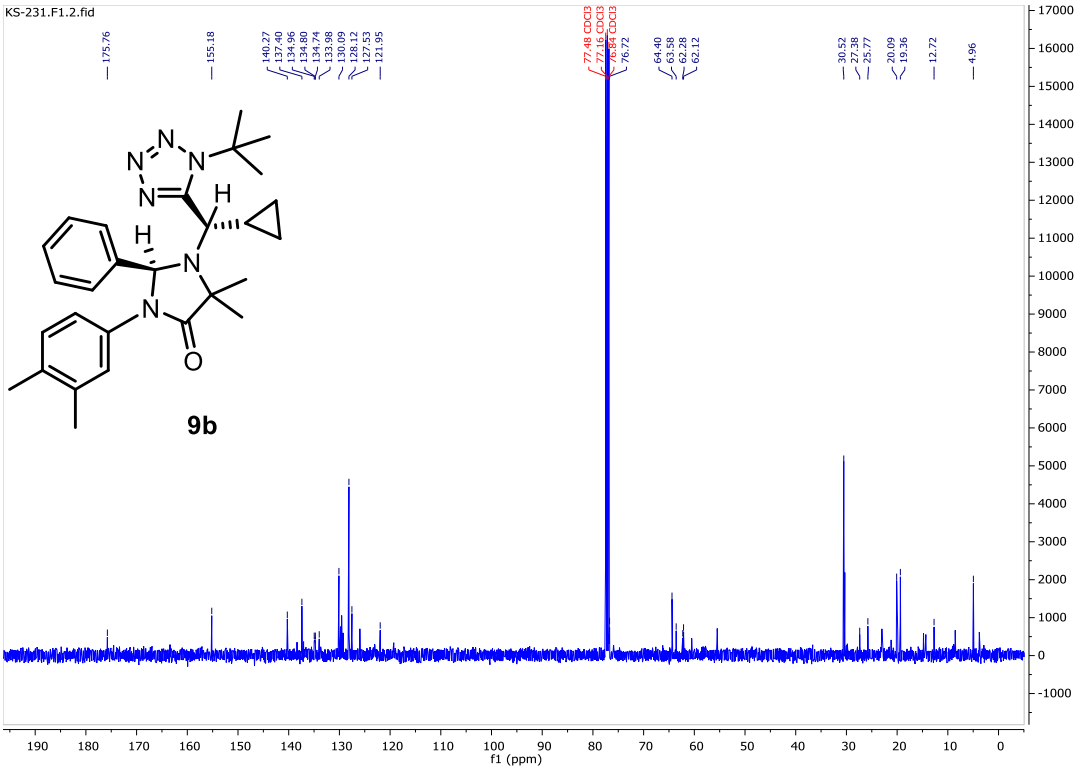


Figure S49. ^{13}C NMR (101 MHz $CDCl_3$) of **9b**.

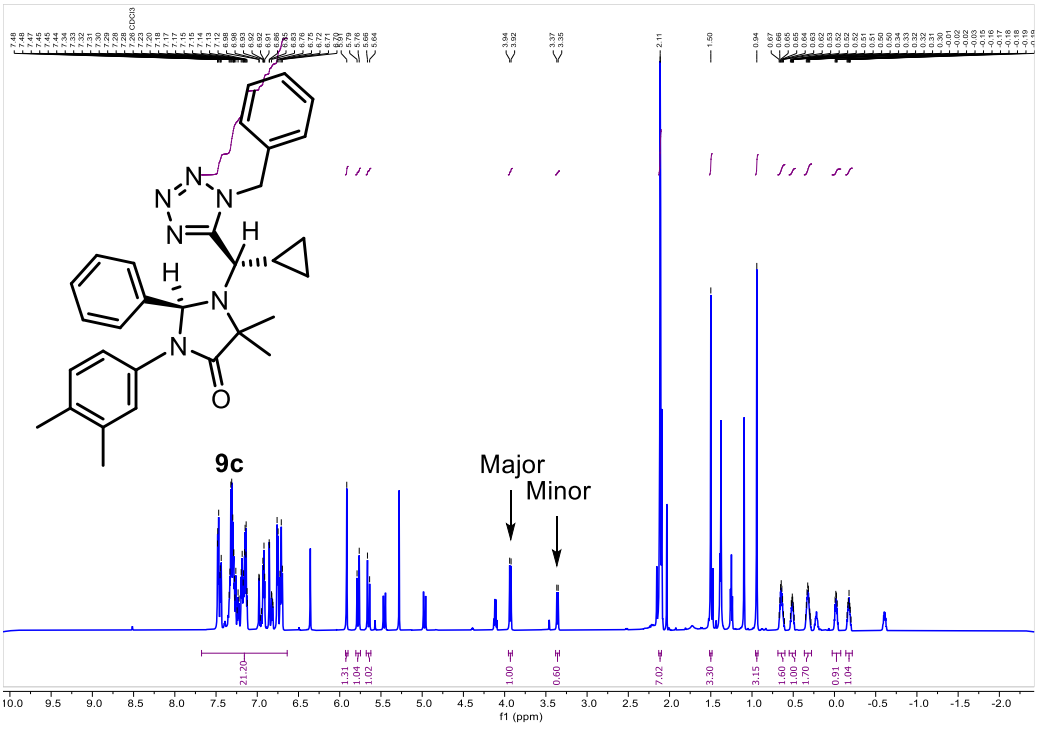


Figure S50. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **9c**.

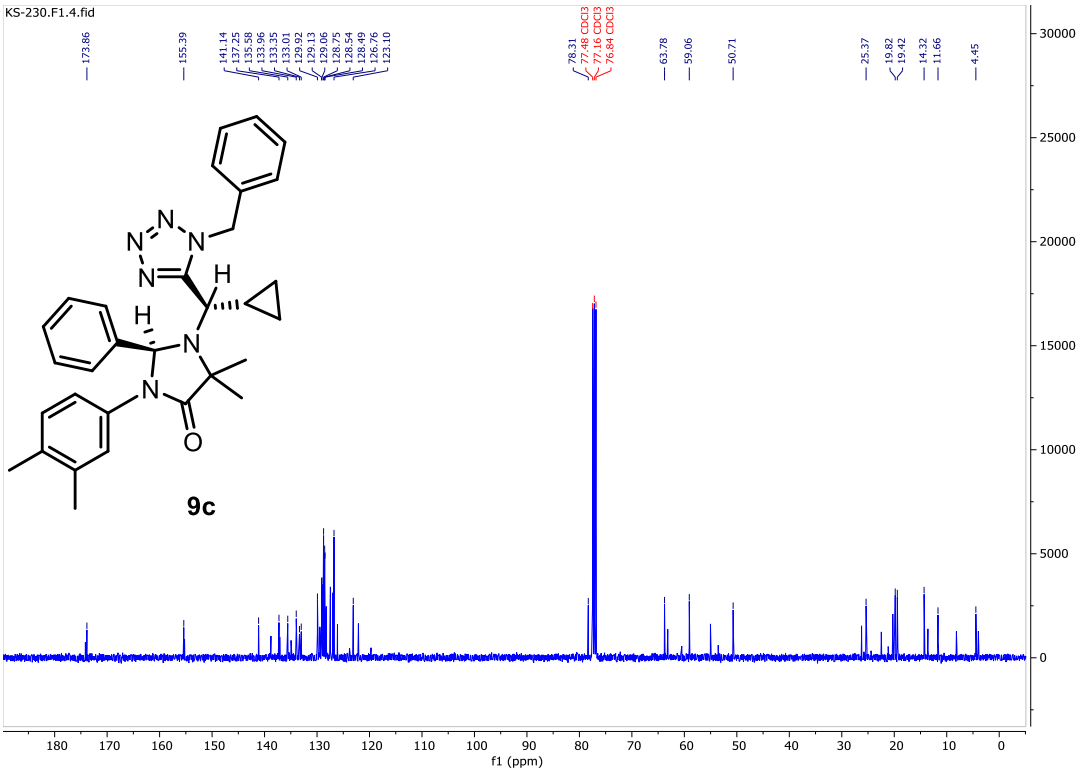


Figure S51. ^{13}C NMR (101 MHz $CDCl_3$) of **9c**.

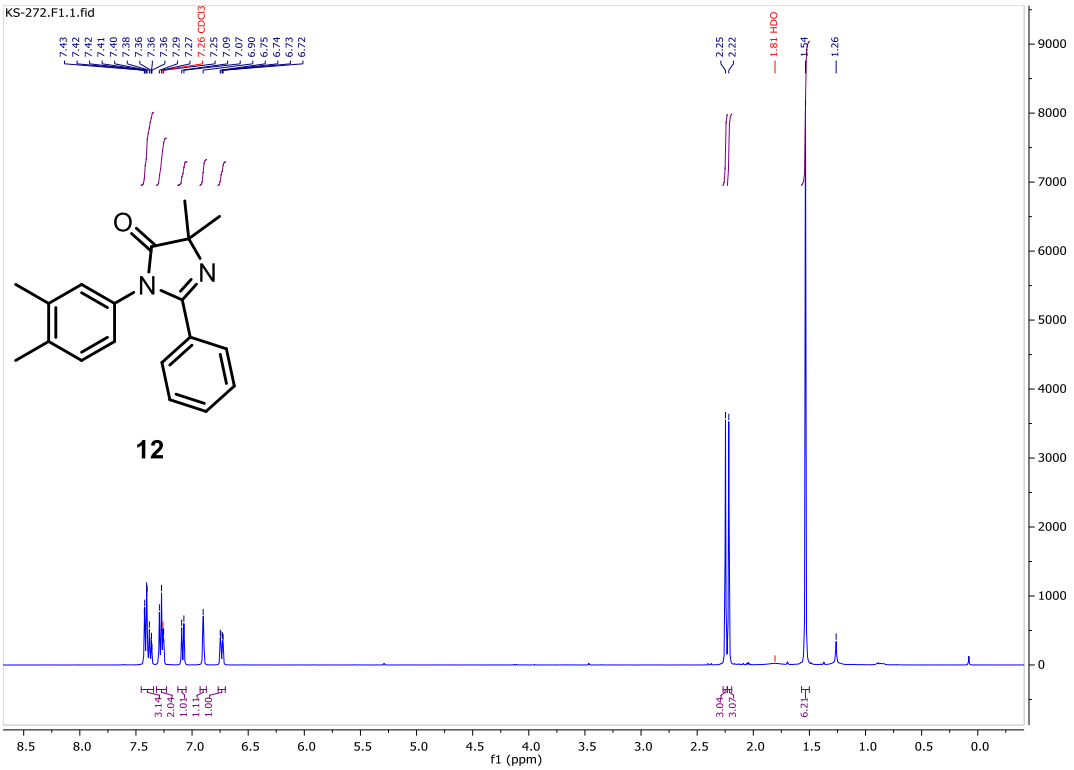


Figure S52. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **12**.

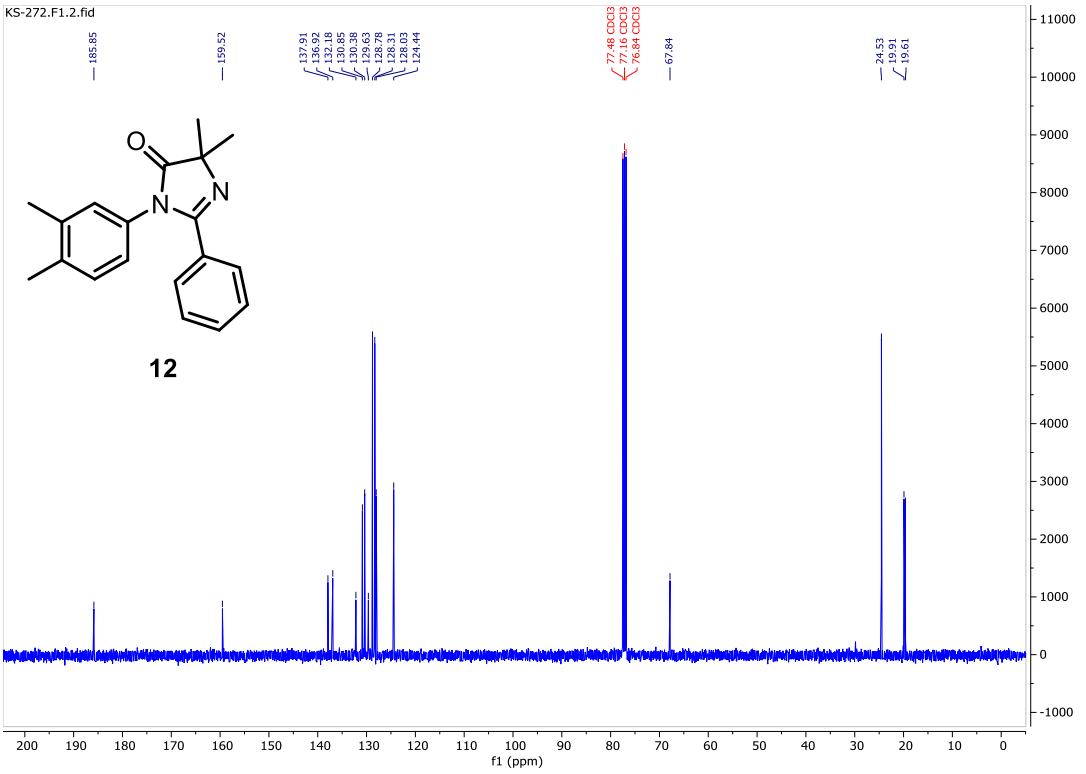


Figure S53. ^{13}C NMR (101 MHz $CDCl_3$) of **12**.

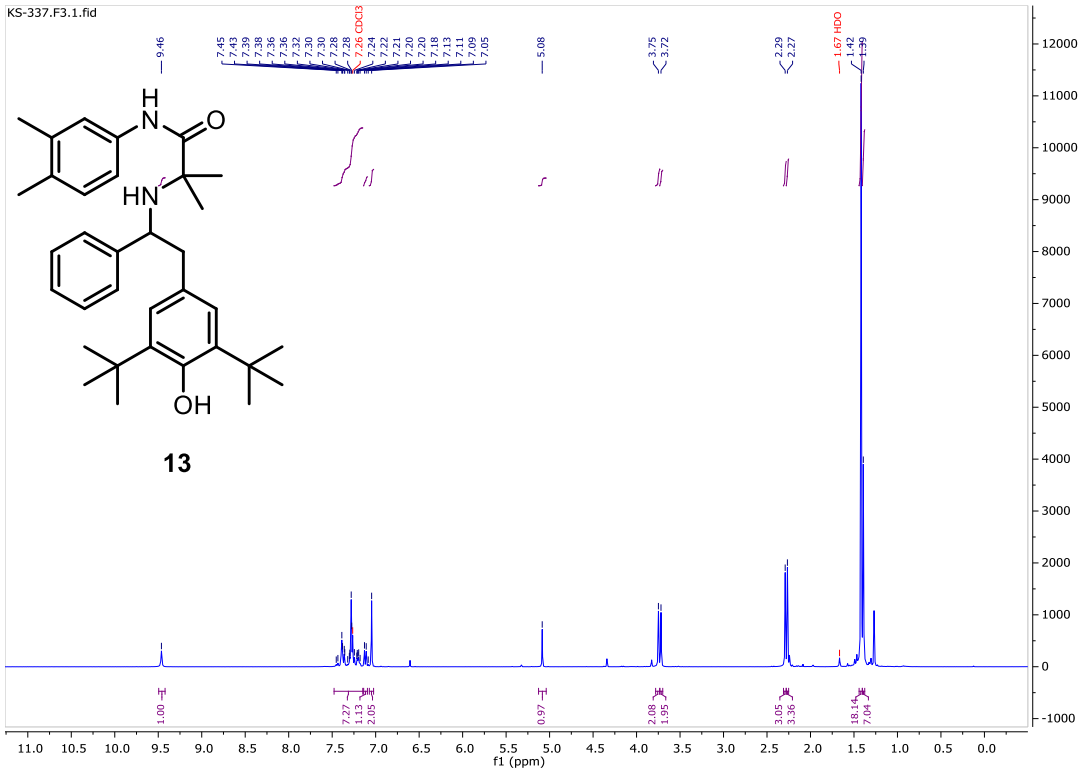


Figure S54. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **13**.

