Supporting Information

Synthesis of spirobenzoxazine frameworks from biomass-derived chloromethylfurfural *via* a key intramolecular aza-Piancatelli reaction.

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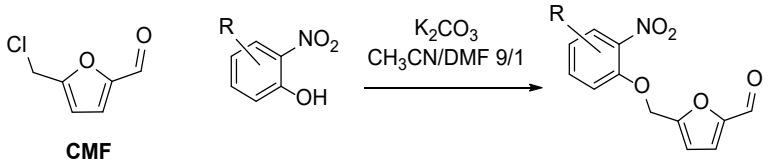
- **General Information**

Reagents and solvents were supplied by Sigma Aldrich and Alfa Aesar. NMR spectra were recorded on Brucker AV300 or Jeol ECZ 400 or Bruker AV 500 (^{1}H 300, 400 or 500 MHz; ^{13}C 75, 100 or 126 MHz) spectrometers using deuterated solvents as specified. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in a standard fashion. The following abbreviations are used to explain the multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q= quadruplet, bq = broad quadruplet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets. NMR peak assignments were performed for each compound using classical 1D and 2D NMR (COSY, HSQC and HMBC) with Mestrenova software. The high-resolution mass spectrometry (HRMS) analyses were performed using a hybrid Quadrupole - Time-of-Flight (QTOF) mass spectrometer (Impact II, Bruker) equipped with an electrospray ion source (ESI) operated in positive or negative ion mode. Capillary voltage used is ± 4500 V, end plate offset used is ± 500 V, nebulizer gas pressure is 0.3 bar, dry gas pressure used is 4.0 L/min, dry gas temperature is set at 200°C. Analytical thin-layer chromatography was carried out on silica gel Macherey-Nagel silica gel 60 (0.2 mm) with UV detection at 254 nm and spraying with appropriate reagent. Column chromatography was performed on silica 60 M (0.04 mm-0.064 mm) from Macherey-Nagel.

NMR Spectra for compounds 5 to 11' are given from page S23 to S97

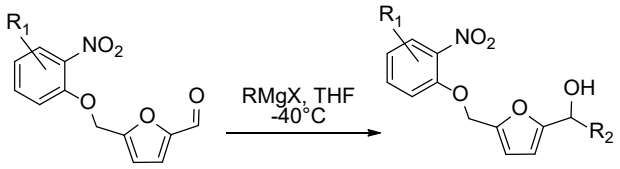
- **General procedure A : Synthesis of substituted 5-[(2-nitrophenoxy) methyl] furan-2-carbaldehydes**[1]



[1] a) D. S. Khachatryan, A. L. Razinov, A. V. Kolotaev, S. K. Belus´ and K. R. Matevosyan, *Russ. Chem. Bull.*, 2015, **64**, 395-404 ; b) CAS: 438221-76-2.

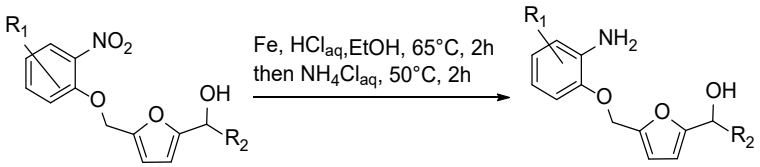
To a solution of 5-chloromethylfurfural (5-CMF)[2] (1 equiv.) in CH_3CN/DMF (9/1) (0.5 M), was added anhydrous K_2CO_3 (1.4 equiv.) and (substituted) 2-nitrophenol (1.1 equiv.). The reaction mixture was stirred for 6h at 80°C. After cooling and addition of ethyl acetate (3,75 mL/mmol), the organic phase was washed with an aqueous saturated solution of ammonium chloride (3 times with 5 mL/mmol) and the aqueous phase extracted with ethyl acetate (twice with 5 mL/mmol). The combined organic phases were dried with Na_2SO_4, filtered and concentrated under *vacuum*. The residual solid was washed with MeOH/H_2O (30/70), filtered and dried under *vacuum*.

- **General procedure B : Synthesis of furyl carbinols, 5-[(2-nitrophenoxy)methyl]furan-2-yl}(vinyl or aryl)methanol**



To a solution of 5-[(2-nitrophenoxy) methyl] furan-2-carbaldehyde or a R_1 substituted analog (1 equiv.) in anhydrous THF (0.3M) was added dropwise under N_2 at -40°C, a solution of Grignard reagent in THF (1.4 equiv.). The reaction was monitored by TLC and an additional reagent might be added when required. After completion, the reaction was quenched by addition of a NH_4Cl saturated solution and let under stirring for 15 minutes. The mixture might be concentrated to remove THF or directly extracted with ethyl acetate or Et_2O and the organic phases washed with water, dried with Na_2SO_4, filtered and concentrated before purification by flash chromatography on silica.

- **General procedure C : Reduction of the nitro group towards {5-[(2-aminophenoxy) methyl] furan-2-yl}(aryl)methanol[3]**



An ethanolic solution (1.5 mL/mmol) containing iron (5 equiv.) and an aqueous HCl solution (37% wt) (0.5 equiv. /mmol) was heated at 65°C for 2h before adding a saturated aqueous NH_4Cl solution and a 0.2 M ethanolic solution of {5-[(2-nitrophenoxy) methyl] furan-2-yl}(aryl)methanol (1 equiv.). The reaction mixture was heated at 50°C under stirring for 2h. After cooling, the mixture was filtered on Celite, washed with EtOH then CH_2Cl_2 and concentrated. The residue was dissolved in EtOAc, washed with a saturated aqueous $NaHCO_3$ solution, then with a saturated aqueous NaCl solution. The organic phase was dried over Na_2SO_4, filtered then concentrated under *vacuum*. The residual crude oil might be purified by flash chromatography on SiO_2 if required.

- **General procedure D: Piancatelli reaction**

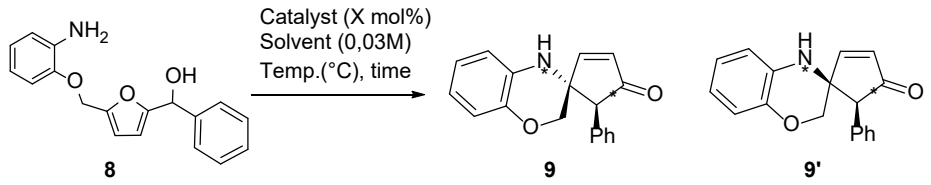
Conditions D1: A solution of furylcarbinol (1 equiv.) in CH_3CN (0.03M) with $Dy(OTf)_3$ (5 mol%) and 1,3,5-trimethoxybenzene as internal standard (0.33 equiv.) stirred at 80°C till completion, monitored by TLC (petroleum ether/EtOAc 7/3).

[2] A. Bredihhin, U. Maeorg and L. Vares, *Carbohydr. Res.*, 2013, **375**, 63-67.
[3] Y. Liu, Y. Lu, M. Prashad, O. Repi and T. J. Blacklock, *Adv. Synth. Catal.*, 2005, **347**, 217-219.

Conditions D2: A solution of furylcarbinol (1 equiv.) in CH_3CN (0.03M) with *p*-TSA (5mol%) and 1,3,5-trimethoxybenzene as internal standard (0.33 equiv.) was stirred at 80°C till completion, monitored by TLC (petroleum ether/EtOAc 7/3).

For both conditions, after the addition of ethyl acetate, the organic phase was washed with an aqueous solution of sodium carbonate, the aqueous phase extracted with ethyl acetate. The combined organic phases were dried with Na_2SO_4, filtered and concentrated under *vacuum* before purification by flash chromatography.

▪ **Table 1. Optimization of the reaction conditions[a]**



8 **9** **9'**

Entry	Cat (mol%)	Solvent	Temp (°C)	Time (h)	Yield[b](dr[c])
1	$Dy(OTf)_3$ (5)	CH_3NO_2	80°C	0.5	49% (80/20, 78/22)
2	$Ca(NTf_2)_2$ (5)[d], nBu_4NPF_6 (5)	CH_3NO_2	100°C	0.5	53% (72/28, 75/25)
3	$Ca(NTf_2)_2$ (5)[e], nBu_4NPF_6 (5)	CH_3NO_2	100°C	0.5	50% (71/29, 68/32)
4	*p*-TSA (5)	CH_3NO_2	80°C	0.5	57% (87/13, 82/18)
5	*N*Tf -phosphoramidate (10)	DCE	80°C	4	54% (85/15, 85/15)
6	$Dy(OTf)_3$ (10)	CH_3NO_2	80°C	0.5	66% (75/25, 63/37)
7	$Dy(OTf)_3$ (5)	CH_3CN	80°C	0.5	82% (71/29)
8	*p*-TSA (5)	CH_3CN	80°C	0.5	77% (81/19, 78/22)
9	$Yb(OTf)_3$ (5)	CH_3CN	80°C	0.5	67% (74/26,71/29)
10	$Y(OTf)_3$ (5)	CH_3CN	80°C	1	68% (69/31, 71/29)
11	$Sc(OTf)_3$ (5)	CH_3CN	80°C	0.5	65% (76/24, 75/25)
12	$DyCl_3$[4] (5)	CH_3CN	80°C	1	34% (67/33)
13	$CeCl_3$ (5)	CH_3CN	80°C	6	Partial conversion and degradation
14	$Ca(NTf_2)_2$ (5)[f], nBu_4NPF_6 (5)	CH_3CN	80°C	0.5	No conversion
15	$Ca(NTf_2)_2$ (5)[f], nBu_4NPF_6 (5)	CH_3CN	80°C	7	Partial conversion
16	trifluoromethylphenyl boronic acid (20)	CH_3CN	80°C	>one week	Partial conversion
17	$Dy(OTf)_3$ (5)	HFIP	rt	24	57% (28/72, 33/67)
18	$Ca(NTf_2)_2$ (5)[f], nBu_4NPF_6 (5)	HFIP	r.t.	5	67% (36/64, 31/69)
19	$Ca(NTf_2)_2$ (5)[g], nBu_4NPF_6 (5)	HFIP	r.t	5	55% (29/71, 32/68)
20	*p*-TSA (5)	HFIP	rt	5	50% (30/70, 37/63)
21	$Dy(OTf)_3$ (5)	Toluene	80°C	4	<24%[f]
22	$Ca(NTf_2)_2$ (5)[e], nBu_4NPF_6 (5)	Toluene	80°C	0.5	<36%[f]
23	diphenylphosphate (5)	DCE	r.t then 80°C	57	Partial conversion
24	None	CH_3NO_2	80°C		n.d[g]
25	None	CH_3CN	80°C		n.d[g]
26	$Dy(OTf)_3$ (5)	CH_3CN	33°C	48h	43% (74/26)[h]

[a] Conditions : **8** (about 0.34 mmol), and catalyst in the corresponding solvent (0.03M, about 11mL) at 80°C for the indicated time.

[b] Isolated yield

[c] dr in all cases determined by ^1H NMR in CDCl3 at 298K analysis of the isolated mixture of both diasteromers and compared to dr in the crude material.

[d] Commercial $Ca(NTf_2)_2$

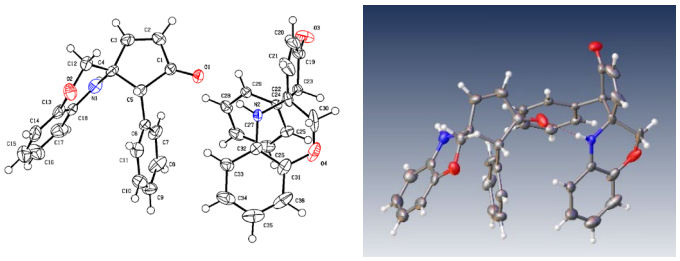
[e] Lab-made $Ca(NTf_2)_2$

[f] Unidentified compound not separated from the mixture of diastereomers

[g] Starting material was recovered

[h] Reaction carried out under white light (P=23W)

[4] F. Cacheux, G. Le Goff, J. Ouazzani, J. Bignon, P. Retailleau, A. Marinetti, A. Voituriez and J.-F. Betzer, *Org. Chem. Front.*, 2021, 2449-2455.

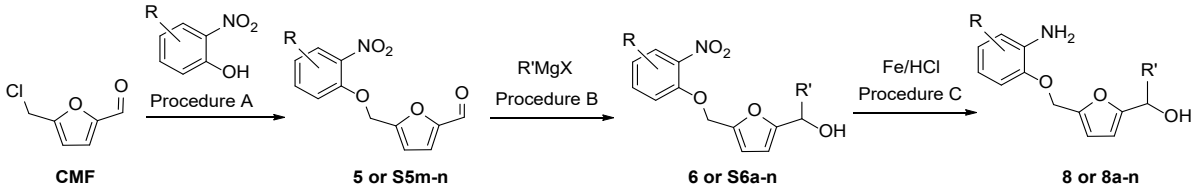


X-ray of **9'**

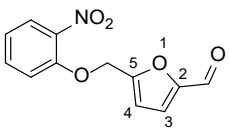
CCDC 2454517

Figure S1. Crystal structure of compound **9'** (thermal ellipsoids at 50% probability, two independent molecules in the asymmetric unit)

- **Characterization of compounds 5 to 8n**



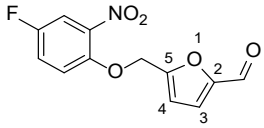
- **5-[(2-Nitrophenoxy) methyl] furan-2-carbaldehyde 5**[1]



Brown solid (1.5 g, 89 %) obtained from 5-CMF (1.0 g, 6.9 mmol) and 2-nitrophenol (1.06 g, 7.6 mmol) following general procedure A.

^{1}H NMR (CDCl$_3$, 500MHz): δ 9.65 (s, 1H, CHO), 7.87 (dd, 1H, *J* 8.3, 1.7 Hz, H_{Ar}), 7.56 (ddd, 1H, *J* 8.3, 7.5 and 1.7 Hz, H_{Ar}), 7.25 (dd, 1H, *J* 3.5 Hz, H_3), 7.18-7.10 (m, 2H, H_{Ar}), 6.72 (d, 1H, *J* 3.5 Hz, H_4), 5.27 (s, 2H, Fur CH_2O); **^{13}C NMR (CDCl$_3$, 125MHz) :** 177.8 (CHO), 155.4 (C_5), 152.9 (C_2), 151.2 ($C_{q\ Ar\ –C-O}$), 140.7 ($C_{q\ Ar\ –C-N}$), 134.4, 126.0, 122.2, 122.0 (4xCH_{Ar}), 115.6 (C_3), 112.3 (C_4), 64.4 (CH_2O); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{12}H_9NNaO_5$ 270.0374; found 270.0373. mp 119°C (litt[1] mp 130°C).

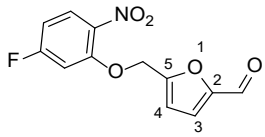
- **5-[(4-Fluoro-2-nitrophenoxy) methyl] furan-2-carbaldehyde S5m**



Brown solid (573 mg, 80%) obtained from 5-CMF (400 mg, 2.8 mmol) and 4-fluoro-2-nitrophenol (467 mg, 3.0 mmol) following general procedure A.

^{1}H NMR (CDCl$_3$, 400MHz): δ 9.60 (s, 1H, CHO), 7.57 (dd, 1H, J_{H-F} 7.6 and *J* 3.7 Hz, $H_{Ar\ nitrophenoxy}$), 7.25 (ddd, 1H, J_{H-F} 7.6, *J* 9.2 and 3.7 Hz, $H_{Ar\ nitrophenoxy}$), 7.21 (d, 1H, *J* 3.6 Hz, H_3), 7.12 (dd, 1H, *J* 9.2 and J_{H-F} 4.3 Hz, $H_{Ar\ nitrophenoxy}$), 6.66 (broad d, 1H, *J* 3.6 Hz,H_4), 5.18 (s, 2H, CH_2); **^{13}C NMR (CDCl$_3$, 100MHz):** δ 177.8 (CHO), 156.4 ($C_{q\ Ar,}$ d, J_{C-F} 250 Hz), 155.0 (C_q, C_5), 153.0 (C_q, C_2), 147.7 ($C_{q\ Ar\ –C-O}$, d, J_{C-F} 3.0 Hz), 140.6 ($C_{q\ Ar\ –C-N}$), 122.2 (C_3), 121.3 (CHAr, d, J_{C-F} 22.8 Hz), 117.9 (CH_{Ar}, d, J_{C-F} 7.9 Hz), 113.2 (CH_{Ar}, d, J_{C-F} 27.4 Hz), 112.6 (C_4), 65.2 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{12}H_8FNNaO_5$: 288.0279; found 288.0278; mp 92°C

- **5-[(5-Fluoro-2-nitrophenoxy) methyl] furan-2-carbaldehyde S5n**

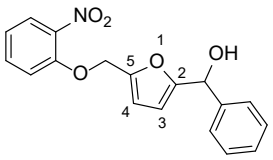


Brown solid (668 mg, 87%) obtained from 5-CMF (417 mg, 2.9 mmol) and 5-fluoro-2-nitrophenol (500 mg, 3.2 mmol) following general procedure A.

^{1}H NMR (CDCl$_3$, 400MHz): δ 9.65 (s, 1H, CHO), 7.98 (dd, 1H, *J* 9.1 and J_{H-F} 5.9 Hz, $H_{Ar\ nitrophenoxy}$), 7.26 (d, 1H, *J* 3.5 Hz, H_3), 6.87 (dd, 1H, J_{H-F} 9.9 Hz and 2.5 Hz, $H_{Ar\ nitrophenoxy}$), 6.81 (ddd, 1H,*J* 9.1, 7.2 and 2.5 Hz, $H_{Ar\ nitrophenoxy}$), 6.77-6.70 (m, 1H, H_4), 5.23 (2H, s, CH_2O); **^{13}C NMR (CDCl$_3$, 100MHz):** δ 177.9 (CHO), 165.7 ($C_{q\ Ar}$, J_{C-F} 257.3 Hz), 154.4

(C_q, C_5), 153.4 ($C_{q\ Ar-C-O}$, d, J_{C-F} 11.0 Hz), 153.1 (C_q, C_2), 136.7 ($C_{q\ Ar-C-N}$), 128.5 (CH_{Ar}, d, J_{C-F} 11.2 Hz), 122.0 (C_3), 112.6 (C_4), 109.0 (CH_{Ar}, d, J_{C-F} 23.3 Hz), 103.2 (CH_{Ar}, d, J_{C-F} 26.9 Hz), 64.4 (CH_2O); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{12}H_8FNNaO_5$: 288.0279; found 288.0279; mp 115°C.

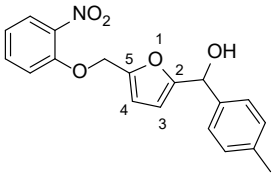
- **{5-[(2-Nitrophenoxy) methyl] furan-2-yl} (phenyl)methanol 6**



Yellow oil (1.15 g, 88%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (1.0 g, 4 mmol) with PhMgCl (2 M in THF, 1.4 equiv., 5.6 mmol) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.81 (dd, 1H, *J* 8.3, 1.4 Hz, H_{Ar}), 7.54 – 7.27 (m, 6H, H_{Ar}), 7.16 (dd, 1H, *J* 8.3, 1.4 Hz, H_{Ar}), 7.06 (ddd, 1H, *J* 8.3, 7.5, 1.4 Hz, H_{Ar}), 6.40 (d, 1H, *J* 3.2 Hz, H_4), 6.10 (d, 1H, *J* 3.2 Hz, H_3), 5.82 (d, 1H, C<u>H</u>OH), 5.12 (s, 2H, Fur C<u>H_2</u>O), 2.44 (s, 1H, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 157.0 (C_2), 151.6 ($C_{q\ Ar-C-O}$), 149.1 (C_q, C_5), 140.6 (2x$C_{q\ Ar}$), 134.0 (2xCH_{Ar}), 128.7 (CH_{Ar}), 128.3 (CH_{Ar}), 126.8 (2xCH_{Ar}), 125.7 (CH_{Ar}), 121.4 (CH_{Ar}), 116.3 (CH_{Ar}), 111.7 (C_4), 108.7 (C_3), 70.2 (CHOH), 64.5 (CH_2O); **HRMS (ESI)** [M+Na] calcd for $C_{18}H_{15}NNaO_5$, 348.0840; found, 348.0842. $[2M+Na]^+$: calcd for 673.1792; found, 673.1793.

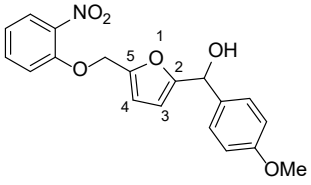
- **{5-[(2-Nitrophenoxy) methyl]furan-2-yl} (4-methylphenyl) methanol S6a**



Yellow oil (217 mg, 80%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with 4-MePhMgBr (1 M in THF, 1.4 equiv., 1.2 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 300MHz): δ 7.81 (dd, 1H, *J* 8.3 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 7.48 (ddd, 1H, *J* 8.3, 7.4 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 7.31 (broad d, 2H, *J* 8.3Hz, 2xH_{Ar}), 7.19-7.14 (m, 3H, $H_{Ar\ nitrophenoxy}$, 2xH_{Ar}), 7.06-7.01 (ddd, 1H, *J* 8.3, 7.4 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 6.39 (d, 1H, *J* 3.2 Hz, H_4), 6.09 (dd, 1H, *J* 3.2 and 0.8Hz, H_3), 5.78 (d, 1H, *J* 3.4 Hz, C<u>H</u>OH), 5.12 (s, 2H, CH_2), 2.41 (d, 1H, *J* 4.4 Hz, CHO<u>H</u>), 2.36 (s, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 157.3 (C_2), 151.7 ($C_{q\ Ar-C-O}$), 149.0 (C_5), 140.9 ($C_{q\ Ar-C-N}$), 138.1 and 137.7 (2x$C_{q\ Ar}$), 134.0 (CH_{Ar}), 129.4 (2xCH_{Ar}), 126.7 (2xCH_{Ar}), 125.7 (CH_{Ar}), 121.4 (CH_{Ar}), 116.3 (CH_{Ar}), 111.6 (C_4), 108.5 (C_3), 70.2 (CHOH), 64.5 (CH_2O), 21.3 (CH_3); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{17}NNaO_5$: 362.0999; found 362.1000.

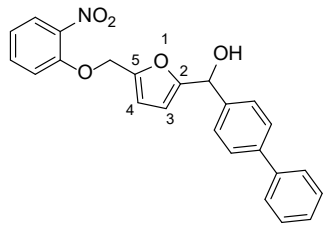
- **{5-[(2-Nitrophenoxy)methyl]furan-2-yl}(4-methoxyphenyl)methanol S6b**



Yellow oil (244 mg, 86%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with 4-MeOPhMgBr (0.5 M in THF, 1.4 equiv., 2.3 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 300MHz): δ 7.79 (dd, 1H, *J* 8.3 and 1.4Hz, $H_{Ar\ nitrophenoxy}$), 7.48(ddd, 1H, *J* 8.3, 7.4 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 7.36-7.32 (m, 2H, 2xH_{Ar}), 7.16 (dd, 1H, *J* 8.3 and 1.4Hz, $H_{Ar\ nitrophenoxy}$), 7.06 (ddd, 1H, *J* 8.3, 7.4 and 1.4Hz, $H_{Ar\ nitrophenoxy}$), 6.94-6.81 (m, 2H, 2xH_{Ar}), 6.38 (d, 1H, *J* 3.2 Hz, H_4), 6.07 (dd, 1H, *J* 3.2 and 0.8Hz, H_3), 5.73 (bd, 1H, C<u>H</u>OH), 5.09 (s, 2H, CH_2), 3.80 (s, 3H, OCH_3), 2.64 (bs, 1H, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 159.6 ($C_{q\ Ar}$), 157.3 (C_q, C_2), 151.6 ($C_{q\ Ar-C-O}$), 148.9 (C_q, C_5), 140.9 ($C_{q\ Ar-C-N}$), 134.0 (CH_{Ar}), 132.9 ($C_{q\ Ar}$), 128.2 (2x CH_{Ar}), 125.7 (CH_{Ar}), 121.4 (CH_{Ar}), 116.3 (CH_{Ar}), 114.0 (2x CH_{Ar}), 111.6 (C_4), 108.4 (C_3), 69.9 (<u>C</u>HOH), 64.5 (CH_2O), 55.5 (OCH_3); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{17}NNaO_6$: 378.0948; found 378.0947

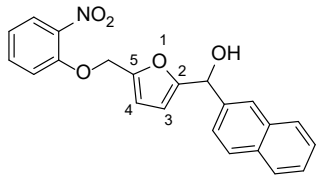
- **{5-[(2-Nitrophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol S6c**



Orange oil (283 mg, 87%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.81 mmol) with 1,1'-biphenylMgBr (0.5 M in THF, 1.4 equiv., 2.3 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 300MHz) : δ 7.80 (dd, 1H, *J* 8.1 and 1.7Hz, $H_{Ar\ nitrophenoxy}$), 7.61-7.55 (m, 4H, 4x$H_{Ar\ biphenyl}$), 7.50-7.41 and 7.39-7.32 (m, 6H, 5 $H_{Ar\ biphenyl}$ and 1x$H_{Ar\ nitrophenoxy}$), 7.16 (dd, 1H, *J* 8.3 and 1.4Hz, $H_{Ar\ nitrophenoxy}$), 7.03 (ddd, 1H, *J* 8.3, 7.4 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 6.41 (d, 1H, *J* 3.2 Hz, H_4), 6.15 (dd, 1H, *J* 3.2 and 0.7Hz, H_3), 5.85 (d, 1H, *J* 3.6 Hz, C<u>H</u>OH), 5.11 (s, 2H, CH_2), 2.72 (bs, 1H, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 75MHz) :** δ 157.0 (C_q, C_2), 151.6 ($C_{q\ Ar-C-O}$), 149.1 (C_q, C_5), 141.1, 140.9, 140.8, 139.7 (4$C_{q\ Ar}$, 3x$C_{q\ biphenyl}$, $C_{q\ Ar-C-N}$), 134.0 (CH_{Ar}), 128.9(2), 127.5, 127.3(2), 127.2(4) (9x$CH_{Ar\ biphenyl}$), 125.6 (CH_{Ar}), 121.4 ($CH_{Ar'}$), 116.3 (CH_{Ar}), 111.6 (C_4), 108.6 (C_3), 70.0 (CHOH), 64.5 (CH_2O); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{24}H_{19}NNaO_5$: 424.1155; found 424.1149

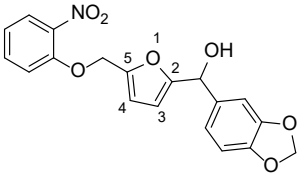
- **2-(Naphthalen-2-yl)-1-{5-[(3-nitrophenoxy) methyl] furan-2-yl}ethan-1-ol S6d**



Yellow oil (230 mg, 77% containing less than 2% remaining aldehyde) isolated after chromatography (petroleum ether/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy) methyl] furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with prepared naphthylMgBr (1 M in THF, 3.8 equiv., 3 mL), following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.88 and 7.86-7.79 (2m, 4H, $H_{Ar\ naphthyl}$), 7.76 (dd, 1H, *J* 8.3 and 1.8 Hz, $H_{Ar\ nitrophenoxy}$), 7.51-7.47 (m, 3H, $H_{Ar\ naphthyl}$), 7.37 (ddd, 1H, *J* 8.3, 7.4 and 1.8 Hz, $H_{Ar\ nitrophenoxy}$), 7.09 (dd, 1H, *J* 8.3 and 1.2 Hz, $H_{Ar\ nitrophenoxy}$), 6.98 (ddd, 1H, *J* 8.3, 7.4 and 1.2 Hz, $H_{Ar\ nitrophenoxy}$), 6.38 (d, 1H, *J* 3.2 Hz, H_4), 6.10 (dd, 1H, *J* 3.2 and 0.7 Hz, H_3), 5.95 (m, 1H, C<u>H</u>OH), 5.07 (s, 2H, CH_2O), 2.89 (d, 1H, *J* 4.0 Hz, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 157.0 (C_q, C_2), 151.5 ($C_{q\ Ar-C-O}$), 149.0 (C_q, C_5), 140.8 ($C_{q\ Ar-C-N}$), 138.0 (C_q, $C_{1'}$), 134.0 ($CH_{Ar\ nitrophenoxy}$), 133.2 (2x$C_{q\ Ar\ naphthyl}$), 128.3, 128.2, 127.8, 126.3 (2) (5x$CH_{Ar\ naphthyl}$), 125.6 and 125.5 ($CH_{Ar\ nitrophenoxy}$ and $CH_{Ar\ naphthyl}$), 124.7 ($CH_{Ar\ naphthyl}$), 121.3 and 116.2 (2 $CH_{Ar\ nitrophenoxy}$), 111.6 (C_4), 108.7 (C_3), 70.2 (CHOH), 64.4 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{22}H_{17}NNaO_5$: 398.0999; found 398.1000.

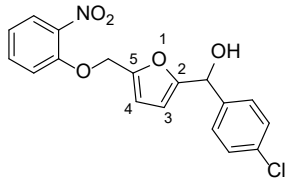
- **{5-[(2-Nitrophenoxy) methyl] furan-2-yl}(3,4-methylenedioxyphenyl) methanol S6e**



Yellow oil (253 mg, 85% containing less than 2% remaining aldehyde) isolated after chromatography on SiO_2(petroleum ether/EtOAc 8/2 to 7/3), obtained from 5-[2-nitrophenoxy) methyl] furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with 3,4-methylenedioxyphenylmagnesiumbromide (0.8 M in THF, 2.8 equiv., 2.8 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.80 (dd, 1H, *J* 8.3 and 1.7 Hz, $H_{Ar\ nitrophenoxy}$), 7.49 (ddd, 1H, *J* 8.3, 7.4 and 1.7 Hz, $H_{Ar\ nitrophenoxy}$), 7.16 (dd, 1H, *J* 8.3 and 1.2 Hz, $H_{Ar\ nitrophenoxy}$), 7.05 (ddd, 1H, *J* 8.3, 7.4 and 1.2 Hz, $H_{Ar\ nitrophenoxy}$), 6.91 (d, 1H, *J* 1.7 Hz, H_{Ar}), 6.86 (ddd, 1H, *J* 8.0, 1.7 and 0.7 Hz, H_{Ar}), 6.78 (d, 1H, *J* 8.3Hz, H_{Ar}), 6.39 (d, 1H, *J* 3.2 Hz, H_4), 6.11 (d, 1H, *J* 3.2 Hz, H_3), 5.95 (s, 2H, OCH_2O), 5.71 (s, 1H, C<u>H</u>OH), 5.11 (s, 2H, OCH_2O), 2.53 (s, 1H, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz)**: δ 157.0 (C_q, C_2), 151.6 ($C_{q\ Ar-C-O}$), 149.0 (C_q, C_5), 147.9, 147.6 (2$C_{q\ Ar-OCH_2O}$), 140.9 ($C_{q\ Ar-C-N}$), 134.6 ($C_{q\ Ar}$), 134.0, 125.7 and 121.4 (3x$CH_{Ar\ nitrophenoxy}$), 120.4 (CH_{Ar}), 116.3 ($CH_{Ar\ nitrophenoxy}$), 111.6 (C_4), 108.4 (CH_{Ar}), 108.3 (C_3), 107.4 (CH_{Ar}), 101.3 (OCH_2O), 70.0 (CHOH), 64.4 (CH_2O); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{15}NNaO_7$: 392.0741; found 392.0740

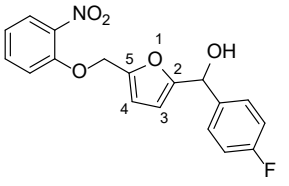
- **{5-[(2-Nitrophenoxy) methyl]furan-2-yl}(4-chlorophenyl) methanol S6f**



Orange oil (244 mg, 86%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with 4-ClPhMgCl (1 M in THF, 1.5 equiv., 1.2 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.80 (dd, 1H, *J* 8.2 and 1.7 Hz, $H_{Ar\ nitrophenoxy}$), 7.48 (ddd, 1H, *J* 8.2, 7.4 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 7.36-7.30 (m, 4H, $H_{Ar\ chlorophenyl}$), 7.14 (dd, 1H, *J* 8.2 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 7.06 (ddd, 1H, *J* 8.2, 7.4 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 6.39 (d, 1H, *J* 3.3 Hz, H_4), 6.09 (dd, 1H, *J* 3.3 and 0.7 Hz, H_3), 5.79 (d, 1H, *J* 4.3 Hz, C<u>H</u>OH), 5.11 (s, 2H, OCH_2), 2.54 (d, 1H, *J* 4.3 Hz, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz) :** δ 156.6 (C_q, C_2), 151.5 ($C_{q\ Ar\ –C-O}$), 149.2 (C_q, C_5), 141.0 ($C_{q\ Ar\ –C-N}$), 139.0 ($C_{q\ Ar}$), 134.0 (CH_{Ar}), 128.8(2x$CH_{Ar\ chlorophenyl}$), 128.1(2x$CH_{Ar\ chlorophenyl}$), 126.8 ($C_{q\ Ar}$)125.7 (CH_{Ar}), 121.5 (CH_{Ar}), 116.3 (CH_{Ar}), 111.7 (C_4), 108.7 (C_3), 69.5 (CHOH), 64.4 (OCH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}ClNNaO_5$: 382.0453; found 382.0457.

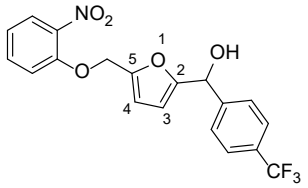
- **{5-[(2-Nitrophenoxy)methyl]furan-2-yl}(4-fluorophenyl) methanol S6g**



Orange oil (232 mg, 85%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with 4-F-PhMgBr (1 M in THF, 1.4 equiv, 1.2 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.78 (dd, 1H, *J* 8.1 and 1.7Hz, $H_{Ar\ nitrophenoxy)}$, 7.47 (ddd, 1H, *J* 8.9, 7.5 and 1.8 Hz, $H_{Ar\ nitrophenoxy}$), 7.42-7.31 (m, 2H, $H_{Ar\ fluorophenyl}$), 7.14 (dd, 1H, *J* 8.5 and 1.1 Hz, $H_{Ar\ nitrophenoxy}$), 7.11-6.92 (m, 3H, $H_{Ar\ nitrophenoxy}$ and 2 $H_{Ar\ fluorophenyl}$), 6.37 (d, 1H, *J* 3.3 Hz, H_4), 6.06 (d, 1H, *J* 3.3 Hz, H_3), 5.75 (s, 1H, C<u>H</u>OH), 5.08 (s, 2H, CH_2), 2.87 (s, 1H, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 125MHz):** δ 162.5 (d, J_{C-F} 246.4 Hz, $C_{q\ Ar}$), 156.8 (C_2), 151.5 ($C_{q\ Ar\ –C-O}$), 149.0 (C_q, C_5), 140.7 ($C_{q\ Ar\ –C-N}$), 136.4 ($C_{q\ Ar}$), 134.1 ($CH_{Ar\ nitrophenoxy}$), 128.5 (2x$CH_{Ar\ fluorophenyl,}$ *J* 8.3 Hz), 125.6 (CH_{Ar}), 121.4 (CH_{Ar}), 116.1 (CH_{Ar}), 115.4 (2x$CH_{Ar\ fluorophenyl,}$ *J* 21.5 Hz), 111.6 (C_4), 108.5 (C_3), 69.4 (CHOH), 64.3 (CH_2); **^{19}F NMR ($CDCl_3$, 282MHz):** δ -114.1 (tt, *J* 8.5, 5.4 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}FNNaO_5$: 366.0748; found 366.0747.

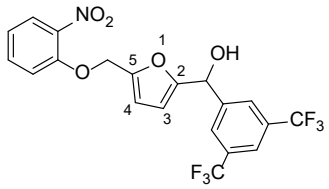
- **{5-[(2-Nitrophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol S6h**



Yellow oil (248 mg, 70%) isolated after chromatography on SiO_2 (petroleum ether/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with 4-trifluoromethylphenylmagnesium chloride (1M in THF, 1.8 equiv., 1.5mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.80 (dd, 1H, *J* 8.3 and 1.7 Hz, $H_{Ar\ nitrophenoxy}$), 7.63 and 7.55 (2d, 2x2H, *J* 8.0 Hz,$H_{Ar\ \textit{ortho and meta trifluoromethylphenyl}}$), 7.47 (ddd, 1H, *J* 8.3, 7.4 and 1.5 Hz, $H_{Ar\ nitrophenoxy}$), 7.14 (dd, 1H, *J* 8.3 and 1.5 Hz, $H_{Ar\ nitrophenoxy}$), 6.40 (d, 1H, *J* 3.3 Hz, H_4), 6.11 (d, 1H, *J* 3.3 Hz, H_3), 5.88 (d, 1H, *J* 3.5 Hz, C<u>H</u>OH), 5.11 (s, 2H, CH_2), 2.63 (d, 1H, *J* 3.5 Hz, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz)**: δ 156.2 (C_q, C_2), 151.5 ($C_{q\ Ar\ –C-O}$), 149.4 (C_q, C_5), 144.4 ($C_{q\ Ar}$), 141.0 ($C_{q\ Ar\ –C-N}$), 134.0 ($CH_{Ar\ nitrophenoxy}$), 130.3 (broad q, *J* 32 Hz, $C_{q\ Ar\ C\text{-}CF_3}$), 127.0 (2x$CH_{Ar\ \textit{ortho}}$), 125.7 (CH_{Ar}), 125.6(q, *J* 4.0 Hz, 2x$CH_{Ar\ \textit{meta}}$), 124.3 (C_q, broad q, *J* 270 Hz, CF_3), 121.6 and 116.3 (2x$CH_{Ar\ nitrophenoxy}$), 111.7 (C_4), 109.0 (C_3), 69.5 (CHOH), 64.4 (CH_2); ^{19}F NMR ($CDCl_3$, 376MHz): -62.4(s); HRMS (ESI) [M+Na]+: calcd for $C_{19}H_{14}F_3NNaO_5$: 416.0716 ; found 416.0718.

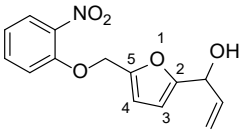
- **{5-[(2-Nitrophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl) methanol S6i**



Orange oil (282 mg, 77%) isolated after chromatography (petroleum ether/EtOAc (8/2), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with 3,5-di-trifluoromethyl-PhMgBr (0.5 M in THF, 1.4 equiv., 2.3 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.92 (m, 2H, H_{Ar}), 7.84 (m, 1H, H_{Ar}), 7.84-7.79 (m, 1H, $H_{Ar\ nitrophenoxy}$), 7.52-7.47 (m, 1H, H_{Ar}), 7.16-7.13 (m, 1H, H_{Ar}), 7.10-7.06 (m, 1H, H_{Ar}), 6.43 (d, 1H, *J* 3.2 Hz, H_4), 6.16 (d, 1H, *J* 3.2 Hz, H_3), 5.95 (d, 1H, *J* 4.1 Hz, CHOH), 5.12 (s, 2H, CH_2), 2.72 (d, 1H, *J* 4.1 Hz, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz)**: δ 155.4 (C_q, C_2), 151.5 ($C_{q\ Ar\ –C-O}$), 149.9 (C_q, C_5), 143.0 and 141.1 ($C_{q\ Ar\ –C-N}$ and $C_{q\ Ar}$), 134.0 ($CH_{Ar\ nitrophenoxy}$), 132.0 ($2xC_{q\ Ar\ C-CF_3}$, broad q, *J* 33.4Hz), 126.9 ($2xCH_{Ar}$), 125.8 (CH_{Ar}), 125.5 ($2C_q$, broad q, *J* 250 Hz, $2xCF_3$), 122.3 (CH_{Ar}), 121.8 and 116.4 ($3xCH_{Ar\ nitrophenoxy}$), 111.8 (C_4), 109.4 (C_3), 68.9 (CHOH), 64.5 (CH_2); ^{19}F NMR ($CDCl_3$, 282MHz): -62.8 (s); HRMS(ESI)[M+Na]$^+$: calcd for $C_{20}H_{13}F_6NNaO_5$: 484.0590; found 484.0589.

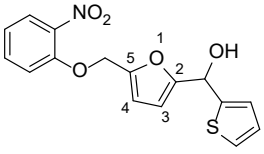
- **1-{5-[(2-Nitrophenoxy) methyl]furan-2-yl}prop-2-en-1-ol S6j**



Yellow oil (360 mg, 65%) isolated after chromatography on SiO_2(petroleum ether/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy) methyl]furan-2-carbaldehyde (500 mg, 2.02 mmol) with vinylmagnesium bromide (1 M in THF, 1.4 equiv., 2.8 mL) following general procedure B.

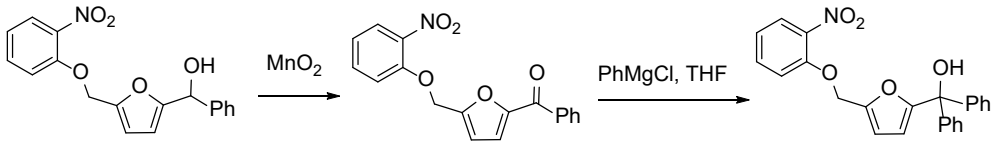
^{1}H NMR ($CDCl_3$, 400MHz): δ 7.81 (dt, 1H, *J* 8.2 and 1.6 Hz, H_{Ar}), 7.54-7.49 (m, 1H, $H_{Ar\ nitrophenoxy}$), 7.20 (dt, 1H, *J* 8.2 and 1.6 Hz, H_{Ar}), 7.09-7.04 (m, 1H, H_{Ar}), 6.41 (dd, 1H, *J* 3.3 and 1.3 Hz, H_4), 6.24 (dd, 1H, *J* 3.3 and 1.3 Hz, H_3), 6.15-6.05 (m, 1H, $CH_{\ ethylene}$), 5.43 (dq, 1H, *J* 17.1 and 1.5 Hz, $CH_{2\ ethylene}$), 5.30 (dq, 1H, *J* 10.4 and 1.5 Hz, $CH_{2\ ethylene}$), 5.22 (m, 1H, C<u>H</u>OH), 5.13 (bs, 2H, CH_2O), 2.22 (s, 1H, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 156.2 (C_q, C_2), 151.7 ($C_{q\ Ar\ –C-O}$), 148.9 ($C_{q,}C_5$), 140.9 ($C_{q\ Ar\ –C-N}$), 136.6 (<u>C</u>H=CH_2), 134.1 (CH_{Ar}), 125.7 (CH_{Ar}), 121.4 (CH_{Ar}), 117.0 (CH_2=), 116.2 (CH_{Ar}), 111.7 (C_4), 107.9 (C_3), 68.7 (CHOH), 64.5 (CH_2); **HRMS (ESI)** [M+Na]$^+$: calcd for $C_{14}H_{13}NNaO_5$: 298.0686; found 298.0688

- **{5-[(2-Nitrophenoxy)methyl]furan-2-yl}(thiophen-2-yl)methanol S6k**



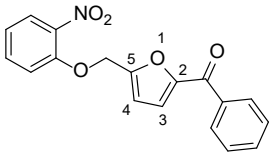
Orange oil (205 mg, 78%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde **5** (200 mg, 0.8 mmol) with thienylMgBr (1 M in THF, 1.4 equiv., 1.2 mL) following general procedure B.

^{1}H NMR ($CDCl_3$, 300MHz): δ 7.81 (dd, 1H, *J* 8.2 and 1.6 Hz, $H_{Ar\ nitrophenoxy}$), 7.50 (ddd, 1H, *J* 8.2, 7.4 and 1.6 Hz, $H_{Ar\ nitrophenoxy}$), 7.30 (dd, 1H, *J* 4.9 and 1.4 Hz, $CH_{\ thienyl}$), 7.18 (dd, 1H, *J* 8.4 and 1.4 Hz, $H_{Ar\ nitrophenoxy}$), 7.08-7.04 (m, 1H, $H_{Ar\ nitrophenoxy}$), 7.03-6.95 (m, 2H, $2CH_{\ thienyl}$), 6.43 (d, 1H, *J* 3.2 Hz, H_4), 6.28 (d, 1H, *J* 3.2 Hz, H_3), 6.05 (d, 1H, *J* 5.1 Hz, C<u>H</u>OH), 5.14 (s, 2H, CH_2), 2.62 (d, 1H, *J* 5.1 Hz, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 75MHz) :** δ 156.0 (C_q, C_2), 151.6 ($C_{q\ Ar\ –C-O}$), 149.2 (C_q, C_5), 144.2 ($C_{q\ thienyl}$), 141.0 ($C_{q\ Ar\ –C-N}$), 134.0 (CH_{Ar}), 126.9 (CH_{Ar}), 125.9 (CH_{Ar}), 125.7 (CH_{Ar}), 125.6 (CH_{Ar}), 121.5 (CH_{Ar}), 116.4 (CH_{Ar}), 111.7 (C_4), 108.6 (C_3), 66.4 (CHOH), 64.5 (CH_2); **HRMS (ESI)** [M+Na]$^+$: calcd for $C_{16}H_{13}NNaO_5S$: 354.0407; found 354.0407.



6 **S6l**

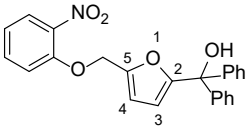
- **{5-[(2-Nitrophenoxy) methyl]furan-2-yl} (phenyl)methanone**



A solution of {5-[(2-nitrophenoxy) methyl] furan-2-yl}(phenyl)methanol **6** (300 mg, 0.92 mmol, 1 equiv) and MnO_2 (1.2 g, 15 equiv) in CH_3CN [0.1M] was heated at 80°C under stirring for 1h. After cooling, the mixture was filtered on Celite, washed with CH_2Cl_2 and the filtrate concentrated under *vacuum*. The residual crude was purified by flash chromatography on SiO_2 with petroleum ether / EtOAc (8/2-7/3) leading to a brown solid (256 mg, 81%).

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.94-7.90 (m, 2H, H_{Ar}), 7.84 (dd, 1H, *J* 8.1 and 1.7 Hz, $H_{Ar\ nitrophenoxy}$), 7.62-7.55 (m, 1H, H_{Ar}), 7.55-7.51 (m, 1H, H_{Ar}), 7.50-7.46 (m, 2H, H_{Ar}), 7.20-7.18 (m, 2H, H_{Ar} and H_3), 7.09 (ddd, 1H, *J* 8.4, 7.4 and 1.1 Hz, $H_{Ar\ nitrophenoxy}$), 6.68 (d, 1H, *J* 3.5 Hz, H_4), 5.27 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 182.5 (CO), 154.1 (C_q, C_5), 152.3 (C_q, C_2), 151.2 ($C_{q\ Ar-C-O}$), 140.5 ($C_{q\ Ar-C-N}$), 137.1 ($C_{q\ Ar}$), 134.3 and 132.8 ($CH_{Ar\ nitrophenoxy}$ and CH_{Ar}), 129.4 (CH_{Ar}), 128.6 (CH_{Ar}), 125.8 ($CH_{Ar\ nitrophenoxy}$), 121.7 and 121.5 (C_3 and $CH_{Ar\ nitrophenoxy}$), 115.5 ($CH_{Ar\ nitrophenoxy}$), 112.1 (C_4), 64.2 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{13}NNaO_5$: 346.0686 found 346.0690; mp 89°C.

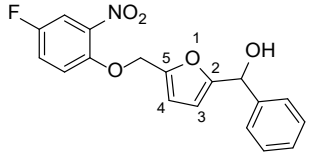
- **{5-[(2-Nitrophenoxy) methyl]furan-2-yl} (diphenyl)methanol S6l**



Orange oil (103 mg, 65%) isolated after chromatography (petroleum ether/EtOAc (8/2) from {5-[(2-nitrophenoxy) methyl] furan-2-yl}(phenyl)methanone (130 mg, 0.40 mmol) with PhMgCl (2 M in THF, 1.5 equiv., 300µL) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.83 (dd, 1H, *J* 8.2 and 1.5 Hz, $H_{Ar\ nitrophenoxy}$), 7.48-7.44 (m, 1H, $H_{Ar\ nitrophenoxy}$), 7.39-7.29 (m, 10H, $H_{Ar\ diphenyl}$), 7.13 (d, 1H, *J* 8.2Hz, $H_{Ar\ nitrophenoxy}$), 7.05 (d, 1H, *J* 7.7 Hz, $H_{Ar\ nitrophenoxy}$), 6.42 (d, 1H, *J* 3.1 Hz, H_4), 5.94 (d, 1H, *J* 3.1 Hz, H_3), 5.13 (s, 2H, CH_2), 3.09 (s, 1H, OH); **^{13}C NMR ($CDCl_3$, 100MHz)**: δ 158.7 (C_q, C_2), 151.3 ($C_{q\ Ar-C-O}$), 149.1 (C_q, C_5), 144.3 ($2C_q$), 140.6 ($C_{q\ Ar-C-N}$), 133.9 ($CH_{Ar\ nitrophenoxy}$), 128.0($4xCH_{Ar\ diphenyl}$), 127.7($2xCH_{Ar\ diphenyl}$) and 127.1($4xCH_{Ar\ diphenyl}$), 125.6, 121.1 and 115.9 ($3xCH_{Ar\ nitrophenoxy}$), 111.3 (C_4), 110.6 (C_3), 77.9 (C_q, Ph_2C-OH), 64.1 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{24}H_{19}NNaO_5$: 424.1155 found 424.1162.

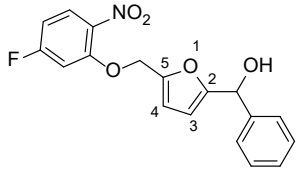
- **{5-[(2-Nitro-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6m**



Yellow oil (195 mg, 76%) isolated after chromatography (pentane/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitro-4-fluoro-phenoxy)methyl]furan-2-carbaldehyde **S5m** (200 mg 0.75 mmol) with PhMgCl (2 M in THF, 1.4 equiv., 525 µL) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.53 (dd, 1H, *J* 7.5 and 3.1Hz, $H_{Ar\ nitrophenoxy}$), 7.41-7.29 (m, 5H, H_{Ar}), 7.17 (ddd, 1H, *J* 9.2, 7.5 and 3.1 Hz, $H_{Ar\ nitrophenoxy}$), 7.09 (dd, 1H, *J* 9.2 and 4.4 Hz, $H_{Ar\ nitrophenoxy}$), 6.37 (d, 1H, *J* 3.2 Hz, H_4), 6.09 (dd, 1H, *J* 3.3 and 0.7 Hz, H_3), 5.82-5.71 (m, 1H, C<u>H</u>OH), 5.07 (s, 2H, CH_2), 2.74 (d, 1H, *J* 3.7 Hz, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz**) : δ 157.2 (C_q, C_2), 156.0 ($C_{q\ C-F}$, d, J_{CF} 244 Hz), 148.8 (C_q, C_5), 148.0 ($C_{q\ Ar-C-O}$, d, J_{C-F} 2.9 Hz,), 140.8 ($C_{q\ Ar-C-N}$, d, J_{C-F} 8.2 Hz,), 140.6 ($C_{q\ Ar}$), 128.6 ($2xCH_{Ar}$), 128.3 (CH_{Ar}), 126.7 ($2xCH_{Ar}$), 121.0 (CH_{Ar}, d, J_{C-F} 22.8 Hz), 118.8 (CH_{Ar}, d, J_{C-F} 7.8 Hz), 112.8 (CH_{Ar}, J_{C-F} 27.4 Hz), 111.9 (C_4), 108.5 (C_3), 70.1 (CHOH), 65.4 (CH_2); **^{19}F NMR ($CDCl_3$, 376MHz):** -118.8 (td, *J* 7.3, 4.5 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for: $C_{18}H_{14}FNNaO_5$: 366.0748; found 366.0745.

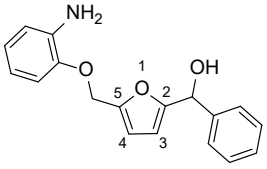
- **{5-[(2-Nitro-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6n**



Brown oil (346 mg, 89%) isolated after chromatography (petroleum ether/EtOAc 8/2 to 7/3), obtained from 5-[(2-nitro-5-fluoro-phenoxy)methyl]furan-2-carbaldehyde **S5n** (300 mg 1.13 mmol) with PhMgCl (2 M in THF, 1.4 equiv., 800 µL) following general procedure B.

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.91 (dd, 1H, *J* 9.1, $J_{H\text{-}F}$ 5.9 Hz, $H_{Ar\ nitrophenoxy}$), 7.46-7.28 (m, 5H, H_{Ar}), 6.89 (dd, 1H, $J_{H\text{-}F}$ 10.2 and *2*.5 Hz, $H_{Ar\ nitrophenoxy}$), 6.74 (ddd, 1H, *J* 9.1, $J_{H\text{-}F}$ 7.3 and 2.5 Hz, $H_{Ar\ nitrophenoxy}$), 6.42 (d, 1H, *J* 3.2 Hz, H_4), 6.11 (dd,1H, *J* 3.2 and 0.8 Hz, H_3), 5.80 (s, 1H, C<u>H</u>OH), 5.10 (s, 2H, CH_2), 2.59 (s, 1H, CHO<u>H</u>); **^{13}C NMR ($CDCl_3$, 100MHz)** δ 165.5 ($C_{q\ C\text{-}F}$, d, $J_{C\text{-}F}$ 256.4 Hz), 157.3 (C_q, C_2), 153.9 ($C_{q\ Ar\ –C\text{-}O}$,d, $J_{C\text{-}F}$ 11.3 Hz), 148.3 (C_q, C_5), 140.5 ($C_{q\ Ar}$), 136.8 ($C_{q\ Ar\ –C\text{-}N}$), 128.7 (2x$CH_{Ar\ phenyl}$), 128.4 ($CH_{Ar\ phenyl}$), 128.1 (CH_{Ar}, d, $J_{C\text{-}F}$ 11.3 Hz), 126.7 (2x$CH_{Ar\ phenyl}$), 112.1 (C_4), 108.6 (C_3), 108.3 (CH_{Ar}, d, $J_{C\text{-}F}$ 23.4 Hz), 103.6 (CH_{Ar}, d, $J_{C\text{-}F}$ 26.7 Hz), 70.2 (CHOH), 64.5 (CH_2); **^{19}F NMR ($CDCl_3$, 376MHz):** δ -100.4 (ddd, *J* 10.1, 7.3, 5.9 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for: $C_{18}H_{14}FNNaO_5$: 366.0748; found 366.0750.

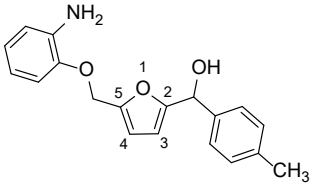
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(phenyl)methanol 8**



Brown solid (876 mg, 93% yield) obtained from {5-[(2-nitrophenoxy)methyl]furan-2-yl}(phenyl)methanol **6** (1.04 g, 3.2 mmol) following general procedure C without further purification.

^{1}H NMR ($CDCl_3$, 400MHz): 7.47-7.29 (m, 5H, $H_{Ar\ phenyl}$), 6.90-6.79 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.74-6.67 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.31 (d, 1H, *J* 3.2Hz, H_4), 6.06 (d, 1H, *J* 3.2Hz, H_3), 5.80 (s, 1H, C<u>H</u>OH), 4.96 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 100MHz)**; 156.7 (C_q, C_2), 150.6 (C_q, C_5), 146.1 ($C_{q\ Ar\ –C\text{-}O}$), 140.8 (C_q, $C_{1'}$), 137.1 ($C_{q\ Ar\ –C\text{-}N}$), 128.6 (2x$CH_{Ar\ phenyl}$), 128.2 ($CH_{Ar\ phenyl}$), 126.8 (2x$CH_{Ar\ phenyl}$), 122.3 ($CH_{Ar\ aminophenoxy}$), 118.6 ($CH_{Ar\ aminophenoxy}$), 115.7 ($CH_{Ar\ aminophenoxy}$), 113.6 ($CH_{Ar\ aminophenoxy}$), 110.7 (C_4), 108.4 (C_3), 70.2 (<u>C</u>HOH), 63.5 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for: $C_{18}H_{17}NNaO_3$: 318.1101 ; found 318.1100; $[M+H]^+$: calcd for $C_{18}H_{18}NO_3$: 296.1281; found 296.1281; mp 74°C.

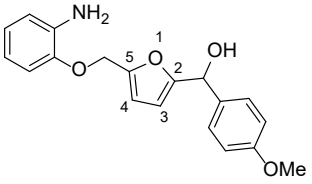
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(4-methylphenyl)methanol 8a**



Yellow oil (146 mg, 89% yield) obtained from {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-methylphenyl)methanol **S6a** (181 mg, 0.53 mmol) following general procedure C without further purification.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.31 and 7.19 (2m, 2x2H, H_{Ar}), 6.93-6.79 and 6.77-6.63 (2m, 2x2H, $H_{Ar\ aminophenoxy}$), 6.31 (d, 1H, *J* 3.2 Hz, H_4), 6.05 (dd, 1H, *J* 3.2 and 0.8Hz, H_3), 5.75 (s, 1H, C<u>H</u>OH), 4.95 (s, 2H, CH_2), 3.47 (bs, 2H, NH_2), 2.38 (s, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 157.0 (C_q, C_2), 150.4 (C_q, C_5), 146.1 ($C_{q\ Ar\ –C\text{-}O}$), 137.9 ($C_{q\ Ar}$), 137.8 ($C_{q\ Ar}$), 136.9 ($C_{q\ Ar\ –C\text{-}N}$), 129.2 (2xCH_{Ar}), 126.7 (2xCH_{Ar}), 122.2 (CH_{Ar}), 118.6 (CH_{Ar}), 115.7 (CH_{Ar}), 113.5 (CH_{Ar}), 110.7 (C_4), 108.1 (C_3), 69.9 (CHOH), 63.5 (CH_2), 21.2 (CH_3); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{19}NNaO_3$: 332.1257; found 332.1258; $[M+H]^+$: calcd for $C_{19}H_{20}NO_3$: 310.1438; found 310.1438 .

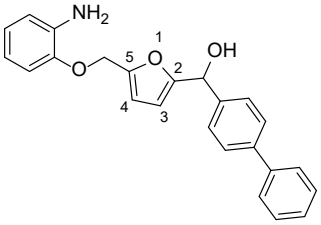
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(4-methoxyphenyl)methanol 8b**



Yellow oil (154 mg, 90% yield) obtained from 5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-methoxyphenyl)methanol **S6b** (170 mg, 0.53 mmol) following general procedure C without further purification.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.37-7.33 (m, 2H, H_{Ar}), 6.92-6.79 (m, 4H, 2x H_{Ar} and 2x$H_{Ar\ aminophenoxy}$), 6.74-6.64 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.32 (d, 1H, *J* 3.2 Hz, H_4), 6.05 (d, 1H, *J* 3.2Hz, H_3), 5.76 (s, 1H, C<u>H</u>OH), 4.97 (s, 2H, CH_2O), 3.82 (s, 3H, OMe); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 159.6 (C_q, $C_{4'}$), 157.0 (C_q, C_2), 150.5 (C_q, C_5), 146.1 ($C_{q\ Ar\ –C-O}$), 137.1 ($C_{q\ Ar\ –C-N}$), 133.0 ($C_{q\ Ar}$), 128.1 (2xCH_{Ar}), 122.3 ($CH_{Ar\ aminophenoxy}$), 118.6 ($CH_{Ar\ aminophenoxy}$), 115.7 ($CH_{Ar\ aminophenoxy}$), 114.0 (2xCH_{Ar}), 113.5 ($CH_{Ar\ aminophenoxy}$), 110.7 (C_4), 108.2 (C_3), 69.9 (CHOH), 63.5 (CH_2O), 55.4 (OMe); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{19}NNaO_4$: 348.1206 found 348.1205.

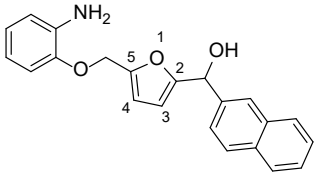
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol 8c**



Yellow solid (134 mg, 82% isolated yield) obtained from {5-[(2-nitrophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol **S6c** (183 mg, 0.46 mmol), purified with chromatography on SiO_2 (pentane/EtOAc 8/2 to 7/3) following general procedure C.

^{1}H NMR ($CDCl_3$, 300MHz): δ 7.66-7.56 and 7.55-7.41 (2m, 2x4H, $H_{Ar\ biphenyl}$), 7.41-7.30 (m, 1H, $H_{Ar\ biphenyl}$), 6.90-6.87 (m, 1H, $H_{Ar\ aminophenoxy}$), 6.84-6.81 (m, 1H, $H_{Ar\ aminophenoxy}$), 6.73- 6.69 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.34 (d, 1H, *J* 3.2 Hz, H_4), 6.13 (d, 1H, *J* 3.2 Hz, H_3), 5.86 (s, 1H, C<u>H</u>OH), 4.99 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 75MHz):** δ 156.6 (C_q, C_2), 150.8 (C_q, C_5), 146.1 ($C_{q\ Ar\ –C-O}$), 141.2 ($C_{q\ biphenyl}$), 140.9 ($C_{q\ biphenyl}$), 139.8 ($C_{q\ biphenyl}$), 137.2 ($C_{q\ Ar\ –C-N}$), 128.9 (2x$CH_{Ar\ biphenyl}$), 127.5 ($CH_{Ar\ biphenyl}$), 127.4 (2x$CH_{Ar\ biphenyl}$), 127.2 (4x$CH_{Ar\ biphenyl}$), 122.3 ($CH_{Ar\ aminophenoxy}$), 118.6 ($CH_{Ar\ aminophenoxy}$), 115.7 ($CH_{Ar\ aminophenoxy}$), 113.6 ($CH_{Ar\ aminophenoxy}$), 110.8 (C_4), 108.5 (C_3), 70.1 (CHOH), 63.6 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{24}H_{21}NNaO_3$: 394.1414 found 394.1410; $[M+H]^+$: calcd for $C_{24}H_{22}NO_3$: 372.1594; found 372.1589; mp 87°C.

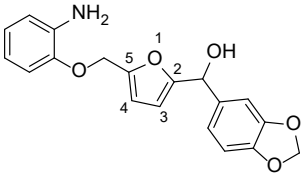
- **1-{5-[(3-Aminophenoxy)methyl]furan-2-yl}-2-(naphthalen-2-yl)ethan-1-ol 8d**



Orange oil (160 mg, 82%) obtained from 2-(naphthalen-2-yl)-1-{5-[(3-nitrophenoxy)methyl]furan-2-yl}ethan-1-ol **S6d** (149 mg, 0.4 mmol) following general procedure C without further purification.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.90-7.81 and 7.53-7.48 (2m, 4H and 3H, $H_{Ar\ naphthyl}$), 6.87-6.80 and 6.71-6.67 (2m, 2x2H, $H_{Ar\ aminophenoxy}$), 6.31 (d, 1H, *J* 2.9 Hz, H_4), 6.07 (d, 1H, *J* 2.9 Hz, H_3), 5.97 (s, 1H, C<u>H</u>OH), 4.96 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 156.7 (C_q, C_2), 150.7 (C_q, C_5), 146.1 ($C_{q\ Ar\ –C-O}$), 138.2 ($C_{q\ Ar}$), 137.0 ($C_{q\ Ar\ –C-N}$), 133.3 and 133.2 (2x$C_{q\ naphthyl}$), 128.3 (2x $CH_{Ar\ naphthyl}$), 127.8 ($CH_{Ar\ naphthyl}$), 126.3 (2x$CH_{Ar\ naphthyl}$), 125.6 ($CH_{Ar\ naphthyl}$) 124.7 ($CH_{Ar\ naphthyl}$), 122.3 $CH_{Ar\ aminophenoxy}$), 118.6 $CH_{Ar\ aminophenoxy}$), 115.7 $CH_{Ar\ aminophenoxy}$), 113.5 ($CH_{Ar\ aminophenoxy}$), 110.8 (C_4), 108.6 (C_3), 70.2 (<u>C</u>HOH), 63.5 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{22}H_{19}NNaO_3$: 368.1257; found 368.1258; $[M+H]^+$: calcd for $C_{22}H_{20}NO_3$: 346.1438; found 346.1441; mp 95°C

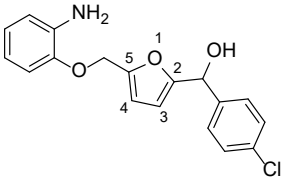
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(3,4-methylenedioxyphenyl)methanol 8e**



Yellow oil (27 mg, 32% isolated yield) obtained after purification with chromatography on SiO_2 (petroleum ether/EtOAc 8/2 to 7/3) from {5-(2-nitrophenoxy)methylfuran-2-yl}(3,4-methylenedioxyphenyl)methanol **S6e** (91 mg, 0.25 mmol) following general procedure C.

^{1}H NMR ($CDCl_3$, 400MHz): δ 6.94, 6.90-6.85, 6.85-6.76 and 6.74-6.66 (4m, 7H, 4xH_{Ar}), 6.32 (d, 1H, *J* 3.2 Hz, H_4), 6.09 (d, 1H, *J* 3.2 Hz, H_3), 5.97 (broad AB system, 2H, OCH_2O), 5.72 (s, 1H, C<u>H</u>OH), 4.97 (s, 2H, CH_2O); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 156.7 (C_q, C_2), 150.6 (C_q, C_5), 147.9 and 147.6 (2 $C_{q\ Ar\text{-}OCH_2O}$), 146.1 ($C_{q\ Ar-C-O}$), 137.1 ($C_{q\ Ar-C-N}$), 134.8 ($C_{q\ Ar}$), 122.3 (CH_{Ar}), 120.4 (CH_{Ar}), 118.6 (CH_{Ar}), 115.7 (CH_{Ar}), 113.5 (CH_{Ar}), 110.8 (C_4), 108.2 (CH_{Ar} and C_3), 107.4 (CH_{Ar}), 101.3 (OCH_2O), 70.1 (CHOH), 63.5 (CH_2O); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{17}NNaO_5$: 362.0999 found 362.1003; $[M+H]^+$: calcd for $C_{19}H_{18}NO_5$: 340.1179; found 340.1183

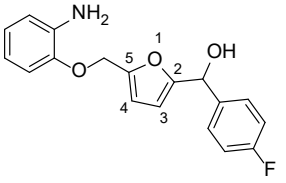
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol 8f**



Yellow oil (134 mg, 95% yield) obtained from {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol **S6f** (156 mg, 0.43 mmol) following general procedure C without further purification.

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.36 (4d, 4H, *J* 8.6 Hz, $H_{Ar\ chlorophenyl}$), 6.87 (dd, 1H, *J* 7.8, 1.3 Hz, $H_{Ar\ aminophenoxy}$), 6.83 (ddd, 1H, *J* 7.8, 7.5, 1.3 Hz, $H_{Ar\ aminophenoxy}$), 6.73-6.68 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.32 (d, 1H, *J* 3.1 Hz, H_4), 6.06 (d, 1H, *J* 3.1 Hz, H_3), 5.80 (s, 1H, C<u>H</u>OH), 4.97 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 125MHz):** δ 156.2 (C_q, C_2), 150.9 (C_q, C_5), 146.1 ($C_{q\ Ar-C-O}$), 139.1(C_q, $C_{1'}$), 137.1 ($C_{q\ Ar-C-N}$), 134.0 ($C_{q\ Ar}$), 128.8 (2x$CH_{Ar\ meta\ Cl}$), 128.2 (2x$CH_{Ar\ ortho\ Cl}$), 122.4 ($CH_{Ar\ aminophenoxy}$), 118.6 ($CH_{Ar\ aminophenoxy}$), 115.7 ($CH_{Ar\ aminophenoxy}$), 113.6 ($CH_{Ar\ aminophenoxy}$), 110.8 (C_4), 108.6 (C_3), 69.6 (<u>C</u>HOH), 63.5 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{16}ClNNaO_3$: 352.0711; found 352.0709; $[M+H]^+$: calcd for $C_{18}H_{17}ClNO_3$: 330.0891; found 330.0891; mp 115°C.

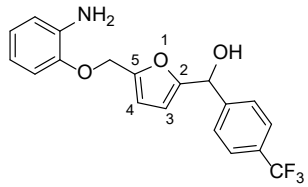
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol 8g**



Yellow solid (158 mg, 75% isolated yield) obtained after purification with chromatography on SiO_2 (pentane/EtOAc 8/2 to 7/3) from {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol **S6g** (233 mg, 0.68 mmol) following general procedure C.

^{1}H NMR ($CDCl_3$, 500MHz): δ 7.42-7.38 (m, 2H, $H_{Ar\ fluorophenyl\ ortho}$), 7.06-7.02 (2d, 2H, *J* 8.6Hz, $H_{Ar\ fluorophenyl\ meta}$), 6.87 (dd,1H, *J* 8.3 and 1.4 Hz, H_{Ar}), 6.82 (pseudo td, 1H, *J* 7.6 and 1.3 Hz, $H_{Ar\ aminophenoxy}$), 6.72-6.68 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.32 (d, 1H, *J* 3.2 Hz, H_4), 6.04 (d, 1H, *J* 3.2 Hz, H_3), 5.79 (bs, 1H, C<u>H</u>OH), 4.97 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 125MHz):** δ 162.6 ($C_{q\ C-F}$, d, J_{C-F} 246.5Hz,'), 156.5 (C_q, C_2), 150.8 (C_q, C_5), 146.1 ($C_{q\ Ar-C-O}$), 137.0 ($C_{q\ Ar-C-N}$), 136.5 ($C_{q\ Ar}$, d, *J* 3.1 Hz), 128.5 (2x$CH_{Ar\ ortho\ F}$, d, J_{C-F} 8.2 Hz), 122.3 ($CH_{Ar\ aminophenoxy}$), 118.6 ($CH_{Ar\ aminophenoxy}$), 115.7 ($CH_{Ar\ aminophenoxy}$), 115.4 (2x$CH_{Ar\ meta\ F}$, d, J_{C-F} 21.5 Hz,), 113.5 ($CH_{Ar\ aminophenoxy}$), 110.7 (C_4), 108.4 (C_3), 69.6 (CHOH), 63.5 (CH_2); **^{19}F NMR ($CDCl_3$, 282MHz):** δ -114.1–114.2 (m);**HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{16}FNNaO_3$: 336.1006 found 336.1003. mp : 100°C.

