Rh(III) Catalyzed Aldehydic and Aryl C-H Alkylation with Cyclopropanols *via* C-H/C-C Bond Activation

Om Prakash Dash, Divya Garg and Chandra M. R. Volla*

Department of Chemistry, Indian Institute of Technology Bombay

Powai, Mumbai-400076, India.

E–mail: chandra.volla@chem.iitb.ac.in

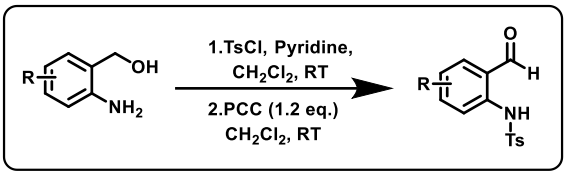
Supporting Information

Table of contents

1. General considerations.

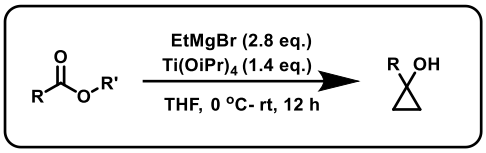
All reactions were carried out under air in screw cap reaction tubes. Unless otherwise noted, all the chemicals were purchased from commercial suppliers and used as received. Reactions were monitored using thin-layer chromatography (SiO_2). A gradient elution using petroleum ether and ethyl acetate was performed based on Merck aluminum TLC sheets (silica gel $60F_{254}$). TLC plates were visualized with UV light (254 nm) or $KMnO_4$ stain. For column chromatography, silica gel (100–200 mesh) from Finar Co. was used. All isolated compounds are characterized by ^{1}H NMR, ^{13}C NMR spectroscopy. In addition, all the compounds are further characterized by HRMS. HRMS were recorded with Bruker MaXis impact mass spectrometer using ESI-TOF techniques. Copies of ^{1}H NMR and ^{13}C NMR can be found in the supporting information. Nuclear magnetic resonance spectra were recorded either on a Bruker 500 or a 400 MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm), and was measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra was reported in ppm relative to deuterochloroform (77.16 ppm) unless otherwise stated, and all was obtained with 1 H decoupling.

2. (a) General procedure for the synthesis of starting materials.[1]



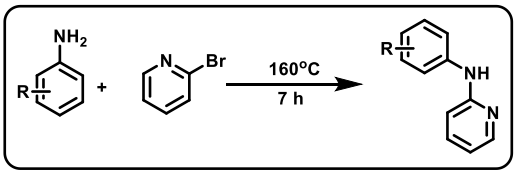
A dry and nitrogen-flushed 250-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-aminobenzyl alcohol (1.23 g, 10 mmol) in CH_2Cl_2 (100 mL). TsCl (2.09 g, 1.1 equiv) and pyridine (0.1 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. Thereafter, the solvent was removed by evaporation in vacuum. Without purification, the crude product was dissolved in dichloromethane (30 mL) and then PCC (2.6 g, 1.2 equiv) was added. The reaction mixture was stirred for 4 h at room temperature and then filtered through Celite followed by washing with CH_2Cl_2. Thereafter, the solvent was removed by evaporation in vacuum. Purification by column chromatography (ethyl acetate/hexanes: 1/2) furnished 2-tosylaminobenzaldehyde.

(b) General Procedure for the Preparation of Cyclopropanol.[2]



To a stirred solution of ester (5.0 mmol) in THF (10 mL), $Ti(OiPr)_4$ (7 mmol, 1.4 equiv, 2 mL) was added under N_2 atmosphere, which was treated with alkylmagnesuim bromide (2.8 equiv) dropwise via syringe at 0 °C. The black solution was allowed to warm to room temperature and stirred for 12 h. After completion, the reaction mixture was cooled to 0 °C and quenched with slow addition of sulfuric acid solution (2.0 M, 20 mL) and stirred until all the solid dissolved to give a clear two-phase liquid. The liquid was separated and the aqueous solution was extracted with diethyl ether (3×30 mL). The organic layer was collected, washed with brine, and dried over anhydrous Na_2SO_4. The organic solution was filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc, 5:1) to provide the cyclopropanol product.

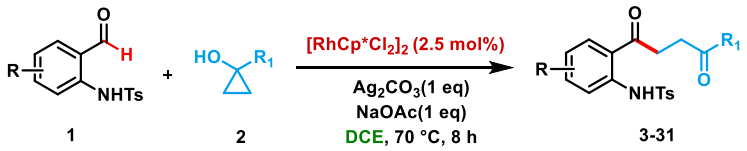
(c) General procedure for the synthesis of pyridinyl arylamines.[3]



A 25 mL Schlenk tube with a magnetic stir bar was charged with aniline (1.4 g, 15 mmol), 2-bromopyridine (2.4 g, 15 mmol). The reaction mixture was stirred at 160 °C (oil bath) for 7 h under an atmosphere of argon. Upon completion, saturated $NaHCO_3$ was added, and the mixture was extracted with EtOAc (3×15 mL). The combined organic phase was washed with brine and dried over Na_2SO_4. The solid was filtered off and the filtrate was evaporated in vacuum. The crude product was purified by flash column chromatography (n-hexanes/EtOAc) to give N-phenylpyridin-2-amine.

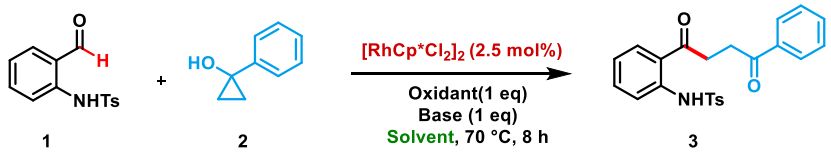
3. Procedure and Optimization of the reaction protocols

(a) General procedure for the synthesis of 1.4-diketones.



In an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), and Ag_2CO_3 (0.2 mmol), NaOAc (0.2 mmol), 2-tosylaminobenzaldehyde **1** (0.2 mmol,1 eq.) and cyclopropanol 2 (0.3 mmol, 1.5 eq.) were added followed by addition of 2 ml of 1,2-dichloroethane via syringe. The reaction mixture was allowed to stir at 70 ^oC for 8 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product **3** to **31**.

Optimization table

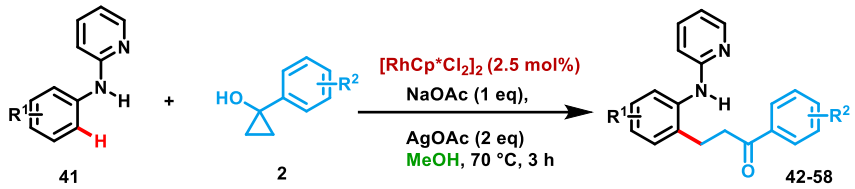


Entry	Solvent	Base	Oxidant	Yield (3)(%)
1	TFE	NaOAc	Ag_2CO_3	Trace
2	MeOH	NaOAc	Ag_2CO_3	N.R
3	MeCN	NaOAc	Ag_2CO_3	Trace
4	Toluene	NaOAc	Ag_2CO_3	42
5	THF	NaOAc	Ag_2CO_3	75
6	**DCE**	**NaOAc**	**Ag_2CO_3**	**78**
7	DCE	NaOAc	$Cu(OAc)_2.H_2O$	51
8	DCE	NaOAc	Ag_2O	58
9	DCE	Na_2CO_3	Ag_2CO_3	46
10	DCE	Na_2HPO_4	Ag_2CO_3	54
11	DCE	Cs_2CO_3	Ag_2CO_3	Trace
12	DCE	CsOAc	Ag_2CO_3	Trace

13	DCE	K_2CO_3	Ag_2CO_3	42
14	DCE	NaOAc	-	Trace
15[b]	DCE	NaOAc	Ag_2CO_3	N.R
16[c]	DCE	NaOAc	Ag_2CO_3	N.R
17[c]	TFE	NaOAc	Ag_2CO_3	N.R
18[d]	DCE	NaOAc	Ag_2CO_3	63
19[e]	DCE	NaOAc	Ag_2CO_3	57

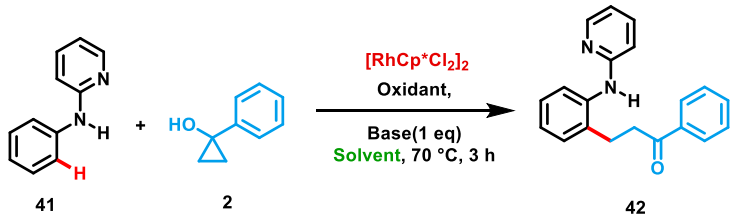
reaction condition: [a] $[RhCp^*Cl_2]_2$ (2.5 mol%) , 1a (1 equiv), 2a (1.5 equiv), Base (1 equiv.), oxidant (1 equiv.). yield are isolated yield at 70 °C, [b] without $[RhCp^*Cl_2]_2$ [c] With $[Cp^*CoCOI_2]$ (10 mol%) and $AgSbF_6$ (20 mol%). [d] reaction at 90 °C. [e]Reaction at 110 °C.

(b) General procedure for the C-H alkylation of anilines.



In an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), AgOAc (2 eq.), NaOAc (1 eq.), N-aryl aminopyridine **41** (0.2 mmol, 1 eq.) and cyclopropanol **2** (0.3 mmol, 2 eq.) were added followed by addition of 2 ml of MeOH via syringe. The reaction mixture was allowed to stir at room temperature for 3 h. On the completion of the reaction, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product **42-58**.

Optimization of the reaction



Entry	Solvent	Base	Oxidant	%Yield (42)

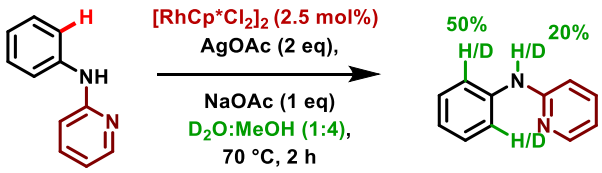
1	THF	NaOAc	$Cu(OAc)_2.H_2O$	Trace
2	DCE	NaOAc	$Cu(OAc)_2.H_2O$	66
3	MeCN	NaOAc	$Cu(OAc)_2.H_2O$	24
4	DMSO	NaOAc	$Cu(OAc)_2.H_2O$	N.R
5	TFE	NaOAc	$Cu(OAc)_2.H_2O$	Trace
6	MeOH	NaOAc	$Cu(OAc)_2.H_2O$	68
7	MeOH	NaOAc	Ag_2CO_3	30
8	MeOH	NaOAc	Ag_2O	Trace
9	**MeOH**	**NaOAc**	**AgOAc**	**90**
10	MeOH	Cs_2CO_3	AgOAc	Trace
11	MeOH	CsOAc	AgOAc	25
12	MeOH	K_2CO_3	AgOAc	N.R
13	MeOH	NaOAc	-	Trace
14[b]	MeOH	NaOAc	AgOAc	N.R

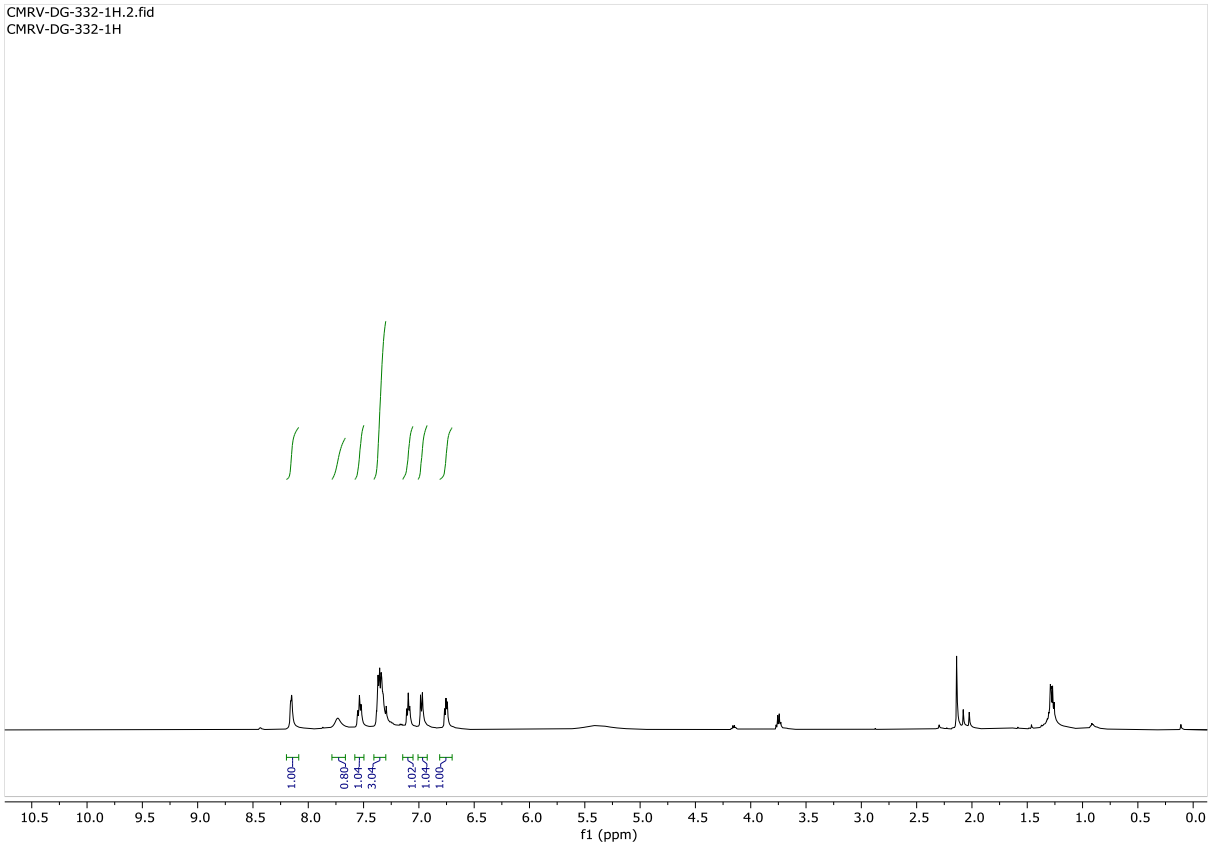
reaction condition: [a] $[RhCp^*Cl_2]_2$ (2.5 mol%) , **41** (1 equiv), **2** (2.0 equiv), Base (1 equiv.), oxidant (2 equiv.). yields are isolated yield at 70°C, [b] without $[RhCp^*Cl_2]_2$.

4. Mechanistic studies

(a) Deuterium exchange experiment

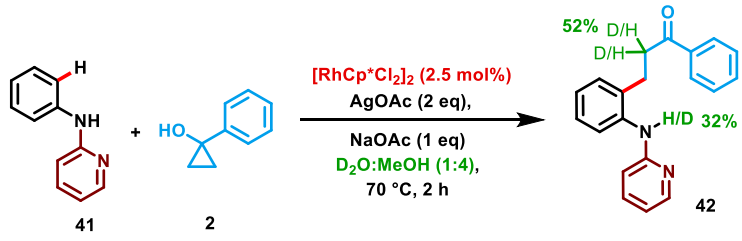
In an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), AgOAc (2 eq.), NaOAc (1 eq.), N-aryl aminopyridine 1 (34 mg, 0.2 mmol) were added followed by addition of MeOH/D_2O (1.6/0.4 ml), via syringe. The reaction mixture was allowed to stir at room temperature for 2 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford recovered substrate 1a with incorporation of deuterium.

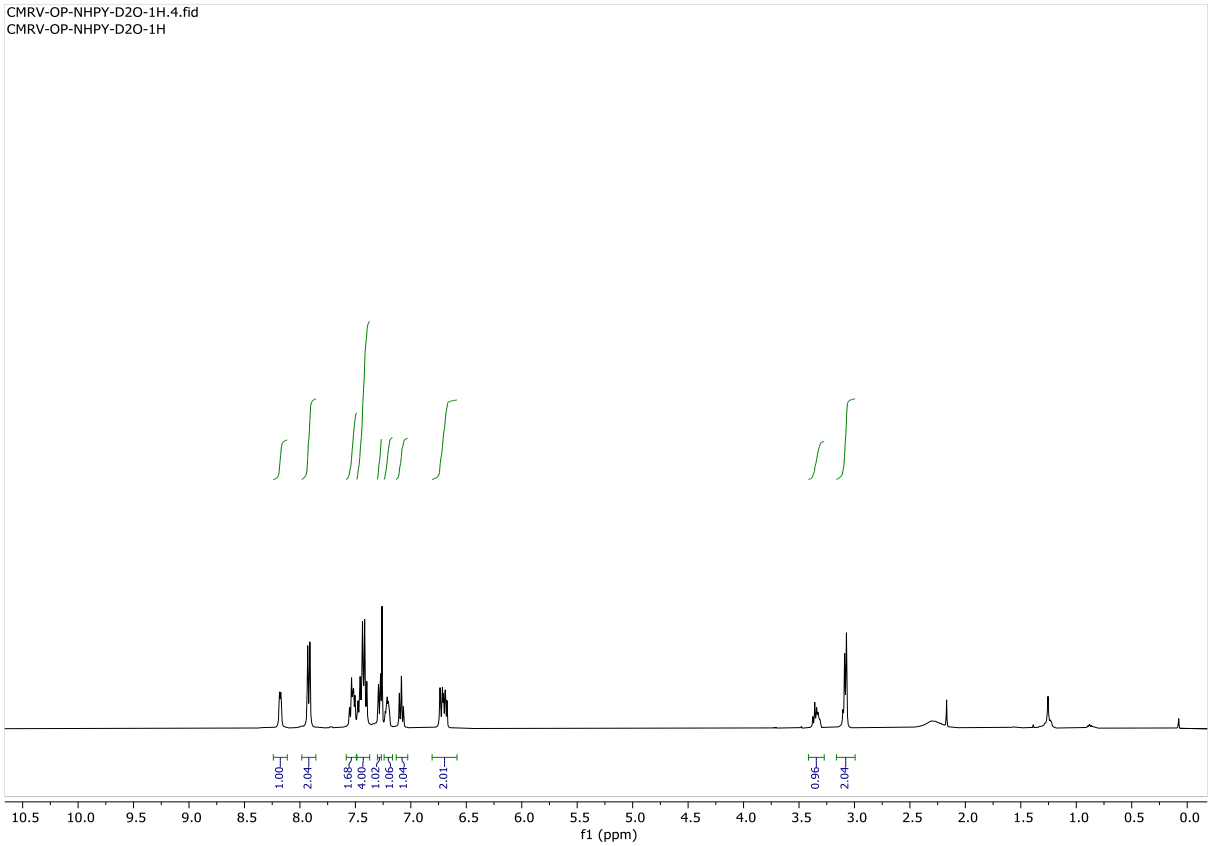




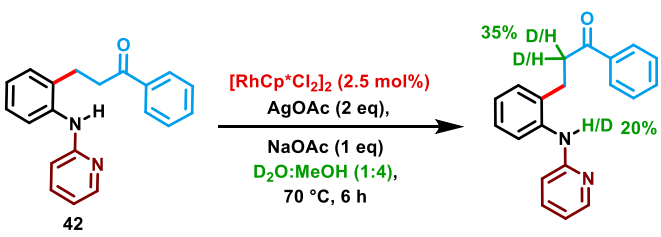
Deuterium exchange experiment with coupling partner

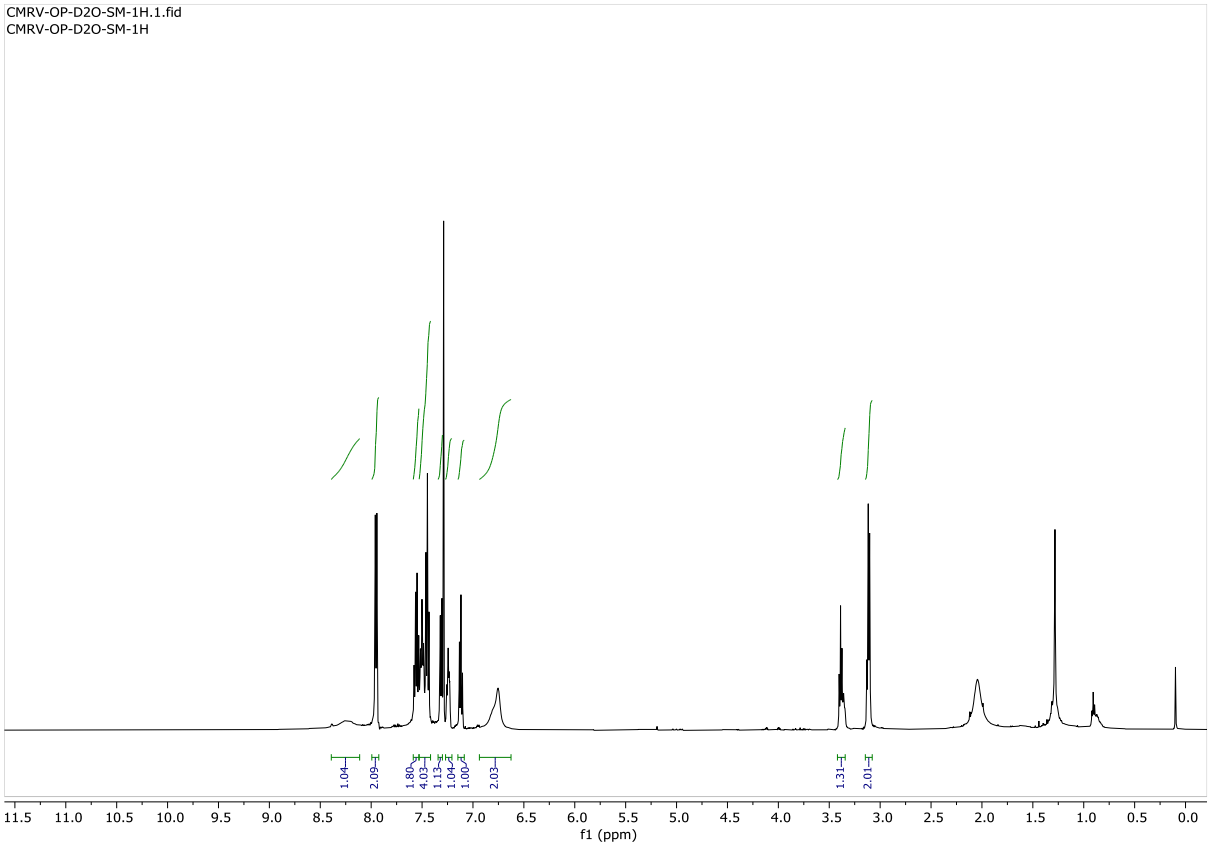
In an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), AgOAc (2 eq.), NaOAc (1 eq.), N-aryl aminopyridine **41** (1 eq.) and cyclopropanol **2** (2 eq.) were added followed by addition of MeOH/D_2O (1.6/0.4 ml), via syringe. The reaction mixture was allowed to stir at 70 ^{o} C for 2 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford product **42** with incorporation of deuterium.





After this duteration study with coupling partner, we have taken an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), AgOAc (2 eq.), NaOAc (1 eq.), **42** (1 eq.) were added followed by addition of MeOH/D_2O (1.6/0.4 ml), via syringe. The reaction mixture was allowed to stir at 70 ^{o}C for 6 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford product **42** with incorporation of deuterium. From here we can clearly confirm that duteration obtained due to acidic nature of α-proton to the carbonyl.





(b) control experiment

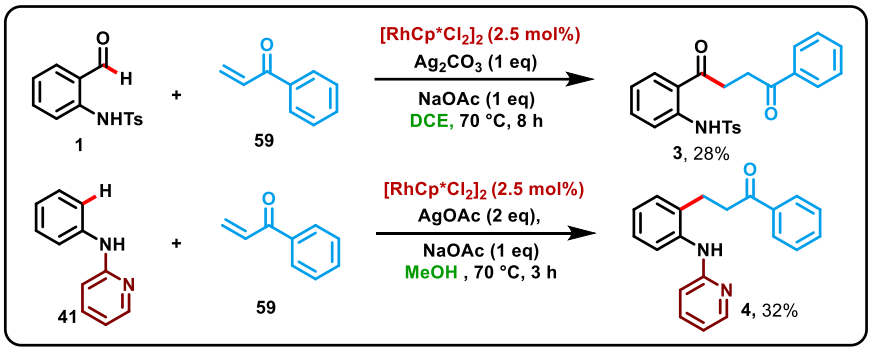
1. Reaction with 2-tosylaminobenzaldehyde:

In an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), Ag_2CO_3 (0.2 mmol), NaOAc (0.2 mmol), 2-tosylaminobenzaldehyde **1** (0.2 mmol,1 eq.) and phenyl vinyl ketone **59** (0.2 mmol, 1 eq.) were added followed by addition of 2 ml of 1,2-dichloroethane via syringe. The reaction mixture was allowed to stir at 70 ^oC for 8 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product 3 in 28% yield.

2. Reaction with N-phenyl aminopyridine

In an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), AgOAc (2 eq.), NaOAc (1 eq.), N-phenyl aminopyridine 1 (34 mg, 0.2 mmol) and phenyl vinyl ketone **59** (0.2 mmol, 1 eq.) were added followed by addition of 2 ml of MeOH via syringe. The reaction mixture was allowed to stir at room temperature for 3 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and

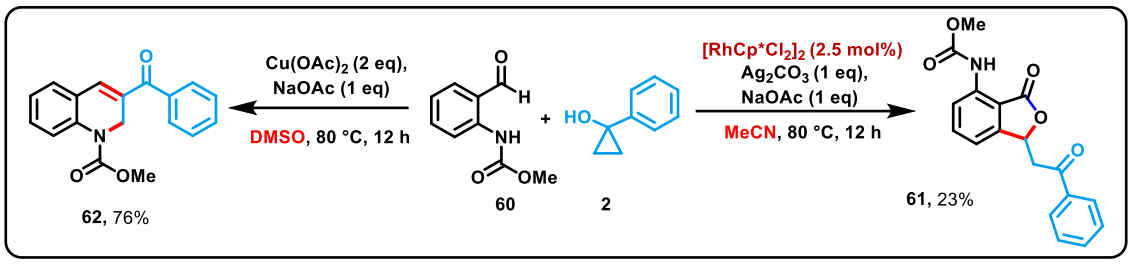
washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product 42 in 32% yield. This indicated that the presence of an *α,β*-unsaturated ketone intermediate in the catalytic cycle.



(c) Reaction with other protecting group

1. In an oven-dried reaction tube, charged with magnetic stir-bar, $[RhCp^*Cl_2]_2$ (2.5 mol%), Ag_2CO_3 (0.2 mmol), NaOAc (0.2 mmol), methyl (2-formylphenyl)carbamate **60** (0.2 mmol,1 eq.) and cyclopropanol 2 (0.3 mmol, 1.5 equiv) were added followed by addition of 2 ml of MeCN *via* syringe. The reaction mixture was allowed to stir at 80 ^oC temperature for 12 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (85:15) as eluent to afford the butenolide derivative **61** in 23% yield.

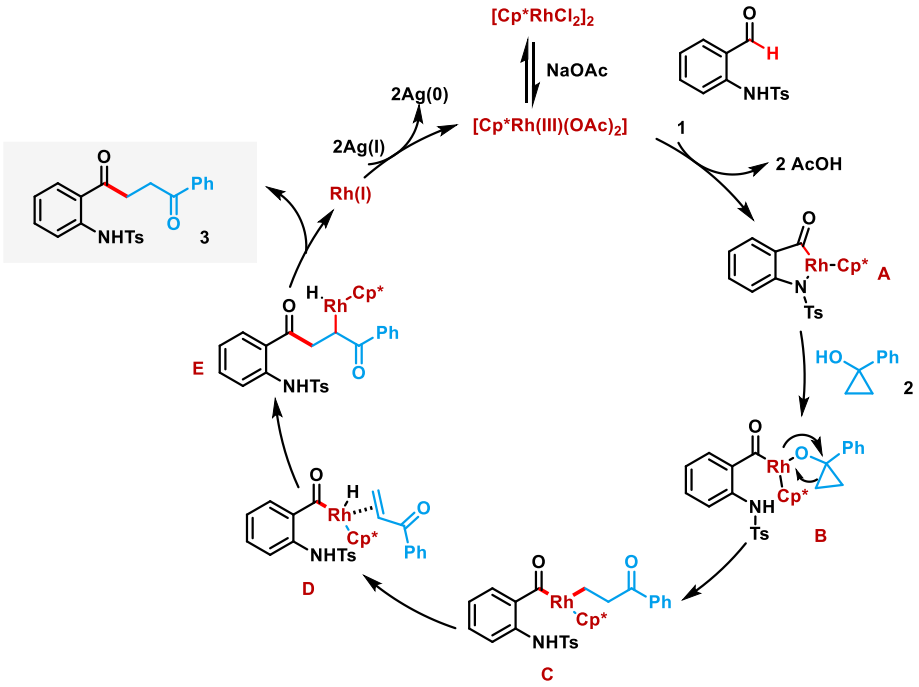
2. In an oven-dried reaction tube, charged with magnetic stir-bar, $Cu(OAc)_2.H_2O$ (0.4 mmol), NaOAc (0.2 mmol), methyl (2-formylphenyl)carbamate **60** (0.2 mmol,1 eq.) and cyclopropanol 2 (0.3 mmol, 1.5 equiv) were added followed by addition of 2 ml of DMSO *via* syringe. The reaction mixture was allowed to stir at 80 ^oC temperature for 12 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (80:20) as eluent to afford the methyl 3-benzoylquinoline-1(2H)-carboxylate **62** in 76% yield.



5. Proposed mechanism

1. Mechanism for 1,4-diketones

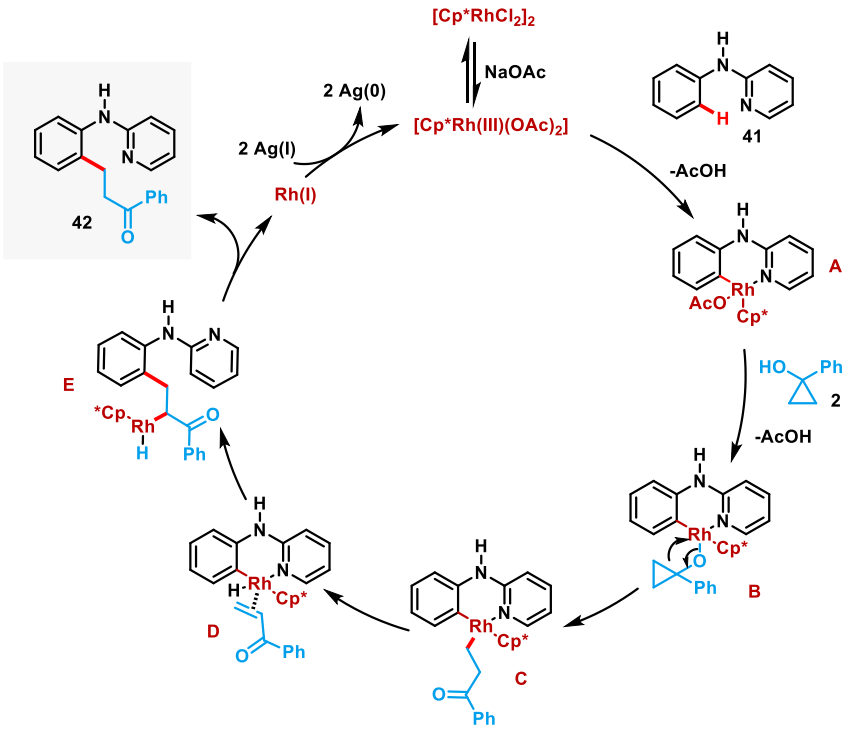
N-tosyl 2-amino benzaldehyde undergoes anion exchange followed by the subsequent C–H activation with active Rh(III) catalyst to form the five-membered rhodacycle **A**. Intermediate **A** on ligand exchange with the cyclopropanol **2** forms **B** and subsequent *β*-carbon elimination leads to the Rh(III) alkyl species **C**. Intermediate **C** then undergoes *β*-hydride elimination to form **D**, which can undergo migratory insertion to form **E** which under reductive elimination to furnish the 1,4-diketone **3** alongwith a Rh(I) species, which can be oxidized by Ag(I) to regenerate the active catalyst.



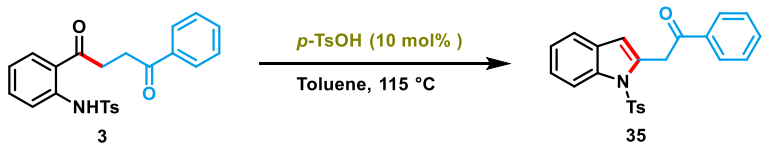
2. Mechanism for *β*-aryl ketone

Active catalyst **I** is generated from [RhCp*Cl_2]$_2$ in the presence of NaOAc undergoes directed ortho-metalation to N-aryl aminopyridine in a reversible manner to generate six-membered rhodacycle **A,** which undergoes ligand exchange with the cyclopropanol **2** forms **B** and subsequent *β*-carbon elimination leads to the Rh(III) alkyl species **C**. Intermediate **C** then

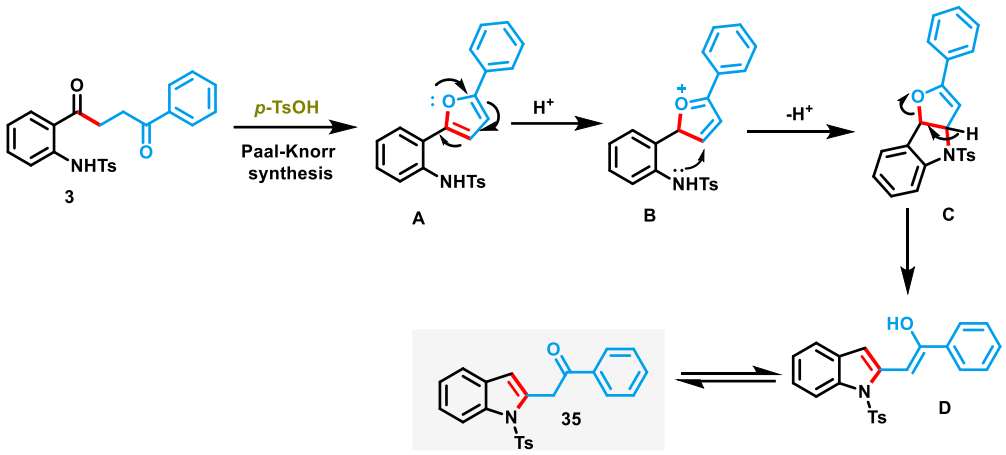
undergoes β-hydride elimination to form **D**, which can undergo migratory insertion to form **E** which under reductive elimination to furnish the β-aryl ketone **3** along with a Rh(I) species, which can be oxidized by Ag(I) to regenerate the active catalyst.



3. Mechanism for 2-alkyl indole derivative

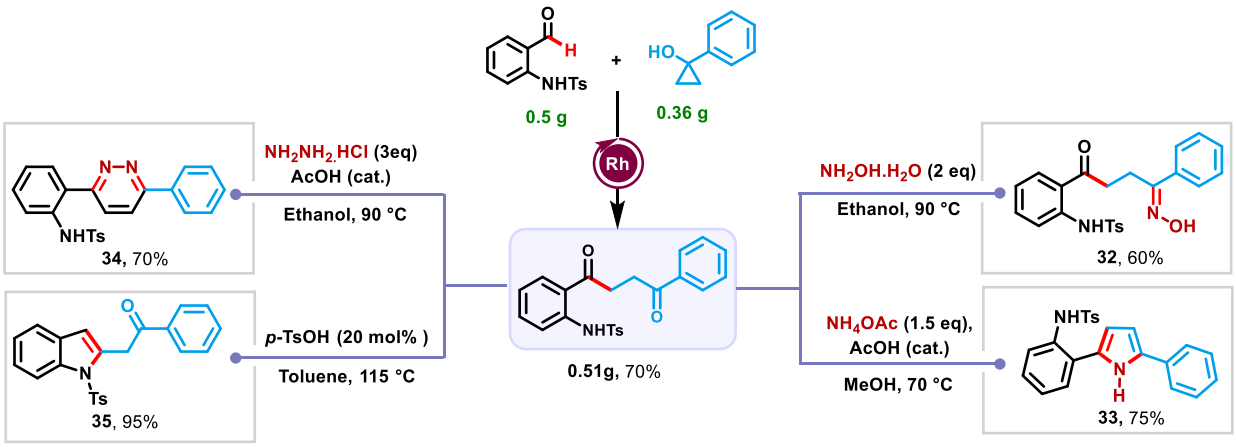


In presence of acid, **3** undergoes Paal-Knorr synthesis to generate furan **A** which rearranges to generate **B**. From intermediate **B**, nucleophilic addition happens to generate **C** which on subsequent ring opening deliver **D**. The intermediate **D** tautomerise to give **35**.



6. Scale up and functionalization:

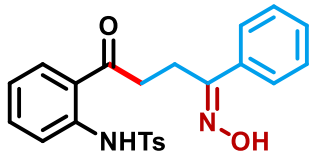
(a) Scale-up reaction: An oven-dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%), 2-aminobenzaldehyde **1** (0.5 g, 1 eq.) and cyclopropanol **2a** (1.5 equiv), Ag_2CO_3 (1 equiv.), NaOAc (1 equiv.), were added followed by addition of 10 ml of 1,2-dichloroethane via syringe The reaction mixture was allowed to stir at 70 °C for 14 h. On completion The mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 15 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the corresponding product **3** was isolated as white solid with yield of **70%** (0. 51g).



Synthesis of 32

To a 25 mL round bottom flask was added **3** (1.0 equiv) in 3 ml ethanol as reaction solvent followed by $NH_2OH.H_2O$ (2.0 equiv). The resulting reaction mixture was stirred at 90 °C for 10 h. On completion of the reaction, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography (PE/EA = 85/15) to afford compound 32 as light yellow oil with 60% yield.

(Z)-N-(2-(4-(hydroxyimino)-4-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide



32, 60%

Purified by (petroleum ether/EtOAc: 75/25), 51 mg, 60%, light yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.44 (dd, *J* = 7.2, 1.5 Hz, 2H), 7.41 – 7.39 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.02 (t, *J* = 7.7 Hz, 1H), 3.22 – 3.16 (m, 2H), 3.14 – 3.07 (m, 2H), 2.33 (s, 3H).

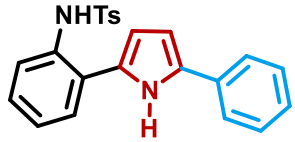
^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 158.6, 143.9, 140.0, 136.6, 135.0, 134.9, 131.0, 129.7, 128.8, 127.3, 126.2, 122.7, 122.1, 119.5, 35.9, 21.5, 21.3

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}N_2O_4S$ 423.1373, found 423.1382

Synthesis of 33

To a 25 mL round bottom flask was added **3** (1.0 equiv) in 3 ml methanol as reaction solvent followed by NH_4OAc (2.0 equiv). Then AcOH (2-3 drops) was added in the rb. The resulting reaction mixture was stirred at 70 ^oC for 12 h. On completion of the reaction, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography (PE/EA = 80/20) to afford compound 32 as white sticky solid with 75% yield.

4-methyl-N-(2-(5-phenyl-1H-pyrrol-2-yl)phenyl)benzenesulfonamide



33, 75%

Purified by (petroleum ether/EtOAc: 80/20), 58 mg, 75%, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.26 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 3.5 Hz, 1H), 6.21 (d, *J* = 3.5 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 136.0, 133.9, 133.1, 132.2, 129.7, 129.4, 128.99, 128.35, 128.22, 127.78, 127.37, 126.63, 126.28, 124.5, 123.9, 110.3, 107.2, 21.5

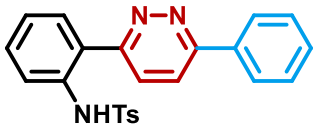
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}N_2O_2S$ 389.1318, found 389.1321

Synthesis of 34

A 25 mL round bottom flask was charged with 3 (1.0 equiv) in 3 mL ethanol as reaction solvent and NH_2NH_2. HCl (3.0 equiv) was added in one portion. The resulting mixture was stirred for

16 h at 90 °C. On completion of the reaction, the solvent was removed under reduced pressure followed by purification by flash column chromatography (PE/EA = 85/15) to afford compound 34 light yellow oil with 70% yield.

4-methyl-N-(2-(6-phenylpyridazin-3-yl)phenyl)benzenesulfonamide



34, 70%

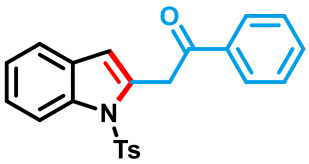
Purified by (petroleum ether/EtOAc: 80/20), 56 mg, 70%, white sticky solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.45 (s, 1H), 8.10 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.54 (m, 4H), 7.50 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.44 (td, *J* = 7.9, 1.8 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 157.5, 143.0, 136.7, 136.5, 135.5, 131.1, 130.6, 129.3, 129.2, 128.6, 127.0, 126.9, 126.2, 125.7, 125.2, 124.7, 124.6, 21.4

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}N_2O_2S$ 402.1271, found 402.1269

Synthesis of 35



35, 95%

To a 25 mL round bottom flask was charged with **3** (1.0 equiv) in 3 ml toluene as solvent followed by PTSA. H_2O (10 mol%) was added in the rb. The resulting reaction mixture was stirred at 115 °C for 6 h. On completion of the reaction, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography (PE/EA = 80/20) to afford compound 32 as white sticky solid with 95% yield.

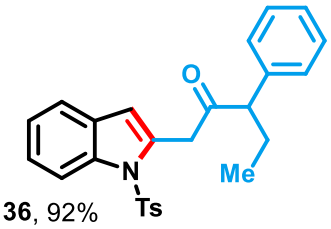
Purified by (petroleum ether/EtOAc: 95/5), 74 mg, 95%, white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.45 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.24 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 3H), 6.53 (s, 1H), 4.74 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 144.9, 136.8, 136.49, 136.04, 134.3, 133.3, 129.82, 129.35, 128.73, 128.46, 126.8, 124.3, 123.4, 120.6, 114.4, 112.2, 39.2, 21.6

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{20}NO_3S$ 390.1158, found 390.1160

3-phenyl-1-(1-tosyl-1H-indol-2-yl)pentan-2-one



36, 92%

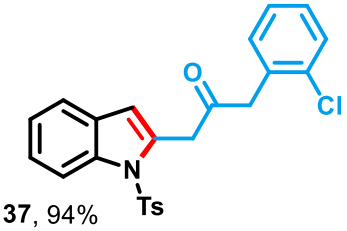
Purified by (petroleum ether/EtOAc: 80/20), 80 mg, 92%, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.40 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 7.21 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.20 – 7.14 (m, 3H), 6.34 (s, 1H), 4.23 (d, *J* = 17.8 Hz, 1H), 3.81 (d, *J* = 17.8 Hz, 1H), 3.76 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.33 (s, 3H), 2.15 (m, 1H), 1.80 – 1.72 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 144.8, 138.8, 136.6, 136.0, 134.1, 129.8, 129.3, 128.92, 128.66, 127.3, 126.6, 124.3, 123.4, 120.5, 114.4, 112.4, 60.4, 42.1, 25.2, 21.6, 11.9

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{26}NO_3S$ 432.1628, found 432.1632

1-(2-chlorophenyl)-3-(1-tosyl-1H-indol-2-yl)propan-2-one



37, 94%

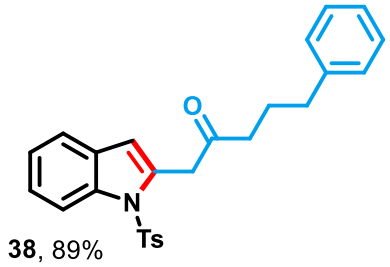
Purified by (petroleum ether/EtOAc: 80/20), 82 mg, 94%, white sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.33 – 7.29 (m, 1H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.21 (dd, *J* = 3.4, 1.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.52 (s, 1H), 4.17 (s, 2H), 4.04 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 144.9, 136.7, 135.9, 134.5, 133.7, 132.7, 132.2, 129.9, 129.5, 129.3, 128.7, 127.1, 126.7, 124.4, 123.5, 120.6, 114.4, 112.7, 47.2, 42.6, 21.6

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{21}ClNO_3S$ 438.0925, found 438.0927

5-phenyl-1-(1-tosyl-1H-indol-2-yl)pentan-2-one



38, 89%

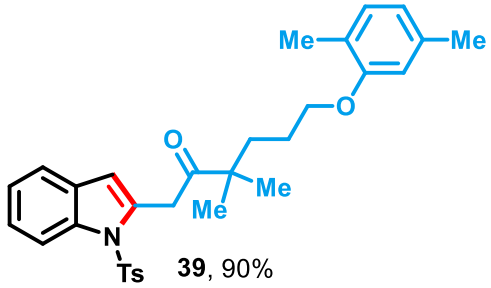
Purified by (petroleum ether/EtOAc: 80/20), 77 mg, 89%, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 6.5, 1.4 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.23 – 7.20 (m, 3H), 7.19 – 7.17 (m, 3H), 6.49 (s, 1H), 4.08 (s, 2H), 2.66 – 2.60 (m, 4H), 2.33 (s, 3H), 2.00 – 1.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 144.9, 141.7, 136.6, 135.96, 134.1, 129.85, 129.27, 128.53, 128.38, 126.7, 125.9, 124.4, 123.5, 120.6, 114.4, 112.3, 43.1, 41.4, 35.1, 25.1, 21.6

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{26}NO_3S$ 432.1628, found 432.1630.

6-(2,5-dimethylphenoxy)-3,3-dimethyl-1-(1-tosyl-1H-indol-2-yl)hexan-2-one



39, 90%

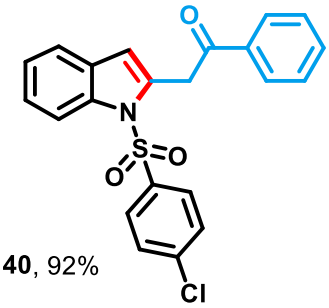
Purified by (petroleum ether/EtOAc: 80/20), 93 mg, light yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 6.41 (s, 1H), 4.33 (s, 2H), 3.94 (t, *J* = 6.0 Hz, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 1.86 – 1.82 (m, 2H), 1.80 – 1.75 (m, 2H), 1.30 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.7, 156.9, 144.7, 136.8, 136.55, 136.17, 134.7, 130.3, 129.75, 129.37, 126.8, 124.1, 123.54, 123.34, 120.76, 120.47, 114.4, 112.0, 67.9, 47.6, 37.9, 36.6, 24.9, 24.8, 21.5, 21.4, 15.9

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{36}NO_4S$ 518.2360, found 518.2368.

2-(1-((4-chlorophenyl)sulfonyl)-1H-indol-2-yl)-1-phenylethan-1-one



40, 92%

Purified by (petroleum ether/EtOAc: 75/25), 75 mg, light yellow liquid.

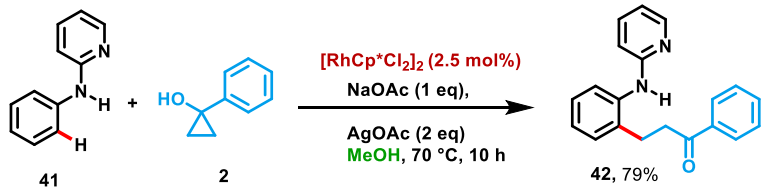
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.93 – 7.89 (m, 1H), 7.82 – 7.78 (m, 2H), 7.66 – 7.61 (m, 1H), 7.56 – 7.49 (m, 3H), 7.43 – 7.40 (m, 2H), 7.28 – 7.22 (m, 2H), 6.60 (s, 1H), 4.77 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 140.4, 137.3, 136.6, 136.4, 134.4, 133.5, 129.51, 129.38, 128.80, 128.40, 128.36, 124.5, 123.8, 120.8, 114.2, 112.9, 39.2

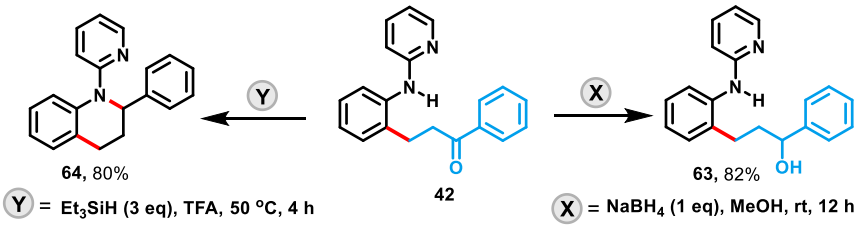
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{17}ClNO_3S$ 410.0612, found 410.0615.

(b) Scale up and functionalization of N-phenyl aminopyridine:

Scale-up reaction: An oven-dried 25 mL round bottom flask equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (2.5 mol%), AgOAc (2 eq.), NaOAc (1 eq.) N-phenyl aminopyridine **41** (0.5g, 1 eq.) and cyclopropanol **2** (2 eq.) were added followed by addition of 10 ml of MeOH via syringe. The reaction mixture was allowed to stir at 70 °C for 6 h. Then, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). On completion the mixture was filtered through a Celite pad and washed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the corresponding product **42** was isolated as white solid with yield of **79%** (0. 7g).



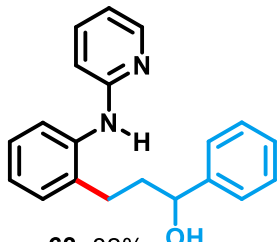
Functionalization:



Reduction of 42:

A 25 mL round bottom flask was charged with **42** (0.2 mmol, 1.0 equiv) in 3 mL methanol as reaction solvent and $NaBH_4$ (1 eq.) was added slowly within 10-15 minutes at low tempereture. The resulting mixture was stirred for 10 h at room temperature. On completion of the reaction, the solvent was removed under reduced pressure followed by purification by flash column chromatography (PE/EA = 80/20) to afford compound **63** light brown oil with 82% yield.

1-phenyl-3-(2-(pyridin-2-ylamino)phenyl)propan-1-ol



63, 82%

Purified by (petroleum ether/EtOAc: 80/20), 50 mg, light brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.2, 2.3 Hz, 1H), 7.52 – 7.34 (m, 3H), 7.31 – 7.25 (m, 4H), 7.25 – 7.18 (m, 3H), 7.08 (t, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.67 – 6.60 (m, 1H), 4.62 (dd, *J* = 9.3, 4.0 Hz, 1H), 3.38 (s, 1H), 2.89 – 2.71 (m, 2H), 2.11 – 2.02 (m, 1H), 1.97 – 1.88 (m, 1H).

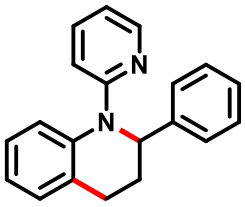
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 147.9, 144.9, 138.6, 138.0, 134.9, 130.6, 128.5, 127.5, 126.97, 125.9, 124.5, 123.0, 114.5, 108.2, 72.8, 39.9, 27.6

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{20}N_2NaO$ 327.1468, found 327.1469

Synthesis of 64:

A 25 mL round bottom flask was charged with **42** (0.2 mmol, 1.0 eq.) was dissolved in TFA (1 mL) in a round bottomed flask. Et_3SiH (3 eq.) was added, and the mixture was stirred at 50 °C under argon for 4 h. On completion of the reaction, the solvents were removed under reduced pressure. The mixture was extracted with EtOAc (3× 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and evaporated in vacuo. The product was purified by silica gel column chromatography (petroleum ether/EtOAc: 95/5) to give the pure **64** as a colorless oil in 80% yield.

2-phenyl-1-(pyridin-2-yl)-1,2,3,4-tetrahydroquinoline



64, 80%

Purified by (petroleum ether/EtOAc: 95/5), 46 mg, colourless liquid.

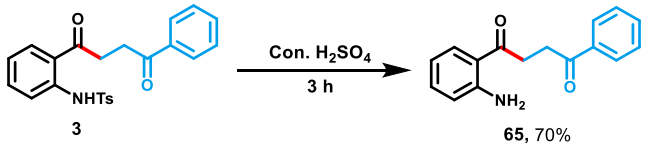
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 5.3, 2.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.19 – 7.15 (m, 1H), 7.14 – 7.10 (m, 2H), 7.07 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.90 (td, *J* = 7.3, 1.2 Hz, 1H), 6.75 (dd, *J* = 7.2, 4.0 Hz, 1H), 5.68 (t, *J* = 5.4 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.64 – 2.56 (m, 1H), 2.46 – 2.39 (m, 1H), 2.22 – 2.16 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 148.5, 143.5, 140.8, 137.2, 129.5, 129.2, 128.5, 126.5, 126.4, 126.4, 121.7, 120.8, 116.2, 113.1, 59.1, 30.5, 24.6.

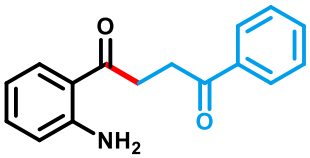
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}N_2$ 287.1543, found 287.1543.

(c) Removal of tosyl protecting group:

A 25 mL round bottom flask was charged with **3** (0.2 mmol) was dissolved in TFA (1 mL) in a round bottomed flask 1.0 mmol) was added to conc. H_2SO_4 (5 mL) at 0 °C. The mixture was stirred for 3 h. After completion, the reaction mixture was quenched with $NaHCO_3$ solution and the resulting mixture was extracted with EtOAc (3 × 10 mL). The organic layers were dried over anhydrous Na_2SO_4, and was concentrated under vacuum to give **65** as white solid in 70 % yield.



1-(2-aminophenyl)-4-phenylbutane-1,4-dione



65, 70%

Purified by (petroleum ether/EtOAc: 90/10), 35 mg, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.89 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 6.72 – 6.61 (m, 2H), 3.49 – 3.44 (m, 2H), 3.44 – 3.39 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 199.2, 150.3, 137.0, 134.5, 133.2, 131.3, 128.7, 128.3, 118.0, 117.5, 116.1, 33.2, 32.8.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}NNaO_2$ 276.0995, found 276.0996.

7. References:

1. (a) Wang, H.; Xie, F.; Qi, Z.; Li, X. *Org. Lett.* **2015**, *17*, 920–923. (b) Debbarma, S.; Sudan Maji, M. *E. J. Org. Chem.* **2017**, *2017*, 3699–3706. (c) Ai, W.; Wu, Y.; Tang, H.; Yang, X.; Yang, Y.; Li, Y.; Zhou, B. *Chem. Commun.* **2015**, *51*, 7871–7874.

2. (a) Rosa, D.; Orellana, A. *Chem. Commun*. **2013**, *49*, 5420. (b) Zhou, X.; Yu, S.; Kong, L.; Li, X. *ACS Catal.* **2016**, *6*, 647. (c) Zhou, X.; Qi, Z.; Yu, S.; Kong, L.; Li, Y.; Tian, W.-F.; Li, X. *Adv. Synth. Catal.* **2017**, *359*, 1620. (d) Zhan, J.-L.; Wu, M.-W.; Wei, D.; Wei, B.- Y.; Jiang, Y.; Yu, W.; Han, B. *ACS Catal.* **2019**, *9*, 4179. (e) Ganiu, M. O.; Cleveland, A. H.; Paul, J. L.; Kartika, R. *Org. Lett.* **2019**, *21*, 5611. (f) Pati, B. V.; Ghosh, A.; Ravikumar, P. C. *Org. Lett.* **2020**, *22*, 2854. (g) Fang, L.; Fan, S.; Wu, W.; Li, T.; Zhu, J. *Chem. Commun.* **2021**, *57*, 7386. (h) Lou, C.; Wang, X.; Lv, L.; Li, Z. *Org. Lett.* **2021**, *23*, 7608.

3. (a) X. Huang, S. Xu, Q. Tan, M. Gao, M. Lia and B. Xu, *Chem. Commun*., 2014, 50, 1465. (b) Ackermann, L.; Lygin, A. V. *Org. Lett.* **2012**, *14*, 764–767. (c) Qian, G.; Liu, B.; Tan, Q.; Zhang, S.; Xu, B. *Eur. J. Org. Chem*. **2014**, *2014*, 4837−4843. (d) Lv, S.; Han, X.; Wang, J.-Y.; Zhou, M.; Wu, Y.; Ma, L.; Niu, L.; Gao, W.; Zhou, J.; Hu, W.; Cui, Y.; Chen, J. *Angew. Chem., Int. Ed.* **2020**, *59*, 11583–11590. (e) Wang, Y.; Jia, D.; Zeng, J.; Liu, Y.; Bu, X.; Yang, X. *Org. Lett.* **2021**, *23*, 7740–7745. (f) Yan, X.; Ye, R.; Sun, H.; Zhong, J.; Xiang, H.; Zhou, X *Org. Lett.* **2019**, *21*, 7455–7459.

8. (a) X-ray Crystallography data for the compound of 7

Crystal of the compound **7** was obtained after slow evaporation of chloroform solvent. Molecular structure of **7** with 50% ellipsoid probability.

Datablock cmrv_dg_200_re_autored - ellipsoid plot

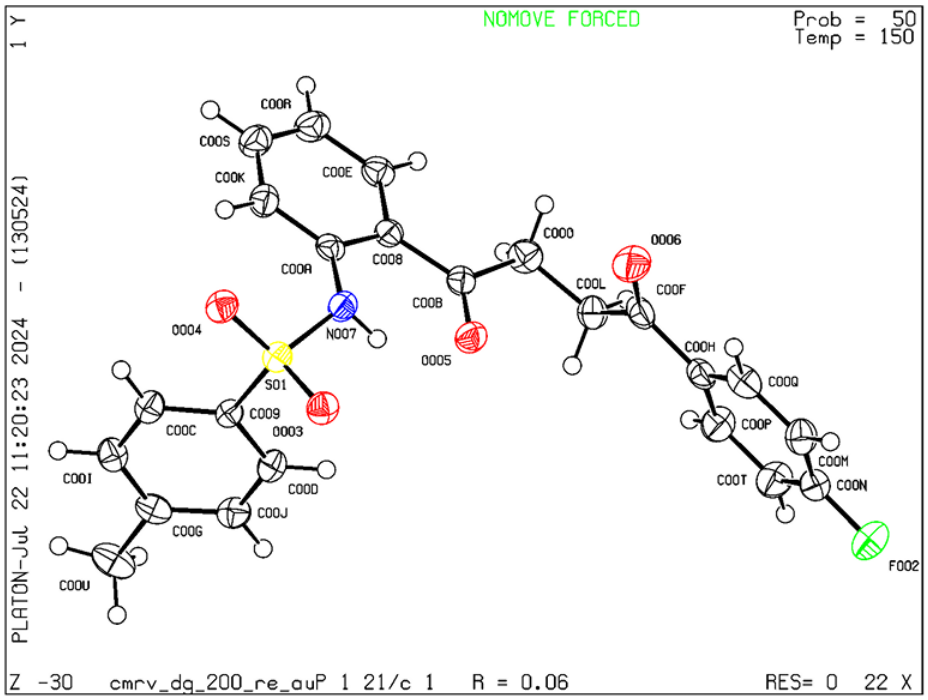


Table 1 Crystal data and structure refinement for CMRV_DG_200_RE_autored.	
Identification code	CMRV_DG_200_RE_autored
Empirical formula	$C_{23}H_{20}FNO_4S$
Formula weight	425.46
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.0724(16)
b/Å	8.3789(4)
c/Å	11.4598(7)
α/°	90
β/°	101.066(6)
γ/°	90
Volume/Å^3	1985.8(2)
Z	4
ρ_{calc}g/cm^3	1.423
μ/mm^{-1}	0.203
F(000)	888.0

Crystal size/mm^3	0.087 × 0.067 × 0.045
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.938 to 49.996
Index ranges	-25 ≤ h ≤ 25, -9 ≤ k ≤ 9, -13 ≤ l ≤ 13
Reflections collected	40038
Independent reflections	3476 [R_{int} = 0.1664, R_{sigma} = 0.0679]
Data/restraints/parameters	3476/0/272
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1280
Final R indexes [all data]	R_1 = 0.0893, wR_2 = 0.1520
Largest diff. peak/hole / e Å^{-3}	0.25/-0.54

(b) X-ray Crystallography data for the compound of 35 Crystal of the compound **35** was obtained after slow evaporation of chloroform solvent. Molecular structure of **35** with 50% ellipsoid probability.

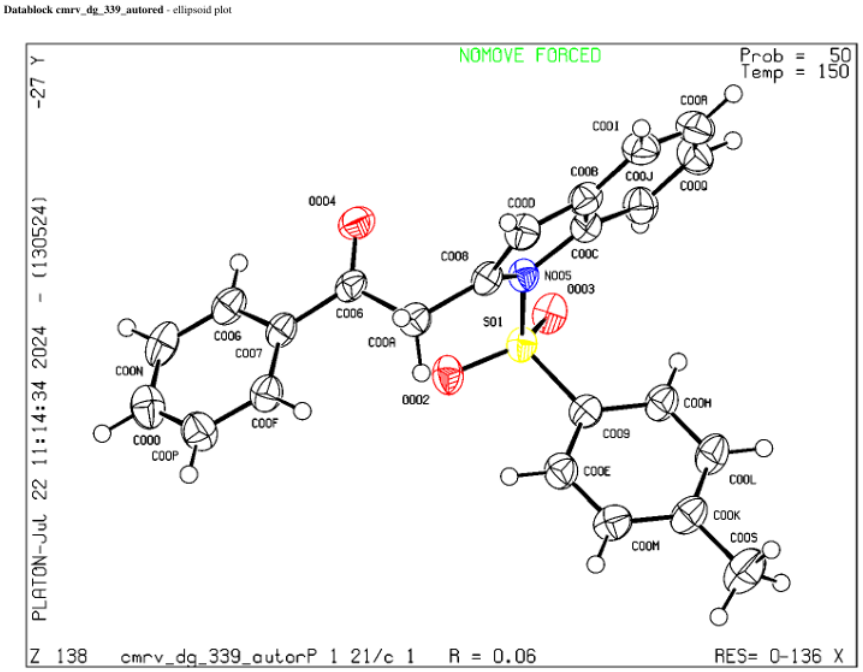


Table 2 Crystal data and structure refinement for CMRV_DG_339_autored.	
Identification code	CMRV_DG_339_autored
Empirical formula	$C_{23}H_{19}NO_3S$

Formula weight	389.45
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.7427(6)
b/Å	20.8546(7)
c/Å	10.5793(6)
α/°	90
β/°	114.951(7)
γ/°	90
Volume/Å^3	1948.9(2)
Z	4
ρ_{calc}g/cm^3	1.327
μ/mm^{-1}	0.190
F(000)	816.0
Crystal size/mm^3	0.098 × 0.076 × 0.043
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.906 to 50
Index ranges	$-11 \leq h \leq 11$, $-24 \leq k \leq 24$, $-12 \leq l \leq 11$
Reflections collected	31561
Independent reflections	3436 [R_{int} = 0.1468, R_{sigma} = 0.0633]
Data/restraints/parameters	3436/0/254
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1474
Final R indexes [all data]	R_1 = 0.0731, wR_2 = 0.1657
Largest diff. peak/hole / e Å^{-3}	0.23/-0.46

(c) X-ray Crystallography data for the compound of 42 Crystal of the compound **42** was obtained after slow evaporation of chloroform solvent. Molecular structure of **42** with 50% ellipsoid probability.

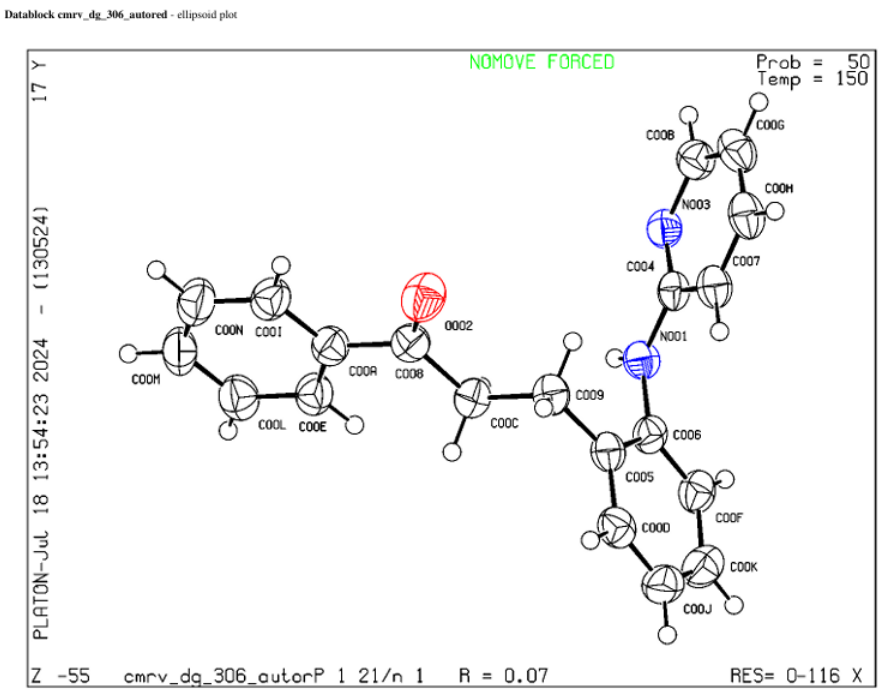


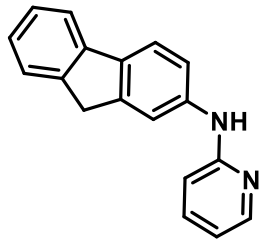
Table 3 Crystal data and structure refinement for CMRV_DG_306_RE_autored.

Identification code	CMRV_DG_306_autored
Empirical formula	$C_{20}H_{18}N_2O$
Formula weight	302.36
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.3251(7)
b/Å	19.6723(16)
c/Å	10.6280(11)
α/°	90
β/°	104.751(10)
γ/°	90
Volume/Å³	1683.2(3)
Z	4

ρ_{calc}g/cm^3	1.193
μ/mm^{-1}	0.074
F(000)	640.0
Crystal size/mm^3	0.078 × 0.067 × 0.054
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.14 to 49.992
Index ranges	-9 ≤ h ≤ 9, -23 ≤ k ≤ 23, -12 ≤ l ≤ 12
Reflections collected	49288
Independent reflections	2959 [R_{int} = 0.1552, R_{sigma} = 0.0527]
Data/restraints/parameters	2959/0/208
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0689, wR_2 = 0.1823
Final R indexes [all data]	R_1 = 0.1037, wR_2 = 0.2143
Largest diff. peak/hole / e Å^{-3}	0.22/-0.34

9. Spectroscopic data of the new starting materials

41b



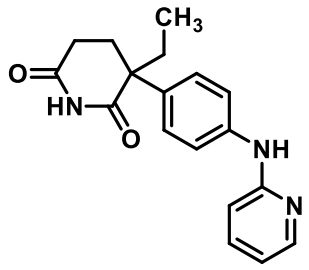
N-(9H-fluoren-2-yl)pyridin-2-amine

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 5.9 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.55 – 7.44 (m, 2H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 6.75 (dd, *J* = 7.2, 5.0 Hz, 1H), 3.90 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 144.8, 143.1, 141.7, 138.0, 138.0, 126.9, 126.2, 125.1, 120.6, 119.7, 119.7, 119.4, 117.4, 117.4, 115.0, 108.6, 37.1.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{15}N_2$ 259.1230; Found 259.1237

41c



(E)-3-ethyl-3-(1-(pyridin-2-yl)-2-styryl-1H-indol-5-yl)piperidine-2,6-dione

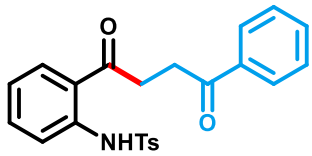
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.27 (s, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.39 – 7.17 (m, 5H), 7.00 – 6.71 (m, 2H), 2.65 – 2.42 (m, 2H), 2.38 – 2.17 (m, 2H), 2.12 – 1.90 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.0, 173.2, 155.7, 148.2, 140.1, 138.1, 132.5, 127.3, 120.1, 115.4, 108.7, 50.6, 33.0, 29.5, 27.2, 9.2.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{20}N_3O_2$ 310.1550; Found 310.1547

10. ^{1}H and ^{13}C spectral data of the compounds

4-methyl-N-(2-(4-oxo-4-phenylbutanoyl)phenyl) benzenesulfonamide



3, 78%

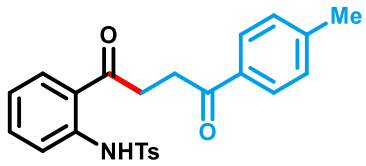
Purified by (petroleum ether/EtOAc: 80/20), 64 mg, white sticky solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.03 (d, *J* = 7.3 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 3.39 (s, 4H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.7, 198.4, 144.0, 140.1, 136.8, 136.7, 134.9, 133.5, 131.2, 129.8, 128.8, 128.2, 127.4, 122.8, 122.4, 119.4, 33.6, 32.5, 21.7

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{22}NO_4S$ 408.1264, found 408.1271.

4-methyl-N-(2-(4-oxo-4-(p-tolyl) butanoyl)phenyl) benzenesulfonamide



4, 80%

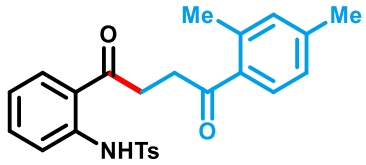
Purified by (petroleum ether/EtOAc: 95/5), 67 mg, white sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 7.97 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.04 (m, 1H), 3.40 – 3.34 (m, 4H), 2.44 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 197.8, 144.2, 143.8, 140.0, 136.6, 134.7, 134.1, 131.0, 129.6, 129.4, 128.2, 127.3, 122.7, 122.4, 119.3, 33.5, 32.3, 21.7, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{24}NO_4S$ 422.1421, found 422.1428.

N-(2-(4-(2,4-dimethylphenyl)-4-oxobutanoyl)phenyl)-4-methylbenzenesulfonamide



5, 82%

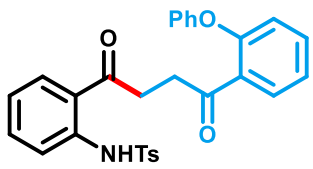
Purified by (petroleum ether/EtOAc: 80/20), 71 mg, light sticky liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.36 (s, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.68 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.13 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.10 – 7.06 (m, 2H), 3.39 – 3.34 (m, 2H), 3.30 – 3.26 (m, 2H), 2.50 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 201.3, 143.8, 142.3, 139.9, 138.8, 136.5, 134.77, 134.46, 133.0, 131.0, 129.67, 129.23, 127.3, 126.5, 122.67, 122.27, 119.2, 34.71, 33.8, 21.6, 21.5, 21.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{26}NO_4S$ 436.1577, found 436.1579.

4-methyl-N-(2-(4-oxo-4-(2-phenoxyphenyl)butanoyl)phenyl)benzenesulfonamide



6, 84%

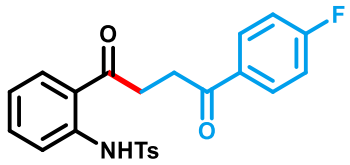
Purified by (petroleum ether/EtOAc: 80/20), 84 mg, white sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.67 (m, 3H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.41 (m, 3H), 7.22 – 7.17 (m, 4H), 7.08 (m, 3H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.42 (t, *J* = 5.9 Hz, 2H), 3.31 (t, *J* = 5.9 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 199.4, 156.5, 156.3, 143.8, 139.8, 136.5, 134.6, 133.8, 131.0, 130.65, 130.15, 129.84, 129.65, 127.3, 124.1, 123.5, 122.7, 122.5, 119.35, 119.25, 119.15, 37.3, 33.9, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{29}H_{26}NO_5S$ 500.1526, found 500.1534.

