Supporting information

Selective Synthesis of Trisubstituted Pyrroles through the Reactions of Alkynyl Fischer Carbene Complexes with Oxazolones

Julio Lopez,[1] Iván Velazco-Cabral ,[1] Eloy Rodríguez-De León,[1] Clarisa Villegas Gómez,[1] Francisco Delgado,[2] Ana Arrieta,[3,4] Fernando P. Cossío,[3,4] Miguel A. Vázquez.[1*]

[1]Departament of Chemistry, University of Guanajuato, Noria Alta S/N, 36050 Guanajuato, Gto., México.
[2]Departament of Organic Chemistry, National School of Biological Sciences-IPN, Prol. Carpio y Plan de Ayala S/N, 11340, CDMX, México.
[3]Departament of Organic Chemistry I and Centro de Innovación en Química Avanzada (ORFEO-CINQA) Universidad del País Vasco/Euskal Herriko Unibertsitatea (UPV/EHU), Manuel Lardizabal Ibilbidea 3, 20018 San Sebastian/Donostia, Spain.
[4]Donostia International Physics Center (DIPC), Manuel Lardizabal Ibilbidea 4, 20018 San Sebastian/Donostia, Spain.

Table of contents

SECTION 1

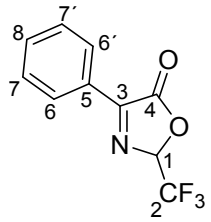
The organometallic reactions were carried out under nitrogen. THF was purchased in TEDIA (www.T2-P2.com, #TS2123-001, with 0.02% of water). On the other hand, the Et_2O was acquired in Merck (#296082) and was distilled over Na, as well as, dichloromethane (Sigma-Aldrich, #34859) was distilled over $CaCl_2$. The products were purified by column chromatography on silica gel (MN Kieselgel 60, 230-400 mesh). Mixtures of ethyl acetate and hexane were used as eluents. Analytical TLC was employed on aluminum sheets (silica gel 60 F/UV254) with visualization carried out with UV light and iodine. Melting points were determined on a digital Electrothermal 90100 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra ($CDCl_3$, DMSO-d_6) were recorded with a Varian Gemini 300 MHz, a Varian VNMR System 500 MHz, a Bruker Ascend 400 MHz, or a Bruker Ultrashield 500 MHz spectrometer. All chemical shifts are reported in ppm relative to Me_4Si and $CHCl_3$ used as the internal standard. IR spectra were recorded on potassium bromide plates with a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were determined with electrospray ionization on a Bruker micrOTOF-Q II or electronebulization ionization on a Bruker QTOF mass spectrometer. X-ray data were collected on an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector.

SECTION 2.

General method for the synthesis of oxazolones 2a-d:

In a 25 mL round-bottom flask containing a stirring bar, 1.3 mmol (1.0 equiv) of the appropriate amino acid was added. Then 3.9 mmol (3.0 equiv, ρ = 1.511 g/mL) of trifluoroacetic anhydride was incorporated dropwise and the mixture was stirred for 4 h at room temperature. After this time, the reaction crude was poured into a separation funnel, washed with a saturated solution of $NaHCO_3$ (3 x 15 mL) and then extracted with CH_2Cl_2. The organic fractions were evaporated under reduced pressure and the pure compounds **2a-d** were recuperated as viscous liquids.

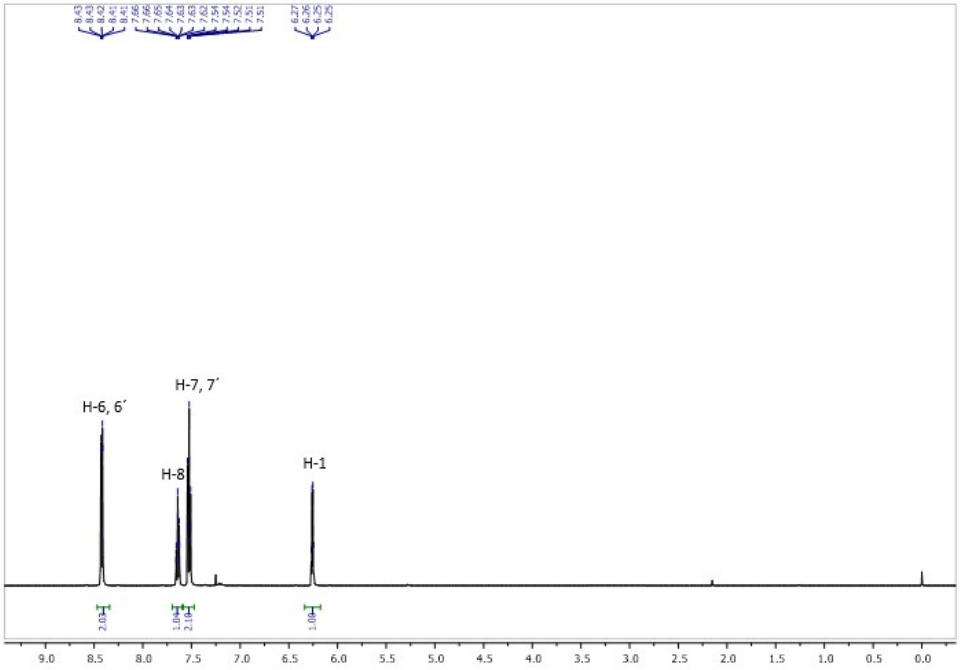
Compound **2a**.



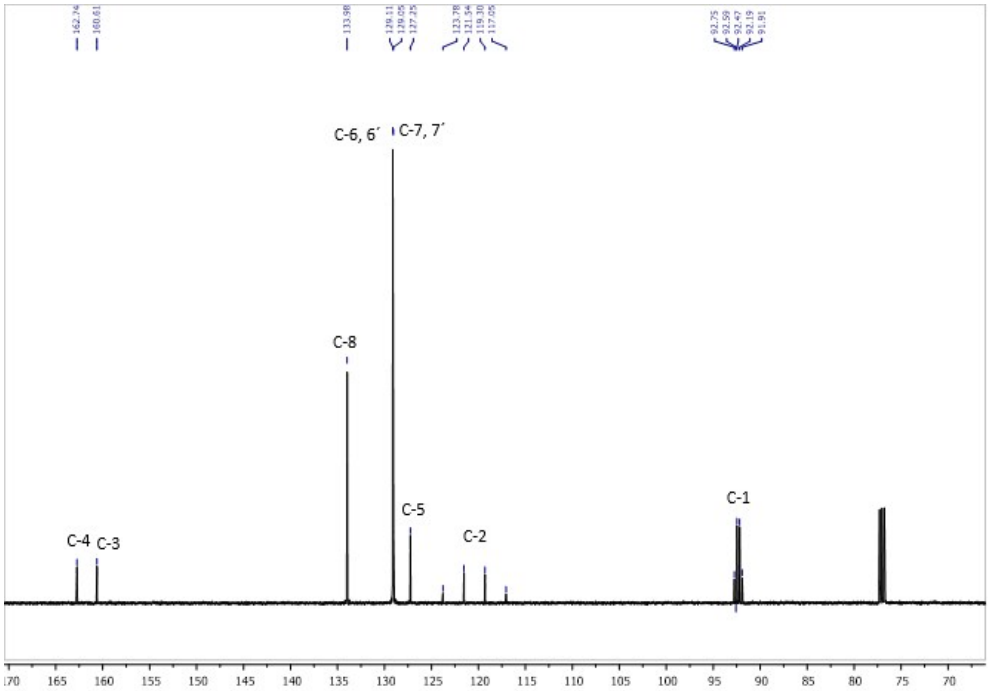
4-phenyl-2-(trifluoromethyl)oxazol-5(2H)-one

CCDC 1912568

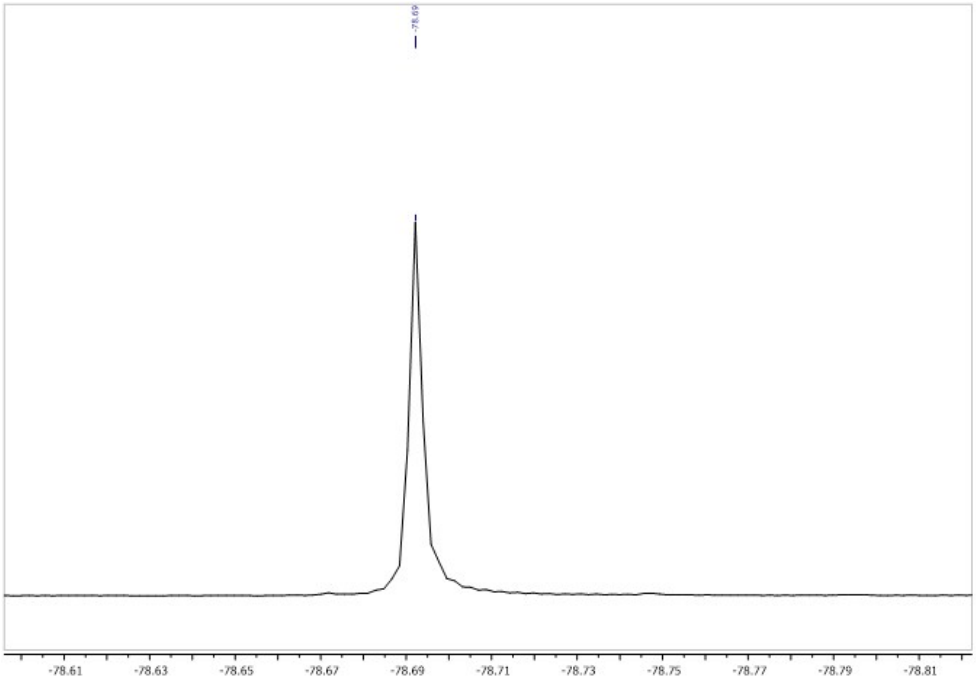
Yield: 95%; yellow solid; mp: 87 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.42 (d, $^{3}J_{H-H}$ = 5.0 Hz, 2H, H-6,6´), 7.64 (t, $^{3}J_{H-H}$ = 7.5 Hz, 1H, H-8), 7.53 (t, $^{3}J_{H-H}$ = 7.8 Hz, 2H, H-7,7´), 6.25 (q, $^{3}J_{H-F}$ = 5.0 Hz, 1H, H-1). ^{13}C NMR (125 MHz ($CDCl_3$) δ: 162.7 (C=O), 160.6 (C-3), 133.9 (C-8), 129.1 (C-6) 129.0 (C-7), 127.2 (C-5), 120.4 (q, $^{1}J_{C-F}$ = 280.0 Hz, C-2), 92.4 (q, $^{1}J_{C-C}$ = 91.5 Hz, C-1).



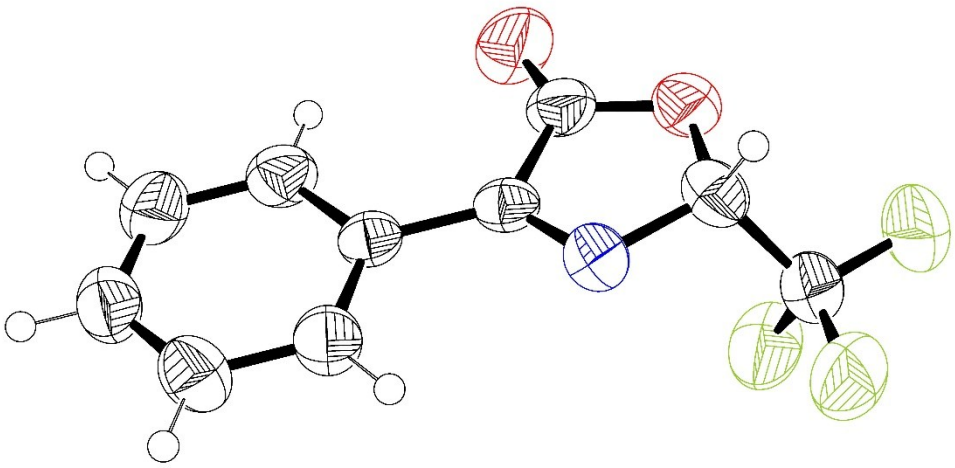
2a NMR ^{1}H ($CDCl_3$, 500 MHz)



2a NMR ^{13}C ($CDCl_3$, 125 MHz)



2a NMR ^{19}F ($CDCl_3$, 470 MHz)



2a, X-Ray Data CCDC 1912568

Table 1. Crystal data and structure refinement for **2a**.

Identification code	**2a**	
Empirical formula	C10 H6 F3 N O2	
Formula weight	229.16	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P bca	
Unit cell dimensions	a = 10.5916(4) Å	□= 90°.
	b = 8.1713(3) Å	□= 90°.
	c = 22.3051(8) Å	□ = 90°.
Volume	1930.44(12) $Å^3$	
Z	8	
Density (calculated)	1.577 Mg/m^3	
Absorption coefficient	0.148 mm^{-1}	
F(000)	928	
Crystal size	0.60 x 0.47 x 0.21 mm^3	
Theta range for data collection	2.65 to 25.34°.	
Index ranges	-11<=h<=12, -9<=k<=9, -25<=l<=26	
Reflections collected	6374	
Independent reflections	1764 [R(int) = 0.0133]	
Completeness to theta = 25.34°	99.9 %	
Max. and min. transmission	0.9695 and 0.9163	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1764 / 0 / 146	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0874	
R indices (all data)	R1 = 0.0417, wR2 = 0.0923	
Extinction coefficient	0.0125(10)	
Largest diff. peak and hole	0.154 and -0.177 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	3381(2)	3869(2)	1408(1)	54(1)
C(4)	4143(1)	2936(2)	955(1)	41(1)
C(6)	4628(2)	2007(2)	1846(1)	50(1)
C(7)	5816(2)	2392(2)	2194(1)	56(1)
C(11)	4062(1)	3143(2)	303(1)	40(1)
C(12)	4853(2)	2218(2)	-62(1)	52(1)
C(13)	4775(2)	2333(2)	-676(1)	60(1)
C(14)	3916(2)	3366(2)	-935(1)	59(1)
C(15)	3139(2)	4297(2)	-584(1)	65(1)
C(16)	3209(2)	4198(2)	35(1)	55(1)
N(5)	4865(1)	1908(2)	1215(1)	47(1)
O(1)	3733(1)	3269(2)	1951(1)	60(1)
O(3)	2623(1)	4936(2)	1353(1)	83(1)
F(8)	6666(1)	1231(2)	2123(1)	86(1)
F(9)	5581(1)	2521(2)	2775(1)	83(1)
F(10)	6322(1)	3793(1)	2022(1)	82(1)

Table 3. Bond lengths [Å] and angles [°] for **2a**.

C(2)-O(3)	1.191(2)
C(2)-O(1)	1.358(2)
C(2)-C(4)	1.502(2)
C(4)-N(5)	1.2758(19)
C(4)-C(11)	1.4664(19)
C(6)-O(1)	1.4203(19)
C(6)-N(5)	1.4331(18)
C(6)-C(7)	1.511(2)

C(6)-H(6)	0.9800
C(7)-F(8)	1.317(2)
C(7)-F(10)	1.3207(19)
C(7)-F(9)	1.3260(18)
C(11)-C(16)	1.384(2)
C(11)-C(12)	1.391(2)
C(12)-C(13)	1.376(2)
C(12)-H(12)	0.9300
C(13)-C(14)	1.369(2)
C(13)-H(13)	0.9300
C(14)-C(15)	1.368(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.385(2)
C(15)-1H5	0.9300
C(16)-H(16)	0.9300

O(3)-C(2)-O(1)	122.73(15)
O(3)-C(2)-C(4)	131.58(16)
O(1)-C(2)-C(4)	105.68(13)
N(5)-C(4)-C(11)	124.22(13)
N(5)-C(4)-C(2)	110.45(13)
C(11)-C(4)-C(2)	125.32(13)
O(1)-C(6)-N(5)	108.65(12)
O(1)-C(6)-C(7)	108.71(13)
N(5)-C(6)-C(7)	111.68(13)
O(1)-C(6)-H(6)	109.3
N(5)-C(6)-H(6)	109.3
C(7)-C(6)-H(6)	109.3
F(8)-C(7)-F(10)	108.21(15)
F(8)-C(7)-F(9)	107.63(14)
F(10)-C(7)-F(9)	106.89(15)
F(8)-C(7)-C(6)	110.98(14)
F(10)-C(7)-C(6)	111.71(13)
F(9)-C(7)-C(6)	111.22(15)
C(16)-C(11)-C(12)	118.70(14)
C(16)-C(11)-C(4)	122.53(13)

C(12)-C(11)-C(4)	118.76(13)
C(13)-C(12)-C(11)	120.54(15)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	120.20(16)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	120.05(16)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.44(16)
C(14)-C(15)-1H5	119.8
C(16)-C(15)-1H5	119.8
C(11)-C(16)-C(15)	120.07(15)
C(11)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(4)-N(5)-C(6)	107.75(13)
C(2)-O(1)-C(6)	107.37(11)

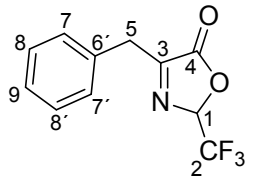
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	40(1)	68(1)	54(1)	-14(1)	1(1)	4(1)
C(4)	34(1)	39(1)	49(1)	-6(1)	2(1)	-5(1)
C(6)	57(1)	48(1)	46(1)	1(1)	7(1)	-8(1)
C(7)	61(1)	59(1)	48(1)	8(1)	0(1)	-1(1)
C(11)	35(1)	38(1)	48(1)	-2(1)	0(1)	-5(1)
C(12)	54(1)	51(1)	51(1)	-3(1)	1(1)	10(1)
C(13)	70(1)	61(1)	51(1)	-7(1)	8(1)	5(1)

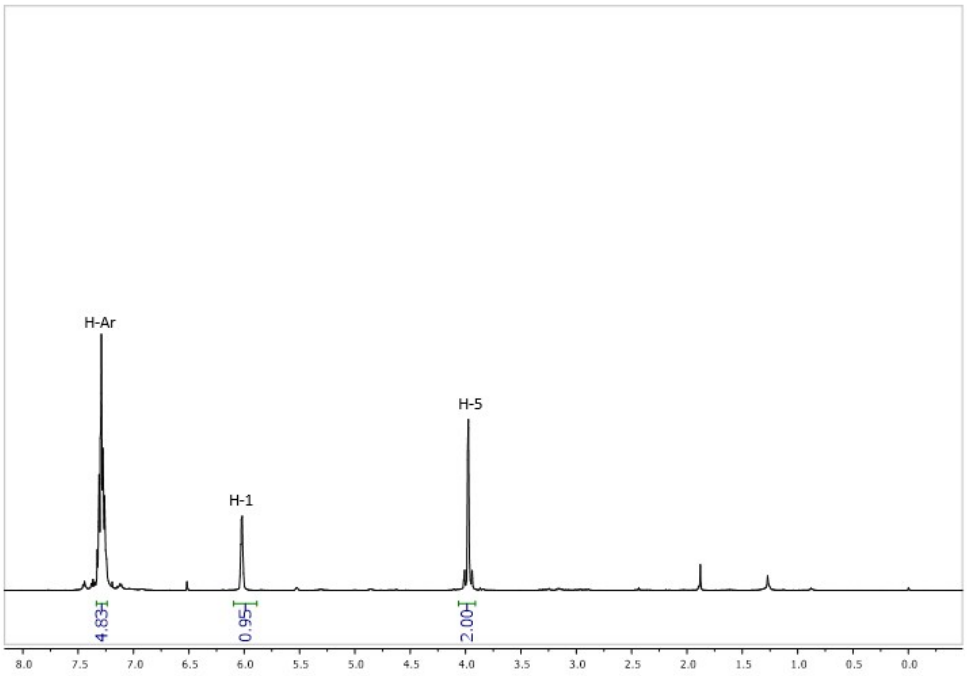
C(14)	66(1)	65(1)	47(1)	5(1)	-3(1)	-9(1)
C(15)	59(1)	72(1)	63(1)	14(1)	-8(1)	8(1)
C(16)	46(1)	56(1)	62(1)	0(1)	2(1)	10(1)
N(5)	53(1)	42(1)	45(1)	-2(1)	3(1)	0(1)
O(1)	52(1)	81(1)	48(1)	-12(1)	7(1)	5(1)
O(3)	65(1)	109(1)	74(1)	-23(1)	-2(1)	43(1)
F(8)	83(1)	98(1)	77(1)	12(1)	-6(1)	33(1)
F(9)	92(1)	111(1)	45(1)	-2(1)	-5(1)	-4(1)
F(10)	79(1)	79(1)	87(1)	23(1)	-24(1)	-31(1)

Compound 2b

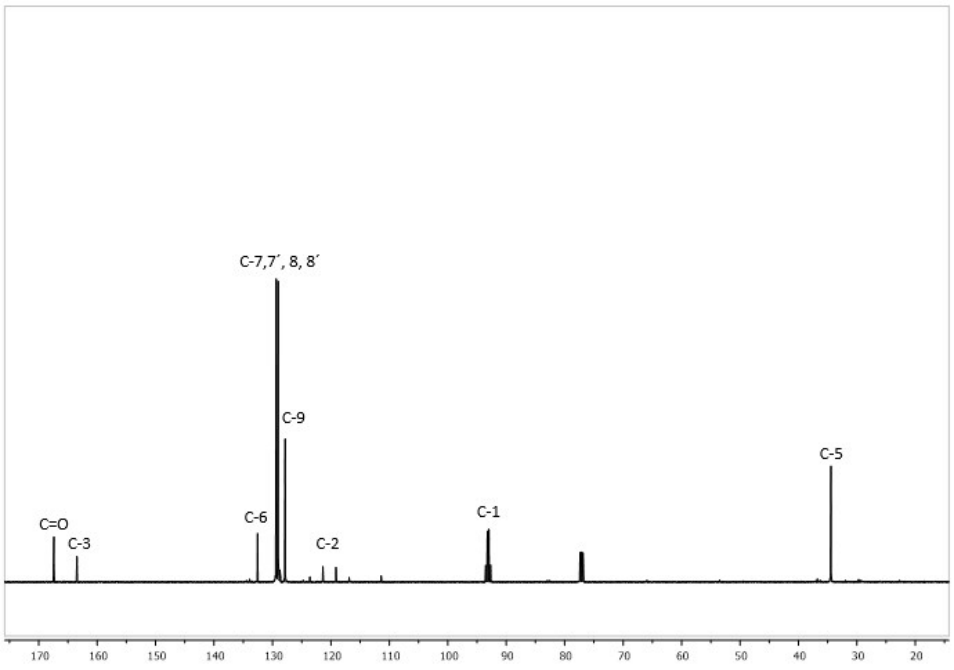


4-benzyl-2-(trifluoromethyl)oxazol-5(2H)-one (2b).

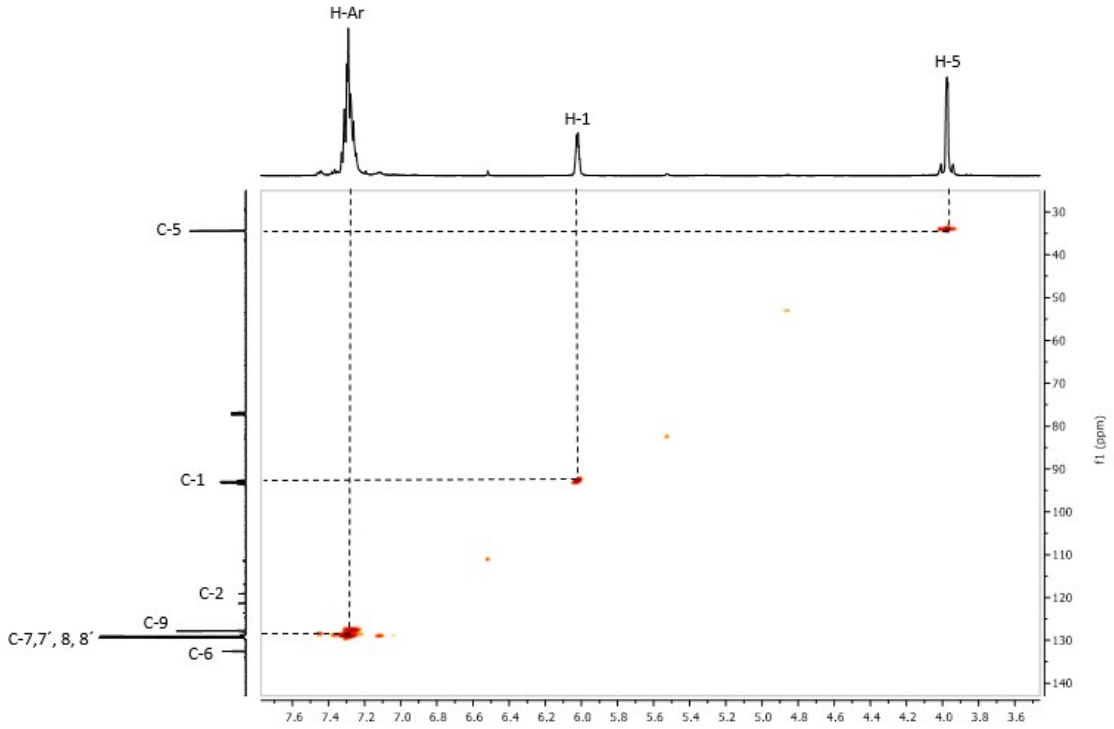
Yield: 60%; yellow liquid.^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25-7.20 (m, 5H, H-7-9, 7′,8′), 5.99-5.96 (m, 1H, H-1), 3.96-3.89 (dd, $^{2}J_{H\text{-}H}$ = 5.0 Hz, 2H, H-5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.7 (C=O), 160.6 (C-3), 133.5 (C-6), 129.8 (C-7, 7′) 129.6 (C-8, 8′), 127.2 (C-9), 120.4 (q, $^{2}J_{C\text{-}F}$ = 280.0 Hz, C-2), 92.4 (q, $^{1}J_{C\text{-}C}$ = 91.5 Hz, C-1), 34.8 (C-5).



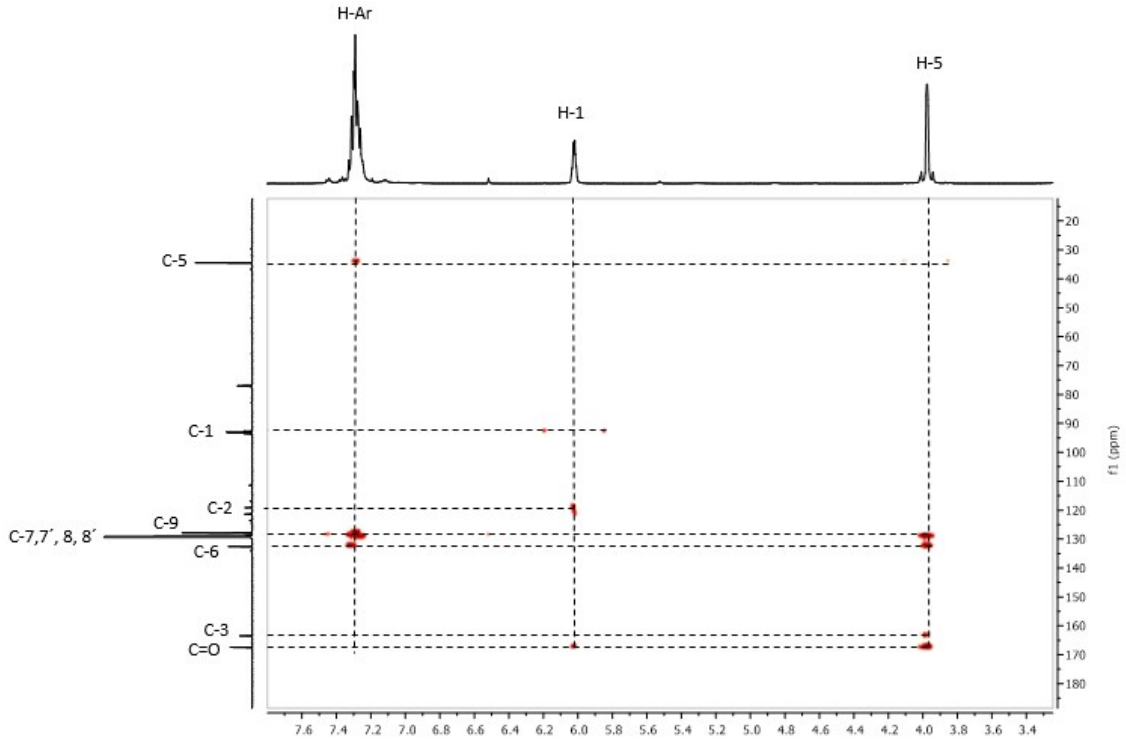
2b NMR ^{1}H ($CDCl_3$, 500 MHz)



2b NMR ^{13}C ($CDCl_3$, 125 MHz)

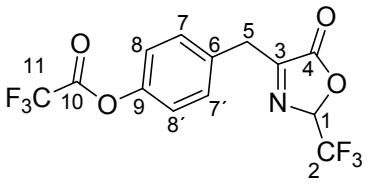


2b NMR-HSQC ($CDCl_3$, 500 MHz)



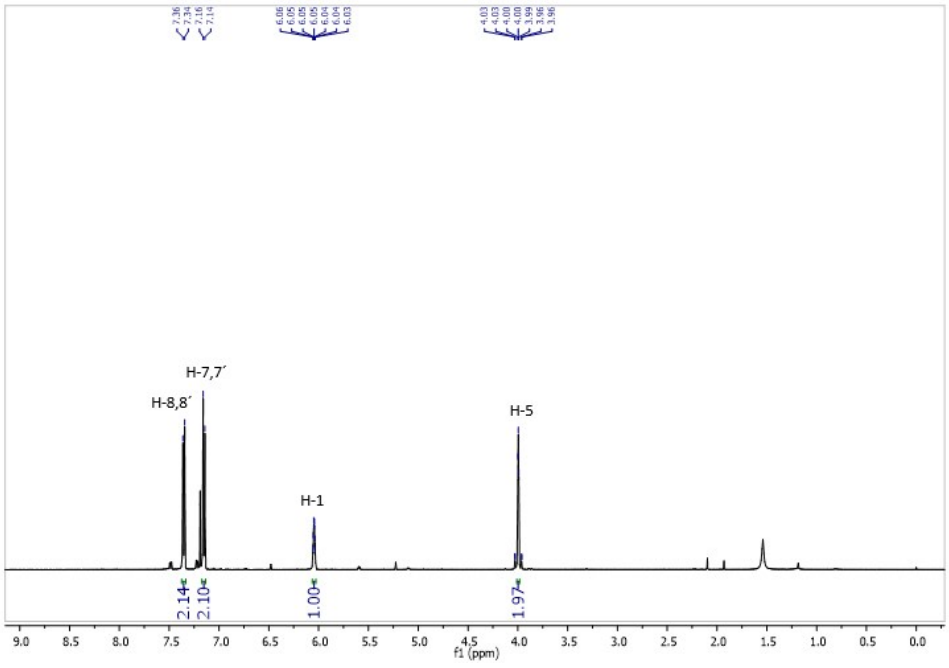
2b NMR-HMBC ($CDCl_3$, 500 MHz)

Compund 2c

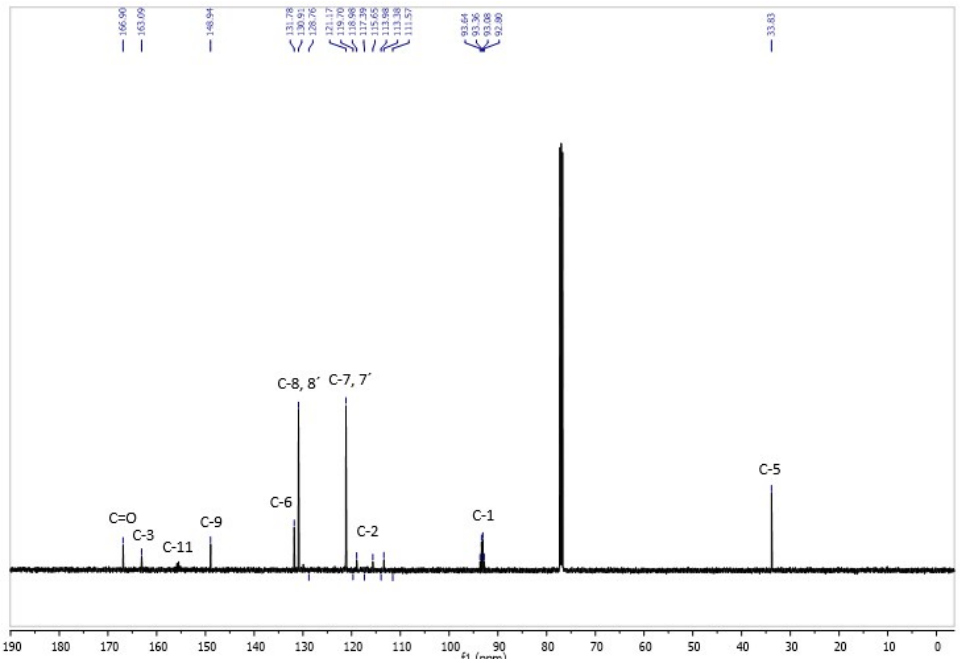


4-((5-oxo-2-(trifluoromethyl)-2,5-dihydrooxazol-4-yl)methyl)phenyl 2,2,2-trifluoroacetate.

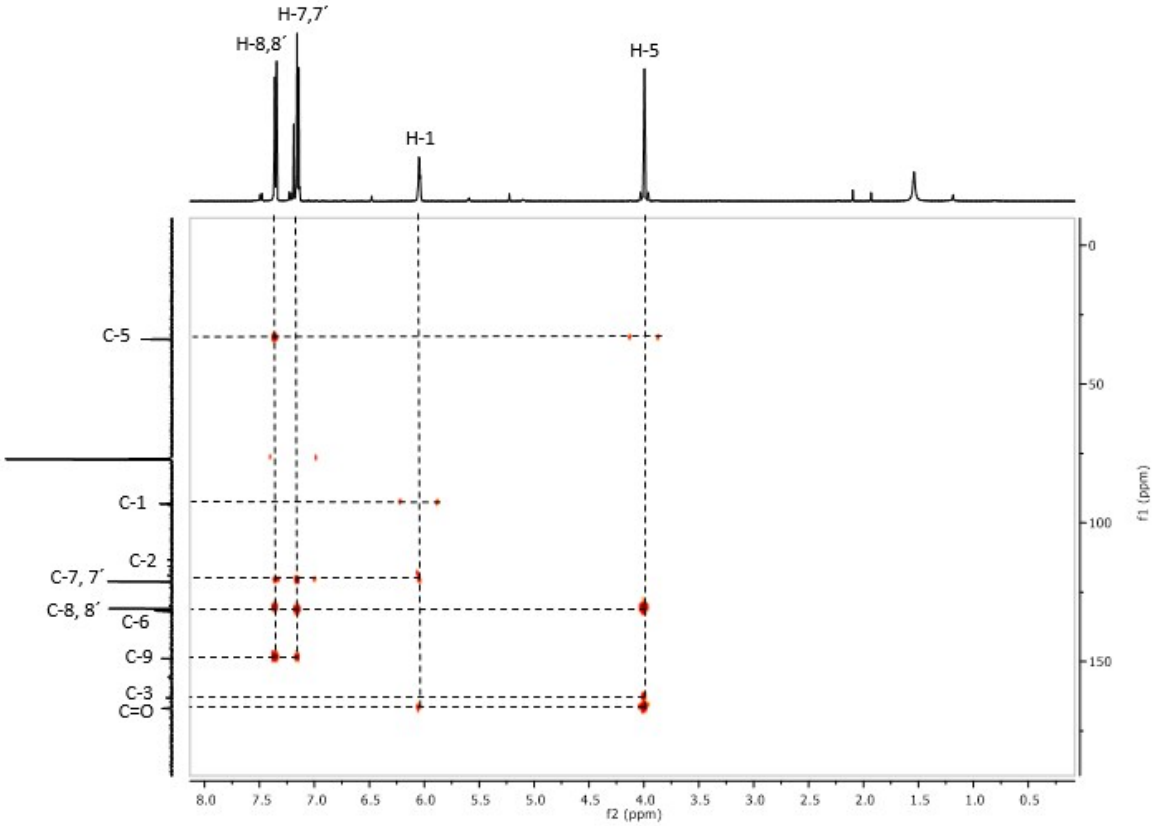
Yield: 89%; orange liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-8,8´), 7.15 (d, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-7,7´), 6.06-6.03 (m, 1H, H-1), 4.03-3.96 (m, 1H, H-5). ^{13}C NMR (125 MHz ($CDCl_3$) δ: 166.9 (C=O), 163.0 (C-3), 148.9 (C-9), 131.7 (C-6), 130.9 (C-8, 8´), 121.1 (C-7, 7´), 117.5 (q, $^{2}J_{C\text{-}F}$ = 283.7 Hz, C-2), 93.2 (q, $^{1}J_{C\text{-}C}$ = 70.0 Hz, C-1), 33.8 (C-5).



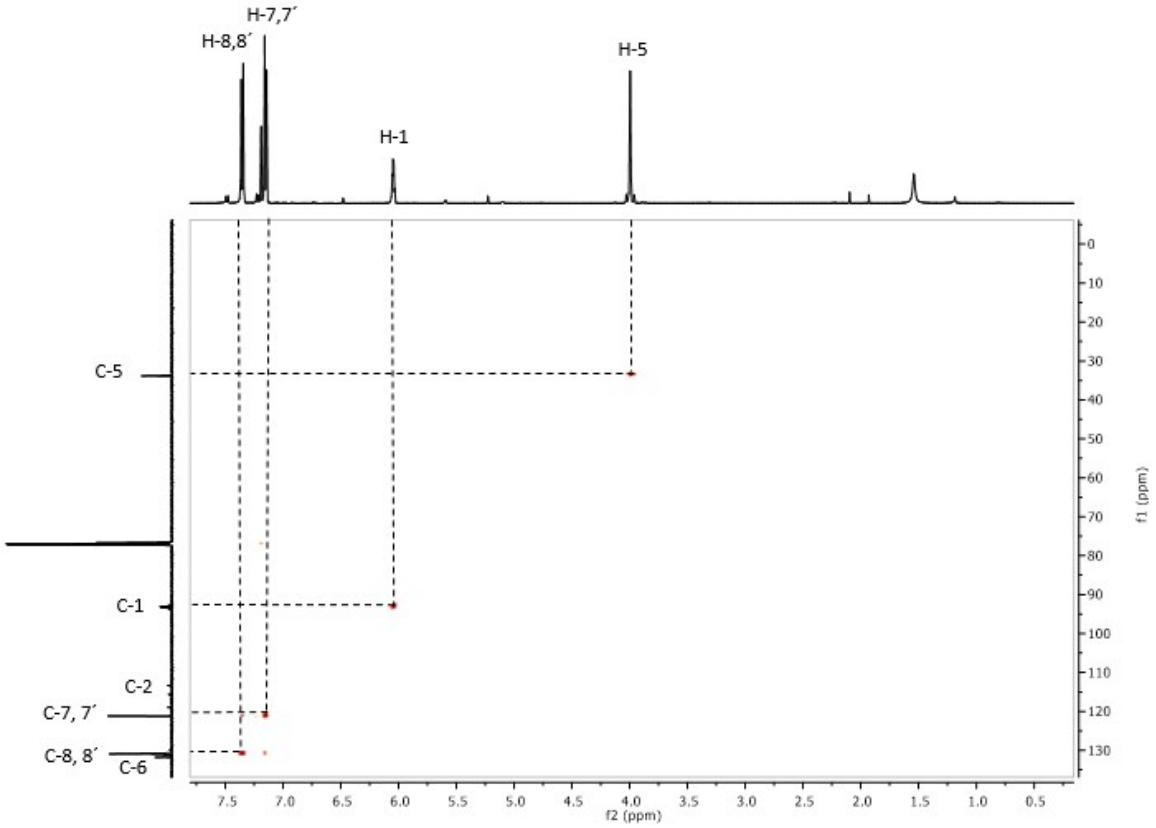
2c NMR ^{1}H ($CDCl_3$, 500 MHz)



2c NMR ^{13}C ($CDCl_3$, 125 MHz)

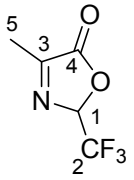


2c NMR-HMBC ($CDCl_3$, 500 MHz)

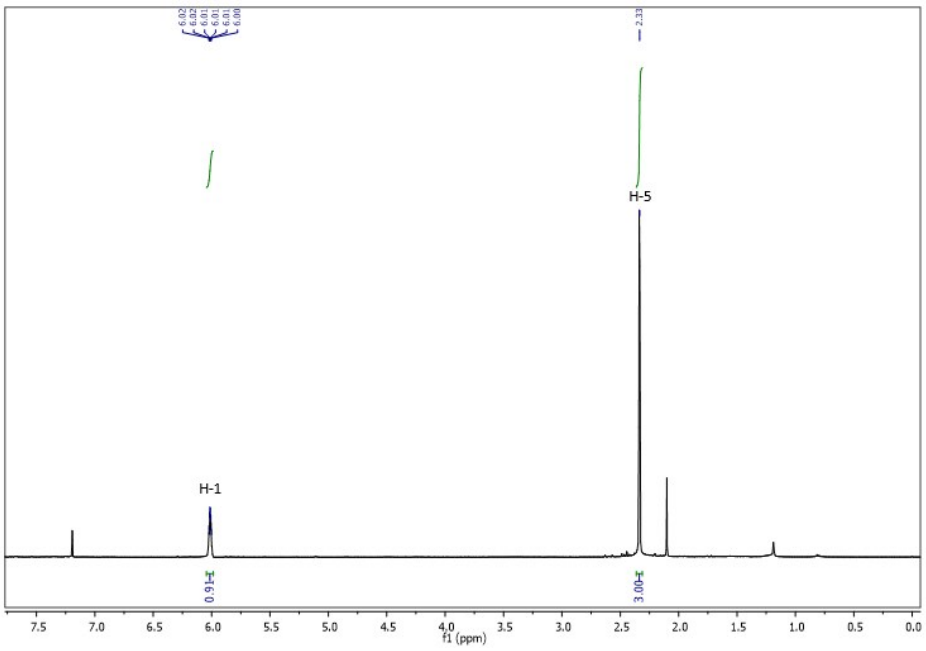


2c NMR-HSQC ($CDCl_3$, 500 MHz)

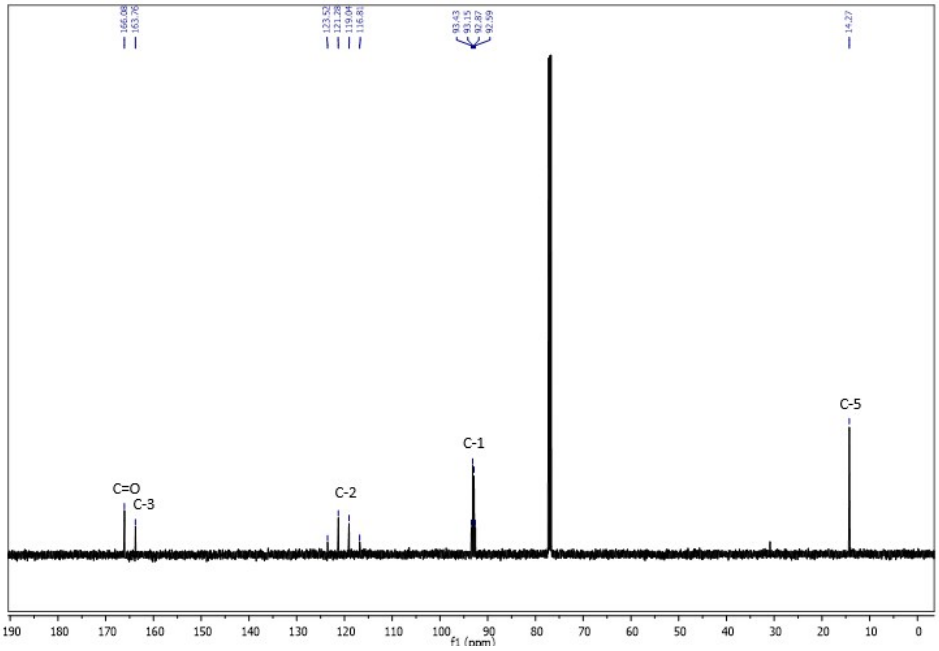
Compound 2d



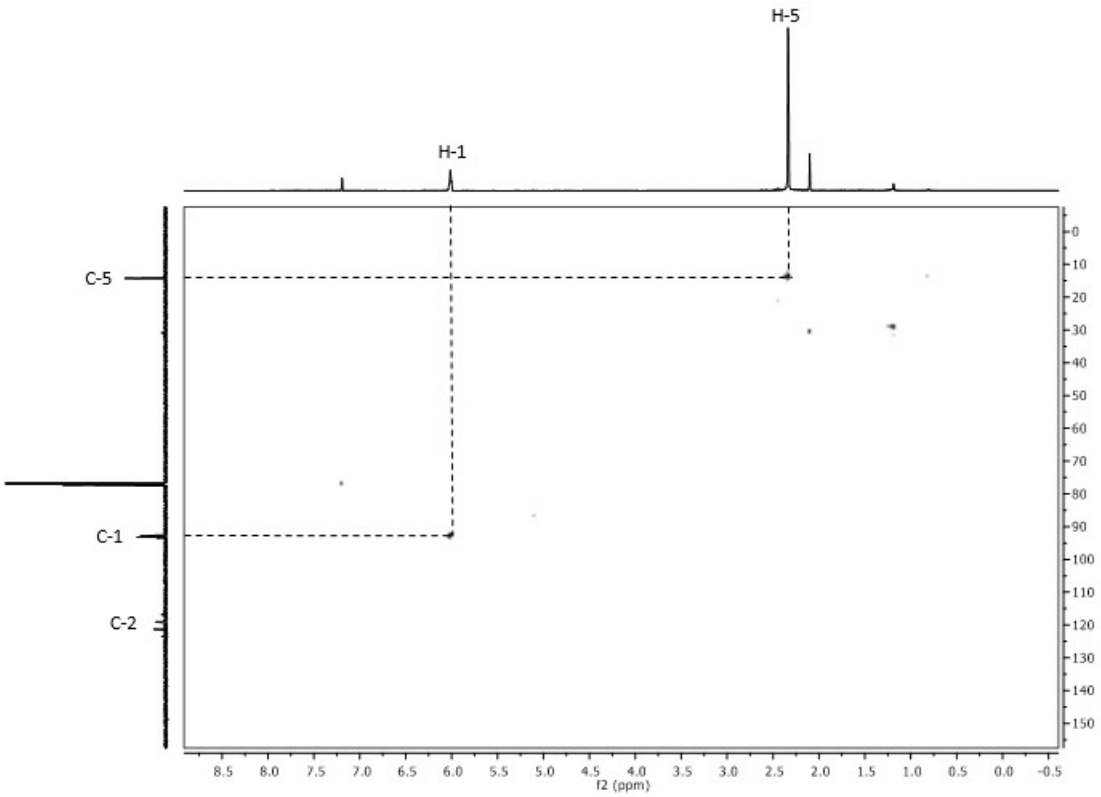
4-methyl-2-(trifluoromethyl)oxazol-5(2H)-one (2d). Yield: 95%; orange liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.02-6.00 (m, 1H, H-1), 2.33 (s, 3H, H-5). ^{13}C NMR (125 MHz ($CDCl_3$) δ: 166.0 (C=O), 163.7 (C-3), 120.0 (q, $^{2}J_{C\text{-}F}$ = 280.0 Hz, C-2), 93.2 (q, $^{1}J_{C\text{-}C}$ = 70.0 Hz, C-1), 14.2 (C-5).



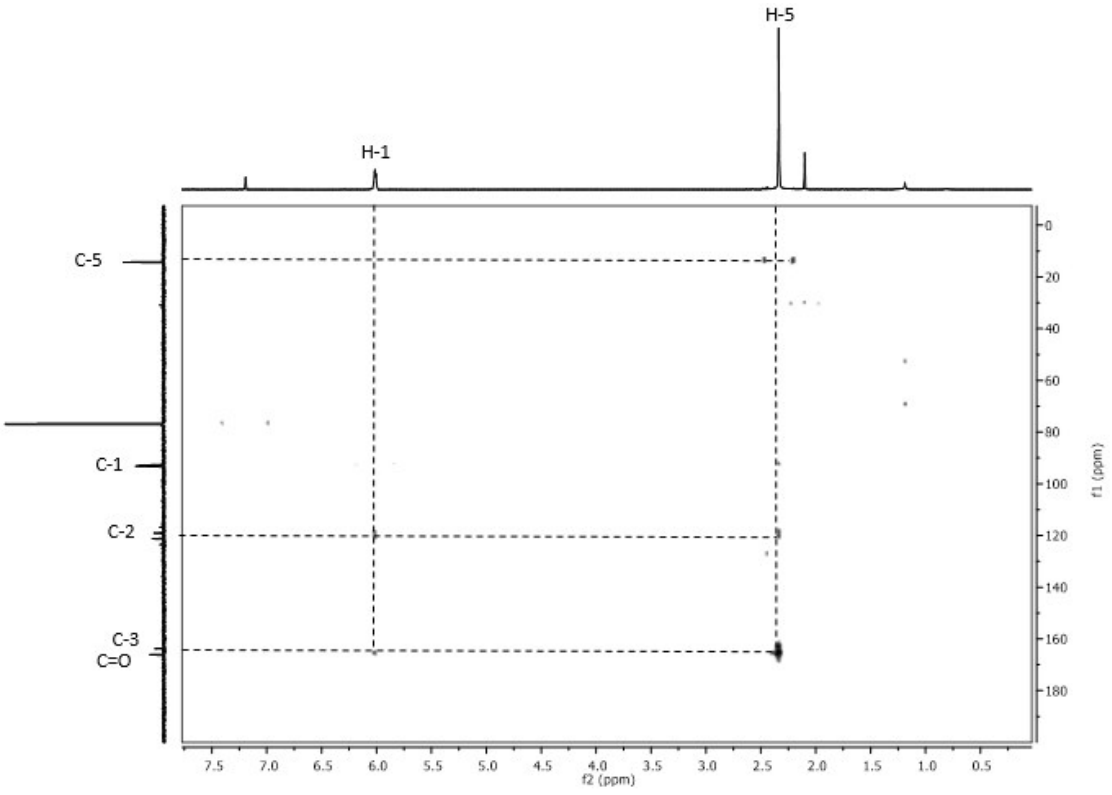
2d NMR ^{1}H ($CDCl_3$, 500 MHz)



2d NMR ^{13}C ($CDCl_3$, 125 MHz)



2d NMR-HSQC ($CDCl_3$, 500 MHz)

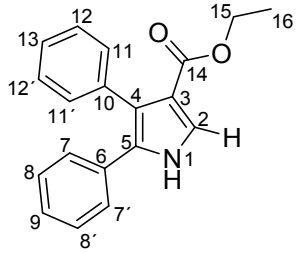


2d NMR-HBBC ($CDCl_3$, 500 MHz)

SECTION 3

General method for the synthesis of pyrroles 4a-f, 4g and 4h-q: In a 100 mL dried round-bottom flask provided with a stirring bar, 0.9 mmol (1.1 equiv) of the corresponding oxazolone **2a-d** and 0.095 mmol of AgOAc (10 mol%) were added and this mixture was purged for 5 min under a nitrogen flow. Later, 40 mL of THF (TEDIA, www.T2-P2.com, #TS2123-001, with 0.02% of water) were added into the container and 0.9 mmol of Et_3N (0.5% water, Sigma-Aldrich #T0886) was finally incorporated into the mixture, which was then stirred for a further 30 min at room temperature. Meanwhile, in a separate flask, 0.86 mmol (1.0 equiv) of the corresponding alkynyl Fischer carbene **1a-h** was dissolved in 10 mL of THF and maintained under an inert atmosphere. Once the required reaction time, the solution of the carbene was slowly transferred via cannula into the flask with the oxazolone and then allowed to react for 20–180 min, as judged by TLC monitoring. For **4g**, the D_2O was added to the mixture of reaction using 5 ml anhydrous THF. The crude reaction mixture was purified by column chromatography (silica gel, 9:1 Hex:AcOEt) and isolated products were recovered under reduced pressure.