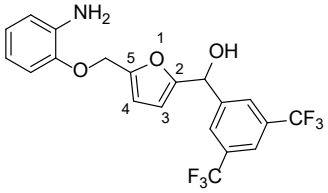
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol 8h**



Yellow solid (238 mg, 95% yield) obtained from {5-(2-nitrophenoxy)methylfuran-2-yl}(4-trifluoromethylphenyl)methanol **S6h** (270 mg, 0.69 mmol) following general procedure C without further purification.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.66-7.60 (2d, 4H, *J* 8.0 Hz, $H_{Ar\ trifluoromethylphenyl}$), 6.91-6.78 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.75-6.65 (2H, m, $H_{Ar\ aminophenoxy}$), 6.33 (1H, d, *J* 3.2 Hz, H_4), 6.06 (d, 1H, *J* 3.2 Hz, H_3), 5.86 (s, 1H, C<u>H</u>OH), 4.97 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 155.9 (C_q, C_2), 151.0 (C_q, C_5), 146.1 ($C_{q\ Ar\ –C\text{-}O}$), 144.5 ($C_{q\ Ar}$, d, J_{CF} 1.4 Hz), 136.9 ($C_{q\ Ar\ –C\text{-}N}$), 130.3 ($C_{q\ C\text{-}CF_3}$, $J_{C\text{-}F}$ 32 Hz), 127.0 ($2xCH_{Ar\ ortho\ CF_3}$), 125.5 ($2xCH_{Ar\ meta\ CF_3}$, $J_{C\text{-}F}$ 3.8Hz), 124.2 ($C_{q\ CF_3}$, bq, *J* 270 Hz), 122.4 ($CH_{Ar\ aminophenoxy}$), 118.8 ($CH_{Ar\ aminophenoxy}$), 115.8 ($CH_{Ar\ aminophenoxy}$), 113.6 ($CH_{Ar\ aminophenoxy}$), 110.8 (C_4), 108.8 (C_3), 69.5 (CHOH), 63.5 (CH_2); **^{19}F NMR ($CDCl_3$, 282MHz):** δ -62.4 (s); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{16}F_3NNaO_3$: 386.0974 found 386.0971; $[M+H]^+$: calcd for $C_{19}H_{17}F_3NO_3$: 364.1155; found 364.1152; mp 129°C.

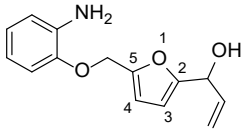
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol 8i**



Yellow solid (220 mg, 84% yield) obtained from {5-[(2-nitrophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol **S6i** (170 mg, 0.43 mmol) following general procedure C without further purification.

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.92 (s, 2H, H_{Ar}), 7.84 (s, 1H, H_{Ar}), 6.91-6.79 and 6.75-6.65 (2m, 2x2H, $4xH_{Ar\ aminophenoxy}$), 6.35 (d, 1H, *J* 3.2 Hz, H_4), 6.12 (d, 1H, *J* 3.2 Hz, H_3), 5.94 (s, 1H, C<u>H</u>OH), 4.98 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 155.0 (C_q, C_2), 151.4 (C_q, C_5), 146.0 ($C_{q\ Ar\ –C\text{-}O}$), 143.2 ($C_{q\ Ar}$), 136.8 ($C_{q\ Ar\ –C\text{-}N}$), 131.9 ($2C_{q\ C\text{-}CF_3}$, q, $J_{C\text{-}F}$ 33.4 Hz,), 126.9 ($2xCH_{Ar}$), 123.4 ($2xC_{q\ CF_3}$, bq, $J_{C\text{-}F}$ 270 Hz), 122.6 ($CH_{Ar\ aminophenoxy}$), 122.1 (CH_{Ar}), 118.8 ($CH_{Ar\ aminophenoxy}$), 115.9 ($CH_{Ar\ aminophenoxy}$), 113.6 ($CH_{Ar\ aminophenoxy}$), 110.9 (C_4), 109.1 (C_3), 68.8 (CHOH), 63.4 (CH_2); **^{19}F NMR ($CDCl_3$, 282MHz**): δ -62.8 (s); **HRMS (ESI)** [M+Na]+: calcd for $C_{10}H_{15}F_6NNaO_3$: 454.0848; found 454.0848; [M+H]+: calcd for $C_{20}H_{16}F_6NO_3$: 432.1029; found 432.1028; mp 121°C.

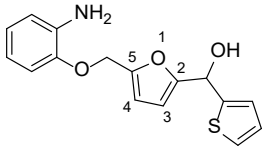
- **1-{5-[(2-Aminophenoxy)methyl]furan-2-yl}prop-2-en-1-ol 8j**



Yellow solid (100 mg, 55% isolated yield) obtained from 1-{5-[(2-nitrophenoxy)methyl]furan-2-yl}prop-2-en-1-ol **S6j** (209 mg, 0.76 mmol), with chromatography on SiO_2 (pentane/EtOAc 8/2 to 7/3) following general procedure C.

^{1}H NMR ($CDCl_3$, 400MHz): δ 6.90-6.88 (m, 1H, H_{Ar}), 6.85-6.80 (m, 1H, H_{Ar}), 6.74-6.69 (m, 2H, $2xH_{Ar}$), 6.35 (d, 1H, *J* 3.2 Hz, H_4), 6.23 (d, 1H, *J* 3.2 Hz, H_3), 6.13 (ddd, 1H, *J* 17.2, 10.4 and 5.7 Hz, $CH_{ethylene}$), 5.44 (dt, 1H, *J* 17.2 and 1.3 Hz, CH_2=), 5.30 (dt, 1H, *J* 10.4 and 1.3 Hz, $CH_{2\ ethylene}$), 5.23 (m, 1H, C<u>H</u>OH), 4.99 (s, 2H, CH_2O); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 155.7 ($C_{q\ Ar}$), 150.6 ($C_{q\ Ar}$), 146.2 ($C_{q\ Ar}$), 137.1 ($C_{q\ Ar}$), 136.7 ($CH_{ethylene}$), 122.3 (CH_{Ar}), 118.6 (CH_{Ar}), 116.9 ($CH_{2\ ethylene}$), 115.7 (CH_{Ar}), 113.4 (CH_{Ar}), 110.8 (C_4), 107.8 (C_3), 68.8 (<u>C</u>HOH), 63.5 (<u>C</u>H_2O); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{14}H_{15}NNaO_3$: 268.0944 found 268.0946; $[M+H]^+$: calcd for $C_{14}H_{16}NO_3$: 246.1125; found 246.1126; mp 74°C

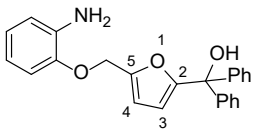
- **{{5-[(2-Aminophenoxy)methyl]furan-2-yl}(thiophen-2-yl)methanol 8k**



Yellow solid (125 mg, 73% isolated yield) obtained from {5-[(2-nitrophenoxy)methyl]furan-2-yl}(thiophen-2-yl)methanol **S6k** (190 mg, 0.57 mmol), with chromatography on SiO_2 (pentane/EtOAc 8/2 to 7/3) following general procedure C.

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.30 (dd, 1H, *J* 5.0 and 1.2 Hz, $H_{Ar\ thienyl}$), 7.02 (pseudo dt, 1H, *J* 3.5 and 1.2 Hz, $H_{Ar\ thienyl}$), 6.98 (dd, 1H, *J* 5.0 and 3.5 Hz, $H_{Ar\ thienyl}$), 6.89 (dd, 1H, *J* 8.3 and 1.4 Hz, $H_{Ar\ aminophenoxy}$), 6.84-6.80 and 6.74-6.69 (2m, 3H, $H_{Ar\ aminophenoxy}$), 6.35 (d, 1H, *J* 3.2 Hz, H_4), 6.24 (dd, 1H, *J* 3.2 and 0.7 Hz, H_3), 6.04 (bs, 1H, CHOH), 4.98 (s, 2H, CH_2); **^{13}C NMR (CDCl$_3$, 100MHz):** δ 155.7 (C_q, C_2), 150.7 (C_q, C_5), 146.1 ($C_{q\ Ar-C-O}$), 144.4 ($C_{q\ Ar}$), 137.0 ($C_{q\ Ar-C-N}$), 126.8 ($CH_{Ar\ thienyl}$), 125.7 ($CH_{Ar\ thienyl}$), 125.5 ($CH_{Ar\ thienyl}$), 122.3 ($CH_{Ar\ aminophenoxy}$), 118.7 ($CH_{Ar\ aminophenoxy}$), 115.8 ($CH_{Ar\ aminophenoxy}$), 113.5 ($CH_{Ar\ aminophenoxy}$), 110.8 (C_4), 108.4 (C_3), 66.3 (CHOH), 63.5 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{16}H_{15}NNaO_3S$: 324.0665; found 324.0666; mp 79°C.

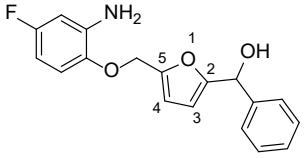
- **{5-[(2-Aminophenoxy)methyl]furan-2-yl}(diphenyl)methanol 8l**



Yellow oil (95 mg, 99% yield) obtained from {5-[(2-nitrophenoxy)methyl]furan-2-yl}di(phenyl)methanol **S6l** (100 mg, 0.26 mmol) according to procedure C without further purification.

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.41-7.27 (m, 10H, $H_{Ar\ phenyl}$), 6.88-6.81 and 6.72-6.68 (2m, 2x2H, $H_{Ar\ aminophenoxy}$), 6.33 (d, 1H, *J* 3.2 Hz, H_4), 5.9 (d, 1H, *J* 3.2 Hz, H_3), 4.99 (s, 2H, CH_2O); **^{13}C NMR (CDCl$_3$, 100MHz):** δ 158.4 (C_q, C_2), 150.9 (C_q, C_5), 146.0 ($C_{q\ Ar-C-O}$), 144.6 (2x$C_{q\ Ar}$), 137.1 ($C_{q\ Ar-C-N}$), 128.5-127.1 (m, 10x$CH_{Ar\ phenyl}$), 122.4 ($CH_{Ar\ aminophenoxy}$), 118.5 ($CH_{Ar\ aminophenoxy}$), 115.8 ($CH_{Ar\ aminophenoxy}$), 113.8 ($CH_{Ar\ aminophenoxy}$), 110.6, 110.4 (C_3 and C_4), 78.0 ($C_{q\ C-OH}$), 63.6 (CH_2O); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{24}H_{21}NNaO_3$: 394.1414 found 394.1419.

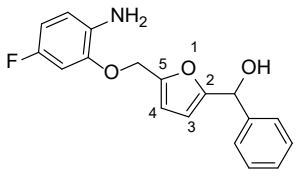
- **{5-[(2-Amino-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8m**



Yellow oil (71 mg, 62% isolated yield) obtained from {5-[(2-nitro-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol **S6m** (126mg, 0.37 mmol), with chromatography on SiO_2 (pentane/EtOAc 8/2 to 7/3) following general procedure C.

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.49-7.28 (m, 5H, $H_{Ar\ phenyl}$), 6.75 (dd, 1H, *J* 8.7 and J_{H-F} 5.1 Hz, $H_{Ar\ aminophenoxy}$), 6.39-6.31 (m, 2H, $H_{Ar\ aminophenoxy}$), 6.29 (d, 1H, *J* 3.2 Hz, H_4), 6.07 (d, 1H, *J* 3.2 Hz, H_3), 5.80 (s, 1H, CHOH), 4.91 (s, 2H, CH_2); **^{13}C NMR (CDCl$_3$, 100MHz):** δ 158.6 ($C_{q\ C-F}$, d, J_{C-F} 238 Hz), 156.8 (C_q, C_2), 150.5 (C_q, C_5), 142.0 ($C_{q\ Ar-C-O}$, d, J_{C-F} 2.2 Hz,), 140.7 ($C_{q\ Ar}$), 138.8 ($C_{q\ Ar-C-N}$, d, J_{C-F} 11.2 Hz,), 128.6(2x$CH_{Ar\ phenyl}$), 128.3 ($CH_{Ar\ phenyl}$), 126.7 (2x$CH_{Ar\ phenyl}$), 115.0 (CH_{Ar}, d, J_{C-F} 10.0 Hz), 110.9 (C_4), 108.4 (C_3), 103.8 (CH_{Ar}, d, J_{C-F} 23.2 Hz), 102.5 (CH_{Ar}, d, J_{C-F} 26.5 Hz), 70.2 (CHOH), 64.4 (CH_2); **^{19}F NMR (CDCl$_3$, 282MHz):** δ -121.00 (ddd, *J* 10.0, 8.2 and 5.1 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{16}FNNaO_3$: 336.1006 found 336.1005; $[M+H]^+$: calcd for $C_{18}H_{17}FNO_3$: 314.1187 found 314.1186 ; mp 70°C

- **{5-[(2-Amino-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8n**

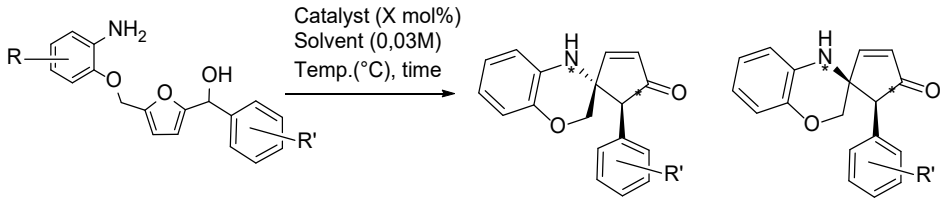


Brown solid (264 mg, 98% yield) obtained from {5-[(2-nitro-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol **S6n** (300mg, 0.87 mmol) following general procedure C without further purification.

^{1}H NMR (CDCl$_3$, 400MHz): δ 7.44-7.32 (m, 5H, $H_{Ar\ phenyl}$), 6.65 (dd, 1H, J_{H-F}≈ $J_{ortho\ H-H}$ 9.4 and 2.6 Hz, H_{Ar}), 6.60 (dd, 1H, *J* 9.4 and 5.8 Hz, H_{Ar}), 6.53 (pseudo td, 1H, J_{H-F}≈ $J_{ortho\ H-H}$ 9.4 and 2.6 Hz $H_{Ar\ aminophenoxy}$), 6.34 (d, 1H, *J* 3.2 Hz, H_4), 6.07 (d, 1H, *J* 3.2 Hz, H_3), 5.80 (s, 1H, CHOH), 4.94 (s, 2H, CH_2); **^{13}C NMR (CDCl$_3$, 100MHz):** δ 156.9 (C_q, C_2), 156.2 ($C_{q\ C-F}$, d, J_{C-F} 230 Hz),149.9 (C_q, C_5), 146.4 ($C_{q\ Ar-C-O}$, d, J_{C-F} 9.6 Hz,), 140.7 ($C_{q\ Ar}$), 132.9 ($C_{q\ Ar-C-N}$,d, J_{C-F} 2.7 Hz), 128.6(2xCH_{Ar}), 128.3 (CH_{Ar}), 126.7(2xCH_{Ar}), 115.4 (CH_{Ar}, d, J_{C-F} 9.2 Hz), 111.2 (C_4), 108.5 (C_3), 107.8 (CH_{Ar}, d, J_{C-F} 21.9 Hz), 101.6 (CH_{Ar} d, J_{C-F} 26.3 Hz), 70.2 (CHOH), 63.6 (CH_2); **^{19}F NMR (CDCl$_3$, 282MHz):** δ -123.94 (ddd, *J*

10.2, 8.2 and 5.9 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{16}FNNaO_3$: 336.1006 found 336.1005; $[M+H]^+$: calcd for $C_{18}H_{17}FNO_3$: 314.1187 found 314.1187; m.p. 85°C

- **Characterization of compounds 9, 9a-9n, 10**

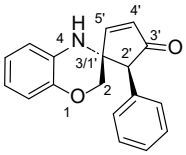


8 and 8a-8n **9/9' and 9/9'a-n and 10**

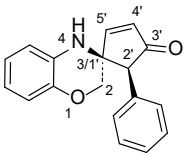
- **{2'-Phenyl-*2H*, *4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9/9'**

Conditions D1: Mixture of diastereomers obtained as orange oil (74.4 mg, 73%, dr = 73/27) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}(phenyl)methanol (108.2 mg, 0.37 mmol).

Conditions D2: Mixture of diastereomers obtained as orange oil (72.8 mg, 77%, dr = 78/22) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}(phenyl)methanol (98.8 mg, 0.34 mmol)



Major diastereomer **9** obtained after separation **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.74 (d, 1H, *J* 6.0 Hz, $H_{5'}$), 7.56 – 7.28 (m, 3xH_{Ar}), 7.17 – 7.06 (m, 2xH_{Ar}), 6.91 – 6.58 (m, 4xH_{Ar}), 6.41 (d, 1H, *J* 6.0 Hz, $H_{4'}$), 3.84 and 3.49 (2d, 1H, *J* 11.0 Hz, CH_2), 3.61 (s, 1H, $H_{2'}$); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 206.1(CO), 162.5($C_{5'}$), 143.3(C_q), 133.3(C_q), 133.1($C_{4'}$), 131.8 (C_q), 129.5 (2xCH_{Ar}), 128.8 (2xCH_{Ar}), 128.0 (CH_{Ar}), 122.1 (CH_{Ar}), 119.7 (CH_{Ar}), 116.8 (CH_{Ar}), 116.0 (CH_{Ar}), 71.0 (CH_2), 62.4 (CH), 61.8 ($C_{q\ spiro}$). **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{15}NNaO_2$: 300.0995 found 300.100.

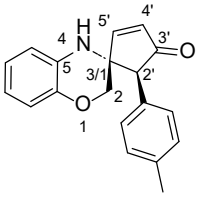


Minor diastereomer **9'** obtained after separation and recrystallized from CH_2Cl_2/Et_2O (Structure confirmed by X-Ray diffraction analysis) **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.57 (d, 1H, *J* 5.7 Hz, $H_{5'}$), 7.56 – 7.28 (m, 3xH_{Ar}), 7.17 – 7.06 (m, 2xH_{Ar}), 6.91 – 6.58 (m, 4xH_{Ar}), 6.53 (d, 1H, *J* 5.7 Hz, $H_{4'}$), 4.25 and 4.1 (2d, 1H, *J* 10.4 Hz, OCH_2), 3.80 (s, 1H, $H_{2'}$); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 207.2 (CO), 162.8 ($C_{5'}$), 143.5 (C_q), 135.9 ($C_{4'}$), 135.8 (C_q), 131.3 (C_q), 129.3 (2xCH_{Ar}), 128.7 (2xCH_{Ar}), 127.7 (CH_{Ar}), 122.0 (CH_{Ar}), 119.4 (CH_{Ar}), 116.6 (CH_{Ar}), 115.6 (CH_{Ar}), 72.1 (CH_2), 60.5 (CH), 61.9 ($C_{q\ spiro}$). **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{15}NNaO_2$: 300.0995 found 300.100.

- **2'-(4-Methylphenyl)-*2H*,*4H*-spiro [1,4] benzoxazine-3,1'-cyclopent[4]en]-3'-one 9a/9'a**

Conditions D1: Mixture of diastereomers obtained as an orange oil (48.2 mg, 60%, dr = 76/24) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl] furan-2-yl} (4-methylphenyl) methanol (87.8 mg, 0.28 mmol).

Conditions D2: Mixture of diastereomers obtained as orange oil (46.9 mg, 58%, dr = 88/12) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl] furan-2-yl} (4-methylphenyl) methanol (88.3 mg, 0.28 mmol).



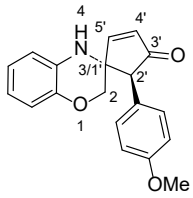
Major diastereomer obtained after separation as a yellow oil **^{1}H NMR ($CDCl_3$, 400MHz)** δ 7.73 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.12 (d, 2H, *J* 8.0 Hz, $H_{Ar\ p\text{-tolyl}}$), 7.05-6.94 (m, 2H, $H_{Ar\ p\text{-tolyl}}$), 6.87-6.75 and 6.74-6.64 (2m, 2x2H, $H_{Ar\ benzoxazine}$), 6.40 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 4.07 (s, 1H, NH), 3.83 (d, 1H, *J* 11.0 Hz, CH_2O), 3.56 (s, 1H, $H_{2'}$), 3.50 (d, 1H, *J* 10.9 Hz, CH_2O), 2.32 (s, 3H, CH_3); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 206.2 (CO), 162.4

($C_{5'}$), 143.4 ($C_{q\ Ar\ C\text{-}O}$), 137.7 ($C_{q\ Ar}$), 133.2 ($C_{4'}$), 131.9 ($C_{q\ Ar\ –C\text{-}N}$), 130.2 ($C_{q\ Ar}$), 129.5-129.4 (4x$CH_{Ar\ p\text{-}tolyl}$), 122.1-116.1 (4x$CH_{Ar\ benzoxazine}$), 71.1 (CH_2), 62.2 (CH), 61.8 ($C_{q\ spiro}$), 21.2 (CH_3); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{17}NNaO_2$: 314.1151 found 314.1154

- **<u>2'-(4-Methoxyphenyl)-*2H,4H*-spiro [[1,4] benzoxazine-3,1'-cyclopent[4] en]-3'-one 9b/9'b</u>**

Conditions D1: Mixture of diastereomers obtained as yellow solid (65 mg, 67%, dr = 87/13) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl] furan-2-yl}(4-methoxyphenyl) methanol **8b** (103.5 mg, 0.32 mmol).

Conditions D2: Mixture of diastereomers obtained as yellow oil (61.2 mg, 65%, dr = 91/9) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl]furan-2-yl}(4-methoxyphenyl) methanol **8b** (102.2 mg, 0.31 mmol).

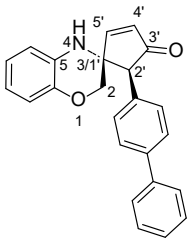


9b Major diastereomer obtained after separation as a yellow oil **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.72 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.08-6.97 (m, 2H, $H_{Ar\ methoxyphenyl}$), 6.90-6.75 (m, 4H, $2H_{Ar\ methoxyphenyl}$ and $2H_{Ar\ benzoxazine}$), 6.75-6.61 (m, 2H, $H_{Ar\ benzoxazine}$), 6.40 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 4.09 (s, 1H, NH), 3.82 (dd, 1H, *J* 10.9 and 1.4 Hz, CH_2O), 3.78 (s, 3H, CH_3), 3.55 (s, 1H, $H_{2'}$), 3.50 (d, 1H, *J* 10.9 Hz, CH_2O); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 206.3 (CO), 162.4 ($C_{5'}$), 159.3 (C_q, $C_{4''}$), 143.4 ($C_{q\ Ar\ C\text{-}O}$), 133.1 ($C_{4'}$), 131.9 ($C_{q\ Ar\ –C\text{-}N}$), 130.6 (2x$CH_{Ar\ methoxyphenyl}$), 125.2 (C_q, $C_{1''}$), 121.1-116.1 (4x$CH_{Ar\ benzoxazine}$), 114.3 (2x$CH_{Ar\ methoxyphenyl}$), 71.2 (CH_2), 61.8 ($C_{2'}$ and $C_{q\ spiro}$), 55.4 (CH_3); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{17}NNaO_3$: 330.1101 found 330.1098.

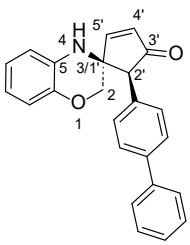
- **<u>2'-Biphenyl-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9c/9'c</u>**

Conditions D1: Mixture of diastereomers obtained as yellow oil (67.8 mg, 64%, dr = 72/28) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol **8c** (112.7 mg, 0.3 mmol).

Conditions D2: Mixture of diastereomers obtained as yellow solid (71.8 mg, 59%, dr = 81/19) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol **8c** (129 mg, 0.35 mmol).



Major diastereomer 9c obtained after separation as a yellow oil **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.77 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.60-7.51 (m, 4H, $H_{Ar\ biphenyl}$), 7.48-7.39 (m, 2H, $H_{Ar\ biphenyl}$), 7.39-7.31 (m, 1H, $H_{Ar\ biphenyl}$), 7.20 (d, 2H, *J* 8.2Hz, $H_{Ar\ biphenyl}$), 6.88-6.77 and 6.76-6.66 (2m, 2x2H, $H_{Ar\ benzoxazine}$), 6.44 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 3.89 (d, 1H, *J* 10.9 Hz, CH_2), 3.65 (s, 1H, $H_{2'}$), 3.58 (d, 1H, *J* 10.9 Hz, CH_2); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 206.0 (CO), 162.5 ($C_{5'}$), 143.4 ($C_{q\ Ar\ C\text{-}O}$), 140.9 and 140.6 (2$C_{q\ Ar}$), 133.2 ($C_{4'}$), 132.3 ($C_{q\ Ar}$), 131.8 ($C_{q\ Ar\ –C\text{-}N}$), 129.9-127.2 (9x$CH_{Ar\ biphenyl}$), 122.1-116.1 (4x$CH_{Ar\ benzoxazine}$), 71.1 (CH_2), 62.3 (CH), 61.9 ($C_{q\ spiro}$); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{24}H_{19}NNaO_2$: 376.1308 found 376.1307.

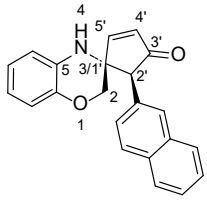


Minor diastereomer 9'c obtained after separation as a yellow solid **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.60 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.53-7.47 (m, 2H, $H_{Ar\ biphenyl}$), 7.45-7.37 (m, 4H, $H_{Ar\ biphenyl}$), 7.37-7.30 (m, 1H, $H_{Ar\ biphenyl}$), 7.01-6.93 (m, 2H, $H_{Ar\ biphenyl}$), 6.83 (dd, 1H, *J* 7.9 and 1.5 Hz, $H_{Ar\ benzoxazine}$), 6.68-6.56 (m, 2H, $H_{Ar\ benzoxazine}$), 6.55 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 6.12 (dd, 1H, *J* 7.8 and 1.6 Hz, $H_{Ar\ benzoxazine}$), 4.28 and 4.12 (2d, 2H, *J* 10.4 Hz, CH_2O), 3.85 (s, 1H, $H_{2'}$); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 207.2 (CO), 162.8 ($C_{5'}$), 143.5 ($C_{q\ Ar\ C\text{-}O}$), 140.6 (2x$C_{q\ Ar}$), 135.9 ($C_{4'}$), 134.7 ($C_{q\ Ar}$), 131.3 ($C_{q\ Ar\ –C\text{-}N}$), 129.7-127.2 (9x$CH_{Ar\ biphenyl}$), 122.1-115.7 (4x$CH_{Ar\ benzoxazine}$), 72.1 (CH_2), 61.9 ($C_{q\ spiro}$), 60.1 (CH); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{24}H_{19}NNaO_2$: 376.1308 found 376.1310; mp 123°C.

- **2'-(2-Naphtalenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9d/9'd**

Conditions D1: Mixture of diastereomers obtained as yellow solid (55 mg, 57%, dr = 71/29) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}(naphtalen-2-yl) methanol **8d** (102.8 mg, 0.30 mmol).

Conditions D2: Mixture of diastereomers obtained as yellow oil (51.4 mg, 55%, dr = 75/25) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl]furan-2-yl}(naphtalen-2-yl) methanol **8d** (98.7 mg, 0.29 mmol).

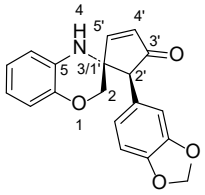


Major diastereomer **14a** obtained after separation as a yellow solid **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.87-7.72 (m, 4H, 3$H_{Ar\ naphthyl}$ and $H_{5'}$), 7.63 (m,1H, $H_{Ar\ naphthyl}$), 7.48 (dd, 2H, *J* 7.2 and 3.3 Hz, $H_{Ar\ naphthyl}$), 7.21 (dd, 1H, *J* 8.5 and 1.8 Hz, H_{Ar}), 6.88-6.80 and 6.79-6.65 (2m, 1H and 3H, $H_{Ar\ benzoxazine}$), 6.46 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 4.14 (s, 1H, NH), 3.87 (d, 1H, *J* 11.0 Hz, CH_2O), 3.77 (s, 1H, $H_{2'}$), 3.51 (d, 1H, *J* 11.0 Hz, CH_2O); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 206.1 (CO), 162.6 ($C_{5'}$), 143.4 ($C_{q\ Ar\ C\text{-}O}$), 133.4 and 133.3 ($C_{q\ Ar\ –C\text{-}N}$ and $C_{4'}$), 132.9, 131.8 and 130.8 (3x$C_{q\ naphthyl}$), 128.8, 128.6, 128.0, 127.8, 127.0, 126.5 and 126.4 (7x$CH_{Ar\ naphthyl}$), 122.1, 119.9, 116.9 and 116.1 (4xCH_{Ar} benzoxazine), 71.1 (CH_2), 62.5 (CH), 62.0 ($C_{q\ spiro}$); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{22}H_{17}NNaO_2$: 350.1151 found 350.1153; mp 87°C

- **2'-(Methylenedioxyphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9e/9'e**

Conditions D1: Mixture of diastereomers obtained as yellow solid (68 mg, 69%, dr = 85/15) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}(2*H*-1,3-benzodioxol-5-yl)methanol **8e** (105 mg, 0.31 mmol).

Conditions D2: Mixture of diastereomers obtained as yellow solid (60.1 mg, 61%, dr = 86/14) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from from {5-[(2-aminophenoxy)methyl]furan-2-yl}(2*H*-1,3-benzodioxol-5-yl)methanol **8e** (105.7 mg, 0.31 mmol).

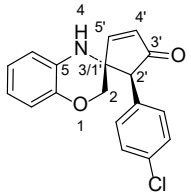


Major Diastereomer 9e obtained after separation as a yellow solid **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.74 (d, 1H, *J* 5.9 Hz, $H_{5'}$), 6.86-6.78 (m, 2H, $H_{Ar\ benzoxazine}$), 6.76 (1H, dd, *J* 7.5 and 0.8 Hz, H_{Ar}), 6.74-6.66 (2H, m, H $_{Ar\ benzoxazine}$), 6.62 (dt, 2H, *J* 8.8 and 0.8 Hz, H_{Ar}), 6.40 (d, 1H, *J* 5.9 Hz, $H_{4'}$), 5.94 (2d, 2H, *J* 1.5 Hz, OCH_2O), 4.02 (s, 1H, NH), 3.90-3.82 (m, 1H, CH_2O), 3.57 (d, 1H, *J* 11.0 Hz, CH_2), 3.53 (s, 1H, $H_{2'}$); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 205.8 (CO), 162.4 ($C_{5'}$), 148.0 and 147.4 (2x$C_{q\ Ar\text{-}OCH2O}$), 143.4 ($C_{q\ Ar\ C\text{-}O}$), 133.1 ($C_{4'}$), 131.8 ($C_{q\ Ar\ –C\text{-}N}$), 126.6 ($C_{q\ Ar'}$), 123.1 (CH_{Ar}), 122.1, 119.9, 116.9 and 116.1 (4x$CH_{Ar\ benzoxazine}$), 109.6 and 108.7 (2xCH_{Ar}), 101.3 (OCH_2O), 71.1 (CH_2), 62.2 (CH), 61.9 ($C_{q\ spiro}$); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{19}H_{15}NNaO_4$: 344.0893 found 344.0895; mp 77°C

- **2'-(4-Chlorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9f/9'f**

Conditions D1: Mixture of diastereomers obtained as a yellow oil (61.1 mg, 57%, dr = 64/36) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol **8f** (114.8 mg, 0.35 mmol).

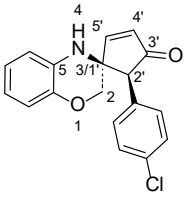
Conditions D2: Mixture of diastereomers obtained as a orange oil (51.2 mg, 61%, dr = 76/24) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol (90.2 mg, 0.27 mmol).



Major diastereomer **9f** obtained after separation as a yellow oil

^{1}H NMR ($CDCl_3$, 400MHz): δ 7.72 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.33-7.27 and 7.09-7.03 (2m, 2x2H,$H_{Ar\ chlorophenyl}$), 6.87-6.63 (m, 4H, $H_{Ar\ benzoxazine}$), 6.41 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 4.09 (s, 1H, NH), 3.81 (d, 1H, *J* 10.9 Hz, CH_2O), 3.58 (s, 1H, $H_{2'}$), 3.50 (d, 1H, *J* 10.9 Hz, CH_2O); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 205.3 (CO), 162.3 ($C_{5'}$), 143.4 ($C_{q\ Ar\ C\text{-}O}$), 134.0 ($C_{q\ Ar\ –C\text{-}N}$),

133.3 ($C_{4'}$), 131.9 and 131.6 (2x$C_{q\ Ar\ chlorophenyl}$), 130.8 (2x$CH_{Ar\ chlorophenyl}$), 129.0 (2x$CH_{Ar\ chlorophenyl}$), 122.2 ($CH_{Ar\ benzoxazine}$), 120.0 ($CH_{Ar\ benzoxazine}$), 116.9 ($CH_{Ar\ benzoxazine}$), 116.1 ($CH_{Ar\ benzoxazine}$), 70.9 (CH_2O), 61.9 and 61.8 (CH and $C_{q\ spiro}$); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}ClNNaO_2$: 334.0605 found 334.0605.

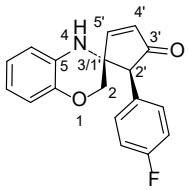


Minor diastereomer **9'f** obtained after separation as a yellow solid. **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.55 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.14 (d, 2H, *J* 8.4 Hz, $H_{Ar\ chlorophenyl}$), 6.87-6.76 (m, 3H, 2x$H_{Ar\ chlorophenyl}$ and H_{Ar}), 6.69-6.58 (m, 2H, $H_{Ar\ benzoxazine}$), 6.52 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 6.16-6.08 (m, 1H, $H_{Ar\ benzoxazine}$), 4.23 (d, 1H, *J* 10.4 Hz, CH_2O), 4.08 (d, 1H, *J* 10.4 Hz, CH_2O), 3.78 (s, 1H, $H_{2'}$); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 206.7 (CO), 162.5 ($C_{5'}$), 143.5 ($C_{q\ Ar\ C\text{-}O}$), 136.1 ($C_{4'}$), 134.3, 133.6 and 131.1 (2x$C_{q\ Ar\ chlorophenyl}$ and $C_{q\ Ar\ C\text{-}N}$), 130.7 (2xCH_{Ar}), 128.7 (2x$CH_{Ar\ chlorophenyl}$), 122.2 ($CH_{Ar\ benzoxazine}$), 119.6 ($CH_{Ar\ benzoxazine}$), 116.6 ($CH_{Ar\ benzoxazine}$), 115.5 ($CH_{Ar\ benzoxazine}$), 72.0 (CH_2O), 62.0 ($C_{q\ spiro}$), 60.0 (CH); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}ClNNaO_2$: 334.0605 found 334.0607; mp 142°C

- **<u>2'-(4-Fluorophenyl)-*2H,4H*-spiro[[1,4] benzoxazine-3,1'-cyclopent[4]en]-3'-one 9g/9'g</u>**

Conditions D1: Mixture of diastereomers obtained as an orange oil (91.8 mg, 70%, dr = 73/27) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl] furan-2-yl}(4-fluorophenyl) methanol **8g** (142.7 mg, 0.45 mmol).

Conditions D2: Mixture of diastereomers obtained as an orange oil, (61.3 mg, 57%, dr = 83/17) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl]furan-2-yl}(4-fluorophenyl) methanol **8g** (115 mg, 0.37 mmol).

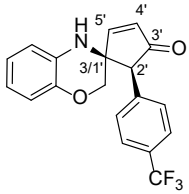


Major diastereomer **9g** obtained after separation as a yellow solid **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.73 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.16-7.06 and 7.06-6.96 (2m, 2x2H, $H_{Ar\ fluorophenyl}$), 6.89-6.64 (m, 4H, $H_{Ar\ benzoxazine}$), 6.42 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 4.04 (s, 1H, NH), 3.85-3.77 (m, 1H, CH_2O), 3.60 (s, 1H, $H_{2'}$), 3.50 (d, 1H, *J* 10.9Hz, CH_2O); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 205.5 (CO), 162.5 ($C_{q\ Ar}$, d, $J_{C\text{-}F}$ 240 Hz), 162.3 ($C_{5'}$), 143.4 ($C_{q\ Ar\ C\text{-}O}$), 133.3 ($C_{4'}$), 131.7 ($C_{q\ Ar\ C\text{-}N}$), 131.1 (d, CH_{Ar}, $J_{C\text{-}F}$ 8.1 Hz,), 129.1 ($C_{q\ Ar}$, d, J_{CF} 3.4Hz), 122.2, 120.0, 116.9 and 116.1 (4x$CH_{Ar\ benzoxazine}$), 115.8 (d, $J_{C\text{-}F}$ 21.5 Hz, 2x$CH_{Ar\ ortho\text{-}C\text{-}F}$), 71.0 ($CH_2$), 61.9 (CH), 61.8 ($C_{q\ spiro}$); **^{19}F NMR ($CDCl_3$, 282MHz):** δ -113.8 (tt, *J* 8.6 and 5.2 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}FNNaO_2$: 318.0901 found 318.0899; mp 56°C

- **<u>2'-(4-Trifluoromethylphenyl)-*2H,4H*-spiro[[1,4] benzoxazine-3,1'-cyclopent [4] en]-3'-one 9h/9'h</u>**

Conditions D1: Mixture of diastereomers obtained as an orange oil (53.4 mg, 60%, dr = 40/60) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl] furan-2-yl}(4-(trifluoromethyl) phenyl) methanol **8h** (93.6 mg, 0.26 mmol).

Conditions D2: Mixture of diastereomers obtained as an orange oil (29.3 mg, 30%, dr = 38/62) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy) methyl]furan-2-yl}(4-(trifluoromethyl) phenyl) methanol **8h** (104.6 mg, 0.29 mmol).

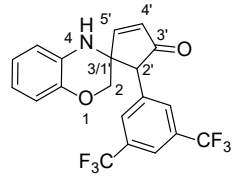


Major diastereomer **9h** obtained after separation as a yellow oil contaminated by the minor diastereomer (<10%) **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.55 (d, 1H, *J* 5.8 Hz, H_{Ar}), 7.39 (d, 2H, *J* 8.0 Hz, H_{Ar}), 7.01 (d, 2H, *J* 8.0 Hz, H_{Ar}), 6.79 (dd, 1H, *J* 7.9 and 1.6 Hz, $H_{Ar\ benzoxazine}$), 6.67-6.51 (m, 3H, 2x$H_{Ar\ benzoxazine}$ and $H_{4'}$), 6.03 (dd, 1H, *J* 7.9 Hz and 1.6 Hz, $H_{Ar\ benzoxazine}$), 4.18 (2d, 2H, *J* 10.4 Hz, CH_2O), 3.88 (s, 1H, s, CH); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 206.4 (CO), 162.3 ($C_{5'}$), 143.6 ($C_{q\ Ar\ C\text{-}O}$), 139.9 ($C_{q\ Ar}$,), 136.3 ($C_{4'}$), 130.9 ($C_{q\ Ar\ C\text{-}N}$), 130.0 (d, $C_{q\ Ar}$, *J* 1.6 Hz), 129.5 (2xCH_{Ar}, *J* 33 Hz), 125.3 (2x CH_{Ar}, *J* 4 Hz), 124.1(q, CF_3, *J* 270 Hz), 122.2 (CH_{Ar}), 119.8 (CH_{Ar}) 116.5 (CH_{Ar}) 115.4 (CH_{Ar}), 72.0 (CH_2), 62.1 ($C_{q\ spiro}$), 60.5 (C_H); **^{19}F NMR ($CDCl_3$, 282MHz):** δ -62.5 (minor, s), -62.6 (s); HRMS $[M+Na]^+$: calcd for $C_{19}H_{14}F_3NNaO_2$: 368.0869 found 368.0871

- **2'-(3,5-Ditrifluoromethyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9/9'i**

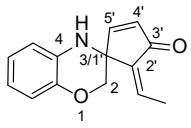
Conditions D1: Mixture of diastereomers obtained as a yellow oil (29.2 mg, 31%, dr = 23/77) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}[(3,5-bis(trifluoromethyl)phenyl]methanol **8i** (100.7 mg, 0.23 mmol).

Conditions D2: Mixture of diastereomers obtained as a yellow oil, (18.8 mg, 13%, dr 29/71) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminophenoxy)methyl]furan-2-yl}[(3,5-bis(trifluoromethyl)phenyl]methanol **8i** (101.1 mg, 0.23 mmol).



Assignment of NMR Signals for the major diastereomer 9i from mixture of 9/9'i ^{1}H NMR (CDCl$_3$, 400MHz): δ 7.58 (m, 1H, H_{Ar}), 7.51 (dd, 1H, *J* 5.8 and 0.7 Hz, $H_{5'}$), 7.33 (m, 2H, H_{Ar}), 6.75 (m, 1H, $H_{Ar\ benzoxazine}$), 6.60 (d, 1H, *J* 5.8 Hz, $H_{4'}$), 6.58 (m, 1H,$H_{Ar\ benzoxazine}$), 6.51 (m, 1H, $H_{Ar\ benzoxazine}$), 5.93 (m, 1H, H_{Ar}), 4.25 and 4.19 (2d, 2H, *J* 11.4 Hz, CH_2O), 3.99 (s, 1H, $H_{2'}$), 3.55 (s, 1H, NH); **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 206.0 (CO), 161.3 ($C_{5'}$), 144.0($C_{q\ Ar\ C\text{-}O}$), 138.4 ($C_{q,\ Ar\ C\text{-}N}$), 137.3 ($C_{4'}$), 134.3 ($CH_{Ar(CF3)2}$), 131.6 (q, 2x$C_{q\ Ar}$, *J* 33 Hz), 130.5 ($C_{q\ Ar}$), 130.2 (m, $CH_{Ar(CF3)2}$), 123.4 (q, 2xCF_3, *J* 270 Hz), 122.6 ($CH_{Ar\ benzoxazine}$), 121.7 (m, $CH_{Ar(CF3)2}$), 120.4 ($CH_{Ar\ benzoxazine}$), 116.9($CH_{Ar\ benzoxazine}$), 115.2 ($CH_{Ar\ benzoxazine}$), 72.3 (CH_2), 62.7 (CH), 61.5 ($C_{q\ spiro}$); **^{19}F NMR (CDCl$_3$, 282MHz):** δ -62.80(major), -62.85 (minor); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{20}H_{13}F_6NNaO_2$: 436.0743 found 436.0740

- **2'-Ethylidene-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 10**



Conditions D1: Mixture of isomers obtained as a yellow oil (25.5 mg, 31%, 47/53 according to respective integrations of 1H signals for CH_3) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from 1-{5-[(2-aminophenoxy)methyl]furan-2-yl}prop-2-en-1-ol **8j** (91.3 mg, 0.37 mmol).

Conditions D2: Mixture of isomers obtained as a yellow oil (19.3 mg, 20%, 76/24 according to respective integrations of 1H signals for CH_3)) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from 1-{5-[(2-aminophenoxy)methyl]furan-2-yl}prop-2-en-1-ol **8j** (103 mg, 0.42 mmol).

10/10' could not be assigned as Z/E isomers without X-ray diffraction analysis.

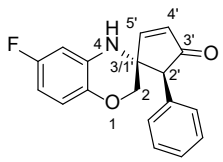
Isomer **10** obtained after separation as a yellow oil **^{1}H NMR (CDCl$_3$, 400MHz):** δ 7.44 (d, 1H, *J* 6.0 Hz, $H_{5'}$), 6.92-6.79 (m, 2H, H_{Ar}), 6.73 (ddd, 1H, *J* 8.0, 7.4 and 1.6 Hz, H_{Ar}), 6.63 (dd, 1H, *J* 7.8 and 1.5 Hz, H_{Ar}), 6.40-6.28 (m, 2H, $H_{4'}$ and H $_{vinyl}$), 4.07 (d, 2H, *J* 1.7 Hz, CH_2), 3.86 (s, 1H, NH), 2.27 (d, 3H, *J* 7.4 Hz, CH_3); **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 196.2 (CO), 156.3 ($C_{5'}$), 143.0 ($C_{q\ Ar\ C\text{-}O}$), 138.5 (CH), 136.8 (C_q, $C_{2'}$), 136.5 ($C_{4'}$), 132.4 ($C_{q\ Ar\ –C\text{-}N}$), 122.2, 119.4, 117.0 and 115.7 (4xCH_{Ar}), 72.1 (CH_2), 59.6 ($C_{q\ spiro}$), 14.1 (CH_3); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{14}H_{13}NNaO_2$: 250.0838 found 250.0839

Isomer **10'** obtained after separation as a yellow solid **^{1}H NMR (CDCl$_3$, 400MHz):** δ 7.67 (dd, 1H, *J* 6.1 and 0.8 Hz, $H_{5'}$), 6.94-6.80 (m, 3H, H $_{vinyl}$ and 2xH_{Ar}), 6.79-6.70 (m, 1H, H_{Ar}), 6.66 (dd, 1H, *J* 7.7 and 1.6Hz, H_{Ar}), 6.38 (dd, 1H, *J* 6.1 and 0.6 Hz, $H_{4'}$), 4.46 and 4.03 (dd, 1H, *J* 10.7 and 0.6 Hz, CH_2O), 3.97 (s, 1H, NH), 2.11-1.92 (m, 3H, CH_3); **^{13}C NMR (CDCl$_3$, 100 MHz)**: δ 194.4 (CO), 159.1 ($C_{5'}$), 142.9 ($C_{q\ Ar\ C\text{-}O}$), 136.2 (C_q, $C_{2'}$), 136.1 (CH), 133.9 ($C_{4'}$), 131.7 ($C_{q\ Ar\ –C\text{-}N}$), 122.3, 119.4, 117.1, 115.7 (4xCH_{Ar}), 69.5 (CH_2), 60.4 ($C_{q\ spiro}$), 14.1 (CH_3); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{14}H_{13}NNaO_2$: 250.0838 found 250.0842, mp 120°C

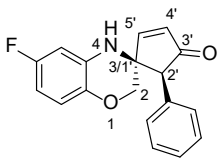
- **6-Fluoro-2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9m/9'm**

Conditions D1: Mixture of diastereomers obtained as an orange solid (53.8 mg, 83%, dr 82/18) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-amino-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol **8m** (69.3 mg, 0.22 mmol).

Conditions D2: Mixture of diastereomers obtained as an orange oil, (69 mg, 74%, dr 85/15) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-amino-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol **8m** (99.8 mg, 0.32 mmol).



Major Diastereomer **9m** obtained as a yellow solid after separation. **^{1}H NMR ($CDCl_3$; 400MHz):** δ 7.70 (d, 1H, *J* 5.8 Hz, $H_{5'}$), 7.37-7.27 (m, 3H, H_{Ar}), 7.10 (dd, 2H, *J* 7.4 and 2.1 Hz, H_{Ar}), 6.71-6.64 (m, 1H, H_{Ar}), 6.46-6.33 (m, 3H, H_4 and 2xH_{Ar}), 4.23 (s, 1H, NH), 3.81 (dd, 1H, *J* 11.0 and 1.9 Hz, CH_2O), 3.59 (s, 1H, $H_{2'}$), 3.44 (d, 1H, *J* 11.0 Hz, CH_2O); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 205.8 (CO), 162.2 ($C_{5'}$), 158.1 (d, $C_{qAr\ C\text{-}F}$, $J_{C\text{-}F}$ 238.2 Hz), 139.3 (d, $C_{q\ Ar}$, $J_{C\text{-}F}$ 2.1Hz,), 133.4 ($C_{4'}$), 133.2 ($C_{q\ Ar}$), 132.6 ($C_{q\ Ar}$, $J_{C\text{-}F}$ 10.8 Hz), 129.5 (2xCH_{Ar}), 128.9 (2xCH_{Ar}), 128.1 (CH_{Ar}), 117.3 (d, CH_{Ar}, $J_{C\text{-}F}$ 9.6 Hz), 105.7 (d, $J_{C\text{-}F}$ 23.3 Hz, $CH_{Ar\ benzoxazine}$), 102.6 (d, $J_{C\text{-}F}$ 26.9 Hz, $CH_{Ar\ benzoxazine}$), 71.0 (CH_2O), 62.4 (CH), 61.8 ($C_{q\ spiro}$); **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -121.2 (ddd, *J* 9.5, 8.0 and 5.6 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}FNNaO_2$: 318.0901 found 318.0904; mp 103°C



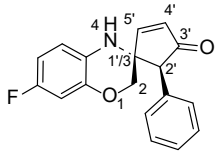
Minor Diastereomer **9'm** obtained as a yellow solid after separation

^{1}H NMR ($CDCl_3$; 400MHz): δ 7.53 (dd, 1H, *J* 5.8 and 0.8 Hz, $H_{5'}$), 7.24-7.15 (m, 3H, H_{Ar}), 6.95-6.85 (m, 2H, H_{Ar}), 6.72 (dd, 1H, *J* 8.8 and 5.2 Hz, H_{Ar}), 6.53 (dd, 1H, *J* 5.8 and 0.8 Hz, $H_{4'}$), 6.31 (td, 1H, *J* 8.5 and 2.9 Hz, H_{Ar}), 5.82 (ddd, 1H, *J* 9.6, 2.9 and 0.8 Hz, H_{Ar}), 4.20 and 4.05 (2d, 2H, *J* 10.4 Hz, CH_2O), 3.79 (s, 1H, $H_{2'}$), 3.56 (s, 1H, NH); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 206.9 (CO), 162.2 ($C_{5'}$), 158.0 (d, C_q, $J_{C\text{-}F}$ 238 Hz), 139.5 (d, $C_{q\ Ar\ C\text{-}O}$, $J_{C\text{-}F}$ 2.2 Hz), 136.3 ($C_{4'}$), 135.7 ($C_{q\ Ar}$), 131.2 (d, $C_{q\ Ar\ C\text{-}N}$, $J_{C\text{-}F}$ 10.9 Hz), 129.3 (2xCH_{Ar}), 128.8 (2xCH_{Ar}), 127.9 (CH_{Ar}), 117.0 (d, $J_{C\text{-}F}$ 9.7Hz, C_9), 105.3 (d, $J_{C\text{-}F}$ 23.4Hz, C_8), 101.9 (d, $J_{C\text{-}F}$ 26.9 Hz, C_6), 72.0 (CH_2), 61.8 ($C_{q\ spiro}$), 60.5 (CH); **^{19}F NMR ($CDCl_3$, 376MHz):** δ -121.5 (ddd, *J* 9.5, 8.0 and 5.6 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}FNNaO_2$: 318.0901 found 318.0901; mp 128°C

- **7-Fluoro-2'-phenyl-2*H*,4*H*-spiro[[1,4] benzoxazine-3,1'-cyclopent[4]en]-3'-one 9n/9'n**

Conditions D1: Mixture of diastereomers obtained as a yellow oil (47.7 mg, 58%, dr 71/29) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-amino-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol **8n** (86.7 mg, 0.28 mmol).

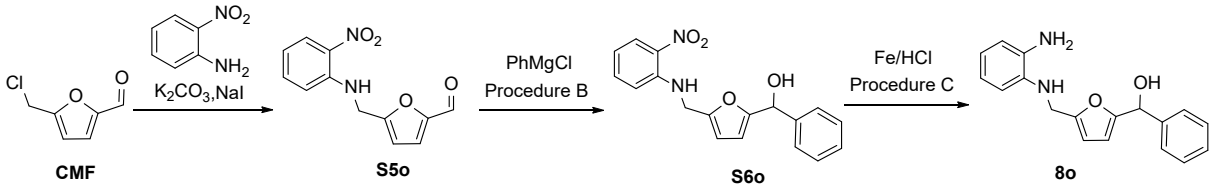
Conditions D2: Mixture of diastereomers obtained as an orange oil (54 mg, 63 %, dr 80/20) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-amino-5-fluoro-phenoxy) methyl]furan-2-yl}(phenyl)methanol **8n** (91.7 mg, 0.29 mmol).



Major diastereomer **9n** obtained as a yellow solid after separation

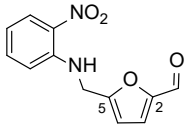
^{1}H NMR ($CDCl_3$; 400MHz): δ 7.71 (d, 1H, *J* 5.9 Hz, $H_{5'}$), 7.36-7.29 (m, 3H, H_{Ar}), 7.16-7.05 (m, 2H, H_{Ar}), 6.63-6.49 (m, 3H, $H_{Ar\ benzoxazine}$), 6.43 (d, 1H, *J* 5.9 Hz, $H_{4'}$), 3.96 (s, 1H, NH), 3.83 (d, 1H, *J* 11.0Hz, CH_2O), 3.59 (s, 1H, $H_{2'}$), 3.49 (d, 1H, *J* 11.0 Hz, CH_2O); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 205.8 (CO), 161.9 ($C_{5'}$), 156.8 (d, $C_{q\ Ar}$, $J_{C\text{-}F}$ 237. 5Hz), 143.8 (d, $C_{q\ Ar\ C\text{-}O}$, $J_{C\text{-}F}$ 11.5 Hz), 133.5 ($C_{4'}$), 133.3 ($C_{q\ Ar}$), 129.5, 128.9 and 128.1 (5xCH_{Ar}), 127.9 (d, $C_{q\ Ar\ C\text{-}N}$, $J_{C\text{-}F}$ 2.6 Hz), 116.3 (d, $J_{C\text{-}F}$ 9.2 Hz, CH_{Ar}), 108.6 (d, $J_{C\text{-}F}$ 22.6 Hz, CH_{Ar}), 104.4 (d, $J_{C\text{-}F}$ 25.8 Hz, CH_{Ar}), 71.2 (CH_2O), 62.6 (CH, $C_{2'}$), 61.7 ($C_{q\ spiro}$); **^{19}F NMR ($CDCl_3$, 376MHz):** δ -123.1 (ddd, *J* 9.5, 8.0 and 5.6 Hz); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{18}H_{14}FNNaO_2$: 318.0901 found 318.0895 ; mp 158°C

- **Synthetic procedures for the synthesis of spiroquinoxaline compound 11**



- **5-[(2-Nitroanilino) methyl] furan-2-carbaldehyde S5o**

To a solution of 5-chloromethylfurfural (5-CMF) (633 mg, 4.4 mmol, 1 equiv.) in CH_3CN (9mL), was added K_2CO_3 (2.5 equiv.), NaI (1 equiv.) and 2-nitroaniline (2.5 equiv.). The reaction mixture was stirred for 6h at 80°C. After the addition of ethyl acetate (30 mL), the organic phase was washed with an aqueous saturated solution of ammonium chloride (3 x 20 mL), the aqueous phase extracted with ethyl acetate (2x20 mL). The combined organic phases were dried with Na_2SO_4, filtered and concentrated under *vacuum*. The residual crude was purified by flash chromatography on SiO_2 with petroleum ether / EtOAc (8/2 to 7/3) to afford a brown solid (330 mg, 31%).

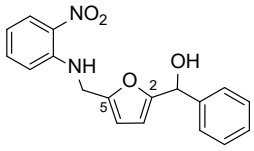


^{1}H NMR ($CDCl_3$, 400MHz): δ 9.60 (s, 1H, CHO), 8.39 (bs, 1H, NH), 8.20 (dd, 1H, *J* 8.5 and 1.4 Hz, H_{Ar}), 7.45 (ddd, 1H, *J* 8.5, 7.0 and 1.4 Hz, H_{Ar}), 7.20 (d, 1H, *J* 3.6 Hz, H_3), 6.83 (dd, 1H, *J* 8.5 and 1.4 Hz, H_{Ar}), 6.75 (ddd, 1H, *J* 8.5, 7.0 and 1.4 Hz, H_{Ar}), 6.47 (dt, 1H, *J* 3.6 and 1.0 Hz, H_4), 4.65 (dd, 2H, *J* 6.0 and 1.0 Hz, CH_2); **^{13}C NMR ($CDCl_3$, 100MHz) :** δ 177.5 (CHO), 158.0 (C_q, C_5), 152.7 (C_q, C_2), 144.4 ($C_{q\ C\text{-}NH}$), 136.5 (CH_{Ar}), 133.0 ($C_{q\ C\text{-}NO_2}$), 127.1 (CH_{Ar}), 122.7 (C_3), 116.8 (CH_{Ar}), 113.7 (CH_{Ar}), 110.3 (C_4), 40.7 (CH_2); **HRMS (ESI)** $[M+Na]^+$: calcd for $C_{12}H_{10}N_2NaO_4$ 269.0533 found 269.0536; mp 127°C

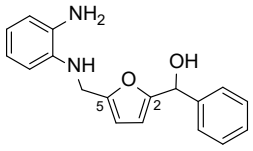
- **{5-[(2-Aminoanilino)methyl]furan-2-yl}(phenyl)methanol 8o**

Orange oil (102 mg, 43%) isolated after chromatography (petroleum ether / EtOAc (8/2 to 6/4) after a two-step sequence from 5-[(2-nitroanilino)methyl]furan-2-carbaldehyde **S5o** (187 mg, 0.76 mmol) with PhMgCl (1.5 M in THF, 1.6 ml, 2.28 mmol, 3 equiv.) following general procedure B, then reduction of **S6o** with Fe/NH_4Cl in EtOH following general procedure C.

{5-[(2-Nitroanilino) methyl] furan-2-yl}(phenyl)methanol S6o



^{1}H NMR ($CDCl_3$, 500MHz): δ 8.29 (s, 1H, NH), 8.18 (dd, 1H, *J* 8.6 and 1.4 Hz, $H_{Ar\ nitroaniline}$), 7.48-7.30 (m, 6H, $H_{Ar\ nitroaniline}$ and 5xH_{Ar}), 6.90 (dd, 1H, *J* 8.6 and 1.4 Hz, $H_{Ar\ nitroaniline}$), 6.73-6.63 (m, 1H, $H_{Ar\ nitroaniline}$), 6.20 and 6.05 (2d, 2H, *J* 3.3 Hz, H_3 and H_4), 5.81 (s, 1H, C<u>H</u>OH), 4.49 (2xbs, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 125MHz):** δ 156.0 (C_q, C_2), 151.0 (C_q, C_5), 144.9 ($C_{q\ C\text{-}NH}$), 140.7 ($C_{q\ Ar}$), 136.3 ($CH_{Ar\ nitroaniline}$), 132.6 ($C_{q\ C\text{-}NO_2}$), 128.7 (3xCH_{Ar}), 128.3 (CH_{Ar}), 127.0 ($CH_{Ar\ nitroaniline}$), 126.8 (2xCH_{Ar}), 116.1 ($CH_{Ar\ nitroaniline}$), 114.0 ($CH_{Ar\ nitroaniline}$), 108.6 and 108.4 (C_3 and C_4), 70.3 (CHOH), 40.5 (CH_2); **HRMS (ESI)** [M+Na] calcd for $C_{18}H_{16}N_2NaO_4$, 347.1002; found 347.1004.



^{1}H NMR ($CDCl_3$, 400MHz): δ 7.47-7.28 (m, 5H, H_{Ar}), 6.80 (ddd, 1H, *J* 7.7, 6.8 and 2.2Hz, $H_{Ar\ aminoaniline}$), 6.75-6.63 (m, 3H, $H_{Ar\ aminoaniline}$), 6.15 (d, 1H, *J* 3.2 Hz, H_4), 6.02-5.95 (m, 1H, H_3), 5.77 (s, 1H, C<u>H</u>OH), 4.23 (s, 2H, CH_2); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 155.6 (C_q, C_2), 153.0 (C_q, C_5), 140.9 ($C_{q\ Ar}$), 137.0 ($C_{q\ C\text{-}NH}$), 134.8 ($C_{q\ C\text{-}NO_2}$), 128.5 (2xCH_{Ar}), 128.1 (CH_{Ar}), 126.7 (2xCH_{Ar}), 120.7 ($CH_{Ar\ aminoaniline}$), 119.7 ($CH_{Ar\ aminoaniline}$), 116.8

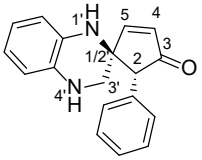
($CH_{Ar\ aminoaniline}$),112.9 ($CH_{Ar\ aminoaniline}$), 108.5 (C_3), 107.9 (C_4), 70.1 (CHOH), 41.9 (CH_2); **HRMS (ESI)** [M+Na] calcd for $C_{18}H_{18}N_2NaO_2$, 317.1260; found 317.1259.

- **<u>2-Phenyl-3',4'-dihydro-1'H-spiro[cyclopent-4-ene-1,2'-quinoxalin]-3-one 11</u>**

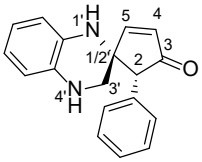
Conditions D1: Mixture of diastereomers obtained as orange oil (23.8 mg, 32%,) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminoanilino)methyl]furan-2-yl}(phenyl)methanol **10o** (80.7 mg, 0.27 mmol).

Conditions D2 : Mixture of diastereomers obtained as orange oil (25.1 mg, 29%,) isolated after chromatography (petroleum ether/EtOAc (10/3), obtained from {5-[(2-aminoanilino)methyl]furan-2-yl}(phenyl)methanol **10o** (94 mg, 0.32 mmol).

N.B. In both cases, the minor diastereomer might recrystallize during purification as determined dr in crude (64/36) evolved to 86/14 in the purified mixture.



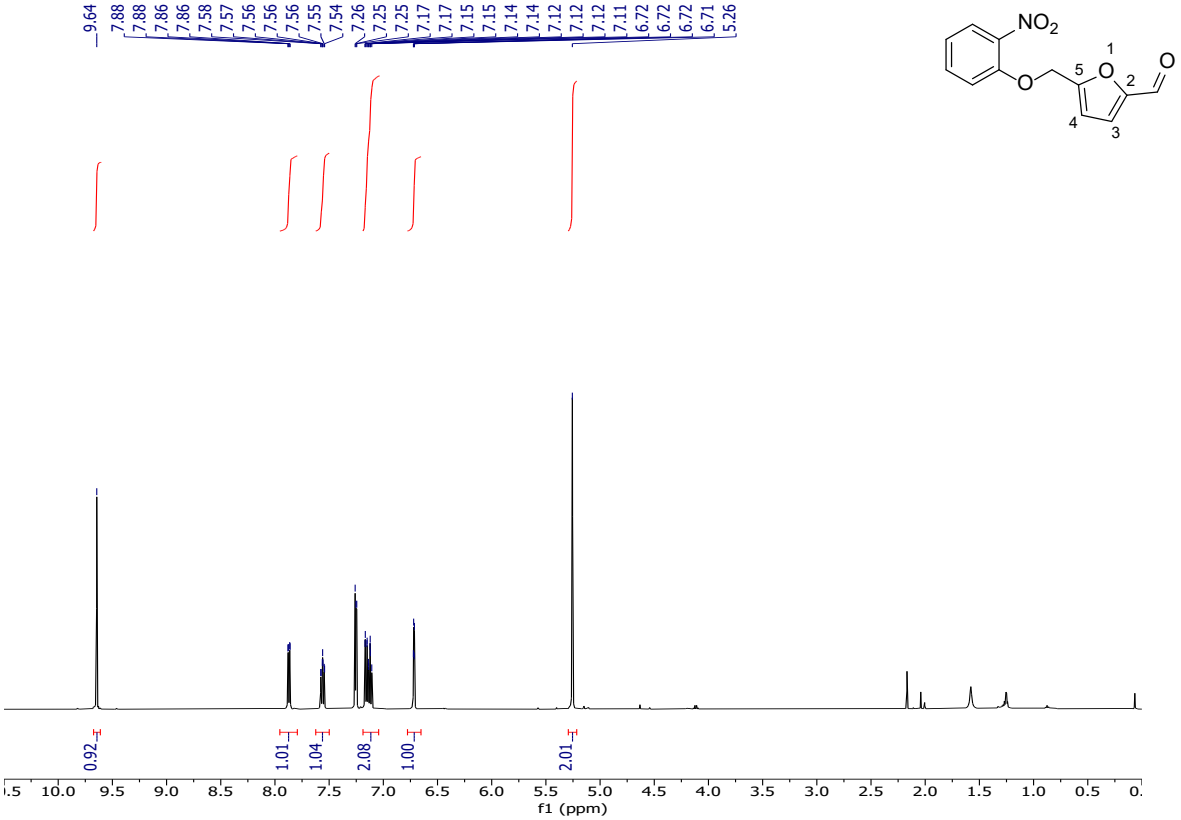
Major diastereomer **11** obtained after separation as an orange oil. **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.81 (d, 1H, *J* 5.8 Hz, H_5), 7.37-7.24 (m, 3H, $H_{Ar\ phenyl}$), 7.14-7.05 (m, 2H, $H_{Ar\ phenyl}$), 6.73-6.57 (m, 3H, H_{Ar}), 6.54-6.44 (m, 1H, H_{Ar}), 6.37 (d, 1H, *J* 5.8 Hz, H_4), 3.57 (s, 1H, CH), 2.96 and 2.82 (2d, 2H, *J* 11.5 Hz, CH_2N); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 206.8 (CO), 164.4 (C_5), 134.6 (2x$C_{q\ Ar}$), 132.4 ($C_{q\ Ar}$ and C_4), 129.6 (2x$CH_{Ar\ phenyl}$), 128.7 ($CH_{Ar\ phenyl}$), 127.8 (2x$CH_{Ar\ phenyl}$), 119.9 (CH_{Ar}), 119.4 (CH_{Ar}), 115.4 (CH_{Ar}), 115.1 (CH_{Ar}), 63.4 (CH), 62.2 ($C_{q\ spiro}$), 48.7 (CH_2); **HRMS (ESI)** [M+Na] calcd for $C_{18}H_{16}N_2NaO$, 299.1155; found 299.1153.



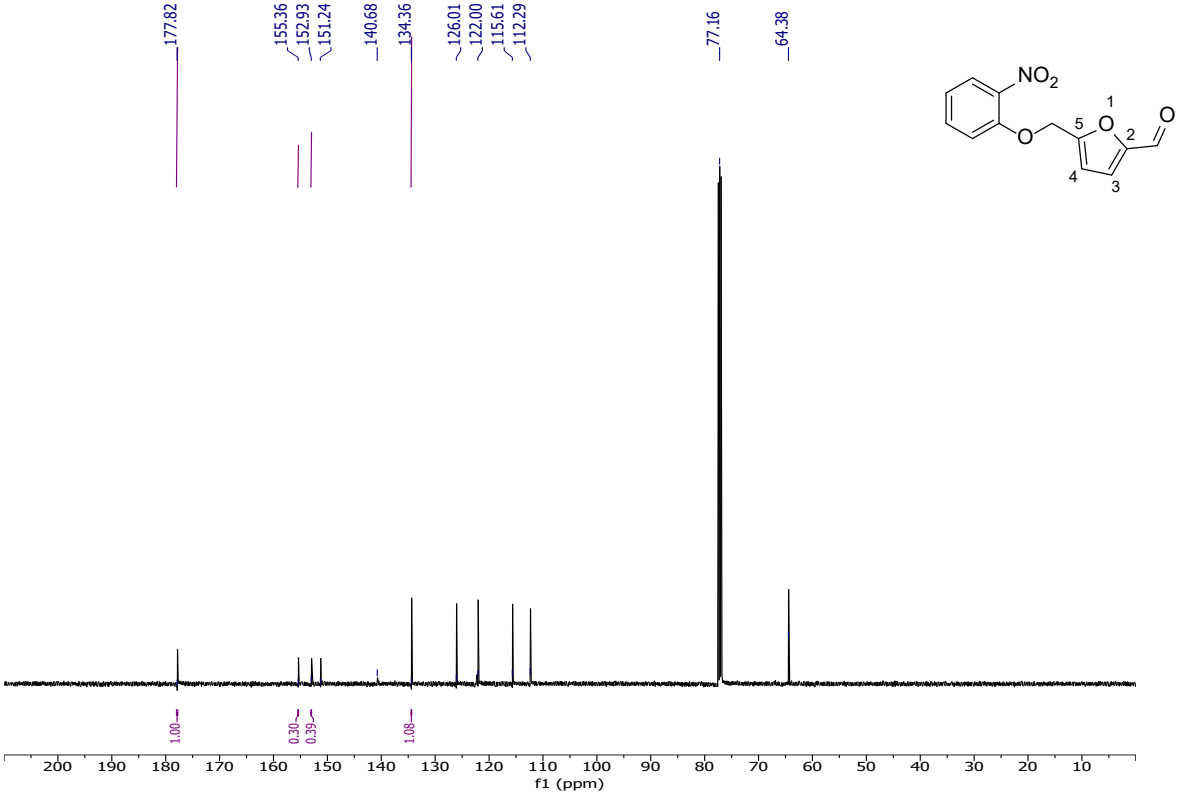
Minor diastereomer **11'** obtained after separation as a brown solid. **^{1}H NMR ($CDCl_3$, 400MHz):** δ 7.63 (d, 1H, *J* 5.7 Hz, H_5), 7.21-7.11 (m, 3H, $H_{Ar\ phenyl}$), 6.98-6.86 (m, 2H, $H_{Ar\ phenyl}$), 6.62-6.49 (m, 2H, H_{Ar}), 6.46 (d, 1H, *J* 5.7 Hz, H_4), 6.41 (pseudo td, 1H, *J* 7.3 and 1.8 Hz, H_{Ar}), 5.98 (dd, 1H, *J* 7.9 and 1.2 Hz, H_{Ar}), 3.75 (s, 1H, CH), 3.52 and 3.25 (2d, 2x1H, *J* 10.6 Hz, CH_2N); **^{13}C NMR ($CDCl_3$, 100MHz):** δ 208.1 (CO), 165.3 ($C_{q\ Ar}$), 136.4 ($C_{q\ Ar}$), 134.7 ($C_{q\ Ar}$), 132.6 ($C_{q\ Ar\ C\text{-}O}$), 131.5 ($C_{q\ Ar\ –C\text{-}N}$), 129.3, 128.6, 127.5 (5x$CH_{Ar\ phenyl}$), 119.4 (CH_{Ar}), 119.2 (CH_{Ar}), 114.7 (CH_{Ar}), 114.4 (CH_{Ar}), 62.4 (CH), 62.0 ($C_{q\ spiro}$), 50.8 (CH_2); **HRMS (ESI)** [M+Na] calcd for $C_{18}H_{16}N_2NaO$, 299.1155; found 299.1156; m.p 193°C.

