SUPPLEMENTARY INFORMATION

Thiocyanate: A Visible Light Driven Traceless Auxiliary for Stereoselective Cyclopropyl Ketone Construction

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1. General Considerations:

All commercially available chemicals and reagents were used without any further purification unless otherwise stated. Solvents for extraction or column chromatography were of technical quality. All water used was purified via a Merck Millipore reverse osmosis purification system prior to use. All reactions were performed in oven-dried glassware under a positive pressure of argon with freshly distilled anhydrous solvents.[1] Solvents were transferred *via* syringe and were introduced into the reaction vessels through a rubber septum Solvents were removed under reduced pressure using Büchi Rotavapor apparatus.

Thin-layer chromatography (TLC): The progress of the reaction was monitored by thin layer chromatography (TLC) using SiO_2-60 UV254 coated aluminium sheets (Merck, TLC Silica gel 60 F_{254}). Visualization was achieved using UV light, iodine, and/or chemical staining with vanillin or basic potassium permanganate solutions as appropriate.

Flash column chromatography (FC): Purification of reaction mixture was carried out with flash column chromatography on silica gel 230-400 mesh (Merck, 37-63 µm). Solvents for extraction and chromatography were of technical quality. Eluting solvent mixtures are individually reported in parenthesis.

NMR spectra: Proton, Carbon, and Fluorine nuclear magnetic resonance (^{1}H, ^{13}C, and ^{19}F NMR) spectra were recorded on a Bruker Avance III HD (400, 101, and 377 MHz) spectrometer at 25 ºC. Chemical shifts (δ) are given in ppm and reported as follows: multiplicity (s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), and m (multiplet)), coupling constants (J) in Hz, number of protons; suggested assignment. The residual deuterated solvent was used as internal standard ($CDCl_3$: δ_H = 7.26 ppm; δ_C = 77.16 ppm).

Melting point (Mp): Melting points were measured by Tempstar melting point instrument using open glass capillaries in a Remco-Kolkata apparatus and are reported uncorrected.

High-resolution mass spectrometry (HRMS): HRMS were recorded using Waters XEVO G2-XS QTOF and Agilent Technologies 6530 Accurate-Mass QTOF by ESI technique.

Photoreactions: Photoreactions were carried out in borosilicate made culture tube using blue light source (PAR38 24 W blue LED bulb).

Electrochemical Measurements: Cyclic Voltammetry was performed using CH Instruments (model: Gamry Interface 1010T).

UV-Vis Spectrophotometer: UV-Vis absorption spectra were recorded using Shimadzu UV Spectrophotometer (model: UV-1800).

Luminescence spectrometer: Fluorescence quenching studies were carried out using a PerkinElmer LS 55 Fluorescence Spectrometer.

2. Preparation of Starting Materials:

2.1. Preparation of alkenes:

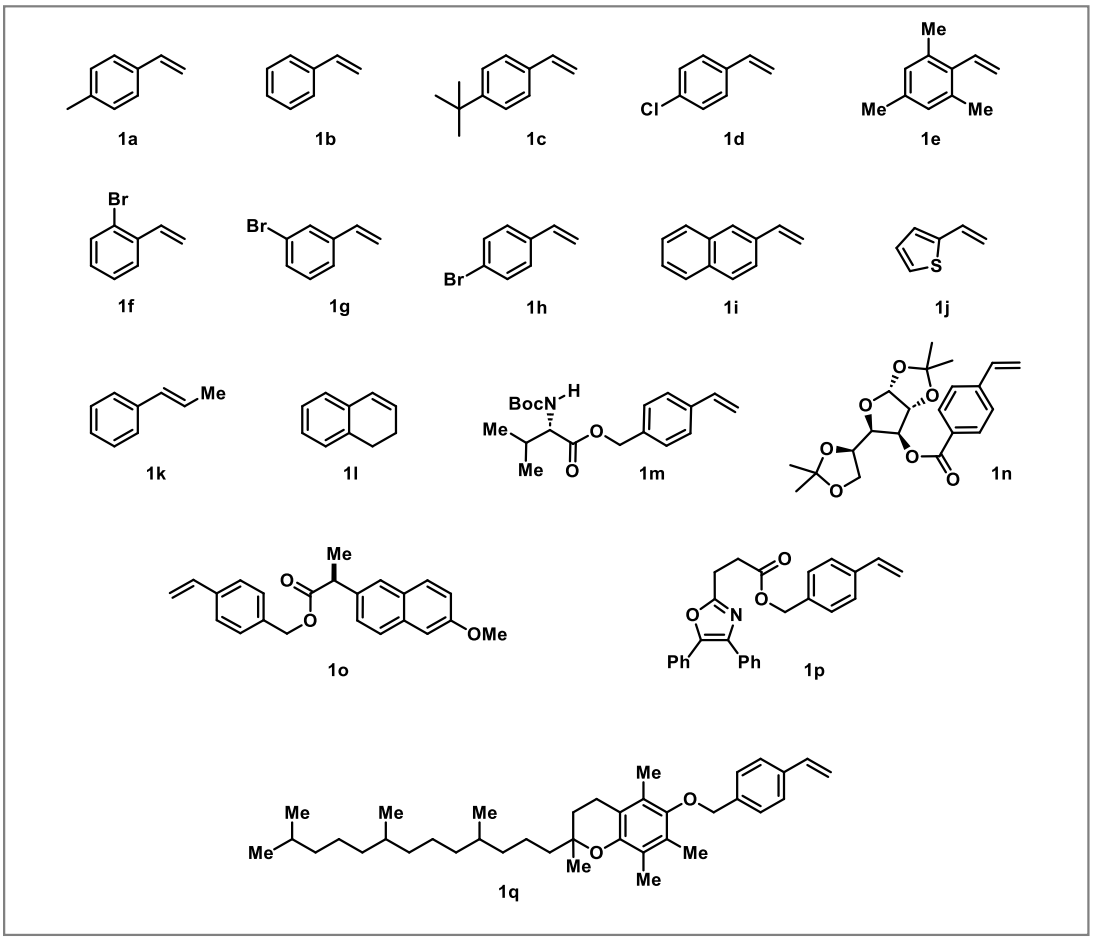


Figure S1: Alkene included in the manuscript.

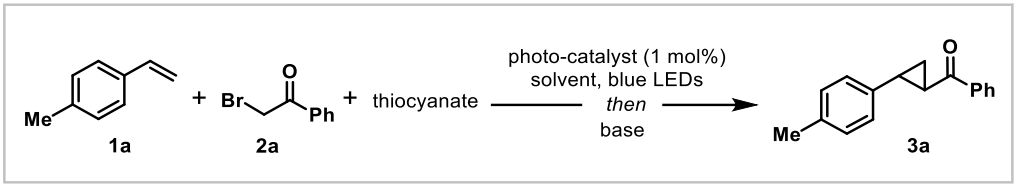
Most of the alkenes were purchased from commercial sources and used as received. 1m-1q were prepared according to the literature procedures, and all the spectroscopic data are in agreement with the literature reports.

3. Reaction Optimization:

General procedure for optimization of reaction conditions:

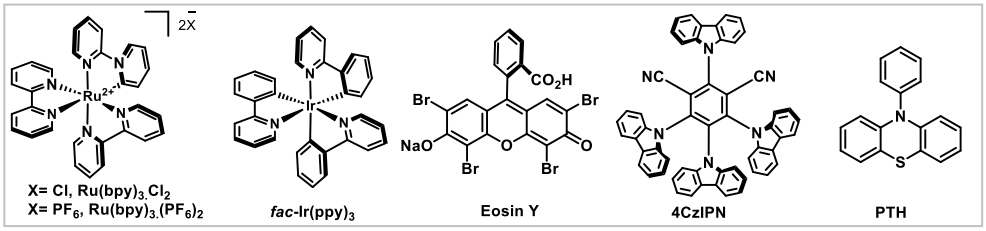
An oven-dried culture tube equipped with a magnetic stir bar was charged with photo-catalyst (1 mol%), phenacyl bromide **2a** (0.2 mmol, 1 equiv.), thiocyanate (0.4 mmol, 2 equiv.) and dry solvent (0.1 M). 4-methylstyrene **1a** (0.4 mmol, 2 equiv.) was added to it, and the tube was sealed with a Teflon screw cap. Then, the reaction mixture was degassed by Freeze-Pump-Thaw cycles with argon and irradiated at rt with 24 W blue LEDs at a distance of approximately 5 cm for a specific time. A high-speed fan was used to maintain the temperature. After completion of Atom Transfer Radical Addition (ATRA) reaction (confirmed by TLC), base was added to the reaction mixture and was stirred for another 2 h. The crude reaction mixture was diluted with water, extracted with ethyl acetate (2×2 mL), washed with brine (3 mL), and dried over anhydrous Na_2SO_4. The organic portion was concentrated, purified by flash column chromatography and the isolated yield was measured.

Table S1: Optimized reaction conditions:[a]



Entry	Catalyst	Solvent	Thiocyanate	Base	3a (%)[b]
1	$Ru(bpy)_3.Cl_2$	MeCN	KSCN	Cs_2CO_3	NR
2	$Ru(bpy)_3.(PF_6)_2$	MeCN	KSCN	Cs_2CO_3	NR
3	*fac*-Ir(ppy)$_3$	MeCN	KSCN	Cs_2CO_3	57
4	Eosin Y	MeCN	KSCN	Cs_2CO_3	NR
5	4CzIPN	MeCN	KSCN	Cs_2CO_3	36
6[c]	PTH	MeCN	KSCN	Cs_2CO_3	51
7	*fac*-Ir(ppy)$_3$	$MeNO_2$	KSCN	Cs_2CO_3	NR
8	*fac*-Ir(ppy)$_3$	Toluene	KSCN	Cs_2CO_3	23
9	*fac*-Ir(ppy)$_3$	DCM	KSCN	Cs_2CO_3	26
10	*fac*-Ir(ppy)$_3$	DMF	KSCN	Cs_2CO_3	13
11	*fac*-Ir(ppy)$_3$	DMSO	KSCN	Cs_2CO_3	NR
12	*fac*-Ir(ppy)$_3$	1,2-DCE	KSCN	Cs_2CO_3	68
13	*fac*-Ir(ppy)$_3$	THF	KSCN	Cs_2CO_3	45
14	*fac*-Ir(ppy)$_3$	$PhCF_3$	KSCN	Cs_2CO_3	trace
15	*fac*-Ir(ppy)$_3$	1,2-DCE	NH_4SCN	Cs_2CO_3	62
16	*fac*-Ir(ppy)$_3$	1,2-DCE	NaSCN	Cs_2CO_3	59
17	*fac*-Ir(ppy)$_3$	1,2-DCE	KSCN	DBU	trace
18	*fac*-Ir(ppy)$_3$	1,2-DCE	KSCN	2,6-lutidine	NR
19	*fac*-Ir(ppy)$_3$	1,2-DCE	KSCN	KOH	35
20	*fac*-Ir(ppy)$_3$	1,2-DCE	KSCN	NaH	42
21[d]	*fac*-Ir(ppy)$_3$	1,2-DCE	KSCN	Cs_2CO_3	72
22[c,d]	PTH	1,2-DCE	KSCN	Cs_2CO_3	61
23	-	1,2-DCE	KSCN	Cs_2CO_3	NR
24[e]	*fac*-Ir(ppy)$_3$	1,2-DCE	KSCN	Cs_2CO_3	NR

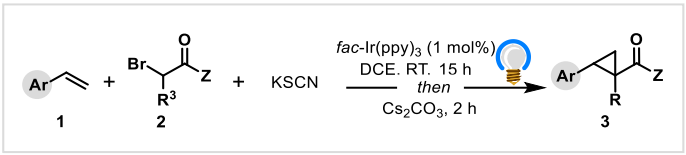
[a]Conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), thiocyanate (0.4 mmol), photo-catalyst (1 mol%), solvent (2 mL), degassed condition, irradiation with 24 W blue LEDs light in rt; [b]isolated yield (%); [c]irradiated with violet LED; [d]KSCN (0.6 mmol); [e] reaction performed in dark.



4. Reaction Generality:

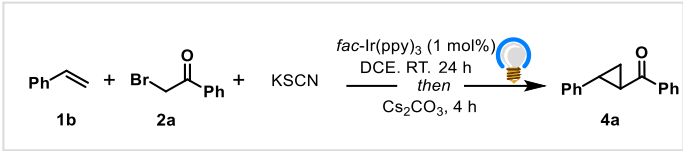
4.1. Synthetic Procedures:

General procedure for photocatalytic cyclopropanation:



An oven-dried culture tube equipped with a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (1 mol%), *α*-bromocarbonyls **2** (0.2 mmol, 1.0 equiv.), KSCN (0.6 mmol, 3.0 equiv.) and dry DCE (0.1 M). olefin **1** (0.4 mmol, 2.0 equiv.) was added to it, and the tube was sealed with a Teflon screw cap. Then, the reaction mixture was degassed by Freeze-Pump-Thaw cycles with argon and irradiated at rt with 24 W blue LEDs at a distance of approximately 5 cm for 15 h. A high-speed fan was used to maintain the temperature. After completion of ATRA reaction (confirmed by TLC), Cs_2CO_3 was added to the reaction mixture and was stirred for another 2 h. The crude reaction mixture was diluted with water, extracted with ethyl acetate (2×2 mL), washed with brine (3 mL), and dried over anhydrous Na_2SO_4. The organic portion was concentrated, purified by flash column chromatography using EtOAc/petroleum ether as eluent to afford the corresponding cyclopropyl ketone **3**.

Scale up reaction of compound 4a:



An oven-dried round bottom flask equipped with a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (1 mol%), *α*-bromocarbonyls **2a** (5.02 mmol, 1 g, 1.0 equiv.), KSCN (15.06 mmol, 1.46 g, 3.0 equiv.) and dry DCE (50 mL, 0.1 M). olefin **1b** (10.04 mmol, 1.15 mL, 2.0 equiv.) was added to it, and the tube was sealed with a rubber septum. Then, the reaction mixture was degassed by Freeze-Pump-Thaw cycles with argon and irradiated at rt with 24 W blue LEDs at a distance of approximately 5 cm for 24 h. A high-speed fan was used to maintain the temperature. After completion of ATRA reaction (confirmed by TLC), Cs_2CO_3 was added to the reaction mixture and was stirred for another 4 h. The crude reaction mixture was diluted with water, extracted with ethyl acetate (30×2 mL), washed with brine (30 mL), and dried over anhydrous Na_2SO_4. The organic portion was concentrated, purified by flash column chromatography using EtOAc/petroleum ether as eluent to afford the corresponding cyclopropyl ketone **4a** in 60% yield (0.68 g).

4.2. Compound characterization data:

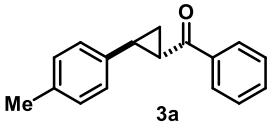
Phenyl(2-(*p*-tolyl)cyclopropyl)methanone (3a):[2]

Yield: 72% (34 mg).

Nature: Pale yellow solid.

Mp: 72-75 ºC

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3a

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.92 – 2.87 (m, 1H), 2.72 – 2.67 (m, 1H), 2.36 (s, 3H), 1.97 – 1.92 (m, 1H), 1.58 – 1.54 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.8, 137.8, 137.5, 136.3, 133.0, 129.3, 128.6, 128.2, 126.2, 30.0, 29.4, 21.1, 19.2.

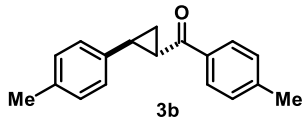
_p_-Tolyl(2-(_p_-tolyl)cyclopropyl)methanone (3b):[3]

Yield: 54% (27 mg).

Nature: Light yellow solid.

Mp: 75-78 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3b

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.87 – 2.83 (m, 1H), 2.68 – 2.63 (m, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 1.92 – 1.87 (m, 1H), 1.54 – 1.49 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.4, 143.8, 137.7, 136.3, 135.3, 129.3, 128.4, 126.3, 29.8, 29.3, 21.8, 21.2, 19.1.

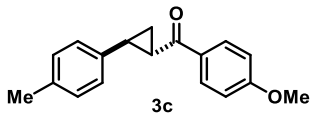
(4-Methoxyphenyl)(2-(_p_-tolyl)cyclopropyl)methanone (3c):[4]

Yield: 49% (26 mg).

Nature: White solid.

Mp: 39-42 ºC

TLC: R_f = 0.2 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3c

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.00 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.86 – 2.81 (m, 1H), 2.68 – 2.63 (m, 1H), 2.35 (s, 3H), 1.92 – 1.87 (m, 1H), 1.53 – 1.48 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.1, 163.5, 137.7, 136.2, 130.8, 130.4, 129.3, 126.2, 113.8, 76.8, 55.5, 29.5, 29.0, 21.1, 18.9.

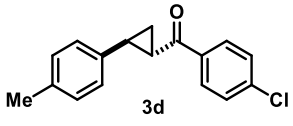
(4-Chlorophenyl)(2-(_p_-tolyl)cyclopropyl)methanone (3d):[3]

Yield: 76% (41 mg).

Nature: Pale yellow solid.

Mp: 51-54 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 4:6 (v/v)], visualized by UV.



3d

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 2.83 – 2.78 (m, 1H), 2.70 – 2.65 (m, 1H), 2.35 (s, 2H), 1.95 – 1.90 (m, 1H), 1.59 – 1.54 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.5, 139.4, 137.3, 136.5, 136.1, 129.6, 129.4, 129.0, 126.2, 30.3, 29.5, 21.2, 19.4.

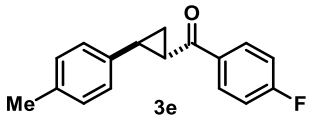
(4-Fluorophenyl)(2-(*p*-tolyl)cyclopropyl)methanone (3e):

Yield: 71% (36 mg).

Nature: White solid.

Mp: 59-52 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3e

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.15 – 7.13 (m, 2H), 7.11 (d, *J* = 6.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.83 – 2.78 (m, 1H), 2.69 – 2.64 (m, 1H), 2.34 (s, 3H), 1.93 – 1.89 (m, 1H), 1.57 – 1.52 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.2, 165.8 (d, *J* = 254.3 Hz), 134.3 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 9.2 Hz), 129.4, 126.2, 115.8 (d, *J* = 21.7 Hz), 30.1, 29.4, 21.2, 19.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm): -105.6.

HRMS (ESI) *m/z* calcd for $C_{17}H_{16}FO$ $[M+H]^+$: 255.1185; found: 255.1191.

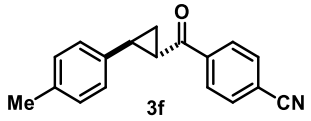
4-(2-(*p*-Tolyl)cyclopropane-1-carbonyl)benzonitrile (3f):

Yield: 65% (34 mg).

Nature: Light yellow solid.

Mp: 80-83 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3f

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.05 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.83 – 2.79 (m, 1H), 2.73 – 2.68 (m, 1H), 2.34 (s, 3H), 1.99 – 1.94 (m, 1H), 1.65 – 1.61 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.5, 140.9, 136.8, 136.8, 132.6, 129.5, 128.6, 126.2, 118.1, 116.2, 31.1, 30.0, 21.2, 19.8.

HRMS (ESI) *m/z* calcd for $C_{18}H_{16}NO$ $[M+H]^+$: 262.1232; found: 262.1239.

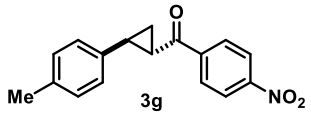
(4-Nitrophenyl)(2-(*p*-tolyl)cyclopropyl)methanone (3g):

Yield: 62% (35 mg).

Nature: Pale yellow solid.

Mp: 84-87 ºC

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3g

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 7.13 (s, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.86 – 2.82 (m, 1H), 2.76 – 2.71 (m, 1H), 2.35 (s, 3H), 2.01 – 1.96 (m, 1H), 1.68 – 1.64 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.3, 150.2, 142.3, 136.8, 136.7, 129.5, 129.2, 126.2, 123.9, 31.3, 30.2, 21.2, 20.0.

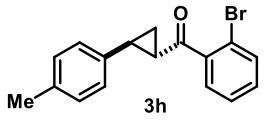
HRMS (ESI) *m/z* calcd for $C_{17}H_{16}NO_3$ $[M+H]^+$: 282.1130; found: 282.1135.

(2-Bromophenyl)(2-(*p*-tolyl)cyclopropyl)methanone (3h):

Yield: 73% (46 mg).

Nature: Colourless liquid.

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3h

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 (td, *J* = 7.7, 1.8 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.82 – 2.77 (m, 1H), 2.71 – 2.66 (m, 1H), 2.34 (s, 3H), 2.00 – 1.96 (m, 1H), 1.63 – 1.58 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 202.3, 142.2, 137.0, 136.4, 133.6, 131.7, 129.3, 129.1, 127.5, 126.2, 119.3, 33.6, 31.7, 21.1, 20.7.

HRMS (ESI) *m/z* calcd for $C_{17}H_{16}BrO$ $[M+2+H]^+$: 317.0364; found: 317.0384.

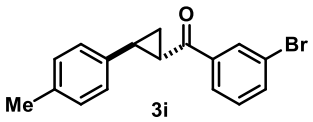
(3-Bromophenyl)(2-(*p*-tolyl)cyclopropyl)methanone (3i):

Yield: 68% (43 mg).

Nature: White solid.

Mp: 62-65 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3i

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (t, *J* = 1.8 Hz, 1H), 7.92 – 7.89 (m, 1H), 7.69 – 7.67 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.82 – 2.77 (m, 1H), 2.72 – 2.67 (m, 1H), 2.34 (s, 3H), 1.94 – 1.89 (m, 1H), 1.60 – 1.56 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.5, 139.6, 137.1, 136.6, 135.8, 131.2, 130.3, 129.4, 126.8, 126.3, 123.0, 30.5, 29.5, 21.2, 19.7.

HRMS (ESI) *m/z* calcd for $C_{17}H_{16}BrO$ $[M+H]^+$: 315.0385; found: 315.0380.

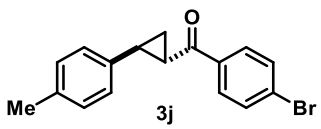
(4-Bromophenyl)(2-(*p*-tolyl)cyclopropyl)methanone (3j):

Yield: 65% (41 mg).

Nature: White solid.

Mp: 73-76 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3j

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.81 – 2.77 (m, 1H), 2.69 – 2.64 (m, 1H), 2.34 (s, 3H), 1.94 – 1.89 (m, 1H), 1.58 – 1.53 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 197.7, 137.3, 136.5, 132.0, 129.8, 129.4, 128.2, 126.2, 30.4, 29.5, 21.2, 19.4.

HRMS (ESI) *m/z* calcd for $C_{17}H_{16}BrO$ $[M+H]^+$: 315.0385; found: 315.0379.

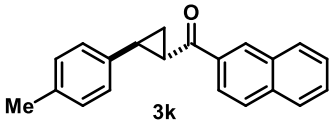
Naphthalen-2-yl(2-(*p*-tolyl)cyclopropyl)methanone (3k):

Yield: 63% (36 mg).

Nature: White solid.

Mp: 116-119 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:1 (v/v)], visualized by UV.



3k

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.89 (t, *J* = 8.4 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.05 – 3.01 (m, 1H), 2.78 – 2.73 (m, 1H), 2.36 (s, 3H), 1.99 – 1.95 (m, 1H), 1.63 – 1.58 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 198.7, 137.6, 136.4, 135.6, 135.2, 132.6, 129.9, 129.7, 129.4, 128.5, 128.5, 127.9, 126.9, 126.3, 124.1, 30.1, 29.5, 21.2, 19.4.

HRMS (ESI) *m/z* calcd for $C_{21}H_{19}O$ $[M+H]^+$: 287.1436; found: 287.1463.

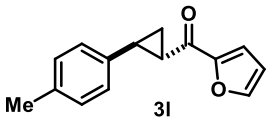
Furan-2-yl(2-(*p*-tolyl)cyclopropyl)methanone (3l):

Yield: 58% (26 mg).

Nature: White solid.

Mp: 61-64 ºC

TLC: R_f = 0.3 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3l

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, *J* = 1.1 Hz, 1H), 7.22 (d, *J* = 3.3 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.54 (dd, *J* = 3.5, 1.8 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.72 – 2.67 (m, 1H), 2.33 (s, 3H), 1.89 – 1.85 (m, 1H), 1.53 – 1.48 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 187.5, 153.3, 146.5, 137.4, 136.4, 129.3, 126.3, 116.9, 112.4, 29.5, 29.2, 21.1, 19.1.

HRMS (ESI) *m/z* calcd for $C_{15}H_{15}O_2$ $[M+H]^+$: 227.1072; found: 227.1075.

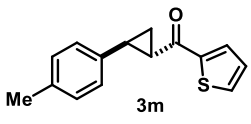
Thiophen-2-yl(2-(*p*-tolyl)cyclopropyl)methanone (3m):

Yield: 62% (30 mg).

Nature: Pale yellow solid.

Mp: 70-73 ºC

TLC: R_f = 0.2 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3m

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.79 (dd, *J* = 3.8, 0.9 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.14 – 7.11 (m, 3H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.74 – 2.68 (m, 2H), 2.33 (s, 3H), 1.91 – 1.86 (m, 1H), 1.55 – 1.50 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 191.2, 145.0, 137.4, 136.4, 133.7, 131.9, 129.4, 128.3, 126.4, 30.1, 29.5, 21.2, 19.1.

HRMS (ESI) *m/z* calcd for $C_{15}H_{15}OS$ $[M+H]^+$: 243.0844; found: 243.0846.

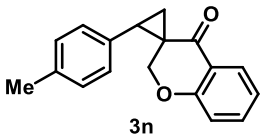
2'-(*p*-Tolyl)spiro[chromane-3,1'-cyclopropan]-4-one (3n):

Yield: 61% (32 mg).

Nature: White solid.

Mp: 55-58 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3n

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.15 (s, 4H), 7.08 – 7.04 (m, 1H), 6.95 (dd, *J* = 8.3, 0.7 Hz, 1H), 4.34 (d, *J* = 12.0 Hz, 1H), 3.95 (d, *J* = 12.0 Hz, 1H), 3.01 (dd, *J* = 8.5, 7.5 Hz, 1H), 2.35 (s, 3H), 2.03 (dd, *J* = 8.9, 4.8 Hz, 1H), 1.40 (dd, *J* = 7.1, 4.8 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 192.7, 161.9, 137.1, 135.8, 132.5, 129.3, 129.2, 127.1, 121.8, 121.5, 118.2, 69.1, 34.0, 32.8, 21.2, 17.0.

HRMS (ESI) *m/z* calcd for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1229; found: 265.1219.

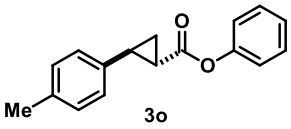
Phenyl 2-(*p*-tolyl)cyclopropane-1-carboxylate (3o):

Yield: 64% (32 mg).

Nature: White solid.

Mp: 76 - 79 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:9 (v/v)], visualized by UV.



3o

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 – 7.36 (m, 2H), 7.25 – 7.21 (m, 1H), 7.14 – 7.11 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 2.69 – 2.64 (m, 1H), 2.34 (s, 3H), 2.13 – 2.09 (m, 1H), 1.76 – 1.71 (m, 1H), 1.48 – 1.43 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 172.3, 150.9, 136.7, 136.5, 129.5, 129.4, 126.3, 125.9, 121.7, 27.0, 24.2, 21.2, 17.8.

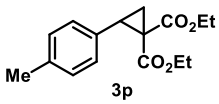
HRMS (ESI) *m/z* calcd for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1229; found: 253.1230.

Diethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate (3p):[5]

Yield: 74% (41 mg).

Nature: Colourless liquid.

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



3p

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.10 – 7.05 (m, 4H), 4.28 – 4.18 (m, 2H), 3.89 – 3.81 (m, 2H), 3.18 (t, *J* = 8.6 Hz, 1H), 2.29 (s, 3H), 2.14 (dd, *J* = 8.0, 5.1 Hz, 1H), 1.68 (dd, *J* = 9.2, 5.1 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 170.1, 166.9, 137.1, 131.6, 128.9, 128.5, 61.8, 61.2, 37.5, 32.1, 21.2, 18.9, 14.2, 13.8.

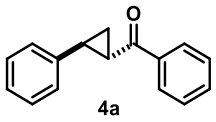
Phenyl(2-phenylcyclopropyl)methanone (4a):[2]

Yield: 65% (29 mg).

Nature: white solid.

Mp: 37-40 ºC

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4a

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.21 – 7.19 (m, 2H), 2.95 – 2.91 (m, 1H), 2.76 – 2.71 (m, 1H), 1.98 – 1.93 (m, 1H), 1.60 – 1.55 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.6, 140.6, 137.8, 133.0, 128.7, 128.2, 126.7, 126.3, 76.8, 30.1, 29.4, 19.3.

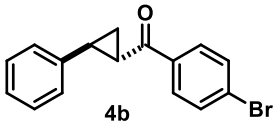
(4-Bromophenyl)(2-phenylcyclopropyl)methanone (4b):[6]

Yield: 71% (43 mg).

Nature: White solid.

Mp: 53-56 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4b

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.19 – 7.16 (m, 2H), 2.85 – 2.81 (m, 1H), 2.73 – 2.68 (m, 1H), 1.95 – 1.91 (m, 1H), 1.61 – 1.56 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.7, 140.3, 136.5, 132.0, 129.8, 128.7, 128.2, 126.9, 126.3, 30.4, 29.4, 19.6.

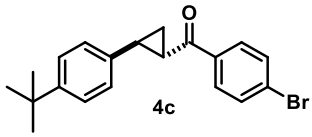
(4-Bromophenyl)(2-(4-(*tert*-butyl)phenyl)cyclopropyl)methanone (4c):

Yield: 49% (35 mg).

Nature: White solid.

Mp: 49-52 ºC

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4c

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 2.85 – 2.80 (m, 1H), 2.71 – 2.66 (m, 1H), 1.94 – 1.89 (m, 1H), 1.60 – 1.55 (m, 1H), 1.32 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.8, 149.9, 137.3, 136.6, 132.0, 129.8, 128.2, 126.0, 125.6, 34.6, 31.5, 30.3, 29.4, 19.6.

HRMS (ESI) *m/z* calcd for $C_{20}H_{22}BrO$ $[M+H]^+$: 357.0854; found: 357.0839.

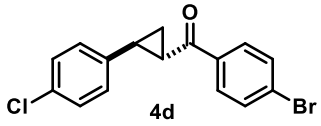
(4-Bromophenyl)(2-(4-chlorophenyl)cyclopropyl)methanone (4d):

Yield: 63% (42 mg).

Nature: White solid.

Mp: 65-68 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4d

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.81 – 2.76 (m, 1H), 2.69 – 2.64 (m, 1H), 1.94 – 1.89 (m, 1H), 1.56 – 1.52 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.3, 138.9, 136.4, 132.6, 132.1, 129.8, 128.9, 128.4, 127.7, 29.6, 29.3, 19.5.

HRMS (ESI) *m/z* calcd for $C_{16}H_{13}BrClO$ $[M+H]^+$: 334.9838; found: 334.9822.

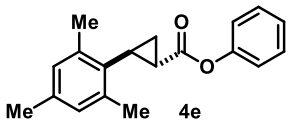
Phenyl 2-mesitylcyclopropane-1-carboxylate (4e):

Yield: 61% (34 mg).

Nature: White solid.

Mp: 40-43 ºC

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.43 (dd, *J* = 10.9, 4.8 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 0.8 Hz, 2H), 6.90 (s, 2H), 2.52 – 2.49 (m, 1H), 2.45 (s, 6H), 2.30 (s, 3H), 2.01 – 1.96 (m, 1H), 1.89 – 1.84 (m, 1H), 1.37 – 1.32 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 173.1, 150.9, 138.4, 136.7, 132.8, 129.5, 129.1, 125.9, 121.7, 24.4, 23.3, 20.9, 20.6, 18.4.

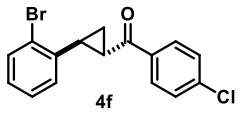
HRMS (ESI) *m/z* calcd for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1542; found: 281.1545.

(2-(2-Bromophenyl)cyclopropyl)(4-chlorophenyl)methanone (4f):

Yield: 72% (48 mg).

Nature: Colourless liquid.

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, *J* = 8.7 Hz, 2H), 7.57 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.16 – 7.11 (m, 2H), 2.90 – 2.85 (m, 1H), 2.72 – 2.68 (m, 1H), 1.94 – 1.89 (m, 1H), 1.65 – 1.61 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.6, 139.5, 139.4, 136.0, 132.8, 129.8, 129.0, 128.6, 128.0, 127.6, 126.7, 31.4, 27.7, 18.1.

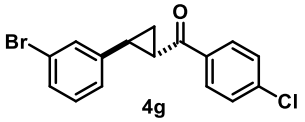
HRMS (ESI) *m/z* calcd for $C_{16}H_{13}BrClO$ $[M+H]^+$: 334.9838; found: 334.9833.

(2-(3-Bromophenyl)cyclopropyl)(4-chlorophenyl)methanone (4g):

Yield: 66% (44 mg).

Nature: Colourless liquid.

TLC: R_f = 0.6 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.28 (t, *J* = 1.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.10 (m, 1H), 2.85 – 2.80 (m, 1H), 2.69 – 2.64 (m, 1H), 1.93 – 1.89 (m, 1H), 1.57 – 1.53 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.0, 142.8, 139.7, 135.9, 130.3, 129.9, 129.7, 129.2, 129.1, 125.3, 122.9, 29.5, 29.3, 19.5.

HRMS (ESI) *m/z* calcd for $C_{16}H_{13}BrClO$ $[M+H]^+$: 334.9838; found: 334.9825.

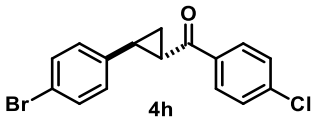
(2-(4-Bromophenyl)cyclopropyl)(4-chlorophenyl)methanone (4h):[7]

Yield: 60% (40 mg).

Nature: Light yellow solid.

Mp: 54-57 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4h

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 3.8 Hz, 2H), 7.42 (d, *J* = 3.6 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 2.82 – 2.77 (m, 1H), 2.68 – 2.63 (m, 1H), 1.94 – 1.89 (m, 1H), 1.56 – 1.51 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.1, 139.6, 139.4, 135.9, 131.8, 129.6, 129.0, 128.0, 120.5, 29.5, 29.3, 19.4.

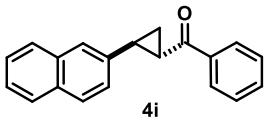
(2-(Naphthalen-2-yl)cyclopropyl)(phenyl)methanone (4i):[2]

Yield: 66% (36 mg).

Nature: White solid.

Mp: 76-79 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4i

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 (d, *J* = 7.2 Hz, 2H), 7.84 – 7.79 (m, 3H), 7.65 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.30 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.03 – 2.99 (m, 1H), 2.90 – 2.85 (m, 1H), 2.06 – 2.01 (m, 1H), 1.74 – 1.69 (m, 1H).

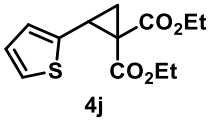
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.6, 138.0, 137.8, 133.5, 133.1, 132.5, 128.7, 128.4, 128.2, 127.8, 127.6, 126.5, 125.7, 124.8, 124.7, 30.4, 29.6, 19.2.

Diethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (4j):[5]

Yield: 71% (38 mg).

Nature: Colourless liquid.

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4j

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.02 (dd, *J* = 1.9, 1.0 Hz, 1H), 6.95 (dd, *J* = 5.0, 0.9 Hz, 1H), 4.28 – 4.17 (m, 2H), 3.91 (q, *J* = 7.1 Hz, 2H), 3.13 (t, *J* = 8.5 Hz, 1H), 2.05 (dd, *J* = 7.8, 5.0 Hz, 1H), 1.72 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 69.9, 166.9, 136.1, 128.2, 125.5, 122.6, 61.9, 61.4, 37.4, 27.6, 20.1, 14.2, 13.8.

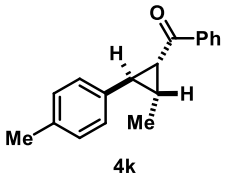
(2-Methyl-3-(*p*-tolyl)cyclopropyl)(phenyl)methanone (4k):

Yield: 58% (29 mg).

Nature: white solid.

Mp: 87-89 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4k

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (d, *J* = 7.1 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.53 – 7.49 (m, 2H), 7.18 – 7.13 (m, 4H), 3.01 (dd, *J* = 9.5, 4.8 Hz, 1H), 2.85 (t, *J* = 4.7 Hz, 1H), 2.35 (s, 3H), 2.10 – 2.02 (m, 1H), 1.06 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 199.6, 138.2, 136.2, 133.9, 132.9, 129.1, 129.0, 128.7, 128.1, 35.3, 32.0, 27.0, 21.2, 13.1.

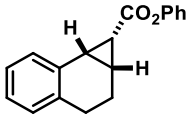
HRMS (ESI) *m/z* calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1436; found: 251.1429.

Phenyl 1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene-1-carboxylate (4l):

Yield: 59% (31 mg).

Nature: Colourless liquid.

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



4l

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40 – 7.34 (m, 3H), 7.25 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 7.14 – 7.11 (m, 2H), 7.07 (d, *J* = 6.9 Hz, 1H), 2.74 – 2.69 (m, 2H), 2.58 – 2.49 (m, 1H), 2.35 – 2.27 (m, 3H), 1.92 – 1.83 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 171.9, 151.0, 134.8, 133.9, 129.5, 129.1, 128.9, 126.5, 126.4, 125.9, 121.7, 27.4, 25.5, 25.3, 23.2, 18.8.

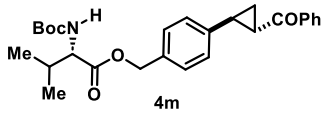
HRMS (ESI) *m/z* calcd for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1229; found: 265.1233.

4-(2-Benzoylcyclopropyl)benzyl (*tert*-butoxycarbonyl)-*L*-valinate (4m):

Yield: 40% (36 mg).

Nature: Colourless liquid.

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:9 (v/v)], visualized by UV.



4m

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, *J* = 7.1 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 5.14 (q, *J* = 12.3 Hz, 2H), 5.02 (d, *J* = 9.1 Hz, 1H), 4.28 – 4.24 (m, 1H), 2.92 – 2.88 (m, 1H), 2.72 – 2.67 (m, 1H), 2.15 (dd, *J* = 11.9, 6.7 Hz, 1H), 1.95 – 1.91 (m, 1H), 1.58 – 1.53 (m, 1H), 1.44 (s, 9H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.5, 172.5, 141.0, 137.7, 133.9, 133.1, 128.9, 128.7, 128.2, 126.5, 79.9, 66.7, 58.67, 31.4, 29.8, 29.5, 28.4, 19.4, 19.2, 17.6.

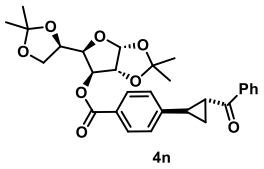
HRMS (ESI) *m/z* calcd for $C_{27}H_{33}NO_5Na$ $[M+Na]^+$: 474.2256; found: 474.2259.

(3a*R*,5*R*,6*R*,6a*R*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-(2-benzoylcyclopropyl)benzoate (4n):

Yield: 46% (47 mg).

Nature: Gummy solid.

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 3:17 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.97 (t, *J* = 8.3 Hz, 4H), 7.60 – 7.56 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.95 (d, *J* = 3.7 Hz, 1H), 5.49 (d, *J* = 2.6 Hz, 1H), 4.63 (d, *J* = 3.7 Hz, 1H), 4.34 (d, *J* = 4.6 Hz, 2H), 4.10 (d, *J* = 4.7 Hz, 2H), 2.98 – 2.93 (m, 1H), 2.77 – 2.72 (m, 1H), 2.01 – 1.96 (m, 1H), 1.63 – 1.59 (m, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.27 (d, *J* = 2.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.0, 165.1, 146.9, 137.6, 133.3, 130.2, 128.8, 128.3, 126.4, 126.3, 112.5, 109.5, 105.3, 83.6, 80.1, 72.8, 67.4, 58.6, 29.8, 29.6, 27.0, 26.9, 26.4, 25.4, 19.8, 19.8, 18.6.

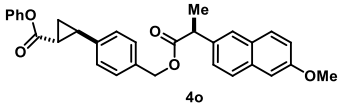
HRMS (ESI) *m/z* calcd for $C_{29}H_{32}O_8Na$ $[M+Na]^+$: 531.1995; found: 531.1997.

Phenyl 2-(4-((((*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)methyl)phenyl)cyclopropane-1-carboxylate (4o):

Yield: 42% (40 mg).

Nature: White solid.

Mp: 122-125 ºC



TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 (t, *J* = 8.8 Hz, 2H), 7.64 (s, 1H), 7.42 – 7.36 (m, 3H), 7.26 – 7.21 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.11 (m, 4H), 7.07 (d, *J* = 8.2 Hz, 2H), 5.10 (q, *J* = 12.4 Hz, 2H), 3.93 – 3.88 (m, 1H), 3.92 (s, 3H), 2.69 – 2.64 (m, 1H), 2.13 – 2.09 (m, 1H), 1.77 – 1.73 (m, 1H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.46 – 1.41 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 174.6, 172.0, 157.8, 150.9, 139.8, 135.6, 134.7, 133.8, 129.5, 129.4, 129.1, 128.5, 127.3, 126.5, 126.4, 126.1, 125.9, 121.7, 119.1, 105.7, 66.3, 55.4, 45.6, 26.9, 24.3, 18.6, 17.9.

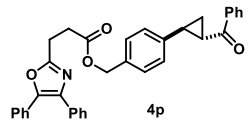
HRMS (ESI) *m/z* calcd for $C_{31}H_{29}O_5$ $[M+NH_4]^+$: 498.2280; found: 498.2285.

4-(2-Benzoylcyclopropyl)benzyl 3-(4,5-diphenyloxazol-2-yl)propanoate (4p):

Yield: 33% (35 mg).

Nature: Colourless liquid.

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:9 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.53 (m, 5H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.27 (m, 8H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.15 (s, 2H), 3.20 (t, *J* = 7.4 Hz, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.87 – 2.83 (m, 1H), 2.68 – 2.64 (m, 1H), 1.93 – 1.89 (m, 1H), 1.53 – 1.48 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.6, 172.0, 161.8, 145.5, 140.8, 137.7, 135.2, 134.3, 133.1, 132.6, 129.1, 128.8, 128.7, 128.7, 128.6, 128.2, 128.2, 128.0, 126.6, 126.5, 66.4, 31.3, 29.8, 29.5, 23.6, 19.4.

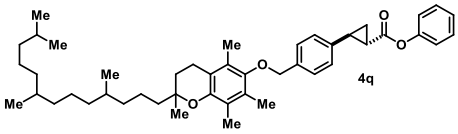
HRMS (ESI) *m/z* calcd for $C_{35}H_{30}NO_4$ $[M+H]^+$: 528.2175; found: 528.2172.

Phenyl 2-(4-(((2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)cyclopropane-1-carboxylate (4q):

Yield: 28% (38 mg).

Nature: Colourless liquid

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:9 (v/v)], visualized by UV.



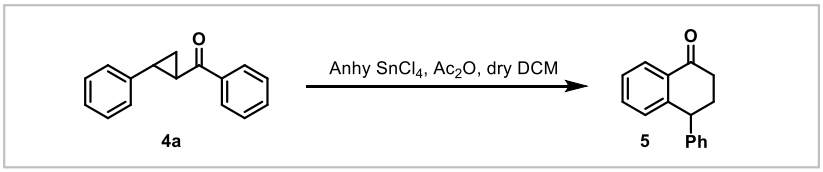
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.23 (dd, *J* = 16.7, 7.1 Hz, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 4.69 (s, 2H), 2.76 – 2.71 (m, 1H), 2.61 (t, *J* = 6.7 Hz, 2H), 2.23 (s, 3H), 2.20 – 2.15 (m, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 1.86 – 1.76 (m, 3H), 1.57 – 1.48 (m, 4H), 1.46 – 1.37 (m, 4H), 1.31 – 1.22 (m, 11H), 1.18 – 1.07 (m, 6H), 0.89 – 0.85 (m, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 172.1, 150.9, 148.2, 148.1, 139.4, 136.8, 129.5, 128.1, 128.0, 126.5, 126.1, 125.9, 123.1, 121.7, 117.7, 77.4, 75.0, 74.5, 40.2, 40.1, 39.5, 37.72, 37.71, 37.63, 37.60, 37.55, 37.53, 37.48, 37.4, 32.93, 32.92, 32.84, 32.82, 31.44, 31.39, 28.1, 27.0, 24.9, 24.6, 24.3, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 19.8, 19.7, 17.9, 13.0, 12.1, 12.0.

HRMS (ESI) *m/z* calcd for $C_{46}H_{65}O_4$ $[M+H]^+$: 681.4883; found: 681.4881.

5. Synthetic Transformations of cyclopropyl ketone products:

5.1. Reaction procedure for synthesis of tetralone derivative:



In an oven-dried culture tube acyl cyclopropane **4a** (0.2 mmol, 1.0 equiv.) was taken and was dissolved in dry DCM. Acetic anhydride (0.2 mmol, 1.0 equiv.) and anhydrous $SnCl_4$ (0.2 mmol, 1.0 equiv.) were added under inert atmosphere. Resultant reaction mixture was stirred at room temperature for 3 h. After completion (checked by TLC), it was poured into 5% NaOH and extracted with dichloromethane. The organic layer was washed with water and dried over Na_2SO_4 and concentrated under vacuum. The crude reaction mixture further purified with flash column chromatography to yield **5**.

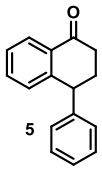
4-Phenyl-3,4-dihydronaphthalen-1(2*H*)-one (5):[8]

Yield: 73% (32 mg).

Nature: Light yellow solid.

Mp: 49-52 ºC

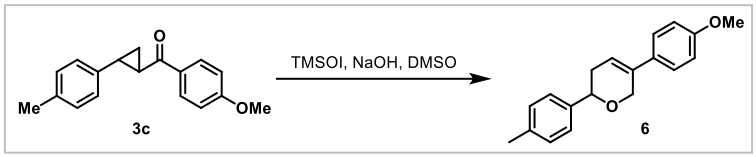
TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:9 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 1.6 Hz, 1H), 7.38 – 7.35 (dt, *J* = 3.2, 1.2 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.12 (d, *J* = 6.9 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 4.31 (dd, *J* = 8.0, 4.6 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.67 – 2.59 (m, 1H), 2.52 – 2.44 (m, 1H), 2.35 – 2.27 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 198.2, 146.4, 143.8, 133.7, 132.9, 129.6, 128.7, 128.7, 127.2, 127.1, 126.9, 45.4, 36.8, 31.9.

