Supporting Information

Copper-Catalyzed Cross Coupling of Benzylic C–H Bonds and Azoles with Controlled *N*-Site Selectivity

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1. General Considerations

All reagents were purchased and used as received unless otherwise noted. Cu salts were purchased from Aldrich. Benzylic C–H substrates were purchased from Alfa Aesar, Ambeed, Ark Pharm, AstaTech, Chem-Impex, Combi-Blocks, Enamine, Matrix Chemicals, Millipore Sigma, Oakwood Chemicals and TCI America. Additives were purchased from Aldrich or TCI America. N-Fluorobenzenesulfonimide (NFSI) was purchased from Ark Pharm and Combi-Blocks. Diisopropyl phosphites were purchased from Aldrich, Oakwood Chemicals, Alfa Aesar and TCI America. All the reagents were used without further purification. Substrate **1q** was prepared with the procedure reported in literature.[1]

^{1}H, ^{13}C, ^{19}F and all the 2D NMR spectra were recorded on Bruker 400 MHz or Bruker 500 MHz spectrometers and chemical shifts are reported in parts per million (ppm). ^{1}H NMR spectra were referenced to tetramethylsilane at 0.00 ppm and ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.16 ppm. Column chromatography was performed using a Biotage Isolera One® with reusable 25 g SNAP Ultra® cartridges, 25 g Sfär® cartridges or standard silica cartridges. Further purification of impure samples was conducted using preparative thin-layer chromatography with Analtech® Glass-Backed Silica G UNIPLATES®. High-resolution mass spectra were obtained using a Thermo Q Exactive™ Plus (ESI or ASAP-MS) by the mass spectrometry facility at the University of Wisconsin. Melting points were determined using a DigiMelt MPA160 SRS melting point apparatus.

2. Experimental Procedures for Cross-Coupling Reactions

General Procedure (I) for Cross Coupling of N–H Nucleophiles and Benzylic C–H Substrates (pressure tube, temperature ≥ 50 °C)

Copper(I) chloride (2.0 mg, 0.020 mmol, 10 mol%), tetrabutylammonium chloride (2.8 mg, 0.020 mmol, 10 mol% or 16.8 mg, 0.060 mmol, 30 mol%), NFSI (94.6 mg, 0.30 mmol, 1.5 equiv), N–H nucleophile (0.50 mmol, 2.5 equiv) and benzylic substrate (if solid, 0.20 mmol, 1.0 equiv) were added to a glass pressure tube under air. The pressure tube was then moved to a glove box under N_2 atmosphere. Solvent (1.0 mL), benzylic substrate (if liquid, 0.20 mmol, 1.0 equiv) and diisopropyl phosphite (16.3 μL, 0.10 mmol, 0.5 equiv) were added to the tube. The tube was sealed in the glove box and taken out to a hot plate. The sealed tube was heated at 50 °C with stirring for 16 h. When the reaction finished, the mixture was cooled down to room temperature. Then the mixture was evaporated under vacuum and the crude mixture was purified by column chromatography (silica gel, eluted by pentane:ethyl acetate = 20:1 to 4:1).
Trimethylsilyl triflate (3.6 μL, 0.020 mmol, 10 mol%) or BF_3•OEt_2 (2.5 μL, 0.020 mmol, 10 mol%) was added in the glove box when they were used as an additive instead of tetrabutylammonium chloride.

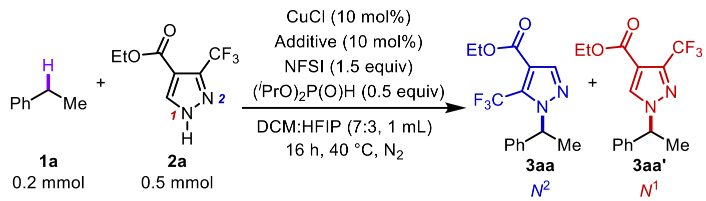
General Procedure (II) for Cross Coupling of N–H nucleophiles and Benzylic C–H Substrates (glass vial, temperature ≤ 40°C)

Copper(I) chloride (2.0 mg, 0.020 mmol, 10 mol%), tetrabutylammonium chloride (5.6 mg, 0.020 mmol, 10 mol% or 16.8 mg, 0.060 mmol, 30 mol%), NFSI (94.6 mg, 0.30 mmol, 1.5 equiv), N–H nucleophile (0.50 mmol, 2.5 equiv) and benzylic substrate (if solid, 0.20 mmol, 1.0 equiv) were added under air to a 4 ml borosilicate glass vial containing a magnetic stir bar. Then the vial was capped with a pierceable Teflon cap. A needle was pierced through the cap to facilitate exchange of the vial headspace with the atmosphere. Then the vial was moved into a glove box, through three vacuum-nitrogen-backfill cycles. The needle was removed, and the vial was taken out of the glove box (now sealed under an inert gas). Solvent (1.0 mL), benzylic substrate (if liquid, 0.20 mmol, 1.0 equiv), and diisopropyl phosphite (16.3 μL, 0.10 mmol, 0.5 equiv) were added into the vial by injection through the cap. The sealed vial was heated at 30 °C and stirred for 16 h. When the reaction finished, the mixture was cooled down to room temperature. Then the mixture was evaporated under vacuum and the crude mixture was purified by column chromatography (silica gel, eluted by pentane:ethyl acetate = 20:1 to 4:1).

3. Optimization of the Reaction Conditions

Optimization of reaction conditions were conducted according to general procedure (I) or (II), with variations specified in each table. Reaction yields were monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the internal standard.

Table S1a. Assessment of Ancillary Ligands



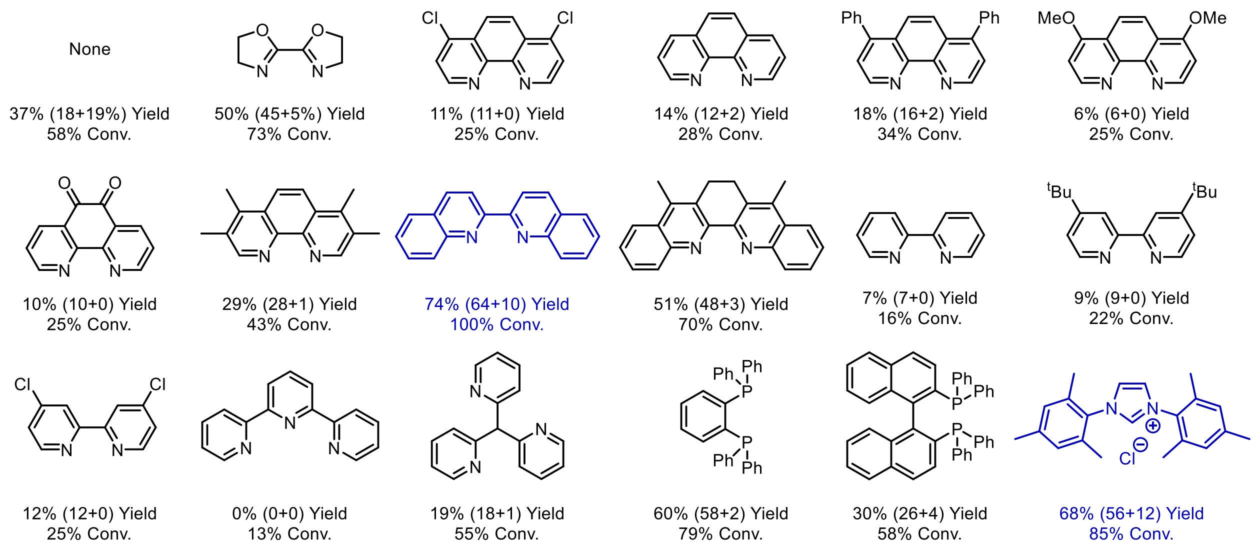
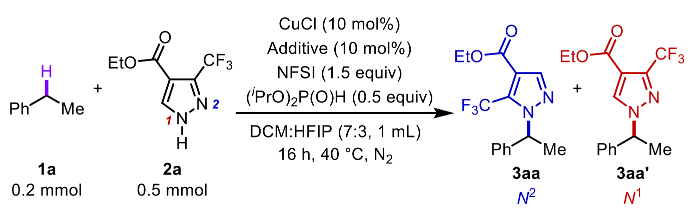


Table S2b. Ligand Comparison with Selected Nucleophiles



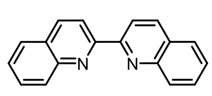
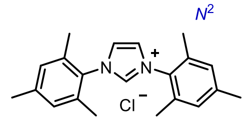
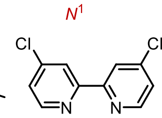
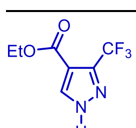
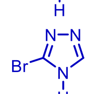
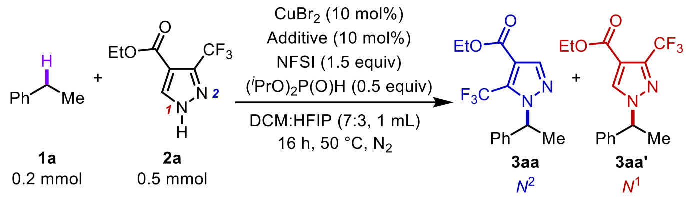
			
	74% (64+10) Yield 100% Conv.	68% (56+12) Yield 85% Conv.	12% (12+0) Yield 25% Conv.
	0% Yield 4% Conv.	61% (52+9) Yield 88% Conv.	25% (20+5) Yield 40% Conv.

Table S2. Effect of Different Additives in Controlling the Regioselectivity[a]

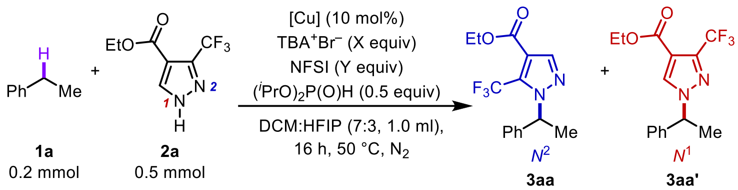


Entry	Additive	Conv. of **1a** (%)	Yield of ***N-2*** (%)	Yield of ***N-1*** (%)	***N-2*:*N-1***
1	$IMes^+Cl^-$	100	63	7	9.0:1
2	TBA^+Br^-	100	72	4	18:1
3	$TBA^+NO_3^-$	91	54	2	13:1
4	TBA^+Cl^-	100	70	6	11.7:1
5	(none)	89	57	5	9.3:1
6	$TBA^+PF_6^-$	91	57	11	5.8:1
7	$TBA^+HSO_4^-$	100	57	10	5.7:1
8	$TBA^+BH_2^-$	88	52	24	2.2:1
9	TBA^+OTf^-	96	45	23	2.1:1
10	$TBA^+ClO_4^-$	100	63	34	1.7:1
11	TBDMSCl	94	44	27	1.6:1
12	TMSCN	91	42	28	1.5:1
13	TIPSCl	91	36	29	1.2:1
14	$TBA^+BF_4^-$	100	26	34	1:1.3
15	$TEA^+BF_4^-$	97	35	43	1:1.2
16	$(Ph)_3SiCl$	97	34	37	1:1.1
17	TMSCl	94	30	47	1:1.8
18	BF_3•OEt_2	91	6	60	1:10
19	TMSOTf	42	2	38	1:19
20[b]	TMSOTf	100	1	66	1:66

[a]TBA, tetrabutylammonium; TEA, tetraethylammonium; TMS, trimethylsilyl; TIPS, triisopropylsilyl; TBDMS, *tert*-butyldimethyl; DCM, dichloromethane; HFIP, hexafluoroisopropanol; Conv., conversion. [b]Reaction conducted at 60 °C.

Note: The screening of salts in this study indicate the imidazolium cation identified in previous screening results does not play an important role in reactivity or N^1/N^2 regioselectivity and can be replaced by tetrabutylammonium cation. When the additive contains a Lewis acid, such as TMSCl or BF_3•OEt_2, the regioselectiviy switiches to favor N^1.

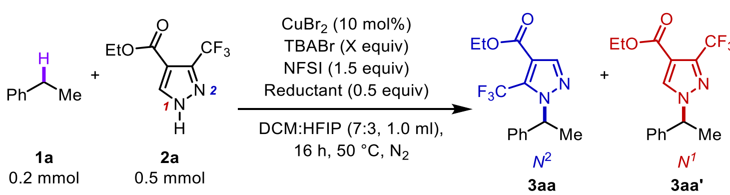
Table S3. Optimization of the Reaction Conditions with Various Solvents, Cu Salts and Temperature[a]



Entry	[Cu]	Solvent	X	Y	Z	Conv. of **1** (%)	Yield of ***N-2*** (%)	Yield of ***N-1*** (%)	***N-2*:*N-1***
1	CuCl	DCE	0.1	1.5	2.5	94	60	3	20:1
2	CuCl	PhH	0.1	1.5	2.5	58	12	0	–
3	CuCl	PhCl	0.1	1.5	2.5	91	48	0	–
4	CuCl	$PhCF_3$	0.1	1.5	2.5	64	24	1	24:1
5	CuCl	$PhNO_2$	0.1	1.5	2.5	64	12	1	12:1
6	CuCl	$MeNO_2$	0.1	1.5	2.5	97	21	34	1:1.6
7	CuCl	DCM	0.1	1.5	2.5	100	48	8	6:1
8	CuCl	HFIP	0.1	1.5	2.5	91	2	39	1:19.5
10	CuCl	DCM:HFIP=8:2	0.1	1.5	2.5	100	63	9	7:1
11	CuCl	DCM:HFIP=6:4	0.1	1.5	2.5	100	45	16	2.8:1
12	CuCl	DCM:HFIP=7:3	0.1	1.5	2.5	100	63	8	7.9:1
13	CuOAc	DCM:HFIP=7:3	0.1	1.5	2.5	94	66	6	11:1
14	CuI	DCM:HFIP=7:3	0.1	1.5	2.5	100	57	11	5.2:1
15	CuBr	DCM:HFIP=7:3	0.1	1.5	2.5	100	57	11	5.2:1
16	$CuCl_2$	DCM:HFIP=7:3	0.1	1.5	2.5	100	60	10	6:1
17	$CuBr_2$	DCM:HFIP=7:3	0.1	1.5	2.5	100	63	11	5.7:1
18	$CuBr_2$	DCM:HFIP=7:3	0.1	1.0	2.5	94	60	8	7.5:1
19	$CuBr_2$	DCM:HFIP=7:3	0.1	2.0	2.5	100	63	8	7.9:1
20	$CuBr_2$	DCM:HFIP=7:3	0.1	1.5	2.5	100	69	6	11.5:1
21	$CuBr_2$	DCM:HFIP=7:3	0.3	1.5	2.5	97	72	2	36:1
22	CuCl	DCM:HFIP=7:3	0.3[a]	1.5	2.5	100	76	4	19:1
23	CuCl	DCM:HFIP=7:3	0.1[a]	1.5	2.5	100	75	4	19:1

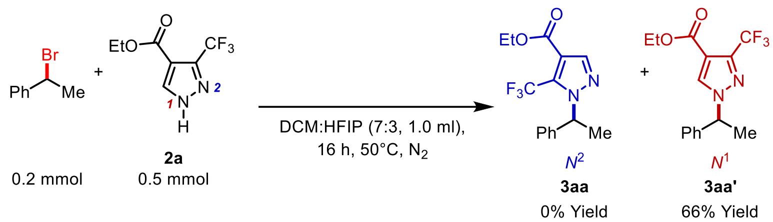
[a]Reactions were conducted with TBA^+Cl^- instead of TBA^+Br^-. DCE, 1,2-dichloroethane; DCM, DCM; HFIP, hexafluoroisopropanol; T, temperature; Conv., conversion.

Table S4. Investigation of various reductants with ethylbenzene as the substrate



Entry	Reductant	Conv. of **1** (%)	Yield of ***N-2*** (%)	Yield of ***N-1*** (%)	***N-2*:*N-1***
1	-	100	63	5	13:1
2	$(MeO)_2P(O)H$	100	33	5	6.6:1
3	$(EtO)_2P(O)H$	100	42	7	6.0:1
4	$(^iPrO)_2P(O)H$	100	68	4	17:1
5	$(^tBuO)_2P(O)H$	76	45	4	11:1
6	$(^nBuO)_2P(O)H$	100	51	7	7.3:1
7	$(MeO)_2MeSiH$	91	48	3	16:1
8	$(EtO)_2MeSiH$	94	51	5	10:1
9	PhNHNHPh	28	4	0	-
10	$EtCO_2NHNHCO_2Et$	100	51	2	26:1
11	$P(^nBu)_3$	88	54	6	9.0:1
12	Sodium Ascorbate	100	36	11	3.3:1

4. Displacement of Benzylic Bromide with 2a



2a (104 mg, 0.50 mmol, 2.5 equiv) was added to a glass pressure tube under air. The pressure tube was then moved to a glove box under N_2 atmosphere. DCM:HFIP (7:3, 1.0 mL) and (1-Bromoethyl)benzene (27.3 μL, 0.20 mmol, 1.0 equiv) and were added to the tube. The tube was sealed in the glove box and taken out to a hot plate. The sealed tube was heated at 50 °C with stirring for 16 h. When the reaction finished, the mixture was cooled down to room temperature. Then an aliquot of the mixture was taken, diluted with $CDCl_3$. Reaction yield was monitored by ^1H NMR spectroscopy with 0.2 mmol mesitylene as the internal standard.

5. Additional Screening Data with Benzylic C–H Substrates and Azoles

Not all substrates tested afforded good reactivity in the cross-coupling reactions, and a survey of suboptimal results are provided in Figure S1. Ethylbenzene derivatives with electron-deficient *para*-substituents are less reactive toward C–H activation, and lower conversions and yields are observed (Figure S1A and B). Pyridine-containing substrates do afford the desirable products but often with low yield (Figure S1C). More electron-rich azoles appear to inhibit the C–N cross coupling reactivity, possibly reflecting coordination/inhibition of the copper catalyst or because they undergo side reactions with NFSI (Figure S1D). The presence of large substituents near the benzylic C–H site also inhibits the conversion of the starting material (Figure S1E). Reaction yields were monitored by ^{1}H NMR spectroscopy with 0.2 mmol mesitylene as the internal standard.

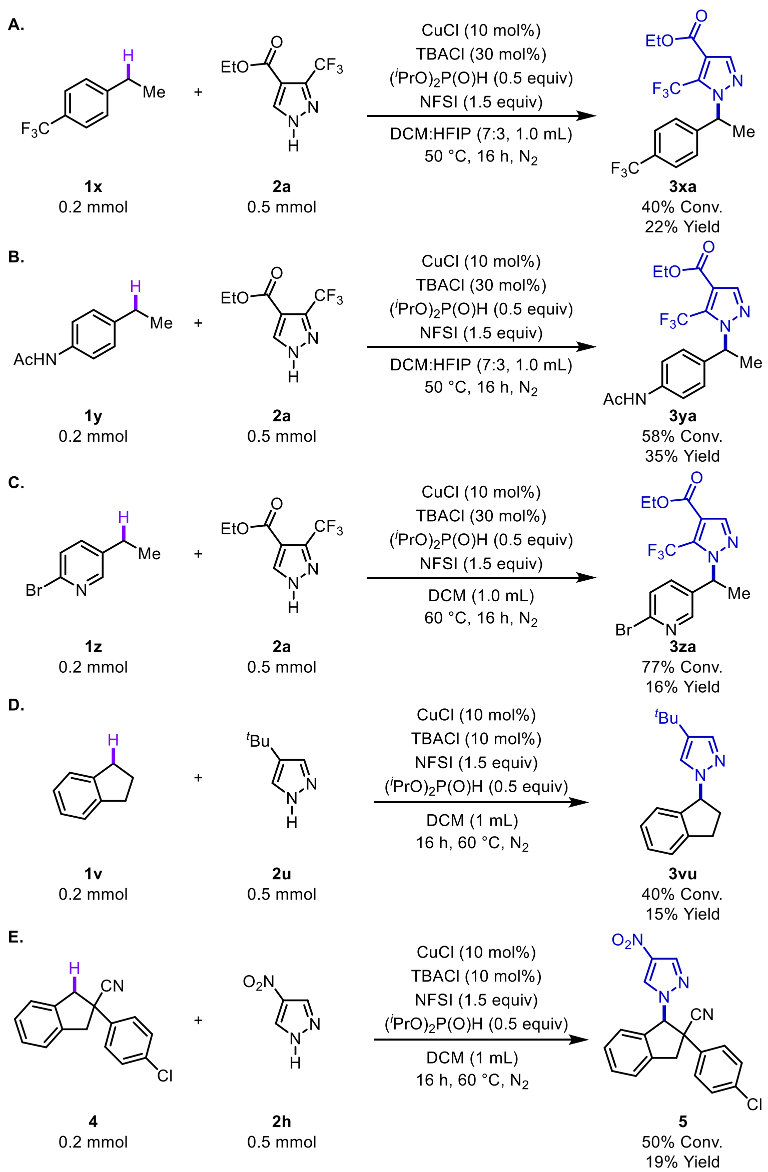


Figure S1. Screening data with additional benzylic C–H substrates and azoles.

A selection of cross coupling reactions of benzylic C–H substrates and azoles were further analyzed to insight the mass balance of this method.

- While TBABr has shown high selectivity for *N*-2 regioisomer in coupling reactions with **2a**, when electron-rich substrates like **1h** were employed, formation of brominated products on the arene were observed. Replacing TBABr with TBACl avoided this side reactivity (Figure S2A).
- Minor side products were observed where the byproduct benzenesulfonimide from NFSI was introduced to the benzylic sites, especially when cyclic substrates were engaged (Figure S2B and S2C).

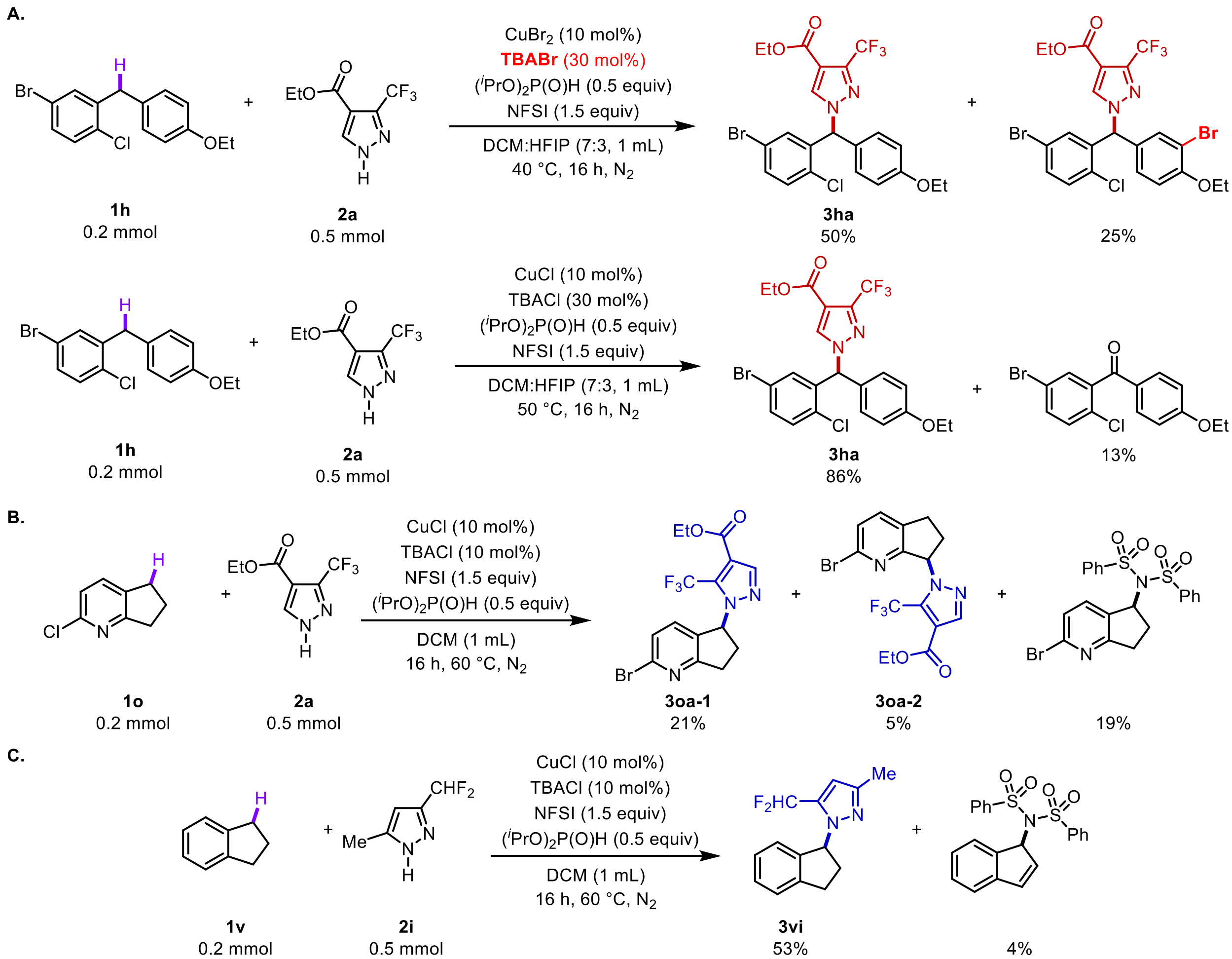


Figure S2. Further analyses of reaction outcomes of cross couplings of benzylic C–H bonds and azoles

6. Characterization of Regioselectivity

A. Benzylic C–H cross coupling products with 2a

All the *N*-1 and *N*-2 regioisomers were assigned based on 2D NMR spectra (HSQC and HMBC), along with additional characteristics in the ^{13}C and ^{19}F NMR spectra.

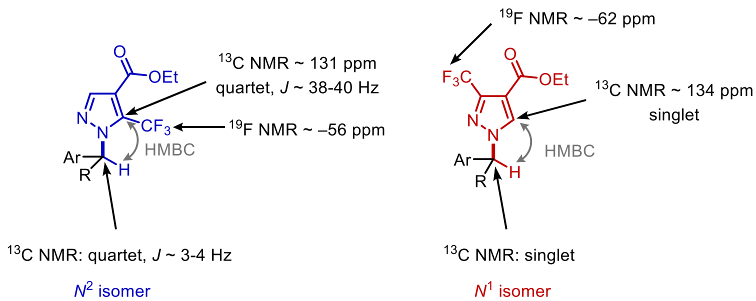


Figure S3. Evidence for regioisomer assignment of benzylic C–H cross coupling products with **2a**

B. Benzylic C–H cross coupling products with other ambidentate azoles

Regioisomers with other azoles were assigned based on 2D NMR spectra (HSQC and HMBC), literature values and/or the number of peaks in ^{13}C NMR spectra.

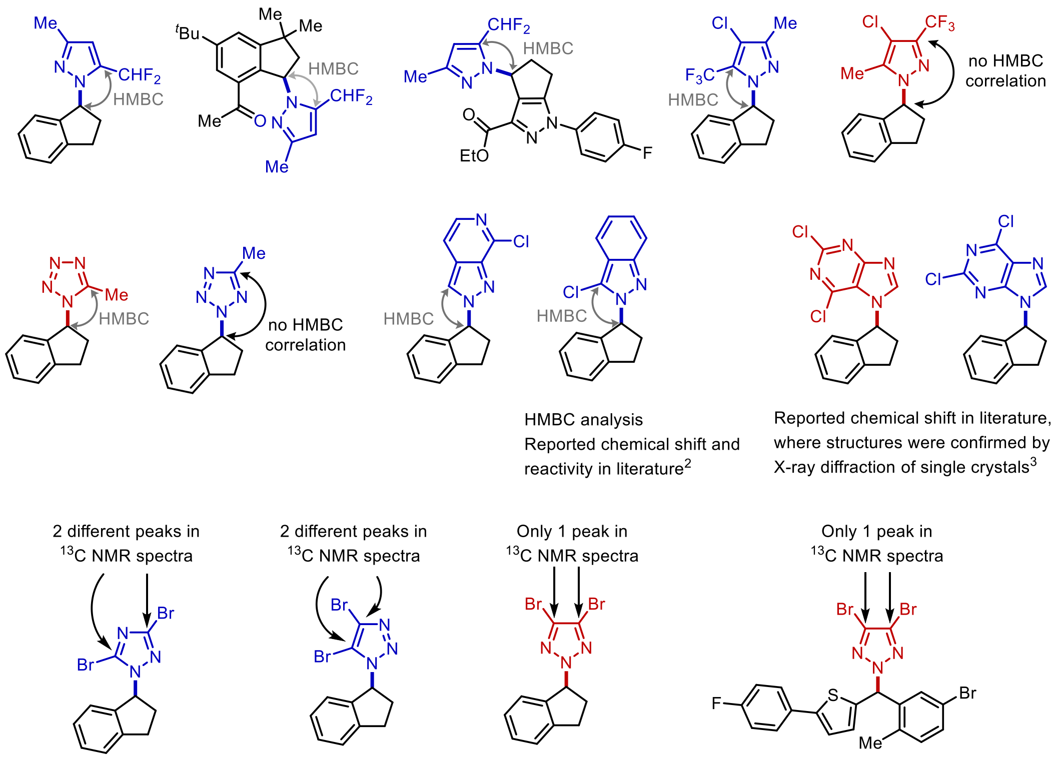


Figure S4. Proof of regioisomer assignment for benzylic C–H cross coupling products with other ambidentate azoles

7. Crystallization and Crystallographic Data for $[(C_6H_5)N(CH_3)_3]_2[CuBr_4]$ and 2a

Preparation

Copper(I) bromide (28.7 mg, 0.2 mmol, 1.0 equiv) and trimethylphenylammonium bromide (129.7 mg, 0.6 mmol, 3.0 equiv) were weighed into a 4 mL borosilicate glass vial in a glove box under nitrogen atmosphere, followed by the addition of 1 mL 1,1,1,3,3,3-hexafluoroisopropanol. N-fluorobenzenesulfonimide (31.5 mg, 0.1 mmol, 0.5 equiv) was then added into the solution. The vial was then sealed with a Teflon cap and the reaction mixture was then heated at 50℃ for 30 min. After that, **2a** (166.5 mg, 0.4 mmol, 4.0 equiv) was added into the solution. The reaction mixture was then removed from the glovebox and heated at 50℃ on a hot plate for 16 h before cooling down to room temperature. The 4 mL glass vial was uncapped and placed in a 15 mL borosilicate glass vial containing pentane. The 15 mL glass vial was then sealed with a 15 mL Teflon cap to allow vapor diffusion. Two kinds of crystals were found in the glass vial: blue crystal $[(C_6H_5)N(CH_3)_3]_2[CuBr_4]$ and colorless crystal **2a**.

Crystallographic Data for $[(C_6H_5)N(CH_3)_3]_2[CuBr_4]$

Data Collection

A blue crystal with approximate dimensions 0.14 x 0.01 x 0.005 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and a diffractometer to crystal distance of 4.96 cm.[4]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 30 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 5662 strong reflections from the actual data collection.

The data were collected by using a full sphere data collection routine to survey reciprocal space to the extent of a full sphere to a resolution of 0.80 Å. A total of 28817 data were harvested by collecting 4 sets of frames with 0.6º scans in ω and φ with exposure times of 180 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[5]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups *Pn* and *P*2/*n*. The *E*-statistics strongly suggested the centrosymmetric space group *P*2/*n* that yielded chemically reasonable and computationally stable results of refinement.[6-11]

A successful solution by direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The structure crystallizes as an inorganic salt with the formula $[(C_6H_5)N(CH_3)_3]_2[CuBr_4]$. Atom Br4 in the $[CuBr_4]^{2-}$ anion is disordered over two positions, with a major component occupancy of 58.5(16) %.

The structure also contains two trimethylaniline cations. One of these cations resides on a crystallographic general position and is fully occupied. The second cation is disordered over two different crystallographic sites. Both of these sites are crystallographic special positions corresponding to two-fold axes. Thus, this cation presents itself in the symmetry-independent unit as being 50% occupied at two different crystallographic sites and is equally disordered across the crystallographic two-fold axis at each site. This cation was refined with 1,2 and 1,3 distance restraints, as well as with atomic displacement parameter restraints and constraints.

The final least-squares refinement of 305 parameters against 4749 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0453 and 0.0962, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{18}H_{28}Br_4CuN_2$ (M =655.60 g/mol): monoclinic, space group *P*2/*n* (no. 13), a = 9.247(4) Å, b = 8.397(3) Å, c = 29.837(10) Å, β = 93.608(11) °, V = 2312.2(14) Å^3, Z = 4, T = 99.99 K, μ(Mo Kα) = 7.862 mm^{-1}, *Dcalc* = 1.883 g/cm^3, 28817 reflections measured (2.736° ≤ 2Θ ≤ 52.85°), 4749 unique (R_{int} = 0.0705, R_{sigma} = 0.0545) which were used in all calculations. The final R_1 was 0.0453 (I > 2σ(I)) and wR_2 was 0.0962 (all data).

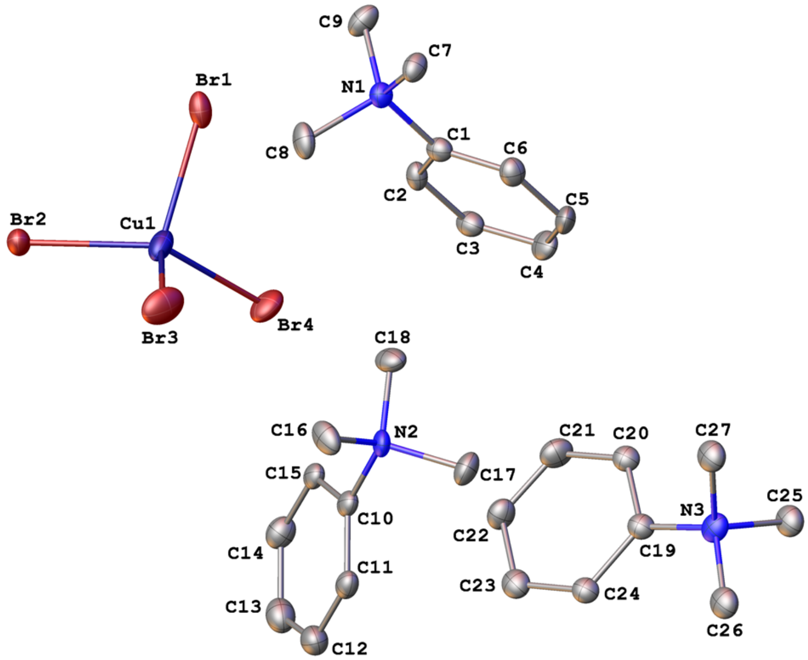


Figure S5. A molecular drawing of $[(C_6H_5)N(CH_3)_3]_2[CuBr_4]$. The N,N,N-trimethylanilinium cations containing atoms N2 and N3 are 50% occupied. All atoms are shown with 50% probability ellipsoids. All H atoms and minor disorder components are omitted.

Table S5. Crystal data and structure refinement for $[(C_6H_5)N(CH_3)_3]_2[CuBr_4]$.

Empirical formula	$[(C_6H_5)N(CH_3)_3]_2[CuBr_4]$
Formula weight	655.60
Temperature/K	99.99
Crystal system	monoclinic
Space group	*P*2/*n*
a/Å	9.247(4)
b/Å	8.397(3)
c/Å	29.837(10)
α/°	90
β/°	93.608(11)
γ/°	90
Volume/Å^3	2312.2(14)
Z	4
ρ_{calc}g/cm^3	1.883
μ/mm^{-1}	7.862
F(000)	1276.0
Crystal size/mm^3	0.14 × 0.01 × 0.005
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	2.736 to 52.85
Index ranges	$-11 \le h \le 11$, $-10 \le k \le 9$, $-37 \le l \le 35$
Reflections collected	28817
Independent reflections	4749 [R_{int} = 0.0705, R_{sigma} = 0.0545]
Data/restraints/parameters	4749/95/305
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.0879
Final R indexes [all data]	R_1 = 0.0727, wR_2 = 0.0962
Largest diff. peak/hole / e Å^{-3}	0.70/-1.02

Crystallographic Data for 2a

Data Collection

A colorless crystal with approximate dimensions 0.50 x 0.40 x 0.40 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu K_α (λ = 1.54178 Å) radiation and the diffractometer to crystal distance of 4.03 cm.[4]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 50 frames collected at intervals of 0.5º in a 25º range about ω with an exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX3 program. The final cell constants were calculated from a set of 2234 strong reflections from the actual data collection.

The data were collected by using a full sphere data collection routine to survey reciprocal space to the extent of a full sphere to a resolution of 0.81 Å. A total of 3882 data were harvested by collecting 9 sets of frames with 0.6º scans in ω and φ with an exposure time 5-20 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[5]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P2_1/m$ and $P2_1$. The *E*-statistics strongly suggested the centrosymmetric space group $P2_1/m$ that yielded chemically reasonable and computationally stable results of refinement.[6-11]

A successful solution by direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients.

The molecule resides on a crystallographic mirror plane.

The final least-squares refinement of 99 parameters against 912 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0305 and 0.0814, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_7H_7F_3N_2O_2$ (M =208.15 g/mol): monoclinic, space group $P2_1/m$ (no. 11), a = 6.7889(11) Å, b = 6.6884(5) Å, c = 9.9202(8) Å, β = 105.469(11)°, V = 434.13(9) $Å^3$, Z = 2, T = 99.97 K, μ(Cu Kα) = 1.420 mm^{-1}, $Dcalc$ = 1.592 g/cm^3, 3882 reflections measured (9.25° ≤ 2Θ ≤ 144.162°), 912 unique (R_{int} = 0.0278, R_{sigma} = 0.0202) which were used in all calculations. The final R_1 was 0.0305 (I > 2σ(I)) and wR_2 was 0.0814 (all data).

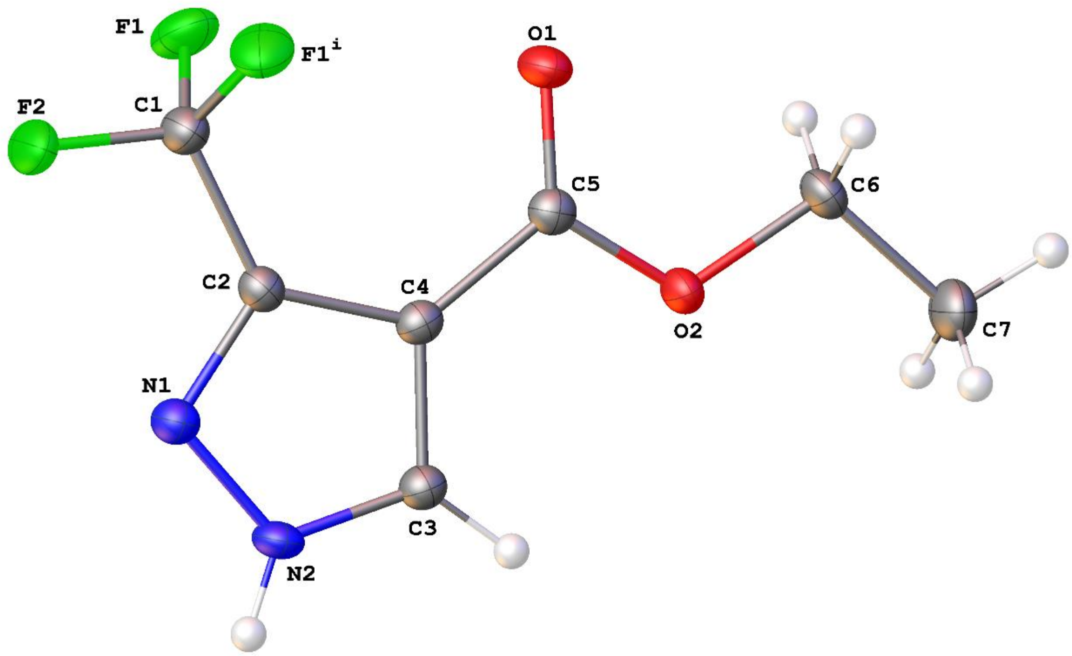
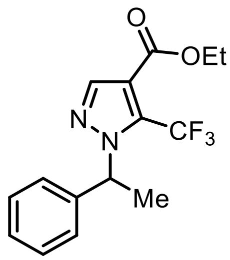


Figure S6. A molecular drawing of **2a** shown with 50% probability ellipsoids for non-hydrogen atoms. [Symmetry code: (i) x, $3/2 - y$, z.]

Table S6. Crystal data and structure refinement for 2a.

Empirical formula	$C_7H_7F_3N_2O_2$
Formula weight	208.15
Temperature/K	99.97
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	6.7889(11)
b/Å	6.6884(5)
c/Å	9.9202(8)
α/°	90
β/°	105.469(11)
γ/°	90
Volume/Å^3	434.13(9)
Z	2
ρ_{calc}g/cm^3	1.592
μ/mm^{-1}	1.420
F(000)	212.0
Crystal size/mm^3	0.5 × 0.4 × 0.4
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	9.25 to 144.162
Index ranges	$-7 \leq h \leq 8$, $-8 \leq k \leq 8$, $-12 \leq l \leq 12$
Reflections collected	3882
Independent reflections	912 [R_{int} = 0.0278, R_{sigma} = 0.0202]
Data/restraints/parameters	912/0/99
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0788
Final R indexes [all data]	R_1 = 0.0343, wR_2 = 0.0814
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27

8. Characterization of Compounds



Ethyl 1-(1-phenylethyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3aa**

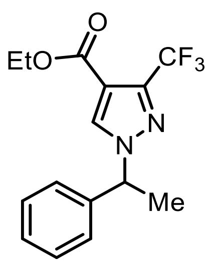
Reaction run using ethylbenzene **1a** (24.5 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 47.3 mg (76%) of pale-yellow liquid. TLC (Pentane:EtOAc, 9:1 v/v): R_f = 0.71.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.99 (s, 1H), 7.40 – 7.19 (m, 5H), 5.79 (q, *J* = 6.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.94 (d, *J* = 6.9 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.2, 141.5, 140.5, 131.4 (q, *J* = 40.1 Hz), 128.7, 128.1, 126.3, 119.7 (q, *J* = 271.2 Hz), 115.8 (q, *J* = 1.5 Hz), 61.1, 61.0 (q, *J* = 3.6 Hz), 22.1, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.9 ppm.

HRMS Calculated for $[C_{15}H_{15}F_3N_2O_2+H]^+$: 313.1158, Found: 313.1153.



Ethyl 1-(1-phenylethyl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3aa'**

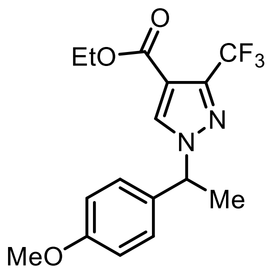
Reaction run using ethylbenzene **1a** (24.5 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and TMSOTf (3.6 μL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 39.6 mg (63%) of clear colorless liquid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.38.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.91 (s, 1H), 7.42 – 7.32 (m, 3H), 7.28 – 7.26 (m, 2H), 5.56 (q, *J* = 7.1 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.92 (d, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.0, 141.2 (q, *J* = 38.3 Hz), 139.4, 134.1, 129.1, 128.8, 126.7, 120.5 (q, *J* = 269.6 Hz), 113.2, 62.6, 61.0, 21.1, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -61.9 ppm.

HRMS Calculated for $[C_{15}H_{15}F_3N_2O_2+H]^+$: 313.1158, Found: 313.1157.



Ethyl 1-(1-(4-methoxyphenyl)ethyl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ba'**

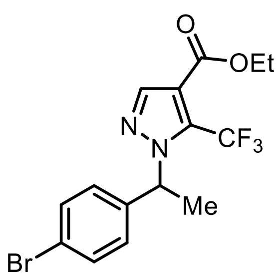
Reaction run using 4-ethylanisole **1b** (29.3 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and trimethylsilyl triflate (3.6 μL, 0.02 mmol, 0.1 equiv) at 60°C following the general procedure I (pressure tube). Yield = 54.7 mg (80%) of clear colorless liquid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.42.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.84 (s, 1H), 7.26 – 7.20 (m, 2H), 6.94 – 6.86 (m, 2H), 5.51 (q, *J* = 7.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.89 (d, *J* = 7.0 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.0, 159.8, 141.1 (q, *J* = 38.4 Hz), 133.8, 131.1, 128.1, 120.5 (q, *J* = 269.6 Hz), 114.4, 113.0, 62.1, 60.8, 55.3, 21.1, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -61.9 ppm.

HRMS Calculated for $[C_{16}H_{17}F_3N_2O_3+Na]^+$: 365.1083, Found: 365.1089.



Ethyl 1-(1-(4-bromophenyl)ethyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ca**

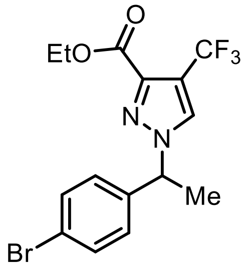
Reaction run using 4-bromoethylbenzene **1c** (27.5 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 57.6 mg (74%) of clear colorless liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.61.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.98 (s, 1H), 7.52 – 7.39 (m, 2H), 7.24 – 7.05 (m, 2H), 5.73 (q, *J* = 6.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.92 (d, *J* = 6.9 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.1, 141.7, 139.5, 131.9, 131.4 (q, *J* = 39.9 Hz), 128.2, 122.3, 119.6 (q, *J* = 271.3 Hz), 115.9 (q, *J* = 1.6 Hz), 61.2, 60.5 (q, *J* = 3.4 Hz), 22.1, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.9 ppm.

HRMS Calculated for $[C_{15}H_{14}BrF_3N_2O_2+H]^+$: 391.0264, Found: 391.0257.



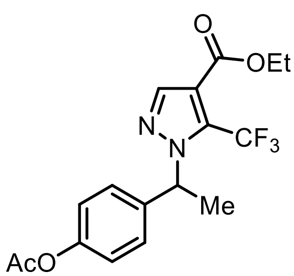
Ethyl 1-(1-(4-bromophenyl)ethyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ca'**
Reaction run using 4-bromoethylbenzene **1c** (27.5 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and trimethylsilyl triflate (3.6 μL, 0.02 mmol, 0.1 equiv) at 60°C following the general procedure I (pressure tube). Yield = 78.2 mg (35%) of pale-yellow semisolid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.31. Mp: 89-90 °C

^{1}H NMR ($CDCl_3$, 500 MHz): 7.92 (s, 1H), 7.71 – 7.41 (m, 2H), 7.18 – 7.11 (m, 2H), 5.51 (q, J = 7.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.90 (d, J = 7.1 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 160.9, 141.4 (q, J = 38.6 Hz), 138.5, 134.0, 132.3, 128.3, 122.8, 120.4 (q, J = 269.7 Hz), 113.4 (d, J = 1.2 Hz), 62.0, 61.0, 21.0, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -61.94 ppm.

HRMS Calculated for $[C_{15}H_{14}BrF_3N_2O_2+Na]^+$: 413.0083, Found: 413.0083.



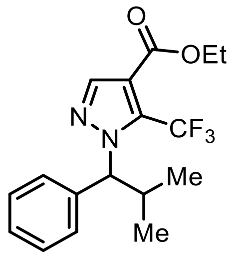
Ethyl 1-(1-(4-acetoxyphenyl)ethyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3da**
Reaction run using 4-ethylphenyl acetate **1d** (32.0 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 51.5 mg (70%) of brown solid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.33. Mp: 88-90 °C

^{1}H NMR ($CDCl_3$, 500 MHz): 7.98 (s, 1H), 7.34 – 7.28 (m, 2H), 7.10 – 7.01 (m, 2H), 5.77 (q, J = 6.9 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.93 (d, J = 6.9 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 169.3, 161.1, 150.4, 141.6, 137.9, 131.3 (q, J = 40.0 Hz), 127.7, 121.8, 119.6 (q, J = 271.2 Hz), 115.8 (q, J = 1.6 Hz), 61.1, 60.5 (q, J = 3.4 Hz), 22.2, 21.1, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.8 ppm.

HRMS Calculated for $[C_{17}H_{17}F_3N_2O_4+H]^+$: 371.1213, Found: 371.1218.



Ethyl 1-(2-methyl-1-phenylpropyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylat, **3ea**

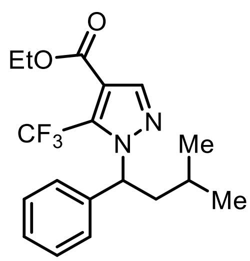
Reaction run using isobutylbenzene **1e** (31.4 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 45.8 mg (67%) of yellow liquid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.47.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.98 (s, 1H), 7.57 – 7.46 (m, 2H), 7.41 – 7.26 (m, 3H), 4.96 (d, *J* = 10.6 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.94 (dh, *J* = 12.6, 6.4, 5.8 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 4H), 0.82 (d, *J* = 2.3 Hz, 3H), 0.80 (d, *J* = 2.0 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.3, 141.7, 138.1, 131.9 (q, *J* = 39.6 Hz), 128.5, 128.4, 128.2, 119.7 (q, *J* = 271.3 Hz), 115.1 (q, *J* = 1.5 Hz), 72.7 (q, *J* = 3.0 Hz), 61.1, 33.6, 19.9, 19.7, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -54.9 ppm.

HRMS Calculated for $[C_{17}H_{19}F_3N_2O_2+H]^+$: 341.1471, Found: 341.1470.



Ethyl 1-(3-methyl-1-phenylbutyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3fa**

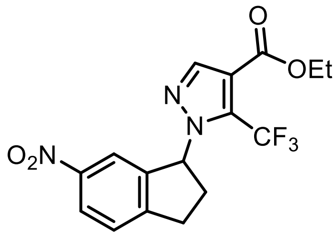
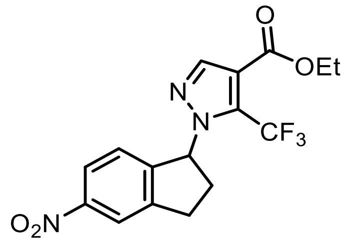
Reaction run using isopentylbenzene **1f** (34.7 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 42.1 mg (59%) of pale-yellow semisolid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.67.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.99 (s, 1H), 7.38 – 7.25 (m, 5H), 5.63 (dd, *J* = 9.1, 6.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.50 (ddd, *J* = 14.5, 9.1, 5.8 Hz, 1H), 2.00 (ddd, *J* = 14.0, 7.9, 6.0 Hz, 1H), 1.42 – 1.36 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 141.5, 139.7, 131.72 (q, *J* = 39.7 Hz), 128.7, 128.2, 127.0, 119.7 (q, *J* = 271.3 Hz), 115.6 (q, *J* = 1.5 Hz), 63.9 (q, *J* = 3.1 Hz), 61.1, 45.1, 29.7, 24.9, 22.5, 21.9, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.6 ppm.

HRMS Calculated for $[C_{18}H_{21}F_3N_2O_2+Na]^+$: 377.1447, Found: 377.1444.

	
Ethyl 1-(6-nitro-2,3-dihydro-1H-inden-1-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ga-1**	Ethyl 1-(5-nitro-2,3-dihydro-1H-inden-1-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ga-2**

Reaction run using 5-nitroindane **1g** (32.7 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), copper(II) bromide (4.5 mg, 0.02 mmol, 0.1 equiv.), and tetrabutylammonium bromide (19.3 mg, 0.06 mmol, 0.3 equiv) following the general procedure I (pressure tube) and two regioisomers were isolated.

3ga-1: Yield = 14.5 mg (20%) of pale-yellow semisolid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.47.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.20 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.90 (s, 1H), 7.89 (d, *J* = 2.1 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 6.16 (dd, *J* = 7.9, 6.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.40 (ddd, *J* = 17.0, 8.9, 5.2 Hz, 1H), 3.11 (ddd, *J* = 16.9, 8.8, 6.2 Hz, 1H), 2.80 (dtd, *J* = 13.6, 8.4, 5.2 Hz, 1H), 2.61 (ddt, *J* = 12.7, 9.0, 6.1 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H) ppm

^{13}C NMR ($CDCl_3$, 126 MHz): δ 160.9, 151.5, 147.7, 142.5, 141.9, 131.9 (q, *J* = 40.0 Hz), 125.8, 124.6, 120.0, 119.7 (q, *J* = 271.3 Hz), 115.9 (q, *J* = 1.3 Hz), 65.4 (q, *J* = 3.5 Hz), 61.3, 33.7, 31.0, 14.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): -55.5 ppm.

HRMS Calculated for $[C_{16}H_{14}F_3N_3O_4+NH_4]^+$: 387.1275, Found: 387.1271.

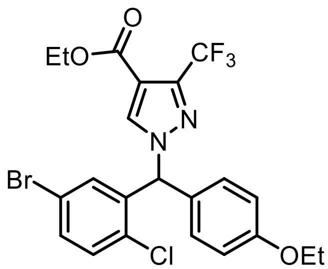
3ga-2: Yield = 9.8 mg (13%) of pale-yellow liquid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.59.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19 (d, *J* = 2.1 Hz, 1H), 8.09 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.90 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.15 (dd, *J* = 8.2, 6.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.40 (ddd, *J* = 16.3, 9.0, 5.0 Hz, 1H), 3.12 (dt, *J* = 15.9, 7.6 Hz, 1H), 2.81 (dtd, *J* = 13.4, 8.4, 5.0 Hz, 1H), 2.64 (ddt, *J* = 13.1, 8.9, 6.3 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 160.9, 148.8, 147.0, 145.7, 142.4, 131.9 (q, *J* = 40.0 Hz), 125.1, 122.8, 120.5, 119.7 (q, *J* = 271.5 Hz), 115.9 (q, *J* = 1.3 Hz), 65.4 (q, *J* = 3.5 Hz), 61.3, 33.6, 30.7, 14.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): -55.6 ppm.

HRMS Calculated for $[C_{16}H_{14}F_3N_3O_4+NH_4]^+$: 387.1275, Found: 387.1271.



Ethyl 1-((5-bromo-2-chlorophenyl)(4-ethoxyphenyl)methyl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ha'**

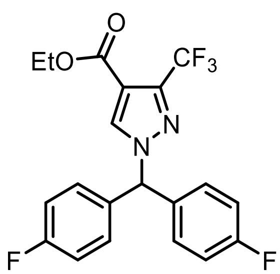
Reaction run using 4-(5-bromo-2-chlorobenzyl)phenyl ethyl ether **1h** (65.1 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 91.5 mg (86%) of yellow solid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.44. Mp: 84-87 °C

^{1}H NMR ($CDCl_3$, 500 MHz): 7.74 (s, 1H), 7.44 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.98 (s, 1H), 6.95 – 6.88 (m, 2H), 6.81 (d, *J* = 2.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 160.9, 159.7, 142.3 (q, *J* = 38.5 Hz), 138.0, 136.1, 132.9, 132.5, 131.6, 131.3, 129.9, 126.7, 121.1, 120.2 (q, *J* = 269.9 Hz), 115.2, 113.2, 67.1, 63.6, 61.1, 14.8, 14.0 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -62.0 ppm.

HRMS Calculated for $[C_{22}H_{19}BrClF_3N_2O_3+Na]^+$: 553.0112, Found: 553.0112.



Ethyl 1-(bis(4-fluorophenyl)methyl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ia'**

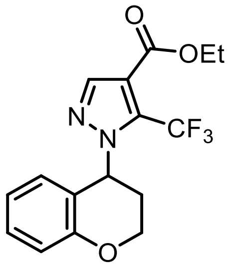
Reaction run using 4,4'-difluorodiphenylmethane **1i** (40.8 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), copper(II) bromide (4.5 mg, 0.02 mmol, 0.1 equiv.), and tetrabutylammonium bromide (19.3 mg, 0.06 mmol, 0.3 equiv) following the general procedure I (pressure tube). Yield = 78.3 mg (95%) of yellow solid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.30. Mp: 96-97 °C

^{1}H NMR ($CDCl_3$, 500 MHz): 7.83 – 7.78 (m, 1H), 7.12 – 7.03 (m, 8H), 6.78 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 162.8 (d, *J* = 249.1 Hz), 161.8, 160.8, 142.0 (q, *J* = 38.6 Hz), 135.4, 133.3 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 8.3 Hz), 120.3 (q, *J* = 269.8 Hz), 116.2 (d, *J* = 21.8 Hz), 113.5, 69.3, 61.1, 14.0 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -61.97, -112.26 ppm.

HRMS Calculated for $[C_{20}H_{15}F_5N_2O_2+Na]^+$: 433.0946, Found: 433.0951.



Ethyl 1-(chroman-4-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ja**

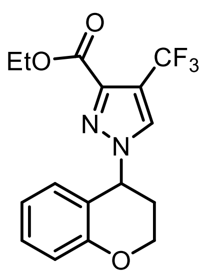
Reaction run using chroman **1j** (25.3 µL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate 2a (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (16.8 mg, 0.06 mmol, 0.3 equiv) following the general procedure I (pressure tube). Yield = 29.4 mg (43%) of yellow semisolid. TLC (pentane:EtOAc, 15:1 v/v): R_f = 0.51. **3ja'** (9.7 mg, 14%) was also isolated in this reaction.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.91 (s, 1H), 7.22 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 6.92 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.85 (td, *J* = 7.6, 1.1 Hz, 1H), 6.75 (dd, *J* = 7.9, 0.9 Hz, 1H), 5.82 (t, *J* = 5.7 Hz, 1H), 4.51 (dt, *J* = 11.6, 5.7 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.28 (dt, *J* = 10.8, 5.0 Hz, 1H), 2.45 (q, *J* = 5.6 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.1, 155.2, 141.9, 132.0 (q, *J* = 39.9 Hz), 130.0, 128.6, 120.9, 119.8 (q, *J* = 271.2 Hz), 119.1, 117.6, 115.7 (d, *J* = 1.6 Hz), 62.8, 61.3, 55.4 (q, *J* = 3.6 Hz), 30.1, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.7 ppm.

HRMS Calculated for $[C_{16}H_{15}F_3N_2O_3+Na]^+$: 363.0927, Found: 363.0918.



Ethyl 1-(chroman-4-yl)-4-(trifluoromethyl)-1H-pyrazole-3-carboxylate, **3ja'**

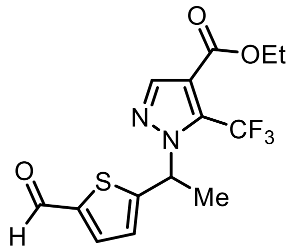
Reaction run using chroman **1j** (25.3 µL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate 2a (104.1 mg, 0.50 mmol, 2.5 equiv), and trimethylsilyl triflate (3.6 µL, 0.02 mmol, 0.1 equiv) at 60℃ following the general procedure I (pressure tube). Yield = 25.4 mg (37%) of white solid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.94. Mp: 86-88 °C

^{1}H NMR ($CDCl_3$, 500 MHz): 7.71 (s, 1H), 7.33 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.08 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.97 (m, 2H), 5.58 (t, *J* = 4.3 Hz, 1H), 4.34 – 4.23 (m, 3H), 3.92 (td, *J* = 11.5, 2.5 Hz, 1H), 2.53 (dtd, *J* = 14.6, 3.9, 2.5 Hz, 1H), 2.43 (ddt, *J* = 14.7, 11.4, 4.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 160.9, 155.5, 142.0 (q, *J* = 38.4 Hz), 135.3, 131.2, 130.5, 121.4, 120.4 (q, *J* = 269.8 Hz), 118.0, 116.4, 112.9, 61.5, 61.0, 56.7, 28.9, 14.0 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -62.0 ppm.

HRMS Calculated for $[C_{16}H_{15}F_3N_2O_3+Na]^+$: 363.0927, Found: 363.0922.



Ethyl 1-(1-(5-formylthiophen-2-yl)ethyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ka**

Reaction run using 5-ethyl-2-thiophenecarboxaldehyde **1k** (25.1 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate 2a (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (16.8 mg, 0.06 mmol, 0.3 equiv) following the general procedure I (pressure tube). Yield = 37.7 mg (54%) of pale-yellow liquid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.52.

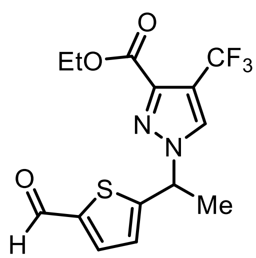
3ka' (13%) was observed in ^{1}H NMR analysis of the reaction crude, with 0.2 mmol mesitylene as the external standard.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.86 (s, 1H), 8.00 (s, 1H), 7.61 (d, J = 3.9 Hz, 1H), 7.05 (d, J = 3.9 Hz, 1H), 6.05 (q, J = 6.8 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.03 (d, J = 6.8 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 182.8, 160.8, 153.1, 143.8, 142.2, 135.7, 131.2 (q, J = 40.2 Hz), 126.5, 116.1 (q, J = 1.3 Hz), 119.5 (q, J = 271.4 Hz), 61.3, 56.8 (q, J = 3.7 Hz), 22.9, 14.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): -55.9 ppm.

HRMS Calculated for $[C_{14}H_{13}BF_3N_2O_3S+Na]^+$: 369.0491, Found: 369.0485.



Ethyl 1-(1-(5-formylthiophen-2-yl)ethyl)-4-(trifluoromethyl)-1H-pyrazole-3-carboxylate, **3ka'**

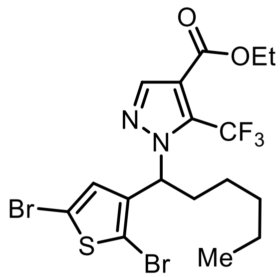
Reaction run using 5-ethyl-2-thiophenecarboxaldehyde **1k** (25.1 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and trimethylsilyl triflate (3.6 μL, 0.02 mmol, 0.1 equiv) at 60°C following the general procedure I (pressure tube). Yield = 34.6 mg (50%) of yellow semisolid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.91.

^{1}H NMR ($CDCl_3$, 500 MHz): 9.88 (s, 1H), 8.04 (s, 1H), 7.66 (d, J = 3.8 Hz, 1H), 7.11 (d, J = 3.8 Hz, 1H), 5.83 (q, J = 7.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.02 (d, J = 7.1 Hz, 3H), 1.34 (t, J = 7.1 Hz, 4H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 182.8, 160.6, 152.2, 143.9, 141.8 (q, J = 38.7 Hz), 136.1, 133.7, 126.94, 120.2 (q, J = 269.8 Hz), 113.8, 61.1, 58.3, 21.8, 14.0 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -62.0 ppm.

HRMS Calculated for $[C_{14}H_{13}F_3N_2O_3S+Na]^+$: 369.0491, Found: 369.0487.



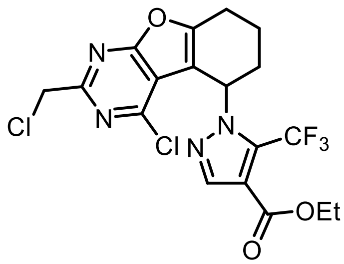
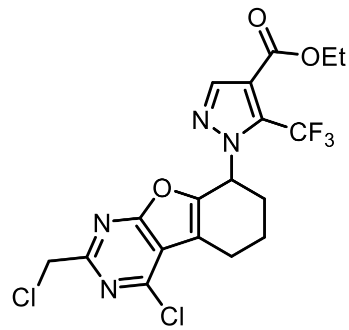
Ethyl 1-(1-(2,5-dibromothiophen-3-yl)hexyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3la**
Reaction run using 2,5-dibromo-3-hexylthiophene **1l** (42 μL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv, and tetrabutylammonium chloride (16.8 mg, 0.06 mmol, 0.3 equiv) following the general procedure I (pressure tube). Yield = 68.7 mg (65%) of pale-yellow liquid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.59.

^{1}H NMR ($CDCl_3$, 500 MHz): 8.00 (s, 1H), 7.14 (s, 1H), 5.69 (dd, *J* = 8.7, 6.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.35 (dtd, *J* = 14.2, 9.2, 5.3 Hz, 1H), 2.03 (ddt, *J* = 13.5, 9.8, 6.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.32 – 1.25 (m, 4H), 1.26 – 1.19 (m, 1H), 1.16 – 1.08 (m, 1H), 0.88 – 0.83 (m, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.1, 142.0, 139.9, 132.0 (q, *J* = 40.1 Hz), 129.8, 119.5 (q, *J* = 271.6 Hz), 115.6, 111.7, 110.0, 61.2, 60.1 (q, *J* = 3.4 Hz), 36.0, 31.0, 25.5, 22.3, 14.1, 13.9 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.7 ppm.

HRMS Calculated for $[C_{17}H_{19}BrF_3N_2O_2S+H]^+$: 530.9559, Found: 530.9554.

	
Ethyl 1-(4-chloro-2-(chloromethyl)-5,6,7,8-tetrahydrobenzofuro[2,3-d]pyrimidin-5-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ma-1**	Ethyl 1-(4-chloro-2-(chloromethyl)-5,6,7,8-tetrahydrobenzofuro[2,3-d]pyrimidin-8-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ma-2**

Reaction run using 3-chloro-5-(chloromethyl)-8-oxa-4,6-diazatricyclo[7.4.0.0{2,7}]trideca-1(9),2,4,6-tetraene **1m** (51.4 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (16.8 mg, 0.06 mmol, 0.3 equiv) following the general procedure II (glass vial) at 40 °C and two regioisomers were isolated.

3ma-1: Yield = 72.3 mg (45%) of yellow semisolid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.32.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.89 (s, 1H), 5.87 (t, *J* = 5.6 Hz, 1H), 4.73 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.11 (dtd, *J* = 17.0, 5.5, 1.6 Hz, 1H), 2.92 (dddd, *J* = 17.0, 7.3, 5.5, 1.7 Hz, 1H), 2.43 (q, *J* = 5.9 Hz, 2H), 2.30 – 2.18 (m, 1H), 2.00 (dh, *J* = 17.2, 5.6 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 167.0, 161.1, 160.7, 153.4, 149.7, 142.0, 132.0 (q, *J* = 40.3 Hz), 119.6 (q, *J* = 271.4 Hz), 117.2, 116.3 (q, *J* = 1.6 Hz), 116.1, 61.3, 54.5 (q, *J* = 3.9 Hz), 46.2, 30.8, 21.0, 19.4, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.8 ppm.

HRMS Calculated for $[C_{18}H_{15}Cl_2F_3N_4O_3+H]^+$: 463.0546, Found: 463.0543.

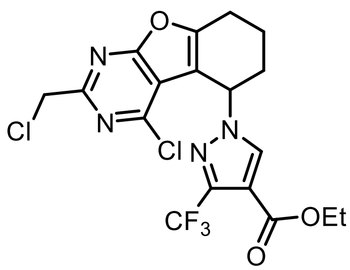
3ma-2: Yield = 8.1 mg (9%) of yellow semisolid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.39.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.84 (s, 1H), 6.07 (t, *J* = 4.5 Hz, 2H), 4.73 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.05 (dt, *J* = 18.1, 5.1 Hz, 1H), 2.86 (dt, *J* = 17.5, 7.2 Hz, 1H), 2.34 (ddt, *J* = 16.8, 8.7, 2.8 Hz, 1H), 2.26 – 2.09 (m, 2H), 2.08 – 1.95 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 167.1, 160.9, 160.2, 159.7, 151.6, 141.4, 131.4 (q, *J* = 40.3 Hz), 119.8 (q, *J* = 271.6 Hz), 116.7, 115.5, 109.3, 61.3, 54.2 (q, *J* = 3.8 Hz), 46.3, 31.2, 23.1, 18.2, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -56.0 ppm.

HRMS Calculated for $[C_{18}H_{15}Cl_2F_3N_4O_3+H]^+$: 463.0546, Found: 463.0545.



Ethyl 1-(4-chloro-2-(chloromethyl)-5,6,7,8-tetrahydrobenzofuro[2,3-d]pyrimidin-5-yl)-3-(trifluoro-methyl)-1H-pyrazole-4-carboxylate, **3ma'-1**

Reaction run using 3-chloro-5-(chloromethyl)-8-oxa-4,6-diazatricyclo[7.4.0.0{2,7}]trideca-1(9),2,4,6-tetraene **1m** (51.4 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and BF_3•Et_2O (2.5 μL, 0.02 mmol, 0.1 equiv) at 60°C following the general procedure I (pressure tube) and two regioisomers were isolated.

3ma'-1: Yield = 52.6 mg (58%) of colorless semisolid. TLC (pentane:Et_2O, 1:1 v/v): R_f = 0.18.

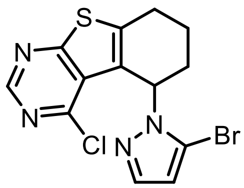
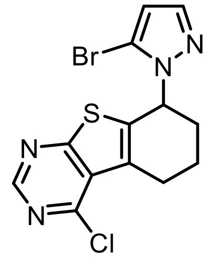
^{1}H NMR ($CDCl_3$, 400 MHz): 7.93 (s, 1H), 5.65 (t, *J* = 5.0 Hz, 1H), 4.76 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.12 (dt, *J* = 17.4, 5.3 Hz, 1H), 2.97 – 2.82 (m, 1H), 2.57 (dq, *J* = 14.3, 4.7 Hz, 1H), 2.48 – 2.31 (m, 1H), 2.04 (p, *J* = 5.2 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 167.3, 161.7, 160.6, 153.9, 148.6, 142.2 (q, *J* = 38.8 Hz), 135.1, 120.2 (q, *J* = 269.8 Hz), 118.4, 115.9, 113.6, 61.1, 55.4, 46.2, 29.9, 21.1, 18.8, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -62.1 ppm.

HRMS Calculated for $[C_{18}H_{15}Cl_2F_3N_4O_3+H]^+$: 463.0546, Found: 463.0539.

3ma-1: Yield = 12.9 mg (14%) of yellow semisolid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.32.

	
5-(5-bromo-*1H*-pyrazol-1-yl)-4-chloro-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidine, **3nb-1**	8-(5-bromo-*1H*-pyrazol-1-yl)-4-chloro-5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-d]pyrimidine, **3nb-2**

Reaction run using 4-chloro-5,6,7,8-tetrahydro[1]benzothieno[2,3-*d*]pyrimidine **1n** (44.8 mg, 0.2 mmol, 1.0 equiv), 3-bromopyrazle **2b** (73.5 mg, 0.50 mmol, 2.5 equiv), copper(II) bromide (4.5 mg, 0.02 mmol, 0.1 equiv.), and tetrabutylammonium bromide (19.3 mg, 0.06 mmol, 0.3 equiv) following the general procedure I (pressure tube) and two regioisomers were isolated.

3nb-1: Yield = 28.1 mg (38%) of white solid. (pentane:EtOAc, 2:1 v/v): R_f = 0.48.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.72 (s, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 6.39 (d, *J* = 1.9 Hz, 1H), 6.18 (t, *J* = 2.4 Hz, 1H), 3.19 (ddd, *J* = 17.8, 5.4, 2.1 Hz, 1H), 3.02 – 2.81 (m, 1H), 2.33 (ddt, *J* = 13.8, 5.0, 2.7 Hz, 1H), 2.15 (tdd, *J* = 13.7, 4.5, 2.9 Hz, 1H), 2.04 (tddd, *J* = 13.6, 11.3, 5.3, 2.5 Hz, 1H), 1.96 – 1.86 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 168.8, 152.8, 152.0, 145.6, 139.8, 127.9, 122.7, 112.0, 109.2, 52.7, 29.9, 26.1, 17.0 ppm.

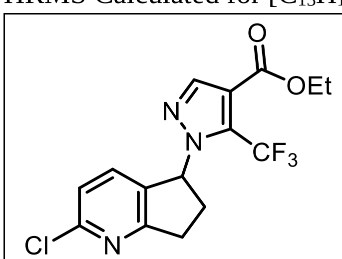
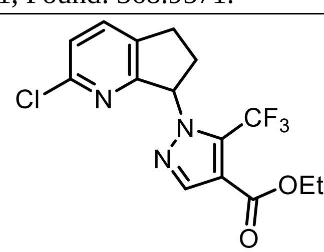
HRMS Calculated for $[C_{13}H_{10}BrClN_4S+H]^+$: 368.9571, Found: 368.9570.

3nb-2: Yield = 18.8 mg (25%) of white solid. (pentane:EtOAc, 2:1 v/v): R_f = 0.06.

^{1}H NMR ($CDCl_3$, 500 MHz): 8.75 (s, 1H), 7.56 (d, *J* = 1.8 Hz, 1H), 6.40 (d, *J* = 1.9 Hz, 1H), 5.86 (dd, *J* = 7.7, 5.4 Hz, 1H), 3.37 – 3.14 (m, 2H), 2.52 – 2.40 (m, 1H), 2.42 – 2.27 (m, 2H), 2.07 – 1.95 (m, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 169.6, 154.5, 152.5, 141.3, 137.7, 131.0, 128.3, 112.8, 109.1, 55.6, 29.9, 26.1, 20.5 ppm.

HRMS Calculated for $[C_{13}H_{10}BrClN_4S+H]^+$: 368.9571, Found: 368.9571.

	
Ethyl 1-(2-chloro-6,7-dihydro-5H-cyclopenta[b]pyridin-5-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3oa-1**	Ethyl 1-(2-chloro-6,7-dihydro-5H-cyclopenta[b]pyridin-7-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3oa-2**

Reaction run using 2-chloro-6,7-dihydro-5H-cyclopenta[b]pyridine **1o** (30.7 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60 °C and two regioisomers were isolated.

3oa-1: Yield = 14.0 mg (20%) of light-yellow liquid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.27.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.09 (dd, *J* = 8.4, 5.2 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.41 (ddd, *J* = 17.1, 9.3, 5.5 Hz, 1H), 3.11 (ddd, *J* = 17.3, 8.9, 6.1 Hz, 1H), 2.77 (dtd, *J* = 14.0, 8.7, 5.5 Hz, 1H), 2.57 (ddt, *J* = 14.3, 9.3, 5.7 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 165.6, 160.9, 152.5, 142.3, 135.1, 132.3, 131.7 (q, *J* = 39.9 Hz), 122.4, 119.7 (q, *J* = 271.2 Hz), 115.9, 63.7 (q, *J* = 3.5 Hz), 61.4, 32.4, 31.6, 14.2 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): -55.6 ppm.

HRMS Calculated for $[C_{15}H_{13}ClF_3N_3O_2+H]^+$: 360.0721, Found: 360.0717.

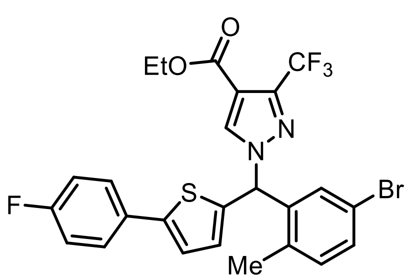
3oa-2: Yield = 4.0 mg (6%) of light-yellow liquid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.16.

^{1}H NMR ($CDCl_3$+DCM, 400 MHz): δ 7.89 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 3H), 6.05 (dd, *J* = 8.6, 4.9 Hz, 1H), 4.33 (qd, *J* = 7.1, 1.7 Hz, 2H), 3.24 (ddd, *J* = 15.4, 9.0, 5.7 Hz, 1H), 2.99 (ddd, *J* = 16.3, 8.8, 5.2 Hz, 1H), 2.77 (dtd, *J* = 14.3, 8.7, 5.8 Hz, 1H), 2.48 (ddt, *J* = 14.1, 9.6, 5.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 161.1, 160.1, 150.7, 142.2, 136.4, 135.7, 131.7 (q, *J* = 39.9 Hz), 124.3, 119.7 (q, *J* = 271.2 Hz), 115.9, 65.52 (q, *J* = 3.9 Hz), 61.1, 31.7, 27.9, 14.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): -55.7 ppm.

HRMS Calculated for $[C_{15}H_{13}ClF_3N_3O_2+Na]^+$: 382.0541, Found: 382.0538.



Ethyl 1-((5-bromo-2-methylphenyl)(5-(4-fluorophenyl)thiophen-2-yl)methyl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3pa'**

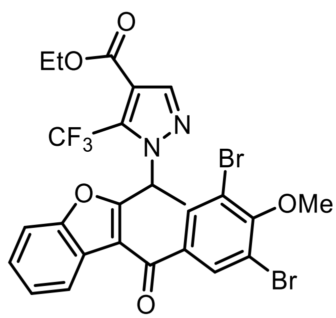
Reaction run using 2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene **1p** (68.6 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure II (glass vial) at 30 °C. . Yield = 101.6 mg (90%) of yellow solid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.56. Mp: 115-118 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.94 (s, 1H), 7.57 – 7.49 (m, 2H), 7.43 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.15 (d, *J* = 3.7 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.08 (t, *J* = 8.6 Hz, 2H), 7.02 (s, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.80 (dd, *J* = 3.8, 0.9 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.23 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 162.7 (d, *J* = 248.6 Hz), 160.8, 146.0, 142.3 (q, *J* = 38.6 Hz), 138.2, 137.4, 135.5, 134.87, 132.8, 132.1, 130.0, 129.7 (d, *J* = 3.4 Hz), 128.7, 127.7 (d, *J* = 8.2 Hz), 123.1, 120.4, 120.2 (q, *J* = 270.0 Hz), 116.1 (d, *J* = 21.9 Hz), 113.6, 63.1, 61.2, 18.8, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -62.0, -113.2 ppm.

HRMS Calculated for $[C_{25}H_{19}BrF_4N_2O_2S+NH_4]^+$: 584.0625, Found: 584.0617.



Ethyl 1-(1-(3-(3,5-dibromo-4-methoxybenzoyl)benzofuran-2-yl)ethyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3qa**

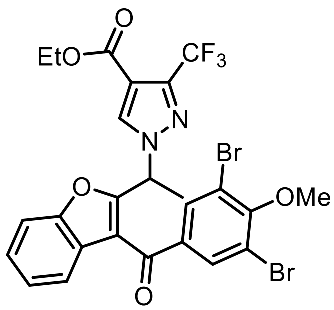
Reaction run using benzbromarone methyl ether **1q** (87.6 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 99.0 mg (77%) of pale-yellow semisolid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.42.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (s, 1H), 7.94 (s, 2H), 7.60 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.39 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.27 (td, *J* = 7.5, 7.1, 0.8 Hz, 2H), 7.23 (dd, *J* = 8.0, 0.7 Hz, 1H), 6.37 (q, *J* = 6.9 Hz, 1H), 4.31 (qd, *J* = 7.2, 1.1 Hz, 2H), 3.98 (s, 3H), 2.08 (d, *J* = 6.9 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 187.4, 160.9, 158.8, 158.3, 154.0, 141.9, 136.1, 133.7, 131.4 (q, *J* = 40.0 Hz), 126.0, 125.2, 124.4, 121.4, 119.4 (q, *J* = 271.3 Hz), 118.7, 117.1, 116.3 (q, *J* = 1.3 Hz), 112.2, 61.2, 60.9, 54.1 (q, *J* = 3.6 Hz), 19.5, 14.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): -56.4 ppm.

HRMS Calculated for $[C_{25}H_{19}Br_2F_3N_2O_5+H]^+$: 642.9686, Found: 642.9687.



Ethyl 1-(1-(3-(3,5-dibromo-4-methoxybenzoyl)benzofuran-2-yl)ethyl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3qa'**

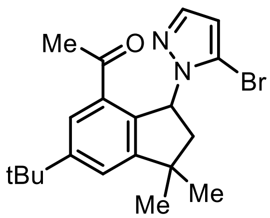
Reaction run using benzbromarone methyl ether **1q** (87.6 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and BF_3•Et_2O (2.5 μL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60 °C. Yield = 58.0 mg (45%) of pale-yellow semisolid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.56. Mp: 152-155 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.31 (s, 1H), 8.01 (s, 2H), 7.59 (dt, J = 8.4, 0.9 Hz, 1H), 7.42 (ddd, J = 8.5, 4.7, 3.8 Hz, 1H), 7.30 (t, J = 1.0 Hz, 1H), 7.29 (d, J = 0.8 Hz, 1H), 6.06 (q, J = 7.1 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.00 (s, 3H), 2.06 (d, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ 187.3, 160.8, 158.5, 158.2, 154.0, 141.7 (q, J = 38.7 Hz), 135.9, 134.8, 133.9, 126.3, 125.2, 124.6, 121.6, 120.3 (q, J = 269.9 Hz), 118.8, 117.7, 113.6, 112.2, 61.0, 60.9, 55.0, 18.8, 14.1 ppm.

^{19}F NMR (377 MHz, $CDCl_3$): -62.0 ppm.

HRMS Calculated for $[C_{25}H_{19}Br_2F_3N_2O_5+H]^+$: 642.9686, Found: 642.9687.



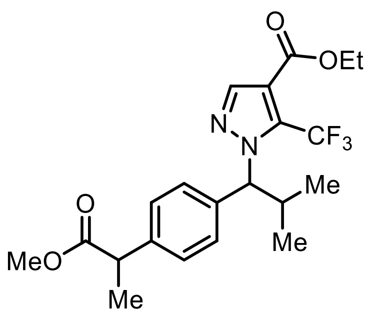
1-(3-(4-bromo-1H-pyrazol-1-yl)-6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one, **3rb**

Reaction run using celestolide **1r** (48.9 mg, 0.2 mmol, 1.0 equiv), 3-bromopyrazole **2b** (73.5 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 54.2 mg (70%) of white solid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.46 . Mp: 88-90 °C

^{1}H NMR ($CDCl_3$, 500 MHz): 7.63 (s, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.36 (d, *J* = 1.9 Hz, 1H), 6.40 (dd, *J* = 8.2, 6.5 Hz, 1H), 6.26 (d, 1H), 2.53 (dd, *J* = 13.1, 8.3 Hz, 1H), 2.35 (s, 3H), 2.09 (dd, *J* = 13.1, 6.5 Hz, 1H), 1.42 (s, 3H), 1.37 (s, 9H), 1.32 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 199.9, 154.2, 152.4, 139.6, 135.4, 135.1, 125.1, 123.0, 113.8, 107.6, 61.6, 49.3, 42.4, 34.9, 31.4, 30.3, 29.3, 27.6.ppm.

HRMS Calculated for $[C_{20}H_{25}BrN_2O+H]^+$: 389.1223, Found: 389.1220.



Ethyl 1-(1-(4-(1-methoxy-1-oxopropan-2-yl)phenyl)-2-methylpropyl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3sa**

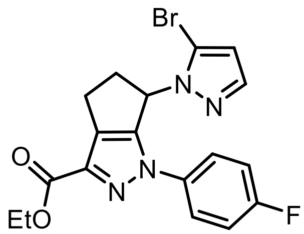
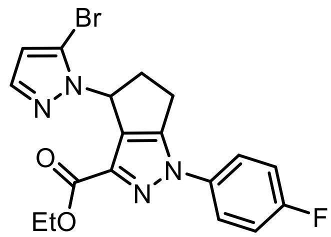
Reaction run using ibuprofen methyl ester **1s** (41.6 µL, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure II (glass vial) at 40 °C. . Yield = 55.7 mg (65%) of white solid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.45. Mp: 83-86 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.97 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.94 (d, *J* = 10.6 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 3.65 (s, 3H), 2.97 – 2.86 (m, 1H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 174.8 (d, *J* = 1.3 Hz), 161.3, 141.7, 140.6 (d, *J* = 1.0 Hz), 136.9, 131.9 (q, *J* = 39.8 Hz), 128.5, 127.6, 119.7 (q, *J* = 271.3 Hz), 115.1 (q, *J* = 1.5 Hz), 72.3 (q, *J* = 2.9 Hz), 61.1, 52.1, 45.1, 33.6, 20.0, 19.7, 18.5, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -54.9 ppm.

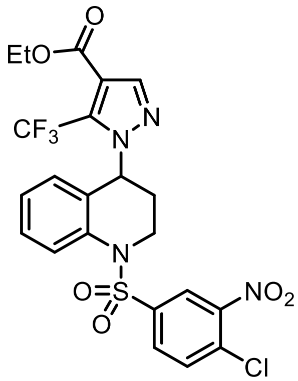
HRMS Calculated for $[C_{21}H_{25}F_3N_2O_4+NH_4]^+$: 444.2105, Found: 444.2101.

	
Ethyl 6-(5-bromo-1H-pyrazol-1-yl)-1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate, **3tb-1**	Ethyl 4-(5-bromo-1H-pyrazol-1-yl)-1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate, **3tb-2**

Reaction run ethyl 1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate **1t** (54.5 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate 2a (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) and two regioisomers were isolated.

3tb-1: Yield = 36.0 mg (43%) of light yellow amorphous solid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.17.
^{1}H NMR ($CDCl_3$, 500 MHz): 7.99 – 7.61 (m, 2H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.22 – 7.10 (m, 2H), 6.30 (d, *J* = 1.9 Hz, 1H), 6.09 (dd, *J* = 8.4, 3.8 Hz, 1H), 4.23 (qt, *J* = 7.4, 3.8 Hz, 2H), 3.38 (dddd, *J* = 15.4, 8.9, 5.1, 1.3 Hz, 1H), 3.22 (dtd, *J* = 13.6, 8.6, 5.1 Hz, 1H), 3.03 (ddd, *J* = 15.4, 8.9, 4.4 Hz, 1H), 2.80 (ddt, *J* = 13.2, 8.6, 4.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm.
^{13}C NMR ($CDCl_3$, 126 MHz): 161.5 (d, *J* = 247.6 Hz), 161.4, 151.3, 140.6, 138.3, 135.7 (d, *J* = 3.1 Hz), 129.2, 122.2 (d, *J* = 8.6 Hz), 116.3 (d, *J* = 23.0 Hz), 112.4, 108.0, 60.9, 55.8, 39.5, 25.1, 14.2 ppm.
^{19}F NMR ($CDCl_3$, 377 MHz): -114.2 ppm.
HRMS Calculated for $[C_{18}H_{16}BrFN_4O_2+H]^+$: 419.0513, Found: 419.0508.

3tb-2: Yield = 5.1 mg (6%) of light-yellow semisolid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.25.
^{1}H NMR ($CDCl_3$, 500 MHz): 7.45 (d, *J* = 1.9 Hz, 1H), 7.21 – 7.14 (m, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 6.24 (d, *J* = 1.9 Hz, 1H), 6.07 (q, *J* = 4.4 Hz, 1H), 4.42 (qd, *J* = 7.1, 1.3 Hz, 2H), 3.21 (qd, *J* = 7.9, 3.8 Hz, 2H), 3.02 – 2.89 (m, 1H), 2.86 – 2.74 (m, 1H), 1.40 (t, *J* = 7.1 Hz, 3H) ppm.
^{13}C NMR ($CDCl_3$, 126 MHz): 162.2, 161.8 (d, *J* = 248.1 Hz), 146.6, 141.4, 138.4, 135.1, 134.7, 123.5 (d, *J* = 8.7 Hz), 116.0 (d, *J* = 23.1 Hz), 112.2, 108.9, 61.0, 56.9, 40.1, 22.4, 14.4 ppm.
^{19}F NMR ($CDCl_3$, 377 MHz): -113.6 ppm.
HRMS Calculated for $[C_{18}H_{16}BrFN_4O_2+H]^+$: 419.0513, Found: 419.0509.



Ethyl 1-(1-((4-chloro-3-nitrophenyl)sulfonyl)-1,2,3,4-tetrahydroquinolin-4-yl)-5-(trifluoromethyl)-1H-pyrazole-4-carboxylate, **3ua**

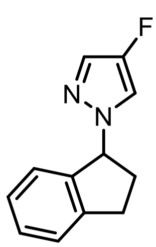
Reaction run using 1-(4-chloro-3-nitrobenzenesulfonyl)-1,2,3,4-tetrahydroquinoline **1u** (70.6 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 47.0 mg (42%) of yellow semisolid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.40 .

^{1}H NMR ($CDCl_3$, 500 MHz): 8.08 (d, *J* = 2.2 Hz, 1H), 7.90 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.78 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.71 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.35 (ddd, *J* = 8.5, 7.2, 1.1 Hz, 2H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 5.59 (t, *J* = 7.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 3H), 4.32 – 4.25 (m, 1H), 3.95 (ddd, *J* = 13.9, 9.3, 3.9 Hz, 1H), 2.22 – 2.09 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz) δ 160.7, 148.0, 142.1, 139.3, 136.2, 133.0, 132.1 (q, *J* = 39.8 Hz), 132.1, 131.2, 129.3, 128.5, 127.1, 126.5, 124.7, 124.7, 119.5 (q, *J* = 271.4 Hz), 115.7, 61.4, 56.9 (q, *J* = 3.2 Hz), 44.7, 28.5, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -55.93 ppm.

HRMS Calculated for $[C_{22}H_{18}ClF_3N_4O_6S+Na]^+$: 581.0480, Found: 581.0478.



1-(2,3-dihydro-1*H*-inden-1-yl)-4-fluoro-1*H*-pyrazole, **3vc**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 4-fluoropyrazole **2c** (43.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60 °C. Yield = 33.4 mg (82%) of yellow liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.50.

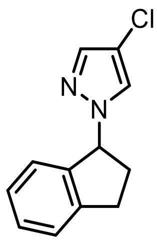
^{1}H NMR ($CDCl_3$, 400 MHz): 7.36 (d, *J* = 4.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.22 (td, *J* = 7.0, 6.3, 2.3 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 4.7 Hz, 1H), 5.76 (t, *J* = 7.0 Hz, 1H), 3.12 (ddd, *J* = 16.0, 8.7, 5.2 Hz, 1H), 2.96 (ddd, *J* = 15.8, 8.4, 6.6 Hz, 1H), 2.68 (dtd, *J* = 13.5, 8.2, 5.2 Hz, 1H), 2.30 (ddt,

J = 13.4, 8.7, 6.2 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 149.6 (d, J = 246.0 Hz), 143.8, 140.6, 129.0, 127.1, 126.1 (d, J = 13.5 Hz), 125.2, 124.8, 113.6 (d, J = 27.8 Hz), 68.0, 33.7, 30.4 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -176.5 ppm.

HRMS Calculated for $[C_{12}H_{11}FN_2+H]^+$: 203.0979, Found: 203.0978.



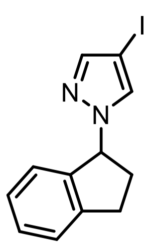
4-chloro-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole, **3vd**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 4-chloropyrazole **2d** (51.3 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 28.8 mg (66%) of colorless liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.57.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.45 (s, 1H), 7.32 (m, 2H), 7.23 (ddd, J = 8.0, 6.5, 2.1 Hz, 1H), 7.17 (m, 2H), 5.81 (dd, J = 7.9, 5.6 Hz, 1H), 3.13 (ddd, J = 14.4, 8.6, 5.6 Hz, 1H), 2.96 (ddd, J = 15.7, 8.2, 6.4 Hz, 1H), 2.68 (dtd, J = 13.6, 8.2, 5.6 Hz, 1H), 2.33 (ddt, J = 11.9, 8.6, 5.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 144.0, 140.4, 137.7, 129.0, 127.1, 125.6, 125.2, 124.9, 109.8, 67.7, 33.7, 30.4 ppm.

HRMS Calculated for $[C_{12}H_{11}ClN_2N_2+H]^+$: 219.0684, Found: 219.0684.



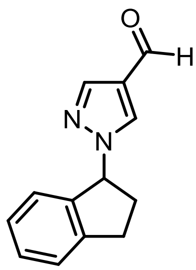
1-(2,3-dihydro-1*H*-inden-1-yl)-4-iodo-1*H*-pyrazole, **3ve**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 4-iodopyrazole **2e** (97.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 37.5 mg (60%) of light-yellow liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.60.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.54 (s, 1H), 7.37 – 7.28 (m, 2H), 7.27 – 7.19 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 5.87 (dd, J = 7.9, 5.5 Hz, 1H), 3.13 (ddd, J = 16.0, 8.6, 5.6 Hz, 1H), 2.96 (ddd, J = 15.7, 8.4, 6.1 Hz, 1H), 2.68 (dtd, J = 13.7, 8.2, 5.6 Hz, 1H), 2.33 (ddt, J = 14.1, 8.6, 5.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 144.4, 144.0, 140.4, 132.1, 129.1, 127.2, 125.2, 125.0, 67.5, 56.1, 33.9, 30.4 ppm.

HRMS Calculated for $[C_{12}H_{11}IN_2+H]^+$: 311.0040, Found: 311.0036.



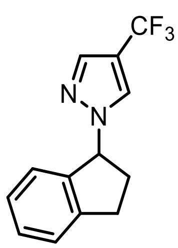
1-(2,3-dihydro-1*H*-inden-1-yl)-1*H*-pyrazole-4-carbaldehyde, **3vf**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), pyrazole-4-carboxaldehyde **2f** (48.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 30.2 mg (71%) of light-yellow liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.17.

^{1}H NMR ($CDCl_3$, 400 MHz): 9.80 (s, 1H), 8.01 (s, 1H), 7.73 (s, 1H), 7.39 – 7.34 (m, 2H), 7.30 – 7.23 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 5.90 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.16 (ddd, *J* = 15.2, 8.5, 6.2 Hz, 1H), 3.00 (ddd, *J* = 16.1, 8.5, 5.4 Hz, 1H), 2.73 (dtd, *J* = 14.2, 8.2, 6.2 Hz, 1H), 2.41 (ddt, *J* = 13.7, 8.5, 5.2 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 184.1, 144.3, 141.0, 139.6, 131.1, 129.4, 127.3, 125.4, 125.0, 124.2, 67.5, 33.7, 30.4 ppm.

HRMS Calculated for $[C_{13}H_{12}N_2O+H]^+$: 213.1022, Found: 213.1021.



1-(2,3-dihydro-1H-inden-1-yl)-4-(trifluoromethyl)-1H-pyrazole, **3vg**

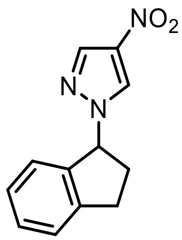
Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 4-trifluoromethylpyrazole **2g** (68.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 36.0 mg (71%) of colorless liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.61.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.74 (s, 1H), 7.48 (s, 1H), 7.39 – 7.31 (m, 2H), 7.30 – 7.21 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 5.89 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.15 (ddd, *J* = 15.9, 8.6, 5.7 Hz, 1H), 2.99 (ddd, *J* = 15.9, 8.5, 5.9 Hz, 1H), 2.72 (dtd, *J* = 13.9, 8.2, 5.8 Hz, 1H), 2.38 (ddt, *J* = 13.9, 8.6, 5.6 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 144.1, 139.9, 137.1 (q, *J* = 2.8 Hz), 129.3, 127.3, 126.9 (q, *J* = 3.6 Hz), 125.3, 124.9, 122.7 (q, *J* = 265.9 Hz), 113.5 (q, *J* = 38.1 Hz), 67.5, 33.8, 30.4 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): –56.3 ppm.

HRMS Calculated for $[C_{13}H_{11}F_3N_2+H]^+$: 253.0947, Found: 253.0944.



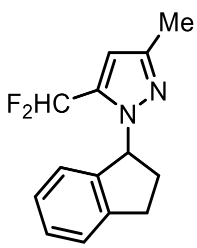
1-(2,3-dihydro-1*H*-inden-1-yl)-4-nitro-1*H*-pyrazole, **3vh**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 4-nitropyrazole **2h** (56.5 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 38.2 mg (83%) of dark yellow liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.40.

^{1}H NMR ($CDCl_3$, 400 MHz): 8.11 (s, 1H), 7.89 (s, 1H), 7.38 (d, *J* = 3.9 Hz, 2H), 7.29 (dt, *J* = 8.5, 4.2 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.87 (dd, *J* = 7.9, 4.6 Hz, 1H), 3.17 (ddd, *J* = 15.4, 8.5, 6.5 Hz, 1H), 3.02 (ddd, *J* = 16.2, 8.6, 5.1 Hz, 1H), 2.74 (dtd, *J* = 14.5, 8.2, 6.5 Hz, 1H), 2.41 (ddt, *J* = 13.5, 8.4, 4.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 144.4, 138.8, 136.0, 129.8, 127.5, 127.0, 125.5, 125.0, 68.3, 33.6, 30.3 ppm.

HRMS Calculated for $[C_{12}H_{11}N_3O_2+Na]^+$: 252.0743, Found: 252.0740.



5-(difluoromethyl)-1-(2,3-dihydro-1H-inden-1-yl)-3-methyl-1*H*-pyrazole, **3vi**

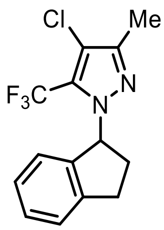
Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 3-(difluoromethyl)-5-methyl-1*H*-pyrazole **2i** (66.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) in DCM. Yield = 25.7 mg (52%) of while solid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.47. Mp: 75-77 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.29 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 54.1 Hz, 1H), 6.28 (s, 1H), 5.93 (t, *J* = 7.9 Hz, 1H), 3.23 (ddd, *J* = 15.9, 9.1, 3.5 Hz, 1H), 2.97 (dt, *J* = 16.2, 8.3 Hz, 1H), 2.70 – 2.62 (m, 1H), 2.57 (dq, *J* = 13.1, 8.3 Hz, 1H), 2.22 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 148.3, 143.3, 141.3, 136.1 (t, *J* = 26.0 Hz), 128.4, 126.8, 125.1, 124.1, 108.8 (t, *J* = 235.5 Hz), 106.4, 65.2, 32.9, 30.5, 13.6 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -109.1 (d, *J* = 307.2 Hz), -111.7 (d, *J* = 307.2 Hz) ppm.

HRMS Calculated for $[C_{14}H_{14}F_2N_2+H]^+$: 249.1198, Found: 249.1193.



4-chloro-1-(2,3-dihydro-1H-inden-1-yl)-3-methyl-5-(trifluoromethyl)-1*H*-pyrazole, **3vj**

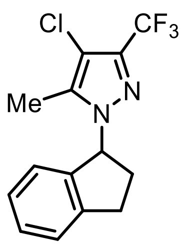
Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 4-Chloro-3-trifluoromethyl-5-(methyl) pyrazole **2j** (92.3 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) in DCM. Yield = 32.7 mg (55%) of colorless liquid**.** TLC (pentane:Et_2O, 20:1 v/v): R_f = 0.56.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.30 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.89 (t, *J* = 7.4 Hz, 1H), 3.26 (ddd, *J* = 15.7, 9.0, 4.3 Hz, 1H), 2.97 (dt, *J* = 15.8, 7.9 Hz, 1H), 2.62 (dtt, *J* = 12.4, 8.5, 4.2 Hz, 1H), 2.54 (ddd, *J* = 13.1, 6.7, 1.7 Hz, 1H), 2.17 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 146.9, 143.5, 140.6, 128.6, 127.8 (q, *J* = 37.6 Hz), 126.9, 125.1, 124.1, 120.0 (q, *J* = 270.2 Hz), 110.4, 65.7 (q, *J* = 2.3 Hz), 32.8, 30.6, 11.3 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -57.3 ppm.

HRMS Calculated for $[C_{14}H_{12}ClF_3N_2+Na]^+$: 323.0533, Found: 323.0529.



4-chloro-1-(2,3-dihydro-1H-inden-1-yl)-5-methyl-3-(trifluoromethyl)-1*H*-pyrazole, **3vj'**

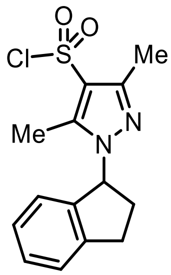
Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 4-Chloro-3-trifluoromethyl-5-(methyl) pyrazole **2j** (92.3 mg, 0.50 mmol, 2.5 equiv), and BF_3●Et_2O (2.5 μL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 27.9 mg (46%) of colorless liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.63.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.33 – 7.26 (m, 2H), 7.19 (td, *J* = 7.2, 1.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 5.90 (t, *J* = 7.9 Hz, 1H), 3.23 (ddd, *J* = 16.0, 9.2, 3.7 Hz, 1H), 3.01 (dt, *J* = 16.2, 8.2 Hz, 1H), 2.68 (dtd, *J* = 13.5, 8.5, 3.7 Hz, 1H), 2.50 (ddt, *J* = 13.4, 9.3, 7.8 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 143.4, 140.1, 137.7, 137.6 (q, *J* = 37.3 Hz), 129.0, 127.2, 125.4, 124.1, 120.9 (q, *J* = 269.3 Hz), 107.5, 66.6, 32.1, 30.7, 9.6 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -62.3 ppm.

HRMS Calculated for $[C_{14}H_{12}ClF_3N_2+H]^+$: 301.0714, Found: 301.0710.



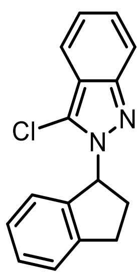
1-(2,3-dihydro-1H-inden-1-yl)-3,5-dimethyl-1*H*-pyrazole-4-sulfonyl chloride, **3vk**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 3,5-dimethyl-1*H*-pyrazole-4-sulfonyl chloride **2k** (97.3 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) in DCM. Yield = 32.7 mg (53%) of white solid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.37. Mp: 69-71 °C.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.33 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.83 (t, *J* = 7.7 Hz, 1H), 3.28 (ddd, *J* = 16.0, 9.0, 3.9 Hz, 1H), 3.02 (dt, *J* = 16.0, 8.1 Hz, 1H), 2.66 (m, 1H), 2.63 (s, 3H), 2.57 (dq, *J* = 13.2, 7.6 Hz, 1H), 2.42 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 148.4, 143.4, 142.9, 139.9, 128.9, 127.1, 125.4, 123.8, 121.6, 64.2, 32.1, 30.7, 13.3, 10.9 ppm.

HRMS Calculated for $[C_{14}H_{15}ClN_2O_2S+H]^+$: 311.0616, Found: 311.0609.



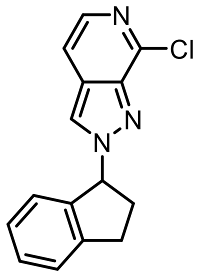
3-chloro-2-(2,3-dihydro-1H-inden-1-yl)-2H-indazole, **3vl**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 3-chloroindazole **2l** (38.2 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 17.2 mg (32%) of colorless semisolid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.71.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.68 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.22 (t, *J* = 7.9 Hz, 1H), 3.27 (ddd, *J* = 15.9, 9.1, 3.4 Hz, 2H), 3.06 (dt, *J* = 16.2, 8.3 Hz, 1H), 2.73 (ddt, *J* = 16.8, 8.4, 4.2 Hz, 2H), 2.56 (dq, *J* = 13.3, 8.2 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 143.3, 140.8, 140.3, 133.0, 128.6, 127.2, 126.9, 125.2, 124.4, 121.8, 121.2, 112.0, 110.1, 65.3, 32.1, 30.6 ppm.

HRMS Calculated for $[C_{16}H_{13}ClN_2+H]^+$: 269.0840, Found: 269.0838.



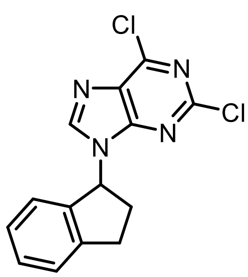
7-chloro-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazolo[3,4-c]pyridine, **3vm**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 7-Chloro-1H-pyrazolo[3,4-*c*]pyridine **2m** (76.8 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 16.0 mg (30%) of yellow semisolid**.** TLC (DCM:MeOH, 19:1 v/v): R_f = 0.60.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.90 (d, J = 5.8 Hz, 1H), 7.70 (s, 1H), 7.44 – 7.37 (m, 2H), 7.36 (d, J = 6.0 Hz, 1H), 7.31 – 7.22 (m, 3H), 6.31 (dd, J = 8.1, 4.7 Hz, 1H), 3.21 (ddd, J = 15.3, 8.4, 6.4 Hz, 1H), 3.07 (ddd, J = 16.2, 8.6, 5.2 Hz, 1H), 2.90 (dtd, J = 14.5, 8.3, 6.3 Hz, 1H), 2.50 (ddt, J = 13.6, 8.6, 5.0 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 144.5, 142.9, 142.9, 139.5, 137.2, 129.7, 127.5, 125.6, 125.5, 125.3, 122.3, 113.6, 69.5, 34.7, 30.5 ppm.

HRMS Calculated for $[C_{15}H_{12}ClN_3+Na]^+$: 292.0612, Found: 292.0607.



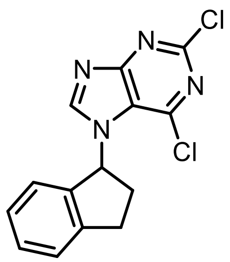
2,6-dichloro-9-(2,3-dihydro-1H-inden-1-yl)-9H-purine, **3vn**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 2,6-dichloropurine **2n** (94.5 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) in DCM. Yield = 21.5 mg (35%) of white solid**.** TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.26. Mp: 140-143 °C. **3vn'** (13.9 mg, 23%) was also isolated in this reaction.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.79 (s, 1H), 7.46 – 7.35 (m, 2H), 7.27 (d, J = 7.7 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 6.25 (dd, J = 7.8, 5.5 Hz, 1H), 3.22 (ddd, J = 14.7, 8.5, 5.9 Hz, 1H), 3.10 (ddd, J = 16.0, 8.2, 6.4 Hz, 1H), 2.87 (dtd, J = 13.9, 8.1, 5.8 Hz, 1H), 2.28 (ddt, J = 14.0, 8.5, 5.7 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 153.2, 153.0, 151.8, 144.3, 144.1, 138.7, 131.0, 129.8, 127.7, 125.6, 124.6, 59.9, 34.1, 30.5 ppm.

HRMS Calculated for $[C_{14}H_{10}Cl_2N_4+H]^+$: 305.0355, Found: 305.0353.



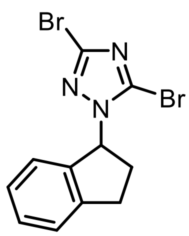
2,6-dichloro-7-(2,3-dihydro-1H-inden-1-yl)-7H-purine, **3vn'**

Reaction run using indane **1v** (24.5 µL, 0.2 mmol, 1.0 equiv), 2,6-dichloropurine **2n** (94.5 mg, 0.50 mmol, 2.5 equiv), and BF_3●Et_2O (2.5 µL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 38.5 mg (63%) of white solid**.** TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.11. Mp: 167-170 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.79 (s, 1H), 7.54 – 7.41 (m, 2H), 7.36 (dt, *J* = 8.3, 4.0 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 6.47 (dd, *J* = 7.6, 4.2 Hz, 1H), 3.36 – 3.00 (m, 2H), 2.87 (dq, *J* = 15.1, 7.7 Hz, 1H), 2.28 (ddt, *J* = 13.1, 8.4, 4.6 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 164.0, 157.9, 153.2, 148.4, 144.7, 143.8, 137.5, 130.3, 128.0, 125.9, 125.2, 62.8, 35.5, 30.1 ppm.

HRMS Calculated for $[C_{14}H_{10}Cl_2N_4+Na]^+$: 327.0175, Found: 327.0173.



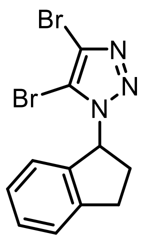
3,5-dibromo-1-(2,3-dihydro-1H-inden-1-yl)-1H-1,2,4-triazole, **3vo**

Reaction run using indane **1v** (24.5 µL, 0.2 mmol, 1.0 equiv), 3,5-dibromo-1*H*-1,2,4-triazole **2o** (113.4 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 53.1 mg (77%) of white solid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.52. Mp: 83-86 °C.

^{1}H NMR ($CDCl_3$+DCM, 500 MHz): 7.37 – 7.28 (m, 2H), 7.24 – 7.16 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.01 (dd, *J* = 8.2, 6.0 Hz, 1H), 3.32 (ddd, *J* = 15.9, 8.9, 4.9 Hz, 1H), 3.01 (ddd, *J* = 15.6, 8.5, 6.6 Hz, 1H), 2.67 (dtd, *J* = 13.4, 8.4, 5.0 Hz, 1H), 2.56 (ddt, *J* = 13.2, 8.9, 6.3 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 143.8, 140.4, 139.2, 129.3, 129.0, 127.1, 125.3, 124.1, 64.9, 31.9, 30.7 ppm.

HRMS Calculated for $[C_{11}H_9Br_2N_3+H]^+$: 341.9236, Found: 341.9233.



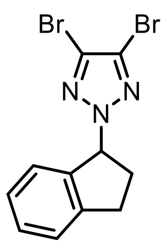
4,5-dibromo-1-(2,3-dihydro-1H-inden-1-yl)-1H-1,2,3-triazole, **3vp**

Reaction run using indane **1v** (24.5 µL, 0.2 mmol, 1.0 equiv), 4,5-dibromo-1*H*-1,2,3-triazole **2p** (113.4 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) in DCM. Yield = 25.4 mg (37%) of colorless liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.47. **3vp'** (59 mg, 8%) was also isolated in this reaction.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.55 – 7.28 (m, 2H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.19 (dd, *J* = 8.4, 5.7 Hz, 1H), 3.38 (ddd, *J* = 15.8, 8.9, 5.3 Hz, 1H), 3.07 (ddd, *J* = 15.7, 8.6, 6.1 Hz, 1H), 2.77 (dtd, *J* = 13.9, 8.5, 5.4 Hz, 1H), 2.63 (ddt, *J* = 14.4, 8.8, 5.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 144.0, 138.9, 129.4, 127.2, 125.3, 124.4, 123.4, 111.7, 66.1, 32.2, 30.9 ppm.

HRMS Calculated for $[C_{11}H_9Br_2N_3+Na]^+$: 363.9055, Found: 363.9053.



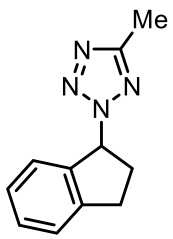
4,5-dibromo-2-(2,3-dihydro-1H-inden-1-yl)-2H-1,2,3-triazole, **3vp'**

Reaction run using indane **1v** (24.5 µL, 0.2 mmol, 1.0 equiv), 4,5-dibromo-1*H*-1,2,3-triazole **2p** (113.4 mg, 0.50 mmol, 2.5 equiv), and BF_3●Et_2O (2.5 µL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C in DCM. Yield = 5.9 mg (8%) of colorless liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.73.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.34 – 7.30 (m, 1H), 7.24 – 7.18 (m, 1H), 6.10 (dd, *J* = 7.5, 5.9 Hz, 1H), 3.48 – 3.22 (m, 1H), 3.10 – 2.94 (m, 1H), 2.90 – 2.57 (m, 1H). ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 144.0, 138.9, 129.4, 127.2, 125.3, 124.4, 123.4, 111.7, 66.1, 32.2, 30.9 ppm.

HRMS Calculated for $[C_{11}H_9Br_2N_3+Na]^+$: 363.9052, Found: 363.9055.



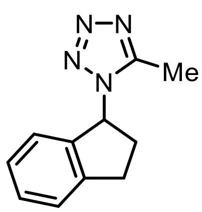
2-(2,3-dihydro-1H-inden-1-yl)-5-methyl-2H-tetrazole, **3vq**

Reaction run using indane **1v** (24.5 µL, 0.2 mmol, 1.0 equiv), 5-methyl tetrazole **2q** (42.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C in DCM. Yield = 20.0 mg (50%) of colorless liquid**.** TLC (pentane:Et_2O, 20:1 v/v): R_f = 0.30. **3vq'** (3.6 mg, 18%) was also isolated in this reaction.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.56 – 7.29 (m, 2H), 7.24 – 6.93 (m, 2H), 6.36 (dd, *J* = 8.1, 5.2 Hz, 1H), 3.37 (ddd, *J* = 15.3, 8.6, 6.1 Hz, 1H), 3.07 (ddd, *J* = 15.9, 8.4, 5.8 Hz, 1H), 2.88 – 2.64 (m, 2H), 2.50 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 163.1, 144.0, 139.2, 129.4, 127.1, 125.2, 124.8, 68.0, 32.1, 30.8, 11.0 ppm.

HRMS Calculated for $[C_{11}H_{12}N_4+H]^+$: 201.1135, Found: 201.1132.



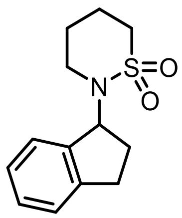
1-(2,3-dihydro-1H-inden-1-yl)-5-methyl-1H-tetrazole, **3vq'**

Reaction run using indane **1v** (24.5 µL, 0.2 mmol, 1.0 equiv), 5-methyl tetrazole **2q** (42.0 mg, 0.50 mmol, 2.5 equiv), and BF_3●Et_2O (2.5 µL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 16.7 mg (42%) of colorless liquid**.** TLC (pentane:Et_2O, 20:1 v/v): R_f = 0.30. **3vq** (15.2 mg, 37%) was also isolated in this reaction.

^{1}H NMR ($CDCl_3$, 600 MHz): 7.37 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 0H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.13 (dd, *J* = 8.4, 6.2 Hz, 1H), 3.33 (ddd, *J* = 16.2, 9.0, 4.8 Hz, 1H), 3.09 (ddd, *J* = 15.9, 8.8, 6.5 Hz, 1H), 2.81 (dtd, *J* = 13.5, 8.5, 4.8 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.43 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 151 MHz): 150.9, 143.6, 138.5, 129.5, 127.4, 125.5, 124.1, 63.1, 32.6, 30.7, 9.5 ppm.

HRMS Calculated for $[C_{11}H_{12}N_4+Na]^+$: 223.0954, Found: 223.0952.