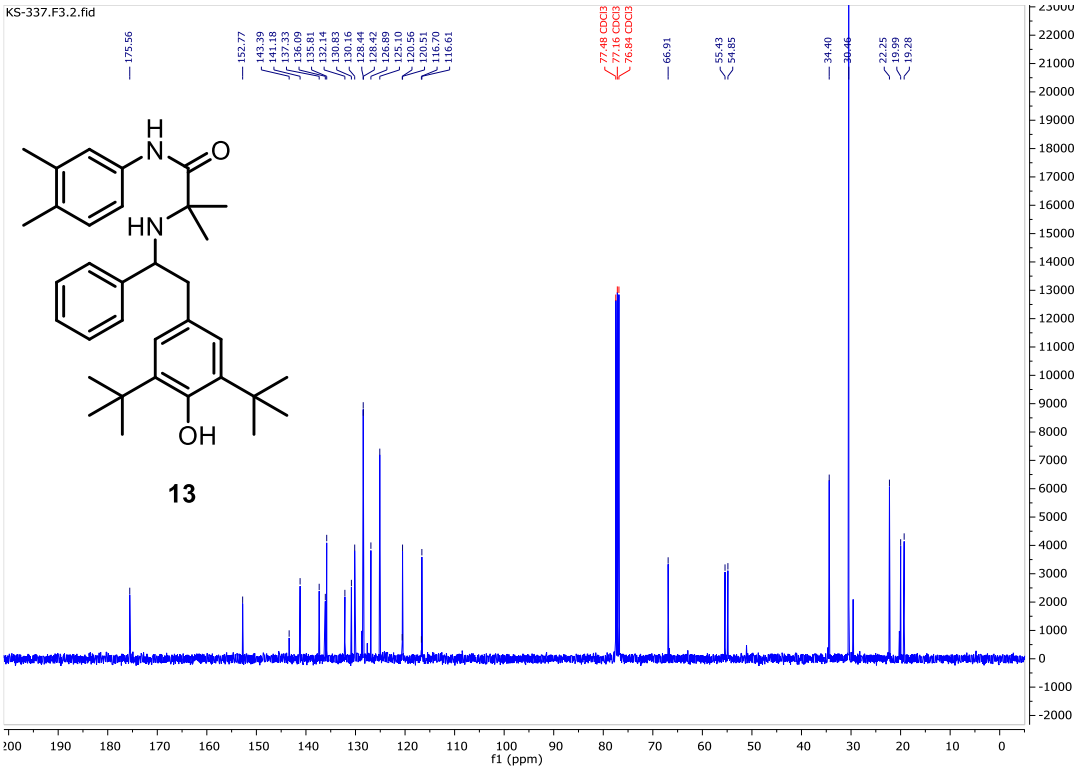


Figure S55. ^{13}C NMR (101 MHz $CDCl_3$) of **13**.

8. Radical Inhibition Studies

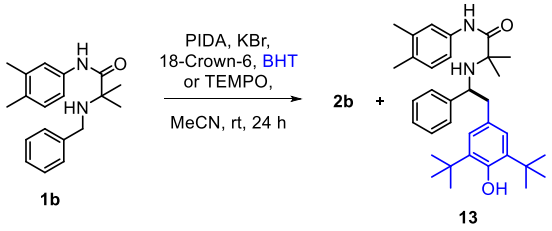


Table S7. Radical inhibition of **1b**.

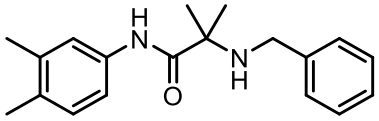
Entry	Additive (equiv.)	Yield (%, 2b)	Recovery (%, 1b)	Yield (%, 11)
1	-	84	0	-
2	Light	83	0	-
3	TEMPO (1)	62	0	-
4	TEMPO (2)	62	12	-
5	TEMPO (5)	66	22	-
6	TEMPO (10)	62	26	-
7	BHT (1)	0	20	40
8	BHT (2)	0	38	48
9	BHT (5)	rt	40	55

***BHT= Butylated Hydroxytoluene**

9. References

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

10. High Resolution Mass Spectrometry



1b

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{25}N_2O$ 297.1961; found 297.1953.

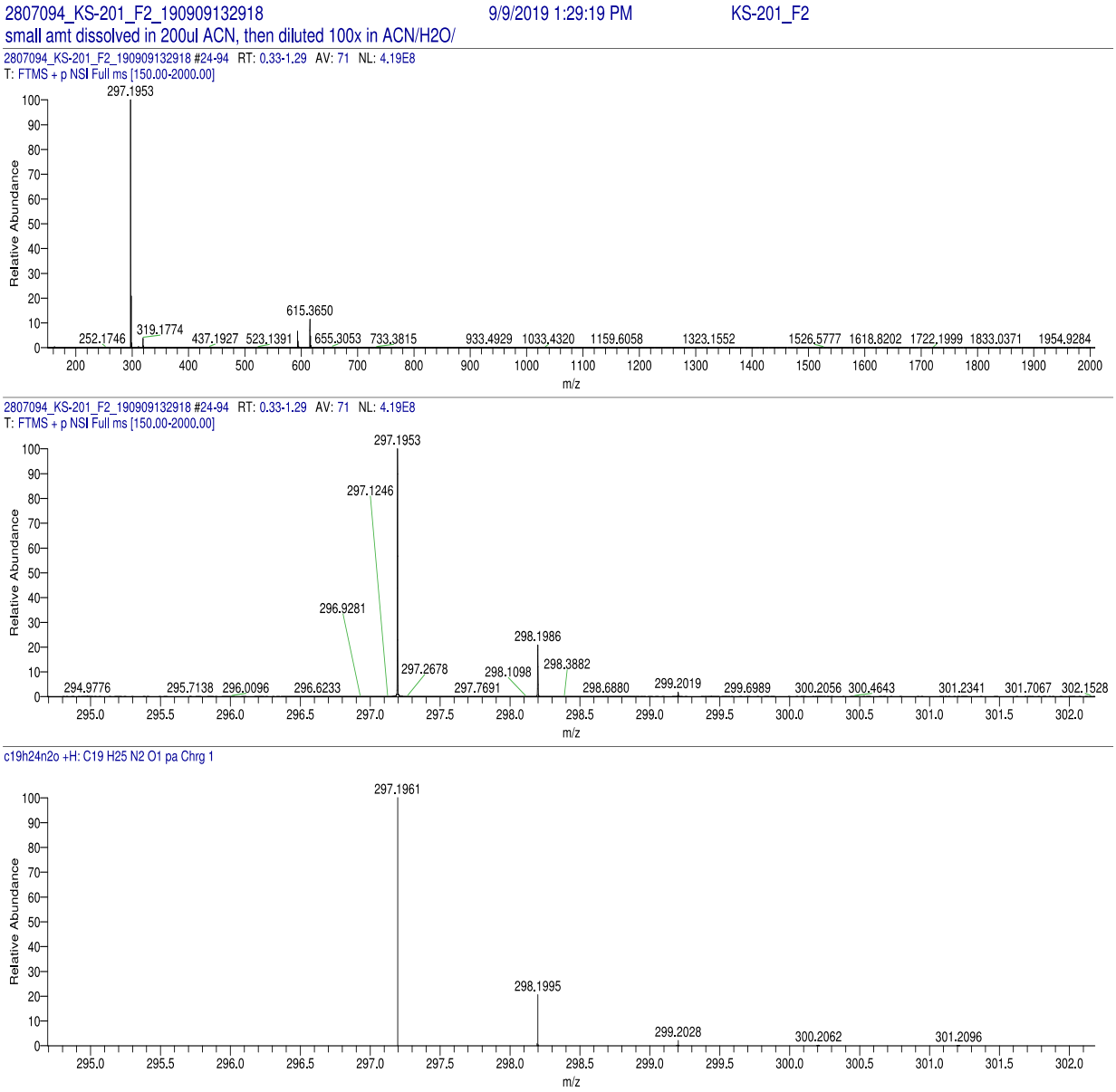
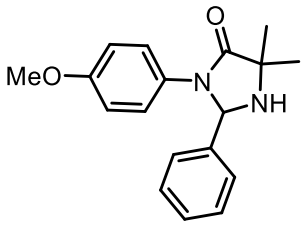


Figure S56. HRMS (ESI) spectra of **1b**.



2a

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{18}H_{21}N_2O_2$ 297.1598; found 297.1602.

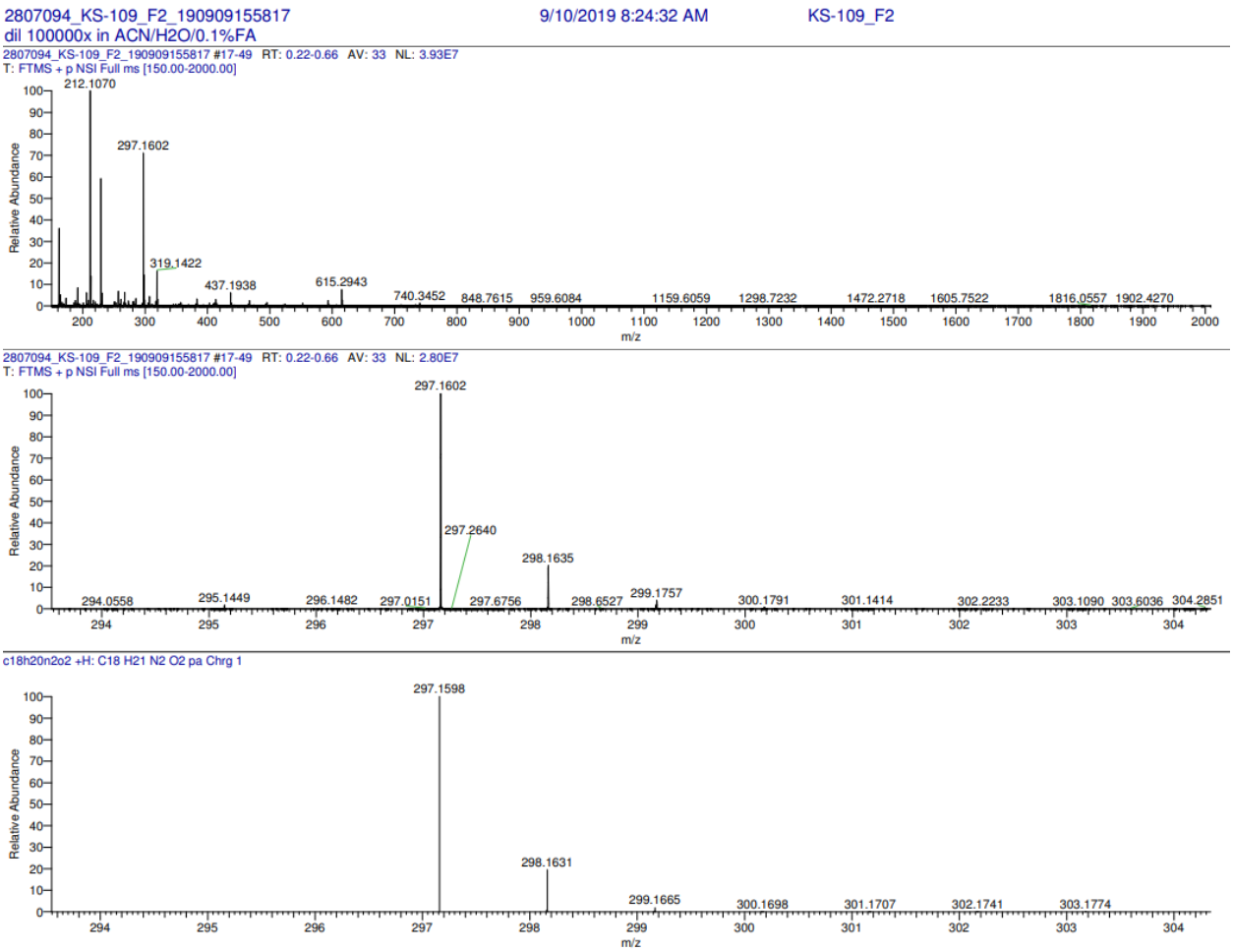
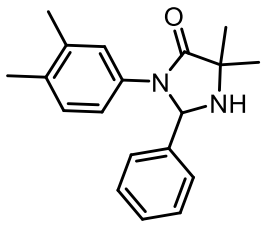


Figure S57. HRMS (ESI) spectra of **2a.**



2b

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{23}N_2O$ 295.1805; found 295.1804.

