

SUPPORTING INFORMATION

Blaise Reaction: Synthesis, skeletal diversification of C(4) substituted 5-ylidenepyrrol-(5*H*)-ones and the role of the strategically located ester on the reactivity of the nitriles

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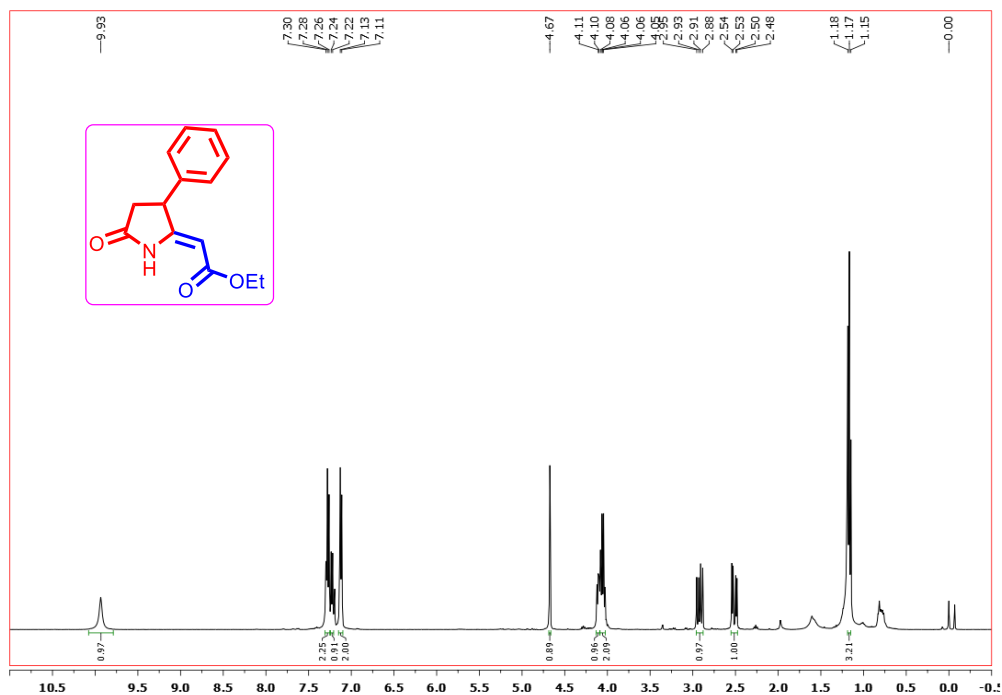
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hspr.che@pondiuni.edu.in; hspr@yahoo.com

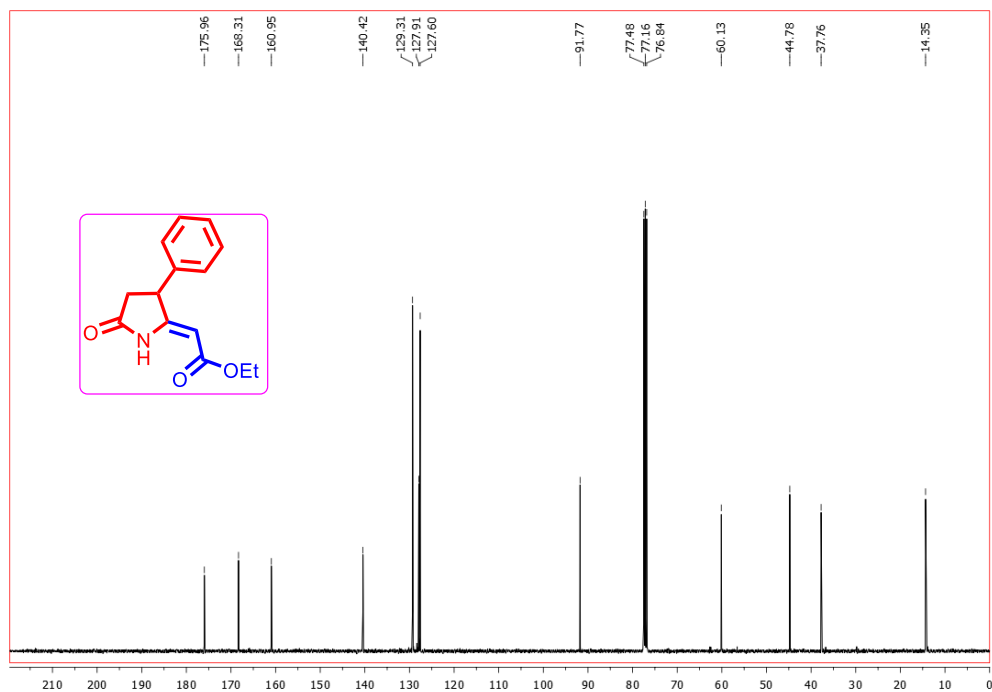
[b] Department of Chemistry and Biochemistry, Sharda University, Knowledge Park III, Greater Noida (Delhi NCR) 201306 UP, India.

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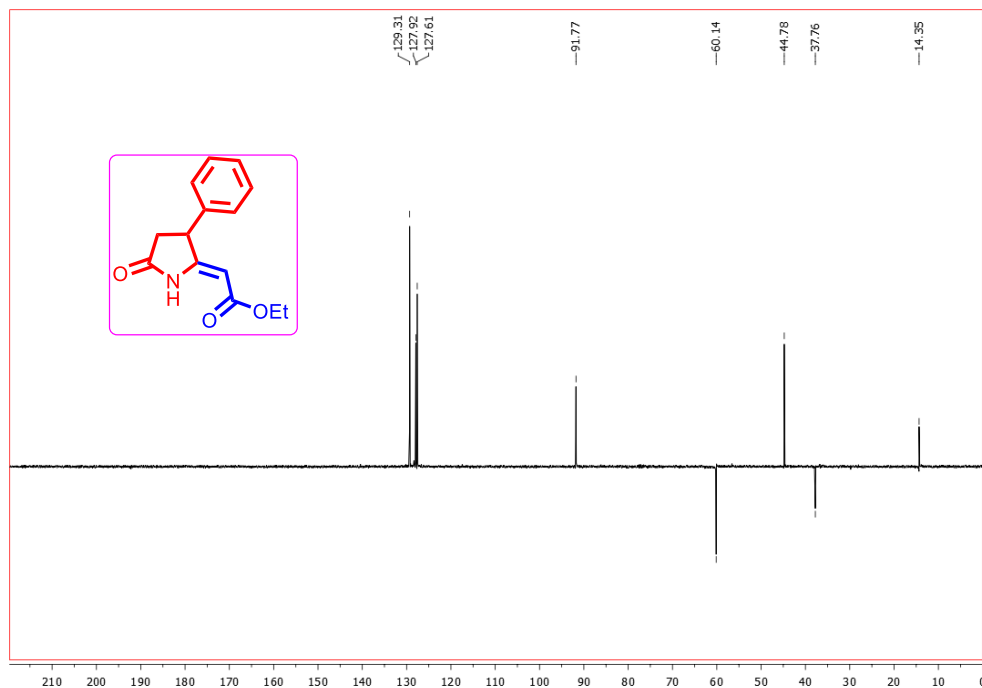
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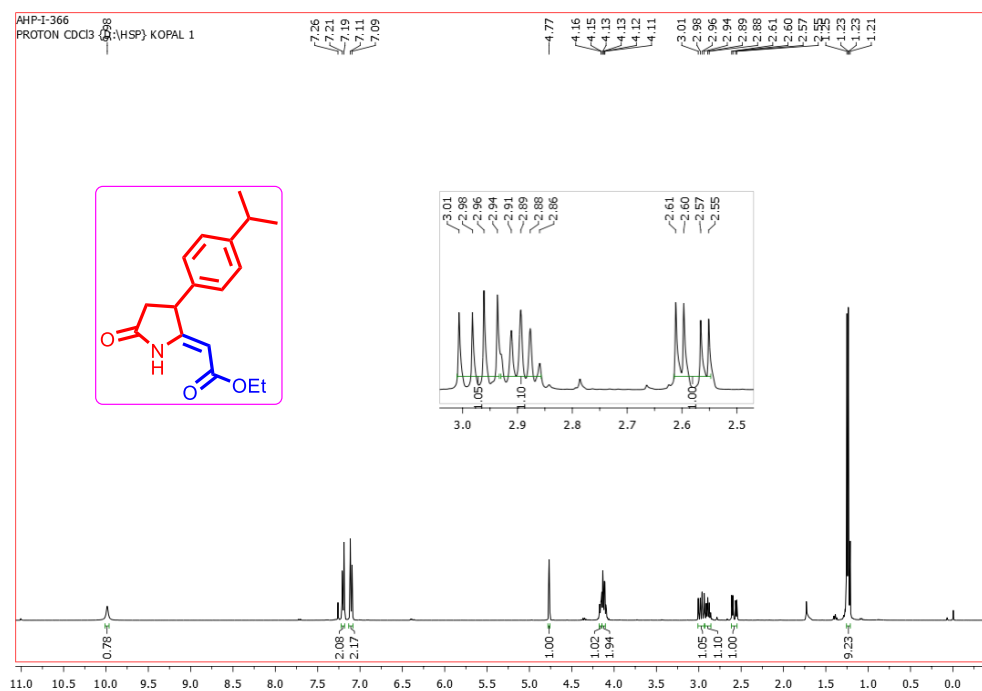
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-phenylpyrrolidin-2-ylidene)acetate **12a**.



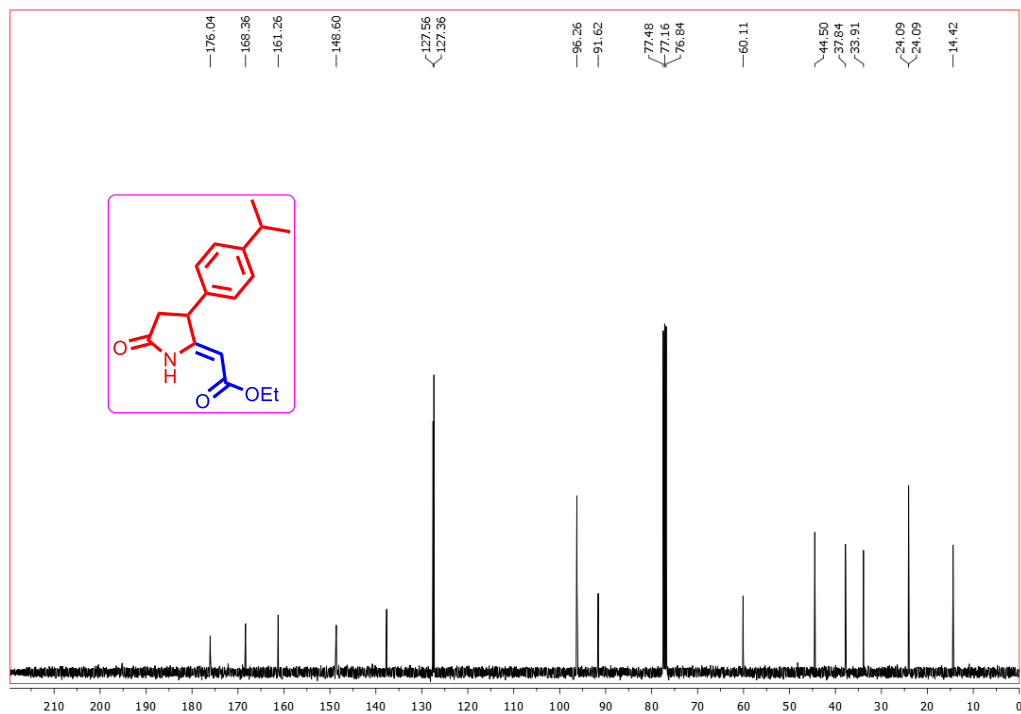
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-phenylpyrrolidin-2-ylidene)acetate **12a**.



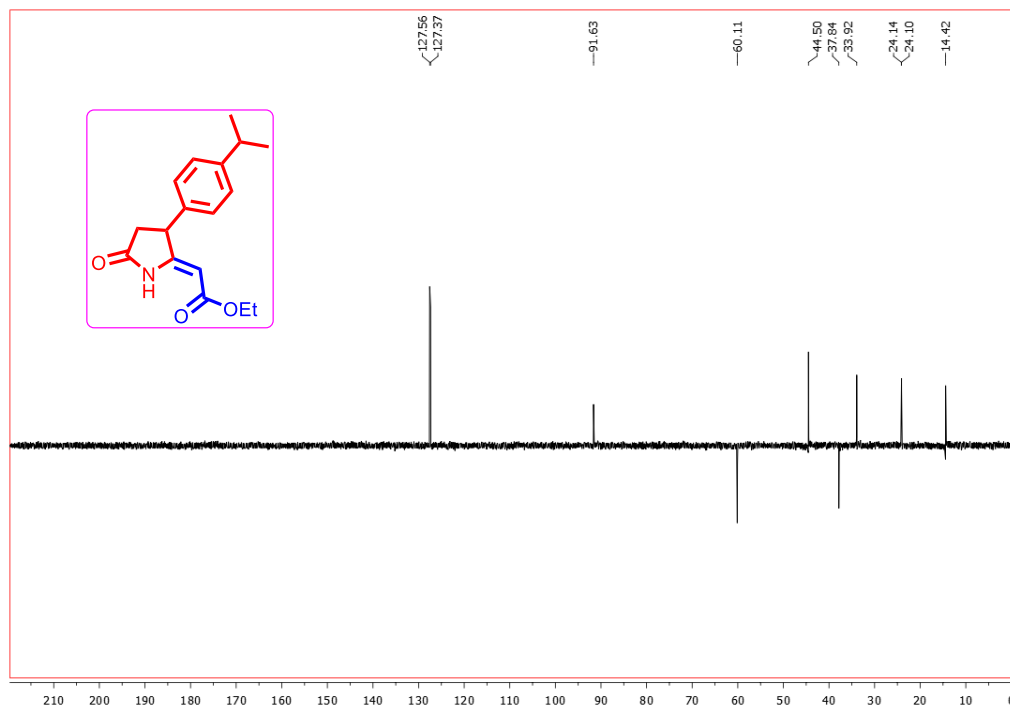
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-phenylpyrrolidin-2-ylidene)acetate **12a**.



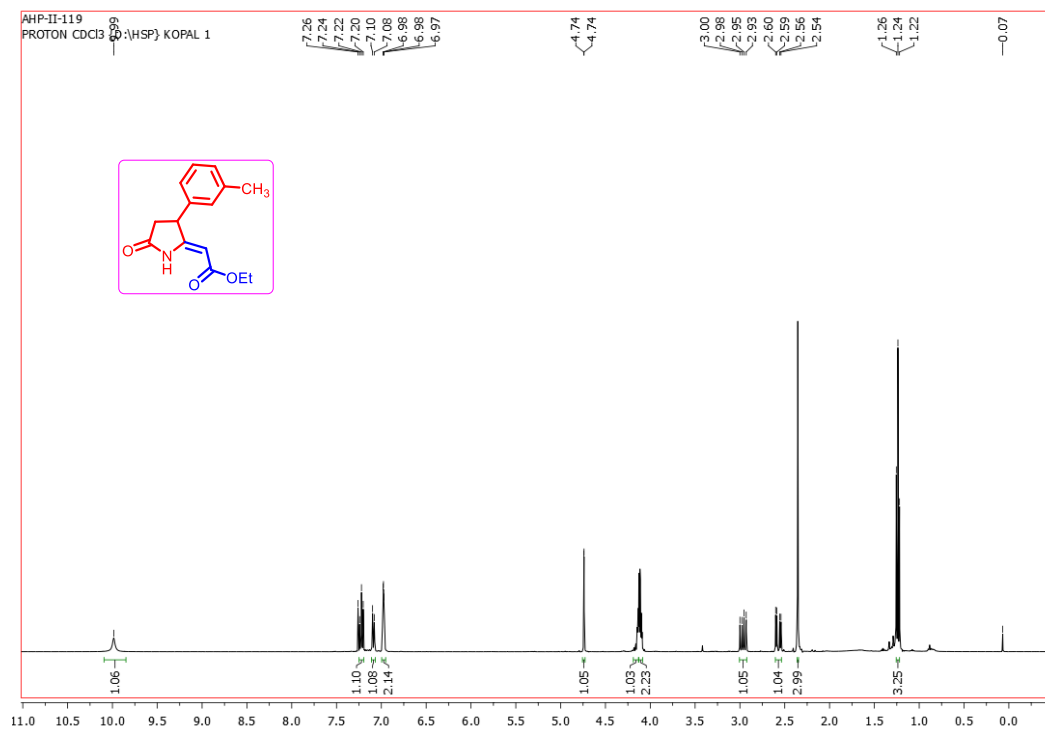
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-isopropylphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12b**.



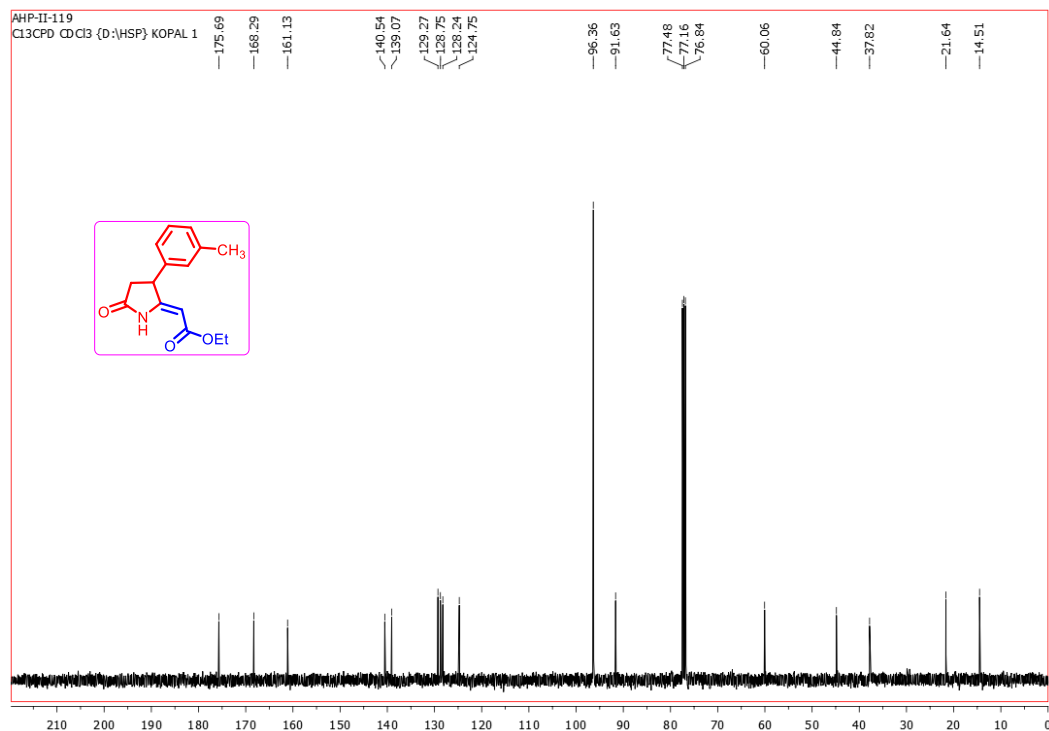
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-isopropylphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12b**.



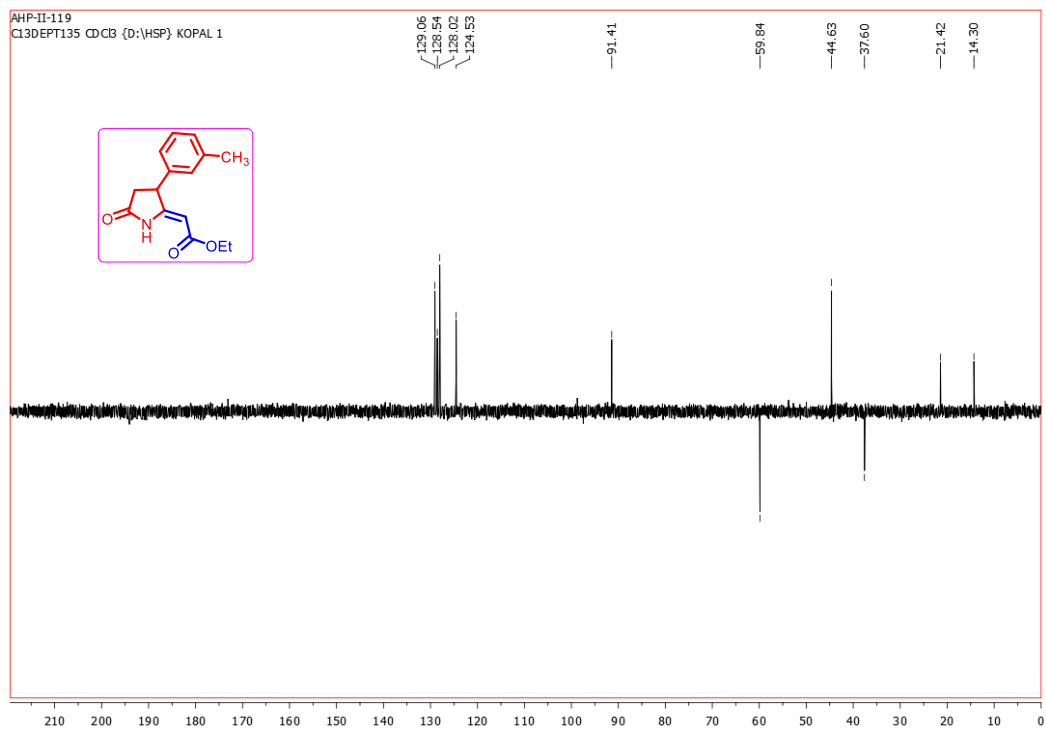
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-isopropylphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12b**.



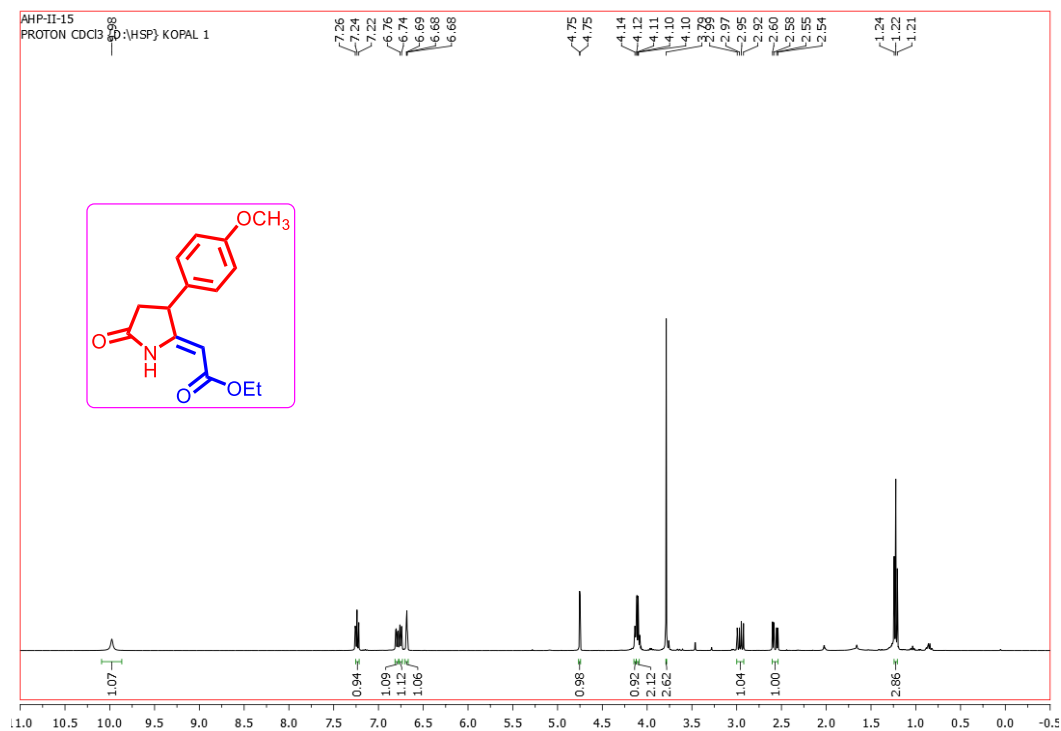
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-(m-tolyl)pyrrolidin-2-ylidene)acetate **12c**.



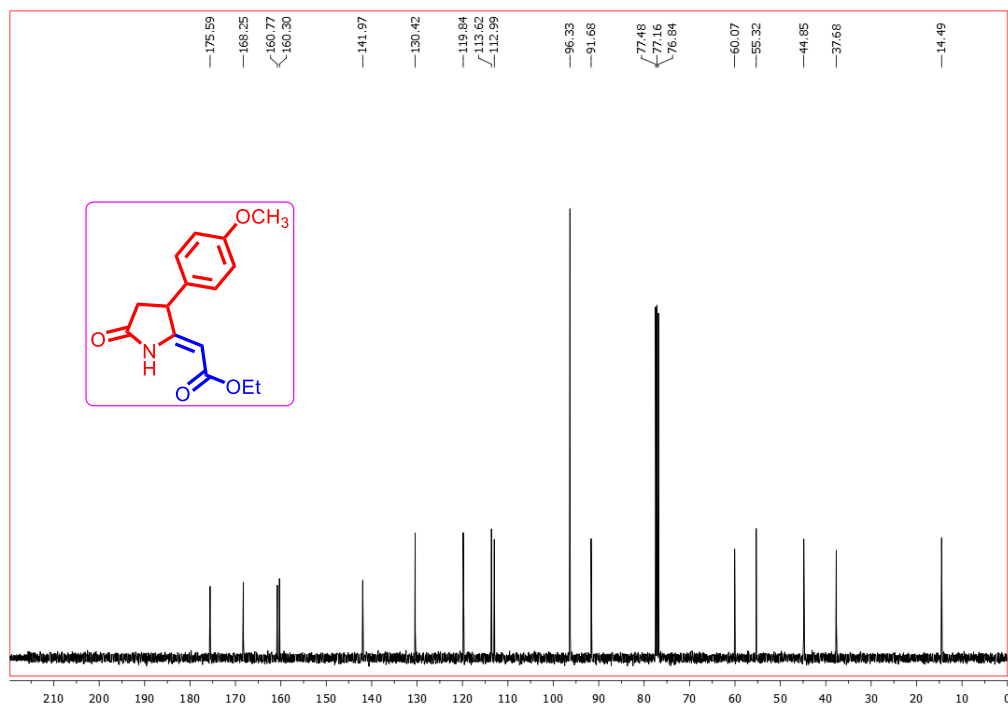
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-(m-tolyl)pyrrolidin-2-ylidene)acetate **12c**.



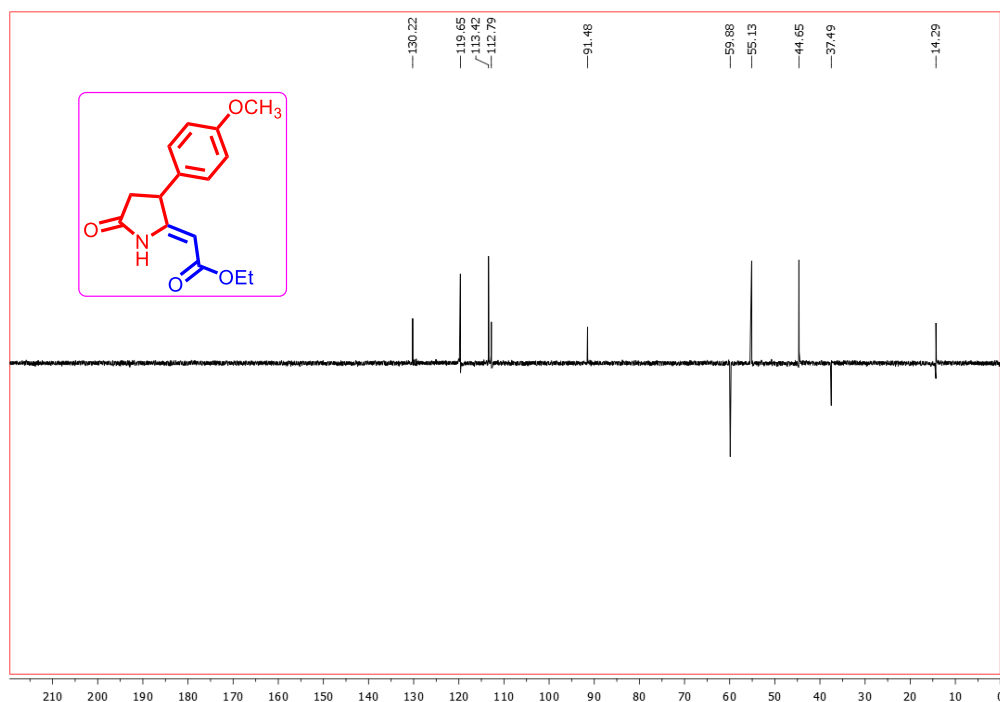
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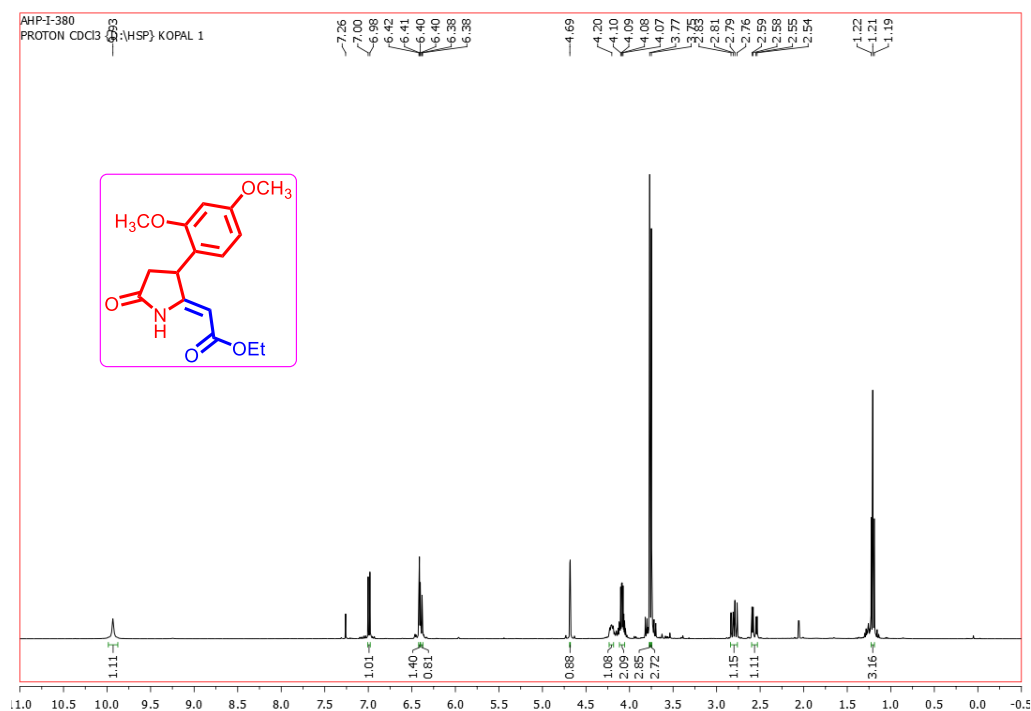
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-methoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12d**.



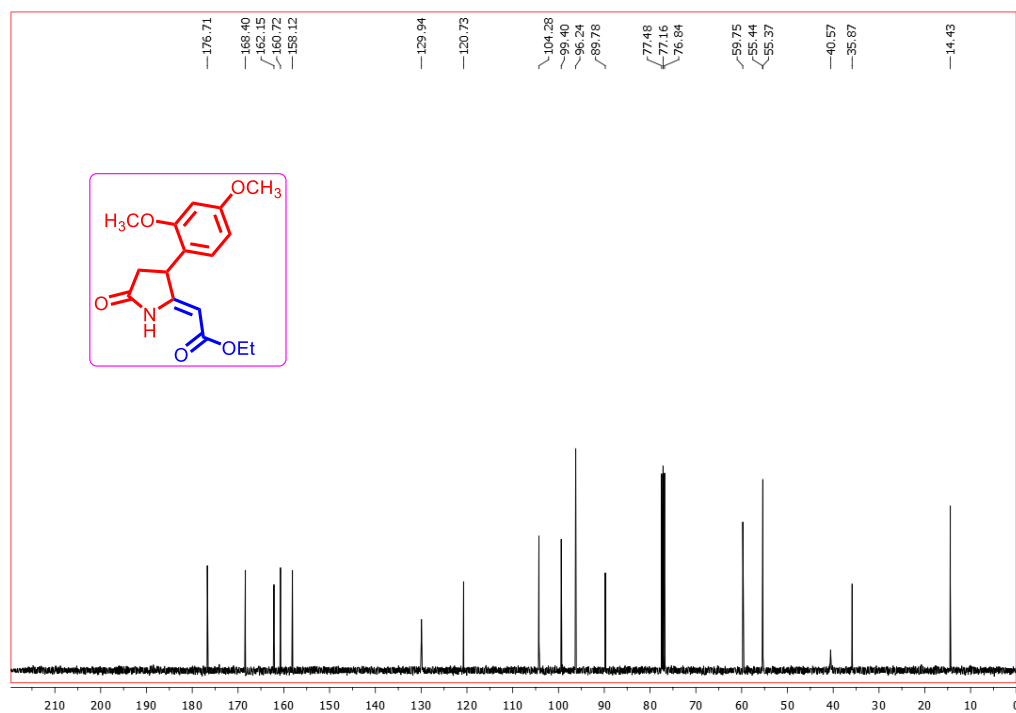
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(4-methoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12d**.