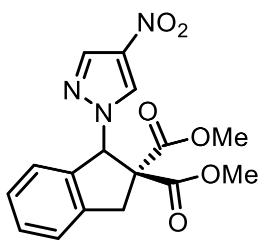
2-(2,3-dihydro-1H-inden-1-yl)-1,2-thiazinane 1,1-dioxide, **3vr**

Reaction run using indane **1v** (24.5 μL, 0.2 mmol, 1.0 equiv), 1,4-propanesultam **2r** (67.5 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) in DCM. Yield = 23.5 mg (47%) of colorless liquid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.13.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.40 – 7.30 (m, 1H), 7.28 – 7.19 (m, 3H), 5.67 (t, *J* = 8.0 Hz, 1H), 3.24 – 3.11 (m, 2H), 3.07 (ddd, *J* = 16.7, 8.8, 4.4 Hz, 1H), 3.03 – 2.90 (m, 2H), 2.85 (dt, *J* = 16.3, 8.4 Hz, 1H), 2.46 – 2.34 (m, 1H), 2.31 – 2.15 (m, 2H), 2.03 (dq, *J* = 13.3, 8.5 Hz, 1H), 1.64 (ddtq, *J* = 22.3, 13.6, 9.0, 4.1 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 143.6, 140.3, 128.1, 126.8, 124.9, 124.6, 59.7, 51.1, 43.8, 30.4, 29.3, 24.9, 24.2 ppm.

HRMS Calculated for $[C_{13}H_{17}NO_2S+Na]^+$: 274.0872, Found: 274.0868.



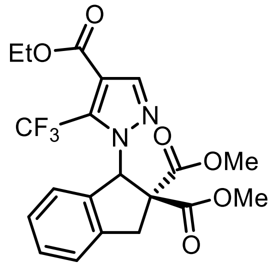
Dimethyl 1-(4-nitro-1H-pyrazol-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate, **3wh**

Reaction run using 2,2-dimethyl 1,3-dihydroindene-2,2-dicarboxylate **1w** (46.9 mg, 0.2 mmol, 1.0 equiv), 4-Nitropyrazole **2h** (56.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube). Yield = 44.7 mg (65%) of yellow semisolid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.10.

^{1}H NMR ($CDCl_3$, 400 MHz): 8.03 (dd, *J* = 10.6, 0.6 Hz, 1H), 7.42 (td, *J* = 7.4, 1.2 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.60 (s, 1H), 4.09 (d, *J* = 16.8 Hz, 1H), 3.79 (s, 3H), 3.51 (s, 3H), 3.47 (d, *J* = 16.9 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 170.1, 167.6, 140.6, 136.3, 136.1, 135.9, 130.5, 129.4, 128.3, 125.23, 125.18, 71.3, 65.0, 53.6, 53.3, 38.8. ppm.

HRMS Calculated for $[C_{16}H_{15}N_3O_6S+Na]^+$: 368.0853, Found: 368.0846.



Dimethyl 1-(4-(ethoxycarbonyl)-5-(trifluoromethyl)-1*H*-pyrazol-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate, **3wa**

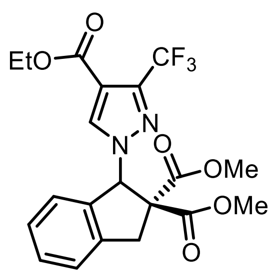
Reaction run using 2,2-dimethyl 1,3-dihydroindene-2,2-dicarboxylate **1w** (46.9 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and BF_3●Et_2O (2.5 µL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C in DCM. Yield = 45.1 mg (51%) of yellow semisolid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.20.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.79 (s, 1H), 7.41 – 7.29 (m, 2H), 7.25 – 7.16 (m, 2H), 6.82 (s, 1H), 4.39 (d, *J* = 16.8 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.51 (d, *J* = 16.8 Hz, 1H), 3.46 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 170.1, 167.4, 160.9, 142.6, 140.9, 138.4, 132.5 (q, *J* = 39.9 Hz), 129.9, 127.8, 125.0, 124.6, 119.6 (q, *J* = 271.8 Hz), 115.4, 68.4 (q, *J* = 4.3 Hz), 65.2, 61.2, 53.7, 53.0, 39.9, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -56.6 ppm.

HRMS Calculated for $[C_{20}H_{19}F_3N_2O_6+H]^+$: 441.1268, Found: 441.1262.



Dimethyl 1-(4-(ethoxycarbonyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate, **3wa'**

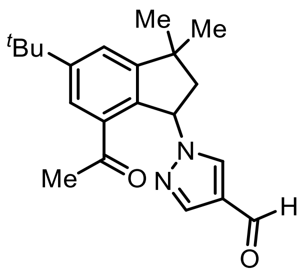
Reaction run using 2,2-dimethyl 1,3-dihydroindene-2,2-dicarboxylate **1w** (46.9 mg, 0.2 mmol, 1.0 equiv), ethyl 3-(trifluoromethyl)-1H-pyrazole-4-carboxylate **2a** (104.1 mg, 0.50 mmol, 2.5 equiv), and BF_3●Et_2O (2.5 µL, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 40.6 mg (46%) of white semisolid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.13.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.79 (s, 1H), 7.41 – 7.29 (m, 2H), 7.25 – 7.16 (m, 2H), 6.82 (s, 1H), 4.39 (d, *J* = 16.8 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.51 (d, *J* = 16.8 Hz, 1H), 3.46 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 170.1, 167.4, 160.9, 142.6, 140.9, 138.4, 132.5 (q, *J* = 39.9 Hz), 129.9, 127.8, 125.0, 124.6, 119.6 (q, *J* = 271.8 Hz), 115.4, 68.4 (q, *J* = 4.3 Hz), 65.2, 61.2, 53.7, 53.0, 39.9, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -56.6 ppm.

HRMS Calculated for $[C_{20}H_{19}F_3N_2O_6+H]^+$: 441.1268, Found: 441.1262.

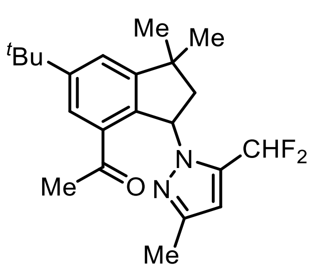


1-(7-acetyl-5-(tert-butyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-yl)-1H-pyrazole-4-carbaldehyde, **3rf**
Reaction run using celestolide **1r** (48.9 mg, 0.2 mmol, 1.0 equiv), pyrazole-4-carboxaldehyde **2f** (48.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C. Yield = 61.0 mg (90%) of colorless semisolid**.** TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.29.

^{1}H NMR ($CDCl_3$, 500 MHz): 9.79 (s, 1H), 7.93 (s, 1H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.74 (s, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 6.29 (dd, *J* = 8.4, 3.9 Hz, 1H), 2.54 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.45 (s, 3H), 2.37 (dd, *J* = 13.8, 3.9 Hz, 1H), 1.40 (s, 10H), 1.34 (s, 3H), 1.30 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 199.2, 184.3, 155.4, 153.8, 140.8, 134.4, 132.7, 126.2, 124.0, 123.1, 65.0, 49.0, 42.7, 35.1, 31.4, 30.3, 29.9, 27.8 ppm.

HRMS Calculated for $[C_{21}H_{26}N_2O_2+Na]^+$: 361.1887, Found: 361.1880.



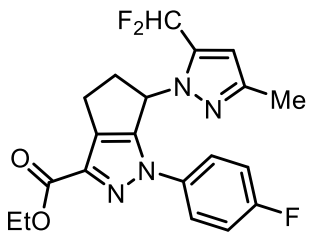
1-(6-(tert-butyl)-3-(5-(difluoromethyl)-3-methyl-1H-pyrazol-1-yl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one, **3ri**
Reaction run using celestolide **1r** (48.9 mg, 0.2 mmol, 1.0 equiv), 3-(difluoromethyl)-5-methyl-1*H*-pyrazole **2i** (66.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 60°C in DCM. Yield = 38.7 mg (52%) of white solid**.** TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.56. Mp: 113-116 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.54 (d, *J* = 1.8 Hz, 1H), 7.39 (d, *J* = 1.7 Hz, 1H), 7.09 (dd, *J* = 58.3, 53.1 Hz, 1H), 6.19 (d, *J* = 2.2 Hz, 1H), 6.08 (t, *J* = 7.9 Hz, 1H), 2.51 (dd, *J* = 12.9, 8.0 Hz, 1H), 2.30 (s, 3H), 2.21 (dd, *J* = 12.9, 7.9 Hz, 1H), 2.14 (s, 3H), 1.47 (s, 3H), 1.36 (s, 9H), 1.27 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 200.5, 153.8, 152.3, 147.4, 137.5 (dd, *J* = 33.0, 24.4 Hz), 135.7, 135.4, 124.4, 122.8, 109.8 (dd, J = 235.3 Hz, J = 235.4 Hz), 104.4 (dd, J = 3.7, 2.4 Hz), 61.9 (d, J = 2.0 Hz), 50.0, 42.1, 34.9, 31.5, 30.3, 28.8, 27.8, 13.6 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -106.96 (d, J = 307.0 Hz), -121.35 (d, J = 307.0 Hz) ppm.

HRMS Calculated for $[C_{22}H_{28}F_2N_2O+Na]^+$: 397.2062, Found: 297.2057.



Ethyl 6-(5-(difluoromethyl)-3-methyl-1H-pyrazol-1-yl)-1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate, **3ti**

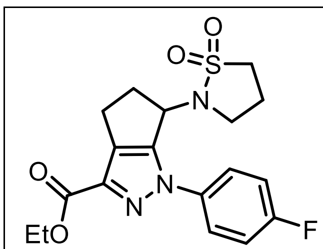
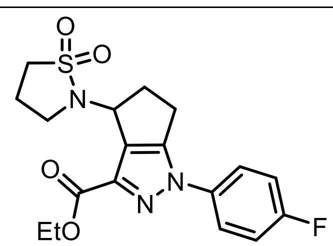
Reaction run using ethyl 1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate **1t** (54.5 mg, 0.2 mmol, 1.0 equiv), 3-(difluoromethyl)-5-methyl-1*H*-pyrazole **2i** (66.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 50 °C in DCM. Yield = 33.6 mg (42%) of pale yellow amorphous solid. TLC (DCM:MeOH, 50:1 v/v): R_f = 0.18.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.72 – 7.65 (m, 2H), 7.20 – 7.13 (m, 2H), 6.99 (dd, J = 56.5, 53.2 Hz, 1H), 6.25 (d, J = 1.9 Hz, 1H), 5.86 (dd, J = 8.6, 3.8 Hz, 1H), 4.36 – 4.14 (m, 2H), 3.40 (dddd, J = 15.1, 8.7, 5.1, 1.3 Hz, 1H), 3.20 (dtd, J = 13.6, 8.4, 5.0 Hz, 1H), 2.99 (ddd, J = 15.2, 8.6, 4.5 Hz, 1H), 2.90 (ddt, J = 13.2, 8.7, 4.2 Hz, 1H), 2.21 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.7, 161.6 (d, J = 247.6 Hz), 151.5, 148.1, 138.2, 136.1 (dd, J = 30.2, 25.0 Hz), 135.7 (d, J = 3.0 Hz), 129.6, 122.3 (d, J = 8.4 Hz), 116.3 (d, J = 23.1 Hz), 109.2 (t, J = 235.7 Hz), 105.5 (t, J = 3.8 Hz), 61.0, 56.2 (d, J = 2.4 Hz), 39.8, 25.2, 14.1, 13.7 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -108.15 (d, J = 307.6 Hz), -114.20, -116.86 (d, J = 307.8 Hz) ppm.

HRMS Calculated for $[C_{20}H_{19}F_3N_4O_2+H]^+$: 405.1533, Found: 405.1529.

	
Ethyl 4-(1,1-dioxidoisothiazolidin-2-yl)-1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate, **3tt-1**	Ethyl 4-(1,1-dioxidoisothiazolidin-2-yl)-1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate, **3tt-2**

Reaction run using ethyl 1-(4-fluorophenyl)-1,4,5,6-tetrahydrocyclopenta[*c*]pyrazole-3-carboxylate **1t** (54.5 mg, 0.2 mmol, 1.0 equiv), 1,3-propanesultam **2t** (50.0 μL, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure I (pressure tube) at 40 °C in DCM, and two regioisomers were isolated.

3tt-1: Yield = 39.0 mg (47%) of colorless semisolid. TLC (pentane:EtOAc, 1:2 v/v): R_f = 0.33.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.92 – 7.56 (m, 2H), 7.19 – 6.96 (m, 2H), 5.66 – 4.99 (m, 1H), 4.42 (qd, *J* = 7.1, 3.0 Hz, 2H), 3.36 – 3.11 (m, 5H), 3.03 – 2.89 (m, 2H), 2.85 (ddt, *J* = 13.6, 5.2, 2.8 Hz, 1H), 2.32 (dddd, *J* = 13.3, 9.0, 6.4, 2.6 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 161.8, 161.6 (d, *J* = 247.9 Hz), 151.4, 139.0, 135.6 (d, *J* = 3.0 Hz), 128.4, 122.2 (d, *J* = 8.5 Hz), 116.4 (d, *J* = 23.0 Hz), 61.3, 51.3, 47.3, 42.7, 37.0, 25.2, 18.6, 14.4 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -113.9 ppm.

HRMS Calculated for $[C_{18}H_{20}FN_3O_4S+H]^+$: 394.1231, Found: 394.1226.

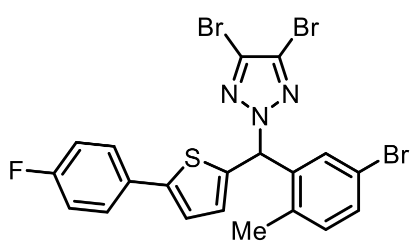
3tt-2: Yield = 4.0 mg (5%) of pale yellow amorphous solid. TLC (pentane:EtOAc, 1:1 v/v): R_f = 0.33.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.90 – 7.76 (m, 2H), 7.21 – 7.11 (m, 2H), 5.38 (dd, *J* = 8.1, 3.2 Hz, 1H), 4.42 (qd, *J* = 7.1, 1.4 Hz, 2H), 3.18 (dt, *J* = 9.1, 7.3 Hz, 1H), 3.11 (ddd, *J* = 12.7, 8.2, 6.8 Hz, 1H), 3.01 (dddd, *J* = 24.5, 13.6, 9.0, 7.1 Hz, 2H), 2.94 – 2.84 (m, 2H), 2.81 – 2.69 (m, 2H), 2.33 – 2.22 (m, 1H), 2.18 – 2.07 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): 162.1, 161.7 (d, *J* = 247.8 Hz), 145.6, 138.2, 135.1 (d, *J* = 3.0 Hz), 134.6, 122.4 (d, *J* = 8.4 Hz), 116.2 (d, *J* = 23.0 Hz), 61.1, 51.1, 46.8, 40.7, 36.0, 22.8, 18.4, 14.1 ppm.

^{19}F NMR ($CDCl_3$, 377 MHz): -114.1 ppm.

HRMS Calculated for $[C_{18}H_{20}FN_3O_4S+H]^+$: 394.1231, Found: 394.1229.



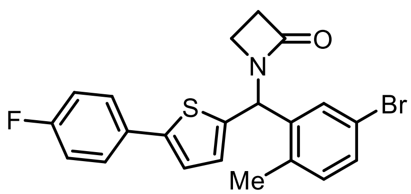
4,5-dibromo-2-((5-bromo-2-methylphenyl)(5-(4-fluorophenyl)thiophen-2-yl)methyl)-2H-1,2,3-triazole, **3pp'**

Reaction run using 2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene **1p** (68.6 mg, 0.2 mmol, 1.0 equiv), 4,5-Dibromo-1*H*-1,2,3-triazole **2p** (113.4 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure II (glass vial) procedure at 30 °C. Yield = 81.8 mg (70%) of colorless liquid. TLC (pentane:EtOAc, 9:1 v/v): R_f = 0.51.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.58 – 7.46 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.20 (s, 1H), 7.09 (d, *J* = 3.2 Hz, 2H), 7.08 – 6.94 (m, 2 H), 6.84 (d, *J* = 3.7 Hz, 1H), 2.29 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 162.6 (d, *J* = 248.1 Hz), 145.5, 137.6, 137.5, 134.6, 132.5, 132.1, 130.00, 129.95, 129.6, 127.6 (d, *J* = 8.1 Hz), 125.6, 122.8, 120.3, 116.0 (d, *J* = 21.9 Hz), 65.9, 18.9.

^{19}F NMR ($CDCl_3$, 377 MHz): -113.6 ppm.
HRMS Calculated for $[C_{20}H_{13}Br_3FN_3S+H]^+$: 583.8437, Found: 583.8444.



4,5-dibromo-2-((5-bromo-2-methylphenyl)(5-(4-fluorophenyl)thiophen-2-yl)methyl)-2H-1,2,3-triazole, **3ps**

Reaction run using 2-(5-bromo-2-methylbenzyl)-5-(4-fluorophenyl)thiophene **1p** (68.6 mg, 0.2 mmol, 1.0 equiv), azetidin-2-one **2s** (35.0 mg, 0.50 mmol, 2.5 equiv), and tetrabutylammonium chloride (5.6 mg, 0.02 mmol, 0.1 equiv) following the general procedure II (glass vial) procedure at 30 °C. Yield = 68.5 mg (80%) of light-yellow liquid. TLC (pentane:EtOAc, 4:1 v/v): R_f = 0.10.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.57 – 7.48 (m, 2H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.38 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.15 – 7.06 (m, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 3.8 Hz, 1H), 6.43 (s, 1H), 3.38 (q, *J* = 5.1, 4.5 Hz, 1H), 3.24 (dt, *J* = 5.7, 4.0 Hz, 1H), 3.01 (t, *J* = 4.2 Hz, 2H), 2.29 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz): 167.2, 162.5 (d, *J* = 247.7 Hz), 143.7, 140.7, 139.2, 135.1, 132.7, 131.3, 130.2 (d, *J* = 3.5 Hz), 129.9, 127.7, 127.4 (d, *J* = 8.1 Hz), 122.9, 119.8, 115.9 (d, *J* = 21.8 Hz), 53.8, 38.4, 36.1, 19.0 ppm.

^{19}F NMR ($CDCl_3$, 471 MHz): -114.0 ppm.
HRMS Calculated for $[C_{21}H_{17}BrFNOS+H]^+$: 452.0091, Found: 452.0089.

9. References

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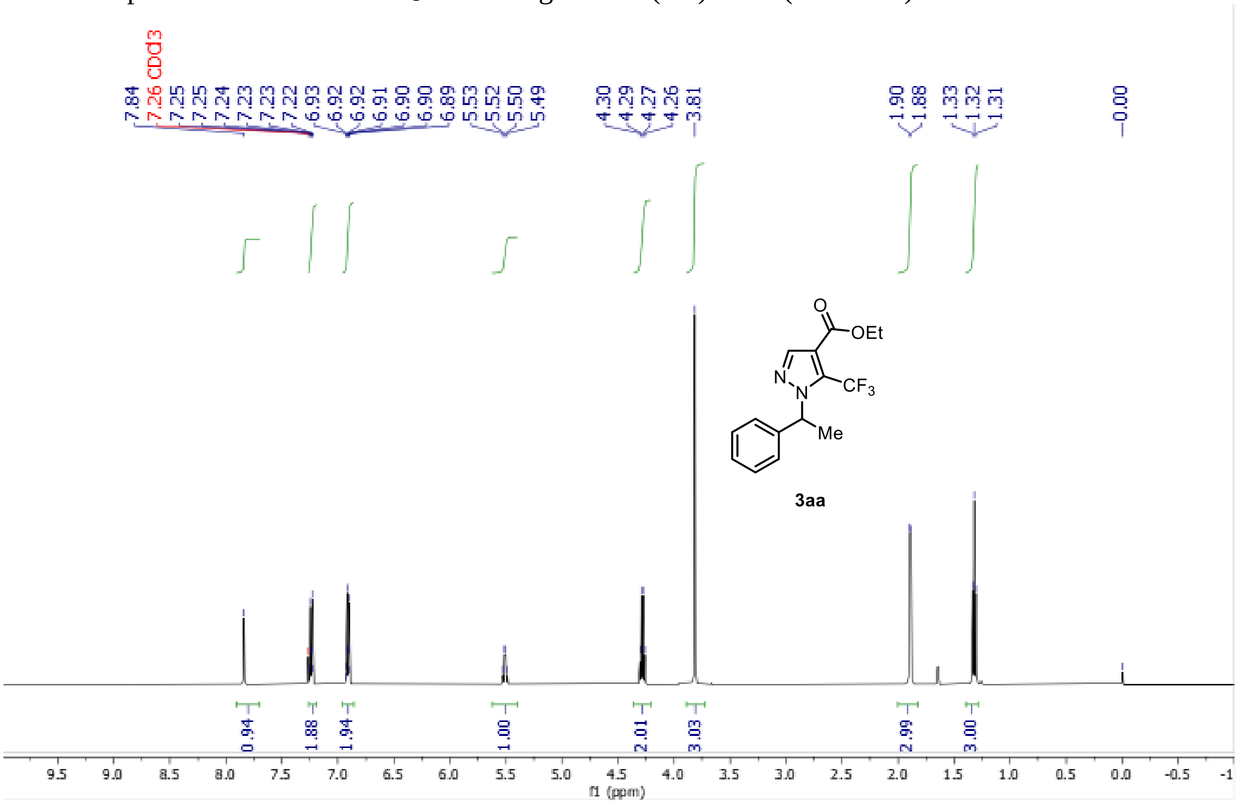
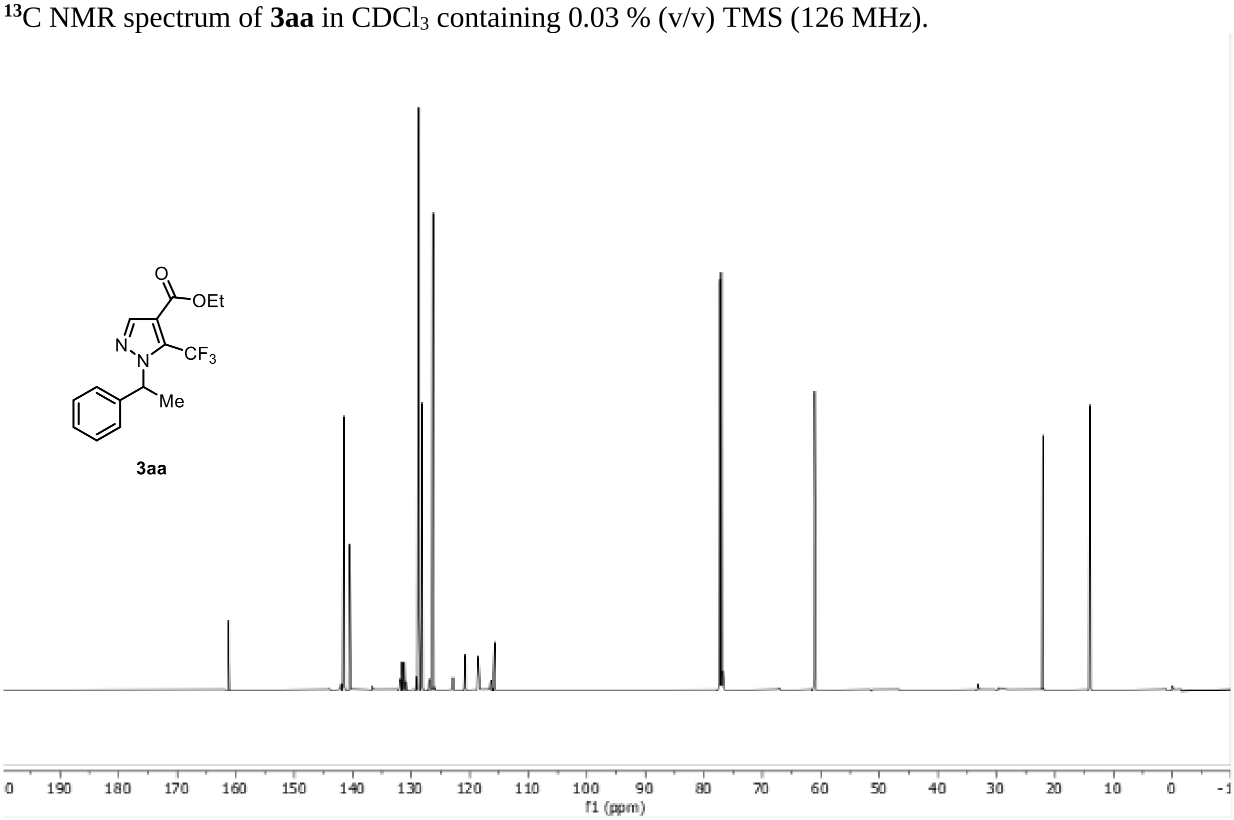
10. NMR Spectroscopic Data

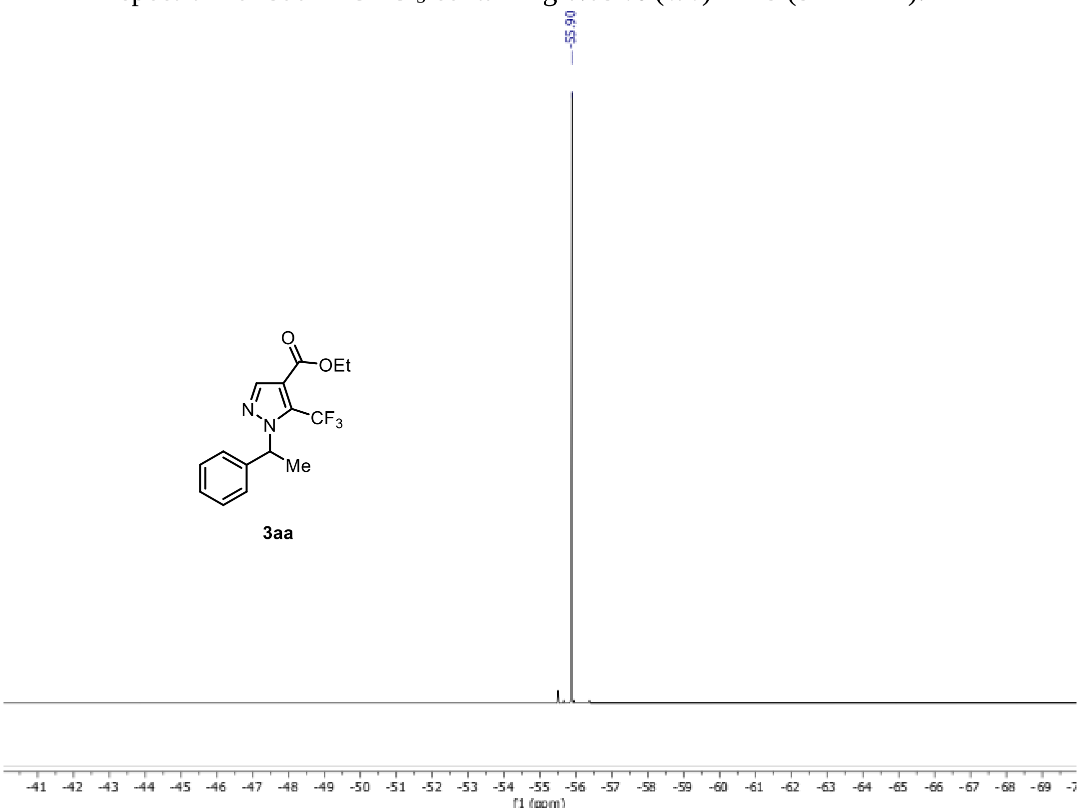
^{1}H NMR spectrum of **3aa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



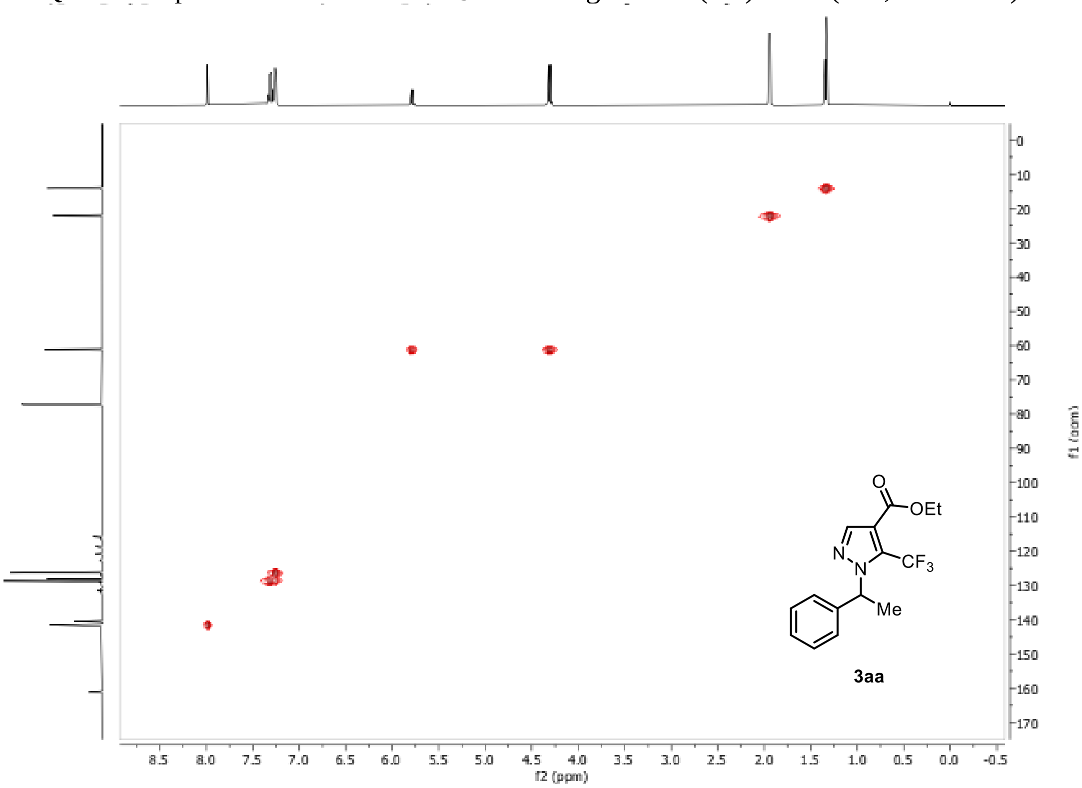
^{13}C NMR spectrum of **3aa** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



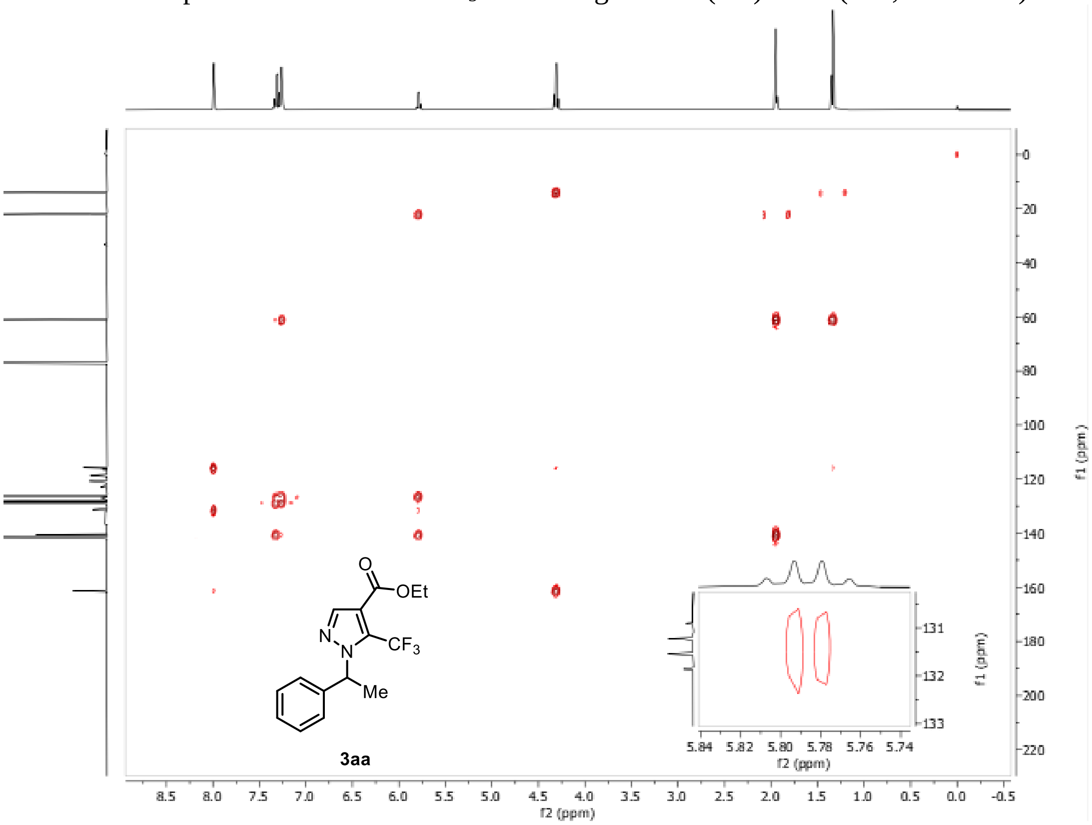
^{19}F NMR spectrum of **3aa** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



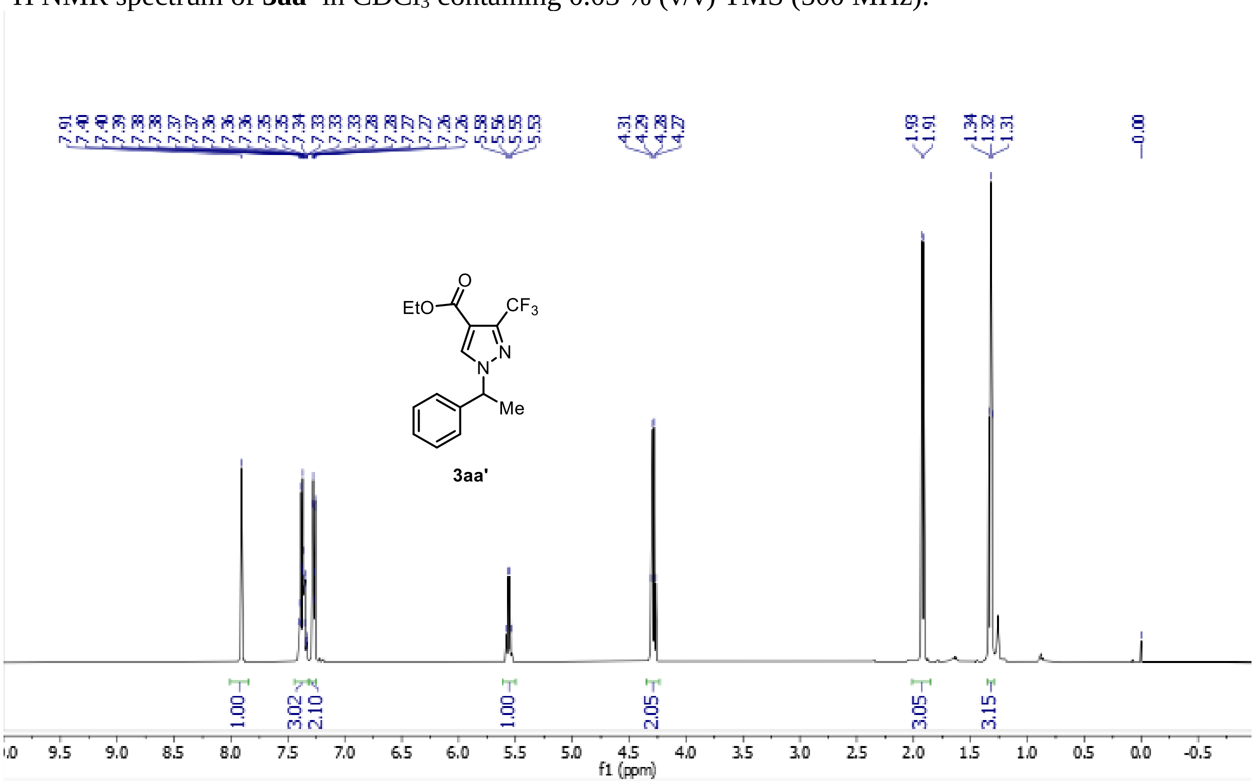
HSQC NMR spectrum of **3aa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



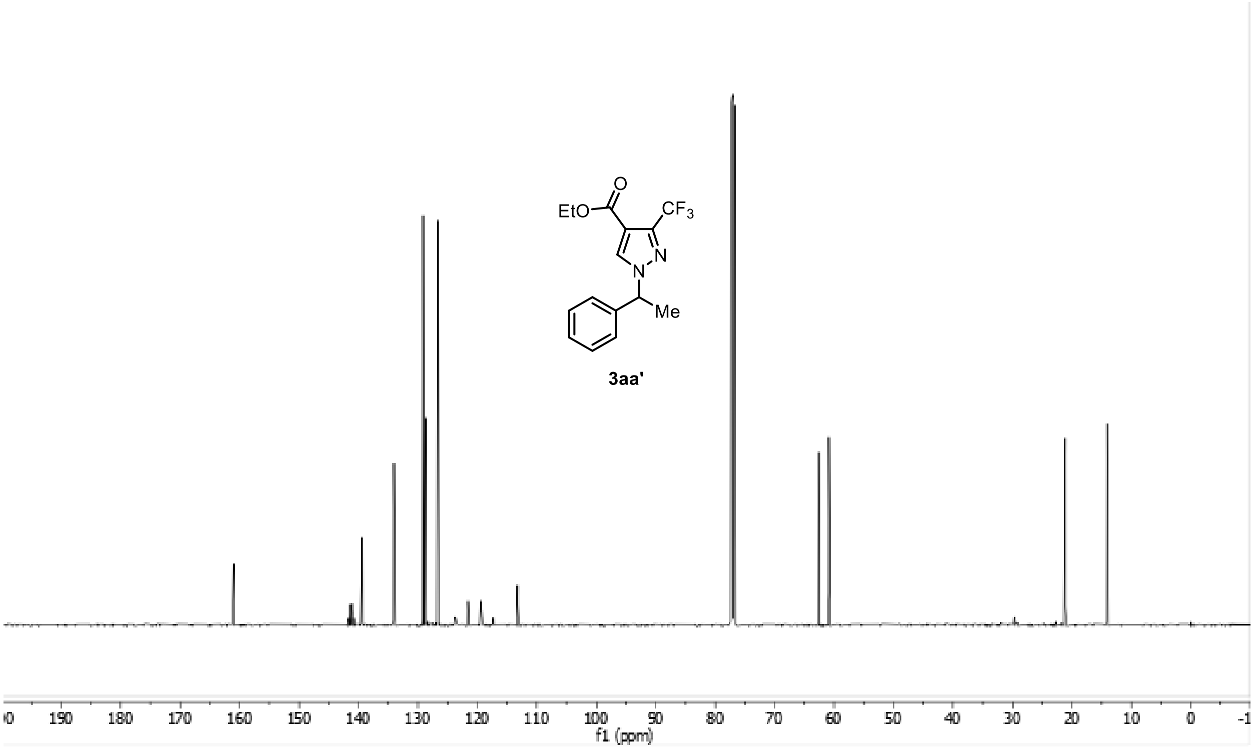
HMBC NMR spectrum of **3aa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



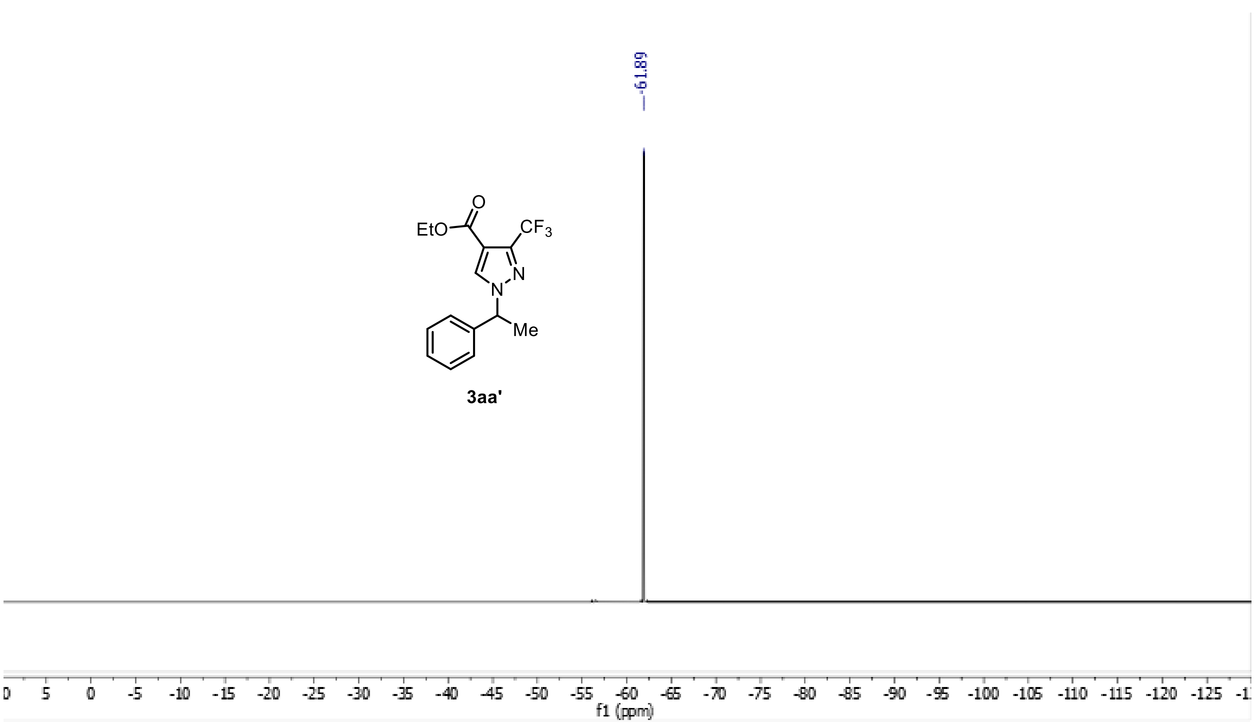
[1]H NMR spectrum of **3aa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



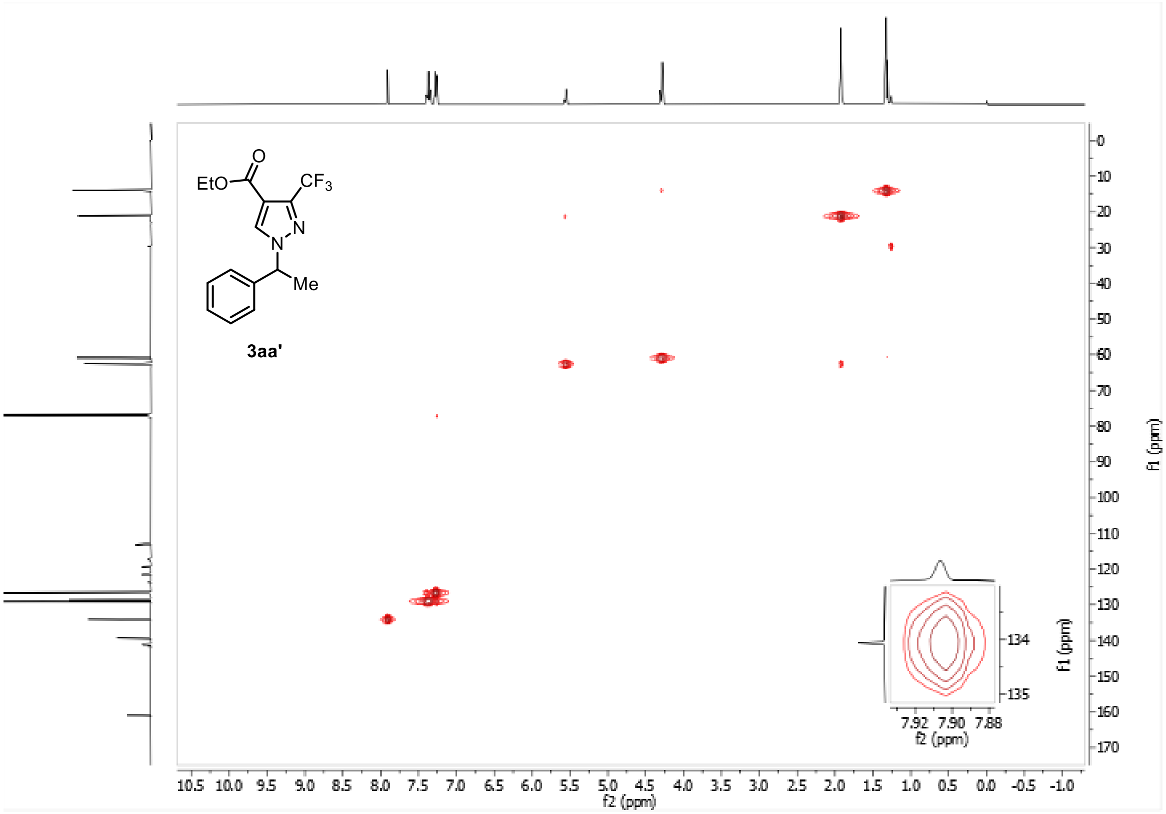
^{13}C NMR spectrum of **3aa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



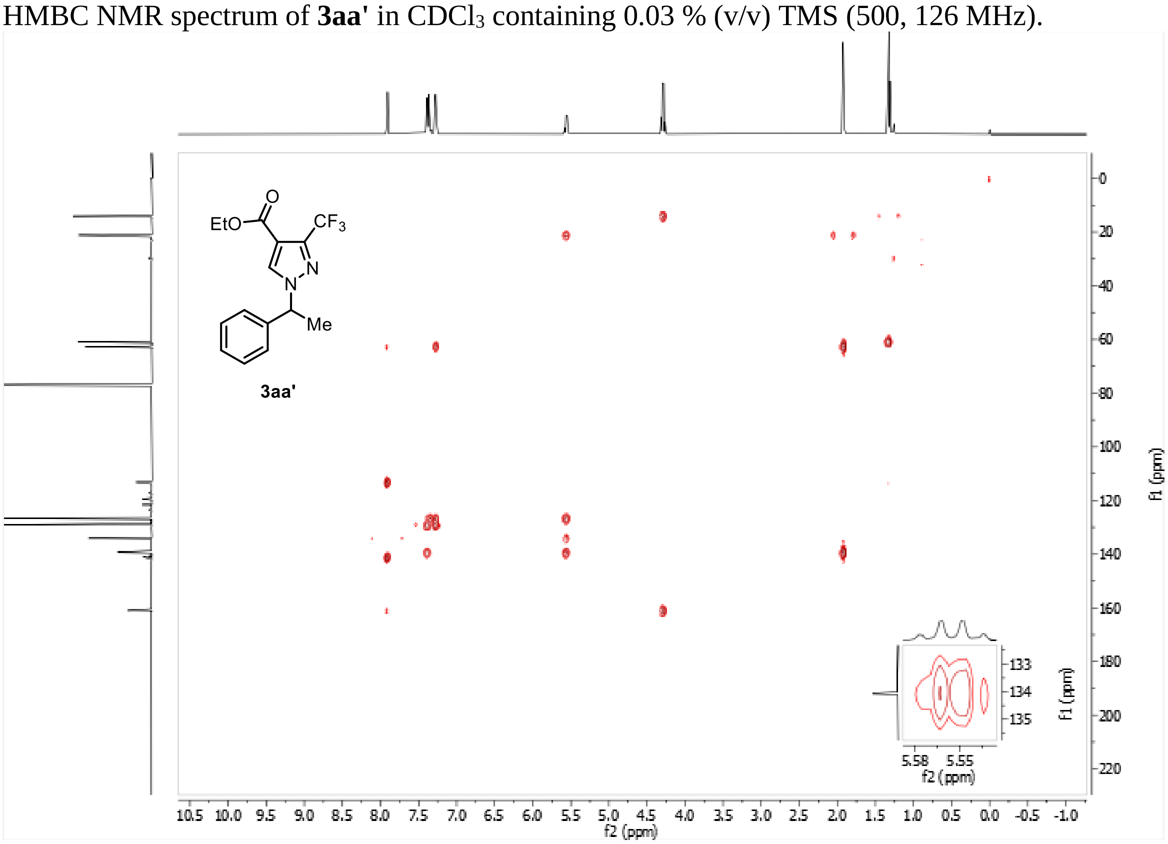
^{19}F NMR spectrum of **3aa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



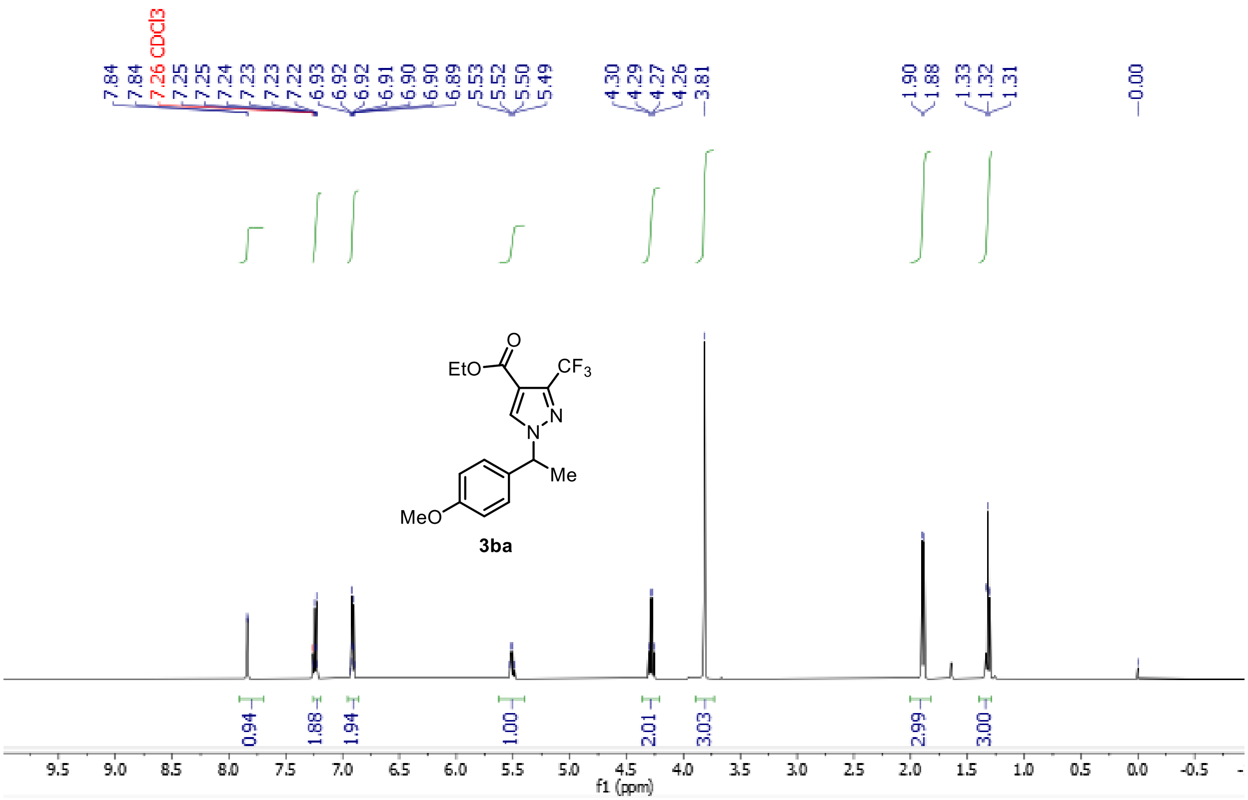
HSQC NMR spectrum of **3aa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



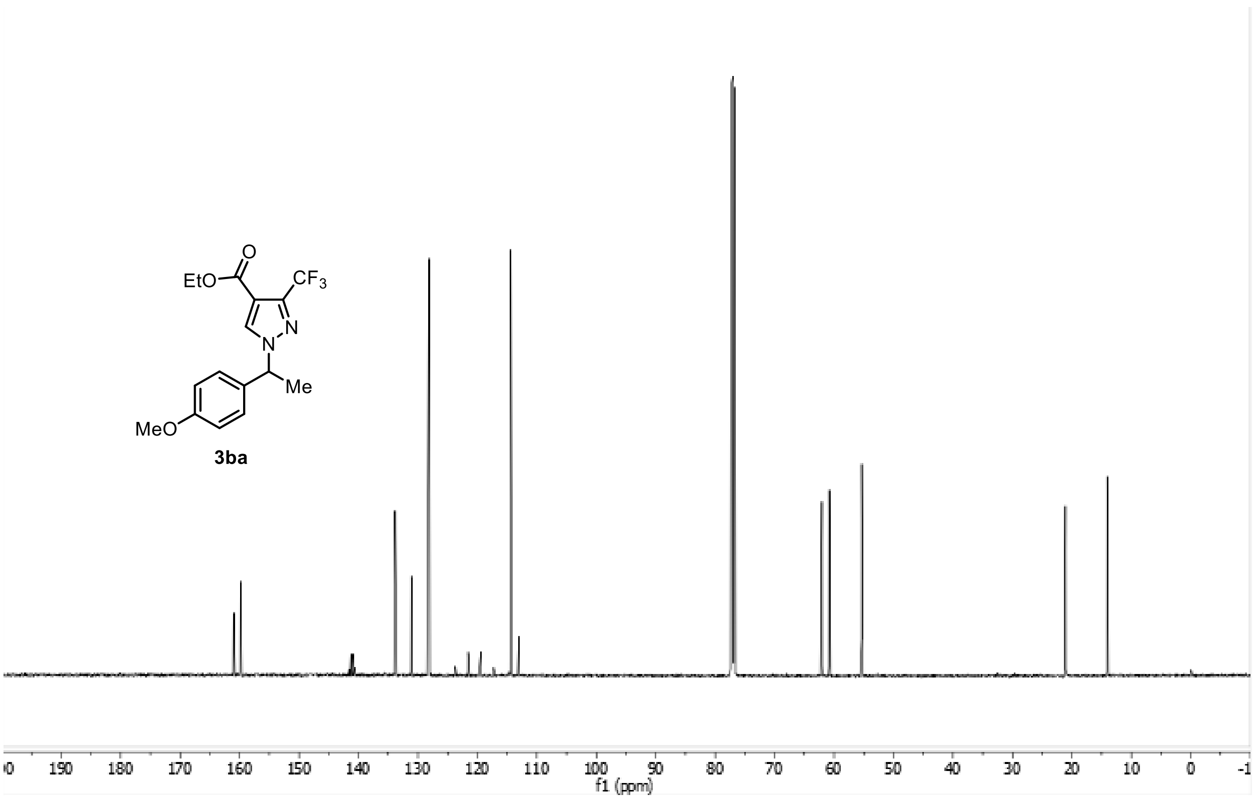
HMBC NMR spectrum of **3aa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



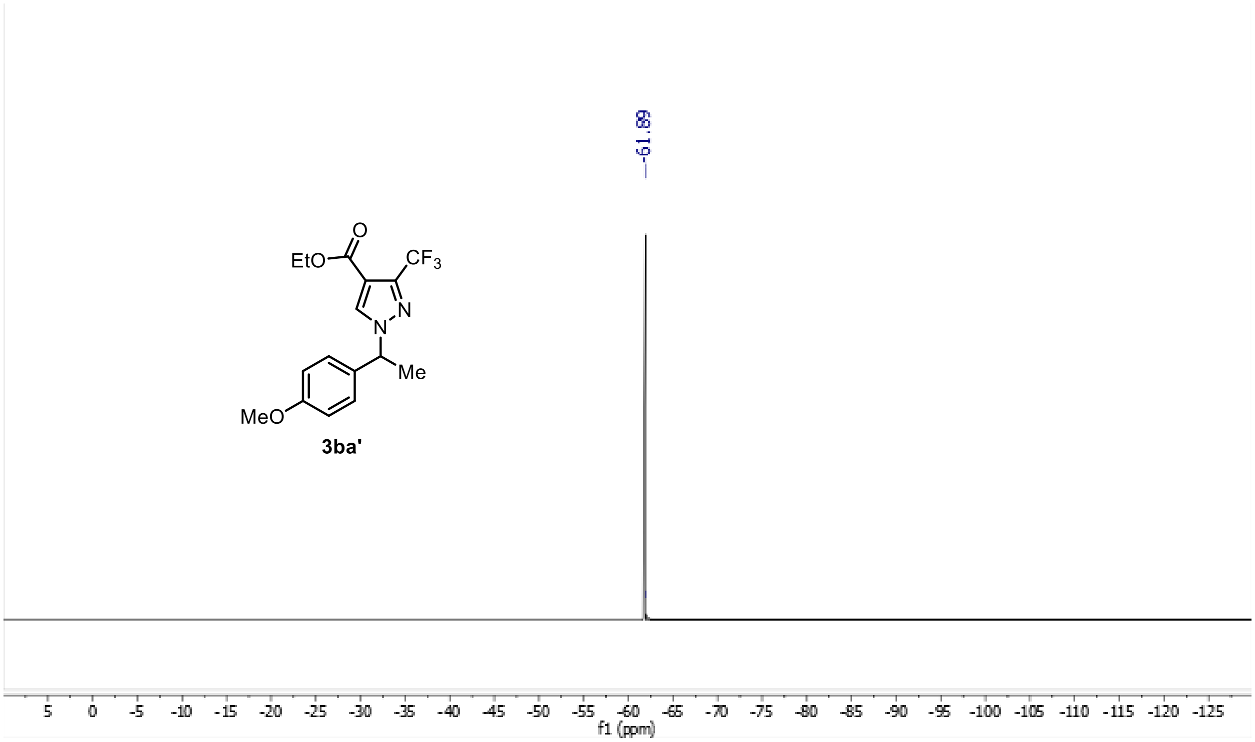
[1]H NMR spectrum of **3ba'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



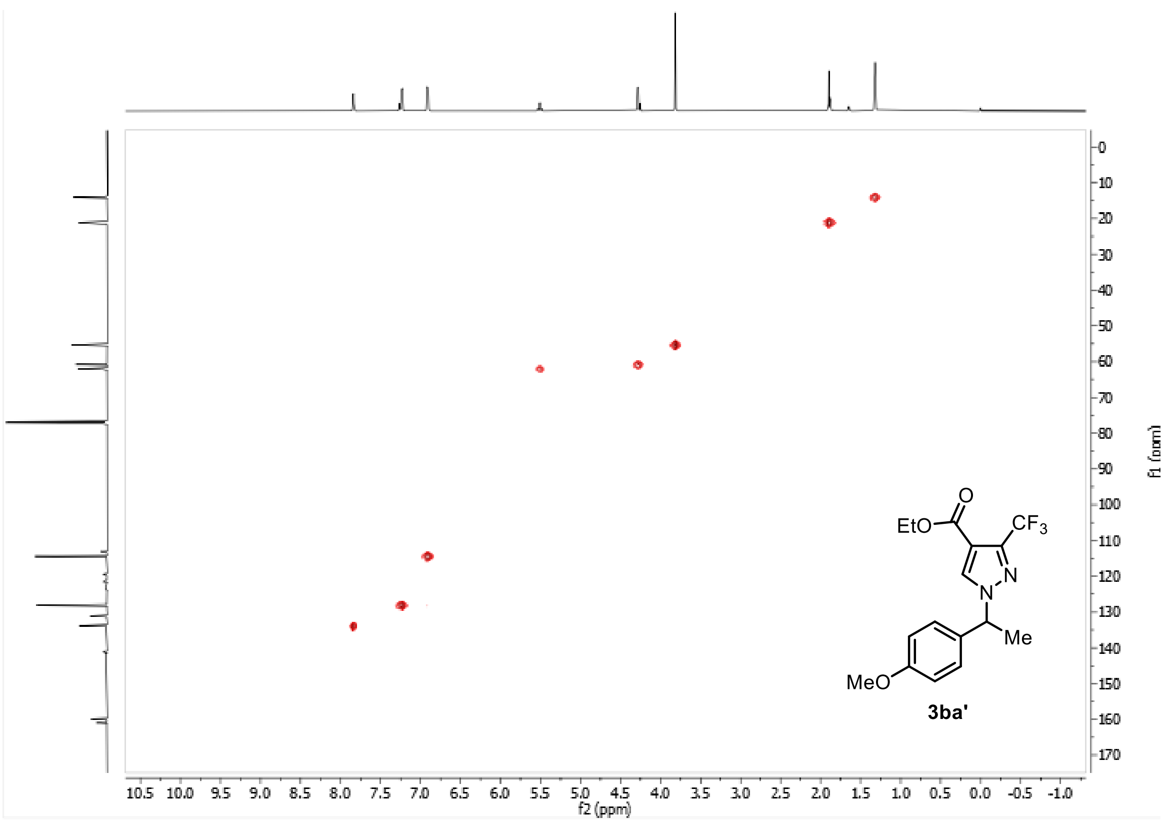
[13]C NMR spectrum of **3ba'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



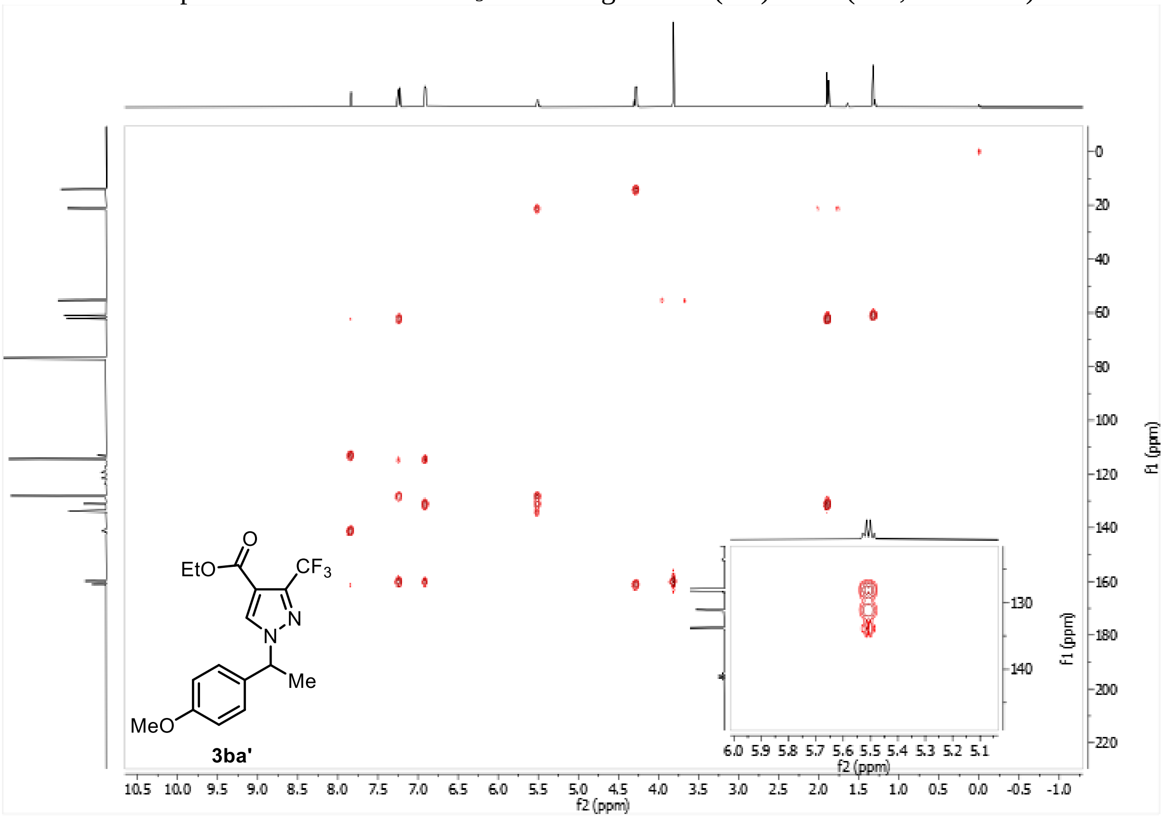
^{19}F NMR spectrum of **3ba'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



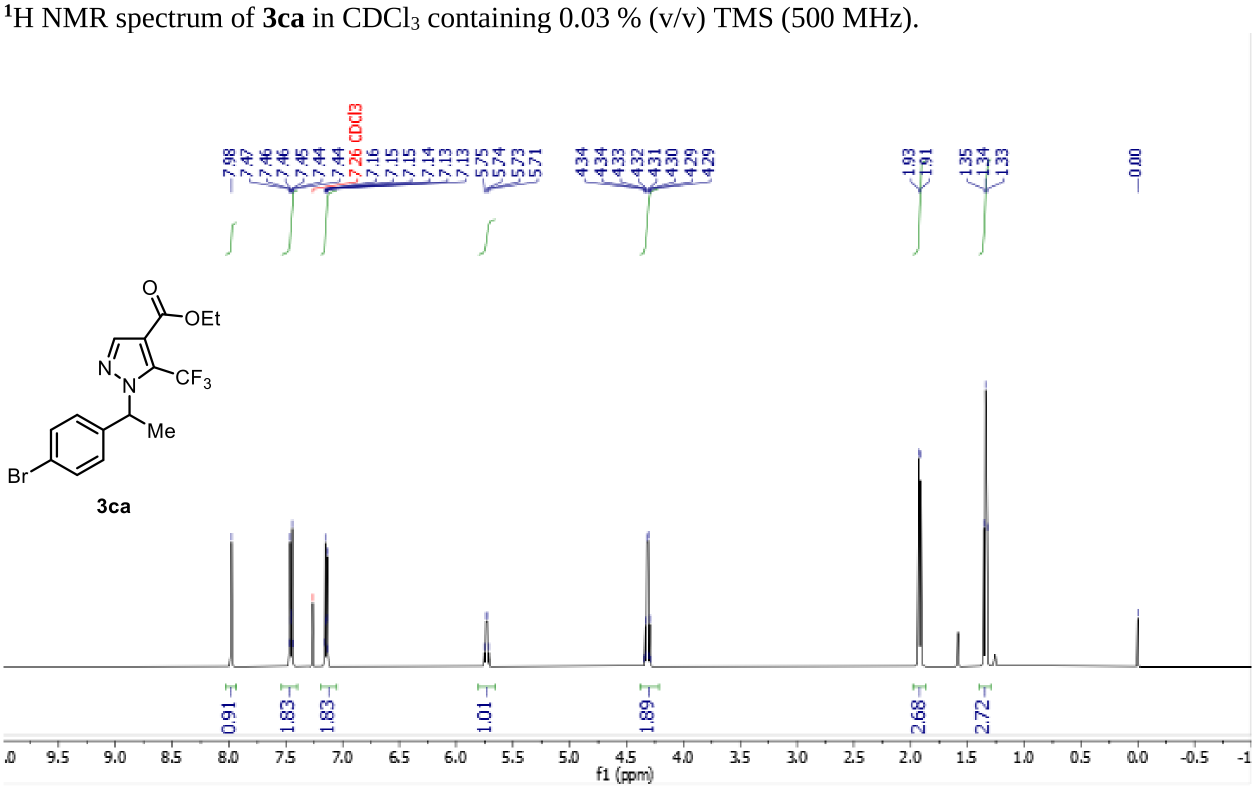
HSQC NMR spectrum of **3ba'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



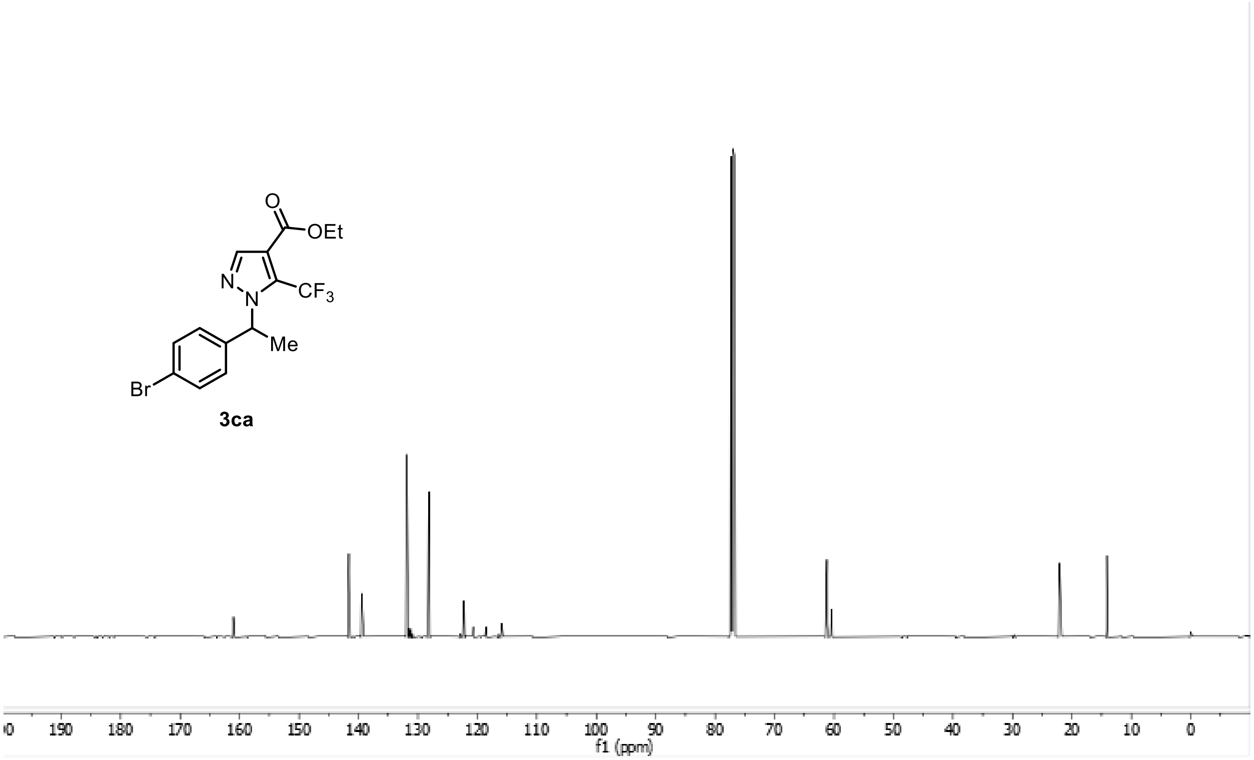
HMBC NMR spectrum of **3ba'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



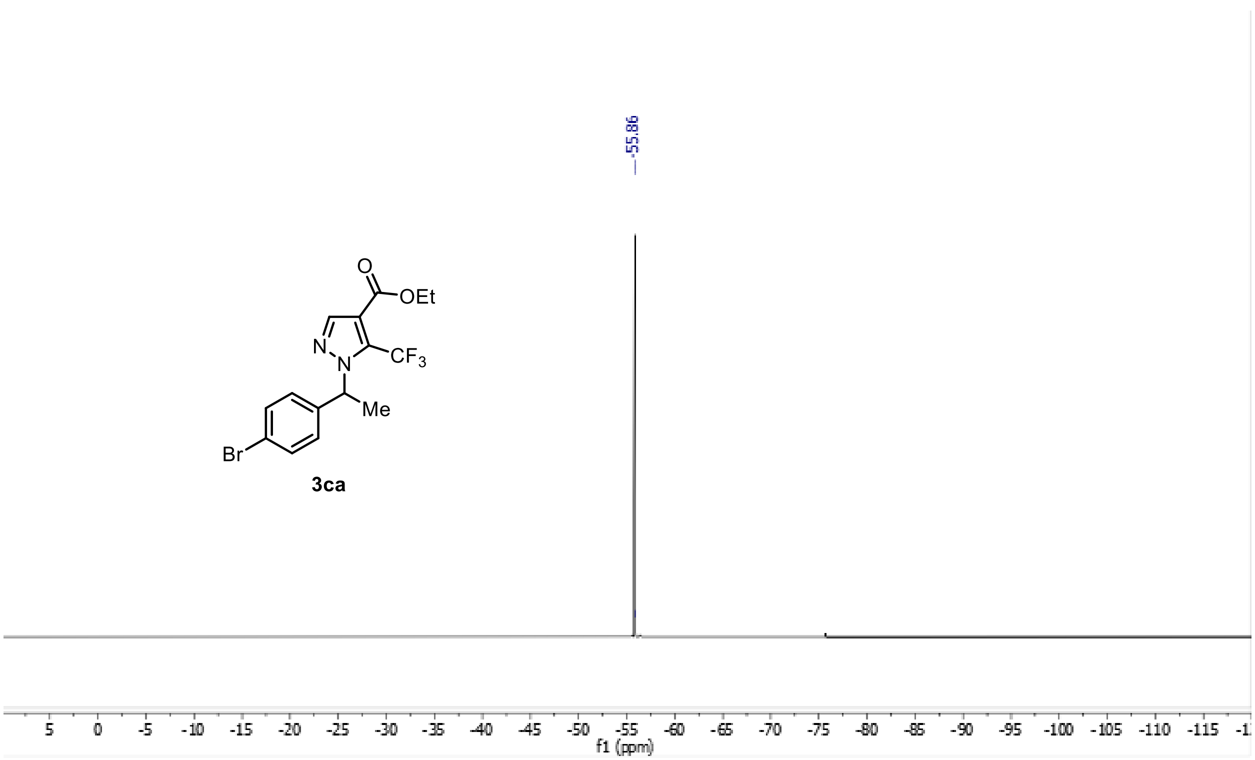
[1]H NMR spectrum of **3ca** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



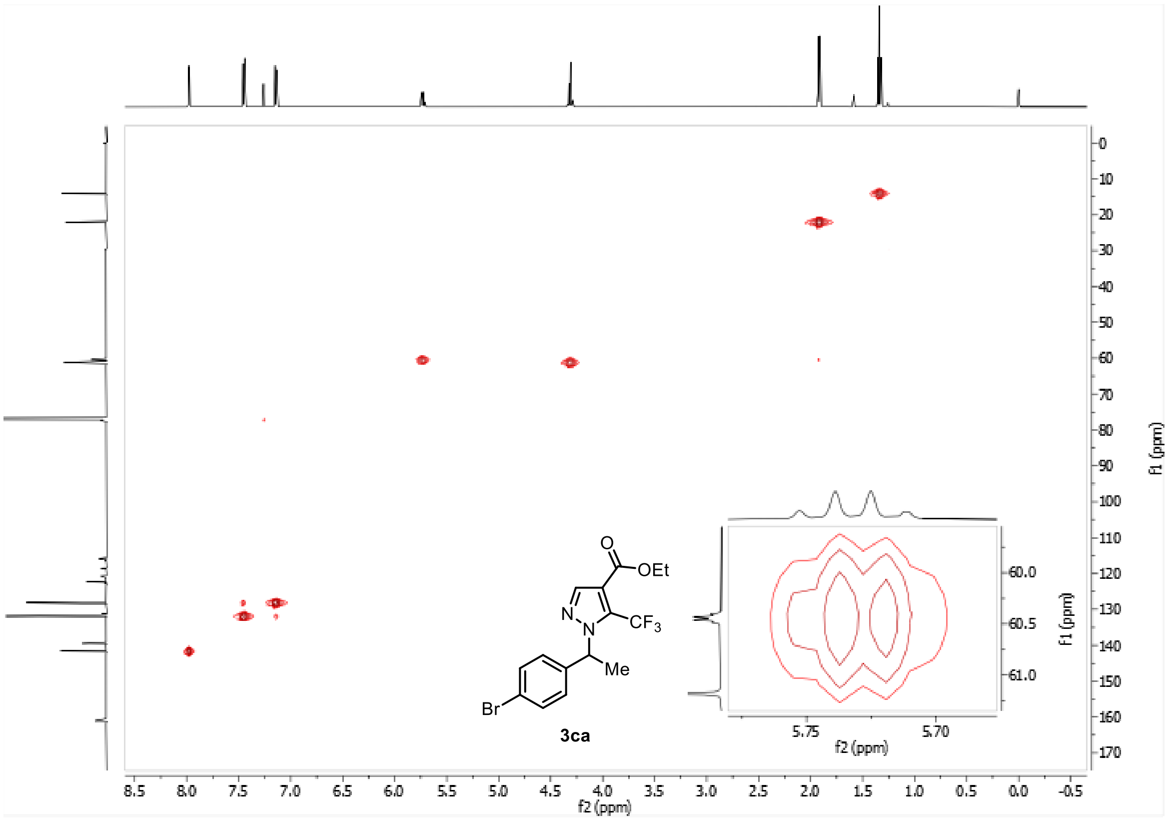
[13]C NMR spectrum of **3ca** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



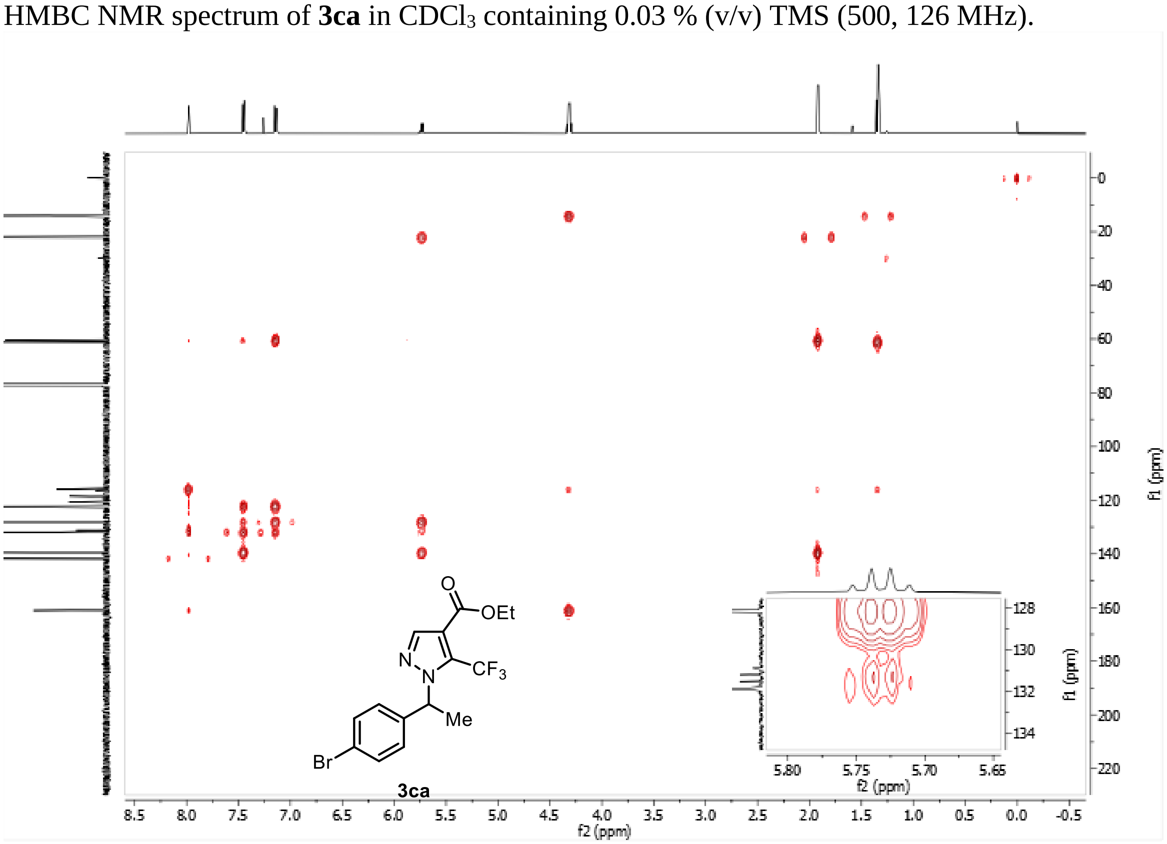
[19]F NMR spectrum of **3ca** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



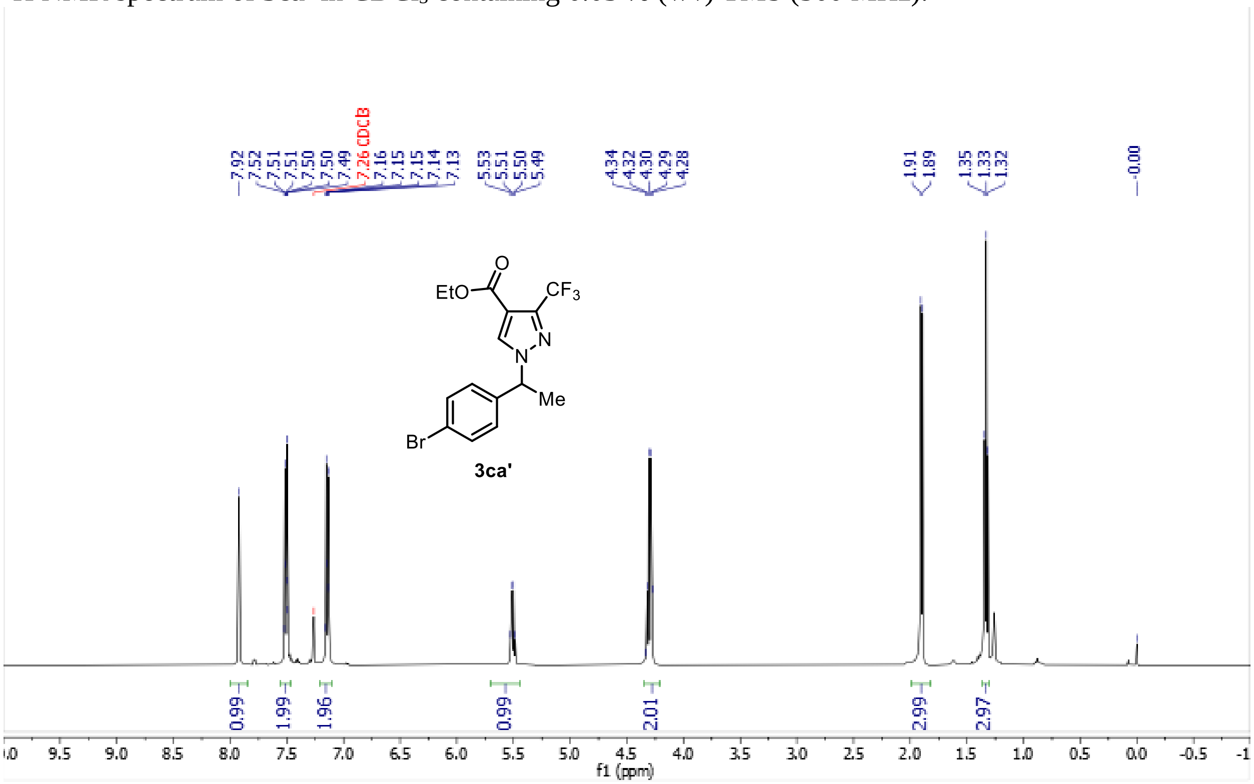
HSQC NMR spectrum of **3ca** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



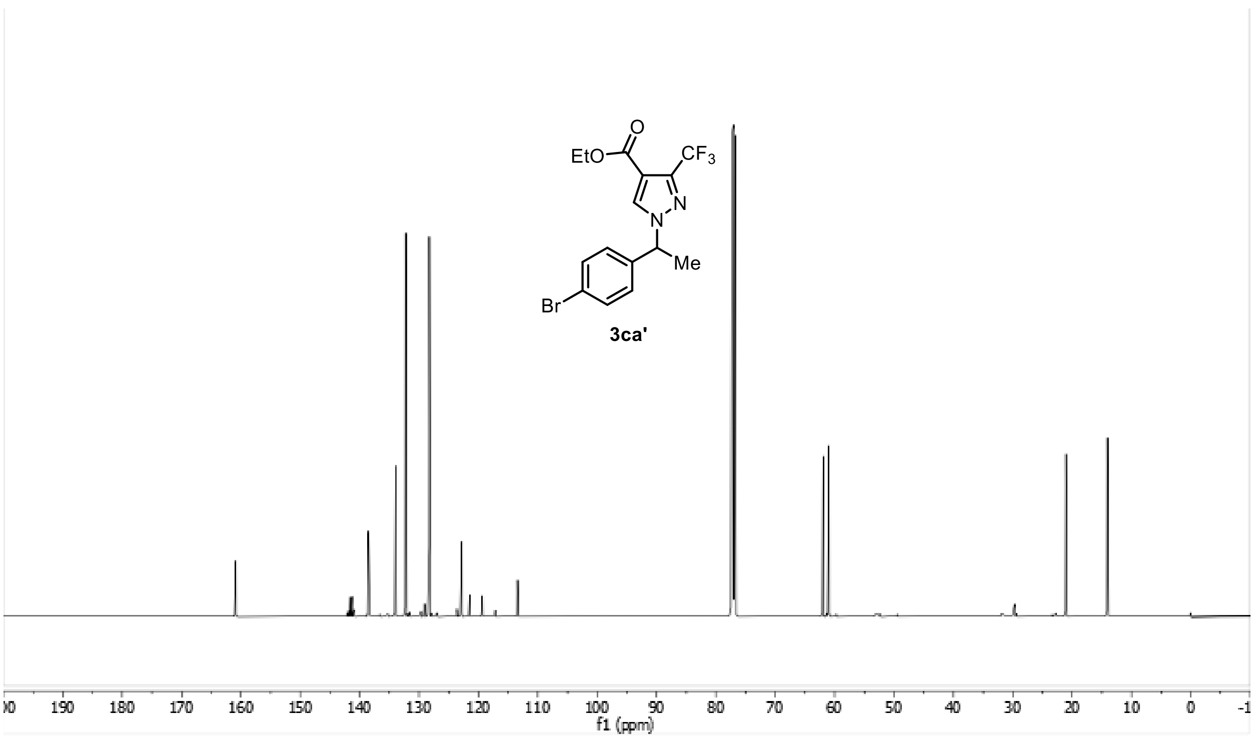
HMBC NMR spectrum of **3ca** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



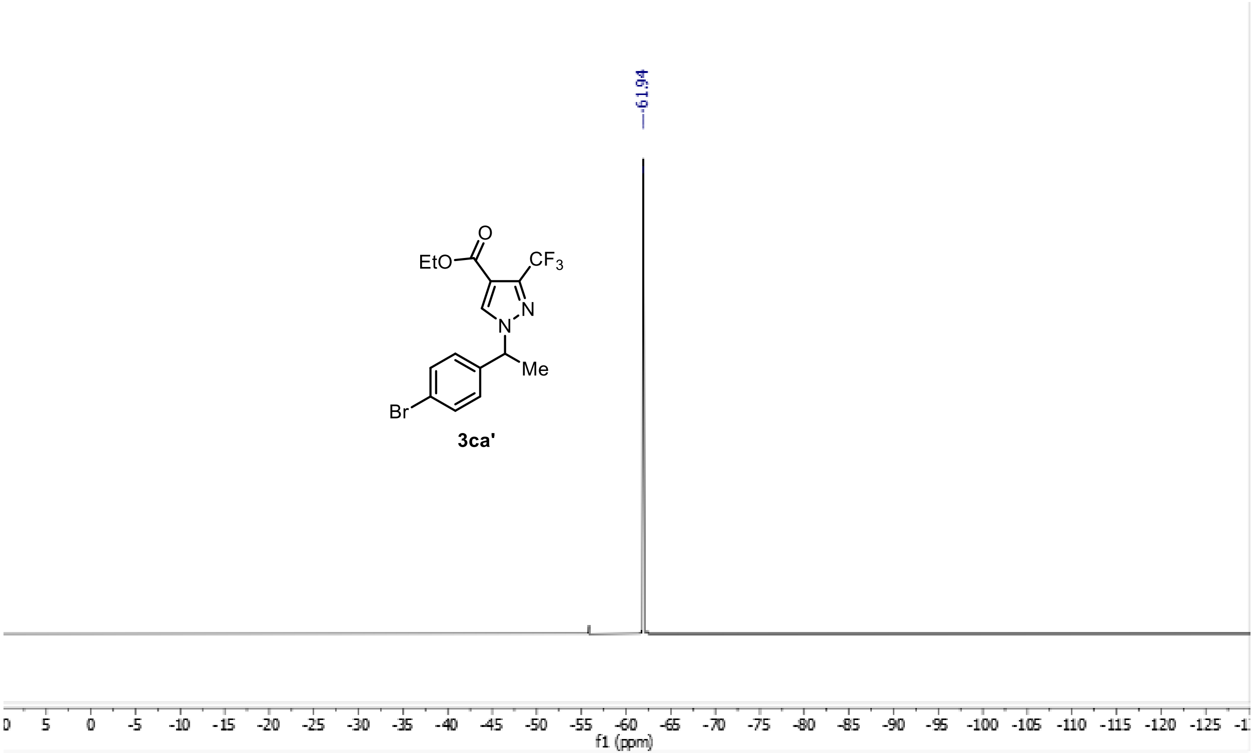
^{1}H NMR spectrum of **3ca'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



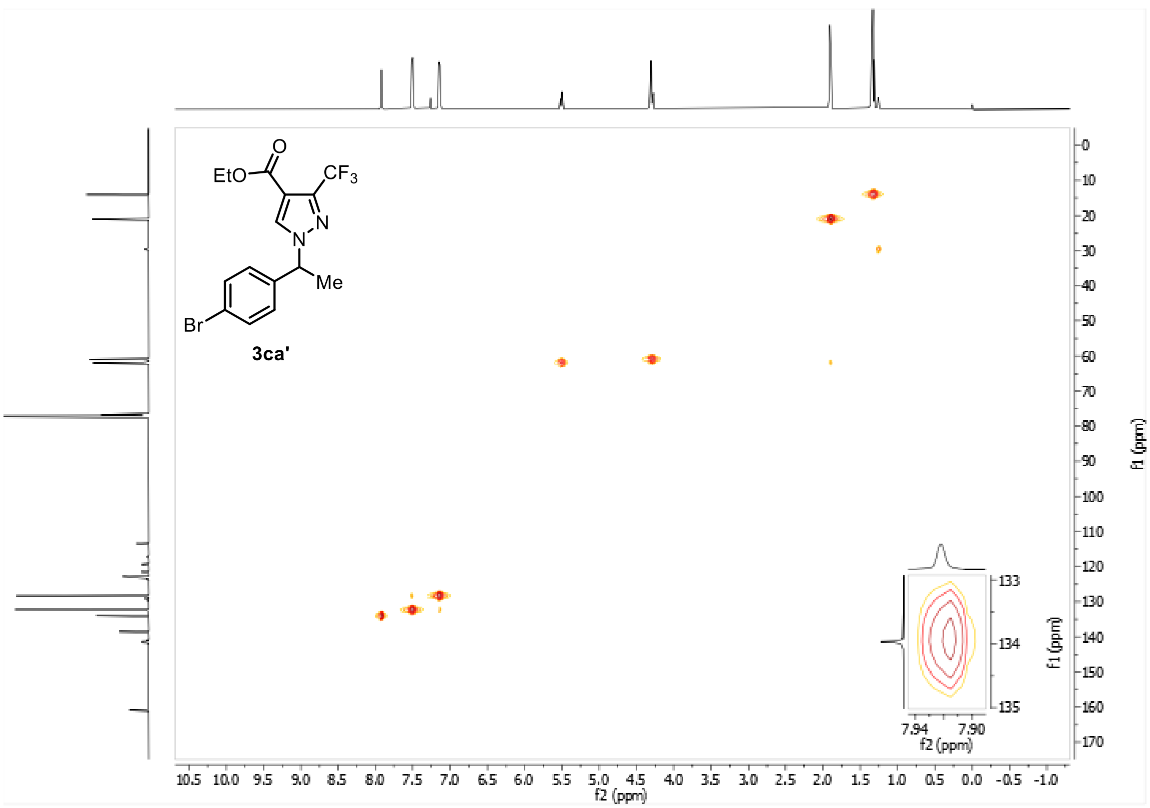
^{13}C NMR spectrum of **3ca'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



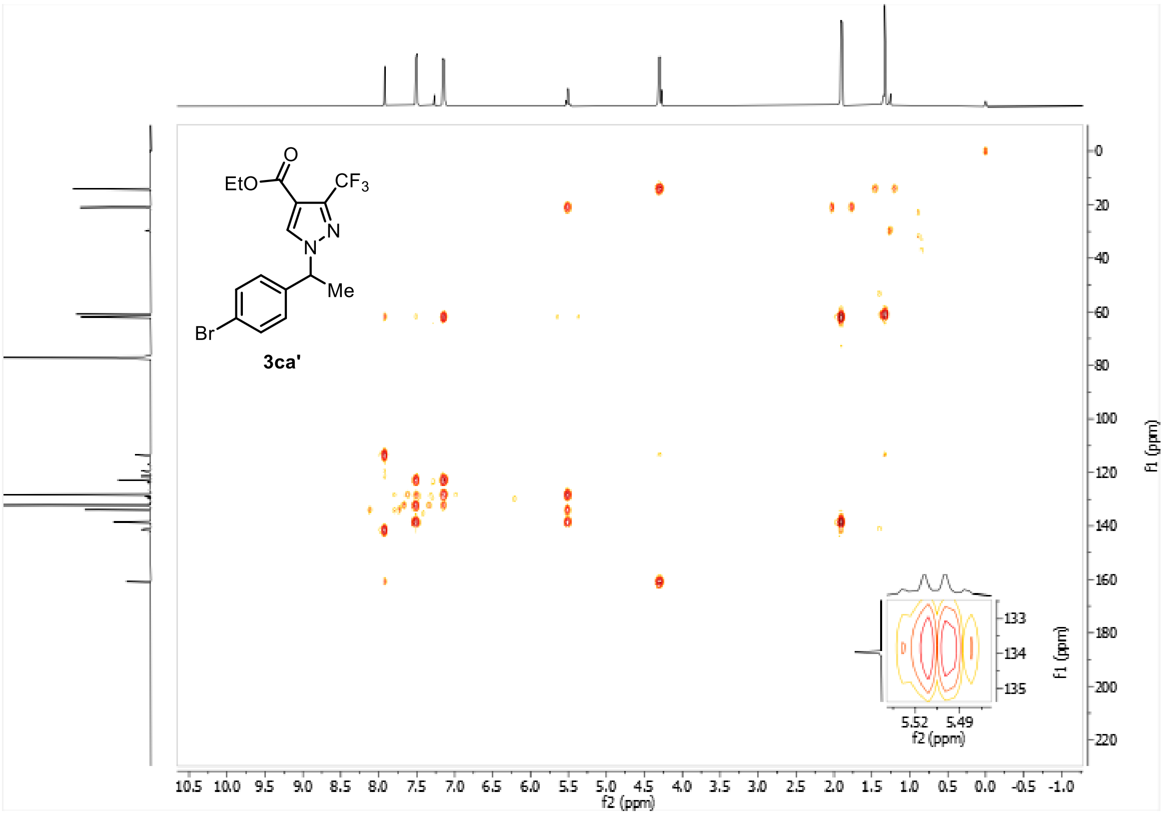
^{19}F NMR spectrum of **3ca'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



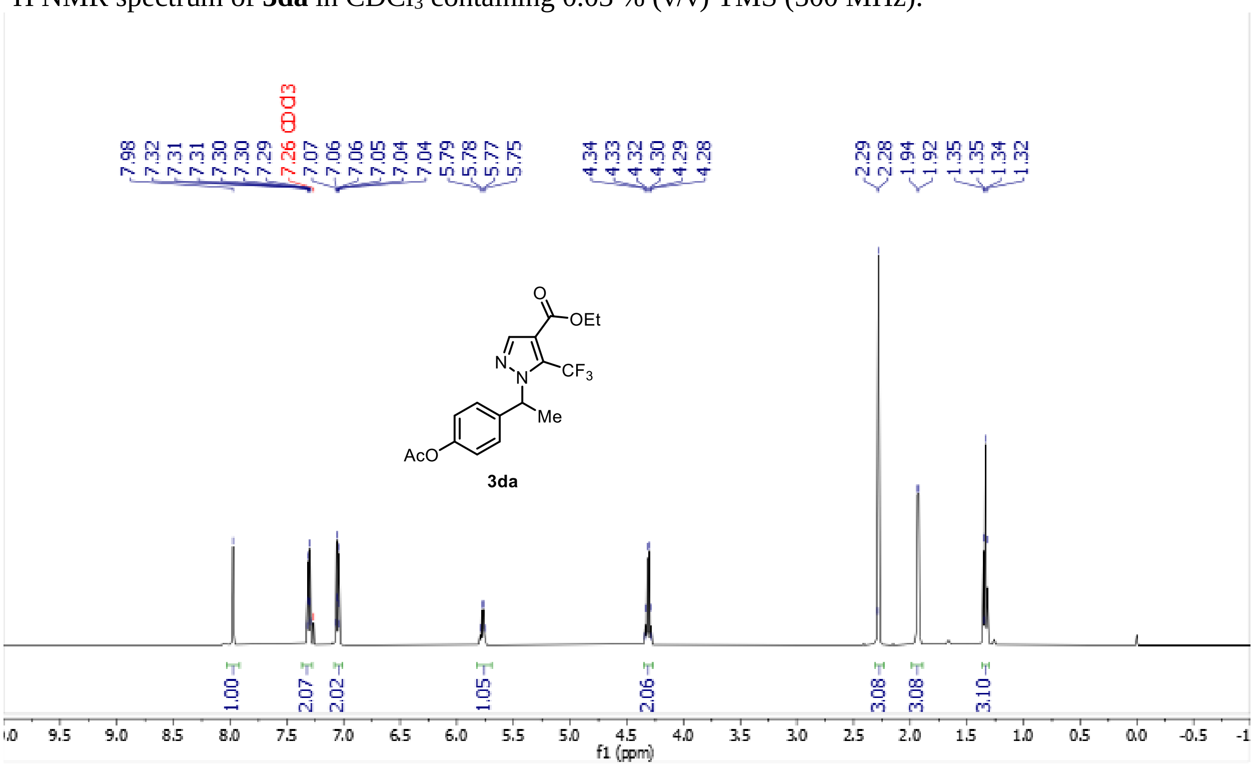
HSQC NMR spectrum of **3ca'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



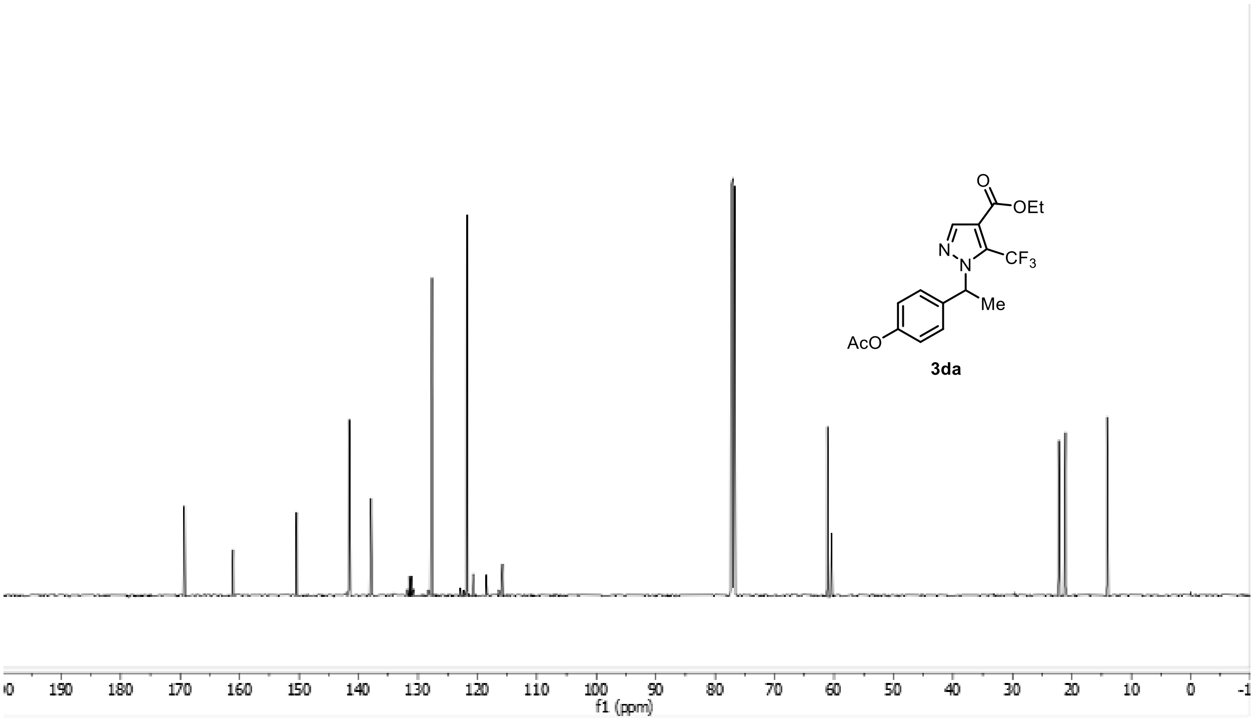
HMBC NMR spectrum of **3ca'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



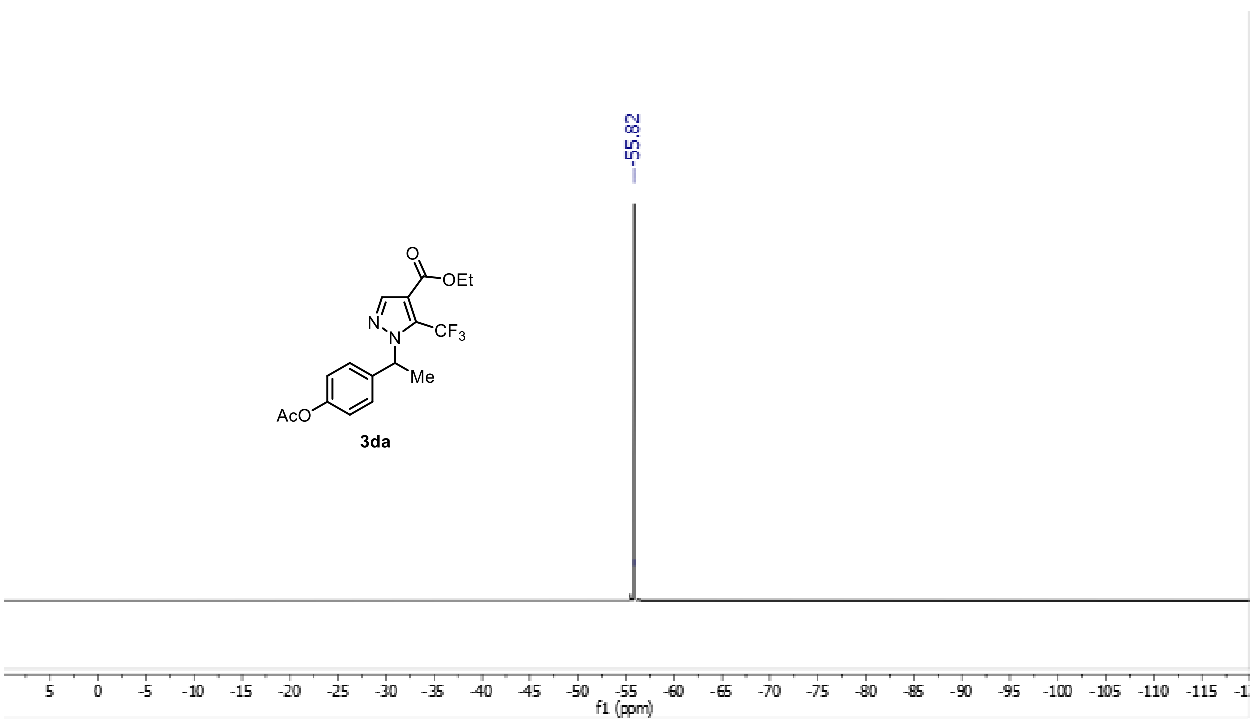
^{1}H NMR spectrum of **3da** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



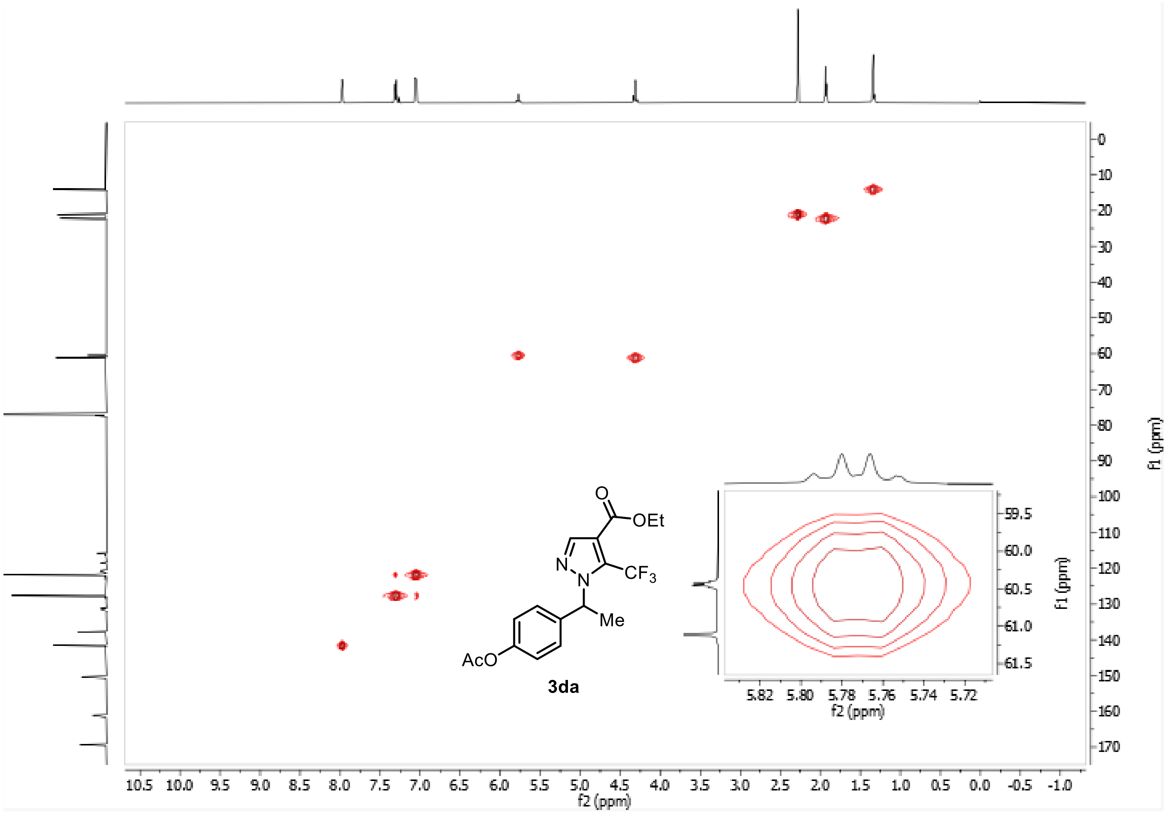
^{13}C NMR spectrum of **3da** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



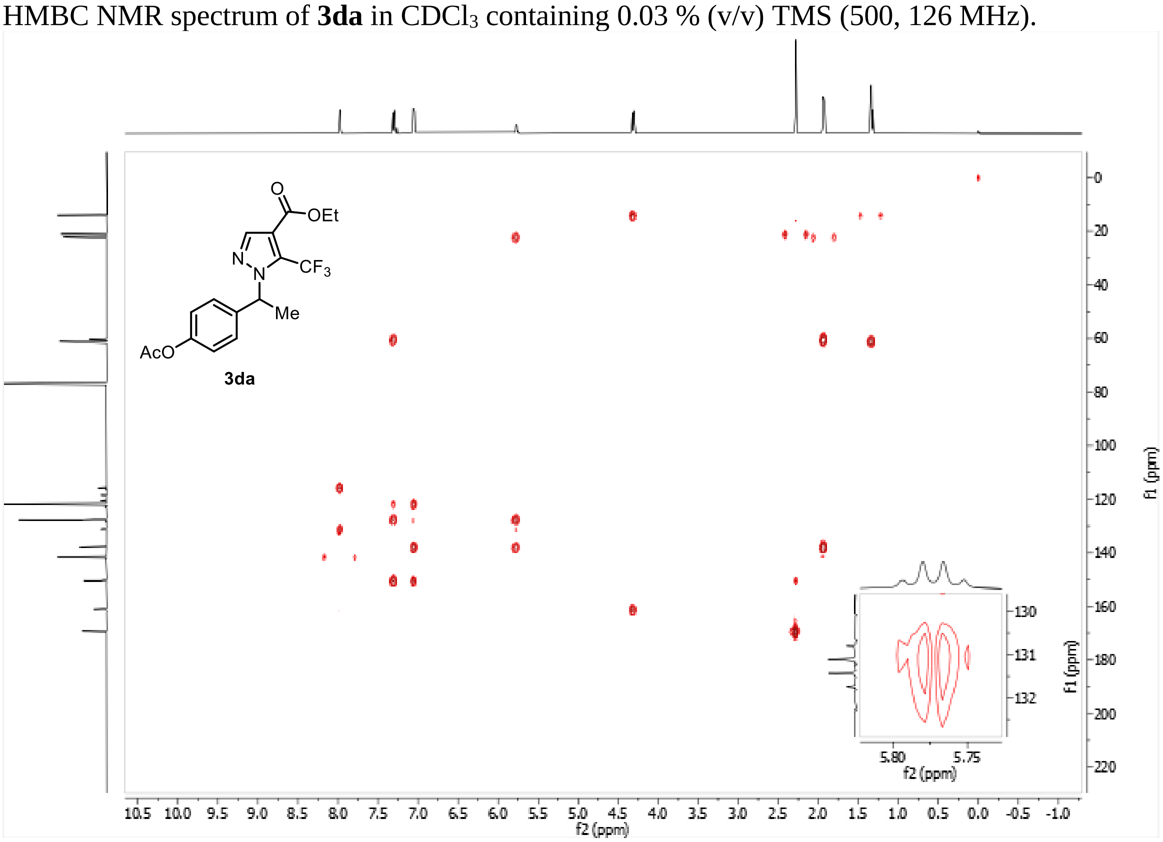
^{19}F NMR spectrum of **3da** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



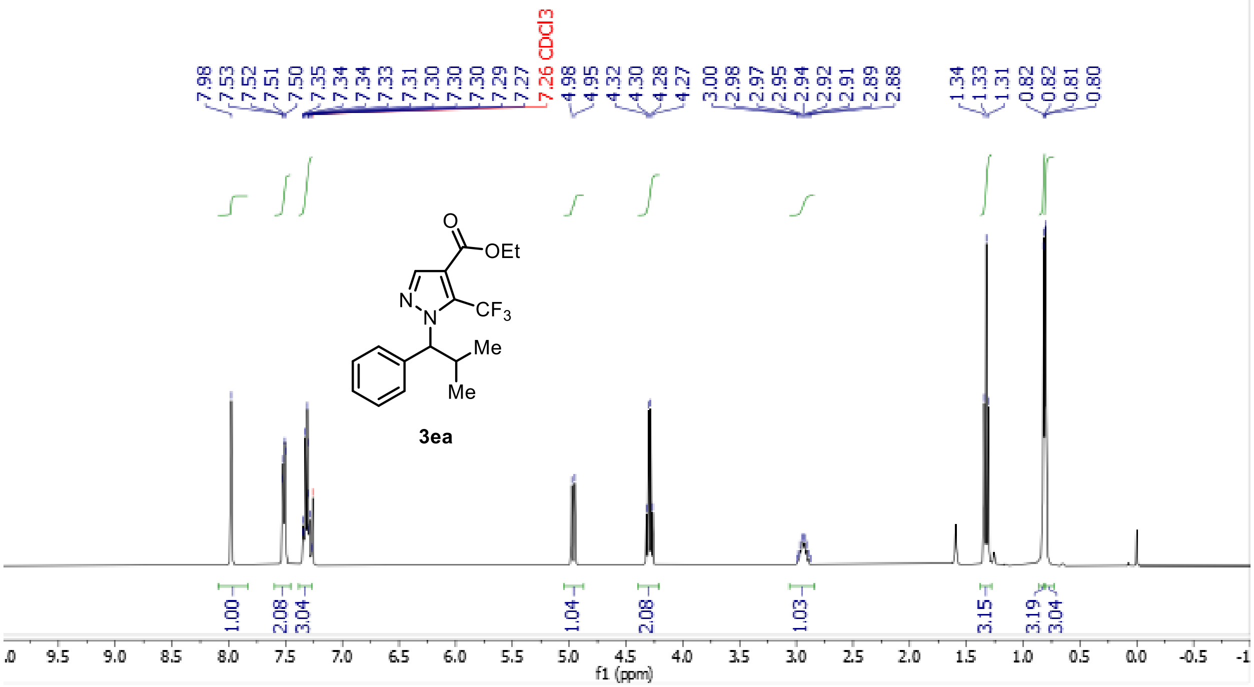
HSQC NMR spectrum of **3da** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



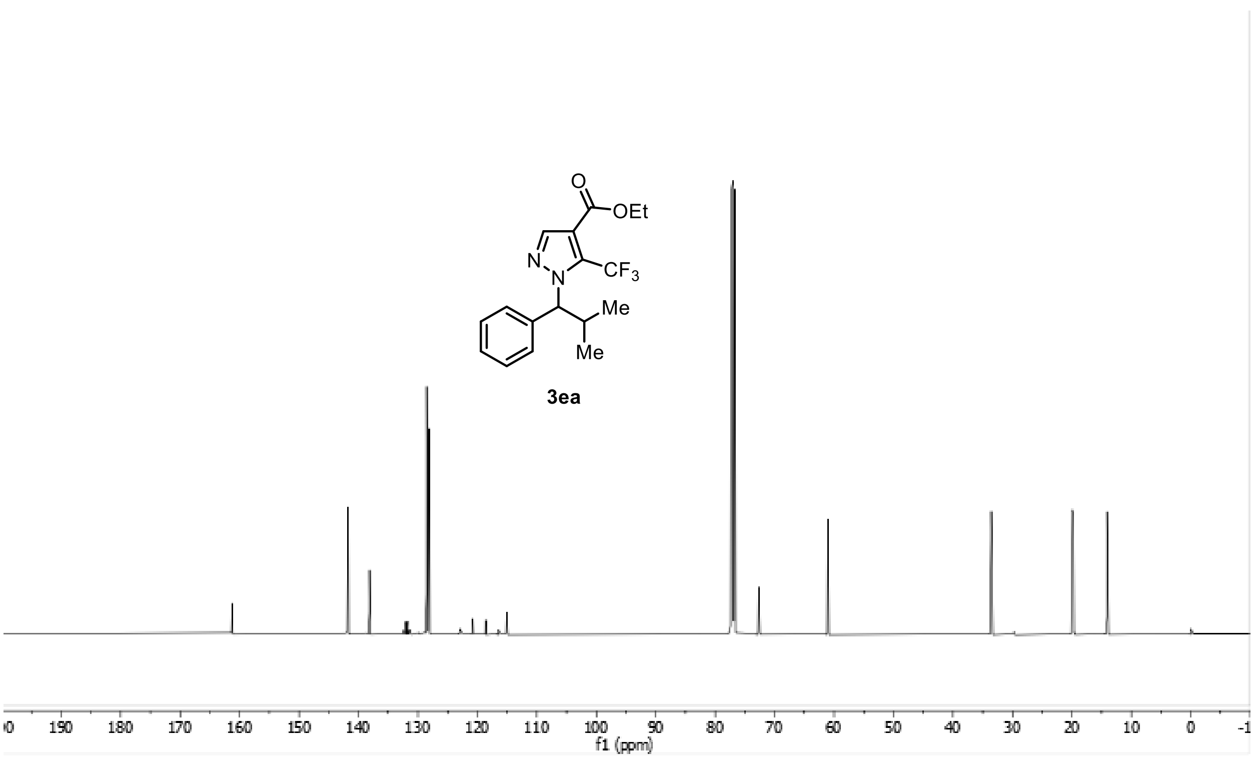
HMBC NMR spectrum of **3da** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