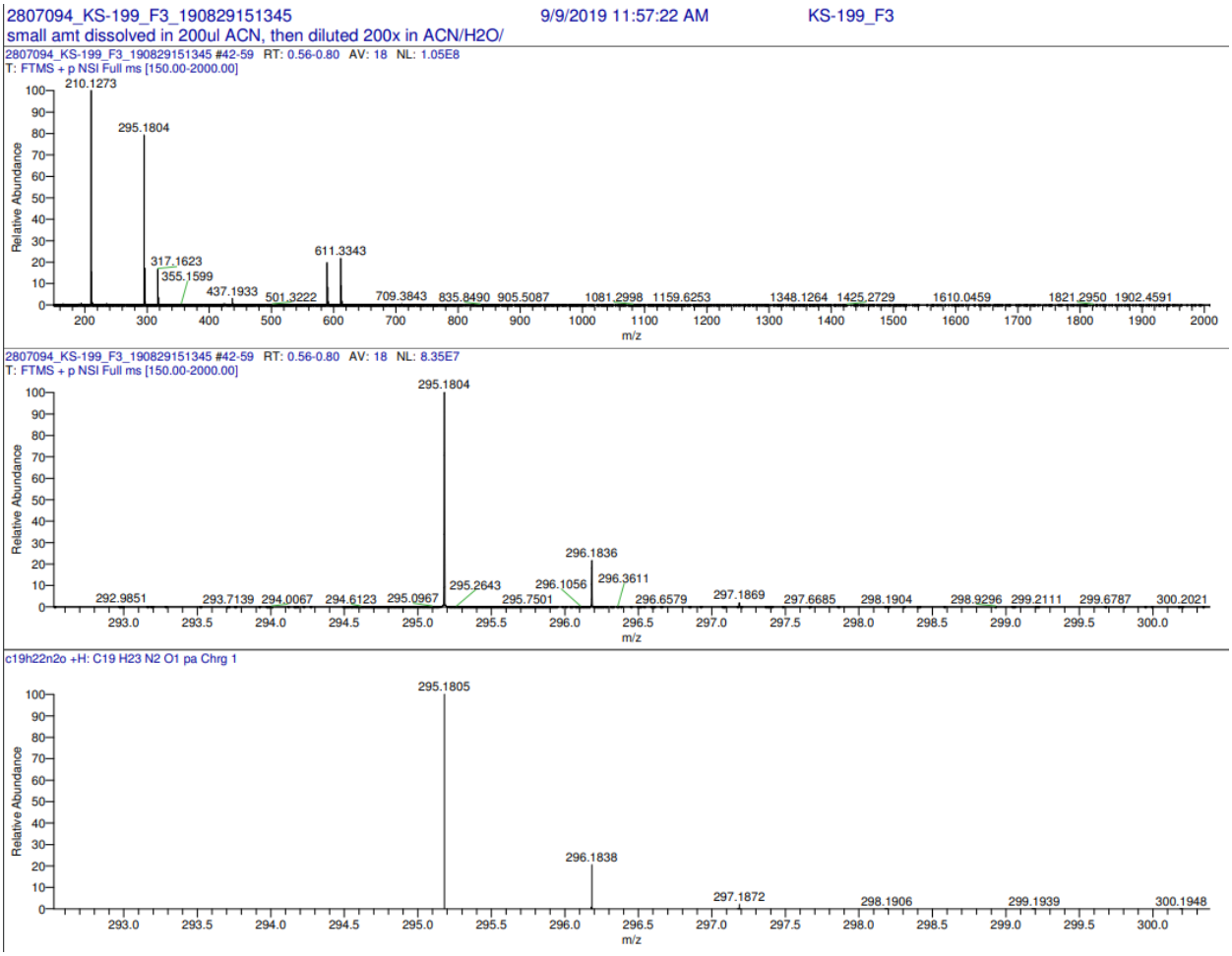
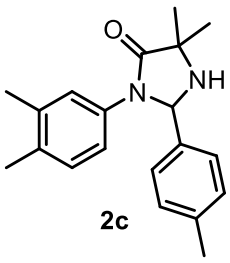


Figure S58. HRMS (ESI) spectra of **2b.**



2c

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{20}H_{25}N_2O$ 309.1961; found 309.1960.

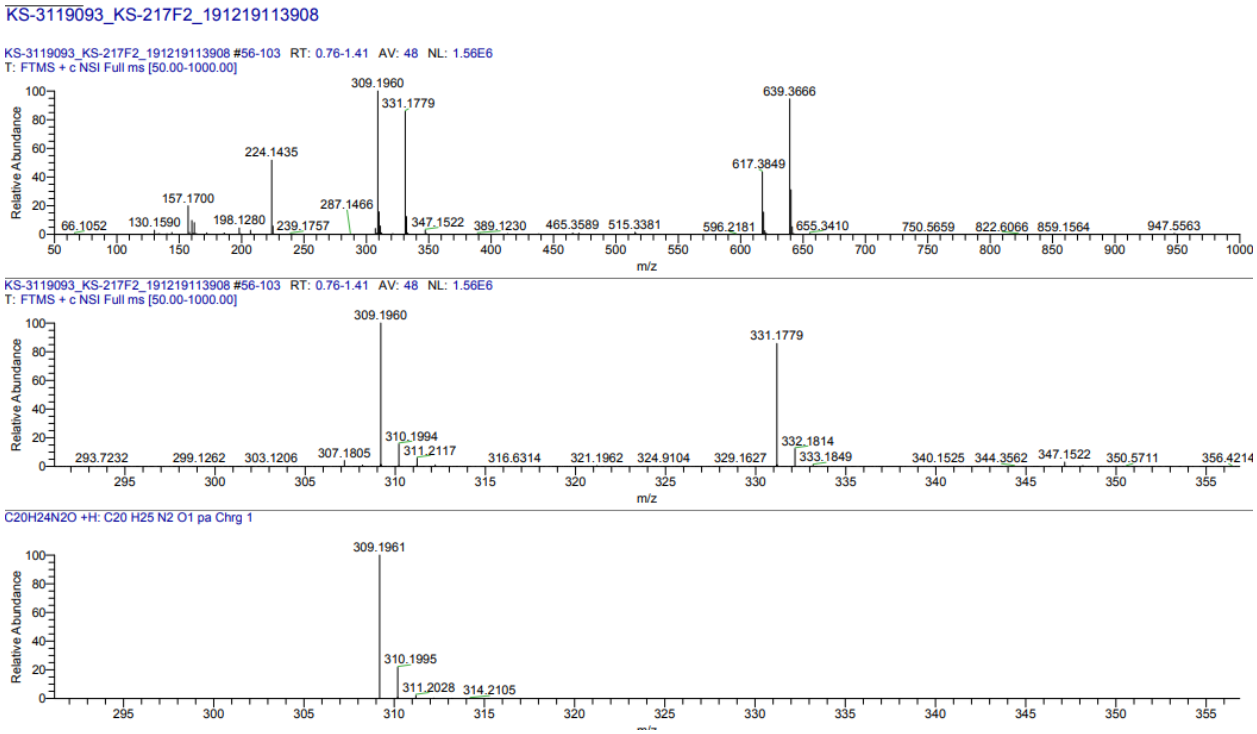
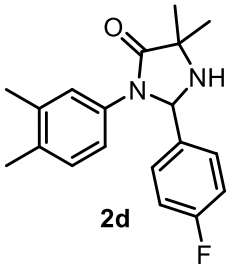


Figure S59. HRMS (ESI) spectra of **2c.**



2d

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{22}FN_2O$ 313.1711; found 313.1709.

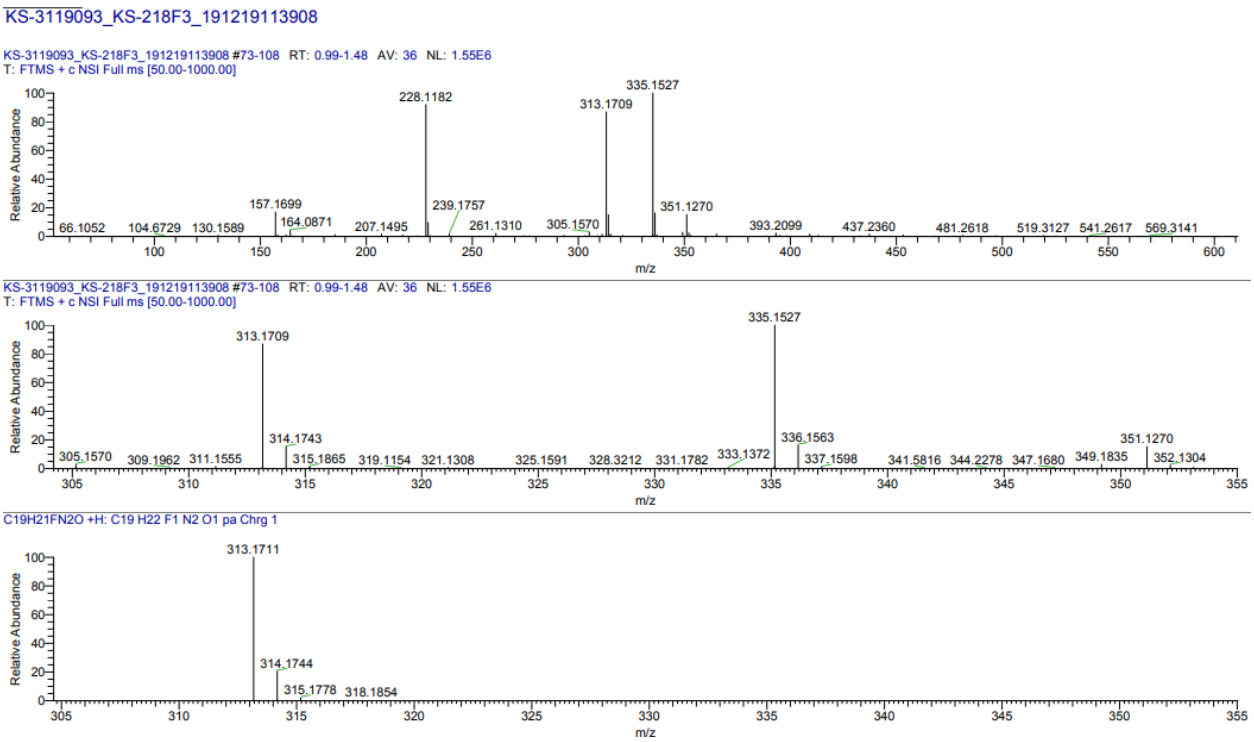
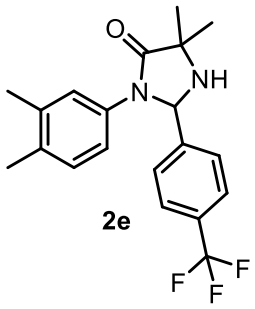


Figure S60. HRMS (ESI) spectra of **2d.**



2e

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{20}H_{22}F_3N_2O$ 363.1679; found 363.1677.

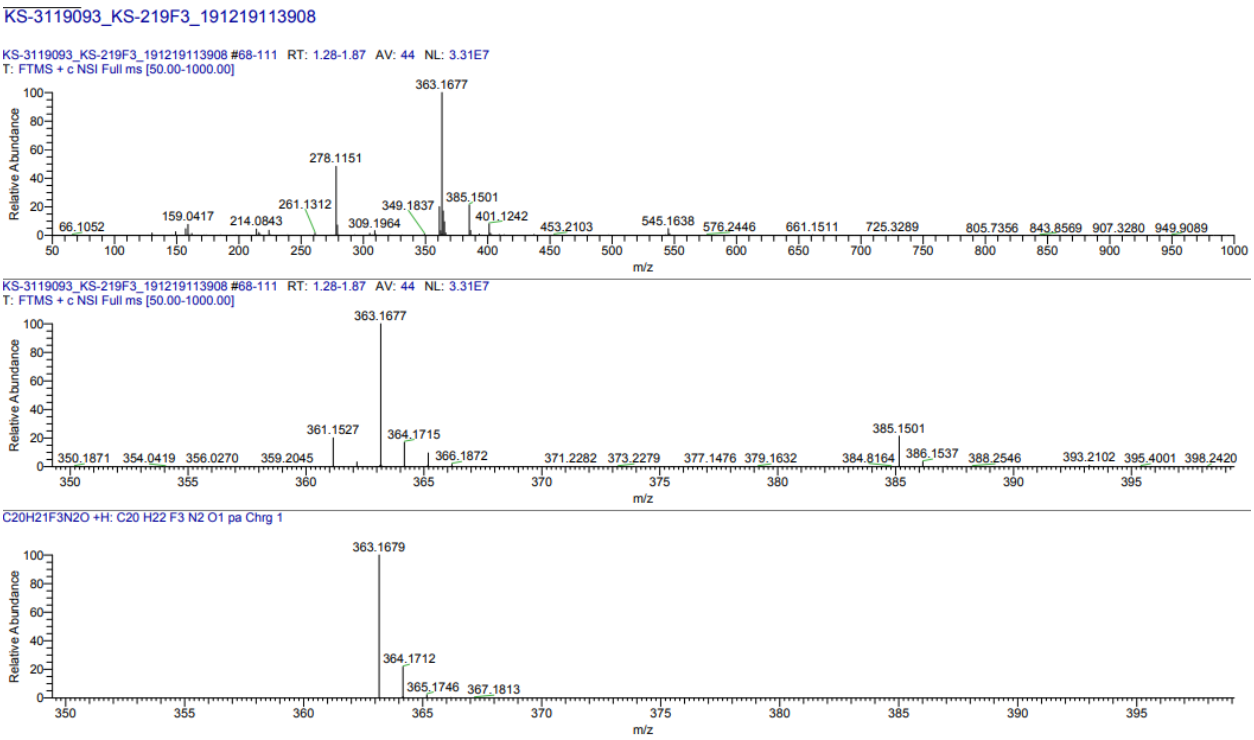
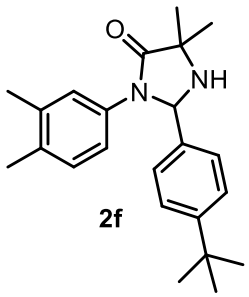


Figure S61. HRMS (ESI) spectra of **2e.**



2f

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{23}H_{31}N_2O$ 351.2431; found 351.2427.

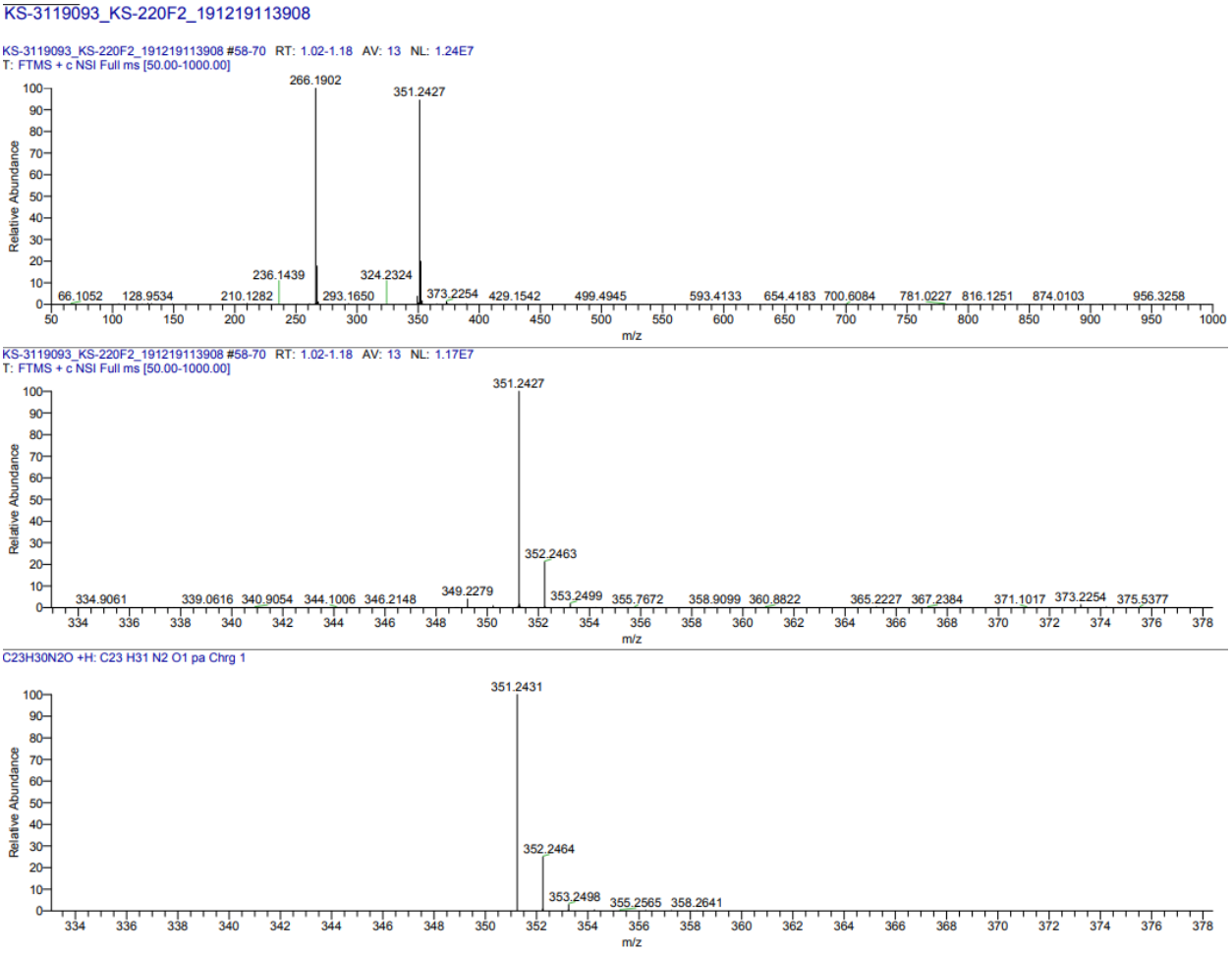
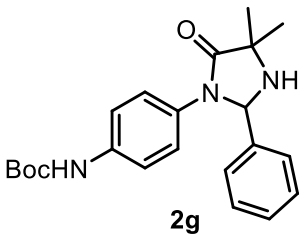


Figure S62. HRMS (ESI) spectra of **2f.**



2g

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{22}H_{28}N_3O_3$ 382.2125; found 382.2126.

