

**Visible-light promoted α,α -dibromination in minutes: efficient route for
construction of quaternary carbon centers**

Kuili Zhang[†], Rui Ma[†], Yanxia Wang[†], Zhihao Shi*[†], Tao Lu[†] and Jie Feng*[†]

[†]State Key Laboratory of Natural Medicines,

Department of Organic Chemistry, China Pharmaceutical University,

No. 24 Tongjiaxiang Road, Nanjing, 210009, P.R. China.

E-mail: 1020162519@cpu.edu.cn

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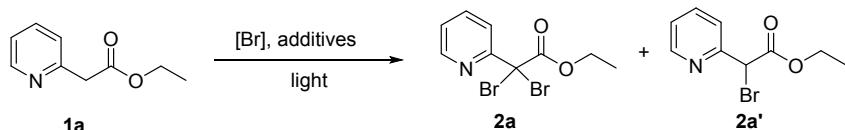
1. General Information

Unless otherwise noted, all reactions were performed under an atmosphere of air. All reactions were carried out in a transparent sample vial (4 mL) equipped with a Teflon-coated magnetic stir bar. NBS was recrystallized from EtOH/H₂O before use. Other commercially available reagents were used without further purification. Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F25 plates (Merck, 0.25 mm thick). LEDs was commercially available (blue LED bulbs, household, 9W). GC-MS data were recorded on an Agilent Technologies 7890A GC system coupled with Agilent Technologies 5975C mass spectrometer using HP-5MS column (30 m x 0.250 mm, 0.25 μ) purchased from Agilent Technologies. ¹H and ¹³C NMR spectra were obtained in CDCl₃ or DMSO using 300 MHz, 400 MHz Varian NMR spectrometer. Chemical shifts in ¹H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual CDCl₃ (7.27 ppm) or the central peak of DMSO-*d*₆ (2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet), integration, and coupling constant in Hertz (Hz). Chemical shifts in ¹³C NMR spectra are reported in ppm on the δ scale from the central peak of residual CDCl₃ (77.00 ppm) or the central peak of DMSO-*d*₆ (39.51 ppm).

2. Optimization of Reaction Parameters

a) Optimizations

Table S1 Optimization of substrate ethyl 2-(pyridin-2-yl)acetate **1a**^a



	Modified conditions	Yield/% ^b 2a/2a'
1	NBS (2.2 equiv), BrCH ₂ COOH (0%), 15 min	10/85
2	NBS (2.2 equiv), BrCH ₂ COOH (50%), Blue LEDs, 30 min	98/2
3	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, 15 min	99/trace
4	NBS (2.2 equiv), BrCH ₂ COOH (5%), darkness, 15 min	73/11
5	NBS (2.2 equiv), BrCH ₂ COOH (5%), sunlight, 15 min	81/8
6	NBS (2.2 equiv), BrCH ₂ COOH (5%), White LEDs, 15 min	98/trace
7	NBS (2.2 equiv), BrCH ₂ COOEt (5%), Blue LEDs, 15 min	75/20
8	NBS (2.2 equiv), CH ₂ COOH(5%), Blue LEDs, 15 min	75/18
9	NBS (2.2equiv), BrCH ₂ COOH (5%), sunlight, 15 min	81/8
10	NBS (1.1 equiv), CH ₂ COOH(5%), Blue LEDs, 15 min	32/37
11	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, 120 min	70/5 (20 ^c)
12	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, 90 min	88/5
13	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, 60 min	87/5
14	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, 30 min	99/trace
15	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, 15 min	99/trace ^d
16	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, 5 min	95/3
17	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, <2.5 min	80/10 ^e
18	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, H ₂ O,15 min	96/3
19	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, DMF,15 min	80/15
20	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, THF,15 min	89/8
21	NBS (2.2 equiv), BrCH ₂ COOH (5%), Blue LEDs, Toluene,15 min	50/47

^aReaction conditions: ethyl 2-(pyridin-2-yl)acetate (0.5 mmol), NBS (1.1 mmol), CH₃CN (2 mL), LEDs irritation (9W), RT, air; ^b isolated yield; ^c yield of ethyl 2-(2,5-dioxopyrrolidin-1-yl)-2-(pyridin-2-yl)acetate; ^d **2a'** was used as starting materials; ^e stopped just after stirring a few minutes.

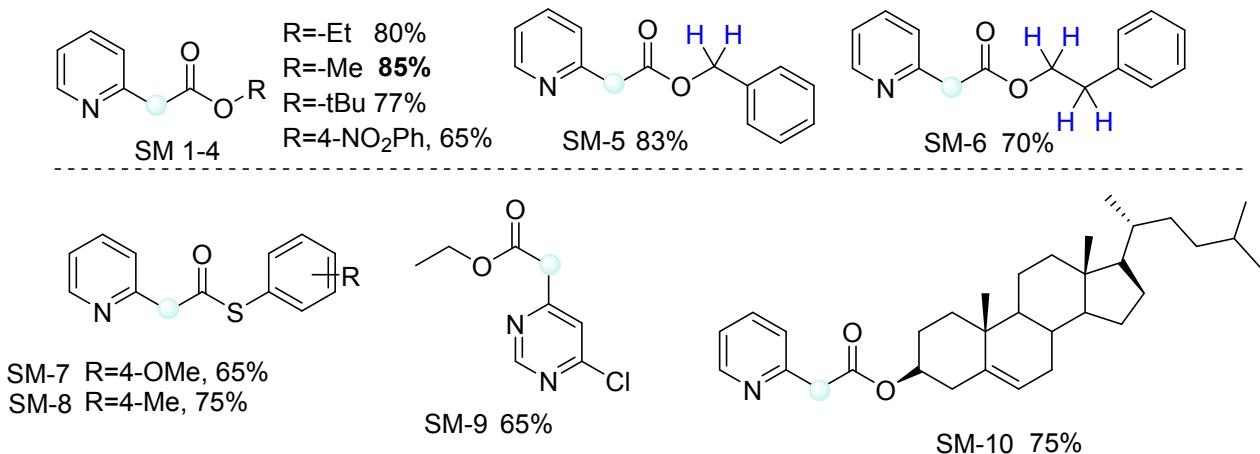
Table S2 Optimization of substrate ethyl 2-(pyridin-2-yl)acetate **1b**^a

	Modified conditions	Yield/% ^b 2b/2b'/others
1	NBS (2.5 equiv), BrCH ₂ COOH (0%), 15 min	trace/15/trace
2	NBS (2.5 equiv), BrCH ₂ COOH (0%), 12 h	75/5/5
3	NBS (2.5 equiv), BrCH ₂ COOH (5%), Blue LEDs, 15 min	75/4/trace
4	NBS (2.5 equiv), BrCH ₂ COOH (5%), Blue LEDs, darkness, 15 min	12/30/trace
5	NBS (2.5 equiv), BrCH ₂ COOH (5%), Blue LEDs, darkness, 12 h	60/15/10 ^c

^aReaction conditions: 1-phenylpentane-2,4-dione (0.5 mmol), NBS (1.1 mmol), CH₃CN (2 mL), Blue LEDs irritation (9W), RT, air; ^b isolated yield; ^c NMR yield from ¹H NMR.

3. General Experimental details

3.1 Preparation of substrates



Scheme S1 preparations of starting materials

Starting materials **1-8**, **10** was prepared via condensation using DCC as condensation agent ¹; Substrates **9** was synthesized according to the literature²; other starting materials were commercially available.

3.2 General procedure for α,α -dibrominations

General procedures

A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under air atmosphere was sequentially charged with carbonyl compound (0.5 mmol), bromoacetic acid (0.025mmol) and CH₃CN (2 mL). Next, fresh recrystallized NBS (1.1 mmol) was added at once. The

reaction tube was placed under the irritation of 9W blue LEDs and stirred for 5-15 min to give a brown solution.

Workup A (for substrates **2a**, **2c-2e**, **2j**, **2k**, **2l-2o**, **2q**, **2s**, **2t**, **3h**, 0.5 mmol scale): after completion, stirring was stopped. CH₃CN was removed by vacuum evaporation, the resulting mixture was diluted with EtOAc (1 mL), washed with H₂O (3 mL), stirred gently and briefly, allowed to separate. This protocol was repeated two times. The combined organic layers were concentrated in vacuo and afforded the dibromide product without extra chromatography.

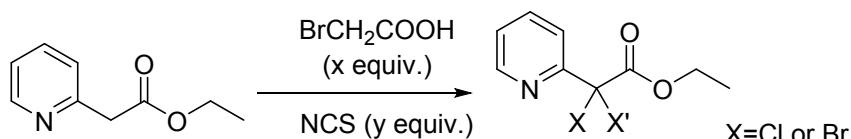
Workup B (for substrates **2a**, 10 mmol scale): after completion, stirring was stopped. CH₃CN was removed by vacuum evaporation, the resulting mixture was diluted with EtOAc (0.5 mL), washed with H₂O (3 mL), stirred gently and briefly, allowed to separate. This protocol was repeated two times. The combined organic layers were concentrated in vacuo and afforded the dibromide product without extra chromatography.

Workup C (for substrates **2b**, **2f-2i**, **2p**, **2r**, **2u-2z**, **3a-3g**, 0.5 mmol scale): after completion, stirring was stopped. CH₃CN was removed by vacuum evaporation, the resulting mixture was diluted with EtOAc (0.5 mL), washed with H₂O (3 mL), stirred gently and briefly, allowed to separate. The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography (PE/EA=10/1).

3.3 Controlled experiments

a) A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under air atmosphere was sequentially charged with carbonyl compound (0.5 mmol), bromoacetic acid (x mmol) and CH₃CN (2 mL). Next, fresh recrystallized NCS (y mmol) was added at once. The reaction tube was placed under the irritation of 9W blue LEDs and stirred for 5-15 min to give a brown solution. After completion, stirring was stopped. CH₃CN was removed by vacuum evaporation, the resulting mixture was diluted with EtOAc (0.5 mL), washed with H₂O (3 mL), stirred gently and briefly, allowed to separate. This protocol was repeated two times. The combined organic layers were concentrated in vacuo and afforded the dibromide product without extra chromatography. ¹H NMR test was then taken to identify the ratio of α , α -di-chloride, α -chloride- α -bromide and α , α -di-bromide products.

Table S3 Controlled experiments for identify the Br source



x=0.05, y=2	99%	0%	0%
x=1, y=2	90%	trace	0%
X=2, y=1	34% (32% mono-Cl)	trace	0%

From the results listed above. The main bromide source didn't come from BrCH₂COOH. But BrCH₂COOH may participate the formation of trace amount of Br₂.

b) A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under air atmosphere was sequentially charged with bromoacetic acid or acetic acid (0.025 mmol) and CH₃CN (2 mL). Next, fresh recrystallized NBS (0.5 mmol) was added at once. The reaction tube was immediately placed under the irritation of 9W blue LEDs or put in dark, and stirred for 5 min. After completion, a picture was taken immediately.

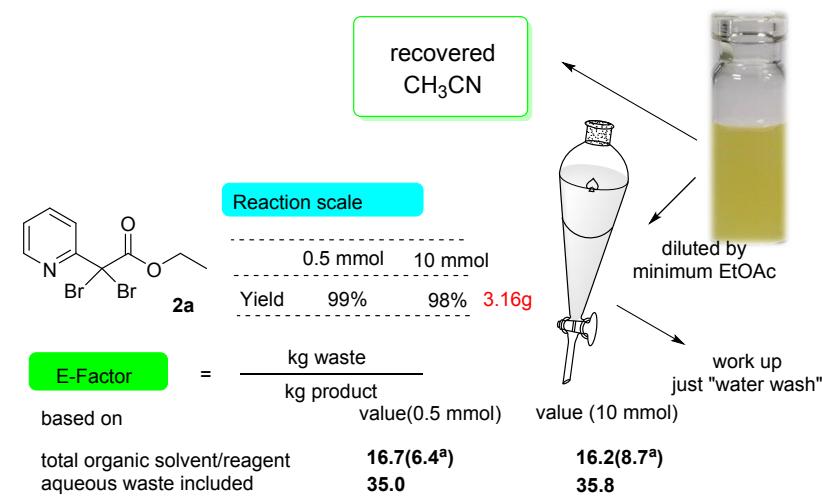
Table S4 Controlled experiments for identify the Br₂ formation.



A	B	C	D
			
BrCH ₂ COOH after Blue LED irritation (5 mins)	BrCH ₂ COOH Dark (5 mins)	CH ₃ COOH after Blue LED irritation (5 mins)	CH ₃ COOH Dark (5 mins)
yellow	Pale yellow	yellow	colorless
pKa of BrCH ₂ COOH= 2.86; pKa of CH ₃ COOH= 4.74			

It can be concluded that yellow solution would appear when the reaction was put under Blue LED irritation. In comparison, no color change occurred when using CH₃COOH in darkness and light yellow color occurred when using BrCH₂COOH in darkness. It means Blue LED irritation was conducive to the formation of small amount Br₂. By directly comparing BrCH₂COOH and CH₃COOH, BrCH₂COOH may react with NBS to produce trace amount Br₂ even in darkness.

3.4 Gram scale experiment, Recycling experiment, and E Factor test



Scheme S1 Gram scale experiment, Recycling experiment, and E Factor test

Gram scale experiment

A 100 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under air atmosphere was sequentially charged with ethyl 2-(pyridin-2-yl)acetate (1.65g, 10 mmol), bromoacetic acid (69.5 mg, 0.5 mmol) and CH₃CN (30 mL). The reaction tube was placed under the irritation of blue LEDs. Next, fresh recrystallized NBS (3.9g, 22 mmol) was added in portion. The mixture was stirred vigorously for 15 min to give a brown solution. After completion, stirring was stopped. CH₃CN was recycled via vacuum evaporation, the resulting mixture was diluted with EtOAc (30 mL), washed with H₂O (20 mL), stirred gently and briefly, allowed to separate. This protocol was repeated two times. The combined organic layers were concentrated in vacuo and afforded the dibromide product (3.16g, 98% yield) without extra chromatography. The purity is 98% (from ¹H NMR).

E Factor calculations:

Note: Density of each liquid at 25 °C; CH₃CN=0.790 g/mL; EtOAc= 0.902 g/mL; water = 1.00 g/mL

For 0.5 mmol scale

a) For 0.5 mmol scale, organic solvent (not considering recycled CH₃CN and aqueous wastes)

Wastes: CH₃CN 2mL, EtOAc 1 mL, excess NBS 0.1 mmol, Succinimide 1 mmol, BrCH₂COOH 0.025mmol

$$\begin{aligned} \text{E-Factor} &= \frac{\text{kg waste}}{\text{kg product}} \\ &= \frac{(0.79*2+0.902*1)*1000+0.1*178+1*99+0.025*139}{322.9*0.5*99\%} \\ &= 16.7 \end{aligned}$$

For 0.5 mmol scale, organic solvent (recycled CH₃CN and not considering aqueous wastes)

$$\begin{aligned} \text{E-Factor} &= \frac{\text{kg waste}}{\text{kg product}} \\ &= \frac{0.902*1*1000+0.1*178+1*99+0.025*139}{322.9*0.5*99\%} \\ &= 6.4 \end{aligned}$$

For 0.5 mmol scale, organic solvent including water (not considering recycled CH₃CN)

Wastes: CH₃CN 2mL, EtOAc 1 mL, excess NBS 0.1 mmol, Succinimide 1 mmol, BrCH₂COOH 0.025mmol, water 1.0 mL *3=3 mL

$$\begin{aligned} \text{E-Factor} &= \frac{\text{kg waste}}{\text{kg product}} \\ &= \frac{(0.79*2+0.902*1)*1000+0.1*178+1*99+0.025*139+3*1000}{322.9*0.5*99\%} \\ &= 35.0 \end{aligned}$$

b) For 10 mmol scale, organic solvent (recycled CH₃CN and not considering aqueous wastes)

Wastes: EtOAc 30 mL, excess NBS 2 mmol, Succinimide 20 mmol, BrCH₂COOH 0.5mmol

$$\begin{aligned}
 \text{E-Factor} &= \frac{\text{kg waste}}{\text{kg product}} \\
 &= \frac{0.902*30*1000+2*178+2*99+0.5*139}{322.9*10*98\%} \\
 &= 8.7
 \end{aligned}$$

c) For 10 mmol scale, organic solvent (not considering aqueous wastes)

Wastes: EtOAc 30 mL, excess NBS 2 mmol, Succinimide 20 mmol, BrCH₂COOH 0.5mmol

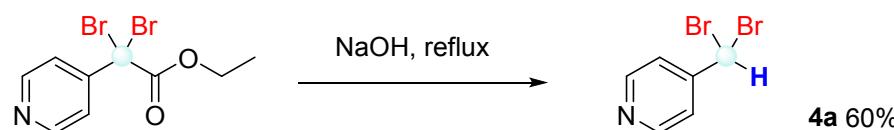
$$\begin{aligned}
 \text{E-Factor} &= \frac{\text{kg waste}}{\text{kg product}} \\
 &= \frac{0.902*30*1000+2*178+2*99+0.5*139+0.79*30*1000}{322.9*10*98\%} \\
 &= 16.2
 \end{aligned}$$

For 10 mmol scale, organic solvent (recycled CH₃CN and considering aqueous wastes)

Wastes: EtOAc 30 mL, excess NBS 2 mmol, Succinimide 20 mmol, BrCH₂COOH 0.5mmol, H₂O 20 mL*3

$$\begin{aligned}
 \text{E-Factor} &= \frac{\text{kg waste}}{\text{kg product}} \\
 &= \frac{0.902*30*1000+2*178+20*99+0.5*139+3*20*1000+0.79*30*1000}{322.9*10*98\%} \\
 &= 35.8
 \end{aligned}$$

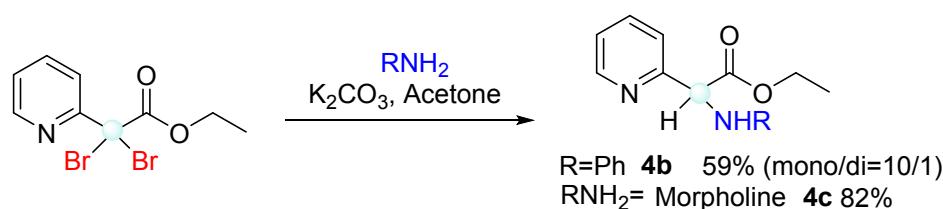
3.5 Decarboxylative reaction of substrates **2q**



Scheme S2 Decarboxylative reaction of substrates **2q**

A 25 mL reaction flask equipped with a Teflon® stir bar, fitted with a reflux condenser and under argon atmosphere was sequentially charged with ethyl 2-(pyridin-4-yl)acetate **2q** (0.2 mmol), aqueous NaOH solution (10%, 1 mL) and acetone (5 mL). The mixture was refluxed for 4 h. TLC monitored the reaction. After completion, stirring was stopped. The solution was acidified, the resulting mixture was extracted with EtOAc (3 mLx3), washed with H₂O (5 mLx3). The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography to give relative product (29.8 mg, 60%).

3.6 Aminations of substrates **2a**

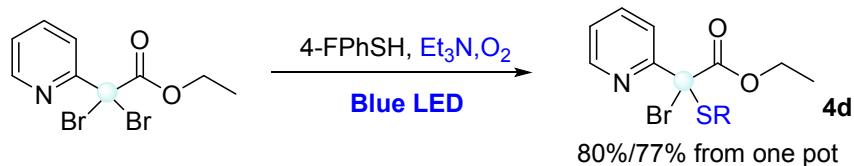


Scheme S3 Aminations of substrates **2a**

A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under argon atmosphere was sequentially charged with ethyl 2-(pyridin-2-yl)acetate **2a** (0.2 mmol), aniline (0.25 mmol) and acetone (2 mL). Next, K₂CO₃ (0.25 mmol) were added. The mixture was stirred at room temperature. TLC monitored

the reaction. After completion, stirring was stopped. acetone was removed via vacuum evaporation, the resulting mixture was diluted with EtOAc (3 mL), washed with H₂O (5 mLx3). The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography (from PE/EA=10/1 to 5/1) to give relative product.

3.7 photo-redox one-pot or stepwise thiolation of substrate **2a**



Scheme S4 thiolation of substrate **2a**

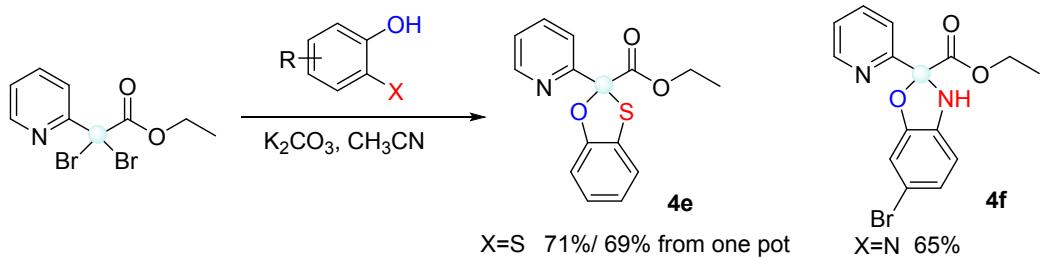
Stepwise procedure

A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under argon atmosphere was sequentially charged with ethyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2a** (65 mg, 0.2 mmol), 4-fluorothiophenol (32 mg, 0.25 mmol) and CH₃CN (2 mL). Next, triethylamines (30 mg, 0.3 mmol) were added. The mixture was stirred under the irritation of Blue LEDs. TLC monitored the reaction. After completion, stirring was stopped. CH₃CN was removed via vacuum evaporation, the resulting mixture was diluted with EtOAc (3 mL), washed with H₂O (5 mLx3). The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography (from PE/EA=10/1 to 5/1) to give thiolation product (59.2 mg, 80%).

Synthesis in one pot

A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under air atmosphere was sequentially charged with ethyl 2-(pyridin-2-yl)acetate (33 mg, 0.2 mmol), bromoacetic acid (1.4 mg, 0.01 mmol) and CH₃CN (2 mL). Next, fresh recrystallized NBS (78 mg, 0.44 mmol) was added at once. The reaction tube was placed under the irritation of blue LEDs and stirred for 15 min to give a brown solution. After that 4-fluorothiophenol (32 mg, 0.25 mmol) and triethylamines (30 mg, 0.3 mmol) were added in sequence. TLC monitored the reaction. After completion, stirring was stopped. CH₃CN was removed via vacuum evaporation, the resulting mixture was diluted with EtOAc (3 mL), washed with H₂O (5 mLx3). The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography (from PE/EA=10/1 to 5/1) to give thiolation product (57.0 mg, 77%).

3.8 construction of carbon-hetero quaternary carbon products **4e**, **4f**.



Scheme S5 construction of carbon-hetero quaternary carbon products **4e**, **4f**

Stepwise procedure

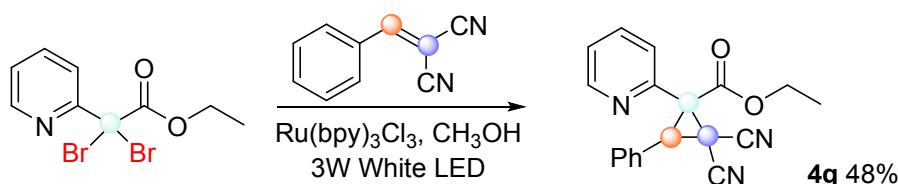
A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under argon atmosphere was sequentially charged with ethyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2a** (65 mg, 0.2 mmol), 2-mercaptophenol (25.2 mg, 0.2 mmol) or 5-bromo-2-aminophenol (37.6 mg, 0.2 mmol) and CH₃CN (2 mL). Next, K₂CO₃ (55.2 mg, 0.4 mmol) were added. The mixture was stirred at room temperature overnight. TLC monitored

the reaction. After completion, stirring was stopped. CH₃CN was removed via vacuum evaporation, the resulting mixture was diluted with EtOAc (3 mL), washed with H₂O (5 mL×3). The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography (from PE/EA=10/1 to 5/1) to give product: ethyl 2-(pyridin-2-yl)benzo[d][1,3]oxathiole-2-carboxylate (40.8 mg, 71%); ethyl 6-bromo-2-(pyridin-2-yl)-2,3-dihydrobenzo[d]oxazole-2-carboxylate (45.4 mg, 65%).

Synthesis of ethyl 2-(pyridin-2-yl)benzo[d][1,3]oxathiole-2-carboxylate in one pot

A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under air atmosphere was sequentially charged with ethyl 2-(pyridin-2-yl)acetate (33 mg, 0.2 mmol), bromoacetic acid (1.4 mg, 0.01 mmol) and CH₃CN (2 mL). Next, fresh recrystallized NBS (78 mg, 0.44 mmol) was added at once. The reaction tube was placed under the irritation of blue LEDs and stirred for 15 min to give a brown solution. After that 2-mercaptophenol (25.2 mg, 0.2 mmol) and K₂CO₃ (55.2 mg, 0.4 mmol) were added in sequence. TLC monitored the reaction. After completion, stirring was stopped. CH₃CN was removed via vacuum evaporation, the resulting mixture was diluted with EtOAc (3 mL), washed with H₂O (5 mL×3). The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography (from PE/EA=10/1 to 5/1) to give product (39.7 mg, 69%).

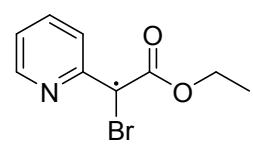
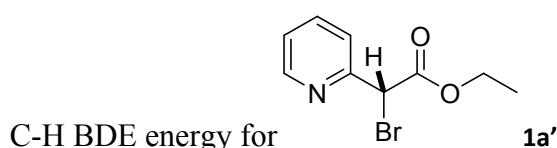
3.9 construction of all carbon quaternary carbon product 4g



Scheme S6 the formation of product 4g

A 5 mL transparent reaction tube equipped with a Teflon® stir bar, fitted with a rubber septum and under air atmosphere was sequentially charged with ethyl 2,2-dibromo-2-(pyridin-2-yl) acetate (65 mg, 0.2 mmol), 2-benzylidenemalononitrile (62 mg, 0.4 mmol), tris(2,2'-bipyridyl)rutheniumchloridehexahydrate (2 mg, 0.002 mmol), N,N-Diisopropyl-ethylamin (51.7 mg, 0.4 mmol), 10 mL methanol. Next, the reaction tube was placed under the irritation of White LEDs and stirred for 6h. After that stirring was stopped. solvent was removed via vacuum evaporation, the resulting mixture was diluted with EtOAc (3 mL), washed with H₂O (5 mL×3). The combined organic layers were concentrated in vacuo and the crude material further purified via chromatography and prep. TLC to give product (30.4 mg, 48%).

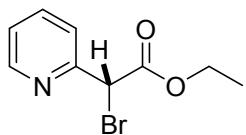
3.10 calculations for C-H BDE energy



Zero-point correction=	0.165879 (Hartree/Particle)
Thermal correction to Energy=	0.178642
Thermal correction to Enthalpy=	0.179587
Thermal correction to Gibbs Free Energy=	0.123442
Sum of electronic and zero-point Energies=	-3124.786976
Sum of electronic and thermal Energies=	-3124.774213
Sum of electronic and thermal Enthalpies=	-3124.773269

Sum of electronic and thermal Free Energies=

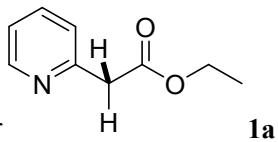
-3124.829413



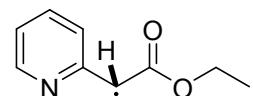
Zero-point correction=	0.179481 (Hartree/Particle)
Thermal correction to Energy=	0.192134
Thermal correction to Enthalpy=	0.193078
Thermal correction to Gibbs Free Energy=	0.138155
Sum of electronic and zero-point Energies=	-3125.419920
Sum of electronic and thermal Energies=	-3125.407267
Sum of electronic and thermal Enthalpies=	-3125.406323
Sum of electronic and thermal Free Energies=	-3125.461245

C-H BDE for **1a'**= 3125.406323-(0.487949+3124.773269)=0.145105 Hartree=91.1 Kcal/mmol

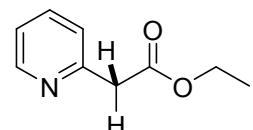
C-H BDE energy for



1a'



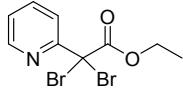
Zero-point correction=	0.176433 (Hartree/Particle)
Thermal correction to Energy=	0.187562
Thermal correction to Enthalpy=	0.188506
Thermal correction to Gibbs Free Energy=	0.137328
Sum of electronic and zero-point Energies=	-553.811838
Sum of electronic and thermal Energies=	-553.800710
Sum of electronic and thermal Enthalpies=	-553.799766
Sum of electronic and thermal Free Energies=	-553.850943



Zero-point correction=	0.189576 (Hartree/Particle)
Thermal correction to Energy=	0.200974
Thermal correction to Enthalpy=	0.201918
Thermal correction to Gibbs Free Energy=	0.149473
Sum of electronic and zero-point Energies=	-554.437858
Sum of electronic and thermal Energies=	-554.426459
Sum of electronic and thermal Enthalpies=	-554.425515
Sum of electronic and thermal Free Energies=	-554.477961

C-H BDE for 1a= 554.425515-(0.487949+553.799766)=0.137801 Hartree=86.4 Kcal/mmol

6. Analytic data



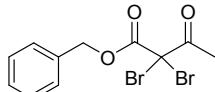
ethyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2a**

The title compound was obtained according to the general procedure A using the following amounts and conditions: ethyl 2-(pyridin-2-yl) acetate (82.6 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified via workup A to provide the desired compound as a colorless oil liquid (159.8 mg, 99% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.53 (d, *J* = 4.1 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.81 (td, *J* = 7.9, 1.6 Hz, 1H), 7.25 (dd, *J* = 7.0, 4.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 165.6, 158.5, 148.2, 137.6, 123.8, 121.9, 64.4, 58.7, 13.8.

HRMS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₉H₁₀Br₂NO₂]⁺: 321.9073; found: 321.9070.



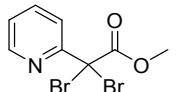
benzyl 2,2-dibromo-3-oxobutanoate **2b**

The title compound was obtained according to the general procedure A using the following amounts and conditions: benzyl 3-oxobutanoate (96.1 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 30 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow oil liquid (142.6 mg, 81% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.38 (s, 5H), 5.31 (s, 2H), 2.50 (d, *J* = 13.6 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 190.8, 163.5, 134.0, 129.0, 128.8, 128.4, 70.1, 59.7, 23.5.

HRMS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₁H₁₁Br₂O₃]⁺: 348.9069; found: 348.9070.



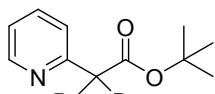
methyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2c**

The title compound was obtained according to the general procedure A using the following amounts and conditions: methyl 2-(pyridin-2-yl) acetate (75.5 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow oil liquid (141.5 mg, 91% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.53 (d, *J* = 4.1 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.82 (td, *J* = 7.9, 1.7 Hz, 1H), 7.29 – 7.21 (m, 1H), 3.92 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 166.2, 158.5, 148.2, 137.7, 123.9, 122.0, 58.1, 55.0.

HRMS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₈H₈Br₂NO₂]⁺: 307.8916; found: 307.8915.



tert-butyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2d**

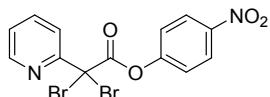
The title compound was obtained according to the general procedure A using the following amounts and conditions: tert-butyl 2-(pyridin-2-yl) acetate (97.06 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane

5-10%) to provide the desired compound as a yellow oil liquid (173.2 mg, 97.8% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.55 (d, *J* = 4.2 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.23 (dd, *J* = 7.4, 4.9 Hz, 1H), 1.49 (s, 9H).

¹³C NMR (75 MHz, CDCl₃) δ 164.1, 158.7, 148.2, 137.4, 123.6, 121.7, 85.0, 60.6, 27.5.

HRMS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₁H₁₄Br₂NO₂]⁺: 349.9386; found: 349.9387.



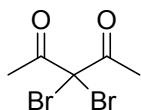
4-nitrophenyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2e**

The title compound was obtained according to the general procedure A using the following amounts and conditions: 4-nitrophenyl 2-(pyridin-2-yl) acetate (129.06mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 10-15%) to provide the desired compound as a brown oil liquid (177.7 mg, 85% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.57 (s, 1H), 8.24 (d, *J* = 39.8 Hz, 3H), 7.91 (s, 1H), 7.37 (d, *J* = 26.3 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 168.5, 165.5, 162.2, 157.0, 148.3, 138.6, 138.5, 136.1, 126.1, 126.0, 122.7, 122.6, 115.9, 115.6, 62.8.

HRMS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₃H₉Br₂N₂O₄]⁺: 414.8924; found: 414.8927.



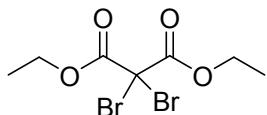
3,3-dibromopentane-2,4-dione **2f**

The title compound was obtained according to the general procedure A using the following amounts and conditions: pentane-2,4-dione (50.06 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow oil liquid (107.95 mg, 83% yield).

¹H NMR (300 MHz, CDCl₃) δ 2.61 (s, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 193.4, 68.2, 24.6.

The result is in accordance with literature³



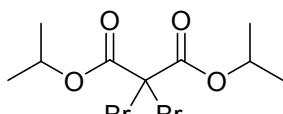
diethyl 2,2-dibromomalonate **2g**

The title compound was obtained according to the general procedure A using the following amounts and conditions: diethyl malonate (80.1 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a colorless oil liquid (121.6 mg, 76% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.37 (q, *J* = 7.1 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 163.2, 64.8, 50.7, 13.7.

The result is in accordance with literature⁴



diisopropyl 2,2-dibromomalonate **2h**

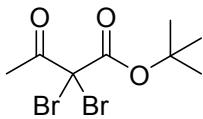
The title compound was obtained according to the general procedure A using the following amounts and conditions: diisopropyl malonate (94.1 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2

mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow oil liquid (140.2 mg, 81 % yield).

¹H NMR (300 MHz, CDCl₃) δ 5.14 (hept, *J* = 6.2 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 163.2, 64.8, 13.7.

The result is in accordance with literature⁴



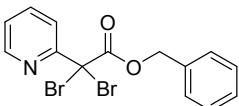
tert-butyl 2,2-dibromo-3-oxobutanoate **2i**

The title compound was obtained according to the general procedure A using the following amounts and conditions: tert-butyl 3-oxobutanoate (79.0 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 2-5%) to provide the desired compound as a pale-yellow oil liquid (130 mg, 82% yield).

¹H NMR (300 MHz, CDCl₃) δ 2.55 (s, 3H), 1.53 (s, 9H).

¹³C NMR (75 MHz, CDCl₃) δ 190.8, 162.2, 86.3, 61.7, 27.5, 23.5.

The result is in accordance with literature⁵



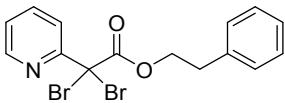
benzyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2j**

The title compound was obtained according to the general procedure A using the following amounts and conditions: benzyl 2-(pyridin-2-yl) acetate (129.0 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 10-15%) to provide the desired compound as a yellow oil liquid (177.7 mg, 85% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.48 (m, 1H), 8.04-7.96 (m, 1H), 7.77 (td, *J* = 7.8, 1.8 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 5H), 7.22 (m, 1H), 5.33 (d, *J* = 4.9 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 165.4, 158.5, 148.1, 137.6, 134.7, 128.5, 128.5, 128.1, 123.8, 122.0, 69.6, 58.5.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₄H₁₂Br₂NO₂]⁺: 383.9229; found: 383.9235.



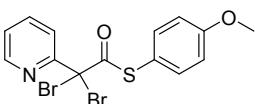
phenethyl 2,2-dibromo-2-(pyridin-2-yl)acetate **2k**

The title compound was obtained according to the general procedure A using the following amounts and conditions: phenethyl 2-(pyridin-2-yl) acetate (121.1 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 2-5%) to provide the desired compound as a pale-yellow oil liquid (197.3 mg, 98.1% yield, 1Br:2Br=1:8).

¹H NMR (300 MHz, CDCl₃) δ 8.47 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.01 – 7.95 (m, 1H), 7.77 (td, *J* = 7.8, 1.8 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.23 – 7.20 (m, 2H), 7.17 – 7.12 (m, 2H), 4.51 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 165.6, 158.3, 148.2, 137.6, 129.0, 128.5, 127.9, 126.7, 123.8, 121.9, 68.7, 48.7, 34.6.

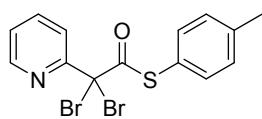
HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₅H₁₄Br₂NO₂]⁺: 397.9386; found: 397.9385.



S-(4-methoxyphenyl)-2,2-dibromo-2-(pyridin-2-yl)ethanethioate **2l**

The title compound was obtained according to the general procedure A using the following amounts and conditions:

S-(4-methoxyphenyl) 2-(pyridin-2-yl)ethanethioate (130.5 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow liquid (185.5 mg, 89% yield).
¹H NMR (400 MHz, CDCl₃) δ 8.63 (dd, *J* = 12.8, 8.8 Hz, 1H), 8.00 (dd, *J* = 15.1, 4.8 Hz, 1H), 7.78 (td, *J* = 7.8, 1.8 Hz, 1H), 7.40 (dd, *J* = 2.0 Hz, 2H), 7.28 – 7.24 (m, 1H), 6.95 (dd, *J* = 2.0 Hz, 2H), 3.81 (s, 3H).
¹³C NMR (101 MHz, CDCl₃) δ 192.2, 161.1, 157.7, 148.7, 137.5, 136.3, 124.1, 122.7, 118.7, 115.1, 65.5, 55.4.
HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₄H₁₂Br₂NO₂S]⁺: 415.8590; found: 415.8588.



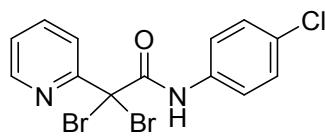
S-(p-tolyl) 2,2-dibromo-2-(pyridin-2-yl)ethanethioate **2m**

The title compound was obtained according to the general procedure A using the following amounts and conditions: S-(p-tolyl)-2-(pyridin-2-yl)ethanethioate (122.5 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow liquid (174 mg, 87% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.61 (d, *J* = 4.6 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.78 (dt, *J* = 9.4, 4.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.24 (dd, *J* = 9.6, 6.8 Hz, 3H), 2.36 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 191.8, 157.6, 148.7, 140.4, 137.5, 134.6, 130.3, 124.6, 124.1, 122.7, 77.5, 77.1, 76.8, 65.6, 21.4.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₄H₁₂Br₂NOS]⁺: 399.9001; found: 399.9004.



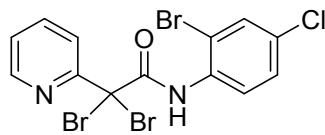
2,2-dibromo-N-(4-chlorophenyl)-2-(pyridin-2-yl)acetamide **2n**

The title compound was obtained according to the general procedure A using the following amounts and conditions: N-(4-chlorophenyl)-2-(pyridin-2-yl)acetamide (123.3 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-20%) to provide the desired compound as a yellow oil liquid (165 mg, 82% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 9.76 (s, 1H), 8.61 (ddd, *J*=4.8, 1.8, 0.9, 1H), 8.20 (dt, *J*=8.1, 1.0, 1H), 7.84 (td, *J*=7.9, 1.8, 1H), 7.60 – 7.55 (m, 2H), 7.36 – 7.30 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 162.8, 158.1, 148.0, 138.0, 135.8, 130.4, 129.2, 124.1, 123.6, 121.4, 62.0.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₃H₁₀Br₂ClN₂O]⁺: 402.8843; found: 402.8846.