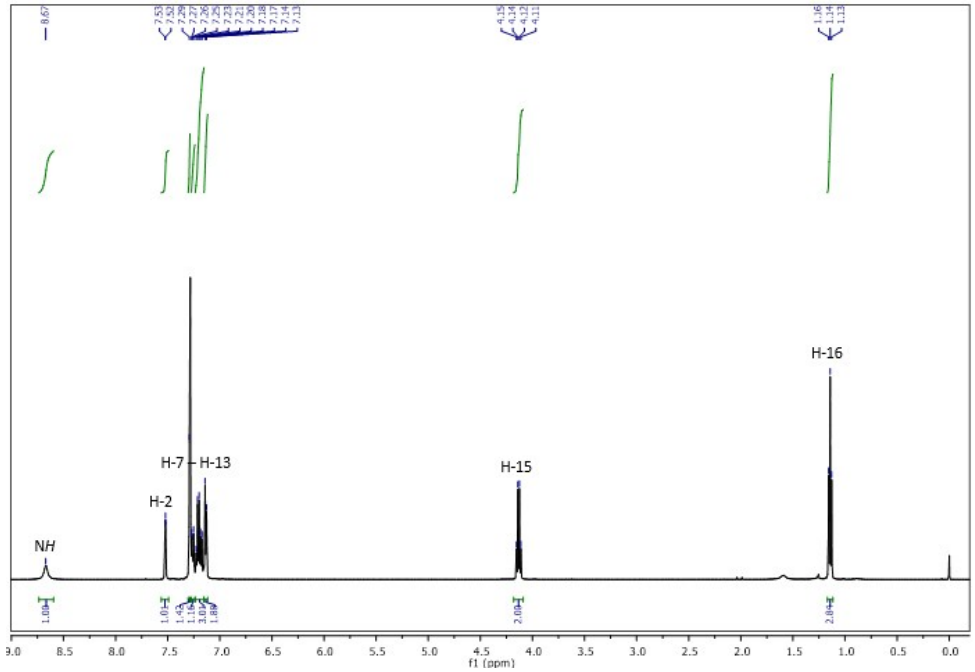
Compound 4a.



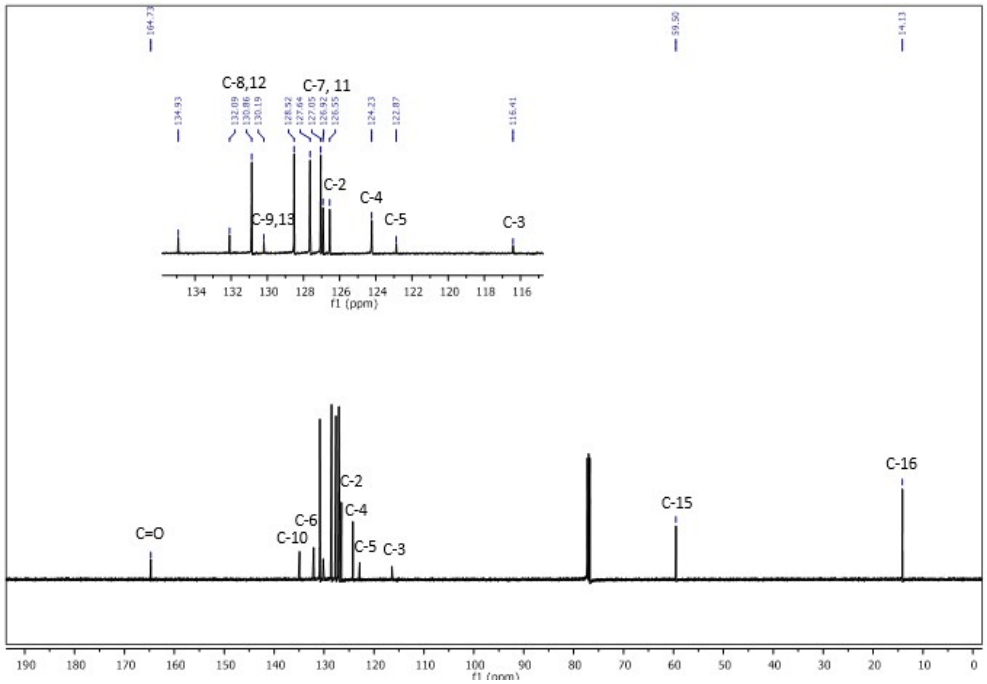
Ethyl 4,5-diphenyl-1*H*-pyrrole-3-carboxylate (4a). CCDC 1912115

Yield: 88%; white crystals; mp: 192-194 °C. IR (ν cm^{-1}) 3327 (N-H), 1685 (C=O). ^1H NMR (500 MHz, $CDCl_3$) δ: 8.67 (s, 1H, H-1), 7.52 (d, $^3J_{H-H}$ = 5.0 Hz, 1H, H-2), 7.29-7.13 (m, 10H, Ph-*H*), 4.13 (q, $^3J_{H-H}$ = 7.5 Hz, 2H, H-15), 1.14 (t, $^3J_{H-H}$ = 7.5 Hz, 3H, H-16). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.7 (C-14), 134.9 (C-10), 132.0 (C-6), 130.8 (C-8), 130.1 (C-12), 128.5 (C-9), 127.6 (C-7), 127.0 (C-13), 126.9 (C-11), 126.5 (C-2), 124.2 (C-4),

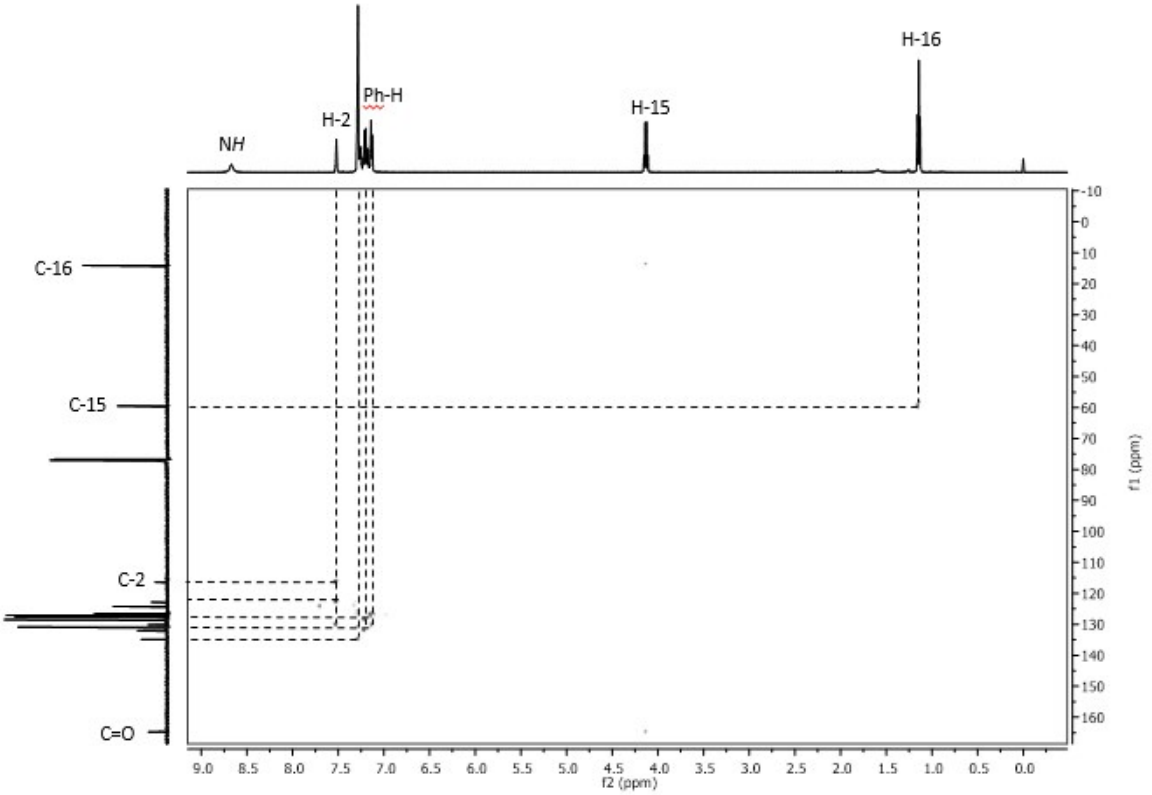
122.8 (C-5), 116.4 (C-3), 59.5 (C-15), 14.1 (C-16). HRMS (ESI$^+$): m/z calcd. for $C_{19}H_{17}NO_2$ $[M+Na]^+$ 314.1157, found 314.1159.



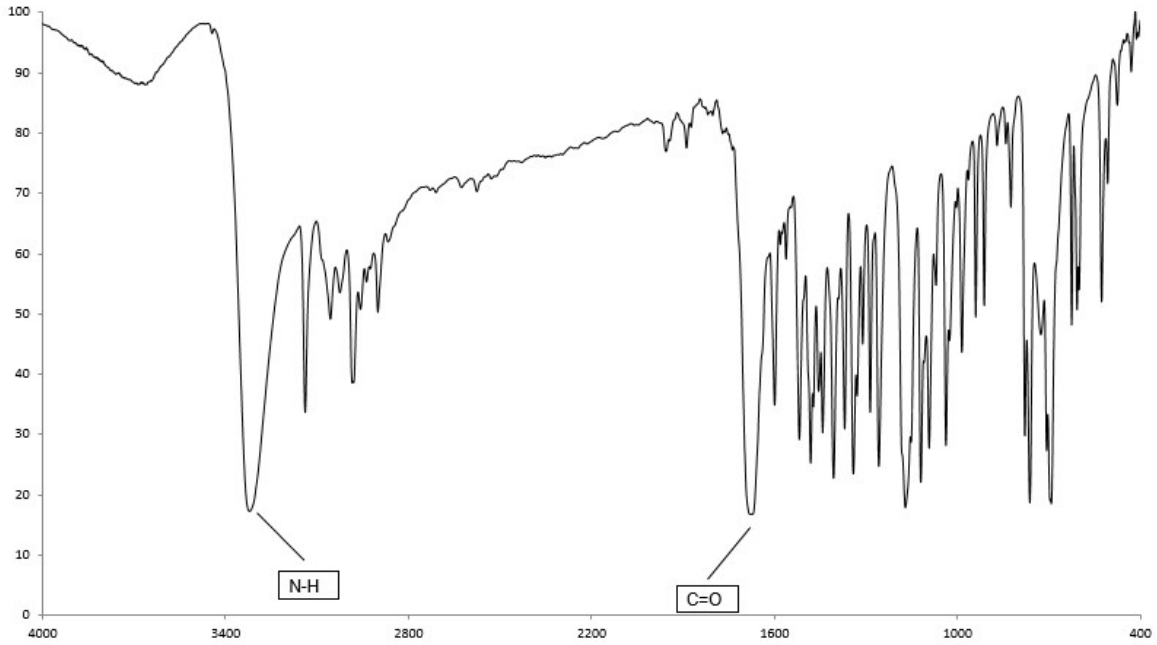
4a NMR ^{1}H ($CDCl_3$, 500 MHz)



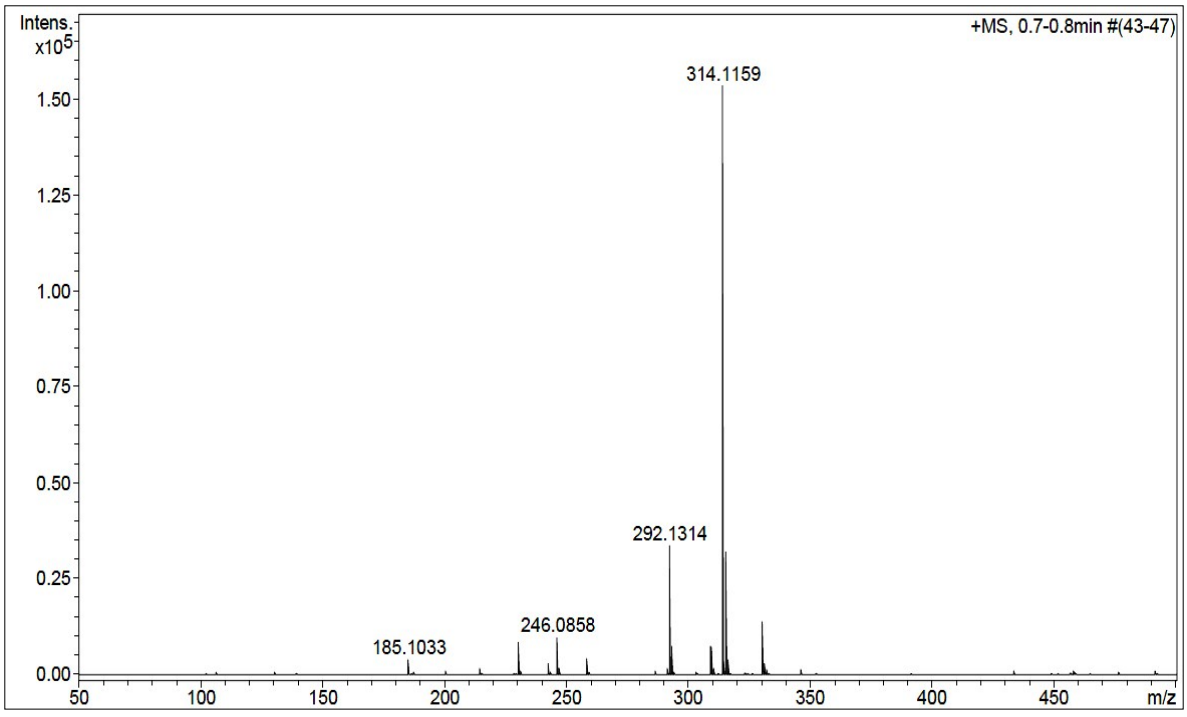
4a NMR ^{13}C ($CDCl_3$, 125 MHz)



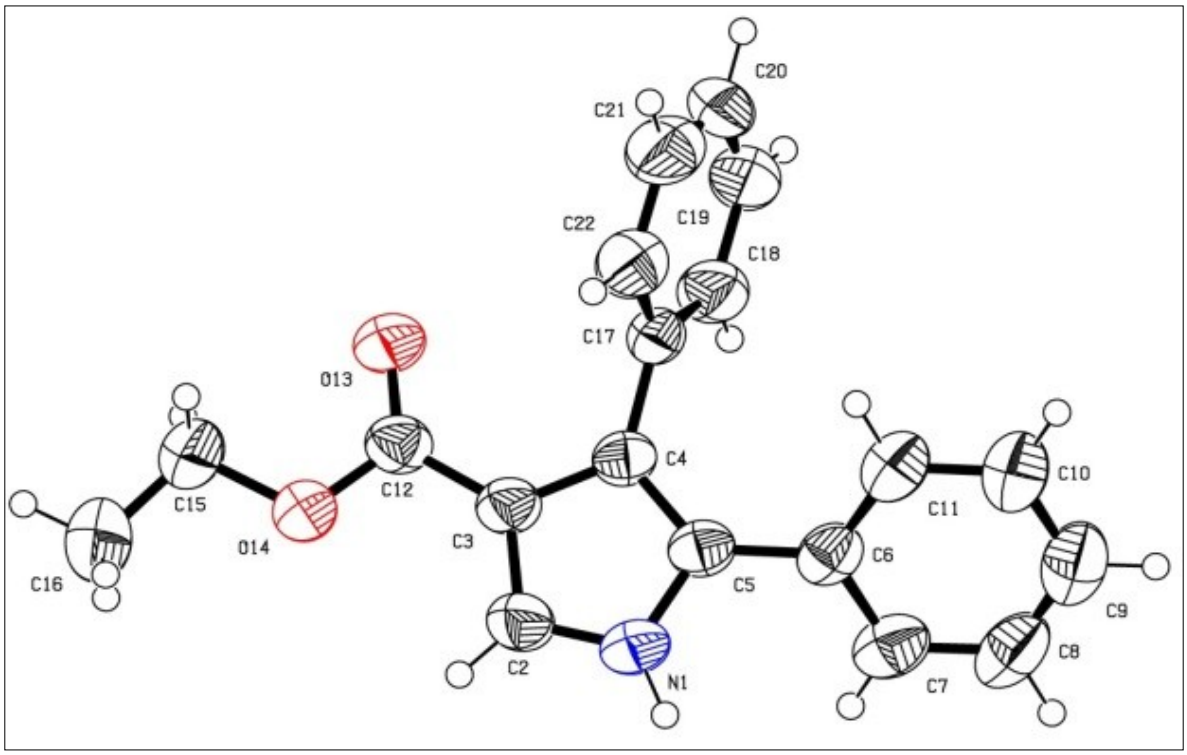
4a NMR-HSQC ($CDCl_3$, 500 MHz)



4a, IR-KBr pellet.



4a, HRMS



4a, X-Ray Data CCDC 1912115

Table 1. Crystal data and structure refinement for **4a**.

Identification code	**4a**	
Empirical formula	C19 H17 N O2	
Formula weight	291.34	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.7993(3) Å	α= 90°.
	b = 13.4017(7) Å	β= 90°.
	c = 20.2659(11) Å	γ = 90°.
Volume	1575.08(14) $Å^3$	
Z	4	
Density (calculated)	1.229 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	616	

Theta range for data collection	3.65 to 26.05°.
Index ranges	-6<=h<=7, -10<=k<=16, -20<=l<=25
Reflections collected	7871
Independent reflections	3083 [R(int) = 0.0216]
Completeness to theta = 26.05°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3083 / 1 / 203
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0847
R indices (all data)	R1 = 0.0585, wR2 = 0.0930
Absolute structure parameter	-0.4(14)
Largest diff. peak and hole	0.085 and -0.120 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	5338(4)	1343(1)	7690(1)	62(1)
C(3)	4893(3)	378(1)	7499(1)	54(1)
C(4)	6371(3)	167(1)	6951(1)	49(1)
C(5)	7668(3)	1009(1)	6839(1)	54(1)
C(6)	9431(3)	1253(1)	6344(1)	55(1)
C(7)	11243(3)	1896(1)	6489(1)	68(1)
C(8)	12892(3)	2114(2)	6019(1)	78(1)
C(9)	12799(4)	1699(2)	5405(1)	80(1)
C(10)	11026(4)	1064(2)	5254(1)	76(1)
C(11)	9358(3)	842(2)	5712(1)	64(1)
C(12)	3265(3)	-295(1)	7811(1)	56(1)
C(15)	237(4)	-472(2)	8587(1)	80(1)
C(16)	-971(5)	126(2)	9090(1)	99(1)
C(17)	6459(3)	-768(1)	6563(1)	49(1)
C(18)	8369(3)	-1378(1)	6577(1)	68(1)
C(19)	8456(5)	-2232(2)	6199(1)	90(1)
C(20)	6670(6)	-2494(2)	5809(1)	93(1)
C(21)	4758(5)	-1898(2)	5786(1)	90(1)
C(22)	4638(4)	-1041(2)	6165(1)	69(1)
O(13)	3021(3)	-1167(1)	7677(1)	75(1)
O(14)	1972(3)	149(1)	8273(1)	74(1)
N(1)	7004(3)	1709(1)	7303(1)	63(1)

Table 3. Bond lengths [Å] and angles [°] for **4a**.

C(2)-N(1)	1.338(2)
C(2)-C(3)	1.374(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.432(2)
C(3)-C(12)	1.450(3)
C(4)-C(5)	1.375(2)
C(4)-C(17)	1.480(2)
C(5)-N(1)	1.383(2)
C(5)-C(6)	1.468(2)
C(6)-C(7)	1.390(3)
C(6)-C(11)	1.396(3)
C(7)-C(8)	1.381(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.364(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.370(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.372(3)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300
C(12)-O(13)	1.209(2)
C(12)-O(14)	1.338(2)
C(15)-O(14)	1.452(2)
C(15)-C(16)	1.475(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-C(18)	1.377(2)
C(17)-C(22)	1.379(3)
C(18)-C(19)	1.378(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.350(4)

C(19)-H(19)	0.9300
C(20)-C(21)	1.368(4)
C(20)-H(20)	0.9300
C(21)-C(22)	1.384(3)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
N(1)-H(1F)	0.883(15)

N(1)-C(2)-C(3)	108.40(17)
N(1)-C(2)-H(2)	125.8
C(3)-C(2)-H(2)	125.8
C(2)-C(3)-C(4)	106.97(16)
C(2)-C(3)-C(12)	125.79(17)
C(4)-C(3)-C(12)	127.23(16)
C(5)-C(4)-C(3)	107.12(15)
C(5)-C(4)-C(17)	125.96(16)
C(3)-C(4)-C(17)	126.90(15)
C(4)-C(5)-N(1)	106.92(15)
C(4)-C(5)-C(6)	132.58(16)
N(1)-C(5)-C(6)	120.49(15)
C(7)-C(6)-C(11)	117.44(18)
C(7)-C(6)-C(5)	121.36(17)
C(11)-C(6)-C(5)	121.20(16)
C(8)-C(7)-C(6)	120.6(2)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(9)-C(8)-C(7)	121.0(2)
C(9)-C(8)-H(8)	119.5
C(7)-C(8)-H(8)	119.5
C(8)-C(9)-C(10)	119.1(2)
C(8)-C(9)-H(9)	120.4
C(10)-C(9)-H(9)	120.4
C(9)-C(10)-C(11)	120.9(2)
C(9)-C(10)-H(10)	119.6
C(11)-C(10)-H(10)	119.6
C(10)-C(11)-C(6)	120.91(19)

C(10)-C(11)-H(11)	119.5
C(6)-C(11)-H(11)	119.5
O(13)-C(12)-O(14)	121.43(17)
O(13)-C(12)-C(3)	125.42(17)
O(14)-C(12)-C(3)	113.14(15)
O(14)-C(15)-C(16)	108.72(18)
O(14)-C(15)-H(15A)	109.9
C(16)-C(15)-H(15A)	109.9
O(14)-C(15)-H(15B)	109.9
C(16)-C(15)-H(15B)	109.9
H(15A)-C(15)-H(15B)	108.3
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	118.08(17)
C(18)-C(17)-C(4)	121.29(16)
C(22)-C(17)-C(4)	120.61(17)
C(17)-C(18)-C(19)	120.7(2)
C(17)-C(18)-H(18)	119.6
C(19)-C(18)-H(18)	119.6
C(20)-C(19)-C(18)	121.0(2)
C(20)-C(19)-H(19)	119.5
C(18)-C(19)-H(19)	119.5
C(19)-C(20)-C(21)	119.3(2)
C(19)-C(20)-H(20)	120.3
C(21)-C(20)-H(20)	120.3
C(20)-C(21)-C(22)	120.5(2)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8
C(17)-C(22)-C(21)	120.5(2)
C(17)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(12)-O(14)-C(15)	116.10(15)

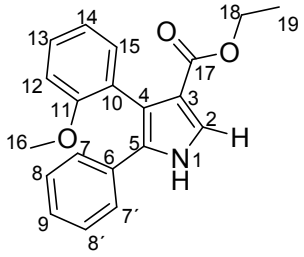
C(2)-N(1)-C(5)	110.57(15)
C(2)-N(1)-H(1F)	125.6(14)
C(5)-N(1)-H(1F)	123.2(14)

Symmetry transformations used to generate equivalent atoms:

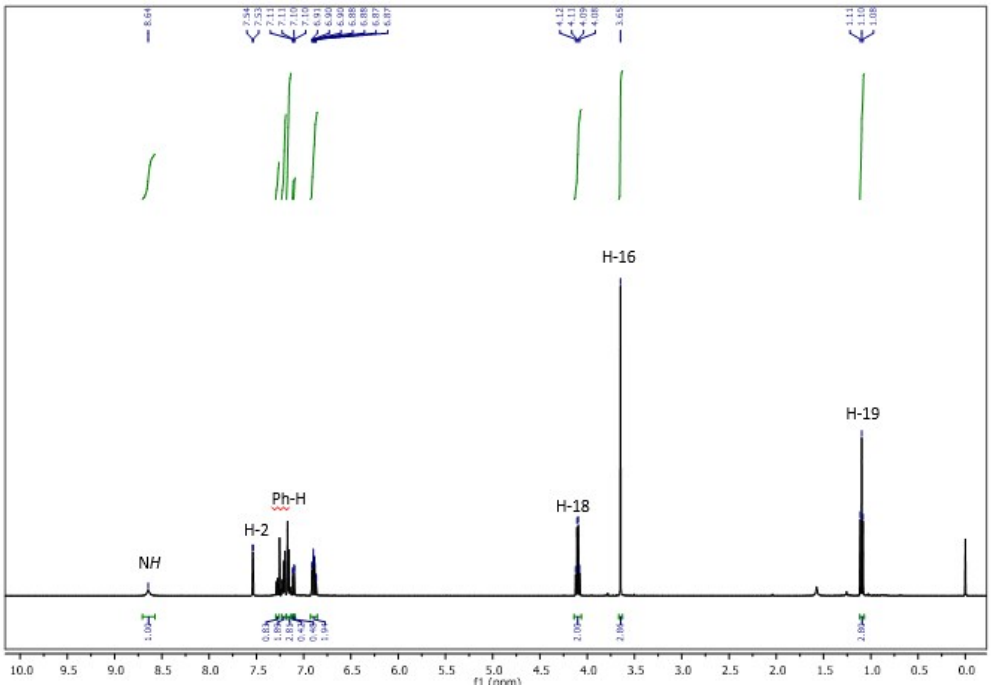
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	79(1)	46(1)	63(1)	-4(1)	9(1)	1(1)
C(3)	65(1)	40(1)	57(1)	2(1)	2(1)	1(1)
C(4)	55(1)	37(1)	54(1)	3(1)	-2(1)	2(1)
C(5)	59(1)	41(1)	61(1)	2(1)	-2(1)	2(1)
C(6)	52(1)	41(1)	70(1)	12(1)	-2(1)	4(1)
C(7)	62(1)	52(1)	90(1)	4(1)	-9(1)	-2(1)
C(8)	53(1)	62(1)	120(2)	17(1)	2(1)	-7(1)
C(9)	64(1)	79(2)	97(2)	22(1)	15(1)	3(1)
C(10)	69(1)	84(2)	75(1)	16(1)	7(1)	-4(1)
C(11)	58(1)	63(1)	72(1)	14(1)	-4(1)	-6(1)
C(12)	70(1)	44(1)	54(1)	2(1)	-1(1)	3(1)
C(15)	94(2)	72(1)	75(1)	2(1)	21(1)	-23(1)
C(16)	101(2)	99(2)	97(2)	5(1)	35(2)	-14(2)
C(17)	57(1)	43(1)	47(1)	4(1)	3(1)	-4(1)
C(18)	63(1)	53(1)	88(1)	-5(1)	5(1)	5(1)
C(19)	95(2)	54(1)	120(2)	-16(1)	40(2)	0(1)
C(20)	139(2)	68(2)	71(1)	-24(1)	45(2)	-26(2)
C(21)	124(2)	93(2)	53(1)	-7(1)	-6(1)	-40(2)
C(22)	75(1)	71(1)	61(1)	3(1)	-7(1)	-7(1)
O(13)	102(1)	42(1)	83(1)	0(1)	19(1)	-8(1)
O(14)	90(1)	54(1)	77(1)	-6(1)	26(1)	-12(1)
N(1)	77(1)	39(1)	73(1)	-2(1)	5(1)	-6(1)

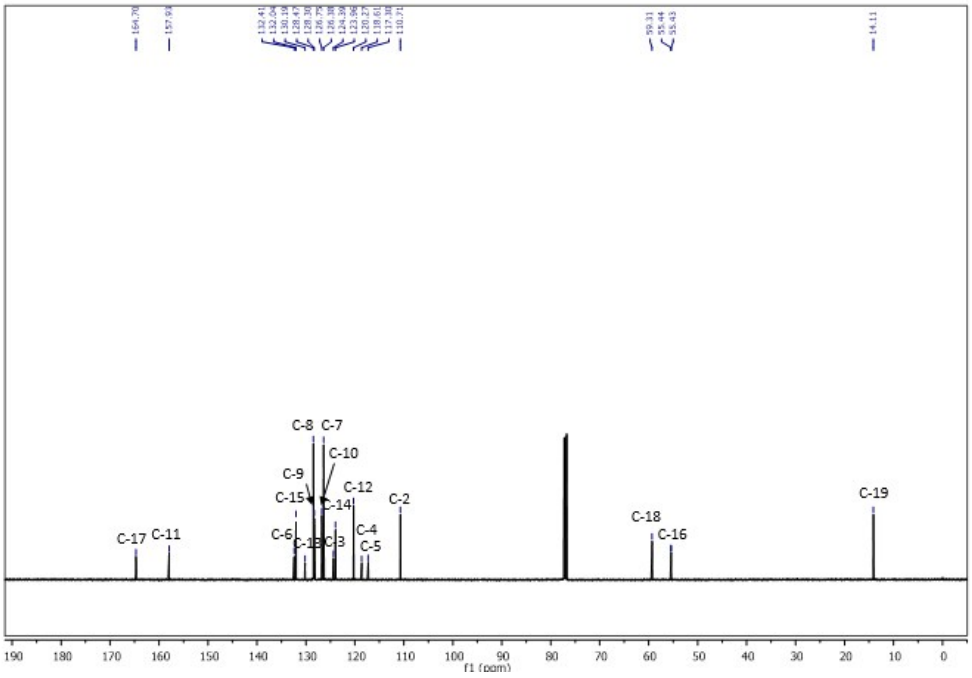
Compound 4b



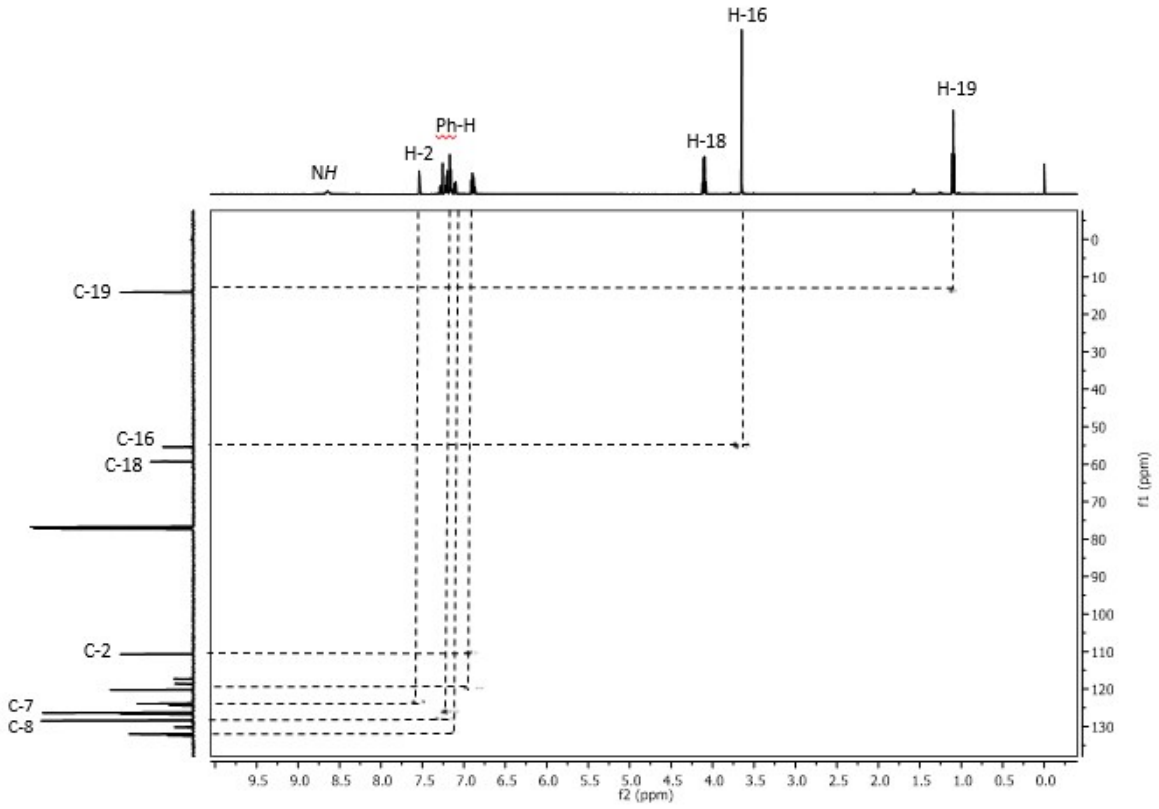
Ethyl 4-(2-methoxyphenyl)-5-phenyl-1*H*-pyrrole-3-carboxylate (4b). CCDC 1912414 Yield: 80%; colorless crystals; mp: 171-172 °C. IR (ν cm^{-1}) 3281 (N-H), 1692 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.68 (s, 1H, H-1), 7.52 (d, $^{3}J_{H-H}$ = 3.0 Hz, 1H, H-2), 7.27-7.09 (m, 7H, C*H* Ar), 6.91-6.86 (m, 2H, C*H* Ar) 4.10 (q, $^{3}J_{H-H}$ = 7.0 Hz, 2H, H-18), 3.61 (s, 3H, H-16) 1.09 (t, $^{3}J_{H-H}$ = 7.0 Hz, 3H, H-19). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.7 (C-17), 157.9 (C-11), 132.4 (C-6), 132.0 (C-15), 130.1 (C-13), 128.4 (C-8), 128.3 (C-9), 126.7 (C-10), 126.3 (C-7), 124.3 (C-3), 123.9 (C-14), 120.2 (C-12), 118.6 (C-4), 117.3 (C-5), 110.7 (C-2), 59.3 (C-18), 55.4 (C-16), 14.1 (C-19). HRMS (ESI^{+}): m/z calcd for $C_{20}H_{19}NO_3$ $[M+Na]^{+}$ 344.1263, found 344.1269.



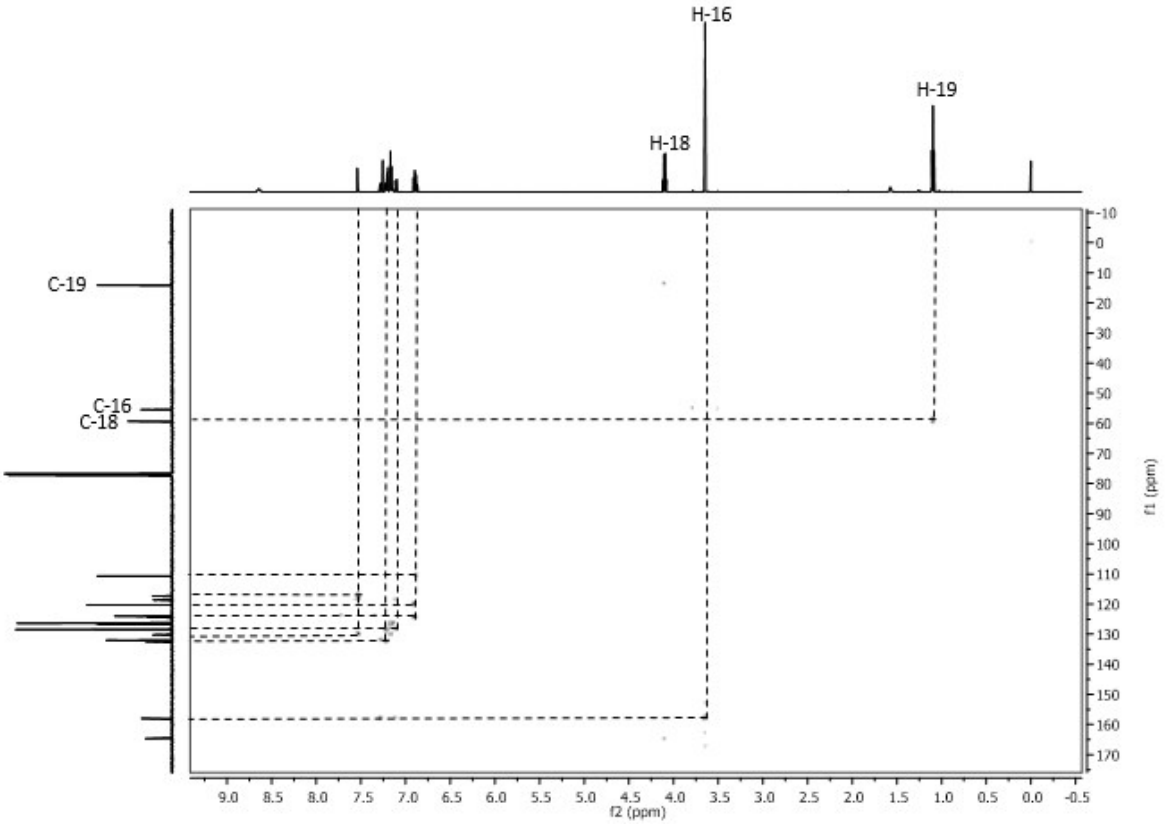
4b NMR ^{1}H ($CDCl_3$, 500 MHz).



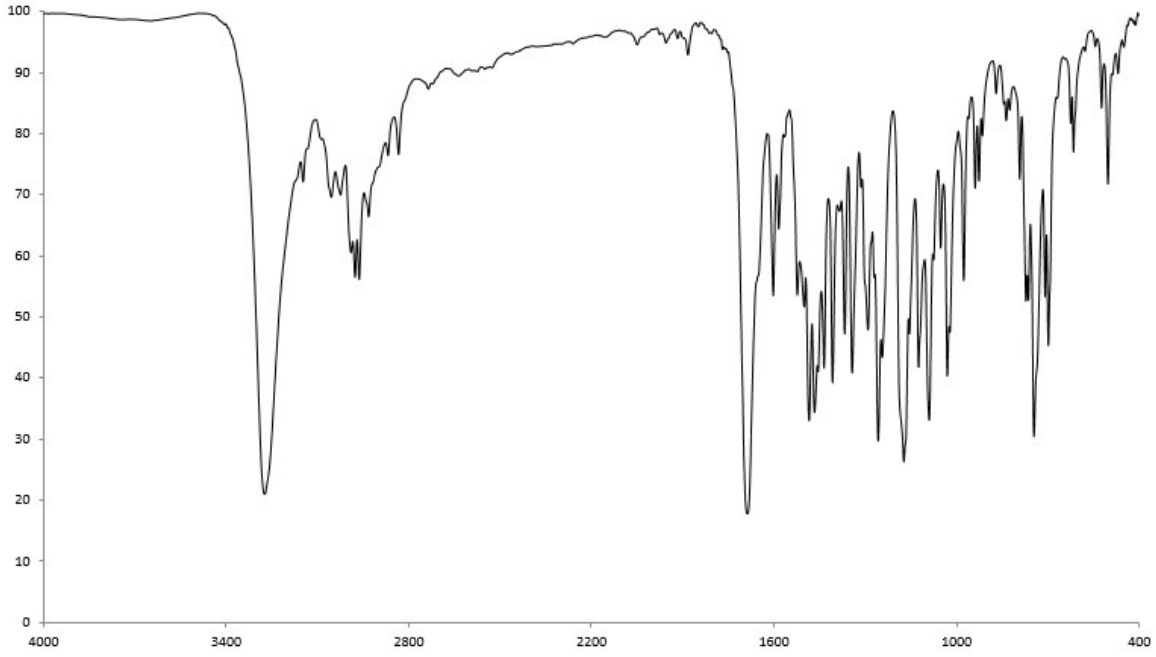
4b NMR ^{13}C ($CDCl_3$, 125 MHz).



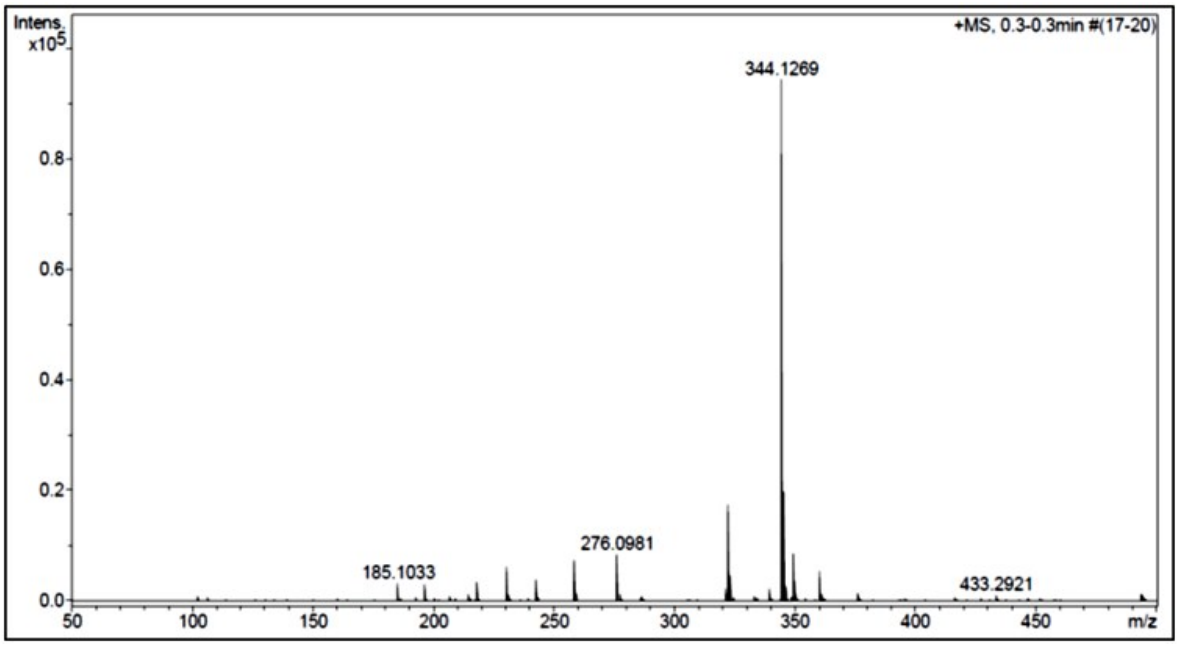
4b NMR-HSQC ($CDCl_3$, 500 MHz).



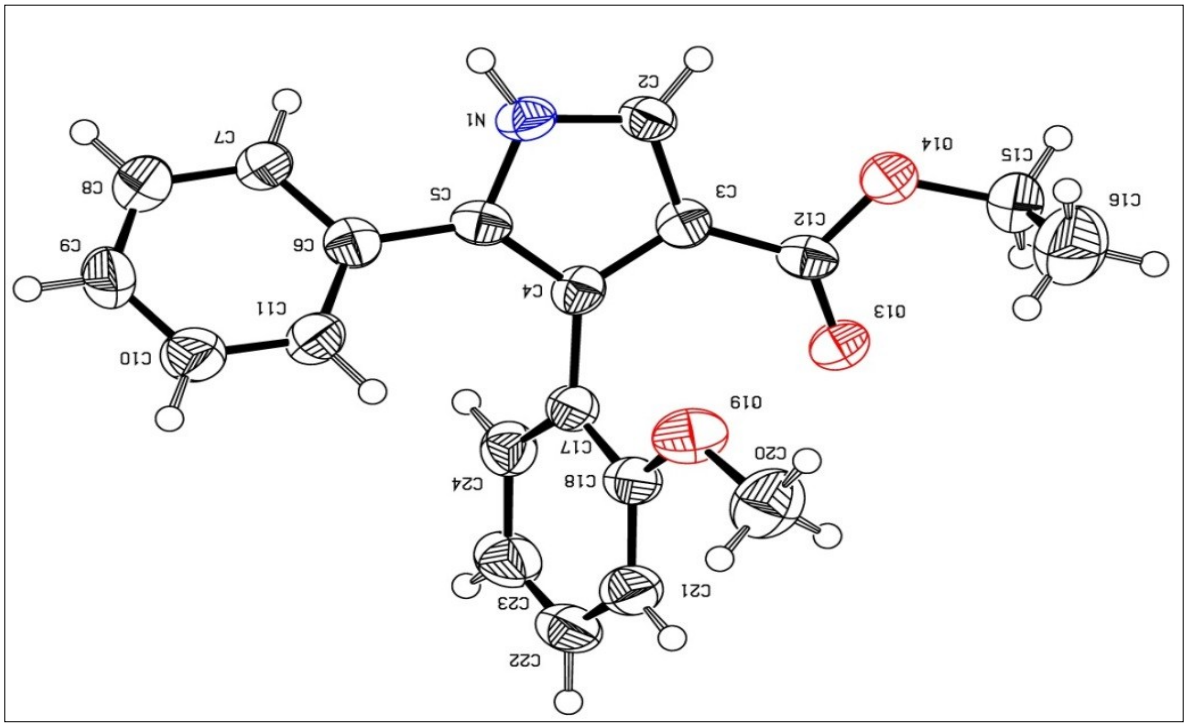
4b NMR-HMBC ($CDCl_3$, 500 MHz).



4b IR-KBr pellet.



4b HRMS



4b, X-Ray Data CCDC 1912414

Table 1. Crystal data and structure refinement for **4b**.

Identification code	**4b**	
Empirical formula	C20 H19 N O3 S0	
Formula weight	321.36	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P na21	
Unit cell dimensions	a = 20.686(3) Å	α= 90°.
	b = 10.2939(12) Å	β= 90°.
	c = 7.9226(13) Å	γ = 90°.
Volume	1687.0(4) $Å^3$	
Z	4	
Density (calculated)	1.265 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	680	
Theta range for data collection	3.39 to 25.34°.	
Index ranges	-24<=h<=24, -9<=k<=12, -5<=l<=9	
Reflections collected	4470	
Independent reflections	2543 [R(int) = 0.0532]	
Completeness to theta = 25.34°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2543 / 2 / 222	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0588, wR2 = 0.1118	
R indices (all data)	R1 = 0.1094, wR2 = 0.1356	
Absolute structure parameter	-1(2)	
Largest diff. peak and hole	0.177 and -0.216 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	-7337(2)	-7150(4)	-2963(6)	39(1)
C(3)	-7241(2)	-5894(4)	-3521(6)	36(1)
C(4)	-7762(2)	-5123(4)	-2903(6)	36(1)
C(5)	-8162(2)	-5952(4)	-2004(6)	38(1)
C(6)	-8751(2)	-5745(4)	-1013(6)	38(1)
C(7)	-9214(2)	-6716(4)	-832(6)	44(1)
C(8)	-9754(2)	-6526(5)	185(7)	59(2)
C(9)	-9830(2)	-5379(5)	1048(7)	61(2)
C(10)	-9383(2)	-4409(5)	879(7)	56(1)
C(11)	-8843(2)	-4578(4)	-151(6)	45(1)
C(12)	-6698(2)	-5458(4)	-4528(6)	38(1)
C(15)	-5663(2)	-6044(5)	-5611(7)	55(1)
C(16)	-5166(2)	-5454(6)	-4475(9)	87(2)
C(17)	-7872(2)	-3718(4)	-3210(6)	39(1)
C(18)	-7440(2)	-2786(4)	-2604(6)	42(1)
C(20)	-6439(2)	-2381(5)	-1201(8)	71(2)
C(21)	-7530(2)	-1481(4)	-2967(7)	53(1)
C(22)	-8055(3)	-1097(5)	-3930(7)	57(2)
C(23)	-8490(2)	-1986(5)	-4524(7)	60(2)
C(24)	-8403(2)	-3302(4)	-4162(6)	45(1)
O(13)	-6642(1)	-4410(3)	-5206(4)	47(1)
O(14)	-6232(1)	-6372(3)	-4659(4)	49(1)
O(19)	-6945(2)	-3254(3)	-1652(4)	55(1)
N(1)	-7895(2)	-7186(3)	-2078(5)	39(1)

Table 3. Bond lengths [Å] and angles [°] for **4b**.