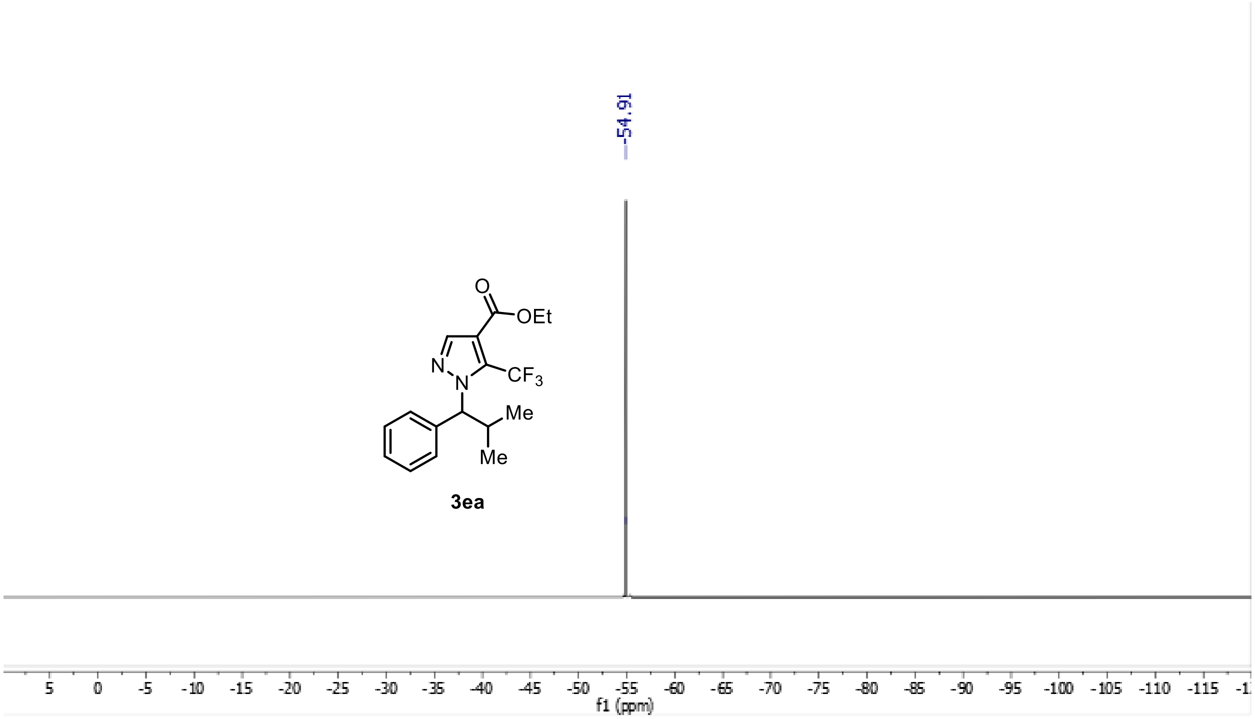
^{1}H NMR spectrum of **3ea** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



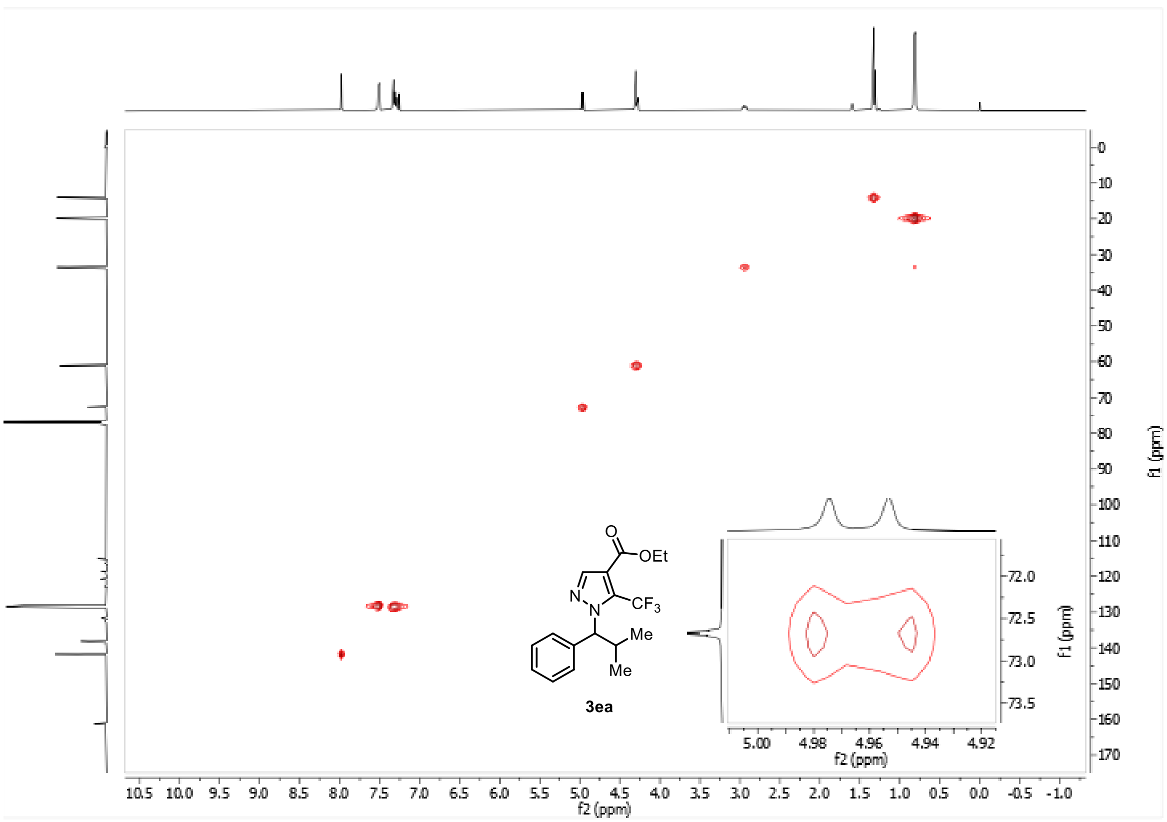
^{13}C NMR spectrum of **3ea** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



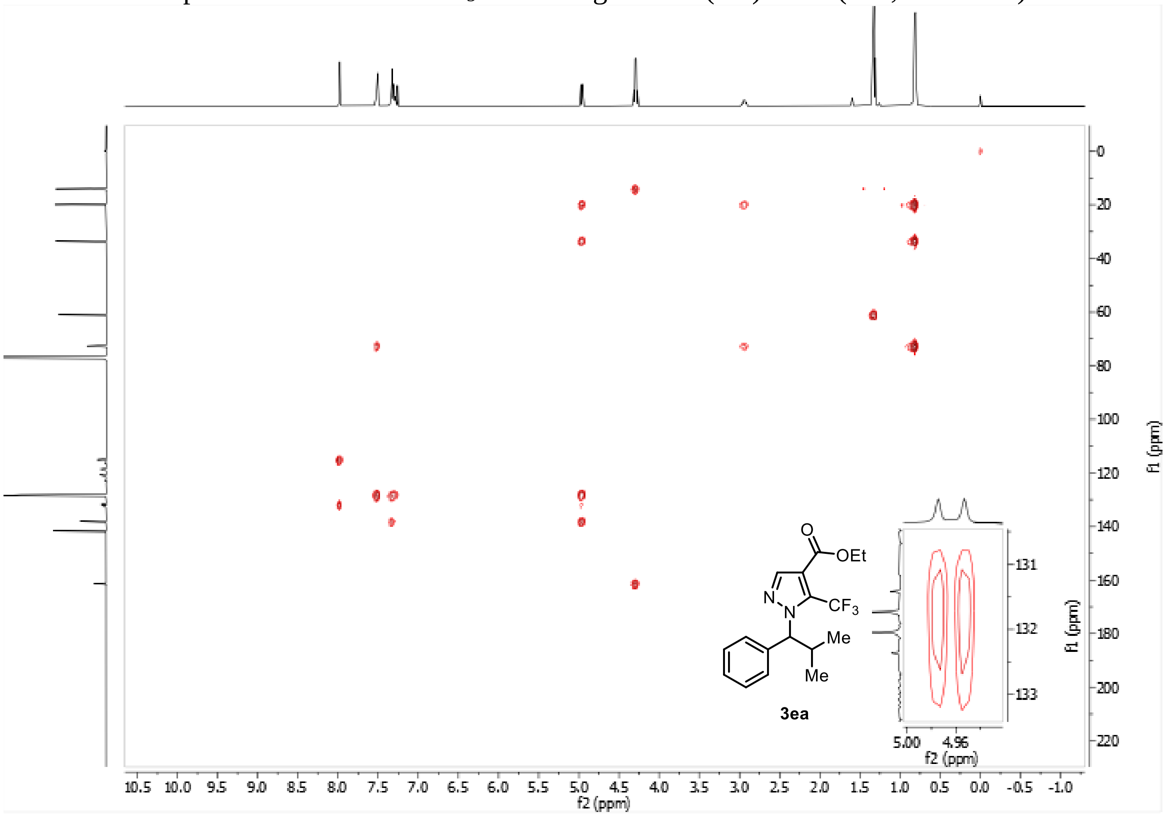
^{19}F NMR spectrum of **3ea** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



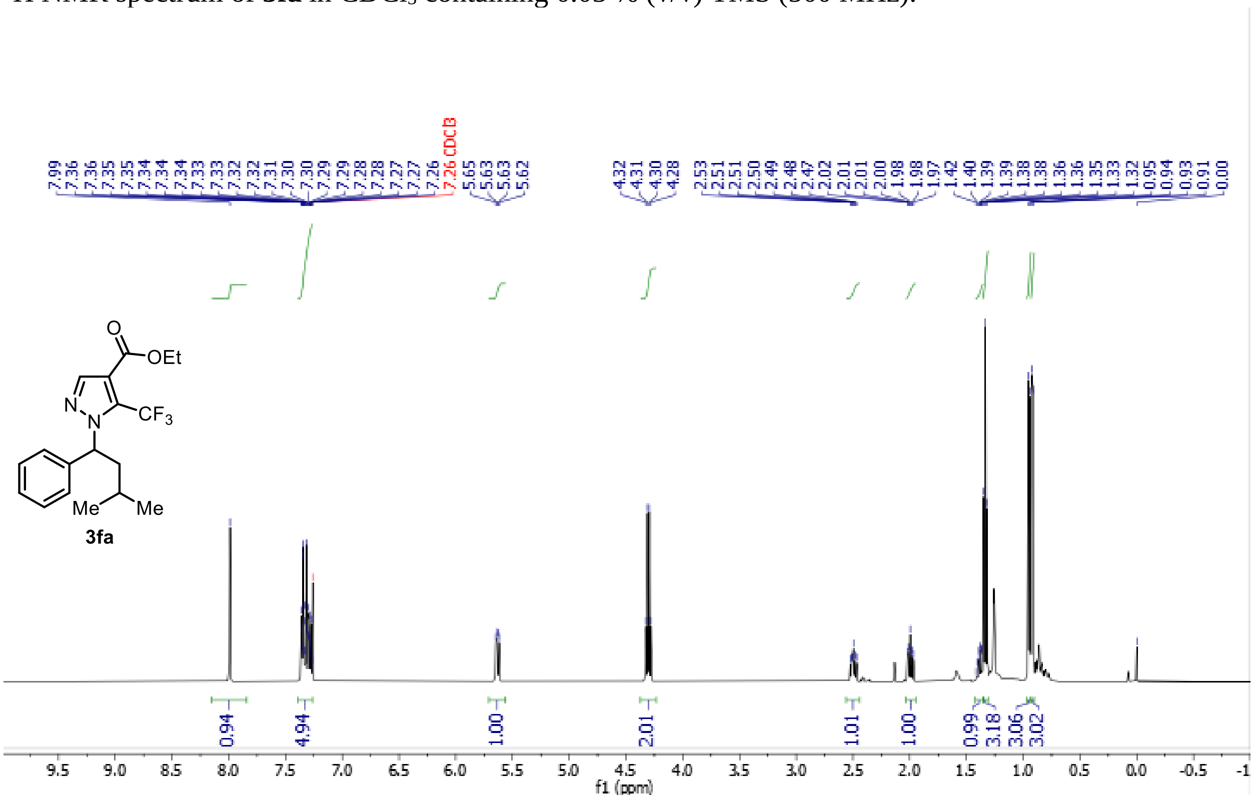
HSQC NMR spectrum of **3ea** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



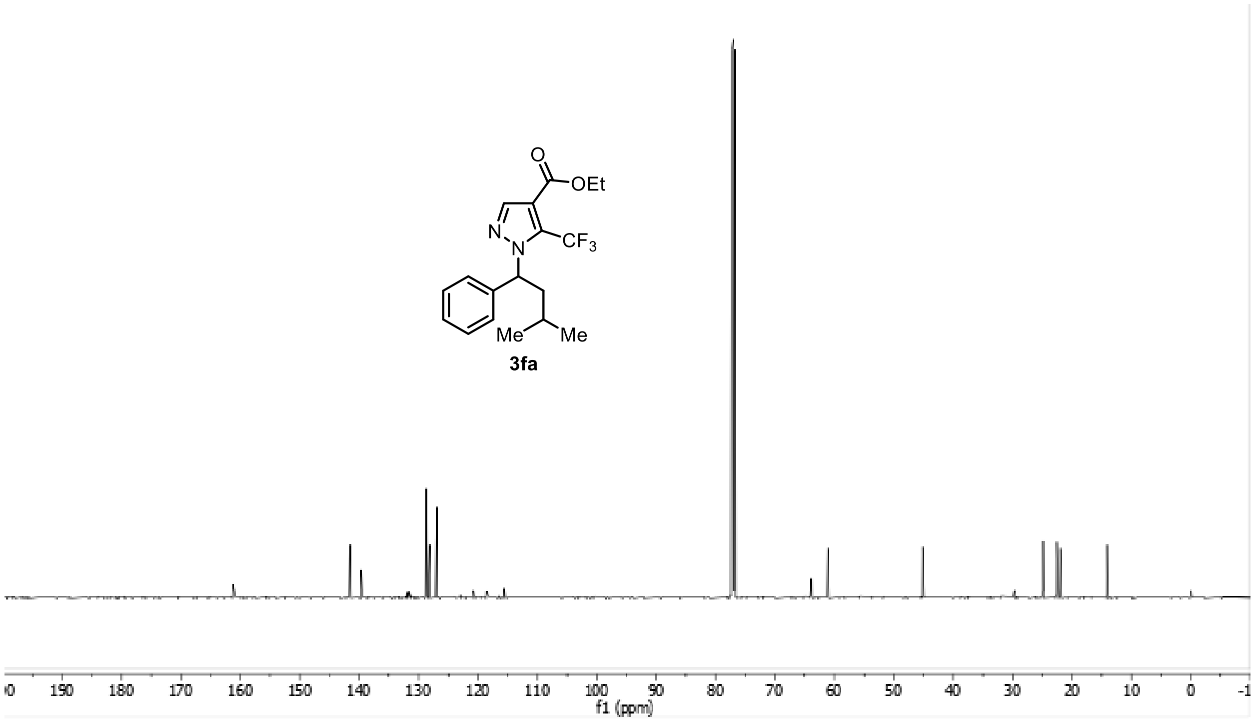
HMBC NMR spectrum of **3ea** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



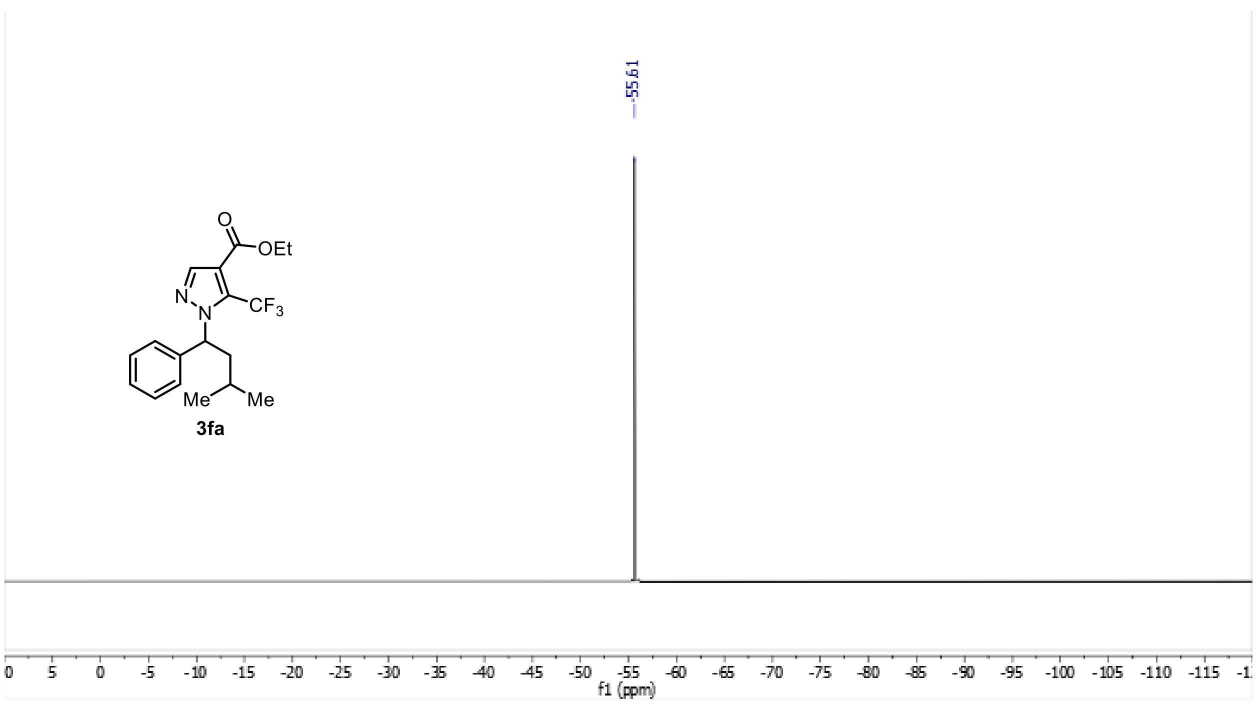
[1]H NMR spectrum of **3fa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



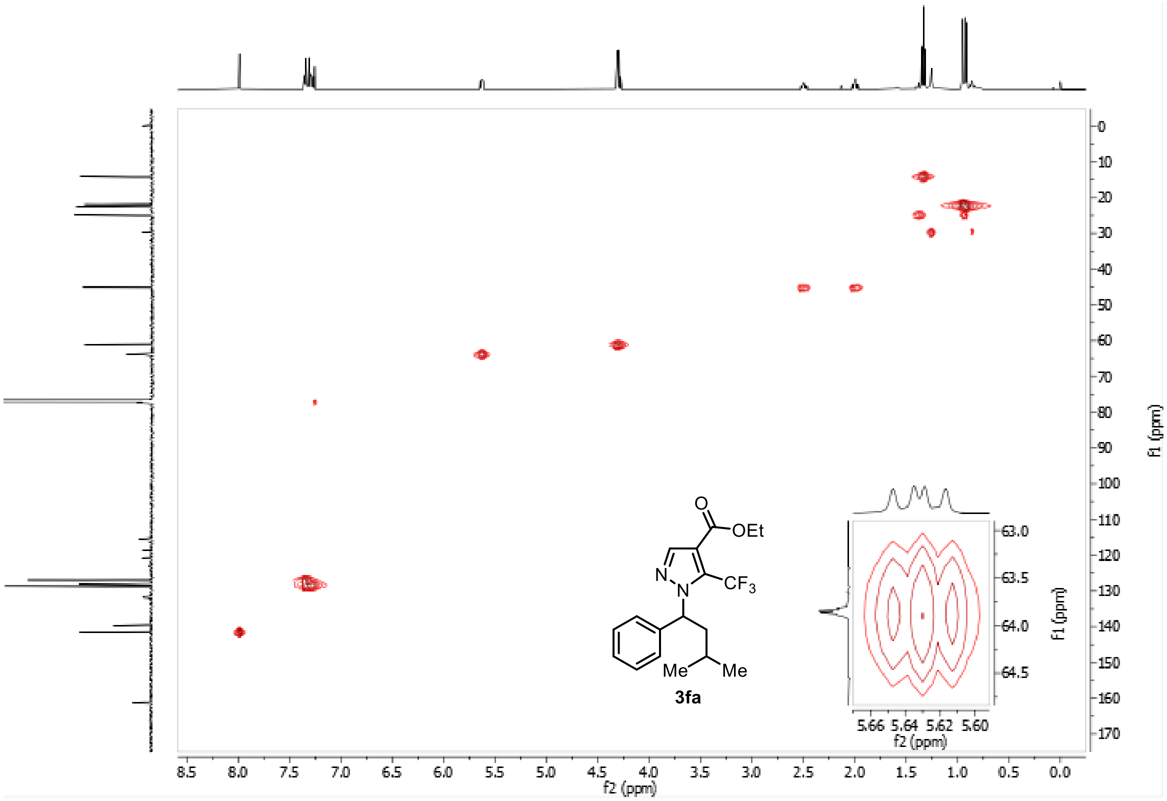
^{13}C NMR spectrum of **3fa** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



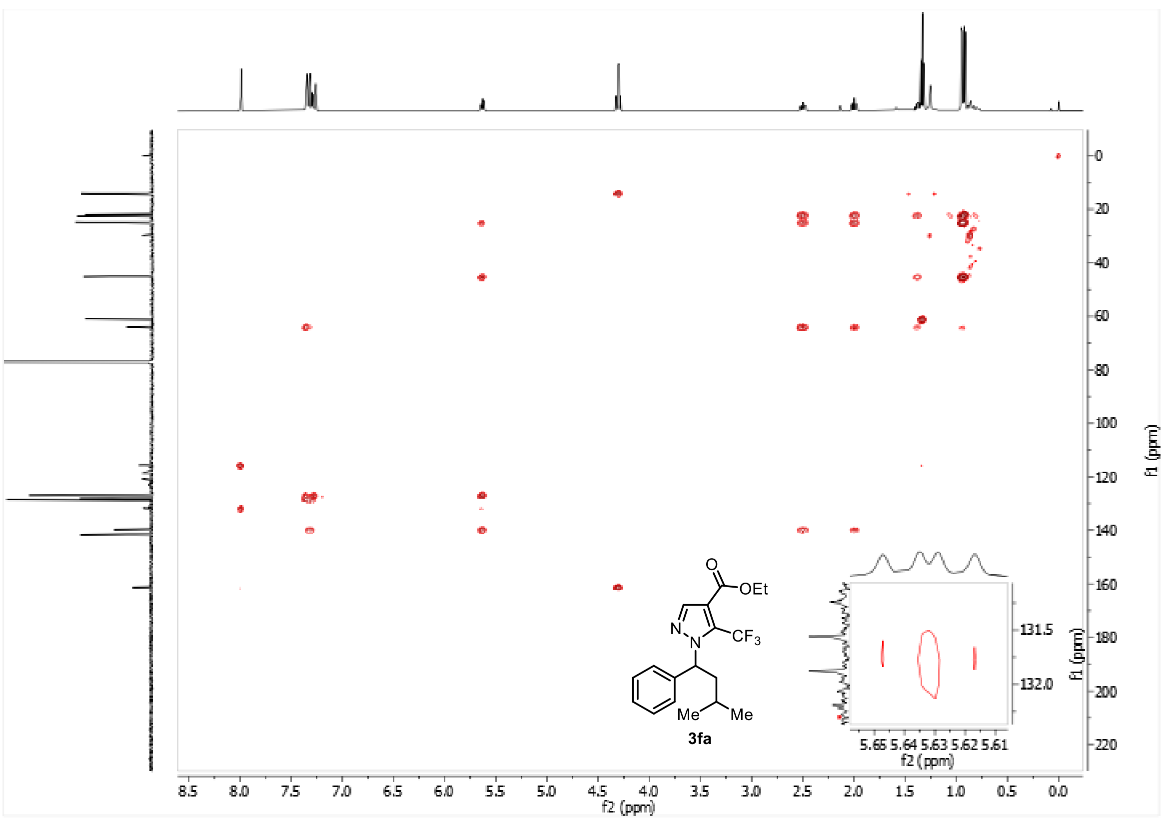
^{19}F NMR spectrum of **3fa** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



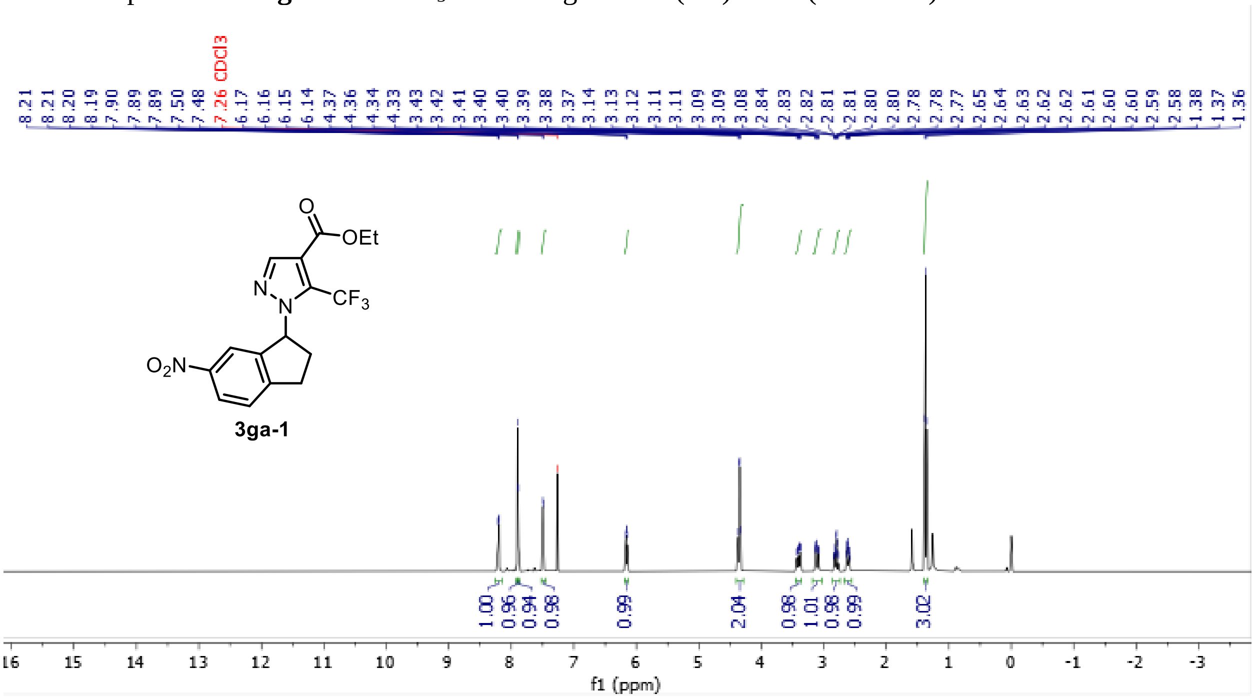
HSQC NMR spectrum of **3fa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



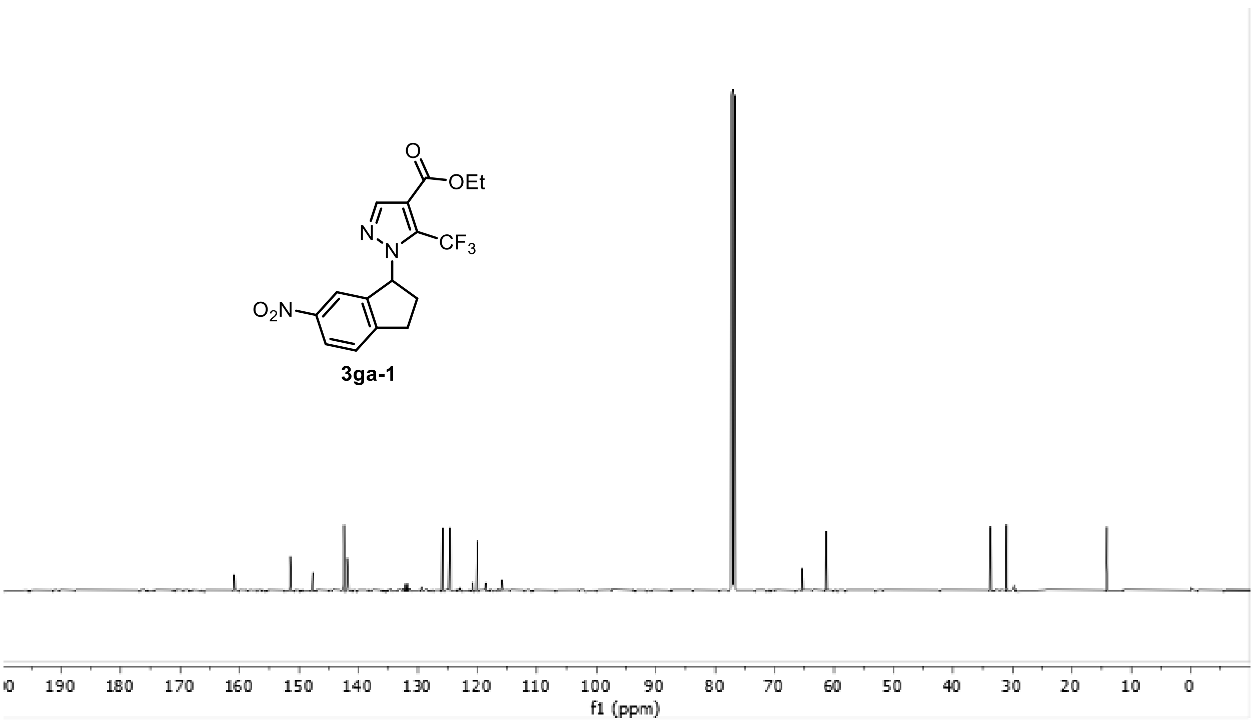
HMBC NMR spectrum of **3fa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



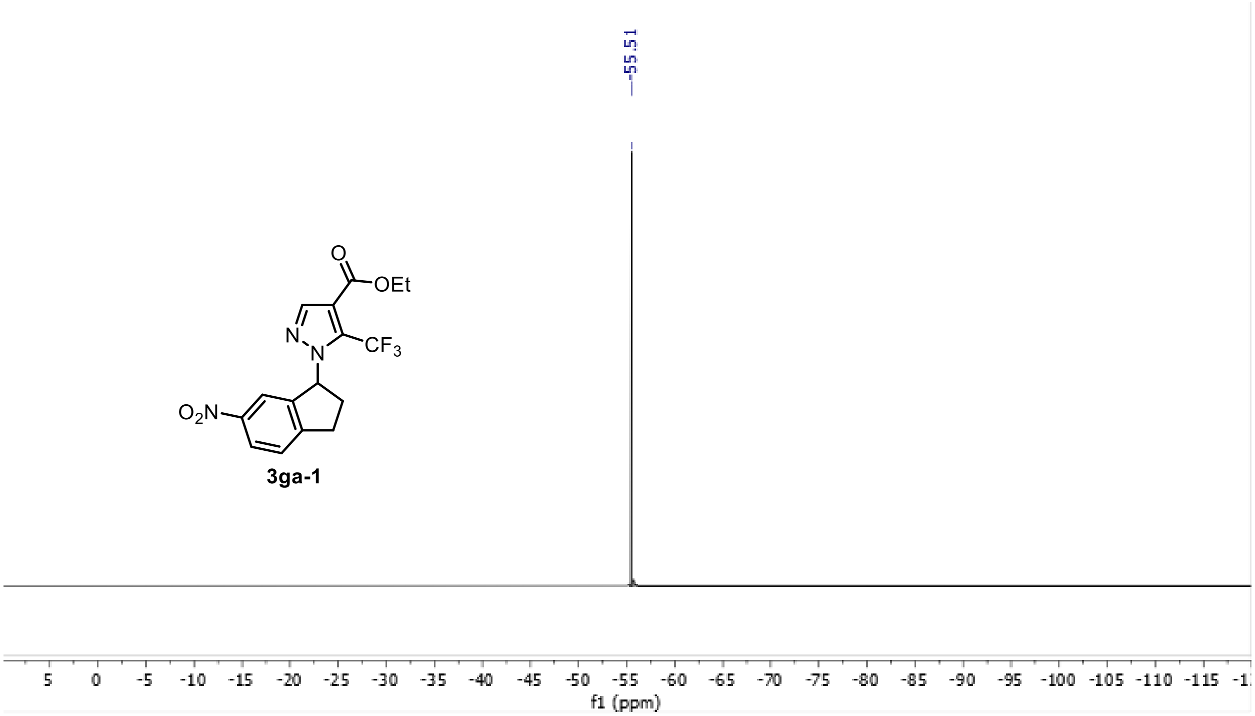
^{1}H NMR spectrum of **3ga-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



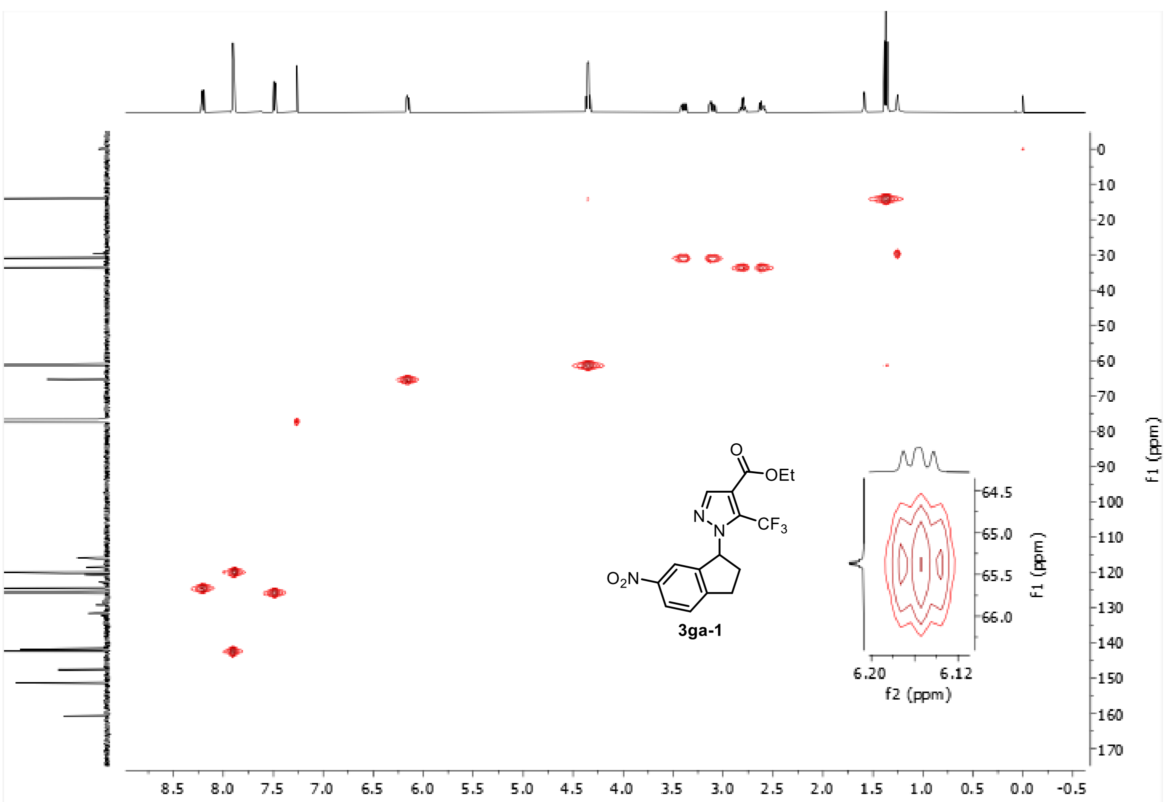
^{13}C NMR spectrum of **3ga-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



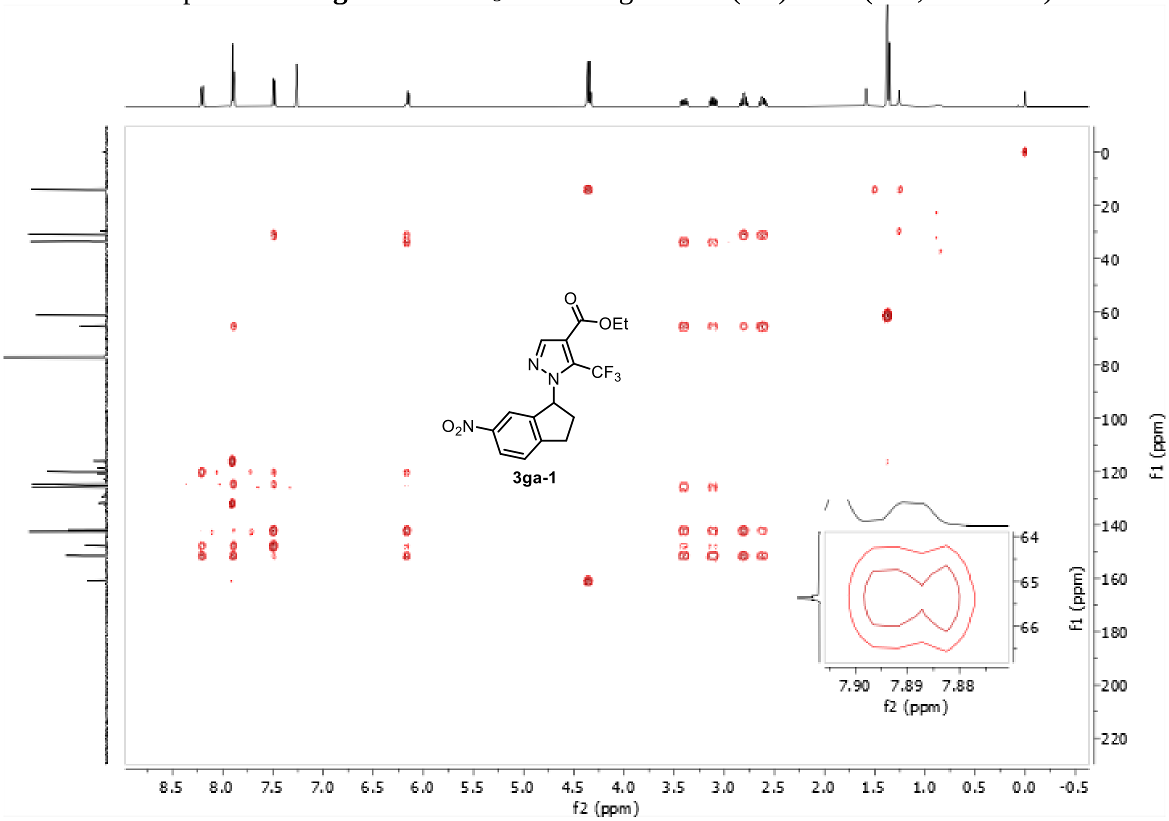
^{19}F NMR spectrum of **3ga-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



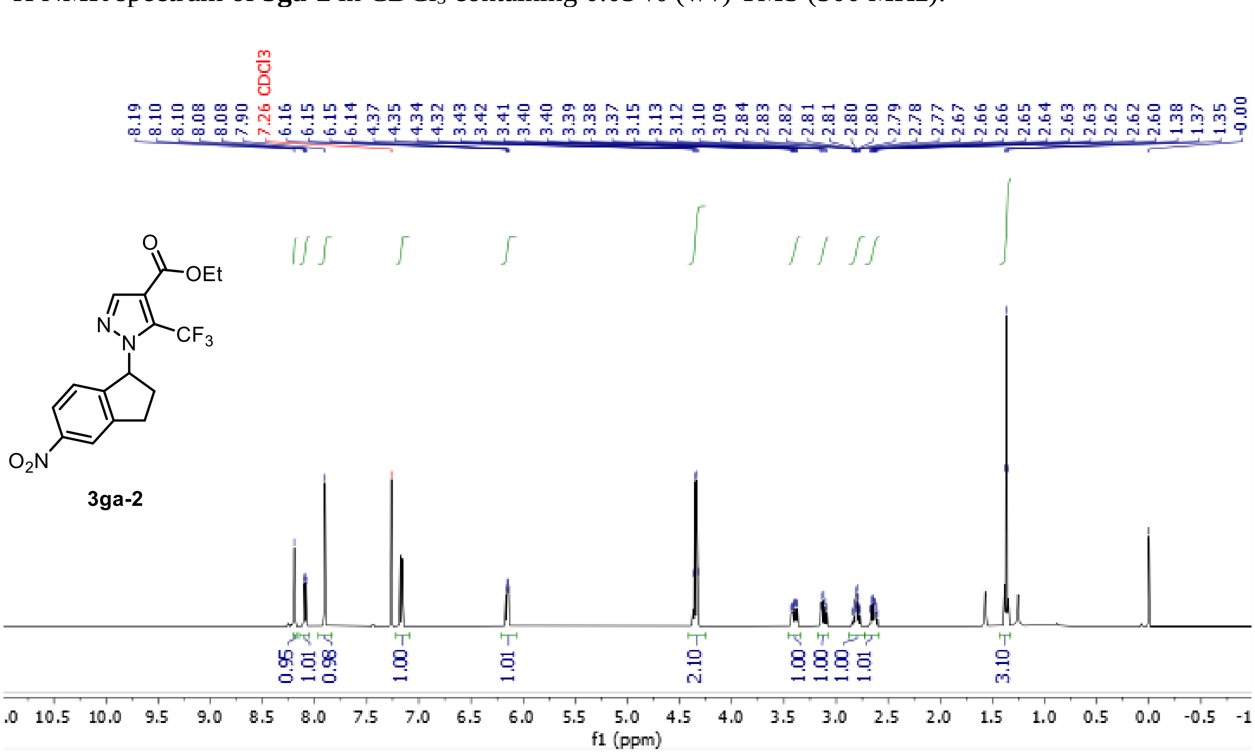
HSQC NMR spectrum of **3ga-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



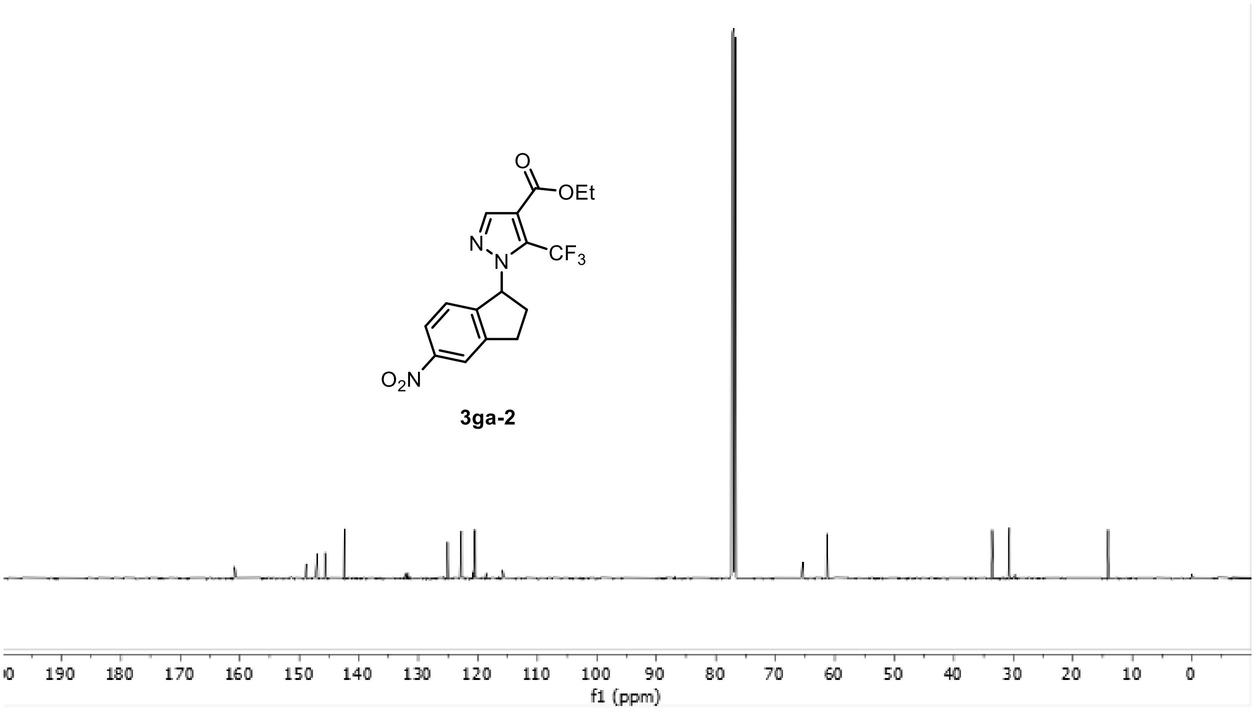
HMBC NMR spectrum of **3ga-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



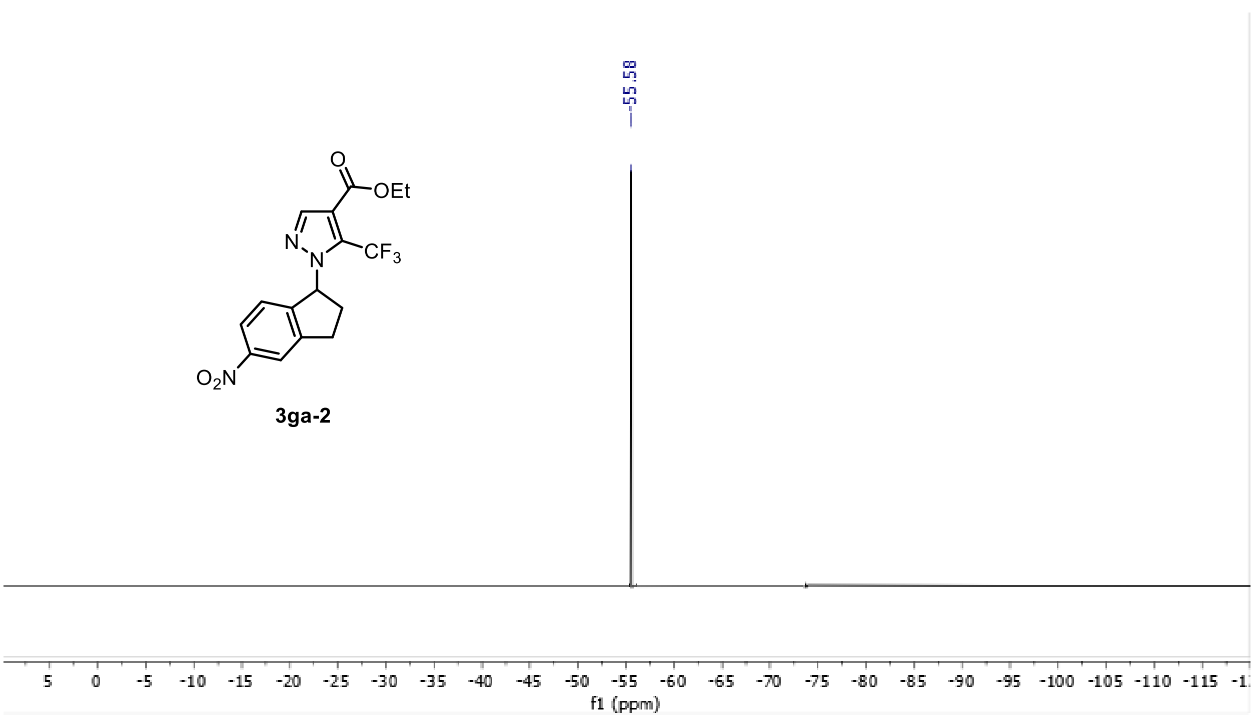
^{1}H NMR spectrum of **3ga-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



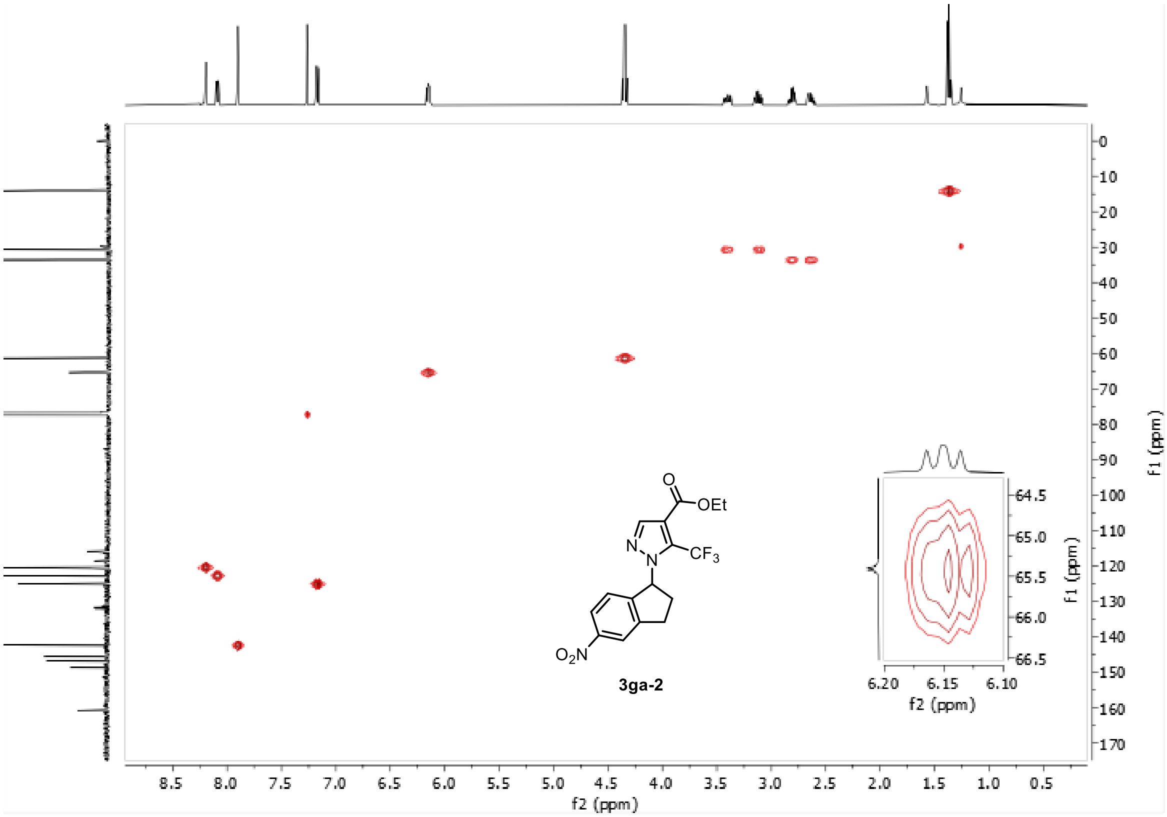
^{13}C NMR spectrum of **3ga-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



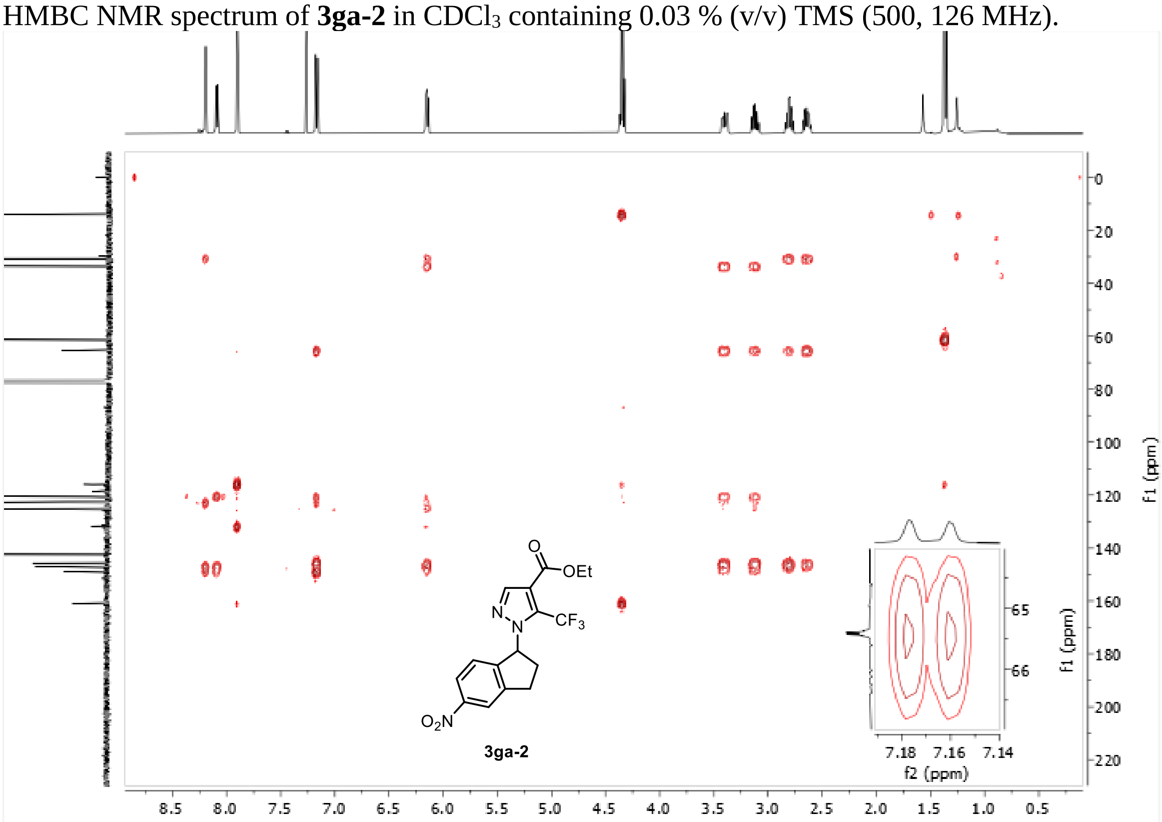
^{19}F NMR spectrum of **3ga-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



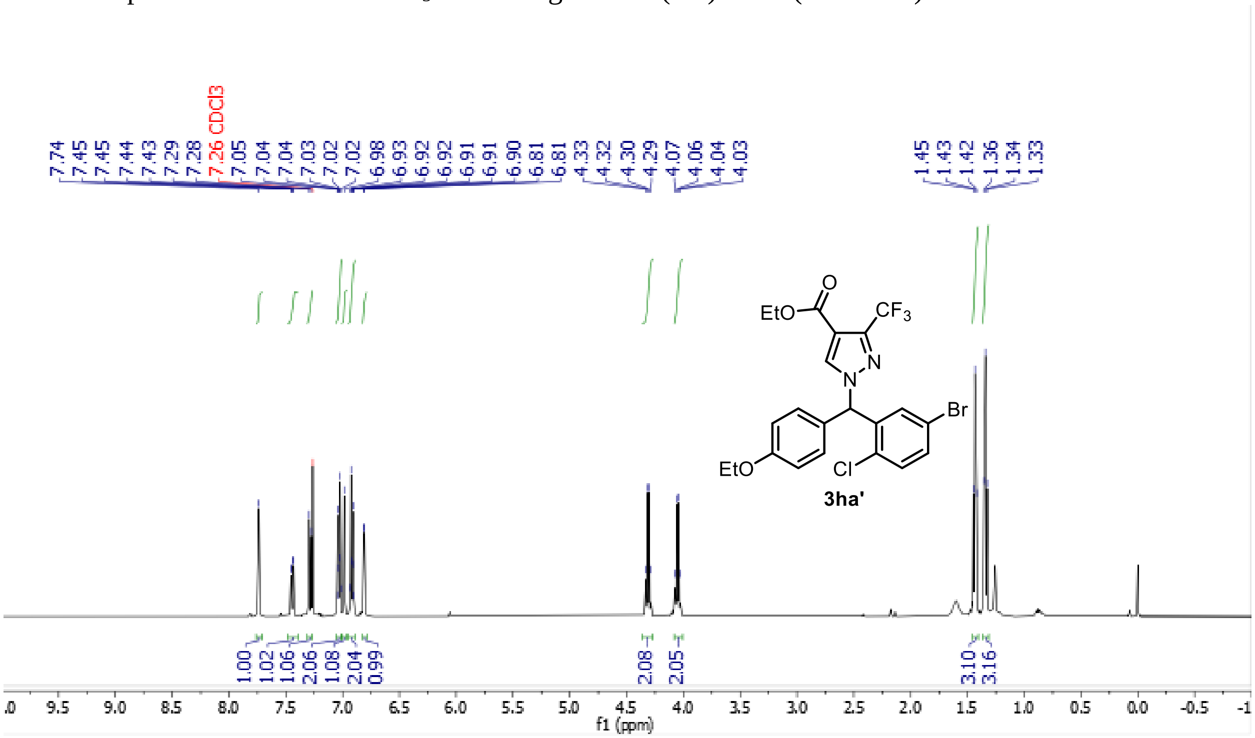
HSQC NMR spectrum of **3ga-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



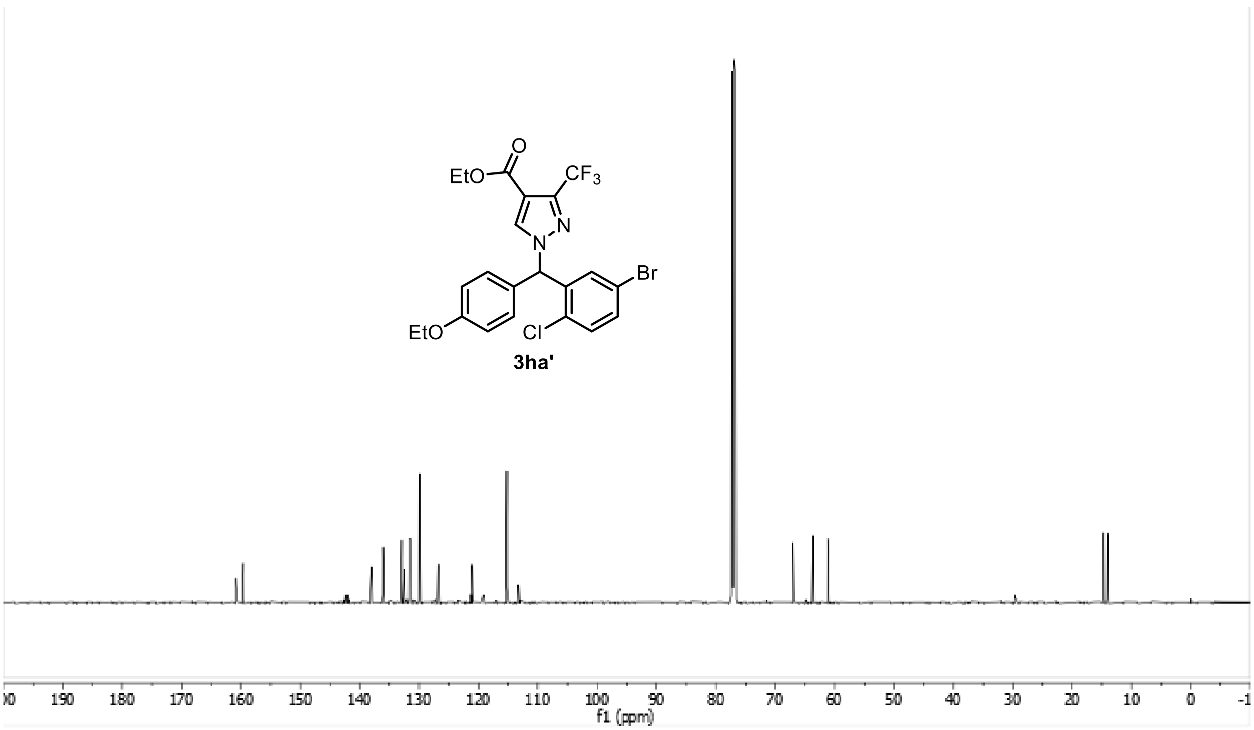
HMBC NMR spectrum of **3ga-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



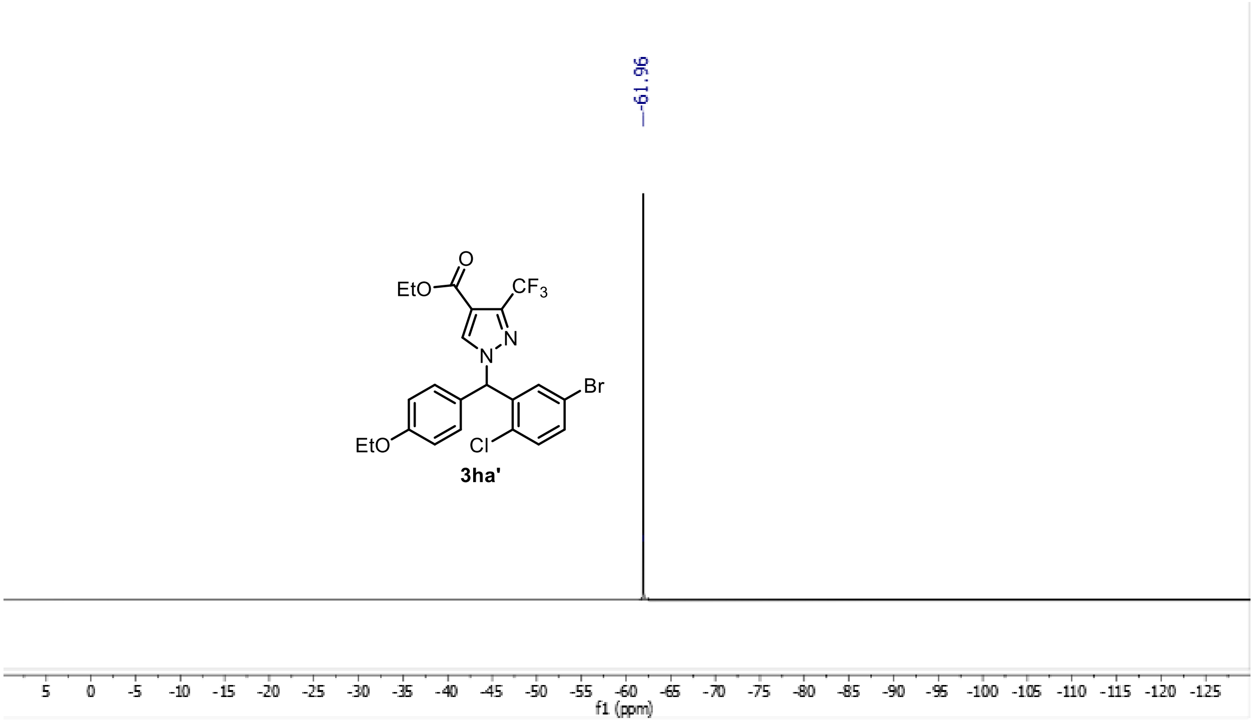
^{1}H NMR spectrum of **3ha'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



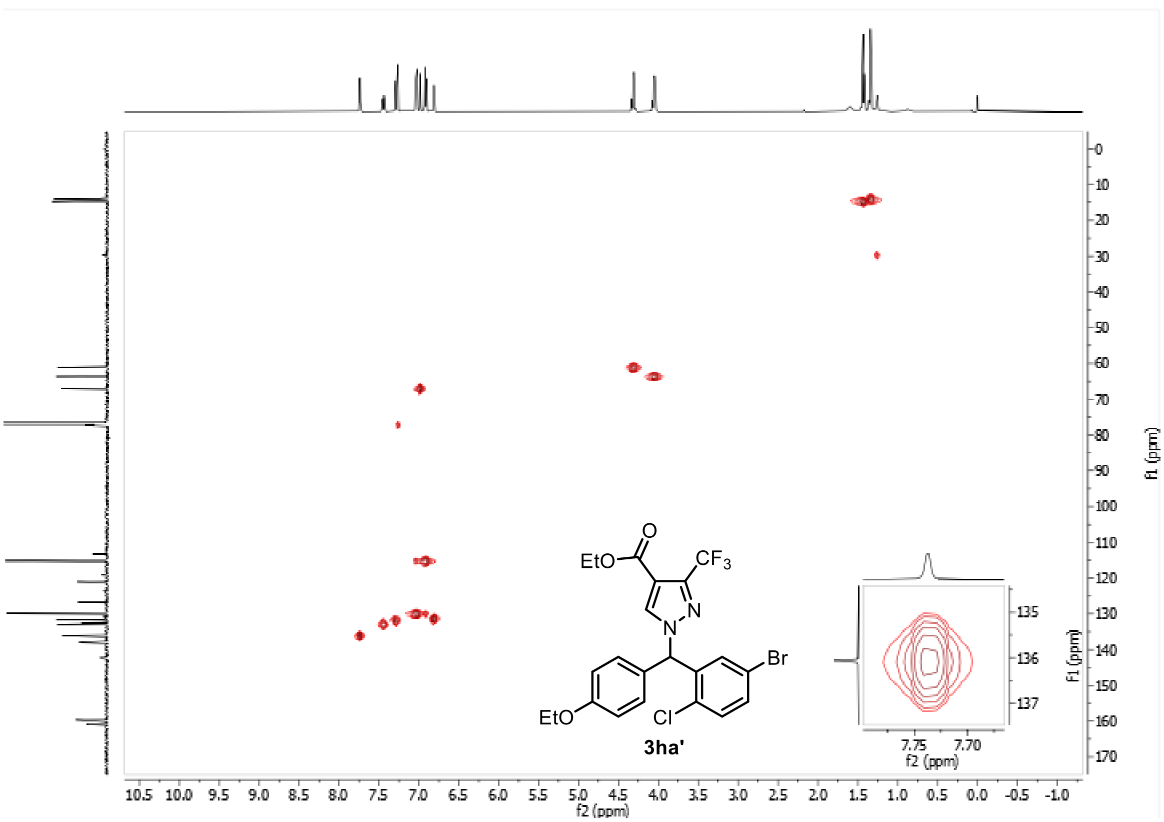
^{13}C NMR spectrum of **3ha'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



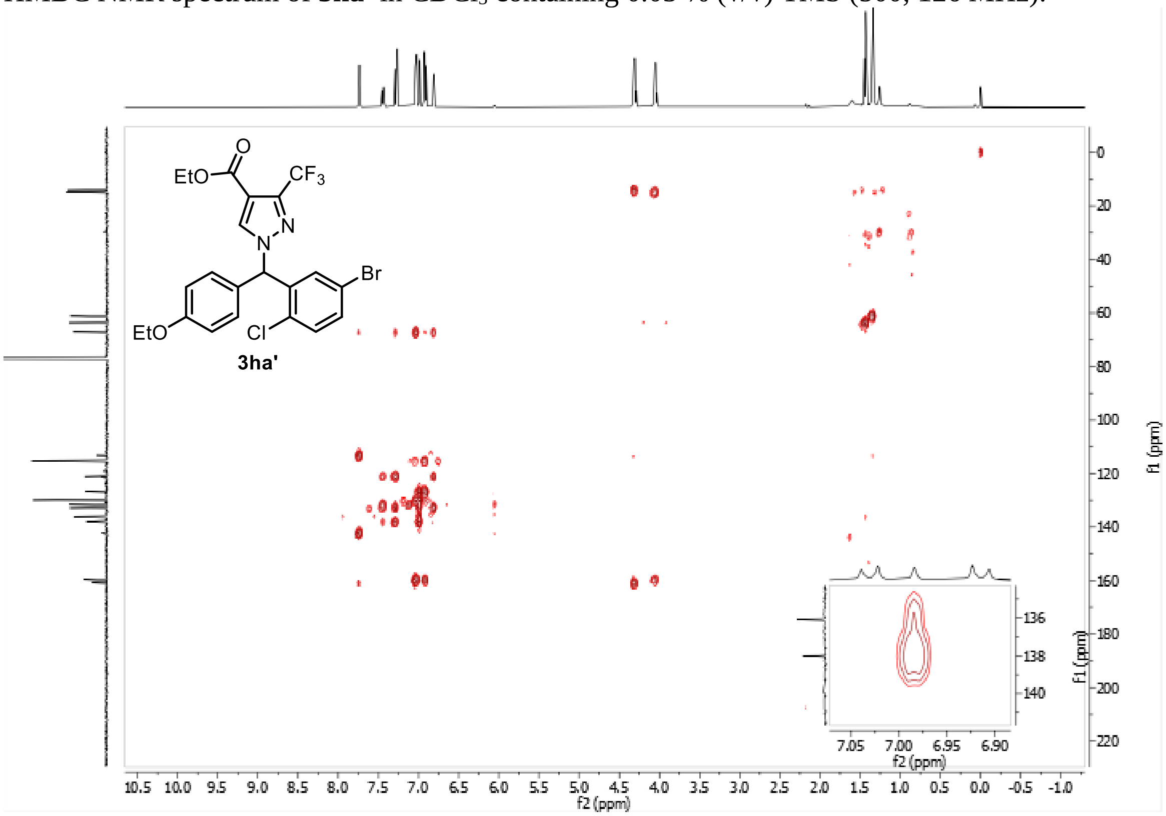
^{19}F NMR spectrum of **3ha'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



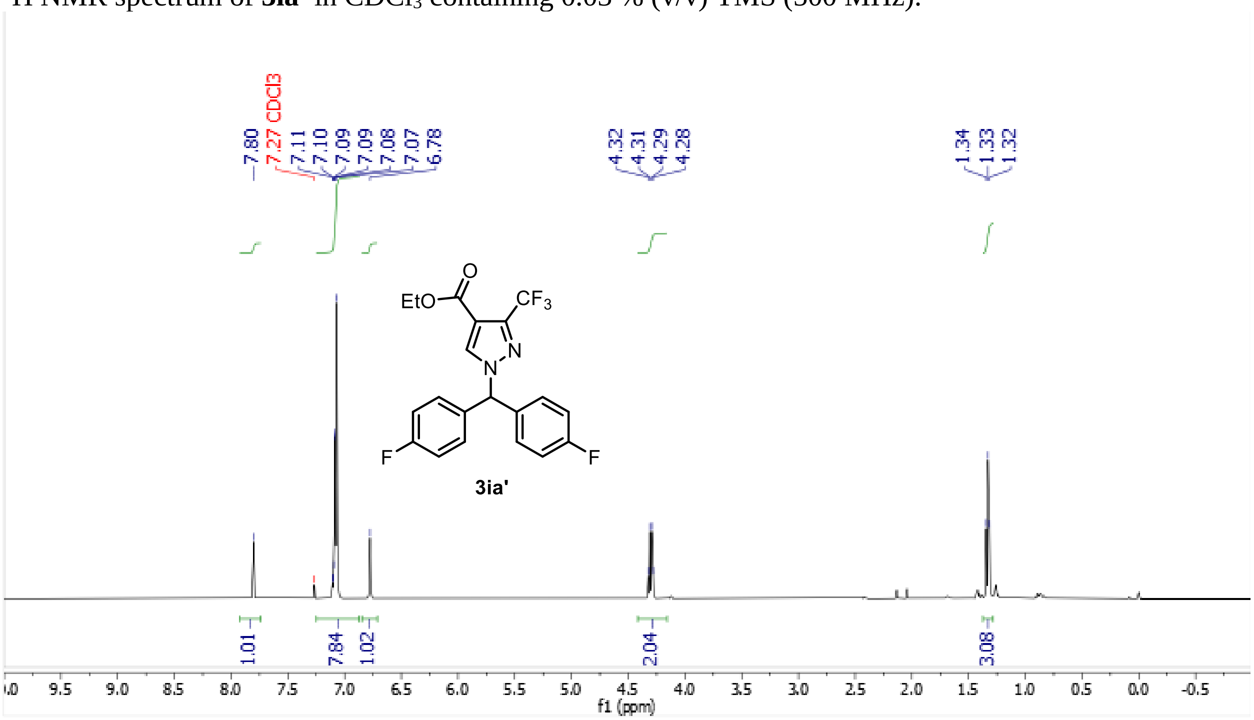
HSQC NMR spectrum of **3ha'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



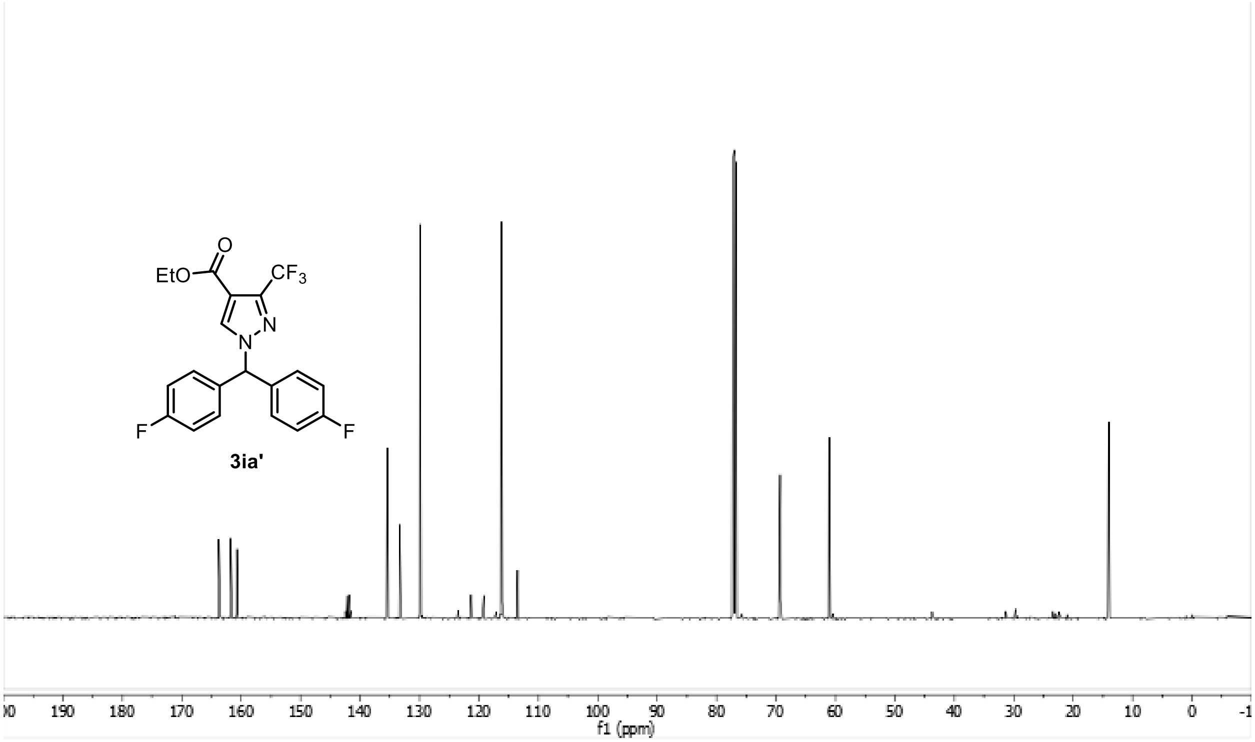
HMBC NMR spectrum of **3ha'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



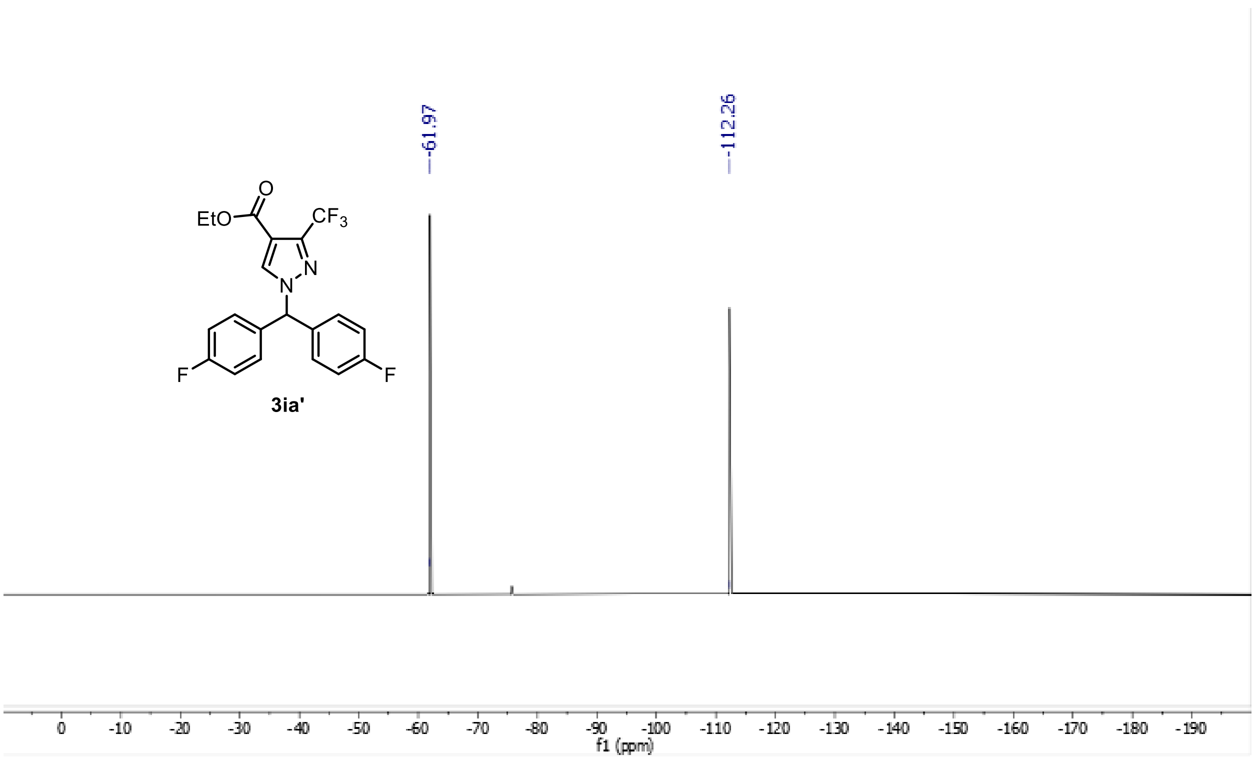
[1]H NMR spectrum of **3ia'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



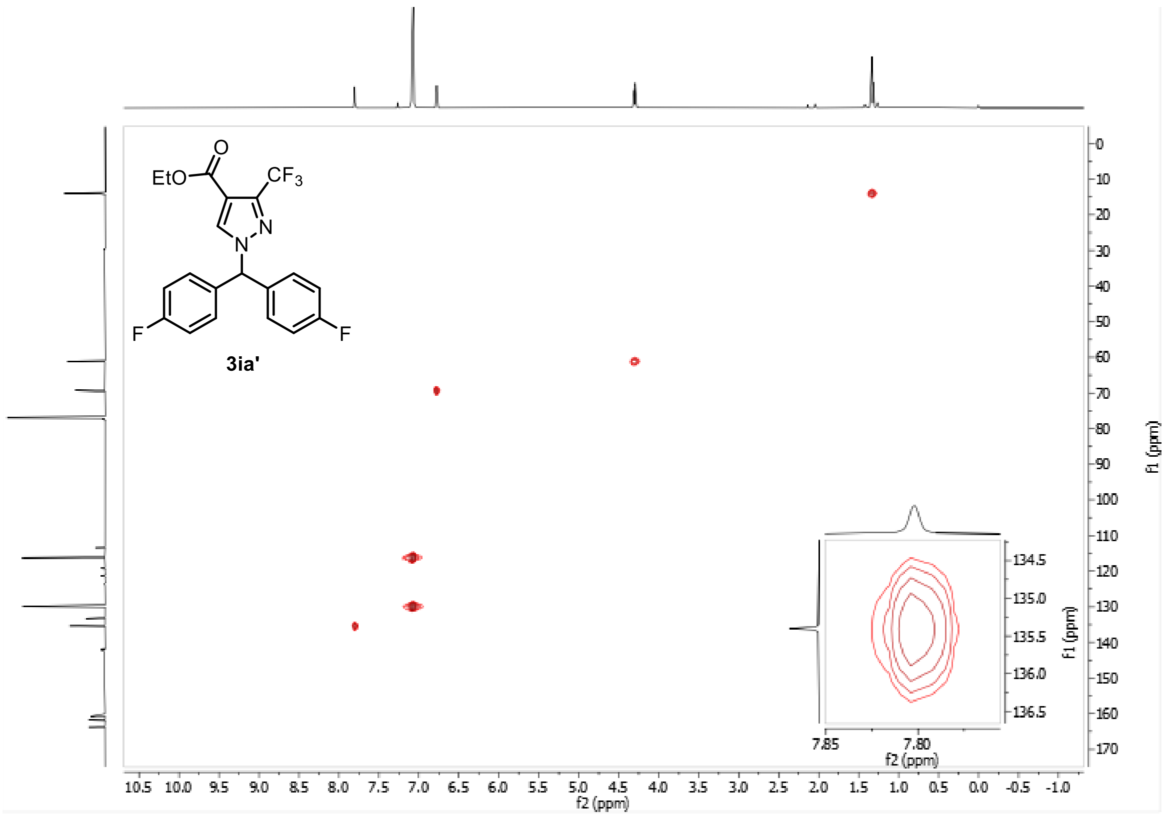
^{13}C NMR spectrum of **3ia'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



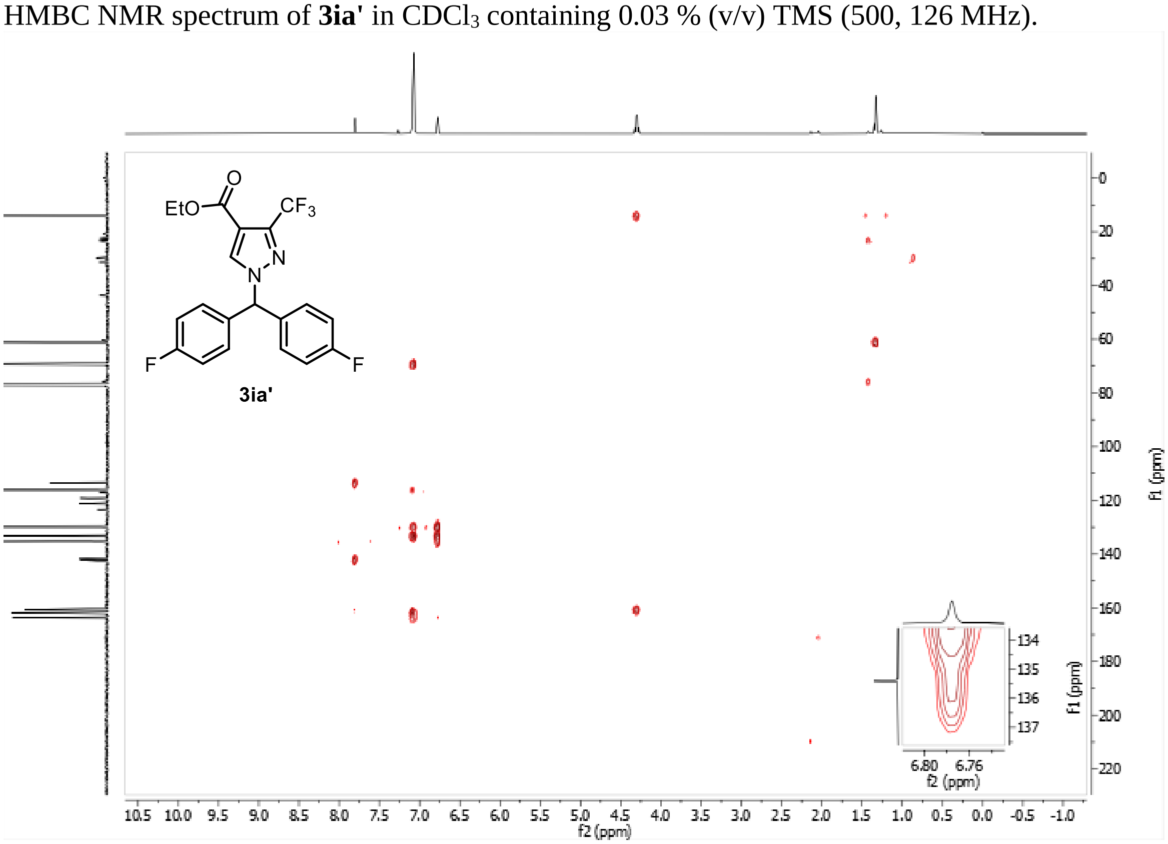
^{19}F NMR spectrum of **3ia'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



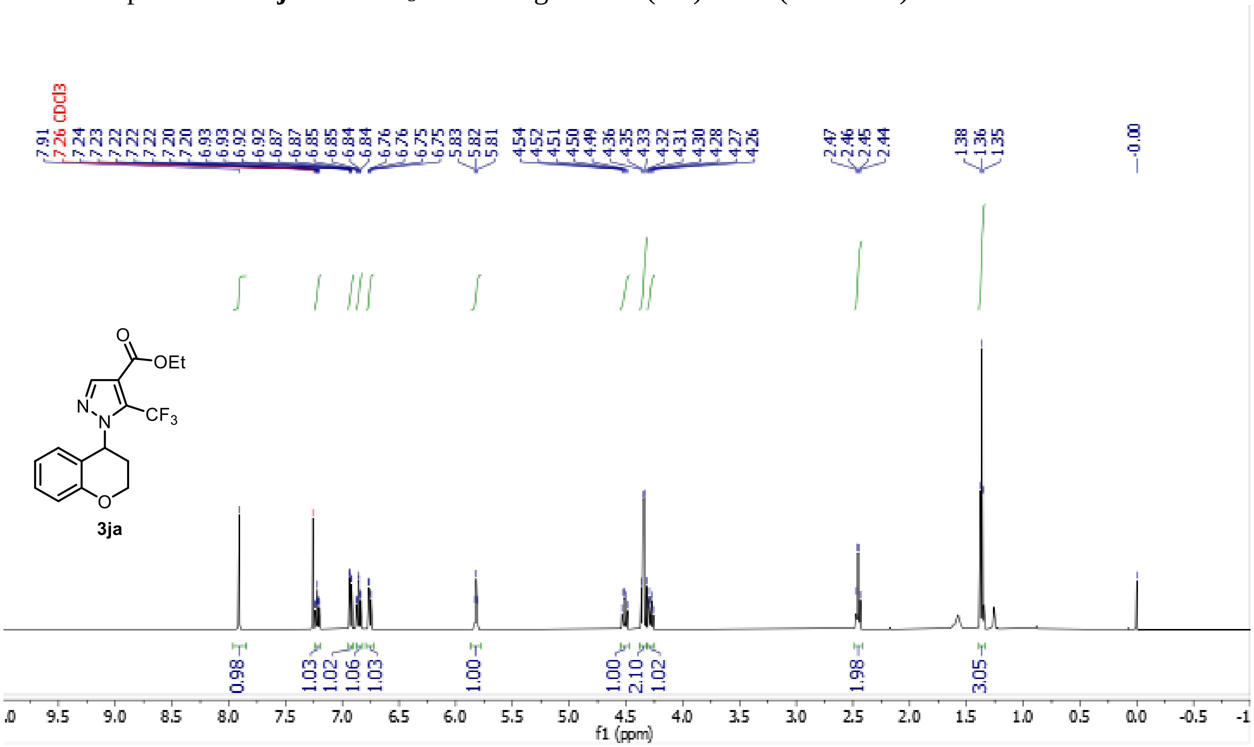
HSQC NMR spectrum of **3ia'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



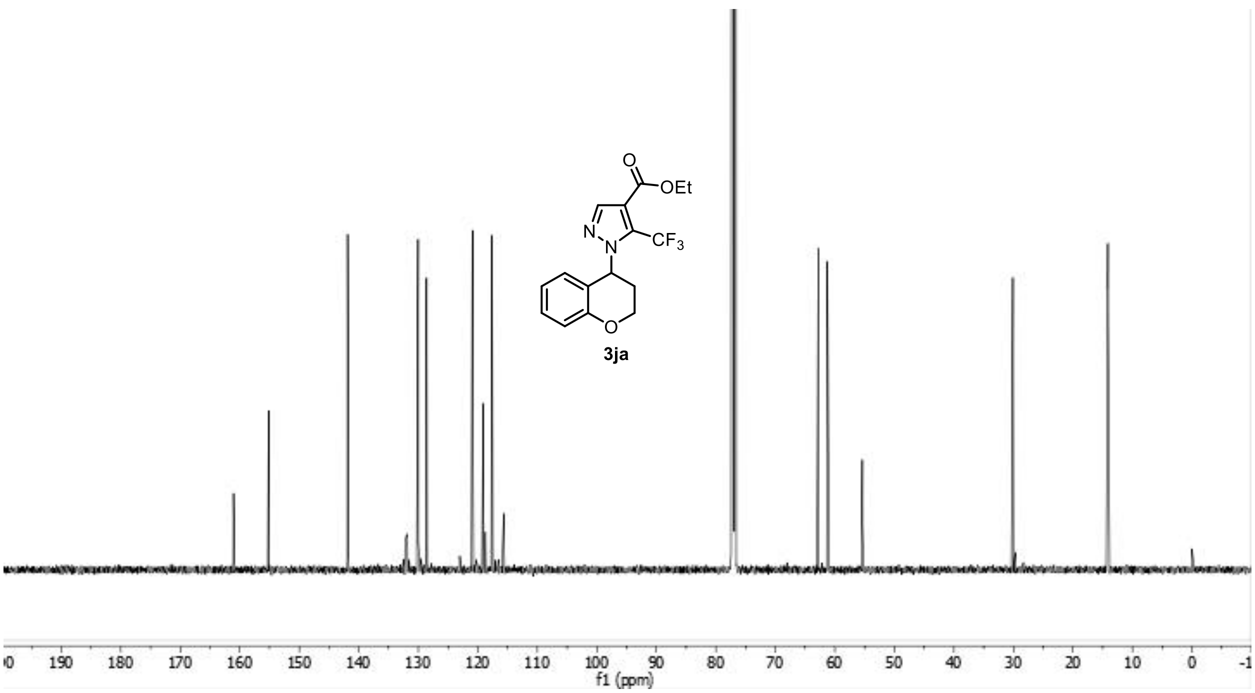
HMBC NMR spectrum of **3ia'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



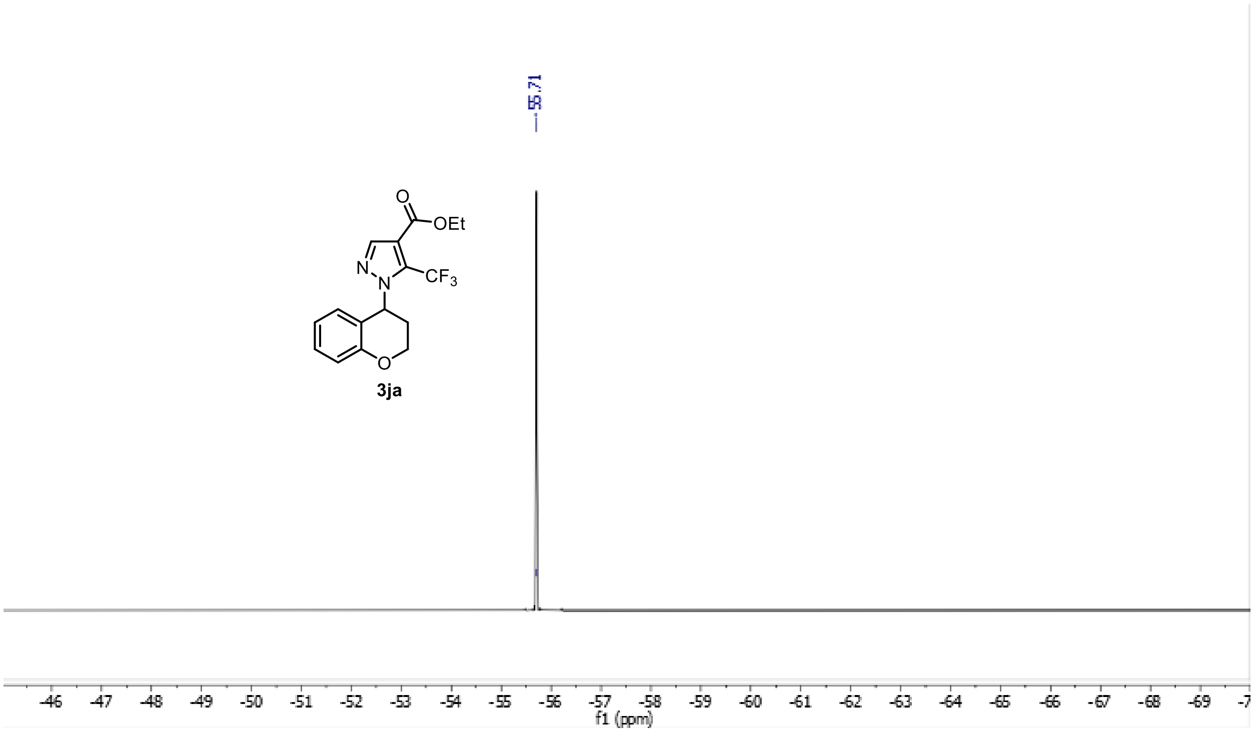
[1]H NMR spectrum of **3ja** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



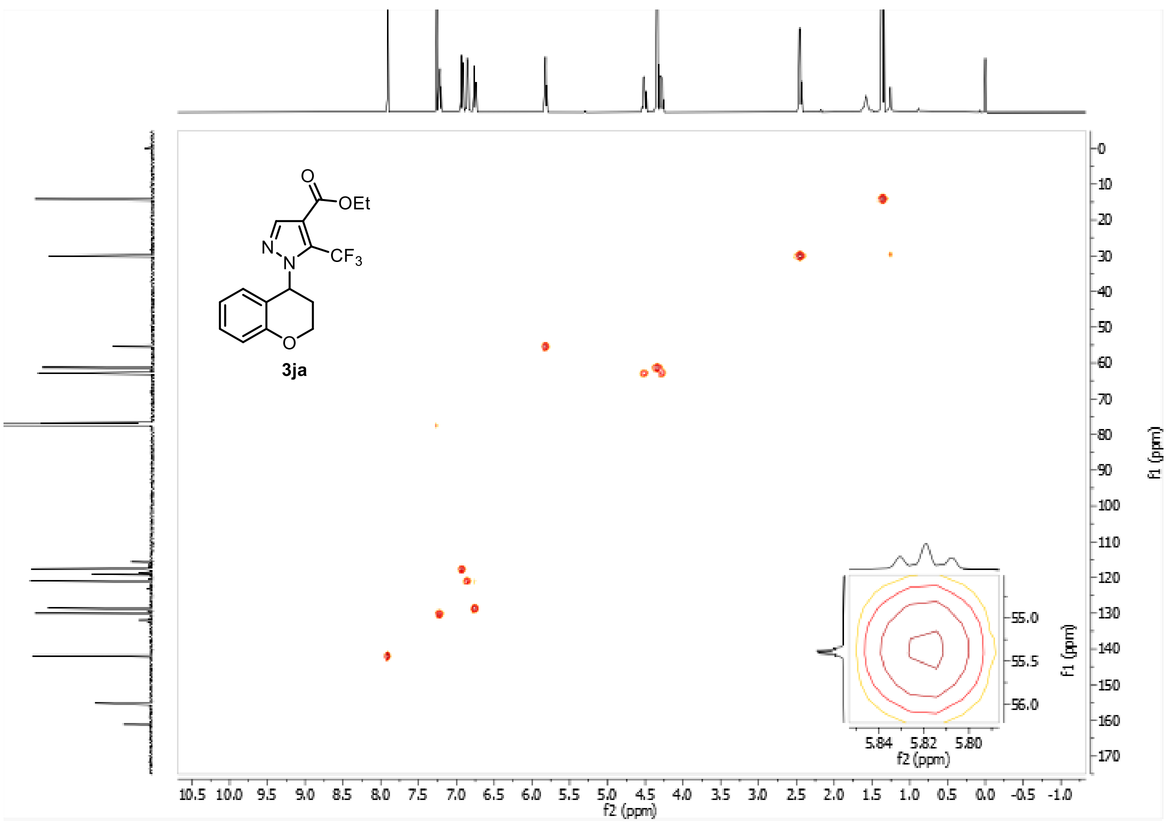
[13]C NMR spectrum of **3ja** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



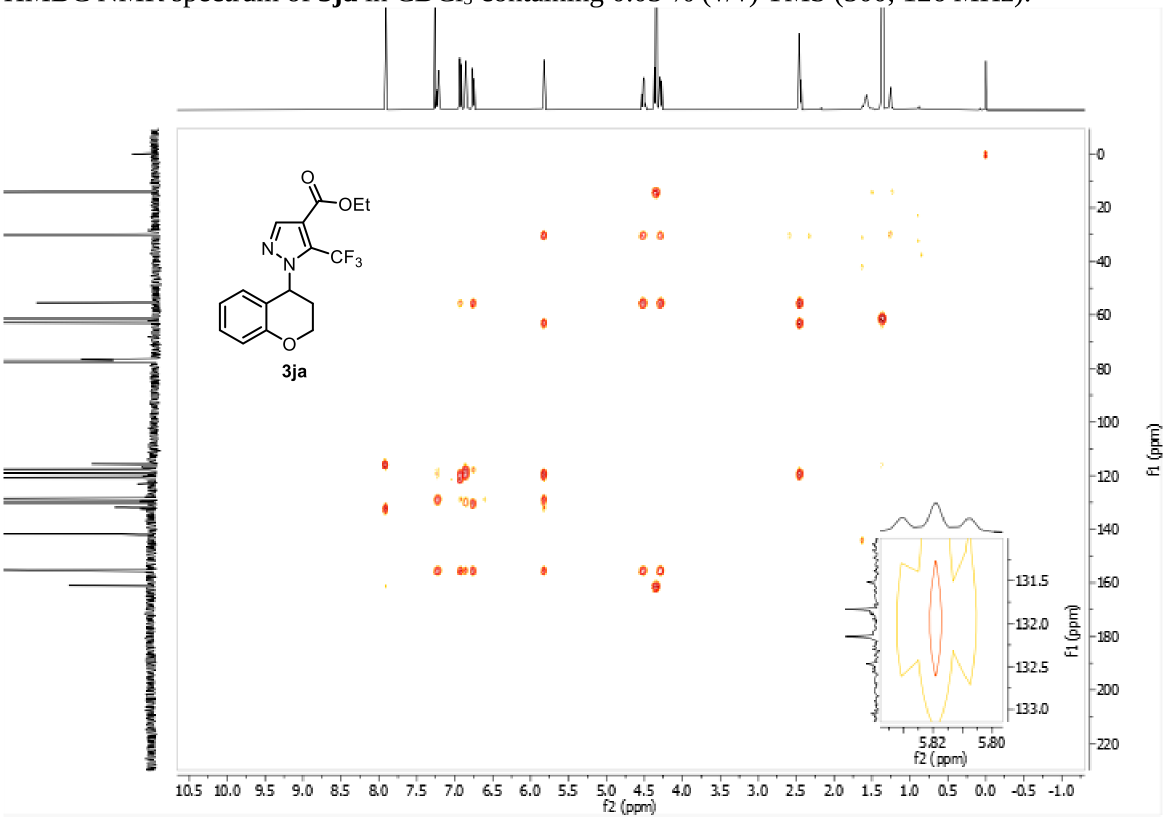
^{19}F NMR spectrum of **3ja** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



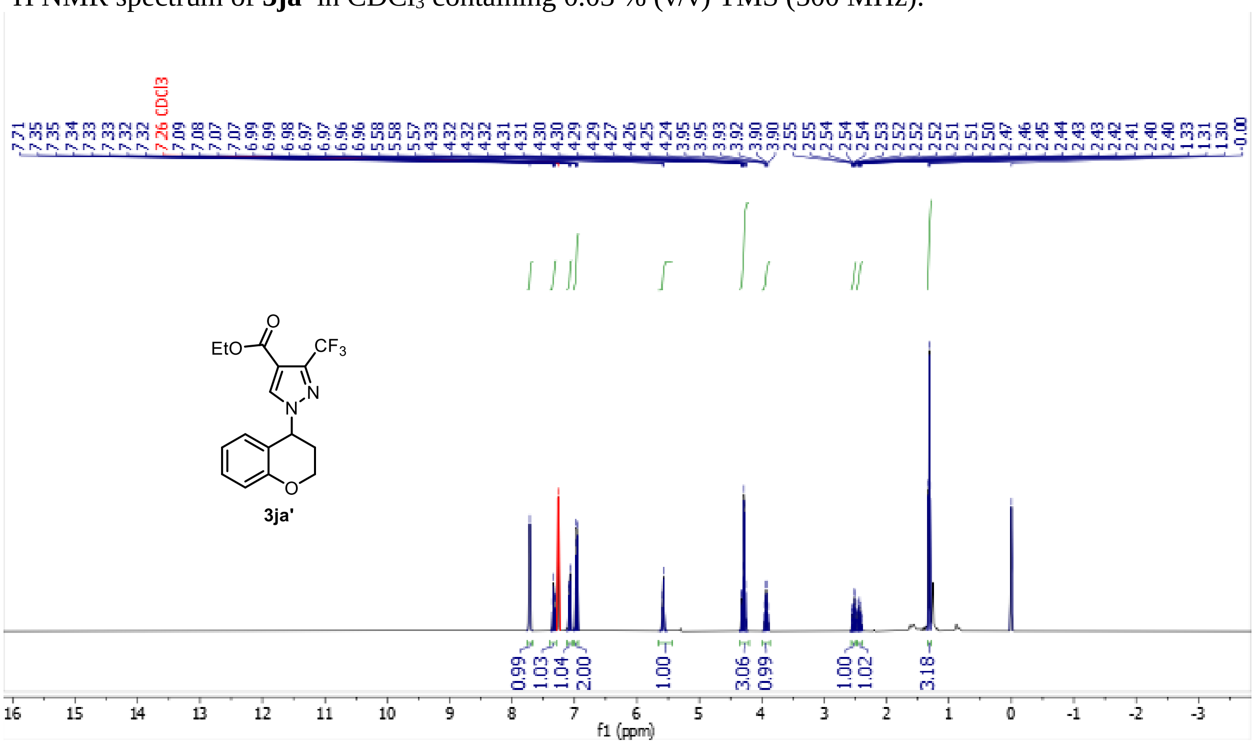
HSQC NMR spectrum of **3ja** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



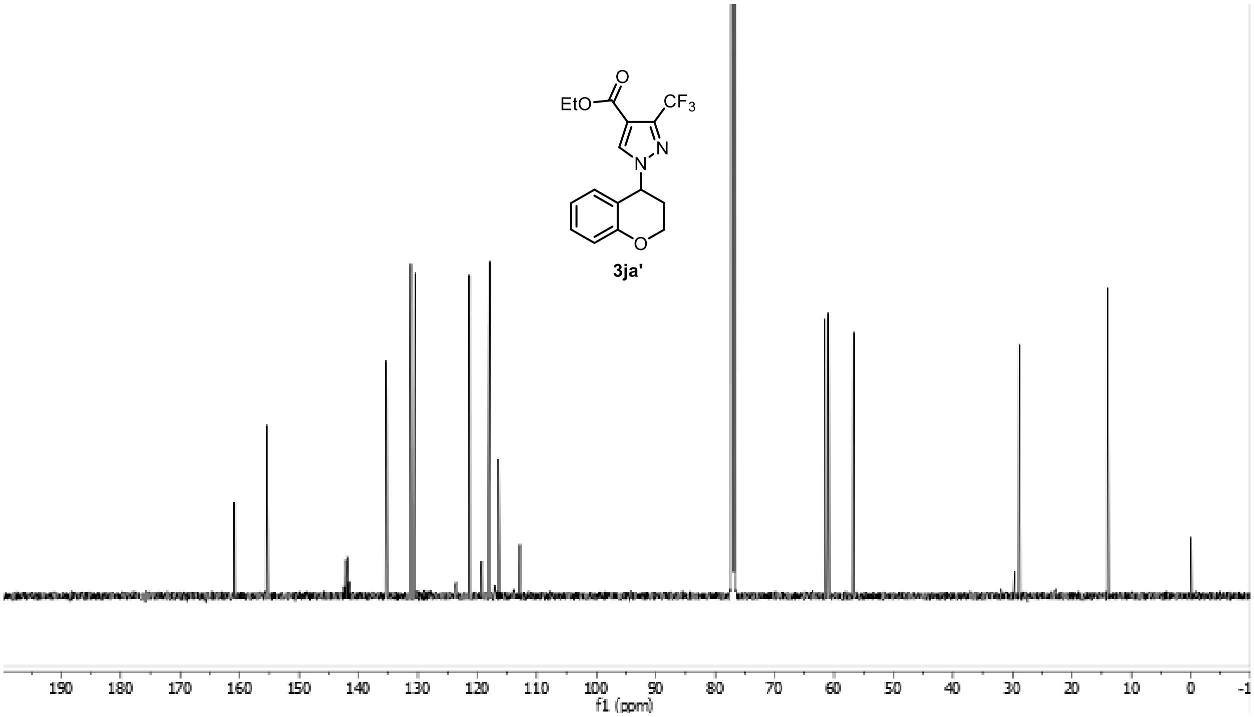
HMBC NMR spectrum of **3ja** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



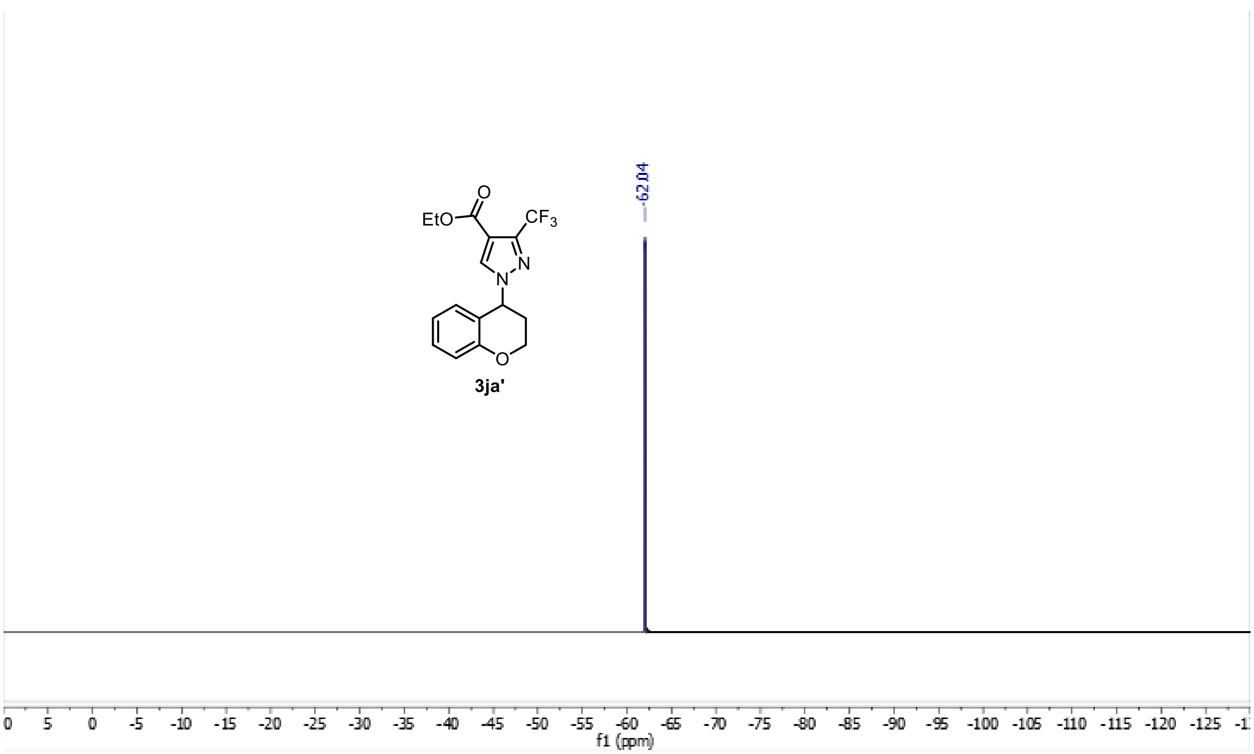
^{1}H NMR spectrum of **3ja'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



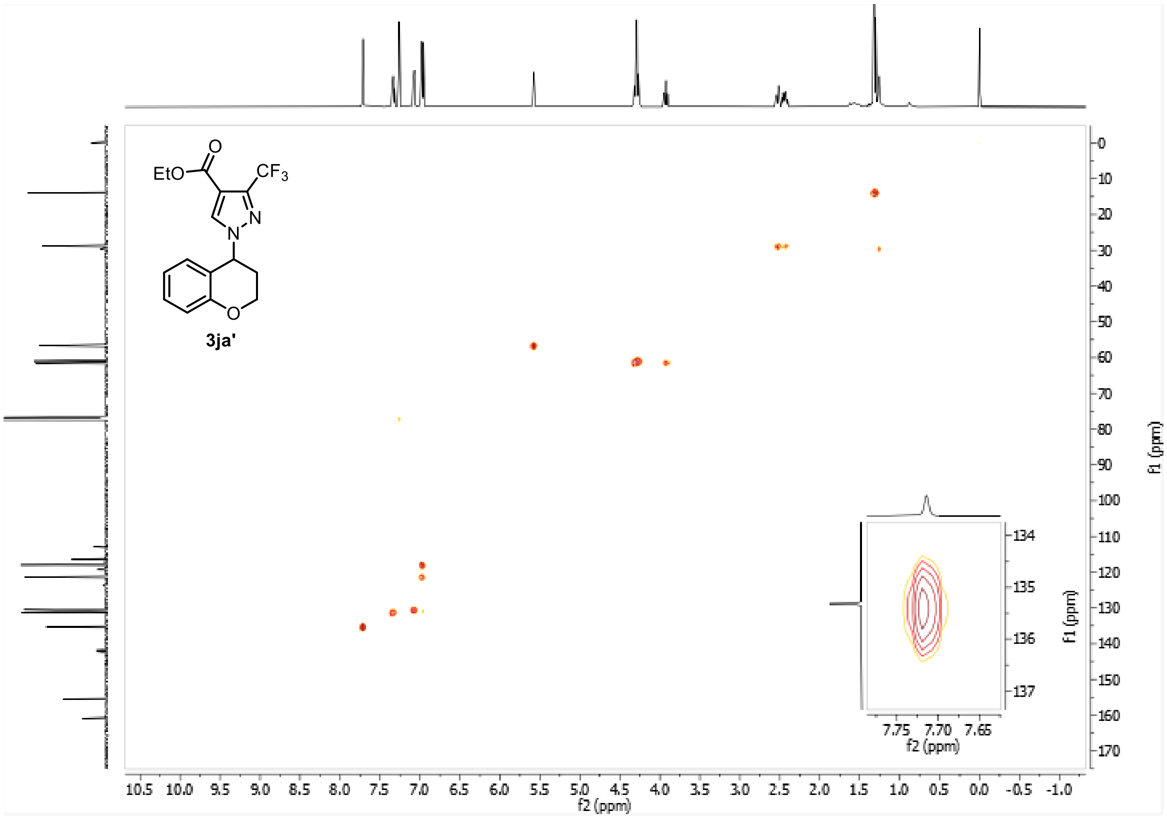
[13]C NMR spectrum of **3ja'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