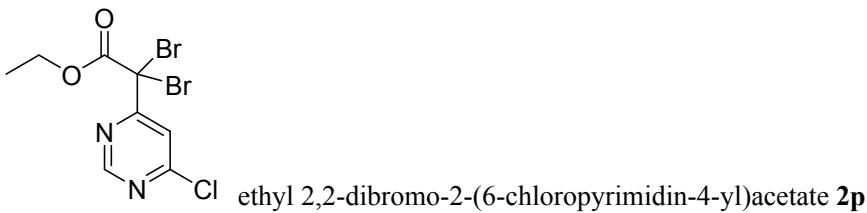
2,2-dibromo-N-(2-bromo-4-chlorophenyl)-2-(pyridin-2-yl)acetamide **2o**

The title compound was obtained according to the general procedure A using the following amounts and conditions: N-(2-bromo-4-chlorophenyl)-2-(pyridin-2-yl)acetamide (162.8 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-20%) to provide the desired compound as a colorless oil liquid (171.5 mg, 71% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 10.35 (s, 1H), 8.62 (ddd, *J*=4.8, 1.8, 0.9, 1H), 8.36 (d, *J*=8.9, 1H), 8.23 – 8.18 (m, 1H), 7.85 (td, *J*=7.9, 1.8, 1H), 7.59 (d, *J*=2.4, 1H), 7.34 (dd, *J*=4.3, 1.7, 1H), 7.33 – 7.29 (m, 1H). ¹³C

NMR (101 MHz, CDCl₃) δ 163.1, 158.0, 148.1, 137.9, 130.4, 128.5, 124.1, 123.5, 122.2, 114.3, 61.9.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₃H₉Br₃ClN₂O]⁺: 480.7948; found: 480.7944.

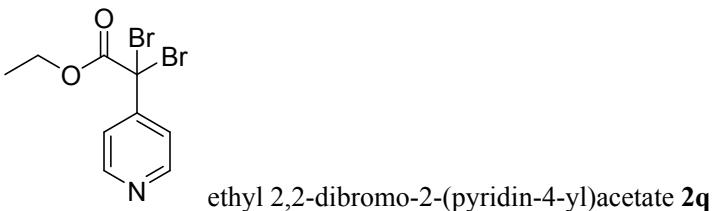


The title compound was obtained according to the general procedure A using the following amounts and conditions: ethyl 2-(6-chloropyrimidin-4-yl) acetate (100.31 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-20%) to provide the desired compound as a yellow liquid (152.1 mg, 85% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.95 (s, 1H), 8.03 (s, 1H), 4.51 – 4.29 (m, 2H), 1.31 (t, J = 7.1, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 167.6, 164.2, 163.2, 158.0, 119.5, 64.9, 13.7.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₈H₈Br₂ClNO₂]⁺: 356.8636; found: 356.8633.

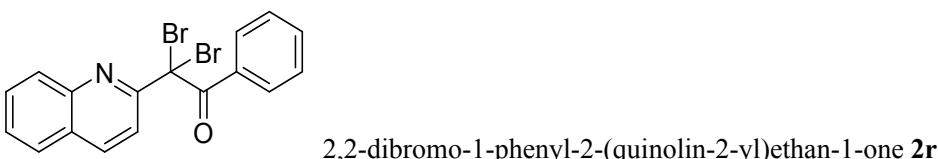


The title compound was obtained according to the general procedure A using the following amounts and conditions: ethyl 2-(pyridin-4-yl)acetate (82.6 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a colorless oil liquid (143.6 mg, 89% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.65 (d, J = 6.1 Hz, 2H), 7.59 (d, J = 6.1 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 165.3, 150.1, 148.5, 121.9, 64.9, 56.3, 13.7.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₉H₁₀Br₂NO₂]⁺: 321.9073; found: 321.9071.

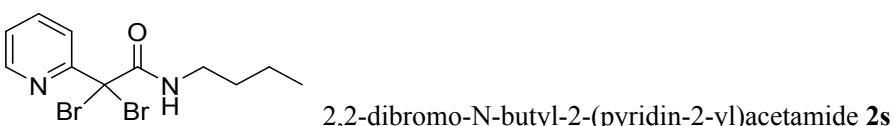


The title compound was obtained according to the general procedure A using the following amounts and conditions: 1-phenyl-2-(quinolin-2-yl)ethan-1-one (123.8 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by flash silica gel filtration (eluent: ether/hexane 1-3%) to provide the desired compound as a colorless oil liquid (135 mg, 67% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 8.32 (d, J=8.6, 1H), 8.15 (d, J=8.7, 1H), 7.86 (t, 2H), 7.73 – 7.64 (m, 3H), 7.58 (ddd, J=8.1, 6.9, 1.3, 1H), 7.42 – 7.36 (m, 1H), 7.25 – 7.20 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 185.9, 158.5, 145.9, 138.3, 132.7, 131.7, 131.2, 130.5, 129.9, 128.1, 127.9, 127.4, 119.6, 119.0, 69.1.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₇H₁₂Br₂NO]⁺: 403.9280; found: 403.9281.



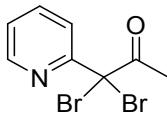
The title compound was obtained according to the general procedure A using the following amounts and conditions: N-butyl-2-(pyridin-2-yl)acetamide (96 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS

(195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-15%) to provide the desired compound as a colorless oil liquid (141.8 mg, 81% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 8.59 (ddd, *J*=4.8, 1.8, 0.9, 1H), 8.04 (dt, *J*=8.1, 1.0, 1H), 7.78 (ddd, *J*=8.1, 7.6, 1.8, 1H), 7.29 – 7.18 (m, 1H), 3.40 (td, *J*=7.1, 5.7, 2H), 1.67 – 1.57 (m, 2H), 1.47 – 1.37 (m, 2H), 0.96 (t, *J*=7.3, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.2, 158.3, 148.5, 137.4, 123.8, 122.5, 62.7, 41.2, 31.1, 20.0, 13.8.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₁H₁₅Br₂N₂O]⁺: 348.9546; found: 348.9549.



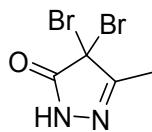
1,1-dibromo-1-(pyridin-2-yl)propan-2-one **2t**

The title compound was obtained according to the general procedure A using the following amounts and conditions: 1-(pyridin-2-yl)propan-2-one (67.5 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow oil liquid (131.8 mg, 90% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 8.53 (ddt, *J*=4.8, 1.6, 0.8, 1H), 8.10 (dt, *J*=8.1, 1.0, 1H), 7.87 (td, *J*=7.8, 1.8, 1H), 7.31 (dd, *J*=4.8, 1.1, 1H), 7.27 (d, *J*=1.0, 0H), 2.48 (d, *J*=0.7, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 192.6, 158.4, 148.2, 138.0, 124.0, 123.0, 69.2, 24.5.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₈H₈Br₂NO]⁺: 291.8967; found: 291.8965.



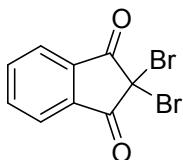
4,4-dibromo-5-methyl-2,4-dihydro-3H-pyrazol-3-one **2u**

The title compound was obtained according to the general procedure A using the following amounts and conditions: 5-methyl-2,4-dihydro-3H-pyrazol-3-one (49 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a white solid (71.5 mg, 56% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 2.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.6, 156.9, 44.0, 13.3.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₄H₅Br₂N₂O]⁺: 254.8763; found: 254.8759.

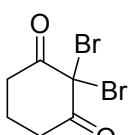


2,2-dibromo-1H-indene-1,3(2H)-dione **2v**

The title compound was obtained according to the general procedure A using the following amounts and conditions: 1H-indene-1,3(2H)-dione (73.07 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow liquid (150.4 mg, 99% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, *J* = 22.9 Hz, 4H).

The result is in accordance with literature⁴



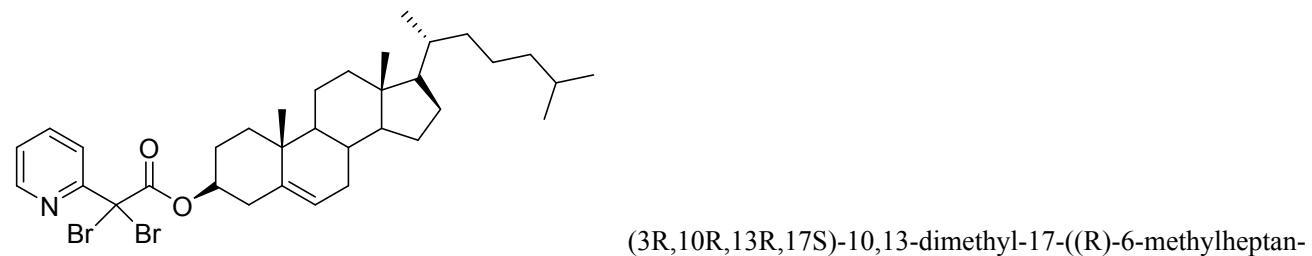
2,2-dibromocyclohexane-1,3-dione **2w**

The title compound was obtained according to the general procedure A using the following amounts and conditions: cyclohexane-1,3-dione (56.1 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 30%) to provide the desired compound as a pale-yellow oil liquid (118.1 mg, 87.1% yield, 1Br:2Br=1:10).

¹H NMR (300 MHz, CDCl₃) δ 3.07 (dd, *J* = 12.7, 5.9 Hz, 4H), 2.08 – 1.99 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 163.2, 64.8, 50.7, 13.7.

The result is in accordance with literature⁴



The title compound was obtained according to the general procedure A using the following amounts and conditions: (3R,10R,13R,17S)-10,13-dimethyl-17-((R)-5-methylhexan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(pyridin-2-yl)acetate (252.83 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a colorless oil liquid (282.2 mg, 84.8% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.57 – 8.50 (m, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.80 (tt, *J* = 7.9, 2.5 Hz, 1H), 7.25 – 7.19 (m, 1H), 5.43 – 5.37 (m, 1H), 4.87 – 4.74 (m, 1H), 2.47 – 2.23 (m, 2H), 2.05 – 1.91 (m, 3H), 1.90 – 1.78 (m, 2H), 1.63 – 1.43 (m, 6H), 1.36 (dt, *J* = 20.3, 8.0 Hz, 5H), 1.22 – 1.09 (m, 6H), 1.06 – 0.95 (m, 6H), 0.93 – 0.81 (m, 10H), 0.74 – 0.62 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 164.9, 158.6, 148.12, 139.1, 137.5, 123.8, 123.12, 121.9, 78.3, 59.2, 56.6, 56.1, 49.9, 42.3, 39.7, 39.5, 37.4, 36.8, 36.6, 36.2, 35.8, 31.9, 31.8, 28.3, 28.0, 27.1, 24.3, 23.9, 22.89, 22.6, 21.0, 19.4, 18.8, 11.9.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₃₄H₅₀Br₂NO₂]⁺: 662.2203; found: 662.2193.

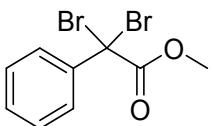


The title compound was obtained according to the general procedure A using the following amounts and conditions: 3-isochromanone (74.1 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow liquid (88.98 mg, 78% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.52 – 7.38 (m, 3H), 7.36 – 7.29 (m, 1H), 5.69 (d, *J* = 14.2 Hz, 1H), 5.44 (s, 1H), 5.28 (d, *J* = 14.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 165.8, 133.4, 131.6, 130.1, 129.5, 128.2, 125.5, 69.8, 38.9.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₉H₈BrO₂]⁺: 226.9702; found: 226.9700.



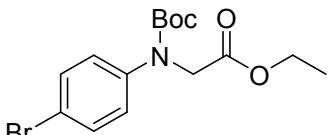
methyl 2,2-dibromo-2-phenylacetate **3a**

The title compound was obtained according to the general procedure A using the following amounts and conditions: methyl 2-phenylacetate (75 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 1-5%) to provide the desired compound as a colorless oil liquid (97 mg, 63% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 8.02 (d, 2H), 7.67 (td, *J*=7.4, 1.5, 1H), 7.52 (td, *J*=7.7, 1.4, 2H), 3.99 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 164.1, 135.0, 132.5, 130.1, 128.9, 52.8, 29.7.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₉H₈Br₂O₂]⁺: 306.8964; found: 306.8960.



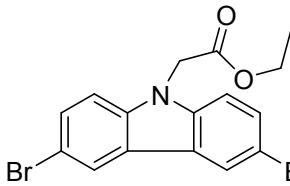
ethyl N-(4-bromophenyl)-N-(tert-butoxycarbonyl)glycinate **3c**

The title compound was obtained according to the general procedure A using the following amounts and conditions: tert-butyl N-(2-ethoxy-2-oxoethyl)-N-phenylglycinate (139.6 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 30min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow liquid (125.7 mg, 70% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 4.24 (s, 2H), 4.23 – 4.17 (m, 2H), 1.44 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.7, 154.3, 141.9, 131.9, 128.3, 119.7, 81.4, 61.3, 52.2, 28.2, 14.2.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₅H₂₁BrNO₄]⁺: 358.0648; found: 358.0654.



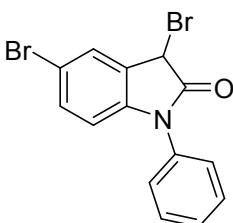
ethyl 2-(3,6-dibromo-9H-carbazol-9-yl)acetate **3d**

The title compound was obtained according to the general procedure A using the following amounts and conditions: ethyl 2-(9H-carbazol-9-yl)acetate (126.5mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 30min. The crude product was purified by silica gel filtration (eluent: ether/hexane 10-15%) to provide the desired compound as a white solid (126 mg, 61% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 1H), 7.57 – 7.48 (m, 1H), 7.16 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.88 (d, *J* = 2.3 Hz, 1H), 4.18 (dt, *J* = 7.0, 5.9 Hz, 1H), 1.24 – 1.18 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 167.8, 139.5, 129.4, 123.8, 123.4, 112.9, 110.1, 62.0, 44.80 14.2.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₆H₁₄Br₂NO₂]⁺: 409.9386; found: 409.9386.



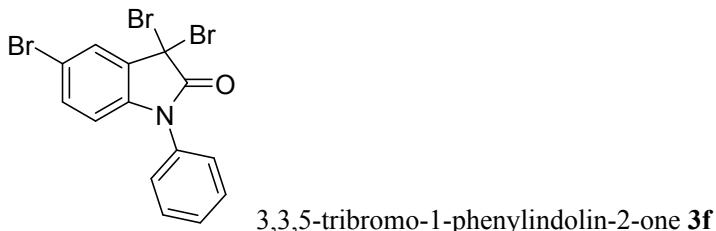
3,5-dibromo-1-phenylindolin-2-one **3e**

The title compound was obtained according to the general procedure A using the following amounts and conditions: 1-phenyloxindole (104.62 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 25min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow solid (115.6mg, 63% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 1.1 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 4.9 Hz, 1H), 7.42 – 7.37 (m, 3H), 6.68 (dd, *J* = 8.4, 5.4 Hz, 1H), 5.41 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 171.1, 142.9, 133.5, 133.2, 129.9, 129.4, 128.8, 127.9, 126.3, 116.3, 111.6, 37.9.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₄H₁₀Br₃NO]⁺: 365.9124; found: 365.9118.

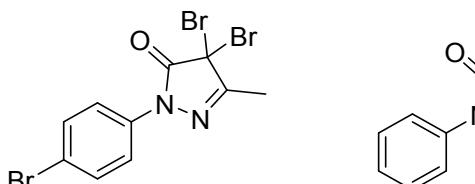


The title compound was obtained according to the general procedure A using the following amounts and conditions: 1-phenyloxindole (104.62 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.025 mmol), NBS (285 mg, 1.6 mmol), 2 mL acetonitrile, r.t, 25min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow solid (126.8 mg, 57% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, *J* = 2.0 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.51 – 7.45 (m, 1H), 7.43 (d, *J* = 1.5 Hz, 1H), 7.40 (d, *J* = 1.6 Hz, 1H), 7.40 – 7.35 (m, 1H), 6.67 (d, *J* = 8.5 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 168.5, 139.0, 134.4, 132.9, 132.5, 130.0, 129.3, 129.1, 126.3, 116.9, 111.9, 43.9.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₄H₉Br₃NO]⁺: 443.8229; found: 443.8225.

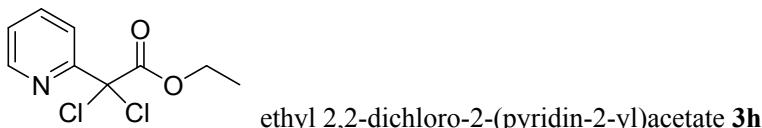


mixture of 4,4-dibromo-2-(4-bromophenyl)-5-methyl-2,4-dihydro-3H-pyrazol-3-one **3g** and 4,4-dibromo-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one **3g'**

The title compound was obtained according to the general procedure A using the following amounts and conditions: 5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (87 mg, 0.5 mmol), bromoacetic acid (3.5 mg, 0.0025 mmol), NBS (195.8 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15 min. The crude product was purified by silica gel filtration (eluent: ether/hexane 1-5%) to provide the desired compound as a yellow oil liquid (130.2 mg, 64% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 7.89 – 7.75 (m, 2H), 7.56 – 7.39 (m, 2H), 2.43 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.1, 156.4, 136.0, 132.1, 129.1, 126.1, 120.2, 118.8, 45.8, 13.2.

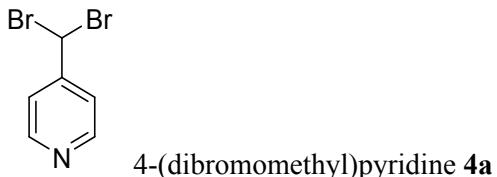


The title compound was obtained according to the general procedure A using the following amounts and conditions: ethyl 2-(pyridin-2-yl) acetate (82.6 mg, 0.5 mmol), bromoacetic acid (13.9 mg, 0.01 mmol), NCS (146.9 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 15min. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a colorless oil liquid (106.02 mg, 91% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.56 (d, *J* = 4.7 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 11.6, 4.0 Hz, 1H), 7.32 (dd, *J* = 7.2, 4.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 165.3, 157.6, 148.6, 137.6, 124.2, 120.7, 83.3, 64.2, 13.8.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₉H₁₀Cl₂NO₂]⁺: 234.0083; found: 234.0080.

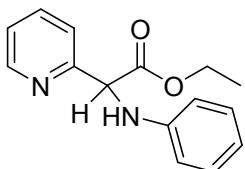


The title compound was obtained according to the general procedure 3.5 as a colorless oil liquid (29.8 mg, 60 % yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 8.69-8.66 (m, 2H), 7.49-7.46 (m, 2H), 6.55 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 150.3, 149.7, 121.0, 38.1.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₆H₆Br₂N]⁺: 249.8862; found: 249.8865.

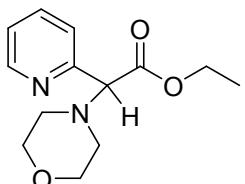


ethyl 2-(phenylamino)-2-(pyridin-2-yl)acetate **4b**

The title compound was obtained according to the general procedure B using the following amounts and conditions: ethyl 2,2-dibromo-2-(pyridin-2-yl) acetate (162.5 mg, 0.5 mmol), aniline (46.56mg, 0.5 mmol), K₂CO₃ (152.03 mg, 1.1 mmol), 5 mL acetone, r.t., 5h. The crude product was purified by silica gel filtration (eluent: ether/hexane 3-5%) to provide the desired compound as a yellow liquid (74.27 mg, 58% yield). Note: mixture of ethyl 2-(phenylamino)-2-(pyridin-2-yl)acetate and ethyl 2,2-bis(phenylamino)-2-(pyridin-2-yl)acetate were obtained due to similar polarity (10/1 according to ¹H NMR).

¹H NMR (300 MHz, CDCl₃) δ 8.62 (d, *J* = 4.8 Hz, 1H), 7.68 (td, *J* = 7.6, 1.6 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 7.3, 5.7 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 5.26 (s, 1H), 4.20 (dd, *J* = 7.2, 3.5 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.3, 156.4, 149.5, 146.1, 137.1, 129.3, 123.2, 122.0, 118.2, 113.6, 62.4, 61.9, 14.1.



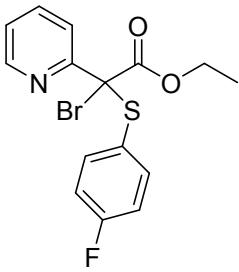
ethyl 2-morpholino-2-(pyridin-2-yl)acetate **4c**

The title compound was obtained according to the general procedure B using the following amounts and conditions: ethyl 2,2-dibromo-2-(pyridin-2-yl) acetate (162.5 mg, 0.5 mmol), morpholine (129.24 mg, 1 mmol), triethylamine (101.19 mg, 1 mmol), 5 mL acetonitrile, r.t, 5h. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow liquid (93.83mg, 75% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.59 (d, *J* = 4.2 Hz, 1H), 7.71 (td, *J* = 7.7, 1.7 Hz, 1H), 7.55 (d, *J* = 4.5 Hz, 1H), 7.25 (dd, *J* = 6.2, 1.1 Hz, 1H), 4.21 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.74 (t, *J* = 4.6 Hz, 4H), 2.57 (d, *J* = 3.3 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 4H).

¹³C NMR (75 MHz, CDCl₃) δ 170.29, 155.83, 149.44, 136.70, 123.29, 123.07, 75.35, 66.98, 61.05, 51.21, 14.18.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₃H₁₉N₂O₃]⁺: 251.1396; found: 251.1390.



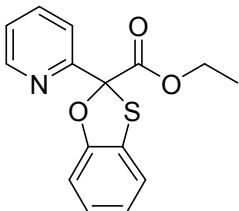
ethyl 2-bromo-2-((4-fluorophenyl)thio)-2-(pyridin-2-yl)acetate **4d**

The title compound was obtained according to the general procedure A using the following amounts and conditions: ethyl 2,2-dibromo-2-(pyridin-2-yl) acetate (162.5 mg, 0.5 mmol), 4-fluorobzenethiol (64.08mg, 0.5 mmol), K_2CO_3 (152.03 mg, 1.1 mmol), 2 mL acetonitrile, r.t, 50min. The crude product was purified by silica gel filtration (eluent: ether/hexane 3-5%) to provide the desired compound as a colorless oil liquid (103.66mg, 56% yield).

1H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, J = 4.8 Hz, 1H), 7.61 (td, J = 8.0, 1.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.20 (dd, J = 4.6, 2.9 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 163.9 ($^1J_{C-F}$ =258 Hz), 157.0, 148.3, 138.6 ($^3J_{C-F}$ =9 Hz), 136.1, 126.1, 122.7, 115.7 ($^2J_{C-F}$ =21 Hz), 69.8, 62.8, 13.8.

HR-MS (ESI $^+$) m/z (%): calcd. for $[M+H]^+$ = $[C_{15}H_{14}BrFNO_2S]^{+}$: 369.9907; found: 369.9902.



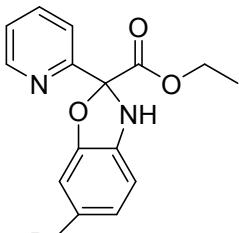
ethyl 2-(pyridin-2-yl)benzo[d][1,3]oxathiole-2-carboxylate **4e**

The title compound was obtained according to the general procedure B using the following amounts and conditions: ethyl 2,2-dibromo-2-(pyridin-2-yl) acetate (162.5 mg, 0.5 mmol), 2-mercaptophenol (63.08mg, 0.5 mmol), K_2CO_3 (152.03 mg, 1.1 mmol), 5 mL acetone, r.t., 10h. The crude product was purified by silica gel filtration (eluent: ether/hexane 3-5%) to provide the desired compound as a yellow liquid (89.64 mg, 62% yield).

1H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, J = 4.8, 1.6, 1.0 Hz, 1H), 7.83 – 7.72 (m, 2H), 7.32 – 7.25 (m, 1H), 7.14 (dd, J = 7.6, 1.1 Hz, 1H), 7.04 (dtd, J = 17.2, 7.7, 1.3 Hz, 2H), 6.93 (td, J = 7.4, 1.4 Hz, 1H), 4.28 (tdd, J = 7.1, 5.7, 3.5 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 156.8, 154.7, 149.4, 137.1, 126.3, 124.4, 124.0, 123.1, 121.6, 120.7, 110.8, 98.4, 62.9, 13.9.

HR-MS (ESI $^+$) m/z (%): calcd. for $[M+H]^+$ = $[C_{15}H_{13}NO_3S]^{+}$: 288.0694; found: 288.0696.



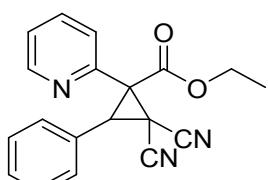
ethyl 6-bromo-2-(pyridin-2-yl)-2,3-dihydrobenzo[d]oxazole-2-carboxylate **4f**

The title compound was obtained according to the general procedure B using the following amounts and conditions: ethyl 2,2-dibromo-2-(pyridin-2-yl) acetate (162.5 mg, 0.5 mmol), 2-aminophenol (54.6 mg, 0.5 mmol), K_2CO_3 (152.03 mg, 1.1 mmol), 5 mL acetone, r.t, 10h. The crude product was purified by silica gel filtration (eluent: ether/hexane 5-10%) to provide the desired compound as a yellow liquid (109.69 mg, 62.3% yield).

¹H NMR (400 MHz, DMSO) δ 8.56 (d, *J*=4.5 Hz, 1H), 7.88 (t, *J*=7.6 Hz, 1H), 7.63 (d, *J*=7.8 Hz, 1H), 7.38 (dd, *J*=6.7, 5.6 Hz, 1H), 6.77 – 6.55 (m, 2H), 6.04 (s, 1H), 4.23 – 4.15 (m, 2H), 1.17 (t, *J*=7.1 Hz, 3H).

¹³C NMR (101 MHz, DMSO) δ 188.5, 168.7, 165.6, 150.5, 149.6, 142.6, 138.8, 129.9, 127.6, 125.4, 123.8, 92.5, 79.9, 62.4, 14.4.

HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₅H₁₄BrN₂O₃]⁺: 349.0182; found: 349.0183.



ethyl 2,2-dicyano-3-phenyl-1-(pyridin-2-yl)cyclopropane-1-carboxylate **4g**

The title compound was obtained according to the general procedure 3.9 to provide the desired compound as a colorless oil (30.4 mg, 48% yield).

¹H NMR (300 MHz, Chloroform-*d*) δ = 8.67 (ddd, *J*=4.9, 1.8, 1.0, 1H), 7.85 (td, *J*=7.7, 1.8, 1H), 7.56 (dt, *J*=7.9, 1.0, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.38 (m, 3H), 4.64 (s, 1H), 4.22 – 4.08 (m, 2H), 1.06 (t, *J*=7.1, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 167.8, 164.5, 150.4, 149.7, 137.5, 129.2, 129.1, 129.1, 129.0, 128.8, 124.7, 112.7, 63.3, 49.7, 39.7, 29.7, 13.5.

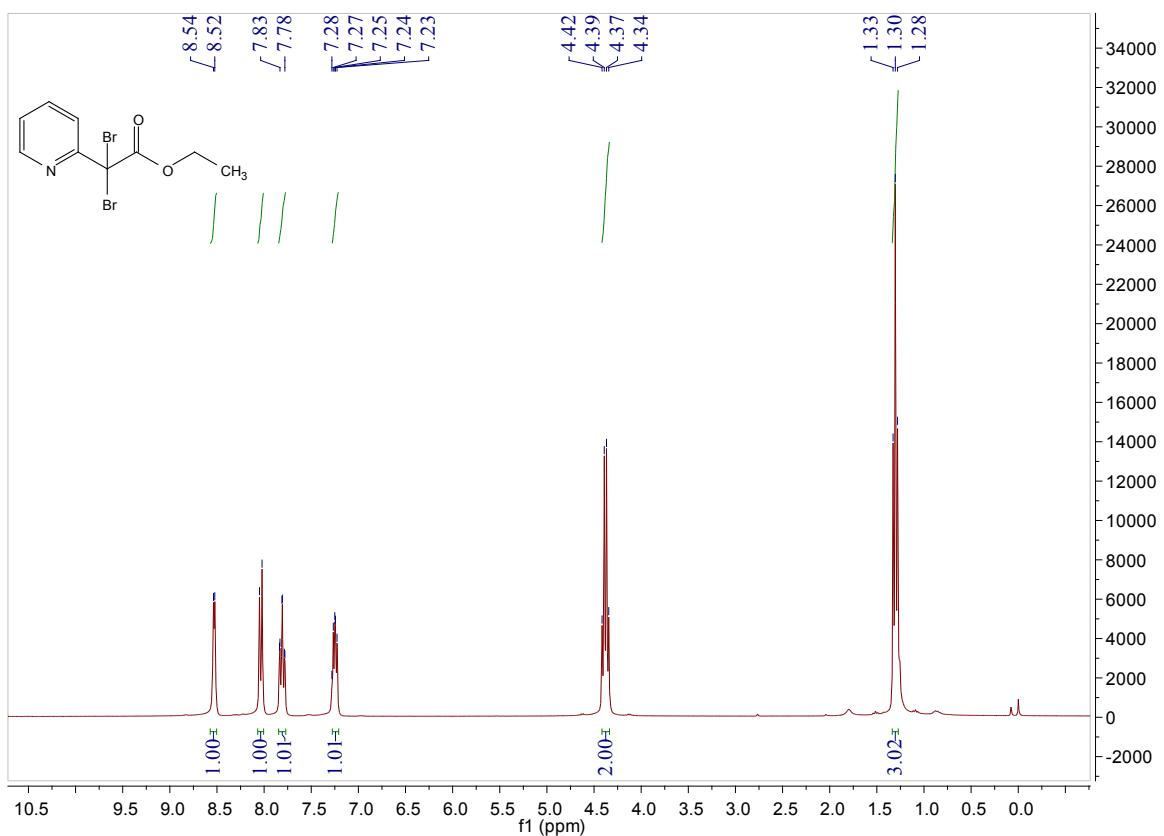
HR-MS (ESI⁺) m/z (%): calcd. for [M+H]⁺ = [C₁₉H₁₆N₃O₂]⁺: 318.1237; found: 318.1244.

References

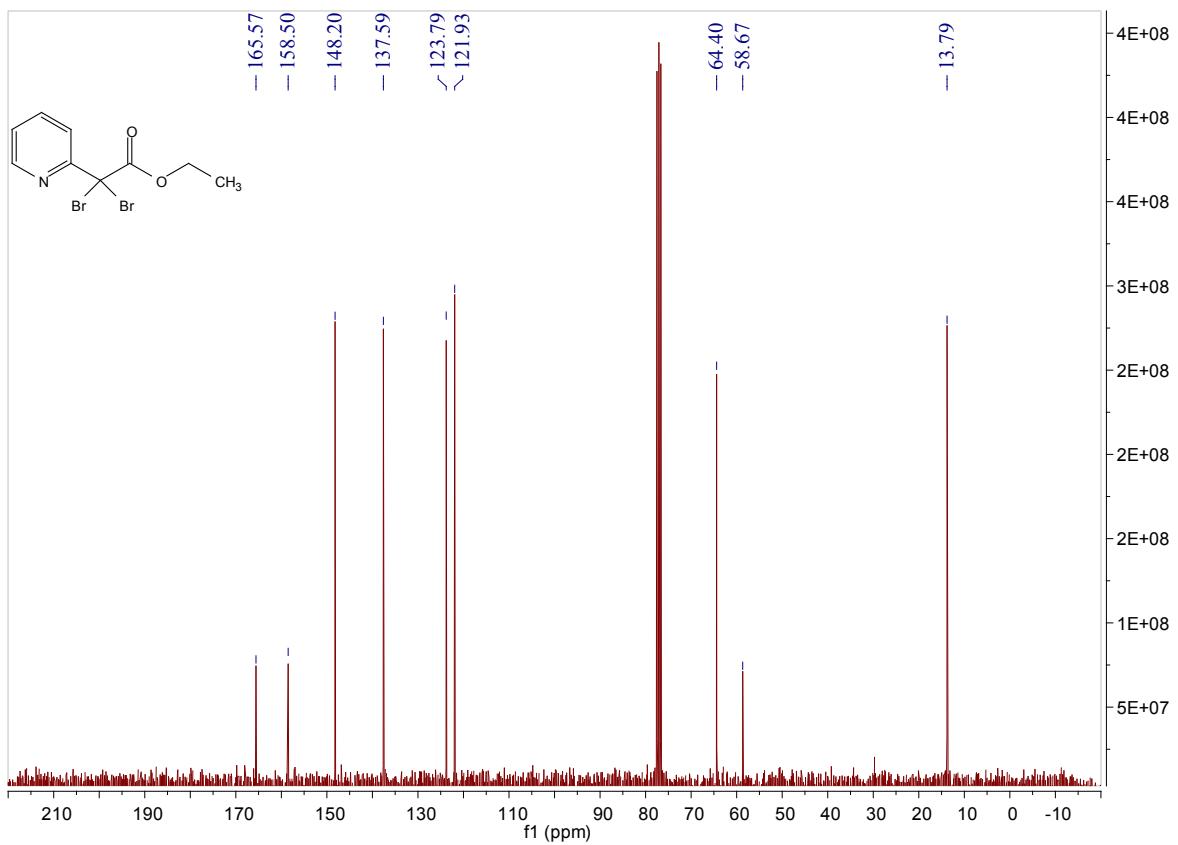
1. Neises, B.; Steglich, W. *Angew. Chem., Int. Ed.* **1978**, *17*, 522-526.
2. Shetty, P.; Praveen, B. M.; Raghavendra, M.; Manjunath, K.; Cheruku, S. *Molecular Diver.* **2016**, *20*(2), 391-398.
3. Cui, X.-M.; Guan, Y.-H.; Li, N.; Lv, H.; Fu, L.-A.; Guo, K.; Fan, X. *Tetrahedron Lett.*, **2014**, *55*(1), 90-93.
4. Zou, L.-H.; Li, Y.-C.; Li, .-G.; Zhou, J.; Wu, Z.-M. *Eur. J. Org. Chem.* **2018**(41), 5639-5643.
5. Wiest, J. M.; Conner, M. L.; Brown, M. K. *Angew. Chem., Int. Ed.*, **2018**, *57*(17), 4647-4651.

NMR spectra

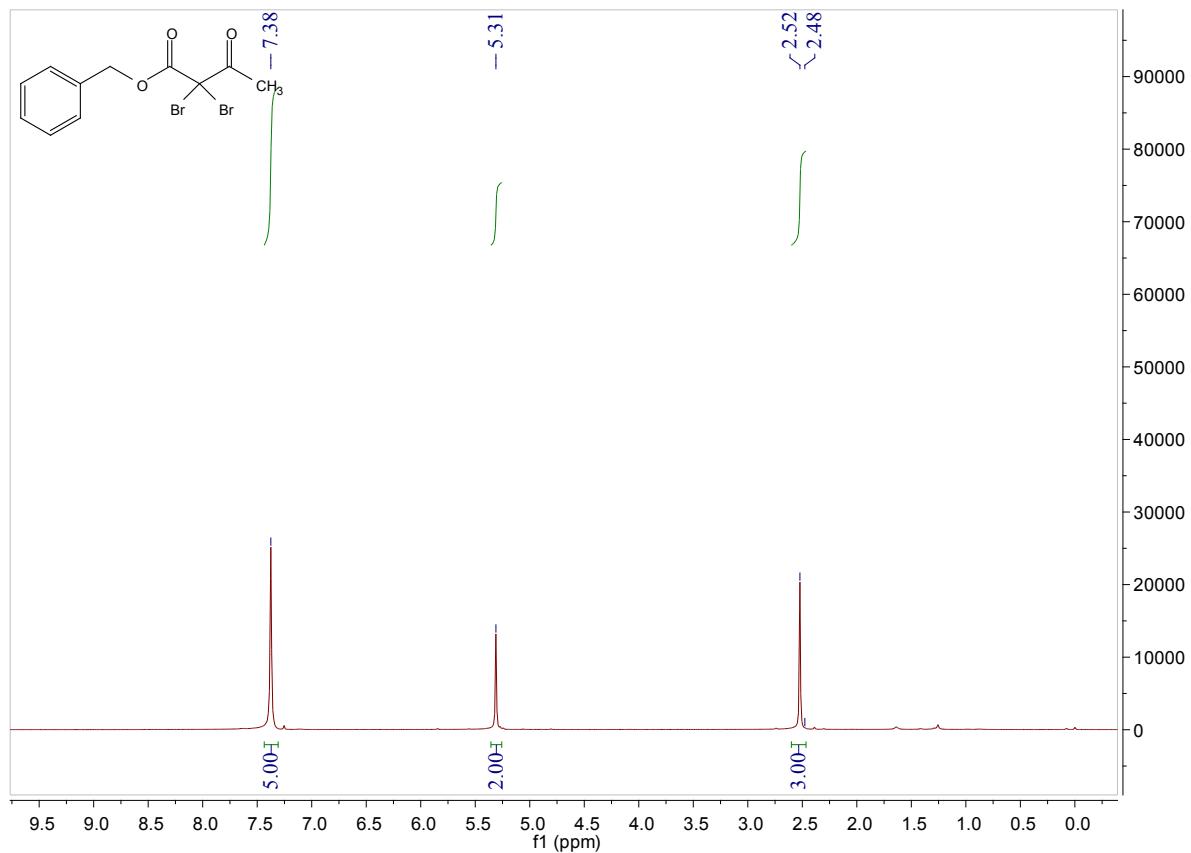
¹H NMR of **2a**



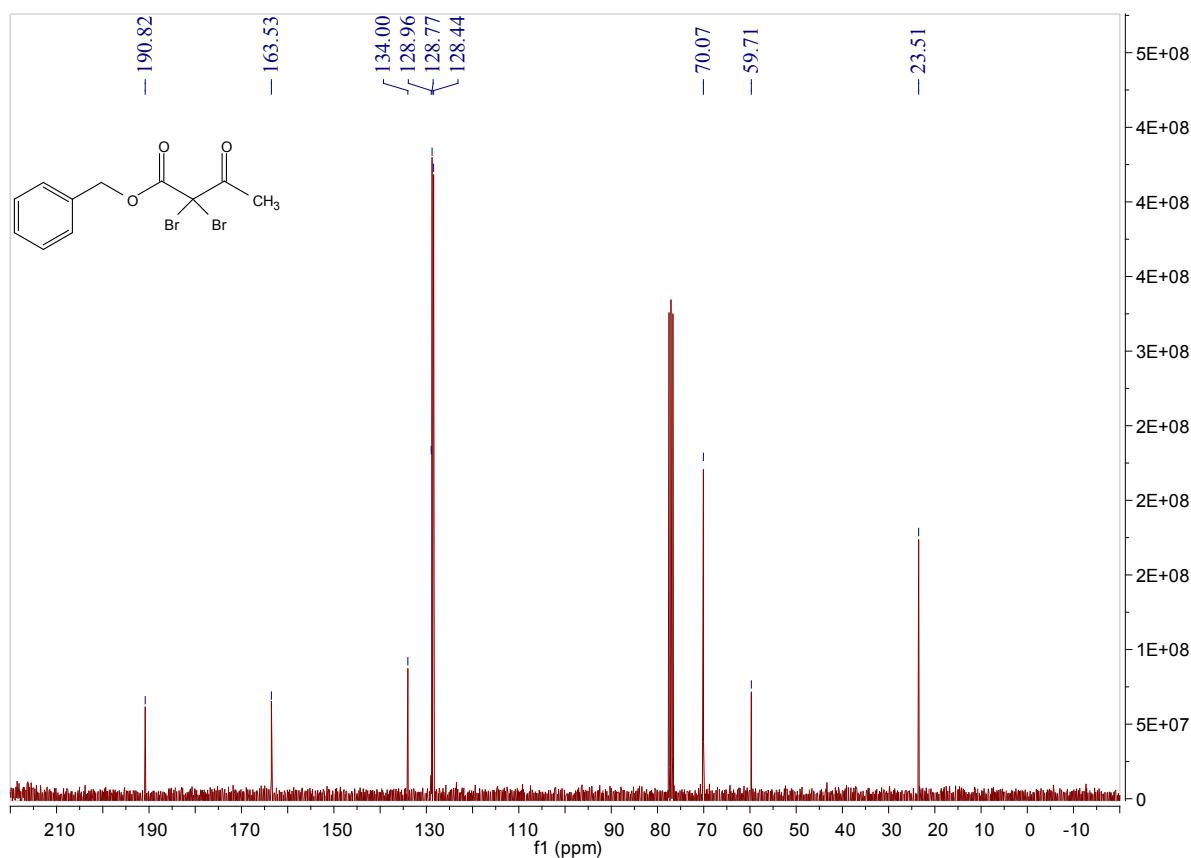
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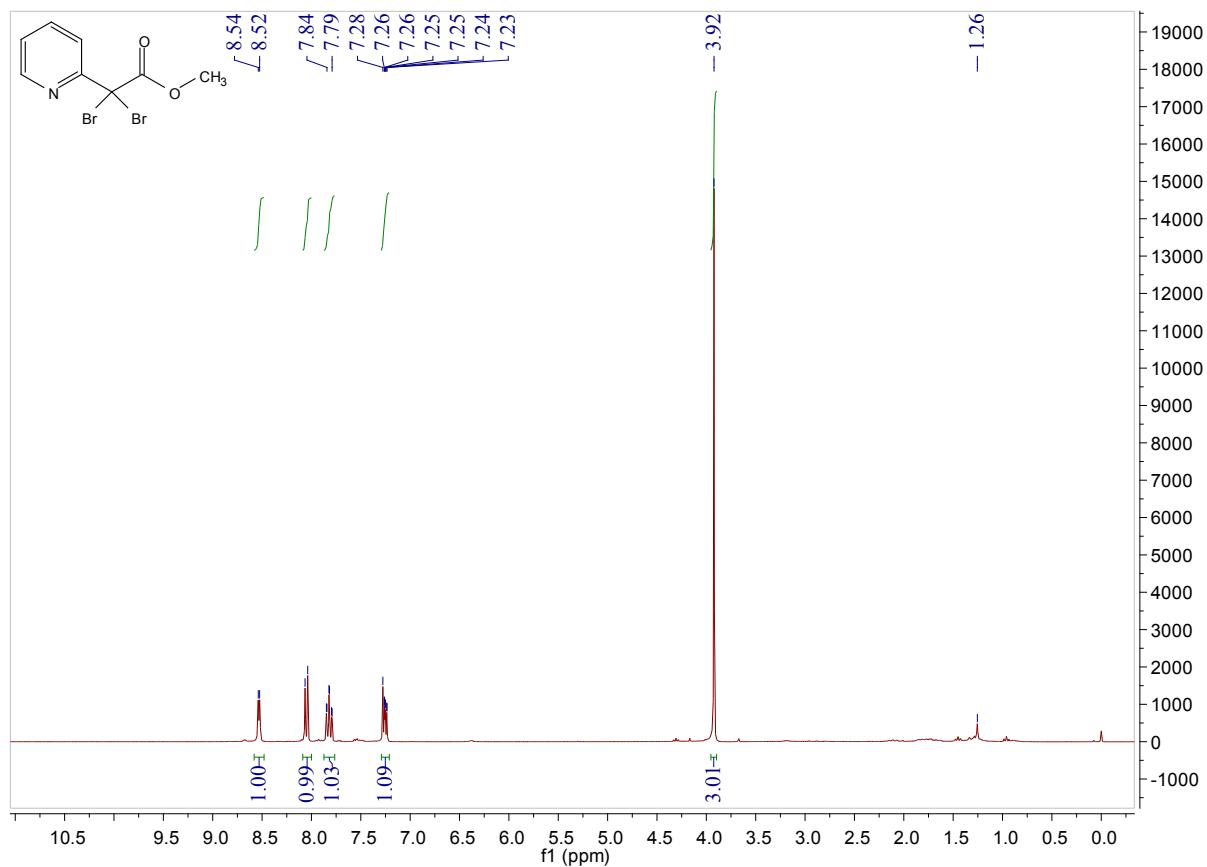
¹H NMR of **2b**