C(2)-N(1)	1.350(5)
C(2)-C(3)	1.381(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.426(6)
C(3)-C(12)	1.449(6)
C(4)-C(5)	1.386(6)
C(4)-C(17)	1.484(5)
C(5)-N(1)	1.387(5)
C(5)-C(6)	1.464(6)
C(6)-C(7)	1.392(6)
C(6)-C(11)	1.395(6)
C(7)-C(8)	1.391(6)
C(7)-H(7)	0.9300
C(8)-C(9)	1.373(6)
C(8)-H(8)	0.9300
C(9)-C(10)	1.366(6)
C(9)-H(9)	0.9300
C(10)-C(11)	1.395(6)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300
C(12)-O(13)	1.211(5)
C(12)-O(14)	1.351(5)
C(15)-O(14)	1.437(5)
C(15)-C(16)	1.496(7)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-C(18)	1.396(6)
C(17)-C(24)	1.400(6)
C(18)-O(19)	1.361(5)
C(18)-C(21)	1.386(6)
C(20)-O(19)	1.425(5)

C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-C(22)	1.386(7)
C(21)-H(21)	0.9300
C(22)-C(23)	1.367(7)
C(22)-H(22)	0.9300
C(23)-C(24)	1.396(6)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
N(1)-H(1F)	0.906(19)

N(1)-C(2)-C(3)	108.4(4)
N(1)-C(2)-H(2)	125.8
C(3)-C(2)-H(2)	125.8
C(2)-C(3)-C(4)	107.6(4)
C(2)-C(3)-C(12)	125.3(4)
C(4)-C(3)-C(12)	127.1(4)
C(5)-C(4)-C(3)	106.6(3)
C(5)-C(4)-C(17)	126.4(4)
C(3)-C(4)-C(17)	127.0(4)
C(4)-C(5)-N(1)	107.7(4)
C(4)-C(5)-C(6)	133.0(4)
N(1)-C(5)-C(6)	119.2(4)
C(7)-C(6)-C(11)	118.3(4)
C(7)-C(6)-C(5)	121.5(4)
C(11)-C(6)-C(5)	120.1(4)
C(8)-C(7)-C(6)	120.8(4)
C(8)-C(7)-H(7)	119.6
C(6)-C(7)-H(7)	119.6
C(9)-C(8)-C(7)	120.0(5)
C(9)-C(8)-H(8)	120.0
C(7)-C(8)-H(8)	120.0
C(10)-C(9)-C(8)	120.2(5)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9

C(9)-C(10)-C(11)	120.5(5)
C(9)-C(10)-H(10)	119.8
C(11)-C(10)-H(10)	119.8
C(6)-C(11)-C(10)	120.2(4)
C(6)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
O(13)-C(12)-O(14)	121.2(4)
O(13)-C(12)-C(3)	126.5(4)
O(14)-C(12)-C(3)	112.3(4)
O(14)-C(15)-C(16)	110.0(5)
O(14)-C(15)-H(15A)	109.7
C(16)-C(15)-H(15A)	109.7
O(14)-C(15)-H(15B)	109.7
C(16)-C(15)-H(15B)	109.7
H(15A)-C(15)-H(15B)	108.2
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(24)	118.5(4)
C(18)-C(17)-C(4)	121.1(4)
C(24)-C(17)-C(4)	120.4(4)
O(19)-C(18)-C(21)	123.9(4)
O(19)-C(18)-C(17)	115.4(4)
C(21)-C(18)-C(17)	120.7(4)
O(19)-C(20)-H(20A)	109.5
O(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-C(22)	119.7(5)
C(18)-C(21)-H(21)	120.2
C(22)-C(21)-H(21)	120.2

C(23)-C(22)-C(21)	120.9(4)
C(23)-C(22)-H(22)	119.5
C(21)-C(22)-H(22)	119.5
C(22)-C(23)-C(24)	119.7(5)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-H(23)	120.2
C(23)-C(24)-C(17)	120.5(4)
C(23)-C(24)-H(24)	119.7
C(17)-C(24)-H(24)	119.7
C(12)-O(14)-C(15)	117.4(3)
C(18)-O(19)-C(20)	118.0(4)
C(2)-N(1)-C(5)	109.7(4)
C(2)-N(1)-H(1F)	125(3)
C(5)-N(1)-H(1F)	125(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **4b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	47(3)	33(2)	38(3)	-1(2)	4(2)	6(2)
C(3)	40(2)	40(2)	28(3)	7(2)	-1(2)	2(2)
C(4)	40(2)	39(2)	29(3)	7(2)	0(2)	-1(2)
C(5)	47(3)	32(2)	33(3)	-2(2)	-4(2)	4(2)
C(6)	41(3)	42(3)	32(3)	7(2)	-3(2)	4(2)
C(7)	40(2)	37(2)	54(4)	5(2)	1(2)	-3(2)
C(8)	49(3)	51(3)	78(4)	10(3)	10(3)	-3(2)
C(9)	51(3)	63(3)	69(4)	9(3)	23(3)	8(3)
C(10)	66(3)	47(3)	55(4)	-4(3)	12(3)	-3(3)
C(11)	49(3)	43(3)	45(3)	-1(2)	4(3)	-8(2)
C(12)	49(3)	31(2)	35(3)	-3(2)	-2(2)	4(2)
C(15)	44(3)	58(3)	64(4)	3(3)	8(3)	-2(2)
C(16)	66(4)	100(4)	94(6)	-5(4)	-1(4)	-15(3)
C(17)	45(3)	35(2)	36(3)	5(2)	11(2)	3(2)
C(18)	54(3)	37(3)	35(3)	2(2)	9(2)	3(2)
C(20)	66(3)	76(4)	71(4)	-7(3)	-7(3)	-17(3)
C(21)	68(3)	39(3)	50(4)	-3(3)	19(3)	-1(3)
C(22)	82(4)	40(3)	49(4)	12(3)	29(3)	17(3)
C(23)	67(3)	53(3)	59(4)	17(3)	11(3)	17(3)
C(24)	42(3)	50(3)	44(3)	6(2)	3(2)	2(2)
O(13)	52(2)	41(2)	49(2)	14(2)	8(2)	-1(1)
O(14)	50(2)	43(2)	53(2)	11(2)	12(2)	4(2)
O(19)	66(2)	48(2)	52(3)	-2(2)	-12(2)	-5(2)
N(1)	50(2)	31(2)	36(2)	5(2)	2(2)	-2(2)

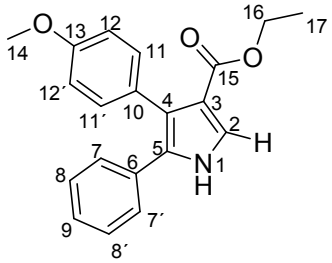
Table 5. Torsion angles [°] for **4b**.

N(1)-C(2)-C(3)-C(4)	1.4(5)
N(1)-C(2)-C(3)-C(12)	-179.5(4)
C(2)-C(3)-C(4)-C(5)	-0.7(5)
C(12)-C(3)-C(4)-C(5)	-179.7(4)
C(2)-C(3)-C(4)-C(17)	-178.7(5)
C(12)-C(3)-C(4)-C(17)	2.3(7)
C(3)-C(4)-C(5)-N(1)	-0.3(5)
C(17)-C(4)-C(5)-N(1)	177.7(4)
C(3)-C(4)-C(5)-C(6)	176.7(4)
C(17)-C(4)-C(5)-C(6)	-5.3(8)
C(4)-C(5)-C(6)-C(7)	151.8(5)
N(1)-C(5)-C(6)-C(7)	-31.5(6)
C(4)-C(5)-C(6)-C(11)	-31.5(7)
N(1)-C(5)-C(6)-C(11)	145.1(4)
C(11)-C(6)-C(7)-C(8)	0.0(7)
C(5)-C(6)-C(7)-C(8)	176.7(4)
C(6)-C(7)-C(8)-C(9)	-1.1(7)
C(7)-C(8)-C(9)-C(10)	1.6(8)
C(8)-C(9)-C(10)-C(11)	-0.9(8)
C(7)-C(6)-C(11)-C(10)	0.8(7)
C(5)-C(6)-C(11)-C(10)	-176.0(4)
C(9)-C(10)-C(11)-C(6)	-0.3(7)
C(2)-C(3)-C(12)-O(13)	170.2(5)
C(4)-C(3)-C(12)-O(13)	-11.0(7)
C(2)-C(3)-C(12)-O(14)	-9.7(6)
C(4)-C(3)-C(12)-O(14)	169.1(4)
C(5)-C(4)-C(17)-C(18)	117.8(5)
C(3)-C(4)-C(17)-C(18)	-64.6(6)
C(5)-C(4)-C(17)-C(24)	-64.0(6)
C(3)-C(4)-C(17)-C(24)	113.5(5)
C(24)-C(17)-C(18)-O(19)	178.3(4)
C(4)-C(17)-C(18)-O(19)	-3.5(6)
C(24)-C(17)-C(18)-C(21)	-1.3(7)
C(4)-C(17)-C(18)-C(21)	176.8(4)

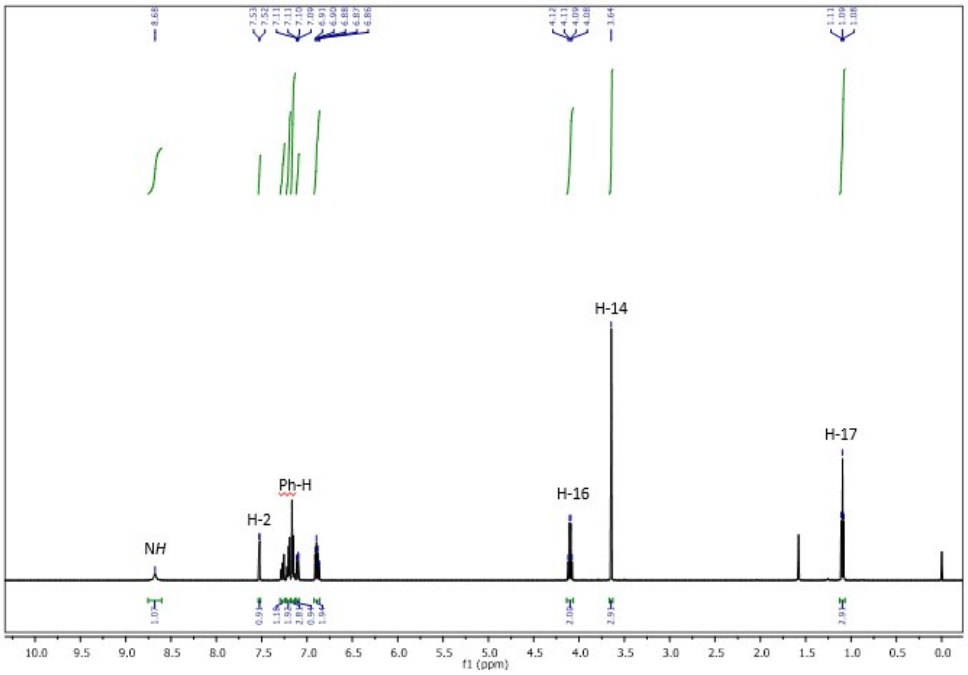
O(19)-C(18)-C(21)-C(22)	-179.1(4)
C(17)-C(18)-C(21)-C(22)	0.5(7)
C(18)-C(21)-C(22)-C(23)	0.3(7)
C(21)-C(22)-C(23)-C(24)	-0.2(8)
C(22)-C(23)-C(24)-C(17)	-0.7(7)
C(18)-C(17)-C(24)-C(23)	1.4(7)
C(4)-C(17)-C(24)-C(23)	-176.7(4)
O(13)-C(12)-O(14)-C(15)	0.9(6)
C(3)-C(12)-O(14)-C(15)	-179.2(4)
C(16)-C(15)-O(14)-C(12)	90.3(5)
C(21)-C(18)-O(19)-C(20)	-9.3(6)
C(17)-C(18)-O(19)-C(20)	171.1(4)
C(3)-C(2)-N(1)-C(5)	-1.6(5)
C(4)-C(5)-N(1)-C(2)	1.2(5)
C(6)-C(5)-N(1)-C(2)	-176.3(4)

Symmetry transformations used to generate equivalent atoms:

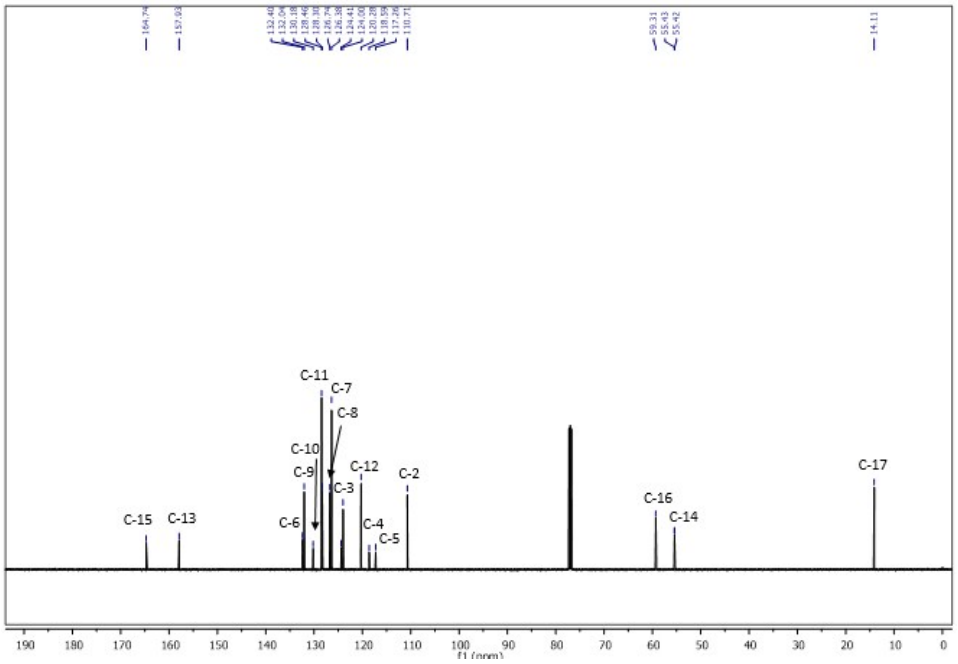
Compound 4c



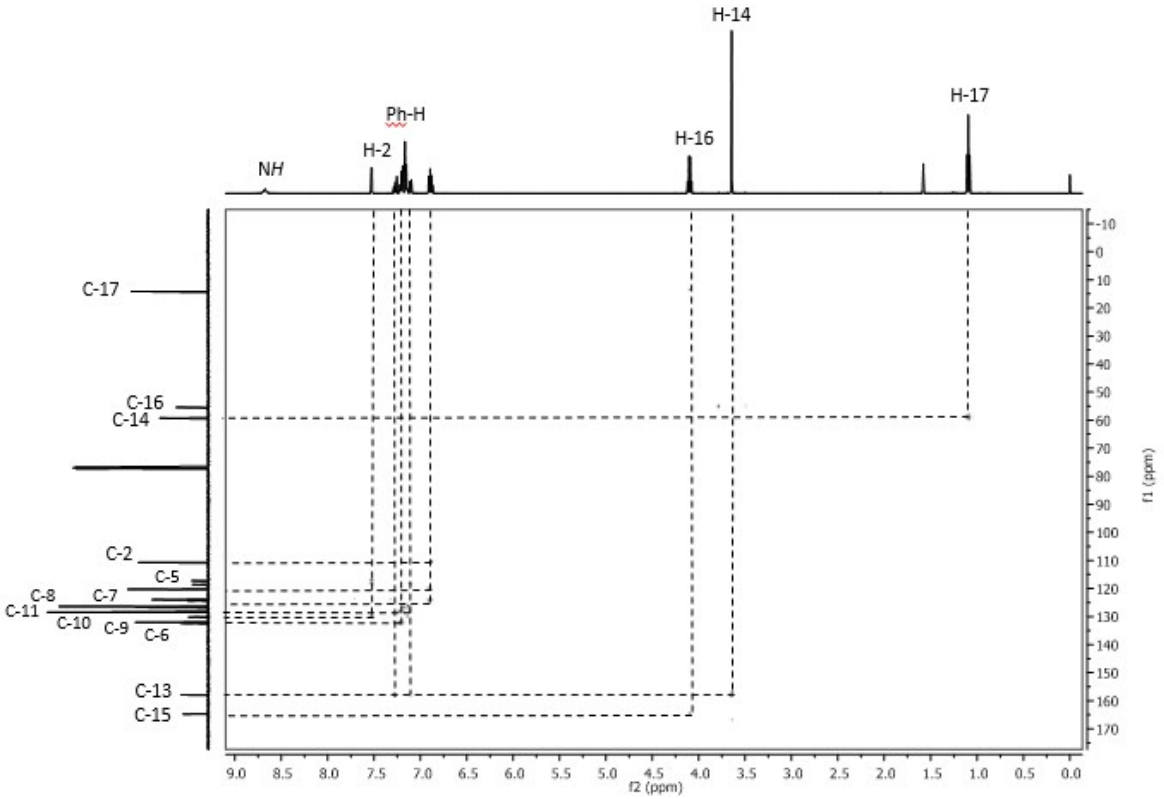
Ethyl 4-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-3-carboxylate (4c). **CCDC 1912422** Yield: 87%; brown solid; mp: 188-190 °C. IR (ν cm^{-1}) 3304 (N-H), 1683 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.68 (s, 1H, H-1), 7.52 (d, $^{3}J_{H-H}$ = 5.0 Hz, 1H, H-2), 7.11-7.09 (m, 7H, C*H* Ar), 6.91-6.86 (m, 2H, C*H* Ar), 4.10 (q, $^{3}J_{H-H}$ = 7.5 Hz, 2H, H-16), 3.64 (s, 3H, H-14), 1.09 (t, $^{3}J_{H-H}$ = 7.5 Hz, 3H, H-17). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.7 (C-15), 157.9 (C-13), 132.4 (C-6), 132.0 (C-9), 130.1 (C-10), 128.4 (C-14), 126.7 (C-8), 126.3 (C-7), 124.0 (C-3), 120.2 (C-12), 118.5 (C-4), 117.2 (C-5), 110.7 (C-2), 59.3 (C-16), 55.4 (C-14), 14.1 (C-17). HRMS (ESI^{+}): m/z calcd for $C_{20}H_{19}NO_3$ $[M+Na]^{+}$ 344.1263, found 344.1270.



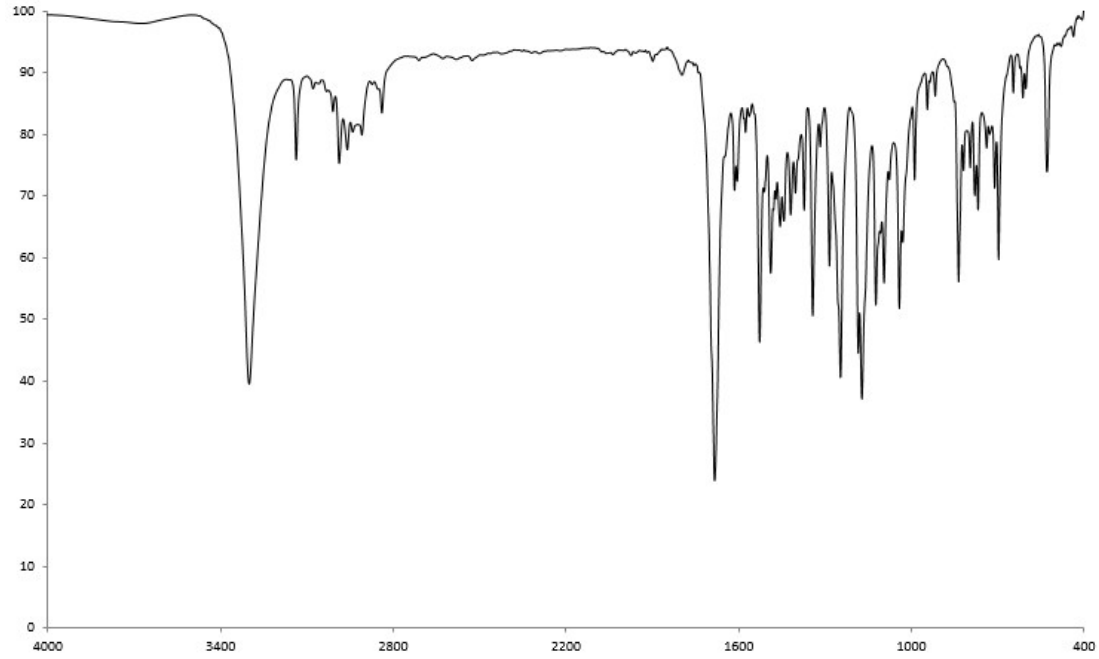
4c NMR ^{1}H ($CDCl_3$, 500 MHz).



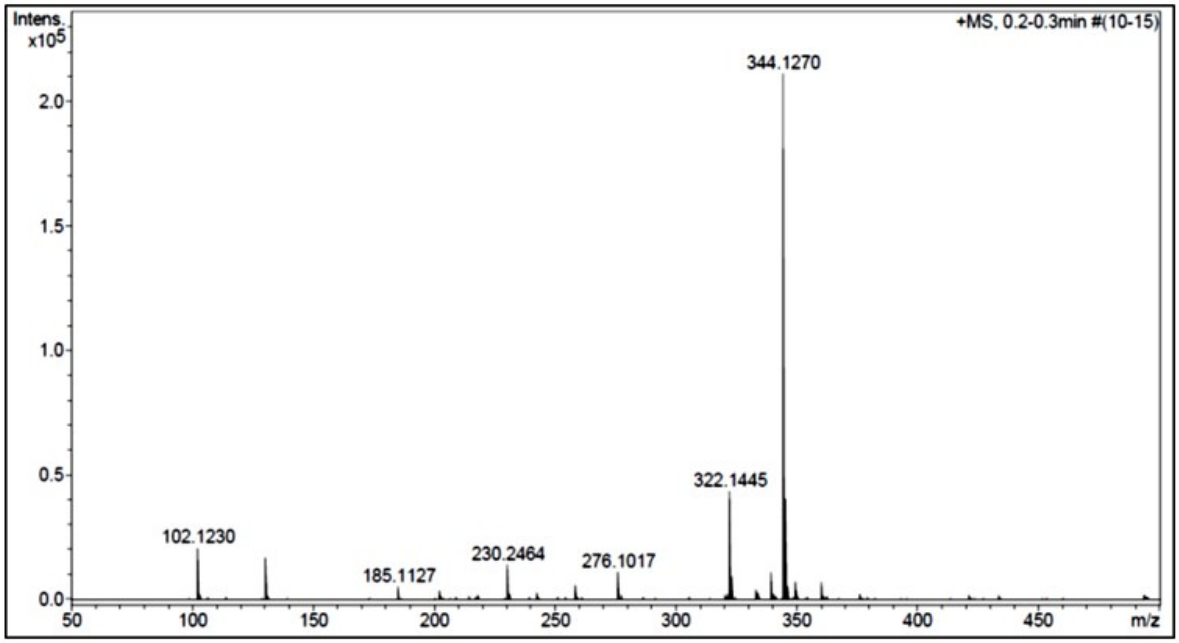
4c NMR ^{13}C ($CDCl_3$, 125 MHz).



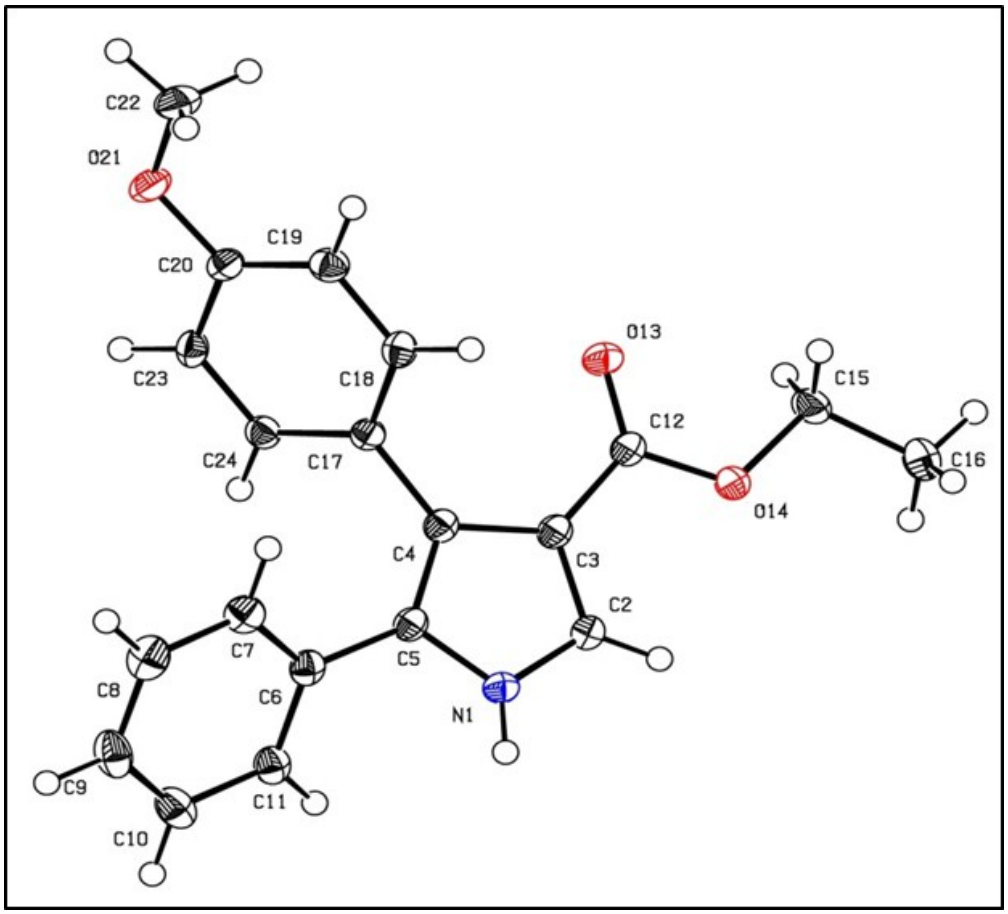
4c NMR-HMBC ($CDCl_3$, 500 MHz).



4c IR-KBr pellet.

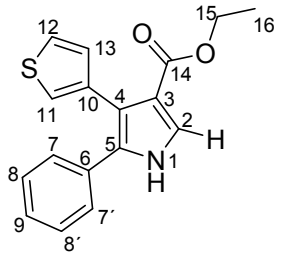


4c HRMS.



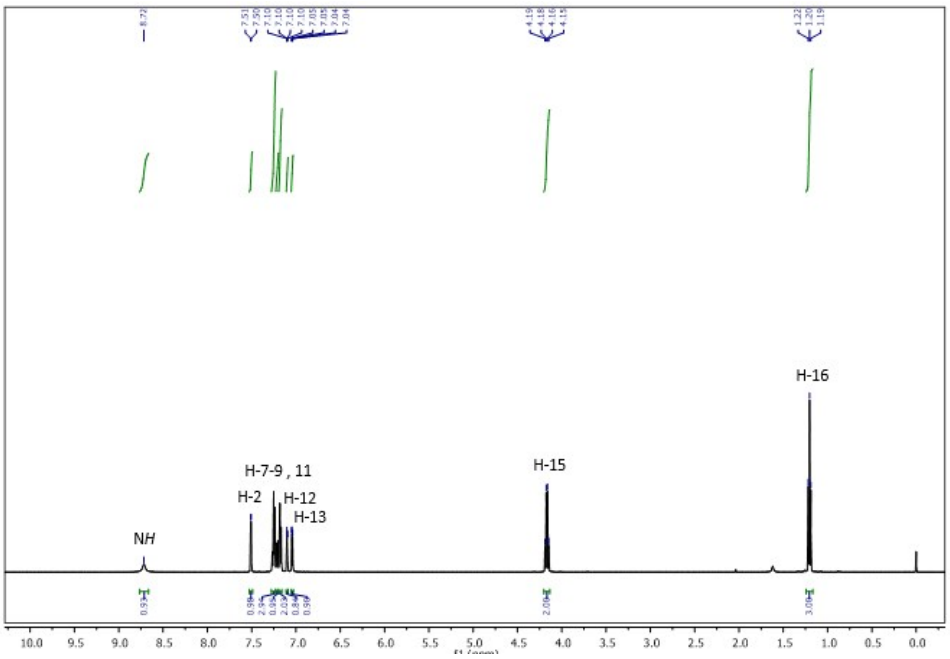
4c, X-Ray Data CDC 1912422

Compound 4d

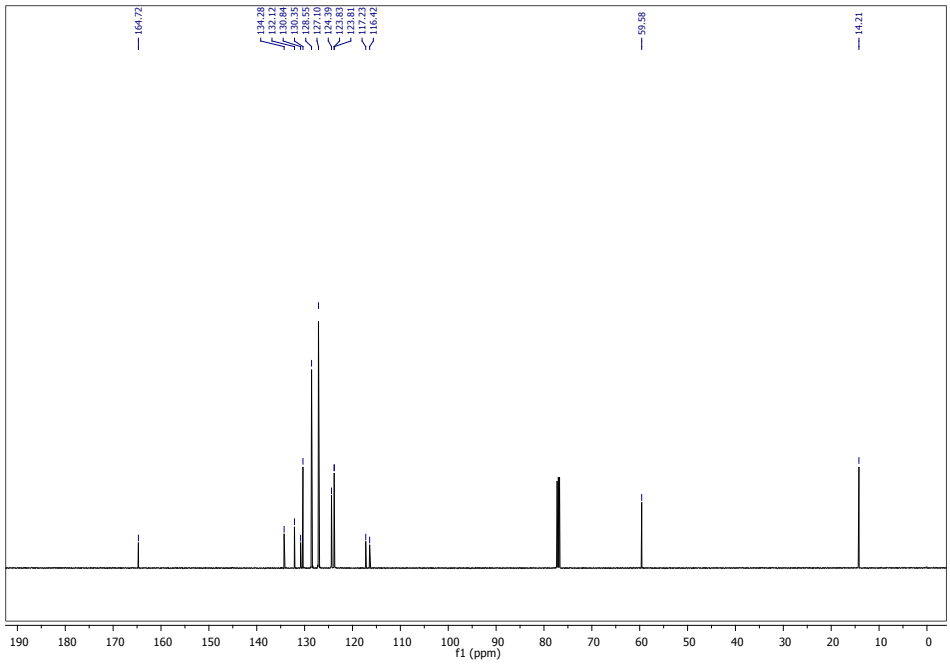


Ethyl 5-phenyl-4-(thiophen-3-yl)-1*H*-pyrrole-3-carboxylate (4d). CCDC 1912423

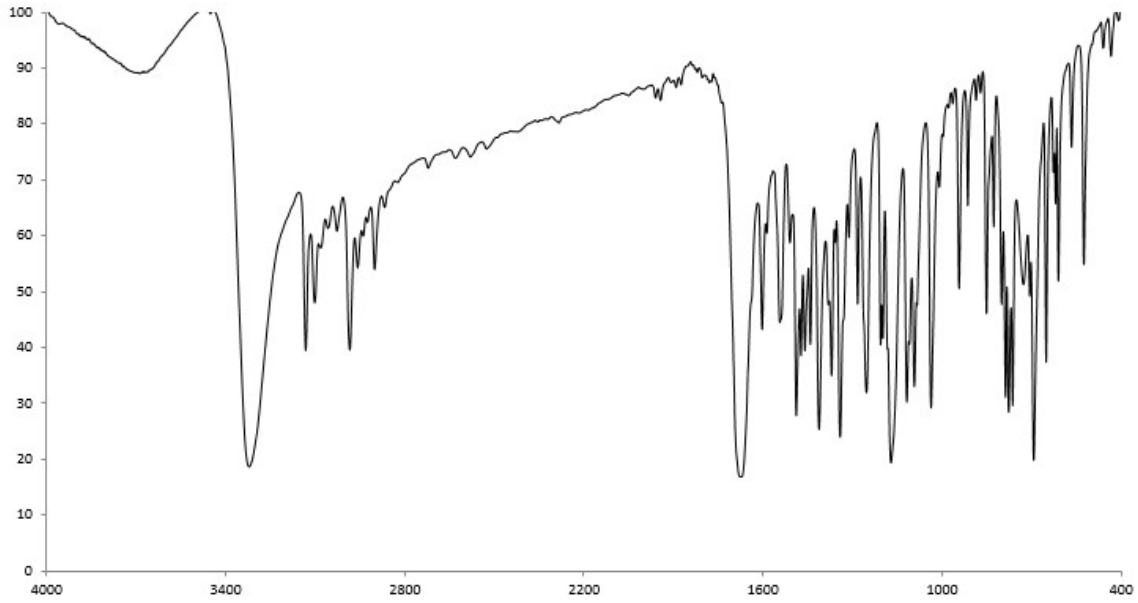
Yield: 90%; brown crystals; mp: 178-179 °C. IR (ν cm^{-1}) 3327 (N-H), 1681 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.72 (s, 1H, H-1), 7.50 (d, $^{3}J_{H\text{-}H}$ = 5.0 Hz, 1H, H-2), 7.27-7.17 (m, 6H, H-7, H-8, H-9 and H-11), 7.10 (dd, $^{2}J_{H\text{-}H}$ = 1.0 Hz, 1H, H-12), 7.05 (dd, $^{2}J_{H\text{-}H}$ = 1.0 Hz, H-13), 4.17 (q, *J* = 7.5 Hz, 2H, H-15), 1.20 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 3H, H-16). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.7 (C-14), 134.2 (C-10), 132.1 (C-6), 130.8 (C-9), 130.5 (C-8), 128.5 (C-12), 127.1 (C-13), 124.3 (C-7), 123.9 (C-11), 123.8 (C-2), 117.2 (C-3), 116.4 (C-4), 59.5 (C-15), 14.2 (C-16). HRMS (ESI^{+}): m/z calcd for $C_{17}H_{15}NO_2S$ $[M+Na]^{+}$ 320.0721, found 320.0724.



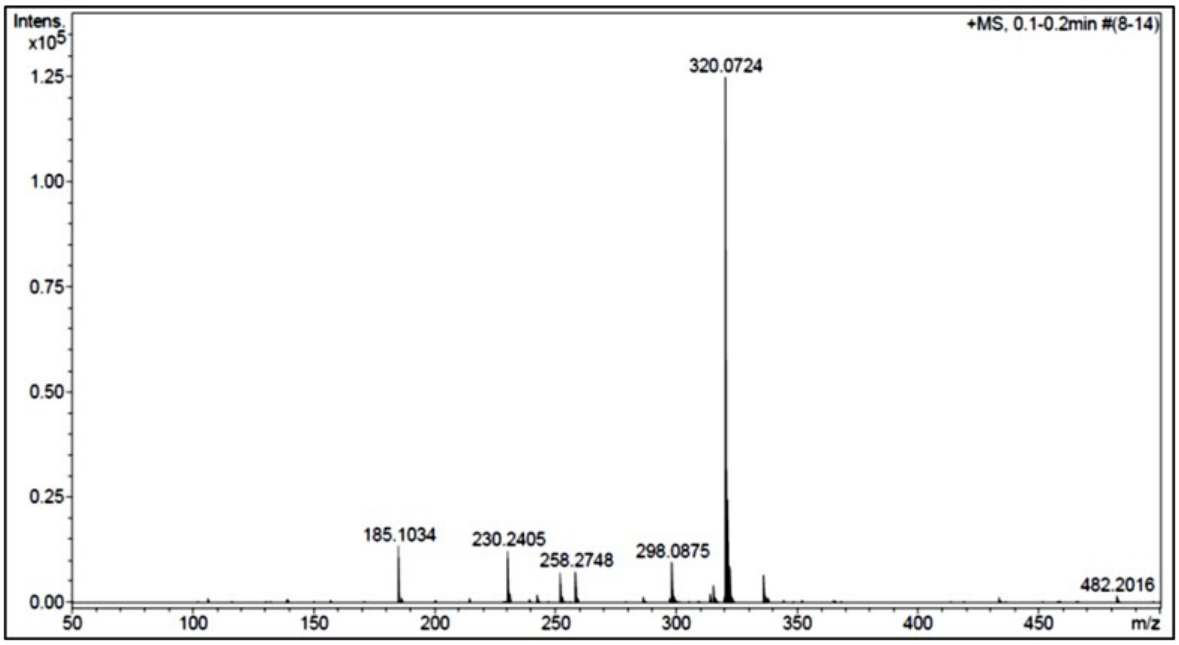
4d NMR ^{1}H ($CDCl_3$, 500 MHz).



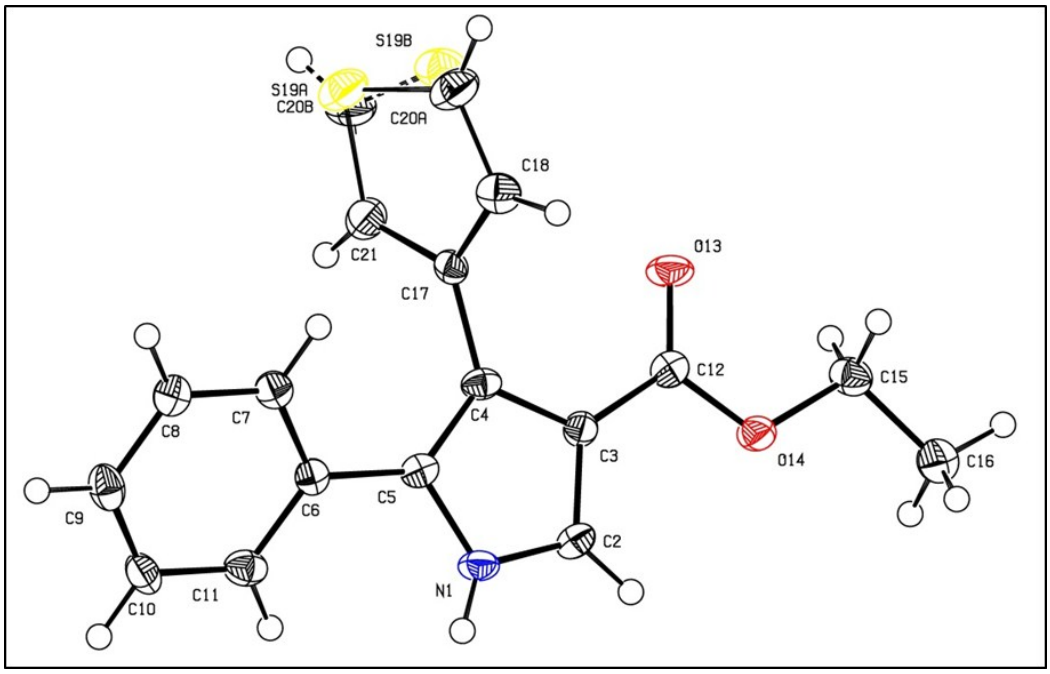
4d NMR ^{13}C ($CDCl_3$, 125 MHz).



4d IR-KBr pellet.



4d HRMS.



4d, X-Ray Data CCDC 1912423

Table 1. Crystal data and structure refinement for **4d**.

Identification code	**4d**	
Empirical formula	C17 H15 N O2 S	
Formula weight	297.36	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.5576(5) Å	α= 90°.
	b = 13.3725(17) Å	β= 90°.
	c = 19.880(3) Å	γ = 90°.
Volume	1477.4(3) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.222 mm^{-1}	
F(000)	624	
Theta range for data collection	3.431 to 26.731°.	
Index ranges	-6<=h<=6, -16<=k<=16, -24<=l<=25	
Reflections collected	11405	
Independent reflections	3084 [R(int) = 0.0886]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3084 / 2 / 201	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.0774	
R indices (all data)	R1 = 0.1093, wR2 = 0.0959	
Absolute structure parameter	-0.07(14)	
Largest diff. peak and hole	0.252 and -0.231 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	5378(7)	6386(3)	7323(2)	21(1)
C(3)	4943(8)	5410(3)	7513(2)	20(1)
C(4)	6500(7)	5189(3)	8069(2)	19(1)
C(5)	7835(7)	6037(3)	8190(2)	20(1)
C(6)	9689(7)	6276(3)	8696(2)	18(1)
C(7)	9689(7)	5805(3)	9327(2)	21(1)
C(8)	11457(7)	6022(3)	9795(2)	23(1)
C(9)	13243(7)	6713(3)	9650(2)	25(1)
C(10)	13257(7)	7187(3)	9035(2)	25(1)
C(11)	11489(7)	6967(3)	8560(2)	24(1)
C(12)	3233(7)	4741(3)	7199(2)	20(1)
C(15)	25(8)	4569(3)	6420(2)	25(1)
C(16)	-1276(7)	5194(4)	5905(2)	30(1)
C(17)	6619(7)	4249(3)	8459(2)	18(1)
C(18)	4858(8)	3933(3)	8907(2)	26(1)
C(21)	8581(8)	3602(3)	8459(2)	28(1)
O(13)	2988(5)	3854(2)	7333(1)	28(1)
O(14)	1864(5)	5195(2)	6727(1)	24(1)
S(19A)	8298(12)	2682(4)	9018(2)	34(1)
C(20A)	5390(50)	3057(14)	9246(12)	34(1)
S(19B)	5591(11)	2873(4)	9319(3)	33(1)
C(20B)	8320(60)	2762(19)	8882(11)	33(1)
N(1)	7134(6)	6752(3)	7723(2)	22(1)

Table 3. Bond lengths [Å] and angles [°] for **4d**.

C(2)-N(1)	1.350(5)
C(2)-C(3)	1.379(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.433(5)
C(3)-C(12)	1.447(6)
C(4)-C(5)	1.377(5)
C(4)-C(17)	1.479(5)
C(5)-N(1)	1.389(5)
C(5)-C(6)	1.475(5)
C(6)-C(11)	1.388(5)
C(6)-C(7)	1.404(5)
C(7)-C(8)	1.383(5)
C(7)-H(7)	0.9500
C(8)-C(9)	1.387(6)
C(8)-H(8)	0.9500
C(9)-C(10)	1.378(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.393(5)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-O(13)	1.224(5)
C(12)-O(14)	1.352(4)
C(15)-O(14)	1.455(5)
C(15)-C(16)	1.506(5)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(21)	1.392(6)
C(17)-C(18)	1.389(5)
C(18)-C(20A)	1.384(16)
C(18)-S(19B)	1.688(6)
C(18)-H(18)	0.9500

C(21)-C(20B)	1.411(19)
C(21)-S(19A)	1.666(6)
C(21)-H(21)	0.9500
S(19A)-C(20A)	1.75(3)
C(20A)-H(20A)	0.9500
S(19B)-C(20B)	1.75(3)
C(20B)-H(20B)	0.9500
N(1)-H(1F)	0.87(4)

N(1)-C(2)-C(3)	108.0(4)
N(1)-C(2)-H(2)	126.0
C(3)-C(2)-H(2)	126.0
C(2)-C(3)-C(4)	107.5(4)
C(2)-C(3)-C(12)	125.6(4)
C(4)-C(3)-C(12)	127.0(4)
C(5)-C(4)-C(3)	106.9(4)
C(5)-C(4)-C(17)	125.7(3)
C(3)-C(4)-C(17)	127.4(4)
C(4)-C(5)-N(1)	107.4(3)
C(4)-C(5)-C(6)	132.4(4)
N(1)-C(5)-C(6)	120.2(4)
C(11)-C(6)-C(7)	118.2(3)
C(11)-C(6)-C(5)	121.0(3)
C(7)-C(6)-C(5)	120.8(4)
C(8)-C(7)-C(6)	120.4(4)
C(8)-C(7)-H(7)	119.8
C(6)-C(7)-H(7)	119.8
C(7)-C(8)-C(9)	120.6(4)
C(7)-C(8)-H(8)	119.7
C(9)-C(8)-H(8)	119.7
C(10)-C(9)-C(8)	119.6(4)
C(10)-C(9)-H(9)	120.2
C(8)-C(9)-H(9)	120.2
C(9)-C(10)-C(11)	120.0(4)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0

C(6)-C(11)-C(10)	121.1(4)
C(6)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
O(13)-C(12)-O(14)	121.6(4)
O(13)-C(12)-C(3)	125.3(4)
O(14)-C(12)-C(3)	113.1(4)
O(14)-C(15)-C(16)	107.6(4)
O(14)-C(15)-H(15A)	110.2
C(16)-C(15)-H(15A)	110.2
O(14)-C(15)-H(15B)	110.2
C(16)-C(15)-H(15B)	110.2
H(15A)-C(15)-H(15B)	108.5
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(21)-C(17)-C(18)	111.3(4)
C(21)-C(17)-C(4)	124.3(4)
C(18)-C(17)-C(4)	124.3(4)
C(20A)-C(18)-C(17)	114.9(12)
C(17)-C(18)-S(19B)	113.4(4)
C(20A)-C(18)-H(18)	122.5
C(17)-C(18)-H(18)	122.5
C(17)-C(21)-C(20B)	114.5(14)
C(17)-C(21)-S(19A)	112.7(4)
C(17)-C(21)-H(21)	123.7
S(19A)-C(21)-H(21)	123.7
C(12)-O(14)-C(15)	115.4(3)
C(21)-S(19A)-C(20A)	92.8(7)
C(18)-C(20A)-S(19A)	108.2(16)
C(18)-C(20A)-H(20A)	125.9
S(19A)-C(20A)-H(20A)	125.9
C(18)-S(19B)-C(20B)	92.2(8)
C(21)-C(20B)-S(19B)	108.4(18)

C(21)-C(20B)-H(20B)	125.8
S(19B)-C(20B)-H(20B)	125.8
C(2)-N(1)-C(5)	110.3(4)
C(2)-N(1)-H(1F)	123(3)
C(5)-N(1)-H(1F)	126(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for **4d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	26(2)	18(2)	18(2)	0(2)	-2(2)	5(2)
C(3)	20(2)	16(2)	22(2)	-2(2)	-3(2)	1(2)
C(4)	23(2)	15(2)	20(2)	1(2)	4(2)	3(2)
C(5)	22(2)	18(2)	18(2)	1(2)	2(2)	2(2)
C(6)	17(2)	14(2)	22(2)	-6(2)	1(2)	4(2)
C(7)	22(2)	18(2)	23(2)	-4(2)	1(2)	1(2)
C(8)	23(2)	25(3)	22(2)	-2(2)	0(2)	2(2)
C(9)	20(2)	27(3)	30(2)	-10(2)	-1(2)	0(2)
C(10)	17(2)	22(2)	36(3)	-5(2)	1(2)	-3(2)
C(11)	26(2)	20(3)	27(2)	1(2)	6(2)	1(2)
C(12)	23(2)	22(3)	15(2)	0(2)	2(2)	2(2)
C(15)	30(2)	23(3)	23(2)	-2(2)	-1(2)	-5(2)
C(16)	29(3)	31(3)	31(3)	0(2)	-3(2)	-3(2)
C(17)	19(2)	16(2)	18(2)	-3(2)	-2(2)	-2(2)
C(18)	32(2)	24(3)	24(2)	-3(2)	1(2)	-1(2)
C(21)	28(2)	26(3)	29(2)	1(2)	-3(2)	2(2)
O(13)	41(2)	13(2)	30(2)	1(1)	-6(2)	-4(2)
O(14)	30(2)	18(2)	24(2)	1(1)	-8(1)	-3(2)
S(19A)	49(2)	24(2)	29(2)	2(2)	-14(2)	2(1)
C(20A)	49(2)	24(2)	29(2)	2(2)	-14(2)	2(1)
S(19B)	46(2)	29(2)	26(2)	5(2)	-3(2)	-7(2)
C(20B)	46(2)	29(2)	26(2)	5(2)	-3(2)	-7(2)
N(1)	29(2)	13(2)	22(2)	1(2)	-2(2)	-2(2)

Table 5.