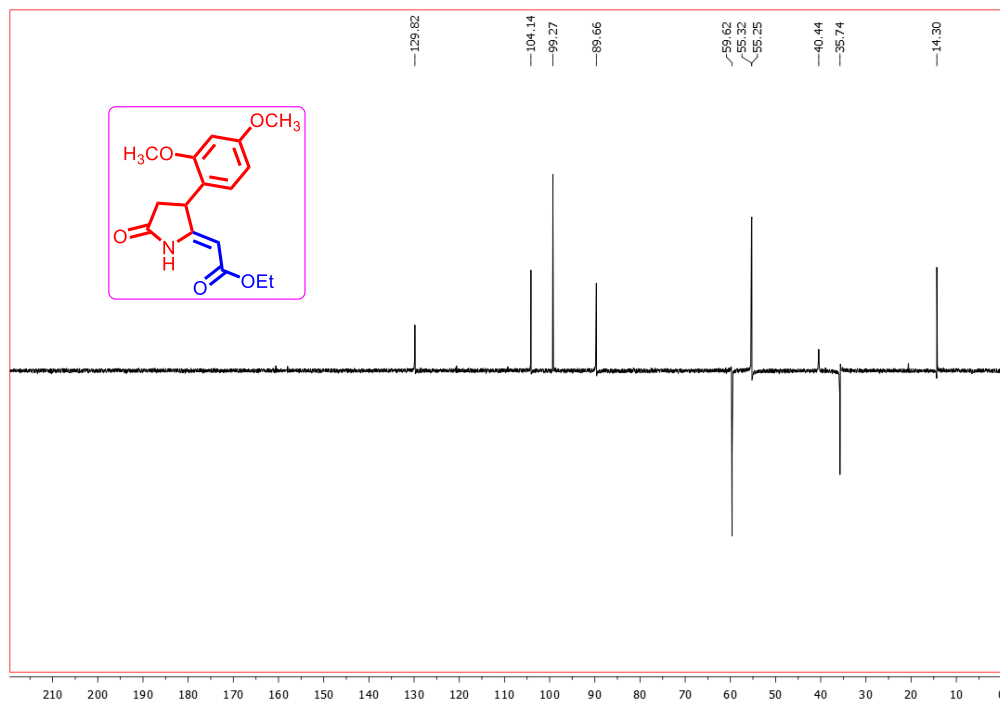
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(4-methoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12d**.



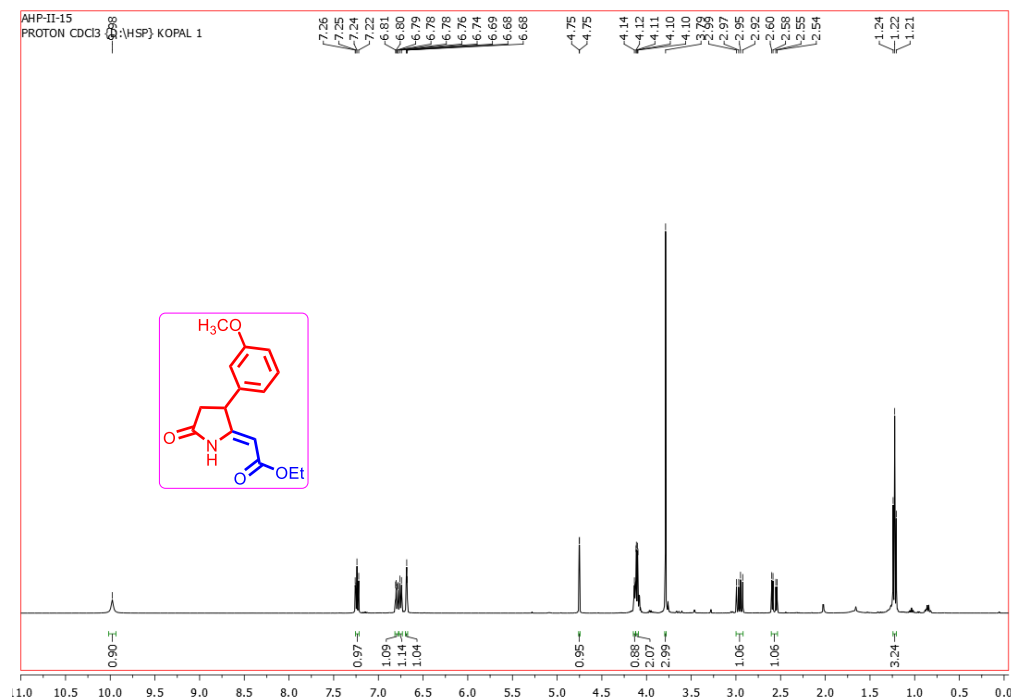
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(2,4-dimethoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12e**.



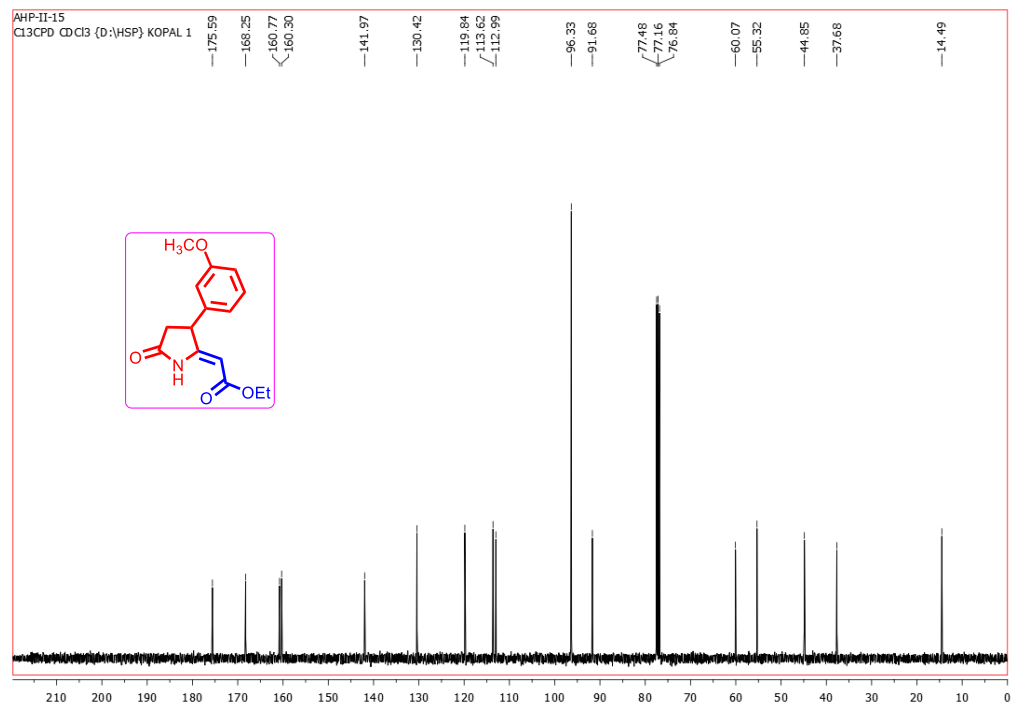
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(2,4-dimethoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12e**.



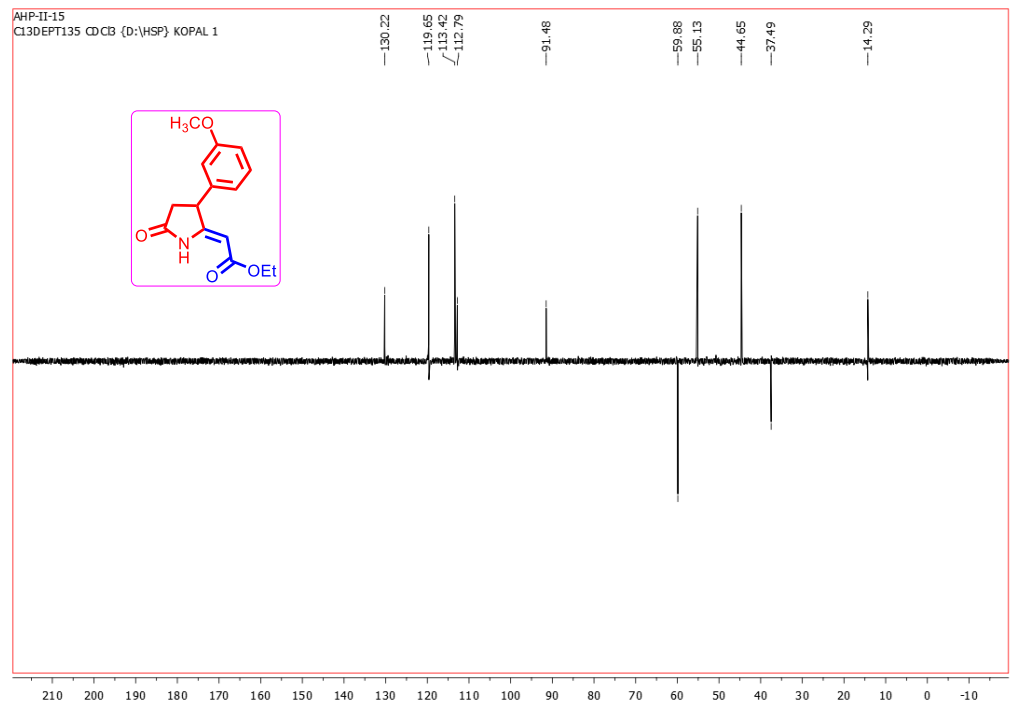
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(2,4-dimethoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12e**.



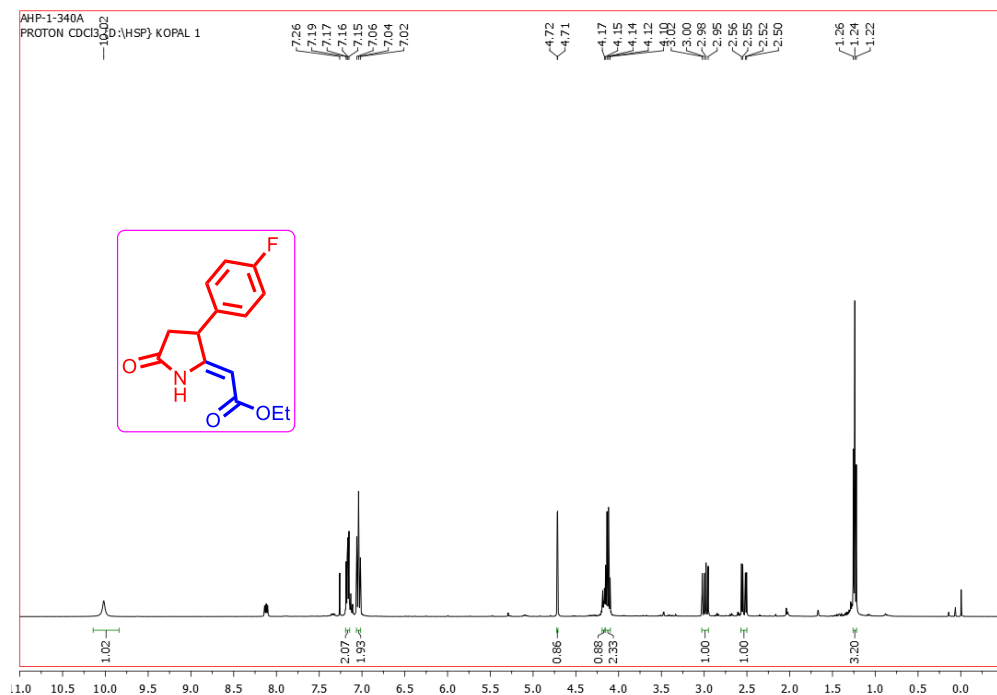
^1H (400 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(3-methoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12f**.



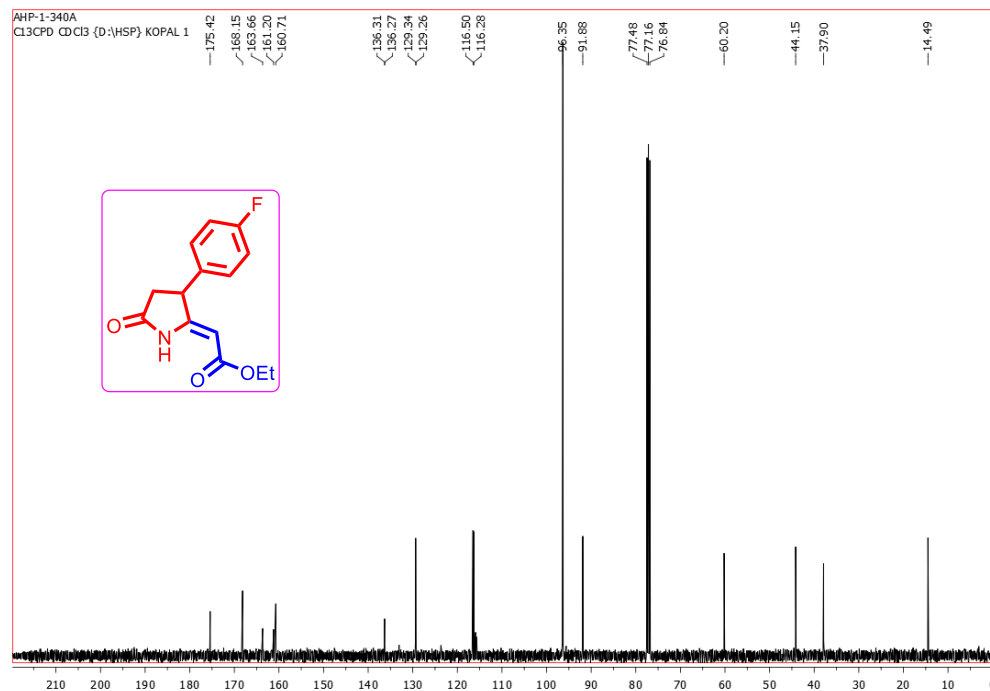
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(3-methoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12f**.



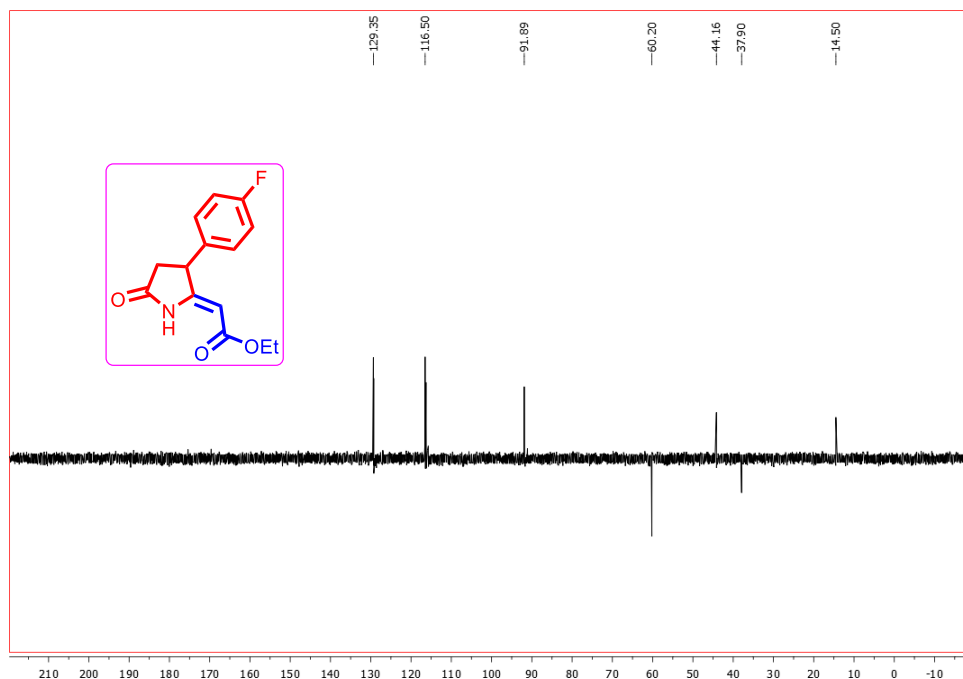
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(3-methoxyphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12f**.



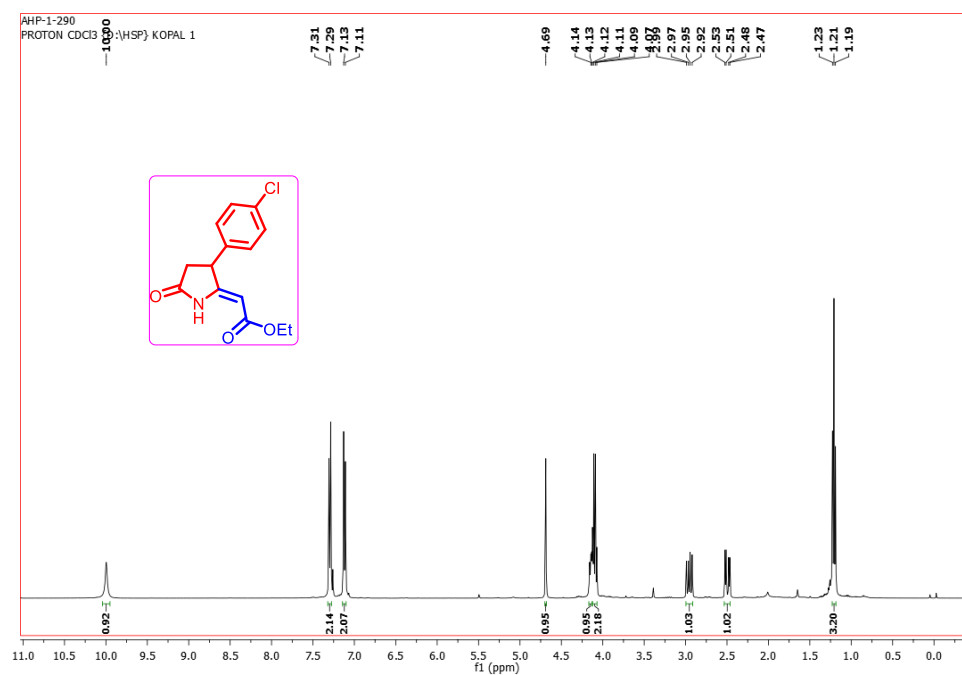
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-fluorophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12g**.



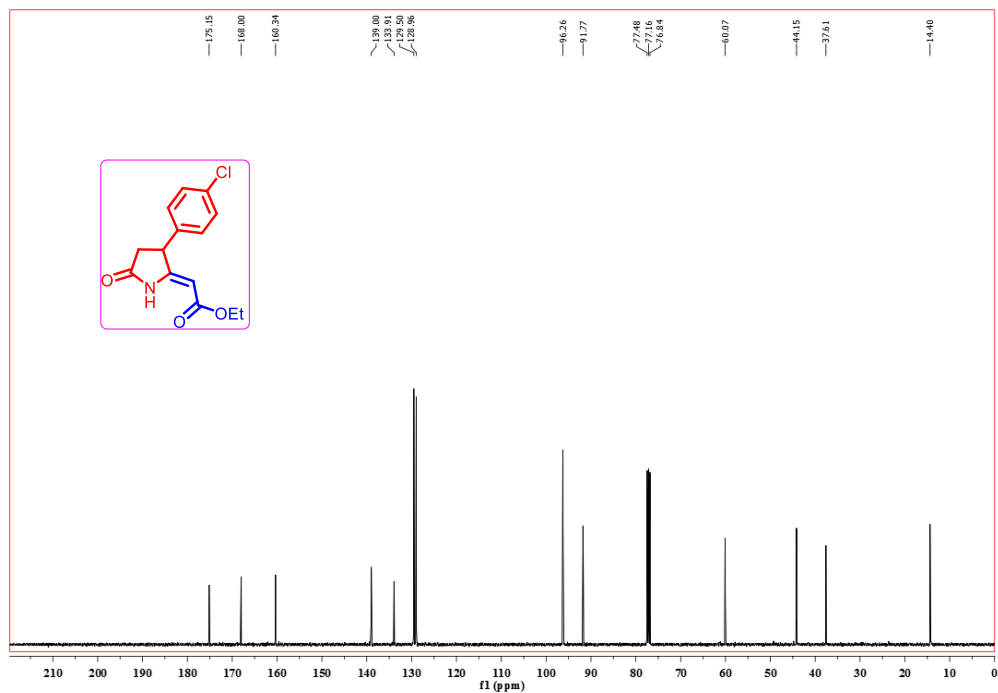
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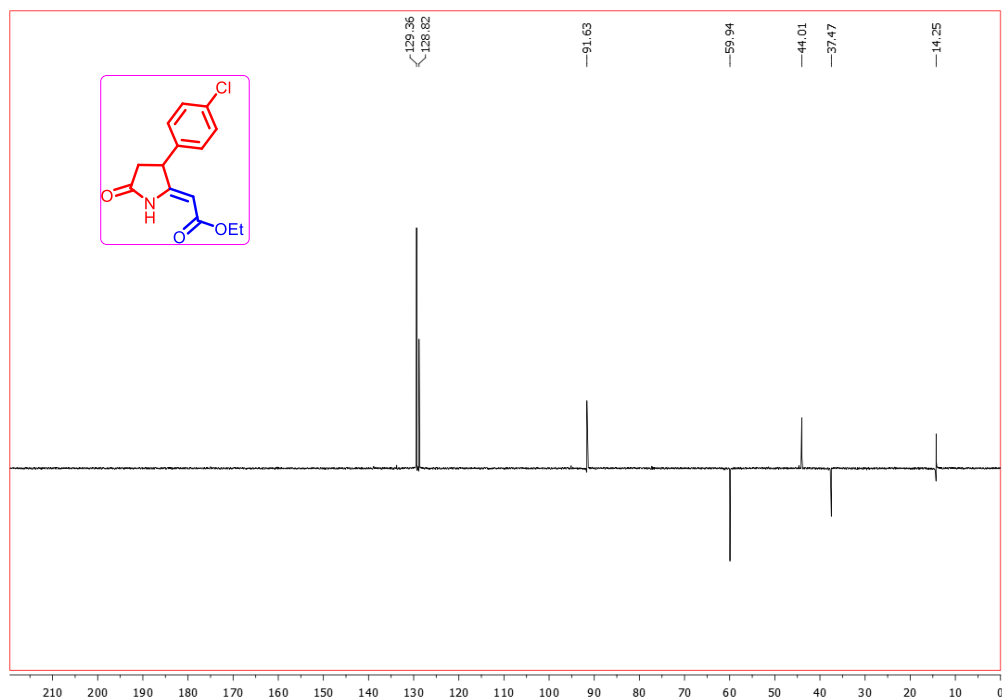
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-fluorophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12g**.



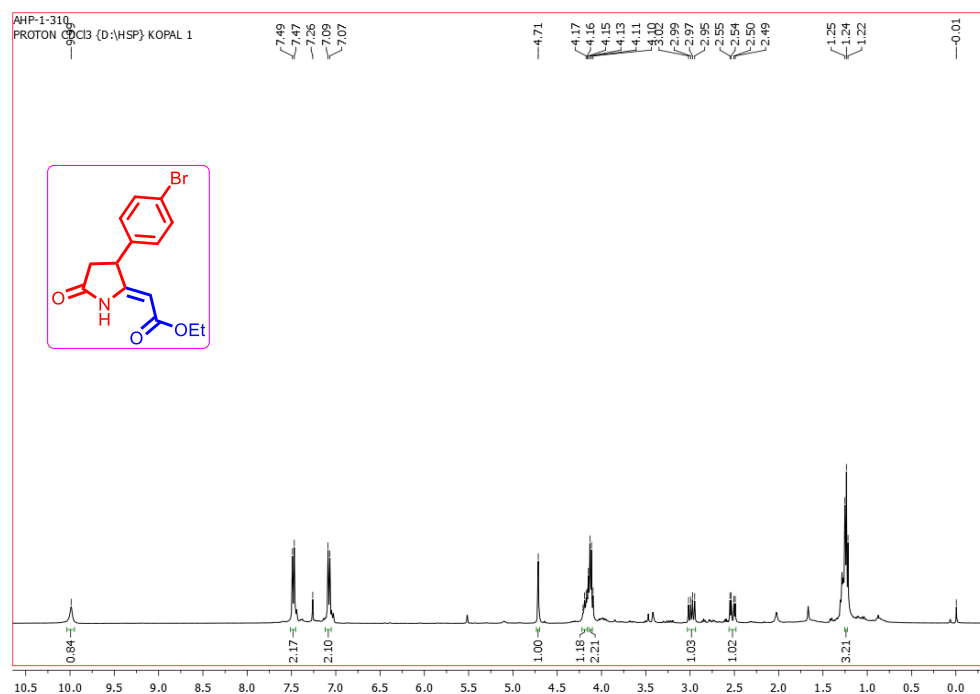
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-chlorophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12h**.



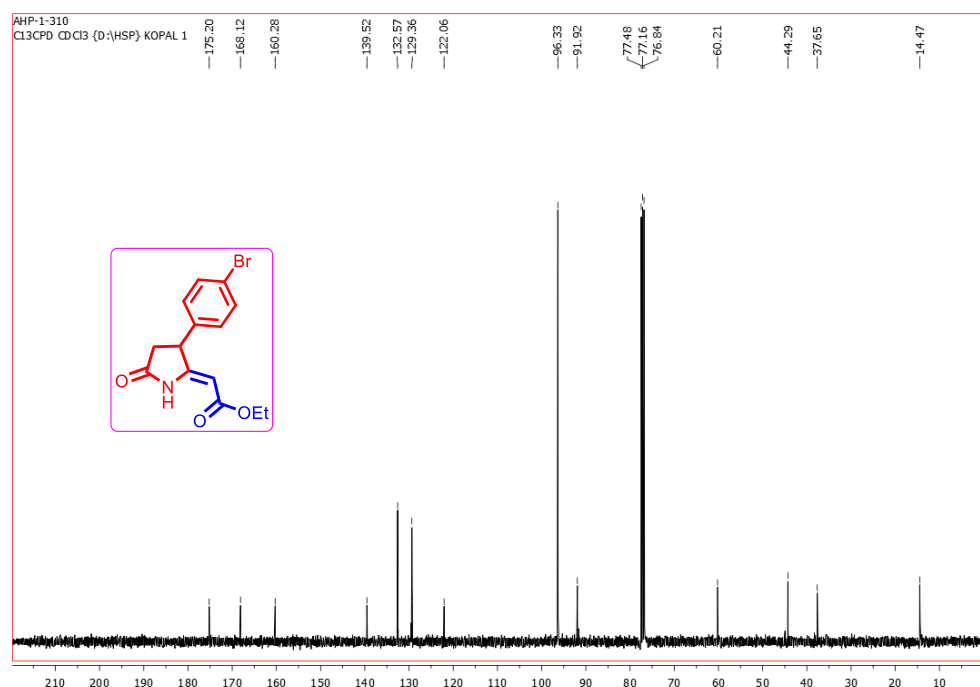
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-chlorophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12h**.



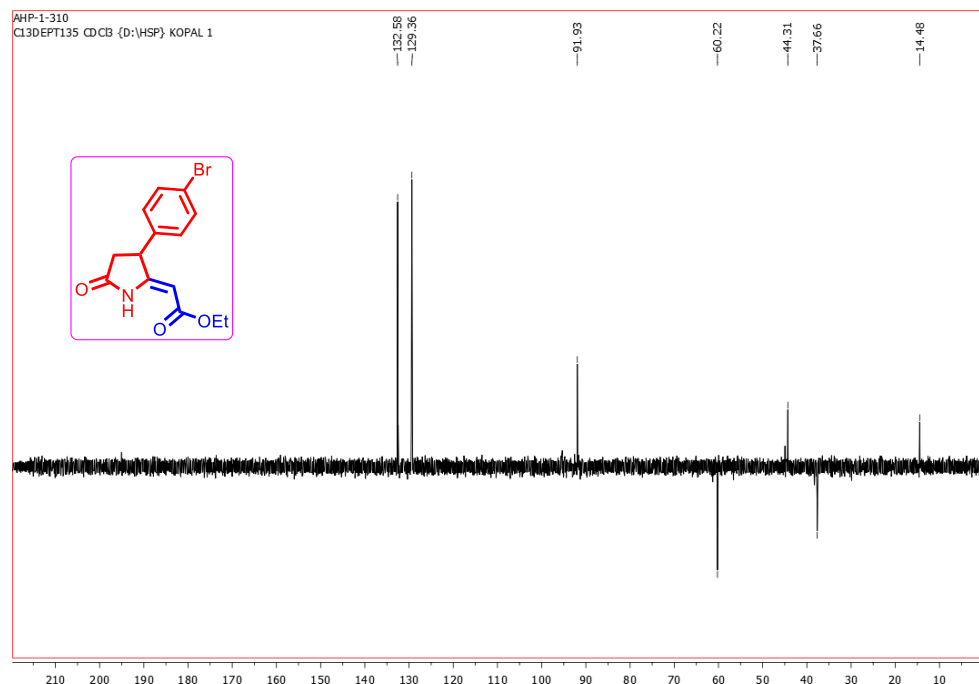
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-chlorophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12h**.



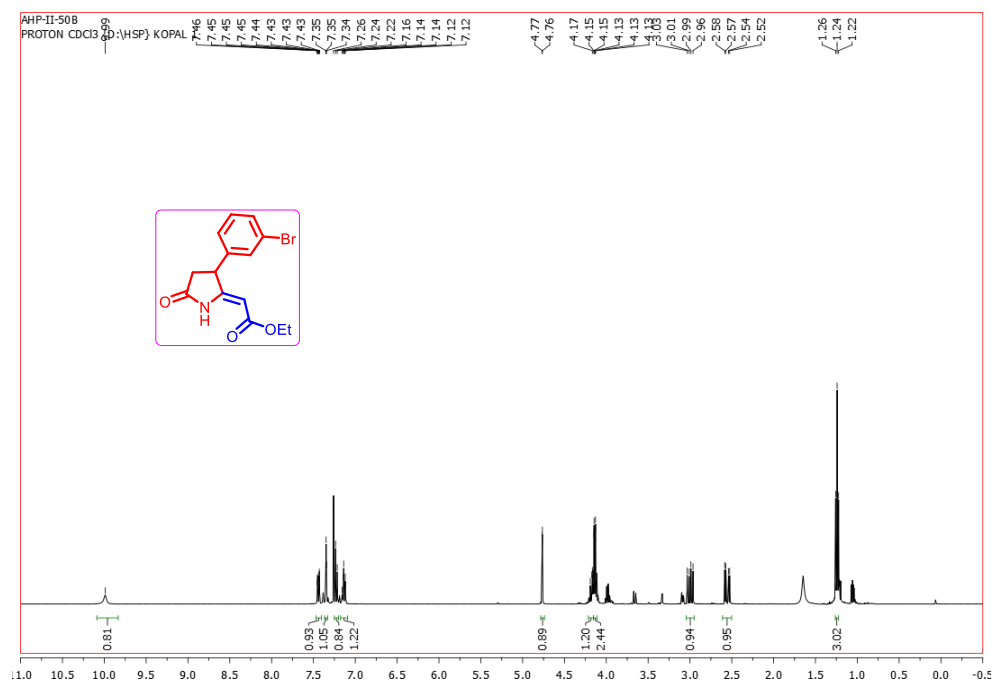
¹H (400 MHz, CDCl₃) NMR spectrum of ethyl (Z)-2-(3-(4-bromophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12i**.