5.2. Reaction procedure for synthesis of dihydro pyran derivative:



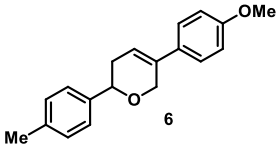
An oven-dried culture tube equipped with magnetic stir bar, NaOH (0.6 mmol, 3.0 equiv.) was taken. Trimethylsulphoxonium iodide (0.6 mmol, 3.0 equiv.) and dry DMSO (1 mL) were added under inert atmosphere. Another solution of **3c** (0.2 mmol, 1.0 equiv.) in anhydrous DMSO (1 mL) was added to the previous solution. The reaction mixture then stirred for 1 h. After completion (monitored by TLC), the reaction mixture was quenched with saturated ammonium chloride solution and was extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated with rotary evaporator. Resulting crude was then purified by flash column chromatography to yield pyran derivative.

5-(4-Methoxyphenyl)-2-(*p*-tolyl)-3,6-dihydro-2*H*-pyran (6):

Yield: 72% (40 mg).

Nature: Gummy solid.

TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.17 (dd, *J* = 5.4, 2.1 Hz, 1H), 4.75 – 4.71 (m, 1H), 4.68 – 4.62 (m, 1H), 4.58 (dd, *J* = 10.0, 3.9 Hz, 1H), 3.82 (s, 3H), 2.58 – 2.48 (m, 1H), 2.46 – 2.39 (m, 1H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.2, 139.4, 137.4, 135.6, 130.9, 129.2, 126.1, 126.0, 120.0, 114.1, 75.7, 68.1, 55.4, 33.2, 21.3.

HRMS (ESI) *m/z* calcd for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1542; found: 281.1538.

5.3. Reaction procedure for synthesis of tetrahydrofuran derivative (7):

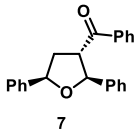
To a stirred solution of 4a (0.2 mmol) in anhydrous DCM was added $BF_3.Et_2O$ (2.0 eq.) and benzaldehyde (3.0 eq). The reaction mixture was the stirred at 0 ºC for 30 min and then at room temperrature for 6 h. The reaction mixture then quenched with water and extracted with EtOAc (10 mL × 2). The organic layer then washed with brine and dried over anhydrous Na_2SO_4. Obtained solvent was concentrated in vacuo and purified by flash column chromatography.

(2,5-Diphenyltetrahydrofuran-3-yl)(phenyl)methanone (7):[9]

Yield: 81% (53 mg).

Nature: Colourless liquid.

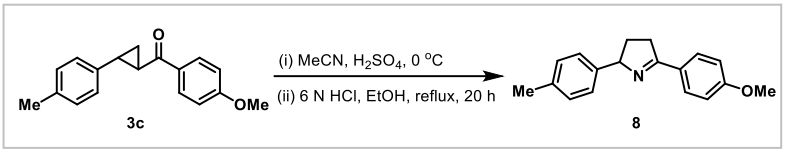
TLC: R_f = 0.4 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.84 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.57 – 7.52 (m, 3H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.38 – 7.28 (m, 4H), 5.47 (d, *J* = 7.2 Hz, 1H), 5.23 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.12 – 4.06 (m, 1H), 2.74 – 2.68 (m, 1H), 2.47 – 2.40 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 200.1, 141.7, 141.3, 136.5, 133.5, 128.7, 128.7, 128.6, 128.6, 128.0, 127.8, 126.4, 126.1, 83.4, 80.8, 55.0, 40.5.

5.4. Reaction procedure for synthesis of Pyrrole derivative:



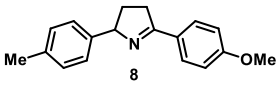
To a stirred solution of conc. H_2SO_4 (0.8 mmol, 4.0 equiv.) was slowly added acetonitrile (1 ml) at 0 ºC and was continuously stirred for 30 minutes. To the above mixture a solution of acyl cyclopropane **3c** (0.2 mmol) in acetonitrile (1 ml) was then slowly added left stirring for 6 h. After completion, the reaction mixture was neutralized with saturated solution of $NaHCO_3$ and extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The obtained crude reaction mixture then dissolved in 1 mL EtOH and 6(N) HCl (0.5 mL) was added sequentially and reflux for 20 h. After completion (monitored by TLC), the reaction mixture was neutralized with NaOH solution and extracted with EtOAc (3×5 mL). The solvent was then evaporated using rotary evaporator and was purified by flash column chromatography to yield **8**.

5-(4-Methoxyphenyl)-2-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole (8):

Yield: 70% (37 mg).

Nature: Brown solid.

Mp: 154-157 ºC



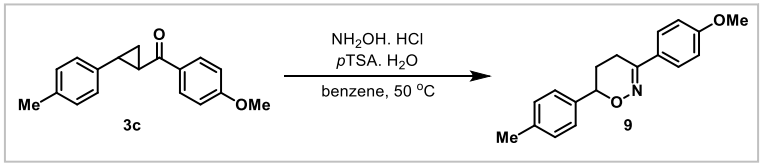
TLC: R_f = 0.3 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.25 (t, *J* = 7.6 Hz, 1H), 3.86 (s, 3H), 3.17 – 3.09 (m, 1H), 3.01 – 2.92 (m, 1H), 2.60 – 2.51 (m, 1H), 2.33 (s, 3H), 1.92 – 1.83 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 172.8, 142.0, 136.4, 129.6, 129.2, 127.6, 126.6, 113.9, 75.8, 55.5, 35.6, 32.7, 21.2.

HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1545; found: 266.1543.

5.5. Reaction procedure for synthesis of oxazine derivative:



Compound **3c** (53 mg, 0.2 mmol), hydroxylamine hydrochloride (0.4 mmol) and 2ml benzene was added sequentially to an oven dried culture tube and reaction mixture was stirred open to air at room temperature for 1 h followed by addition of *p*-toluene sulphonic acid monohydrate (*p*TSA.H_2O, 0.04 mmol). The reaction mixture was then stirred at about 50 ºC for 16 h. After completion (as monitored by TLC), the solvent was extracted by rotary evaporator and purified by column chromatography on silica gel to yield **9**.

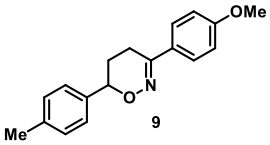
3-(4-Methoxyphenyl)-6-(*p*-tolyl)-5,6-dihydro-4*H*-1,2-oxazine (9):

Yield: 43% (24 mg).

Nature: Brown solid.

Mp: 72-75 ºC

TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:19 (v/v)], visualized by UV.



9

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 9.0 Hz, 2H), 7.27 (t, *J* = 4.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.79 (t, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 3.06 (t, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 2.21 – 2.15 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 199.4, 163.6, 141.6, 137.3, 130.5, 130.0, 129.3, 125.9, 113.8, 73.7, 55.6, 34.6, 33.3, 21.2.

HRMS (ESI) *m/z* calcd for $C_{17}H_{17}BrN$ $[M+H]^+$: 282.1494; found: 282.1492.

6. Mechanistic studies:

6.1. Radical inhibition experiment:

Radical pathway of the reaction mechanism was explored by performing radical trapping experiment with TEMPO (3 equiv.) free radical in the reaction mixture of 4-methyl styrene **1a** (3 equiv.), phenacyl bromide **2a** (1 equiv.) and potassium thiocyanate (3 equiv.) under the standard reaction condition. Astoundingly, instead of getting desired ATRA intermediate **3a'**, TEMPO adducts **10** and **11** was obtained, which was confirmed by HRMS analysis from crude reaction mixture. This radical quenching study confirms that the mechanism involves the photo-induced generation of phenacyl radical which coupled with TEMPO to give corresponding adduct **10** and another benzylic radical adduct **11** as the reaction intermediate.

Reaction procedure: An oven-dried culture tube equipped with a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (1 mol%), phenacyl bromide **2a** (0.2 mmol, 1.0 equiv.), KSCN (0.6 mmol, 3 equiv.) and dry 1,2-DCE (0.1 M). 4-methylstyrene **1a** (0.4 mmol, 2.0 equiv.) and TEMPO free radical (0.6 mmol, 3.0 equiv.) was added to it, and the tube was sealed with a Teflon screw cap. Then the reaction mixture was degassed by Freeze-Pump-Thaw cycles with argon and irradiated at rt with 24 W blue LEDs at a distance of approximately 5 cm for 15 h. A high-speed fan was used to maintain the temperature. After 15 h it was observed that generation of ATRA intermediate was completely ceased and a trace amount of TEMPO adducts **10** and **11** were detected in HRMS analysis from the crude reaction mixture. These results suggested that the reaction passes through radical pathway.

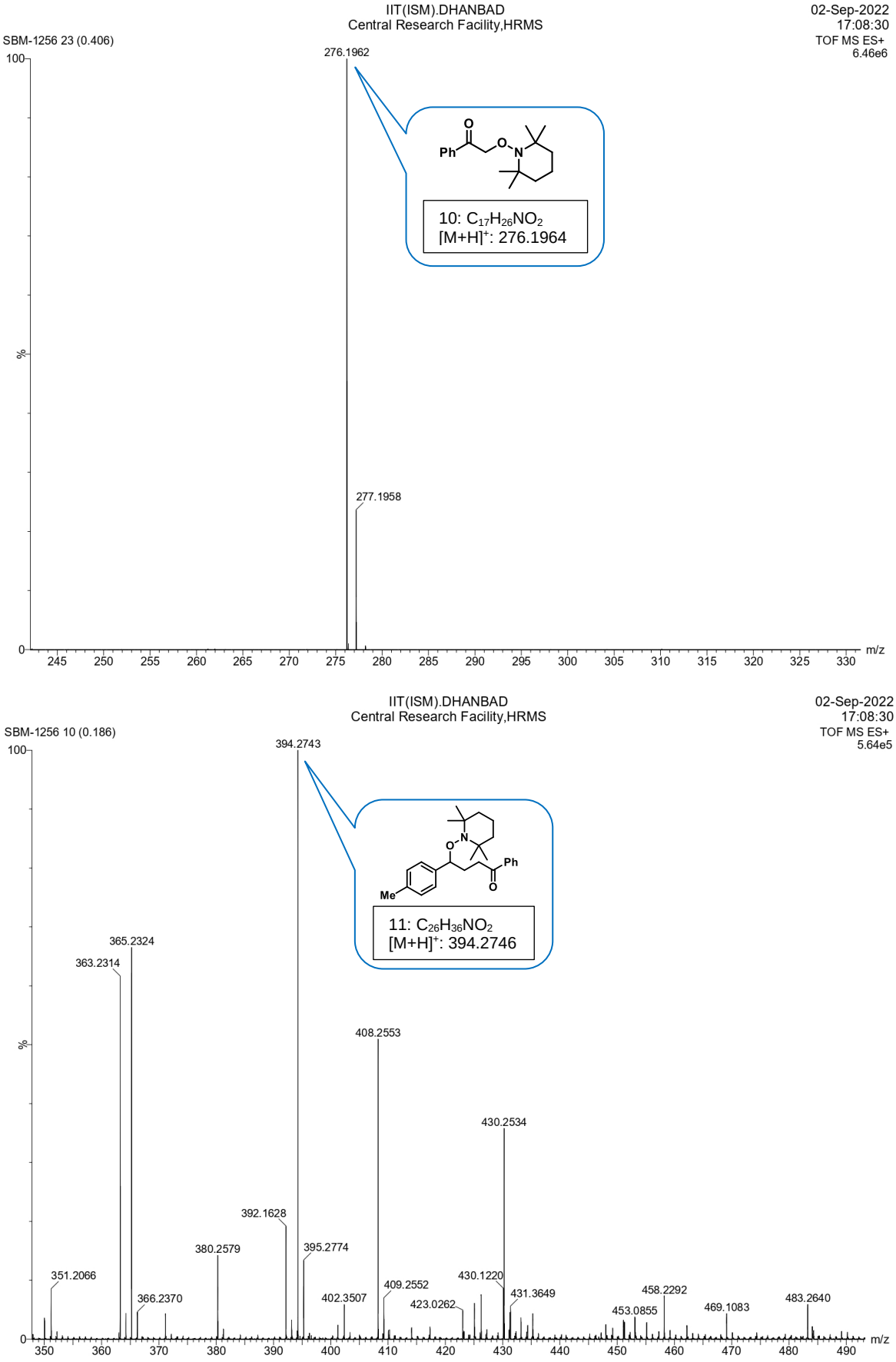
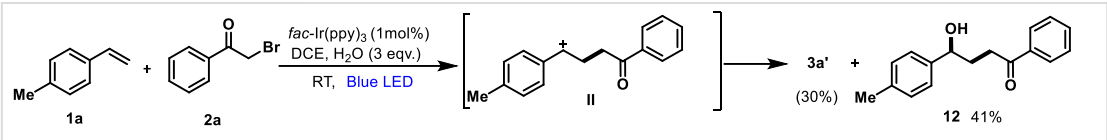


Figure S1. HRMS spectra of crude reaction mixture (compound **10** and **11**).

6.2. Cation Trapping Experiments:

During the reaction between 4-methylstyrene **1a** and phenacyl bromide **2a** in presence of excess water (3 equiv.) under the standard condition, we found the formation of alcohol product **12** in good yield. The alcohol product **12** was formed from hydroxy trapping from water to the cationic intermediate **II**, generated from oxidative transformation of radical to cation after addition of alkyl radical to the styrene.



Reaction procedure:

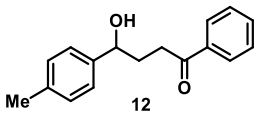
An oven-dried culture tube equipped with a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (1 mol%), phenacyl bromide **2a** (0.2 mmol, 1.0 equiv.), KSCN (0.6 mmol, 3 equiv.), dry 1,2-DCE (0.1 M) and water (3 equiv.). 4-methylstyrene **1a** (0.4 mmol, 2.0 equiv.) was added to it, and the tube was sealed with a Teflon screw cap. Then the reaction mixture was degassed by Freeze-Pump-Thaw cycles with argon and irradiated at rt with 24 W blue LEDs at a distance of approximately 5 cm for 15 h. A high-speed fan was used to maintain the temperature. After the completion of the reaction (confirmed by TLC), the crude reaction mixture was quenched with water, extracted with ethyl acetate (2×2 mL), washed with brine (3 mL), and dried over anhydrous Na_2SO_4. The organic portion was concentrated, and the residue was purified by silica gel column chromatography using EtOAc/petroleum ether as eluent to afford the corresponding product **12** (41%) along with **3a'** (30%).

4-hydroxy-1-phenyl-4-(*p*-tolyl)butan-1-one (12):[10]

Yield: 41% (22 mg).

Nature: Colourless oil.

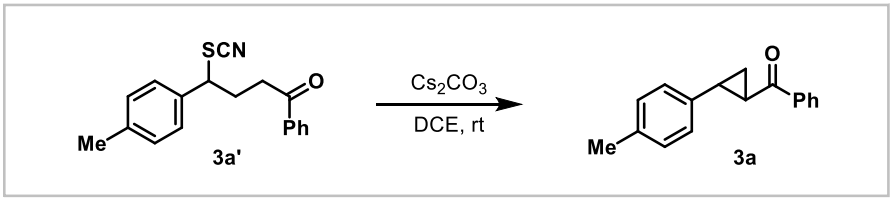
TLC: R_f = 0.5 [EtOAc:Petroleum ether =1:1 (v/v)], visualized by UV.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.79 (t, *J* = 6.3 Hz, 1H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 2.21 – 2.12 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 200.4, 144.0, 141.5, 137.3, 134.5, 129.4, 129.3 128.4, 125.9, 73.6, 34.8, 33.2, 21.8, 21.2.

6.3. Identification of ATRA intermediate 3a':

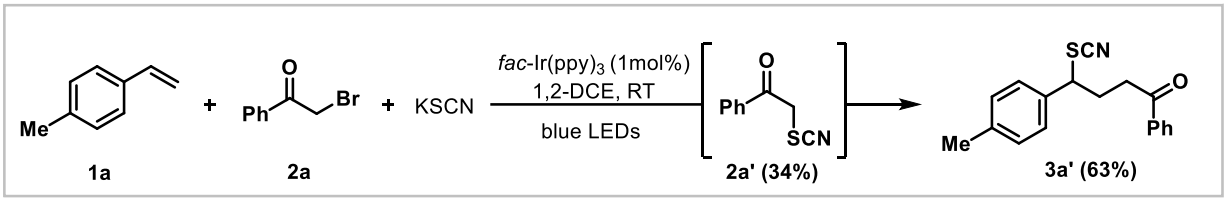


In an oven-dried culture tube ATRA product **3a'** (0.2 mmol, 1.0 equiv.) was taken and was dissolved in dry DCE. Cs_2CO_3 (0.6 mmol, 3.0 equiv.) was added under inert atmosphere. Resultant reaction mixture was stirred at room temperature for 2 h. After completion (checked by TLC), the crude reaction mixture was extracted with ethyl acetate (2×2 mL), washed with brine (3 mL), and dried over anhydrous Na_2SO_4. The organic portion was

concentrated, and the residue was purified by silica gel column chromatography using EtOAc/petroleum ether as eluent to afford the product **3a**.

Conclusion: This result indicates that the cyclopropyl ketone **3a** is formed by an intramolecular nucleophilic substitution after the initial ATRA reaction.

6.4. Evidence for the formation of 2a':

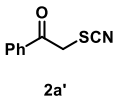


An oven-dried culture tube equipped with a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (1 mol%), phenacyl bromide **2a** (0.2 mmol, 1.0 equiv.), KSCN (0.6 mmol, 3 equiv.), dry 1,2-DCE (0.1 M). 4-methylstyrene **1a** (0.4 mmol, 2.0 equiv.) was added to it, and the tube was sealed with a Teflon screw cap. Then the reaction mixture was degassed by Freeze-Pump-Thaw cycles with argon and irradiated at rt with 24 W blue LEDs at a distance of approximately 5 cm for 9 h. A high-speed fan was used to maintain the temperature. After 9 h the crude reaction mixture was quenched with water, extracted with ethyl acetate (2×2 mL), washed with brine (3 mL), and dried over anhydrous Na_2SO_4. The organic portion was concentrated, and the residue was purified by silica gel column chromatography using EtOAc/petroleum ether as eluent to afford the corresponding product **2a'**.

1-phenyl-2-thiocyanatoethan-1-one (2a'):

Yield: 34% (12 mg).

Nature: White solid.



2a'

Mp: 61-63 ºC

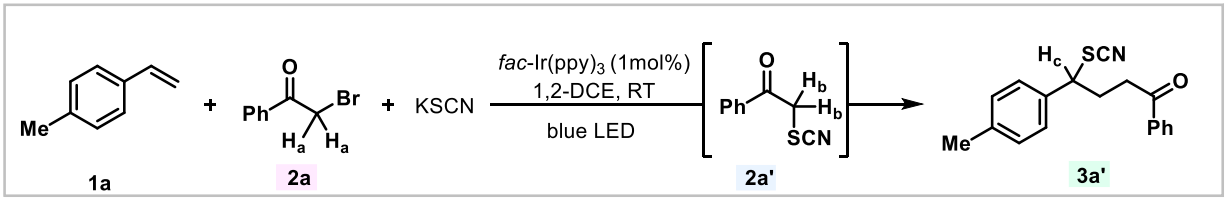
TLC: R_f = 0.5 [EtOAc:Petroleum ether = 1:4 (v/v)], visualized by UV.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.69 – 7.65 (m, 1H), 7.55 – 7.51 (m, 2H), 4.74 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 191.0, 134.9, 134.0, 129.3, 128.5, 112.0, 43.1.

HRMS (ESI) *m/z* calcd for C_9H_8NOS $[M+H]^+$: 178.0327; found: 178.0328.

6.5. Reaction progress monitoring by ^{1}H-NMR study:



Five reactions were set up in 0.2 mmol scale in reaction tube with 4-methylstyrene **1a**, phenacyl bromide **2a**, KSCN and *fac*-Ir(ppy)$_3$ as mentioned in the standard reaction condition. The resulting mixture was irritated with 24 W blue LEDs. At various time intervals (t= 0, 3, 6, 9 and 15 h) one reaction tube was removed from the irradiation setup and crude ^{1}H NMR was taken.

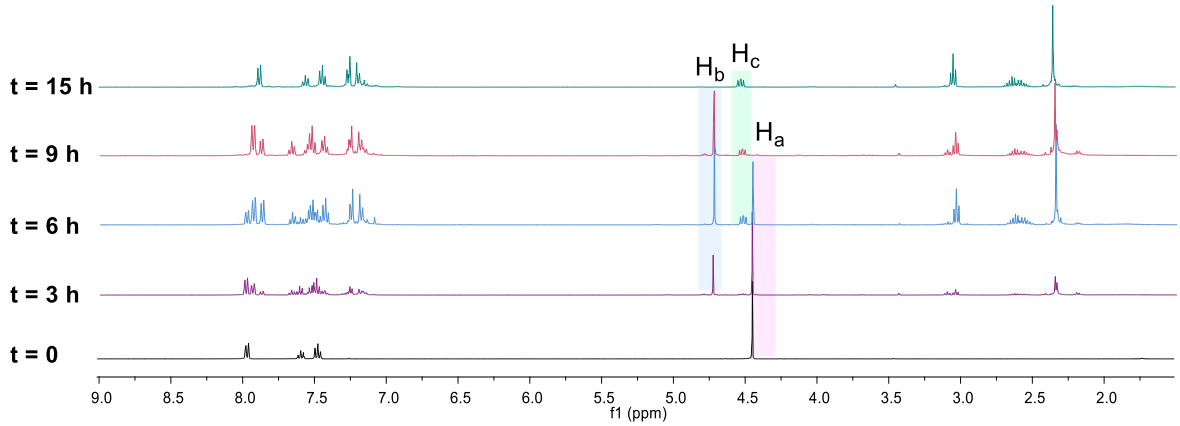


Figure S2: ^{1}H NMR plots.

Conclusion: It was observed that initially **2a** was converted to the active reacting species **2a'** which further underwent ATRA reaction to produce **3a'**.

6.6. Electrochemical Measurements:

Cyclic Voltammetry was performed using CH Instruments (model: CHI1140C) using a glassy carbon working electrode, saturated calomel reference electrode, and a platinum wire counter electrode. Samples were prepared with 2.0 mmol of substrate in 5 mL of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dry and degassed acetonitrile. The potential was scanned at a scan rate 100 mV/s. A background of the electrolyte solution was subtracted from the voltammogram. Reduction was measured by scanning potential in the negative direction and oxidation in the positive direction. The glassy carbon electrode was polished between each scan. Ep/2 is given as the half-wave potential for irreversible oxidation where the current is equal to one-half the peak current of the oxidation event.

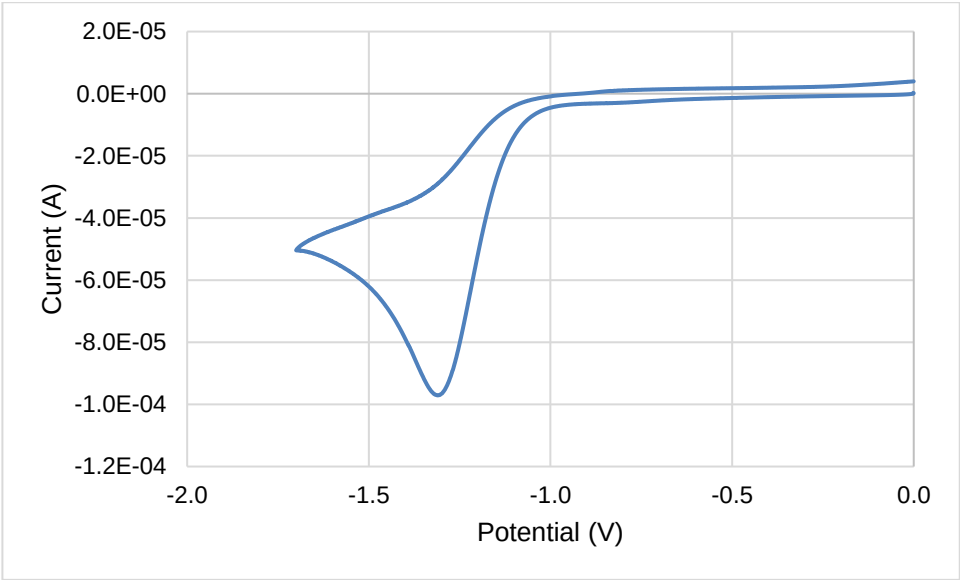


Figure S3: Cyclic voltammogram of **2a'**.

6.7. UV-Visible Study:

UV−Visible absorption spectra were recorded in Shimadzu UV-1800 Spectrophotometer. At first, 1×10^{-4} M solution of *fac*-Ir(ppy)$_3$, 0.02 M solution of 4-methylstyrene **1a** and 0.01 M solution of 1-phenyl-2-thiocyanatoethan-1-one **2a'** was prepared in dry DCE. Then, the absorbance of individual reactants and several combinations of them were measured with the wavelength range from 200 to 800 nm using a quartz cuvette of path length 1.0 cm.

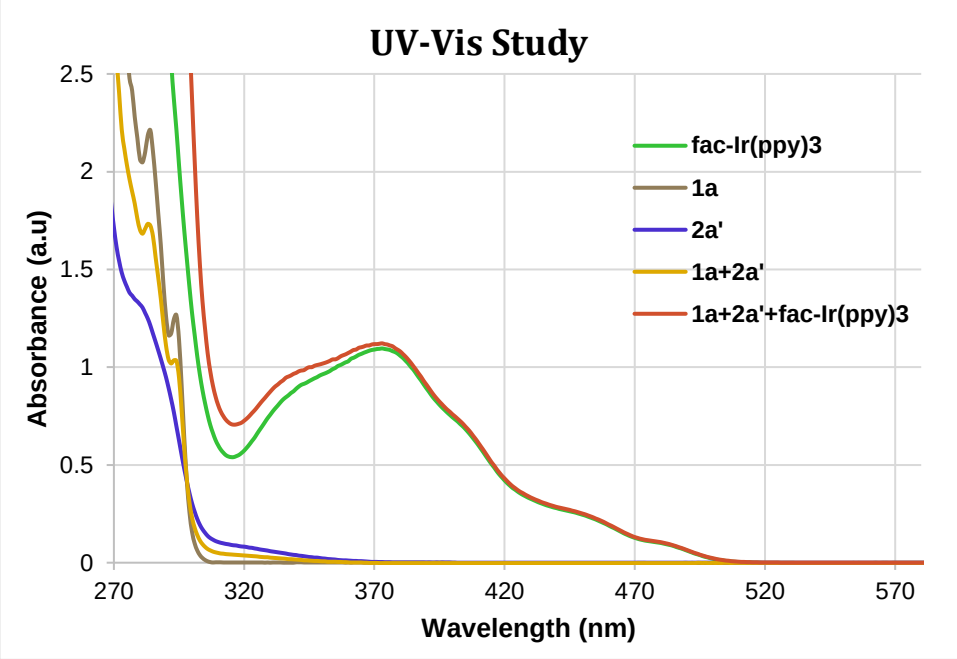


Figure S4: UV-Vis Spectra of *fac*-Ir(ppy)$_3$, individual reactants **1a** and active reacting species **2a'** and their combined mixtures.

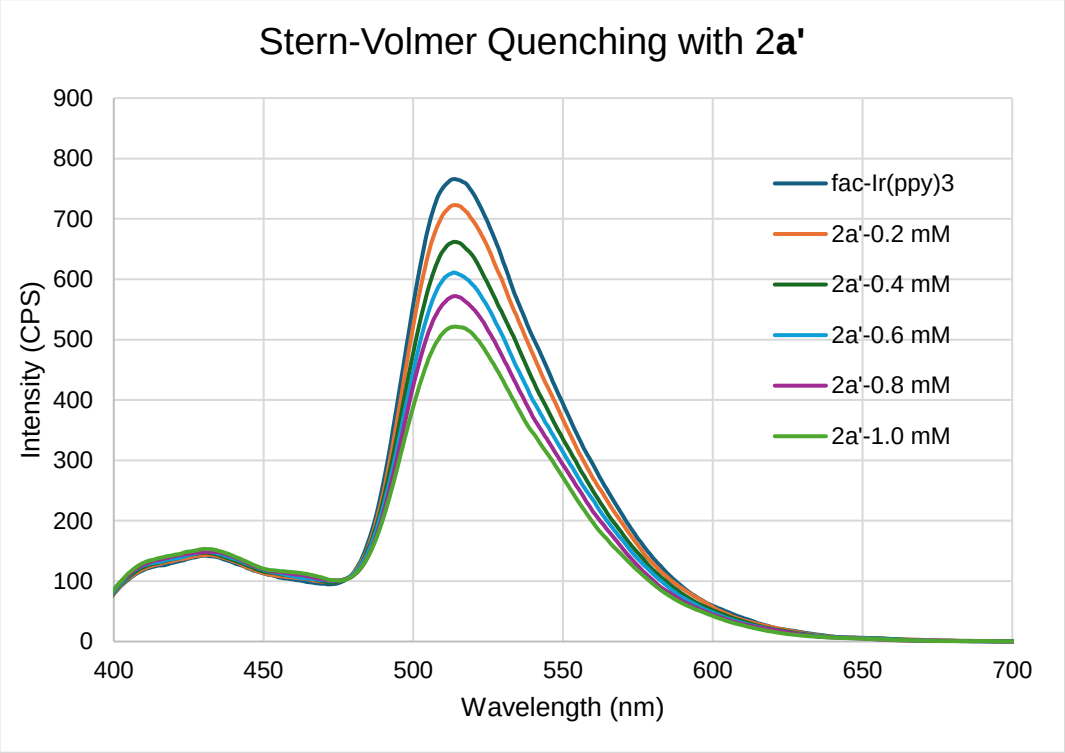
Comments: These spectra indicate that the photocatalyst, *fac*-Ir(ppy)$_3$, shows absorption exclusively at λ_{max}= 375 nm. And there is no new peak generation in the absorption spectra for different combined solutions of the reactants. Hence, the possibility of any electron donor-acceptor (EDA) complex formation is being ruled out.

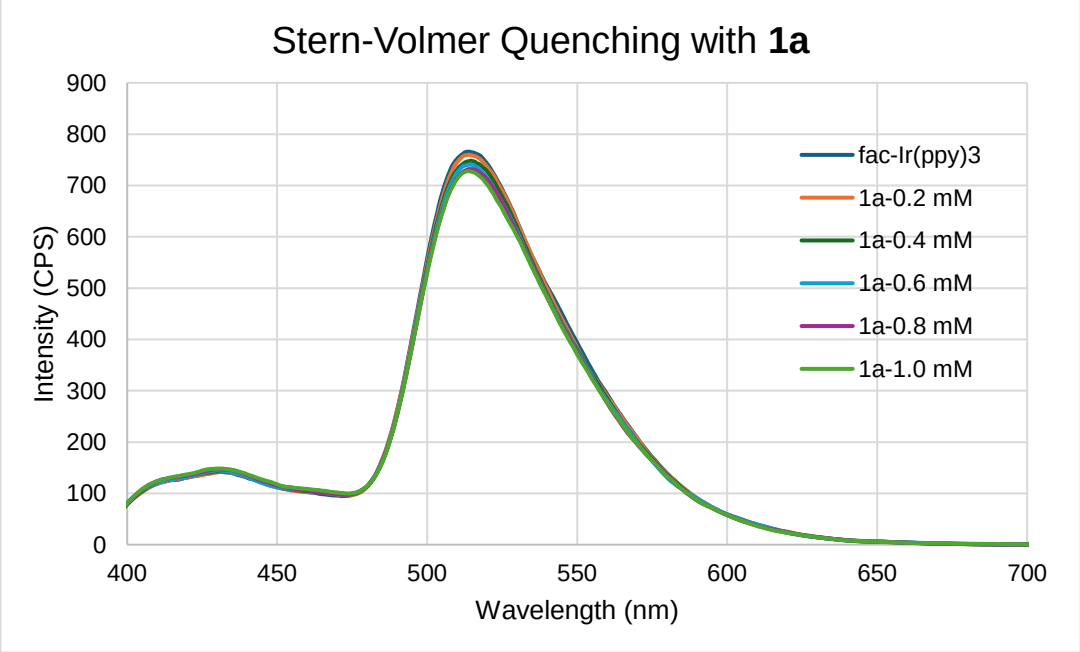
6.8. Stern-Volmer Fluorescence Quenching Experiments:

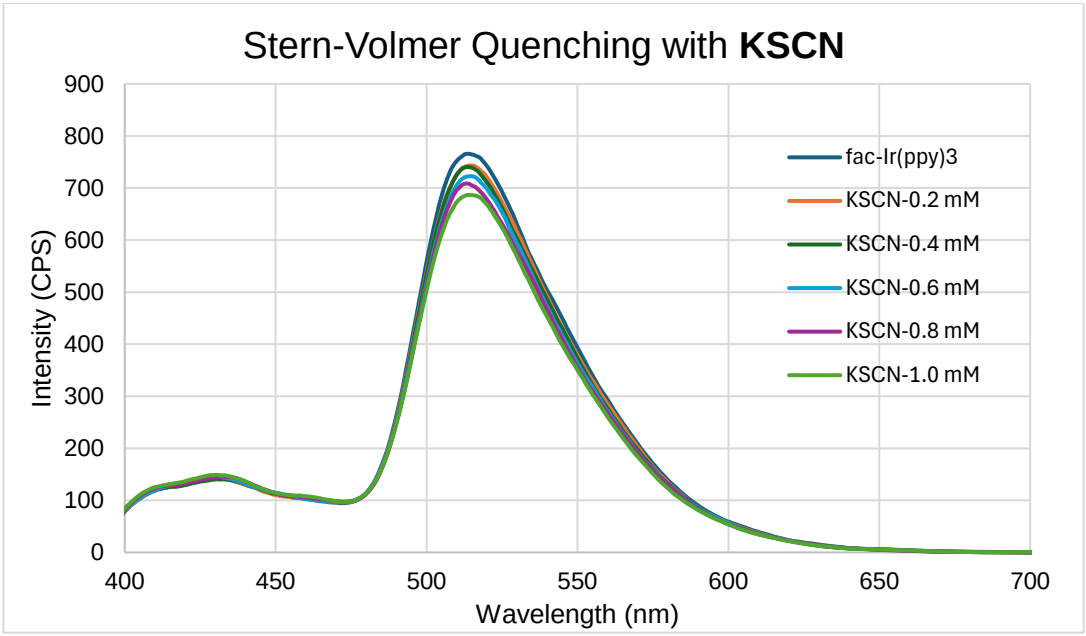
Fluorescence quenching studies were carried out using a PerkinElmer LS 55 Fluorescence Spectrometer. Photocatalyst *fac*-Ir(ppy)$_3$ and different concentrations of added quenchers were prepared in dry DCE in quartz cuvettes. For the quenching experiments, the concentration of *fac*-Ir(ppy)$_3$ was 5.0×10^{-6} M. The solutions were excited at 375 nm, and the emission intensity was measured at 514 nm for *fac*-Ir(ppy)$_3$. Plots were derived according to the Stern–Volmer equation and K_{sv} was calculated.

Stern-Volmer equation: $I_0/I = 1 + K_{sv}[Q]$

Where I_0 is the luminescence intensity of the photocatalyst in the absence of a quencher, I is the intensity of the photocatalyst in the presence of quenchers, [Q] is the concentration of added quencher, and K_{sv} is the Stern– Volmer quenching constant. All emission spectra were recorded after each addition of the quencher.


Stern-Volmer Quenching with 2a'
Intensity (CPS)
Wavelength (nm)
fac-Ir(ppy)3
2a'-0.2 mM
2a'-0.4 mM
2a'-0.6 mM
2a'-0.8 mM
2a'-1.0 mM


Stern-Volmer Quenching with 1a
Intensity (CPS)
Wavelength (nm)
fac-Ir(ppy)3
1a-0.2 mM
1a-0.4 mM
1a-0.6 mM
1a-0.8 mM
1a-1.0 mM



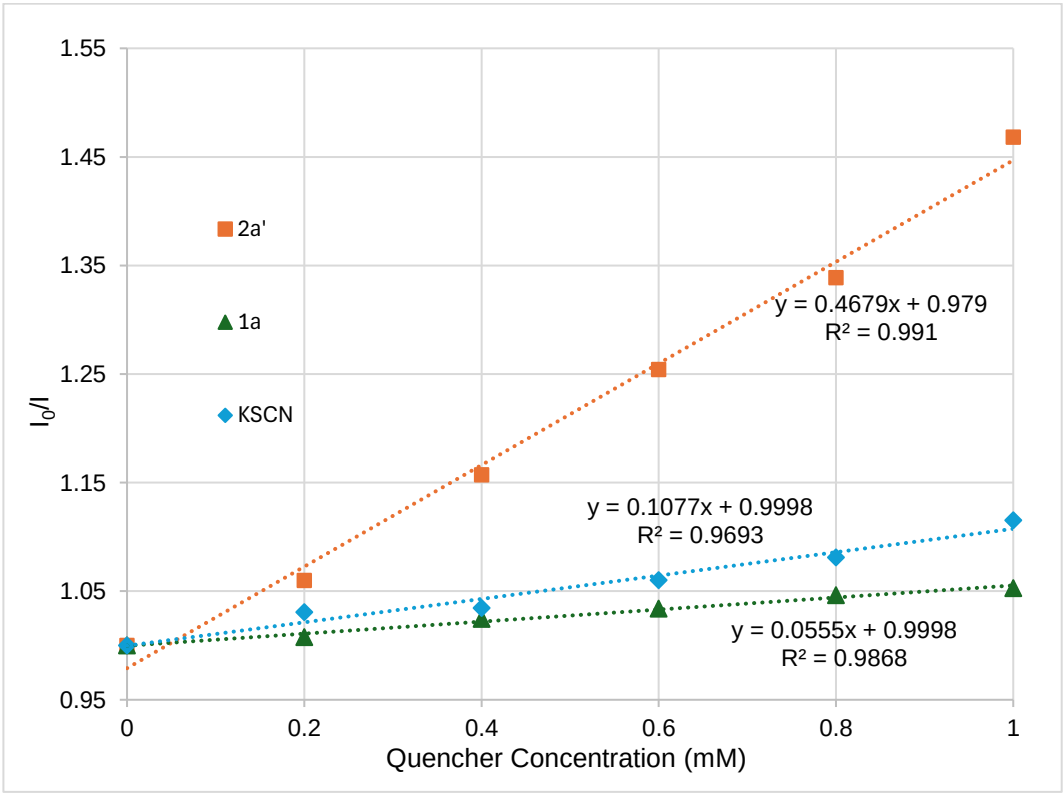


Figure S3: Emission spectra and Stern-Volmer plot of ***fac*-Ir(ppy)$_3$**, quenching with different concentrations of added quenchers- **1a**, **2a'** and **KSCN**.

Comments: The obtained spectra shows that **2a'** is the prominent quencher here and suggests that the mechanism starts with the radical engagement from **2a'**.

7. X-ray Crystal Structures and Data:

PLATON version of 13/05/2024; check.def file version of 04/05/2024

DATABLOCK SHELX - ELLIPSOID PLOT

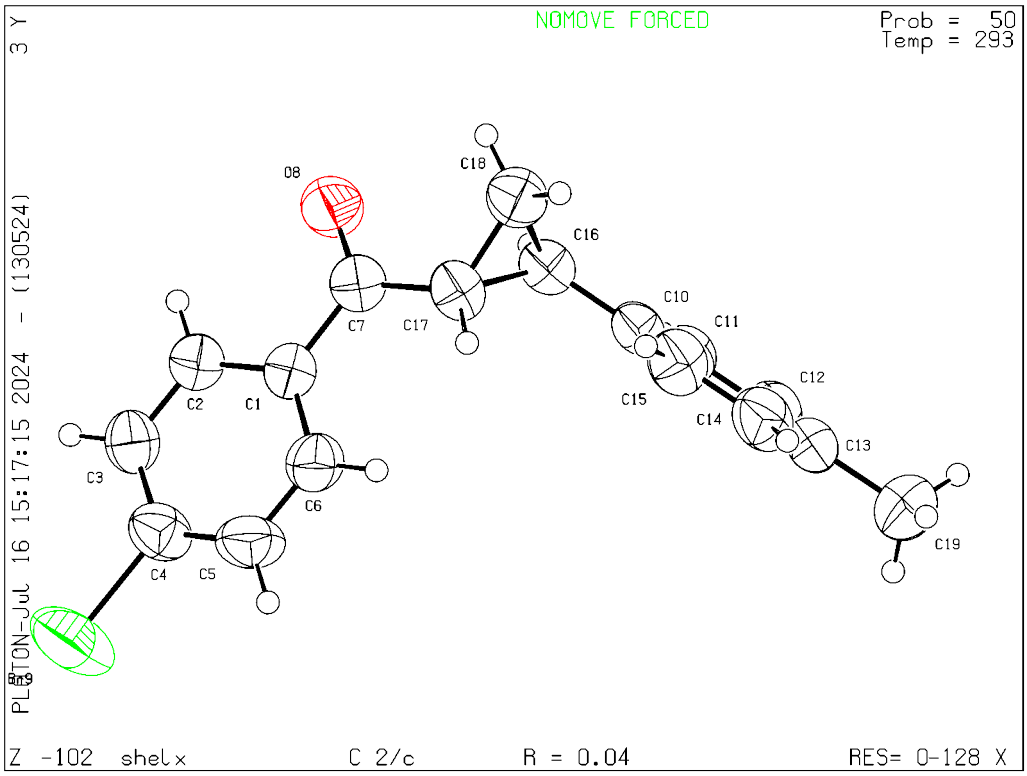


Figure S4. ORTEP plot of compound **3j** with 50% ellipsoid probability.

Crystal growth process for compound 3j: Recrystallization of compound **3j** was performed in a 5 mL glass vial by dissolving 20 mg of the compound **3j** in ethylacetate (0.2 mL) and pentane (3 mL) was slowly added on the top and then the vial was capped and stored at room temperature for the growth of the crystals. After 1 day crystal was formed and was send for the SC-XRD analysis.

Crystal data for compound 3b: X-ray single crystal data were collected using MoKα (λ = 0.71073 Å) radiation on a Rigaku SuperNova diffractometer equipped with an Eos S2 detector. Structure solution/refinement were carried out using Shelx-2013. The structure was solved by direct method and refined in a routine manner. Non-hydrogen atoms were treated anisotropically. All hydrogen atoms were geometrically fixed. CCDC (**CCDC No: 2149906**) contains the supplementary crystallographic data of compound **3b**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Datablock: shelx

BOND PRECISION:	**C-C = 0.0038 A**		**WAVELENGTH=0.71073**
CELL:	**A=23.556(4)**	**B=5.9633(7)**	**C=21.912(3)**
	alpha=90	beta=108.089(15)	gamma=90
TEMPERATURE:	293 K		
	CALCULATED		**REPORTED**
VOLUME	2925.9(8)		2925.9(7)
SPACE GROUP	C 2/c		C 2/c

HALL GROUP	-C 2yc	-C 2yc
MOIETY FORMULA	C17 H15 Br O	?
SUM FORMULA	C17 H15 Br O	C17 H15 Br O
MR	315.19	315.20
DX,G CM-3	1.431	1.431
Z	8	8
MU (MM-1)	2.799	2.799
F000	1280.0	1280.0
F000'	1278.19	
H,K,LMAX	30,7,27	29,7,27
NREF	3195	3150
TMIN,TMAX	0.675,0.735	0.426,1.000
TMIN'	0.651	

CORRECTION METHOD= # REPORTED T LIMITS: TMIN=0.426 TMAX=1.000 ABSCORR = MULTI-SCAN

DATA COMPLETENESS= 0.986 THETA(MAX)= 26.991

R(REFLECTIONS)= 0.0414(1640) WR2(REFLECTIONS)= 0.1041(3150)

S = 1.014 NPAR= 174

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field. Absorption correction given as multi-scan

PLAT031_ALERT_4_C Refined Extinction Parameter Within Range of ... 3.313 Sigma

PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C4 Check

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 16.215 Check

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 4.210 Check

Alert level G

PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K) 293 Check

PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature ..... (K) 293 Check

PLAT793_ALERT_4_G Model has Chirality at C16 (Centro SpGr) R Verify

PLAT793_ALERT_4_G Model has Chirality at C17 (Centro SpGr) R Verify

PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !