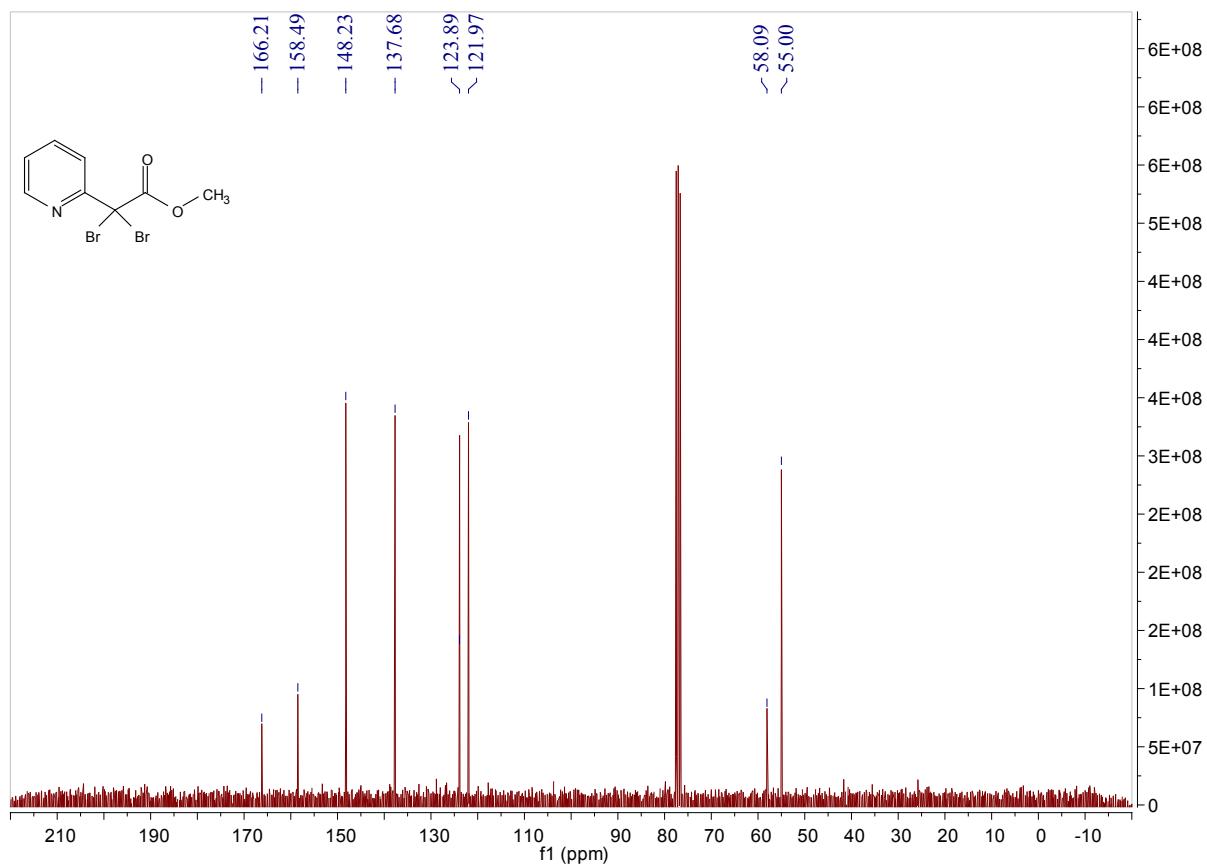
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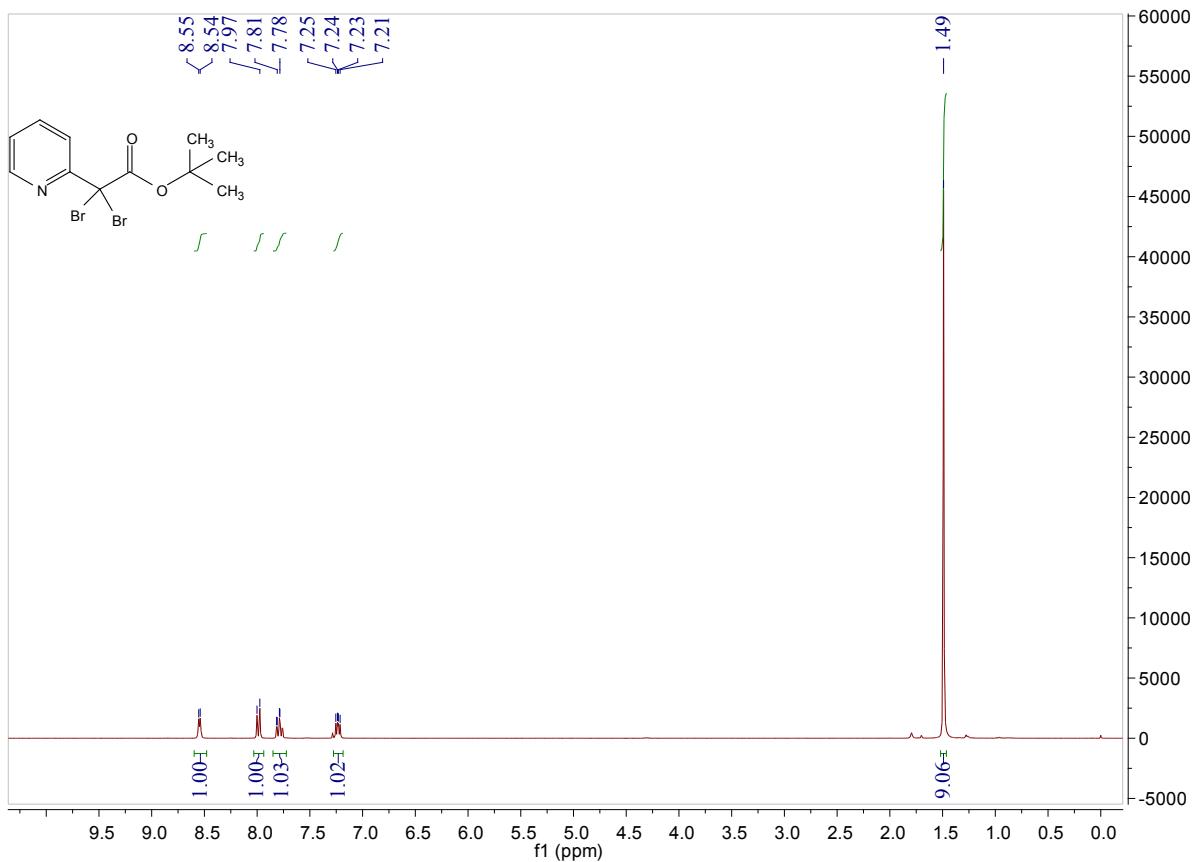
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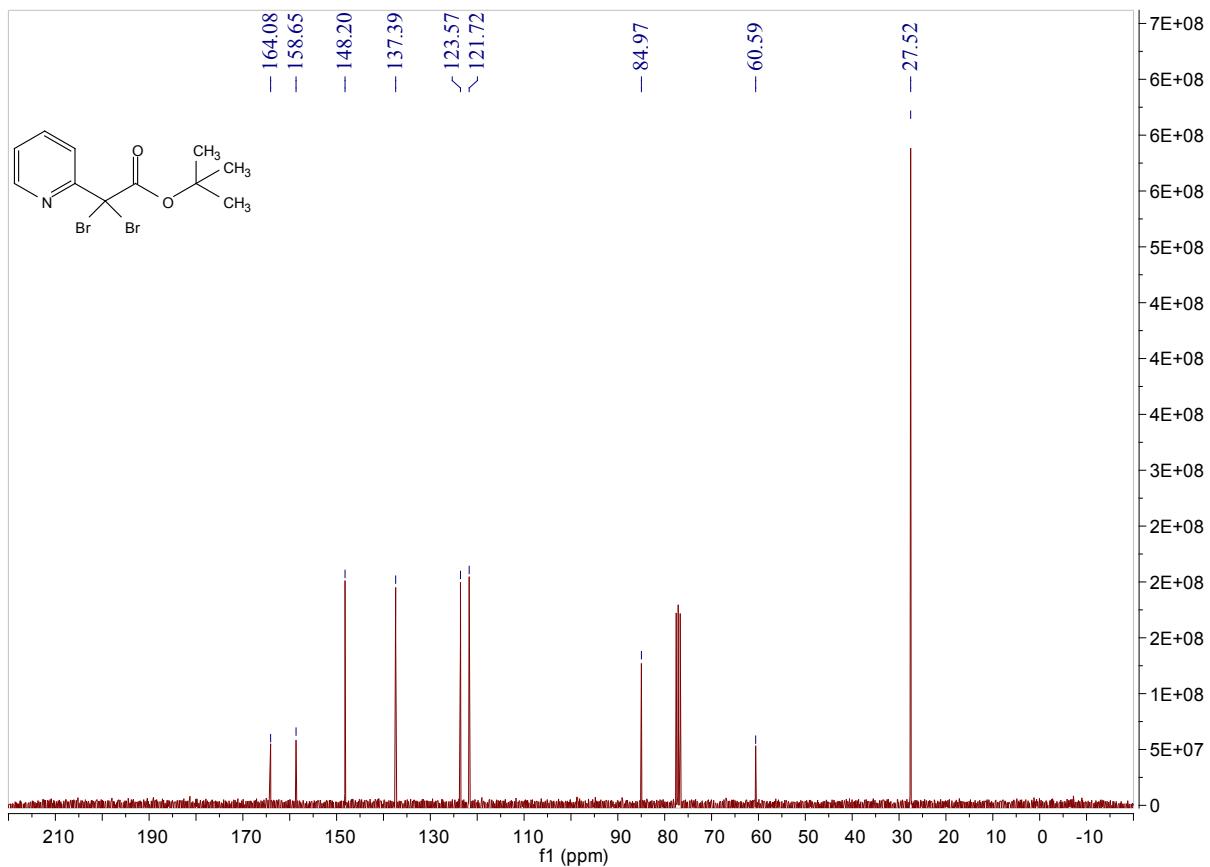
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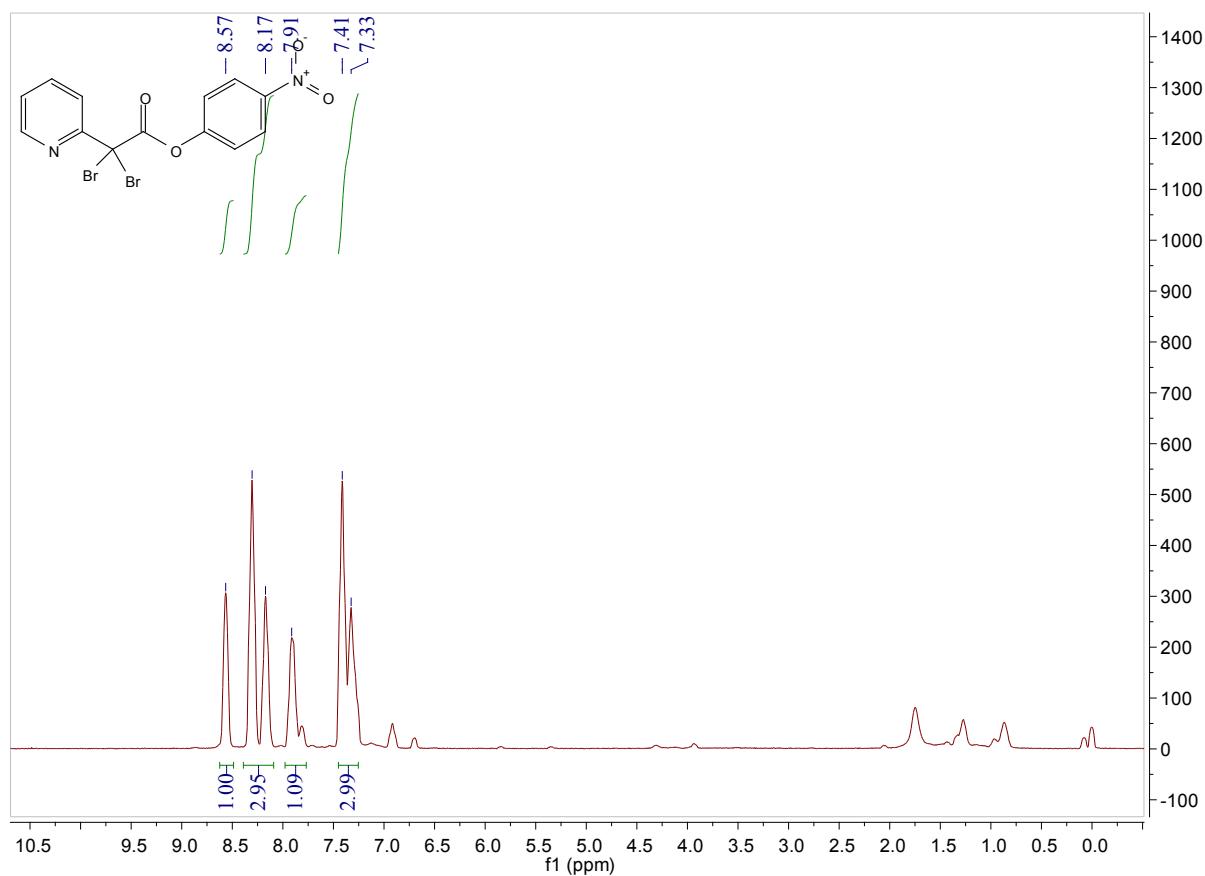
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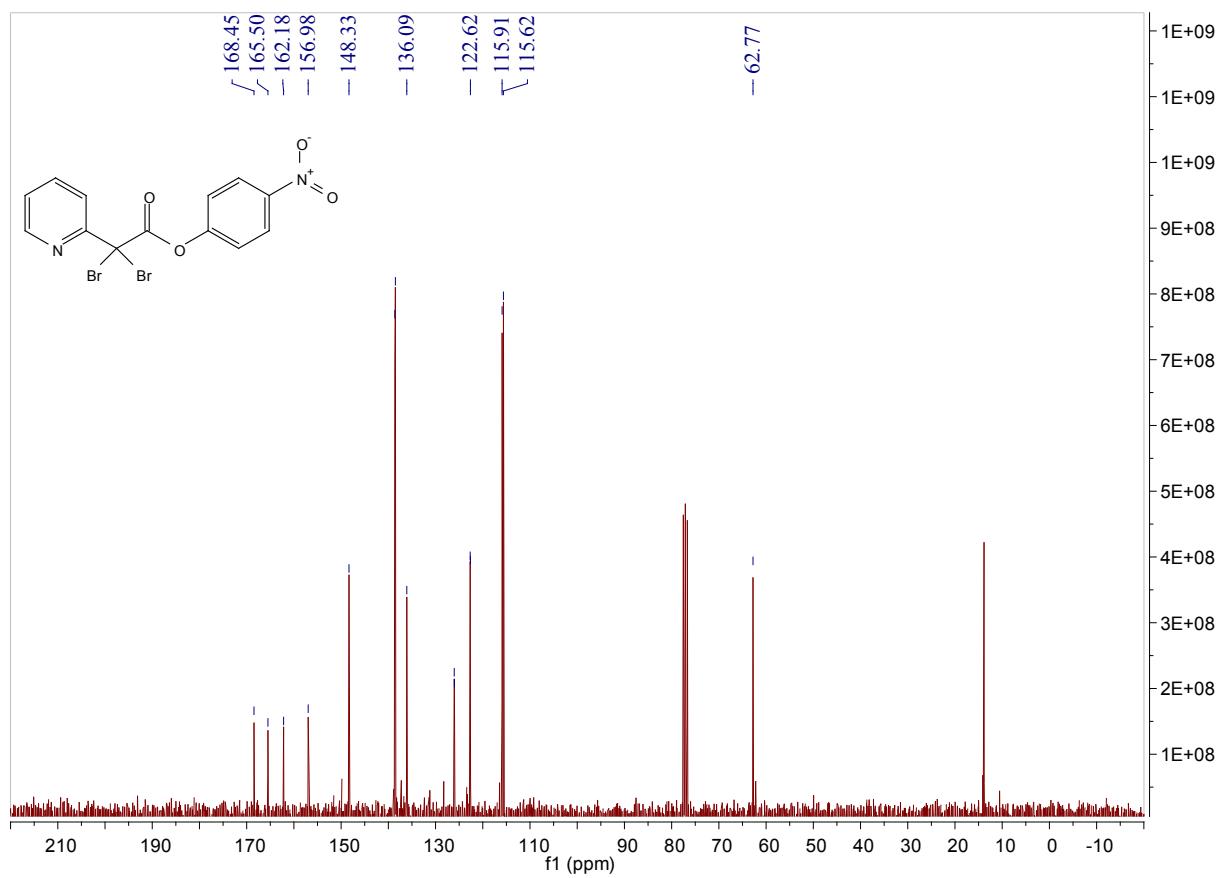
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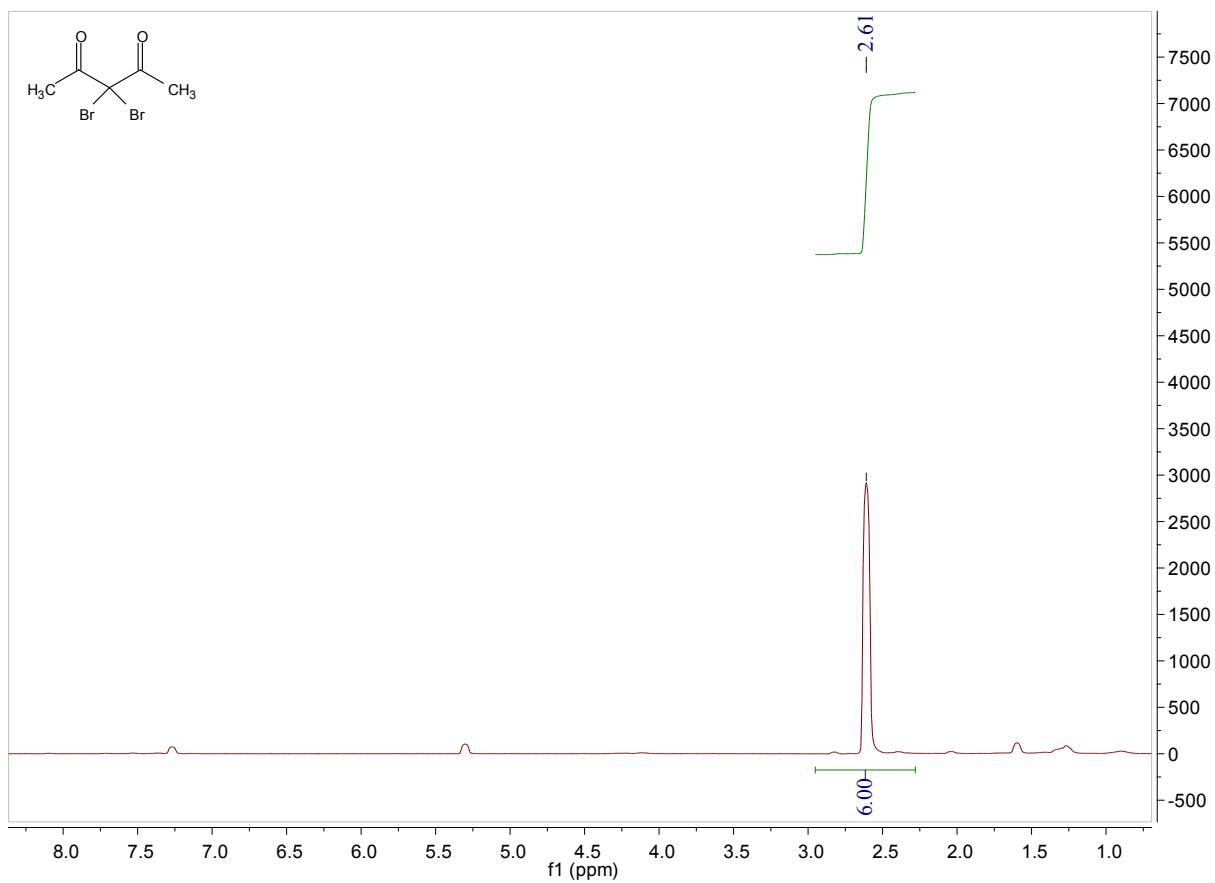
¹H NMR of **2e**



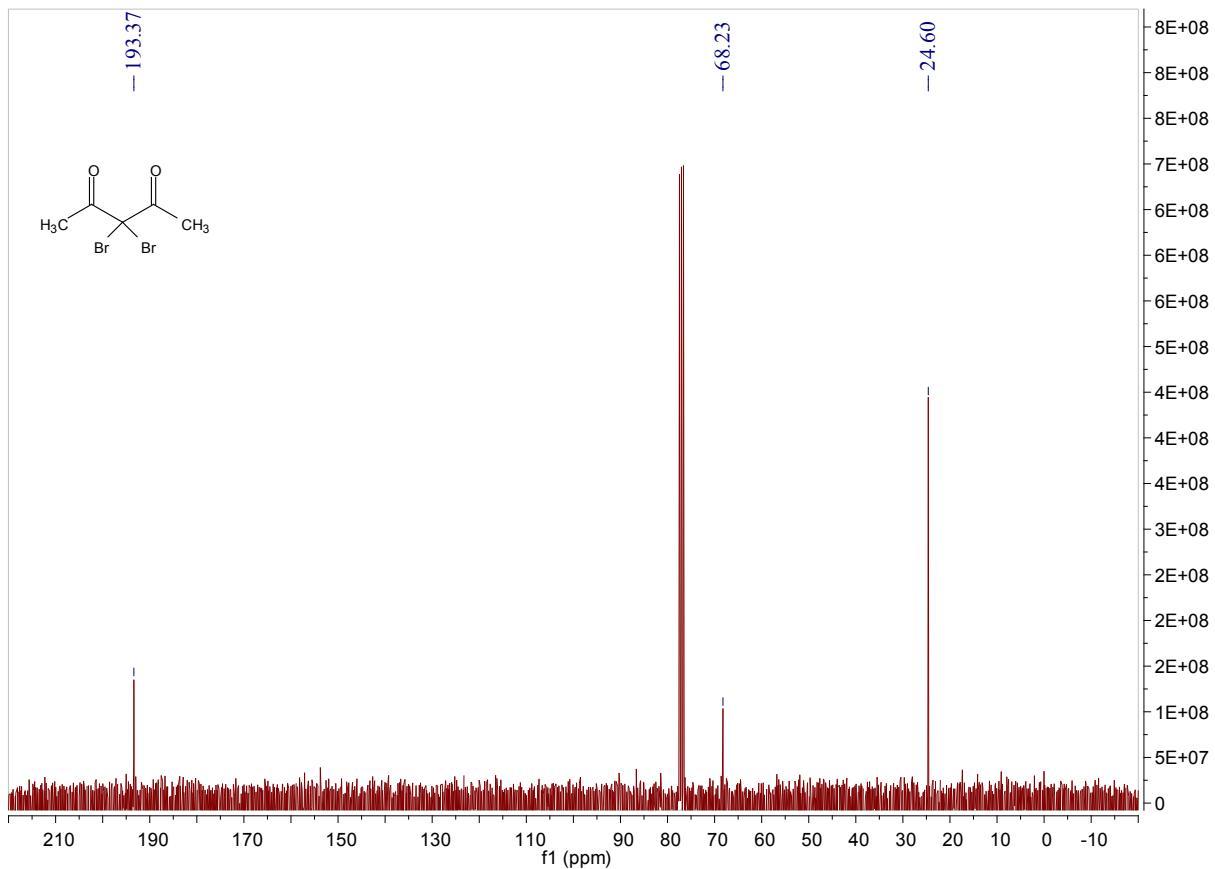
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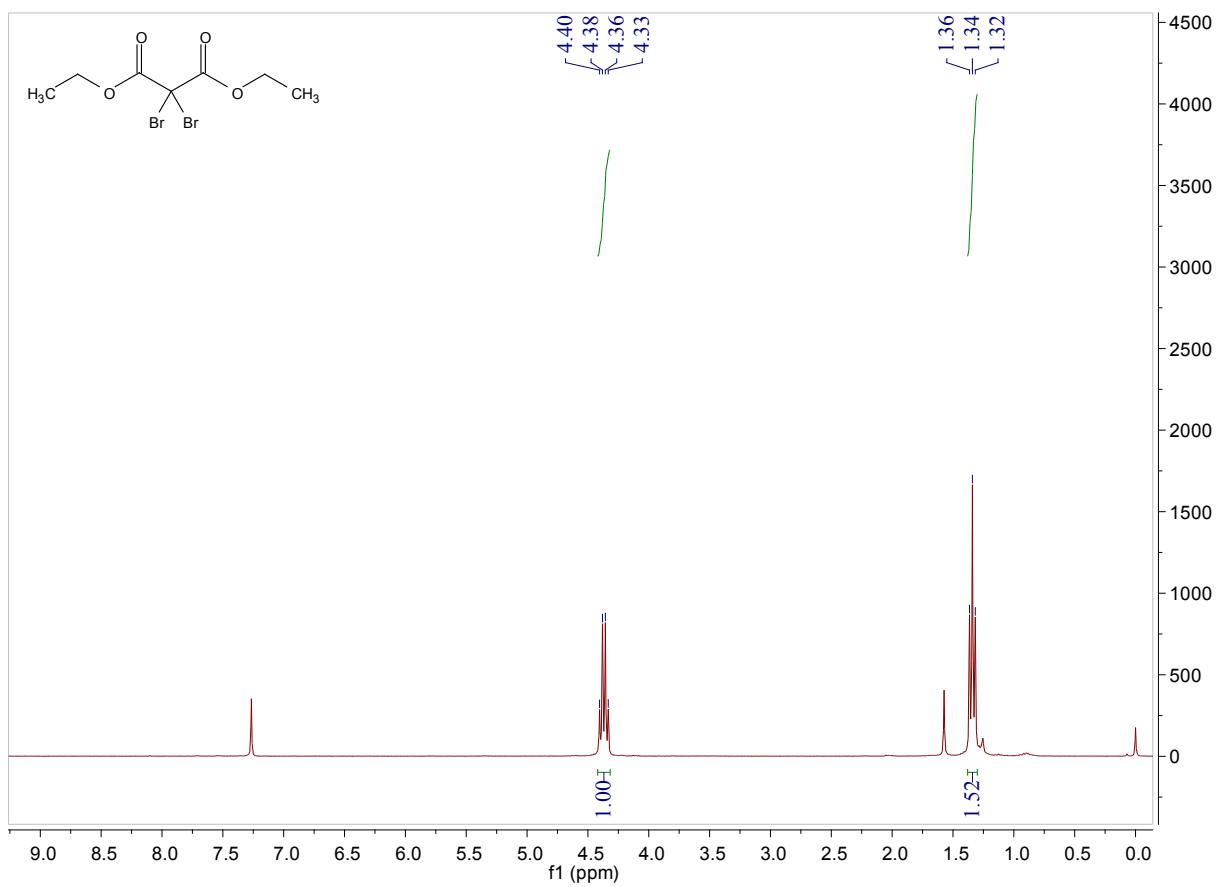
¹H NMR of **2f**