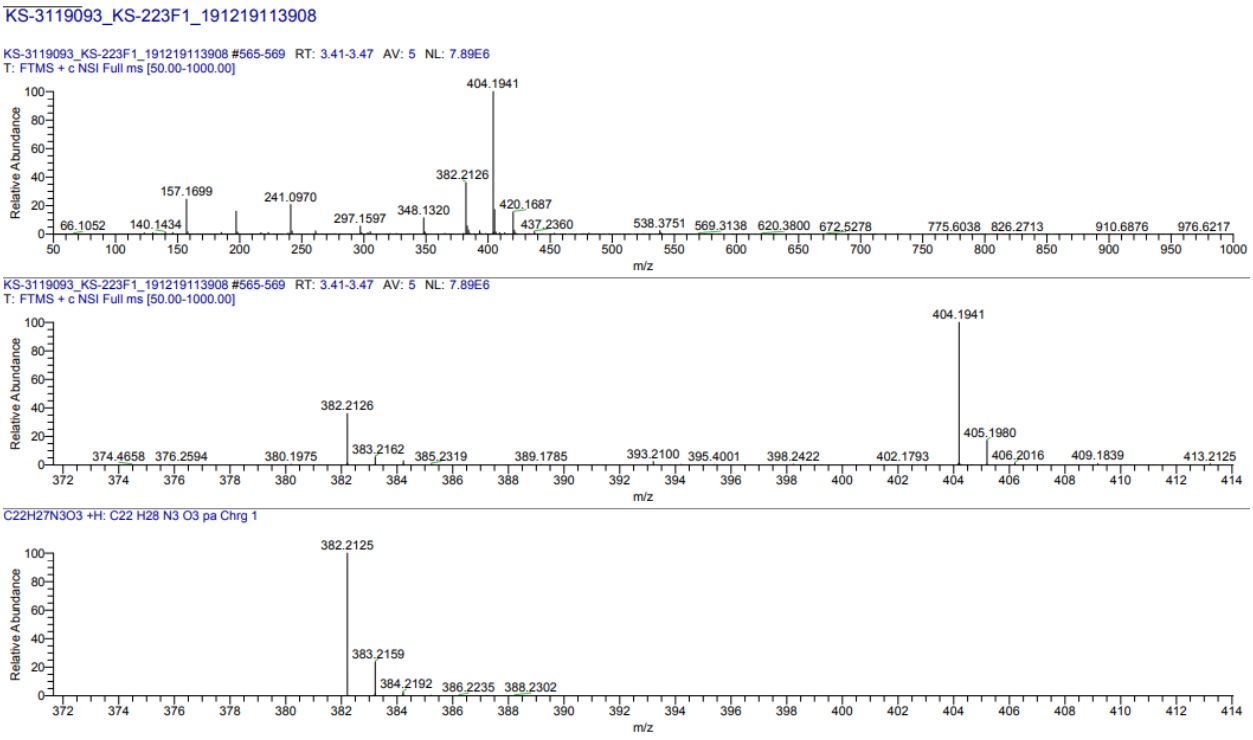
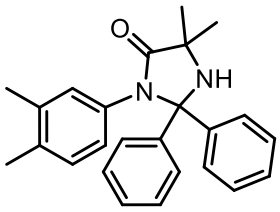


Figure S63. HRMS (ESI) spectra of **2g.**



2h

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{27}N_2O$ 37.2118 found 371.2123.

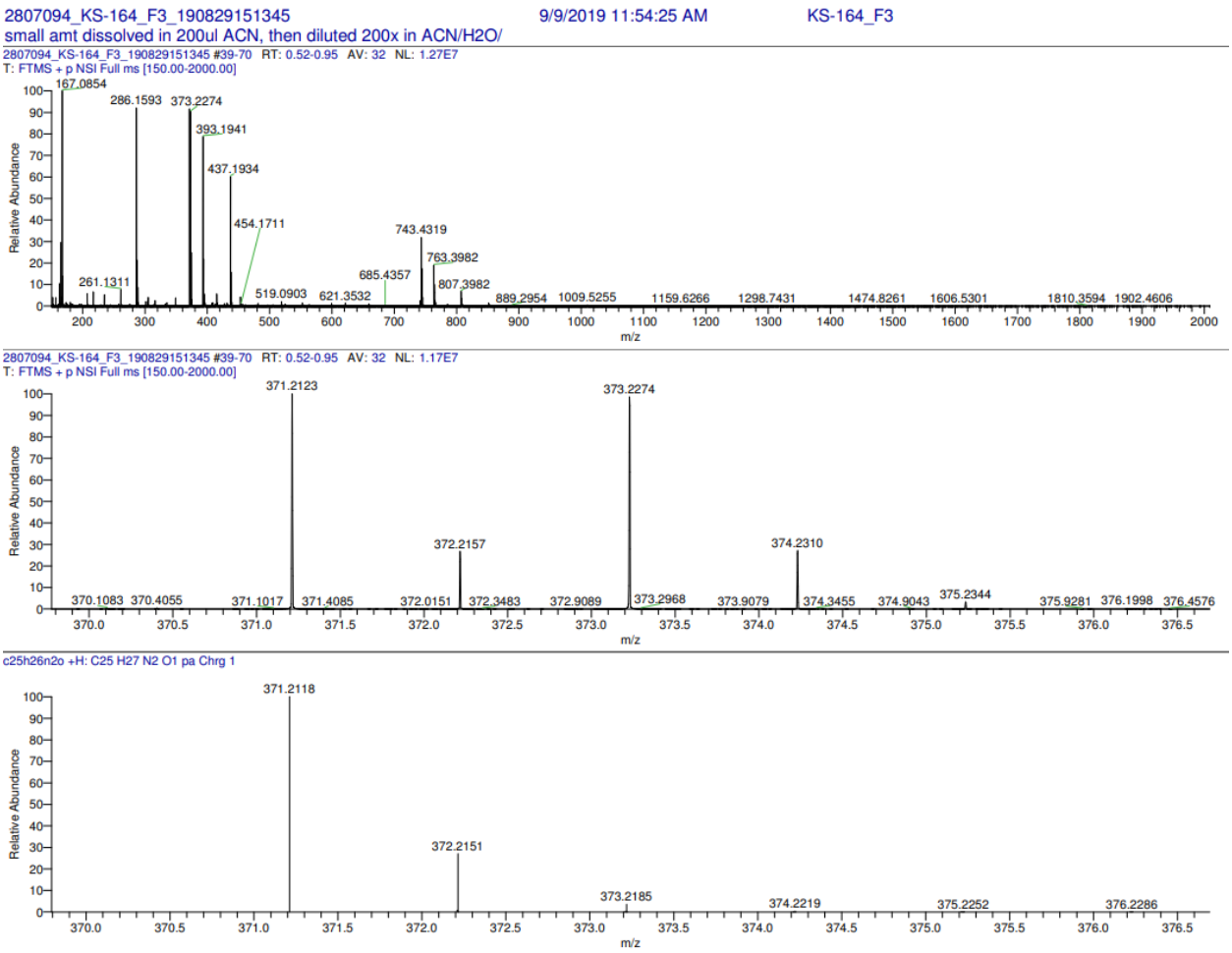
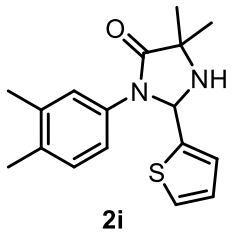


Figure S64. HRMS (ESI) spectra of **2h.**



2i

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{21}N_2OS$ 301.1369; found 301.1369.

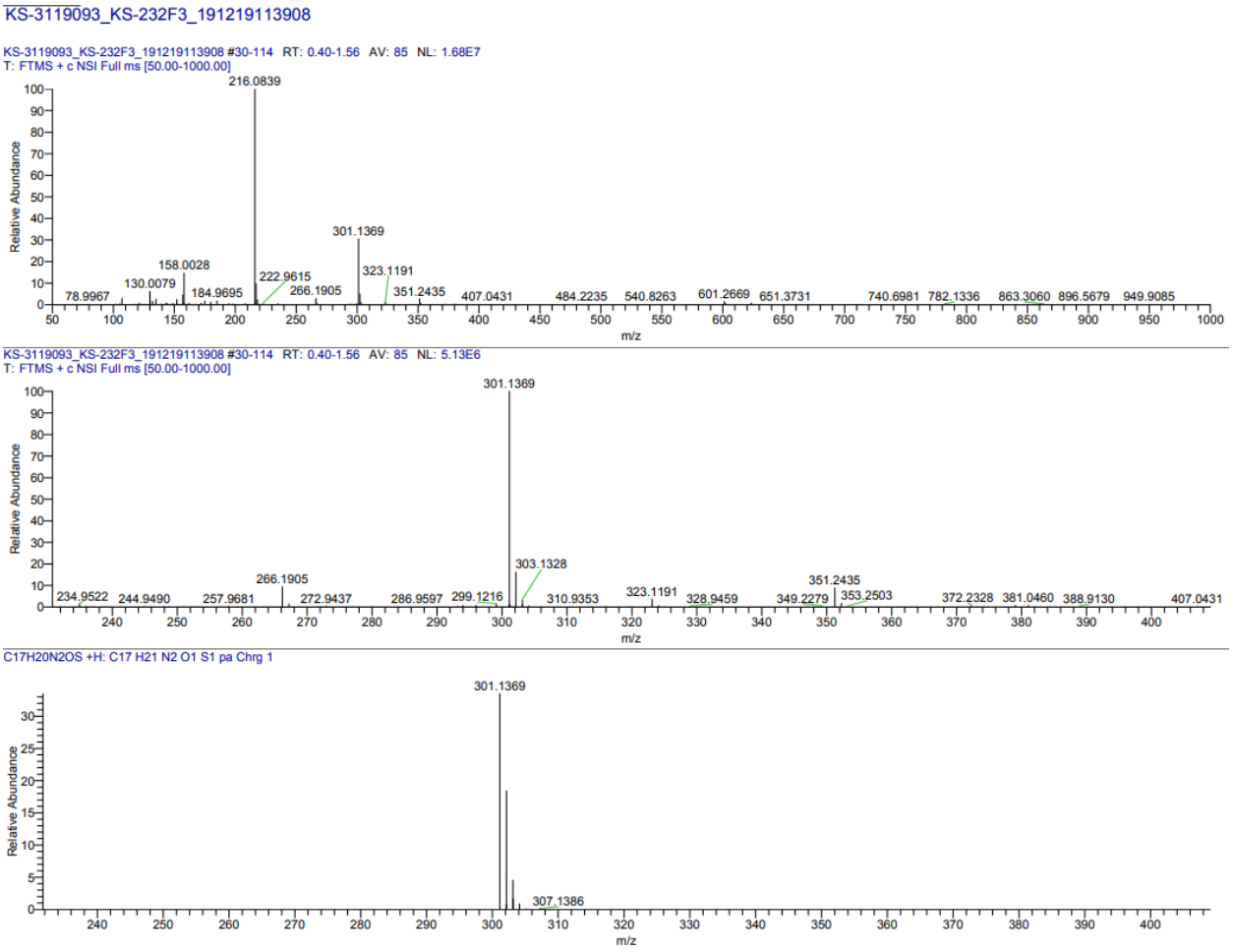
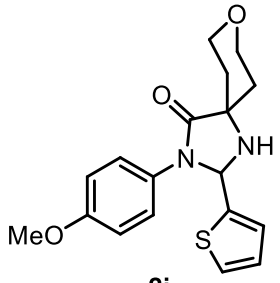


Figure S65. HRMS (ESI) spectra of **2i.**



2j

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{18}H_{21}N_2O_3S$ 345.1267; found 345.1264.

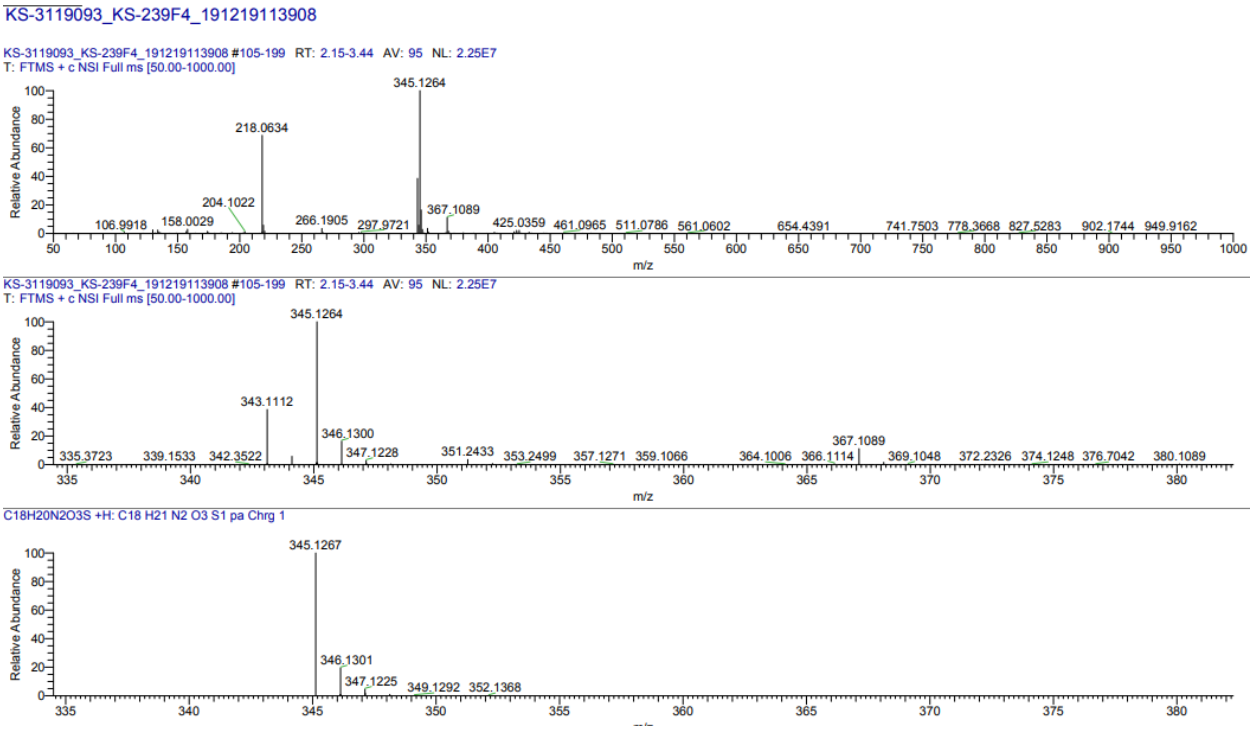
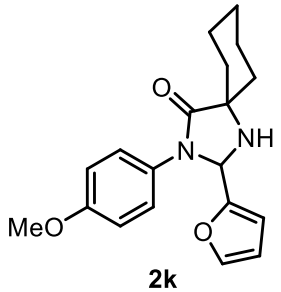


Figure S66. HRMS (ESI) spectra of **2j.**



2k

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{23}N_2O_3$ 327.1703; found 327.1704.