PLAT899_ALERT_4_G SHELXL2018 is Deprecated and Succeeded by SHELXL 2019/3 Note

PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 1 Note

2 0 0,

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 43 Note

PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ..... 2.2 Low

PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... Please Check

PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged Please Check

PLAT967_ALERT_5_G Note: Two-Theta Cutoff Value in Embedded .res .. 54.0 Degree

PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ..... 4.285 Note

Predicted wR2: Based on SigI**2 2.43 or SHELX Weight 10.27

PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 2 Info

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
14 ALERT level G = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low

```
   5 ALERT type 4 Improvement, methodology, query or suggestion
   3 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

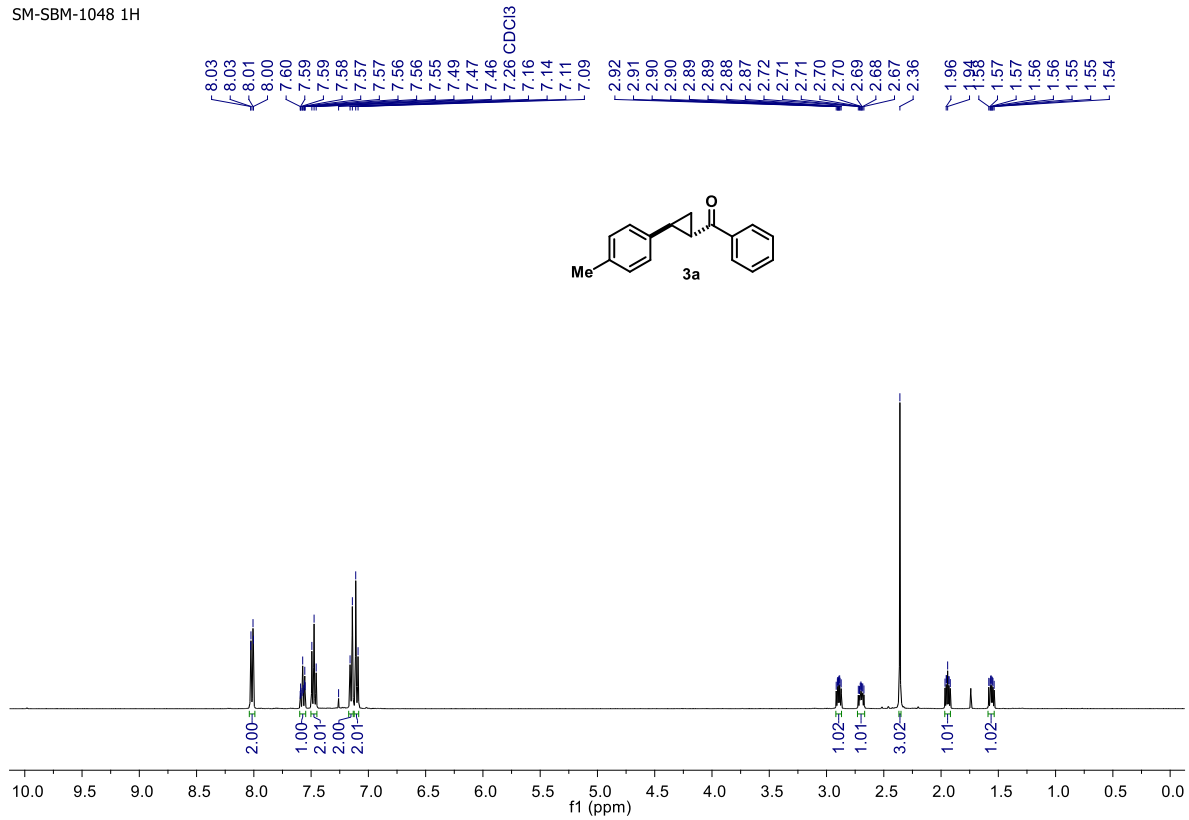
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

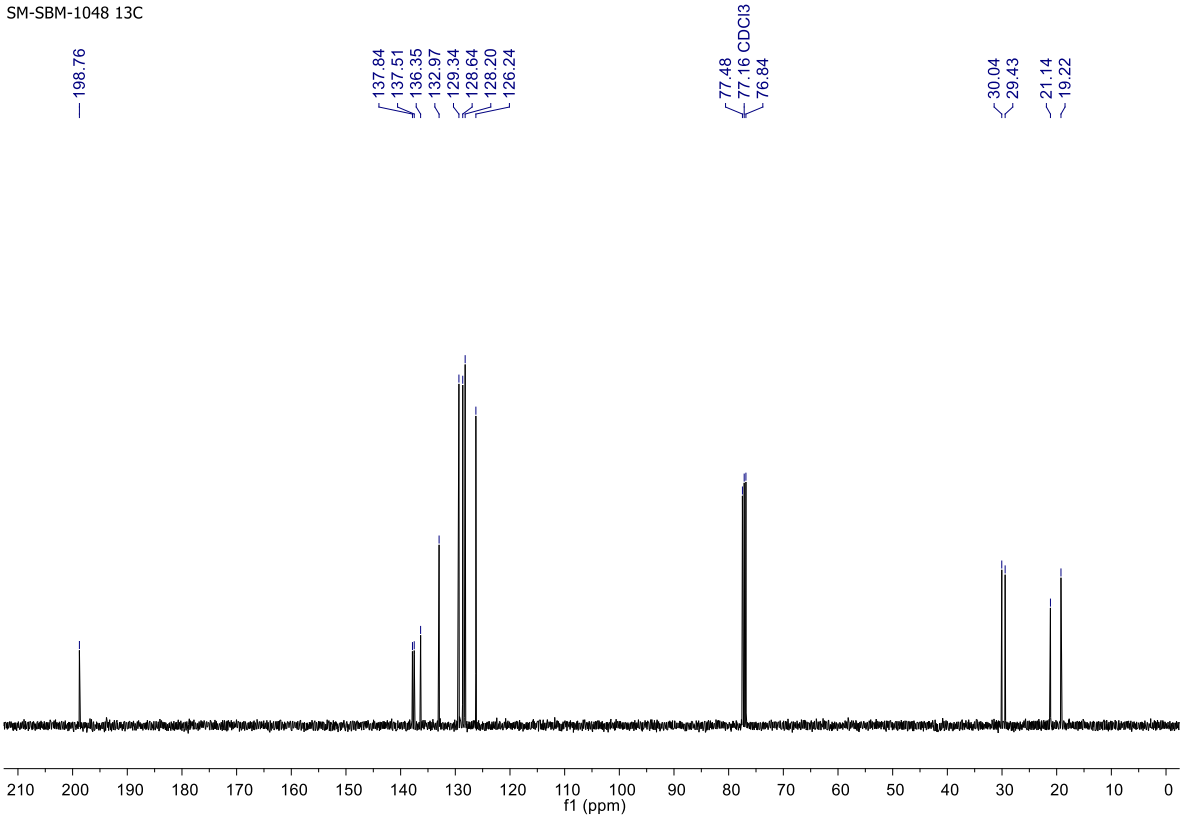
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

8. NMR Spectra:

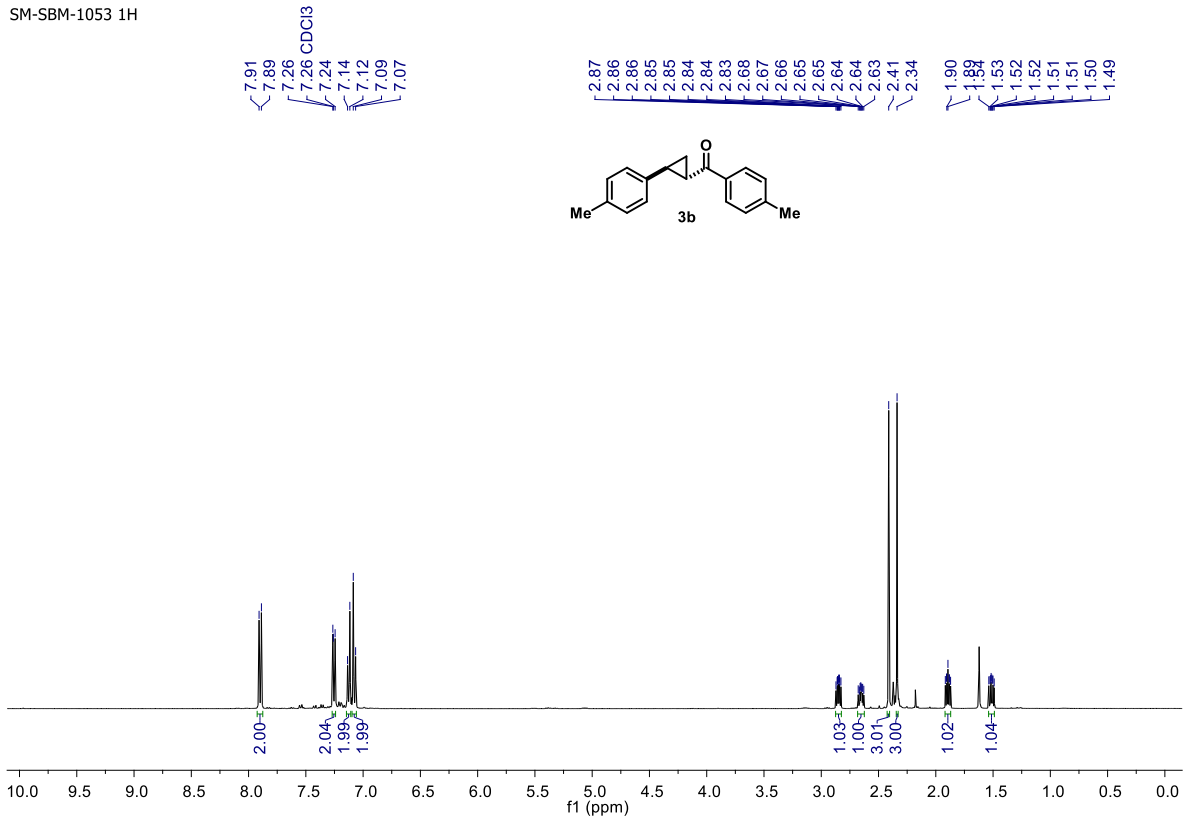
^{1}H NMR of **3a** (400 MHz, $CDCl_3$):



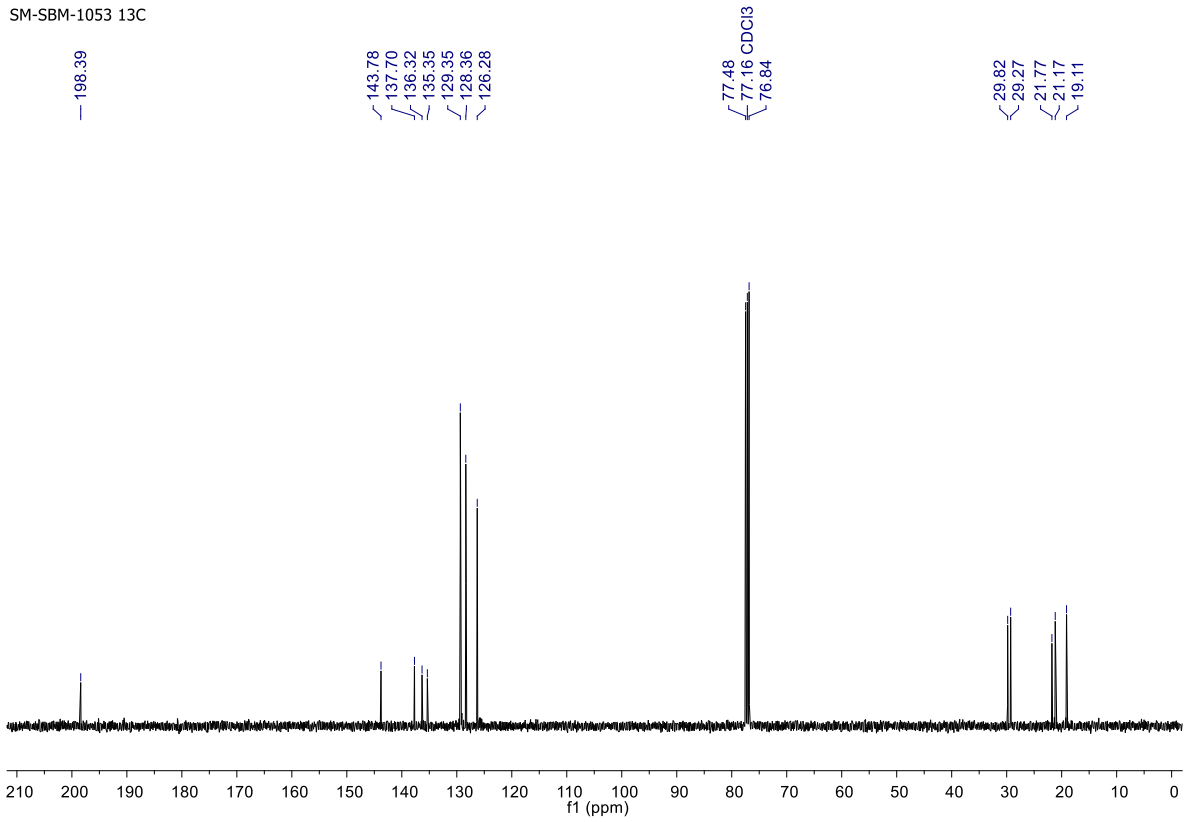
^{13}C{^{1}H} NMR of **3a** (101 MHz, $CDCl_3$):



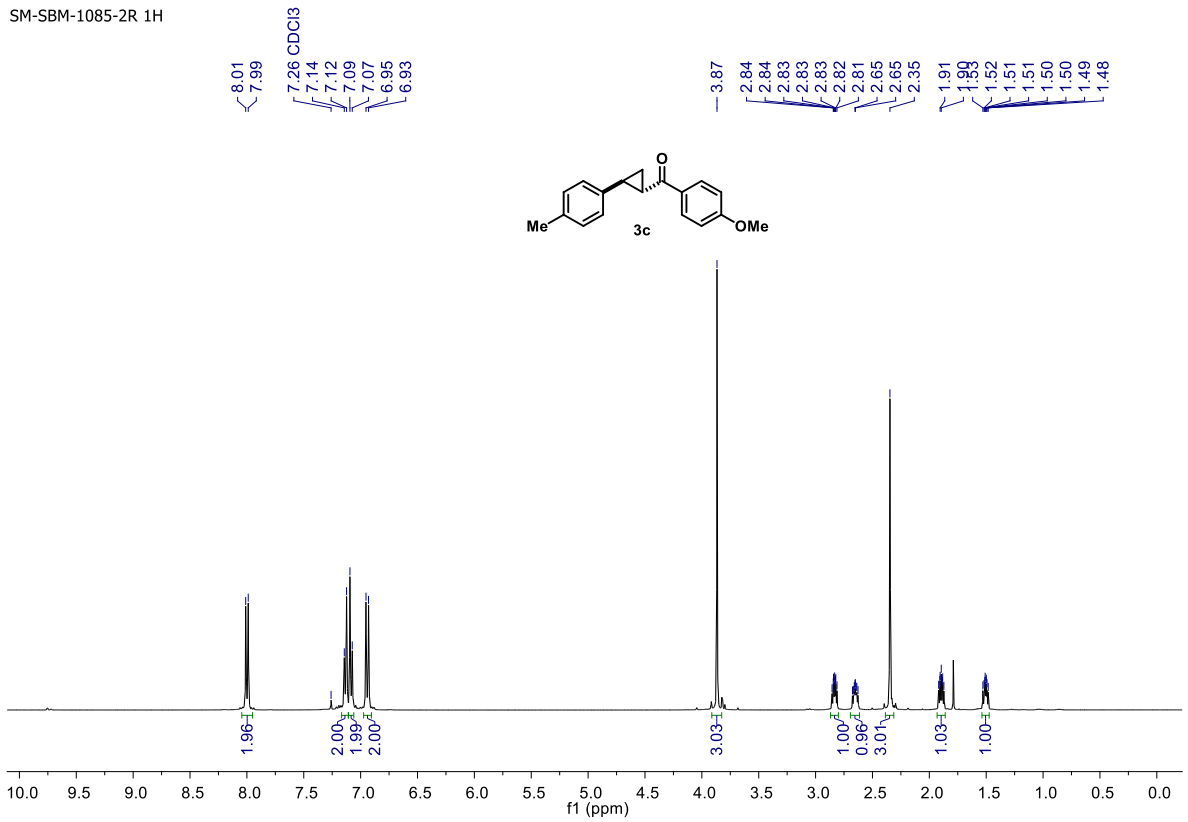
^{1}H NMR of **3b** (400 MHz, $CDCl_3$):



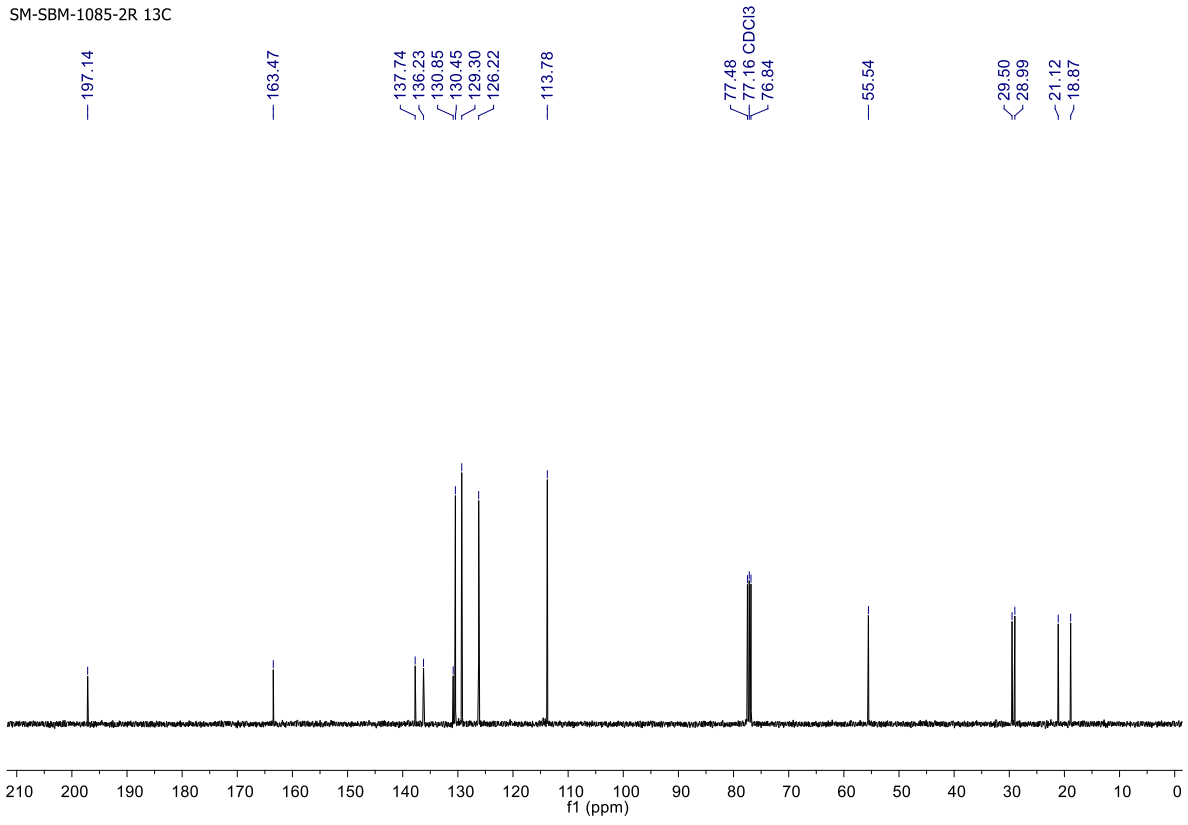