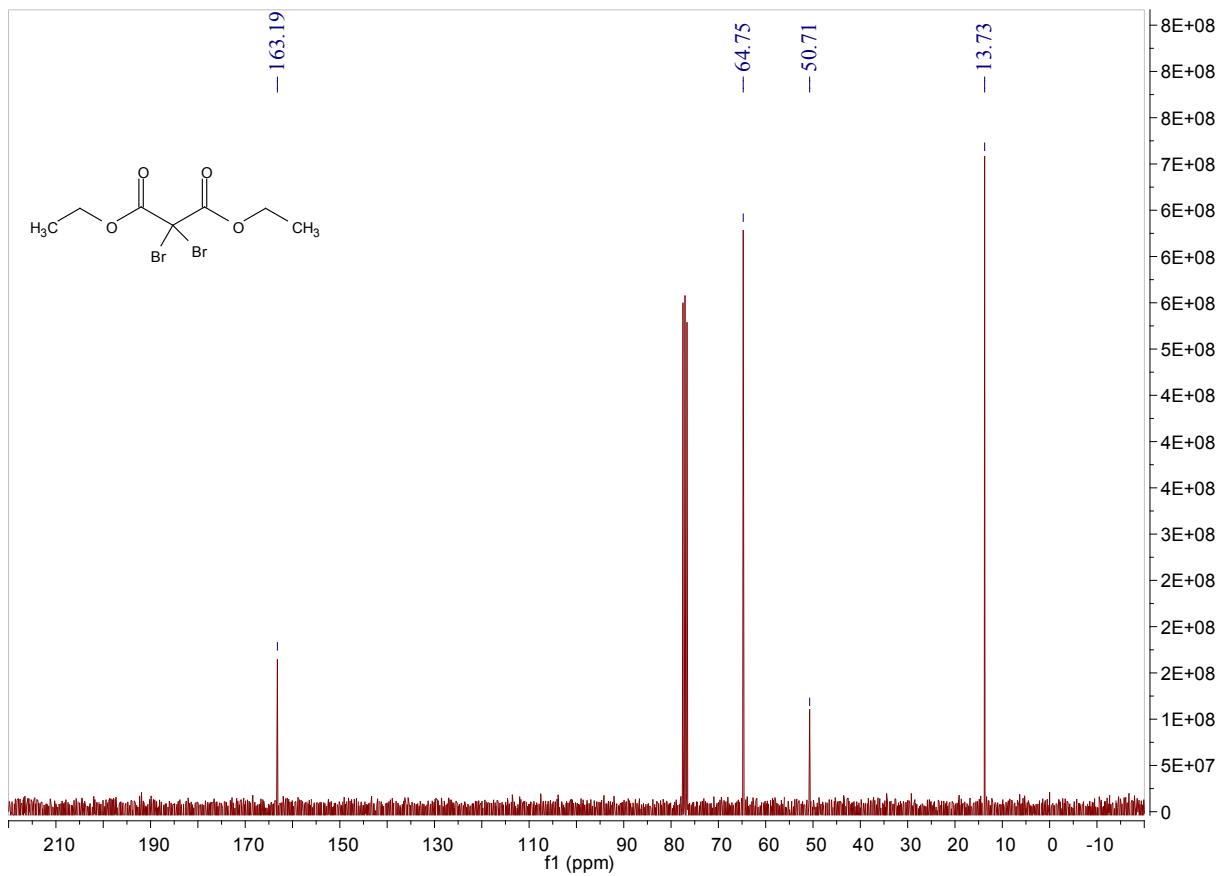
¹³C NMR of **2f**



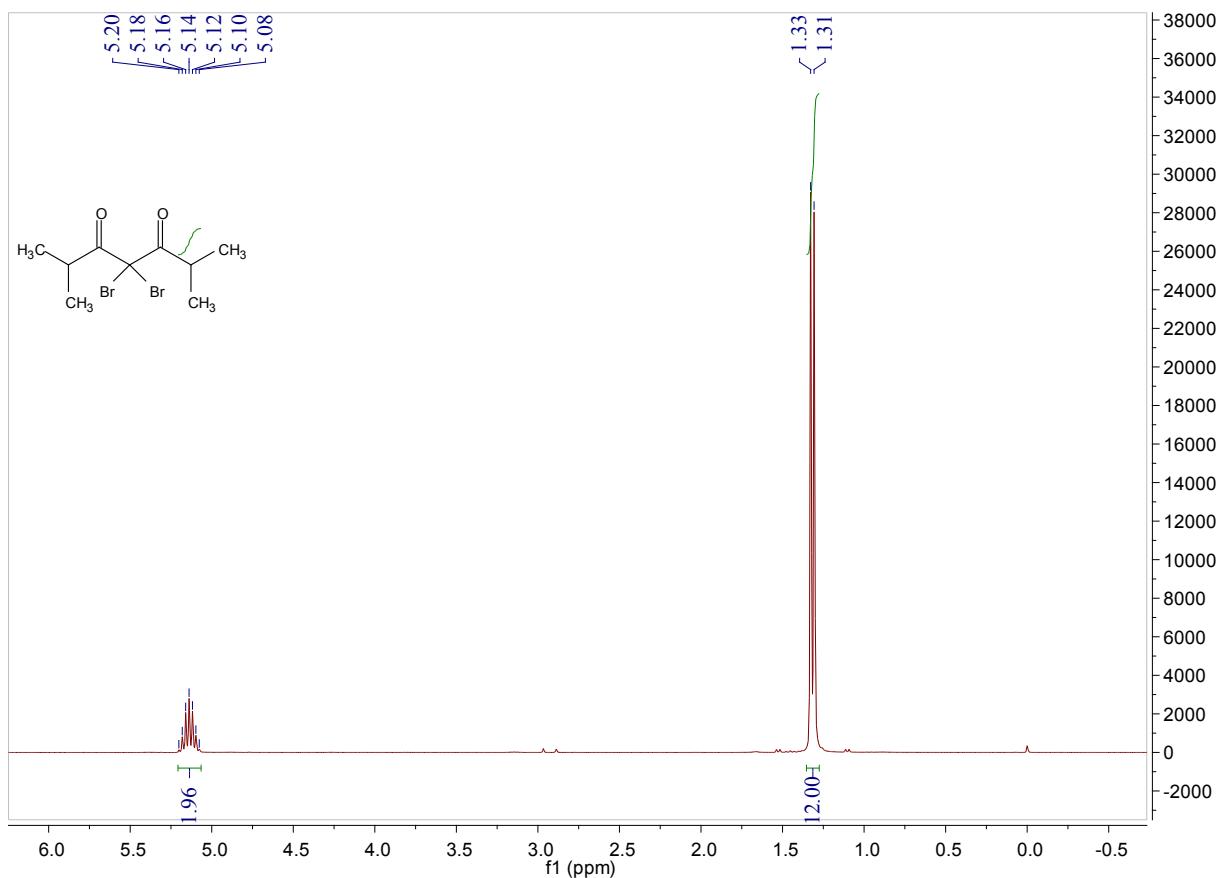
¹H NMR of **2g**



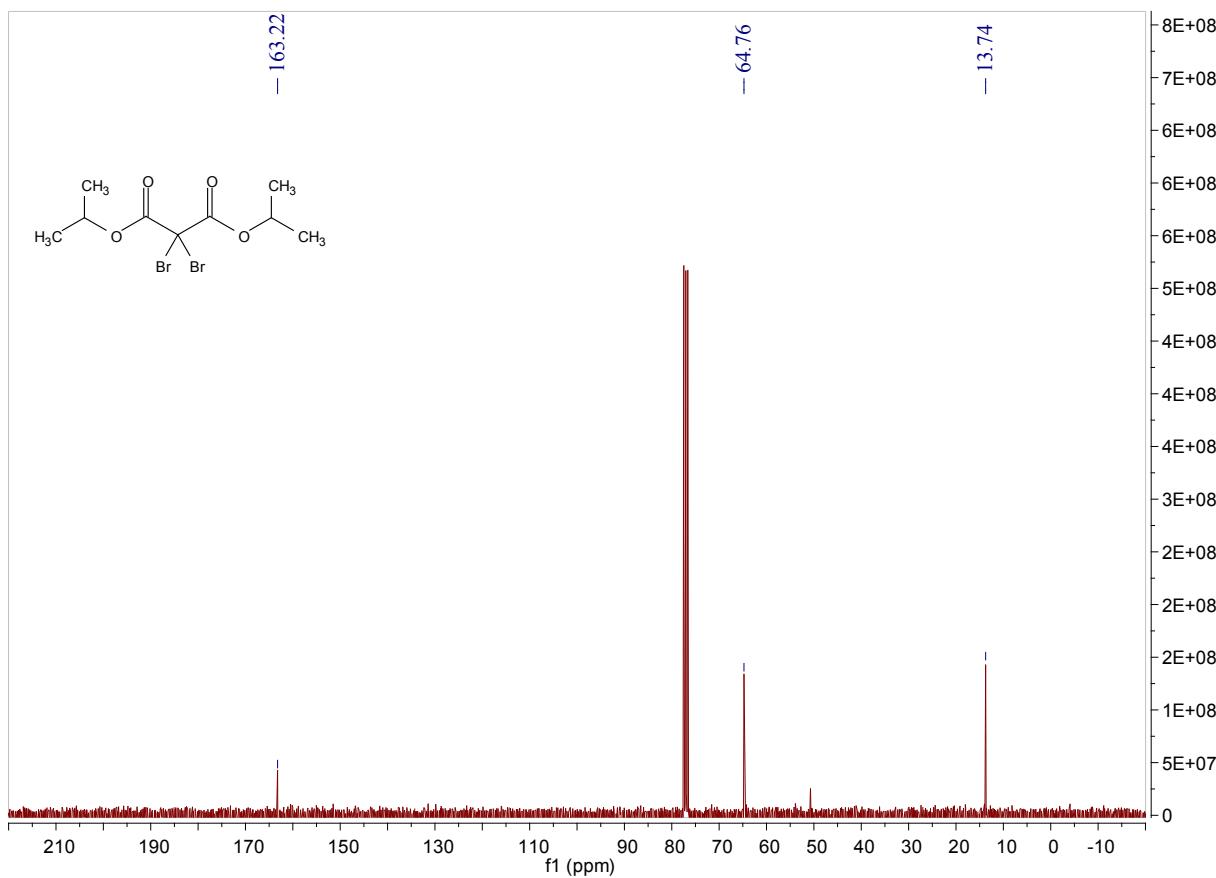
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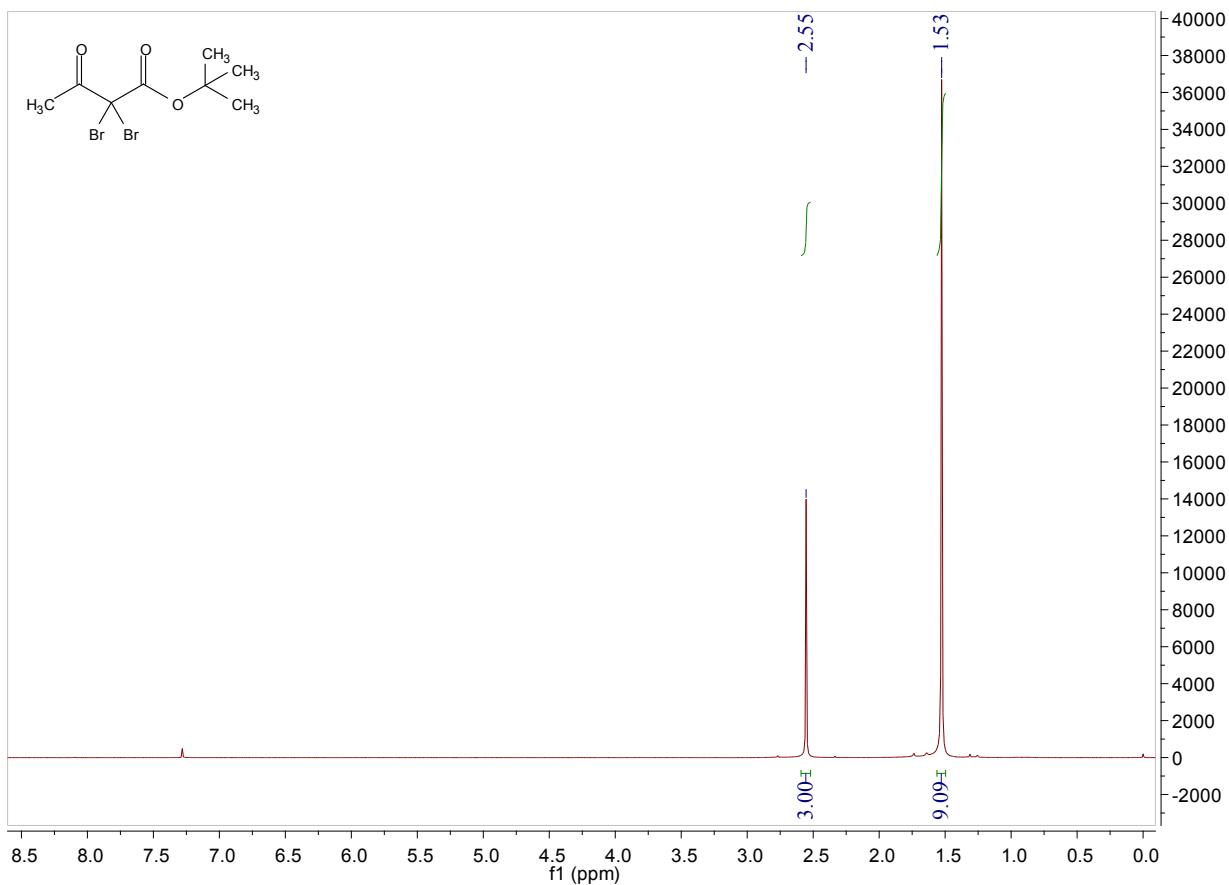
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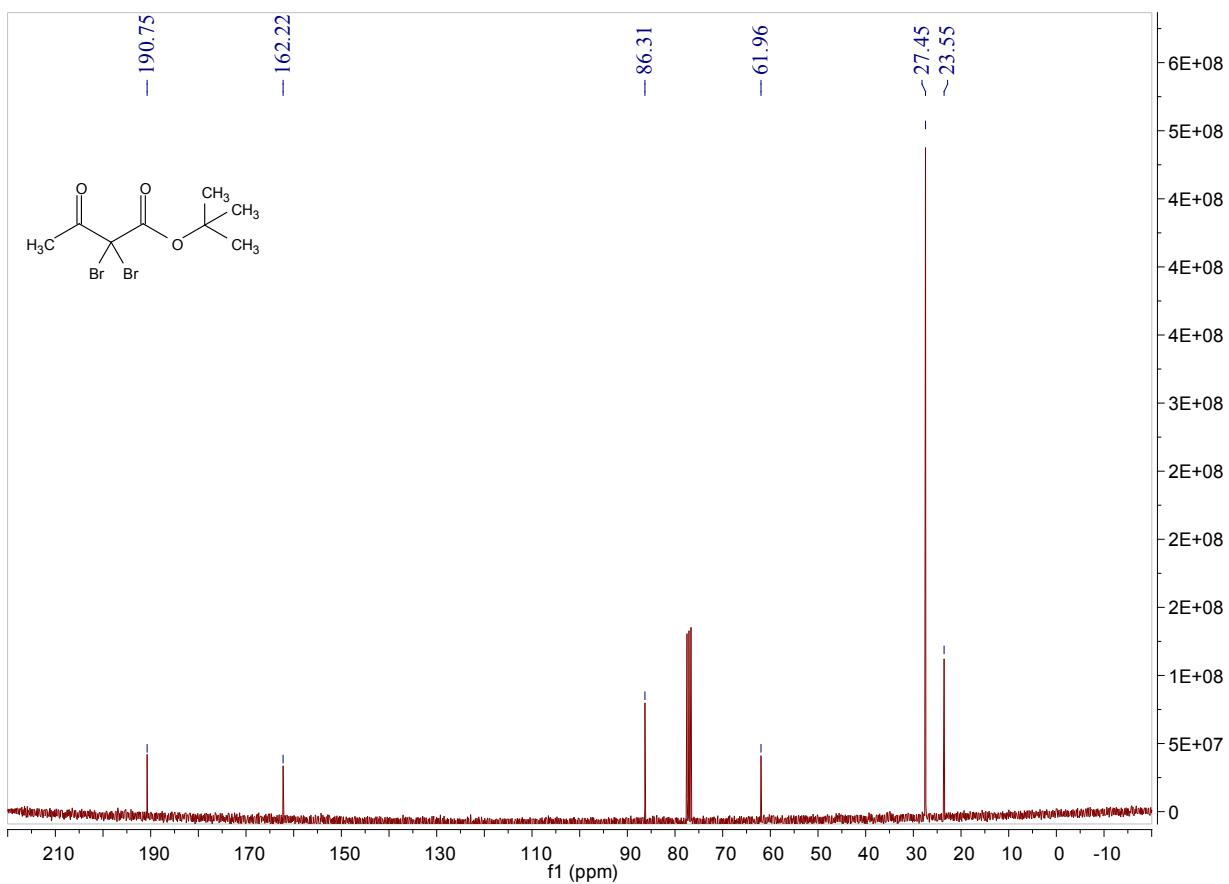
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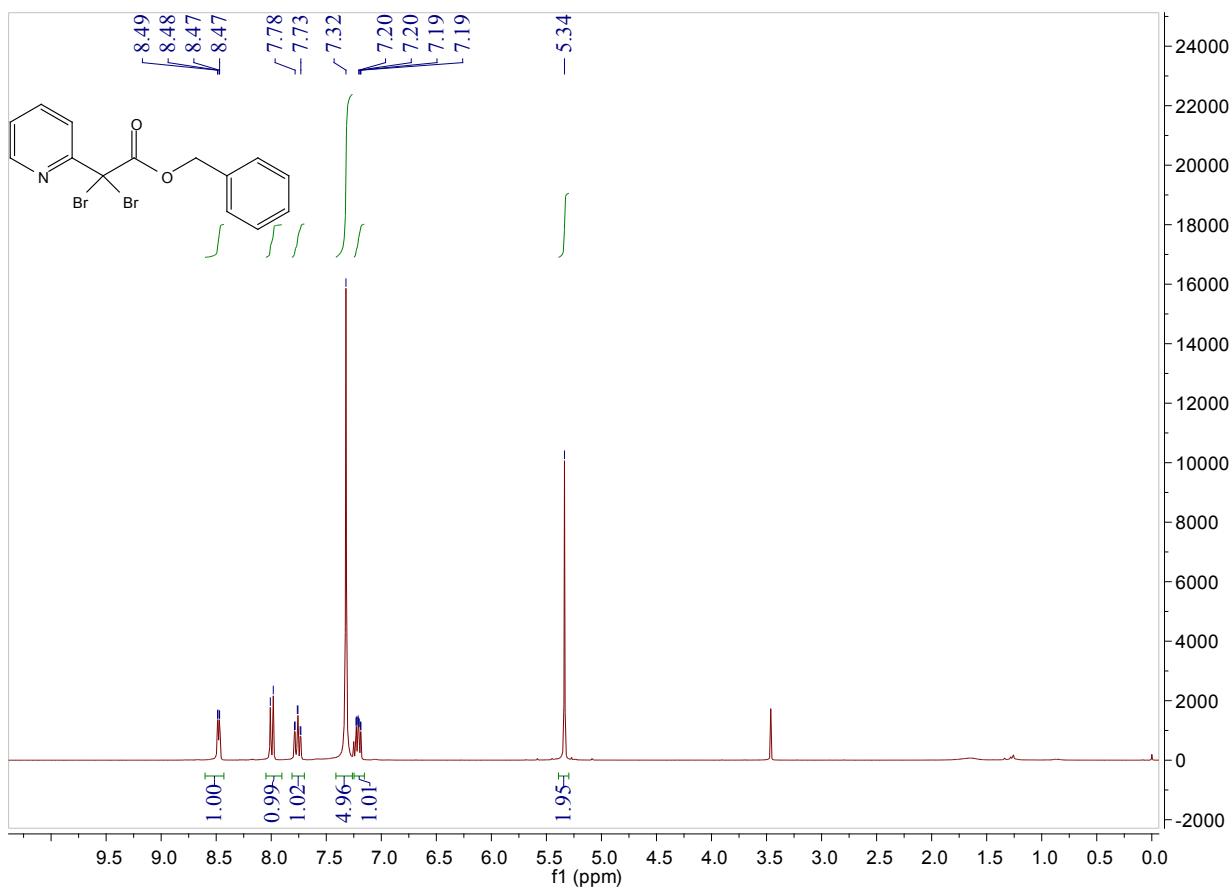
¹H NMR of **2i**



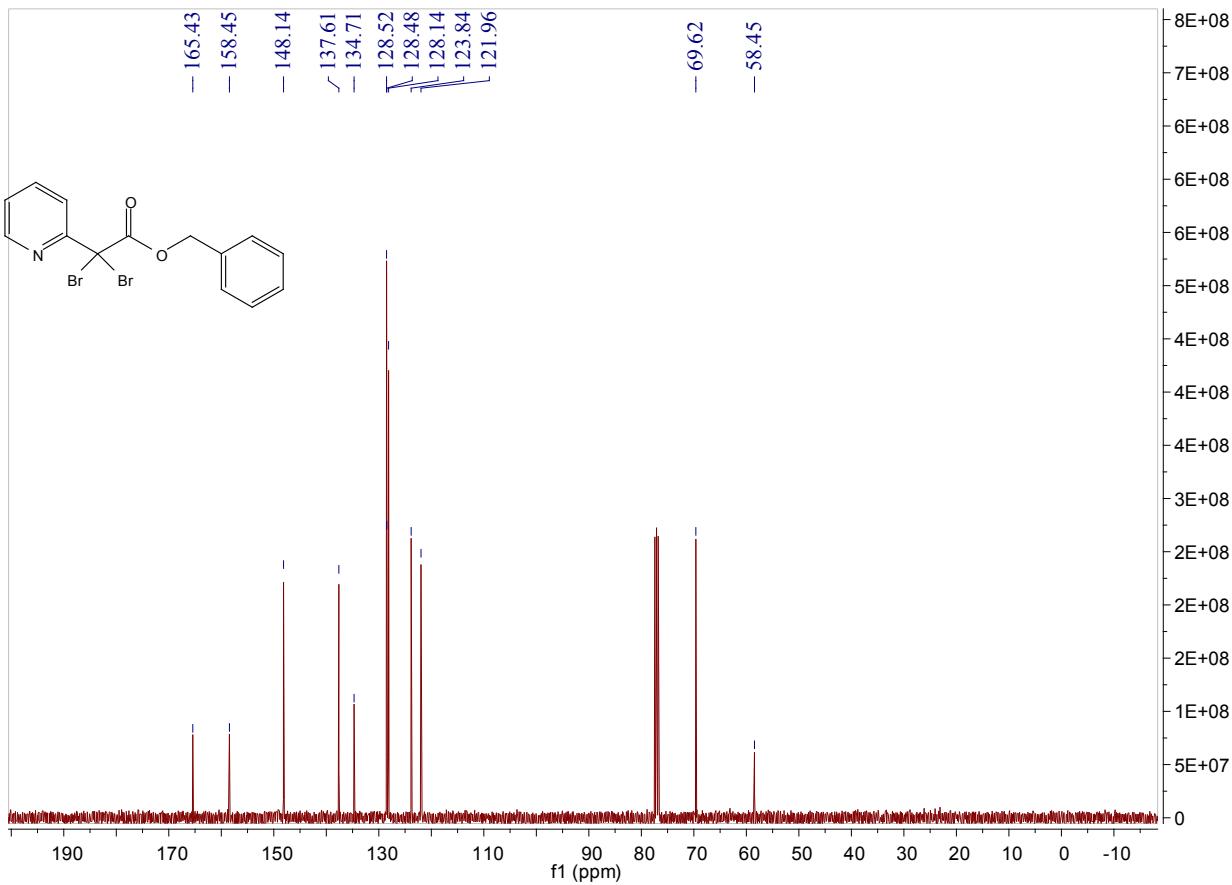
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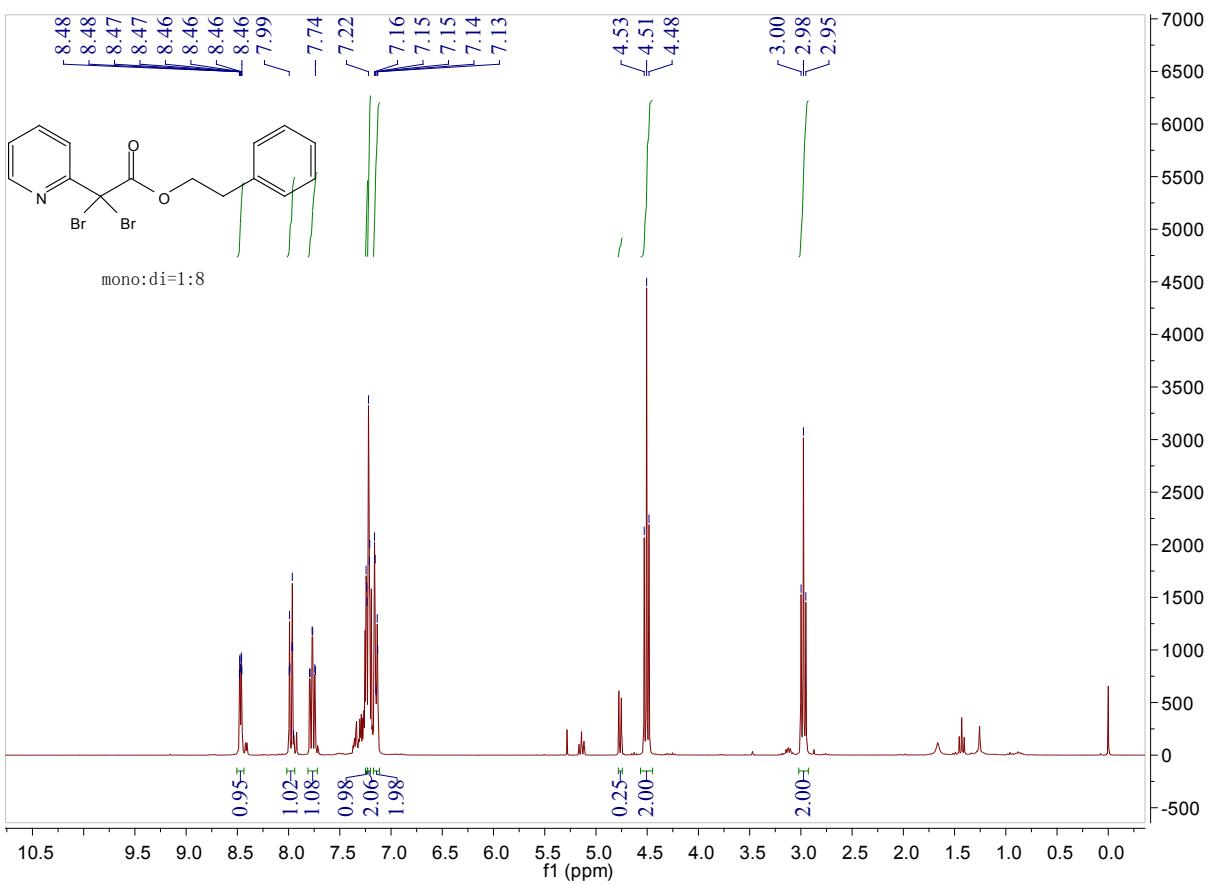
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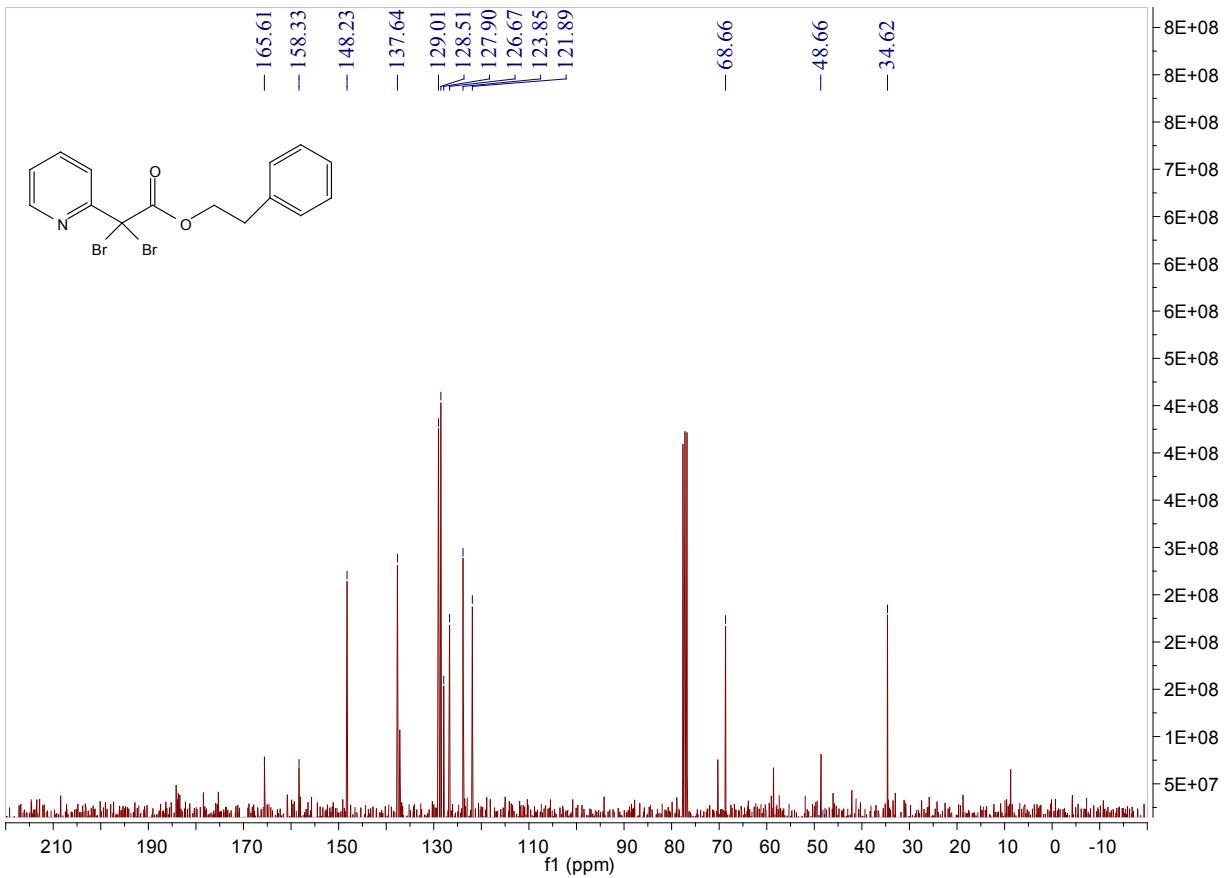
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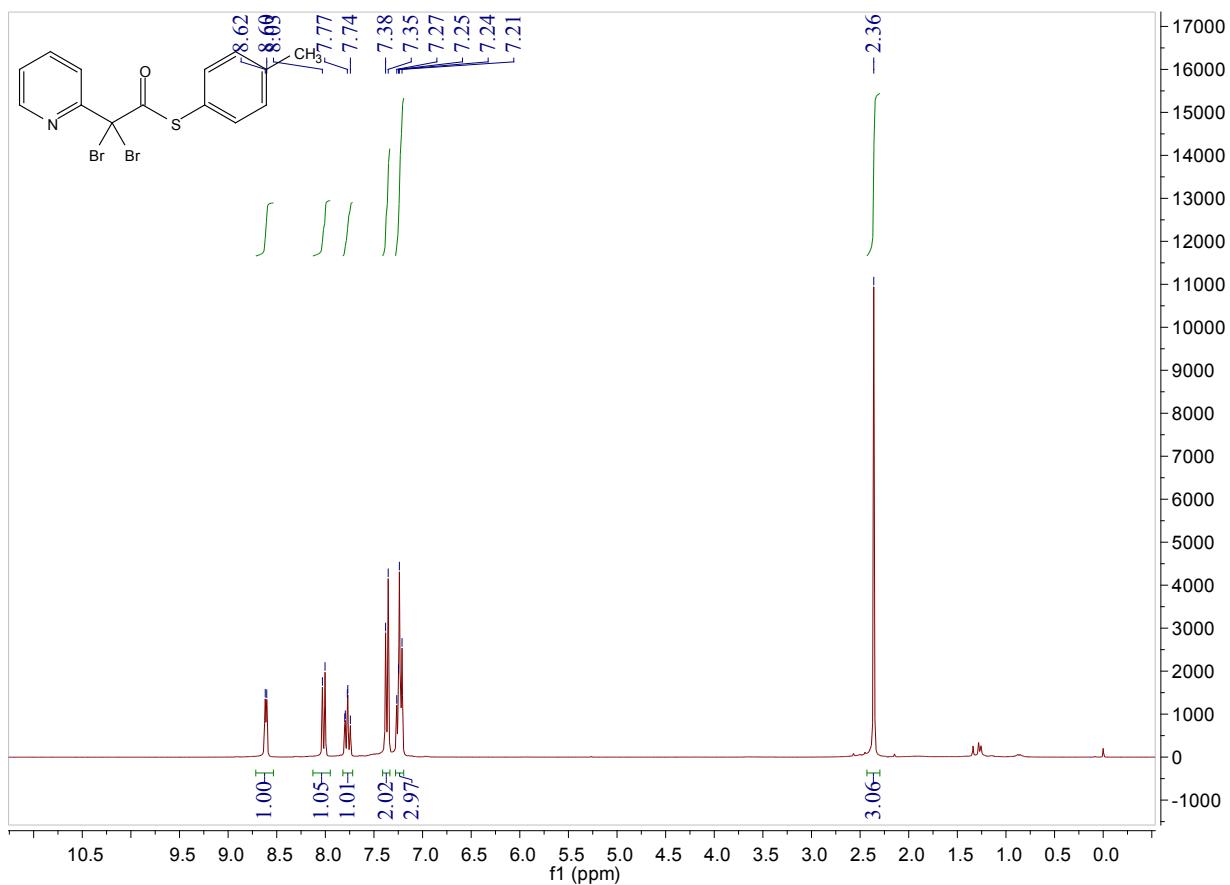
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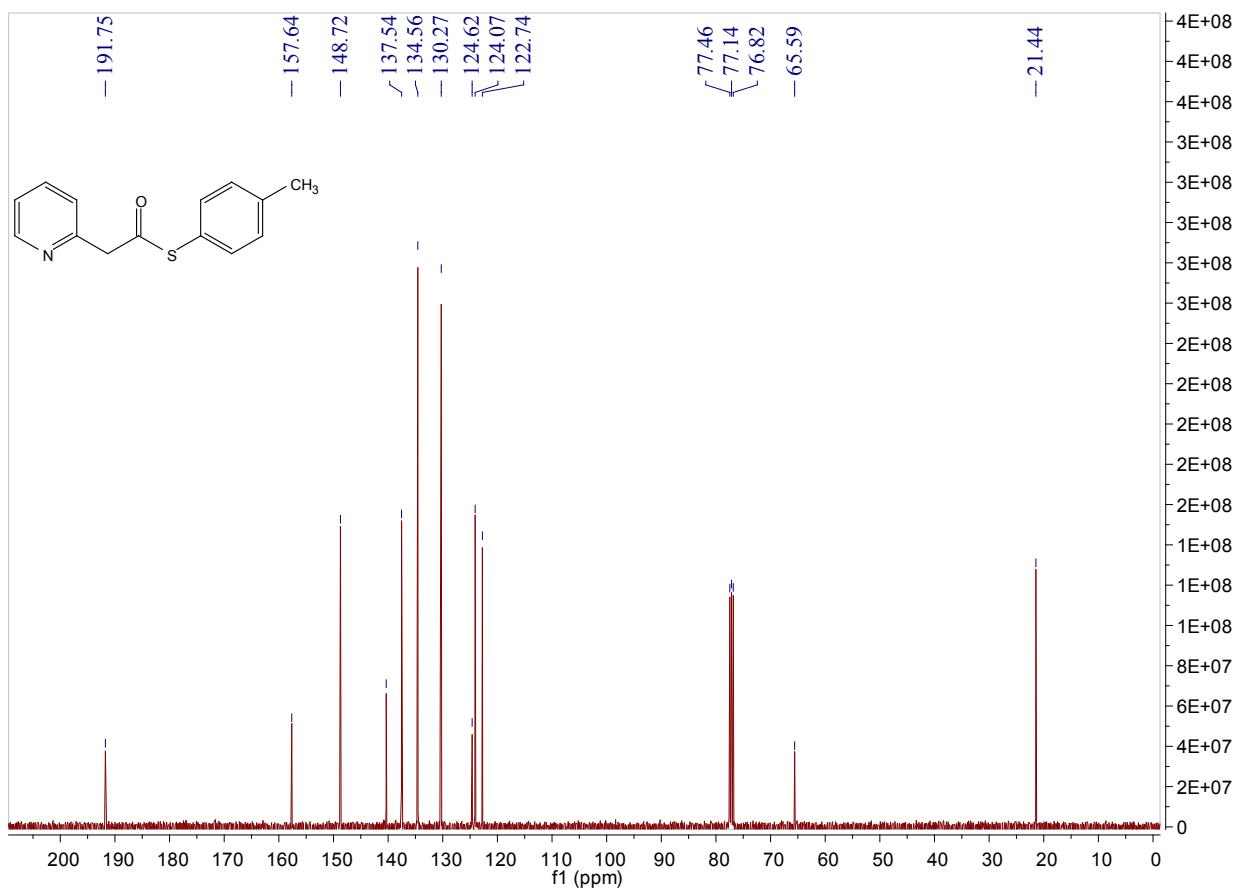
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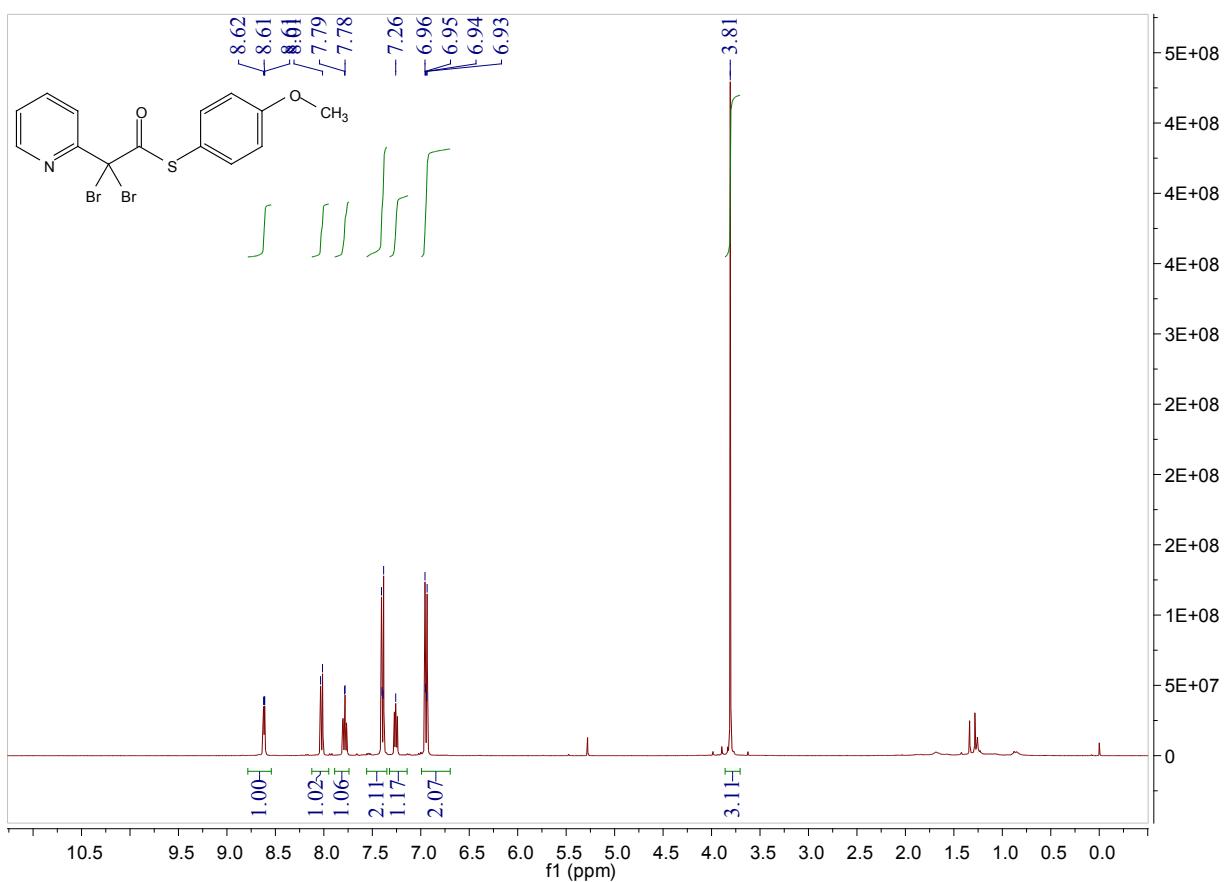
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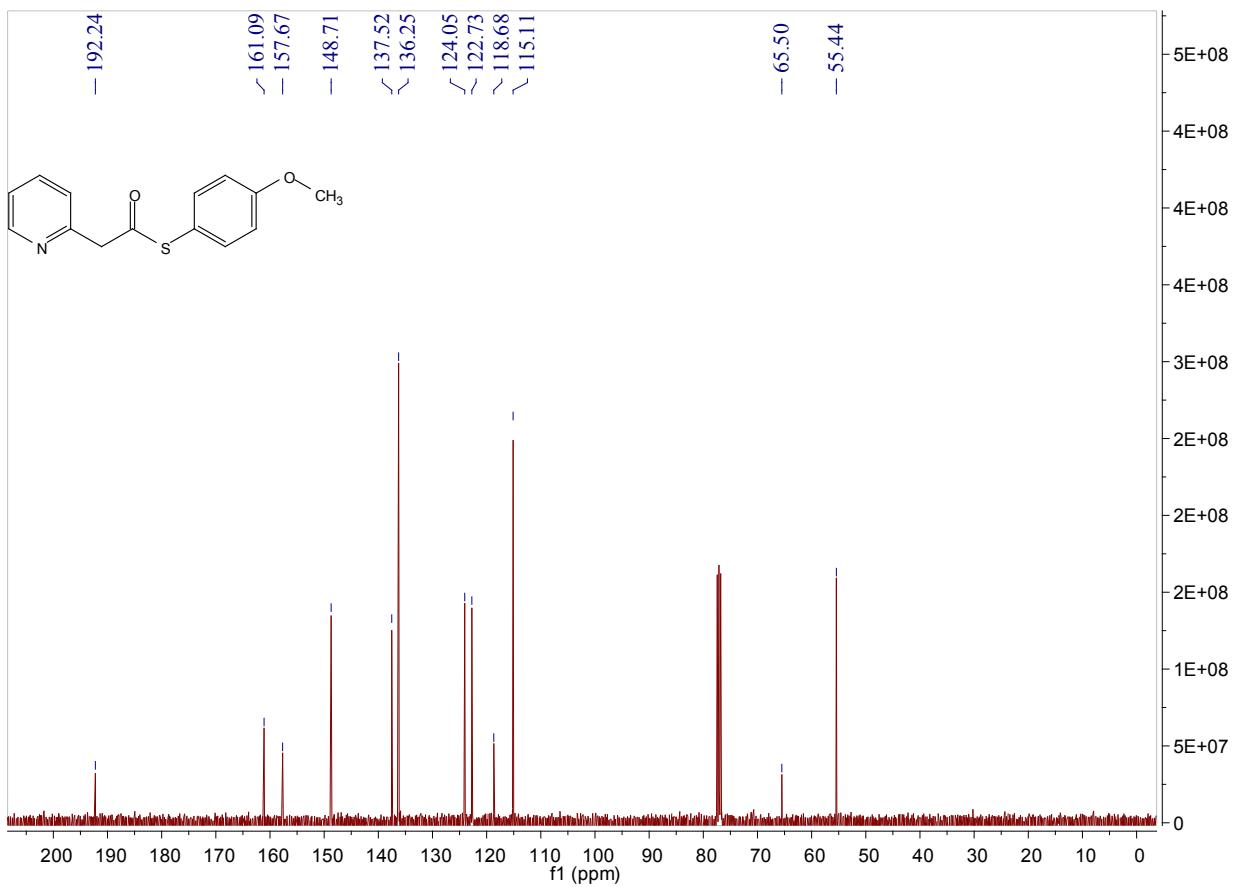
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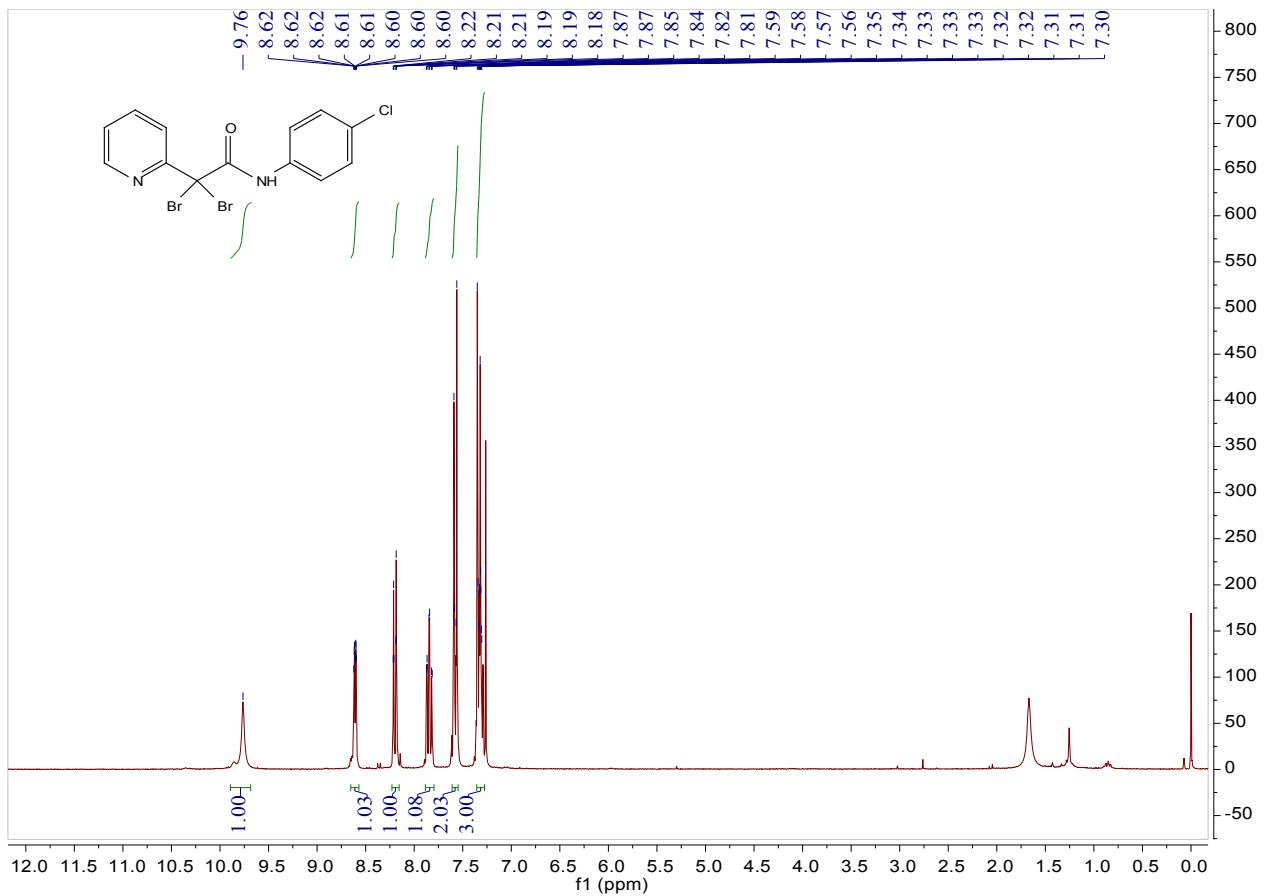
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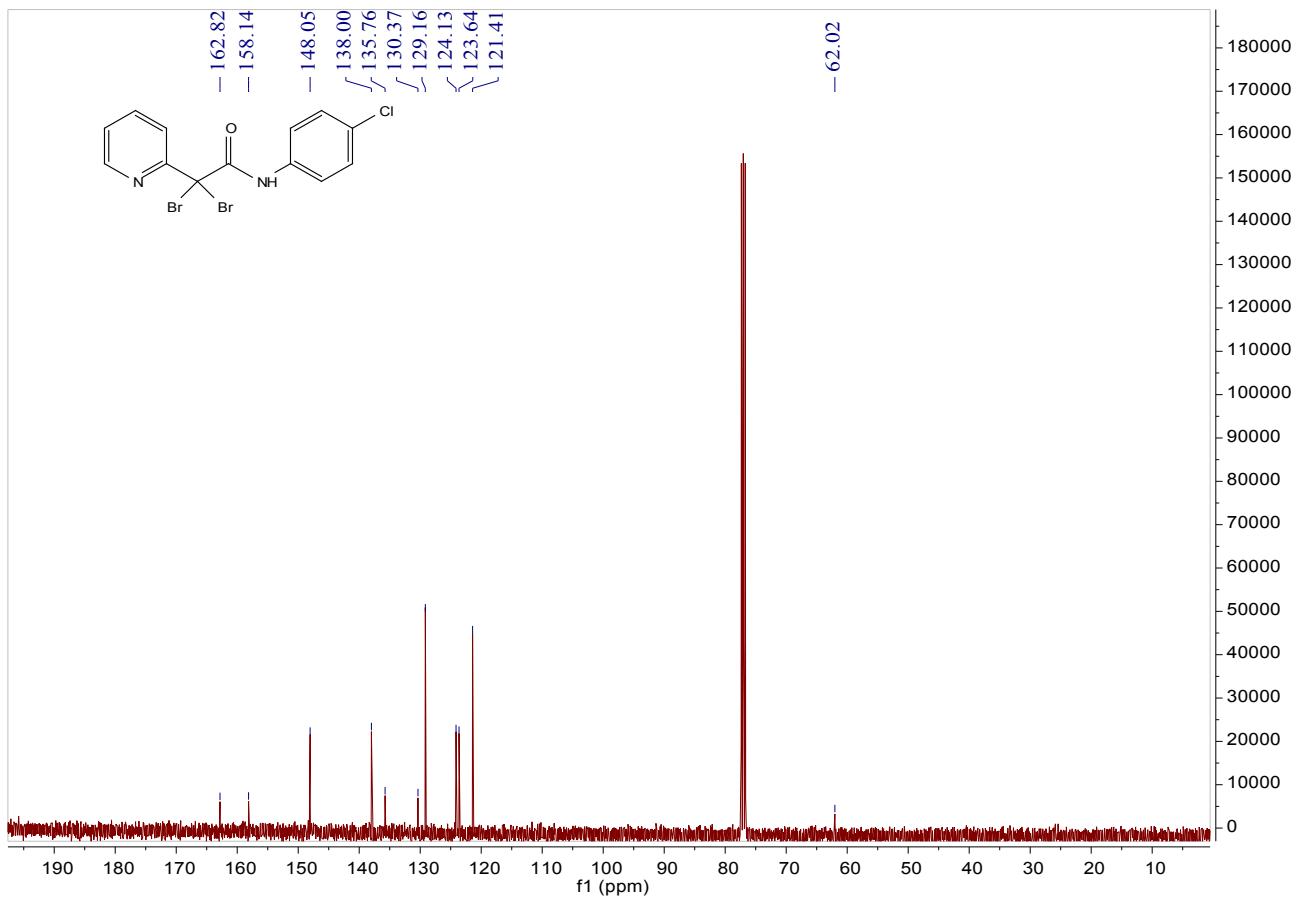
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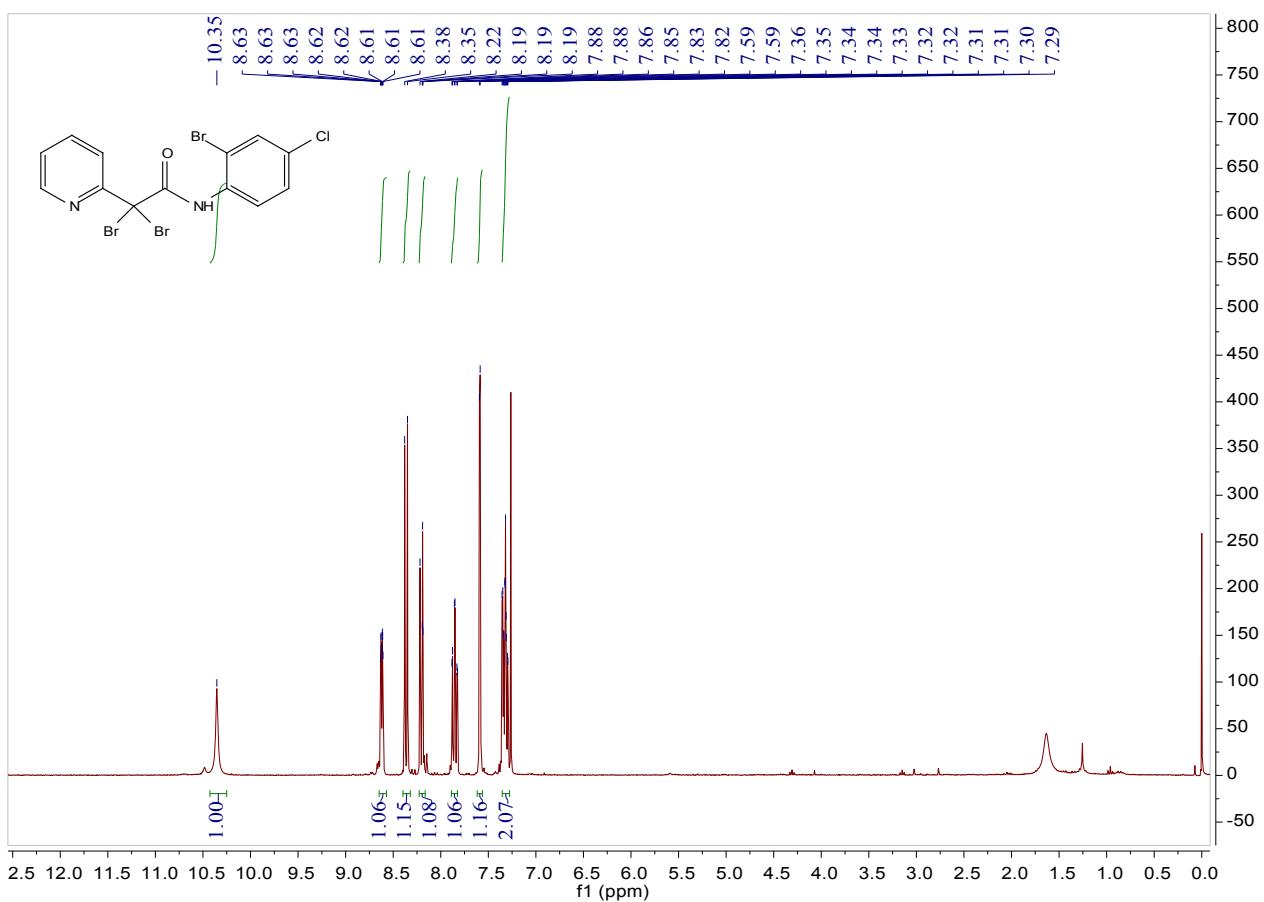
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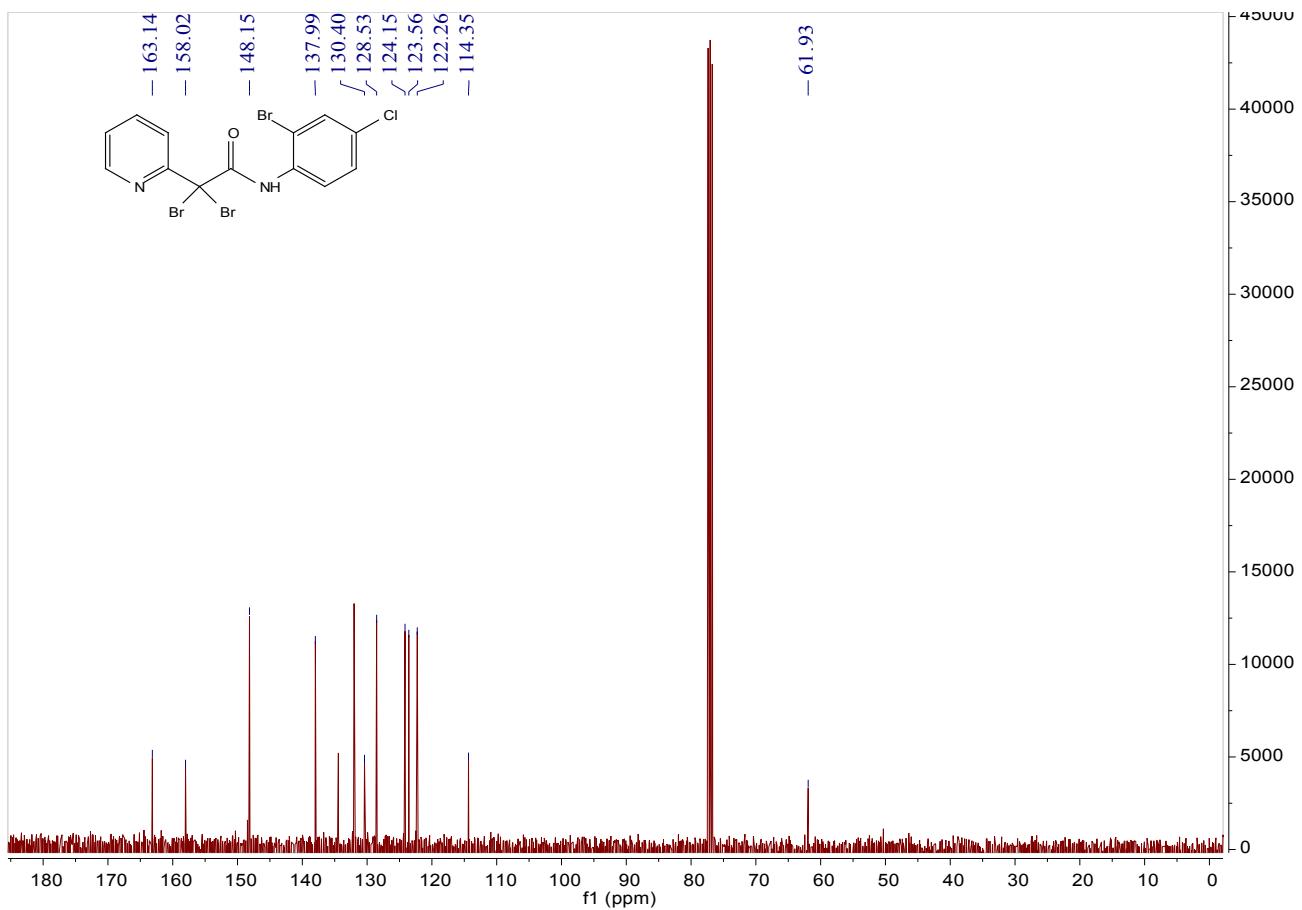
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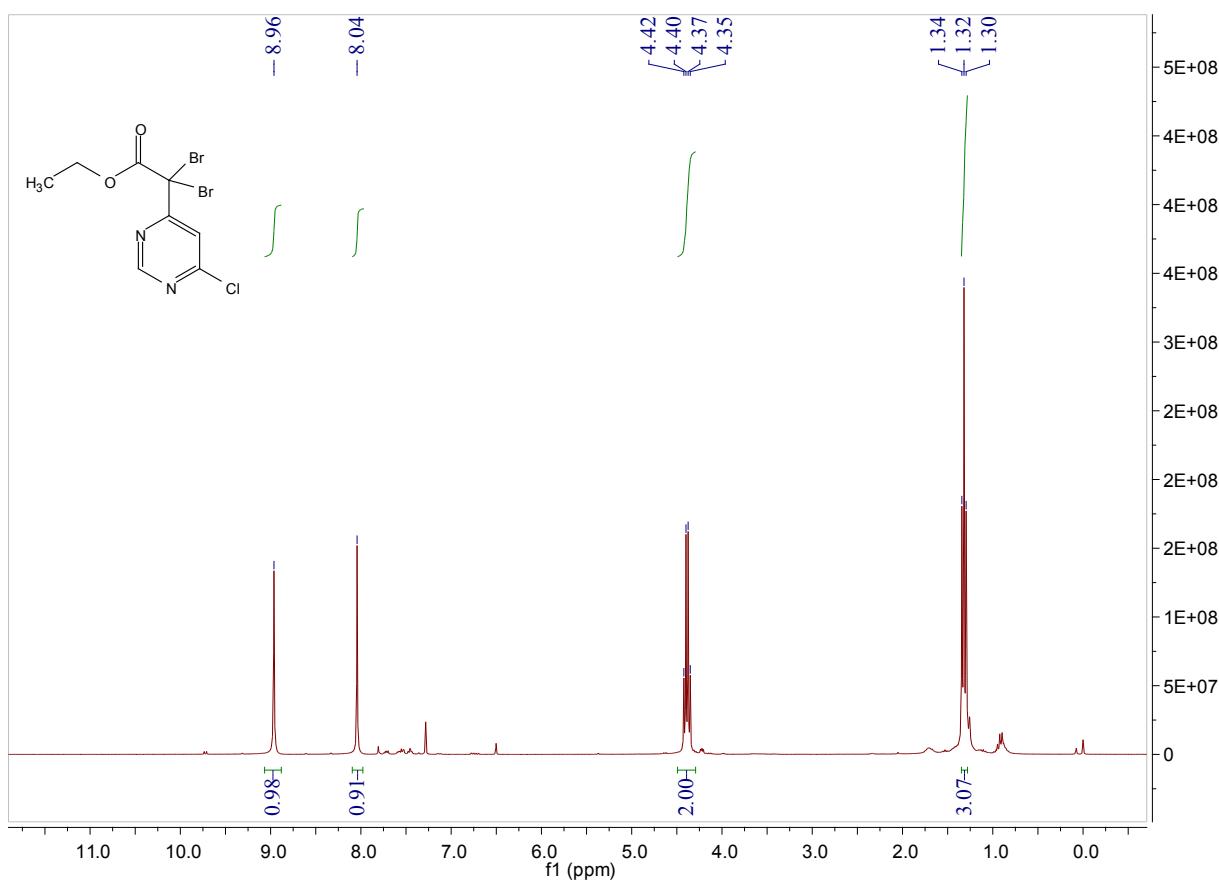
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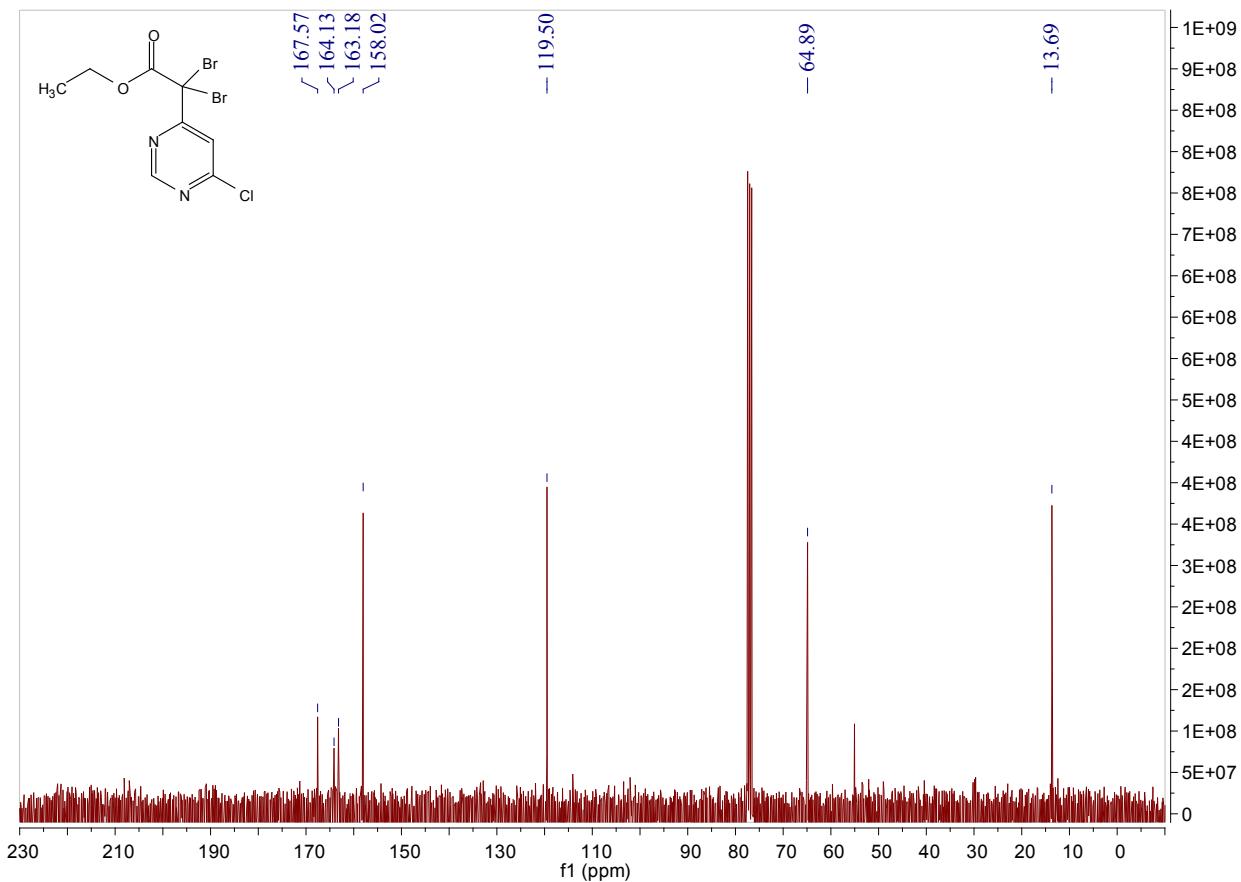
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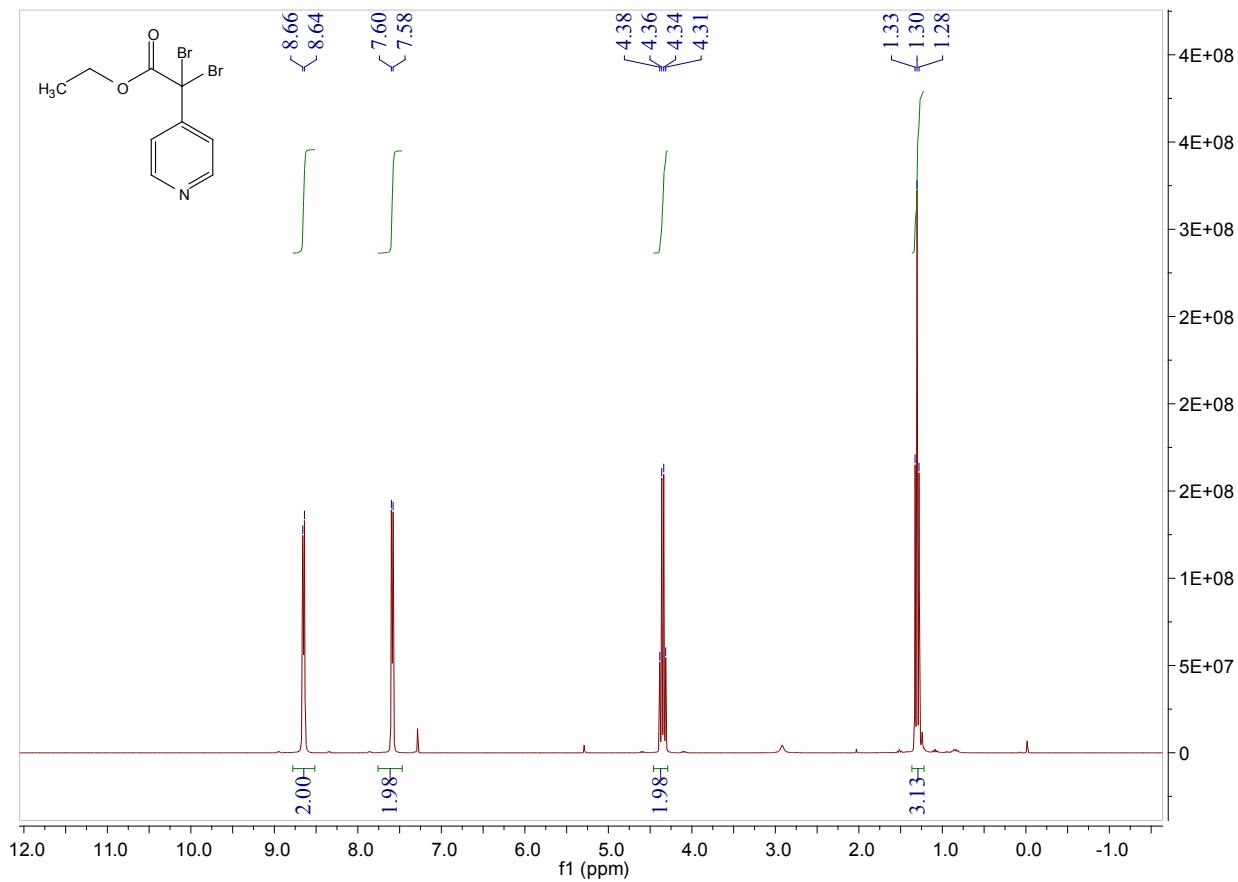
¹H NMR of **2p**



