Supporting Information

The Piancatelli rearrangement of AMF (5-azidomethylfurfural) derivatives: a biobased opportunity for the synthesis of nitrogenous cyclopentenones

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I. General information

Reactions were performed using oven dried glasswares under an atmosphere of argon. Reagents and catalyst were obtained from commercial suppliers and used without further purification. All separations were carried out under flash-chromatographic conditions on silica gel (Redi Sep prepacked column, 230–400 mesh) at medium pressure (20 psi) with use of a CombiFlash Companion or preparative HPLC. Reactions were monitored by thin-layer chromatography on Merck silica gel plates (60 F254 aluminum sheets) which were rendered visible by ultraviolet and spraying with vanillin (15%) + sulfuric acid (2.5%) in EtOH followed by heating. Reagent-grade chemicals were obtained from diverse commercial suppliers and used as received.

Microwave-assisted reactions were performed using an Anton Paar Monowave 300 Microwave Synthesis Reactor, using borosilicate glass standard vials G10 or G30. Sealed reaction vessels were used. The reaction temperature was monitored with an external surface sensor and was maintained in each experiment.

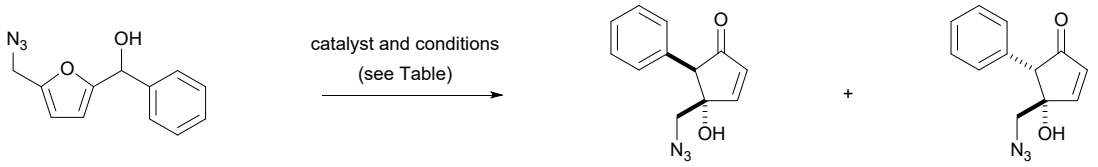
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded with Brüker-Avance 500 MHz and 300 MHz instruments at 298 K unless otherwise stated. Chemical shifts are given in ppm (δ) and are referenced to the internal solvent signal. The following calibration values have been used for ^{1}H NMR: acetone-d_6 (2.05 ppm) and $CDCl_3$ (7.26 ppm); for ^{13}C NMR: acetone-d_6 (29.84 ppm) and $CDCl_3$ (77.16 ppm). Multiplicities are declared as follow: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublet), m (multiplet), bs (broad signal). Coupling constants *J* are given in Hz. Carbon multiplicities were determined by DEPT135 experiment.

Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system using diamond window Dura SamplIR II and the data are reported in reciprocal centimeters (cm^{-1}).

High-resolution mass spectrometry (HRMS) was performed using electrospray ionization (ESI) and time-of-flight (TOF) analyzer, in positive-ion or negative-ion detection mode.

II. Full optimization reaction conditions on substrate 6a

Table S1 Screening and optimization reaction for Piancatelli rearrangement on (5-(azidomethyl)furan-2-yl)phenyl-carbinol **6a**[a]



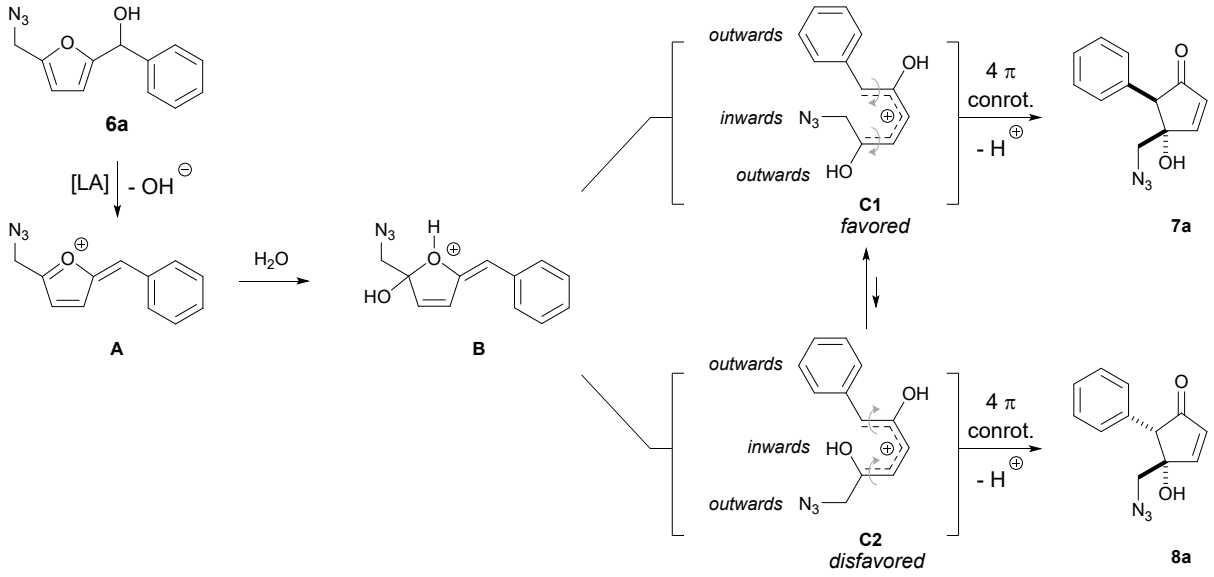
6a **7a** **8a**

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (h)	Conv (%)	NMR Yield (%)[b]	Isolated Yield (%)	d.r.[c] **7a**/**8a**
1	-	*t*-BuOH/H_2O 5:1	MW-190	0.08	decomp.	-	-	-
2	-	*t*-BuOH/H_2O 5:1	MW-100	1.5	0	-	-	-
3	$DyCl_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	40	10	ND	80:20
4	$DyCl_3$ (50)	*t*-BuOH/H_2O 5:1	MW-100	1.5	50	15	ND	80:20
5	$Dy(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	60	50	46	>95:5
6	$Dy(OTf)_3$ (20)	*t*-BuOH/H_2O 5:1	MW-100	1.5	60	45	ND	85:15
7	$Dy(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	3	80	35	ND	85:15
8	$Dy(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-150	1.5	100	30	25	50:50
9	$Dy(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	CH-80	18	35	10	ND	75:25
10	$Dy(OTf)_3$ (10) + TFA (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	75	25	ND	ND
11	$Dy(TMHD)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	0	NA	NA	NA
12	$Yb(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	70	30	ND	85:15
13	$Yb(OTf)_3$ (10)	HFIP/H_2O 2:1	CH-80	16	90	30	ND	70:30
14	$Ce(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	80	20	ND	ND
15	$Sc(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	75	35	ND	80:20
16	$ScCl_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	70	40	37	95:5
17	$ScCl_3$ (10)	*t*-BuOH/H_2O 5:1	MW-150	1.5	80	10	ND	ND
18	$Sc(NTf_2)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	0	NA	NA	NA
19	$Y(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	65	35	ND	90:10
20	$Fe(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	80	20	ND	90:10
21	$Co(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	70	30	ND	85:15
22	$HAuCl_4.3H_2O$ (10)	*t*-BuOH/H_2O 5:1	CH-80	6	100	10	ND	ND
23	$HAuCl_4.3H_2O$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	100	10	ND	ND
24	$Al(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	85	25	ND	85:15
25	$Zn(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	65	10	ND	ND
26	$InCl_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	60	20	ND	90:10
27	$In(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	80	20	ND	90:10
28	$BiCl_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	70	20	ND	90:10
29	$Bi(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	75	15	ND	ND
30	$Ca(NTf_2)_2$ (5) + *n*-Bu_4NPF_6 (5)	HFIP/H_2O 5:1	CH-60	18	80	10	ND	ND
31	$Ca(NTf)_2$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	0	NA	NA	NA
32	$Ba(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	70	20	ND	ND
33	$B(C_6F_5)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	50	25	ND	90:10
34	$(C_6HF_4)B(OH)_2$ (20)	CH_3CN/H_2O 5:1	CH-90	24	70	0	NA	NA
35	BINOL.PA (10)	HFIP/H_2O 2:1	20	18	100	0	NA	NA
36	BINOL.PA (10)	*t*-BuOH/H_2O 5:1	CH-50	18	90	25	ND	ND
37	TFA (20)	*t*-BuOH/H_2O 5:1	MW-100	1.5	100	15	ND	90:10
38[d]	$Dy(OTf)_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	60	50	34[e]	>95:5
39[d]	$ScCl_3$ (10)	*t*-BuOH/H_2O 5:1	MW-100	1.5	65	25	18	95:5

[a] Reactions performed on 0.2 mmol scale at 0.1 *M*. [b] Yield determined by ^1H NMR with trimethoxybenzene as internal standard added at the end of the reaction. [c] The diastereoisomeric ratio (d.r.) was determined by ^1H NMR on the crude mixture. [d] Sodium dithionite ($Na_2S_2O_4$) in a 3 mass percentage was added. [e] 37% of the starting material **6a** was recovered. MW = microwave heating. CH = conventional heating. ND = not determined. NA = not applicable. TMHD = tris(2,2,6,6-tetramethyl-3,5-heptanedionato).

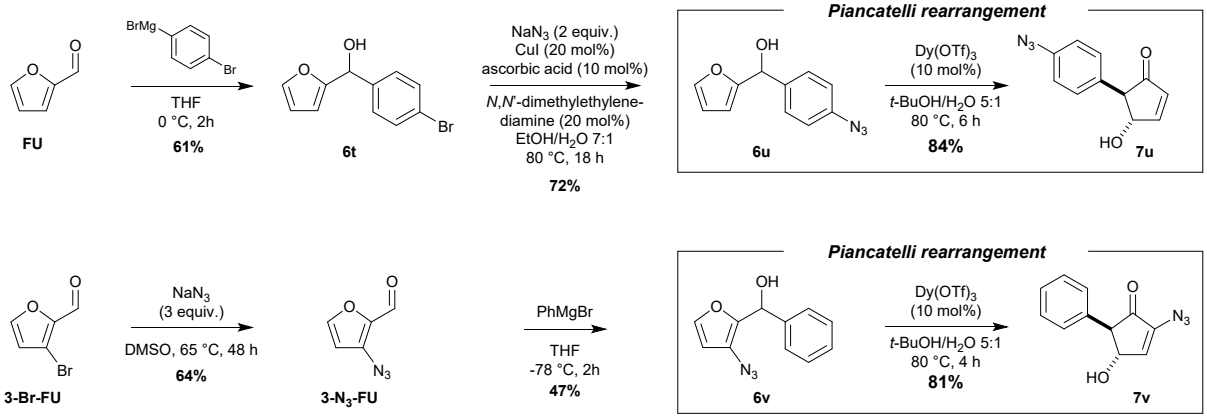
III. Mechanistic considerations for diastereoselectivity rationalization

The proposed reaction pathway to produce the desired 4-(azidomethyl)-4-hydroxycyclopentenone **7a** followed the accepted mechanism of Piancatelli rearrangement.[1] First, substrate **6a** undergoes a dehydration reaction of the carbinol moiety to generate the furanoxonium ion intermediates **A**.[2] The nucleophilic attack of a water molecule on C5 position of furan ring then generates intermediate **B** which undergoes ring opening to generate the pentadienyl cation **C**. At this stage, two pentadienyl cation **C** are in equilibrium. At one end of these pentadienyl cation **C**, the phenyl ring is located *outwards* while the less hindered hydrogen atom (not shown) is located *inwards* with respect to the delocalized charged system. The two pentadienyl cations are distinguished by the geometry of the substituents at the other end. **C1** set up the azidomethyl group in *inwards* position and OH group in *outwards* position. In contrast, **C2** set up OH group in *inwards* position and azidomethyl group in *outwards* position. Considering the destabilizing *syn*-pentane and *syn*-hexane interactions for these two intermediates,[3] pentadienyl cation **C1** is favored compare to **C2**. A pericyclic conrotatory 4π-electrocyclization,[4] closely related to the Nazarov process, is the determining step for the diastereoselectivity: the phenyl arylic and OH groups in the final product **7a** are in a *trans* relative configuration.

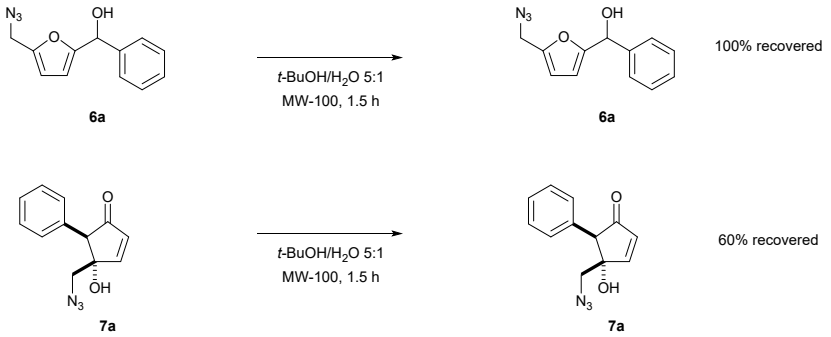


Scheme S1 Reaction pathway for the Piancatelli rearrangement of (5-(azidomethyl)furan-2-yl)-carbinol derivatives and proposed intermediates to rationalize the diastereoselectivity.

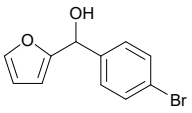
IV. Additional experiments



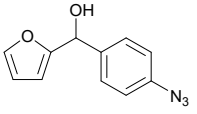
Scheme S2 Changes in the position of the azide function.



Scheme S3 Relative stability test of the substrate **6a** and product **7a** under the reaction conditions.