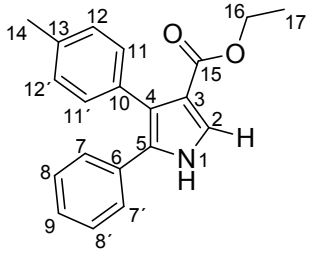
Hydrogen bonds for **4d** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...S(19A)#1	0.95	2.83	3.779(7)	173.3
C(2)-H(2)...S(19B)#1	0.95	2.98	3.860(8)	153.9
C(21)-H(21)...O(13)#2	0.95	2.39	3.335(5)	172.8
C(20A)-H(20A)...S(19A)#3	0.95	2.95	3.77(2)	145.0
N(1)-H(1F)...O(13)#1	0.87(4)	2.00(4)	2.813(5)	156(4)

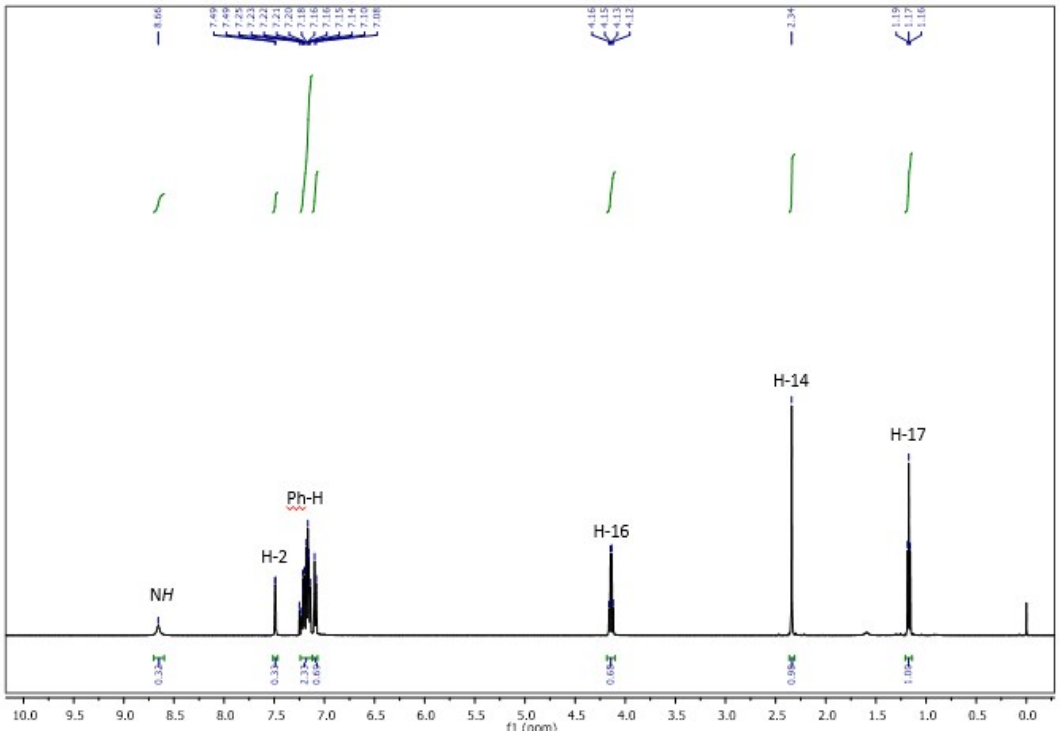
Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+3/2 #2 x+1,y,z #3 x-1/2,-y+1/2,-z+2

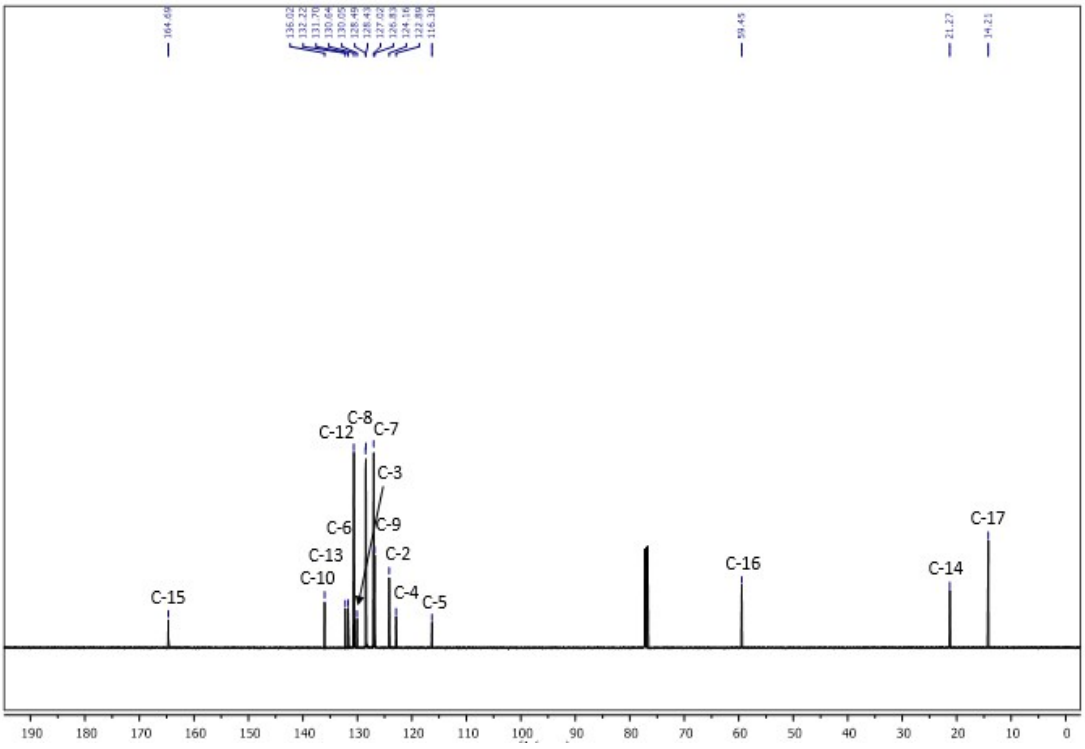
Compound 4e



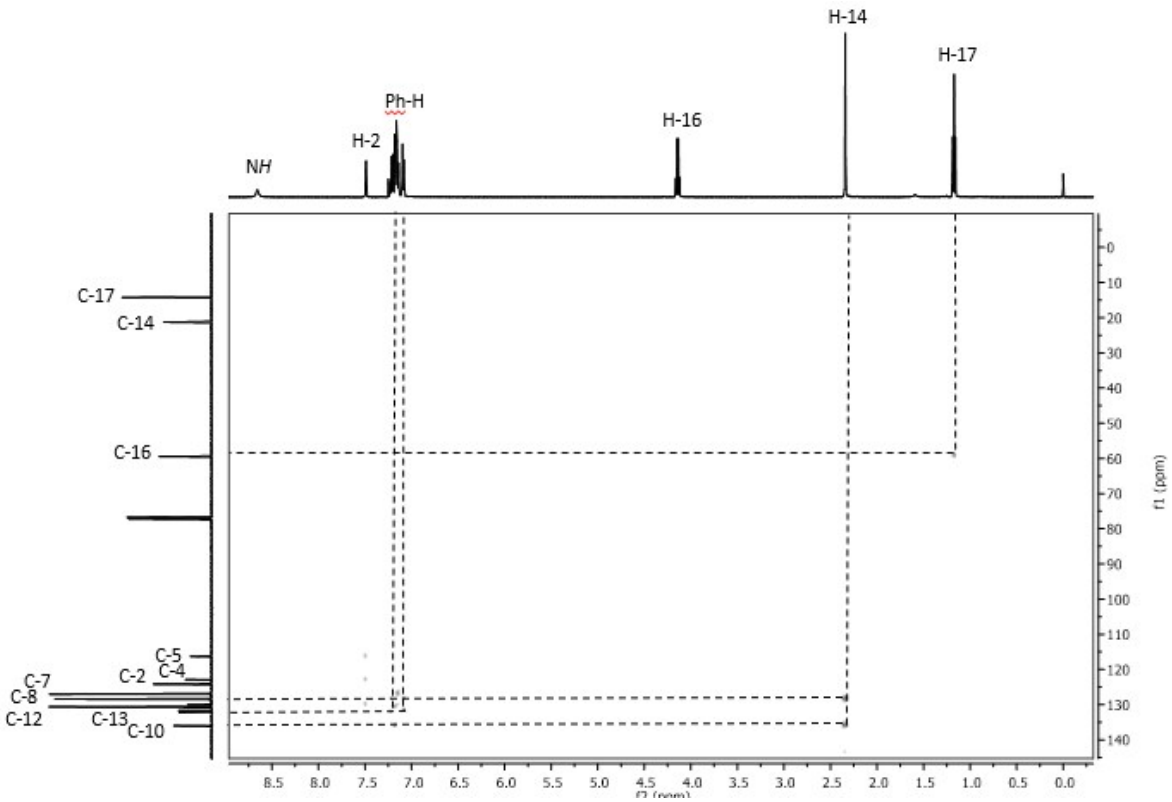
Ethyl 5-phenyl-4-(4-tolyl)-1*H*-pyrrole-3-carboxylate (4e). Yield: 80%; colorless crystals; mp: 206-208 °C. IR (ν cm^{-1}) 3335 (N-H), 1693 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.66 (s, 1H, H-1), 7.49 (d, $^{3}J_{H-H}$ = 4.0 Hz, 1H, H-2), 7.25-7.14 (m, 7H, C*H* Ar), 7.09 (d, $^{3}J_{H-H}$ = 10.0 Hz, 2H, H-11,11´), 4.13 (q, $^{3}J_{H-H}$ = 7.5 Hz, 2H, H-16), 2.34 (s, 3H, H-14), 1.14 (t, $^{3}J_{H-H}$ = 7.5 Hz, 3H, H-17). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.6 (C-15), 136.0 (C-10), 132.2 (C-13), 131.7 (C-6), 130.6 (C-12), 130.0 (C-3), 128.4 (C-8), 127.0 (C-7), 126.8 (C-9), 124.1 (C-2), 122.8 (C-4), 116.3 (C-5), 59.4 (C-16), 21.2 (C-14), 14.2 (C-17). HRMS (ESI^{+}): m/z calcd for $C_{20}H_{19}NO_2$ $[M+Na]^{+}$ 328.1313, found 328.1319.



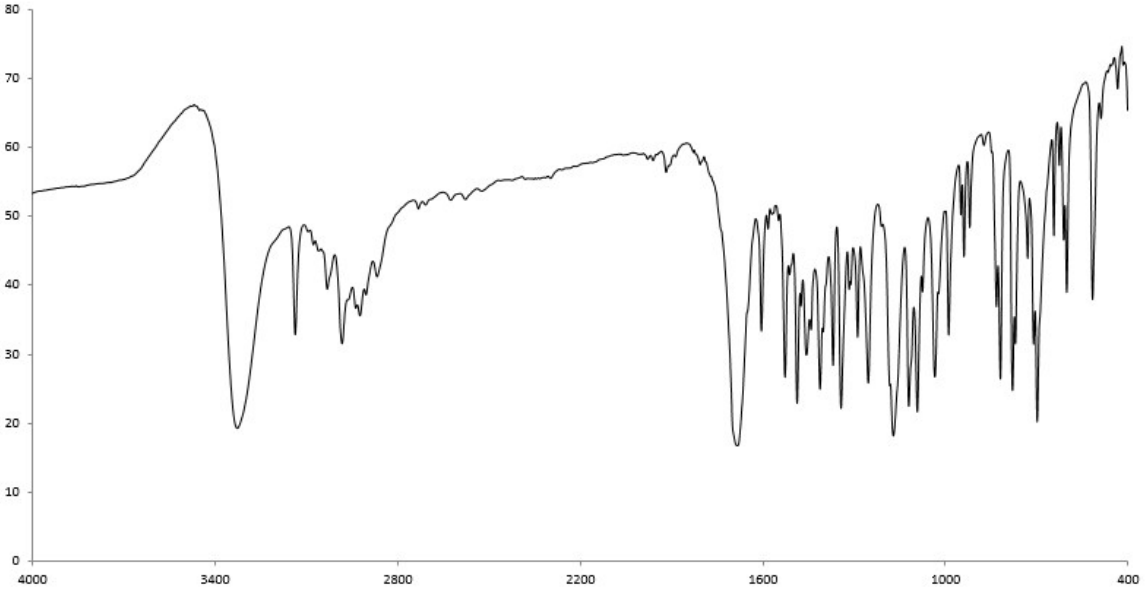
4e NMR ^{1}H ($CDCl_3$, 500 MHz).



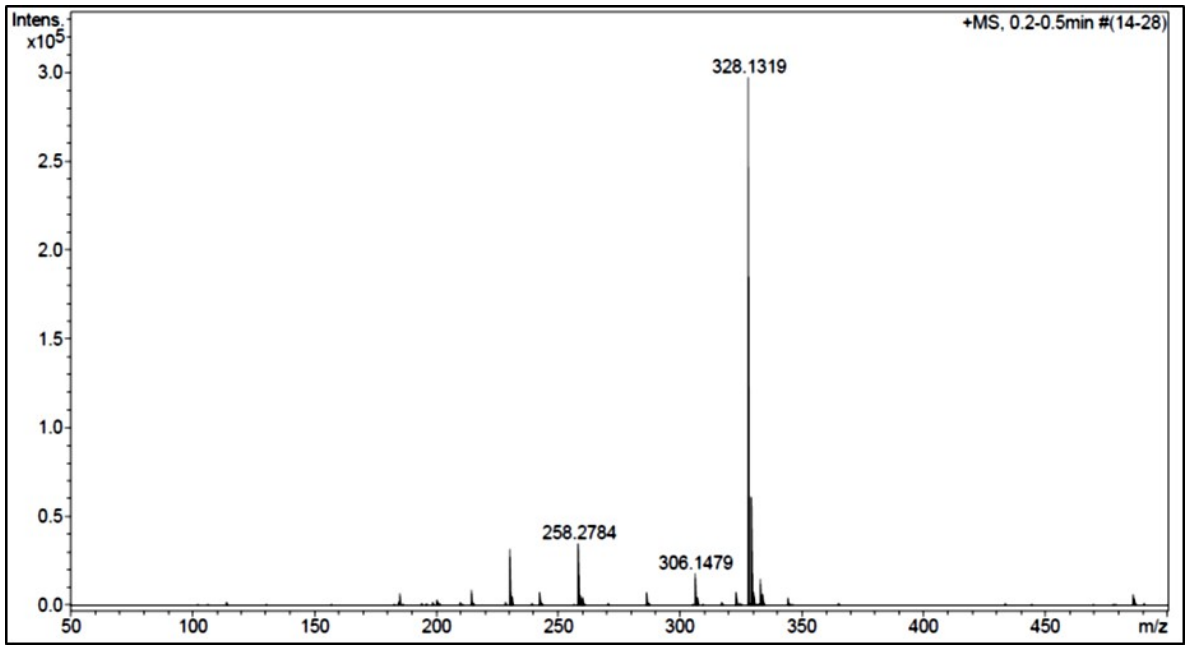
4e NMR ^{13}C ($CDCl_3$, 125 MHz).



4e NMR-HSQC ($CDCl_3$, 500 MHz).

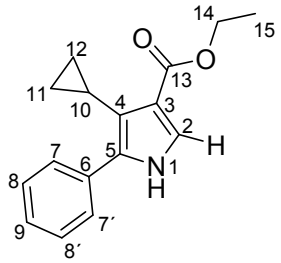


4e IR-KBr pellet.



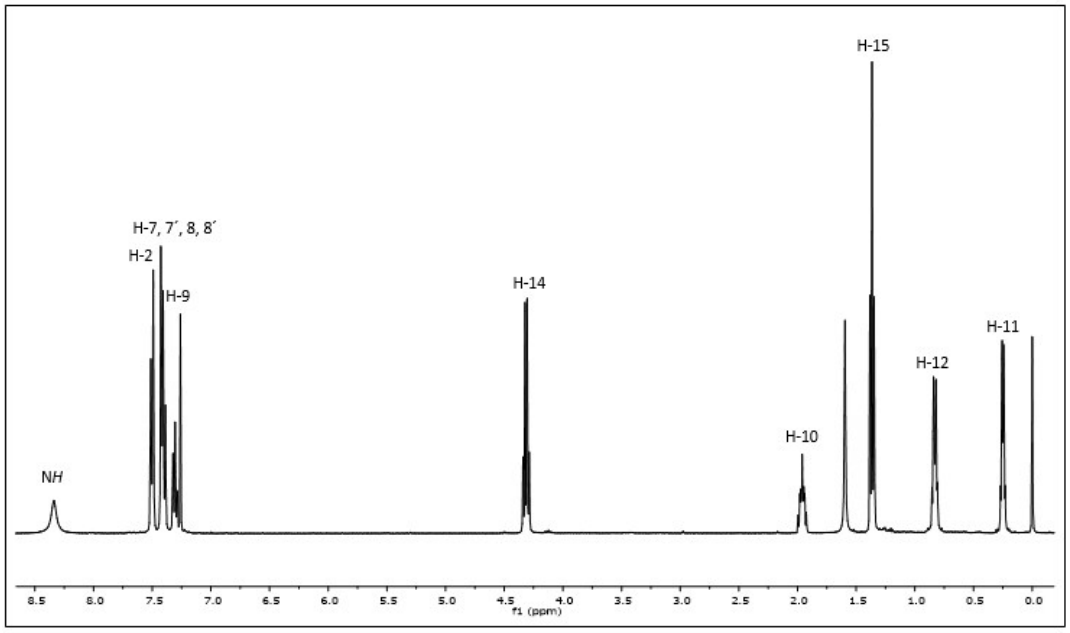
4e HRMS.

Compound 4f.

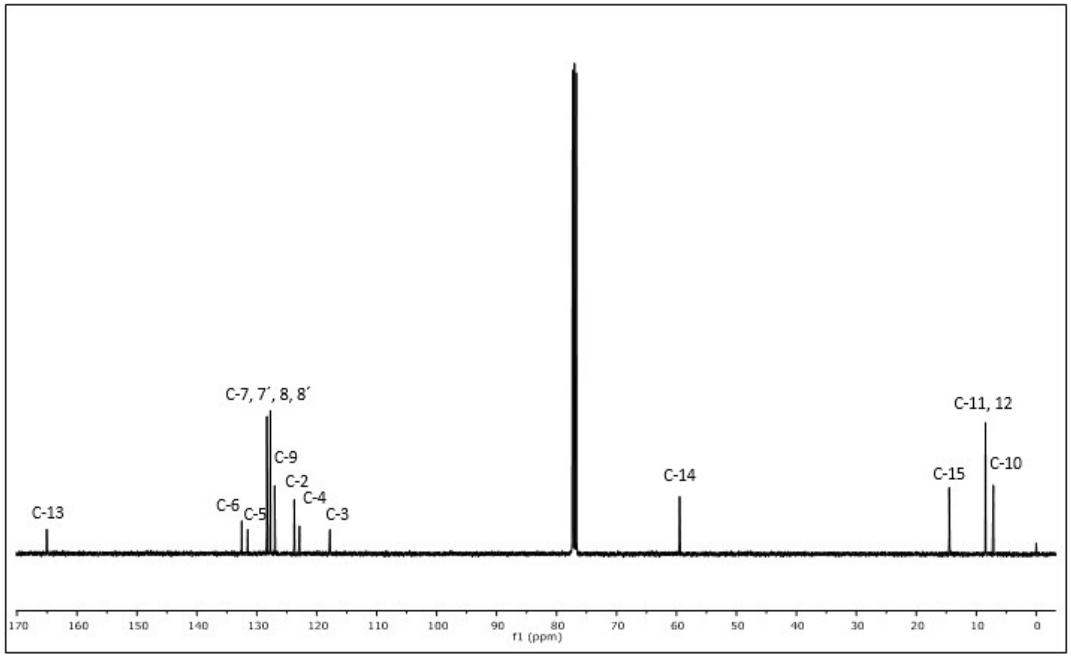


Ethyl 4-cyclopropyl-5-phenyl-1*H*-pyrrole-3-carboxylate (4f).

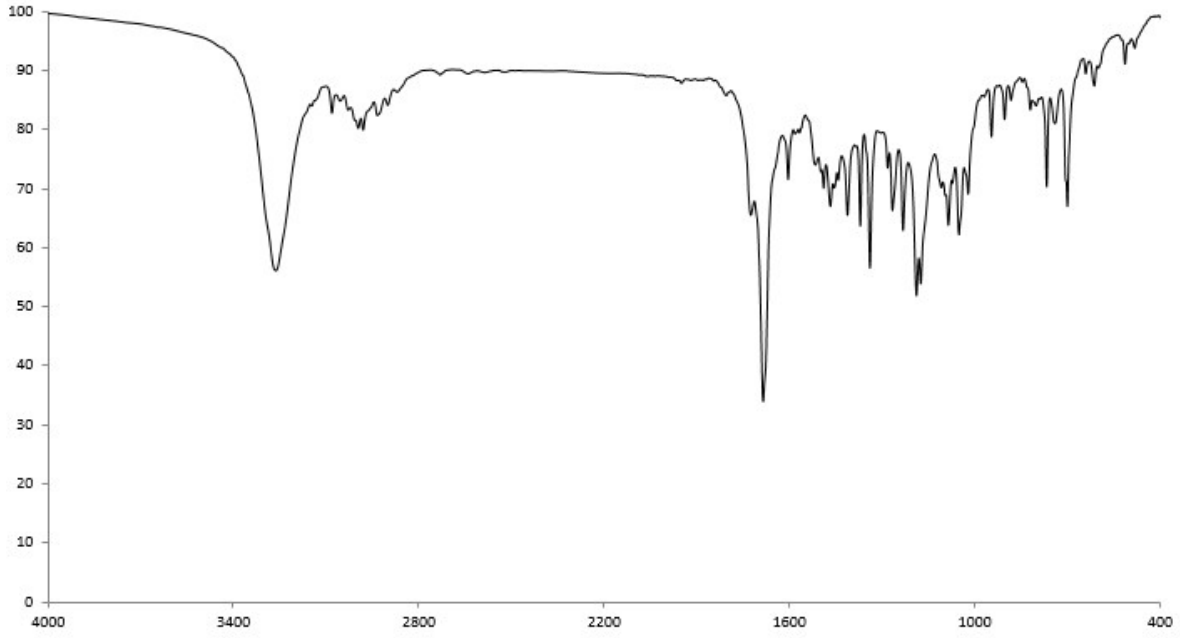
Yield: 72%; white solid; mp: 114-115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (s, 1H, H-1), 7.50 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, H-7,7´), 7.42 (d, $^{3}J_{H\text{-}H}$ = 3.0 Hz, 1H, H-2), 7.40 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, H-8,8´), 7.30 (t, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, H-9), 4.31 (q, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 2H, H-11), 1.96 (q, $^{3}J_{H\text{-}H}$ = 5.6 Hz, 1H, H-10), 1.37 (t, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 3H, H-15), 0.82 (q, $^{3}J_{H\text{-}H}$ = 5.6 Hz, 2H, H-11), 0.24 (q, $^{3}J_{H\text{-}H}$ = 5.6 Hz, H-12). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0 (C-13), 132.5 (C-6), 131.5 (C-5), 128.2 (C-7), 127.3 (C-8), 126.5 (C-9), 123.8 (C-2) 122.9 (C-4), 117.8 (C-3), 59.5 (C-14), 14.5 (C-15), 8.45 (C-11,12), 7.21 (C-10).



4f NMR ^{1}H ($CDCl_3$, 500 MHz).

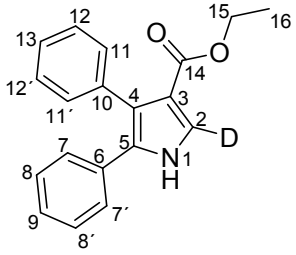


4f NMR ^{13}C ($CDCl_3$, 125 MHz).

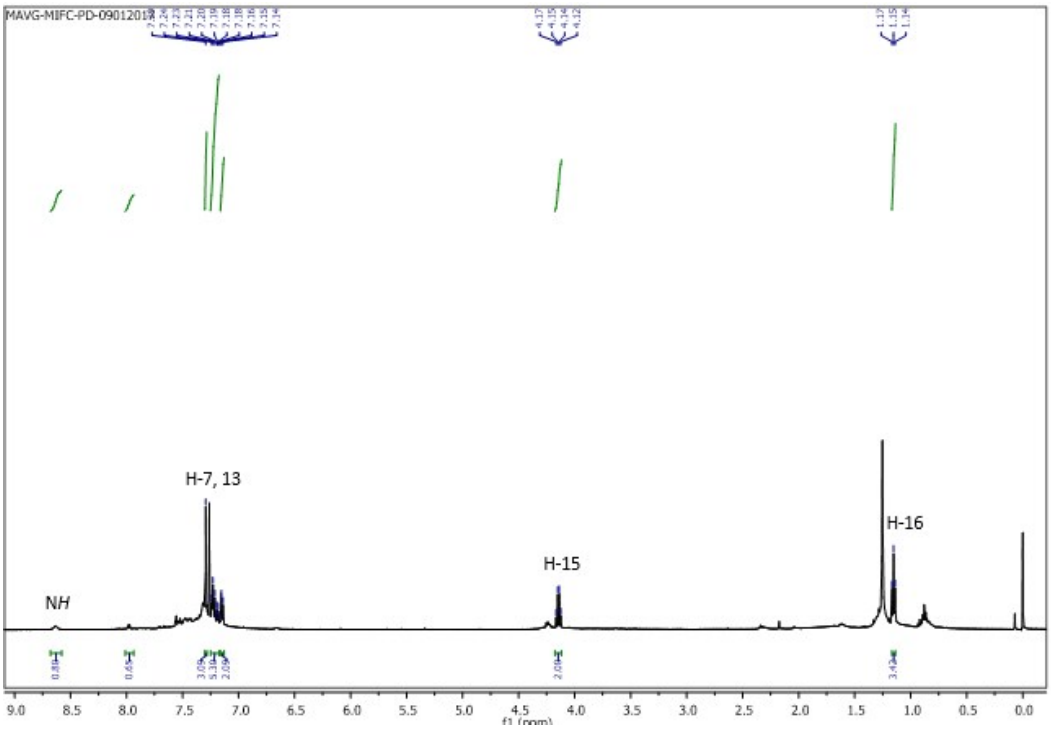


4f IR-KBr pellet.

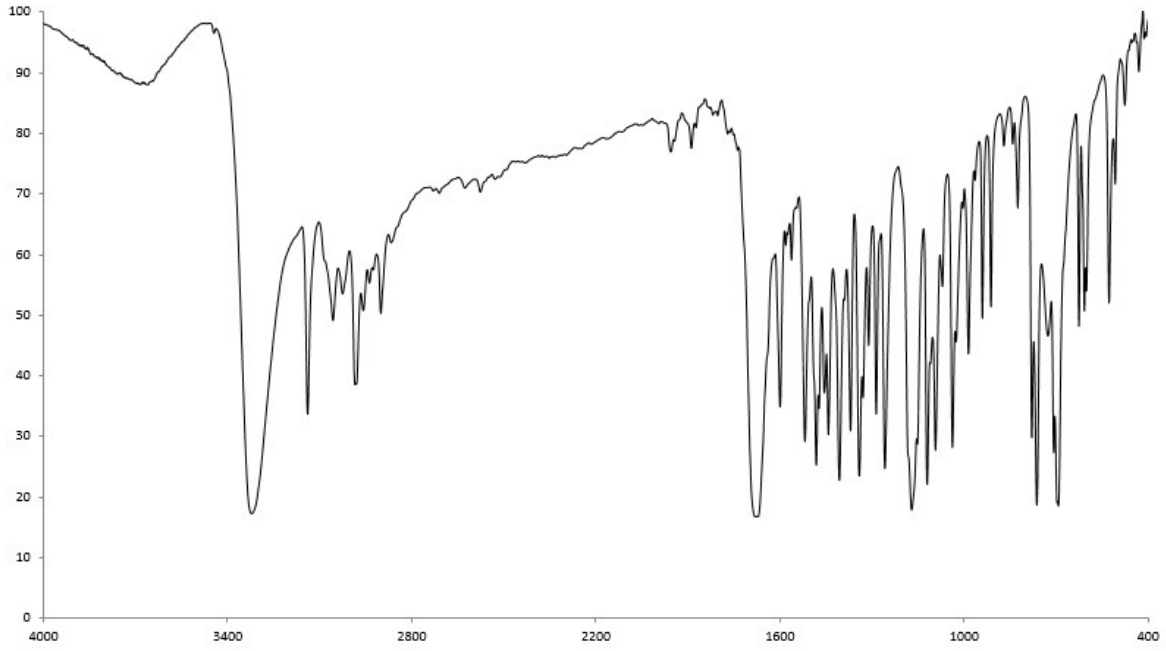
Compound 4g



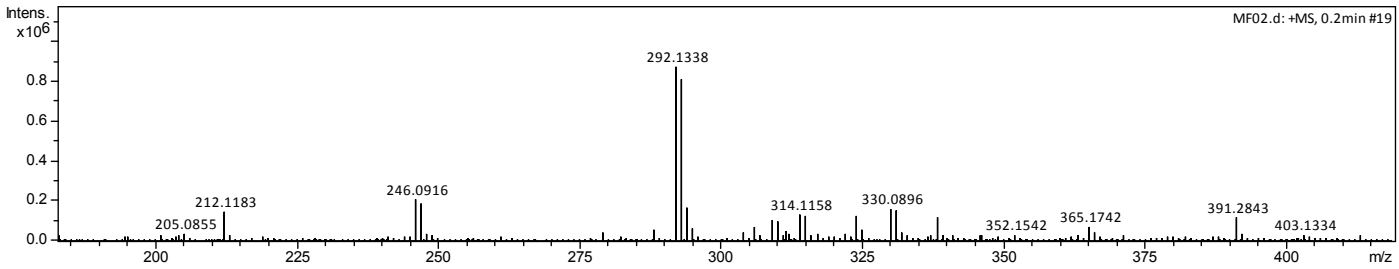
Ethyl 4,5-diphenyl-1*H*-pyrrole-3-carboxylate-2-*d* (4g). Yield: 80%; colorless crystals; mp: 202-204 °C. IR (ν cm^{-1}) 3327 (N-H), 1685 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.52 (s, 1H, H-1), 7.25-7-14 (m, 10H, H-1, Ph-*H*), 4.15 (q, $^{3}J_{H-H}$ = 5.0 Hz, 2H, H-15), 1.15 (t, $^{3}J_{H-H}$ = 5.0 Hz, 3H, H-16). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.7 (C-14), 134.9 (C-10), 132.0 (C-6), 130.8 (C-8), 130.1 (C-12), 128.5 (C-9), 127.6 (C-7), 127.0 (C-13) (C-11), 126.9 (C-2), 126.5 (C-4), 124.2 (C-5), 122.8 (C-3), 116.4, 59.5 (C-15), 14.1 (C-16). HRMS (ESI^{+}): m/z calcd for $C_{19}H_{16}DNO_2$ 292.1322, found 292.1338.



4g NMR ^{1}H ($CDCl_3$, 500 MHz).

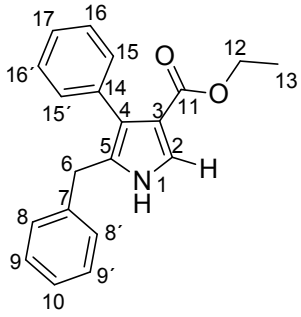


4g IR-KBr pellet.

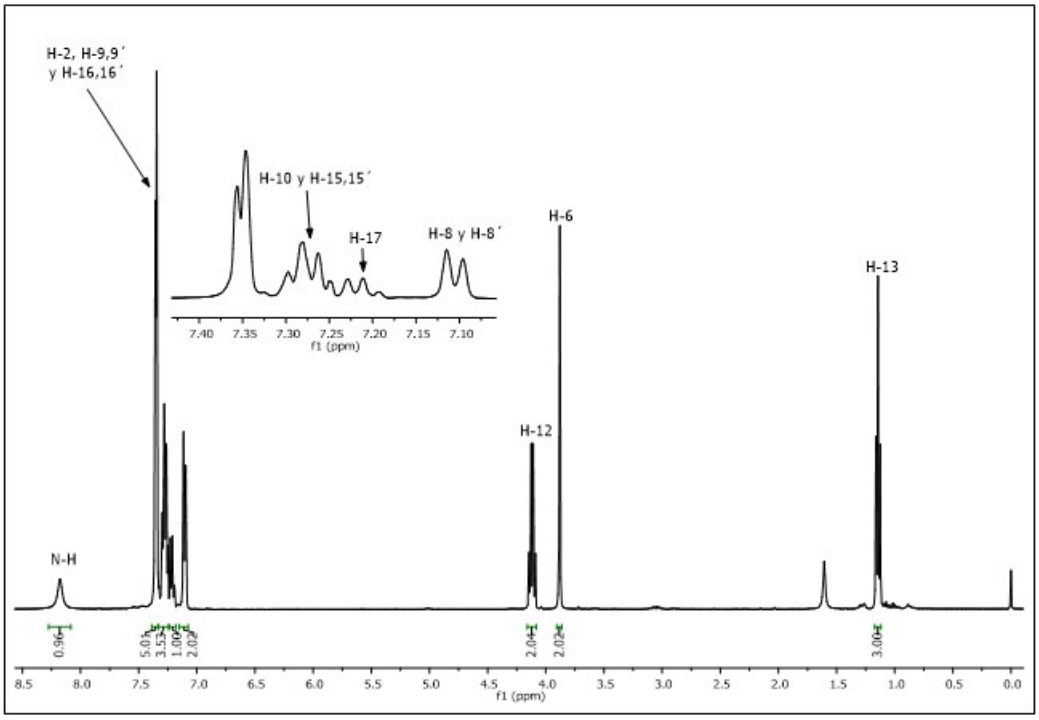


4g HRMS.

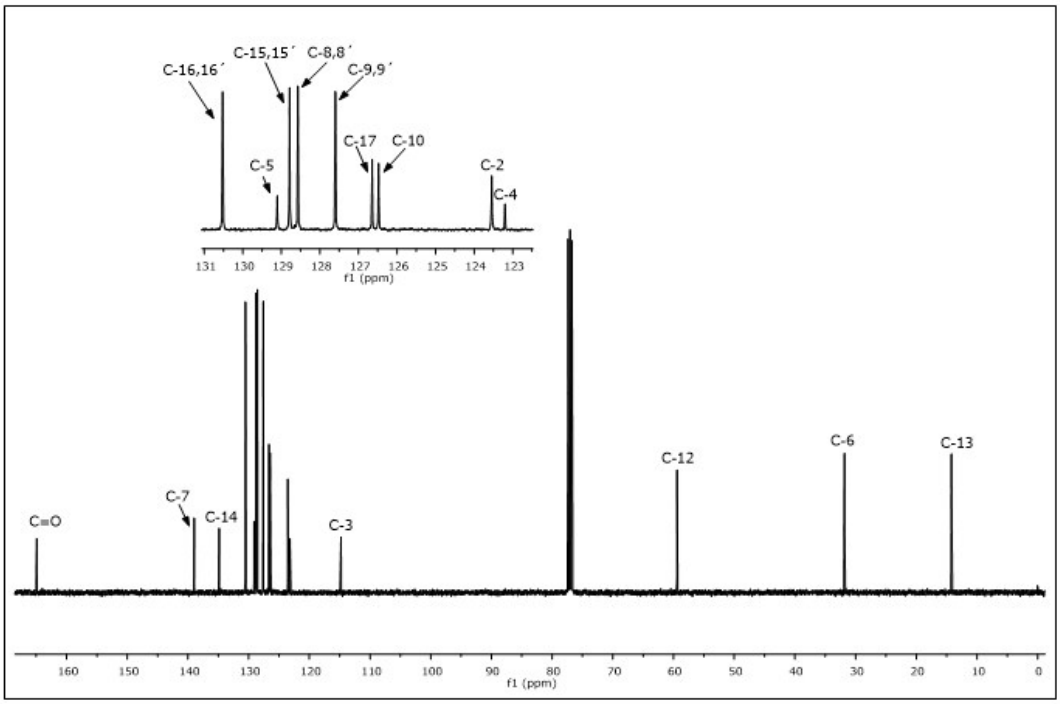
Compound 4h



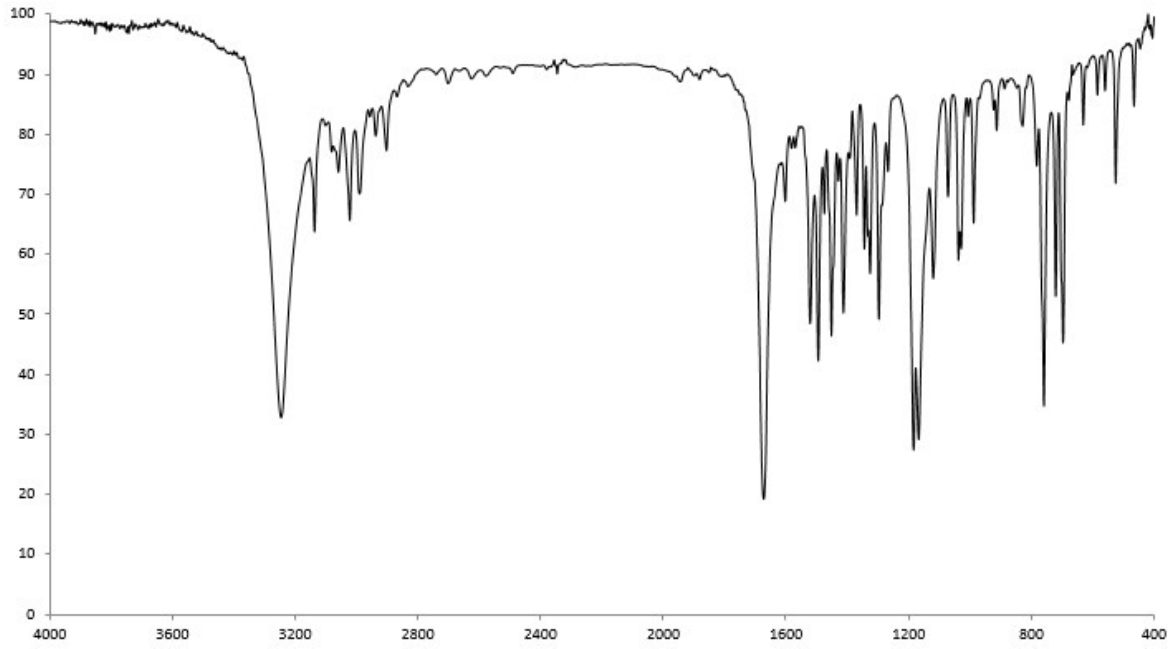
Ethyl 5-benzyl-4-phenyl-1*H*-pyrrole-3-carboxylate (4h) CCDC 1912569. Yield: 50%; white solid; mp: 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 3H, H-13), 3.9 (s, 2H, H-6) 4.14 (c, $^{3}J_{H\text{-}H}$ = 7.1 Hz 2H, H-12), 8.18 (s, 1H, H-1), 7. 20-737 (m, 5H, H-2, H-9,9′ and H-16,16′), 7.17-7.30 (m, 4H, H-10, H-15,15′, H-17),7.12 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, H-8,8′) ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.8 (C-11), 139.0 (C-7), 134.9 (C-14), 130.5 (C-16,16′) 129.1 (C-5), 128.8 (C-15,15′), 128.5 (C-8,8′), 127.6 (C-9,9′), 126.6 (C-17), 126.4 (C-10), 123.5 (C-2), 123.2 (C-4), 114.8 (C-3), 59.3 (C-12), 14.2 (C-13). HRMS (ESI^{+}): m/z calcd for $C_{20}H_{19}NO_2$ $[M+Na]^+$ 328.1313, found 328.1319.



4h NMR ^{1}H ($CDCl_3$, 500 MHz).

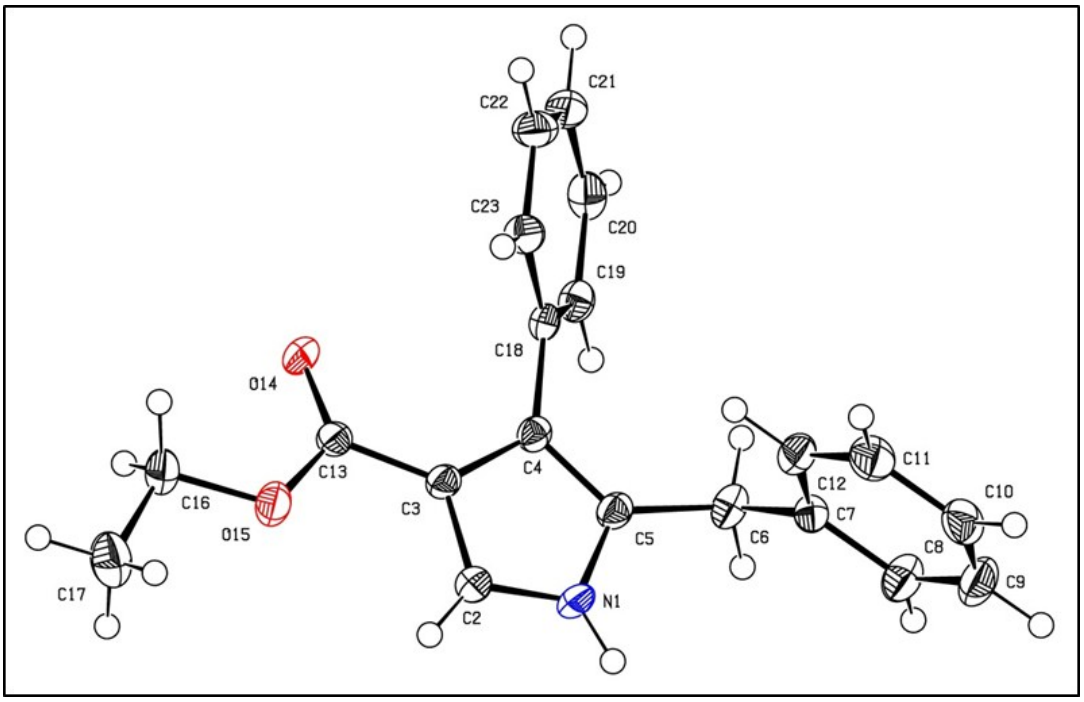


4h NMR ^{13}C ($CDCl_3$, 125 MHz).



4h IR-KBr pellet.

4h HRMS.



4h X-Ray Data CCDC 1912569

Table 1. Crystal data and structure refinement for **4h**.

Identification code	**4h**	
Empirical formula	C20 H19 N O2	
Formula weight	305.36	
Temperature	130(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 6.1237(3) Å	α= 90°.
	b = 21.7422(10) Å	β= 96.668(4)°.
	c = 12.4311(5) Å	γ = 90°.
Volume	1643.91(13) $Å^3$	
Z	4	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	648	
Theta range for data collection	3.431 to 26.354°.	
Index ranges	-7<=h<=7, -27<=k<=22, -14<=l<=15	
Reflections collected	11826	
Independent reflections	3359 [R(int) = 0.0249]	

Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3359 / 0 / 209
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0916
R indices (all data)	R1 = 0.0466, wR2 = 0.0965
Largest diff. peak and hole	0.213 and -0.193 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4h**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	4145(2)	2499(1)	4496(1)	25(1)
C(3)	4387(2)	2267(1)	3486(1)	21(1)
C(4)	2714(2)	1808(1)	3242(1)	20(1)
C(5)	1530(2)	1788(1)	4115(1)	22(1)
C(6)	-302(2)	1377(1)	4369(1)	26(1)
C(7)	341(2)	950(1)	5320(1)	23(1)
C(8)	-1054(2)	852(1)	6103(1)	32(1)
C(9)	-482(3)	446(1)	6952(1)	36(1)
C(10)	1502(2)	140(1)	7031(1)	32(1)
C(11)	2911(2)	235(1)	6261(1)	33(1)
C(12)	2331(2)	637(1)	5409(1)	28(1)
C(13)	5937(2)	2512(1)	2790(1)	21(1)
C(16)	8951(2)	3196(1)	2722(1)	30(1)
C(17)	10222(3)	3637(1)	3481(1)	39(1)
C(18)	2391(2)	1400(1)	2284(1)	20(1)
C(19)	358(2)	1351(1)	1653(1)	24(1)
C(20)	82(2)	959(1)	768(1)	28(1)
C(21)	1819(2)	607(1)	496(1)	31(1)
C(22)	3841(2)	649(1)	1118(1)	30(1)
C(23)	4126(2)	1040(1)	2001(1)	25(1)
N(1)	2429(2)	2210(1)	4864(1)	26(1)
O(14)	5975(2)	2383(1)	1841(1)	29(1)
O(15)	7336(2)	2911(1)	3323(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **4h**.

C(2)-N(1)	1.3487(17)
C(2)-C(3)	1.3769(17)
C(2)-H(2)	0.9500
C(3)-C(4)	1.4375(17)
C(3)-C(13)	1.4570(16)
C(4)-C(5)	1.3744(17)
C(4)-C(18)	1.4800(17)
C(5)-N(1)	1.3761(17)
C(5)-C(6)	1.4960(17)
C(6)-C(7)	1.5189(18)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.3840(18)
C(7)-C(12)	1.3881(19)
C(8)-C(9)	1.390(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.378(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.377(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.387(2)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-O(14)	1.2153(15)
C(13)-O(15)	1.3387(16)
C(16)-O(15)	1.4466(15)
C(16)-C(17)	1.499(2)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.3960(17)

C(18)-C(23)	1.3960(17)
C(19)-C(20)	1.3879(18)
C(19)-H(19)	0.9500
C(20)-C(21)	1.383(2)
C(20)-H(20)	0.9500
C(21)-C(22)	1.384(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.3836(18)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
N(1)-H(1)	0.8800

N(1)-C(2)-C(3)	108.09(12)
N(1)-C(2)-H(2)	126.0
C(3)-C(2)-H(2)	126.0
C(2)-C(3)-C(4)	107.23(11)
C(2)-C(3)-C(13)	123.69(12)
C(4)-C(3)-C(13)	128.78(11)
C(5)-C(4)-C(3)	106.52(11)
C(5)-C(4)-C(18)	125.64(11)
C(3)-C(4)-C(18)	127.71(10)
C(4)-C(5)-N(1)	107.87(11)
C(4)-C(5)-C(6)	131.52(12)
N(1)-C(5)-C(6)	120.43(11)
C(5)-C(6)-C(7)	113.35(10)
C(5)-C(6)-H(6A)	108.9
C(7)-C(6)-H(6A)	108.9
C(5)-C(6)-H(6B)	108.9
C(7)-C(6)-H(6B)	108.9
H(6A)-C(6)-H(6B)	107.7
C(8)-C(7)-C(12)	118.47(12)
C(8)-C(7)-C(6)	121.02(12)
C(12)-C(7)-C(6)	120.50(11)
C(7)-C(8)-C(9)	120.62(13)
C(7)-C(8)-H(8)	119.7
C(9)-C(8)-H(8)	119.7

C(10)-C(9)-C(8)	120.23(13)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(11)-C(10)-C(9)	119.75(13)
C(11)-C(10)-H(10)	120.1
C(9)-C(10)-H(10)	120.1
C(10)-C(11)-C(12)	119.98(13)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-C(7)	120.96(12)
C(11)-C(12)-H(12)	119.5
C(7)-C(12)-H(12)	119.5
O(14)-C(13)-O(15)	123.09(11)
O(14)-C(13)-C(3)	125.38(12)
O(15)-C(13)-C(3)	111.52(10)
O(15)-C(16)-C(17)	106.56(11)
O(15)-C(16)-H(16A)	110.4
C(17)-C(16)-H(16A)	110.4
O(15)-C(16)-H(16B)	110.4
C(17)-C(16)-H(16B)	110.4
H(16A)-C(16)-H(16B)	108.6
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-C(23)	118.10(11)
C(19)-C(18)-C(4)	121.62(11)
C(23)-C(18)-C(4)	120.26(11)
C(20)-C(19)-C(18)	120.71(12)
C(20)-C(19)-H(19)	119.6
C(18)-C(19)-H(19)	119.6
C(21)-C(20)-C(19)	120.46(12)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8

C(20)-C(21)-C(22)	119.40(12)
C(20)-C(21)-H(21)	120.3
C(22)-C(21)-H(21)	120.3
C(23)-C(22)-C(21)	120.36(12)
C(23)-C(22)-H(22)	119.8
C(21)-C(22)-H(22)	119.8
C(22)-C(23)-C(18)	120.97(12)
C(22)-C(23)-H(23)	119.5
C(18)-C(23)-H(23)	119.5
C(2)-N(1)-C(5)	110.29(10)
C(2)-N(1)-H(1)	124.9
C(5)-N(1)-H(1)	124.9
C(13)-O(15)-C(16)	117.32(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **4h**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	33(1)	23(1)	21(1)	-1(1)	8(1)	-3(1)
C(3)	25(1)	20(1)	18(1)	2(1)	5(1)	2(1)
C(4)	22(1)	20(1)	18(1)	3(1)	4(1)	3(1)
C(5)	25(1)	22(1)	20(1)	3(1)	6(1)	4(1)
C(6)	23(1)	33(1)	25(1)	5(1)	7(1)	0(1)
C(7)	25(1)	22(1)	22(1)	0(1)	5(1)	-4(1)
C(8)	28(1)	37(1)	32(1)	7(1)	11(1)	4(1)
C(9)	42(1)	40(1)	29(1)	8(1)	15(1)	-2(1)
C(10)	44(1)	24(1)	28(1)	6(1)	2(1)	0(1)
C(11)	34(1)	26(1)	39(1)	3(1)	5(1)	6(1)
C(12)	28(1)	29(1)	30(1)	2(1)	11(1)	0(1)
C(13)	25(1)	18(1)	21(1)	2(1)	5(1)	3(1)
C(16)	29(1)	28(1)	33(1)	4(1)	10(1)	-6(1)
C(17)	36(1)	37(1)	42(1)	5(1)	2(1)	-12(1)
C(18)	23(1)	20(1)	17(1)	4(1)	5(1)	-1(1)

C(19)	23(1)	26(1)	23(1)	5(1)	4(1)	1(1)
C(20)	29(1)	32(1)	24(1)	4(1)	-3(1)	-8(1)
C(21)	37(1)	32(1)	24(1)	-8(1)	6(1)	-9(1)
C(22)	30(1)	30(1)	32(1)	-8(1)	9(1)	1(1)
C(23)	22(1)	27(1)	25(1)	-2(1)	2(1)	-1(1)
N(1)	36(1)	26(1)	19(1)	0(1)	13(1)	1(1)
O(14)	40(1)	31(1)	20(1)	-3(1)	13(1)	-7(1)
O(15)	32(1)	34(1)	23(1)	-1(1)	7(1)	-12(1)

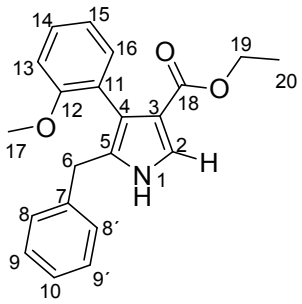
Table 5. Hydrogen bonds for **4h** [Å and

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(14)#1	0.88	1.98	2.8498(13)	168.5

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z+1/2

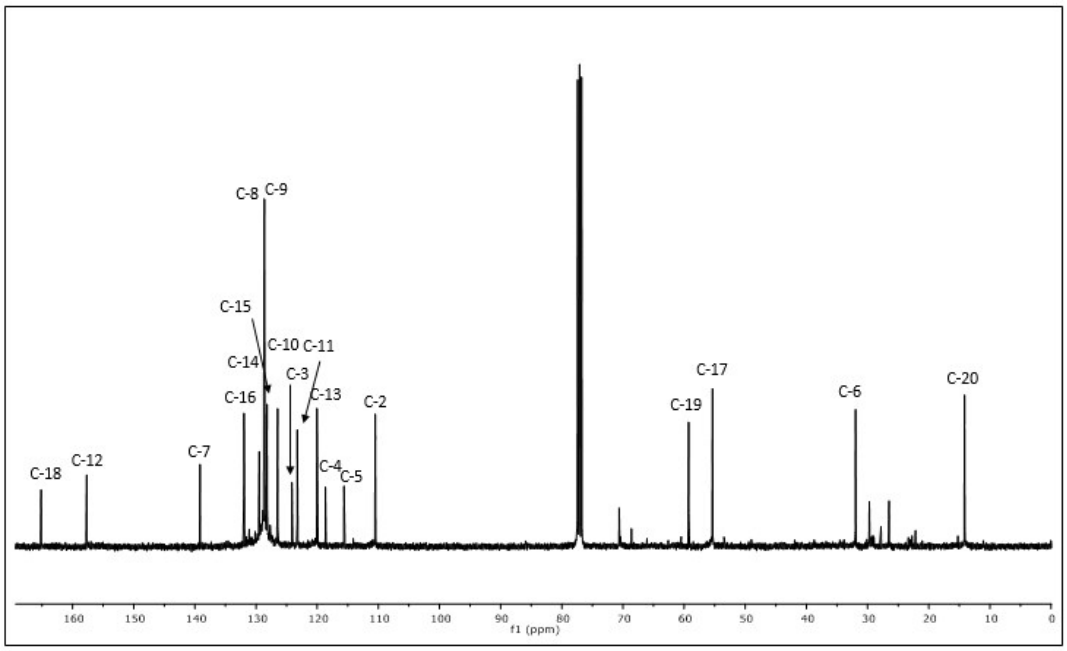
Compound 4i



Ethyl 5-benzyl-4-(2-methoxyphenyl)-1*H*-pyrrole-3-carboxylate (4i).

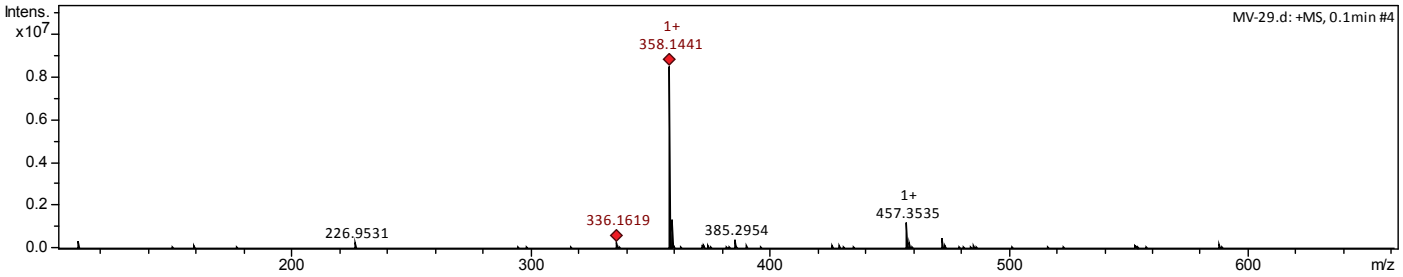
Yield: 48%; brown solid; mp: 190-192 °C. IR (ν cm^{-1}) 3304 (N-H), 1683 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 1H, 1-H), 7.38-6.93 (m, 9H, H-8,8′,9,9′,10, H-13 to H-16), 4.06 (q, $^{3}J_{H-H}$ = 7.0 Hz, 2H, H-19), 3.80 (d, $^{3}J_{H-H}$ = 5.2 Hz, 2H, H-6), 3.71 (s, 3H, H-17), 1.07 (t, $^{3}J_{H-H}$ = 7.0 3H, Hz, H-20). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1 (C-18), 157.7 (C-12), 139.1 (C-7), 129.4 (C-5), 128.7 (C-8), 128.6 (C-6), 126.4 (C-10), 124.1 (C-4), 123.2 (C-2),

118.6 (C-14), 115.6 (C-3), 59.3 (C-19), 55.3 (C-17), 32.0 (C-6), 14.0 (C-20). HRMS (ESI^+): m/z calcd for $C_{21}H_{21}NO_3$ $[M+Na]^+$ 358.1419, found 358.1441.