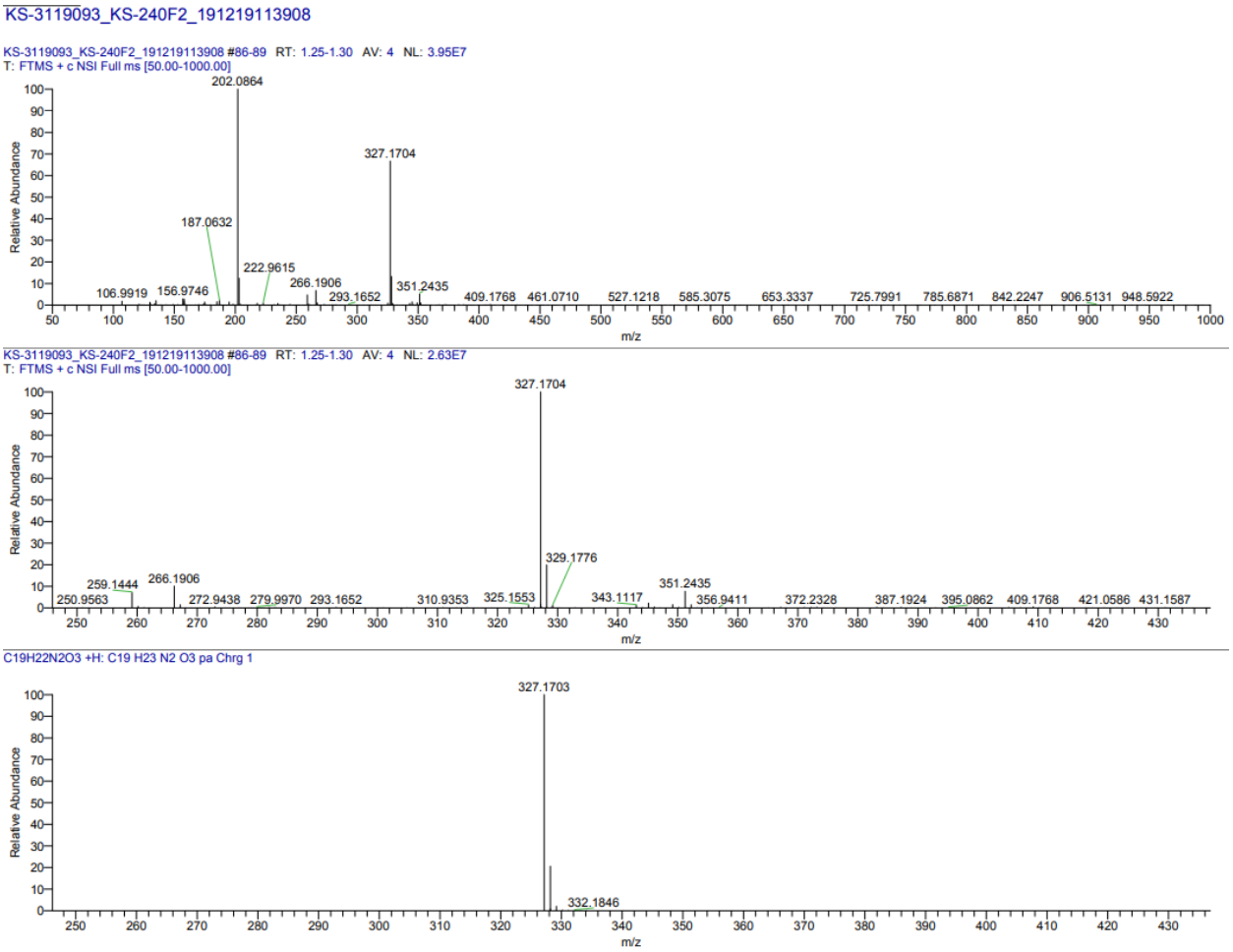
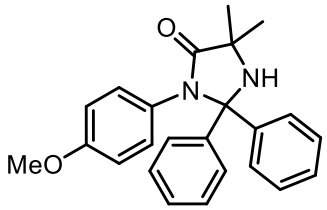


Figure S67. HRMS (ESI) spectra of **2k.**



2l

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{25}N_2O$ 373.1911; found 373.1918.

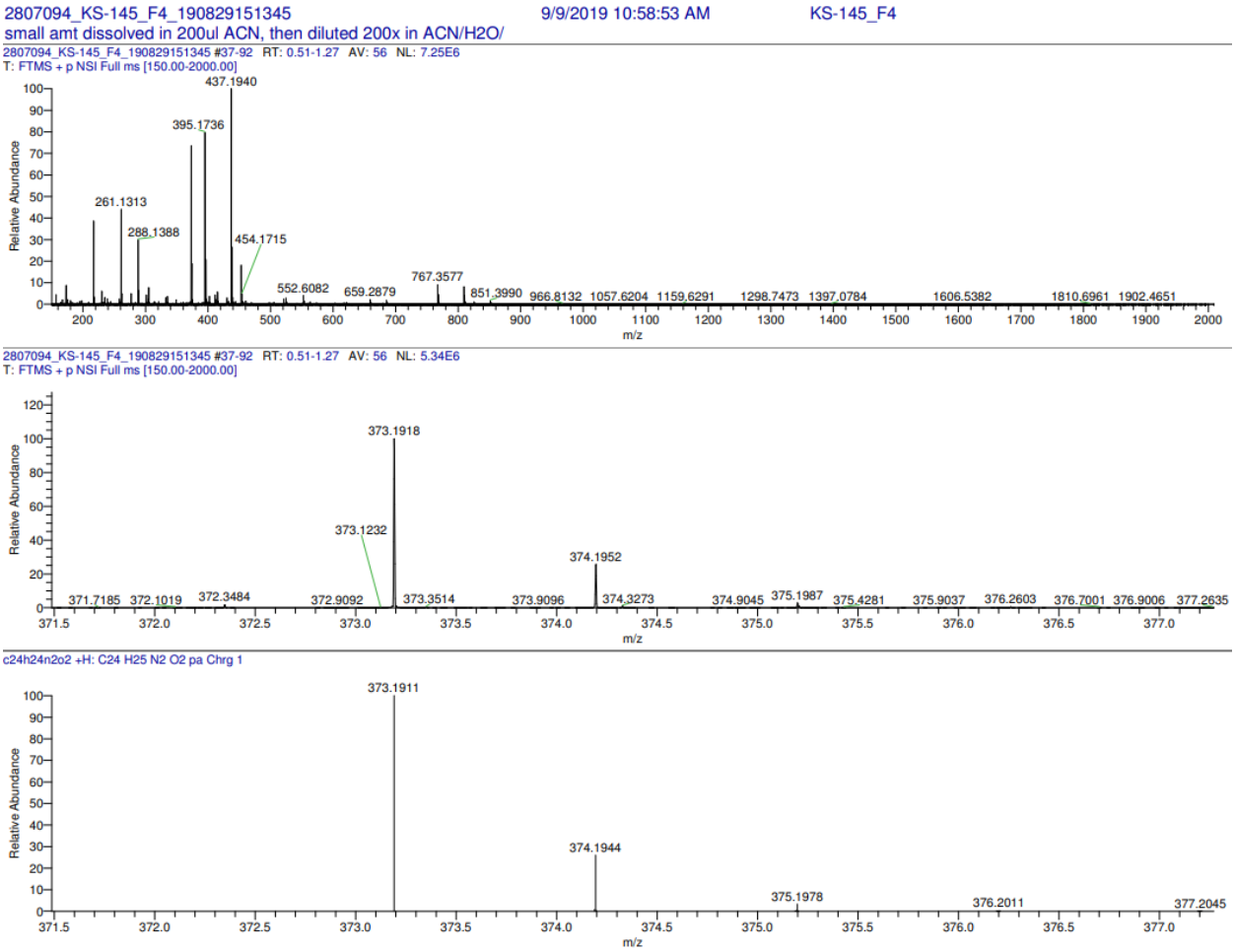
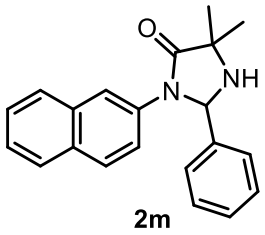


Figure S68. HRMS (ESI) spectra of **2l.**



2m

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{21}H_{21}N_2O$ 317.1648; found 317.1638.

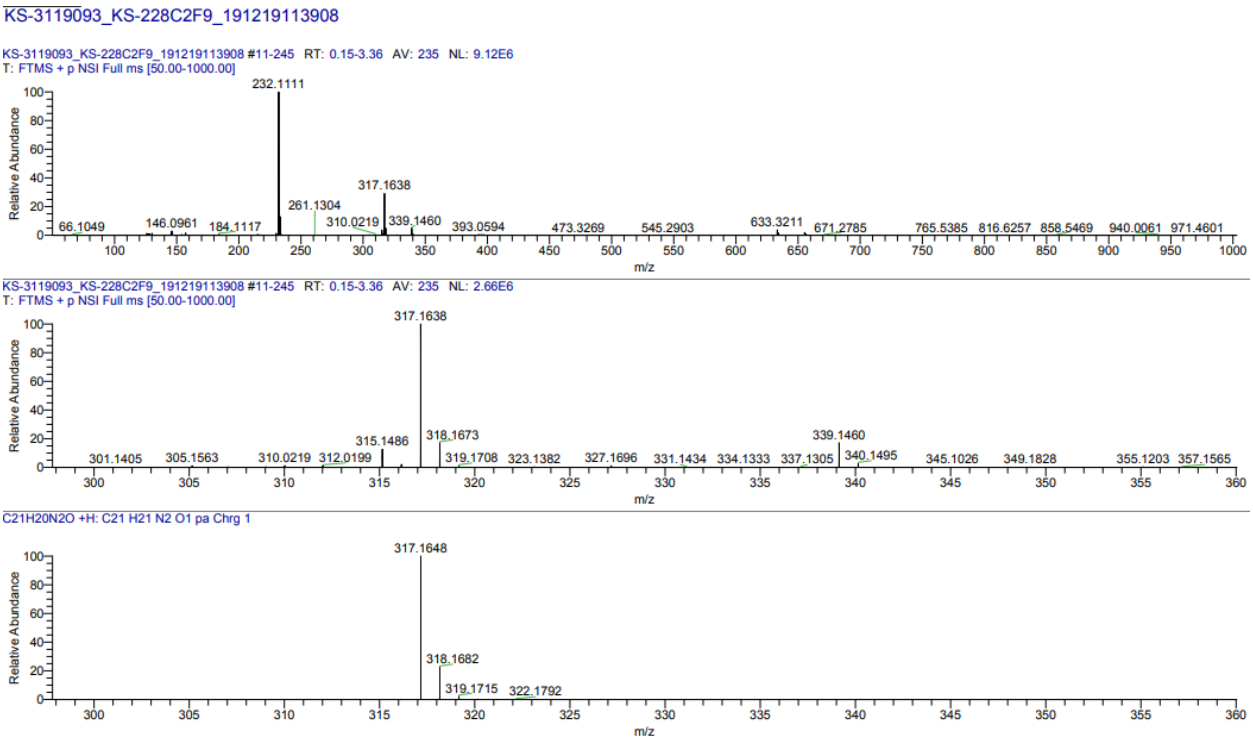
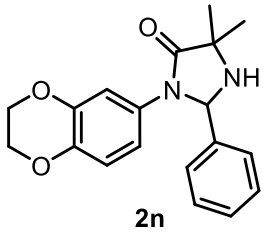


Figure S69. HRMS (ESI) spectra of **2m.**



HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{21}N_2O_3$325.1547; found 325.1535.

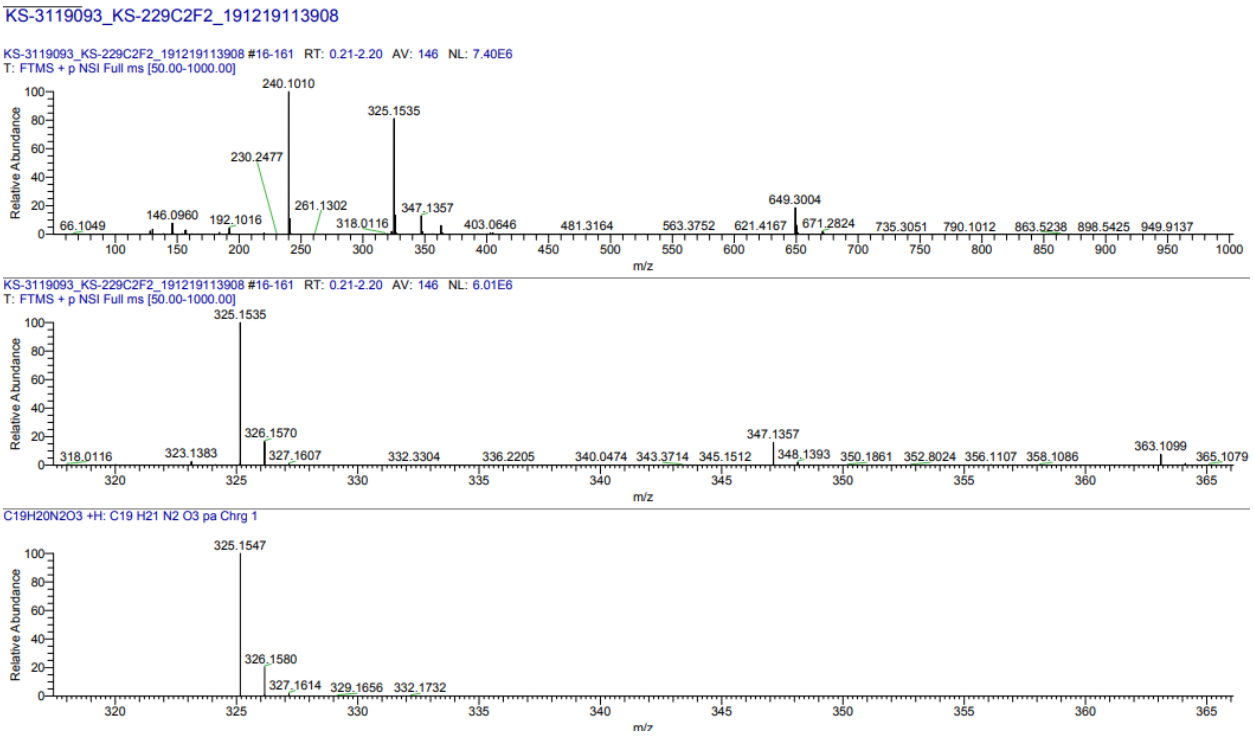
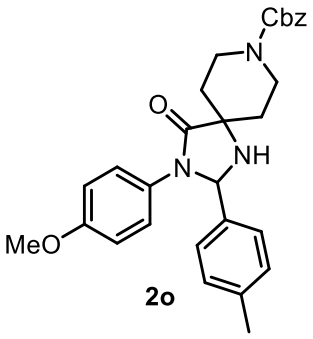


Figure S70. HRMS (ESI) spectra of **2n.**



2o

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{29}H_{32}N_3O$ 486.2387;found 486.2374.