N-(2-(4-(4-fluorophenyl)-4-oxobutanoyl)phenyl)-4-methylbenzenesulfonamide



7, 72%

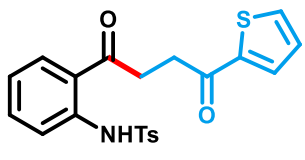
Purified by (petroleum ether/EtOAc: 80/20), 61 mg, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.05 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.95 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.08 (td, *J* = 8.0, 1.3 Hz, 1H), 3.41 – 3.37 (m, 2H), 3.37 – 3.33 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 196.7, δ 165.9 (d, *J* = 254.7 Hz), 143.9, 140.0, 136.5, 134.9, 133.1 (d, *J* = 3.0 Hz), 131.1, 130.8 (d, *J* = 9.3 Hz), 129.7, 127.3, 122.69, 122.12, 119.1, 115.8 (d, *J* = 22.0 Hz), 33.5, 32.2, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}FNO_4S$ 426.1170, found 426.1173.

4-methyl-N-(2-(4-oxo-4-(thiophen-2-yl)butanoyl)phenyl)benzenesulfonamide



8, 75%

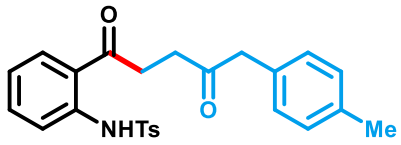
Purified by (petroleum ether/EtOAc: 80/20), 62 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.84 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.45 (td, *J* = 8.0, 1.6 Hz, 1H), 7.23 (d, *J* = 11.2 Hz, 2H), 7.19 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.11 – 7.06 (m, 1H), 3.38 (t, *J* = 5.8 Hz, 2H), 3.33 (t, *J* = 5.8 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 191.1, 143.90, 143.63, 140.0, 136.5, 134.9, 133.8, 132.2, 131.0, 129.7, 128.3, 127.3, 122.71, 122.15, 119.2, 33.5, 32.9, 21.6

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NO_4S_2$ 414.0828, found 414.0837

4-methyl-N-(2-(4-oxo-5-(p-tolyl)pentanoyl)phenyl)benzenesulfonamide



9, 75%

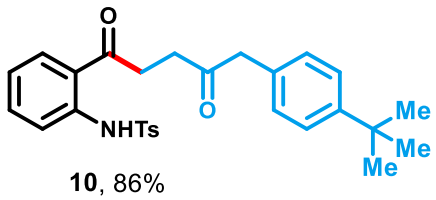
Purified by (petroleum ether/EtOAc: 80/20), 65 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.84 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.22 – 7.15 (m, 6H), 7.04 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 2H), 3.17 (t, *J* = 6.1 Hz, 2H), 2.80 (t, *J* = 6.1 Hz, 2H), 2.35 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 202.4, 143.9, 139.9, 136.8, 136.5, 134.8, 131.1, 131.0, 129.7, 129.5, 129.4, 127.3, 122.62, 122.06, 119.1, 49.9, 35.3, 33.5, 21.5, 21.1

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{26}NO_4S$ 436.1577 found 436.1583

N-(2-(5-(4-(tert-butyl)phenyl)-4-oxopentanoyl)phenyl)-4-methylbenzenesulfonamide



10, 86%

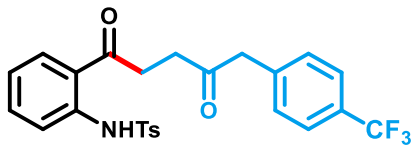
Purified by (petroleum ether/EtOAc: 80/20), 82 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.84 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.43 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.16 (m, 4H), 7.04 (t, *J* = 7.1 Hz, 1H), 3.80 (s, 2H), 3.18 (t, *J* = 6.2 Hz, 2H), 2.83 (t, *J* = 6.1 Hz, 2H), 2.33 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 202.4, 150.0, 143.9, 139.9, 136.4, 134.8, 131.1, 131.0, 129.68, 129.21, 127.3, 125.7, 122.7, 122.1, 119.2, 49.7, 35.4, 34.5, 33.5, 31.4, 21.5

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{28}H_{31}NNaO_4S$ 500.1866 found 500.1876

4-methyl-N-(2-(4-oxo-5-(4-(trifluoromethyl)phenyl)pentanoyl)phenyl)benzenesulfonamide



11, 76%

Purified by (petroleum ether/EtOAc: 70/30), 74 mg, sticky solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.33 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.46 (dt, *J* = 8.5, 4.4 Hz, 2H), 7.38 (d, *J* = 2.3 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.09 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 2H), 3.30 – 3.24 (m, 2H), 2.85 (t, *J* = 6.0 Hz, 2H), 2.37 (s, 3H).

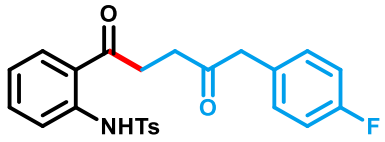
^{13}C NMR (126 MHz, $CDCl_3$) δ 205.5, 202.2, 144.0, 140.0, 136.5, 135.0, 134.1, 131.6, 131.0, 130.6, 129.7, 129.1, 127.3, 122.6, 121.7, 119.0, 48.8, 35.7, 33.6, 21.5.

Coupling carbons corresponding CF_3 groups could not be identified. **^{19}F** NMR was done to confirm presence of CF_3 groups.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{23}F_3NO_4S$ 490.1294, found 490.1295

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.51

N-(2-(5-(4-fluorophenyl)-4-oxopentanoyl)phenyl)-4-methylbenzenesulfonamide



12, 78%

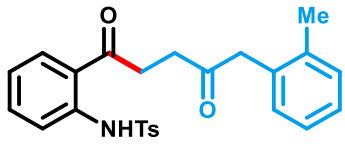
Purified by (petroleum ether/EtOAc: 80/20), 69 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 7.85 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.42 (m, 1H), 7.23 (d, *J* = 5.4 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.08 – 7.02 (m, 3H), 3.82 (s, 2H), 3.24 – 3.19 (m, 2H), 2.84 – 2.79 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.7, 202.4, 162.1 (d, *J* = 245.4 Hz), 144.0, 140.1, 136.5, 135.0, 131.2 (d, *J* = 8.1 Hz), 131.1, 129.9 (d, *J* = 3.4 Hz), 129.8, 127.4, 122.7, 121.98, 119.1, 115.7 (d, *J* = 21.6 Hz), 49.2, 35.6, 33.7, 21.6

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{22}FNNaO_4S$ 462.1146, found 462.1150

4-methyl-N-(2-(4-oxo-5-(o-tolyl)pentanoyl)phenyl)benzenesulfonamide



13, 72%

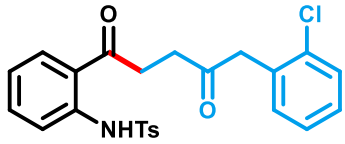
Purified by (petroleum ether/EtOAc: 80/20), 63 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.23 – 7.19 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.1 Hz, 1H), 3.85 (s, 2H), 3.22 – 3.17 (m, 2H), 2.81 – 2.76 (m, 2H), 2.33 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 202.4, 143.9, 139.9, 137.0, 136.4, 134.8, 133.0, 130.94, 130.5, 130.5, 129.7, 127.48, 127.27, 126.3, 122.62, 122.04, 119.1, 48.4, 35.4, 33.5, 21.5, 19.7

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{26}NO_4S$ 436.1577, found 436.1583

N-(2-(5-(2-chlorophenyl)-4-oxopentanoyl)phenyl)-4-methylbenzenesulfonamide



14, 75%

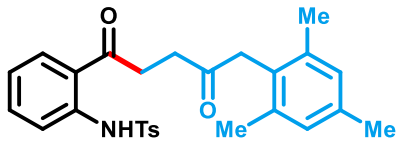
Purified by (petroleum ether/EtOAc: 80/20), 68 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 (dd, *J* = 10.7, 8.3 Hz, 3H), 7.41 (t, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 1H), 3.98 (s, 2H), 3.21 (t, *J* = 6.1 Hz, 2H), 2.86 (t, *J* = 6.1 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4, 202.3, 143.9, 139.9, 136.4, 134.81, 134.48, 132.8, 131.9, 130.9, 129.67, 129.57, 128.8, 127.31, 127.11, 122.67, 122.09, 119.2, 47.7, 35.8, 33.5, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{23}ClNO_4S$ 456.1031, found 456.1037.

N-(2-(5-mesityl-4-oxopentanoyl)phenyl)-4-methylbenzenesulfonamide



15, 85%

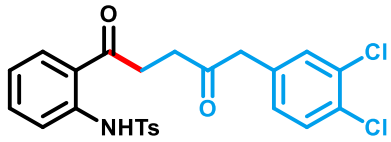
Purified by (petroleum ether/EtOAc: 80/20), 79 mg, white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.68 – 7.64 (m, 3H), 7.45 – 7.40 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.02 (m, 1H), 6.90 (s, 2H), 3.86 (s, 2H), 3.22 – 3.18 (m, 2H), 2.79 – 2.75 (m, 2H), 2.33 (s, 3H), 2.28 (s, 3H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0, 202.5, 143.9, 139.9, 136.91, 136.54, 136.42, 134.8, 131.0, 129.73, 129.06, 127.3, 122.70, 122.12, 119.2, 44.1, 35.4, 33.5, 21.5, 21.9, 20.4

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{30}NO_4S$ 464.1890, found 464.1897

N-(2-(5-(3,4-dichlorophenyl)-4-oxopentanoyl)phenyl)-4-methylbenzenesulfonamide



16, 73%

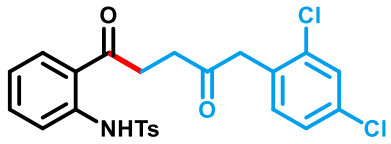
Purified by (petroleum ether/EtOAc: 80/20), 72 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.67 – 7.63 (m, 3H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.06 (ddd, *J* = 8.3, 7.4, 1.2 Hz, 1H), 3.96 (s, 2H), 3.29 – 3.22 (m, 2H), 2.90 – 2.85 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8, 202.3, 144.0, 140.0, 138.1, 136.4, 135.0, 131.0, 130.05, 129.7, 127.32, 127.26, 125.6, 125.6, 122.6, 121.8, 118.9, 49.6, 35.8, 33.6, 21.5.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}Cl_2NO_4S$ 490.0641, found 490.0645.

N-(2-(5-(2,4-dichlorophenyl)-4-oxopentanoyl)phenyl)-4-methylbenzenesulfonamide



17, 70%

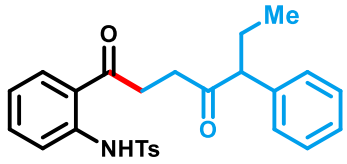
Purified by (petroleum ether/EtOAc: 80/20), 69 mg, sticky solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (s, 1H), 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.29 – 7.26 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.09 – 7.05 (m, 1H), 3.99 (s, 2H), 3.30 – 3.25 (m, 2H), 2.92 – 2.87 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9, 202.2, 143.9, 140.0, 136.4, 135.2, 134.9, 133.8, 132.66, 131.3, 131.0, 129.70, 129.38, 127.38, 127.28, 122.6, 121.9, 119.0, 47.0, 35.8, 33.5, 21.5

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{22}Cl_2NO_4S$ 490.0641 found 490.0651

4-methyl-N-(2-(4-oxo-5-phenylheptanoyl)phenyl)benzenesulfonamide



18, 78%

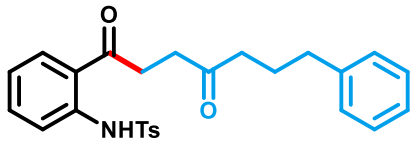
Purified by (petroleum ether/EtOAc: 80/20), 70 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.28 (m, 1H), 7.24 (d, *J* = 1.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.03 (td, *J* = 7.8, 1.2 Hz, 1H), 3.67 (t, *J* = 7.5 Hz, 1H), 3.28 – 3.18 (m, 1H), 3.03 – 2.94 (m, 1H), 2.85 – 2.75 (m, 1H), 2.66 (dt, *J* = 16.9, 5.3 Hz, 1H), 2.34 (s, 3H), 2.18 – 2.09 (m, 1H), 1.80 – 1.72 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 202.5, 143.9, 139.8, 138.9, 136.4, 134.7, 130.9, 129.66, 128.9, 128.4, 127.34, 127.27, 122.69, 122.18, 119.2, 60.9, 35.4, 33.5, 25.2, 21.5, 12.1

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{28}NO_4S$ 450.1734 found 457.1737

4-methyl-N-(2-(4-oxo-7-phenylheptanoyl)phenyl)benzenesulfonamide



19, 80%

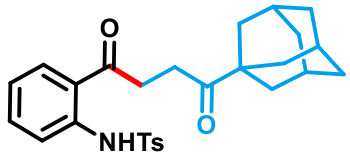
Purified by (petroleum ether/EtOAc: 80/20), 72 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (s, 1H), 7.88 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.34 – 7.28 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 5H), 7.08 – 7.02 (m, 1H), 3.21 (t, *J* = 6.1 Hz, 2H), 2.75 (t, *J* = 6.1 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.35 (s, 3H), 2.01 – 1.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9, 202.5, 143.9, 141.6, 140.0, 136.6, 134.8, 131.0, 129.7, 128.5, 128.4, 127.3, 126.0, 122.60, 122.04, 119.1, 42.0, 36.0, 35.1, 33.4, 25.3, 21.5

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{28}NO_4S$ 450.1734, found 450.1739.

N-(2-adamantan-1-yl)-4-oxobutanoyl)phenyl)-4-methylbenzenesulfonamide



20, 80%

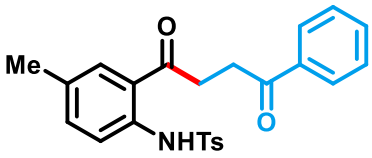
Purified by (petroleum ether/EtOAc: 80/20), 74 mg, light yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.37 (s, 1H), 7.92 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 3.18 (t, *J* = 6.2 Hz, 2H), 2.87 (t, *J* = 6.1 Hz, 2H), 2.38 (s, 3H), 2.13 – 2.08 (m, 3H), 1.91 (d, *J* = 3.2 Hz, 6H), 1.85 – 1.68 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 214.0, 202.9, 143.8, 139.8, 136.5, 134.6, 131.0, 129.7, 127.3, 122.7, 122.4, 119.1, 46.3, 38.4, 36.6, 33.2, 30.2, 28.0, 21.5

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{32}NO_4S$ 466.2047, found 466.2048

4-methyl-N-(4-methyl-2-(4-oxo-4-phenylbutanoyl)phenyl)benzenesulfonamide



21, 75%

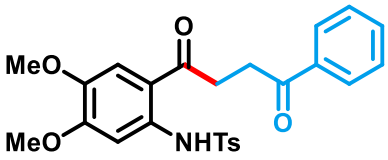
Purified by (petroleum ether/EtOAc: 80/20), 63 mg, sticky solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.10 (s, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 2.1 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.29 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.38 (m, 4H), 2.37 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 198.3, 143.7, 137.3, 136.6, 136.5, 135.5, 133.4, 132.5, 131.1, 129.6, 128.71, 128.11, 127.3, 122.7, 119.8, 33.5, 32.4, 21.5, 20.7.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{24}NO_4S$ 422.1421, found 422.1426

N-(4,5-dimethoxy-2-(4-oxo-4-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide



22, 72%

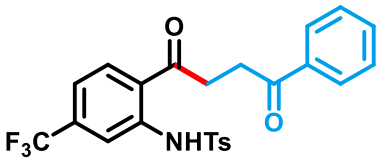
Purified by (petroleum ether/EtOAc: 50/50), 67 mg, white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.45 (s, 1H), 8.06 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 9.8 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 3.95 (s, 3H), 3.90 (s, 3H), 3.39 (t, *J* = 6.6 Hz, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 198.5, 154.3, 144.4, 143.8, 136.6, 136.3, 136.1, 133.4, 129.6, 128.7, 128.1, 127.3, 115.3, 112.4, 103.0, 56.3, 56.2, 33.3, 32.4, 21.6

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{26}NO_6S$ 468.1475, found 468.1479

4-methyl-N-(2-(4-oxo-4-phenylbutanoyl)-5-(trifluoromethyl)phenyl)benzenesulfonamide



23, 82%

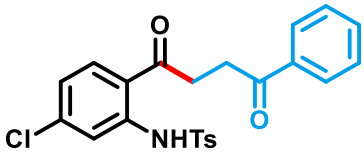
Purified by (petroleum ether/EtOAc: 70/30), 78 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.07 – 8.02 (m, 2H), 8.00 (d, *J* = 2.2 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 3.47 – 3.39 (m, 4H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 198.1, 144.5, 140.4, 136.5, 136.0, 135.8 (q, *J* = 33.4 Hz), 133.6, 131.7, 130.0, 128.8, 128.2, 127.5, 125.8 (q, *J* = 272.5 Hz), 124.2, 119.1 (q, *J* = 3.5 Hz), 116.0 (q, *J* = 3.9 Hz), 33.9, 32.5, 21.7

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{21}F_3NO_4S$ 476.1138, found 476.1144

N-(5-chloro-2-(4-oxo-4-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide



24, 80%

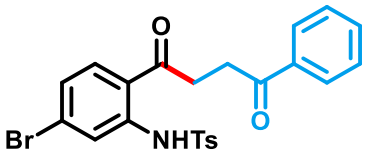
Purified by (petroleum ether/EtOAc: 80/20), 71 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1H), 8.03 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.77 – 7.69 (m, 3H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.05 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.44 – 3.34 (m, 4H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 198.1, 144.3, 141.2, 141.1, 136.5, 136.2, 133.4, 132.2, 129.8, 128.7, 128.1, 127.3, 122.82, 120.22, 118.7, 33.5, 32.4, 21.6

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}ClNO_4S$ 442.0874, found442.0884

N-(5-bromo-2-(4-oxo-4-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide



25, 76%

Purified by (petroleum ether/EtOAc: 80/20), 74 mg, white sticky solid.

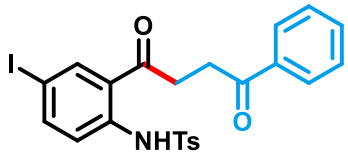
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.04 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.52 (t, *J* =

7.6 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.23 (dd, *J* = 8.6, 2.0 Hz, 1H), 3.45 – 3.33 (m, 4H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 198.1, 144.3, 141.0, 136.48, 136.16, 133.4, 132.1, 129.85, 129.75, 128.74, 128.11, 127.3, 125.8, 121.8, 120.6, 33.5, 32.4, 21.6

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}BrNO_4S$ 486.0369, found 486.0371

N-(4-iodo-2-(4-oxo-4-phenylbutanoyl)phenyl)-4-methylbenzenesulfonamide



26, 74%

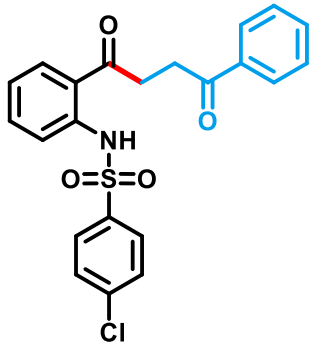
Purified by (petroleum ether/EtOAc: 80/20), 79 mg, sticky solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (s, 1H), 8.06 (d, *J* = 7.0 Hz, 2H), 7.99 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.13 – 7.10 (m, 1H), 3.41 (s, 4H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 198.3, 143.9, 139.9, 136.6, 136.5, 134.8, 133.4, 131.0, 129.7, 128.72, 128.12, 127.3, 122.72, 122.26, 119.2, 33.5, 32.4, 21.5

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}INO_4S$ 534.0231, found 534.0233

4-chloro-N-(2-(4-oxo-4-phenylbutanoyl)phenyl)benzenesulfonamide



27, 78%

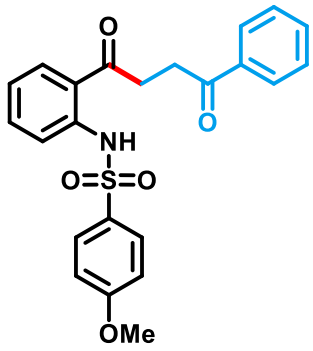
Purified by (petroleum ether/EtOAc: 80/20), 67 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 8.09 – 8.03 (m, 2H), 8.01 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.70 (d, *J* = 1.1 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.56 – 7.51 (m, 2H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.17 – 7.13 (m, 1H), 3.44 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 198.1, 139.55, 139.52, 137.9, 136.5, 134.9, 133.4, 131.2, 129.4, 128.7, 128.1, 123.2, 122.4, 119.4, 33.5, 32.4

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}ClNO_4S$ 428.0718, found 428.0721

4-methoxy-N-(2-(4-oxo-4-phenylbutanoyl)phenyl)benzenesulfonamide



28, 76%

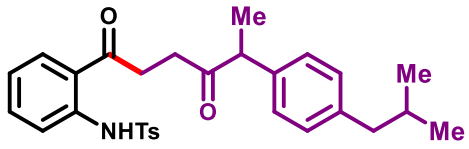
Purified by (petroleum ether/EtOAc: 60/40), 64 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.05 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.98 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (d, *J* = 9.1 Hz, 2H), 7.69 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.55 – 7.50 (m, 2H), 7.49 – 7.45 (m, 1H), 7.10 (ddd, *J* = 8.5, 7.3, 1.2 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 3.41 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 198.3, 163.1, 140.0, 136.6, 134.8, 133.4, 131.1, 129.5, 128.72, 128.66, 128.11, 122.70, 122.25, 119.2, 114.2, 55.6, 33.5, 32.4

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{22}NO_5S$ 424.1213, found 424.1220

N-(2-(5-(4-isobutylphenyl)-4-oxohexanoyl)phenyl)-4-methylbenzenesulfonamide



Ibuprofen

29, 75%

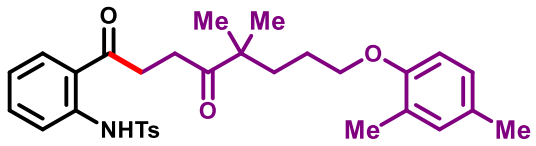
Purified by (petroleum ether/EtOAc: 80/20), 74 mg, light yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.32 (s, 1H), 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.16 (m, 4H), 7.08 – 7.04 (m, 1H), 3.90 (q, *J* = 6.9 Hz, 1H), 3.26 (m, 1H), 3.03 (dt, *J* = 18.3, 5.9 Hz, 1H), 2.81 (ddd, *J* = 18.3, 7.6, 5.4 Hz, 1H), 2.68 (dt, *J* = 18.2, 6.0 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.89 (dt, *J* = 13.6, 6.9 Hz, 1H), 1.47 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 202.6, 143.9, 140.8, 139.9, 137.7, 136.4, 134.8, 130.9, 129.7, 129.7, 127.7, 127.3, 122.7, 122.2, 119.2, 52.7, 45.0, 34.6, 33.7, 30.2, 22.4, 21.6, 17.4

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{29}H_{34}NO_4S$ 492.2203, found 492.2220

N-(2-(8-(2,4-dimethylphenoxy)-5,5-dimethyl-4-oxooctanoyl)phenyl)-4-methyl benzenesulfonamide



Gemfibrozil

30, 78%

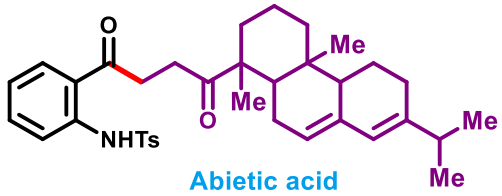
Purified by (petroleum ether/EtOAc: 75/25), 83 mg, light yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.32 (s, 1H), 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.16 (m, 4H), 7.08 – 7.04 (m, 1H), 3.90 (q, *J* = 6.9 Hz, 1H), 3.26 (ddd, *J* = 18.3, 7.7, 5.6 Hz, 1H), 3.03 (dt, *J* = 18.3, 5.9 Hz, 1H), 2.81 (ddd, *J* = 18.3, 7.6, 5.4 Hz, 1H), 2.68 (dt, *J* = 18.2, 6.0 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.89 (dt, *J* = 13.6, 6.9 Hz, 1H), 1.47 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.7, 202.6, 143.9, 140.8, 139.9, 137.7, 136.4, 134.8, 130.9, 129.73, 129.67, 127.66, 127.29, 122.66, 122.16, 119.2, 52.7, 45.0, 34.6, 33.7, 30.2, 22.4, 21.6, 17.4.

HRMS (ESI-TOF) m/z: $[M + NH_4]^+$ calcd for $C_{31}H_{41}N_2O_5S$ 553.2731, found 553.2740

N-(2-(4-(7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthren-1-yl)-4-oxobutanoyl)phenyl)-4-methylbenzenesulfonamide



Abietic acid

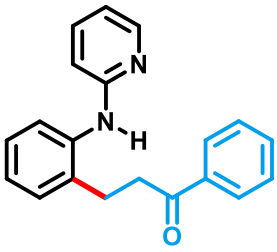
31, 80%

Purified by (petroleum ether/EtOAc: 80/20), 94 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.34 (s, 1H), 7.92 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.74 – 7.67 (m, 3H), 7.47 – 7.42 (m, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.08 (td, *J* = 7.4, 1.2 Hz, 1H), 5.81 (s, 1H), 5.40 (dd, *J* = 5.1, 2.8 Hz, 1H), 3.22 – 3.09 (m, 2H), 2.98 – 2.86 (m, 2H), 2.37 (s, 3H), 2.27 – 2.23 (m, 1H), 2.15 – 2.06 (m, 4H), 2.02 (dd, *J* = 12.0, 1.6 Hz, 2H), 1.86 (d, *J* = 8.6 Hz, 1H), 1.73 – 1.62 (m, 7H), 1.32 (s, 3H), 1.05 (d, *J* = 3.3 Hz, 3H), 1.03 (d, *J* = 3.4 Hz, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6, 203.0, 145.5, 143.9, 140.0, 136.6, 135.8, 134.8, 131.1, 130.0, 129.8, 127.4, 122.8, 122.5, 120.7, 119.3, 51.7, 51.3, 44.4, 38.6, 37.2, 35.0, 34.7, 33.7, 31.3, 27.6, 25.8, 22.7, 21.68, 21.55, 21.0, 18.3, 16.9, 14.4.

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{46}NO_4S$ 588.3142, found 588.3148



42, 90%

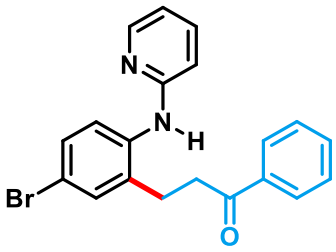
Purified by (petroleum ether/EtOAc: 85/15), 54 mg, white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 5.5, 1.9 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.57 – 7.50 (m, 2H), 7.48 – 7.40 (m, 4H), 7.29 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.21 (td, *J* = 7.7, 1.6 Hz, 1H), 7.09 (td, *J* = 7.5, 1.3 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.71 – 6.66 (m, 1H), 3.36 (t, *J* = 6.9 Hz, 2H), 3.09 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.7, 157.1, 148.2, 138.4, 137.8, 136.6, 134.7, 133.2, 130.39, 128.58, 128.13, 127.2, 124.6, 123.9, 114.4, 108.1, 39.6, 25.3

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}N_2NaO$ 325.1311, found 325.1319

3-(5-bromo-2-(pyridin-2-ylamino)phenyl)-1-phenylpropan-1-one



43, 88%

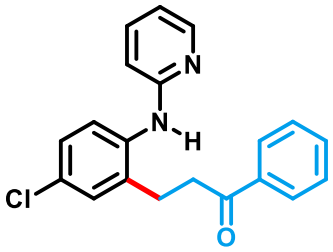
Purified by (petroleum ether/EtOAc: 85/15), 67 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.62 (s, 1H), 7.58 – 7.46 (m, 3H), 7.46 – 7.41 (m, 2H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.29 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.74 – 6.68 (m, 1H), 3.38 (t, *J* = 6.6 Hz, 2H), 3.05 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 156.5, 148.3, 137.9, 137.7, 136.4, 135.99, 133.5, 132.97, 130.0, 128.65, 128.16, 124.6, 116.3, 114.8, 108.8, 39.6, 24.7

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{17}BrN_2NaO$ 403.0416, found 403.0421

3-(5-chloro-2-(pyridin-2-ylamino)phenyl)-1-phenylpropan-1-one



44, 86%

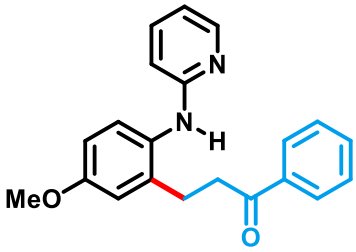
Purified by (petroleum ether/EtOAc: 85/15), 58 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 6.3, 1.6 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.74 – 7.65 (s, 1H), 7.58 – 7.52 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.75 – 6.70 (m, 2H), 3.38 (t, *J* = 6.7 Hz, 2H), 3.05 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 156.7, 148.0, 137.9, 137.2, 136.42, 136.09, 133.4, 130.1, 129.0, 128.65, 128.26, 127.2, 124.7, 114.7, 108.7, 39.5, 24.9

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}ClN_2O$ 337.1102, found 337.1137.

3-(5-methoxy-2-(pyridin-2-ylamino)phenyl)-1-phenylpropan-1-one



45, 80%

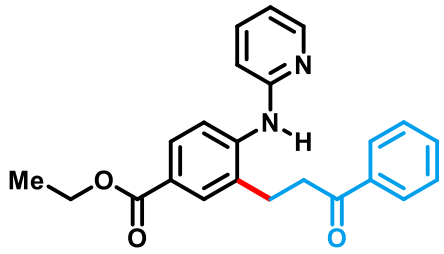
Purified by (petroleum ether/EtOAc: 80/20), 53 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 5.1, 1.9, 0.9 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.36 (m, 4H), 7.27 (d, *J* = 8.7 Hz, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 6.77 (dd, *J* = 8.6, 3.1 Hz, 1H), 6.63 – 6.59 (m, 1H), 6.45 (d, *J* = 8.5 Hz, 1H), 3.78 (s, 3H), 3.28 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 158.3, 157.5, 147.6, 138.84, 138.07, 136.6, 133.1, 130.9, 128.56, 128.12, 127.9, 115.6, 113.7, 112.6, 107.1, 55.4, 39.6, 26.1

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{20}N_2NaO_2$ 355.1417, found 355.1421

ethyl 3-(3-oxo-3-phenylpropyl)-4-(pyridin-2-ylamino)benzoate



46, 86%

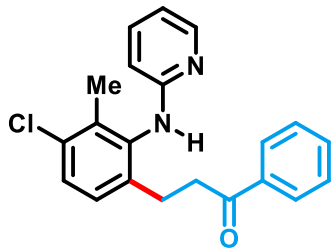
Purified by (petroleum ether/EtOAc: 80/20), 64 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.90 – 7.86 (m, 5H), 7.54 – 7.49 (m, 2H), 7.41 – 7.37 (m, 3H), 6.65 (dd, *J* = 7.0, 5.3 Hz, 1H), 6.30 (d, *J* = 8.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.32 (t, q, *J* = 7.3 Hz 2H), 3.04 (t, q, *J* = 7.3 Hz 2H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$ δ 199.5, 166.3, 157.6, 147.8, 141.0, 140.0, 138.4, 136.5, 133.2, 129.6, 128.82, 128.57, 128.12, 114.3, 107.4, 61.1, 39.6, 26.4, 14.4

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}N_2O_3$ 375.1703, found 375.1708

3-(4-chloro-3-methyl-2-(pyridin-2-ylamino)phenyl)-1-phenylpropan-1-one



47, 80%

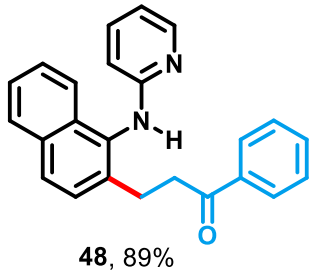
Purified by (petroleum ether/EtOAc: 85/15),56 mg, 72%, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 5.3, 2.1 Hz, 2H), 7.84 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.28 – 7.24 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.63 (td, *J* = 6.1, 1.1 Hz, 1H), 6.09 (d, *J* = 8.3 Hz, 1H), 3.23 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 157.7, 147.2, 138.67, 138.45, 137.6, 136.5, 135.6, 133.36, 133.15, 128.56, 128.28, 128.08, 127.9, 113.8, 106.7, 39.5, 26.3, 15.8

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}ClN_2O$ 351.1259, found 351.1262

1-phenyl-3-(1-(pyridin-2-ylamino)naphthalen-2-yl)propan-1-one



48, 89%

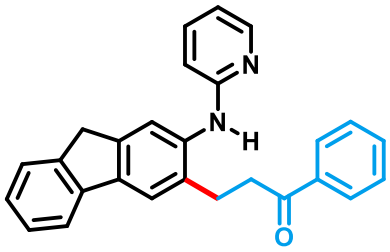
Purified by (petroleum ether/EtOAc: 85/15), 63 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 5.2, 1.1 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.90 – 7.82 (m, 3H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.50 (dd, *J* = 8.8, 7.9 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.43 – 7.36 (m, 3H), 7.34 – 7.28 (m, 1H), 6.65 (ddd, *J* = 7.2, 5.1, 1.0 Hz, 1H), 6.01 (d, *J* = 8.4 Hz, 1H), 3.35 (t, *J* = 6.8 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 158.8, 148.0, 138.1, 136.66, 136.61, 133.52, 133.13, 132.9, 131.7, 128.57, 128.20, 128.11, 128.09, 127.5, 126.7, 125.7, 123.8, 113.9, 106.9, 39.6, 26.5.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{20}N_2NaO$ 375.1468, found 375.1473.

1-phenyl-3-(2-(pyridin-2-ylamino)-9H-fluoren-3-yl)propan-1-one



49, 80%

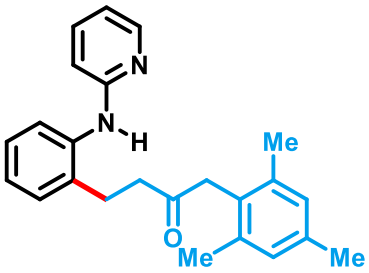
Purified by (petroleum ether/EtOAc: 85/15), 62 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 5.6, 2.0 Hz, 1H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.72 (s, 1H), 7.61 (s, 1H), 7.57 – 7.45 (m, 4H), 7.44 – 7.39 (m, 2H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.29 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.72 – 6.65 (m, 2H), 3.86 (s, 2H), 3.40 (t, *J* = 7.2 Hz, 2H), 3.17 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 157.4, 146.4, 143.4, 142.5, 141.3, 139.2, 138.7, 136.72, 136.66, 134.8, 133.1, 128.5, 128.2, 126.8, 126.4, 125.0, 121.61, 121.58, 119.6, 113.8, 108.4, 40.0, 36.7, 26.2

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{23}N_2O$ 391.1805, found 391.1816

1-mesityl-4-(2-(pyridin-2-ylamino)phenyl)butan-2-one



50, 82%

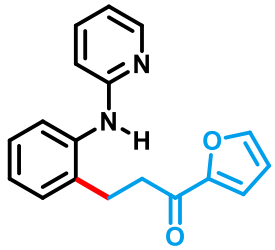
Purified by (petroleum ether/EtOAc: 85/15), 59 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 5.5, 2.4 Hz, 1H), 7.61 (s, 1H), 7.49 – 7.39 (m, 2H), 7.24 – 7.14 (m, 2H), 7.07 (td, *J* = 7.5, 1.5 Hz, 1H), 6.82 (s, 2H), 6.73 – 6.66 (m, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 3.65 (s, 2H), 2.91 (t, *J* = 7.0 Hz, 2H), 2.75 (t, *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 2.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 157.1, 147.4, 138.1, 136.70, 136.43, 135.0, 130.3, 129.36, 129.00, 128.9, 127.2, 124.84, 124.33, 120.6, 114.2, 108.1, 44.3, 42.4, 25.1, 20.9, 20.3

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{26}N_2NaO$ 381.1937, found 381.1931.

1-(furan-2-yl)-3-(2-(pyridin-2-ylamino)phenyl)propan-1-one



51, 82%

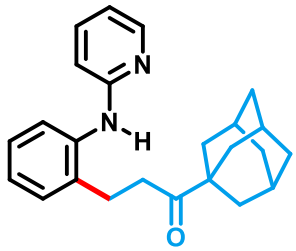
Purified by (petroleum ether/EtOAc: 85/15), 48 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 6.1, 1.9 Hz, 1H), 7.94 (s, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.27 – 7.24 (m, 1H), 7.18 (td, *J* = 7.7, 1.9 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 7.07 (td, *J* = 7.5, 1.5 Hz, 1H), 6.69 – 6.61 (m, 2H), 6.44 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.16 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 157.2, 152.4, 147.2, 146.5, 138.21, 138.14, 135.0, 130.4, 127.3, 124.9, 124.3, 117.4, 114.1, 112.2, 108.2, 39.3, 25.4

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{16}N_2NaO_2$ 315.1104, found 315.1120

1-((1s,3s)-adamantan-1-yl)-3-(2-(pyridin-2-ylamino)phenyl)propan-1-one



52, 88%

Purified by (petroleum ether/EtOAc: 85/15), 63 mg, light yellow liquid.

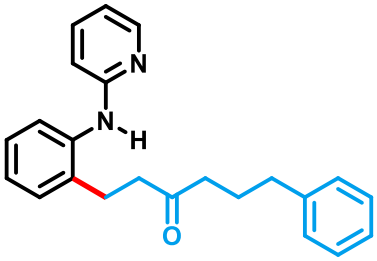
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 5.5 Hz, 1H), 7.50 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.39 (s, 1H), 7.19 (t, *J* = 7.0 Hz, 2H), 7.06 (td, *J* = 7.3, 1.6 Hz, 1H), 6.73 – 6.61

(m, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 6.3 Hz, 2H), 2.00 – 1.95 (m, 3H), 1.69 (d, *J* = 3.0 Hz, 6H), 1.68 – 1.57 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.7, 157.1, 148.1, 137.7, 134.9, 130.3, 127.0, 124.4, 123.8, 120.4, 114.2, 108.1, 46.2, 38.1, 37.2, 36.5, 27.9, 25.1

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{29}N_2O$ 361.2274, found 361.2293

6-phenyl-1-(2-(pyridin-2-ylamino)phenyl)hexan-3-one



53, 92%

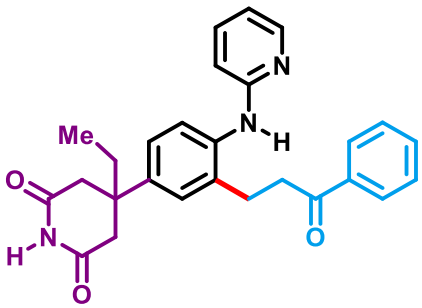
Purified by (petroleum ether/EtOAc: 85/15), 63 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 5.5, 2.0 Hz, 1H), 7.63 (s, 1H), 7.50 – 7.42 (m, 2H), 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 3H), 7.13 – 7.06 (m, 3H), 6.71 – 6.65 (m, 2H), 2.89 (t, *J* = 6.9 Hz, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.90 – 1.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 157.1, 147.6, 141.5, 138.1, 138.0, 134.7, 130.3, 128.46, 128.38, 127.2, 125.9, 124.6, 123.9, 114.2, 108.1, 43.5, 41.9, 35.0, 25.1, 24.9

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{25}N_2O$ 345.1961, found 345.1988

4-ethyl-4-(3-(3-oxo-3-phenylpropyl)-4-(pyridin-2-ylamino)phenyl)piperidine-2,6-dione



Aminoglutethimide

54, 75%

Purified by (petroleum ether/EtOAc: 75/25), 66 mg, sticky solid.

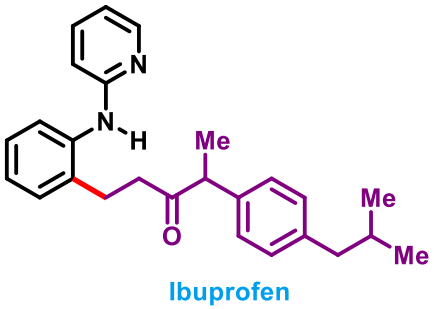
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.21 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.90 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.78 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.40 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.71

(ddd, *J* = 7.3, 5.0, 0.9 Hz, 1H), 3.32 (t, *J* = 6.8 Hz, 2H), 3.08 (t, *J* = 6.8 Hz, 2H), 2.60 – 2.53 (m, 1H), 2.49 – 2.42 (m, 1H), 2.37 – 2.32 (m, 1H), 2.23 – 2.18 (m, 1H), 2.01 (dd, *J* = 14.4, 7.1 Hz, 1H), 1.87 (dd, *J* = 14.4, 7.1 Hz, 1H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 175.5, 172.7, 156.7, 147.9, 137.9, 136.5, 134.55, 134.12, 133.3, 128.61, 128.42, 128.15, 124.9, 123.3, 114.6, 108.7, 50.6, 39.5, 33.0, 29.4, 26.9, 25.7, 9.07

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{27}N_3NaO_3$ 464.1945, found 464.1949

4-(4-isobutylphenyl)-1-(2-(pyridin-2-ylamino)phenyl)pentan-3-one



Ibuprofen

55, 90%

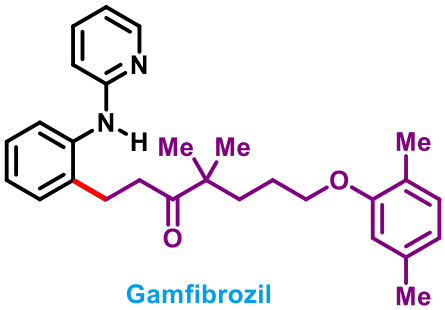
Purified by (petroleum ether/EtOAc: 85/15), 70 mg, light yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 5.3, 2.4 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.19 – 7.13 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.98 (m, 3H), 6.97 – 6.94 (m, 2H), 6.68 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 3.64 (q, *J* = 6.9 Hz, 1H), 2.87 – 2.80 (m, 2H), 2.75 – 2.65 (m, 2H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.88 – 1.78 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.0, 157.1, 148.3, 140.5, 138.3, 137.6, 137.5, 134.4, 130.2, 129.6, 127.47, 127.01, 124.4, 123.7, 114.3, 108.0, 52.7, 45.0, 41.6, 30.2, 25.1, 22.4, 17.3

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{26}H_{30}N_2NaO$ 409.2250, found 409.2248.

7-(2,5-dimethylphenoxy)-4,4-dimethyl-1-(2-(pyridin-2-ylamino)phenyl)heptan-3-one



Gamfibrozil

56, 86%

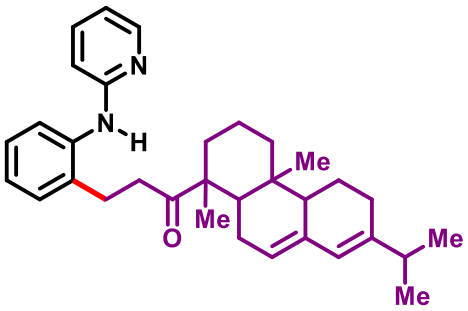
Purified by (petroleum ether/EtOAc: 85/15), 74 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 5.2, 2.3 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.31 (s, 1H), 7.24 – 7.17 (m, 2H), 7.06 (td, *J* = 7.4, 1.3 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.74 – 6.65 (m, 3H), 6.57 (s, 1H), 3.77 (t, *J* = 6.1 Hz, 2H), 3.08 – 2.67 (m, 4H), 2.32 (s, 3H), 2.15 (s, 3H), 1.67 – 1.60 (m, 2H), 1.51 – 1.43 (m, 2H), 1.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.8, 157.2, 156.9, 148.4, 138.4, 137.6, 136.5, 134.6, 130.4, 130.3, 127.1, 124.4, 123.76, 123.51, 120.8, 114.4, 111.9, 108.1, 67.8, 47.3, 38.1, 36.5, 25.2, 24.83, 24.30, 21.5, 15.9

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{35}N_2O_2$ 431.2693, found 431.2713

1-(7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthren-1-yl)-3-(2-(pyridin-2-ylamino)phenyl)propan-1-one



Abietic acid

57, 84%

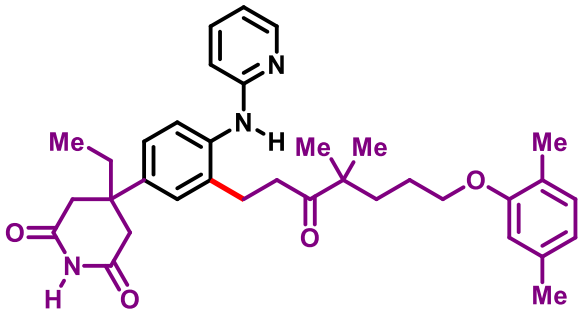
Purified by (petroleum ether/EtOAc: 85/15), 81 mg, light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.46 – 7.40 (m, 1H), 7.33 – 7.32 (m, 1H), 7.22 – 7.17 (m, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.70 – 6.64 (m, 2H), 5.73 (s, 1H), 5.19 (d, *J* = 5.1 Hz, 1H), 2.91 – 2.84 (m, 2H), 2.83 – 2.77 (m, 2H), 2.24 – 2.18 (m, 2H), 2.06 (m, *J* = 7.9, 4.2 Hz, 2H), 1.87 (d, *J* = 1.5 Hz, 3H), 1.53 – 1.47 (m, 2H), 1.44 – 1.39 (m, 1H), 1.32 (d, *J* = 5.3 Hz, 2H), 1.25 (s, 2H), 1.22 (d, *J* = 6.9 Hz, 1H), 1.15 (s, 3H), 1.02 (d, *J* = 3.3 Hz, 3H), 1.00 (d, *J* = 3.3 Hz, 3H), 0.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.2, 157.3, 148.3, 145.3, 138.3, 137.8, 134.9, 130.5, 129.4, 127.2, 124.6, 124.0, 122.6, 120.5, 114.4, 108.1, 51.8, 51.1, 44.2, 38.4, 37.9, 36.2, 35.0, 34.5, 27.6, 25.9, 25.5, 22.6, 21.5, 20.97, 18.2, 16.5, 14.2

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{43}N_2O$ 483.3370, found 483.3381

4-(3-(7-(2,5-dimethylphenoxy)-4,4-dimethyl-3-oxoheptyl)-4-(pyridin-2-ylamino)phenyl)-4-ethylpiperidine-2,6-dione



Aminoglutethimide-Gemfibrozil

58, 88%

Purified by (petroleum ether/EtOAc: 75/25), 100 mg, sticky solid.

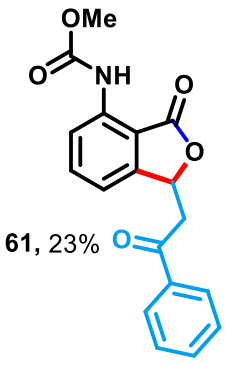
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}N_2$ 297.1386, found 297.1388.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.19 (dd, *J* = 5.9, 2.0 Hz, 1H), 7.88 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.43 (ddd, *J* = 8.8, 7.2, 2.0 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.71 – 6.63 (m, 3H), 6.56 (s, 1H), 3.78 (t, *J* = 6.1 Hz, 2H), 2.95 – 2.88 (m, 2H), 2.86 – 2.80 (m, 2H), 2.61 – 2.55 (m, 1H), 2.51 – 2.43 (m, 1H), 2.37 – 2.32 (m, 1H), 2.29 (s, 3H), 2.20 (dd, *J* = 13.4, 4.8 Hz, 1H), 2.12 (s, 3H), 2.10 – 1.95 (m, 2H), 1.88 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.63 – 1.59 (m, 1H), 1.52 – 1.46 (m, 2H), 1.03 (s, 6H), 0.85 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.5, 175.8, 173.1, 156.9, 156.9, 147.6, 138.2, 137.8, 136.5, 135.2, 134.4, 130.4, 128.5, 125.0, 123.80, 123.47, 120.8, 114.5, 112.0, 108.5, 67.8, 50.6, 47.3, 37.8, 36.2, 33.0, 29.4, 27.0, 25.6, 24.9, 24.3, 24.2, 21.5, 15.9, 9.1

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{35}H_{44}N_3O_4$ 570.3326, found 570.3330

methyl (S)-(3-oxo-1-(2-oxo-2-phenylethyl)-1,3-dihydroisobenzofuran-4-yl)carbamate



61, 23%

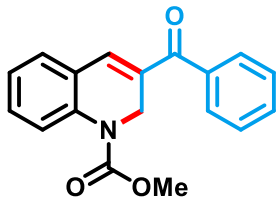
Purified by (petroleum ether/EtOAc: 80/20), 15 mg, sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.95 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.51 – 7.47 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.16 (t, *J* = 6.5 Hz, 1H), 3.82 (s, 3H), 3.73 (dd, *J* = 17.6, 6.1 Hz, 1H), 3.41 (dd, *J* = 17.6, 6.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 171.1, 153.8, 150.1, 139.1, 136.6, 134.1, 130.3, 129.0, 128.3, 117.3, 115.8, 111.4, 77.6, 52.8, 43.6

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{15}NNaO_5$ 348.0842, found 348.0843

methyl 3-benzoylquinoline-1(2H)-carboxylate



62, 76%

Purified by (petroleum ether/EtOAc: 85/15), 45 mg, light brown liquid.

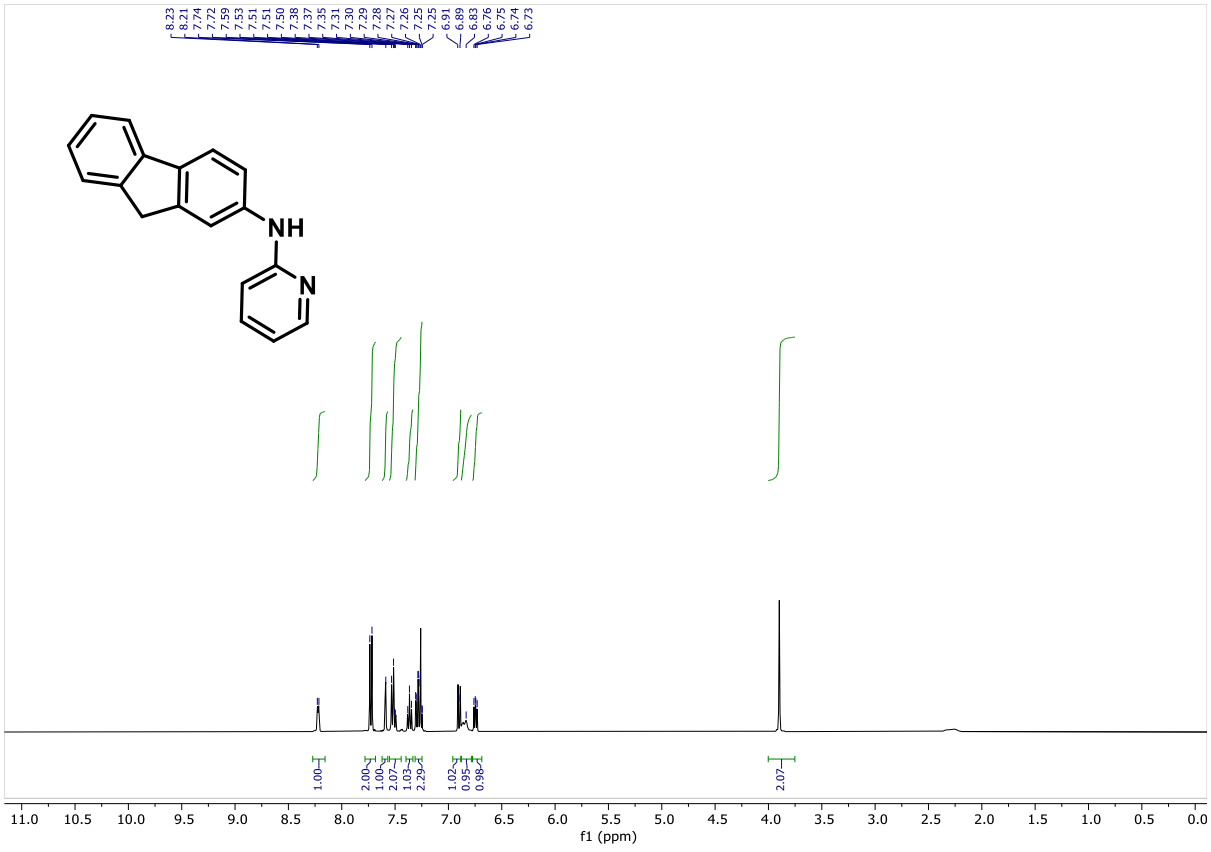
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 3H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.20 – 7.09 (m, 3H), 4.82 (d, *J* = 1.4 Hz, 2H), 3.85 (s, 3H).

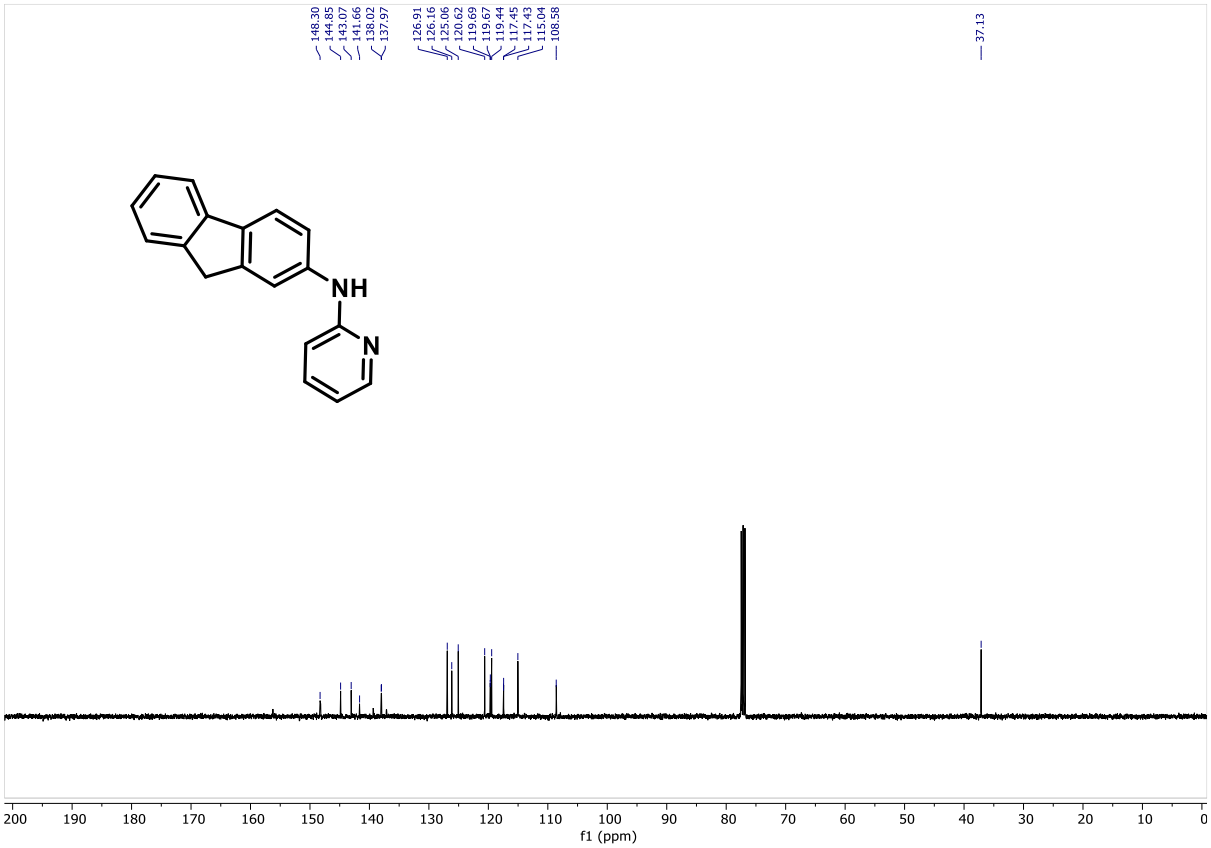
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 154.6, 138.26, 138.16, 137.6, 134.2, 132.2, 130.8, 129.3, 129.1, 128.6, 126.6, 124.6, 123.7, 53.4, 43.3

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3$ 294.1125, found 294.1125.

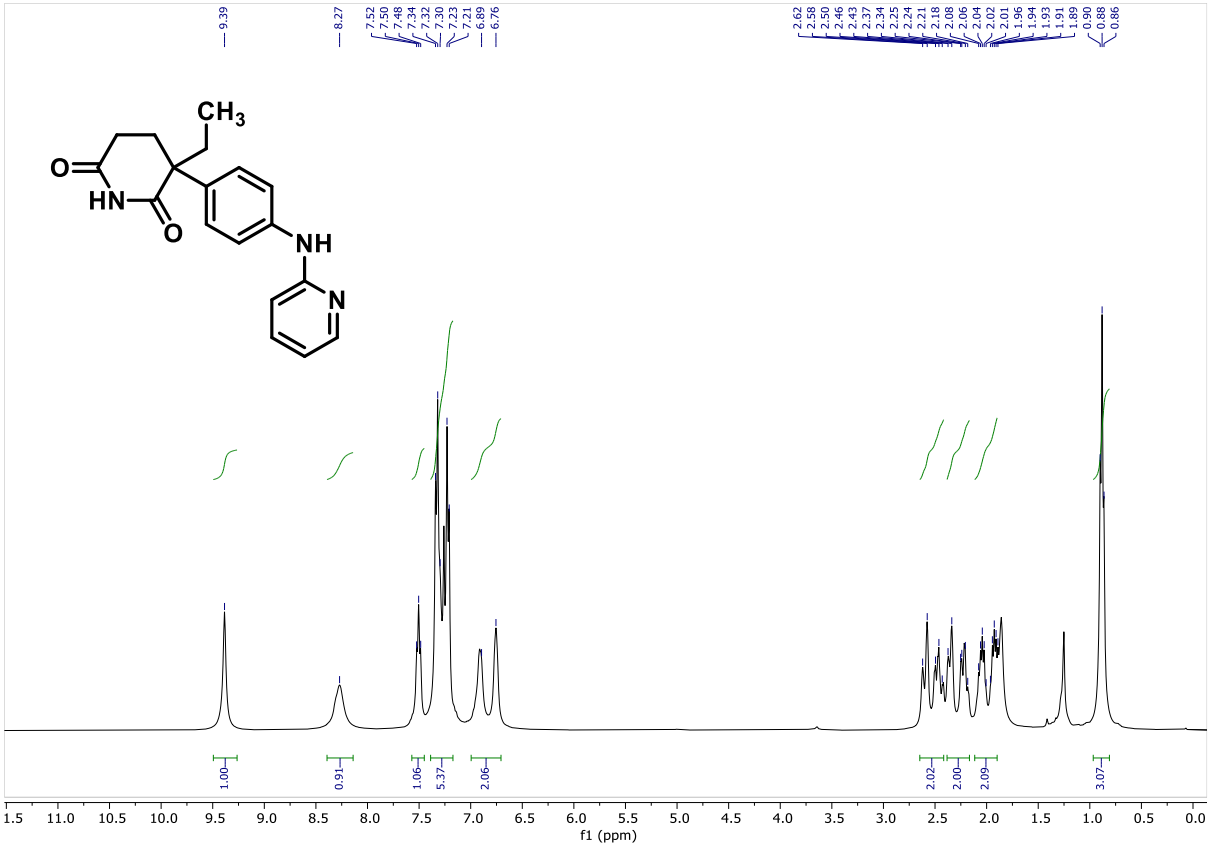
11. ^{1}H and ^{13}C NMR spectra of the compounds

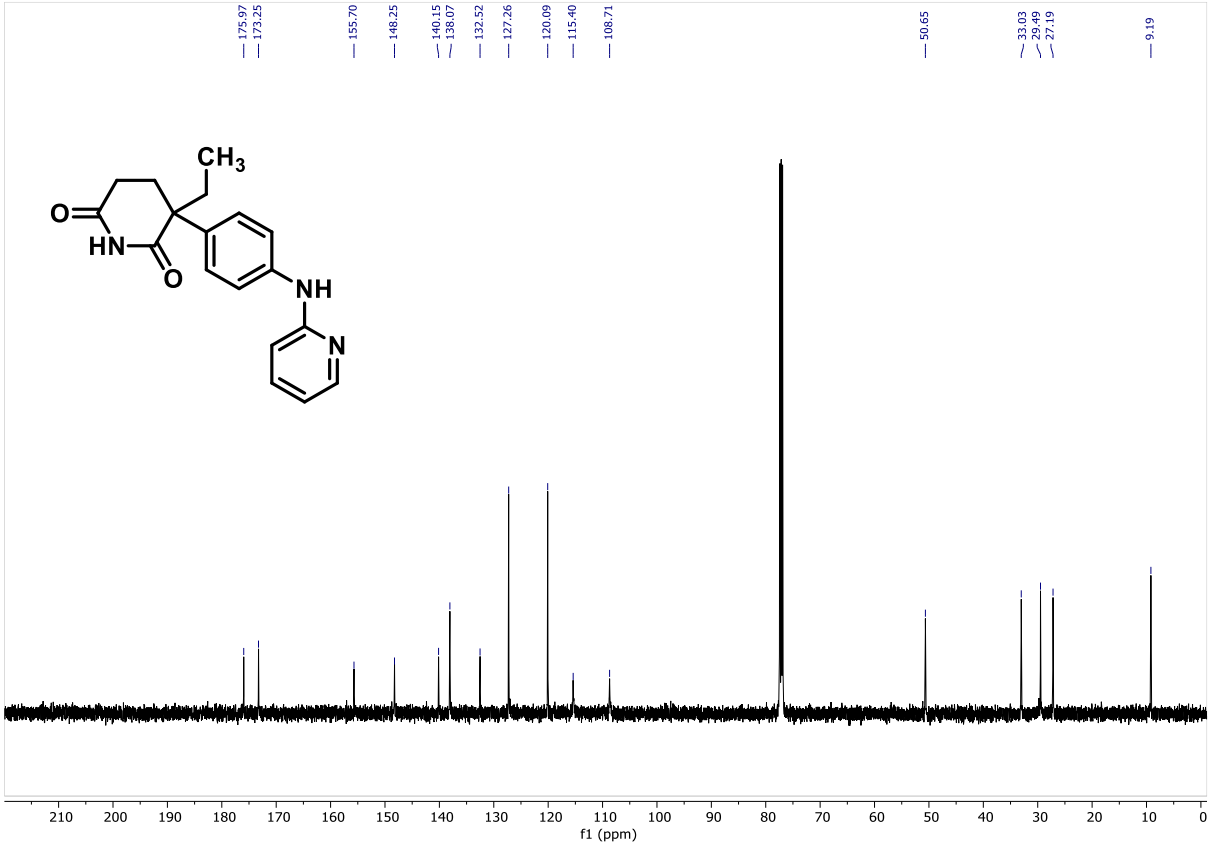
41b



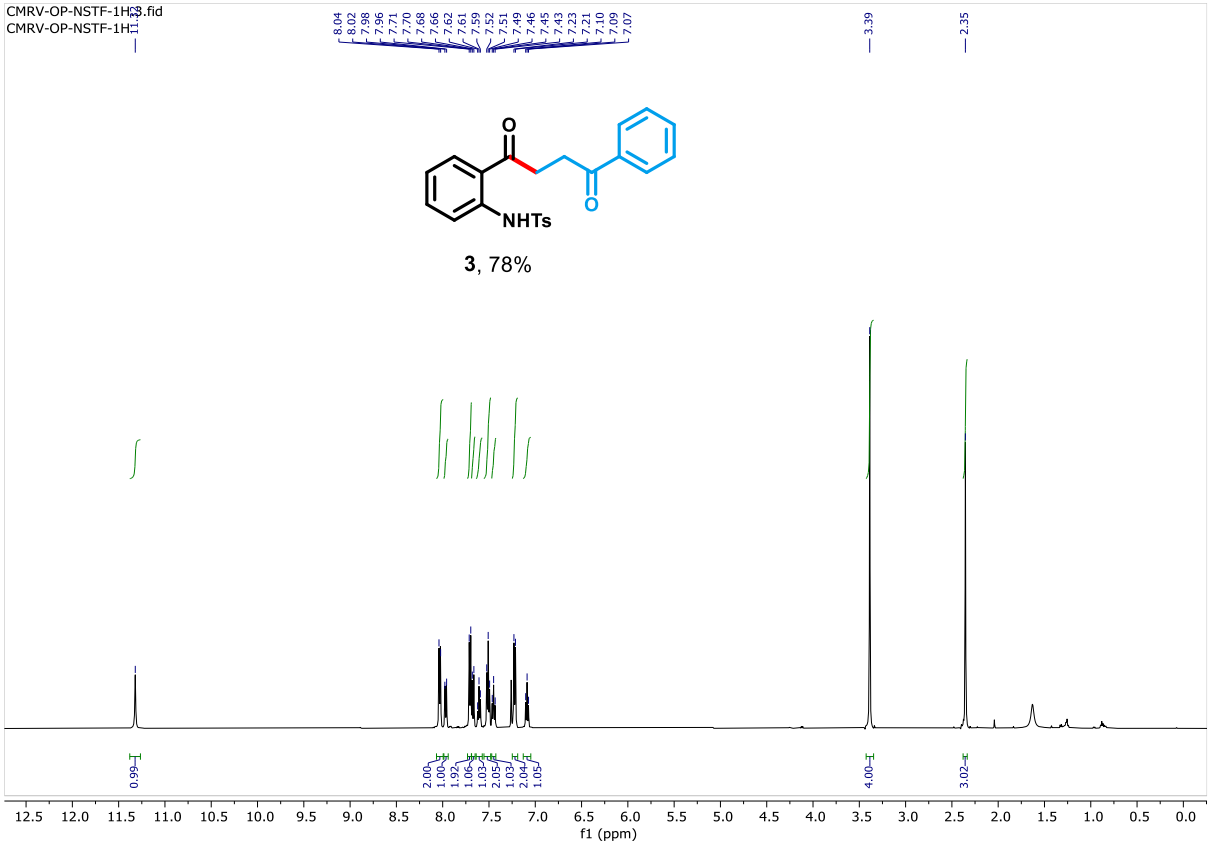

148.30
144.85
143.07
141.66
138.02
137.97
126.91
126.16
125.06
120.62
119.69
119.67
119.44
117.45
117.43
115.04
108.58
37.13
NH
N
f1 (ppm)

41c

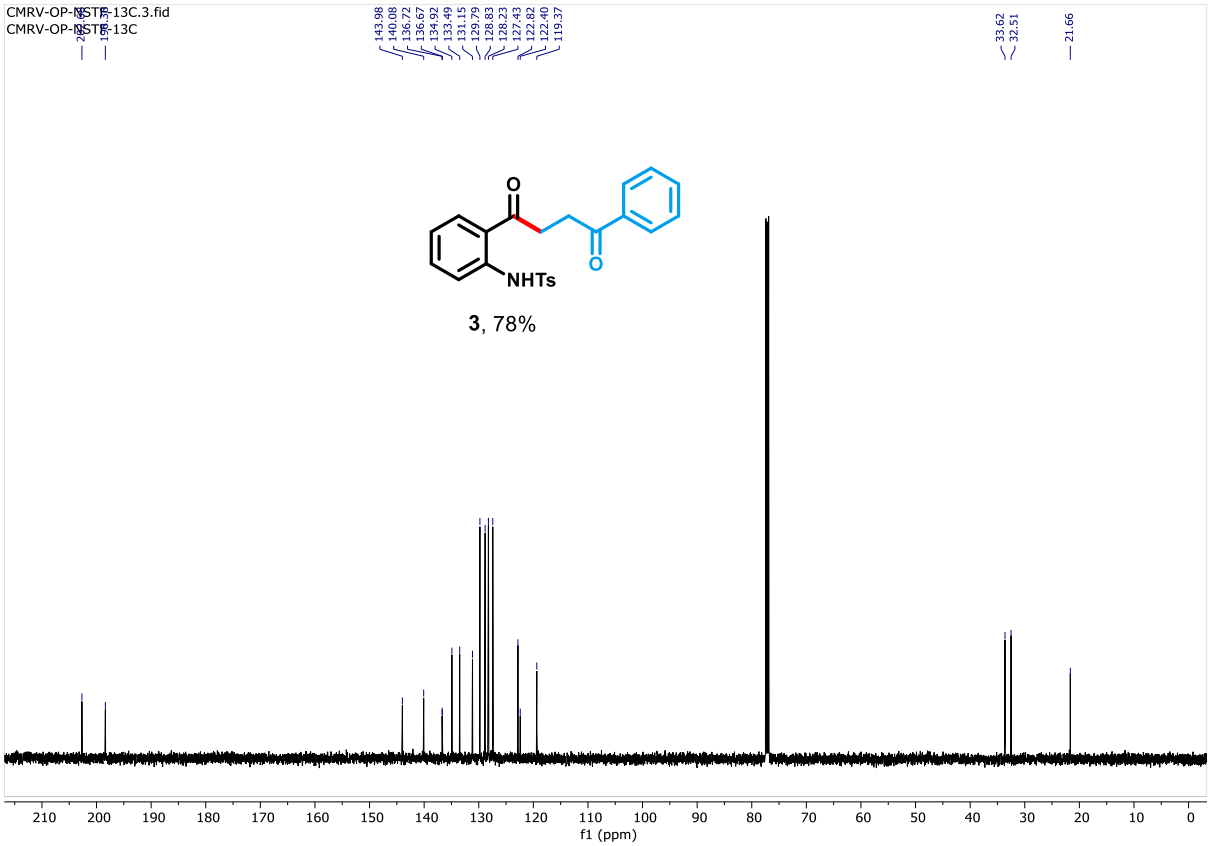

9.39
8.27
7.52
7.50
7.48
7.34
7.32
7.30
7.23
7.21
6.89
6.76
2.62
2.58
2.50
2.46
2.43
2.37
2.34
2.25
2.24
2.21
2.18
2.08
2.06
2.04
2.02
2.01
1.96
1.94
1.93
1.91
1.89
0.90
0.88
0.86
CH3
O
HN
O
NH
N
1.00
0.91
1.06
5.37
2.06
2.02
2.00
2.09
3.07
f1 (ppm)


175.97
173.25
155.70
148.25
140.15
138.07
132.52
127.26
120.09
115.40
108.71
50.65
33.03
29.49
27.19
9.19
CH3
O
HN
O
NH
N
f1 (ppm)