^{13}C{^{1}H} NMR of **3b** (101 MHz, $CDCl_3$):



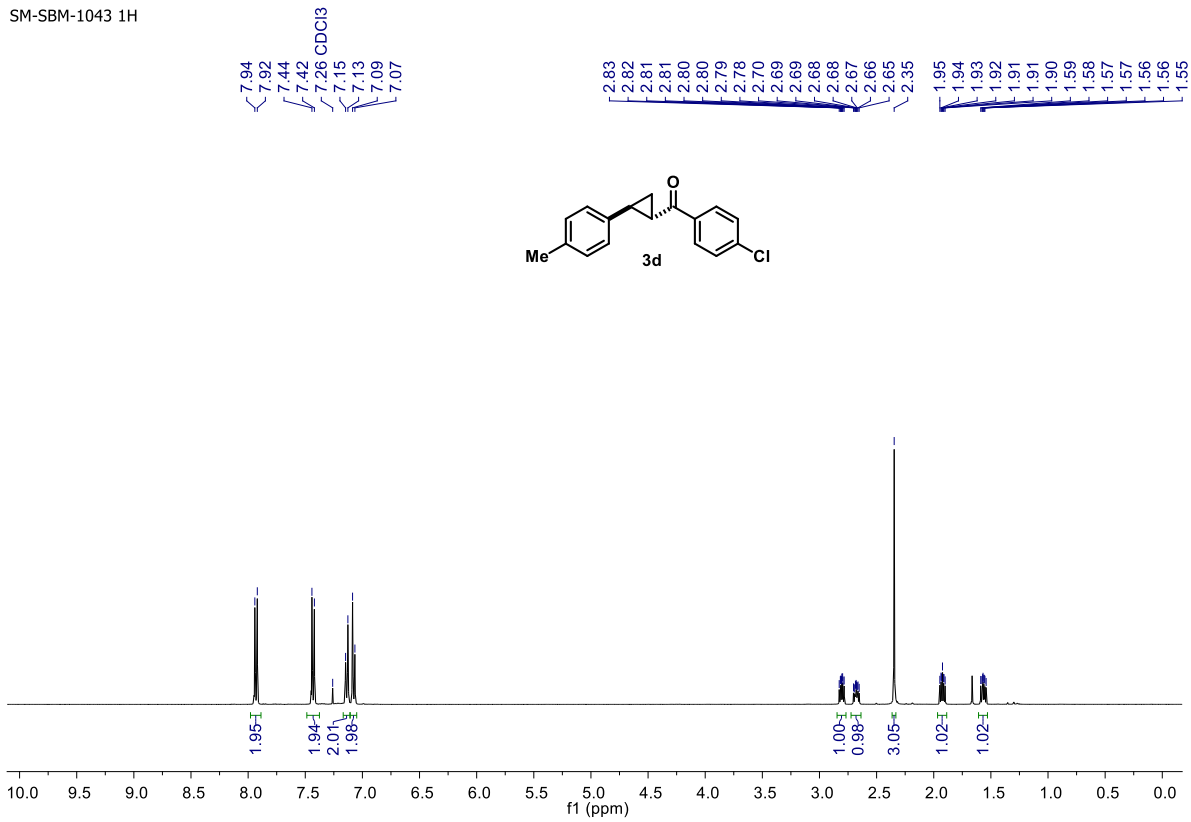
^{1}H NMR of **3c** (400 MHz, $CDCl_3$):



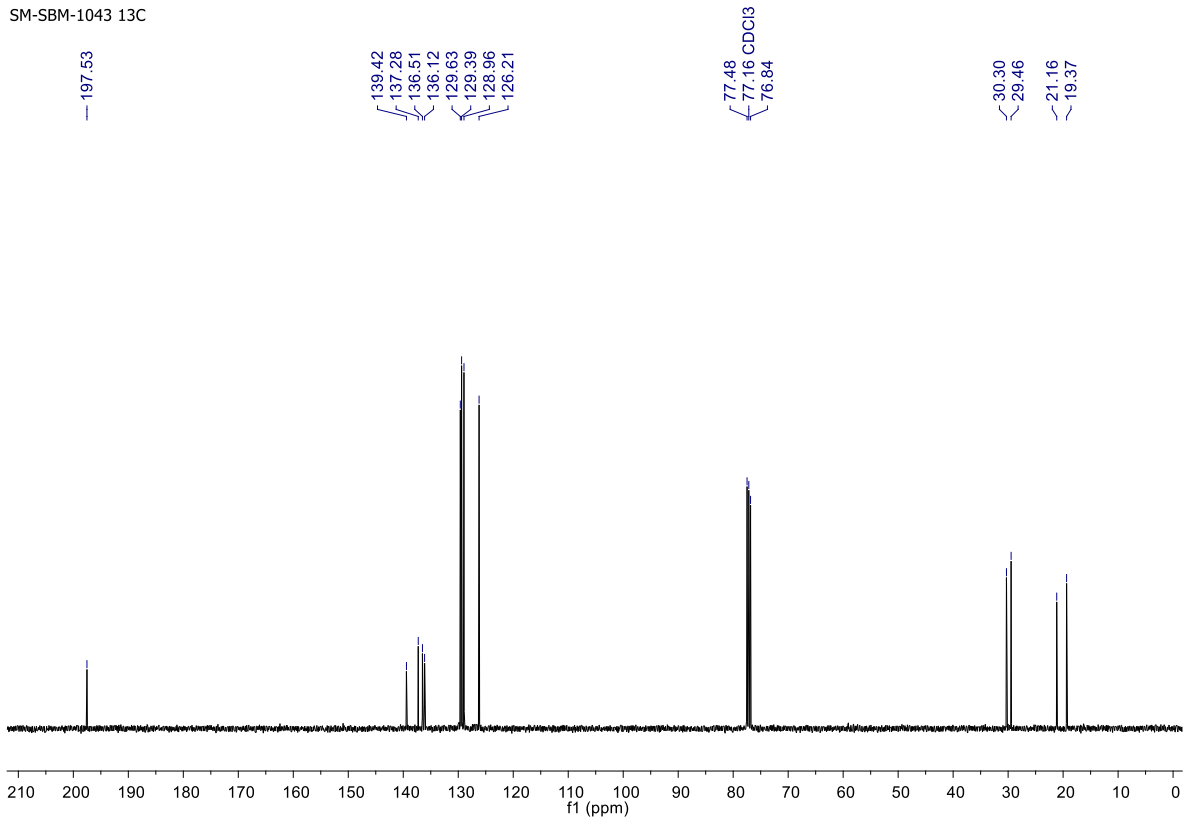
^{13}C{^{1}H} NMR of **3c** (101 MHz, $CDCl_3$):



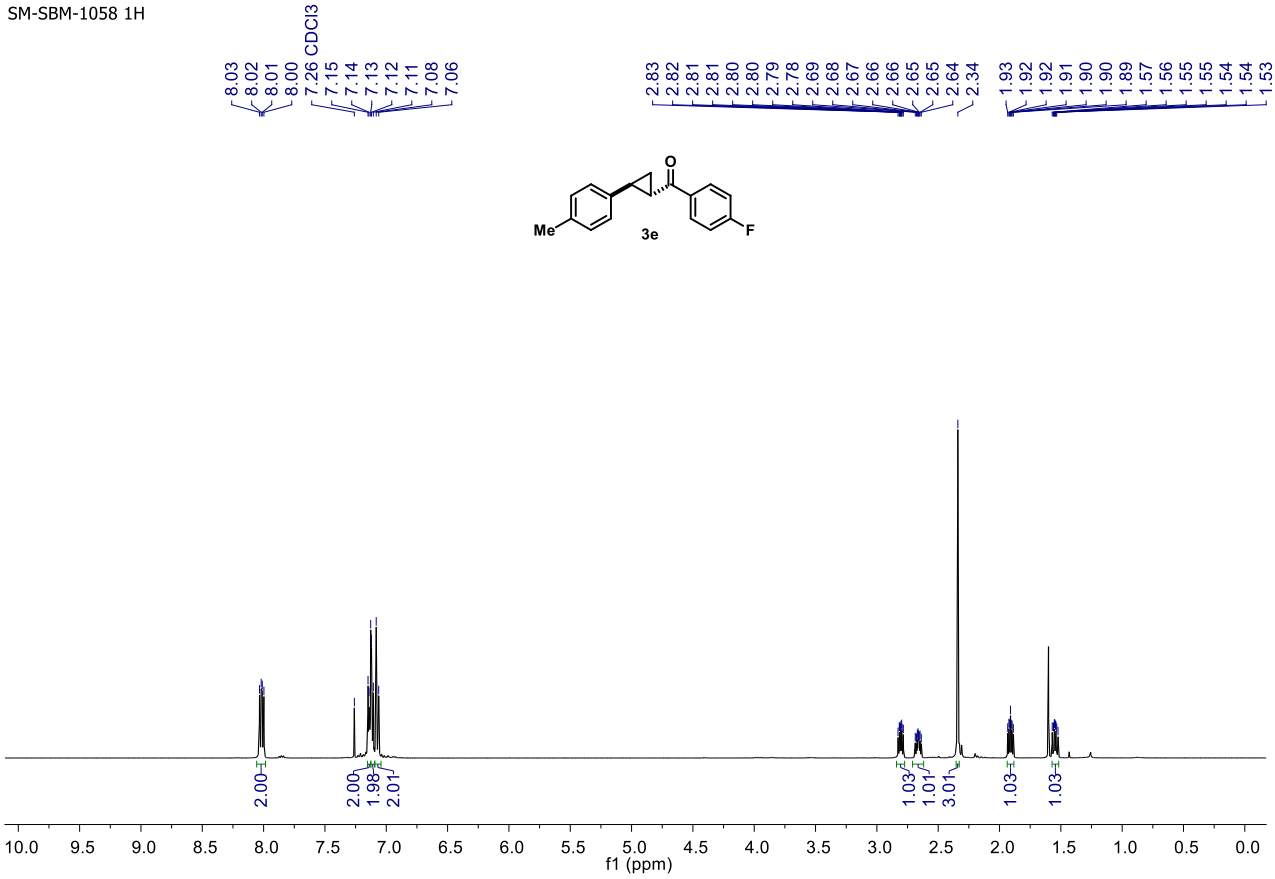
^{1}H NMR of **3d** (400 MHz, $CDCl_3$):



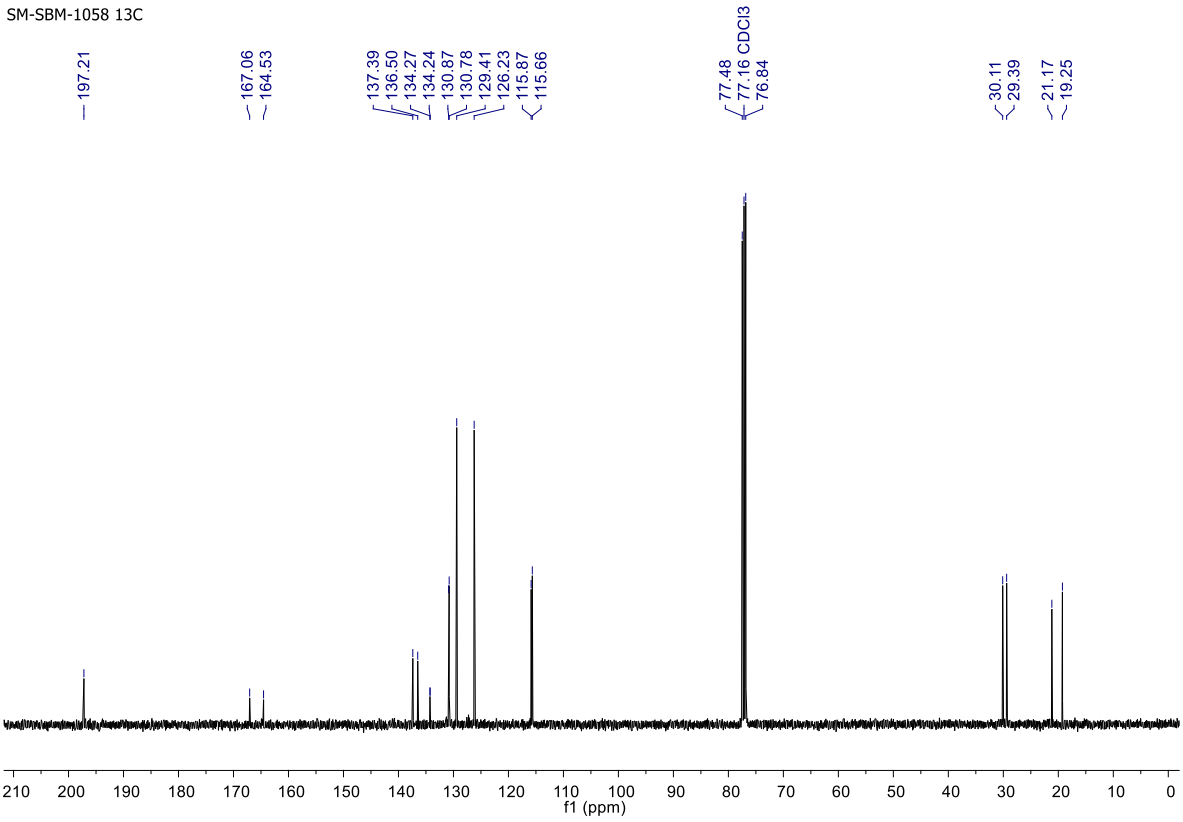
^{13}C{^{1}H} NMR of **3d** (101 MHz, $CDCl_3$):



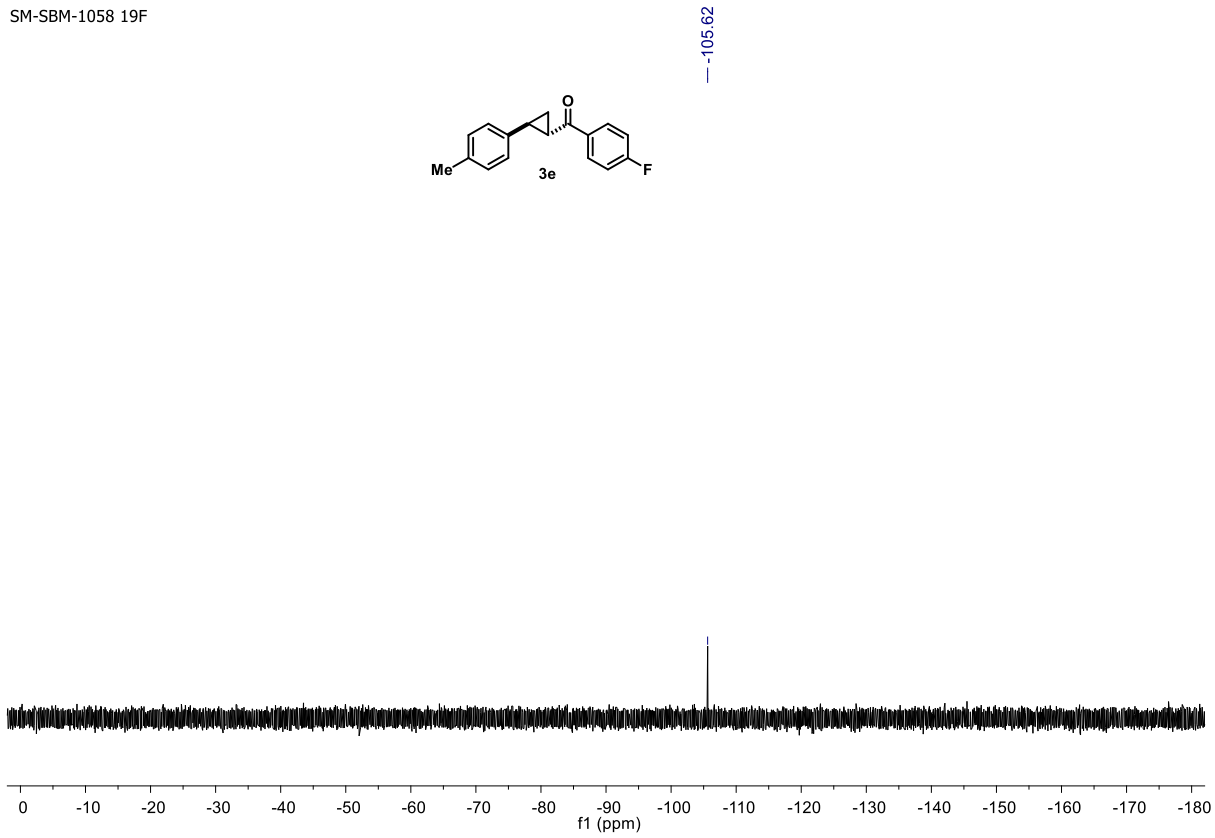
^{1}H NMR of **3e** (400 MHz, $CDCl_3$):



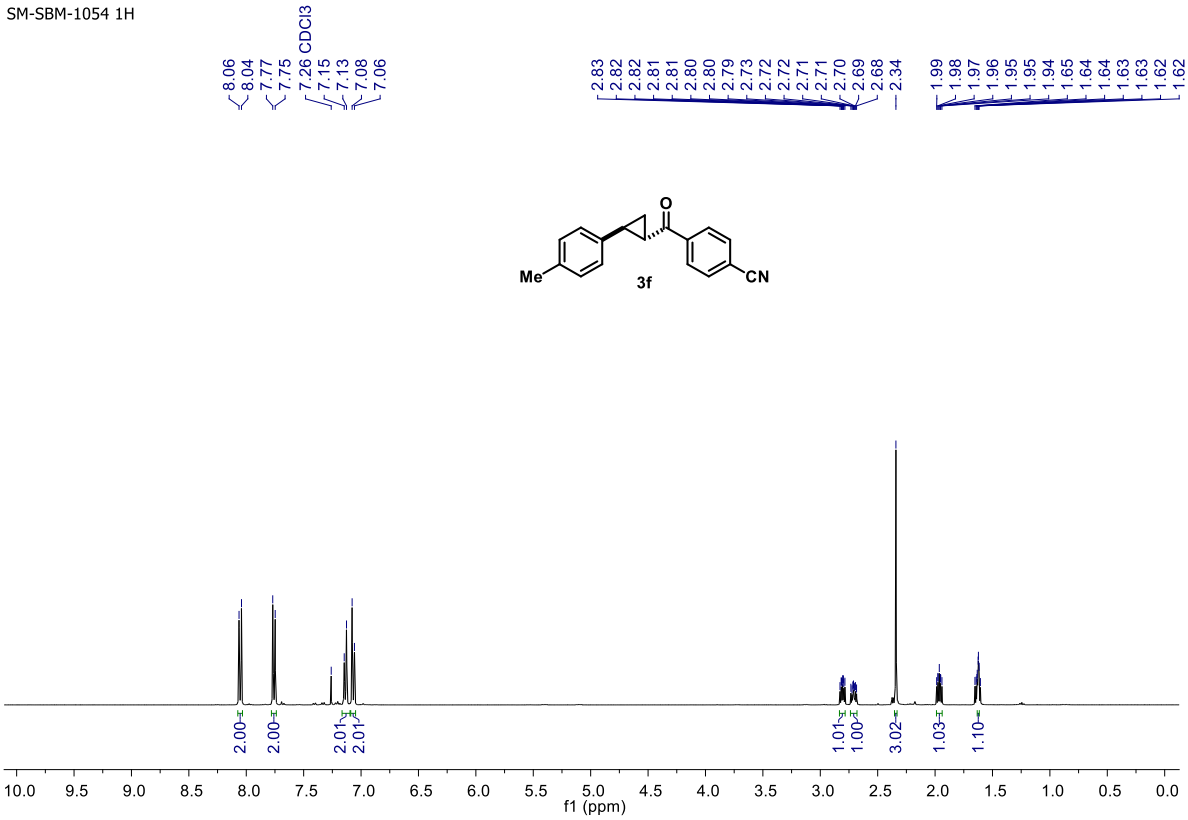
^{13}C{^{1}H} NMR of **3e** (101 MHz, $CDCl_3$):



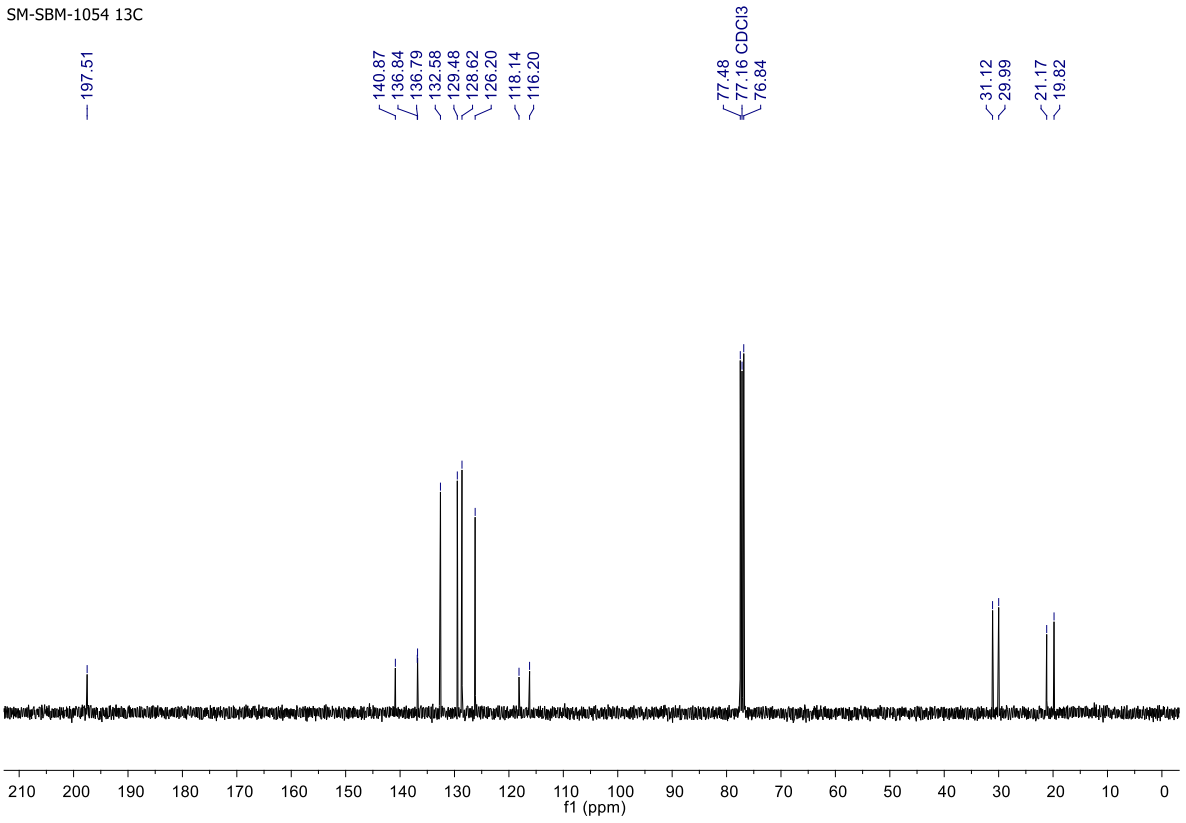
^{19}F NMR of **3e** (377 MHz, $CDCl_3$):



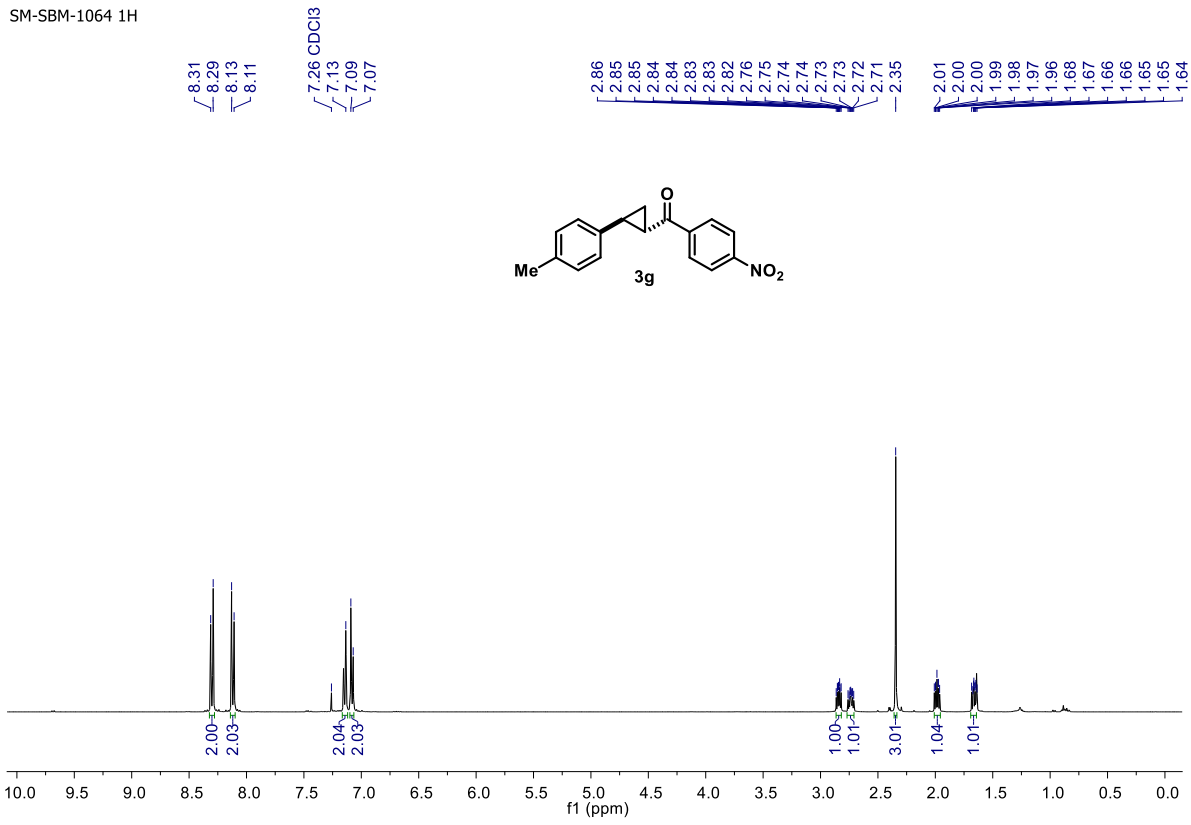
^{1}H NMR of **3f** (400 MHz, $CDCl_3$):



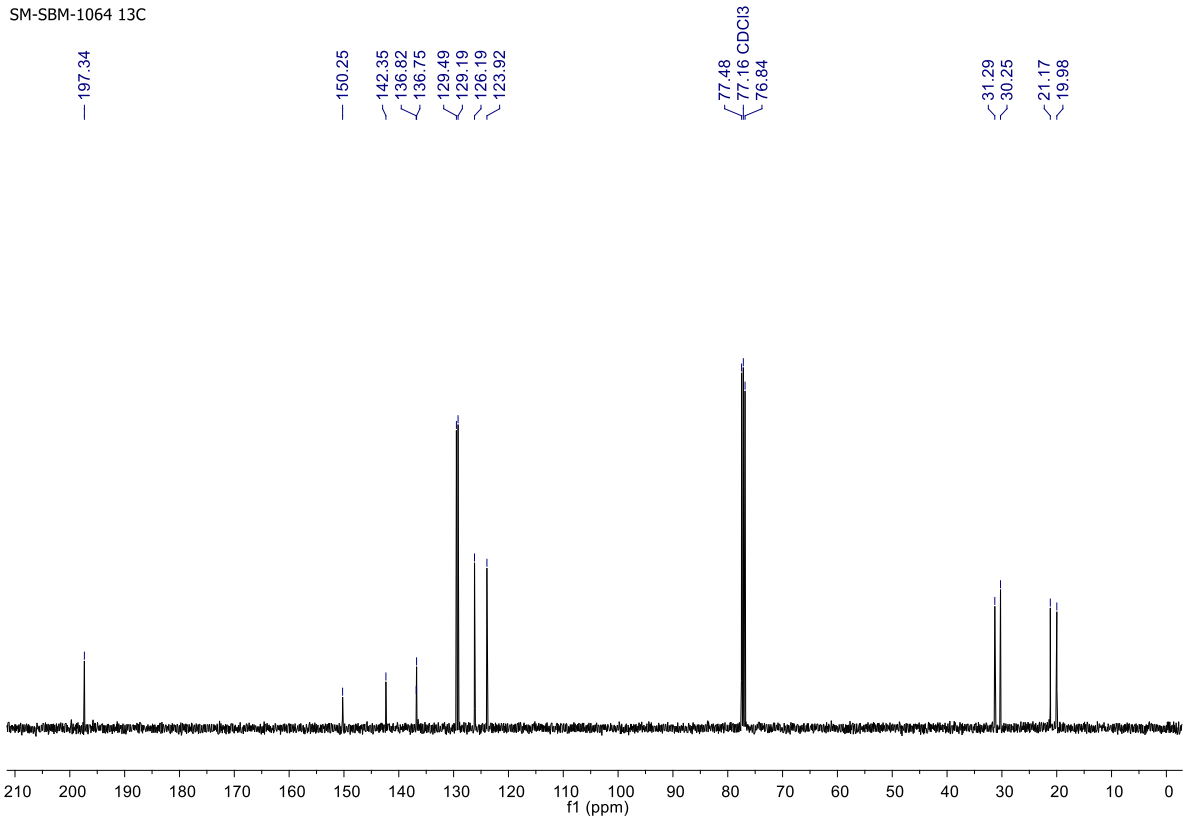
^{13}C{^{1}H} NMR of **3f** (101 MHz, $CDCl_3$):



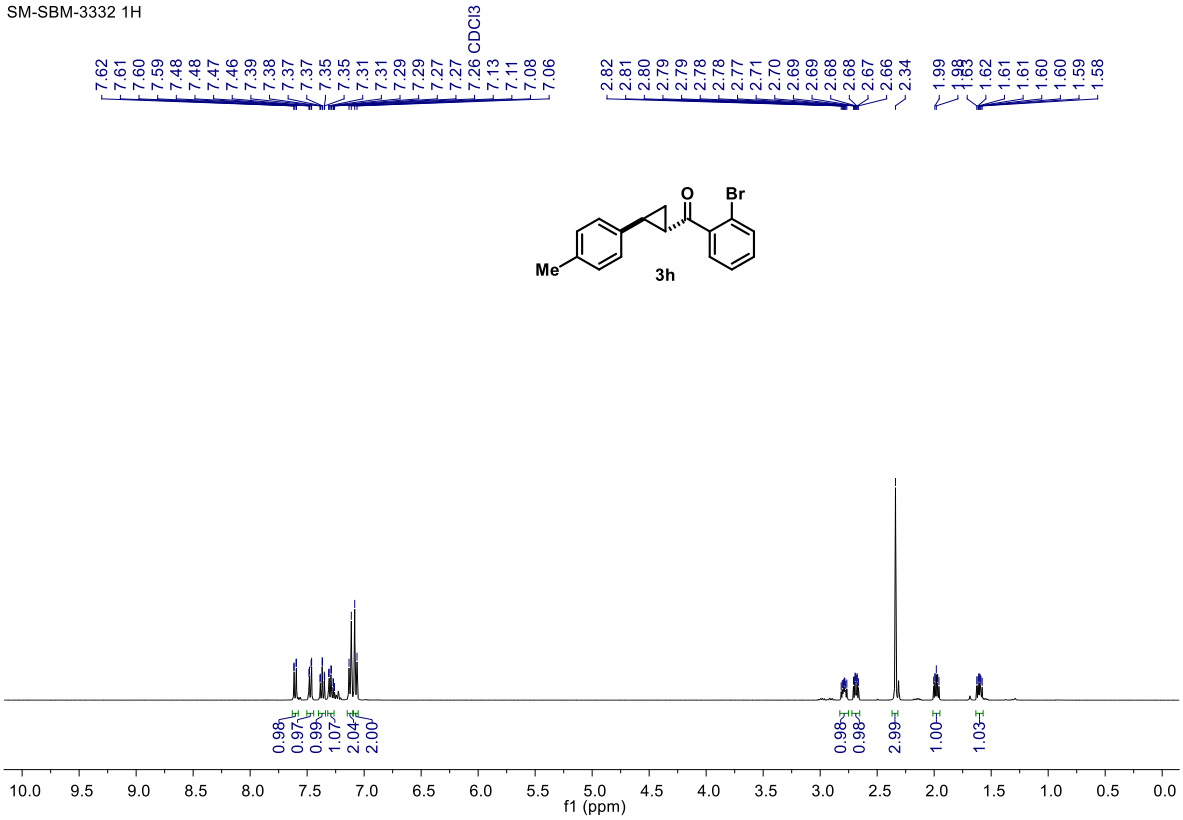
^{1}H NMR of **3g** (400 MHz, $CDCl_3$):



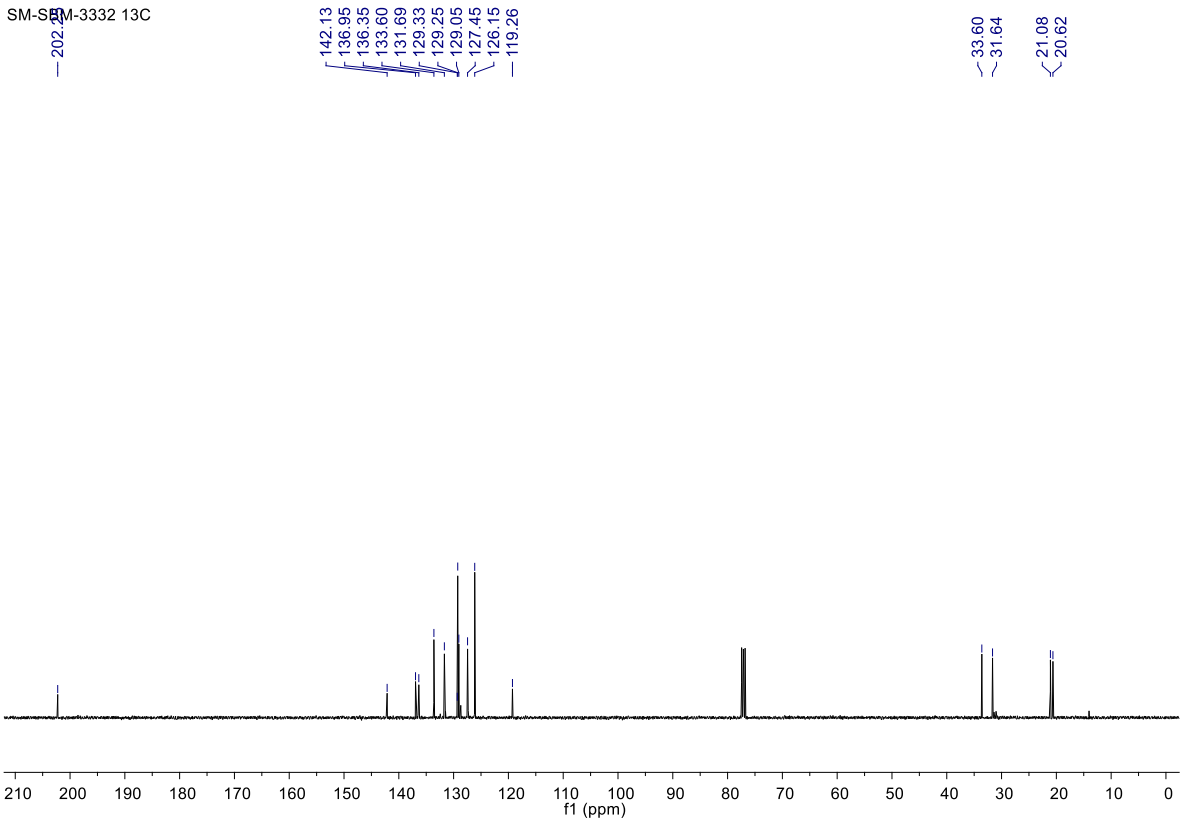
^{13}C{^{1}H} NMR of **3g** (101 MHz, $CDCl_3$):



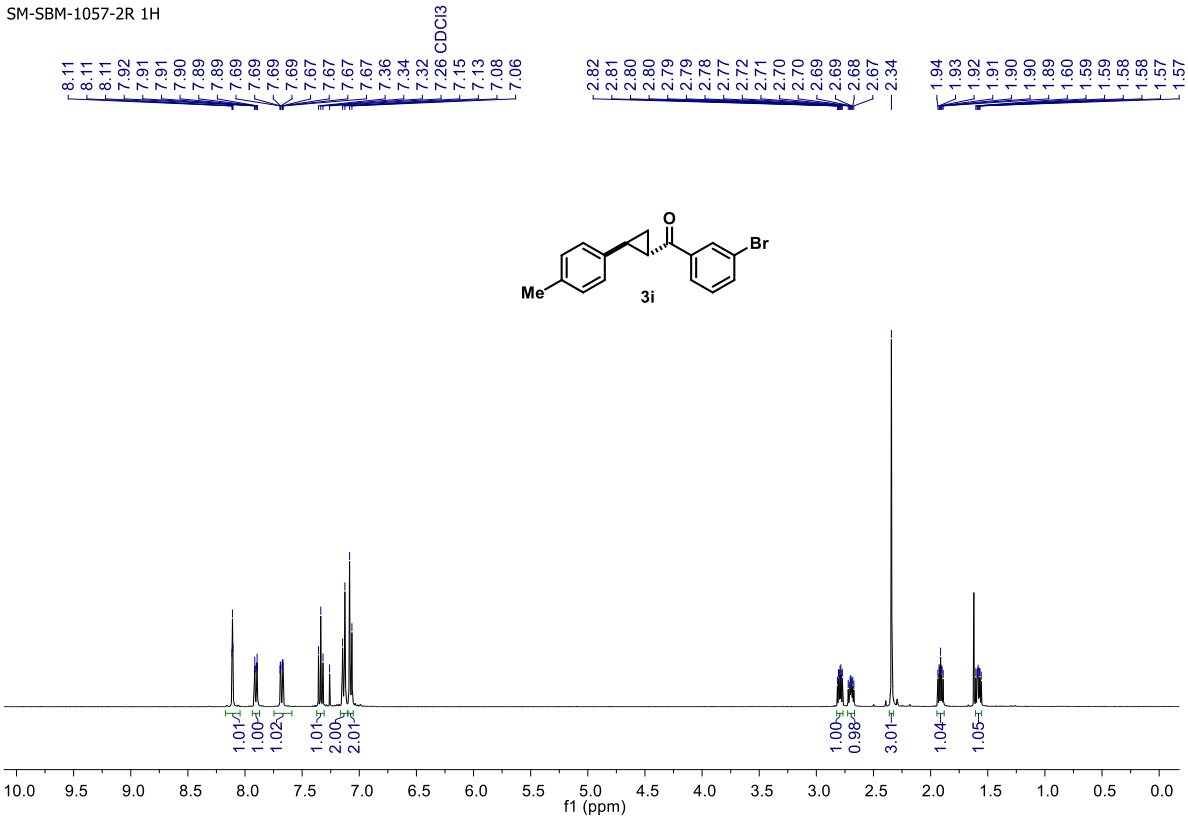
^{1}H NMR of **3h** (400 MHz, $CDCl_3$):



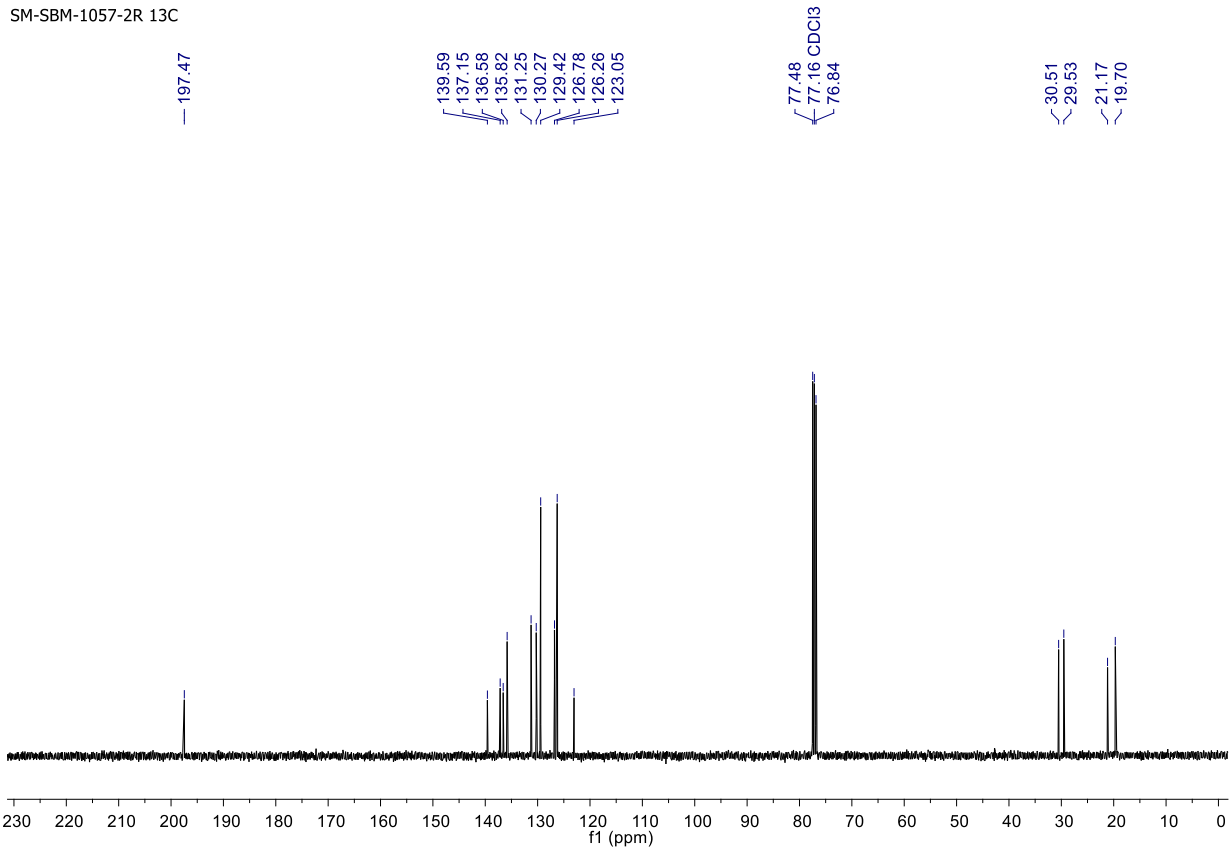
^{13}C{^{1}H} NMR of **3h** (101 MHz, $CDCl_3$):



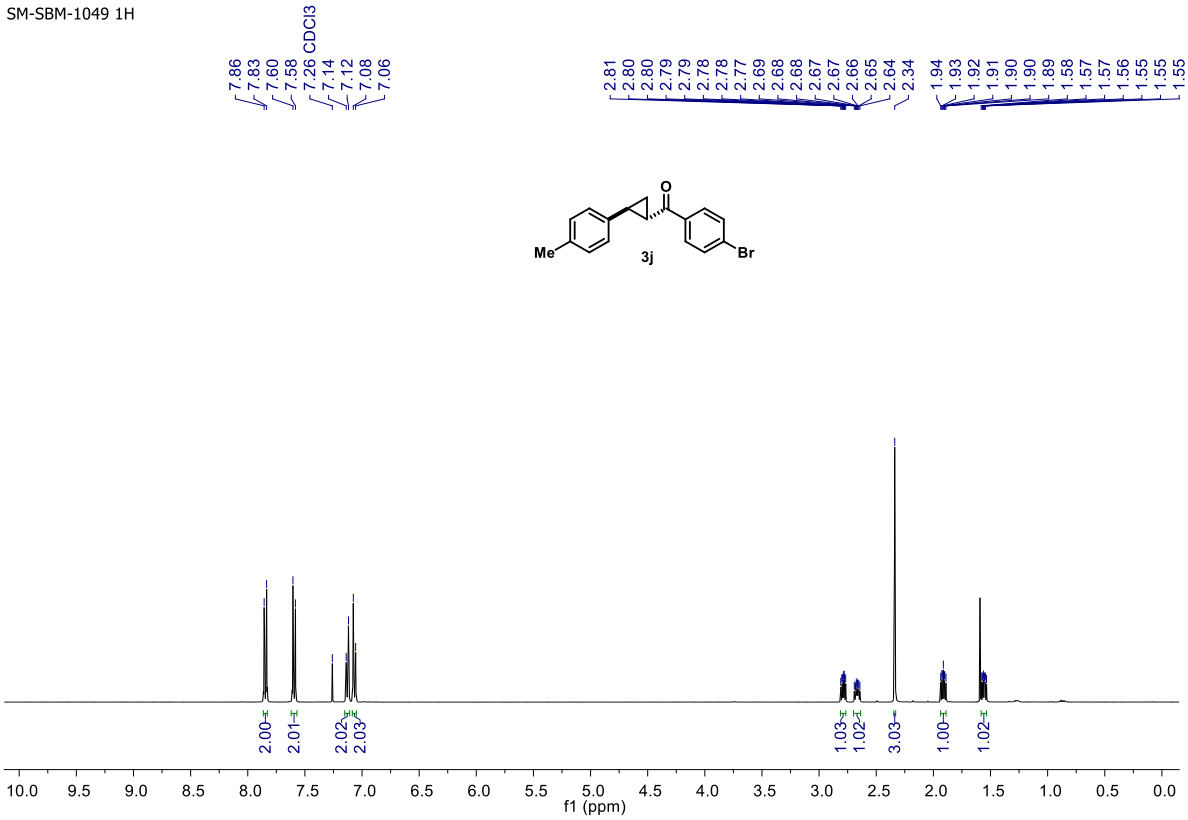
^{1}H NMR of **3i** (400 MHz, $CDCl_3$):



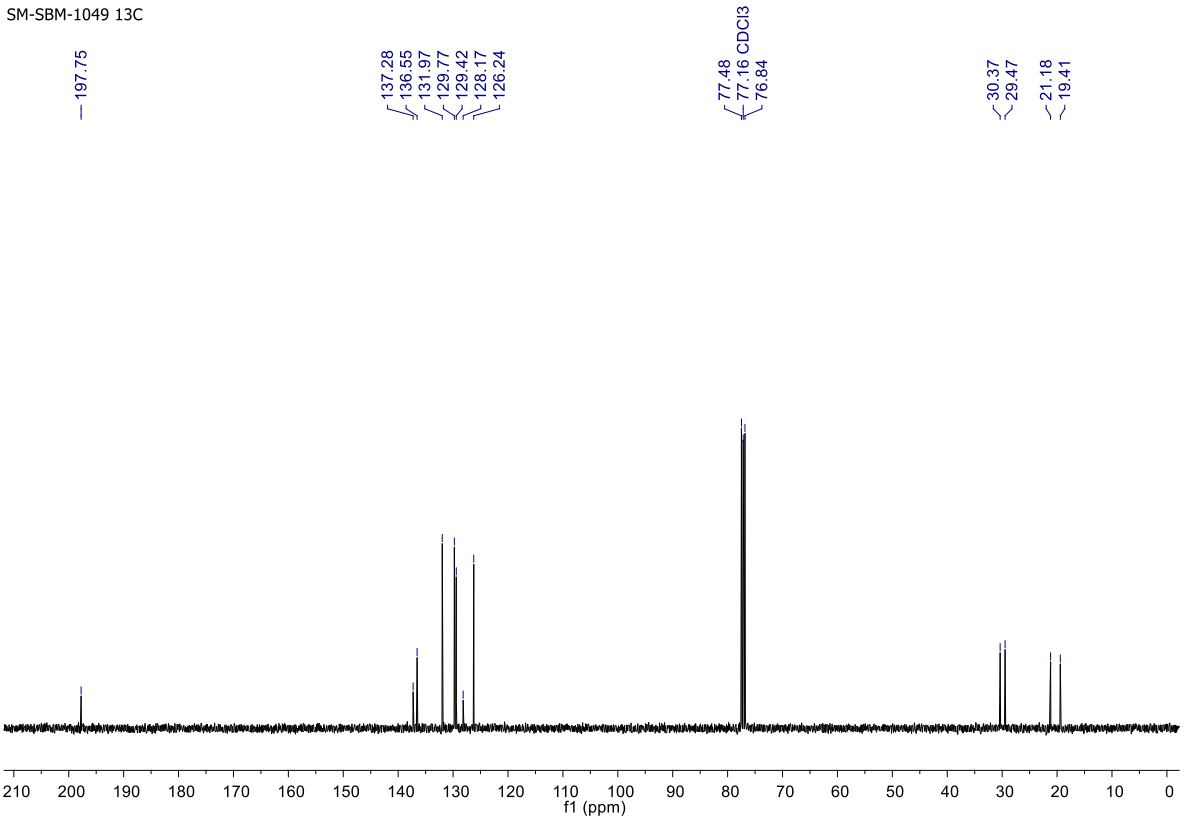
^{13}C{^{1}H} NMR of **3i** (101 MHz, $CDCl_3$):



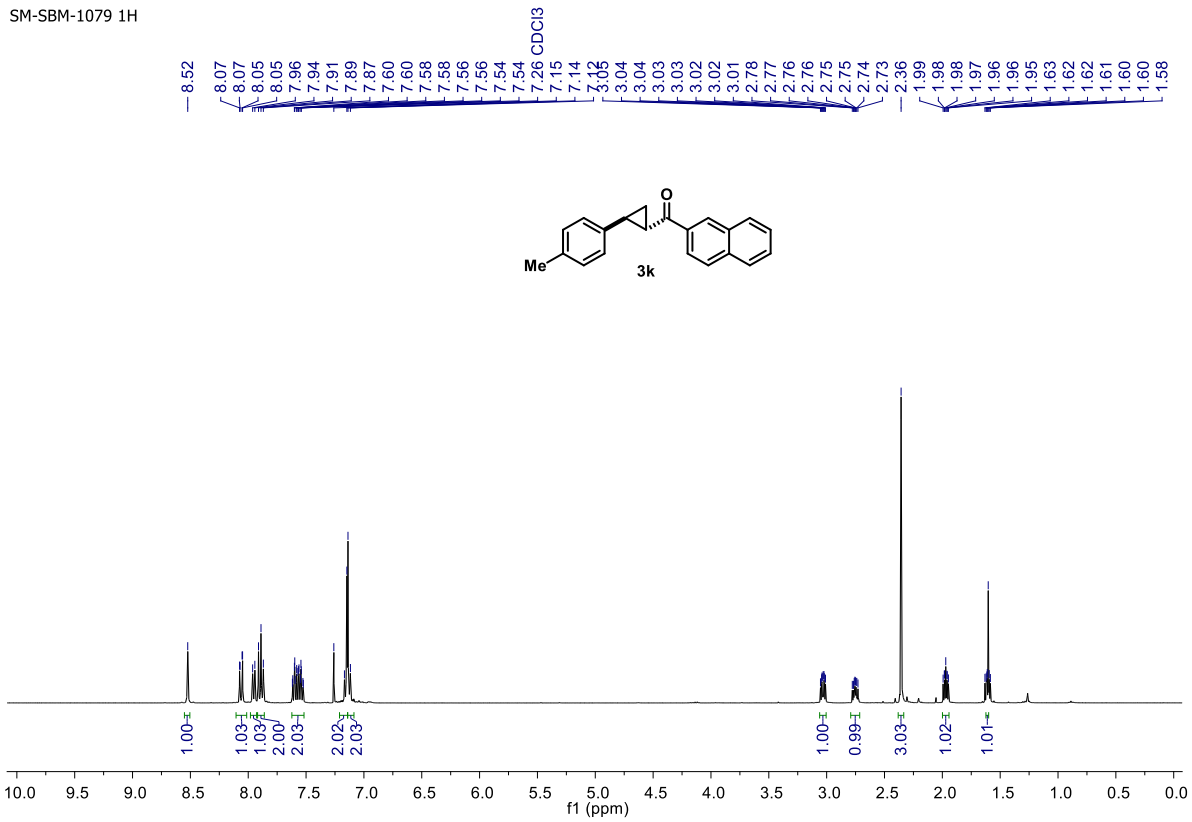
^{1}H NMR of **3j** (400 MHz, $CDCl_3$):