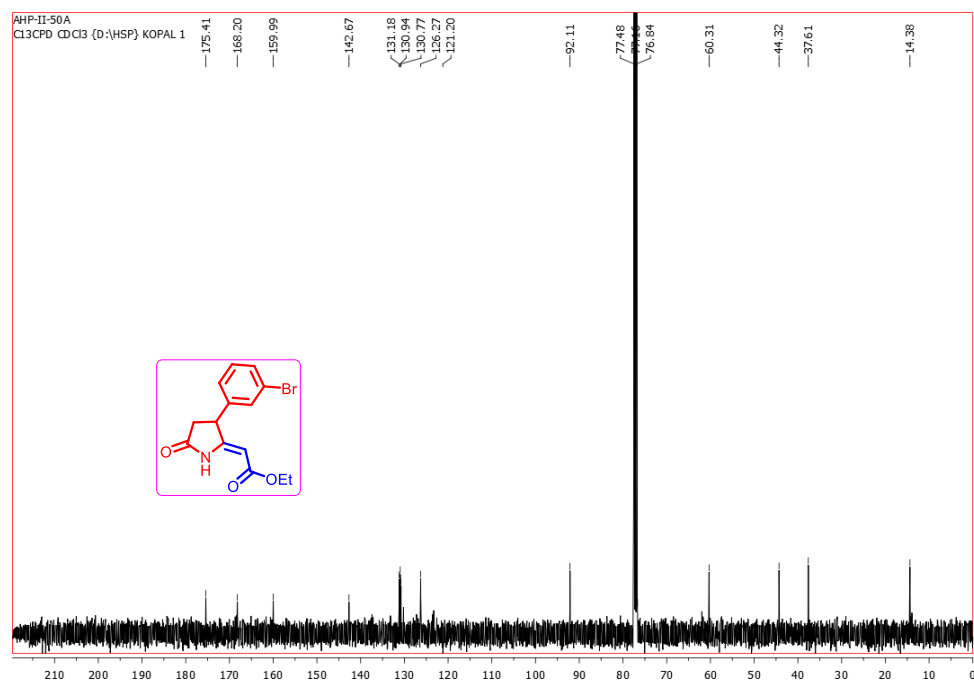
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-bromophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12i**.



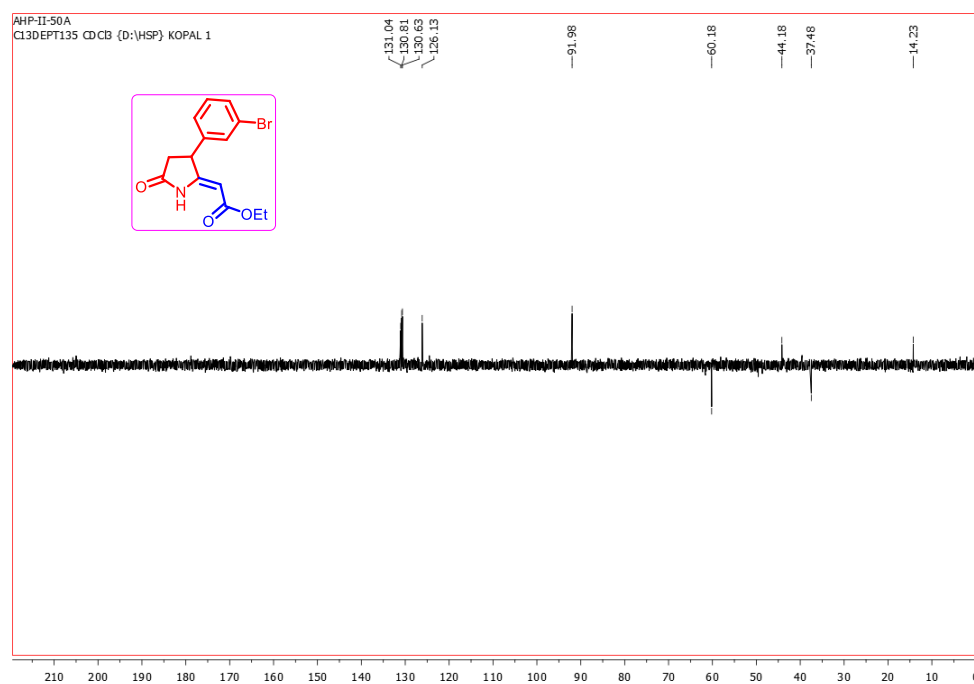
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(4-bromophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12i**.



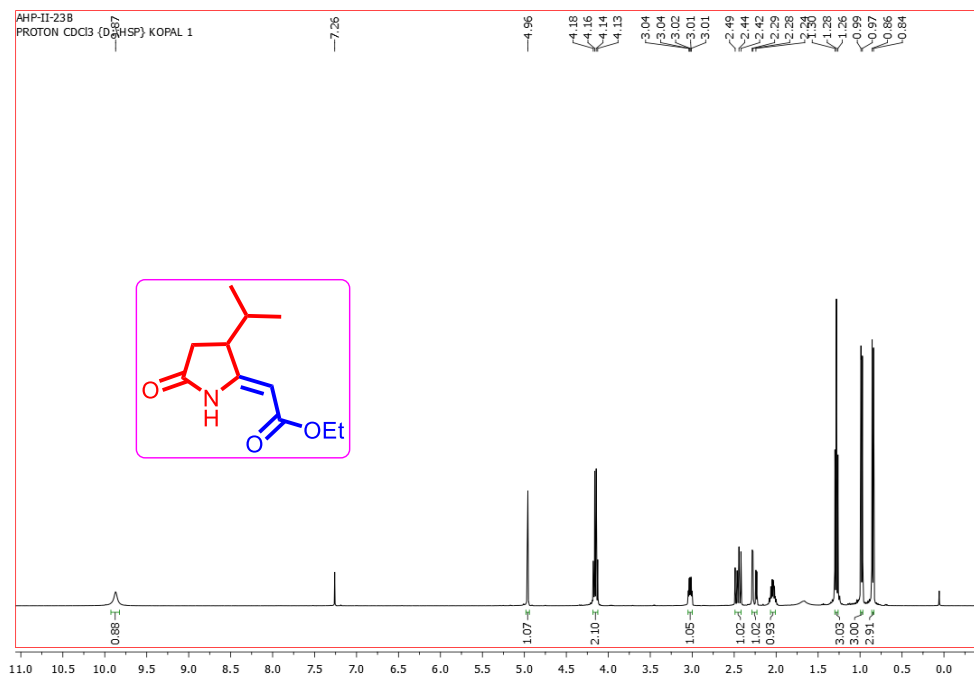
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(3-bromophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12j**.



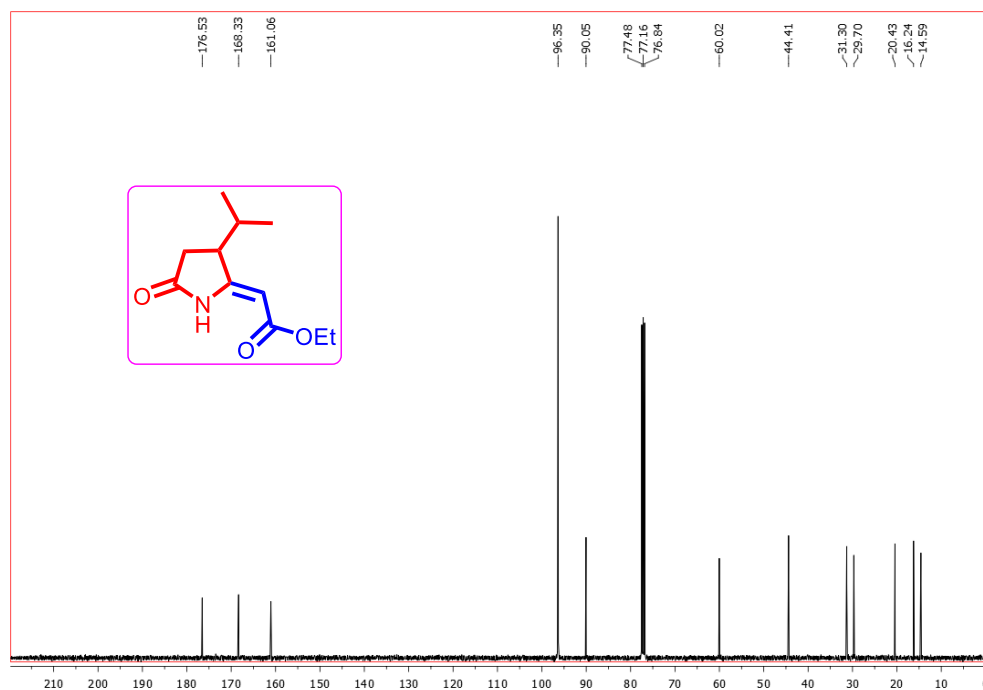
^{13}C (100 MHz, CDCl_3) NMR spectrum of ethyl (Z)-2-(3-(3-bromophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12j**.



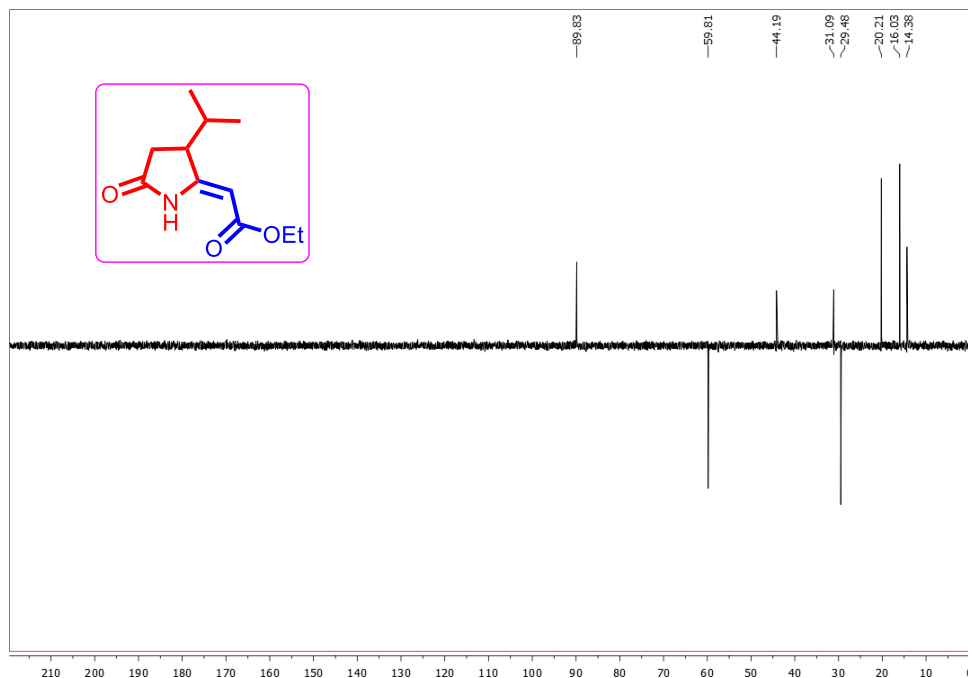
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(3-bromophenyl)-5-oxopyrrolidin-2-ylidene)acetate **12j**.



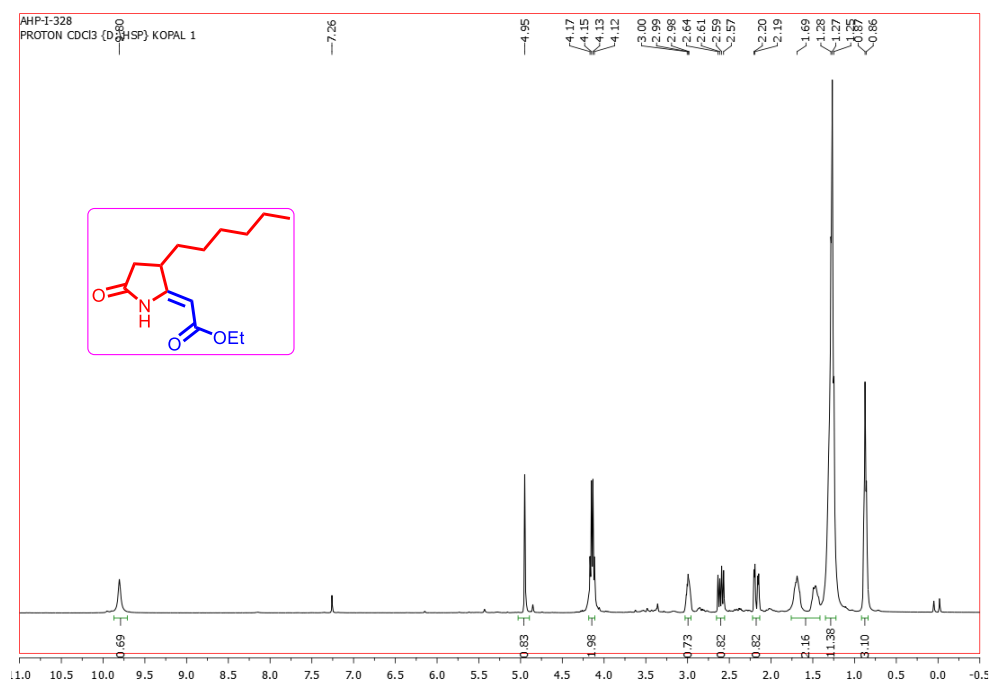
¹H (400 MHz, CDCl₃) NMR spectrum of ethyl (Z)-2-(3-isopropyl-5-oxopyrrolidin-2-ylidene)acetate **12I**.



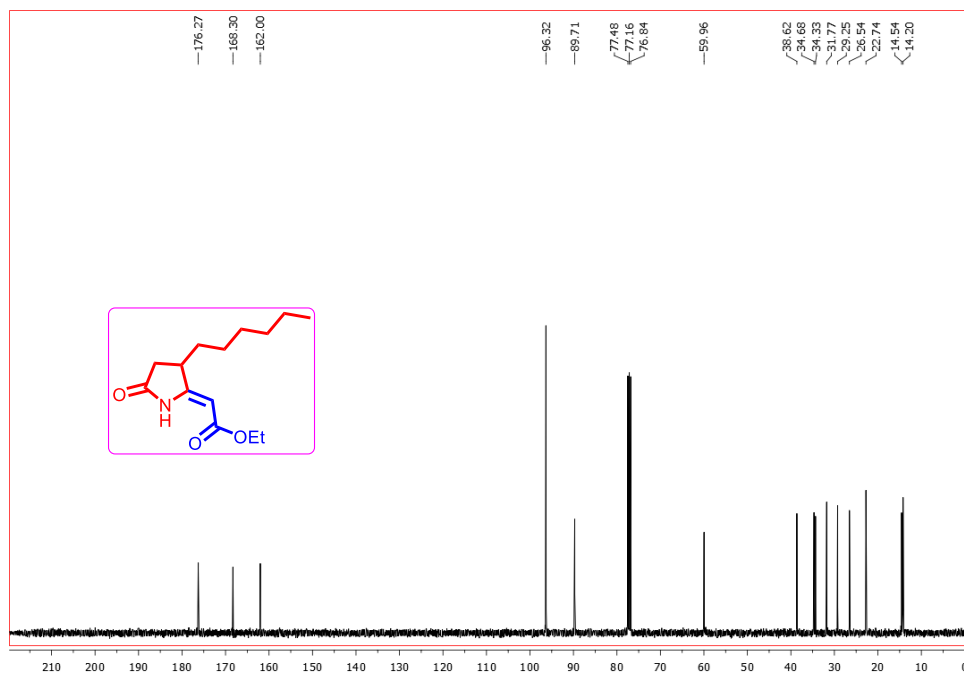
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-isopropyl-5-oxopyrrolidin-2-ylidene)acetate **12I**.



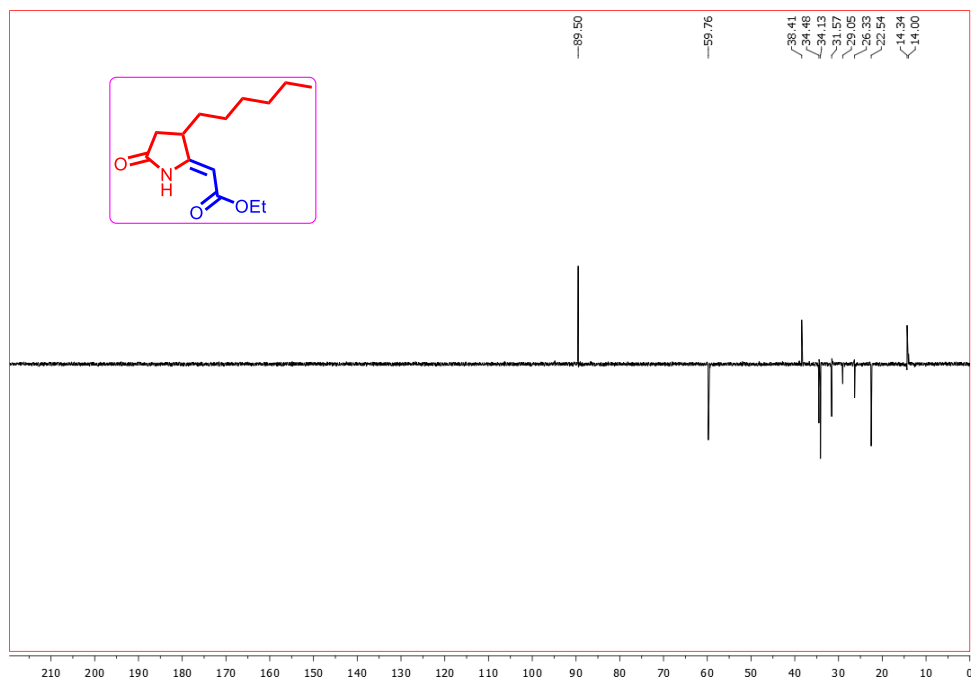
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-isopropyl-5-oxopyrrolidin-2-ylidene)acetate **12l**.



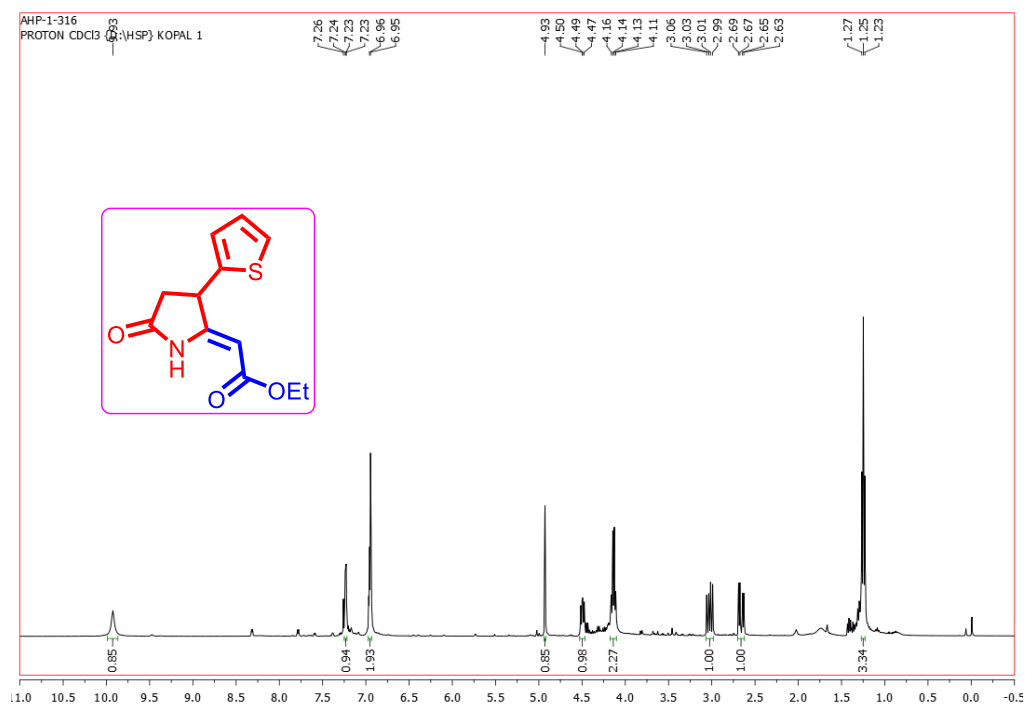
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-hexyl-5-oxopyrrolidin-2-ylidene)acetate **12m**.



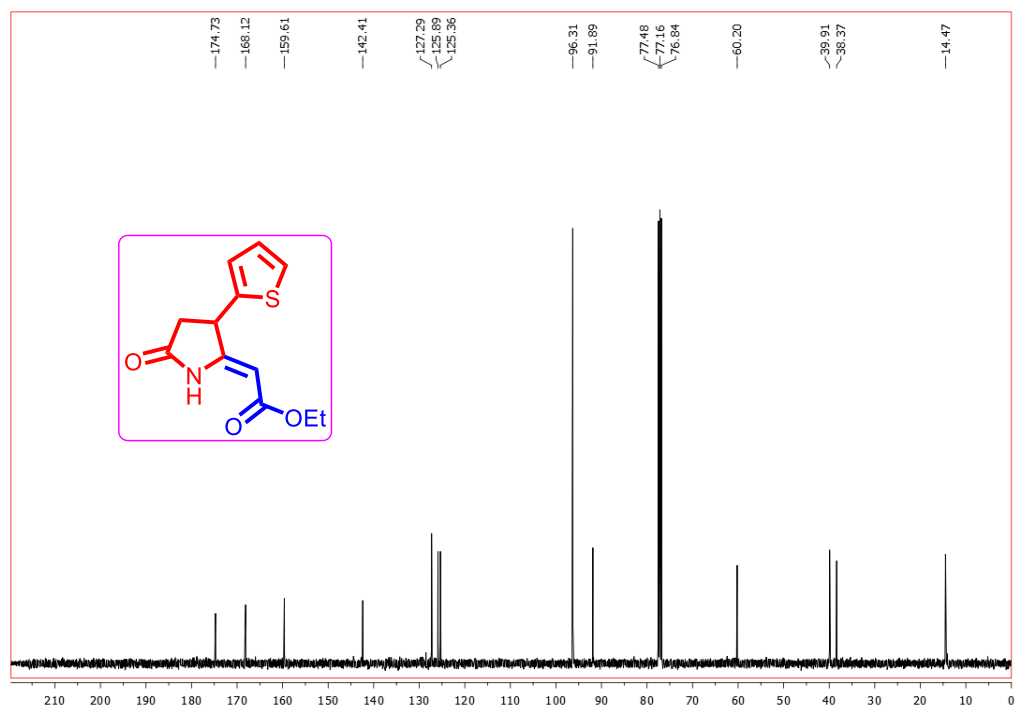
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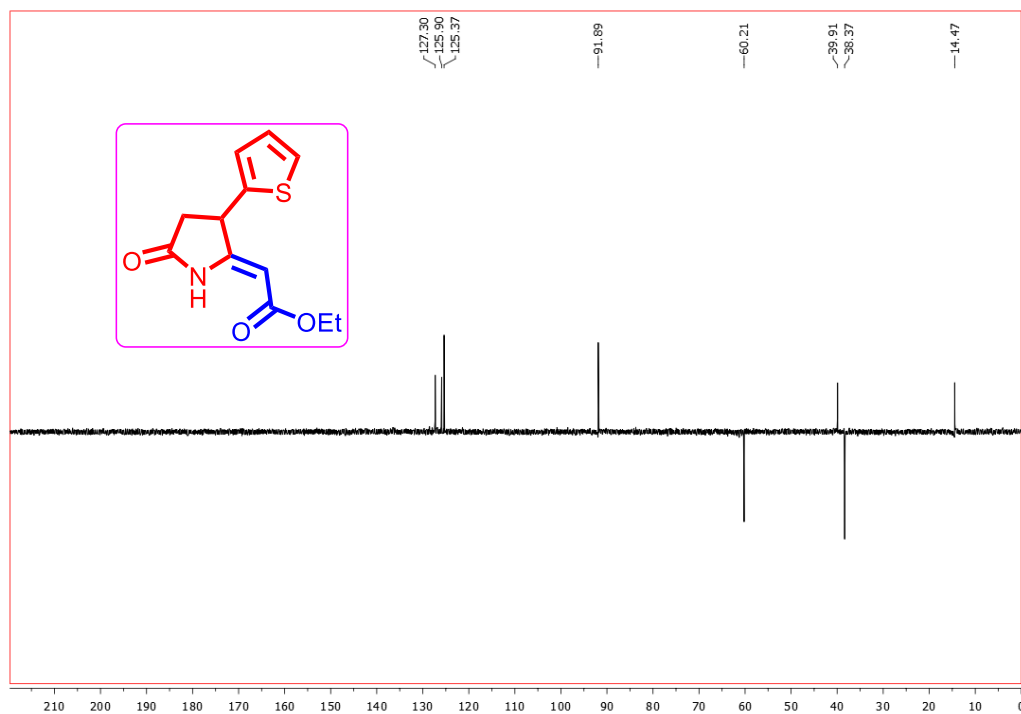
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-hexyl-5-oxopyrrolidin-2-ylidene)acetate **12m**.



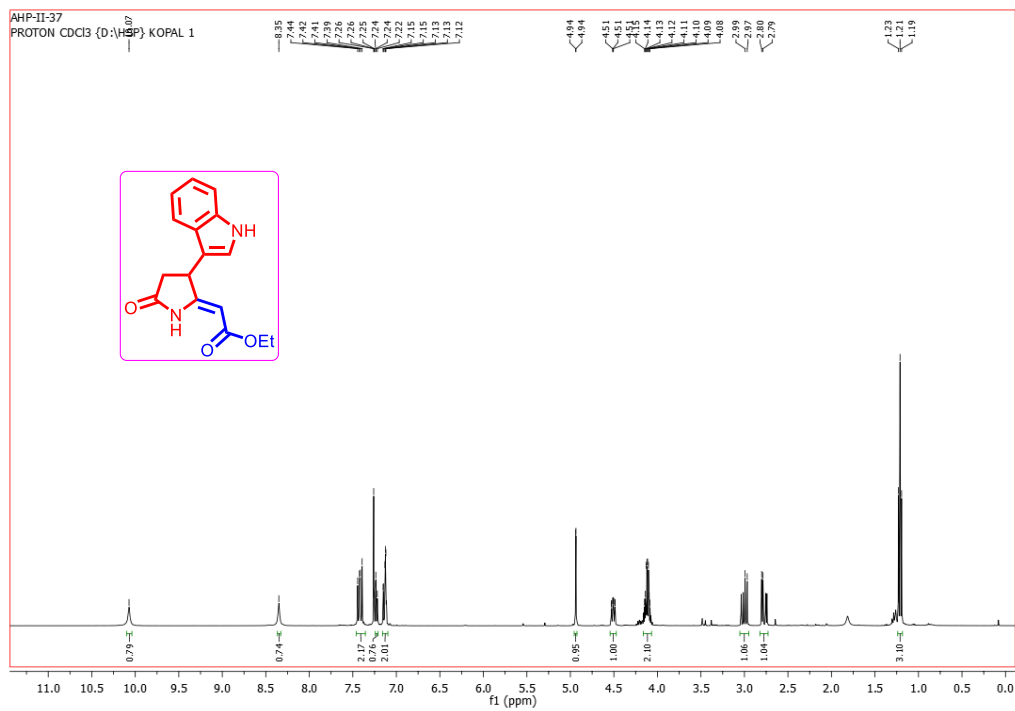
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-(thiophen-2-yl)pyrrolidin-2-ylidene)acetate **12k**.



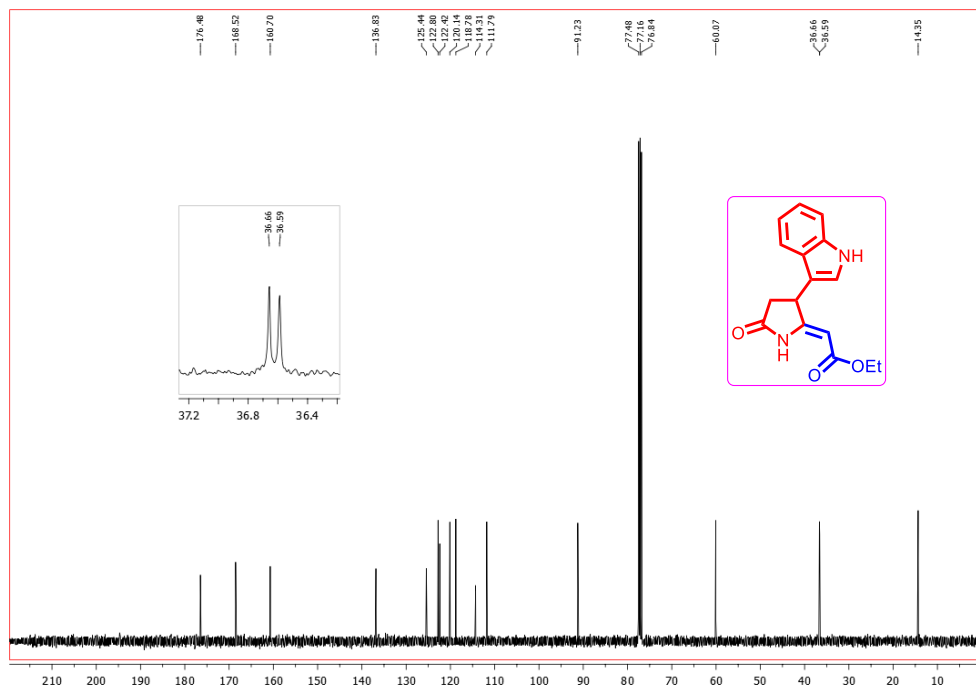
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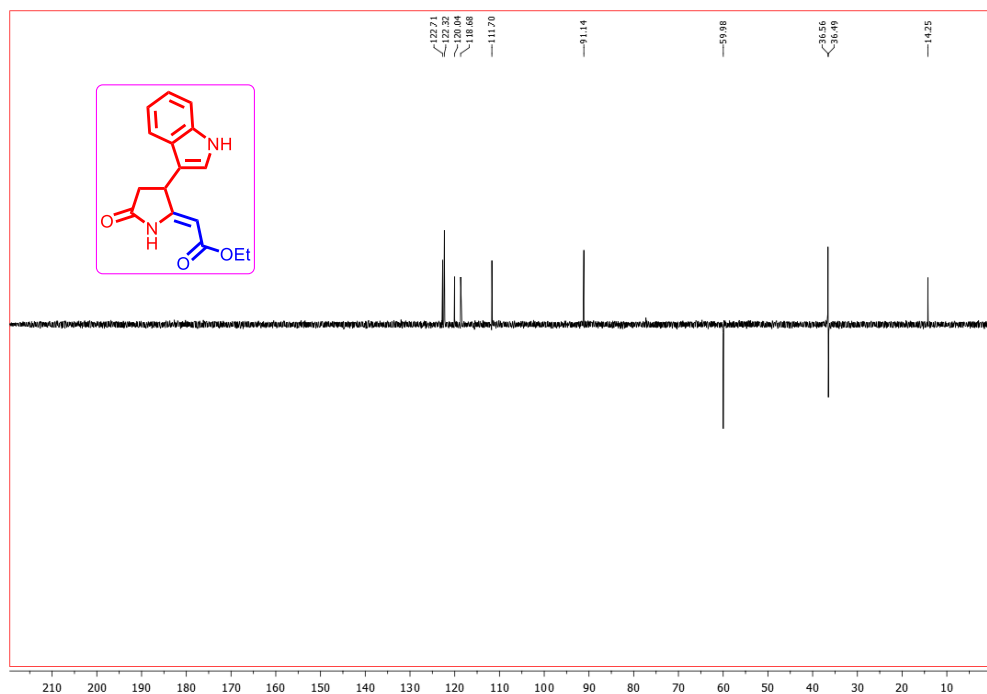
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-(thiophen-2-yl)pyrrolidin-2-ylidene)acetate **12k**.