3

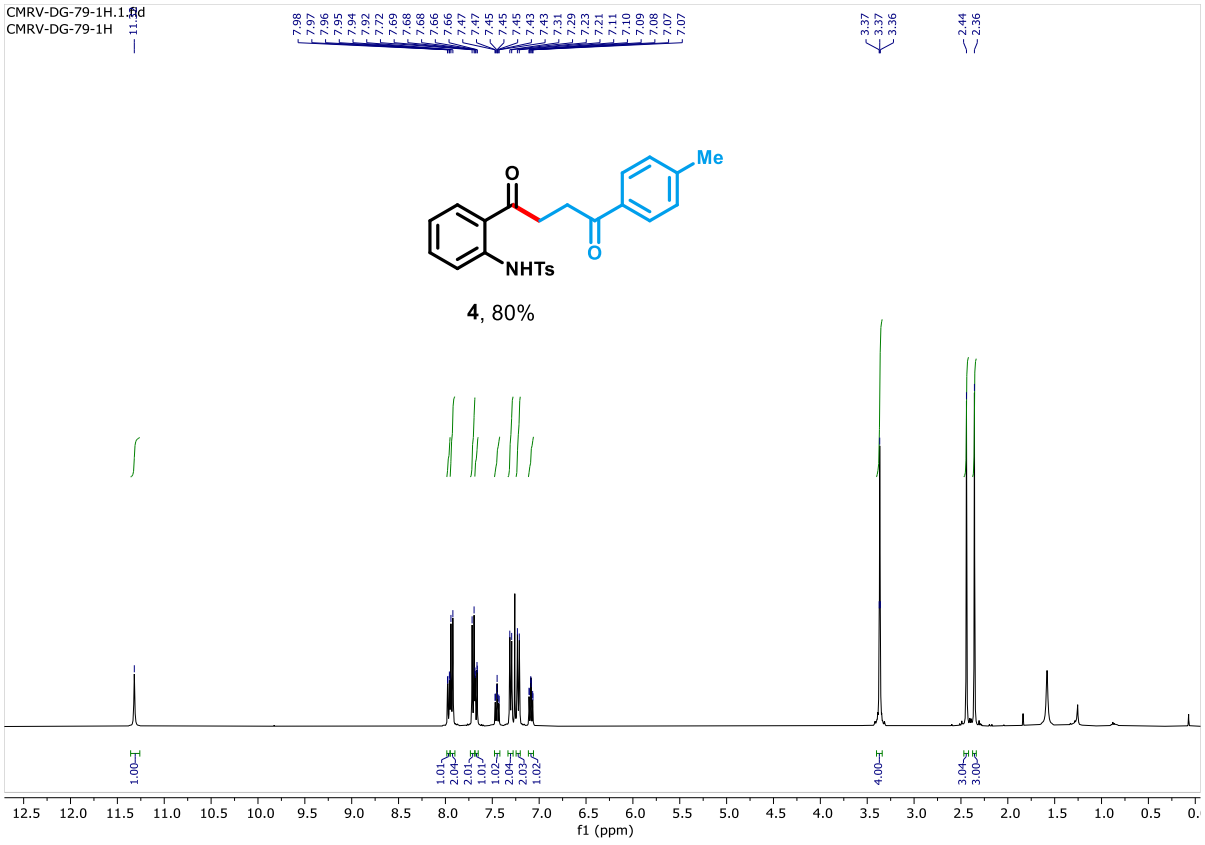

CMRV-OP-NSTF-1H-3.fid
CMRV-OP-NSTF-1H-
11.
8.04
8.02
7.98
7.96
7.71
7.70
7.68
7.66
7.62
7.61
7.59
7.52
7.51
7.49
7.46
7.45
7.43
7.23
7.21
7.10
7.09
7.07
3.39
2.35
O
O
NHTs
0.99
2.00
1.00
1.92
1.06
1.03
2.05
1.03
2.04
1.05
4.00
3.02
f1 (ppm)

3, 78%

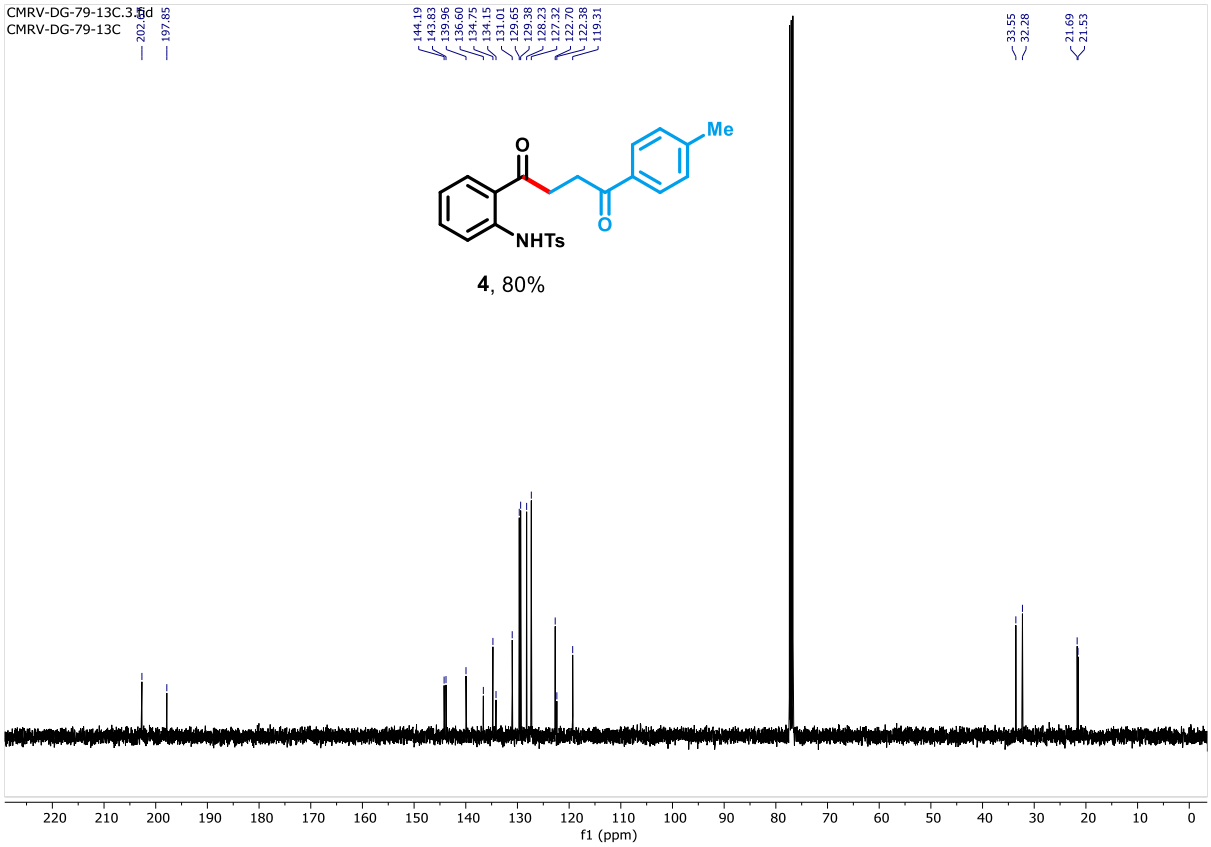

CMRV-OP-NSTF-13C.3.fid
CMRV-OP-NSTF-13C
143.98
140.08
136.72
136.67
134.92
133.49
131.15
129.79
128.83
128.23
127.43
122.82
122.40
119.37
33.62
32.51
21.66
O
O
NHTs
f1 (ppm)

3, 78%

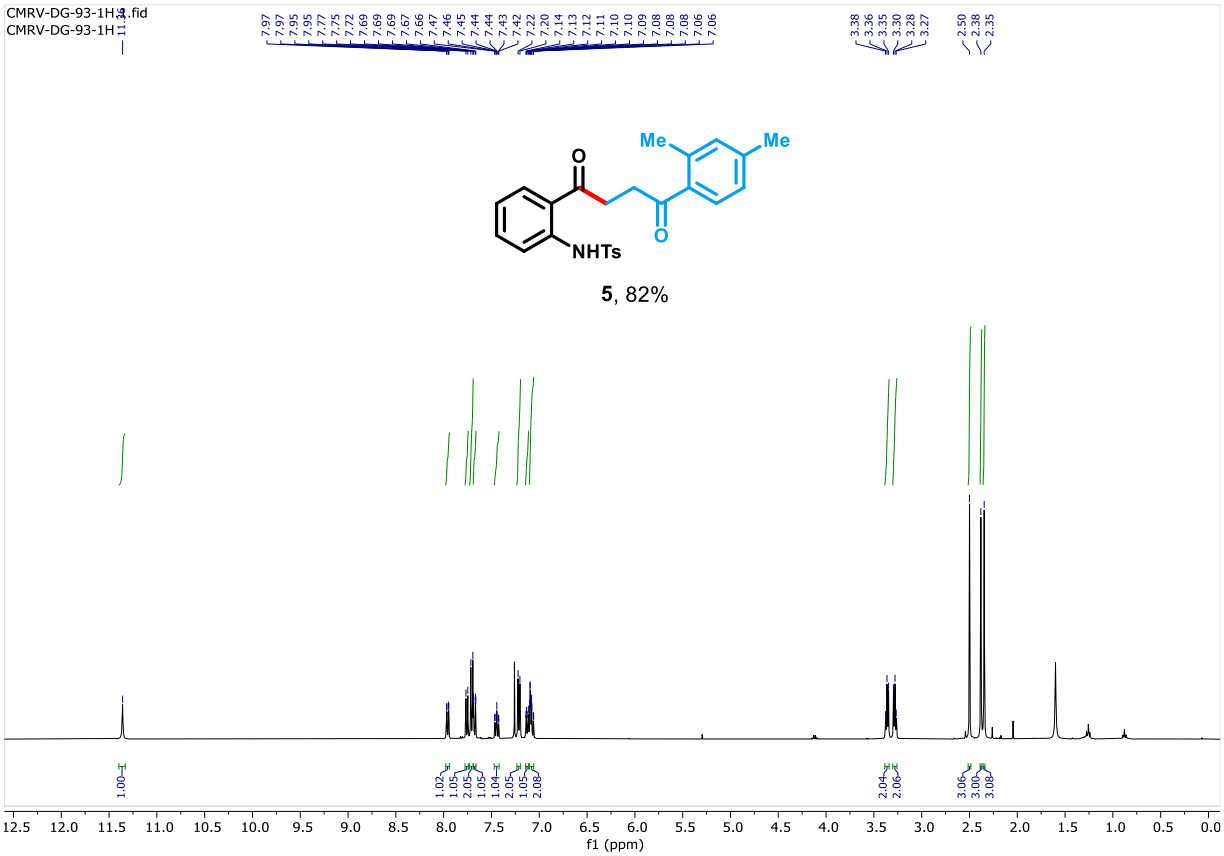
4

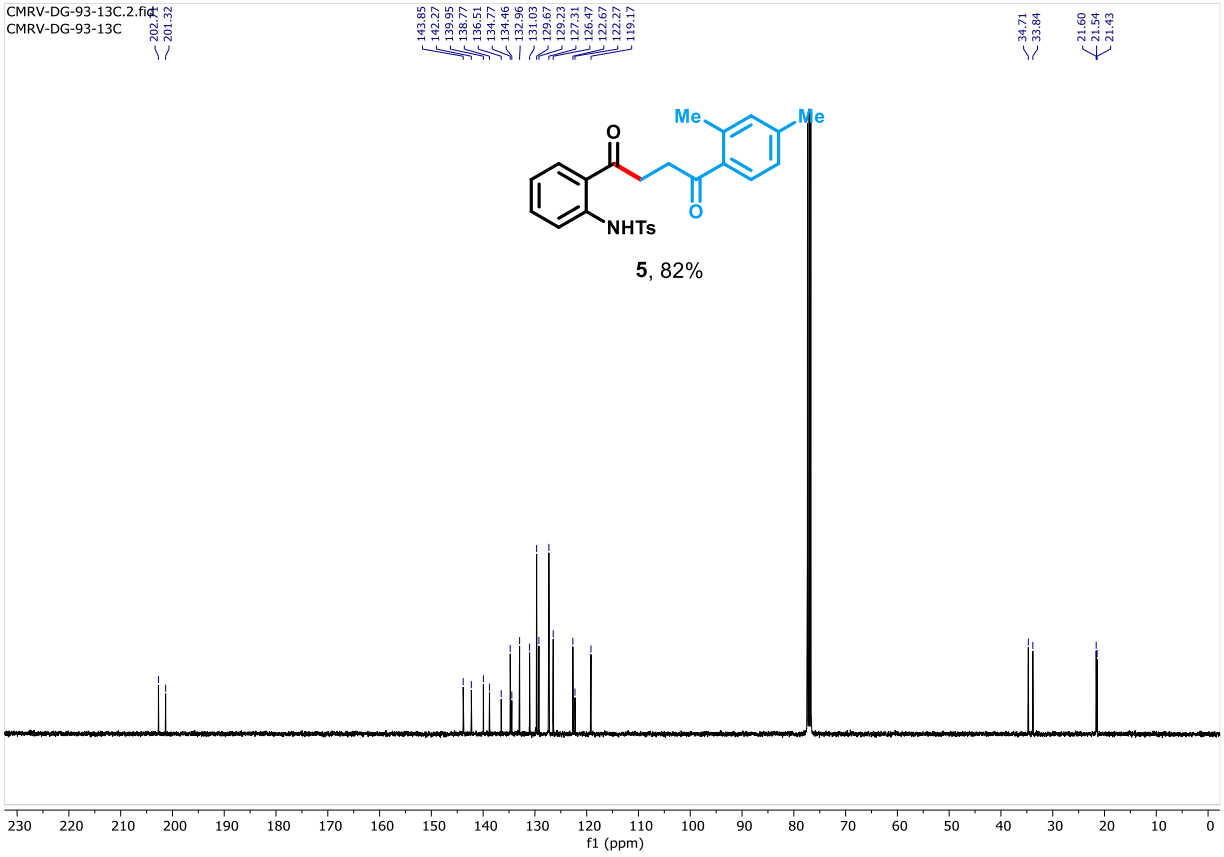

CMRV-DG-79-1H.1.fid
CMRV-DG-79-1H
11.64
7.98
7.97
7.96
7.95
7.94
7.92
7.72
7.69
7.68
7.68
7.66
7.66
7.47
7.47
7.45
7.45
7.45
7.43
7.31
7.29
7.23
7.21
7.11
7.10
7.09
7.08
7.07
7.07
3.37
3.37
3.36
2.44
2.36
Me
O
O
NHTs
1.00
1.01
2.04
2.01
1.01
1.02
2.04
2.03
1.02
4.00
3.04
3.00
f1 (ppm)

4, 80%

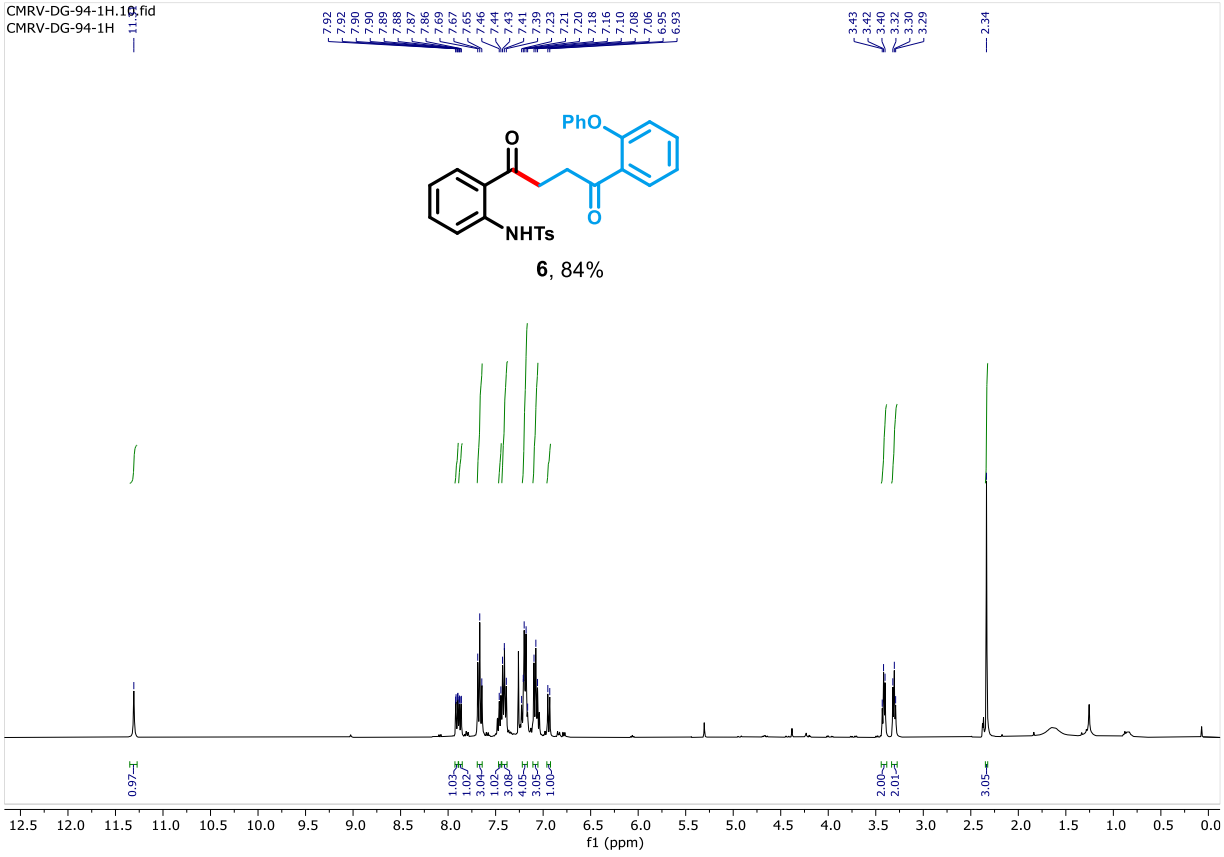

CMRV-DG-79-13C.3.fid
CMRV-DG-79-13C
202.65
197.85
144.19
143.83
139.96
136.60
134.75
134.15
131.01
129.65
129.38
128.23
127.32
122.70
122.38
119.31
33.55
32.28
21.69
21.53
O
Me
O
NHTs
4, 80%
f1 (ppm)

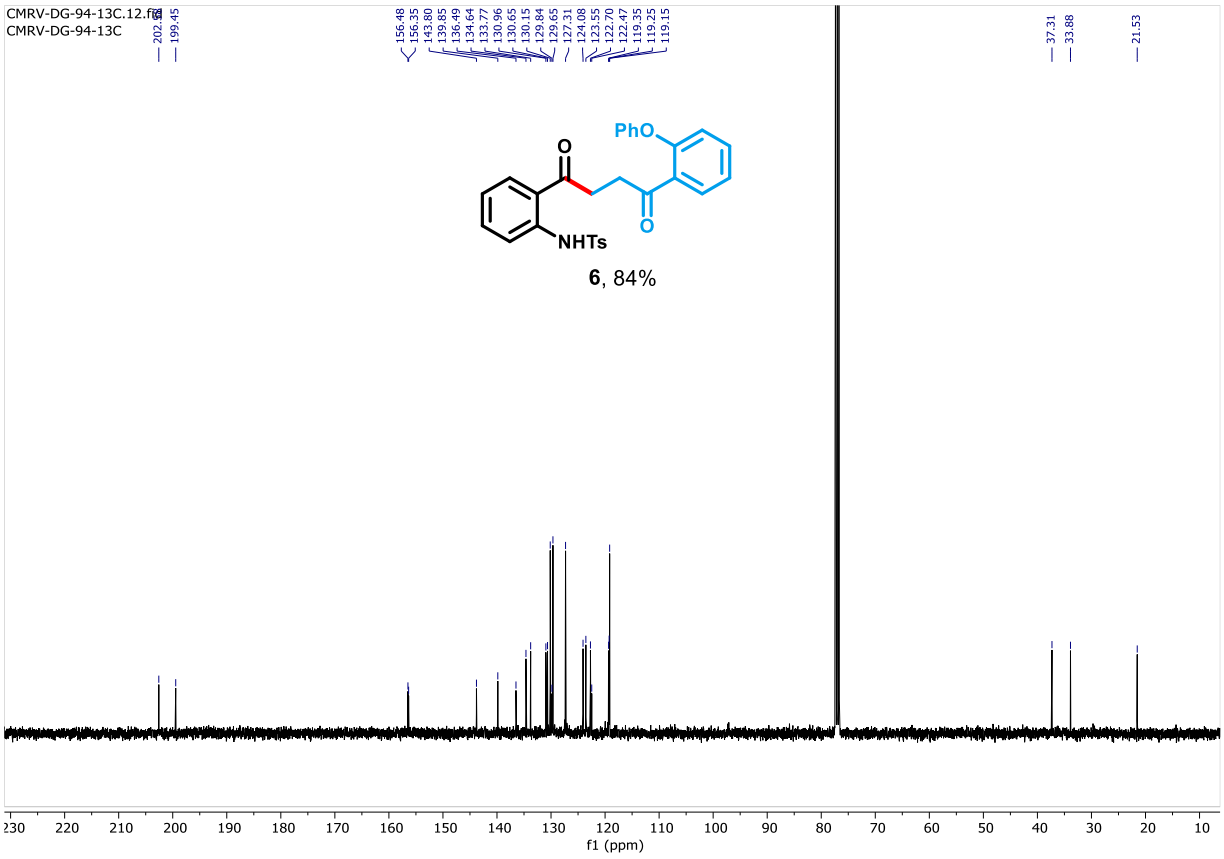
5


CMRV-DG-93-1H.4.fid
CMRV-DG-93-1H
11.34
7.97
7.97
7.95
7.95
7.77
7.75
7.72
7.69
7.69
7.67
7.66
7.47
7.46
7.45
7.44
7.44
7.43
7.42
7.22
7.20
7.14
7.13
7.12
7.11
7.10
7.10
7.09
7.08
7.08
7.08
7.06
7.06
3.38
3.36
3.35
3.30
3.28
3.27
2.50
2.38
2.35
Me
Me
O
O
NHTs
5, 82%
1.00
1.02
1.05
2.05
1.05
1.04
2.05
1.05
2.08
2.04
2.06
3.06
3.00
3.08
f1 (ppm)


CMRV-DG-93-13C.2.fid
CMRV-DG-93-13C
Me
Me
O
O
NHTs
5, 82%
f1 (ppm)

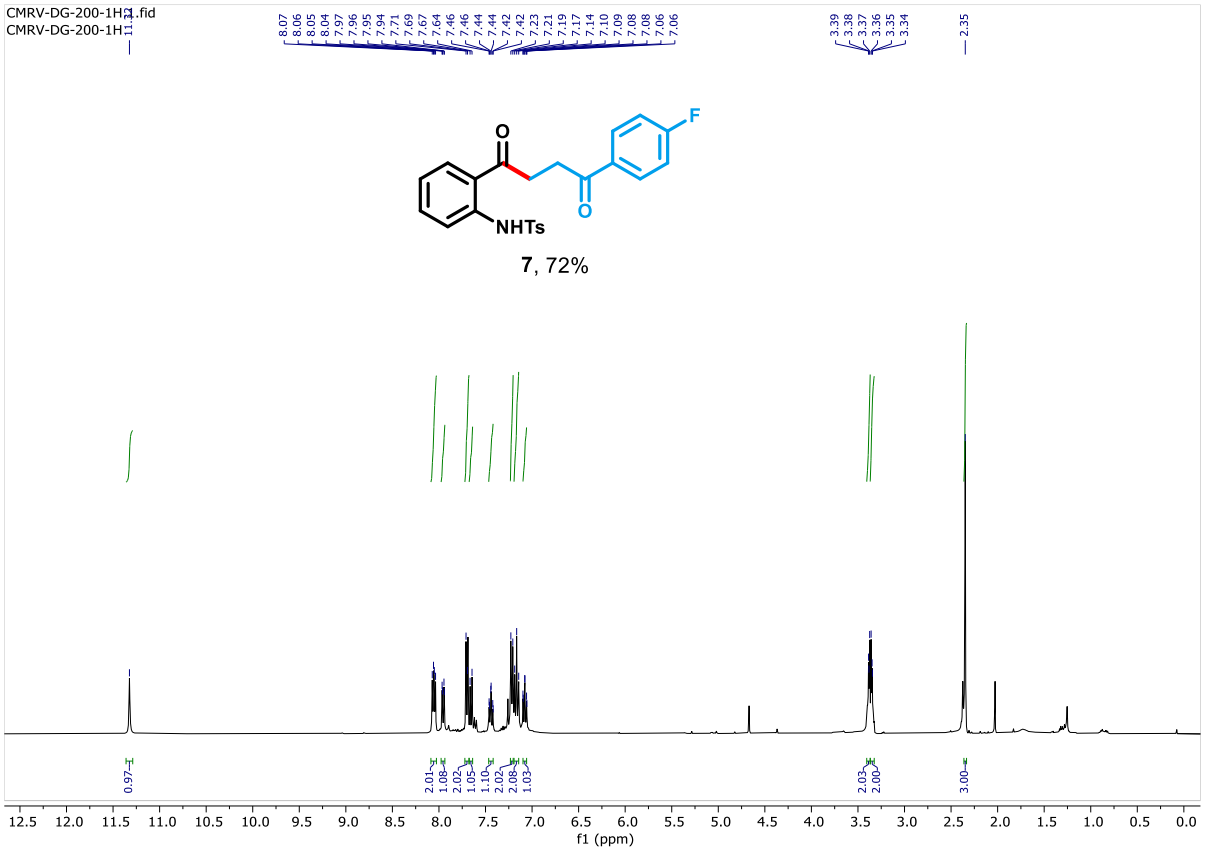
6


CMRV-DG-94-1H.10.fid
CMRV-DG-94-1H
PhO
O
O
NHTs
6, 84%
f1 (ppm)

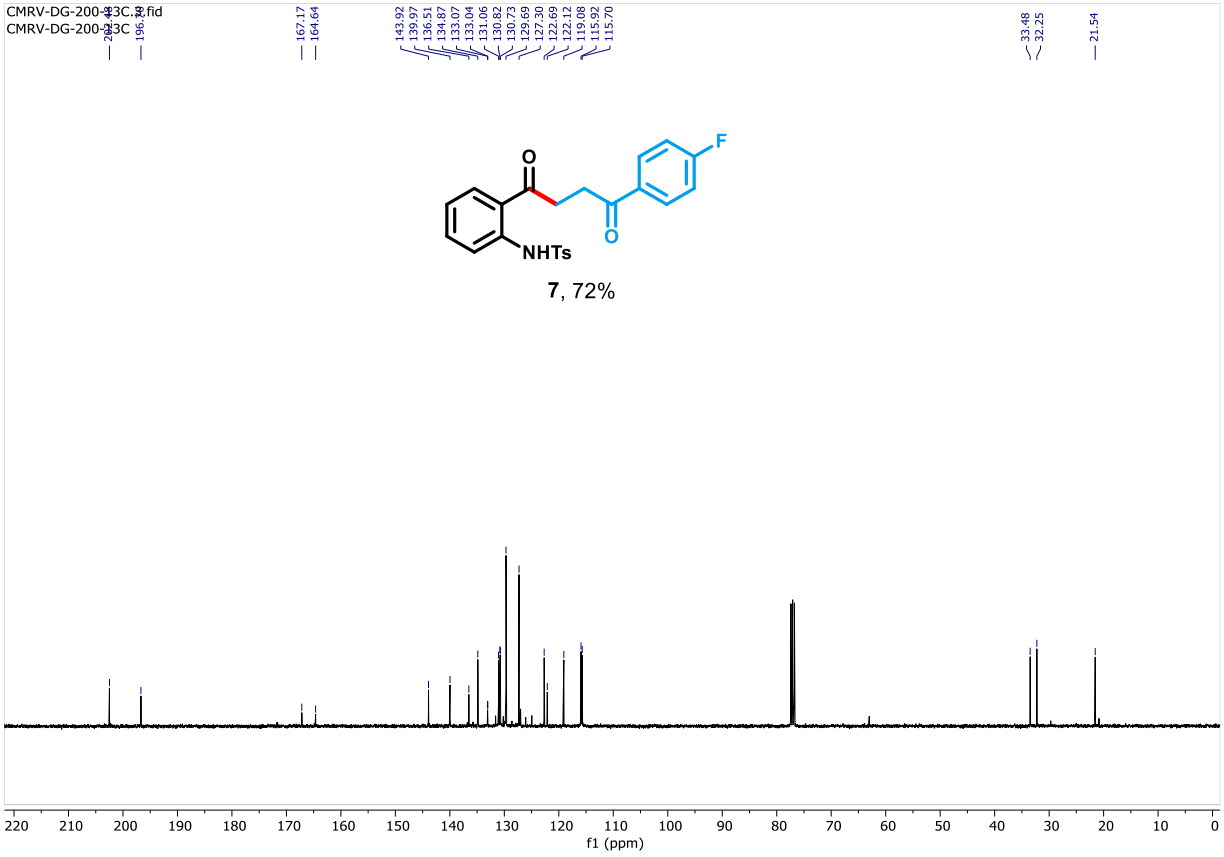

CMRV-DG-94-13C.12.fid
CMRV-DG-94-13C
202.54
199.45
156.48
156.35
143.80
139.85
136.49
134.64
133.77
130.96
130.65
130.15
129.84
129.65
127.31
124.08
123.55
122.70
122.47
119.35
119.25
119.15
37.31
33.88
21.53
PhO
O
O
NHTs
f1 (ppm)

6, 84%

7

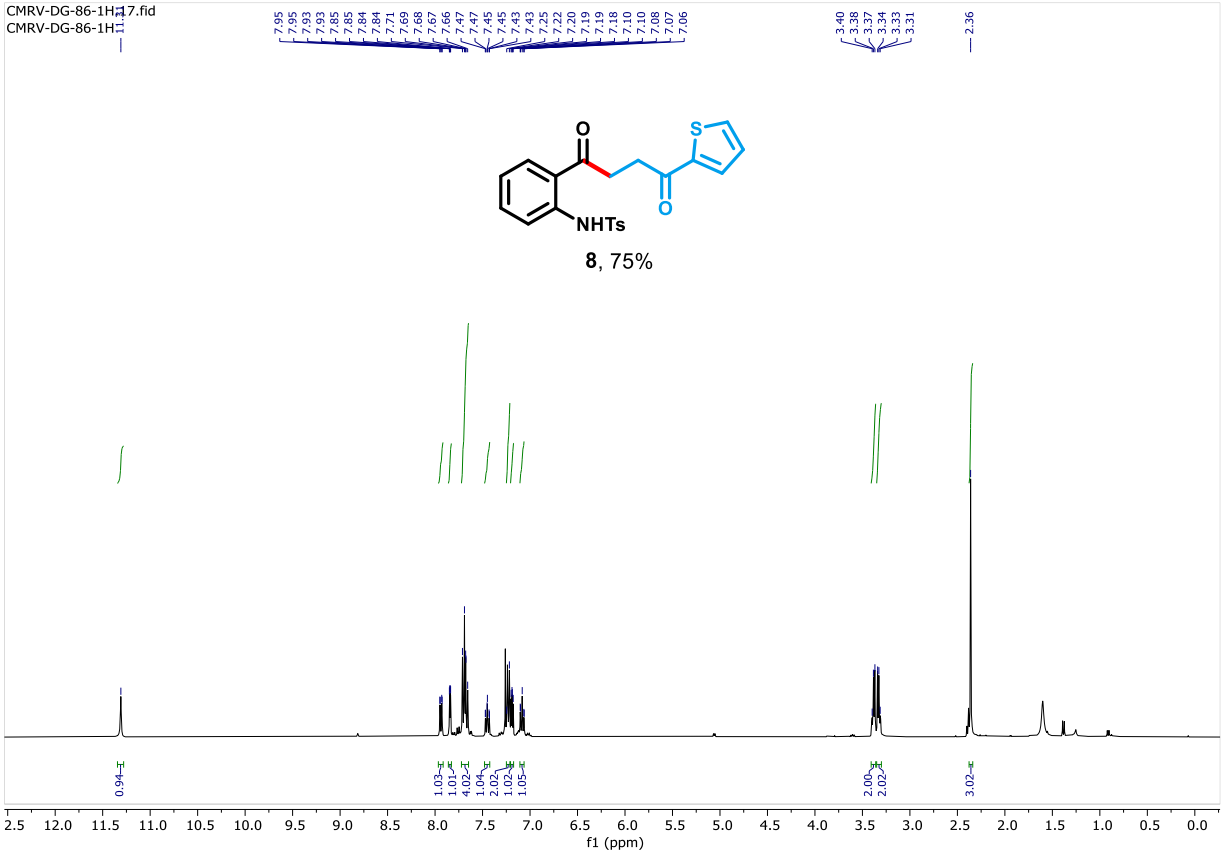

CMRV-DG-200-1H-1.fid
CMRV-DG-200-1H-1
11.54
8.07
8.06
8.05
8.04
7.97
7.96
7.95
7.94
7.71
7.69
7.67
7.64
7.46
7.44
7.44
7.42
7.23
7.21
7.19
7.17
7.14
7.10
7.09
7.08
7.08
7.06
7.06
3.39
3.38
3.37
3.36
3.35
3.34
2.35
F
O
O
NHTs
0.97
2.01
1.08
2.02
1.05
1.10
2.02
2.08
1.03
2.03
2.00
3.00
f1 (ppm)

7, 72%

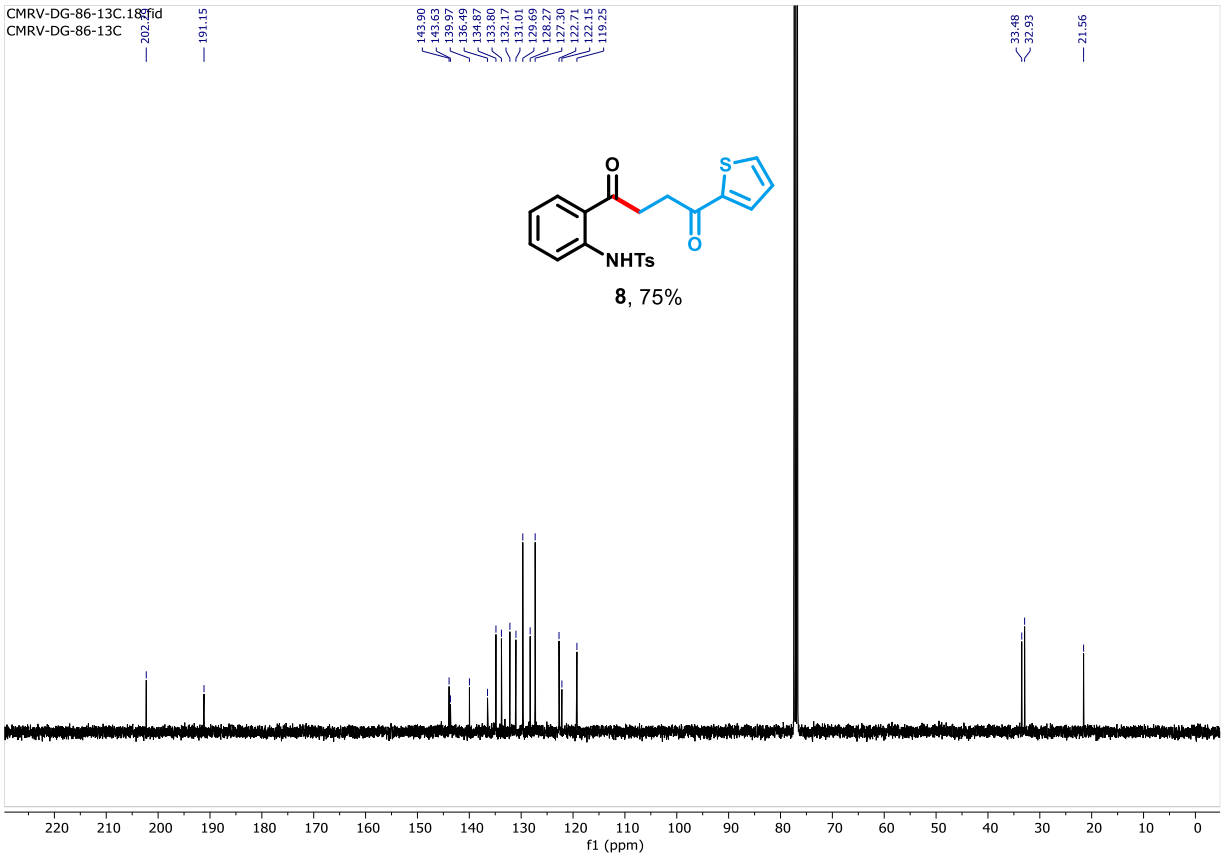

CMRV-DG-200-13C.fid
CMRV-DG-200-13C
196.39
167.17
164.64
143.92
139.97
136.51
134.87
133.07
133.04
131.06
130.82
130.73
129.69
127.30
122.69
122.12
119.08
115.92
115.70
33.48
32.25
21.54
O
F
O
NHTs
f1 (ppm)

7, 72%

8

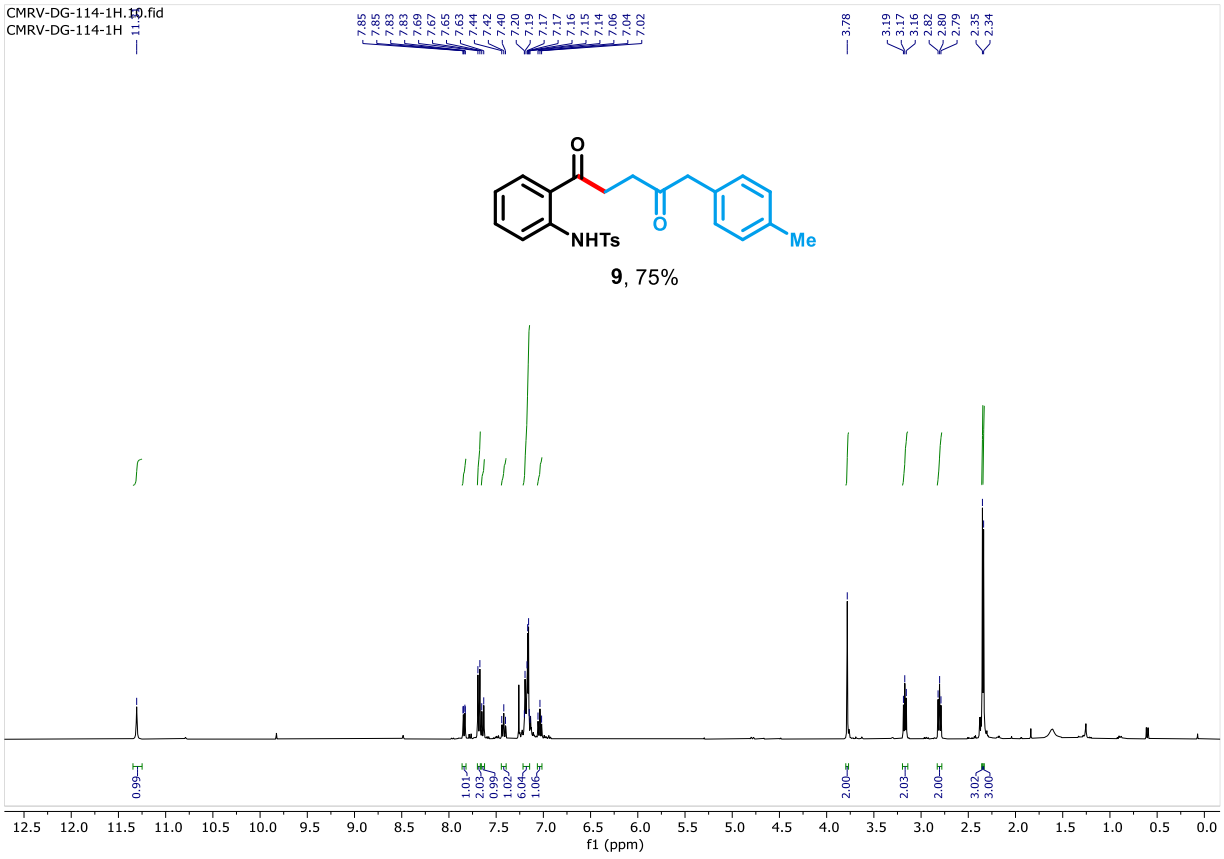

CMRV-DG-86-1H-17.fid
CMRV-DG-86-1H
11.11
7.95
7.95
7.93
7.93
7.85
7.85
7.84
7.84
7.71
7.69
7.68
7.67
7.66
7.47
7.47
7.45
7.45
7.43
7.43
7.25
7.22
7.20
7.19
7.19
7.18
7.10
7.10
7.08
7.07
7.06
3.40
3.38
3.37
3.34
3.33
3.31
2.36
O
S
O
NHTs
0.94
1.03
1.01
4.02
1.04
2.02
1.02
1.05
2.00
2.02
3.02
f1 (ppm)

8, 75%

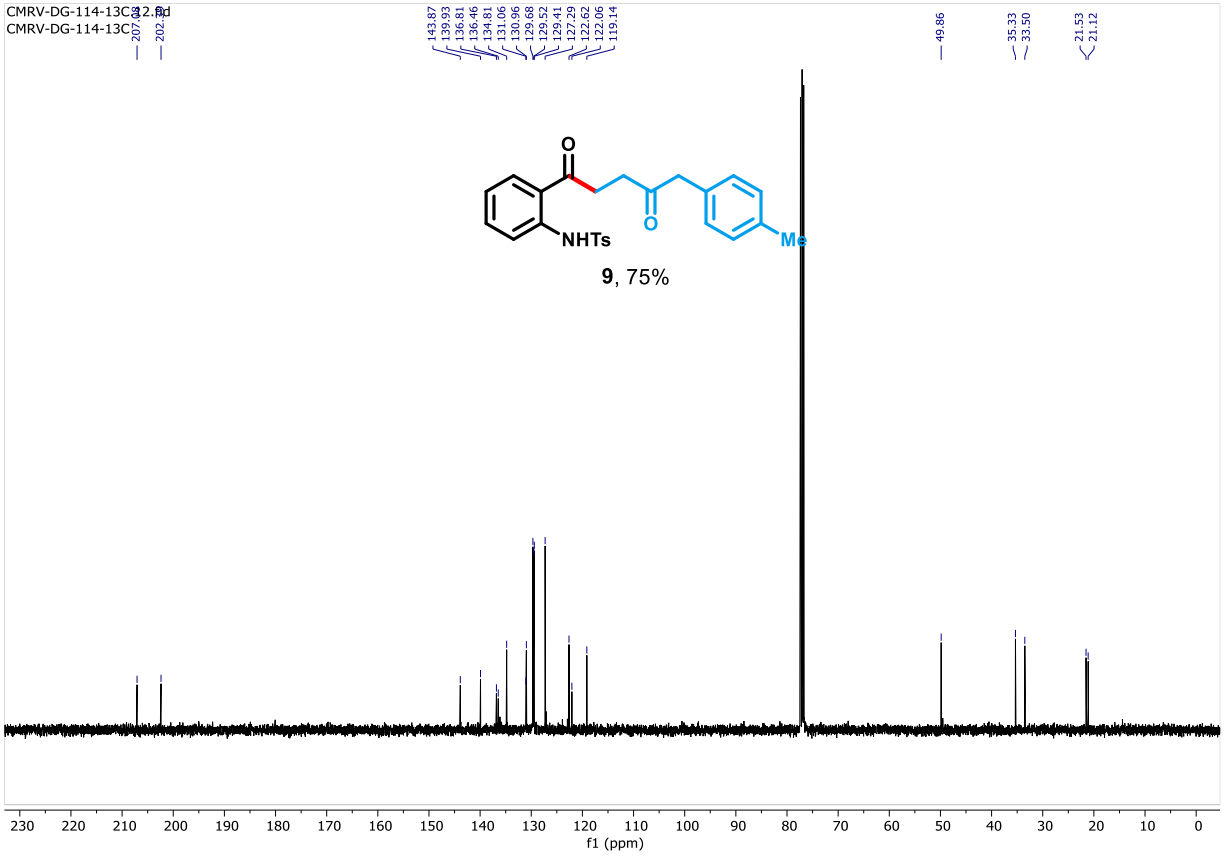

CMRV-DG-86-13C.1
CMRV-DG-86-13C
202.77
191.15
143.90
143.63
139.97
136.49
134.87
133.80
132.17
131.01
129.69
128.27
127.30
122.71
122.15
119.25
33.48
32.93
21.56
O
S
O
NHTs
f1 (ppm)

8, 75%

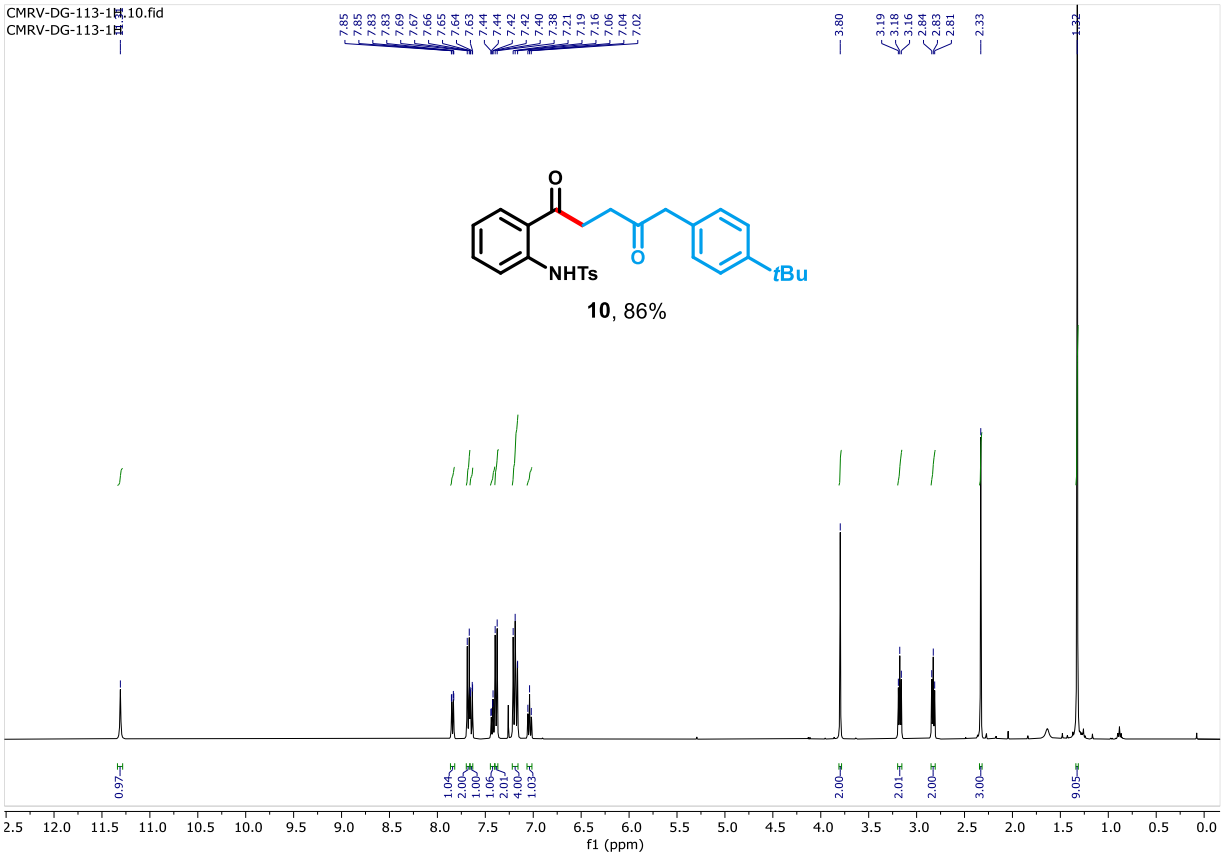
9

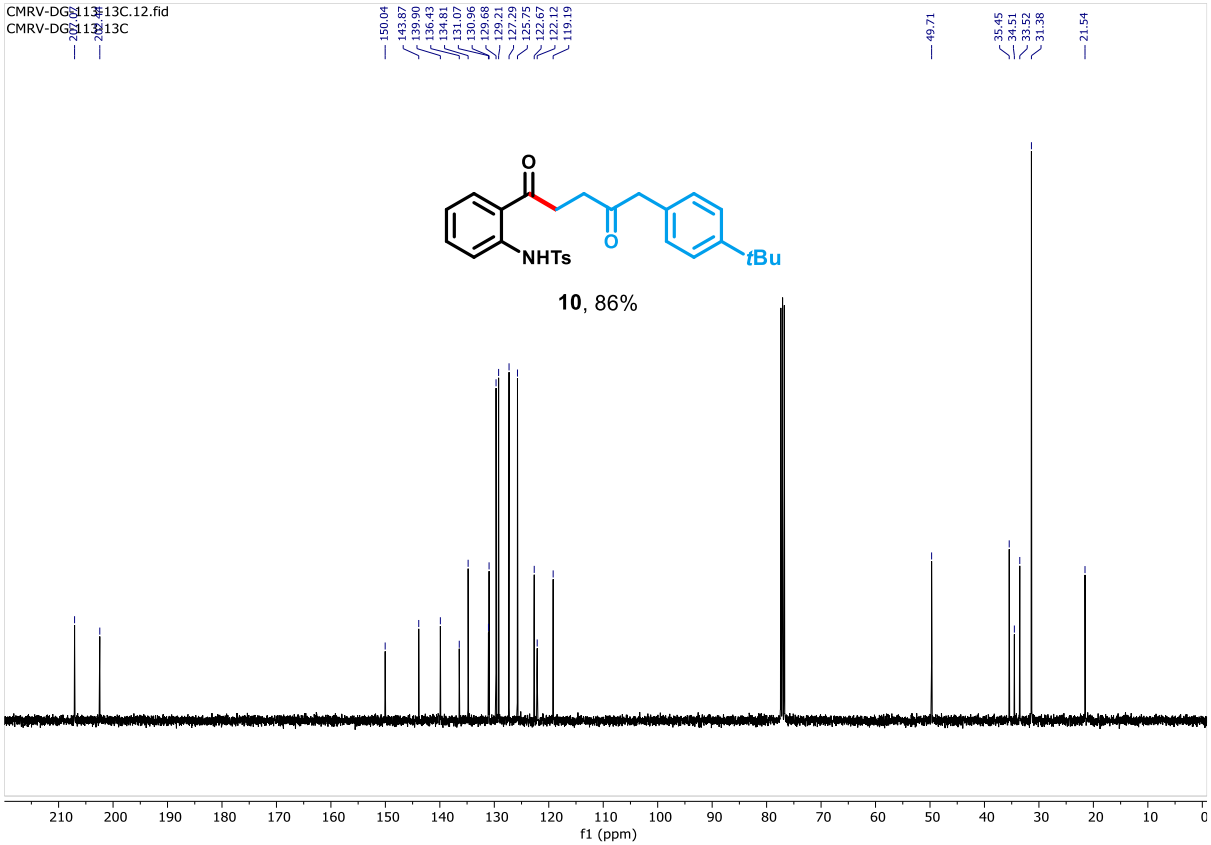

CMRV-DG-114-1H.10.fid
CMRV-DG-114-1H
11.61
7.85
7.85
7.83
7.83
7.69
7.67
7.65
7.63
7.44
7.42
7.40
7.20
7.19
7.17
7.17
7.16
7.15
7.14
7.06
7.04
7.02
3.78
3.19
3.17
3.16
2.82
2.80
2.79
2.35
2.34
O
O
NHTs
Me
0.99
1.01
2.03
0.99
1.02
6.04
1.06
2.00
2.03
2.00
3.02
3.00
f1 (ppm)

9, 75%


CMRV-DG-114-13C.fid
CMRV-DG-114-13C
207.12
202.11
143.87
139.93
136.81
136.46
134.81
131.06
130.96
129.68
129.52
129.41
127.29
122.62
122.06
119.14
49.86
35.33
33.50
21.53
21.12
O
O
NHTs
Me
9, 75%
f1 (ppm)

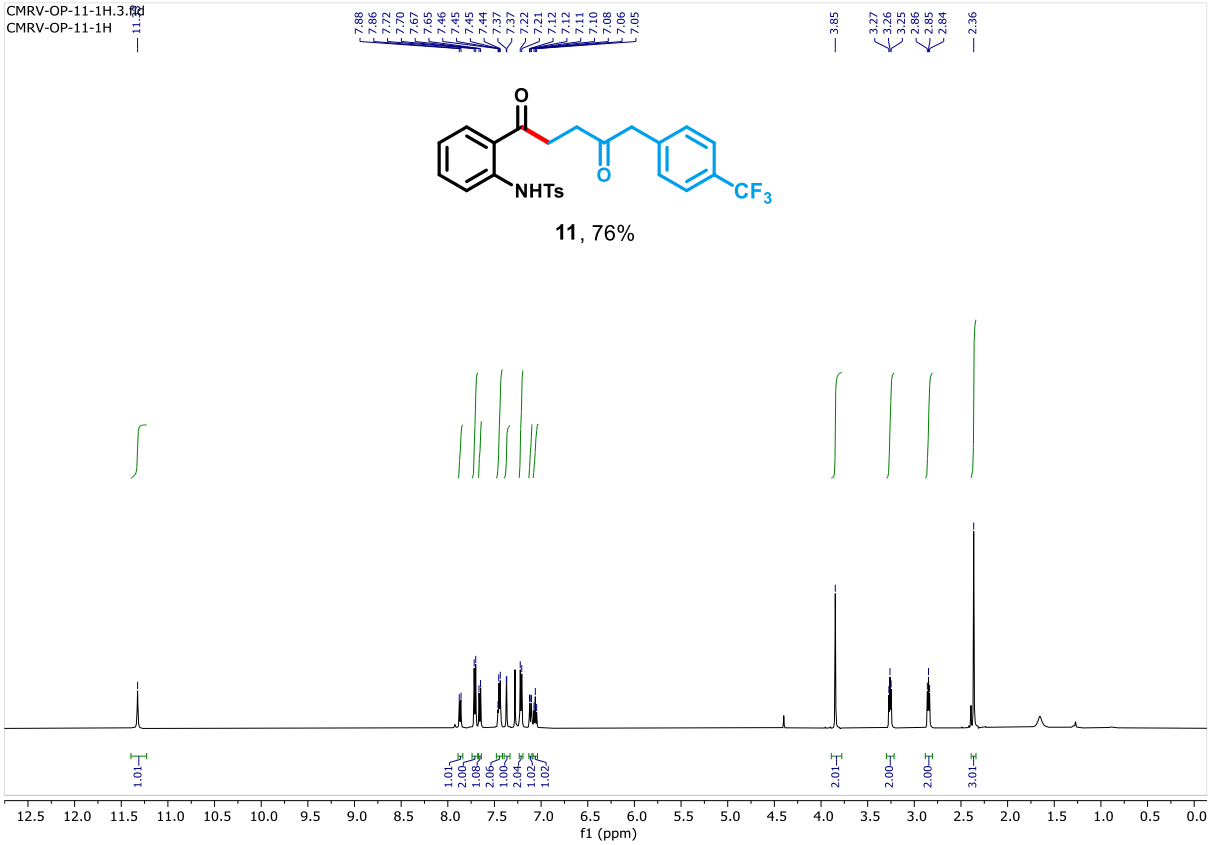
10


CMRV-DG-113-1H.10.fid
CMRV-DG-113-1H
7.85
7.85
7.83
7.83
7.69
7.67
7.66
7.65
7.64
7.63
7.44
7.42
7.42
7.40
7.38
7.21
7.19
7.16
7.06
7.04
7.02
3.80
3.19
3.18
3.16
2.84
2.83
2.81
2.33
1.32
0.97
1.04
2.00
1.00
1.06
2.01
4.00
1.03
2.00
2.01
2.00
3.00
9.05
O
O
NHTs
tBu
10, 86%
f1 (ppm)

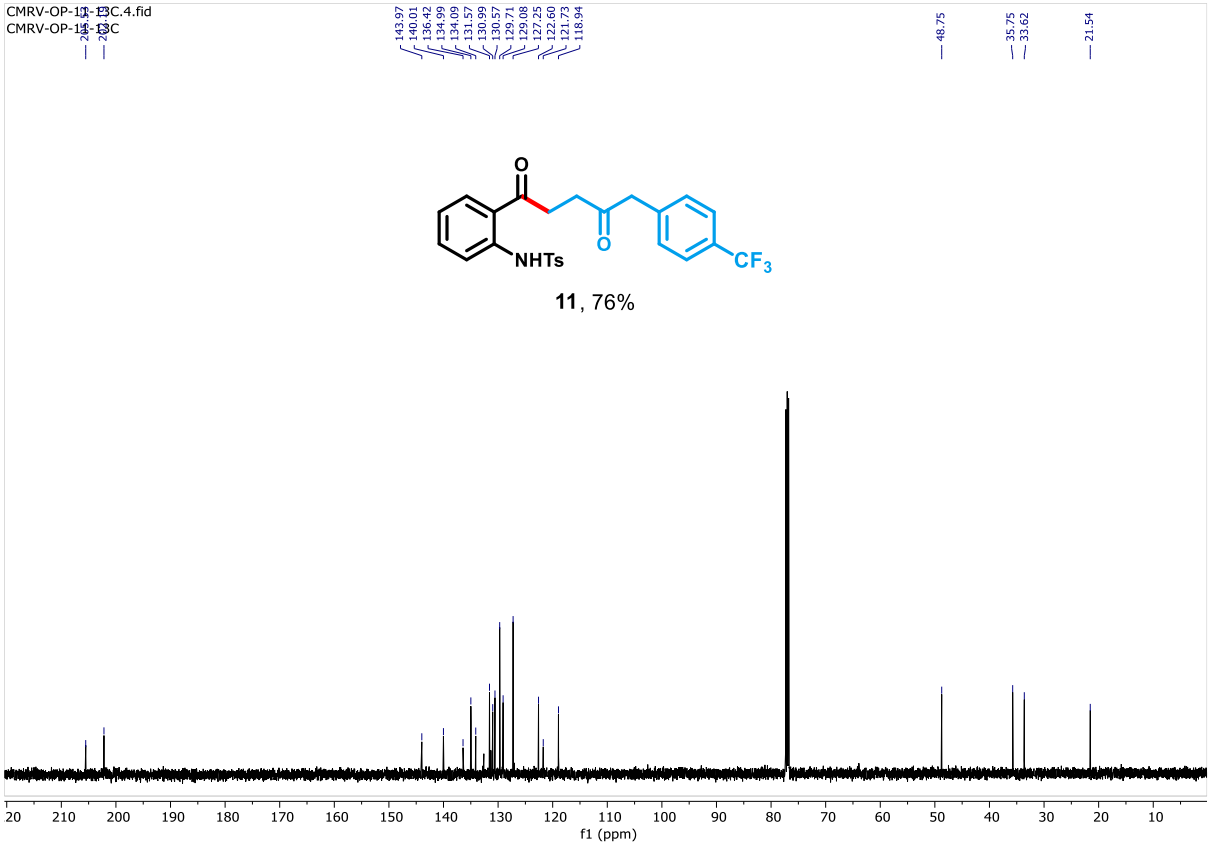

CMRV-DG-11-13C.12.fid
CMRV-DG-11-13C
150.04
143.87
139.90
136.43
134.81
131.07
130.96
129.66
129.21
127.29
125.75
122.67
122.12
119.19
49.71
35.45
34.51
33.52
31.38
21.54
O
O
NHTs
tBu
f1 (ppm)

10, 86%

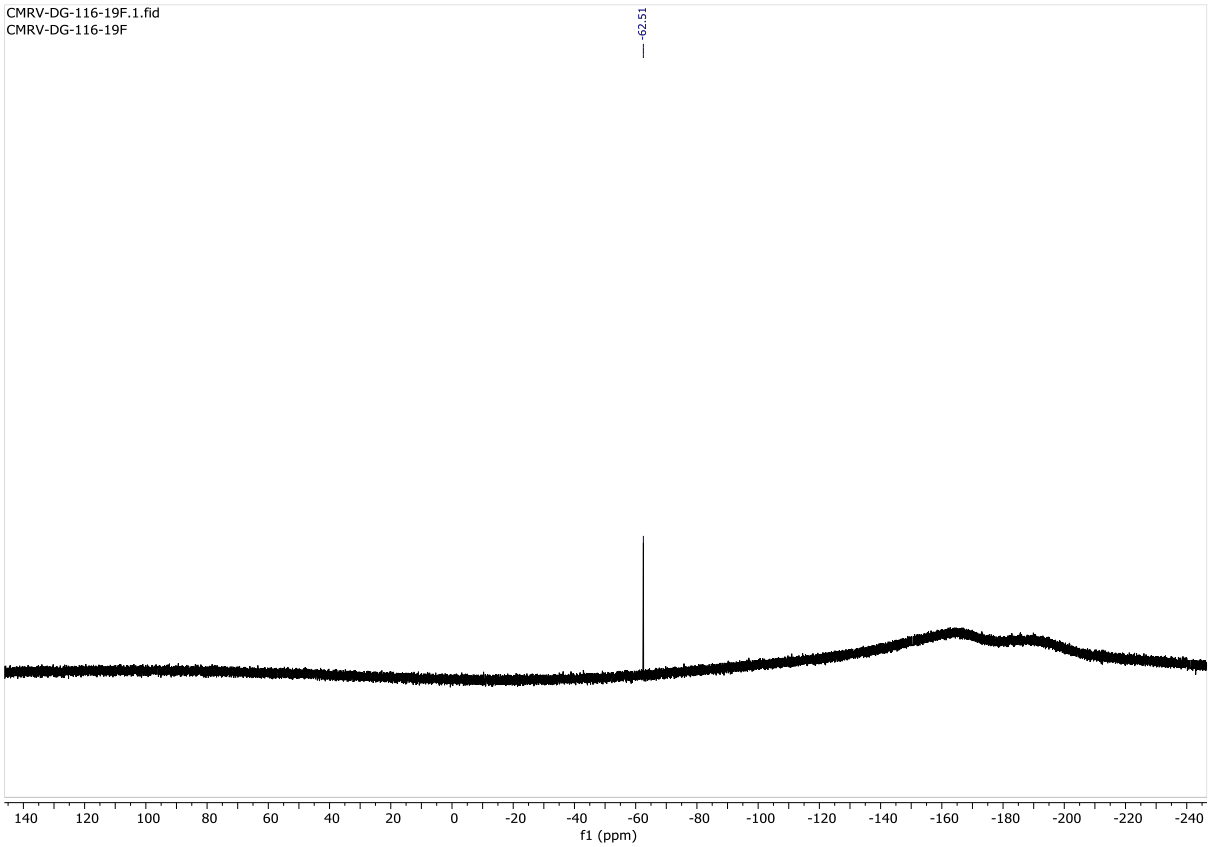
11


CMRV-OP-11-1H.3.fid
CMRV-OP-11-1H
11.52
7.88
7.86
7.72
7.70
7.67
7.65
7.46
7.45
7.44
7.37
7.22
7.21
7.12
7.11
7.10
7.08
7.06
7.05
3.85
3.27
3.26
3.25
2.86
2.85
2.84
2.36
O
O
NHTs
CF3
1.01
2.00
1.08
2.06
1.00
2.04
1.02
1.02
2.01
2.00
2.00
3.01
f1 (ppm)

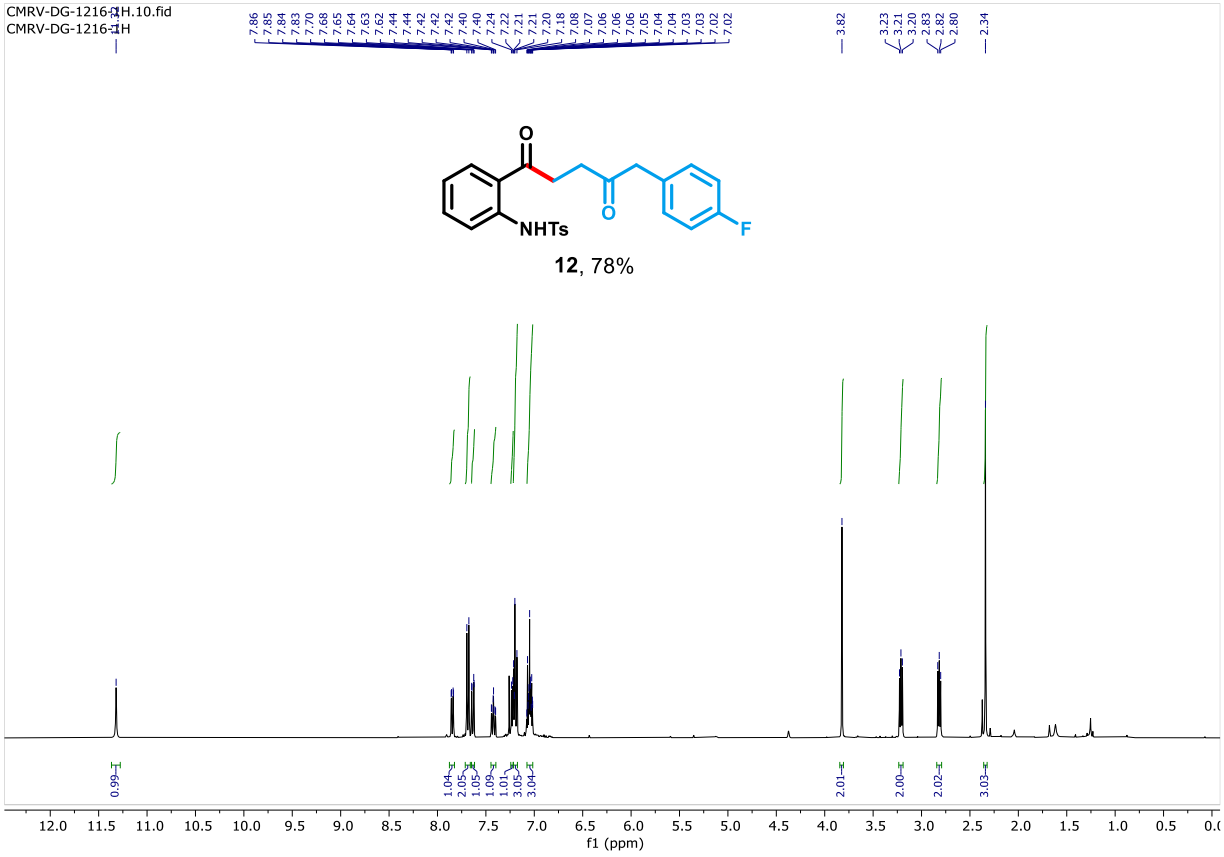
11, 76%

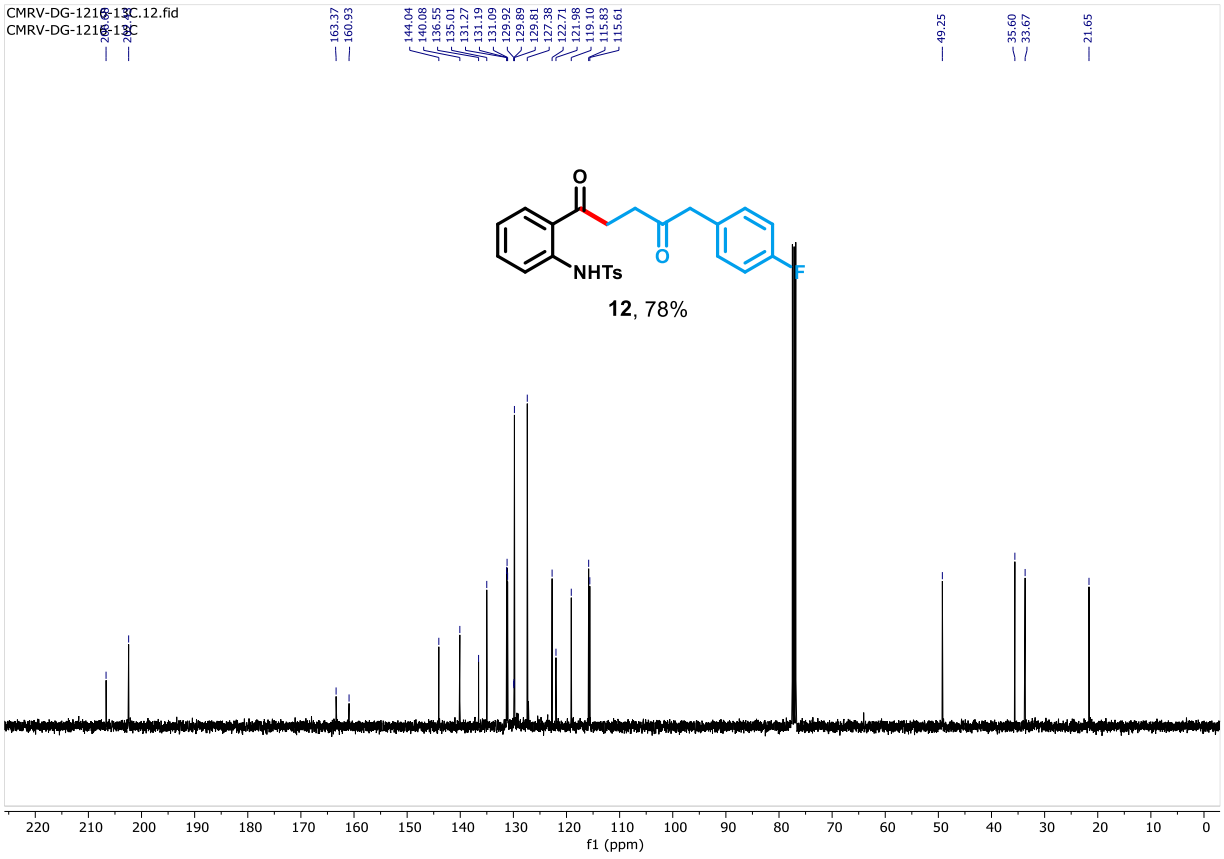

CMRV-OP-116-13C.4.fid
CMRV-OP-116-13C
143.97
140.01
136.42
134.99
134.09
131.57
130.99
130.57
129.71
129.08
127.25
122.60
121.73
118.94
48.75
35.75
33.62
21.54
O
O
NHTs
CF3
f1 (ppm)

11, 76%

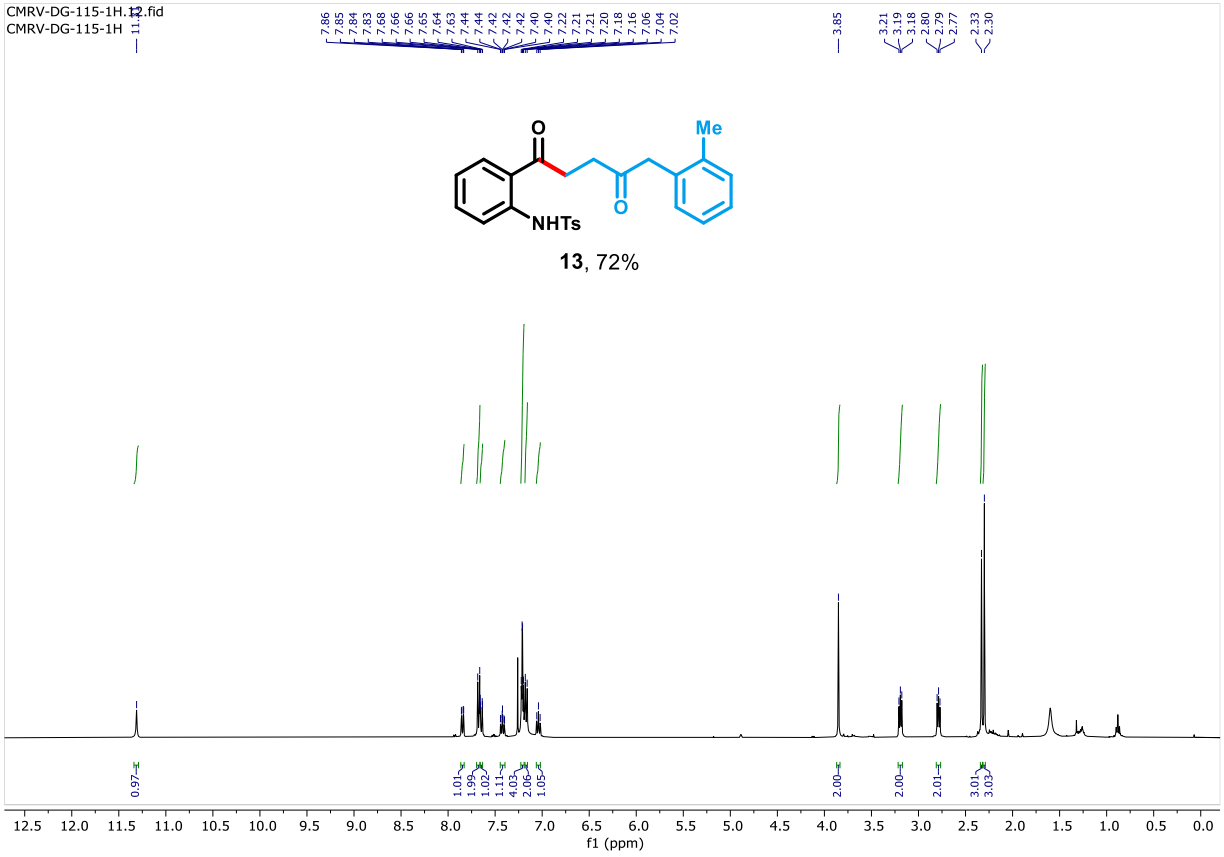

CMRV-DG-116-19F.1.fid
CMRV-DG-116-19F
-62.51
f1 (ppm)