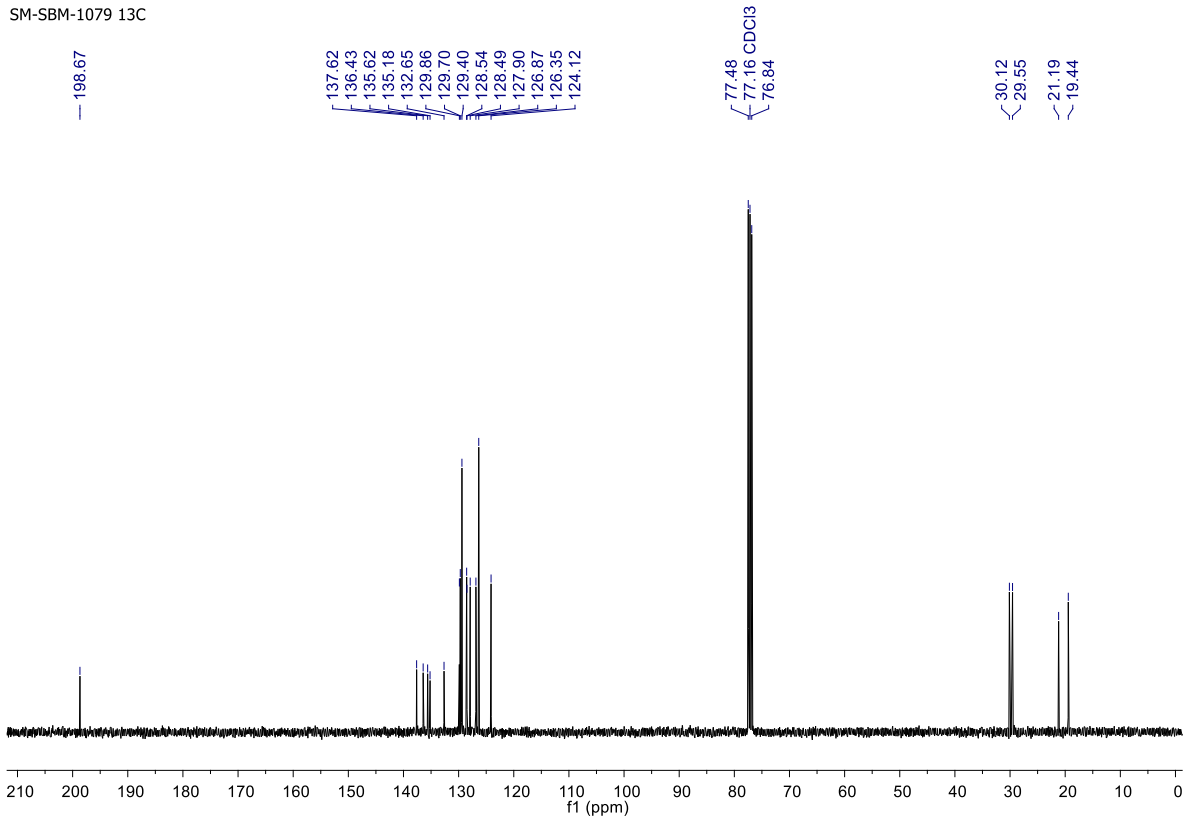
^{13}C{^{1}H} NMR of **3j** (101 MHz, $CDCl_3$):



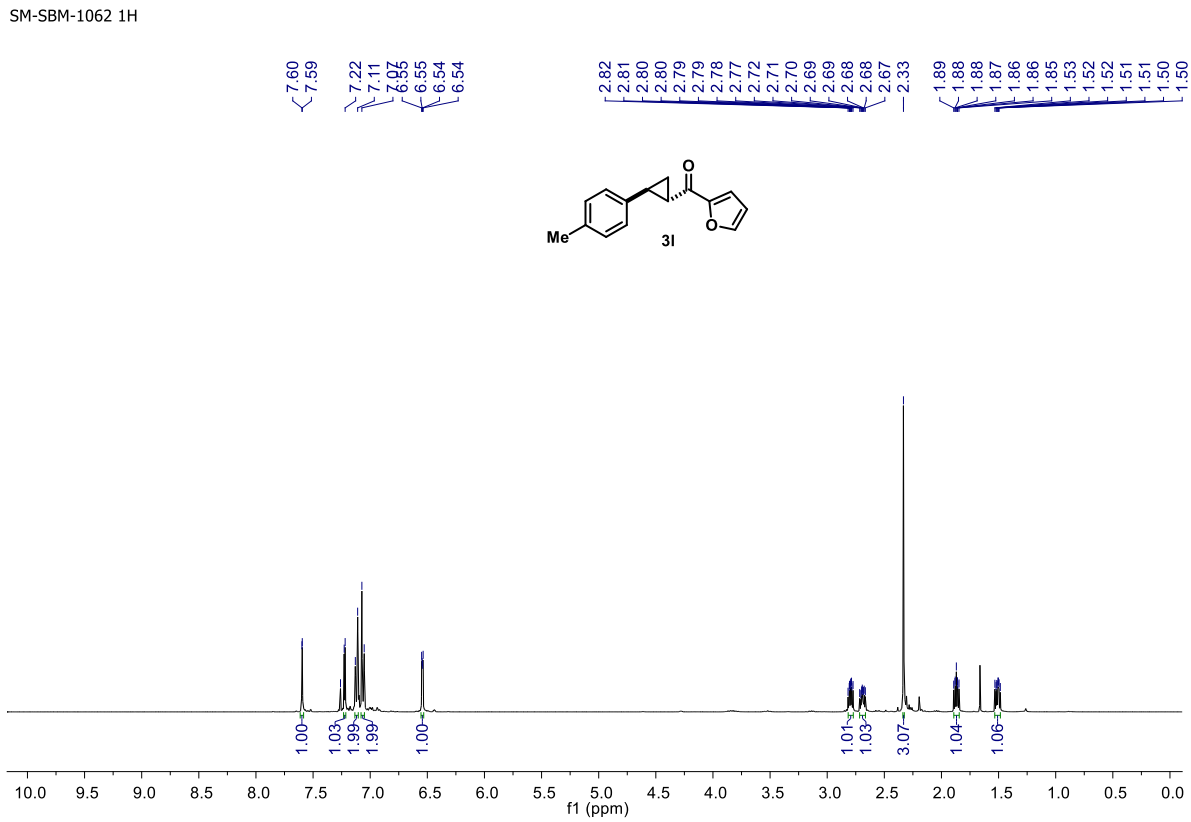
^{1}H NMR of **3k** (400 MHz, $CDCl_3$):



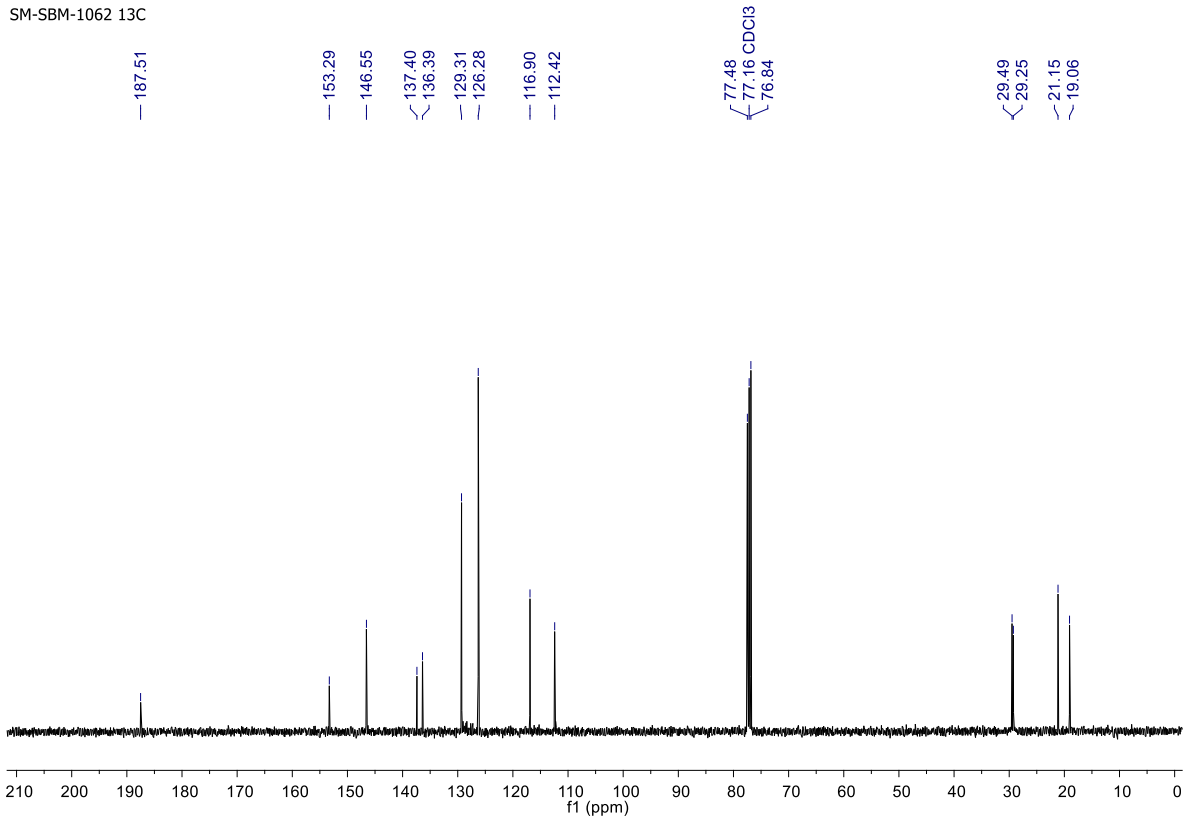
^{13}C{^{1}H} NMR of **3k** (101 MHz, $CDCl_3$):



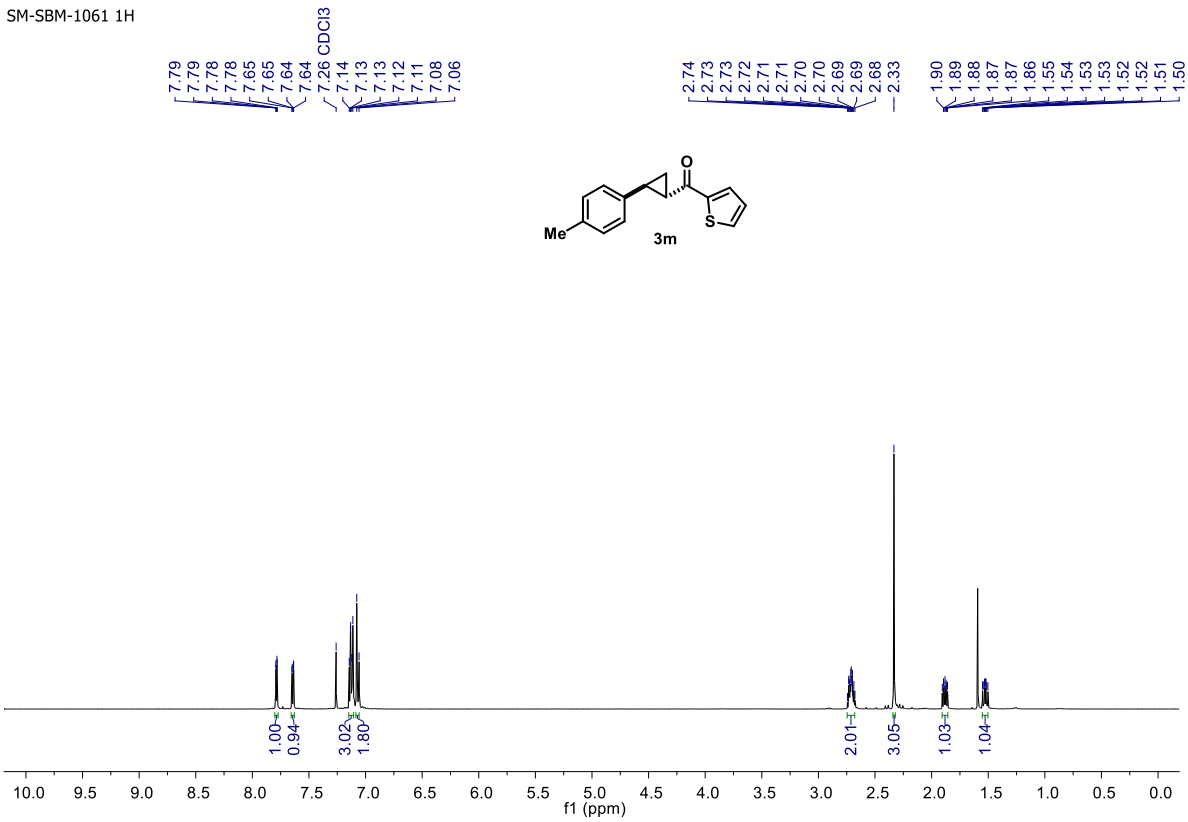
^{1}H NMR of **3l** (400 MHz, $CDCl_3$):



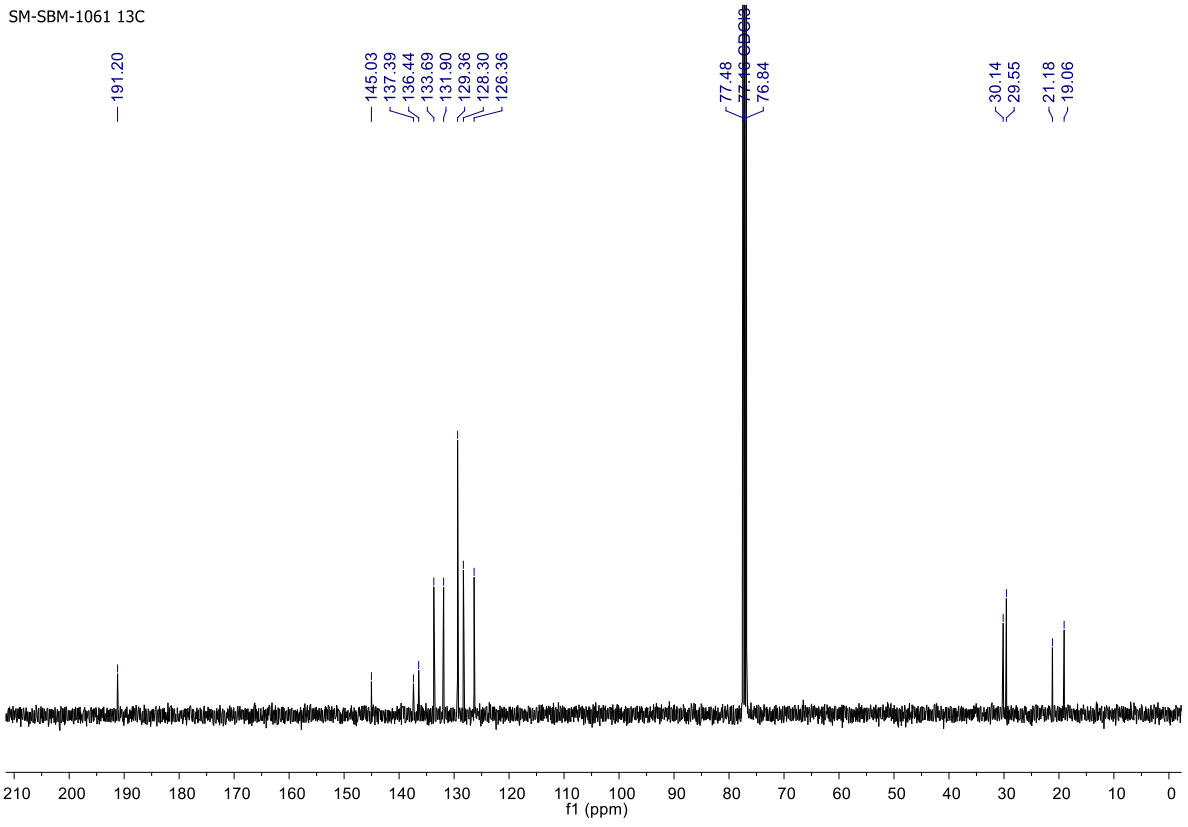
^{13}C{^{1}H} NMR of **3l** (101 MHz, $CDCl_3$):



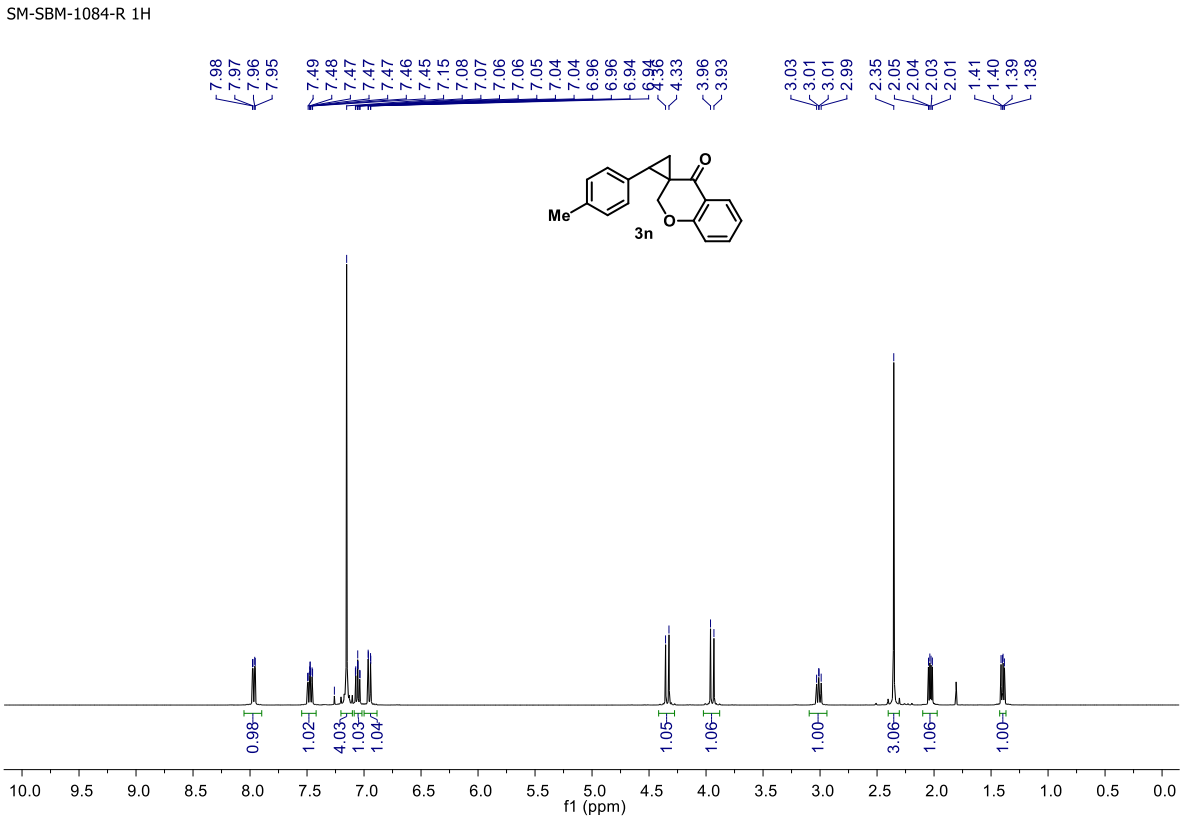
^{1}H NMR of **3m** (400 MHz, $CDCl_3$):



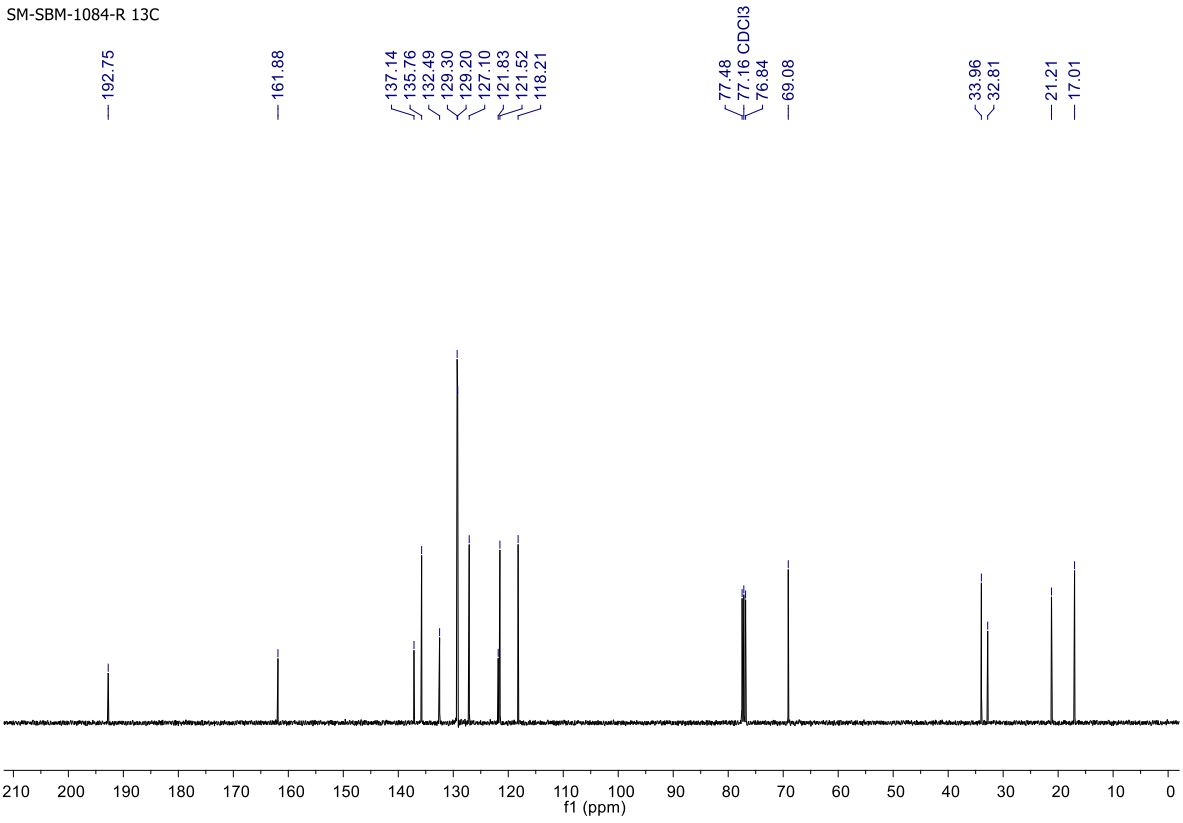
^{13}C{^{1}H} NMR of **3m** (101 MHz, $CDCl_3$):



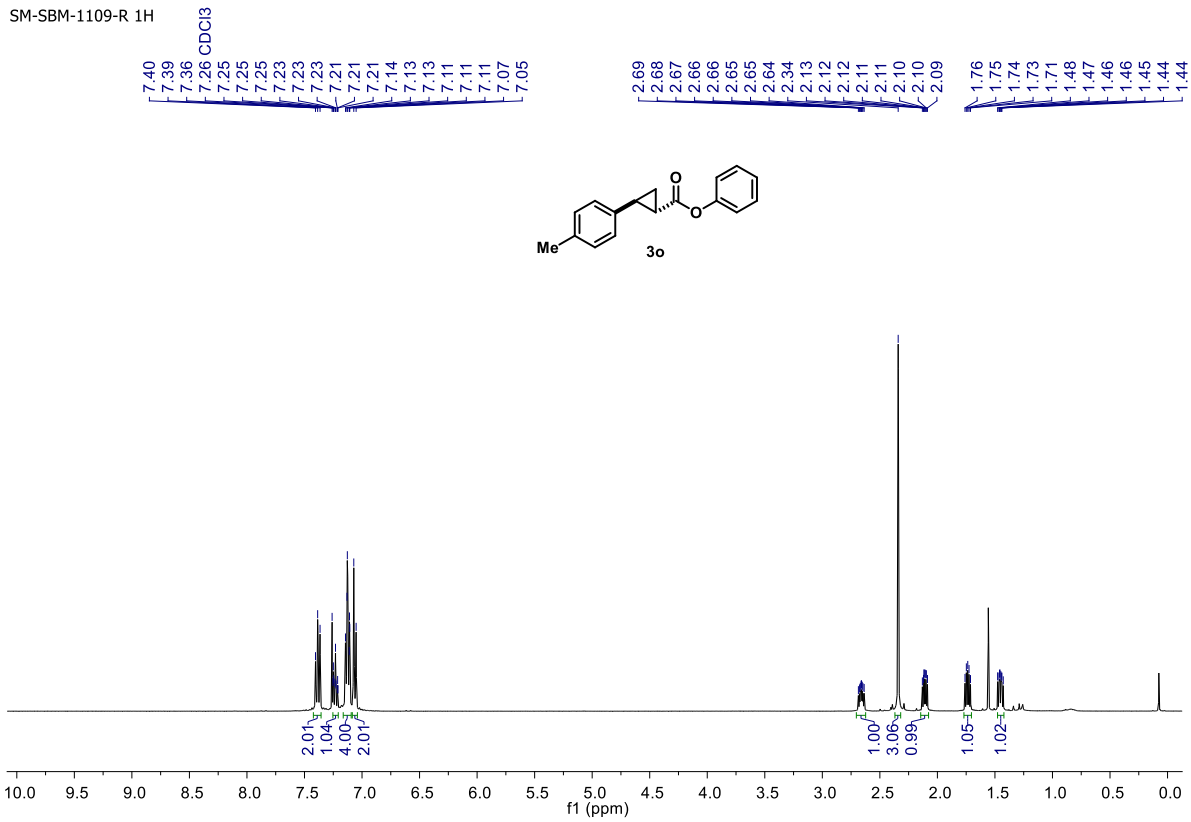
^{1}H NMR of **3n** (400 MHz, $CDCl_3$):



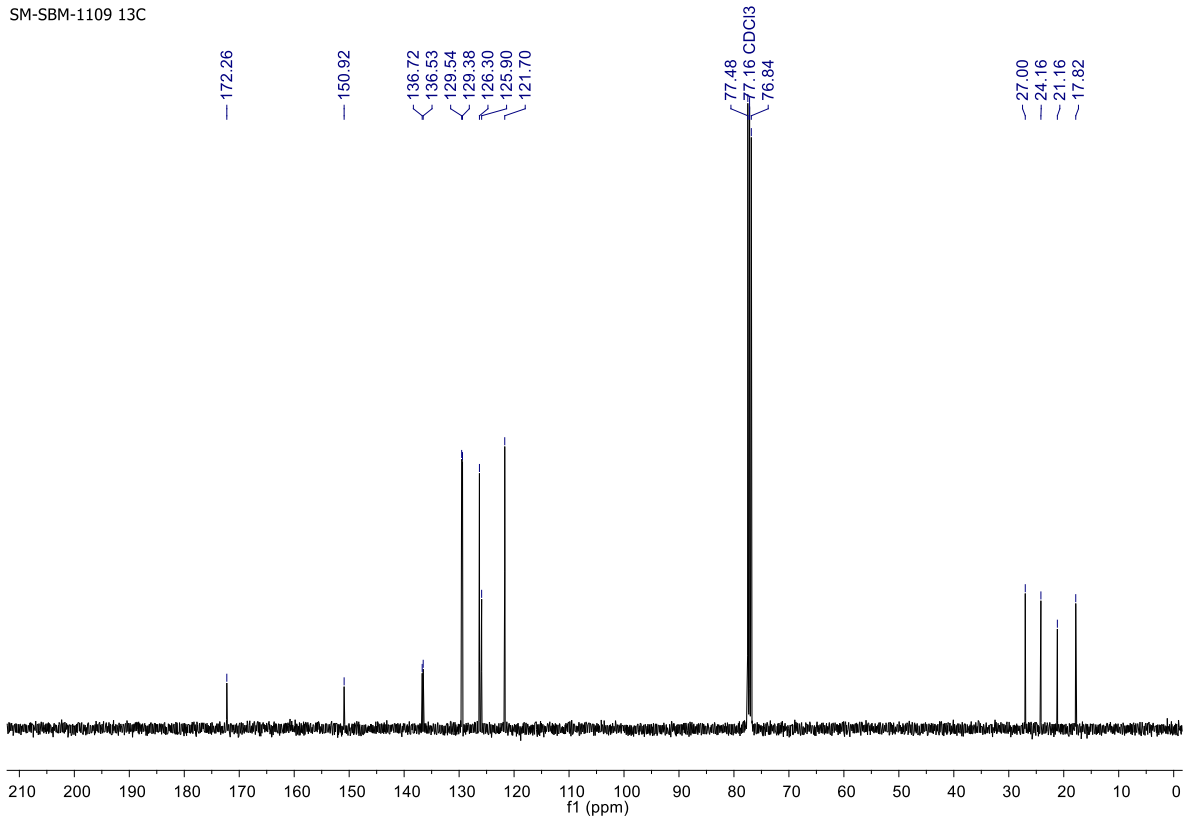
^{13}C{^{1}H} NMR of **3n** (101 MHz, $CDCl_3$):



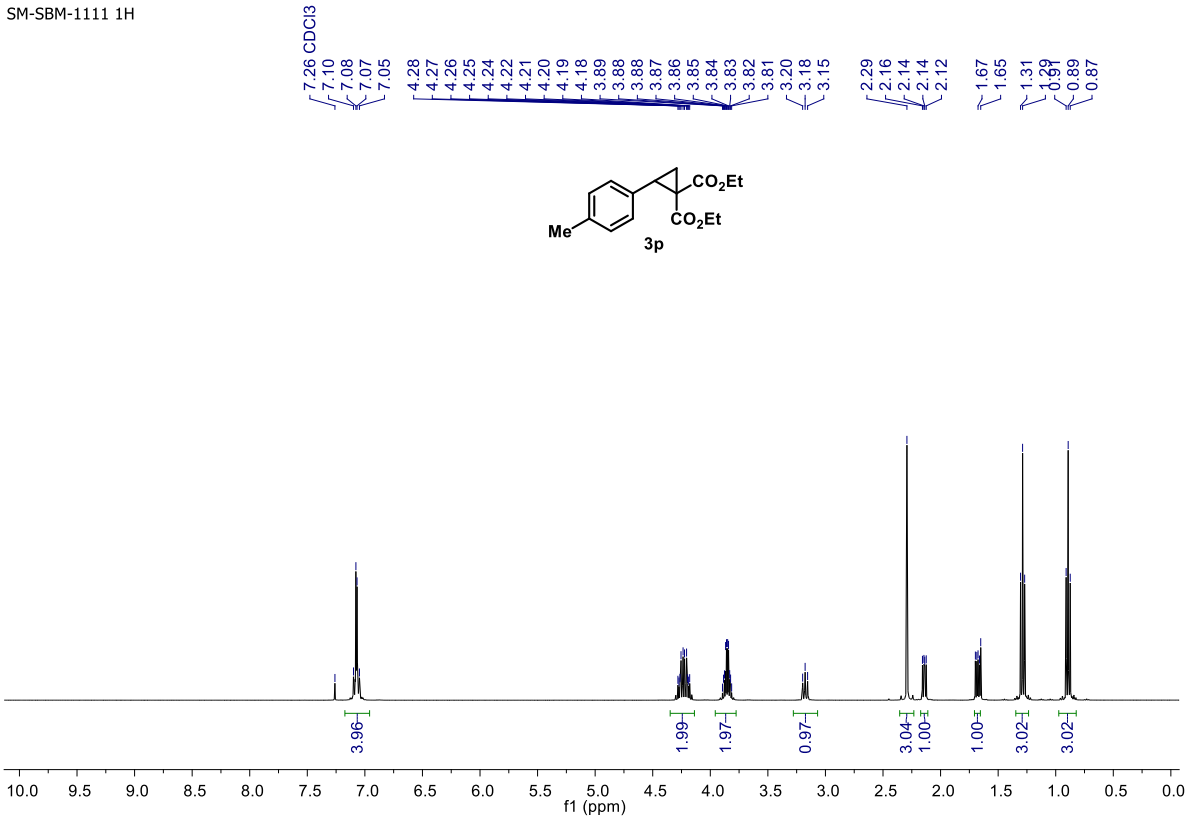
^{1}H NMR of **3o** (400 MHz, $CDCl_3$):



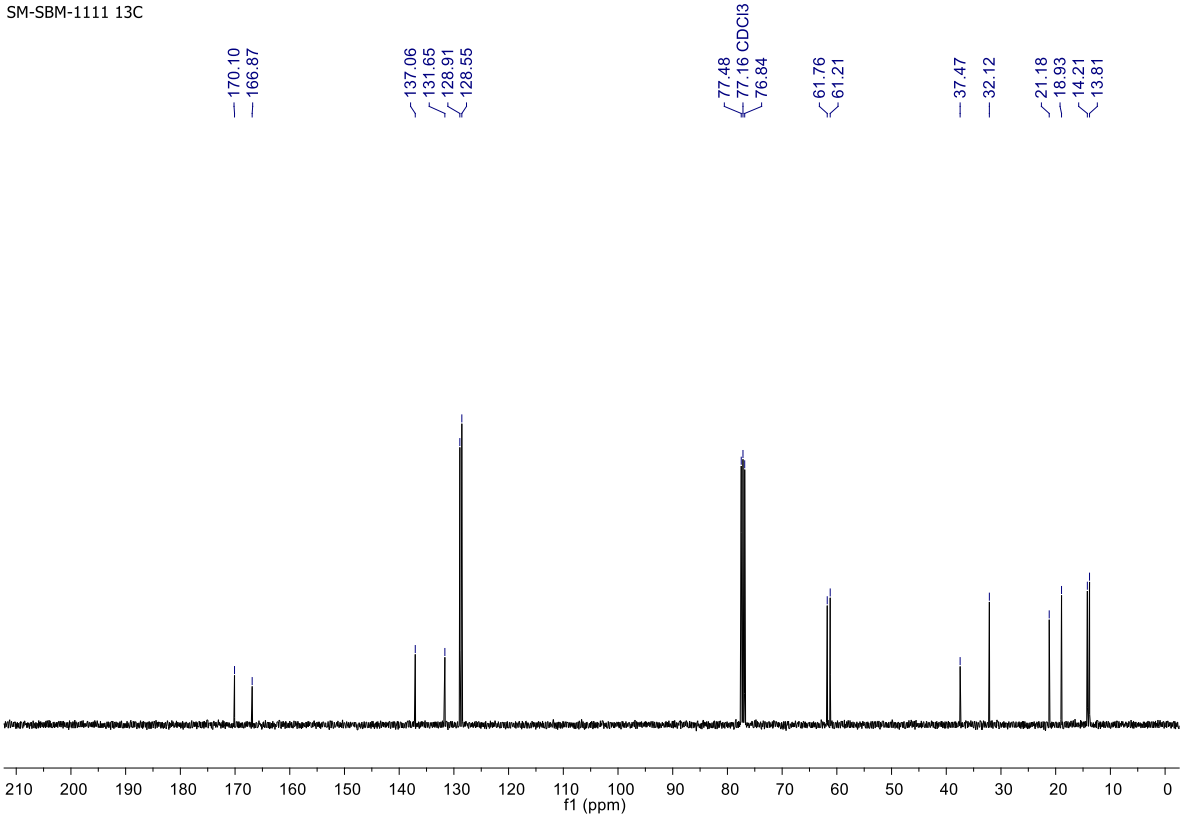
^{13}C{^{1}H} NMR of **3o** (101 MHz, $CDCl_3$):



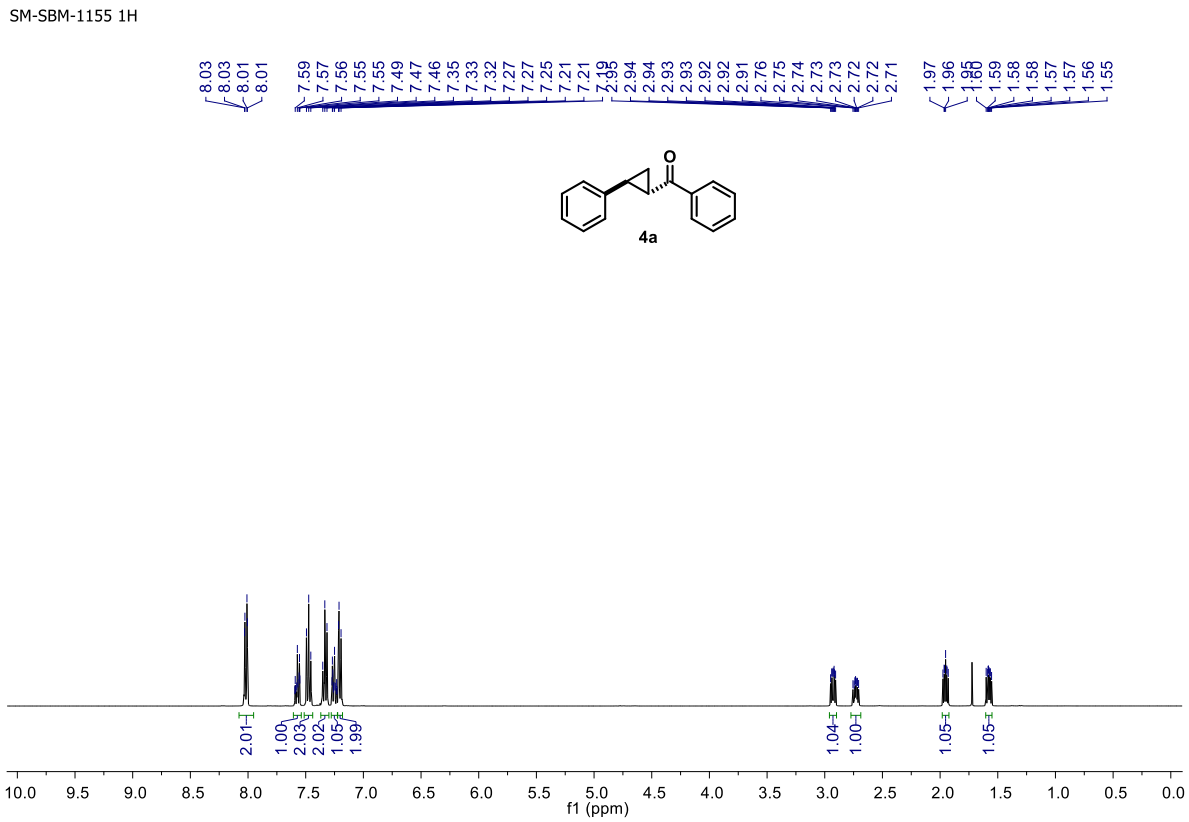
^{1}H NMR of **3p** (400 MHz, $CDCl_3$):



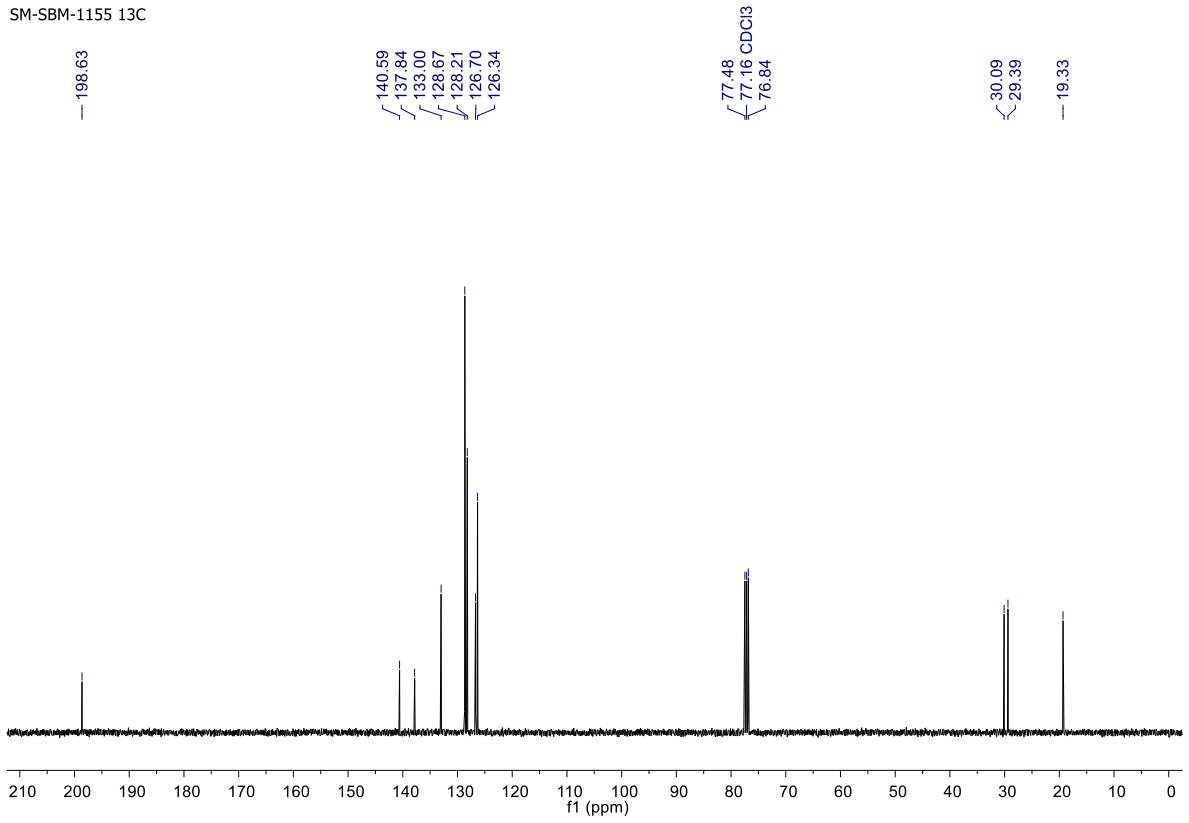
^{13}C{^{1}H} NMR of **3p** (101 MHz, $CDCl_3$):



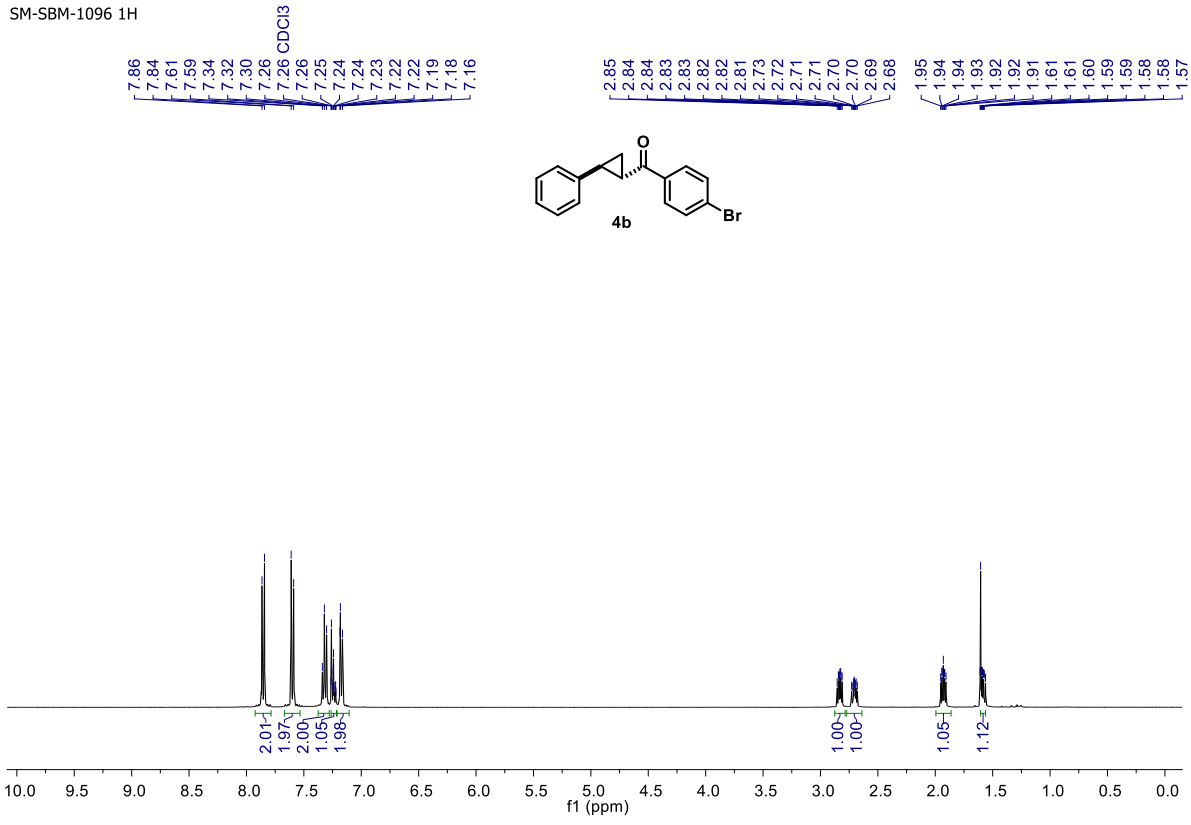
^{1}H NMR of **4a** (400 MHz, $CDCl_3$):



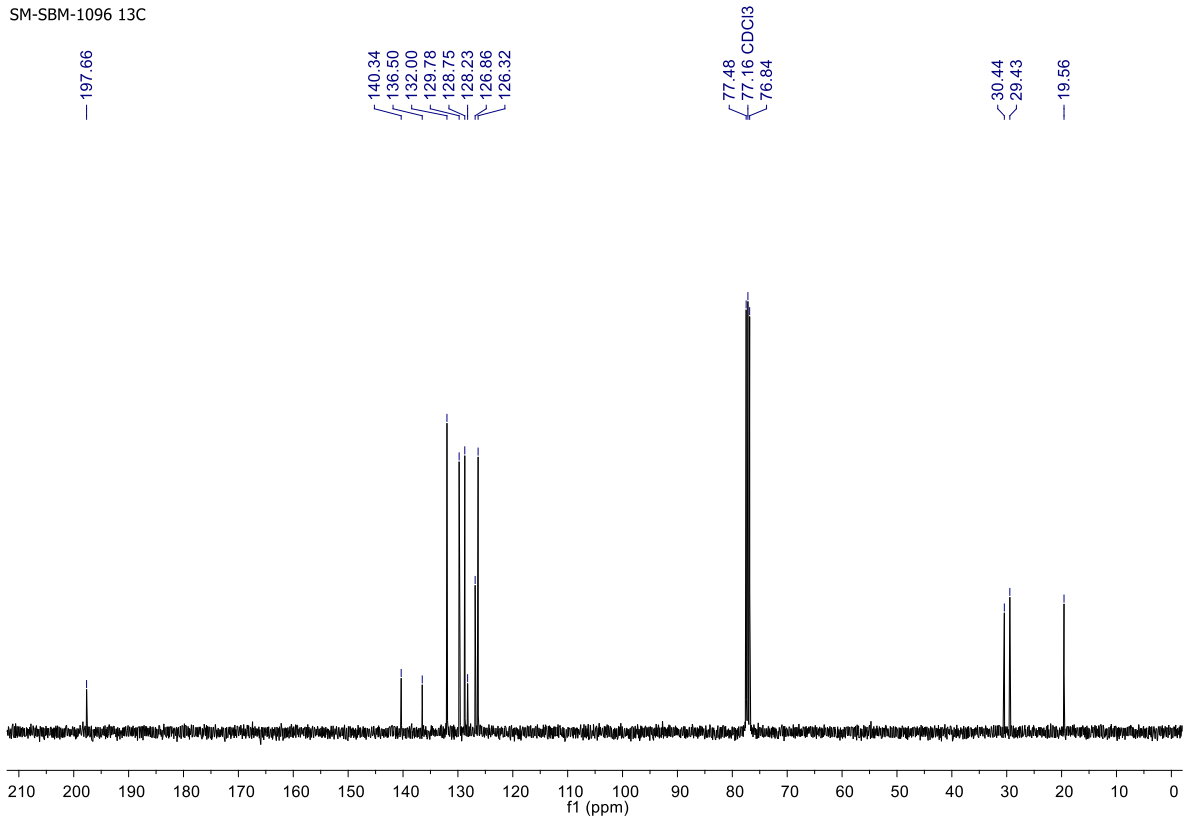
^{13}C{^{1}H} NMR of **4a** (101 MHz, $CDCl_3$):



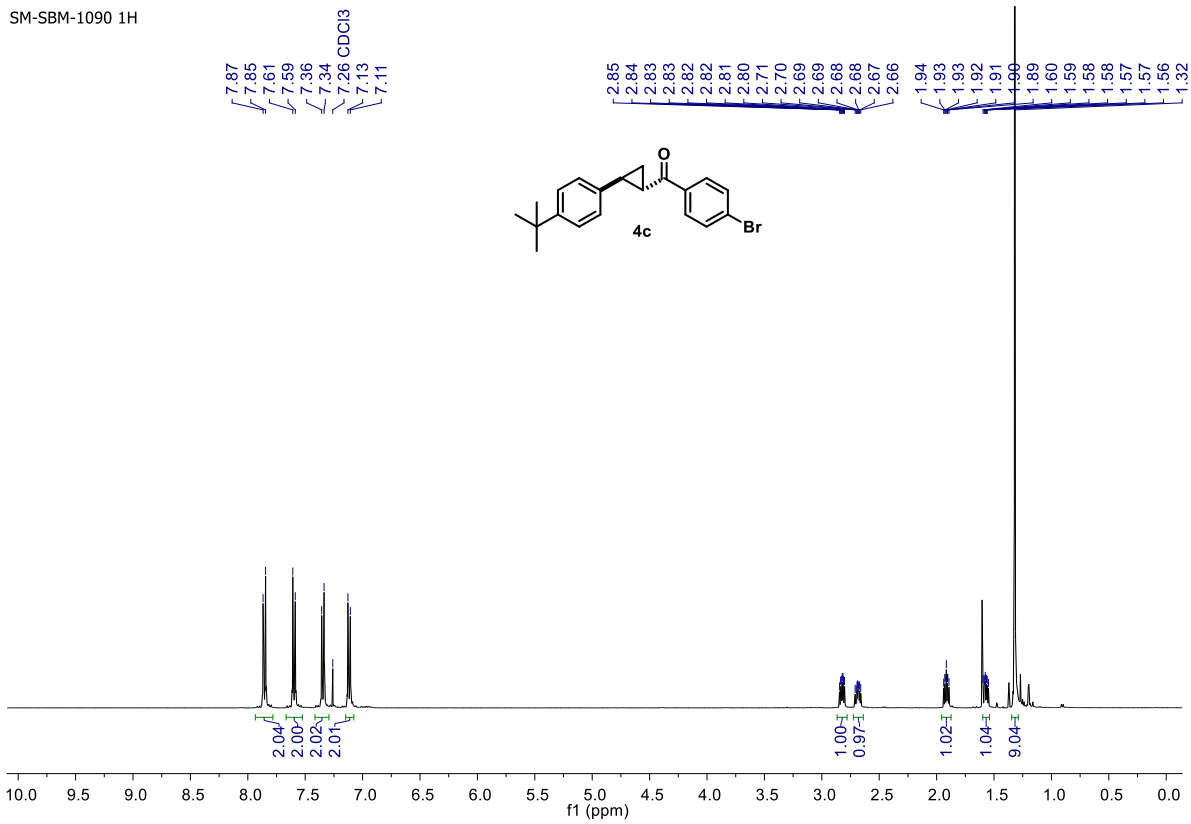
^{1}H NMR of **4b** (400 MHz, $CDCl_3$):



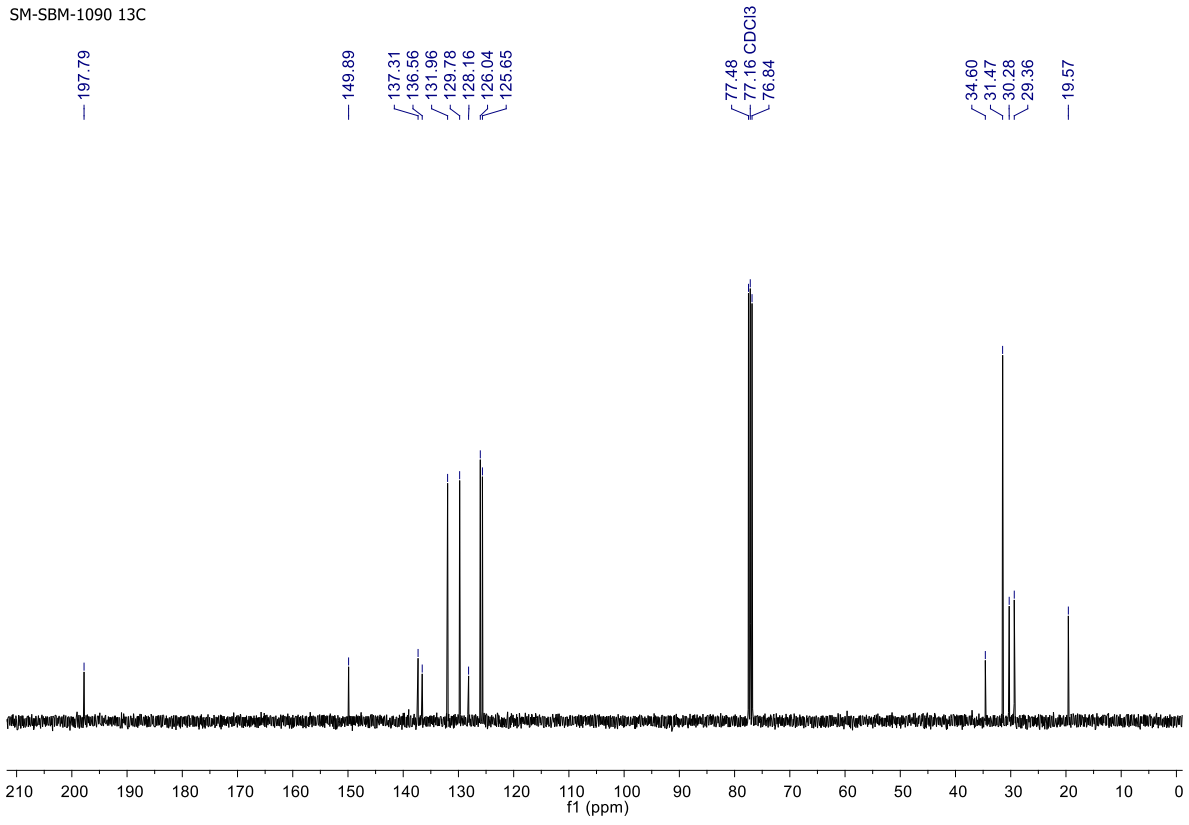