- **NMR Spectra (1H, 13C, 19F) for compounds 5 to 12**

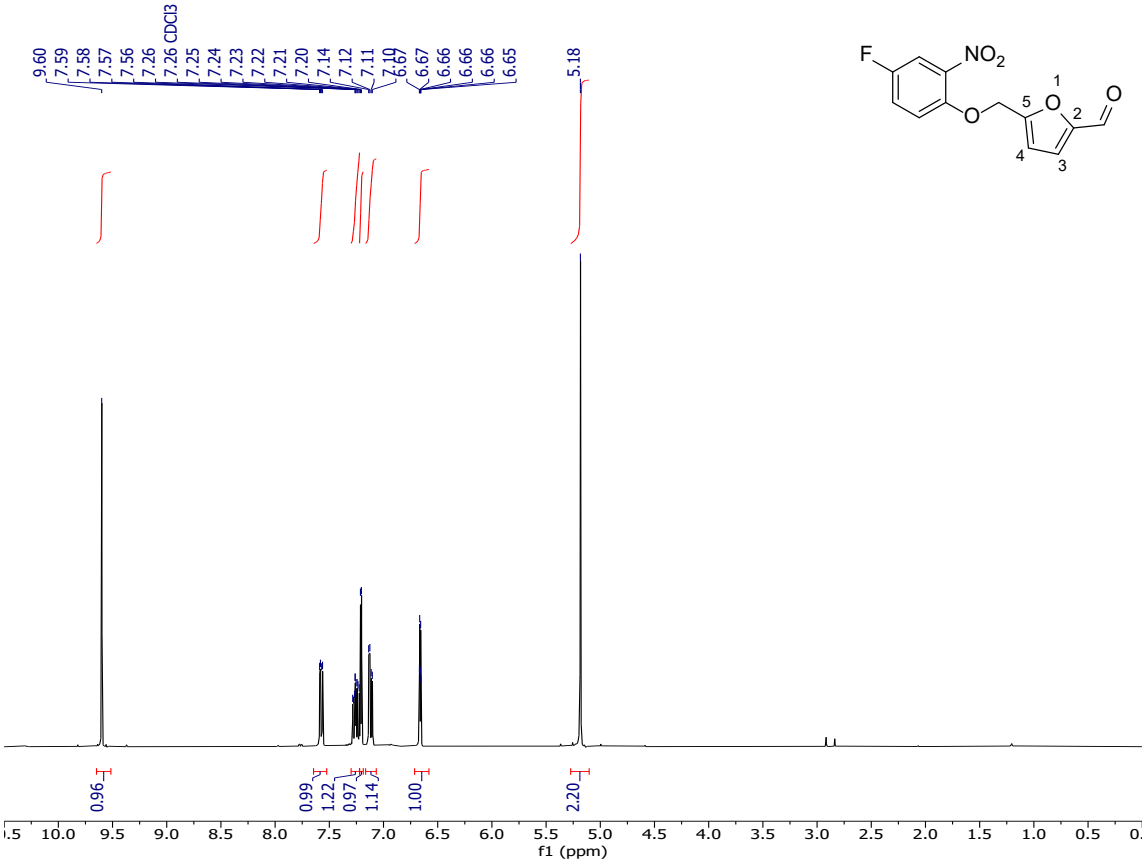
^{1}H NMR spectrum of 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde 5 (500 MHz, $CDCl_3$)



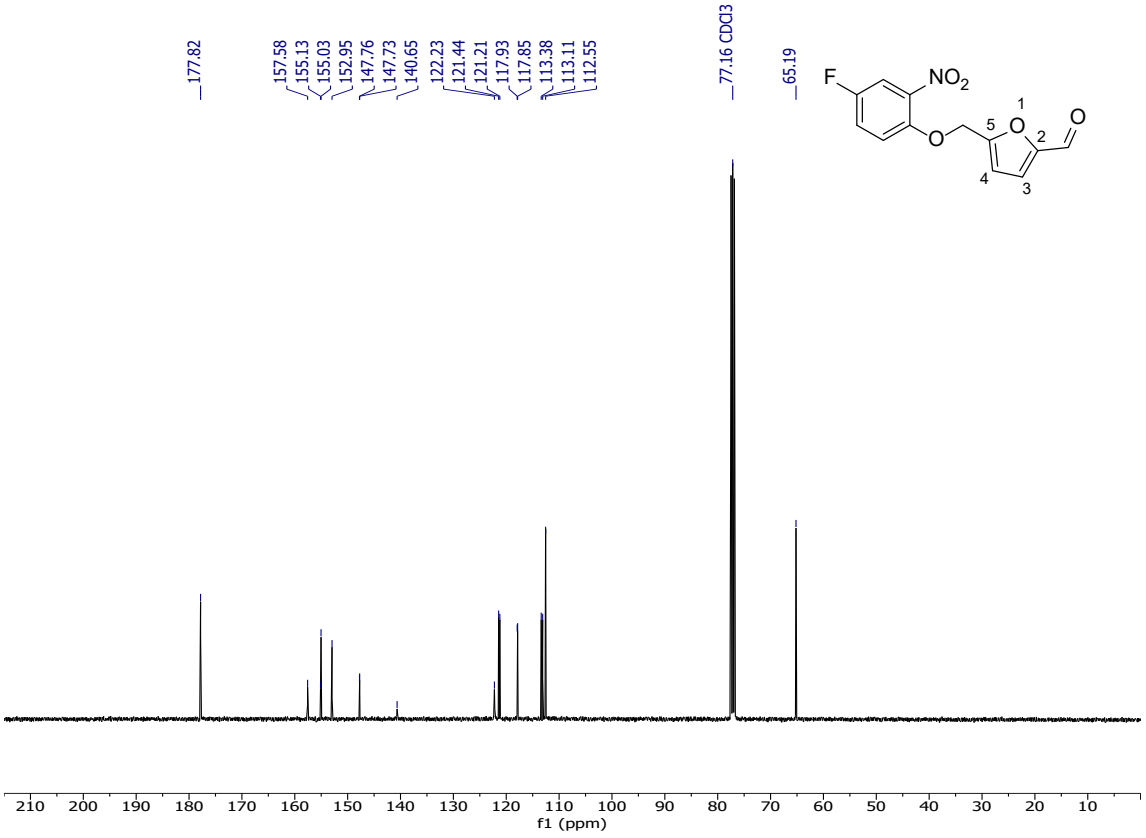
^{13}C NMR spectrum of 5-[(2-nitrophenoxy)methyl]furan-2-carbaldehyde 5 (125 MHz, $CDCl_3$)



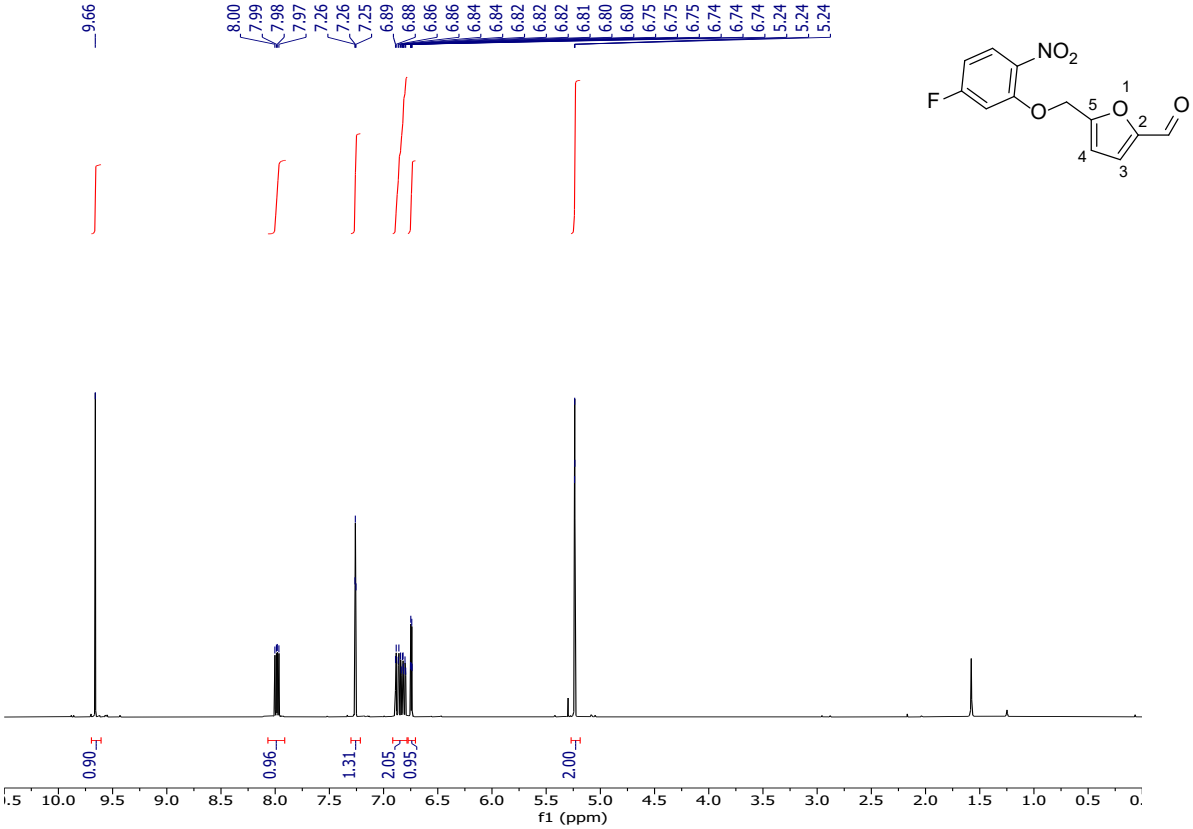
^{1}H NMR spectrum of 5-[(4-fluoro-2-nitrophenoxy)methyl]furan-2-carbaldehyde S5m (400 MHz, $CDCl_3$)



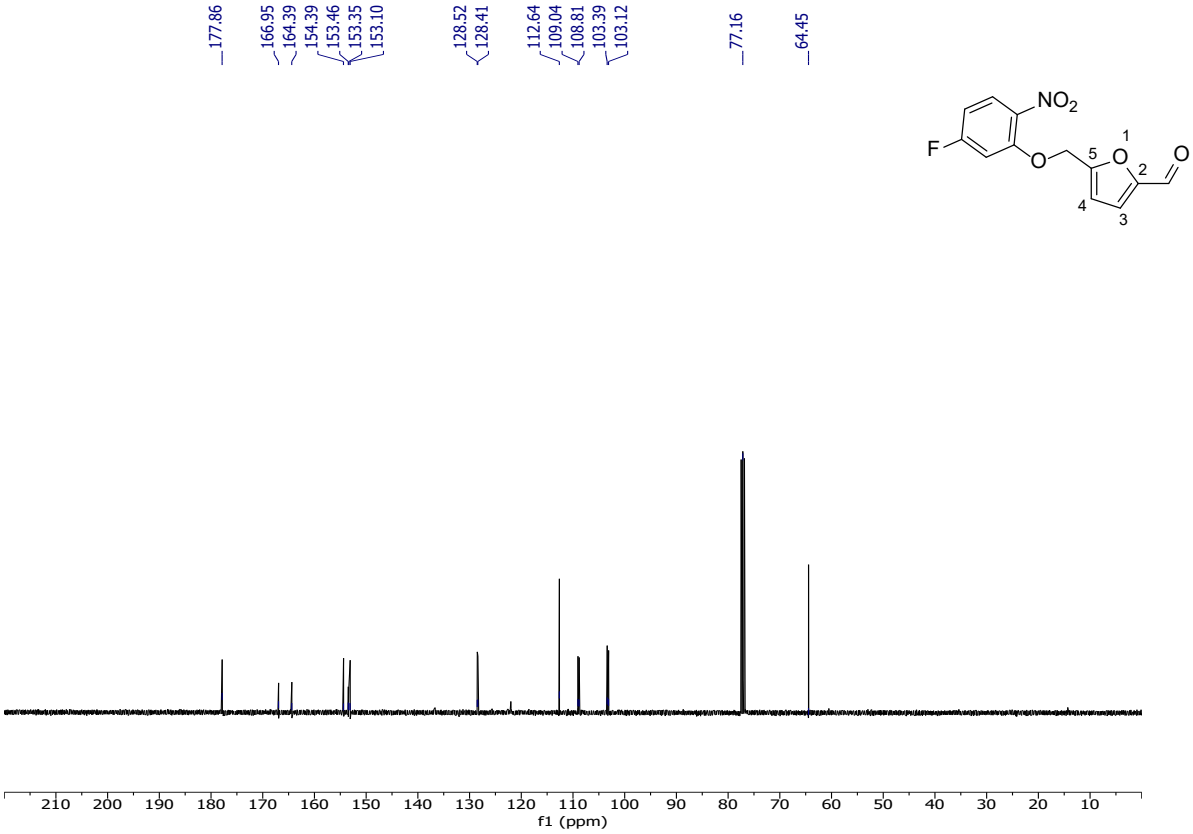
^{13}C NMR spectrum of 5-[(4-fluoro-2-nitrophenoxy)methyl]furan-2-carbaldehyde S5m (100 MHz, $CDCl_3$)



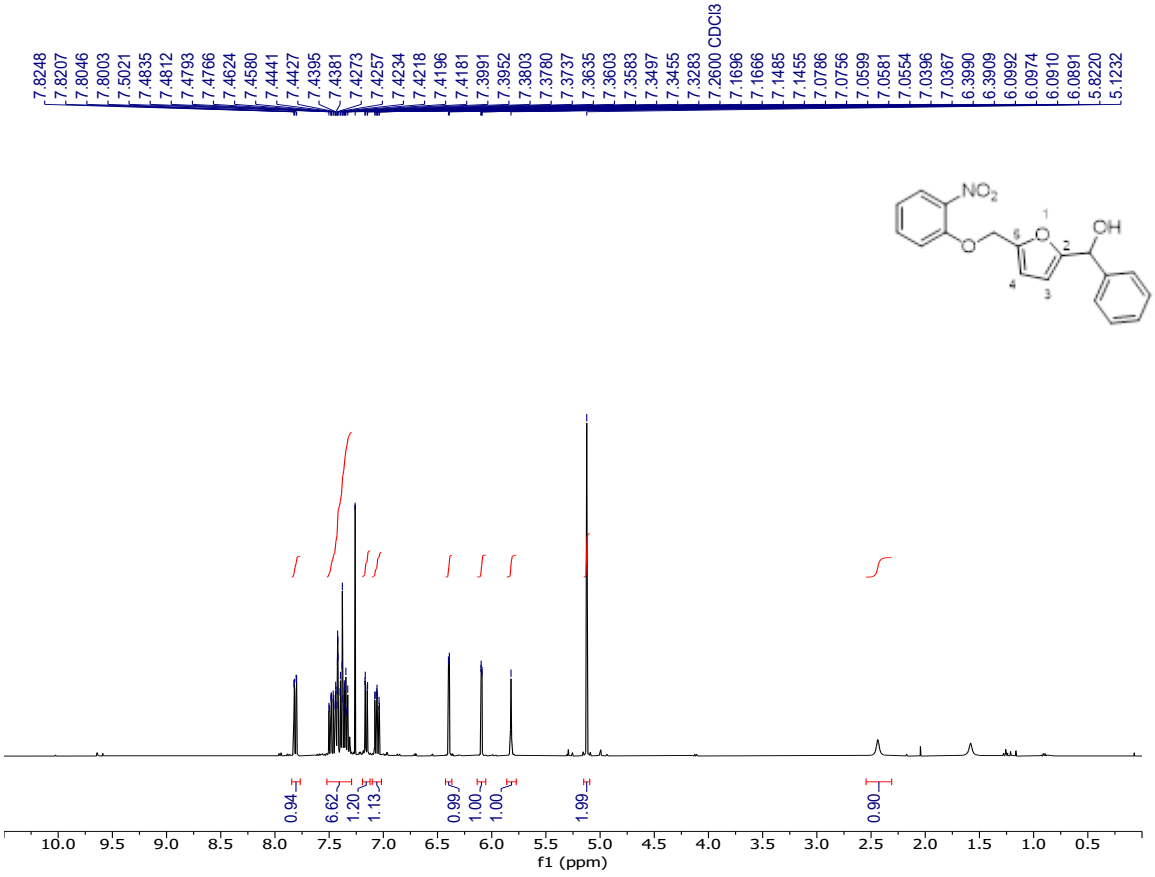
^{1}H NMR spectrum of 5-[(5-fluoro-2-nitrophenoxy)methyl]furan-2-carbaldehyde S5n **(400 MHz, $CDCl_3$)**



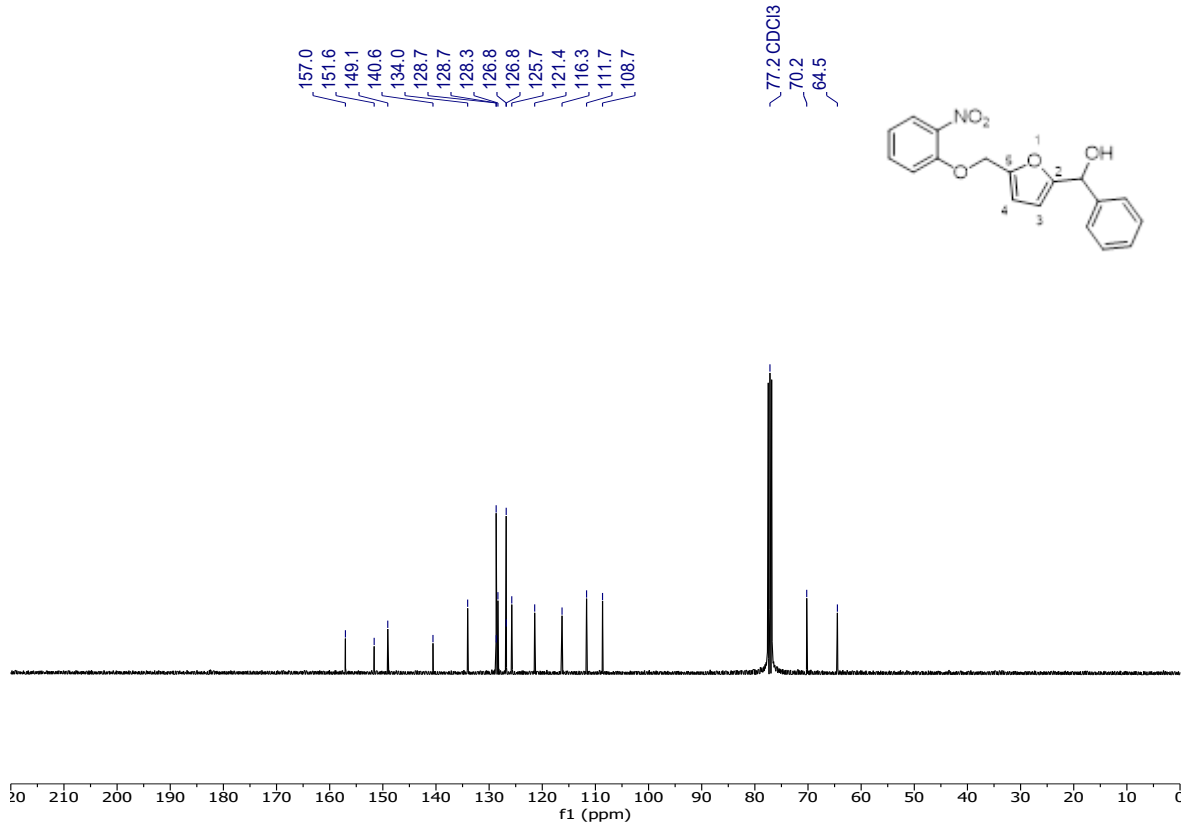
^{13}C NMR **spectrum** of 5-[(5-fluoro-2-nitrophenoxy)methyl]furan-2-carbaldehyde S5n (100 MHz, $CDCl_3$)



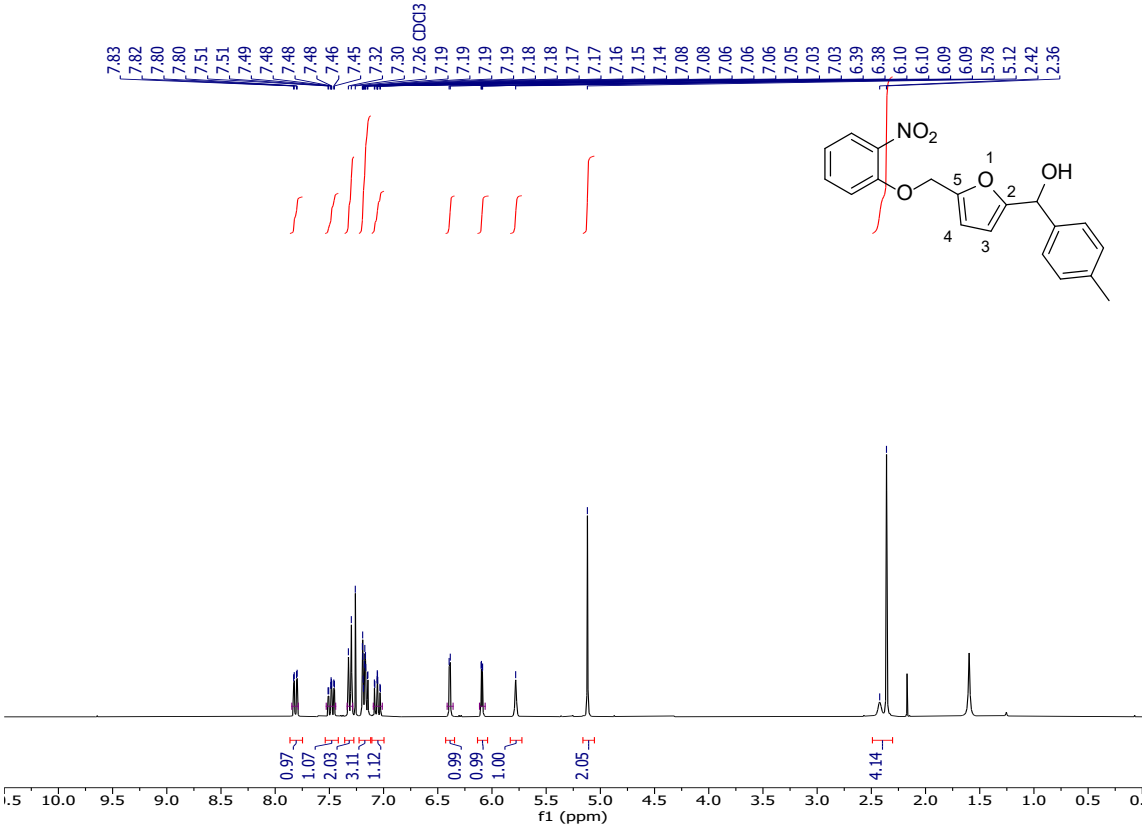
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(phenyl)methanol 6 **(400 MHz, $CDCl_3$)**



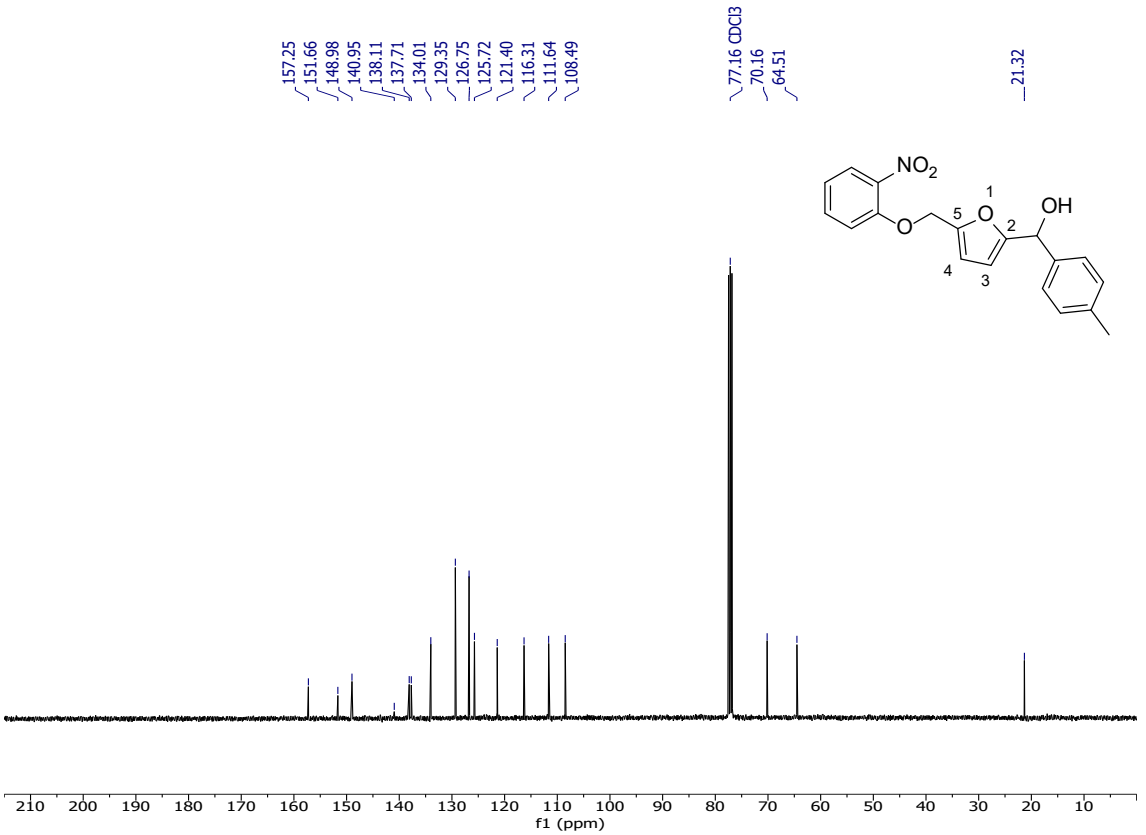
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(phenyl)methanol 6 (100 MHz, $CDCl_3$)



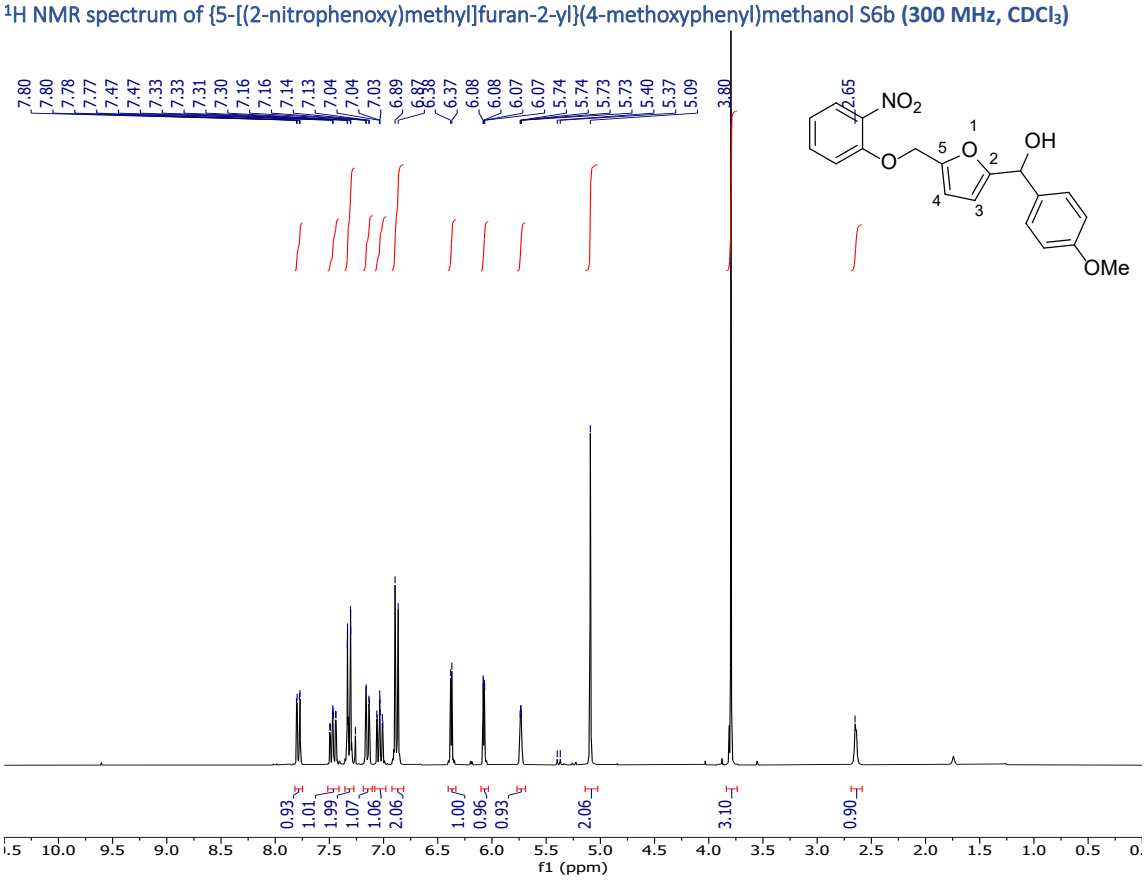
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-methylphenyl)methanol S6a **(300 MHz, $CDCl_3$)**



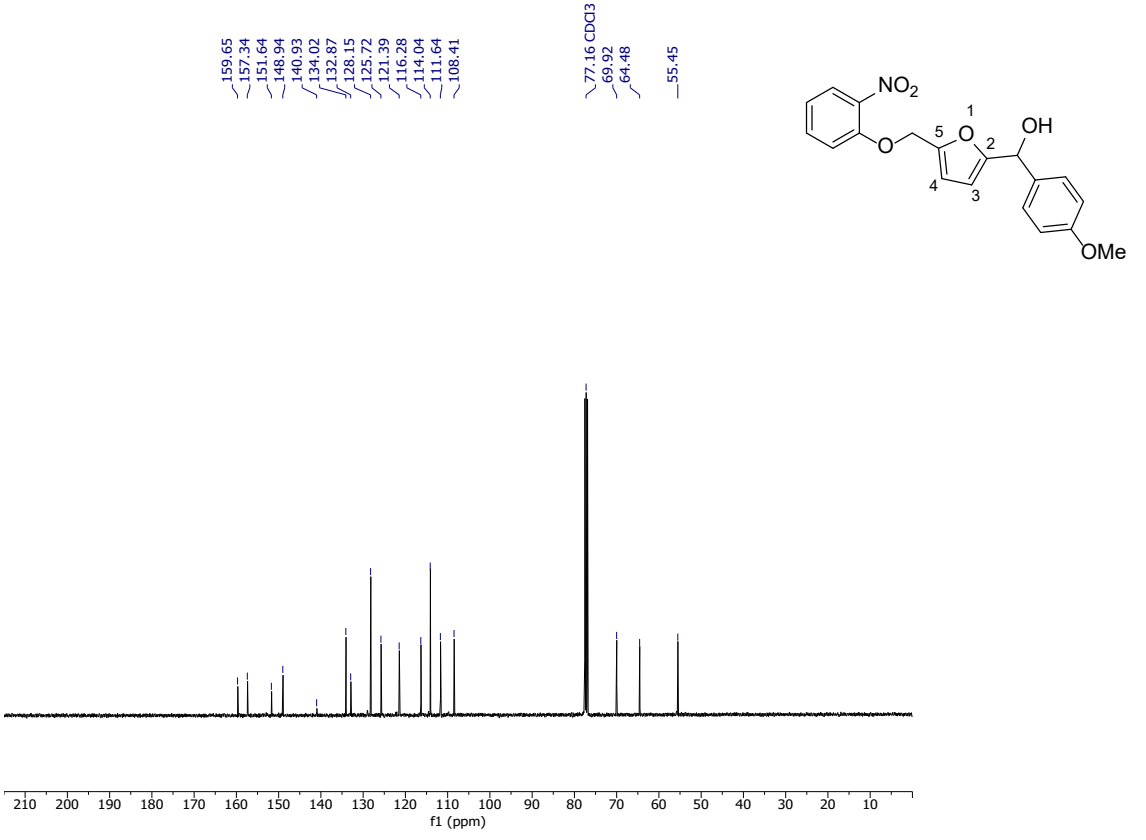
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-methylphenyl)methanol S6a (100 MHz, $CDCl_3$)



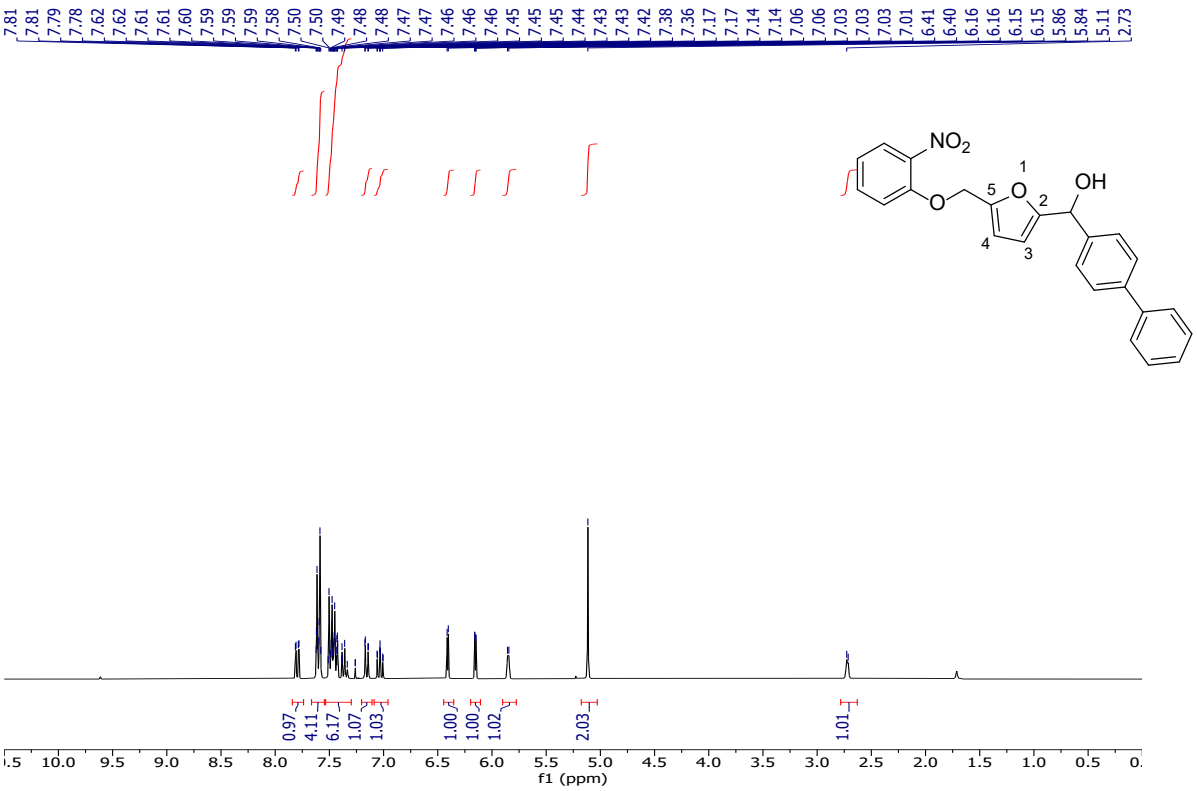
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-methoxyphenyl)methanol S6b **(300 MHz, $CDCl_3$)**



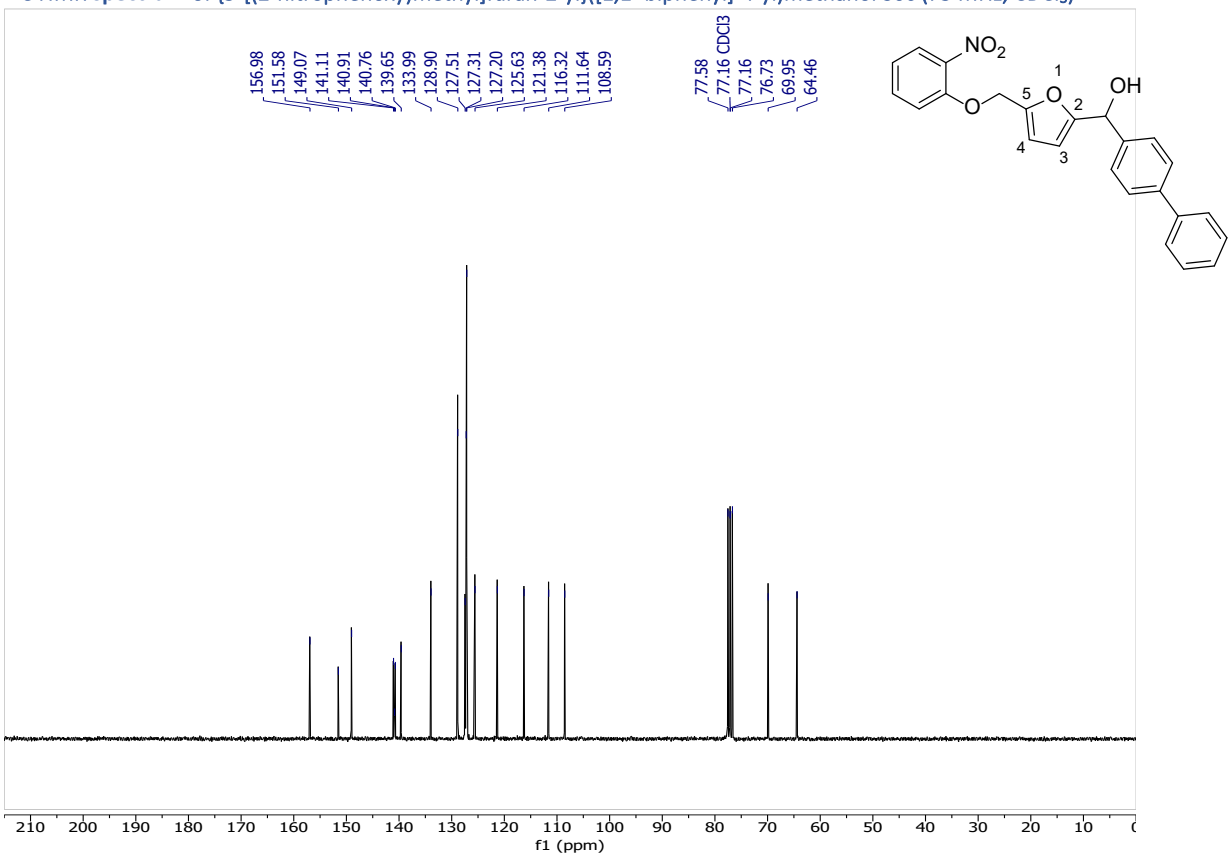
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-methoxyphenyl)methanol S6b (100 MHz, $CDCl_3$)



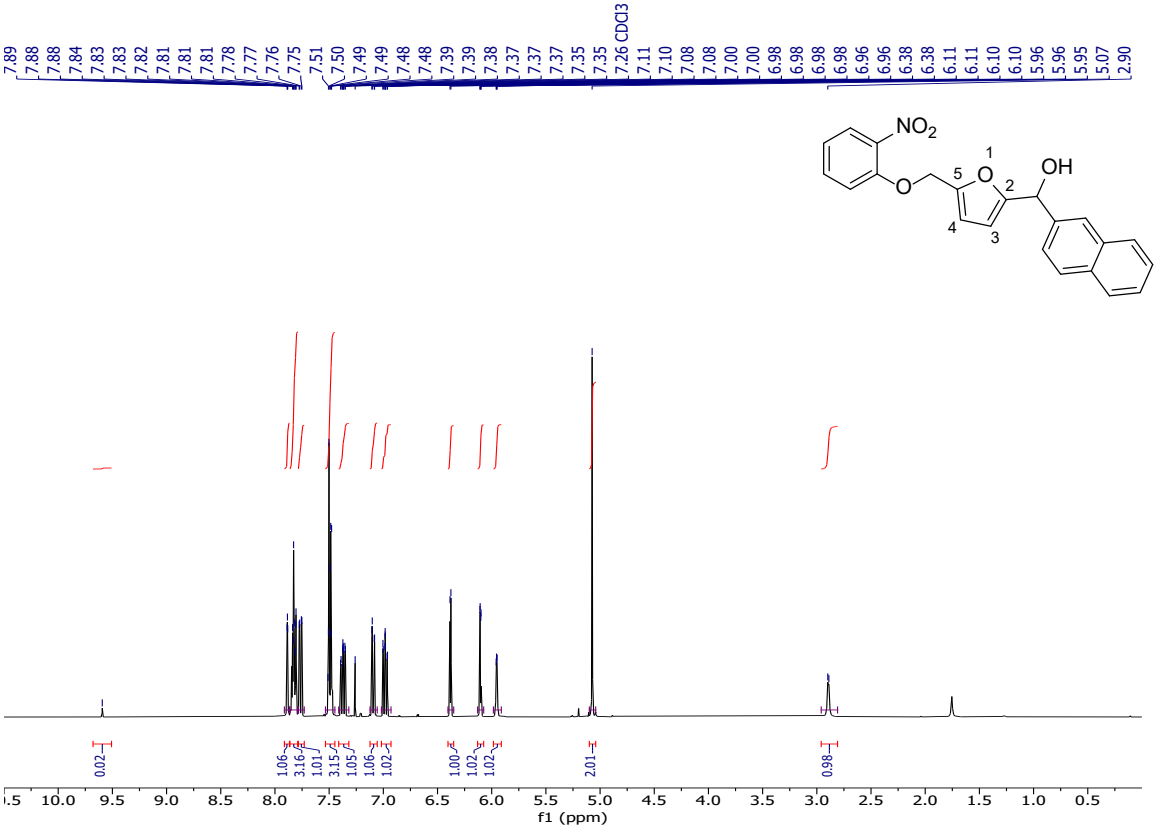
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol S6c **(300 MHz, $CDCl_3$)**



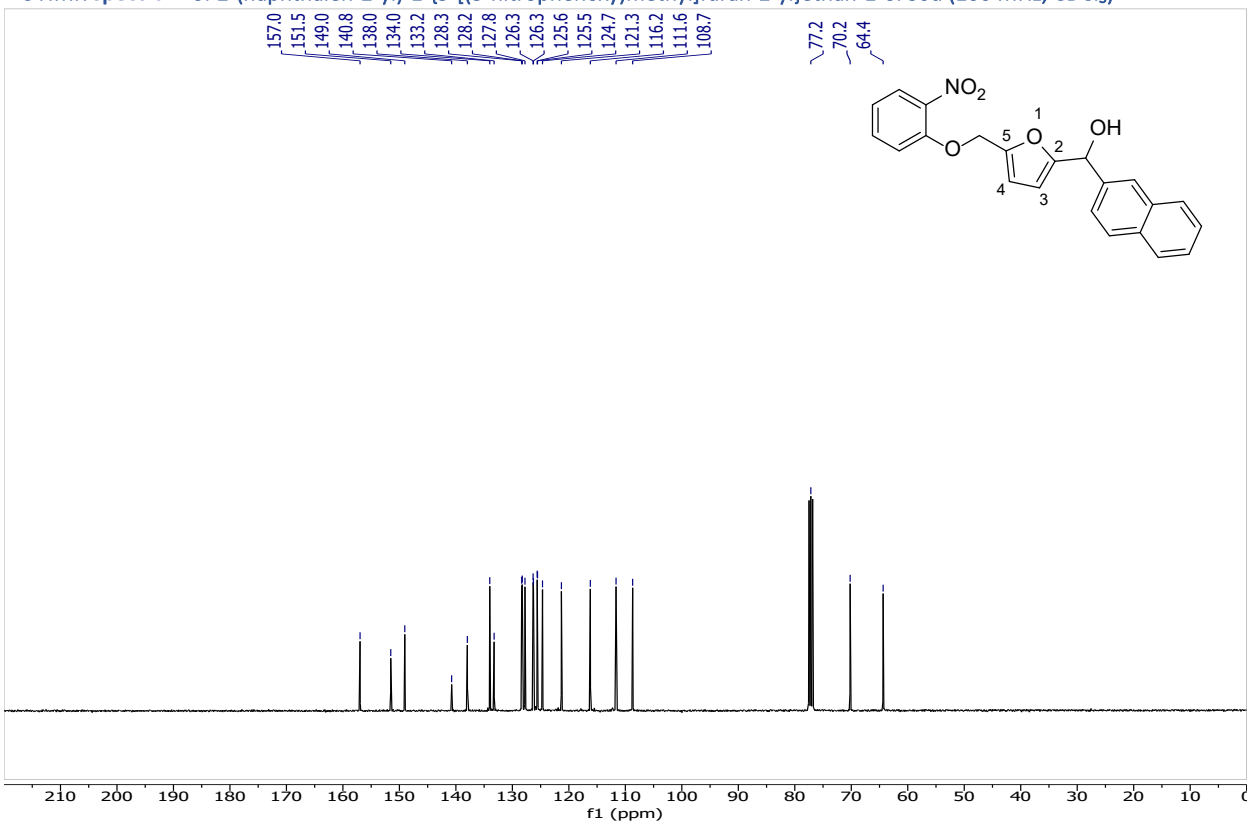
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol S6c (75 MHz, $CDCl_3$)



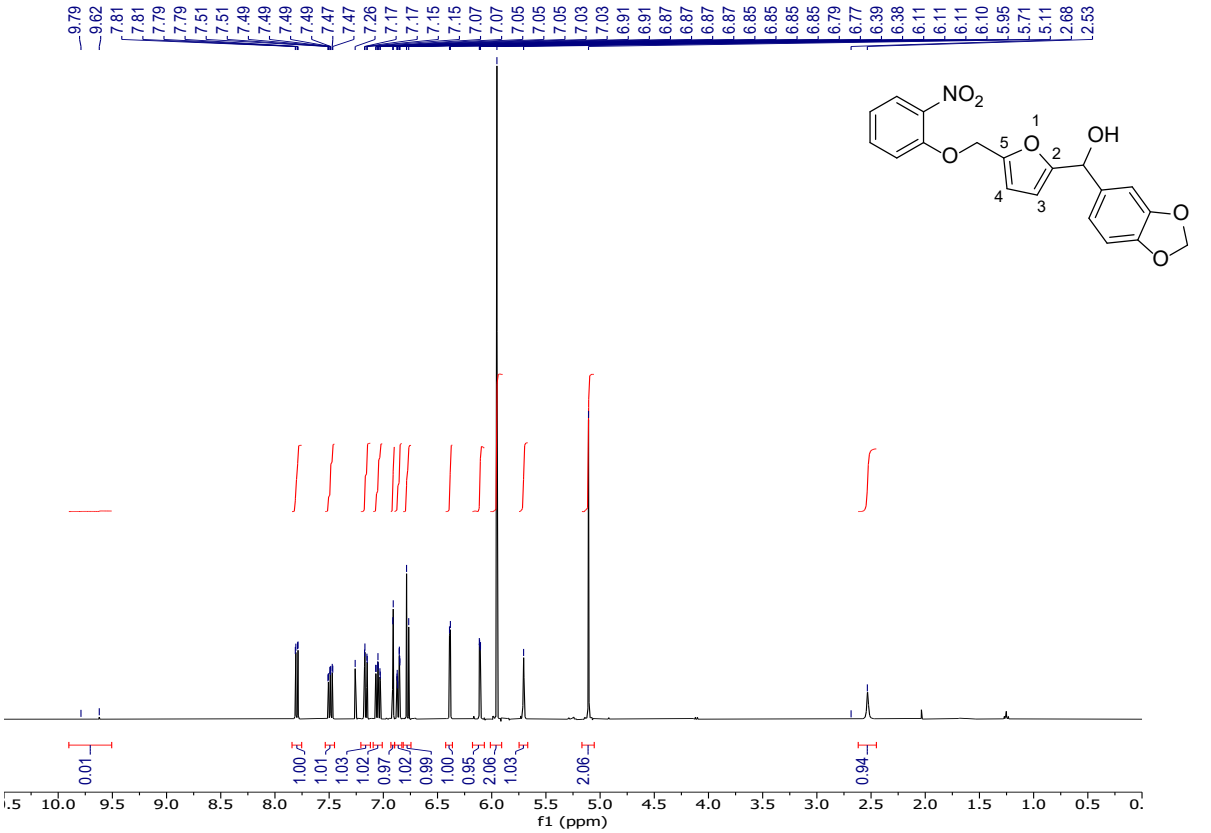
^{1}H NMR spectrum of 2-(naphthalen-2-yl)-1-{5-[(3-nitrophenoxy)methyl]furan-2-yl}ethan-1-ol S6d **(400 MHz, $CDCl_3$)**



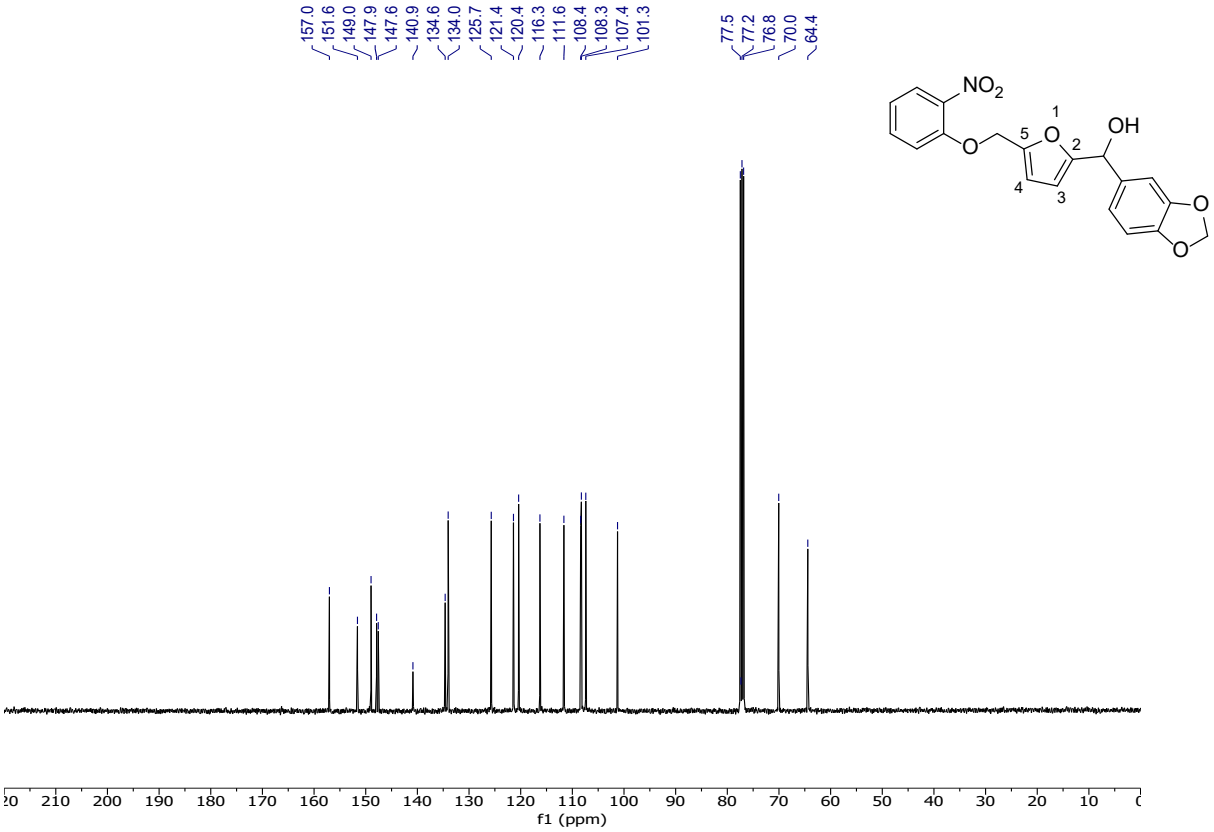
^{13}C NMR **spectrum** of 2-(naphthalen-2-yl)-1-{5-[(3-nitrophenoxy)methyl]furan-2-yl}ethan-1-ol S6d (100 MHz, $CDCl_3$)



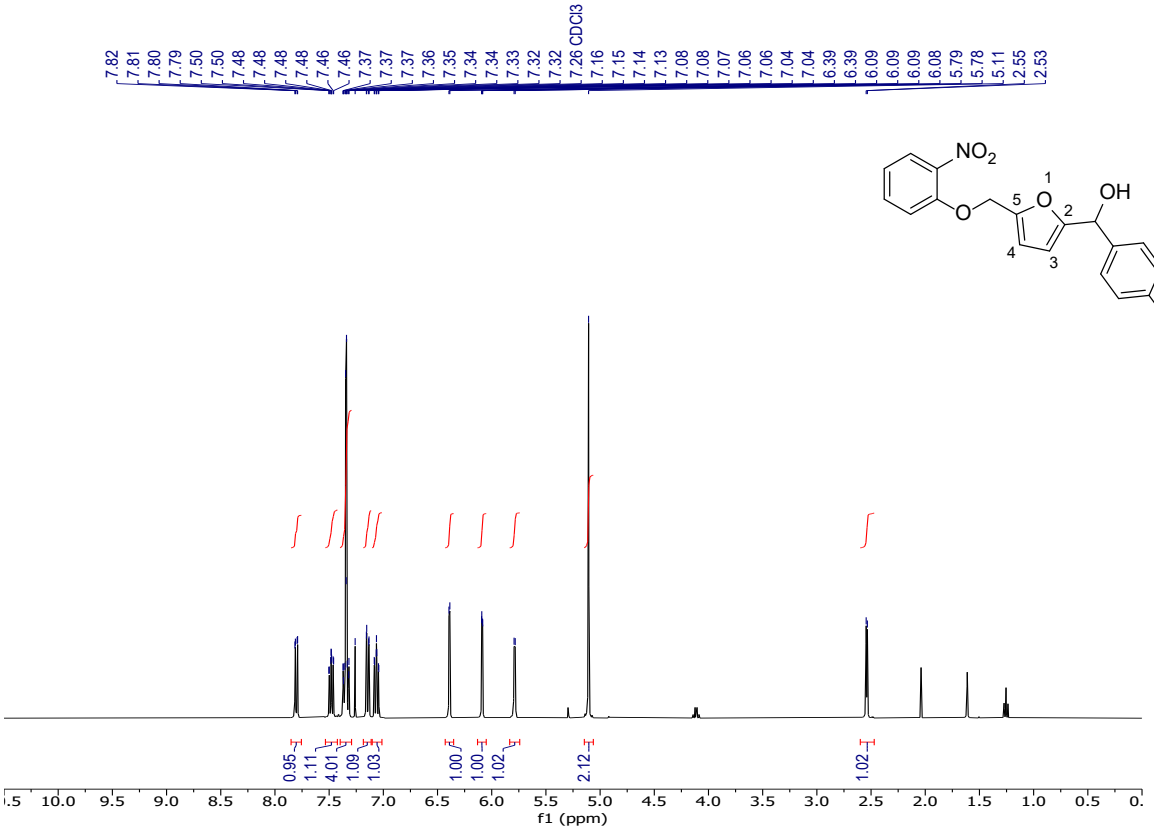
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(3,4-methylenedioxyphenyl)methanol S6e **(400 MHz, $CDCl_3$)**



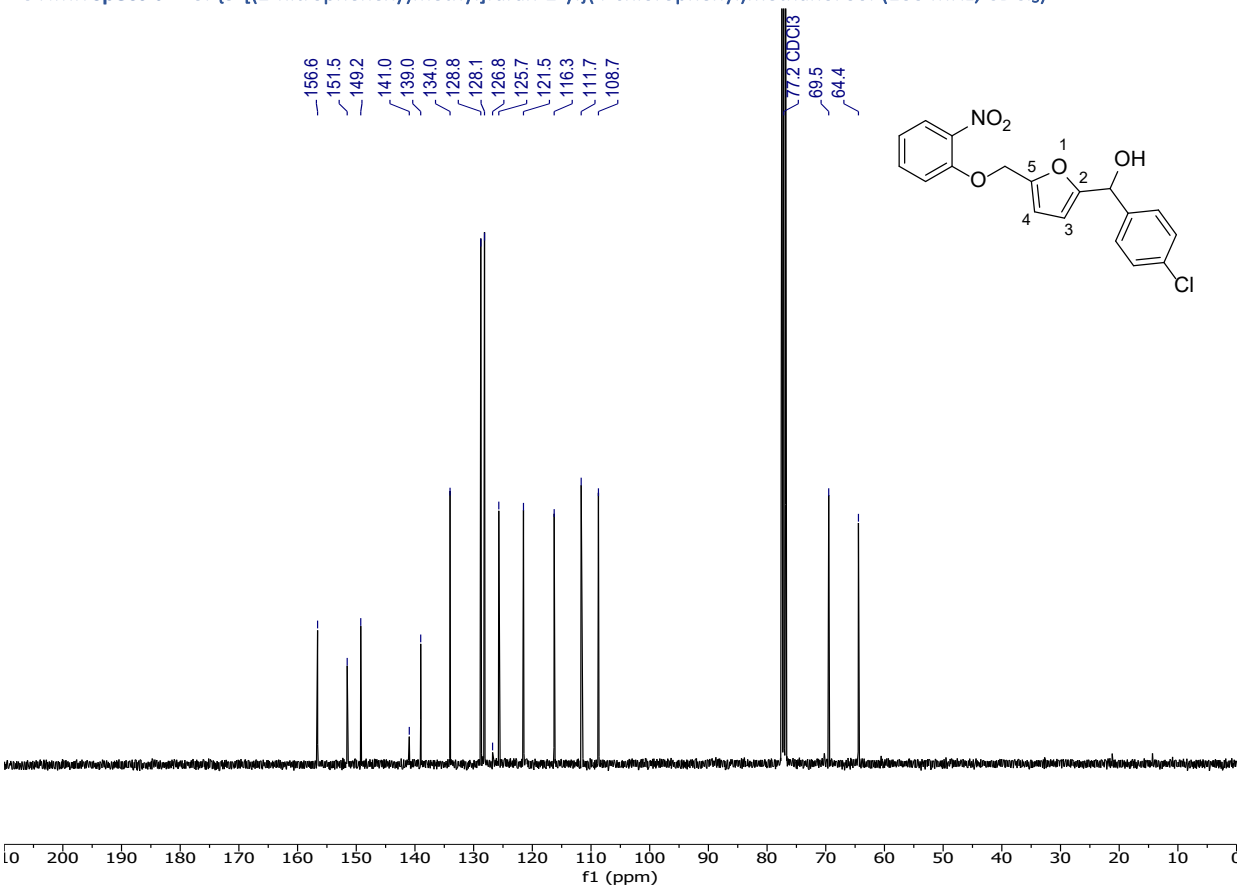
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(3,4-methylenedioxyphenyl)methanol S6e (100 MHz, $CDCl_3$)



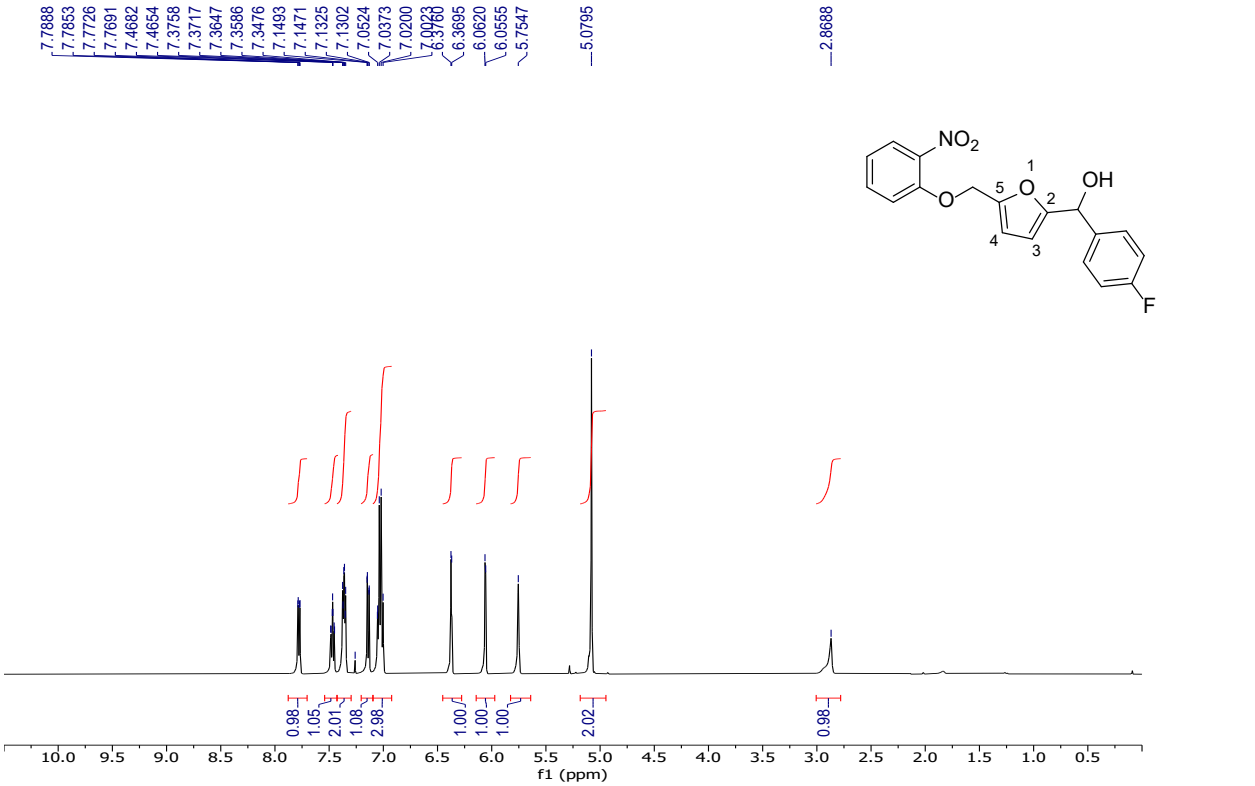
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol S6f **(400 MHz, $CDCl_3$)**



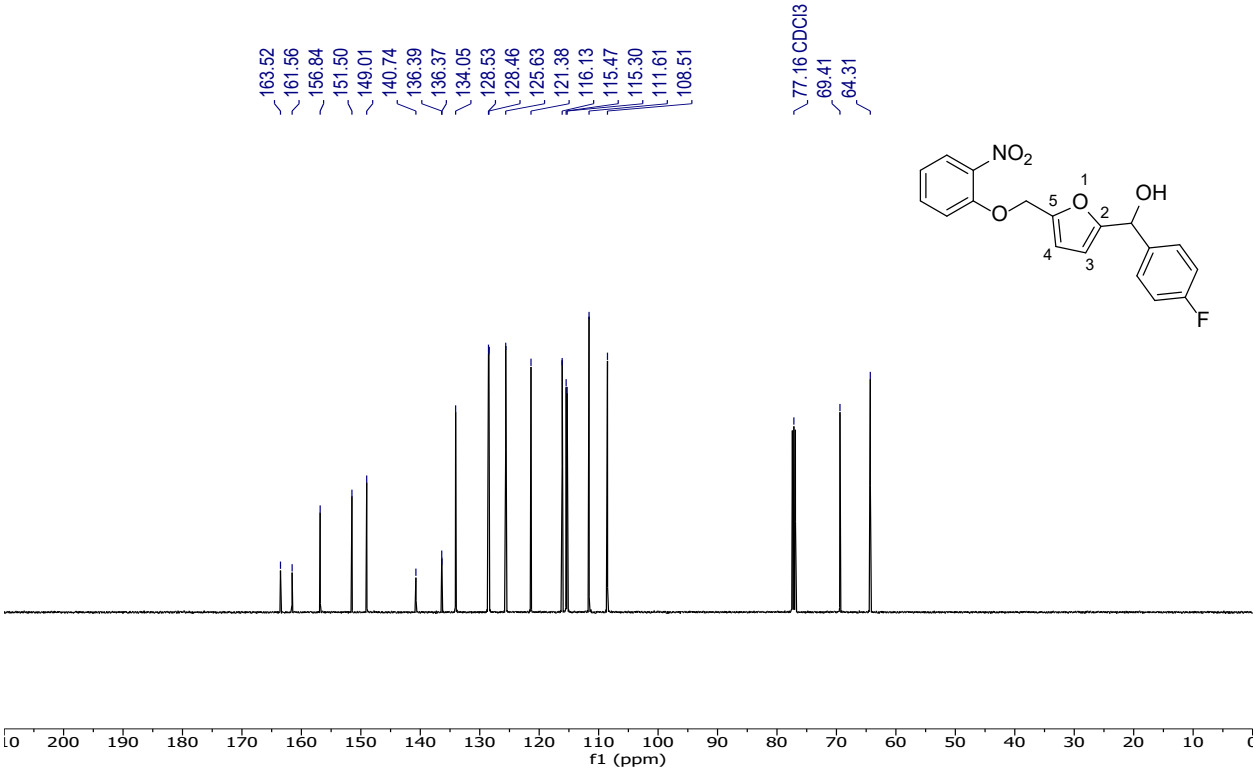
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol S6f (100 MHz, $CDCl_3$)



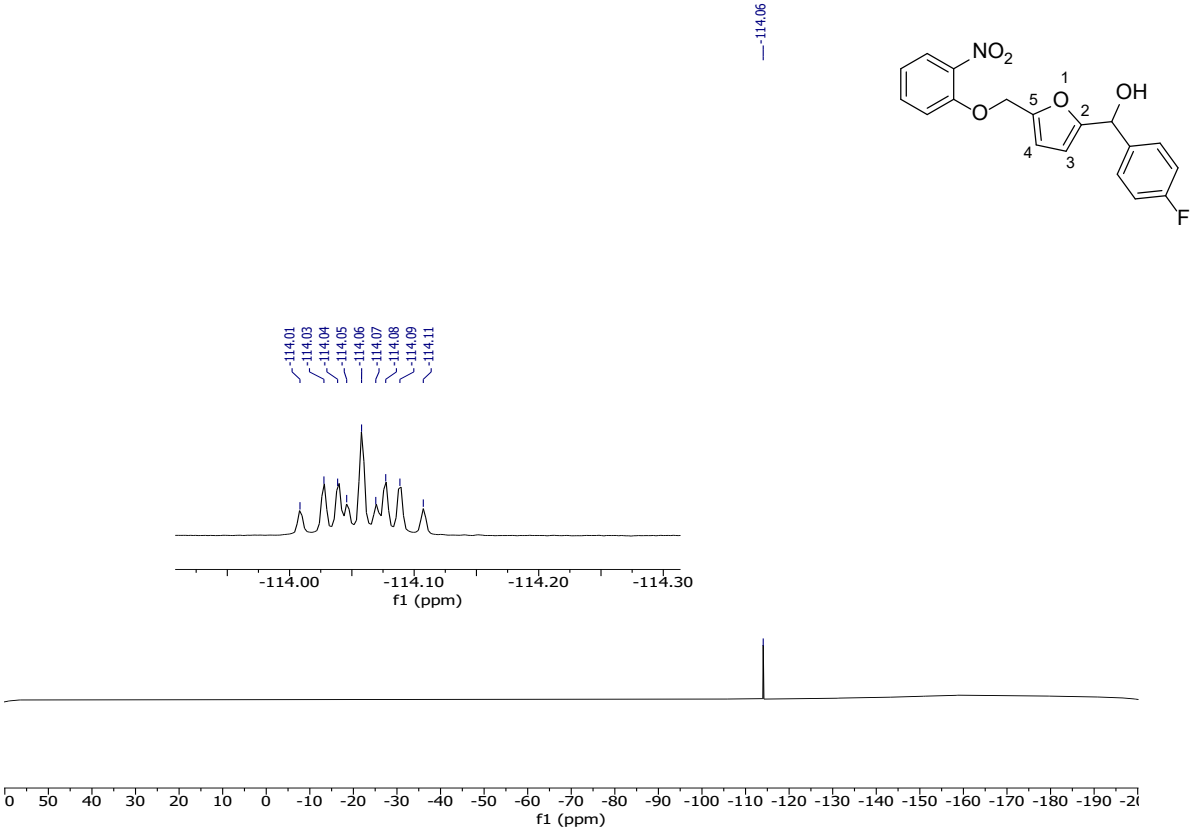
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol S6g **(500 MHz, $CDCl_3$)**



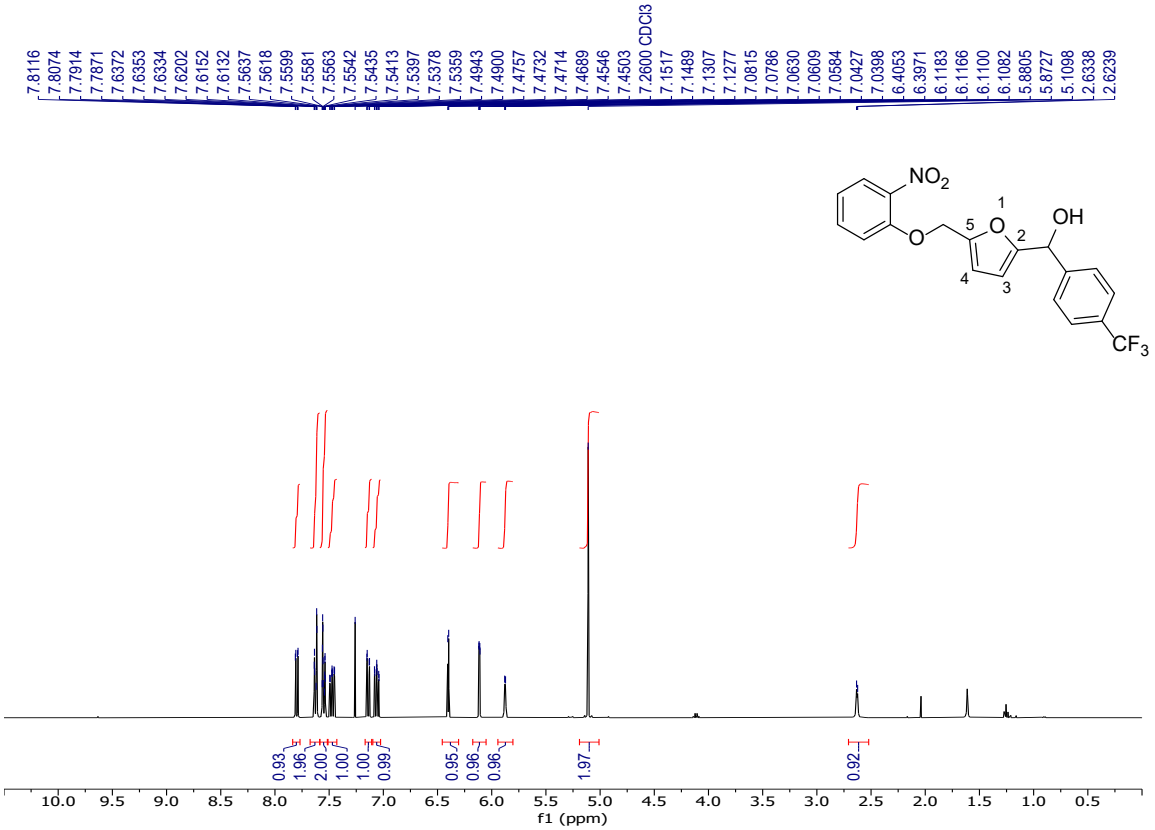
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol S6g (125 MHz, $CDCl_3$)