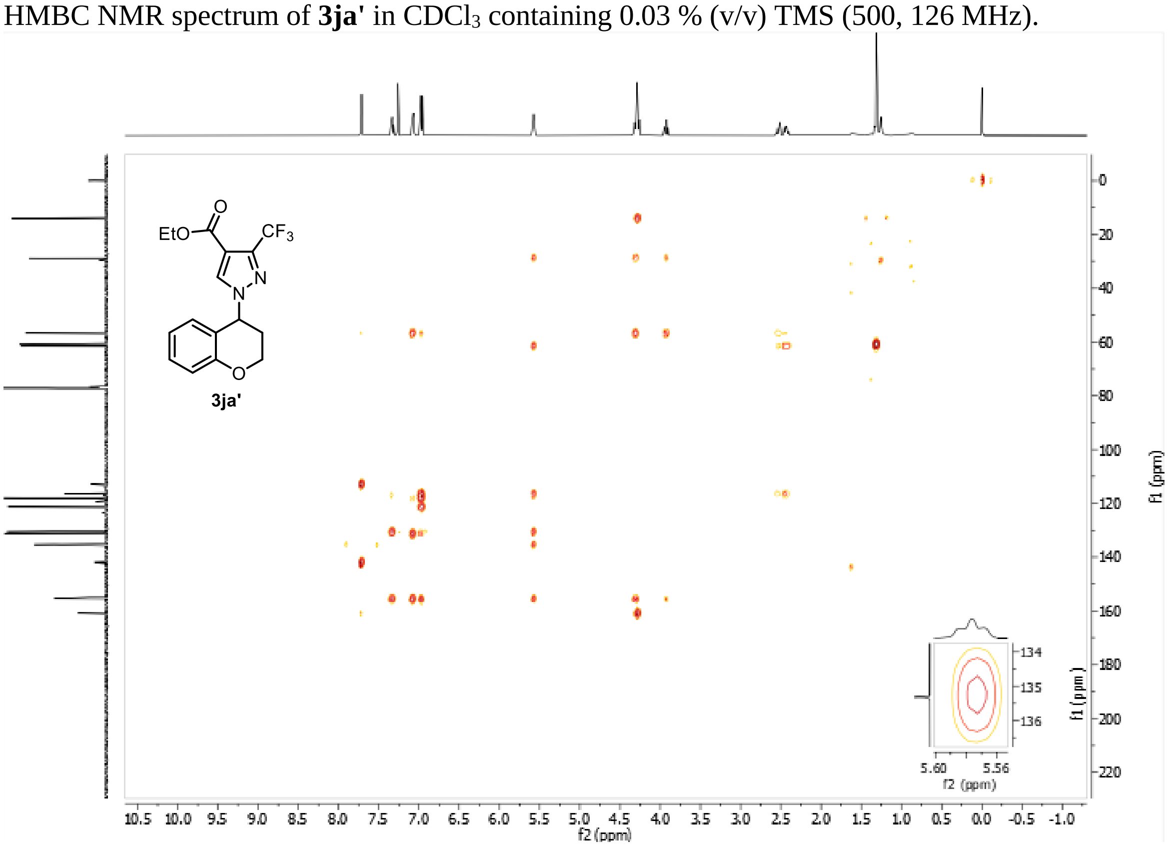
[19]F NMR spectrum of **3ja'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



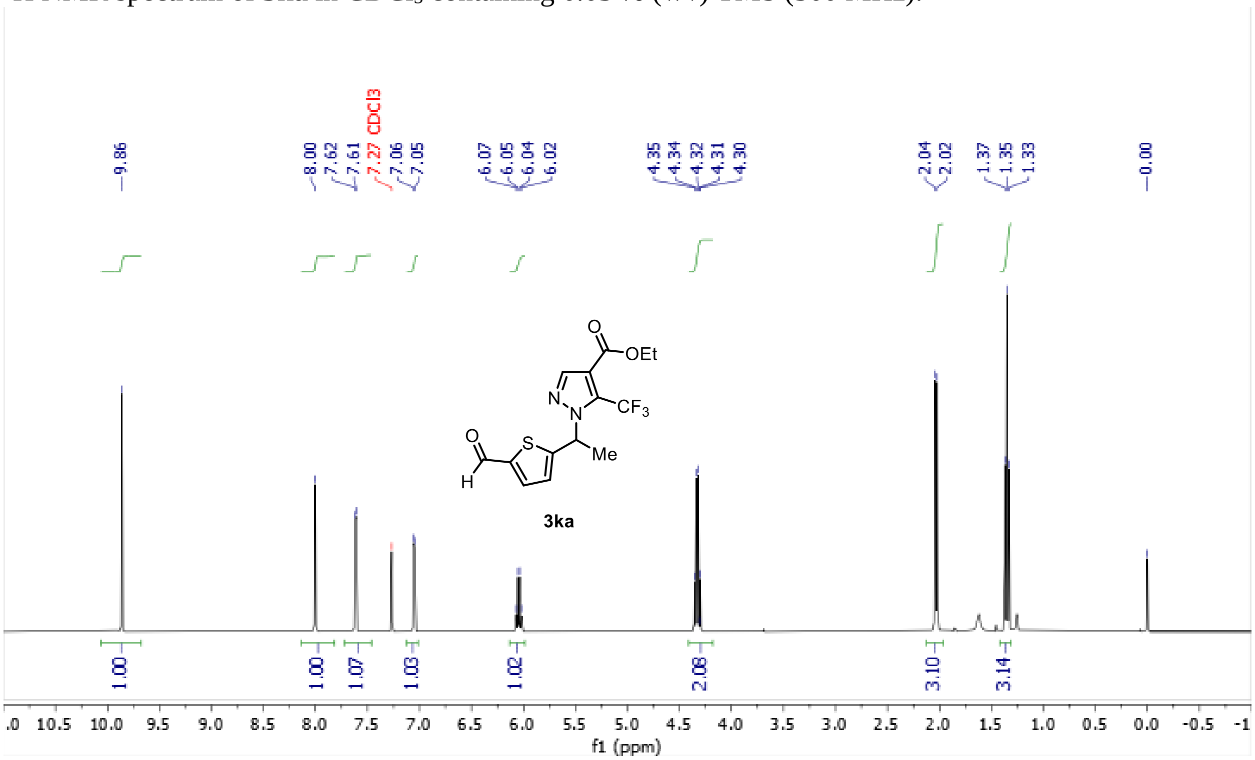
HSQC NMR spectrum of **3ja'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



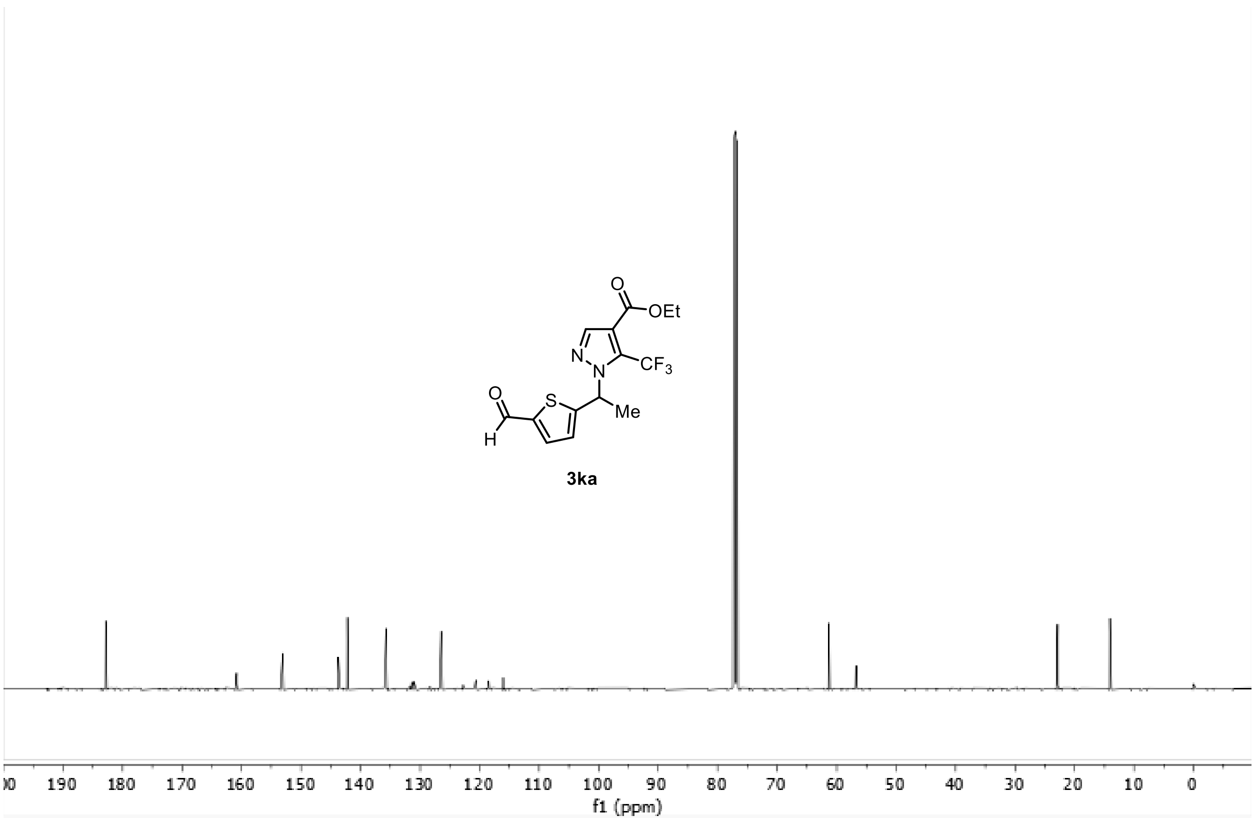
HMBC NMR spectrum of **3ja'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



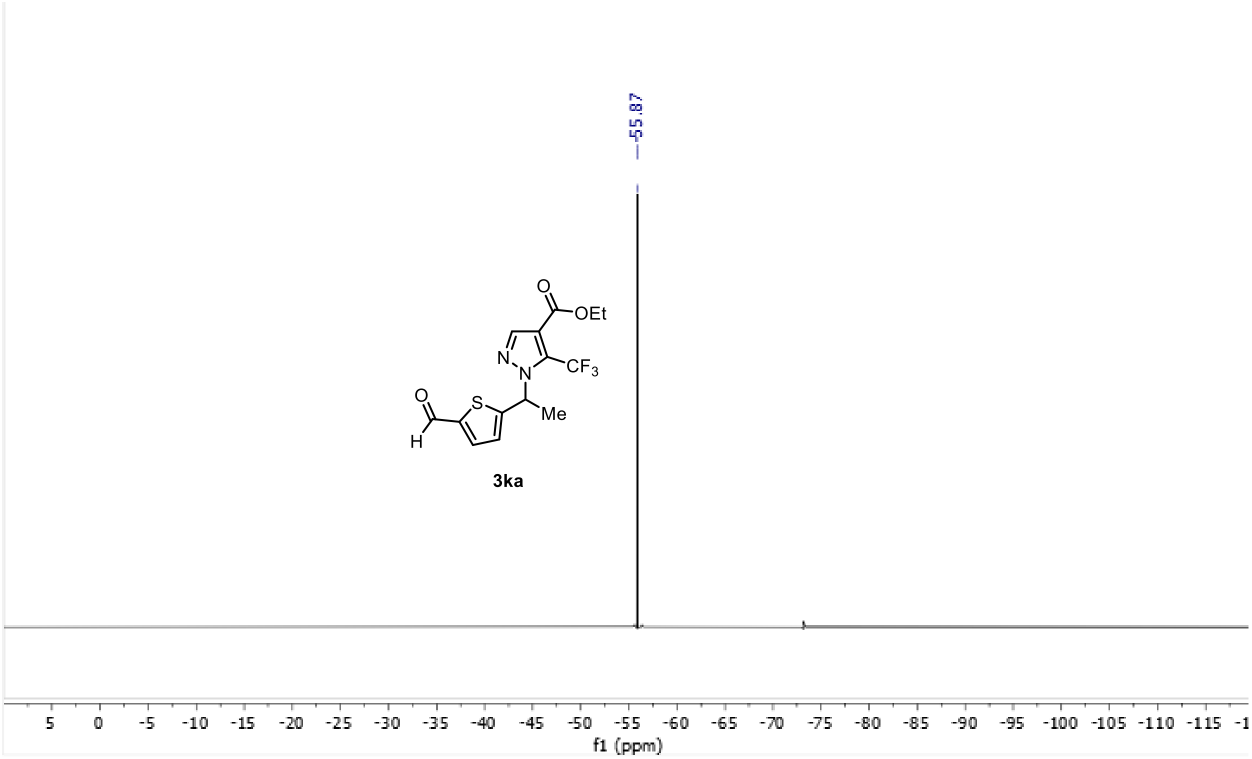
^{1}H NMR spectrum of **3ka** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



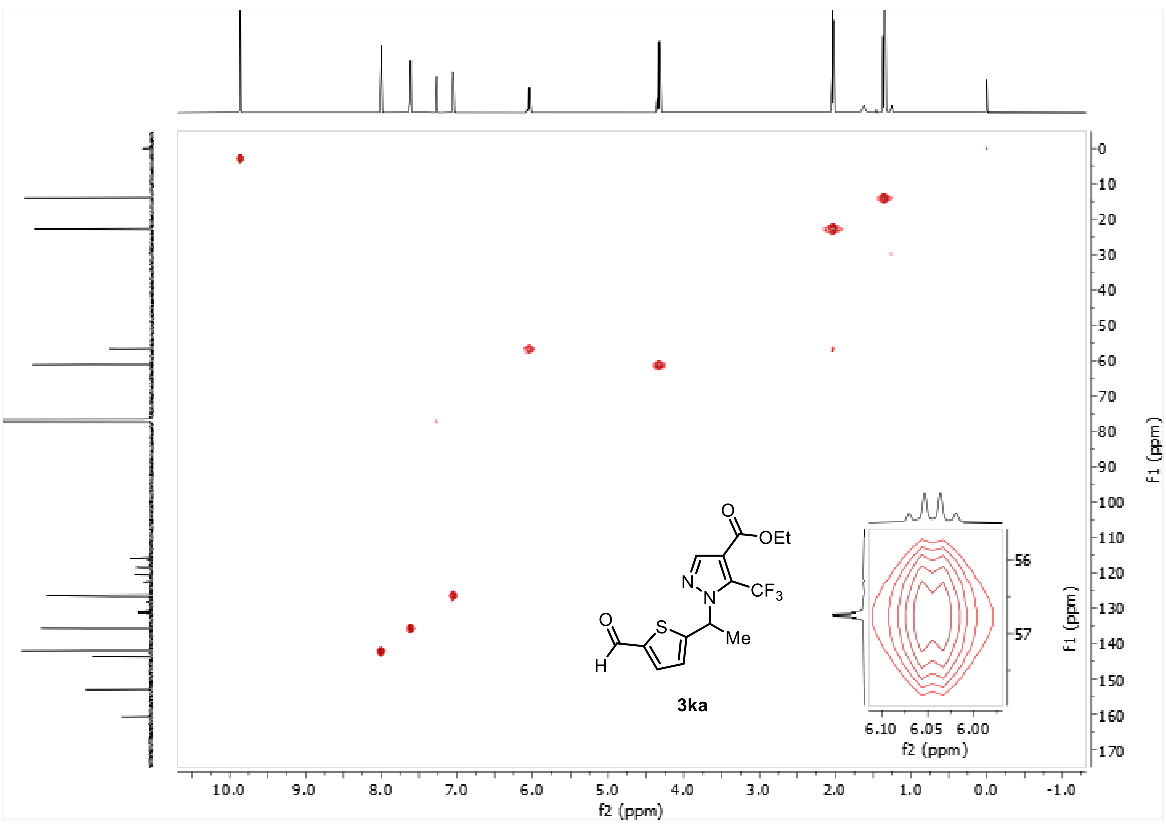
^{13}C NMR spectrum of **3ka** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



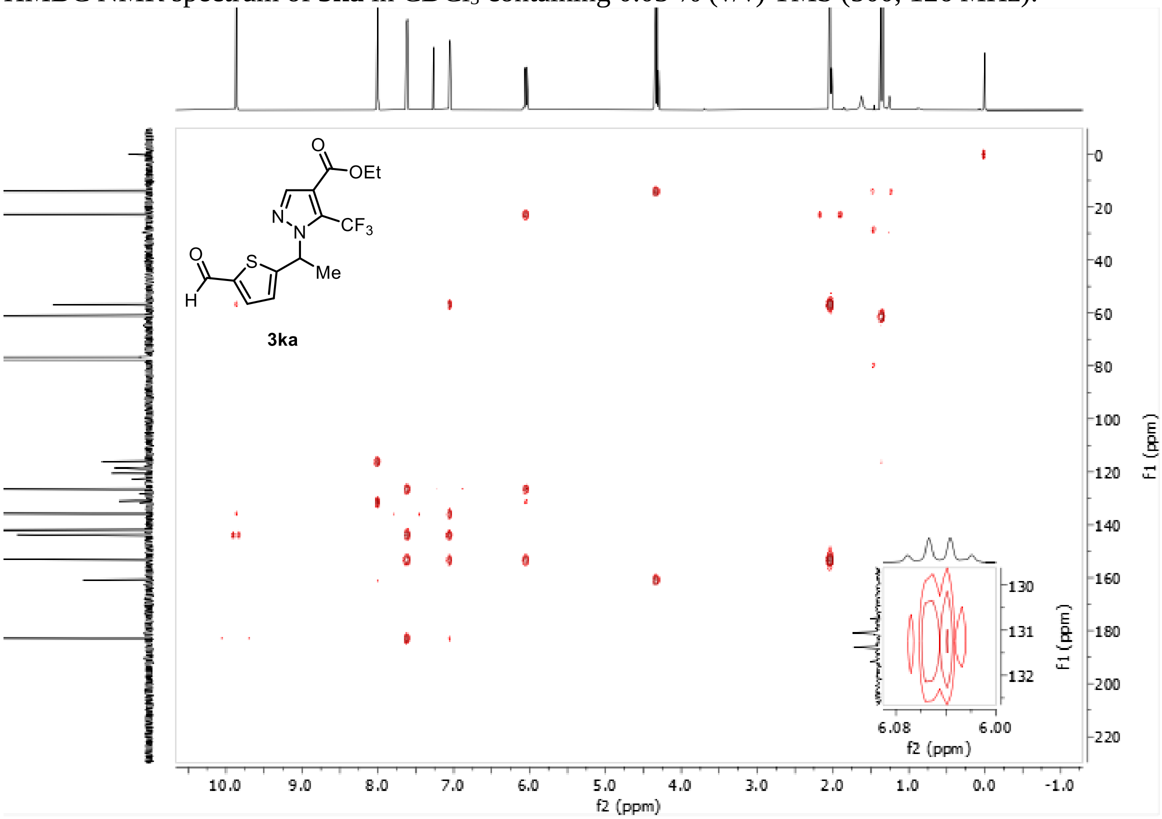
^{19}F NMR spectrum of **3ka** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



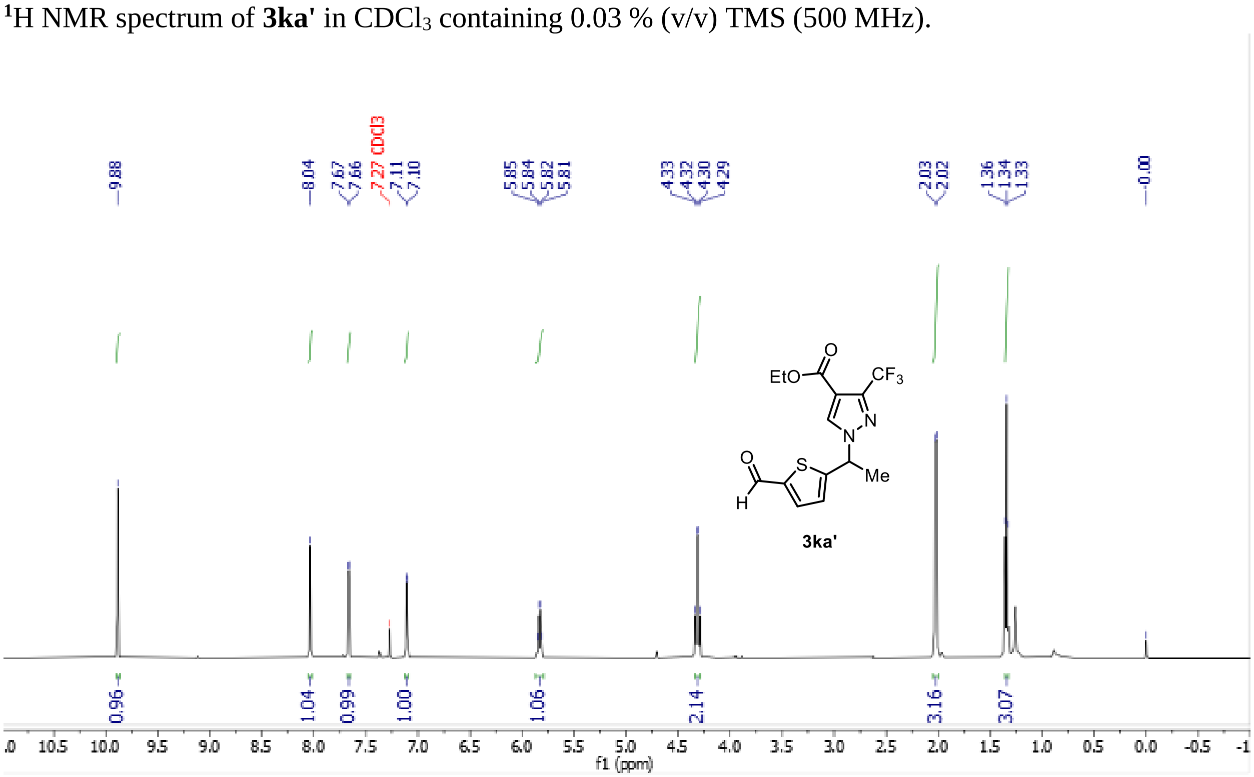
HSQC NMR spectrum of **3ka** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



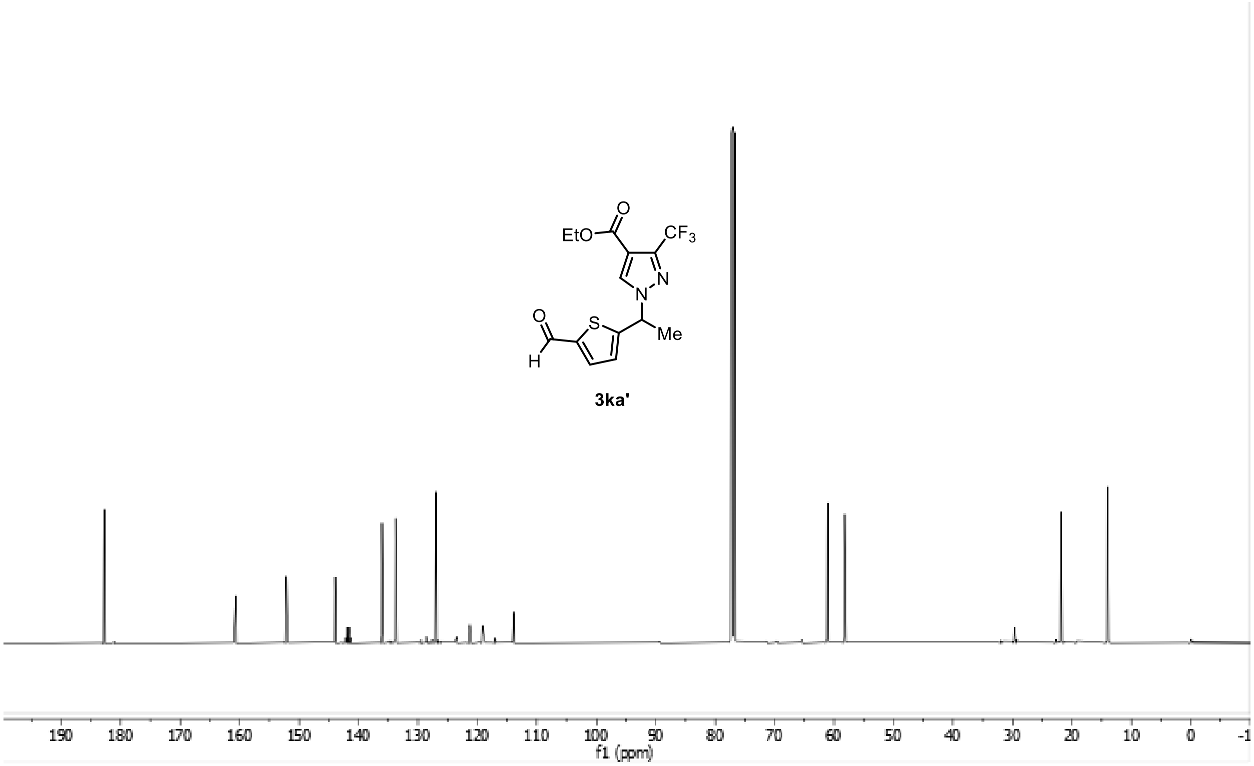
HMBC NMR spectrum of **3ka** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



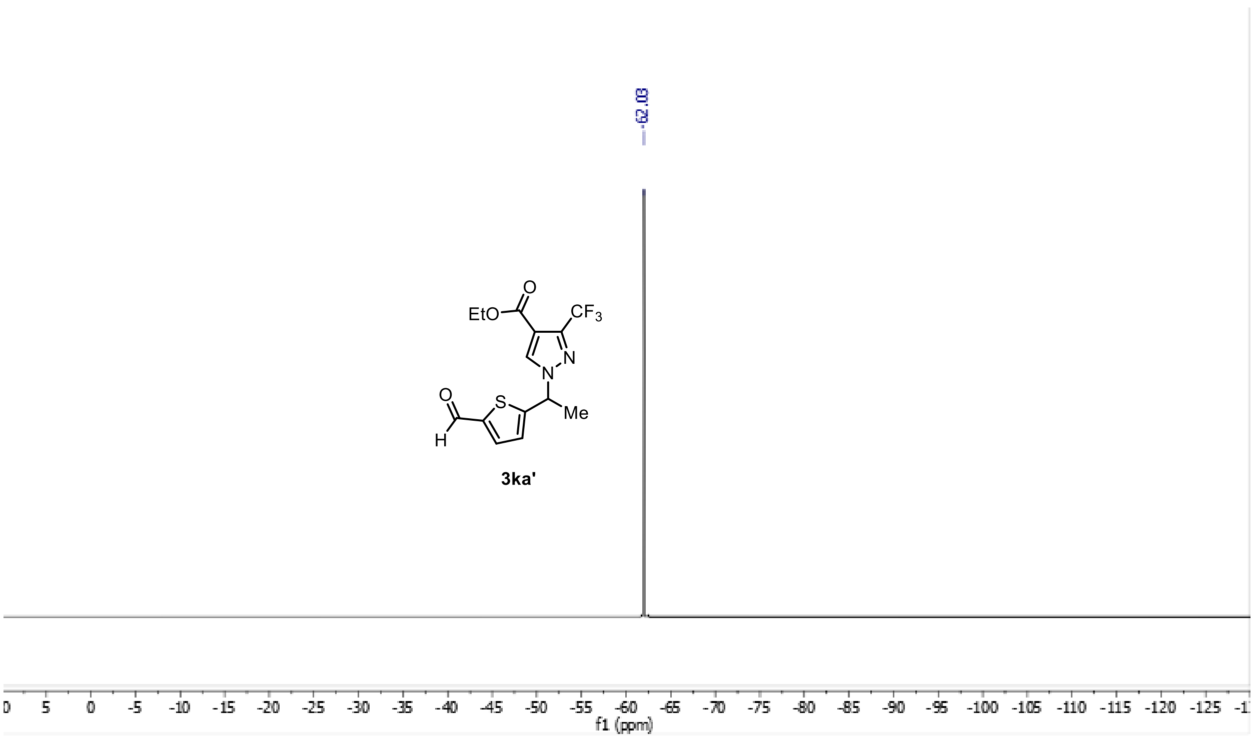
[1]H NMR spectrum of **3ka'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



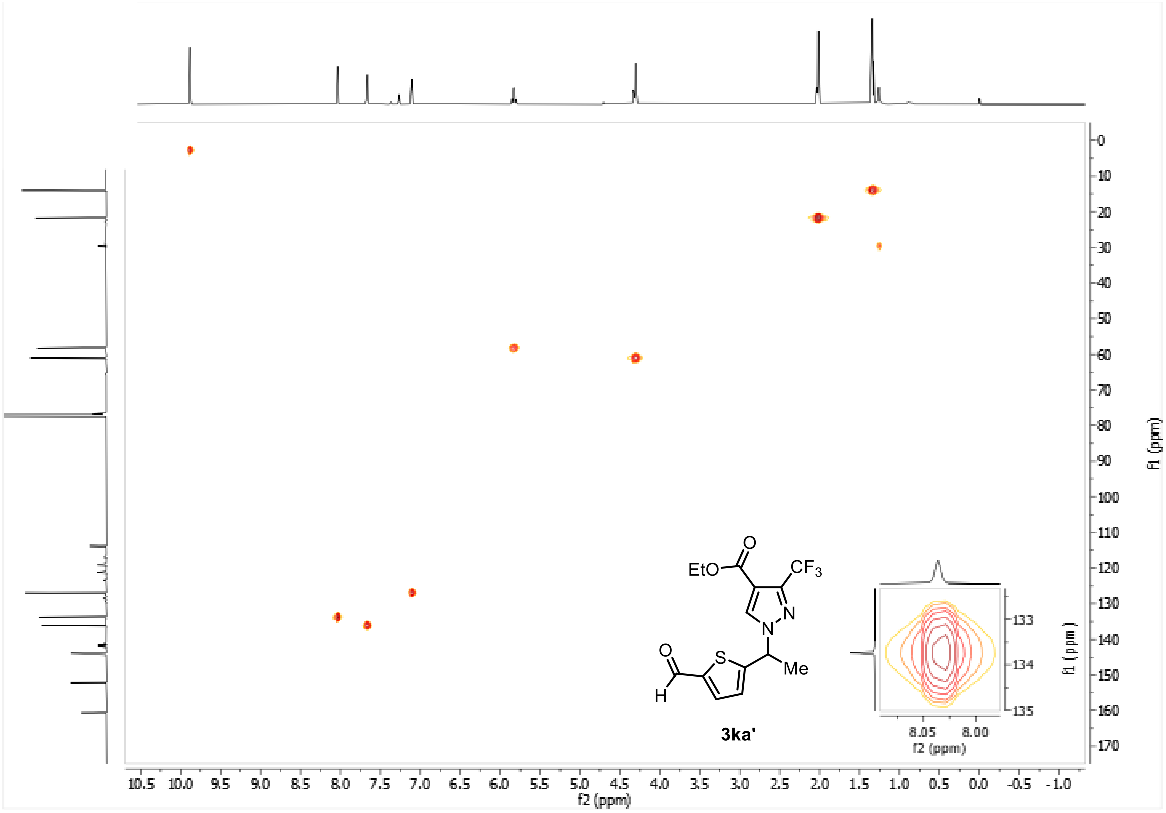
[13]C NMR spectrum of **3ka'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



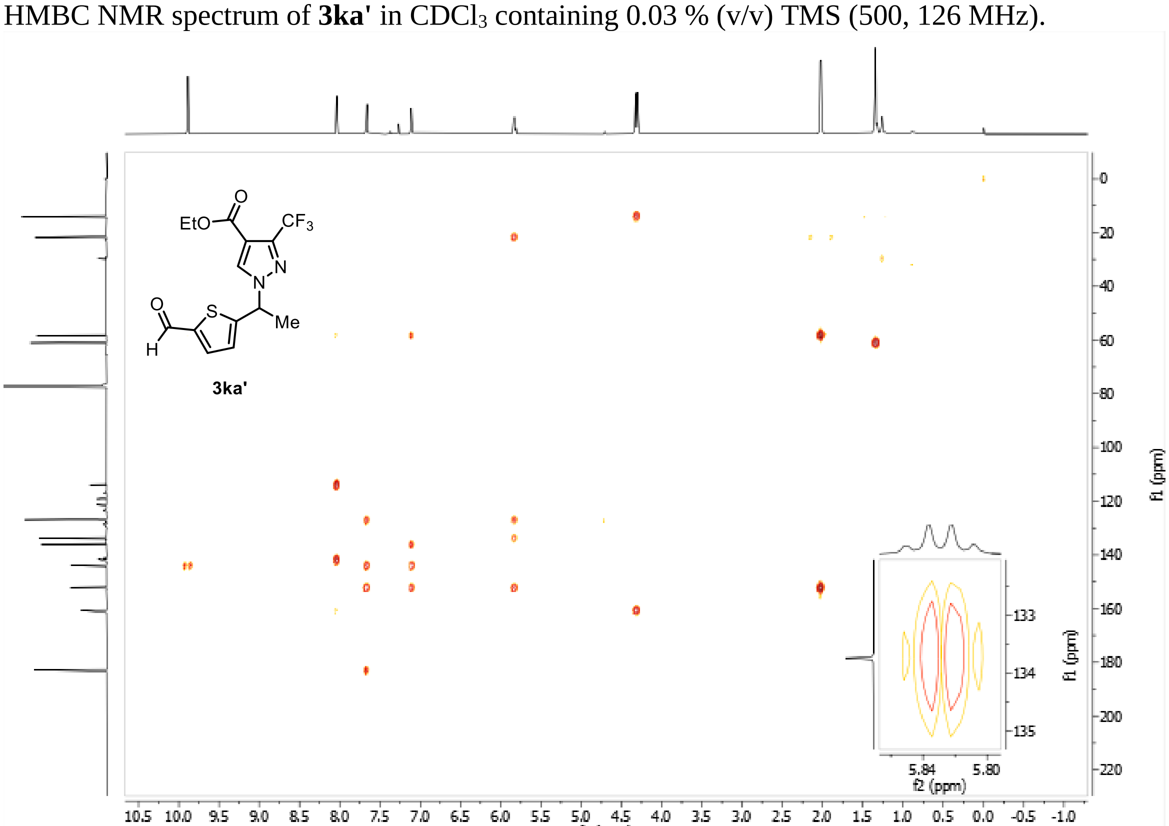
[19]F NMR spectrum of **3ka'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



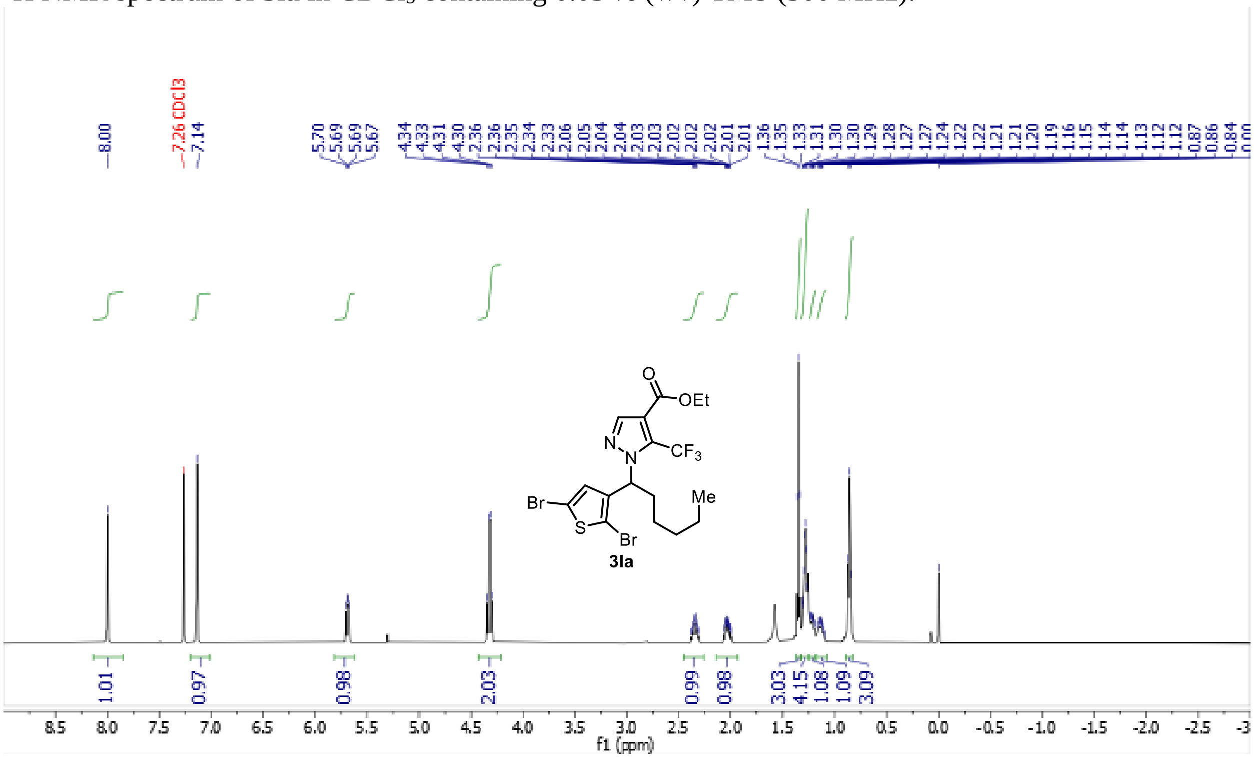
HSQC NMR spectrum of **3ka'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



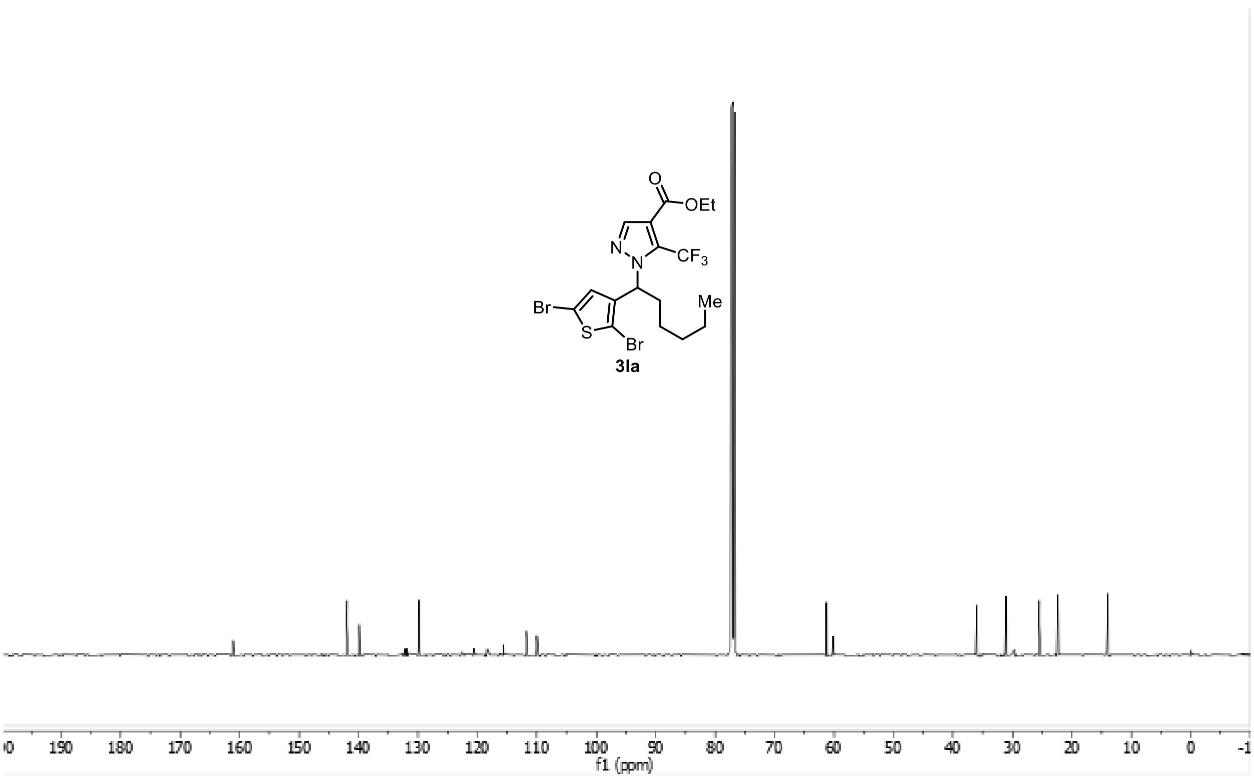
HMBC NMR spectrum of **3ka'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



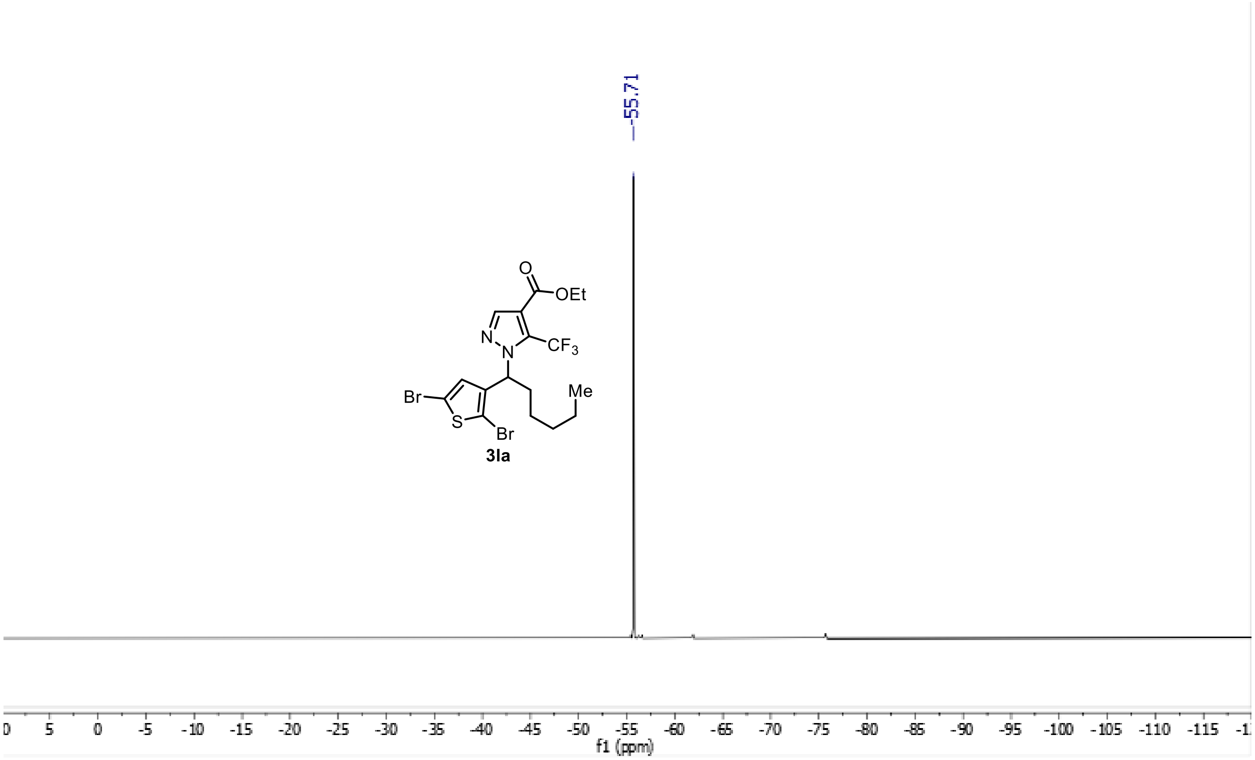
^{1}H NMR spectrum of **3la** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



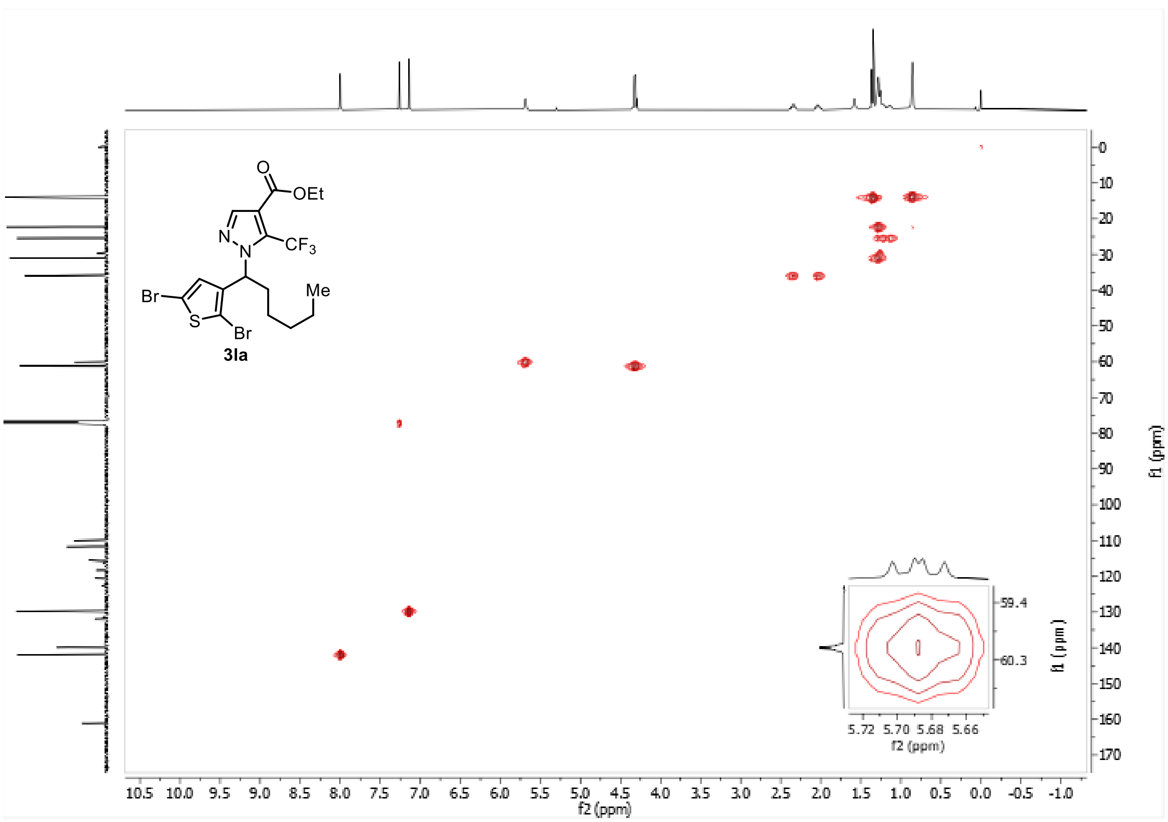
^{13}C NMR spectrum of **3la** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



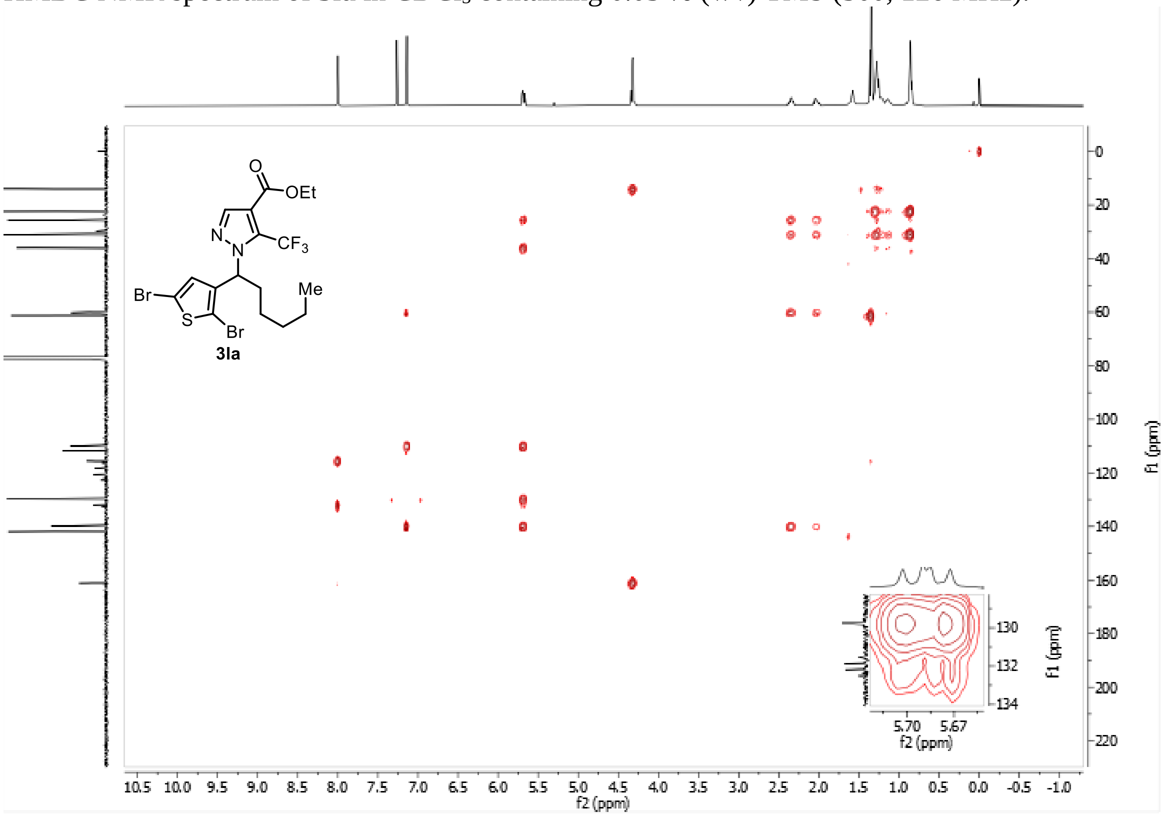
[19]F NMR spectrum of **3la** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



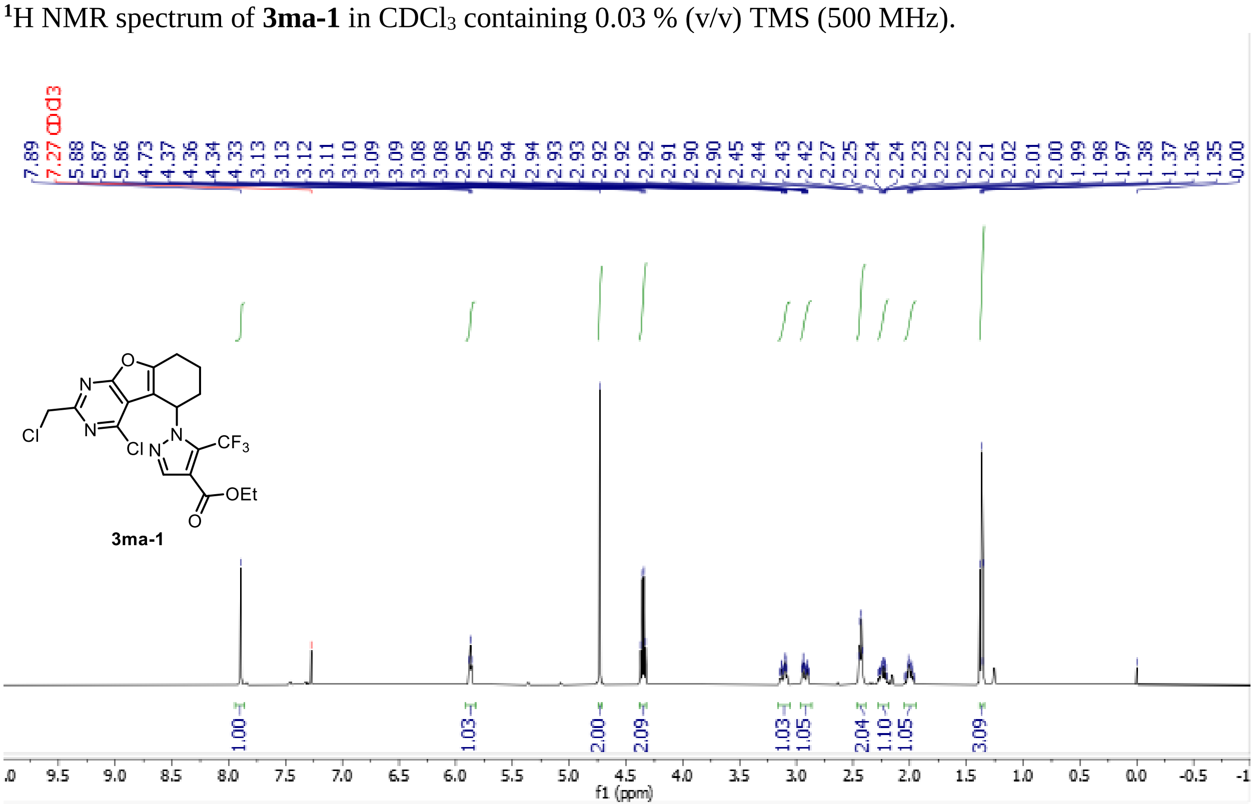
HSQC NMR spectrum of **3la** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



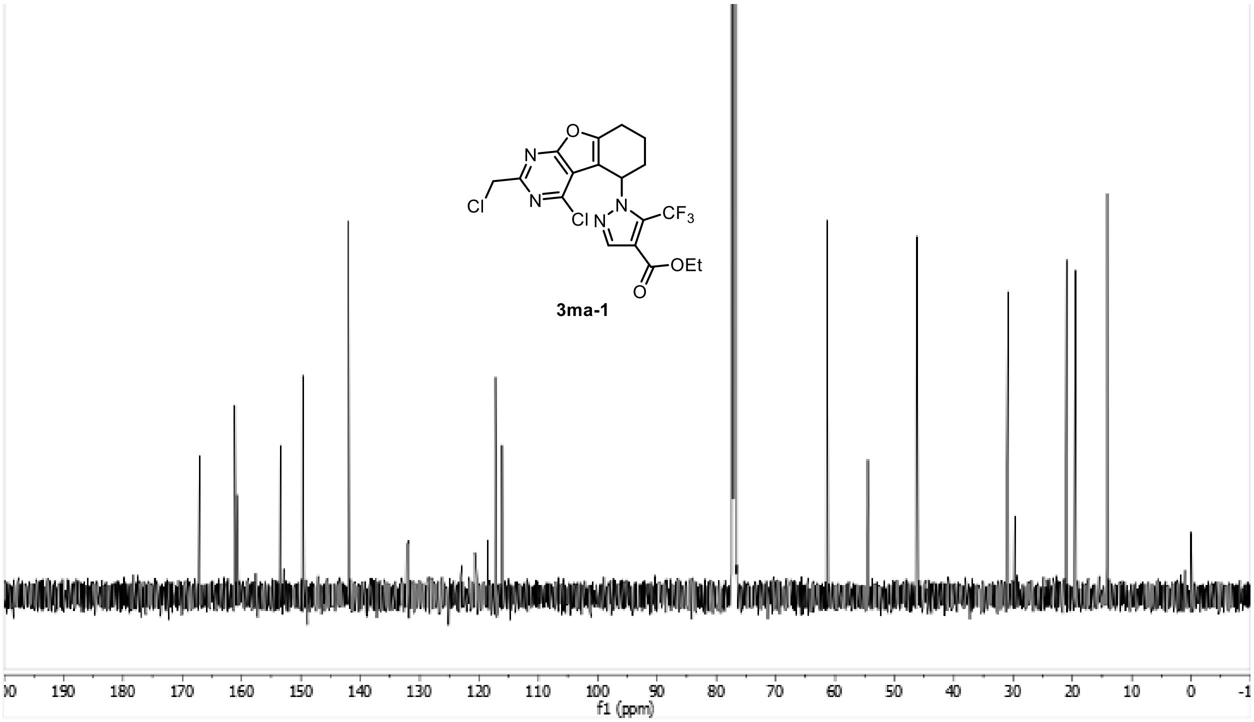
HMBC NMR spectrum of **3la** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



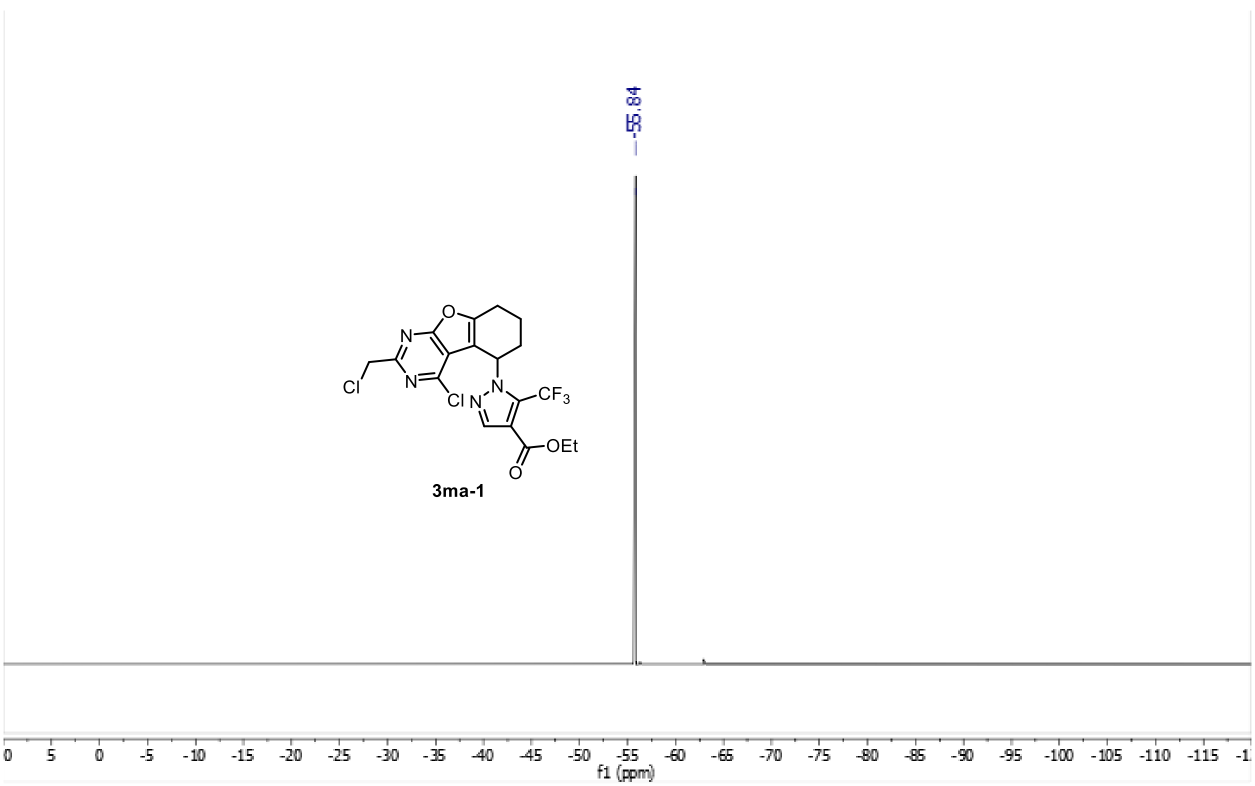
[1]H NMR spectrum of **3ma-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



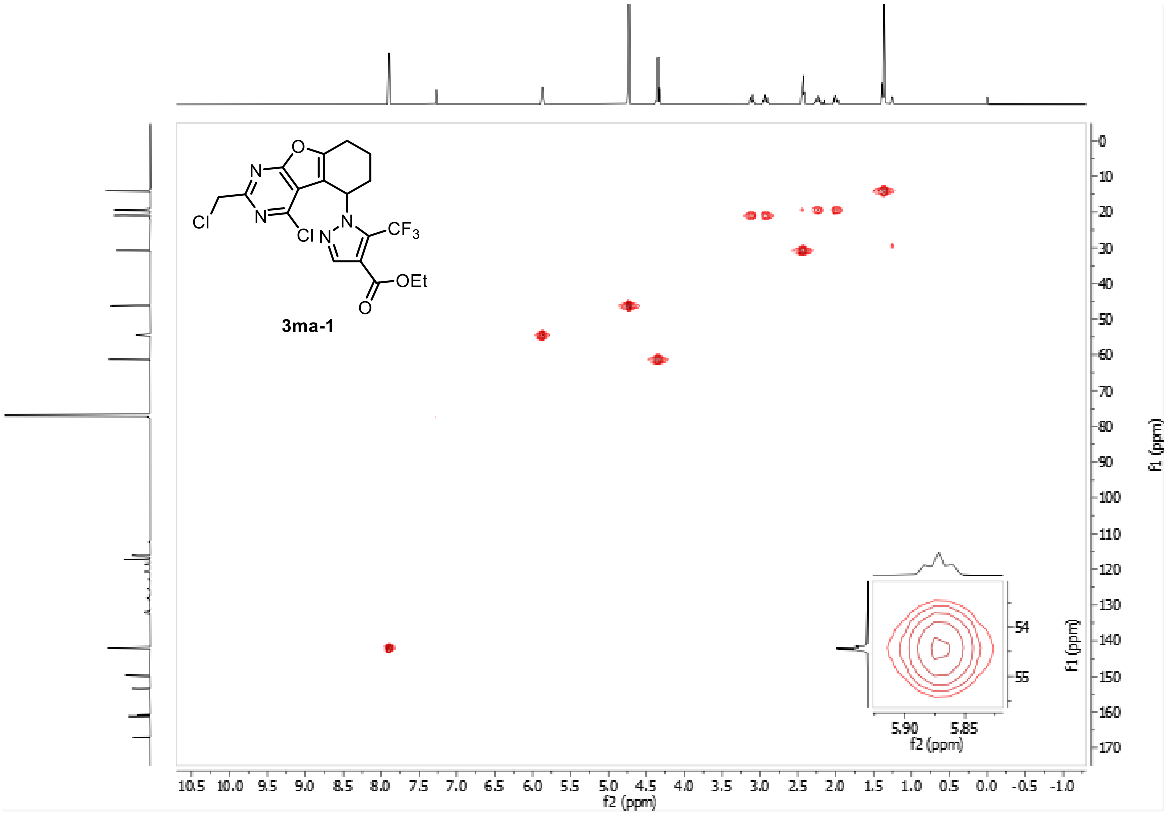
^{13}C NMR spectrum of **3ma-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



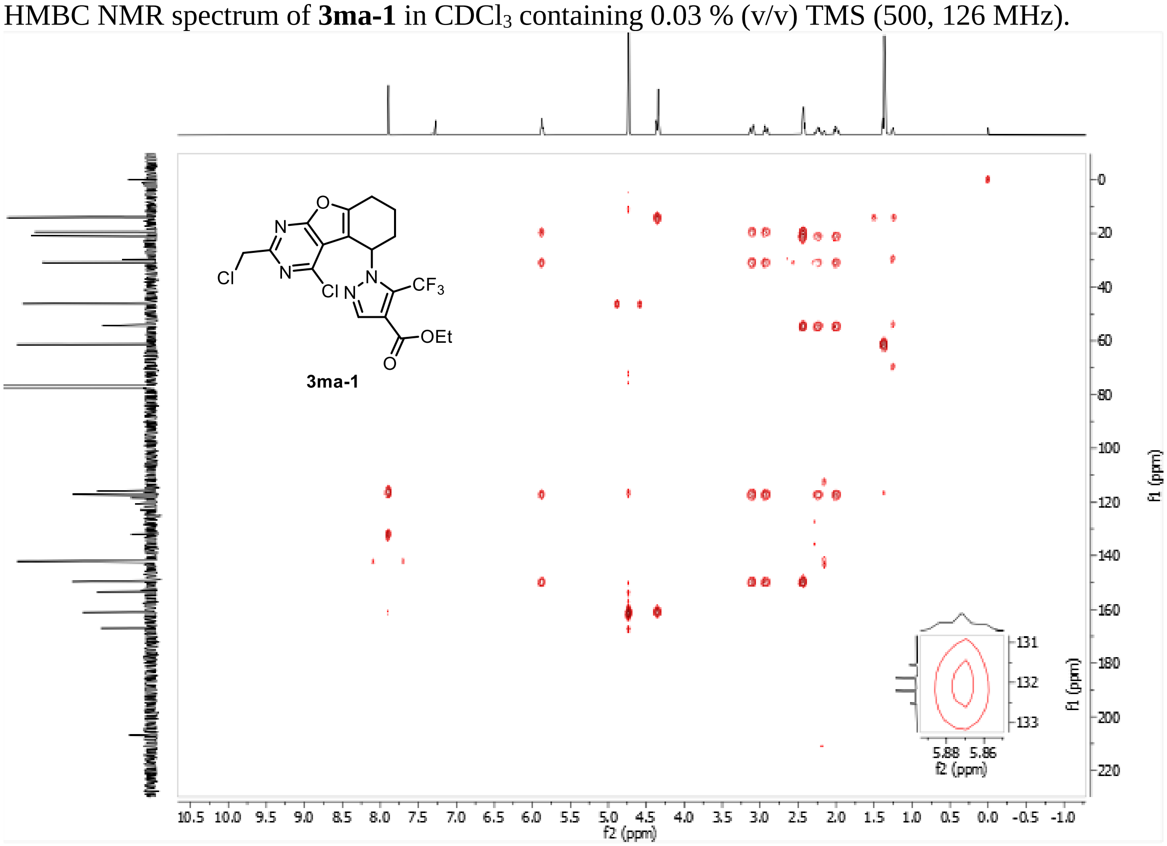
^{19}F NMR spectrum of **3ma-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



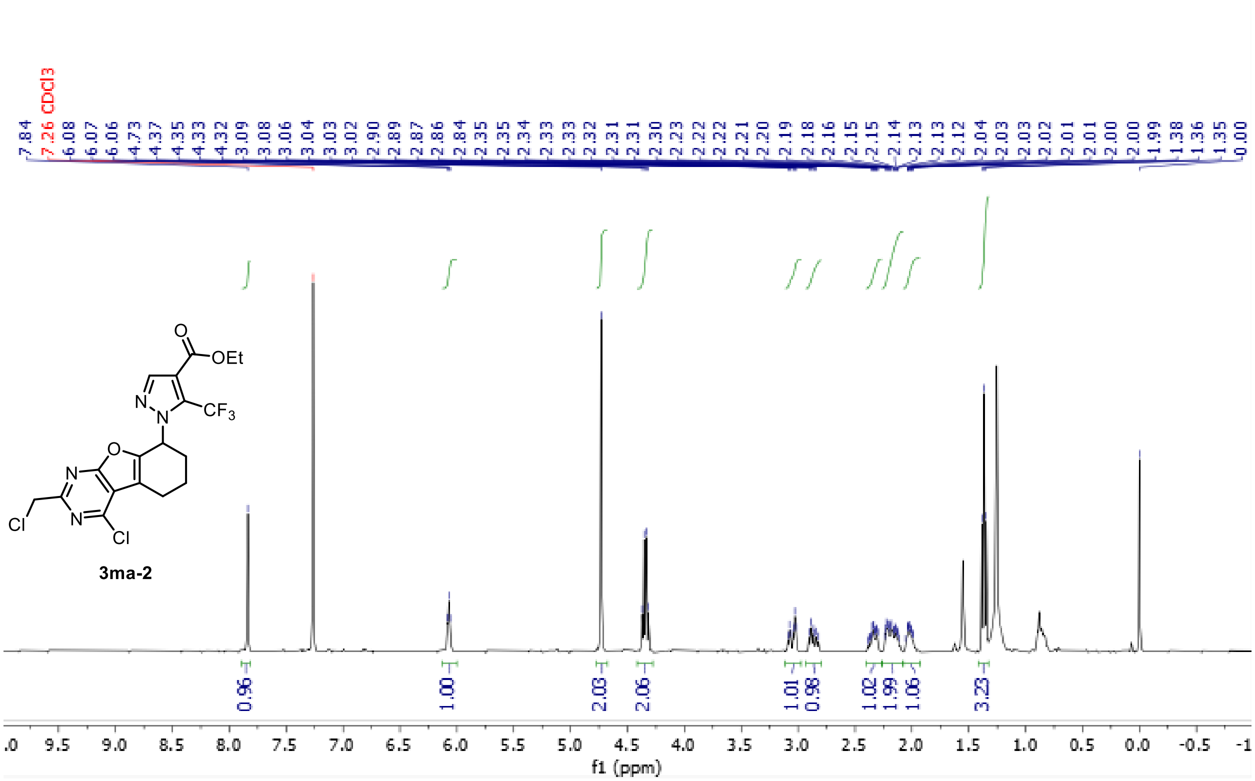
HSQC NMR spectrum of **3ma-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



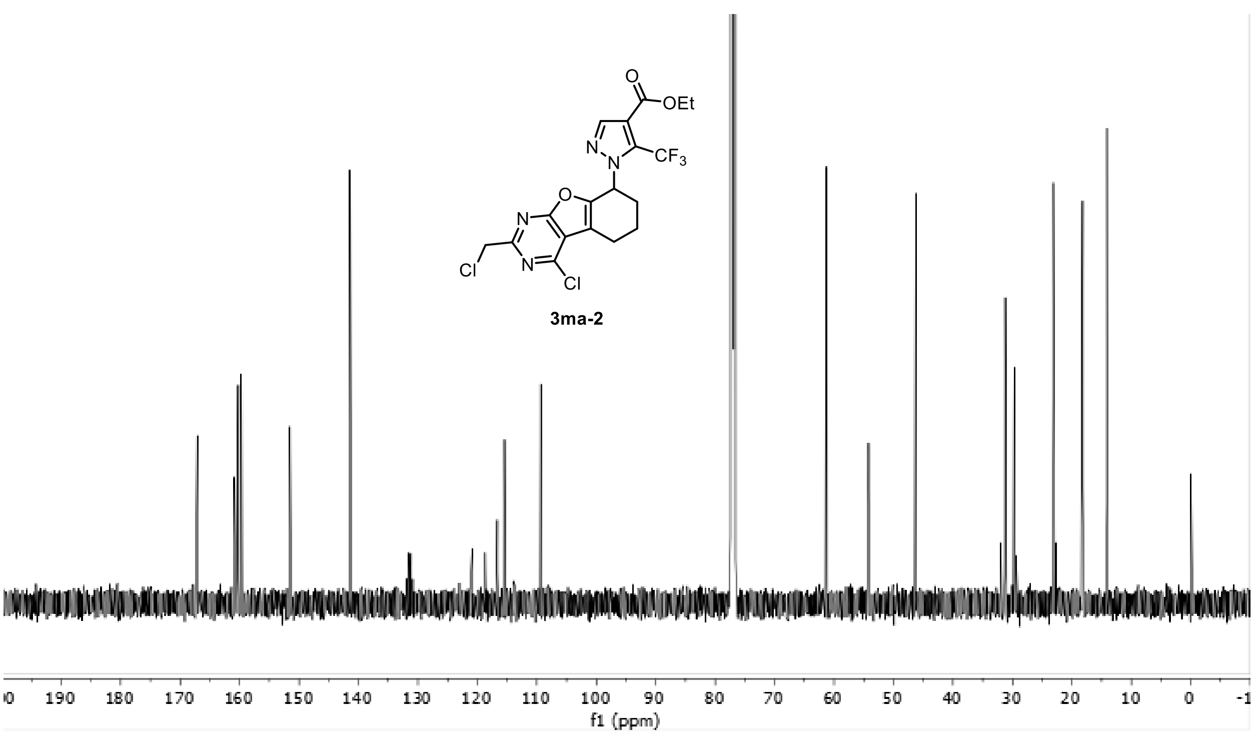
HMBC NMR spectrum of **3ma-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



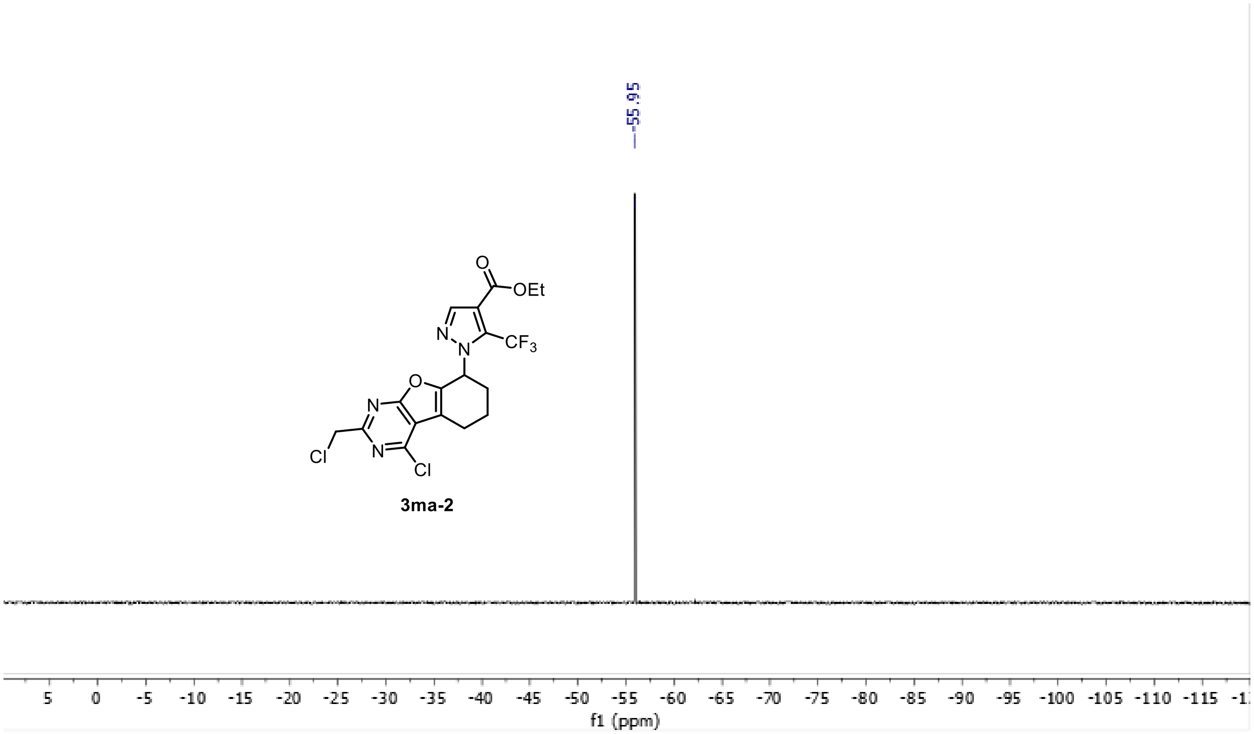
[1]H NMR spectrum of **3ma-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



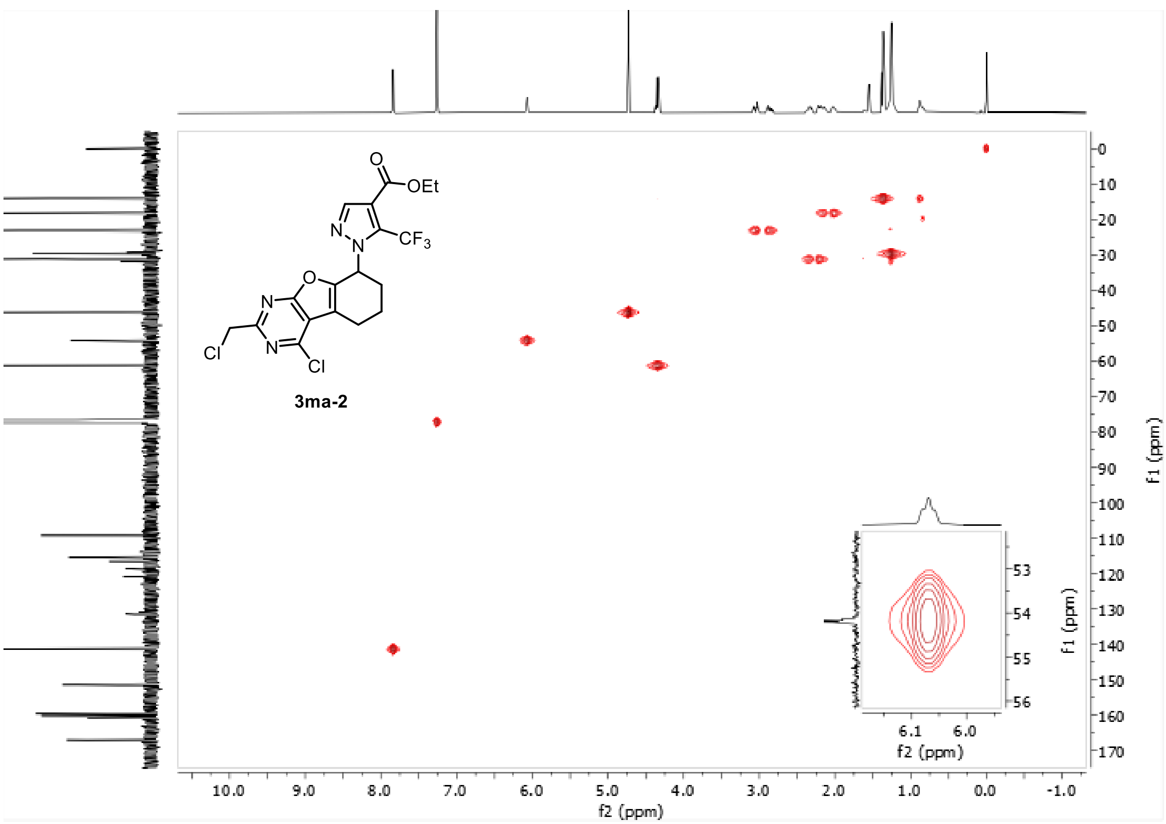
[13]C NMR spectrum of **3ma-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



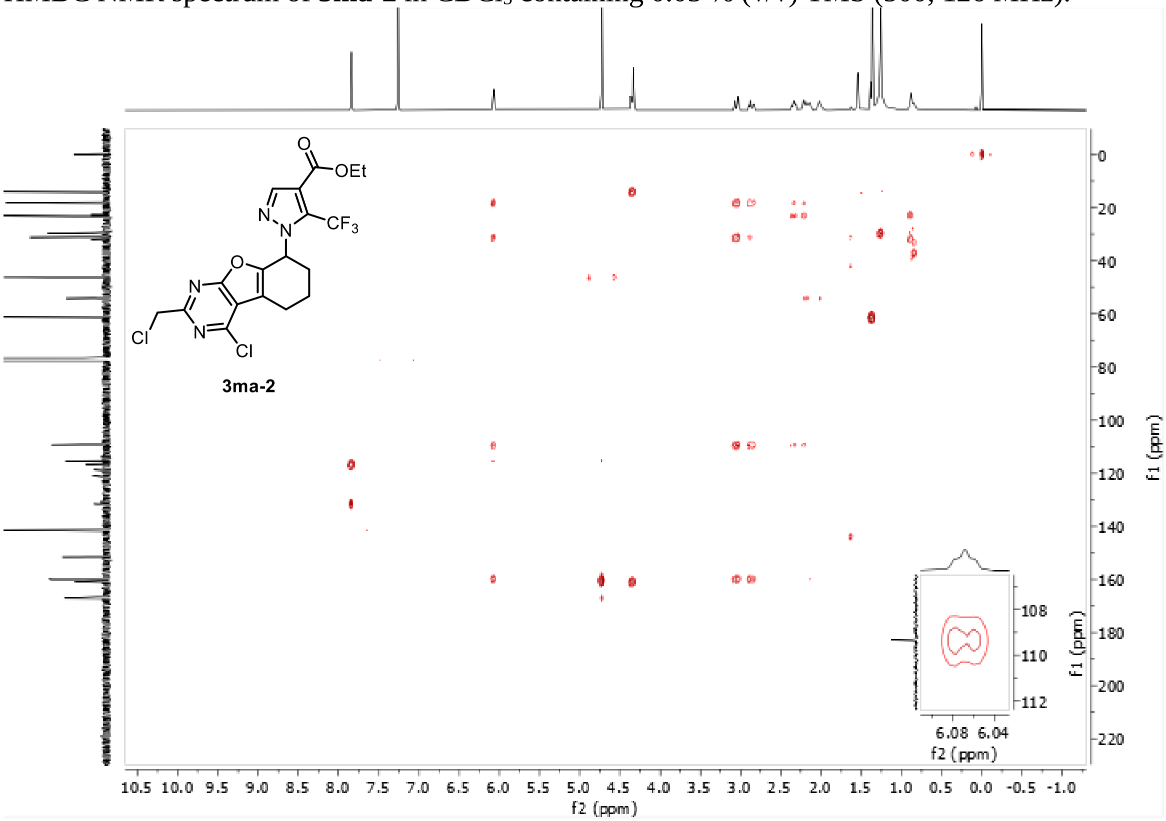
[19]F NMR spectrum of **3ma-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



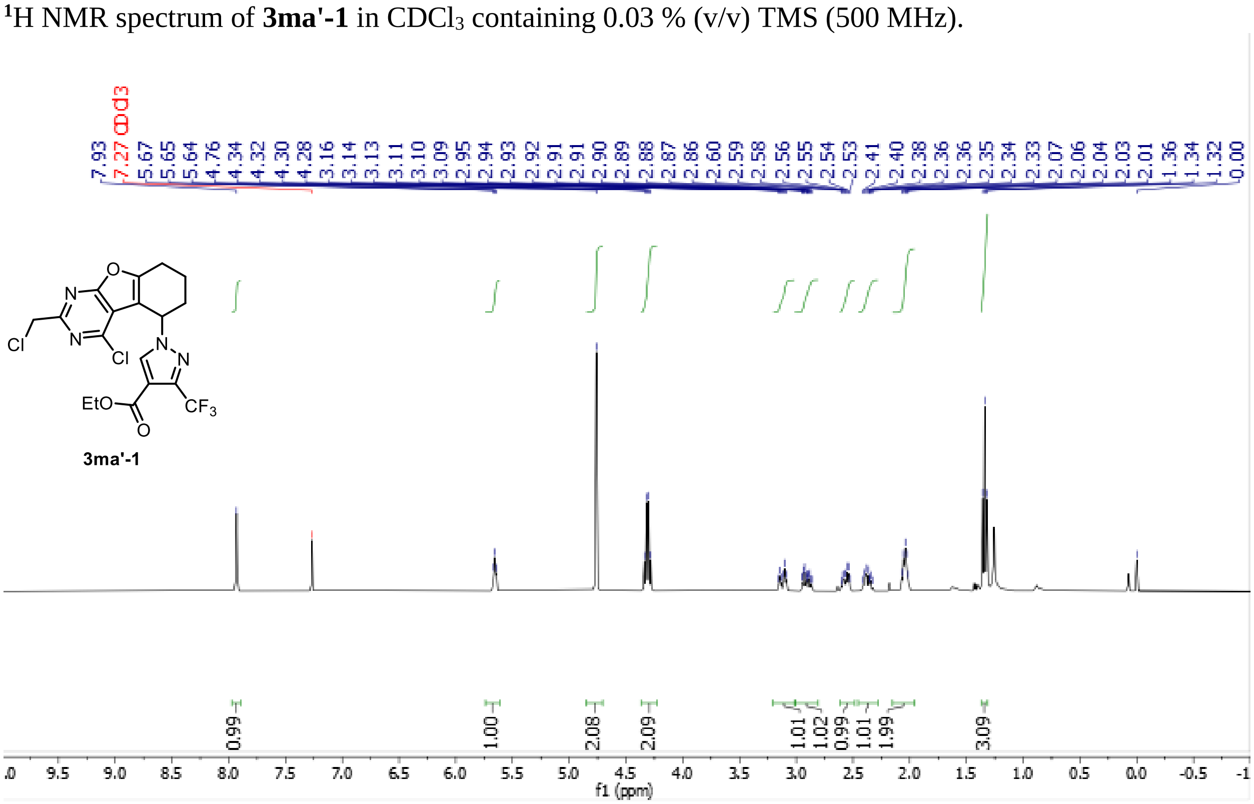
HSQC NMR spectrum of **3ma-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



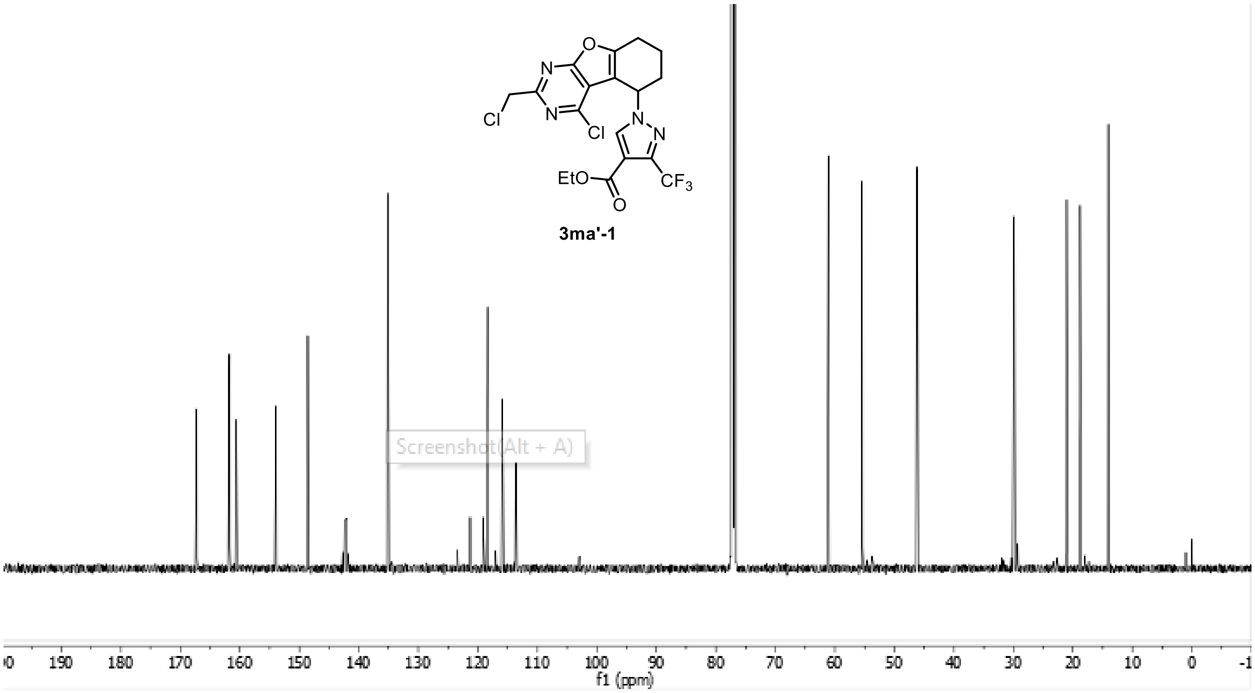
HMBC NMR spectrum of **3ma-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



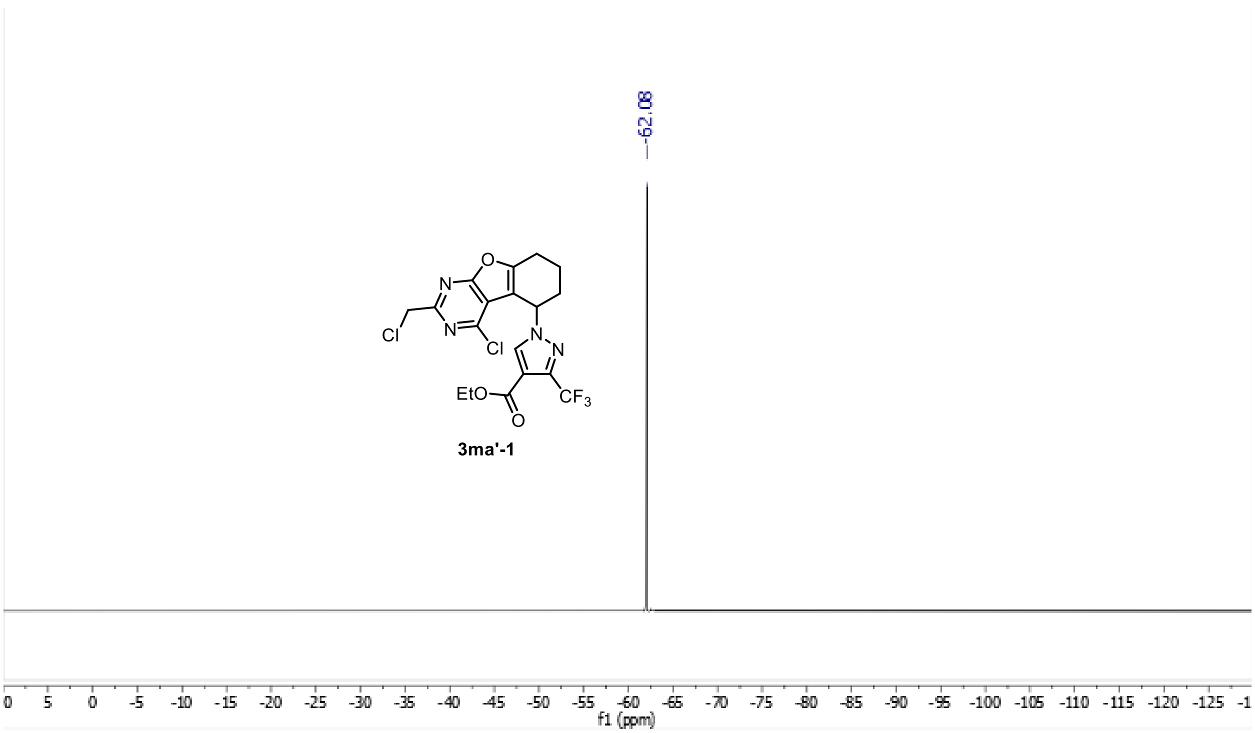
^1H NMR spectrum of **3ma'-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



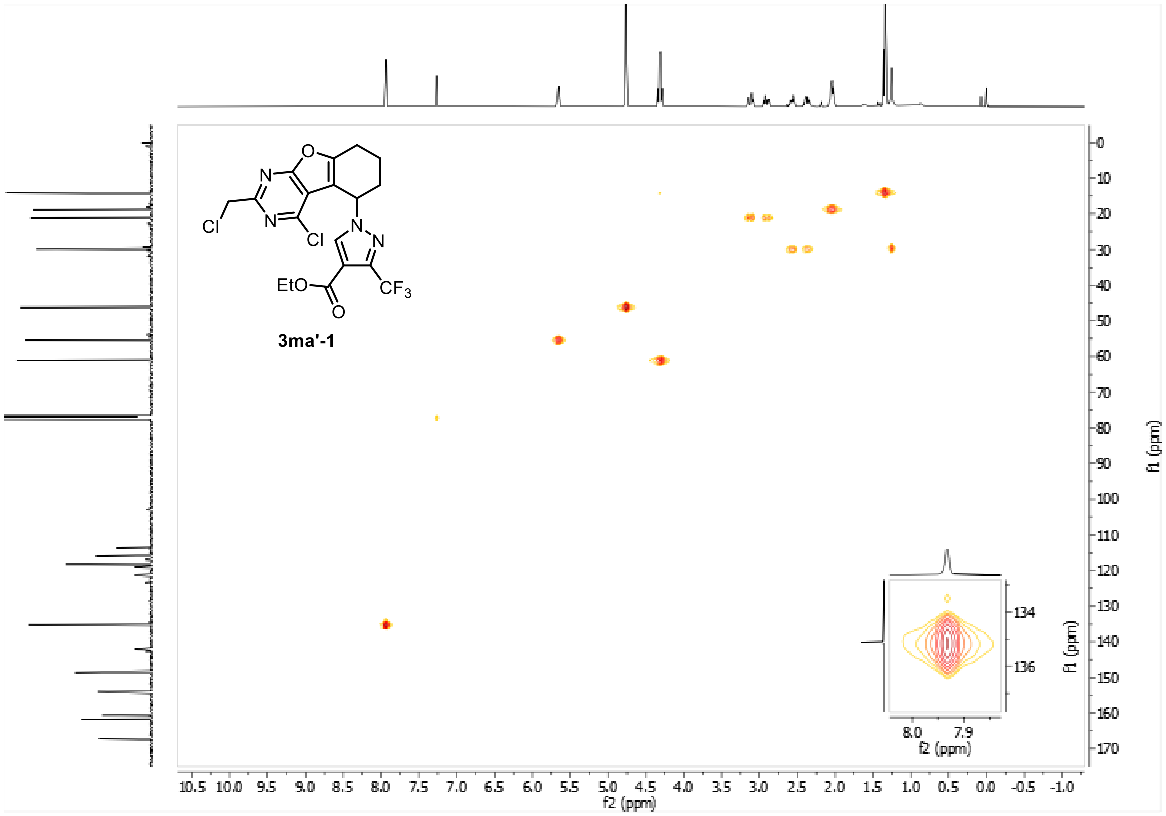
^{13}C NMR spectrum of **3ma'-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



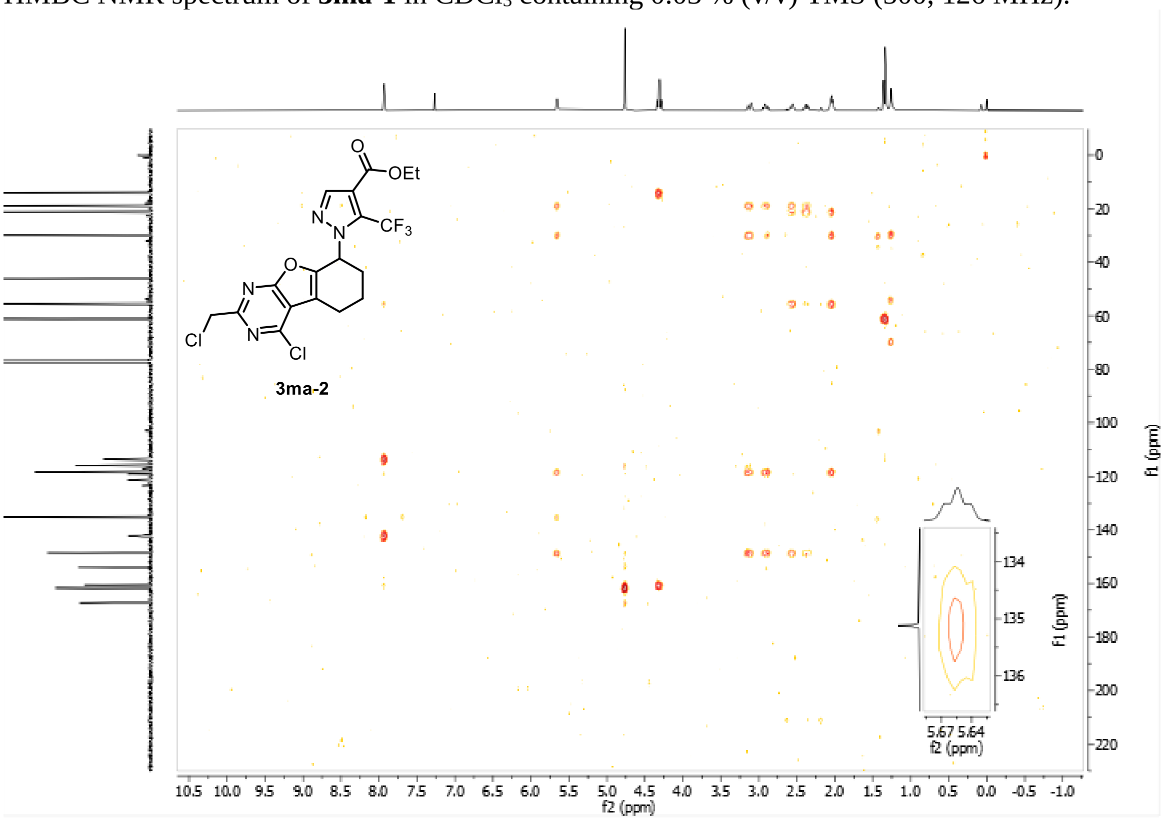
^{19}F NMR spectrum of **3ma'-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



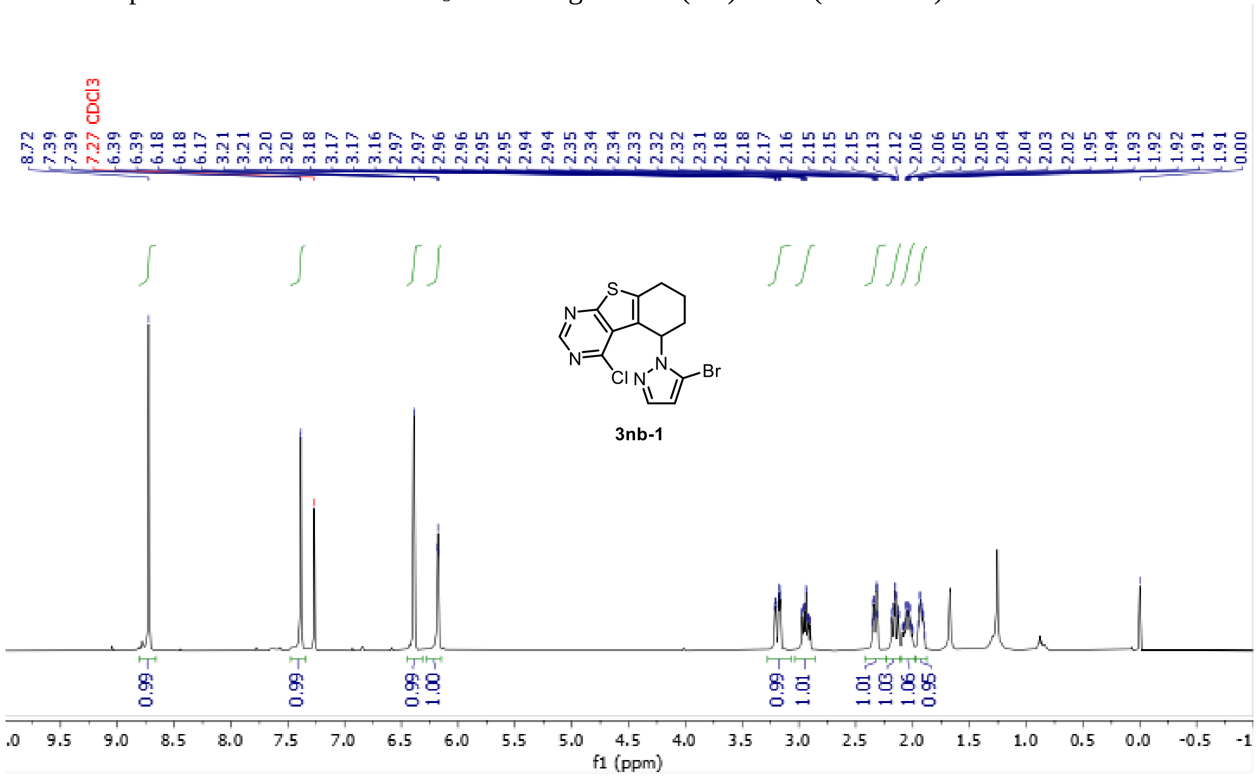
HSQC NMR spectrum of **3ma'-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



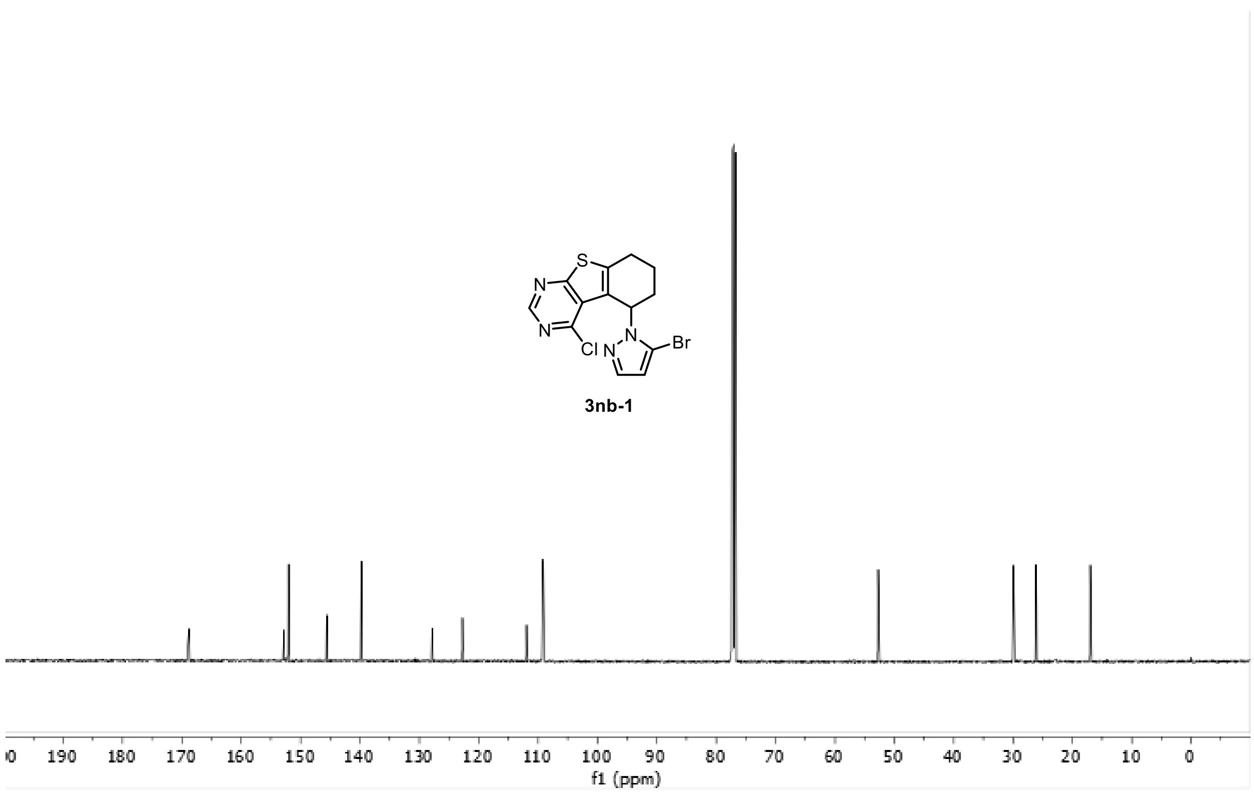
HMBC NMR spectrum of **3ma-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



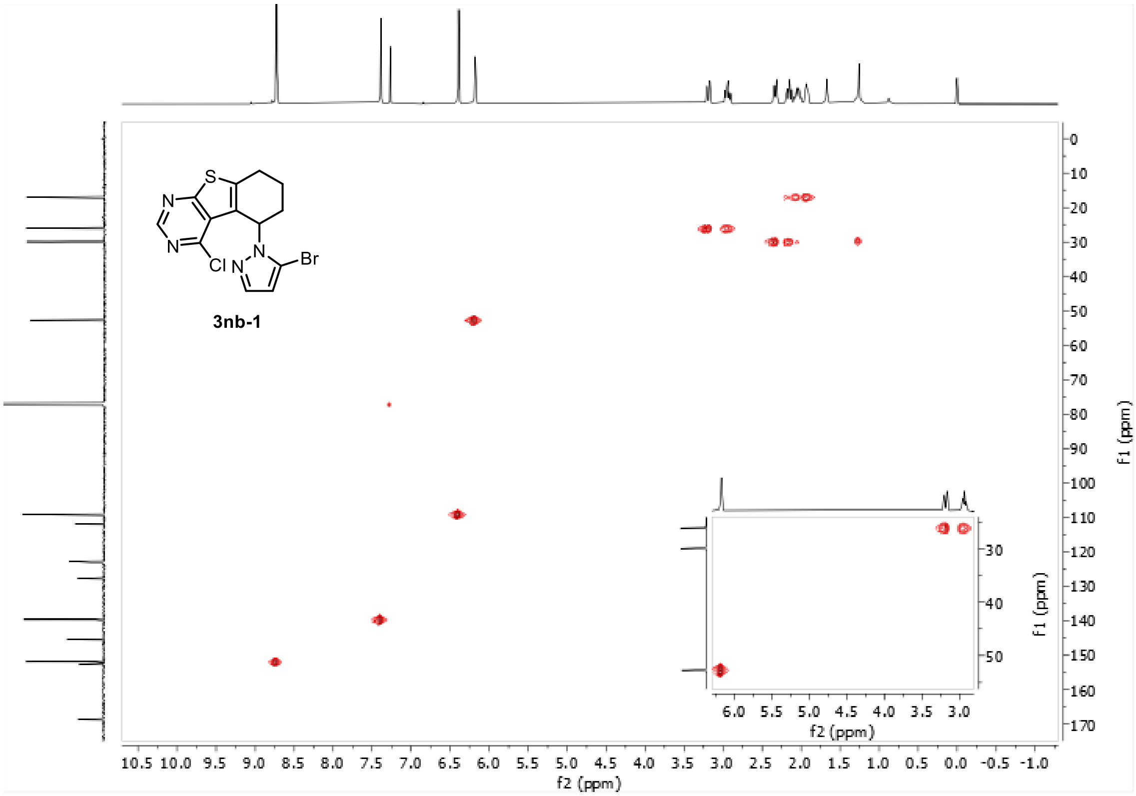
^{1}H NMR spectrum of **3nb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



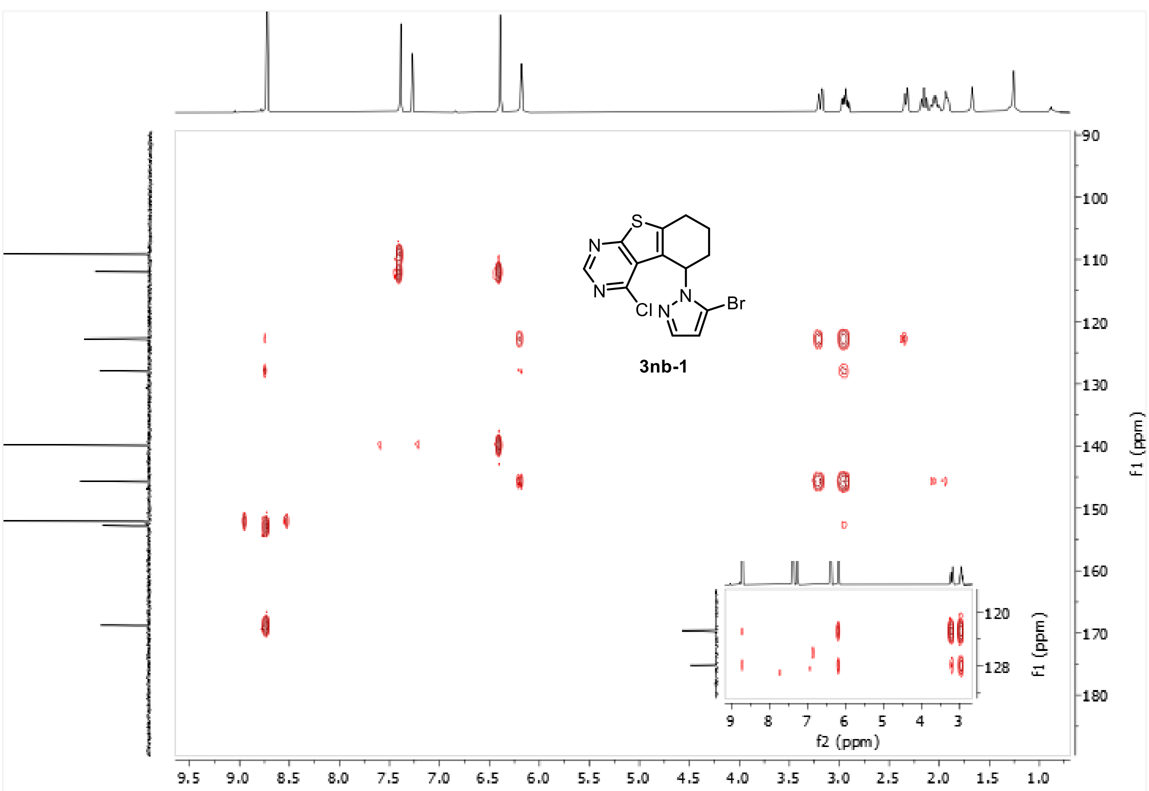
^{13}C NMR spectrum of **3nb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



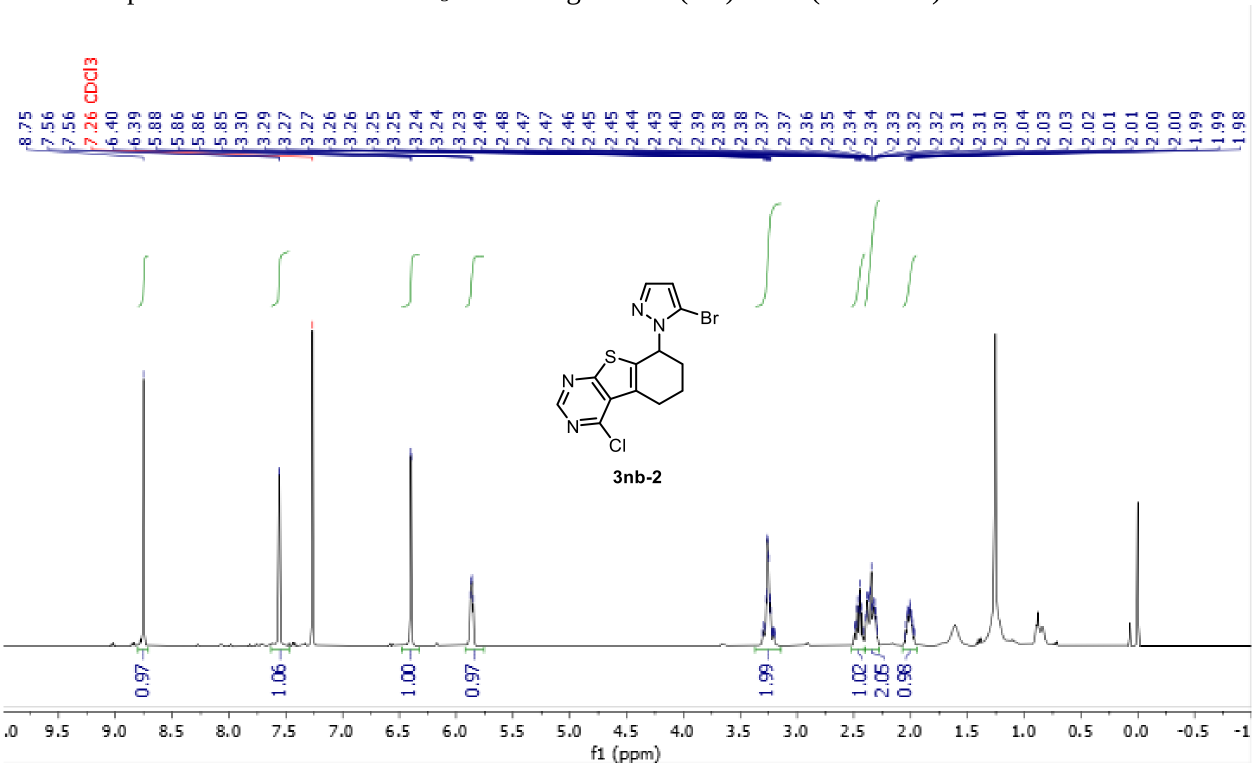
HSQC NMR spectrum of **3nb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



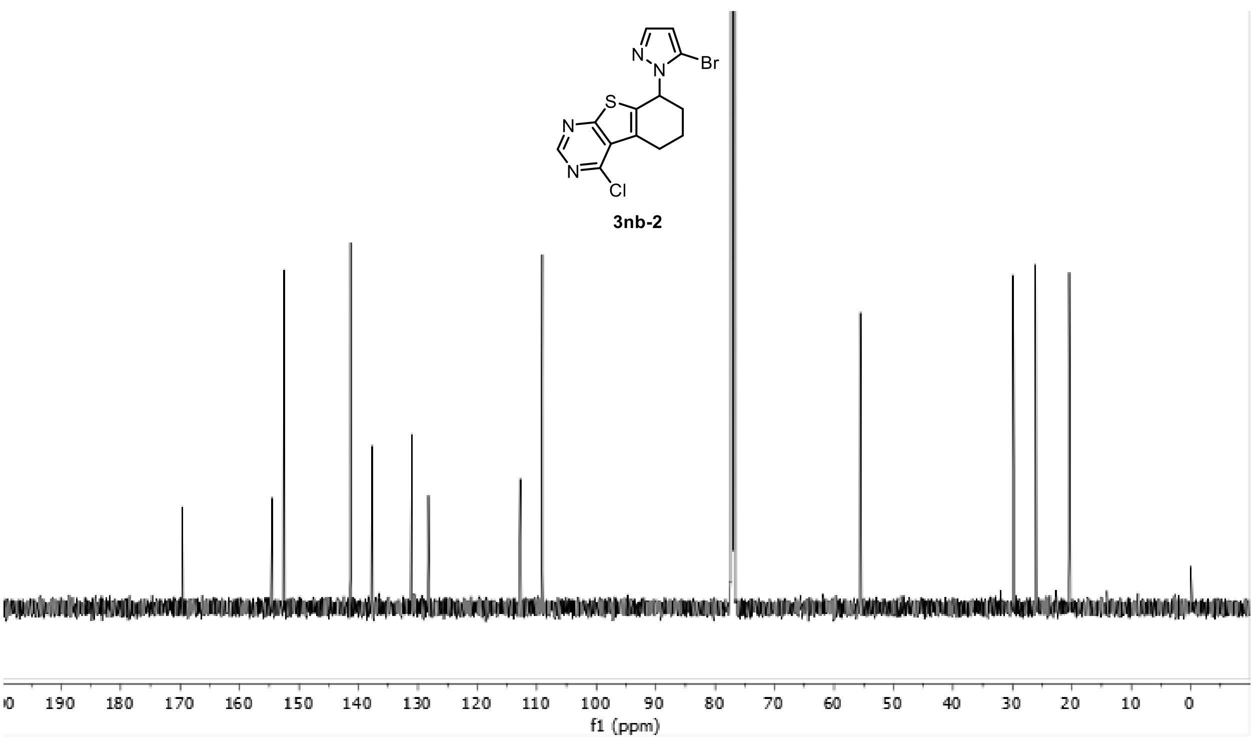
HMBC NMR spectrum of **3nb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