12

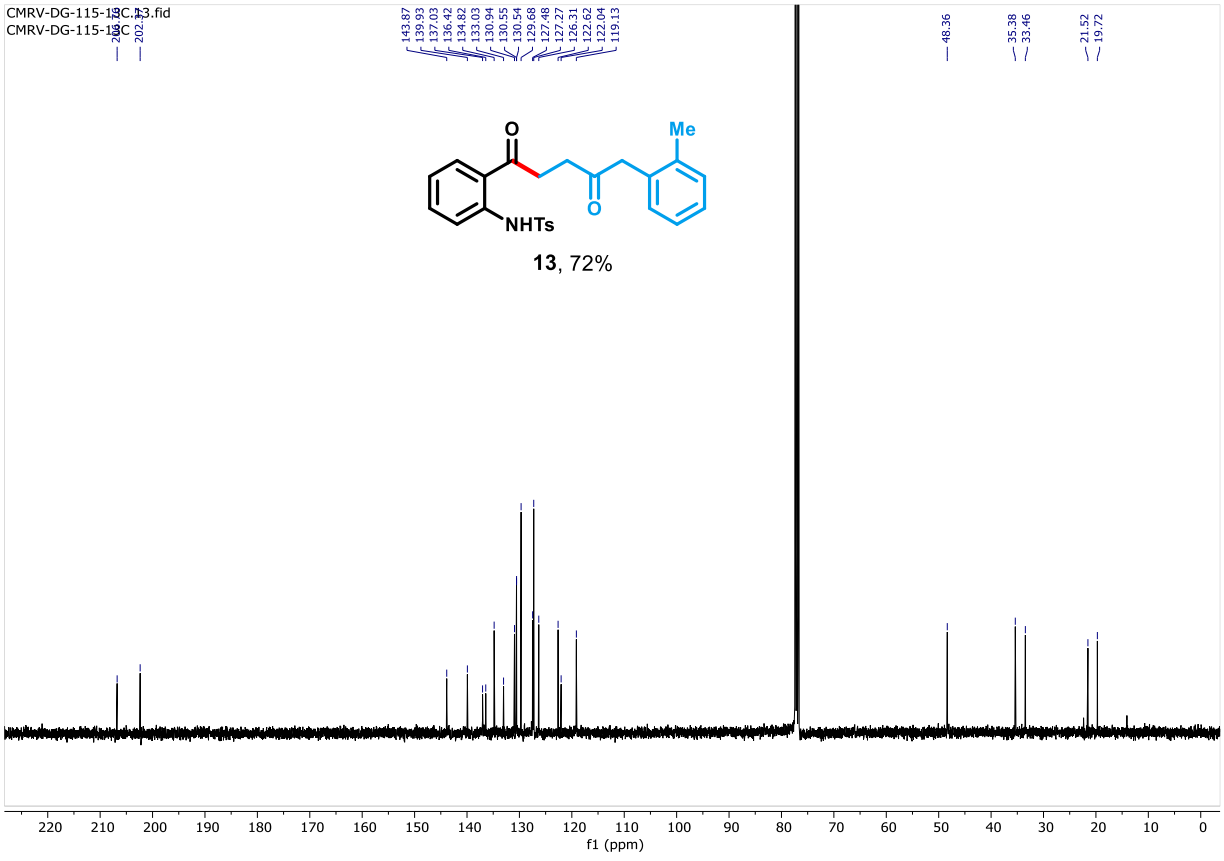

CMRV-DG-1216-1H.10.fid
CMRV-DG-1216-1H
NHTs
F
12, 78%
f1 (ppm)


CMRV-DG-1216-13C.12.fid
CMRV-DG-1216-13C
NHTs
F
12, 78%
f1 (ppm)

13

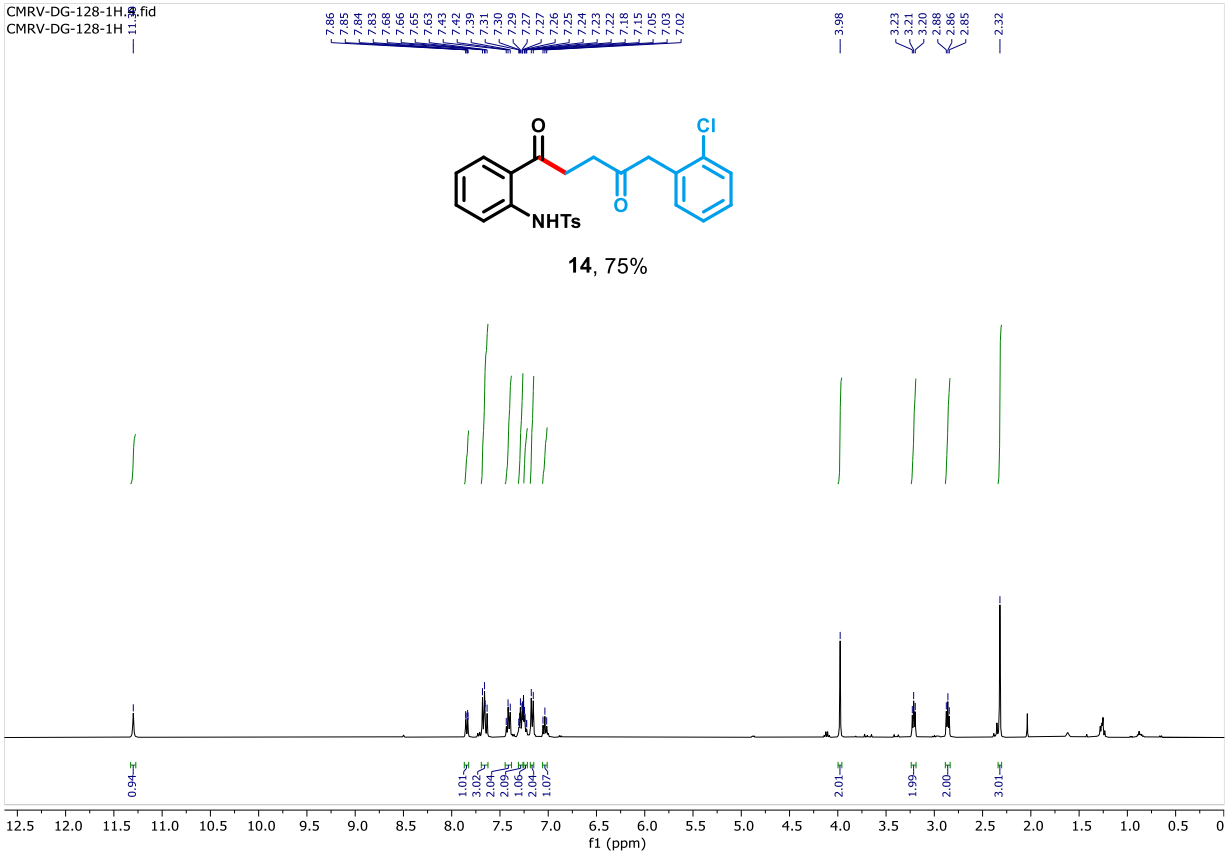

CMRV-DG-115-1H.12.fid
CMRV-DG-115-1H
11.12
7.86
7.85
7.84
7.83
7.68
7.66
7.66
7.65
7.64
7.63
7.44
7.44
7.42
7.42
7.42
7.40
7.40
7.22
7.21
7.21
7.20
7.18
7.16
7.06
7.04
7.02
3.85
3.21
3.19
3.18
2.80
2.79
2.77
2.33
2.30
O
Me
O
NHTs
0.97
1.01
1.99
1.02
1.11
4.03
2.06
1.05
2.00
2.00
2.01
3.01
3.03
12.5 12.0 11.5 11.0 10.5 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 0.0
f1 (ppm)

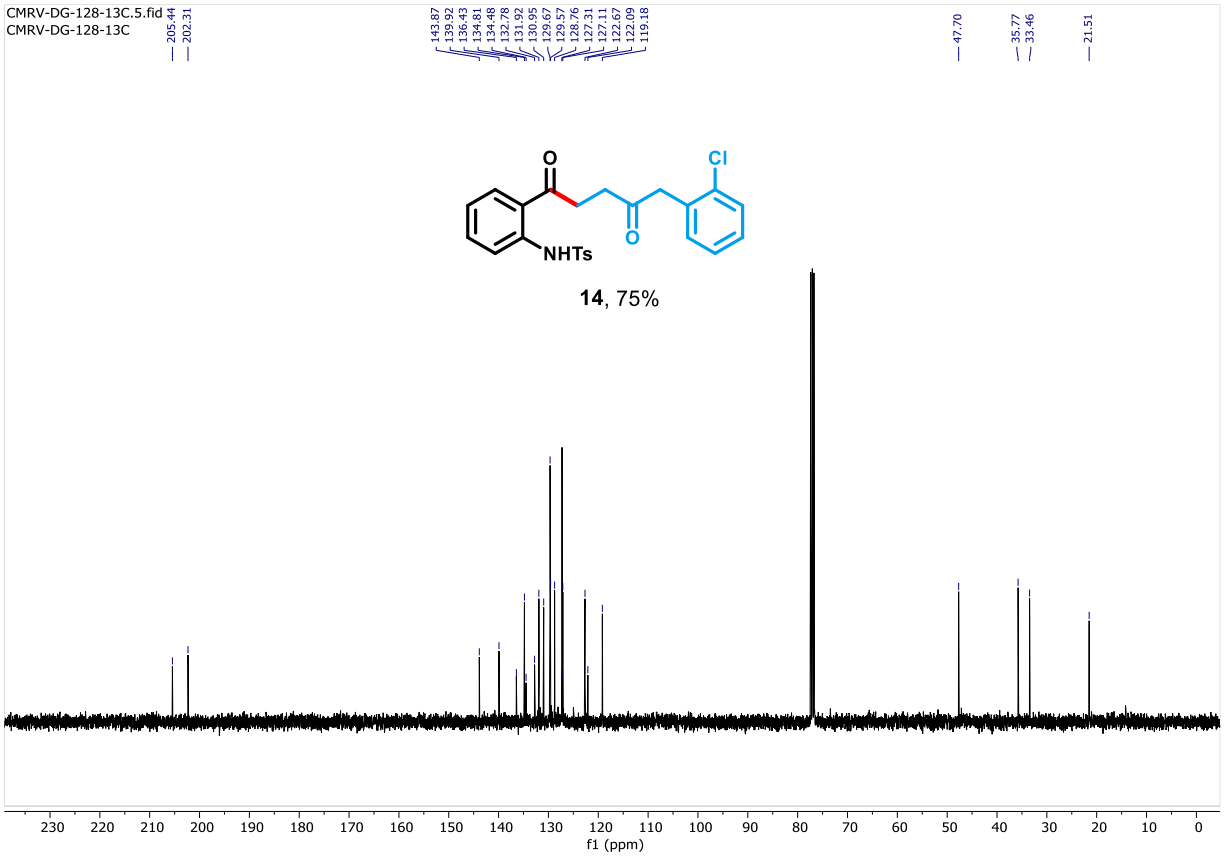
13, 72%


CMRV-DG-115-13C.13.fid
CMRV-DG-115-13C
202.11
202.47
143.87
139.93
137.03
136.42
134.82
133.03
130.94
130.55
130.54
129.68
127.48
127.27
126.31
122.62
122.04
119.13
48.36
35.38
33.46
21.52
19.72
O
Me
O
NHTs
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

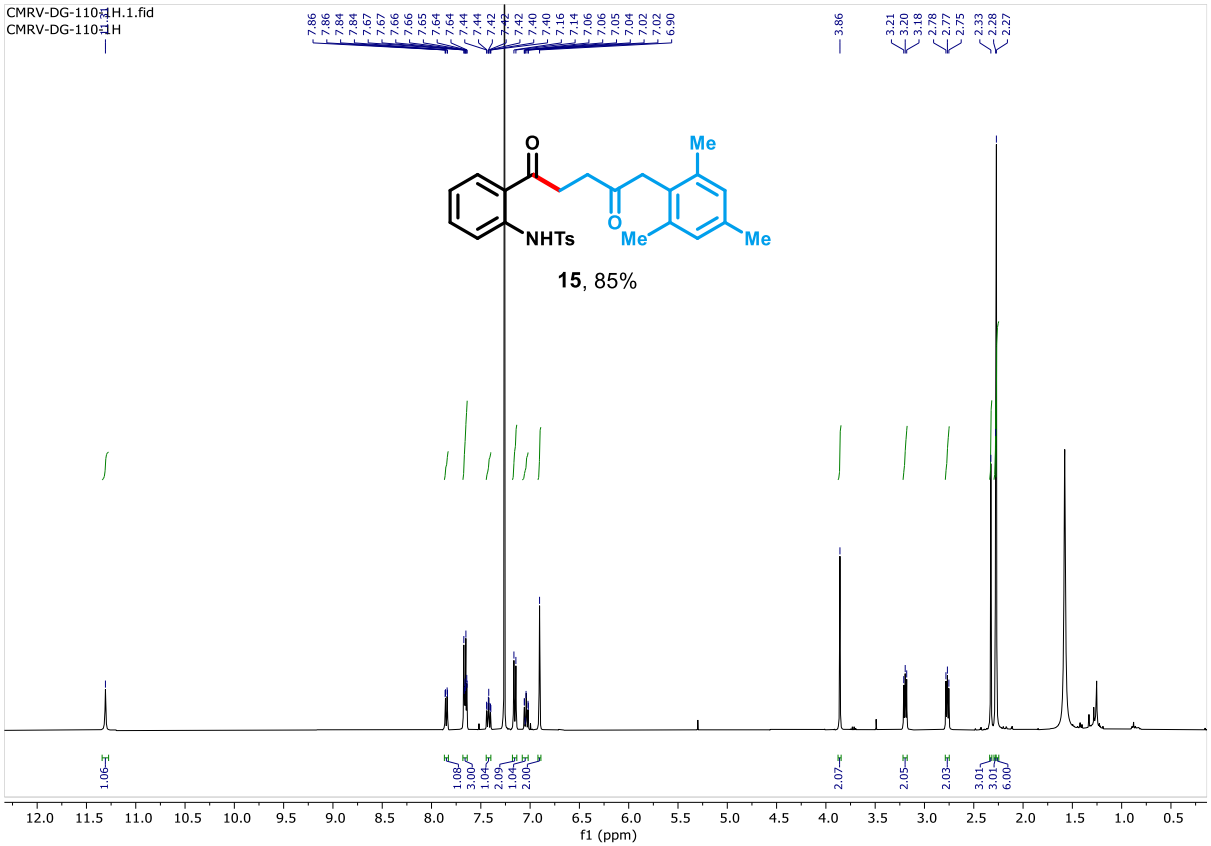
13, 72%

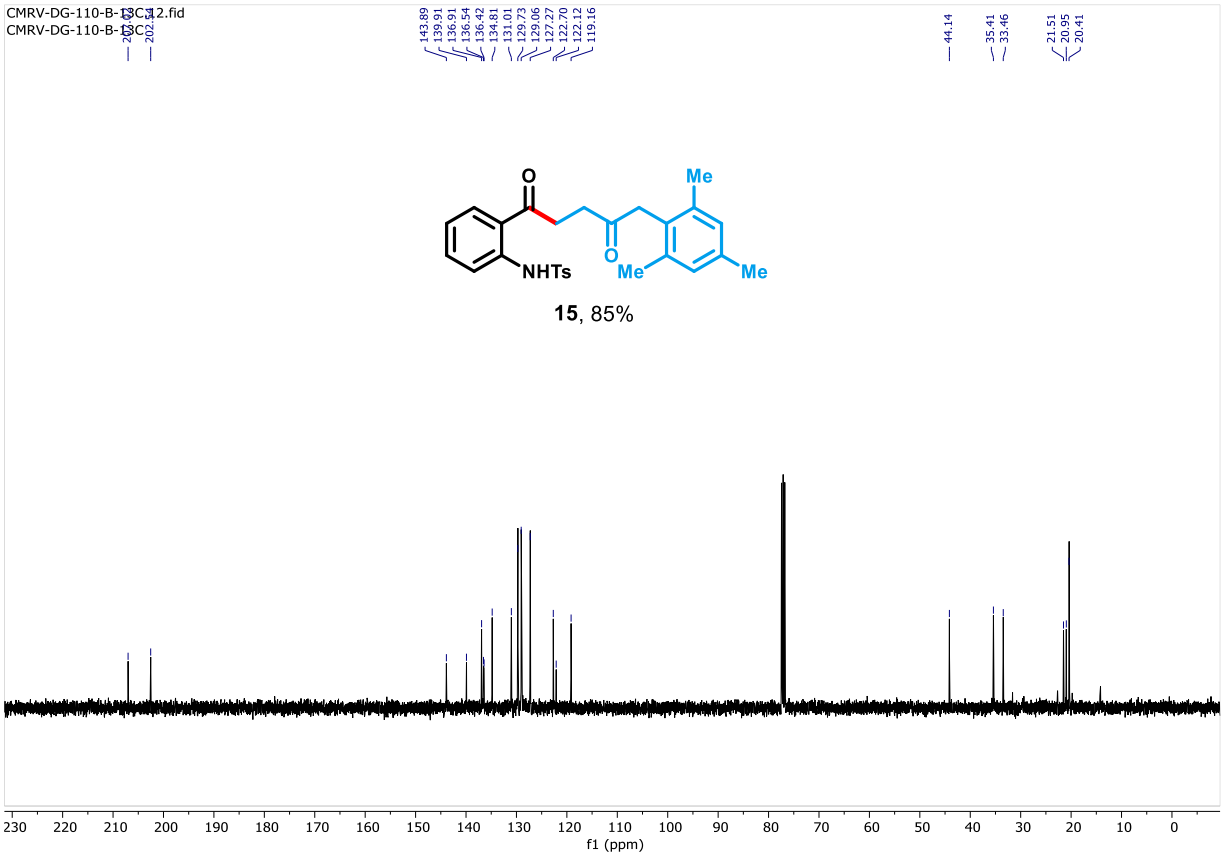
14


CMRV-DG-128-1H.8.fid
CMRV-DG-128-1H
11.14
7.86
7.85
7.84
7.83
7.68
7.66
7.65
7.63
7.43
7.42
7.39
7.31
7.30
7.29
7.27
7.27
7.26
7.25
7.24
7.23
7.22
7.18
7.15
7.05
7.03
7.02
3.98
3.23
3.21
3.20
2.88
2.86
2.85
2.32
O
Cl
O
NHTs
14, 75%
0.94
1.01
3.02
2.04
2.09
1.06
2.04
1.07
2.01
1.99
2.00
3.01
12.5 12.0 11.5 11.0 10.5 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 0
f1 (ppm)

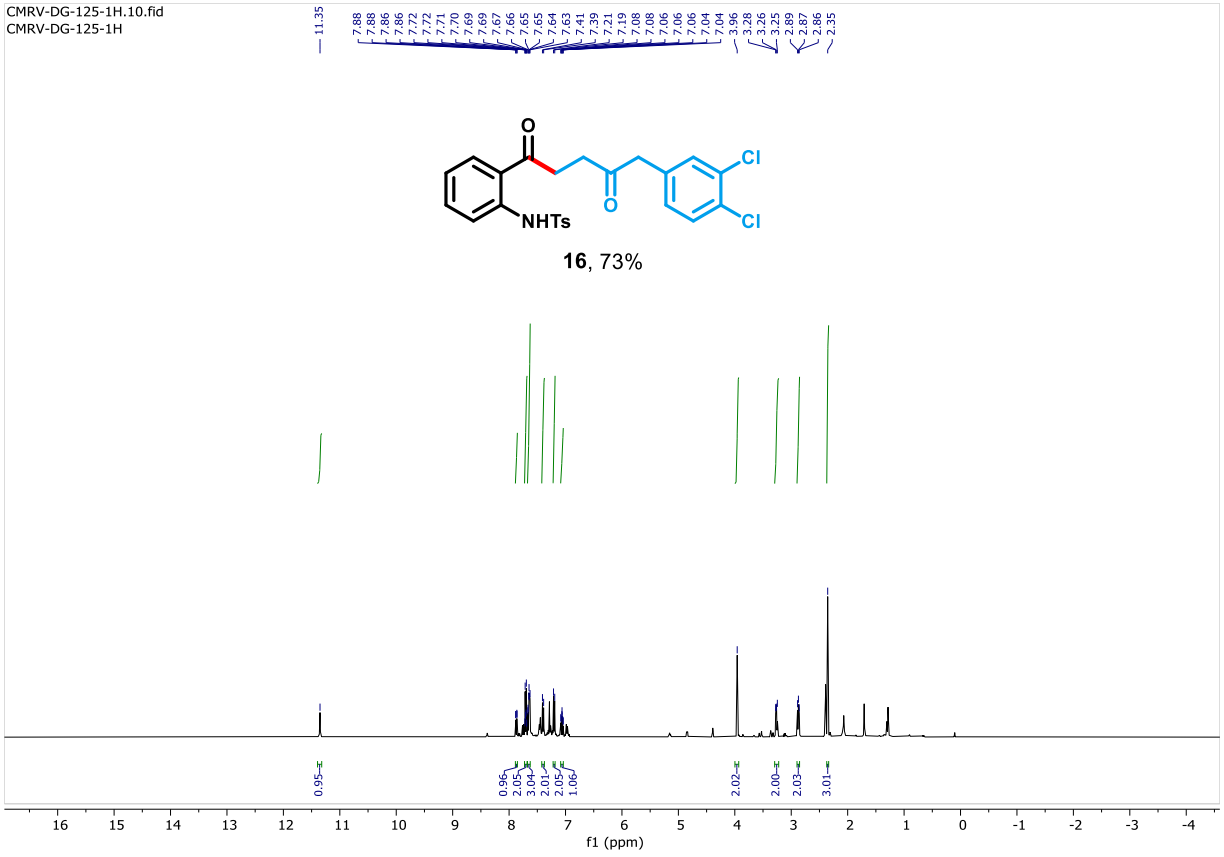

CMRV-DG-128-13C.5.fid
CMRV-DG-128-13C
205.44
202.31
143.87
139.92
136.43
134.81
134.48
132.78
131.92
130.95
129.67
129.57
128.76
127.31
127.11
122.67
122.09
119.18
47.70
35.77
33.46
21.51
O
Cl
O
NHTs
14, 75%
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

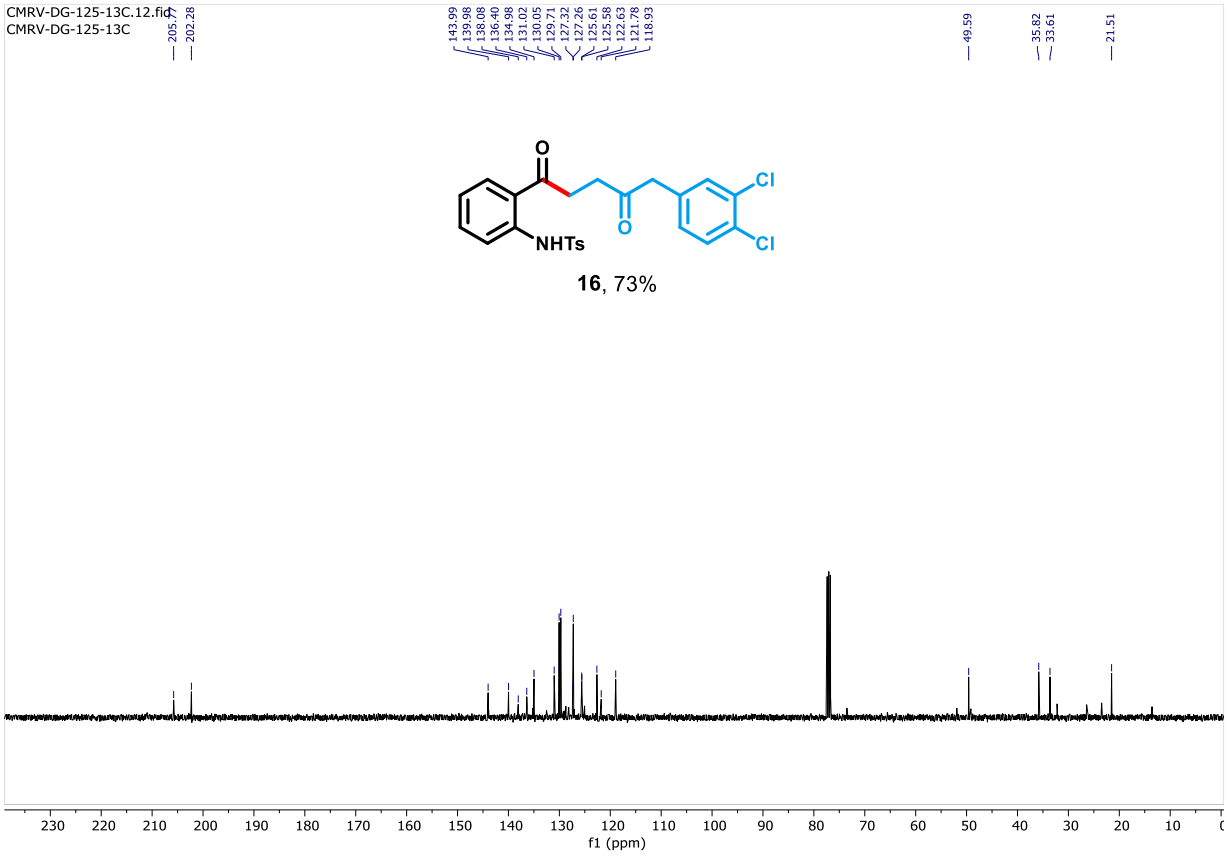
15


CMRV-DG-110-1H.1.fid
CMRV-DG-110-1H
7.86
7.86
7.84
7.84
7.67
7.67
7.66
7.66
7.65
7.64
7.64
7.44
7.44
7.42
7.42
7.42
7.40
7.40
7.16
7.14
7.06
7.06
7.05
7.04
7.02
7.02
6.90
3.86
3.21
3.20
3.18
2.78
2.77
2.75
2.33
2.28
2.27
O
Me
O
Me
Me
NHTs
15, 85%
1.06
1.08
3.00
1.04
2.09
1.04
1.04
2.00
2.07
2.05
2.03
3.01
3.01
6.00
12.0
11.5
11.0
10.5
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)

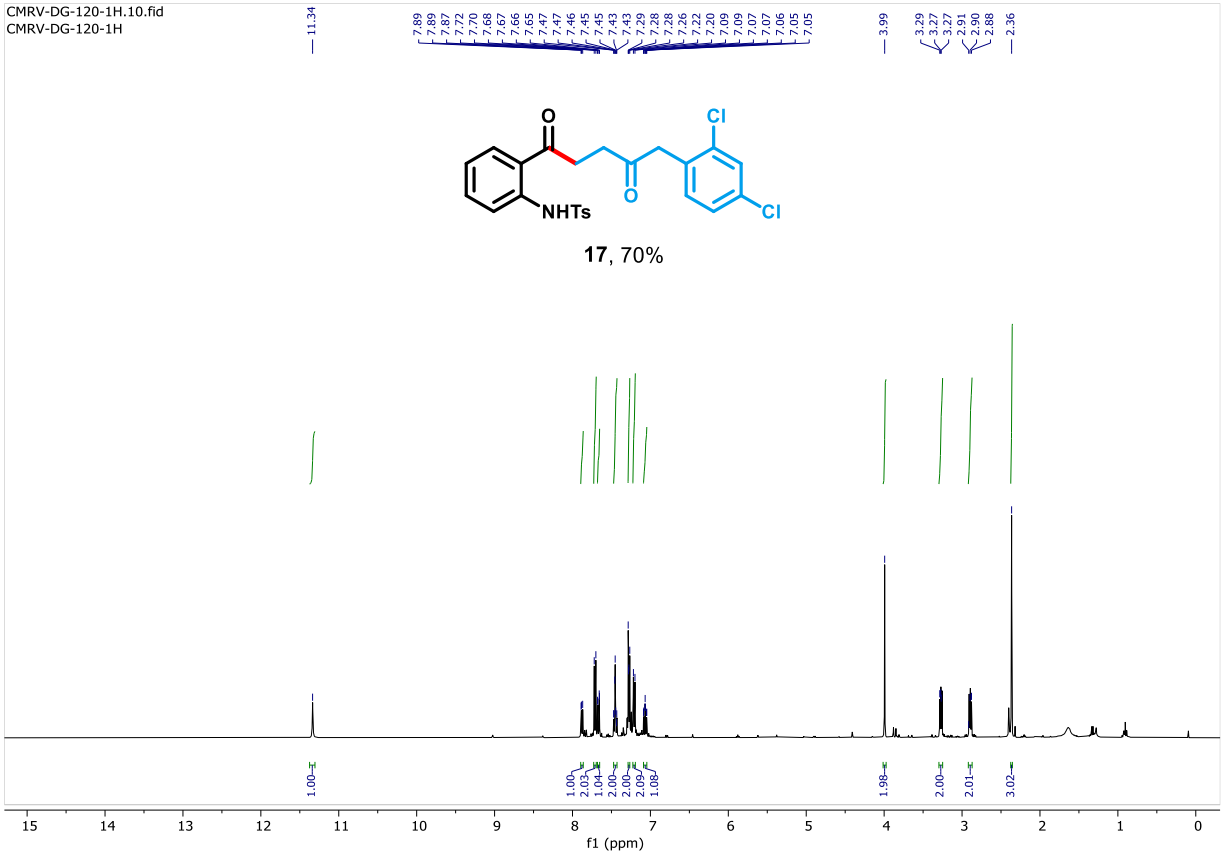

CMRV-DG-110-B-13C.11.2.fid
CMRV-DG-110-B-13C.11
202.14
202.12
143.89
139.91
136.91
136.54
136.42
134.81
131.01
129.73
129.06
127.27
122.70
122.12
119.16
44.14
35.41
33.46
21.51
20.95
20.41
O
Me
O
Me
Me
NHTs
15, 85%
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

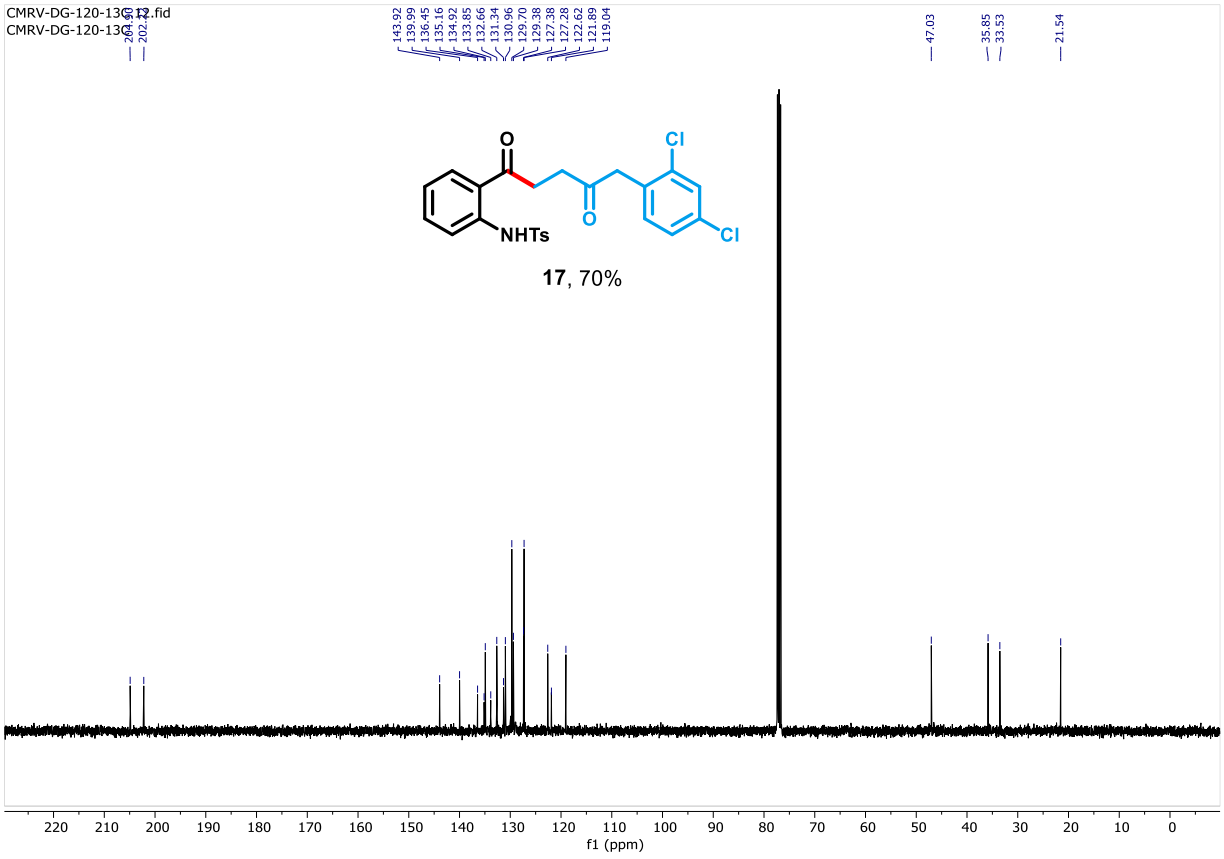
16


CMRV-DG-125-1H.10.fid
CMRV-DG-125-1H
11.35
7.88
7.88
7.86
7.86
7.72
7.72
7.71
7.70
7.69
7.69
7.67
7.66
7.65
7.65
7.64
7.63
7.41
7.39
7.21
7.19
7.08
7.08
7.06
7.06
7.06
7.04
7.04
3.96
3.28
3.26
3.25
2.89
2.87
2.86
2.35
O
Cl
O
Cl
NHTs
16, 73%
0.95
0.96
2.05
3.04
2.01
2.05
1.06
2.02
2.00
2.03
3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

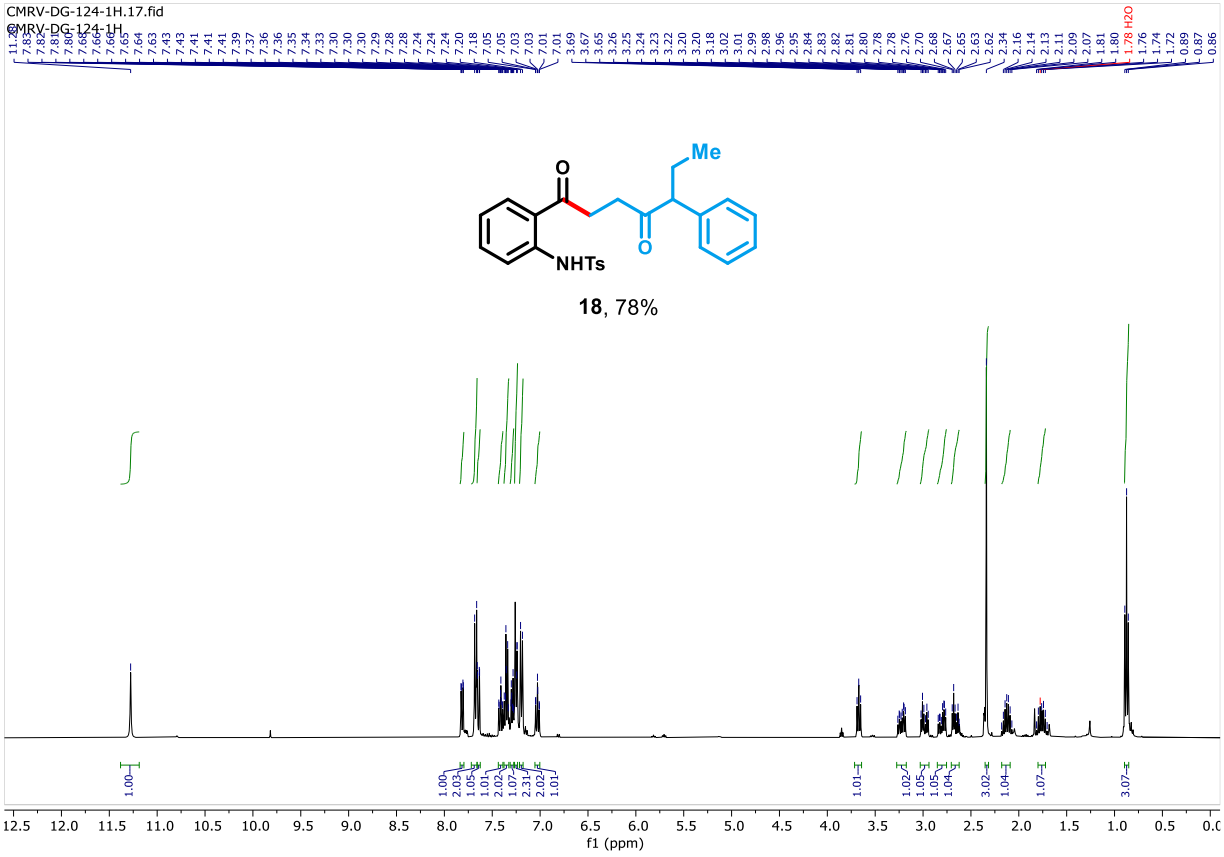

CMRV-DG-125-13C.12.fid
CMRV-DG-125-13C
205.7
202.28
143.99
139.98
138.08
136.40
134.98
131.02
130.05
129.71
127.32
127.26
125.61
125.58
122.63
121.78
118.93
49.59
35.82
33.61
21.51
O
Cl
O
Cl
NHTs
16, 73%
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

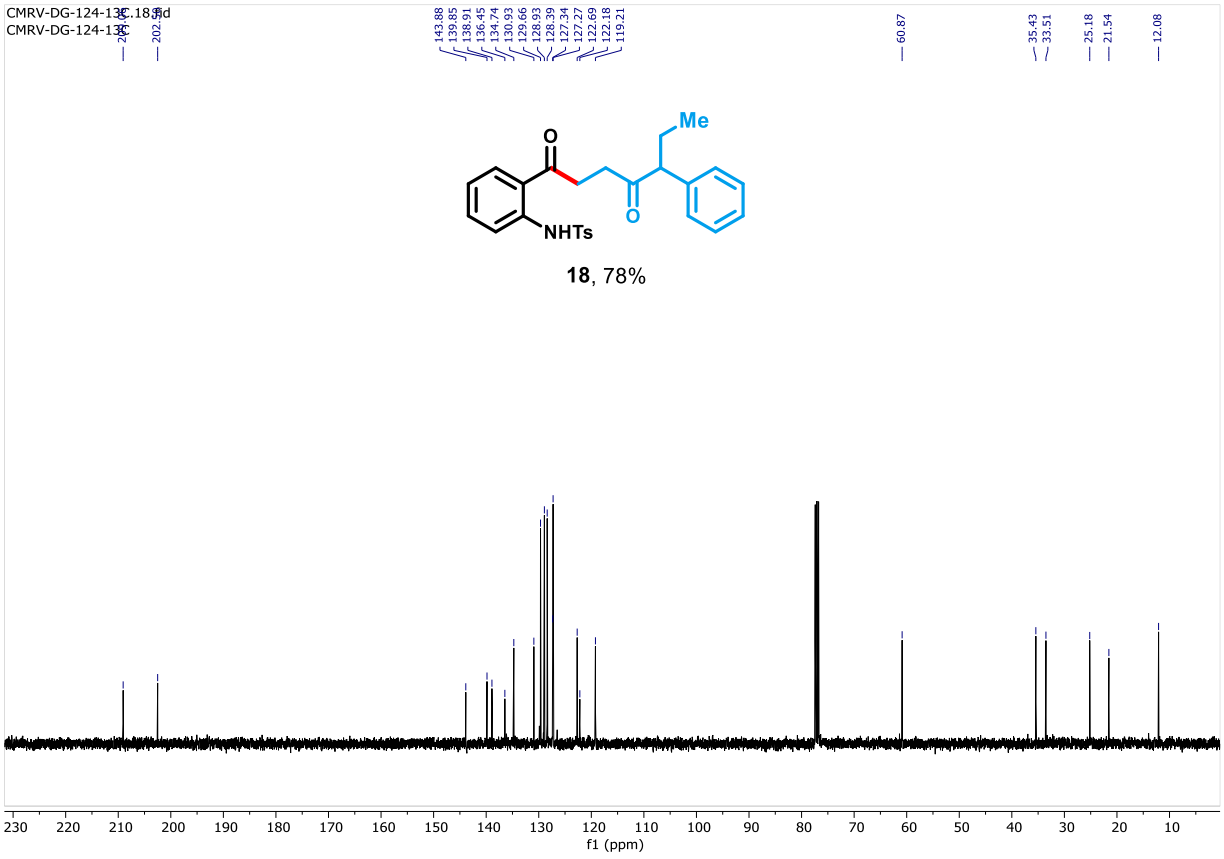
17


CMRV-DG-120-1H.10.fid
CMRV-DG-120-1H
O
Cl
O
NHTs
Cl
17, 70%
f1 (ppm)

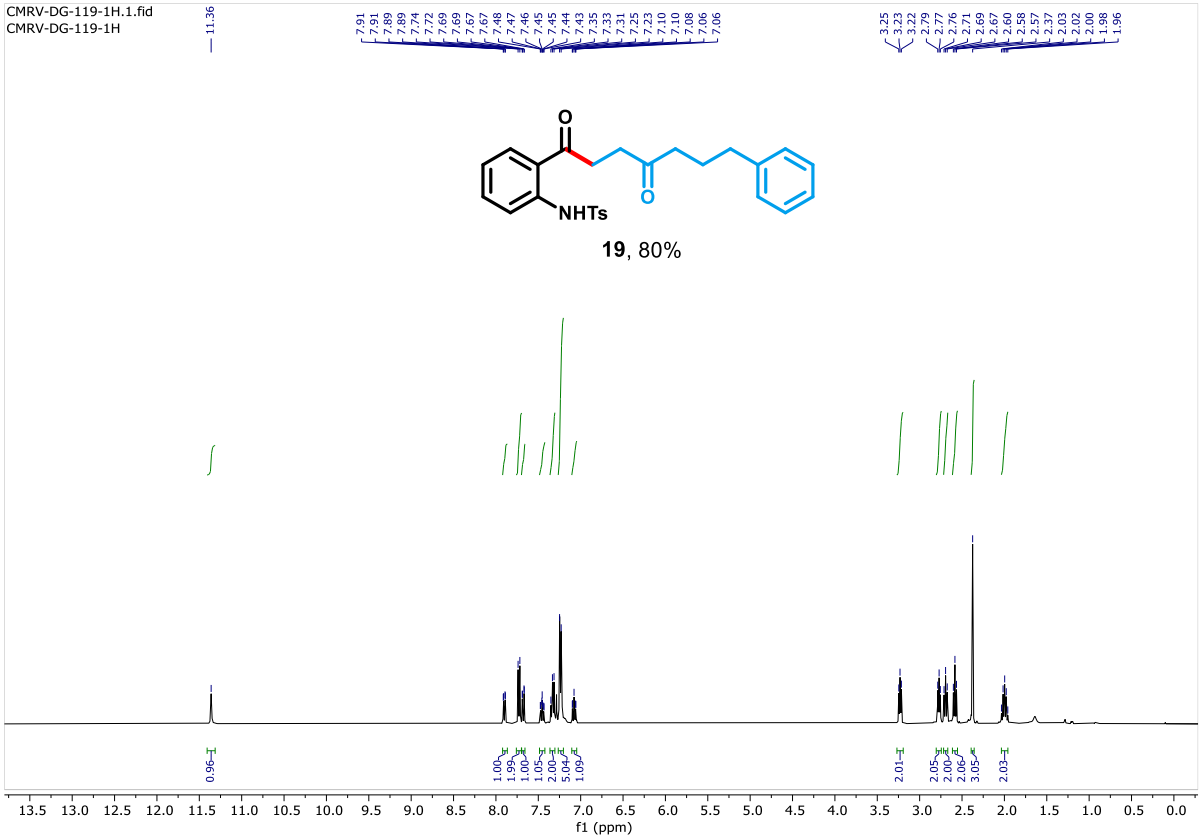

CMRV-DG-120-13C.12.fid
CMRV-DG-120-13C
O
Cl
O
NHTs
Cl
17, 70%
f1 (ppm)

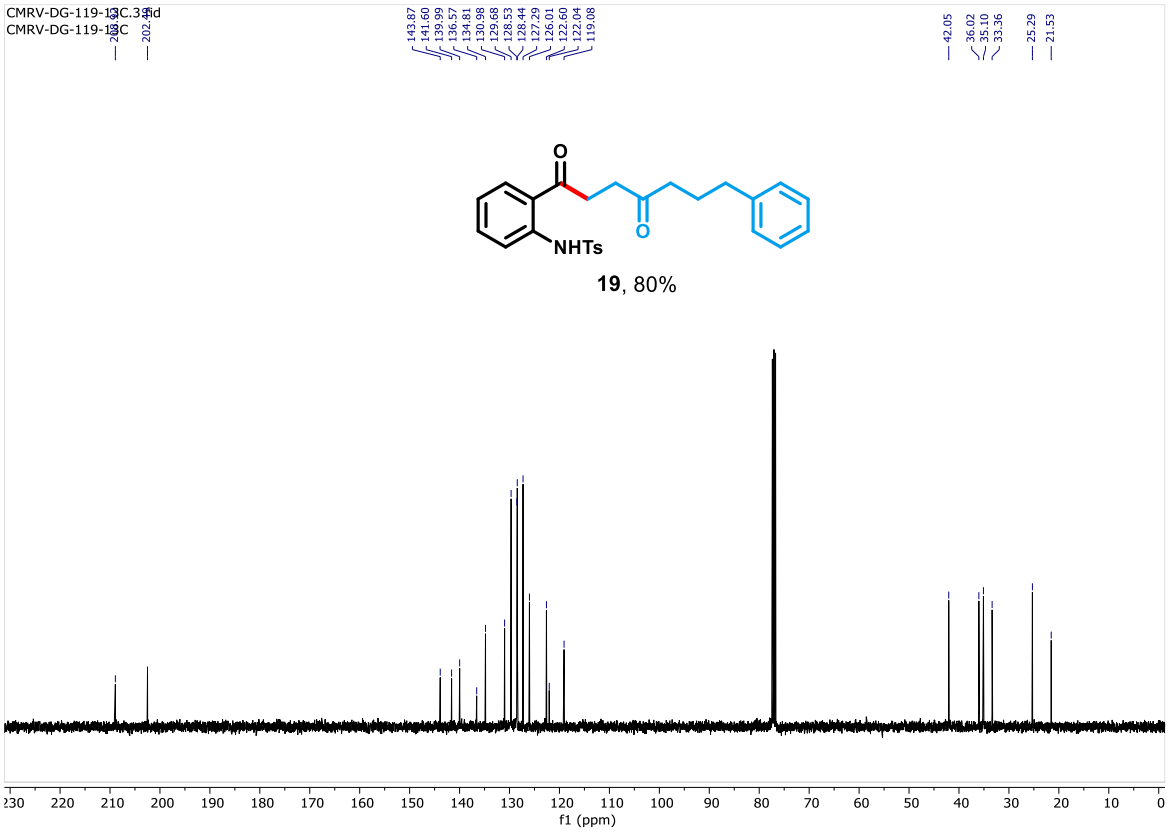
18


CMRV-DG-124-1H.17.fid
CMRV-DG-124-1H
Me
O
O
NHTs
18, 78%
f1 (ppm)

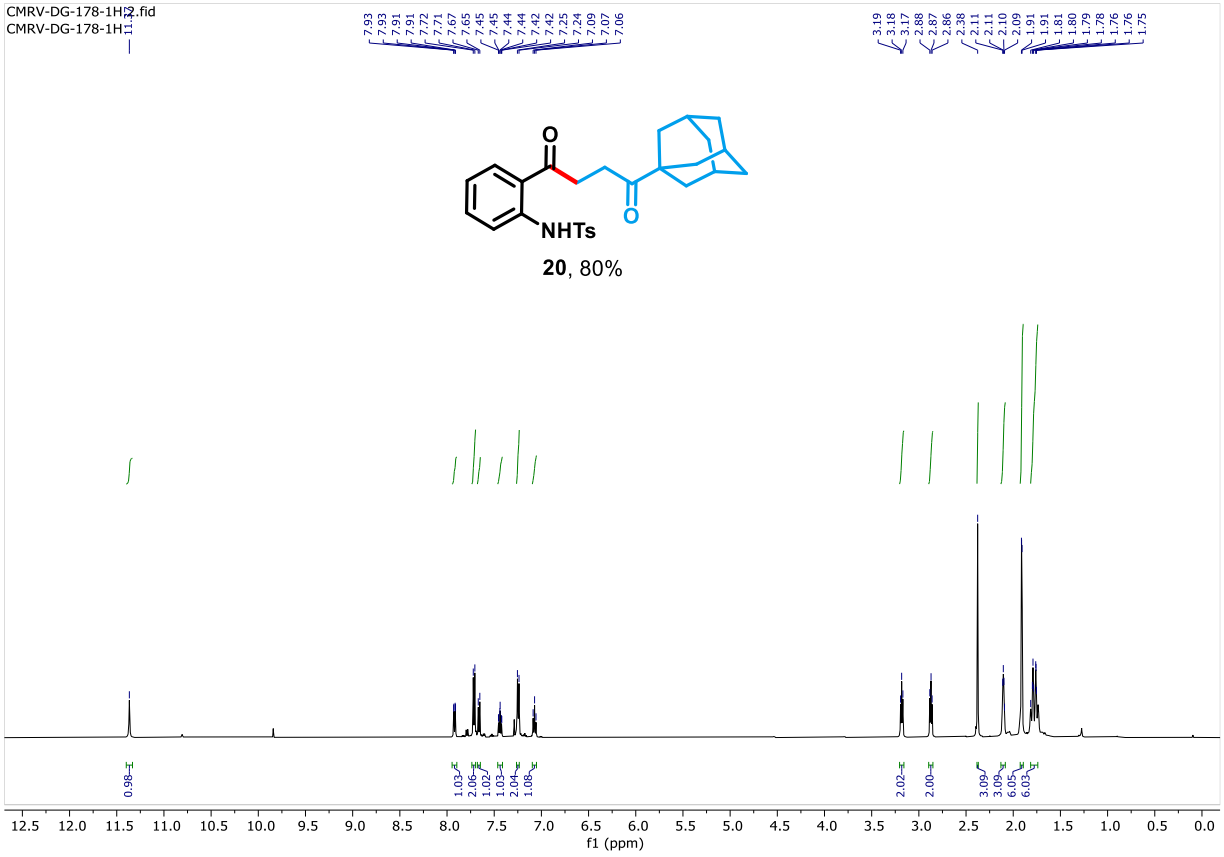

CMRV-DG-124-13C.18.fid
CMRV-DG-124-13C
Me
O
O
NHTs
18, 78%
f1 (ppm)

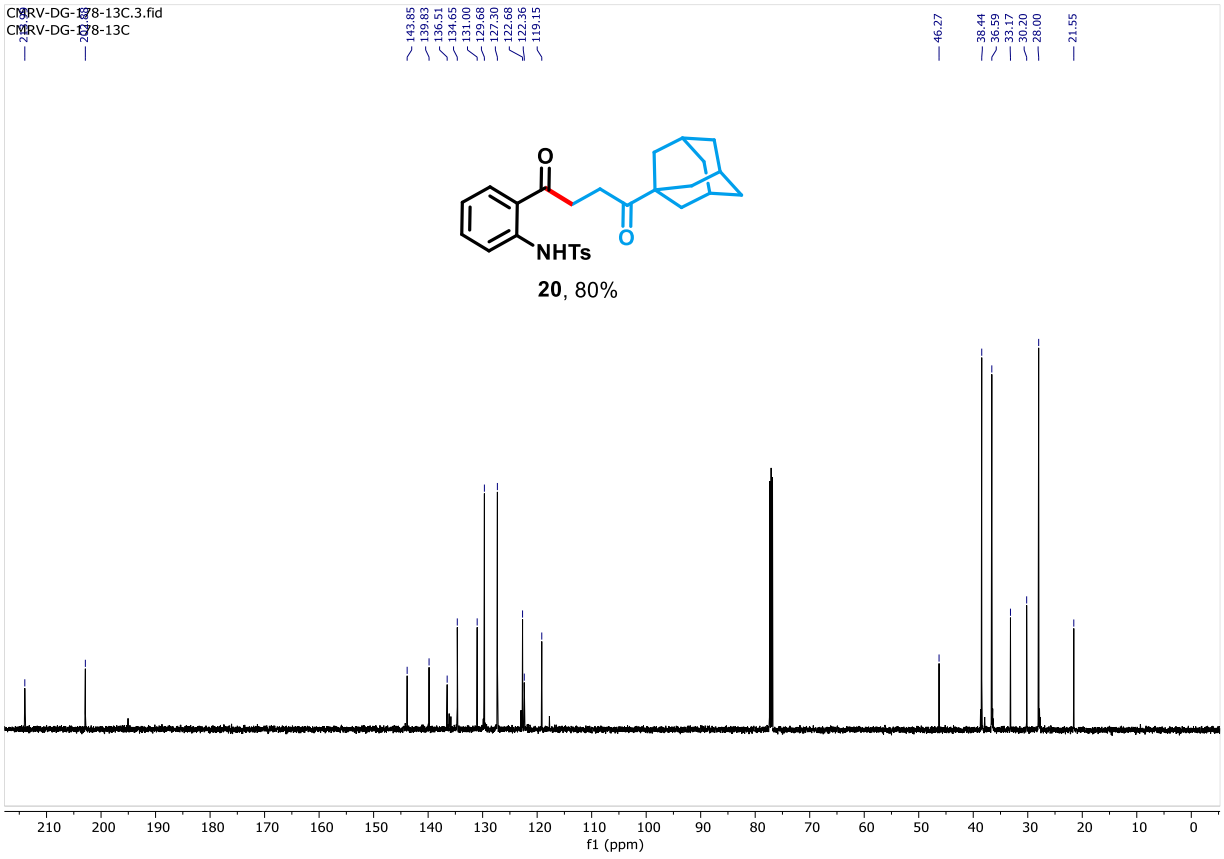
19


CMRV-DG-119-1H.1.fid
CMRV-DG-119-1H
NHTs
19, 80%
f1 (ppm)

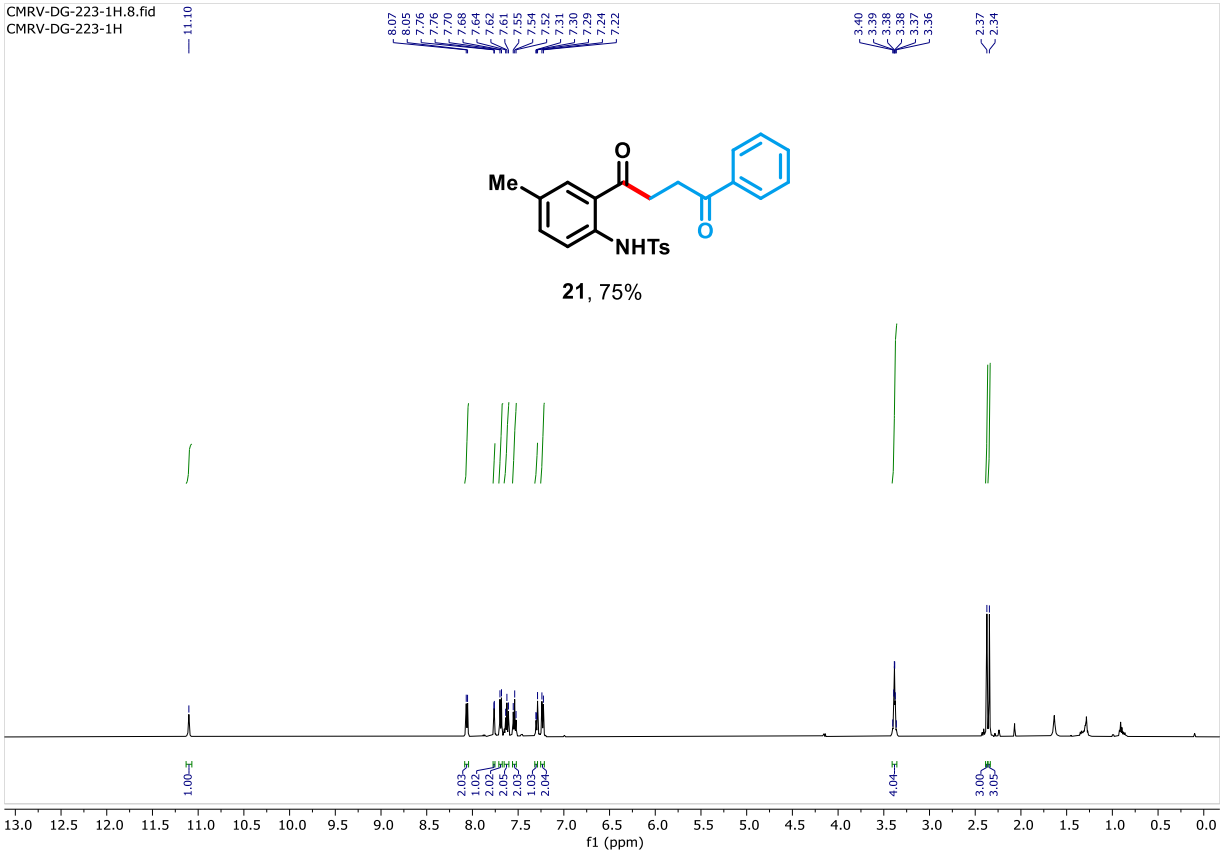

NHTs
19, 80%
f1 (ppm)

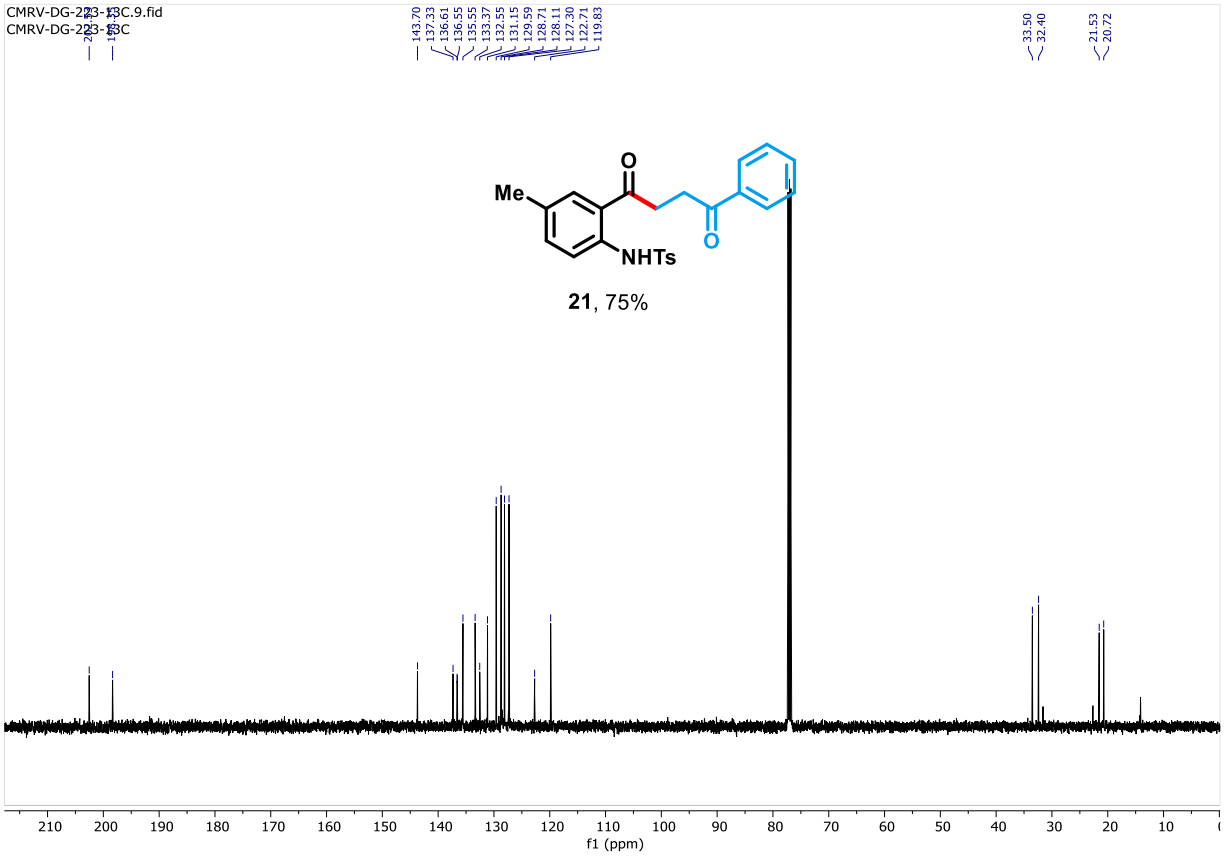
20


CMRV-DG-178-1H.2.fid
CMRV-DG-178-1H.1
O
NHTs
O
20, 80%
f1 (ppm)

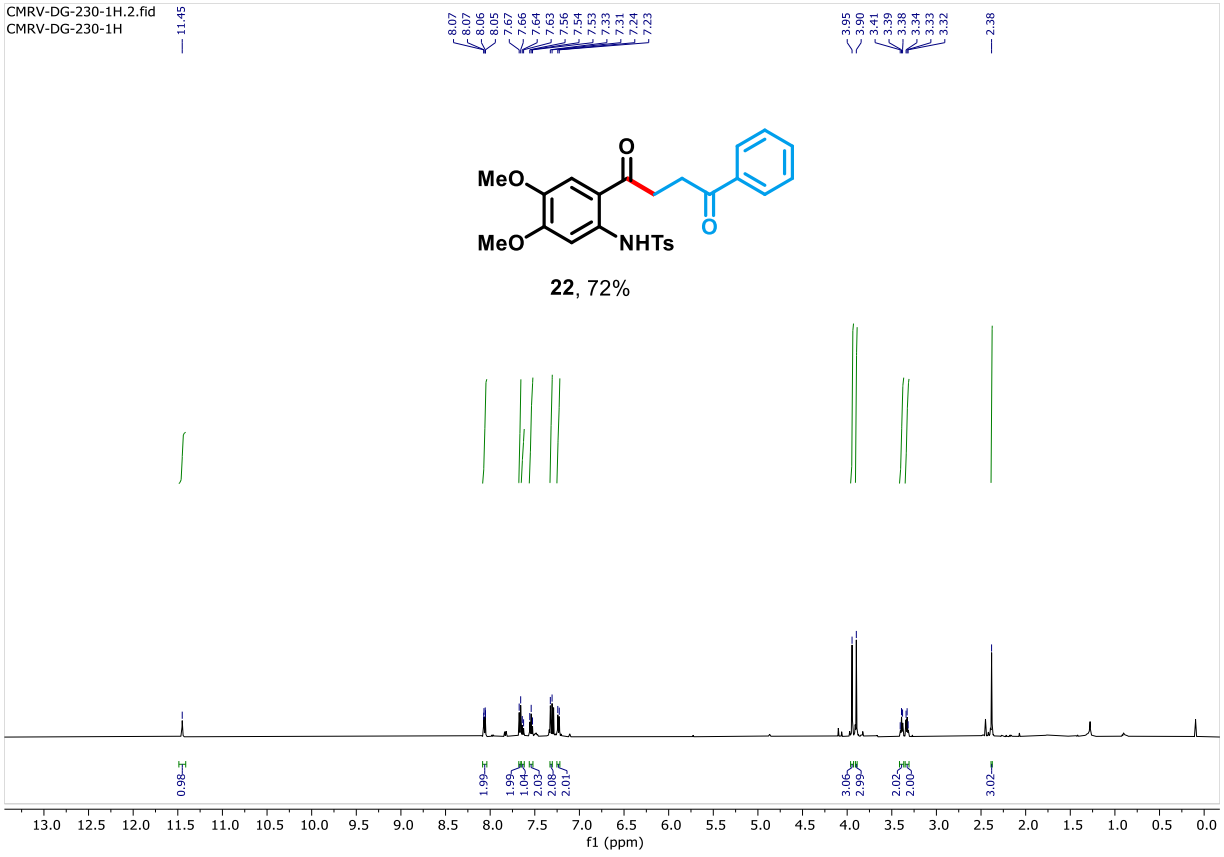

CMRV-DG-178-13C.3.fid
CMRV-DG-178-13C
O
NHTs
O
20, 80%
f1 (ppm)

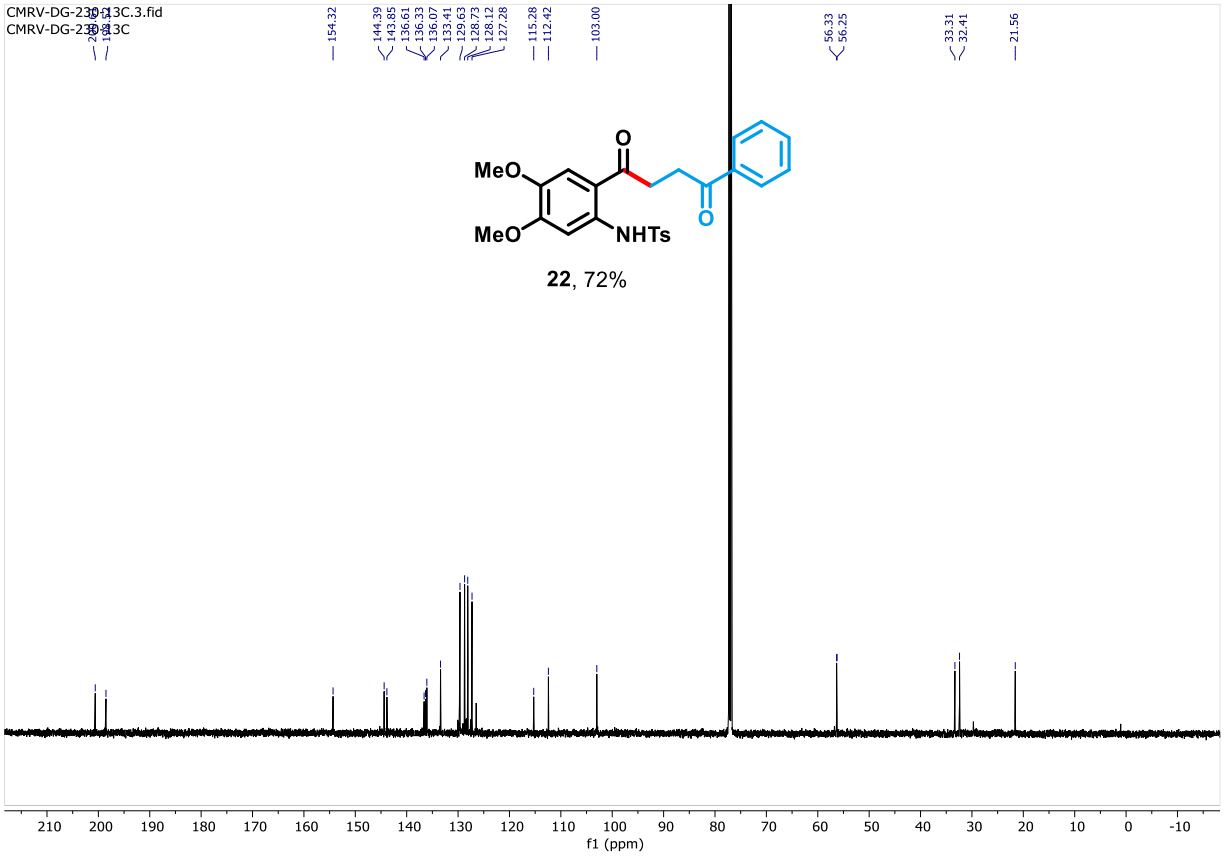
21


CMRV-DG-223-1H.8.fid
CMRV-DG-223-1H
11.10
8.07
8.05
7.76
7.76
7.70
7.68
7.64
7.62
7.61
7.55
7.54
7.52
7.31
7.30
7.29
7.24
7.22
3.40
3.39
3.38
3.38
3.37
3.36
2.37
2.34
Me
O
O
NHTs
21, 75%
1.00
2.03
1.02
2.02
2.05
2.03
1.03
2.04
4.04
3.00
3.05
13.0 12.5 12.0 11.5 11.0 10.5 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 0.0
f1 (ppm)

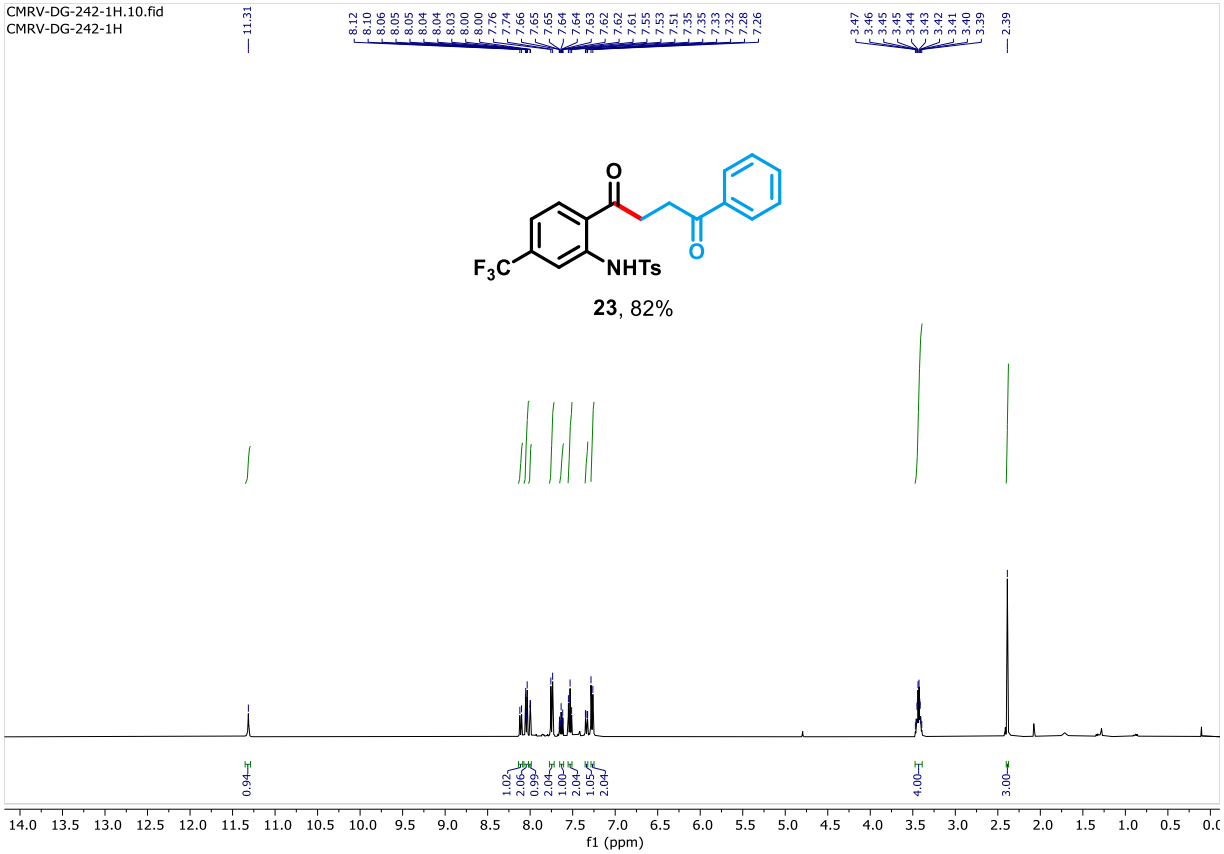

CMRV-DG-223-13C.9.fid
CMRV-DG-223-13C
143.70
137.33
136.61
136.55
135.55
133.37
132.55
131.15
129.59
128.71
128.11
127.30
122.71
119.83
33.50
32.40
21.53
20.72
Me
O
O
NHTs
21, 75%
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