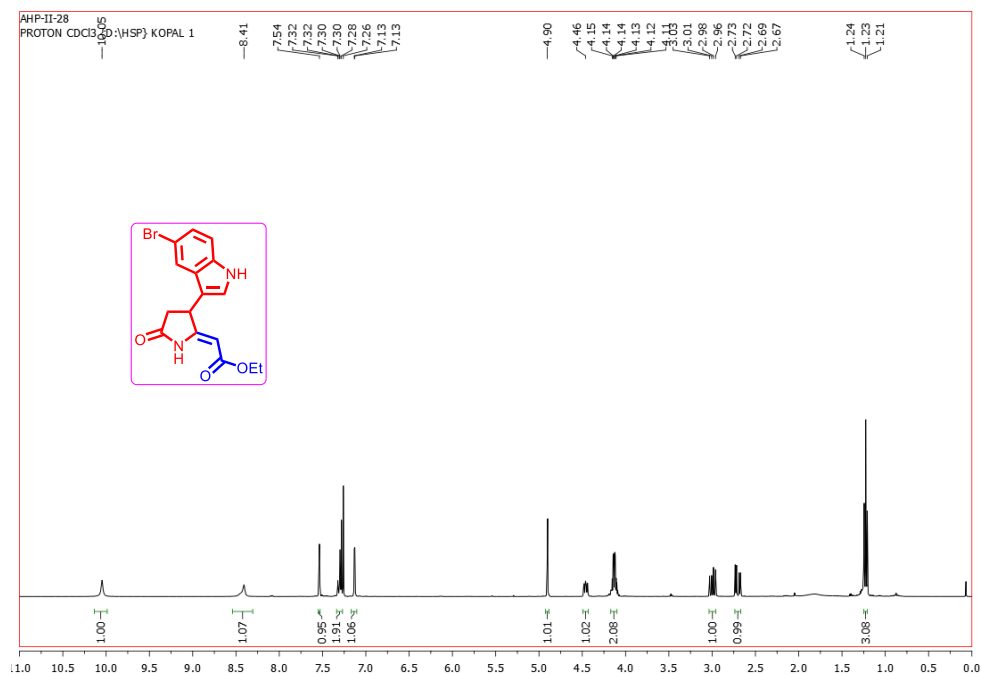
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(1H-indol-3-yl)-5-oxopyrrolidin-2-ylidene)acetate **12n**.



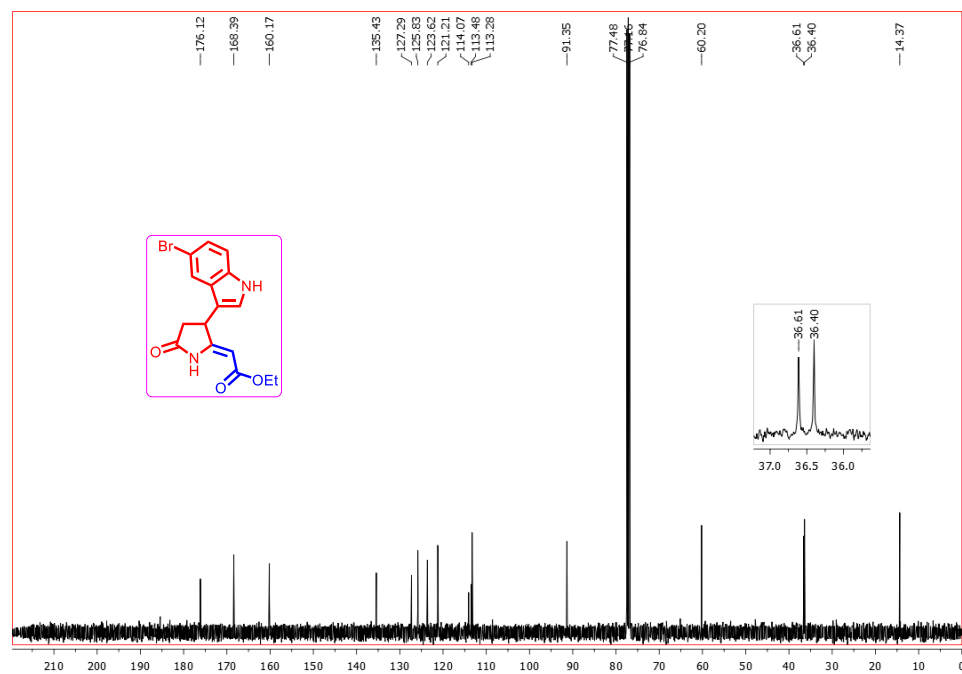
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(1H-indol-3-yl)-5-oxopyrrolidin-2-ylidene)acetate **12n**.



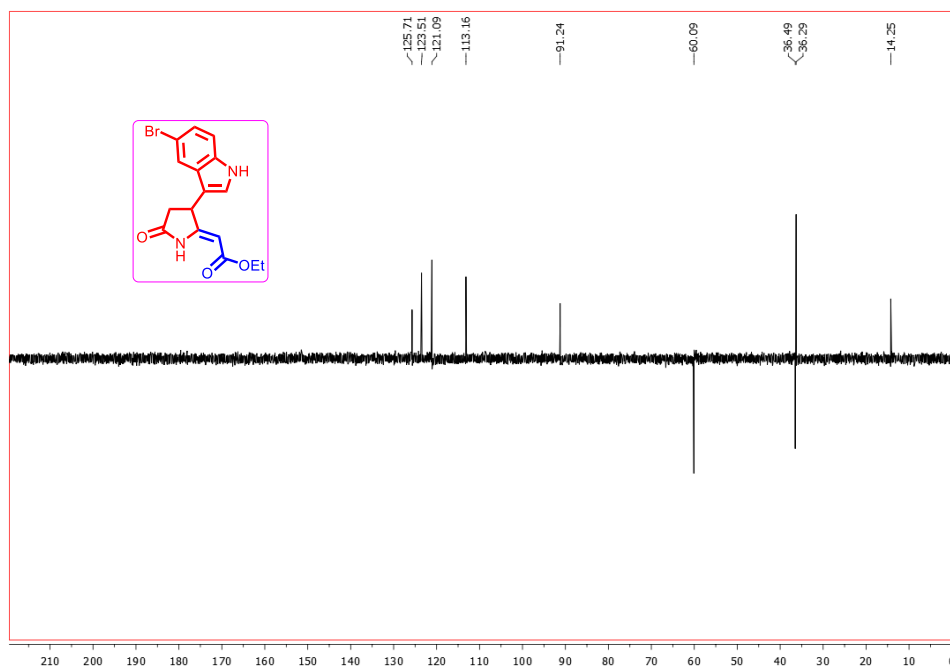
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(1H-indol-3-yl)-5-oxopyrrolidin-2-ylidene)acetate **12n**.



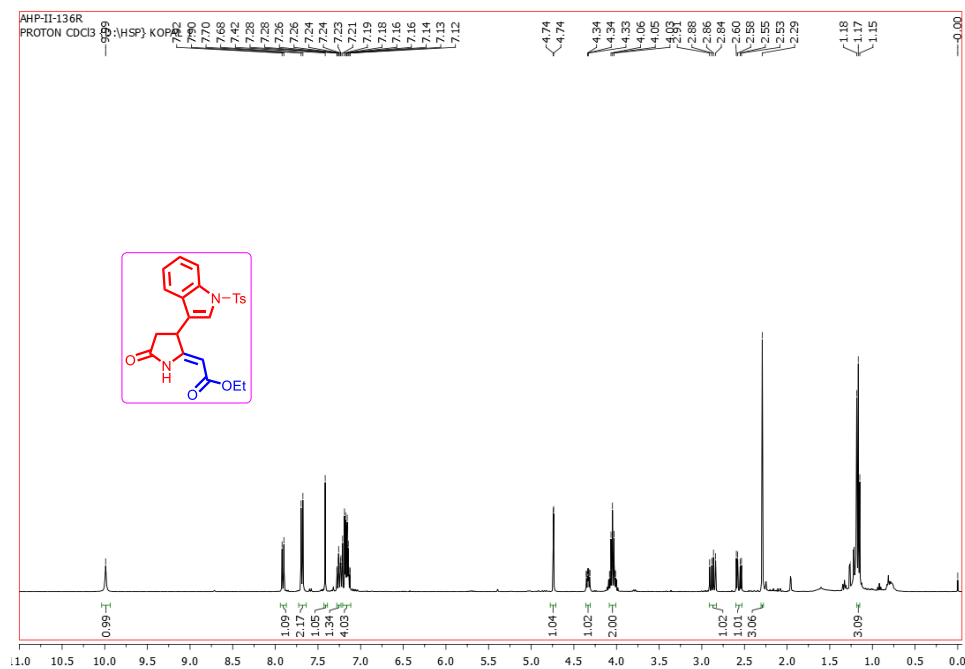
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(5-bromo-1H-indol-3-yl)-5-oxopyrrolidin-2-ylidene)acetate **12o**.



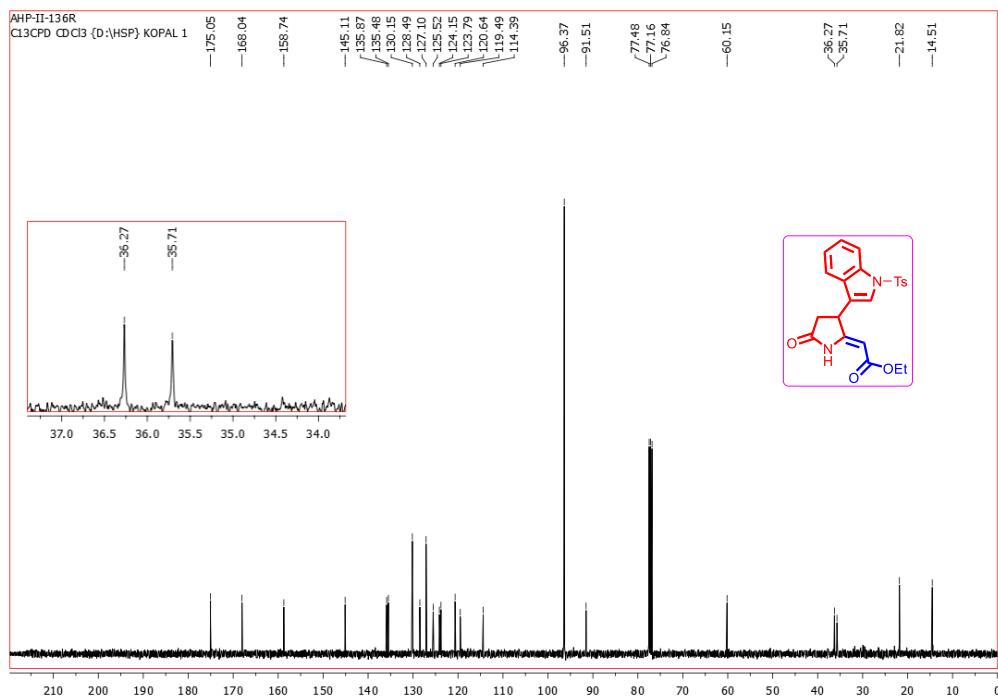
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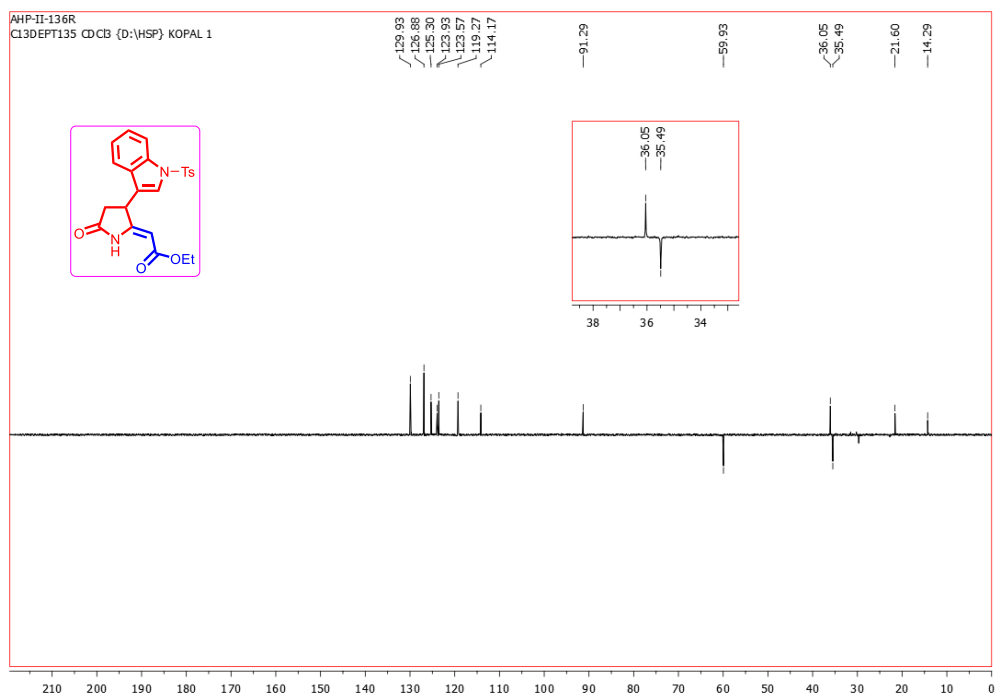
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(5-bromo-1H-indol-3-yl)-5-oxopyrrolidin-2-ylidene)acetate **12o**.



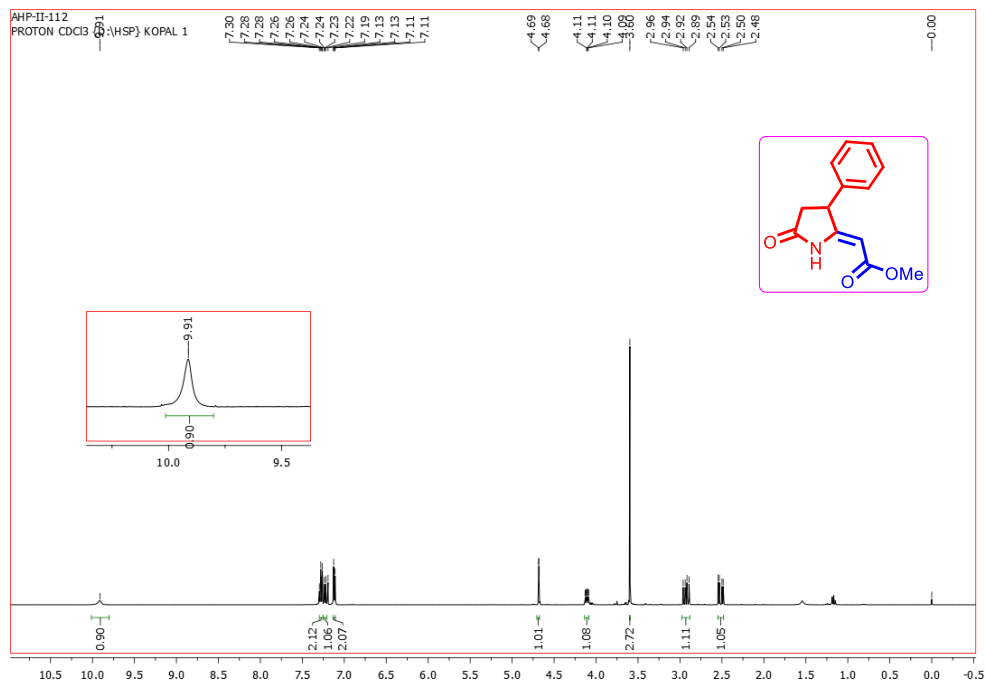
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-(1-tosyl-1H-indol-3-yl)pyrrolidin-2-ylidene)acetate **12p**.



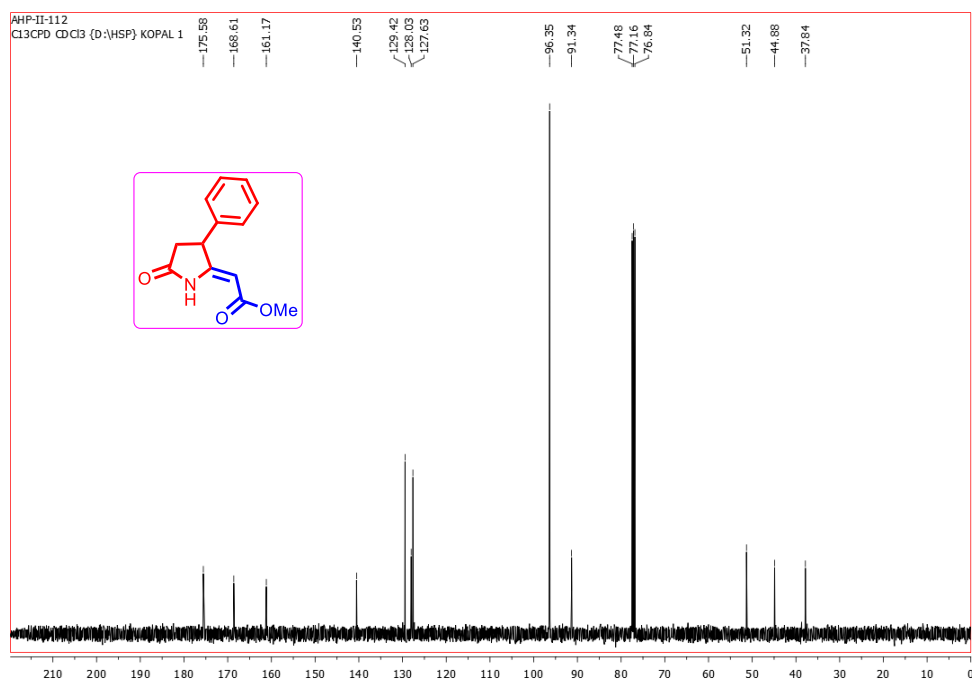
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-(1-tosyl-1H-indol-3-yl)pyrrolidin-2-ylidene)acetate **12p**.



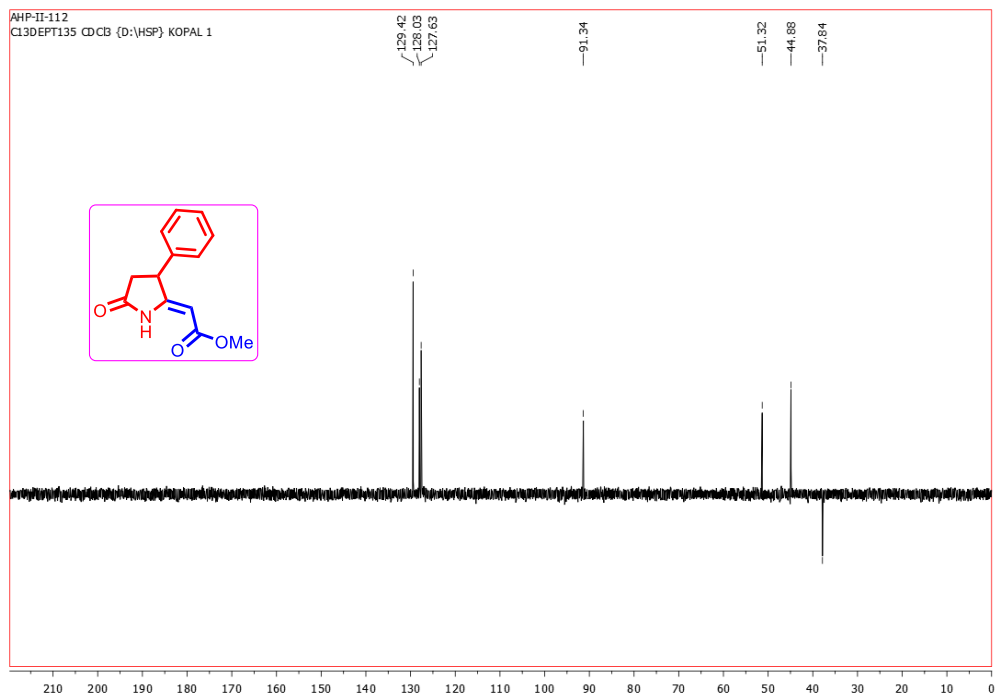
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-(1-tosyl-1H-indol-3-yl)pyrrolidin-2-ylidene)acetate **12p**.



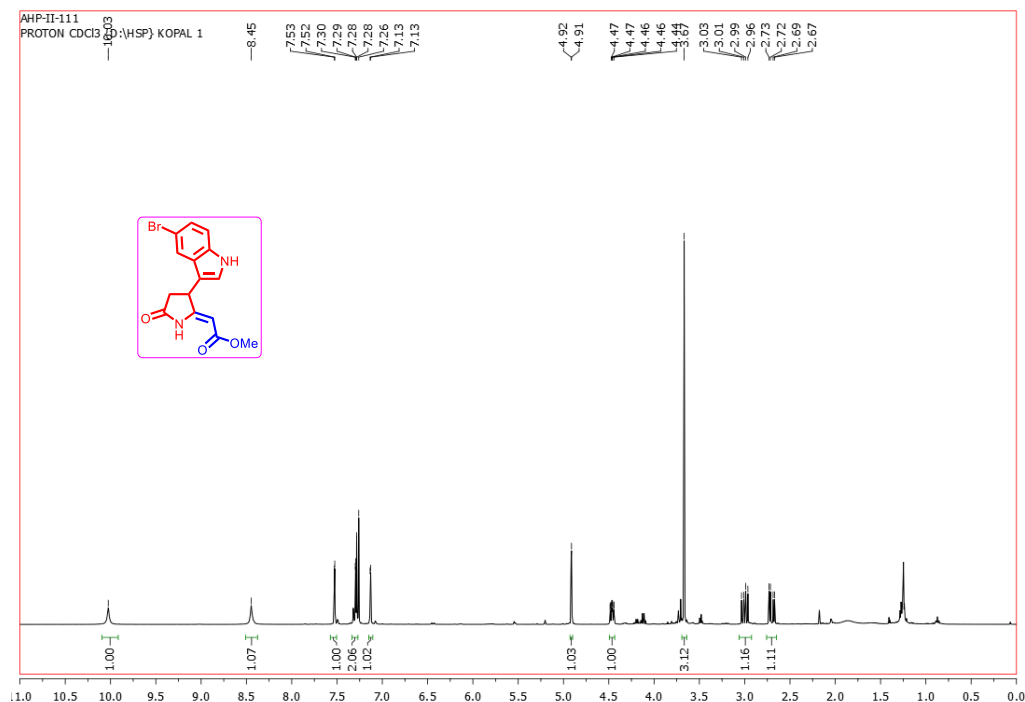
¹H (400 MHz, CDCl₃) NMR spectrum of Methyl (Z)-2-(5-oxo-3-phenylpyrrolidin-2-ylidene)acetate **12q**.



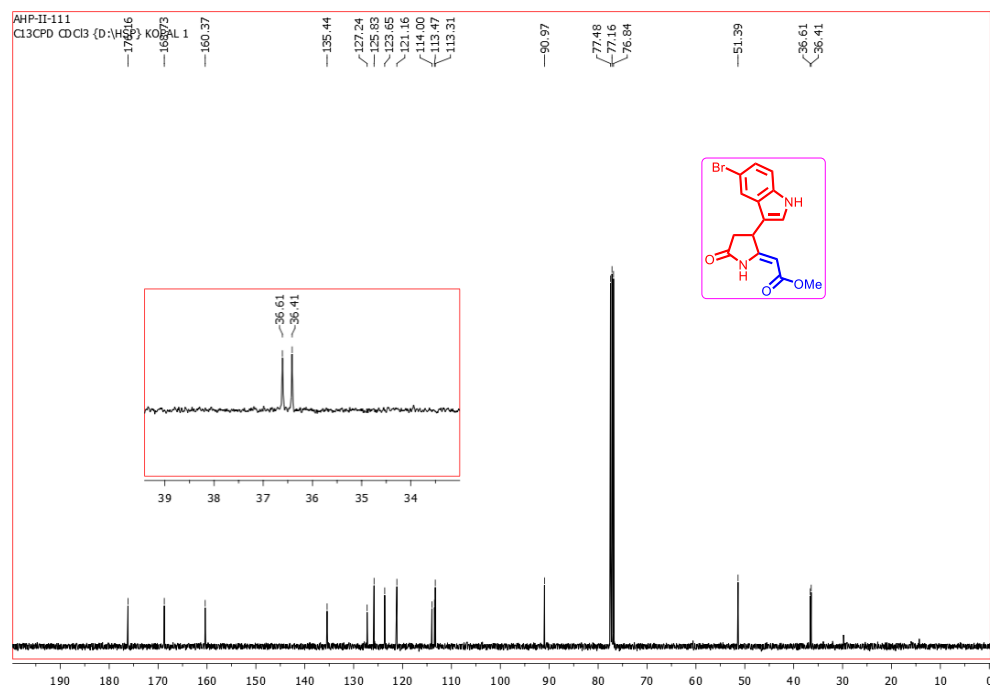
¹³C (100 MHz, CDCl₃) NMR spectrum of Methyl (Z)-2-(5-oxo-3-phenylpyrrolidin-2-ylidene)acetate **12q**.



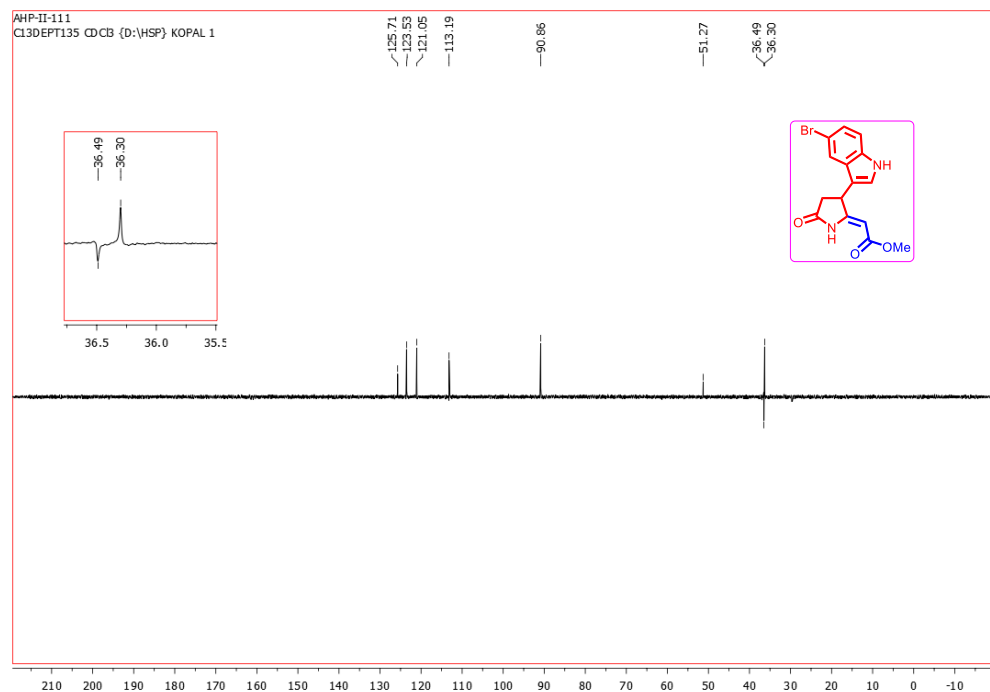
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Methyl (Z)-2-(5-oxo-3-phenylpyrrolidin-2-ylidene)acetate **12q**.



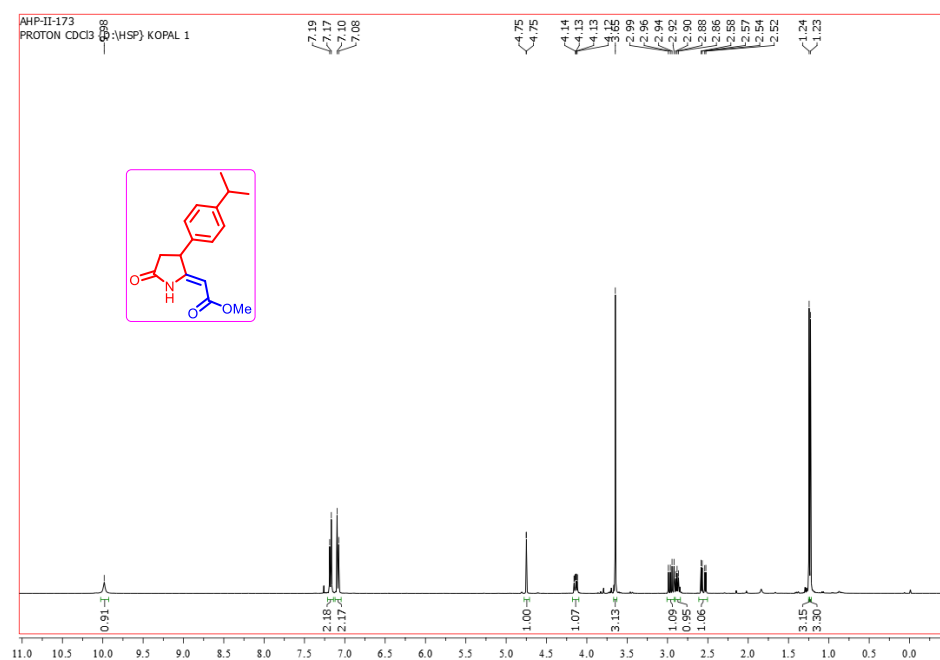
¹H (400 MHz, CDCl₃) NMR spectrum of Methyl (Z)-2-(3-(5-bromo-1H-indol-3-yl)-5-oxopyrrolidin-2-ylidene)acetate **12s**.



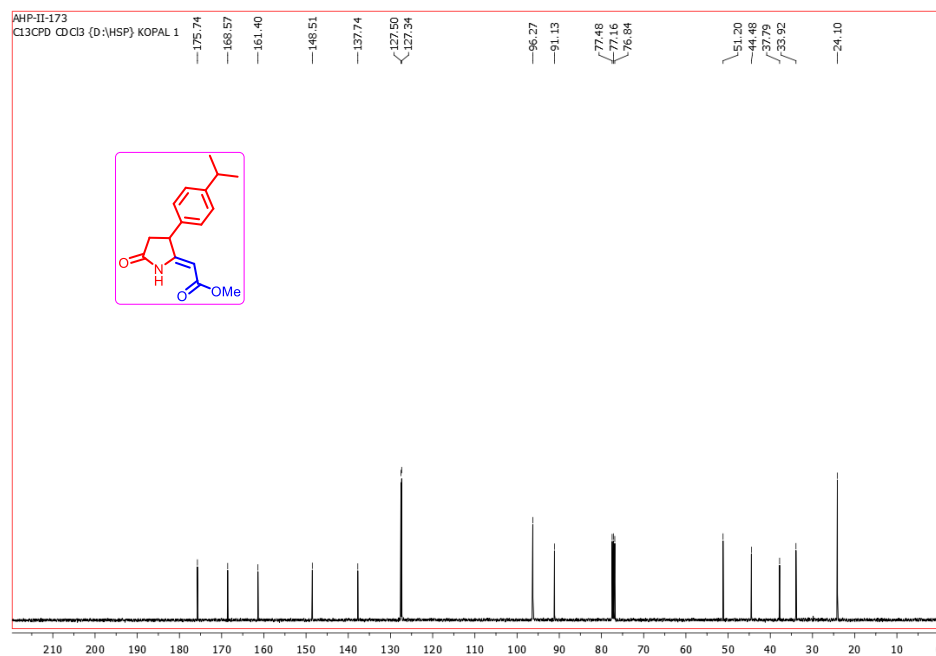
^{13}C (100 MHz, CDCl_3) NMR spectrum of Methyl (Z)-2-(3-(5-bromo-1H-indol-3-yl)-5-oxopyrrolidin-2-ylidene)acetate **12s**.