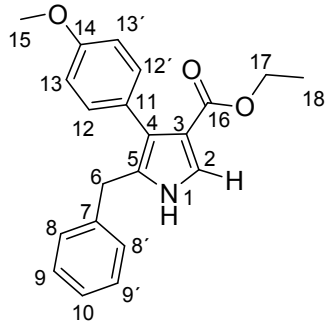
4i NMR ^{13}C ($CDCl_3$, 125 MHz).

4i IR-KBr pellet.

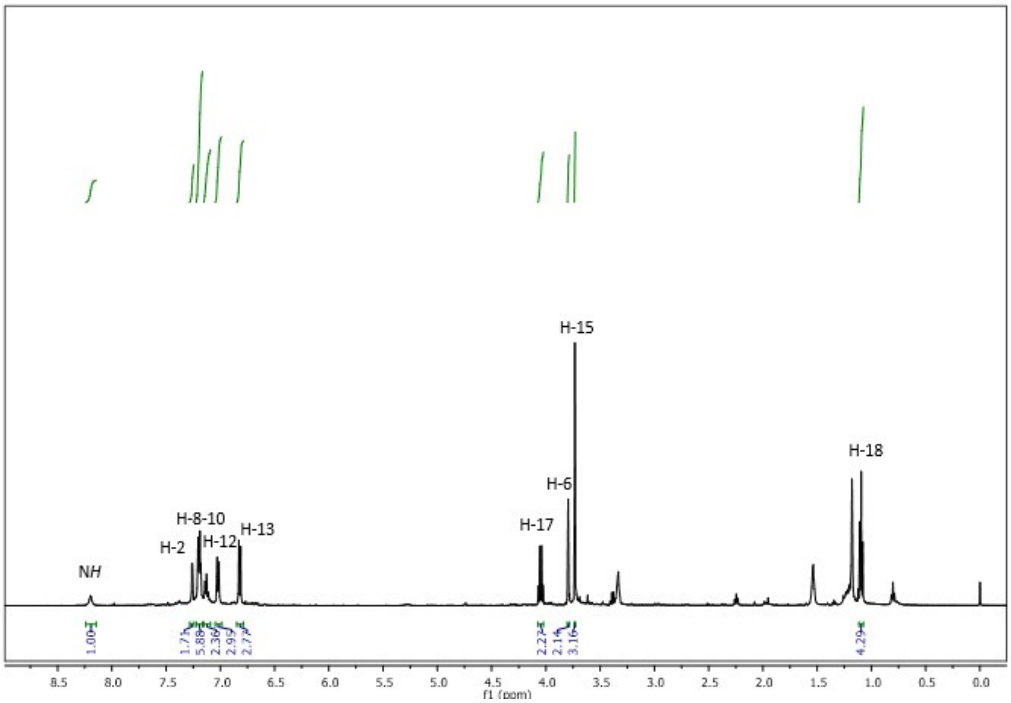


4i HRMS.

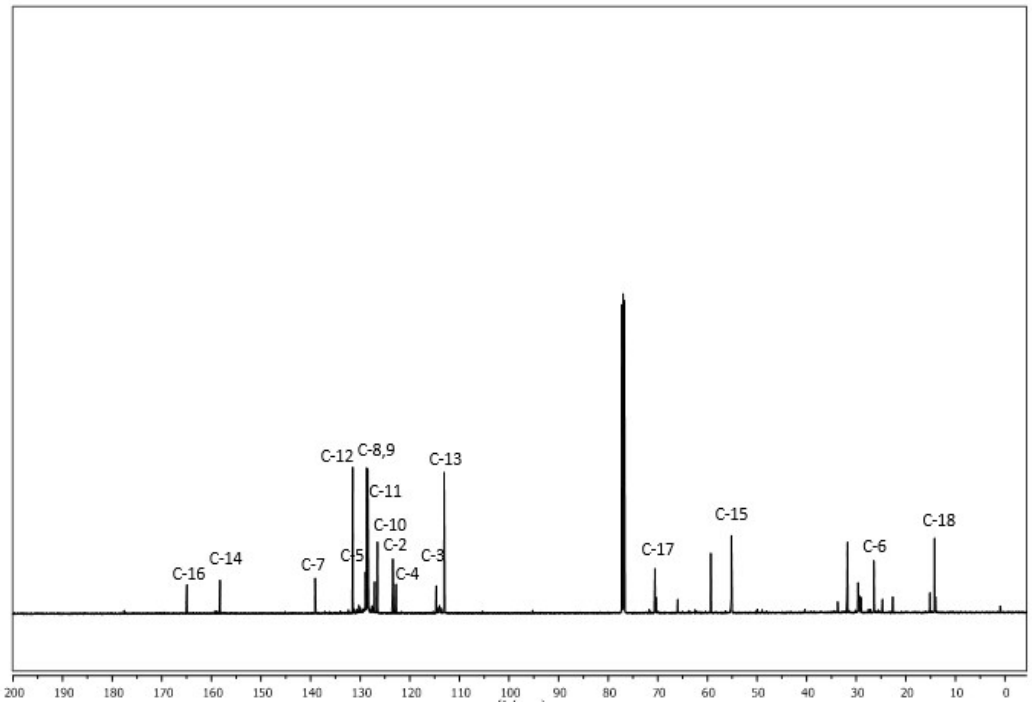
Compound 4j



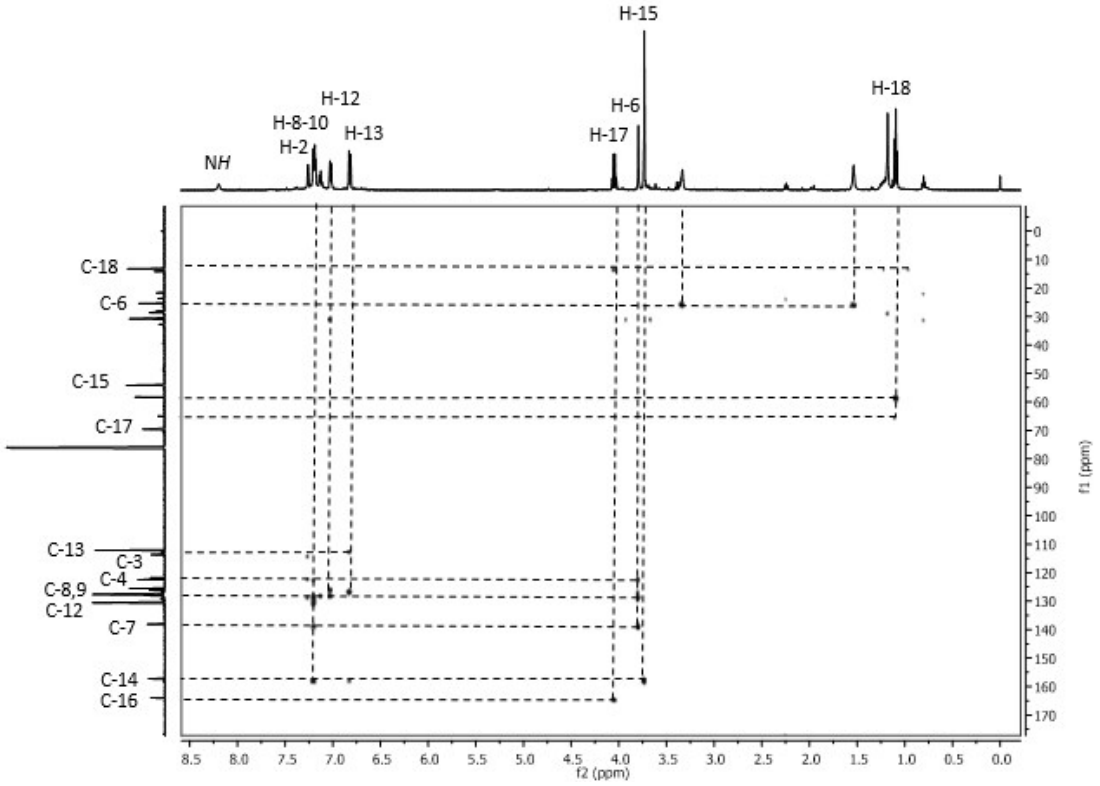
Ethyl 5-benzyl-4-(4-methoxyphenyl)-1*H*-pyrrole-3-carboxylate (4j). Yield: 32%; white solid; mp: 192-193 °C. IR (ν cm^{-1}) 3304 (N-H), 1683 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.20 (s, 1H, H-1), 7.26 (s, 1H, H-2), 7.21-7.13 (m, 5H, H-8-10), 7.03 (d, $^{3}J_{H-H}$ = 10.0 Hz, 2H, H-12), 6.83 (d, $^{3}J_{H-H}$ = 10.0 Hz, 2H, H-13), 4.05 (q, $^{3}J_{H-H}$ = 10.0 Hz, 2H, H-17), 3.79 (s, 2H, H-6), 3.73 (s, 3H, H-15), 1.09 (t, $^{3}J_{H-H}$ =10.0 Hz, 3H, H-18). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9 (C-16), 158.2 (C-14), 139.0 (C-7), 131.4 (C-12), 128.9 (C-5), 128.6 (C-8), 128.4 (C-9), 127.1 (C-11), 126.5 (C-10), 123.4 (C-2), 122.7 (C-4), 114.6 (C-3), 113.0 (C-13), 59.3 (C-17), 55.1 (C-15), 31.7 (C-6), 14.2 (C-18). HRMS (ESI^{+}): m/z calcd for $C_{21}H_{21}NO_3$ $[M+Na]^{+}$ 358.1419, found 358.1440.



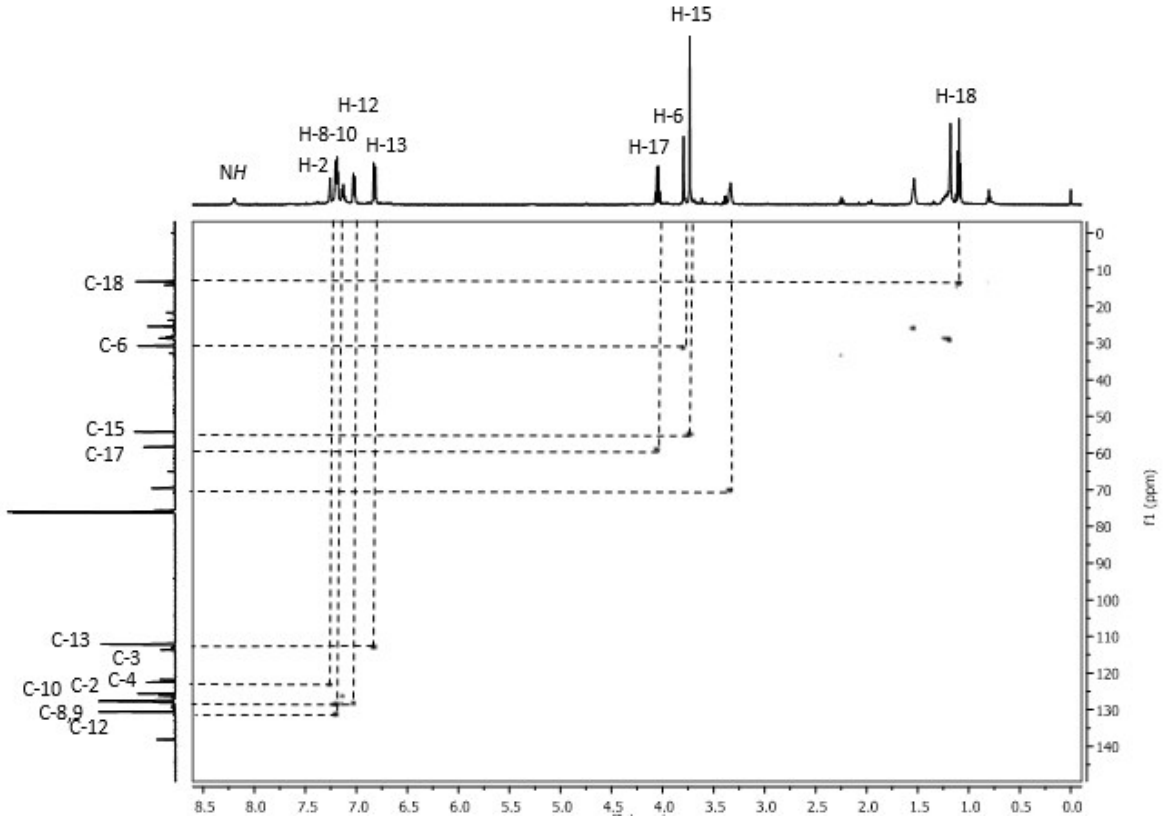
4j NMR ^{1}H ($CDCl_3$, 500 MHz).



4j NMR ^{13}C ($CDCl_3$, 125 MHz).

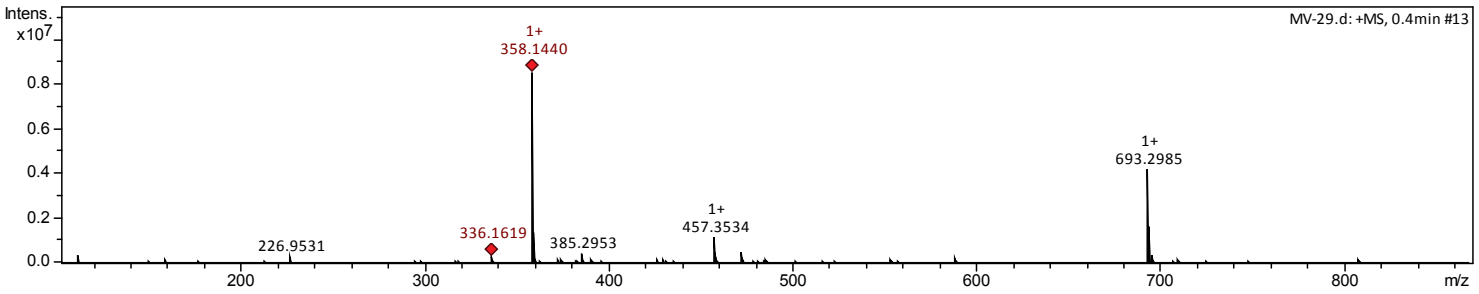


4j NMR-HMBC ($CDCl_3$, 500 MHz).



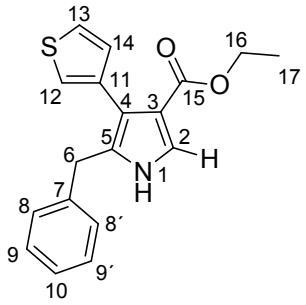
4j NMR-HSQC ($CDCl_3$, 500 MHz).

4j IR-KBr pellet.



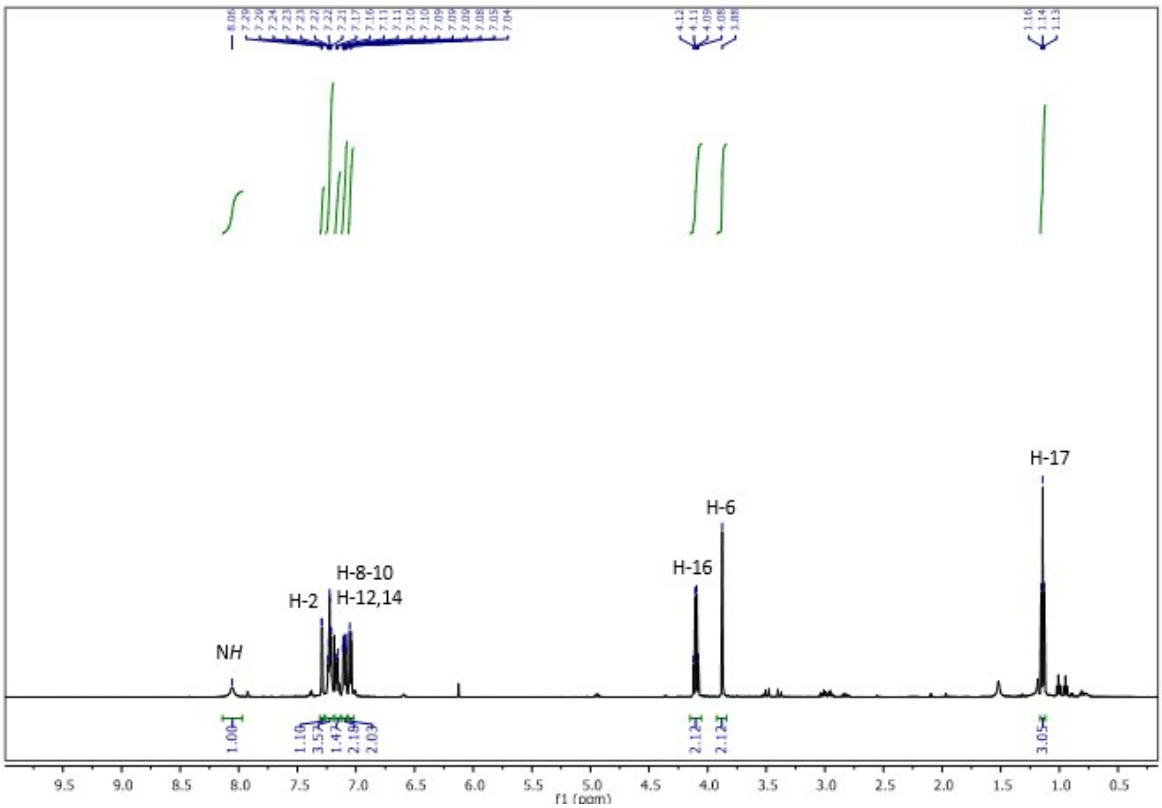
4j HRMS.

Compound 4k.

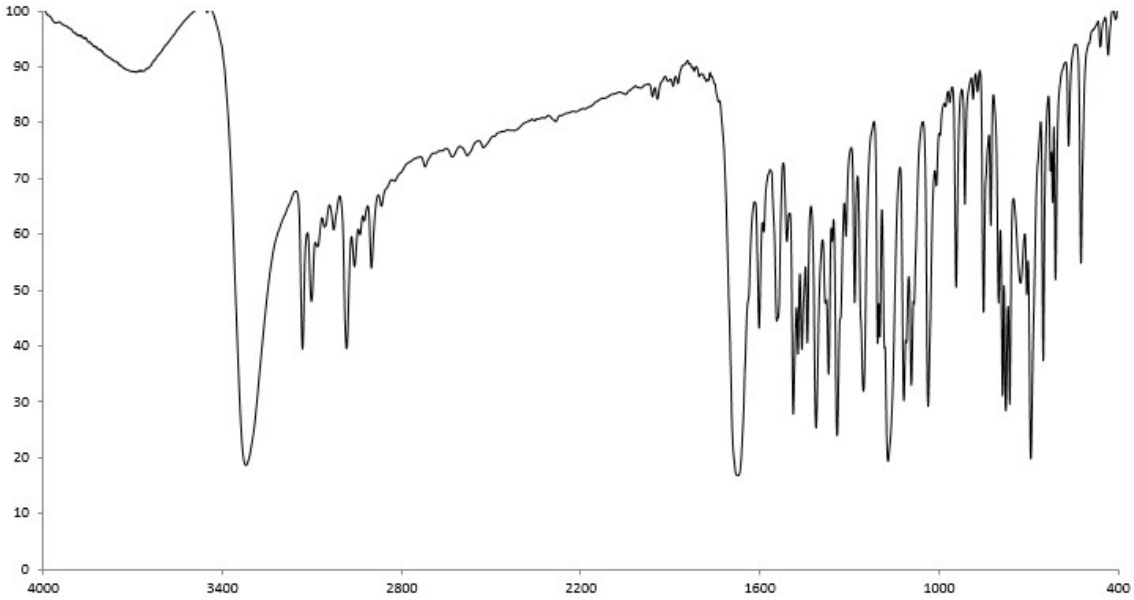


Ethyl 5-benzyl-4-(thiophen-3-yl)-1*H*-pyrrole-3-carboxylate (4k).

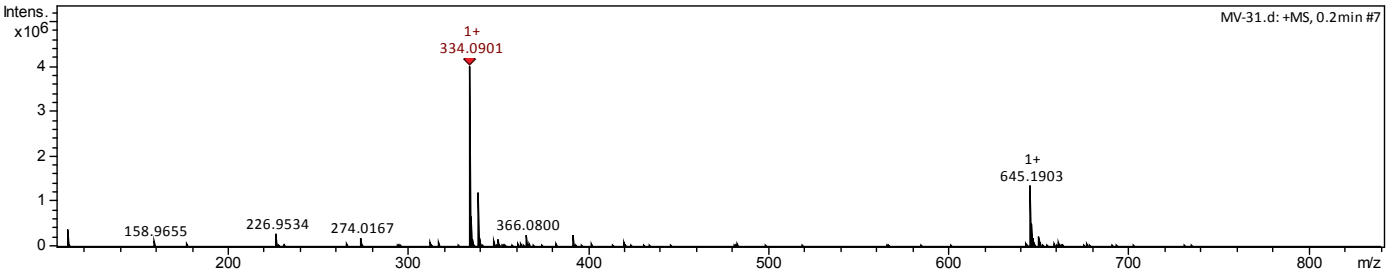
Yield: 45%; white solid; mp: 178-179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06 (s, 1H, H-1), 7.29 (s, 1H, H-2), 7.27-7.17 (m, 6H, H-7, H-8, H-9 and H-14), 7.10 (dd, $^{2}J_{H\text{-}H}$ = 1.0 Hz, 1H, H-12), 7.05 (dd, $^{2}J_{H\text{-}H}$ = 1.0 Hz, H-13), 4.10 (q, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-16), 3.88 (s, 2H, H-6), 3.79 (s, 2H, H-6), 1.14 (t, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 3H, H-17). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9 (C-15), 158.2 (C-14), 139.0 (C-7), 131.4 (C-12), 128.9 (C-5), 128.6 (C-8), 128.4 (C-9), 127.1 (C-11), 126.5 (C-10), 123.4 (C-2), 122.7 (C-4), 114.6 (C-3), 113.0 (C-13), 59.3 (C-17), 55.1 (C-15), 31.7 (C-6), 14.2 (C-17). HRMS (ESI^{+}): m/z calcd for $C_{18}H_{17}NO_2S$ $[M+Na]^{+}$ 334.0878, found 334.0901.



4k NMR ^{1}H ($CDCl_3$, 500 MHz).

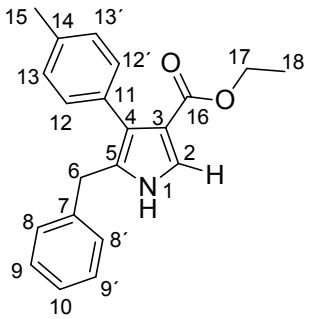


4k IR-KBr pellet.

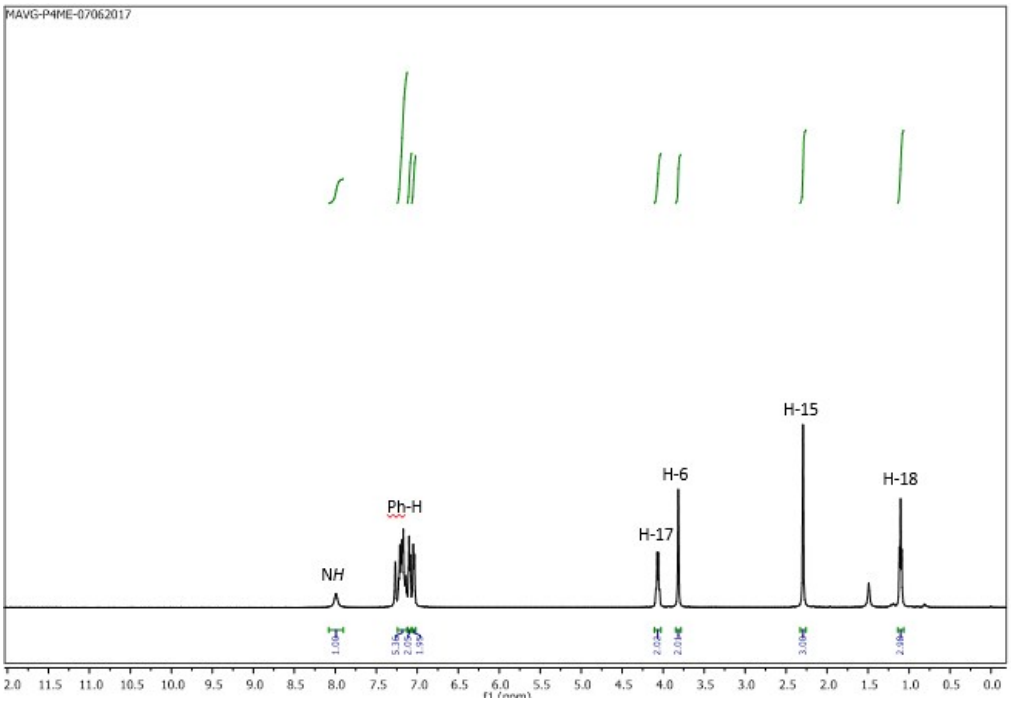


4k HRMS.

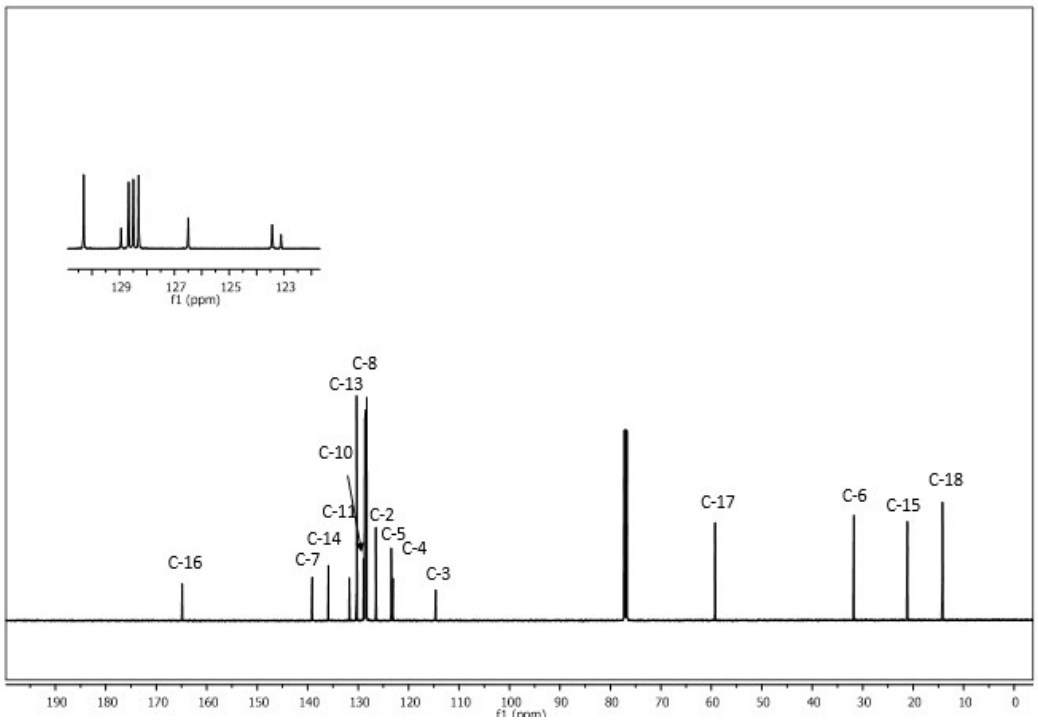
Compound 4l.



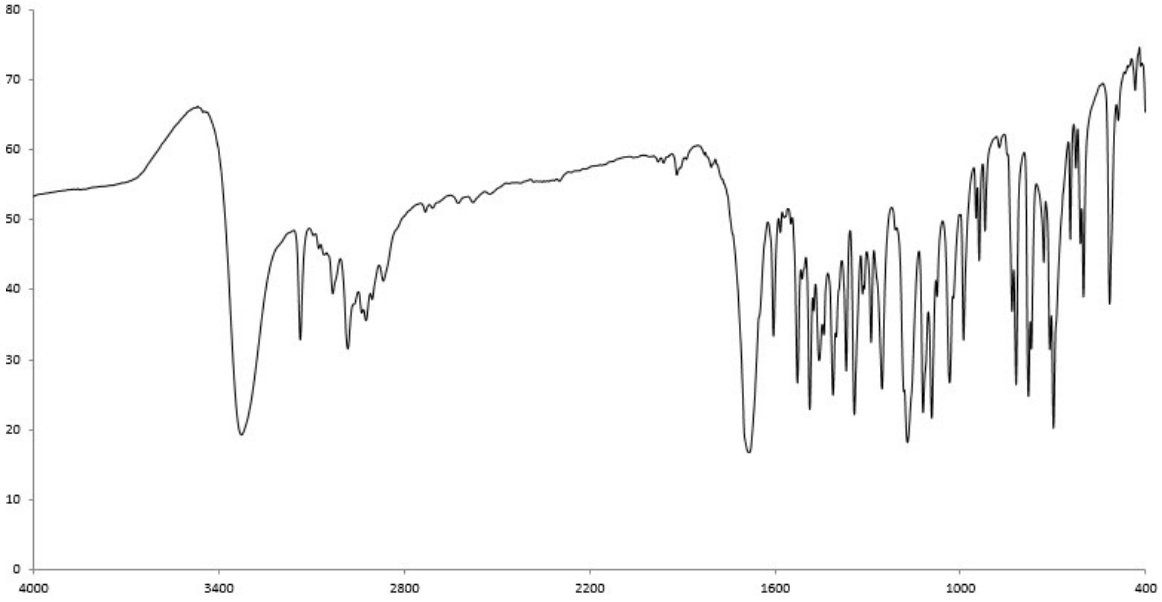
Ethyl 5-benzyl-4-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (4l). Yield: 60%; white solid; mp: 206-208 °C; IR (ν cm^{-1}) 3335 (N-H), 1693 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.99 (s, 1H, H-1), 7.27 (s, 1H, H-2), 7.23-7.14 (m, 5H, H-8-10), 7.10 (d, $^{3}J_{H-H}$ = 5.0 Hz, 2H, H-12), 7.05 (d, $^{3}J_{H-H}$ = 5.0 Hz, 2H, H-13), 4.07 (c, $^{3}J_{H-H}$ = 5.0 Hz, 2H, H-17), 3.82 (s, 2H, H-6), 2.29 (s, 3H, H-15), 1.10 (t, $^{3}J_{H-H}$ =10.0 Hz, 3H, H-18). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.8 (C-16), 139.1 (C-7), 135.8 (C-14), 131.7 (C-11), 130.3 (C-13), 128.9 (C-10), 128.6 (C-8), 128.4 (C-9), 128.3 (C-12), 126.5 (C-2), 123.4 (C-5), 123.1 (C-4), 114.6 (C-3), 59.2 (C-17), 31.7 (C-6), 21.1 (C-15), 14.2 (C-18). HRMS (ESI^{+}): m/z calcd for $C_{21}H_{21}NO_2$ $[M+Na]^{+}$ 342.1470, found 342.1491.



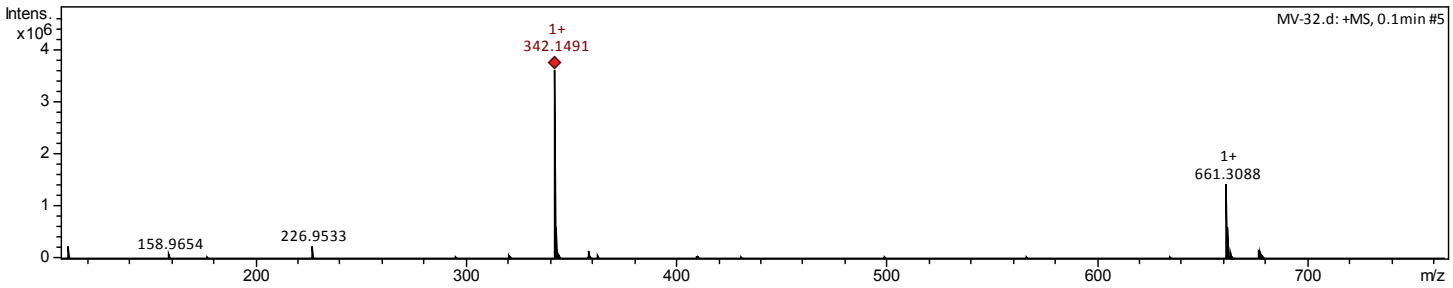
4l NMR ^{1}H ($CDCl_3$, 500 MHz).



4l NMR ^{13}C ($CDCl_3$, 125 MHz).

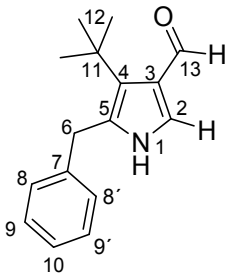


4l IR-KBr pellet.



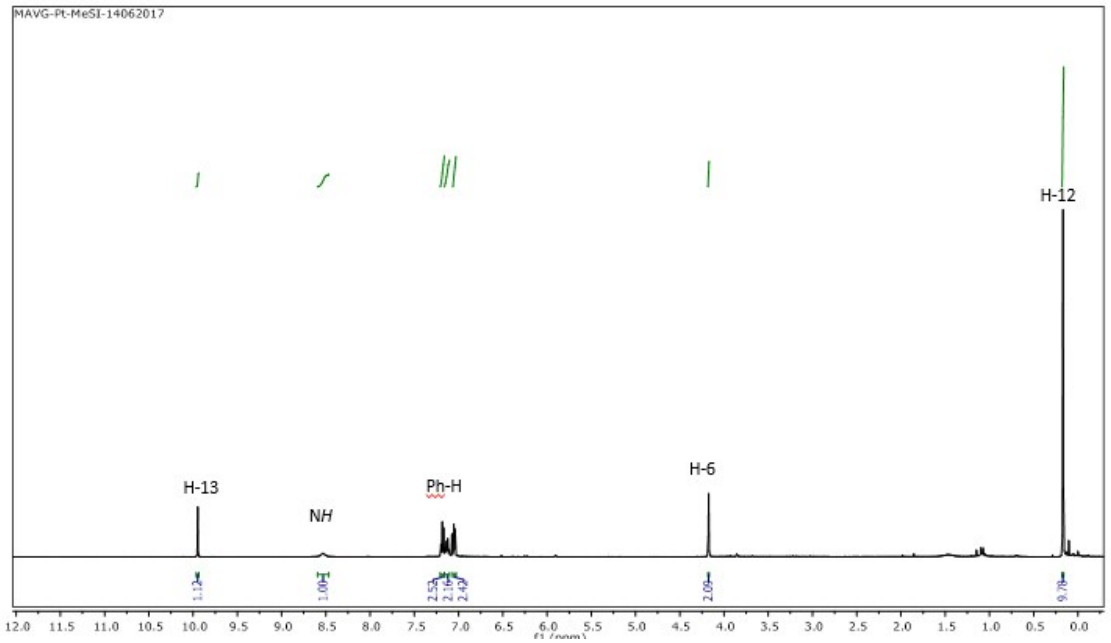
4l HRSM

Compound 4m

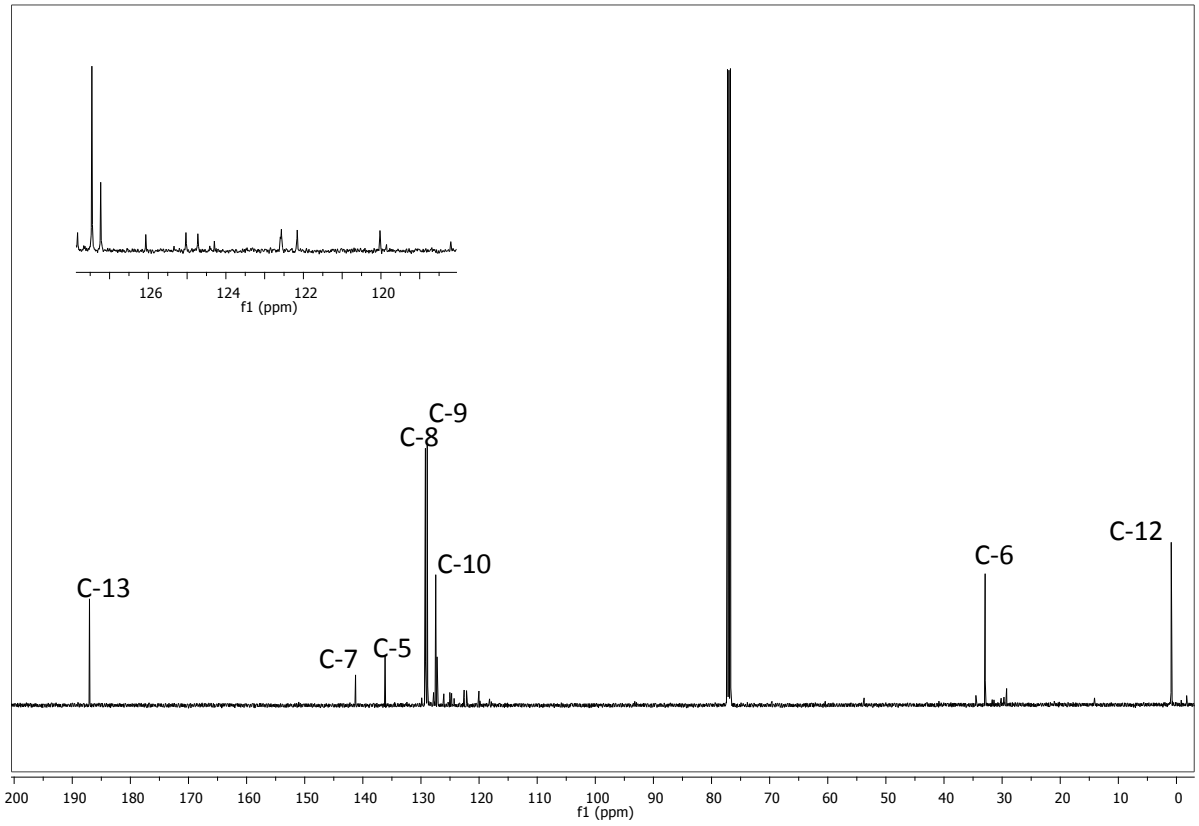


5-benzyl-4-(*tert*-butyl)-1*H*-pyrrole-3-carbaldehyde (4m).

Yield: 38%; white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.95 (s, 1H, H-13), 8.53 (s, 1H, H-1), 7.20-7.04 (m, 5H, H-2,8,9,10), 4.17 (s, 2H, H-6), 0.17 (s, 9H, H-12). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 187.0 (C-13), 141.2 (C-7), 136.1 (C-5), 129.2 (C-8), 128.9 (C-9), 127.4 (C-10), 127.2 (C-2), 126.0 (C-4), 128.3 (C-12), 126.5 (C-2), 123.4 (C-5), 123.1 (C-4), 125.0 (C-3), 32.9 (C-6), 0.90 (C-11), 0.89 (C-12). HRMS (ESI$^+$): m/z calcd for $C_{18}H_{23}NO_2$ $[M+Na]^+$ 308.1626, found 308.1621

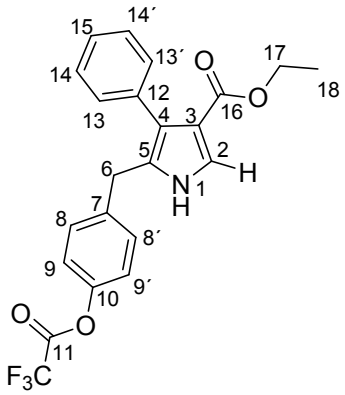


4m NMR ^{1}H ($CDCl_3$, 500 MHz).

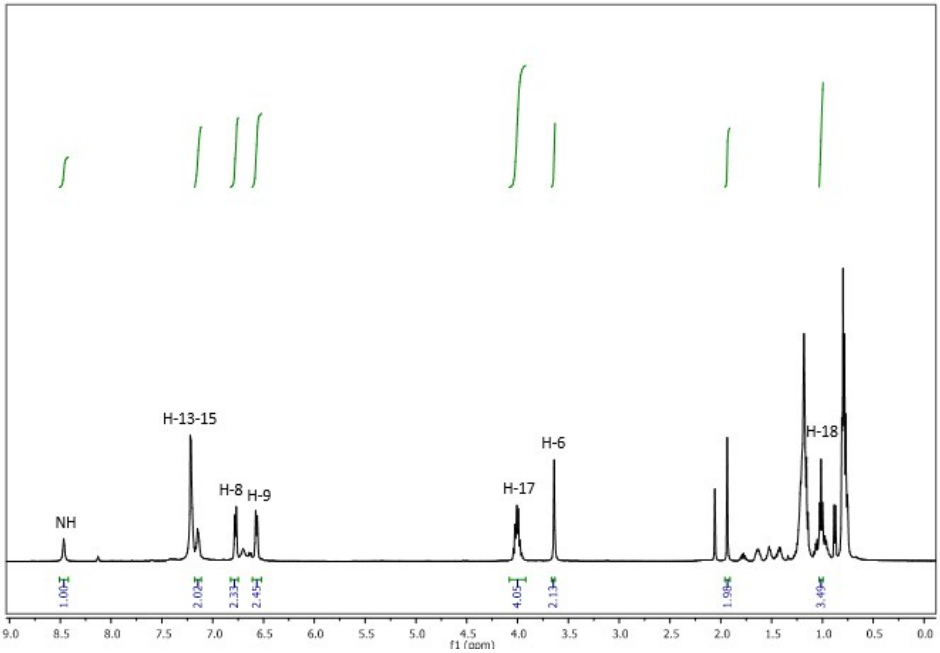


4m NMR ^{13}C ($CDCl_3$, 125 MHz).

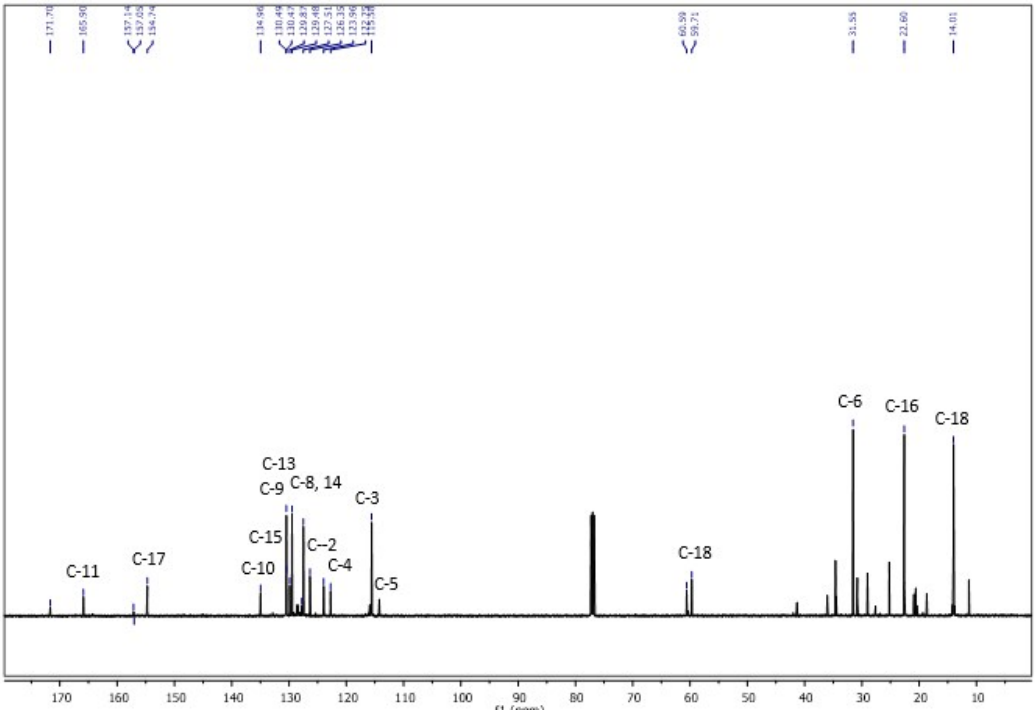
Compound 4n.



Ethyl 4-phenyl-5-(4-(2,2,2-trifluoroacetoxy)benzyl)-1*H*-pyrrole-3-carboxylate (4n). Yield: 45%; white solid; mp: 205-206 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.47 (s, 1H, H-1), 7.22-7.14 (m, 6H, H-2,13-15), 6.77 (d, $^{3}J_{H\text{-}H}$ = 5.0 Hz, 2H, H-9), 6.57 (d, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-8), 4.01 (m, 2H, H-17), 3.64 (s, 2H, H-6), 1.01 (t, $^{3}J_{H\text{-}H}$ =10.0 Hz, 3H, H-18). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.7 (C-11), 165.9 (C-16), 154.7 (C-10), 134.9 (C-7), 130.5 (C-12), 130.4 (C-8), 129.8 (C-15), 129.4 (C-13), 127.5 (C-5), 126.3 (C-2), 123.9 (C-4), 122.7 (CF_3), 115.5 (C-9), 60.6 (C-17), 22.6 (C-6), 14.0 (C-18). HRMS (ESI^{+}): m/z calcd for $C_{20}H_{22}NNaO_4$ $[M+Na]^{+}$ 420.1399, found 420.1402

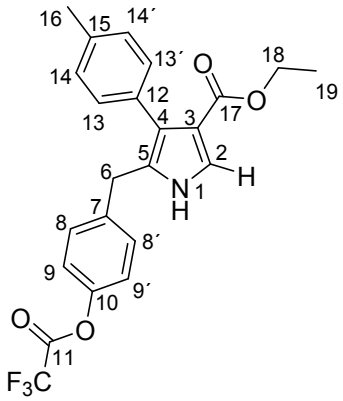


4n NMR ^{1}H ($CDCl_3$, 500 MHz).



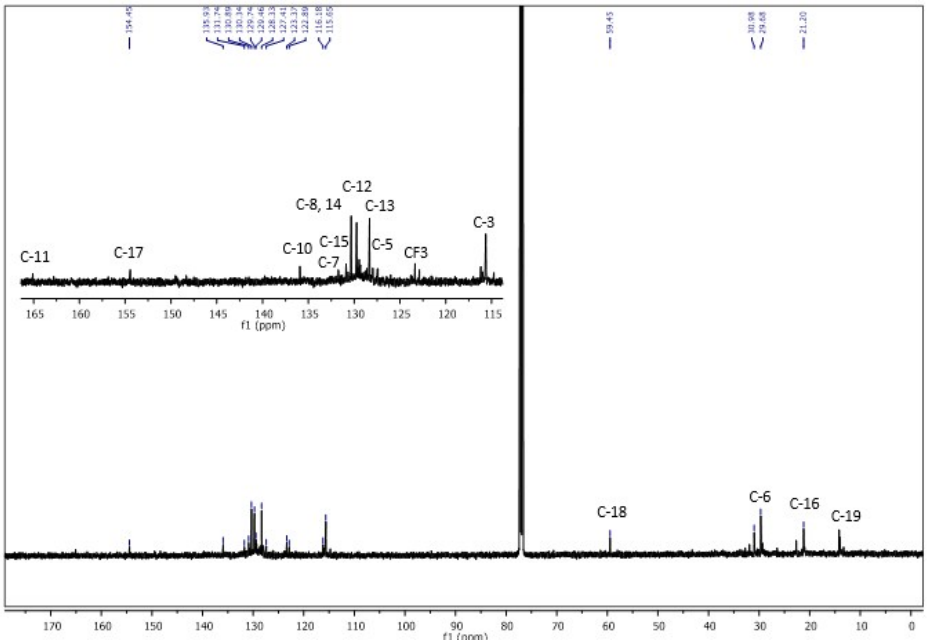
4n NMR ^{13}C ($CDCl_3$, 125 MHz).

Compound 4o.

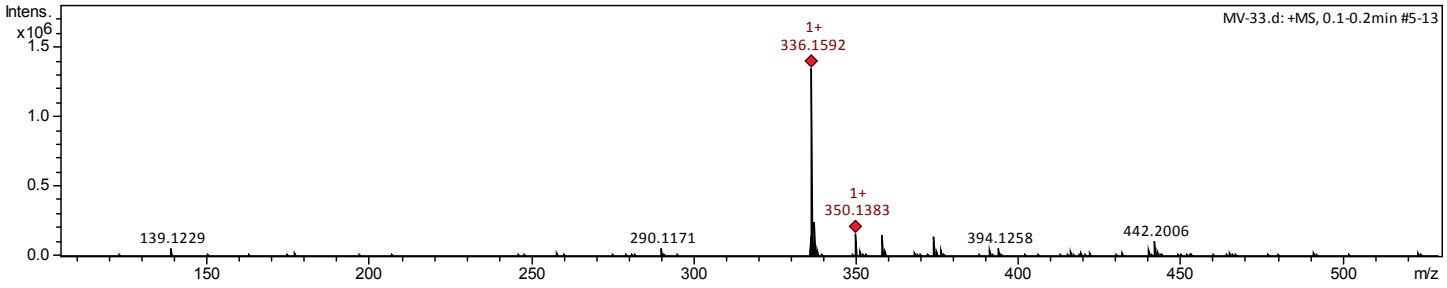


Ethyl 4-(*p*-tolyl)-5-(4-(2,2,2-trifluoroacetoxy)benzyl)-1*H*-pyrrole-3-carboxylate (4o). Yield: 30%; white solid; mp: 196-197 °C. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.04 (s, 1H, H-1), 7.45 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 1H, H-2), 7.28 (d, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H-13), 7.09 (d, $^3J_{H\text{-}H}$ = 10.0 Hz, 2H, H-9), 6.90 (d, $^3J_{H\text{-}H}$ = 10.0 Hz, 2H, H-14), 6.68 (d, $^3J_{H\text{-}H}$ = 10.0 Hz, 2H, H-9), 4.07 (q, $^3J_{H\text{-}H}$ = 5.0 Hz, 2H, H-18), 3.74 (s, 2H, H-6), 2.29 (s, 3H, H-16), 1.10 (t, $^3J_{H\text{-}H}$ = 5.0 Hz,

3H, H-19). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.0 (C-11), 154.4 (C-17), 135.9 (C-10), 131.7 (C-7), 130.8 (C-15), 130.3 (C-8), 129.7 (C-12), 129.4 (C-13), 128.3 (C-5), 127.4 (C-9), 123.3 (C-4), 122.8 (CF_3), 115.6 (C-3), 59.4 (C-18), 29.6 (C-6), 21.2 (C-16), 14.0 (C-19). HRMS (ESI^+): m/z calcd for $C_{20}H_{19}NO_2$ $[M+Na]^+$ 328.1313, found 328.1319.