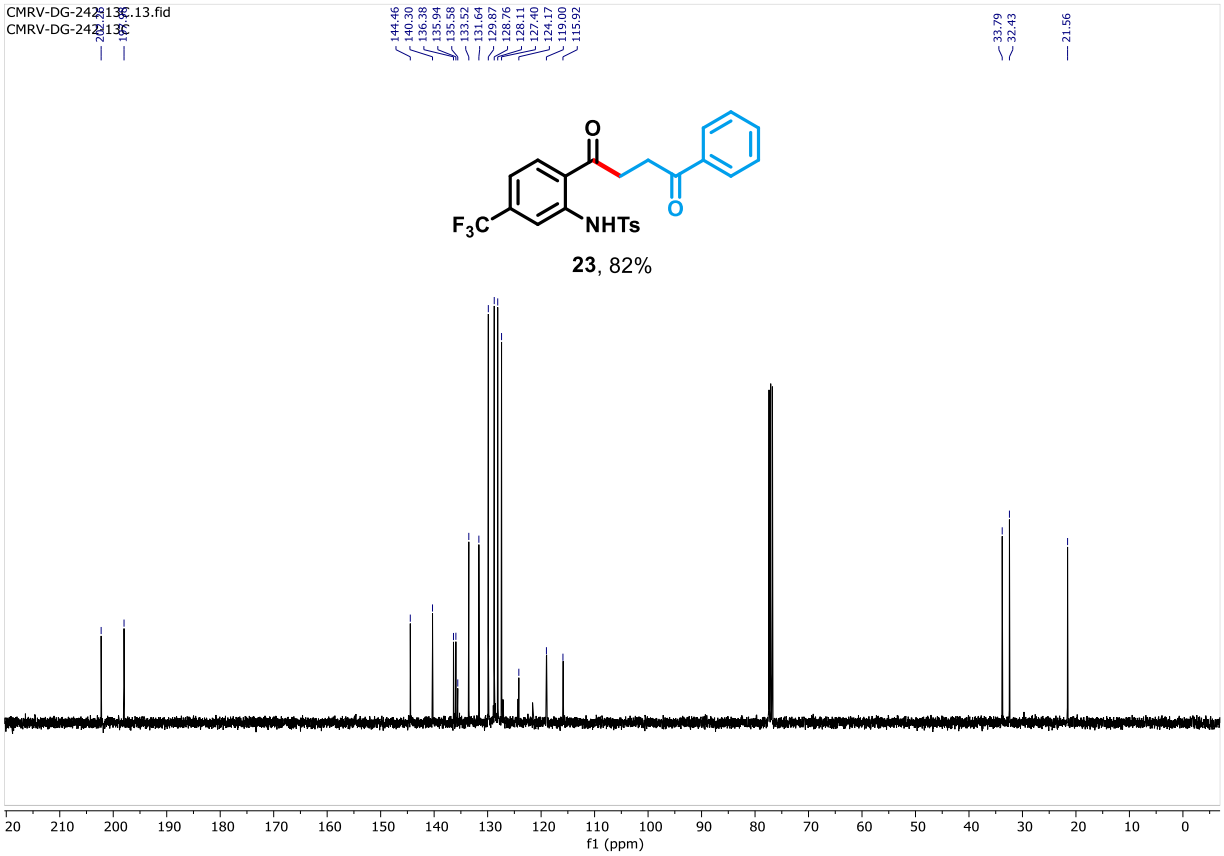
22


CMRV-DG-230-1H.2.fid
CMRV-DG-230-1H
MeO
MeO
NHTs
O
O
22, 72%
f1 (ppm)

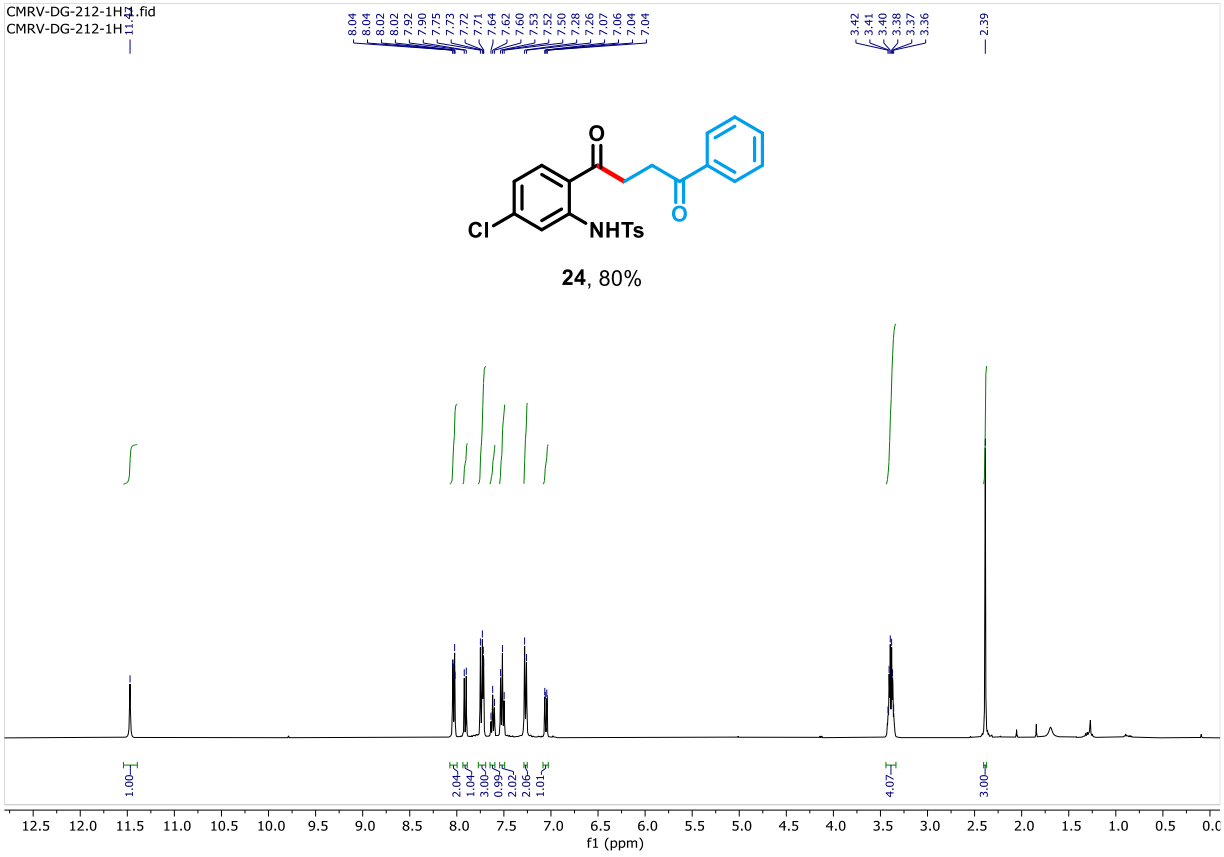

CMRV-DG-230-13C.3.fid
CMRV-DG-230-13C
MeO
MeO
NHTs
O
O
22, 72%
f1 (ppm)

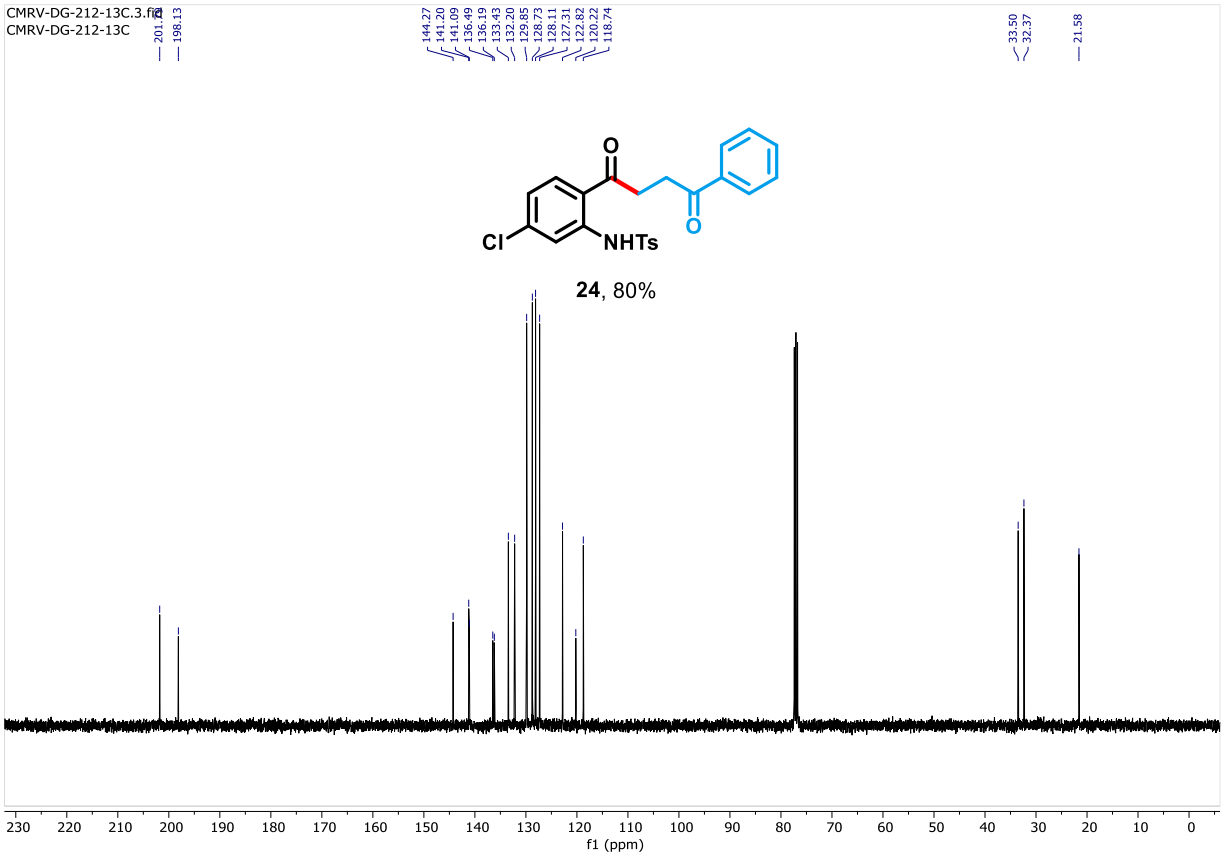
23


CMRV-DG-242-1H.10.fid
CMRV-DG-242-1H
F3C
NHTs
23, 82%
f1 (ppm)

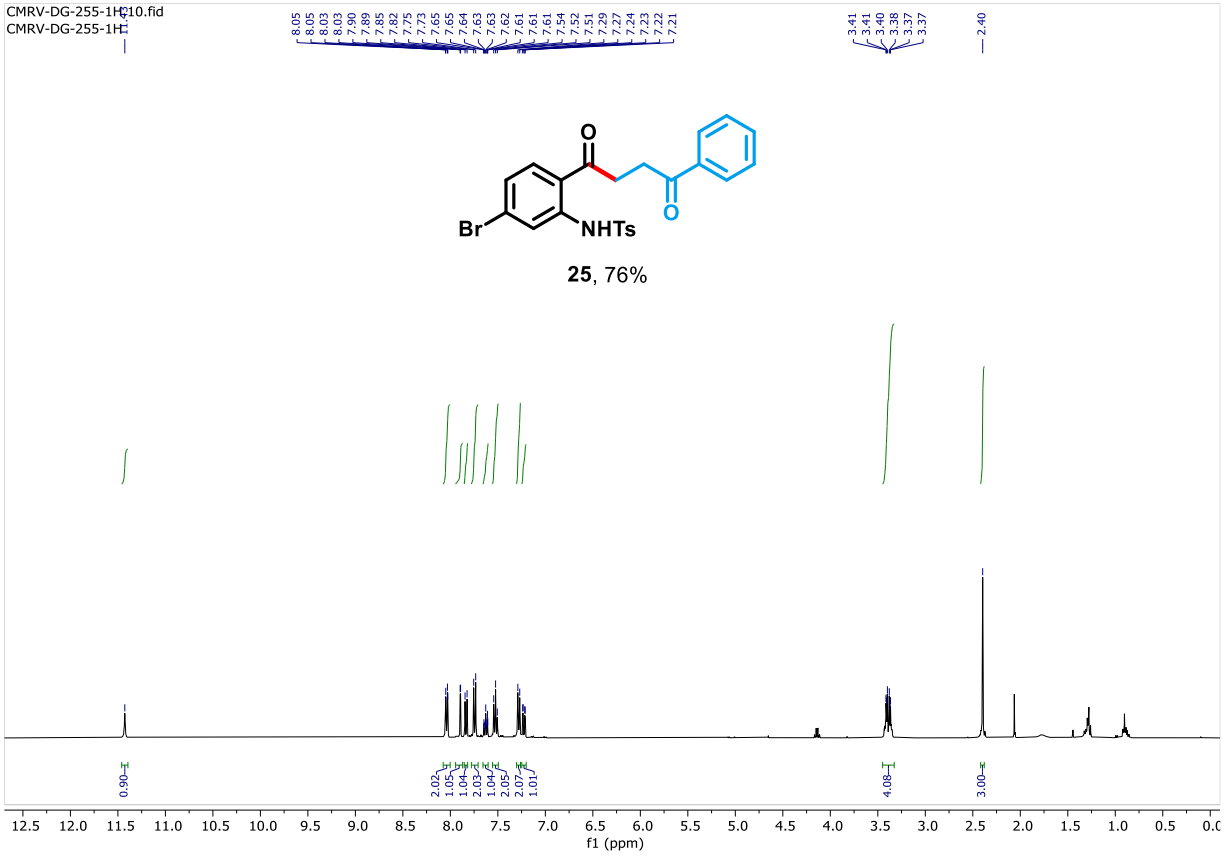

F3C
NHTs
23, 82%
f1 (ppm)

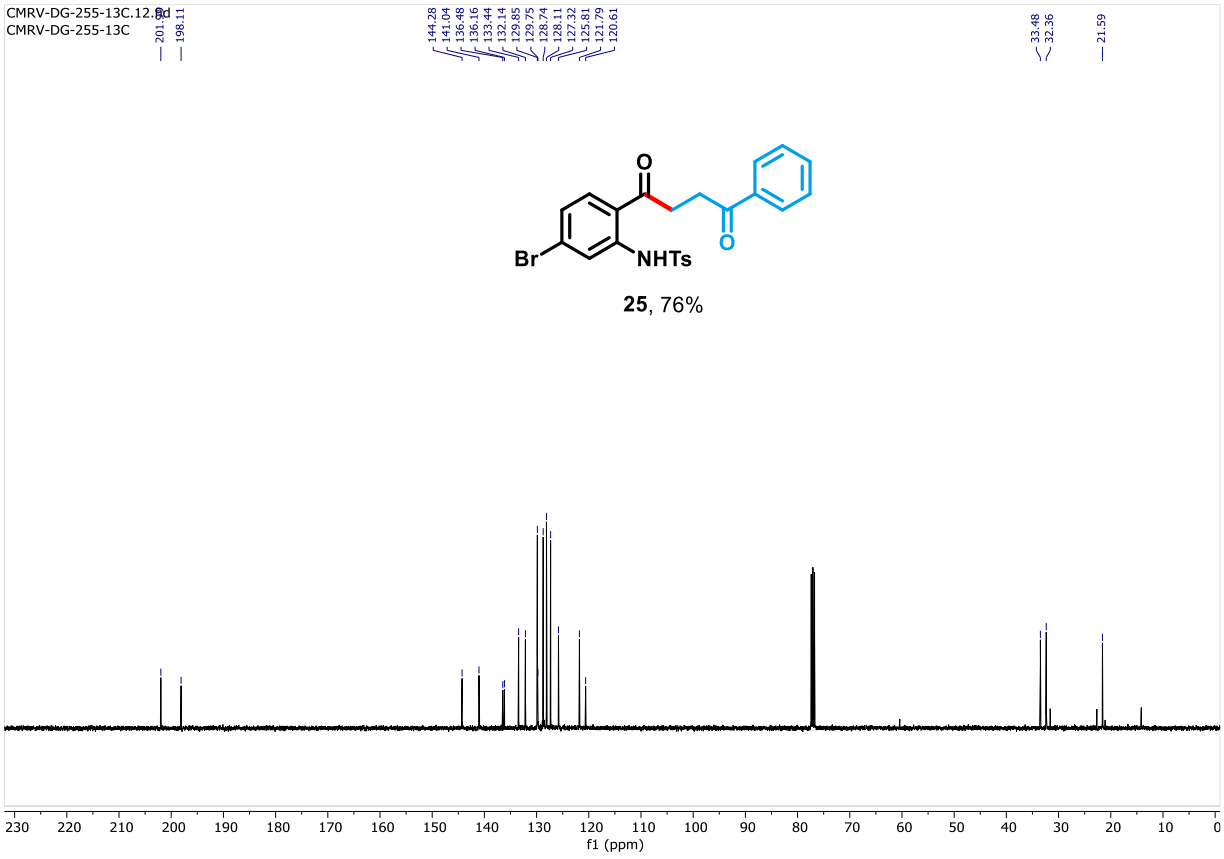
24


CMRV-DG-212-1H-1.fid
CMRV-DG-212-1H
11.47
8.04
8.04
8.02
8.02
7.92
7.90
7.75
7.73
7.72
7.71
7.64
7.62
7.60
7.53
7.52
7.50
7.28
7.26
7.07
7.06
7.04
7.04
3.42
3.41
3.40
3.38
3.37
3.36
2.39
O
O
Cl
NHTs
24, 80%
1.00
2.04
1.04
3.00
0.99
2.02
2.06
1.01
4.07
3.00
12.5 12.0 11.5 11.0 10.5 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 0.0
f1 (ppm)

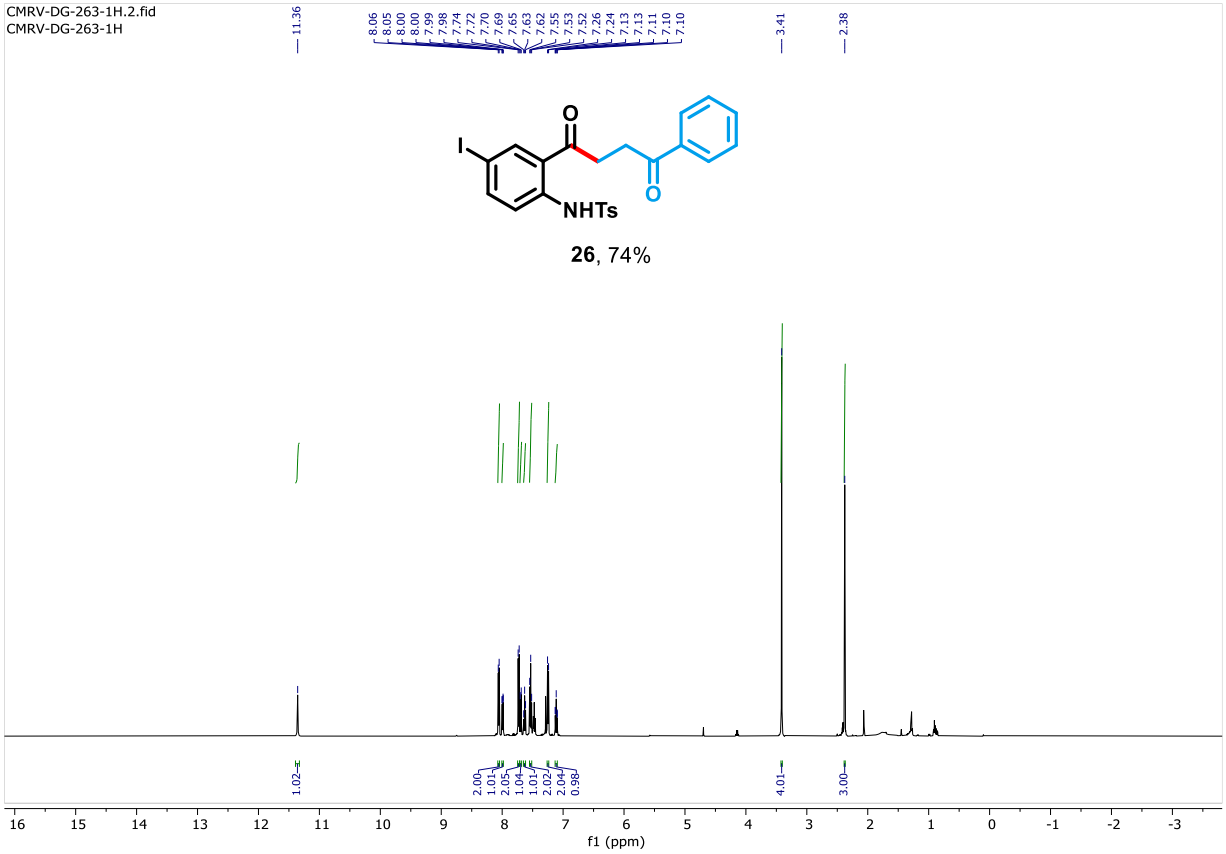

CMRV-DG-212-13C.3.fid
CMRV-DG-212-13C
201.14
198.13
144.27
141.20
141.09
136.49
136.19
133.43
132.20
129.85
128.73
128.11
127.31
122.82
120.22
118.74
33.50
32.37
21.58
O
O
Cl
NHTs
24, 80%
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

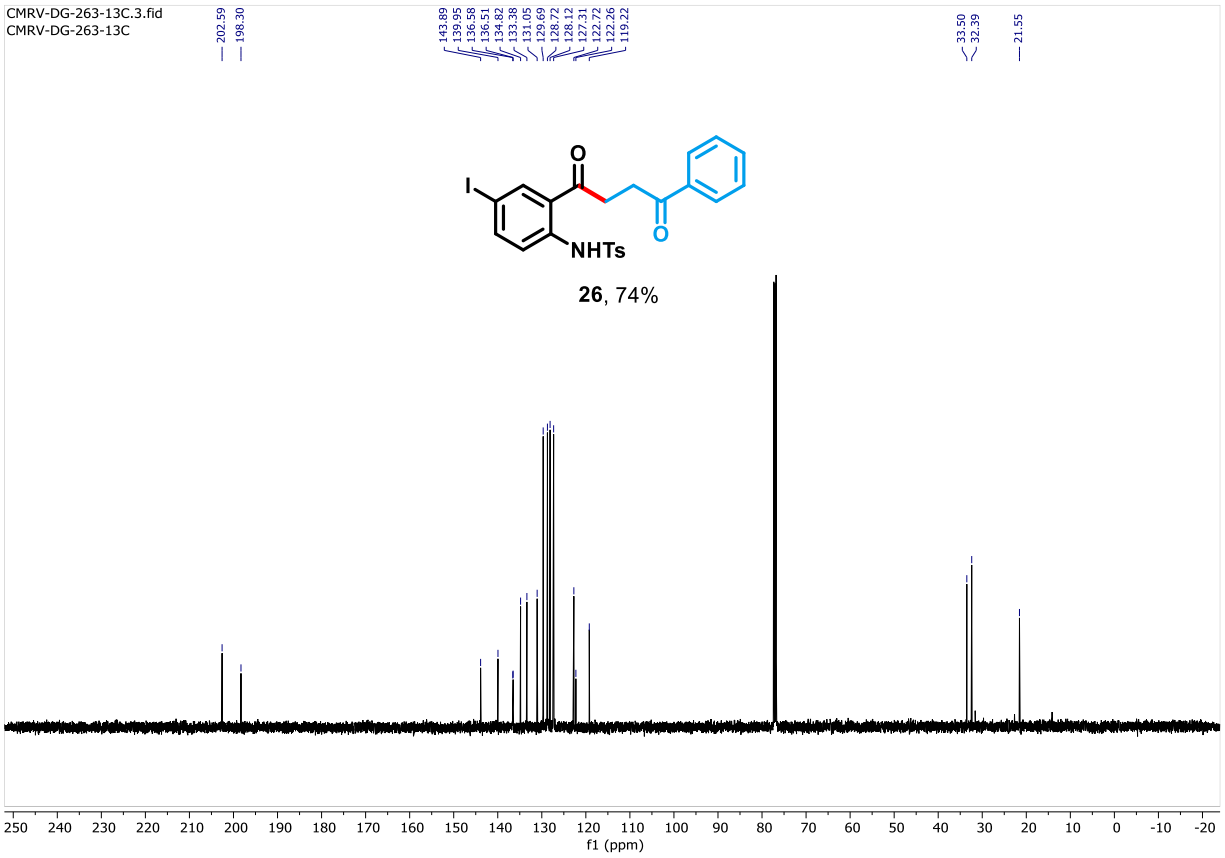
25


CMRV-DG-255-1H-10.fid
CMRV-DG-255-1H
8.05 8.05 8.03 8.03 7.90 7.89 7.85 7.82 7.75 7.73 7.65 7.65 7.64 7.63 7.63 7.62 7.61 7.61 7.61 7.54 7.52 7.51 7.29 7.27 7.24 7.23 7.22 7.21
3.41 3.41 3.40 3.38 3.37 3.37
2.40
O
O
Br
NHTs
25, 76%
0.90
2.02 1.05 1.04 2.03 1.04 2.05 2.07 1.01
4.08
3.00
f1 (ppm)

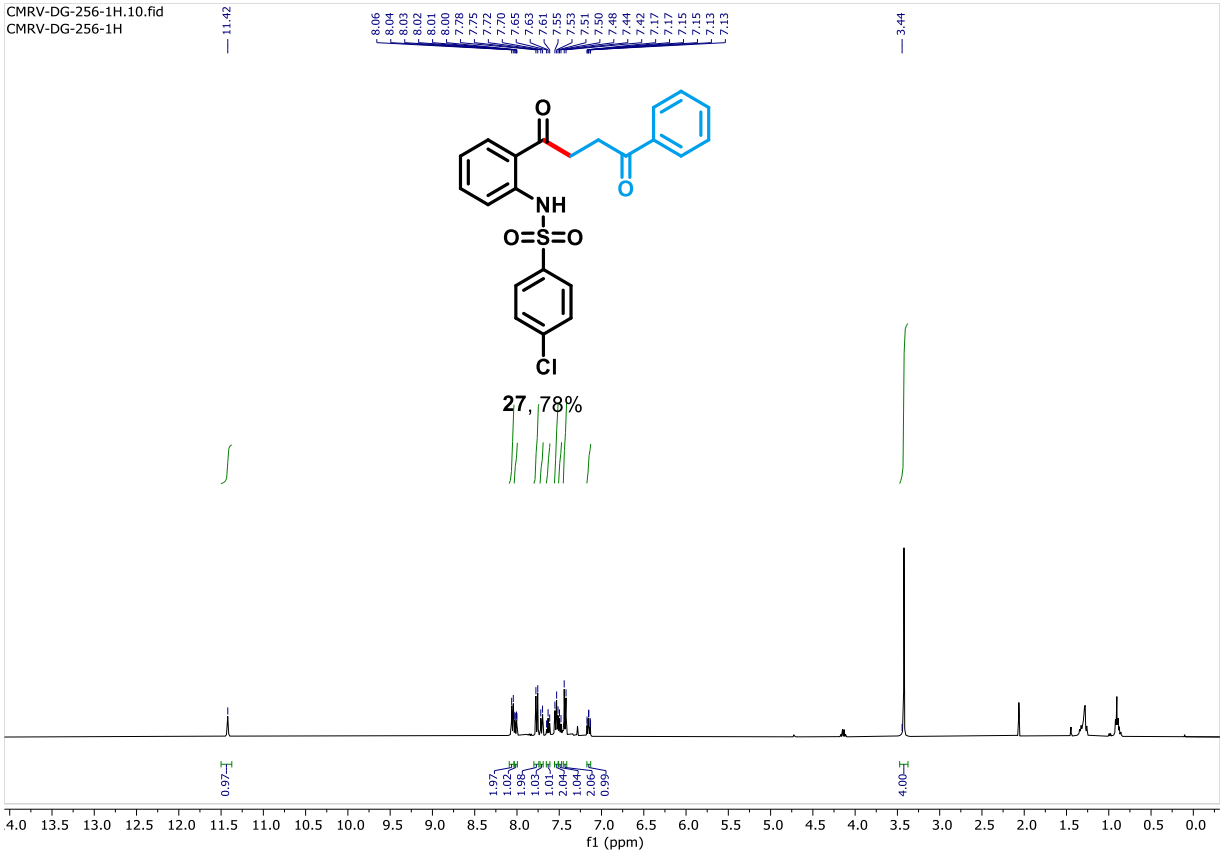

CMRV-DG-255-13C.12.fid
CMRV-DG-255-13C
201.69
198.11
144.28 141.04 136.48 136.16 133.44 132.14 129.85 129.75 128.74 128.11 127.32 125.81 121.79 120.61
33.48
32.36
21.59
O
O
Br
NHTs
25, 76%
f1 (ppm)

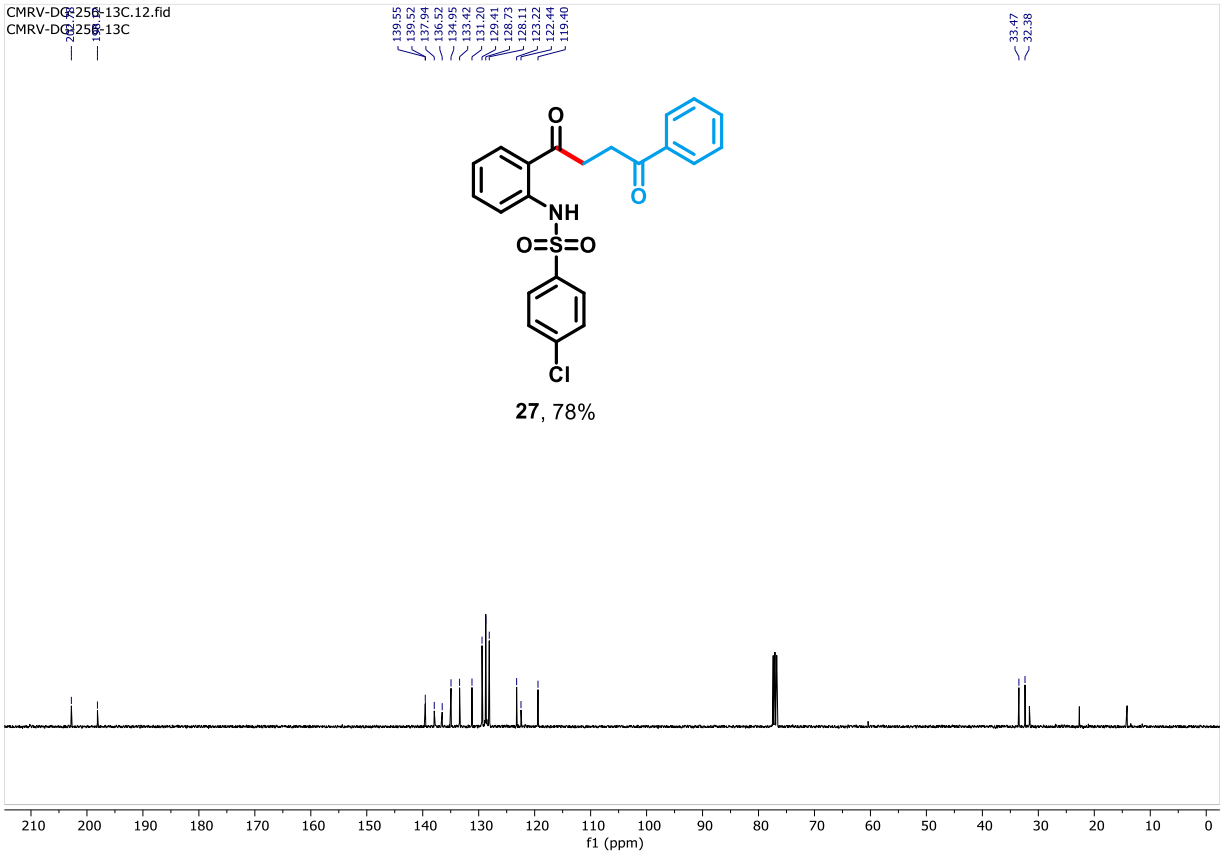
26


CMRV-DG-263-1H.2.fid
CMRV-DG-263-1H
11.36
8.06
8.05
8.00
8.00
7.99
7.98
7.74
7.72
7.70
7.69
7.65
7.63
7.62
7.55
7.53
7.52
7.26
7.24
7.13
7.13
7.11
7.10
7.10
3.41
2.38
O
I
O
NHTs
26, 74%
1.02
2.00
1.01
2.05
1.04
1.01
2.02
2.04
0.98
4.01
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

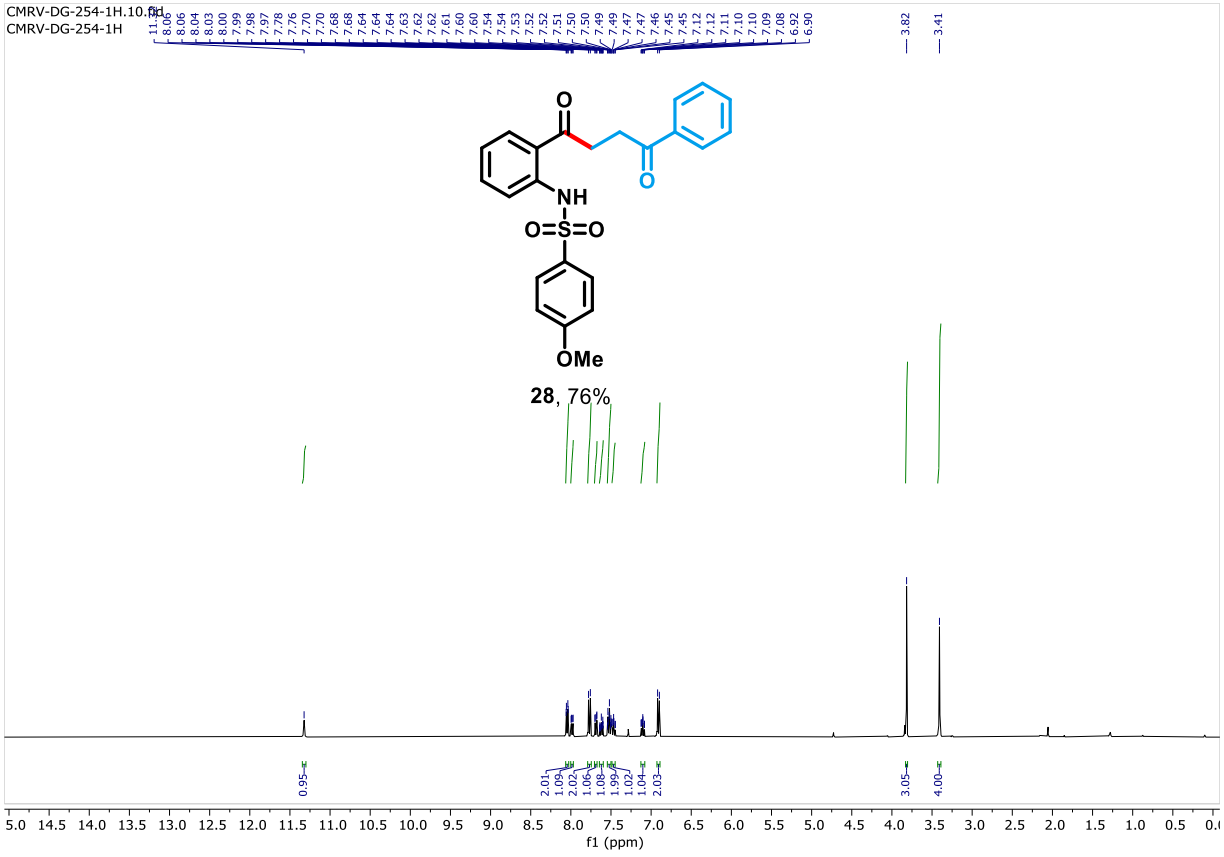

CMRV-DG-263-13C.3.fid
CMRV-DG-263-13C
202.59
198.30
143.89
139.95
136.58
136.51
134.82
133.38
131.05
129.69
128.72
128.12
127.31
122.72
122.26
119.22
33.50
32.39
21.55
O
I
O
NHTs
26, 74%
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

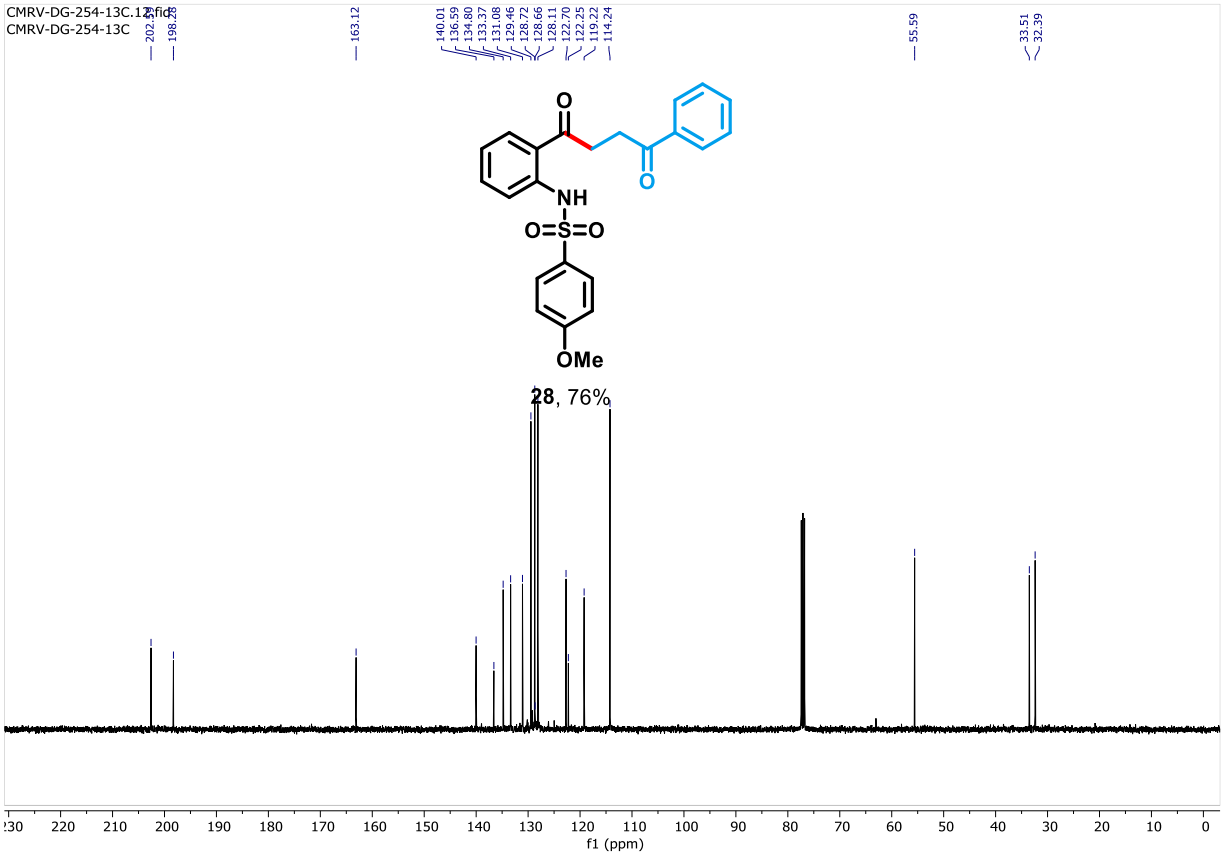
27


CMRV-DG-256-1H.10.fid
CMRV-DG-256-1H
11.42
8.06
8.04
8.03
8.02
8.01
8.00
7.78
7.75
7.72
7.70
7.65
7.63
7.61
7.55
7.53
7.51
7.50
7.48
7.44
7.42
7.17
7.17
7.15
7.15
7.13
7.13
3.44
O
NH
O=S=O
Cl
27, 78%
0.97
1.97
1.02
1.98
1.03
1.01
2.04
1.04
2.06
0.99
4.00
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 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 0.0
f1 (ppm)

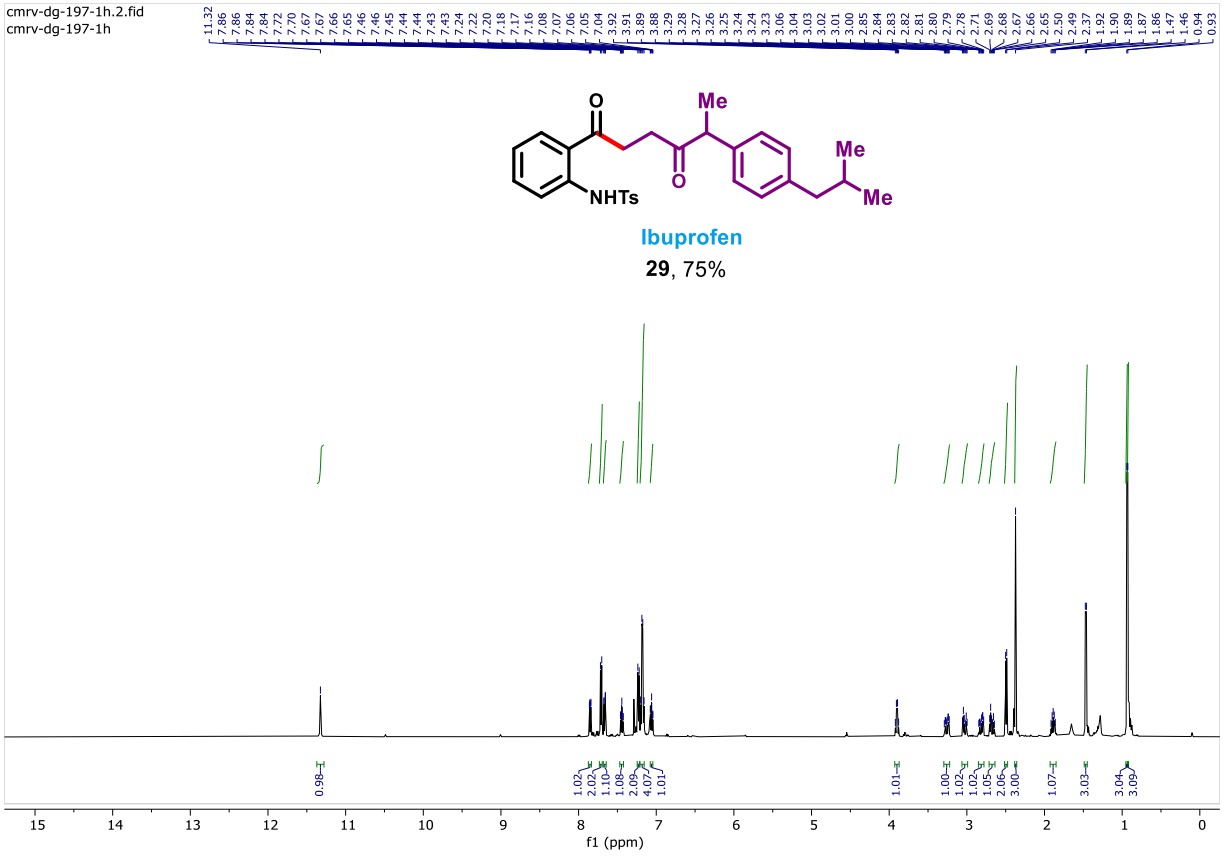

CMRV-DG-256-13C.12.fid
CMRV-DG-256-13C
139.55
139.52
137.94
136.52
134.95
133.42
131.20
129.41
128.73
128.11
123.22
122.44
119.40
33.47
32.38
O
NH
O=S=O
Cl
27, 78%
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

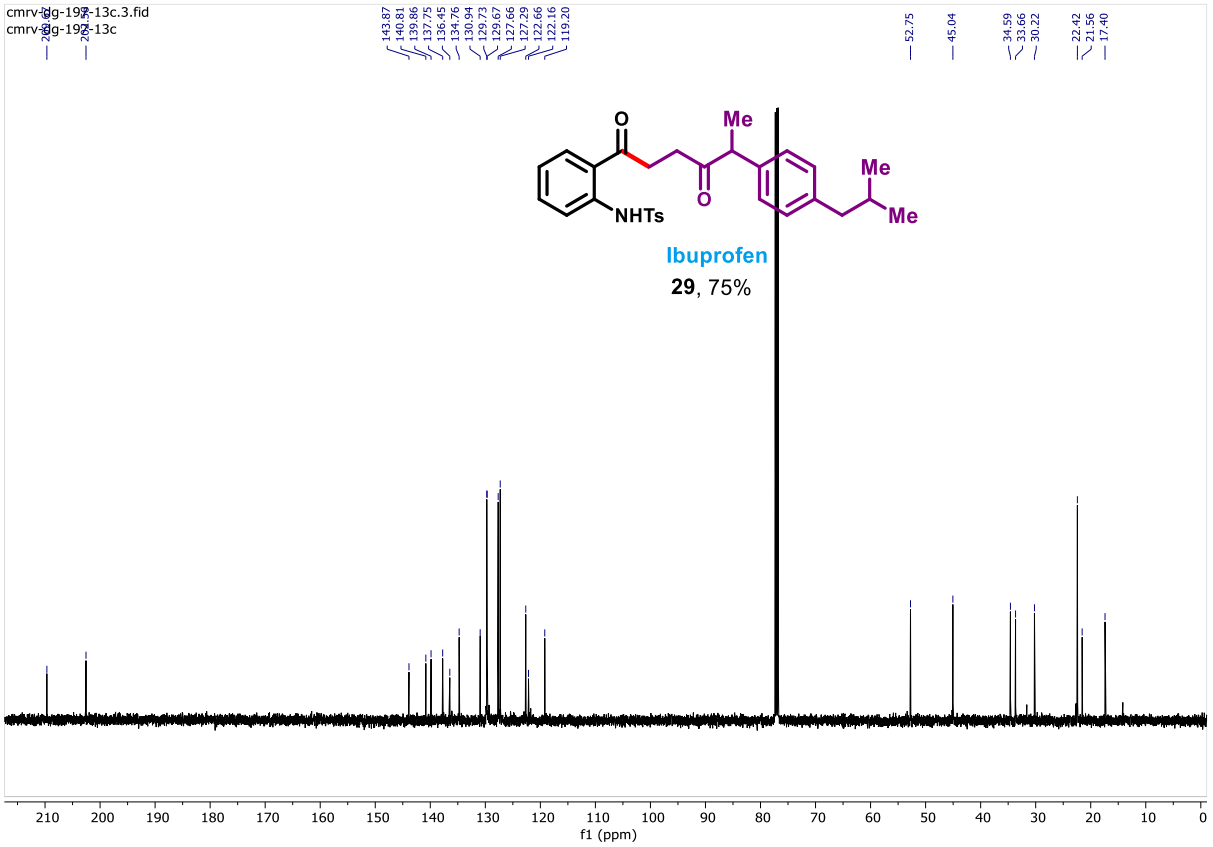
28


CMRV-DG-254-1H.10.fid
CMRV-DG-254-1H
3.82
3.41
O
NH
O=S=O
O
OMe
28, 76%
0.95
2.01
1.09
2.02
1.06
1.08
1.99
1.02
1.04
2.03
3.05
4.00
f1 (ppm)

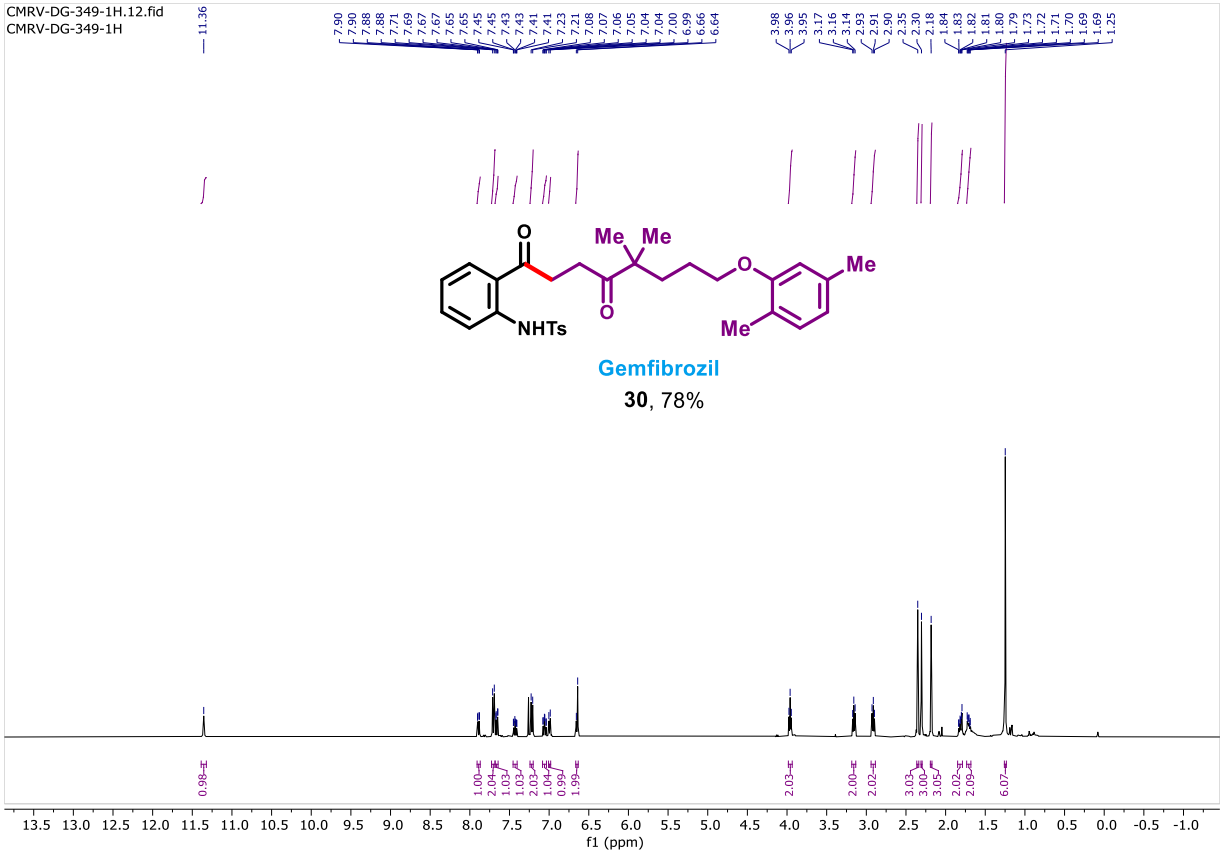

CMRV-DG-254-13C.12.fid
CMRV-DG-254-13C
202.71
198.29
163.12
140.01
136.59
134.80
133.37
131.08
129.46
128.72
128.66
128.11
122.70
122.25
119.22
114.24
55.59
33.51
32.39
O
NH
O=S=O
O
OMe
28, 76%
f1 (ppm)

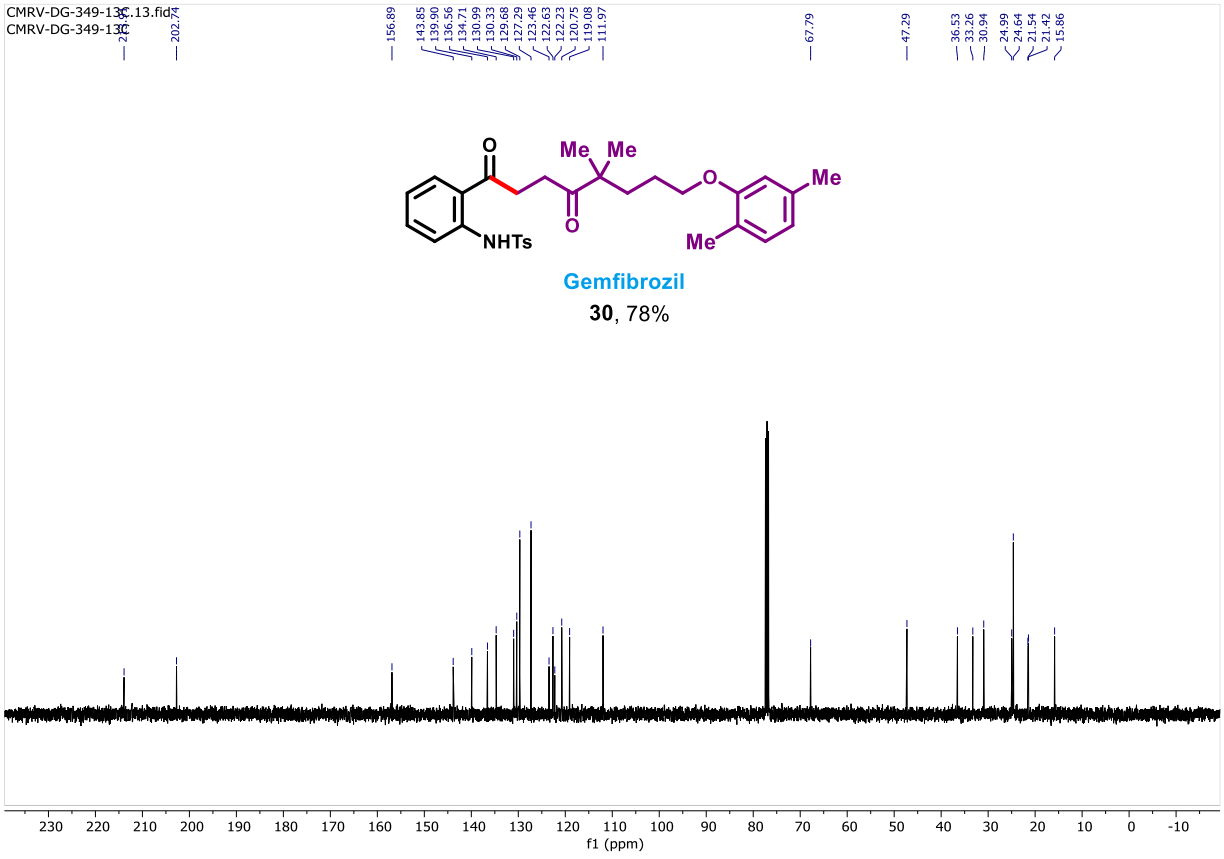
29


cmrv-dg-197-1h.2.fid
cmrv-dg-197-1h
Me
Me
Me
O
O
NHTs
Ibuprofen
29, 75%
f1 (ppm)

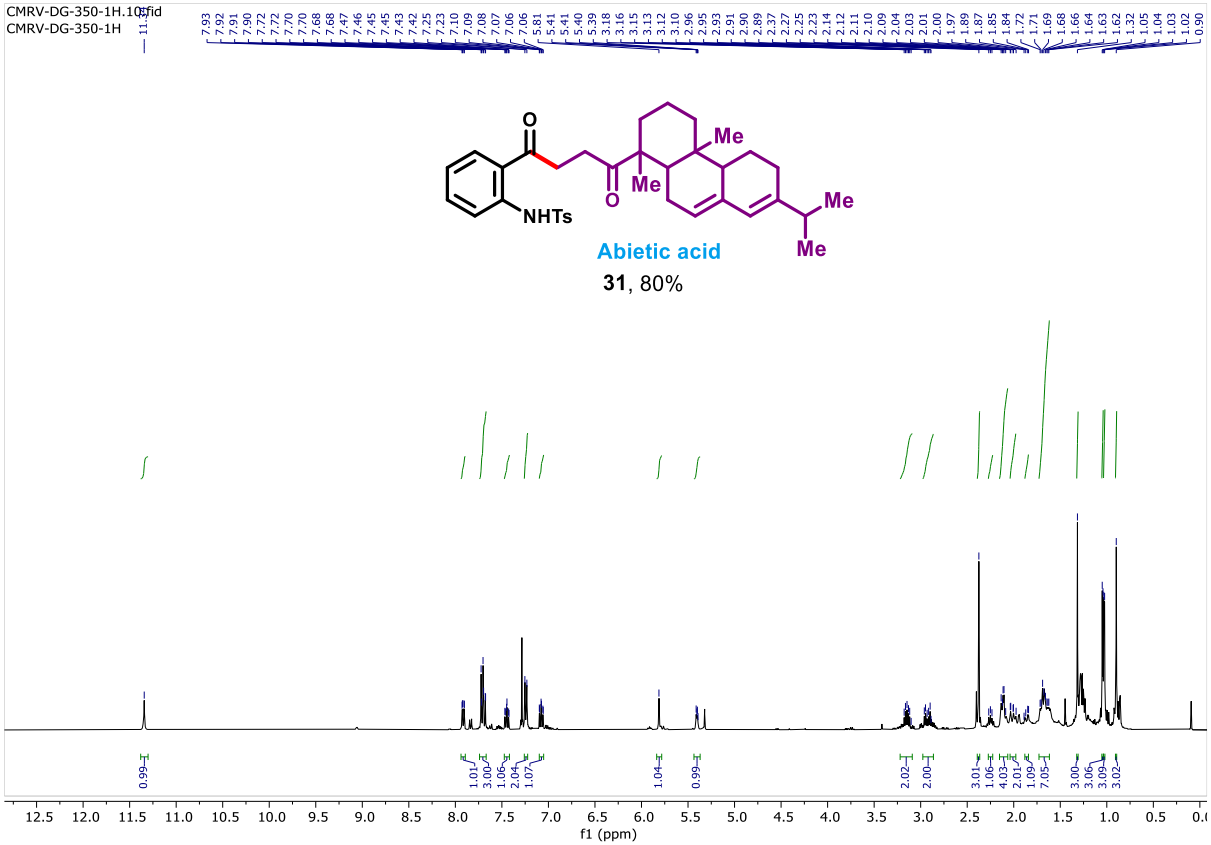

cmrv-dg-197-13c.3.fid
cmrv-dg-197-13c
Me
Me
Me
O
O
NHTs
Ibuprofen
29, 75%
f1 (ppm)

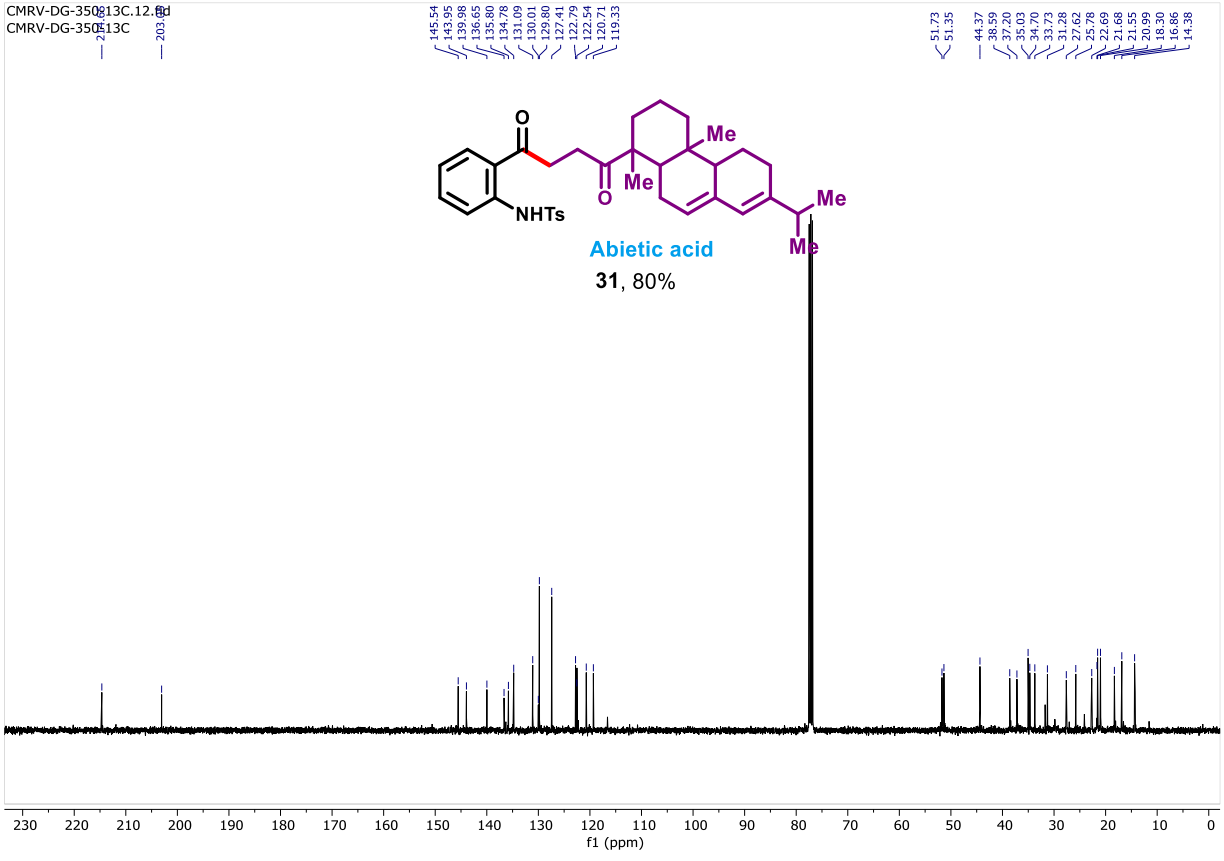
30


CMRV-DG-349-1H.12.fid
CMRV-DG-349-1H
Gemfibrozil
30, 78%
f1 (ppm)

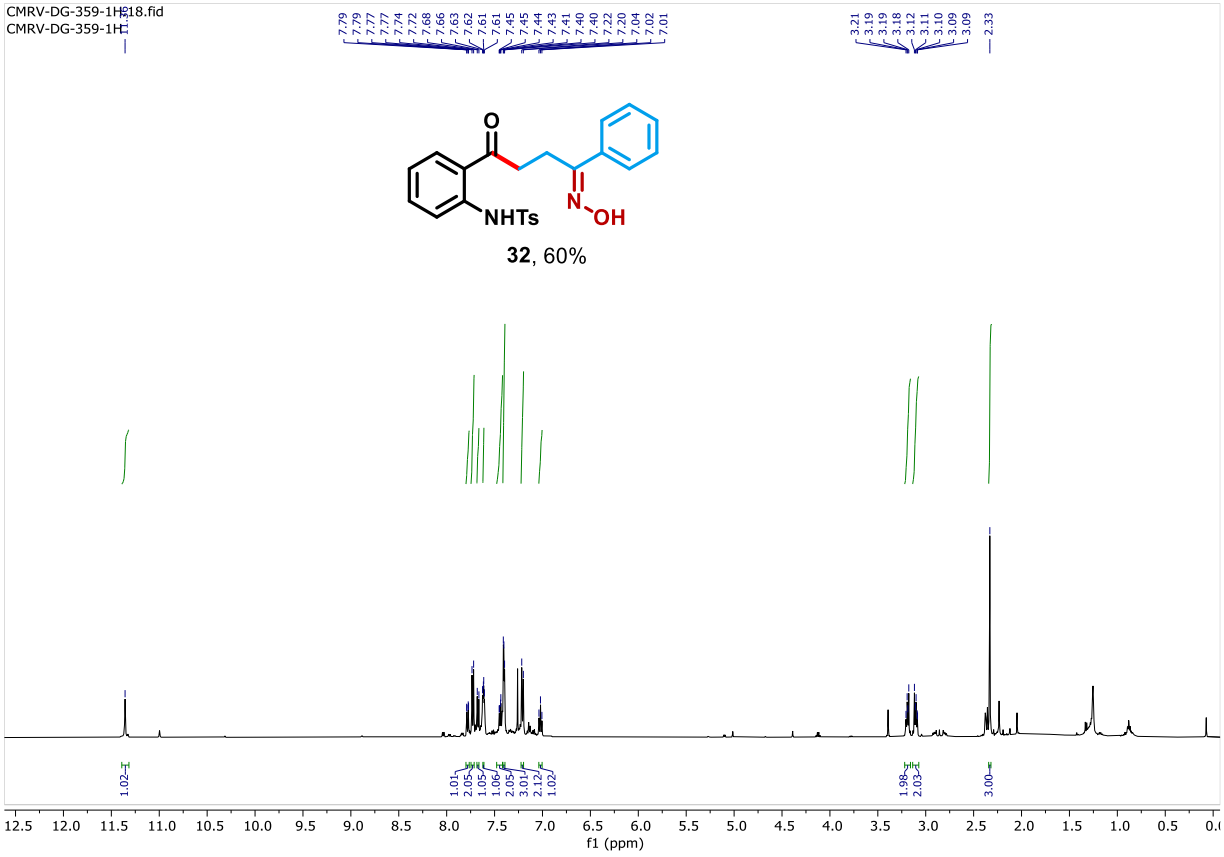

CMRV-DG-349-13C.13.fid
CMRV-DG-349-13C
Gemfibrozil
30, 78%
f1 (ppm)

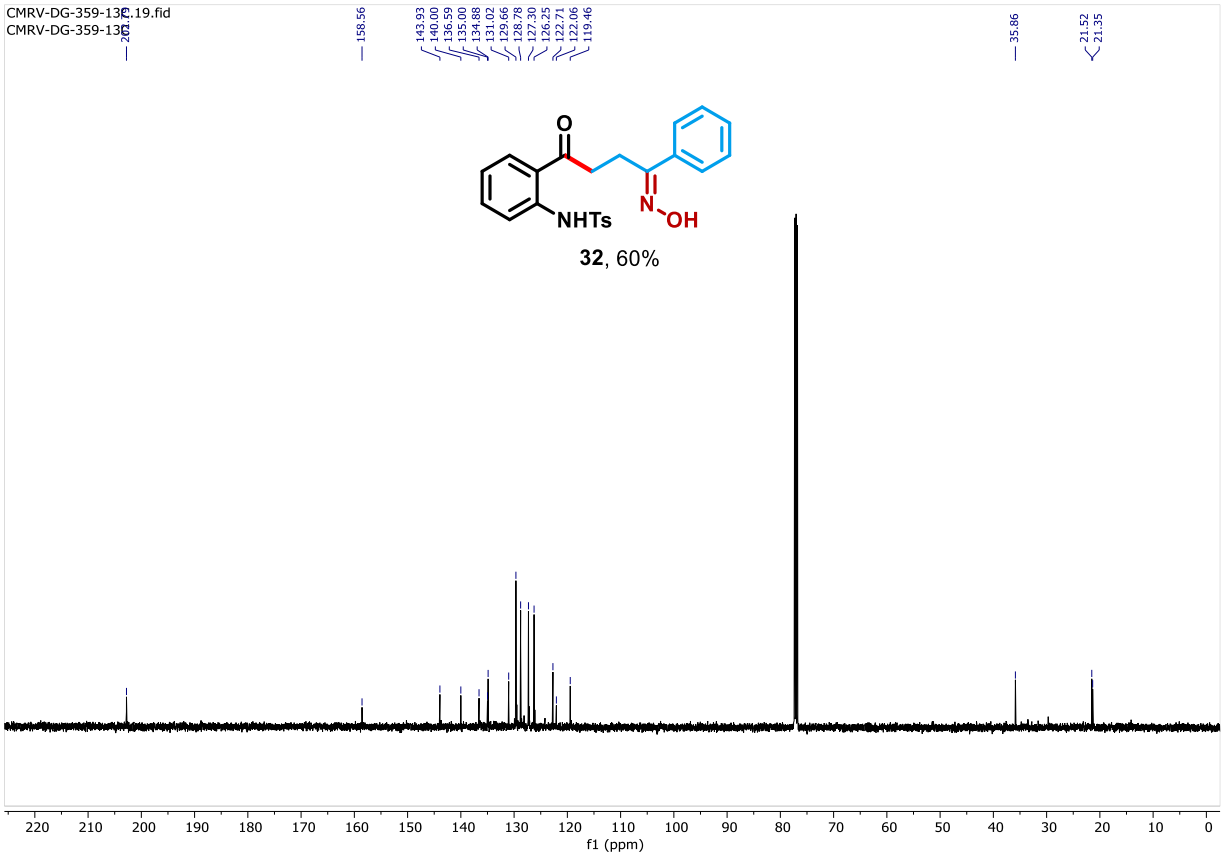
31


CMRV-DG-350-1H.10.fid
CMRV-DG-350-1H
NHTs
Me
Me
Me
Me
Abietic acid
31, 80%
f1 (ppm)

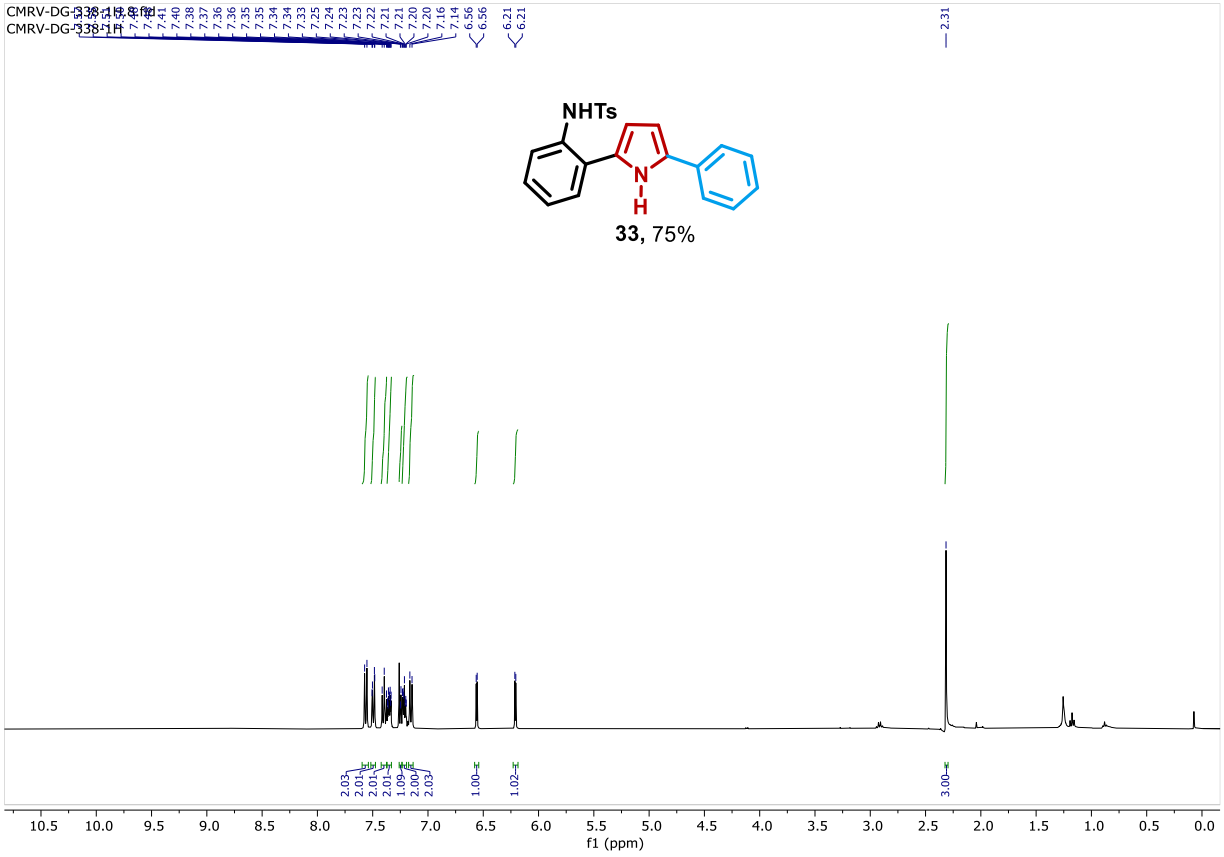

CMRV-DG-350-13C.12.fid
CMRV-DG-350-13C
NHTs
Me
Me
Me
Me
Abietic acid
31, 80%
f1 (ppm)