^{13}C{^{1}H} NMR of **4b** (101 MHz, $CDCl_3$):



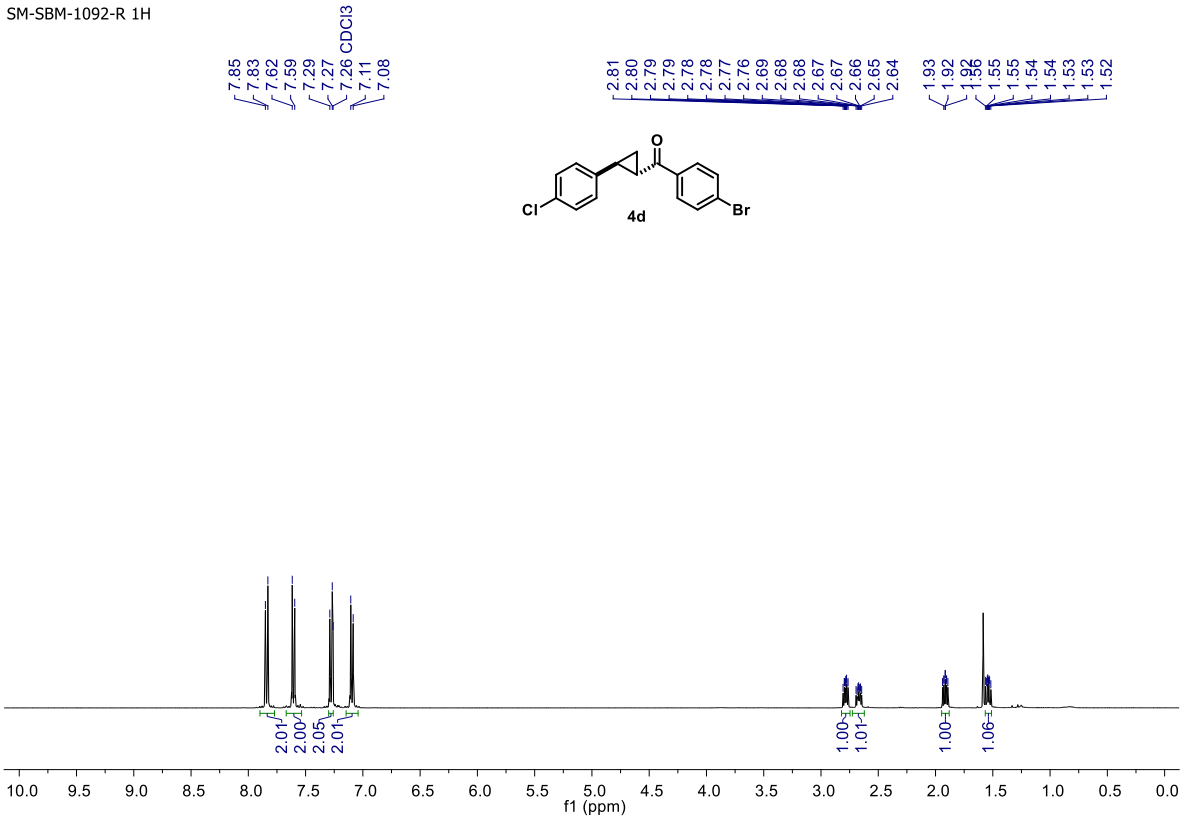
^{1}H NMR of **4c** (400 MHz, $CDCl_3$):



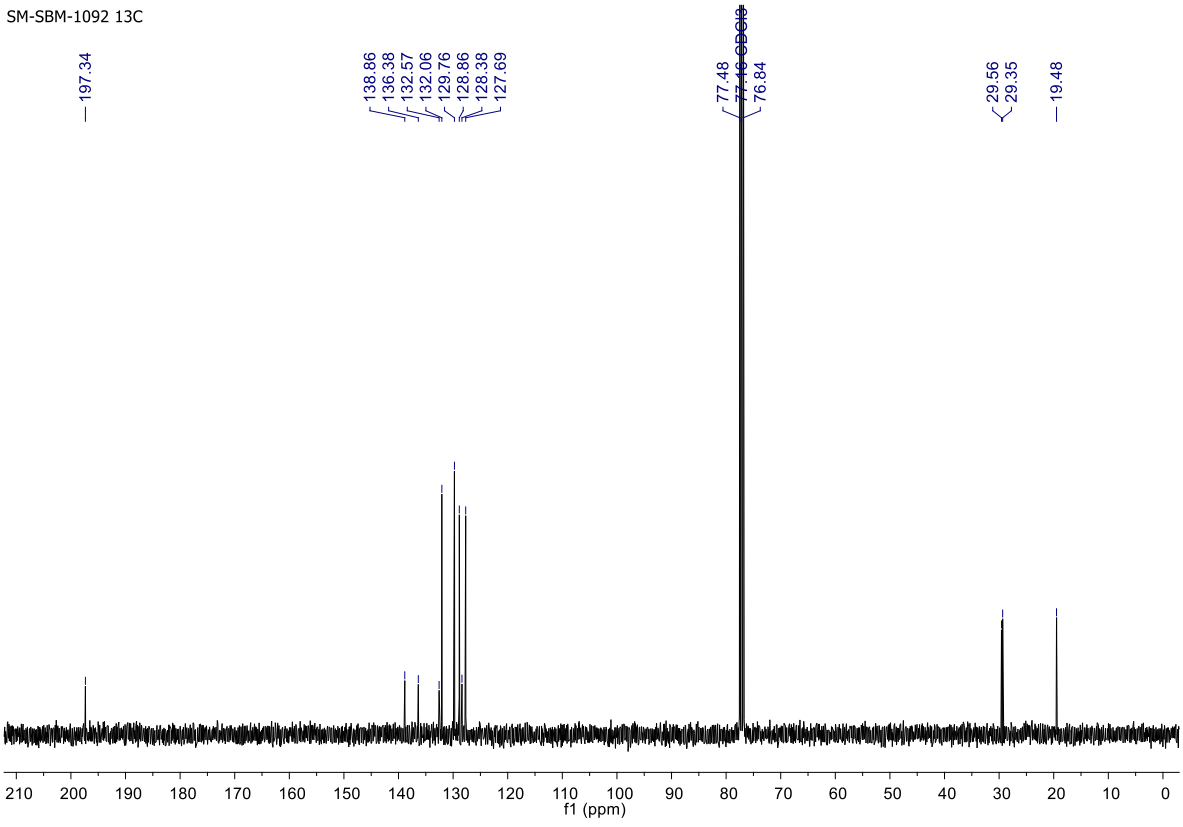
^{13}C{^{1}H} NMR of **4c** (101 MHz, $CDCl_3$):



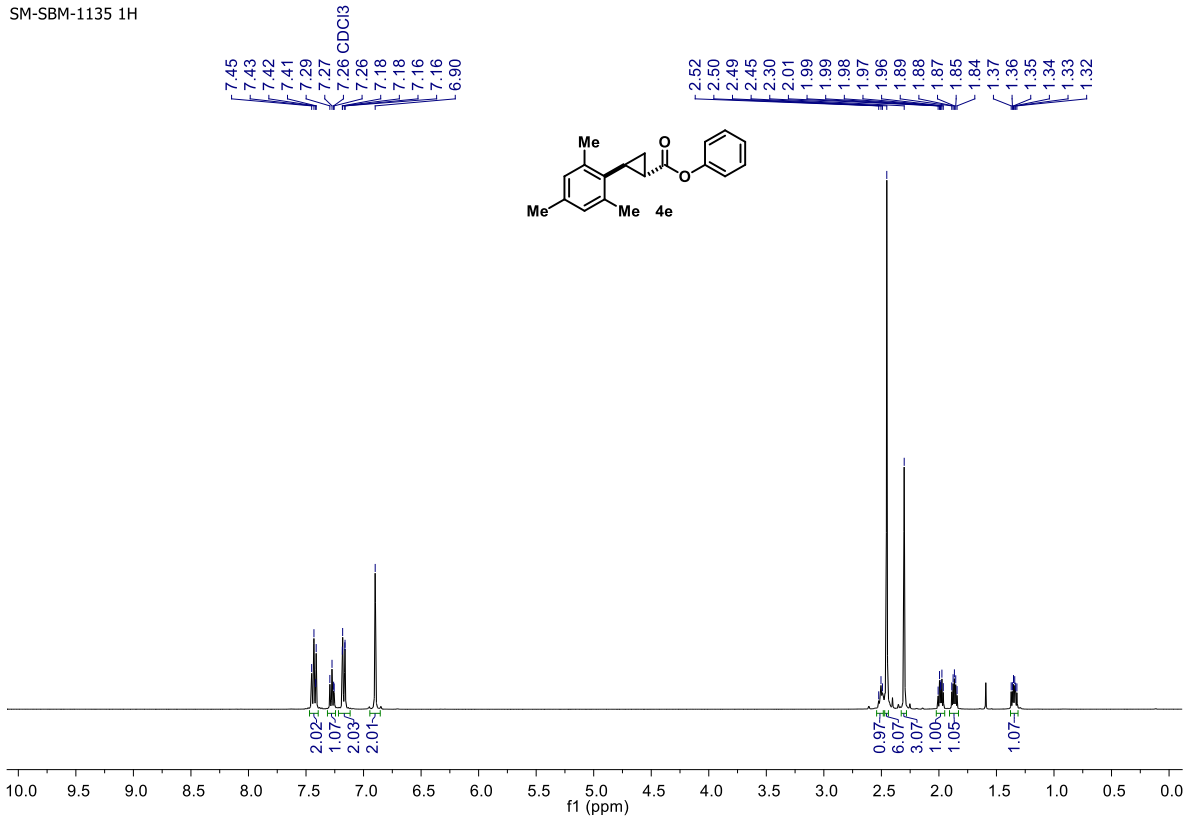
^{1}H NMR of **4d** (400 MHz, $CDCl_3$):



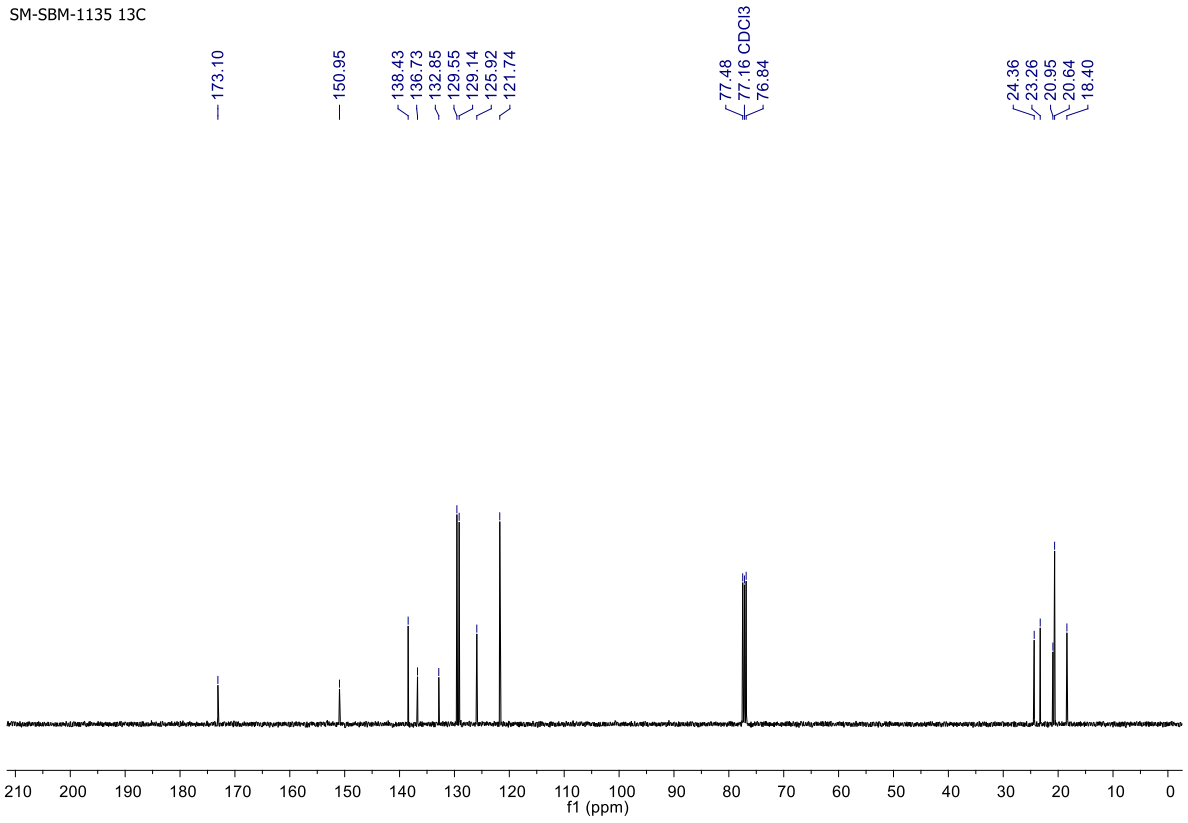
^{13}C{^{1}H} NMR of **4d** (101 MHz, $CDCl_3$):



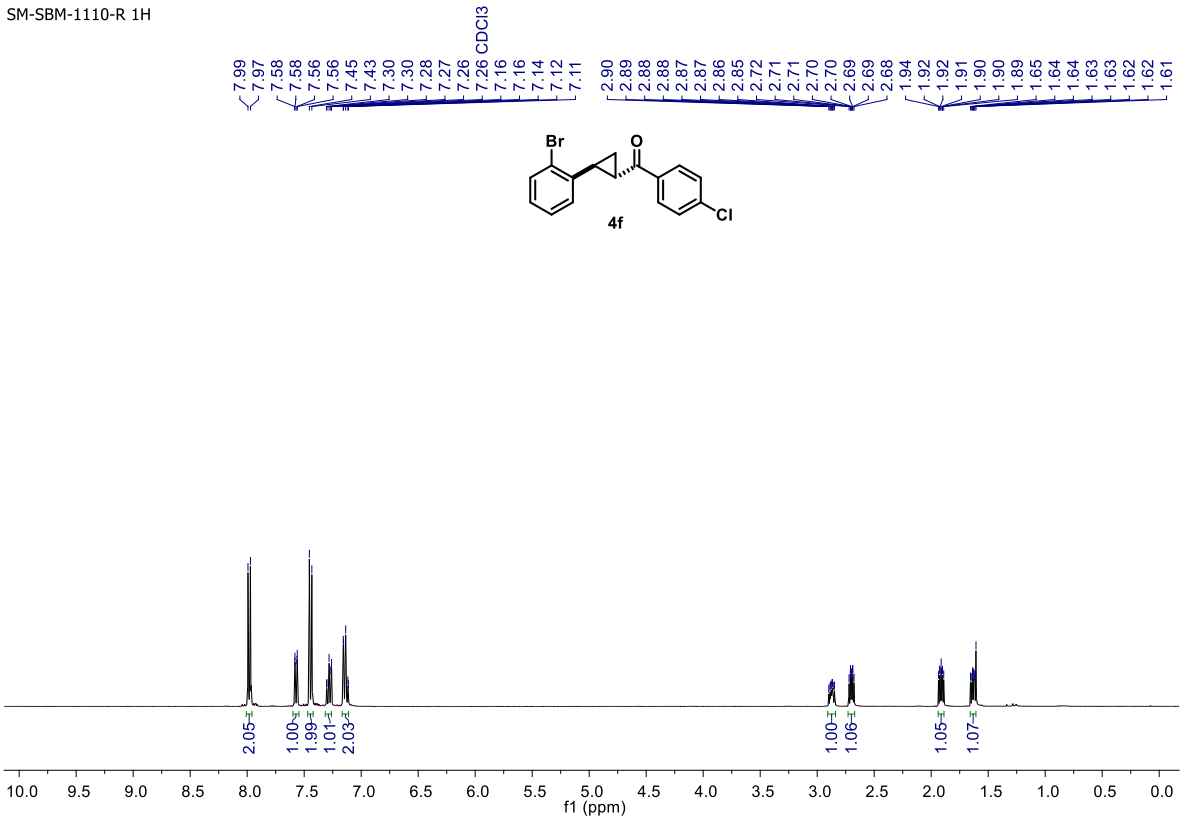
^{1}H NMR of **4e** (400 MHz, $CDCl_3$):



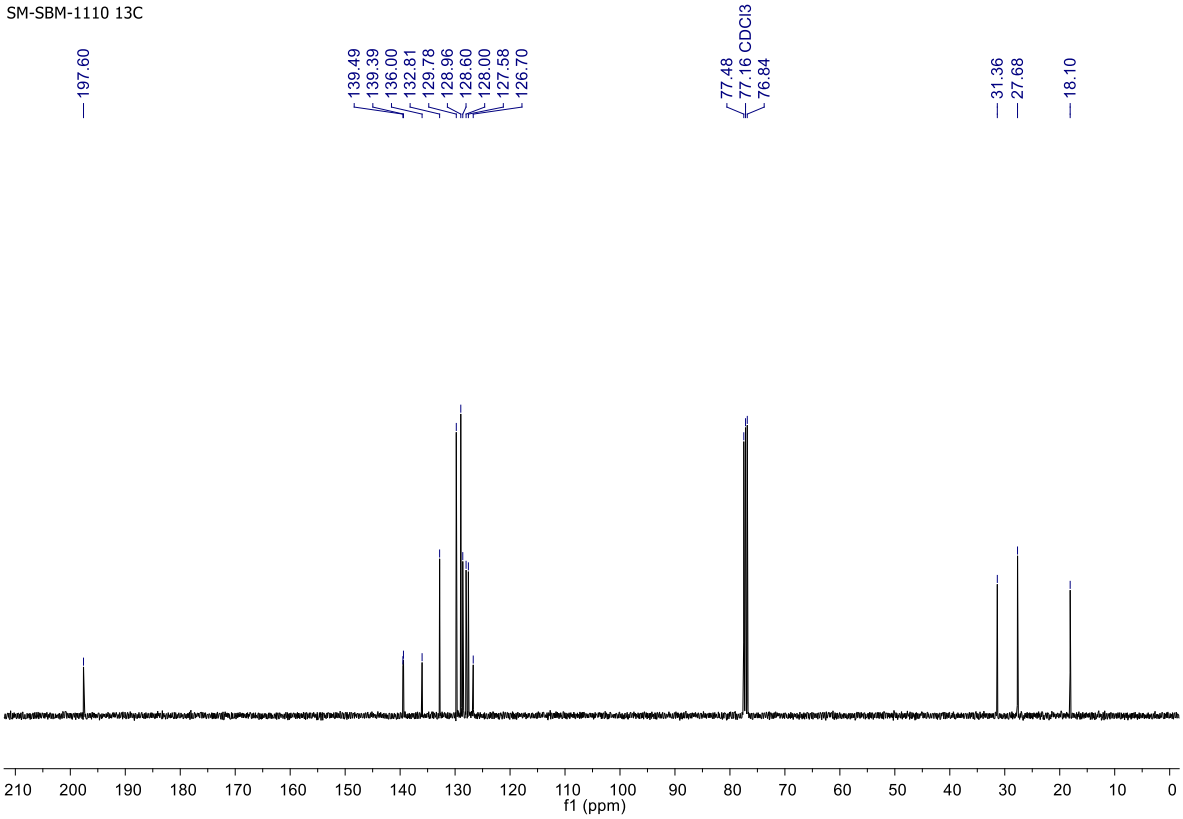
^{13}C{^{1}H} NMR of **4e** (101 MHz, $CDCl_3$):



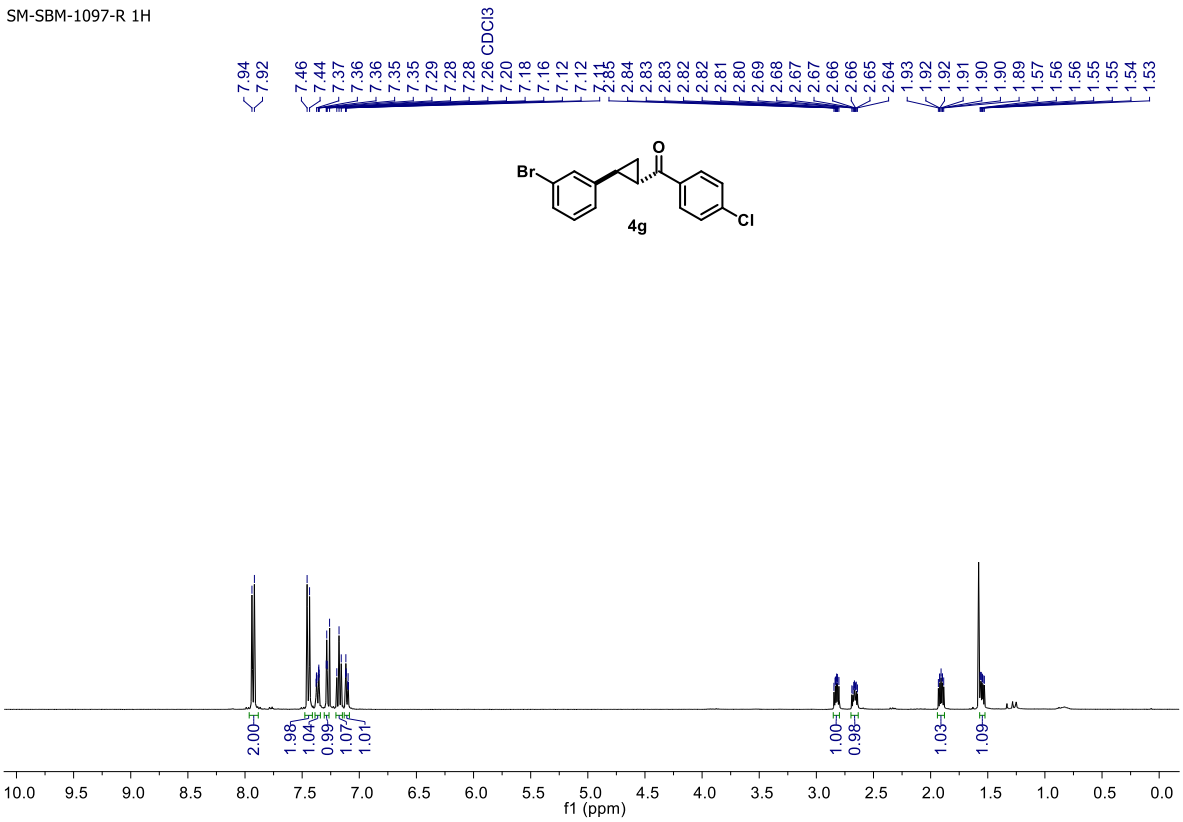
^{1}H NMR of **4f** (400 MHz, $CDCl_3$):



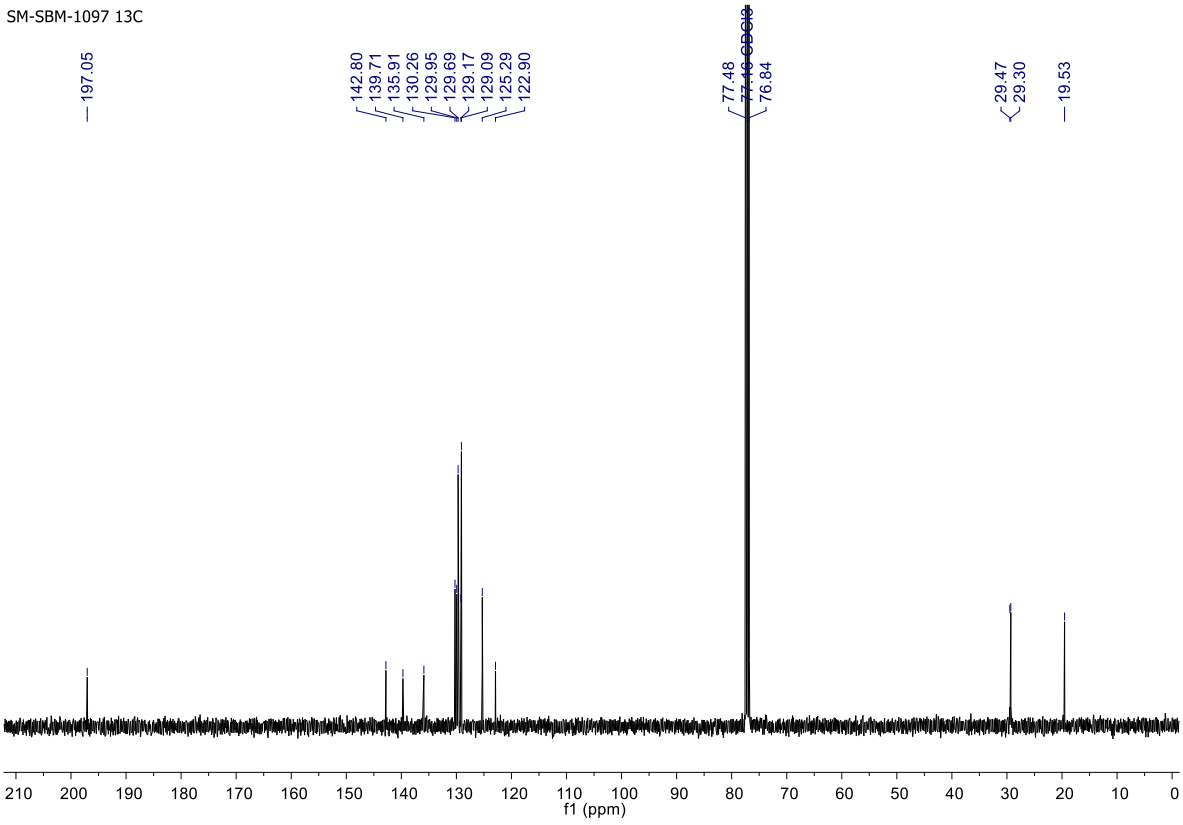
^{13}C{^{1}H} NMR of **4f** (101 MHz, $CDCl_3$):



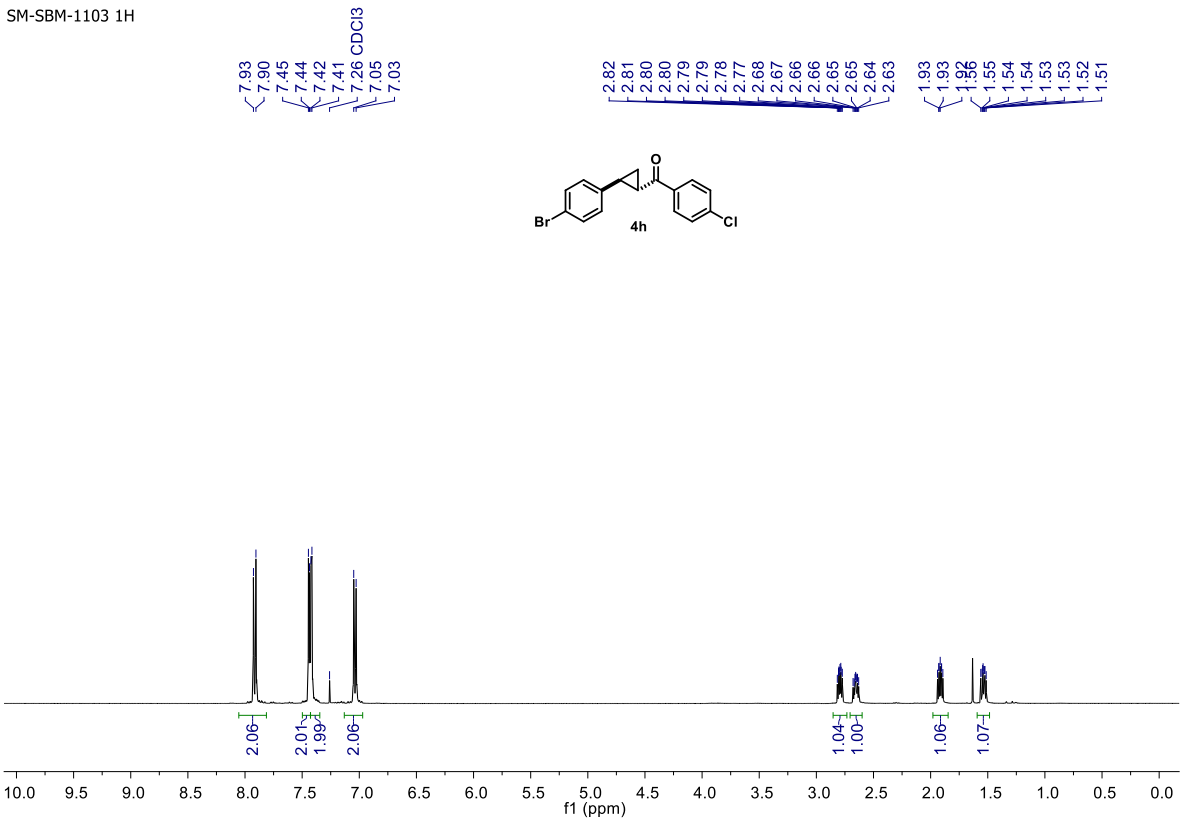
^{1}H NMR of **4g** (400 MHz, $CDCl_3$):



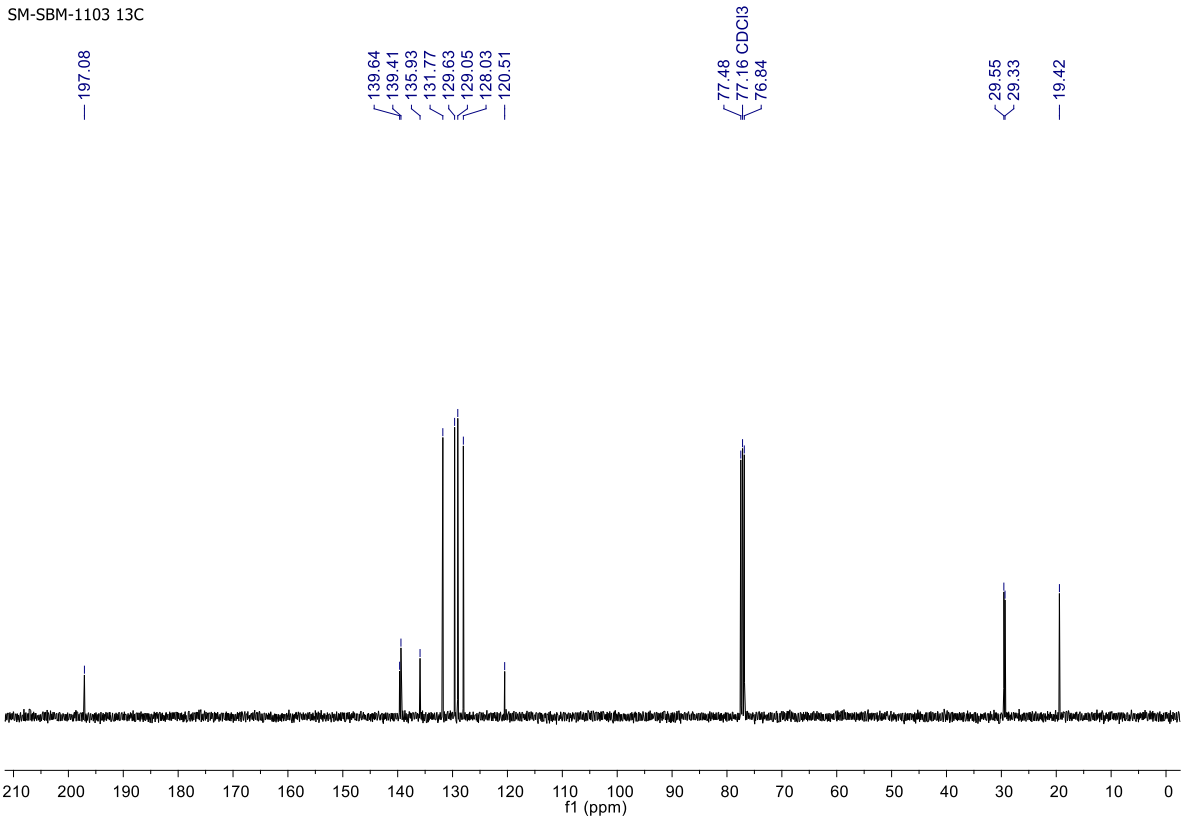
^{13}C{^{1}H} NMR of **4g** (101 MHz, $CDCl_3$):



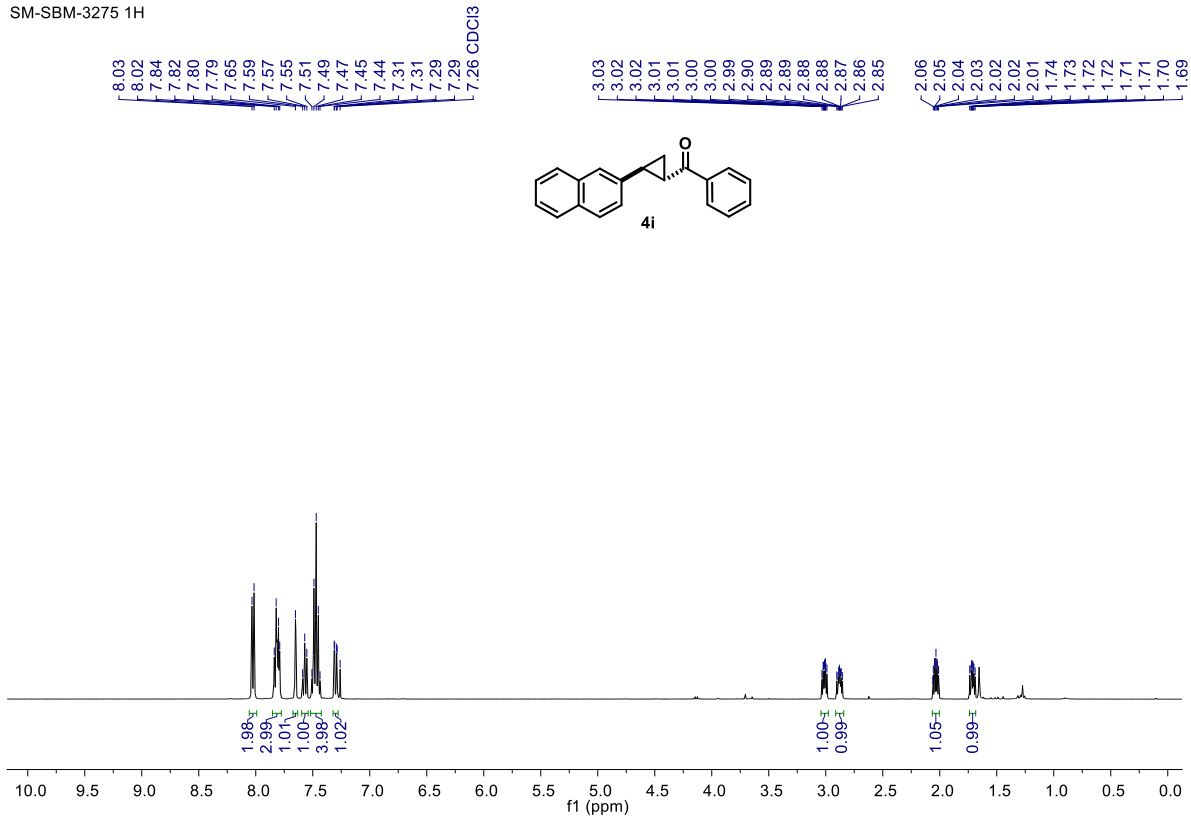
^{1}H NMR of **4h** (400 MHz, $CDCl_3$):



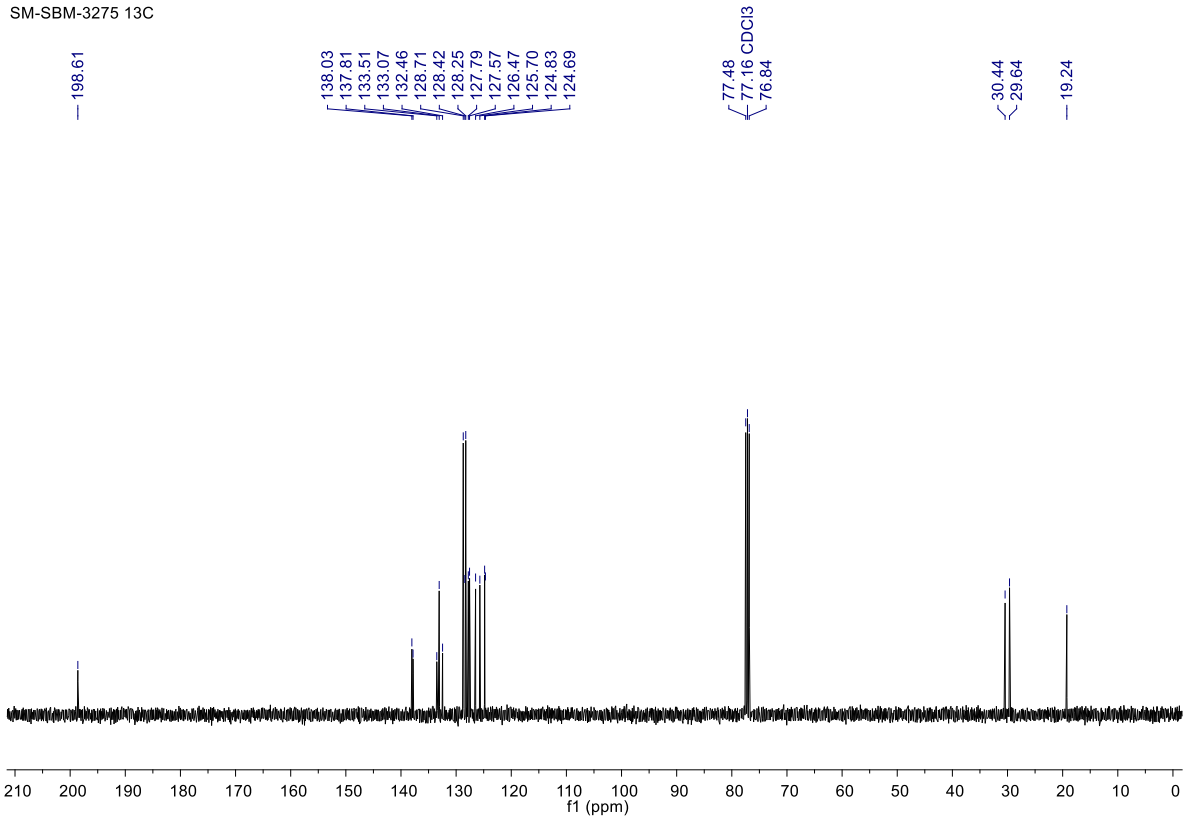
^{13}C{^{1}H} NMR of **4h** (101 MHz, $CDCl_3$):



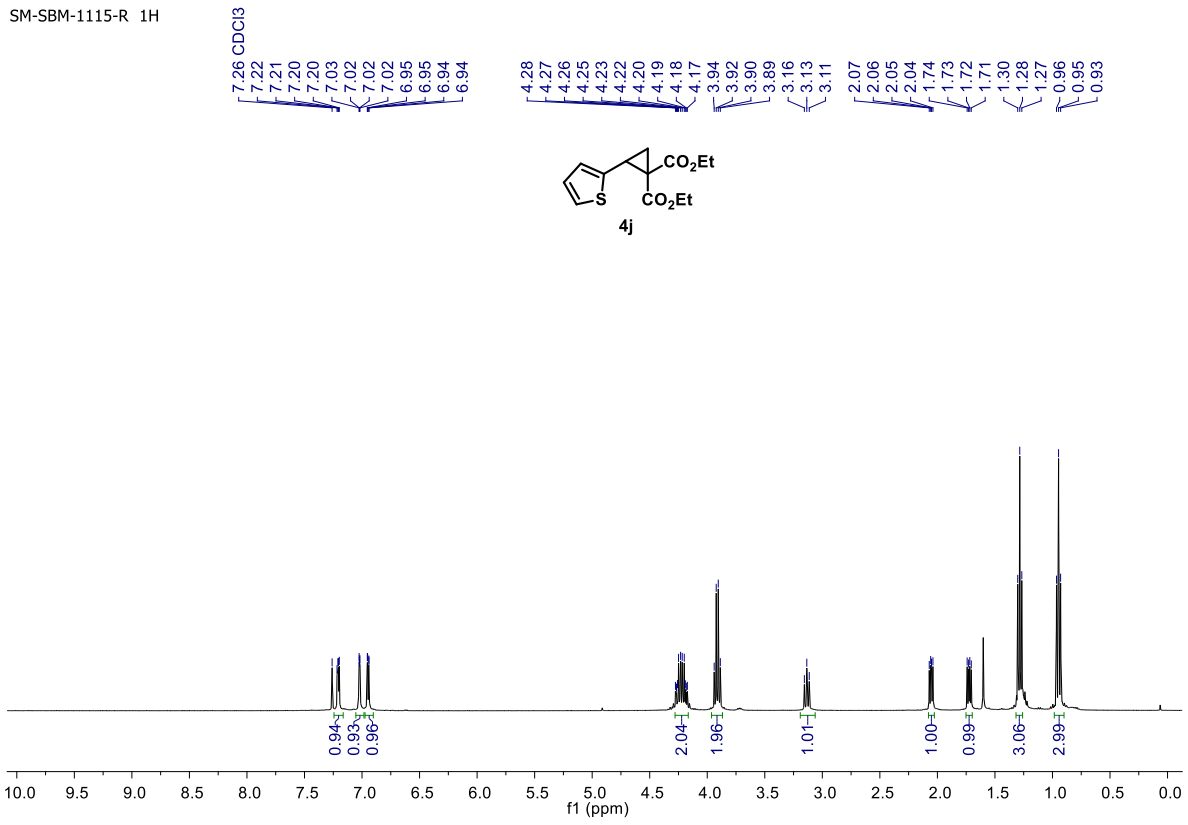
^{1}H NMR of **4i** (400 MHz, $CDCl_3$):



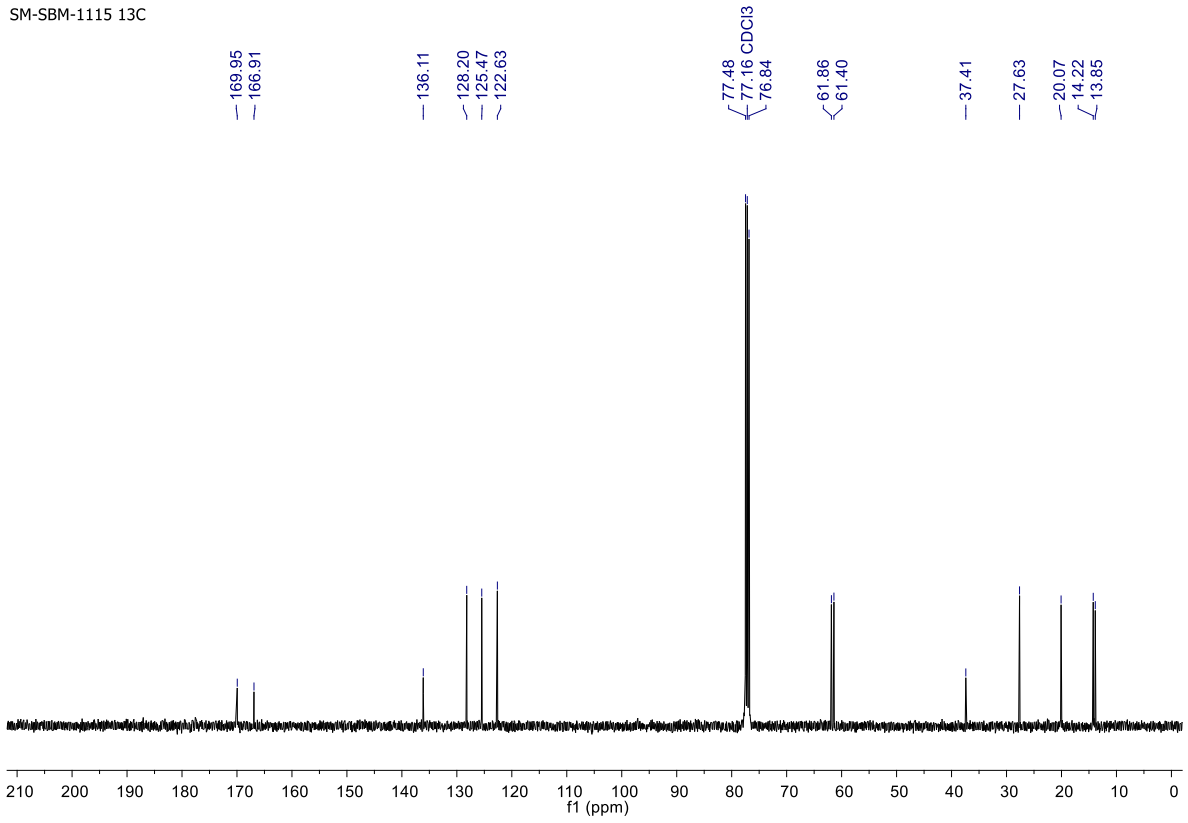
^{13}C{^{1}H} NMR of **4i** (101 MHz, $CDCl_3$):



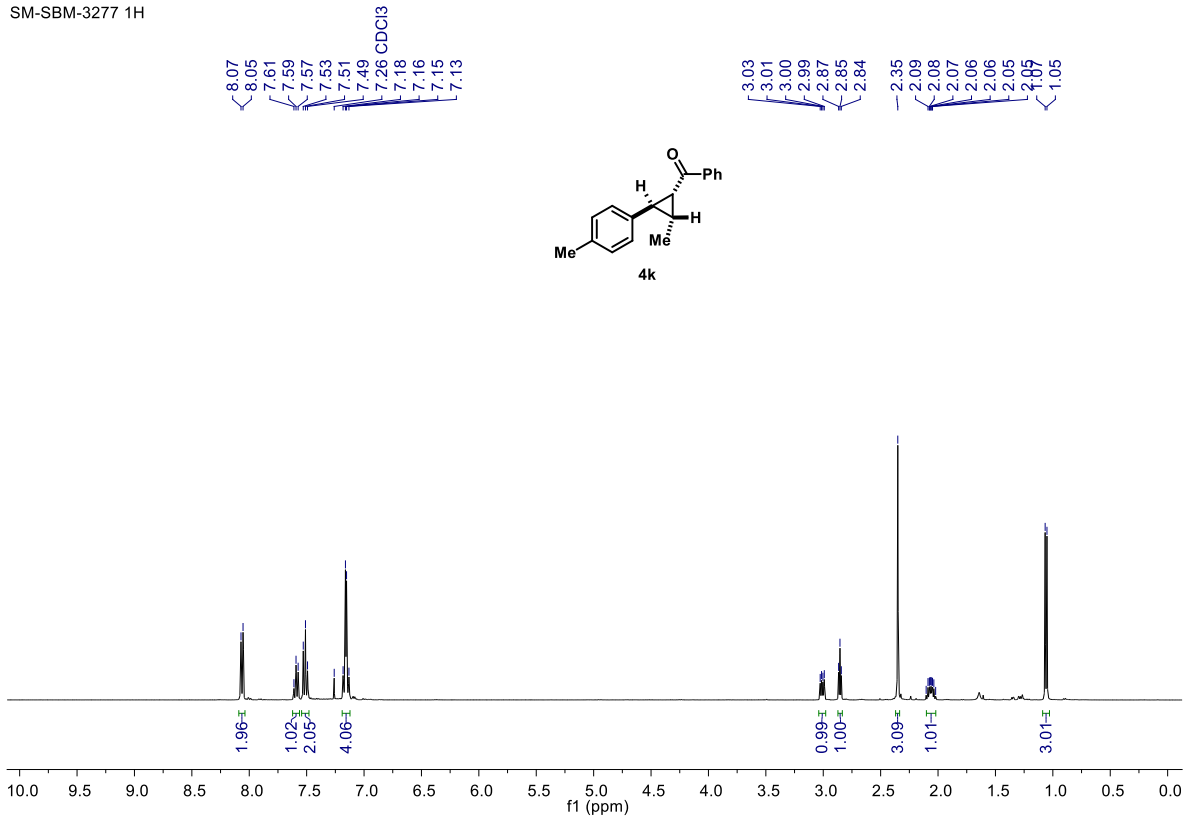
^{1}H NMR of **4j** (400 MHz, $CDCl_3$):



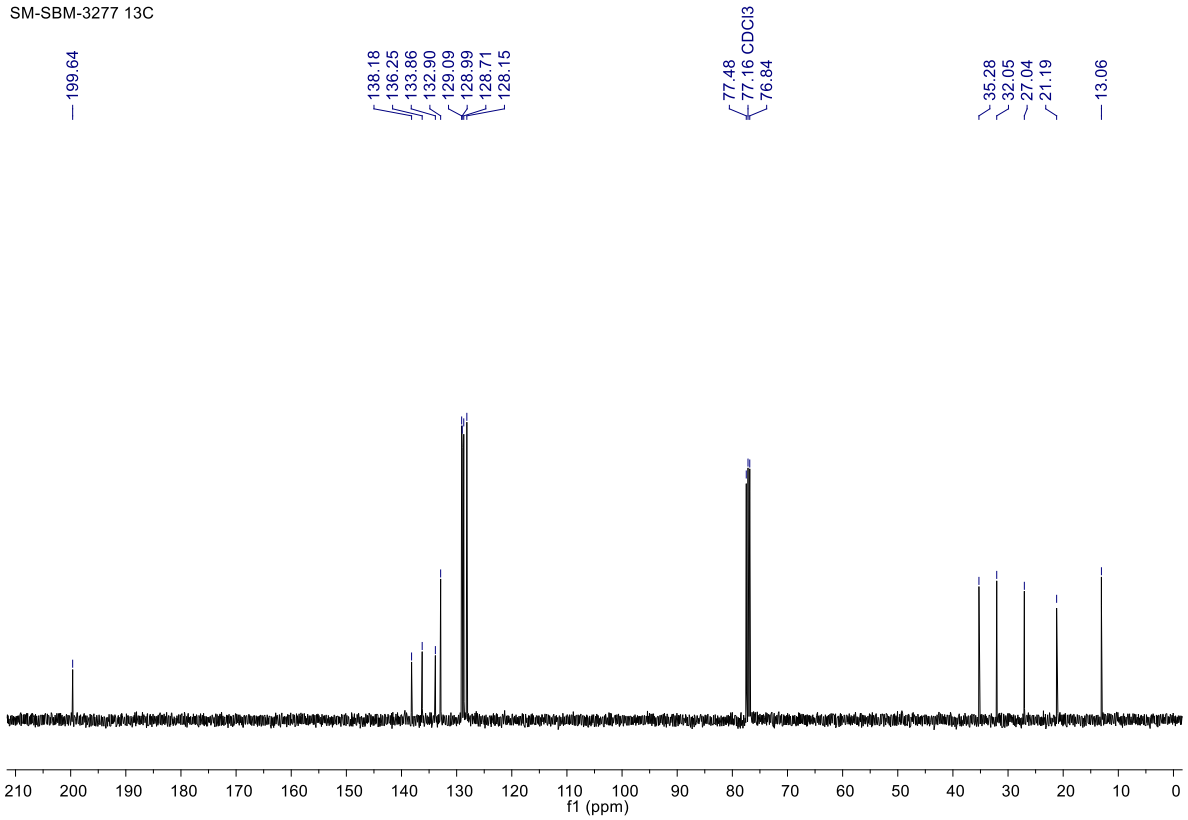
^{13}C{^{1}H} NMR of **4j** (101 MHz, $CDCl_3$):