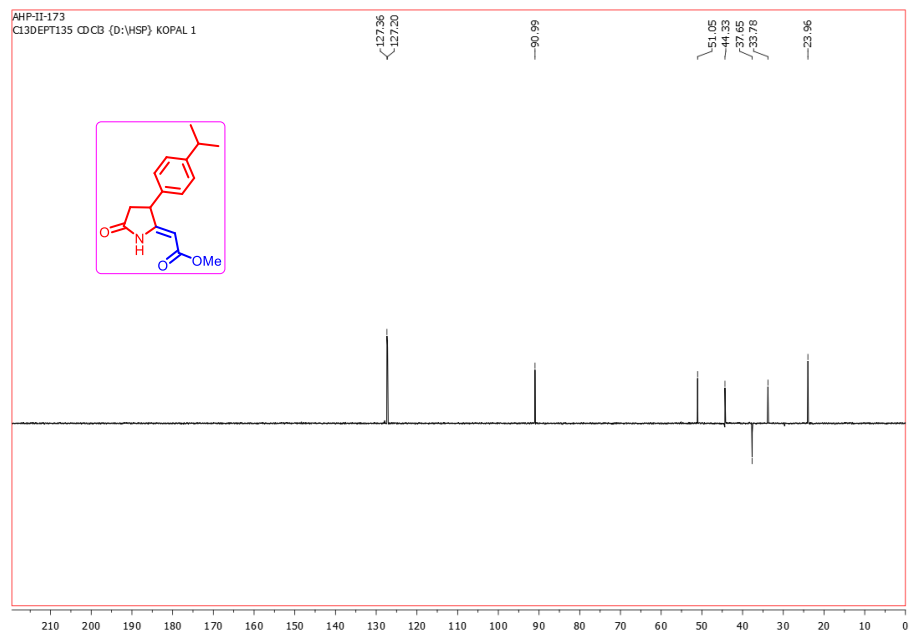
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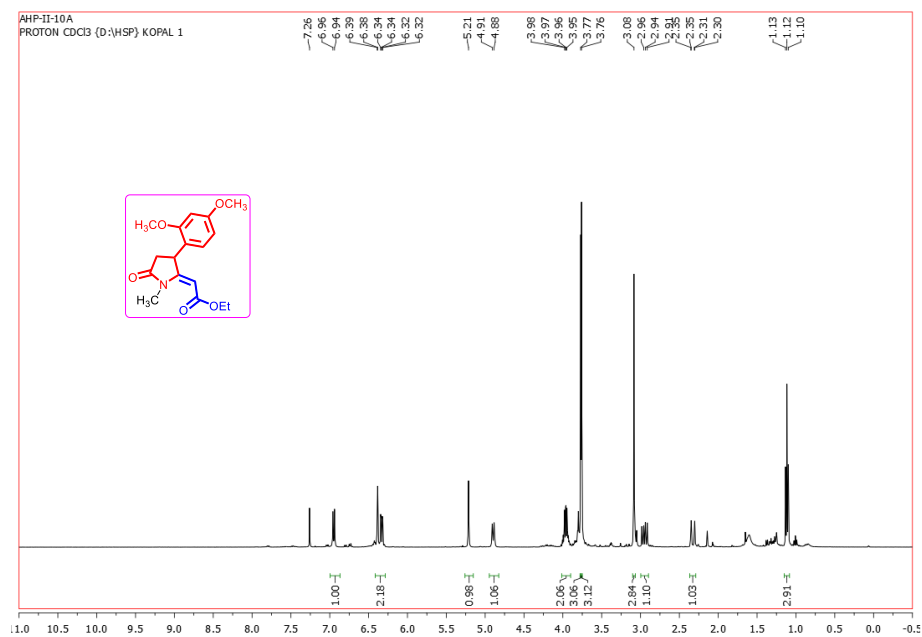
¹H (400 MHz, CDCl₃) NMR spectrum of Methyl (Z)-2-(3-(4-isopropylphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12r**.



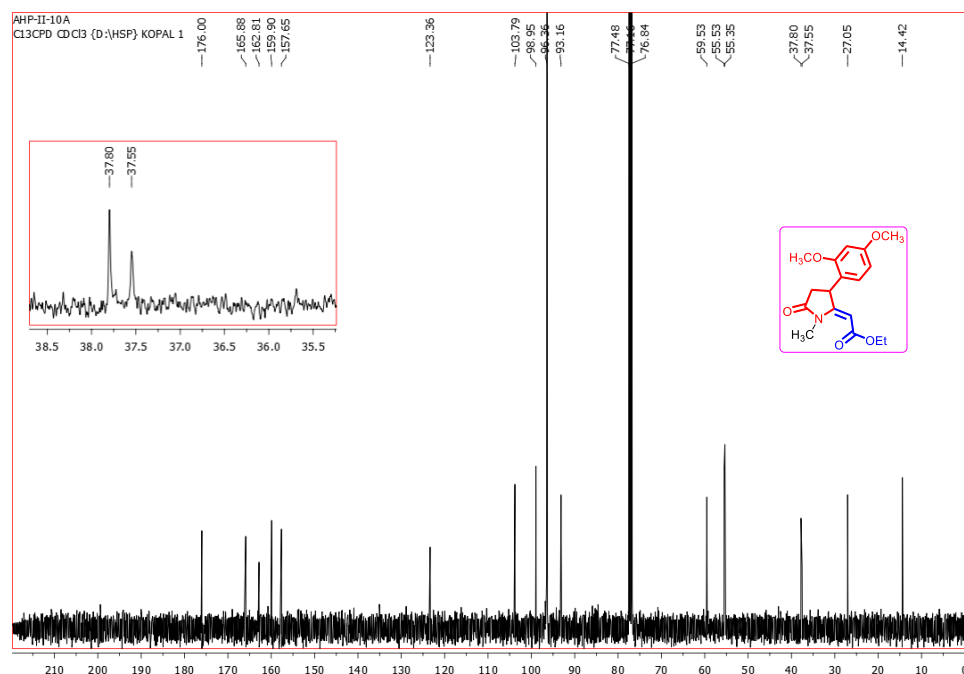
¹³C (100 MHz, CDCl₃) NMR spectrum of Methyl (Z)-2-(3-(4-isopropylphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12r**.



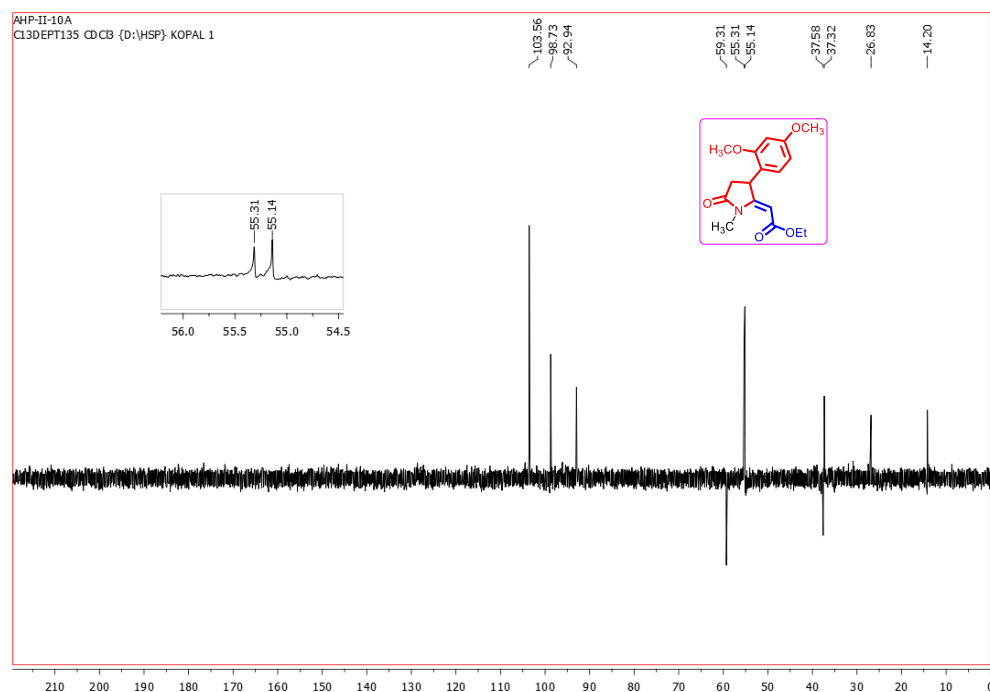
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Methyl (Z)-2-(3-(4-isopropylphenyl)-5-oxopyrrolidin-2-ylidene)acetate **12r**.



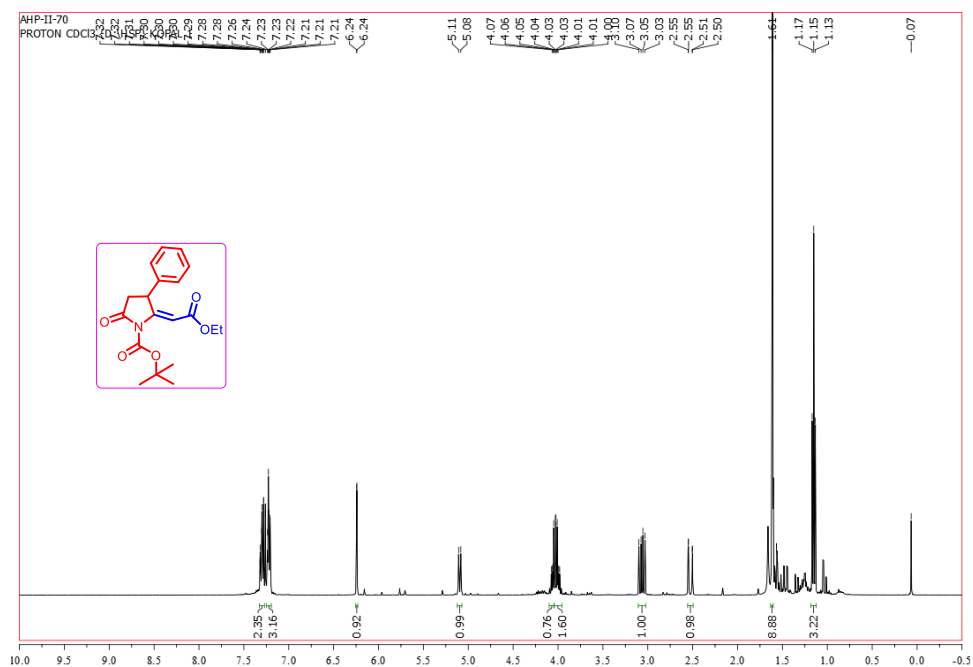
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-(2,4-dimethoxyphenyl)-1-methyl-5-oxopyrrolidin-2-ylidene)acetate **15**.



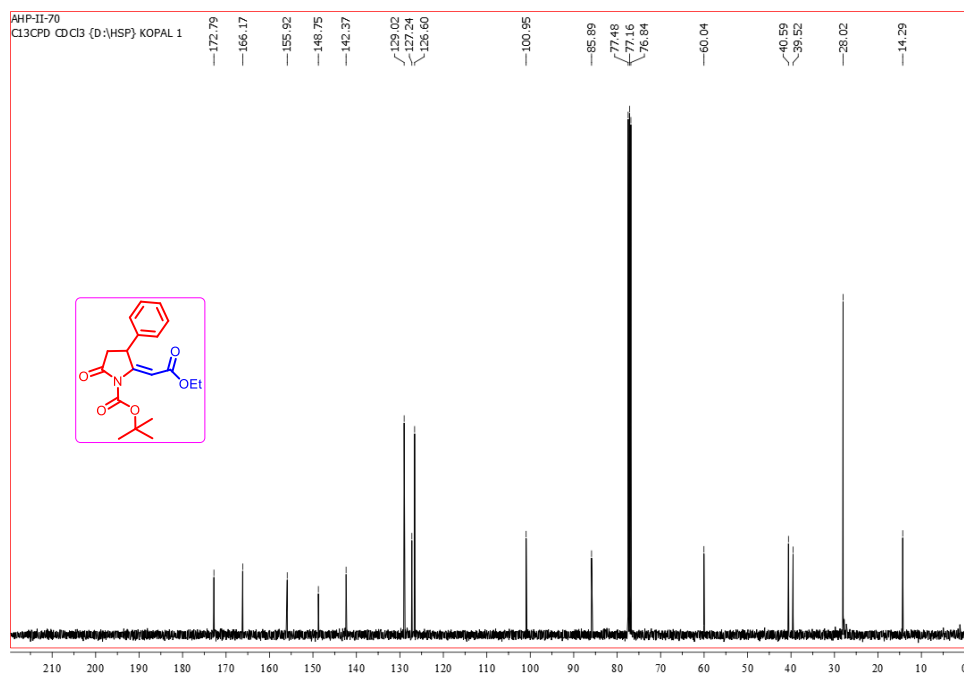
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(2,4-dimethoxyphenyl)-1-methyl-5-oxopyrrolidin-2-ylidene)acetate **15**.



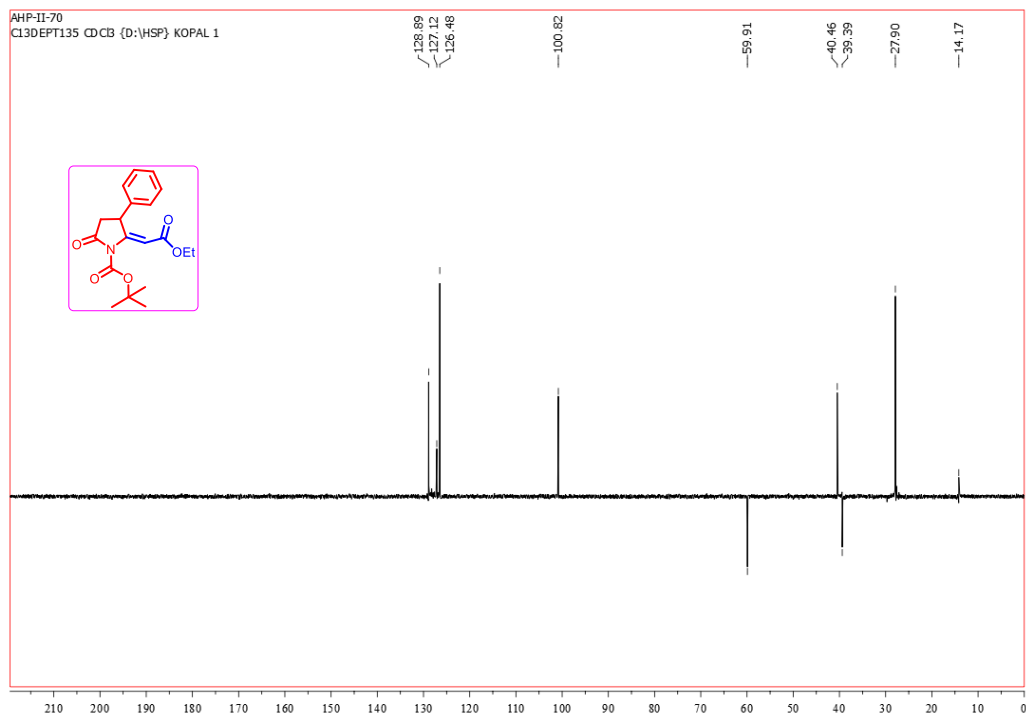
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(2,4-dimethoxyphenyl)-1-methyl-5-oxopyrrolidin-2-ylidene)acetate **15**.



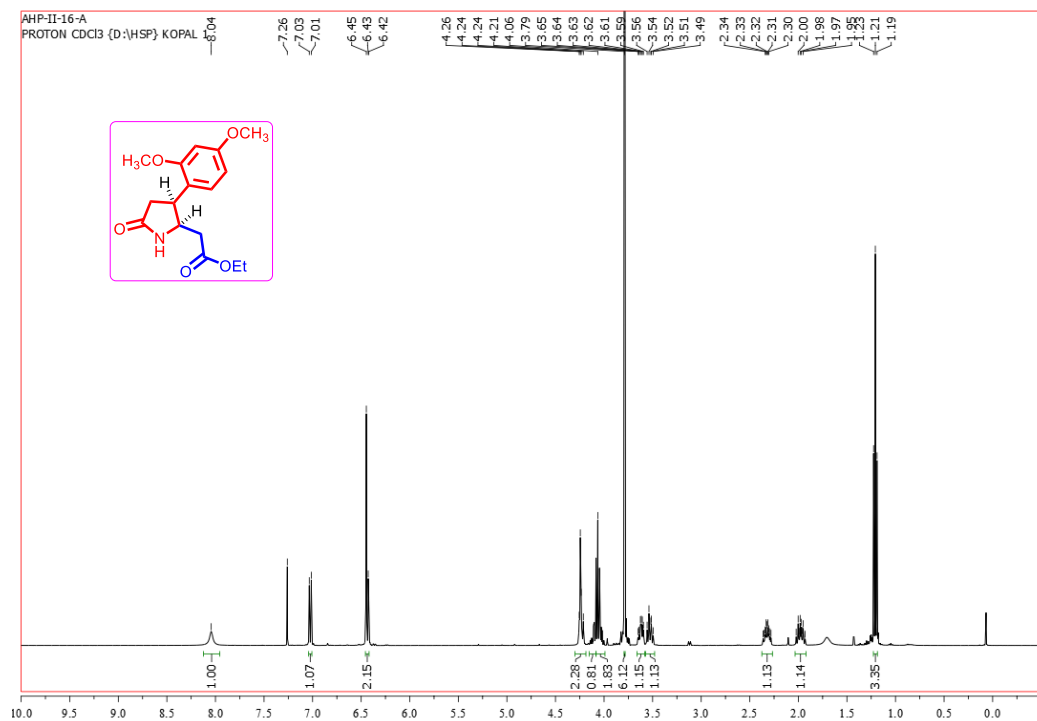
¹H (400 MHz, CDCl₃) NMR spectrum of tert-butyl (E)-2-(2-ethoxy-2-oxoethylidene)-5-oxo-3-phenylpyrrolidine-1-carboxylate **16**.



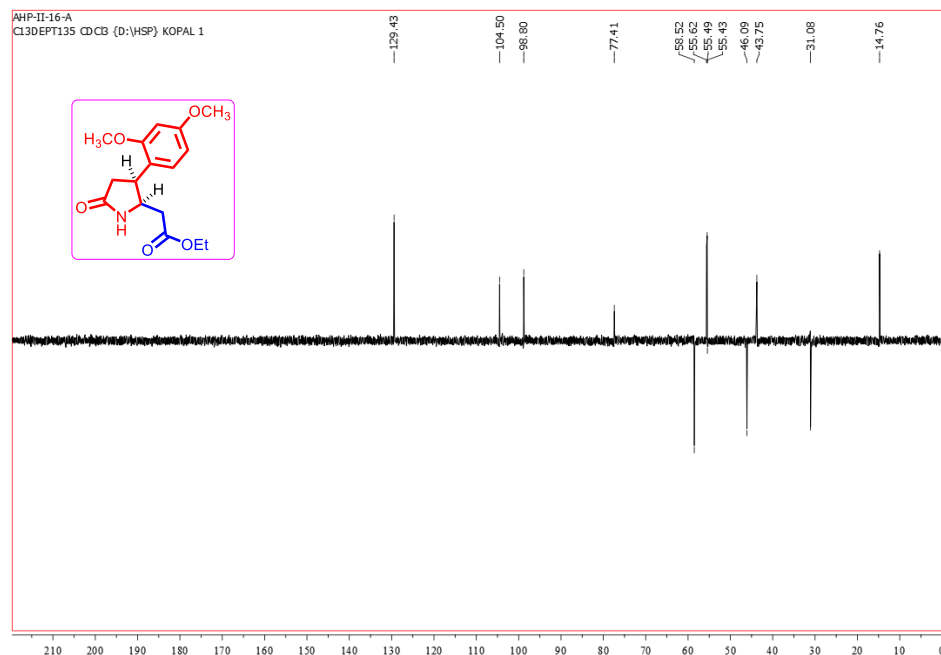
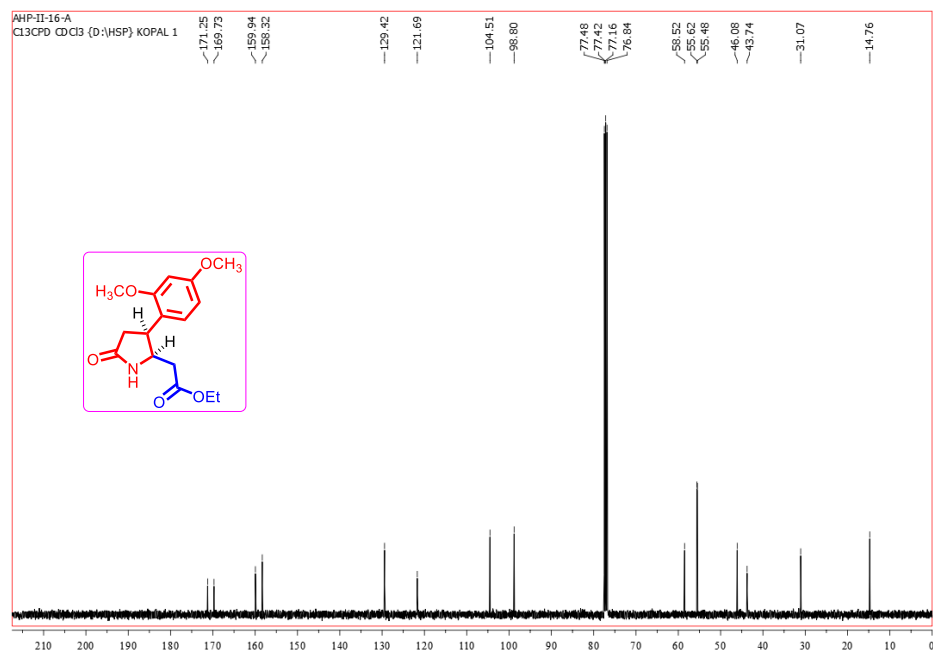
¹³C (100 MHz, CDCl₃) NMR spectrum of tert-butyl (E)-2-(2-ethoxy-2-oxoethylidene)-5-oxo-3-phenylpyrrolidine-1-carboxylate **16**.

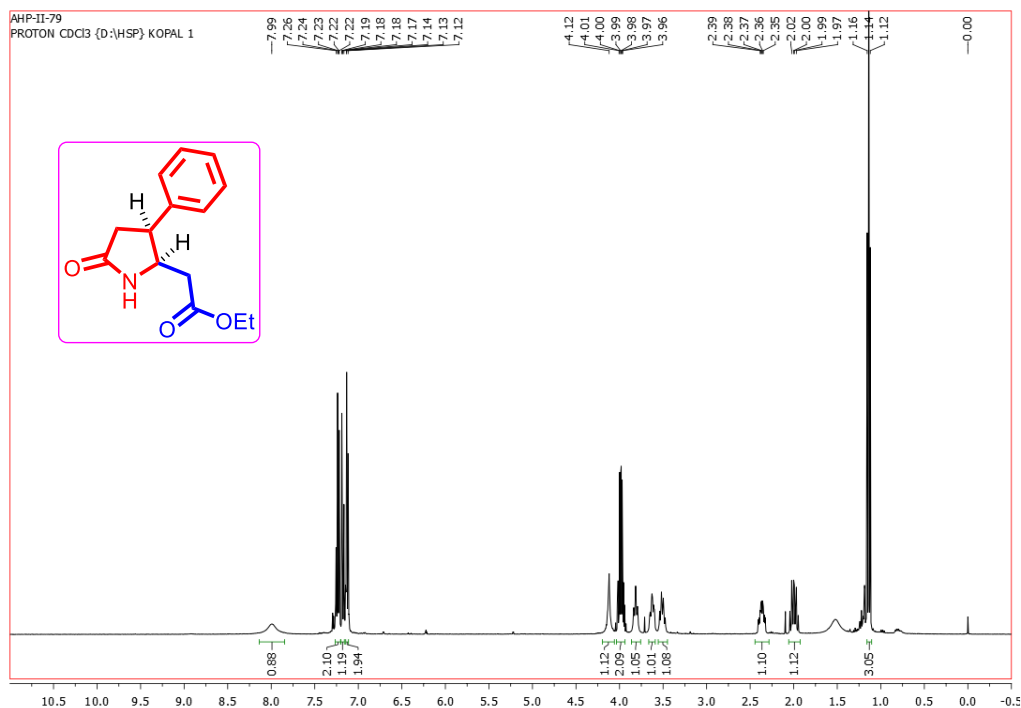


DEPT-135 (100 MHz, CDCl_3) NMR spectrum of tert-butyl (E)-2-(2-ethoxy-2-oxoethylidene)-5-oxo-3-phenylpyrrolidine-1-carboxylate **16**.

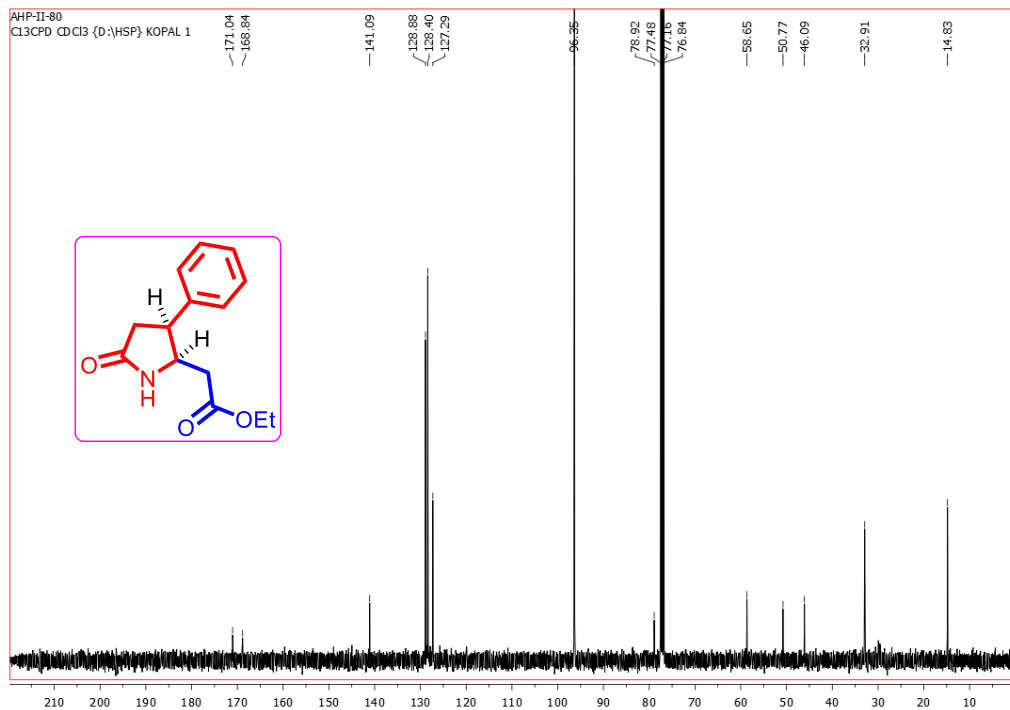


^1H (400 MHz, CDCl_3) NMR spectrum of Ethyl 2-((2R,3S)-3-(2,4-dimethoxyphenyl)-5-oxopyrrolidin-2-yl)acetate **17b**.

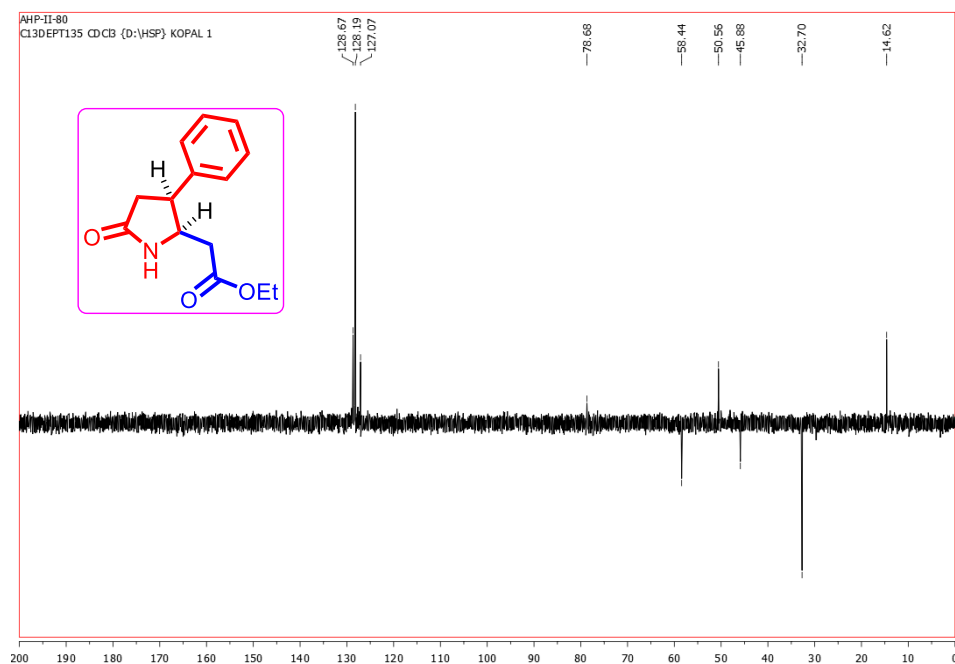




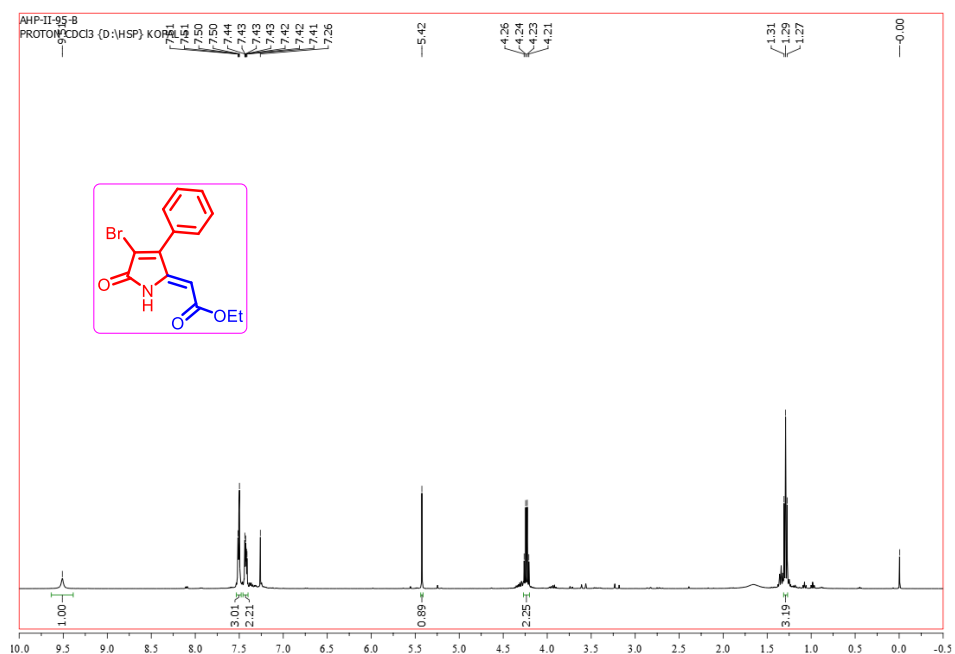
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl 2-((2R,3S)-5-oxo-3-phenylpyrrolidin-2-yl)acetate **17a**.



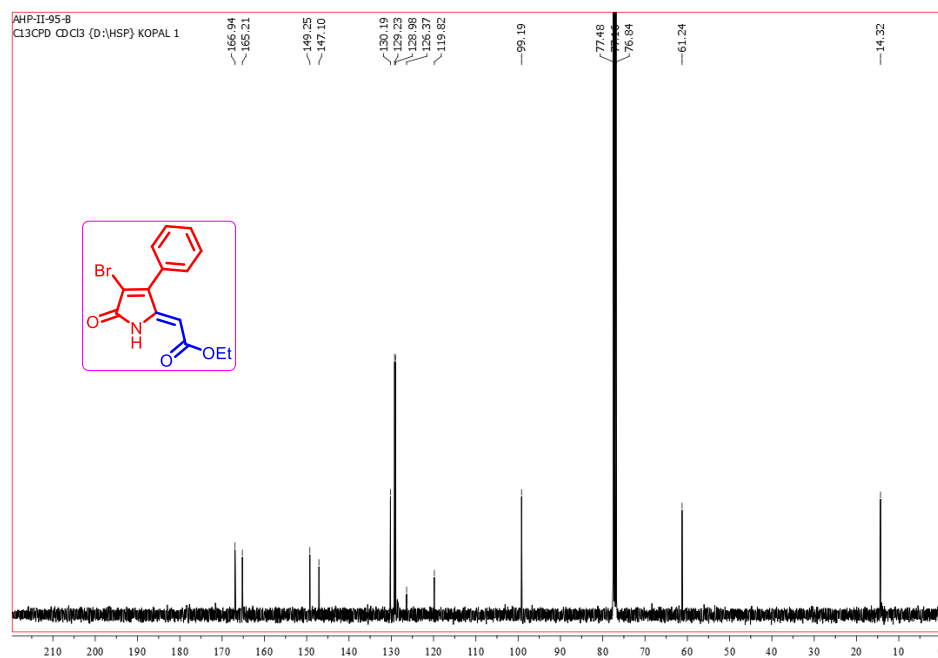
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl 2-((2R,3S)-5-oxo-3-phenylpyrrolidin-2-yl)acetate **17a**.