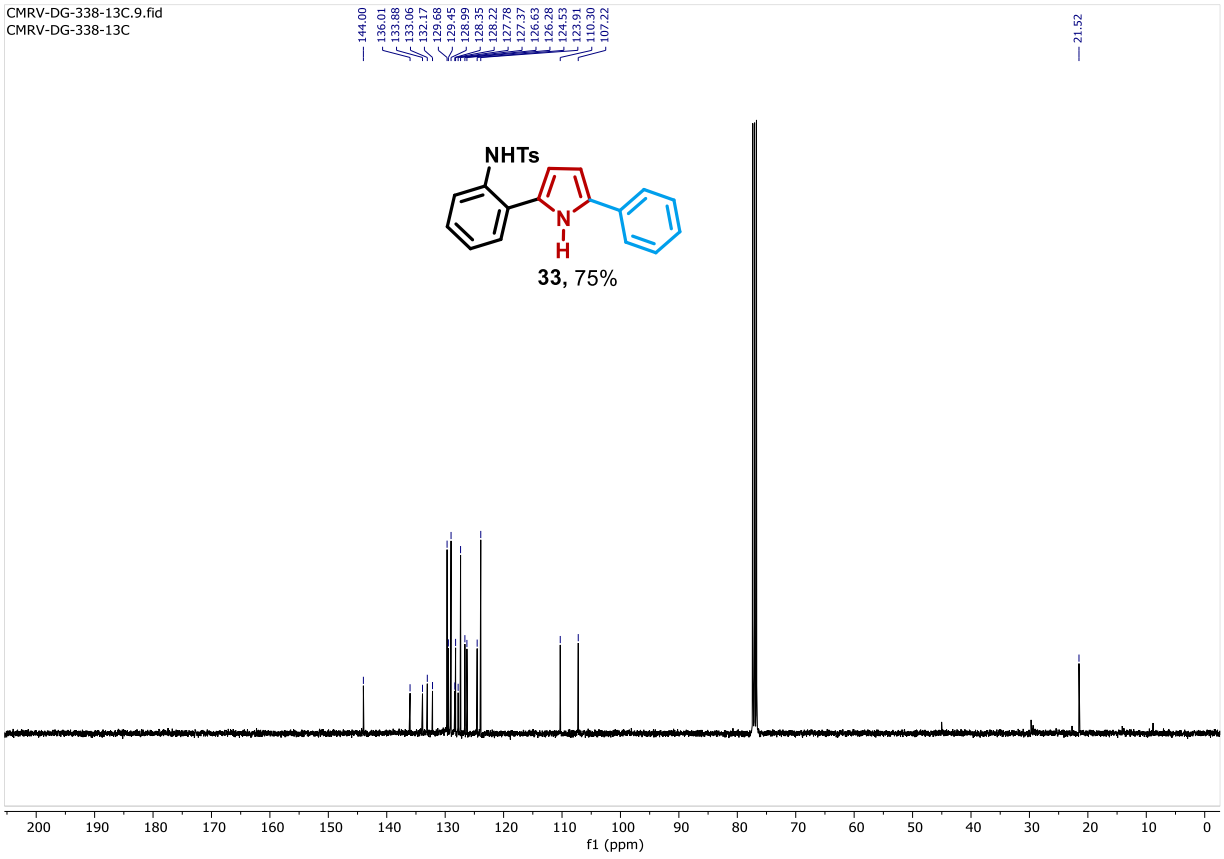
32


CMRV-DG-359-1H-18.fid
CMRV-DG-359-1H
7.79
7.79
7.77
7.77
7.74
7.72
7.68
7.66
7.63
7.62
7.61
7.61
7.45
7.45
7.44
7.43
7.41
7.40
7.40
7.22
7.20
7.04
7.02
7.01
3.21
3.19
3.19
3.18
3.12
3.11
3.10
3.09
3.09
2.33
O
NHTs
N
OH
32, 60%
1.02
1.01
2.05
1.05
1.06
2.05
3.01
2.12
1.02
1.98
2.03
3.00
12.5 12.0 11.5 11.0 10.5 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)

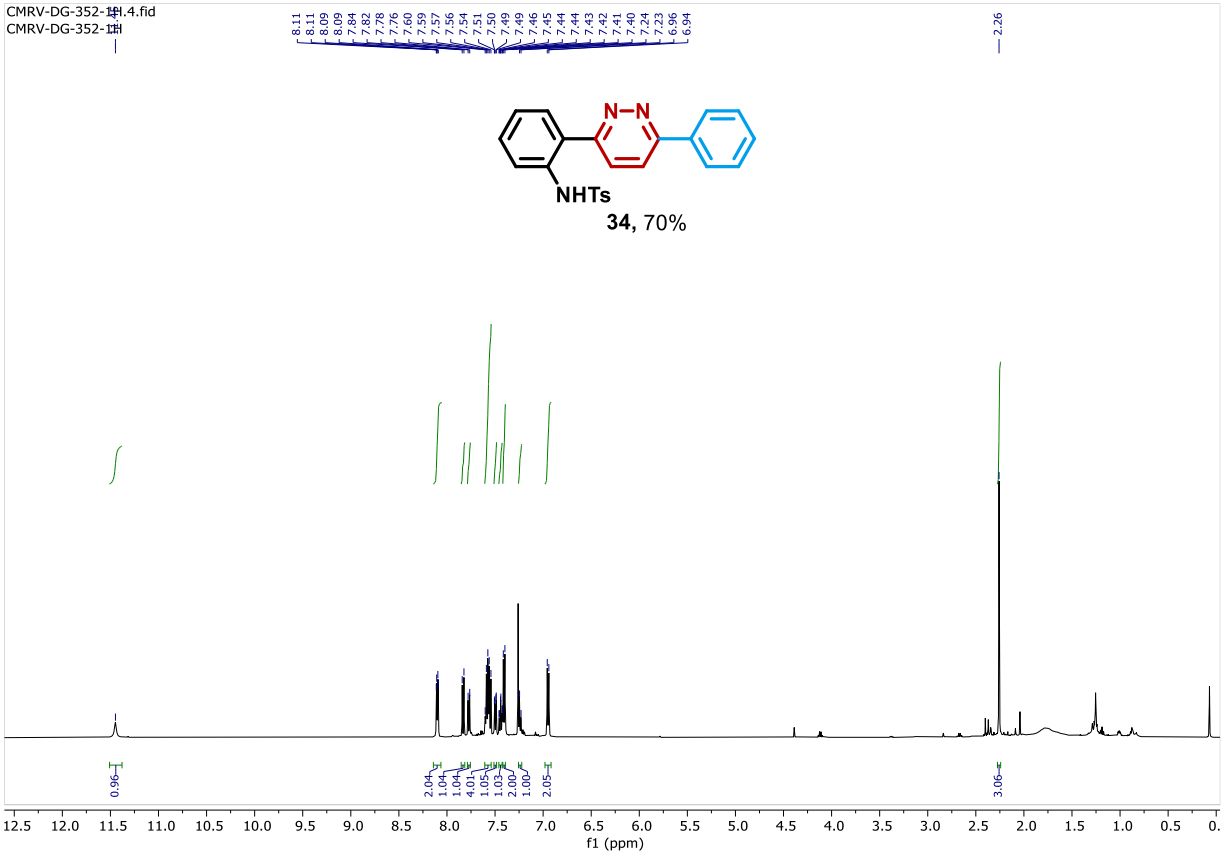

CMRV-DG-359-13C-19.fid
CMRV-DG-359-13C
158.56
143.93
140.00
136.59
135.00
134.88
131.02
129.66
128.78
127.30
126.25
122.71
122.06
119.46
35.86
21.52
21.35
O
NHTs
N
OH
32, 60%
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

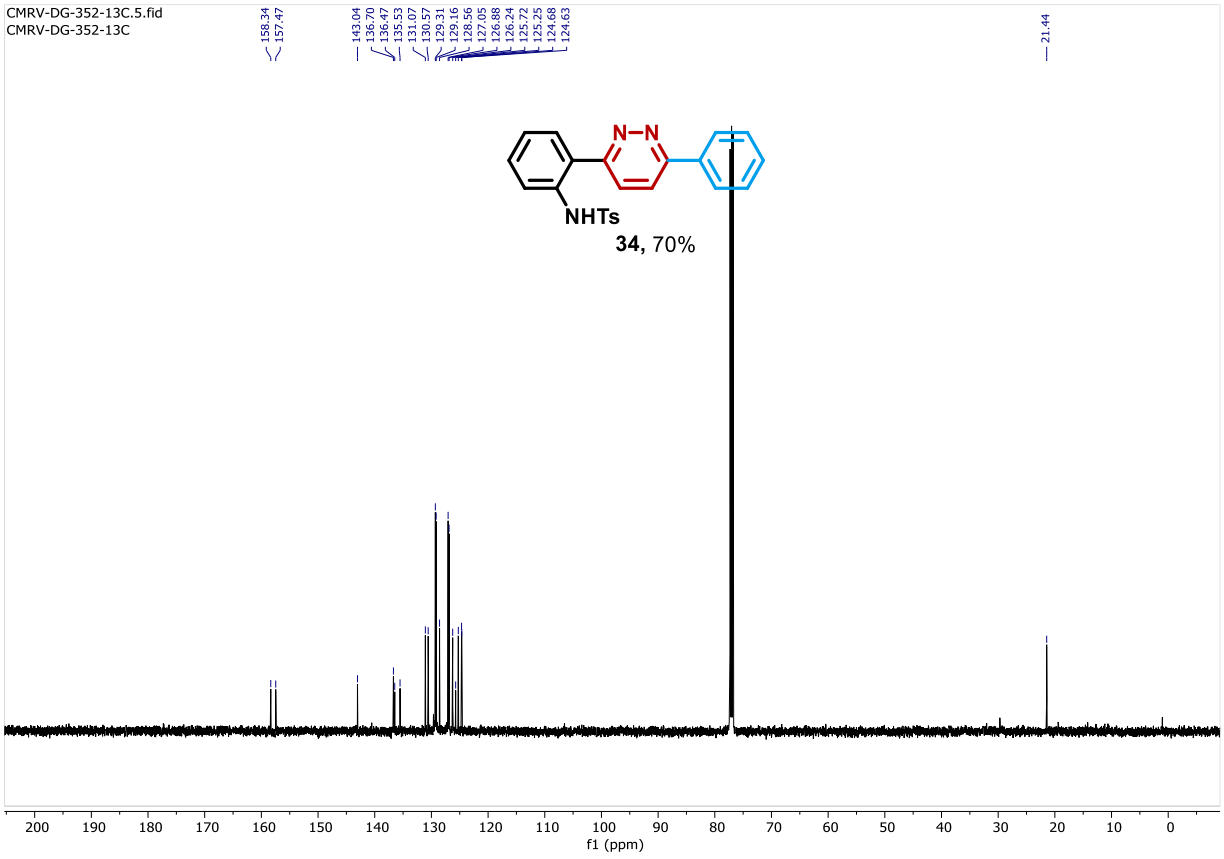
33


CMRV-DG-338-1H.8.fid
CMRV-DG-338-1H
NHTs
N
H
33, 75%
f1 (ppm)

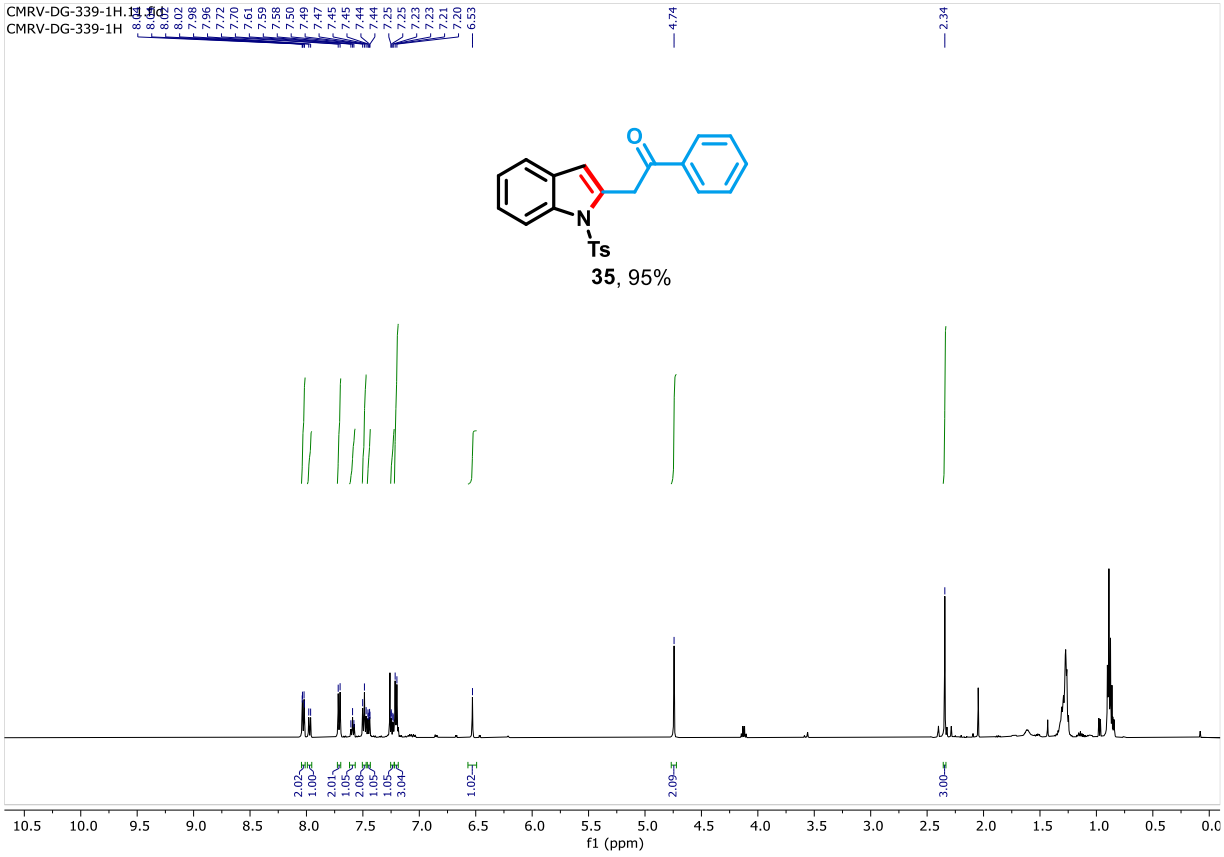

CMRV-DG-338-13C.9.fid
CMRV-DG-338-13C
NHTs
N
H
33, 75%
f1 (ppm)

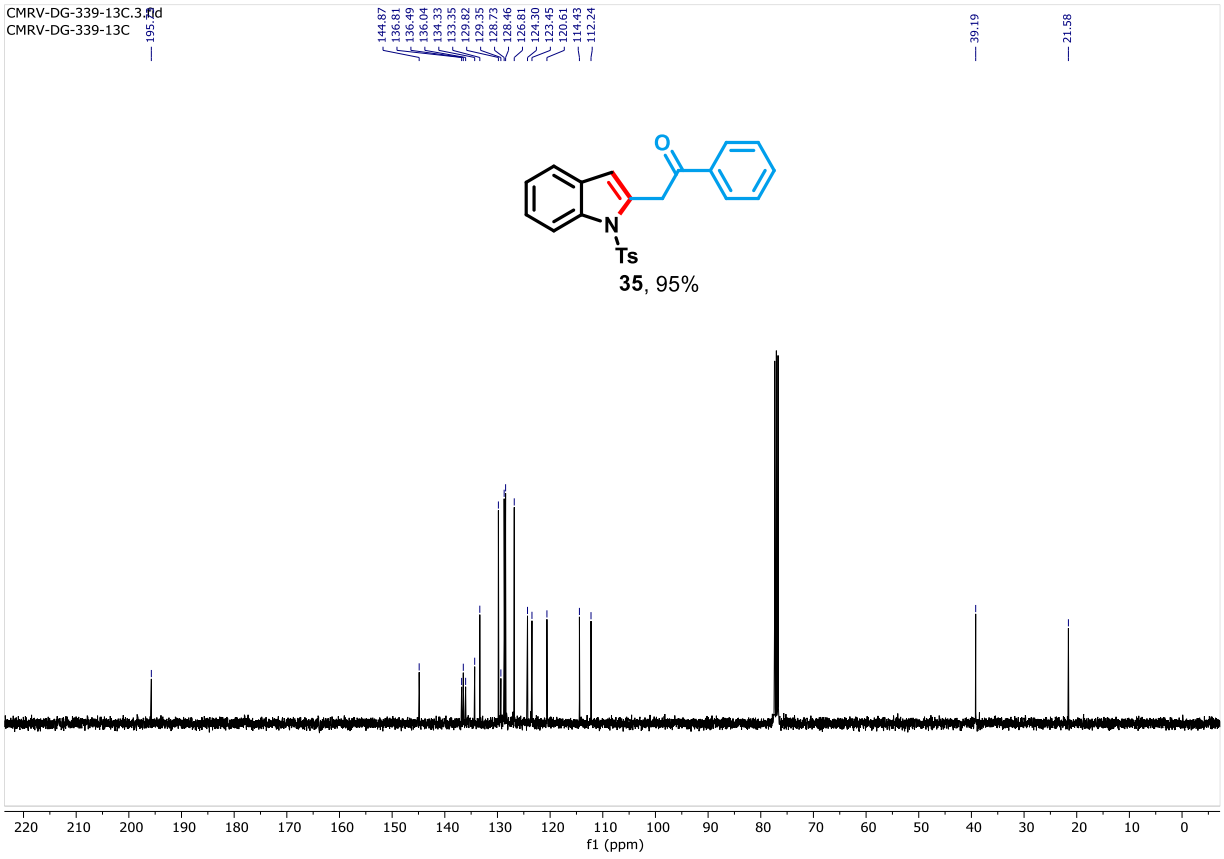
34


CMRV-DG-352-1H.4.fid
CMRV-DG-352-1H
8.11
8.11
8.09
8.09
7.84
7.82
7.78
7.76
7.60
7.59
7.57
7.56
7.54
7.51
7.50
7.49
7.49
7.46
7.45
7.44
7.44
7.43
7.42
7.41
7.40
7.24
7.23
6.96
6.94
2.26
N–N
NHTs
34, 70%
0.96
2.04
1.04
1.04
4.01
1.05
1.03
2.00
1.00
2.05
3.06
f1 (ppm)

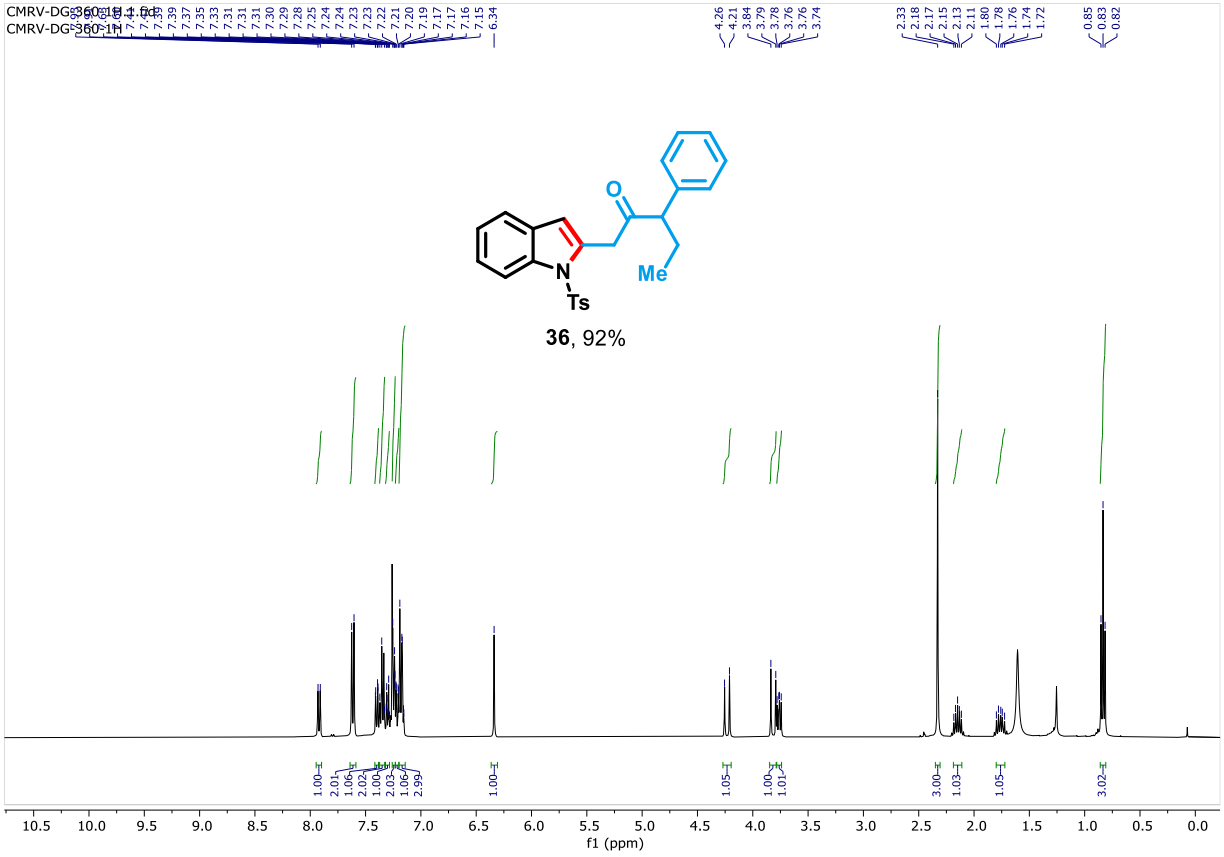

CMRV-DG-352-13C.5.fid
CMRV-DG-352-13C
158.34
157.47
143.04
136.70
136.47
135.53
131.07
130.57
129.31
129.16
128.56
127.05
126.88
126.24
125.72
125.25
124.68
124.63
21.44
N–N
NHTs
34, 70%
f1 (ppm)

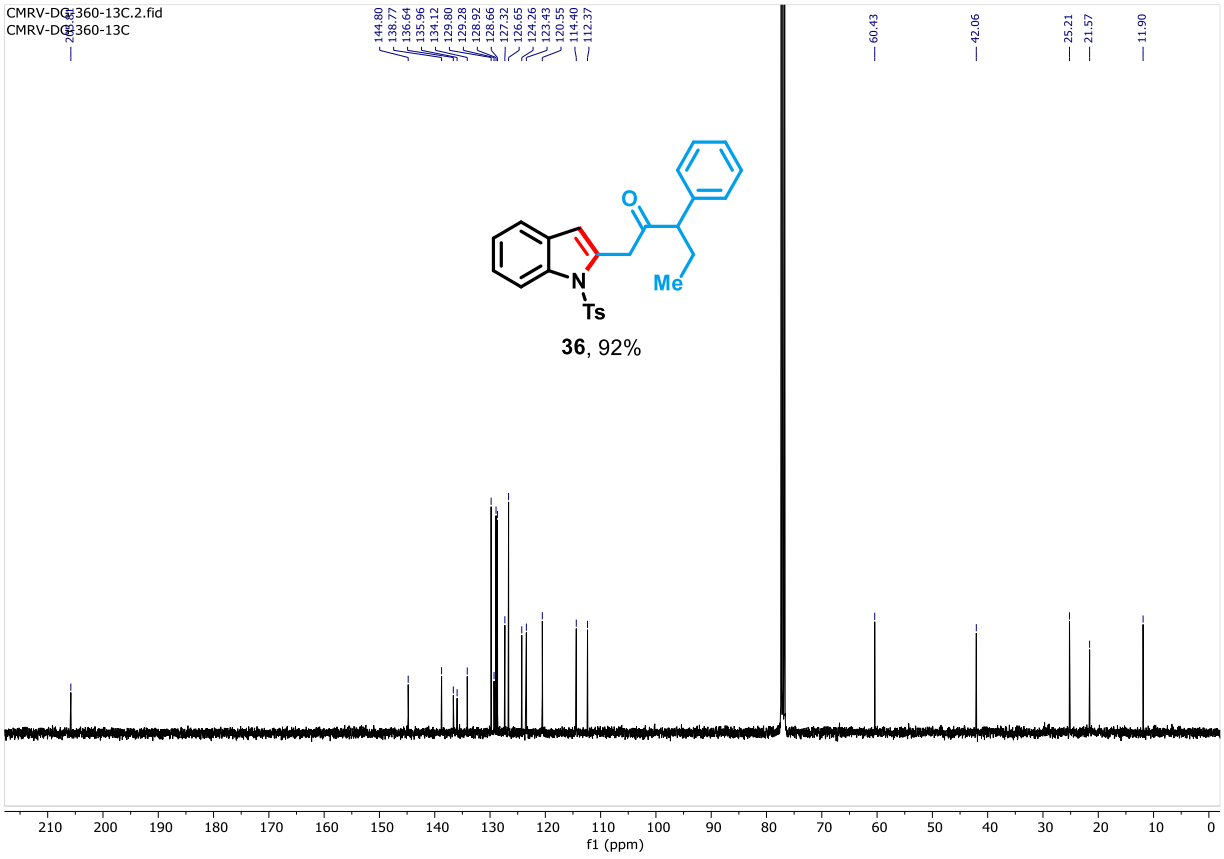
35


CMRV-DG-339-1H
4.74
2.34
O
N
Ts
35, 95%
2.02
1.00
2.01
1.05
2.06
1.05
1.05
3.04
1.02
2.09
3.00
f1 (ppm)

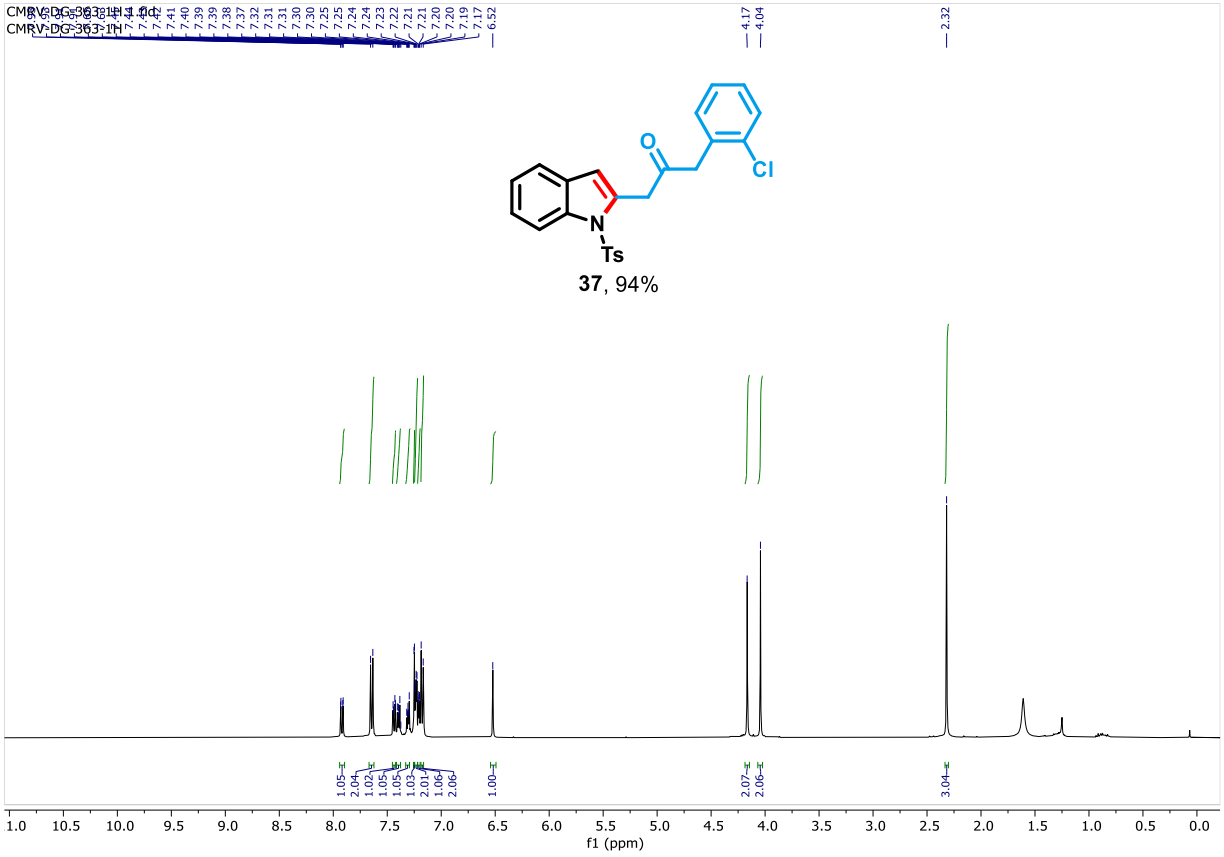

CMRV-DG-339-13C
195.1
144.87
136.81
136.49
136.04
134.33
133.35
129.82
129.35
128.73
128.46
126.81
124.30
123.45
120.61
114.43
112.24
39.19
21.58
O
N
Ts
35, 95%
f1 (ppm)

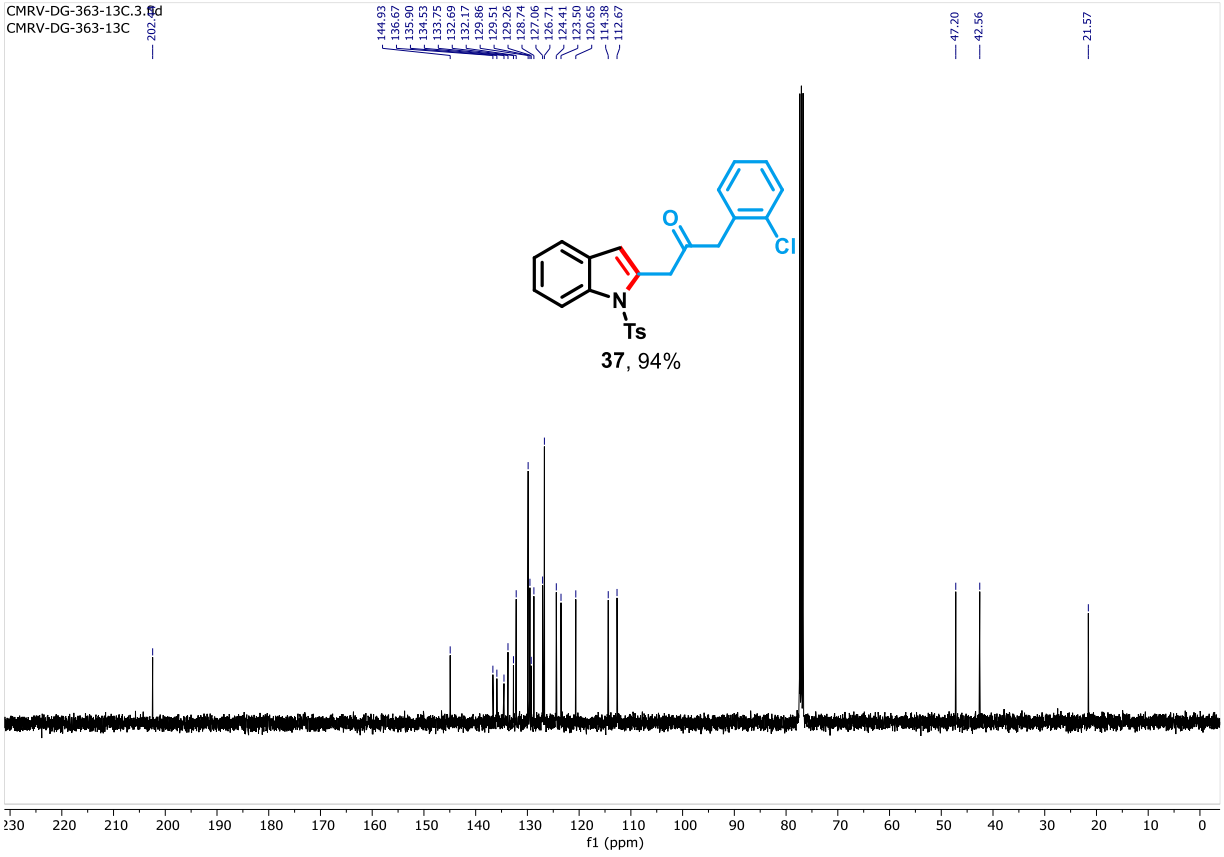
36


CMRV-DG-360-1H-1.fid
CMRV-DG-360-1H
O
N
Ts
Me
36, 92%
f1 (ppm)

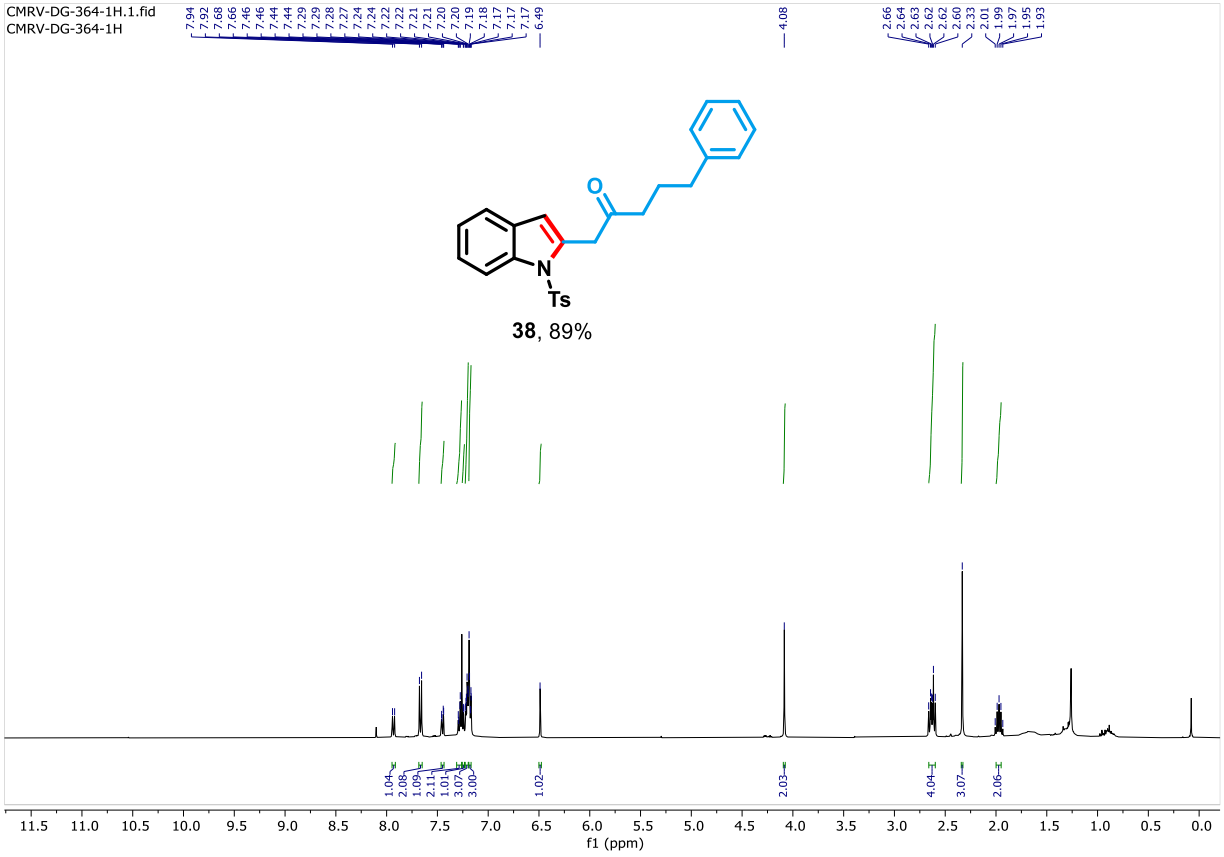

CMRV-DG-360-13C.2.fid
CMRV-DG-360-13C
O
N
Ts
Me
36, 92%
f1 (ppm)

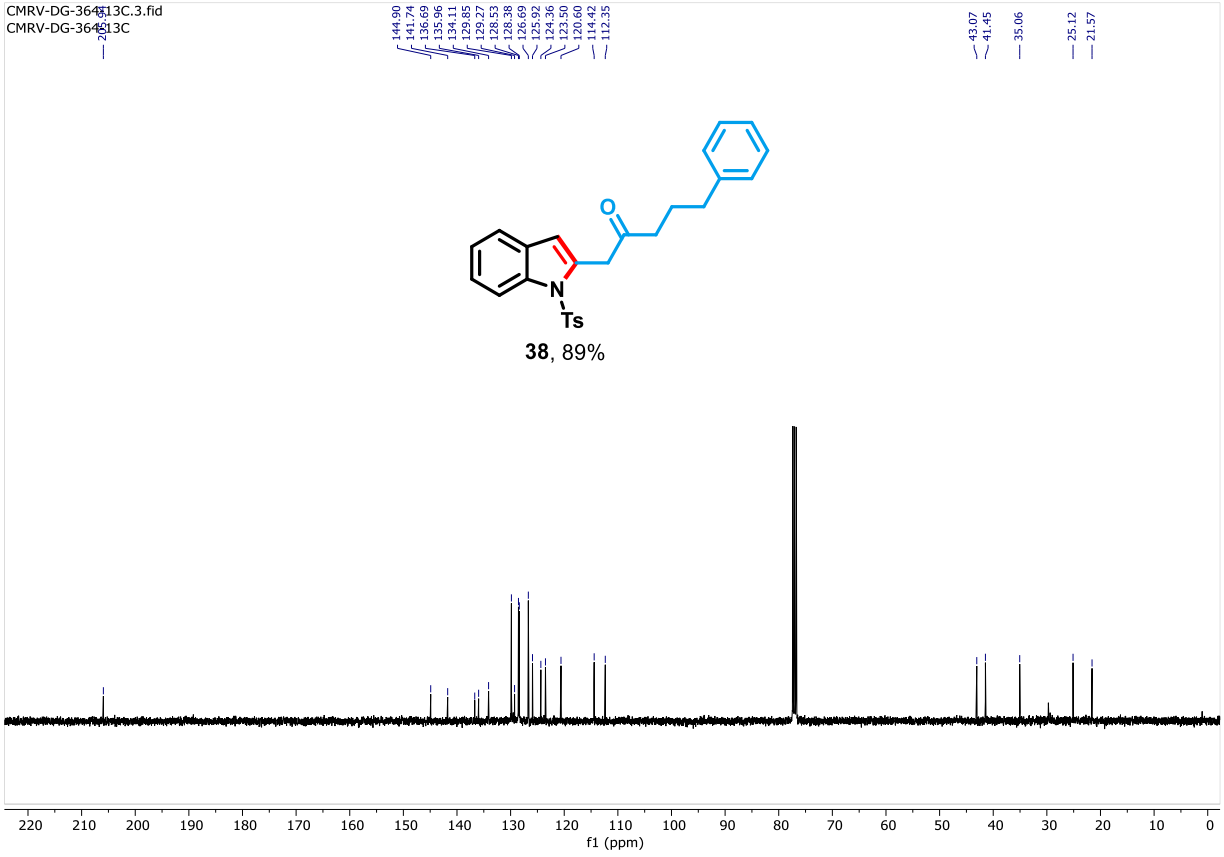
37


CMRV-DG-363-1H
O
Cl
N
Ts
37, 94%
f1 (ppm)

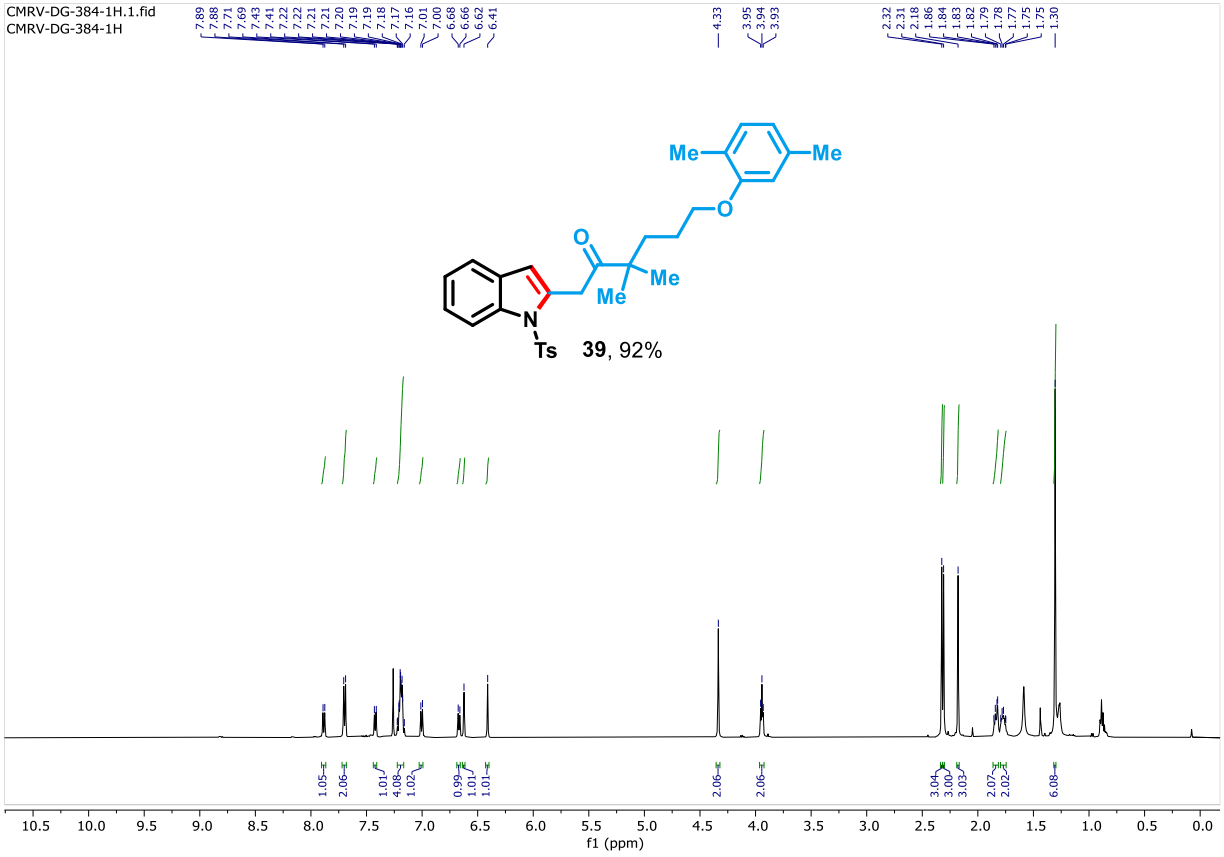

CMRV-DG-363-13C
O
Cl
N
Ts
37, 94%
f1 (ppm)

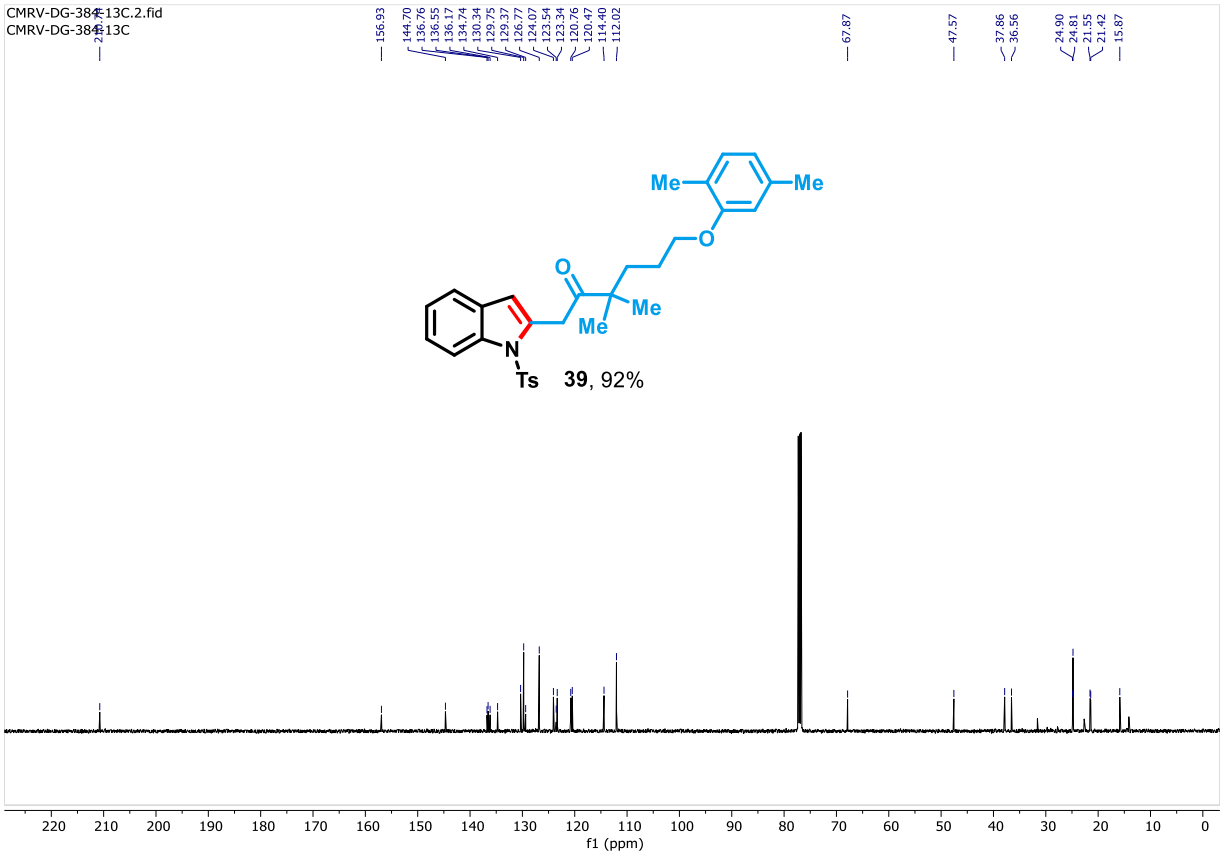
38


CMRV-DG-364-1H.1.fid
CMRV-DG-364-1H
7.94 7.92 7.68 7.66 7.46 7.44 7.29 7.28 7.27 7.24 7.22 7.21 7.20 7.19 7.18 7.17 7.17 6.49
4.08
2.66 2.64 2.63 2.62 2.62 2.60 2.33 2.01 1.99 1.97 1.95 1.93
O
N
Ts
38, 89%
1.04 2.08 1.09 2.11 1.01 3.07 3.00
1.02
2.03
4.04 3.07
2.06
11.5 11.0 10.5 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 0.0
f1 (ppm)

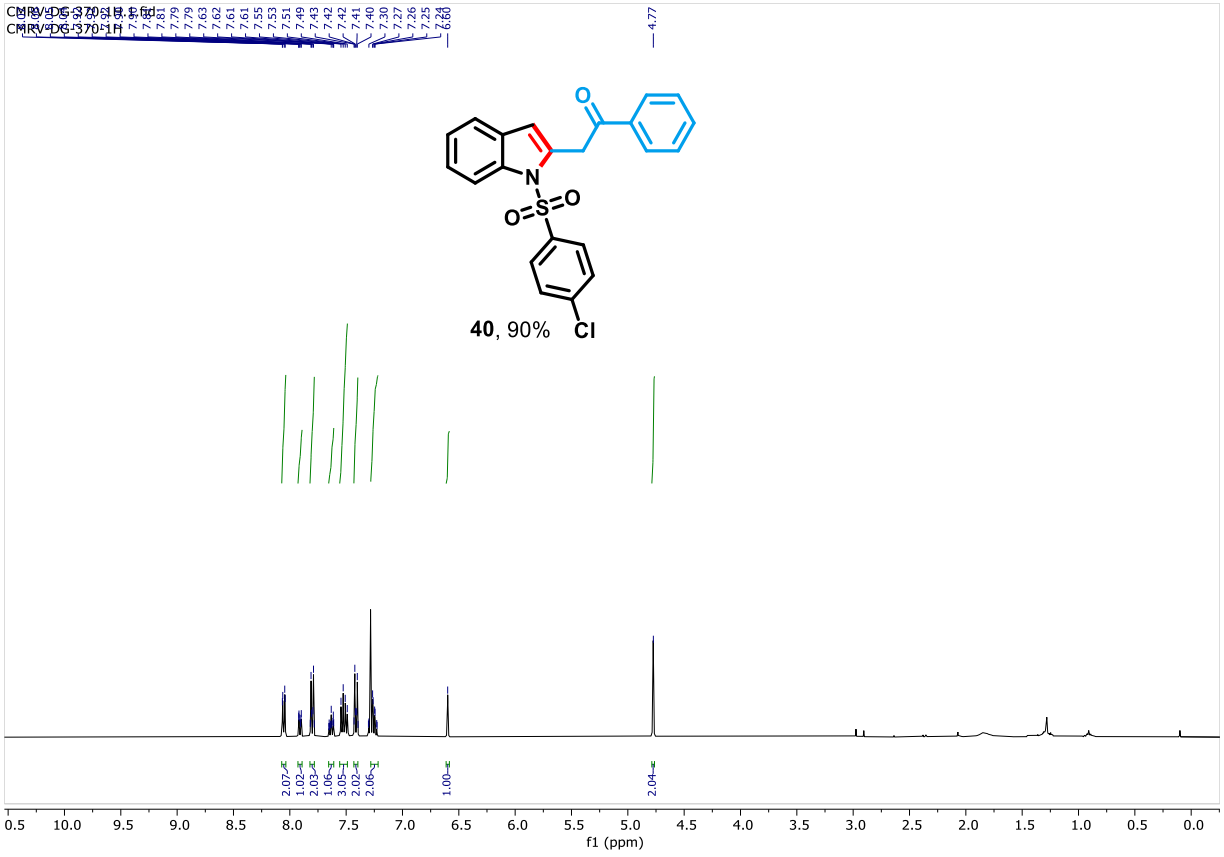

CMRV-DG-364-13C.3.fid
CMRV-DG-364-13C
144.90 141.74 136.69 135.96 134.11 129.85 129.27 128.53 128.38 126.69 125.92 124.36 123.50 120.60 114.42 112.35
43.07 41.45 35.06 25.12 21.57
O
N
Ts
38, 89%
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

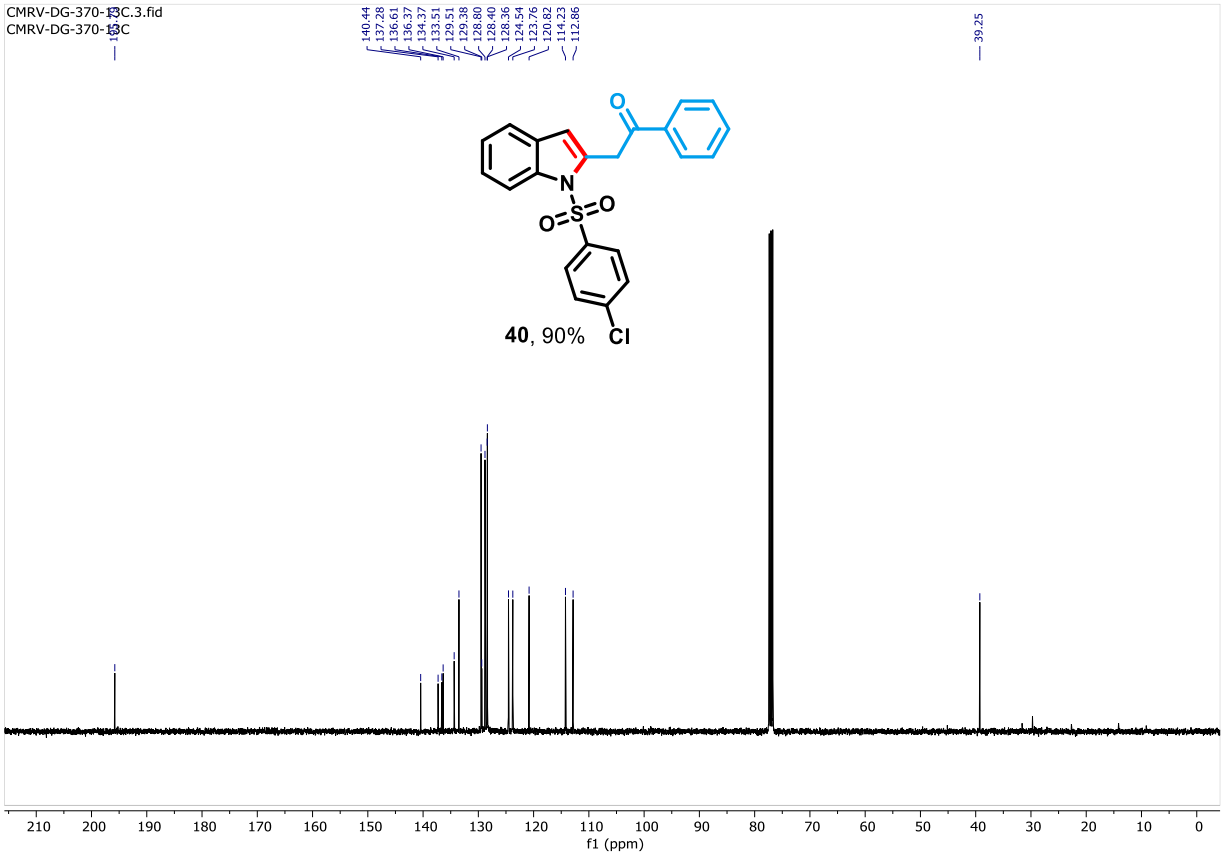
39


CMRV-DG-384-1H.1.fid
CMRV-DG-384-1H
Me
Me
O
O
Me
Me
N
Ts
39, 92%
f1 (ppm)

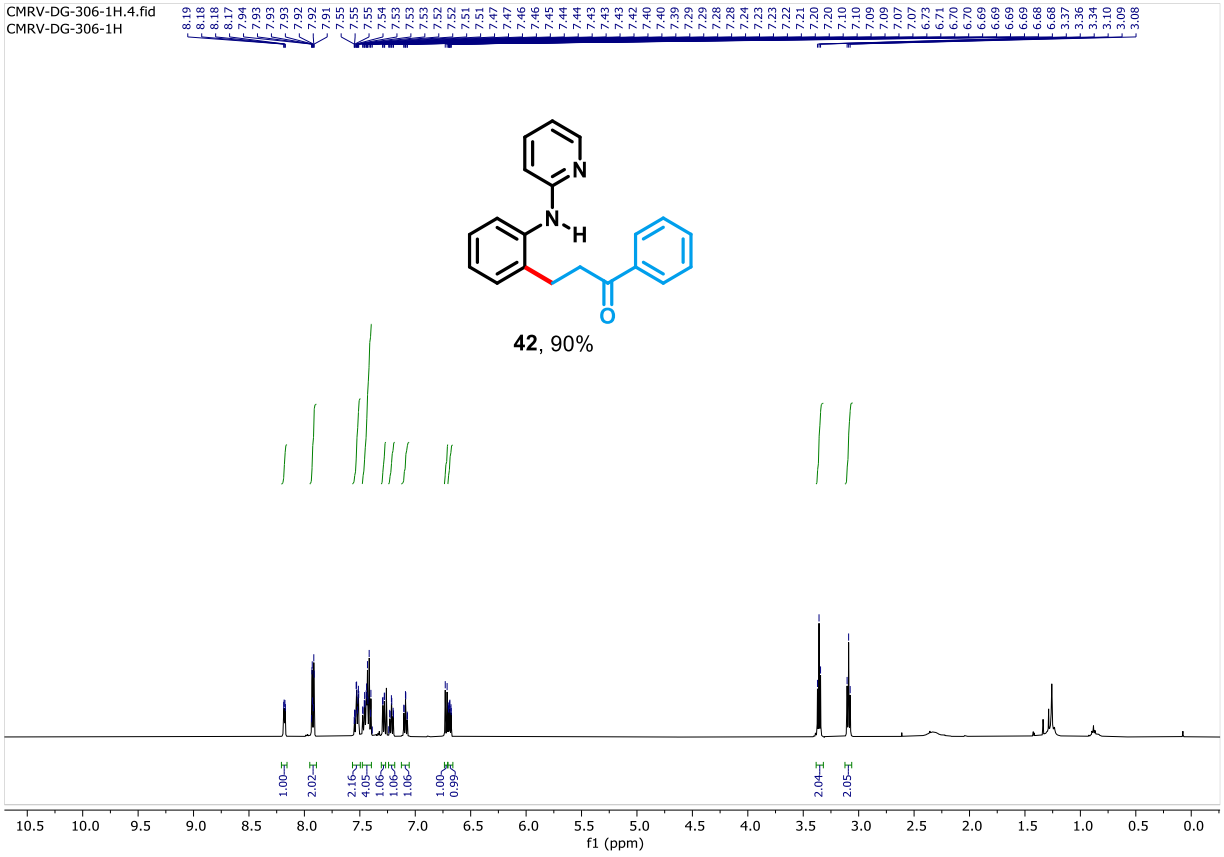

CMRV-DG-384-13C.2.fid
CMRV-DG-384-13C
Me
Me
O
O
Me
Me
N
Ts
39, 92%
f1 (ppm)

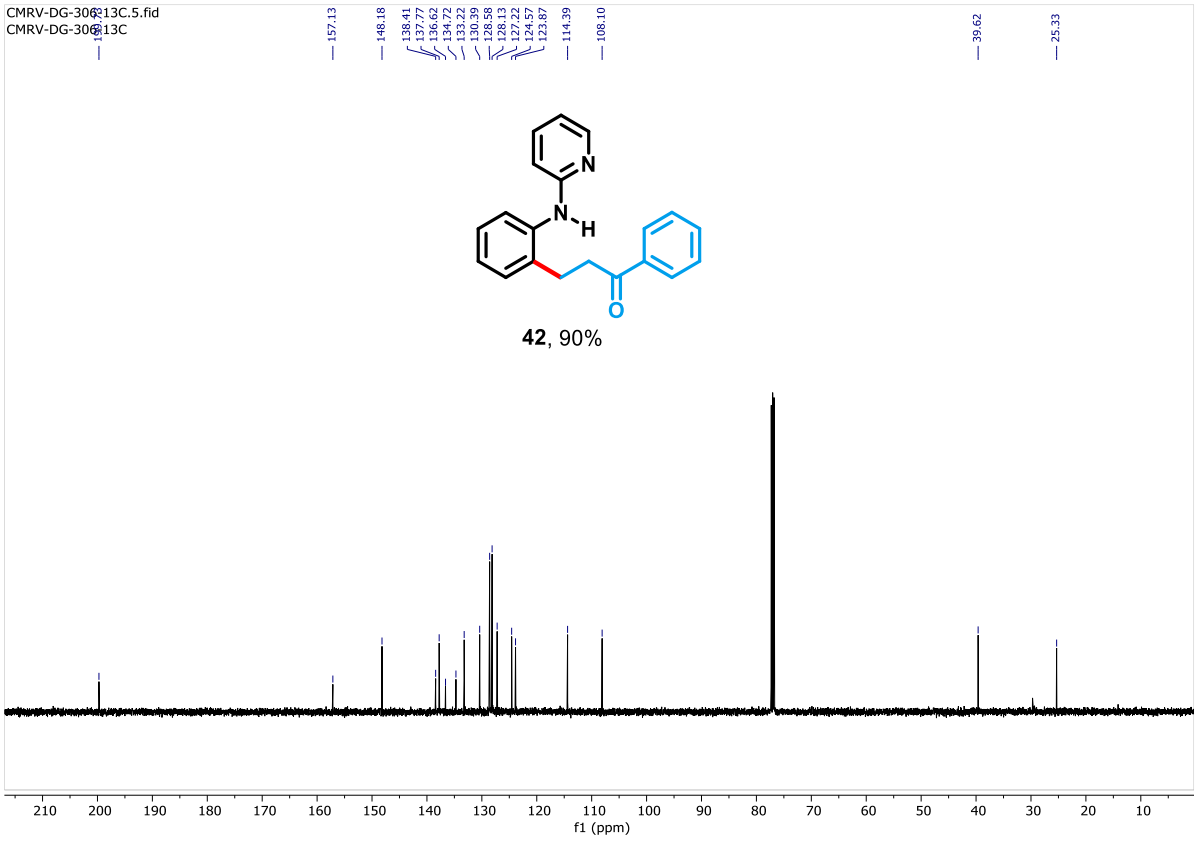
40


CMRV-DG-370-1H.5.fid
CMRV-DG-370-1H
7.83 7.81 7.79 7.79 7.63 7.62 7.61 7.61 7.55 7.53 7.51 7.49 7.43 7.42 7.42 7.41 7.40 7.30 7.27 7.26 7.25 7.24 6.60
4.77
O
N
O=S=O
40, 90% Cl
2.07 1.02 2.03 1.06 3.05 2.02 2.06 1.00 2.04
0.5 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 0.0
f1 (ppm)

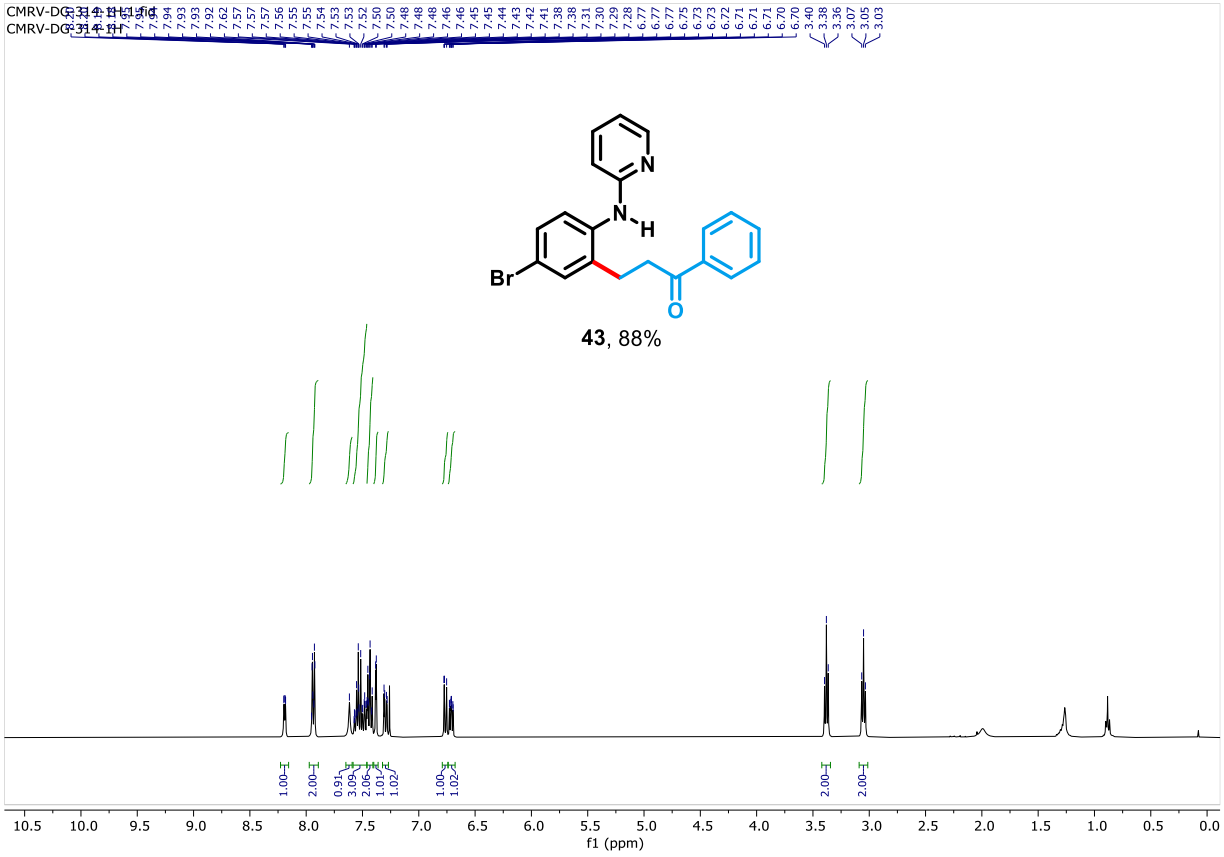

CMRV-DG-370-13C.3.fid
CMRV-DG-370-13C
140.44 137.28 136.61 136.37 134.37 133.51 129.51 129.38 128.80 128.40 128.36 124.54 123.76 120.82 114.23 112.86
39.25
O
N
O=S=O
40, 90% Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

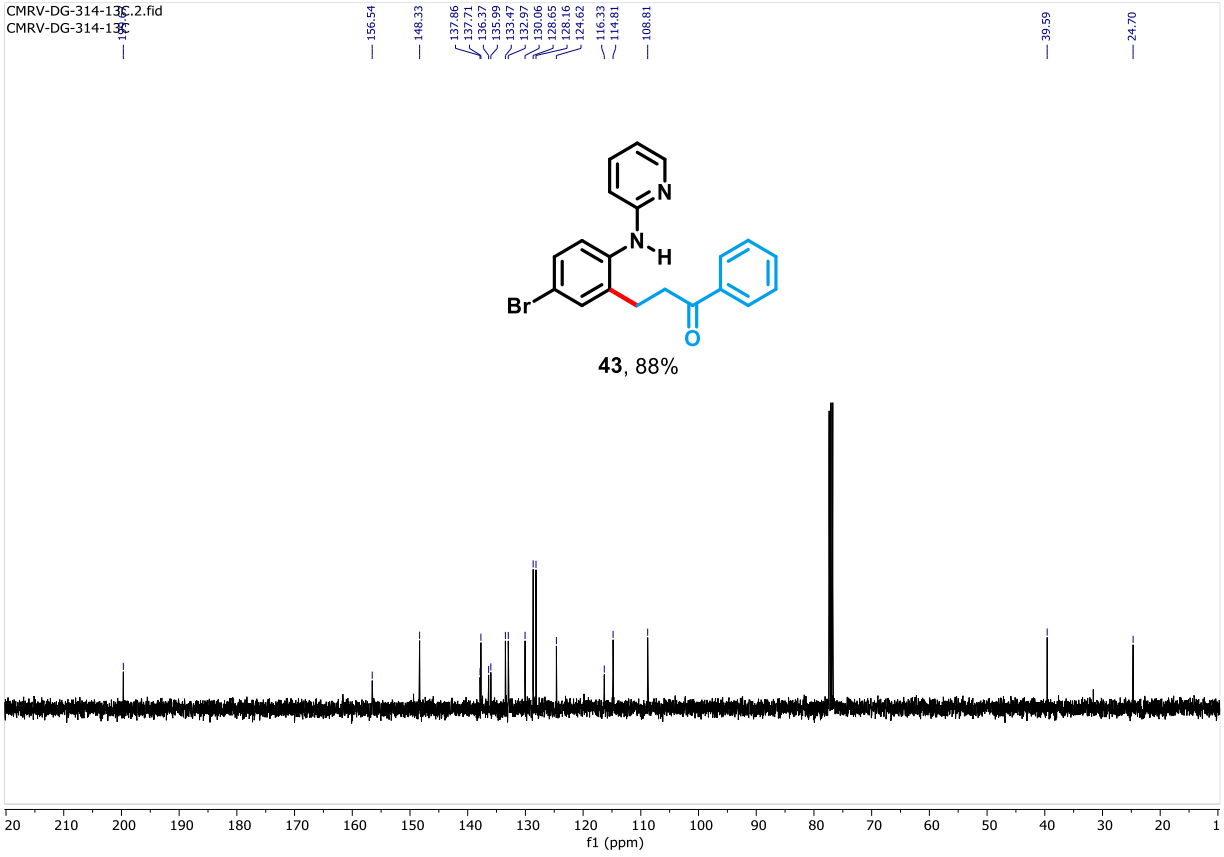
42


CMRV-DG-306-1H.4.fid
CMRV-DG-306-1H
42, 90%
f1 (ppm)

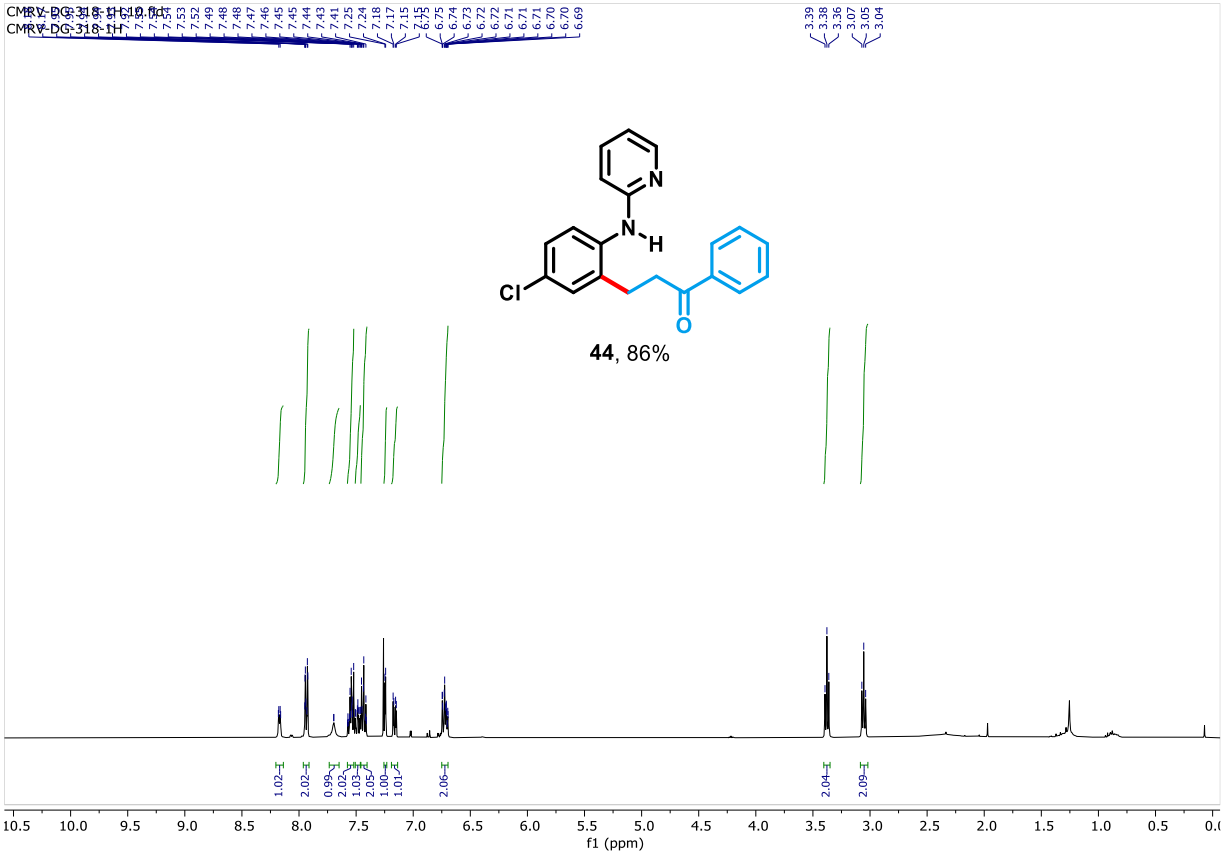

CMRV-DG-306-13C.5.fid
CMRV-DG-306-13C
42, 90%
f1 (ppm)