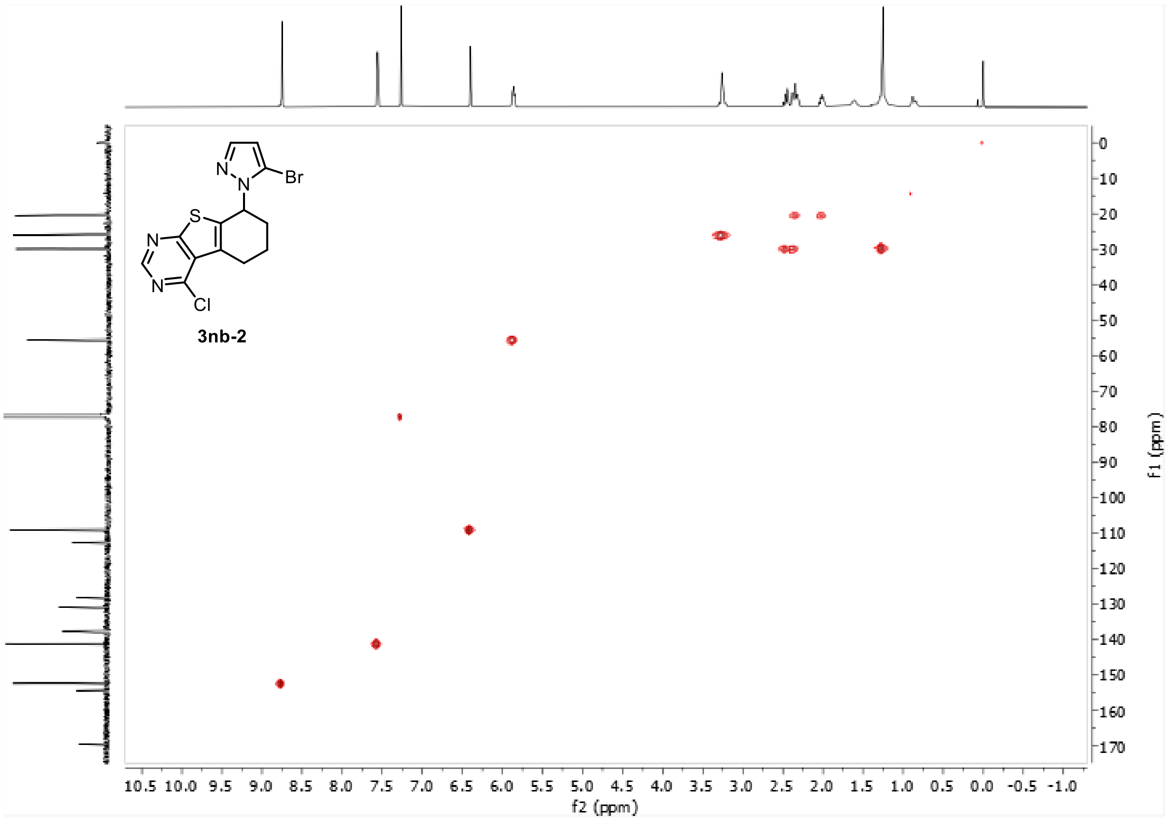
^{1}H NMR spectrum of **3nb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



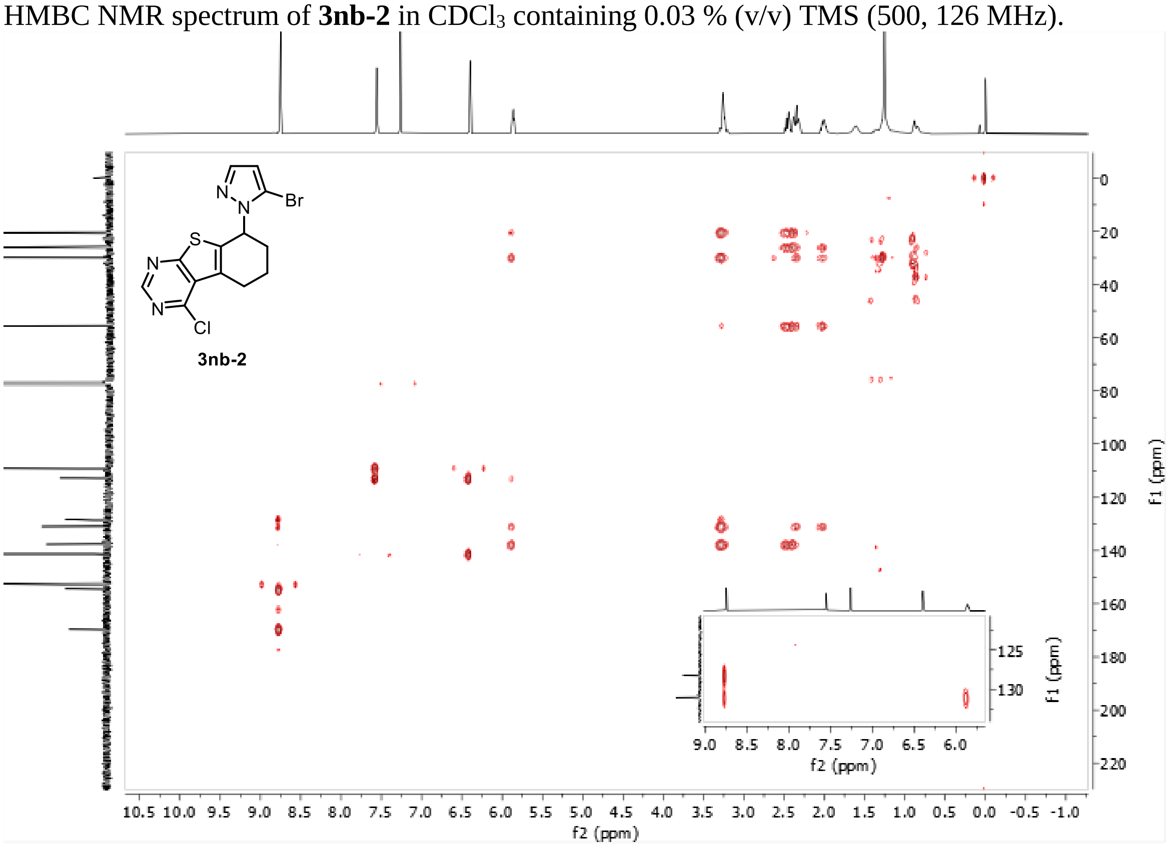
^{13}C NMR spectrum of **3nb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



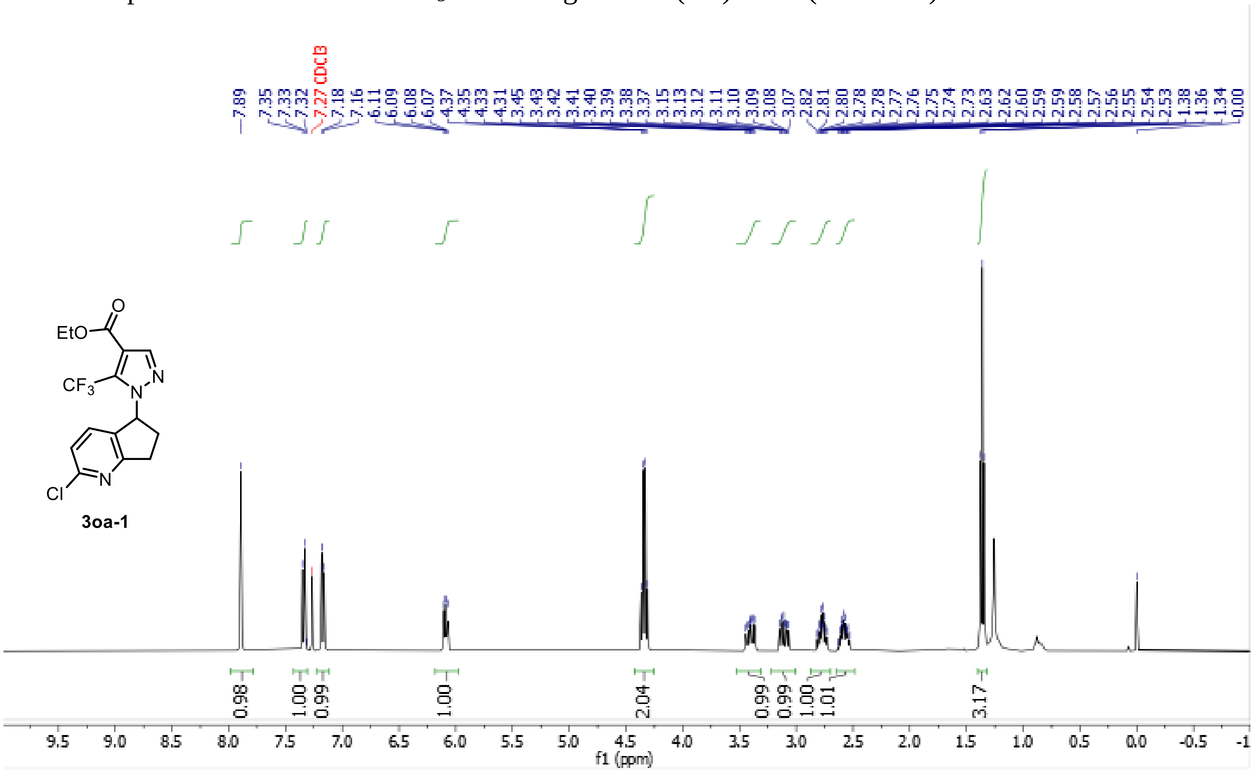
HSQC NMR spectrum of **3nb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



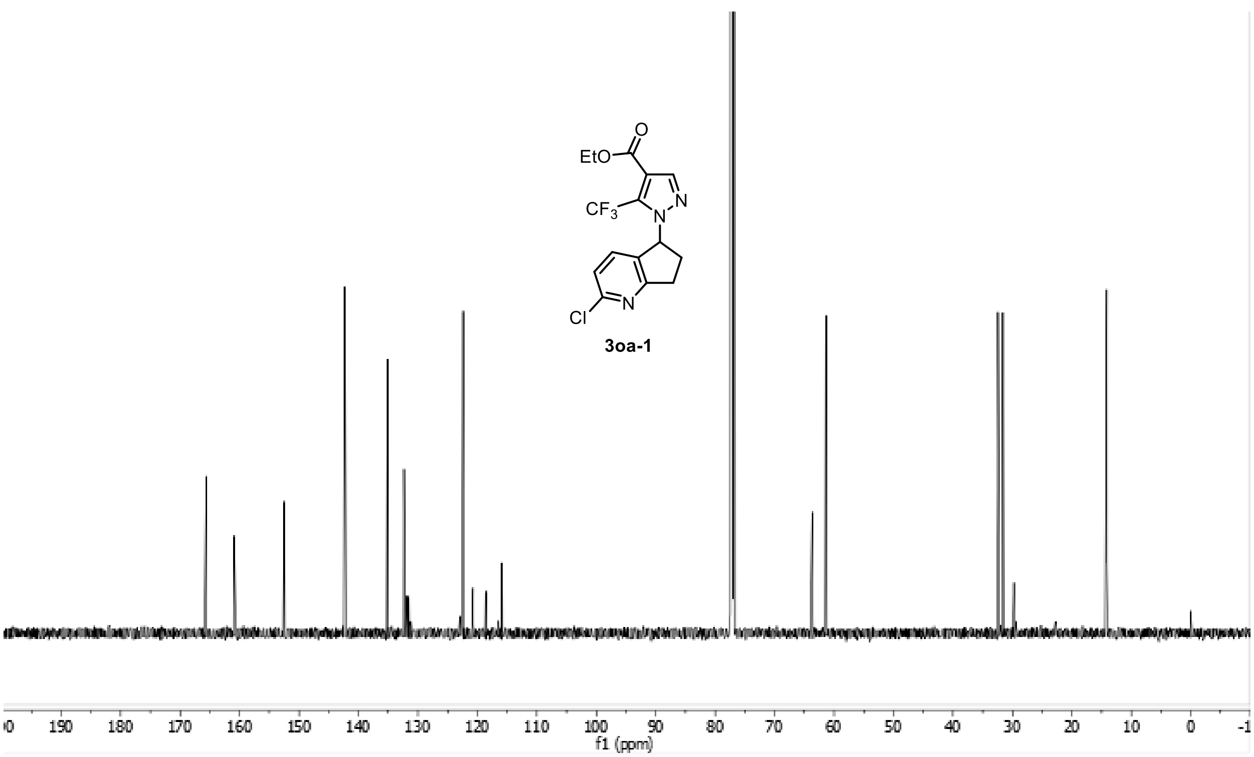
HMBC NMR spectrum of **3nb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



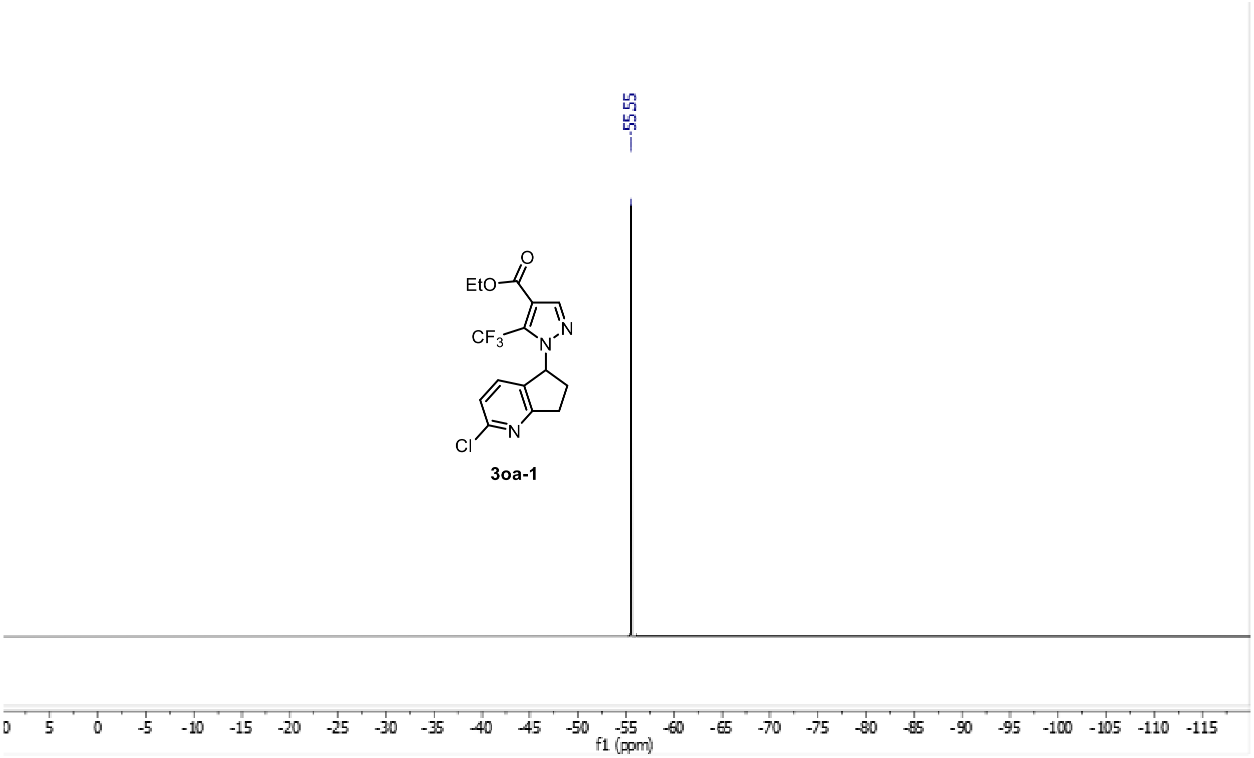
[1]H NMR spectrum of **3oa-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



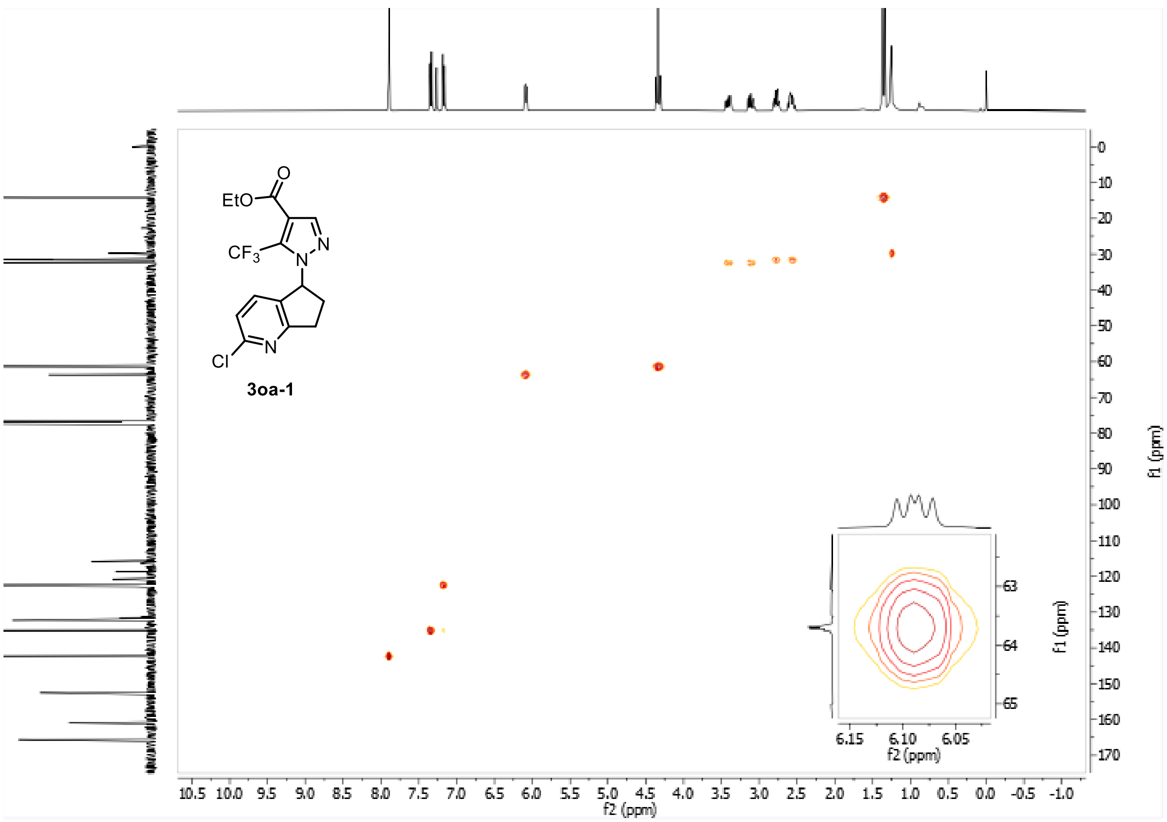
[13]C NMR spectrum of **3oa-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



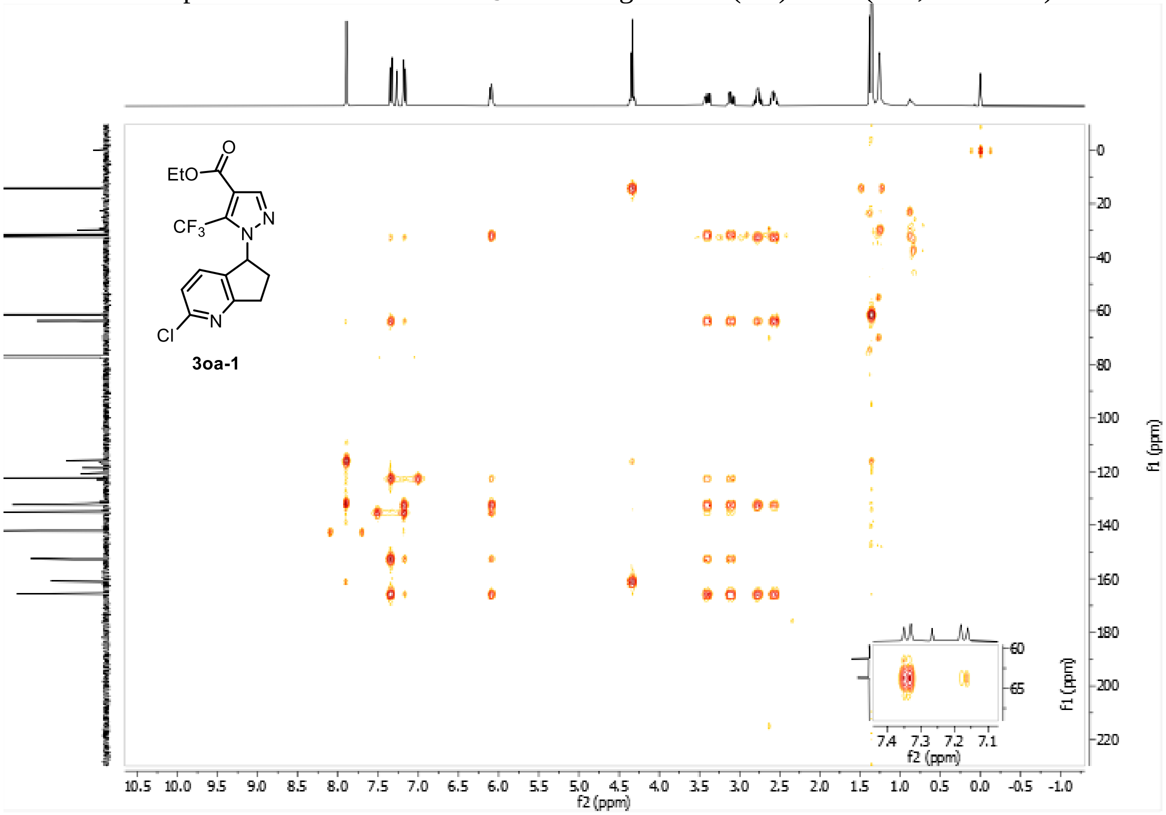
^{19}F NMR spectrum of **3oa-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



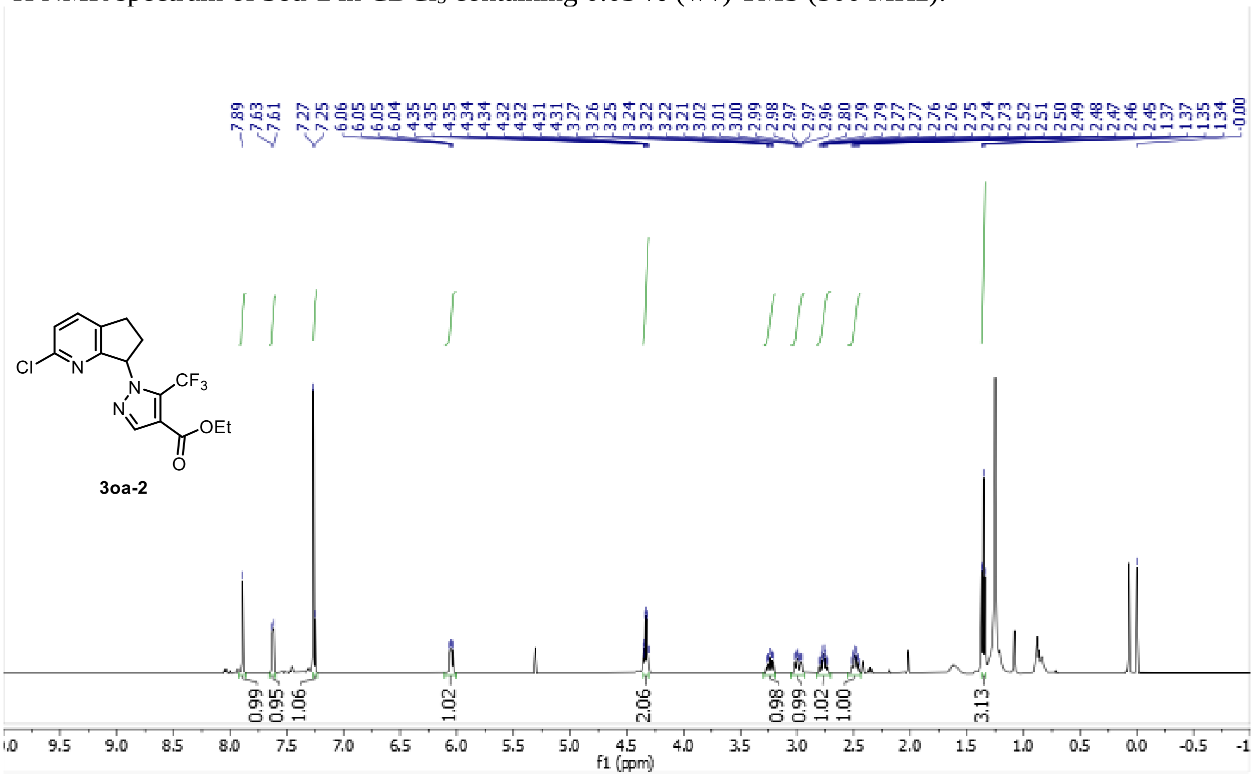
HSQC NMR spectrum of **3oa-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



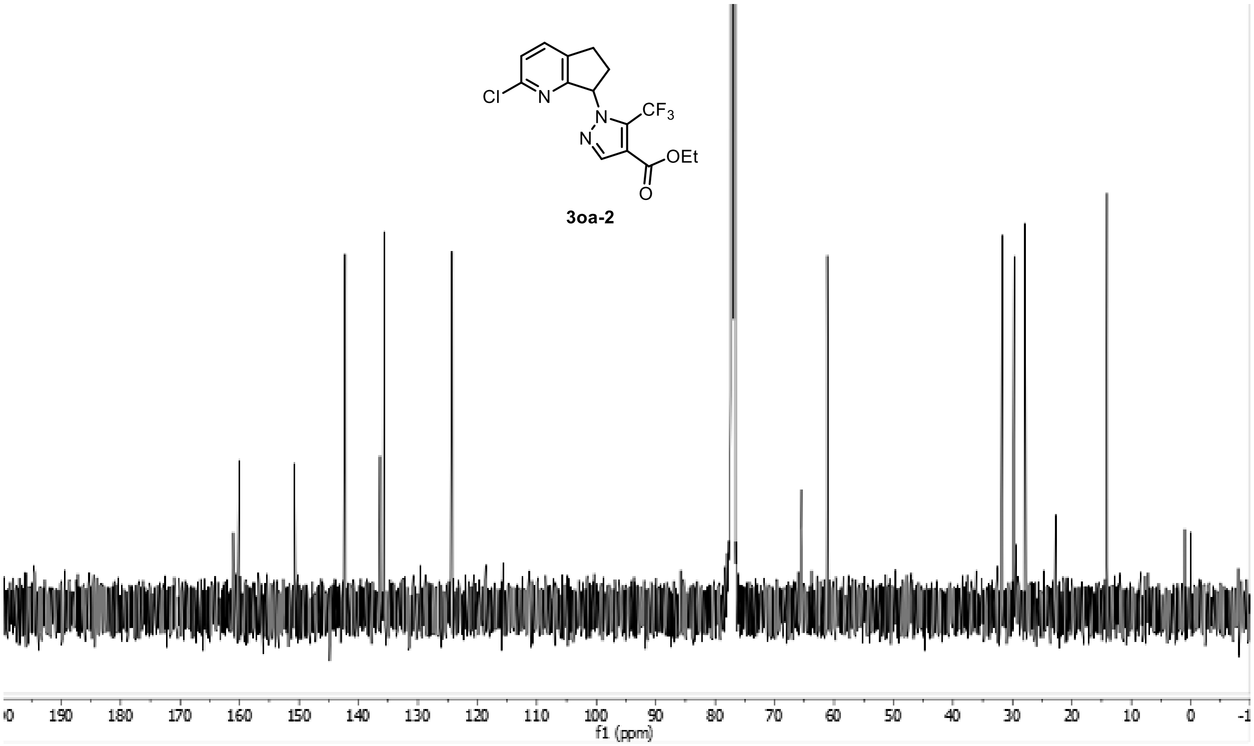
HMBC NMR spectrum of **3oa-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



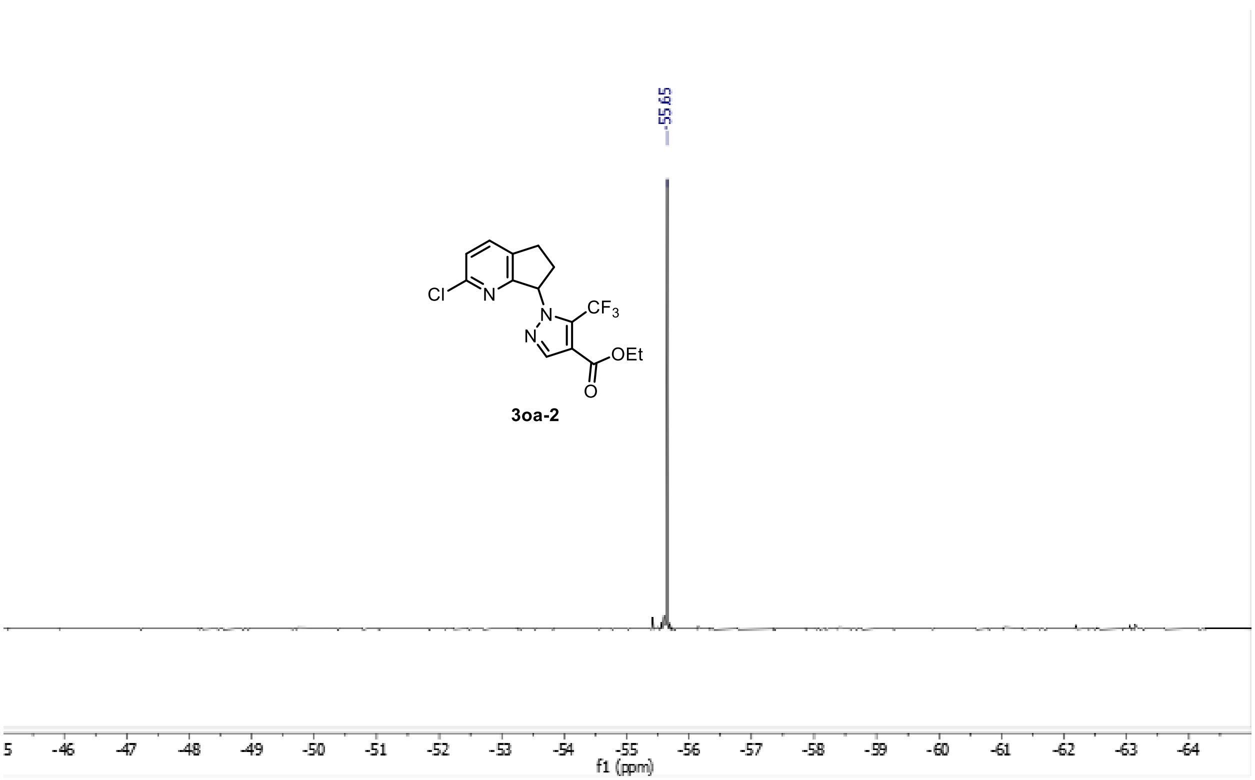
^{1}H NMR spectrum of **3oa-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



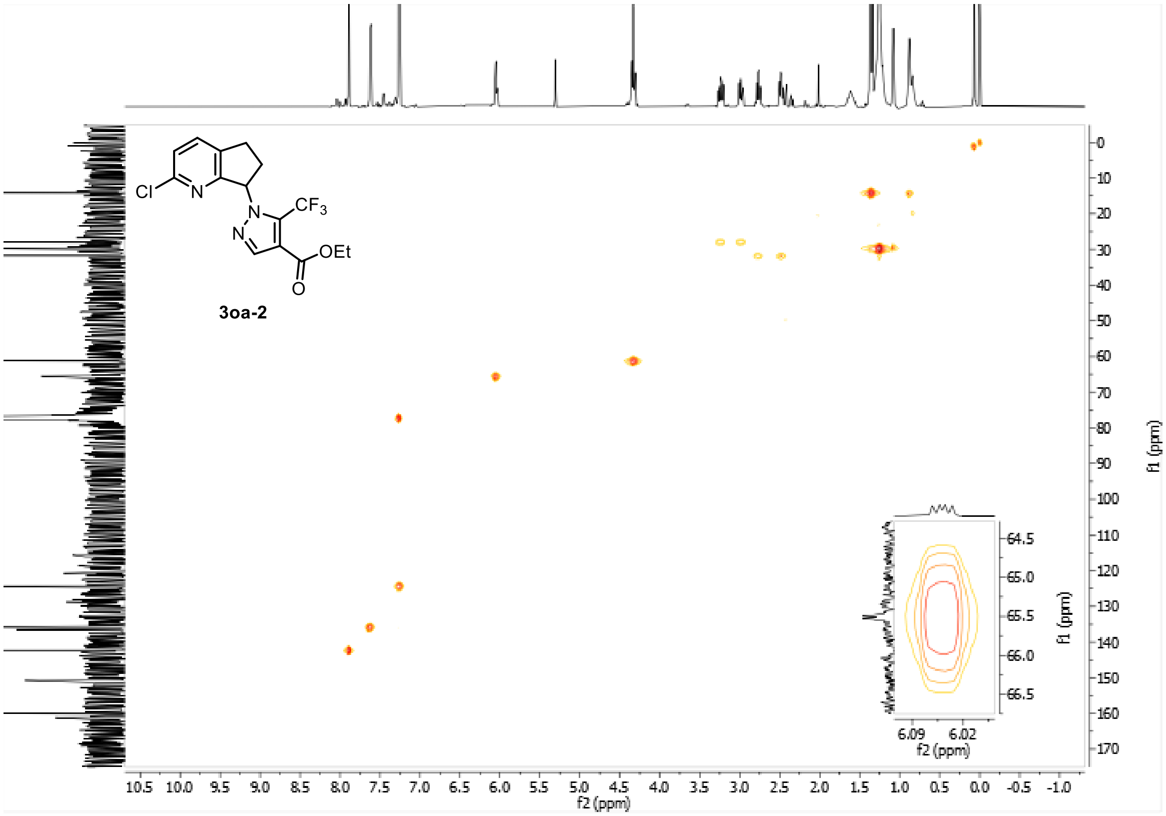
^{13}C NMR spectrum of **3oa-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



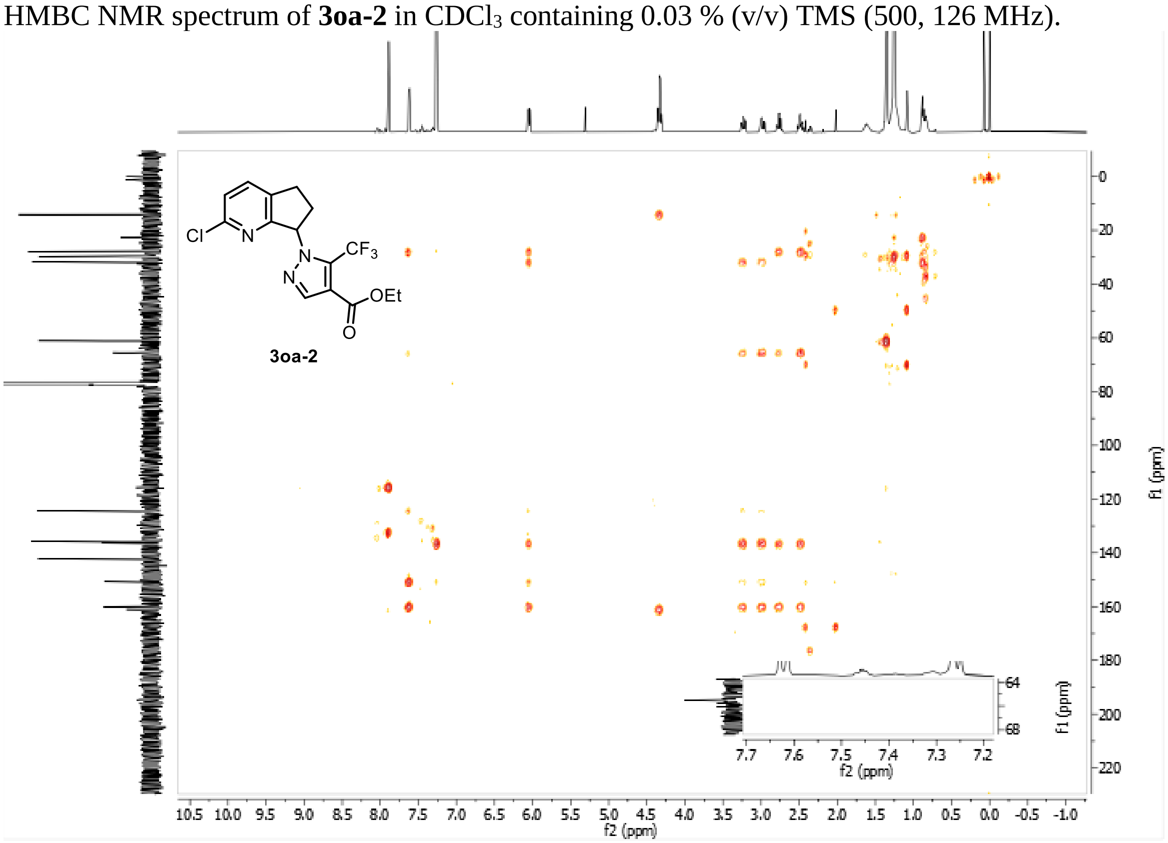
^{19}F NMR spectrum of **3oa-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



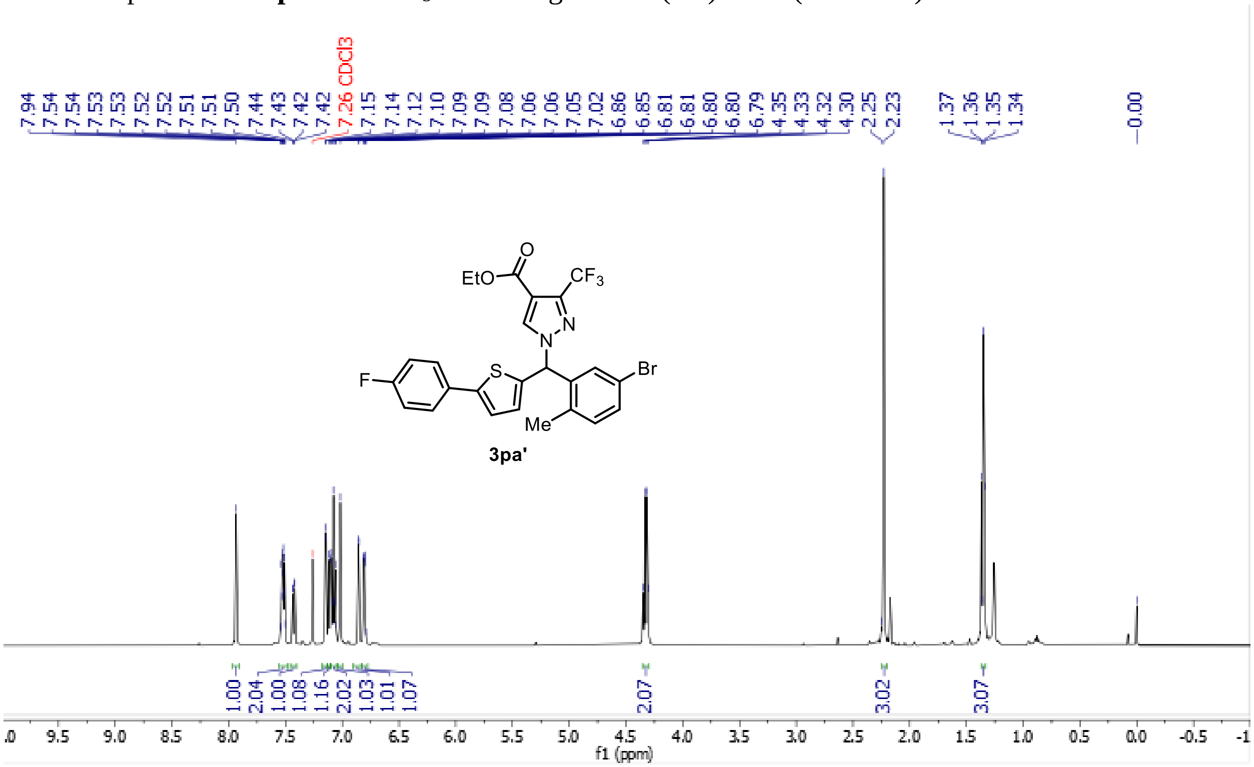
HSQC NMR spectrum of **3oa-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



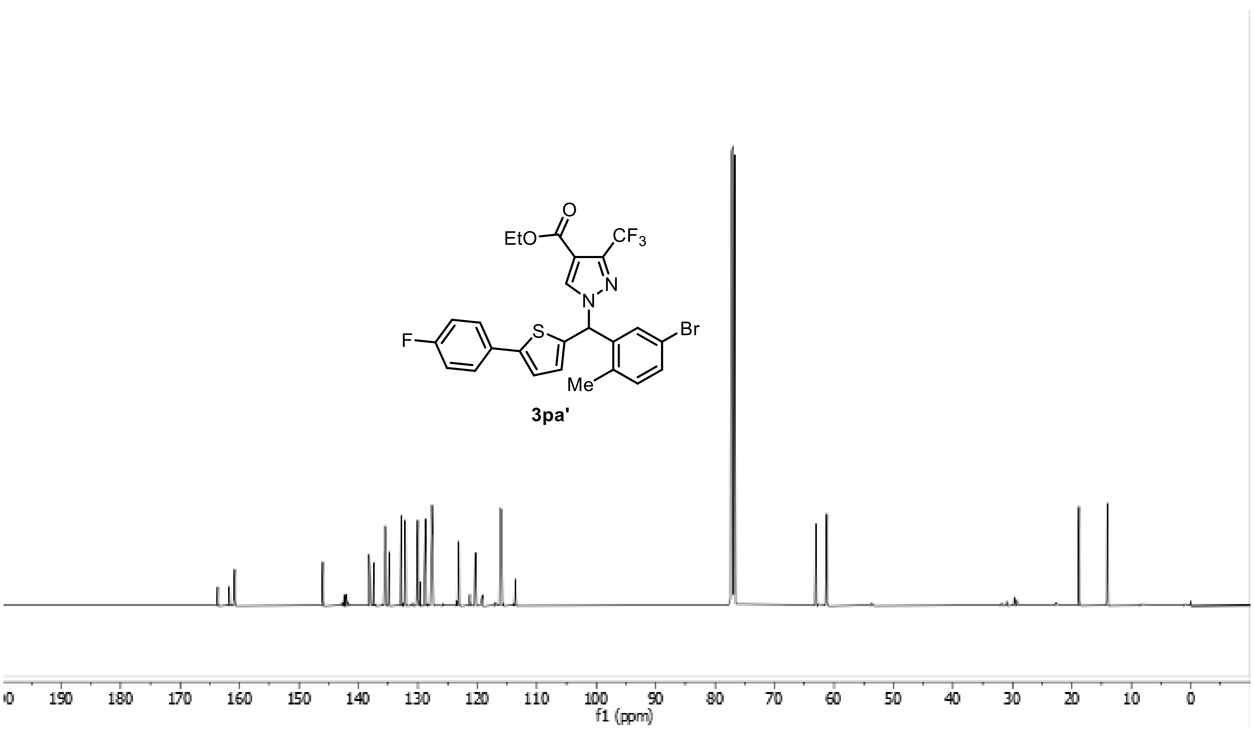
HMBC NMR spectrum of **3oa-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



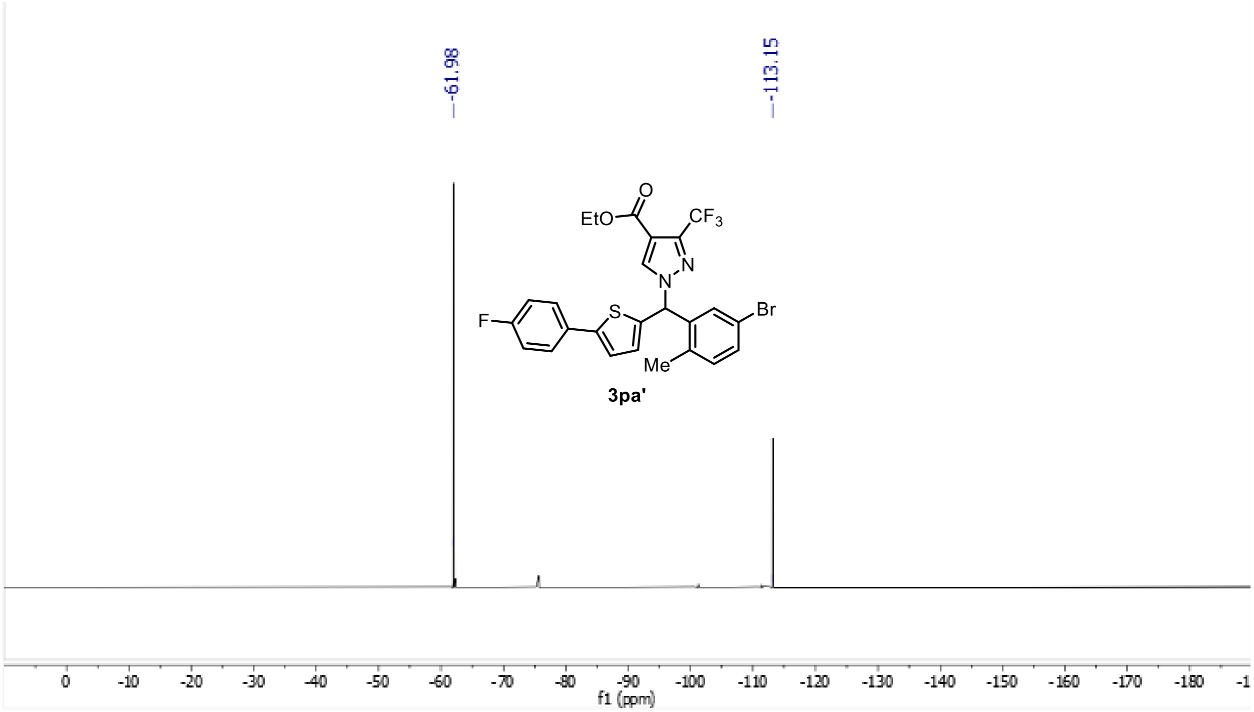
^{1}H NMR spectrum of **3pa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



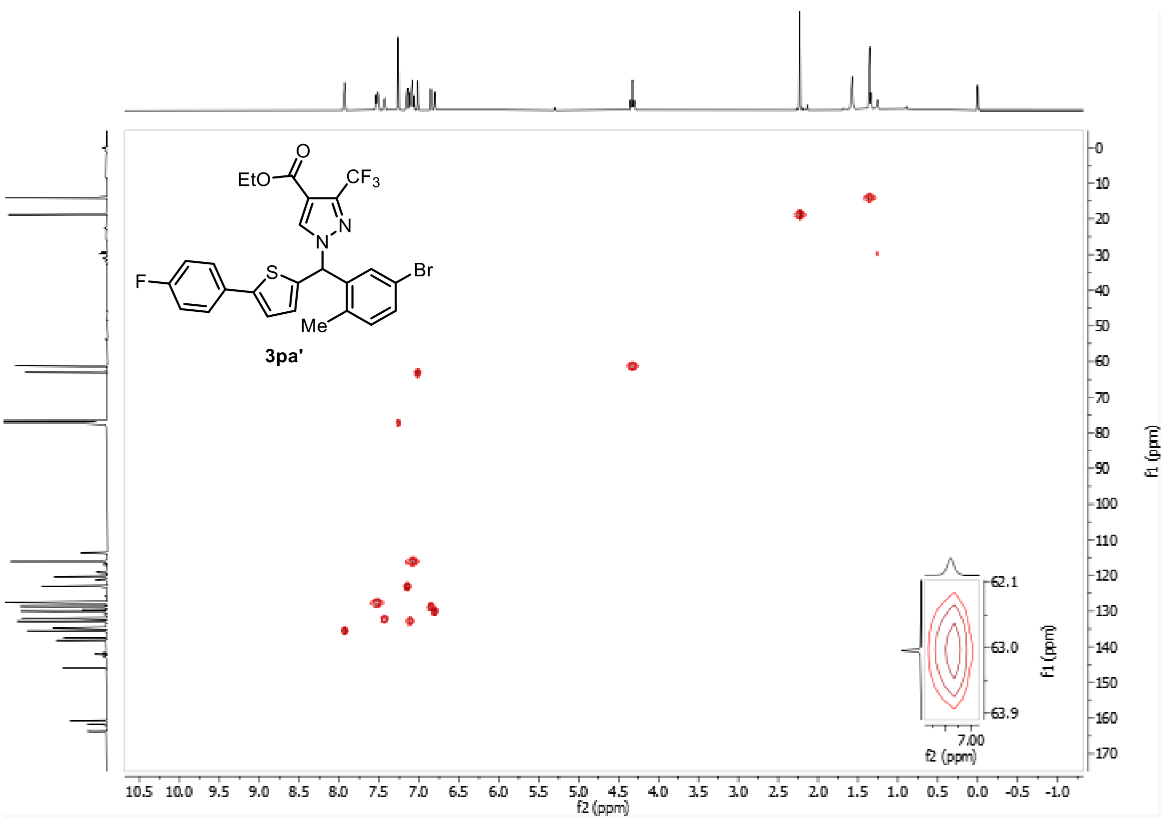
^{13}C NMR spectrum of **3pa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



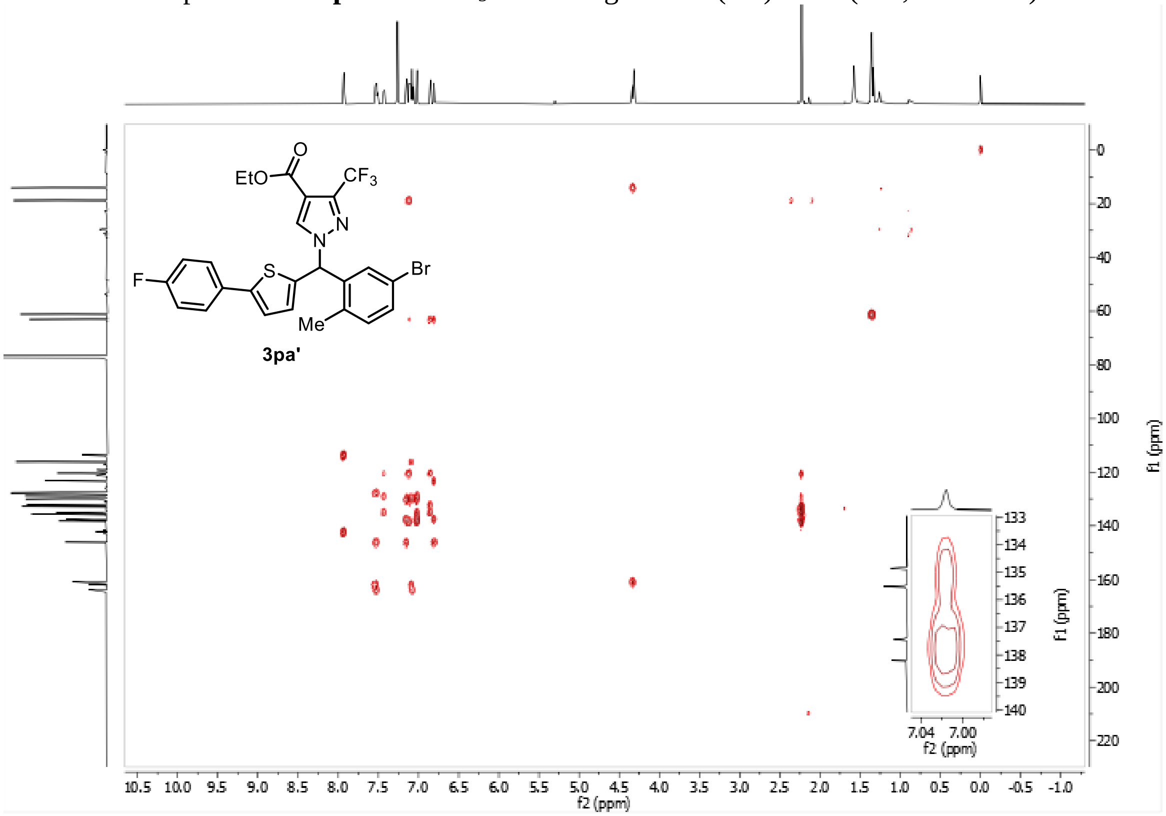
^{19}F NMR spectrum of **3pa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



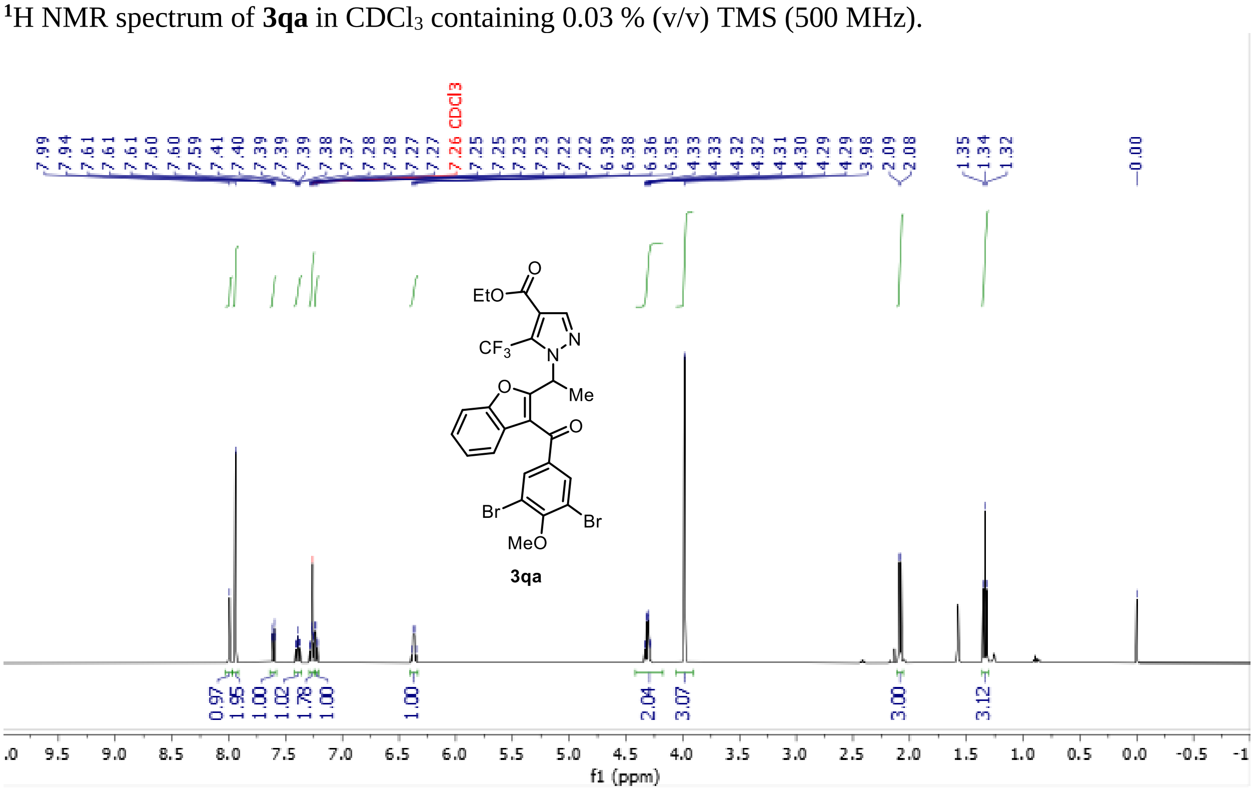
HSQC NMR spectrum of **3pa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



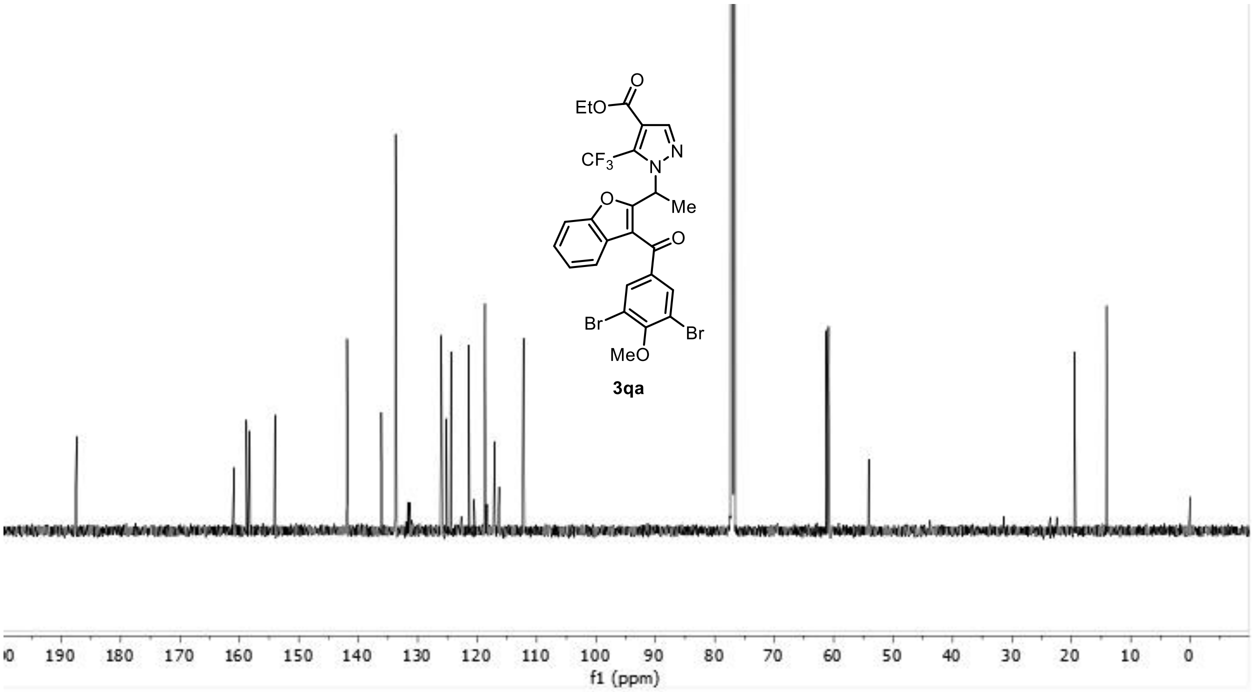
HMBC NMR spectrum of **3pa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



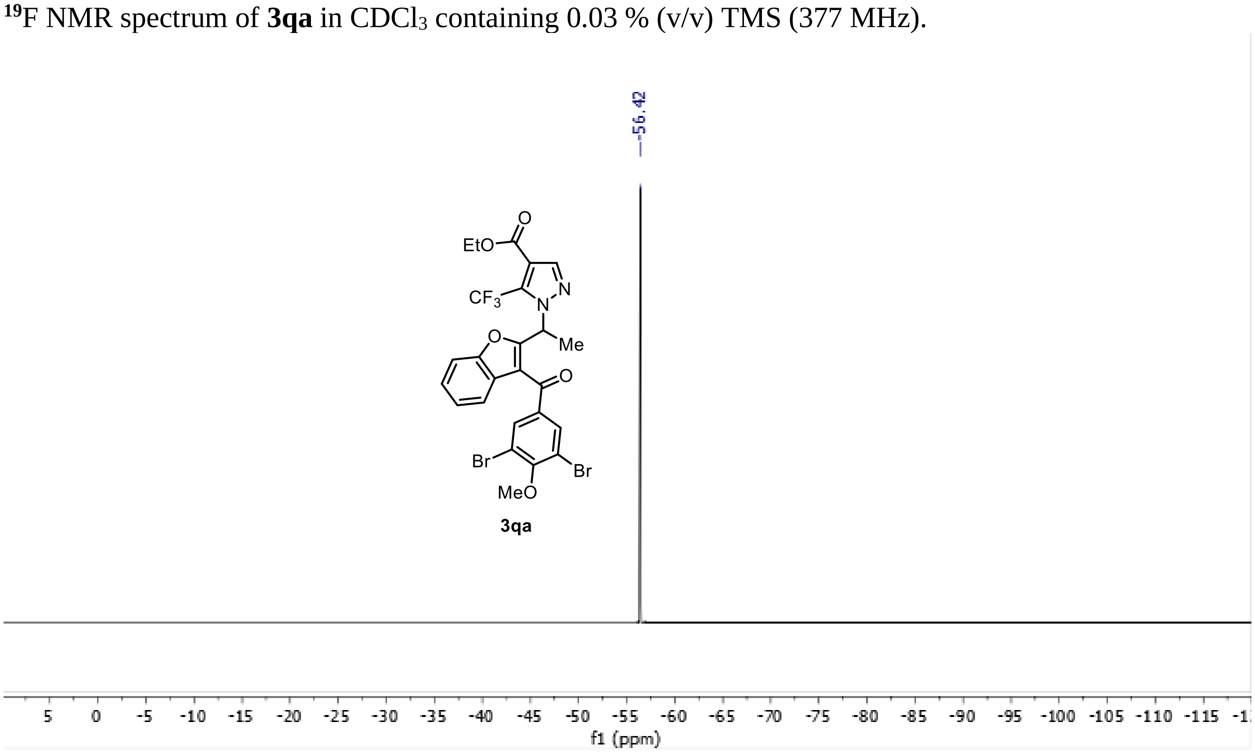
[1]H NMR spectrum of **3qa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



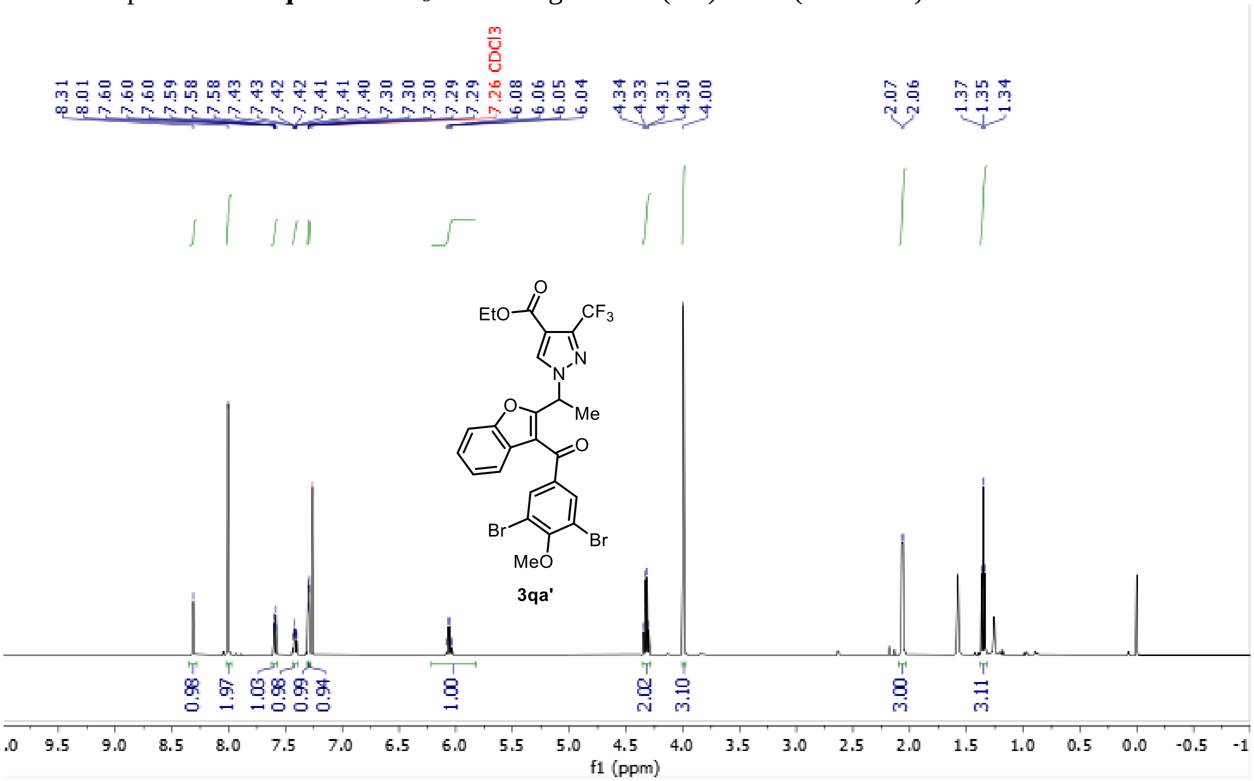
^{13}C NMR spectrum of **3qa** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



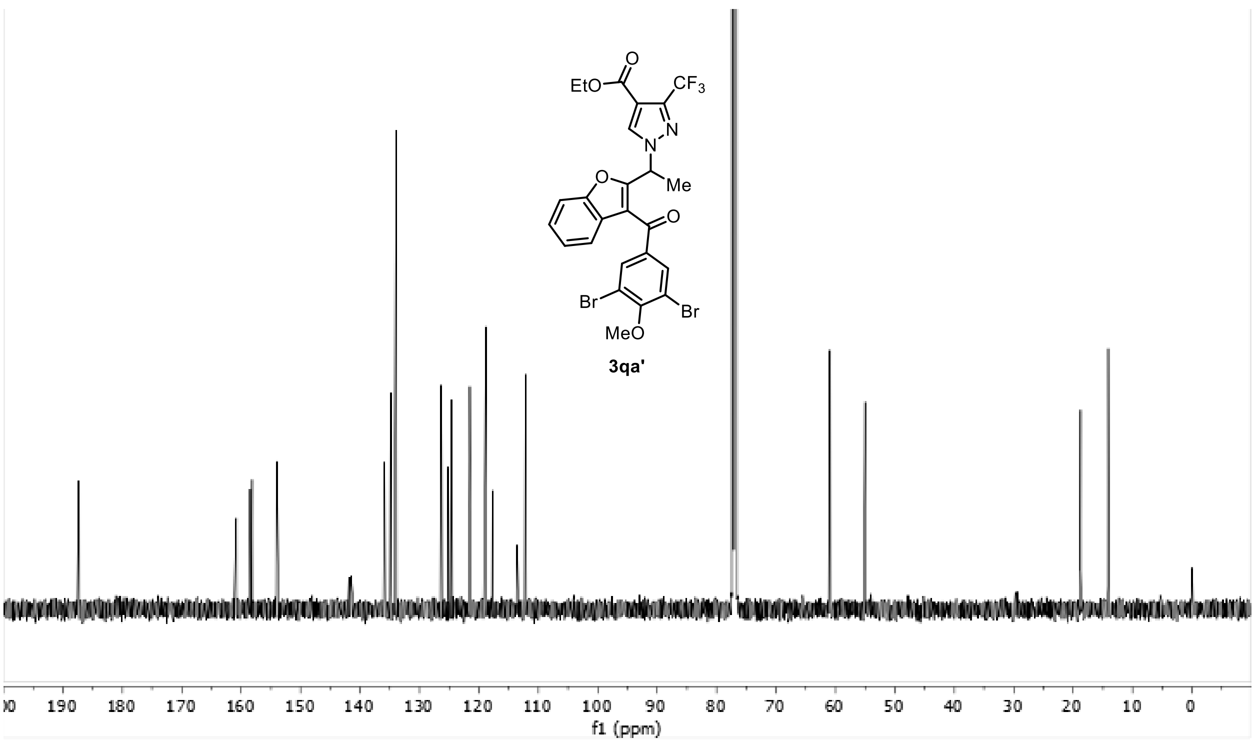
^{19}F NMR spectrum of **3qa** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



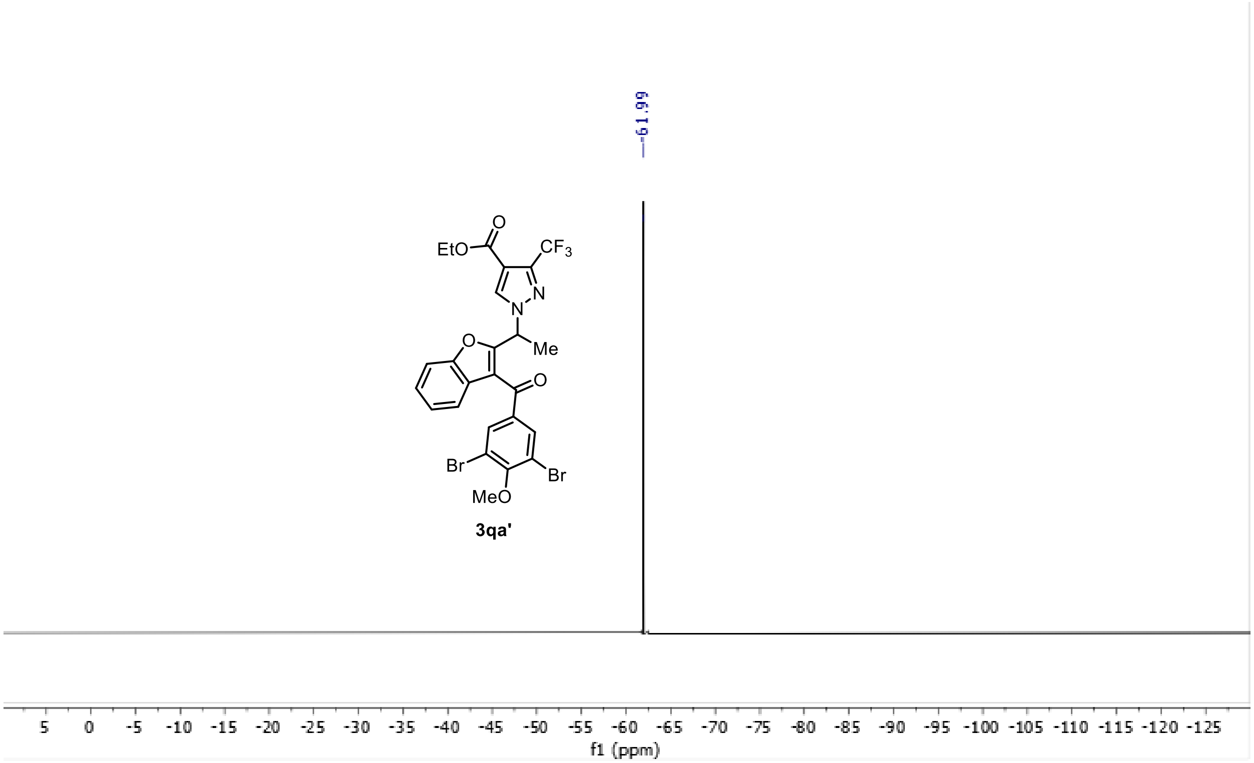
[1]H NMR spectrum of **3qa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



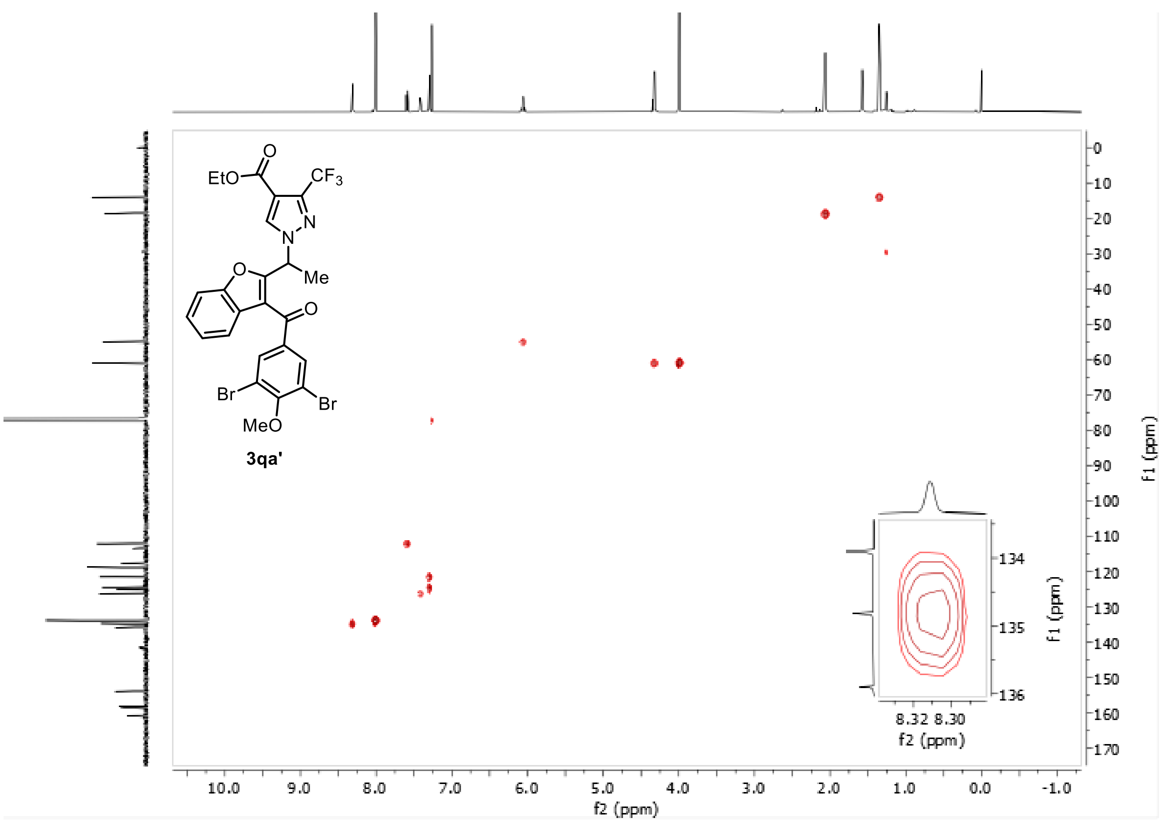
[13]C NMR spectrum of **3qa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



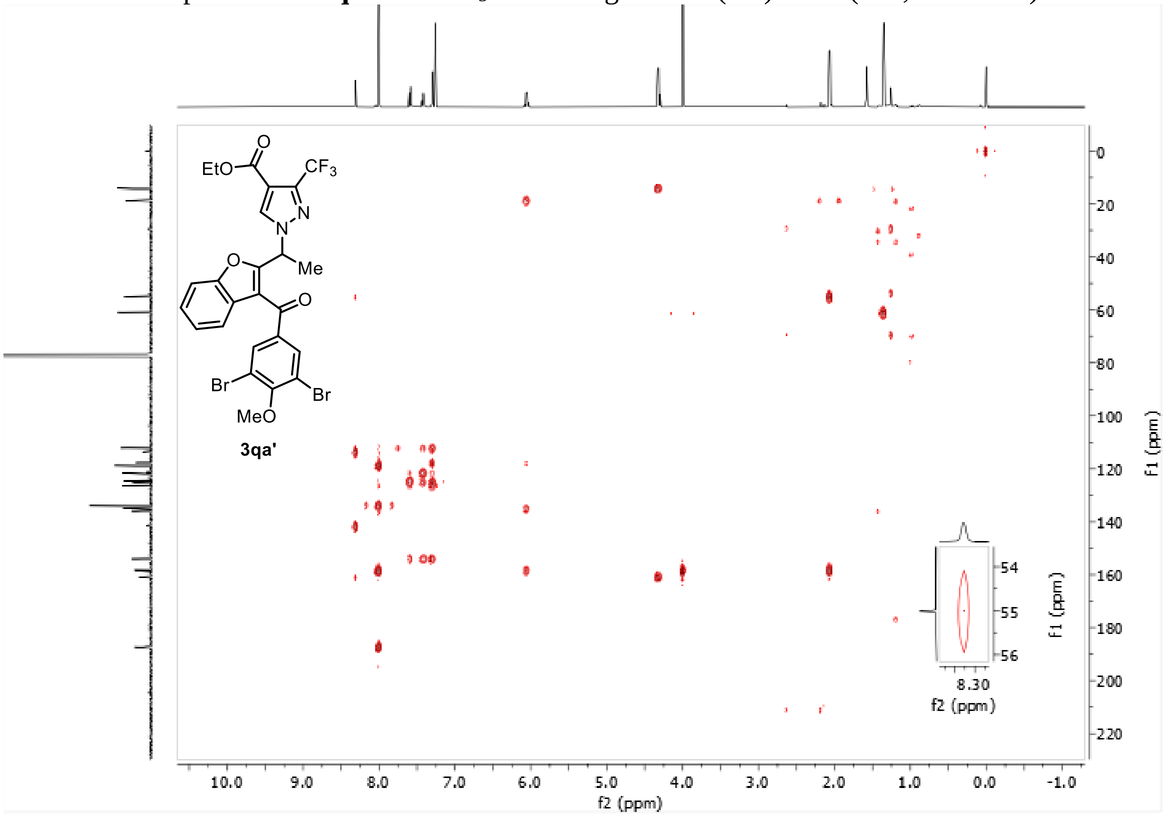
[19]F NMR spectrum of **3qa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



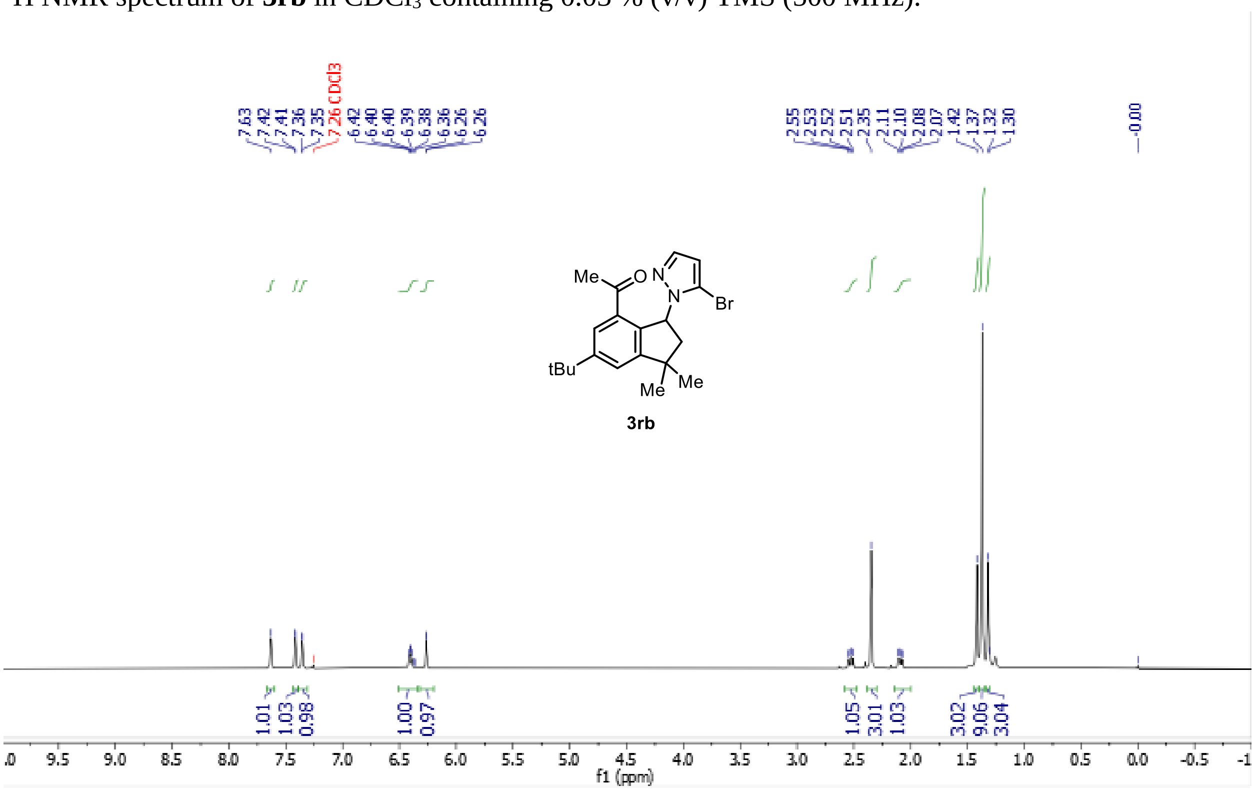
HSQC NMR spectrum of **3qa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



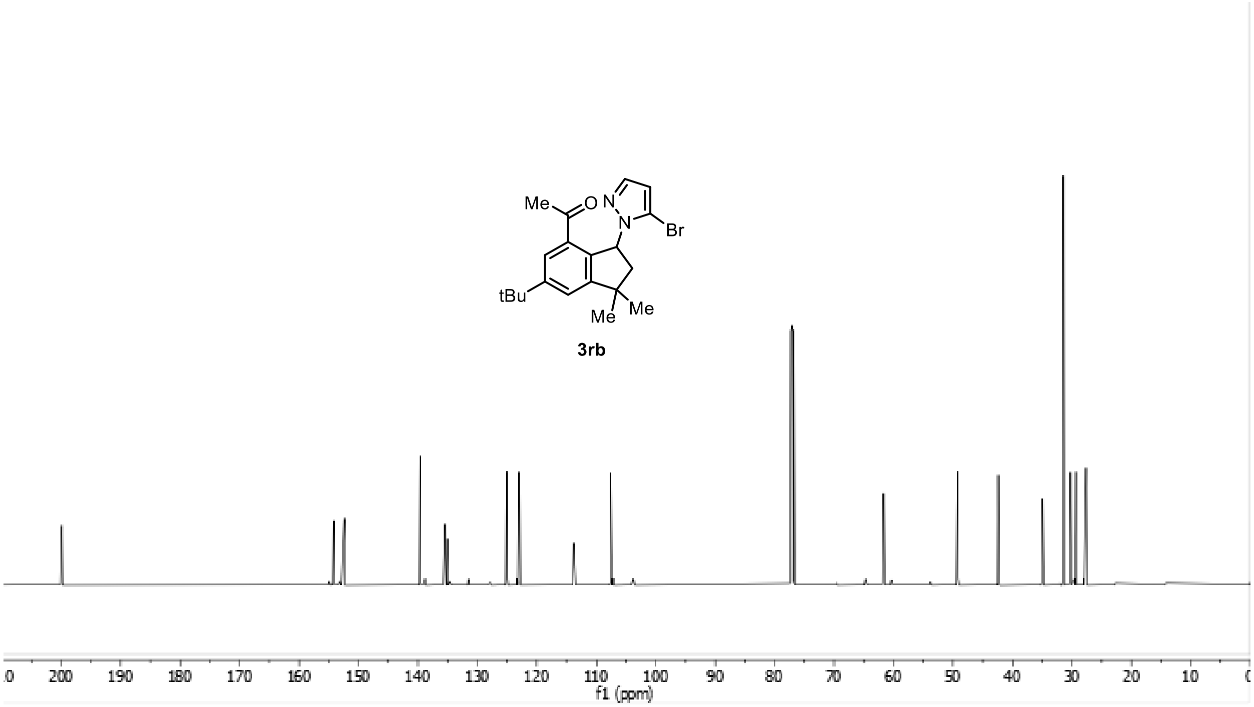
HMBC NMR spectrum of **3qa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



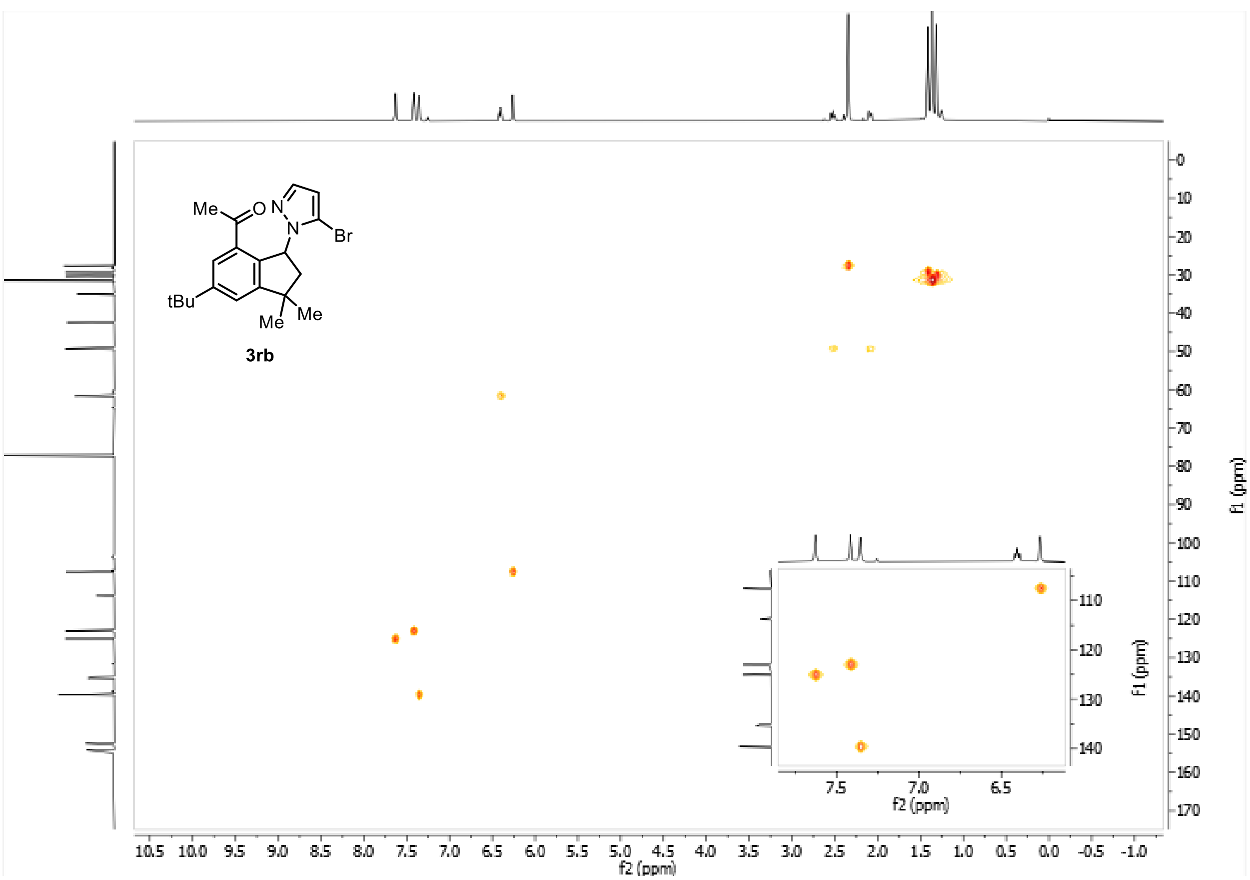
[1]H NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



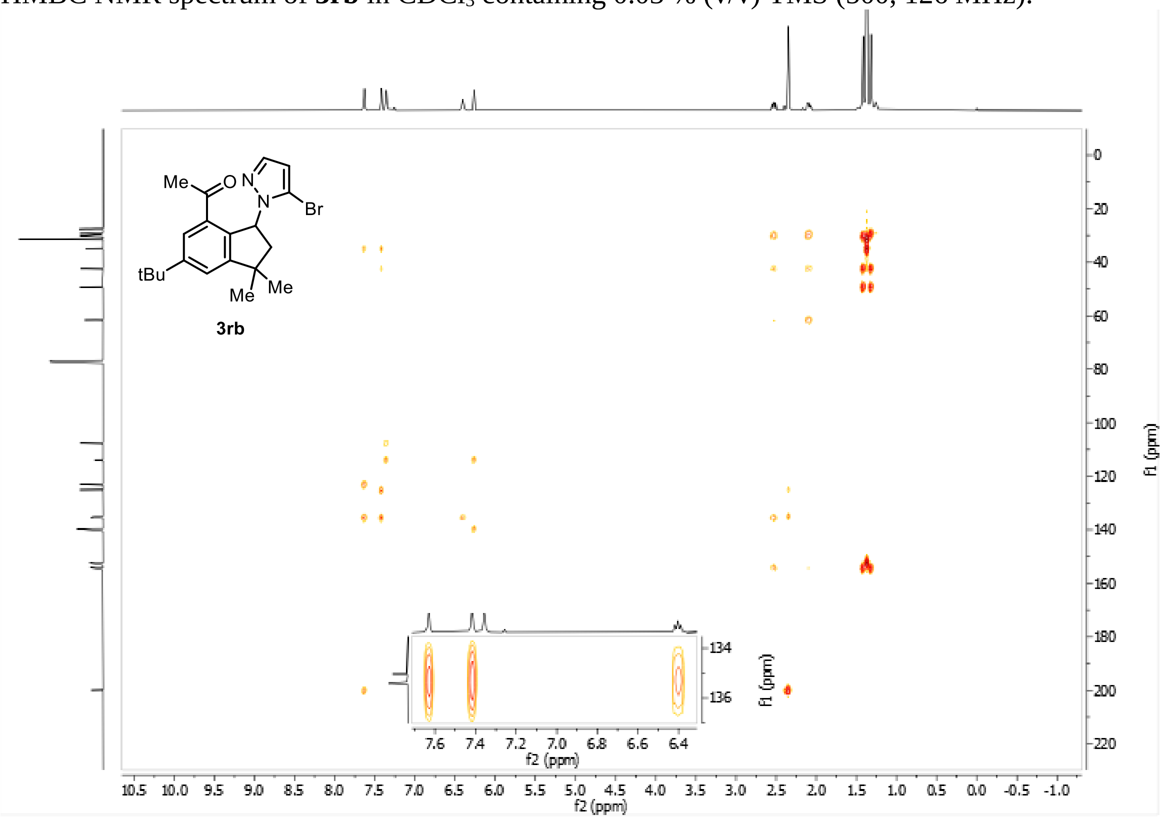
^{13}C NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



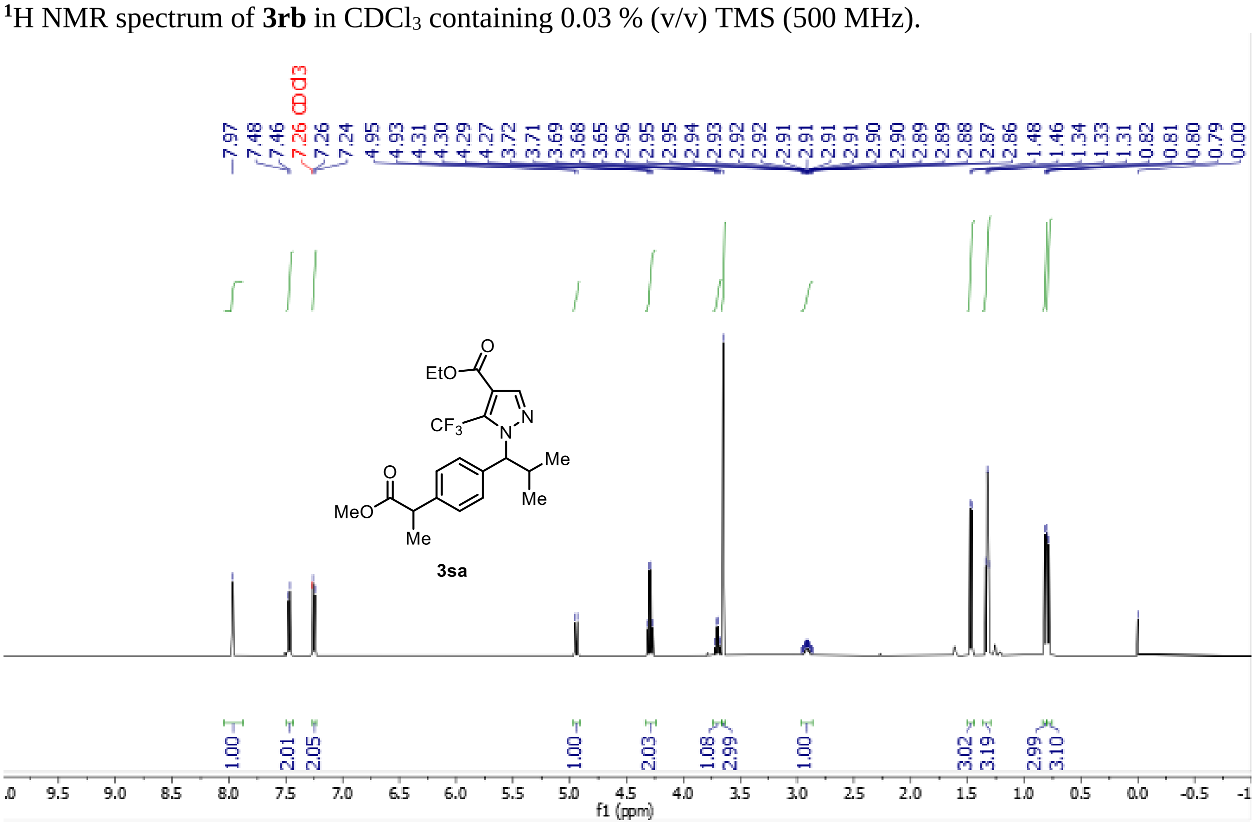
HSQC NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



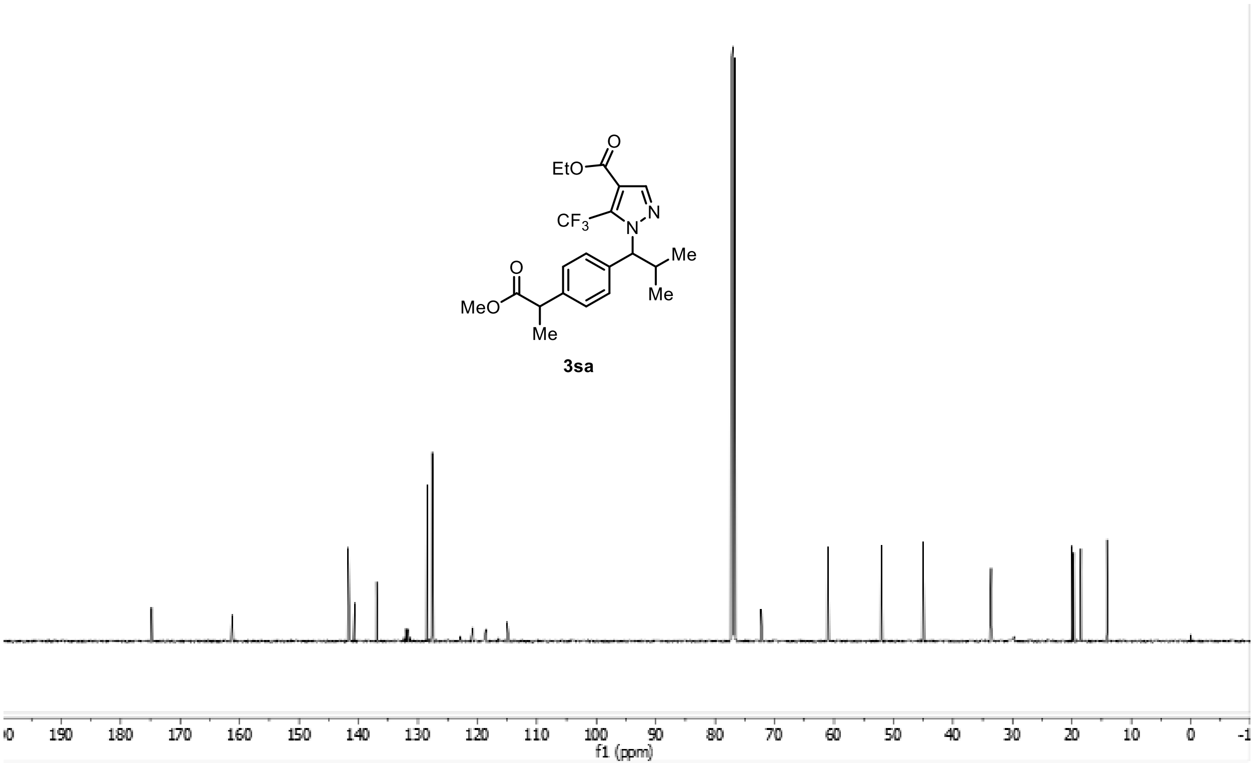
HMBC NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



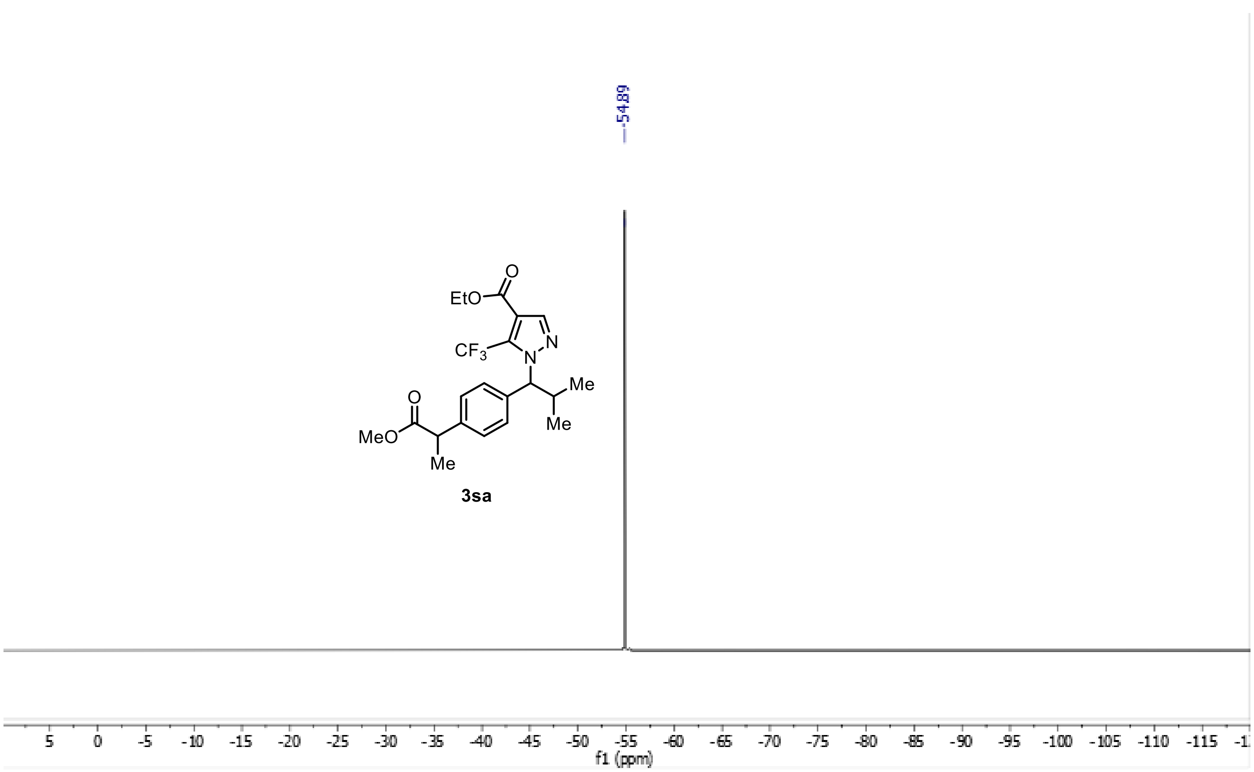
^{1}H NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



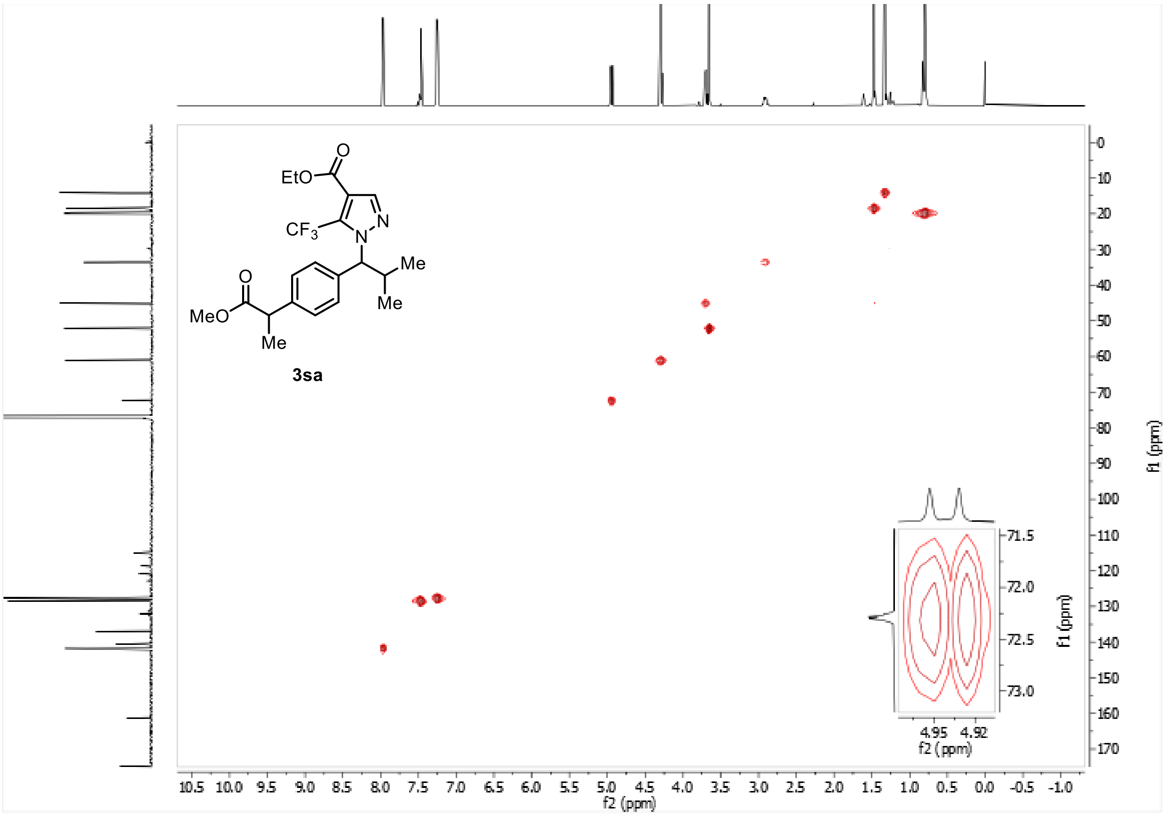
^{13}C NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



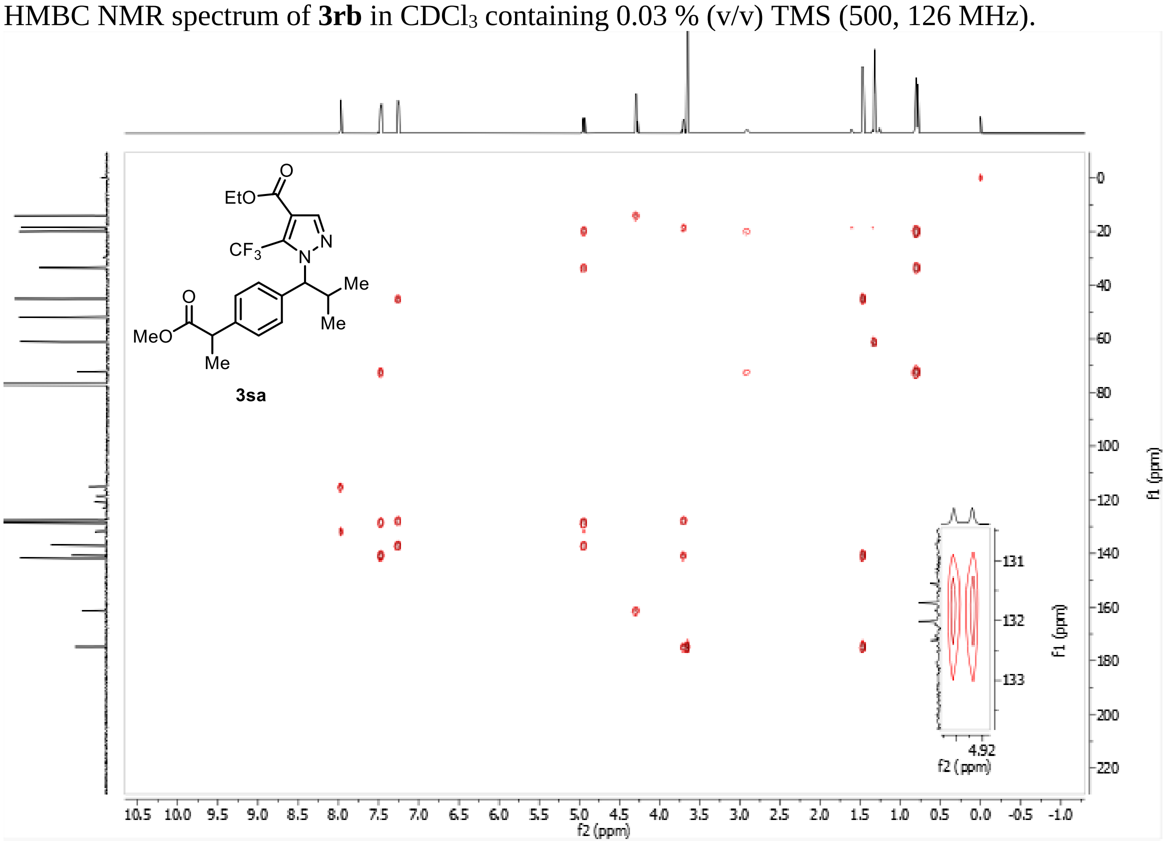
^{19}F NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



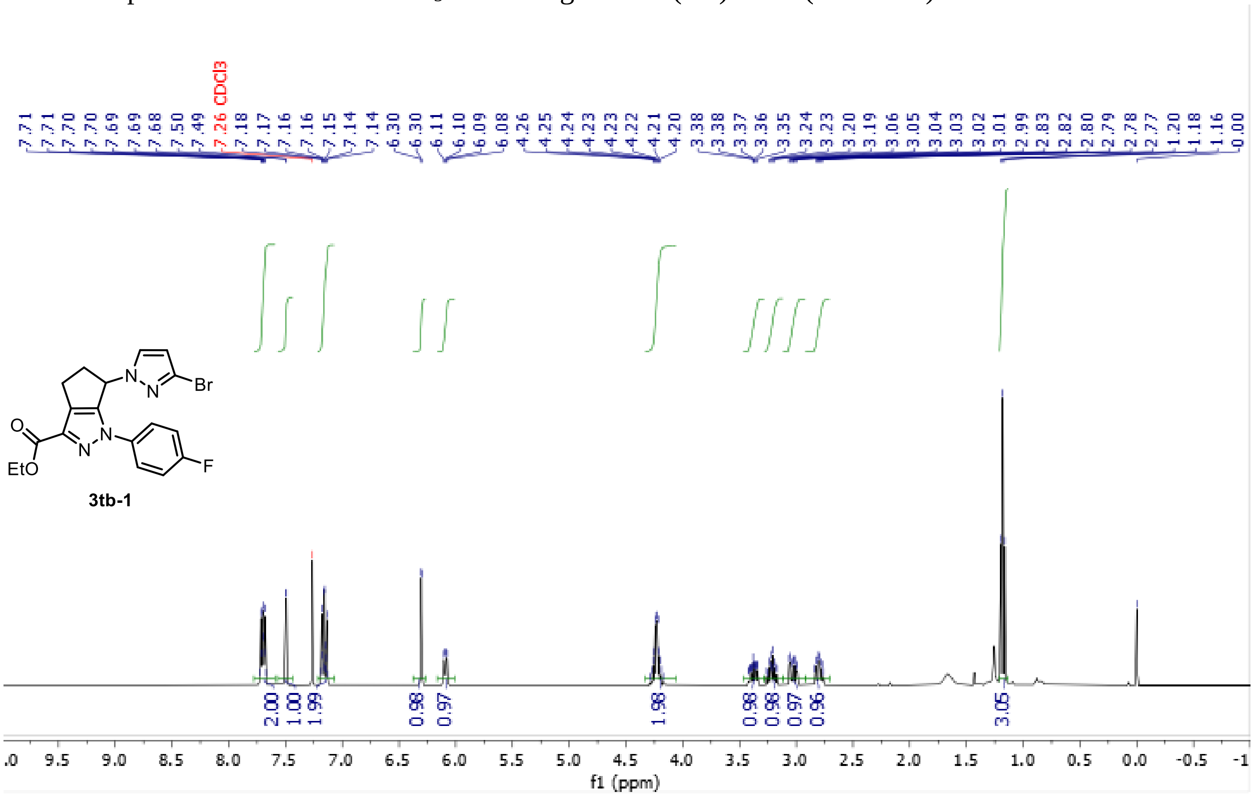
HSQC NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



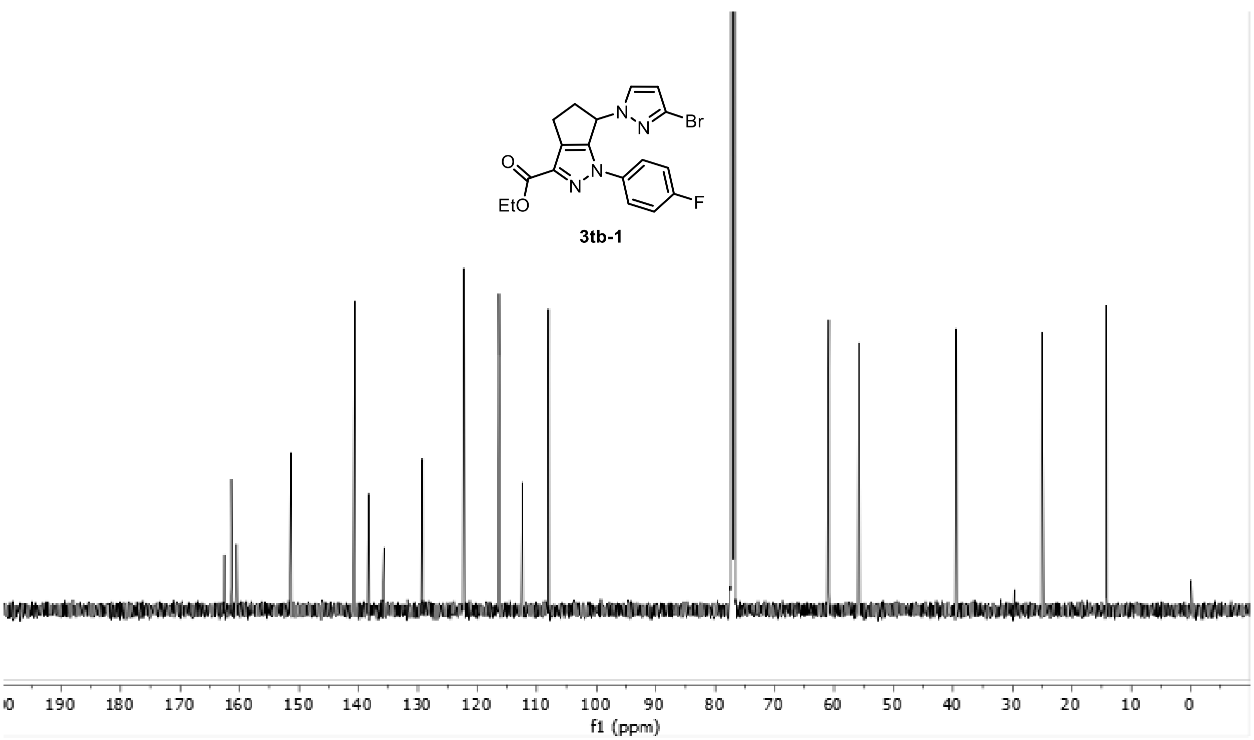
HMBC NMR spectrum of **3rb** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



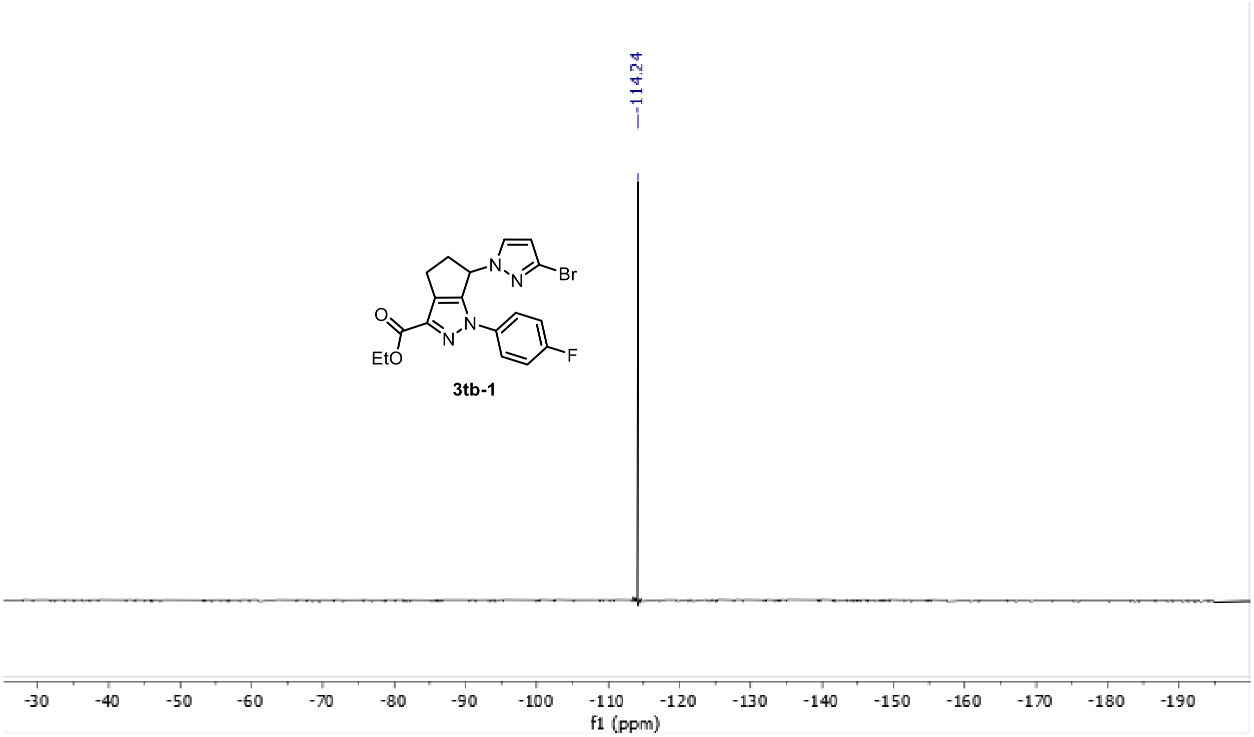
^{1}H NMR spectrum of **3tb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