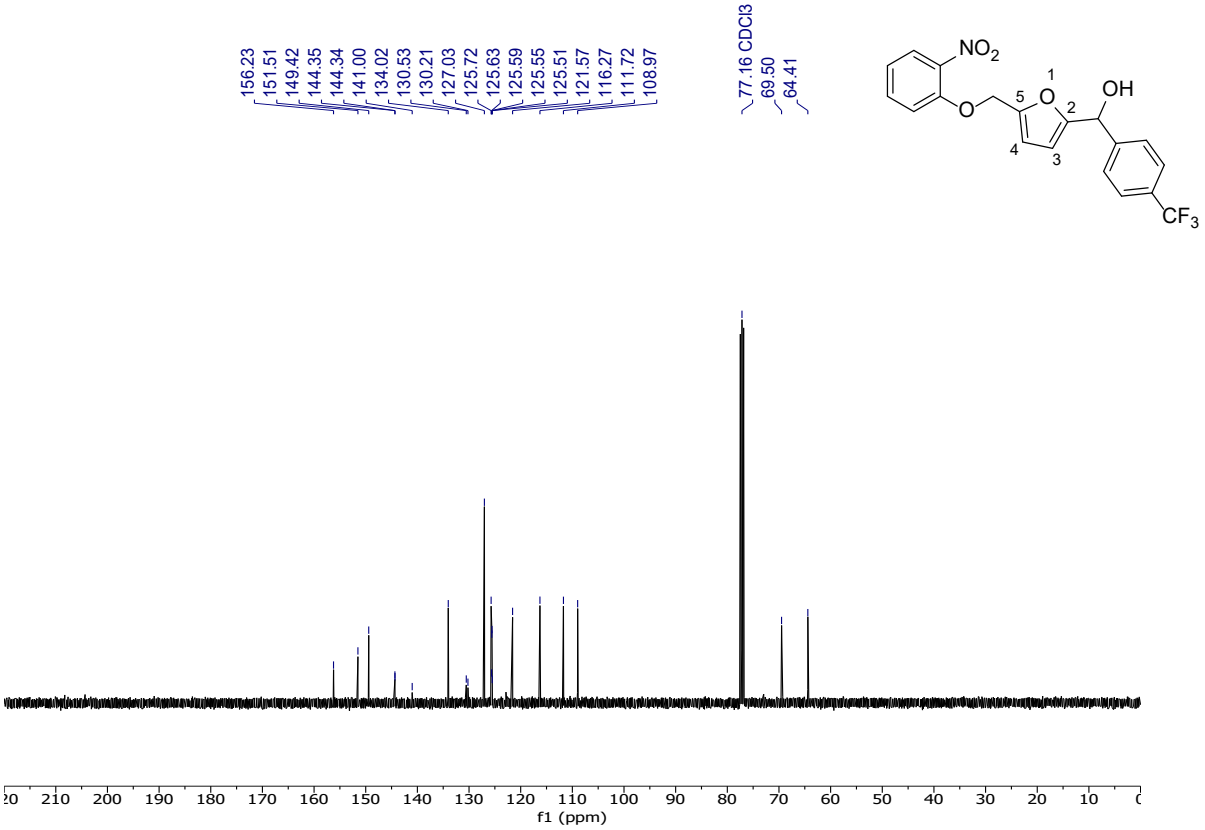
^{19}F NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol S6g (282 MHz, $CDCl_3$)



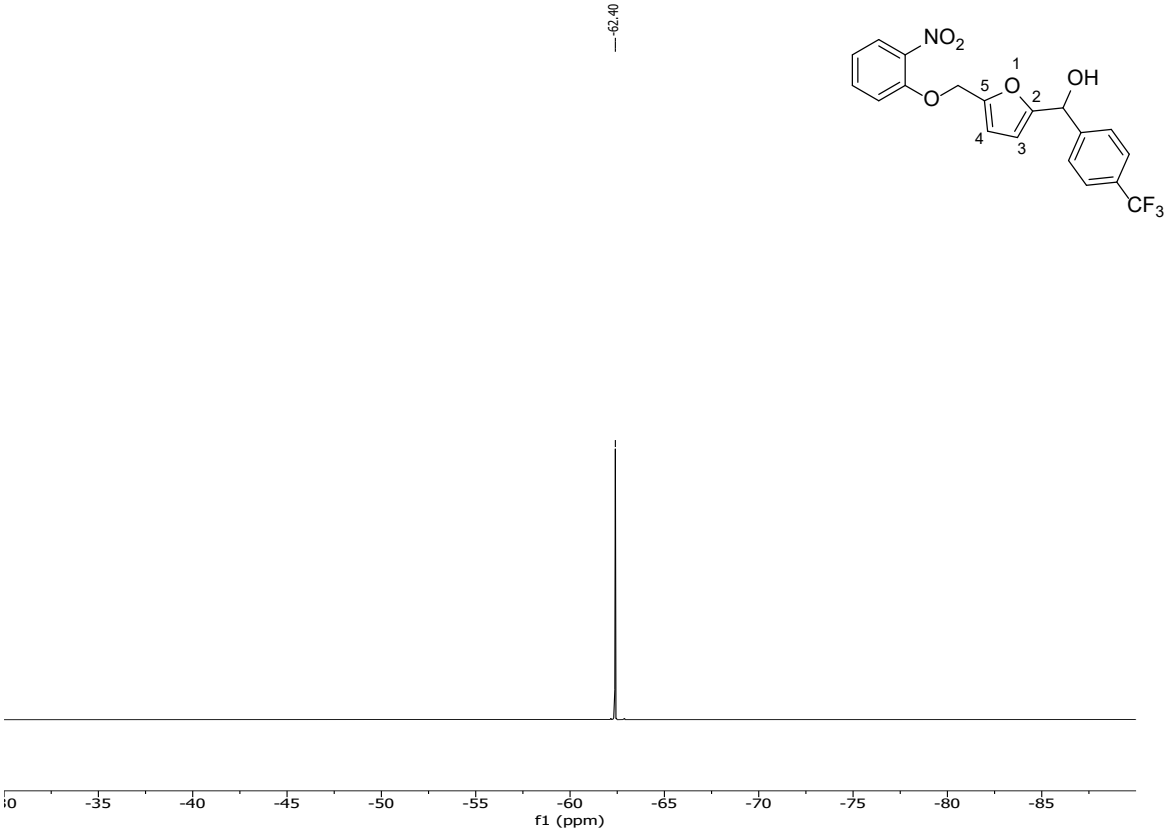
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol S6h **(400 MHz, $CDCl_3$)**



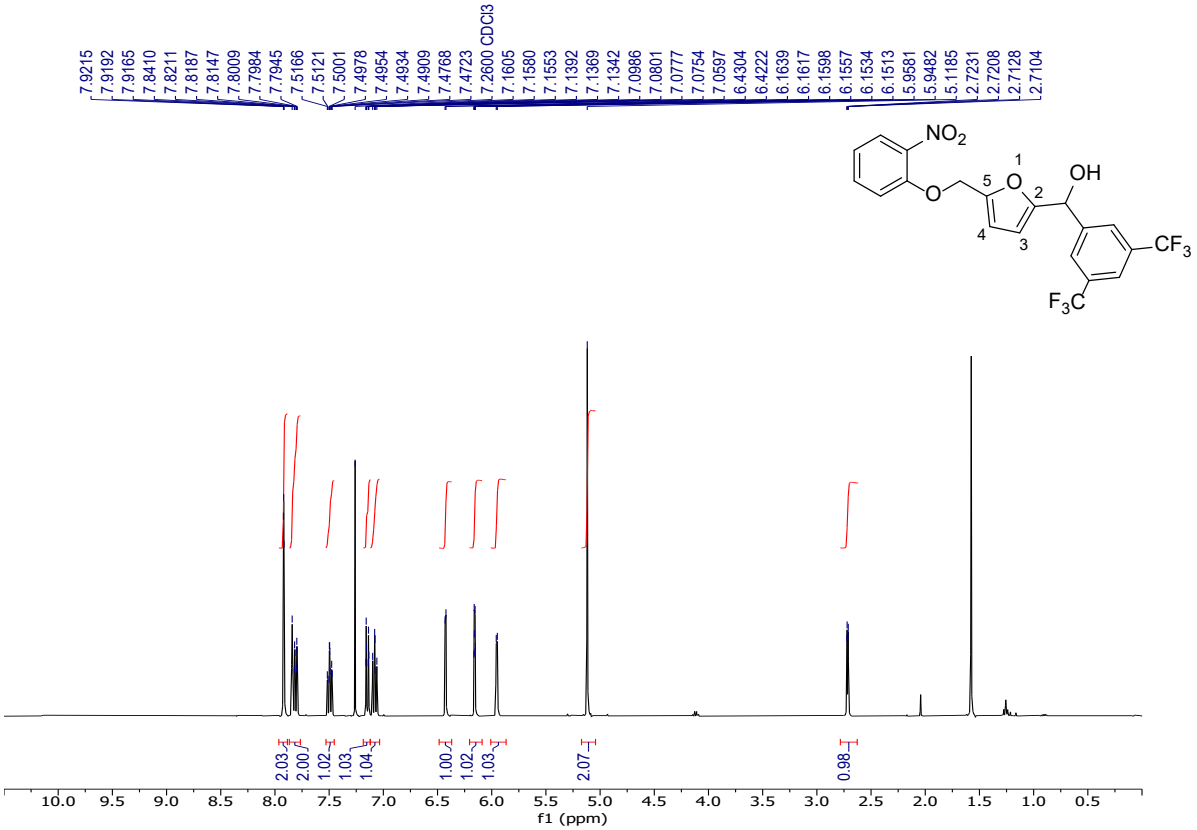
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol S6h (100 MHz, $CDCl_3$)



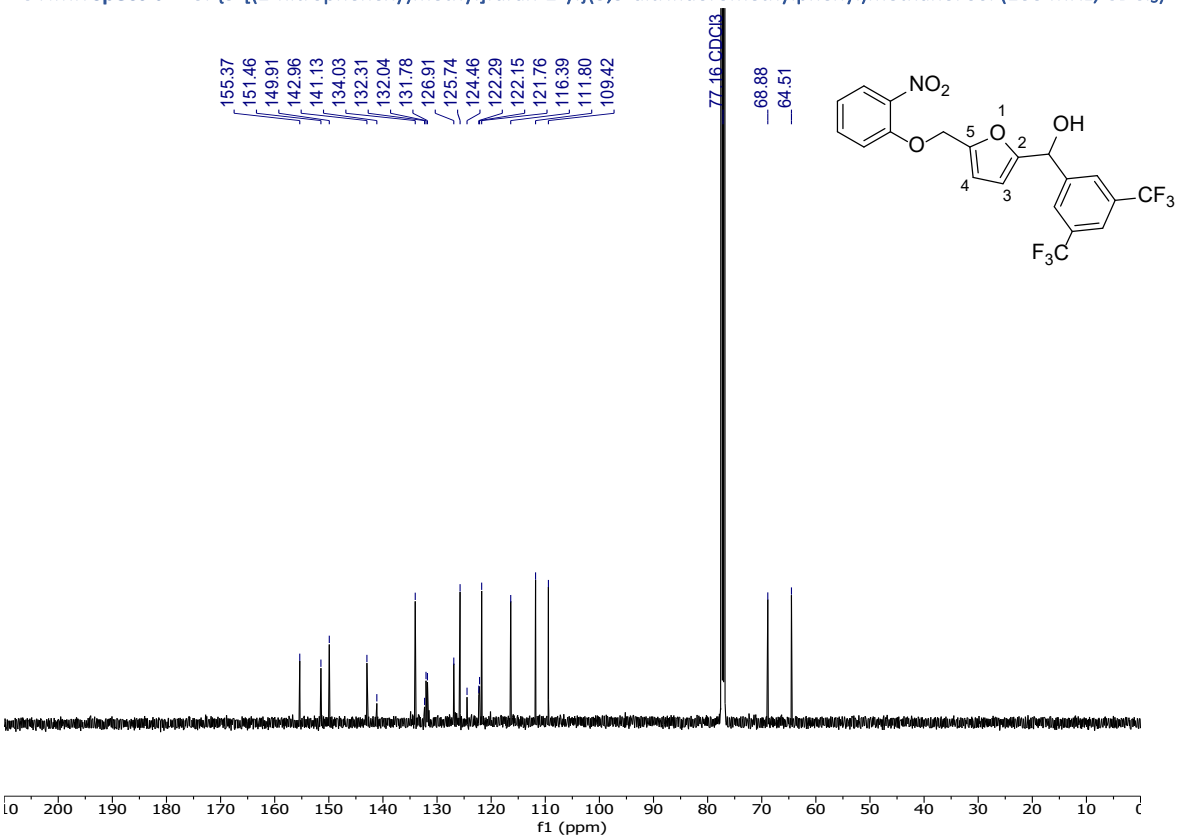
^{19}F NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol S6h (376 MHz, $CDCl_3$)



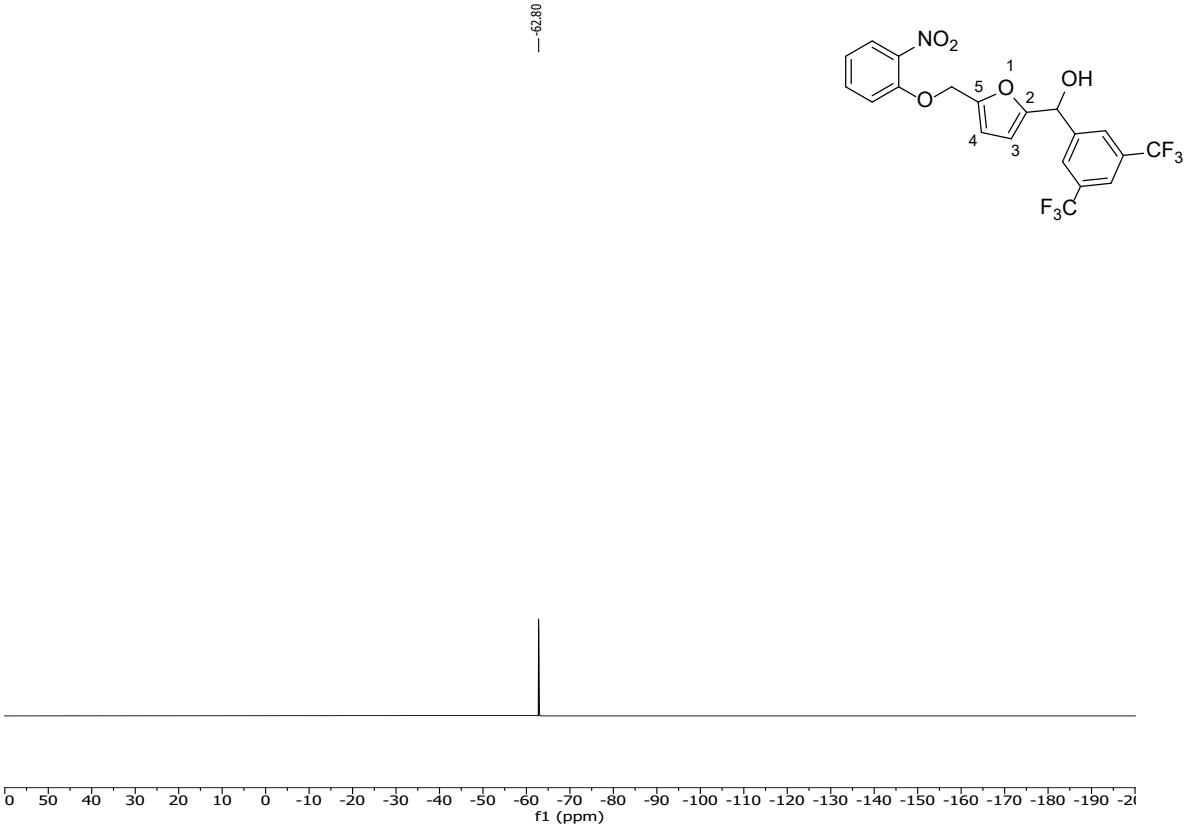
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol S6i **(400 MHz, $CDCl_3$)**



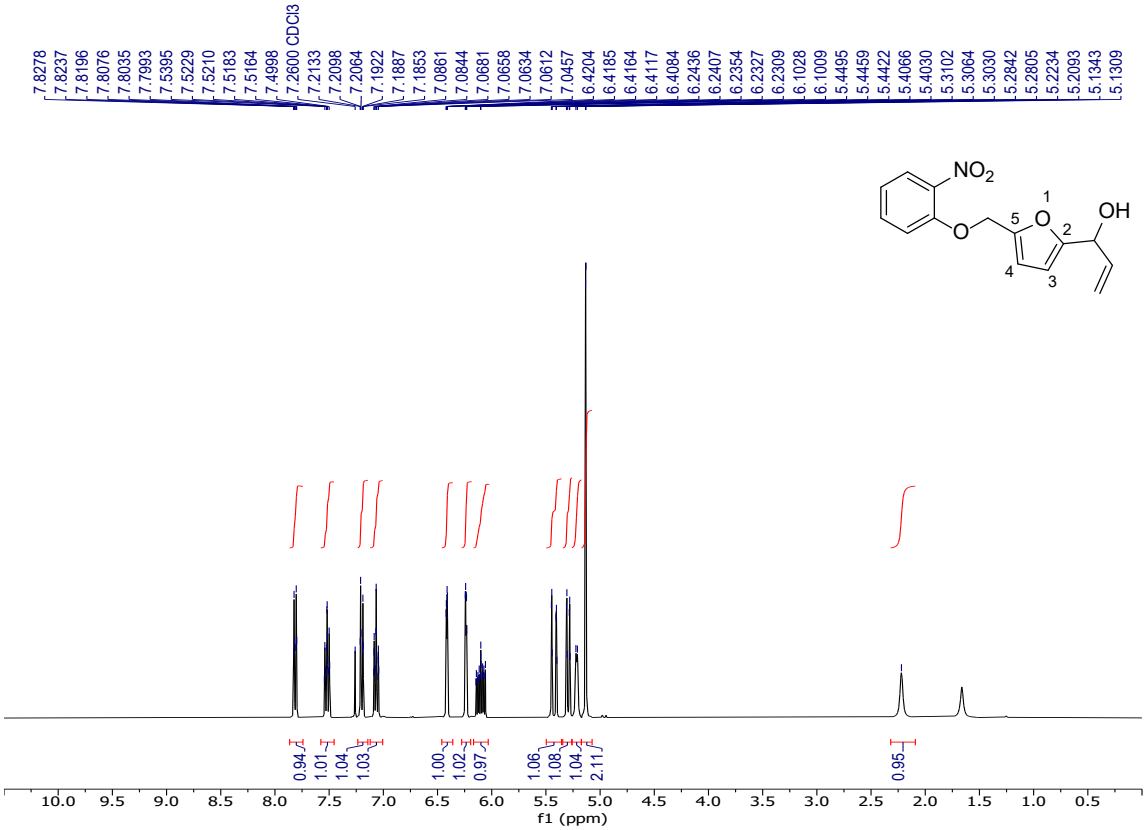
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol S6i (100 MHz, $CDCl_3$)



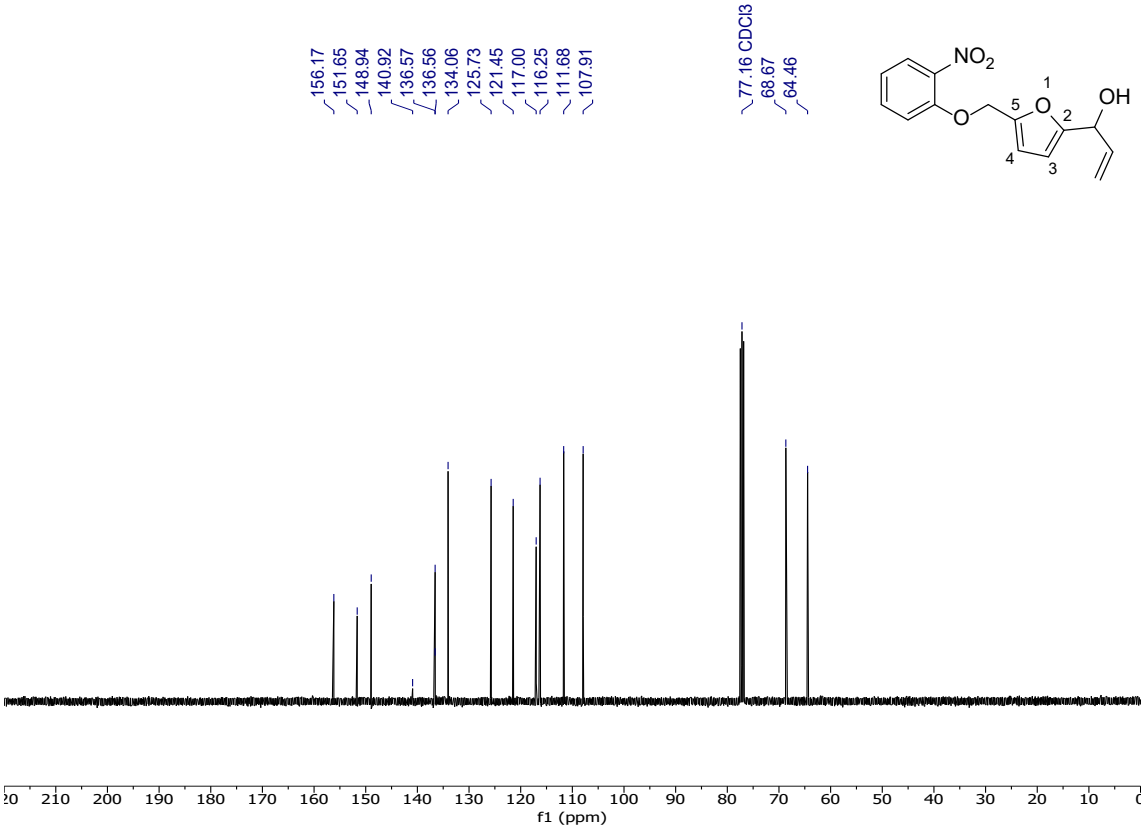
^{19}F NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol S6i (282 MHz, $CDCl_3$)



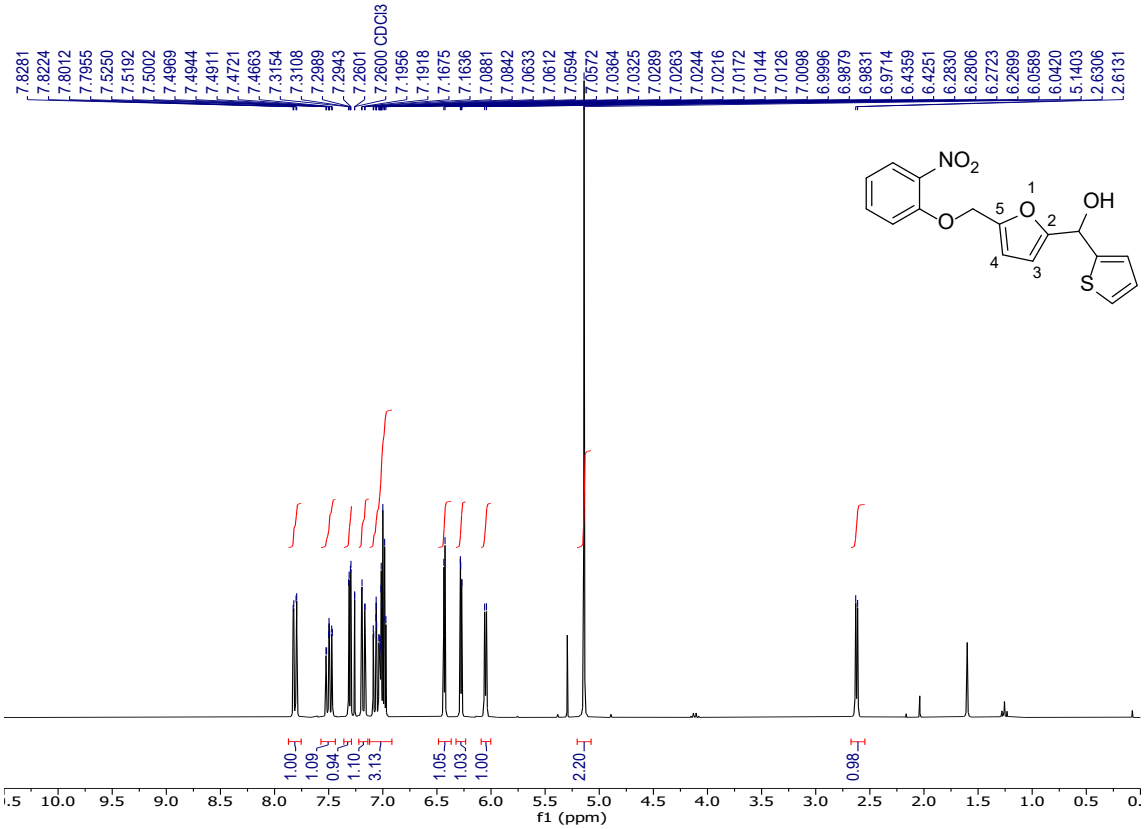
^{1}H NMR spectrum of 1-{5-[(2-nitrophenoxy)methyl]furan-2-yl}prop-2-en-1-ol S6j **(400 MHz, $CDCl_3$)**



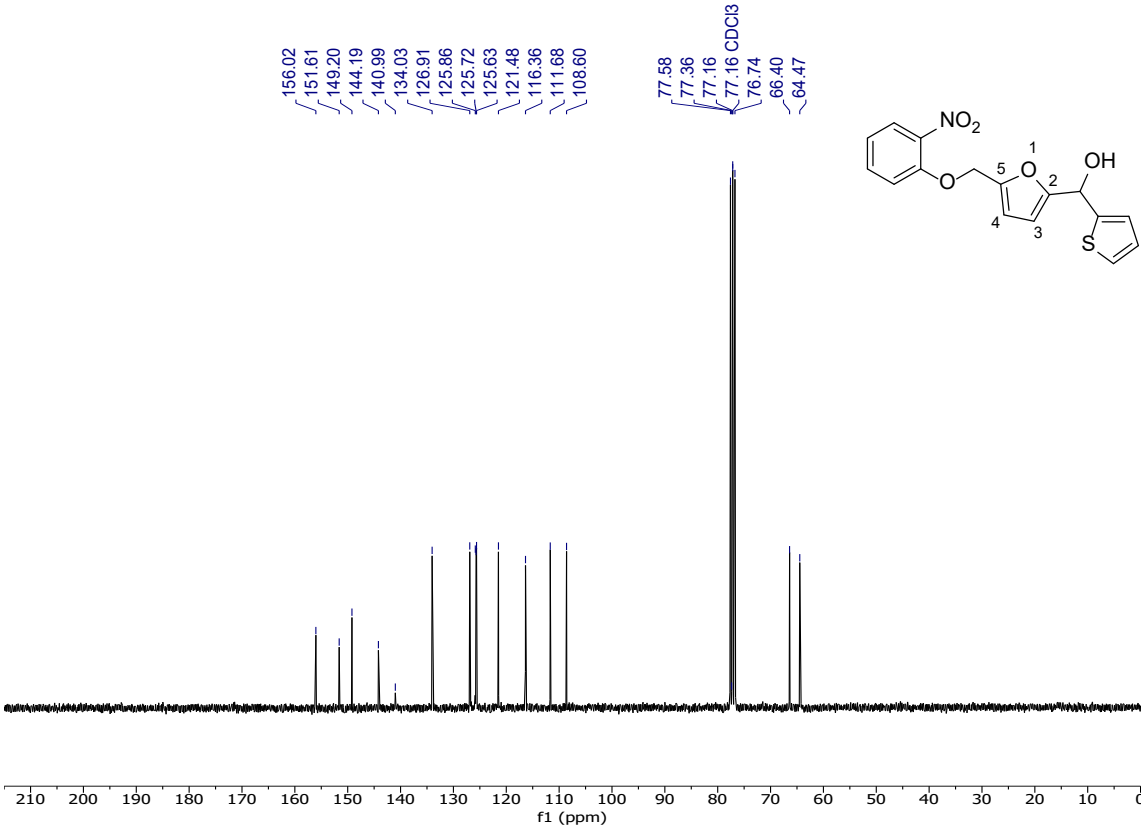
^{13}C NMR **spectrum** of 1-{5-[(2-nitrophenoxy)methyl]furan-2-yl}prop-2-en-1-ol S6j (100 MHz, $CDCl_3$)



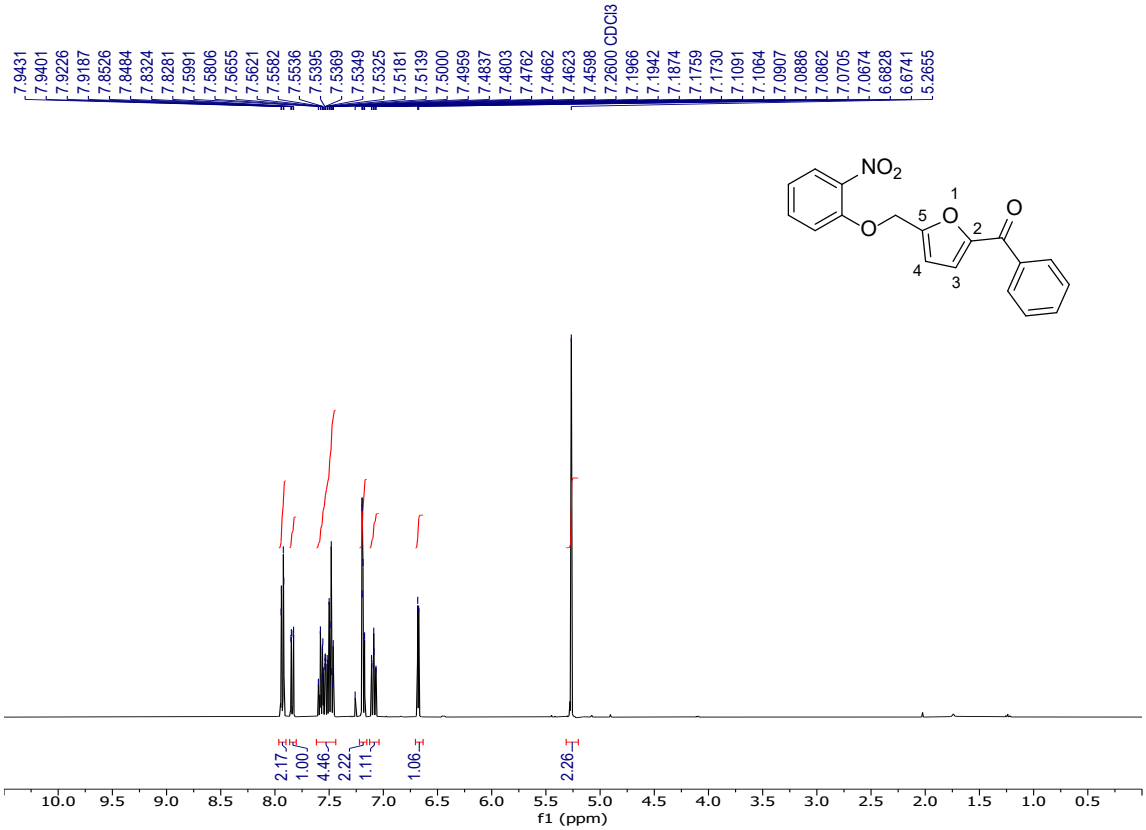
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(thiophen-2-yl)methanol S6k (**(300 MHz, $CDCl_3$)**



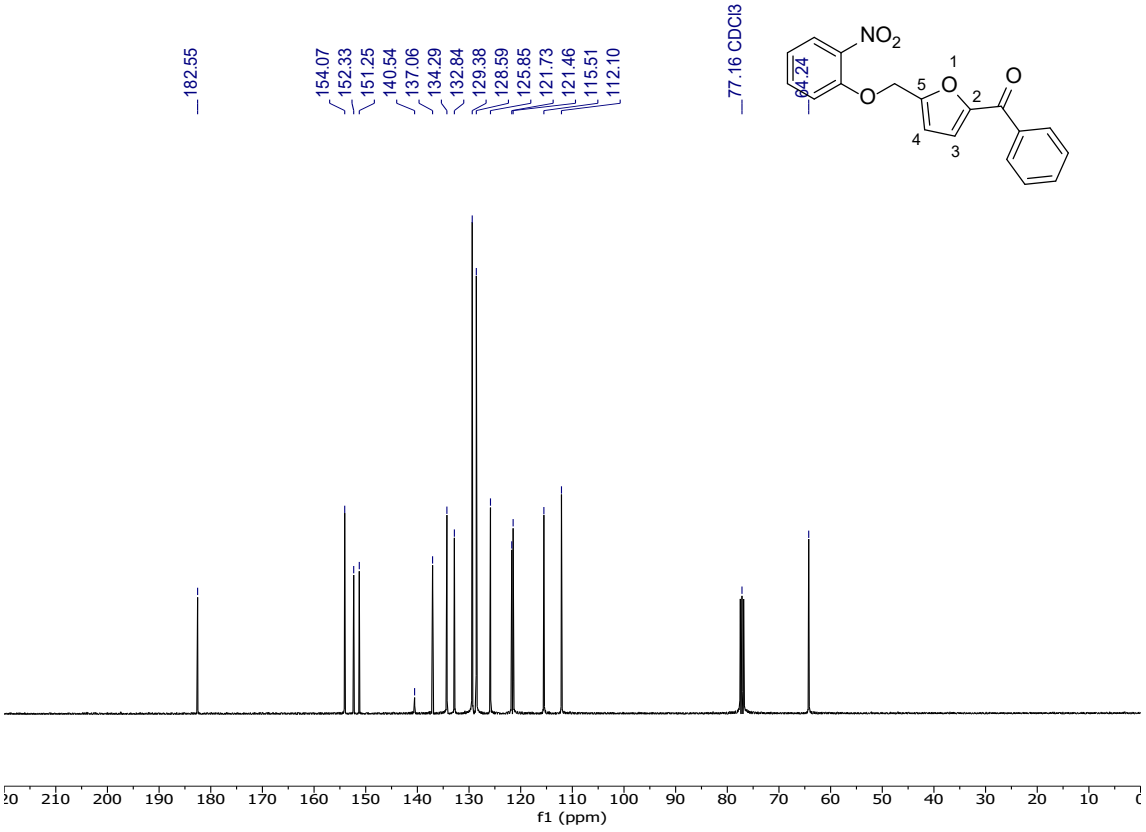
^{13}C NMR spectrum of 5-[(2-nitrophenoxy)methyl]furan-2-yl}(thiophen-2-yl)methanol S6k (75 MHz, $CDCl_3$)



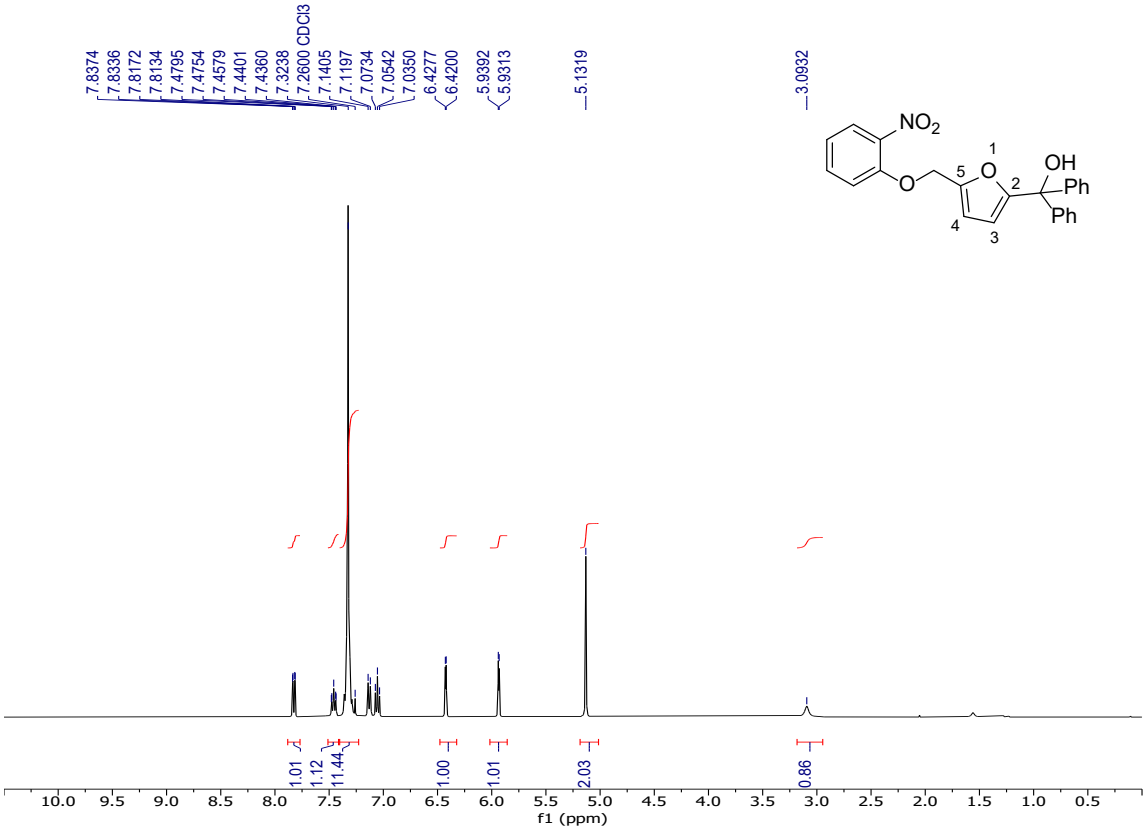
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(phenyl)methanone **(400 MHz, $CDCl_3$)**



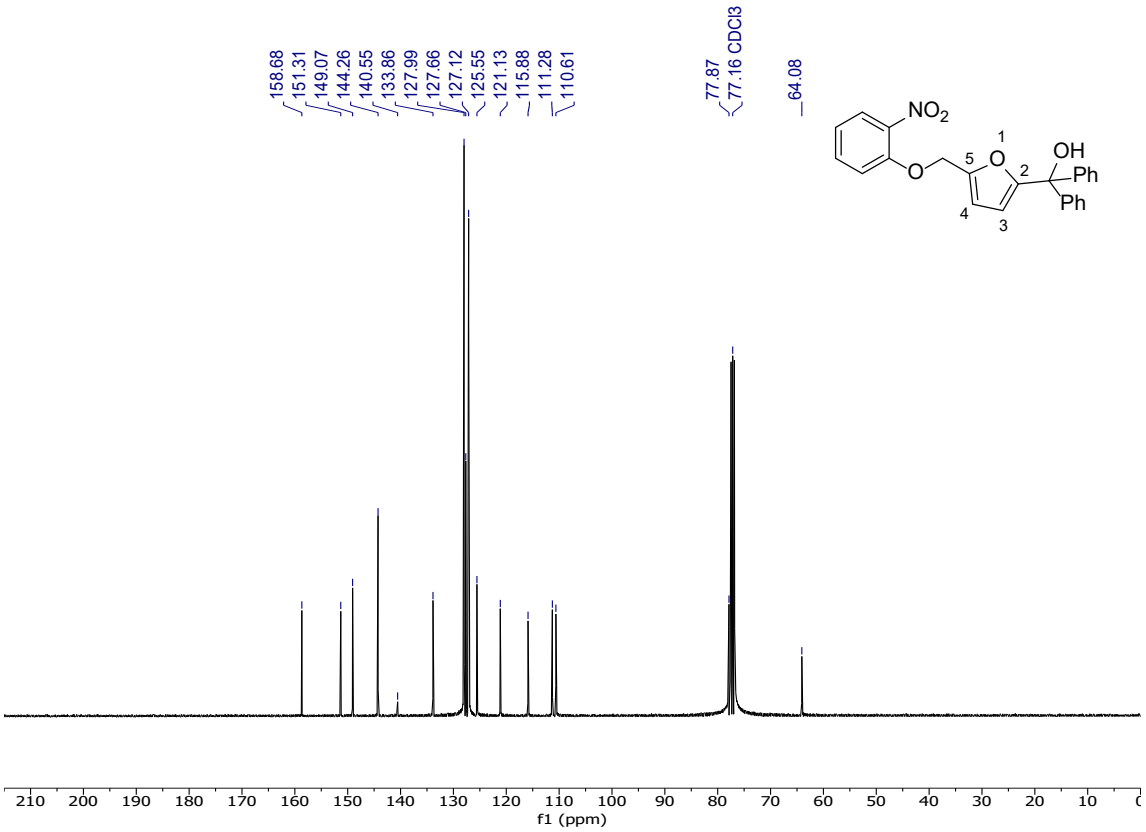
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(phenyl)methanone (100 MHz, $CDCl_3$)



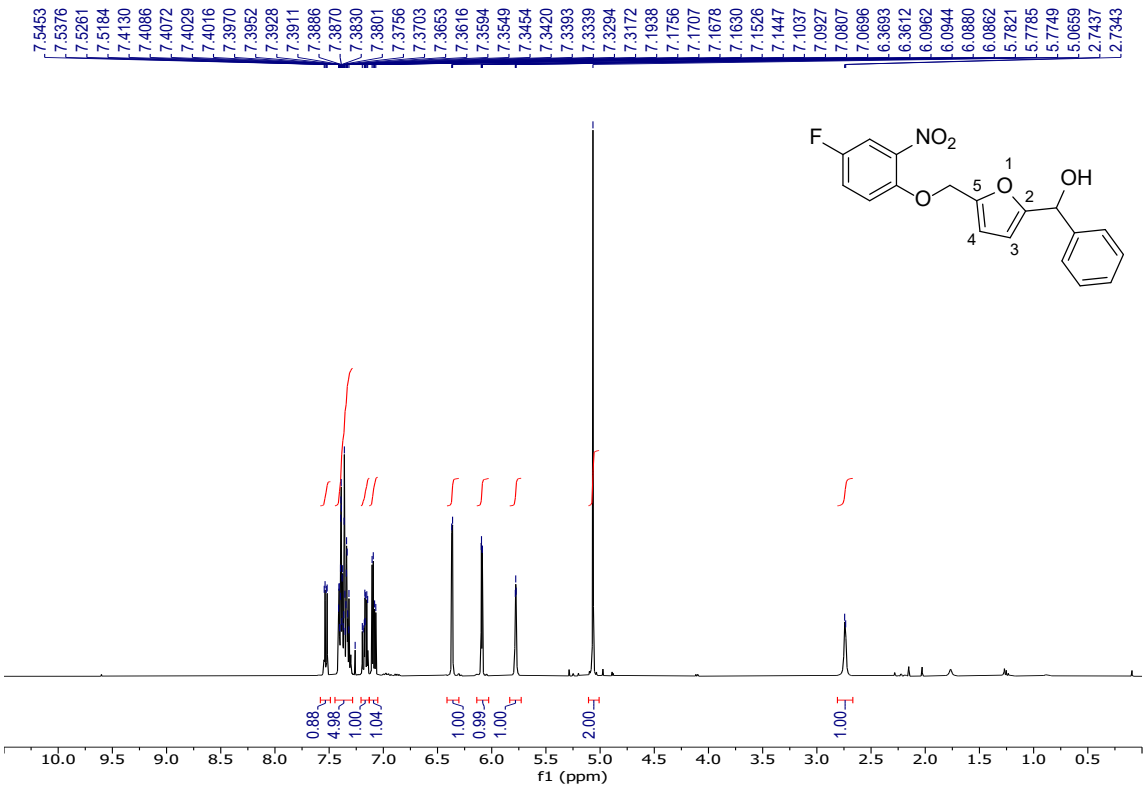
^{1}H NMR spectrum of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(diphenyl)methanol S6l (**400 MHz, $CDCl_3$**)



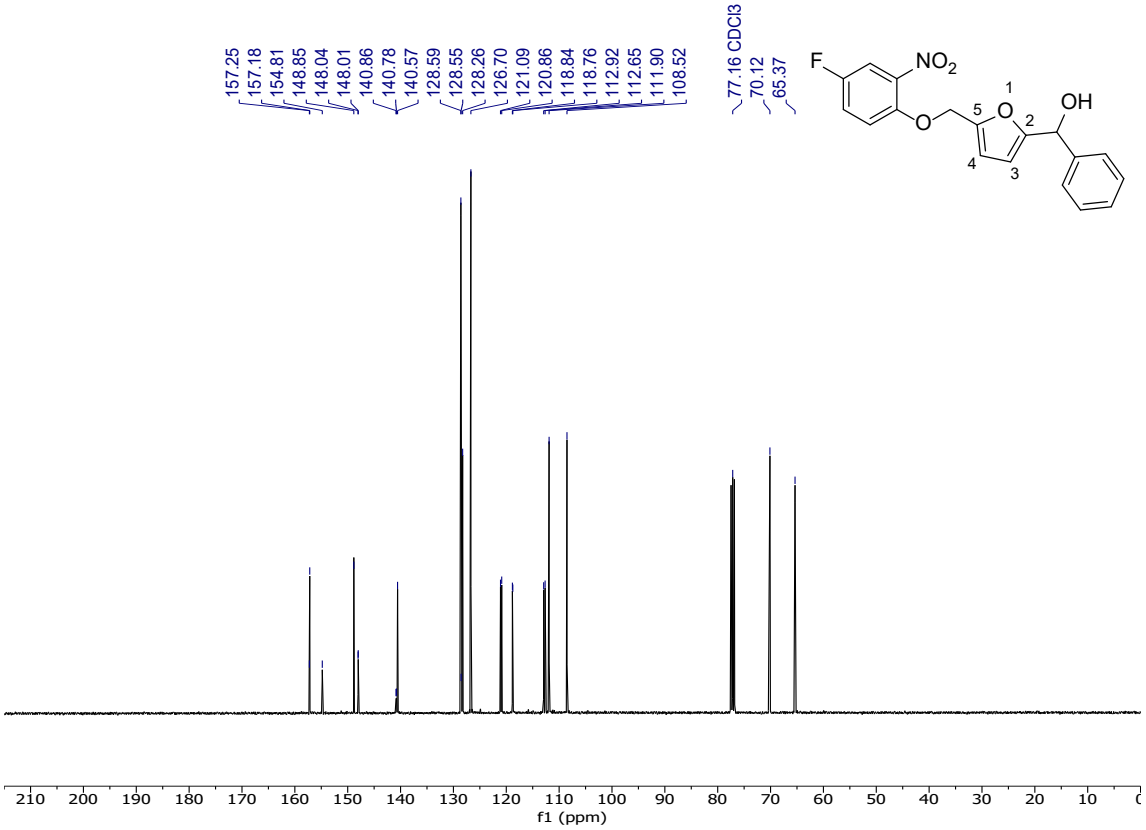
^{13}C NMR **spectrum** of {5-[(2-nitrophenoxy)methyl]furan-2-yl}(diphenyl)methanol S6l (100 MHz, $CDCl_3$)



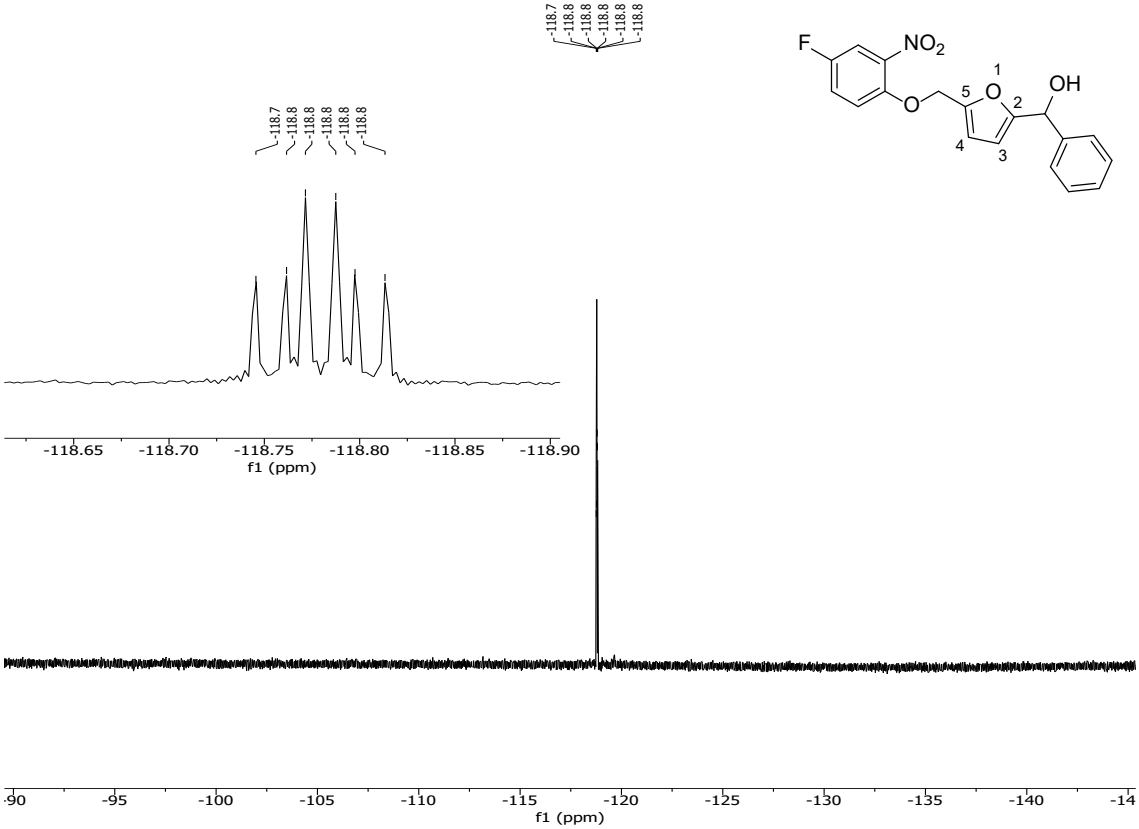
^{1}H NMR spectrum of {5-[(2-nitro-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6m **(400 MHz, $CDCl_3$)**



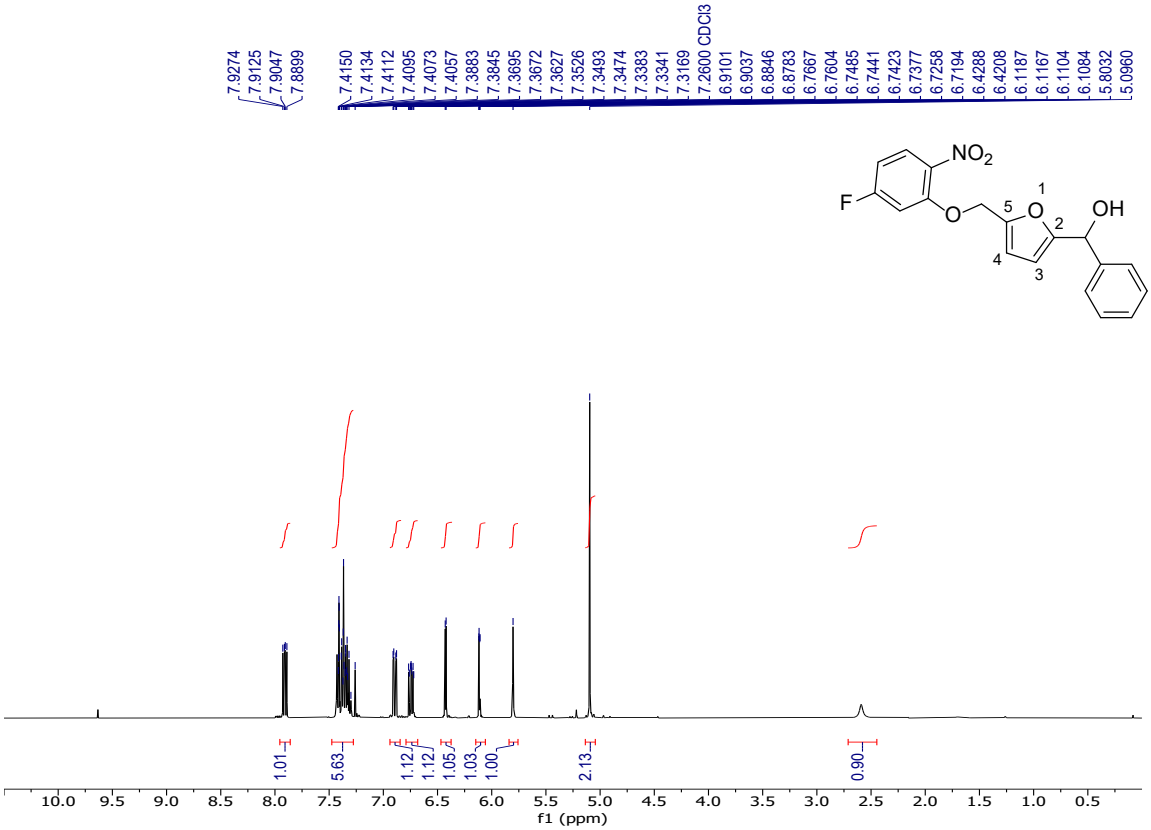
^{13}C NMR **spectrum** of {5-[(2-nitro-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6m (100 MHz, $CDCl_3$)



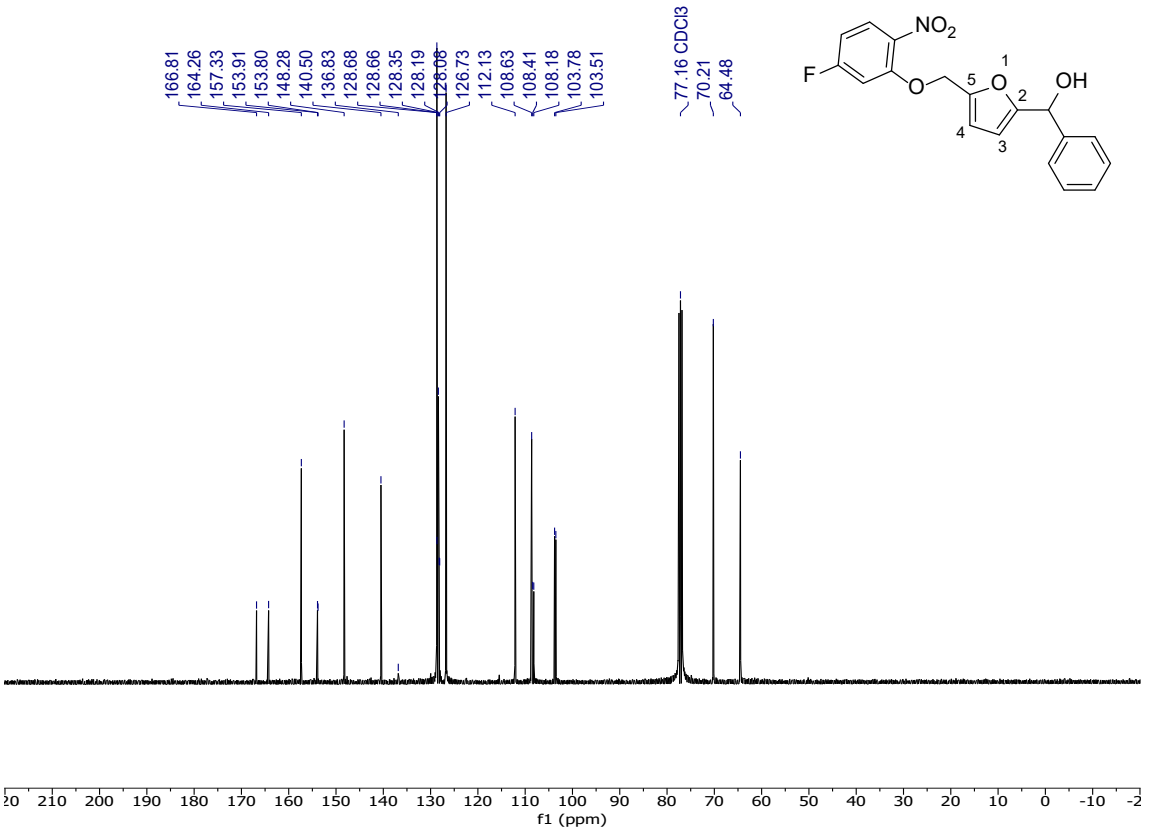
^{19}F NMR **spectrum** of {5-[(2-nitro-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6m (376 MHz, $CDCl_3$)



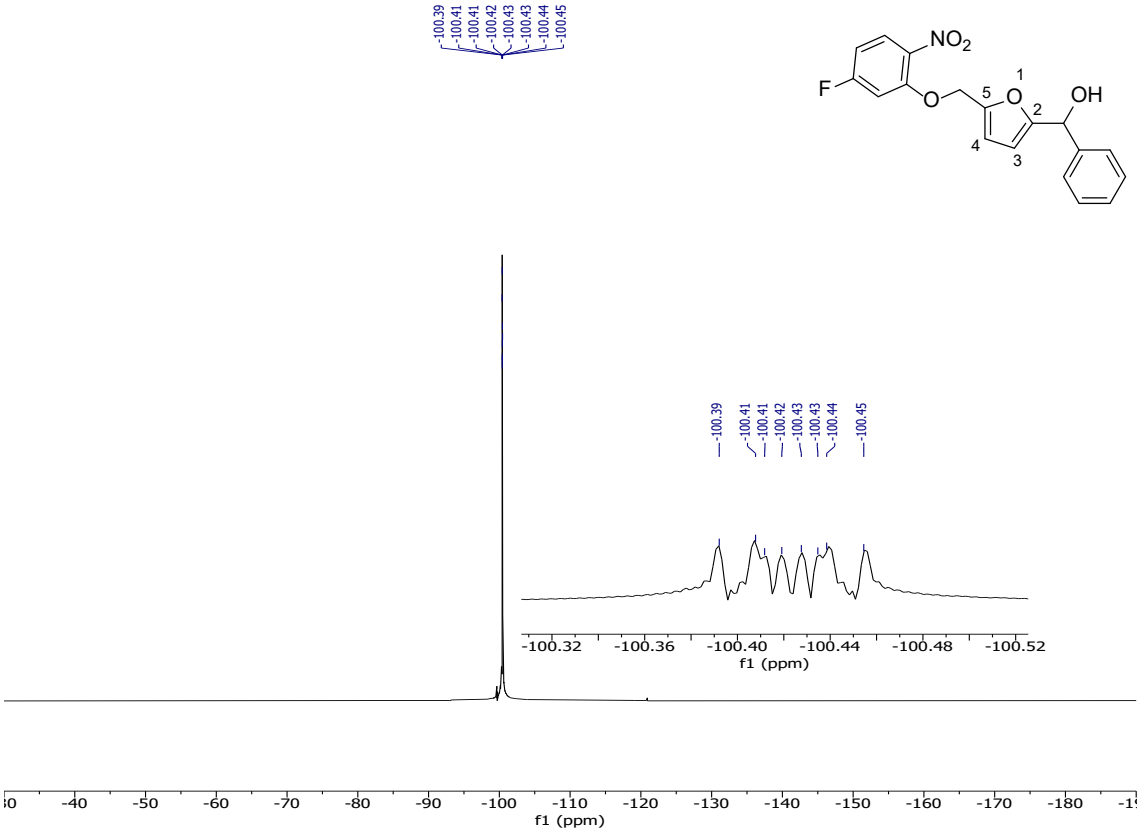
^{1}H NMR spectrum of {5-[(2-nitro-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6n **(400 MHz, $CDCl_3$)**



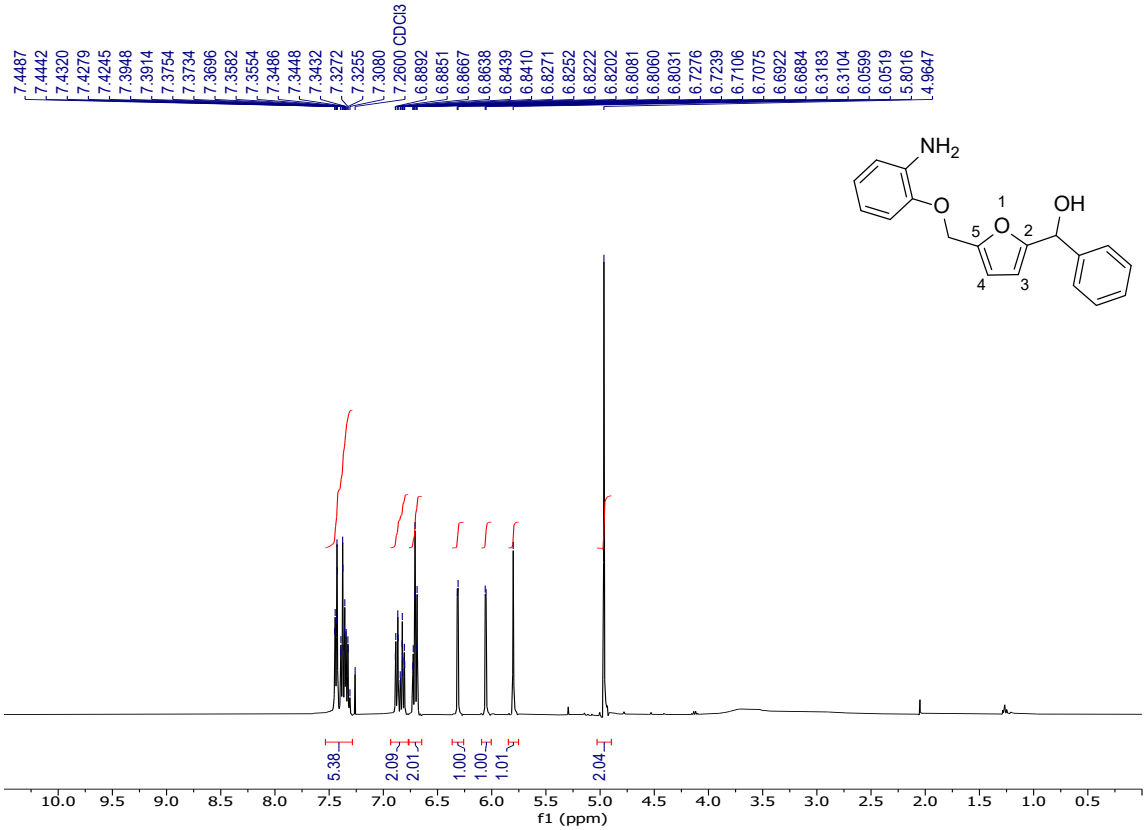
^{13}C NMR **spectrum** of {5-[(2-nitro-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6n (100 MHz, $CDCl_3$)



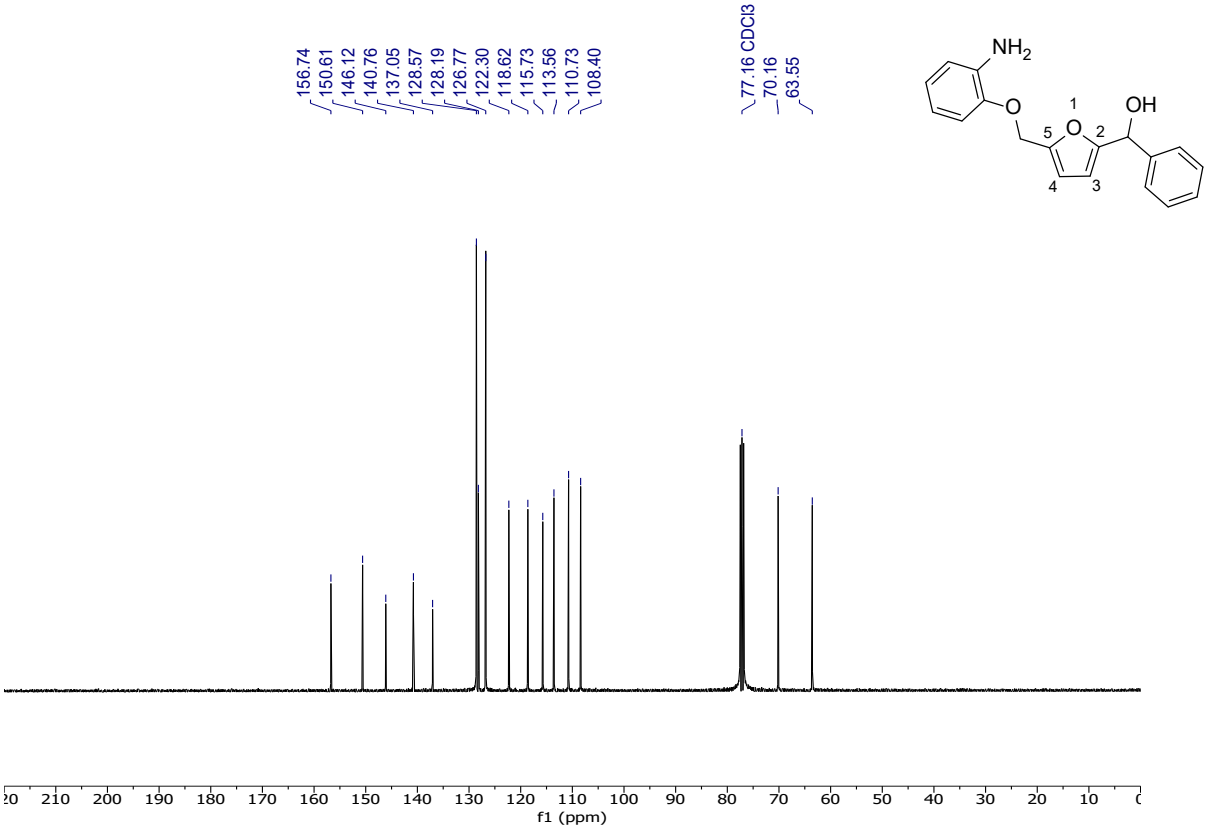
^{19}F NMR spectrum of {5-[(2-nitro-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol S6n (376 MHz, $CDCl_3$)



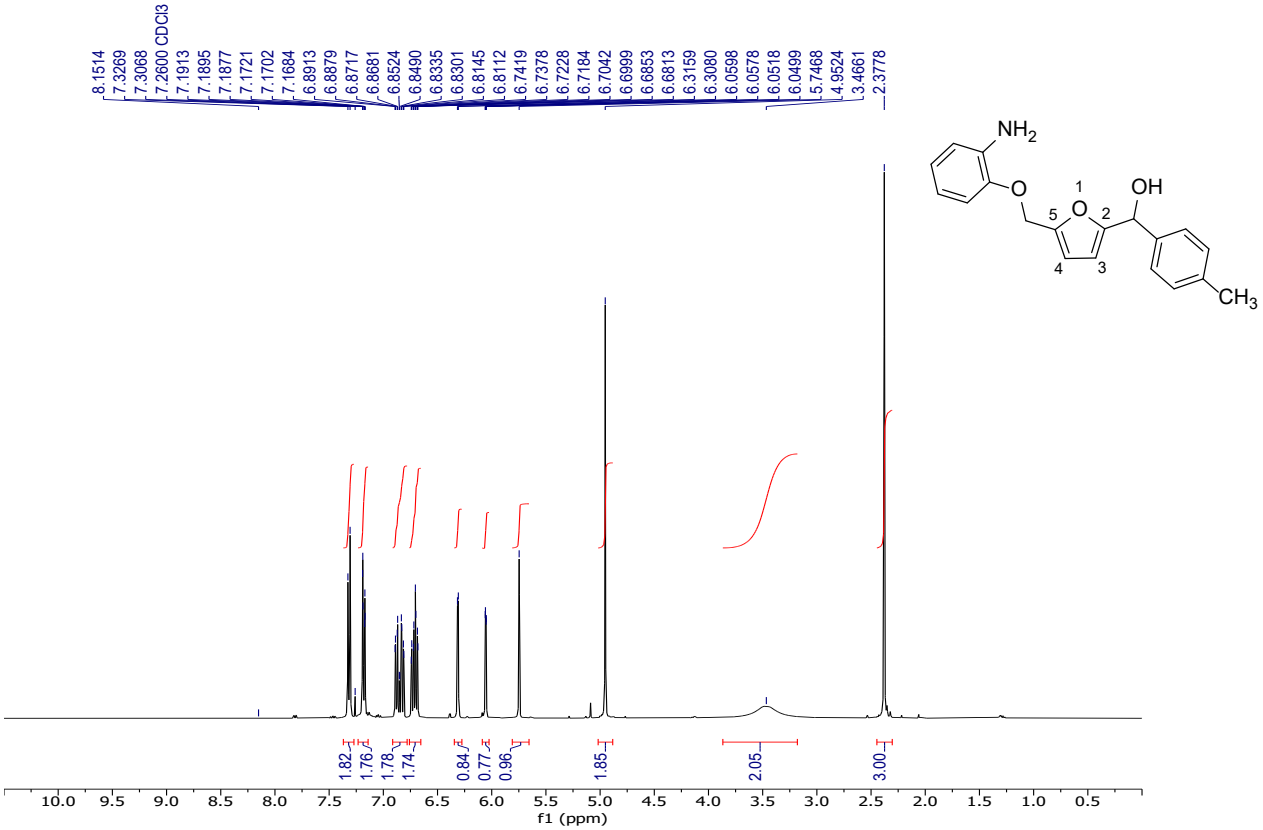
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(phenyl)methanol 8 **(400 MHz, $CDCl_3$)**