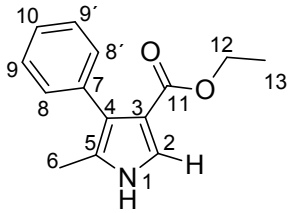


4o NMR ^{13}C ($CDCl_3$, 125 MHz).



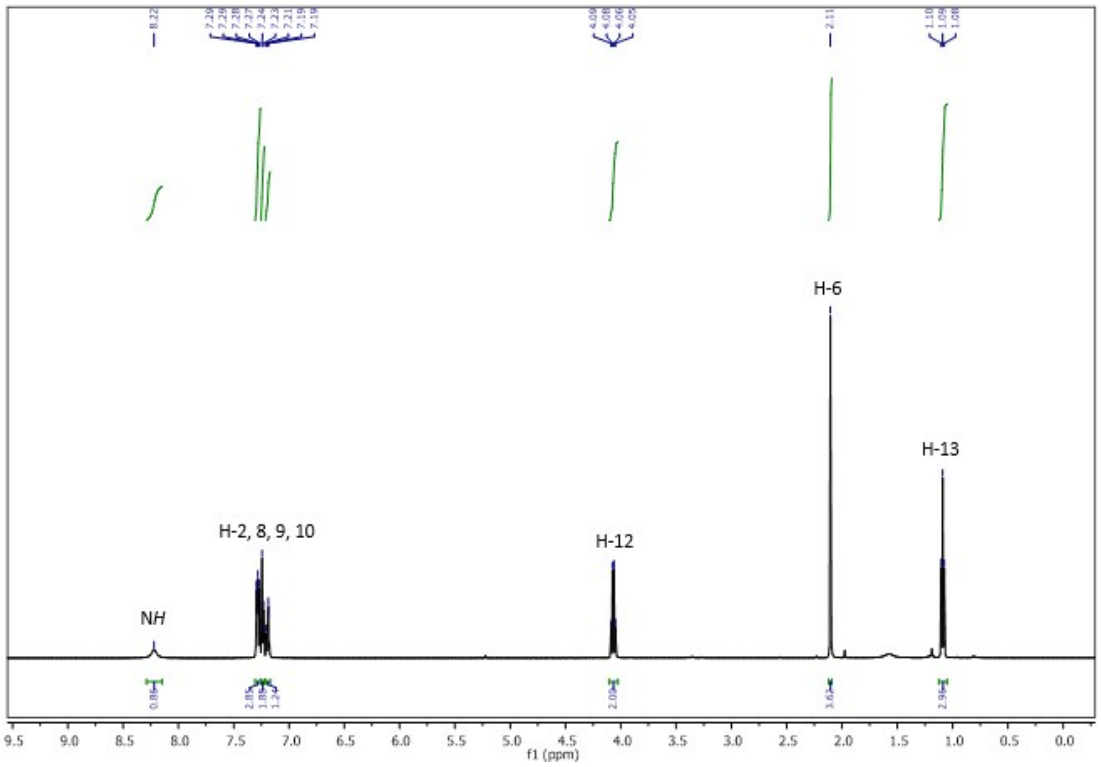
4o HRMS.

Compound 4p

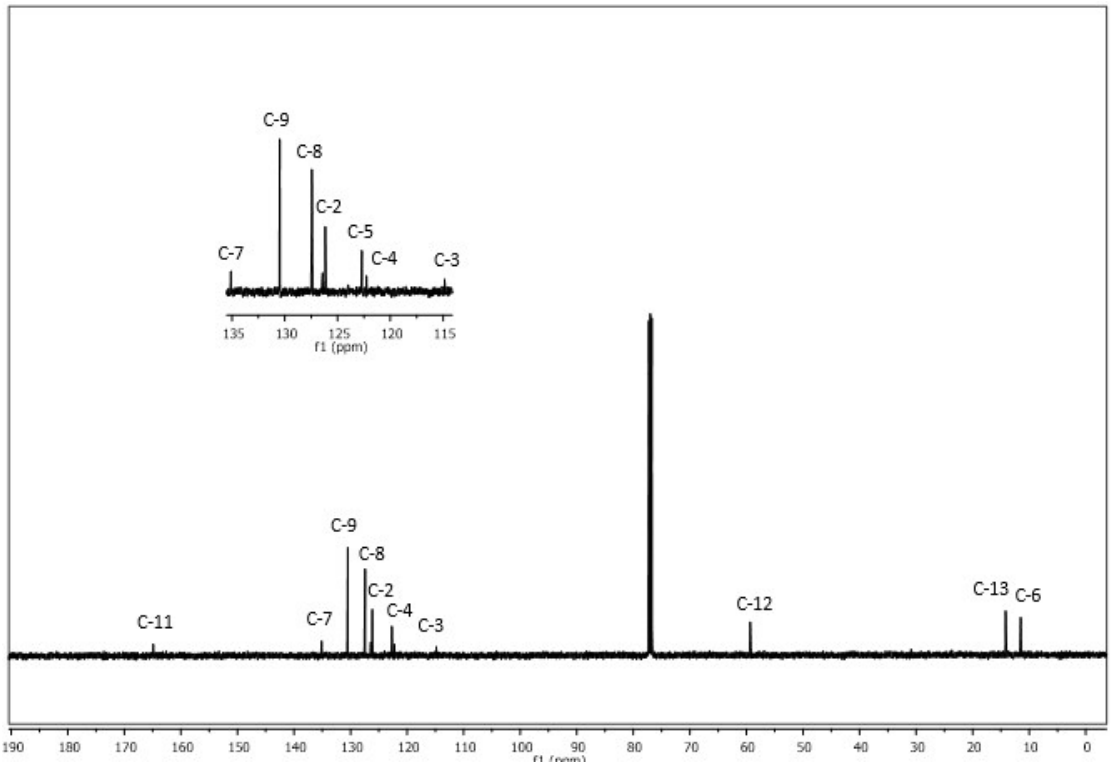


Ethyl 5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (4p).

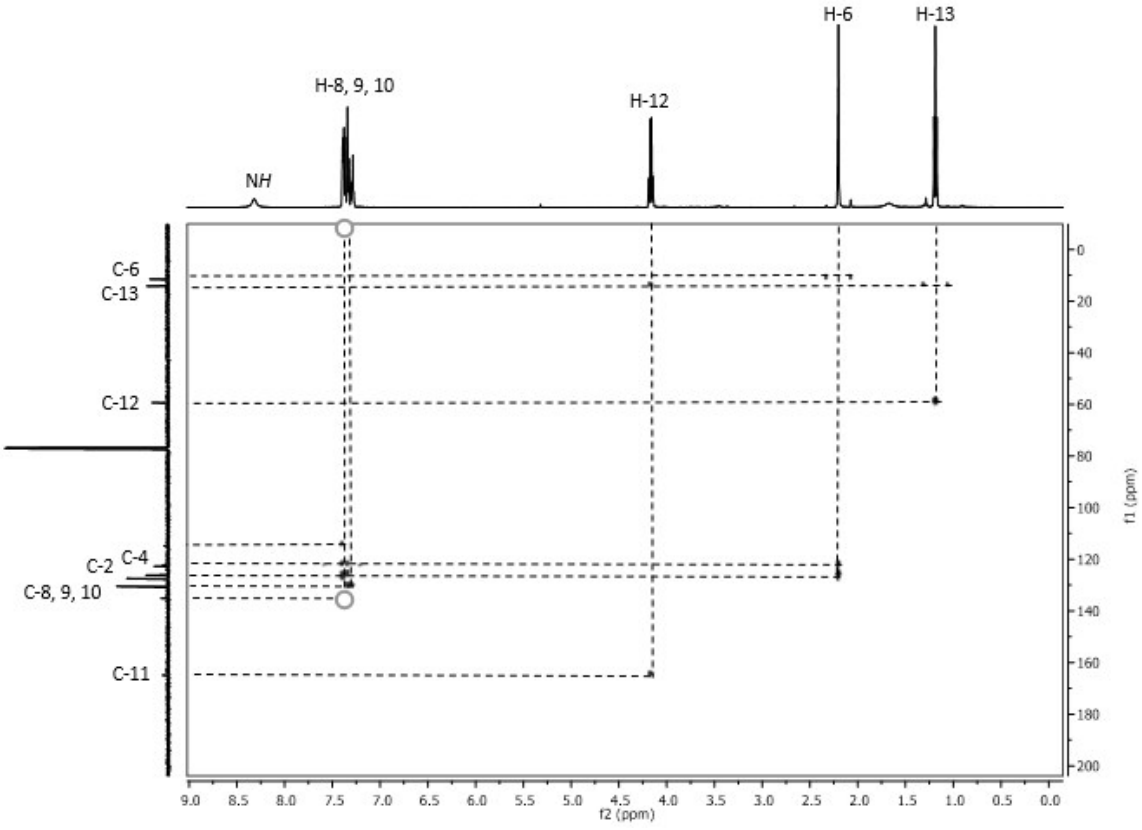
Yield: 60%; white solid; mp: 134-138 °C. IR (ν cm^{-1}) 3304 (N-H), 1683 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.22 (s, 1H, H-1), 7.29-7.19 (m, 6H, H-2,8-10), 4.08 (q, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-12), 2.11 (s, 3H, H-6), 1.09 (t, $^{3}J_{H\text{-}H}$ = 5.0 Hz, 3H, H-13). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.9 (C-11), 135.2 (C-7), 130.4 (C-9), 127.4 (C-8), 126.1 (C-2), 122.7 (C-4), 122.3 (C-5), 123.3 (C-4), 114.8 (C-3), 59.7 (C-12), 14.0 (C-13), 11.4 (C-6).



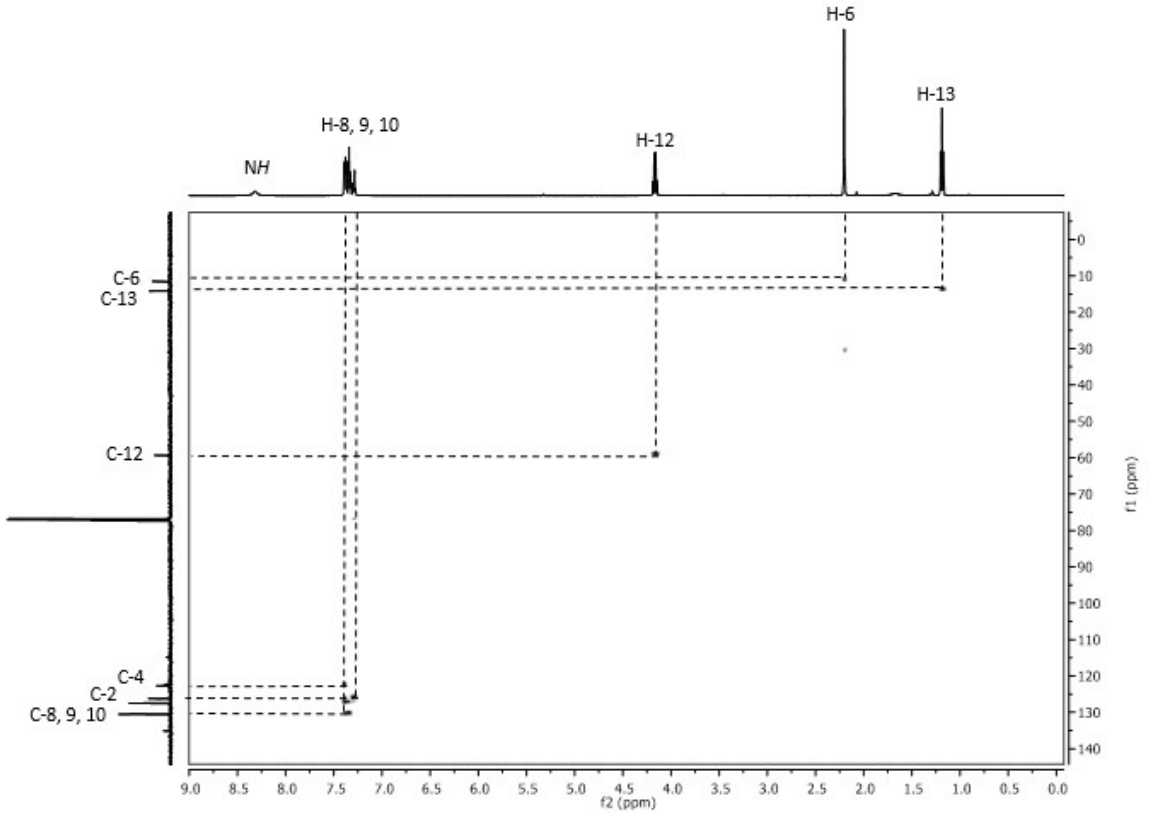
4p NMR ^{1}H ($CDCl_3$, 500 MHz).



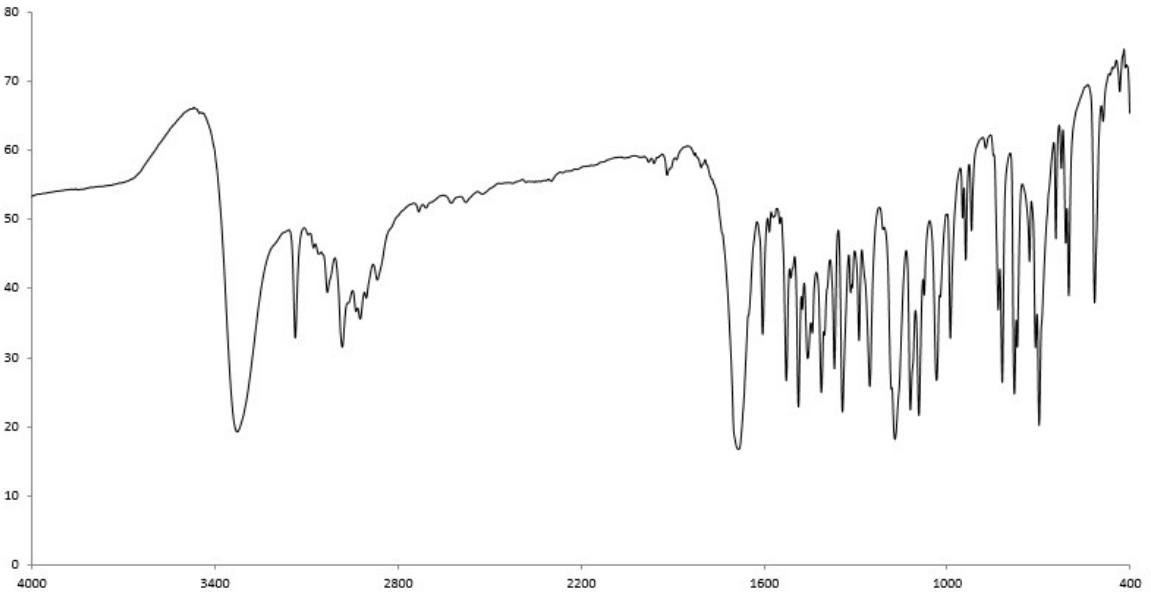
4p NMR ^{13}C ($CDCl_3$, 125 MHz).



4p NMR-HMBC ($CDCl_3$).

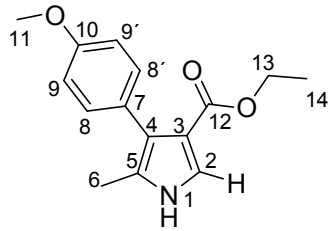


4p NMR-HSQC ($CDCl_3$).



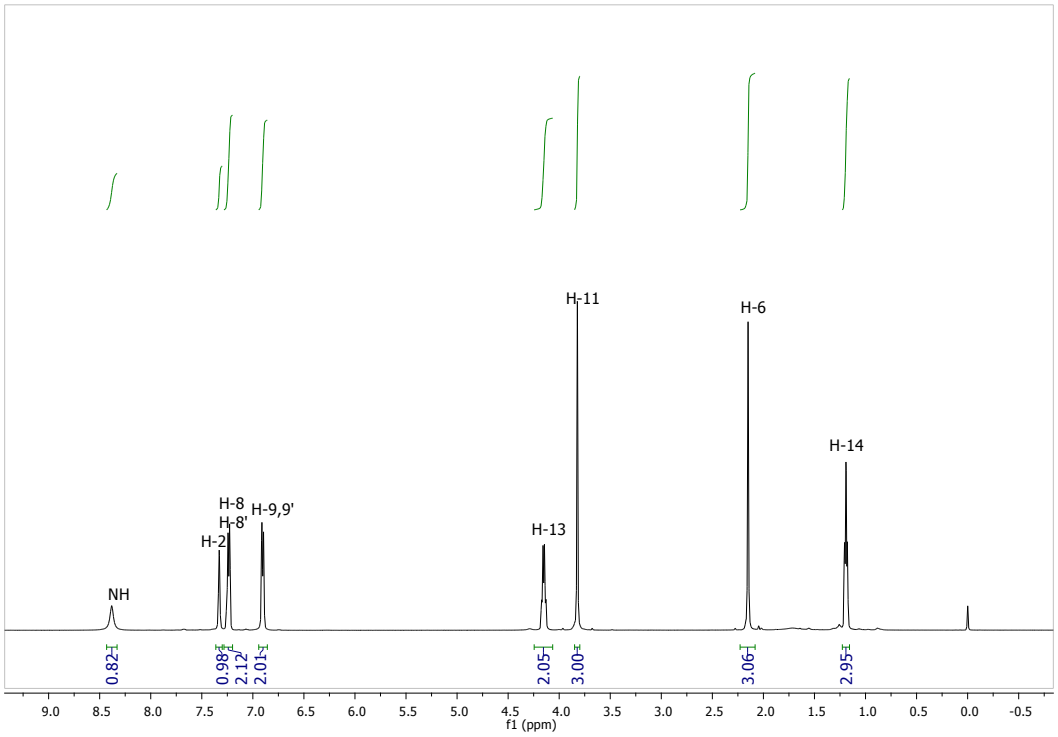
4p IR-KBr pellet.

Compound 4q

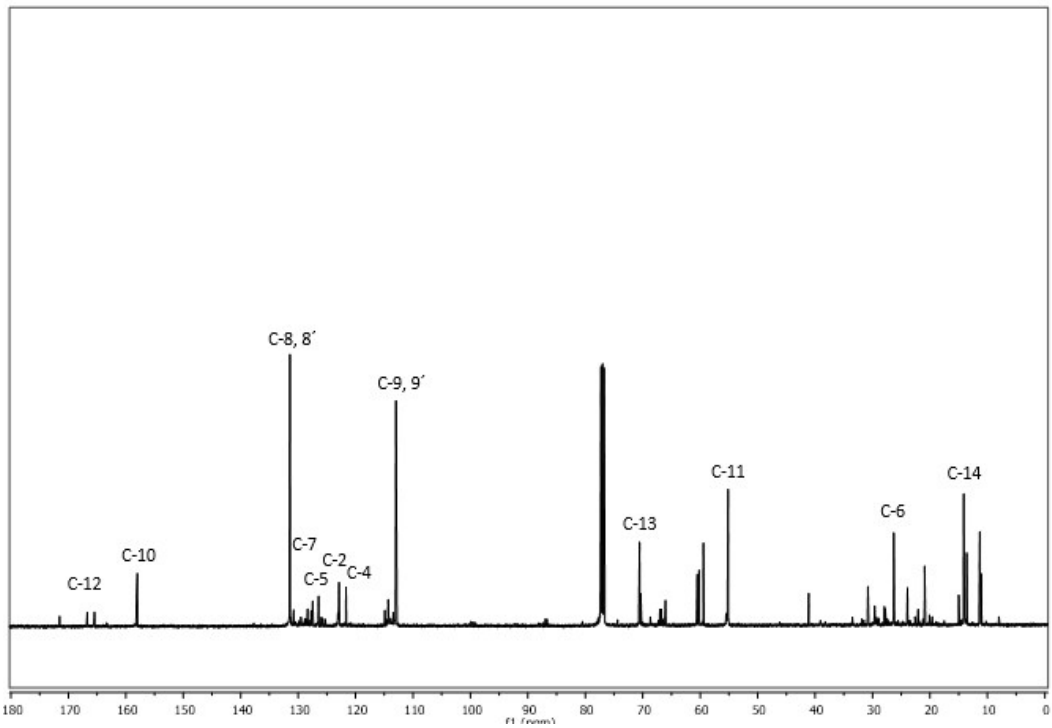


Ethyl 4-(4-methoxyphenyl)-5-methyl-1*H*-pyrrole-3-carboxylate (4q).

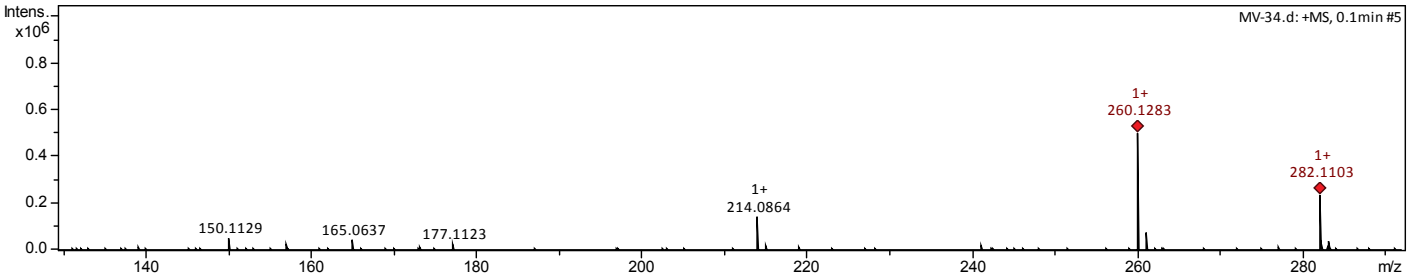
Yield: 55%; white solid; mp: 116-119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.61 (s, 1H, H-1), 7.15 (d, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-8), 7.07 (d, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-2), 6.82 (s, 1H, H-2), 4.05 (q, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 2H, H-13), 3.74 (s, 3H, H-10´), 1.18 (t, $^{3}J_{H\text{-}H}$ = 5.0 Hz, 3H, H-14). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.9 (C-12), 158.0 (C-10), 135.2 (C-7), 130.4 (C-9), 127.4 (C-8), 126.1 (C-2), 122.7 (C-7), 122.3 (C-5), 123.3 (C-5), 114.8 (C-3), 59.7 (C-12), 14.0 (C-13), 11.4 (C-6). HRMS (ESI^{+}): m/z calcd for $C_{15}H_{17}NO_3$ $[M+Na]^{+}$ 282.1106, found 282.1103.



4q NMR ^{1}H ($CDCl_3$, 500 MHz).

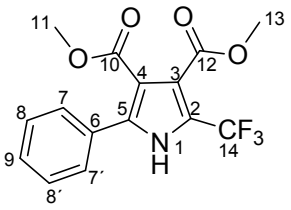


4q NMR ^{13}C ($CDCl_3$, 125 MHz).

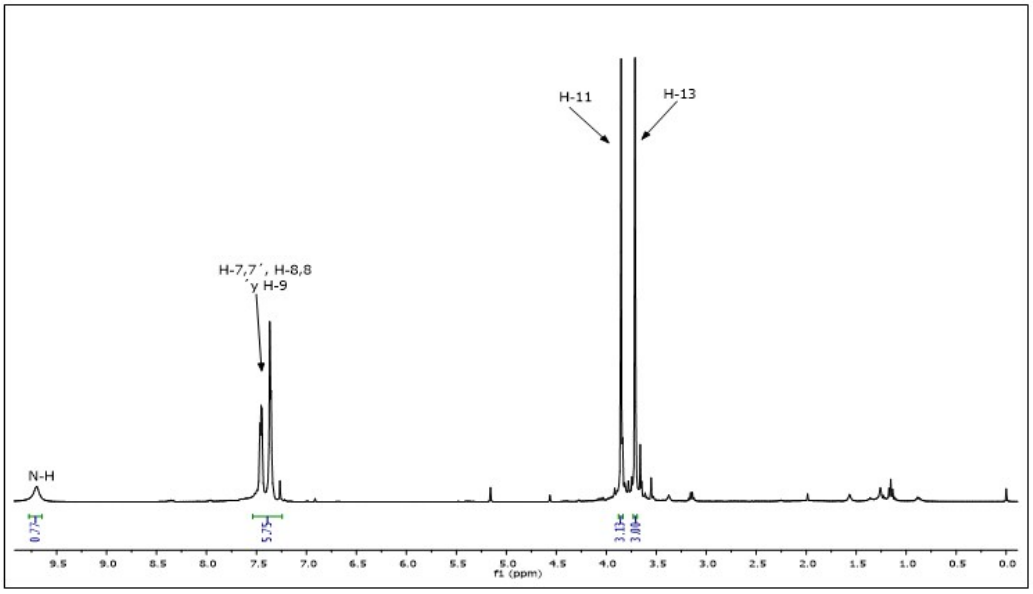


4q HRMS.

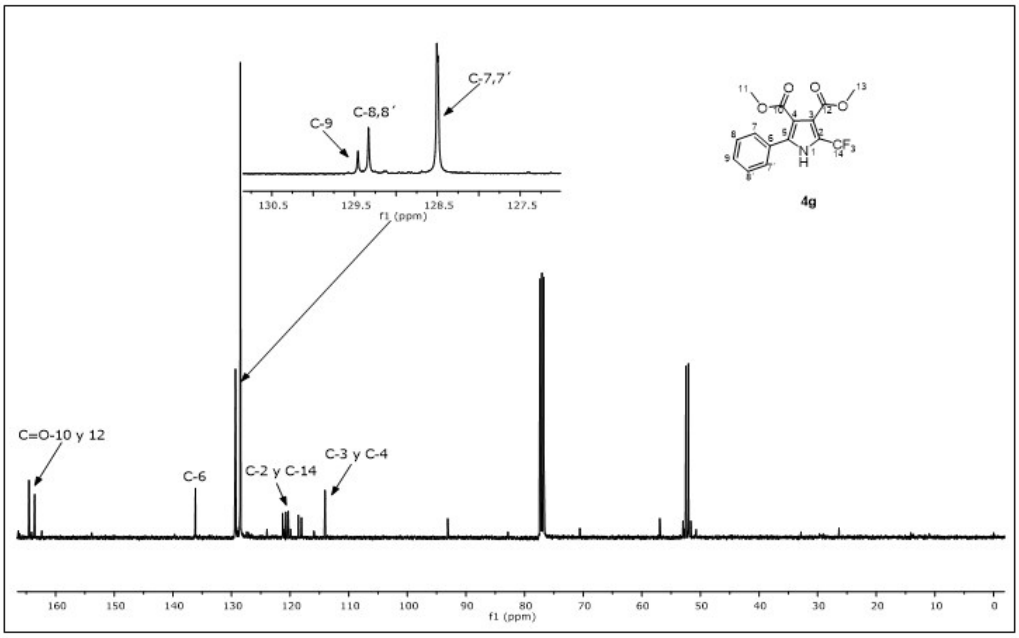
Compound 5.



Dimethyl-2-phenyl-5-(trifluoromethyl)-1*H*-pyrrole-3,4-dicarboxylate (5). Yield: 40%; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.75 (s, 1H, H-1), 7.46-7.35 (m, 5H, H-7, 7´, H-8,8´ and H-9), 3.85 (s, 3H, H-11), 3.70 (s, 3H, H-13). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.5 (C-13), 163.5 (C-11), 136.1 (C-6), 129.4 (C-9), 129.3 (C-8), 128.5 (C-7), 120.4 (q, $^{1}J_{C\text{-}F}$ = 40.0 Hz, C-2), 119.9 (q, $^{2}J_{C\text{-}F}$ = 267.0 Hz, C-14), 114.0 (C-3), 52.5 (C-11), 52.0 (C-13).



5 NMR ^{1}H ($CDCl_3$, 500 MHz).



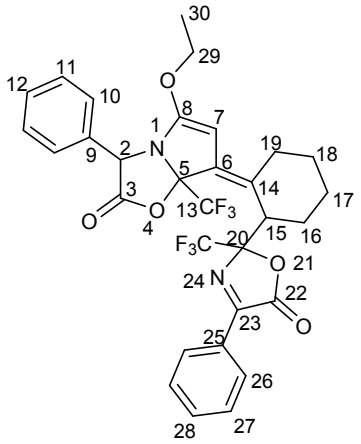
5 NMR ^{13}C ($CDCl_3$, 125 MHz).

SECTION 4

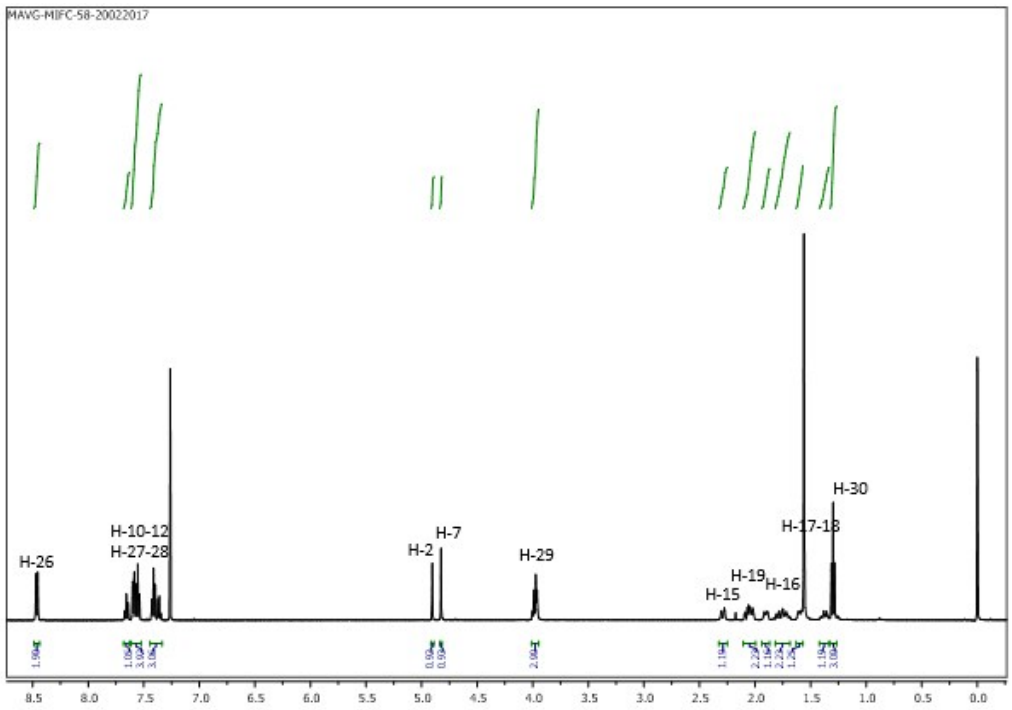
General procedure for the synthesis of compounds 6 and 7

Synthesis of bicyclic compounds 6 and 7: Following the general procedure for the synthesis of pyrroles **4**, compound **6** was obtained in the absence of a catalyst after 180 min of reaction when 1.0 mmol of **1h** and 2.1 mmol of oxazolone **2a** were combined. Compound **7** was isolated from the chloroform-based mixture of **6** stirred for 2 h at room temperature in presence of SiO_2.

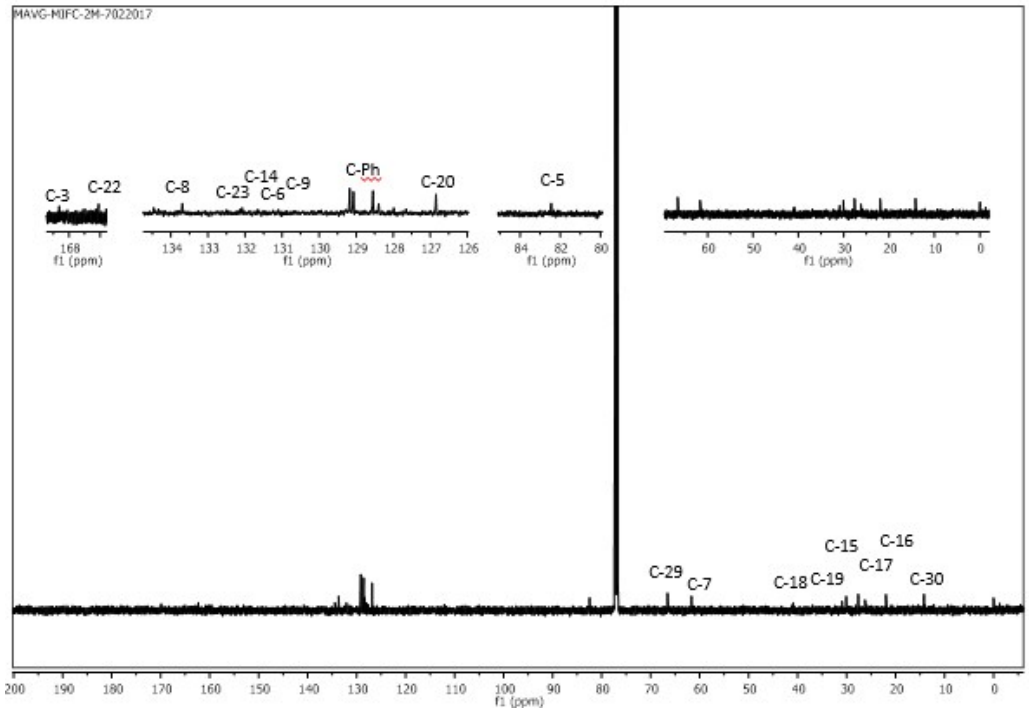
Compound 6



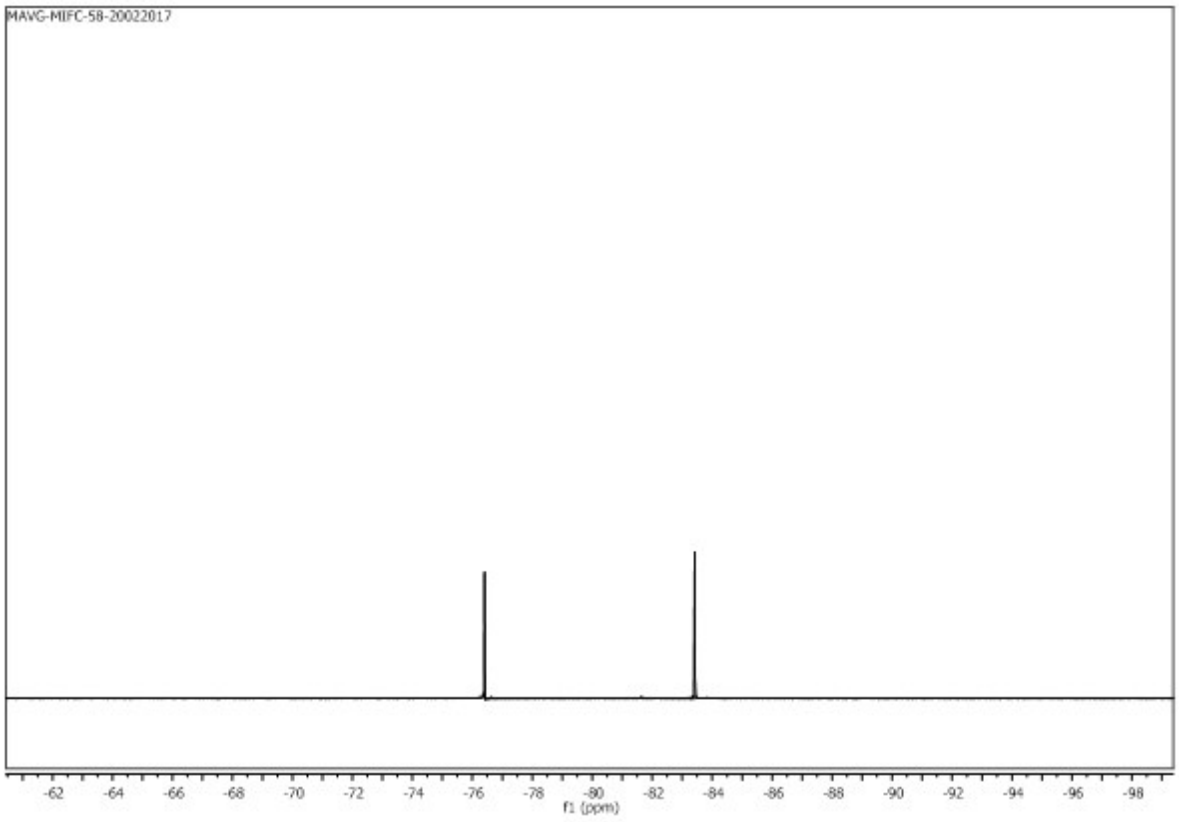
(*Z*)-5-ethoxy-7-(2-(5-oxo-4-phenyl-2-(trifluoromethyl)-2,5-dihydrooxazol-2-yl)cyclohexylidene)-3-phenyl-7a-(trifluoromethyl)-7,7a-dihydropyrrolo[2,1-*b*]oxazol-2(3H)-one (6). CCDC 1911540 Yield: 40%; yellow crystals; mp: 203-205 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 5.0 Hz, 2H, H-26), 7.67-7.35 (m, 8H, H-27, 28, 10-12), 4.90 (s, 1H, H-2), 4.83 (s, 1H, H-7), 4.00-3.96 (q, *J* = 5.0 Hz, 2H, H-29), 2.29 (d, *J* = 10.0 Hz, 1H, H-15), 2.09-2.02 (m, 2H, H-19), 1.92-1.68 (m, 4H, H-16,17), 1.41-1.33 (m, 2H, H-18), 1.30 (t, *J* = 5.0 Hz, 3H, H-30). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.9 (C-3), 162.3 (C-22), 133.6 (C-8), 132.0 (C-23), 131.5 (C-14), 131.2 (C-6), 131.0 (C-9), [129.1, 129.0, 128.5, 128.4, 127.9, 127.6, 126.8 (C-Ph)], 126.8 (C-20), 82.5 (C-5), 66.7 (C-29), 61.7 (C-7), 30.8 (C-18), 30.1 (C-19), 27.7 (C-15), 26.2 (C-17), 22.0 (C-16), 14.2 (C-30).



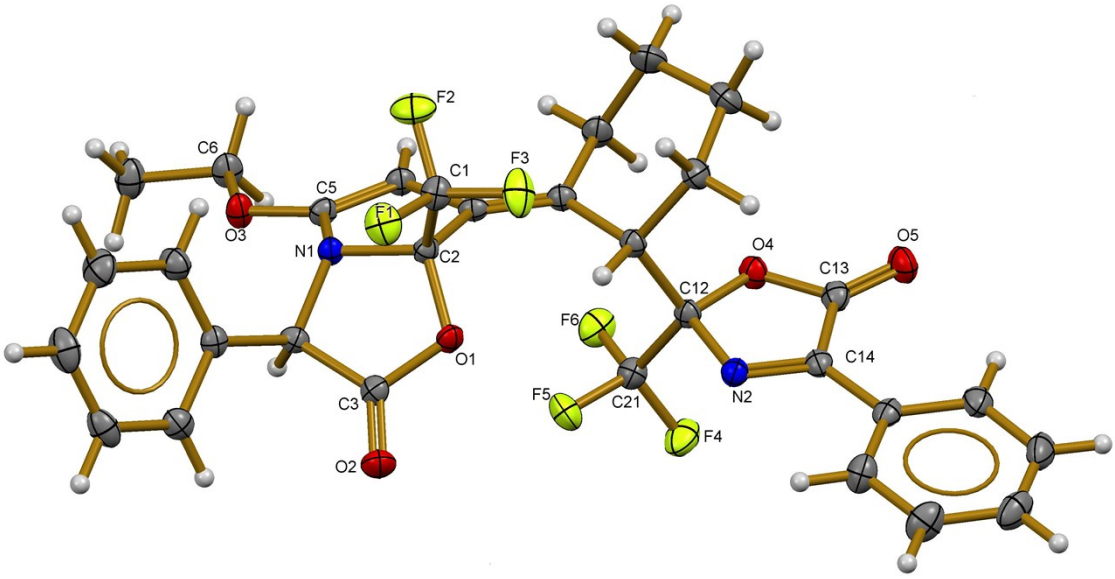
6 NMR ^{1}H ($CDCl_3$, 500 MHz).



6 NMR ^{13}C ($CDCl_3$, 125 MHz).

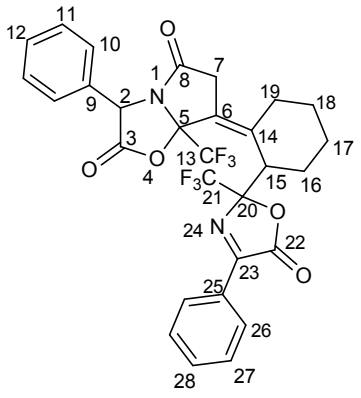


6 NMR ^{19}F ($CDCl_3$, 470 MHz).

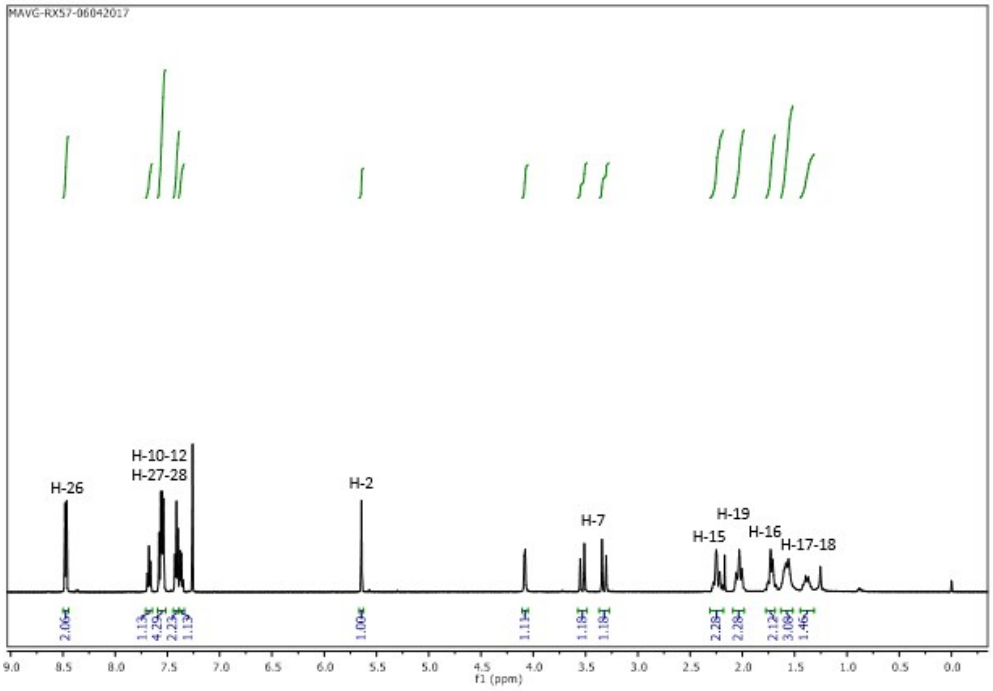


X-Ray Data (CCDC 1911540) CCDC 1911540

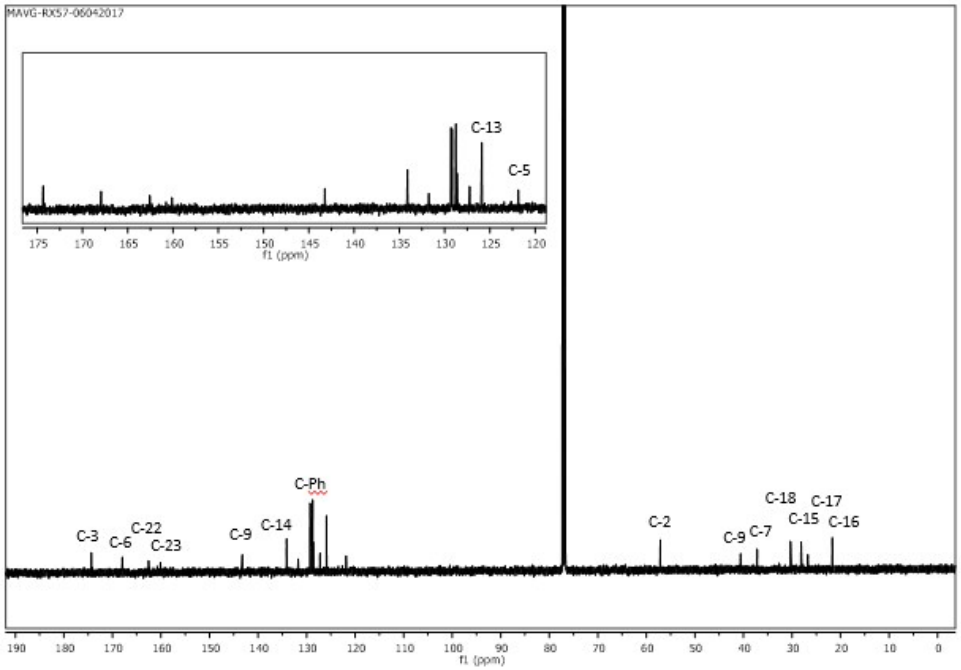
Compound 7.



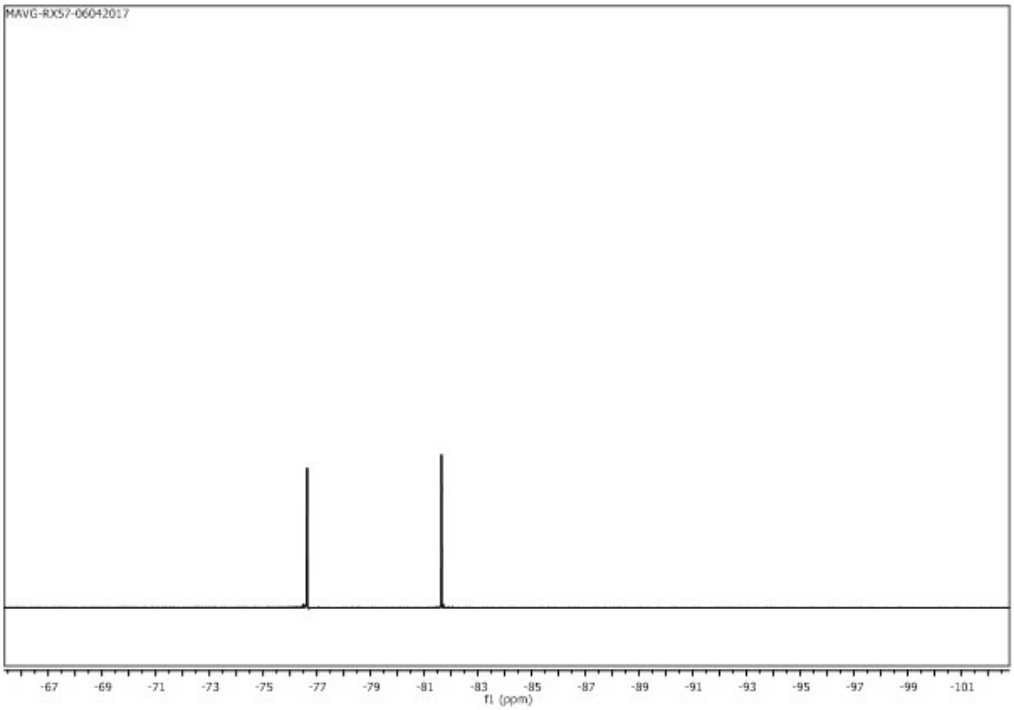
(*Z*)-7-(2-(5-oxo-4-phenyl-2-(trifluoromethyl)-2,5-dihydrooxazol-2-yl)cyclohexylidene)-3-phenyl-7a-(trifluoromethyl)dihydropyrrolo[2,1-*b*]oxazole-2,5(3H,6H)-dione (7). Yield: 40%; white solid; mp: 181-182 °C. IR (ν cm^{-1}) 3327 (N-H), 1685 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.48 (d, J = 5.0 Hz, 2H, H-26), 7.69-7.35 (m, 8H, H-27,28,10-12), 5.64 (s, 1H, H-2), 3.40 (dd , $^{2}J_{H\text{-}H}$ = 20.0, 2H, H-7), 2.28-2.17 (m, 2H, H-15), 2.06-2.01 (m, 2H, H-19), 1.75-1.71 (m, 2H, H-16), 1.58-1.56 (m, 2H, H-17), 1.39-1.36 (m, 2H, H-18). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.3 (C-3), 167.9 (C-8), 162.5 (C-22), 160.1 (C-23), 143.2 (C-9), 134.1 (C-14), 131.7 (C-6, [129.2, 129.1, 128.7, 128.6, 125.8 (C-Ph)], 127.2 (CF_3-21), 121.8 (CF_3-13), 57.1 (C-2), 40.5 (C-9), 37.1 (C-7), 30.3 (C-18), 28.1 (C-15), 26.7 (C-17), 21.7 (C-16). HRMS (ESI^+): m/z calcd for $C_{29}H_{22}F_6N_2O_5$ $[M+Na]^+$ 615.1331, found 615.1432.



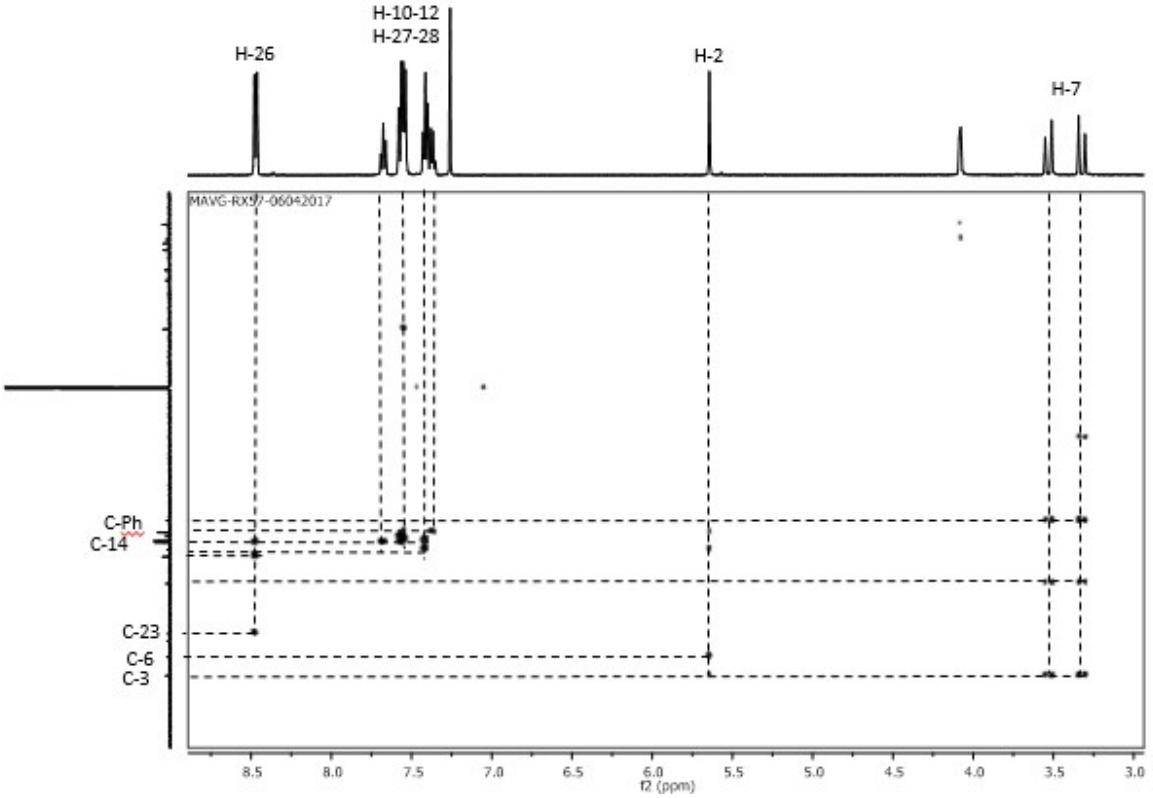
7 NMR ^{1}H ($CDCl_3$, 500 MHz).