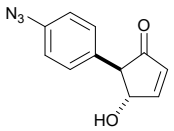


(4-Bromophenyl)(furan-2-yl)methanol (6t). Magnesium turnings (3 eq.) were heated with heatgun for 20 min under vacuum. Flask was then cooled to room temperature, and crystals of diiode were added with THF (1.7 mL/mmol of furan-2-carbaldehyde. To this mixture were added few drops 1,2-dibromoethane under argon to initiate the reaction. 1,4-dibromobenzene (1.7 eq) was then added dropwise, and the reaction mixture was refluxed for 1 h under argon. The mixture was cooled to 0 °C and a solution of furan-2-carbaldehyde (1.72 mL, 20.8 mmol, 1.0 eq) in THF (3.4 mL/mmol of furan-2-carbaldehyde) was added dropwise. After stirring for 2 h at 0 °C, the reaction was quenched with a saturated solution of NH_4Cl. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate 90:10 to 70:30 to afford the desired compound as a pale yellow oil (3.23 g, 61% yield). Characterization data is in accordance with those reported in the literature: Das, M.; O'Shea, D. F. Bu_4N^+ Alkoxide-Initiated/Autocatalytic Addition Reactions with Organotrimethylsilanes. *J. Org. Chem.* **2014**, *79*, 5595-5607. doi:10.1021/jo5007637.

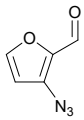


(4-Azidophenyl)(furan-2-yl)methanol (6u). (4-Bromophenyl)(furan-2-yl)methanol (300 mg, 1.19 mmol) **6t** was added to a suspension of ascorbic acid (23 mg, 0.118 mmol, 10 mol%), CuI (45 mg, 0.237 mmol, 20 mol%), *N*,*N*'-

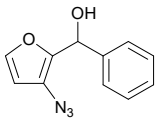
dimethylethylenediamine (25 µL, 0.237 mmol, 20 mol%), NaN_3 (154 mg, 2.37 mmol, 2 eq.) in EtOH/H2O (7:1, 0.07 *M*). The mixture was then heated at 80 °C for 18 h. After cooling to room temperature, the mixture was quenched with $NaHCO_3$, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel petroleum ether/ethyl acetate (98:2 to 70:30) to afford the compound (183 mg, 72% yield) as a yellow oil. R_f 0.5 (70% PET/EtOAc).
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.40-7.44 (m, 2H), 7.39-7.40 (m, 1H), 7.00-7.06 (m, 2H), 6.31-6.34 (m, 1H), 6.12 (d, *J* = 3.2 Hz, 1H), 5.79-5.82 (m, 1H), 2.49 (bs, 1H).
^{13}C-NMR ($CDCl_3$, 126 MHz) δ 155.7 (C), 142.8 (CH), 139.9 (C), 137.6 (C), 128.2 (2xCH), 119.2 (2xCH), 110.4 (CH), 107.6 (CH), 69.6 (CH).
IR (ν/cm^{-1}) 3367, 2115, 1606, 1505, 1284, 1178, 1141, 1128, 1008, 927, 839, 469, 736.
HRMS (ESI) m/z calculated for $C_{11}H_7NO$ ($[M-N_2-H_2O+H]^+$) 170.0600 , found 170.0603.



(4*S,5*R**)-5-(4-Azidophenyl)-4-hydroxycyclopent-2-en-1-one (7u).** (4-azidophenyl)(furan-2-yl)methanol **6u** (50 mg, 0.23 mmol) was diluted in *t*-BuOH/H_20 (5:1, 0.1*M*), and $Dy(OTf)_3$ (14 mg, 0.02 mmol, 10 mol%) was introduced. Reacting mixture was stirred at 80 °C for 6 h. After cooling to room temperature, the mixture was quenched with a saturated solution of $NaHCO_3$, and extracted with EtOAc. The combined organic layers were washed with brine dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel using heptane/ethyl acetate 90:10 to 40:60 to afford the compound **7u** with 84% yield (42 mg). R_f 0.20 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 400 MHz) δ 7.72 (dd, *J* = 5.7 Hz, 2.1 Hz, 1H), 7.20-7.25 (m, 2H), 7.03-7.09 (m, 2H), 6.25 (dd, *J* = 5.7 Hz, 1.1 Hz, 1H), 5.02 (d, *J* = 6.4 Hz, 1H), 4.95-4.99 (m, 1H), 3.42 (d, *J* = 2.6 Hz, 1H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 205.4 (C), 164.3 (CH), 139.4 (C), 136.1 (C), 133.7 (CH), 130.9 (2xCH), 119.9 (2xCH), 79.1 (CH), 62.2 (CH).
IR (ν/cm^{-1}) 3399, 2122, 2090, 1696, 1605, 1506, 1335, 1283, 1185, 1105, 1031, 880, 813, 467.
HRMS (ESI) m/z calculated for $C_{11}H_7NO$ ($[M-N_2-H_2O+H]^+$) 170.0600 , found 170.0602.



3-Azidofuran-2-carbaldehyde (3-N_3-FU). To a solution of 3-bromofuran-2-carbaldehyde (200 mg, 1.14 mmol) in DMSO (0.6 *M*) was added NaN_3 (3 eq.). The mixture was stirred at 65 °C for 48 h. After cooling to room temperature, water (15 mL) was added, and extracted with diethyl ether (2x10 mL). Organic layers were then washed with water (4x5 mL), brine (1x5 mL), dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The final product was obtained as a brown powder (102 mg, 64% yield) and used further without purification. Characterization data is in accordance with those reported in the literature: Liu, J.; Wu, Z.; Yang, Y.; Qian, W.; Wang, L.; Zeng, X. 3-Nitrene-2-formylthiophene and 3-Nitrene-2-formylfuran: Matrix Isolation, Conformation, and Rearrangement Reactions. *J. Phys. Chem. A* **2020**, *124*, 3786-3794. doi:10.1021/acs.jpca.9b11638.



(3-Azidofuran-2-yl)(phenyl)methanol (6v). A solution of phenylmagnesium bromide (2 eq., 1 *M* in THF) was added slowly to a solution of 3-azidofuran-2-carbaldehyde (100 mg, 0.72 mmol) in THF (0.25 *M*) at -78 °C. After stirring for 3 h, the reaction was then quenched with saturated NH_4Cl aqueous solution and extracted with EtOAc. The combined organic layers were washed with brine dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel using

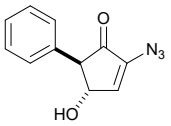
heptane/ethyl acetate 95:5 to 80:20 to afford the compound as a yellow oil with 47% yield (74 mg). Rf 0.7 (50% PET/EtOAc).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.42-7.47 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 2.1 Hz, 1H), 5.81 (d, *J* = 4.6 Hz, 1H), 5.02 (d, *J* = 4.6 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 145.4 (C), 143.3 (CH), 142.7 (C), 128.9 (2xCH), 128.1 (CH), 127.1 (2xCH), 122.9 (C), 105.7 (CH), 66.9 (CH).

IR (ν/cm^{-1}) 3397, 2113, 1611, 1493, 1348, 1193, 1017, 951, 723, 697.

HRMS (ESI) m/z calculated for $C_{11}H_7NO$ ([M-N_2-H_2O+H]$^+$) 170.0600 , found 170.0603.



(4*S,5*R**)-2-Azido-4-hydroxy-5-phenylcyclopent-2-en-1-one (7v).** (3-Azidofuran-2-yl)(phenyl)methanol **6v** (37 mg, 0.172 mmol) was diluted in *t*-BuOH/$H_2$0 (5:1, 0.1 *M*), and Dy(OTf)$_3$ (10 mol%) was introduced. Reacting mixture was stirred at 80 °C for 4 h. After cooling to room temperature, the mixture was quenched with a saturated solution of $NaHCO_3$, and extracted with EtOAc. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel using heptane/ethyl acetate 90:10 to 60:40 to afford the compound **7v** with 81% yield (30 mg). Rf 0.60 (50% PET/EtOAc).

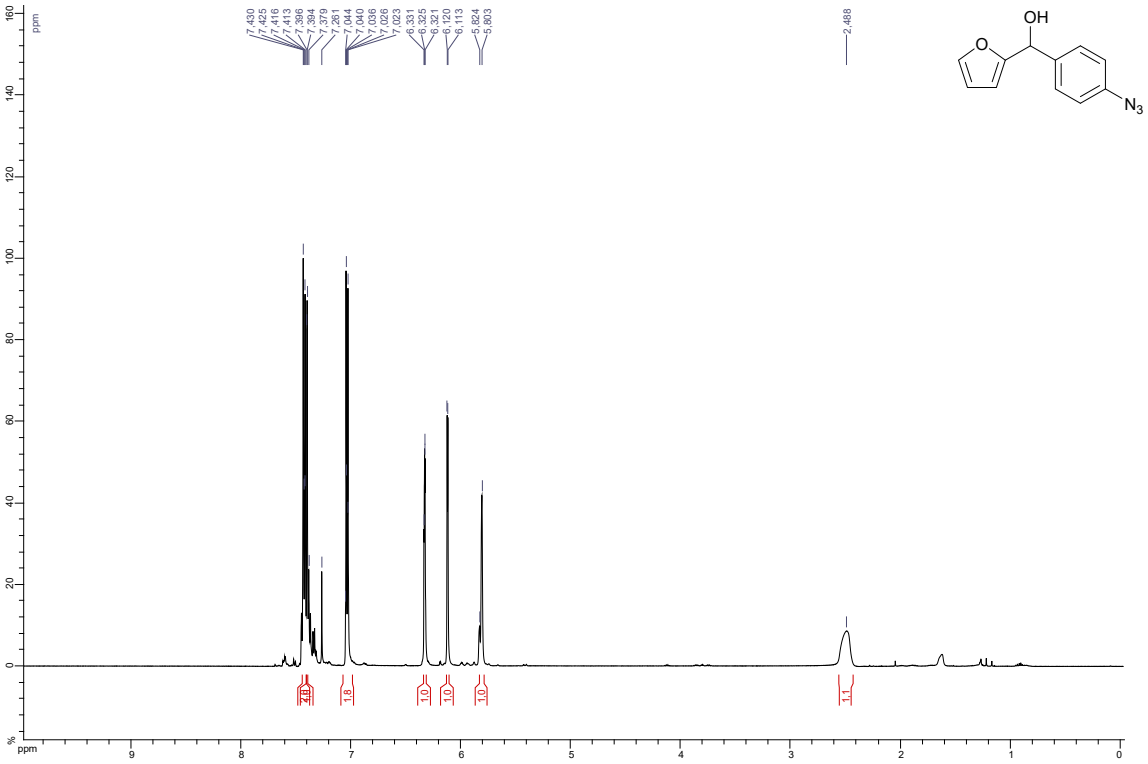
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.32-7.39 (m, 2H), 7.25-7.31 (m, 1H), 7.14-7.24 (m, 2H), 6.95 (d, *J* = 2.7 Hz, 1H), 4.98 (d, *J* = 6.2 Hz, 1H), 4.88-4.93 (m, 1H), 3.58 (d, *J* = 2.4 Hz, 1H).

13C-NMR (Acetone-d_6, 126 MHz) δ 200.3 (C), 142.2 (CH), 139.8 (C), 138.3 (C), 129.4 (2xCH), 129.3 (2xCH), 128.0 (CH), 75.3 (CH), 62.3 (CH).

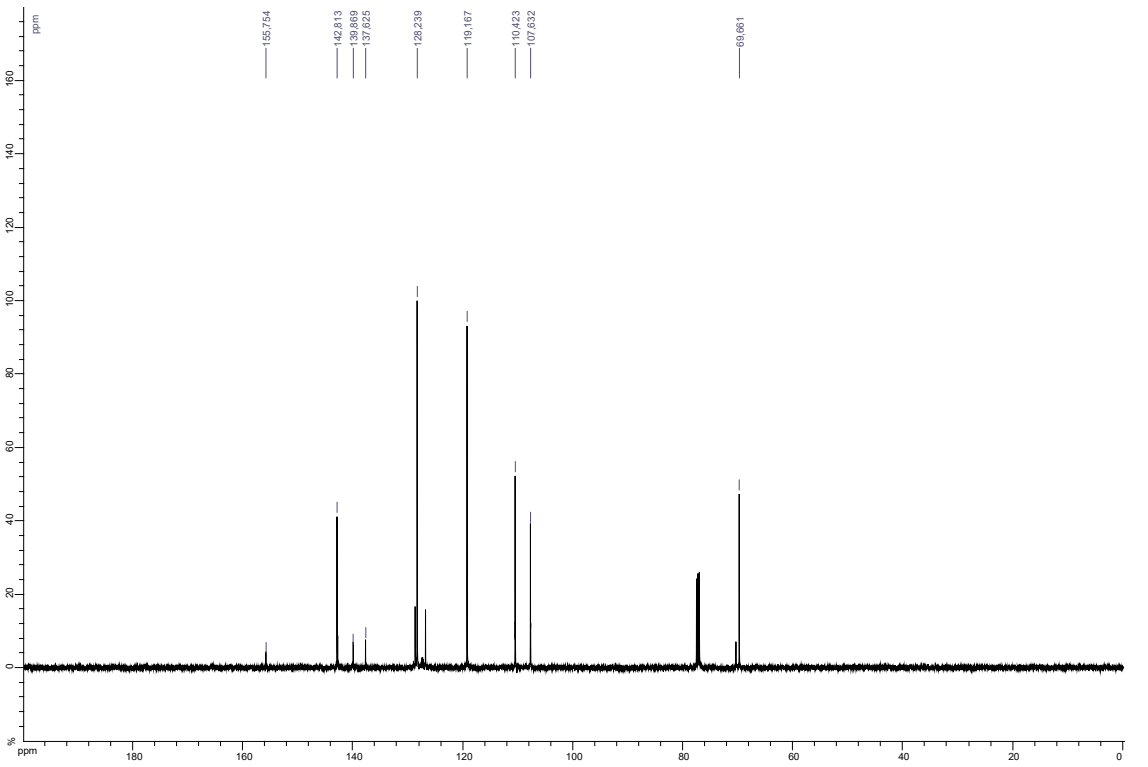
IR (ν/cm^{-1}) 3409, 2110, 1717, 1618, 1497, 1340, 1271, 1152, 1040, 1010, 753, 699.