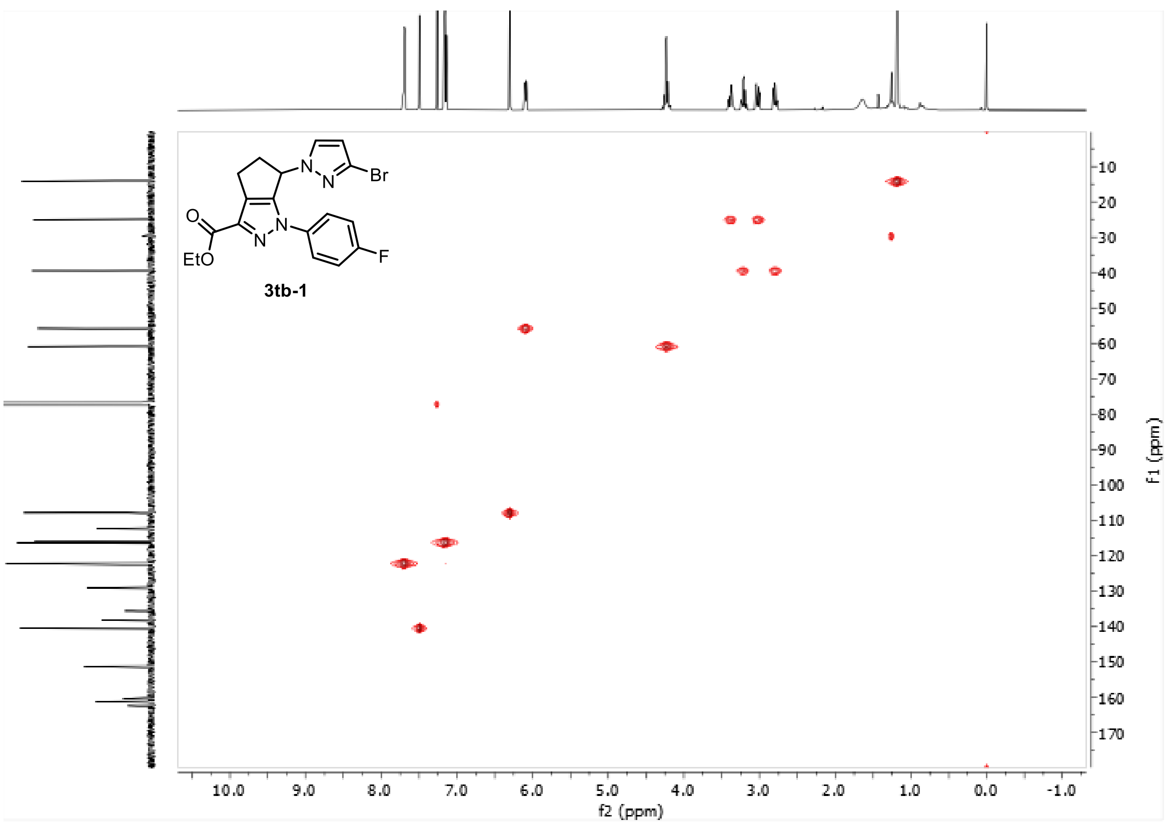
^{13}C NMR spectrum of **3tb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



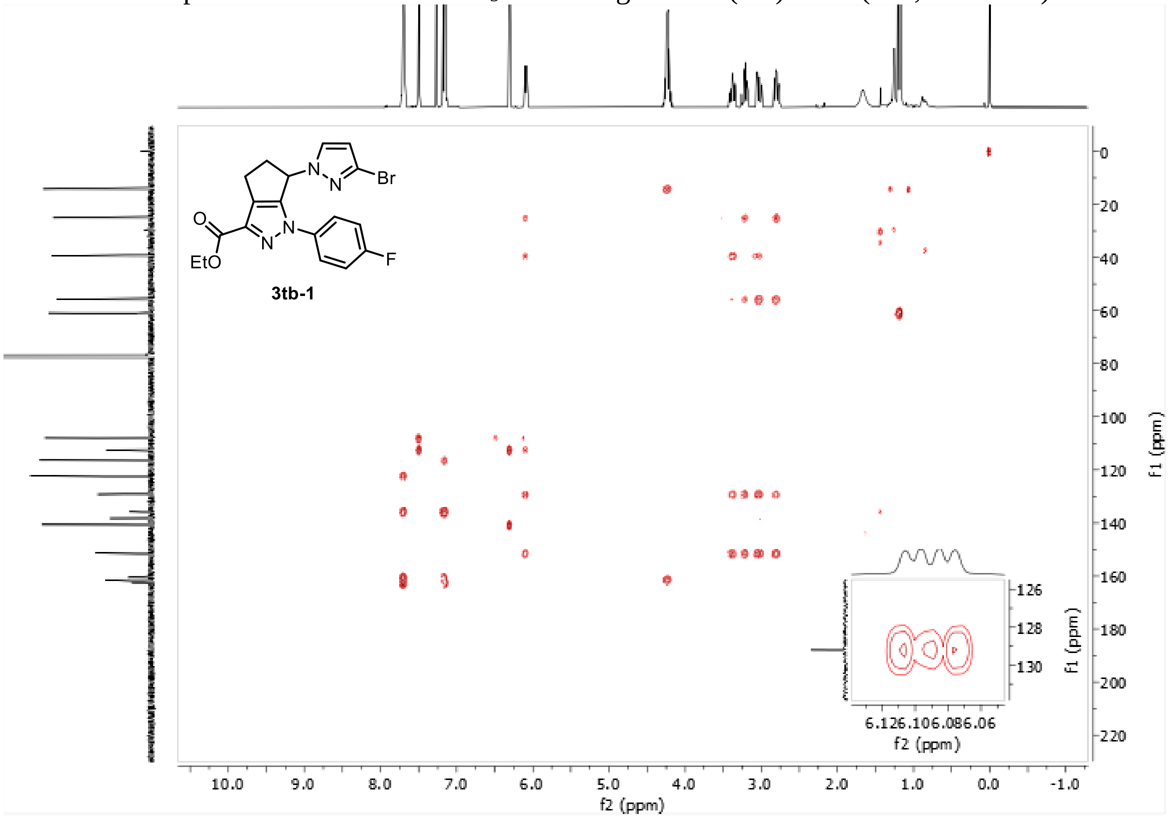
^{19}F NMR spectrum of **3tb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



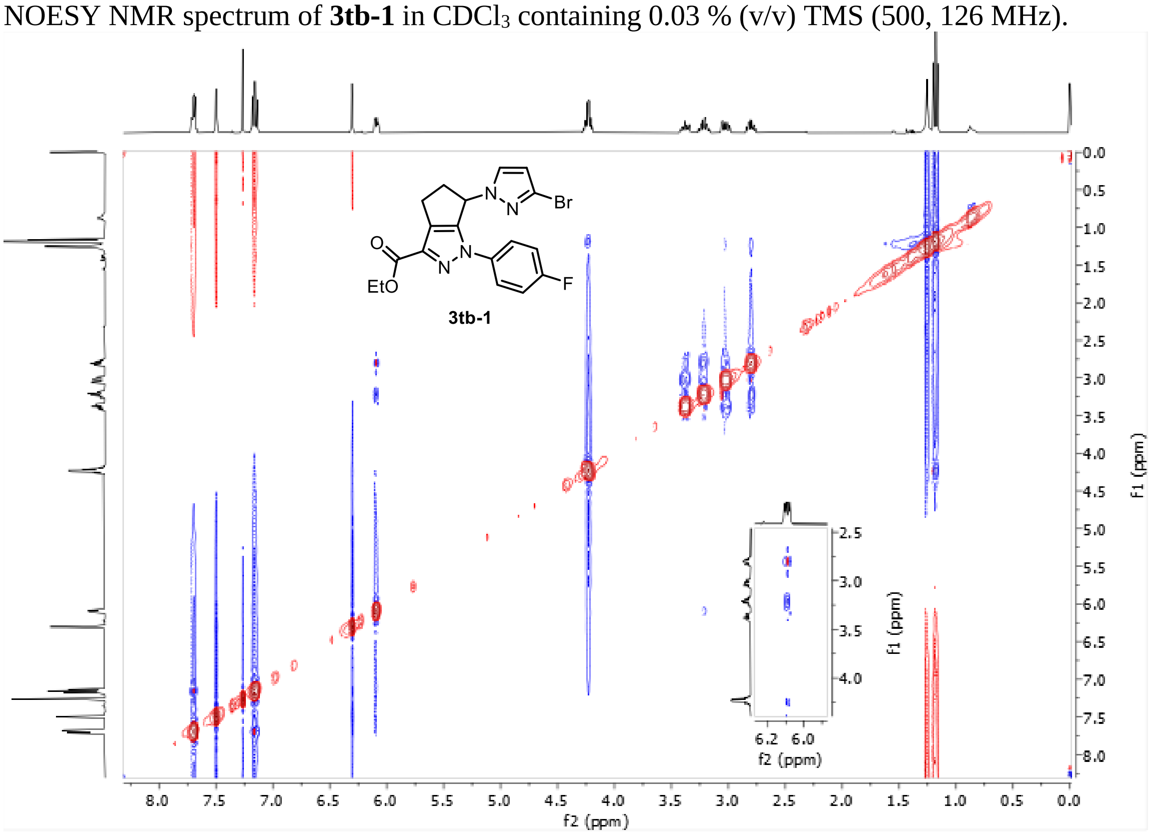
HSQC NMR spectrum of **3tb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



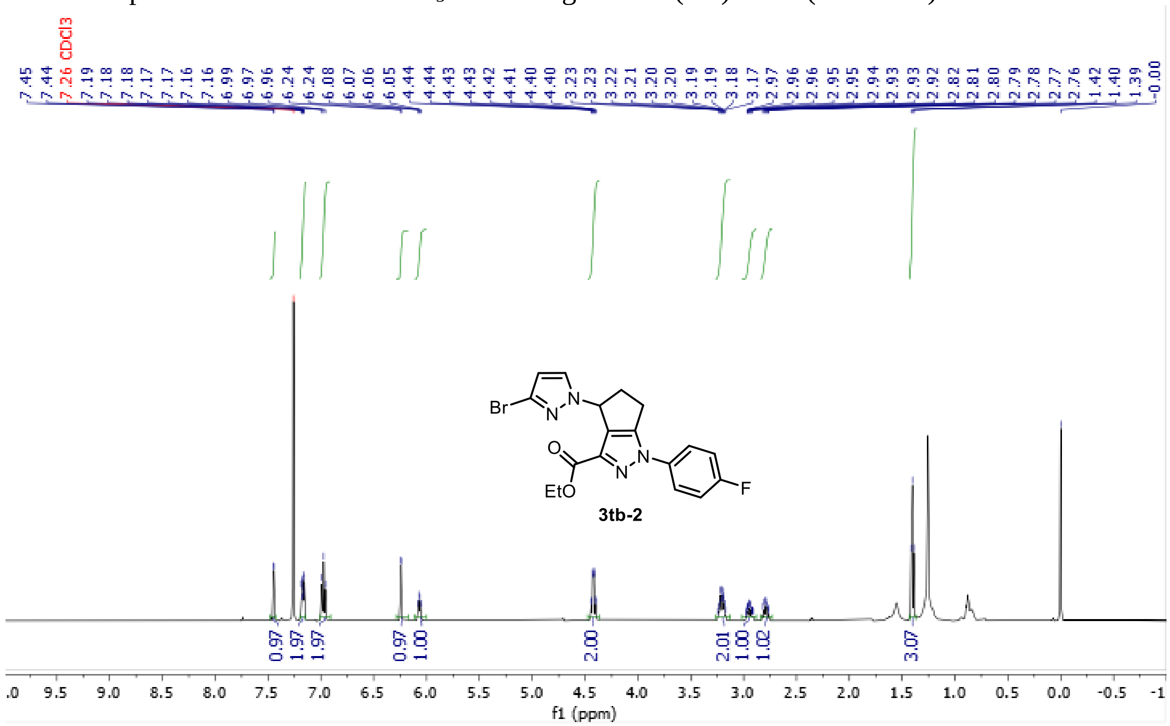
HMBC NMR spectrum of **3tb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



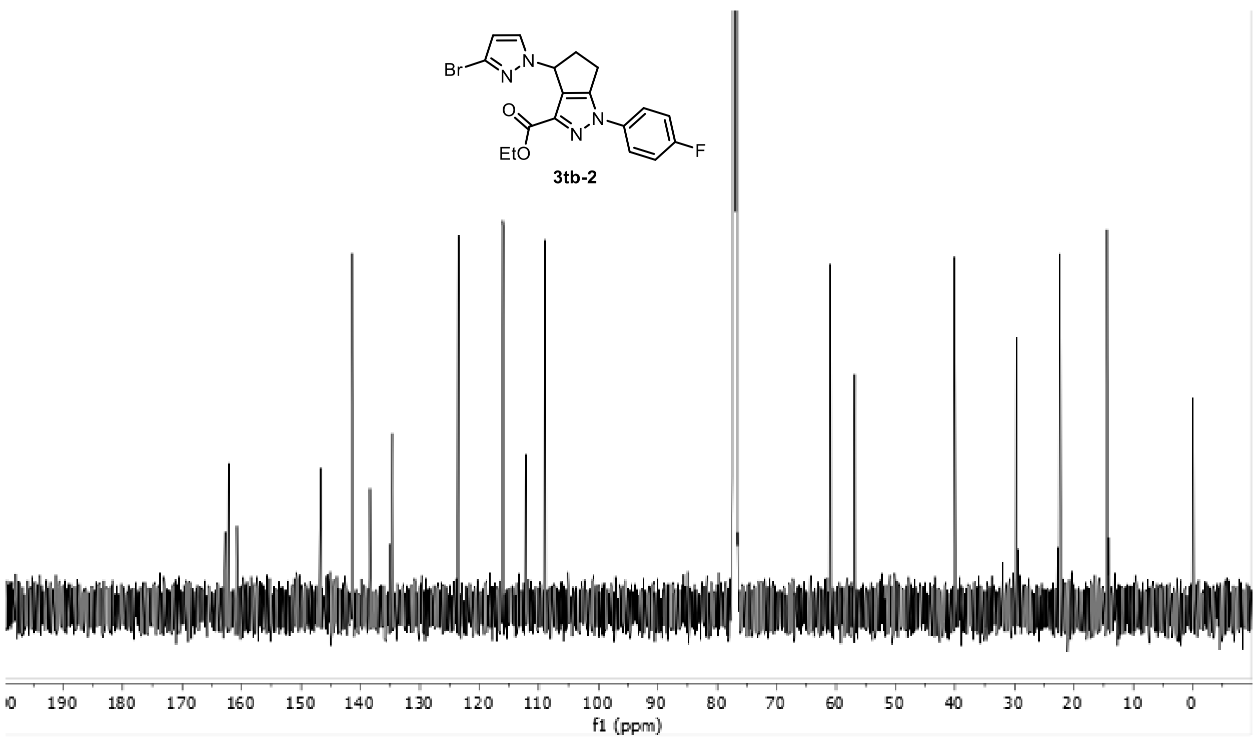
NOESY NMR spectrum of **3tb-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



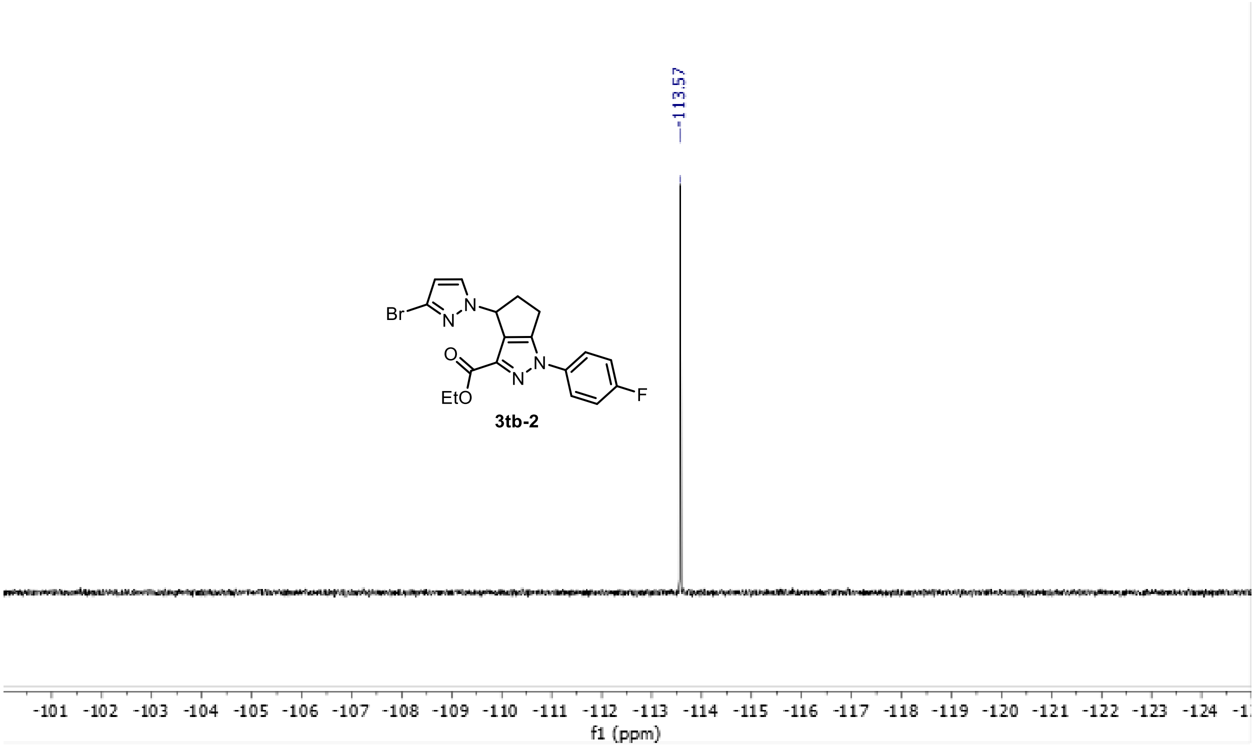
[1]H NMR spectrum of **3tb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



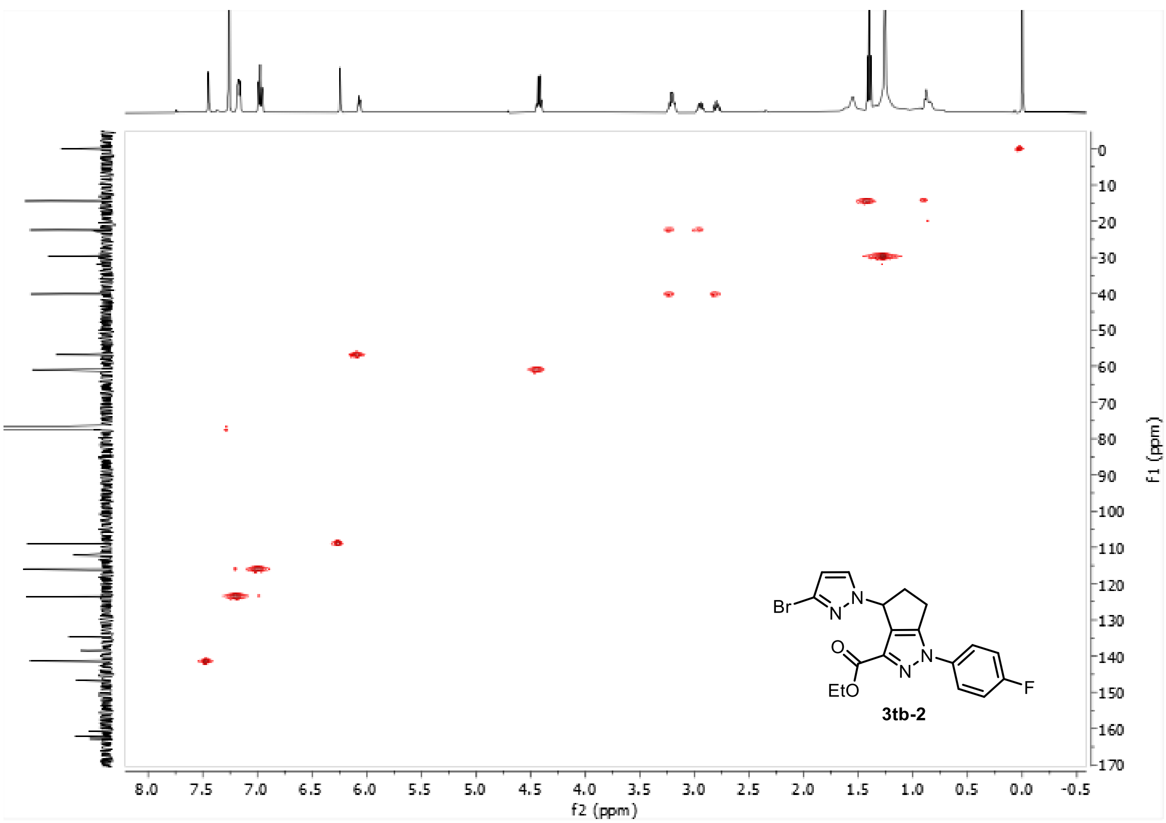
[13]C NMR spectrum of **3tb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



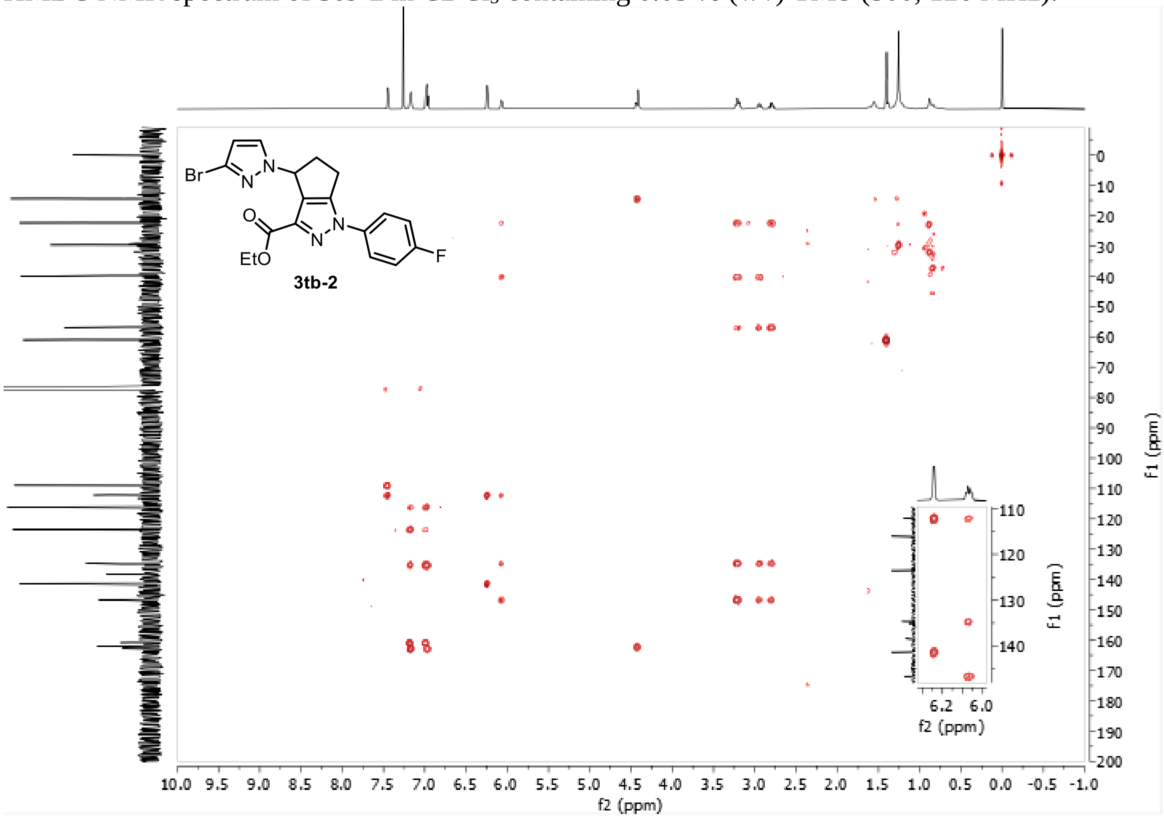
^{19}F NMR spectrum of **3tb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



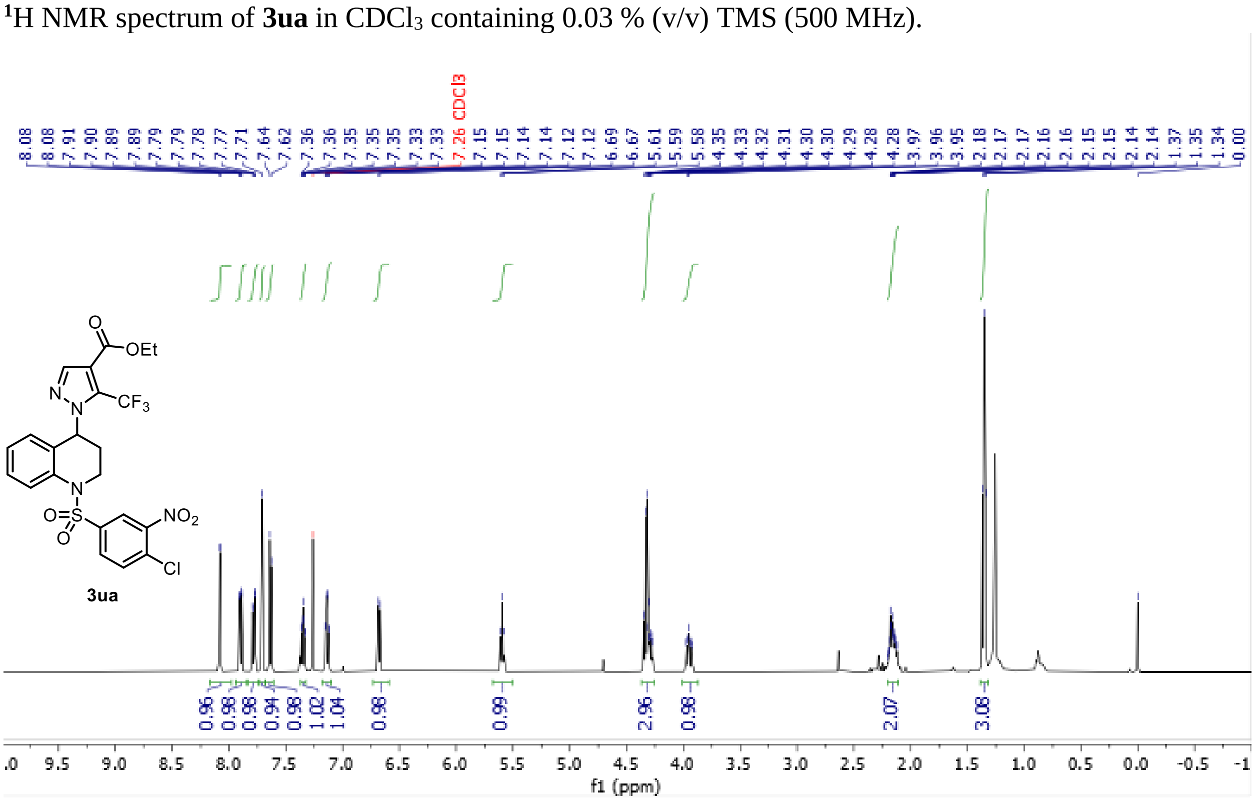
HSQC NMR spectrum of **3tb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



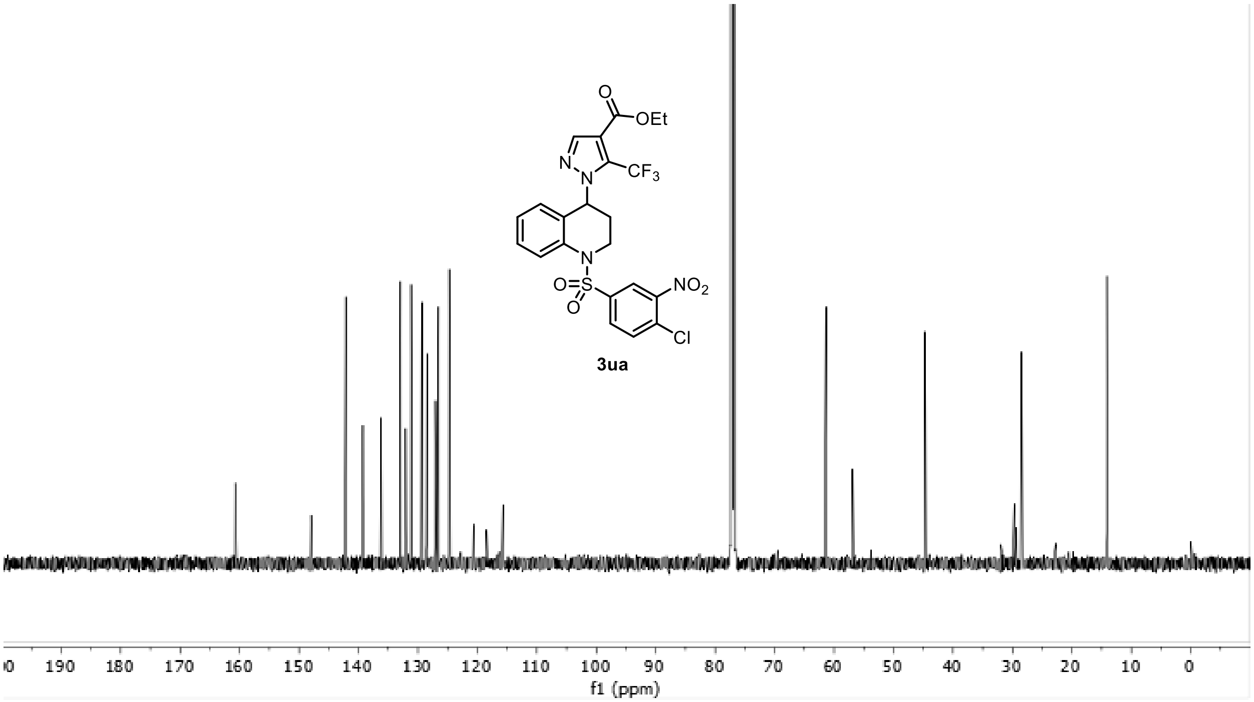
HMBC NMR spectrum of **3tb-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



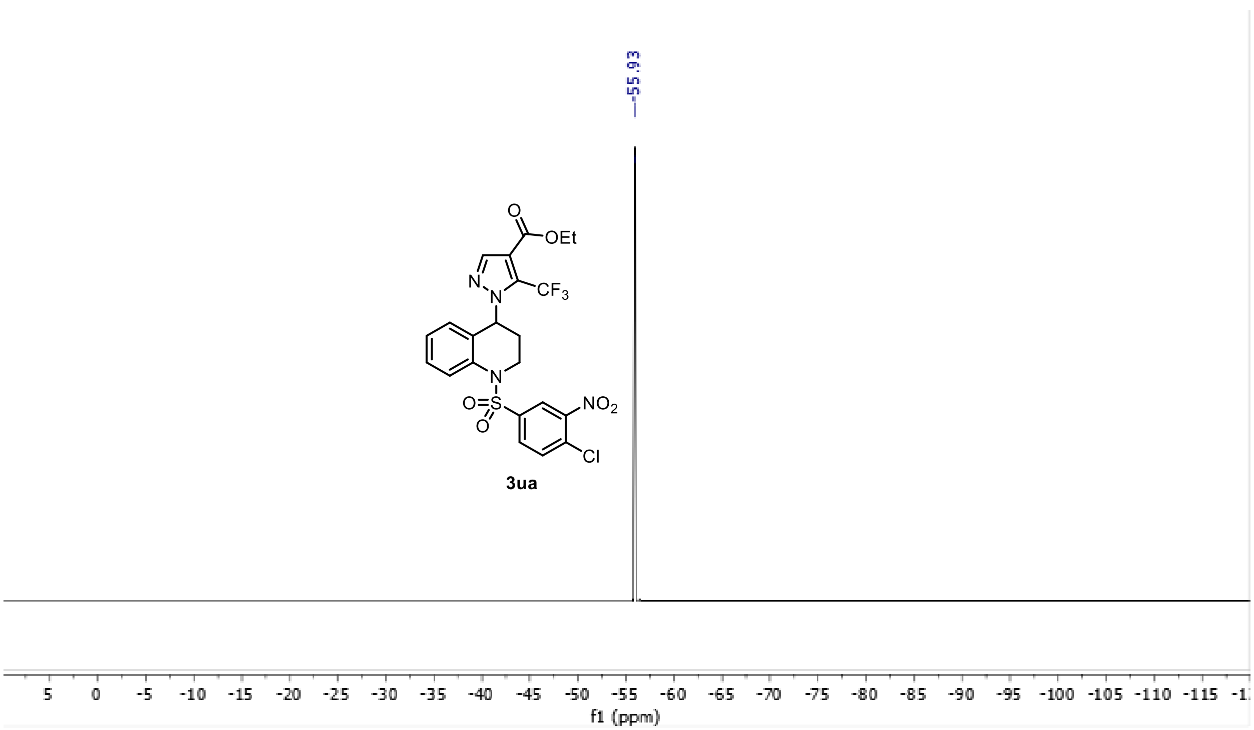
^1H NMR spectrum of **3ua** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



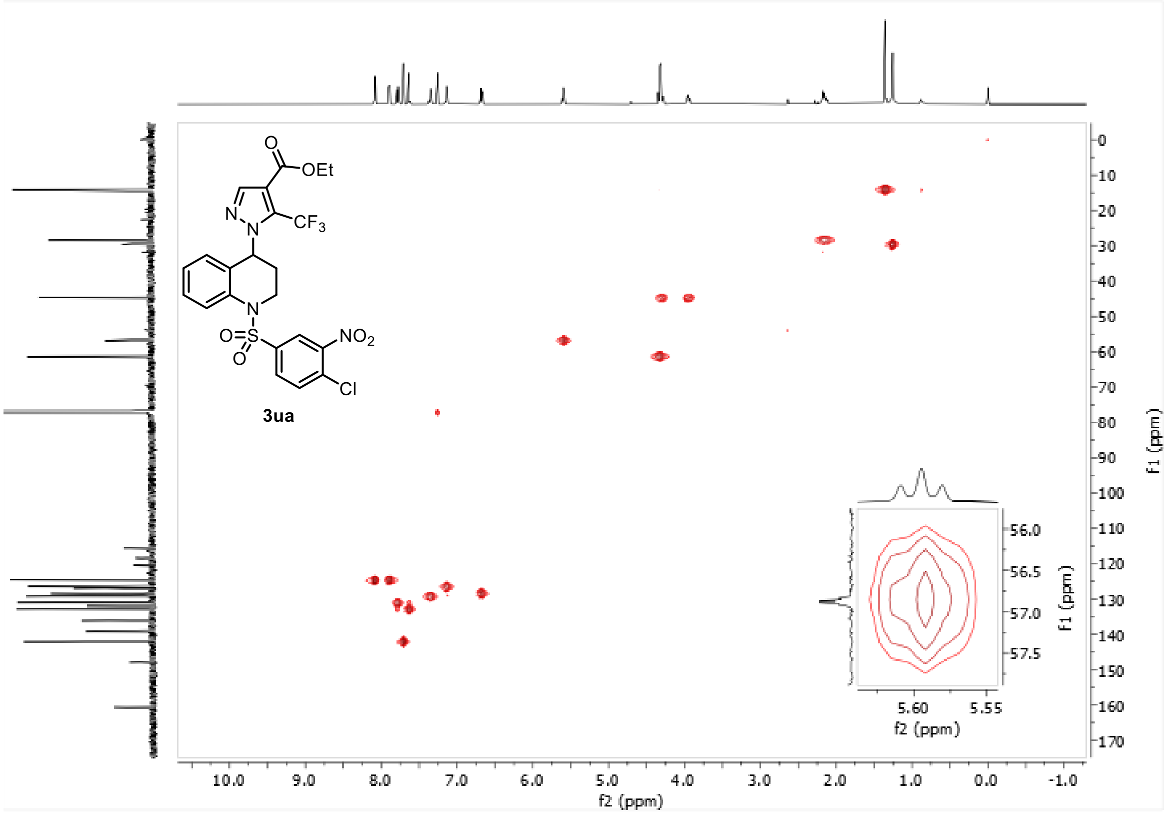
^{13}C NMR spectrum of **3ua** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



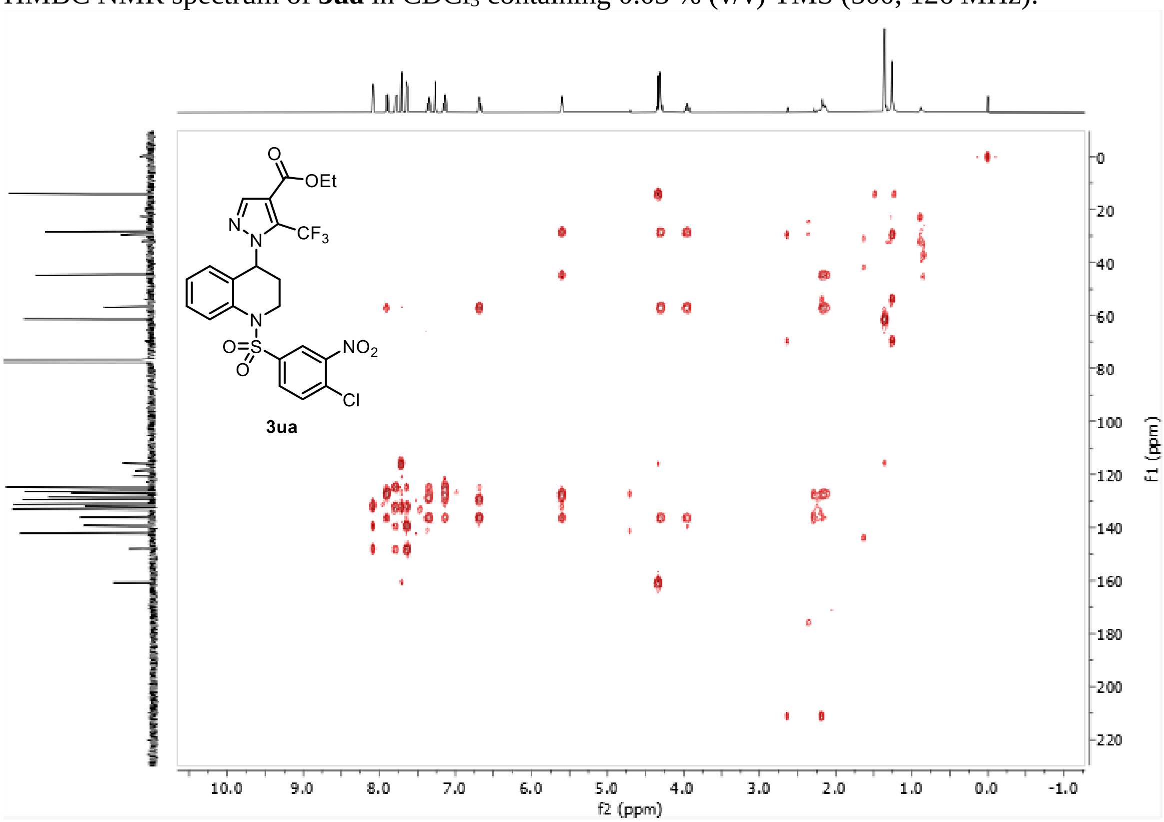
^{19}F NMR spectrum of **3ua** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



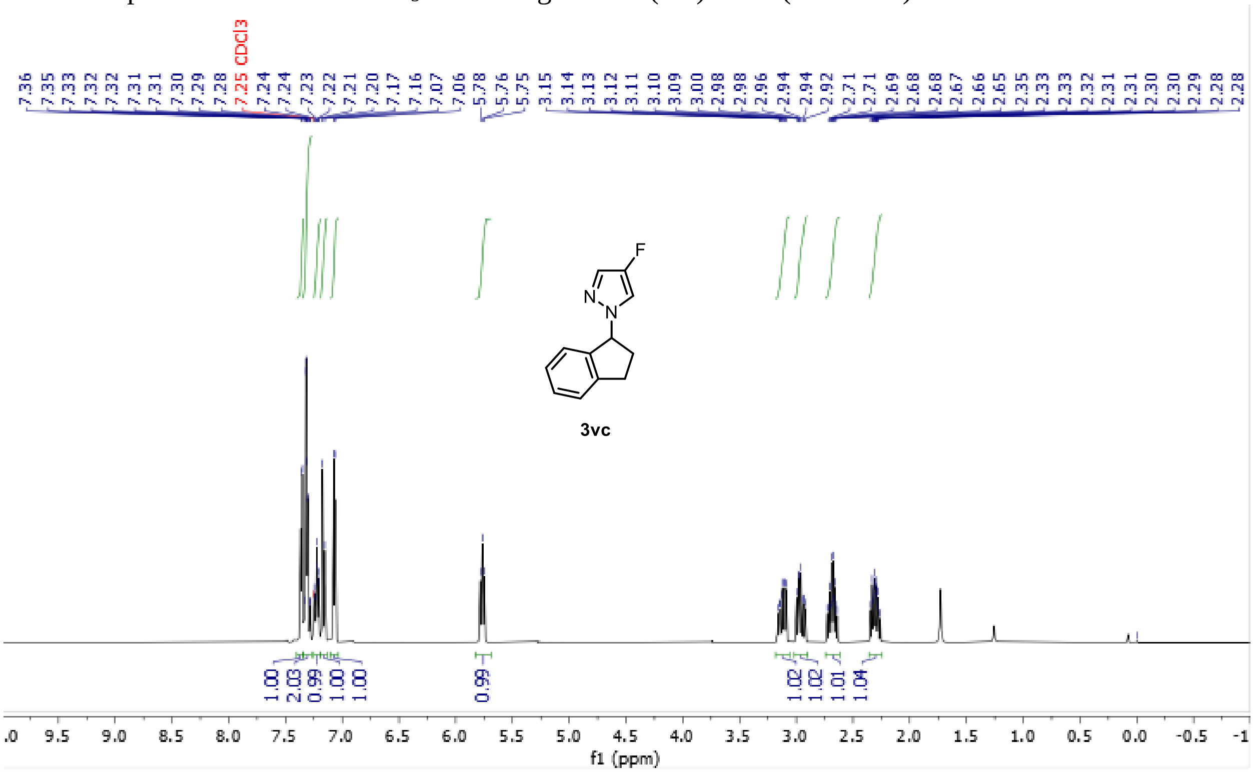
HSQC NMR spectrum of **3ua** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



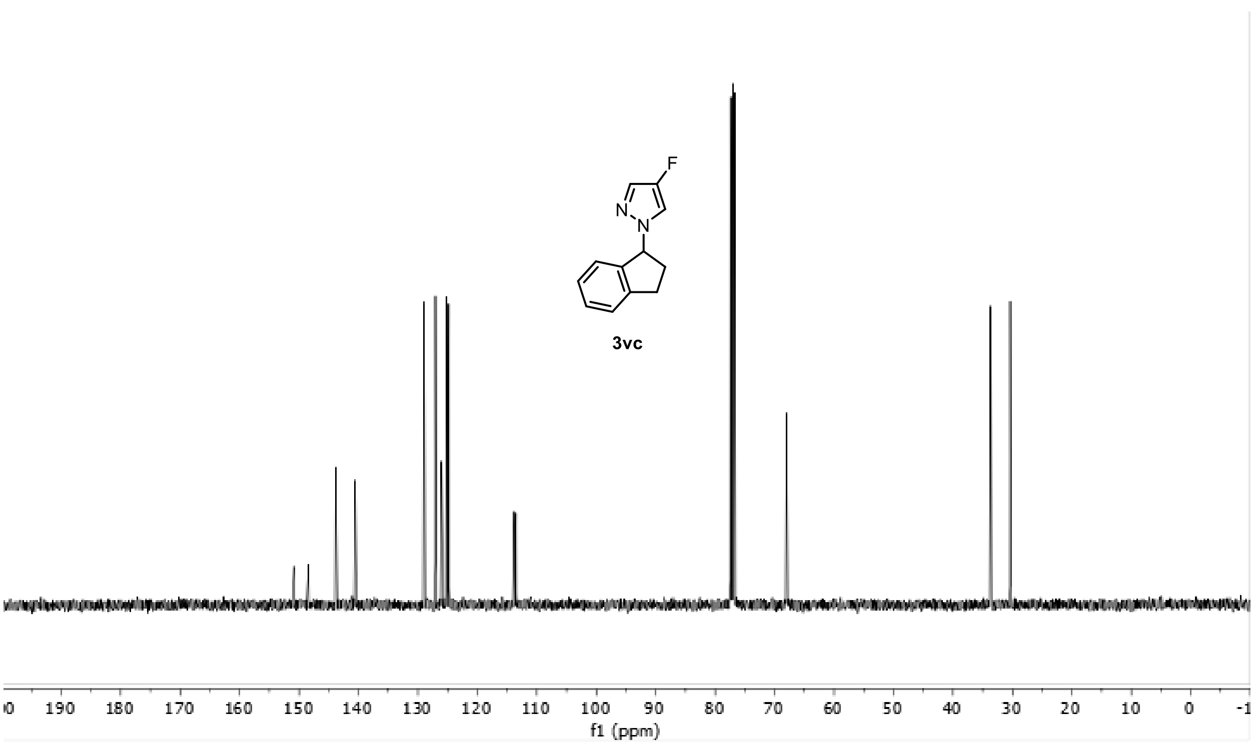
HMBC NMR spectrum of **3ua** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



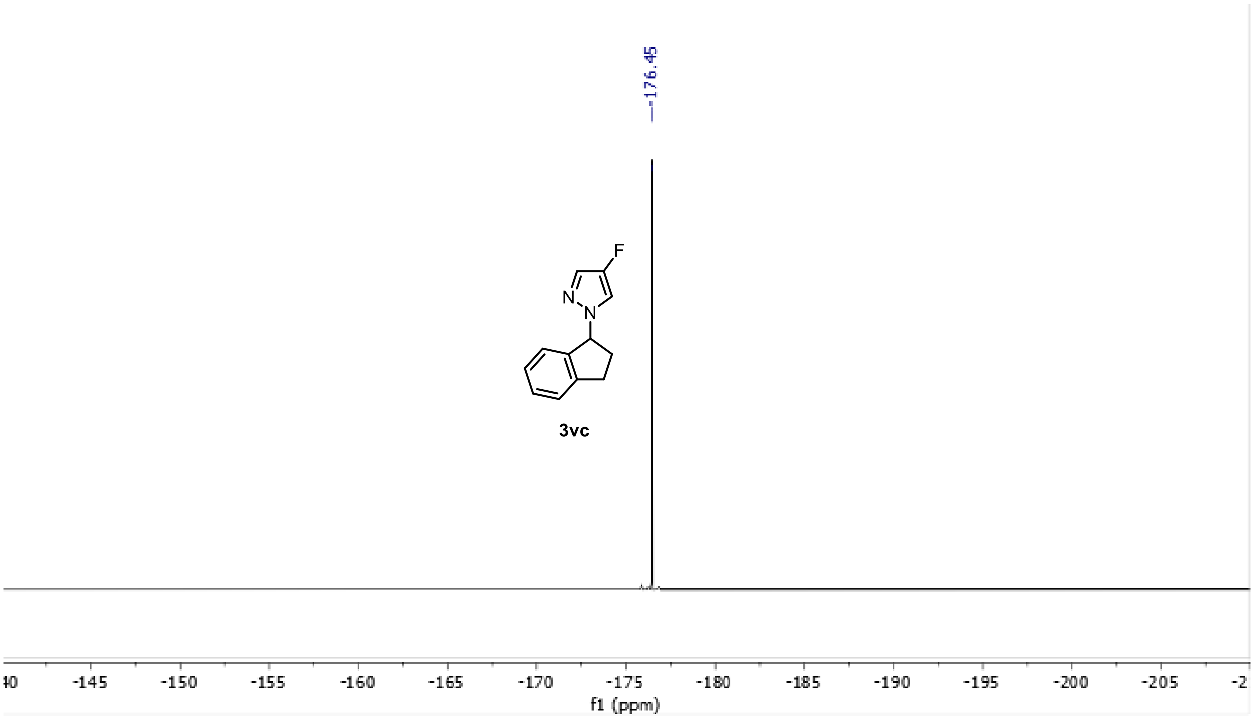
[1]H NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



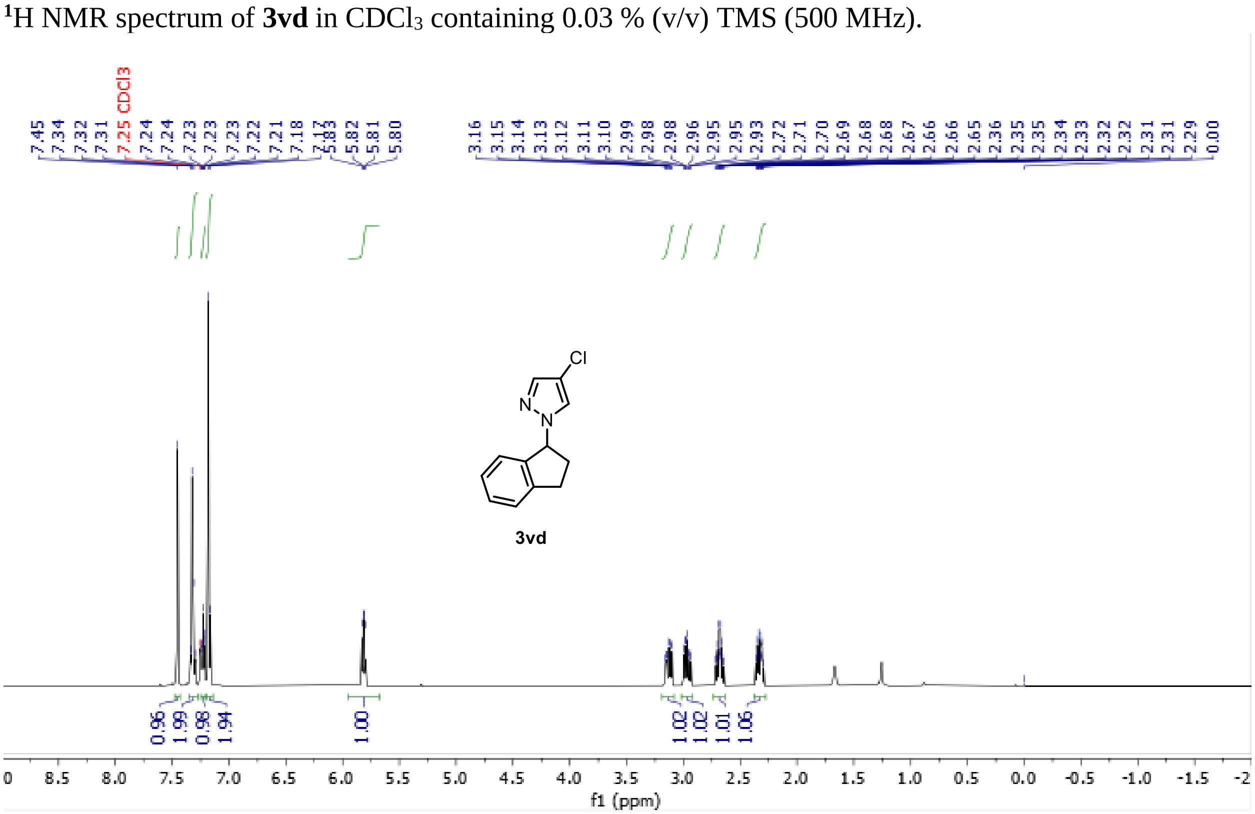
[13]C NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



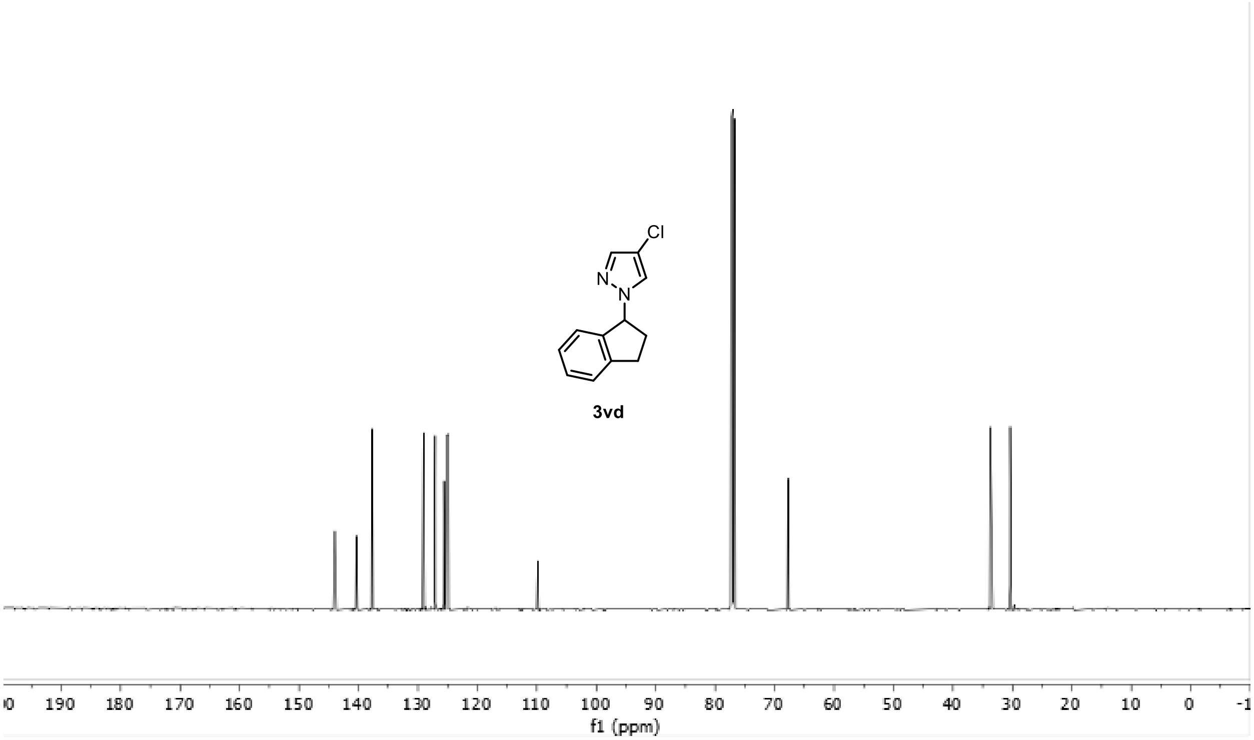
^{19}F NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



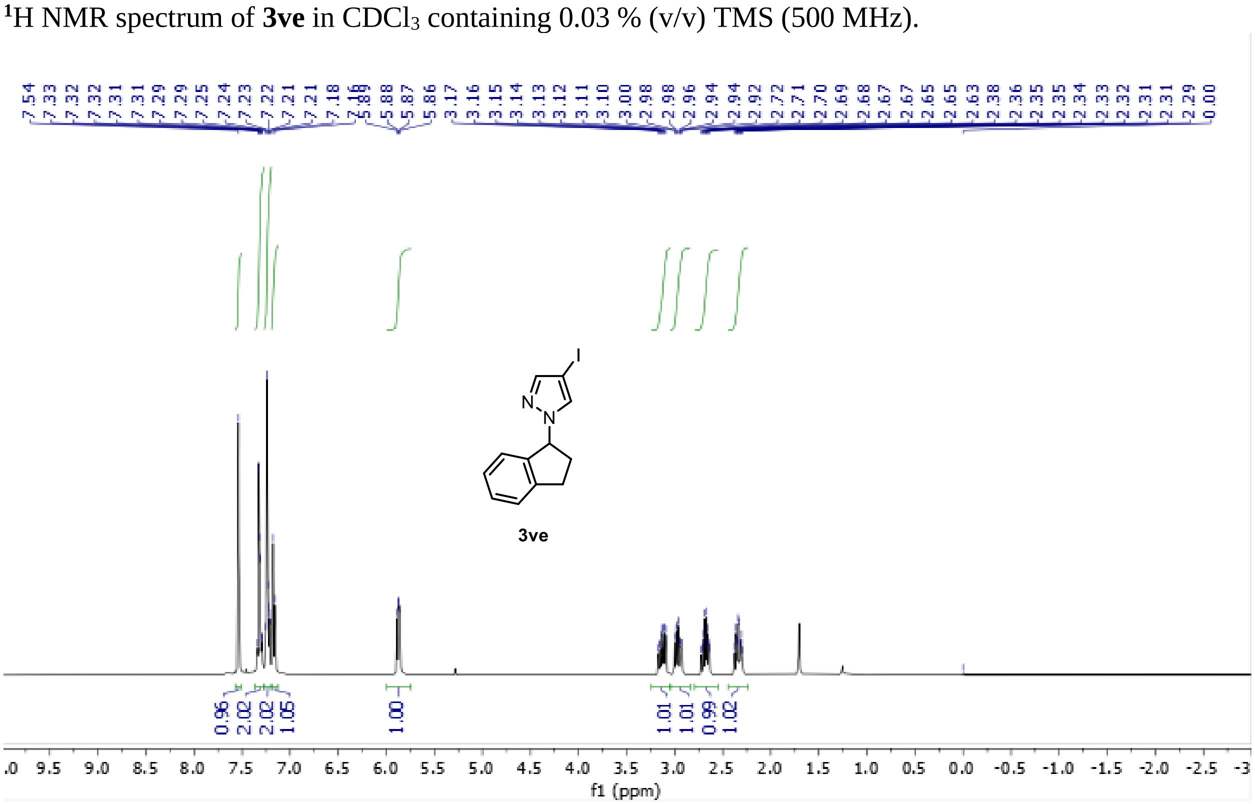
^{1}H NMR spectrum of **3vd** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



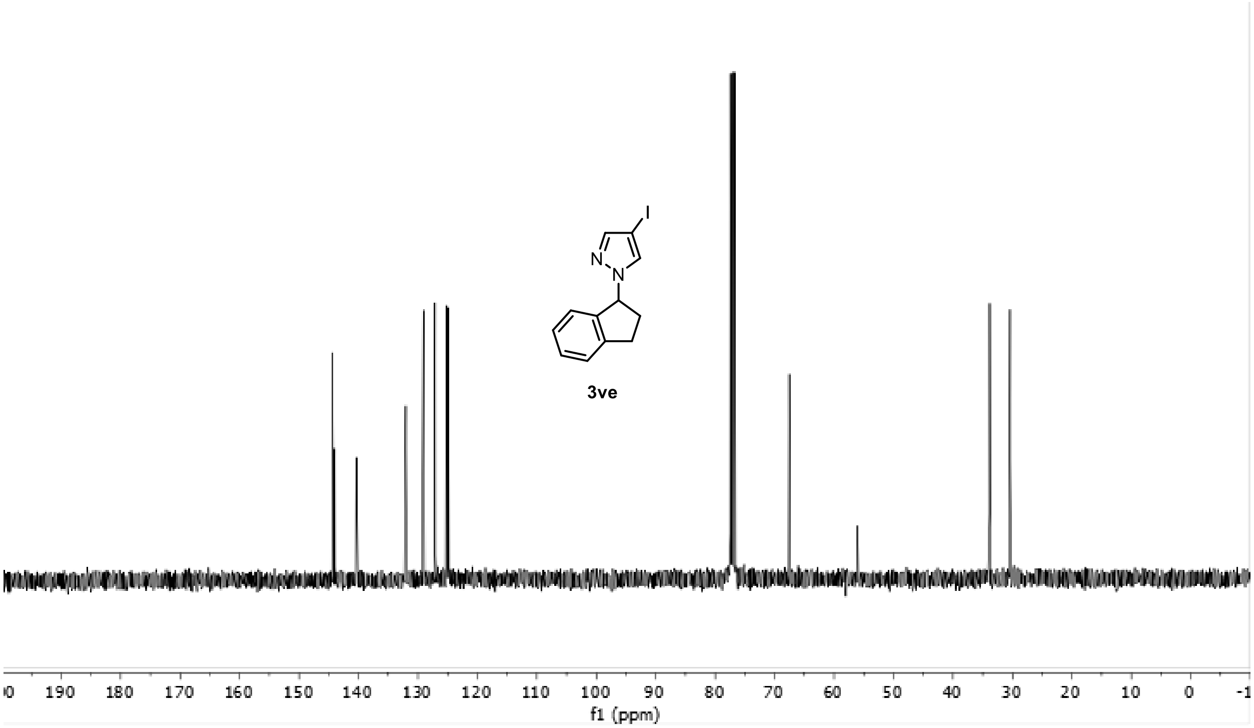
^{13}C NMR spectrum of **3vd** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



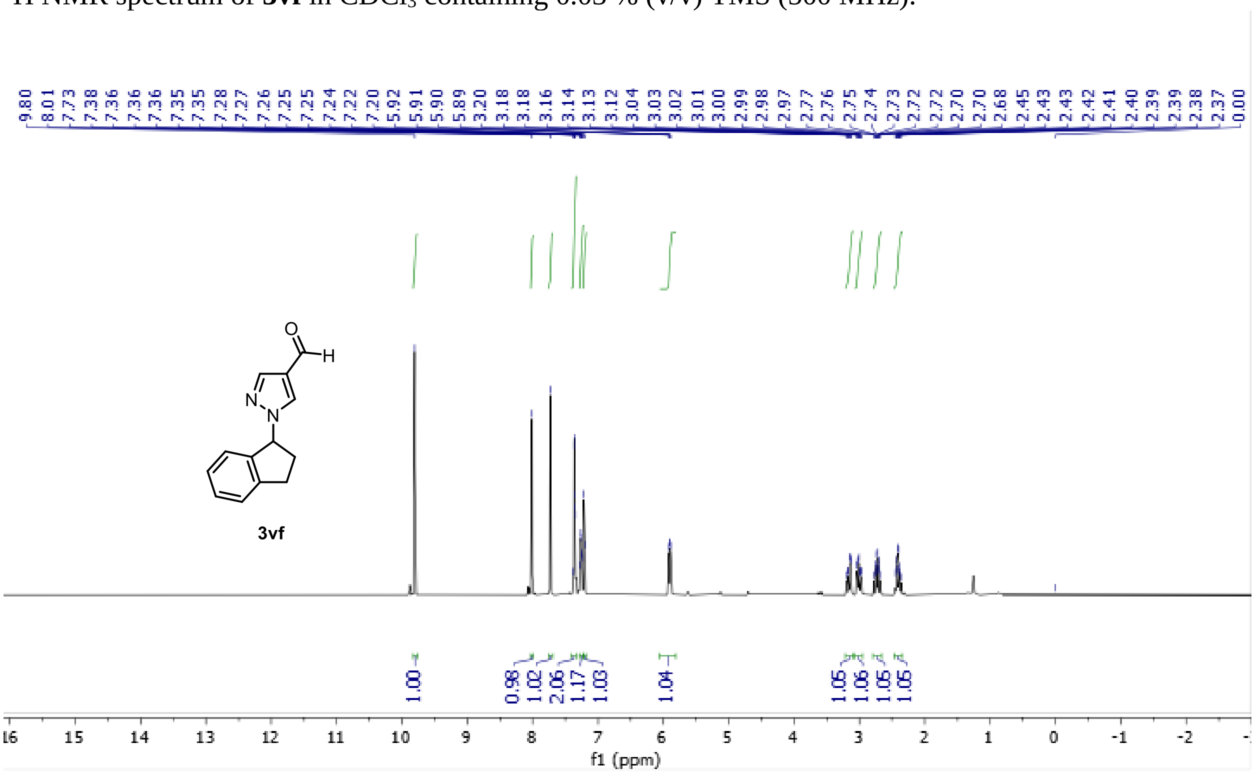
^{1}H NMR spectrum of **3ve** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



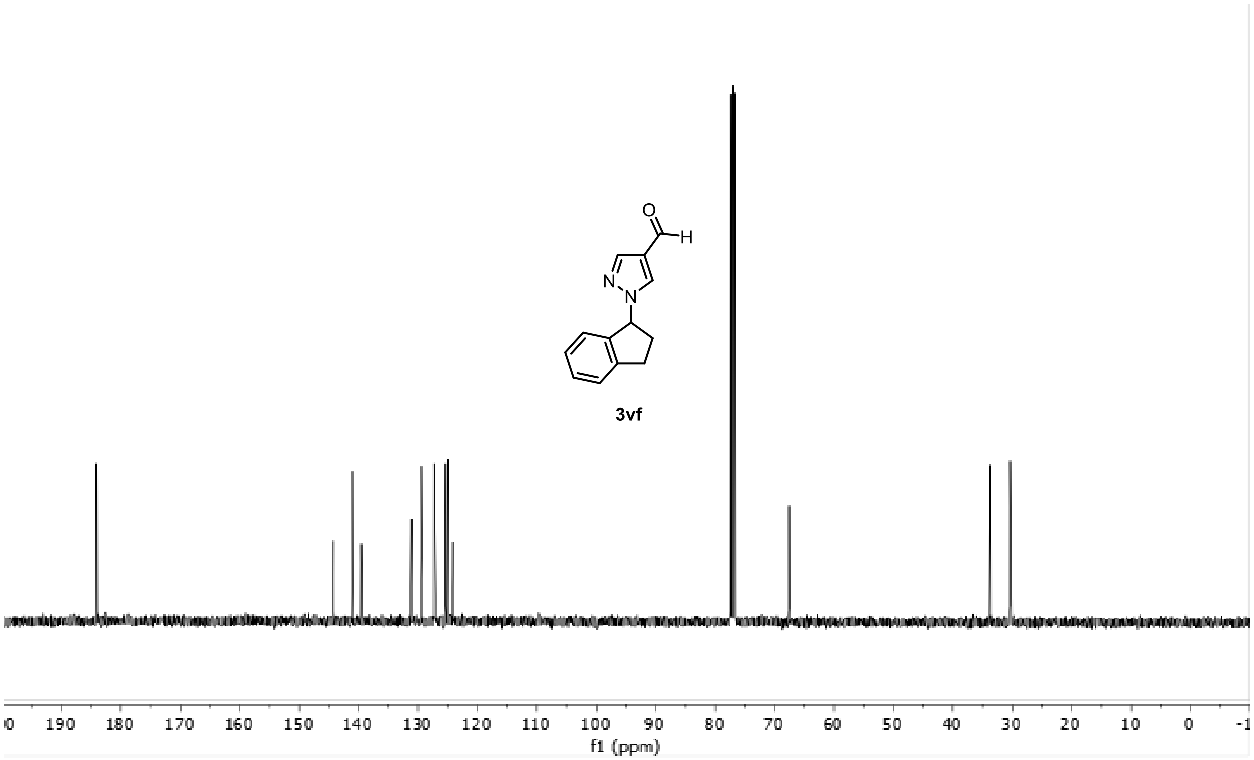
^{13}C NMR spectrum of **3ve** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



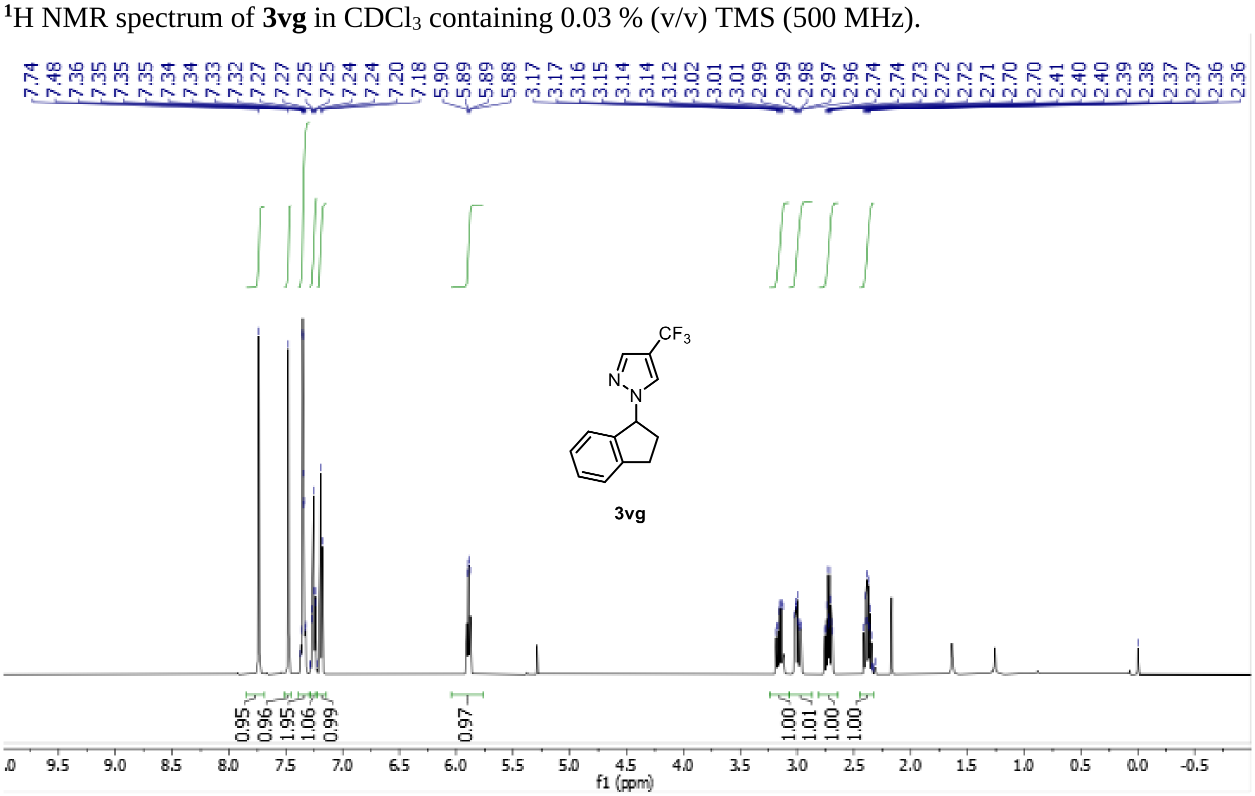
^{1}H NMR spectrum of **3vf** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



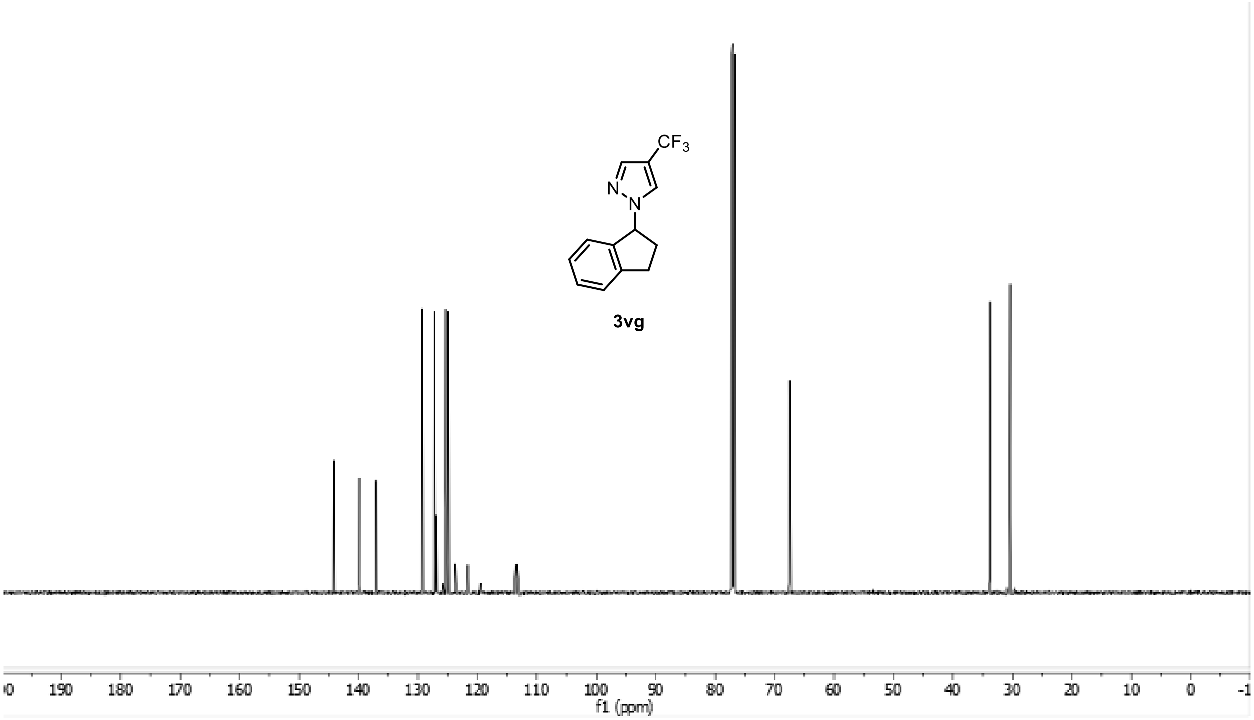
[13]C NMR spectrum of **3vf** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



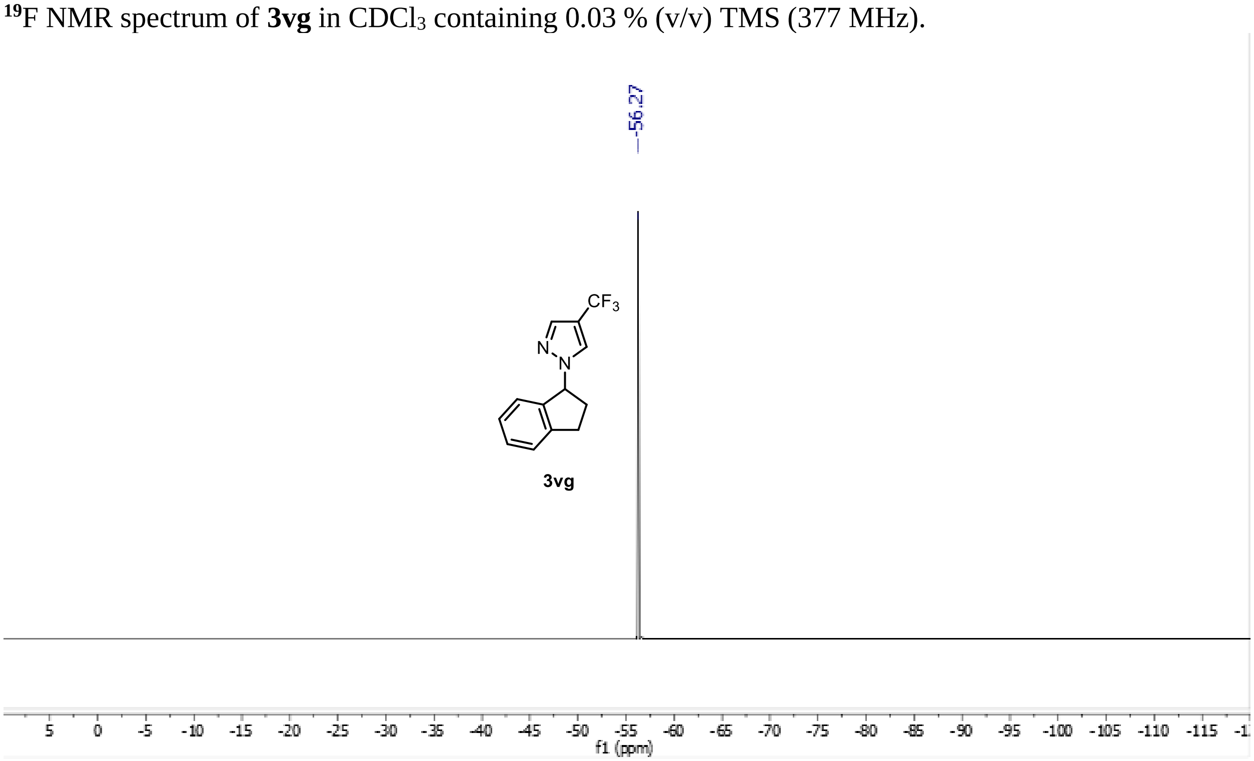
[1]H NMR spectrum of **3vg** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



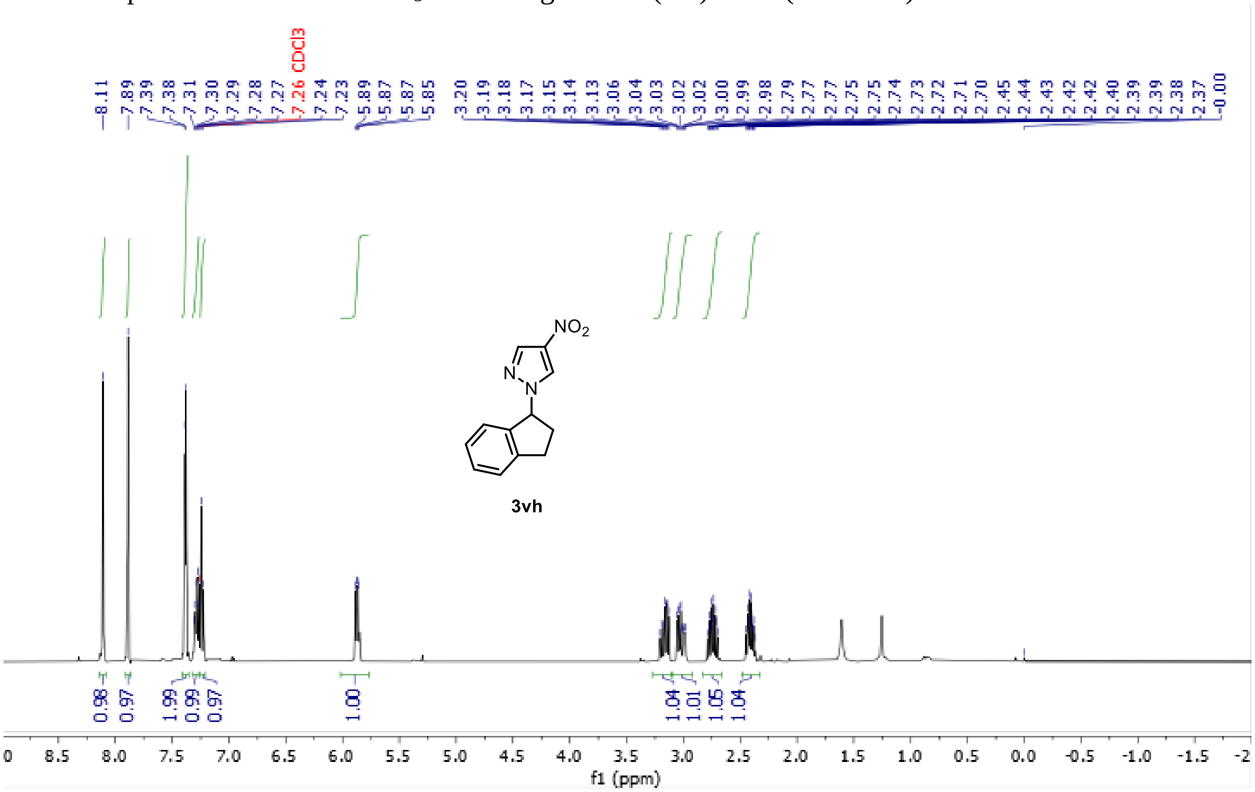
^{13}C NMR spectrum of **3vg** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



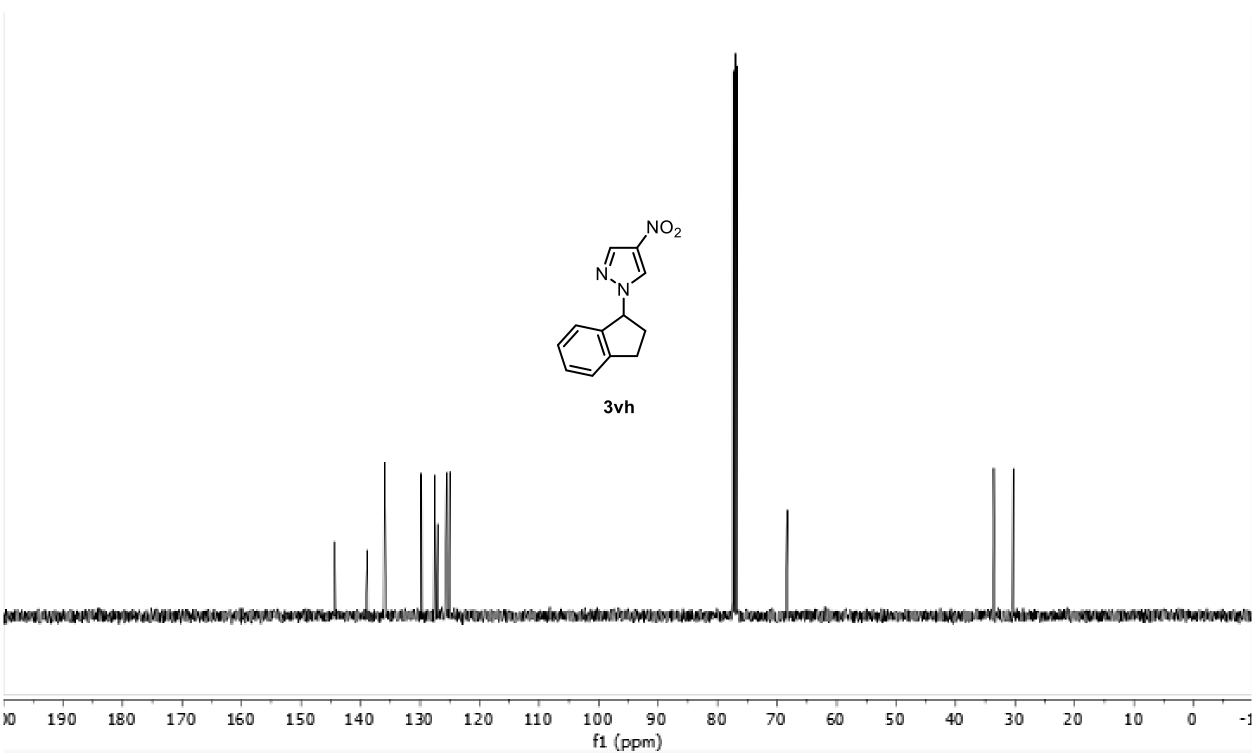
^{19}F NMR spectrum of **3vg** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



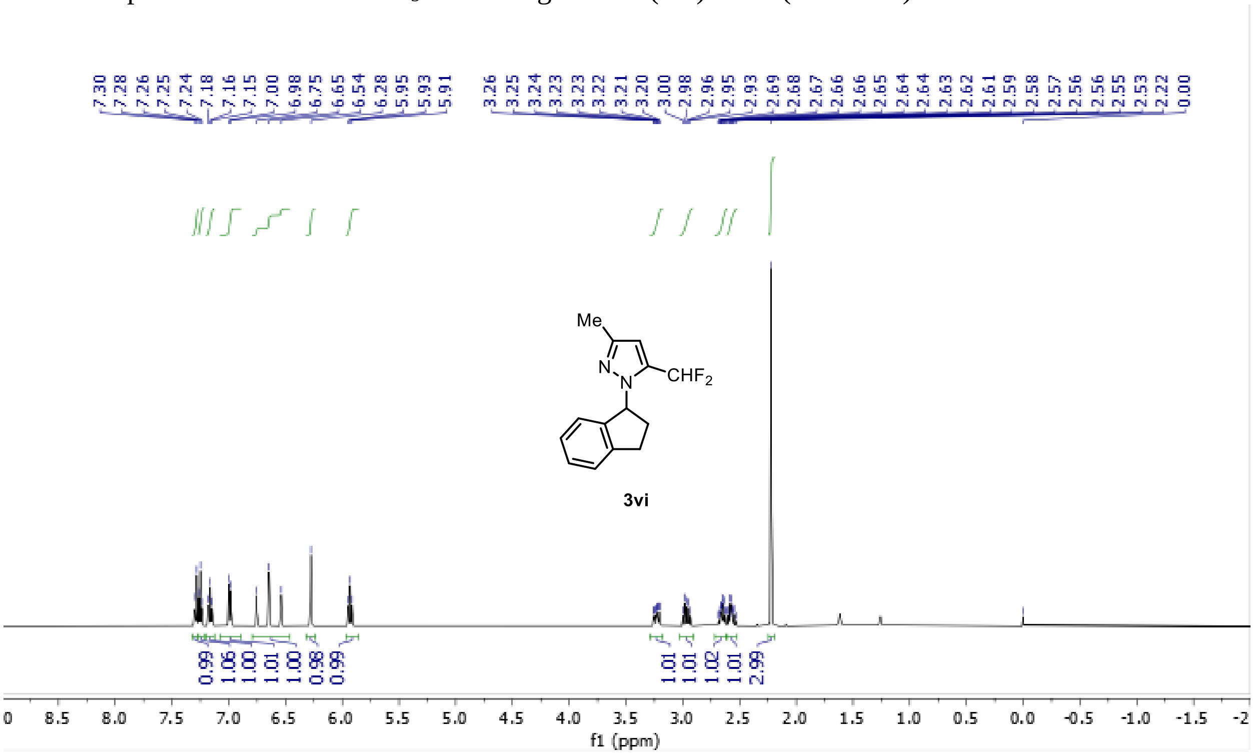
[1]H NMR spectrum of **3vh** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



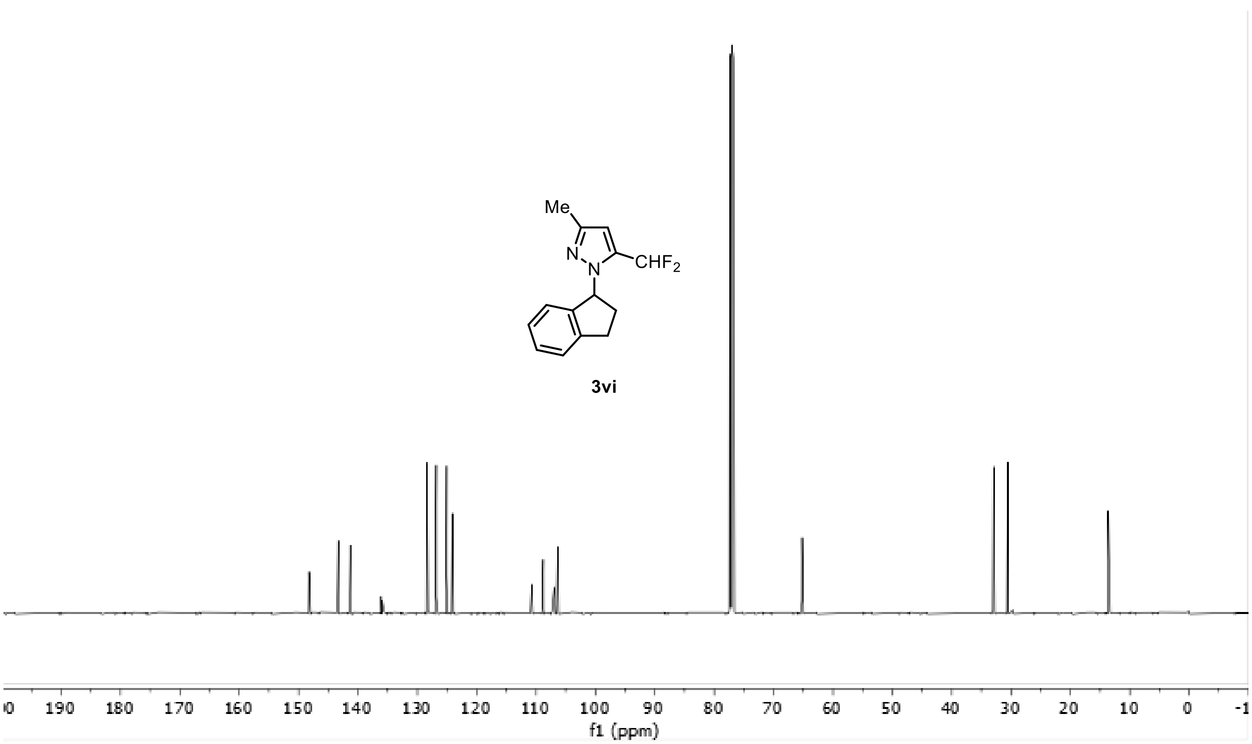
[13]C NMR spectrum of **3vh** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



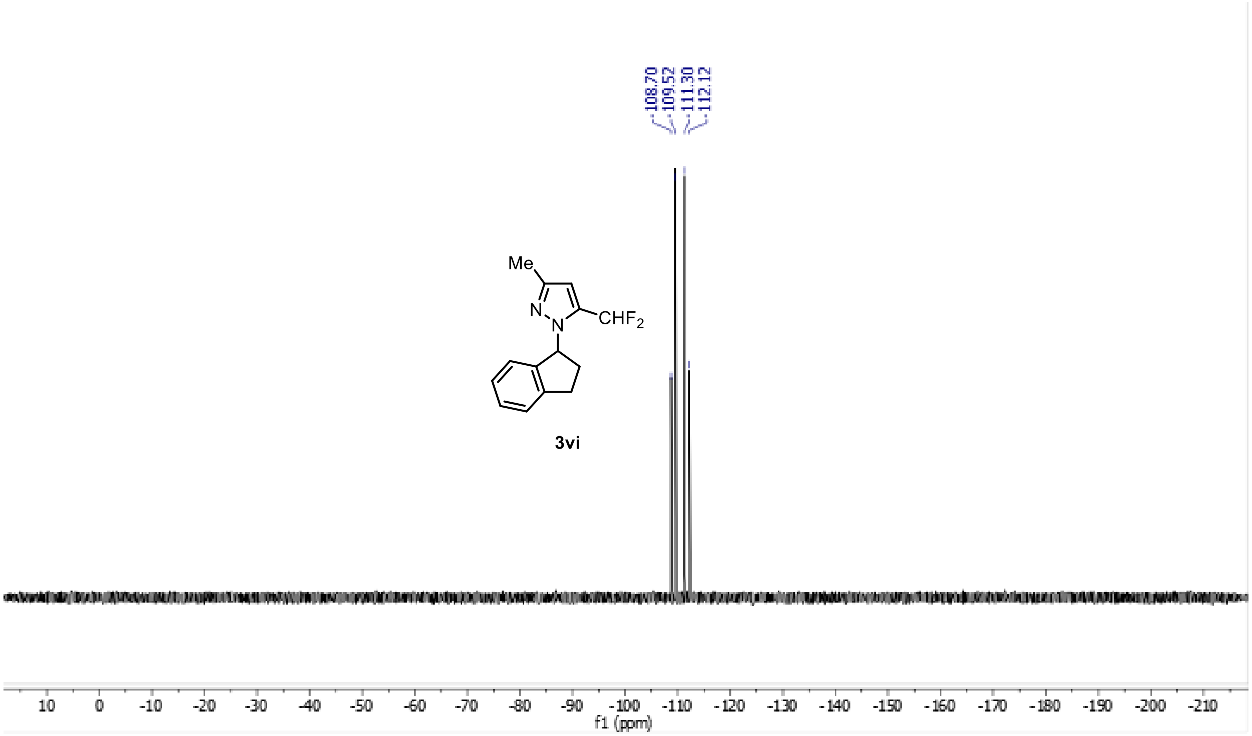
[1]H NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



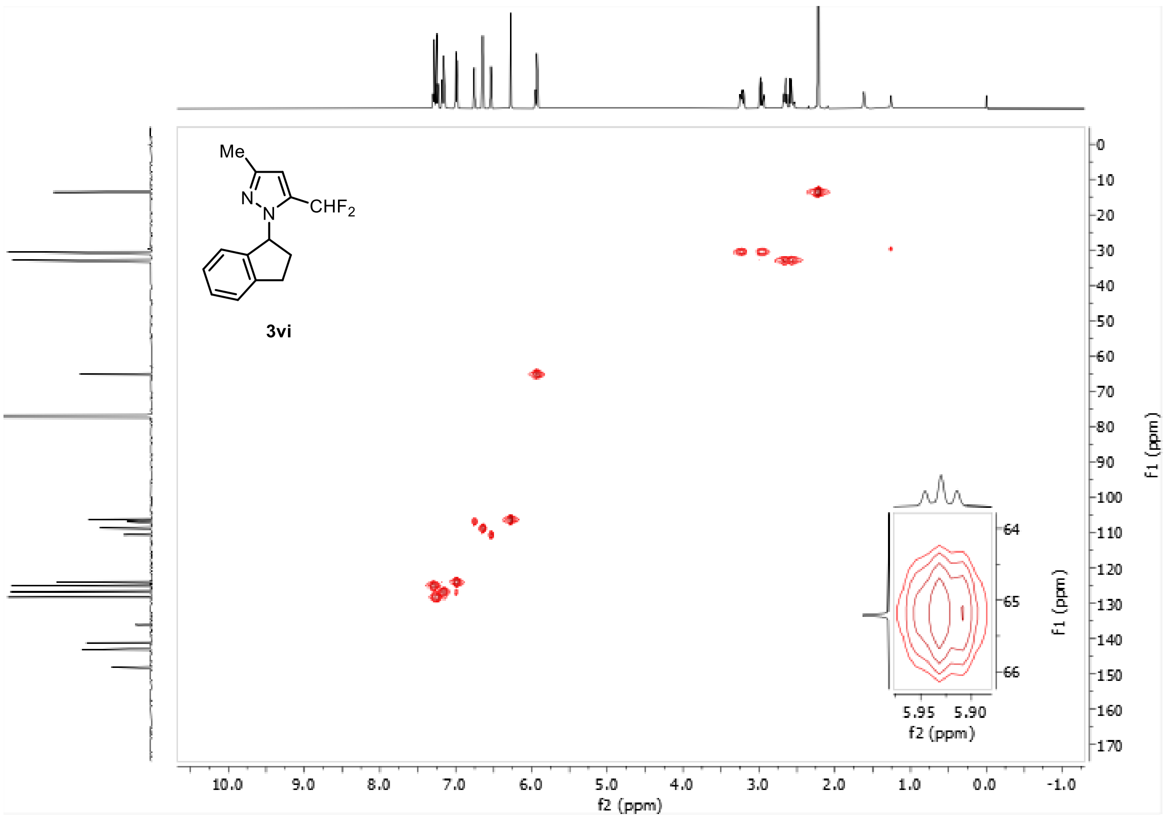
^{13}C NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



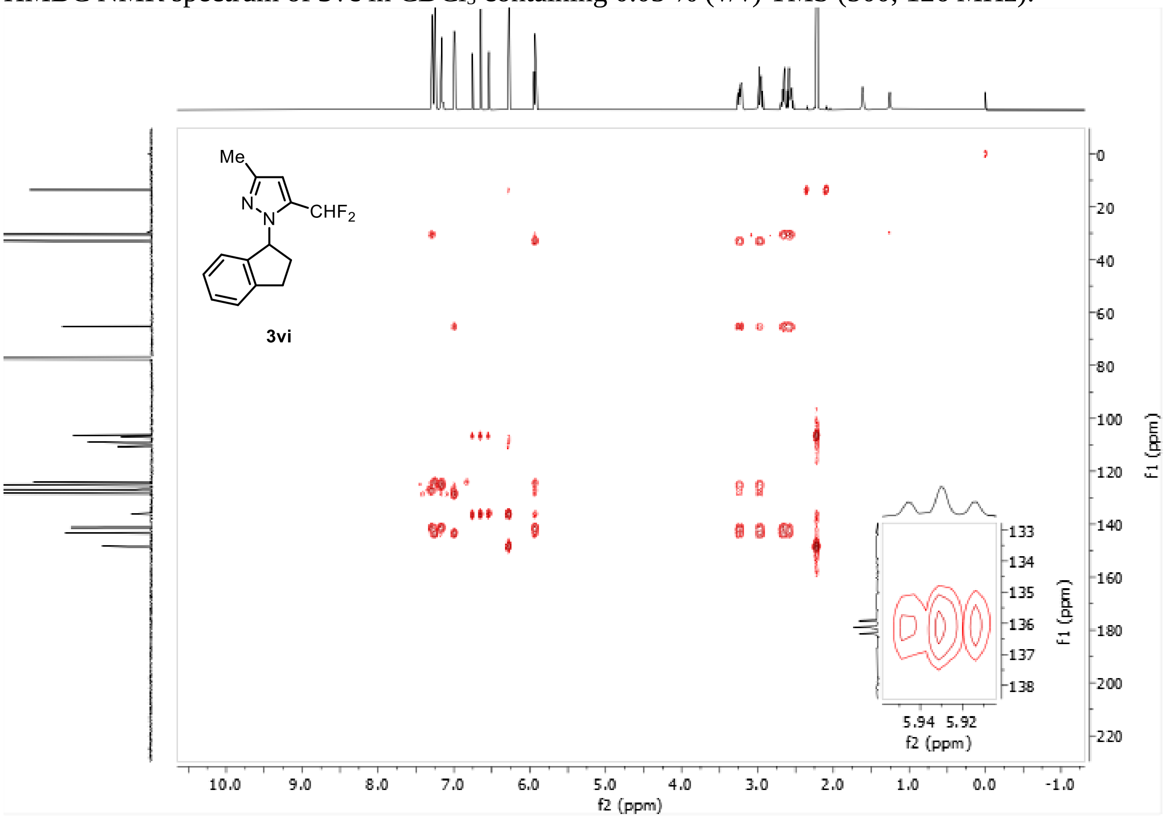
[19]F NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



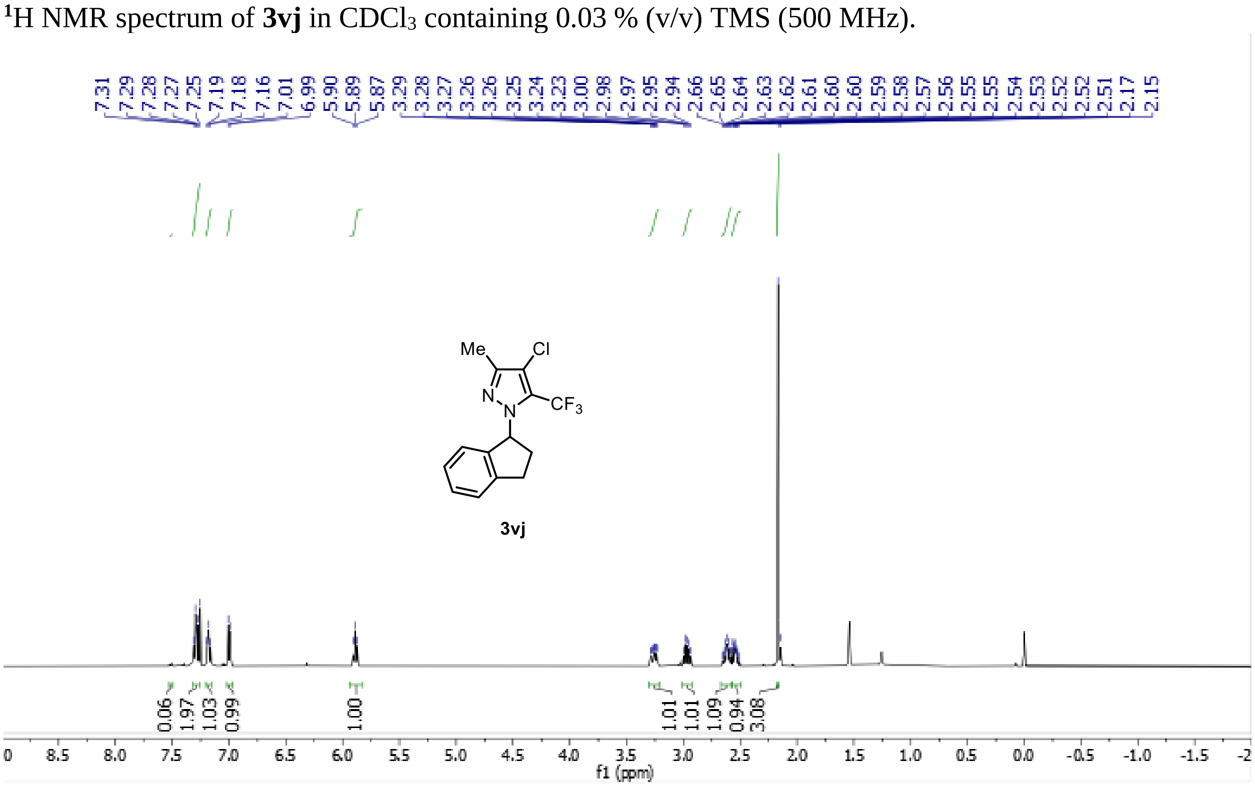
HSQC NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



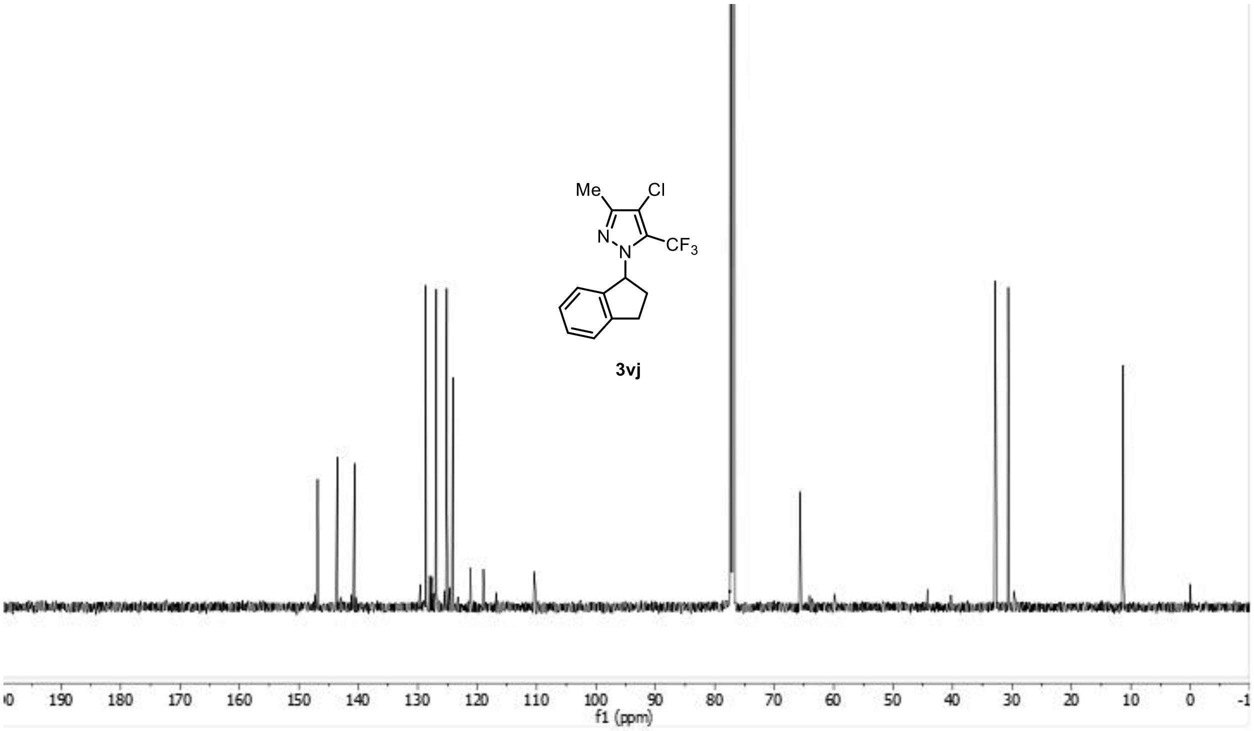
HMBC NMR spectrum of **3vc** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



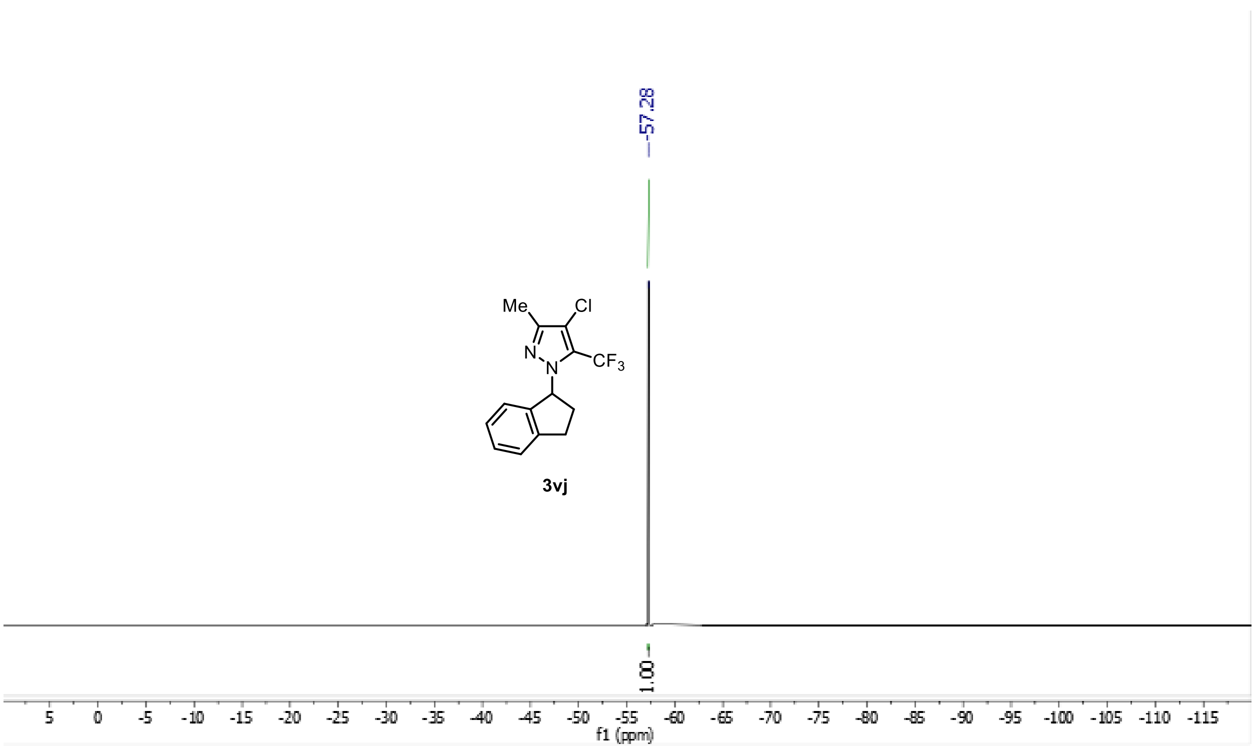
[1]H NMR spectrum of **3vj** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



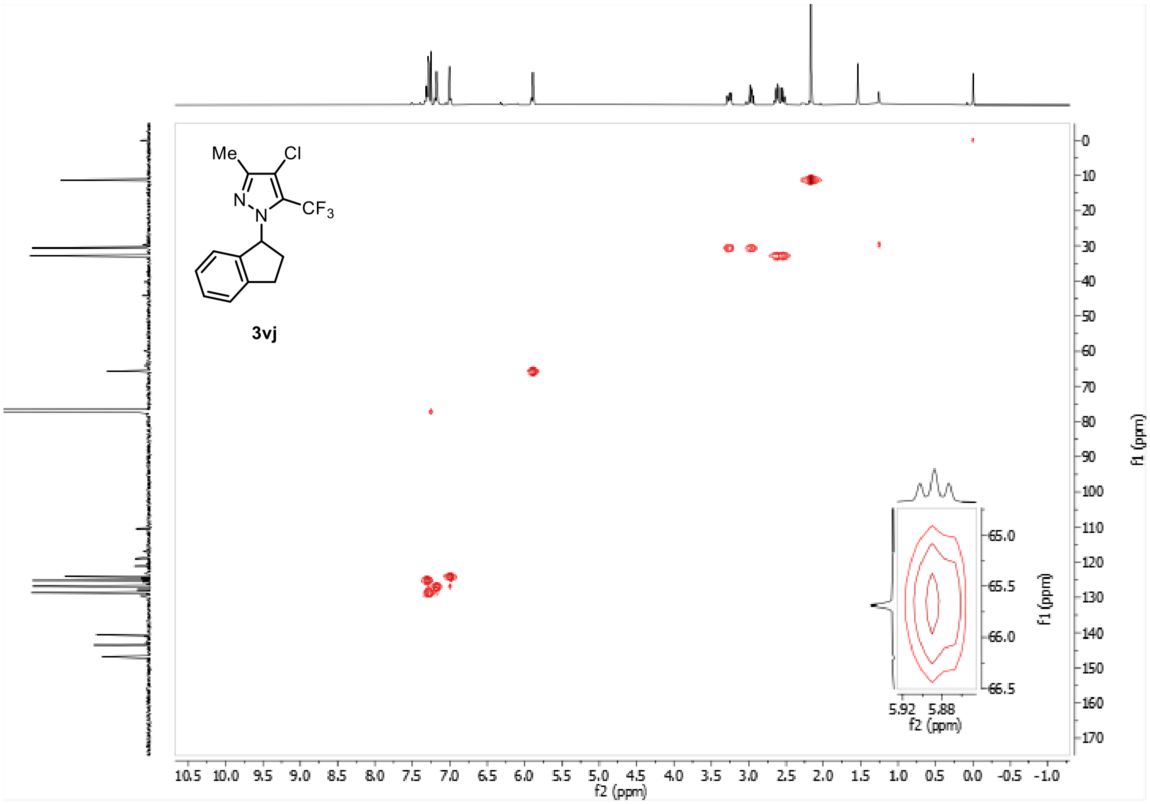
^{13}C NMR spectrum of **3vj** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



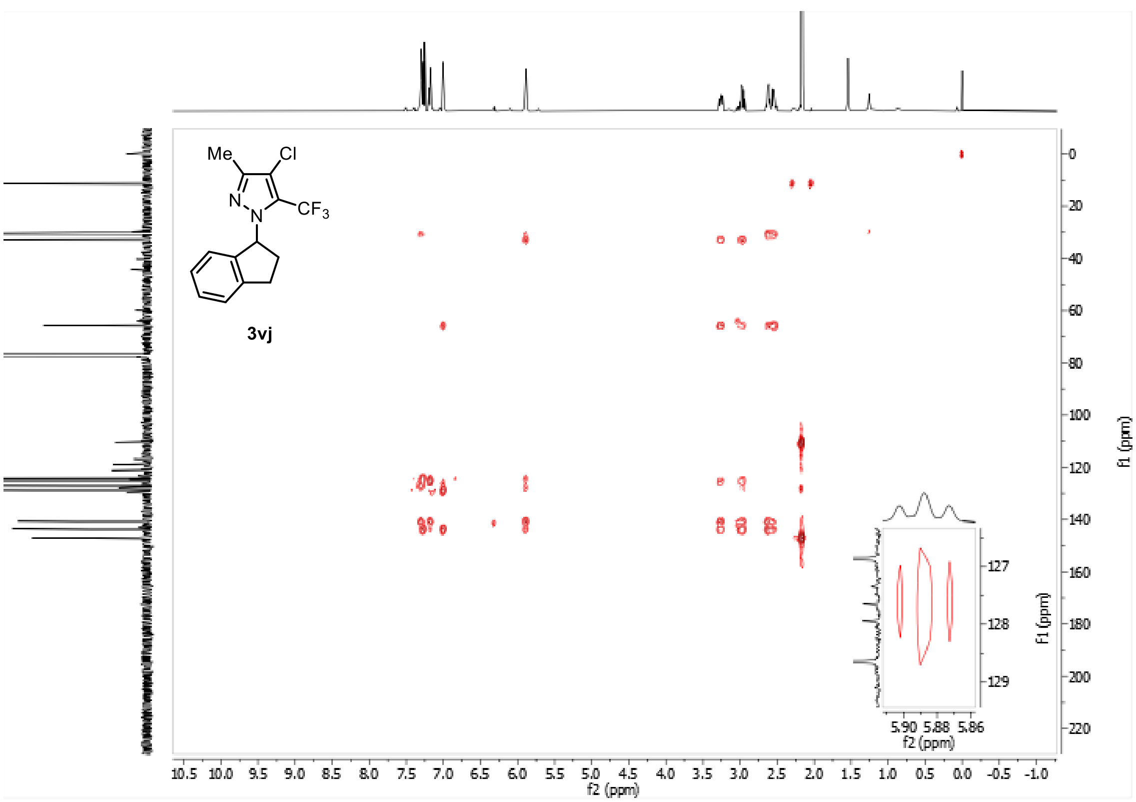
^{19}F NMR spectrum of **3vj** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



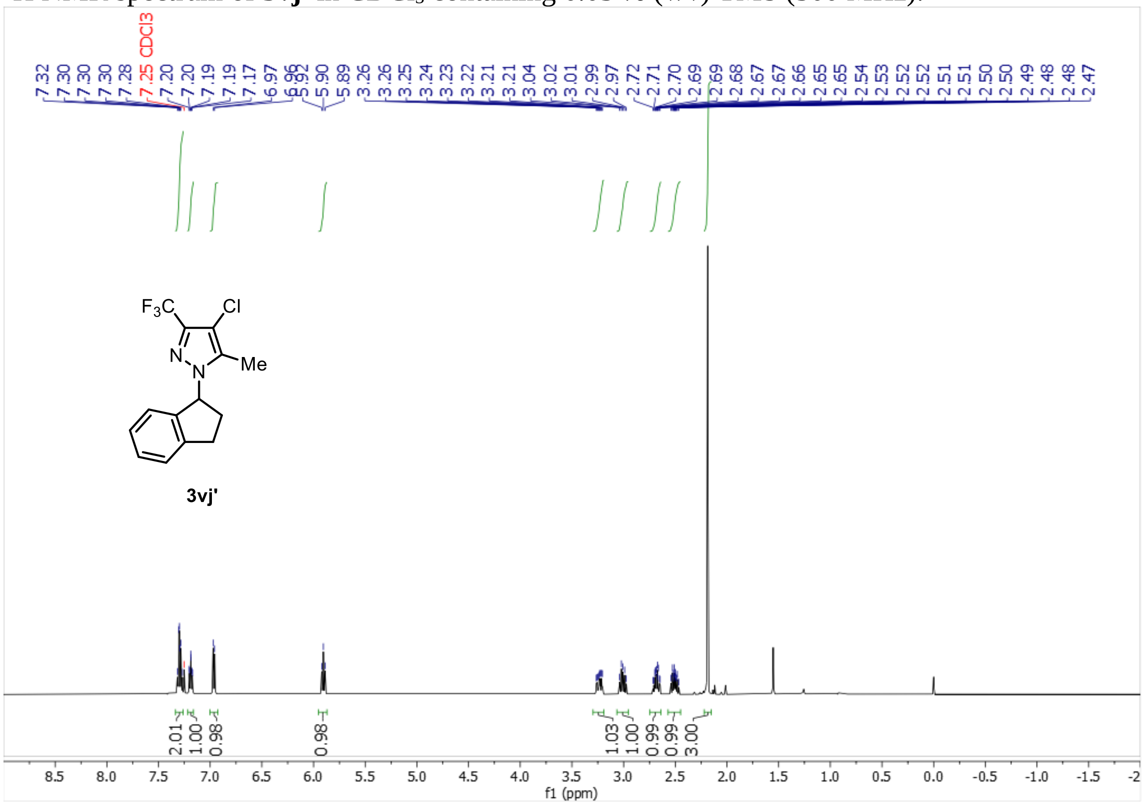
HSQC NMR spectrum of **3vj** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