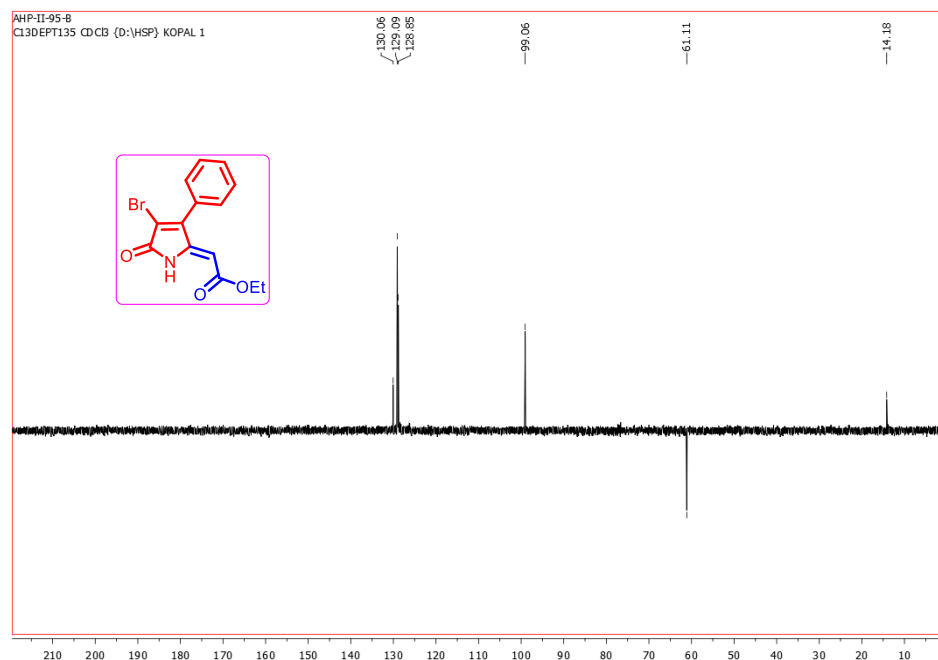
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl 2-((2R,3S)-5-oxo-3-phenylpyrrolidin-2-yl)acetate **17a**.



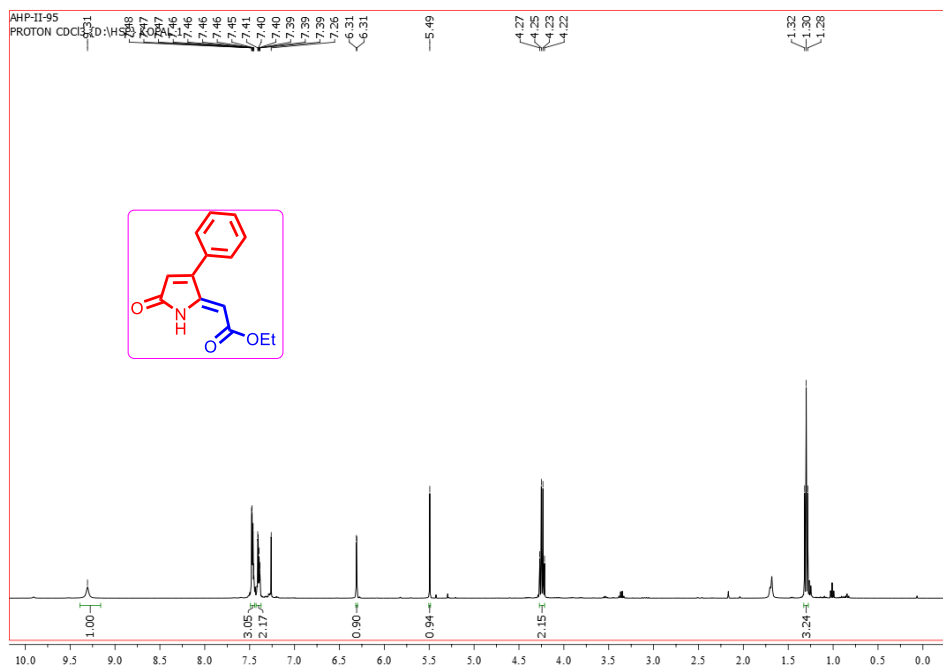
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(4-bromo-5-oxo-3-phenyl-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **19**.



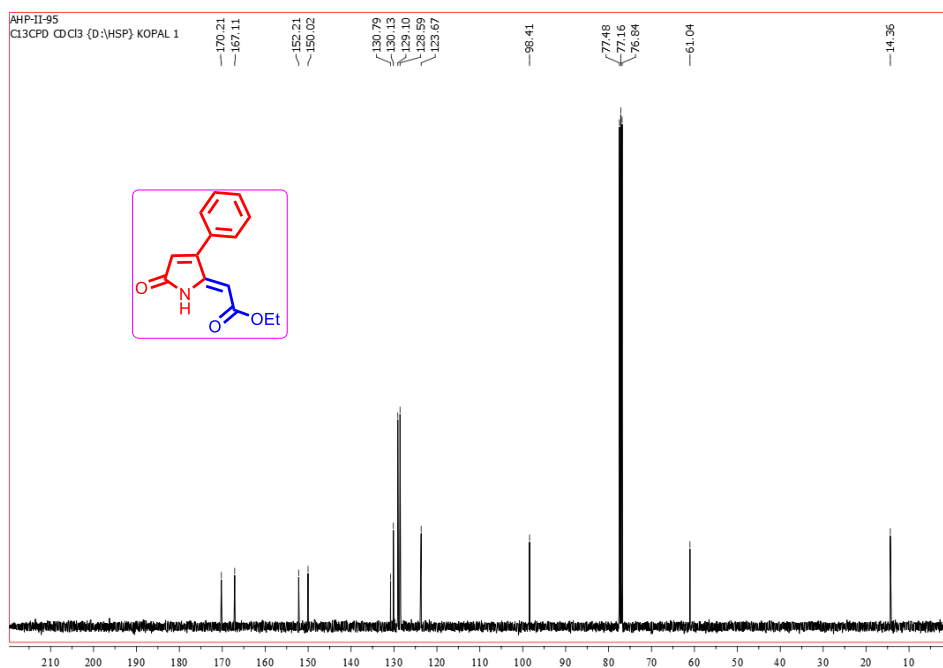
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(4-bromo-5-oxo-3-phenyl-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **19**.



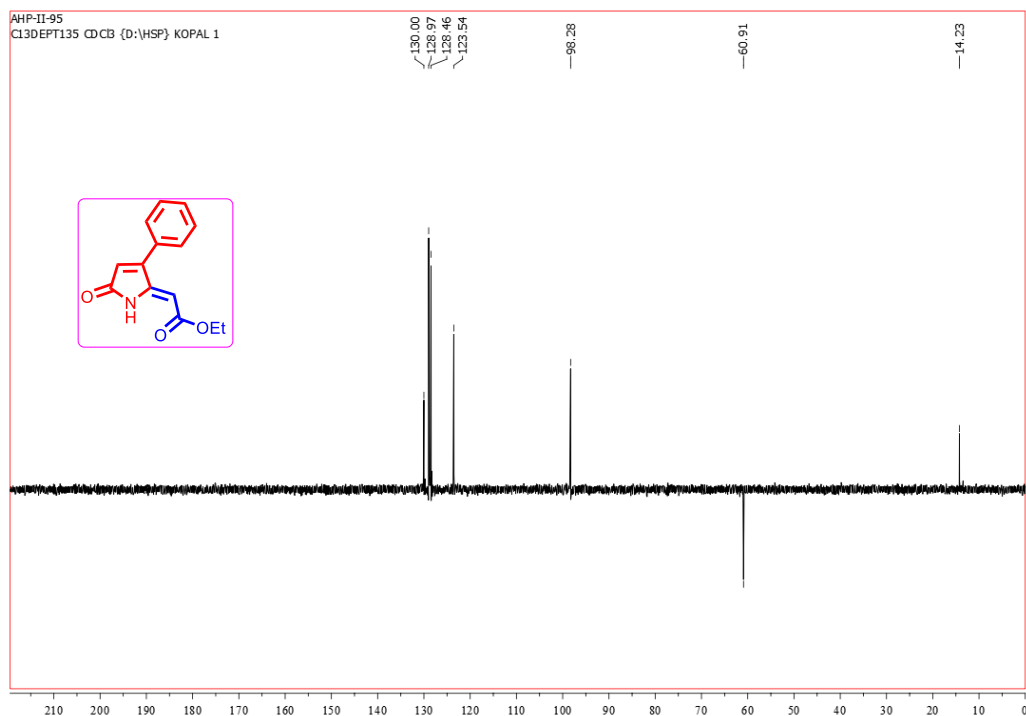
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(4-bromo-5-oxo-3-phenyl-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **19**.



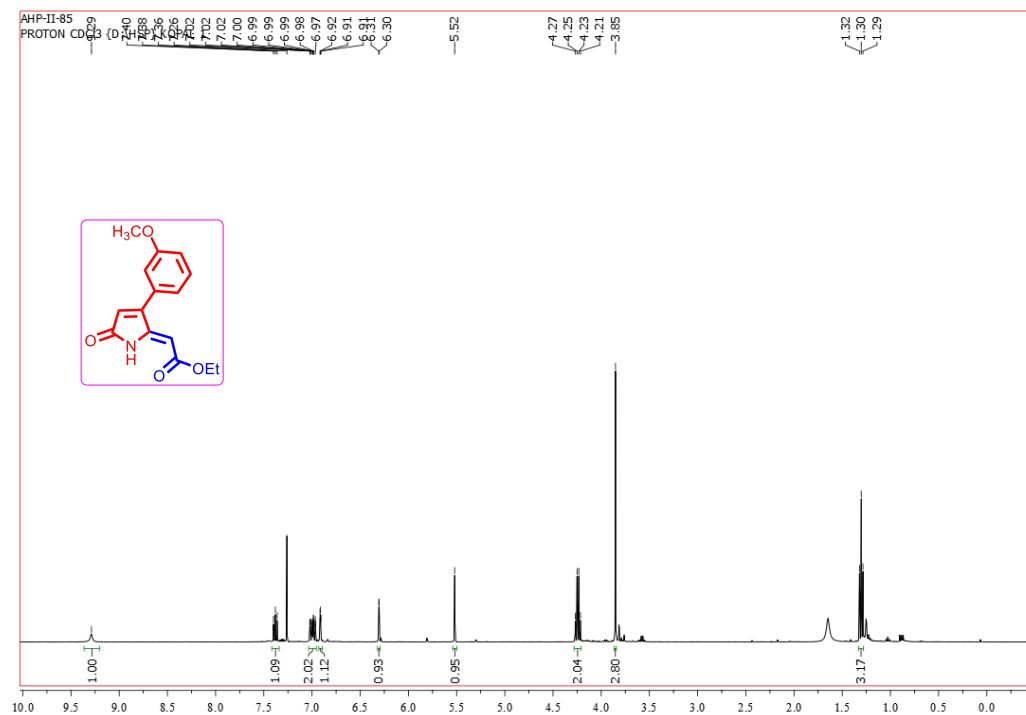
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-phenyl-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **20a**.



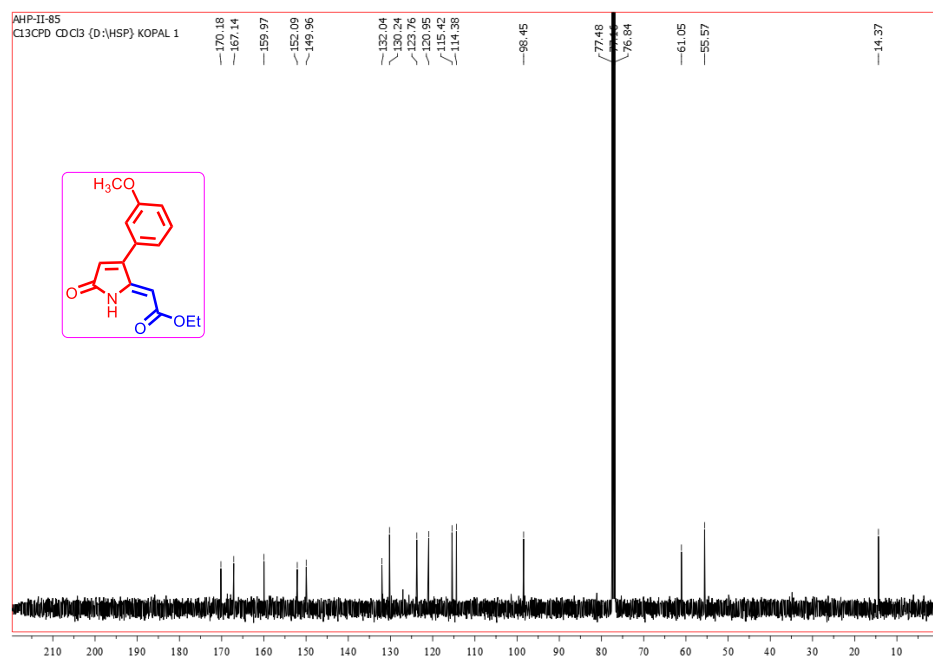
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-phenyl-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **20a**.



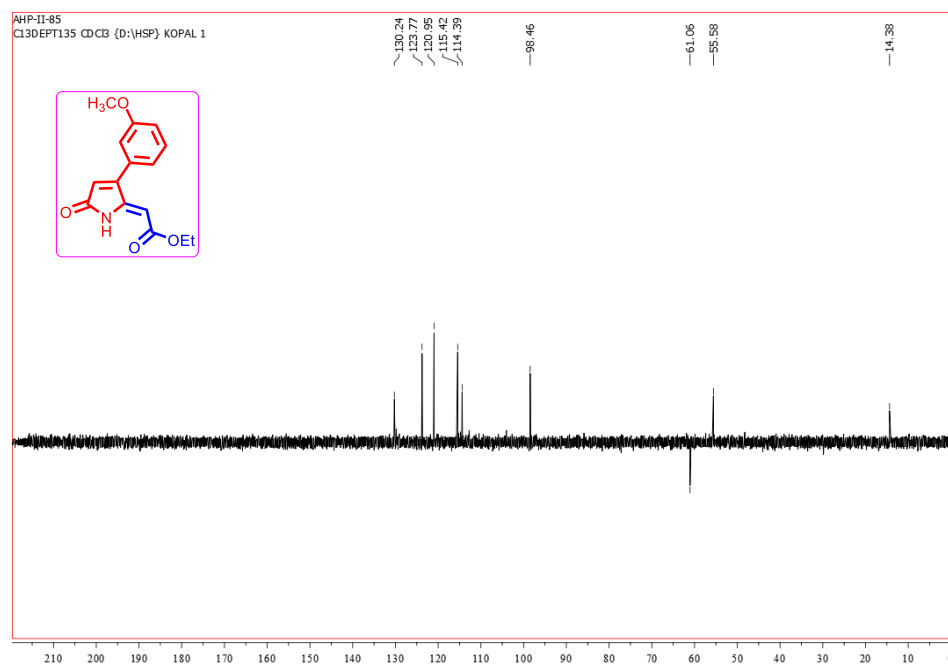
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(5-oxo-3-phenyl-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **20a**.



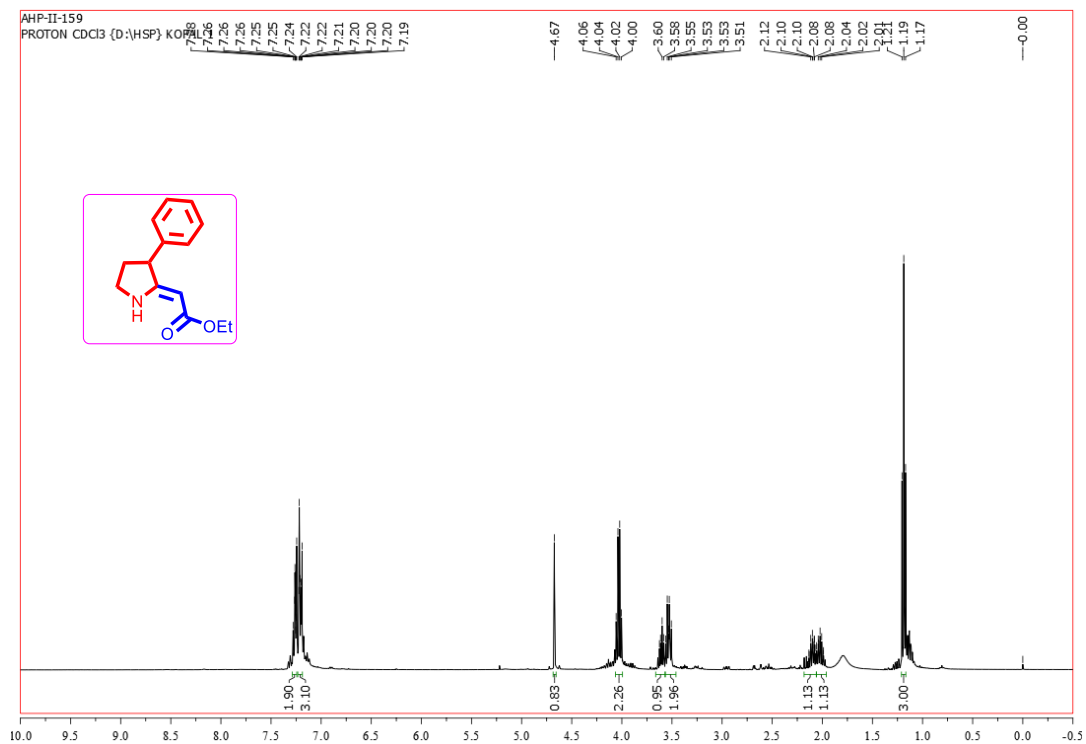
^1H (400 MHz, CDCl_3) NMR spectrum of ethyl (Z)-2-(3-(3-methoxyphenyl)-5-oxo-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **20b**.



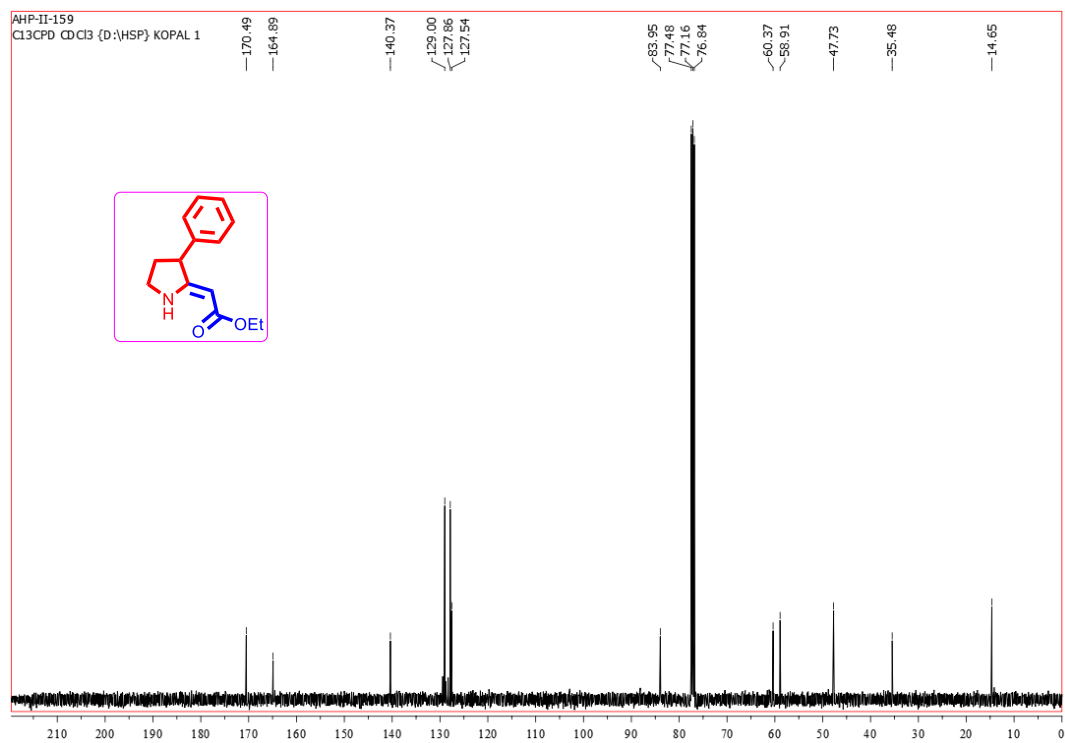
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(3-methoxyphenyl)-5-oxo-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **20b**.



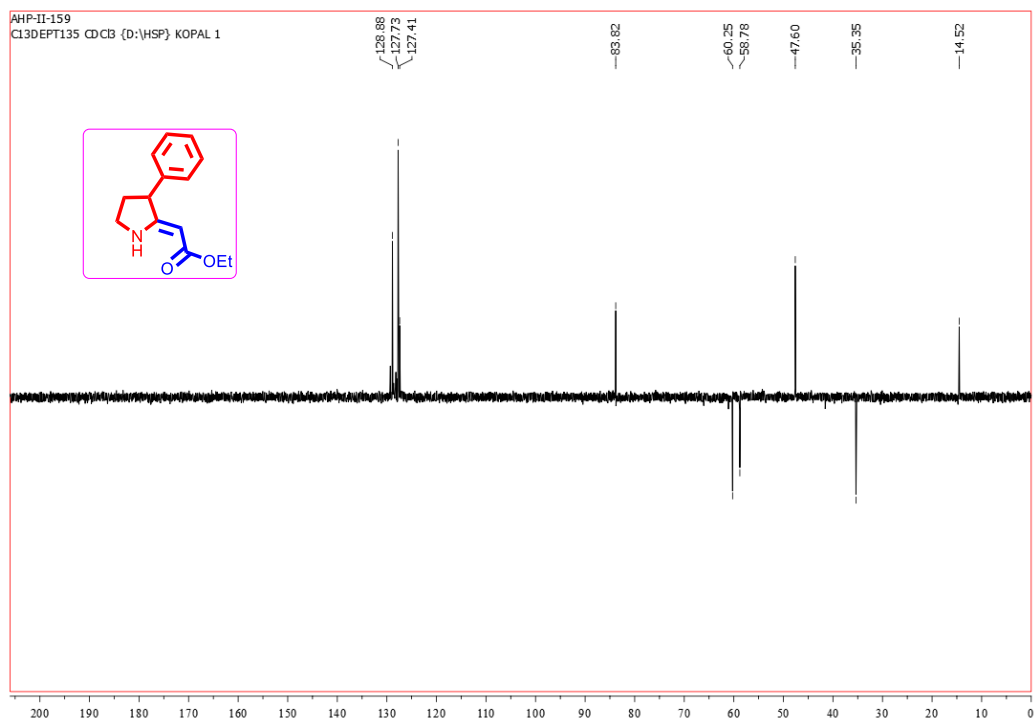
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-2-(3-(3-methoxyphenyl)-5-oxo-1,5-dihydro-2H-pyrrol-2-ylidene)acetate **20b**.



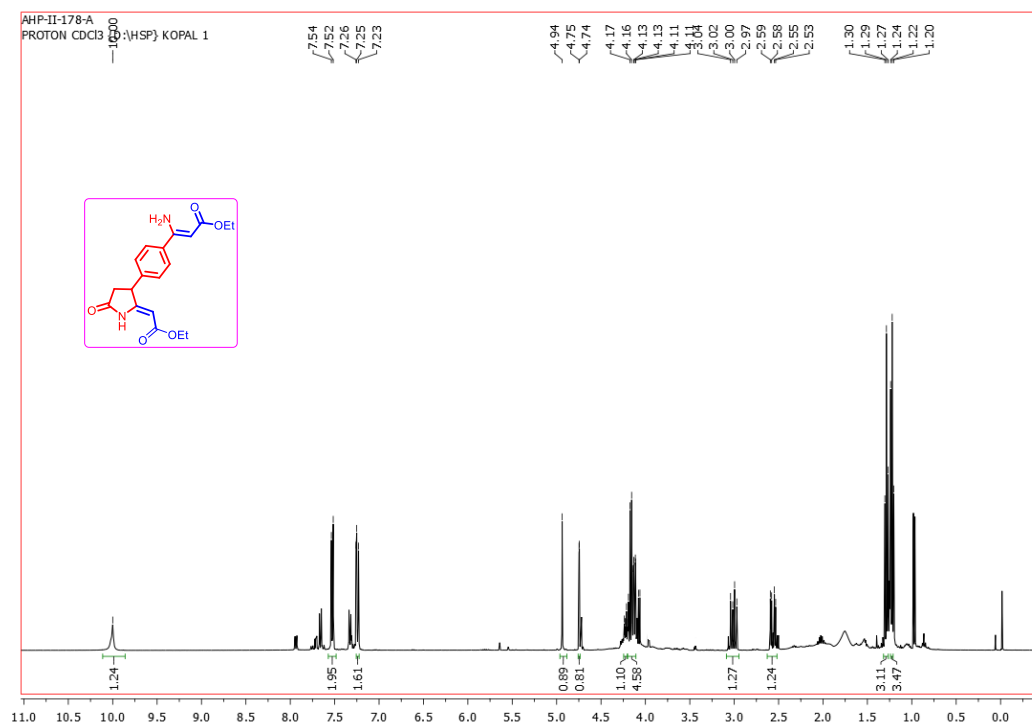
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-phenylpyrrolidin-2-ylidene)acetate **16**.



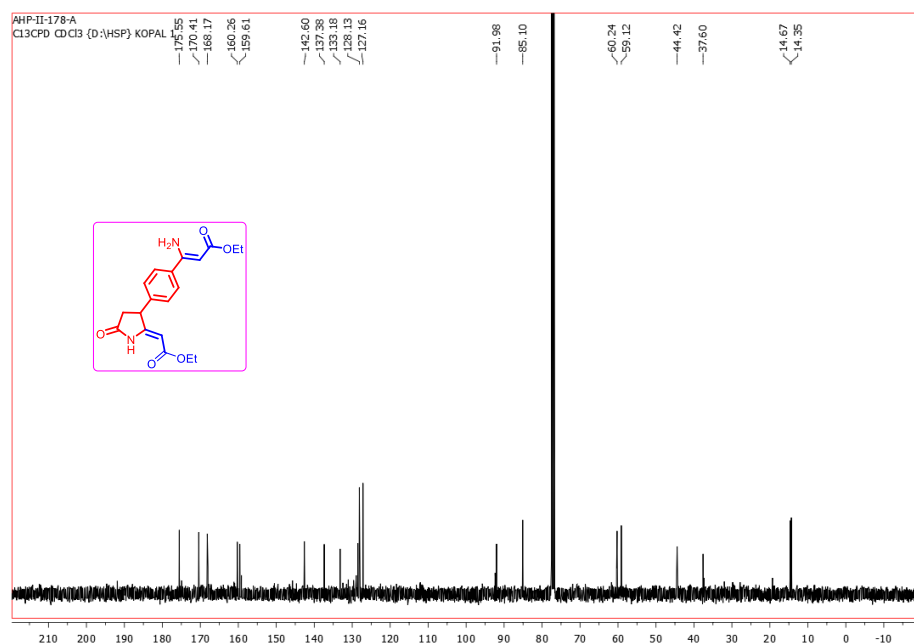
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-phenylpyrrolidin-2-ylidene)acetate **16**.



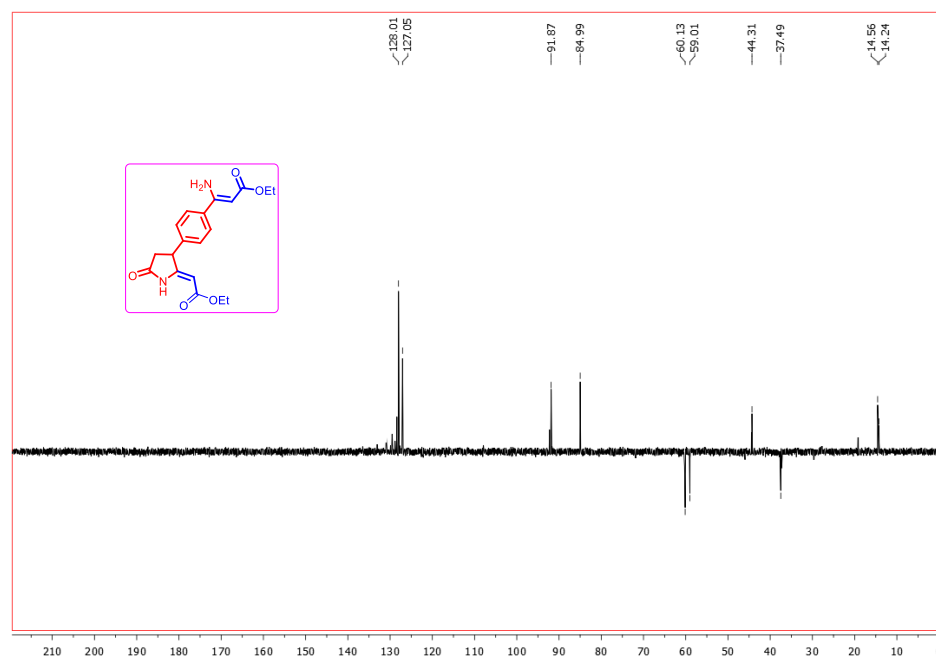
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-2-(3-phenylpyrrolidin-2-ylidene)acetate **16**.



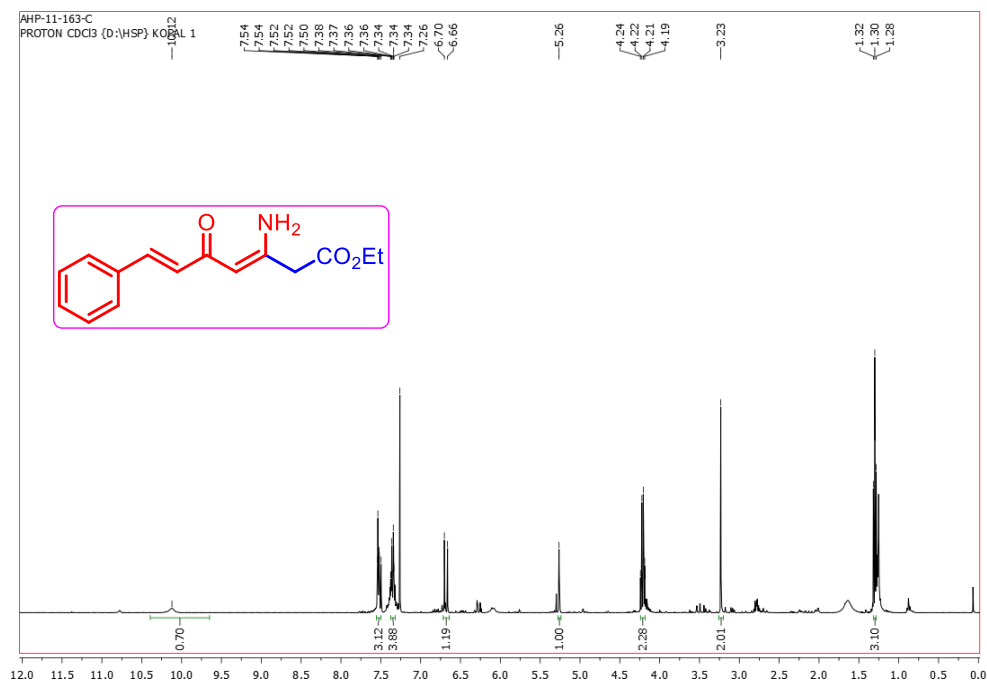
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (Z)-3-amino-3-(4-((Z)-2-(2-ethoxy-2-oxoethylidene)-5-oxopyrrolidin-3-yl)phenyl)acrylate **23**.



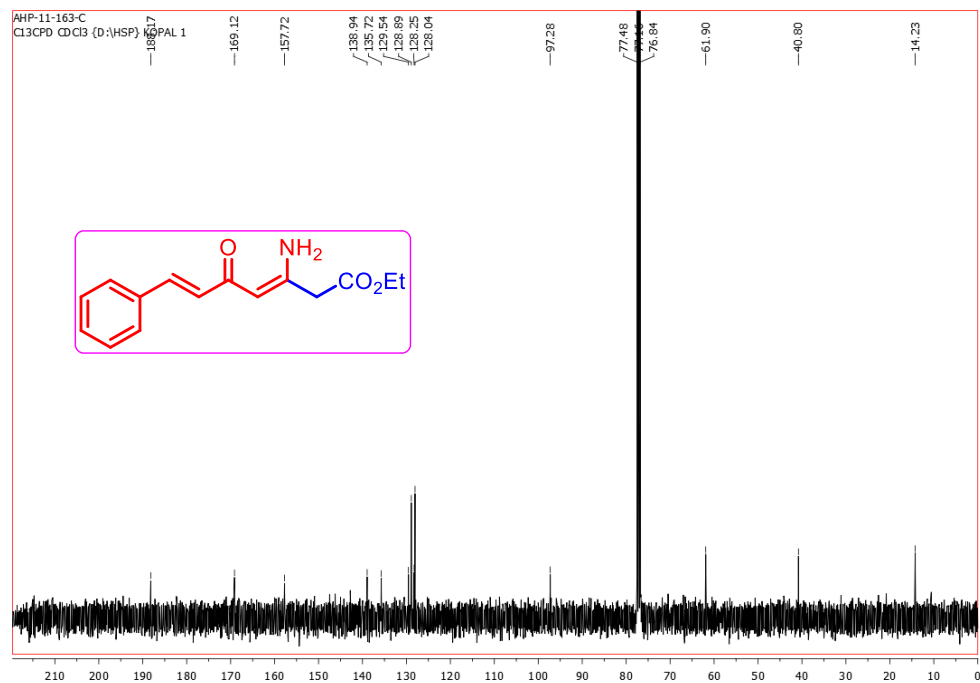
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-3-amino-3-(4-((Z)-2-(2-ethoxy-2-oxoethylidene)-5-oxopyrrolidin-3-yl)phenyl)acrylate **23**.