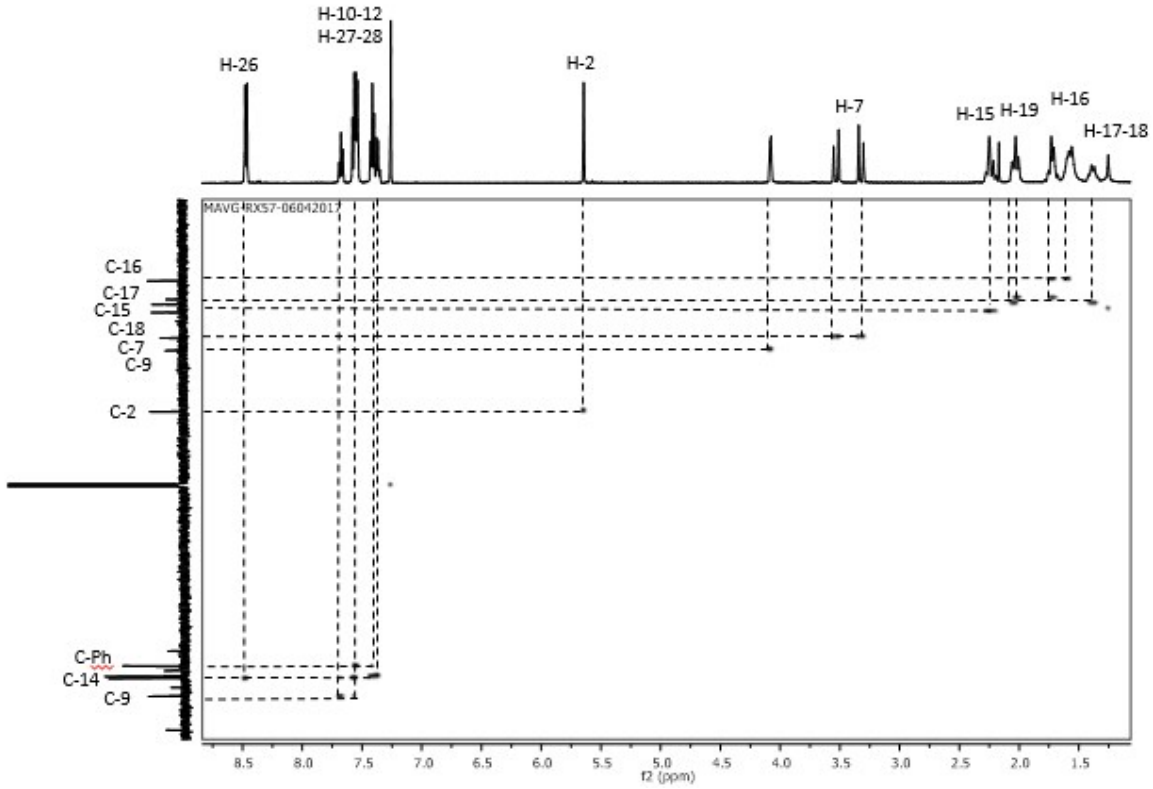
7 NMR ^{13}C ($CDCl_3$, 125 MHz).



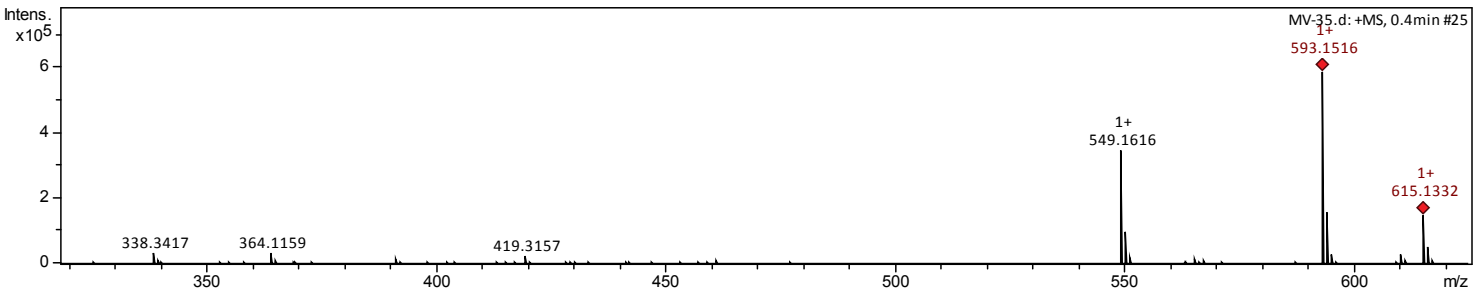
7 NMR ^{19}F ($CDCl_3$, 470 MHz).



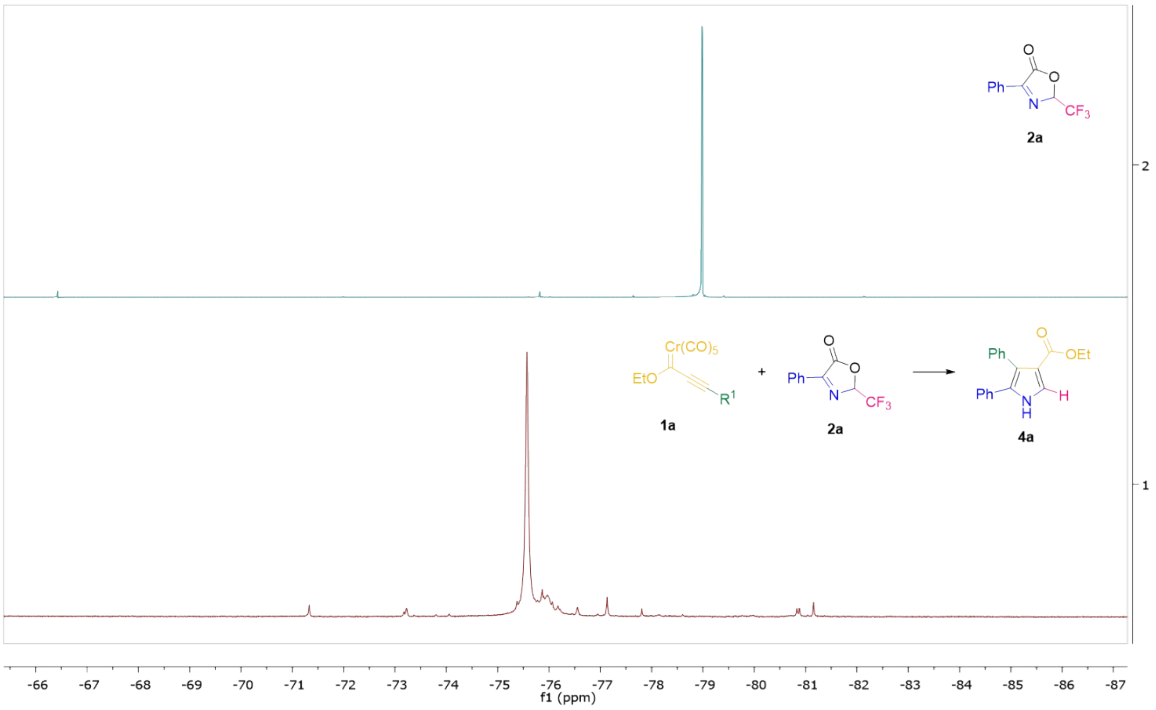
7 NMR-HSQC ($CDCl_3$, 500 MHz).



7 NMR-HMBC ($CDCl_3$, 500 MHz).



7 HRMS.



^{19}F NMR ($CDCl_3$, 470 MHz) of crude reaction of 2a and 1a compared with purified 2a.

SECTION 5

All the stationary points discussed in this work were fully optimized and characterized by means of the Gaussian 09 suite of programs and using the hybrid DFT functional usually referred to as B3LYP with the D3 dispersion empirical correction. In the case of H, C, N, O and F atoms, the 6-31G(d) basis set was used. Metallic centres Ag And Cr were described by the Hay-Wadt (LANL2DZ) effective core potentials and basis sets. All of the stationary points were characterized by harmonic analysis. Reactants and products showed positive definite Hessians (NIMAG=0). Transition structures showed one, and only one, imaginary frequency (NIMAG=1) associated with the reaction coordinate under study. Free energies at 363.15 K were calculated by including the corresponding thermal corrections to Gibbs free energies (TCGE). Non-specific solvent effects were considered by means of the PCM method. The solvent used in the calculations was THF. Natural bonding analysis calculations were performed using the NBO program as implemented in Gaussian 09.

SECTION 6

2a

HF=-889.4297044 hartree

Zero-point correction= 0.149484
(Hartree/Particle)

Thermal correction to Energy= 0.161988

Thermal correction to Enthalpy= 0.162932

Thermal correction to Gibbs Free Energy= 0.108482

Sum of electronic and zero-point Energies= -889.280221

Sum of electronic and thermal Energies= -889.267716

Sum of electronic and thermal Enthalpies= -889.266772

Sum of electronic and thermal Free Energies= -889.321222

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.804002	-0.559129	0.215064
2	9	0	-3.979081	0.090397	0.155898
3	9	0	-2.320079	-0.445752	1.464014
4	9	0	-3.022121	-1.857972	-0.046595
5	6	0	-1.817262	0.025071	-0.806271
6	1	0	-2.253623	-0.067682	-1.805091
7	8	0	-1.634525	1.411166	-0.499980
8	6	0	-0.317692	1.594380	-0.193919
9	8	0	0.137941	2.660741	0.129436
10	6	0	0.329905	0.230248	-0.363111
11	7	0	-0.546724	-0.642785	-0.721191
12	6	0	1.748324	-0.061046	-0.146057
13	6	0	4.450183	-0.681321	0.251848
14	6	0	2.201786	-1.387785	-0.283395

15	6	0	2.663902	0.950981	0.193475
16	6	0	4.008109	0.635619	0.389892
17	6	0	3.542895	-1.693149	-0.085340
18	1	0	1.491683	-2.165599	-0.543628
19	1	0	2.323401	1.972948	0.302508
20	1	0	4.710108	1.421788	0.651422
21	1	0	3.884627	-2.718448	-0.191959
22	1	0	5.498181	-0.922043	0.406476

DEF-N

HF=-1732.0481596 hartree

Zero-point correction= 0.493875
(Hartree/Particle)

Thermal correction to Energy= 0.528382

Thermal correction to Enthalpy= 0.529326

Thermal correction to Gibbs Free Energy= 0.420325

Sum of electronic and zero-point Energies= -1731.554285

Sum of electronic and thermal Energies= -1731.519778

Sum of electronic and thermal Enthalpies= -1731.518834

Sum of electronic and thermal Free Energies= -1731.627835

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.625612	2.965558	0.796970
2	9	0	-2.109663	2.120653	1.736271
3	9	0	-1.941836	4.226000	1.158233
4	9	0	-2.320697	2.710745	-0.349503

5	6	0	-0.160821	2.787873	0.624839
6	8	0	0.517771	3.692820	-0.109264
7	7	0	0.529749	1.724419	0.936417
8	6	0	1.794923	1.899178	0.402670
9	6	0	1.844330	3.128860	-0.303917
10	8	0	2.675297	3.747976	-0.959294
11	6	0	2.853460	0.912505	0.541926
12	6	0	4.855255	-1.083370	0.736516
13	6	0	2.818243	-0.060971	1.564894
14	6	0	3.939097	0.880562	-0.360906
15	6	0	4.919556	-0.105572	-0.262780
16	6	0	3.800315	-1.046408	1.653870
17	1	0	2.020381	-0.031749	2.301666
18	1	0	3.994560	1.635543	-1.138125
19	1	0	5.739213	-0.114176	-0.977246
20	1	0	3.744899	-1.784411	2.450518
21	1	0	5.619705	-1.852165	0.806390
22	47	0	-0.450463	-0.336420	0.861793
23	8	0	0.574732	-2.373011	0.010567
24	8	0	-1.111991	0.101536	-1.602916
25	8	0	-2.600989	-1.308310	1.160926
26	6	0	1.030253	-3.426422	0.896898
27	1	0	0.200575	-4.132093	1.012816
28	1	0	1.265378	-2.992259	1.874612
29	6	0	1.526196	-2.211726	-1.067698
30	1	0	2.280577	-1.468979	-0.786183
31	1	0	0.970927	-1.848474	-1.933585
32	6	0	2.136979	-3.597568	-1.237952
33	1	0	1.453279	-4.247342	-1.796330
34	1	0	3.097800	-3.570531	-1.759749
35	6	0	2.261623	-4.059253	0.224711
36	1	0	2.278575	-5.147144	0.333604

37	1	0	3.178676	-3.653171	0.662118
38	6	0	-2.768807	-2.729651	0.948674
39	1	0	-2.395118	-3.242474	1.839416
40	1	0	-2.165836	-3.038426	0.084725
41	6	0	-3.722497	-0.579555	0.582636
42	1	0	-3.327814	0.164189	-0.114125
43	1	0	-4.236512	-0.064952	1.401893
44	6	0	-4.609077	-1.637390	-0.084266
45	1	0	-4.336056	-1.758005	-1.138165
46	1	0	-5.669616	-1.375629	-0.036388
47	6	0	-4.263012	-2.914311	0.699608
48	1	0	-4.805227	-2.941009	1.651586
49	1	0	-4.485723	-3.832109	0.148043
50	6	0	-0.352706	1.059608	-2.375399
51	1	0	0.717282	0.884460	-2.204784
52	1	0	-0.604978	2.058644	-2.015685
53	6	0	-1.647306	-0.922269	-2.466187
54	1	0	-2.737083	-0.800088	-2.518327
55	1	0	-1.424869	-1.897603	-2.021298
56	6	0	-0.997890	-0.704968	-3.836759
57	1	0	-0.047598	-1.247382	-3.905798
58	1	0	-1.638381	-1.037835	-4.658431
59	6	0	-0.745344	0.811210	-3.831561
60	1	0	0.032340	1.124071	-4.533904
61	1	0	-1.667594	1.351723	-4.074349

DEF-C

HF=-1732.0489885 hartree

Zero-point correction= 0.495224
(Hartree/Particle)

Thermal correction to Energy= 0.529077

Thermal correction to Enthalpy= 0.530022

Thermal correction to Gibbs Free Energy= 0.424239

Sum of electronic and zero-point Energies= -1731.553765

Sum of electronic and thermal Energies= -1731.519911

Sum of electronic and thermal Enthalpies= -1731.518967

Sum of electronic and thermal Free Energies= -1731.624749

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.020952	-3.097965	0.945351
2	9	0	1.181254	-3.489919	0.450955
3	9	0	-0.909902	-4.057890	0.584315
4	9	0	0.067000	-3.119175	2.291776
5	6	0	-0.404612	-1.723845	0.461085
6	8	0	-0.489981	-1.707996	-0.970608
7	6	0	-1.630809	-1.024415	-1.295107
8	8	0	-1.890202	-0.700106	-2.444047
9	6	0	-2.328511	-0.802261	-0.012090
10	7	0	-1.605271	-1.264267	0.979012
11	6	0	-3.627037	-0.147087	0.161994
12	6	0	-6.093461	1.157073	0.533222
13	6	0	-4.057901	0.221373	1.451304
14	6	0	-4.458429	0.136794	-0.936882
15	6	0	-5.679761	0.785102	-0.748052
16	6	0	-5.277324	0.867847	1.633266
17	1	0	-3.420848	0.000974	2.301945
18	1	0	-4.137225	-0.145542	-1.932545
19	1	0	-6.309002	1.000746	-1.607346
20	1	0	-5.591842	1.150969	2.634208

21	1	0	-7.042721	1.666025	0.675954
22	47	0	1.210611	-0.279337	0.948302
23	8	0	2.917772	-0.452922	-1.188009
24	8	0	2.758391	1.303945	1.577287
25	8	0	-0.329002	1.706212	-0.300243
26	6	0	-1.153312	2.359778	0.686863
27	1	0	-0.537027	3.056714	1.271028
28	1	0	-1.524062	1.578631	1.354367
29	6	0	-0.540496	2.358785	-1.560824
30	1	0	-0.271195	1.650697	-2.345866
31	1	0	0.104763	3.248832	-1.636209
32	6	0	-2.021147	2.728288	-1.556459
33	1	0	-2.604781	1.850390	-1.841826
34	1	0	-2.254536	3.544075	-2.247242
35	6	0	-2.277534	3.096839	-0.079432
36	1	0	-2.199347	4.177995	0.073949
37	1	0	-3.268745	2.777386	0.252222
38	6	0	4.170334	0.941795	1.509862
39	1	0	4.301602	0.266034	0.659954
40	1	0	4.424844	0.424251	2.439084
41	6	0	2.578881	2.687066	1.158910
42	1	0	2.374835	3.288943	2.053349
43	1	0	1.715328	2.724361	0.492602
44	6	0	3.898425	3.082223	0.500594
45	1	0	3.906486	2.772284	-0.550531
46	1	0	4.077622	4.160065	0.545234
47	6	0	4.915952	2.260498	1.307732
48	1	0	5.866753	2.118613	0.786357
49	1	0	5.118335	2.743463	2.270470
50	6	0	2.927783	-1.743096	-1.851530
51	1	0	2.200017	-2.379224	-1.344431
52	1	0	3.925126	-2.185512	-1.744735

53	6	0	2.599497	0.570574	-2.148364
54	1	0	3.528857	1.002123	-2.551844
55	1	0	2.046097	1.354186	-1.626391
56	6	0	1.803144	-0.141800	-3.238737
57	1	0	0.769132	-0.299664	-2.915313
58	1	0	1.797803	0.406041	-4.185934
59	6	0	2.543418	-1.487062	-3.318059
60	1	0	1.925451	-2.291550	-3.726559
61	1	0	3.438599	-1.392817	-3.943543

ABC

HF=-1063.923726 hartree

Zero-point correction= 0.274001
(Hartree/Particle)

Thermal correction to Energy= 0.293424

Thermal correction to Enthalpy= 0.294368

Thermal correction to Gibbs Free Energy= 0.224506

Sum of electronic and zero-point Energies= -1063.649725

Sum of electronic and thermal Energies= -1063.630302

Sum of electronic and thermal Enthalpies= -1063.629358

Sum of electronic and thermal Free Energies= -1063.699220

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.977025	0.451210	-0.381855
2	9	0	-3.500187	0.119248	0.837944
3	9	0	-3.015661	-0.671554	-1.134660
4	9	0	-3.822075	1.354203	-0.918141

5	6	0	-1.589493	0.963319	-0.281587
6	8	0	-1.384687	2.194960	0.230286
7	6	0	0.054832	2.321453	0.375536
8	8	0	0.528878	3.354991	0.834700
9	6	0	0.552024	1.084316	-0.114196
10	6	0	1.938957	0.673893	-0.236097
11	6	0	4.631500	-0.190172	-0.421386
12	6	0	2.302458	-0.420998	-1.051544
13	6	0	2.967684	1.344274	0.461558
14	6	0	4.289789	0.915222	0.365477
15	6	0	3.626220	-0.851030	-1.133650
16	1	0	1.538297	-0.909280	-1.649577
17	1	0	2.710711	2.201297	1.074899
18	1	0	5.062188	1.446799	0.916344
19	1	0	3.875222	-1.695756	-1.771937
20	1	0	5.663833	-0.522017	-0.488198
21	7	0	-0.504101	0.273126	-0.493113
22	1	0	-0.374073	-1.434716	-0.094015
23	7	0	-0.309021	-2.342630	0.453287
24	6	0	-1.709578	-2.726045	0.813527
25	1	0	-2.267764	-2.914024	-0.103078
26	1	0	-2.169894	-1.899462	1.354536
27	1	0	-1.682561	-3.621959	1.435689
28	6	0	0.346157	-3.377915	-0.403033
29	1	0	1.359708	-3.049243	-0.632219
30	1	0	-0.229482	-3.486487	-1.323300
31	1	0	0.370449	-4.324486	0.140464
32	6	0	0.506094	-2.031217	1.669987
33	1	0	1.493469	-1.699205	1.348735
34	1	0	0.580450	-2.928521	2.286810
35	1	0	0.011364	-1.230944	2.221036

TS1-H

HF=-2177.9653541 hartree

NIMAG=1 (-301.0111 cm^{-1})

Zero-point correction= 0.465538
(Hartree/Particle)

Thermal correction to Energy= 0.508175

Thermal correction to Enthalpy= 0.509119

Thermal correction to Gibbs Free Energy= 0.386629

Sum of electronic and zero-point Energies= -2177.499816

Sum of electronic and thermal Energies= -2177.457179

Sum of electronic and thermal Enthalpies= -2177.456235

Sum of electronic and thermal Free Energies= -2177.578725

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.621821	-3.579786	-1.345059
2	6	0	-3.326901	-4.281342	-0.362091
3	6	0	-3.124439	-3.982385	0.989657
4	6	0	-2.223798	-2.988589	1.363182
5	6	0	-1.500199	-2.283587	0.376755
6	6	0	-1.718120	-2.584107	-0.984981
7	6	0	-0.629762	-1.218423	0.744211
8	6	0	-2.077336	0.655473	0.864871
9	7	0	-1.038983	1.498197	0.576011
10	6	0	-0.095334	1.269633	1.527069
11	6	0	0.459448	-0.606919	0.973030
12	8	0	-0.738666	0.906186	2.691156
13	6	0	-1.982910	0.364721	2.292946

14	6	0	-3.187242	0.374872	-0.031697
15	6	0	-4.429641	-0.053803	0.466879
16	6	0	-5.461630	-0.369838	-0.415869
17	6	0	-5.271809	-0.263273	-1.796286
18	6	0	-4.031621	0.144711	-2.298022
19	6	0	-2.991108	0.447240	-1.424414
20	6	0	1.036966	2.245117	1.701832
21	9	0	1.999352	1.728701	2.485128
22	8	0	-2.711934	-0.198994	3.080413
23	6	0	1.871833	-0.851801	0.919687
24	24	0	2.922130	-0.773075	-0.840076
25	6	0	4.280239	-1.840360	-0.036911
26	8	0	5.107801	-2.487567	0.439381
27	9	0	1.568855	2.525104	0.494738
28	9	0	0.631446	3.406184	2.252881
29	8	0	2.472665	-1.156017	2.052283
30	6	0	1.726284	-1.311780	3.294339
31	6	0	2.003986	-2.356638	-1.345248
32	8	0	1.436528	-3.320629	-1.632925
33	6	0	1.537843	0.261248	-1.603246
34	8	0	0.673611	0.866765	-2.080312
35	6	0	3.820288	0.772320	-0.191580
36	8	0	4.380493	1.691006	0.225672
37	6	0	3.873288	-0.723524	-2.463727
38	8	0	4.456476	-0.691688	-3.464299
39	7	0	-1.210943	3.512211	-1.371029
40	6	0	-1.317966	3.309157	-2.822125
41	6	0	-2.481099	4.009374	-0.821023
42	6	0	-0.119232	4.449523	-1.069978
43	1	0	-4.573474	-0.141066	1.537223
44	1	0	-2.012124	0.702899	-1.816027
45	1	0	-3.867749	0.204381	-3.370201

46	1	0	-6.418908	-0.699536	-0.022530
47	1	0	-6.080353	-0.510034	-2.478308
48	1	0	-1.174699	-2.031661	-1.743446
49	1	0	-2.080313	-2.734988	2.407883
50	1	0	-3.675106	-4.522302	1.754771
51	1	0	-2.781111	-3.804776	-2.395768
52	1	0	-4.032676	-5.056093	-0.647806
53	1	0	-0.933464	2.077341	-0.304727
54	1	0	-2.389109	4.119604	0.264192
55	1	0	-3.275697	3.287249	-1.029774
56	1	0	-2.764194	4.984193	-1.250956
57	1	0	0.821285	4.049174	-1.456809
58	1	0	-0.024747	4.570142	0.012381
59	1	0	-0.296559	5.440338	-1.520299
60	1	0	-0.393772	2.863923	-3.196795
61	1	0	-1.500201	4.258601	-3.352998
62	1	0	-2.146769	2.630428	-3.039127
63	1	0	2.469675	-1.602478	4.035221
64	1	0	0.971857	-2.091975	3.174704
65	1	0	1.254629	-0.368240	3.567260

INT1-H

HF=-2178.0181078 hartree

Zero-point correction= 0.469699
(Hartree/Particle)

Thermal correction to Energy= 0.511728

Thermal correction to Enthalpy= 0.512673

Thermal correction to Gibbs Free Energy= 0.392483

Sum of electronic and zero-point Energies= -2177.548409

Sum of electronic and thermal Energies= -2177.506379

Sum of electronic and thermal Enthalpies= -2177.505435

Sum of electronic and thermal Free Energies= -2177.625624

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.811293	0.420727	0.236263
2	7	0	1.554643	-0.834877	-0.514047
3	6	0	0.671564	-1.368726	0.476243
4	6	0	0.213697	-2.794276	0.209313
5	9	0	-0.389899	-2.861121	-0.988508
6	9	0	1.255198	-3.645112	0.201989
7	9	0	-0.663304	-3.212868	1.144336
8	6	0	2.212116	-0.206774	1.621735
9	8	0	2.993649	0.160678	2.460727
10	8	0	1.476483	-1.357424	1.739941
11	6	0	0.348850	0.892244	0.495665
12	6	0	-0.369696	-0.244725	0.630464
13	6	0	2.788592	1.361813	-0.403072
14	6	0	4.539515	3.150340	-1.660988
15	6	0	3.493780	2.305220	0.354693
16	6	0	2.955781	1.325059	-1.794303
17	6	0	3.829428	2.215470	-2.419689
18	6	0	4.368060	3.192893	-0.275340
19	1	0	3.364727	2.339294	1.429709
20	1	0	2.393724	0.602944	-2.377471
21	1	0	3.953645	2.179374	-3.498290
22	1	0	4.914113	3.919687	0.319329
23	1	0	5.220092	3.843324	-2.147631
24	6	0	-0.093727	2.276617	0.694228
25	6	0	-1.025732	4.905400	1.052508

26	6	0	0.291054	3.299286	-0.193568
27	6	0	-0.950300	2.597560	1.764208
28	6	0	-1.411298	3.900235	1.941975
29	6	0	-0.177323	4.599350	-0.015266
30	1	0	0.933391	3.069780	-1.035020
31	1	0	-1.246462	1.826283	2.466619
32	1	0	-2.069169	4.128754	2.775425
33	1	0	0.118606	5.374950	-0.715738
34	1	0	-1.384882	5.921399	1.189269
35	1	0	2.441394	-1.386614	-0.534005
36	7	0	4.195324	-2.155159	-0.328635
37	6	0	4.356250	-2.836936	0.959199
38	1	0	3.531736	-3.538262	1.107669
39	1	0	4.330641	-2.101245	1.768223
40	1	0	5.309742	-3.391221	1.018719
41	6	0	4.183455	-3.114668	-1.435720
42	1	0	4.025334	-2.582165	-2.379329
43	1	0	3.359351	-3.820599	-1.295087
44	1	0	5.127012	-3.684180	-1.509708
45	6	0	5.234644	-1.139082	-0.515803
46	1	0	5.068607	-0.610424	-1.458783
47	1	0	6.248415	-1.577662	-0.528530
48	1	0	5.179629	-0.406645	0.295224
49	6	0	-1.819096	-0.417885	0.850808
50	8	0	-2.194302	-0.773755	2.061392
51	6	0	-1.271742	-0.960342	3.175261
52	1	0	-1.892417	-0.906496	4.068223
53	1	0	-0.511044	-0.178637	3.182173
54	1	0	-0.802438	-1.938899	3.088217
55	24	0	-3.161872	-0.269501	-0.646998
56	6	0	-3.104167	1.639340	-0.667684
57	8	0	-3.123042	2.790422	-0.720550

58	6	0	-1.770454	-0.293447	-1.950950
59	8	0	-0.963504	-0.273581	-2.774524
60	6	0	-3.267607	-2.168805	-0.604217
61	8	0	-3.346413	-3.318460	-0.554353
62	6	0	-4.439842	-0.235953	-2.044865
63	8	0	-5.226885	-0.227211	-2.892048
64	6	0	-4.540587	-0.181226	0.660303
65	8	0	-5.382931	-0.116268	1.445513

INT2-H

HF=-2003.5103522 hartree

Zero-point correction= 0.346798
(Hartree/Particle)

Thermal correction to Energy= 0.381714

Thermal correction to Enthalpy= 0.382658

Thermal correction to Gibbs Free Energy= 0.278753

Sum of electronic and zero-point Energies= -2003.163554

Sum of electronic and thermal Energies= -2003.128638

Sum of electronic and thermal Enthalpies= -2003.127694

Sum of electronic and thermal Free Energies= -2003.231599

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.110316	0.217534	-0.404785
2	6	0	-0.021315	-0.544236	-0.673027
3	6	0	-0.402982	-1.951052	-0.133031

4	6	0	-2.156287	-0.759830	0.243809
5	6	0	-1.489754	-1.067030	1.612081
6	8	0	-1.768745	-0.717339	2.725261
7	8	0	-0.385674	-1.839466	1.318561
8	7	0	-1.822468	-2.067561	-0.388914
9	1	0	-2.020367	-2.034353	-1.389611
10	6	0	0.387815	-3.179948	-0.576698
11	9	0	0.005721	-3.500576	-1.836122
12	9	0	1.712975	-2.945393	-0.606743
13	9	0	0.155811	-4.226950	0.214576
14	6	0	-3.617237	-0.412896	0.184170
15	6	0	-6.351933	0.148947	-0.066607
16	6	0	-4.487886	-0.664334	1.251230
17	6	0	-4.127265	0.115477	-1.010761
18	6	0	-5.487270	0.393554	-1.137203
19	6	0	-5.849356	-0.379346	1.124130
20	1	0	-4.106324	-1.068892	2.180920
21	1	0	-3.455772	0.319130	-1.840489
22	1	0	-5.869444	0.804804	-2.066998
23	1	0	-6.516406	-0.572586	1.959290
24	1	0	-7.411267	0.370396	-0.160686
25	6	0	-1.246540	1.672781	-0.459924
26	6	0	-1.419787	4.480810	-0.484678
27	6	0	-2.055676	2.350242	0.473134
28	6	0	-0.533031	2.429402	-1.407497
29	6	0	-0.617826	3.820295	-1.418216
30	6	0	-2.135431	3.740020	0.461256
31	1	0	-2.595816	1.788879	1.227182
32	1	0	0.089043	1.933014	-2.143720
33	1	0	-0.054525	4.384992	-2.154871
34	1	0	-2.754088	4.246199	1.196408
35	1	0	-1.486243	5.564835	-0.492766

36	6	0	1.362438	-0.126400	-0.977933
37	8	0	1.715589	-0.182812	-2.245419
38	6	0	0.810464	-0.624135	-3.302403
39	1	0	1.365527	-0.471028	-4.226333
40	1	0	-0.101359	-0.024546	-3.297224
41	1	0	0.577298	-1.679840	-3.166672
42	24	0	2.681592	0.523776	0.415247
43	6	0	2.721620	2.161324	-0.551050
44	8	0	2.746737	3.143004	-1.156092
45	6	0	3.965051	1.208701	1.628567
46	8	0	4.756866	1.636602	2.353653
47	6	0	4.068137	-0.167525	-0.692477
48	8	0	4.906141	-0.594479	-1.359026
49	6	0	1.294574	1.152526	1.549861
50	8	0	0.475781	1.514917	2.277147
51	6	0	2.651736	-1.115974	1.392257
52	8	0	2.672879	-2.084910	2.016093

TS3

HF=-2003.4869639 hartree

NIMAG=1 (-351.1719 cm^{-1})

Zero-point correction= 0.344919
(Hartree/Particle)

Thermal correction to Energy= 0.379934

Thermal correction to Enthalpy= 0.380878

Thermal correction to Gibbs Free Energy= 0.276676

Sum of electronic and zero-point Energies= -2003.157499

Sum of electronic and thermal Energies= -2003.122484

Sum of electronic and thermal Enthalpies= -2003.121540

Sum of electronic and thermal Free Energies= -2003.225742

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.930292	3.778667	-0.441219
2	6	0	1.210837	4.487087	0.527465
3	6	0	0.476298	3.792943	1.490473
4	6	0	0.462286	2.398124	1.487468
5	6	0	1.182643	1.678333	0.520712
6	6	0	1.920437	2.386852	-0.445952
7	6	0	1.143400	0.211149	0.500101
8	6	0	0.047557	-0.606558	0.769541
9	6	0	0.480510	-1.924876	0.372021
10	8	0	0.375816	-1.771120	-1.418342
11	6	0	1.293875	-1.016939	-1.780316
12	6	0	2.230337	-0.651654	0.063485
13	7	0	1.841764	-1.960152	0.475730
14	6	0	-1.372682	-0.210051	0.972552
15	24	0	-2.664616	0.504178	-0.422498
16	6	0	-2.613052	-1.104714	-1.449055
17	8	0	-2.633491	-2.050603	-2.107619
18	6	0	-0.271098	-3.219491	0.592080
19	9	0	0.183774	-4.184679	-0.221599
20	6	0	3.672016	-0.318154	-0.010394
21	6	0	4.475903	-0.876122	-1.015579
22	6	0	5.843702	-0.600477	-1.058069
23	6	0	6.419865	0.239009	-0.102241
24	6	0	5.624423	0.800647	0.901286
25	6	0	4.259352	0.523253	0.948885
26	8	0	1.792031	-0.527859	-2.756205
27	9	0	-0.095992	-3.643833	1.863689
28	9	0	-1.588566	-3.064267	0.388855

29	8	0	-1.808166	-0.360111	2.207648
30	6	0	-0.970692	-0.819470	3.312725
31	6	0	-2.732426	2.100572	0.606412
32	8	0	-2.783896	3.054932	1.252886
33	6	0	-3.921893	1.225259	-1.637657
34	8	0	-4.698193	1.677209	-2.366403
35	6	0	-4.084127	-0.221054	0.618505
36	8	0	-4.951278	-0.664426	1.236160
37	6	0	-1.280596	1.181238	-1.530016
38	8	0	-0.493841	1.583566	-2.272525
39	1	0	2.333633	-2.757323	0.080880
40	1	0	4.028424	-1.505890	-1.777437
41	1	0	3.643272	0.955845	1.730616
42	1	0	6.067776	1.451464	1.649488
43	1	0	6.455580	-1.035296	-1.843098
44	1	0	7.483452	0.457096	-0.139368
45	1	0	2.451869	1.842452	-1.218966
46	1	0	-0.105084	1.869338	2.246268
47	1	0	-0.090822	4.332535	2.242768
48	1	0	2.493268	4.312700	-1.201134
49	1	0	1.220793	5.573228	0.527850
50	1	0	-1.560792	-0.620964	4.206087
51	1	0	-0.030167	-0.266803	3.335679
52	1	0	-0.780552	-1.886721	3.207633

TS1-Ag

HF=-2846.1270972 hartree

NIMAG=1 (-352.2148 cm^{-1})

Zero-point correction= 0.688243
(Hartree/Particle)

Thermal correction to Energy= 0.745895

Thermal correction to Enthalpy= 0.746839

Thermal correction to Gibbs Free Energy= 0.586179

Sum of electronic and zero-point Energies= -2845.438855

Sum of electronic and thermal Energies= -2845.381202

Sum of electronic and thermal Enthalpies= -2845.380258

Sum of electronic and thermal Free Energies= -2845.540918

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.227577	-5.343696	1.568292
2	6	0	-2.408800	-3.821879	1.555135
3	8	0	-1.496136	-3.326555	0.543422
4	6	0	-0.705573	-4.408342	0.000860
5	6	0	-0.788881	-5.512556	1.050417
6	47	0	-1.516388	-0.986561	0.050941
7	8	0	-3.999582	-1.560080	-0.593111
8	6	0	-3.924279	-2.567725	-1.621249
9	6	0	-3.563776	-1.805688	-2.911509
10	6	0	-4.021789	-0.347996	-2.618884
11	6	0	-4.658028	-0.445559	-1.223170
12	7	0	-0.626877	0.526709	-1.475539
13	6	0	0.303549	0.180360	-2.297904
14	6	0	1.327858	0.912072	0.557443
15	6	0	0.830770	2.041492	0.257040
16	6	0	-0.492204	1.927652	-1.305624
17	6	0	0.470486	2.384495	-2.311246

18	8	0	1.012716	1.172888	-2.858051
19	6	0	0.564040	-1.202662	-2.835722
20	9	0	-0.142825	-1.411124	-3.968275
21	6	0	-1.659827	2.735832	-0.883915
22	6	0	-1.892652	4.007846	-1.430720
23	6	0	-2.981944	4.772609	-1.009404
24	6	0	-3.856514	4.287341	-0.036084
25	6	0	-3.622785	3.028716	0.526045
26	6	0	-2.531714	2.265799	0.112985
27	6	0	1.809345	-0.312197	0.860017
28	8	0	0.858785	-1.040875	1.531233
29	6	0	1.171917	-2.272088	2.181018
30	6	0	0.957336	3.445726	0.619104
31	6	0	0.025076	4.081596	1.459254
32	6	0	0.182354	5.425249	1.793084
33	6	0	1.264615	6.153269	1.288791
34	6	0	2.194734	5.530564	0.451492
35	6	0	2.042977	4.186013	0.115064
36	8	0	0.886474	3.456770	-2.677207
37	9	0	1.862603	-1.367730	-3.123937
38	9	0	0.195350	-2.151309	-1.952568
39	24	0	3.851816	-0.799872	0.368935
40	6	0	3.756121	0.261693	-1.206047
41	8	0	3.810721	0.939443	-2.140290
42	6	0	5.611564	-1.166168	-0.098460
43	8	0	6.711030	-1.404119	-0.394214
44	6	0	4.174513	-1.785872	1.946315
45	8	0	4.465071	-2.382037	2.897239
46	6	0	4.265789	0.785599	1.326813
47	8	0	4.473104	1.763194	1.907114
48	6	0	3.175760	-2.333173	-0.498668
49	8	0	2.738018	-3.285846	-0.992808

50	8	0	-2.226515	-0.450047	2.336670
51	6	0	-3.628054	-0.324002	2.680021
52	6	0	-3.671643	0.521212	3.957071
53	6	0	-2.404165	1.381904	3.820387
54	6	0	-1.420286	0.397206	3.194899
55	1	0	-0.817801	3.517962	1.844082
56	1	0	2.757098	3.694549	-0.537342
57	1	0	3.038189	6.091932	0.059446
58	1	0	-0.541148	5.905159	2.446376
59	1	0	1.383141	7.201634	1.548745
60	1	0	-1.214463	4.402967	-2.177442
61	1	0	-2.334716	1.316478	0.600784
62	1	0	-4.286258	2.644751	1.296346
63	1	0	-3.143827	5.753834	-1.446883
64	1	0	-4.703566	4.884289	0.289484
65	1	0	0.207866	-2.694942	2.463407
66	1	0	1.777362	-2.093773	3.073564
67	1	0	1.691636	-2.961279	1.512491
68	1	0	-4.044036	-1.328768	2.798808
69	1	0	-4.143584	0.168197	1.845866
70	1	0	-0.936562	-0.233223	3.951980
71	1	0	-0.647176	0.858824	2.578979
72	1	0	-3.600283	-0.119450	4.843261
73	1	0	-4.590760	1.109106	4.033006
74	1	0	-2.046686	1.781316	4.773471
75	1	0	-2.582546	2.222372	3.139136
76	1	0	-3.177782	-3.296367	-1.301347
77	1	0	-4.902325	-3.062621	-1.708961
78	1	0	-4.497150	0.434656	-0.598662
79	1	0	-5.736792	-0.652885	-1.284421
80	1	0	-3.160352	0.325200	-2.586803
81	1	0	-4.726744	0.034420	-3.362221

82	1	0	-4.065754	-2.236094	-3.782705
83	1	0	-2.487035	-1.841543	-3.094837
84	1	0	-1.142695	-4.725813	-0.956249
85	1	0	0.301561	-4.028486	-0.180416
86	1	0	-2.133628	-3.356462	2.508488
87	1	0	-3.418881	-3.498372	1.287360
88	1	0	-0.066241	-5.324319	1.852950
89	1	0	-0.592151	-6.504169	0.633837
90	1	0	-2.934858	-5.818570	0.878817
91	1	0	-2.381784	-5.770462	2.563096

INT1-Ag

HF=-2846.1428652 hartree

Zero-point correction= 0.690068
(Hartree/Particle)

Thermal correction to Energy= 0.747971

Thermal correction to Enthalpy= 0.748915

Thermal correction to Gibbs Free Energy= 0.586432

Sum of electronic and zero-point Energies= -2845.452797

Sum of electronic and thermal Energies= -2845.394894

Sum of electronic and thermal Enthalpies= -2845.393950

Sum of electronic and thermal Free Energies= -2845.556434

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.585427	-4.246235	-2.077886

2	6	0	3.291135	-2.772132	-1.776404
3	8	0	2.341099	-2.773398	-0.680256
4	6	0	1.985666	-4.128505	-0.326787
5	6	0	2.317514	-4.952032	-1.567656
6	47	0	1.422758	-0.627352	-0.136701
7	8	0	3.948338	-0.284836	0.510975
8	6	0	4.437979	-1.299986	1.412684
9	6	0	4.366558	-0.695265	2.838510
10	6	0	3.957481	0.778773	2.596275
11	6	0	4.271319	0.977787	1.113381
12	7	0	0.293236	0.820024	1.371257
13	6	0	-0.128554	0.529576	2.533797
14	6	0	-1.455678	0.421099	-0.700538
15	6	0	-1.365563	1.670902	-0.286266
16	6	0	-0.458743	2.021938	0.933101
17	6	0	-1.375740	2.302158	2.129205
18	8	0	-1.093807	1.298114	3.092039
19	6	0	0.374761	-0.596938	3.415050
20	9	0	1.030890	-0.080364	4.470614
21	6	0	0.528185	3.160913	0.657341
22	6	0	0.509095	4.366336	1.364143
23	6	0	1.423123	5.378849	1.054012
24	6	0	2.361902	5.196385	0.039394
25	6	0	2.383923	3.990580	-0.669150
26	6	0	1.473507	2.980147	-0.362905
27	6	0	-1.566191	-0.845718	-1.045120
28	8	0	-0.578389	-1.268613	-1.940776
29	6	0	-0.623669	-2.574716	-2.488754
30	6	0	-2.209342	2.769275	-0.856299
31	6	0	-1.668293	3.877292	-1.529503
32	6	0	-2.503760	4.854738	-2.074020
33	6	0	-3.891481	4.744527	-1.955437

34	6	0	-4.440850	3.645392	-1.289969
35	6	0	-3.606452	2.669562	-0.744657
36	8	0	-2.199175	3.140447	2.331955
37	9	0	-0.649730	-1.330810	3.866117
38	9	0	1.222681	-1.393945	2.747288
39	24	0	-3.156201	-2.008942	-0.056541
40	6	0	-3.387387	-0.627797	1.206286
41	8	0	-3.594496	0.191814	2.000279
42	6	0	-4.474719	-2.913679	0.874279
43	8	0	-5.296655	-3.487894	1.467135
44	6	0	-3.190019	-3.502822	-1.215074
45	8	0	-3.312035	-4.458583	-1.861011
46	6	0	-4.259802	-1.066611	-1.271951
47	8	0	-4.871471	-0.453677	-2.039125
48	6	0	-1.676931	-2.680930	0.876295
49	8	0	-0.707215	-3.041828	1.404108
50	8	0	2.150427	0.339888	-2.332517
51	6	0	3.485846	0.820297	-2.611226
52	6	0	3.399934	1.560052	-3.952682
53	6	0	1.923132	1.985514	-4.004669
54	6	0	1.230877	0.789924	-3.356021
55	1	0	-0.594402	3.969474	-1.643751
56	1	0	-4.032021	1.820040	-0.220873
57	1	0	-5.518863	3.548238	-1.191718
58	1	0	-2.067286	5.700699	-2.598810
59	1	0	-4.539128	5.506651	-2.380532
60	1	0	-0.224252	4.540448	2.142721
61	1	0	1.482918	2.056887	-0.930267
62	1	0	3.106090	3.839953	-1.466475
63	1	0	1.391828	6.312272	1.608422
64	1	0	3.067816	5.985643	-0.202255
65	1	0	0.278204	-2.665582	-3.099518

66	1	0	-1.506509	-2.716723	-3.121188
67	1	0	-0.605480	-3.343031	-1.709485
68	1	0	4.166985	-0.034884	-2.627946
69	1	0	3.785804	1.480376	-1.789402
70	1	0	1.065942	-0.026028	-4.071550
71	1	0	0.283392	1.021417	-2.867668
72	1	0	3.623959	0.876886	-4.779767
73	1	0	4.097573	2.400773	-4.008215
74	1	0	1.564281	2.180237	-5.019158
75	1	0	1.758244	2.886702	-3.402688
76	1	0	3.810990	-2.180609	1.264250
77	1	0	5.472243	-1.548432	1.137910
78	1	0	3.667359	1.742886	0.623241
79	1	0	5.337859	1.201927	0.954354
80	1	0	2.884371	0.912521	2.761923
81	1	0	4.491329	1.483853	3.239718
82	1	0	5.338328	-0.763753	3.335733
83	1	0	3.633187	-1.210110	3.461807
84	1	0	2.586929	-4.443350	0.538114
85	1	0	0.933063	-4.131608	-0.043091
86	1	0	2.822254	-2.252037	-2.618854
87	1	0	4.170796	-2.204094	-1.460337
88	1	0	1.508328	-4.867784	-2.302126
89	1	0	2.472641	-6.010657	-1.341913
90	1	0	4.459538	-4.586190	-1.510824
91	1	0	3.779540	-4.420336	-3.139918

TS2-Ag

HF=-2846.1282252 hartree

NIMAG=1 (-276.7417 cm^{-1})

Zero-point correction= 0.691513
(Hartree/Particle)

Thermal correction to Energy= 0.747424

Thermal correction to Enthalpy= 0.748368

Thermal correction to Gibbs Free Energy= 0.595672

Sum of electronic and zero-point Energies= -2845.436712

Sum of electronic and thermal Energies= -2845.380802

Sum of electronic and thermal Enthalpies= -2845.379857

Sum of electronic and thermal Free Energies= -2845.532553

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.497477	1.271481	-1.431880
2	6	0	0.161482	-0.720441	-1.788107
3	6	0	0.594691	1.298793	-0.233151
4	6	0	1.193506	0.124945	-0.086513
5	7	0	-0.950946	-0.114069	-1.439992
6	6	0	0.248879	-2.232527	-1.952032
7	8	0	0.916485	-0.007579	-2.738116
8	6	0	0.449767	1.298513	-2.629119
9	8	0	0.842575	2.187246	-3.336197
10	47	0	-2.203288	-0.841590	0.292629
11	8	0	-4.668463	-0.739147	-0.434177
12	8	0	-2.785605	-2.976511	1.471414
13	8	0	-2.269182	0.291896	2.462192
14	6	0	-2.005743	-4.107855	1.025842
15	1	0	-1.964560	-4.075122	-0.061751
16	1	0	-2.514928	-5.029061	1.342063
17	6	0	-2.500233	-2.886617	2.883956

18	1	0	-2.838120	-1.908884	3.225514
19	1	0	-3.057100	-3.677531	3.406005
20	6	0	-0.981519	-3.101166	2.984350
21	1	0	-0.465388	-2.139412	2.936020
22	1	0	-0.701148	-3.594657	3.919243
23	6	0	-0.644426	-3.949733	1.724615
24	1	0	0.057555	-3.416795	1.078589
25	1	0	-0.205789	-4.920312	1.972648
26	6	0	-4.838994	0.190797	-1.524005
27	1	0	-4.312941	1.108550	-1.261695
28	1	0	-5.911202	0.408795	-1.637170
29	6	0	-5.005444	-2.025538	-0.990873
30	1	0	-4.624018	-2.783597	-0.304407
31	1	0	-6.100285	-2.110297	-1.056486
32	6	0	-4.278422	-0.528223	-2.765204
33	1	0	-4.856563	-0.286363	-3.661646
34	1	0	-3.240403	-0.230995	-2.935536
35	6	0	-4.359975	-2.035313	-2.387951
36	1	0	-3.357530	-2.469593	-2.340608
37	1	0	-4.948932	-2.620258	-3.100354
38	6	0	-1.134167	0.603658	3.295297
39	1	0	-1.130176	-0.057978	4.174097
40	1	0	-0.238837	0.413038	2.701528
41	6	0	-3.418770	1.043334	2.921572
42	1	0	-4.125263	0.355874	3.401009
43	1	0	-3.894711	1.469603	2.034515
44	6	0	-2.879498	2.110554	3.898707
45	1	0	-3.132913	1.845035	4.929994
46	1	0	-3.297130	3.100594	3.695706
47	6	0	-1.352184	2.059916	3.691087
48	1	0	-1.039526	2.717786	2.874415
49	1	0	-0.790793	2.341972	4.586237

50	6	0	2.179571	-0.578172	0.561854
51	8	0	1.680015	-1.195120	1.655327
52	6	0	2.485667	-2.079517	2.445461
53	1	0	1.863041	-2.352287	3.298205
54	1	0	3.392525	-1.581940	2.794312
55	1	0	2.739377	-2.975289	1.874857
56	24	0	4.182346	-0.408809	-0.171247
57	6	0	4.792913	-2.066440	0.498841
58	8	0	5.250614	-3.073207	0.844616
59	6	0	4.488315	0.466349	1.477724
60	8	0	4.640705	0.993164	2.497150
61	6	0	5.929359	-0.122801	-0.748220
62	8	0	7.024068	0.054209	-1.094208
63	6	0	3.688725	-1.310526	-1.765896
64	8	0	3.409229	-1.871000	-2.736399
65	6	0	3.740307	1.246787	-1.006623
66	8	0	3.546473	2.241719	-1.558237
67	9	0	0.612982	-2.562006	-3.197362
68	9	0	-0.960752	-2.793553	-1.712989
69	9	0	1.118690	-2.801652	-1.096737
70	6	0	0.983312	2.553973	0.438006
71	6	0	1.835780	4.920328	1.721846
72	6	0	0.842904	3.806042	-0.188613
73	6	0	1.575607	2.513786	1.715376
74	6	0	1.995624	3.681168	2.349232
75	6	0	1.263728	4.973410	0.448452
76	1	0	0.428799	3.865097	-1.188710
77	1	0	1.708956	1.557897	2.210408
78	1	0	2.449123	3.620493	3.334840
79	1	0	1.149930	5.927695	-0.058762
80	1	0	2.160437	5.831574	2.216289
81	6	0	-1.627058	2.265685	-1.377241