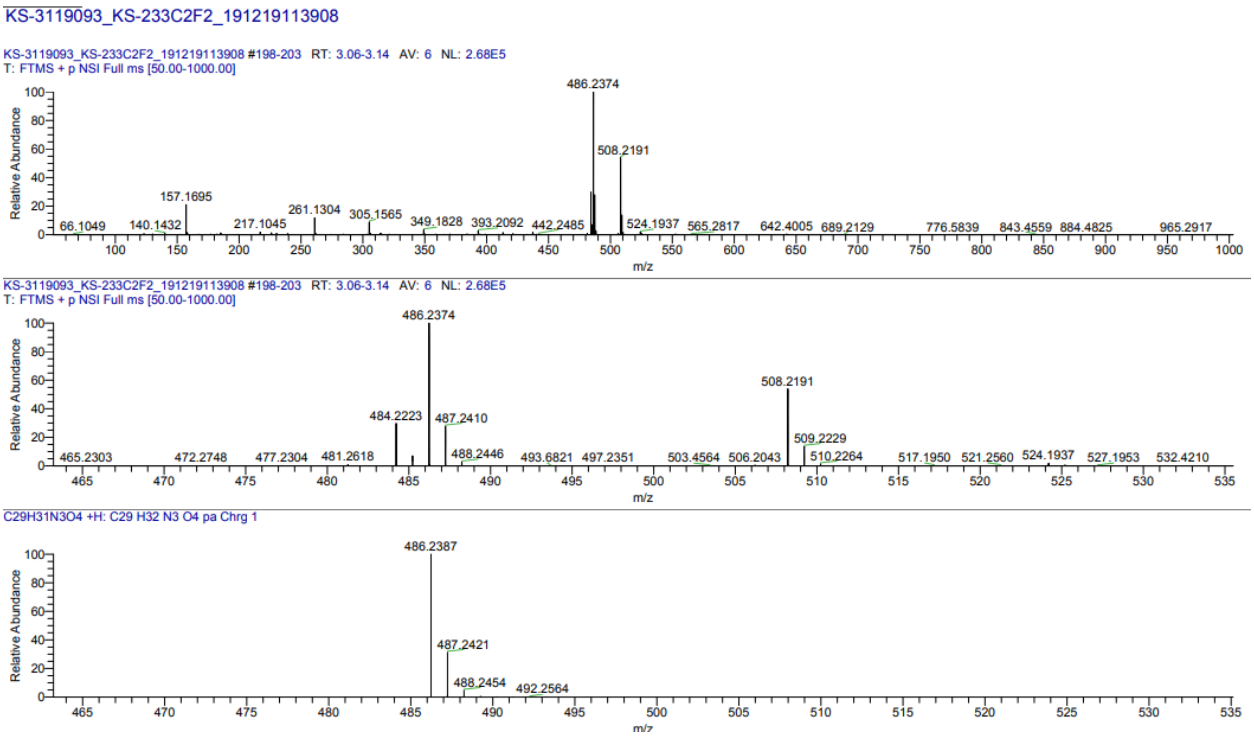
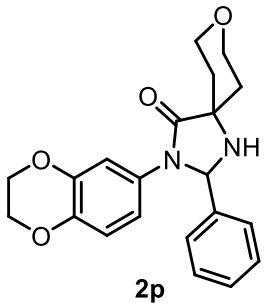


Figure S71. HRMS (ESI) spectra of **2o.**



2p

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{21}H_{23}N_2O_4$ 367.1652; found 367.1638.

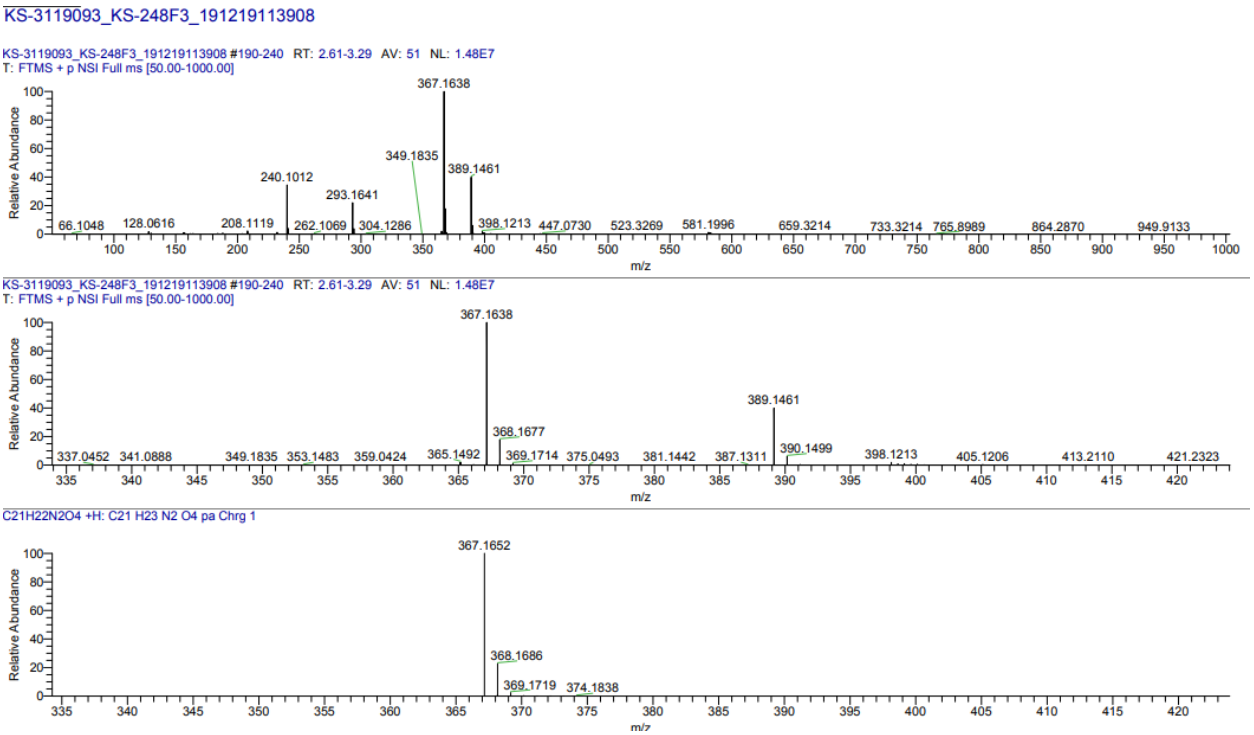
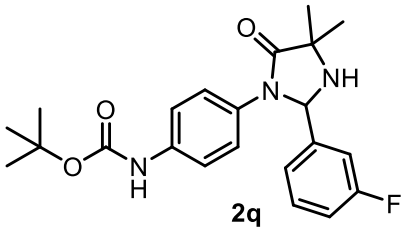


Figure S72. HRMS (ESI) spectra of **2p.**



2q

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{22}H_{27}N_3O_3$ 400.2031; found 400.2024.

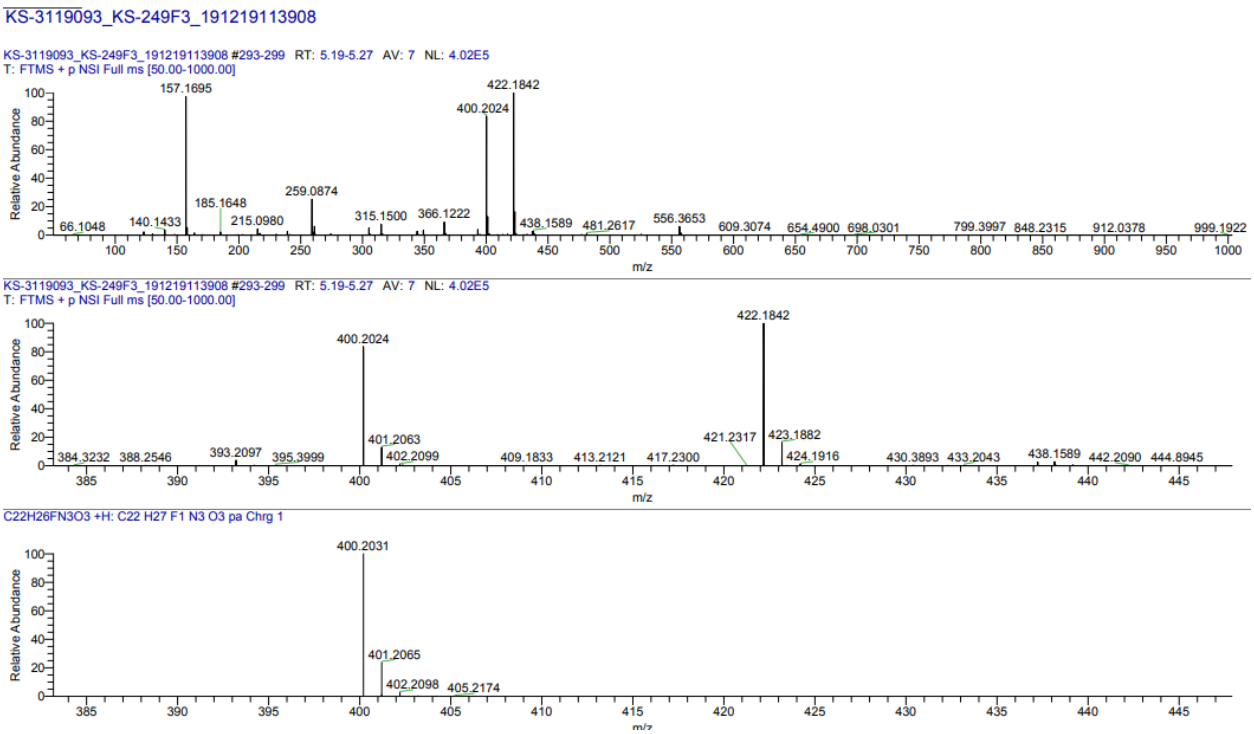
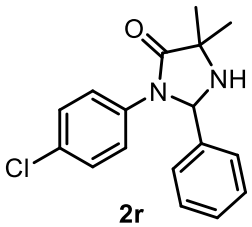


Figure S73. HRMS (ESI) spectra of **2q.**



2r

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{18}ClN_2O$ 301.1102; found 301.1097.

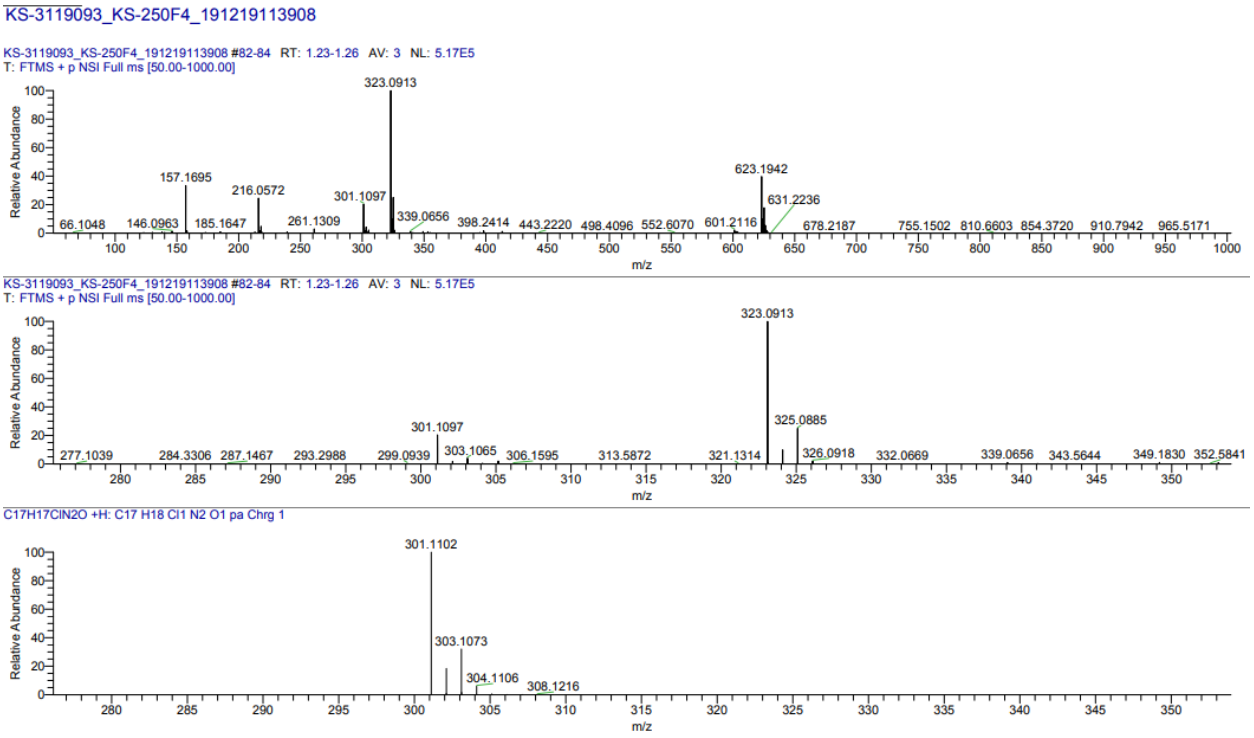
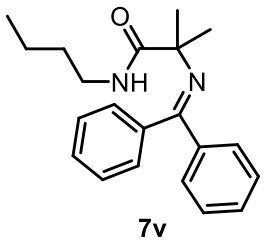


Figure S74. HRMS (ESI) spectra of **2r.**



7v

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{21}H_{27}N_2O$ 323.2118; found 323.2108.