HRMS (ESI) m/z calculated for $C_{11}H_{10}NO_2$ ([M-N_2+H]$^+$) 188.0706 , found 188.0698.

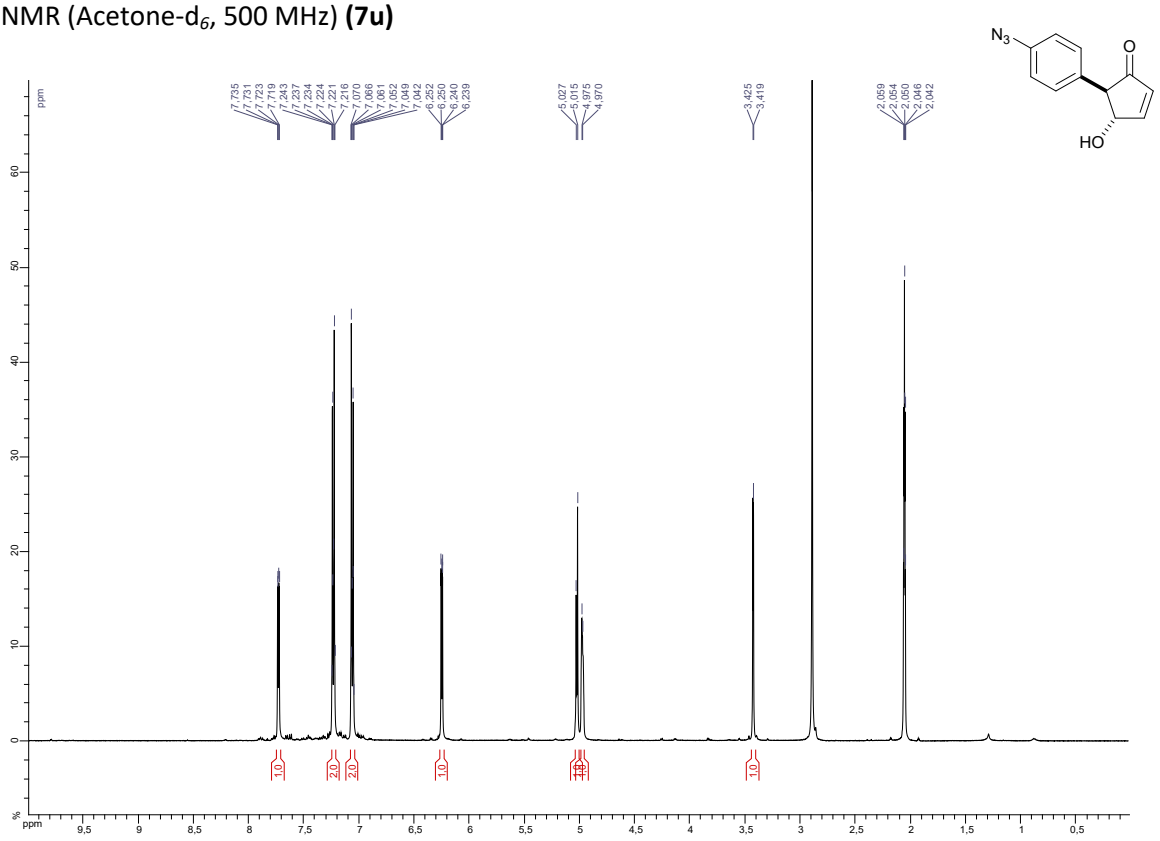
^{1}H-NMR ($CDCl_3$, 500 MHz) **(6u)**



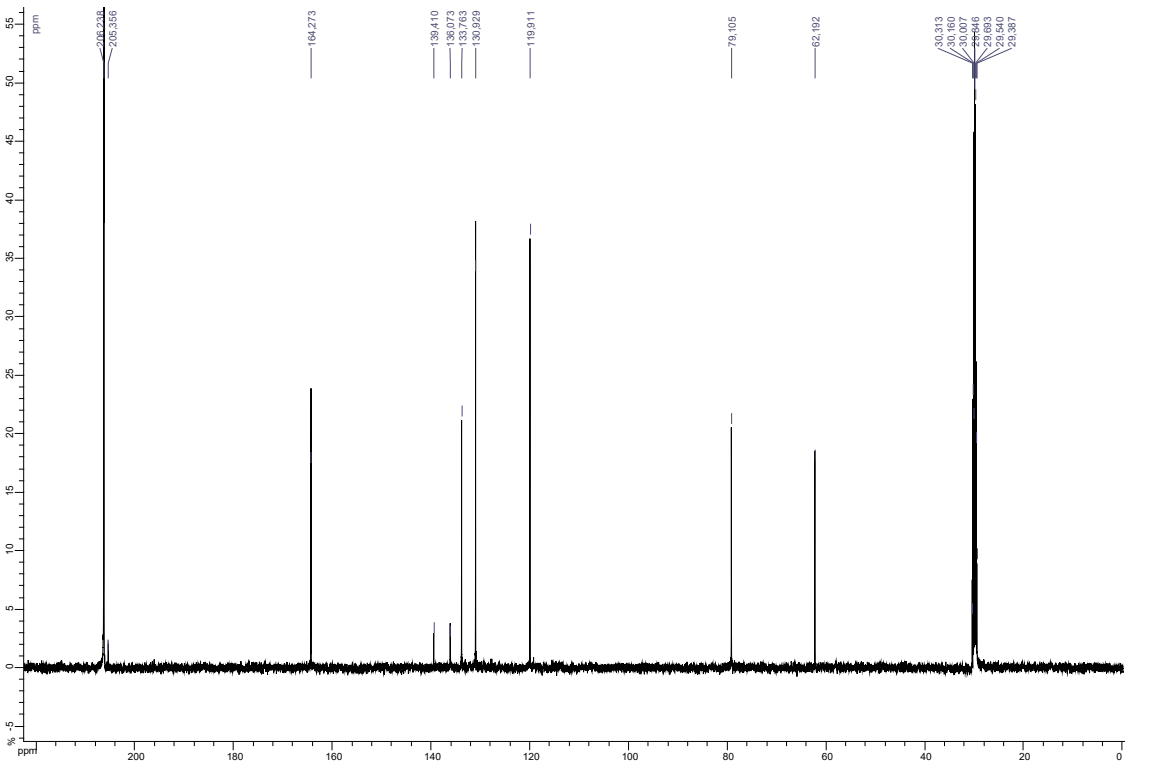
^{13}C-NMR ($CDCl_3$, 126 MHz) **(6u)**



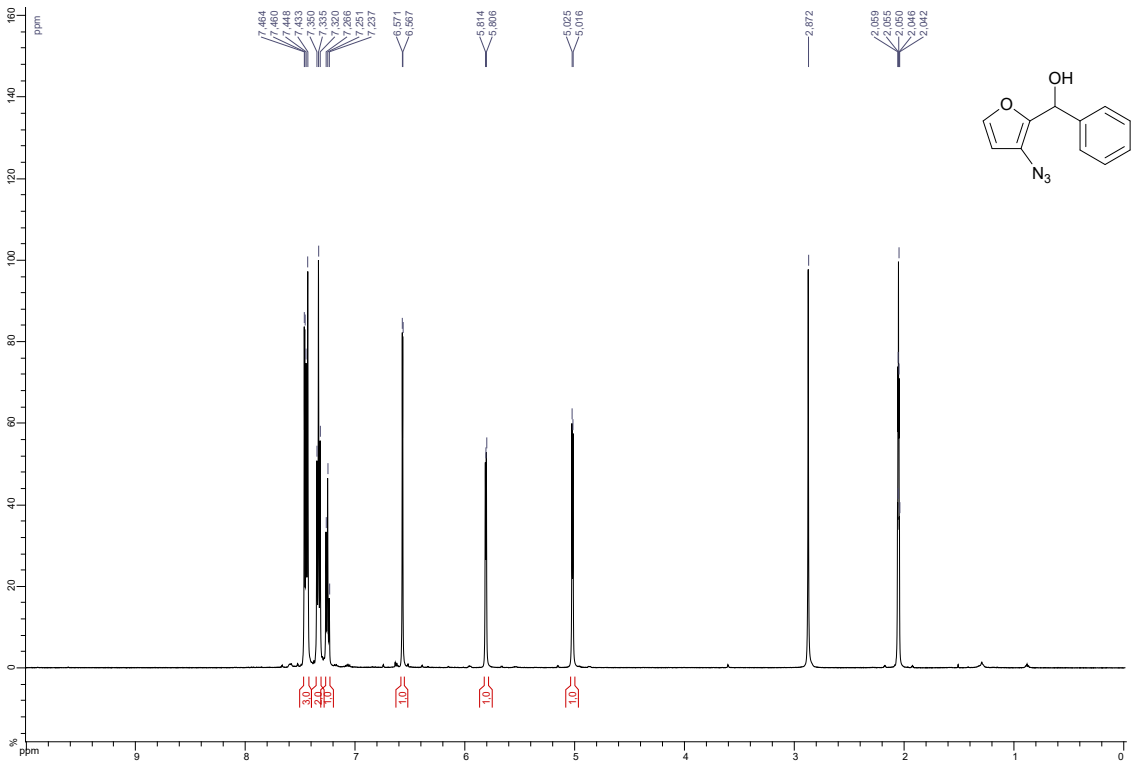
^{1}H-NMR (Acetone-d$_6$, 500 MHz) **(7u)**



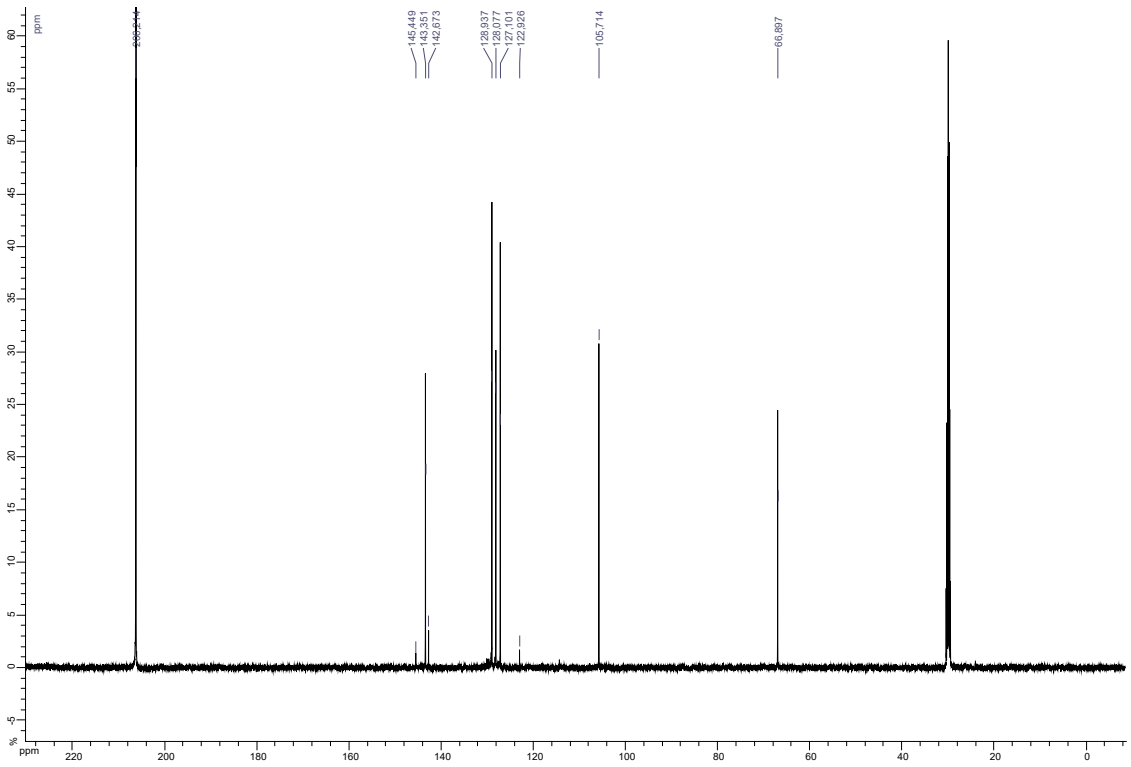
^{13}C-NMR (Acetone-d$_6$, 126 MHz) **(7u)**