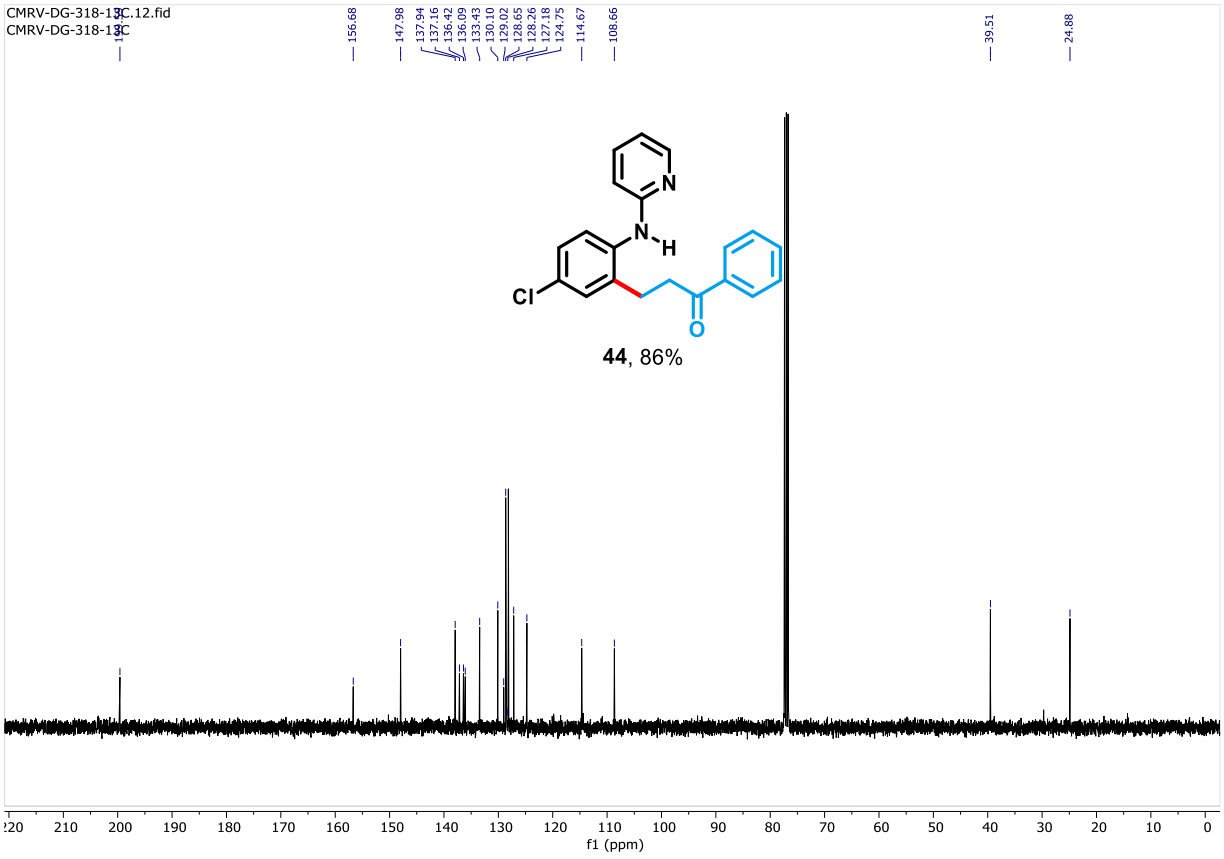
43


CMRV-DG-314-1H.1.fid
CMRV-DG-314-1H
Br
N
N
H
O
43, 88%
f1 (ppm)

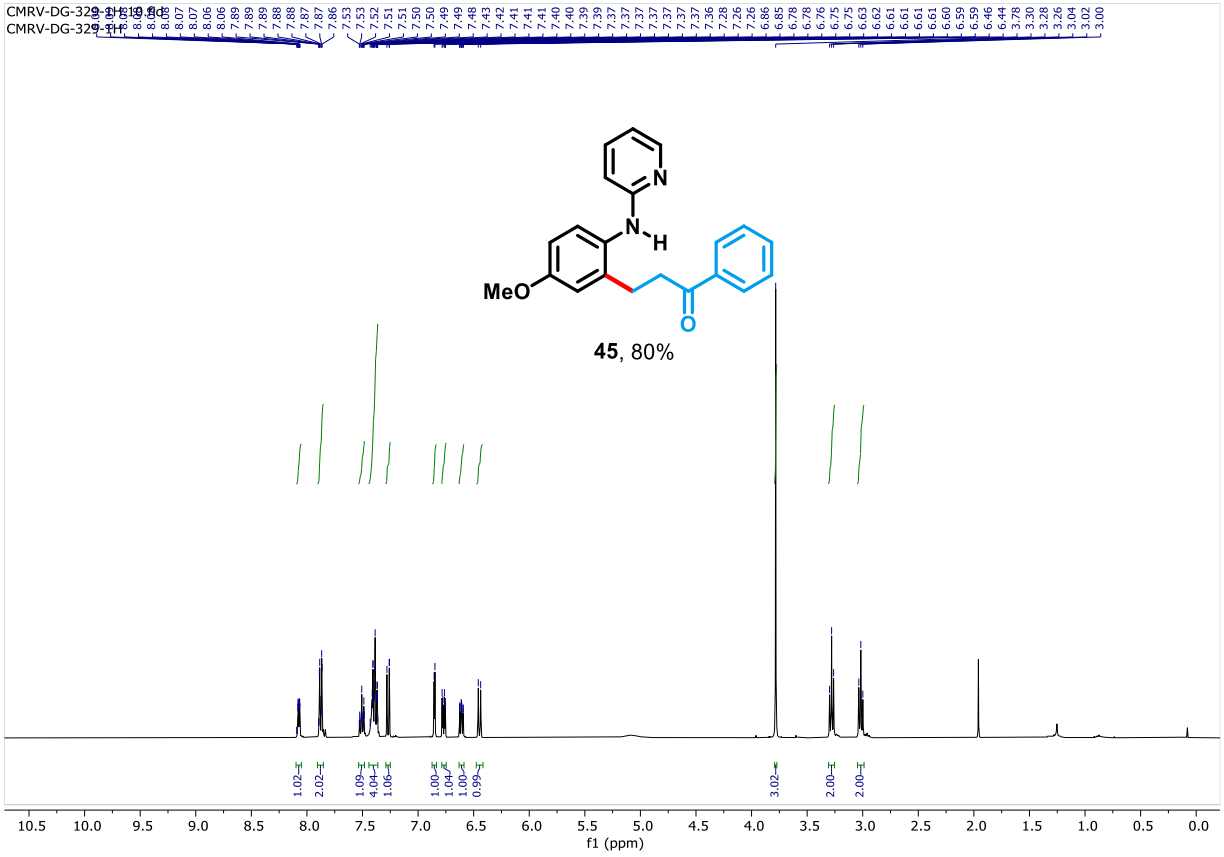

CMRV-DG-314-13C.2.fid
CMRV-DG-314-13C
Br
N
N
H
O
43, 88%
f1 (ppm)

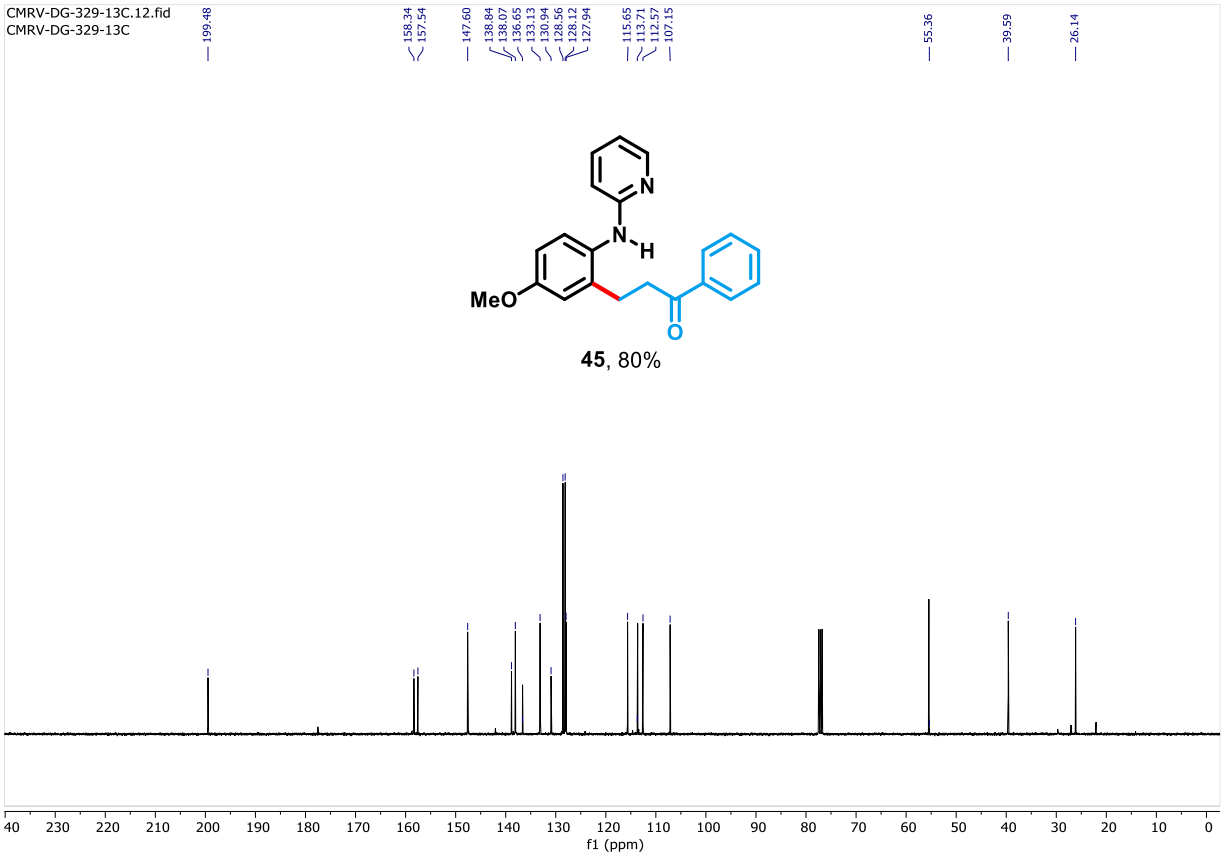
44


CMRV-DG-318-1H.10.fid
CMRV-DG-318-1H
7.55 7.54 7.53 7.52 7.49 7.48 7.48 7.47 7.46 7.45 7.45 7.44 7.43 7.41 7.25 7.24 7.18 7.17 7.15 6.75 6.74 6.73 6.72 6.72 6.71 6.71 6.71 6.70 6.70 6.69
3.39 3.38 3.36 3.07 3.05 3.04
N
N
H
Cl
O
44, 86%
1.02 2.02 0.99 2.02 1.03 2.05 1.00 1.01 2.06
2.04 2.09
10.5 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)

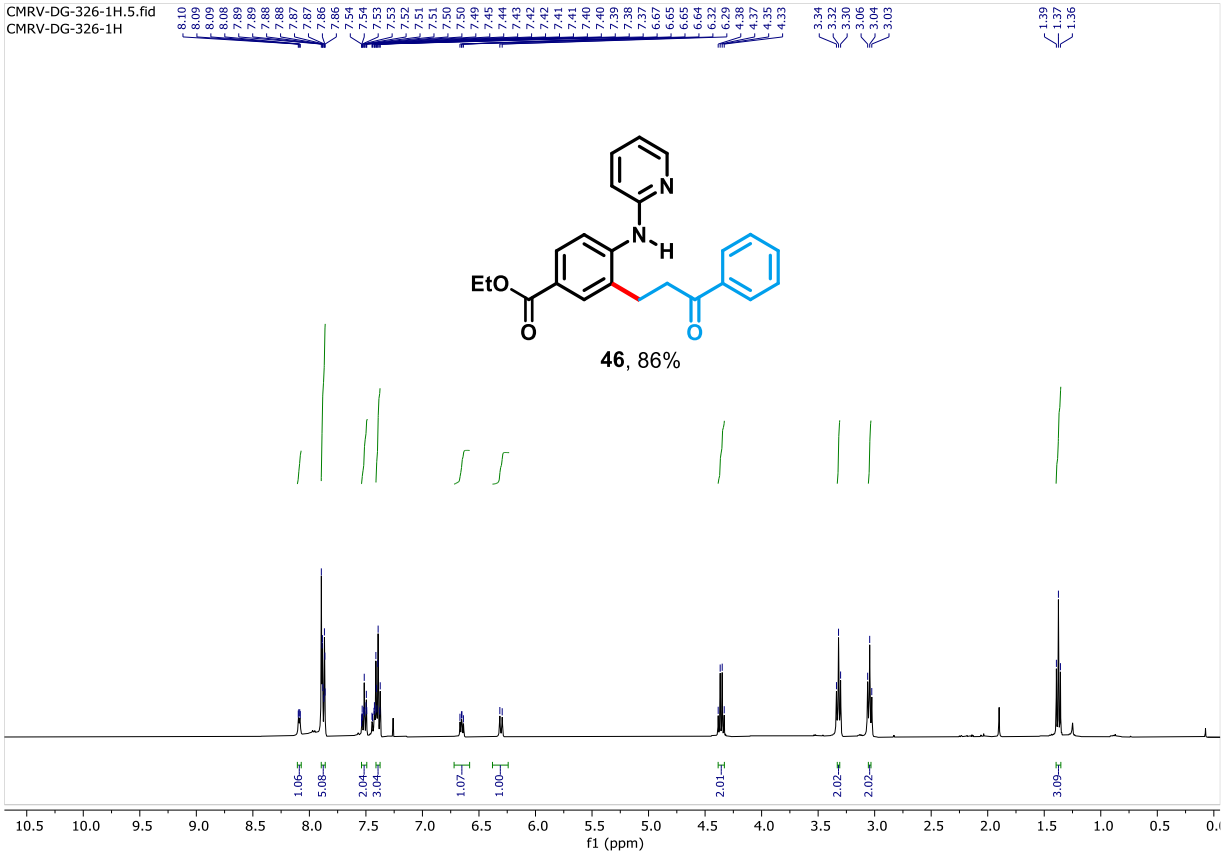

CMRV-DG-318-13C.12.fid
CMRV-DG-318-13C
156.68 147.98 137.94 137.16 136.42 136.09 133.43 130.10 129.02 128.65 128.26 127.18 124.75 114.67 108.66 39.51 24.88
N
N
H
Cl
O
44, 86%
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

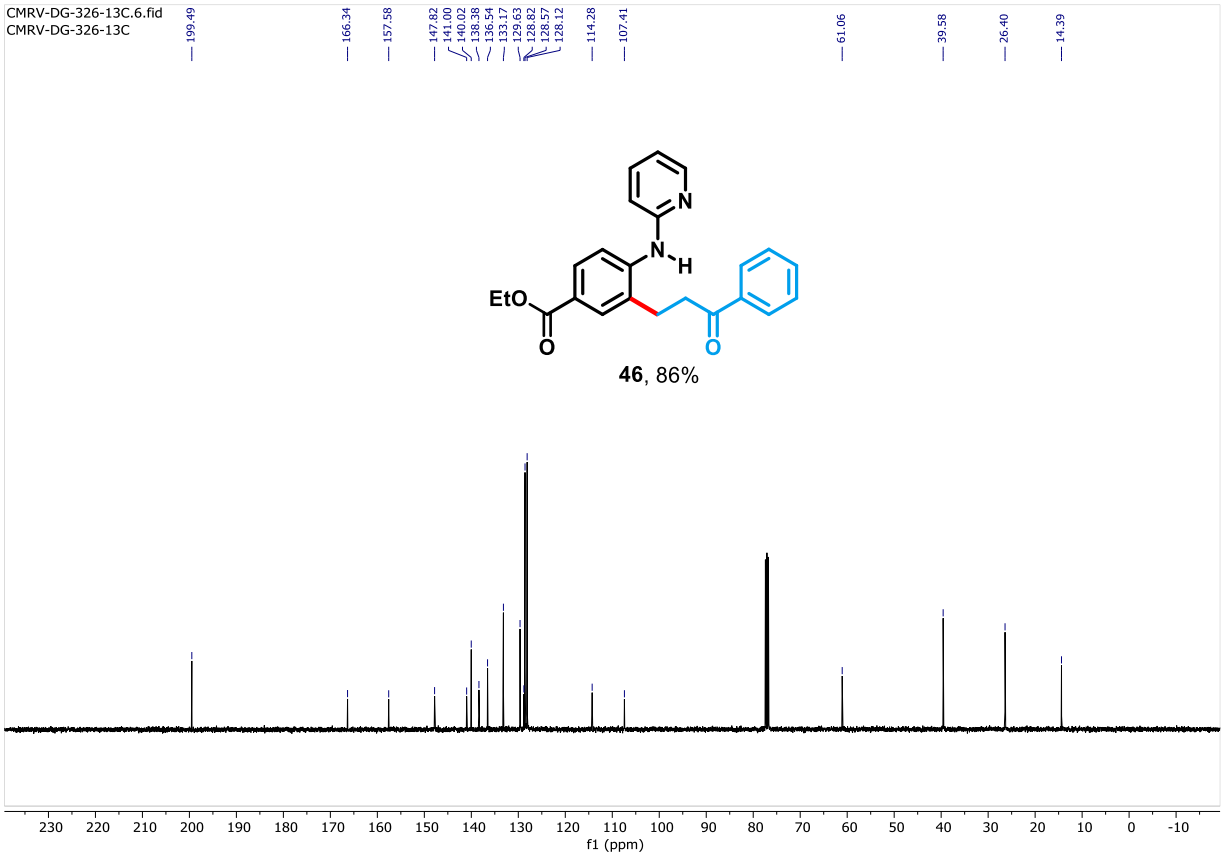
45


CMRV-DG-329-1H.10.fid
CMRV-DG-329-1H
MeO
45, 80%
f1 (ppm)

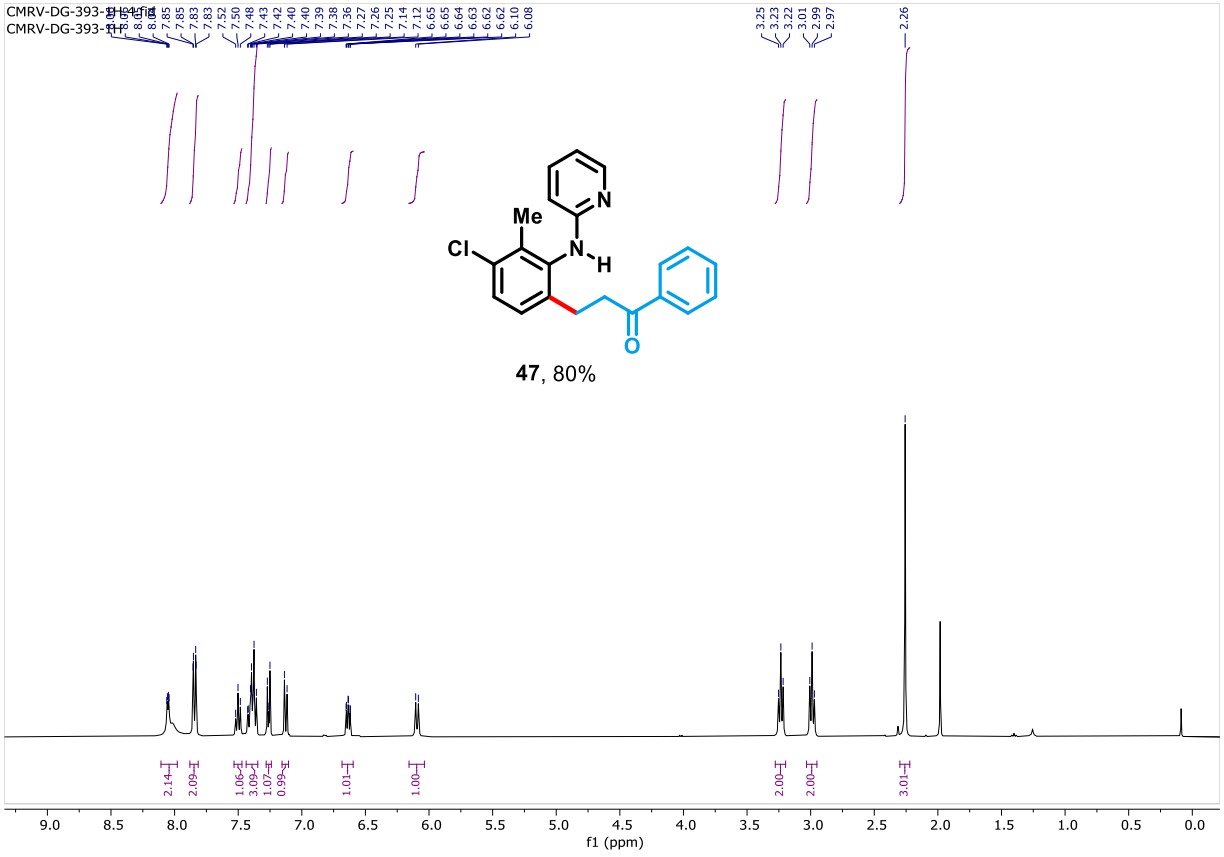

CMRV-DG-329-13C.12.fid
CMRV-DG-329-13C
MeO
45, 80%
f1 (ppm)

46

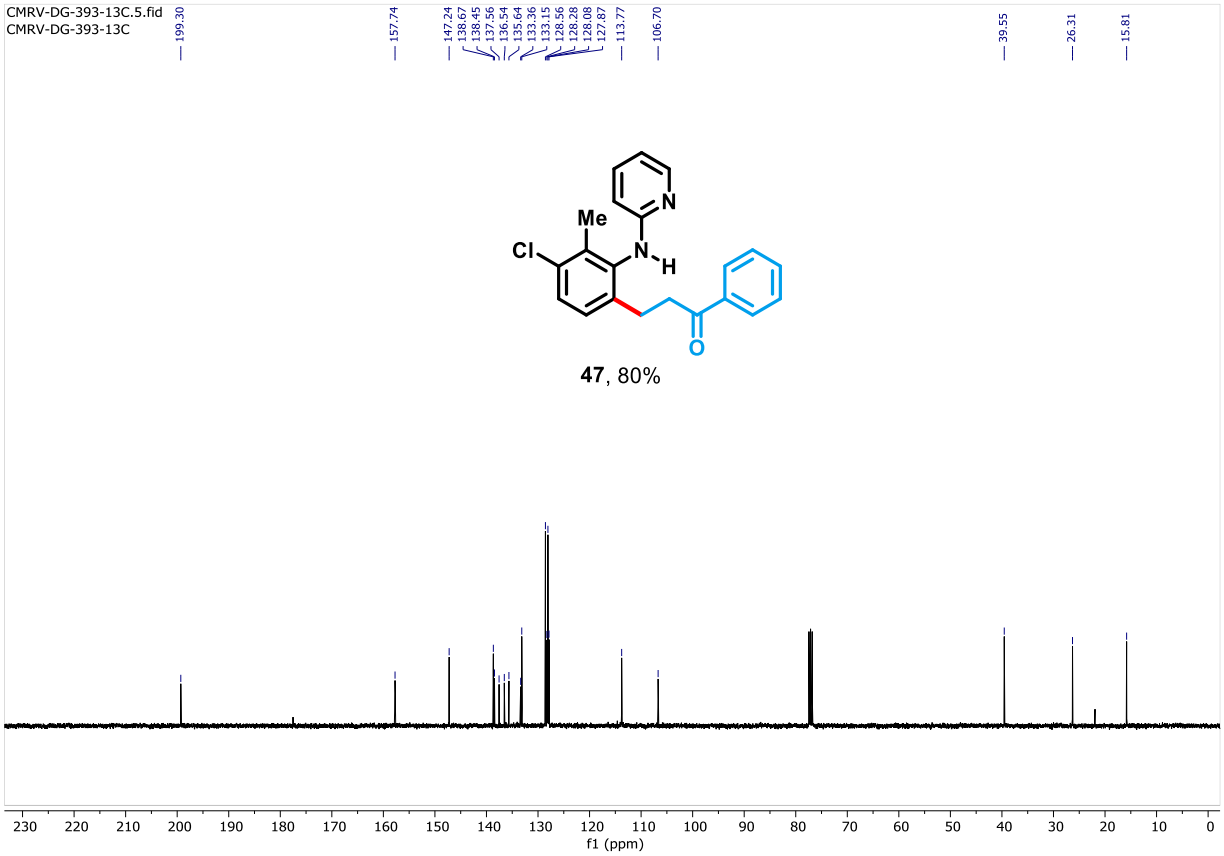

CMRV-DG-326-1H.5.fid
CMRV-DG-326-1H
EtO
O
N
N
H
O
46, 86%
f1 (ppm)


CMRV-DG-326-13C.6.fid
CMRV-DG-326-13C
199.49
166.34
157.58
147.82
141.00
140.02
138.38
136.54
133.17
129.63
128.82
128.57
128.12
114.28
107.41
61.06
39.58
26.40
14.39
EtO
O
N
N
H
O
46, 86%
f1 (ppm)

47

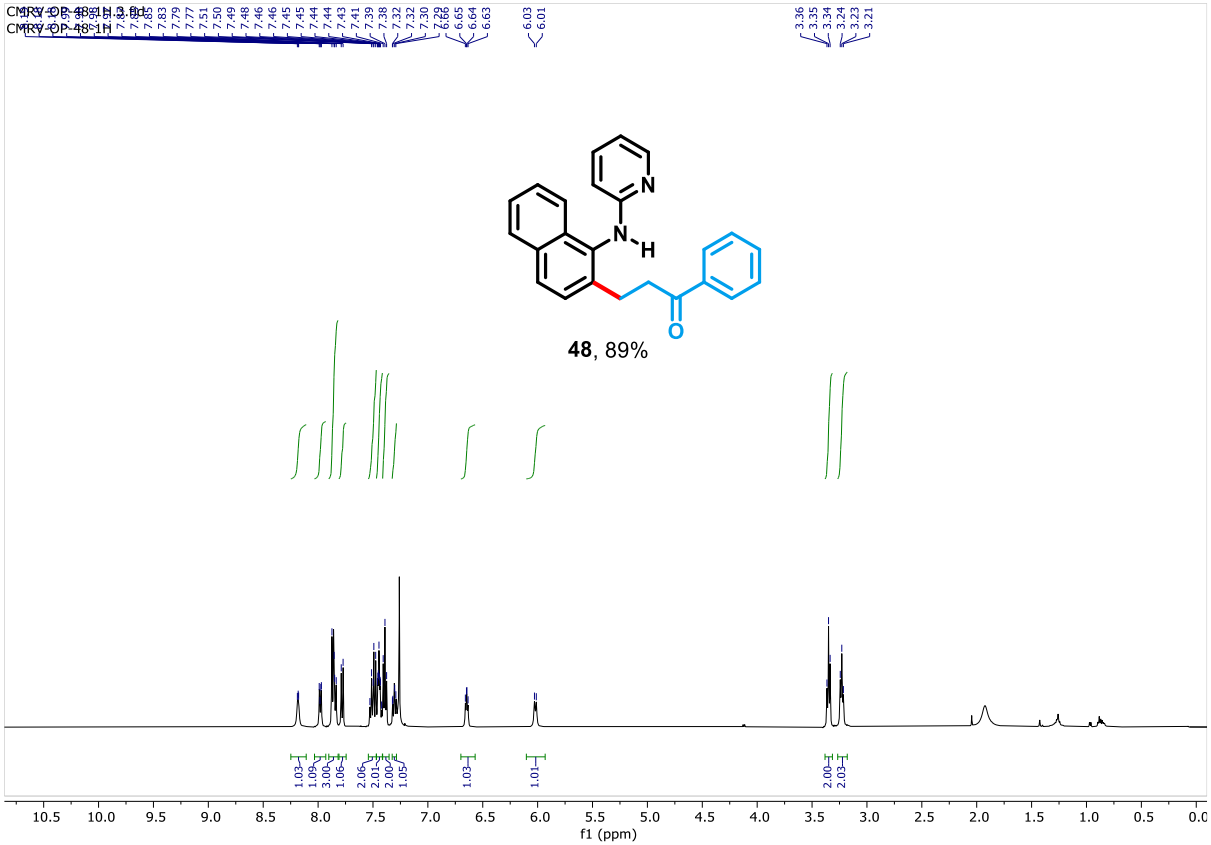

CMRV-DG-393-1H4.fid
CMRV-DG-393-1H
8.08
7.85
7.83
7.52
7.50
7.48
7.43
7.42
7.40
7.39
7.38
7.36
7.27
7.26
7.25
7.14
7.12
6.65
6.64
6.63
6.62
6.62
6.10
6.08
3.25
3.23
3.22
3.01
2.99
2.97
2.26
Me
Cl
N
H
O
2.14
2.09
1.06
3.09
1.07
0.99
1.01
1.00
2.00
2.00
3.01
f1 (ppm)

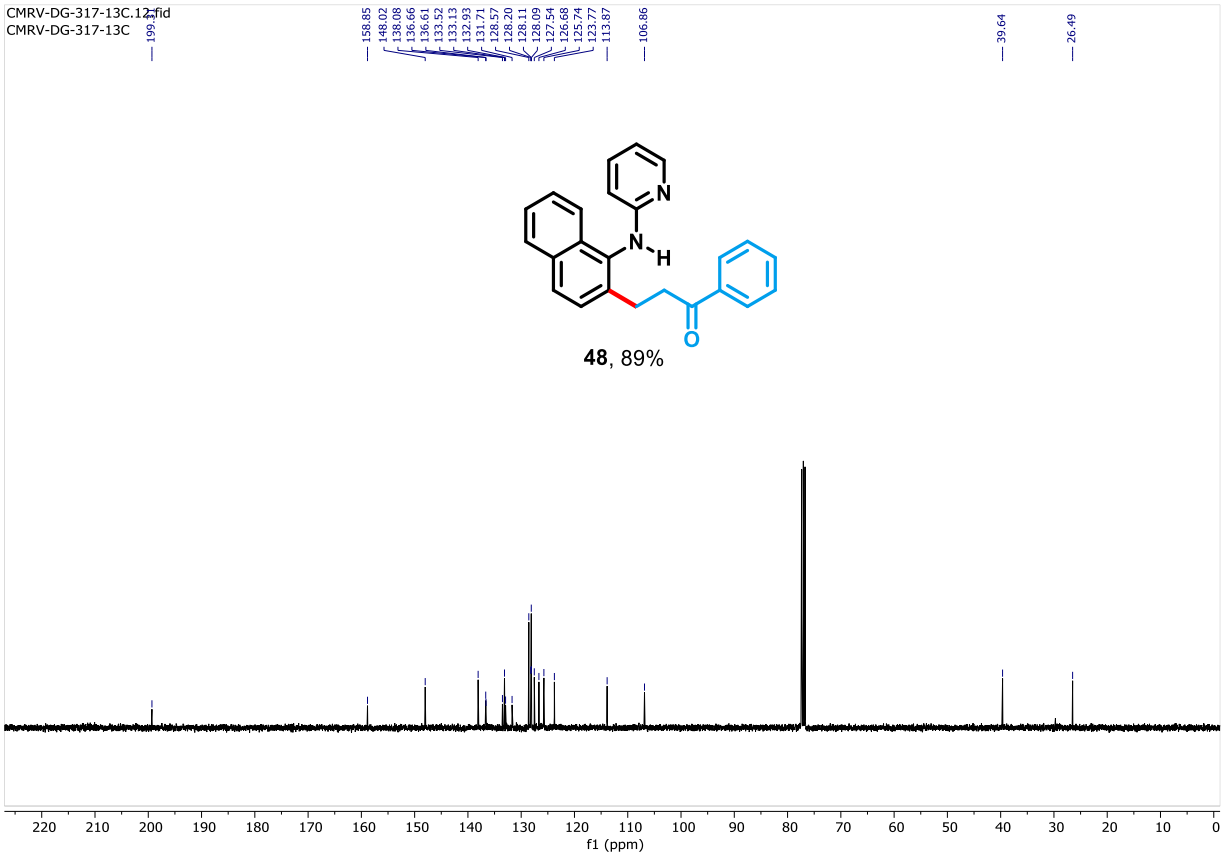
47, 80%


CMRV-DG-393-13C.5.fid
CMRV-DG-393-13C
199.30
157.74
147.24
138.67
138.45
137.56
136.54
135.64
133.36
133.15
128.56
128.28
128.08
127.87
113.77
106.70
39.55
26.31
15.81
Me
Cl
N
H
O
f1 (ppm)

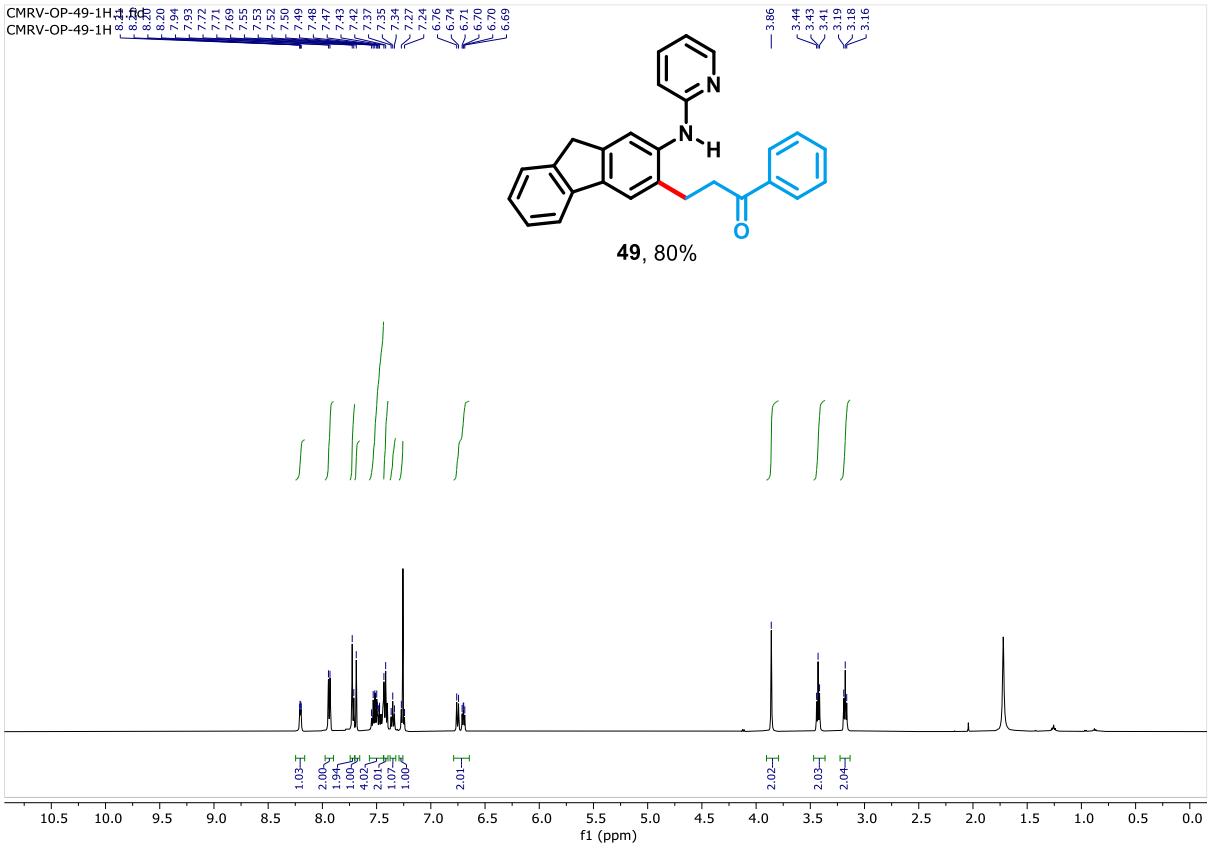
47, 80%

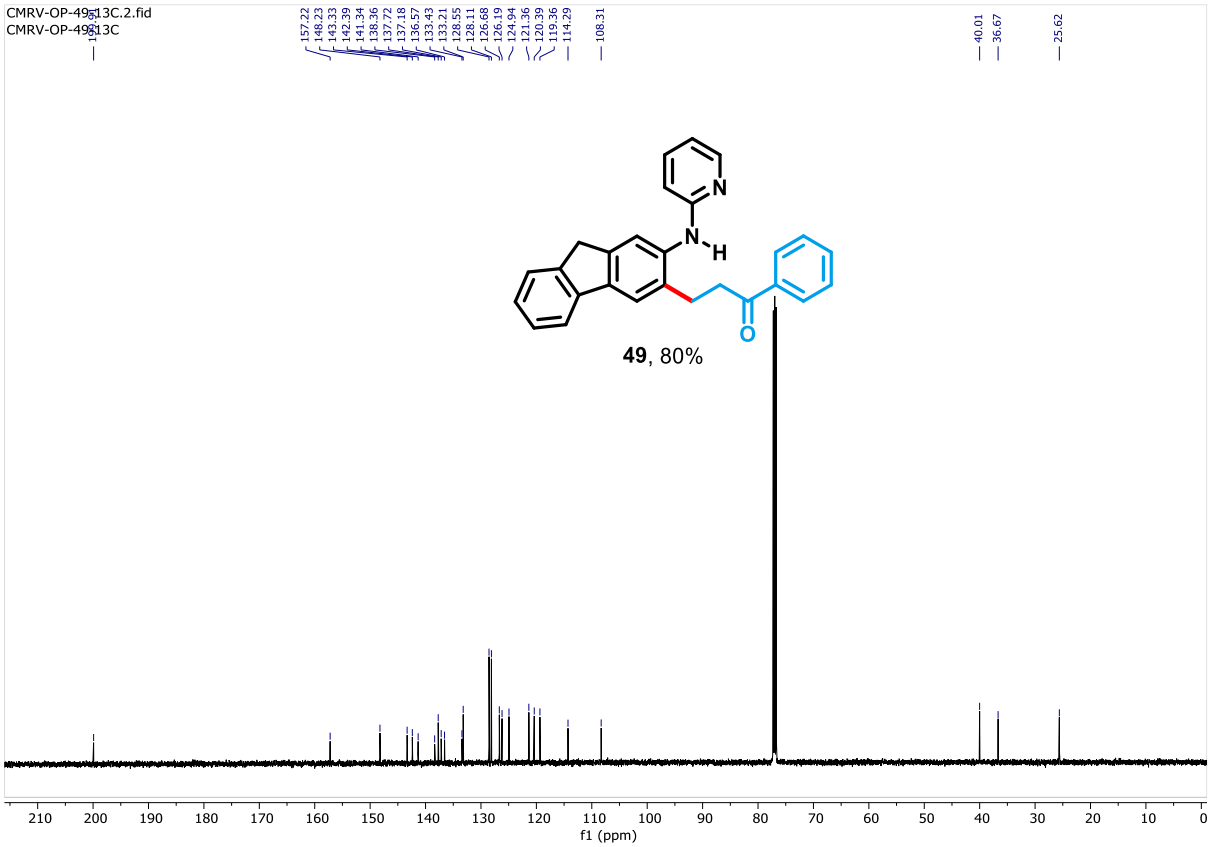
48


CMRV-DP-48-1H-3.fid
CMRV-DP-48-1H
7.85
7.83
7.79
7.77
7.51
7.50
7.49
7.48
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.41
7.39
7.38
7.32
7.30
7.29
6.66
6.65
6.64
6.63
6.03
6.01
3.36
3.35
3.34
3.24
3.23
3.21
N
N
H
O
48, 89%
1.03
1.09
3.00
1.06
2.06
2.01
2.00
1.05
1.03
1.01
2.00
2.03
10.5
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
0.0
f1 (ppm)

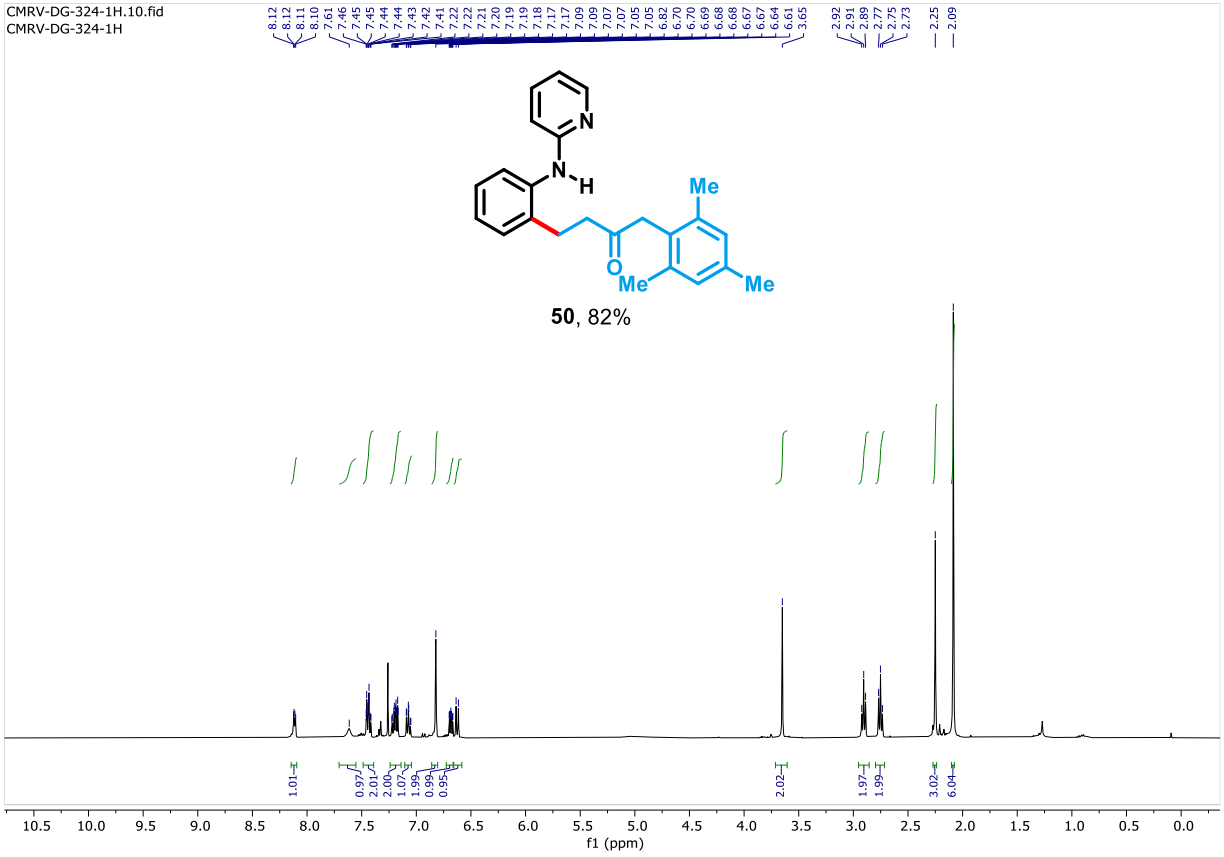

CMRV-DG-317-13C.12.fid
CMRV-DG-317-13C
199.37
158.85
148.02
138.08
136.66
136.61
133.52
133.13
132.93
131.71
128.57
128.20
128.11
128.09
127.54
126.68
125.74
123.77
113.87
106.86
39.64
26.49
N
N
H
O
48, 89%
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

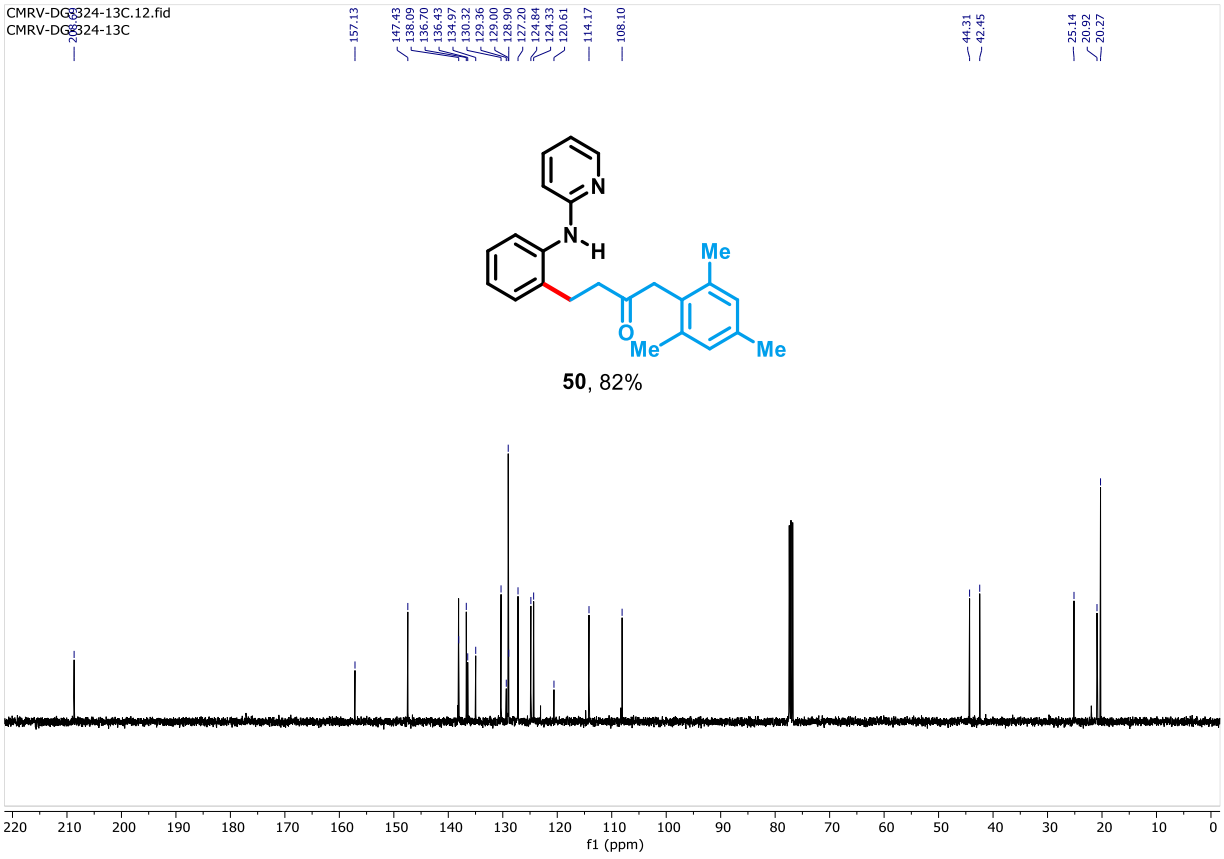
49


CMRV-OP-49-1H-1.fid
CMRV-OP-49-1H
8.21
8.20
8.20
7.94
7.93
7.72
7.71
7.69
7.55
7.53
7.52
7.50
7.49
7.48
7.47
7.43
7.42
7.37
7.35
7.34
7.27
7.24
6.76
6.74
6.71
6.70
6.70
6.69
3.86
3.44
3.43
3.41
3.19
3.18
3.16
N
N
H
O
49, 80%
1.03
2.00
1.94
1.00
4.02
2.01
1.07
1.00
2.01
2.02
2.03
2.04
10.5
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
0.0
f1 (ppm)

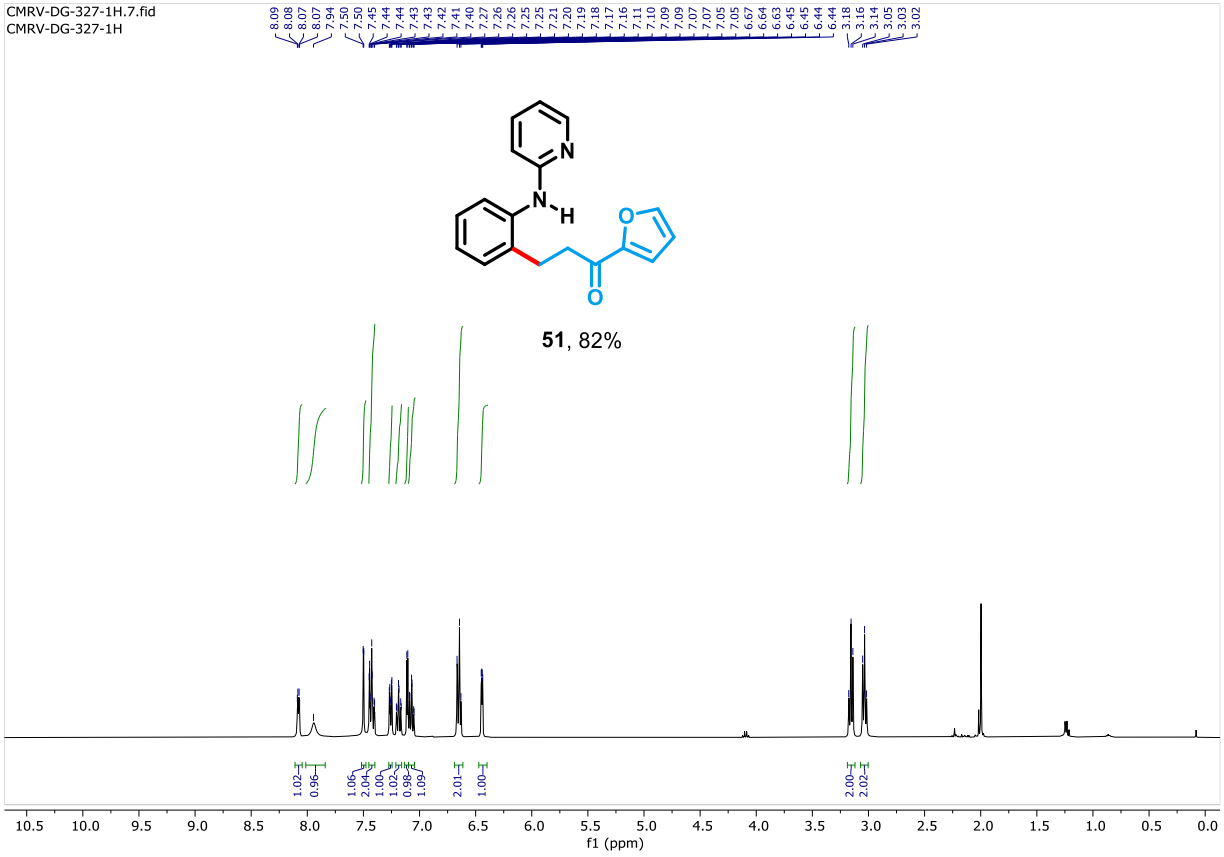

CMRV-OP-49-13C.2.fid
CMRV-OP-49-13C
157.22
148.23
143.33
142.39
141.34
138.36
137.72
137.18
136.57
133.43
133.21
128.55
128.11
126.68
126.19
124.94
121.36
120.39
119.36
114.29
108.31
40.01
36.67
25.62
N
N
H
O
49, 80%
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

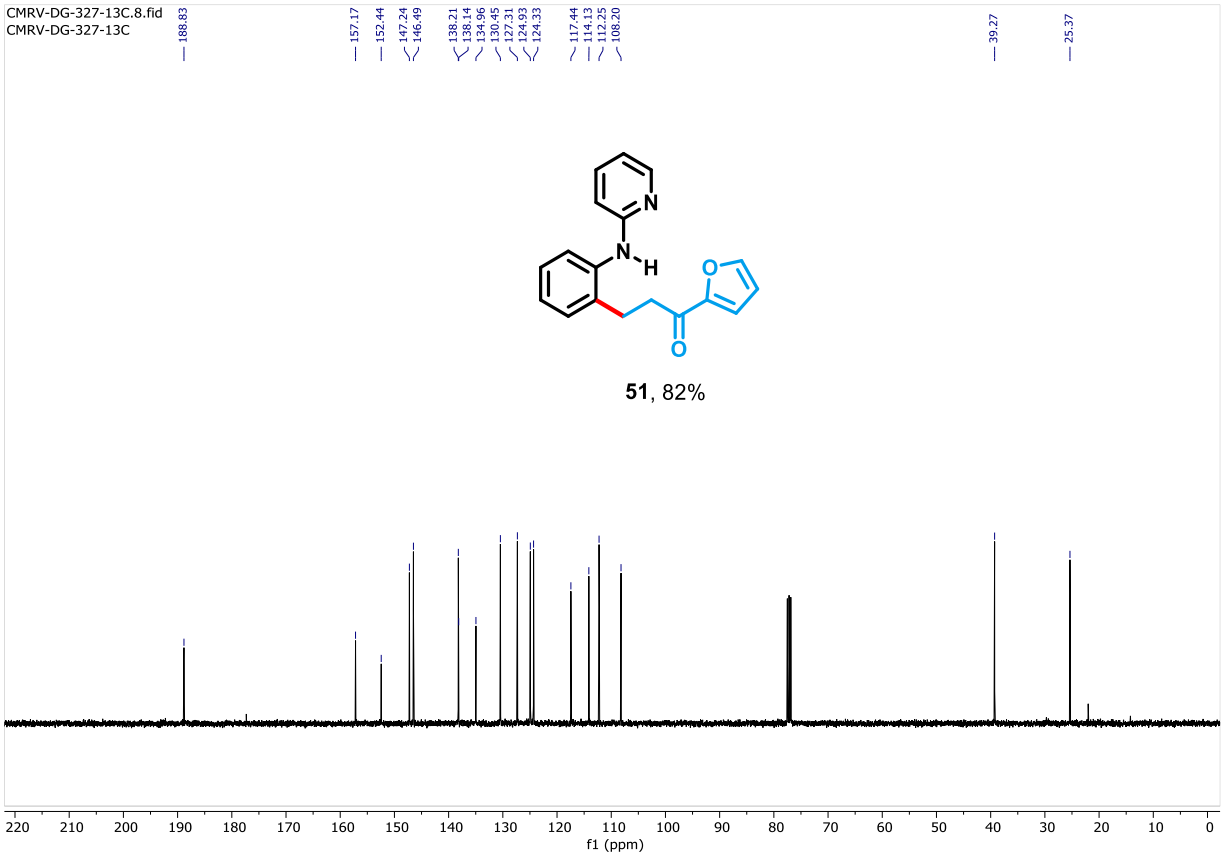
50


CMRV-DG-324-1H.10.fid
CMRV-DG-324-1H
8.12 8.12 8.11 8.10 7.61 7.46 7.45 7.45 7.44 7.44 7.43 7.42 7.41 7.22 7.22 7.21 7.20 7.19 7.19 7.18 7.17 7.17 7.09 7.09 7.07 7.07 7.05 7.05 6.82 6.70 6.70 6.69 6.68 6.68 6.67 6.67 6.64 6.61 3.65 2.92 2.91 2.89 2.77 2.75 2.73 2.25 2.09
N
N H
Me
O
Me
Me
50, 82%
1.01 0.97 2.01 2.00 1.07 1.99 0.99 0.95 2.02 1.97 1.99 3.02 6.04
10.5 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 0.0
f1 (ppm)

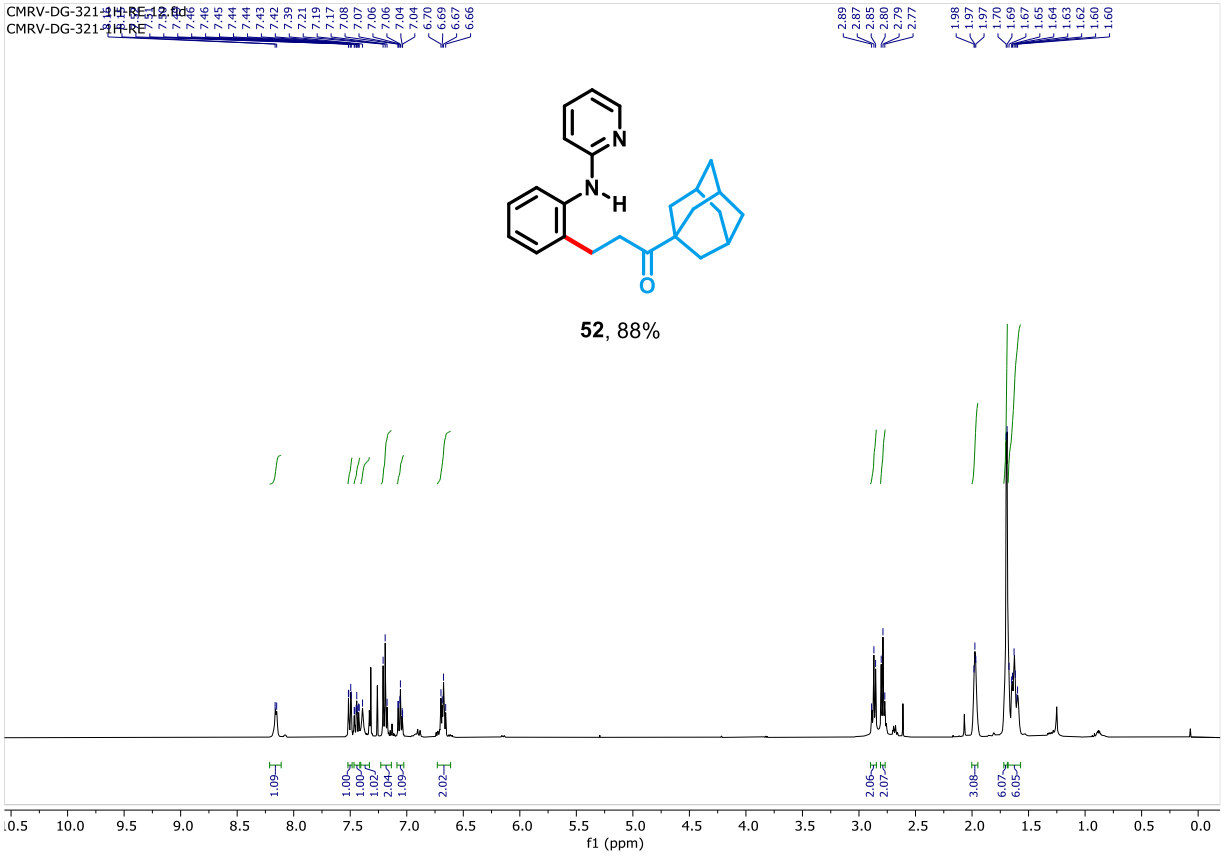

CMRV-DG-324-13C.12.fid
CMRV-DG-324-13C
157.13 147.43 138.09 136.70 136.43 134.97 130.32 129.36 129.00 128.90 127.20 124.84 124.33 120.61 114.17 108.10 44.31 42.45 25.14 20.92 20.27
N
N H
Me
O
Me
Me
50, 82%
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

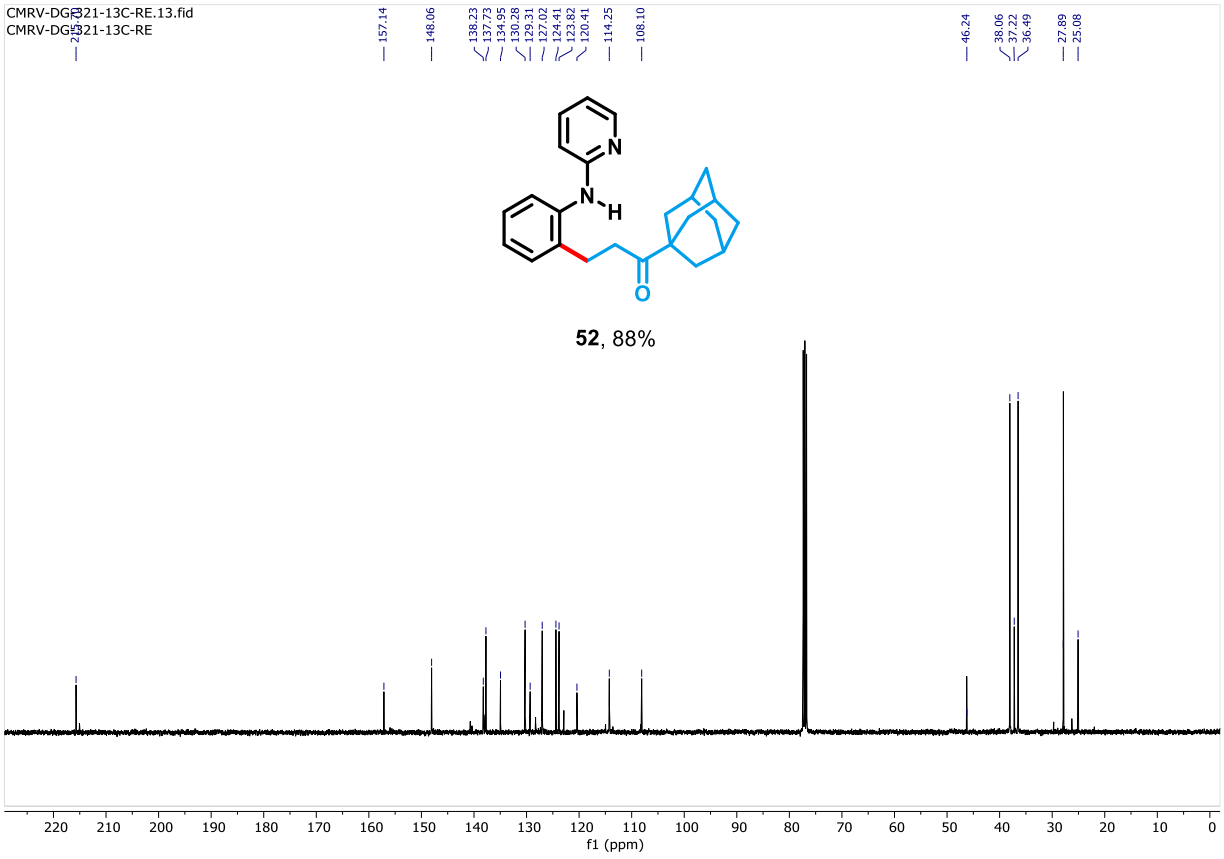
51


CMRV-DG-327-1H.7.fid
CMRV-DG-327-1H
8.09 8.08 8.07 8.07 7.94 7.50 7.50 7.45 7.44 7.44 7.43 7.43 7.42 7.41 7.40 7.27 7.26 7.25 7.25 7.21 7.20 7.19 7.18 7.17 7.16 7.11 7.10 7.09 7.09 7.07 7.07 7.05 7.05 6.67 6.64 6.63 6.45 6.45 6.44 6.44 3.18 3.16 3.14 3.05 3.03 3.02
N
N
H
O
O
51, 82%
1.02 0.96 1.06 2.04 1.00 1.02 0.98 1.09 2.01 1.00 2.00 2.02
10.5 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 0.0
f1 (ppm)

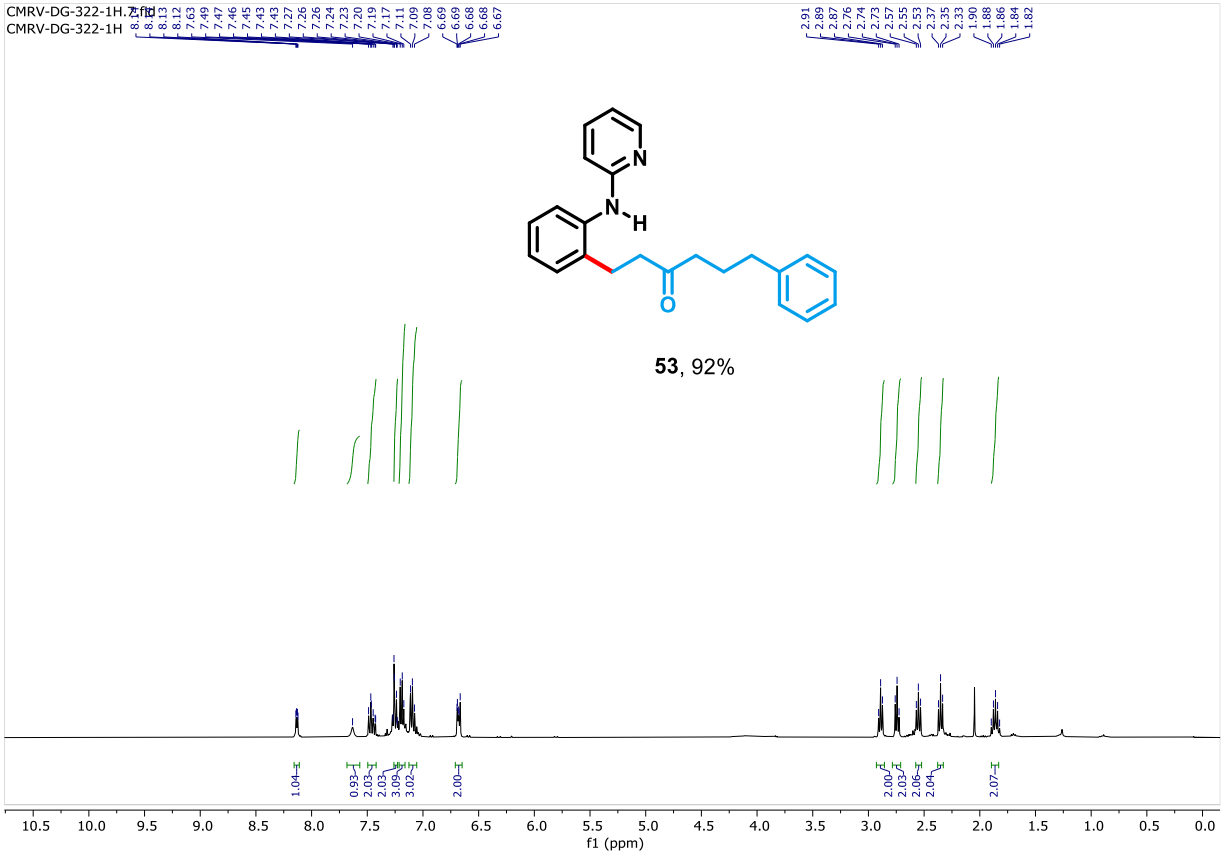

CMRV-DG-327-13C.8.fid
CMRV-DG-327-13C
188.83 157.17 152.44 147.24 146.49 138.21 138.14 134.96 130.45 127.31 124.93 124.33 117.44 114.13 112.25 108.20 39.27 25.37
N
N
H
O
O
51, 82%
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

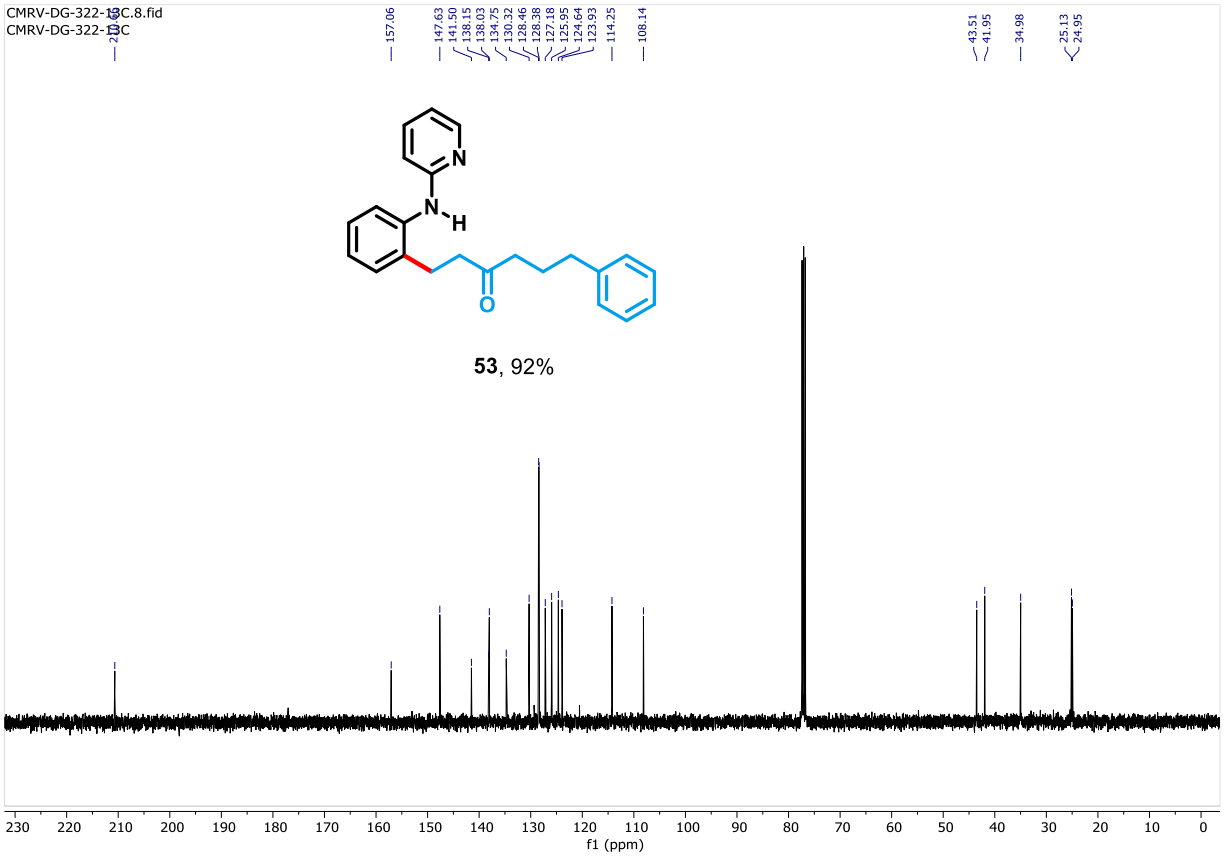
52


CMRV-DG-321-1H-RE.12.fid
CMRV-DG-321-1H-RE
52, 88%
f1 (ppm)