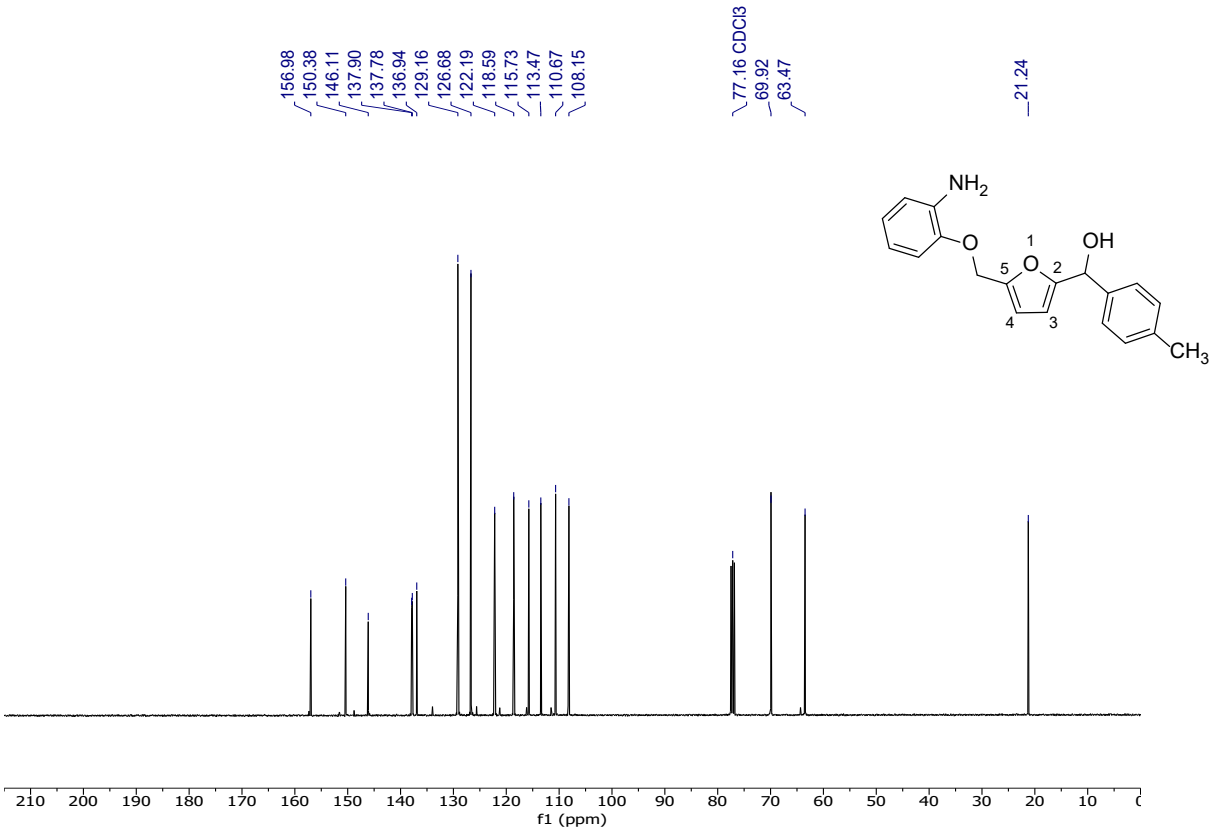
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(phenyl)methanol 8 (100 MHz, $CDCl_3$)



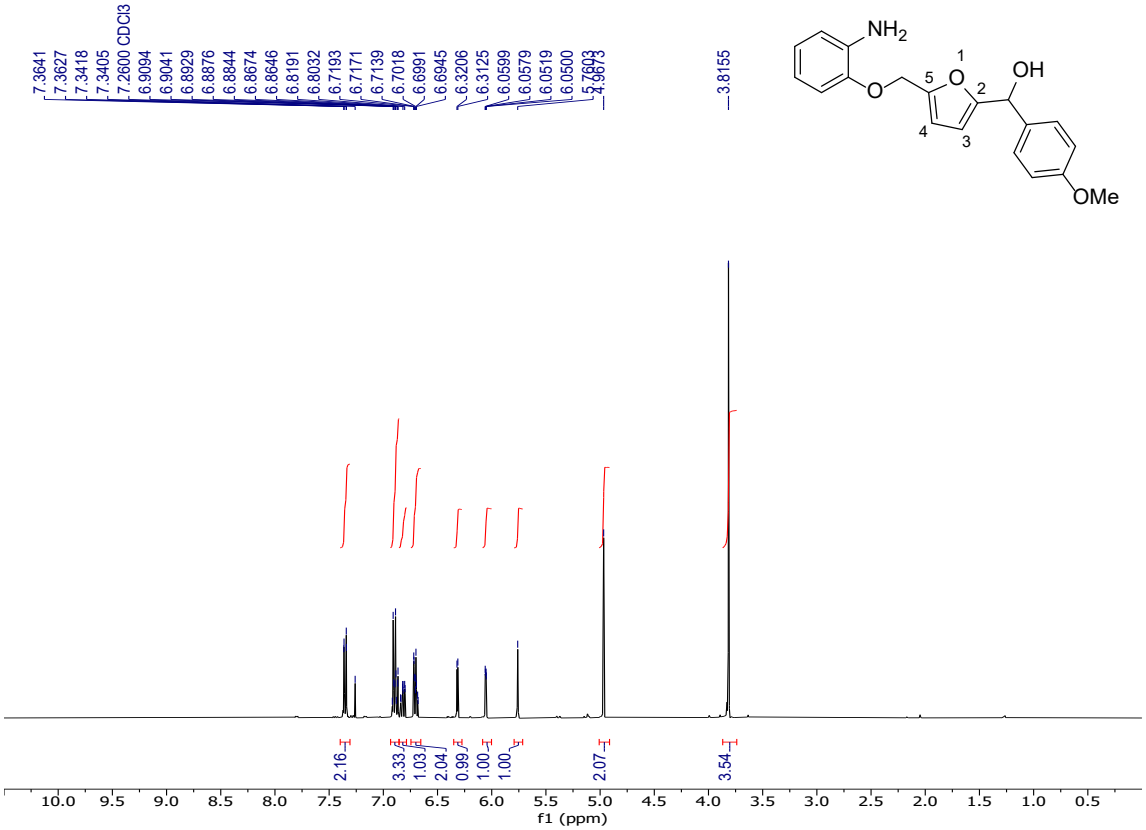
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-methylphenyl)methanol 8a **(400 MHz, $CDCl_3$)**



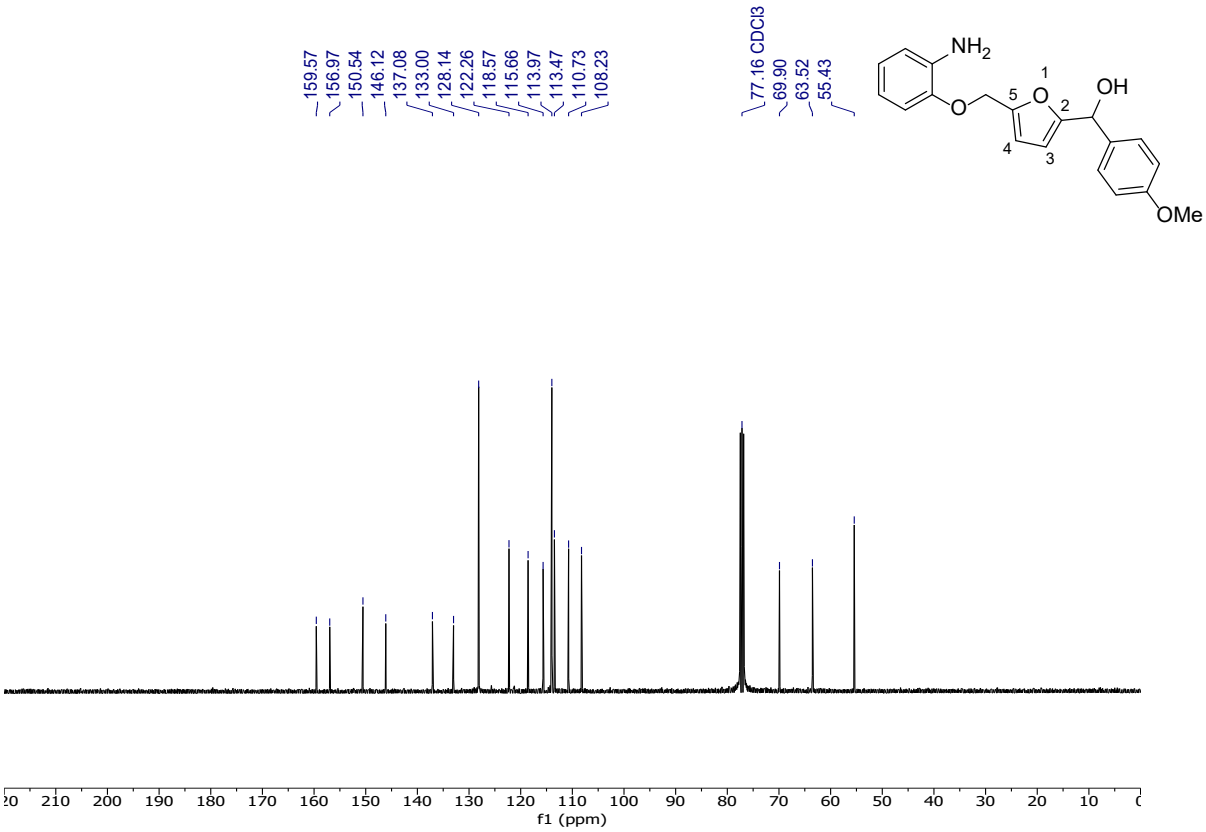
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-methylphenyl)methanol 8a (100 MHz, $CDCl_3$)



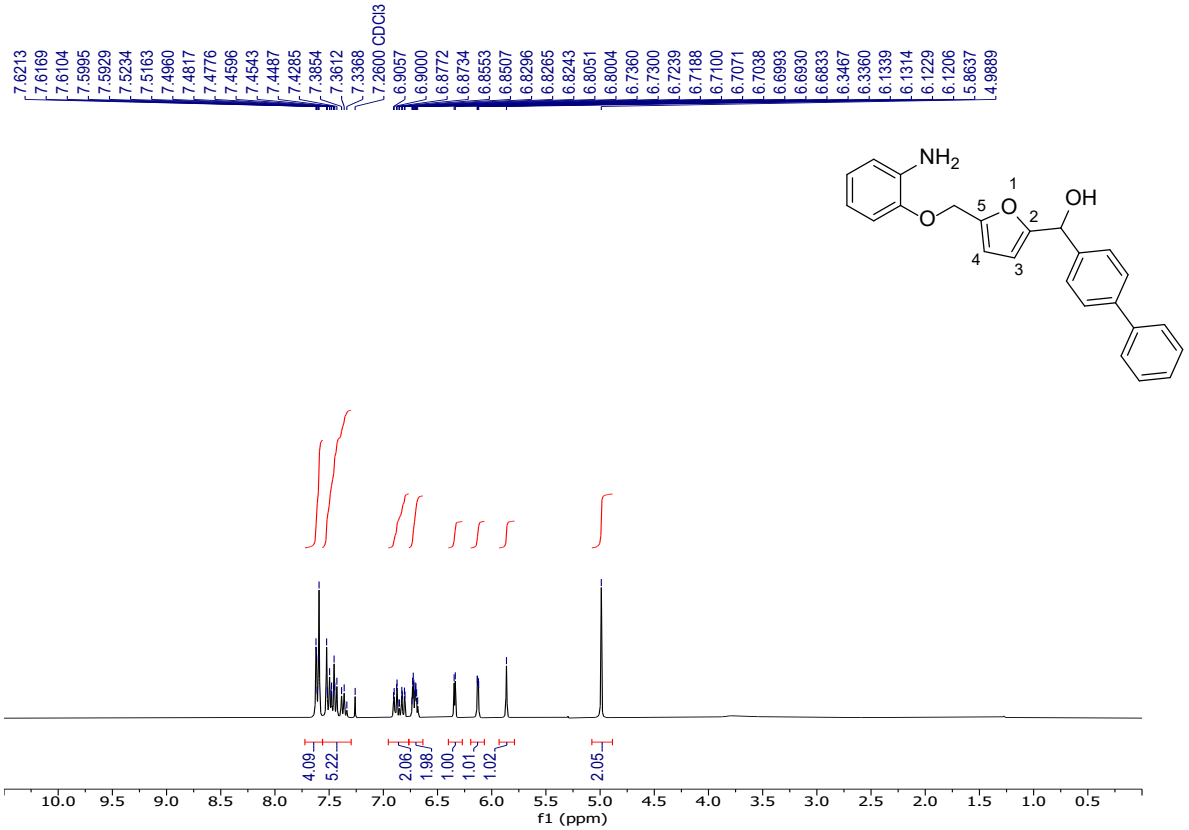
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-methoxyphenyl)methanol 8b **(400 MHz, $CDCl_3$)**



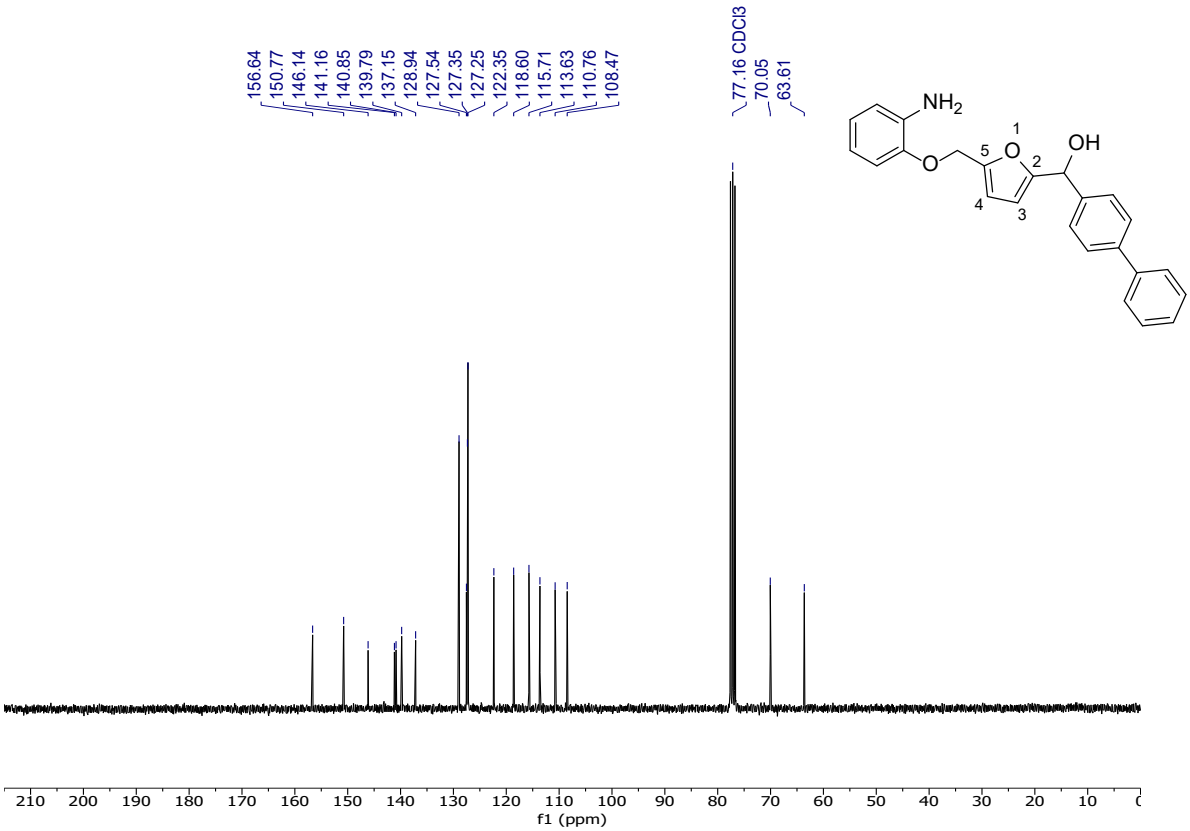
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-methoxyphenyl)methanol 8b (100 MHz, $CDCl_3$)



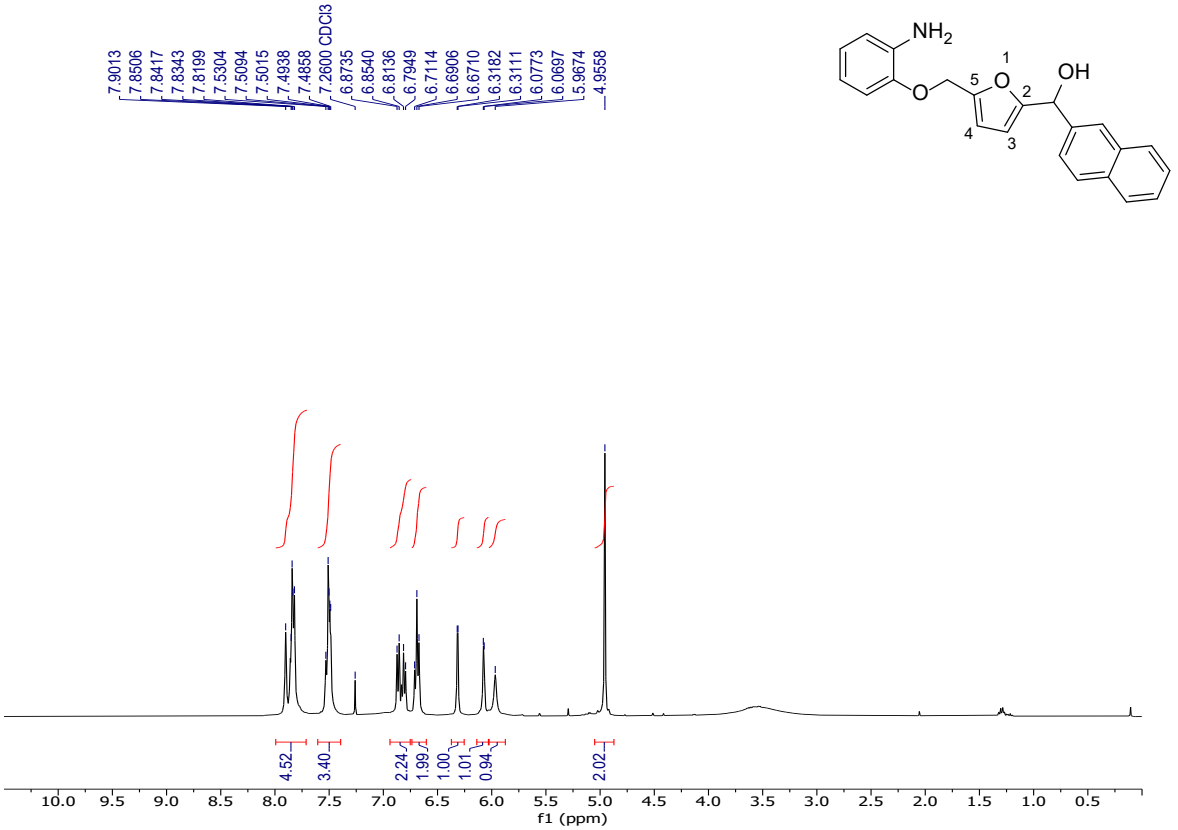
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol 8c **(300 MHz, $CDCl_3$)**



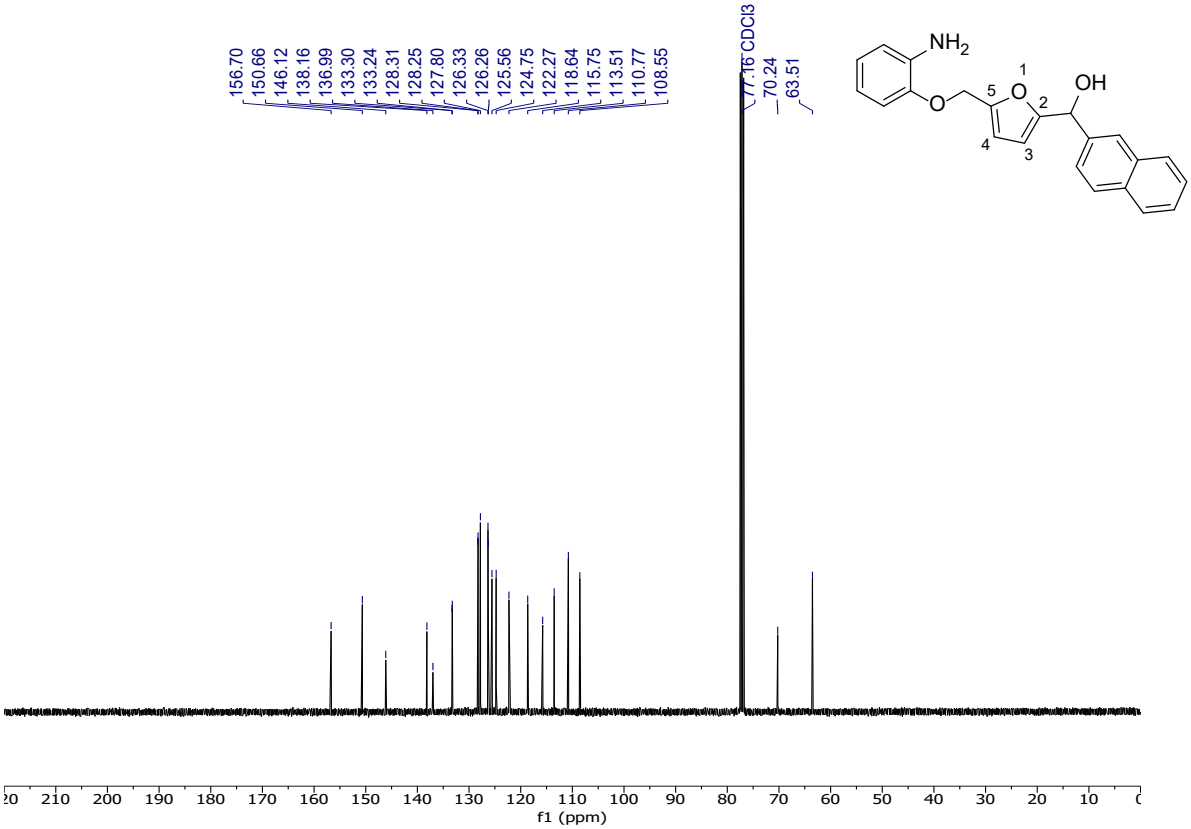
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}([1,1'-biphenyl]-4-yl)methanol 8c (75 MHz, $CDCl_3$)



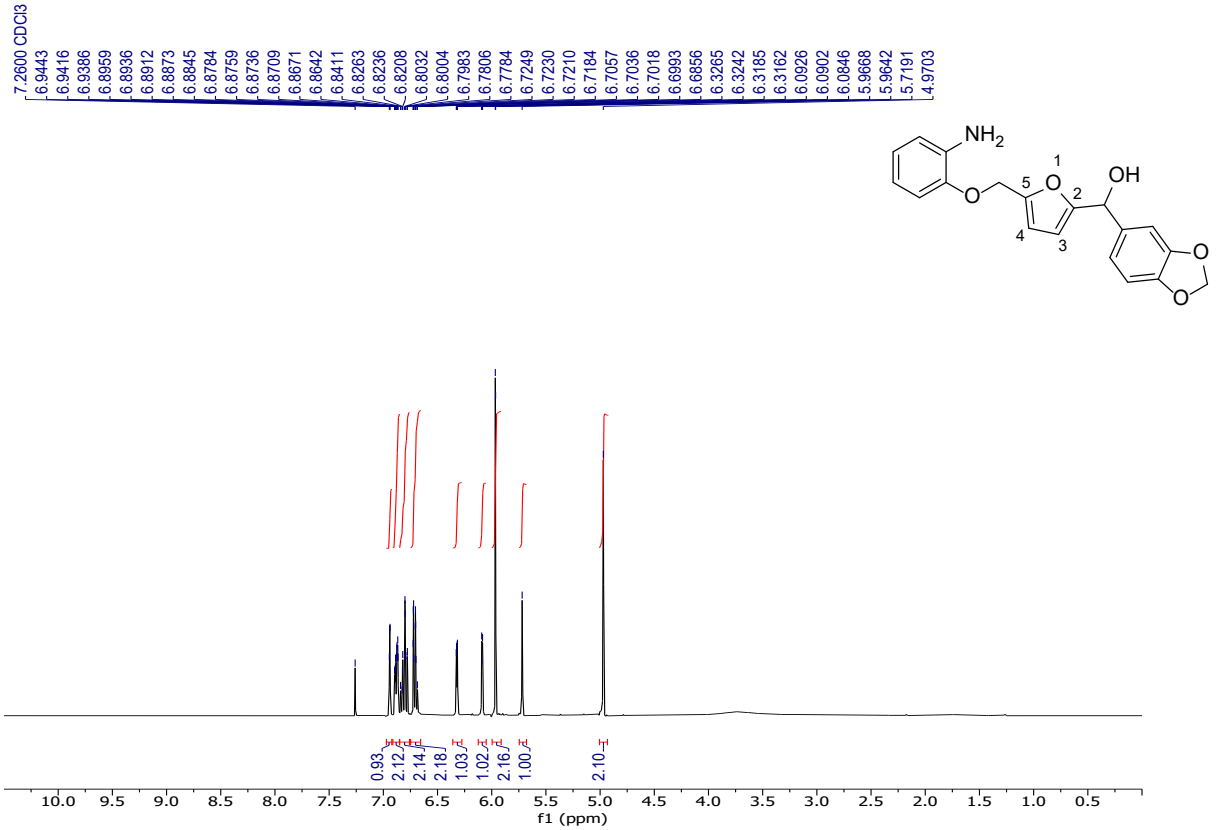
^{1}H NMR spectrum of 1-{5-[(3-aminophenoxy)methyl]furan-2-yl}-2-(naphthalen-2-yl)ethan-1-ol 8d **(400 MHz, $CDCl_3$)**



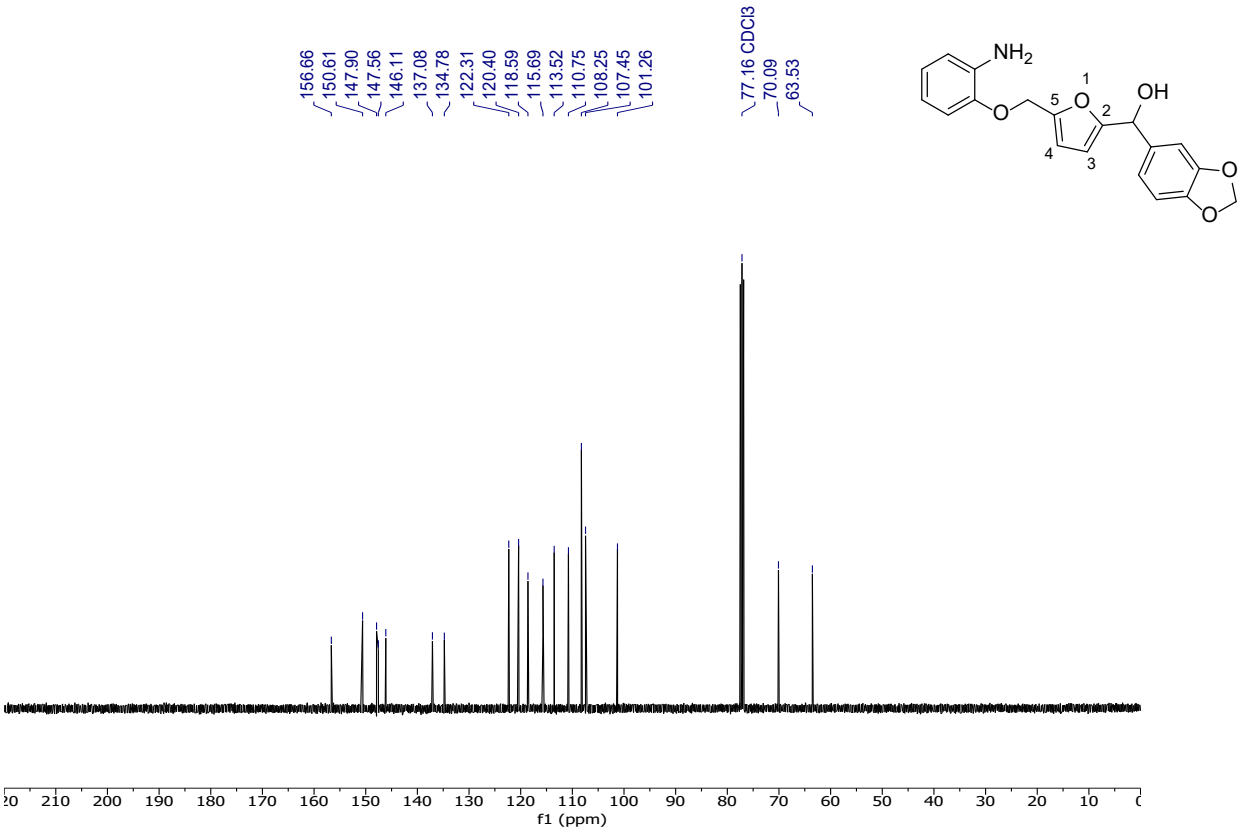
^{13}C NMR **spectrum** of 1-{5-[(3-aminophenoxy)methyl]furan-2-yl}-2-(naphthalen-2-yl)ethan-1-ol 8d (100 MHz, $CDCl_3$)



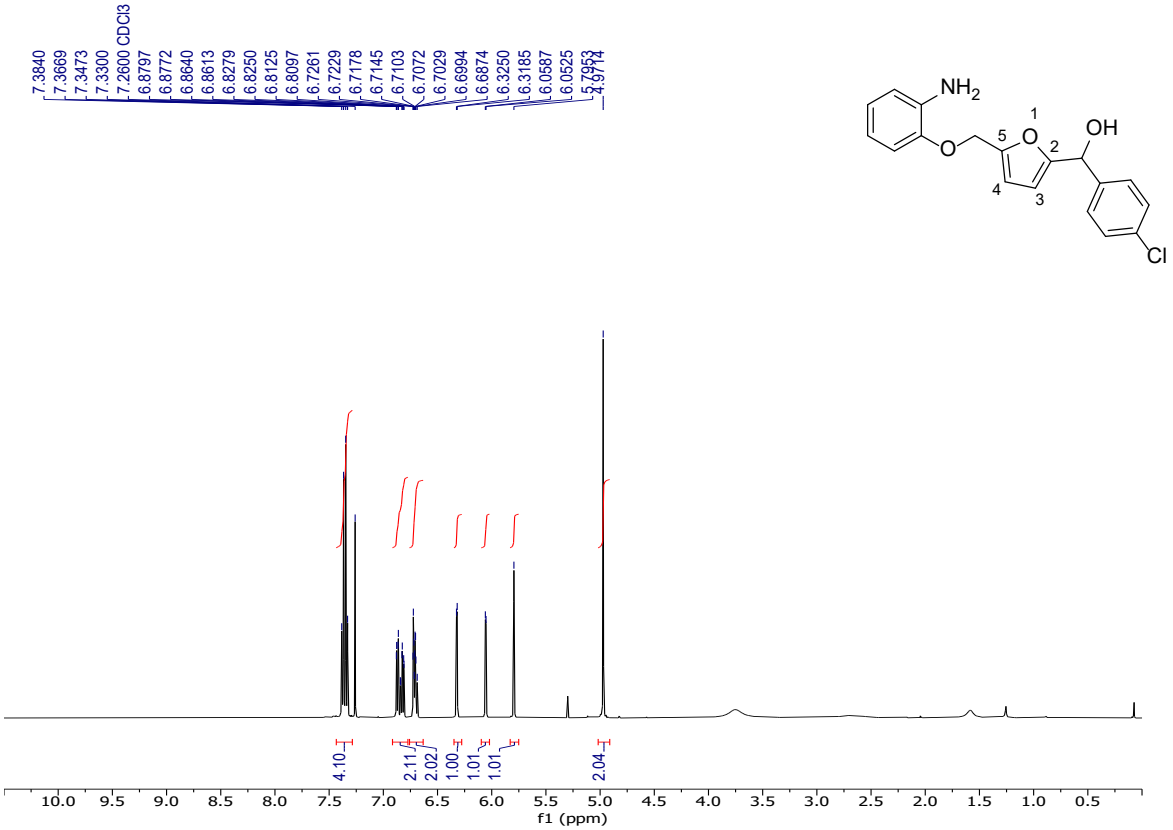
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(3,4-methylenedioxyphenyl)methanol 8e **(400 MHz, $CDCl_3$)**



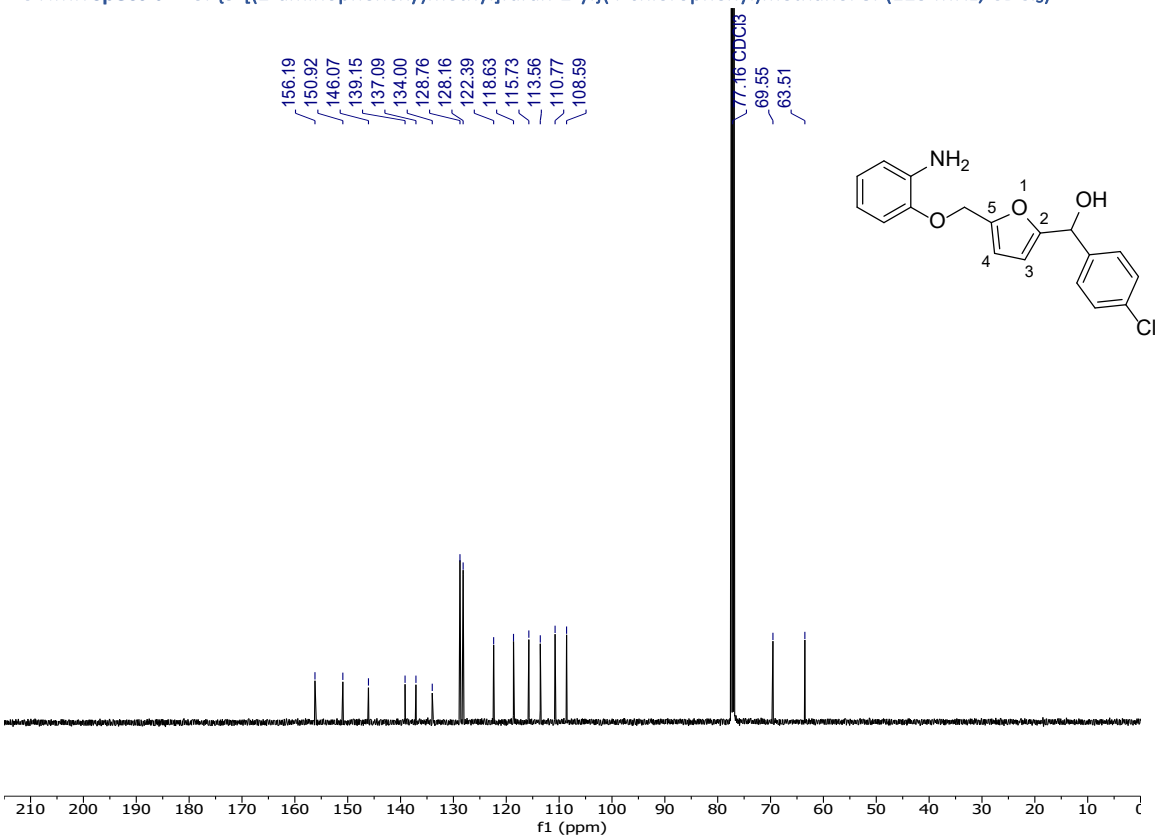
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(3,4-methylenedioxyphenyl)methanol 8e (100 MHz, $CDCl_3$)



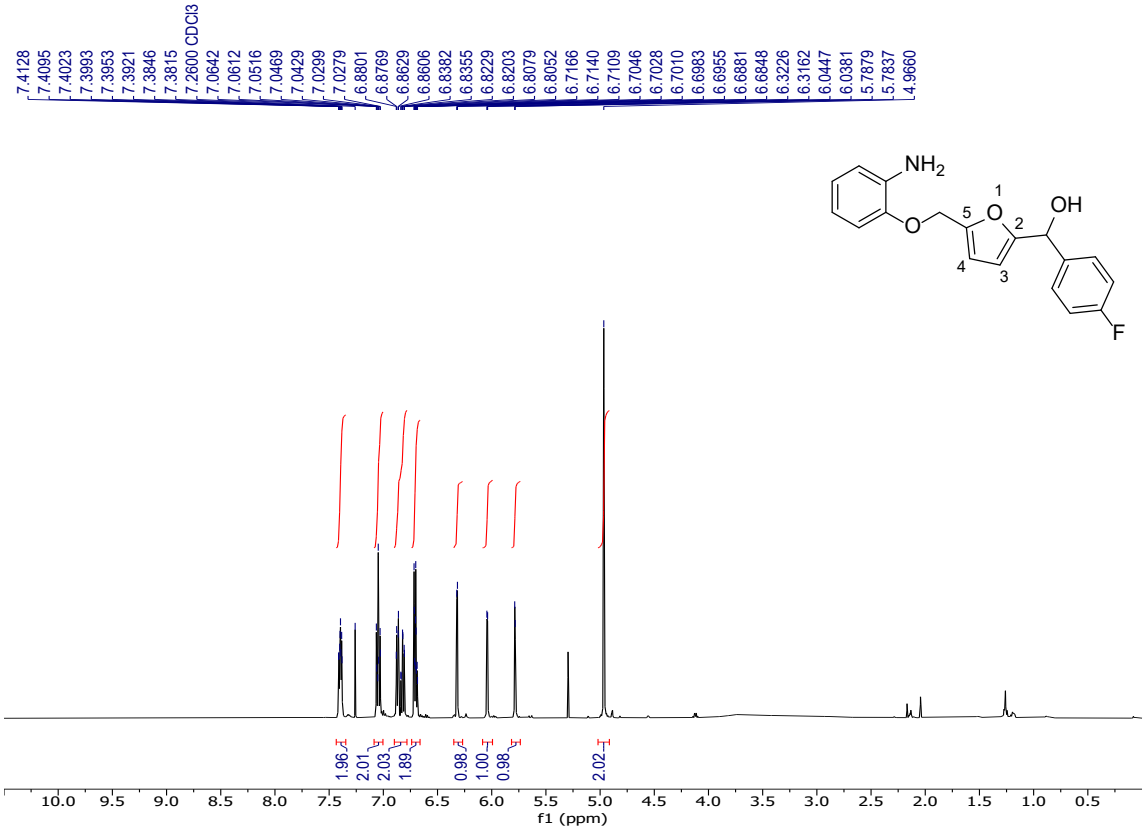
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol 8f **(500 MHz, $CDCl_3$)**



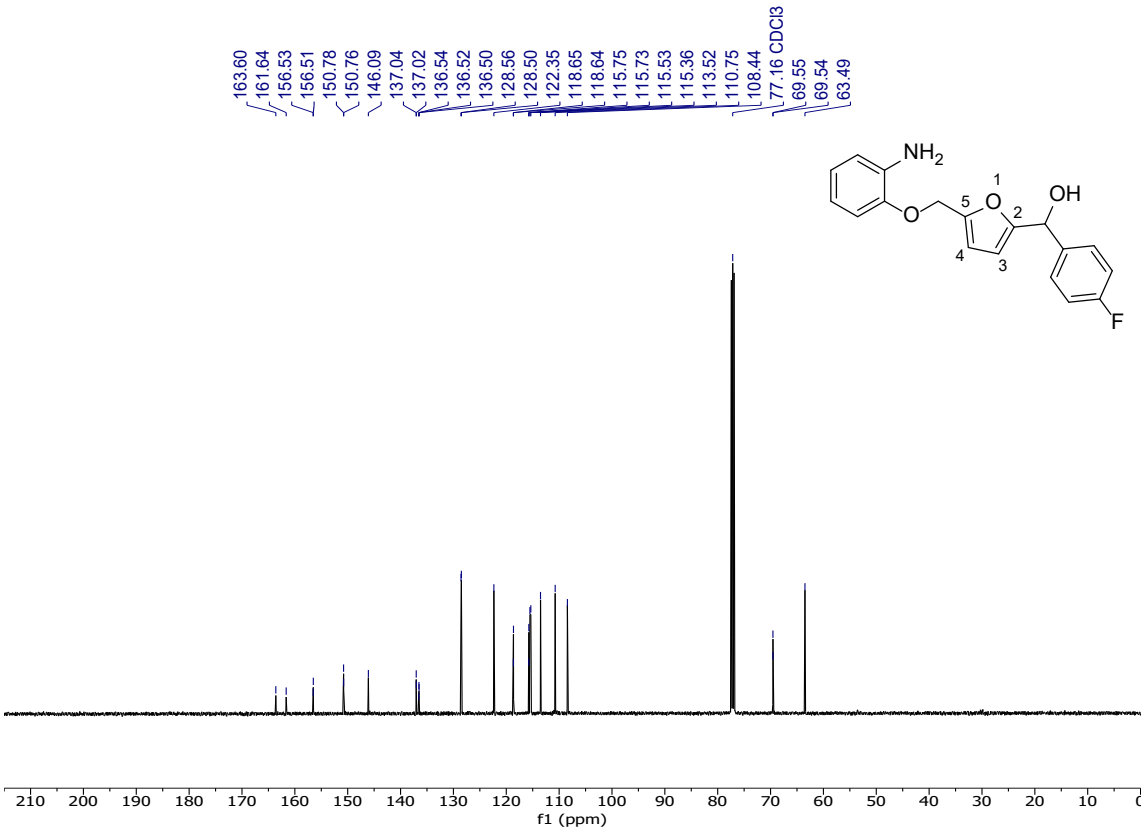
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-chlorophenyl)methanol 8f (125 MHz, $CDCl_3$)



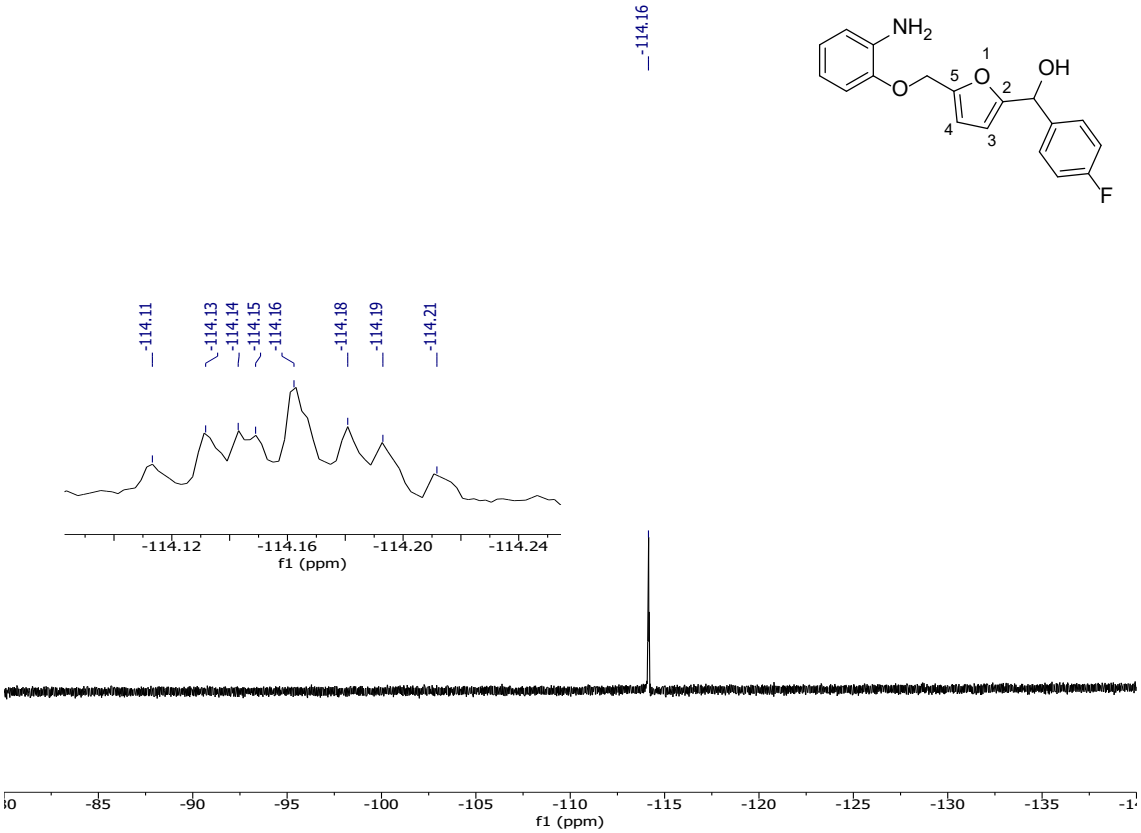
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol 8g **(500 MHz, $CDCl_3$)**



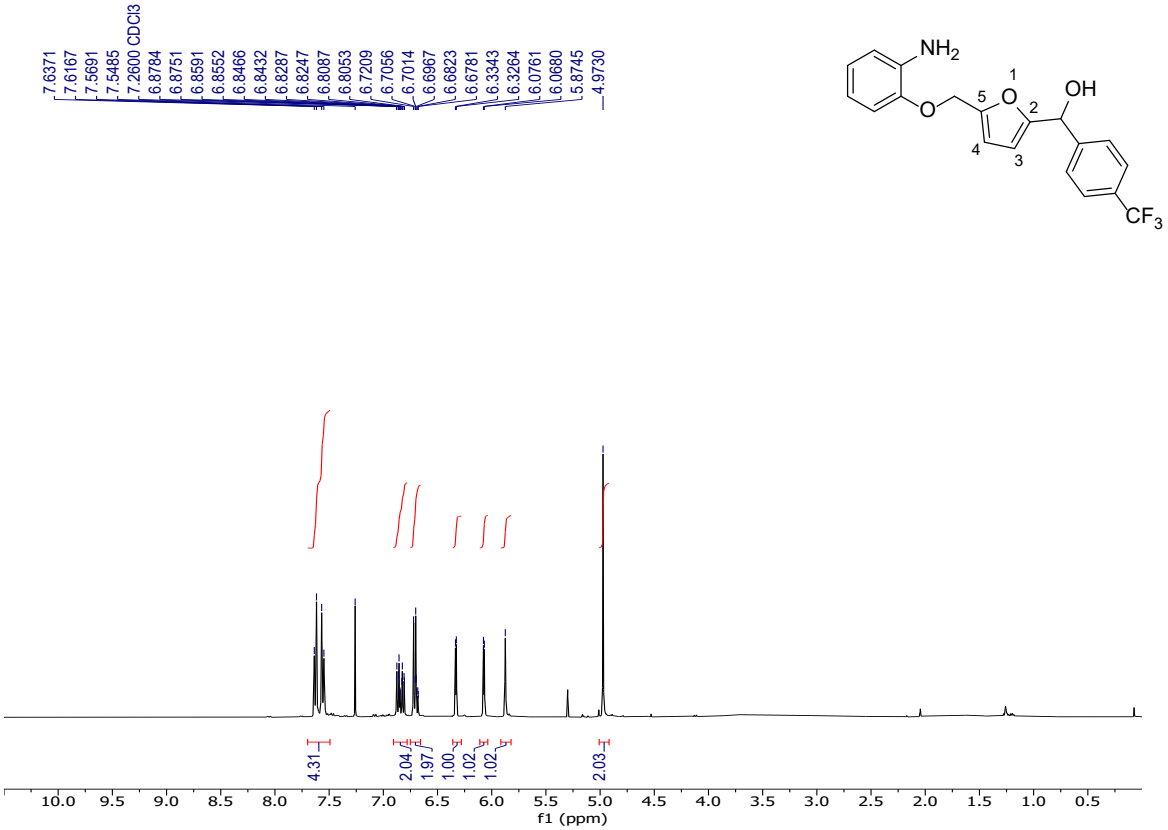
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol 8g (125 MHz, $CDCl_3$)



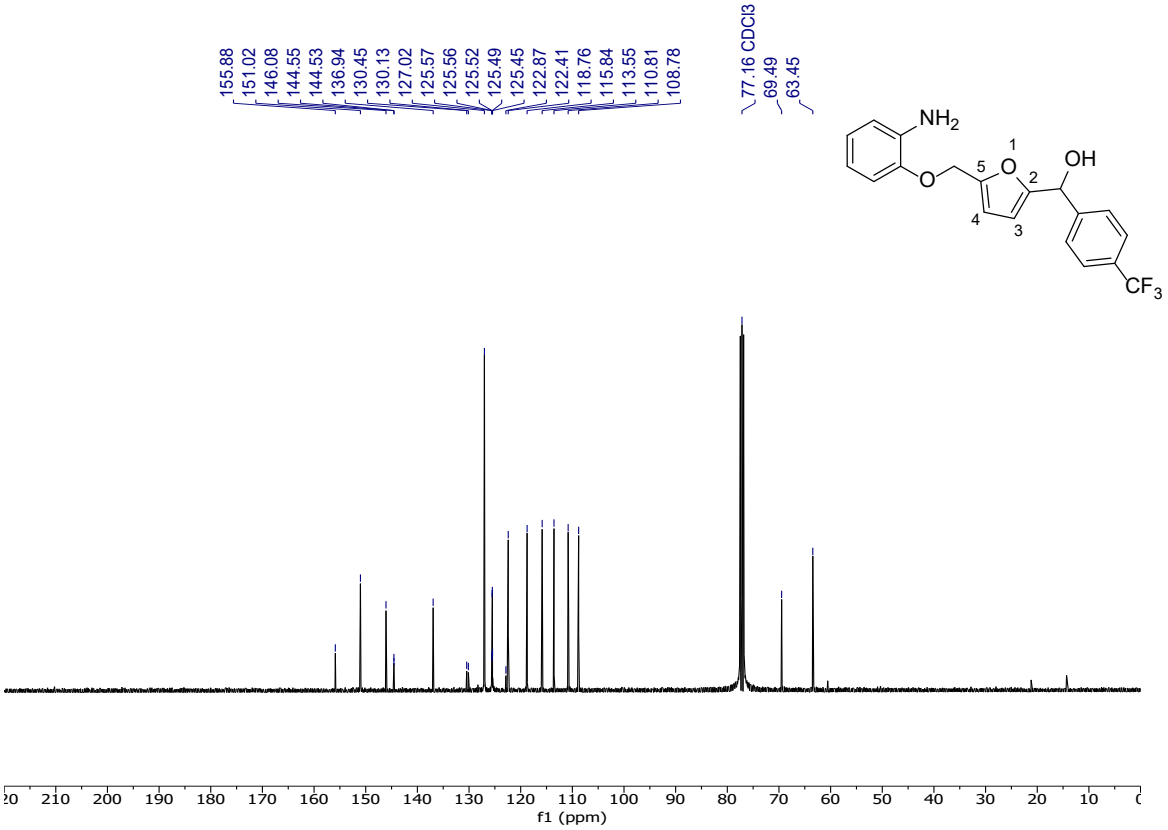
^{19}F NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-fluorophenyl)methanol 8g (282 MHz, $CDCl_3$)



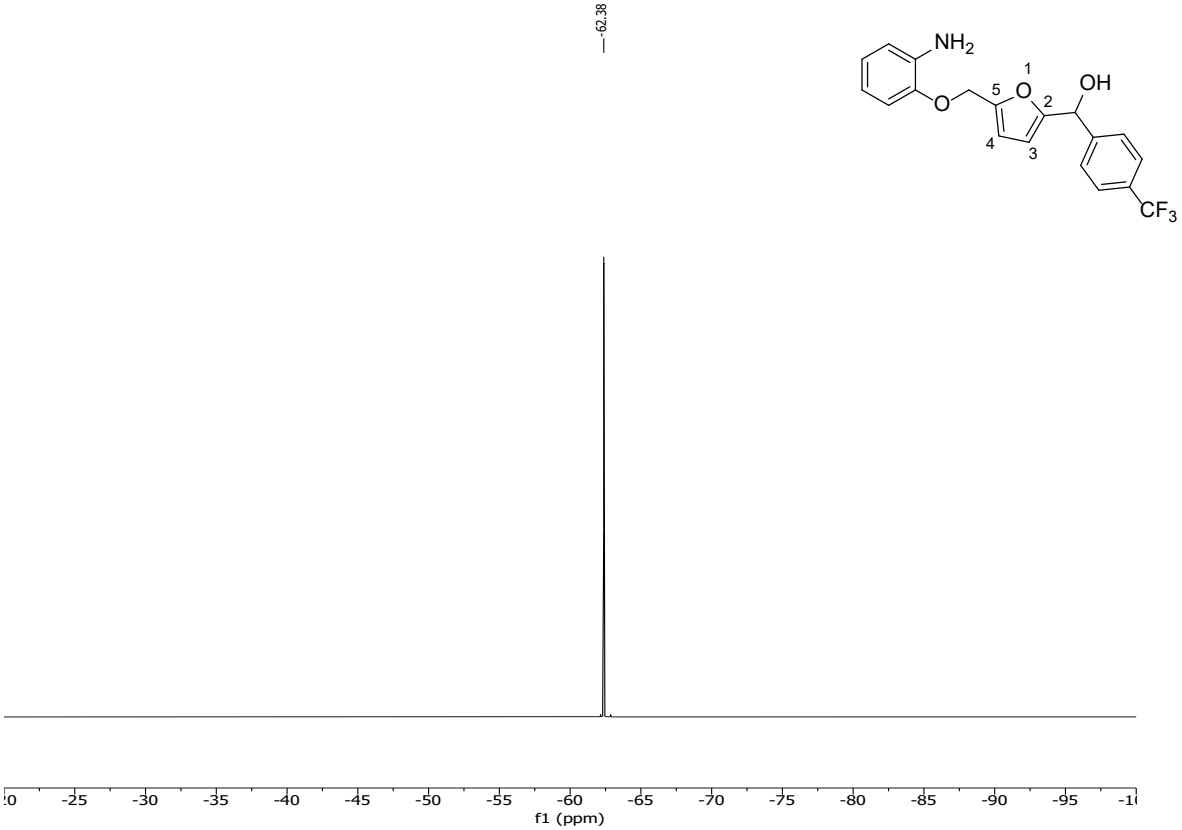
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol 8h (400 MHz, $CDCl_3$)



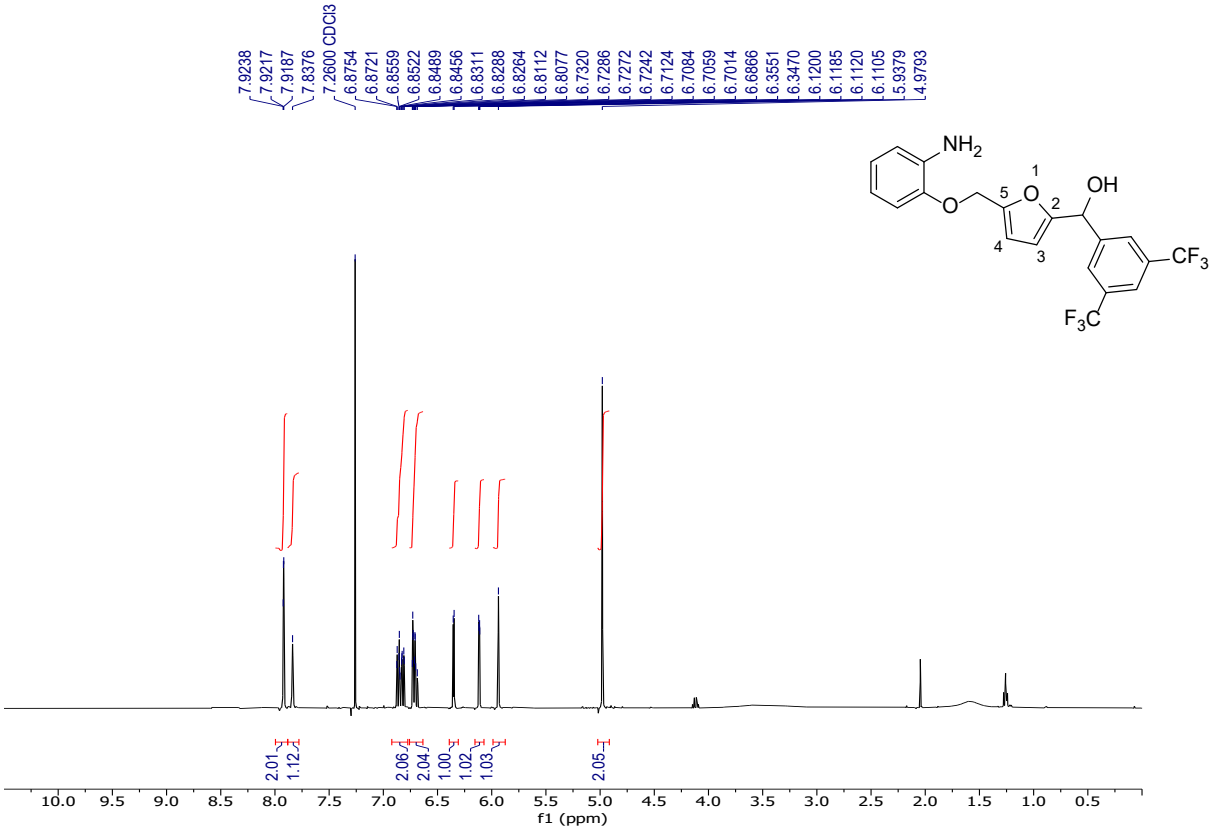
^{13}C NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol 8h (100 MHz, $CDCl_3$)



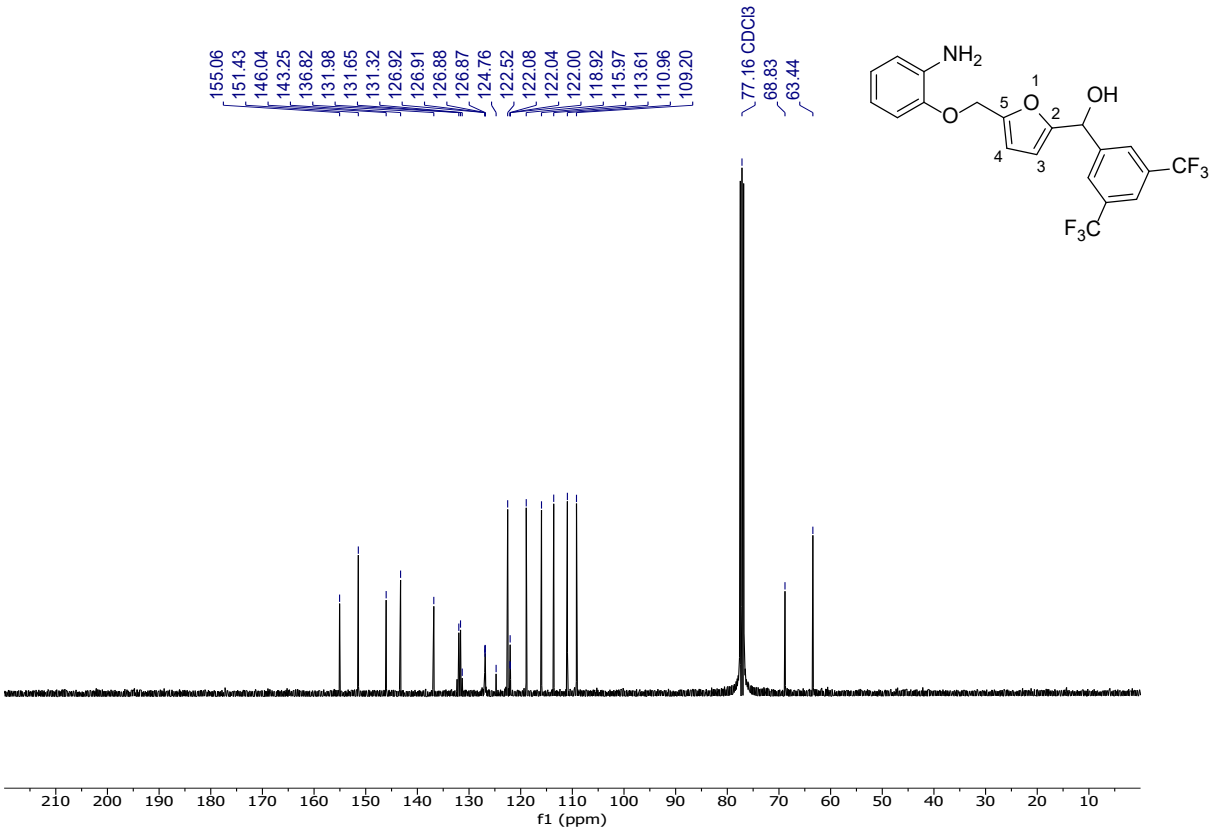
^{19}F NMR spectrum of 5-[(2-aminophenoxy)methyl]furan-2-yl}(4-trifluoromethylphenyl)methanol 8h (282 MHz, $CDCl_3$)



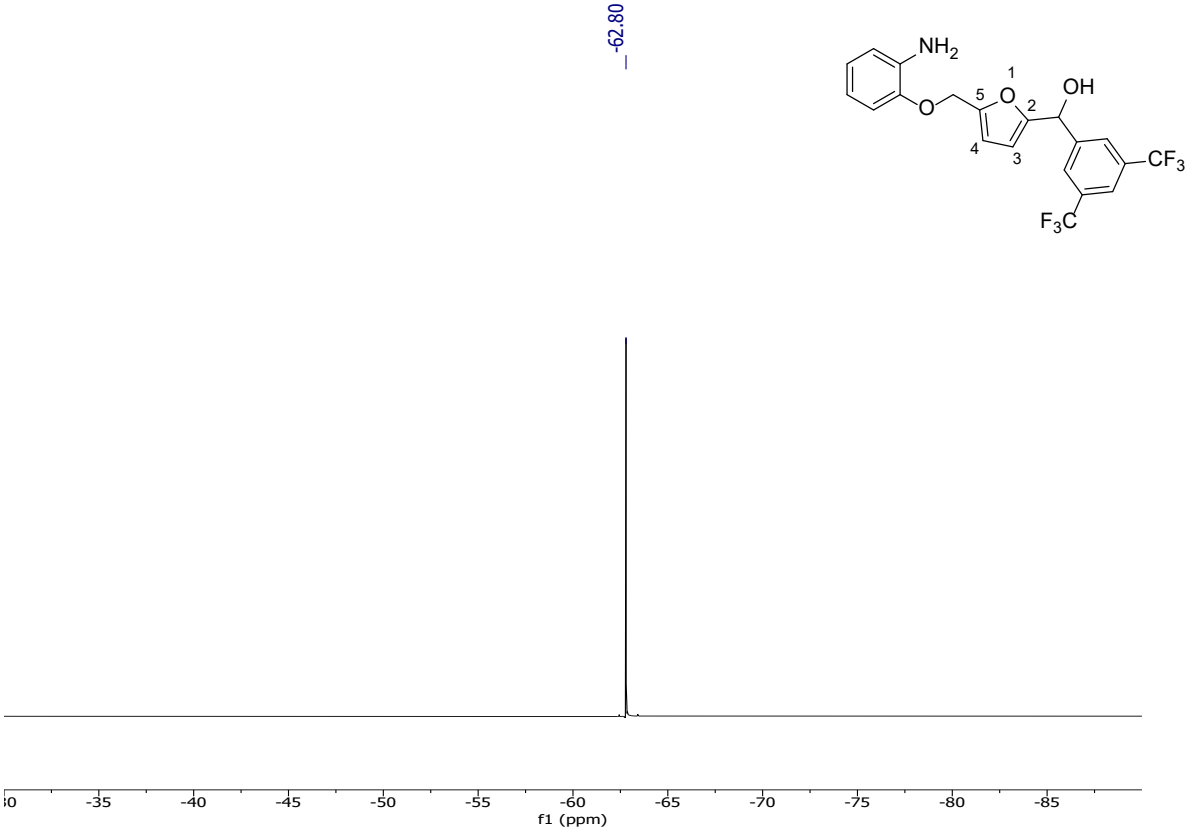
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol 8i **(400 MHz, $CDCl_3$)**



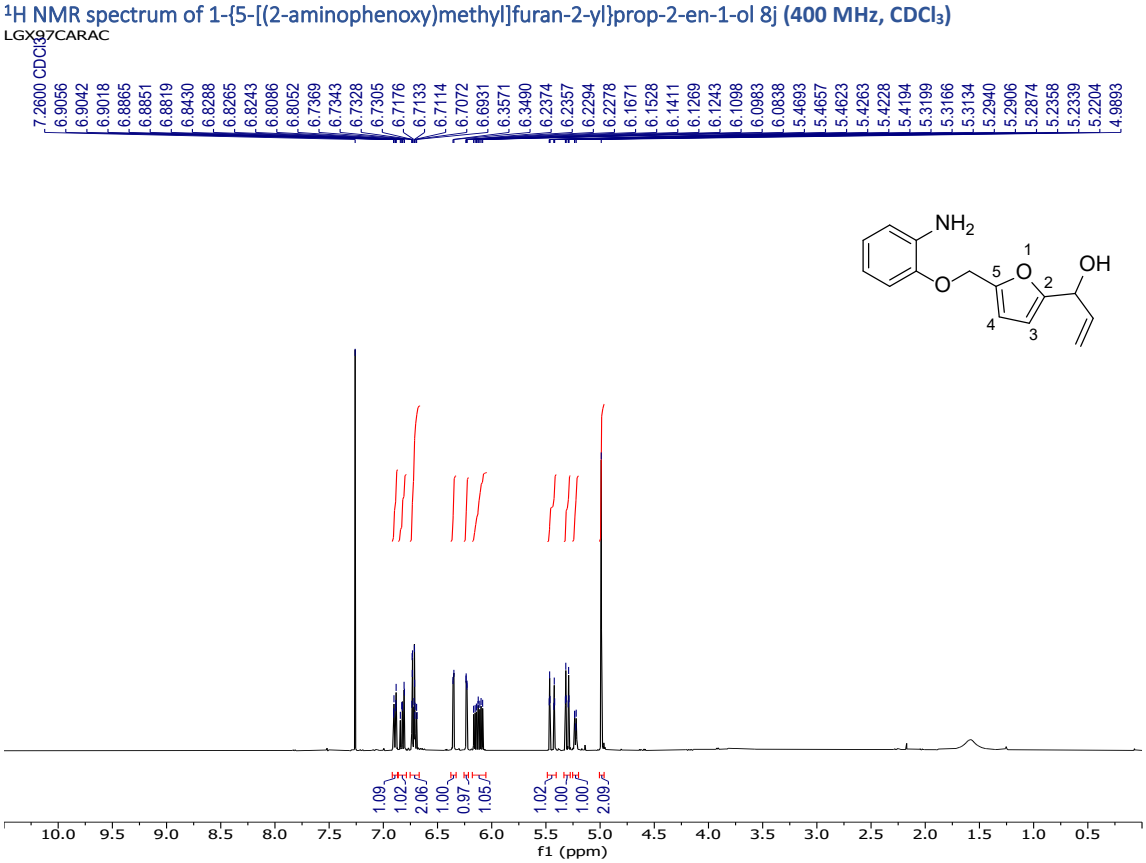
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol 8i (100 MHz, $CDCl_3$)



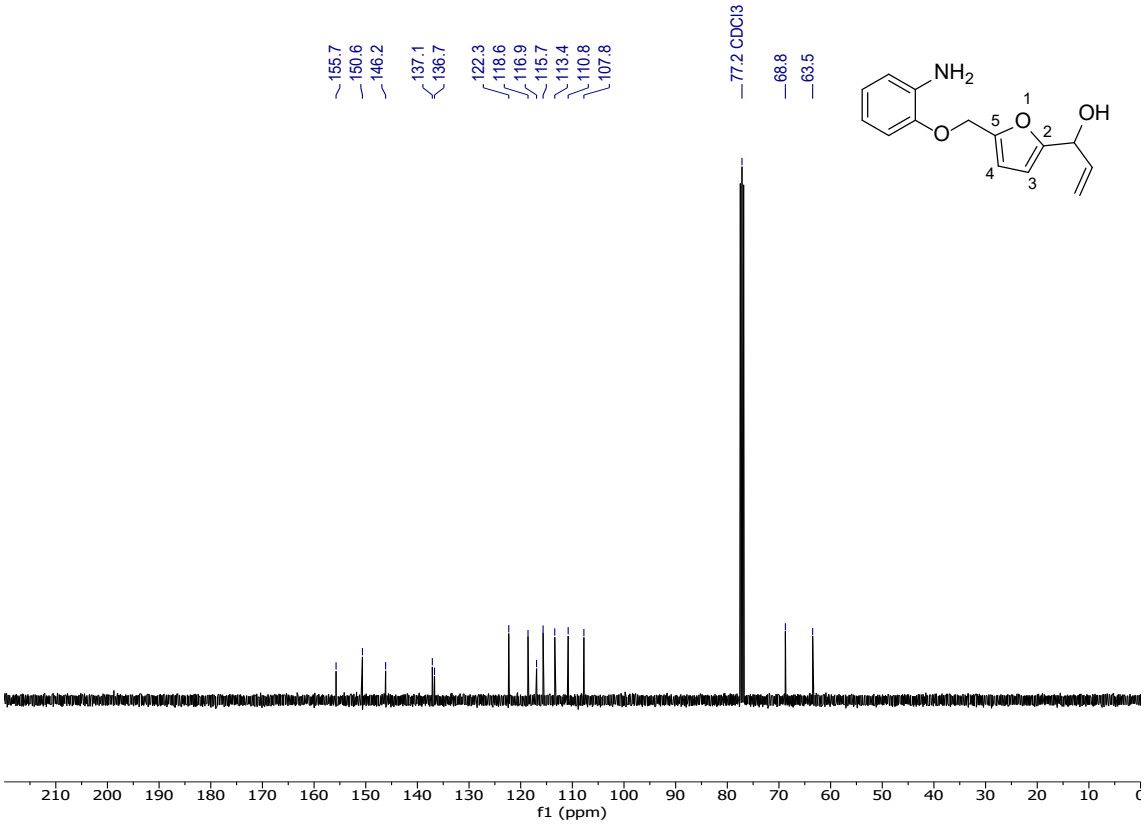
^{19}F NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(3,5-ditrifluoromethylphenyl)methanol 8i (282 MHz, $CDCl_3$)