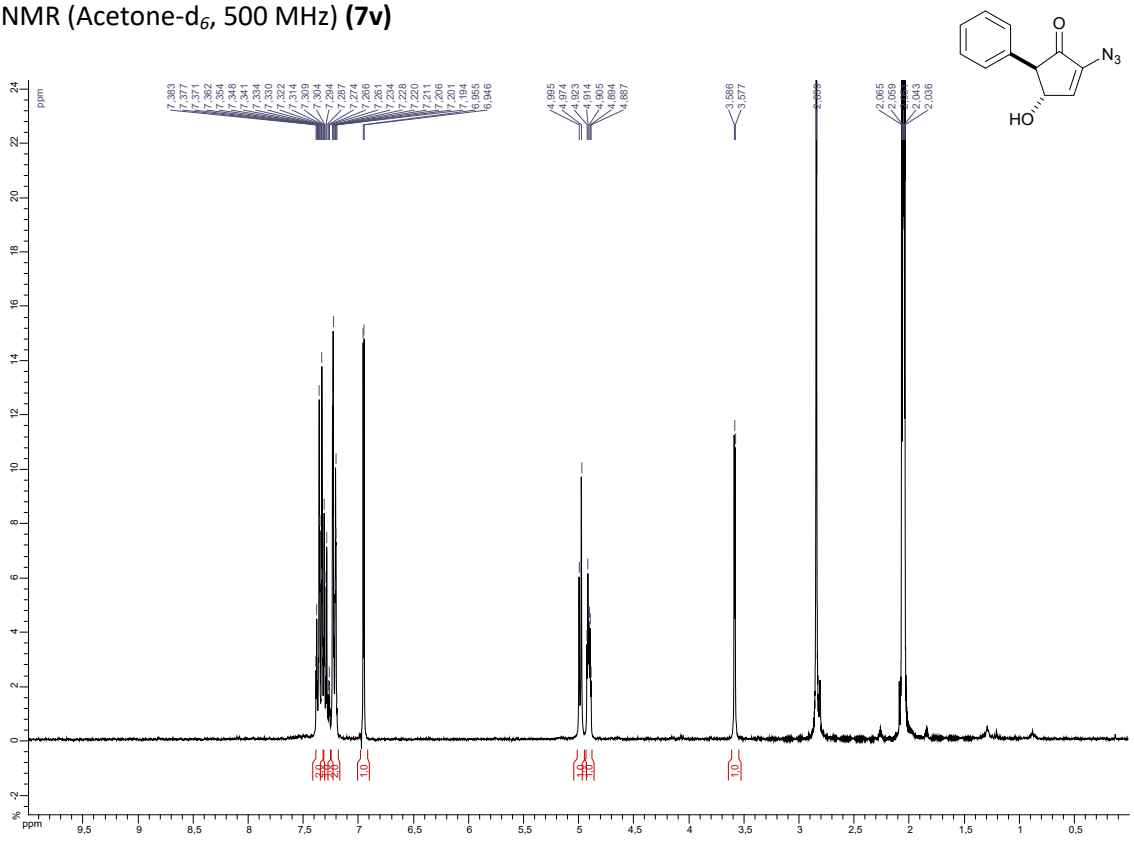
^{1}H-NMR (Acetone-d$_6$, 500 MHz) **(6v)**



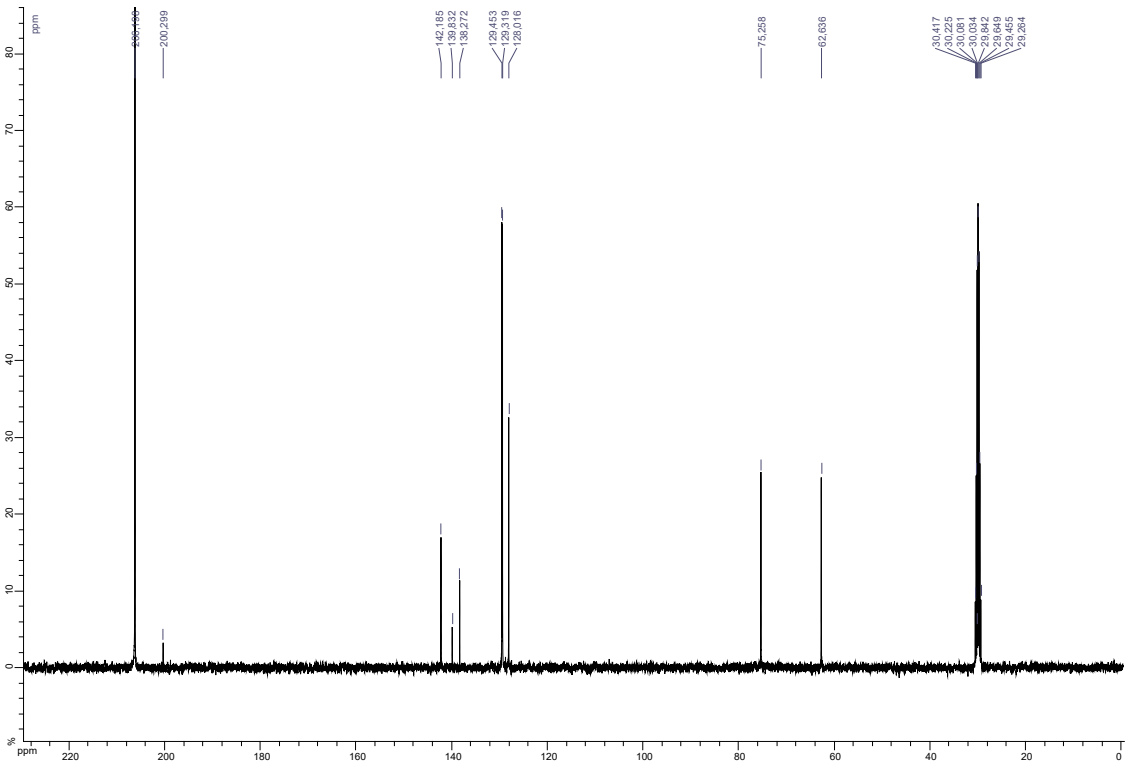
^{13}C-NMR (Acetone-d$_6$, 126 MHz) **(6v)**



^{1}H-NMR (Acetone-d$_6$, 500 MHz) **(7v)**

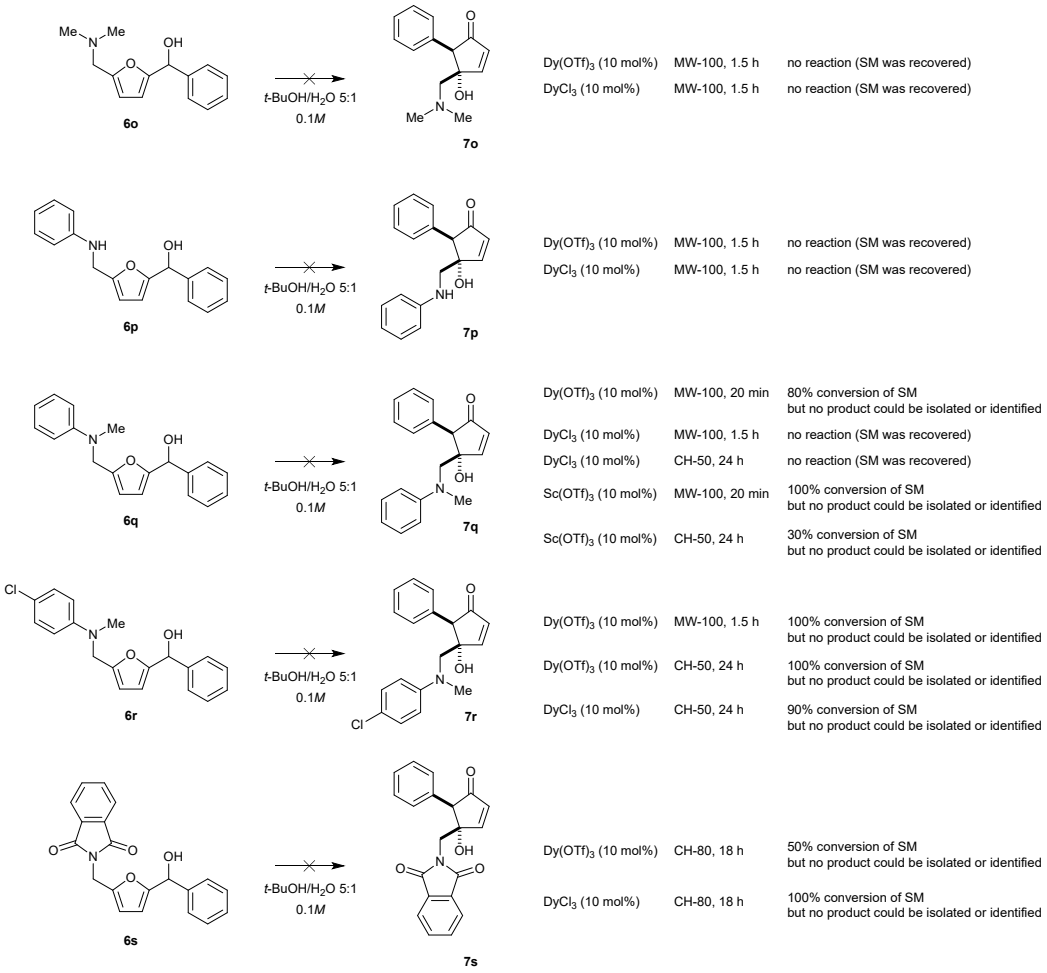


^{13}C-NMR (Acetone-d$_6$, 126 MHz) **(7v)**



V. Unsuccessful Piancatelli rearrangement of substrates with other nitrogen function

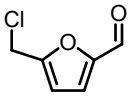
As azide function can be considered a labile and highly reactive functional group, other nitrogen functionalities have been tested, such as aliphatic amines, aromatic amines, and a protected amine function in the form of a phthalimide. The preparation of substrates was easily performed starting from CMF and using a similar route for the preparation of (5-(azidomethyl)furan-2-yl)phenyl-carbinol **6a**, but all attempts for Piancatelli rearrangement on these substrates failed.



Scheme S4 Attempts of Piancatelli rearrangement on compounds 6o-s with an aliphatic amines, aromatic amines, and a protected amine function in the form of a phthalimide side chain at the C-5 position of furan.

VI. Preparation of α-substituted (5-(azidomethyl)furan-2-yl)-carbinol substrates

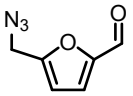
5-(Chloromethyl)furan-2-carbaldehyde (1).



To a solution of HMF (2 g, 15.9 mmol, 1 eq.) in DCM (0.4 *M*) were added *p*-toluenesulfonyl chloride (3.63 mg, 19.0 mmol, 1.2 eq.) and 4-(Dimethylamino)pyridine (116.2 mg, 0.95 mmol, 6 mol %). At 0 °C, trimethylamine (3.1 mL, 22.2 mmol, 1.4 eq.) was added slowly. Reacting mixture was stirred from 0 °C to room temperature for 16 h, and was then quenched with a saturated solution of NH_4Cl. The aqueous layer was extracted thrice with DCM. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel petroleum ether/ethyl acetate (7:3) to afford compound **1** (1.56 g, 68% yield) as a yellow oil.

Characterization data is in accordance with those reported in the literature. The copy of ^{1}H NMR spectra for product **1** is presented below.[1]

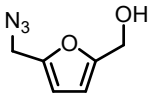
5-(Azidomethyl)furan-2-carbaldehyde (2).



Sodium azide (1.45 g, 22.3 mmol, 2 eq.) was added to a solution of compound **1** (2.0 g, 11.1 mmol, 1 eq.) in acetonitrile (0.2 *M*). The mixture was stirred for 6 h at 60 °C. After cooling to room temperature, mixture was filtered through Celite and washed with diethyl ether to remove inorganic impurities. After evaporation, compound **2** was obtained as a yellow oil (quantitative yield, without further purification).

Characterization data is in accordance with those reported in the literature. The copy of ^{1}H NMR spectra for product **2** is presented below.[2]

5-(Azidomethyl)furan-2-yl)methanol (4).



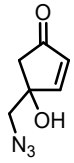
To a solution of 5-(azidomethyl)furfural **2** (200 mg, 1.32 mmol, 1.0 eq.) in MeOH (0.26 *M*), was added at 0 °C sodium borohydride (60.1 mg, 1.59 mmol, 1.2 eq.). After stirring for 1.5 h at 0 °C, the reaction was quenched with a saturated solution of NH_4Cl. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel petroleum ether/ethyl acetate (7:3) to afford compound **4** (192 mg, 95% yield) as a yellow oil. $\mathbf{R_f}$ 0.65 (50% PET/EtOAc).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 6.41 (d, *J* = 3.1 Hz, 1H), 6.28 (d, *J* = 3.1 Hz, 1H), 4.54 (d, *J* = 5.8 Hz, 1H), 4.39 (s, 2H), 4.29 (t, *J* = 6.0 Hz, 2H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 157.46 (C), 149.67 (C), 111.05 (CH), 108.49 (CH), 57.36 (CH_2), 47.57 (CH_2).

HRMS (ESI): m/z calculated for $C_6H_8NO_2$ ($[M-N_2+H]^+$) 126.0550, found 126.0549.

4-(Azidomethyl)-4-hydroxycyclopent-2-en-1-one (5).



100 mg of **2** (0.65 mmol, 1 eq.) were diluted in a mixture of t-BuOH/H_2O 1:5 (0.2 *M*). The reaction mixture was heated under MW irradiation for 5 min at 190 °C. After cooling to room

[1] S. Dutta, *Green Chem*, **2011**, *13*, 40-41.

[2] B.Ya. Karlinskii *et al. Synthesis* **2019**, *51*, 1235-1242.

temperature, the aqueous layer was extracted thrice with *tert*-butyl methyl ether. The combined aqueous layers were concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel petroleum ether/ethyl acetate (3:7) to afford compound **5** (34.3 mg, 37% yield) as an orange oil. $\mathbf{R_f}$ 0.17 (30% PET/EtOAc).

^{1}H-NMR (D_2O, 500 MHz) δ 7.63 (d, *J* = 5.8 Hz, 1H), 6.30 (d, *J* = 5.8 Hz, 1H), 3.70 (d, *J* = 11.7 Hz, 1H), 3.65 (d, *J* = 11.7 Hz, 1H), 2.65 (d, *J* = 18.8 Hz, 1H), 2.49 (s, 1H) 2.43 (d, *J* = 18.8 Hz, 1H).

^{13}C-NMR (D_2O, 126 MHz) δ 211.05 (CO), 165.65 (CH), 134.54 (CH), 79.29 (C), 65.79 (CH_2), 45.46 (CH_2).

IR (ν/cm^{-1}) 3370, 2924, 1709, 1403, 1202, 1036, 805.

HRMS (ESI) m/z calculated for $C_6H_8NO_2$ ($[M-N_2+H]^+$) 126.0555, found 126.0558.

General procedure A.

To a solution of 5-(azidomethyl)furfural **2** (1.0 eq.) in anhydrous THF (0.25 *M*), was added at 0 °C a solution of arylmagnesium bromide in Et_2O or THF (1.3 eq). The reaction mixture was stirred for 2 h at -78 °C. Then, the mixture was quenched with a 0.1 *M* solution of hydrogen chloride. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford compounds **6a-n**.