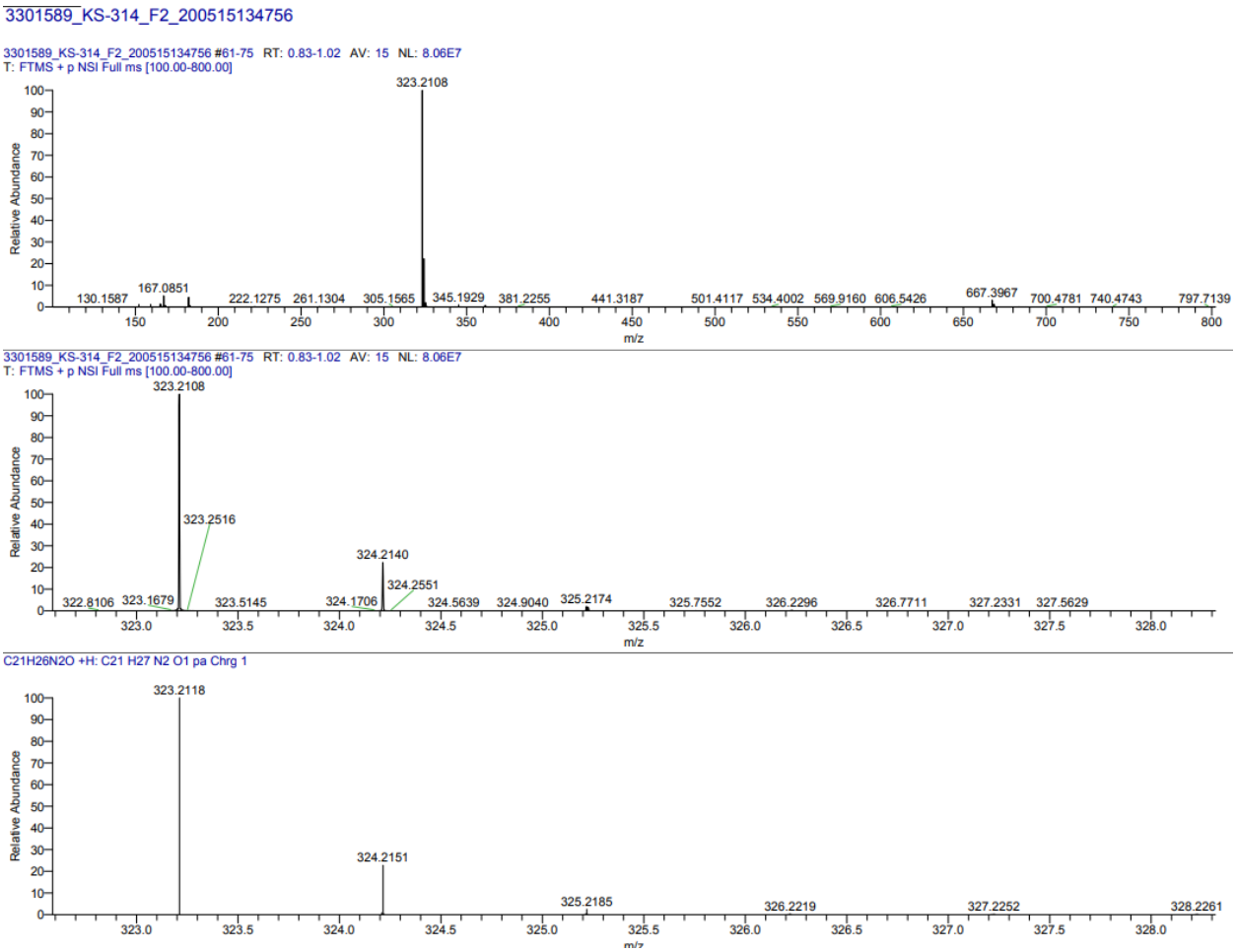
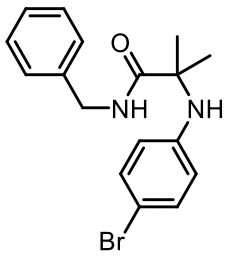


Figure S75. HRMS (ESI) spectra of **7v.**



7w

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{20}BrN_2O$ 347.0754; found 347.0753.

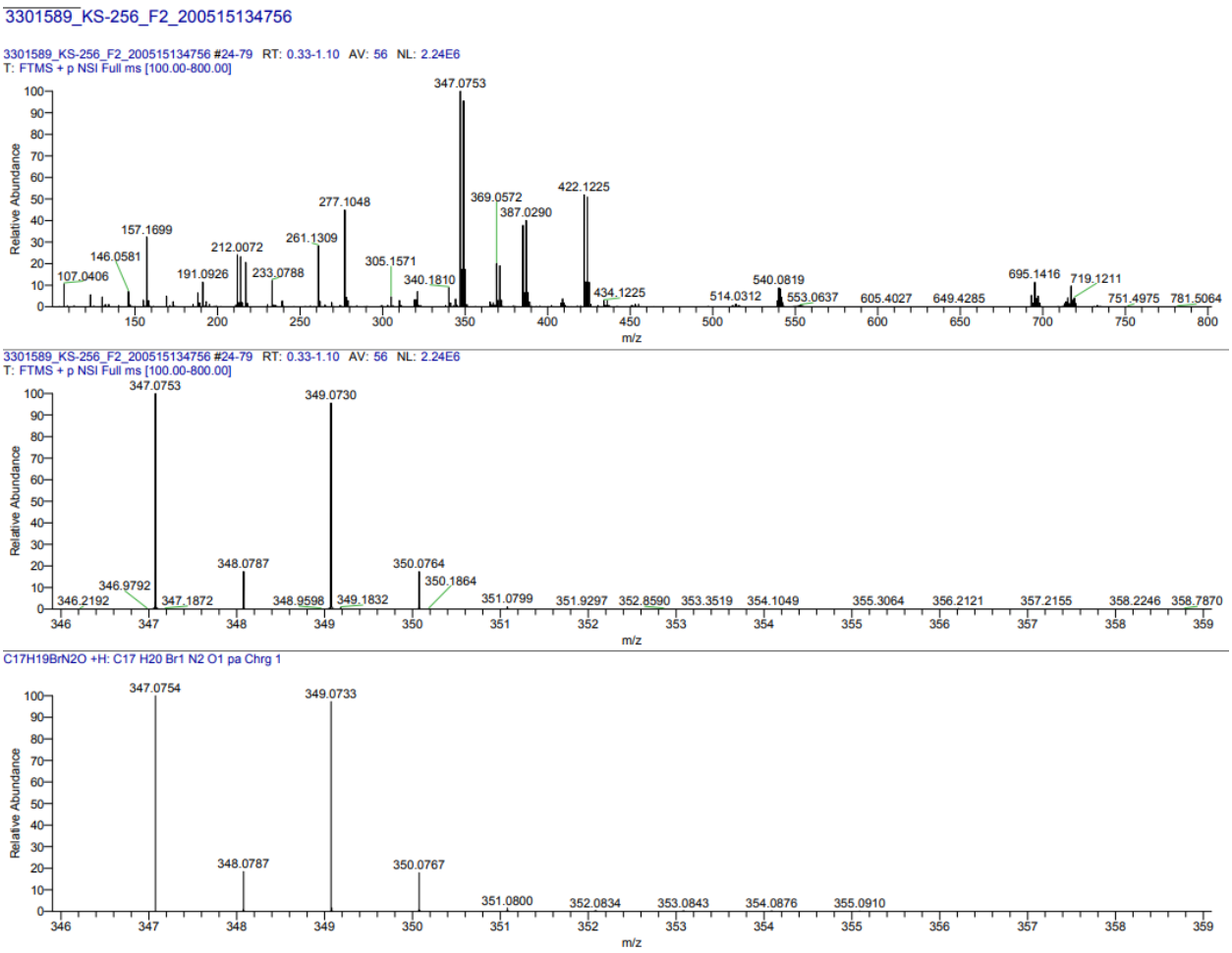
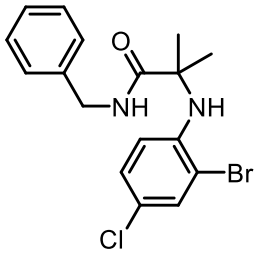


Figure S76. HRMS (ESI) spectra of **7w.**



7x

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{17}H_{19}BrClN_2O$ 381.0364; found 381.0372.

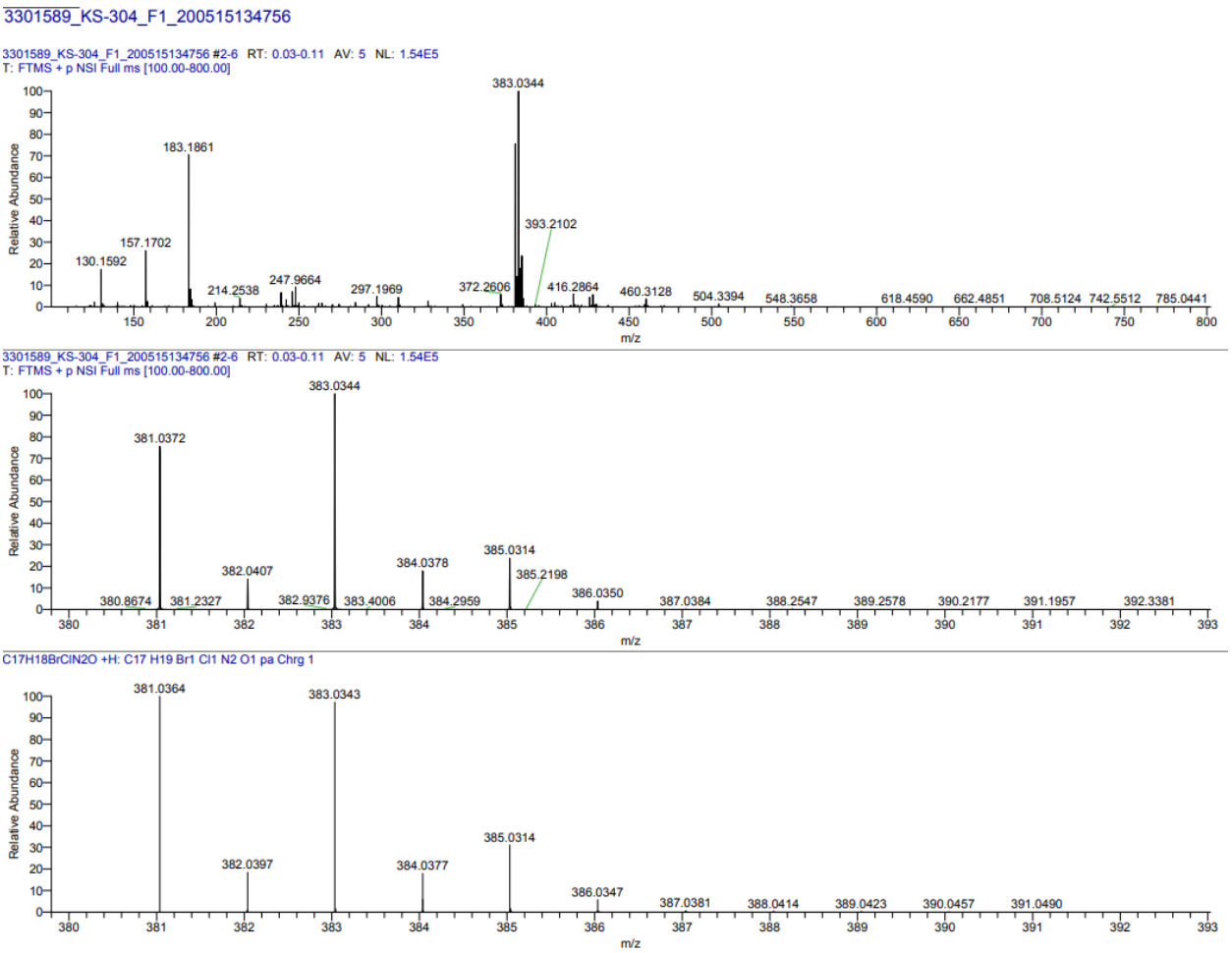
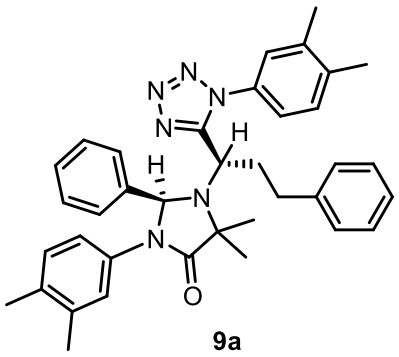


Figure S77. HRMS (ESI) spectra of **7x.**



9a

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{37}H_{41}N_6O$ 585.3336; found 585.3333.

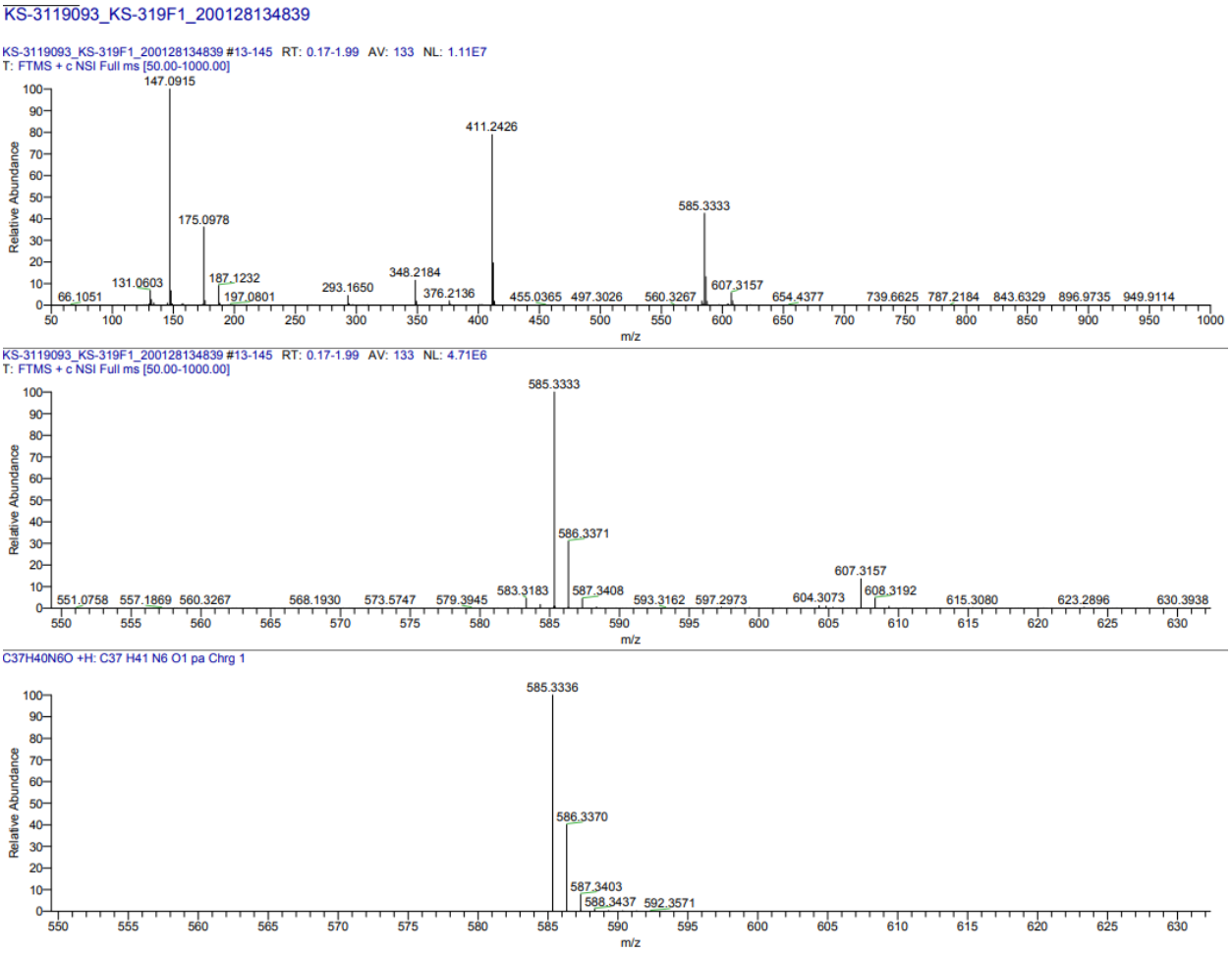
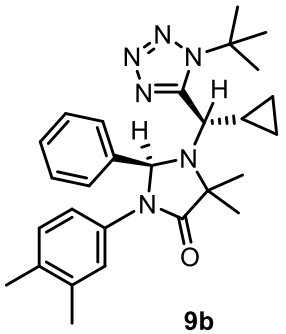


Figure S78. HRMS (ESI) spectra of **9a.**



9b

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{28}H_{37}N_6O$ 473.3023; found 473.3027.