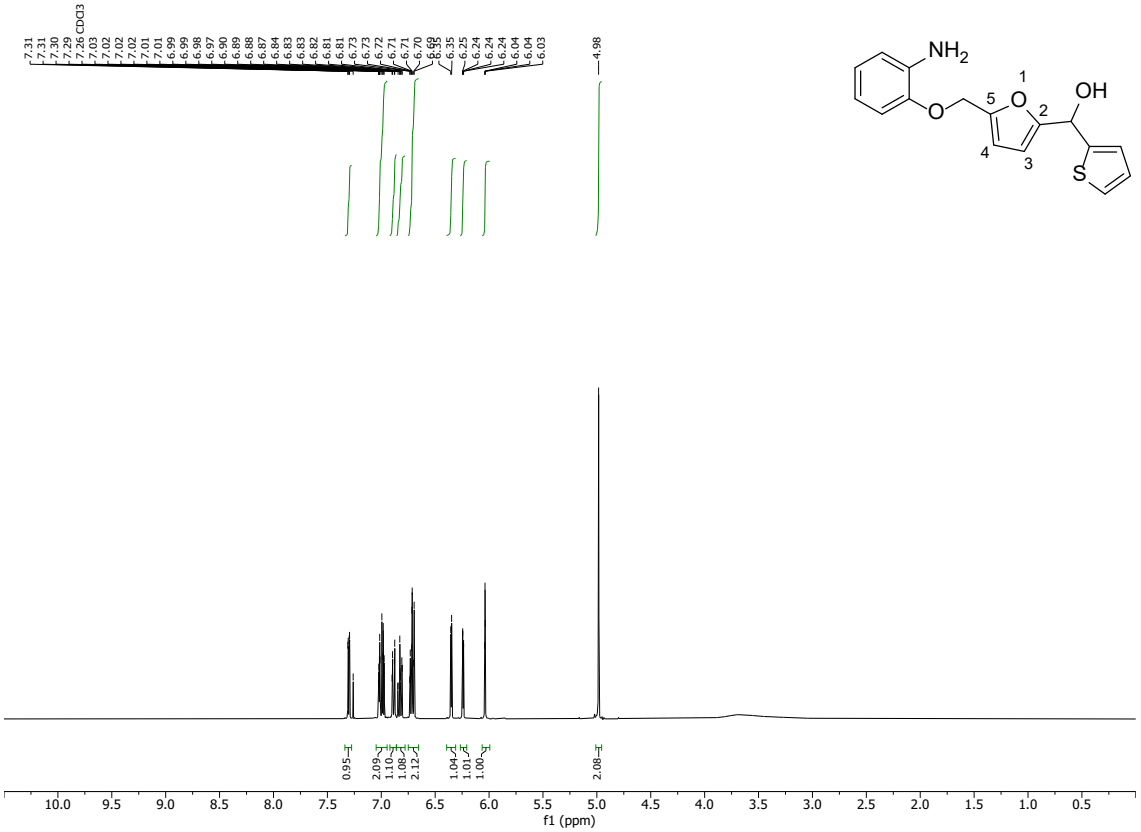
^{1}H NMR spectrum of 1-{5-[(2-aminophenoxy)methyl]furan-2-yl}prop-2-en-1-ol 8j **(400 MHz, $CDCl_3$)**



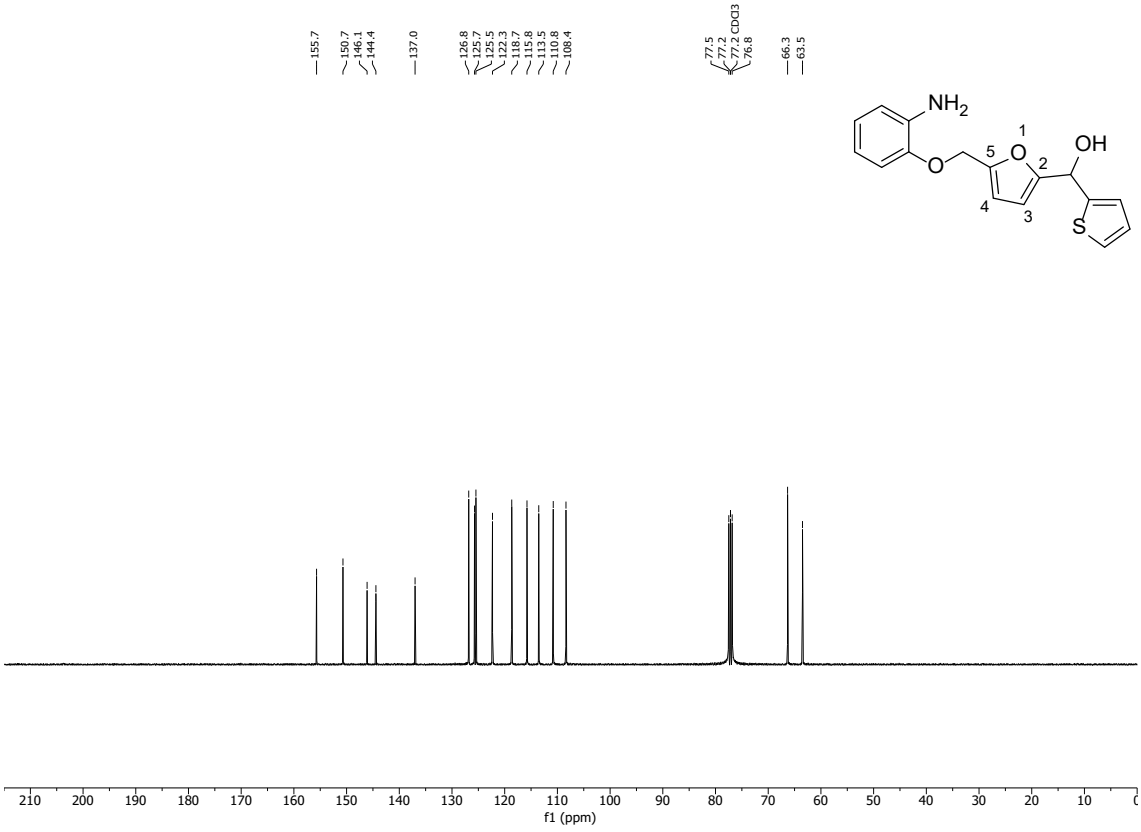
^{13}C NMR **spectrum** of 1-{5-[(2-aminophenoxy)methyl]furan-2-yl}prop-2-en-1-ol 8j (100 MHz, $CDCl_3$)



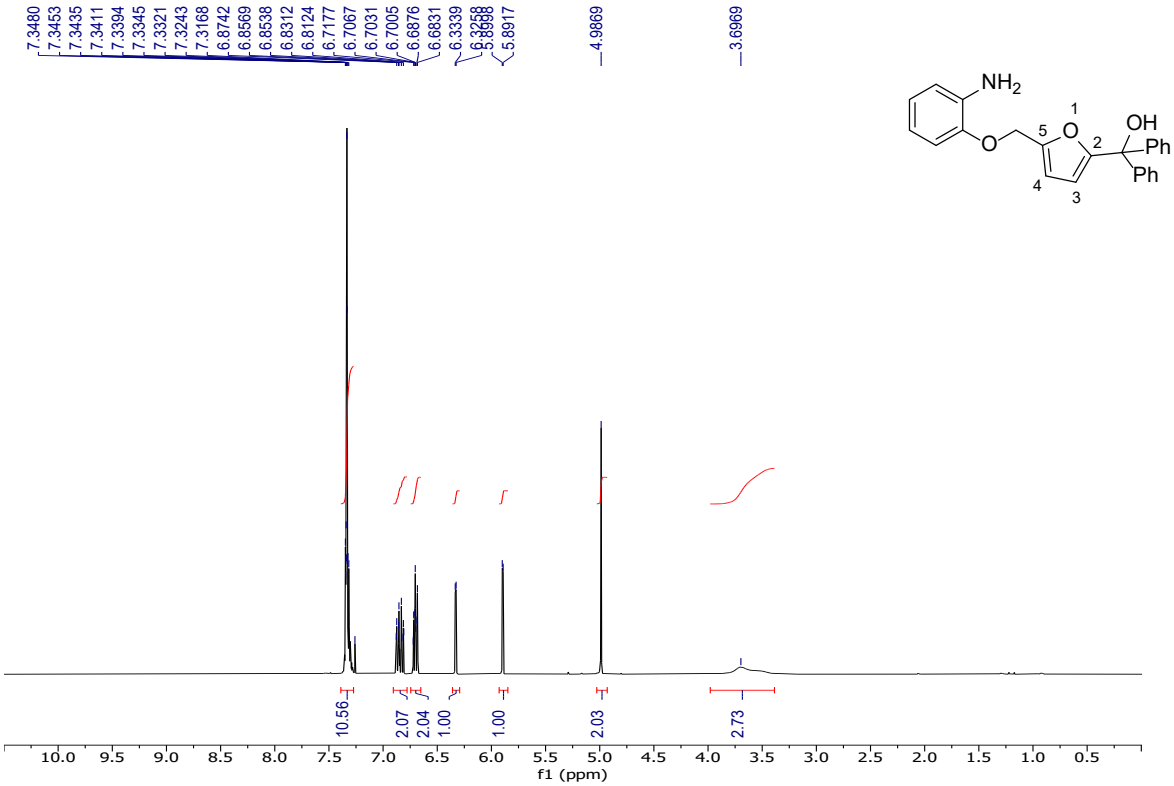
^{1}H NMR spectrum of {{5-[(2-aminophenoxy)methyl]furan-2-yl}(thiophen-2-yl)methanol 8k**(400 MHz, $CDCl_3$)**



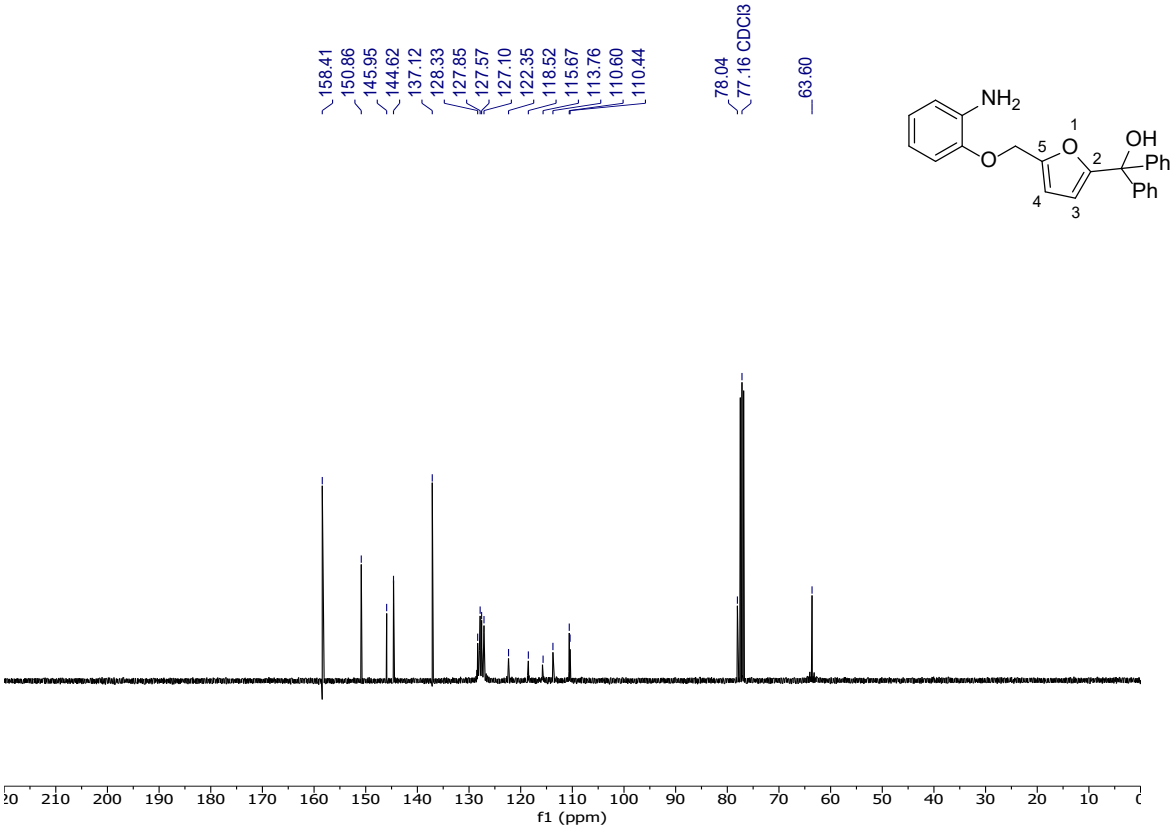
^{13}C NMR **spectrum** of {{5-[(2-aminophenoxy)methyl]furan-2-yl}(thiophen-2-yl)methanol 8k (100 MHz, $CDCl_3$)



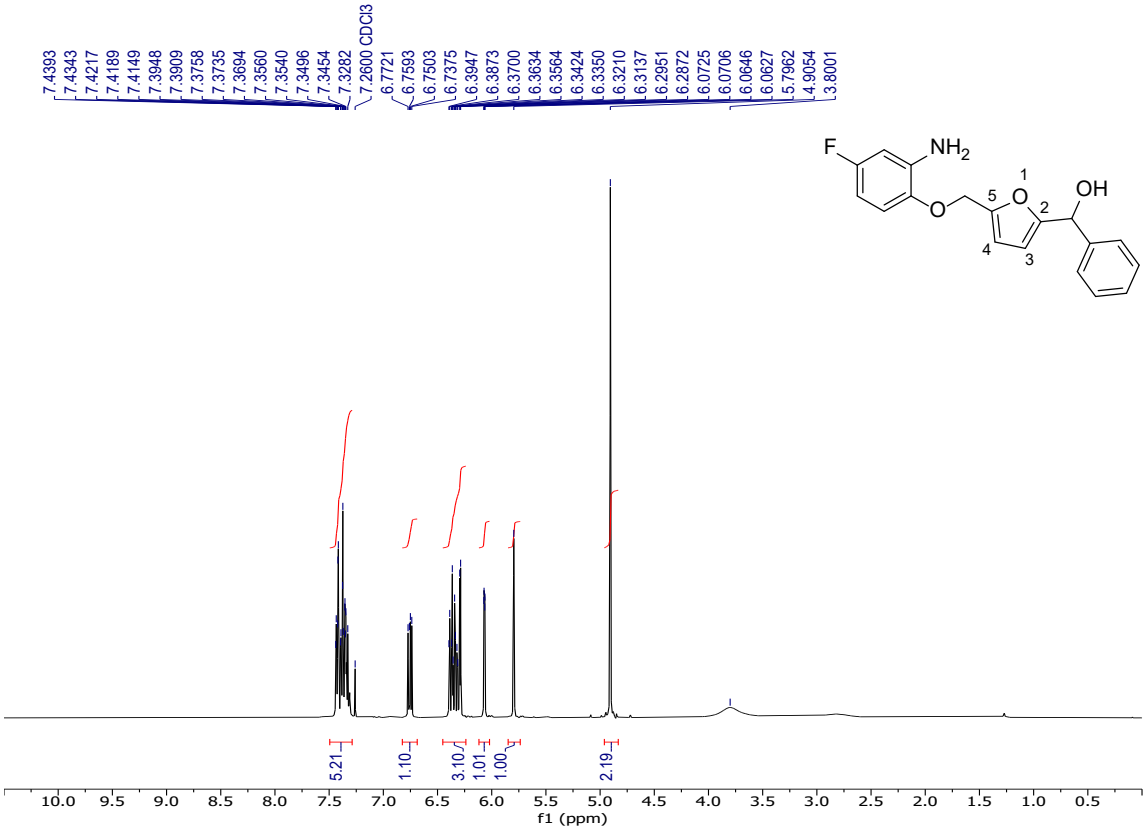
^{1}H NMR spectrum of {5-[(2-aminophenoxy)methyl]furan-2-yl}(diphenyl)methanol 8l **(400 MHz, $CDCl_3$)**



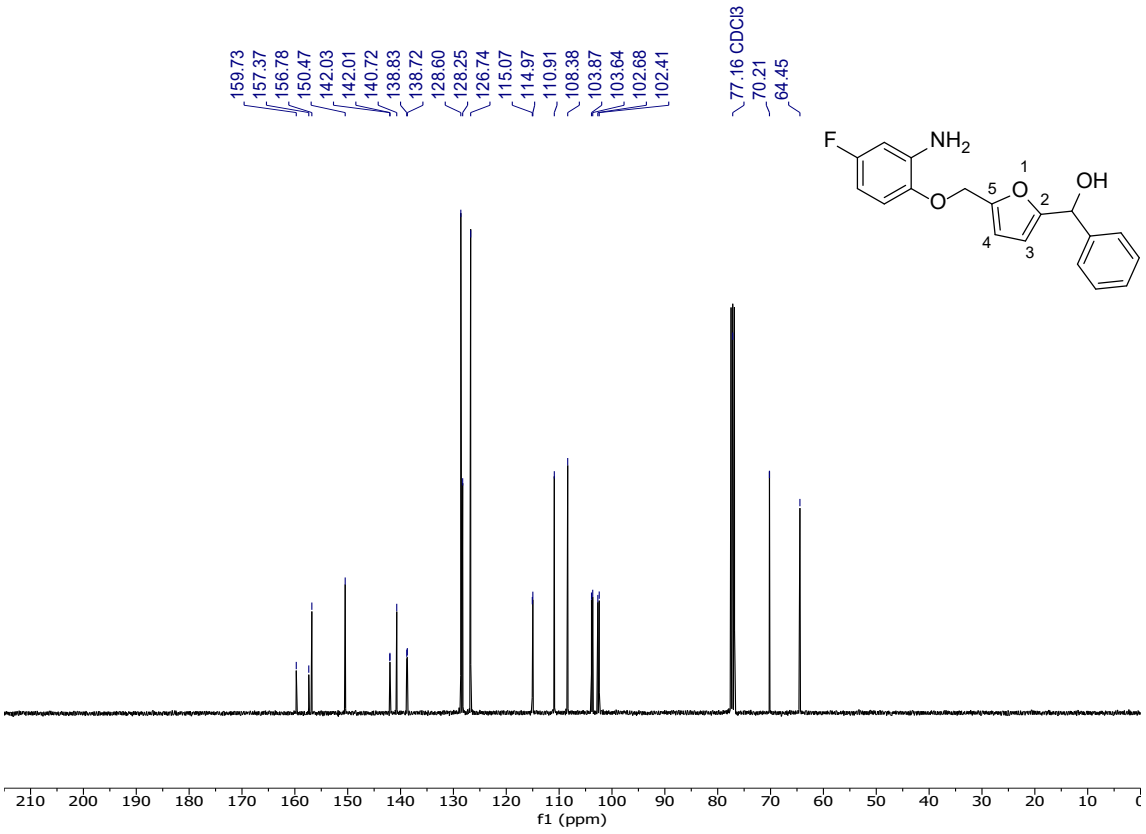
^{13}C NMR **spectrum** of {5-[(2-aminophenoxy)methyl]furan-2-yl}(diphenyl)methanol 8l (100 MHz, $CDCl_3$)



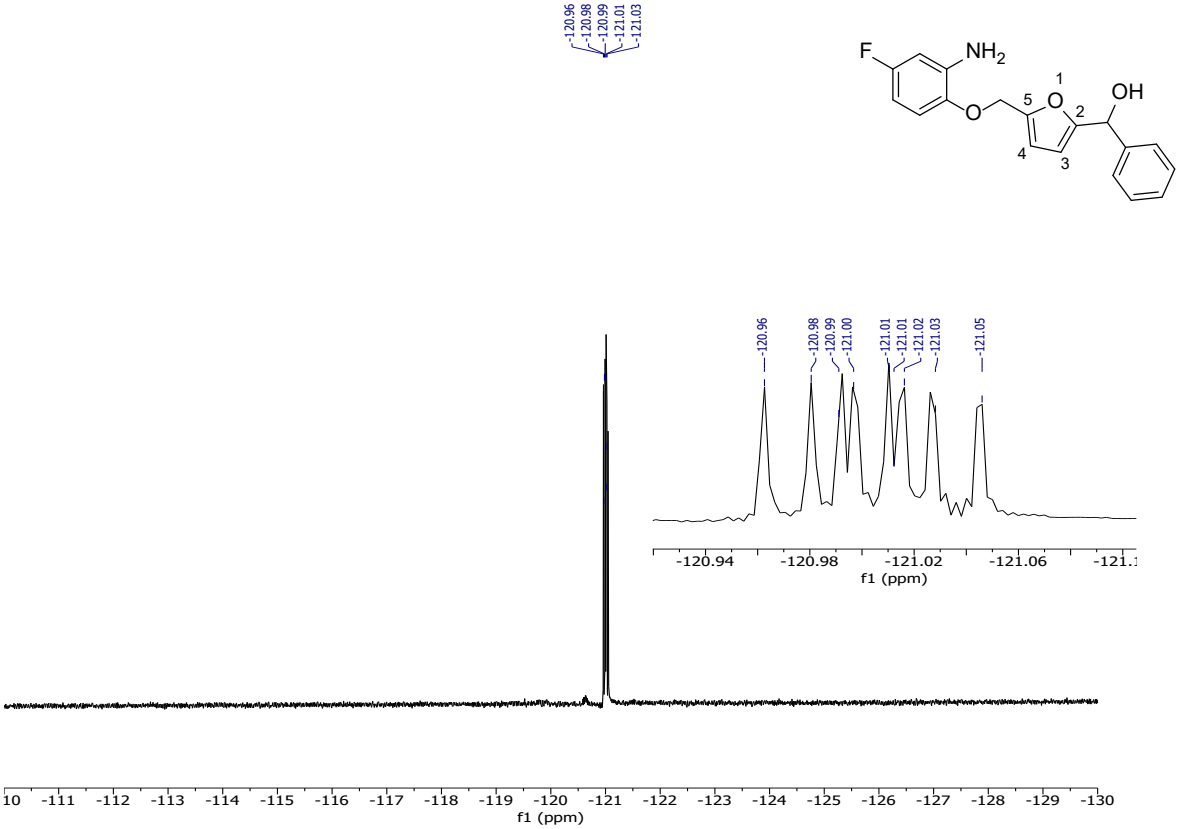
^{1}H NMR spectrum of {5-[(2-amino-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8m **(400 MHz, $CDCl_3$)**



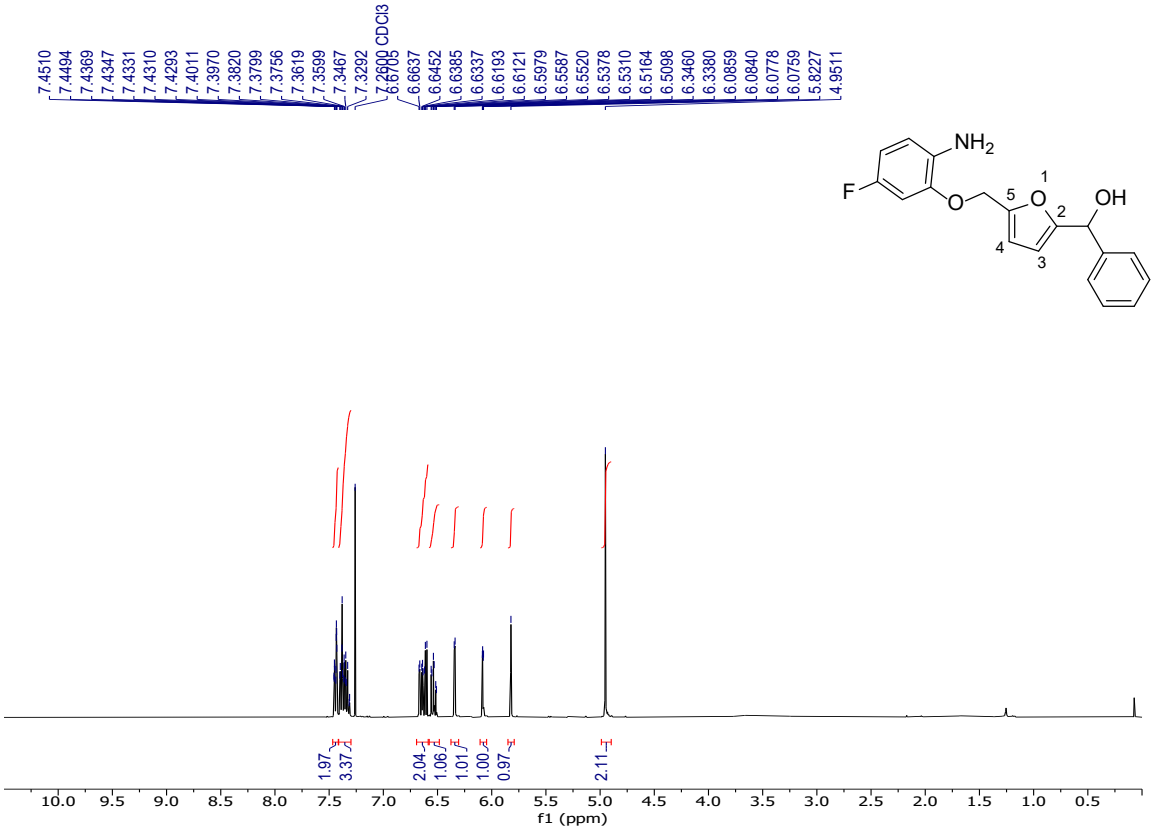
^{13}C NMR **spectrum** of {5-[(2-amino-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8m (100 MHz, $CDCl_3$)



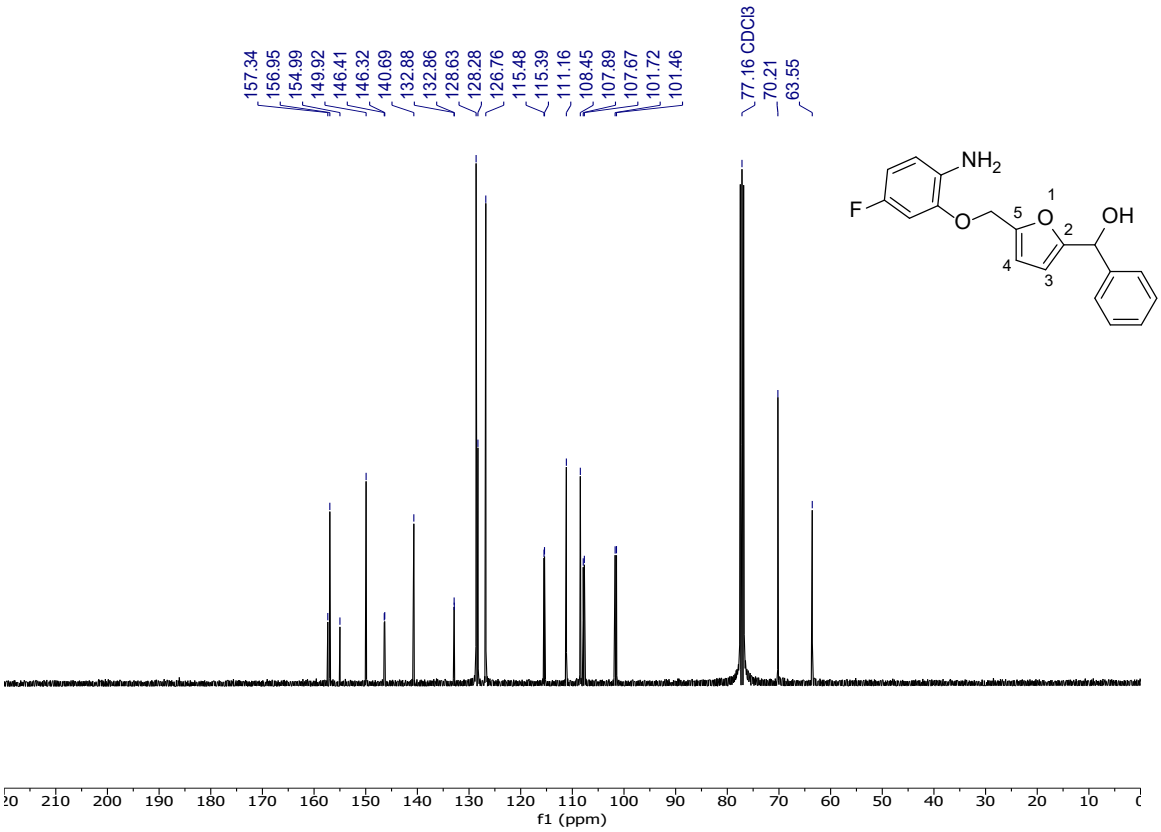
^{19}F NMR spectrum of {5-[(2-amino-4-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8m (282 MHz, $CDCl_3$)



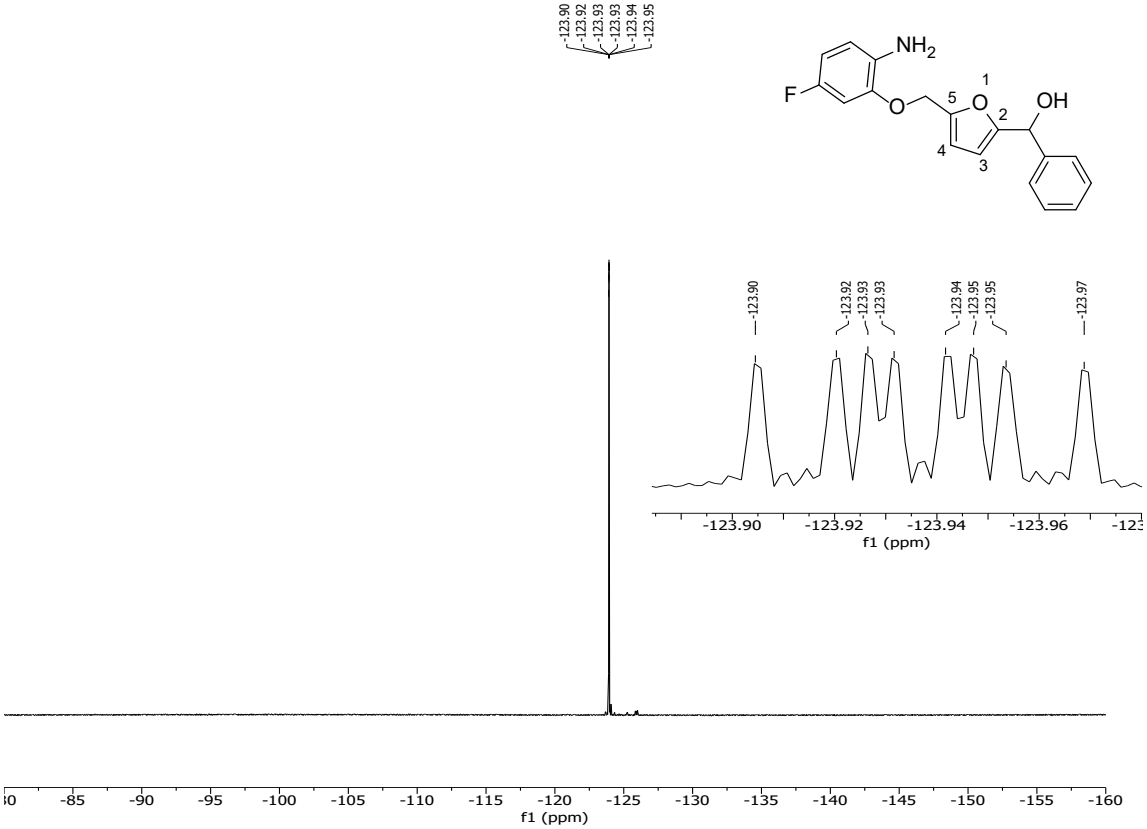
^{1}H NMR spectrum of {5-[(2-amino-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8n **(400 MHz, $CDCl_3$)**



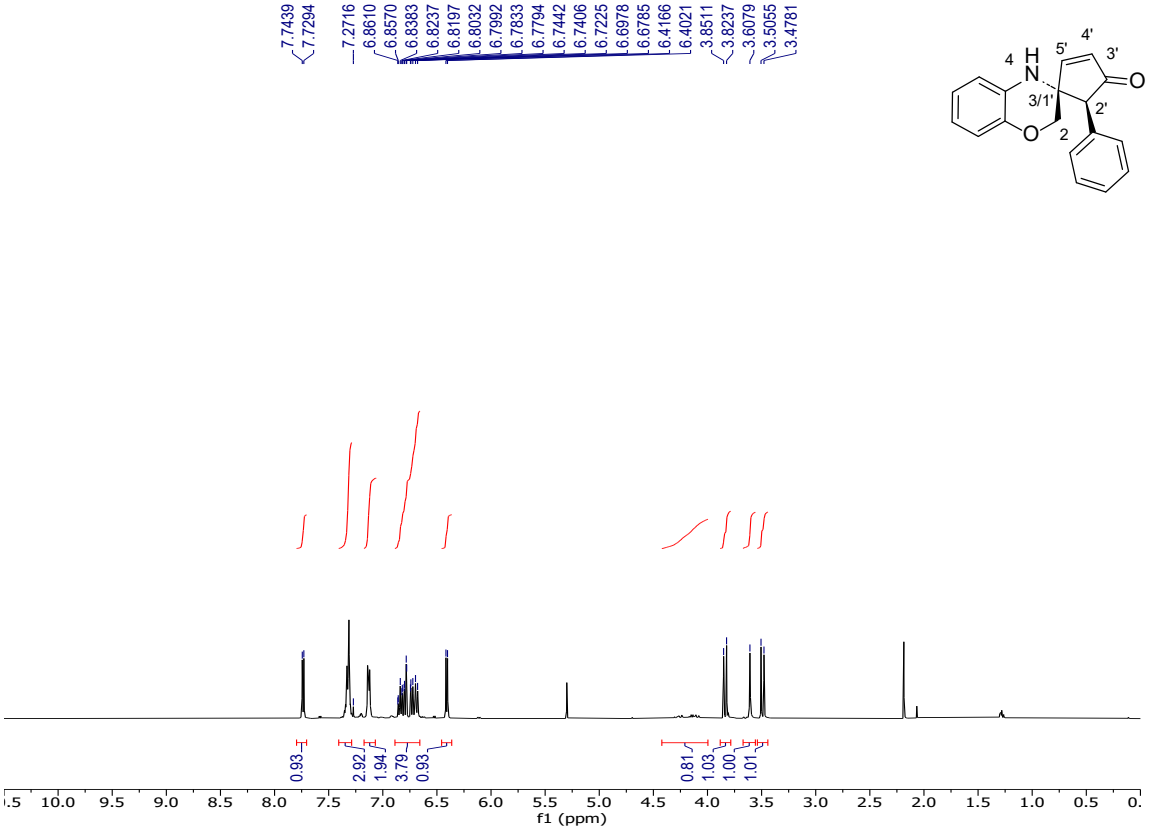
^{13}C NMR **spectrum** of {5-[(2-amino-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8n (100 MHz, $CDCl_3$)



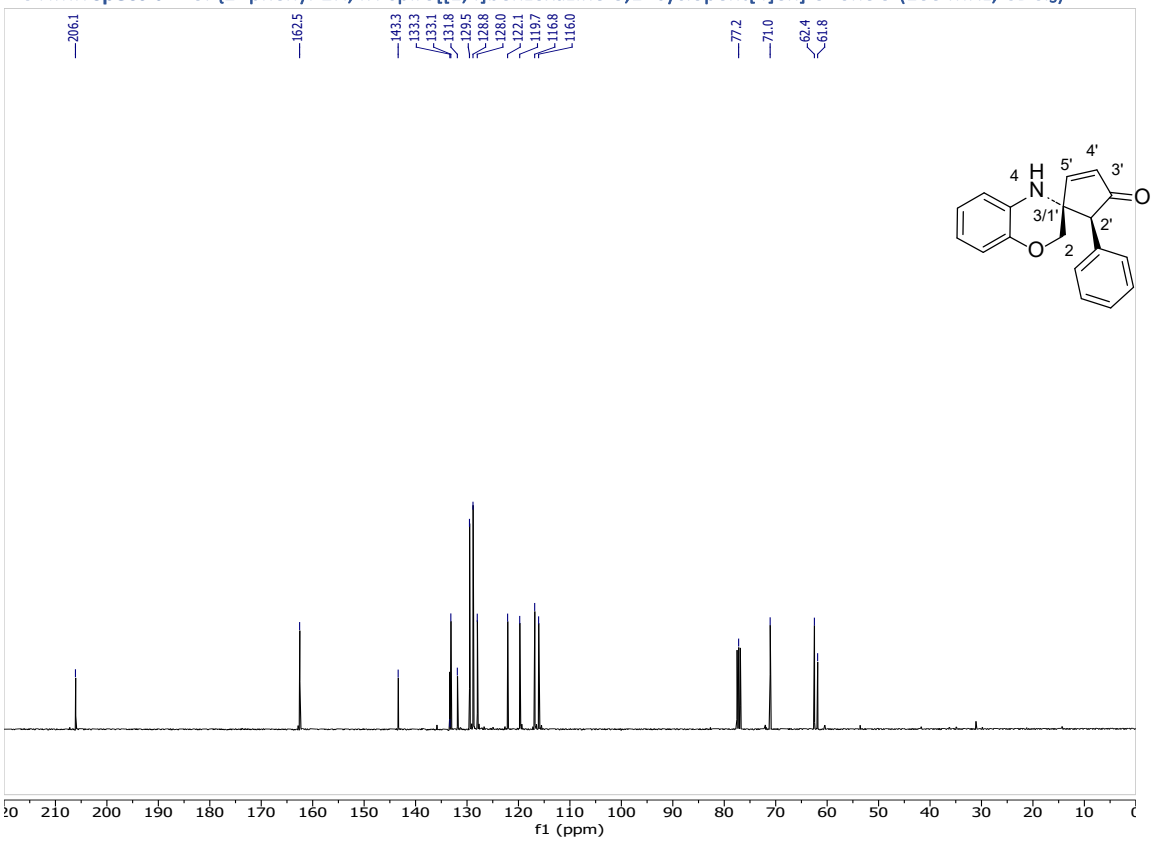
^{19}F NMR **spectrum** of {5-[(2-amino-5-fluoro-phenoxy)methyl]furan-2-yl}(phenyl)methanol 8n (282 MHz, $CDCl_3$)



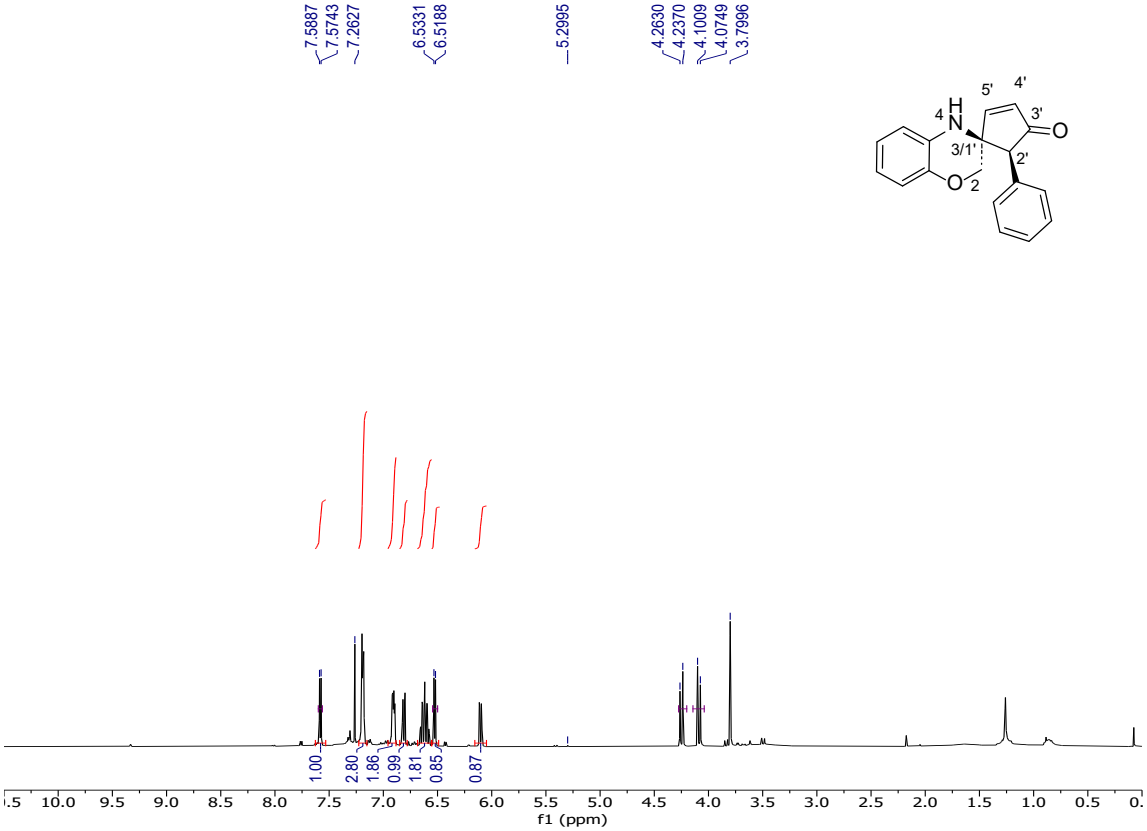
^{1}H NMR spectrum of {2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9 **(400 MHz, $CDCl_3$)**



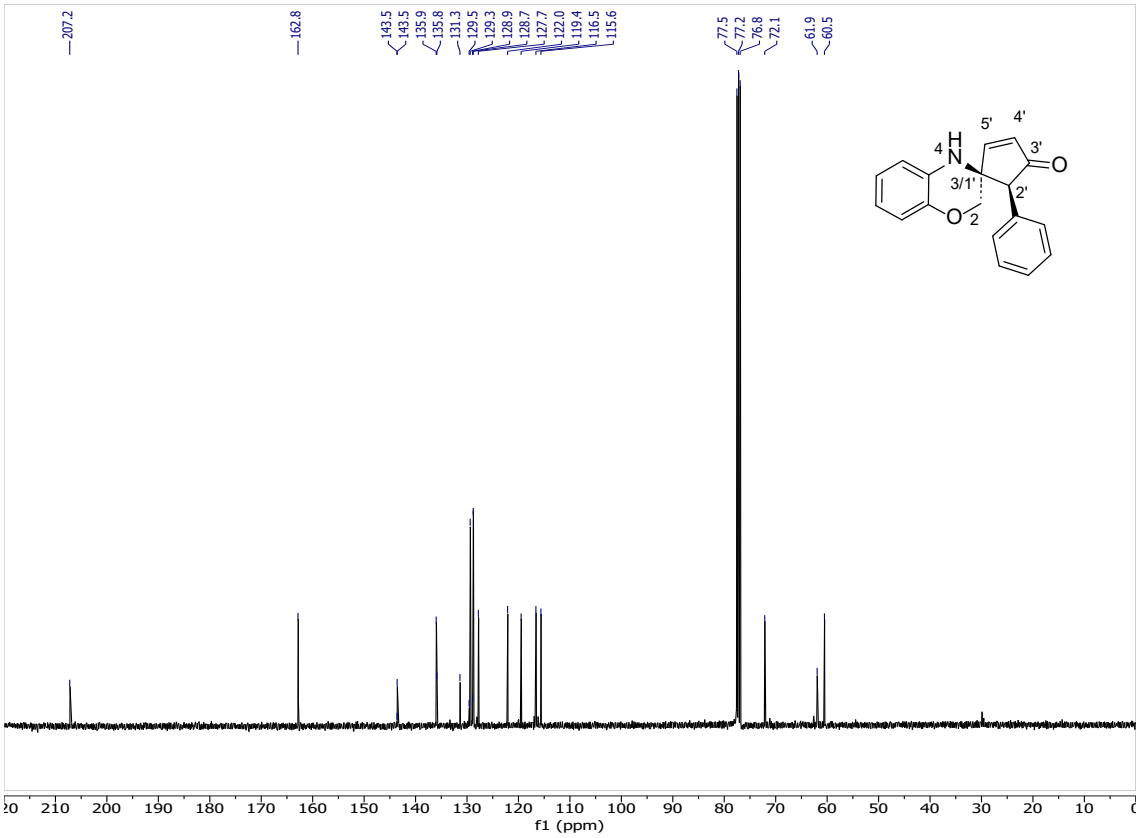
^{13}C NMR **spectrum** of {2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9 (100 MHz, $CDCl_3$)



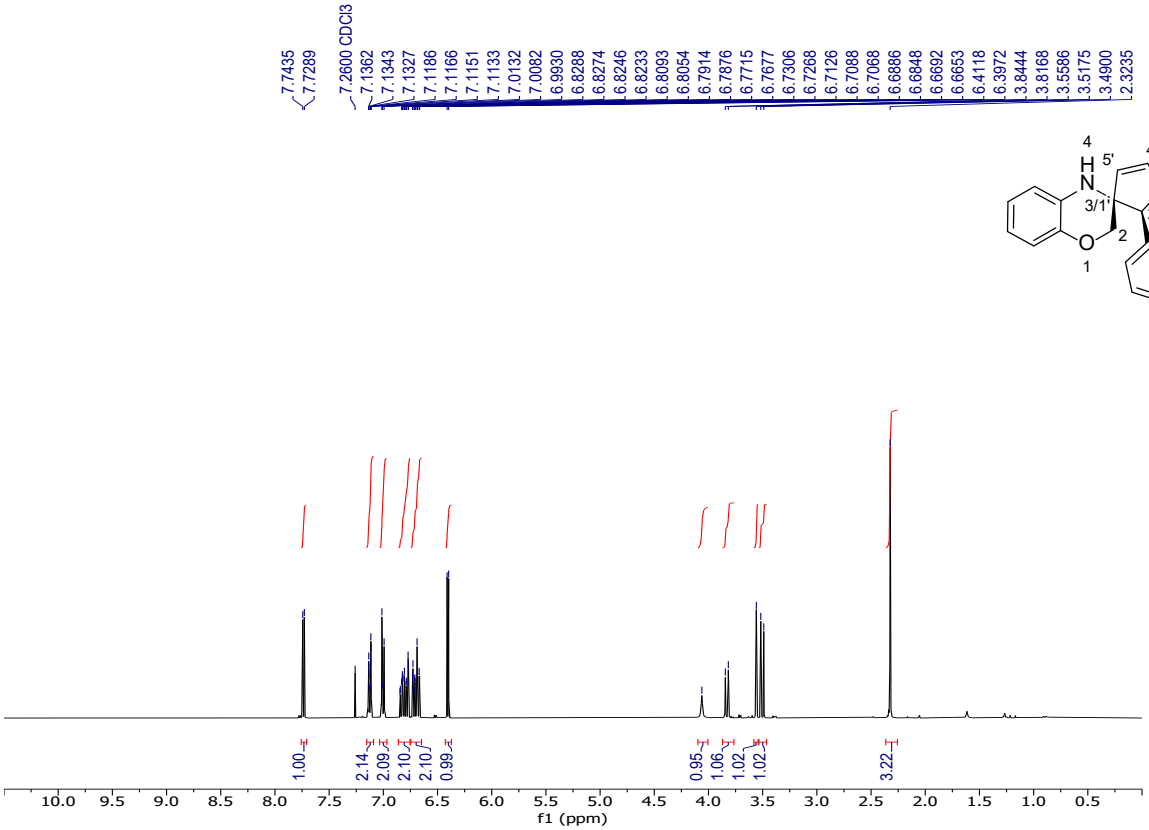
^{1}H NMR spectrum of {2'-phenyl-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9' **(400 MHz, $CDCl_3$)**



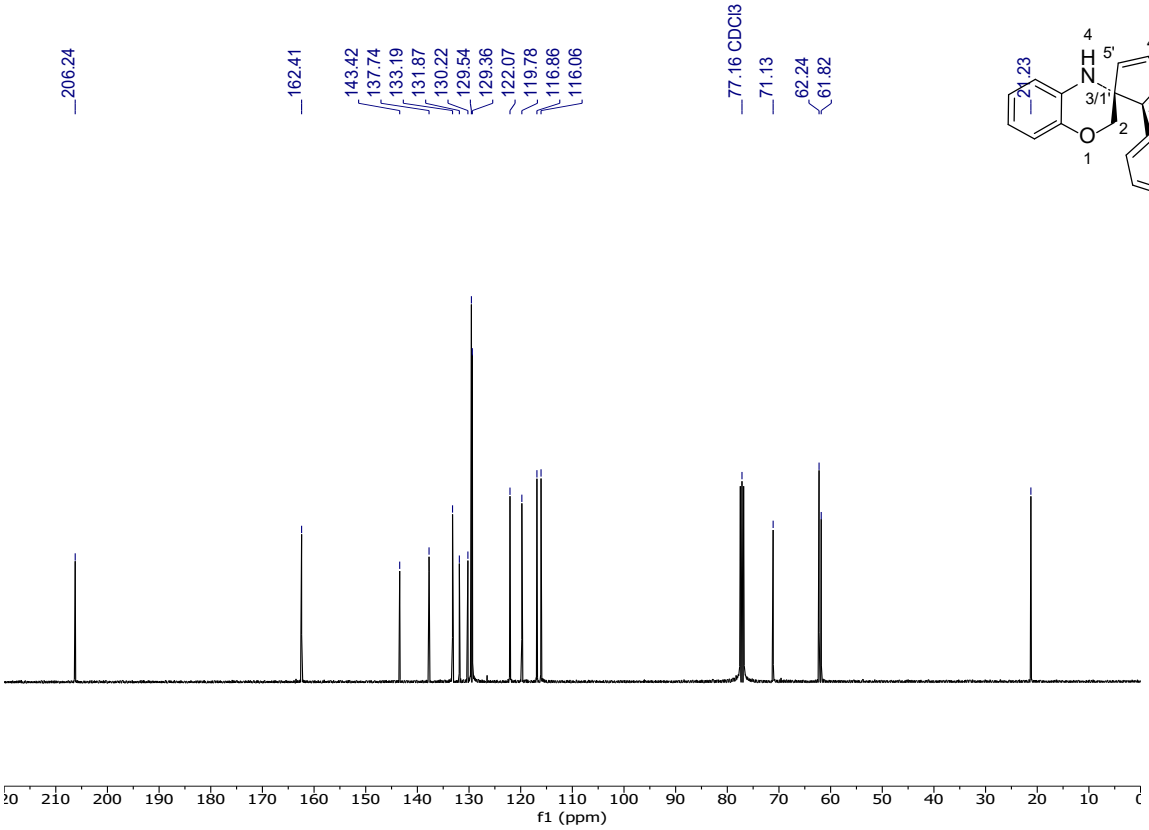
^{13}C NMR **spectrum** of {2'-phenyl-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9' (100 MHz, $CDCl_3$)



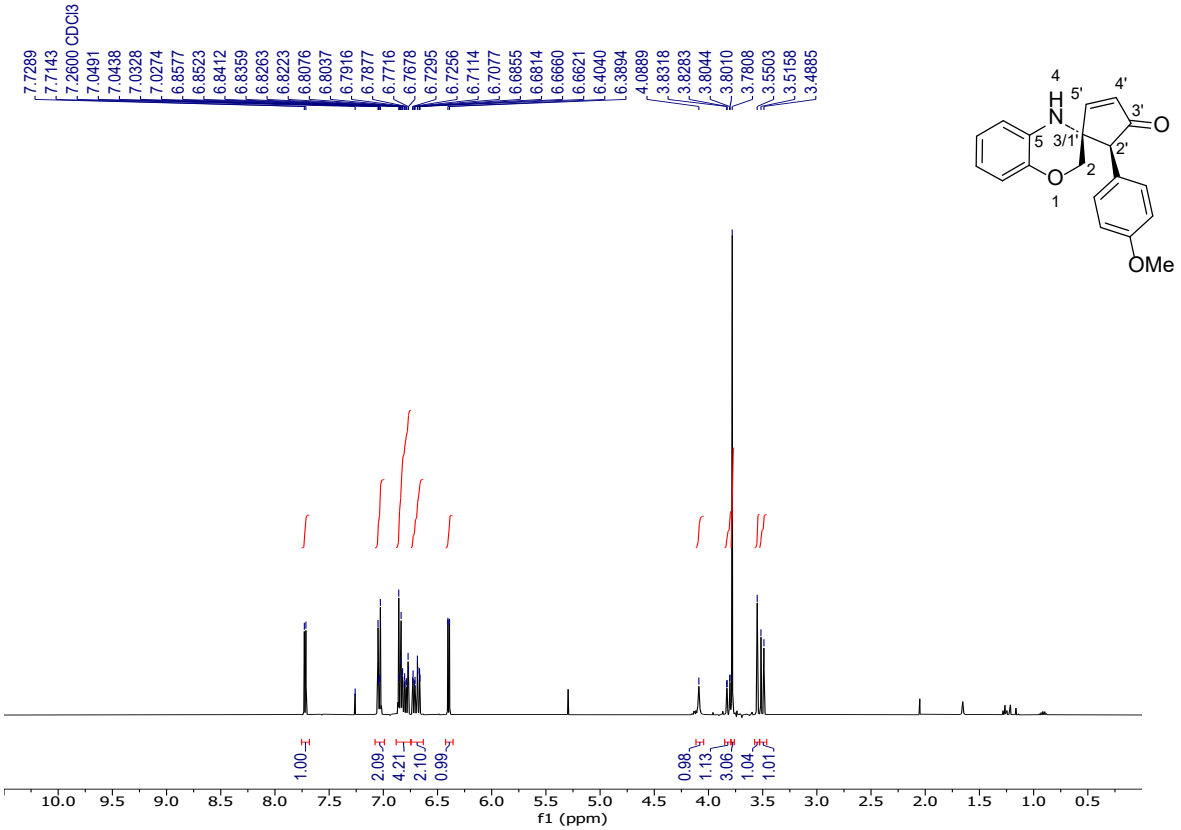
^{1}H NMR spectrum of 2'-(4-methylphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9a **(400 MHz, $CDCl_3$)**



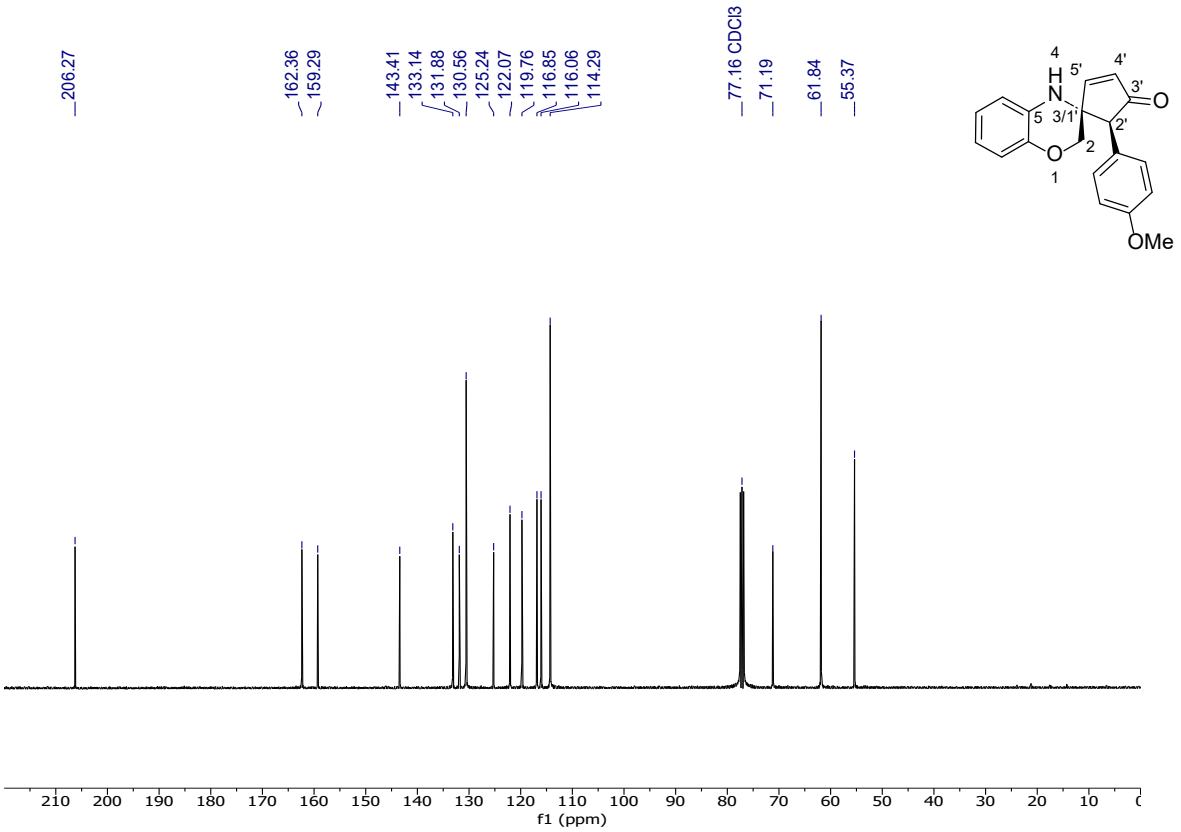
^{13}C NMR **spectrum** of 2'-(4-methylphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9a (100 MHz, $CDCl_3$)



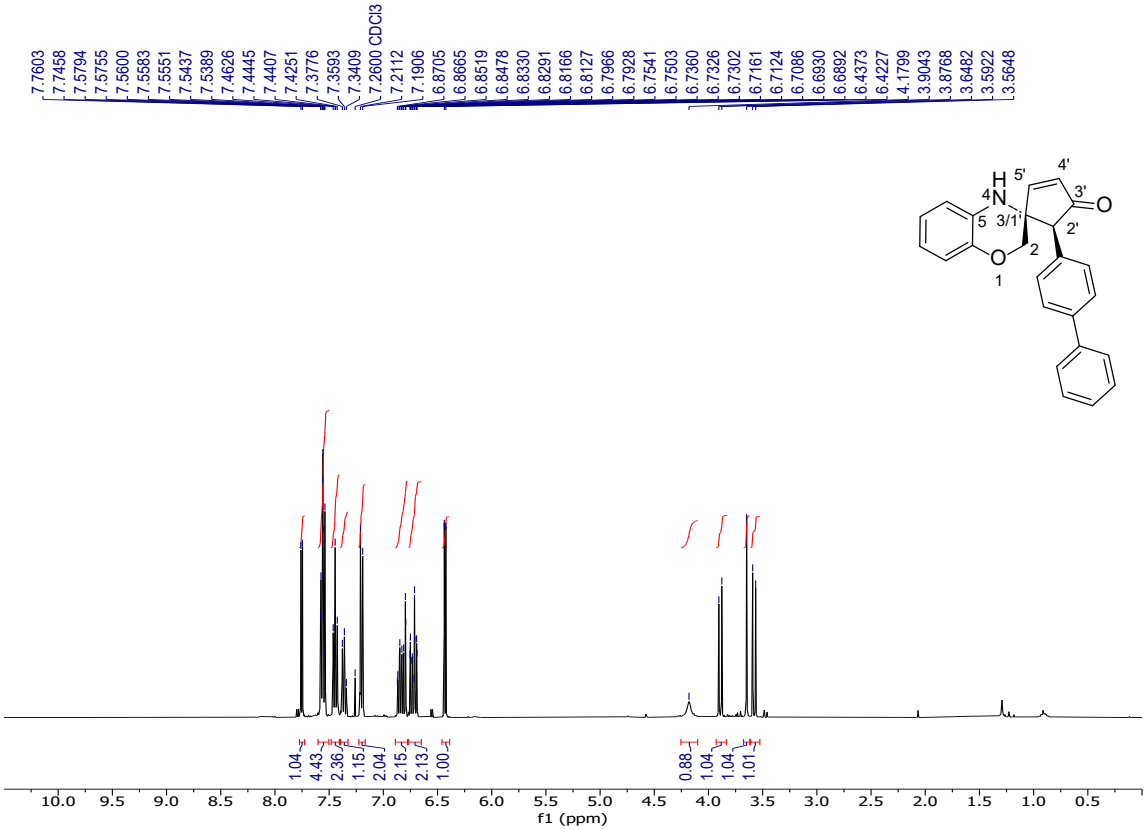
^{1}H NMR spectrum of 2'-(4-methoxyphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9b **(400 MHz, $CDCl_3$)**



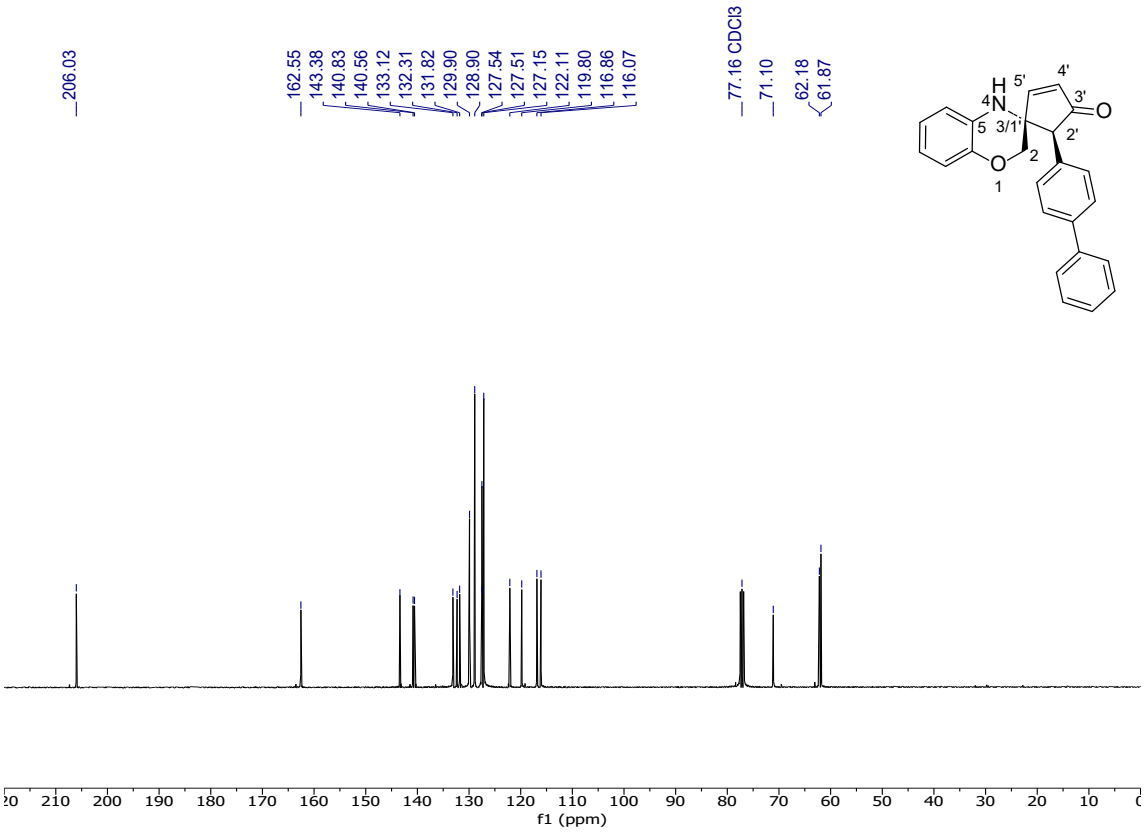
^{13}C NMR **spectrum** of 2'-(4-methoxyphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9b (100 MHz, $CDCl_3$)



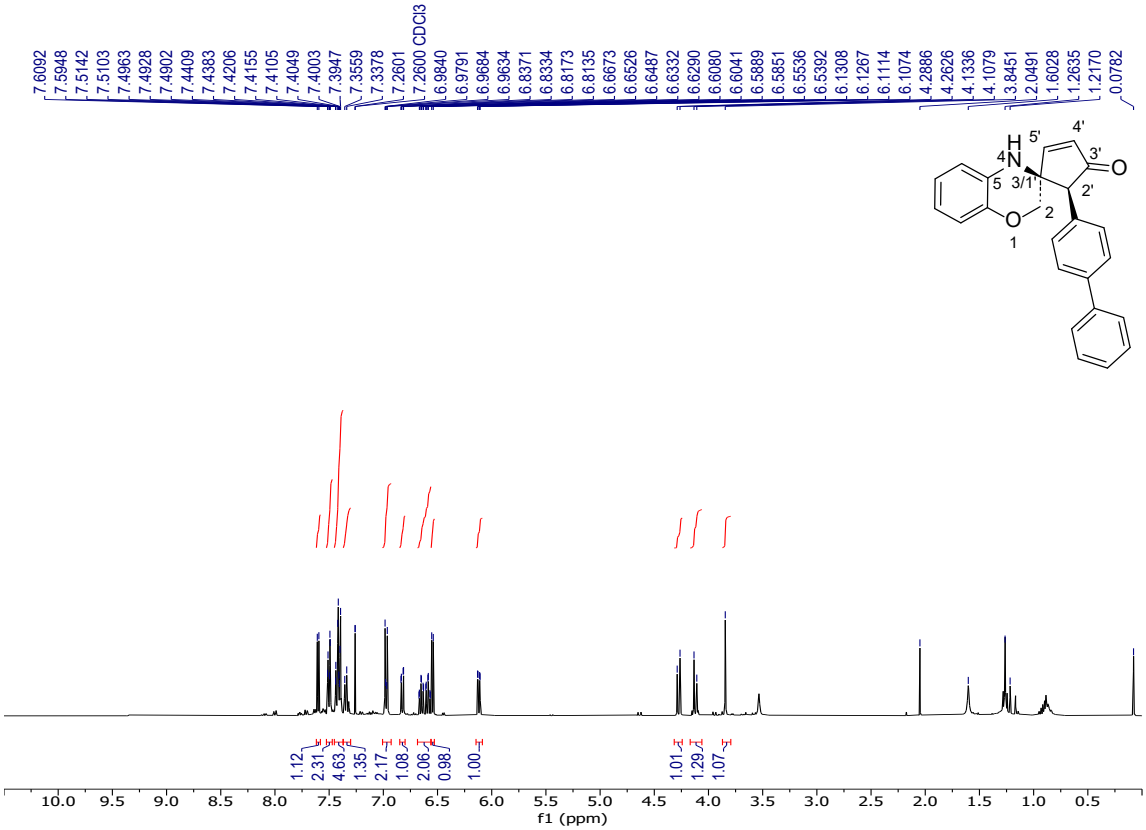
^{1}H NMR spectrum of 2'-biphenyl-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9c **(400 MHz, $CDCl_3$)**



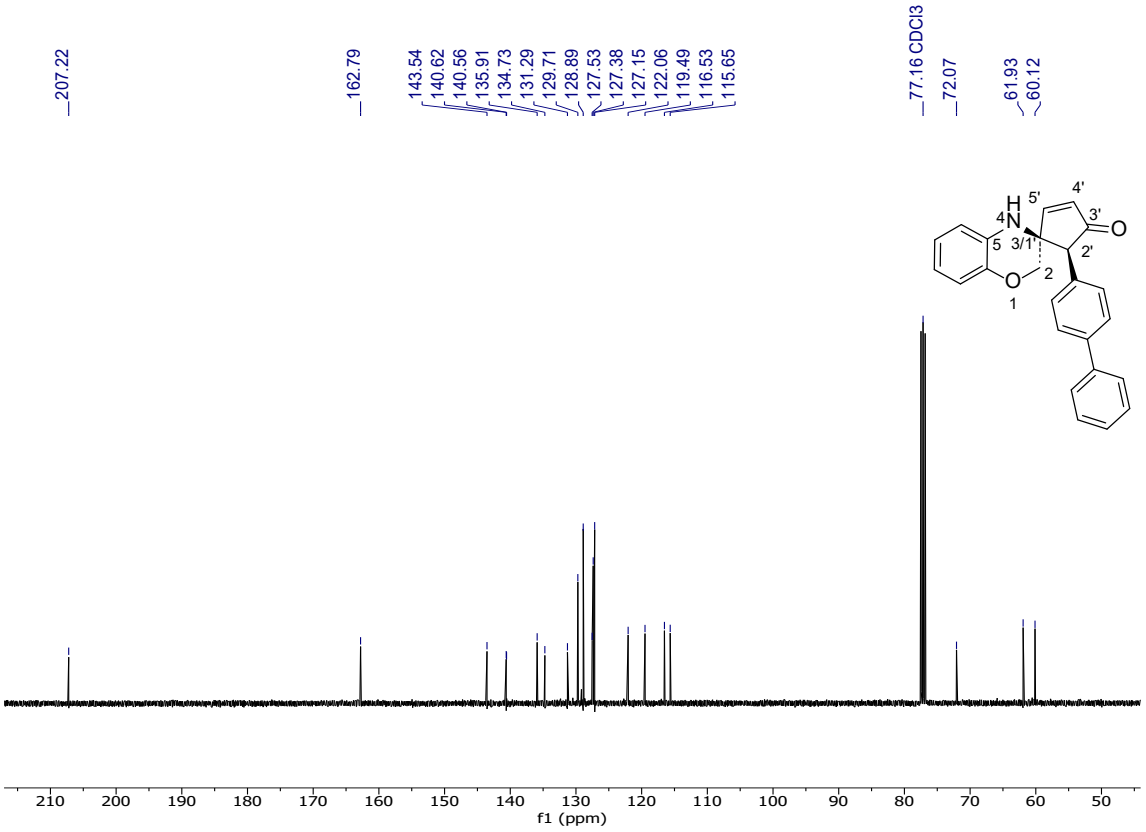
^{13}C NMR **spectrum** of 2'-biphenyl-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9c (100 MHz, $CDCl_3$)