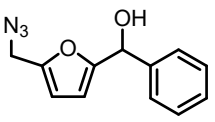
General procedure B.

Magnesium turnings (3 eq.) were heated with heatgun for 20 min under vacuum. Flask was then cooled to room temperature, and crystals of diiode were added with Et_2O (1.7 mL/mmol of 5-(azidomethyl)furfural) **2**. To this mixture were added few drops of 1-bromoaryl substrate and 1,2-dibromoethane under argon to initiate the reaction. 1-bromo-aryl (1.5 eq) was then added dropwise, and the reaction mixture was refluxed for 1 h under argon. The mixture was cooled to 0 °C and a solution of 5-(azidomethyl)furfural (1.0 eq) in Et_2O (3.4 mL/mmol of 5-(azidomethyl) furfural) was added dropwise. After stirring for 2 h at 0 °C, the reaction was quenched with a saturated solution of NH_4Cl. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford compounds **6a-n**.

General procedure C.

To a stirred solution of 5-(azidomethyl)furfural) (1 eq.) in degazed THF (0.2 *M*) were successively added boronic acid (2 eq.), K_2CO_3 (2 eq.), tri-(1-naphthyl)phosphine (5 mol %) and $PdCl_2$ (5 mol %). Reacting mixture was then heaten at room temperature for 16 h. After cooling to room temperature, the mixture was quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford compounds **6a-n**.

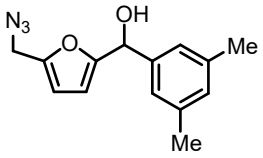
(5-(Azidomethyl)furan-2-yl)(phenyl)methanol (6a)



This product was synthesized according to General Procedure **A** using 1.05 g (6.95 mmol) of **AMF 2**. Pale yellow oil was obtained in 85% yield (1.41 g) using petroleum ether/ethyl acetate (7:3) as the eluent. $\mathbf{R_f}$ 0.50 (50% PET/EtOAc).

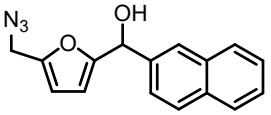
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.46 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 3.1 Hz, 1H), 6.15 (d, *J* = 3.1 Hz, 1H), 5.80 (d, *J* = 4.2 Hz, 1H), 5.04 (d, *J* = 4.2 Hz, 1H), 4.35 (s, 2H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 158.45 (C), 148.88 (C), 142.28 (C), 128.11 (2xCH), 124.44 (CH), 126.65 (2xCH), 110.10 (CH), 107.30 (CH), 69.39 (CH), 46.61 (CH_2).
IR (ν/cm^{-1}) 3394, 2097, 1494, 1453, 1337, 1266, 1017, 791, 747, 700.
HRMS (ESI) m/z calculated for $C_{12}H_{10}N_3O$ ([M-H_2O+H]$^+$) 212.0818, found 212.0819.

(5-(Azidomethyl)furan-2-yl)(3,5-dimethylphenyl)methanol (6b).



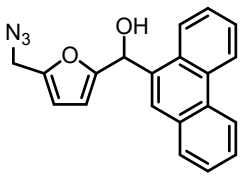
This product was synthesized according to General Procedure **B** using **2** (100 mg, 0.66 mmol). Yellow oil was obtained in 35% yield (60 mg) using petroleum ether/ethyl acetate (8:2) as the eluent. **R_f** 0.68 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.06 (s, 2H), 6.91 (s, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 5.71 (d, *J* = 4.8 Hz, 1H), 4.95 (d, *J* = 4.8 Hz, 1H), 4.34 (s, 2H), 2.27 (s, 6H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 159.47 (C), 149.53 (C), 143.00 (C), 138.21 (2xC), 129.74 (CH), 125.29 (2xCH), 110.95 (CH), 107.95 (CH), 70.28 (CH), 47.40 (CH_2), 21.35 (2xCH_3).
IR (ν/cm^{-1}) 3379, 2097, 1606, 1463, 1266, 1175, 1043, 1016, 855, 778.
HRMS (ESI) m/z calculated for $C_{14}H_{14}N_3O$ ([M-H_2O+H]$^+$) 240.1137, found 240.1127.

(5-(Azidomethyl)furan-2-yl)(naphthalen-2-yl)methanol (6c).



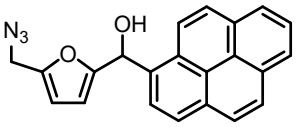
This product was synthesized according to General Procedure **C** using **2** (150 mg, 0.99 mmol). Yellow oil was obtained in 65% yield (48 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. **R_f** 0.67 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.99 (s, 1H), 7.91-7.87 (m, 3H), 7.60 (dd, *J* = 8.6 Hz, 1.5 Hz, 1H), 7.52-7.47 (m, 2H), 6.41 (d, *J* = 3.2 Hz, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 6.00 (d, *J* = 4.8 Hz, 1H), 5.23 (d, *J* = 4.8 Hz, 1H), 4.35 (s, 2H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 159.13 (C), 149.79 (C), 140.62 (C), 134.20 (C), 133.93 (C), 128.81 (CH), 128.62 (CH), 128.46 (CH), 126.92 (CH), 126.72 (CH), 126.02 (CH), 125.85 (CH), 111.01 (CH), 108.34 (CH), 70.31 (CH), 47.40 (CH_2).
IR (ν/cm^{-1}) 3371, 2092, 1675, 1602, 1508, 1336, 1268, 1173, 1122, 1016, 861, 785.
HRMS (ESI) m/z calculated for $C_{16}H_{12}NO$ ([M-H_2O-N_2+H]$^+$) 234.0919, found 234.0916.

(5-(Azidomethyl)furan-2-yl)(phenanthren-9-yl)methanol (6d).



This product was synthesized according to General Procedure **C** using **2** (177 mg, 1.12 mmol). Yellow oil was obtained in 86% yield (313 mg) using petroleum ether/ethyl acetate (8:2) as the eluent. **R_f** 0.66 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 8.12 (s, 1H), 7.94 (dd, *J* = 7.4 Hz, 1.4 Hz, 1 H), 7.64-7.56 (m, 3H), 7.53 (td, *J* = 7.5 Hz, 1.1 Hz, 1H), 6.59 (d, *J* = 3.1 Hz, 1H), 6.33 (d, *J* = 3.2 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 5.43 (d, *J* = 4.4 Hz, 1H), 4.29 (s, 2H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 157.75 (C), 148,68 (C), 135.64 (C), 131.42 (C), 130.57 (C), 130.17 (C), 129.84 (C), 128.79 (CH), 126.82 (CH), 126.78 (CH), 126.45 (CH), 126.29 (CH), 125.15 (CH), 124.60 (CH), 123.08 (CH), 122.49 (CH), 110.34 (CH), 108.31 (CH), 66.97 (CH), 46.46 (CH_2).
IR (ν/cm^{-1}) 3375, 2092, 1693, 1496, 1449, 1336, 1246, 1174, 1065, 1017, 791, 744.
HRMS (ESI) m/z calculated for $C_{20}H_{14}N_3O$ ([M-H_2O+H]$^+$) 312.1137, found 312.1129.

(5-(Azidomethyl)furan-2-yl)(pyren-1-yl)methanol (6e).



This product was synthesized according to General Procedure **C** using **2** (150 mg, 0.99 mmol). Pale yellow solid was obtained in 94% yield (330 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. $\mathbf{R_f}$ 0.58 (60% PET/EtOAc).

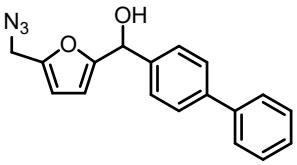
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 8.46 (d, *J* = 9.4 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.3 (d, *J* = 8.0 Hz, 1H), 8.27-8.23 (m, 2H), 8.16-8.12 (m, 3H), 8.04 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 4.2 Hz, 1H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.13 (d, *J* = 3.2 Hz, 1H), 5.5 (d, *J* = 4.7 Hz, 1H), 4.35 (s, 2H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 159.18 (C), 149.77 (C), 136.44 (C), 132.22 (C), 131.81 (C), 131.57 (C), 128.87 (C), 128.33 (CH), 128.294 (CH), 128.15 (CH), 126.95 (CH), 126.16 (CH), 126.02 (CH), 125.75 (CH), 125.68 (CH), 125.50 (C), 125.46 (C), 124.20 (CH), 111.11 (CH), 108.93 (CH), 67.80 (CH), 47.41 (CH_2).

IR (ν/cm^{-1}) 3375, 3042, 2100, 1735, 1675, 1596, 1508, 1264, 1228, 1062, 1017, 857, 714.

HRMS (ESI) m/z calculated for $C_{22}H_{14}NO$ ([M-N_2-H_2O+H]$^+$) 308.1075, found 308.1076.

[1,1'-Biphenyl]-4-yl(5-(azidomethyl)furan-2-yl)methanol (6f).



This product was synthesized according to General Procedure **C** using 5-(azidomethyl)furfural **2** (150 mg, 0.99 mmol). Pale yellow oil was obtained in 50% yield (111 mg) using petroleum ether/ethyl acetate (8:2) as the eluent. $\mathbf{R_f}$ 0.71 (50% PET/EtOAc).

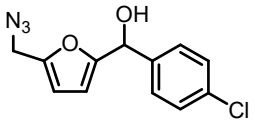
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.63-7.68 (m, 4H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1 H), 6.41 (d, *J* = 3.2 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 5.89 (d, *J* = 4.7 Hz, 1H), 5.22 (d, *J* = 4.7 Hz, 1H), 4.35 (s, 2H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 158.22 (C), 148.85 (C), 141.33 (C), 140.60 (C), 140.09 (C), 128.81 (2xCH), 127.26 (CH), 127.17 (2xCH), 126.78 (2xCH), 126.62 (2xCH), 110.11 (CH), 107.36 (CH), 69.09 (CH), 46.55 (CH_2).

IR (ν/cm^{-1}) 3378, 2092, 1486, 1336, 1261, 1175, 1007, 850, 750.

HRMS (ESI) m/z calculated for $C_{18}H_{14}NO$ ([M-H_2O-N_2+H]$^+$) 260.1075, found 260.1071.

(5-(Azidomethyl)furan-2-yl)(4-chlorophenyl)methanol (6g).



This product was synthesized according to General Procedure **A** using **2** (100 mg, 0.66 mmol). Pale yellow oil was obtained in 84% yield (60 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. $\mathbf{R_f}$ 0.69 (50% PET/EtOAc).

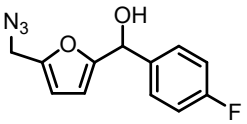
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.4 (d, *J* = 3.2 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 5.83 (d, *J* = 4.9 Hz, 1H), 5.19 (d, *J* = 4.9 Hz, 1H), 4.35 (s, 2H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 158.68 (C), 149.96 (C), 142.04 (C), 133.49 (C), 129.98 (2xCH), 129.01 (2xCH), 110.98 (CH), 108.37 (CH), 69.42 (CH), 47.38 (CH_2).

IR (ν/cm^{-1}) 3372, 2097, 1490, 1407, 1137, 1266, 1175, 1089, 1014, 969, 843, 799, 775.

HRMS (ESI) m/z calculated for $C_{12}H_9NOCl$ ([M-N_2-H_2O+H]$^+$) 218.0373, found 218.0372.

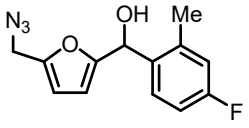
(5-(Azidomethyl)furan-2-yl)(4-fluorophenyl)methanol (6h).



This product was synthesized according to General Procedure **A** using **2** (150 mg, 0.99 mmol). Pale yellow oil was obtained in 65% yield (161 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. $\mathbf{R_f}$ 0.64 (50% PET/EtOAc).

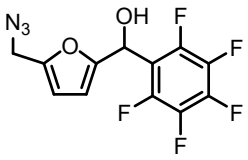
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.52-7.47 (m, 2H), 7.14-7.08 (m, 2H), 6.39 (d, *J* = 3.2 Hz, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 5.83 (d, *J* = 4.8 Hz, 1H), 5.18 (d, *J* = 4.8 Hz, 1H), 4.35 (s, 2H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 162.96 (d, J_{CF} = 243.3 Hz, C), 158.93 (C), 149.82 (C), 139.18 (C), 129.37 (d, J_{CF} = 8.2 Hz, 2xCH), 115.58 (d, J_{CF} = 21.5 Hz, CH), 110.94 (CH), 108.22 (CH), 69.47 (CH), 47.37 (CH_2).
^{19}F-NMR (Acetone-d_6, 300 MHz) 60.72.
IR (ν/cm^{-1}) 3372, 2094, 1604, 1507, 1137, 1210, 1177, 1157, 1014, 969, 842, 802, 776.
HRMS (ESI) m/z calculated for $C_{12}H_9NOF$ ([M-N_2-H_2O+H]$^+$) 202.0668, found 202.0671.

(5-(Azidomethyl)furan-2-yl)(4-fluoro-2-methylphenyl)methanol (6i).



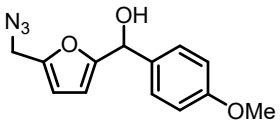
This product was synthesized according to General Procedure **B** using **2** (100 mg, 0.66 mmol). Pale yellow oil was obtained in 96% yield (166 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. **R_f** 0.71 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.60-7.56 (m, 1H), 6.99-6.92 (m, 2H), 6.40 (d, *J* = 3.2 Hz, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 5.96 (d, *J* = 4.9 Hz, 1H), 5.05 (d, *J* = 4.9 Hz, 1H), 4.35 (s, 2H), 2.28 (s, 3H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 162.74 (d, J_{CF} = 242.3 Hz, C), 158.56 (C), 149.77 (C), 138.83 (d, J_{CF} = 8.0 Hz, C), 137.15 (C), 117.28 (d, J_{CF} = 21.4 Hz, CH), 129.99 (d, J_{CF} = 21.4 Hz, CH), 111.04 (CH), 129.28 (d, J_{CF} = 8.6 Hz, CH), 108.47 (CH), 66.77 (CH), 47.39 (CH_2), 19.01 (CH_3).
^{19}F-NMR (Acetone-d_6, 300 MHz) 59.71.
IR (ν/cm^{-1}) 3357, 2097, 1614, 1591, 1495, 1443, 1335, 1247, 1175, 1097, 1017, 851, 866, 783.
HRMS (ESI) m/calculated for $C_{13}H_{11}N_3OF$ ([M-H_2O+H]$^+$) 244.0886, found 244.0885.