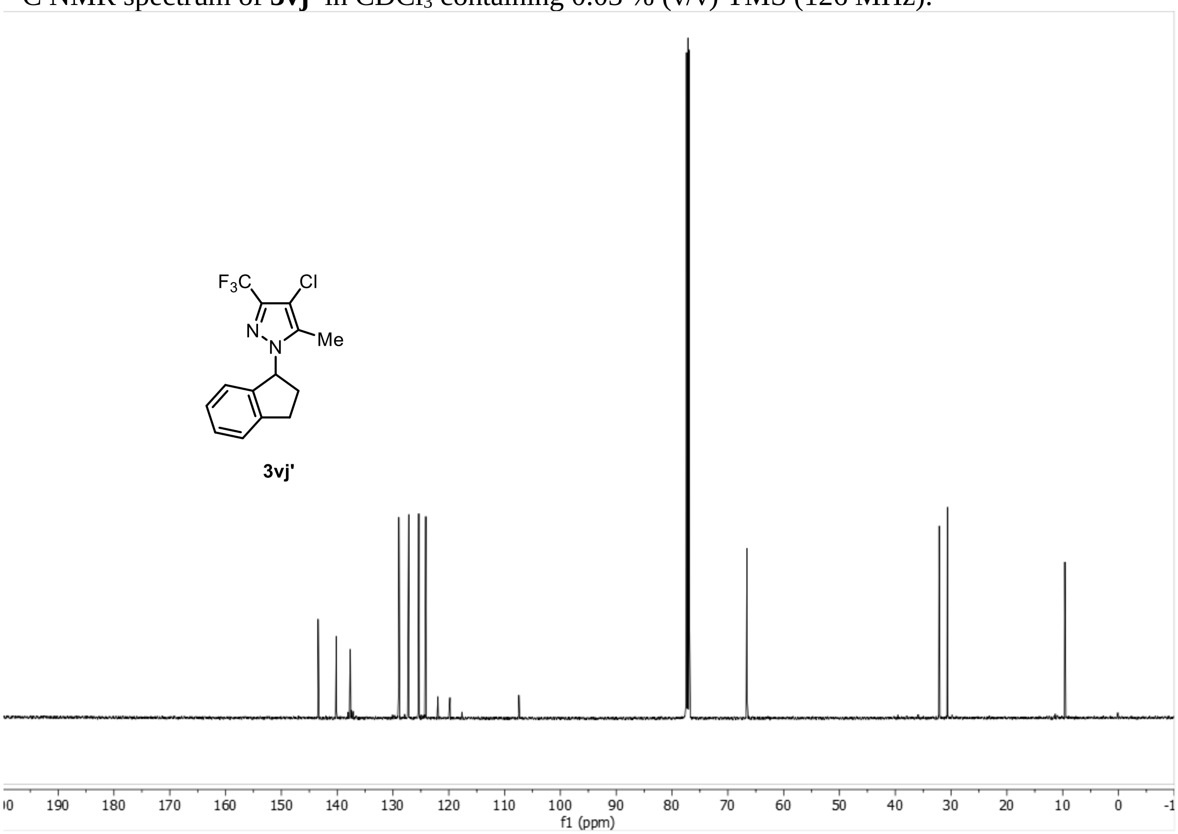
HMBC NMR spectrum of **3vj** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



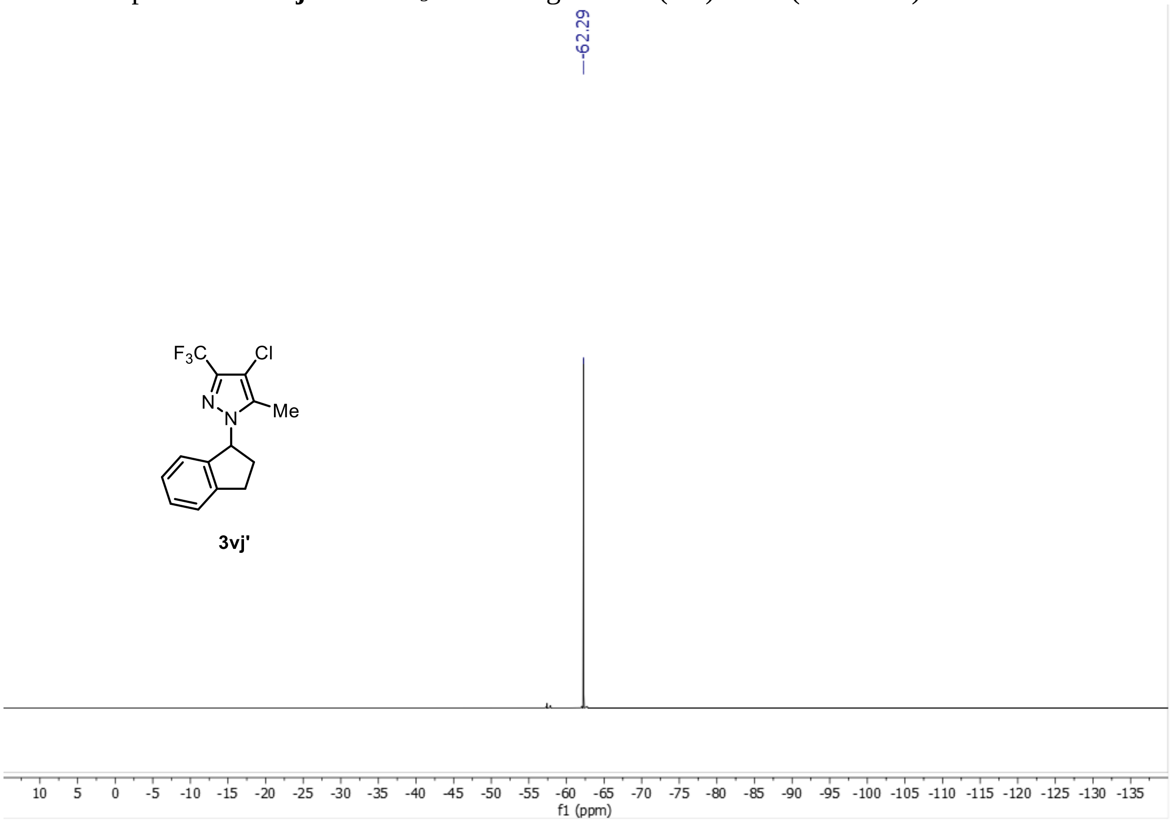
^{1}H NMR spectrum of **3vj'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



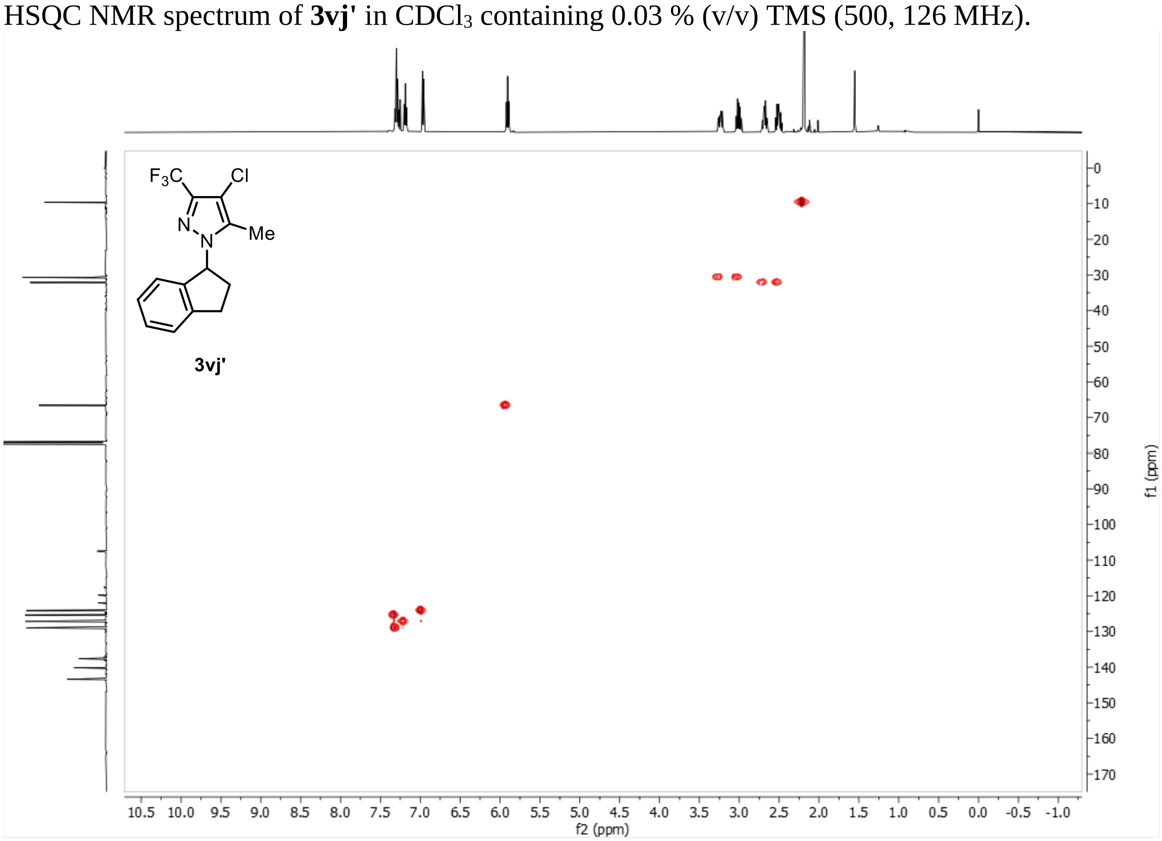
^{13}C NMR spectrum of **3vj'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



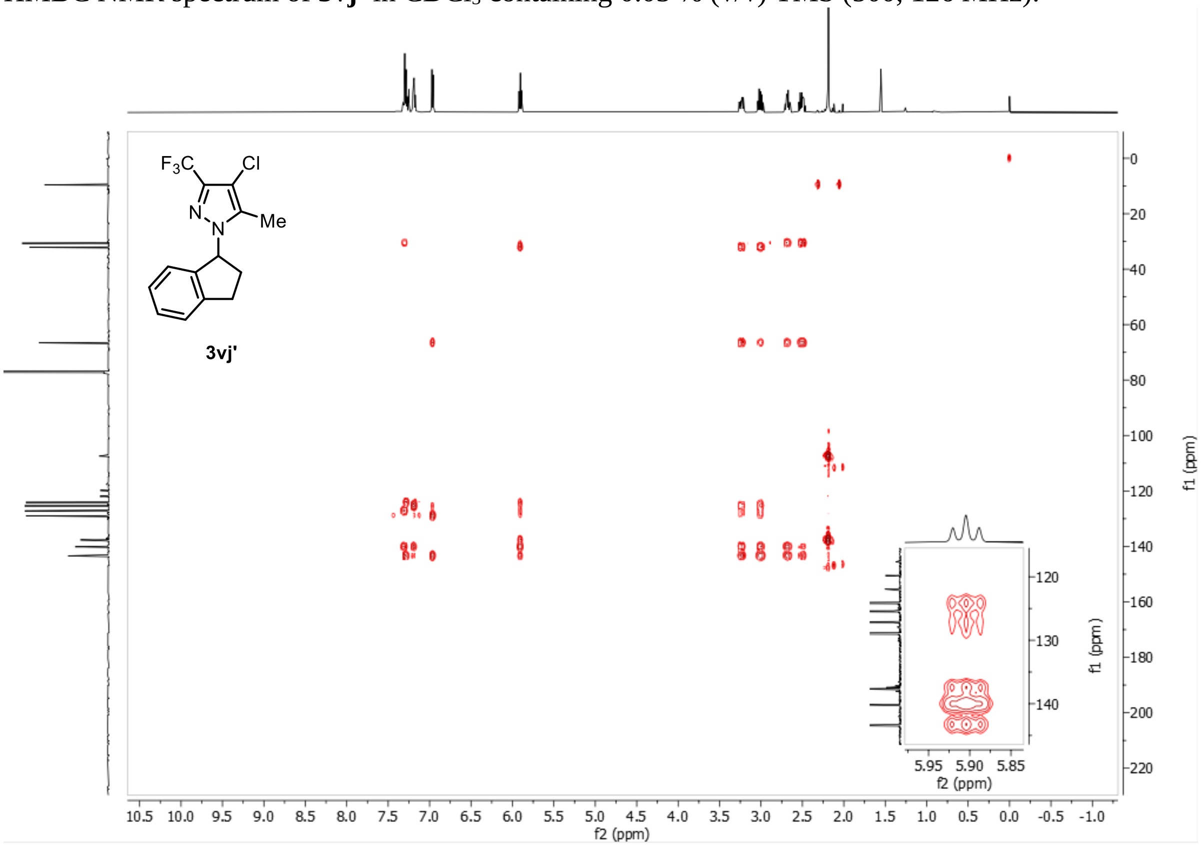
^{19}F NMR spectrum of **3vj'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



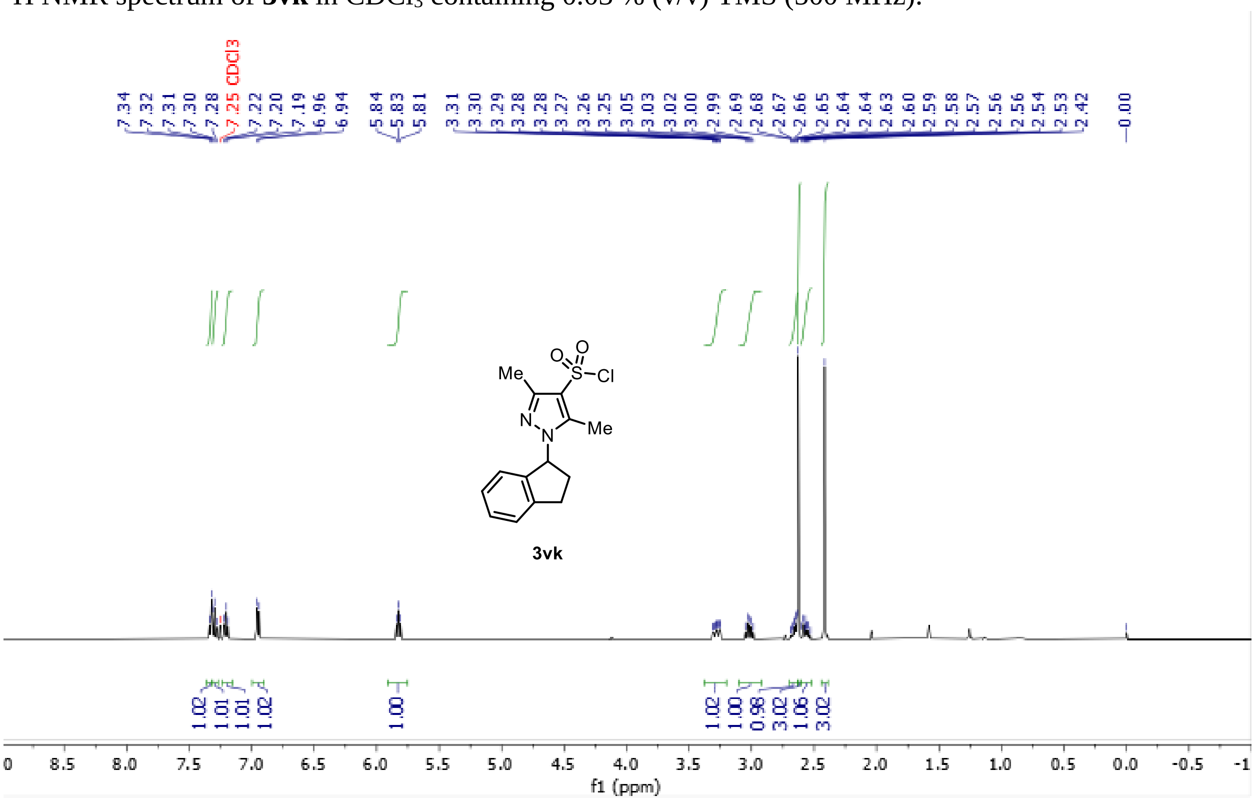
HSQC NMR spectrum of **3vj'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



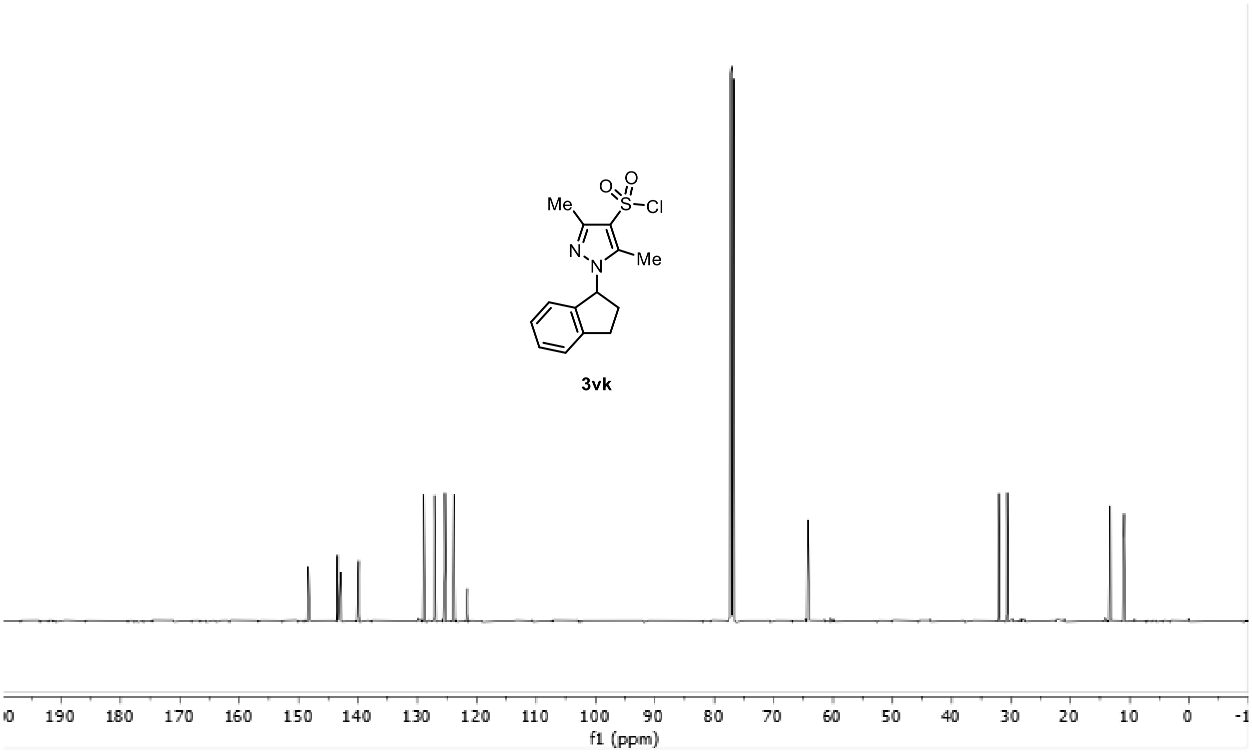
HMBC NMR spectrum of **3vj'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



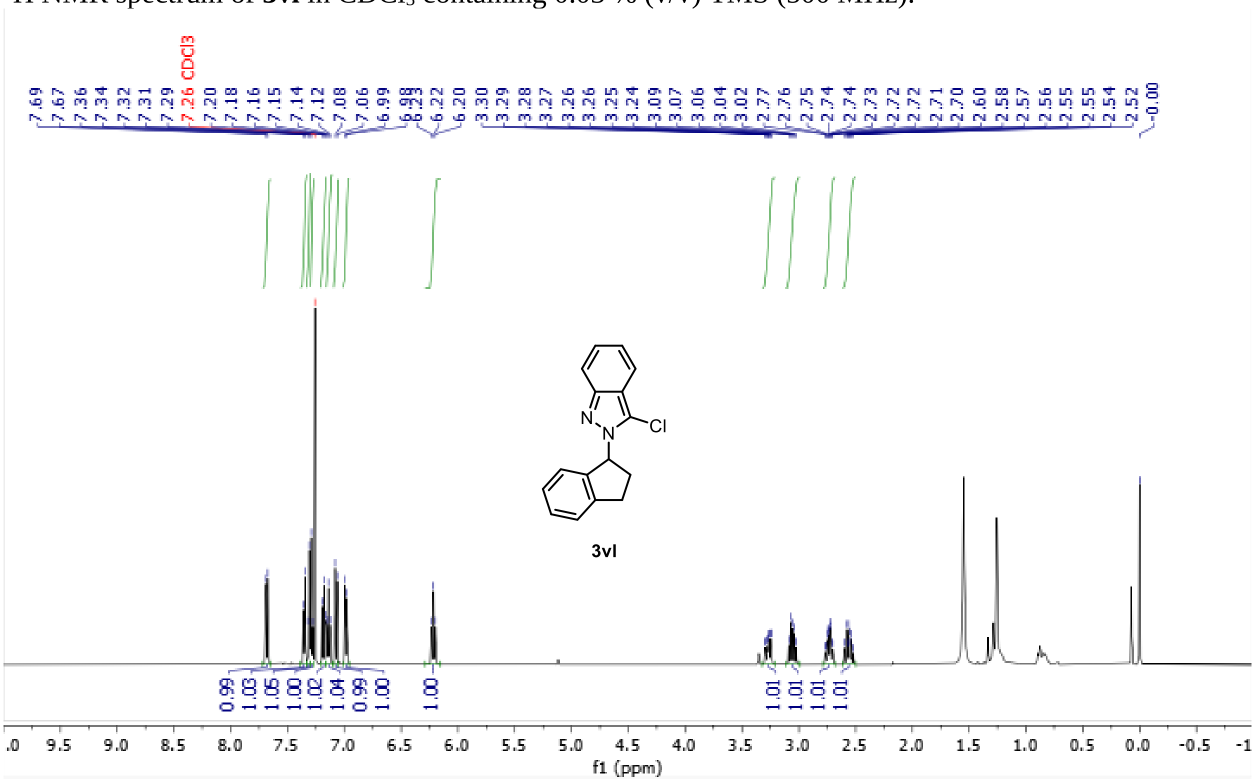
[1]H NMR spectrum of **3vk** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



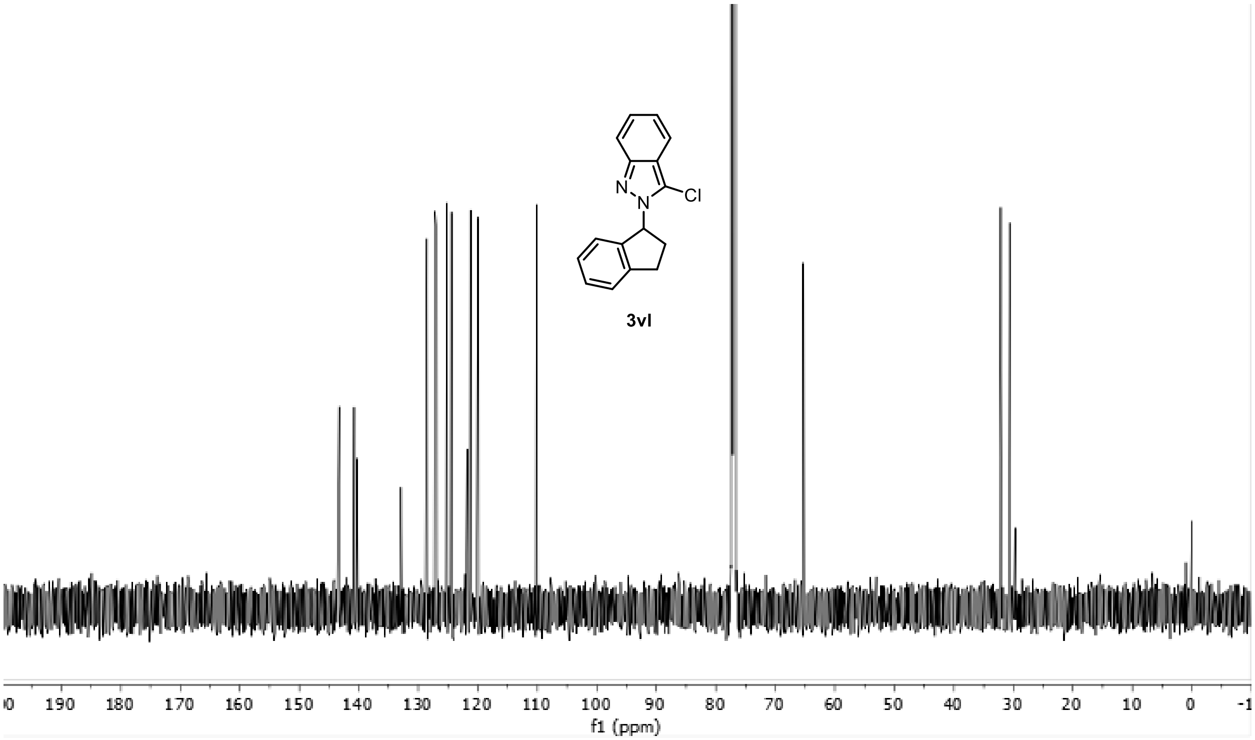
^{13}C NMR spectrum of **3vk** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



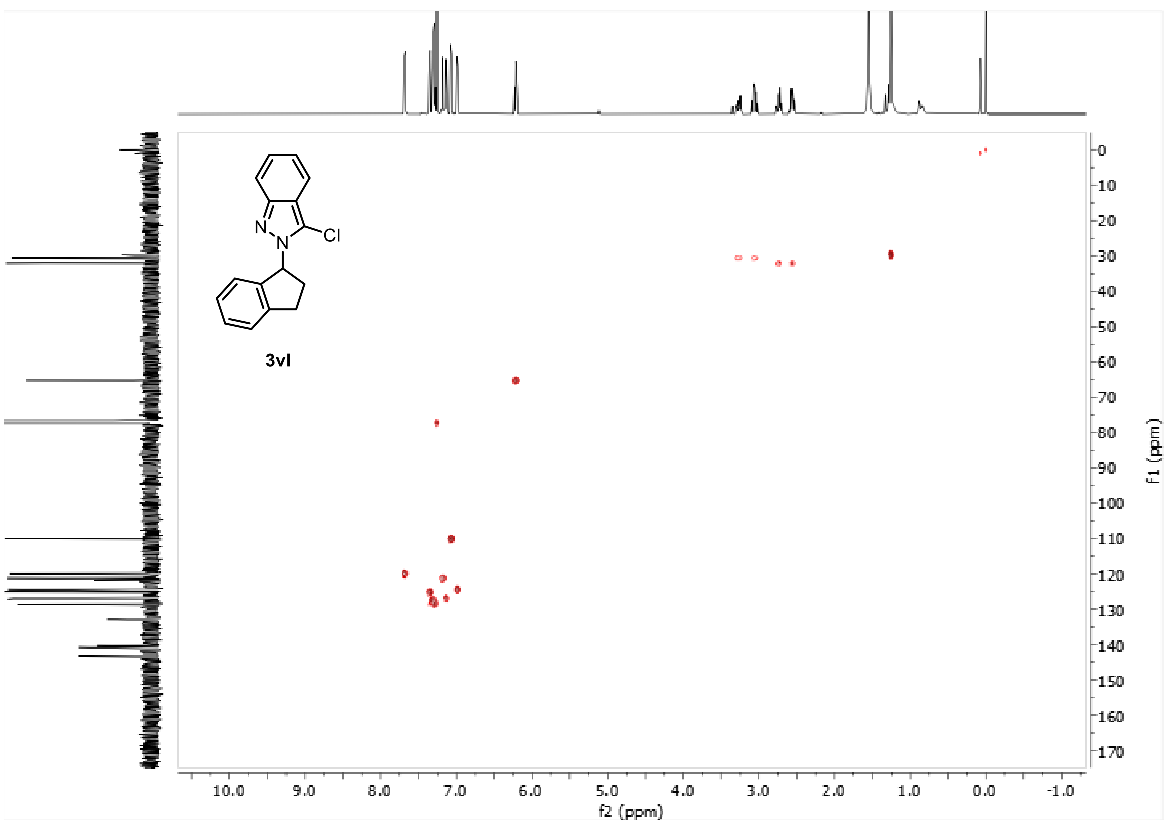
^{1}H NMR spectrum of **3vl** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



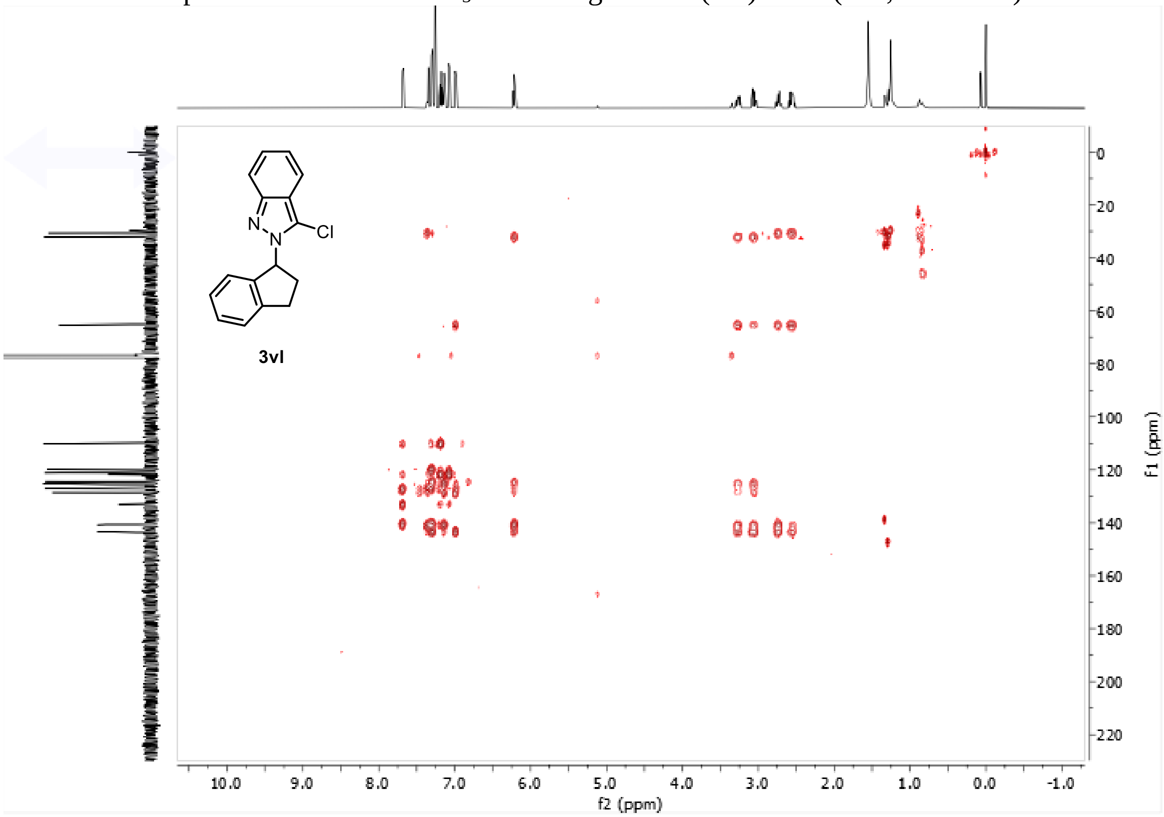
^{13}C NMR spectrum of **3vl** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



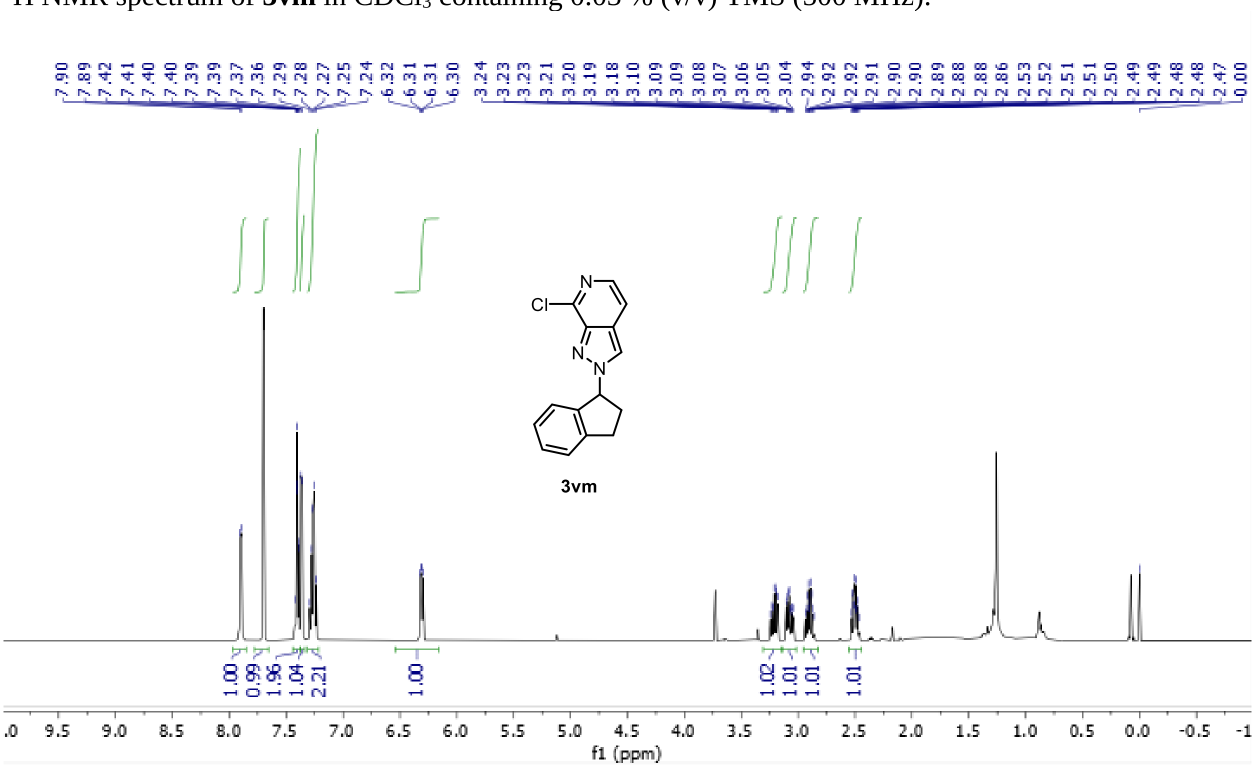
HSQC NMR spectrum of **3vl** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



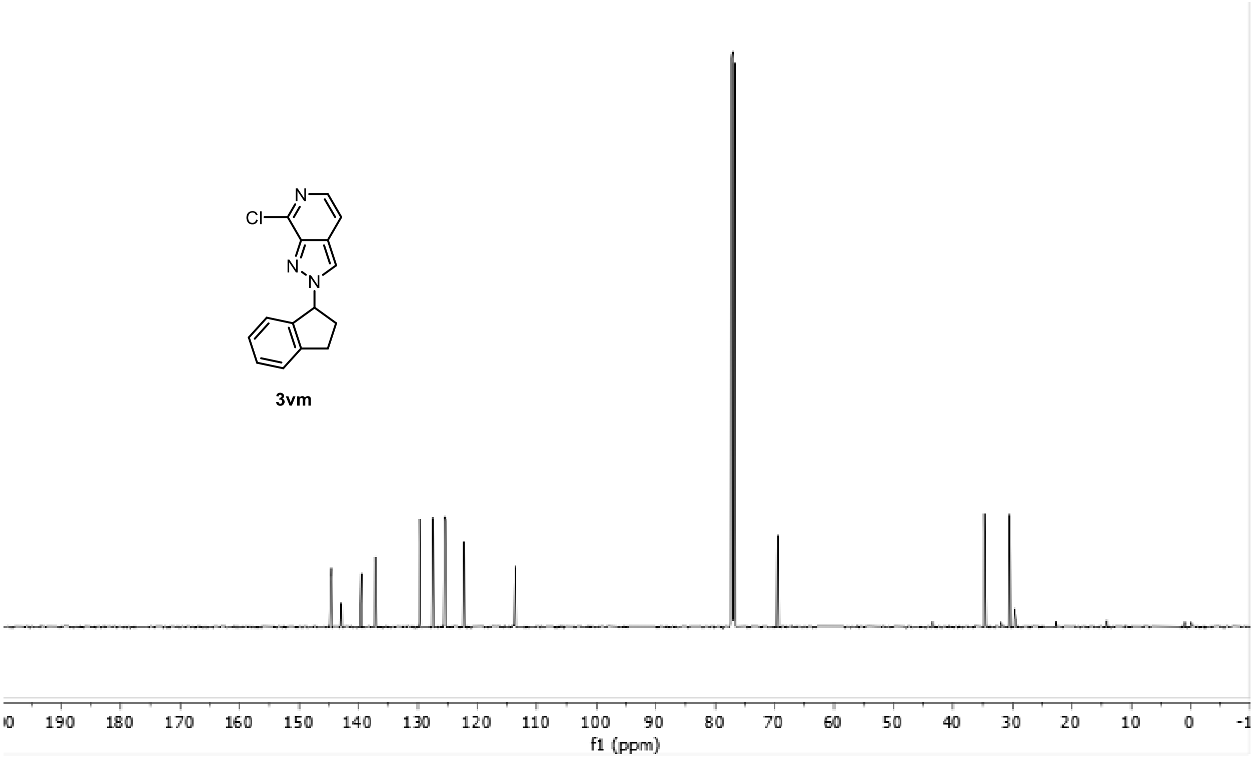
HMBC NMR spectrum of **3vl** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



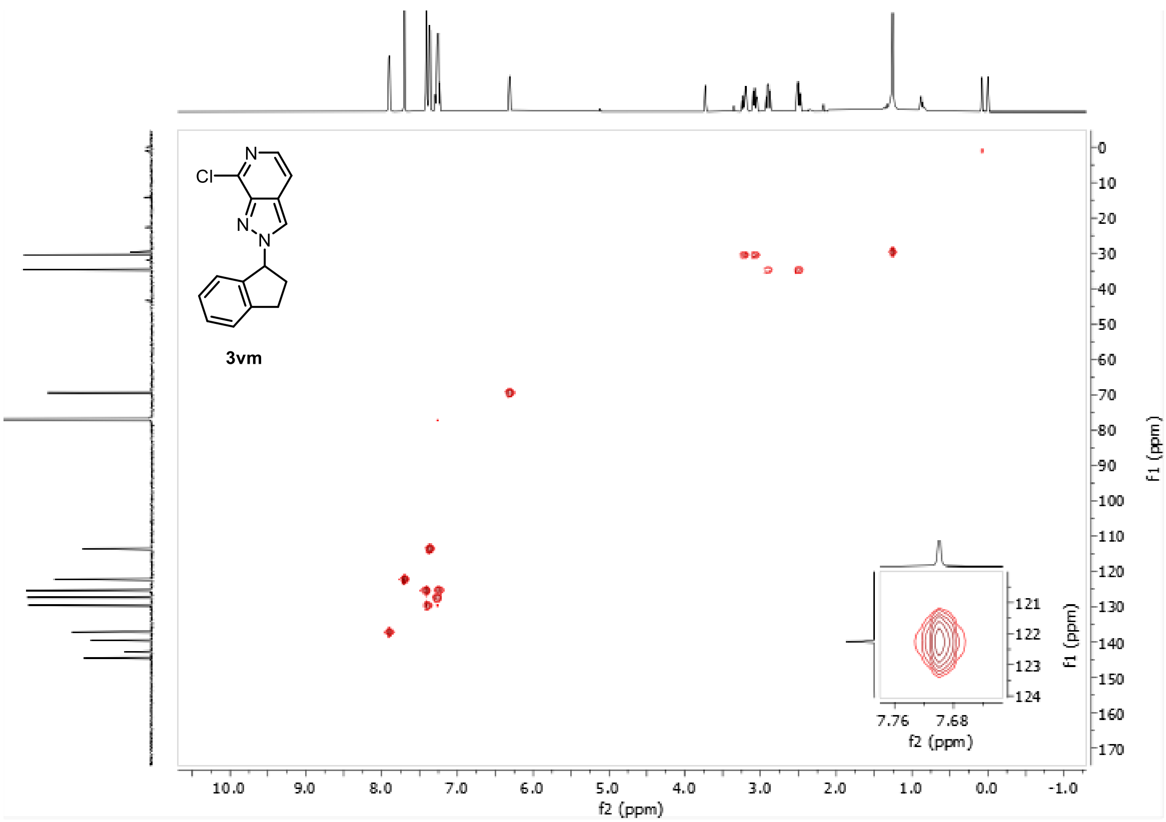
[1]H NMR spectrum of **3vm** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



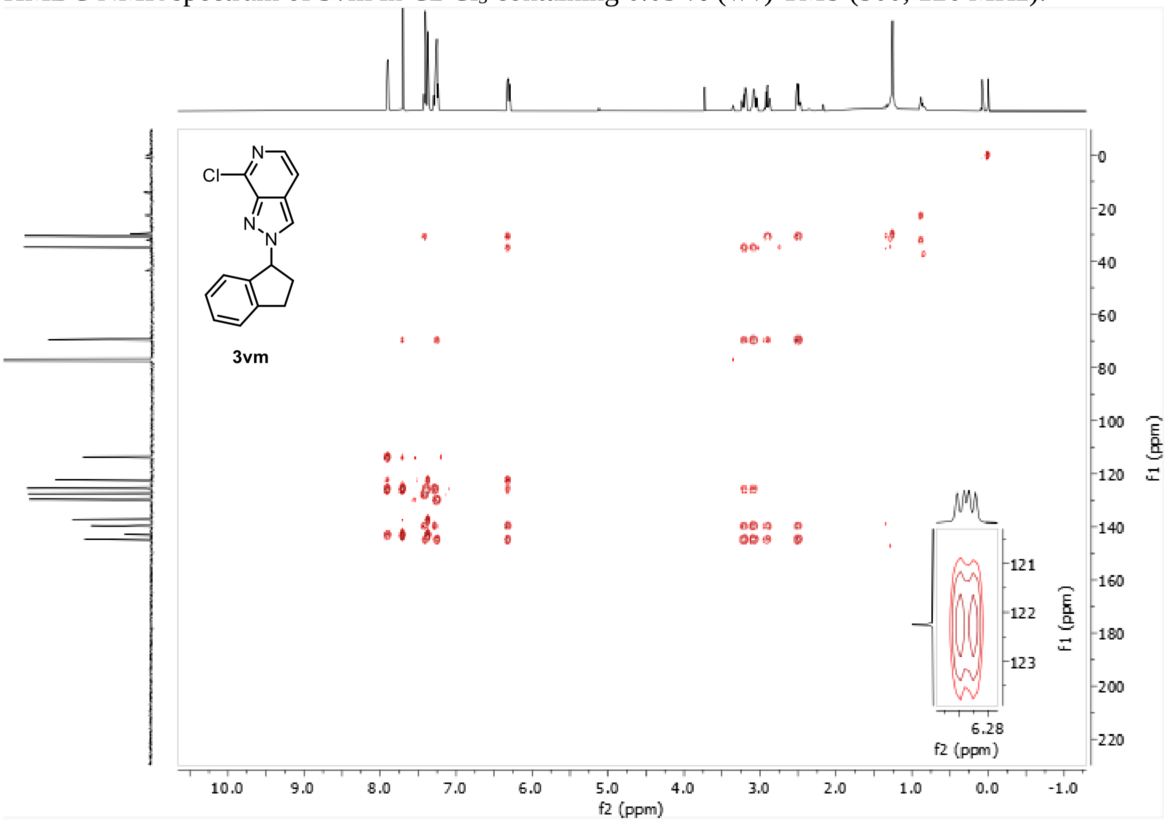
^{13}C NMR spectrum of **3vm** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



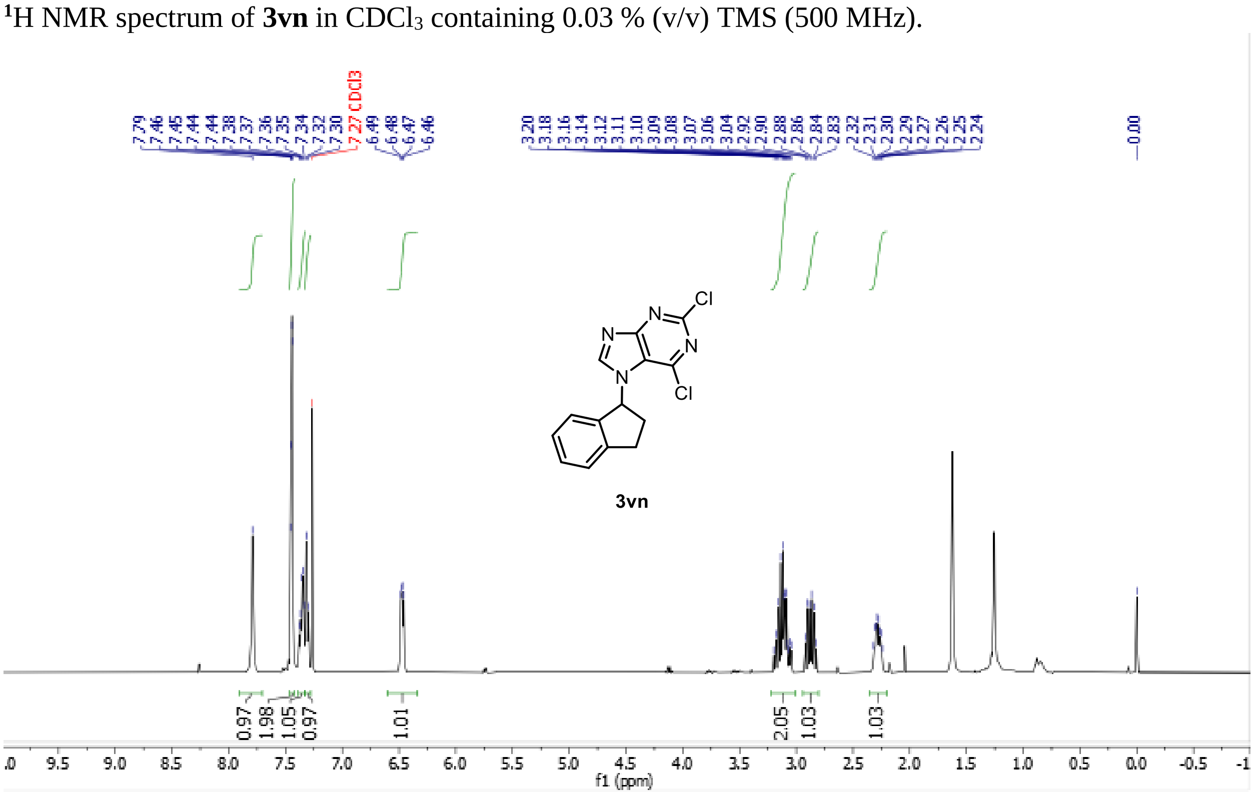
HSQC NMR spectrum of **3vm** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



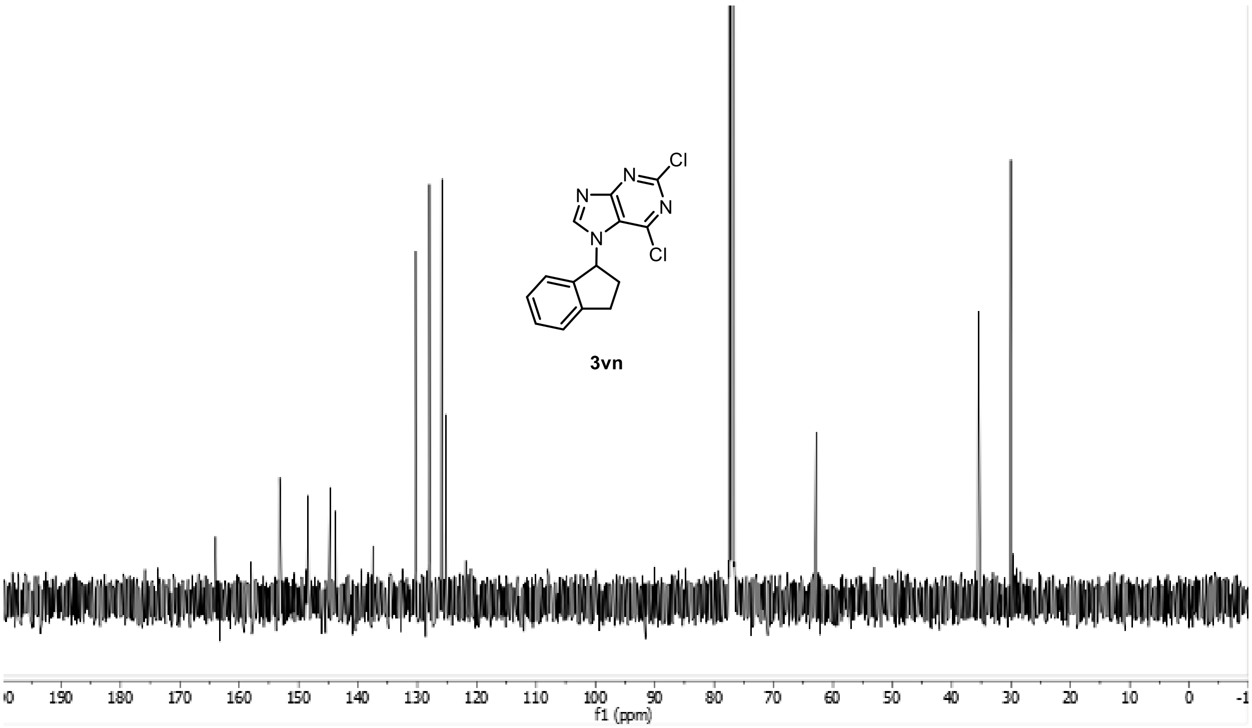
HMBC NMR spectrum of **3vm** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



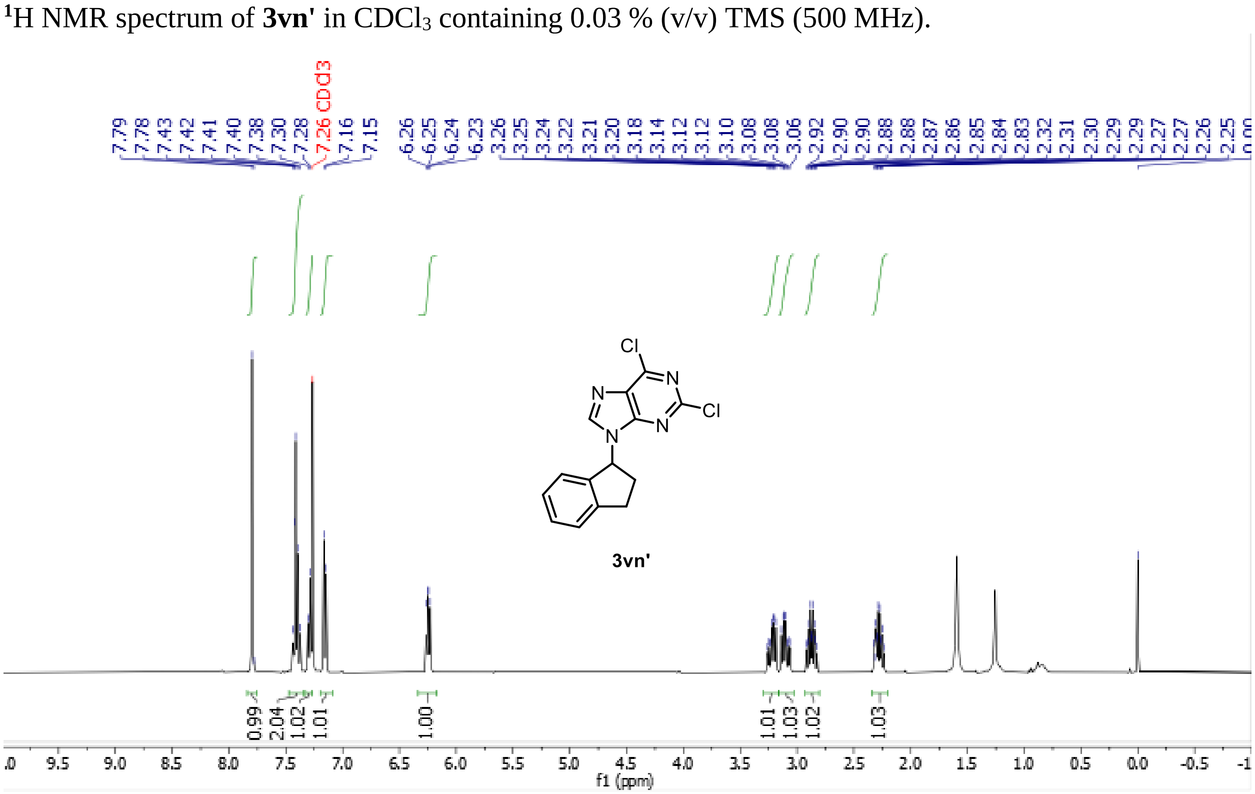
^{1}H NMR spectrum of **3vn** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



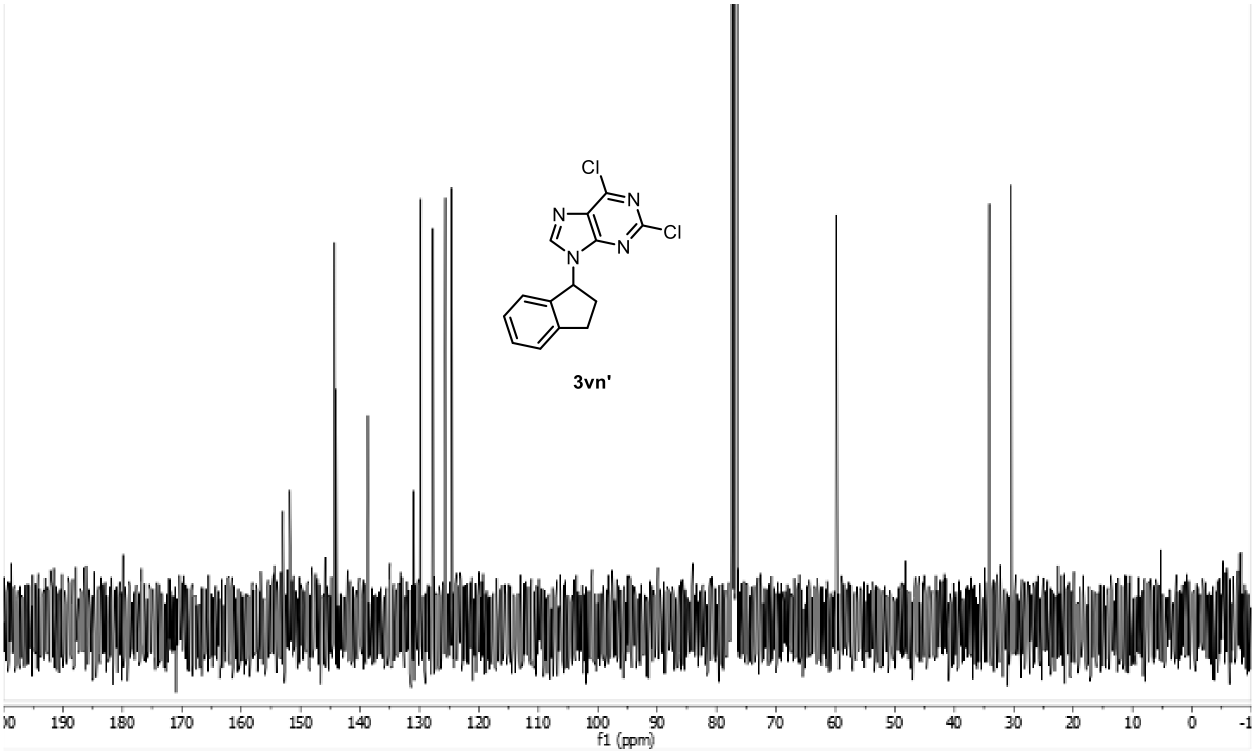
^{13}C NMR spectrum of **3vn** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



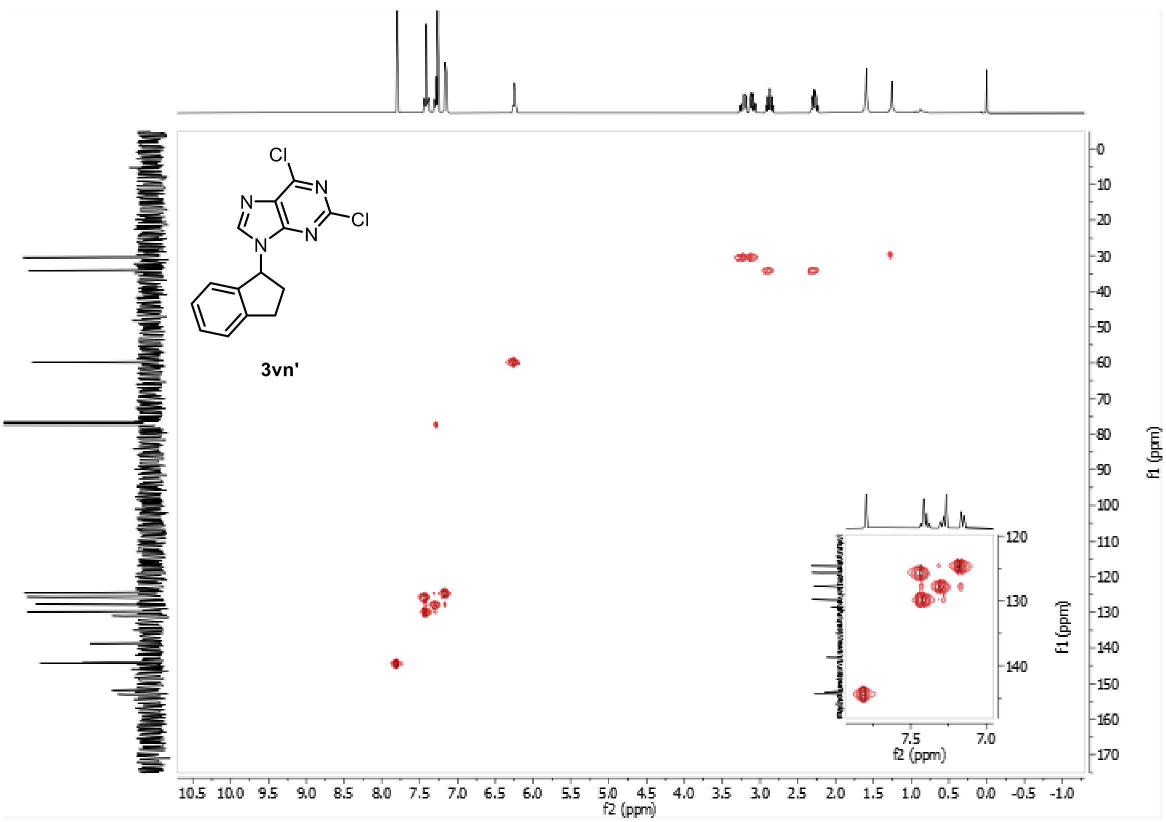
^{1}H NMR spectrum of **3vn'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



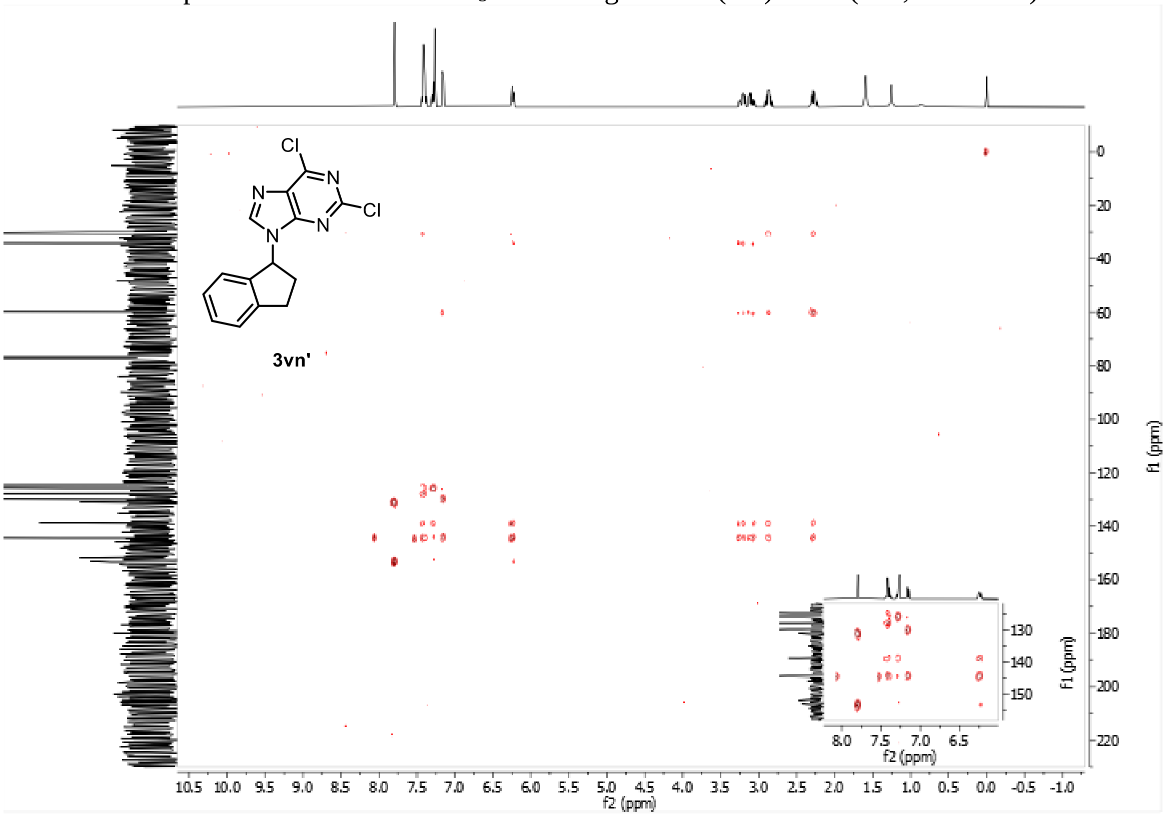
^{13}C NMR spectrum of **3vn'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



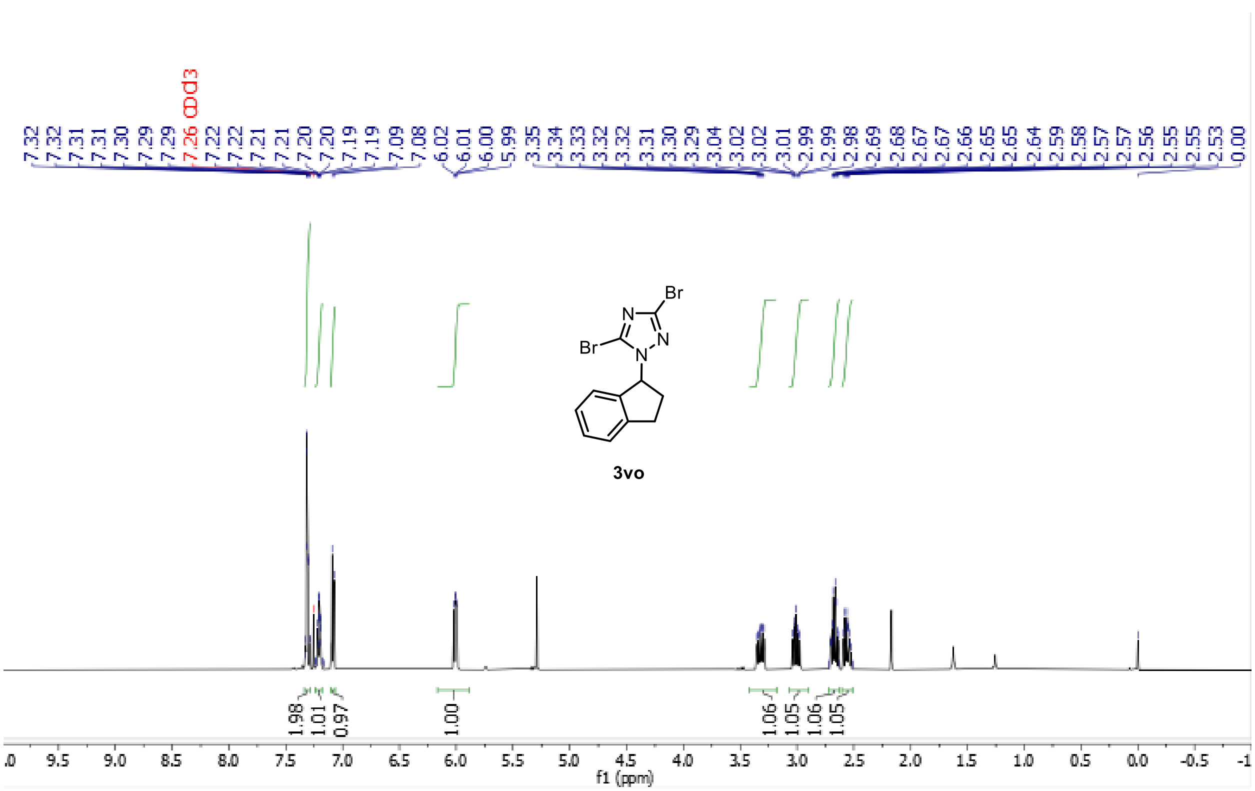
HSQC NMR spectrum of **3vn'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



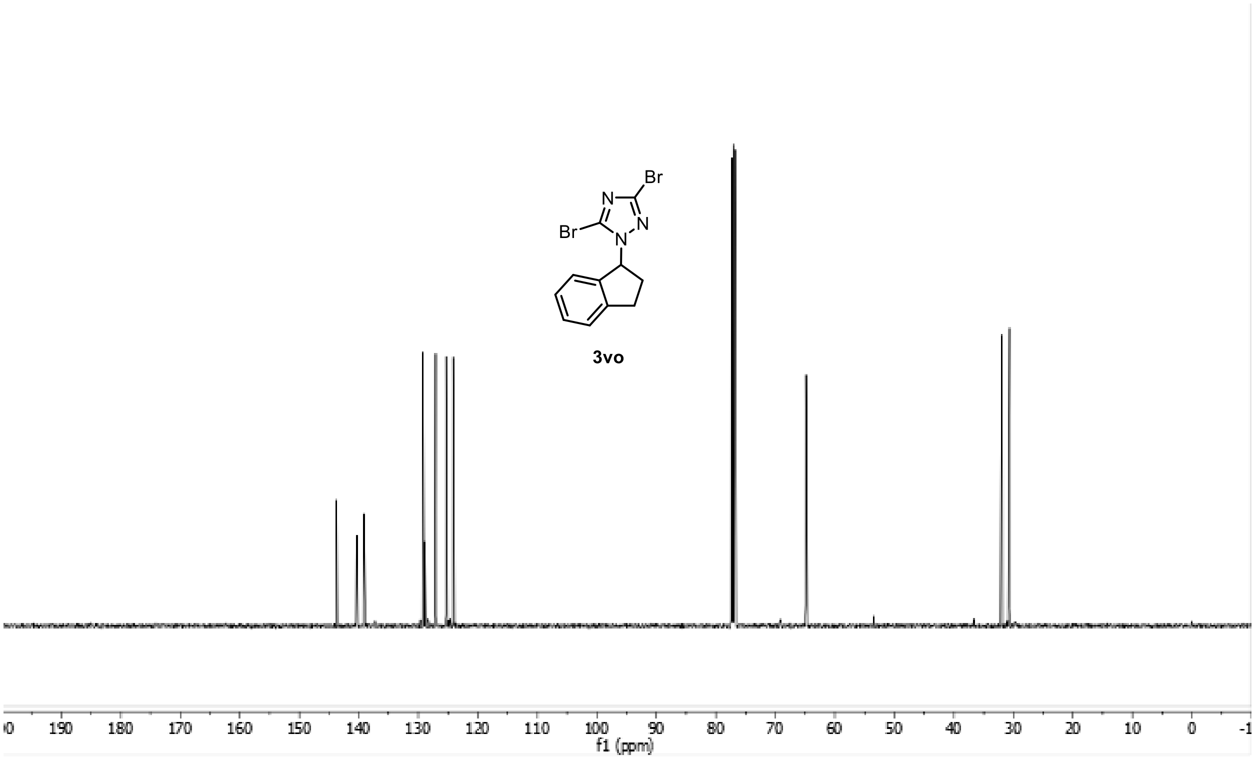
HMBC NMR spectrum of **3vn'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



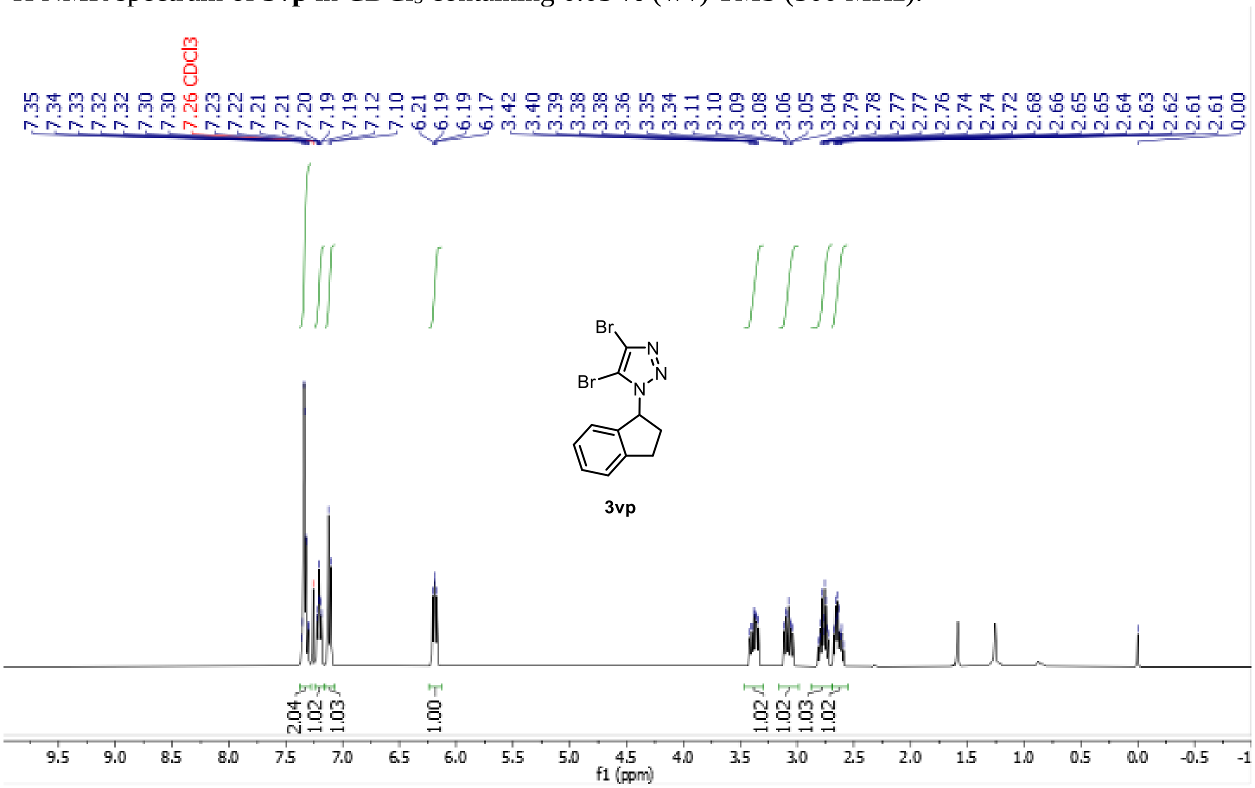
^{1}H NMR spectrum of **3vo** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



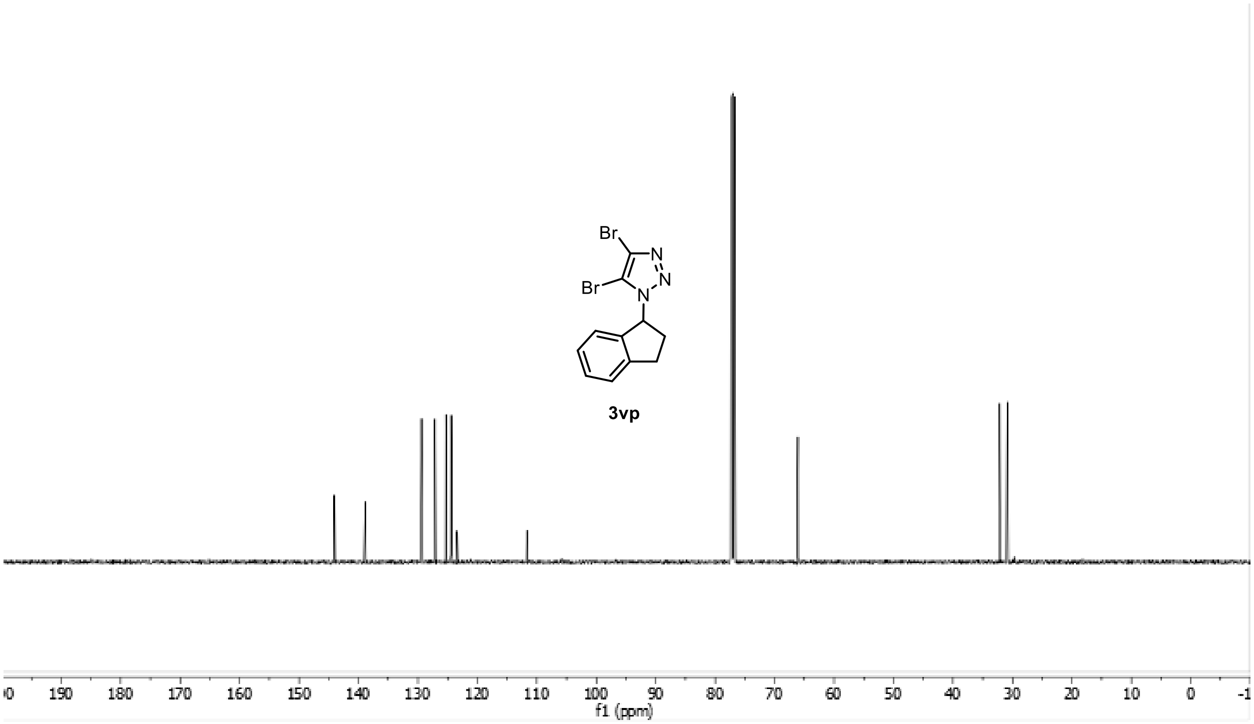
^{13}C NMR spectrum of **3vo** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



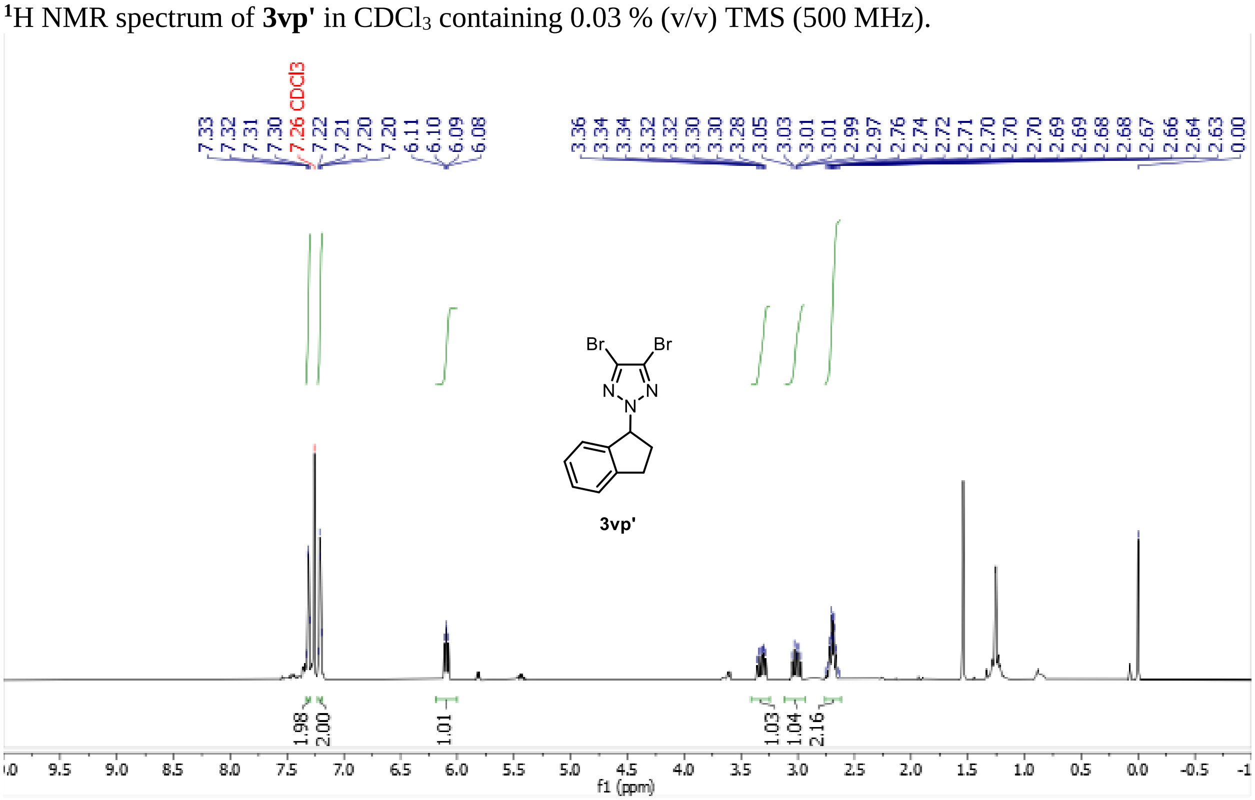
^{1}H NMR spectrum of **3vp** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



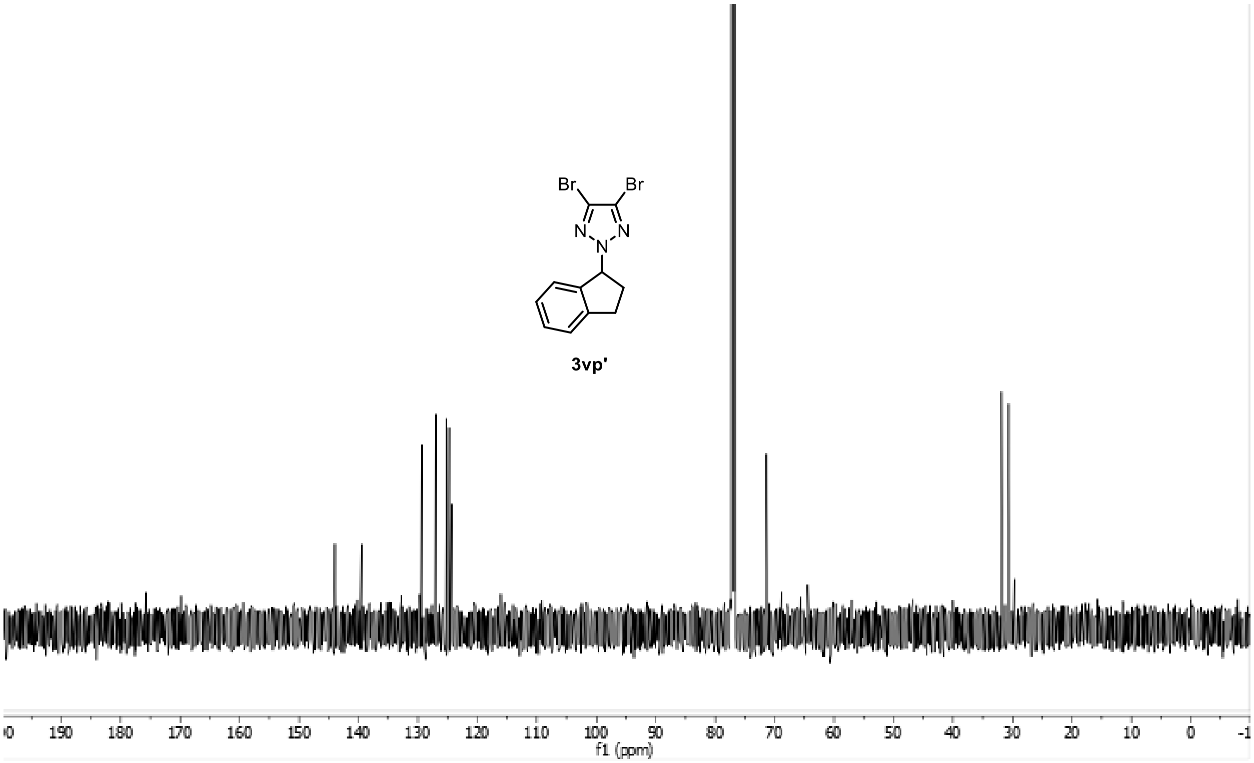
^{13}C NMR spectrum of **3vp** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



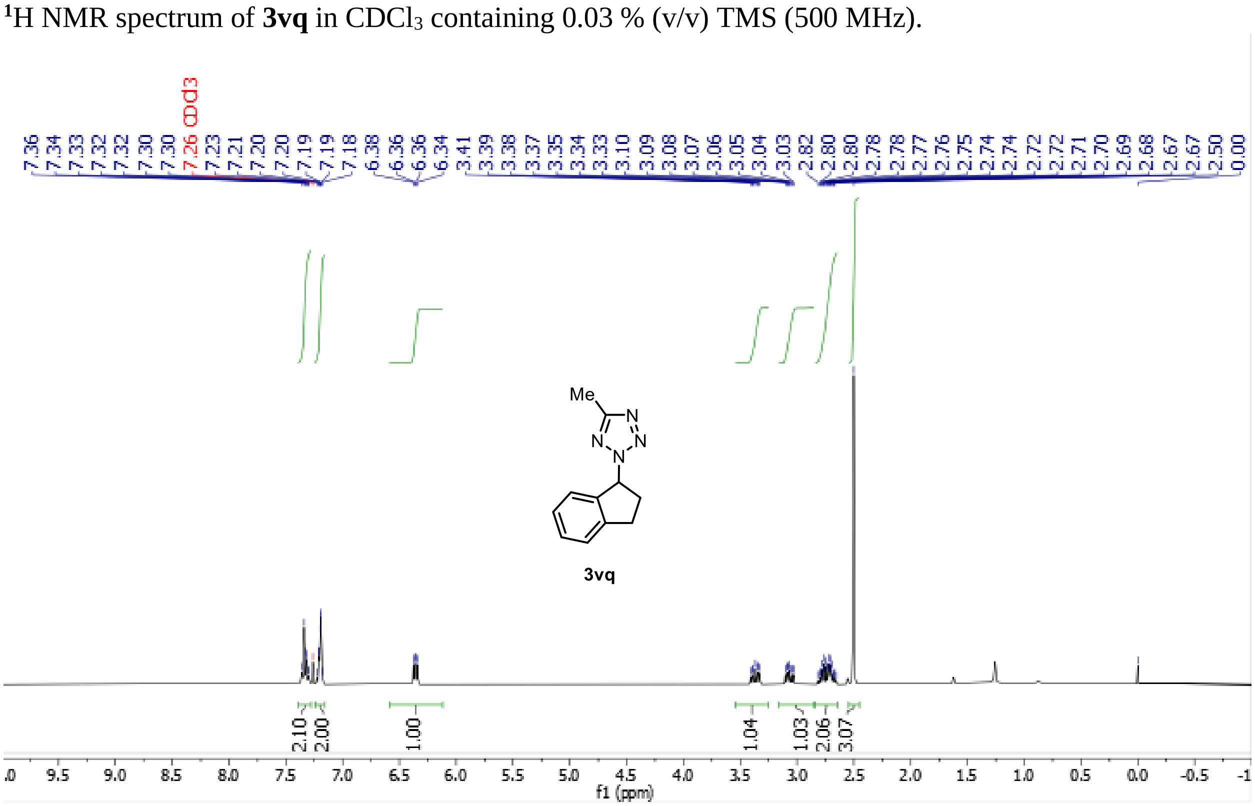
^{1}H NMR spectrum of **3vp'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



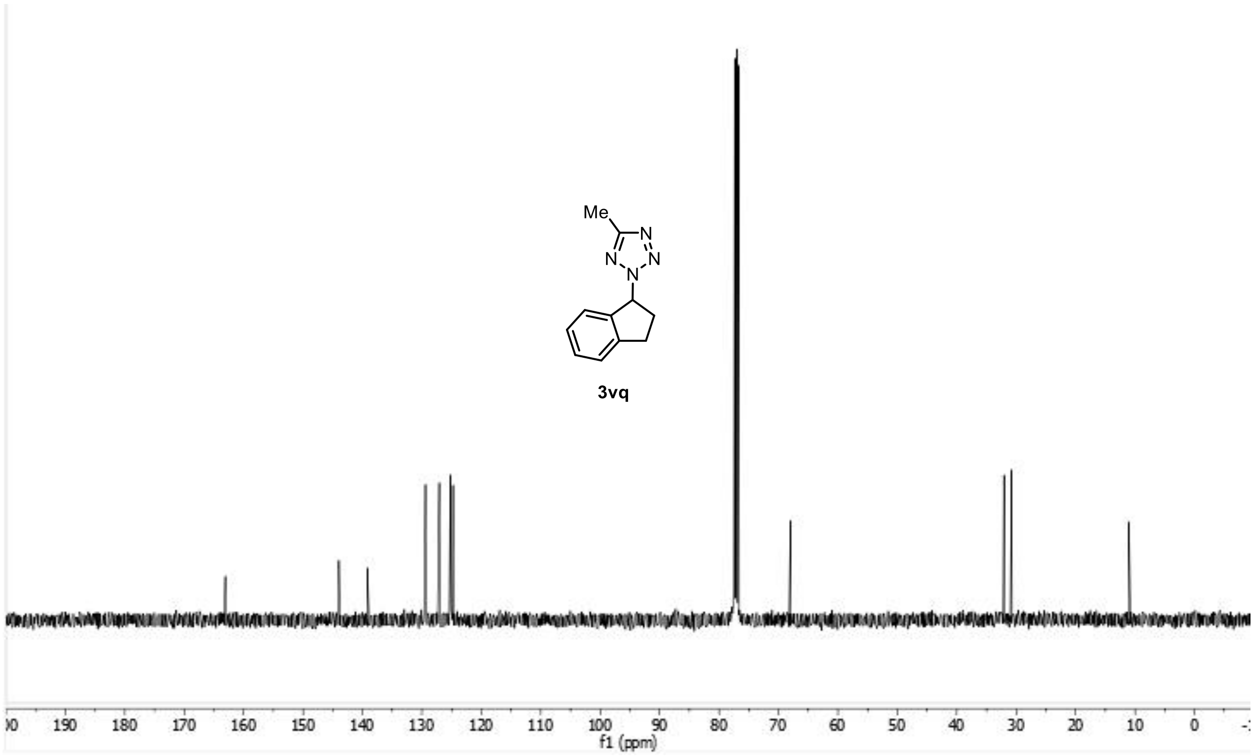
[13]C NMR spectrum of **3vp'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



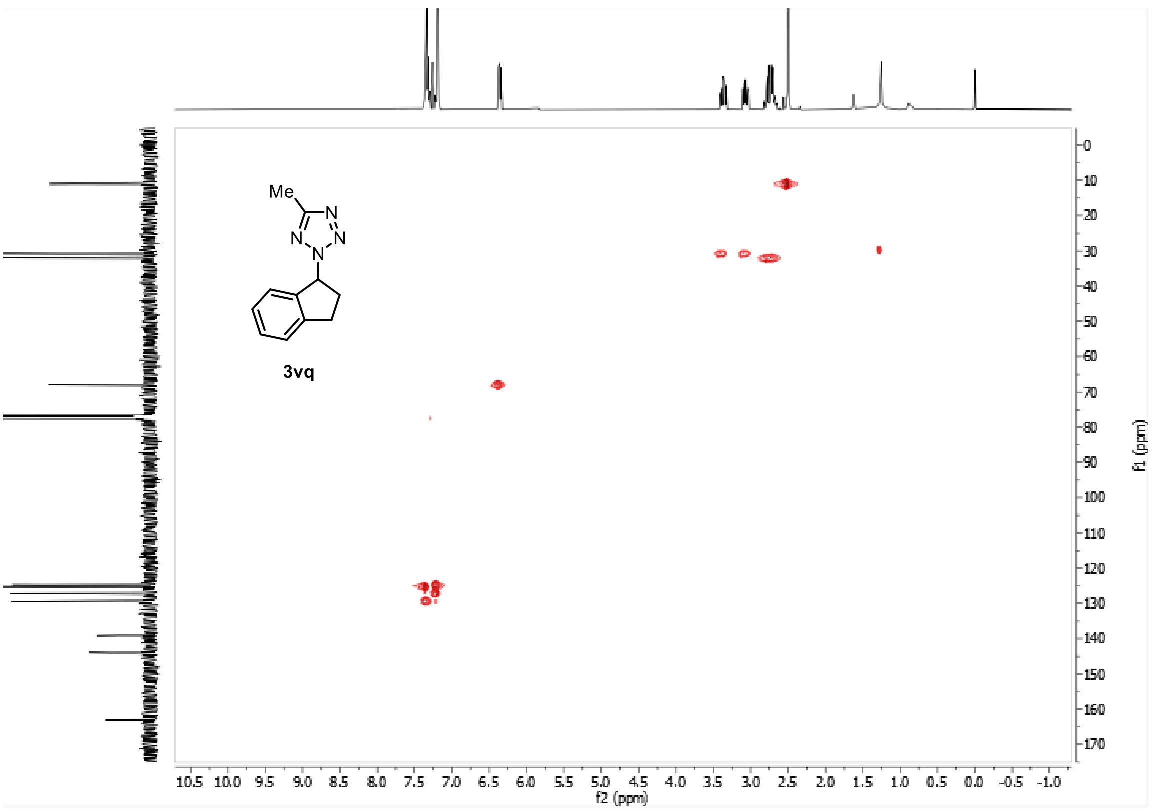
[1]H NMR spectrum of **3vq** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



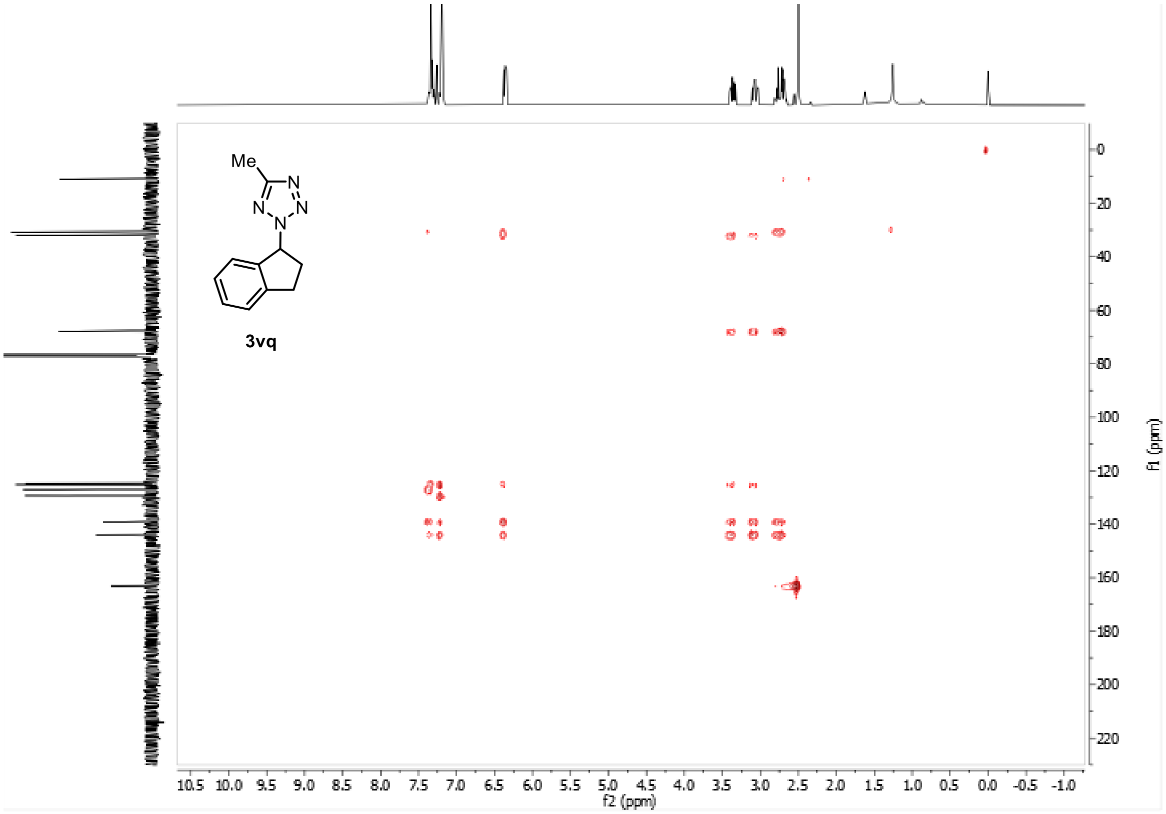
[13]C NMR spectrum of **3vq** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



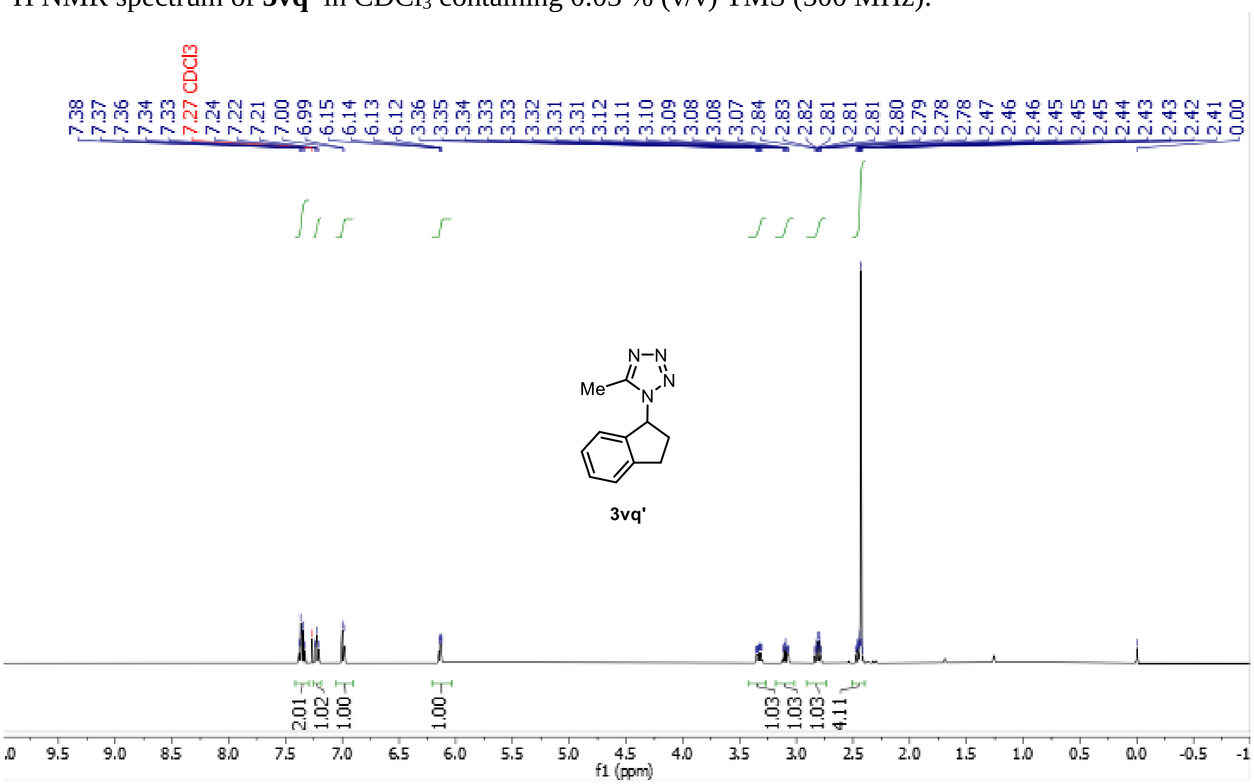
HSQC NMR spectrum of **3vq** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



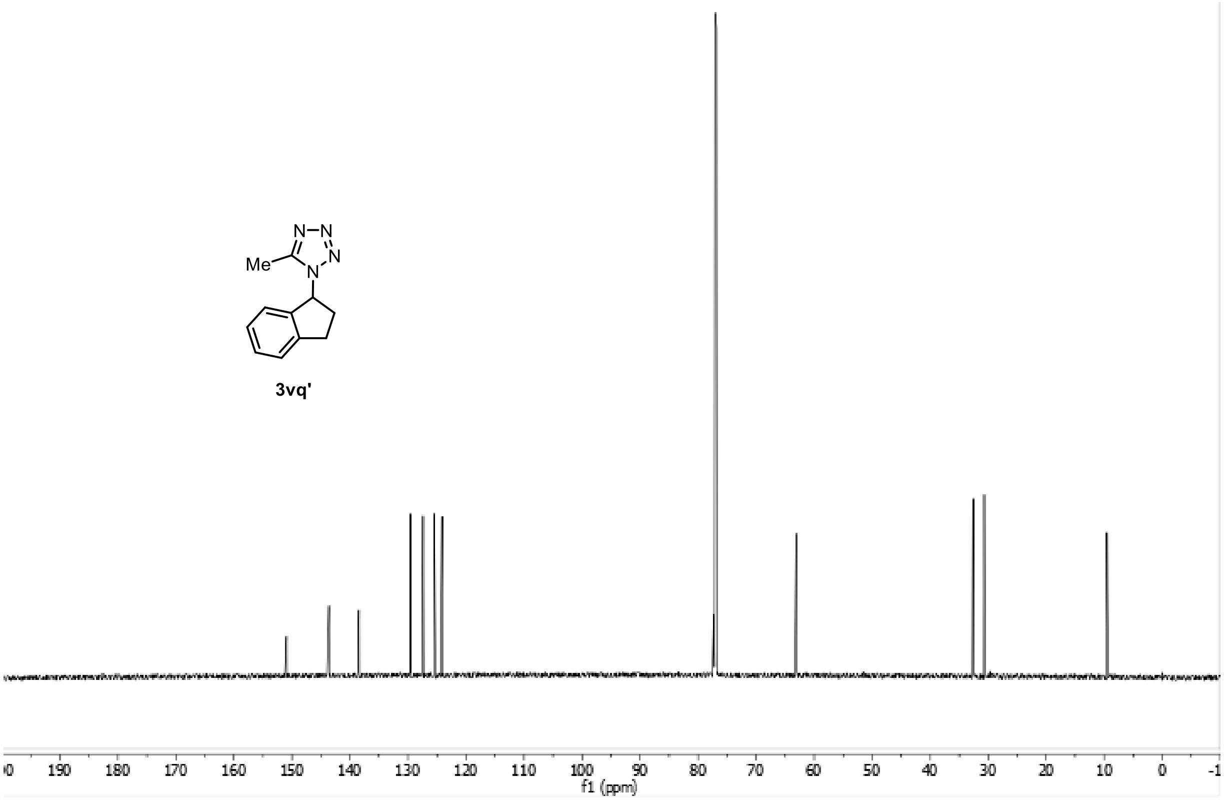
HMBC NMR spectrum of **3vq** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



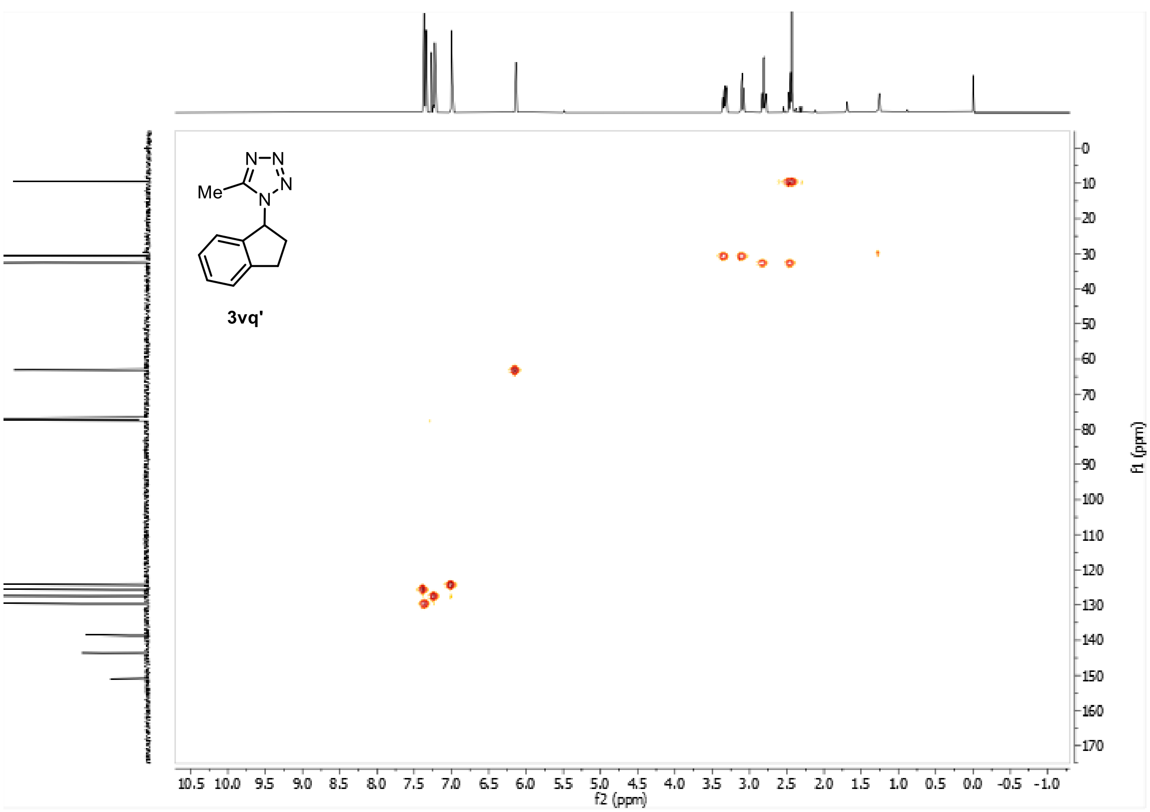
[1]H NMR spectrum of **3vq'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



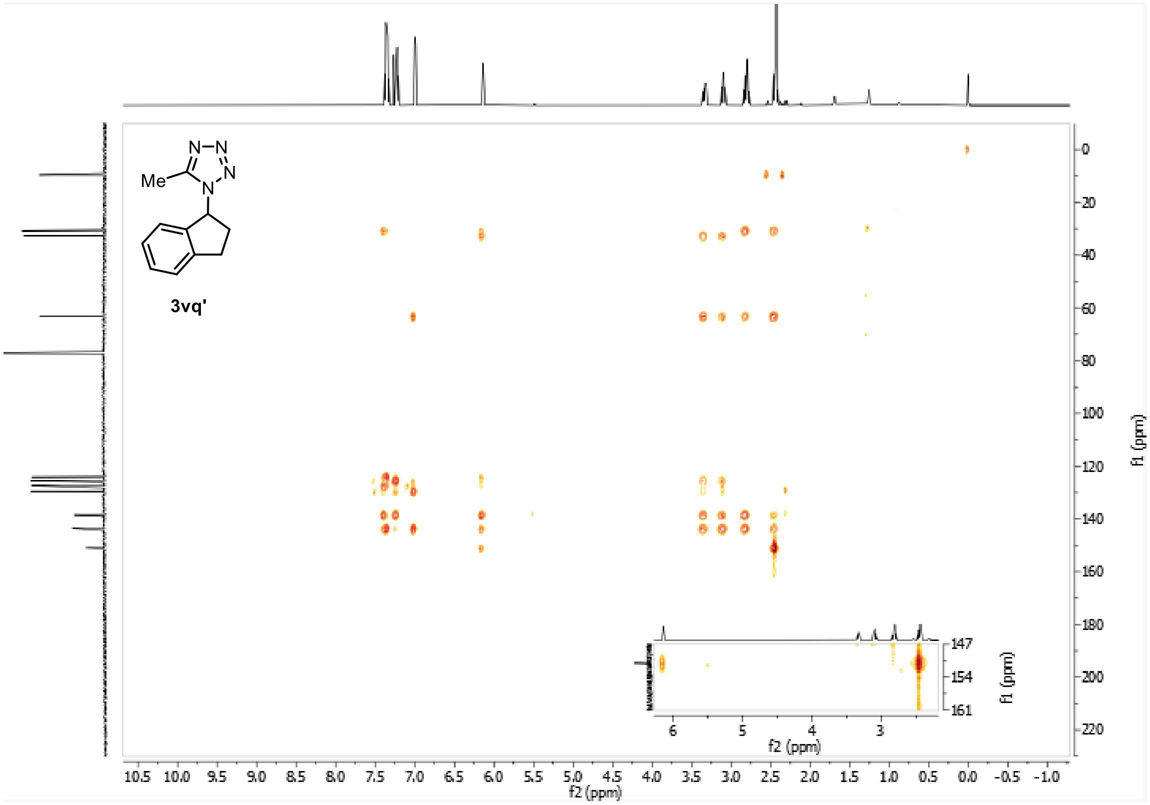
^{13}C NMR spectrum of **3vq'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



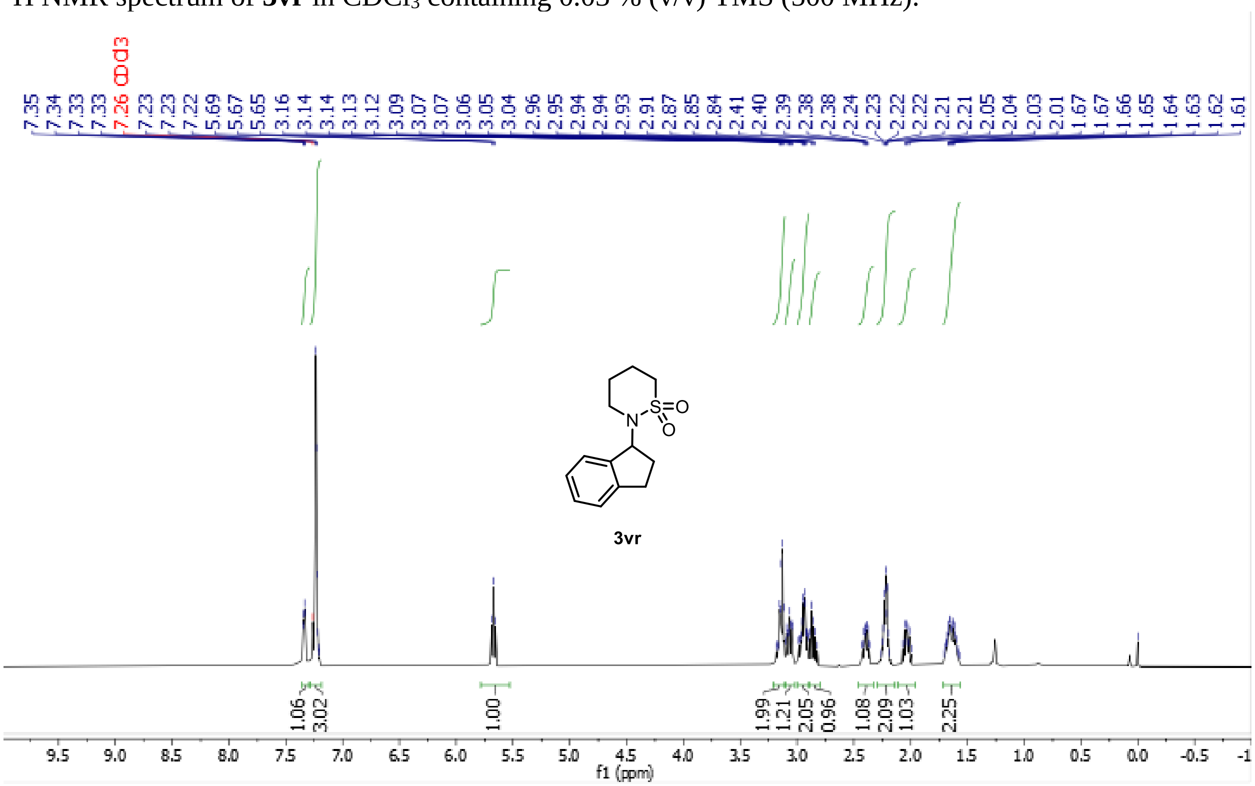
HSQC NMR spectrum of **3vq'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



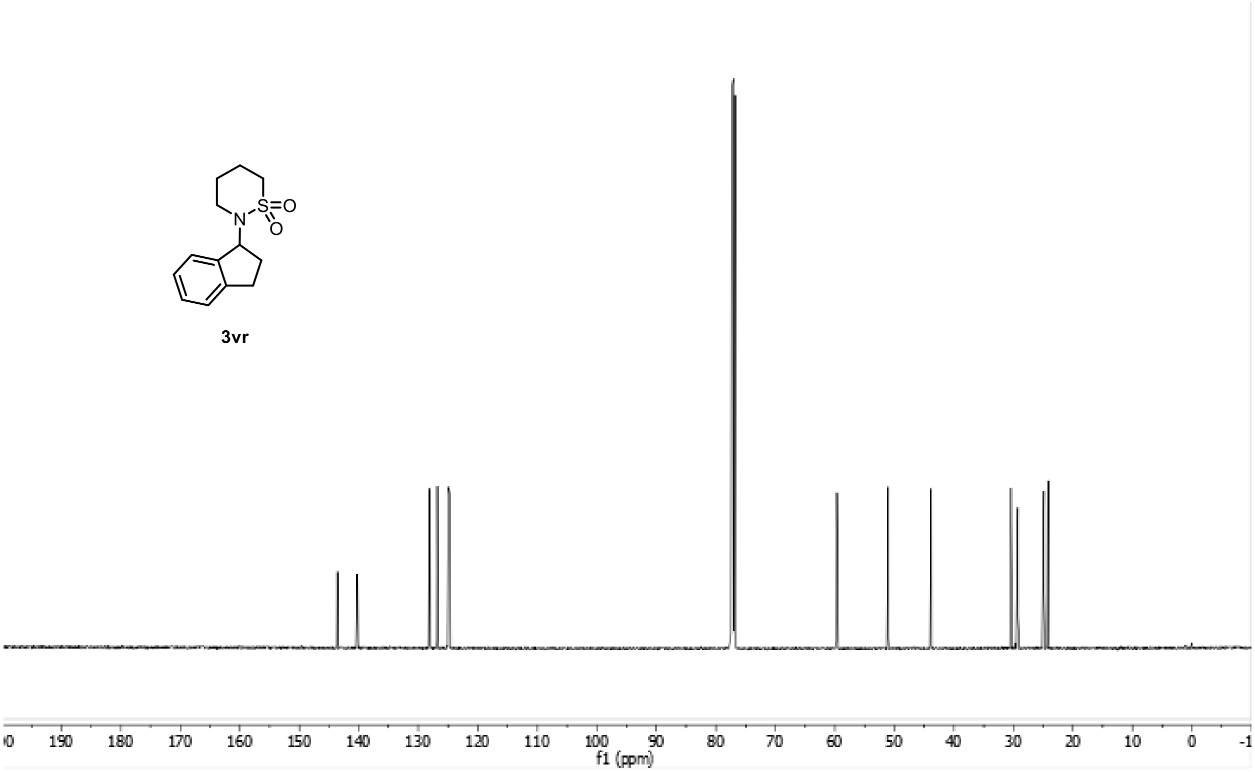
HMBC NMR spectrum of **3vq'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



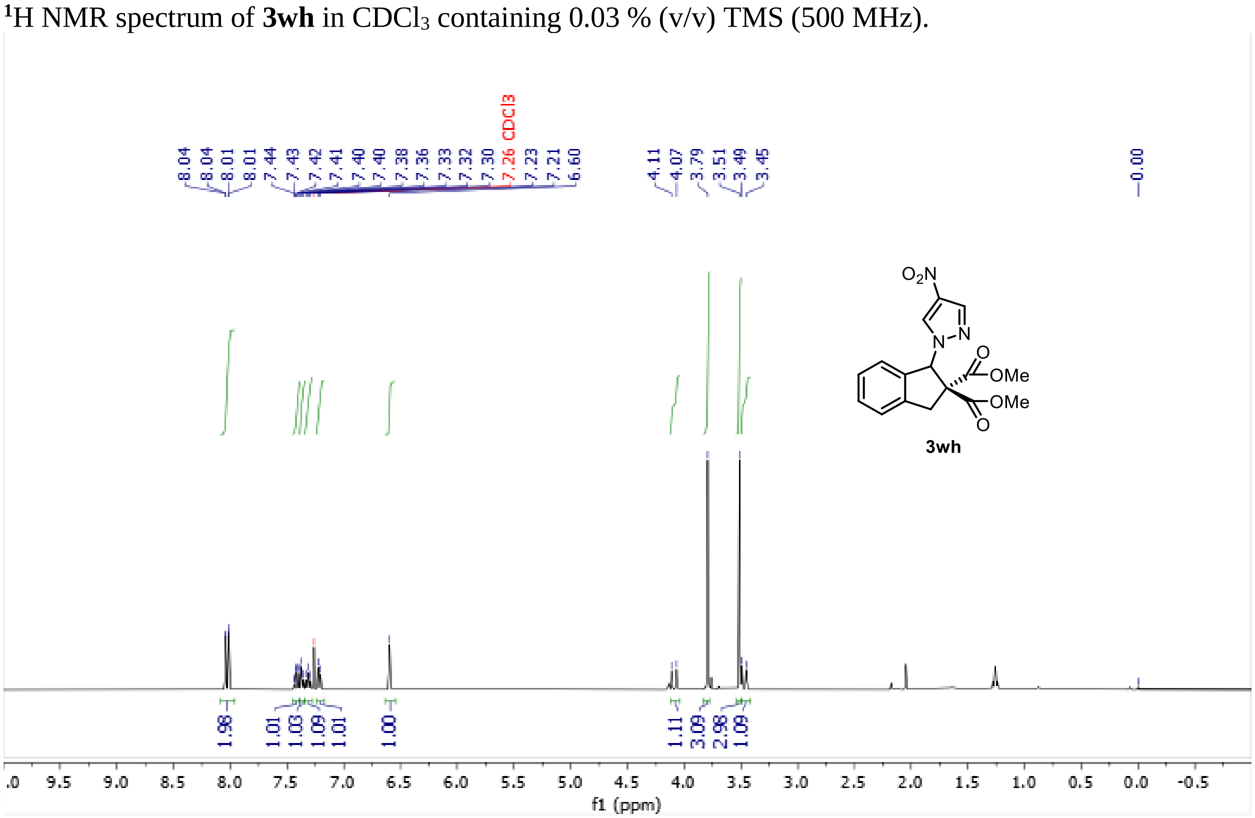
^{1}H NMR spectrum of **3vr** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