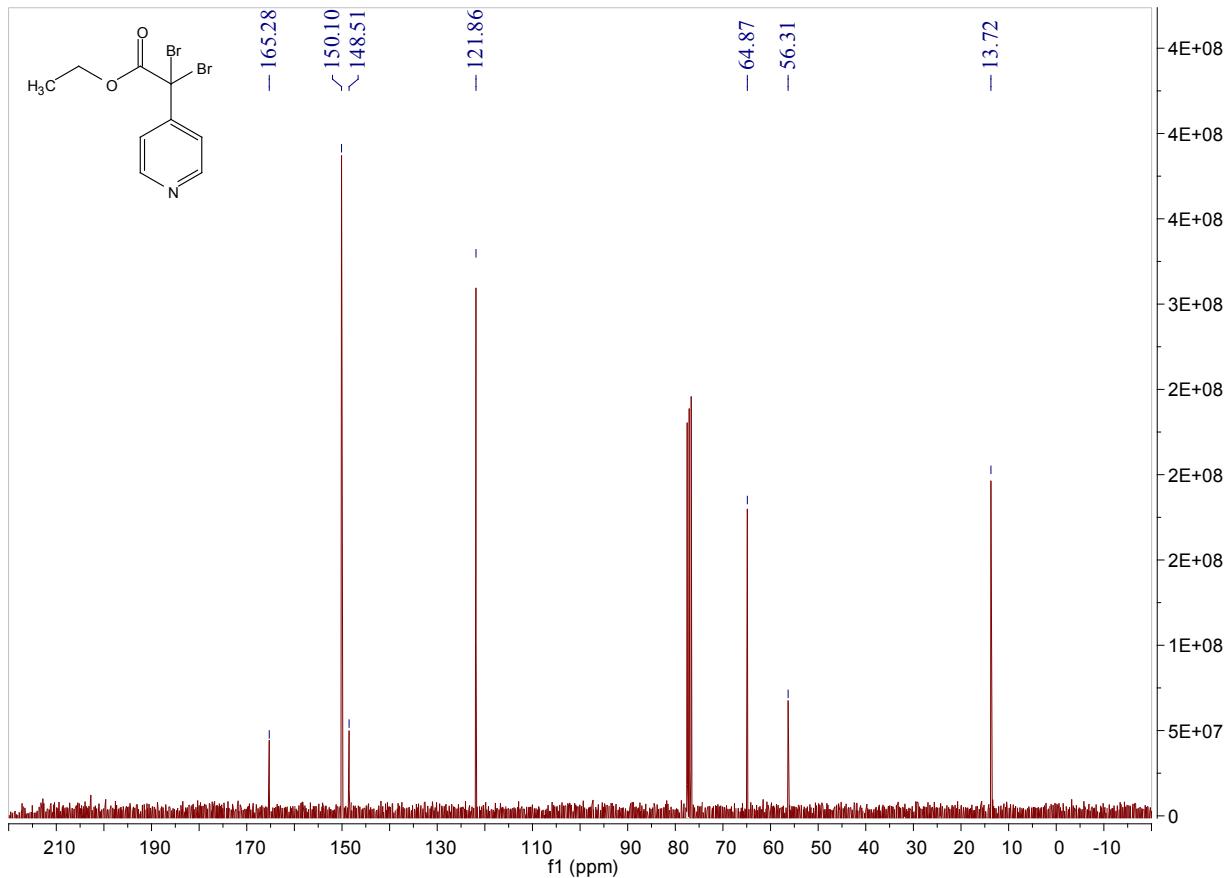
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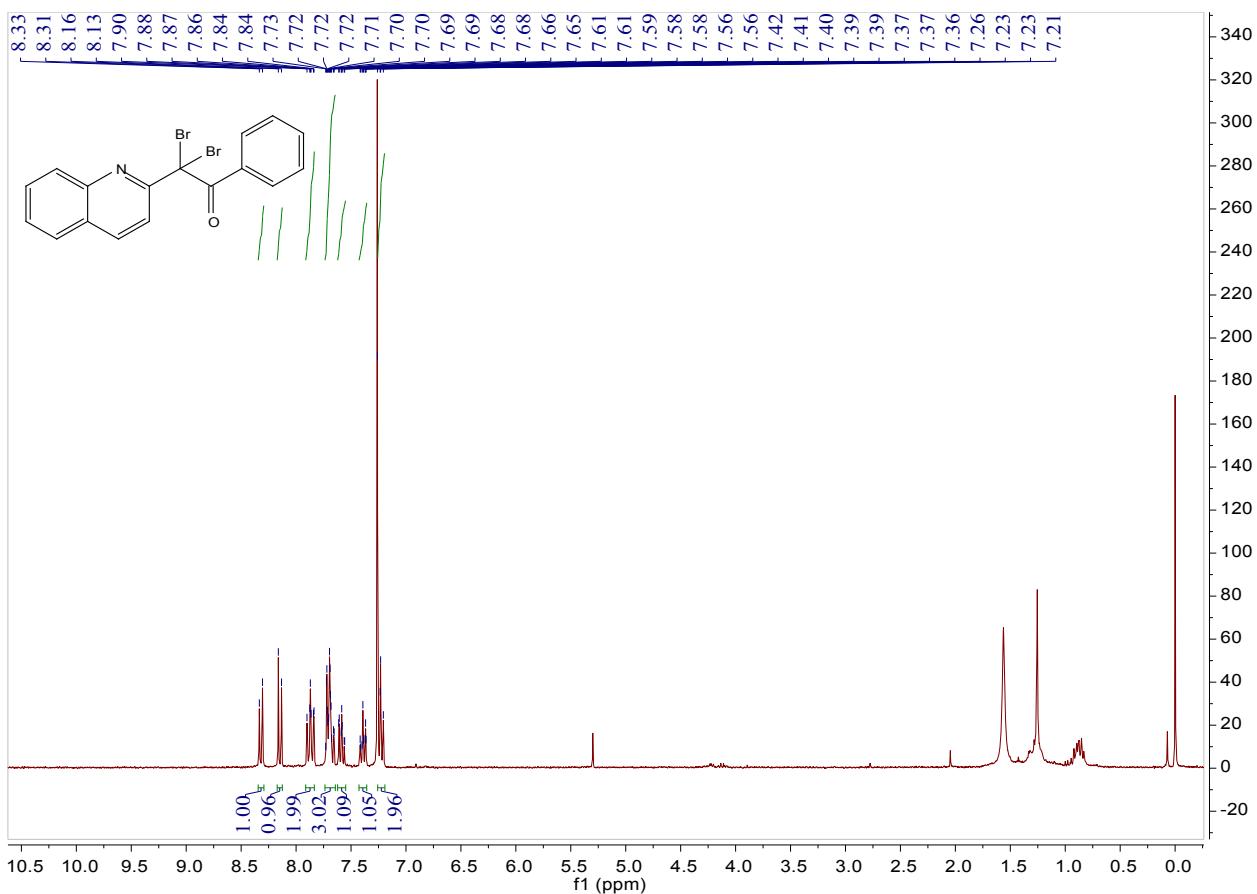
¹H NMR of **2q**



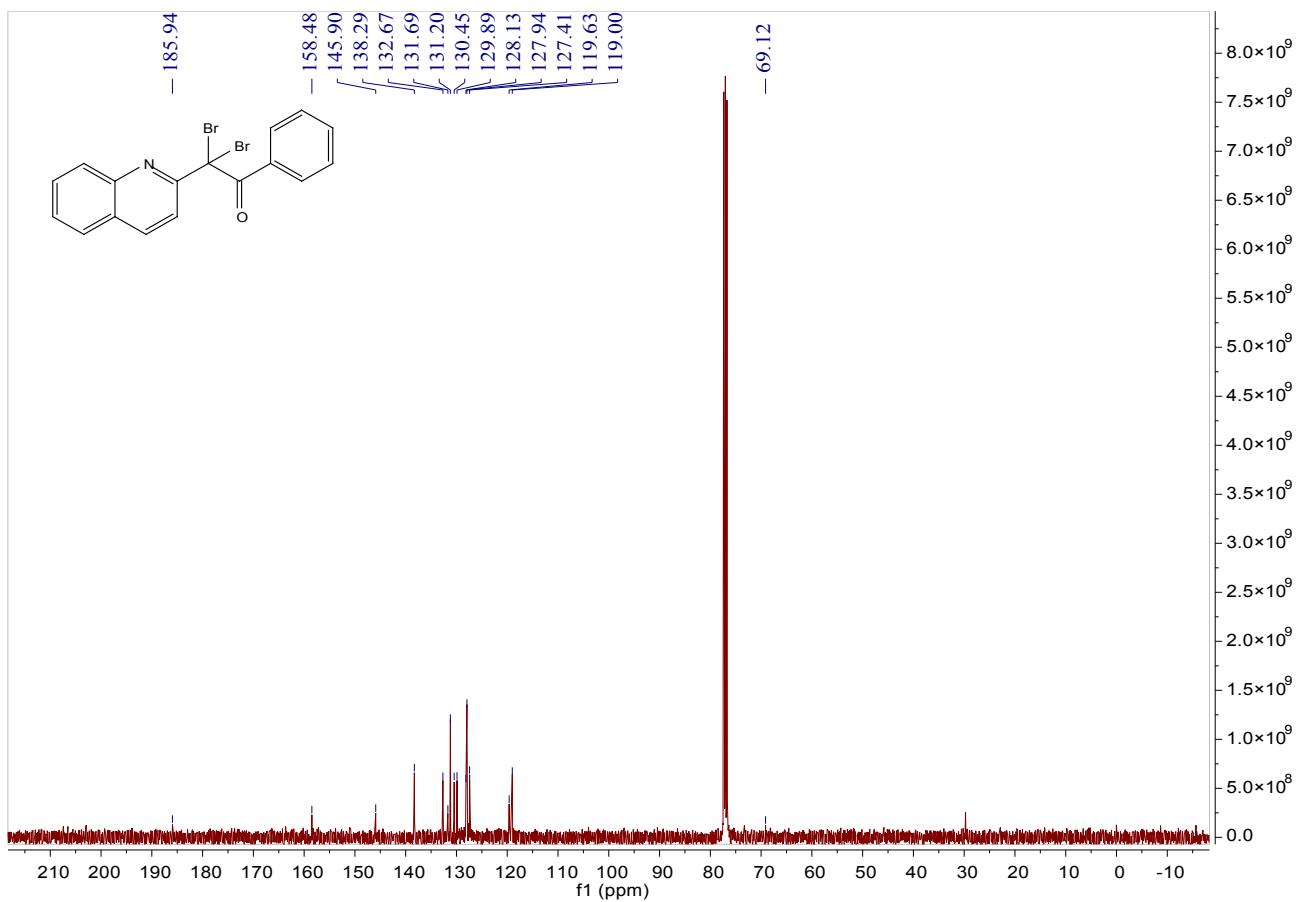
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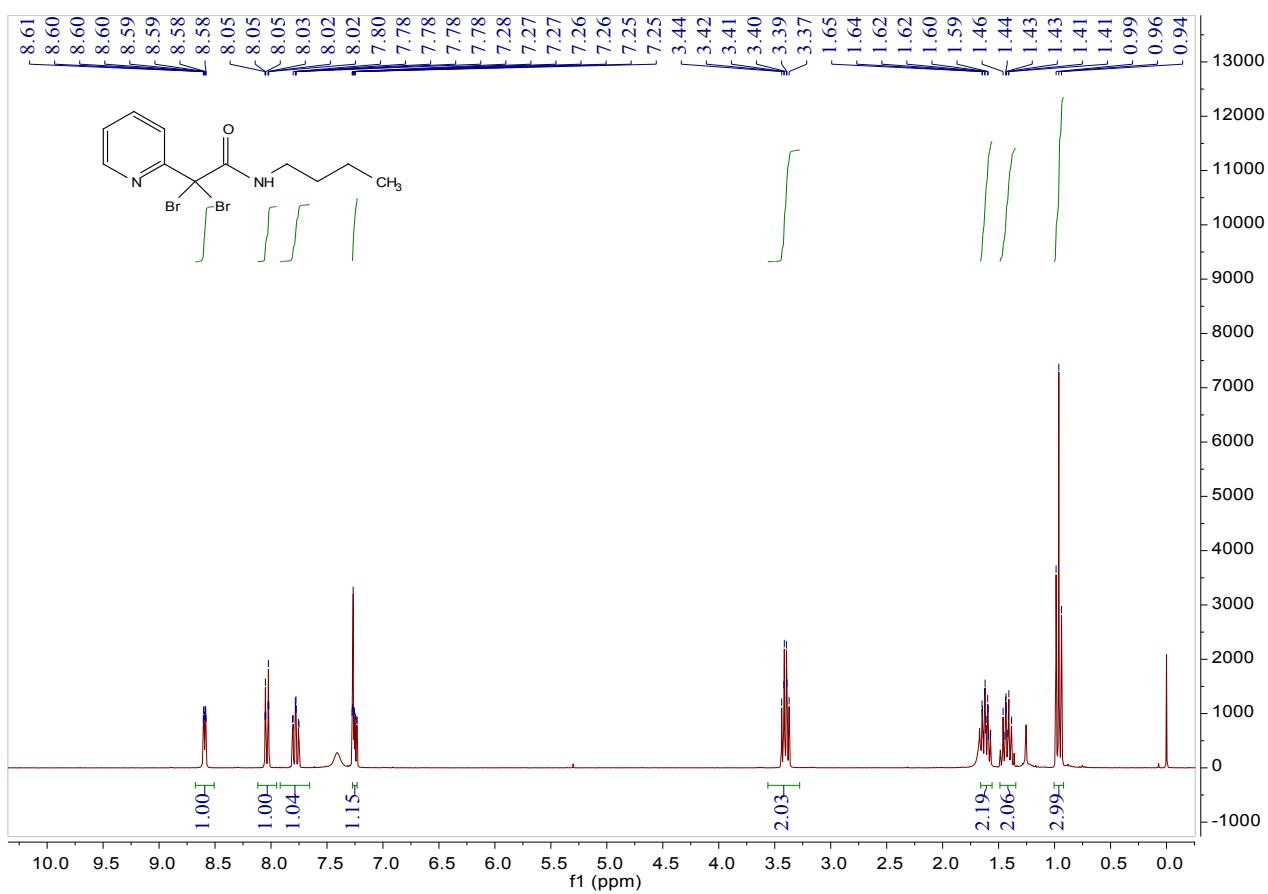
¹H NMR of 2r



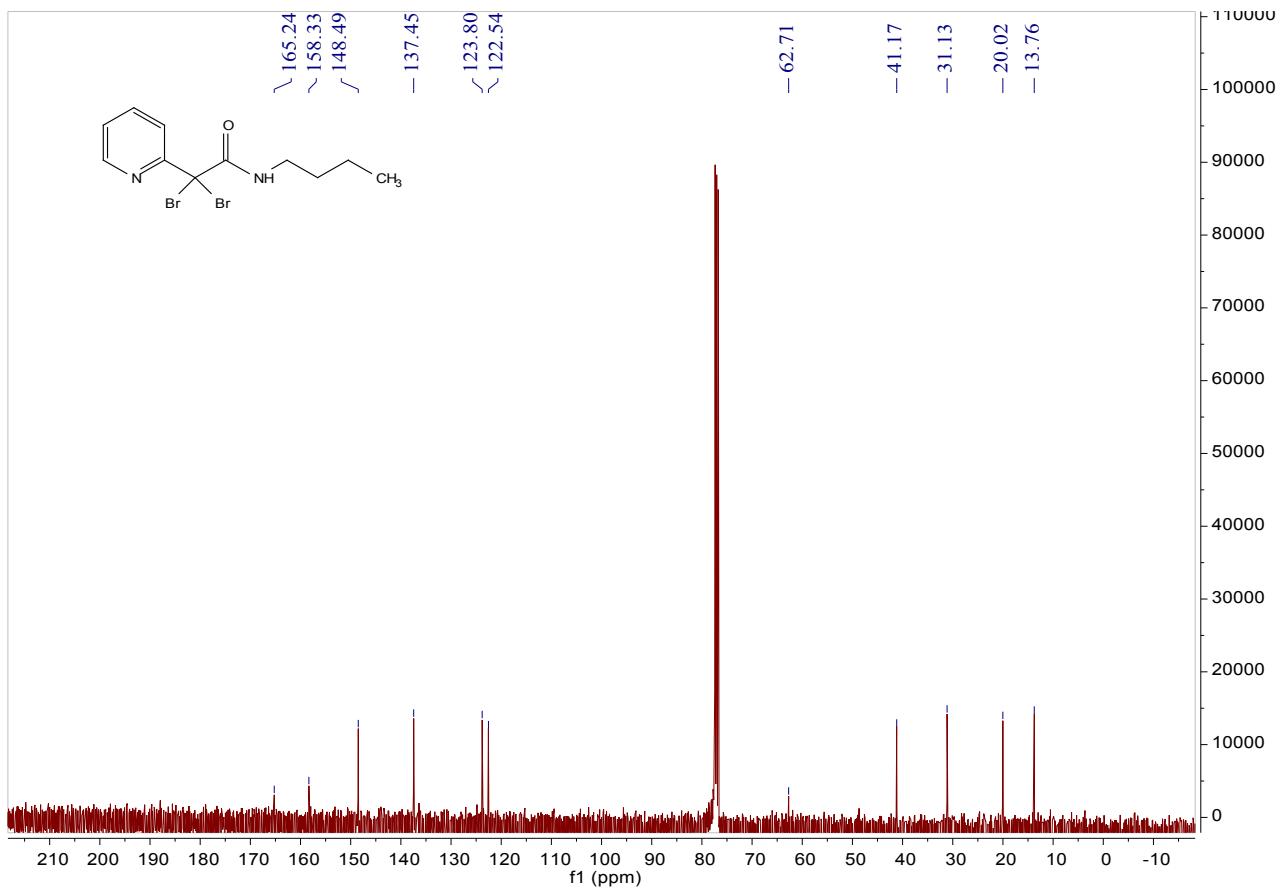
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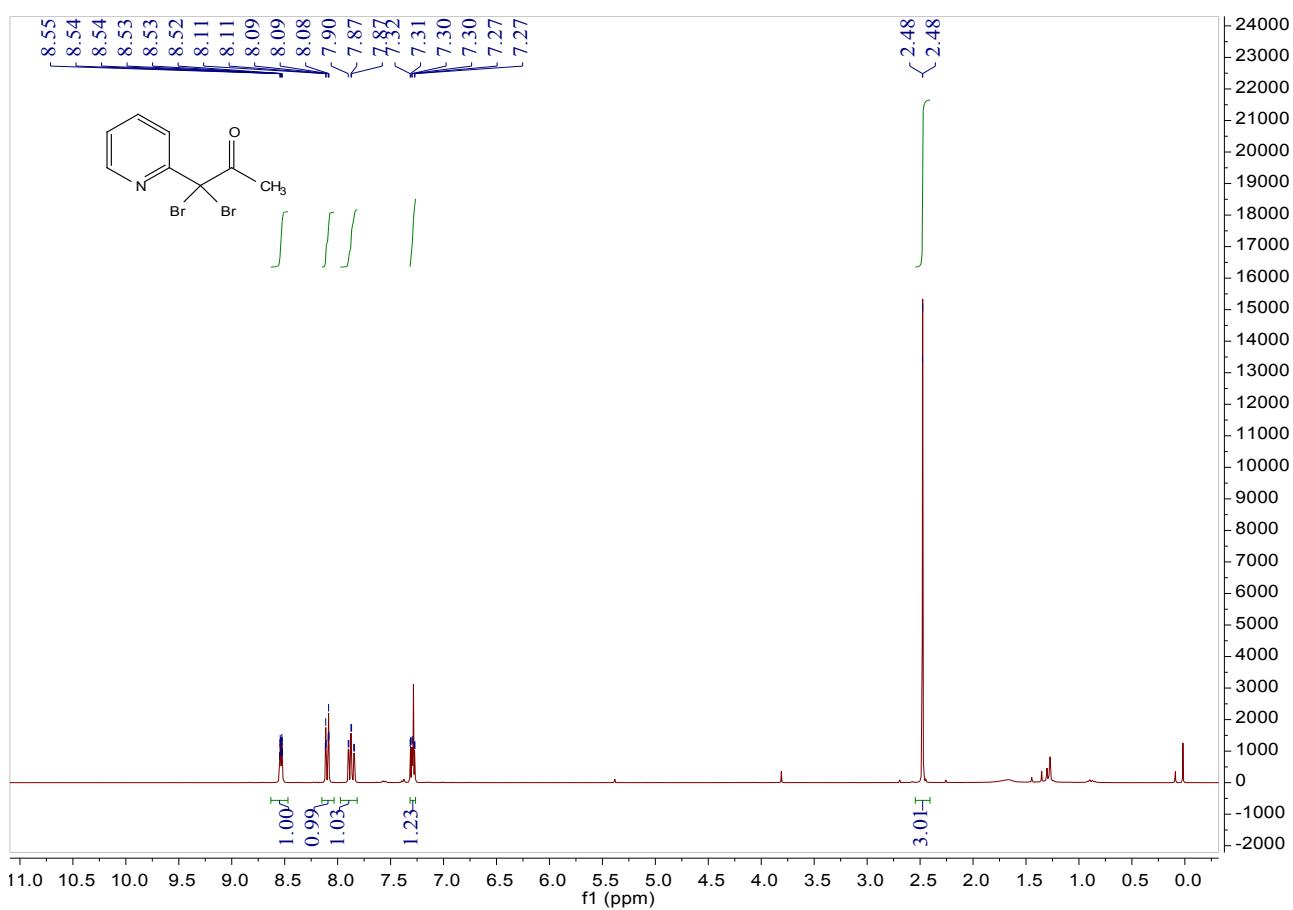
¹H NMR of **2s**