(**5-(Azidomethyl)furan-2-yl)(perfluorophenyl)methanol (6j).**



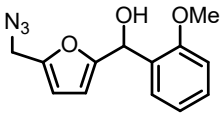
This product was synthesized according to General Procedure **B** using **2** (100 mg, 0.66 mmol). Pale yellow oil was obtained in 85% yield (180 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. **R_f** 0.62 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 6.46 (d, *J* = 3.1 Hz, 1H), 6.41 (d, *J* = 3.1 Hz, 1H), 6.25 (s, 1H), 5.68 (s, 1H), 4.37 (dd, *J* = 20.9 Hz, 14.5 Hz, 2H).
^{13}C-NMR (Acetone-d$_6$, 126 MHz) δ 155.16 (C), 150.47 (C), 147.07-146.80 (m, C), 145.07-144.82, (m, C), 142.85-142.69 (m, C), 140.89-140.61 (m, C), 139.68-139.30 (m, C), 137.72-137.33 (m, C), 111.24 (CH), 108.77 (CH), 61.96 (CH), 47.27 (CH_2).
^{19}F-NMR (Acetone-d_6, 282 MHz) δ 33.46 (dd, *J* = 21.8 Hz, 8.3 Hz), 20.06 (t, *J* = 20.8 Hz), 13.08-12.85 (m).
IR (ν/cm^{-1}) 3391, 2097, 1655, 1655, 1522, 1503, 1338, 1303, 1262, 1121, 993, 1019, 993, 930, 796, 766.
HRMS (ESI) m/z calculated for $C_{12}H_7F_5NO_2$ ([M-N_2+H]$^+$) 292.0391, found 292.0389.

(5-(Azidomethyl)furan-2-yl)(4-methoxyphenyl)methanol (6k).



This product was synthesized according to General Procedure **C** using **2** (150 mg, 0.99 mmol). Pale yellow oil was obtained in 67% yield (110 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. **R_f** 0.70 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.37 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.14 (d, *J* = 3.2 Hz, 1H), 5.74 (d, *J* = 5.0 Hz, 1H), 4.95 (d, *J* = 5.0 Hz, 1H), 4.34 (s, 2H), 3.78 (s, 3H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 160.06 (C), 159.56 (C), 149.51 (C), 135.14 (C), 128.71 (2xCH), 114.27 (2xCH), 110.91 (CH), 107.88 (CH), 69.86 (CH), 55.47 (CH_3), 47.74 (CH_2).
IR (ν/cm^{-1}) 3399, 2093, 1611, 1510, 1441, 1337, 1303, 1243, 1171, 1016, 968, 934, 837, 800, 778.
HRMS (ESI) m/z calculated for $C_{13}H_{12}NO_2$ ([M-N_2-H_2O+H]$^+$) 214.0868, found 214.0849.

(5-(Azidomethyl)furan-2-yl)(2-methoxyphenyl)methanol (6l).



This product was synthesized according to General Procedure **A** using **2** (150 mg, 0.99 mmol). Pale yellow oil was obtained in 68% yield (175 mg) using petroleum ether/ethyl acetate (8:2) as the eluent. $\mathbf{R_f}$ 0.75 (50% PET/EtOAc).

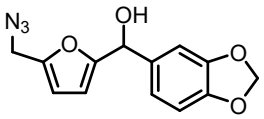
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.56 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.28 (td, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.00-6.95 (m, 2H), 6.35 (d, *J* = 3.1 Hz, 1H), 6.11 (d, *J* = 5.4 Hz, 1H), 5.99 (d, *J* = 3.1 Hz, 1H), 4.82 (d, *J* = 5.4 Hz, 1H), 4.35 (s, 2H), 3.79 (s, 3H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 159.24 (C), 157.29 (C), 149.32 (C), 131.11 (C), 129.47 (CH), 128.22 (CH), 121.17 (CH), 111.39 (CH), 110.91 (CH), 107.93 (CH), 64.27 (CH), 55.81 (CH_3), 47.48 (CH_2).

IR (ν/cm^{-1}) 3417, 2095, 1601, 1492, 1463, 1439, 1285, 1243, 1186, 1018, 969, 755.

HRMS (ESI) m/z calculated for $C_{13}H_{12}N_3O_2$ ([M-H_2O+H]$^+$) 242.0930, found 242.0930.

(5-(Azidomethyl)furan-2-yl)(benzo[d][1,3]dioxol-5-yl)methanol (6m).



This product was synthesized according to General Procedure **C** using **2** (40 mg, 0.25 mmol). Yellow oil was obtained in 46% yield (35 mg) using petroleum ether/ethyl acetate (7:3) as the eluent. $\mathbf{R_f}$ 0.64 (60% PET/EtOAc).

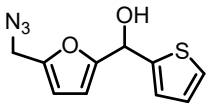
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 6.96 (d, *J* = 1.5 Hz, 1H), 6.92 (dd, *J* = 7.9 H, 1.5 Hz, 1H), 6.8 (d, *J* = 7.9 Hz, 1H), 6.39 (d, *J* = 3.1 Hz, 1H), 6.17 (d, *J* = 3.1 Hz, 1H), 5.92 (s, 2H), 5.72 (d, *J* = 3.9 Hz, 1H), 5.06 (d, *J* = 4.5Hz, 1H), 4.35 (s, 2H)

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 159.27 (C), 149.63 (C), 148.49 (C), 147.88 (C), 137.20 (C), 120.89 (CH), 110.95 (CH), 108.52 (CH), 107.95 (CH), 107.93 (CH), 101.95 (CH_2), 70.02 (CH), 47.42 (CH_2).

IR (ν/cm^{-1}) 3375, 2094, 1610, 1502, 1487, 1442, 1235, 1176, 1094, 1035, 1015, 926, 866, 772.

HRMS (ESI) m/z calculated for $C_{13}H_{10}N_3O_3$ ([M-H_2O+H]$^+$) 256.0722, found 256.0717.

(5-(Azidomethyl)furan-2-yl)(thiophen-2-yl)methanol (6n).



This product was synthesized according to General Procedure **B** using **2** (150 mg, 0.99 mmol). Yellow oil was obtained in 75% yield (183 mg) using petroleum ether/ethyl acetate (8:2) as the eluent. $\mathbf{R_f}$ 0.75 (50% PET/EtOAc).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.39 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 7.02 (d, *J* = 3.5 Hz, 1H), 6.97 (dd, *J* = 5.0 Hz, 3.5 Hz, 1H), 6.43 (d, *J* = 3.2 Hz, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 6.07 (d, *J* = 5.3 Hz, 1H), 5.35 (d, *J* = 5.3 Hz, 1H), 4.38 (s, 2H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 158.36 (C), 149.83 (C), 147.04 (C), 127.22 (CH), 125.88 (CH), 125.44 (CH), 111.04 (CH), 108.14 (CH), 66.45 (CH), 47.41 (CH_2).

IR (ν/cm^{-1}) 3387, 2100, 1437, 1337, 1265, 1230, 1016, 855, 801, 704.

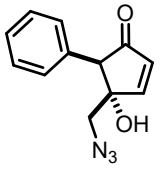
HRMS (ESI) m/z calculated for $C_{10}H_8NOS$ ([M-N_2-H_2O+H]$^+$) 190.0321, found 190.0320.

VII. Experimental procedures for Piancatelli rearrangement

General procedure D: To a solution of furan derivative **6a-n** (1 eq.) in a mixture of *t*-BuOH/H_2O 5:1 (0.1 M), were added $Na_2S_2O_4$ (3 wt %) and $Dy(OTf)_3$ (10 mol %). The reaction mixture was heated under MW irradiation for 1.5 h at 100 °C. After cooling to room temperature, the mixture was quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the cyclopentenone derivatives **7a-n**.

General procedure E: To a solution of furan derivative **6a-n** (1 eq.) in a mixture of *t*-BuOH/H_2O 5:1 (0.1 M), were added $Na_2S_2O_4$ (3 wt %) and $ScCl_3$ (10 mol %). The reaction mixture was heated under MW irradiation for 1.5 h at 100 °C. After cooling to room temperature, the mixture was quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the cyclopentenone derivatives **7a-n**.

(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-phenylcyclopent-2-en-1-one (7a).**



a) General procedure D: the reaction was performed on 100 mg of **6a** (0.44 mmol) and 26.6 mg of $Dy(OTf)_3$ (0.044 mmol). **7a** (33 mg, 46% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (6:4) as the eluent.

b) Procedure E: the reaction was performed on 100 mg of **6a** (0.44 mmol) and 6.6 mg of $ScCl_3$ (0.044 mmol). **7a** (28 mg, 37% yield, dr > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (6:4) as the eluent. $\mathbf{R_f}$ 0.30 (60% PET/EtOAc).

Note relative to NMRs: This *trans* relative stereochemistry was first assigned based upon NMR NOESY 2D-experiments.

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.68 (d, *J* = 6.0 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 6.38 (d, *J* = 6.0 Hz, 1H), 5.37 (s, 1H), 3.86 (s, 1H), 3.20 (d, *J* = 12.6 Hz, 1H), 2.93 (d, *J* = 12.6 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 204.44 (CO), 163.13 (CH), 135.58 (C), 134.73 (CH), 130.92 (2xCH), 129.10 (2xCH), 128.10 (CH), 82.78 (C), 64.92 (CH), 58.41 (CH_2).

IR (ν/cm^{-1}) 3407, 2103, 1700, 1497, 1341, 1287, 1078, 1043, 812, 743, 699.

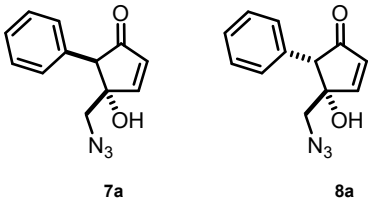
HRMS (ESI) m/z calculated for $C_{12}H_{10}N_3O$ ($[M\text{-}H_2O+H]^+$) 212.0818, found 212.0814.

Preparation of a mixture of 7a and 8a:

This mixture was prepared according to General Procedure **D**. To a solution of furan derivative **6a** (120 mg, 0.52 mmol, 1 eq.) in a mixture of *t*-BuOH/H_2O 5:1 (0.1 *M*), were added $Na_2S_2O_4$ (3 wt %) and $Dy(OTf)_3$ (32 mg, 10 mol %). The reaction mixture was heated under MW irradiation for 1.5 h at 150 °C. After cooling to room temperature, the mixture was quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel using tert-butyl methyl ether/toluene (6:4)

to afford the cyclopentenone derivatives in a mixture of unseparated 2 diastereoisomers **7a** (*cis*) and **8a** (*trans*) (30.6 mg, 25% yield, d.r. 1:1). $\mathbf{R_f}$ 0.30 (60% PET/EtOAc).

Description of a mixture of 7a and 8a:



7a **8a**

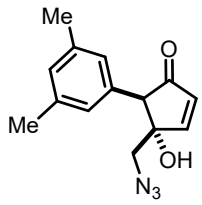
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.75 (d, *J* = 6.0 Hz, 1H$_{trans}$), 7.68 (d, *J* = 6.0 Hz, 1H$_{cis}$), 7.35 (t, *J* = 7.4 Hz, 2H$_{cis}$), 7.32-7.27 (m, 1H$_{cis}$+2H$_{trans}$), 7,26-7.22 (m, 2H$_{cis}$+1H$_{trans}$), 7.14 (d, *J* = 7.4 Hz, 2H$_{trans}$), 6.41 (d, *J* = 6.0 Hz, 1H$_{trans}$), 6.39 (d, *J* = 6.0 Hz, 1H$_{cis}$), 5.38 (s, 1H$_{cis}$), 4.46 (s, 1H$_{trans}$), 3.87 (s, 1H$_{cis}$), 3.77 (d, *J* = 12.6 Hz, 1H$_{trans}$), 3.70 (s, 1H$_{trans}$), 3.60 (d, *J* = 12.6 Hz, 1H$_{trans}$), 3.20 (d, *J* = 12.6 Hz, 1H$_{cis}$), 2.93 (d, *J* = 12.6 Hz, 1H$_{cis}$).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 206.68 (CO$_{trans}$), 204.44 (CO$_{cis}$), 163.46 (CH$_{trans}$), 163.13 (CH$_{cis}$), 136.834 (C$_{trans}$), 135.65 (CH$_{trans}$), 135.52 (C$_{cis}$), 134.71 (CH$_{cis}$), 131.61 (2xCH$_{trans}$), 130.90 (2xCH$_{cis}$), 129.07 (2xCH$_{cis}$), 128.72 (2xCH$_{trans}$), 128.08 (CH$_{cis}$), 127.65 (CH$_{trans}$), 82.75 (C$_{cis}$), 81.23 (C$_{trans}$), 64.88 (CH$_{cis}$), 60.75 (CH$_{trans}$), 59.11 (CH$_{2trans}$), 58.37 (CH$_{2cis}$).

IR (ν/cm^{-1}) 3396, 2923, 2100, 1705, 1497, 1453, 1340, 1284, 1079, 745, 700.

HRMS (ESI) m/z calculated for $C_{12}H_{10}N_3O$ ([M-H$_2$O+H]$^+$) 212.0818, found 212.0817.