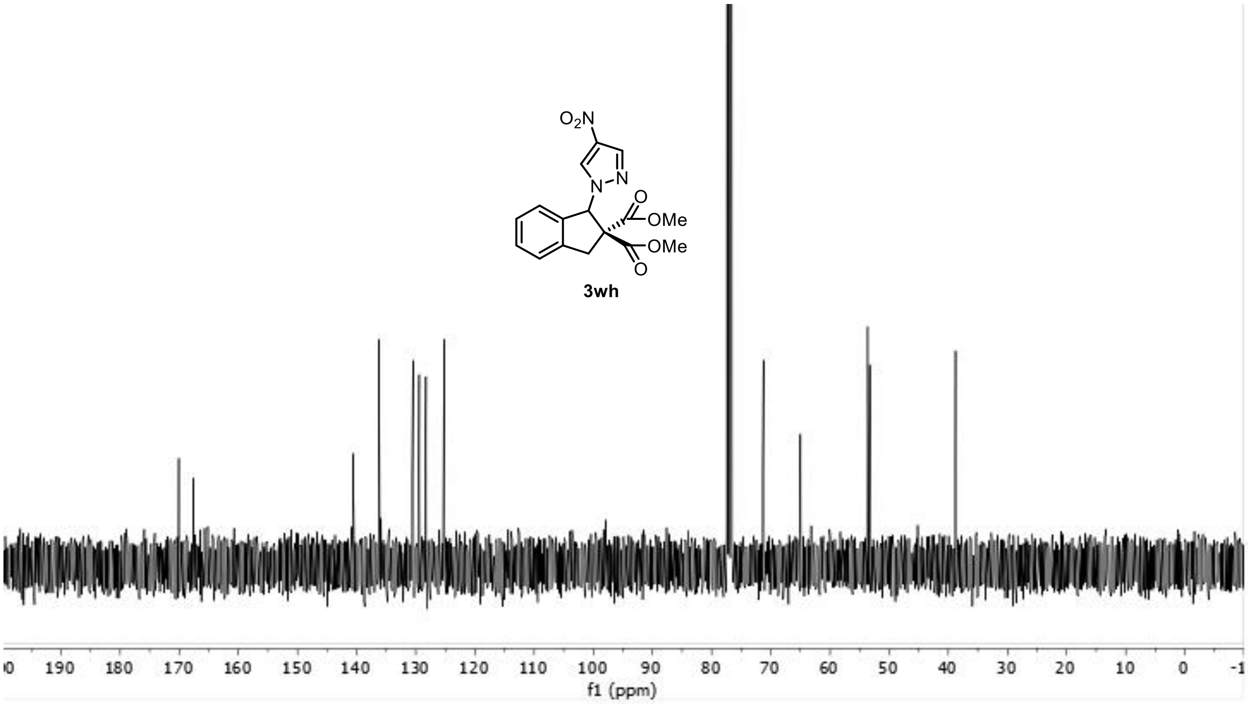
^{13}C NMR spectrum of **3vr** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



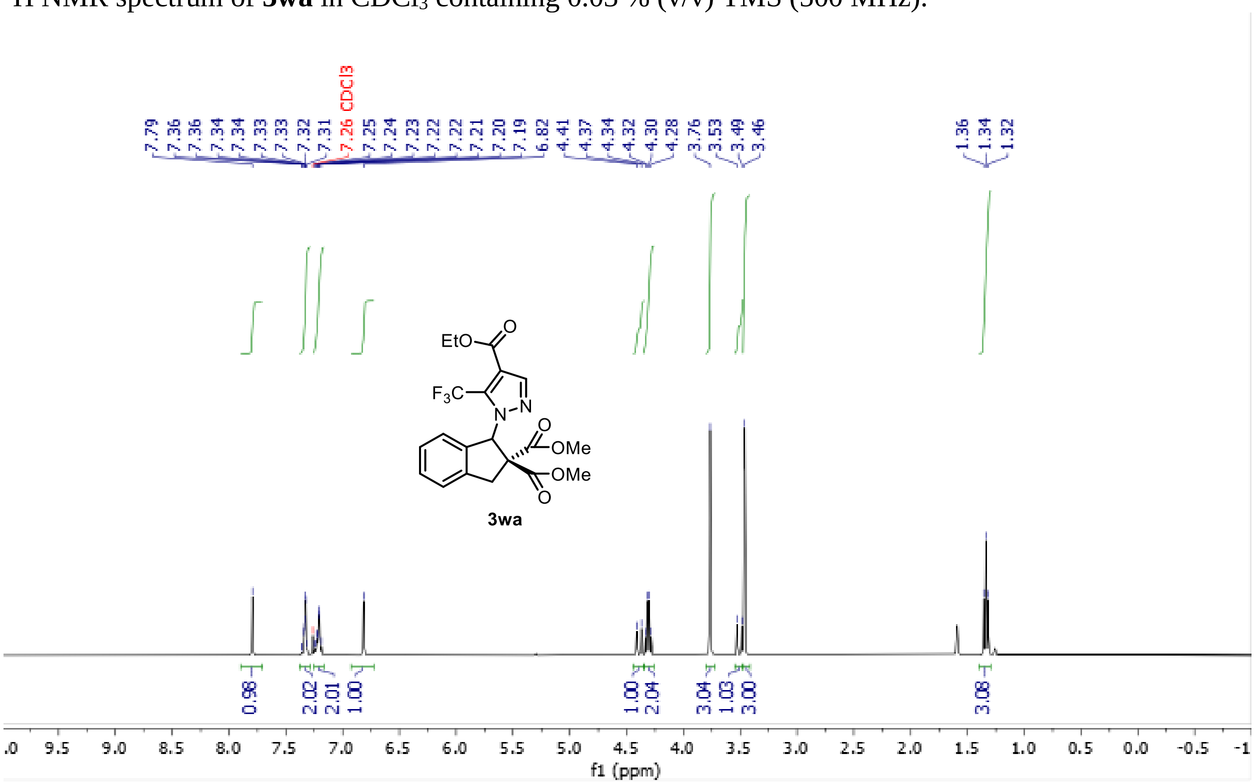
^{1}H NMR spectrum of **3wh** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



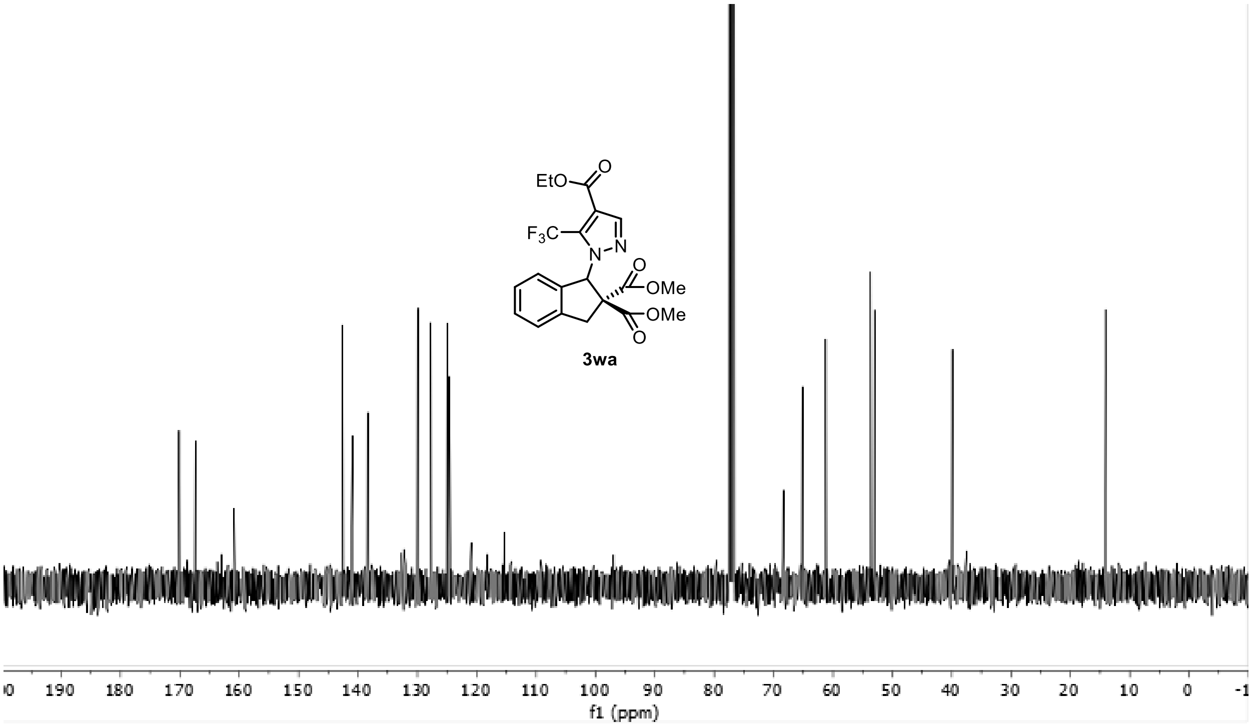
^{13}C NMR spectrum of **3wh** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



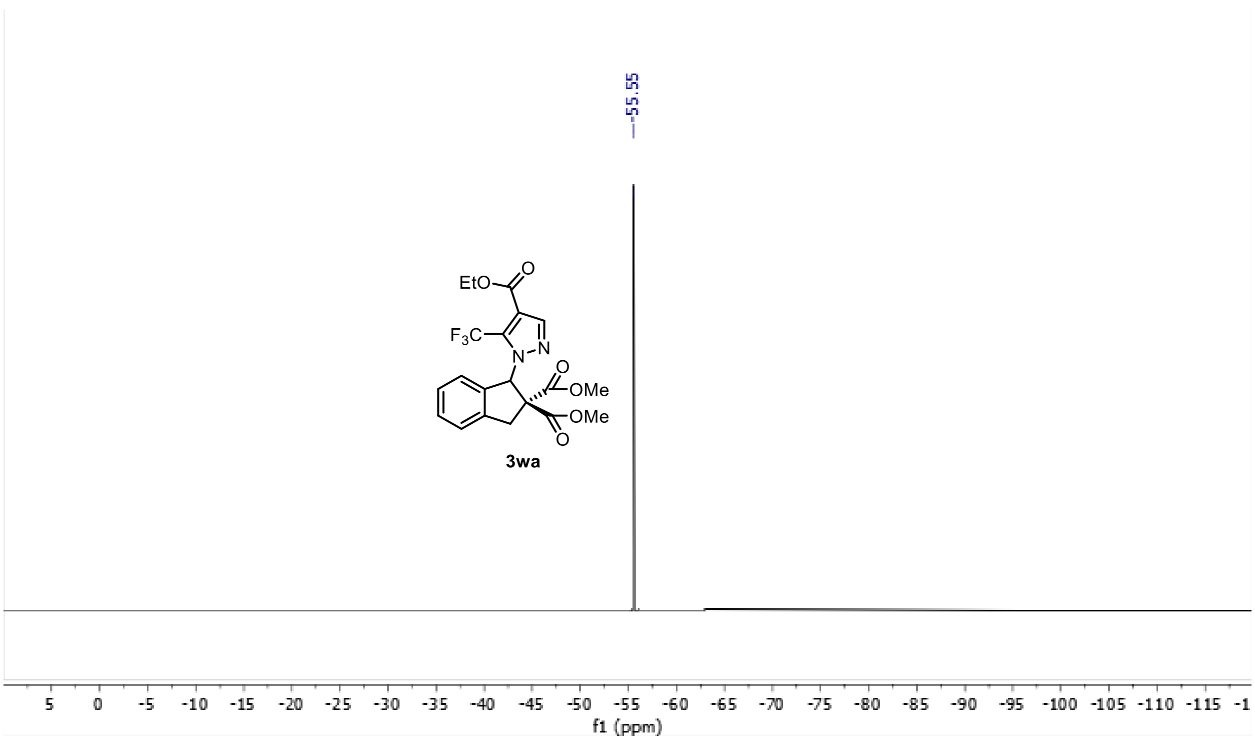
^{1}H NMR spectrum of **3wa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



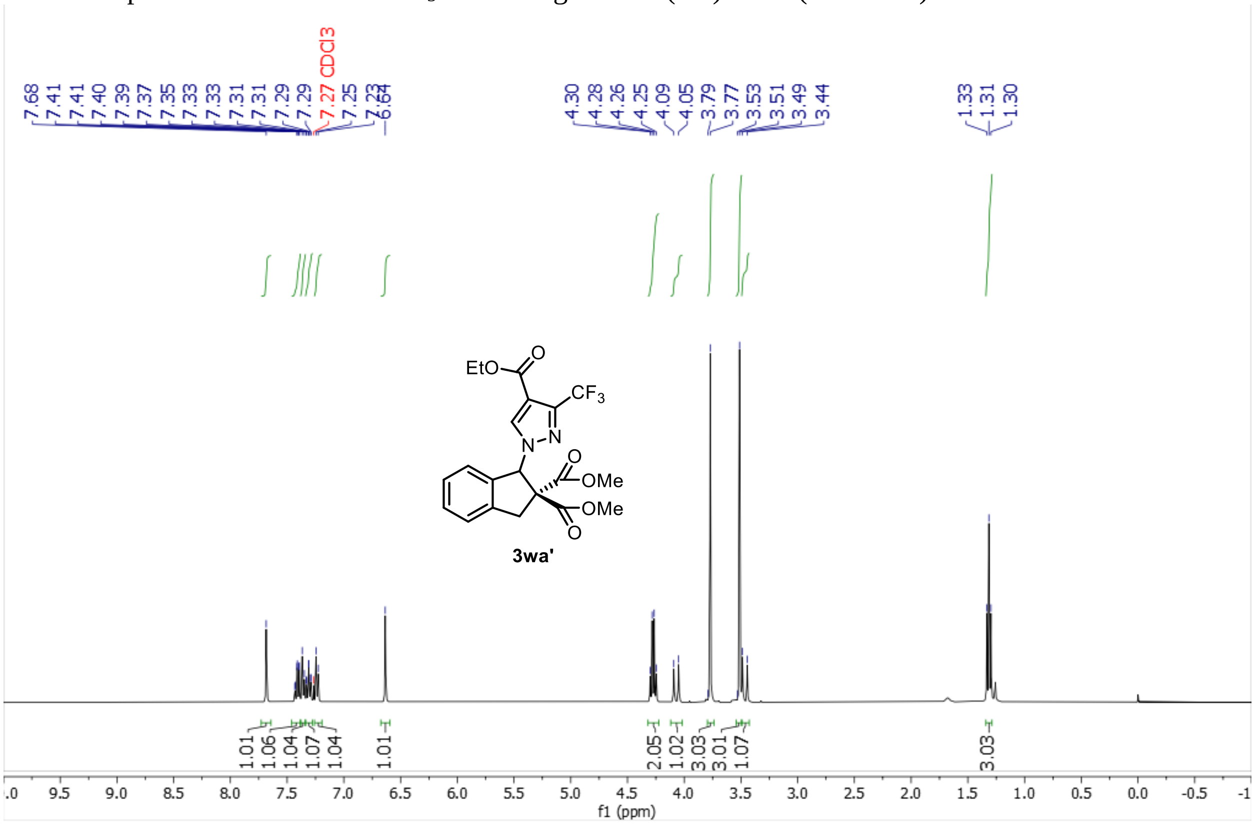
^{13}C NMR spectrum of **3wa** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



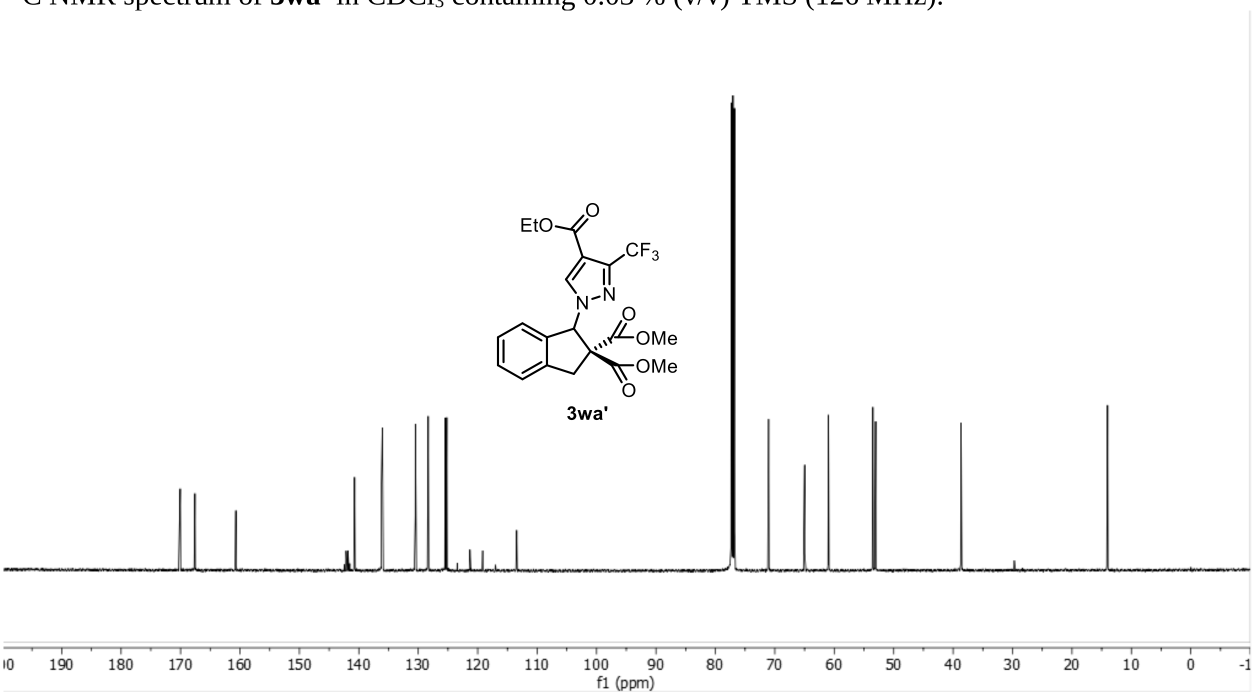
^{19}F NMR spectrum of **3wa** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



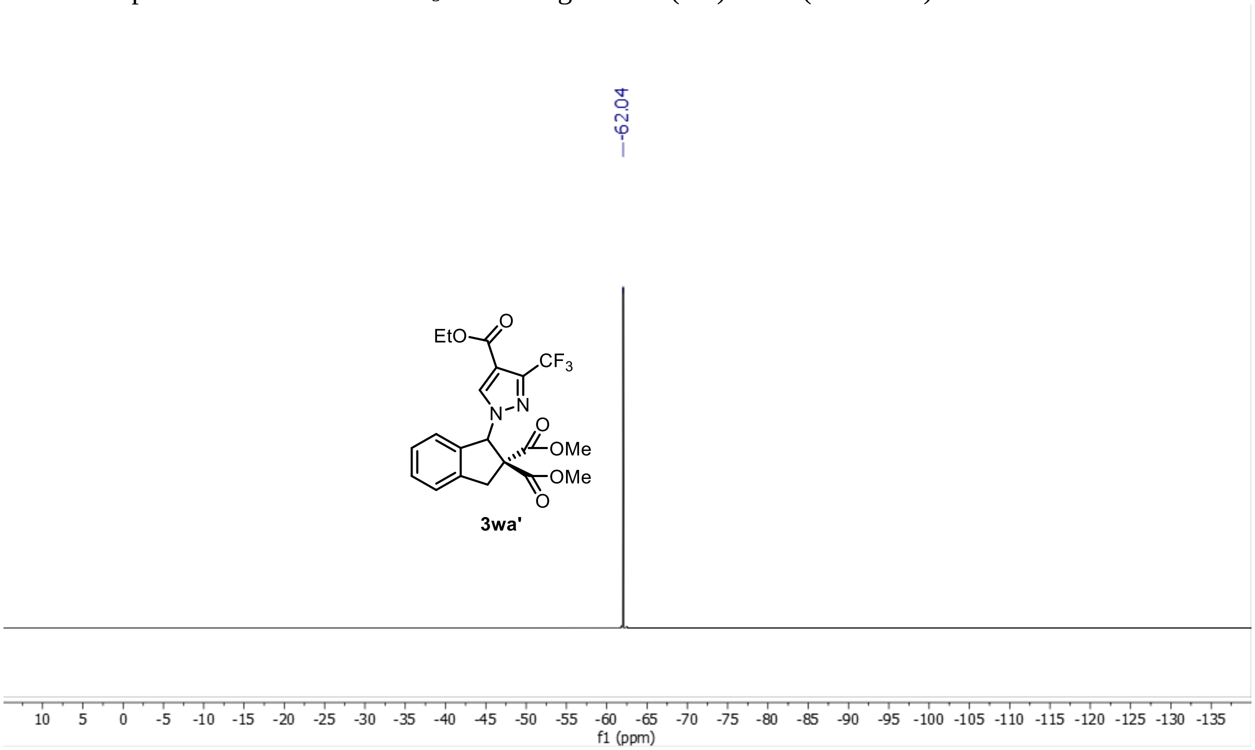
^{1}H NMR spectrum of **3wa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



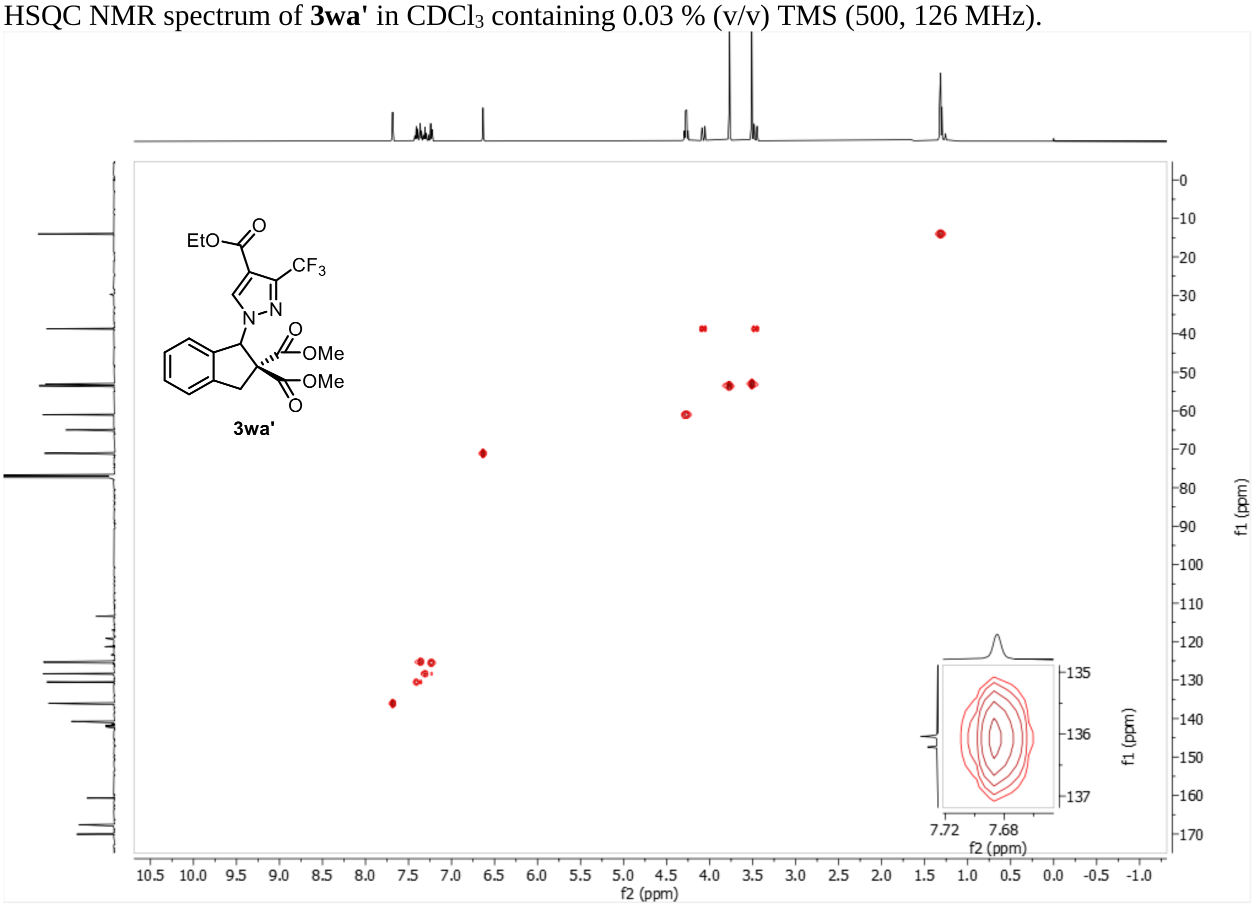
^{13}C NMR spectrum of **3wa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



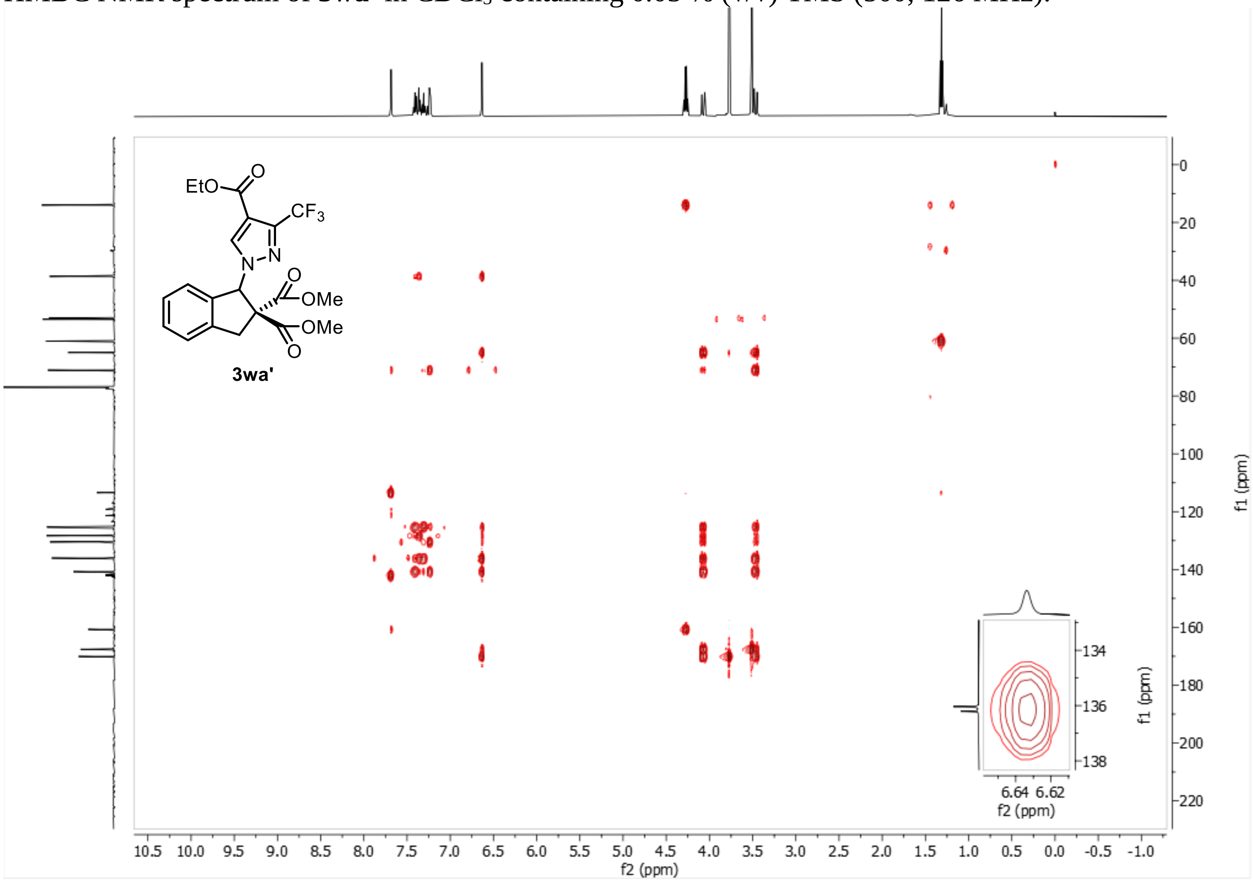
^{19}F NMR spectrum of **3wa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



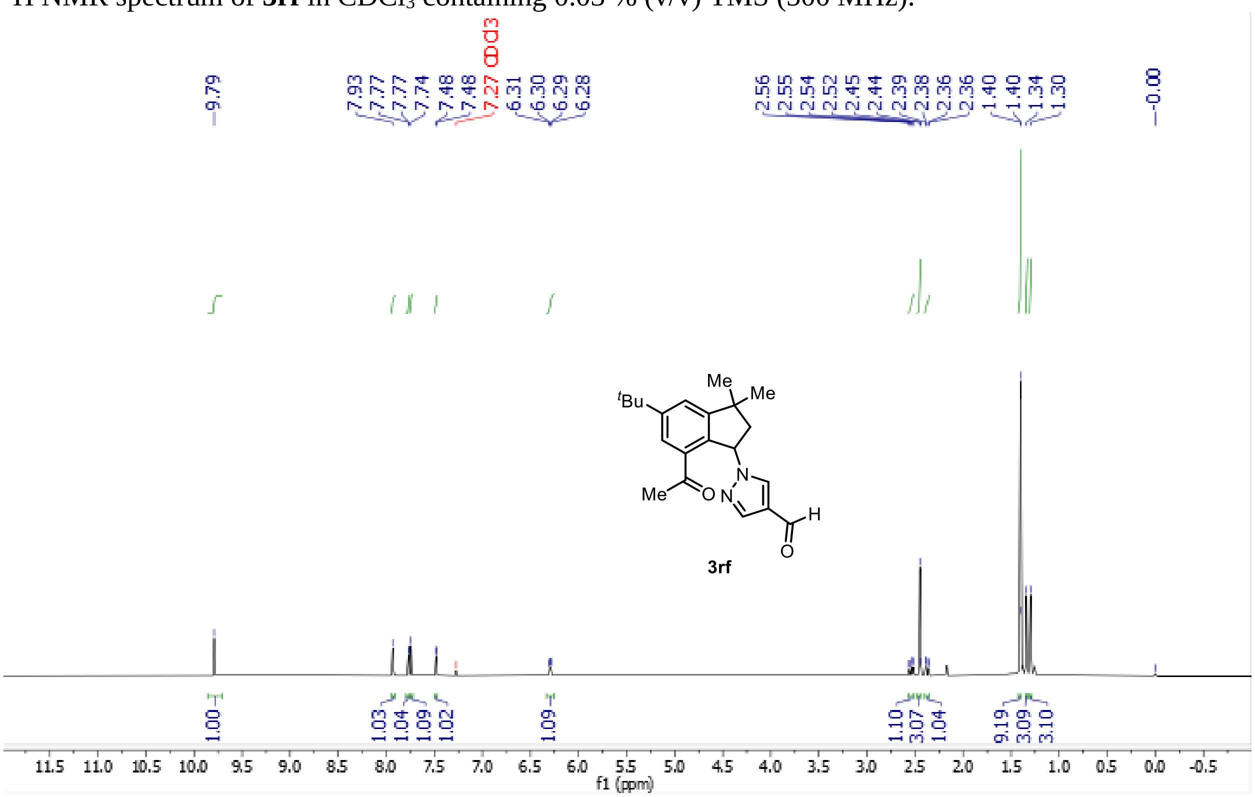
HSQC NMR spectrum of **3wa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



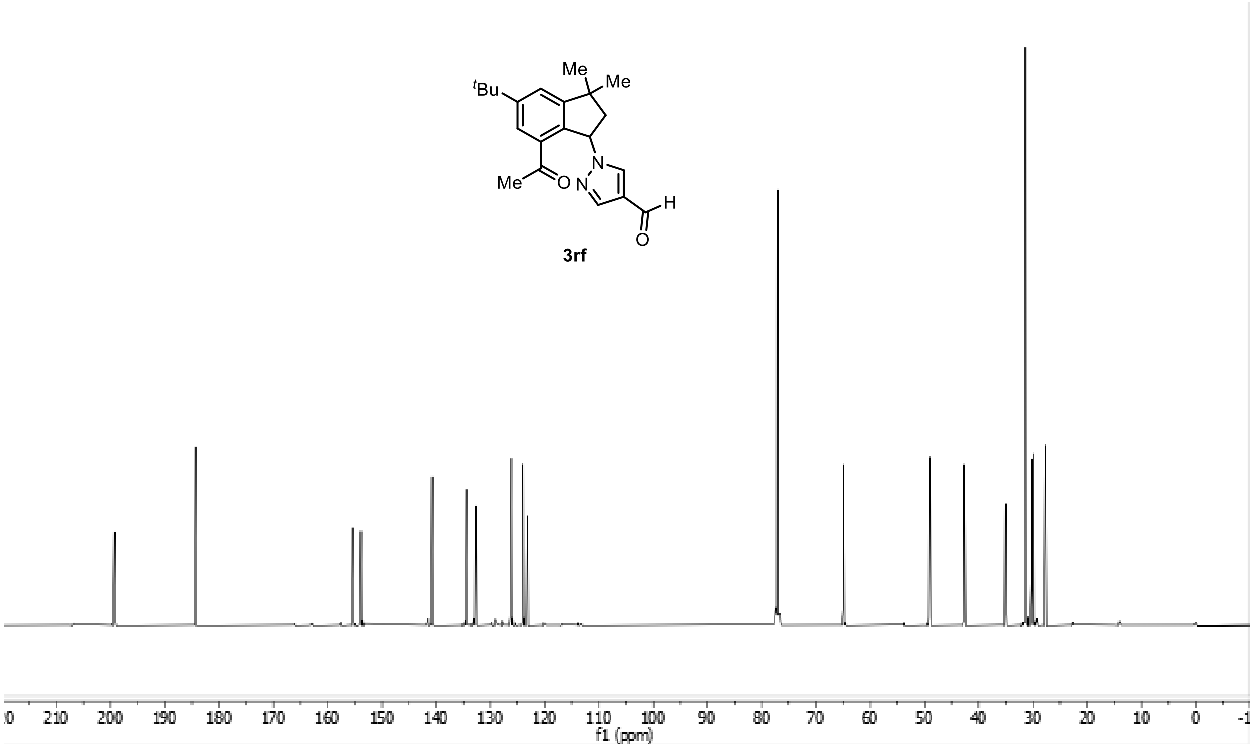
HMBC NMR spectrum of **3wa'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



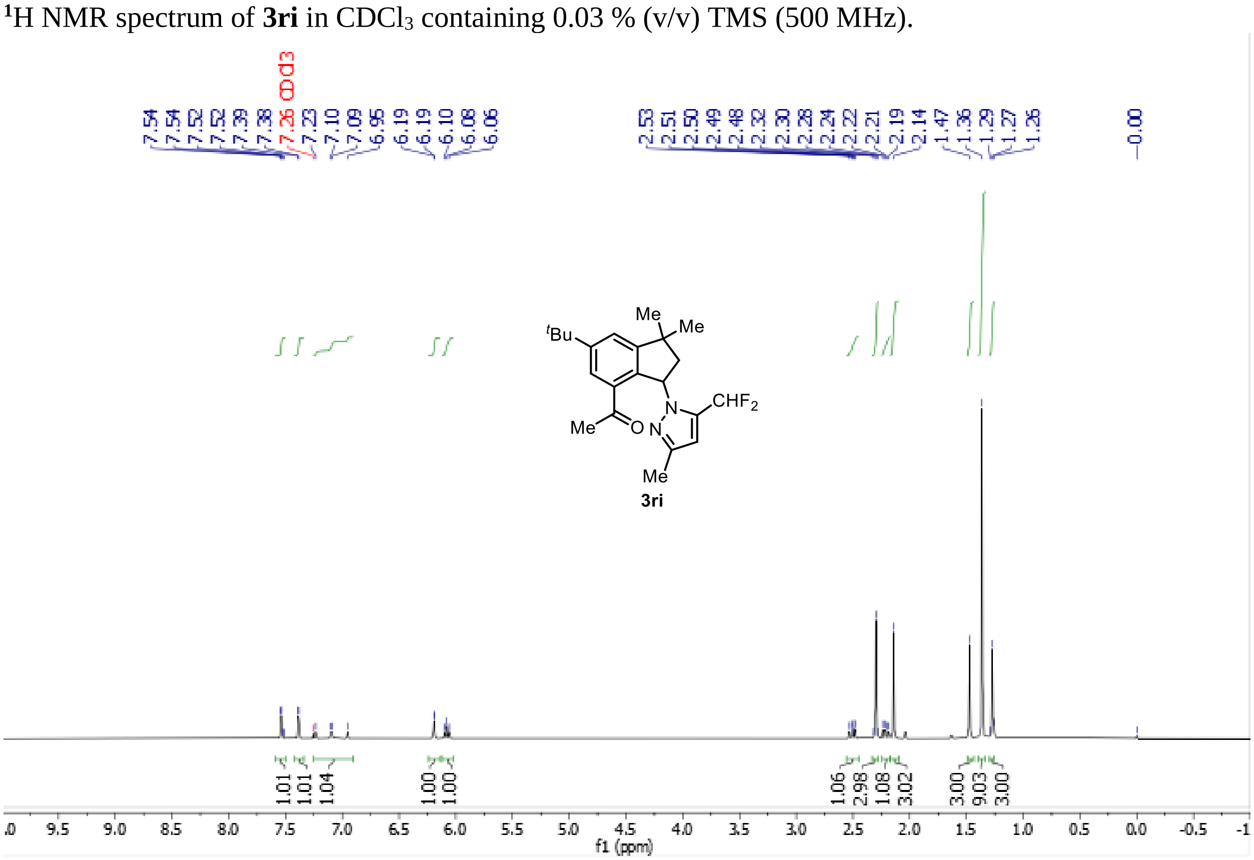
^{1}H NMR spectrum of **3rf** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



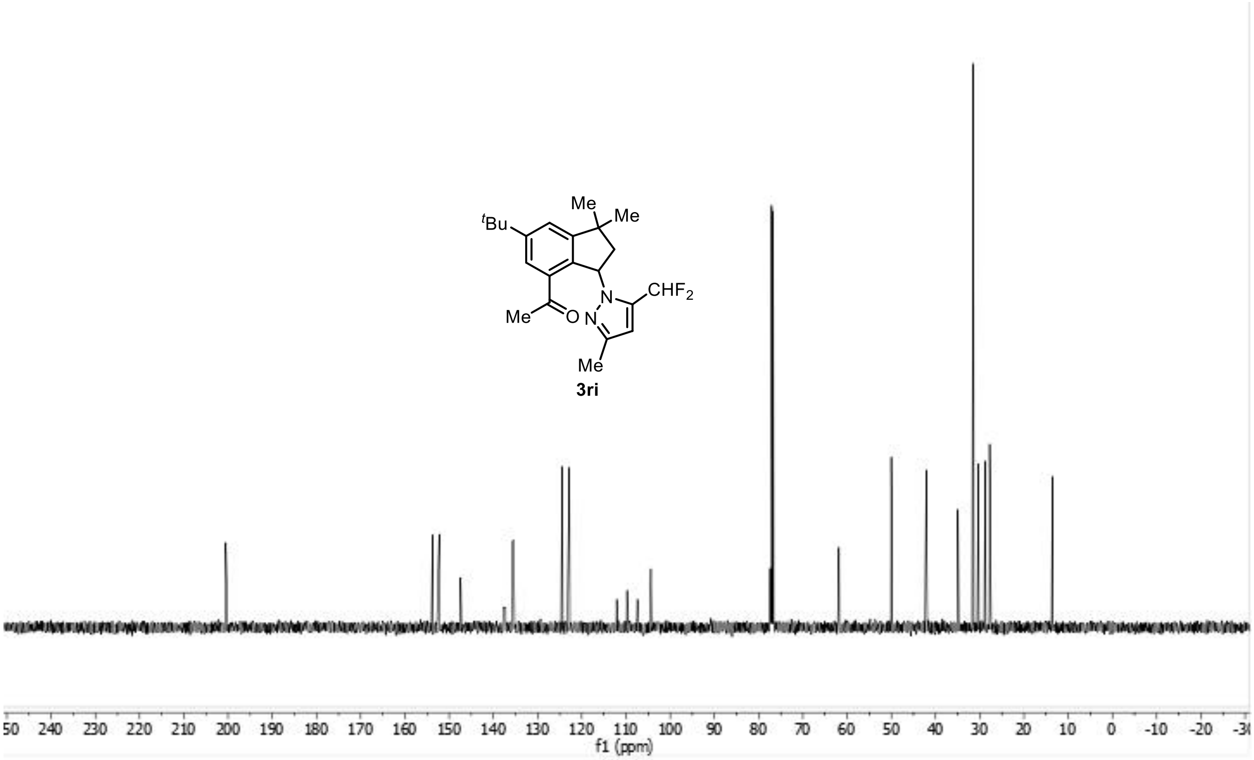
^{13}C NMR spectrum of **3rf** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



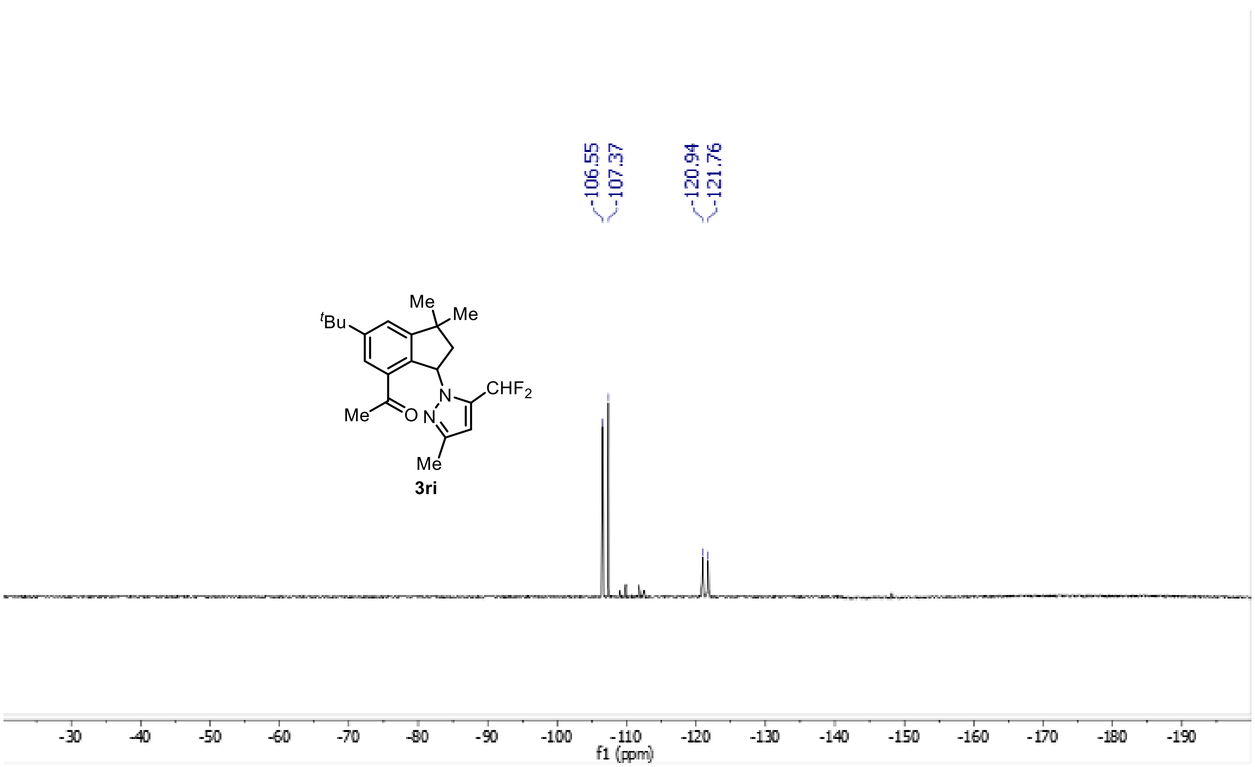
^{1}H NMR spectrum of **3ri** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



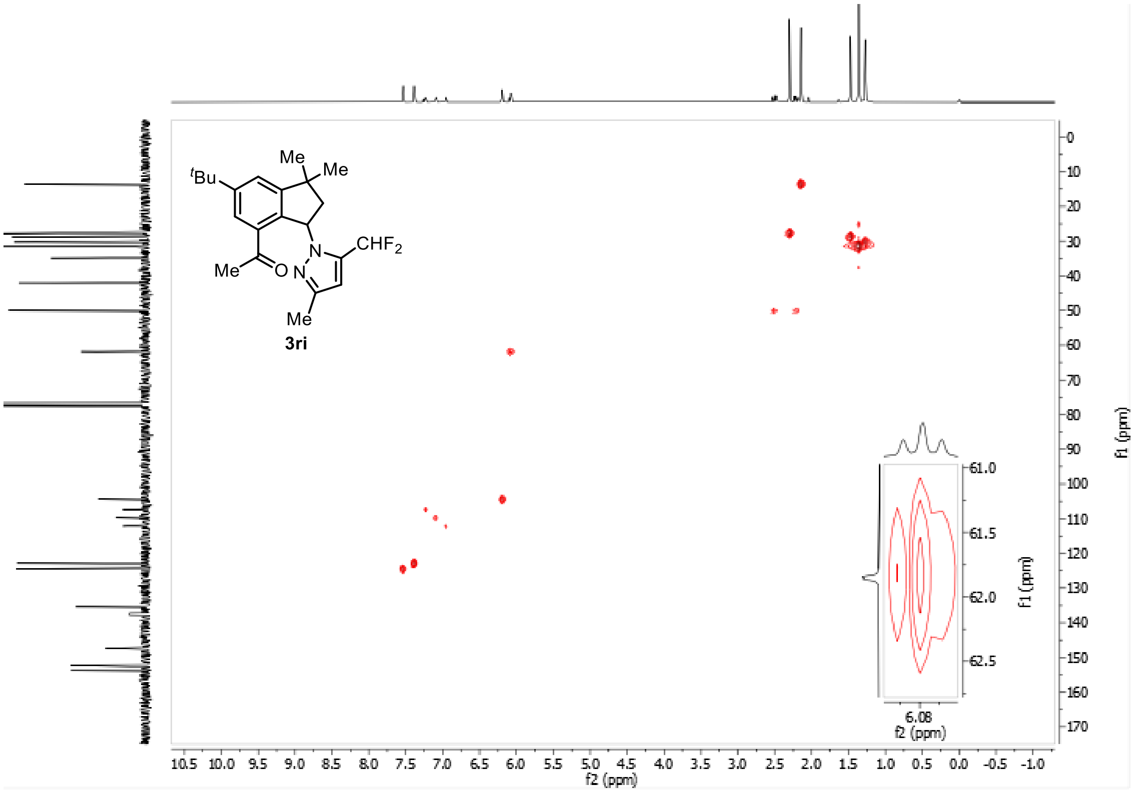
^{13}C NMR spectrum of **3ri** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



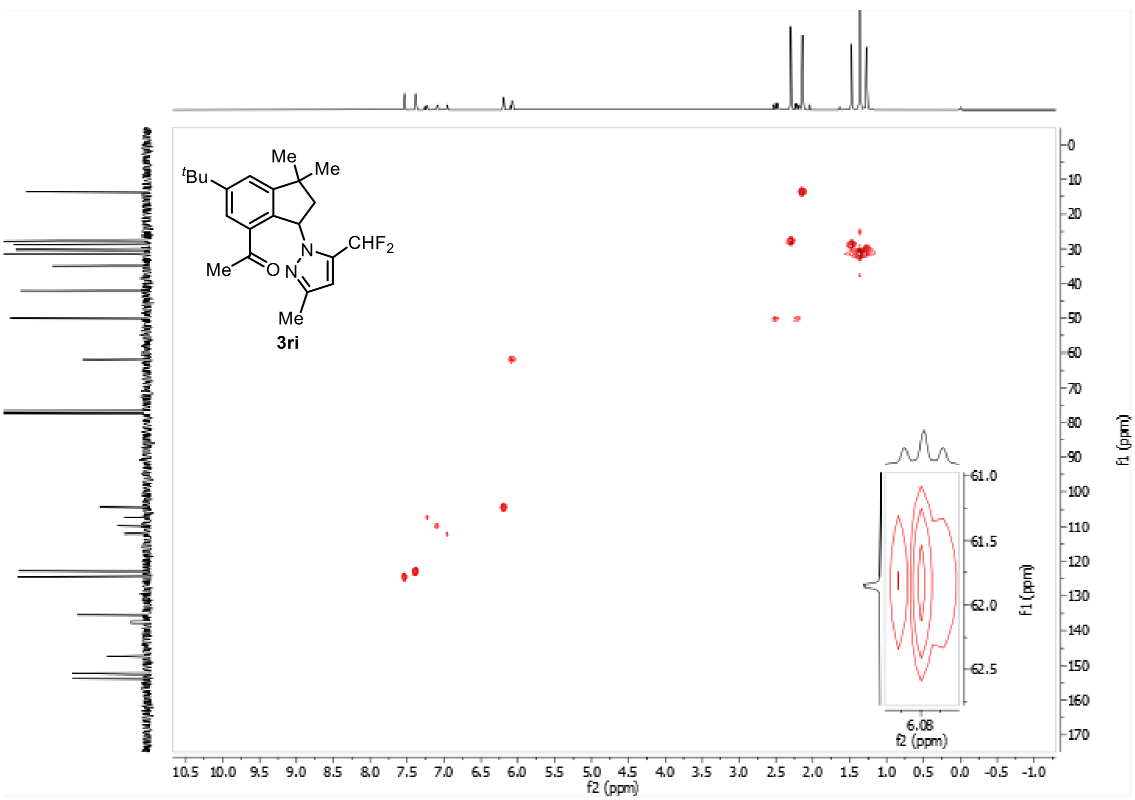
^{19}F NMR spectrum of **3ri** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



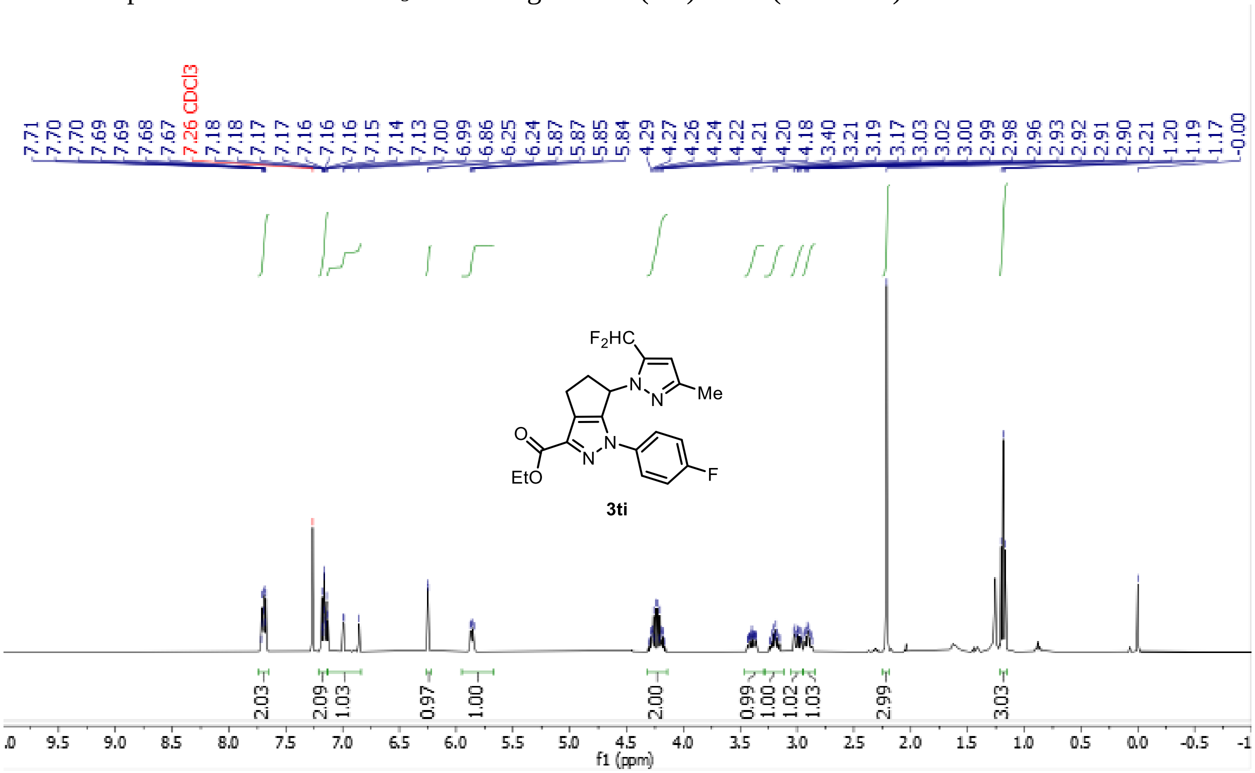
HSQC NMR spectrum of **3wa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



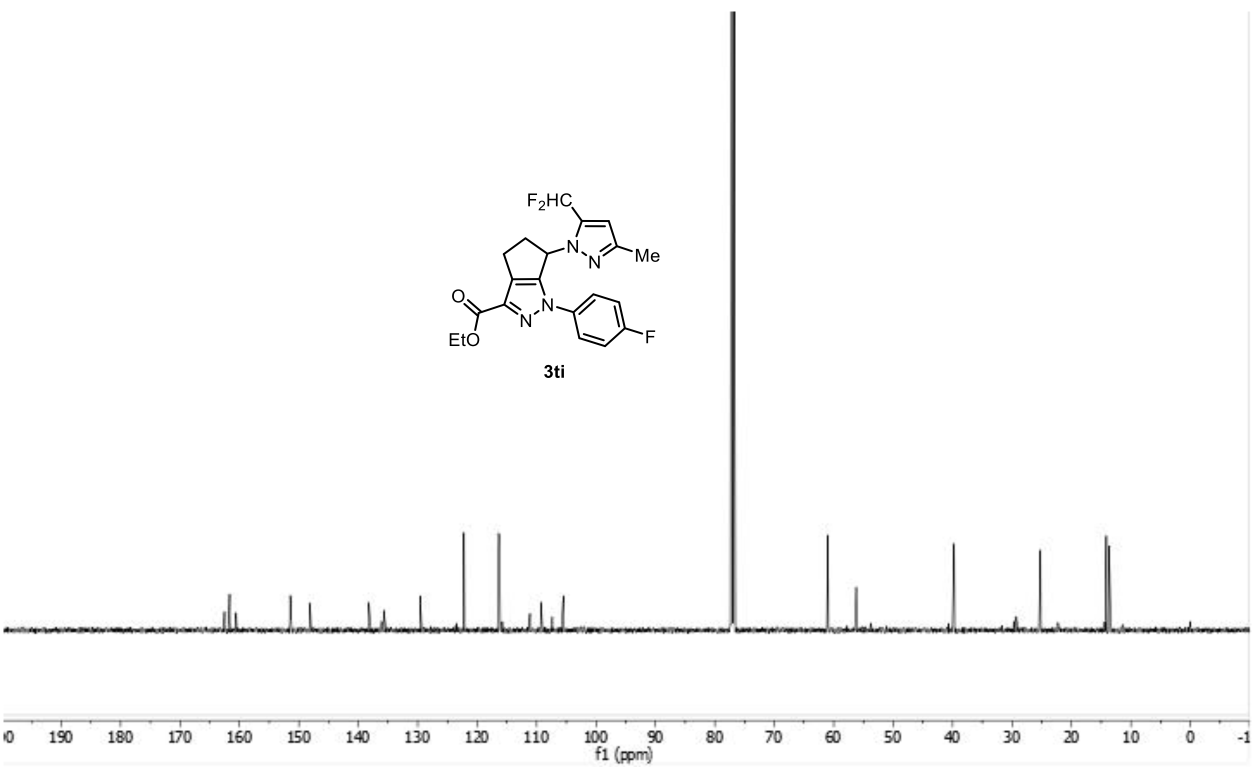
HMBC NMR spectrum of **3wa** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



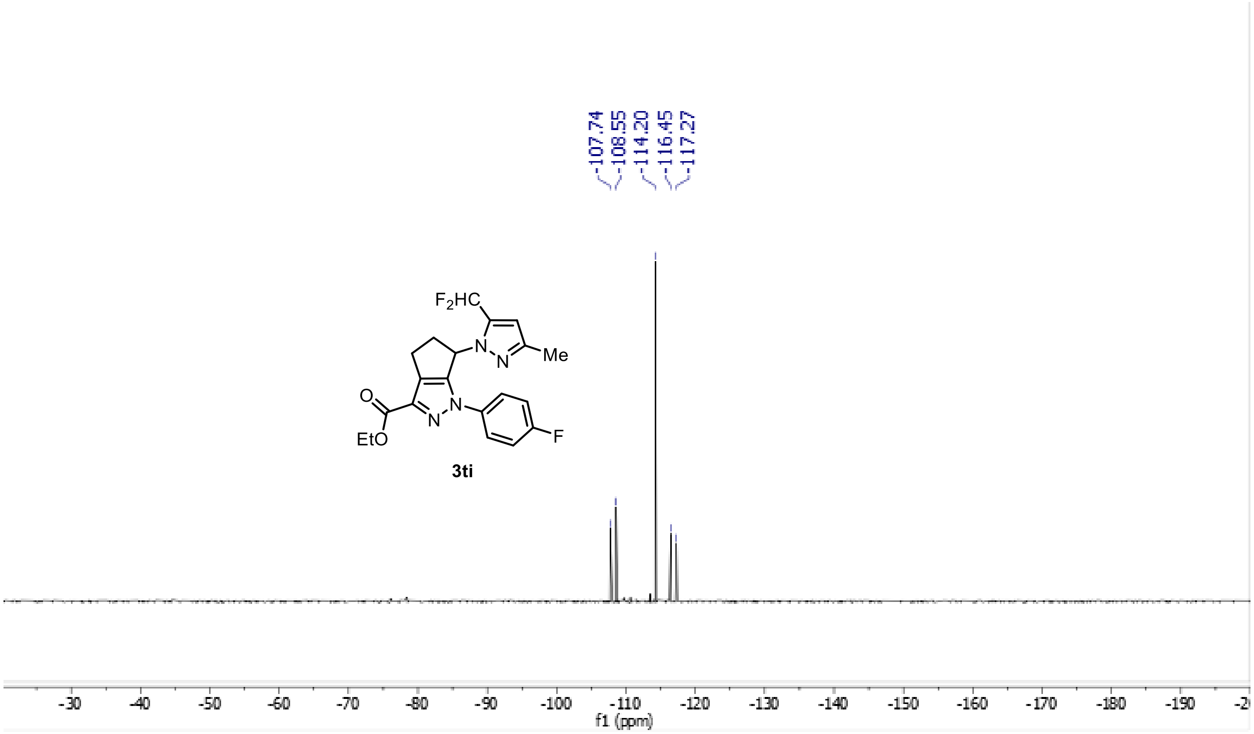
^{1}H NMR spectrum of **3ti** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



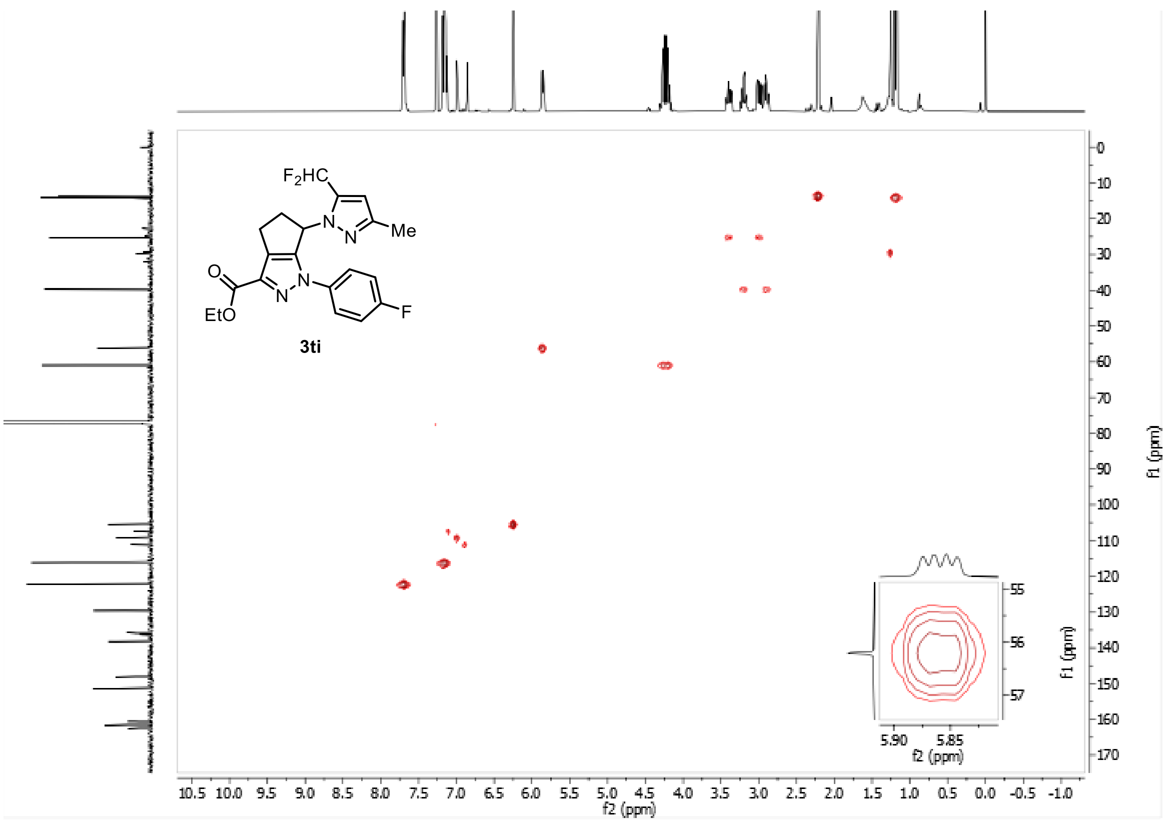
^{13}C NMR spectrum of **3ti** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



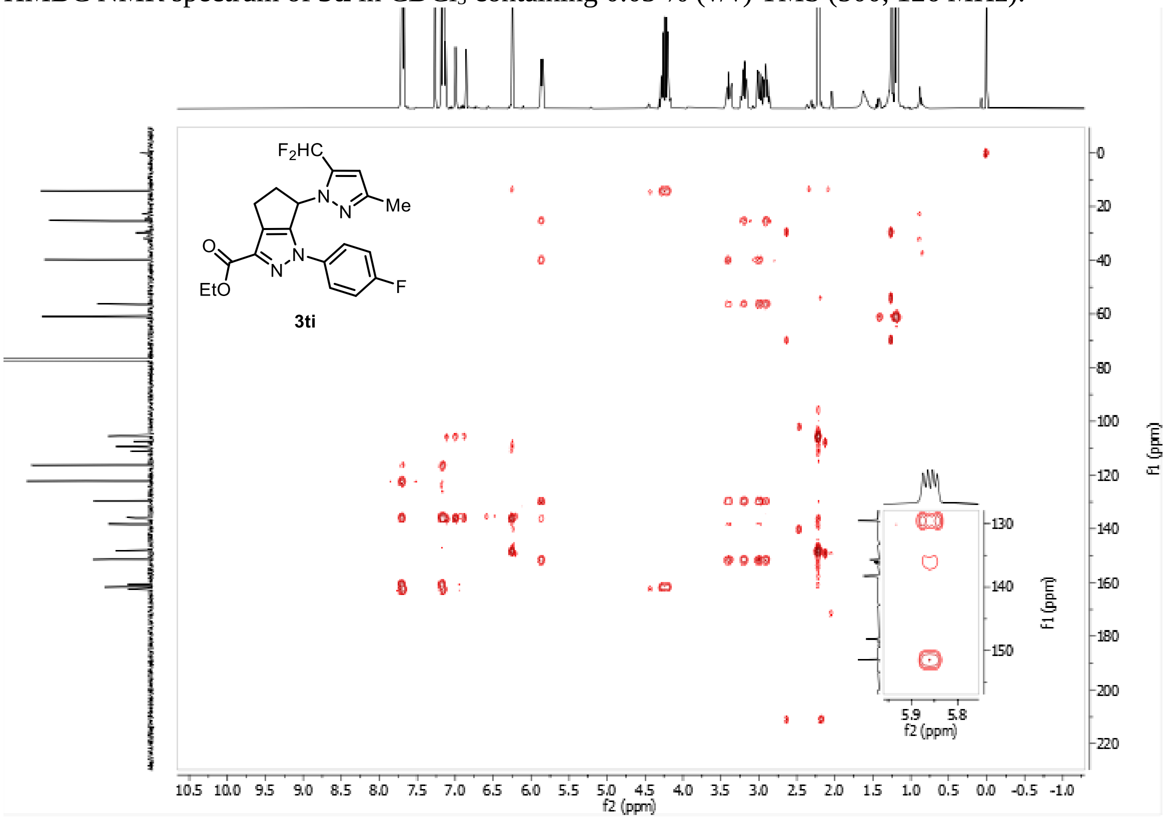
^{19}F NMR spectrum of **3ti** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



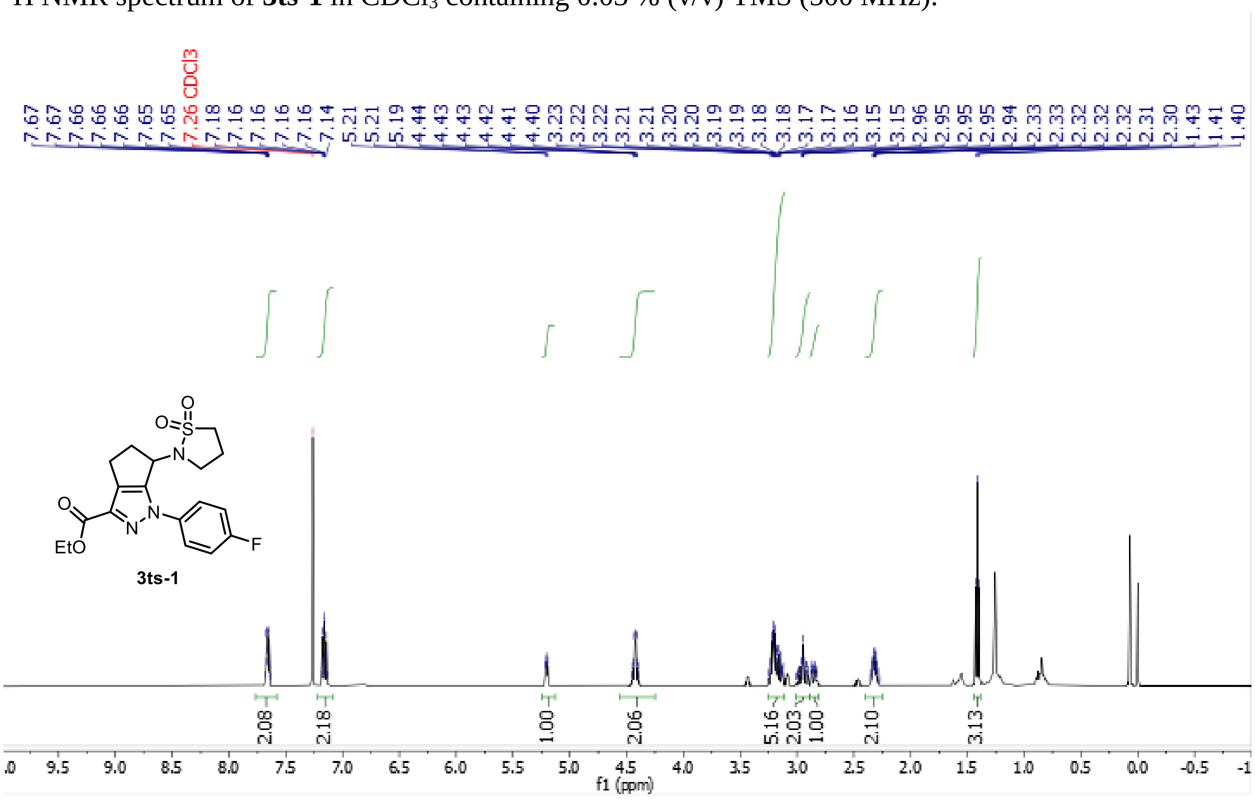
HSQC NMR spectrum of **3ti** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



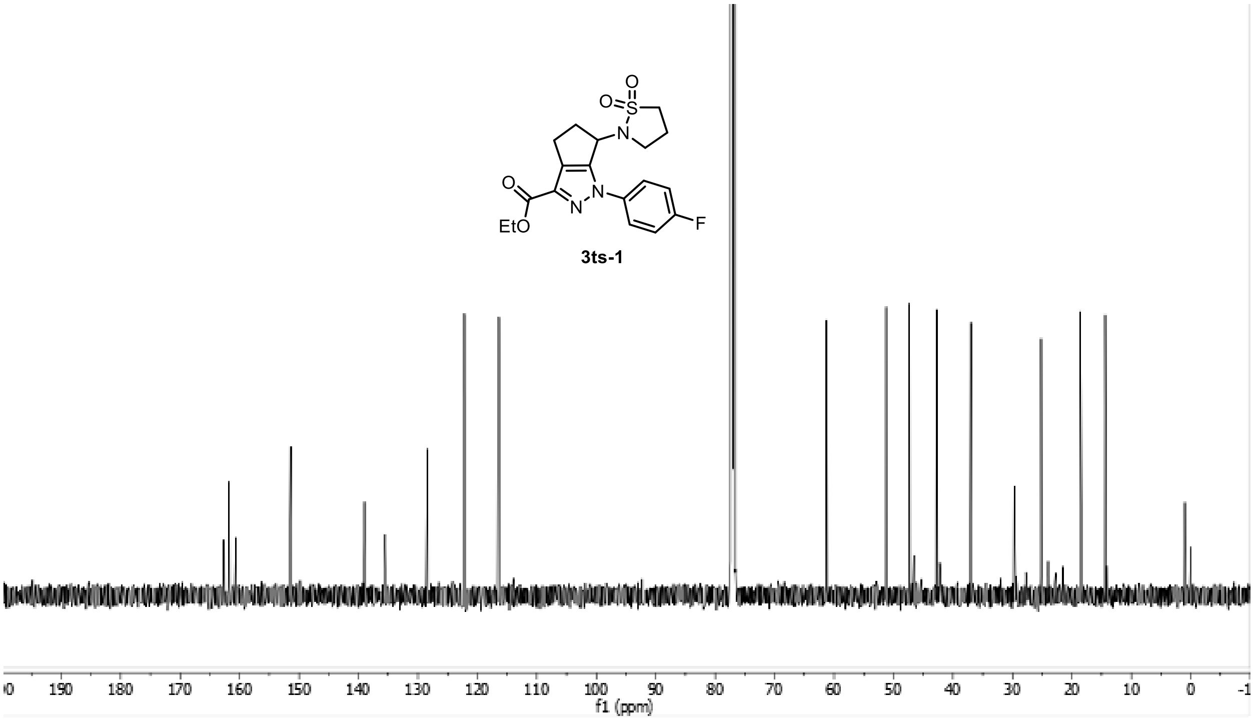
HMBC NMR spectrum of **3ti** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



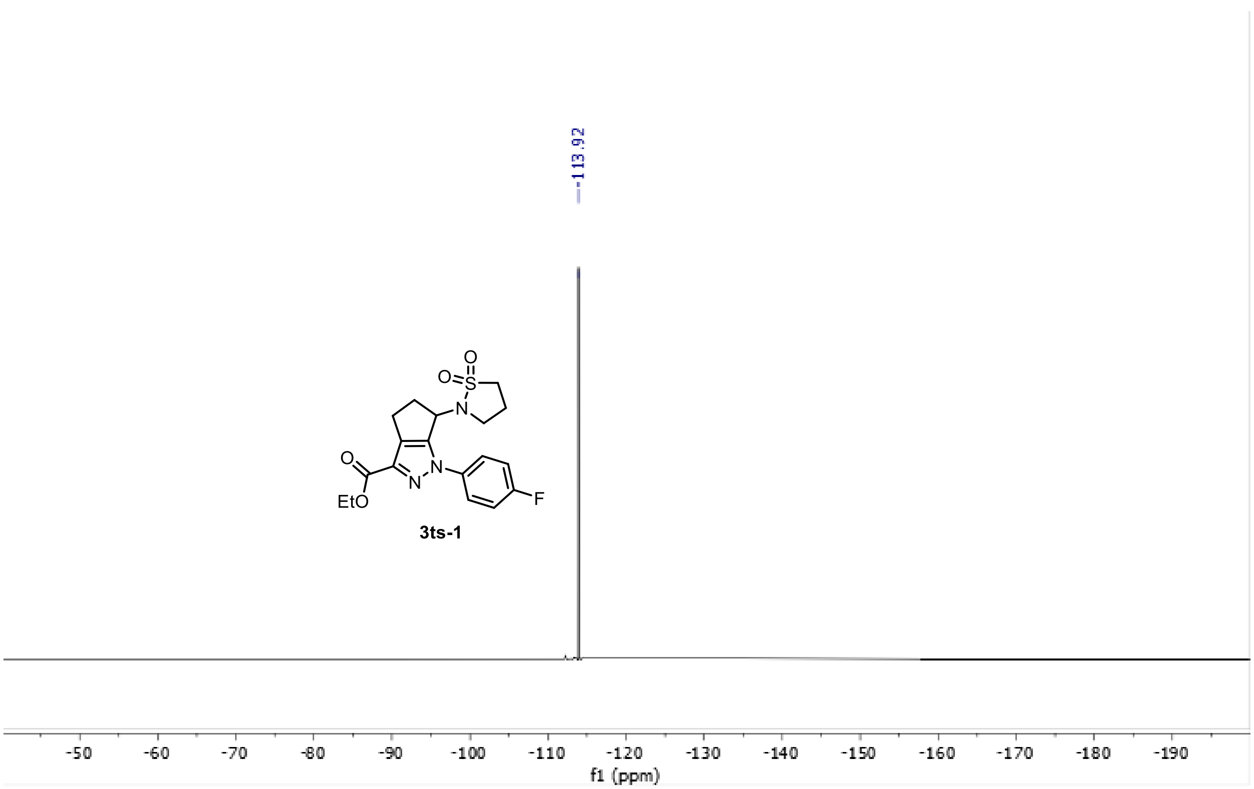
[1]H NMR spectrum of **3ts-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



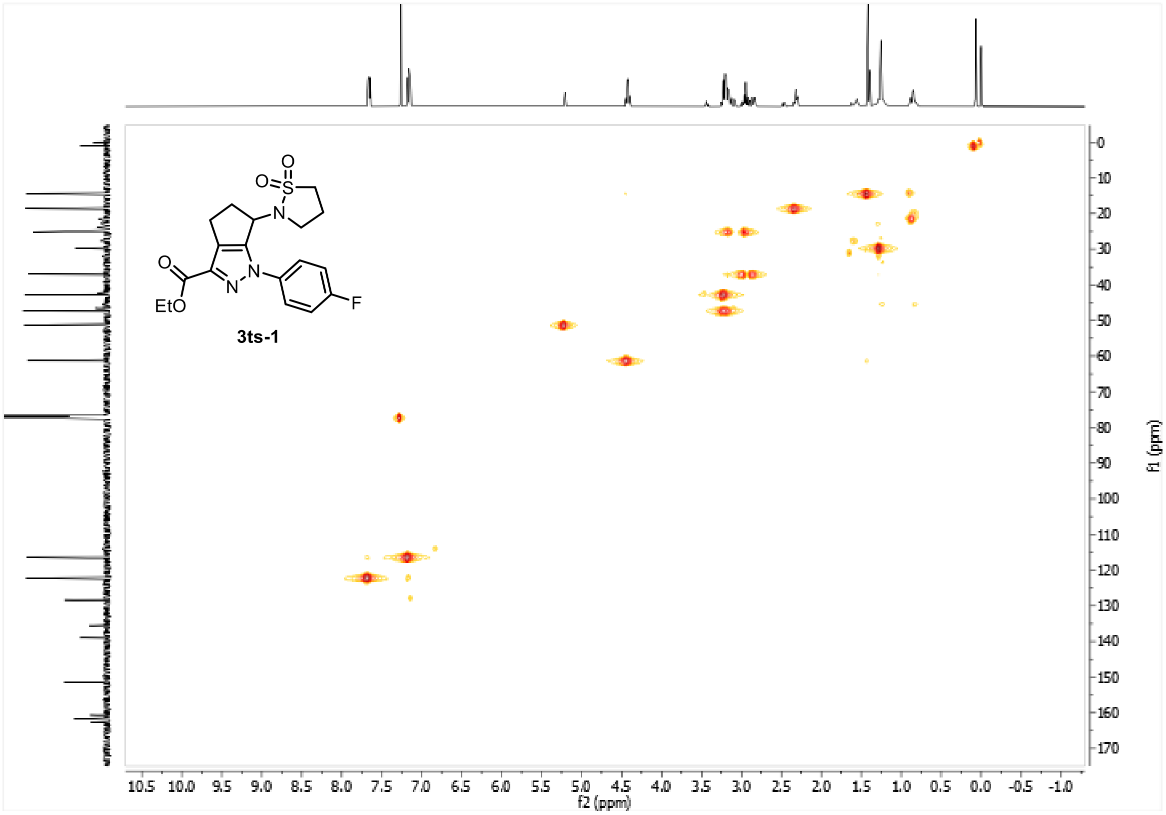
^{13}C NMR spectrum of **3ts-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



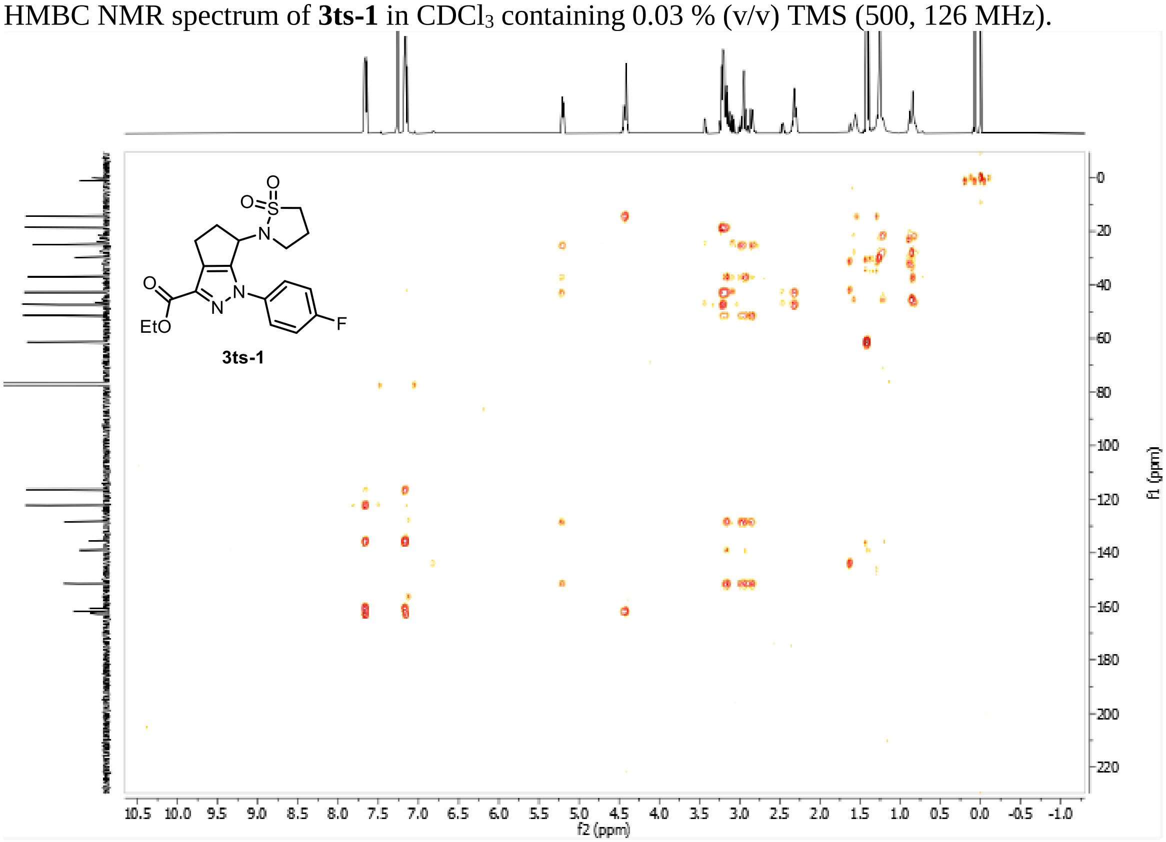
^{19}F NMR spectrum of **3ts-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



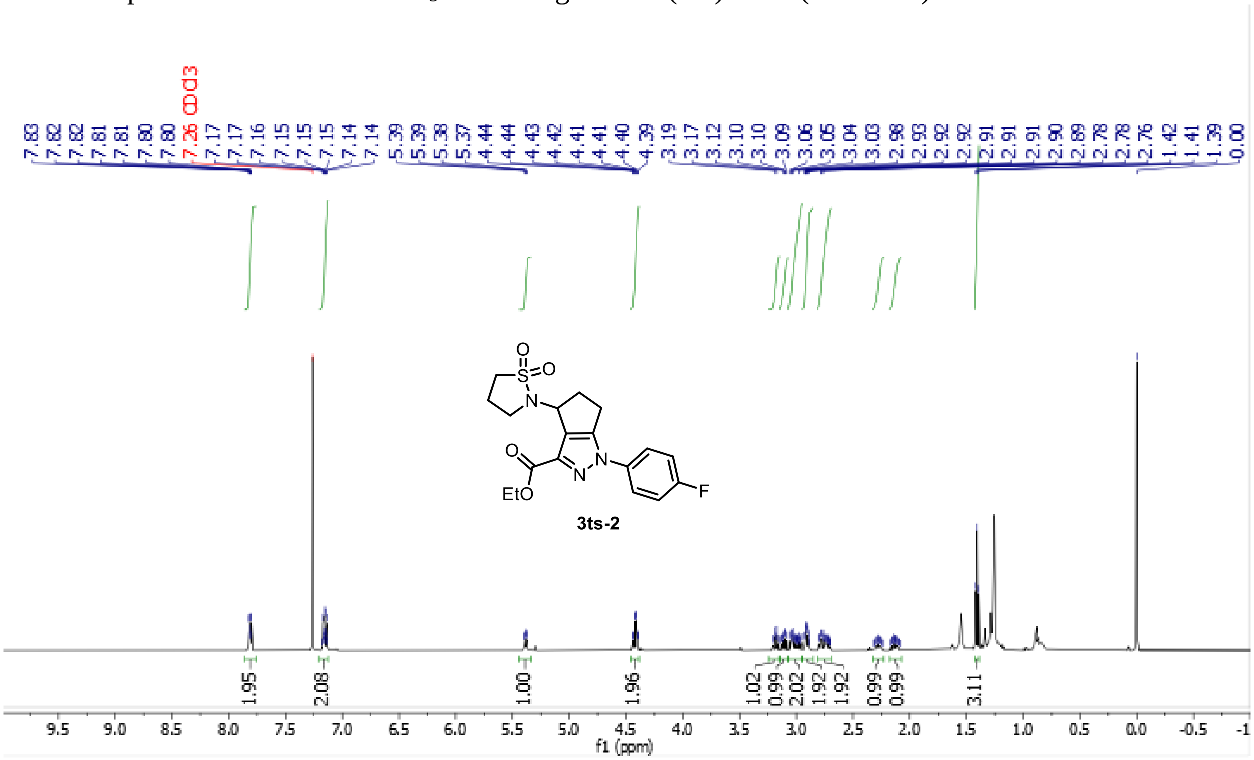
HSQC NMR spectrum of **3ts-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



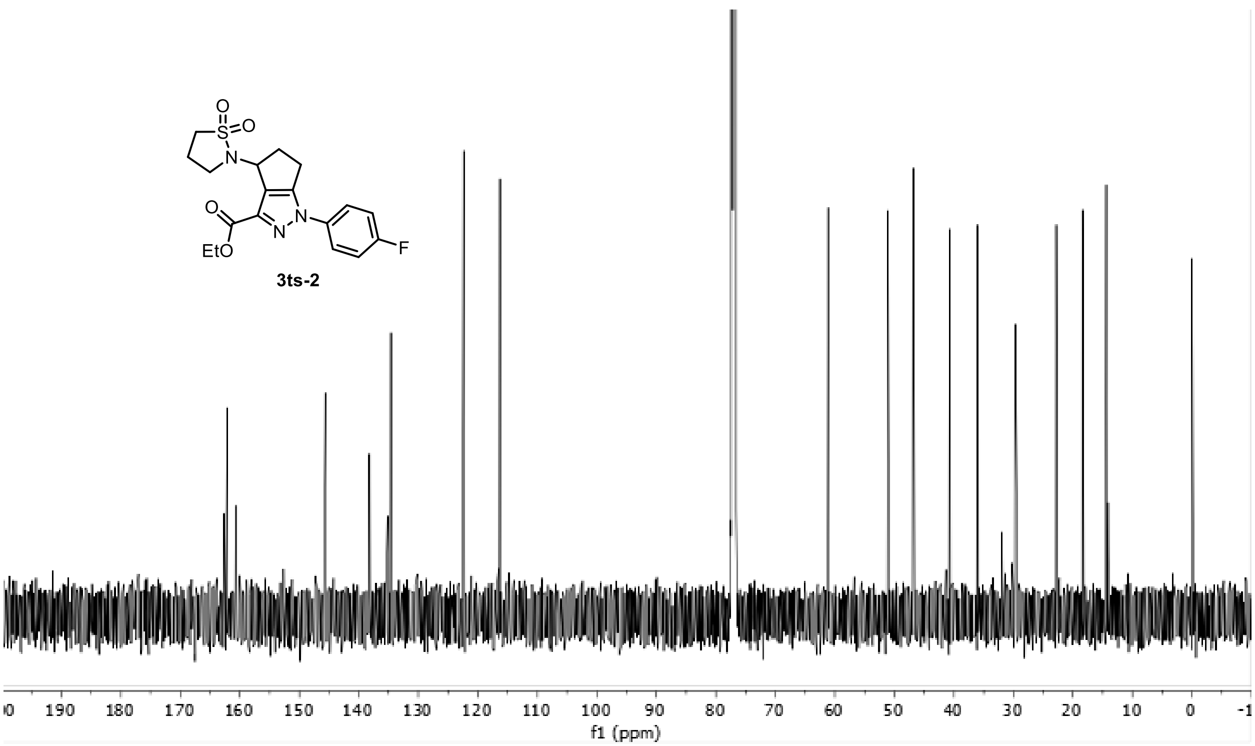
HMBC NMR spectrum of **3ts-1** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



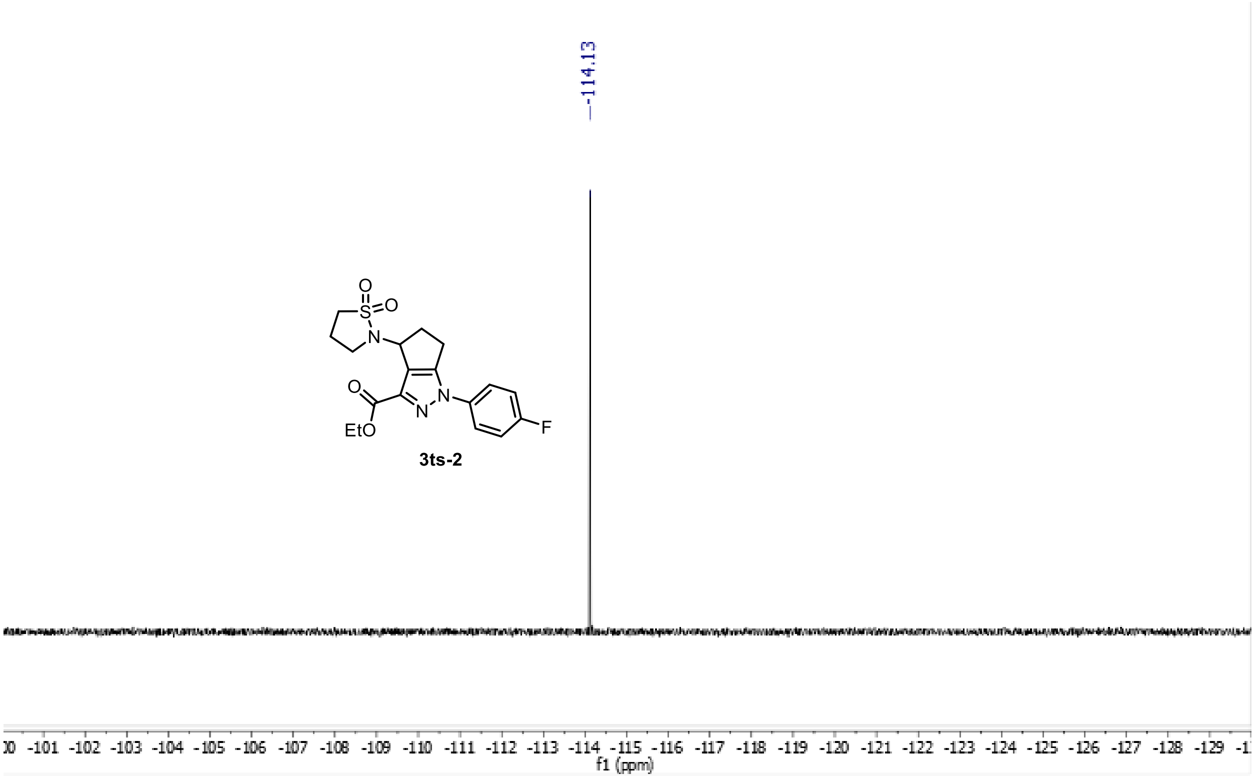
[1]H NMR spectrum of **3ts-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



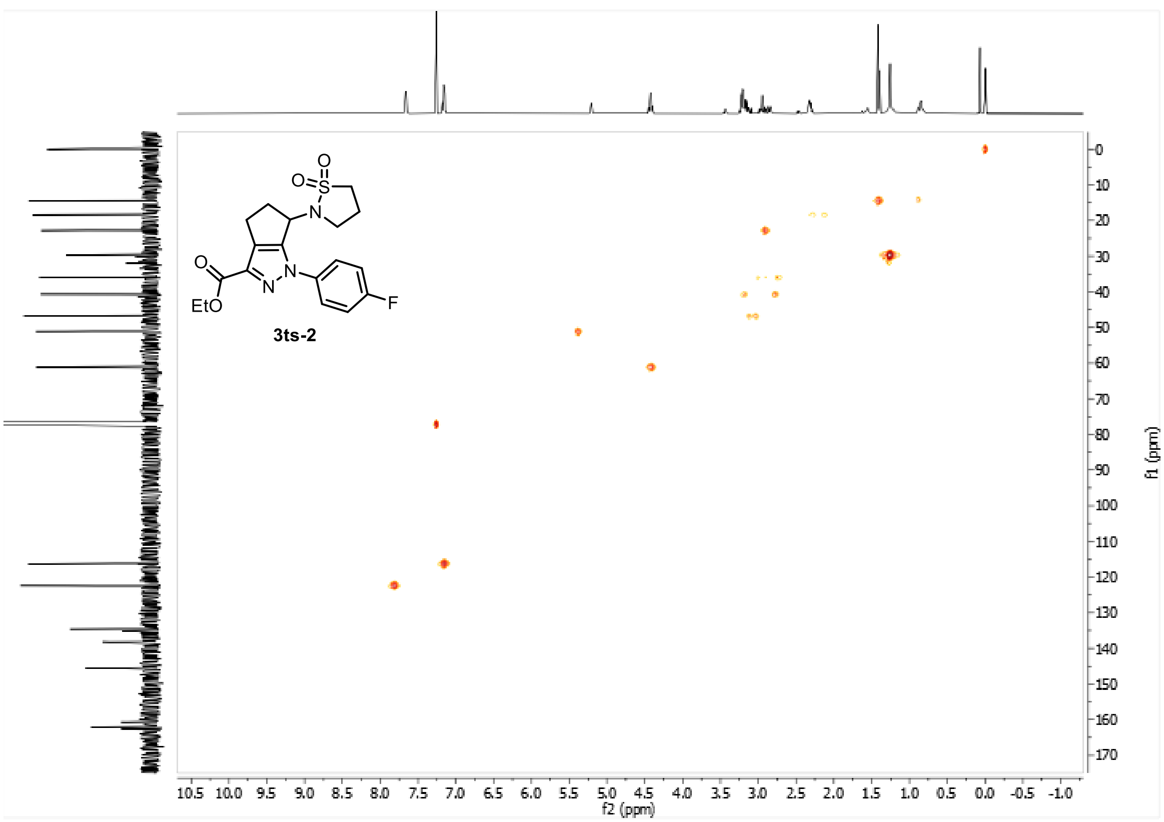
[13]C NMR spectrum of **3ts-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



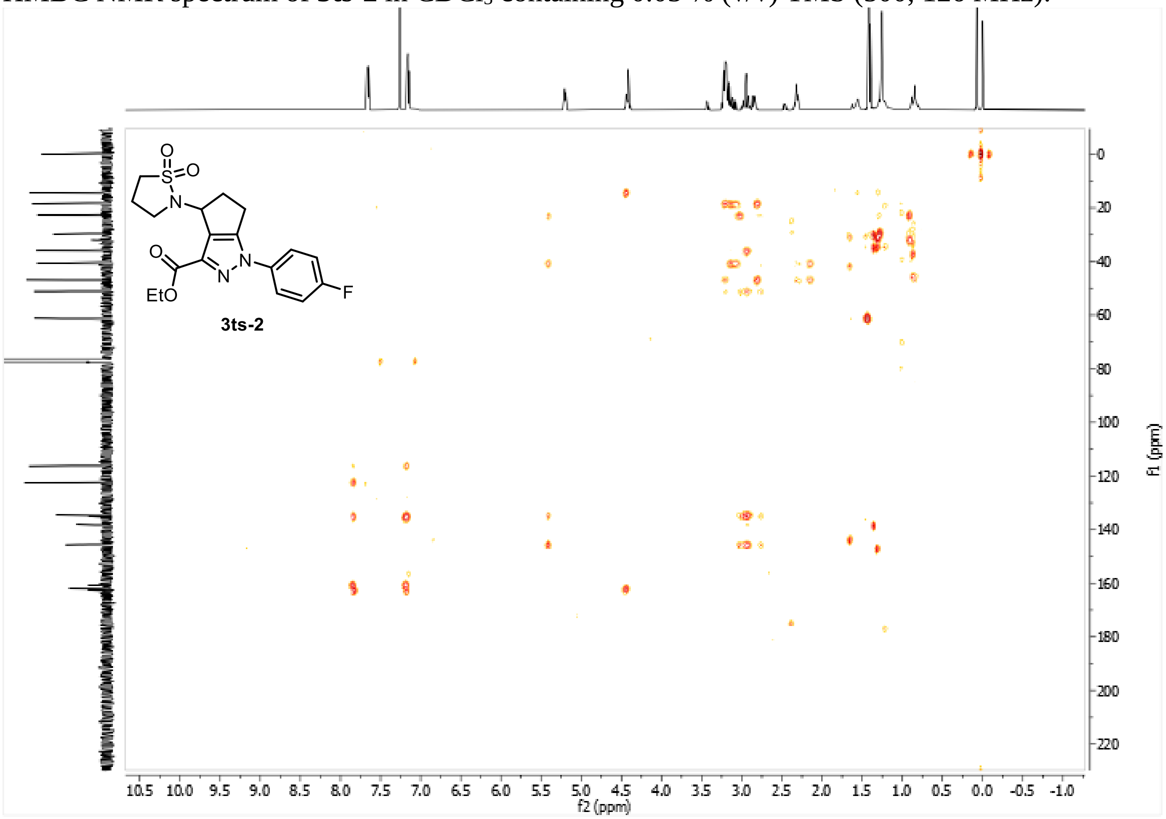
^{19}F NMR spectrum of **3ts-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



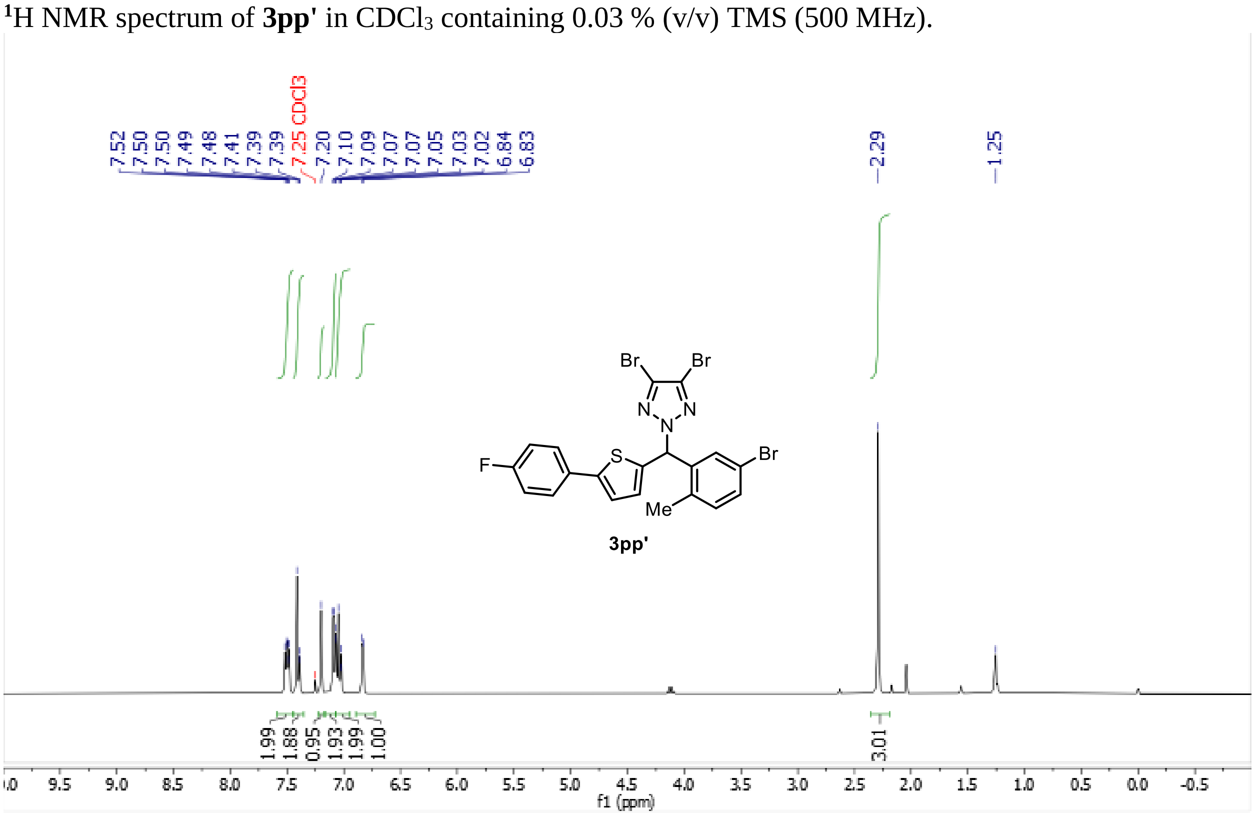
HSQC NMR spectrum of **3ts-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



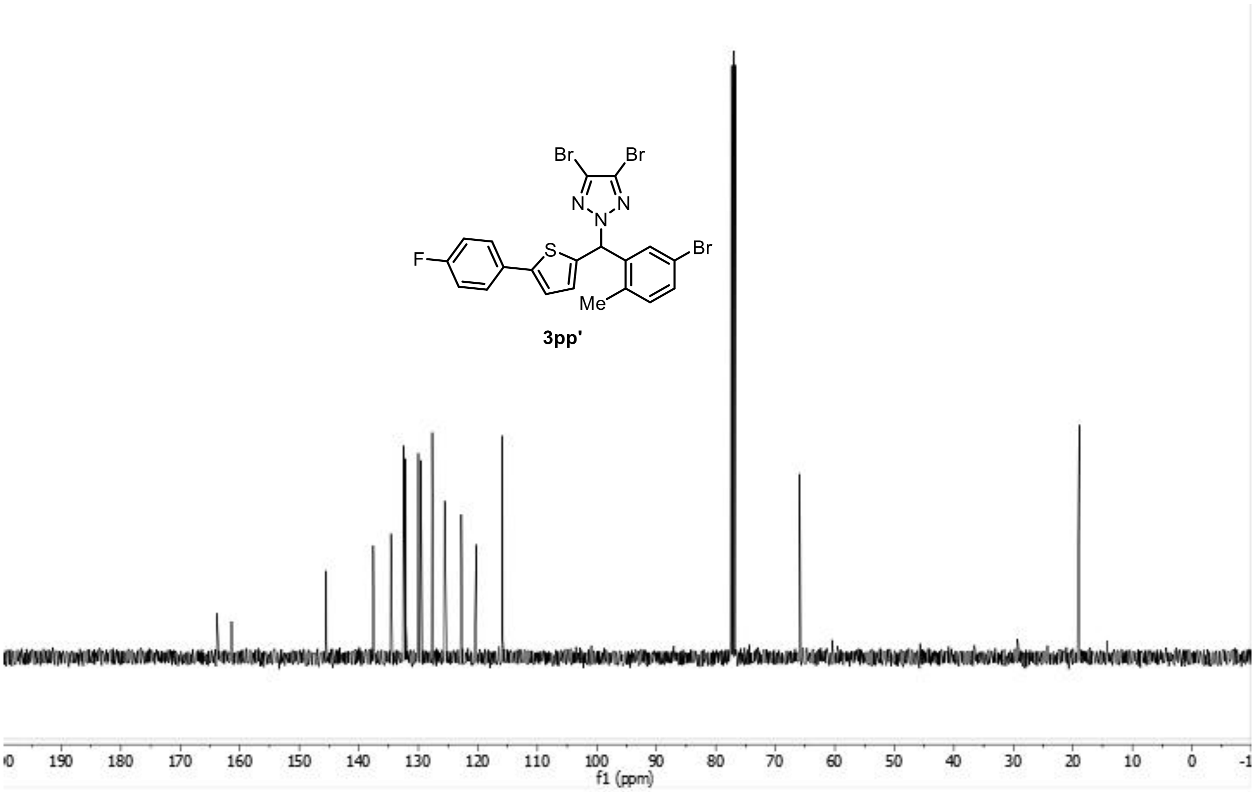
HMBC NMR spectrum of **3ts-2** in $CDCl_3$ containing 0.03 % (v/v) TMS (500, 126 MHz).



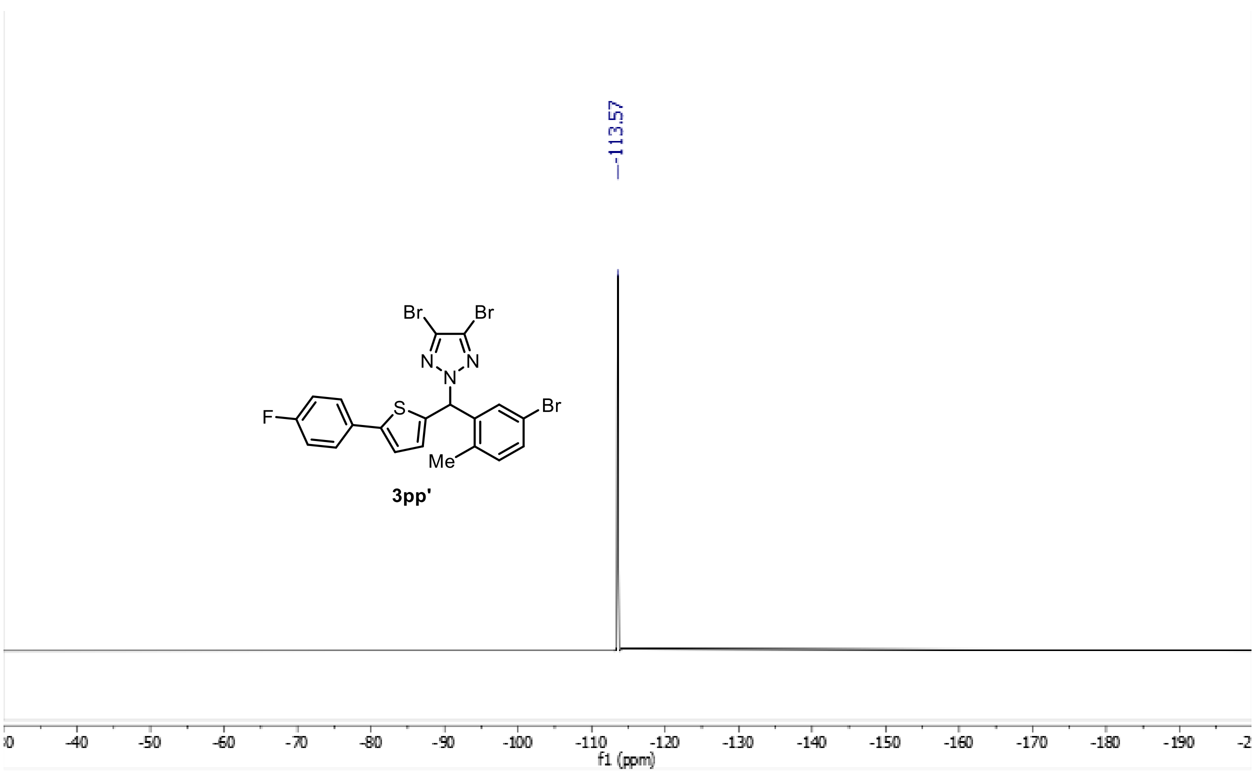
[1]H NMR spectrum of **3pp'** in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



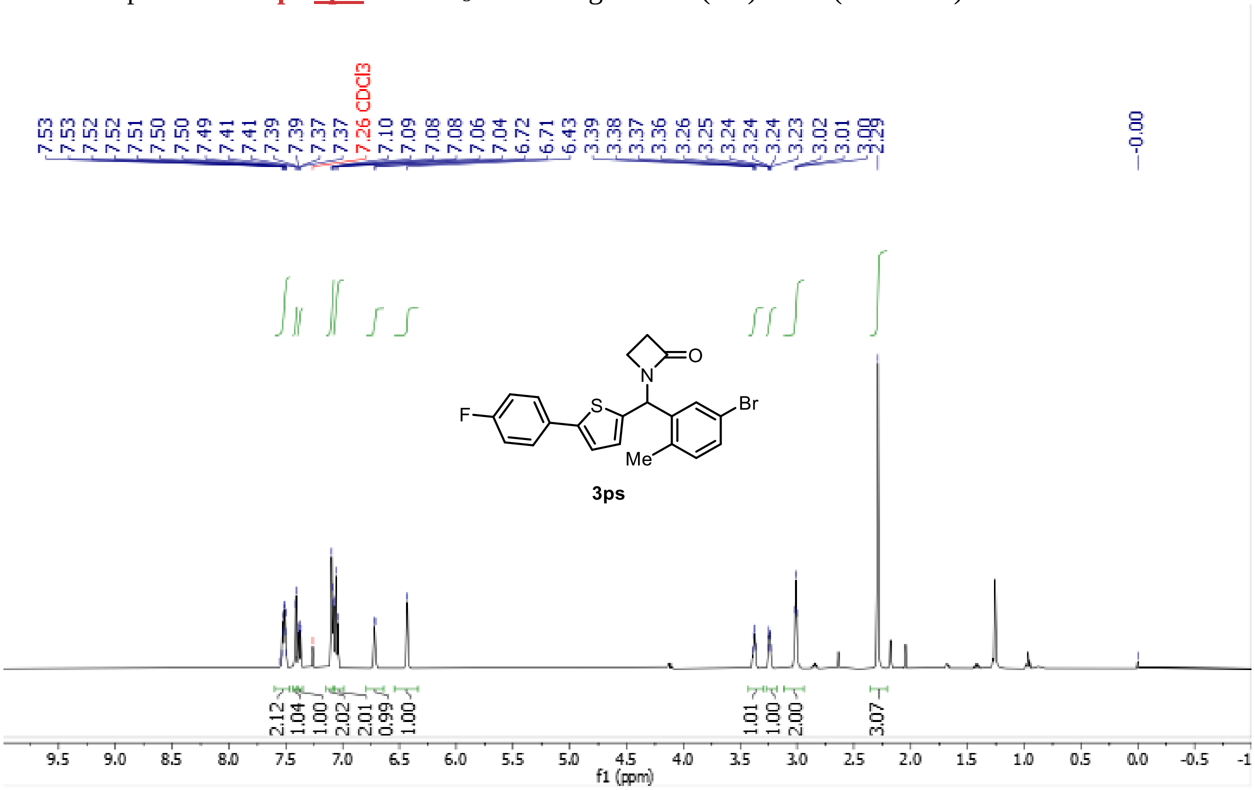
^{13}C NMR spectrum of **3pp'** in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



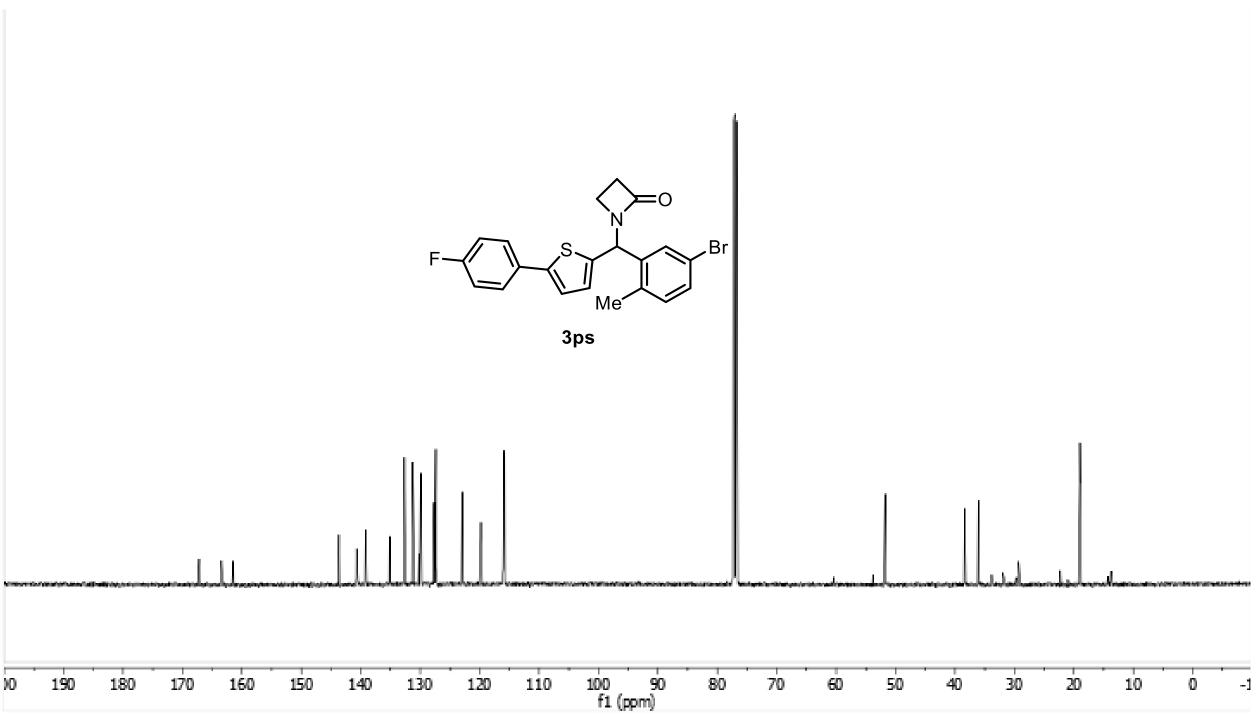
^{19}F NMR spectrum of **3pp'** in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).



[1]H NMR spectrum of ~~3pr~~ 3ps in $CDCl_3$ containing 0.03 % (v/v) TMS (500 MHz).



[13]C NMR spectrum of ~~3pr~~ 3ps in $CDCl_3$ containing 0.03 % (v/v) TMS (126 MHz).



[19]F NMR spectrum of ~~3pr~~ 3ps in $CDCl_3$ containing 0.03 % (v/v) TMS (377 MHz).