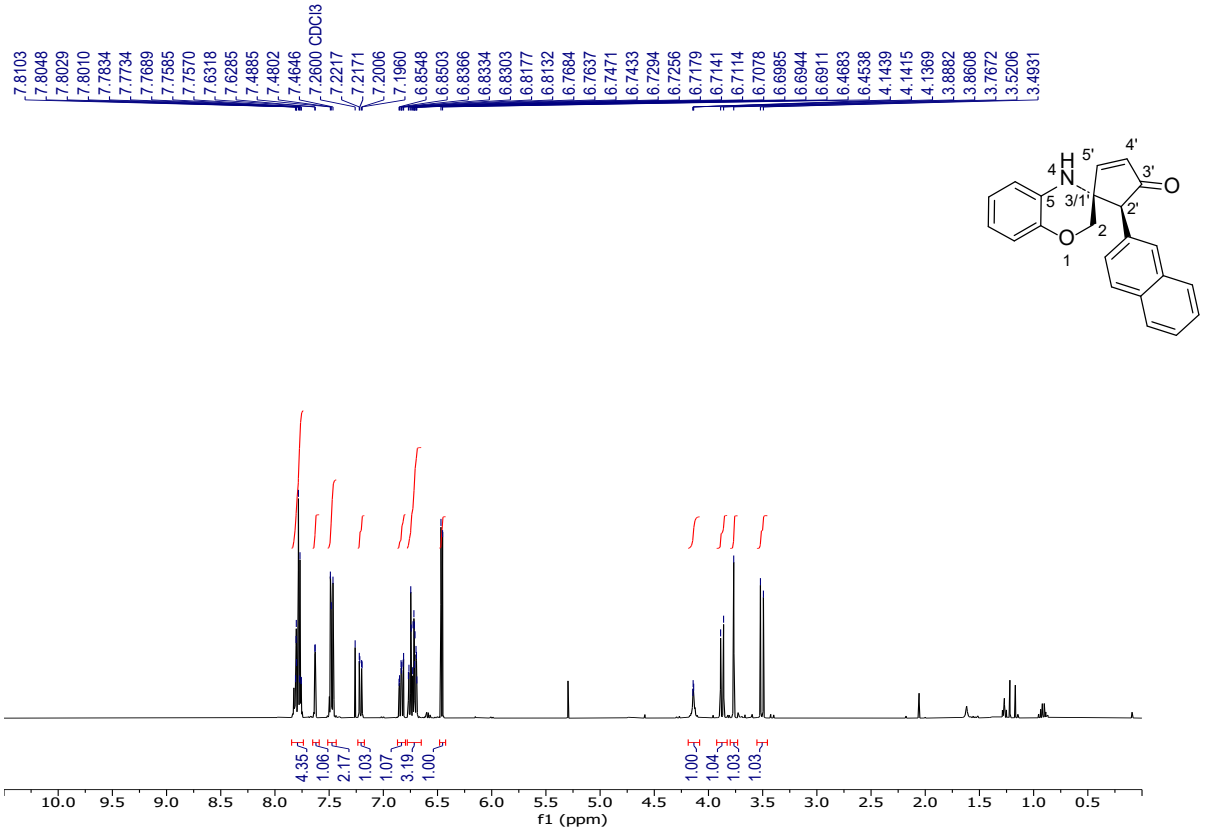
^{1}H NMR spectrum of 2'-biphenyl-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'c **(400 MHz, $CDCl_3$)**



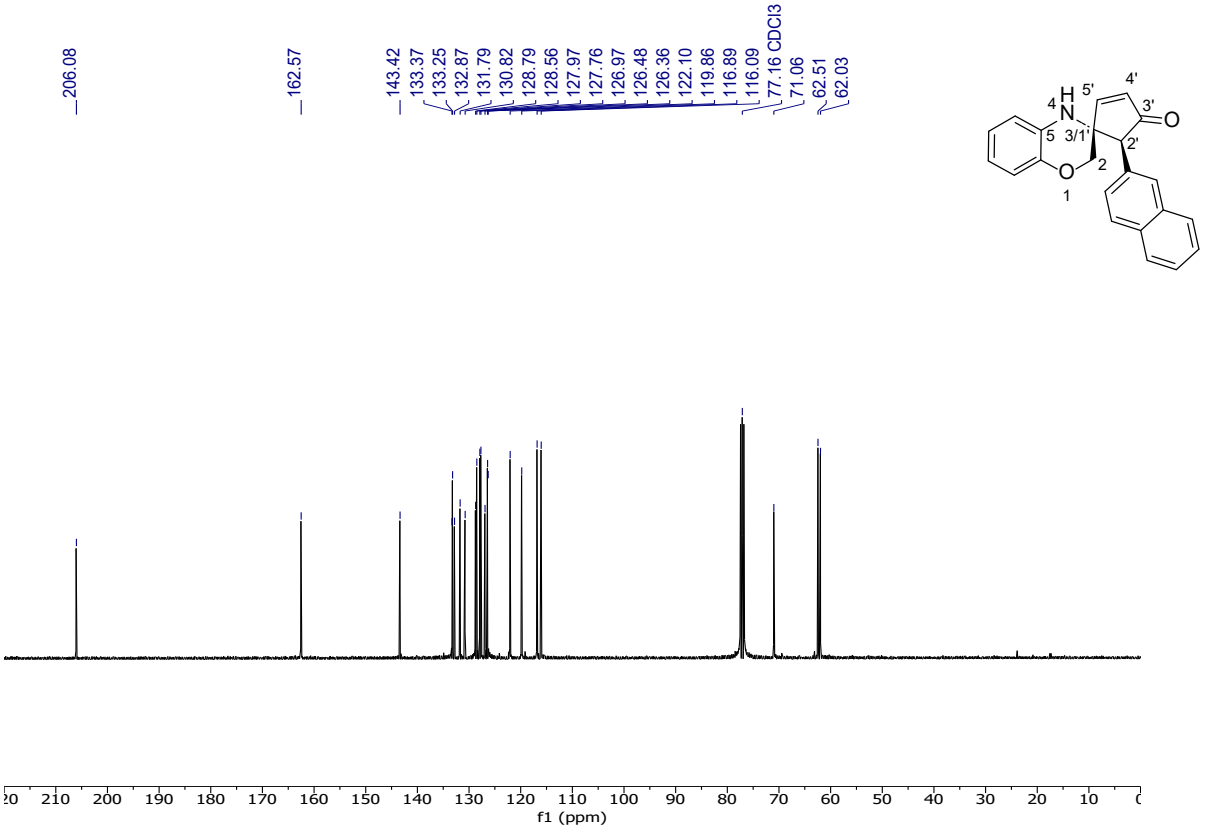
^{13}C NMR **spectrum** of 2'-biphenyl-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'c (100 MHz, $CDCl_3$)



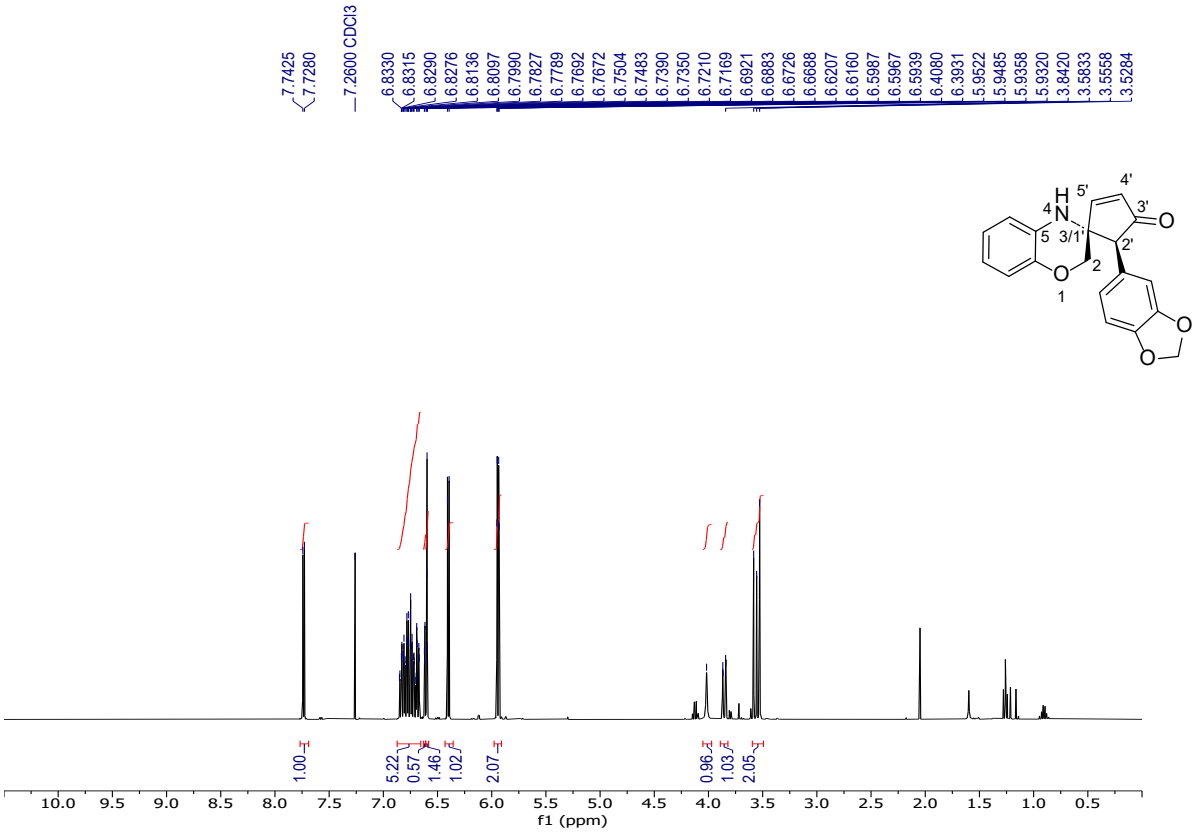
^{1}H NMR spectrum of 2'-(2-naphtalenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9d (400 MHz, $CDCl_3$)



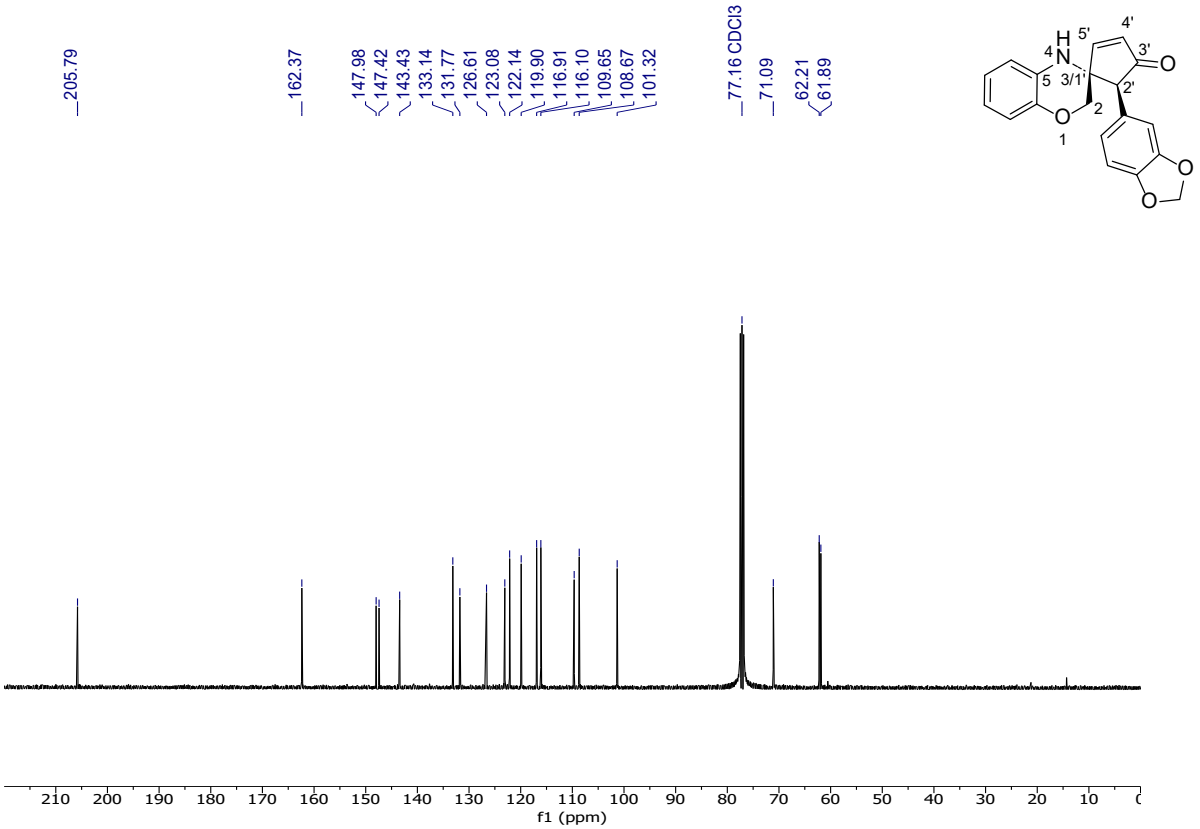
^{13}C NMR spectrum of 2'-(2-naphtalenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9d (100 MHz, $CDCl_3$)



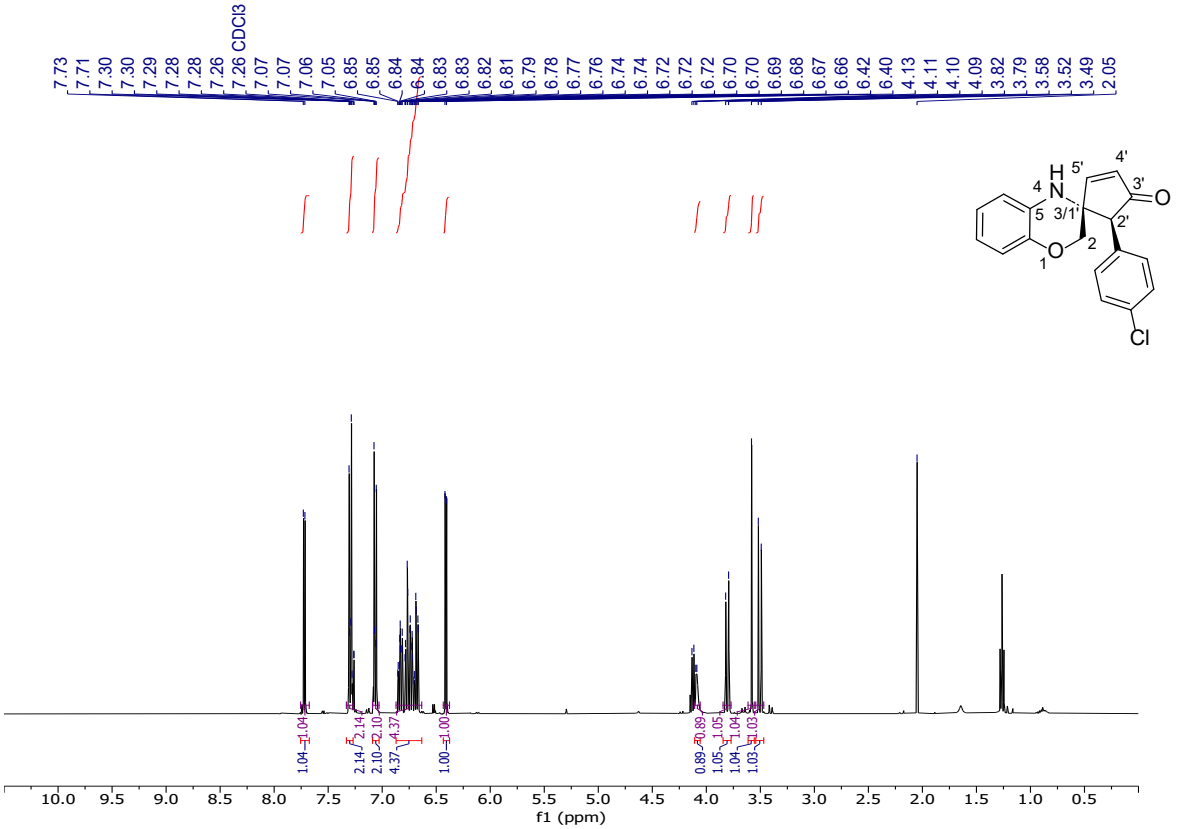
^{1}H NMR spectrum of 2'-(methylenedioxyphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9e (400 MHz, $CDCl_3$)



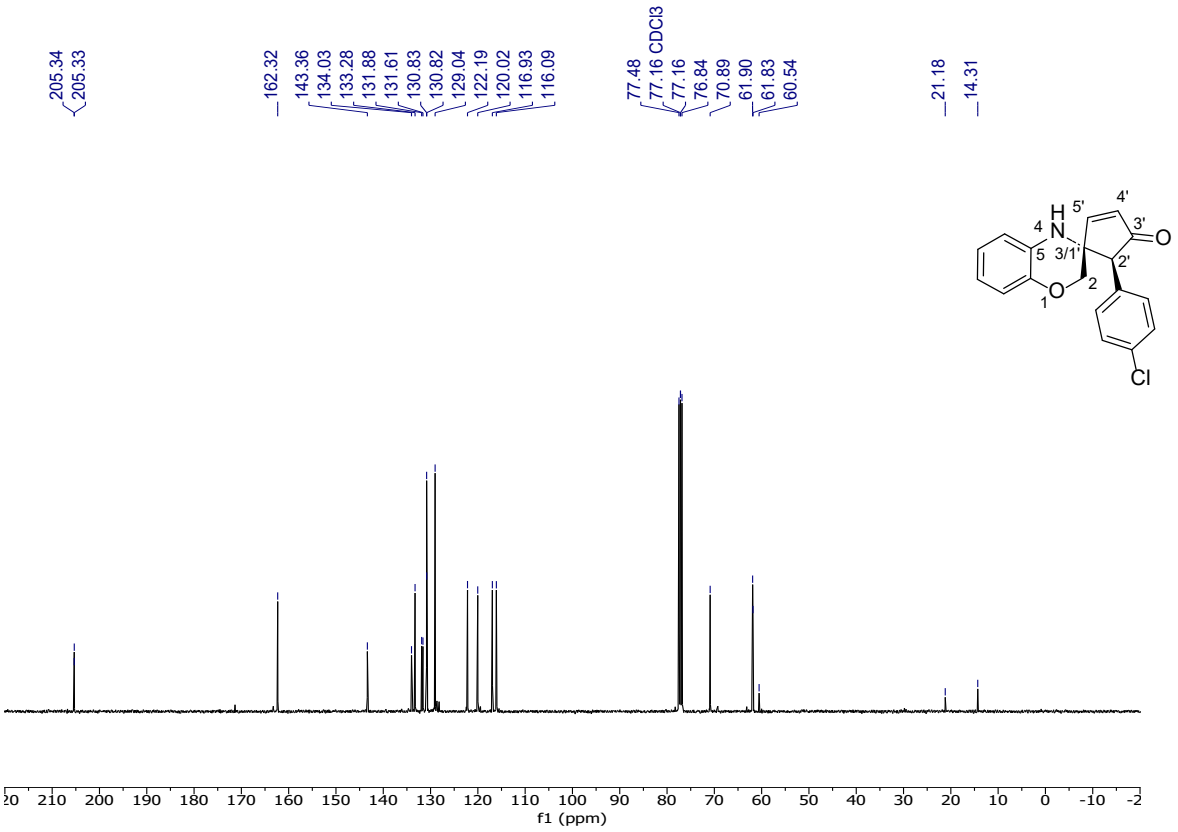
^{13}C NMR spectrum of 2'-(methylenedioxyphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9e (100 MHz, $CDCl_3$)



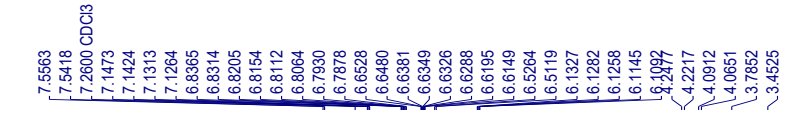
^{1}H NMR spectrum of 2'-(4-chlorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9f **(400 MHz, $CDCl_3$)**

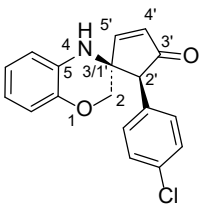


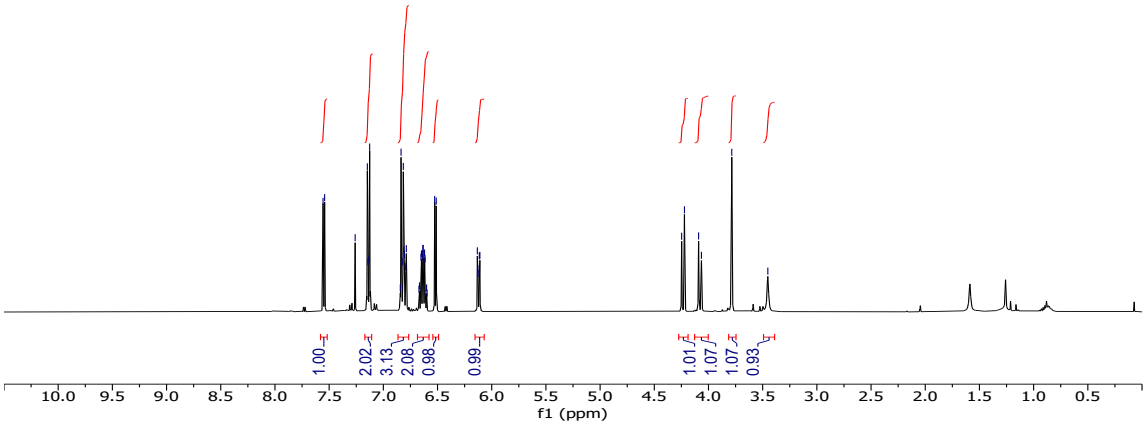
^{13}C NMR **spectrum** of 2'-(4-chlorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9f (100 MHz, $CDCl_3$)



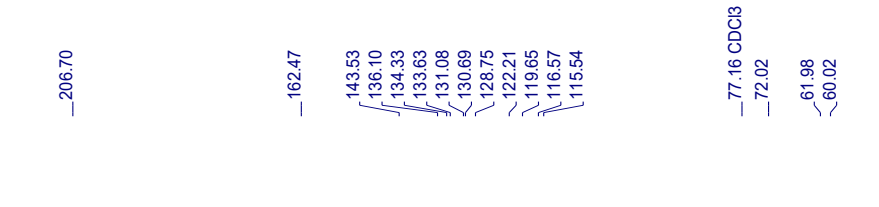
^{1}H NMR spectrum of 2'-(4-chlorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'f **(400 MHz, $CDCl_3$)**

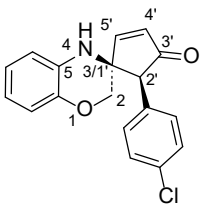


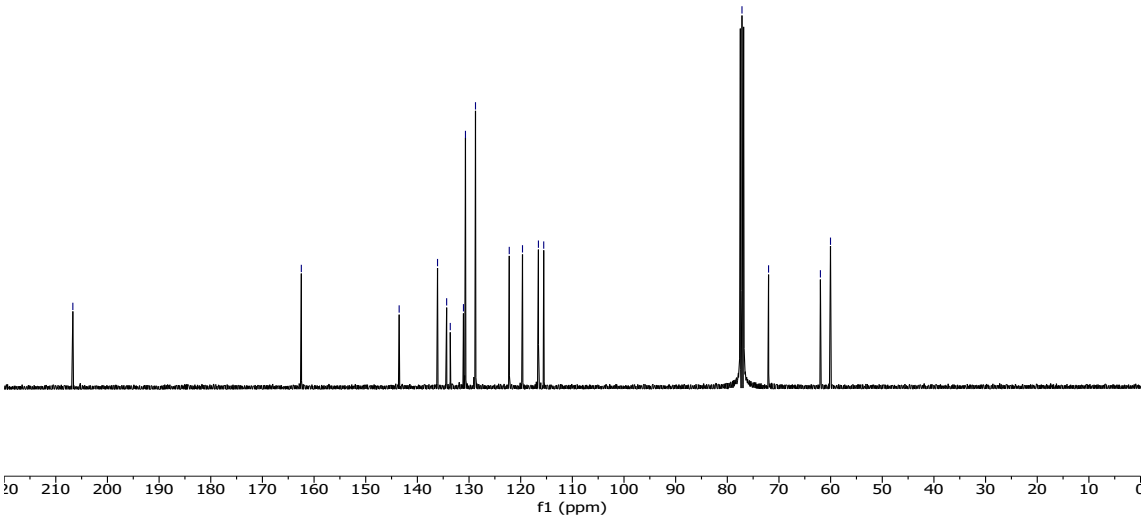




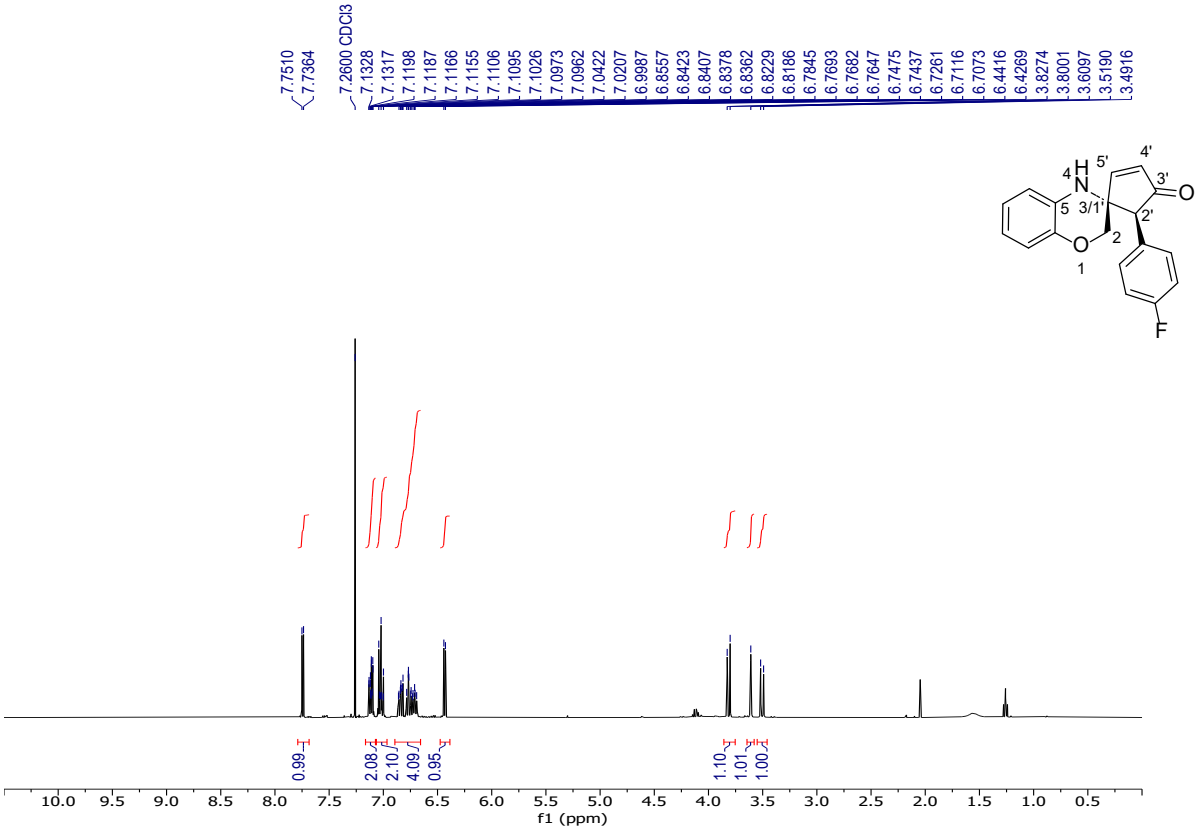
^{13}C NMR **spectrum** of 2'-(4-chlorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'f (100 MHz, $CDCl_3$)



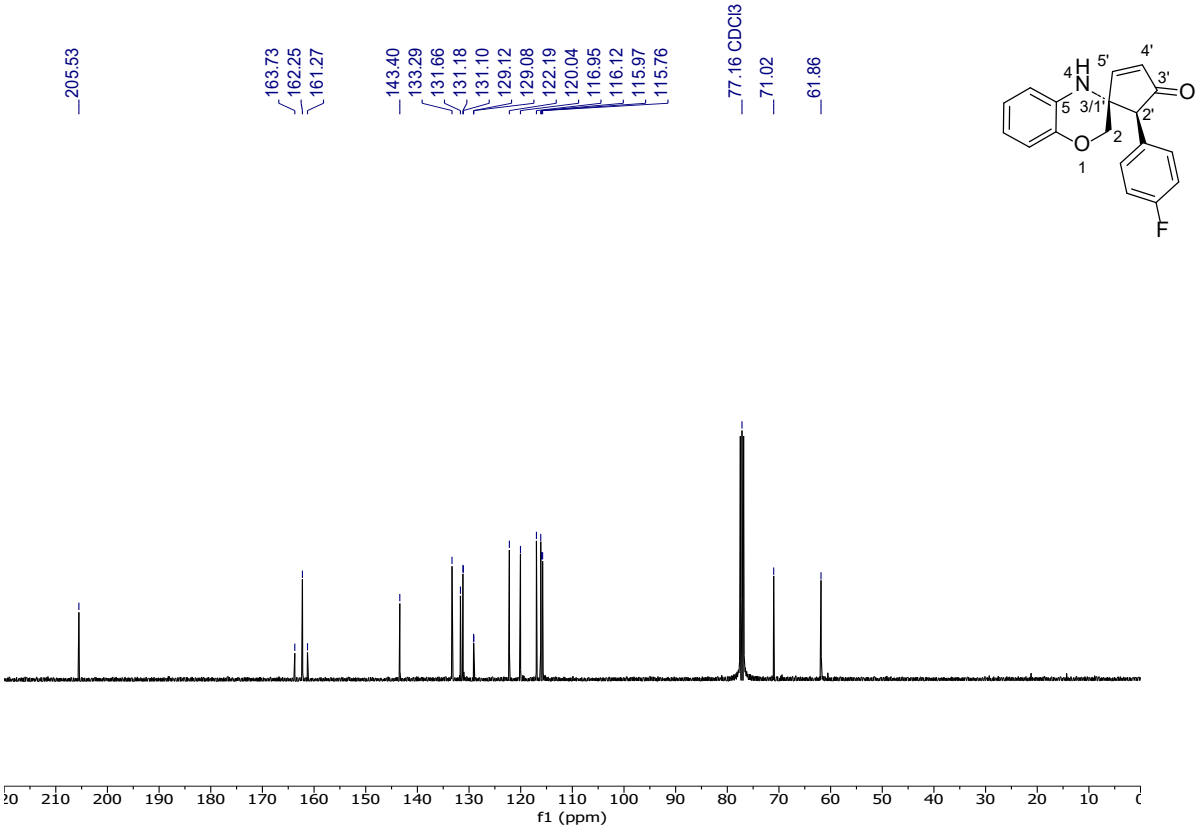




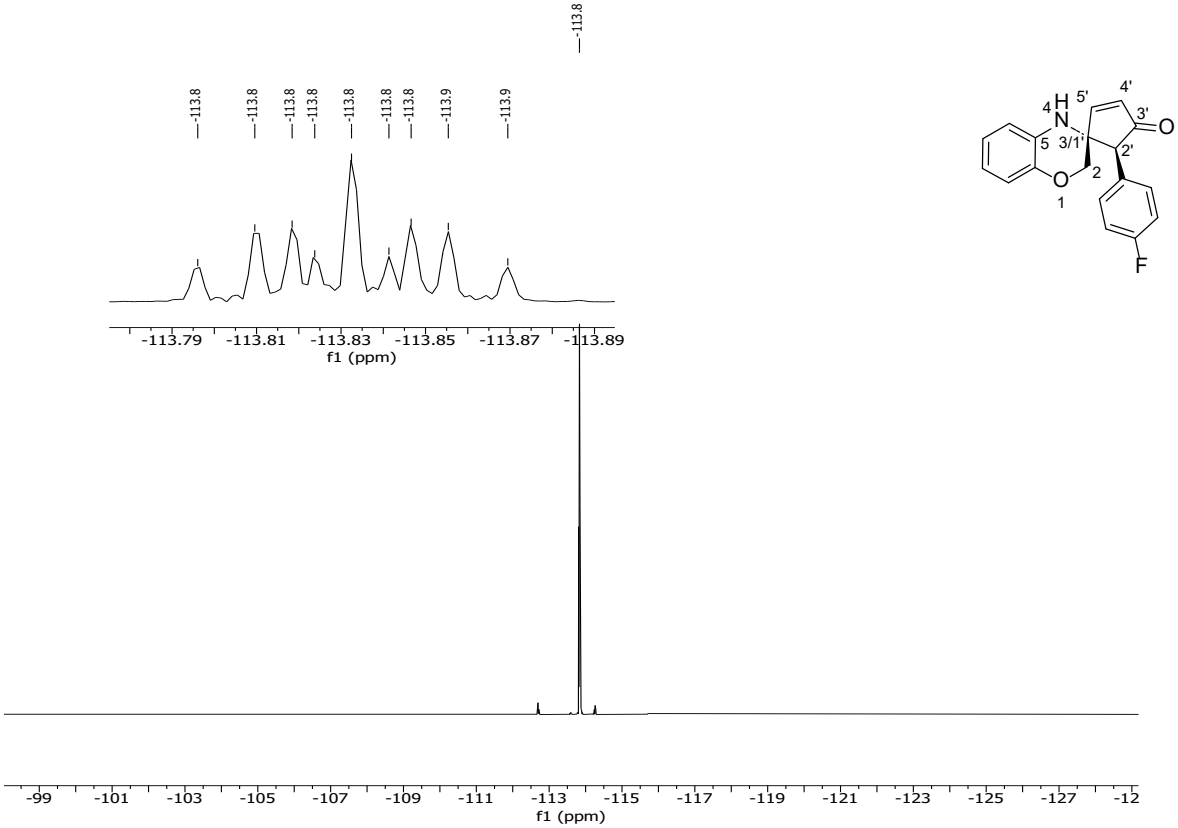
^{1}H NMR spectrum of 2'-(4-fluorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9g **(400 MHz, $CDCl_3$)**



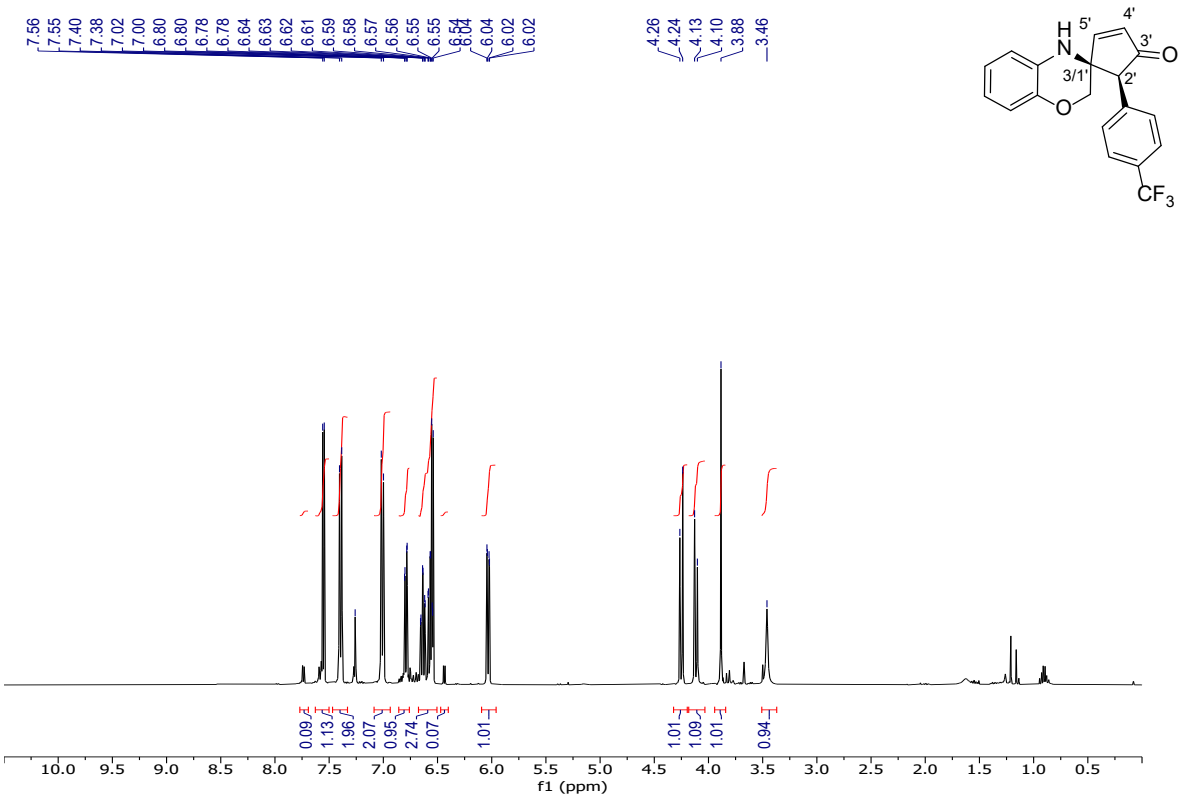
^{13}C NMR **spectrum** of 2'-(4-fluorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9g (100 MHz, $CDCl_3$)



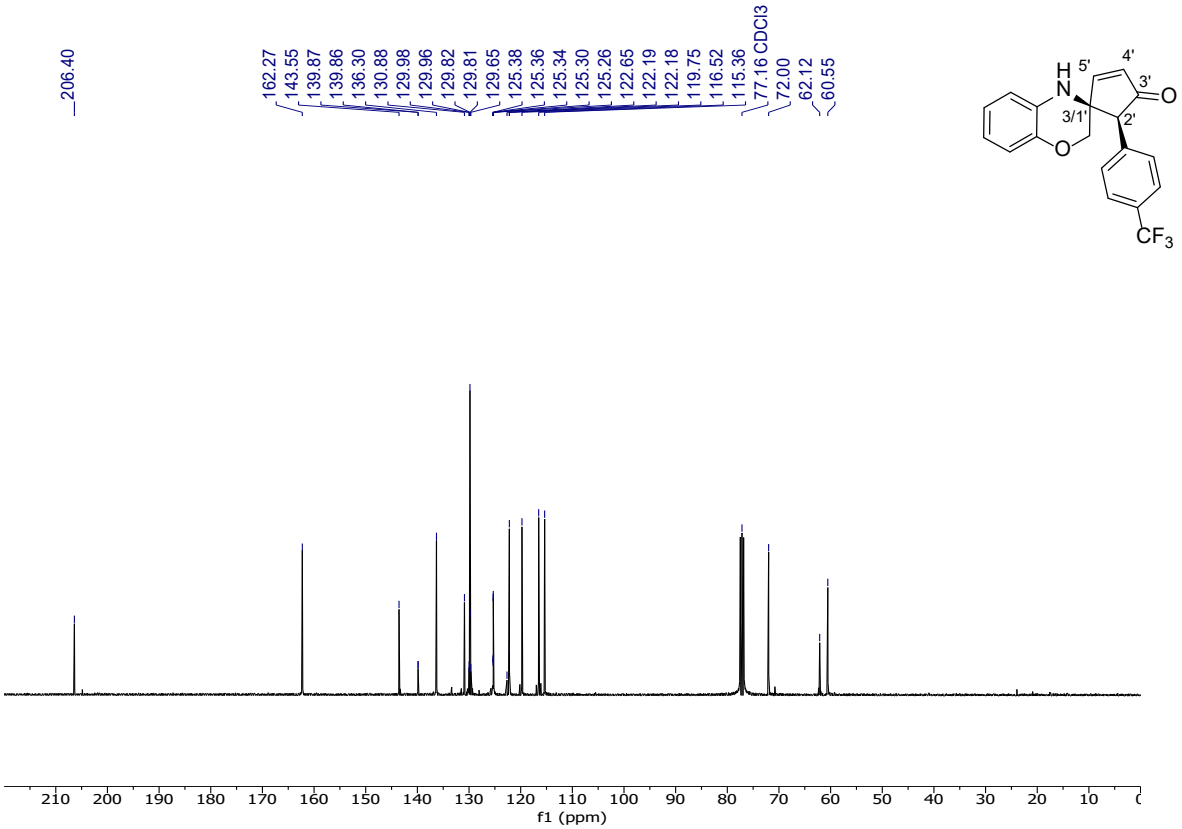
^{19}F NMR spectrum of 2'-(4-fluorophenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9g (282 MHz, $CDCl_3$)



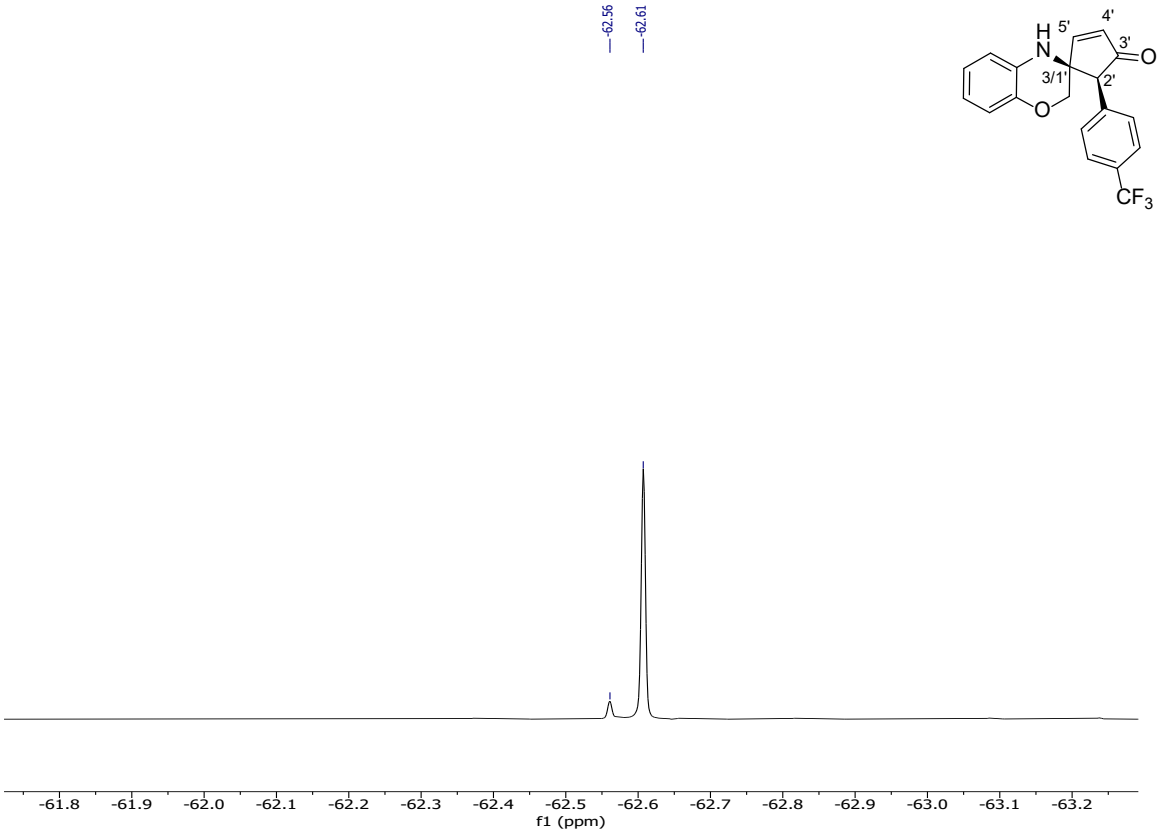
^{1}H NMR spectrum of 2'-(4-trifluoromethylphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'h **(400 MHz, $CDCl_3$ (400 MHz, $CDCl_3$)**



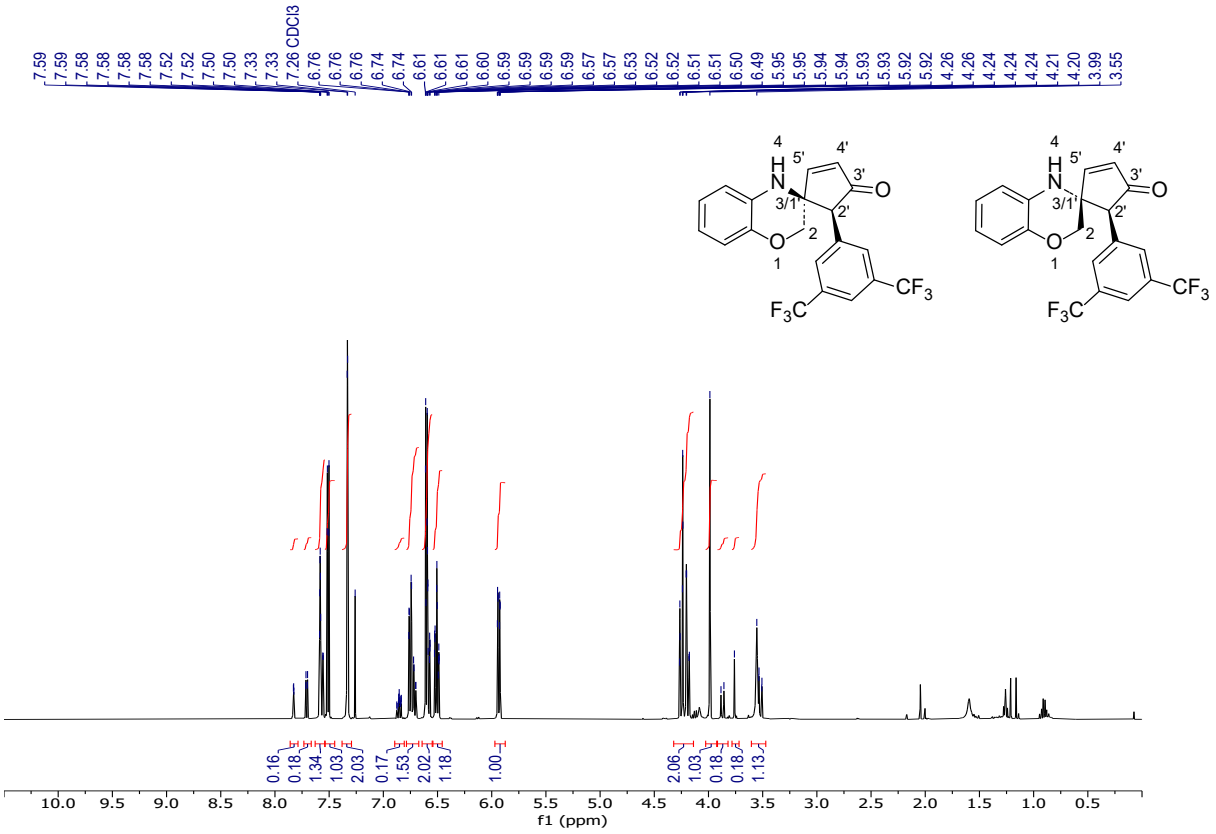
^{13}C NMR **spectrum** of 2'-(4-trifluoromethylphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'h (100 MHz, $CDCl_3$)



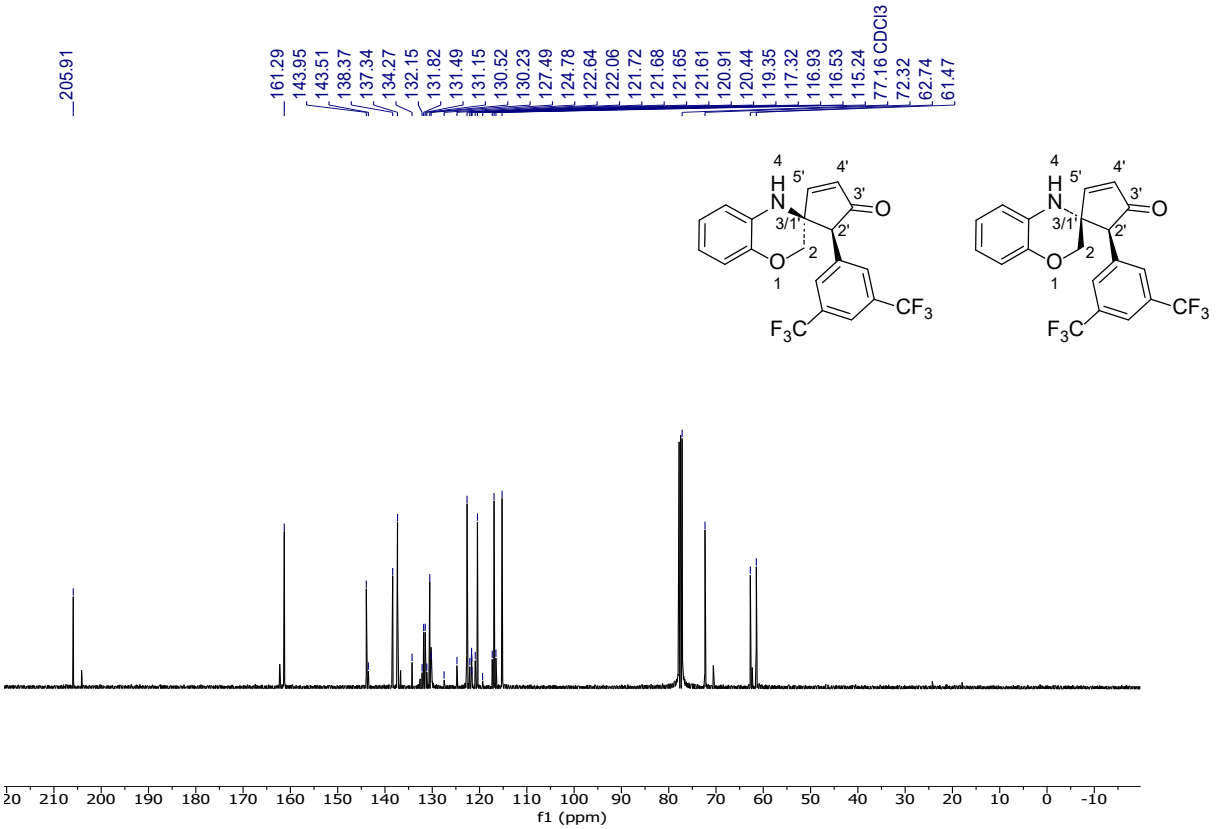
^{19}F NMR spectrum of 2'-(4-trifluoromethylphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'h (282 MHz, $CDCl_3$)



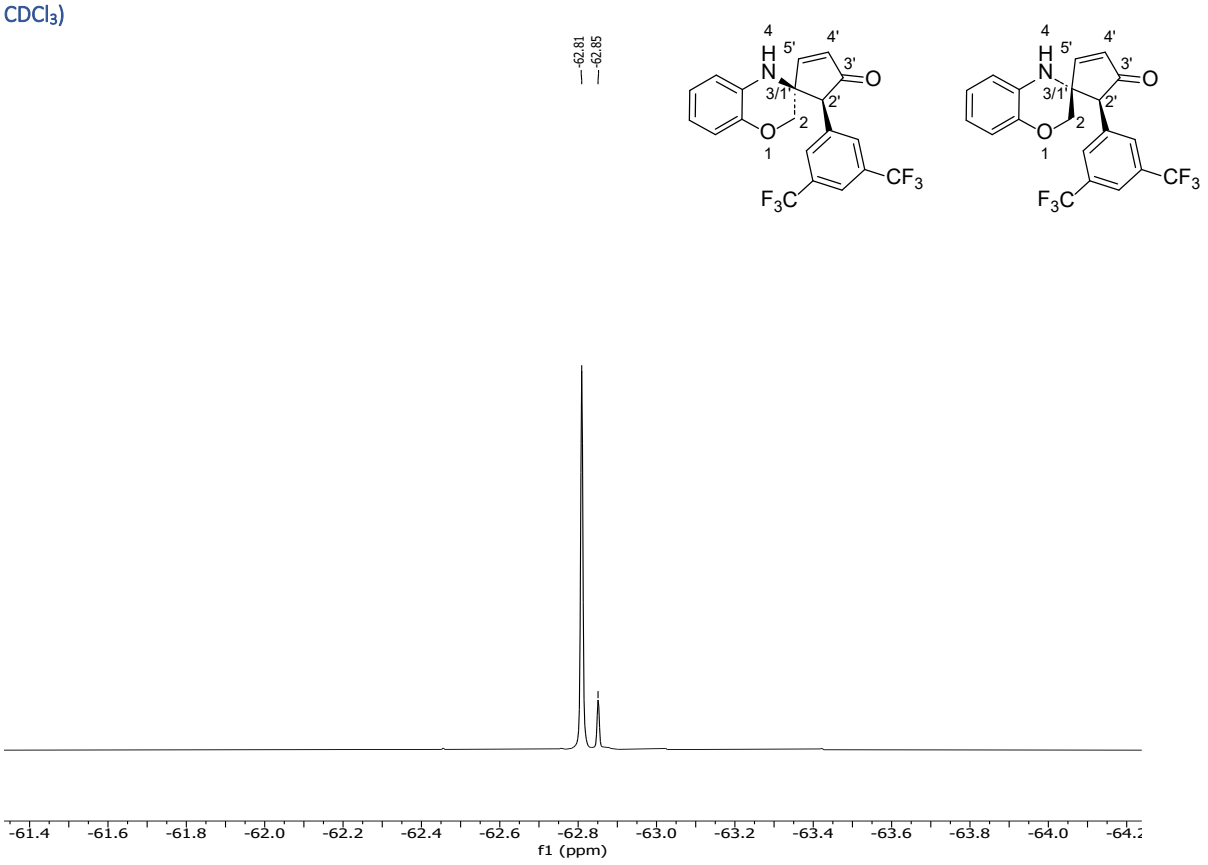
^{1}H NMR spectrum of 2'-(3,5-ditrifluoromethyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9i/9'i (15/85) (400 MHz, $CDCl_3$)



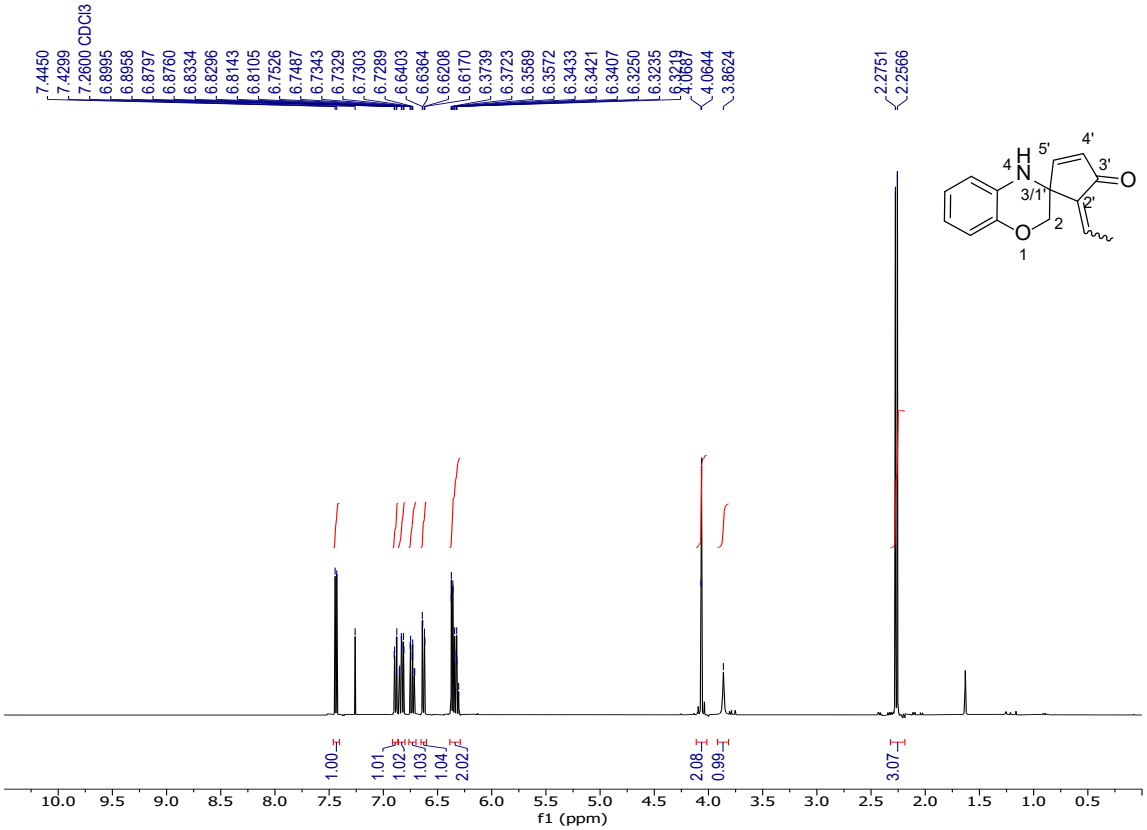
^{13}C NMR spectrum of 2'-(3,5-ditrifluoromethyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9i/9'i (100 MHz, $CDCl_3$)



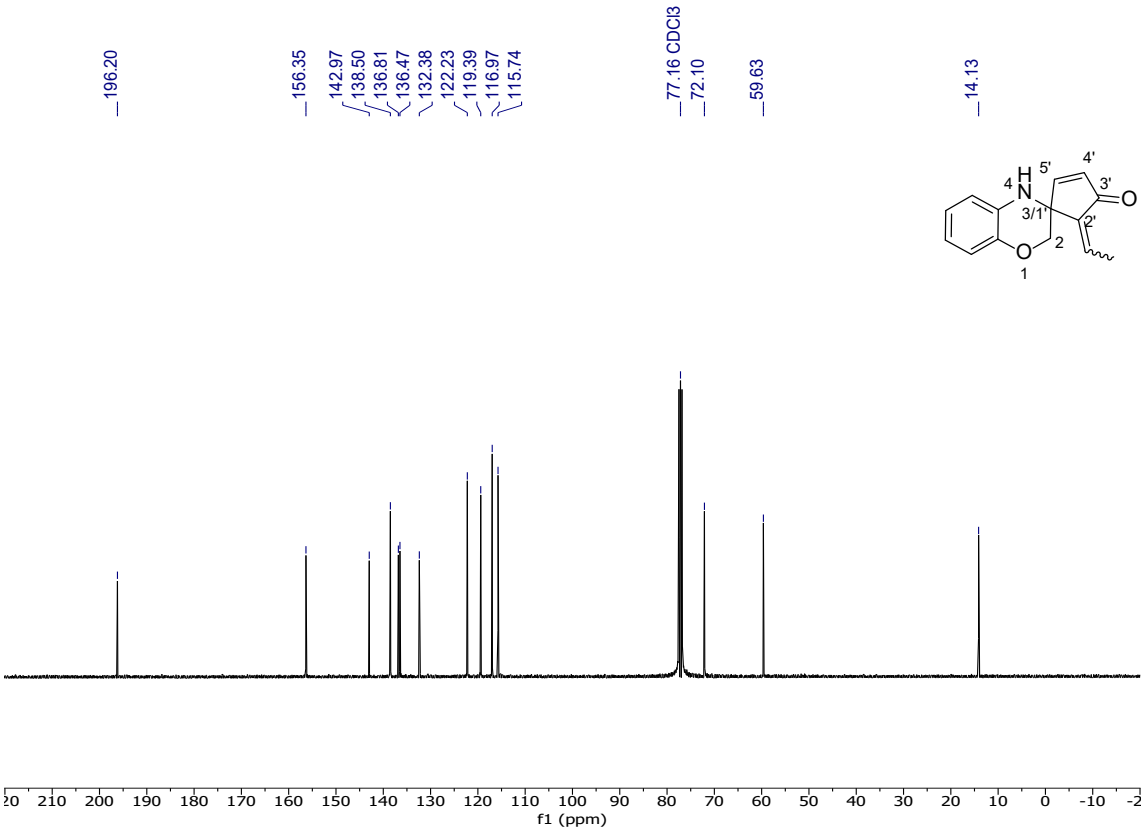
^{19}F NMR spectrum of 2'-(4-trifluoromethylphenyl)-*2H,4H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9i/9'i (282 MHz, $CDCl_3$)



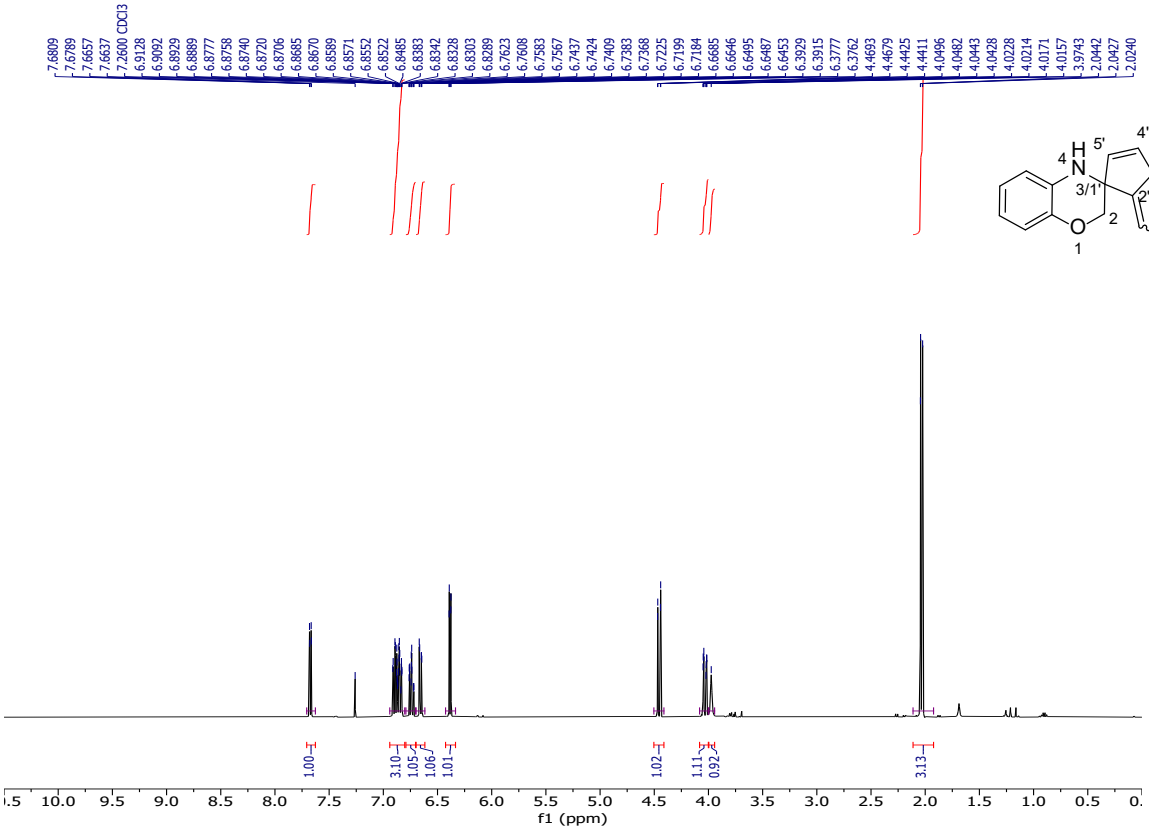
^{1}H NMR spectrum of 2'-ethylidene-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 10 **(400 MHz, $CDCl_3$)**



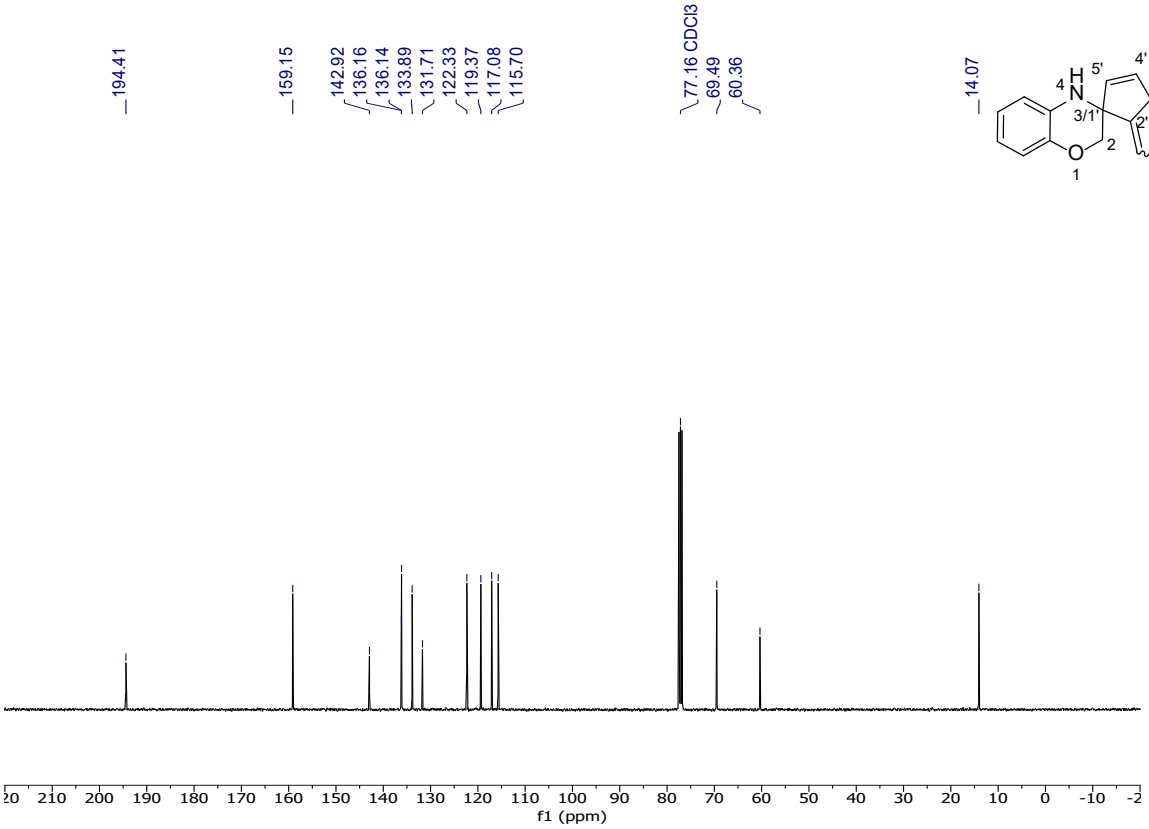
^{13}C NMR spectrum of 2'-ethylidene-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 10 **(100 MHz, $CDCl_3$)**



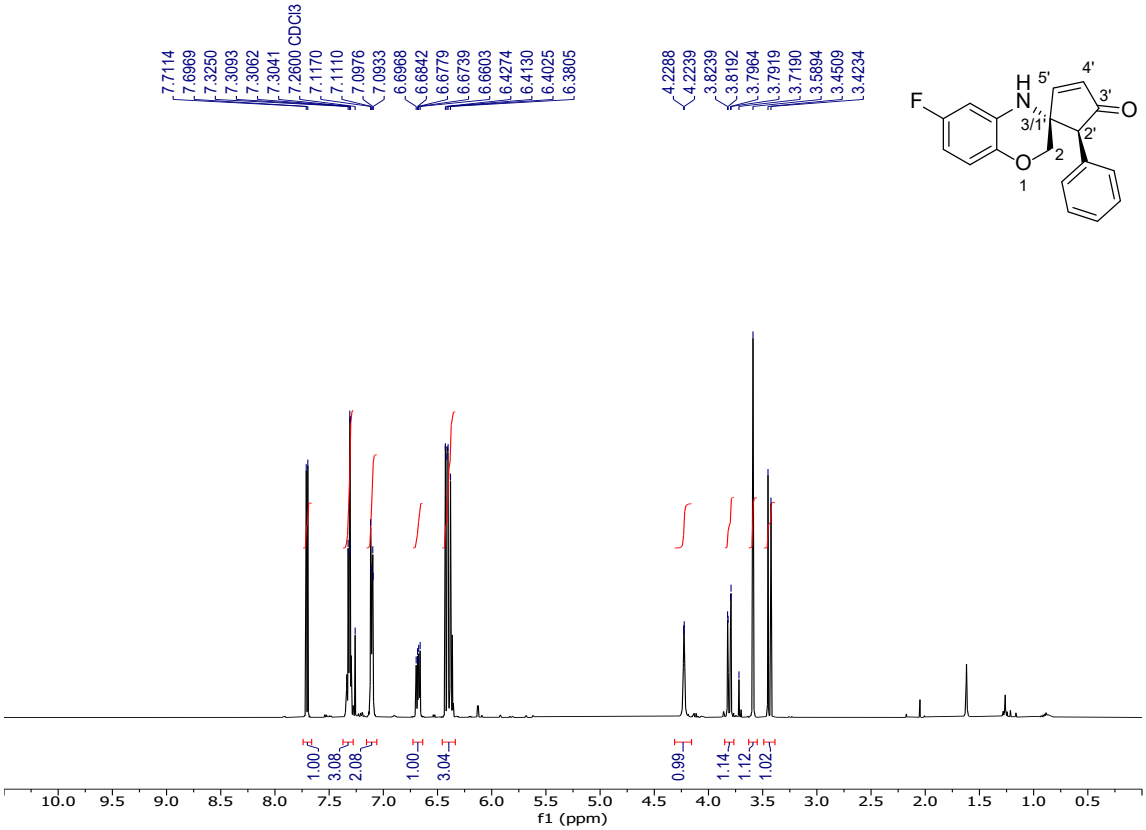
^{1}H NMR spectrum of 2'-ethylidene-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 10′ (400 MHz, $CDCl_3$)



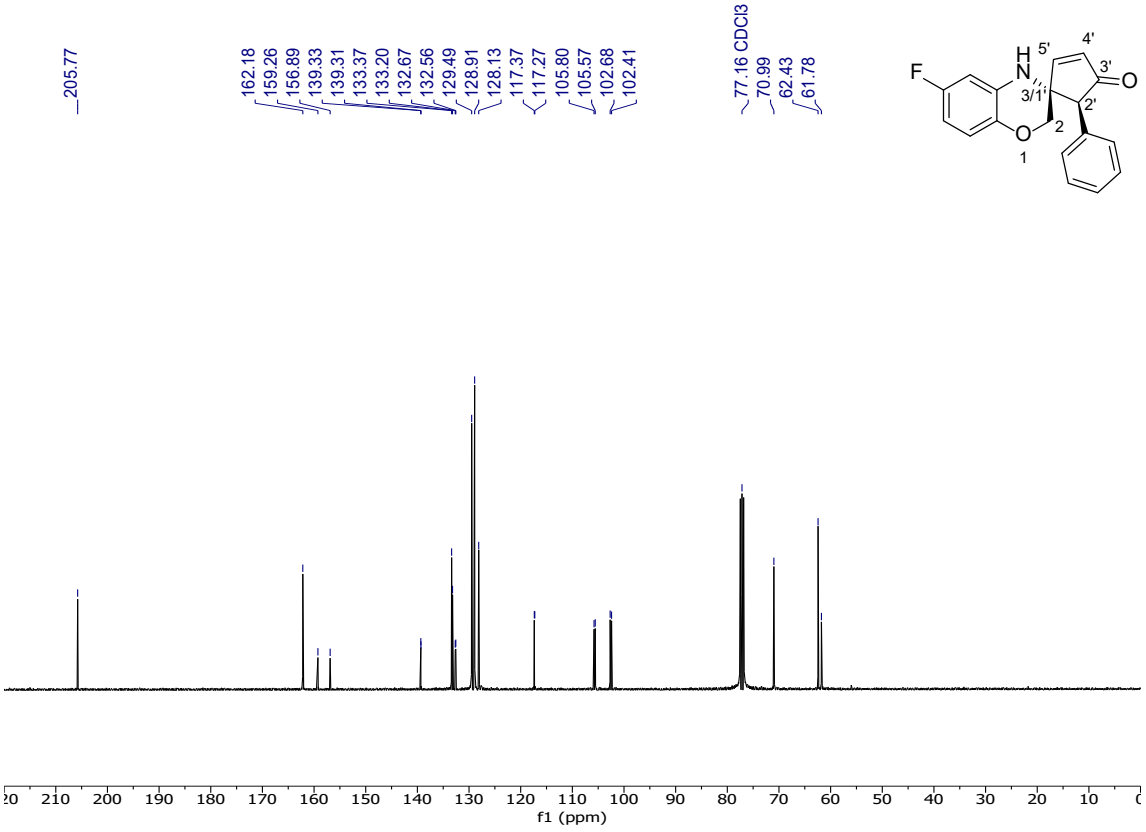
^{13}C NMR spectrum of 2'-ethylidene-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 10′ (100 MHz, $CDCl_3$)