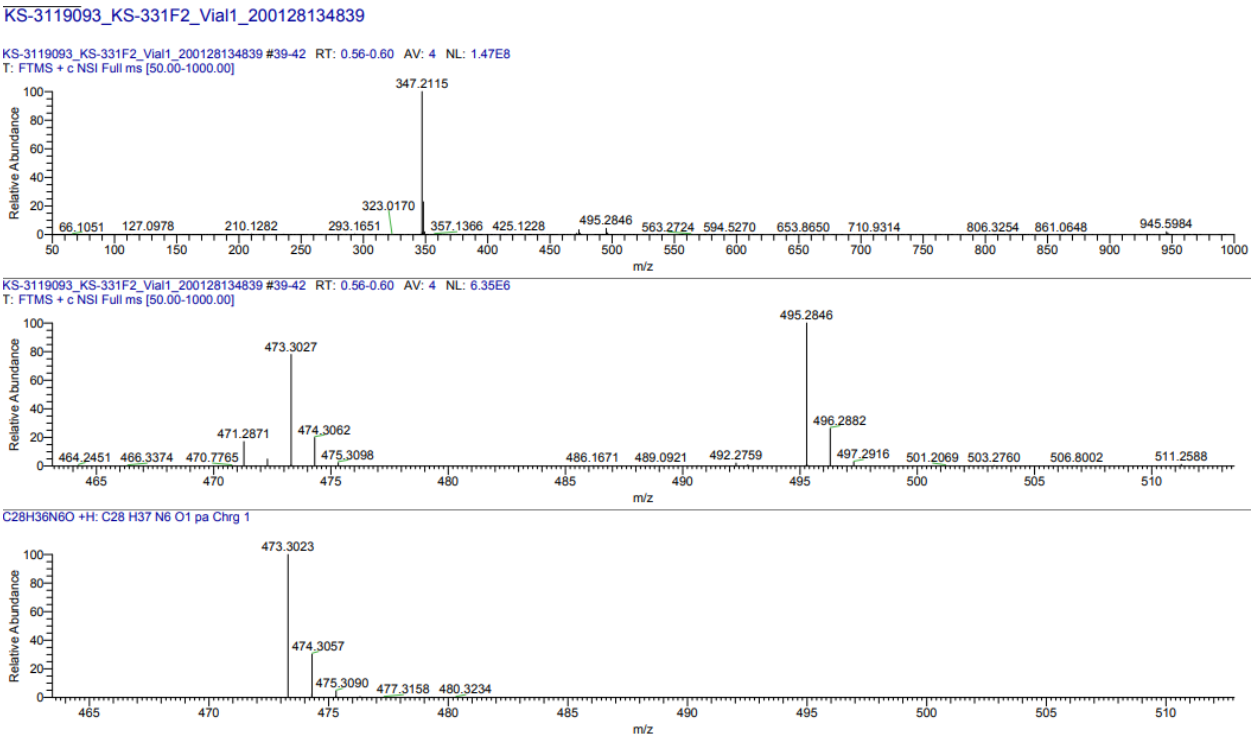
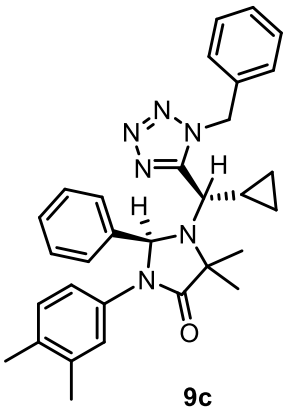


Figure S78. HRMS (ESI) spectra of **9b.**



9c

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{31}H_{35}N_6O$ 507.2867; found 507.2867.

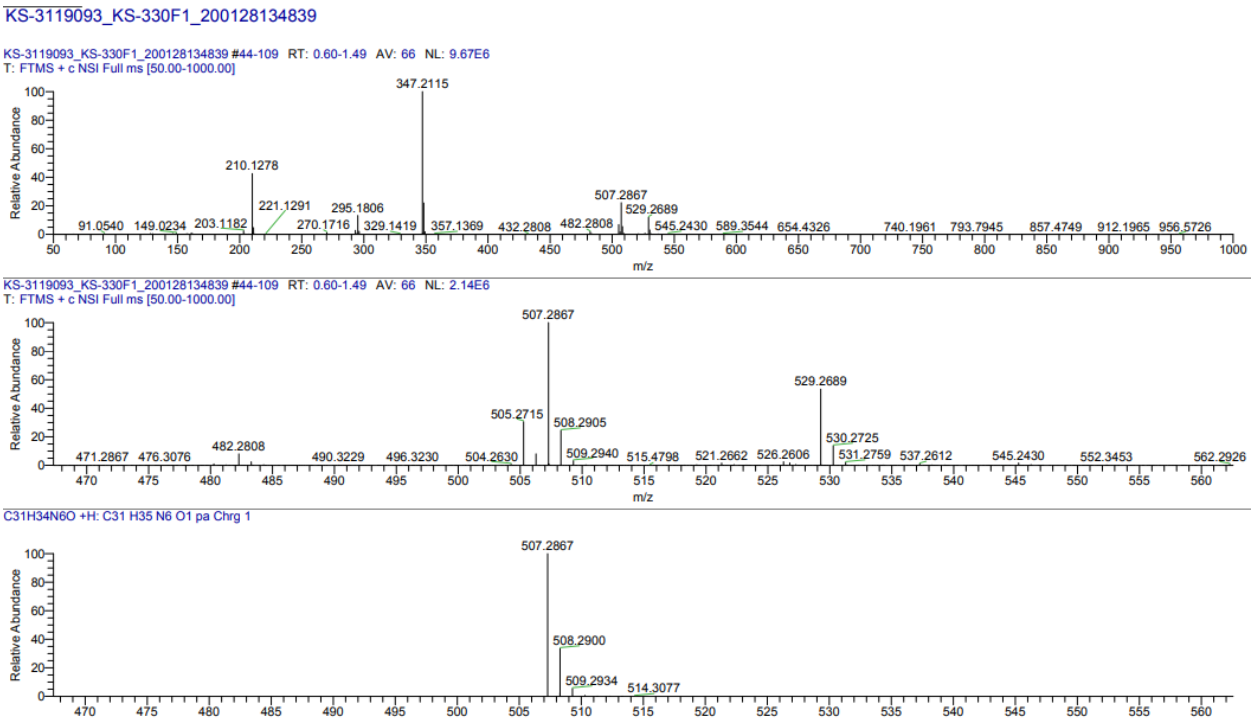
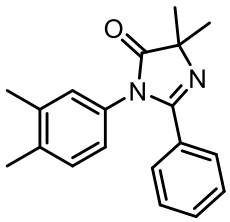


Figure S79. HRMS (ESI) spectra of **9c.**



12

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{21}N_2O$ 293.1648; found 293.1640.

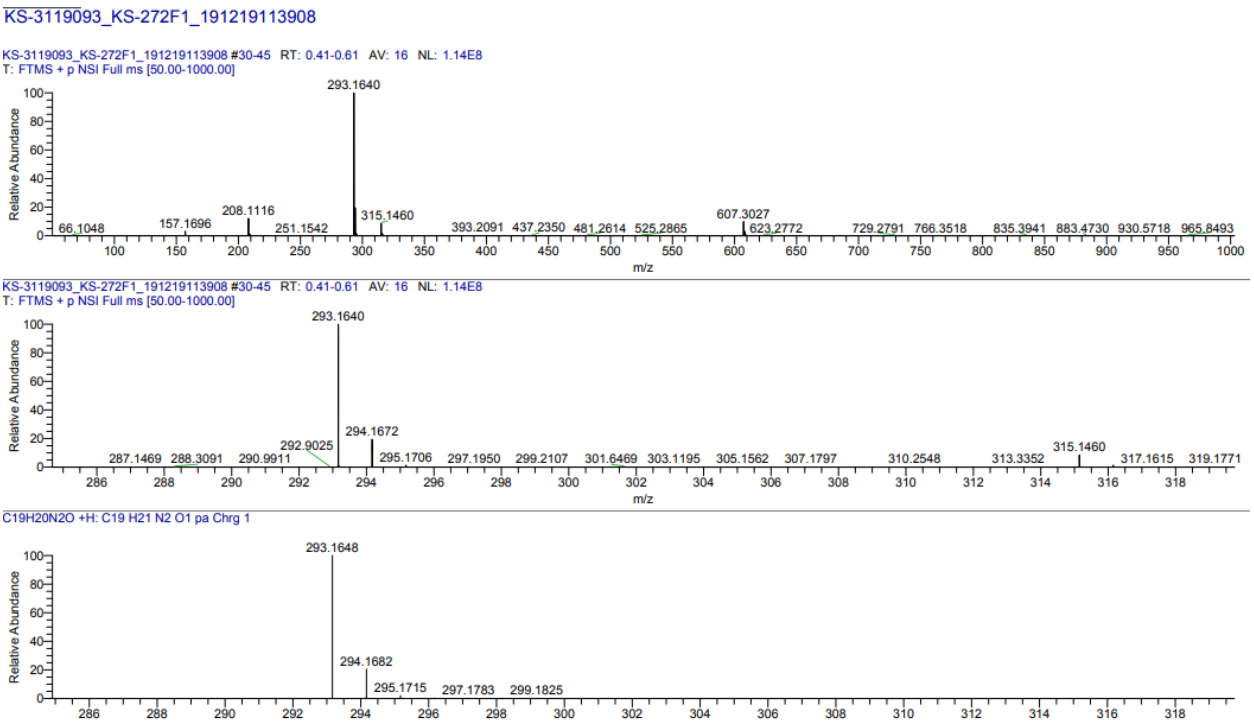
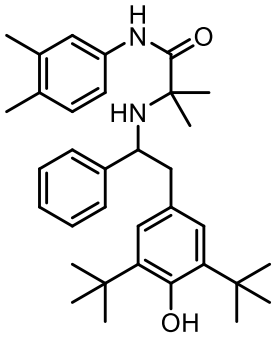


Figure S80. HRMS (ESI) spectra of **12.**



13

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{34}H_{47}N_2O_2$ 515.3632; found 515.3628.

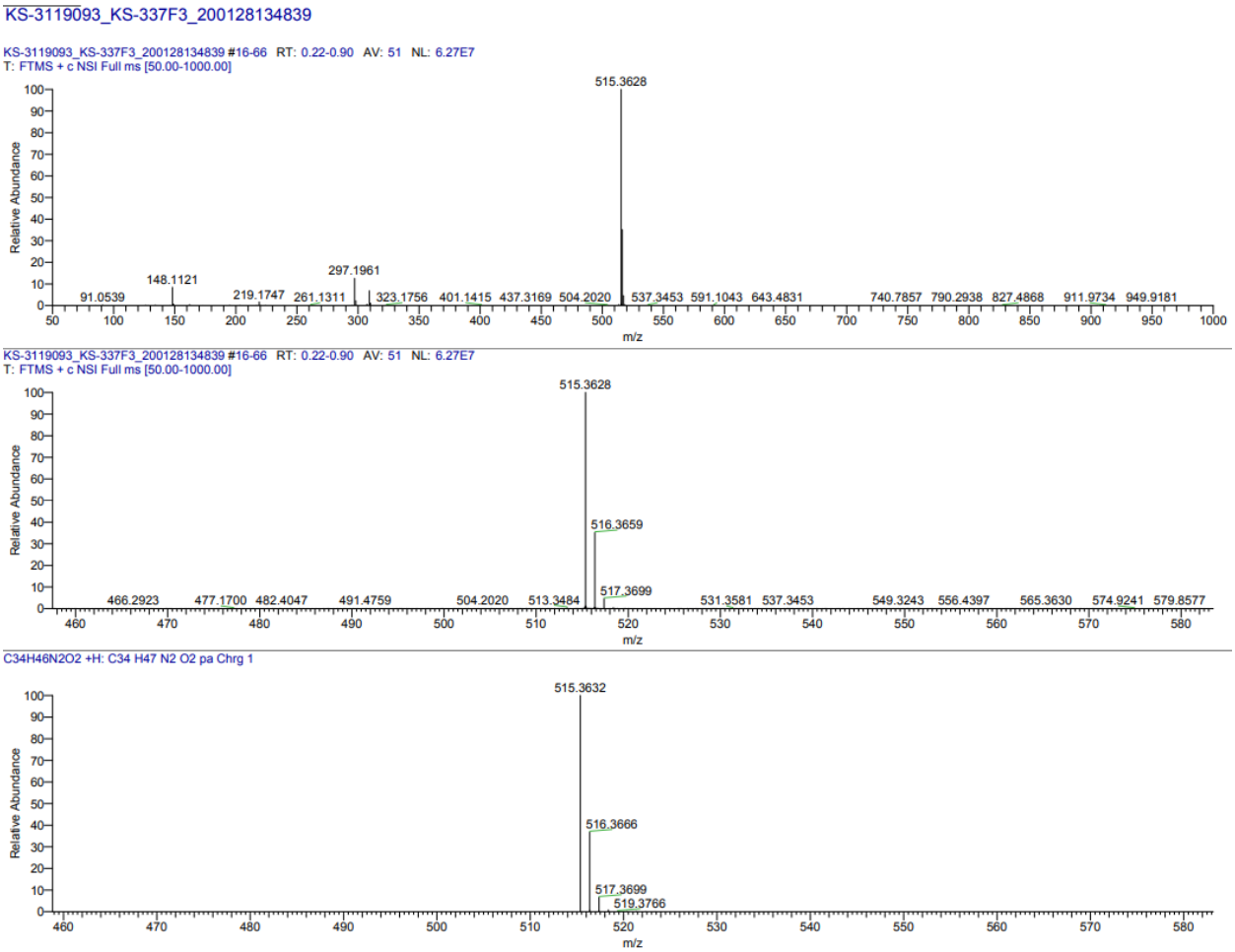


Figure S81. HRMS (ESI) spectra of **13.**