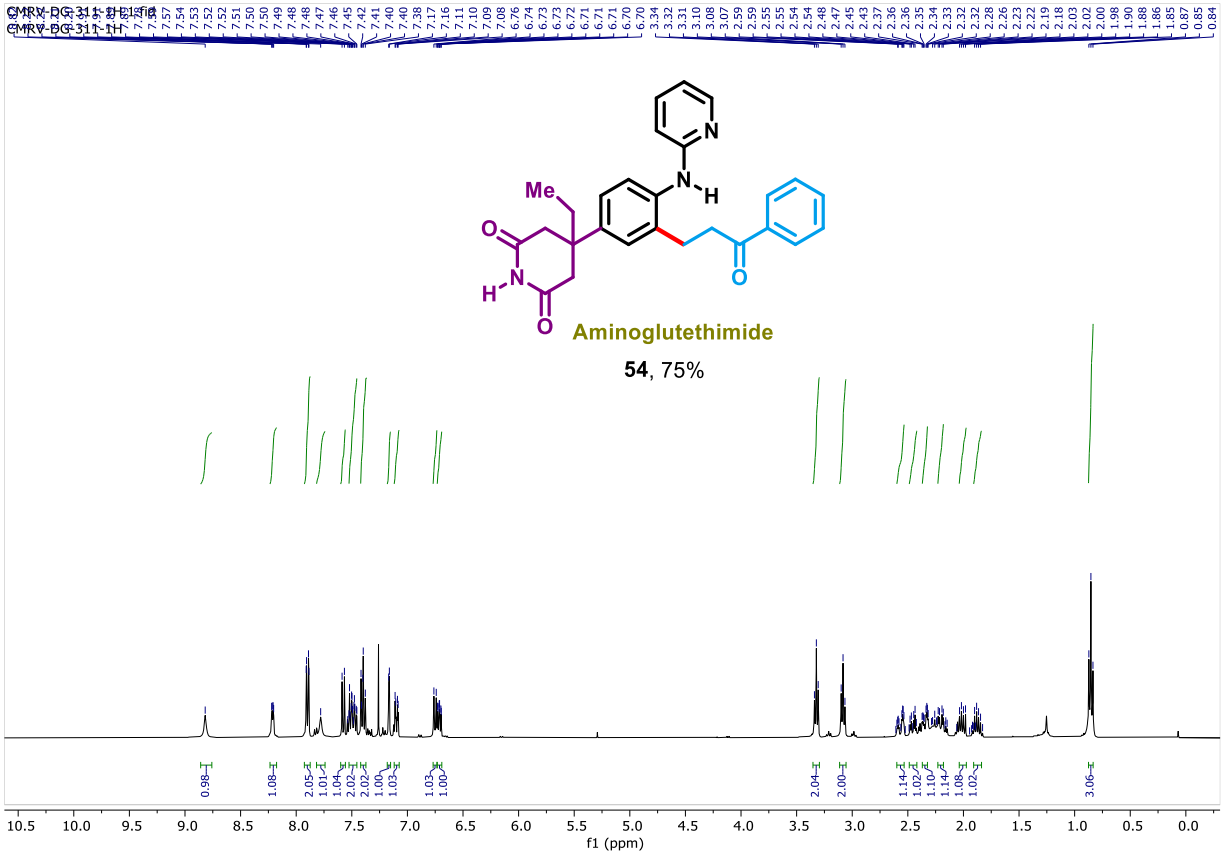

CMRV-DG-321-13C-RE.13.fid
CMRV-DG-321-13C-RE
52, 88%
f1 (ppm)

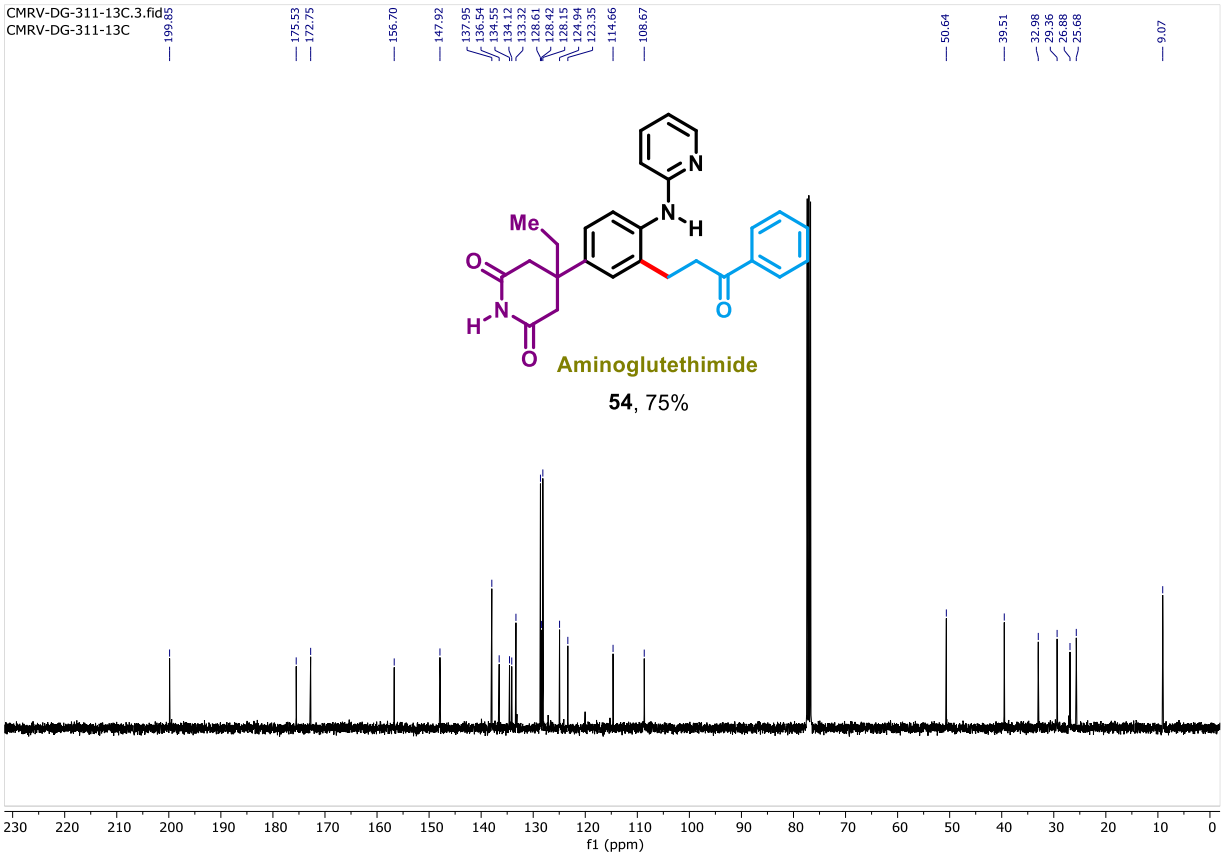
53


CMRV-DG-322-1H.7.fid
CMRV-DG-322-1H
8.14 8.13 8.13 8.12 7.63 7.49 7.47 7.46 7.45 7.43 7.43 7.27 7.26 7.26 7.24 7.23 7.20 7.19 7.17 7.11 7.09 7.08 6.69 6.68 6.68 6.67
2.91 2.89 2.87 2.76 2.74 2.73 2.57 2.55 2.53 2.37 2.35 2.33 1.90 1.88 1.86 1.84 1.82
N
N
H
O
53, 92%
1.04 0.93 2.03 2.03 3.09 3.02 2.00 2.00 2.03 2.06 2.04 2.07
10.5 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 0.0
f1 (ppm)

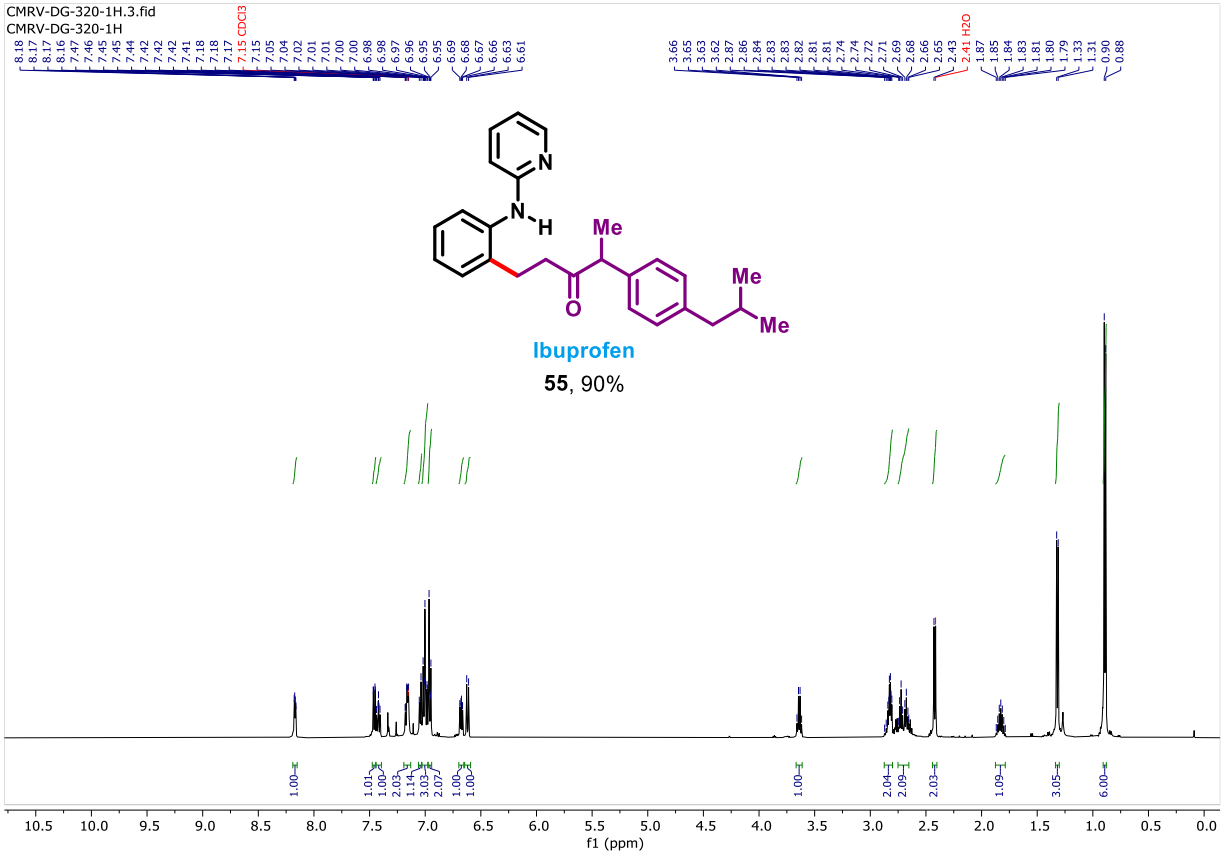

CMRV-DG-322-13C.8.fid
CMRV-DG-322-13C
157.06 147.63 141.50 138.15 138.03 134.75 130.32 128.46 128.38 127.18 125.95 124.64 123.93 114.25 108.14
43.51 41.95 34.98 25.13 24.95
N
N
H
O
53, 92%
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

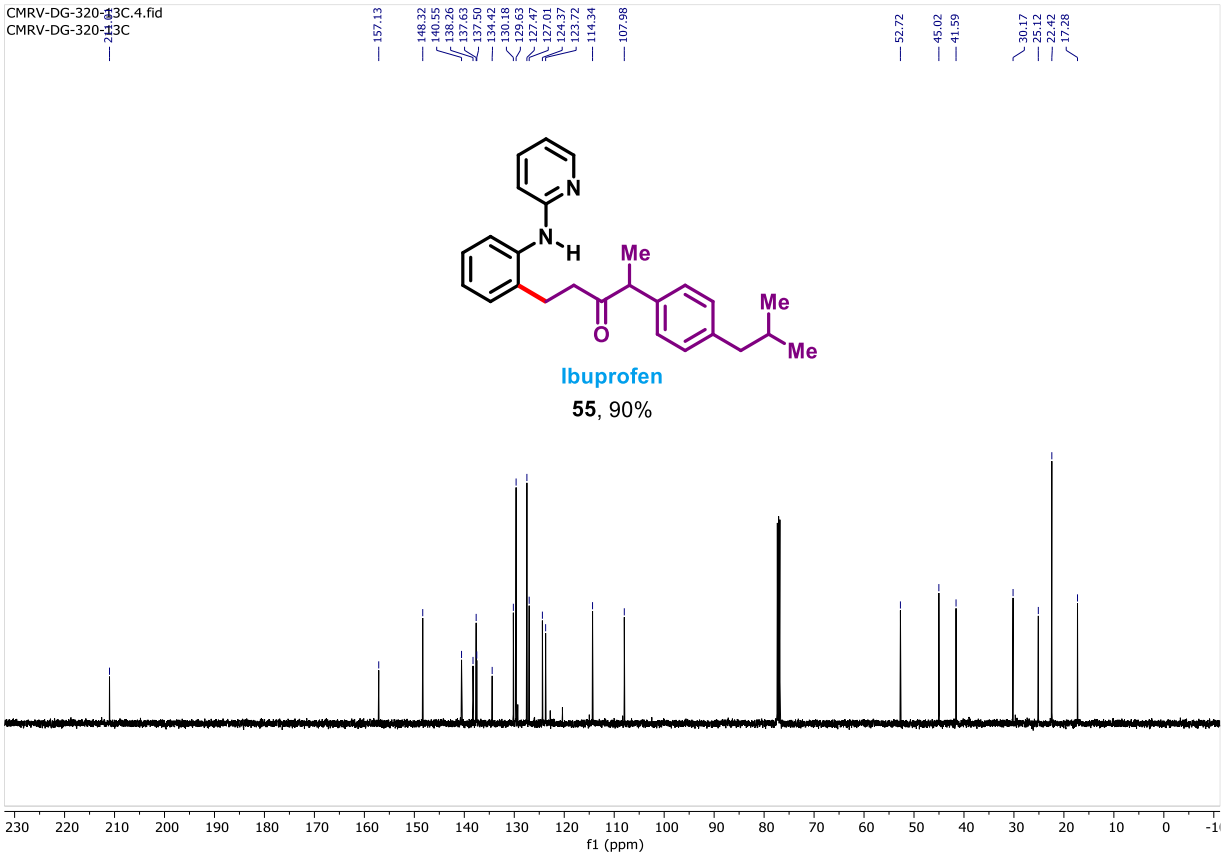
54


CMRV-DG-311-1H.2.fid
CMRV-DG-311-1H
Me
O
N
H
O
N
H
O
Aminoglutethimide
54, 75%
0.98
1.08
2.05
1.01
1.04
2.02
2.02
1.00
1.03
1.03
1.00
2.04
2.00
1.14
1.02
1.10
1.14
1.08
1.02
3.06
10.5 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 0.0
f1 (ppm)

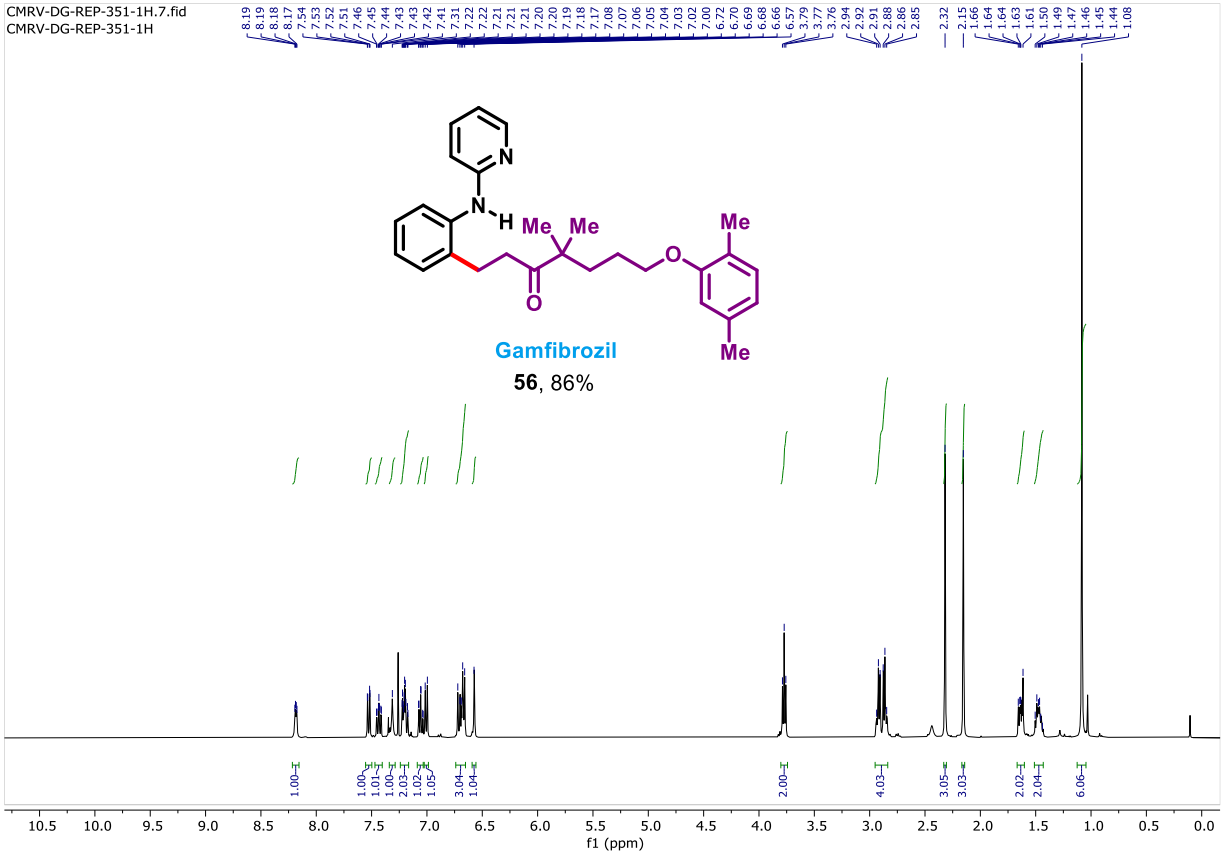

CMRV-DG-311-13C.3.fid
CMRV-DG-311-13C
199.85
175.53
172.75
156.70
147.92
137.95
136.54
134.55
134.12
133.32
128.61
128.42
128.15
124.94
123.35
114.66
108.67
50.64
39.51
32.98
29.36
26.88
25.68
9.07
Me
O
N
H
O
N
H
O
Aminoglutethimide
54, 75%
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

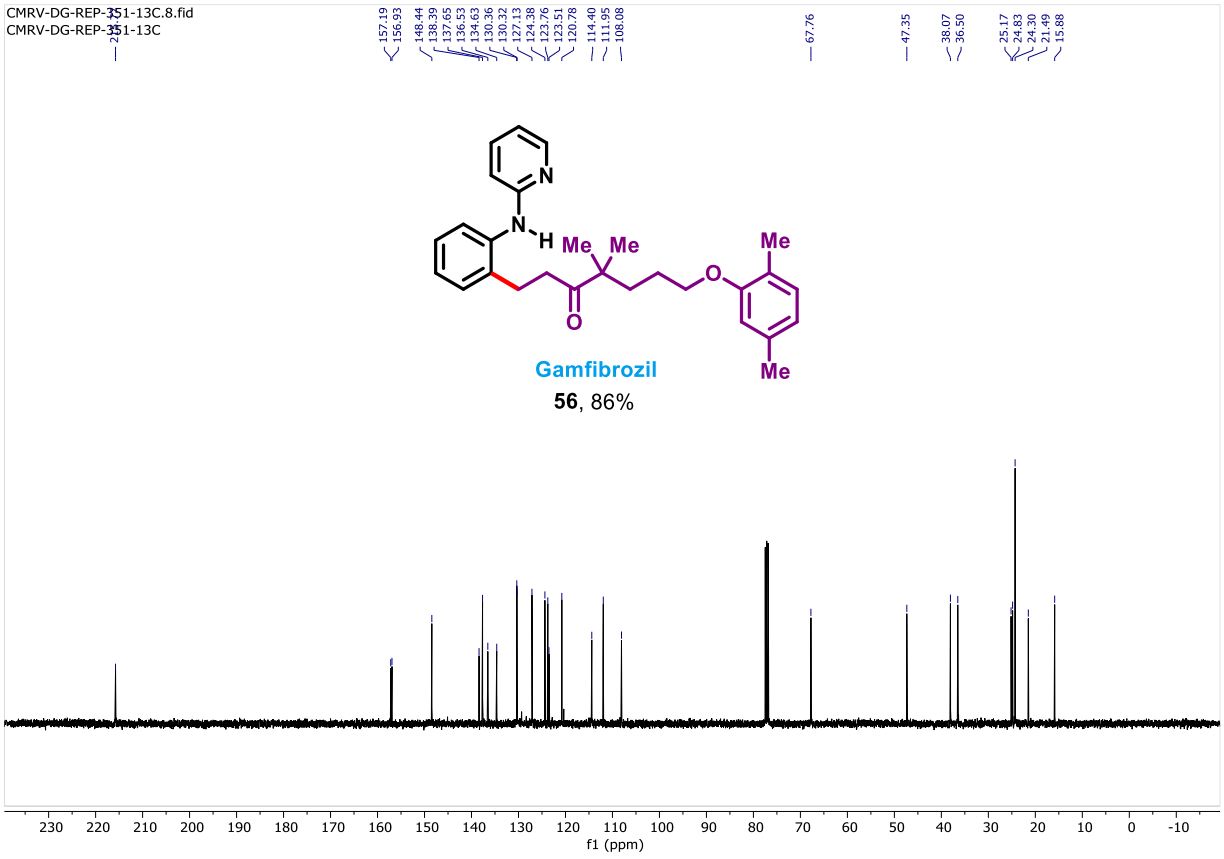
55


CMRV-DG-320-1H.3.fid
CMRV-DG-320-1H
Ibuprofen
55, 90%
f1 (ppm)

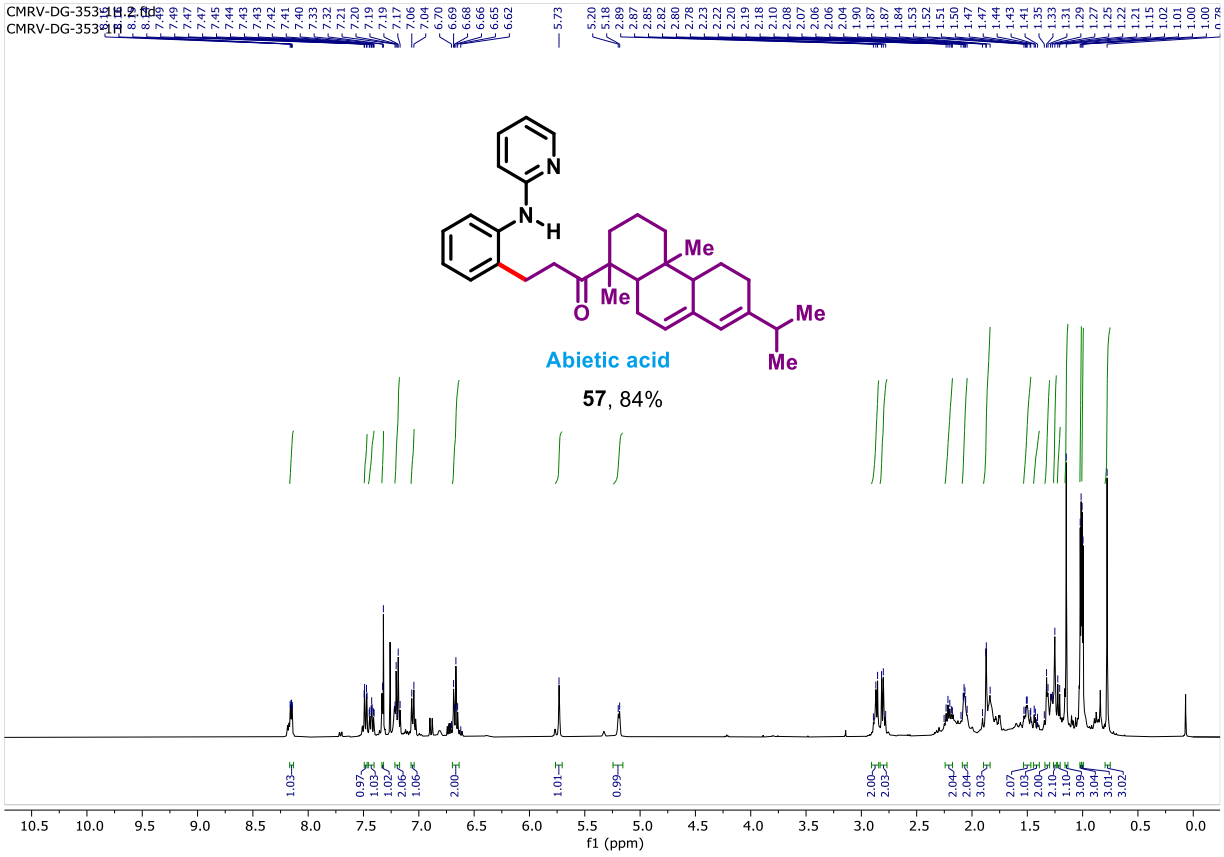

CMRV-DG-320-13C.4.fid
CMRV-DG-320-13C
Ibuprofen
55, 90%
f1 (ppm)

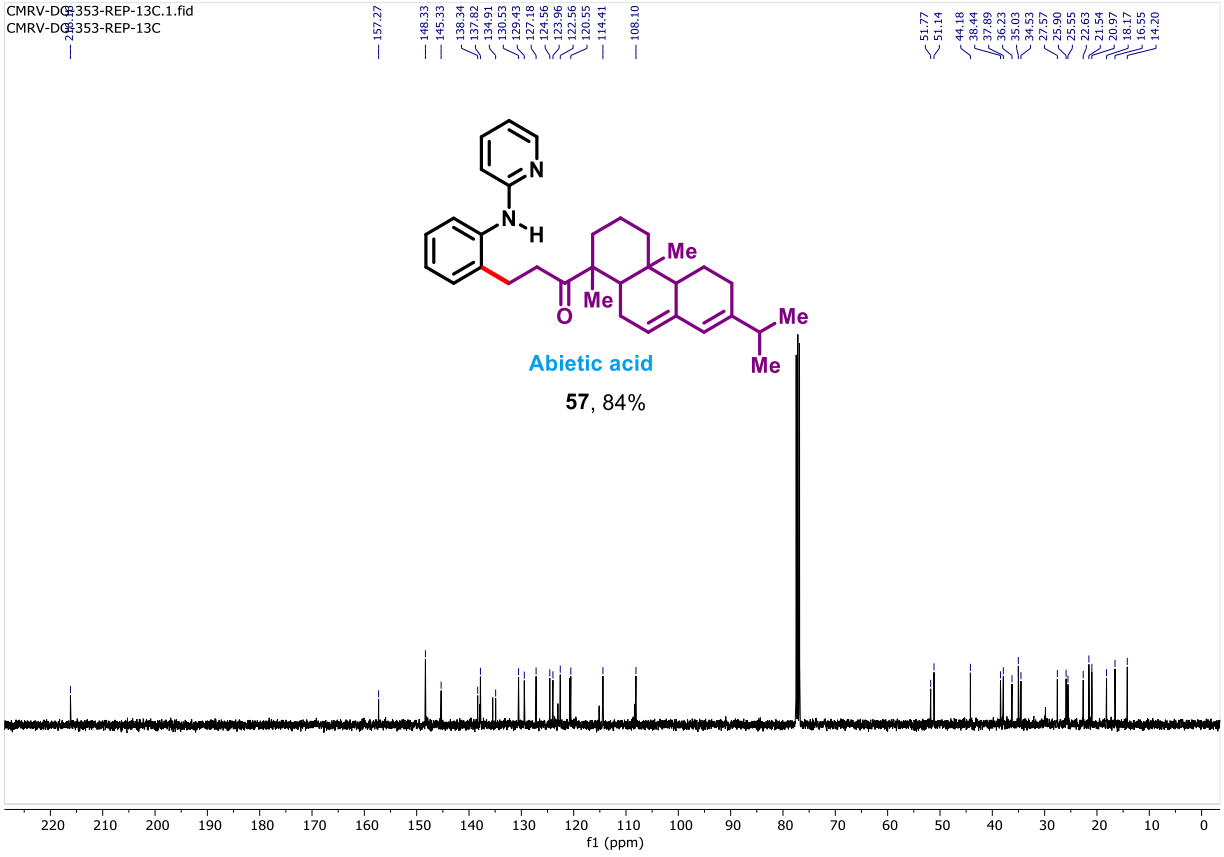
56


CMRV-DG-REP-351-1H.7.fid
CMRV-DG-REP-351-1H
Gamfibrozil
56, 86%
f1 (ppm)

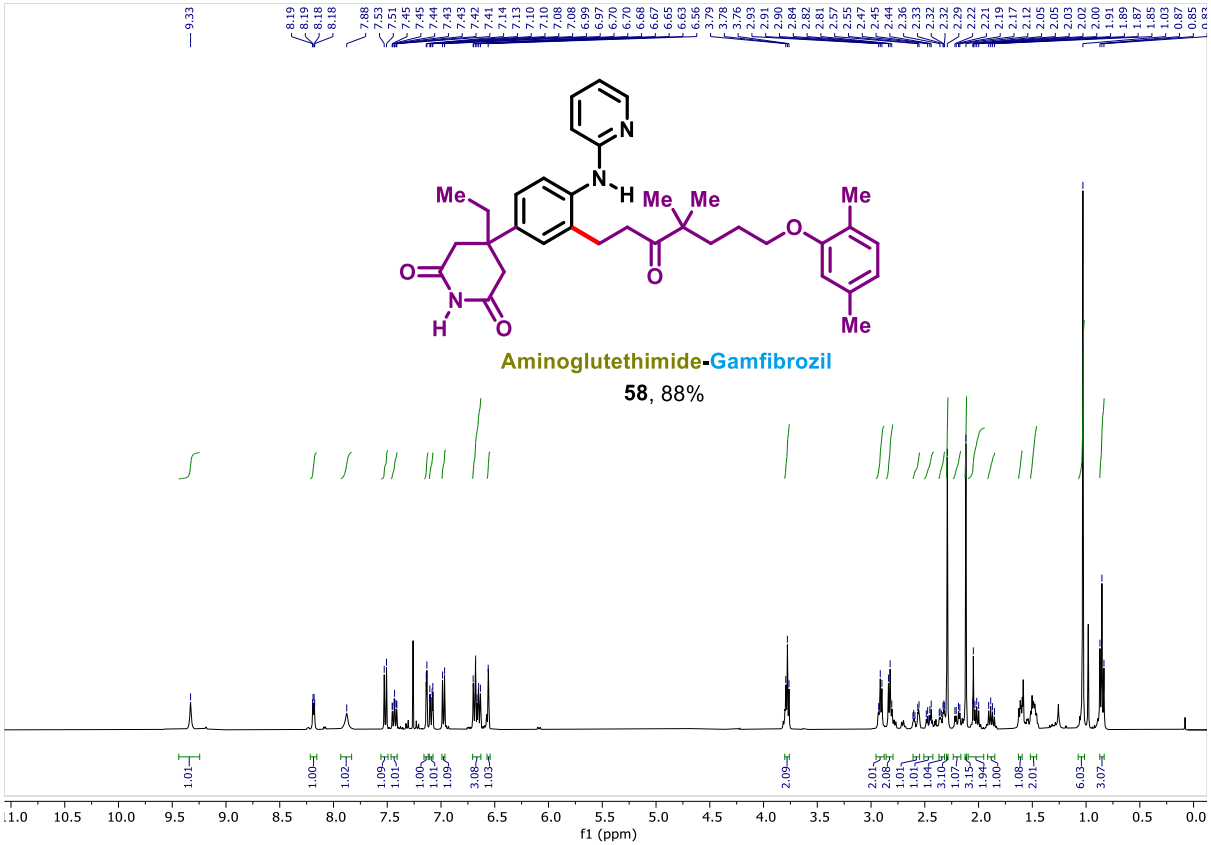

CMRV-DG-REP-351-13C.8.fid
CMRV-DG-REP-351-13C
Gamfibrozil
56, 86%
f1 (ppm)

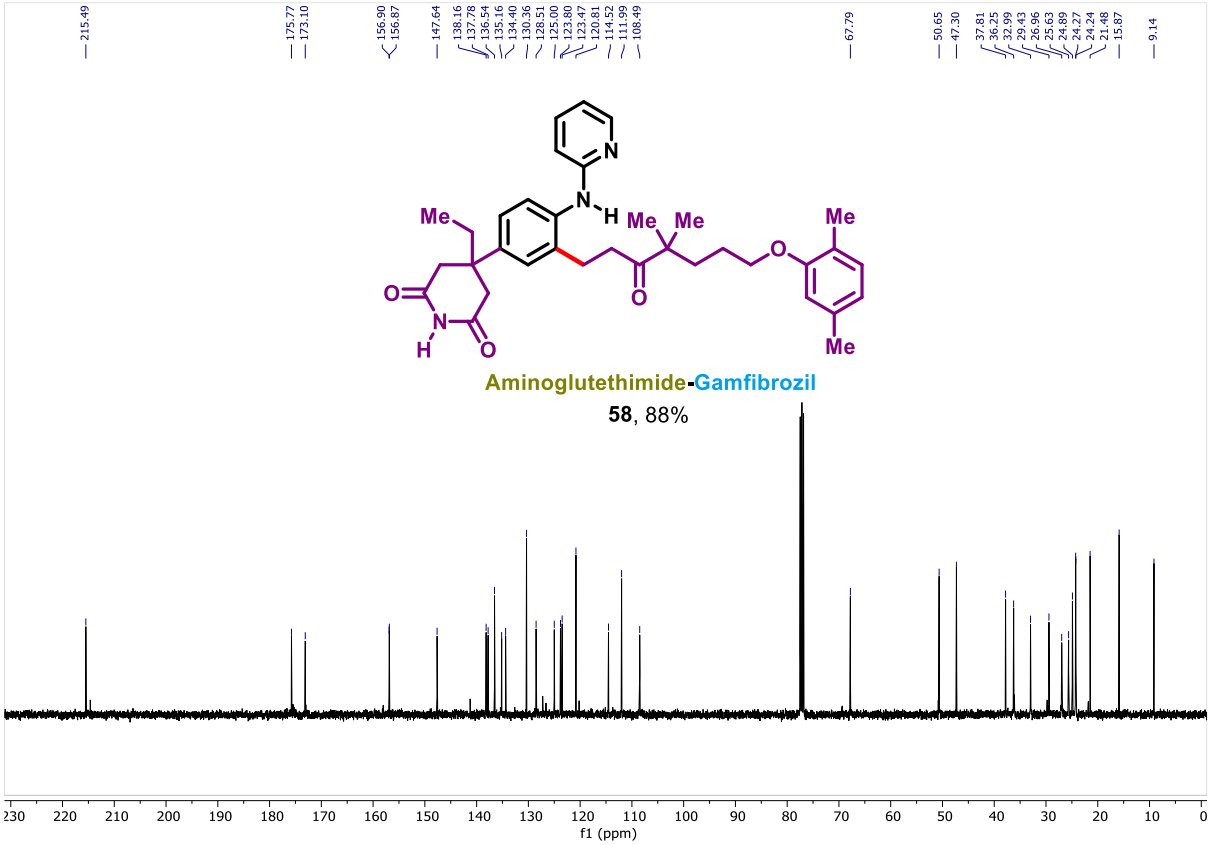
57


CMRV-DG-353-1H.2.fid
CMRV-DG-353-1H
Abietic acid
57, 84%
f1 (ppm)

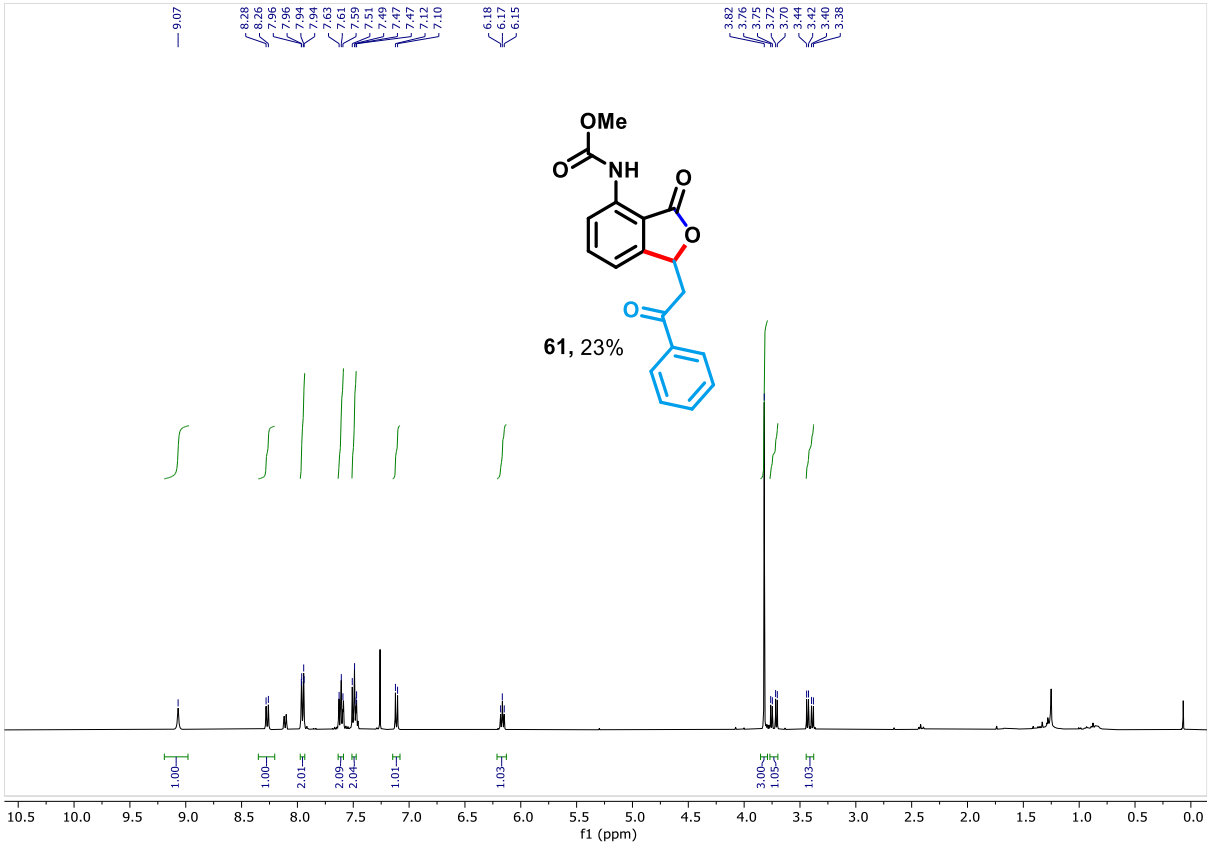

CMRV-DG-353-REP-13C.1.fid
CMRV-DG-353-REP-13C
Abietic acid
57, 84%
f1 (ppm)

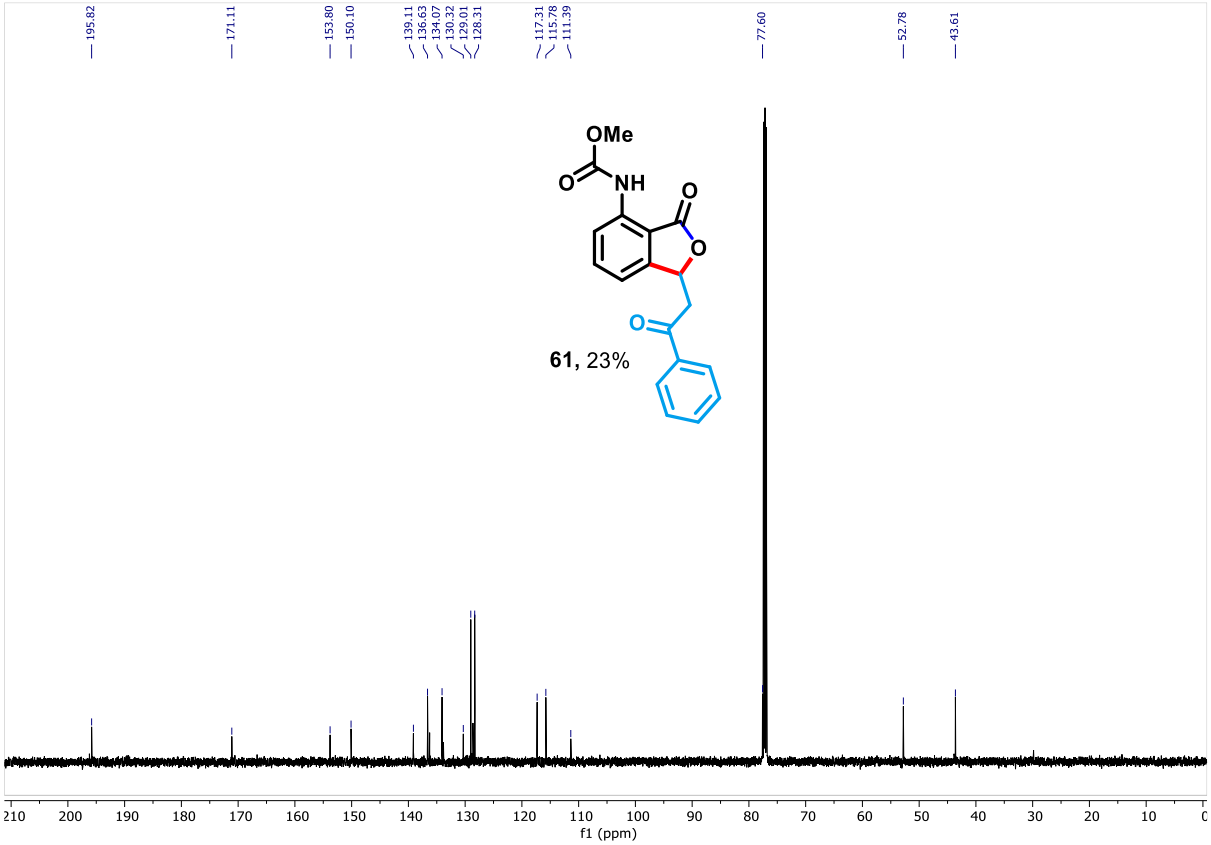
58


Aminoglutethimide-Gamfibrozil
58, 88%
f1 (ppm)

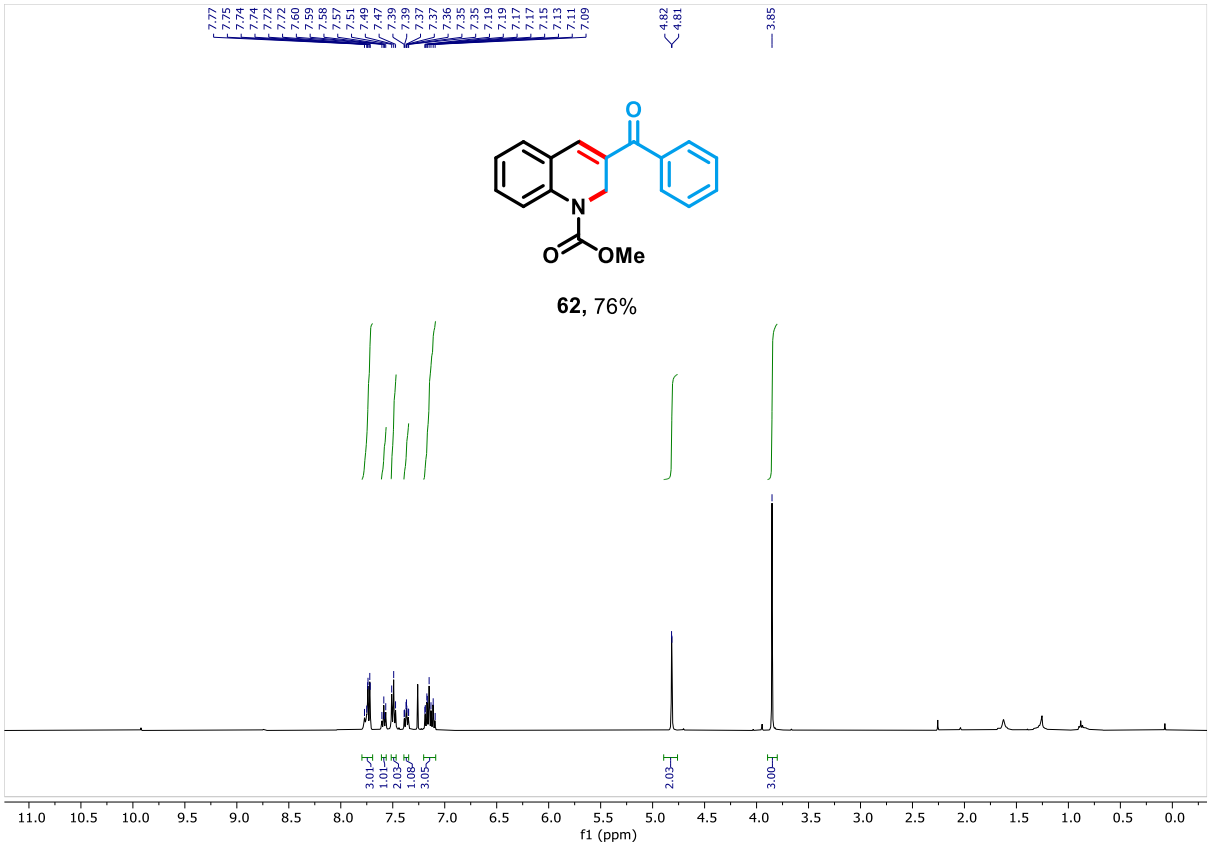

Aminoglutethimide-Gamfibrozil
58, 88%
f1 (ppm)

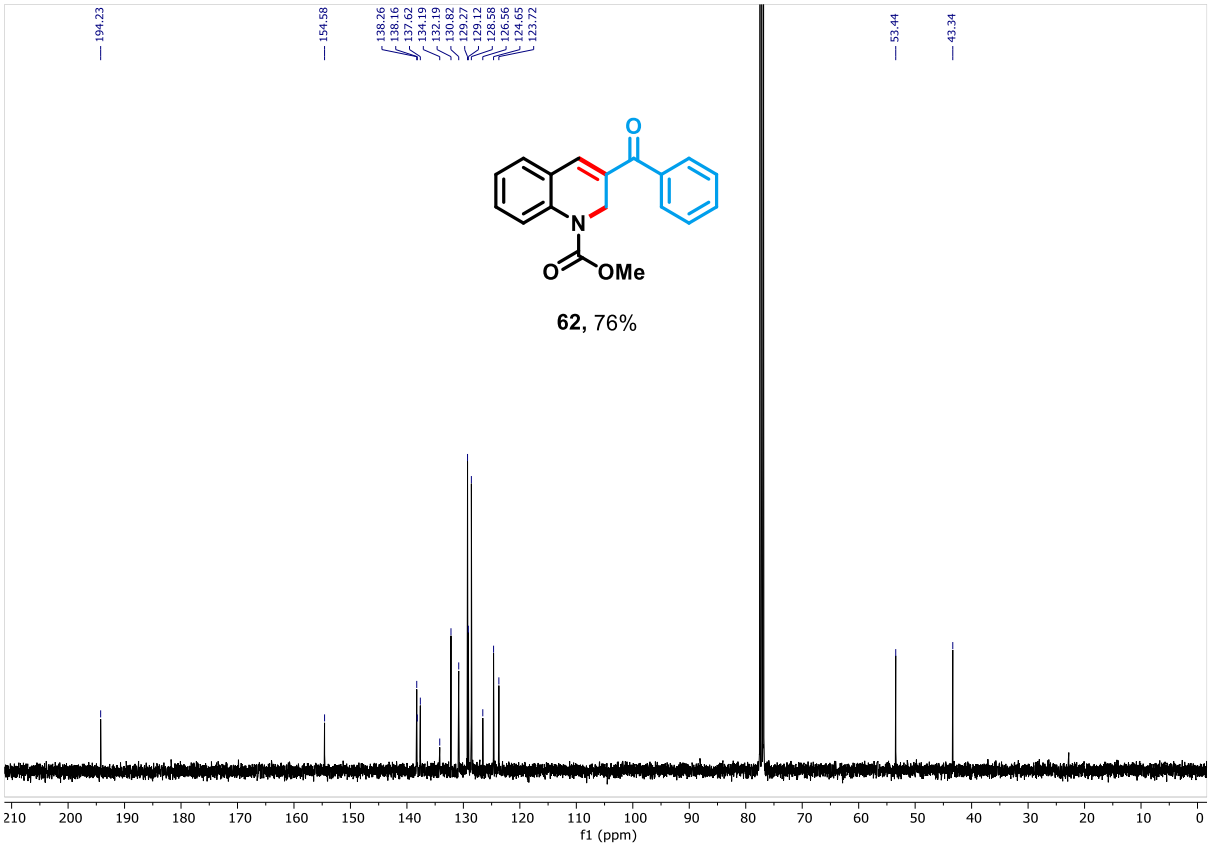
61


9.07
8.28
8.26
7.96
7.96
7.94
7.94
7.63
7.61
7.59
7.51
7.49
7.47
7.47
7.12
7.10
6.18
6.17
6.15
3.82
3.76
3.75
3.72
3.70
3.44
3.42
3.40
3.38
OMe
NH
O
O
O
O
61, 23%
1.00
1.00
2.01
2.09
2.04
1.01
1.03
3.00
1.05
1.03
f1 (ppm)

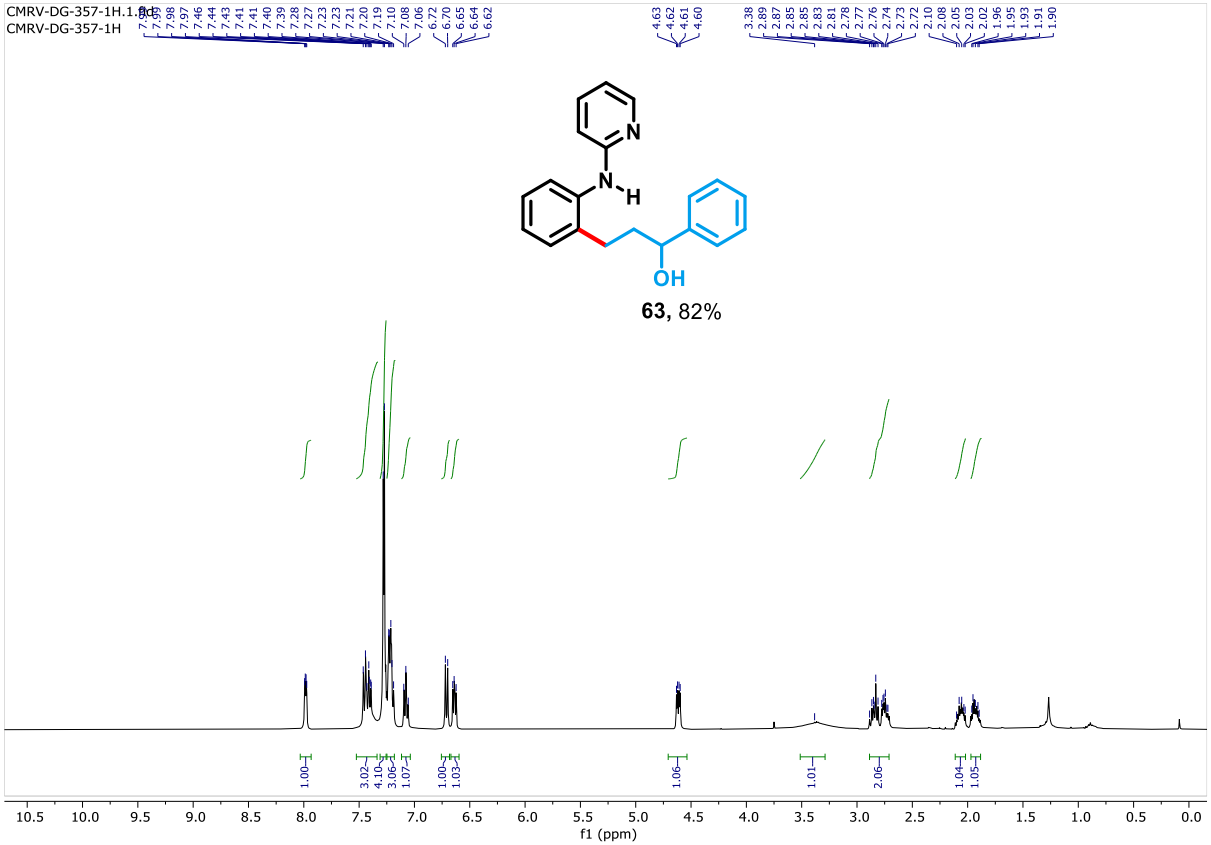

195.82
171.11
153.80
150.10
139.11
136.63
134.07
130.32
129.01
128.31
117.31
115.78
111.39
77.60
52.78
43.61
OMe
NH
O
O
O
O
61, 23%
f1 (ppm)

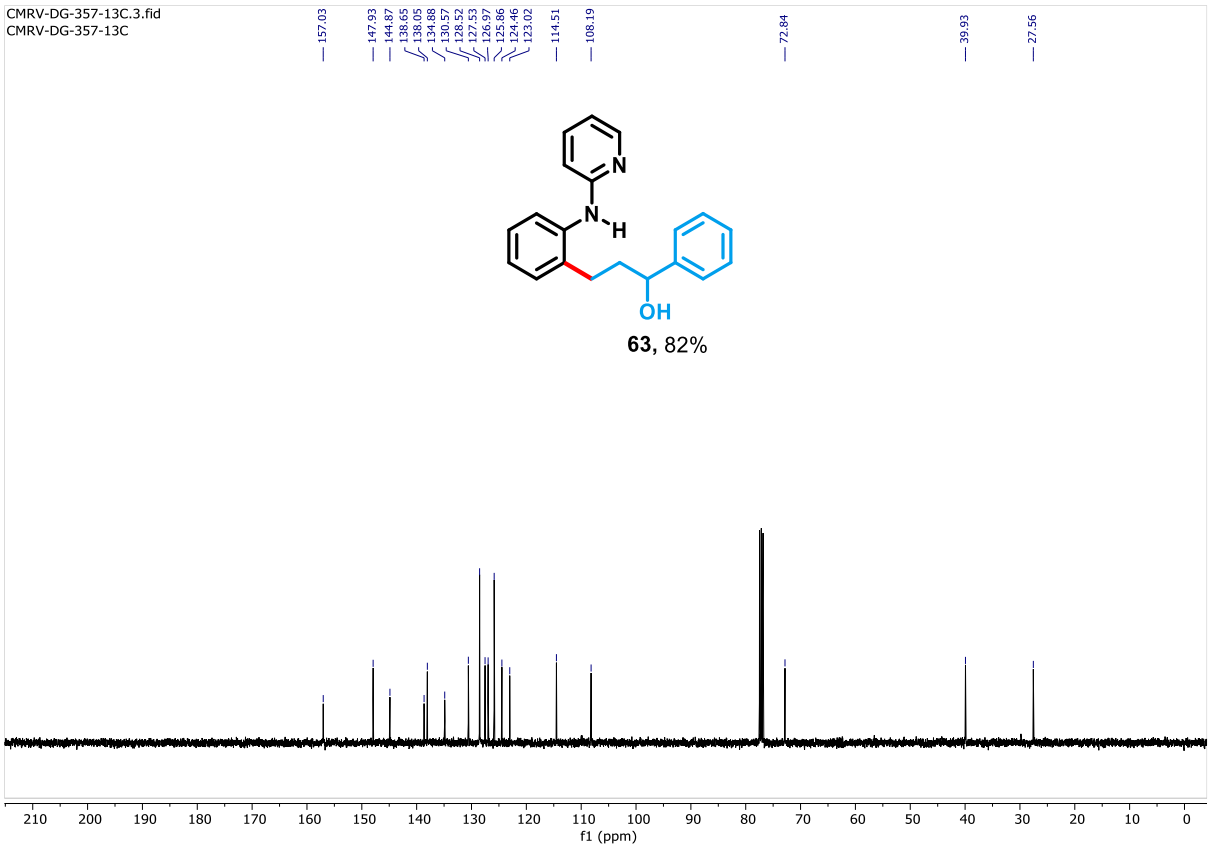
62


7.77
7.75
7.74
7.74
7.72
7.72
7.60
7.59
7.58
7.57
7.51
7.49
7.47
7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.19
7.19
7.17
7.17
7.15
7.13
7.11
7.09
4.82
4.81
3.85
O
N
O
OMe
62, 76%
3.01
1.01
2.03
1.08
3.05
2.03
3.00
11.0 10.5 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 0.0
f1 (ppm)

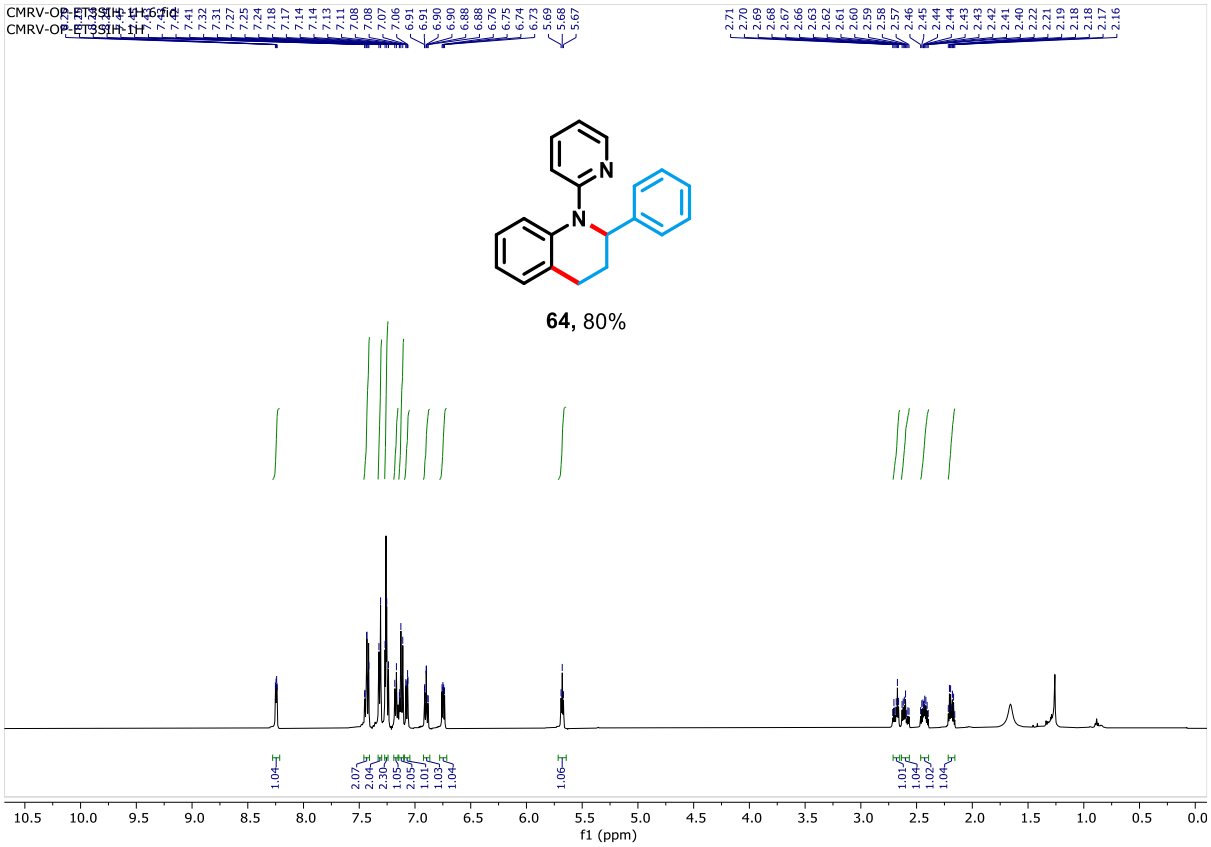

194.23
154.58
138.26
138.16
137.62
134.19
132.19
130.82
129.27
129.12
128.58
126.56
124.65
123.72
53.44
43.34
O
N
O
OMe
62, 76%
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

63

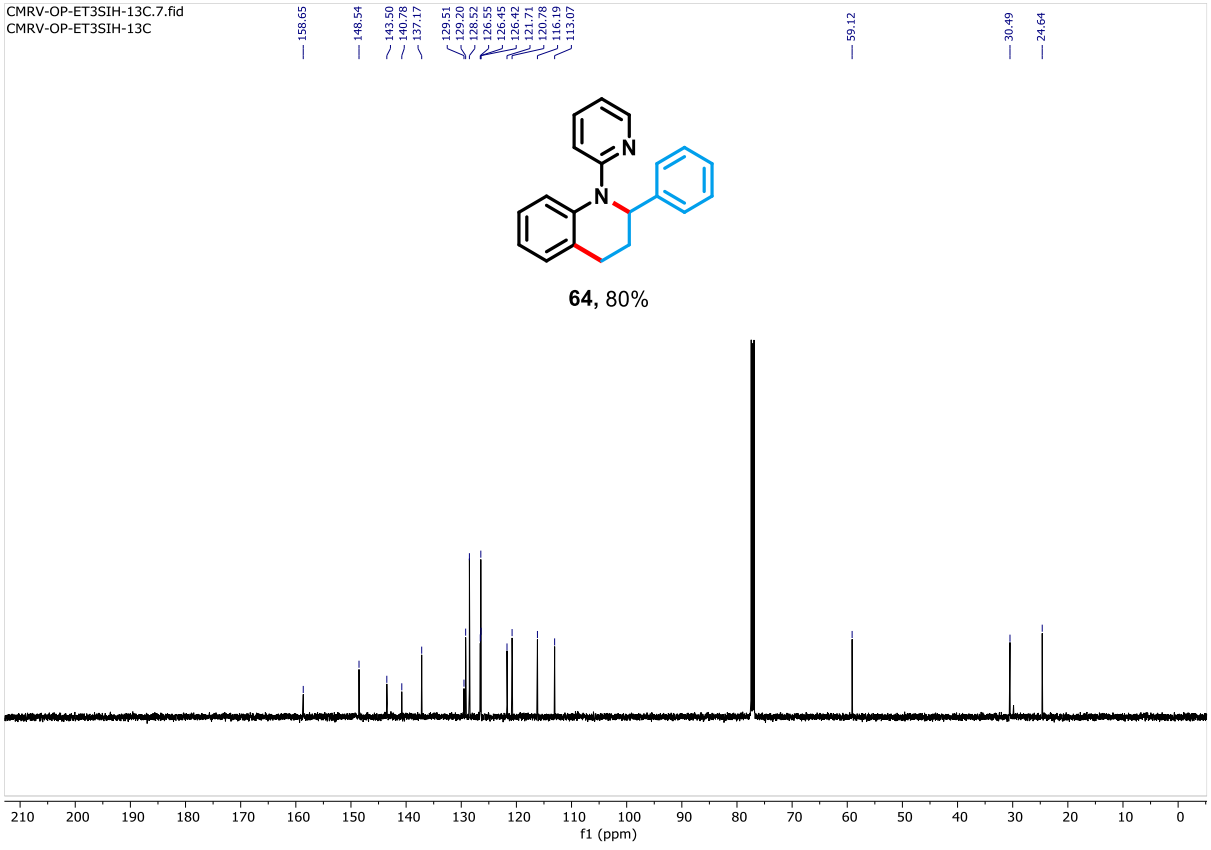

CMRV-DG-357-1H.1.fid
CMRV-DG-357-1H
7.99 7.98 7.97 7.46 7.44 7.43 7.41 7.41 7.40 7.39 7.28 7.27 7.23 7.23 7.21 7.20 7.19 7.10 7.08 7.06 6.72 6.70 6.65 6.64 6.62
4.63 4.62 4.61 4.60
3.38 2.89 2.87 2.85 2.85 2.83 2.81 2.78 2.77 2.76 2.74 2.73 2.72 2.10 2.08 2.05 2.03 2.02 1.96 1.95 1.93 1.91 1.90
N
N
H
OH
63, 82%
1.00 3.02 4.10 3.06 1.07 1.00 1.03 1.06 1.01 2.06 1.04 1.05
10.5 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 0.0
f1 (ppm)


CMRV-DG-357-13C.3.fid
CMRV-DG-357-13C
157.03 147.93 144.87 138.65 138.05 134.88 130.57 128.52 127.53 126.97 125.86 124.46 123.02 114.51 108.19 72.84 39.93 27.56
N
N
H
OH
63, 82%
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

64

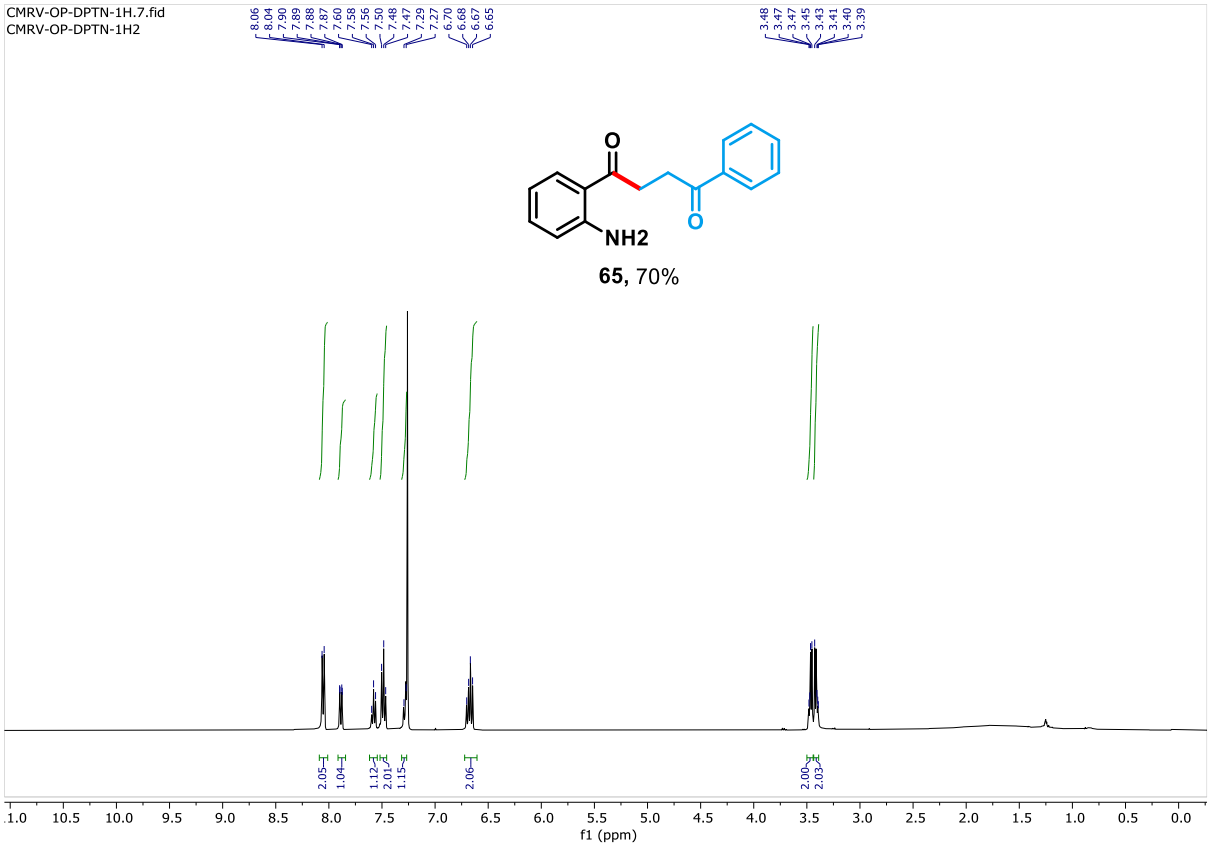

CMRV-OP-ET3SIH-1H.6.fid
CMRV-OP-ET3SIH-1H
f1 (ppm)

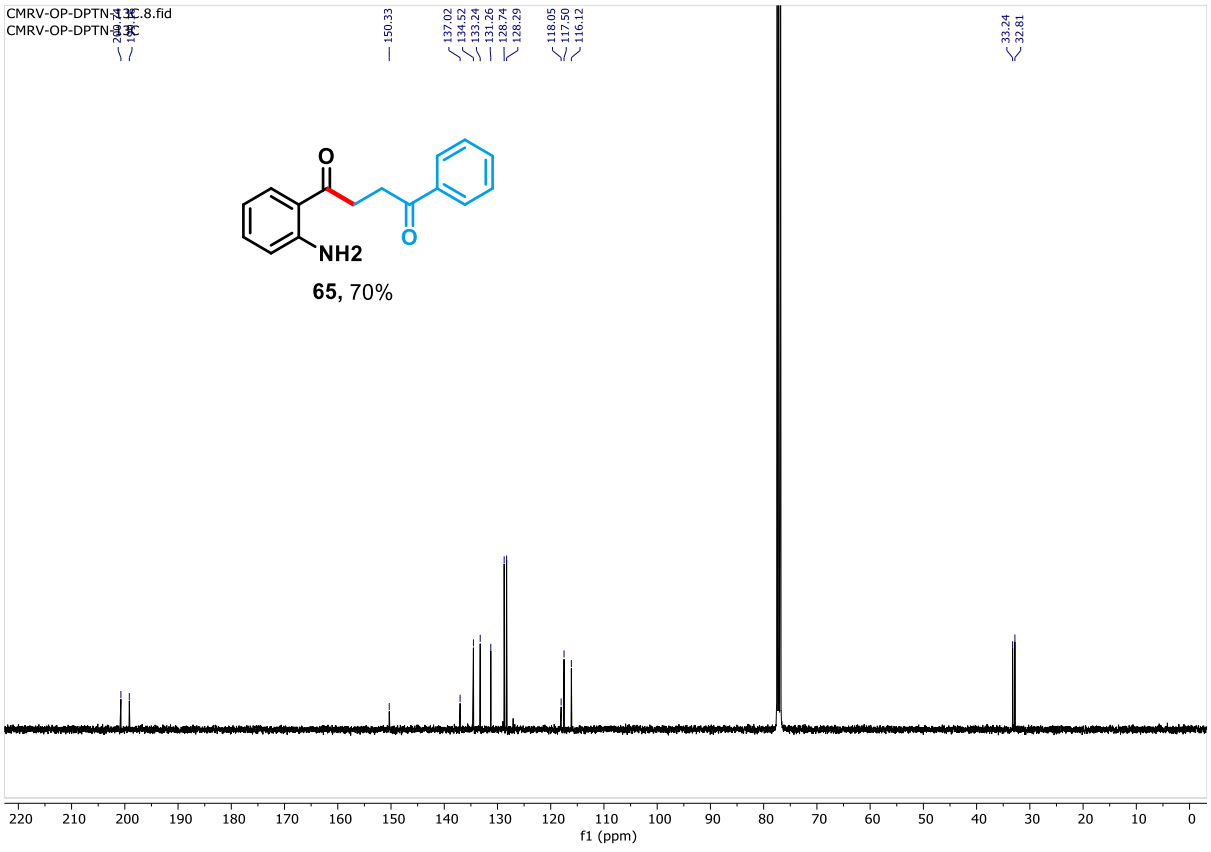
64, 80%


CMRV-OP-ET3SIH-13C.7.fid
CMRV-OP-ET3SIH-13C
158.65
148.54
143.50
140.78
137.17
129.51
129.20
128.52
126.55
126.45
126.42
121.71
120.78
116.19
113.07
59.12
30.49
24.64
f1 (ppm)

64, 80%

65


CMRV-OP-DPTN-1H.7.fid
CMRV-OP-DPTN-1H2
8.06
8.04
7.90
7.89
7.88
7.87
7.60
7.58
7.56
7.50
7.48
7.47
7.29
7.27
6.70
6.68
6.67
6.65
3.48
3.47
3.47
3.47
3.45
3.43
3.41
3.40
3.39
O
O
NH2
65, 70%
2.05
1.04
1.12
2.01
1.15
2.06
2.00
2.03
f1 (ppm)


CMRV-OP-DPTN-13C.8.fid
CMRV-OP-DPTN-13C
150.33
137.02
134.52
133.24
131.26
128.74
128.29
118.05
117.50
116.12
33.24
32.81
O
O
NH2
65, 70%
f1 (ppm)