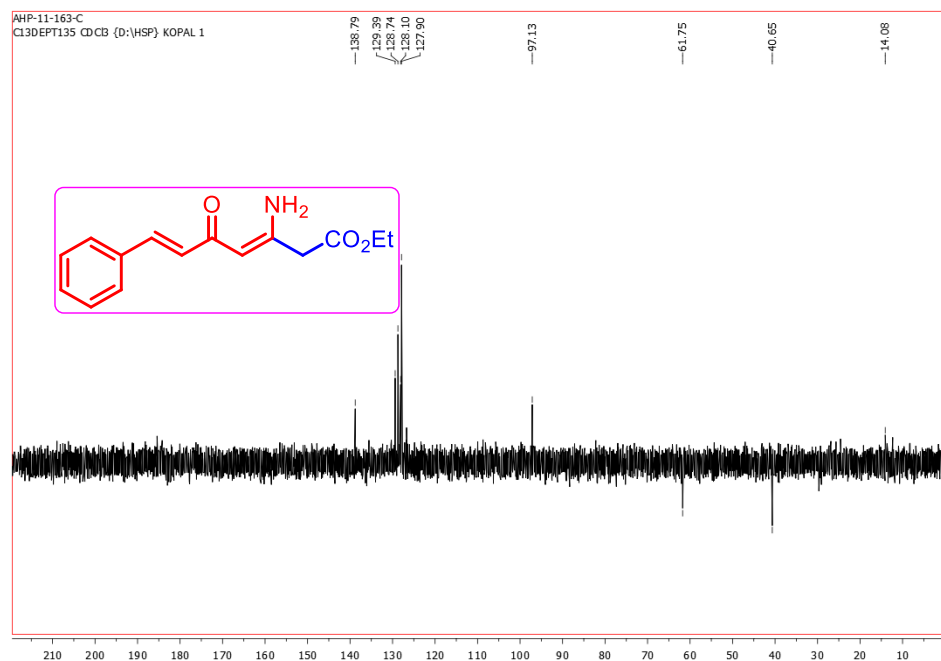
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-3-amino-3-(4-((Z)-2-(2-ethoxy-2-oxoethylidene)-5-oxopyrrolidin-3-yl)phenyl)acrylate **23**.



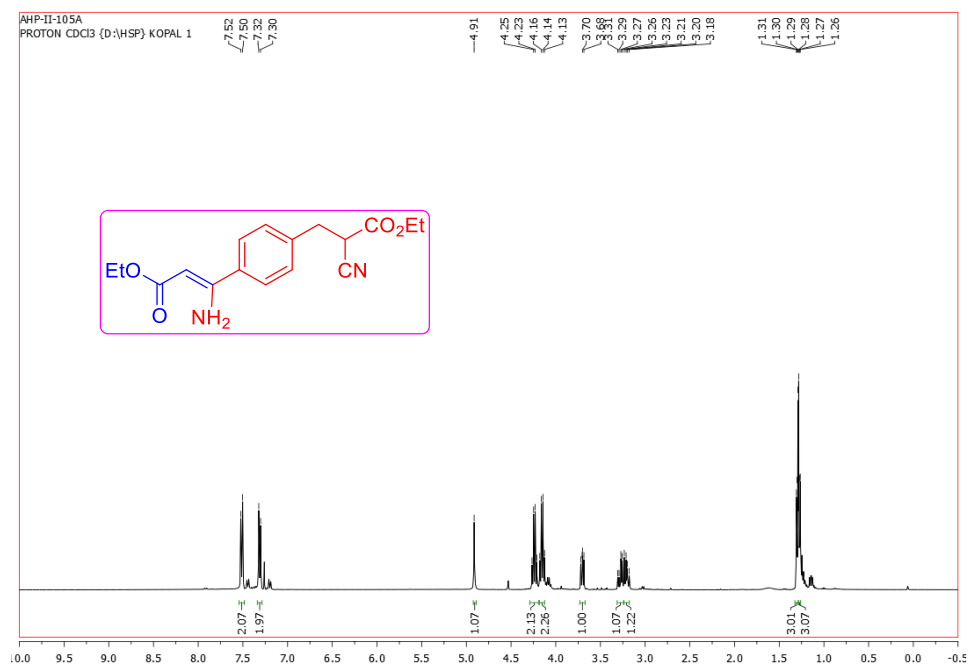
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl (3Z,6E)-3-amino-5-oxo-7-phenylhepta-3,6-dienoate **30**.



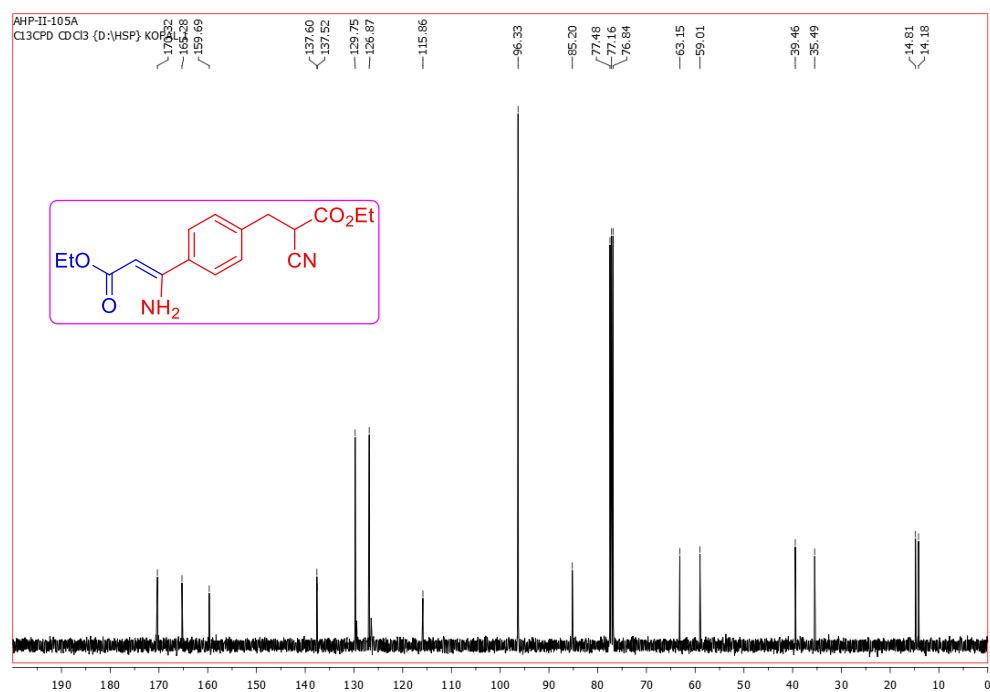
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl (3Z,6E)-3-amino-5-oxo-7-phenylhepta-3,6-dienoate **30**.



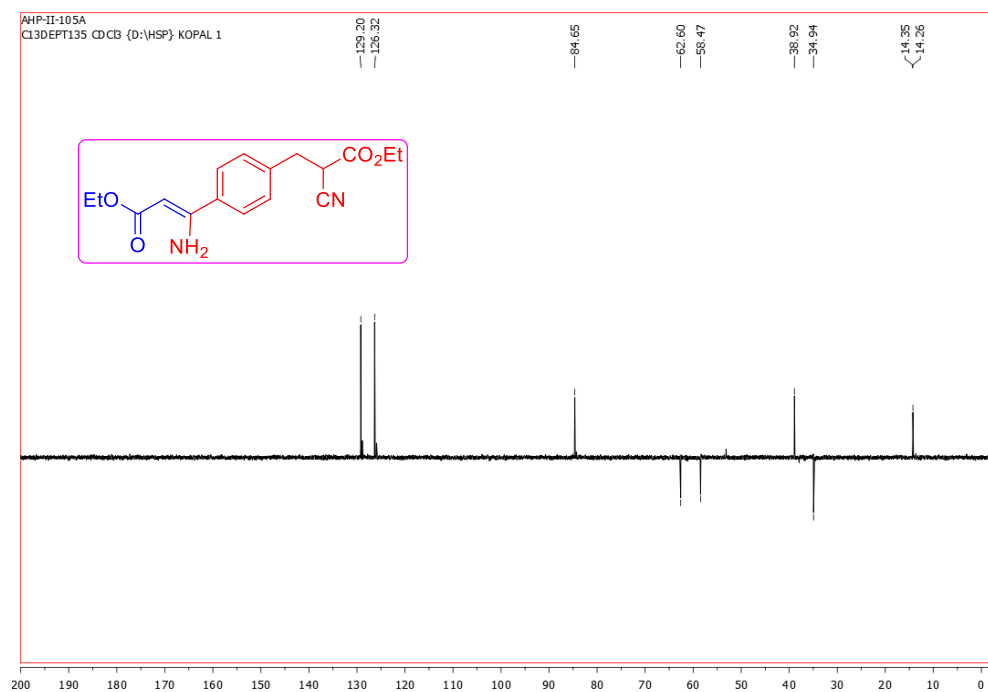
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (3Z,6E)-3-amino-5-oxo-7-phenylhepta-3,6-dienoate **30**.



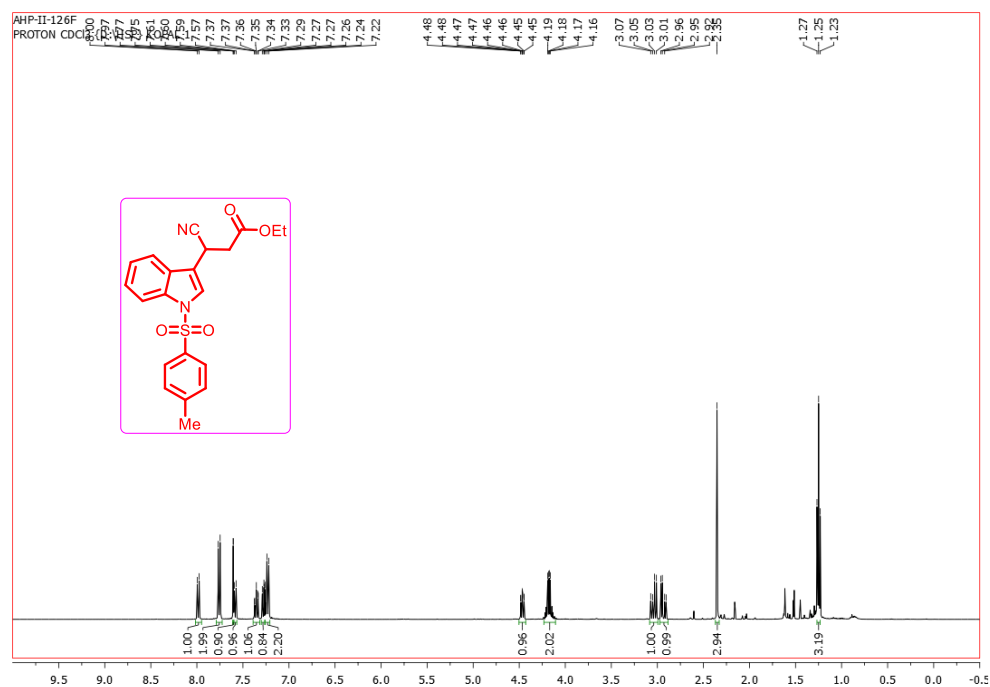
^1H (400 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-3-amino-3-(4-(2-cyano-3-ethoxy-3-oxopropyl)phenyl)acrylate **25**.



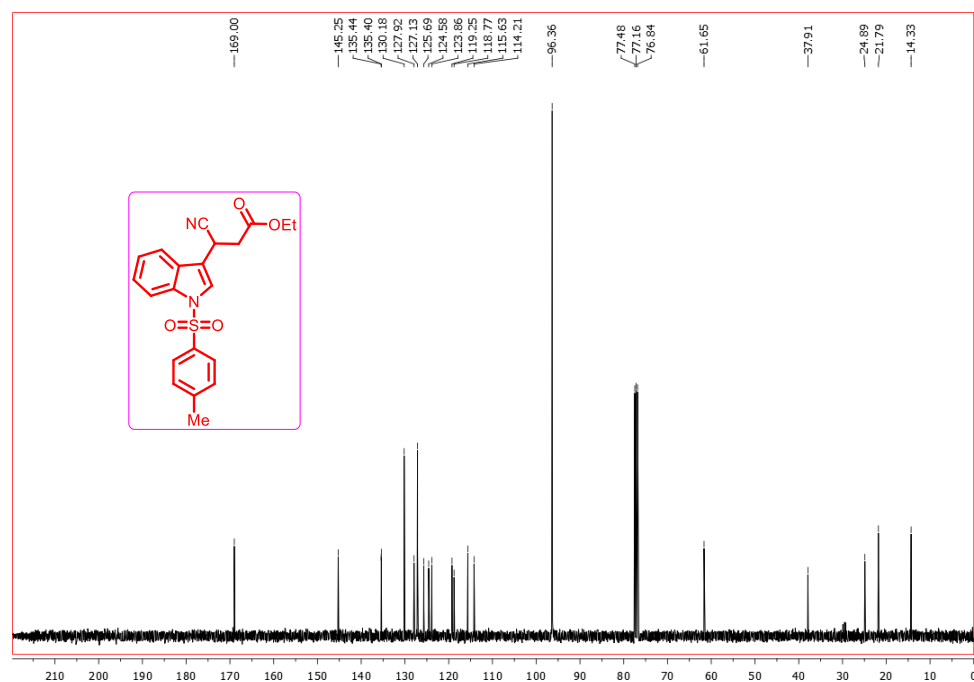
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-3-amino-3-(4-(2-cyano-3-ethoxy-3-oxopropyl)phenyl)acrylate **25**.



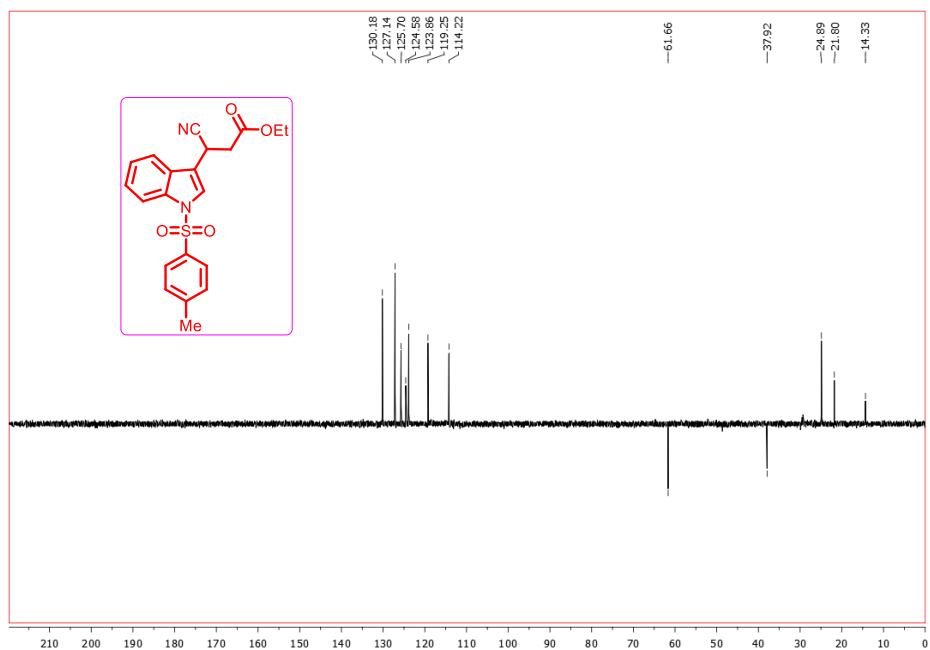
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl (Z)-3-amino-3-(4-(2-cyano-3-ethoxy-3-oxopropyl)phenyl)acrylate **25**.



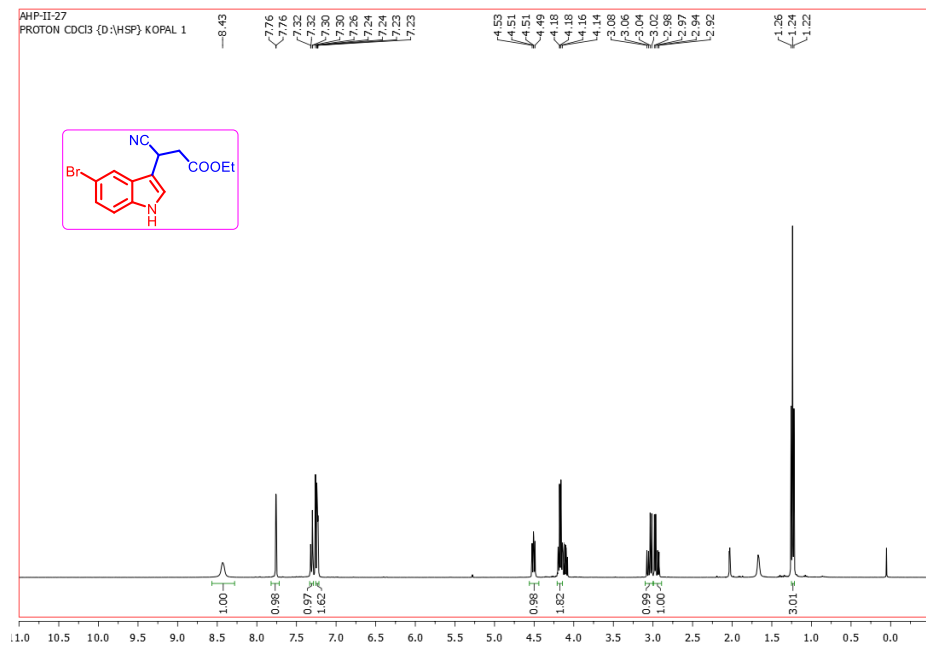
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(1-tosyl-1H-indol-3-yl)propanoate **10n**.



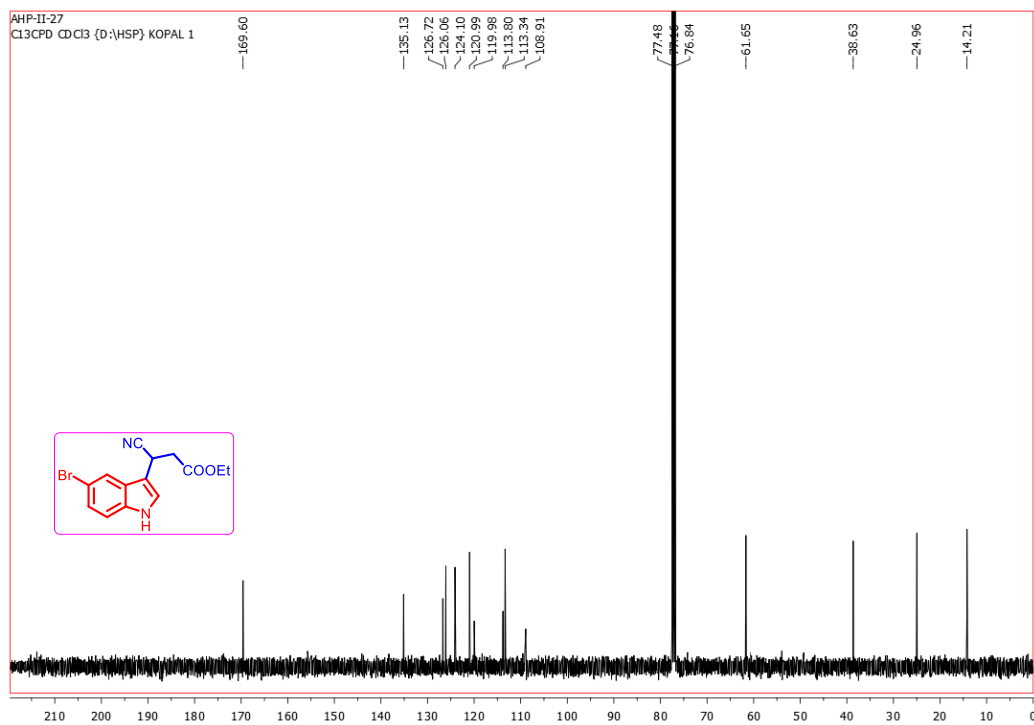
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(1-tosyl-1H-indol-3-yl)propanoate **10n**.



DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(1-tosyl-1H-indol-3-yl)propanoate **10n**.

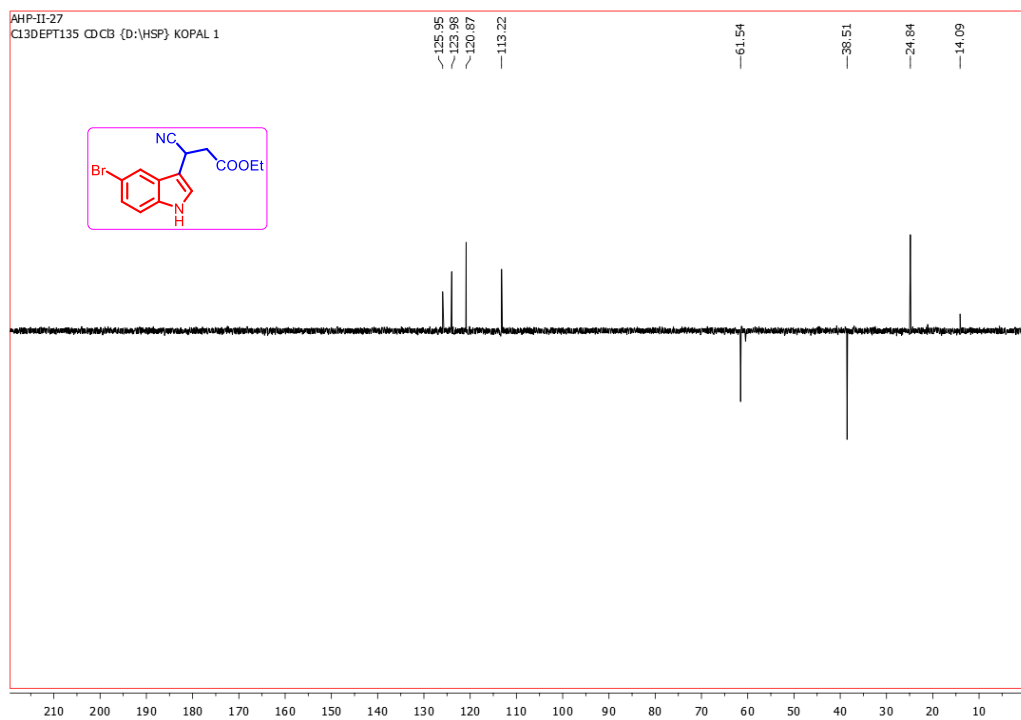


¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl 3-(5-bromo-1H-indol-3-yl)-3-cyanopropanoate **10o**.

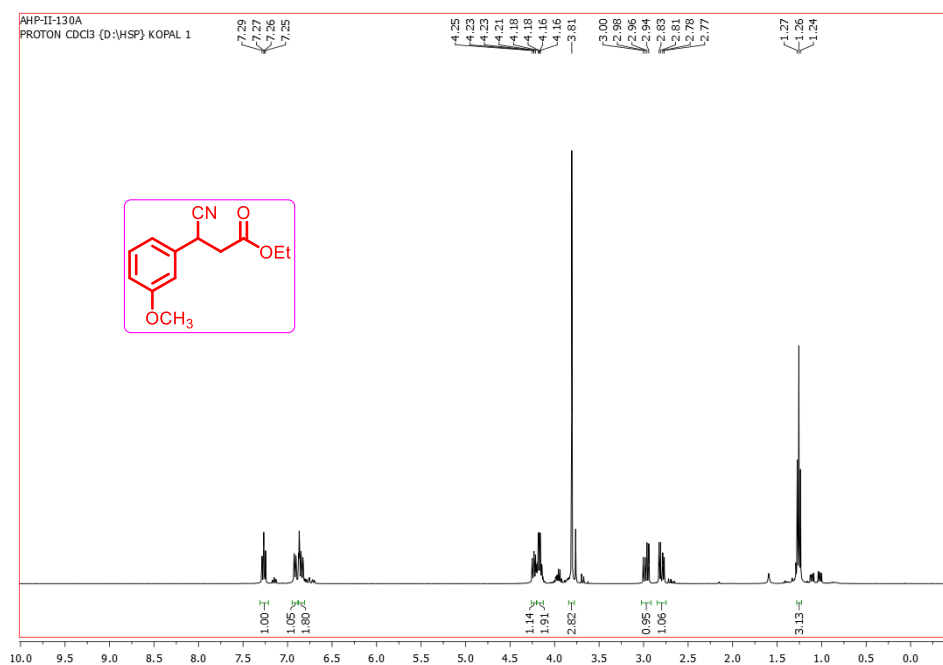


^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl 3-(5-bromo-1H-indol-3-yl)-3-cyanopropanoate

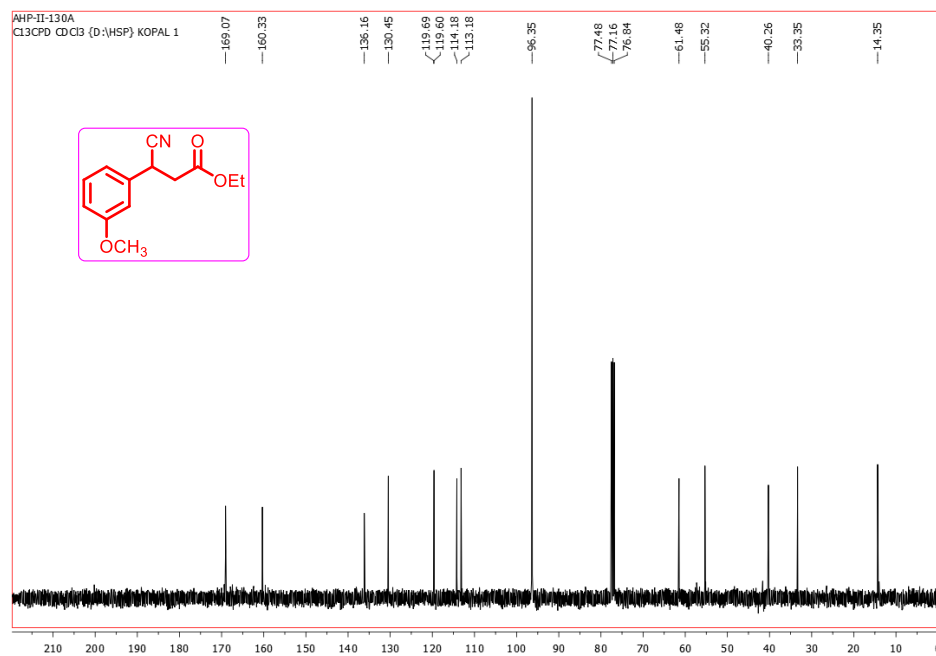
10o.



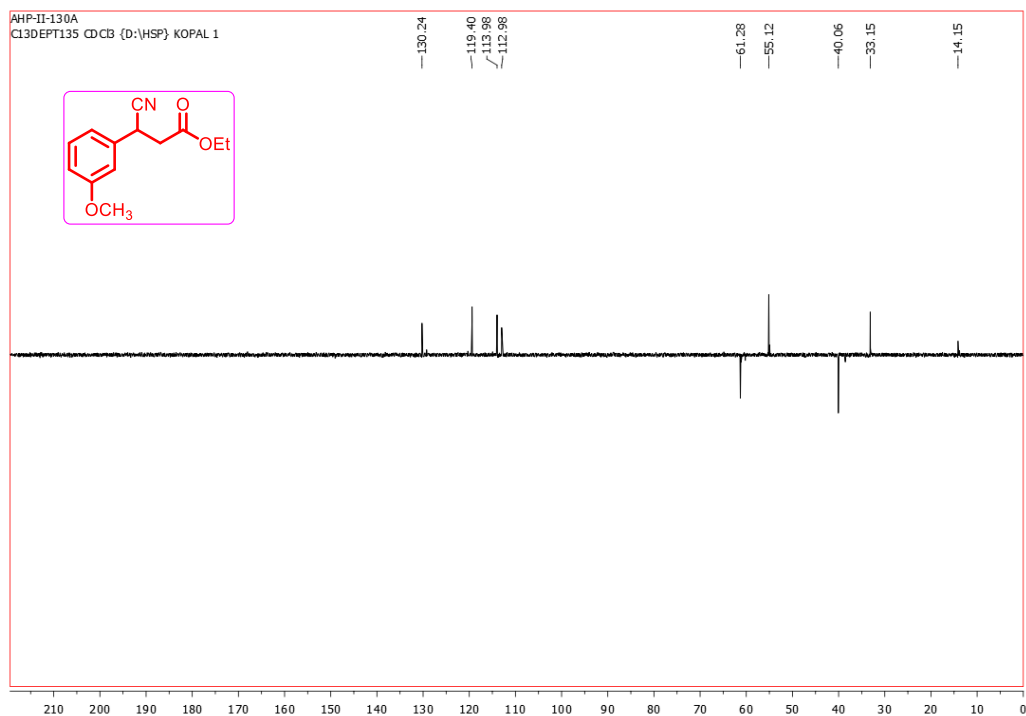
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl 3-(5-bromo-1H-indol-3-yl)-3-cyanopropanoate **10o**.



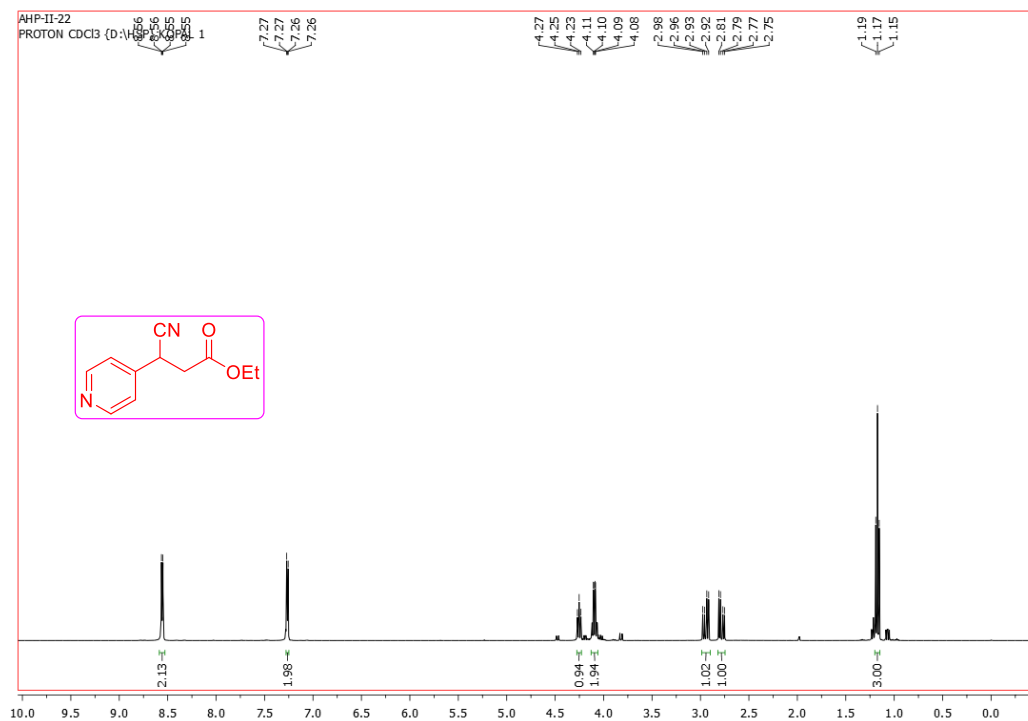
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(3-methoxyphenyl)propanoate **10f**.