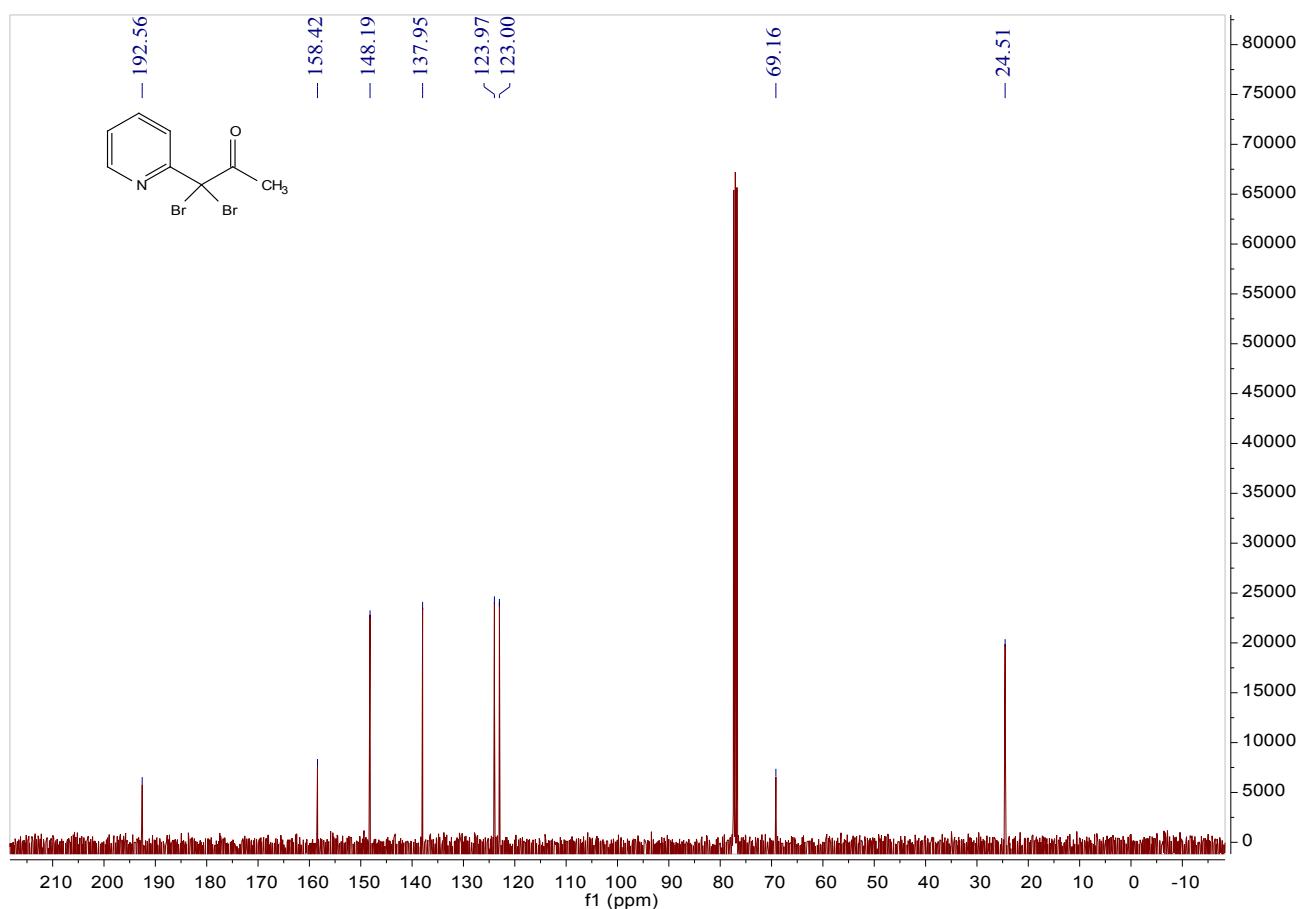
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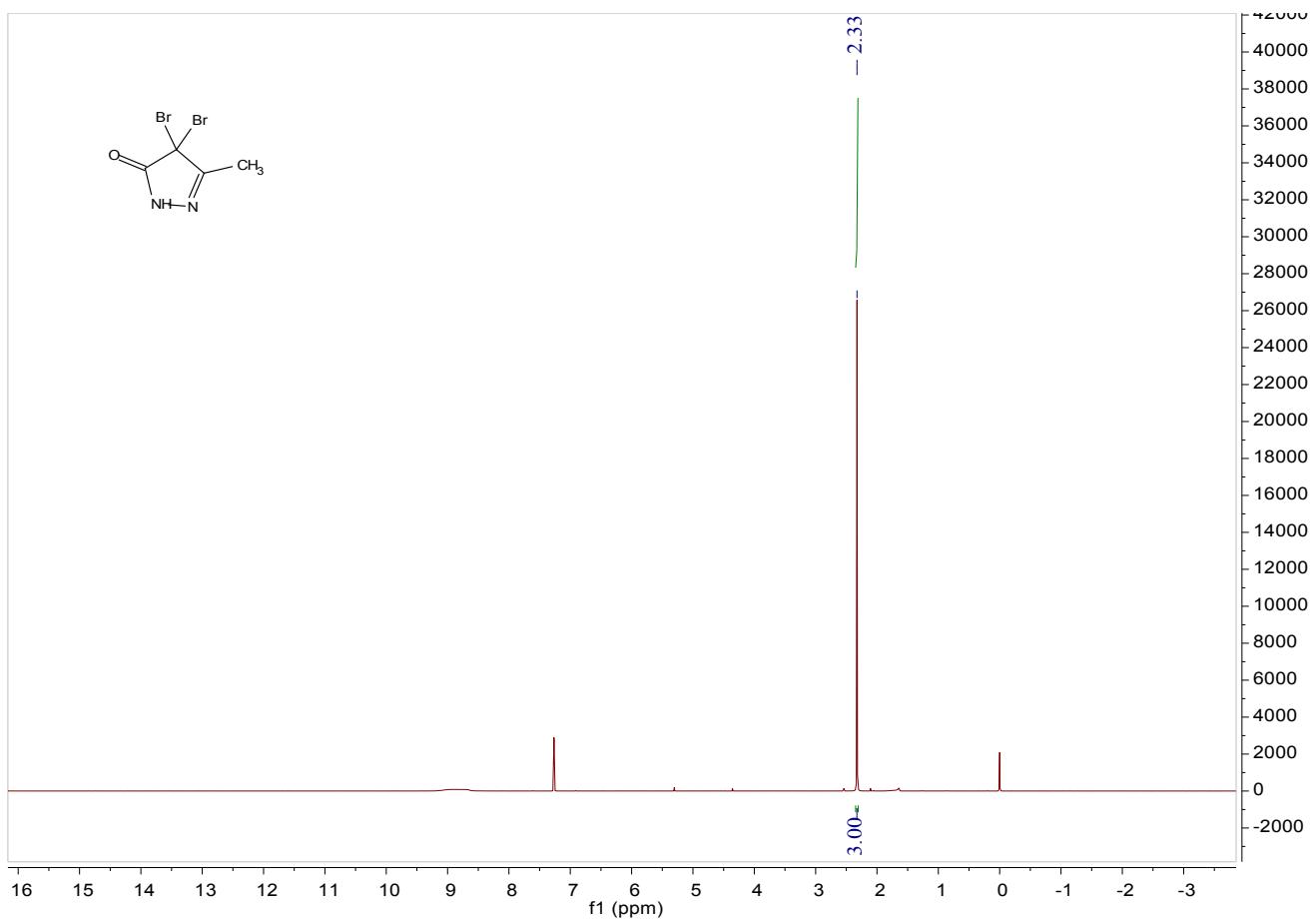
¹H NMR of **2t**



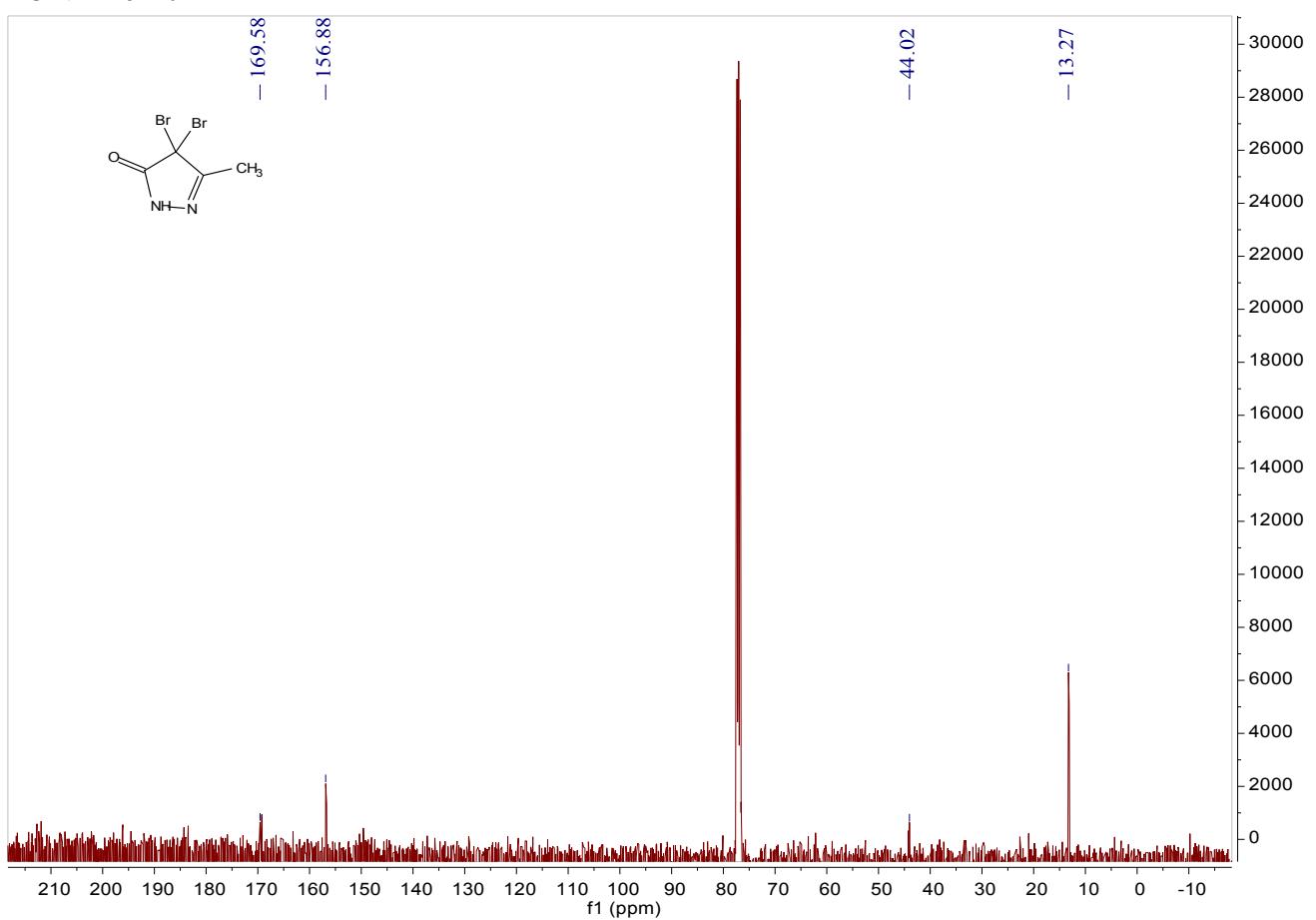
¹³C NMR of **2t**



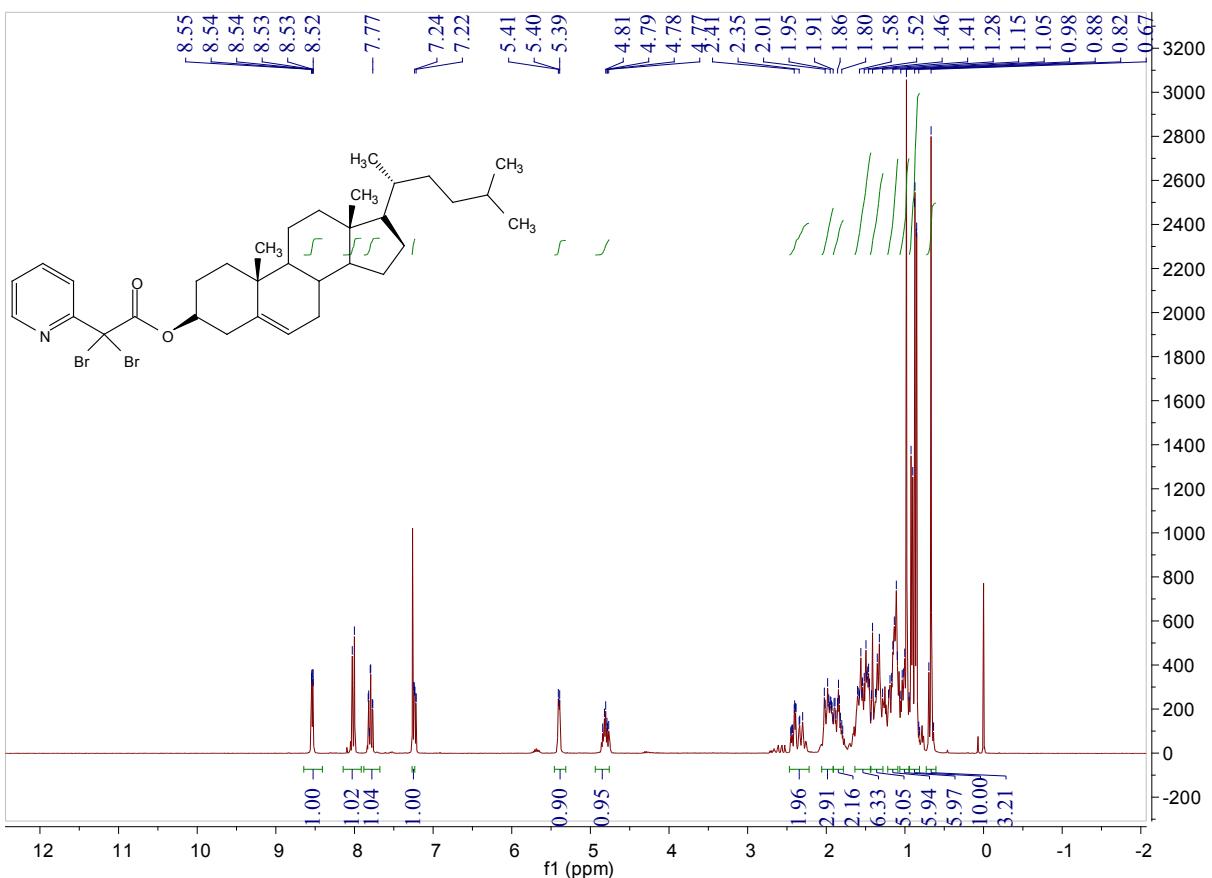
¹H NMR of **2u**



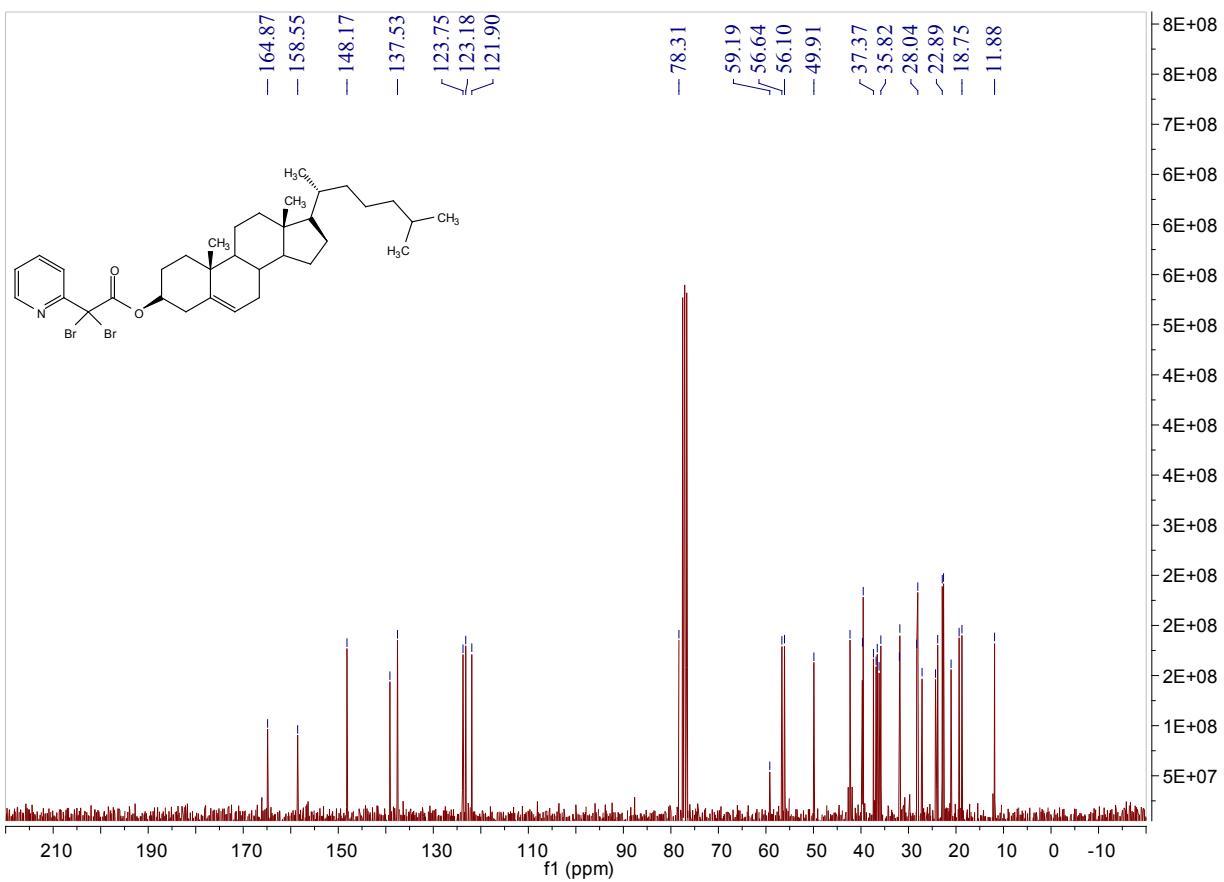
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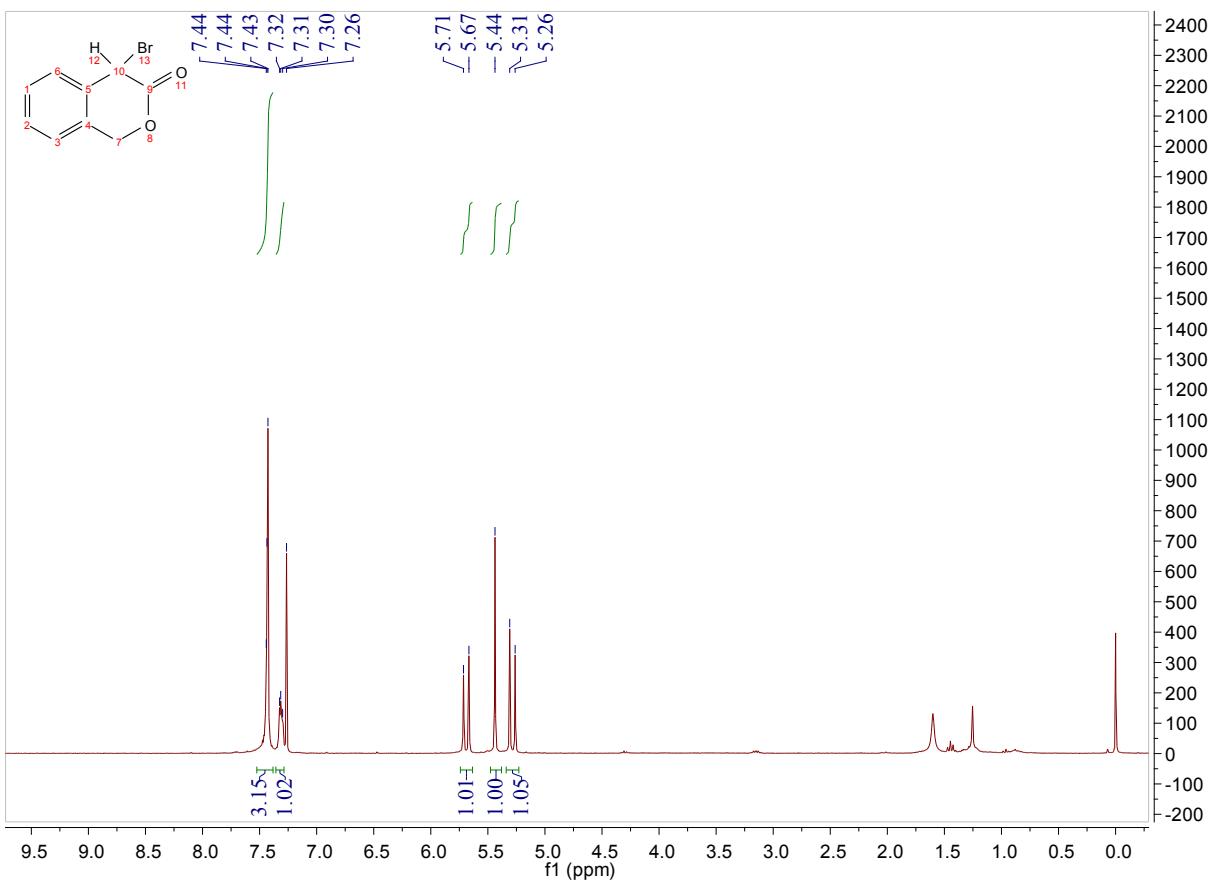
¹H NMR of **2x**



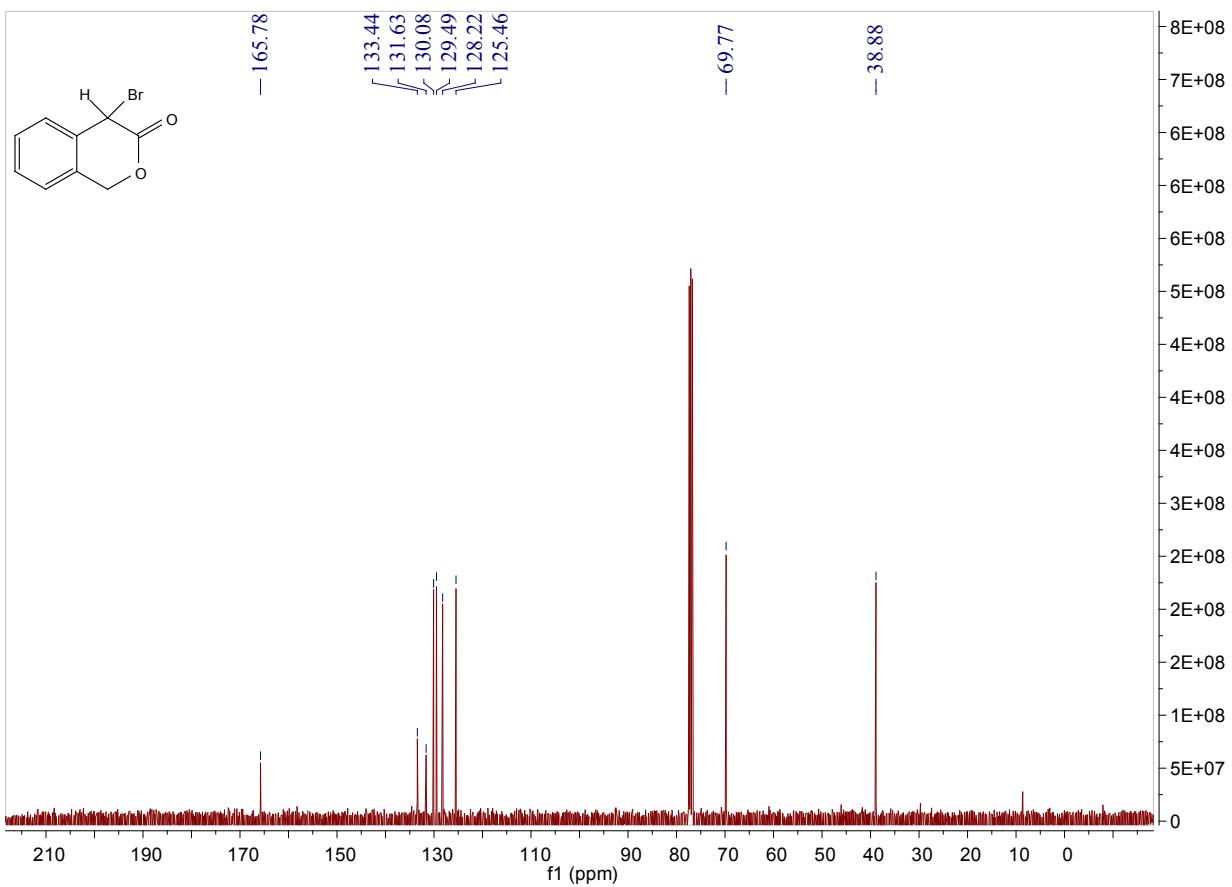
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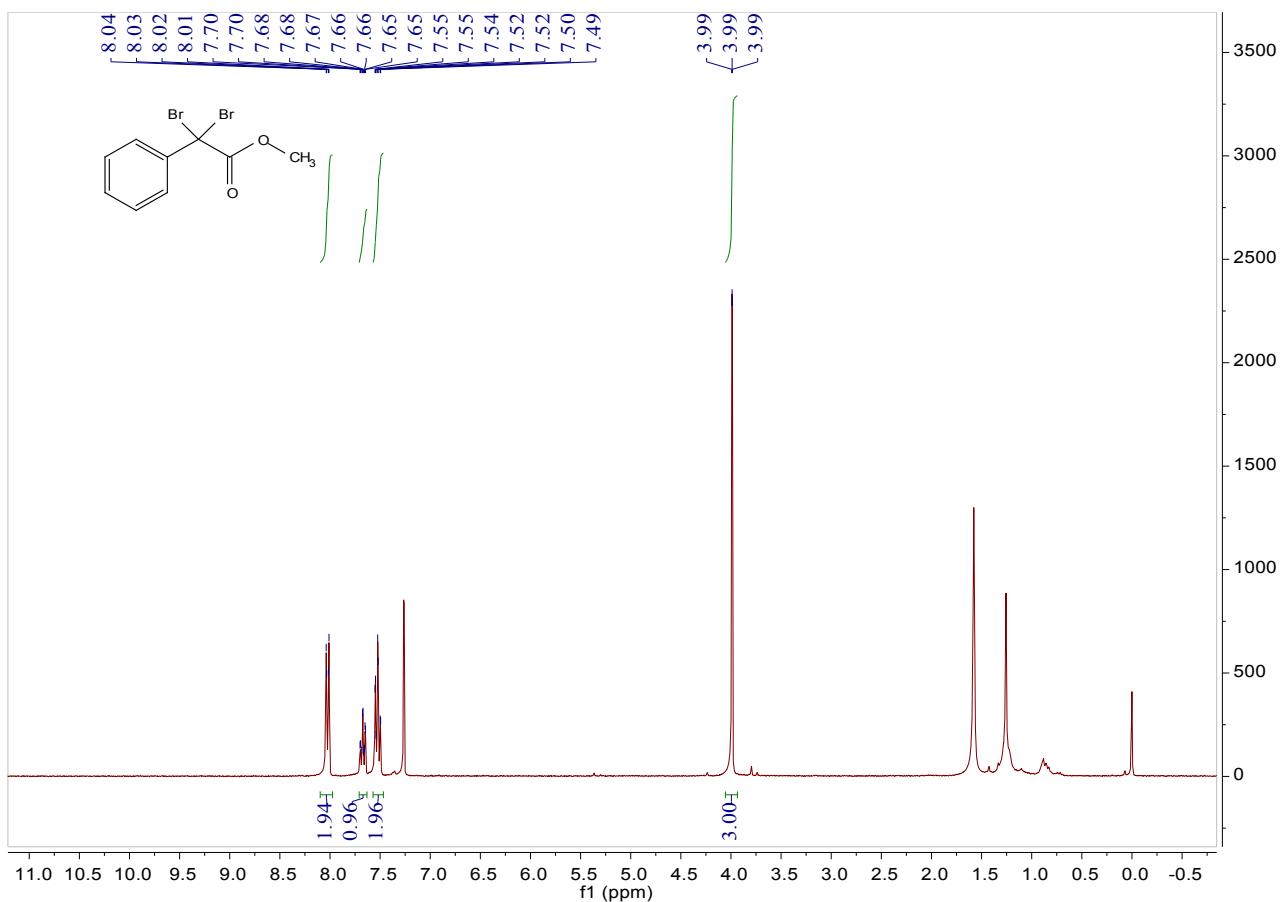
¹H NMR of **2z**



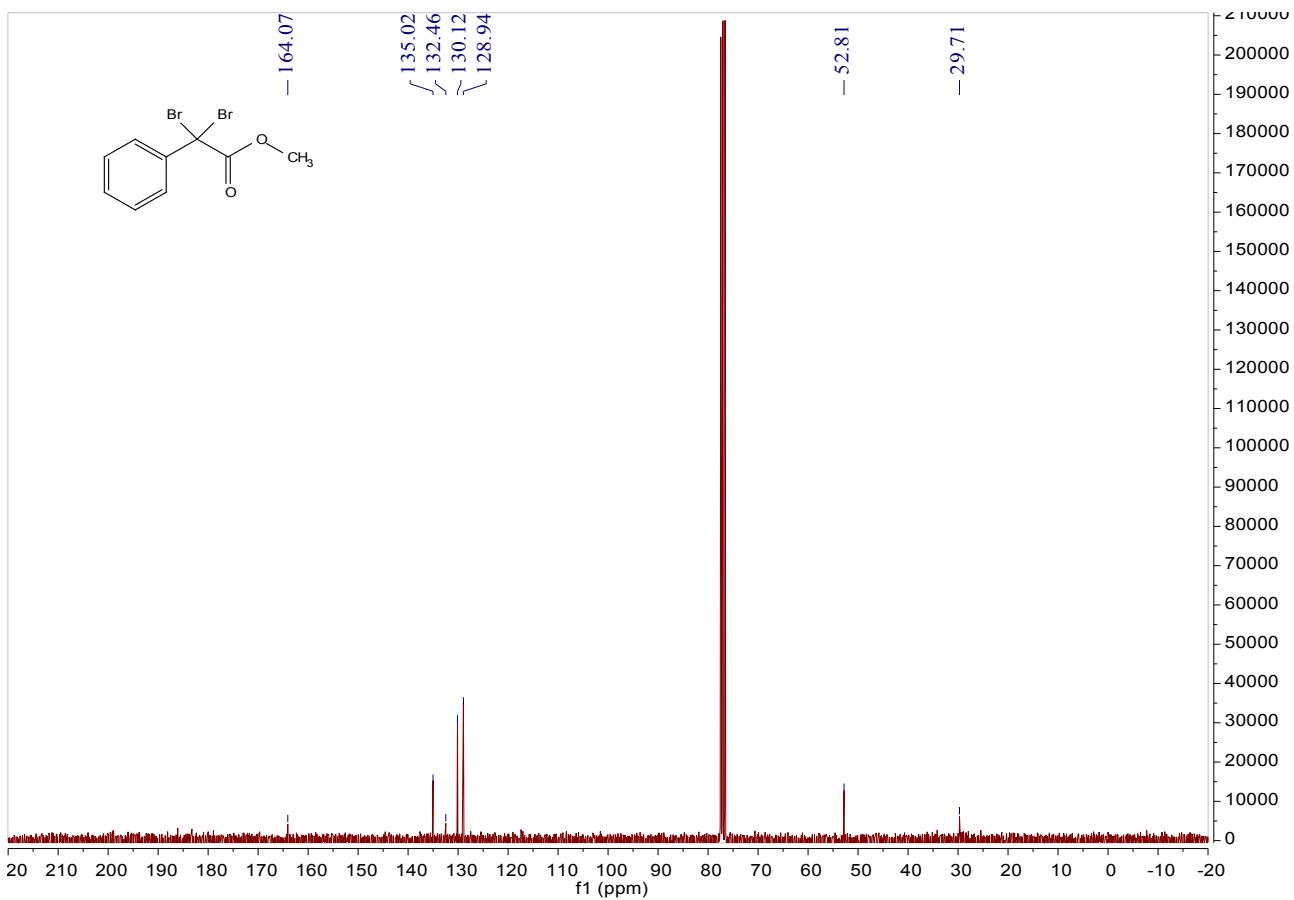
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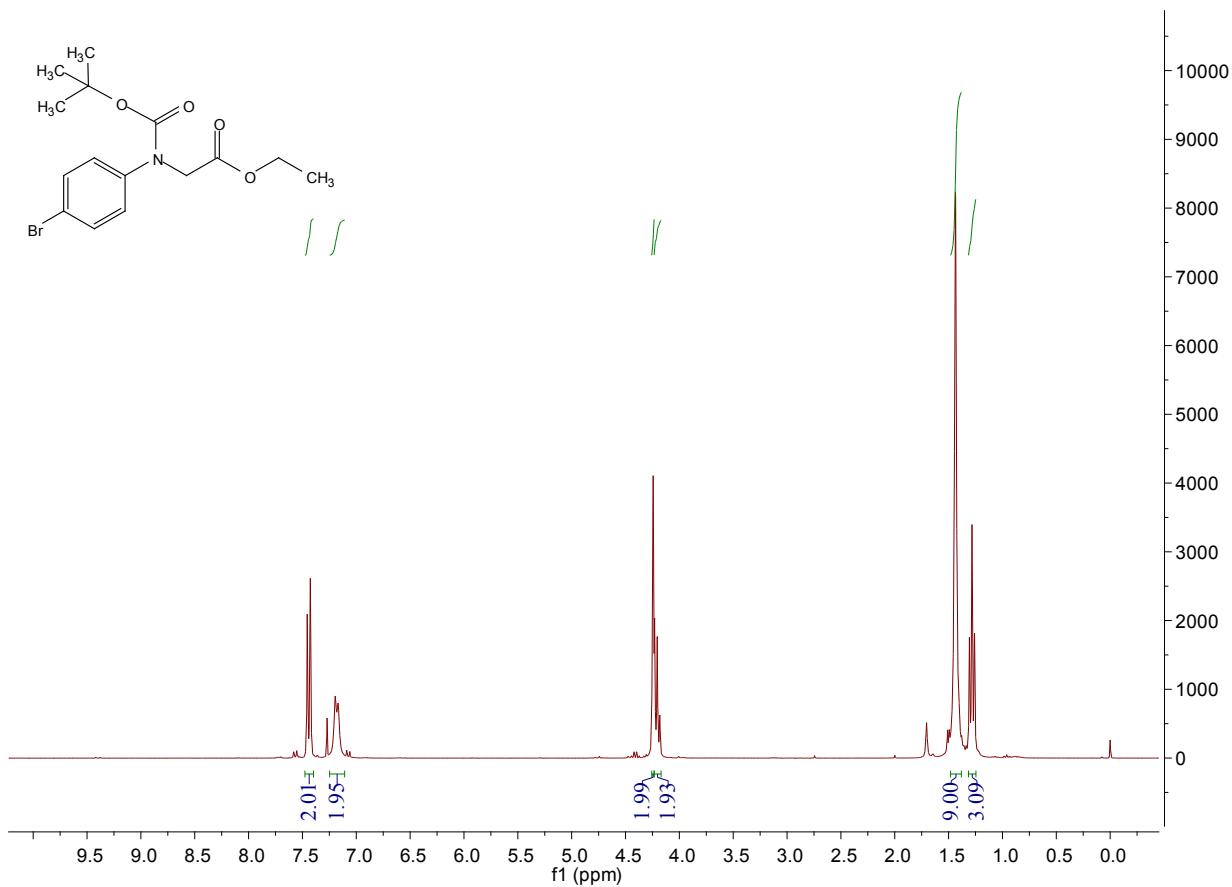
¹H NMR of **3b**