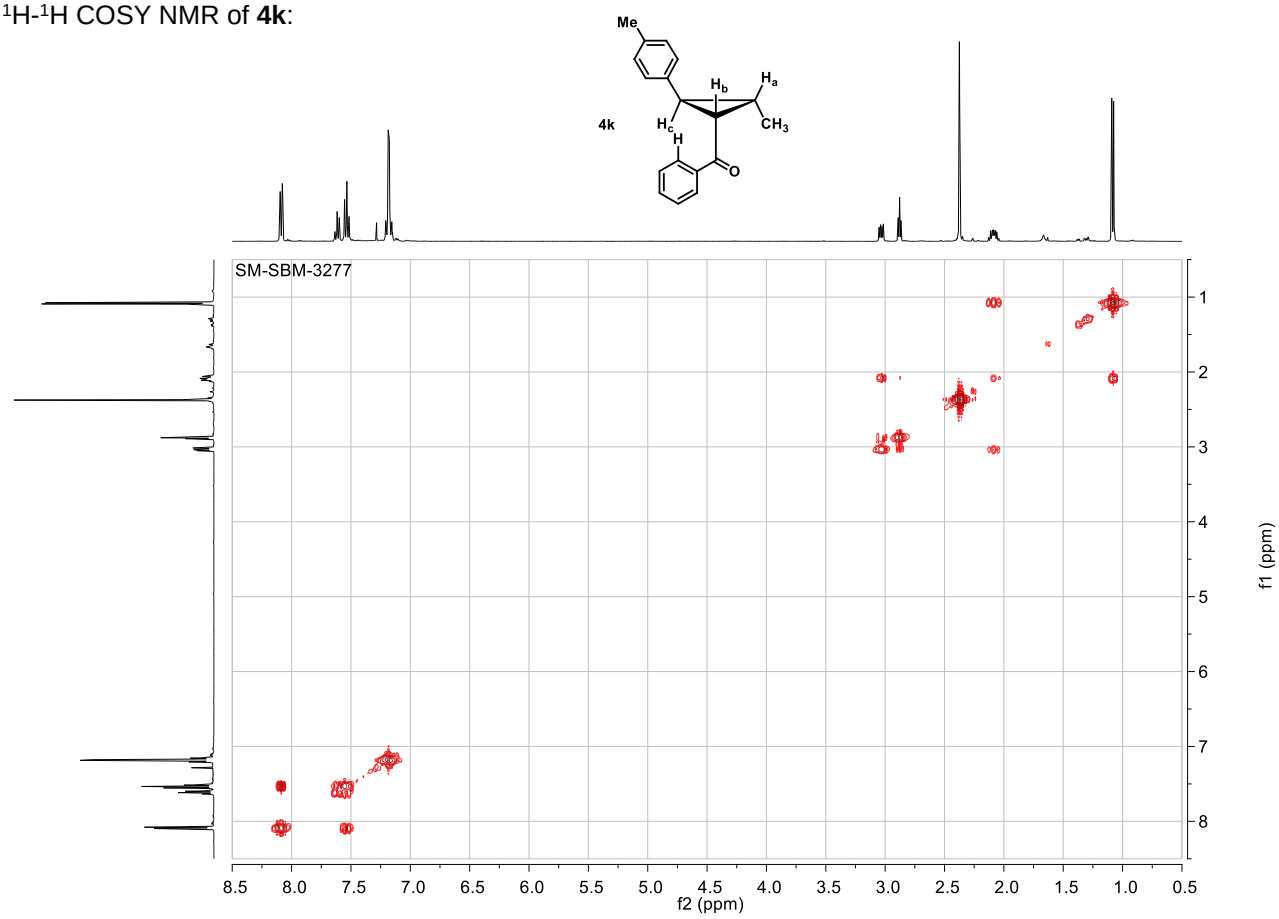
^{1}H NMR of **4k** (400 MHz, $CDCl_3$):



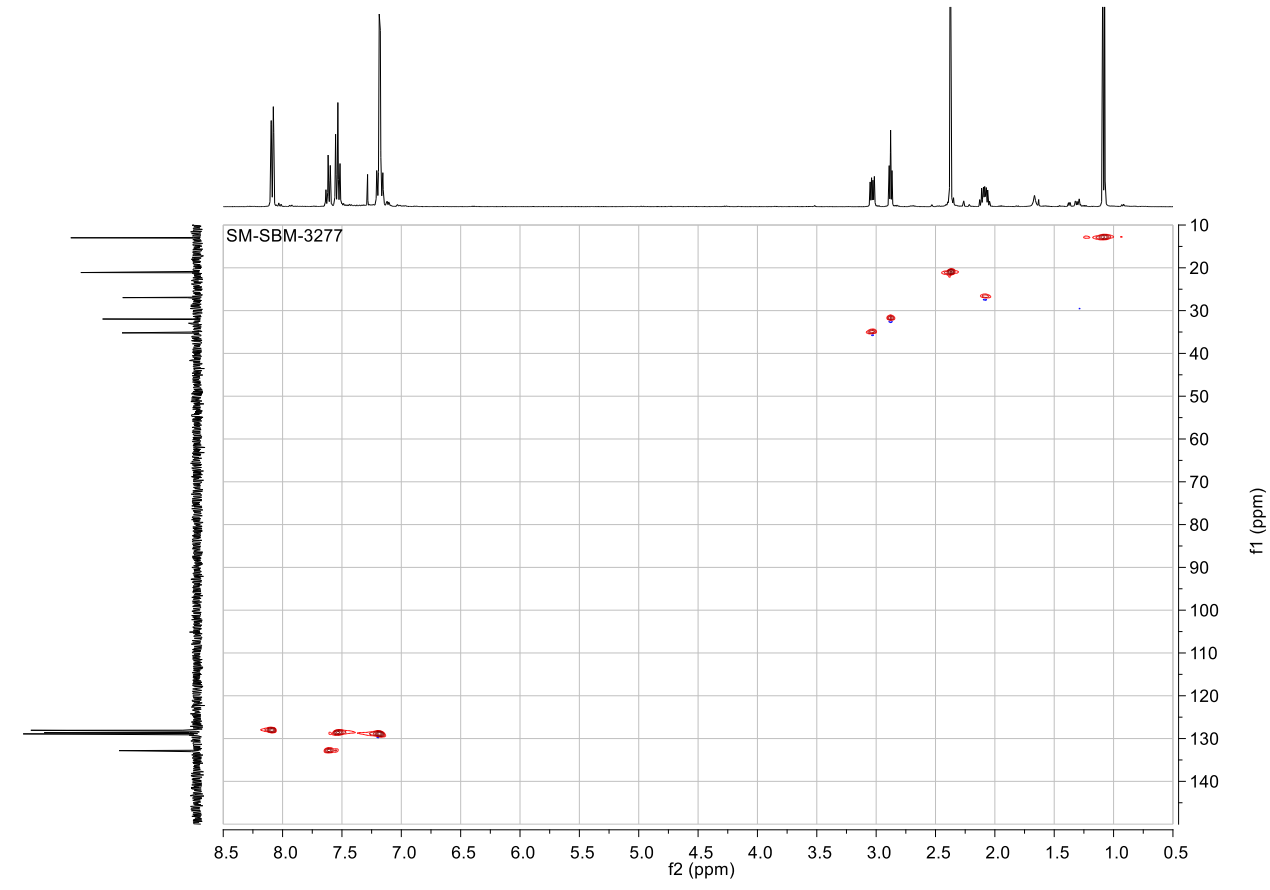
^{13}C{^{1}H} NMR of **4k** (101 MHz, $CDCl_3$):



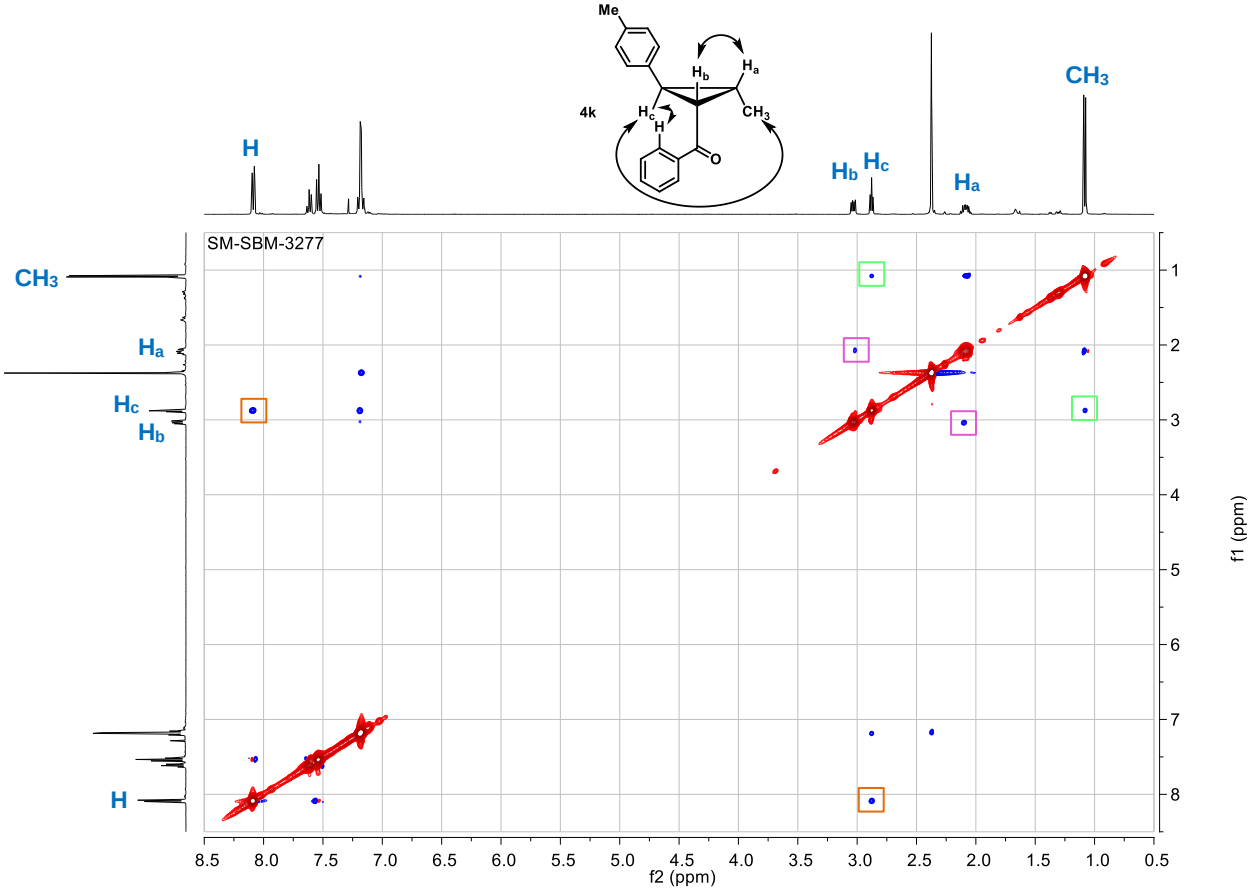
^{1}H-^{1}H COSY NMR of **4k**:



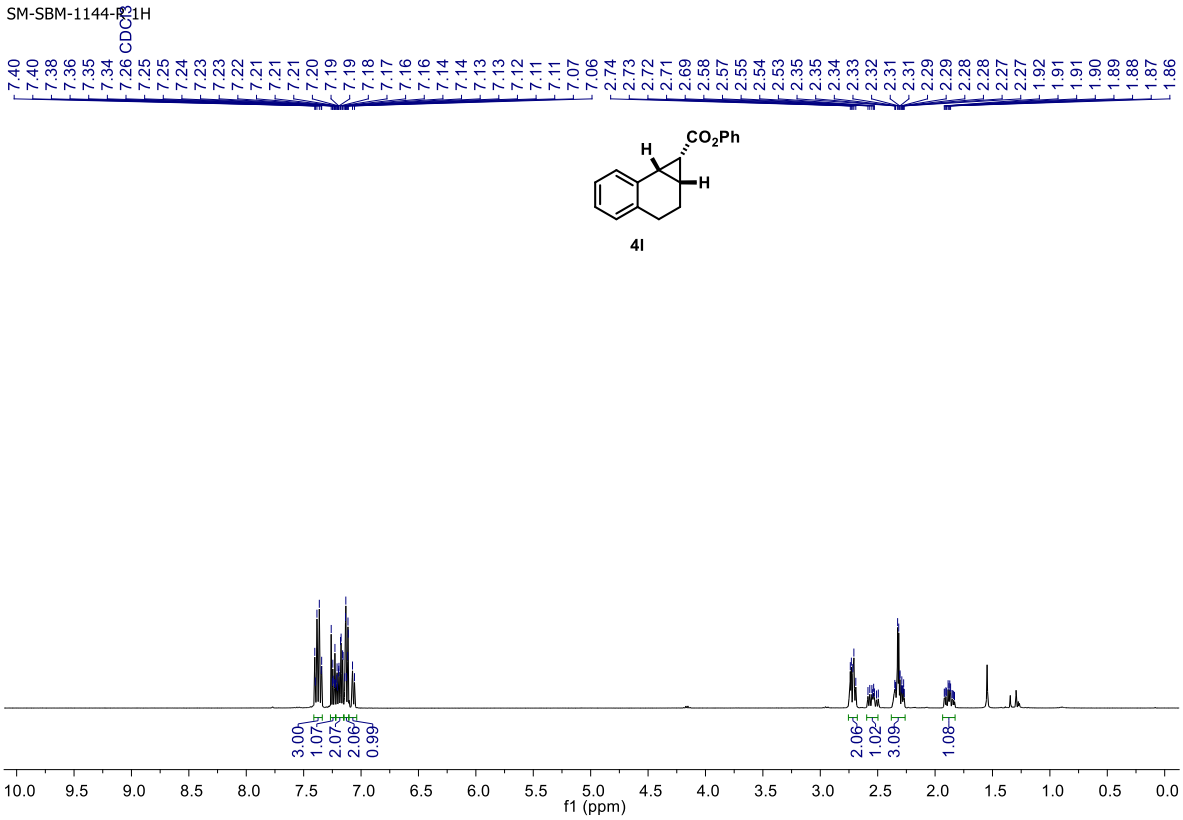
^{1}H-^{13}C HSQC NMR of **4k**:



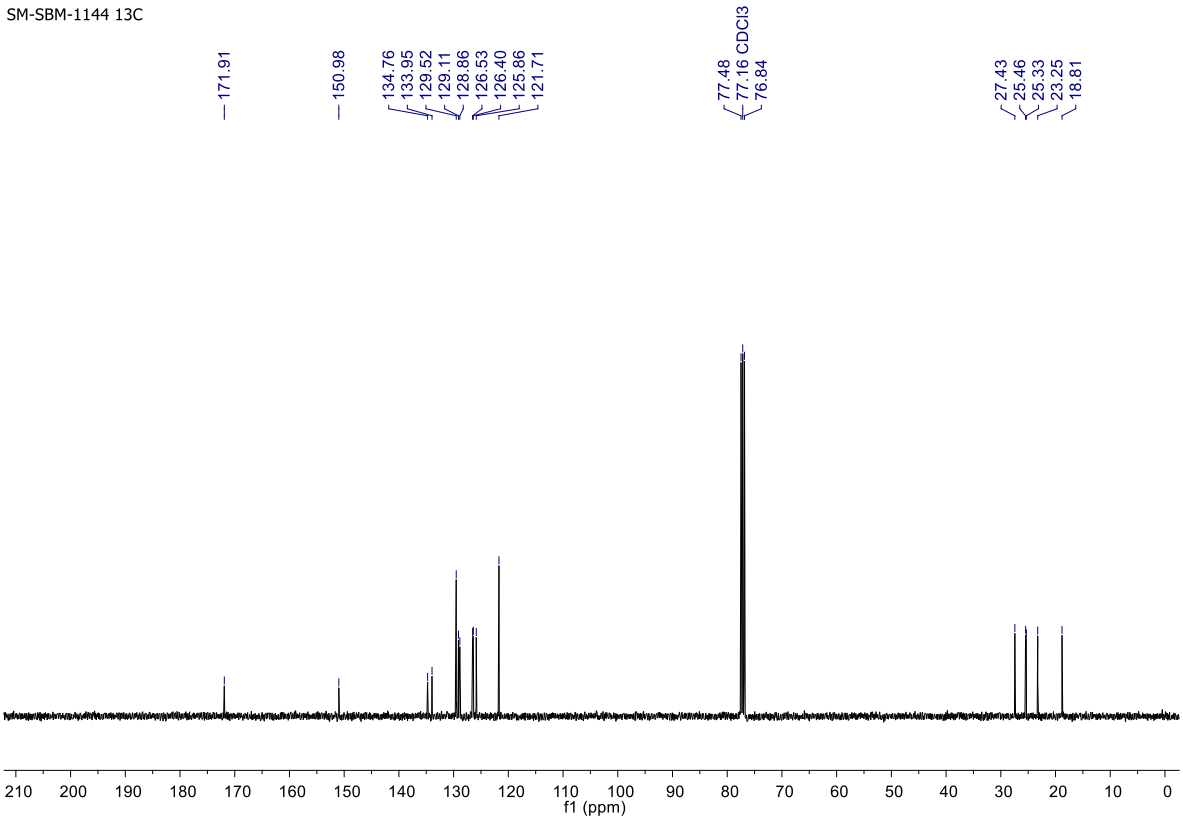
^{1}H-^{1}H NOESY NMR of **4k**:



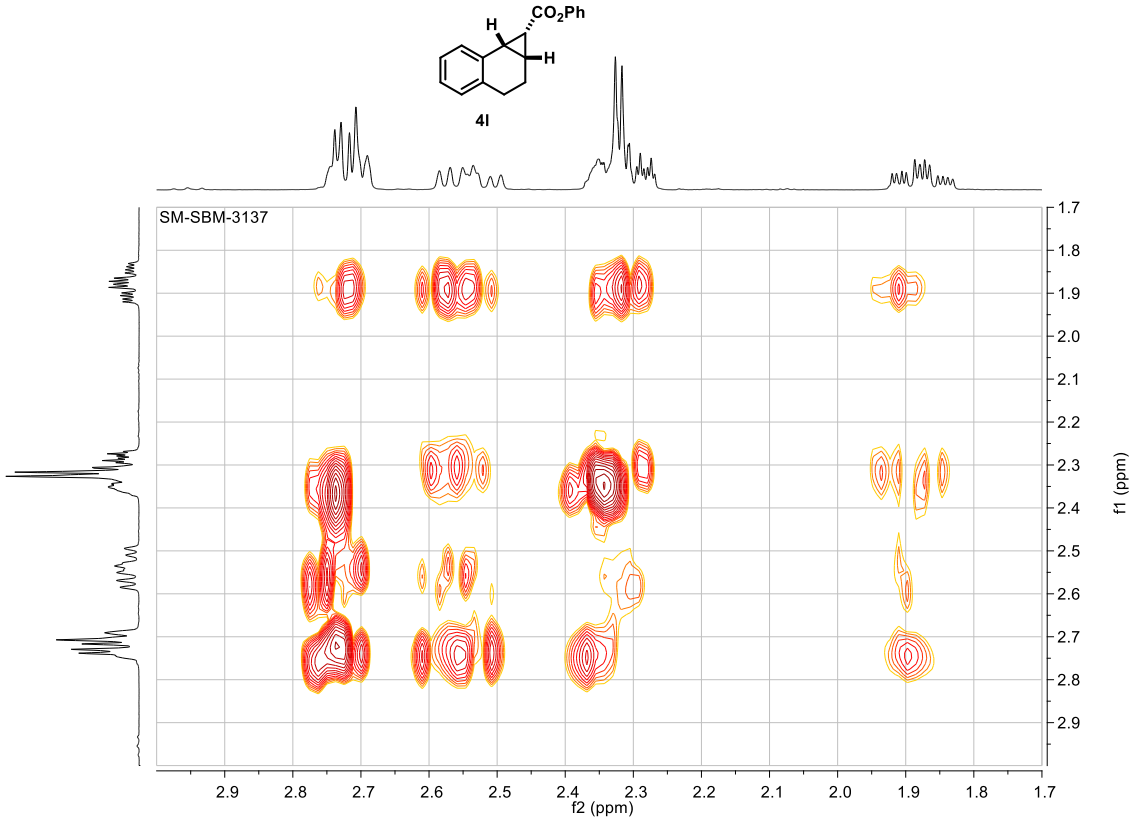
^{1}H NMR of **4l** (400 MHz, $CDCl_3$):



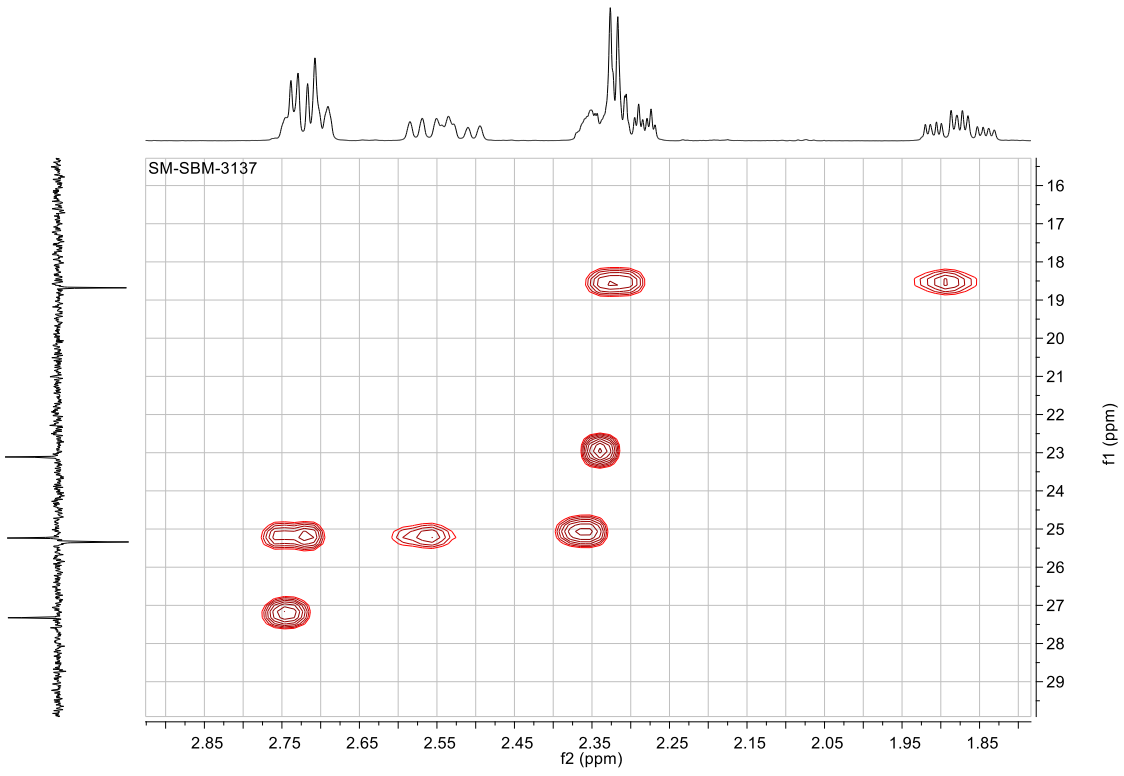
^{13}C{^{1}H} NMR of **4l** (101 MHz, $CDCl_3$):



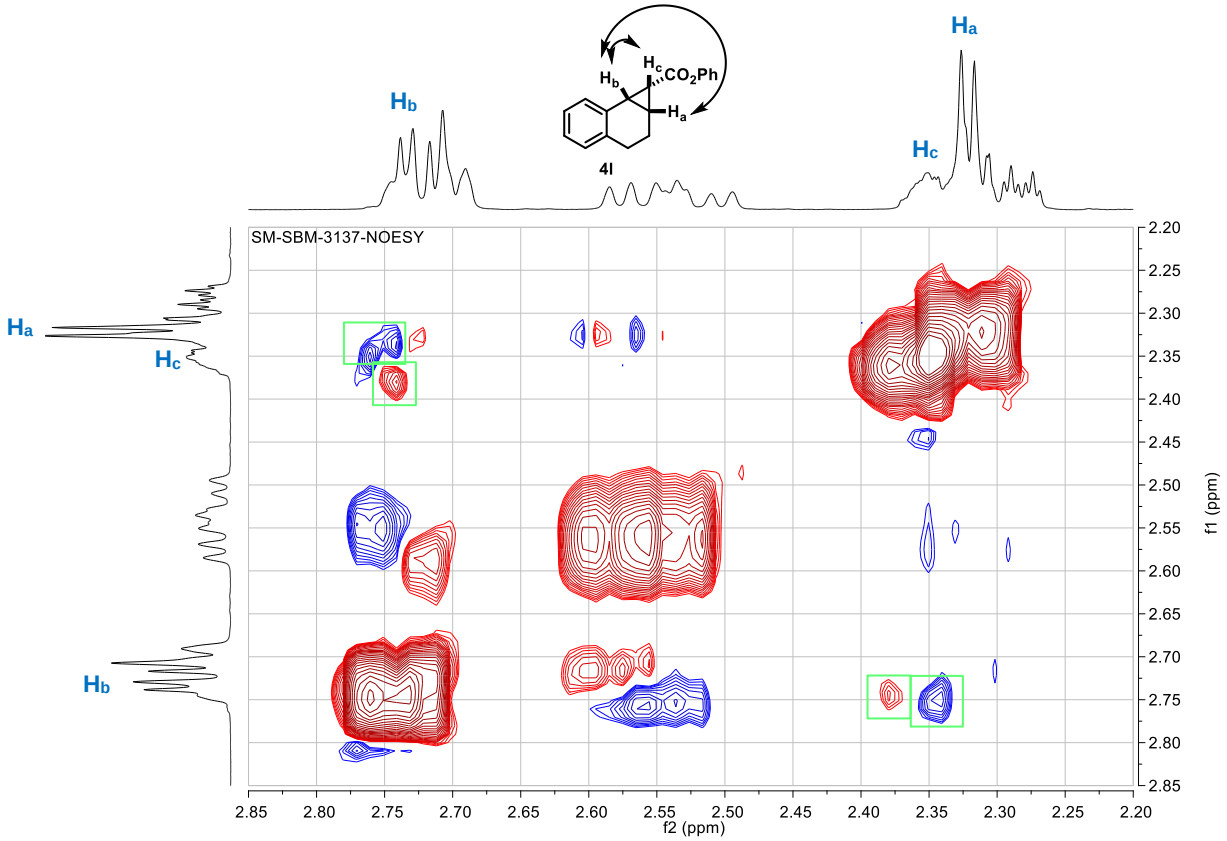
^{1}H-^{1}H COSY NMR of **4l**:



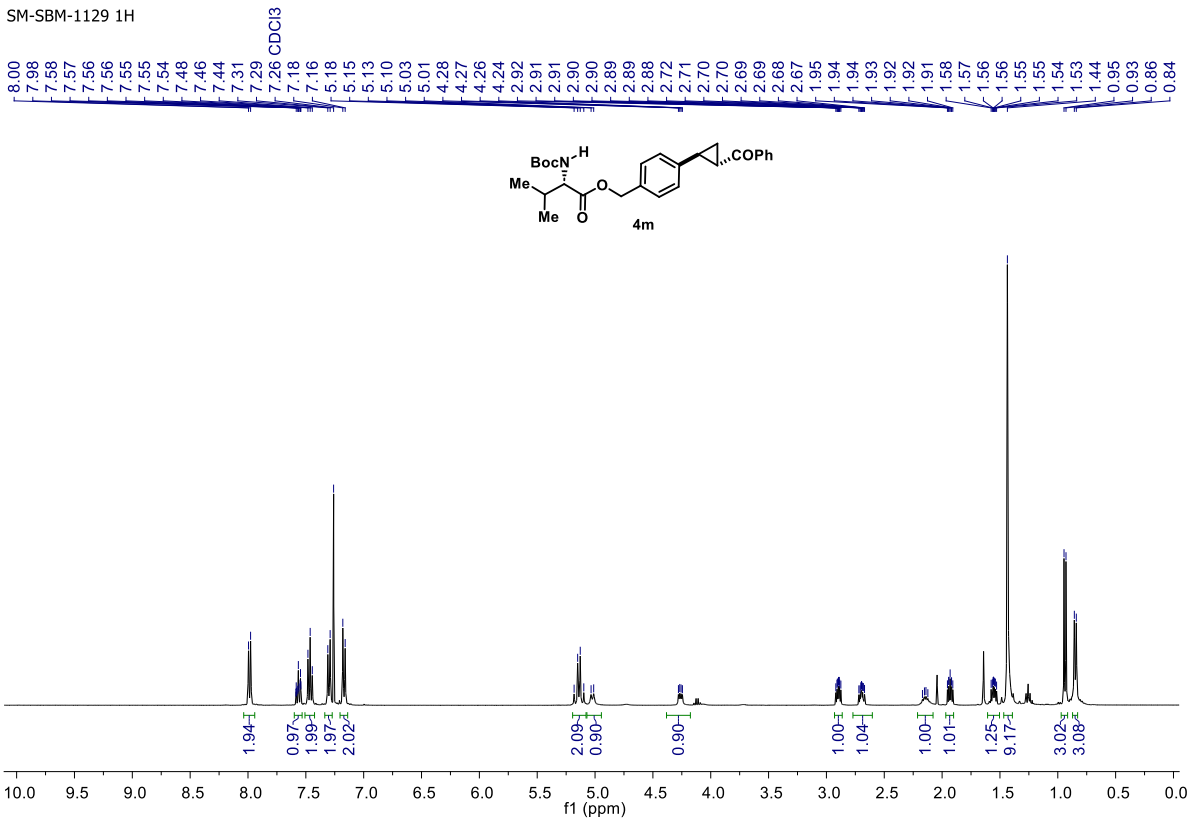
^{1}H-^{13}C HSQC NMR of **4l**:



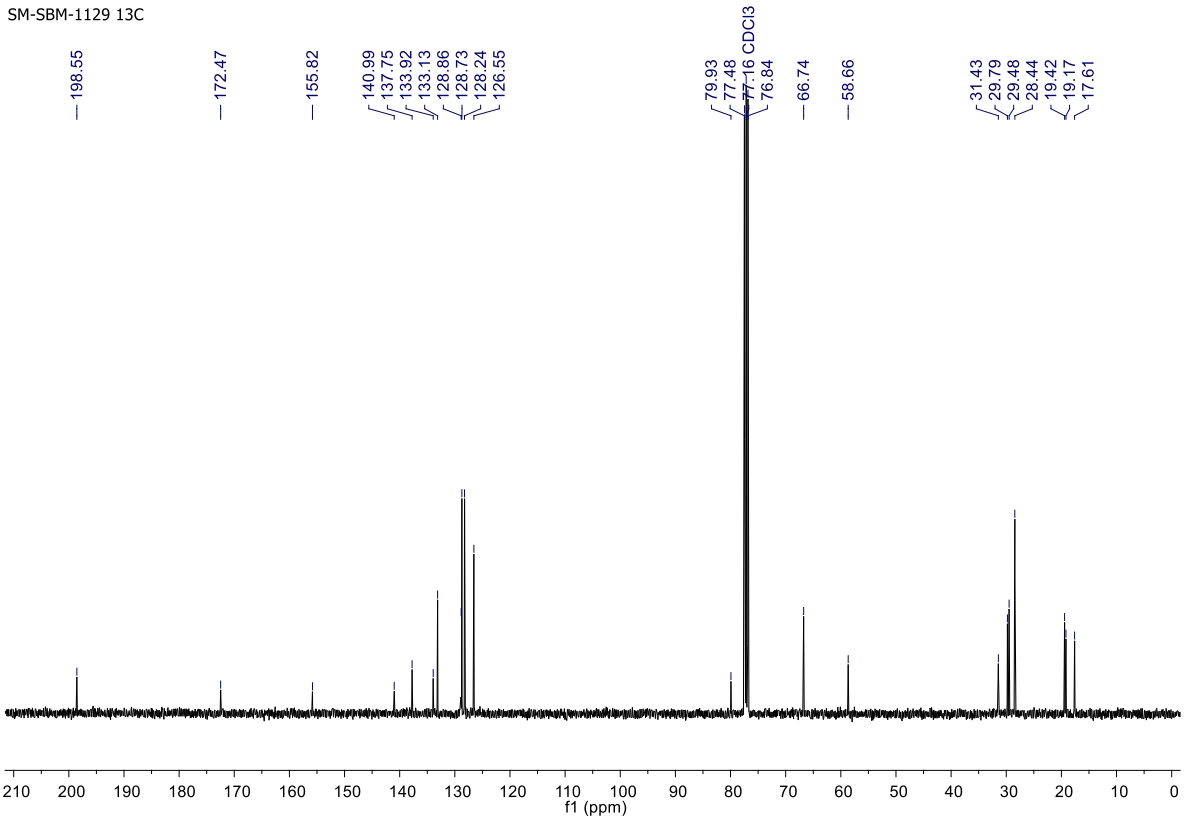
^{1}H-^{1}H NOESY NMR of **4l**:



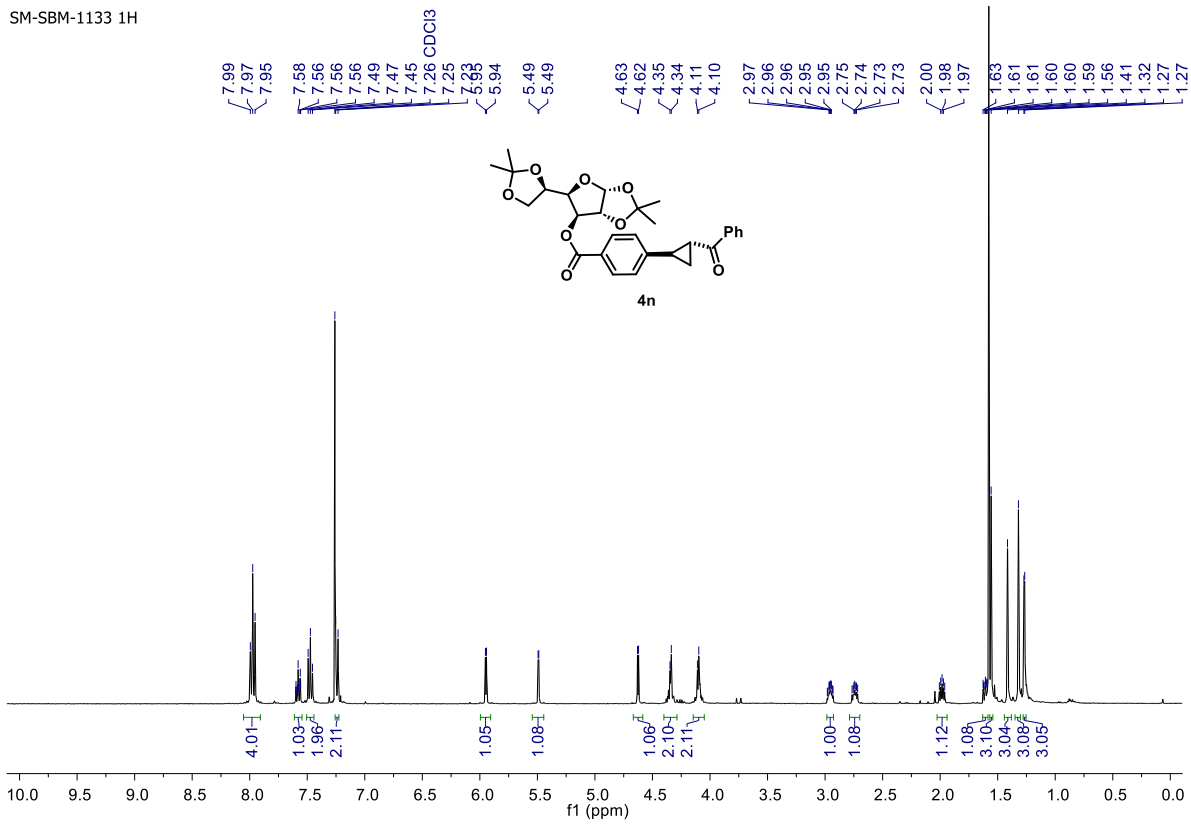
^{1}H NMR of **4m** (400 MHz, $CDCl_3$):



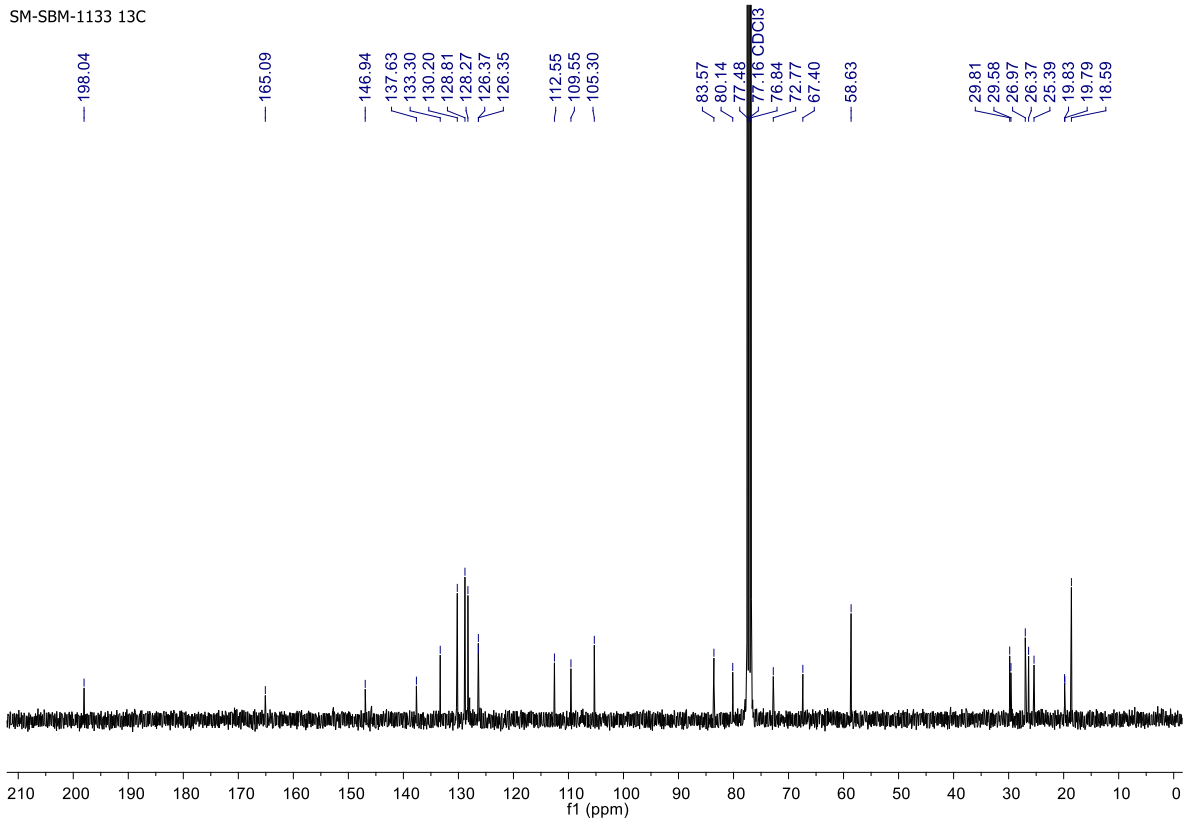
^{13}C{^{1}H} NMR of **4m** (101 MHz, $CDCl_3$):



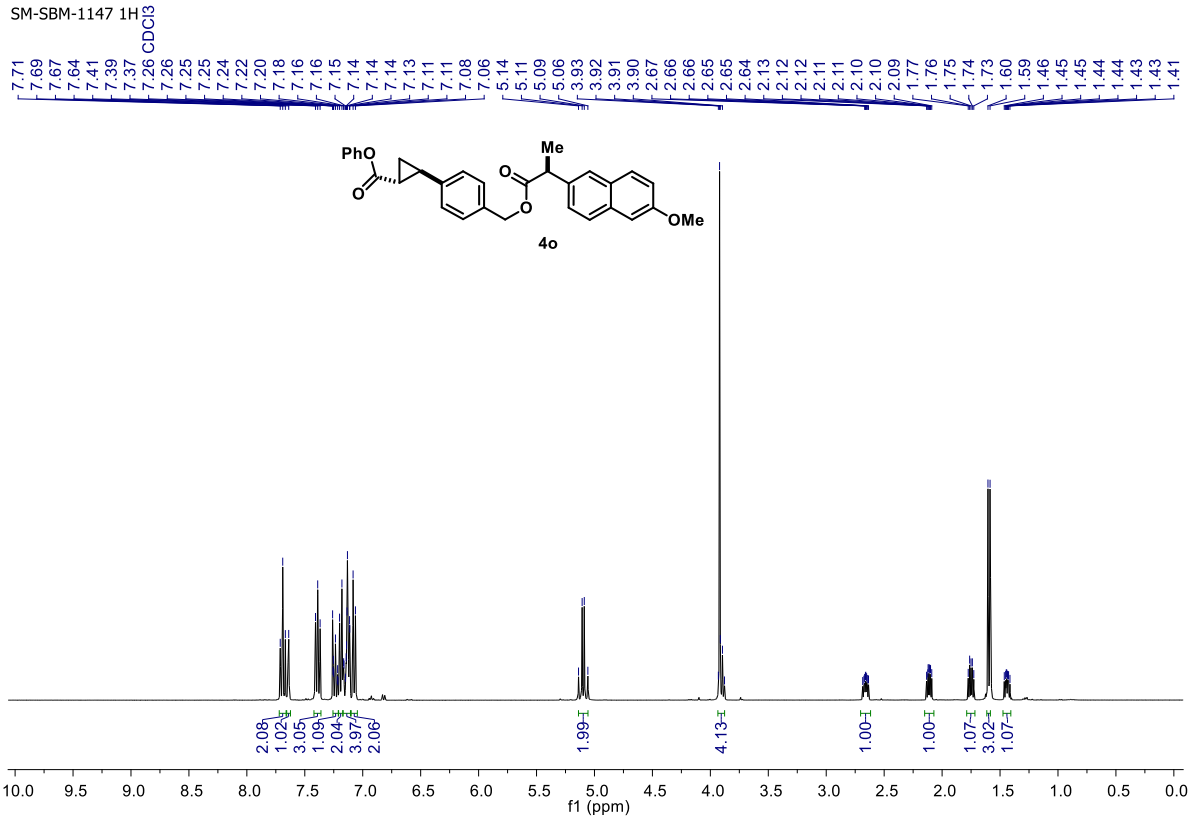
^{1}H NMR of **4n** (400 MHz, $CDCl_3$):



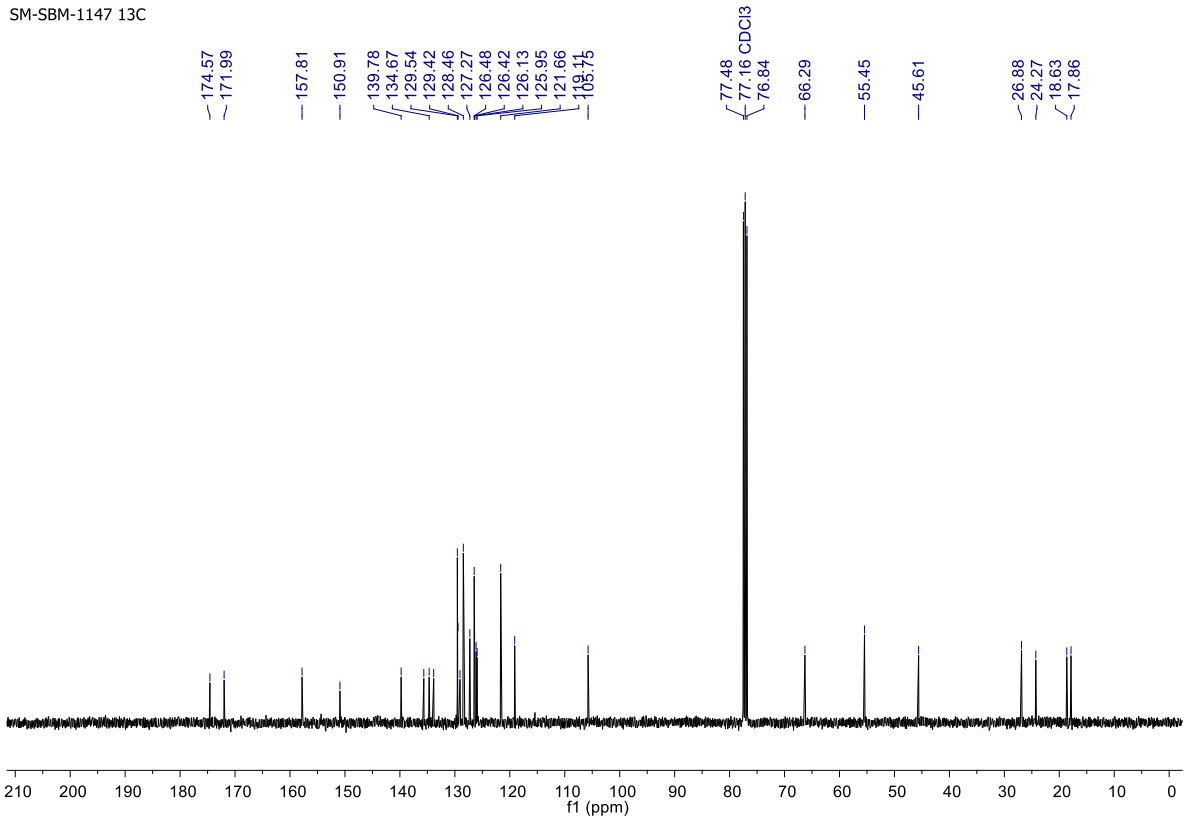
^{13}C{^{1}H} NMR of **4n** (101 MHz, $CDCl_3$):



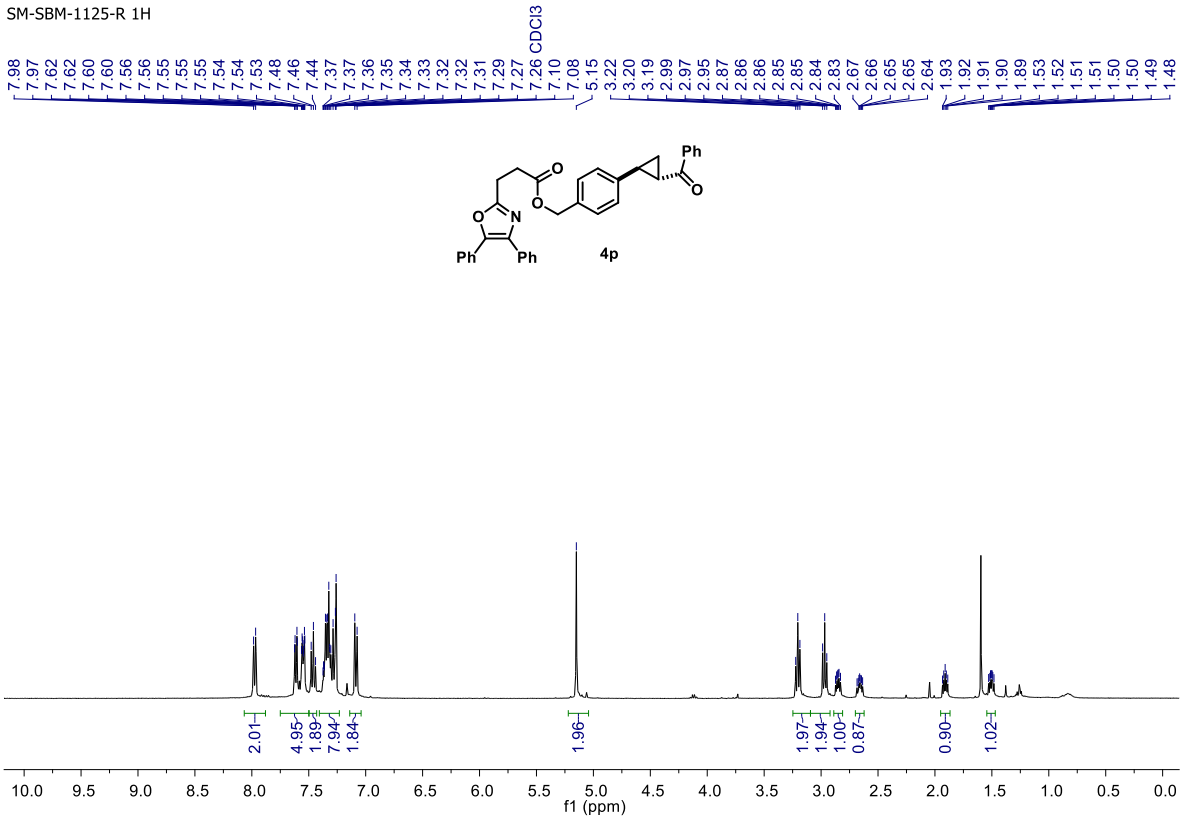
^{1}H NMR of **4o** (400 MHz, $CDCl_3$):



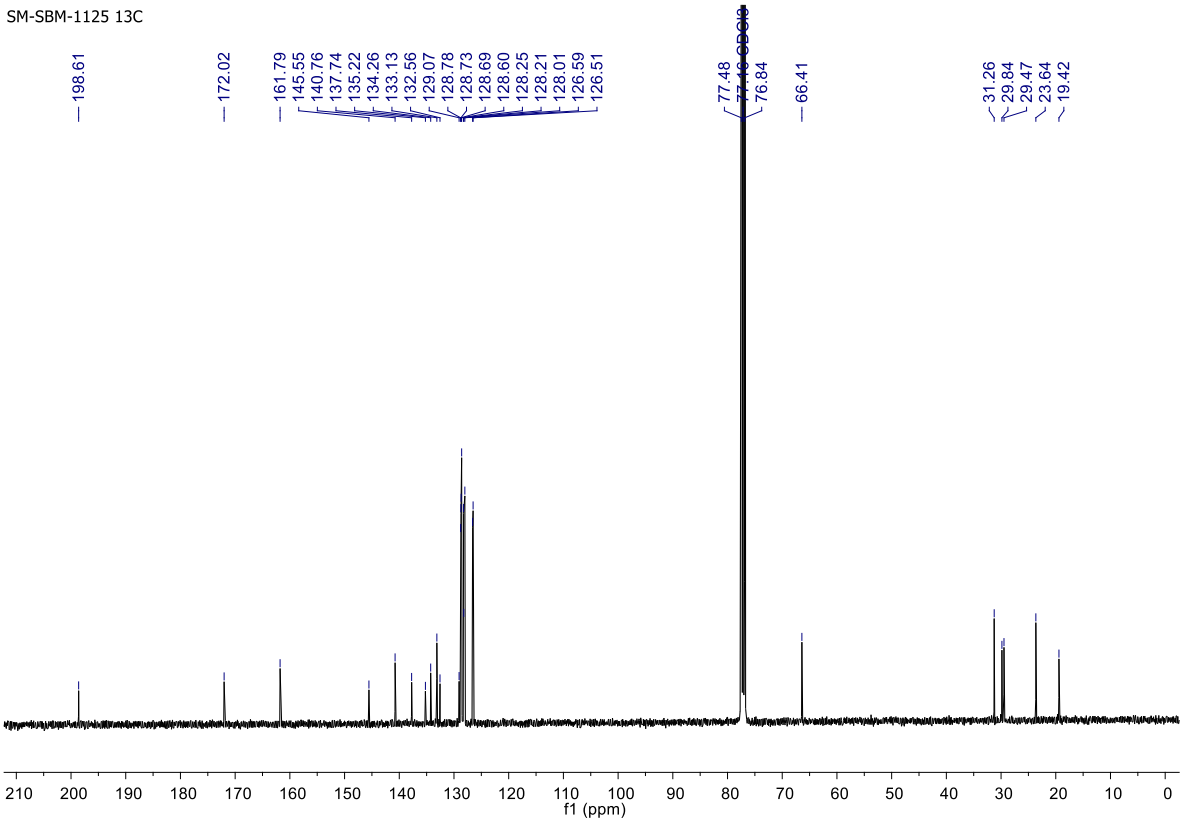
^{13}C{^{1}H} NMR of **4o** (101 MHz, $CDCl_3$):



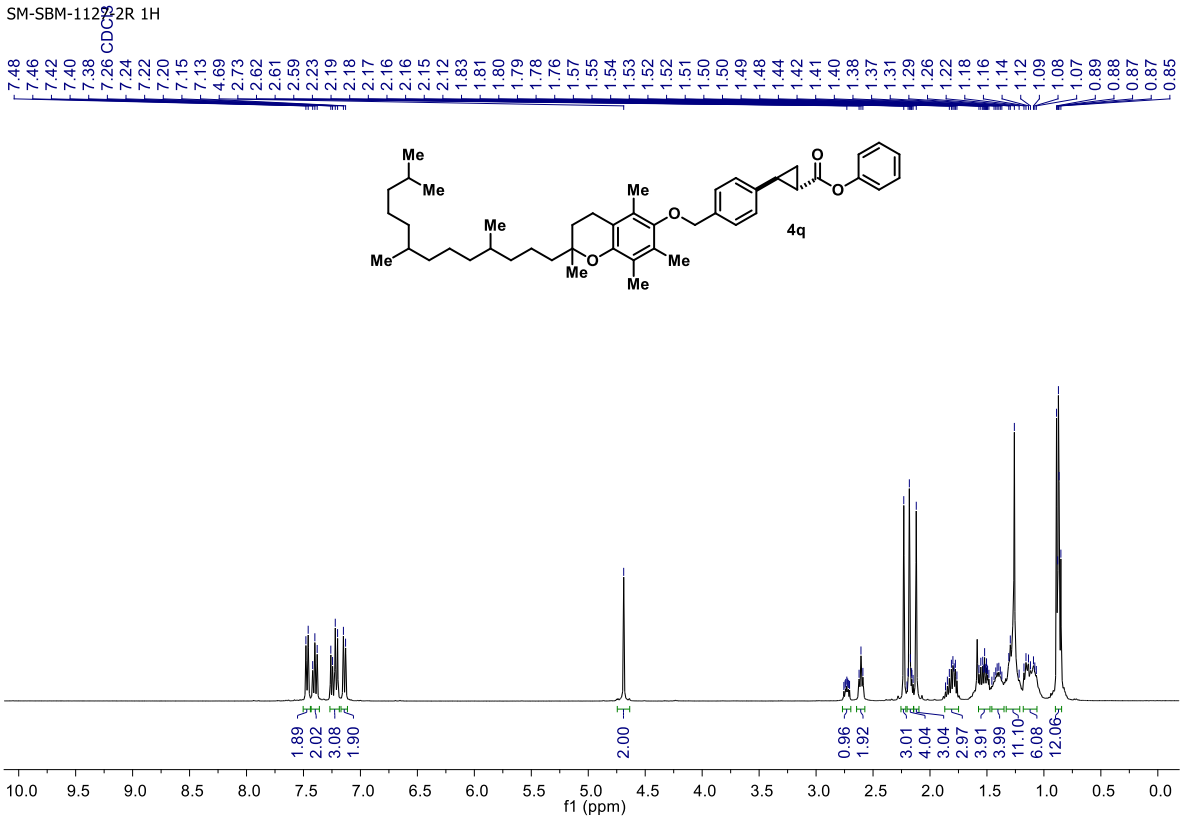
^{1}H NMR of **4p** (400 MHz, $CDCl_3$):



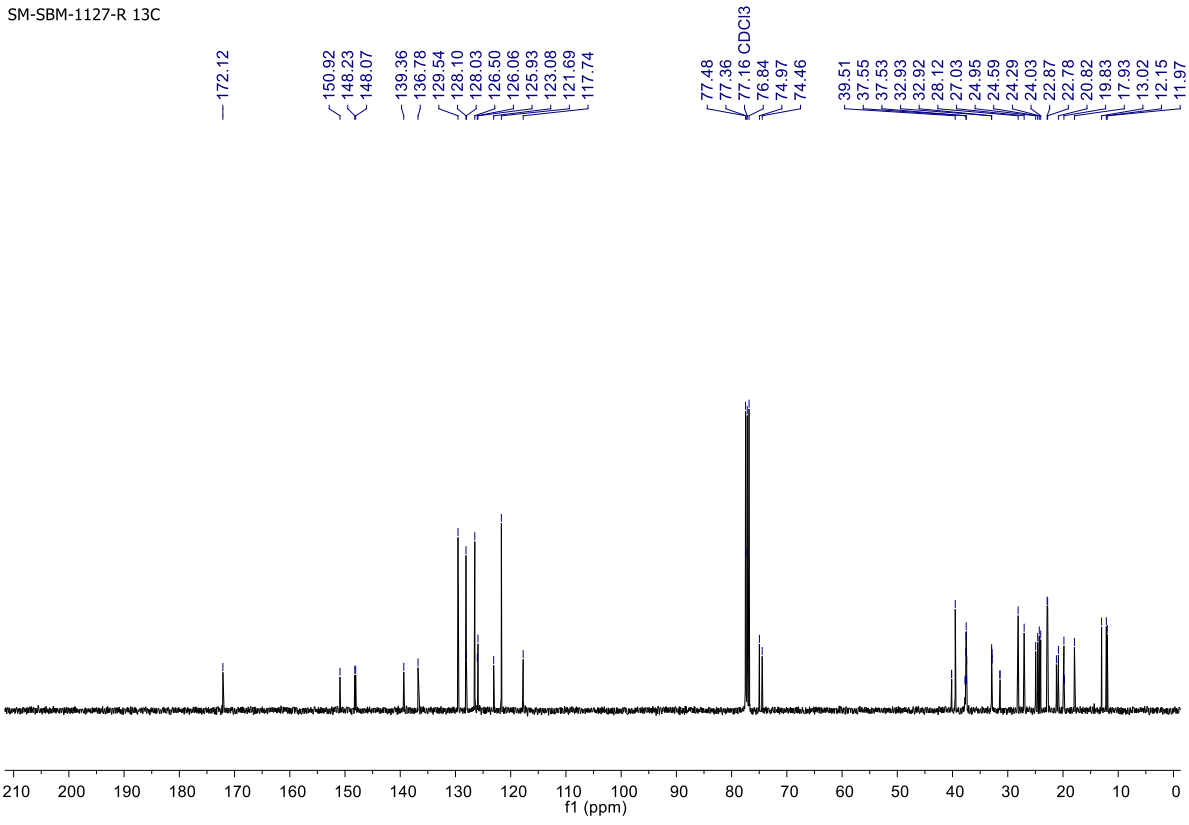