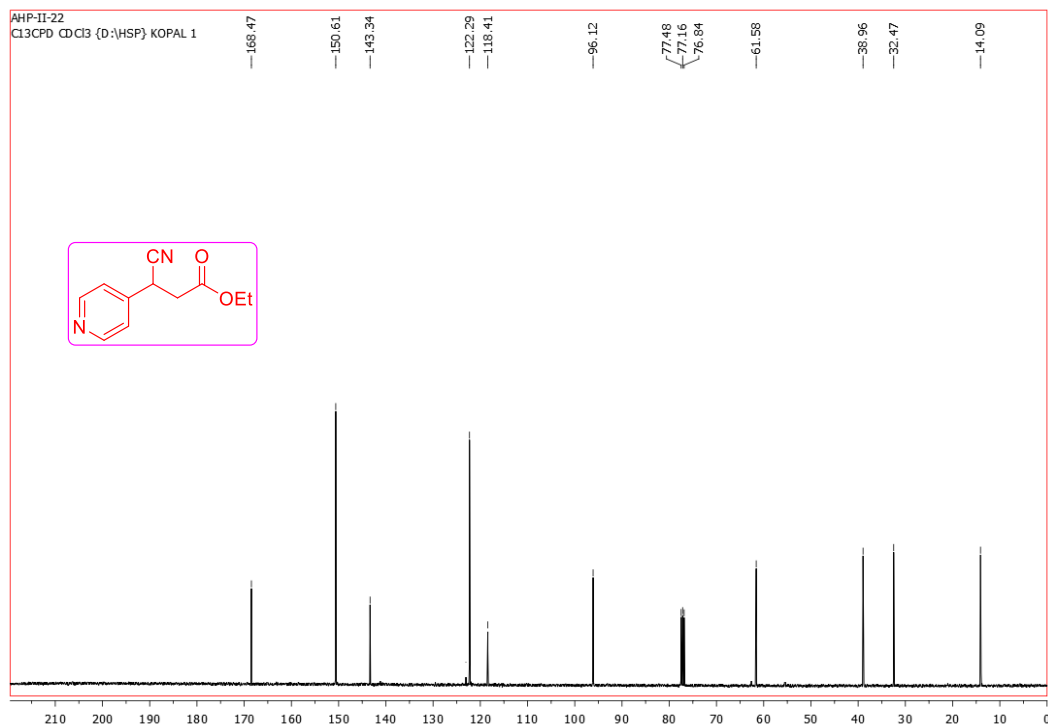
¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(3-methoxyphenyl)propanoate **10f**.



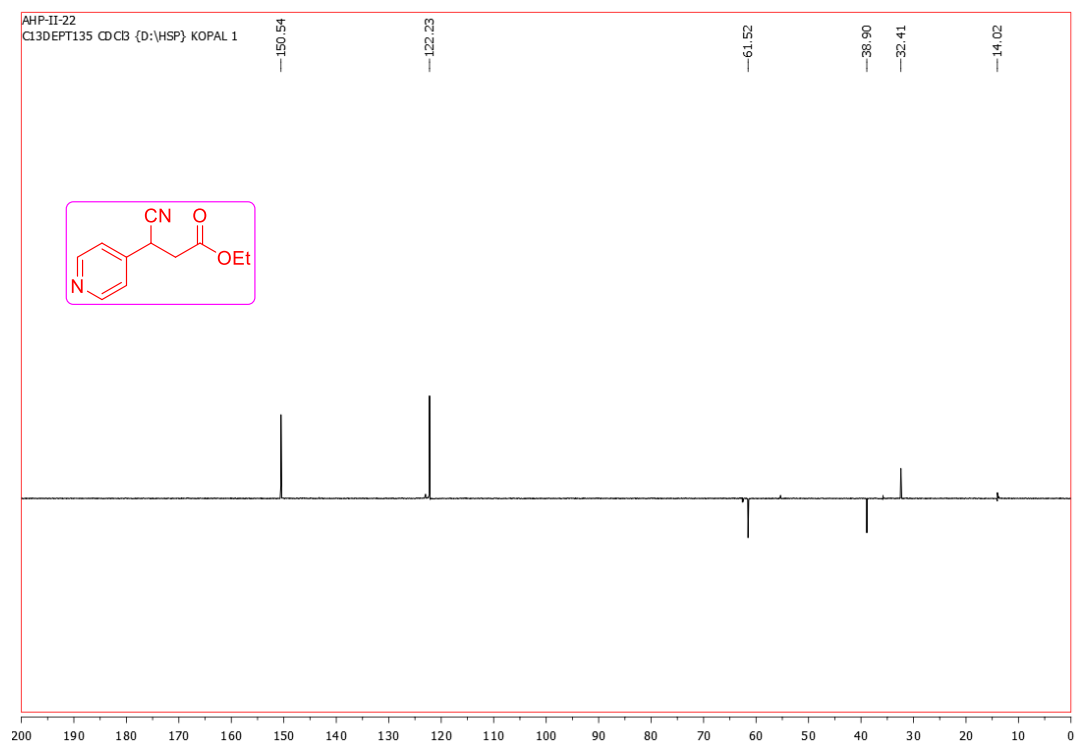
DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(3-methoxyphenyl)propanoate **10f**.



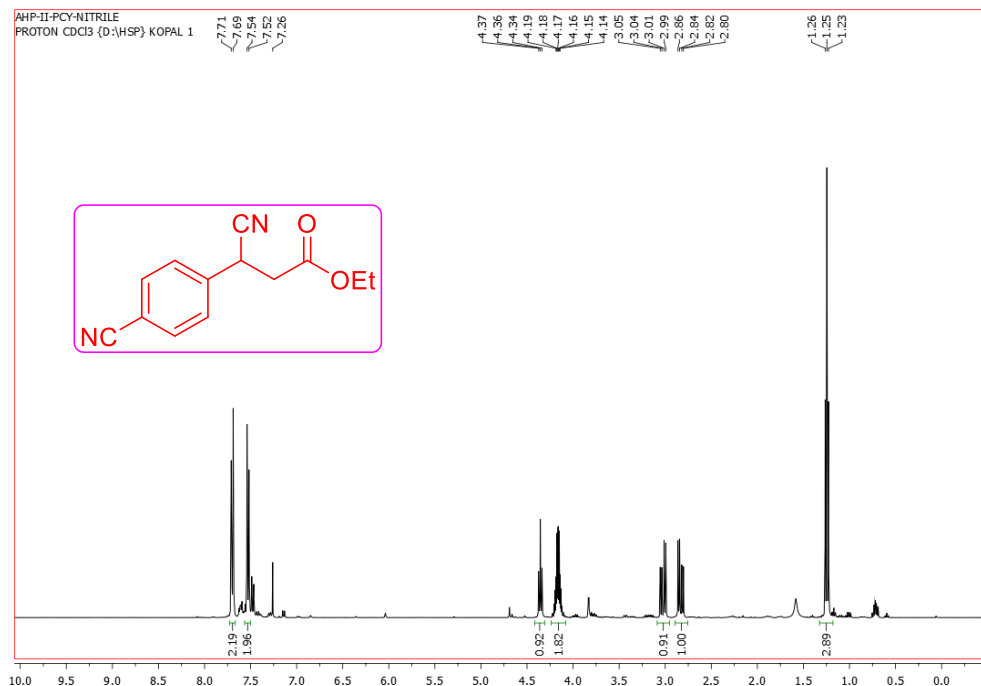
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(pyridin-4-yl)propanoate **10l**.



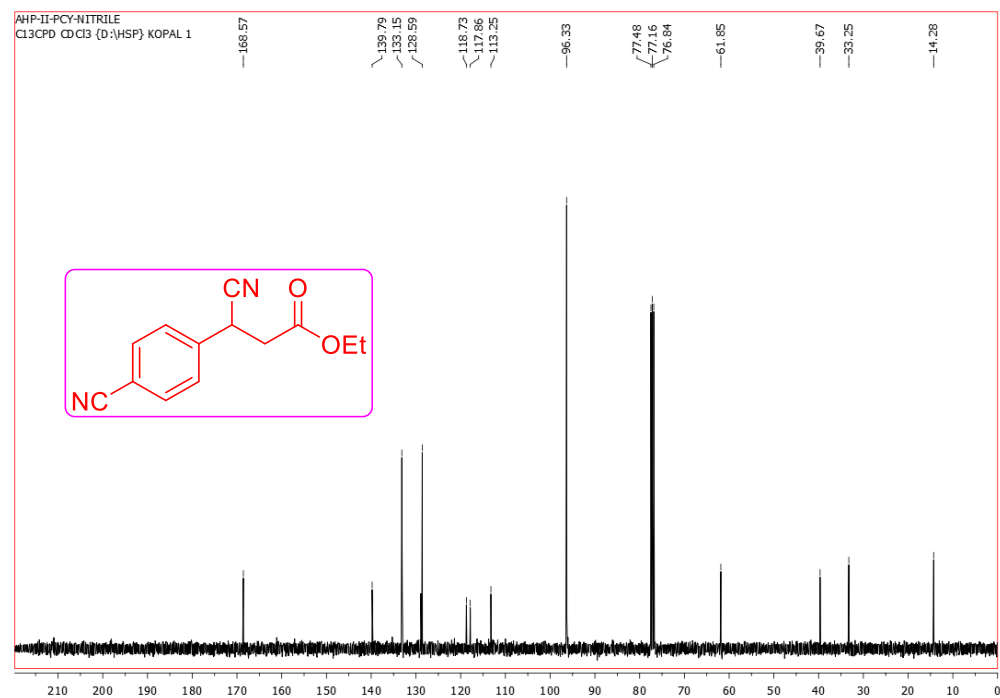
^{13}C (100 MHz, CDCl_3) NMR spectrum of Ethyl 3-cyano-3-(pyridin-4-yl)propanoate **10l**.



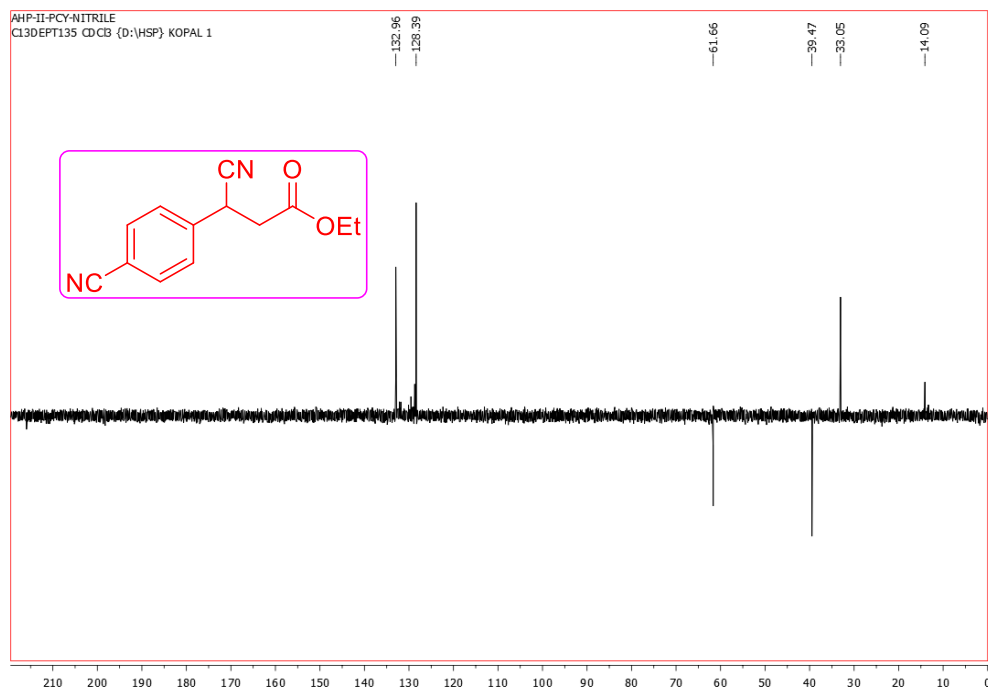
DEPT-135 (100 MHz, CDCl_3) NMR spectrum of Ethyl 3-cyano-3-(pyridin-4-yl)propanoate **10l**.



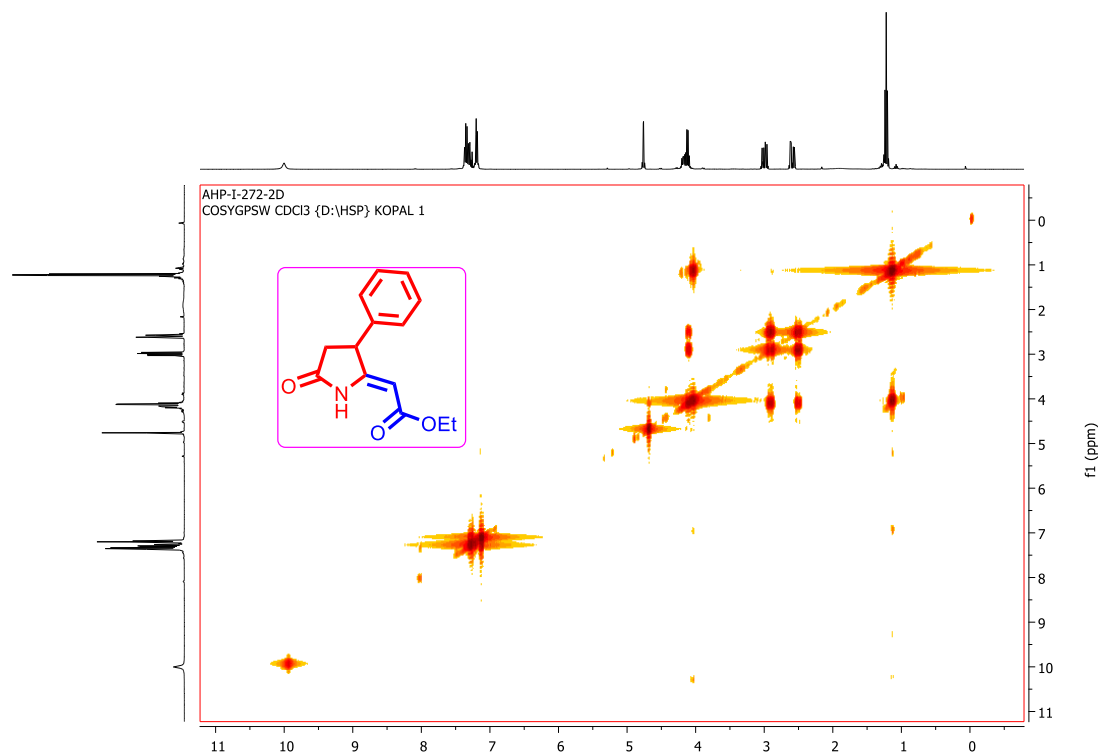
¹H (400 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(4-cyanophenyl)propanoate **10s**.

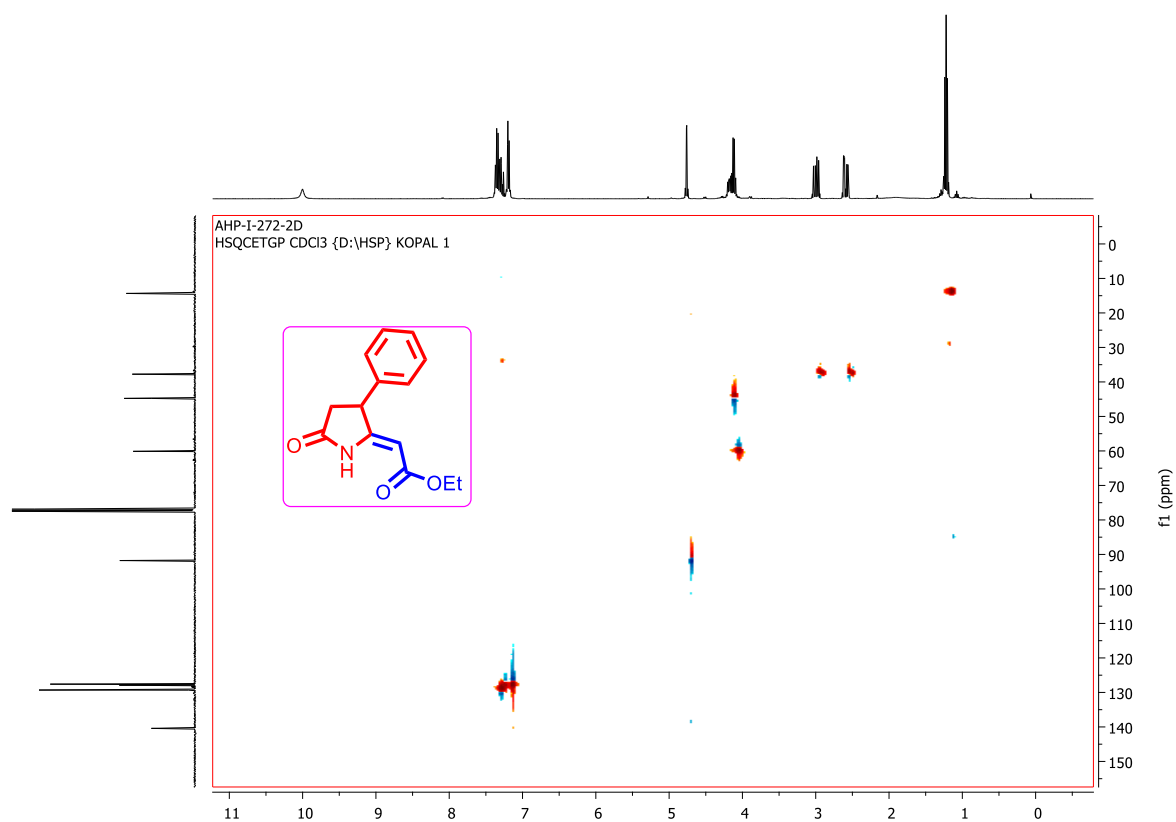
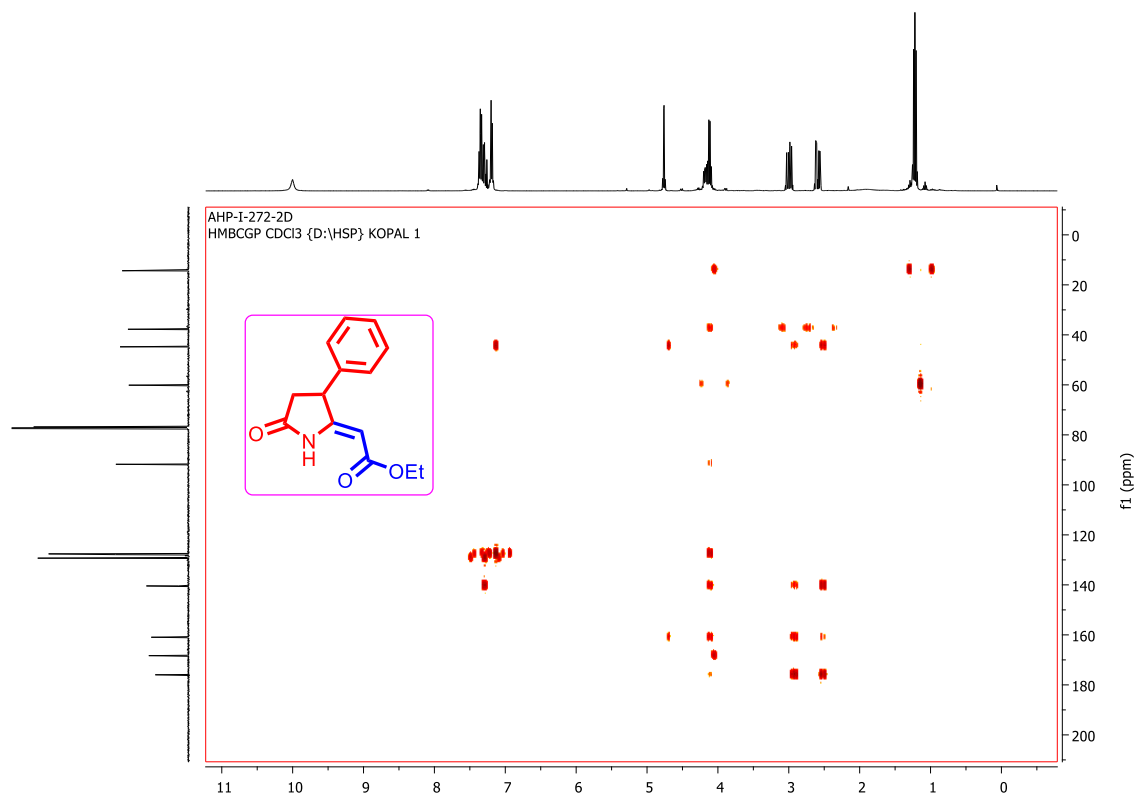


¹³C (100 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(4-cyanophenyl)propanoate **10s**.



DEPT-135 (100 MHz, CDCl₃) NMR spectrum of Ethyl 3-cyano-3-(4-cyanophenyl)propanoate **10s**.





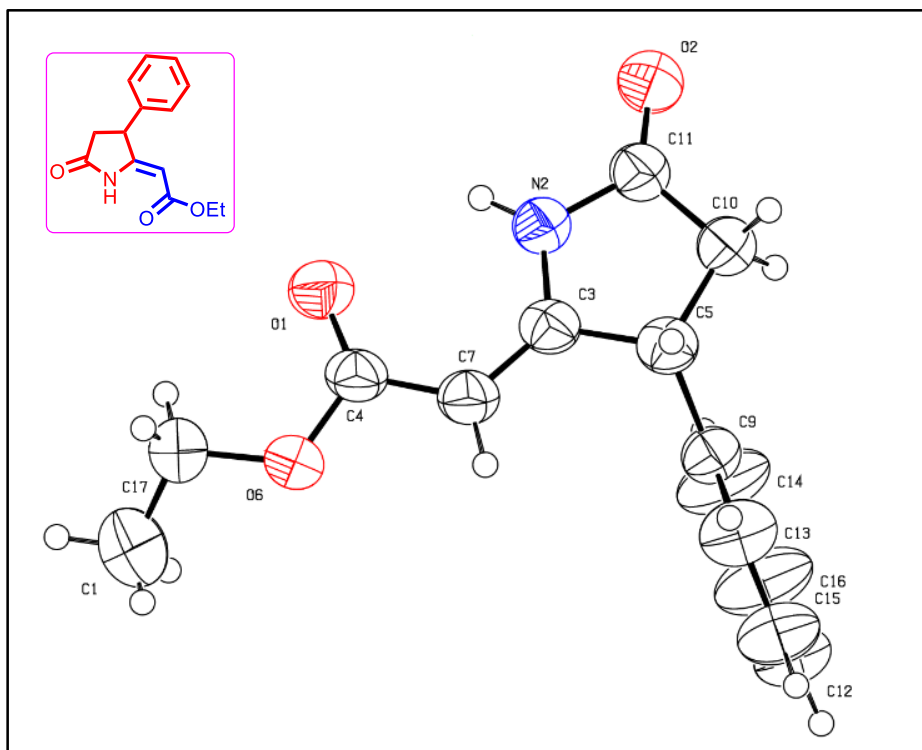


Figure 1. ORTEP diagram of Ethyl (Z)-2-(5-oxo-3-phenylpyrrolidin-2-ylidene)acetate **12a**. Empirical formula, C₁₄H₁₅NO₃; formula weight, 245.27; Crystal color, colourless plate, 295K; Crystal System, monoclinic; lattice parameters, $a = 25.920(3) \text{ \AA}$, $b = 5.4308(6) \text{ \AA}$, $c = 18.988(2) \text{ \AA}$; $\alpha = 90.0$, $\beta = 103.173(13)$, $\gamma = 90.0$; $V = 2602.5(6) \text{ \AA}^3$; space group I 1 2/a 1; $D_{\text{calcd}} = 1.252 \text{ g/cm}^3$; $F_{000} = 1040.52$; $R(I \geq 2\sigma_1) = 0.0615(1786)$, $wR^2 = 0.1904(3012)$; $h, k, l_{\text{max}} = 34, 7, 25$. The detailed X-ray crystallographic data for the compound **12a** is available with CCDC # 1905862 in the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

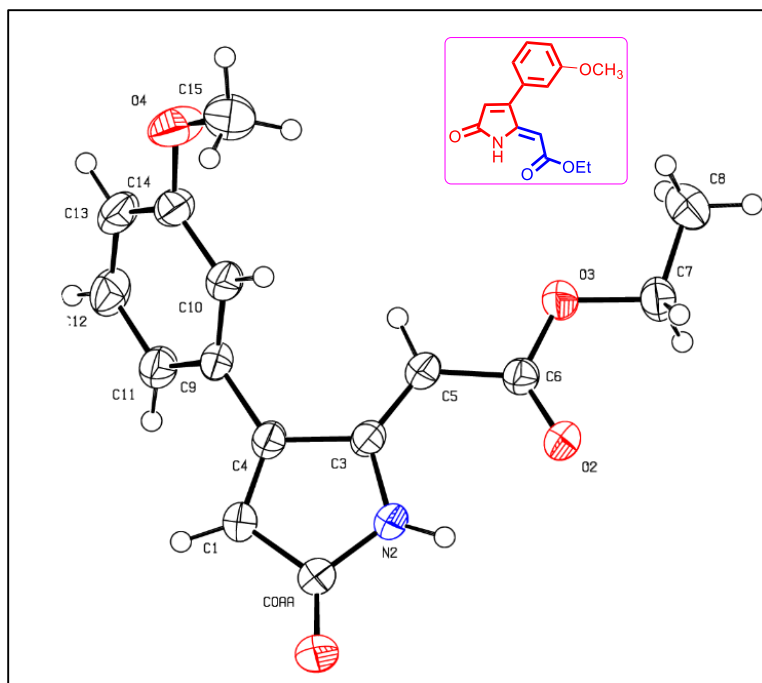
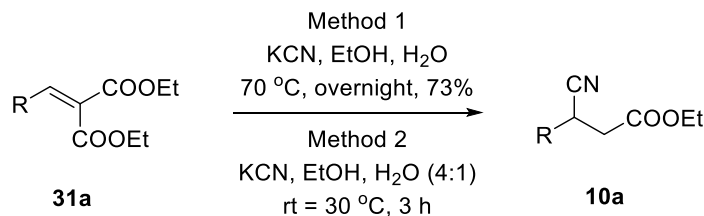


Figure 2. ORTEP diagram of Ethyl (*Z*)-2-(3-(3-Methoxyphenyl)-5-oxo-1,5-dihydro-2*H*-pyrrol-2-ylidene)acetate **20b**.

Empirical formula, C₁₅H₁₅NO₄; formula weight, 273.29; Crystal color, faint yellow color block, 298 K; Crystal System, monoclinic; lattice parameters, *a* = 16.6907(12) Å, *b* = 4.2138(3) Å, *c* = 19.6741(12) Å, α = 90.0, β = 103.083(7), γ = 90.0; *V* = 1347.79(16) Å³; space group *P* 1 21/*n* 1; *D*_{calcd} = 1.3471 g/cm³; *F*₀₀₀ = 576.3; *R* (*I* ≥ 2σ₁) = 0.0379(2553), *wR*² = 0.1054(3011); *h*, *k*, *l* max = 22, 5, 27. The detailed X-ray crystallographic data for the compound **20b** is available with CCDC # 1912295 in the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

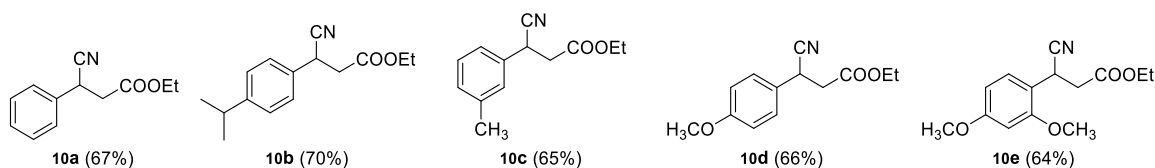
Reference 22

Table S1. Optimization of reaction conditions for the synthesis of β -cyano esters **10a** from diesters.



Entry	KCN (equiv.)	Solvent	Temp °C	Time (h)	Yield (%)
1	1	Ethanol	rt*	3	45
2	1	Ethanol	70	3	25
3	1	Ethanol:H ₂ O (6:1)	70	16	37
4	1.2	Ethanol:H ₂ O (6:1)	70 ^{\$}	16	32
5	1.5	Ethanol	rt	3	50
6	1.5	Ethanol	70	3	35
7	1.2	Ethanol:H ₂ O (6:1)	rt	3	55
8	1.5	Ethanol:H ₂ O (6:1)	rt	3	61
9	1.5	Ethanol:H₂O (4:1)	rt	3	67
10	1.5	Ethanol:H ₂ O (1:1)	rt	3	47
11	2	Ethanol:H ₂ O (4:1)	rt	3	61
12	1.5	Ethanol:H ₂ O (4:1)	70	18	45
13	1.5	Methanol	rt	3	20
14	1.5	Methanol:H ₂ O (4:1)	rt	3	22
15	1.5	Methanol:H ₂ O (4:1)	70	3	15
16	2	Isopropanol	rt	3	no rxn.
17	2	Isopropanol:H ₂ O (4:1)	rt-70	4	no rxn.

* rt = 30-35 °C; ^{\$} Reported conditions (Ref 23);



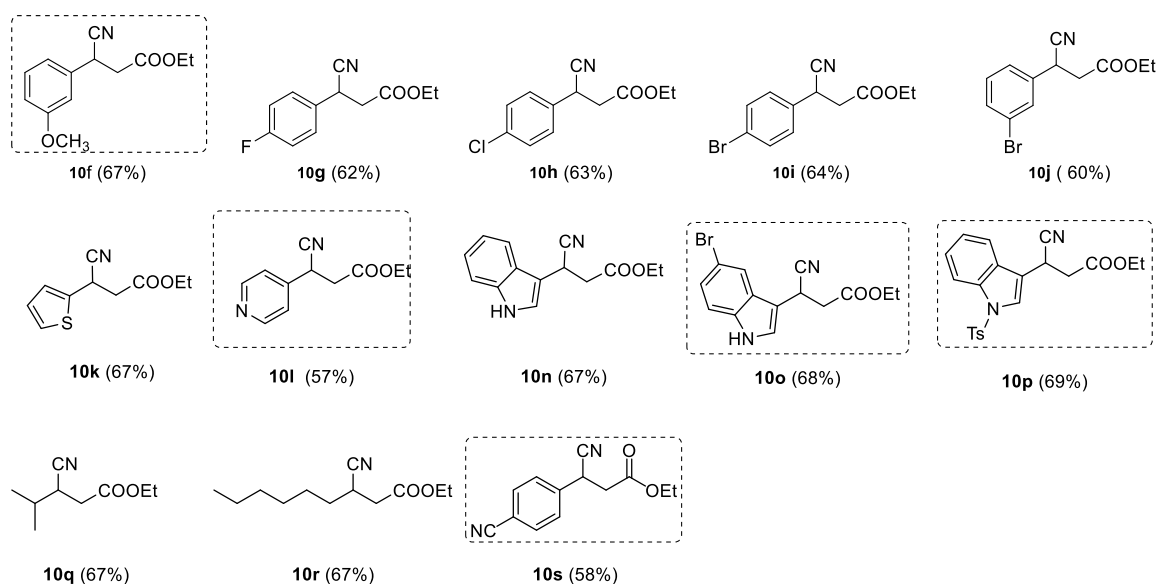


Figure 3. Structures of the nitrile esters **10a-s** prepared in the present work.

Table S2 A series of 2-pyrrolidinones synthesized.

Entry	Nitrile	R ¹	R ²	Time (h)	2-pyrrolidinone	Yield%
1	10a	C ₆ H ₅	Ethyl	6	12a	78
2	10b	4- <i>i</i> -PrC ₆ H ₄	Ethyl	7	12b	77
3	10c	3-MeC ₆ H ₄	Ethyl	7	12c	77
4	10d	4-MeOC ₆ H ₄	Ethyl	7	12d	67
5	10e	2,4-(MeO) ₂ C ₆ H ₃	Ethyl	7	12e	65
6	10f	3-MeOC ₆ H ₄	Ethyl	7	12f	77
7	10g	4-FC ₆ H ₄	Ethyl	5	12g	75
8	10h	4-ClC ₆ H ₄	Ethyl	5	12h	80
9	10i	4-BrC ₆ H ₄	Ethyl	6	12i	77
10	10j	3-BrC ₆ H ₄	Ethyl	6	12j	78
11	10k	2-Thienyl	Ethyl	5	12k	77
12	10q	<i>i</i> -Pr	Ethyl	6	12l	63
13	10r	<i>n</i> -Hexyl	Ethyl	6	12m	68
14	10n	3-indolyl	Ethyl	5	12n	83
15	10o	5-Br-3-indolyl	Ethyl	5	12o	85
16	10p	<i>N</i> -tosyl-3-indolyl	Ethyl	5	12p	82
17	10a	C ₆ H ₅	Methyl	5	12q	78
18	10b	4- <i>i</i> -PrC ₆ H ₄	Methyl	6	12r	77
19	10o	5-Br-3-indolyl	Methyl	4	12s	82
20	10l	4-pyridyl	Ethyl	12	No rxn.	-