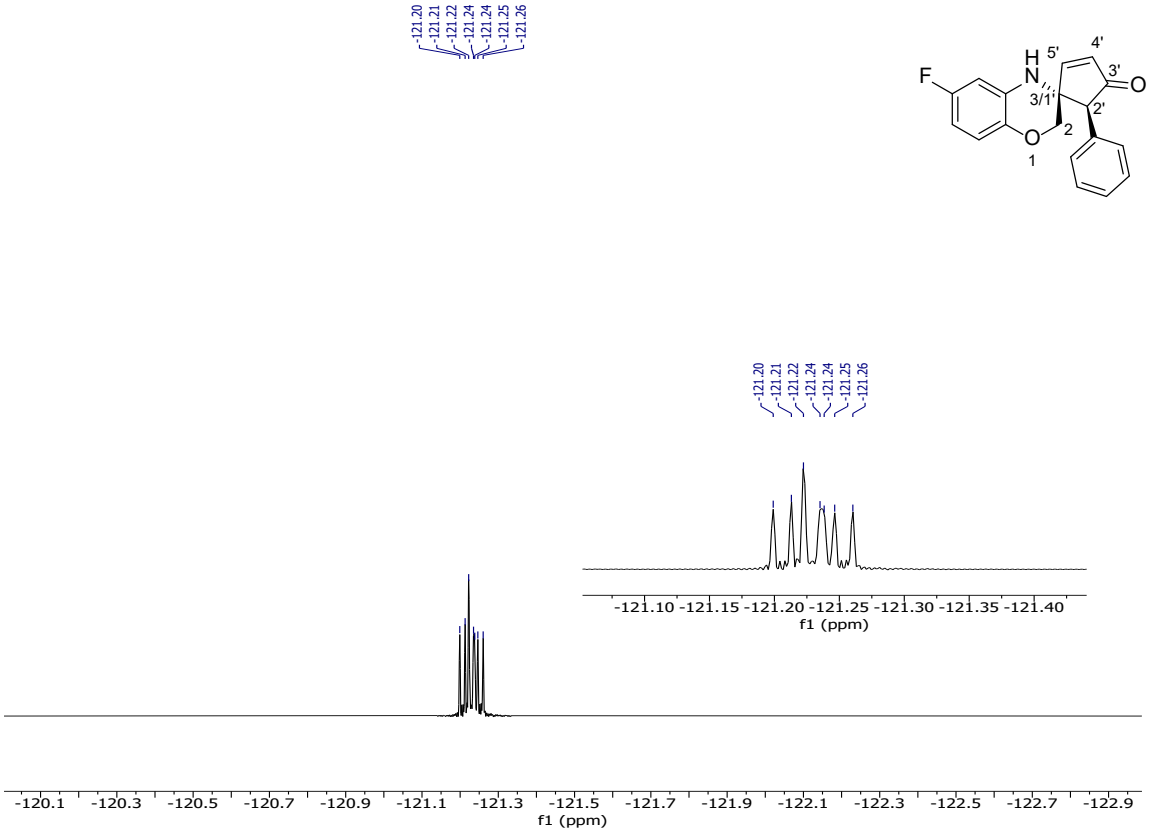
^{1}H NMR spectrum of 6-fluoro-2′-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one **9m (400 MHz, $CDCl_3$)**



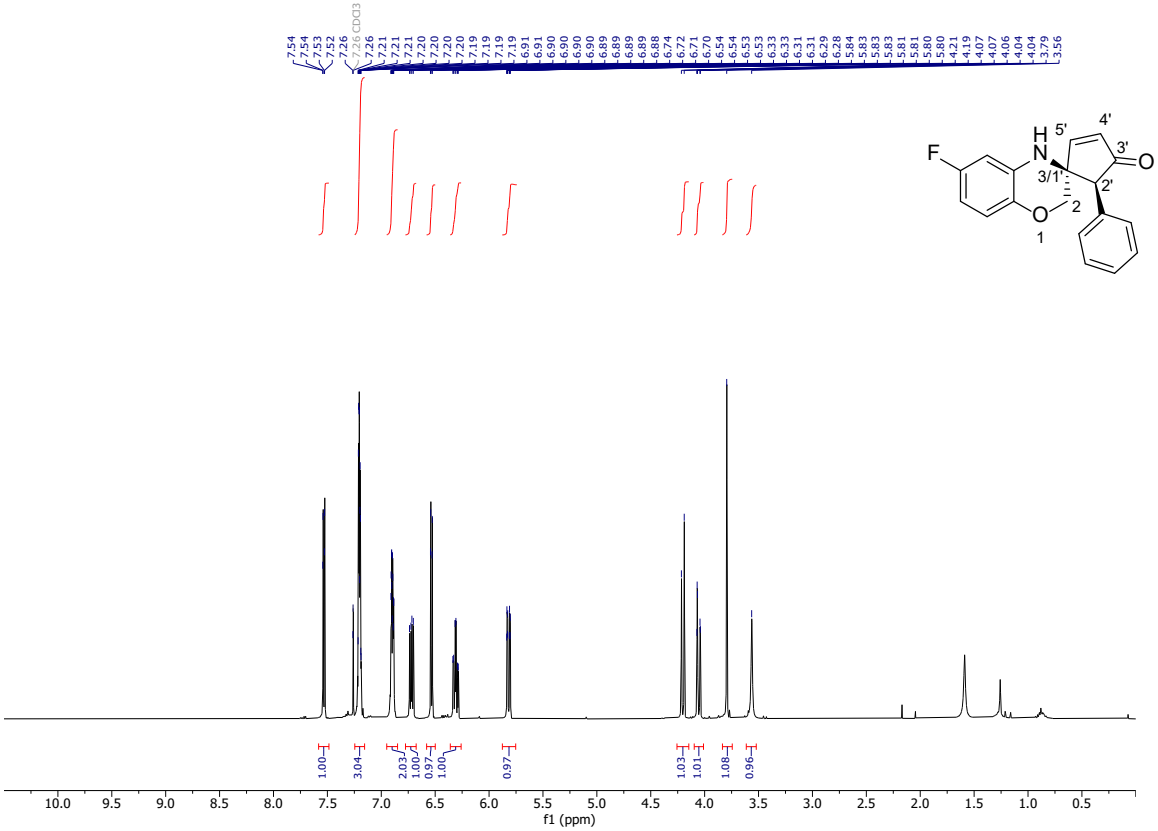
^{13}C NMR spectrum of 6-fluoro-2′-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one **9m (100 MHz, $CDCl_3$)**



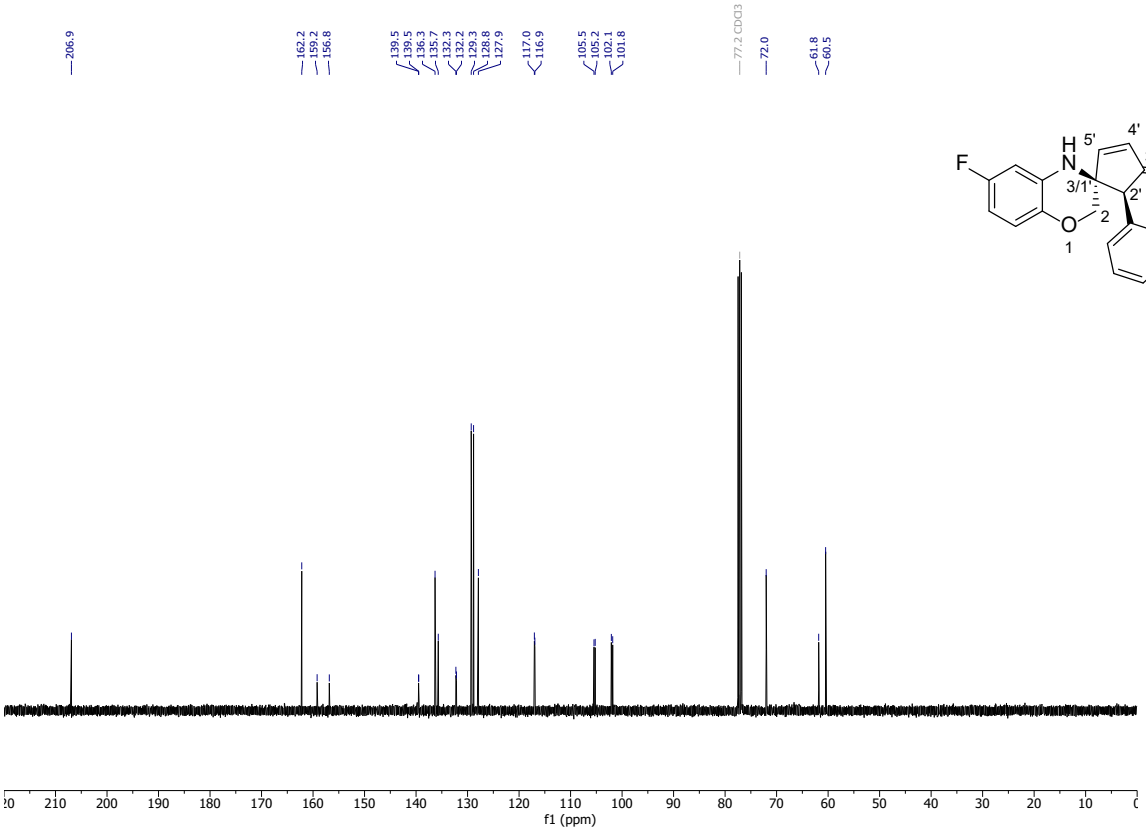
^{19}F NMR spectrum of 6-fluoro-2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one **9m** (376 MHz, $CDCl_3$)



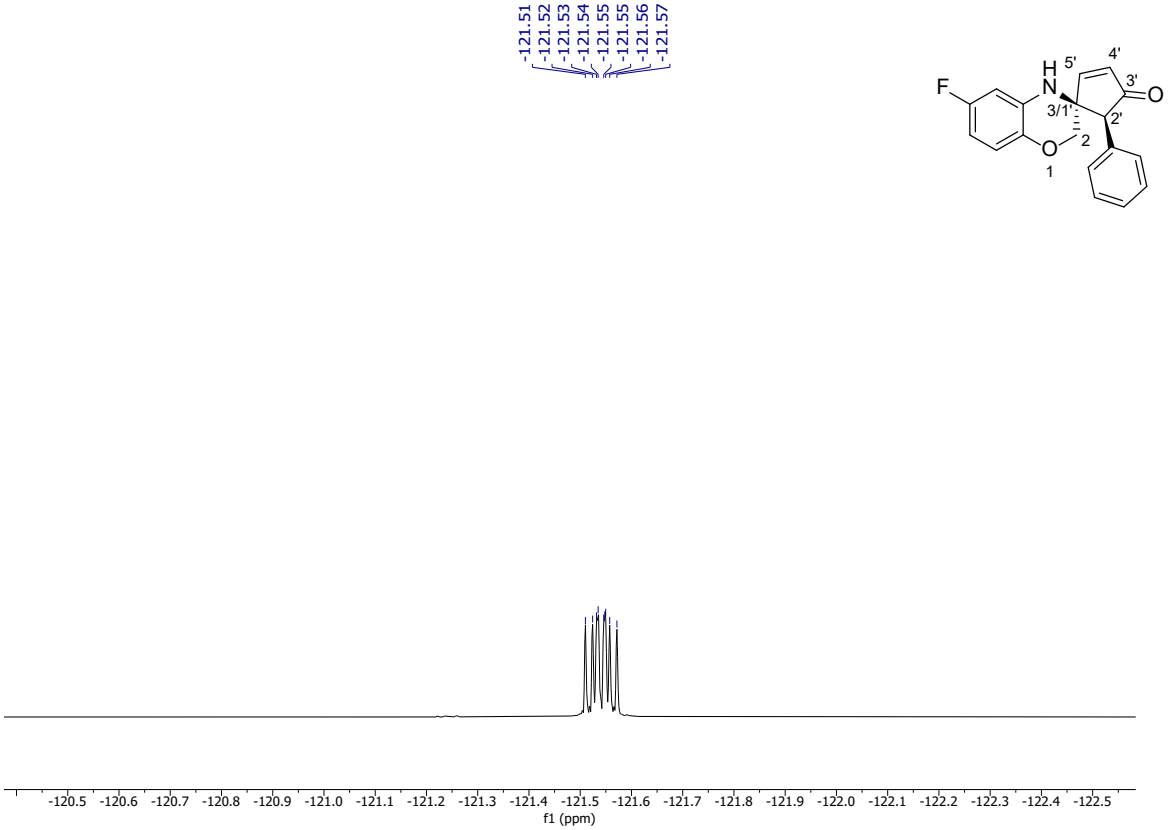
^{1}H NMR spectrum of 6-fluoro-2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'm (400 MHz, $CDCl_3$)



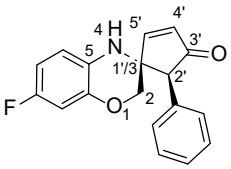
^{13}C NMR spectrum of 6-fluoro-2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9'm (100 MHz, $CDCl_3$)

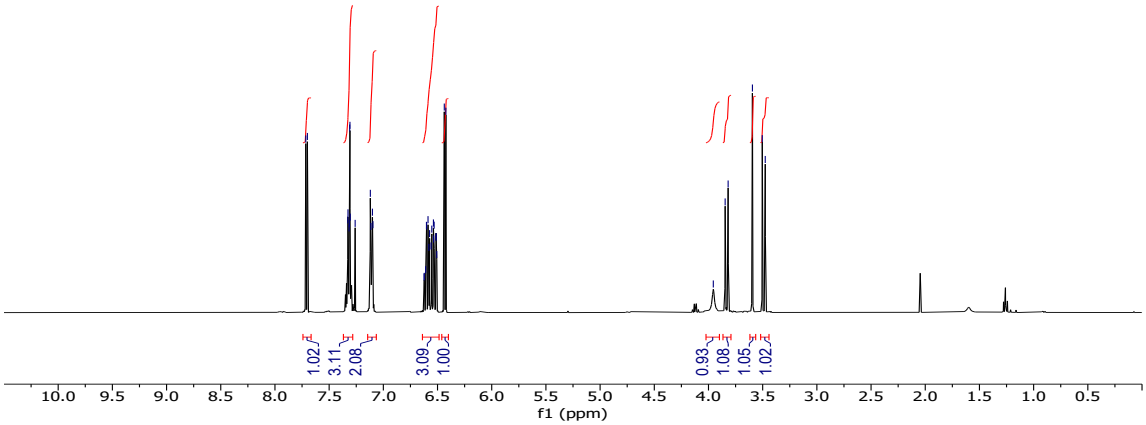


^{19}F NMR spectrum of 6-fluoro-2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one **9'm** (376 MHz, $CDCl_3$)

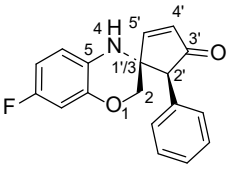


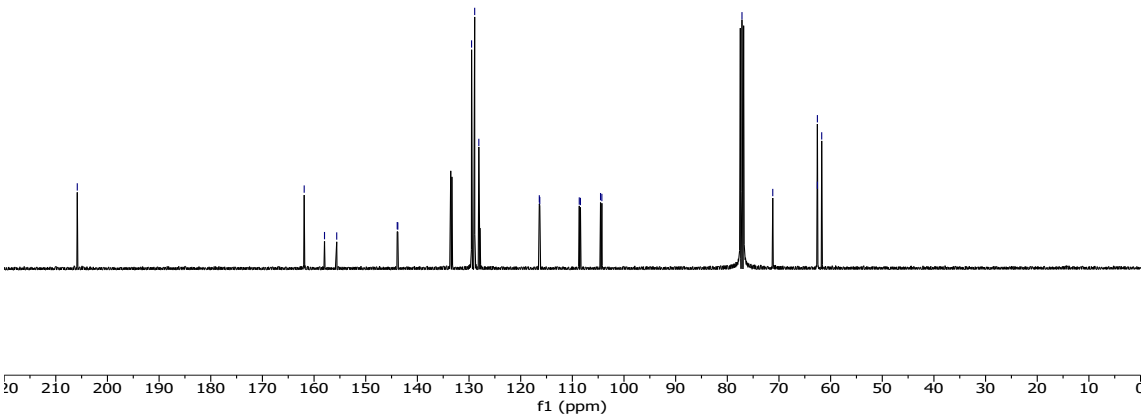
^{1}H NMR spectrum of 7-fluoro-2′-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9n **(400 MHz, $CDCl_3$)**



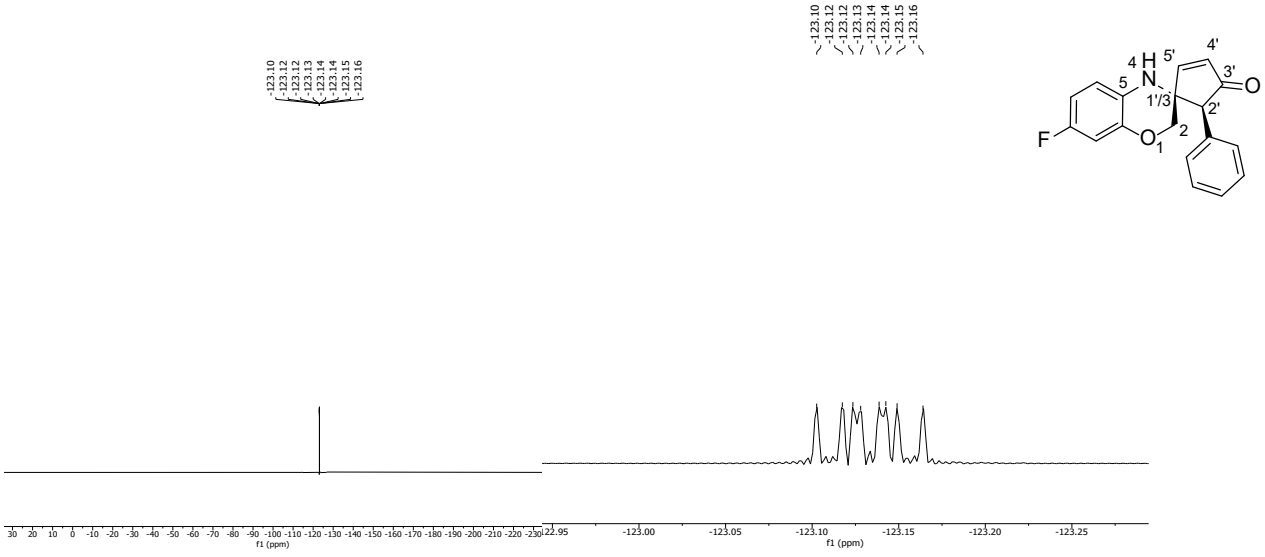


^{13}C NMR spectrum of 7-fluoro-2′-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9n **(100 MHz, $CDCl_3$)**

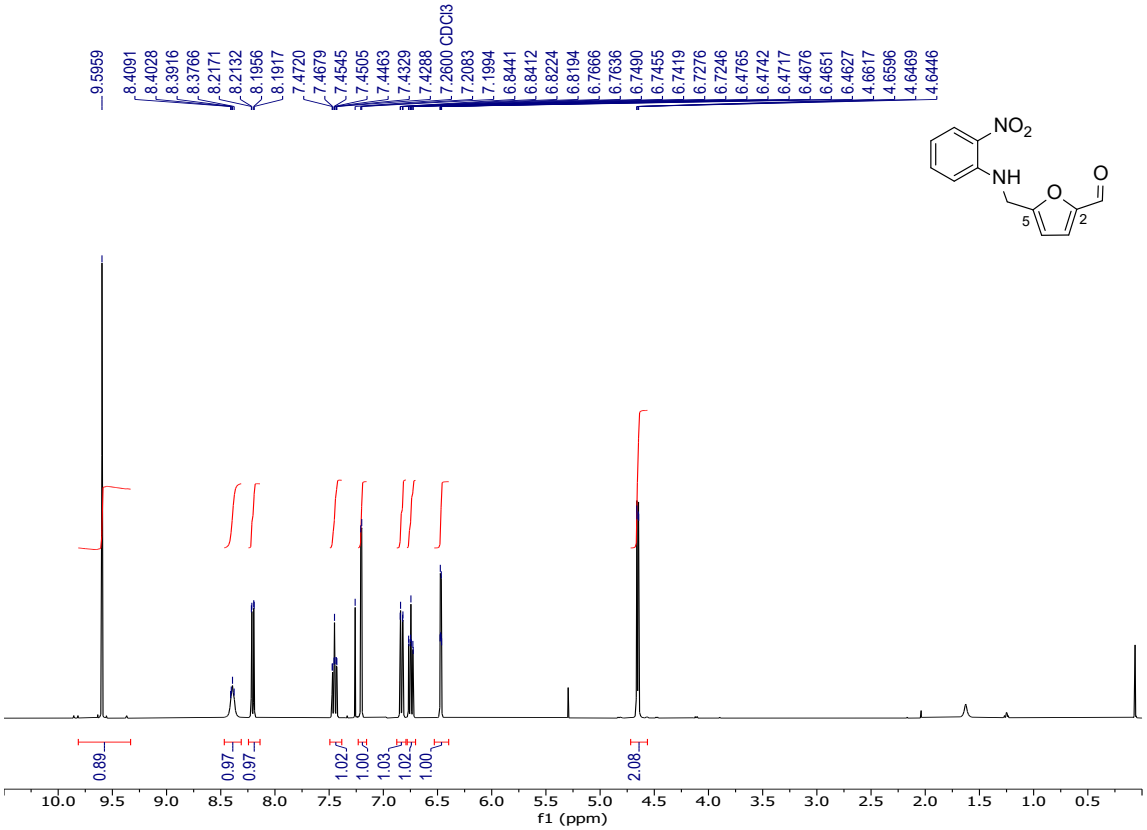




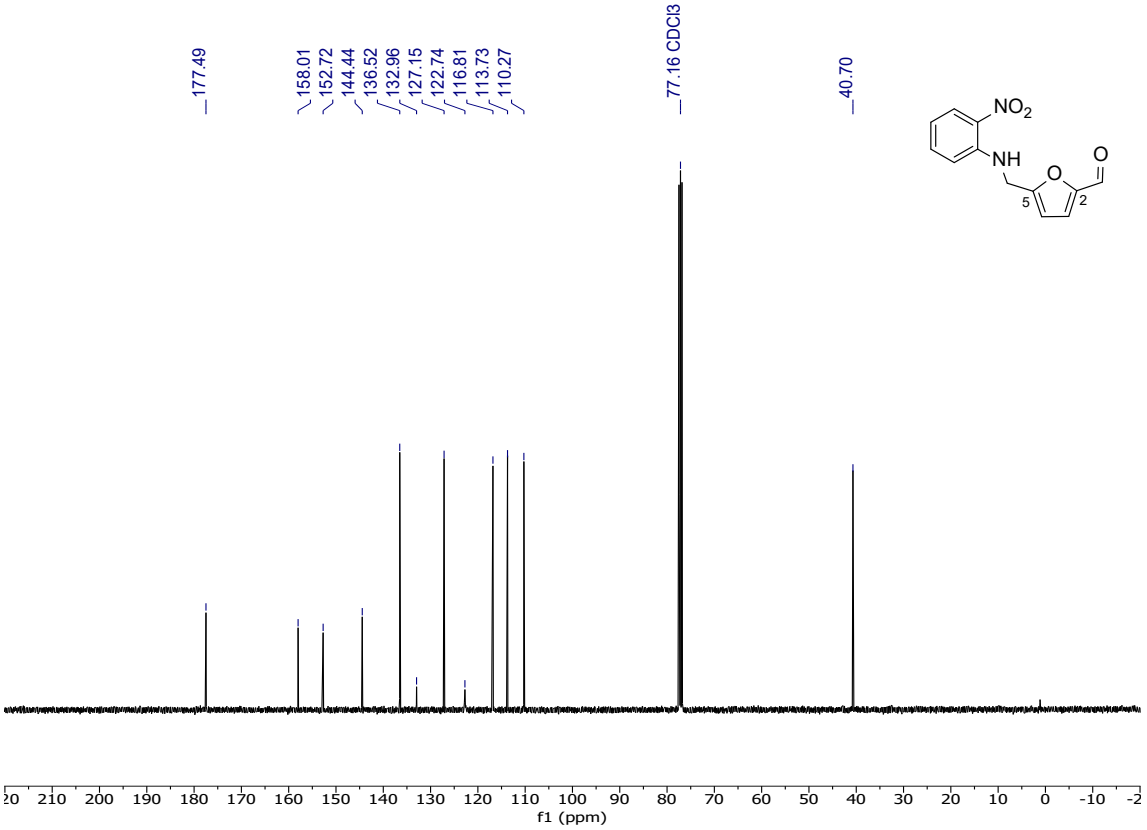
^{19}F NMR spectrum of 7-fluoro-2'-phenyl-2*H*,4*H*-spiro[[1,4]benzoxazine-3,1'-cyclopent[4]en]-3'-one 9n (376 MHz, $CDCl_3$)



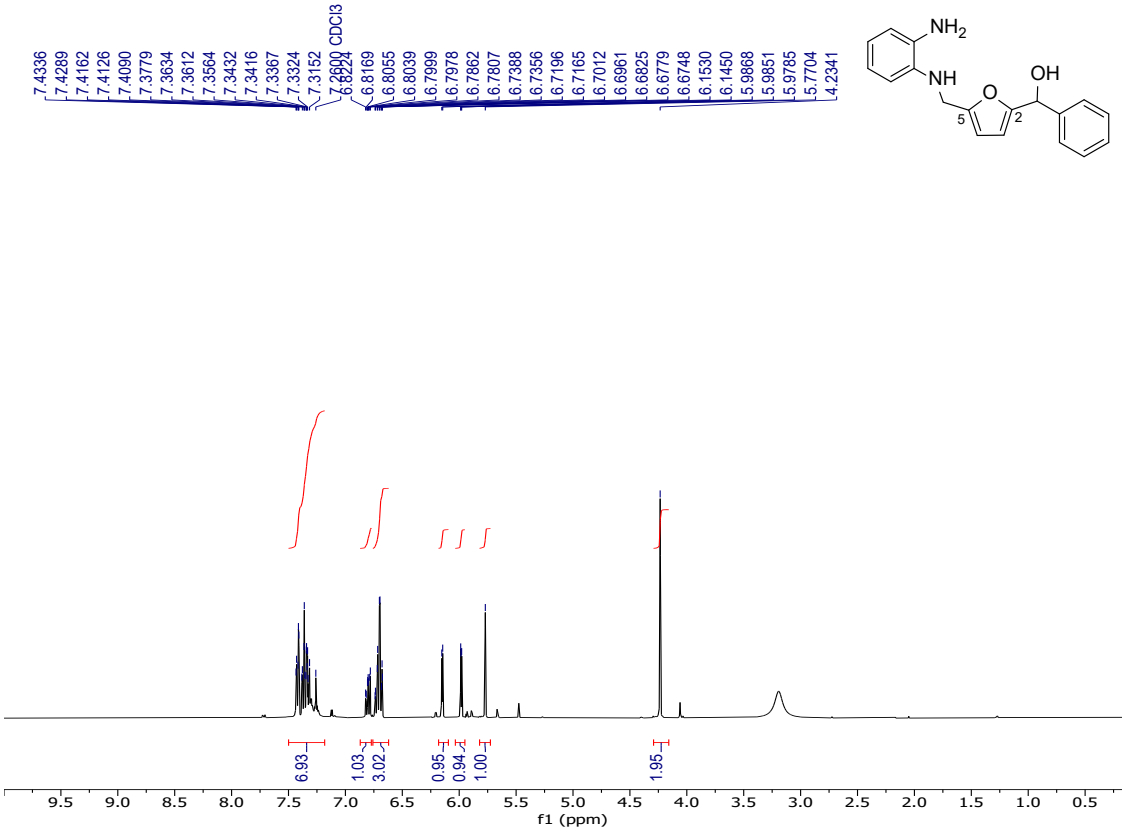
^{1}H NMR spectrum of 5-[(2-nitroanilino)methyl]furan-2-carbaldehyde S5o **(400 MHz, $CDCl_3$)**



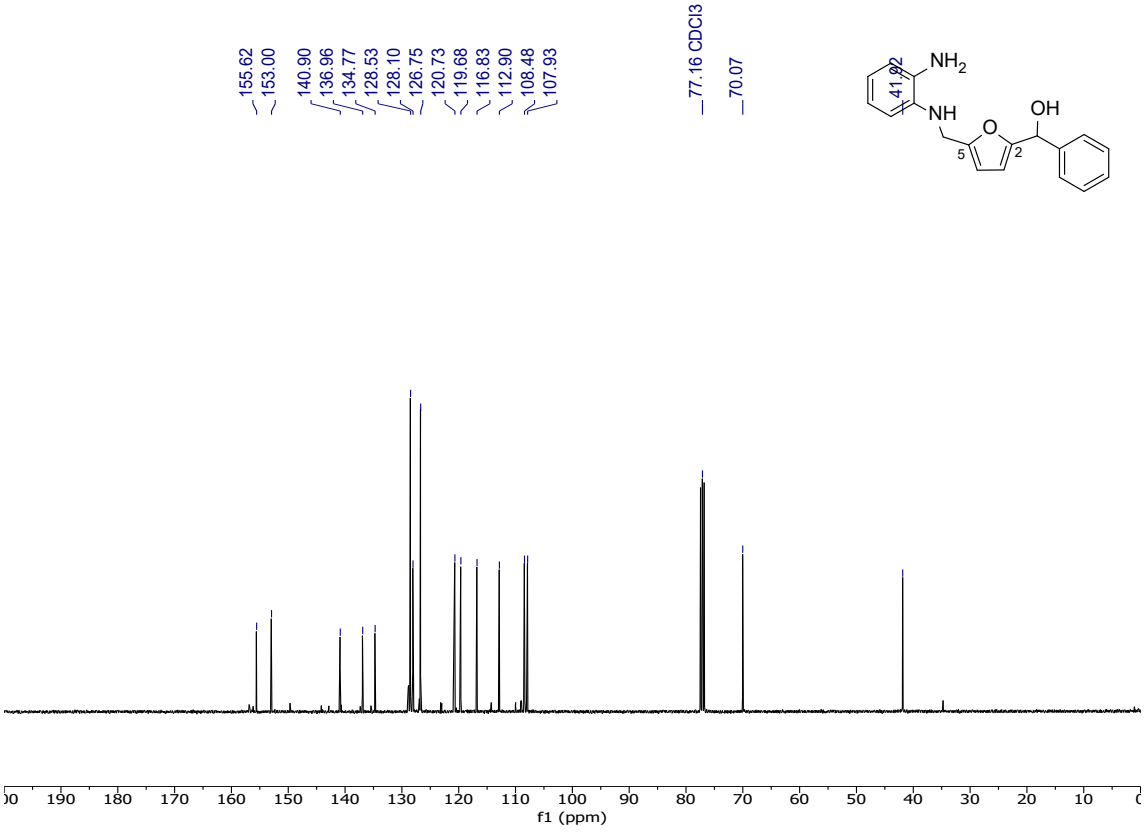
^{13}C NMR spectrum of 5-[(2-nitroanilino)methyl]furan-2-carbaldehyde S5o **(100 MHz, $CDCl_3$)**



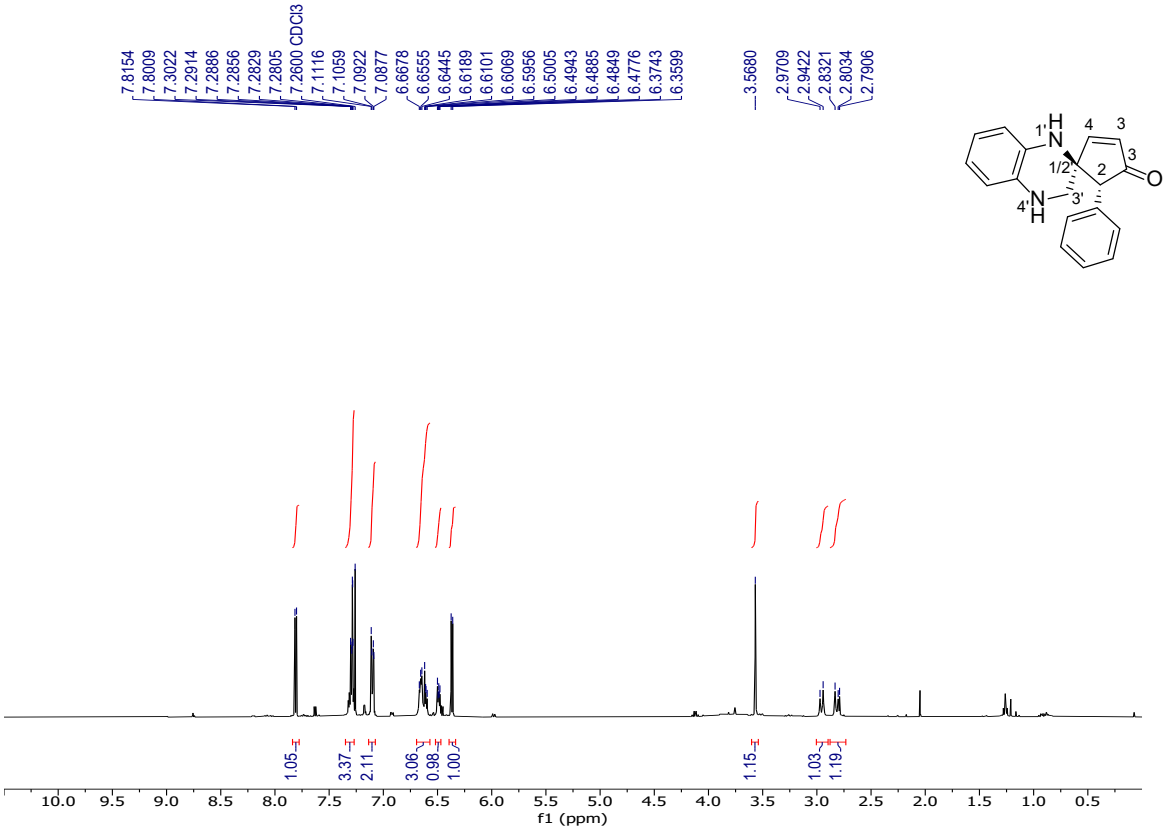
^{1}H NMR spectrum of {5-[(2-aminoanilino)methyl]furan-2-yl}(phenyl)methanol 8o **(400 MHz, $CDCl_3$)**



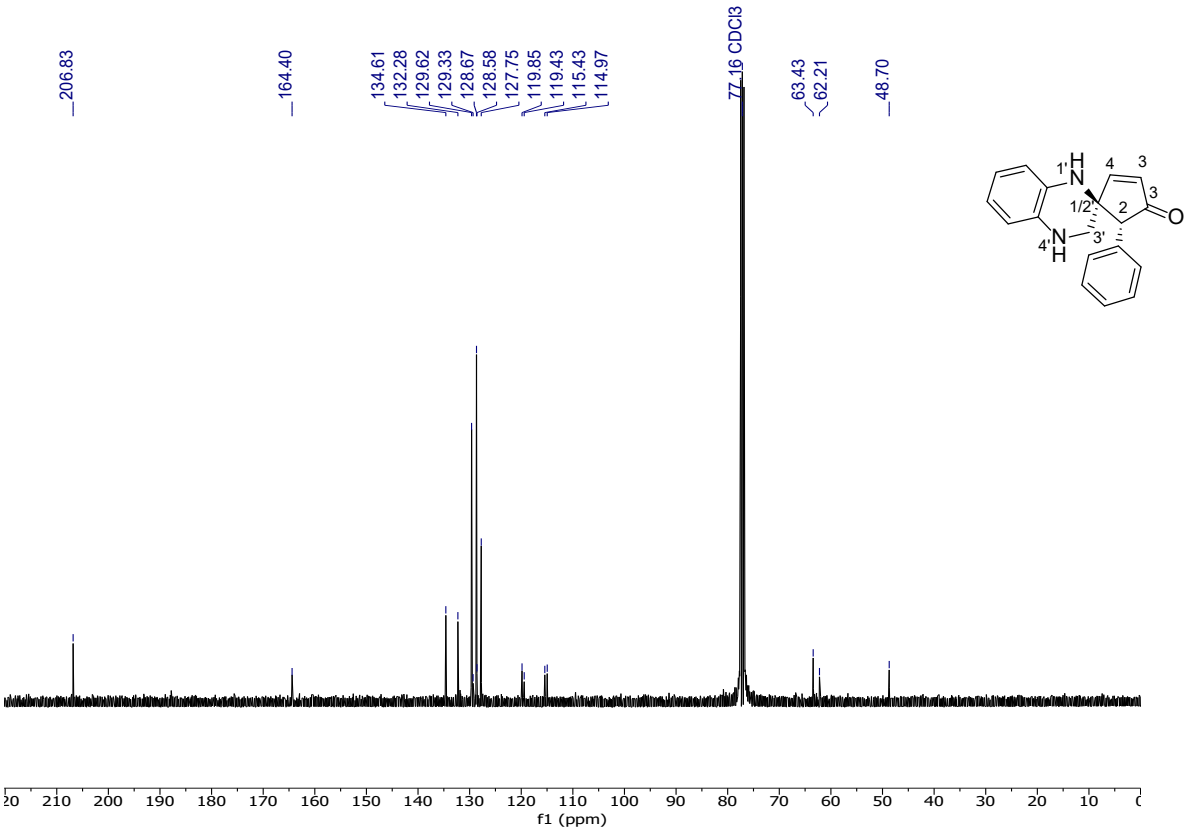
^{13}C NMR spectrum of {5-[(2-aminoanilino)methyl]furan-2-yl}(phenyl)methanol 8o **(100 MHz, $CDCl_3$)**



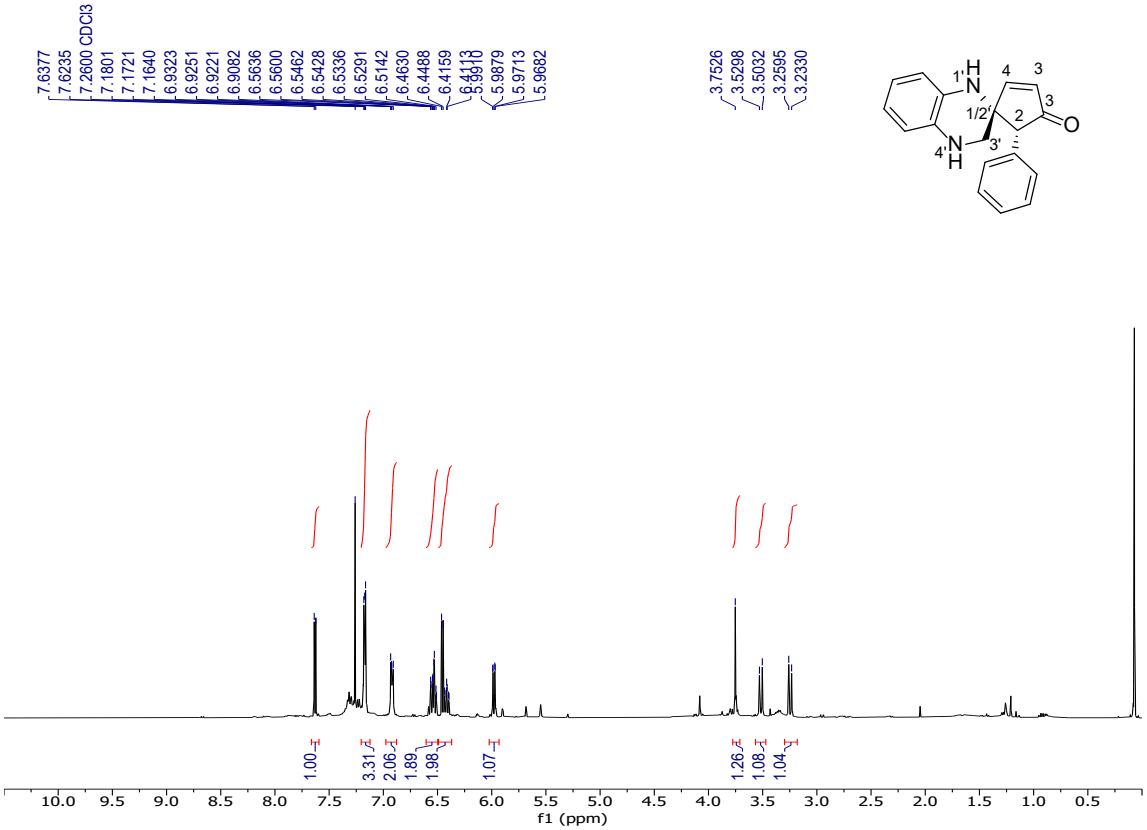
^{1}H NMR spectrum of 2-phenyl-3',4'-dihydro-1'H-spiro[cyclopent-4-ene-1,2'-quinoxalin]-3-one 11 **(400 MHz, $CDCl_3$)**



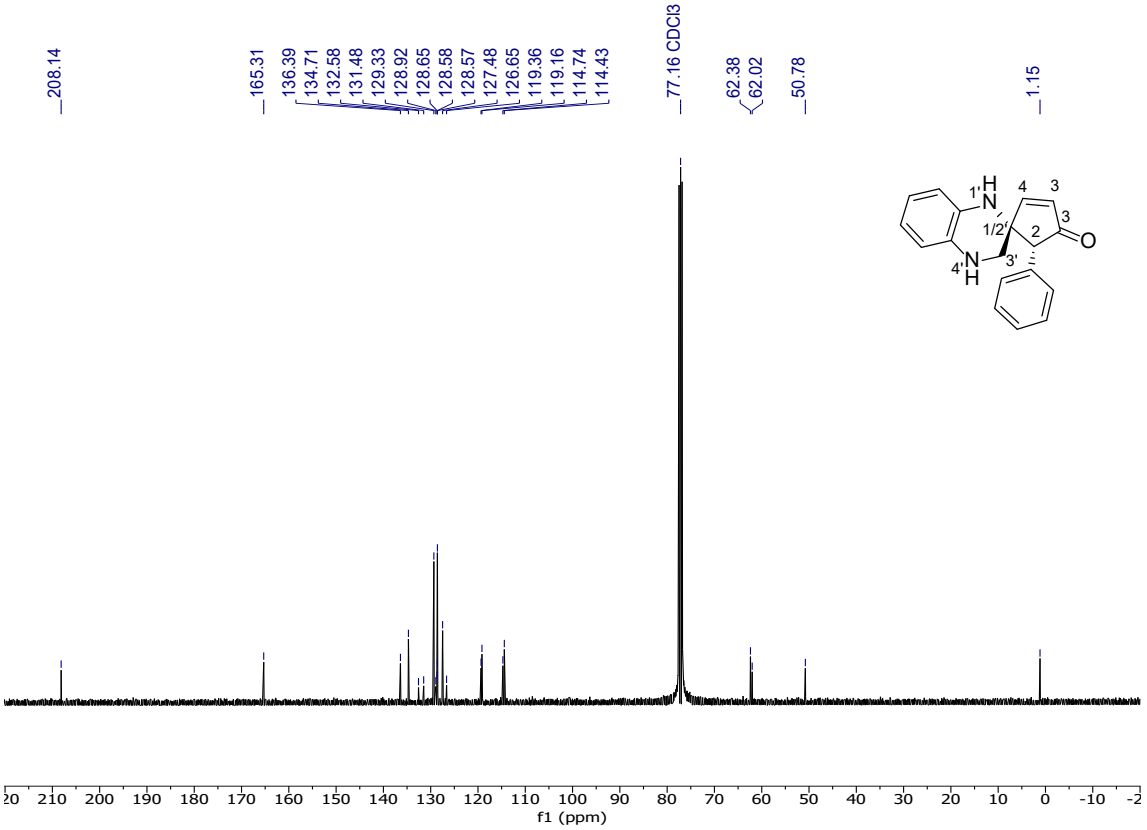
^{13}C NMR spectrum of 2-phenyl-3',4'-dihydro-1'H-spiro[cyclopent-4-ene-1,2'-quinoxalin]-3-one 11 **(100 MHz, $CDCl_3$)**



^{1}H NMR spectrum of 2-phenyl-3',4'-dihydro-1'H-spiro[cyclopent-4-ene-1,2'-quinoxalin]-3-one 11' (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 2-phenyl-3',4'-dihydro-1'H-spiro[cyclopent-4-ene-1,2'-quinoxalin]-3-one 11' (100 MHz, $CDCl_3$)



▪ X-Ray Analysis (CCDC Deposition Number 2454517

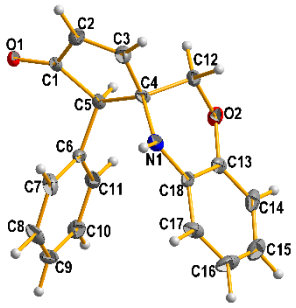
LGSpiroB_2_autored

Submitted by: **Sylvie Moebs-Sanchez**

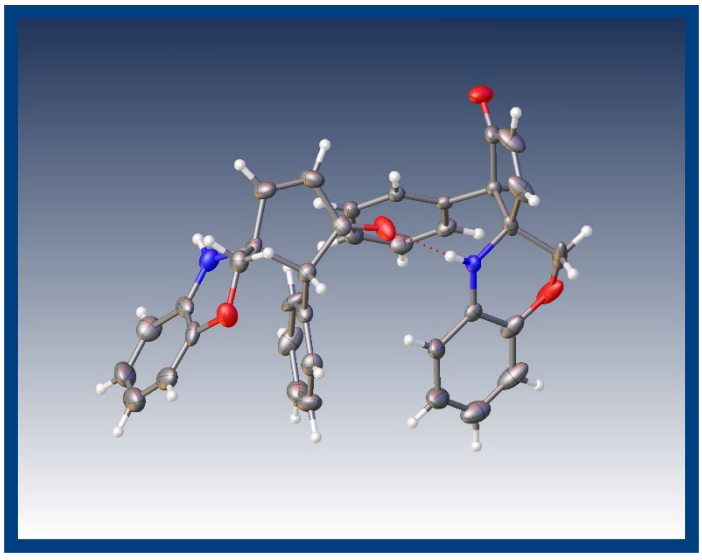
R_1=9.85%

Solved by: **Erwann Jeanneau**

Sample ID: **LGSpiroB** **Compound 9'**



Crystal Data and Experimental



Experimental. Single yellow block-shaped crystals of **LGSpiroB_2_autored** were used as supplied. A suitable crystal with dimensions 0.41 × 0.32 × 0.28 mm^3 was selected and mounted on a nylon loop in perfluoroether oil on a Xcalibur, Eos, Nova diffractometer. The crystal was kept at a steady T = 100.0(3) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{18}H_{15}NO_2$, M_r = 277.31, monoclinic, $P2_1/c$ (No. 14), a = 8.6178(2) Å, b = 25.2539(6) Å, c = 13.1075(3) Å, β = 100.733(2)°, $\alpha = \gamma = 90°$, V = 2802.72(11) Å^3, T = 100.0(3) K, Z = 8, Z' = 2, μ(Mo K$_\alpha$) = 0.086, 37413 reflections measured, 7018 unique (R_{int} = 0.0338) which were used in all calculations. The final wR_2 was 0.2740 (all data) and R_1 was 0.0985 (I≥2 σ(I)).

Compound	**LGSpiroB_2_autored**
Formula	$C_{18}H_{15}NO_2$
$D_{calc.}$/ g cm^{-3}	1.314
μ/mm^{-1}	0.086
Formula Weight	277.31
Colour	yellow
Shape	block-shaped
Size/mm^3	0.41×0.32×0.28
T/K	100.0(3)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	8.6178(2)
b/Å	25.2539(6)
c/Å	13.1075(3)
α/°	90
β/°	100.733(2)
γ/°	90
V/Å^3	2802.72(11)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	3.413
Θ_{max}/°	29.520
Measured Refl's.	37413
Indep't Refl's	7018
Refl's I≥2 σ(I)	5593
R_{int}	0.0338
Parameters	379
Restraints	0
Largest Peak	1.548
Deepest Hole	-0.462
GooF	1.036
wR_2 (all data)	0.2740
wR_2	0.2577
R_1 (all data)	0.1167
R_1	0.0985

Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=59.0° 0.72	I/σ(I) 34.6	Rint 3.38%	Full 50.5° 90% to 59.0° 99.7
Refinement:	Shift 0.001	Max Peak 1.6	Min Peak -0.5	GooF 1.036

A yellow block-shaped-shaped crystal with dimensions 0.41 × 0.32 × 0.28 mm^3 was mounted on a nylon loop in perfluoroether oil. Data were collected using a Xcalibur, Eos, Nova diffractometer operating at T = 100.0(3) K.

Data were measured using ω scans with Mo K$_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.42.54a (Rigaku OD, 2022). The maximum resolution that was achieved was Θ = 29.520° (0.72 Å).

The unit cell was refined using CrysAlisPro 1.171.42.54a (Rigaku OD, 2022) on 14931 reflections, 40% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.42.54a (Rigaku OD, 2022). The final completeness is 99.70 % out to 29.520° in Θ. A gaussian absorption correction was performed using CrysAlisPro 1.171.42.54a (Rigaku Oxford Diffraction, 2022) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient μ of this material is 0.086 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.431 and 1.000.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_exptl_absorpt_process_details: CrysAlisPro 1.171.42.54a (Rigaku Oxford Diffraction, 2022)Numerical absorption correction based on gaussian integration overa multifaceted crystal modelEmpirical absorption correction using spherical harmonics,implemented in SCALE3 ABSPACK scaling algorithm.

The value of Z' is 2. This means that there are two independent molecules in the asymmetric unit.

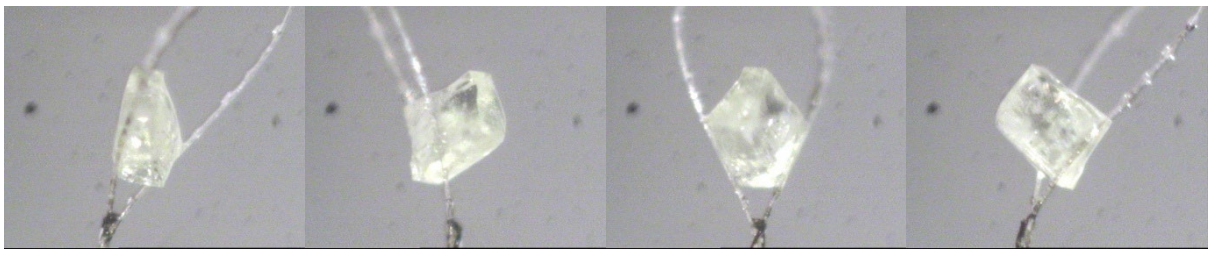


Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **LGSpiroB_2_autored**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	6072(3)	5260.8(8)	7756(2)	39.2(6)
O2	4223(3)	7134.3(9)	9160.7(17)	37.1(5)
N1	3043(3)	6785.7(10)	7121(2)	31.3(6)

Atom	x	y	z	U_{eq}
C1	5765(3)	5726.7(11)	7604(2)	26.8(6)
C2	6336(4)	6083.6(14)	6871(3)	38.1(7)
C3	5698(4)	6557.9(13)	6882(3)	36.0(7)
C4	4600(3)	6612.3(11)	7639(2)	27.1(6)
C5	4700(3)	6058.7(11)	8196(2)	25.7(6)
C6	3138(3)	5793.8(11)	8246(2)	27.7(6)
C7	2137(5)	5590.1(12)	7383(2)	37.2(8)
C8	700(4)	5369.6(14)	7478(3)	42.6(8)
C9	253(4)	5349.0(14)	8426(3)	39.4(8)
C10	1229(4)	5538.5(14)	9279(3)	39.0(8)
C11	2647(4)	5766.7(13)	9203(2)	32.9(7)
C12	5227(4)	7050.7(12)	8423(2)	31.4(6)
C13	2637(4)	7191.9(11)	8736(3)	32.7(7)
C14	1658(5)	7427.9(13)	9317(3)	45.2(9)
C15	88(6)	7474.5(16)	8949(4)	55.7(11)
C16	-512(5)	7307.9(18)	7978(4)	57.6(11)
C17	404(4)	7074.6(16)	7351(3)	44.0(8)
C18	2033(4)	7001.4(11)	7720(3)	33.1(7)
O3	7456(3)	3855.3(11)	5047.4(19)	41.7(6)
O4	4957(4)	3038.8(9)	8219.3(19)	52.1(8)
N2	5609(3)	4116.6(9)	8117.1(17)	21.5(5)
C19	7412(3)	3852.7(12)	5976(2)	28.7(6)
C20	8670(4)	4008.7(16)	6847(3)	44.3(9)
C21	8198(4)	3948.1(16)	7747(3)	44.9(9)
C22	6540(3)	3747.3(11)	7649(2)	25.3(6)
C23	6024(3)	3652.8(10)	6447.3(19)	20.1(5)
C24	4454(3)	3890.5(10)	5965.2(18)	18.2(5)
C25	3112(3)	3573.3(12)	5753(2)	26.3(6)
C26	1638(4)	3794.6(14)	5365(2)	33.4(7)
C27	1496(3)	4332.9(14)	5179(2)	33.2(7)
C28	2824(3)	4650.2(12)	5372(2)	27.3(6)
C29	4289(3)	4431.3(10)	5766.0(19)	20.8(5)
C30	6521(5)	3224.7(14)	8258(2)	47.0(11)
C31	4036(5)	3403.7(12)	8610(2)	37.4(8)
C32	4345(3)	3944.2(11)	8538.4(19)	22.9(5)
C33	3385(4)	4297.8(13)	8951(2)	32.3(6)
C34	2165(4)	4119.9(18)	9414(3)	47.8(9)
C35	1849(5)	3594(2)	9469(3)	54.4(11)
C36	2774(6)	3230.7(17)	9054(3)	52.8(11)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) for **LGSpiroB_2_autored**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	32.6(11)	20.3(10)	67.7(16)	-5.9(10)	17.2(11)	-1.8(8)
O2	40.7(13)	36.9(12)	31.4(11)	-5.2(9)	1.0(9)	7.7(10)
N1	35.0(13)	29.6(13)	26.6(12)	2.0(10)	-0.8(10)	-2.2(10)
C1	24.8(13)	22.5(13)	32.9(14)	-5.7(11)	4.7(11)	-4.5(10)
C2	40.7(17)	38.2(17)	41.1(18)	-7.2(14)	22.5(15)	-1.5(14)
C3	45.4(18)	31.4(16)	36.2(16)	1.3(12)	20.3(14)	-4.8(13)
C4	22.3(13)	21.9(13)	35.7(15)	9.7(11)	1.8(11)	-3.3(10)
C5	27.9(13)	23.2(13)	25.7(13)	-0.3(10)	4.0(11)	-2.9(10)
C6	23.7(13)	20.5(13)	39.9(16)	4.4(11)	8.8(11)	0.3(10)
C7	65(2)	27.3(15)	22.6(14)	2.7(11)	17.9(14)	-7.4(14)
C8	47.4(19)	40.0(18)	32.6(16)	5.4(14)	-12.6(14)	-17.9(15)
C9	26.4(15)	37.7(17)	56(2)	7.5(15)	12.2(14)	-3.0(13)
C10	47.4(19)	42.2(18)	31.7(16)	-2.0(13)	18.8(14)	-0.8(15)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	35.4(16)	33.5(16)	27.2(14)	-4.3(12)	-0.7(12)	-0.5(12)
C12	33.1(15)	24.2(14)	35.4(15)	-0.7(11)	2.5(12)	0.1(11)
C13	30.6(15)	20.0(13)	44.7(17)	12.2(12)	0.1(13)	1.0(11)
C14	68(2)	24.0(15)	49(2)	5.4(14)	25.4(18)	5.8(15)
C15	64(3)	39(2)	71(3)	10.0(19)	31(2)	15.5(18)
C16	36.3(19)	62(3)	78(3)	23(2)	20(2)	18.8(18)
C17	31.8(17)	49(2)	49(2)	3.9(16)	1.7(14)	-9.3(15)
C18	35.4(16)	16.5(12)	51.4(19)	6.2(12)	18.8(14)	0.5(11)
O3	28.0(11)	64.4(17)	34.8(12)	13.8(11)	11.5(9)	4.8(11)
O4	111(3)	20.9(11)	31.5(12)	-1.3(9)	30.5(14)	-5.1(13)
N2	28.8(11)	16.2(10)	20.0(10)	-1.4(8)	5.8(9)	3.2(8)
C19	20.5(13)	32.3(15)	34.0(15)	8.2(12)	7.2(11)	6.9(11)
C20	19.5(14)	51(2)	63(2)	-18.5(18)	9.8(14)	-2.3(13)
C21	22.6(14)	63(2)	45.1(19)	-28.7(17)	-5.3(13)	6.6(14)
C22	29.5(14)	26.7(13)	17.8(12)	-4.3(10)	-0.7(10)	10.8(11)
C23	22.5(12)	20.4(11)	17.7(11)	0.0(9)	4.4(9)	3.0(9)
C24	19.3(11)	22.1(12)	13.8(10)	-0.3(8)	4.5(9)	0.3(9)
C25	27.4(13)	28.0(14)	23.4(13)	2.5(10)	4.7(10)	-6.0(11)
C26	21.5(13)	47.1(18)	30.7(15)	1.2(13)	2.6(11)	-6.5(12)
C27	21.3(13)	50.2(19)	28.1(14)	6.8(13)	4.5(11)	7.7(12)
C28	29.0(14)	30.5(14)	23.7(13)	2.9(11)	8.3(11)	7.5(11)
C29	22.1(12)	22.7(12)	18.2(11)	-0.7(9)	5.1(9)	0.7(9)
C30	91(3)	31.6(16)	16.9(13)	0.6(11)	5.3(16)	34.7(19)
C31	64(2)	25.4(14)	22.0(14)	-0.7(11)	7.1(14)	-7.0(14)
C32	23.8(12)	26.1(13)	16.5(11)	2.2(9)	-2.2(9)	-0.8(10)
C33	24.7(14)	36.8(16)	35.4(15)	9.2(12)	6.0(12)	9.0(12)
C34	26.9(16)	67(3)	51(2)	19.3(18)	12.0(15)	10.8(16)
C35	39.7(19)	78(3)	46(2)	18(2)	8.4(16)	-12.2(19)
C36	75(3)	46(2)	34.0(18)	7.8(15)	3.1(18)	-30(2)

Table 3: Bond Lengths in Å for **LGSpiroB_2_autored**.

Atom	Atom	Length/Å
O1	C1	1.214(4)
O2	C12	1.428(4)
O2	C13	1.384(4)
N1	C4	1.454(4)
N1	C18	1.387(4)
C1	C2	1.467(4)
C1	C5	1.554(4)
C2	C3	1.319(5)
C3	C4	1.499(4)
C4	C5	1.572(4)
C4	C12	1.538(4)
C5	C6	1.515(4)
C6	C7	1.388(5)
C6	C11	1.398(4)
C7	C8	1.385(5)
C8	C9	1.369(5)
C9	C10	1.355(5)
C10	C11	1.372(5)
C13	C14	1.373(5)
C13	C18	1.420(5)
C14	C15	1.354(6)
C15	C16	1.349(7)
C16	C17	1.374(6)
C17	C18	1.410(5)

Atom	Atom	Length/Å
O3	C19	1.224(4)
O4	C30	1.419(6)
O4	C31	1.376(4)
N2	C22	1.440(3)
N2	C32	1.380(4)
C19	C20	1.474(5)
C19	C23	1.531(4)
C20	C21	1.326(6)
C21	C22	1.500(5)
C22	C23	1.573(3)
C22	C30	1.544(4)
C23	C24	1.507(3)
C24	C25	1.391(4)
C24	C29	1.393(4)
C25	C26	1.394(4)
C26	C27	1.382(5)
C27	C28	1.381(4)
C28	C29	1.387(4)
C31	C32	1.397(4)
C31	C36	1.396(5)
C32	C33	1.393(4)
C33	C34	1.384(5)
C34	C35	1.360(6)
C35	C36	1.390(7)

Table 4: Bond Angles in ° for **LGSpiroB_2_autored**.

Atom	Atom	Atom	Angle/°
C13	O2	C12	114.9(2)
C18	N1	C4	118.4(3)
O1	C1	C2	127.8(3)
O1	C1	C5	124.9(3)
C2	C1	C5	107.3(2)
C3	C2	C1	111.1(3)
C2	C3	C4	113.9(3)
N1	C4	C3	111.1(3)
N1	C4	C5	116.8(2)
N1	C4	C12	105.9(2)
C3	C4	C5	103.8(2)
C3	C4	C12	108.8(2)
C12	C4	C5	110.4(2)
C1	C5	C4	103.6(2)
C6	C5	C1	113.3(2)
C6	C5	C4	116.2(2)
C7	C6	C5	123.4(3)
C7	C6	C11	117.9(3)
C11	C6	C5	118.7(3)
C8	C7	C6	120.4(3)
C9	C8	C7	120.3(3)
C10	C9	C8	120.0(3)
C9	C10	C11	120.8(3)
C10	C11	C6	120.6(3)
O2	C12	C4	112.2(2)
O2	C13	C18	120.2(3)
C14	C13	O2	119.0(3)
C14	C13	C18	120.8(3)
C15	C14	C13	121.1(4)
C16	C15	C14	119.4(4)
C15	C16	C17	122.4(4)
C16	C17	C18	119.8(4)
N1	C18	C13	120.3(3)
N1	C18	C17	123.1(3)
C17	C18	C13	116.4(3)
C31	O4	C30	112.0(3)
C32	N2	C22	120.7(2)
O3	C19	C20	127.9(3)
O3	C19	C23	125.0(3)
C20	C19	C23	107.0(3)
C21	C20	C19	110.8(3)
C20	C21	C22	114.1(3)
N2	C22	C21	110.0(2)
N2	C22	C23	116.7(2)
N2	C22	C30	105.8(2)
C21	C22	C23	103.0(2)
C21	C22	C30	110.3(3)
C30	C22	C23	111.1(2)
C19	C23	C22	104.9(2)
C24	C23	C19	114.0(2)
C24	C23	C22	115.1(2)
C25	C24	C23	120.1(2)
C25	C24	C29	118.4(2)
C29	C24	C23	121.4(2)
C24	C25	C26	120.6(3)
C27	C26	C25	120.2(3)
C28	C27	C26	119.7(3)
C27	C28	C29	120.2(3)
C28	C29	C24	121.0(3)
O4	C30	C22	111.4(3)
O4	C31	C32	119.9(3)
O4	C31	C36	119.6(3)
C36	C31	C32	120.5(3)
N2	C32	C31	120.6(3)
N2	C32	C33	121.6(3)
C33	C32	C31	117.7(3)
C34	C33	C32	121.2(3)
C35	C34	C33	121.0(4)
C34	C35	C36	119.3(3)
C35	C36	C31	120.3(4)

Table 5: Torsion Angles in ° for **LGSpiroB_2_autored**.

Atom	Atom	Atom	Atom	Angle/°
O1	C1	C2	C3	177.1(3)
O1	C1	C5	C4	-175.8(3)
O1	C1	C5	C6	-49.1(4)
O2	C13	C14	C15	-177.5(3)
O2	C13	C18	N1	-4.0(4)
O2	C13	C18	C17	179.7(3)
N1	C4	C5	C1	117.7(3)
N1	C4	C5	C6	-7.2(4)
N1	C4	C12	O2	59.3(3)
C1	C2	C3	C4	1.1(4)
C1	C5	C6	C7	-50.3(4)
C1	C5	C6	C11	131.8(3)
C2	C1	C5	C4	5.7(3)
C2	C1	C5	C6	132.4(3)

Atom	Atom	Atom	Atom	Angle/°
C2	C3	C4	N1	-123.7(3)
C2	C3	C4	C5	2.6(4)
C2	C3	C4	C12	120.2(3)
C3	C4	C5	C1	-4.9(3)
C3	C4	C5	C6	-129.8(3)
C3	C4	C12	O2	178.8(2)
C4	N1	C18	C13	18.3(4)
C4	N1	C18	C17	-165.6(3)
C4	C5	C6	C7	69.4(4)
C4	C5	C6	C11	-108.4(3)
C5	C1	C2	C3	-4.4(4)
C5	C4	C12	O2	-67.9(3)
C5	C6	C7	C8	-177.7(3)
C5	C6	C11	C10	178.9(3)
C6	C7	C8	C9	-0.2(5)
C7	C6	C11	C10	0.9(5)
C7	C8	C9	C10	-0.9(6)
C8	C9	C10	C11	2.0(6)
C9	C10	C11	C6	-2.0(5)
C11	C6	C7	C8	0.2(5)
C12	O2	C13	C14	-160.5(3)
C12	O2	C13	C18	20.5(4)
C12	C4	C5	C1	-121.3(3)
C12	C4	C5	C6	113.8(3)
C13	O2	C12	C4	-49.2(3)
C13	C14	C15	C16	-3.0(6)
C14	C13	C18	N1	177.0(3)
C14	C13	C18	C17	0.7(4)
C14	C15	C16	C17	2.1(7)
C15	C16	C17	C18	0.1(6)
C16	C17	C18	N1	-177.7(3)
C16	C17	C18	C13	-1.5(5)
C18	N1	C4	C3	-161.6(3)
C18	N1	C4	C5	79.6(3)
C18	N1	C4	C12	-43.7(3)
C18	C13	C14	C15	1.5(5)
O3	C19	C20	C21	-179.4(3)
O3	C19	C23	C22	-178.7(3)
O3	C19	C23	C24	-51.9(4)
O4	C31	C32	N2	-2.7(4)
O4	C31	C32	C33	-179.7(3)
O4	C31	C36	C35	178.9(3)
N2	C22	C23	C19	116.3(3)
N2	C22	C23	C24	-9.9(4)
N2	C22	C30	O4	58.2(3)
N2	C32	C33	C34	-177.0(3)
C19	C20	C21	C22	-0.7(5)
C19	C23	C24	C25	138.0(3)
C19	C23	C24	C29	-45.0(3)
C20	C19	C23	C22	4.1(3)
C20	C19	C23	C24	130.9(3)
C20	C21	C22	N2	-121.8(3)
C20	C21	C22	C23	3.2(4)
C20	C21	C22	C30	121.8(3)
C21	C22	C23	C19	-4.3(3)
C21	C22	C23	C24	-130.5(3)
C21	C22	C30	O4	177.2(2)
C22	N2	C32	C31	6.3(4)
C22	N2	C32	C33	-176.9(3)
C22	C23	C24	C25	-100.6(3)

Atom	Atom	Atom	Atom	Angle/°
C22	C23	C24	C29	76.4(3)
C23	C19	C20	C21	-2.3(4)
C23	C22	C30	O4	-69.3(3)
C23	C24	C25	C26	176.1(2)
C23	C24	C29	C28	-176.6(2)
C24	C25	C26	C27	0.6(4)
C25	C24	C29	C28	0.4(4)
C25	C26	C27	C28	0.4(5)
C26	C27	C28	C29	-1.0(4)
C27	C28	C29	C24	0.5(4)
C29	C24	C25	C26	-1.0(4)
C30	O4	C31	C32	29.5(4)
C30	O4	C31	C36	-152.1(3)
C30	C22	C23	C19	-122.3(3)
C30	C22	C23	C24	111.5(3)
C31	O4	C30	C22	-58.2(3)
C31	C32	C33	C34	-0.1(5)
C32	N2	C22	C21	-151.2(3)
C32	N2	C22	C23	92.0(3)
C32	N2	C22	C30	-32.1(3)
C32	C31	C36	C35	-2.6(5)
C32	C33	C34	C35	-1.0(5)
C33	C34	C35	C36	0.3(6)
C34	C35	C36	C31	1.5(6)
C36	C31	C32	N2	178.8(3)
C36	C31	C32	C33	1.9(5)

Table 6: Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **LGSpiroB_2_autored**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H1	2747.44	6754.55	6444.11	38
H2	7068.82	5985.97	6445.38	46
H3	5914.36	6839.66	6449.01	43
H5	5282.37	6108.36	8923.65	31
H7	2440.17	5602.01	6722.41	45
H8	21.25	5231.98	6882.31	51
H9	-741.07	5201.92	8485.44	47
H10	926.53	5512.93	9938.44	47
H11	3301.22	5907.58	9805.46	39
H12A	6295.9	6952.98	8795.09	38
H12B	5317.34	7384.83	8043.24	38
H14	2088.72	7560.45	9988.38	54
H15	-584.62	7623.39	9370.77	67
H16	-1608.72	7353.57	7718.25	69
H17	-60.05	6962.85	6670.16	53
H2A	5848.02	4455.62	8134.83	26
H20	9681.2	4135.4	6773.03	53
H21	8853.85	4025.13	8396.25	54
H23	5945.62	3261.55	6331.58	24
H25	3201.27	3202.67	5872.85	32
H26	728.77	3574.82	5228.75	40
H27	489.97	4483.68	4919.3	40
H28	2732.9	5019.39	5235.5	33
H29	5193.24	4653.54	5901.7	25
H30A	7135.84	2953	7960.29	56
H30B	7032.85	3281.83	8990.39	56

Atom	x	y	z	U_{eq}
H33	3570.51	4667.41	8913.01	39
H34	1537.44	4369.01	9699.32	57
H35	1005.59	3476.14	9786.11	65
H36	2546.27	2863.22	9073.75	63

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