82	6	0	-3.849360	3.975466	-1.246885
83	6	0	-2.166027	2.813747	-2.546468
84	6	0	-2.212223	2.577827	-0.142910
85	6	0	-3.315476	3.429290	-0.076310
86	6	0	-3.272733	3.664043	-2.480563
87	1	0	-1.719413	2.584111	-3.507984
88	1	0	-1.800109	2.153101	0.764483
89	1	0	-3.753475	3.670262	0.888287
90	1	0	-3.682439	4.082904	-3.395247
91	1	0	-4.707257	4.640029	-1.197628

4r

HF=-1814.9967867 hartree

Zero-point correction= 0.331317
(Hartree/Particle)

Thermal correction to Energy= 0.364649

Thermal correction to Enthalpy= 0.365593

Thermal correction to Gibbs Free Energy= 0.263963

Sum of electronic and zero-point Energies= -1814.665470

Sum of electronic and thermal Energies= -1814.632138

Sum of electronic and thermal Enthalpies= -1814.631194

Sum of electronic and thermal Free Energies= -1814.732824

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.403012	2.020491	0.481054
2	6	0	0.078439	0.692535	0.713010
3	6	0	1.263617	-0.076399	0.472192

4	6	0	2.270398	0.822979	0.103150
5	7	0	1.716588	2.077736	0.089728
6	1	0	2.233875	2.936346	-0.042768
7	6	0	-0.470967	3.210987	0.386397
8	9	0	-1.000769	3.376579	-0.853551
9	9	0	-1.518246	3.117900	1.241573
10	9	0	0.209765	4.345917	0.668820
11	6	0	3.691706	0.618041	-0.203662
12	6	0	6.420500	0.257298	-0.774585
13	6	0	4.447700	-0.337404	0.498285
14	6	0	4.323043	1.388833	-1.195763
15	6	0	5.678521	1.211960	-1.474453
16	6	0	5.799112	-0.517239	0.210210
17	1	0	3.971781	-0.930991	1.271594
18	1	0	3.745333	2.109937	-1.768119
19	1	0	6.150965	1.812733	-2.246458
20	1	0	6.370822	-1.258268	0.761803
21	1	0	7.474690	0.116204	-0.995440
22	6	0	1.364583	-1.546528	0.532930
23	6	0	1.561230	-4.351069	0.632567
24	6	0	0.894903	-2.258928	1.648208
25	6	0	1.927263	-2.263735	-0.537081
26	6	0	2.027667	-3.652760	-0.485332
27	6	0	0.991221	-3.650026	1.697054
28	1	0	0.460679	-1.721369	2.485752
29	1	0	2.279537	-1.721643	-1.409402
30	1	0	2.463063	-4.191916	-1.322199
31	1	0	0.622481	-4.184500	2.568185
32	1	0	1.636701	-5.434165	0.670213
33	6	0	-1.284053	0.147267	0.937984
34	8	0	-1.719440	0.175849	2.176716
35	6	0	-0.960335	0.753583	3.281015

36	1	0	0.081578	0.432004	3.246002
37	1	0	-1.452338	0.387548	4.180900
38	1	0	-1.024591	1.839677	3.218462
39	24	0	-2.467607	-0.500627	-0.570066
40	6	0	-3.767153	-1.022301	0.714974
41	8	0	-4.562981	-1.349838	1.483867
42	6	0	-1.771084	-2.277585	-0.506023
43	8	0	-1.420125	-3.375288	-0.495663
44	6	0	-3.593778	-1.017503	-1.997791
45	8	0	-4.287706	-1.328731	-2.870250
46	6	0	-1.121705	0.001615	-1.817760
47	8	0	-0.311185	0.289995	-2.587493
48	6	0	-3.253208	1.230712	-0.607868
49	8	0	-3.767145	2.263863	-0.623290

4r-Ag

HF=-2657.6437016 hartree

Zero-point correction= (Hartree/Particle)	0.678056
Thermal correction to Energy=	0.732402
Thermal correction to Enthalpy=	0.733347
Thermal correction to Gibbs Free Energy=	0.580732
Sum of electronic and zero-point Energies=	-2656.965645
Sum of electronic and thermal Energies=	-2656.911299
Sum of electronic and thermal Enthalpies=	-2656.910355
Sum of electronic and thermal Free Energies=	-2657.062969

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.760738	3.777998	0.890733
2	6	0	2.595172	4.935409	0.126581
3	6	0	1.608384	4.967773	-0.863988
4	6	0	0.799171	3.853468	-1.085975
5	6	0	0.961303	2.678896	-0.328841
6	6	0	1.954796	2.659090	0.666216
7	6	0	0.092237	1.510855	-0.587222
8	6	0	-1.317836	1.486208	-0.679323
9	6	0	-1.663041	0.151944	-1.044075
10	6	0	-0.449461	-0.536613	-1.161731
11	7	0	0.605603	0.278363	-0.866003
12	6	0	-0.207273	-1.950082	-1.509043
13	9	0	0.677865	-2.092621	-2.540233
14	6	0	-2.251775	2.604844	-0.467081
15	6	0	-2.082520	3.499483	0.606938
16	6	0	-2.972814	4.552323	0.809377
17	6	0	-4.061678	4.733155	-0.050694
18	6	0	-4.244238	3.852625	-1.118705
19	6	0	-3.345453	2.805327	-1.328285
20	6	0	-3.025109	-0.414795	-1.172433
21	24	0	-4.123176	-0.932818	0.504258
22	6	0	-3.029619	0.195034	1.593932
23	8	0	-2.410222	0.792439	2.362556
24	47	0	2.615327	-0.471595	-0.366372
25	8	0	4.780682	0.651947	-0.308452
26	6	0	5.050105	1.822340	-1.124653
27	6	0	6.033096	2.693352	-0.320195

28	6	0	6.558666	1.732300	0.763422
29	6	0	5.344536	0.841808	1.004653
30	9	0	-1.339921	-2.598767	-1.863091
31	9	0	0.349237	-2.676764	-0.482965
32	8	0	4.042872	-2.388076	0.171805
33	6	0	3.360404	-3.658928	0.096139
34	6	0	3.375144	-4.028991	-1.396481
35	6	0	4.599326	-3.247534	-1.956860
36	6	0	5.168733	-2.529104	-0.722325
37	8	0	-3.273706	-0.529712	-2.458449
38	6	0	-4.516014	-1.053253	-2.973893
39	6	0	-5.270319	-2.184138	-0.327062
40	8	0	-6.007006	-2.983335	-0.726300
41	6	0	-5.343959	0.464198	0.087783
42	8	0	-6.109753	1.282984	-0.187066
43	6	0	-5.033331	-1.339405	2.096709
44	8	0	-5.599346	-1.584448	3.077644
45	6	0	-2.887778	-2.348181	0.776834
46	8	0	-2.160219	-3.227816	0.949855
47	8	0	2.130256	-0.286091	2.295506
48	6	0	0.738520	-0.205965	2.646789
49	6	0	0.300537	-1.664437	2.775017
50	6	0	1.556471	-2.351962	3.365883
51	6	0	2.699254	-1.339803	3.093664
52	1	0	2.363465	-3.525302	0.514403
53	1	0	3.915728	-4.389010	0.701755
54	1	0	5.557342	-1.527857	-0.908105
55	1	0	5.935965	-3.137883	-0.222675
56	1	0	4.278813	-2.517327	-2.706750
57	1	0	5.343101	-3.901267	-2.421001
58	1	0	2.451941	-3.693930	-1.873478
59	1	0	3.462815	-5.109521	-1.540410

60	1	0	0.226672	0.347076	1.858339
61	1	0	0.628177	0.336457	3.598832
62	1	0	3.530624	-1.756191	2.521676
63	1	0	3.083872	-0.914793	4.031708
64	1	0	-0.587811	-1.782380	3.402578
65	1	0	0.073012	-2.061893	1.784807
66	1	0	1.748037	-3.317711	2.888917
67	1	0	1.448501	-2.530899	4.440058
68	1	0	5.473925	1.462549	-2.067746
69	1	0	4.106879	2.338911	-1.325883
70	1	0	5.571241	-0.150944	1.401545
71	1	0	4.605288	1.324105	1.658310
72	1	0	7.391366	1.131945	0.379697
73	1	0	6.891016	2.248673	1.668583
74	1	0	5.499104	3.529812	0.140770
75	1	0	6.829316	3.103396	-0.947428
76	1	0	-4.505304	-0.814704	-4.037260
77	1	0	-5.364532	-0.573741	-2.484336
78	1	0	-4.542978	-2.134130	-2.831157
79	1	0	-1.251826	3.350621	1.289170
80	1	0	-3.483313	2.138030	-2.173935
81	1	0	-5.086247	3.980415	-1.793911
82	1	0	-2.823417	5.228177	1.647658
83	1	0	-4.758871	5.550660	0.112008
84	1	0	2.088729	1.776799	1.282058
85	1	0	0.030216	3.883118	-1.852200
86	1	0	1.468925	5.862311	-1.465386
87	1	0	3.514075	3.744999	1.673850
88	1	0	3.223455	5.804257	0.303235

4s+Cr(CO)5+HCF3

HF=-1891.4808706 hartree

Zero-point correction= 0.358331
(Hartree/Particle)

Thermal correction to Energy= 0.394591

Thermal correction to Enthalpy= 0.395535

Thermal correction to Gibbs Free Energy= 0.285010

Sum of electronic and zero-point Energies= -1891.122540

Sum of electronic and thermal Energies= -1891.086279

Sum of electronic and thermal Enthalpies= -1891.085335

Sum of electronic and thermal Free Energies= -1891.195861

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.220318	2.820495	0.732797
2	6	0	2.043305	1.443888	0.523077
3	6	0	2.142046	0.578705	1.625686
4	6	0	2.403659	1.075840	2.902689
5	6	0	2.572197	2.448534	3.100184
6	6	0	2.480213	3.318611	2.009458
7	6	0	1.785340	0.894990	-0.826041
8	6	0	2.507411	-0.139533	-1.412817
9	7	0	1.911546	-0.423936	-2.631684
10	6	0	0.857177	0.397507	-2.853359
11	6	0	0.732875	1.236921	-1.753748
12	6	0	3.683986	-0.891968	-0.960309
13	6	0	3.782234	-2.273795	-1.203051
14	6	0	4.907712	-2.989590	-0.793169
15	6	0	5.948256	-2.340569	-0.124073

16	6	0	5.856897	-0.967810	0.127995
17	6	0	4.739507	-0.247719	-0.290173
18	6	0	-0.377161	2.185918	-1.665963
19	8	0	-1.168784	2.406479	-2.578551
20	8	0	-0.474980	2.782352	-0.464878
21	6	0	-1.574667	3.692738	-0.291560
22	9	0	-3.939250	1.274744	-1.087834
23	6	0	-3.300905	0.448762	-1.925049
24	9	0	-2.179494	-0.009483	-1.261627
25	24	0	-2.145278	-1.097745	0.757429
26	6	0	-2.002182	-2.000775	2.349922
27	8	0	-1.903406	-2.571903	3.355701
28	9	0	-4.075455	-0.611412	-2.161678
29	6	0	-2.910653	-2.634183	-0.074836
30	8	0	-3.375092	-3.579820	-0.543327
31	6	0	-0.405677	-1.723986	0.262669
32	8	0	0.622364	-2.174430	0.001455
33	6	0	-3.901176	-0.526146	1.243477
34	8	0	-4.957924	-0.220041	1.588089
35	6	0	-1.445800	0.487734	1.592573
36	8	0	-1.087574	1.415712	2.169487
37	1	0	2.270855	-1.096798	-3.294423
38	1	0	4.677274	0.819247	-0.103477
39	1	0	2.959869	-2.794117	-1.686455
40	1	0	4.964739	-4.057460	-0.985905
41	1	0	6.663295	-0.454112	0.644316
42	1	0	6.821951	-2.898964	0.200236
43	1	0	2.145970	3.498762	-0.111296
44	1	0	2.012366	-0.487788	1.473338
45	1	0	2.471607	0.390266	3.743335
46	1	0	2.614261	4.387665	2.152921
47	1	0	2.774254	2.837943	4.094393

48	1	0	-1.506398	4.518727	-1.004514
49	1	0	-1.485014	4.057217	0.731217
50	1	0	-2.524172	3.171058	-0.430799
51	1	0	-2.974696	0.955770	-2.829772
52	1	0	0.261180	0.347165	-3.751439

INT4

HF=-1891.4283774 hartree

Zero-point correction= 0.360071
(Hartree/Particle)

Thermal correction to Energy= 0.394557

Thermal correction to Enthalpy= 0.395501

Thermal correction to Gibbs Free Energy= 0.293150

Sum of electronic and zero-point Energies= -1891.068306

Sum of electronic and thermal Energies= -1891.033820

Sum of electronic and thermal Enthalpies= -1891.032876

Sum of electronic and thermal Free Energies= -1891.135228

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.932896	-1.960508	-0.727309
2	6	0	-3.429498	-0.916216	0.070941
3	6	0	-4.308964	0.101557	0.484306
4	6	0	-5.646322	0.081286	0.094458
5	6	0	-6.134334	-0.954995	-0.708265
6	6	0	-5.272493	-1.975989	-1.115999
7	6	0	-2.016053	-0.935131	0.479047

8	6	0	-1.141715	0.091871	0.674760
9	6	0	0.172904	-0.482793	1.076602
10	6	0	-0.093413	-1.994187	1.253561
11	7	0	-1.411084	-2.194310	0.659671
12	6	0	-1.480217	1.508041	0.381526
13	6	0	-1.851011	1.876095	-0.923519
14	6	0	-2.229367	3.185543	-1.219727
15	6	0	-2.253202	4.152623	-0.212828
16	6	0	-1.909426	3.794870	1.093961
17	6	0	-1.531502	2.485168	1.388948
18	6	0	1.129142	0.132146	1.873570
19	8	0	1.005118	1.409548	2.215505
20	6	0	2.031300	2.057166	2.994458
21	8	0	2.109230	-0.514647	2.529614
22	6	0	0.837480	-3.028721	0.629128
23	9	0	2.129401	-2.870140	1.075553
24	9	0	0.455504	-4.264704	1.002022
25	9	0	0.866072	-2.998801	-0.707389
26	8	0	3.598499	-2.227008	-1.435791
27	6	0	2.956230	-1.302379	-1.176019
28	24	0	2.064868	0.343633	-0.875349
29	6	0	0.584856	-0.265952	-1.919470
30	8	0	-0.282323	-0.666921	-2.564191
31	6	0	3.566256	0.779863	0.188460
32	8	0	4.534754	1.013286	0.777055
33	6	0	1.402912	2.129650	-0.632244
34	8	0	1.163568	3.252487	-0.538918
35	6	0	2.915369	0.973450	-2.374467
36	8	0	3.436392	1.378944	-3.330082
37	1	0	-1.983394	-2.887370	1.130171
38	1	0	-3.942072	0.902408	1.116108
39	1	0	-3.262018	-2.747588	-1.058020

40	1	0	-5.641160	-2.784854	-1.740853
41	1	0	-6.312034	0.874035	0.424611
42	1	0	-7.178026	-0.967269	-1.009861
43	1	0	-1.276242	2.212754	2.406092
44	1	0	-1.848085	1.124735	-1.705079
45	1	0	-2.506040	3.448250	-2.237303
46	1	0	-1.942243	4.536302	1.887992
47	1	0	-2.545466	5.174042	-0.441109
48	1	0	2.111167	1.594983	3.980685
49	1	0	1.693973	3.089183	3.082717
50	1	0	2.994298	2.015589	2.484806
51	1	0	2.266780	-1.393827	2.139439
52	1	0	-0.085590	-2.235858	2.329787

INT5

HF=-1891.3878958 hartree

Zero-point correction= 0.358100
(Hartree/Particle)

Thermal correction to Energy= 0.392559

Thermal correction to Enthalpy= 0.393503

Thermal correction to Gibbs Free Energy= 0.290617

Sum of electronic and zero-point Energies= -1891.029796

Sum of electronic and thermal Energies= -1890.995337

Sum of electronic and thermal Enthalpies= -1890.994393

Sum of electronic and thermal Free Energies= -1891.097279

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	1	0	-1.524456	-0.070318	2.014619
2	6	0	-1.340752	-0.014379	0.926256
3	6	0	-0.018038	-0.785627	0.747918
4	6	0	-0.350041	-1.991182	0.157303
5	6	0	-2.360895	-0.915158	0.261794
6	7	0	-1.717511	-1.998001	-0.125398
7	1	0	-2.159100	-2.797941	-0.568615
8	6	0	0.417615	-3.232589	-0.134823
9	9	0	0.700400	-3.971535	0.959946
10	9	0	1.583552	-2.990860	-0.760303
11	9	0	-0.322465	-4.034458	-0.956591
12	6	0	-3.776125	-0.688038	0.055488
13	6	0	-6.534614	-0.272034	-0.275637
14	6	0	-4.504642	-1.428766	-0.900248
15	6	0	-4.453986	0.276124	0.830805
16	6	0	-5.820775	0.476016	0.665622
17	6	0	-5.870864	-1.222831	-1.058381
18	1	0	-4.001874	-2.142349	-1.546819
19	1	0	-3.909817	0.864256	1.560903
20	1	0	-6.330132	1.218285	1.272529
21	1	0	-6.416614	-1.794874	-1.802432
22	1	0	-7.600360	-0.109616	-0.405536
23	6	0	-1.480548	1.441371	0.513029
24	6	0	-1.968995	4.101737	-0.219514
25	6	0	-1.685001	1.779102	-0.831405
26	6	0	-1.515809	2.445909	1.484695
27	6	0	-1.759744	3.770430	1.120726
28	6	0	-1.924391	3.103526	-1.195563
29	1	0	-1.665336	1.006113	-1.592884
30	1	0	-1.347867	2.190093	2.526503
31	1	0	-1.785246	4.542210	1.884701
32	1	0	-2.080982	3.352916	-2.241173

33	1	0	-2.161251	5.132723	-0.502605
34	6	0	1.221430	-0.375559	1.348306
35	8	0	1.858032	-1.514941	1.873725
36	8	0	1.082447	0.653265	2.304713
37	24	0	2.351737	0.674726	-0.531085
38	6	0	1.489119	2.342957	-0.227869
39	8	0	1.137838	3.431397	-0.066394
40	6	0	1.079609	0.071354	-1.789910
41	8	0	0.319714	-0.324026	-2.571962
42	6	0	3.394041	-0.880953	-0.784927
43	8	0	4.106225	-1.774555	-0.970111
44	6	0	3.555449	1.243711	0.815074
45	8	0	4.287872	1.631538	1.622165
46	6	0	3.342936	1.491859	-1.843737
47	8	0	3.971294	2.009517	-2.677164
48	1	0	0.692945	0.250315	3.108552
49	6	0	3.145220	-1.361201	2.459675
50	1	0	3.316046	-2.266481	3.047108
51	1	0	3.185376	-0.486117	3.115388
52	1	0	3.927607	-1.277204	1.698281

INT6

HF=-1891.3907296 hartree

Zero-point correction= 0.355013
(Hartree/Particle)

Thermal correction to Energy= 0.391261

Thermal correction to Enthalpy= 0.392205

Thermal correction to Gibbs Free Energy= 0.282395

Sum of electronic and zero-point Energies= -1891.035717

Sum of electronic and thermal Energies= -1890.999469

Sum of electronic and thermal Enthalpies= -1890.998524

Sum of electronic and thermal Free Energies= -1891.108335

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.482993	-3.042398	-1.031129
2	6	0	2.913502	-1.704874	-0.982183
3	6	0	4.244714	-1.432766	-0.620041
4	6	0	5.118419	-2.473345	-0.311211
5	6	0	4.683327	-3.801019	-0.368118
6	6	0	3.363646	-4.081305	-0.730779
7	6	0	1.992238	-0.611769	-1.313918
8	6	0	1.861758	0.667185	-0.803886
9	6	0	0.763083	1.281567	-1.528900
10	6	0	0.283374	0.340835	-2.449822
11	7	0	1.025974	-0.764771	-2.310209
12	6	0	2.595927	1.205567	0.362962
13	6	0	2.501916	0.545328	1.599176
14	6	0	3.200022	1.019473	2.710049
15	6	0	4.004692	2.156681	2.600085
16	6	0	4.108363	2.816538	1.372171
17	6	0	3.408835	2.344798	0.260810
18	6	0	0.178885	2.558806	-1.332615
19	8	0	0.878763	3.471892	-0.731588
20	6	0	0.236887	4.712584	-0.321100
21	8	0	-1.012453	2.902897	-1.720809
22	6	0	-2.848548	-0.129520	-2.401548
23	9	0	-2.922626	1.232799	-1.813892
24	9	0	-4.092014	-0.583835	-2.086412
25	9	0	-2.048717	-0.757622	-1.310599

26	8	0	-3.971345	-3.338507	0.497424
27	6	0	-3.383751	-2.355055	0.619507
28	24	0	-2.417780	-0.715755	0.865322
29	6	0	-0.777439	-1.665575	1.008680
30	8	0	0.219821	-2.235543	1.134538
31	6	0	-4.057491	0.263266	0.696575
32	8	0	-5.045183	0.856430	0.676242
33	6	0	-1.494427	0.922260	1.072006
34	8	0	-0.944221	1.925696	1.251841
35	6	0	-2.651063	-0.813634	2.682886
36	8	0	-2.794809	-0.879700	3.835254
37	1	0	0.924099	-1.592341	-2.883400
38	1	0	4.589878	-0.404891	-0.587495
39	1	0	1.447884	-3.270892	-1.268283
40	1	0	3.013666	-5.108982	-0.768302
41	1	0	6.144138	-2.247277	-0.033691
42	1	0	5.367331	-4.610441	-0.129395
43	1	0	3.490319	2.857638	-0.692102
44	1	0	1.881551	-0.341567	1.680165
45	1	0	3.114279	0.500670	3.660868
46	1	0	4.736717	3.698043	1.278240
47	1	0	4.548665	2.526036	3.465069
48	1	0	-0.059365	5.282970	-1.202335
49	1	0	1.002356	5.235440	0.248037
50	1	0	-0.629054	4.480281	0.300097
51	1	0	-1.652296	2.144773	-1.886465
52	1	0	-0.528815	0.392879	-3.160301

TS4

HF=-1891.3396009

NIMAG=1 (-1580.7649 cm^{-1})

Zero-point correction= 0.353879
(Hartree/Particle)

Thermal correction to Energy= 0.387810

Thermal correction to Enthalpy= 0.388754

Thermal correction to Gibbs Free Energy= 0.287370

Sum of electronic and zero-point Energies= -1890.994939

Sum of electronic and thermal Energies= -1890.961008

Sum of electronic and thermal Enthalpies= -1890.960064

Sum of electronic and thermal Free Energies= -1891.061448

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.891485	-3.140509	-1.207947
2	6	0	1.905550	-4.119755	-0.212690
3	6	0	1.686910	-3.758560	1.118795
4	6	0	1.462294	-2.424321	1.457013
5	6	0	1.459832	-1.437819	0.464993
6	6	0	1.673941	-1.804756	-0.871201
7	6	0	1.341082	0.026193	0.807815
8	6	0	0.068096	0.835798	0.670086
9	6	0	0.434239	2.044992	0.144791
10	7	0	1.816098	2.040176	-0.106573
11	6	0	2.404862	0.911549	0.239340
12	6	0	-1.249056	0.440328	1.163293
13	24	0	-2.429597	-0.665007	-0.475676
14	6	0	-3.477753	-1.466324	-1.764139
15	8	0	-4.145082	-1.967388	-2.576031

16	6	0	-0.324150	3.299768	-0.137945
17	9	0	0.413376	4.086497	-0.972038
18	6	0	3.817215	0.639330	0.052251
19	6	0	4.567077	1.345889	-0.910738
20	6	0	5.925056	1.088457	-1.067692
21	6	0	6.552741	0.124001	-0.272667
22	6	0	5.815128	-0.587263	0.679250
23	6	0	4.456369	-0.338337	0.841343
24	9	0	-0.579749	4.036897	0.960338
25	9	0	-1.498124	3.056233	-0.744667
26	8	0	-1.786255	1.548276	1.782960
27	6	0	-3.040619	1.415848	2.442791
28	8	0	-0.842394	-0.643012	2.476115
29	6	0	-1.579564	-2.346809	-0.251826
30	8	0	-1.210812	-3.439735	-0.162867
31	6	0	-1.168039	-0.114136	-1.770609
32	8	0	-0.411520	0.230980	-2.578544
33	6	0	-3.421652	0.924713	-0.750975
34	8	0	-4.079163	1.853695	-0.956472
35	6	0	-3.622808	-1.202813	0.894257
36	8	0	-4.351097	-1.572247	1.714061
37	1	0	1.502732	0.149623	2.192963
38	1	0	2.299116	2.853991	-0.474725
39	1	0	4.085463	2.066912	-1.564846
40	1	0	3.890402	-0.890765	1.582499
41	1	0	6.299980	-1.337029	1.296531
42	1	0	6.491175	1.630550	-1.818610
43	1	0	7.612103	-0.077478	-0.400040
44	1	0	1.674681	-1.045868	-1.647540
45	1	0	1.278464	-2.138934	2.486989
46	1	0	1.690125	-4.516016	1.897371
47	1	0	2.054096	-3.412435	-2.246888

48	1	0	2.081007	-5.159475	-0.473706
49	1	0	-1.179268	-1.484618	2.134675
50	1	0	-3.161288	2.324944	3.036181
51	1	0	-3.030387	0.541477	3.097798
52	1	0	-3.869115	1.340061	1.731591

TS5

HF=-1891.3335922

NIMAG=1 -1481.4718 cm^{-1})

Zero-point correction= 0.352913
(Hartree/Particle)

Thermal correction to Energy= 0.387484

Thermal correction to Enthalpy= 0.388428

Thermal correction to Gibbs Free Energy= 0.285971

Sum of electronic and zero-point Energies= -1890.974558

Sum of electronic and thermal Energies= -1890.939987

Sum of electronic and thermal Enthalpies= -1890.939043

Sum of electronic and thermal Free Energies= -1891.041500

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.239081	1.729074	0.473485
2	6	0	1.447551	1.838675	-0.682397
3	6	0	1.353040	3.092221	-1.310844
4	6	0	2.020043	4.202954	-0.795901
5	6	0	2.800248	4.081665	0.357936

6	6	0	2.909755	2.838722	0.987213
7	6	0	0.716410	0.683188	-1.233350
8	6	0	1.154831	-0.604042	-1.387967
9	7	0	0.101374	-1.420857	-1.842167
10	6	0	-0.949978	-0.601031	-2.308263
11	6	0	-0.714378	0.693144	-1.613615
12	6	0	2.456261	-1.226921	-1.120887
13	6	0	3.658777	-0.545863	-1.379585
14	6	0	4.882794	-1.155967	-1.116399
15	6	0	4.927919	-2.454369	-0.596885
16	6	0	3.738330	-3.142102	-0.345927
17	6	0	2.509758	-2.536073	-0.608454
18	6	0	-1.636180	1.577766	-1.191513
19	24	0	-0.836569	-0.570455	1.891304
20	6	0	-2.592727	-0.000671	1.412919
21	8	0	-3.658439	0.361467	1.155620
22	6	0	-2.284233	-1.324335	-2.373038
23	9	0	-3.145540	-0.801099	-3.248683
24	9	0	-2.064589	-2.610987	-2.744203
25	9	0	-2.895101	-1.368041	-1.161650
26	8	0	-1.456870	2.523273	-0.283071
27	6	0	-1.936049	3.856773	-0.584929
28	6	0	-1.148833	-2.304332	1.126149
29	8	0	-1.323468	-3.357653	0.695889
30	6	0	-0.485070	1.200689	2.544256
31	8	0	-0.297060	2.257159	2.959773
32	6	0	-1.438929	-1.120343	3.535483
33	8	0	-1.821219	-1.468061	4.574239
34	6	0	0.943662	-1.107755	2.350064
35	8	0	2.001468	-1.439427	2.664350
36	8	0	-3.126826	1.469790	-1.762755
37	1	0	0.329250	-2.245601	-2.382829

38	1	0	3.625860	0.457293	-1.790647
39	1	0	1.586859	-3.067668	-0.393956
40	1	0	3.764522	-4.149735	0.059033
41	1	0	5.804671	-0.620057	-1.323875
42	1	0	5.884588	-2.926709	-0.392816
43	1	0	0.753095	3.187744	-2.211722
44	1	0	2.330755	0.768413	0.967502
45	1	0	3.511736	2.732435	1.885612
46	1	0	1.932588	5.163139	-1.297190
47	1	0	3.318224	4.947062	0.761721
48	1	0	-1.352766	4.280024	-1.407286
49	1	0	-1.776170	4.432217	0.325885
50	1	0	-2.994420	3.825678	-0.847214
51	1	0	-3.651933	1.376568	-0.945600
52	1	0	-0.724934	-0.301526	-3.969602

TS6

HF=-1891.3752961 Hartree

NIMAG=1 (-189.3453 cm^{-1})

Zero-point correction= (Hartree/Particle)	0.355504
Thermal correction to Energy=	0.390831
Thermal correction to Enthalpy=	0.391775
Thermal correction to Gibbs Free Energy=	0.284707
Sum of electronic and zero-point Energies=	-1891.024218
Sum of electronic and thermal Energies=	-1890.988891
Sum of electronic and thermal Enthalpies=	-1890.987946
Sum of electronic and thermal Free Energies=	-1891.095015

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.027929	-1.928534	-0.714724
2	6	0	-3.661859	-0.803331	0.047224
3	6	0	-4.511318	0.319182	0.042107
4	6	0	-5.681398	0.318104	-0.713337
5	6	0	-6.034198	-0.804489	-1.470235
6	6	0	-5.203718	-1.927653	-1.465902
7	6	0	-2.426285	-0.815852	0.838098
8	6	0	-1.521095	0.177563	1.112567
9	6	0	-0.455342	-0.430126	1.925762
10	6	0	-0.748193	-1.871174	2.001172
11	7	0	-2.008939	-2.003384	1.460449
12	6	0	-1.553935	1.541657	0.541764
13	6	0	-1.629313	1.706368	-0.852581
14	6	0	-1.672198	2.977568	-1.424866
15	6	0	-1.643529	4.112265	-0.610649
16	6	0	-1.580116	3.962017	0.777689
17	6	0	-1.538115	2.689933	1.349166
18	6	0	0.645092	0.125475	2.522556
19	8	0	0.778708	1.445094	2.638338
20	6	0	2.026078	1.992170	3.108556
21	8	0	1.643899	-0.593008	3.073784
22	6	0	0.628535	-2.825314	0.692962
23	9	0	1.924939	-2.355074	0.962050
24	9	0	0.722142	-4.169836	0.697793
25	9	0	0.377252	-2.452492	-0.592724
26	8	0	3.278285	-2.595176	-2.188641
27	6	0	2.887583	-1.600437	-1.760582

28	24	0	2.291117	0.088169	-1.078928
29	6	0	0.943292	0.155741	-2.439146
30	8	0	0.164941	0.197158	-3.287258
31	6	0	3.591911	-0.032250	0.310409
32	8	0	4.397419	-0.088544	1.134301
33	6	0	1.741189	1.791203	-0.383943
34	8	0	1.532221	2.860732	-0.013264
35	6	0	3.482185	0.958655	-2.165708
36	8	0	4.238197	1.506680	-2.855529
37	1	0	-2.539698	-2.860036	1.462353
38	1	0	-4.248486	1.187127	0.637042
39	1	0	-3.373622	-2.795825	-0.743339
40	1	0	-5.465755	-2.802726	-2.054259
41	1	0	-6.325268	1.193342	-0.705027
42	1	0	-6.948786	-0.802992	-2.056560
43	1	0	-1.483401	2.581015	2.426528
44	1	0	-1.657785	0.825978	-1.484913
45	1	0	-1.721001	3.078655	-2.505908
46	1	0	-1.564688	4.839346	1.419151
47	1	0	-1.671154	5.104588	-1.052657
48	1	0	2.167947	1.762699	4.167562
49	1	0	1.929359	3.066925	2.960386
50	1	0	2.869032	1.604955	2.533341
51	1	0	1.779450	-1.413065	2.561220
52	1	0	-0.502669	-2.461654	2.878128

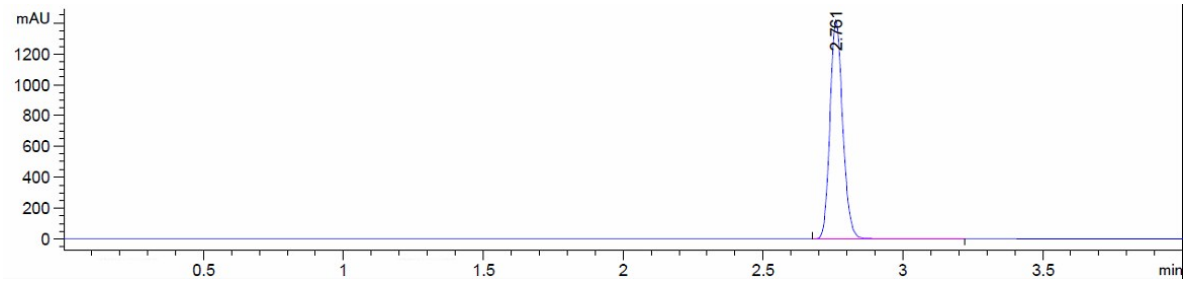
SECTION 7

HPLC analysis of the effect of water on reaction of 1a and 2a.

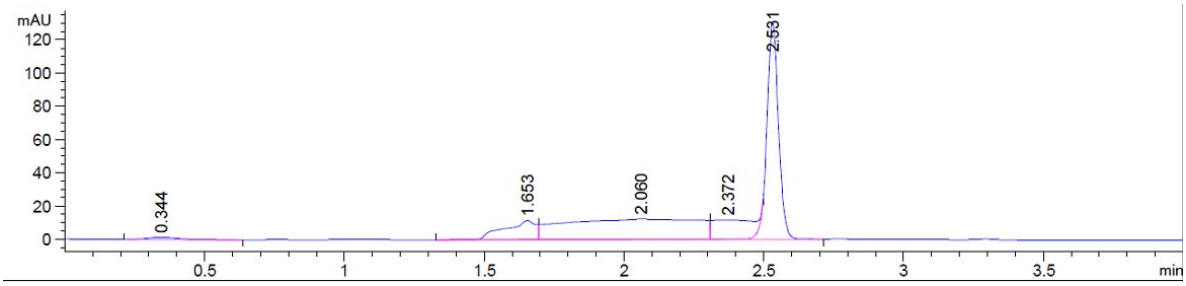
The analysis was performed using HPLC with UV-Visible detector of Agilent Technologies 1260 model with Eclipse XDB-C18 column of 5 µm and 4.6 x 250 mm. All samples were run with flow of 70% MeCN and 30% MeOH (1 mL/min), detected at 280 nm and prepared using commercial grade THF without further purification (TEDIA, www.T2-P2.com, #TS2123-001, with 0.02% of water). The standards for the calibration curve were prepared with 12 mg of compound **4a** in 5.0 mL of THF. Then, 100 µl of the solution were taken and calibrated to 1000 µl to have a final concentration of 0.24 mg/ml, and from here, 1:2 dilutions were made to have concentrations of 0.12 mg/mL, 0.06 mg/ml and 0.03 mg/mL. The reactions were carried out using 100 mg (1 equiv) of carbene **1a** and 99 mg (1.5 equiv) of oxazolone **2a** (1.5 equiv) in 15 mL of THF. The corresponding amounts of water were added, stirring for 5 minutes and after 40 µl of TEA (1 equiv) were also integrated. Then, 15 µl was gauged to 1000 µl, which were injected into the equipment.

Table 1. Reaction performance when adding water to THF.

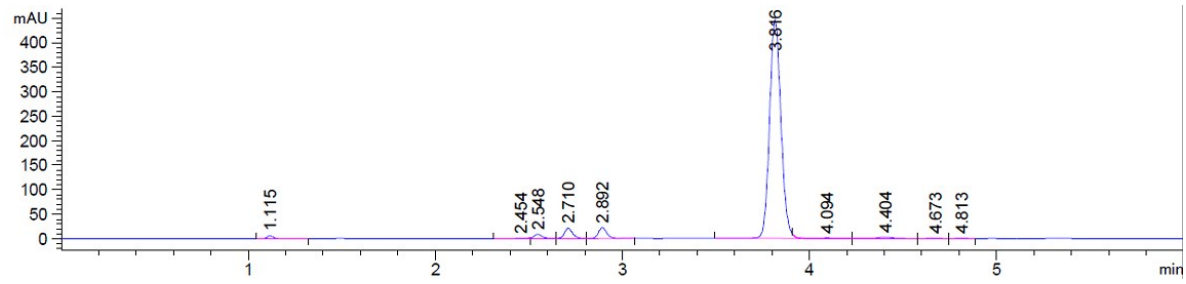
Entry	Eq H_2O	AUC	Yield (%)
1	--	1152.7778	76.30
2	0.02	1156.58875	76.51
3	0.05	1163.18994	76.95
4	0.07	1138.79236	75.31
5	0.1	1046.18591	69.06
6	0.3	573.33301	37.18
7	0.5	373.68301	23.71
8	1	163.49109	09.54



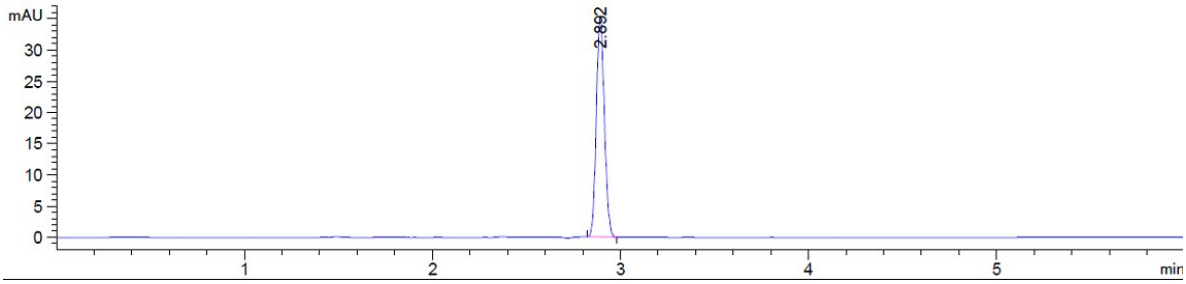
Scheme 1. Chromatogram of pyrrole **4a.**



Scheme 2. Chromatogram of oxazolone **2a**.

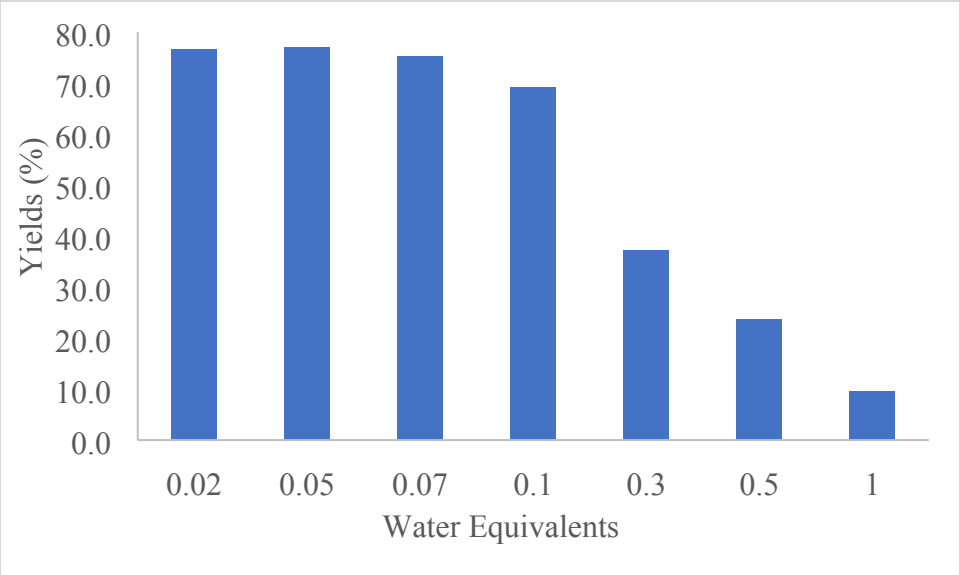


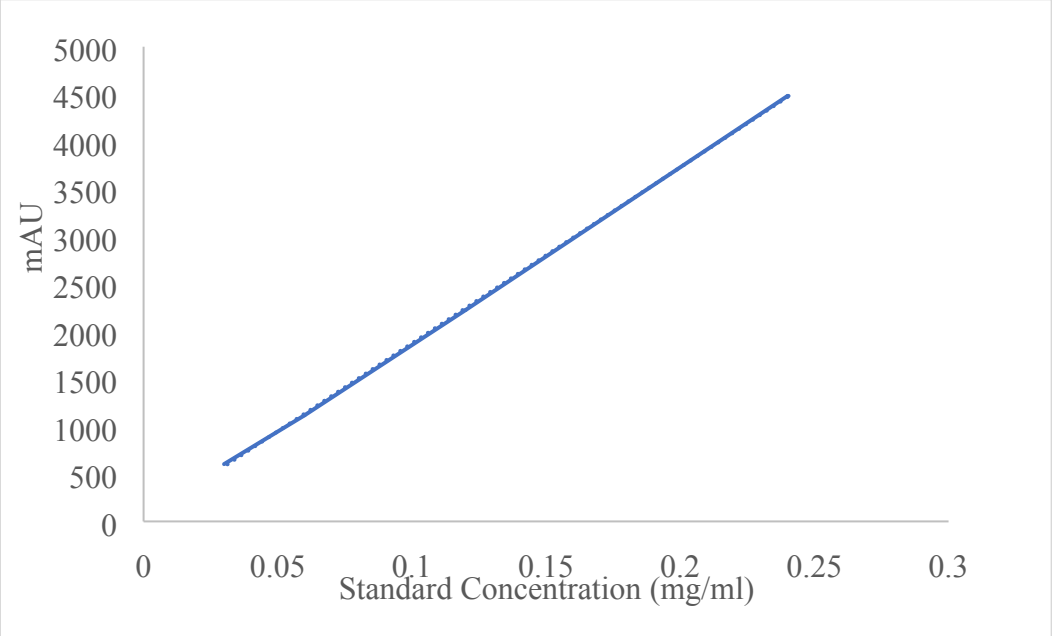
Scheme 3. Chromatogram of carbene **1a**.



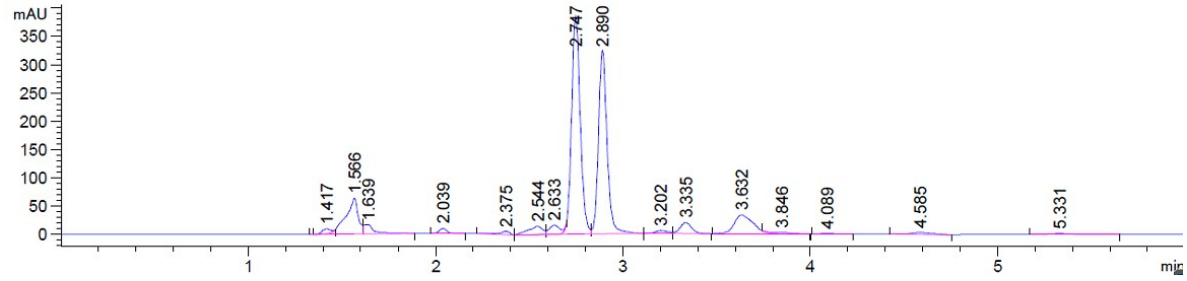
Scheme 4. Chromatogram of **$Cr(CO)_6$**

Graph 1. Reaction performance when adding water to THF.

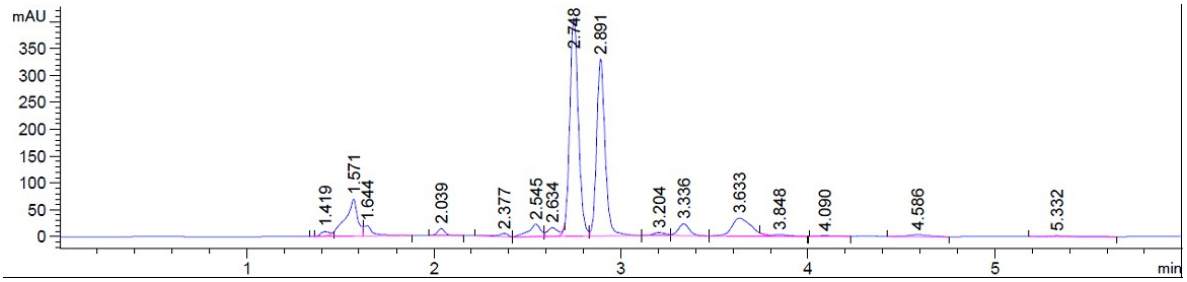




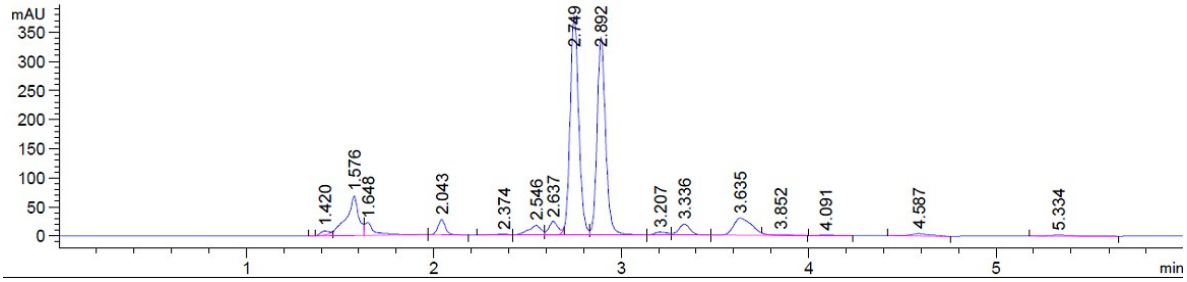
Scheme 5. Calibration curve of compound **4a.**



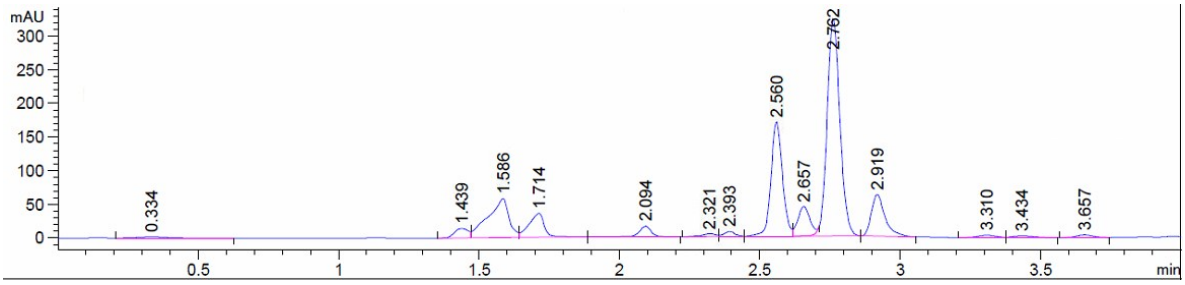
Scheme 6. Chromatogram of reaction crude with 0.02 eq. of H_2O.



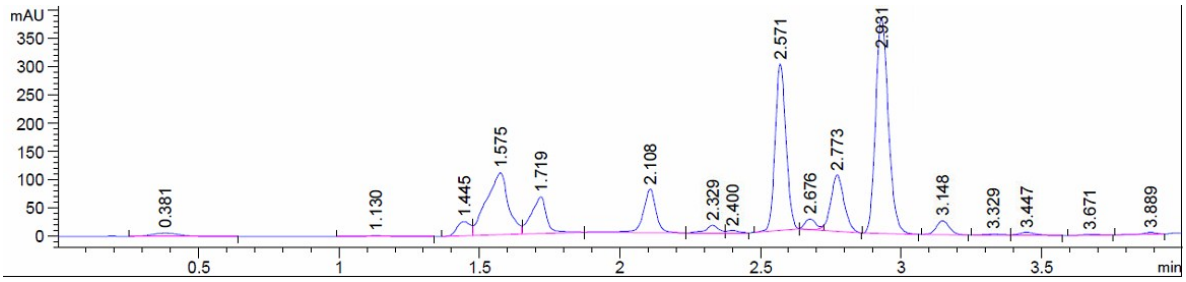
Scheme 7. Chromatogram of reaction crude with 0.05 eq. of H_2O.



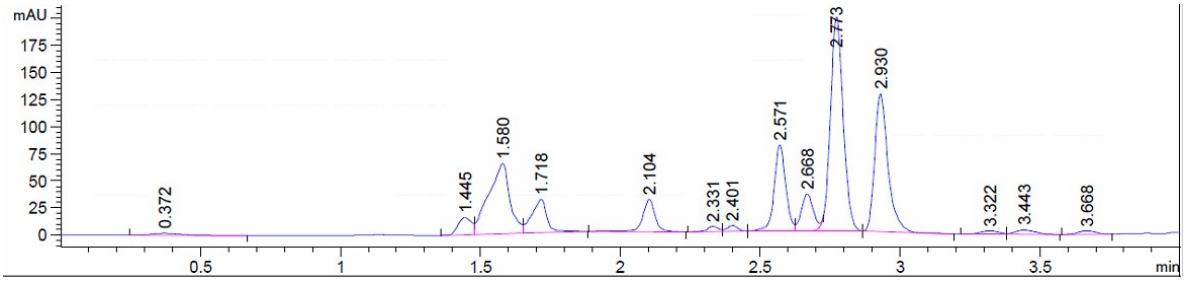
Scheme 8. Chromatogram of reaction crude with 0.07 eq. of H_2O.



Scheme 9. Chromatogram of reaction crude with 0.1 eq. of H_2O.



Scheme 10. Chromatogram of reaction crude with 0.3 eq. of H_2O.



Scheme 11. Chromatogram of reaction crude with 0.5 eq. of H_2O.