(4*S,5*R**)-4-(Azidomethyl)-5-(3,5-dimethylphenyl)-4-hydroxycyclopent-2-en-1-one (7b).**



This compound was prepared according to the General Procedure **D** using 78 mg of **6b** (0.30 mmol) and 18.5 mg of Dy(OTf)$_3$ (0.030 mmol). **7b** (16 mg, 20% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (6:4) as the eluent. $\mathbf{R_f}$ 0.45 (50% PET/EtOAc).

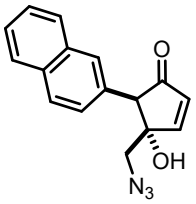
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.67 (d, *J* = 5.9 Hz, 1H), 6.94 (s, 1H), 6.82 (s, 2H), 6.36 (d, *J* = 5.9 Hz, 1H), 5.30 (s, 1H), 3.76 (s, 1H), 3.20 (d, *J* = 12.6 Hz, 1H), 2.93 (d, *J* = 12.6 Hz, 1H), 2.27 (s, 6H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 204.78 (CO), 163.17 (CH), 138.40 (2xC), 135.42 (C), 134.72 (CH), 129.60 (CH), 128.63 (2xCH), 82.76 (C), 64.88 (CH), 58.52 (CH$_2$), 21.32 (2xCH$_3$).

IR (ν/cm^{-1}) 3378, 2921, 2854, 2100, 1712, 1605, 1456, 1341, 1289, 1258, 1078, 1051, 852, 703.

HRMS (ESI) m/z calculated for $C_{14}H_{14}N_3O$ ([M-N$_2$+H]$^+$) 240.1137, found 240.1129.

(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-(naphthalen-2-yl)cyclopent-2-en-1-one (7c)**.



a) General procedure D: the reaction was performed on 100 mg of **6c** (0.36 mmol) and 21.8 mg of Dy(OTf)$_3$ (0.036 mmol). **7c** (25 mg, 25% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (6:4) as the eluent.

b) General procedure E: the reaction was performed on 100 mg of **6c** (0.36 mmol) and 5.42 mg of $ScCl_3$ (0.036 mmol). **7c** (30.5 mg, 36% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (6:4) as the eluent.

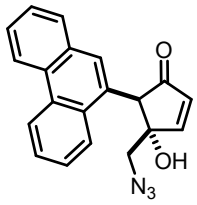
$\mathbf{R_f}$ 0.60 (80% Et$_2$O/toluene).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.92-7.87 (m, 3H), 7.78 (s, 1H), 7.74 (d, *J* = 6.0 Hz, 1H), 7.53-7.48 (m, 2H), 7.36 (dd, *J* = 8.5 Hz, 1.7 Hz, 1H), 6.44 (d, *J* = 6.0 Hz, 1H), 5.47 (s, 1H), 4.05 (s, 1H), 3.23 (d, *J* = 12.6 Hz, 1H), 3.00 (d, *J* = 12.6 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 204.7 (CO), 163.28 (CH), 134.77 (CH), 134.26 (C), 133.57 (C), 133.12 (C), 130.08 (CH), 128.75 (CH), 128.69 (CH), 128.56 (CH), 128.44 (CH), 126.97 (CH), 126.84 (CH), 82.96 (C), 65.02 (CH), 58.44 (CH$_2$).

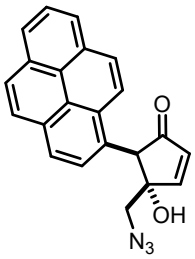
IR (ν/cm^{-1}) 3418, 2105, 1703, 1508, 1341, 1288, 1080, 812.
HRMS (ESI) m/z calculated for $C_{16}H_{12}NO$ ([M-N_2-H_2O+H]$^+$) 234.0919, found 234.0903.

(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-(phenanthren-9-yl)cyclopent-2-en-1-one (7d).**



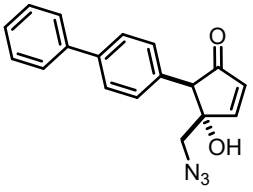
a) General procedure D: the reaction was performed on 150 mg of **6d** (0.45 mmol) and 27.8 mg of Dy(OTf)$_3$ (0.045 mmol). **7d** (63 mg, 40% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent.
b) General procedure E: the reaction was performed on 150 mg of **6d** (0.45 mmol) and 6.89 mg of $ScCl_3$ (0.045 mmol). **7d** (30 mg, 20% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent.
R$_f$ 0.43 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 8.91 (dd, *J* = 8.4 Hz, 1.3 Hz, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), (8.5 (d, *J* = 6.4 Hz, 1H), 7.9 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 6.0 Hz, 1H), 7.77-7.67 (m, 3H), 7.64-7.60 (m, 1H), 7.52 (s, 1H), 6.54 (d, *J* = 6.0 Hz, 1H), 5.63 (d, *J* = 2.1 Hz, 1H), 4.64 (s, 1H), 3.18 (d, *J* = 12.6 Hz, 1H), 3.11 (d, *J* = 12.6 Hz, 1H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 205.74 (CO), 163.64 (CH), 135.90 (CH), 132.25 (C), 131.50 (C), 131.21 (C), 130.77 (C), 129.61 (CH), 129.53 (C), 127.85 (2xCH), 127.71 (CH), 127.56 (CH), 126.07 (CH), 124.10 (CH), 123.39 (2xCH), 83.34 (C), 60.33 (CH), 58.26 (CH_2).
IR (ν/cm^{-1}) 3414, 2103, 1698, 1451, 1291, 1251, 1083, 792, 749, 724.
HRMS (ESI) m/z calculated for $C_{20}H_{14}NO$ ([M-N_2-H_2O+H]$^+$) 284.1075, found 284.1080.

(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-(pyren-1-yl)cyclopent-2-en-1-one (7e)**



This compound was prepared according to the General Procedure **D** using 93 mg of **6e** (0.26 mmol) and 16.1 mg of Dy(OTf)$_3$ (0.026 mmol). **7e** (38 mg, 40% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (6:4) as the eluent. **R$_f$** 0.48 (50% PET/EtOAc).
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 8.62 (s, 1H), 8.29 (d, *J* = 7.6 Hz, 2H), 8.25-8.21 (m, 2H), 8.16 (d, *J* = 3.1 Hz, 2H), 8.07 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 6.1 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 6.1 Hz, 1H), 5.70 (s, 1H), 4.96 (s, 1H), 3.09 (d, *J* = 12.7 Hz, 1H), 2.98 (d, *J* = 12.7 Hz, 1H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 206.03 (CO), 163.71 (CH), 135.03 (CH), 132.24 (C), 131.76 (C), 131.48 (C), 130.47 (C), 128.75 (CH), 128.35 (CH), 128.29 (CH), 128.13 (C), 127.04 (2xCH), 126.23 (CH), 125.98 (CH), 125.78 (C), 125.47 (CH), 125.36 (C), 124.94 (CH), 83.61 (C), 60.92 (CH), 58.44 (CH_2).
IR (ν/cm^{-1}) 3394, 2100, 1694, 1339, 1292, 1247, 1184, 1035, 847, 817, 713.
HRMS (ESI) m/z calculated for $C_{22}H_{16}N_3O_2$ ([M+H]$^+$) 354.1243, found 345.1248.

(4*S,5*R**)-5-([1,1'-Biphenyl]-4-yl)-4-(azidomethyl)-4-hydroxycyclopent-2-en-1-one (7f).**



a) General procedure D: the reaction was performed on 80 mg of **6f** (0.26 mmol) and 16.0 mg of Dy(OTf)$_3$ (0.026 mmol). **7f** (23 mg, 28% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent.

b) General procedure E: the reaction was performed on 80 mg of **6f** (0.26 mmol) and 3.96 mg of $ScCl_3$ (0.026 mmol). **7f** (11.2 mg, 14% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent.

R_f 0.35 (50% PET/EtOAc).

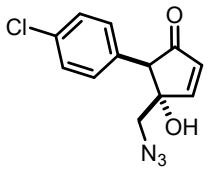
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.71 (d, *J* = 6.0 Hz, 1H), 7.69-7.65 (m, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38-7.32 (m, 3H), 6.41 (d, *J* = 6.0 Hz, 1H), 5.44 (s, 1H), 3.92 (s, 1H), 3.28 (d, *J* = 12.5 Hz, 1H), 3.00 (d, *J* = 12.5 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 204.37 (CO), 163.20 (CH), 141.36 (C), 140.72 (C), 134.74 (CH), 132.19 (C), 131.48 (2xCH), 129.74 (2xCH), 128.23 (CH), 127.64 (2xCH), 127.54 (2xCH), 82.85 (C), 64.64 (CH), 58.38 (CH_2).

IR (ν/cm^{-1}) 3413, 2100, 1703, 1488, 1341, 1291, 1077, 761, 698.

HRMS (ESI) m/z calculated for $C_{18}H_{14}NO$ ($[M-N_2-H_2O+H]^+$) 260.1075, found 260.1065.

(4*S,5*R**)-4-(Azidomethyl)-5-(4-chlorophenyl)-4-hydroxycyclopent-2-en-1-one (7g)**.



a) General procedure D: the reaction was performed on 60 mg of **6g** (0.23 mmol) and 13.9 mg of $Dy(OTf)_3$ (0.023 mmol). **7g** (20 mg, 33% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent.

b) General procedure E: the reaction was performed on 60 mg of **6g** (0.23 mmol) and 3.44 mg of $ScCl_3$ (0.023 mmol). **7g** (10 mg, 17% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent.

R_f 0.46 (50% PET/EtOAc).

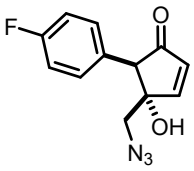
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.67 (d, *J* = 6.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.39 (d, *J* = 6.0 Hz, 1H), 5.48 (s, 1H), 3.89 (s, 1H), 3.25 (d, *J* = 12.6 Hz, 1H), 2.96 (d, *J* = 12.6 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 203.79 (CO), 163.08 (CH), 134.67 (CH), 134.34 (C), 133.53 (C), 132.66 (2xCH), 129.13 (2xCH), 82.70 (C), 64.12 (CH), 58.00 (CH_2).

IR (ν/cm^{-1}) 3389, 2923, 2104, 1706, 1492, 1286, 1120, 1015, 809, 735.

HRMS (ESI) m/z calculated for $C_{12}H_9NOCl$ ($[M-N_2-H_2O+H]^+$) 218.0373, found 218.0639.

(4*S,5*R**)-4-(Azidomethyl)-5-(4-fluorophenyl)-4-hydroxycyclopent-2-en-1-one (7h).**



This compound was prepared according to the General Procedure **D** using 80 mg of **6h** (0.32 mmol) and 19.7 mg of $Dy(OTf)_3$ (0.032 mmol). **7h** (28 mg, 35% yield, d.r. 75:25) was obtained as a yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent. **R_f** 0.48 (50% PET/EtOAc).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.67 (d, *J* = 5.9 Hz, 1H), 7.31-7.26 (m, 2H), 7.14 -7.10 (m, 2H), 6.39 (d, *J* = 5.9 Hz, 1H), 5.40 (s, 1H), 3.89 (s, 1H), 3,24 (d, *J* = 12.5 Hz, 1H), 2.95 (d, *J* = 12.5 Hz, 1H).

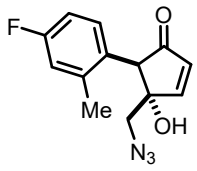
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 203.99 (CO), 162.99 (CH), 162.88 (d, J_{CF} = 243.9 Hz, C), 134.68 (CH), 132.83 (d, J_{CF} = 8.1 Hz, 2xCH), 131.48 (C), 115.80 (d, J_{CF} = 21. Hz, 2xCH), 82.69 (C), 64.07 (CH), 58.12 (CH_2).

^{19}F-NMR (Acetone-d6, 282 MHz) 60.77.

IR (ν/cm^{-1}) 3045, 2105, 1702, 1606, 1509, 1342, 1292, 1223, 1161, 841, 811, 770.

HRMS (ESI) m/z calculated for $C_{12}H_9NOF$ ($[M-N_2-H_2O+H]^+$) 202.0668, found 202.0671.

(4*S,5R*)-4-(Azidomethyl)-5-(4-fluoro-2-methylphenyl)-4-hydroxycyclopent-2-en-1-one (7i)**.



This compound was prepared according to the General Procedure **D** using 160 mg of **6i** (0.61 mmol) and 37.3 mg of $Dy(OTf)_3$ (0.061 mmol). **7i** (13 mg, 22% yield, d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent. $\mathbf{R_f}$ 0.34 (60% MTBE/toluene).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.72 (d, *J* = 6.0 Hz, 1H), 7.03 (dd, *J* = 10.1 Hz, 2.6 Hz, 1H), 6.95-6.37 (m, 2H), 6.39 (d, *J* = 6.0 Hz, 1H), 5.40 (s, 1H), 4.05 (s, 1H), 3.15 (d, *J* = 12.8 Hz, 1H), 2.99 (d, *J* = 12.8 Hz, 1H), 2.47 (s, 3H).

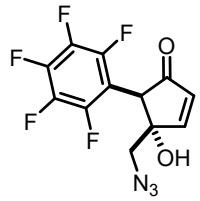
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 205.58 (CO), 163.69 (CH), 162.46 (d, J_{CF} = 243.9 Hz, C), 134.68 (CH), 132.20 (C), 130.85 (d, J_{CF} = 3.2 Hz C), 117.44 (d, J_{CF} = 20.5 Hz, CH), 112.98 (d, J_{CF} = 20.5 Hz, CH), 83.30 (C), 60.77 (CH), 58.42 (CH_2), 20.62 (CH_3).

^{19}F-NMR (Acetone-d6, 282 MHz) 60.15.