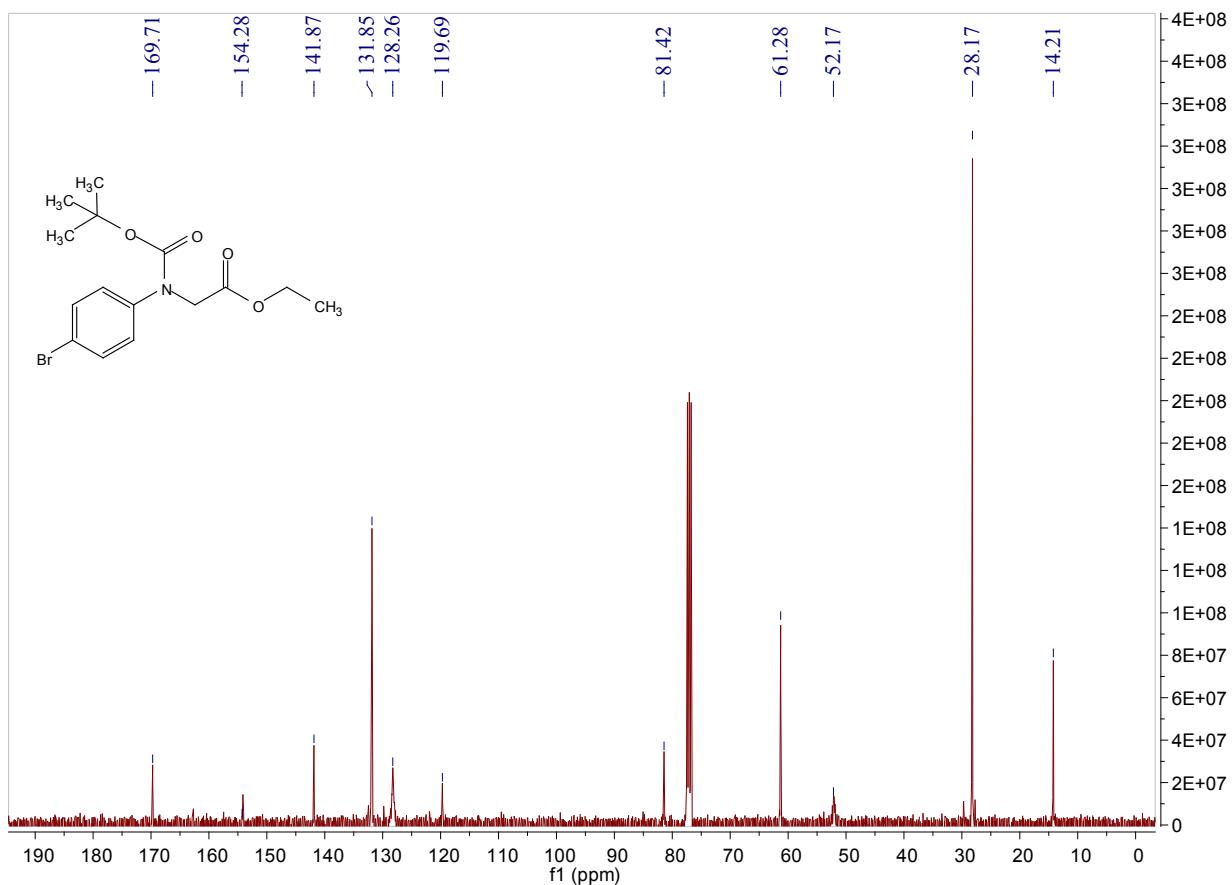
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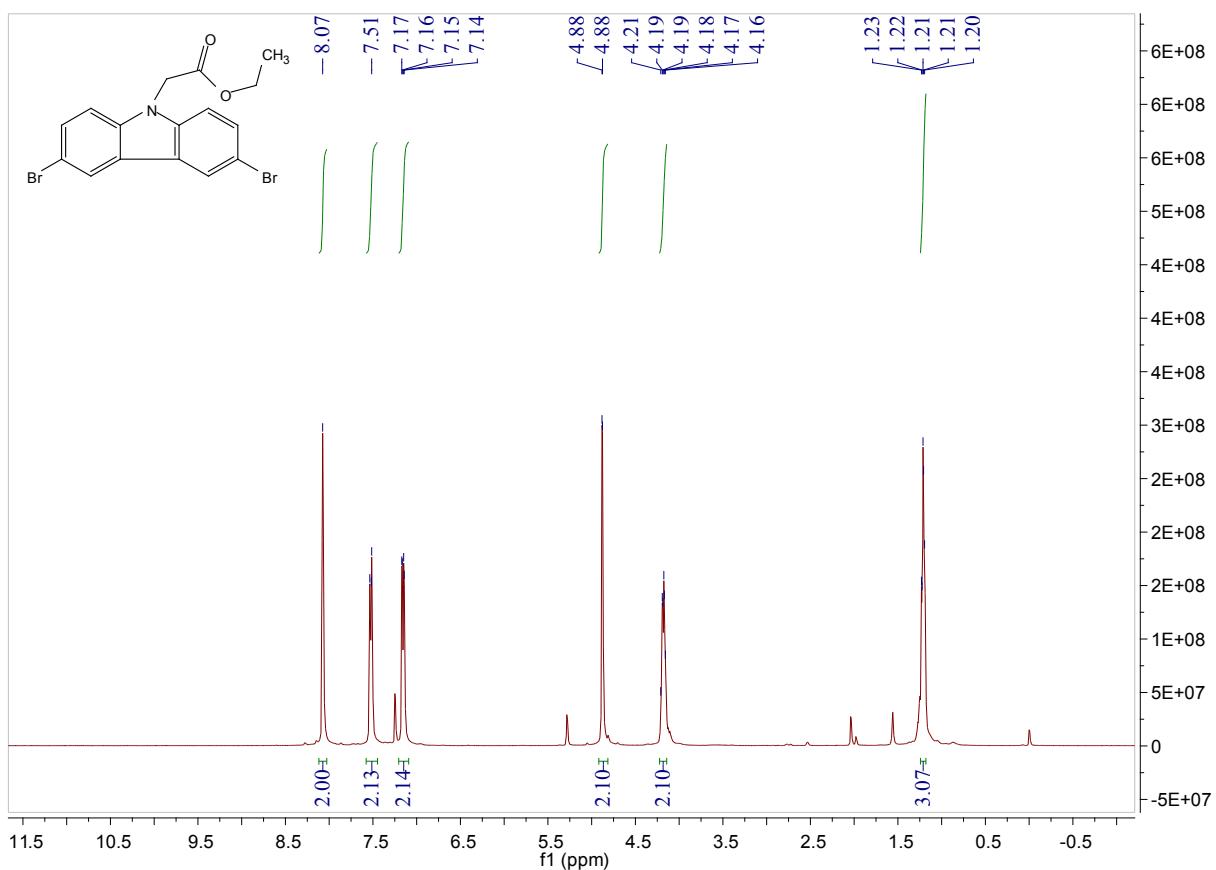
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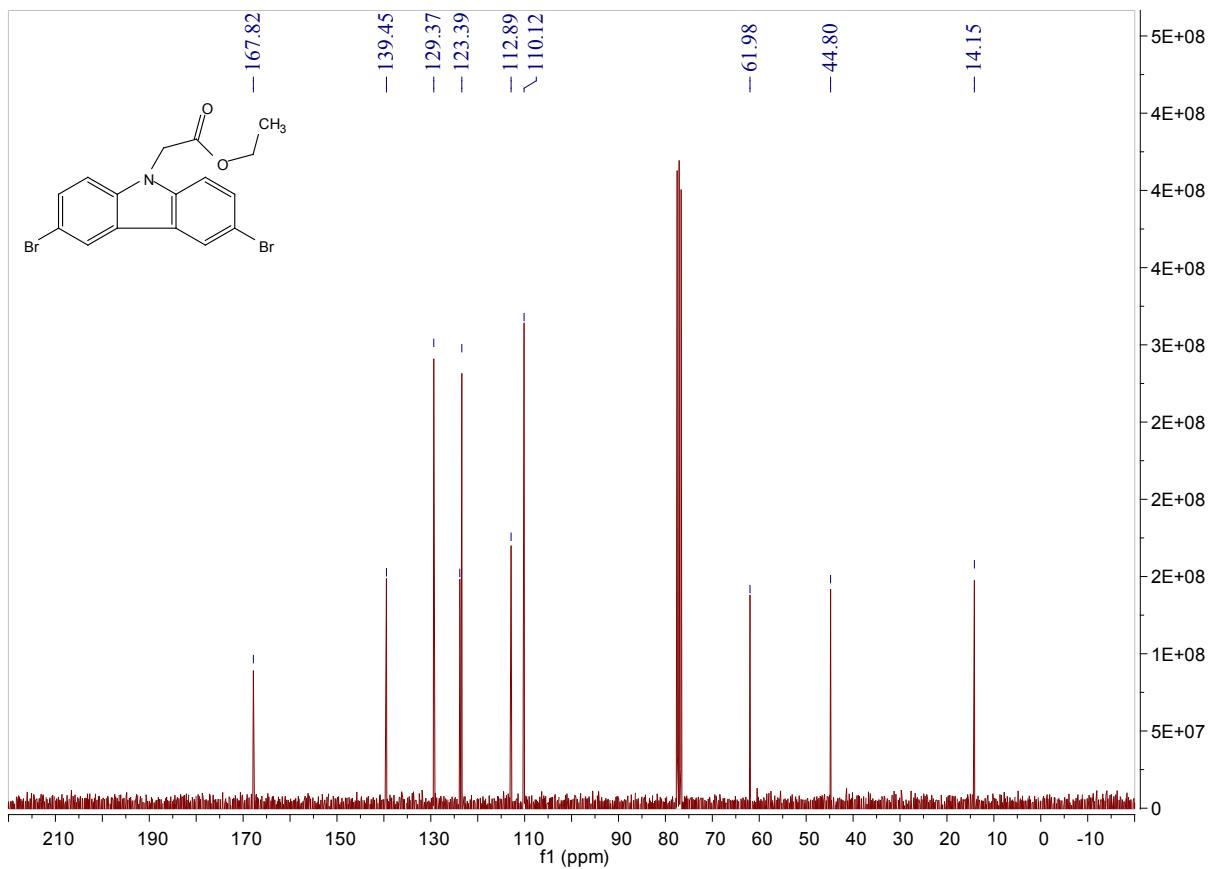
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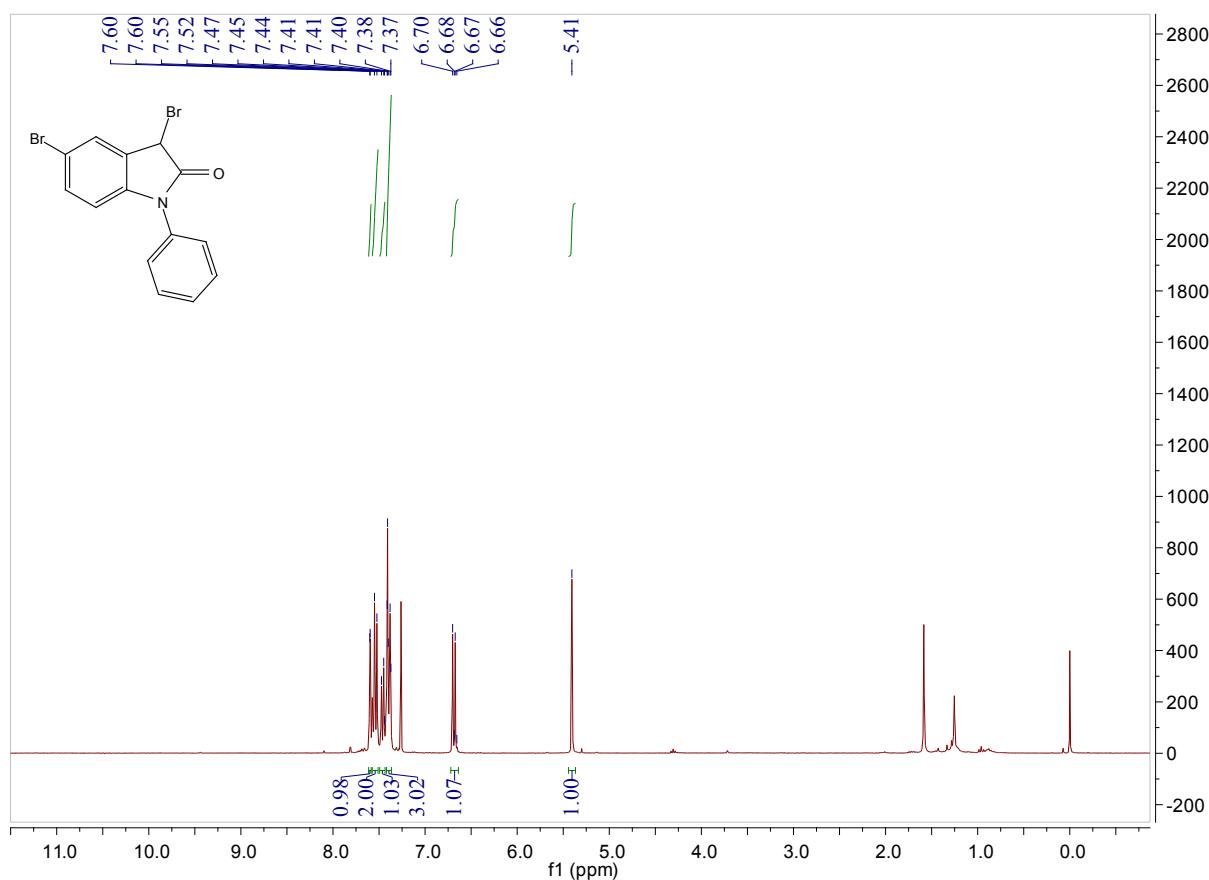
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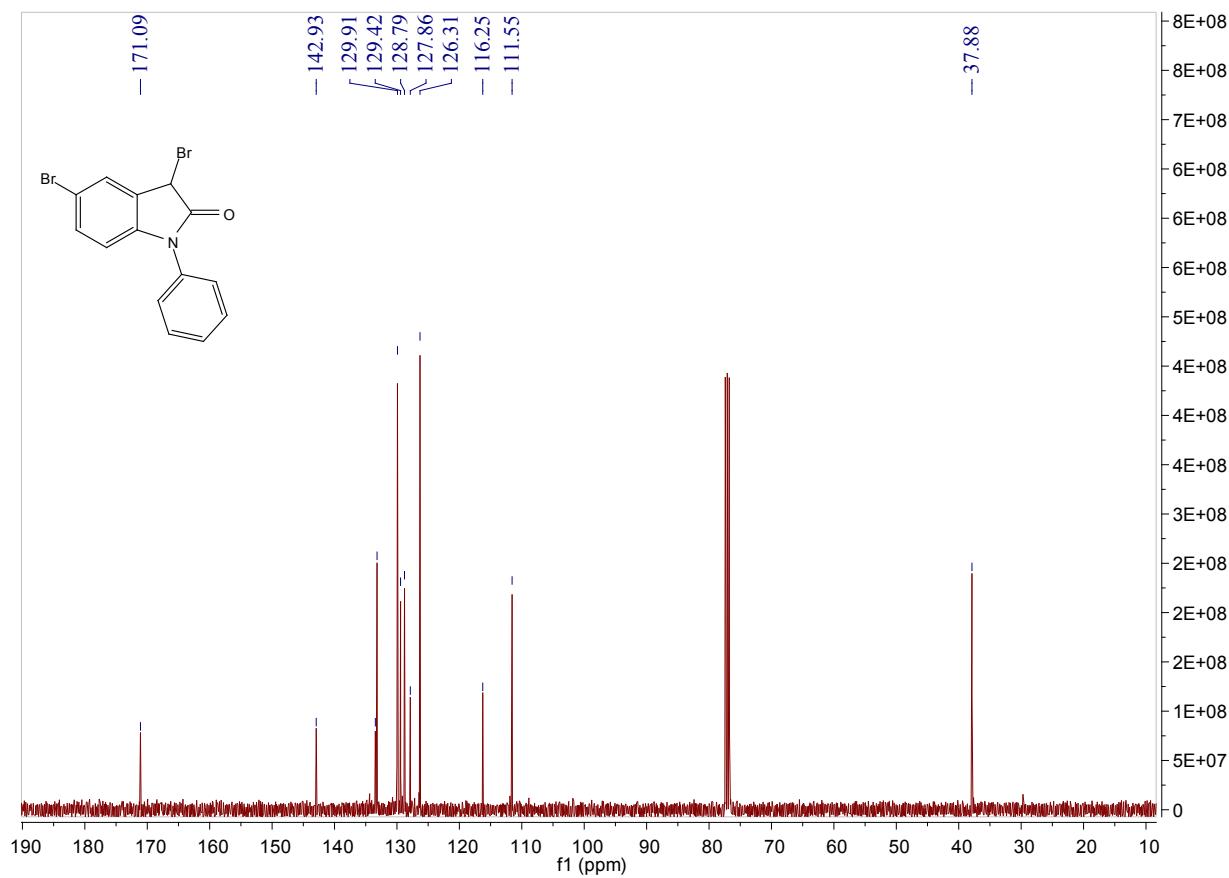
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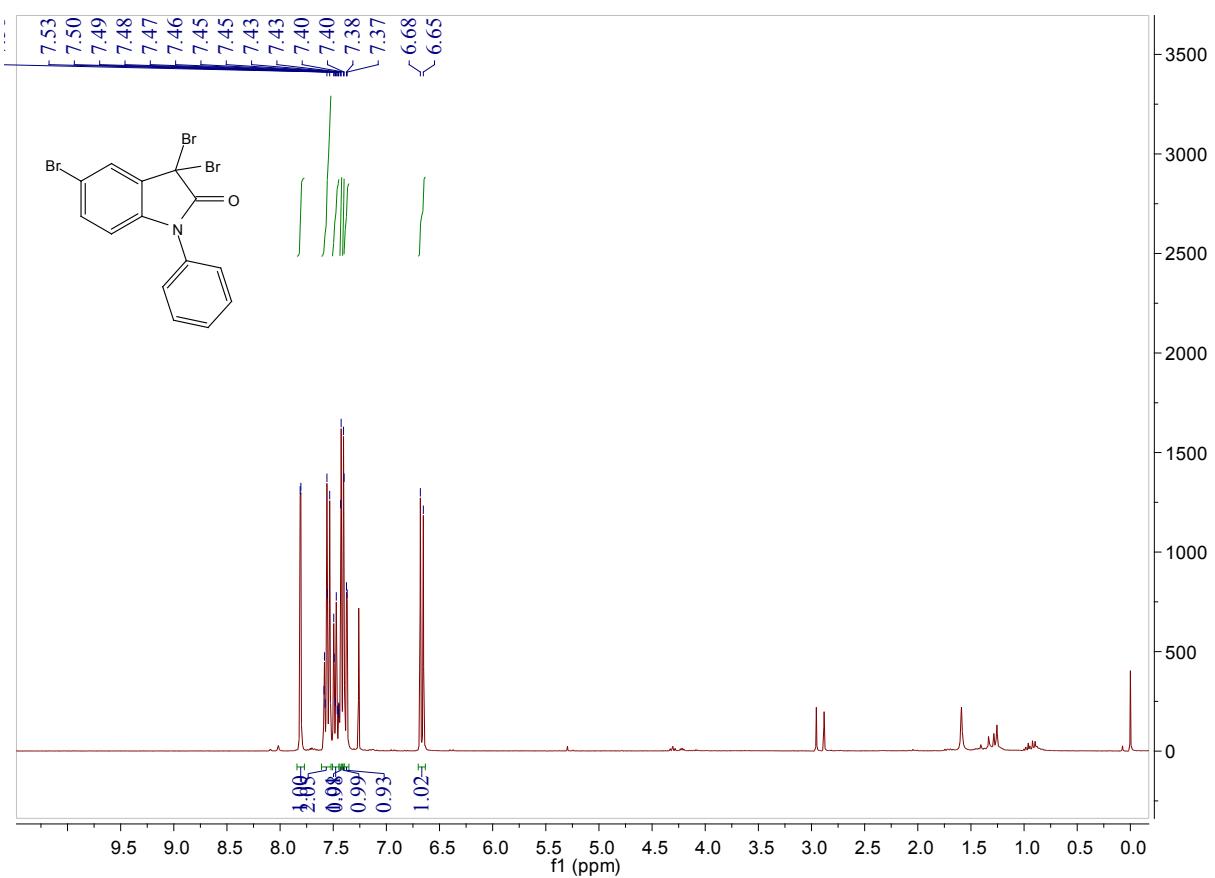
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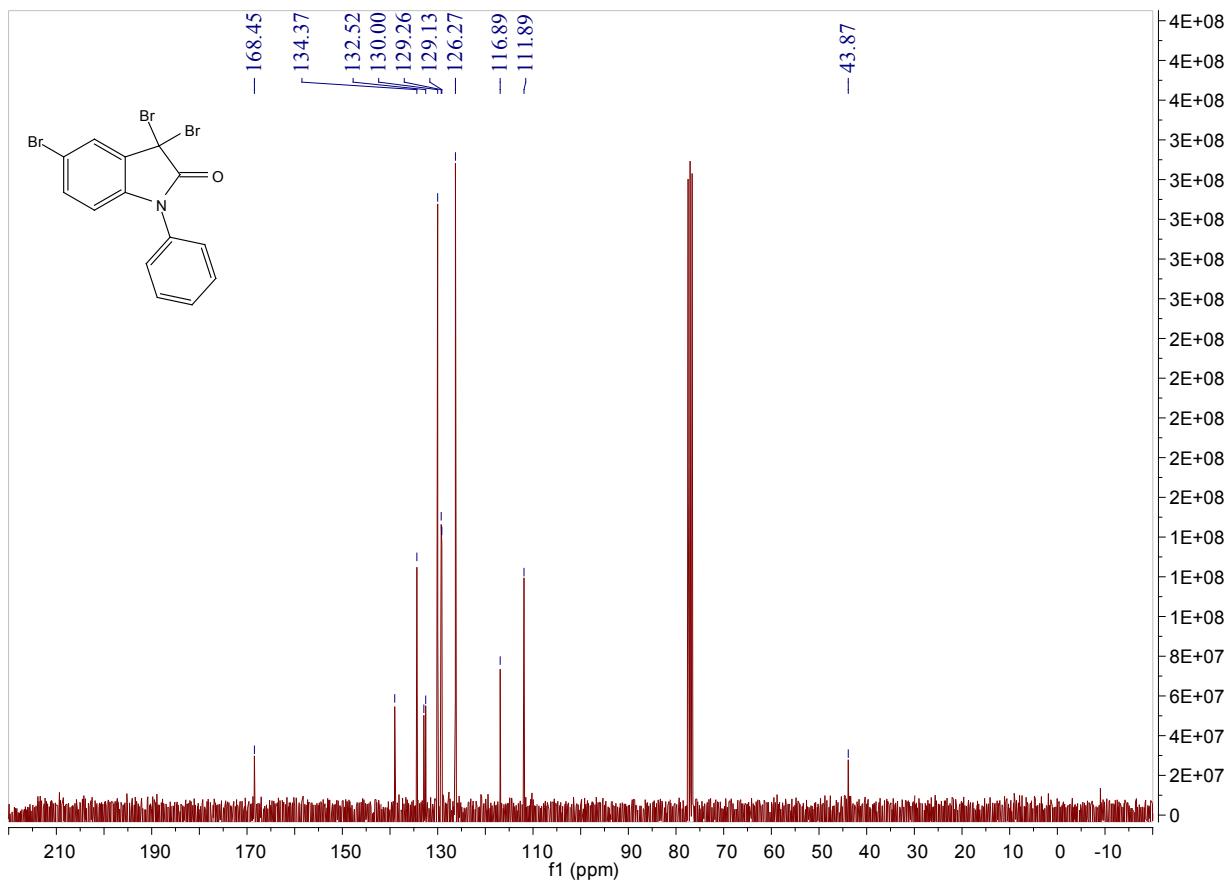
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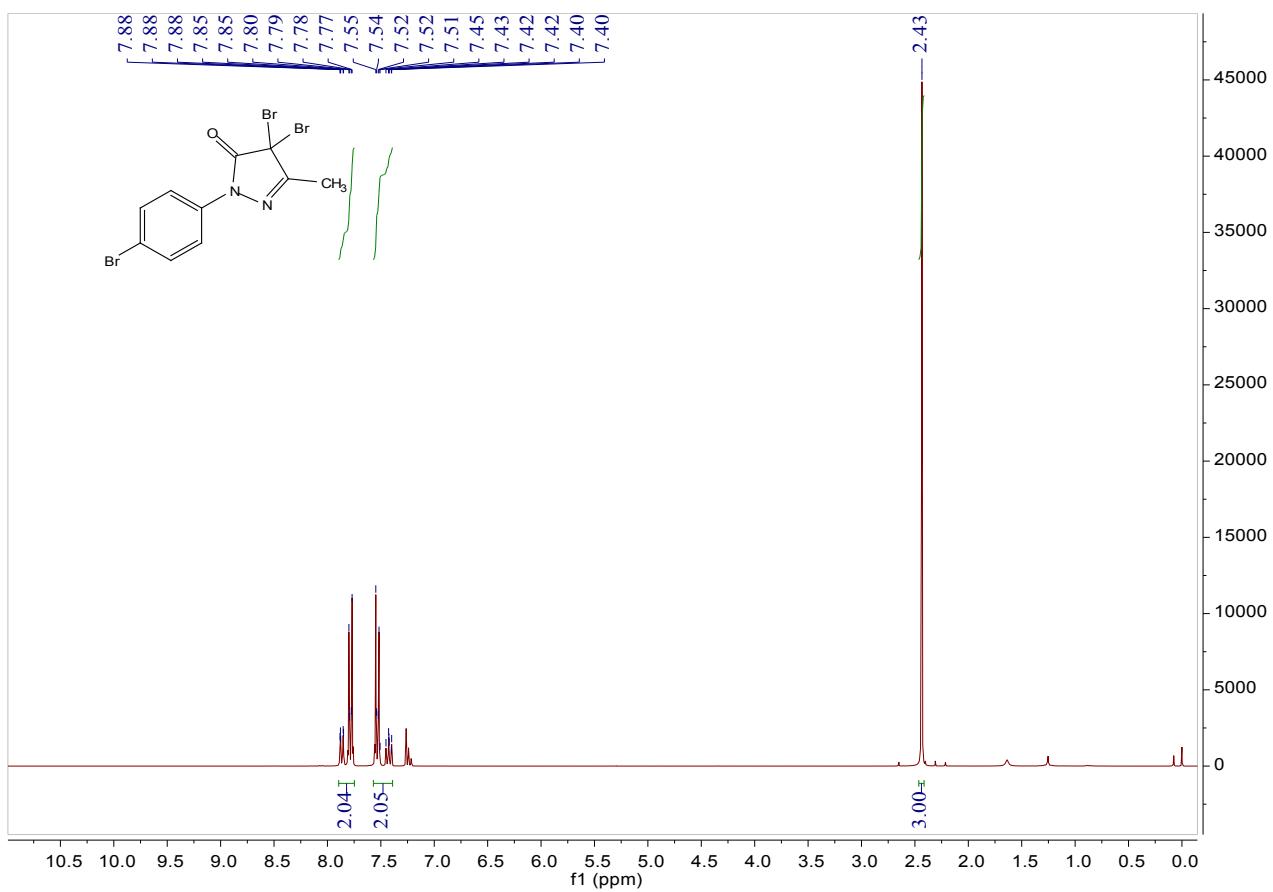
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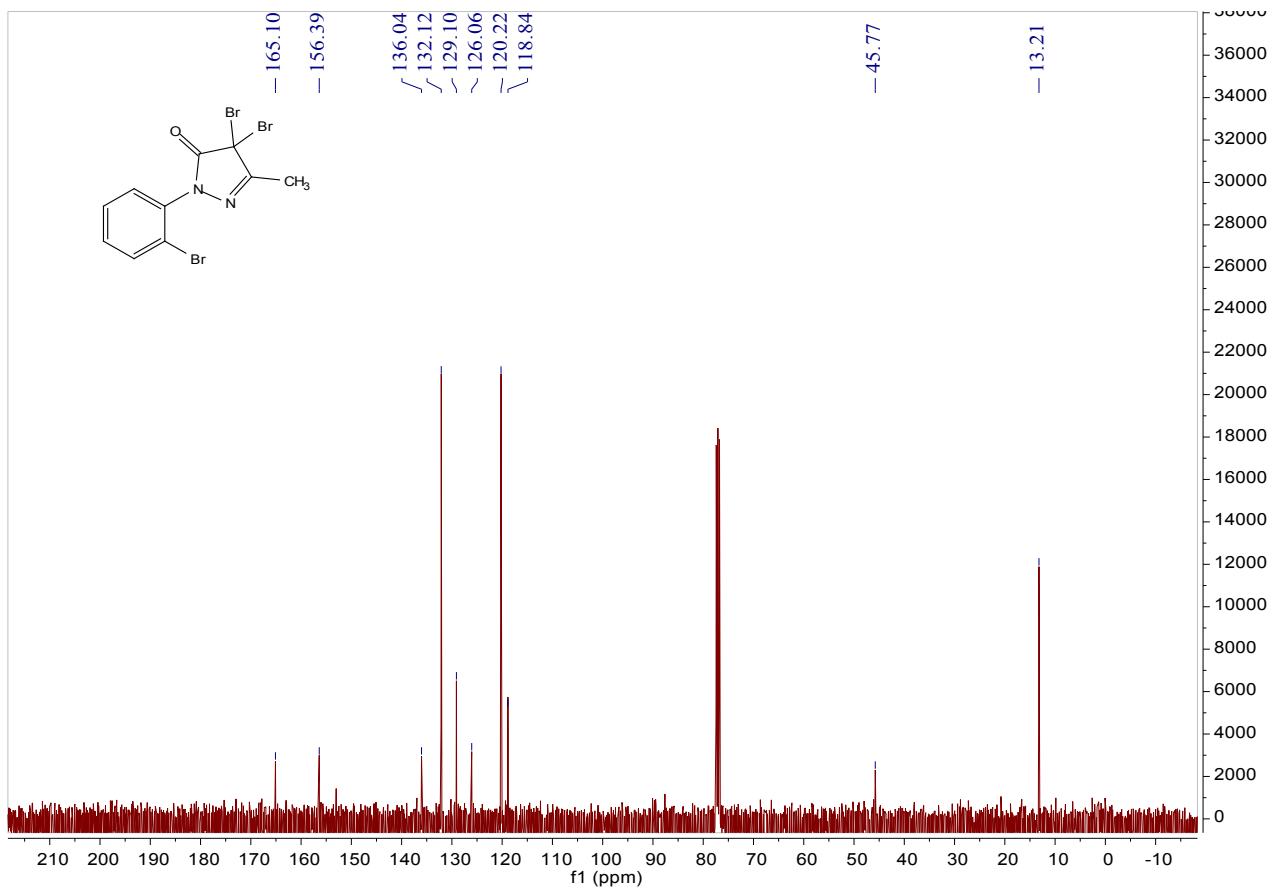
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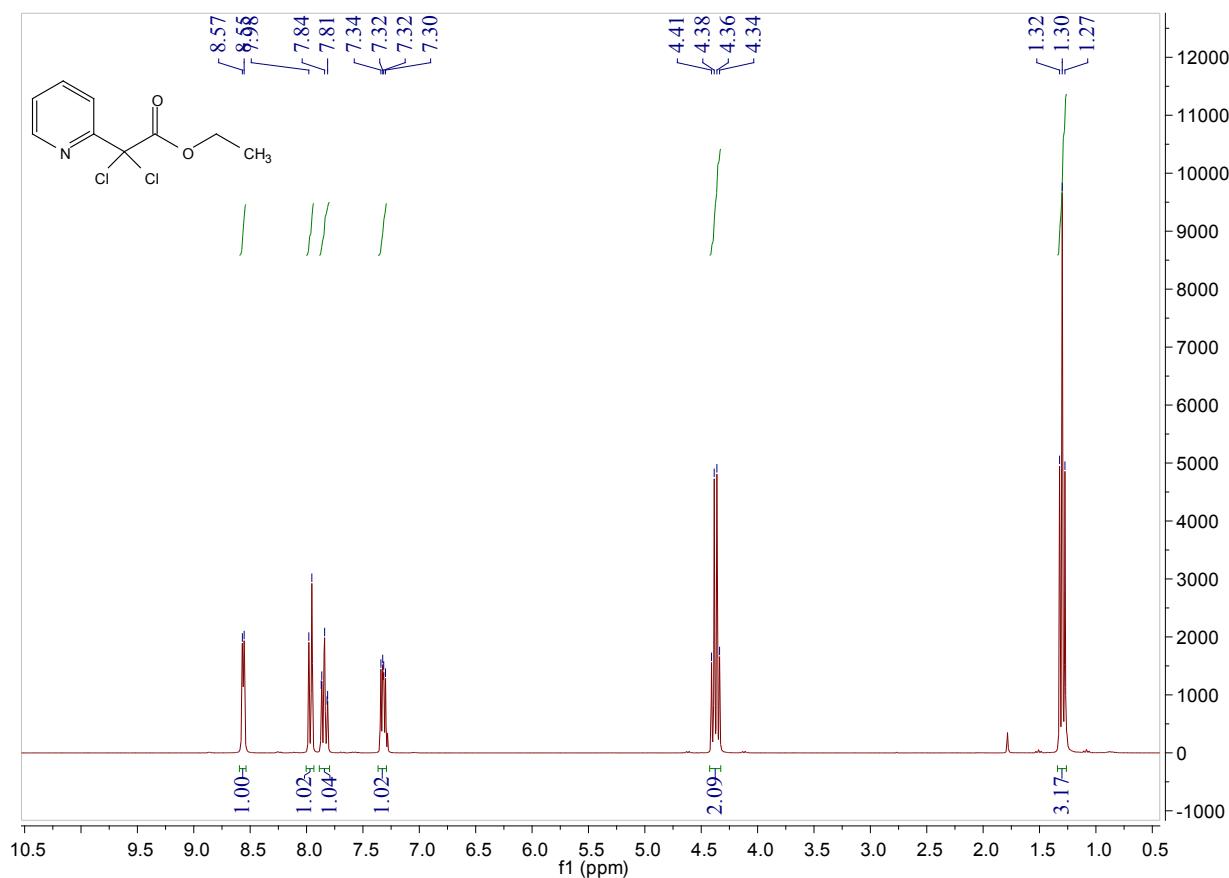
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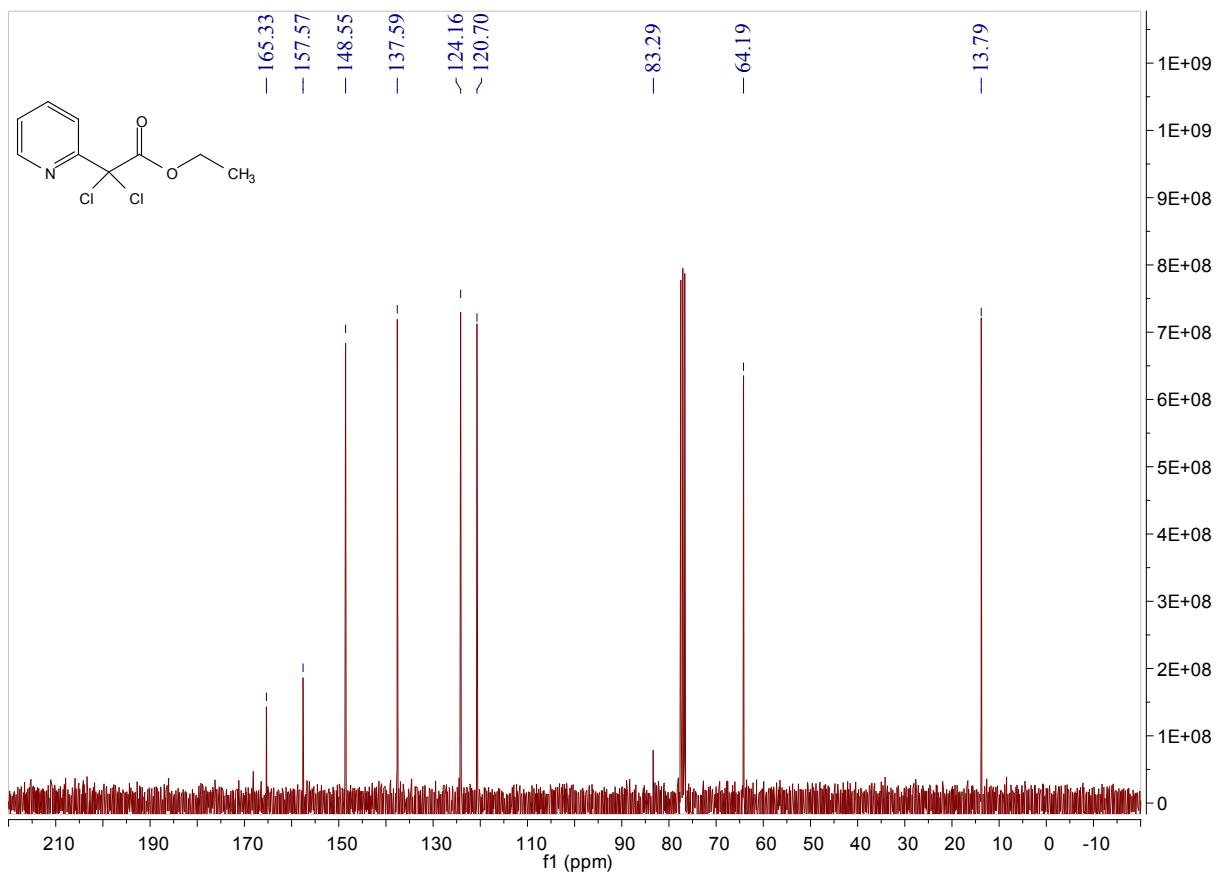
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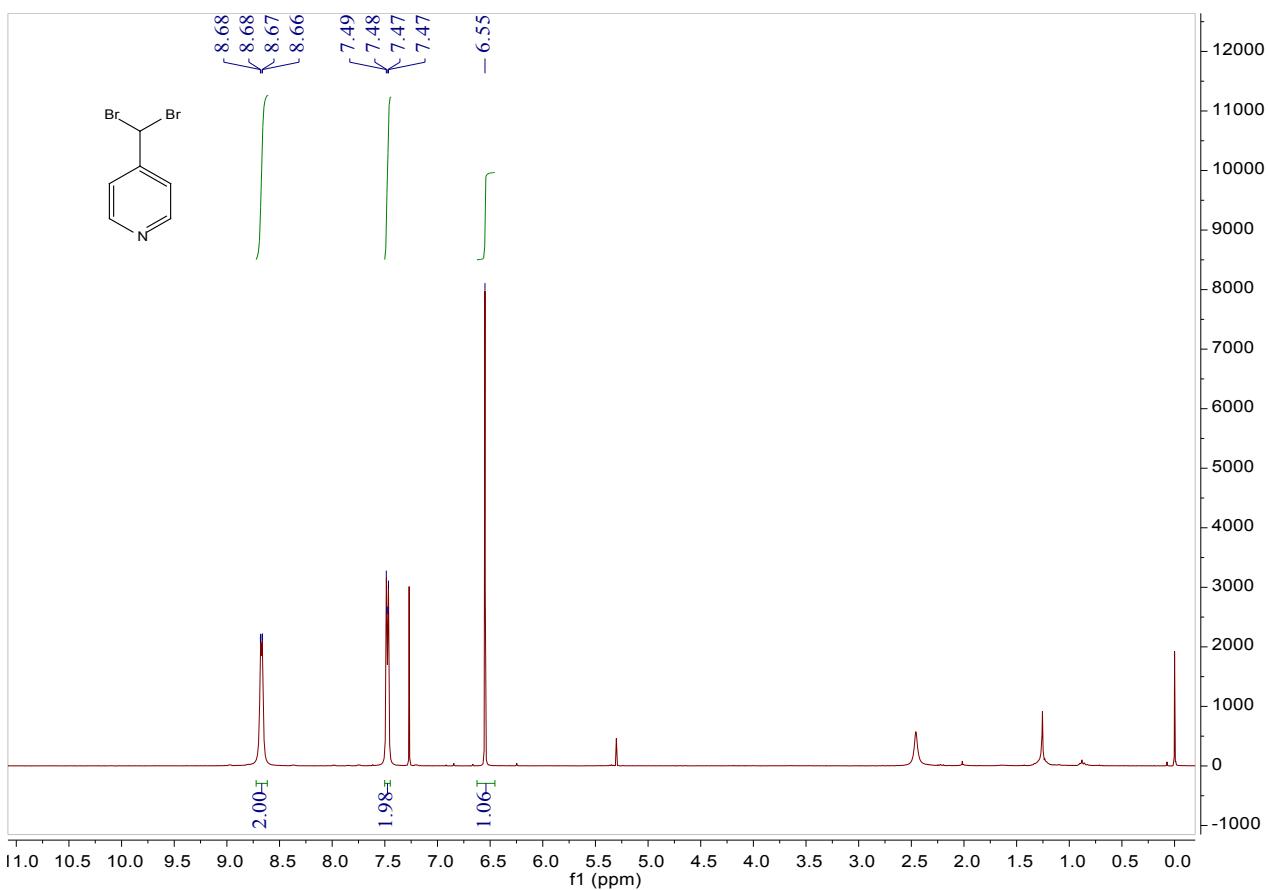
¹H NMR of **3h**