^{13}C{^{1}H} NMR of **4p** (101 MHz, $CDCl_3$):



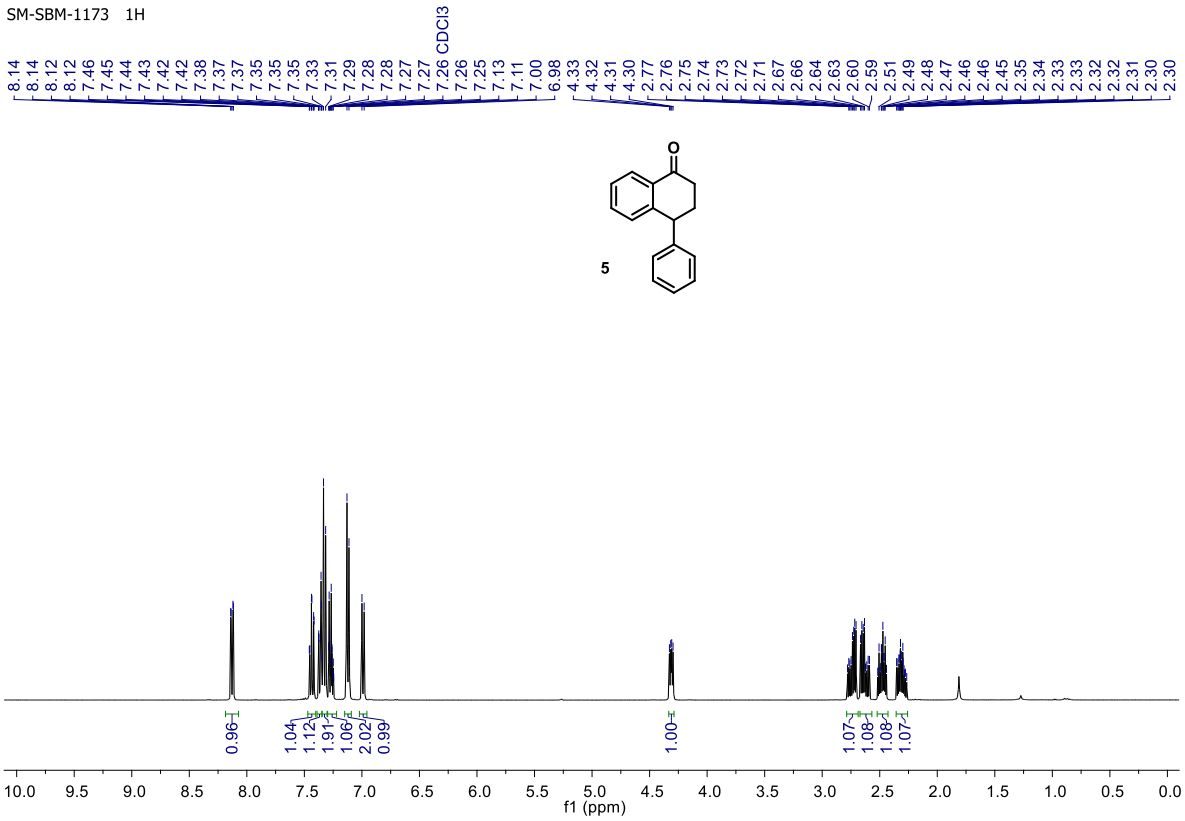
^{1}H NMR of **4q** (400 MHz, $CDCl_3$):



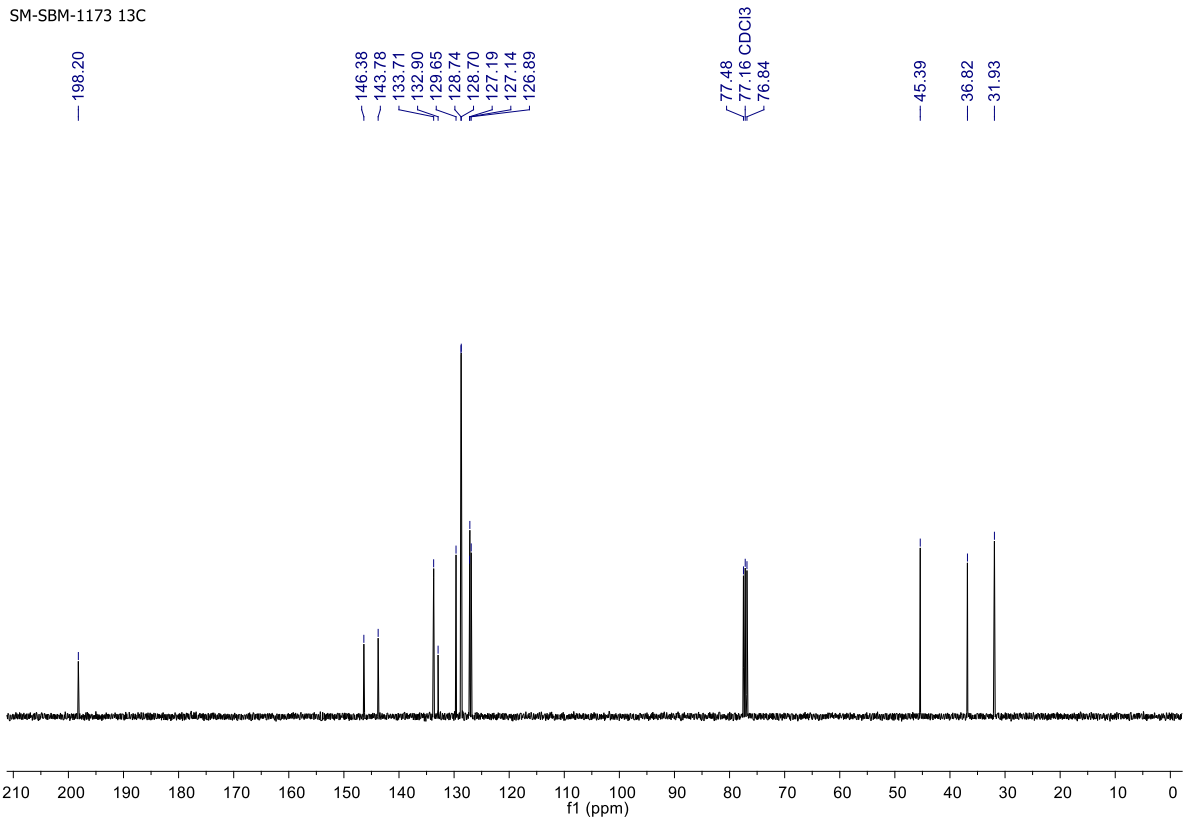
^{13}C{^{1}H} NMR of **4q** (101 MHz, $CDCl_3$):



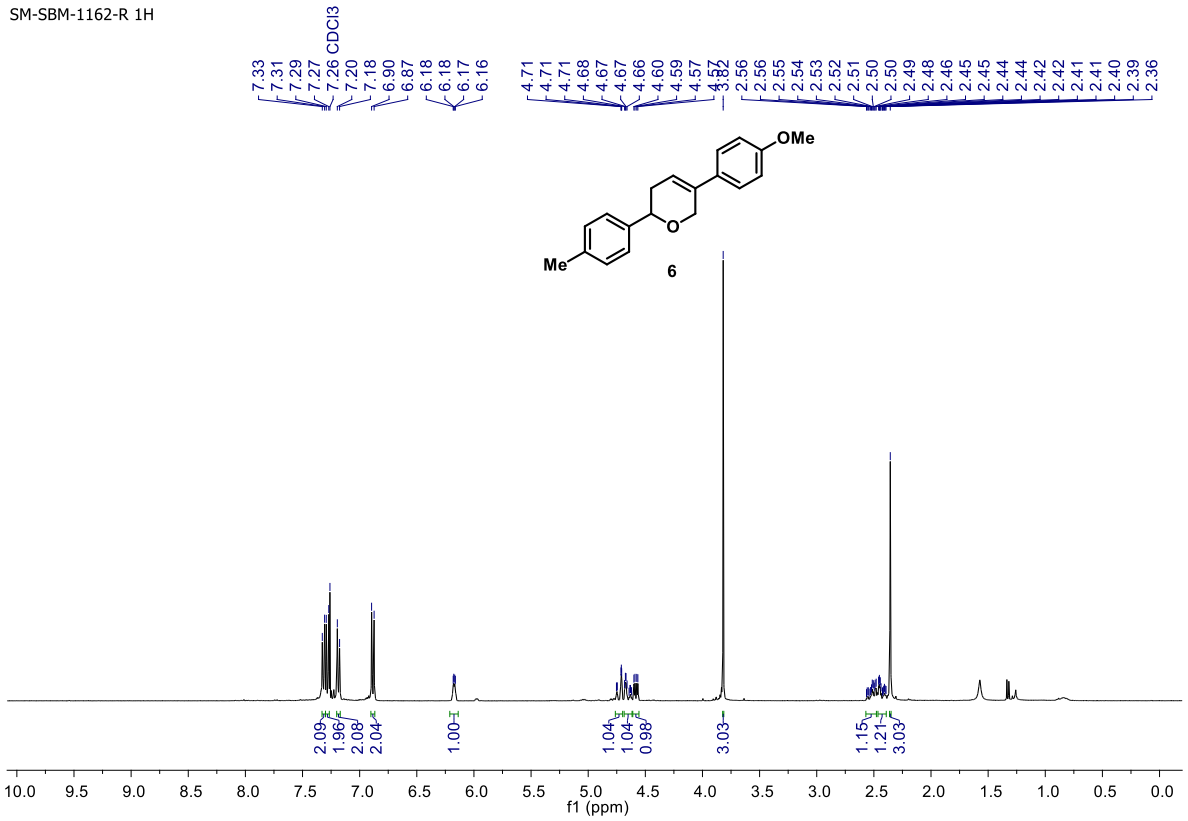
^{1}H NMR of **5** (400 MHz, $CDCl_3$):



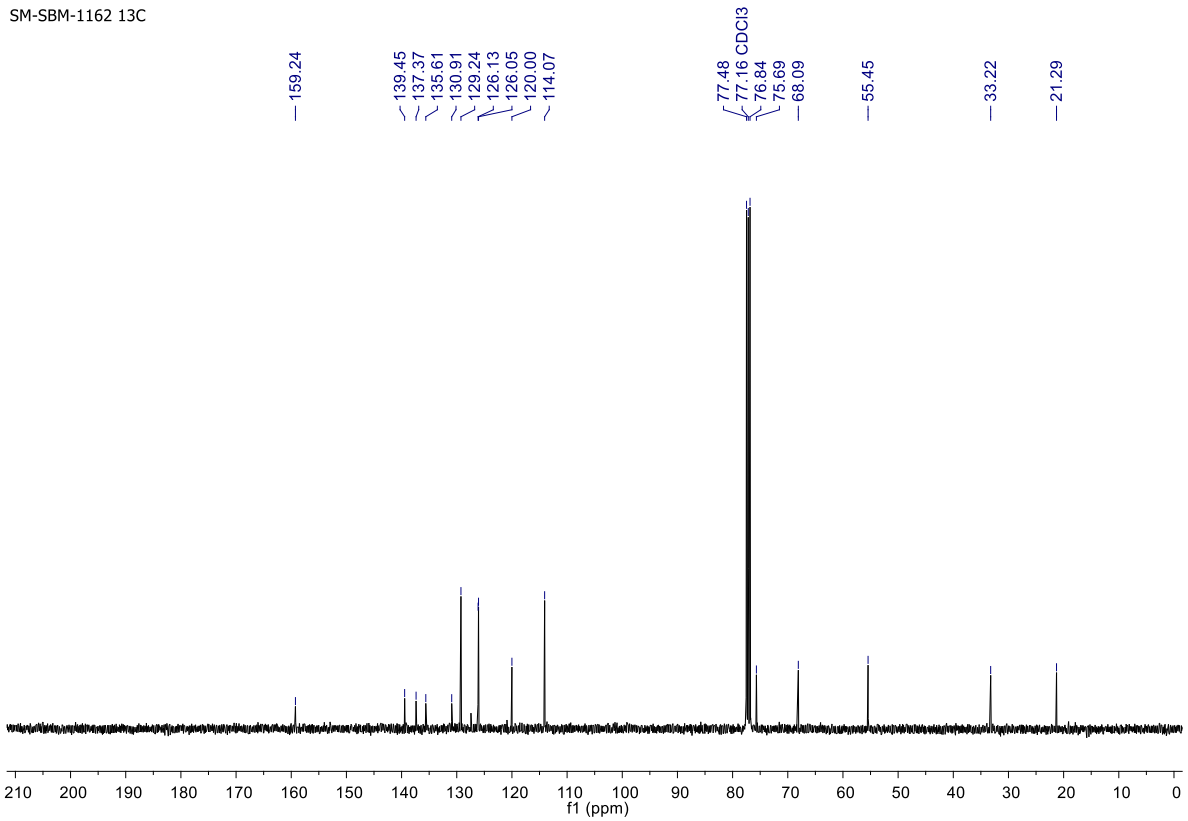
^{13}C{^{1}H} NMR of **5** (101 MHz, $CDCl_3$):



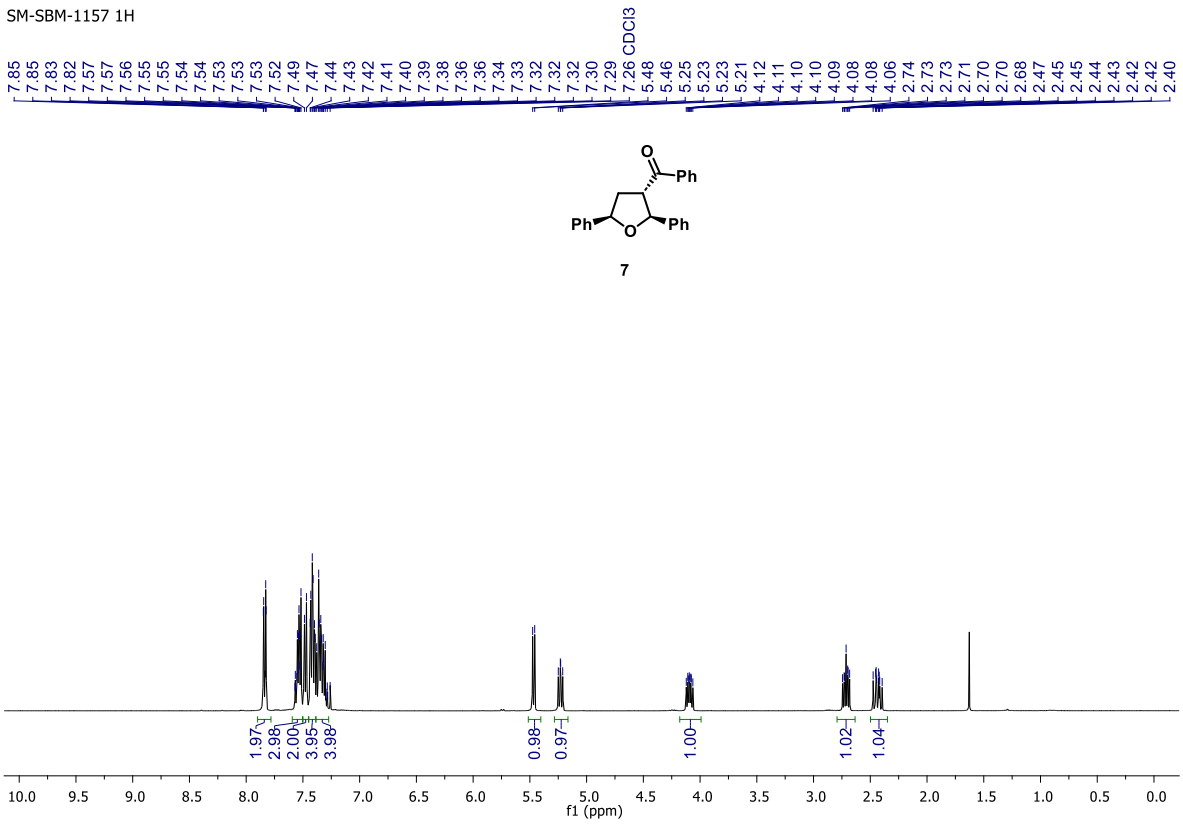
^{1}H NMR of **6** (400 MHz, $CDCl_3$):



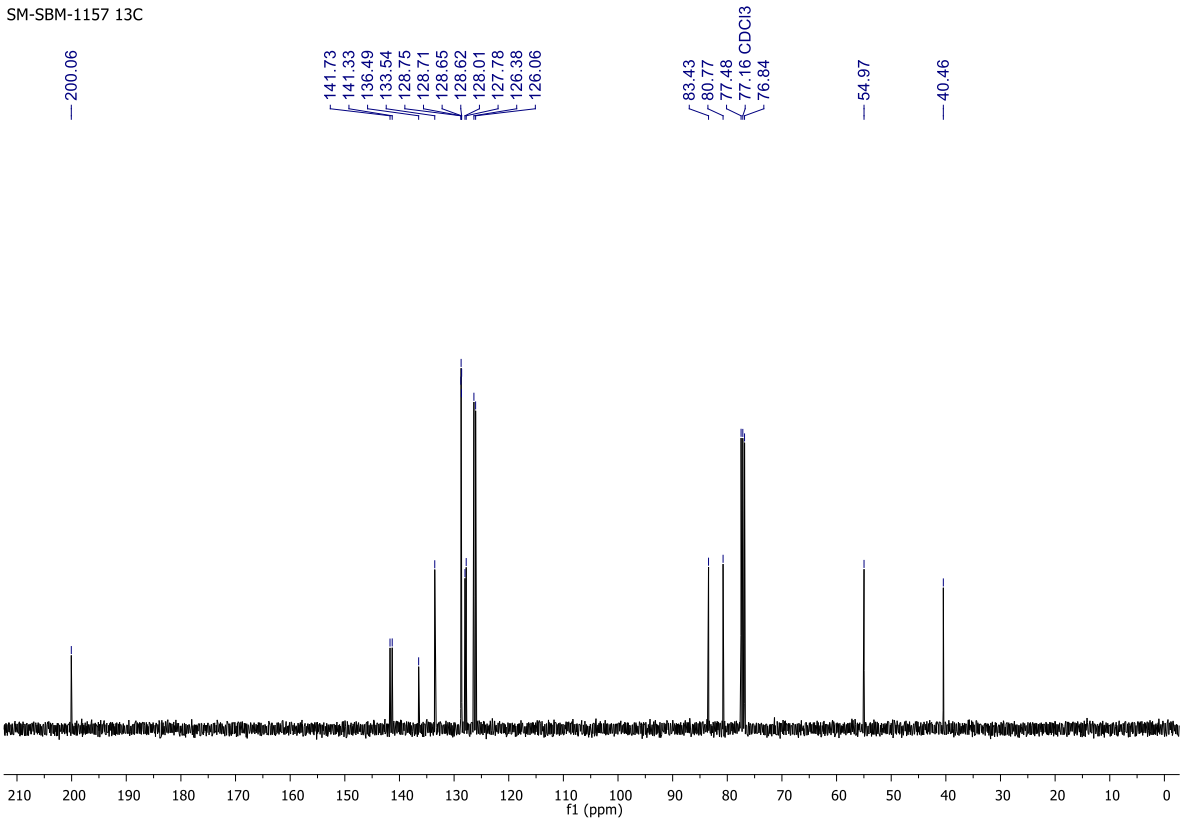
^{13}C{^{1}H} NMR of **6** (101 MHz, $CDCl_3$):



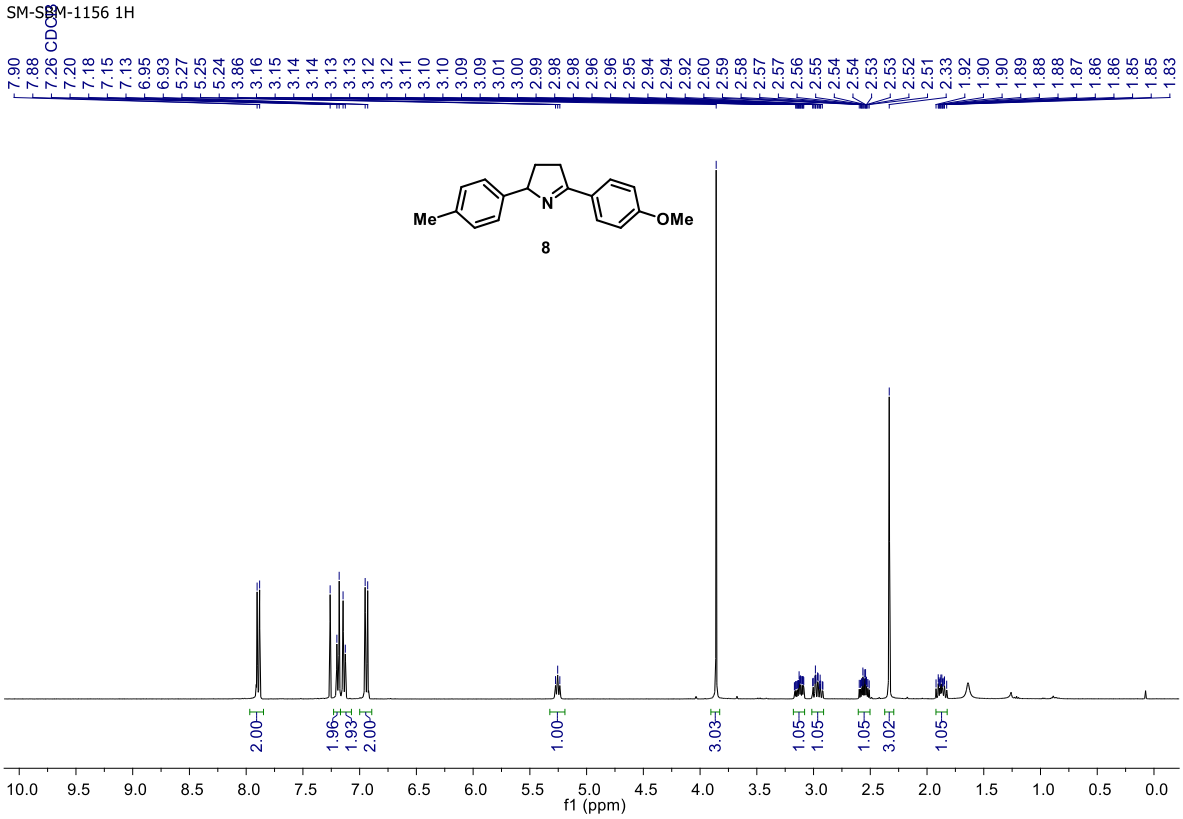
^{1}H NMR of **7** (400 MHz, $CDCl_3$):



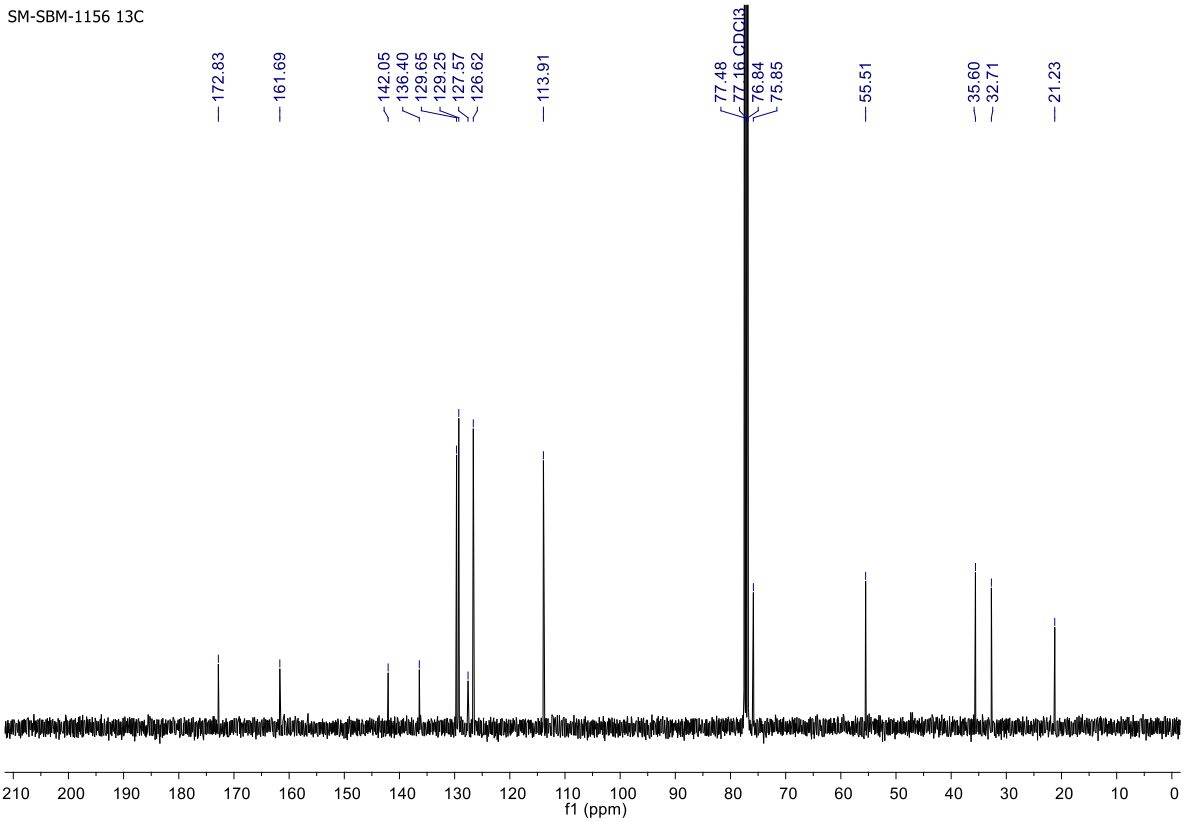
^{13}C{^{1}H} NMR of **7** (101 MHz, $CDCl_3$):



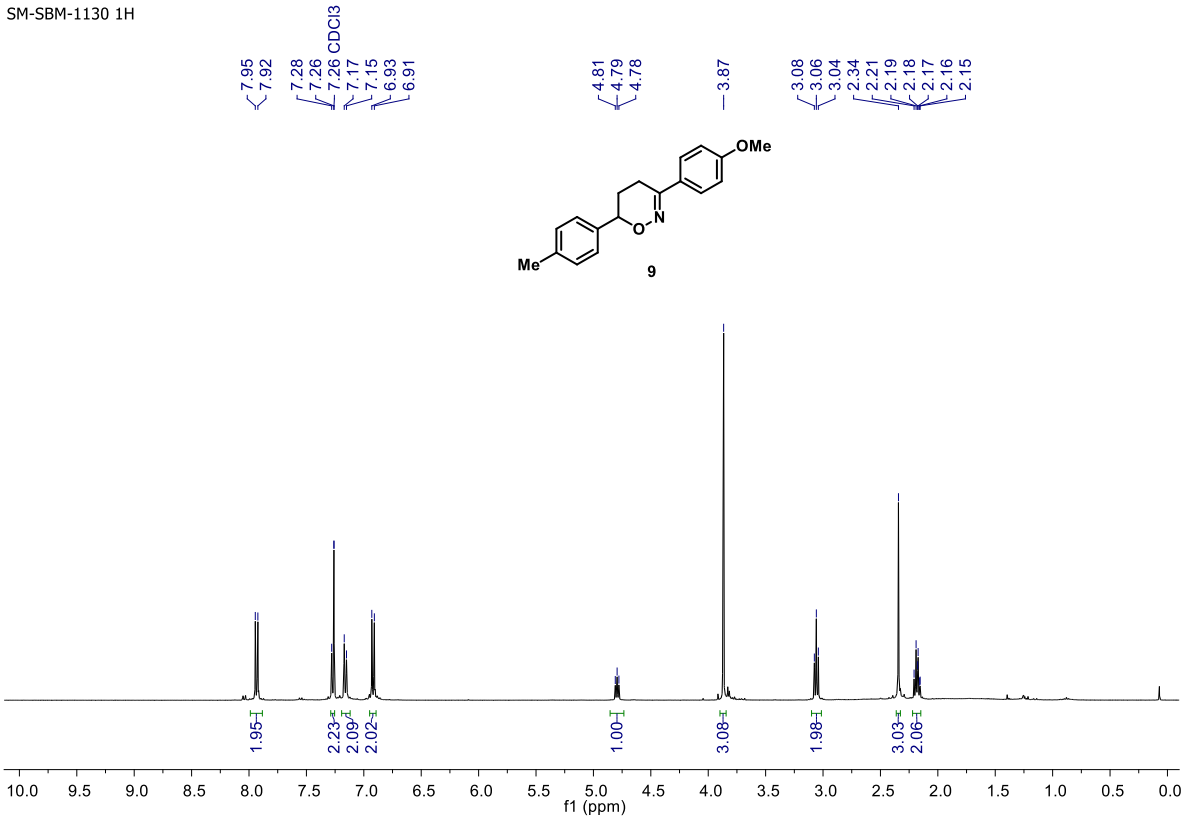
^{1}H NMR of **8** (400 MHz, $CDCl_3$):



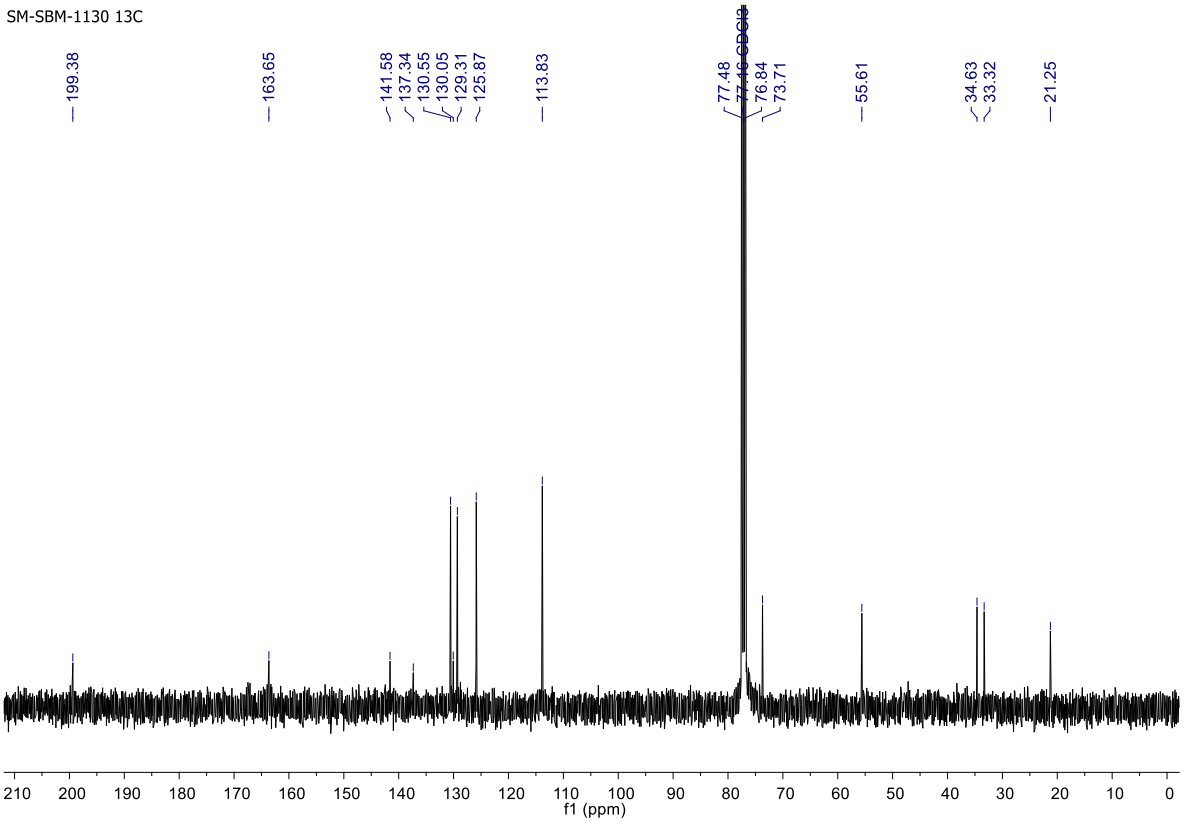
^{13}C{^{1}H} NMR of **8** (101 MHz, $CDCl_3$):



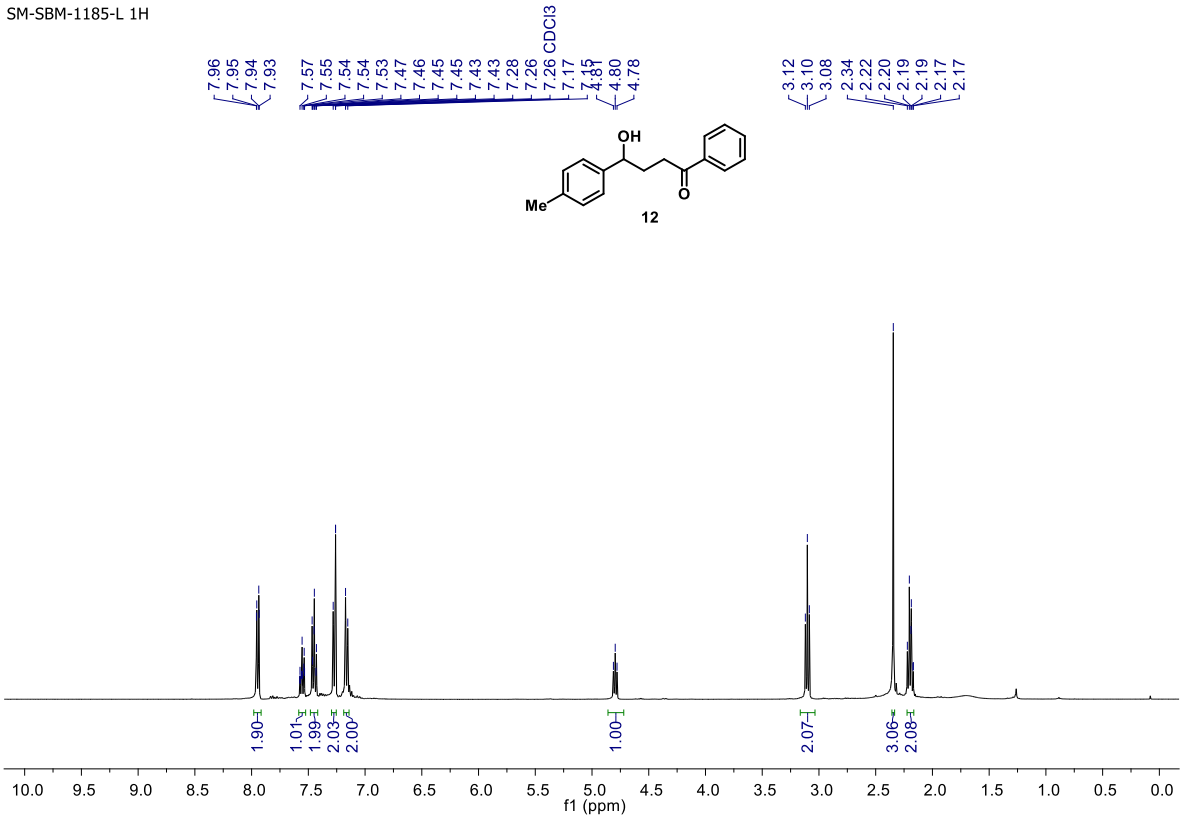
^{1}H NMR of **9** (400 MHz, $CDCl_3$):



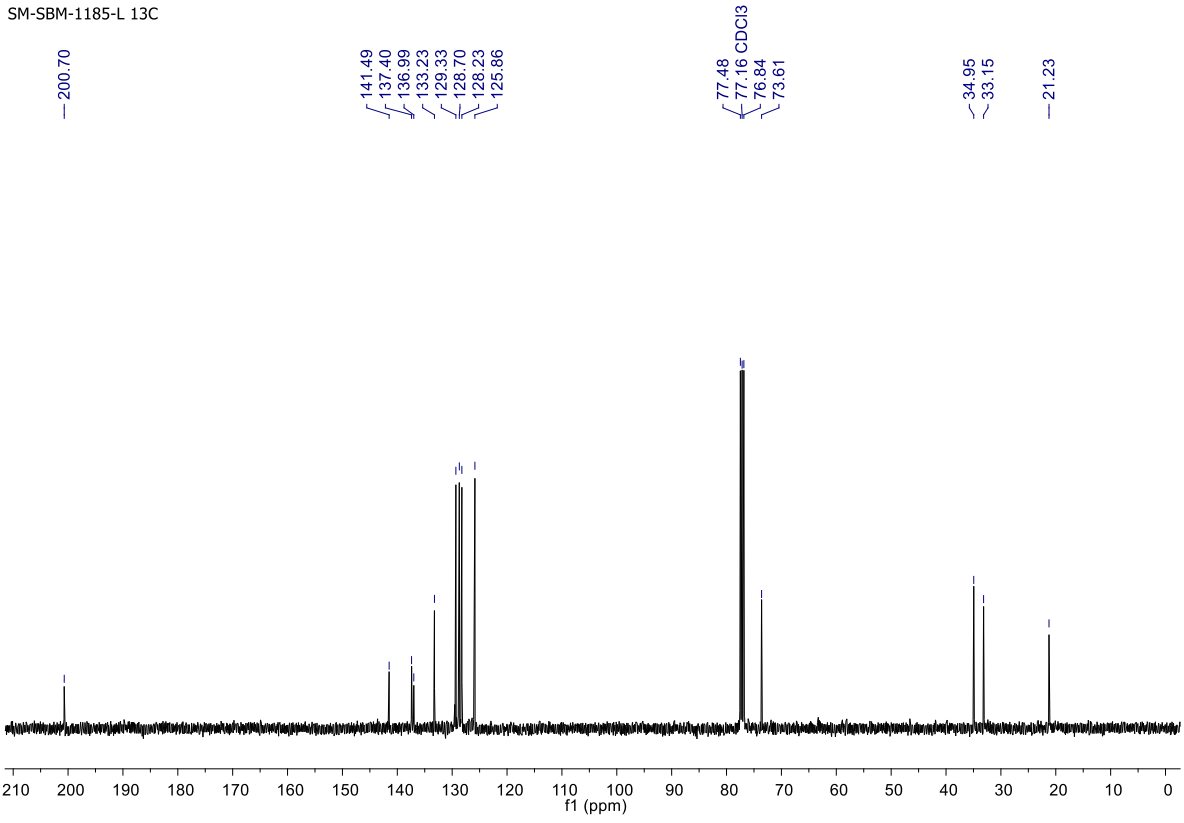
^{13}C{^{1}H} NMR of **9** (101 MHz, $CDCl_3$):



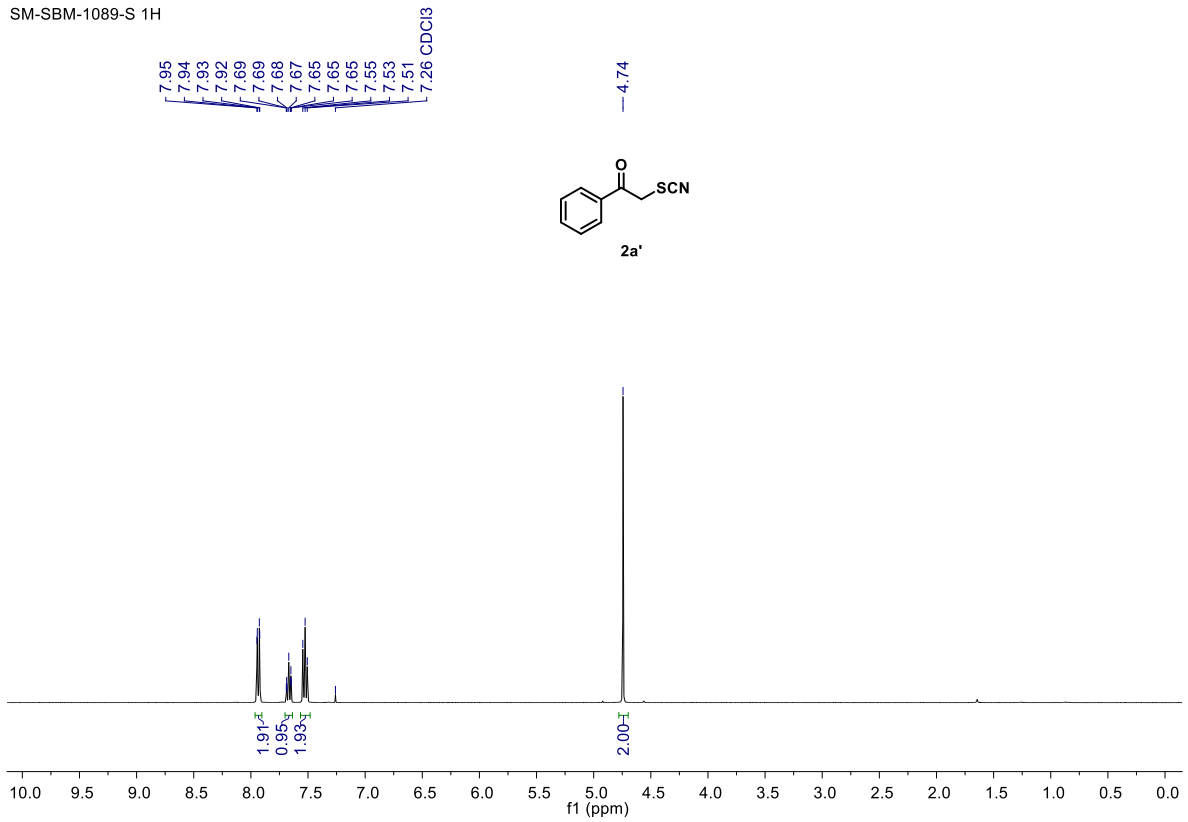
^{1}H NMR of **12** (400 MHz, $CDCl_3$):



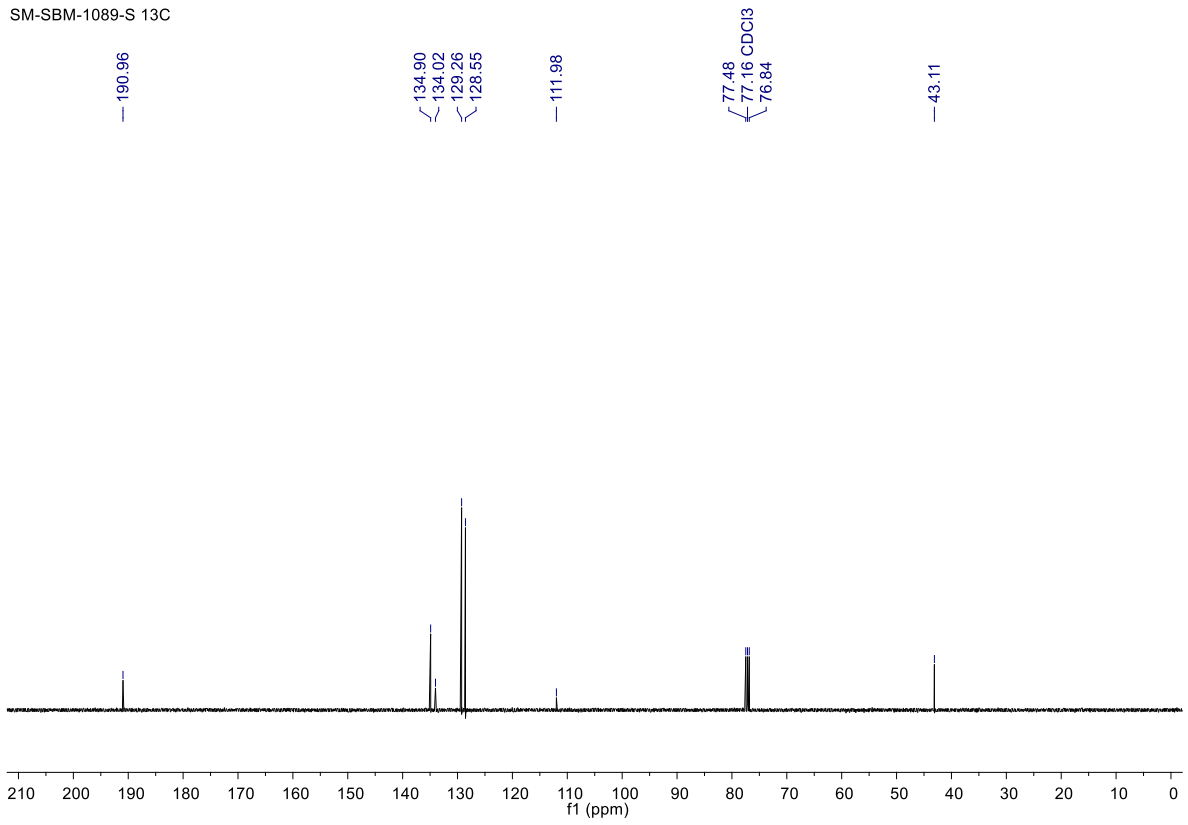
^{13}C{^{1}H} NMR of **12** (101 MHz, $CDCl_3$):



^{1}H NMR of **2a'** (400 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR of **2a'** (101 MHz, $CDCl_3$):



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