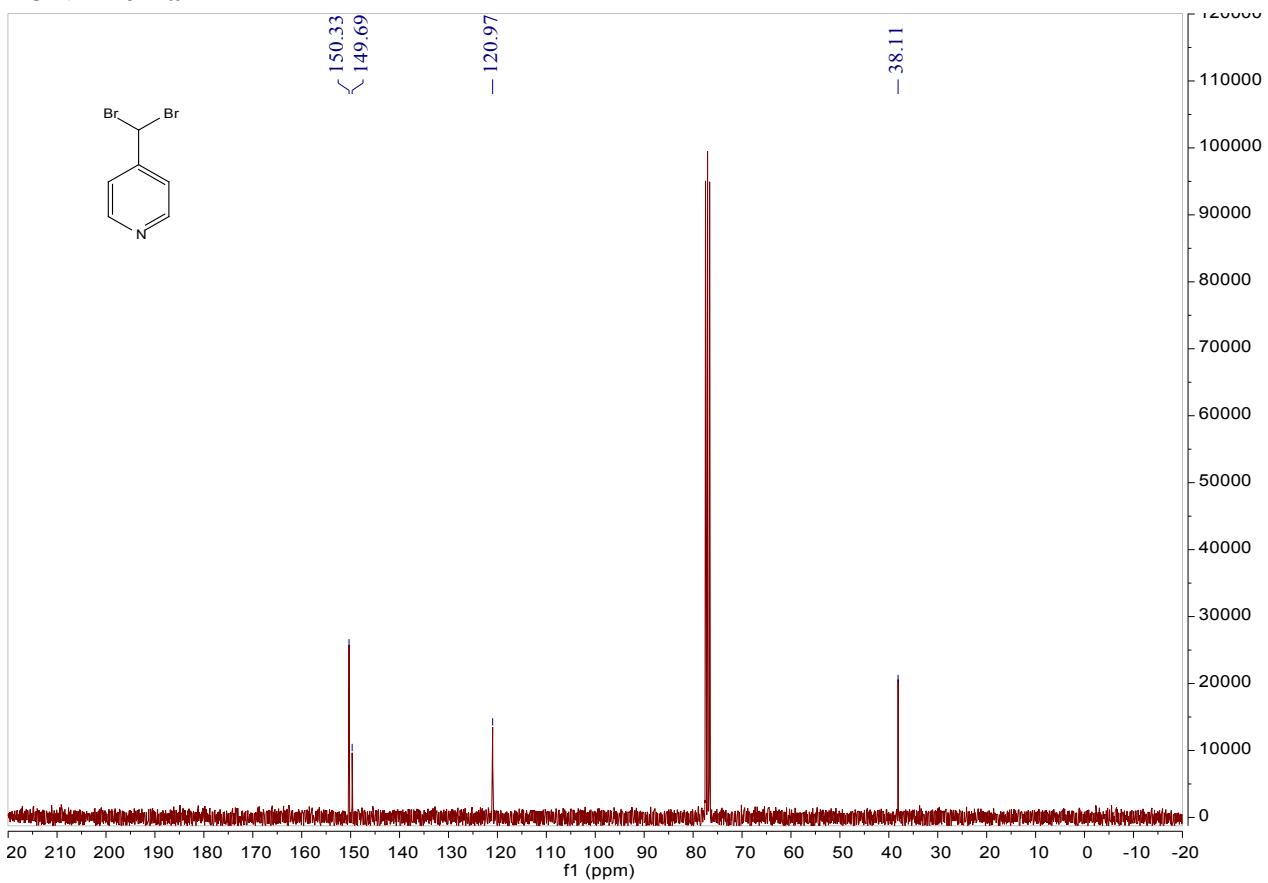
¹³C NMR of **2z**



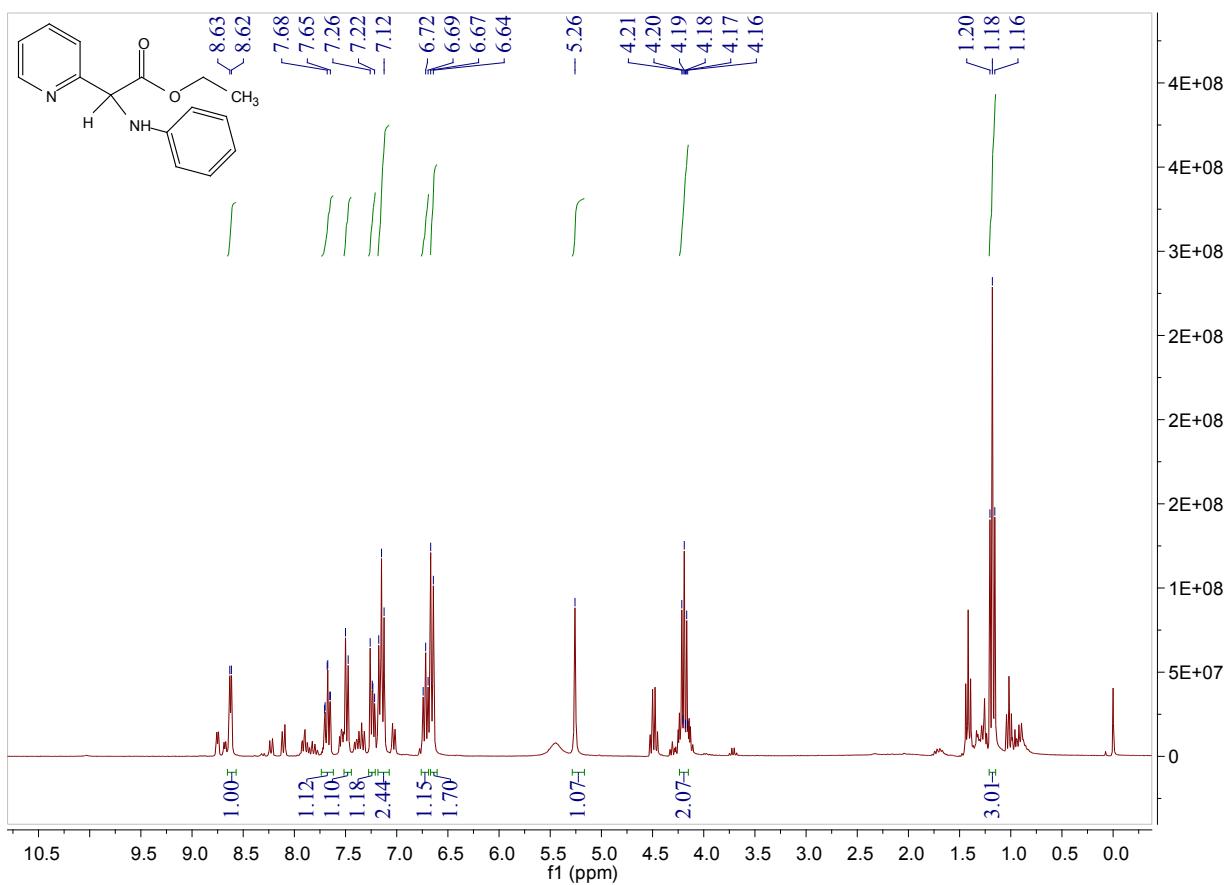
¹H NMR of **4a**



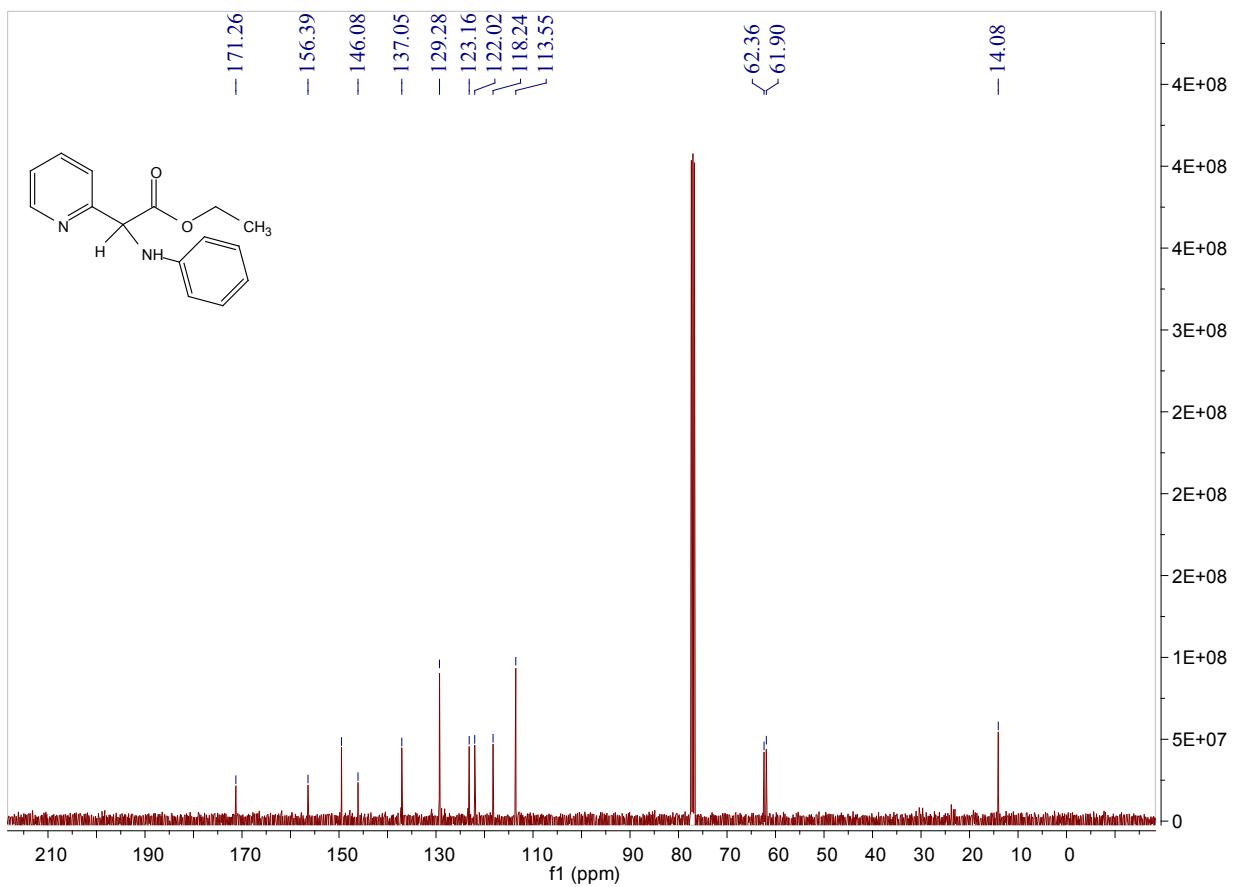
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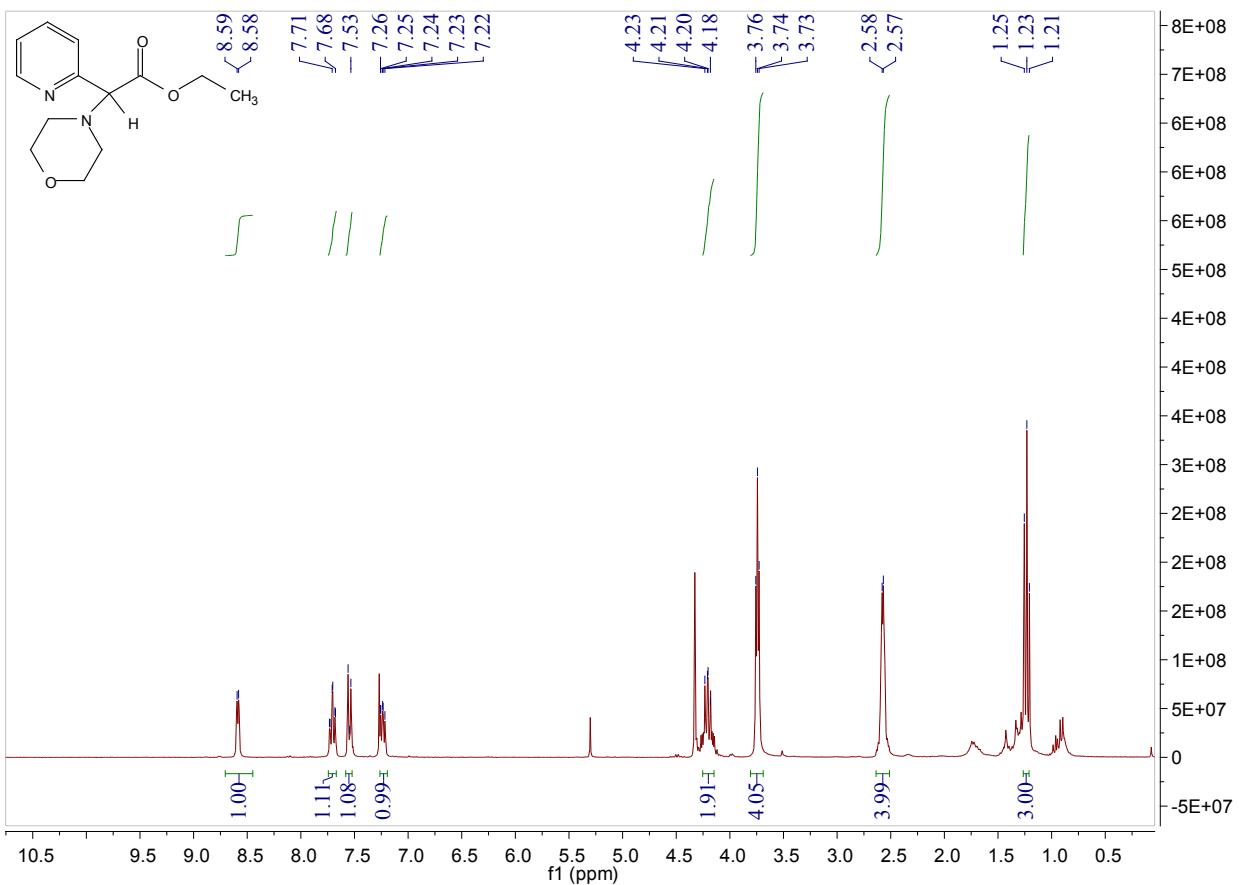
¹H NMR of **4b** (mixture of mono/di substitution)



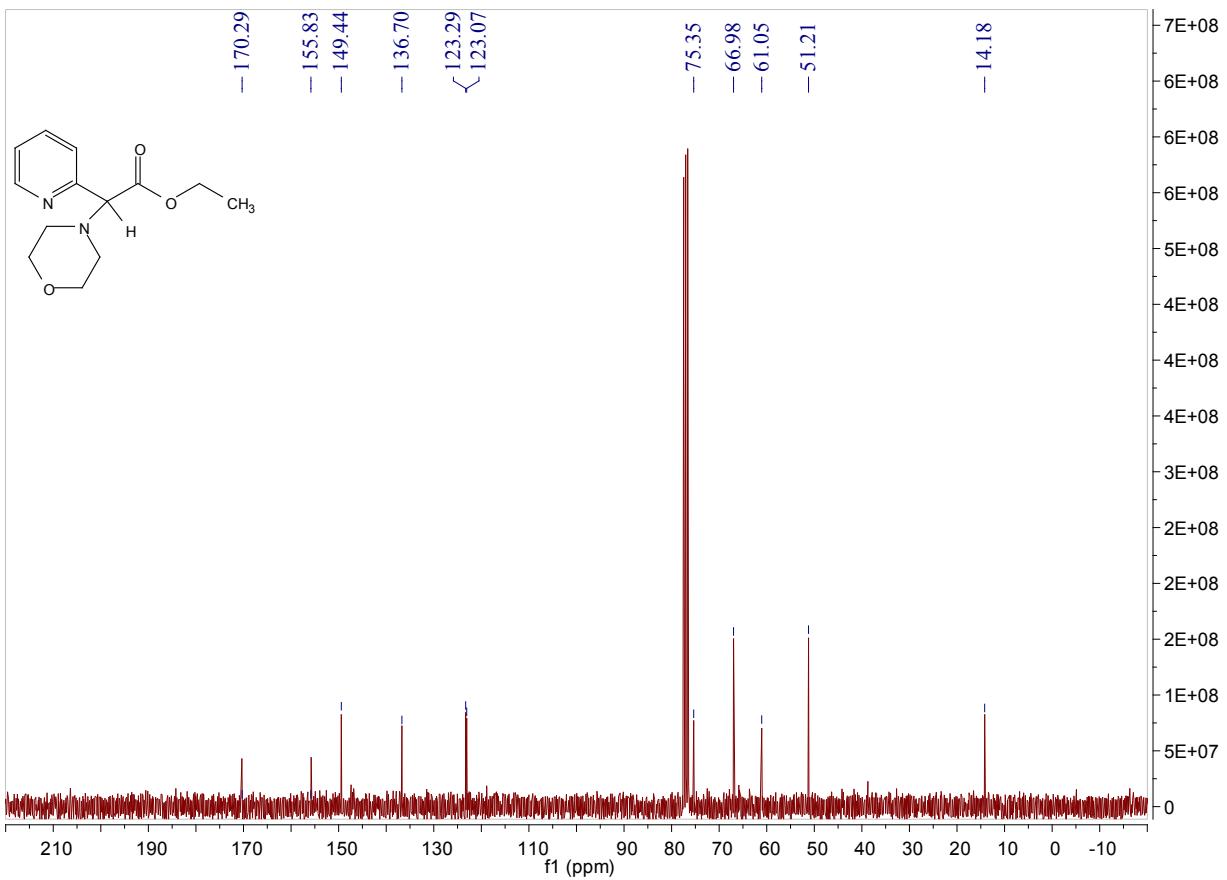
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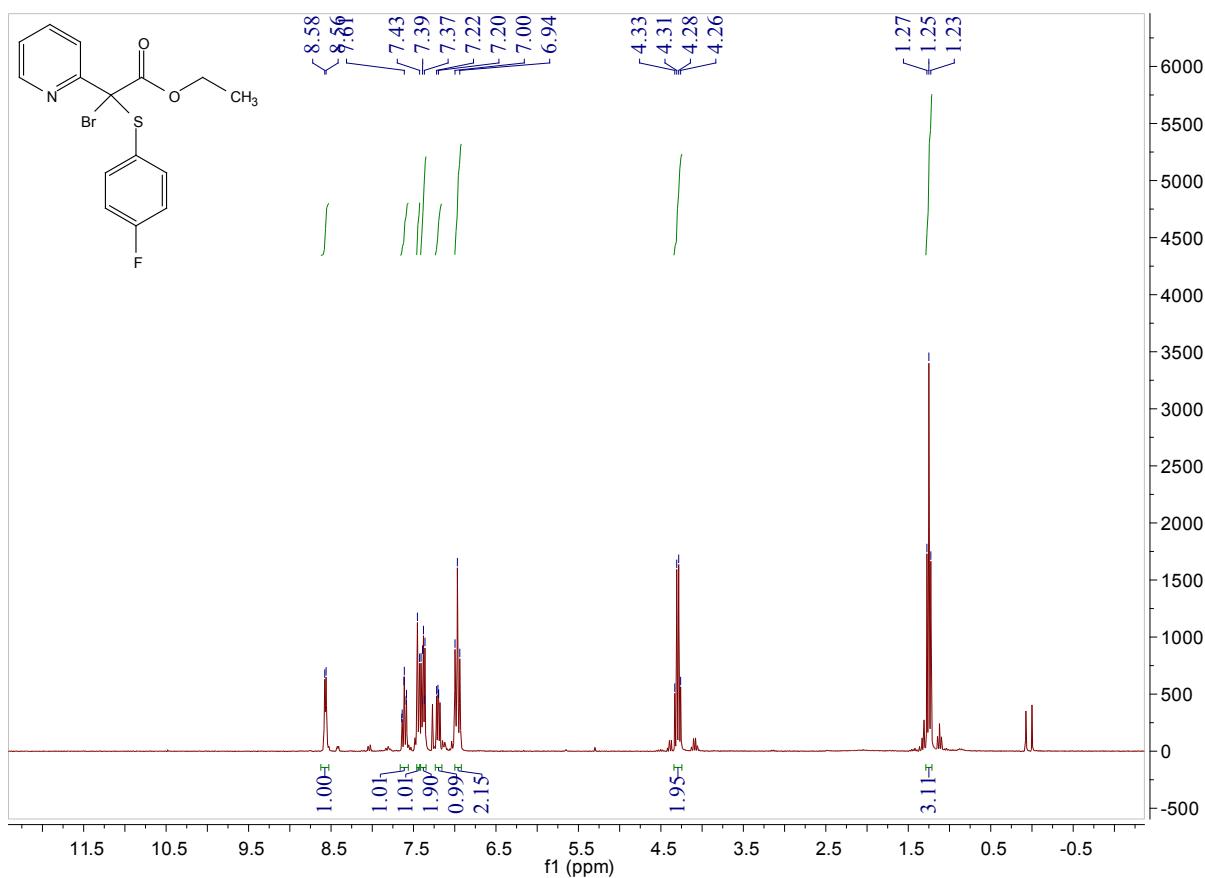
¹H NMR of **4c**



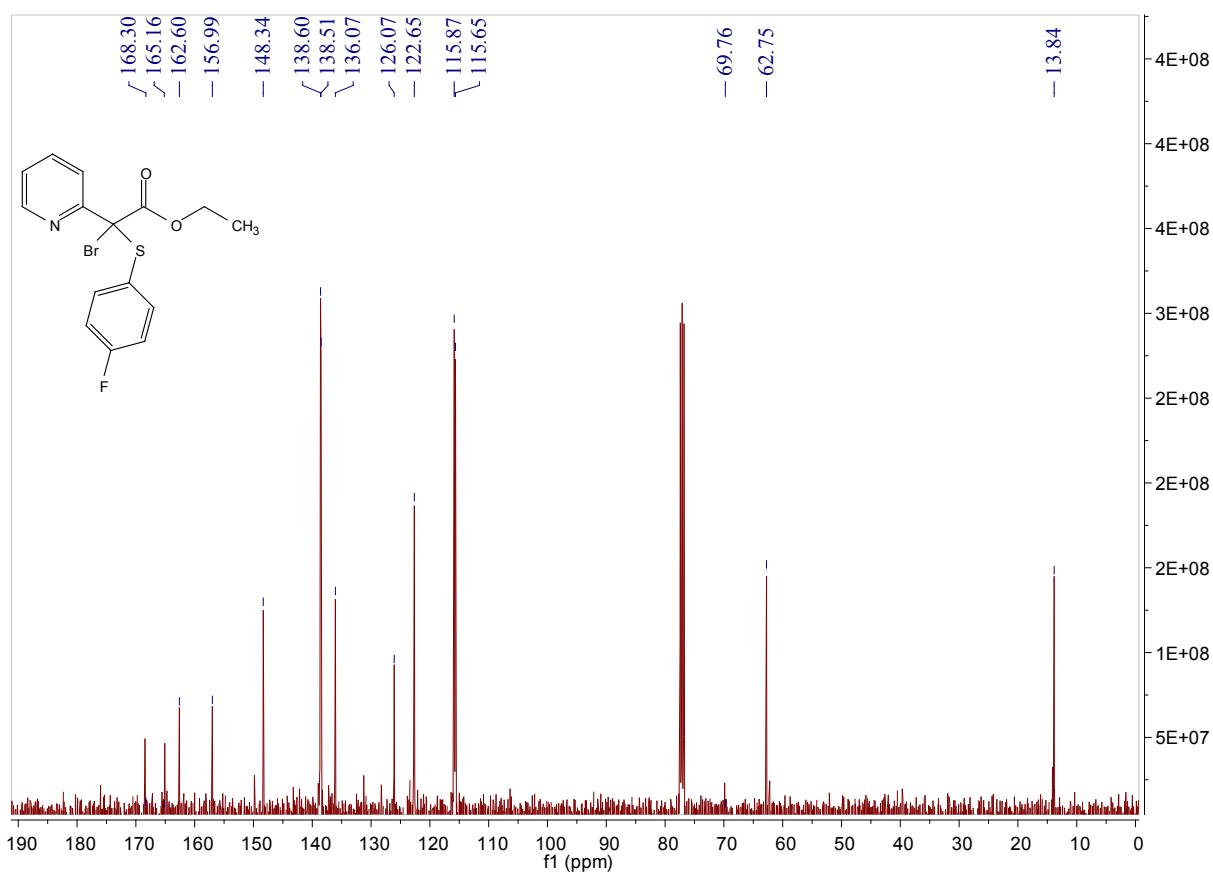
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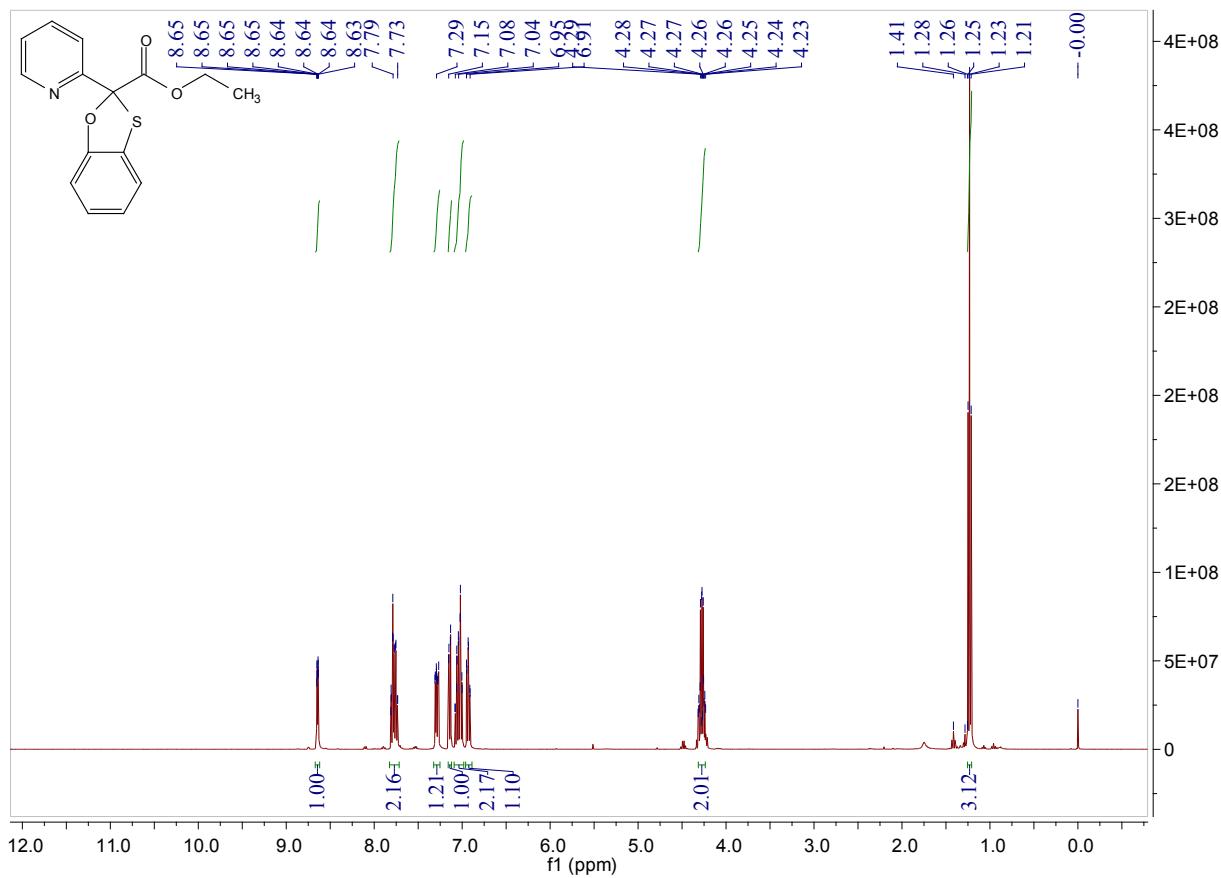
¹H NMR of **4d**



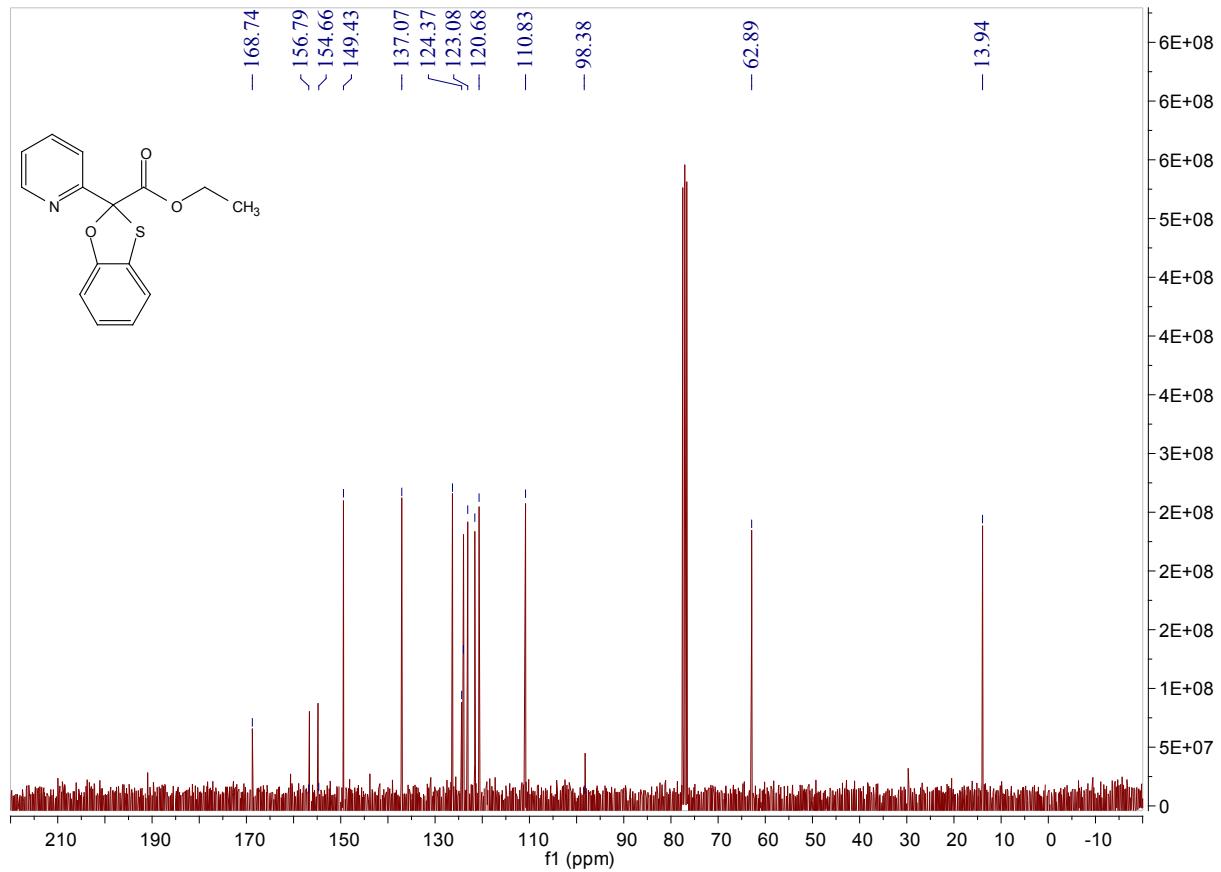
¹³C NMR of **4d**



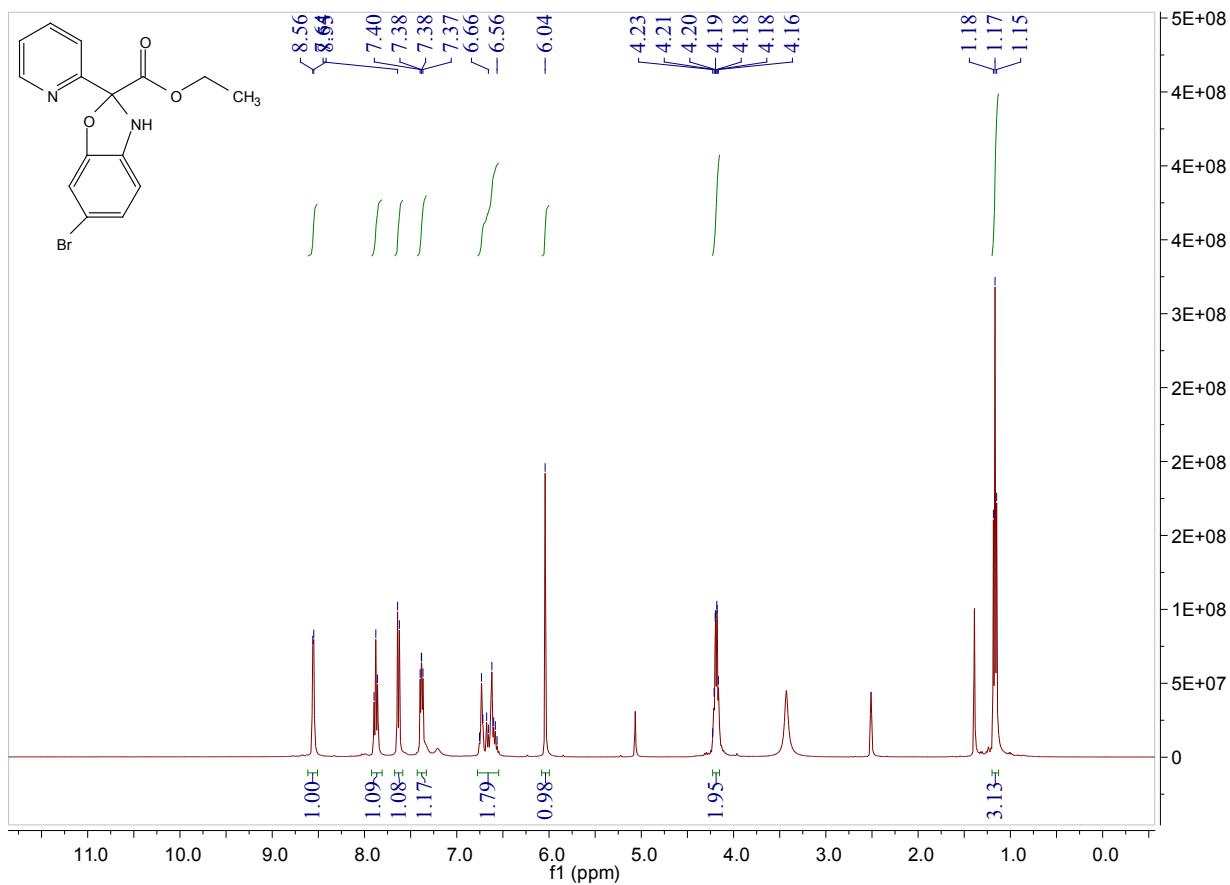
¹H NMR of **4e**



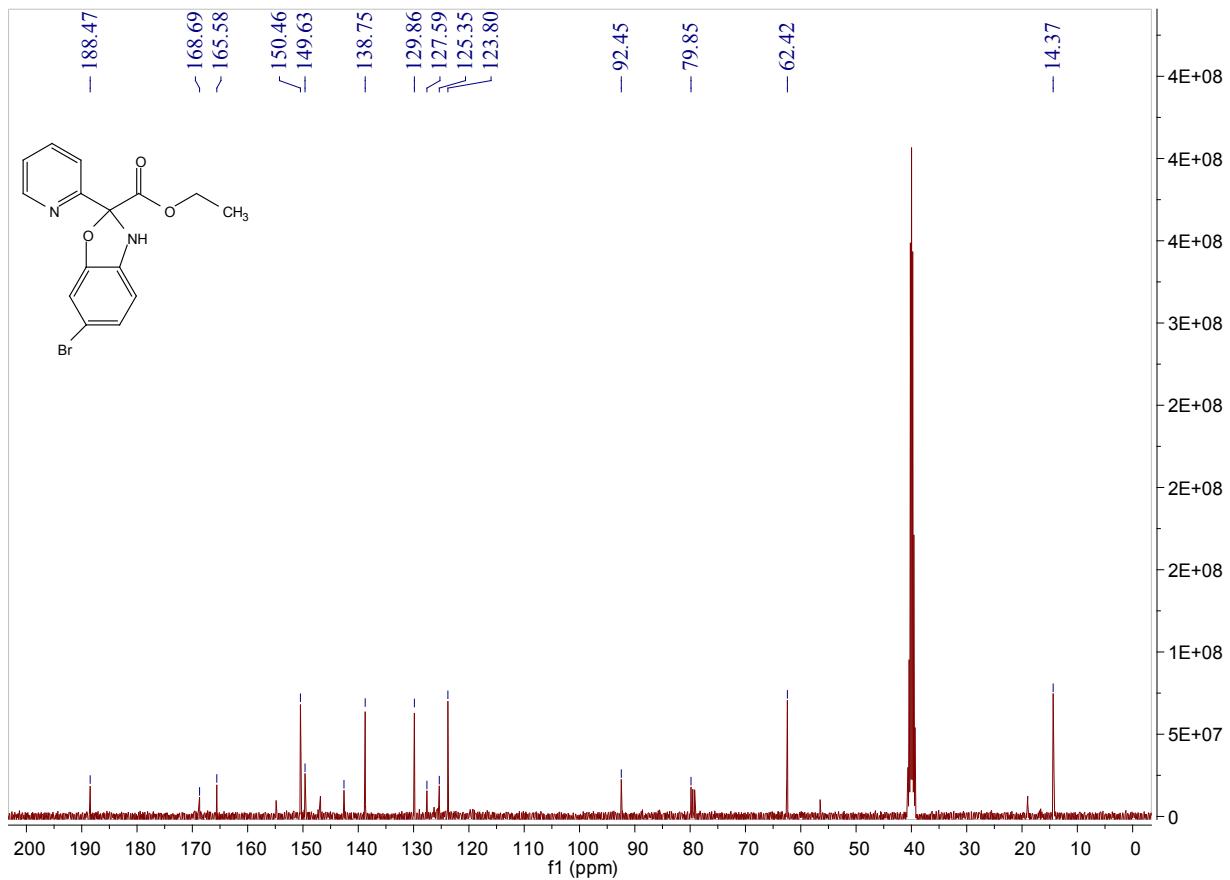
¹³C NMR of **4e**



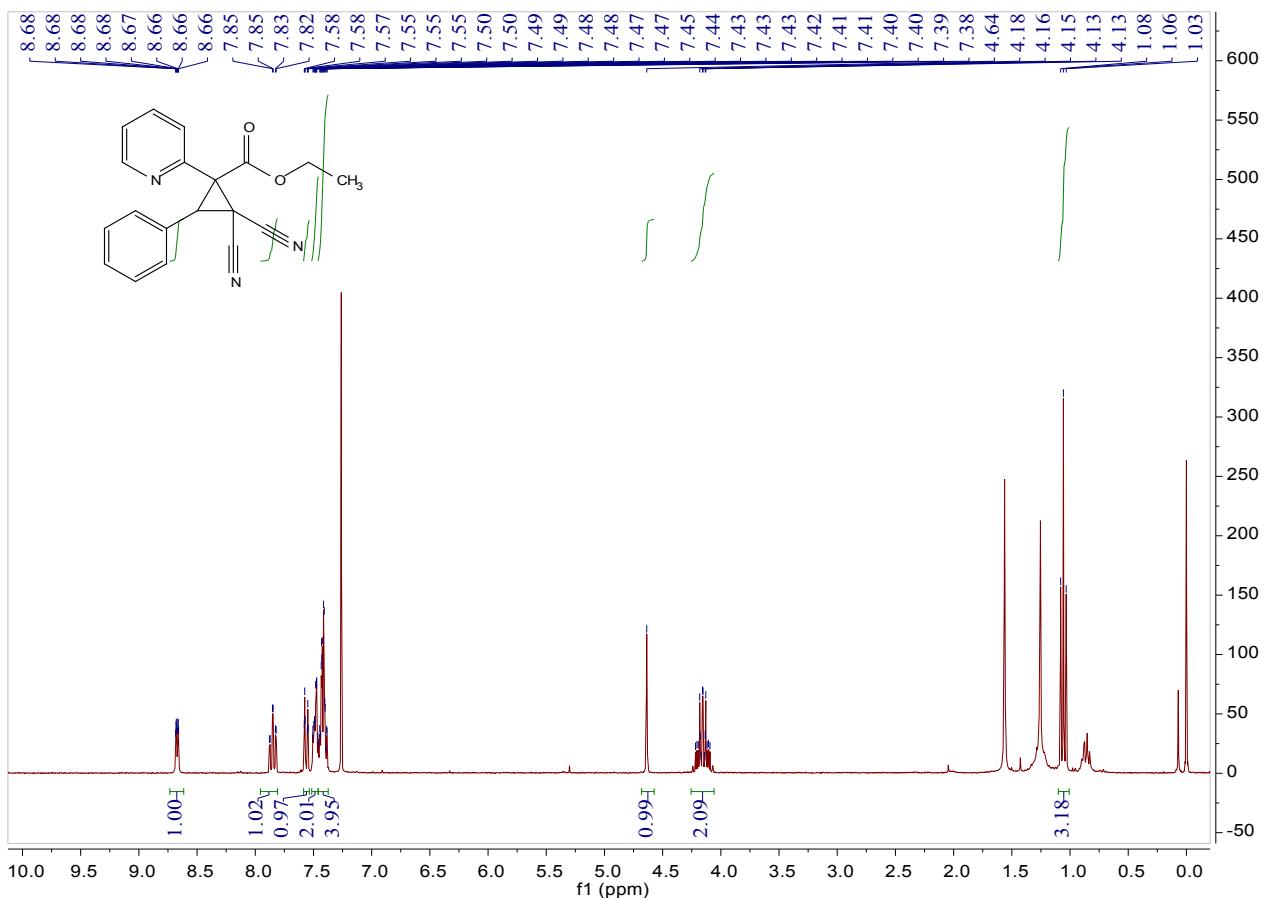
¹H NMR of **4f**



¹³C NMR of **4f**



¹H NMR of **4g**



¹³C NMR of 4g