IR (ν/cm^{-1}) 3395, 2924, 2105, 1705, 1612, 1499, 1446, 1280, 1256, 957, 866.

HRMS (ESI) m/z calculated for $C_{13}H_{13}NO_2F$ ($[M\text{-}N_2+H]^+$) 234.0930, found 234.0931.

(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-(perfluorophenyl)cyclopent-2-en-1-one (7j)**



This compound was prepared according to the General Procedure **E** using **6j** (100 mg, 0.31 mmol) in a mixture of t-BuOH/H_2O 5:1 (0.1 M), were added $Na_2S_2O_4$ (3 wt %) and 30.8 mg of $Sc(OTf)_3$ (0.062 mmol, 20 mol %). The reaction mixture was heated under MW irradiation for 1.5 h at 130 °C. After cooling to room temperature, the mixture was quenched with a saturated solution of $NaHCO_3$. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. **7j** (36 mg, 36% yield, d.r. > 80:20) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (7:3) as the eluent. $\mathbf{R_f}$ 0.75 (50% PET/EtOAc).

^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.64 (d, *J* = 5.9 Hz, 1H), 6.47 (d, *J* = 5.9 Hz, 1H), 3.90 (s, 1H), 3.74 (d, *J* = 12.5 Hz, 1H), 3.57 (d, *J* = 12.5 Hz, 1H), 2.39 (s, 1H).

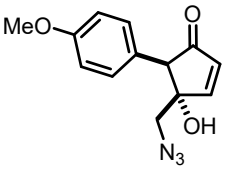
^{13}C-NMR ($CDCl_3$, 126 MHz) δ 202.08 (CO), 160.46 (CH), 136-153 (m, 5xCF *exact peak identification not possible due to multiplicity caused by carbon-fluorine coupling*), 135.10 (CH), 79.96 (C), 49.17 (CH_2), 57.65 (CH).

^{19}F-NMR ($CDCl_3$, 282 MHz) δ -133.97 (d, *J* = 22.0 Hz, dia1), -143.08 (d, *J* = 22.0 Hz, dia2), -152.45 (t, *J* = 21.1 Hz, dia1), -153.4 (t, *J* = 21.1 Hz, dia2), -162.37- -160.87- (m, dia1), -161.36- -161.84 (m, dia2).

IR (ν/cm^{-1}) 3405, 2109, 1271, 1658, 1522, 1504, 1296, 1129, 979.

HRMS (ESI) m/z calculated for $C_{12}H_7F_5NO_2$ ($[M\text{-}N_2+H]^+$) 292.0391, found 292.0406.

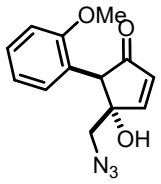
(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-(4-methoxyphenyl)cyclopent-2-en-1-one (7k).**



This compound was prepared according to the General Procedure **D** using 59 mg of **6k** (0.23 mmol) and 13.9 mg of $Dy(OTf)_3$ (0.022 mmol). **7k** (20 mg, 42% yield, d.r. 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent. $\mathbf{R_f}$ 0.52 (50% PET/EtOAc).

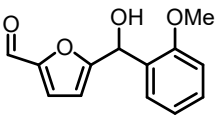
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.66 (d, *J* = 6.0 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.36 (d, *J* = 6.0 Hz, 1H), 5.30 (s, 1H), 3.80 (s, 1H), 3.79 (s, 3H), 3.20 (d, *J* = 12.5 Hz, 1H), 2.92 (d, *J* = 12.5 Hz, 1H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 204.63 (CO), 162.99 (CH), 159.85 (C), 134.70 (CH), 131.95 (2xCH), 127.25 (C), 114.49 (2xCH), 82.76 (C), 64.29 (CH), 58.50 (CH_2), 55.47 (CH_3).
IR (ν/cm^{-1}) 3417, 2105, 1708, 1613, 1514, 1302, 1251, 1180, 1032.
HRMS (ESI) m/z calculated for $C_{13}H_{14}NO_3$ ([M-N_2+H]$^+$) 232.0968, found 232.0962.

(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-(2-methoxyphenyl)cyclopent-2-en-1-one (7l).**



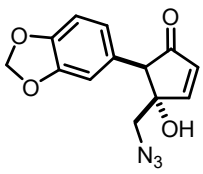
This compound was prepared according to the General Procedure **D** using 85 mg of **6l** (0.33 mmol) and 20.0 mg of Dy(OTf)$_3$ (0.033 mmol). **7l** (25 mg, 29% yield, d.r. > 95:5) was obtained as a pale yellow oil after purification on preparative TLC plate on silica gel using toluene/MTBE (60:40) as the eluent. **R_f** 0.48 (60% toluene/MTBE).
Note relative to NMRs: compound **7l** hasn't a free rotation of the 2-methoxyphenyl group due to the steric hindrance with the ketone, which leads to coalescence making difficult the observation of some expected ^{13}C NMR, due to ^{1}H NMR large broad peaks. HSQC and HMBC experiments provided cross-correlation allowing to identify them.
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.62 (d, *J* = 5.8 Hz, 1H), 7.29 (ddd, *J* = 8.2 Hz, 7.5 Hz, 1.4 Hz, 1H), 7.12 (bs 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.94 (td, J = 7.5 Hz, 1.4 Hz, 1H), 6.31 (d, *J* = 5.8 Hz, 1H), 5.06 (bs, 1H), 3.80 (s, 1H), 3.77 (s, 3H), 3.21 (d, *J* = 12.8 Hz, 1H), 3.10 (bs, 1H).
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 205.06 (CO), 158.82 (C), 157.32 (C), 162.09 (CH), 134.09 (CH), 129.66 (CH), 124.67 (CH), 121.47 (CH), 111.22 (CH), 82.80 (C), 57.46 (CH_2), 55.75 (CH_3). *The signal of the carbon in α-position of the ketone between 60-65 ppm, was not detectable due to the broad proton signal.*
IR (ν/cm^{-1}) 3422, 2924, 2103, 1713, 1494, 1293, 1247, 1024, 756.
HRMS (ESI) m/z calculated for $C_{13}H_{14}NO_3$ ([M-N_2+H]$^+$) 232.0968, found 232.0969.

5-(Hydroxy(2-methoxyphenyl)methyl)furan-2-carbaldehyde (9)



This compound was obtained using the General procedure **D** using 240 mg of **6l** (0.92 mmol) and 56.4 mg of Dy(OTf)$_3$ (0.092 mmol). **9** (11 mg, 5% yield) was obtained as a pale yellow oil after purification on preparative TLC plate on silica gel using toluene/MTBE (60:40) as the eluent. **R_f** 0.50 (60% toluene/MTBE).
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 9.57 (s, 1H), 7.30-7.34 (m, 2H), 7.18 (d, *J* = 3.9 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 3.6 Hz, 1H), 6.07 (d, *J* = 6.2 Hz, 1H), 3.83 (s, 3H), 3.41 (d, *J* = 6.5 Hz, 1H).
^{13}C-NMR ($CDCl_3$, 126 MHz) δ 177.90 (CH), 162.79 (C), 156.86 (C), 152.41 (C), 129.89 (CH), 128.18 (CH), 127.89 (CH), 121.76 (C), 121.19 (CH), 111.04 (CH), 109.63 (CH), 67.10 (CH), 55.64 (CH3).
IR (ν/cm^{-1}) 3403, 2105, 1667, 1601, 1514, 1491, 1243, 1022, 754.
HRMS (ESI) m/z calculated for $C_{13}H_{11}O_3$ ([M-H_2O+H]$^+$ 215.0708, found 215.0711.

(4*S,5*R**)-4-(Azidomethyl)-5-(benzo[d][1,3]dioxol-5-yl)-4-hydroxycyclopent-2-en-1-one (7m).**



This compound was prepared according to the General Procedure **D** using 33 mg of **6m** (0.12 mmol) and 7.4 mg of Dy(OTf)$_3$ (0.012 mmol). **7m** (11 mg, 34% yield,

d.r. > 95:5) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (5:5) as the eluent. $\mathbf{R_f}$ 0.61 (60% PET/EtOAc).

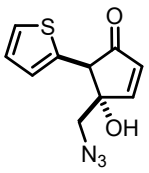
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.66 (d, *J* = 6.1 Hz, 1H), 6.85-6.81 (m, 1H), 6.74-6.70 (m, 2H), 6.36 (d, *J* = 6.1 Hz, 1H), 5.99 (s, 2H), 5.35 (s, 1H), 3.80 (s, 1H), 3.26 (d, *J* = 12.5 Hz, 1H), 2.99 (d, *J* = 12.5 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 126 MHz) δ 204.26 (CO), 162.99 (CH), 148.46 (C), 147.74 (C), 134.62 (CH), 128.84 (C), 124.41 (CH), 110.93 (CH), 108.81 (CH), 102.01 (CH_2), 82.78 (C), 64.58 (CH), 58.34 (CH_2).

IR (ν/cm^{-1}) 3405, 2101, 1698, 1504, 1488, 1442, 1232, 1067, 929, 806, 770.

HRMS (ESI) m/z calculated for $C_{13}H_{10}N_3O_3$ ([M-H_2O+H]$^+$) 256.0722, found 256.0721.

(4*S,5*R**)-4-(Azidomethyl)-4-hydroxy-5-(thiophen-2-yl)cyclopent-2-en-1-one (7n).**



This compound was prepared according to the General Procedure **D** using 110 mg of **6n** (0.47 mmol) and 28.5 mg of Dy(OTf)$_3$ (0.047 mmol). **7n** (34 mg, 31% yield, d.r. 50:50) was obtained as a pale yellow oil after flash chromatography using heptane/ethyl acetate (6:4) as the eluent. $\mathbf{R_f}$ 0.41 (60% PET/EtOAc).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.65 (d, *J* = 6.1 Hz, 1H), 7.37 (dd, *J* = 5.2 Hz, 0.9 Hz, 1H), 6.99 (dd, *J* = 5.2 Hz, 3.5 Hz, 1H), 6.94 (d, *J* = 3.5 Hz, 1H), 6.38 (d, *J* = 6.1 Hz, 1H), 4.70 (s, 1H), 4.02 (s, 1H), 3.41 (d, *J* = 12.5 Hz, 1H), 3.04 (d, *J* = 12.5 Hz, 1H).

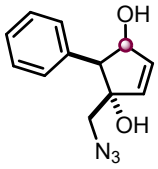
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 201.96 (CO), 162.56 (CH), 135.65 (C), 134.16 (CH), 128.43 (CH), 127.09 (CH), 126.07 (CH), 80.68 (C), 57.72 (CH), 55.56 (CH_2).

IR (ν/cm^{-1}) 3388, 2922, 2103, 1708, 1283, 702.

HRMS (ESI) m/z calculated for $C_{10}H_{10}NO_2S$ ([M-N_2+H]$^+$) 208.0427, found 208.0400.

VIII. Synthetic transformation of 4-(azidomethyl)-cyclopentenones

(4*S,5*R**)-1-(Azidomethyl)-2-phenylcyclopent-4-ene-1,3-diol (10).**



d.r. 1:1

To a solution of **7a** (80 mg, 0.35 mmol, 1 eq.) in MeOH (0.35 M) was added at 0 °C $CeCl_3 \bullet 7H_2O$ (130 mg, 0.35 mmol, 1 eq.). After 0.5 h, $NaBH_4$ (13.2 mg, 0.35 mmol, 1 eq.) was then added in portions, and mixture was stirred for 1.5 h at room temperature. Thereafter, the reaction was quenched with HCl (5 mL of a 1 M aqueous solution), and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (8:2) as the eluent to afford product **10** in two diastereoisomers (76% yield, d.r. 1:1).

Diastereoisomer 1 (31.5 mg, d.r. 5:1); $\mathbf{R_f}$ 0.51 (50% PET/EtOAc):

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.18 (s, 2H), 5.0 (t, *J* = 5.0 Hz, 1H), 4.52 (s, 1H), 3.99 (d, *J* = 5.0 Hz, 1H), 3.31 (d, *J* = 5.7 Hz, 1H), 3.27 (d, *J* = 12.3 Hz, 1H), 3.21 (d, *J* = 12.3 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 500 MHz) δ 140.02 (CH), 137.90 (C), 136.83 (CH), 131.84 (2xCH), 128.37 (2xCH), 127.33 (CH), 86.62 (C), 76.44 (CH), 61.50 (CH), 60.18 (CH_2).

IR (ν/cm^{-1}) 3373, 2921, 2095, 1494, 1282, 1085, 1058, 925, 755, 701.

HRMS (ESI) m/z calculated for $C_{12}H_{14}NO_2$ ($[M\text{-}N_2\text{+}H]^+$) 204.1025, found 204.1023.

Diastereoisomer 2 (30.9 mg, d.r. > 95:5); $\mathbf{R_f}$ 0.42 (50% PET/EtOAc):

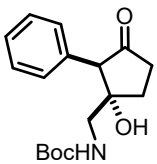
^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.32 (d, *J* = 7.5 Hz, 2H), 7.2 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1 H), 5.92 (dd, *J* = 5.9 Hz, 1.6 Hz, 1H), 5.79 (dd, *J* = 5.9 Hz, 1.6 Hz, 1H), 5.02 (dt, *J* = 7.5 Hz, 1.5 Hz, 1H), 3.18 (d, *J* = 7.6 Hz, 1H), 2.99 (d, J = 12.4 Hz, 1H), 2.78 (d, J = 12.4 Hz, 1H).

^{13}C-NMR (Acetone-d_6, 500 MHz) δ 138.27 (C), 138.03 (CH), 138.01 (CH), 129.91 (2xCH), 129.01 (2xCH), 127.61 (CH), 85.19 (C), 76.90 (CH), 67.29 (CH), 59.58 (CH_2).

IR (ν/cm^{-1}) 3353, 2923, 2097, 1702, 1496, 1407, 1260, 1082, 1038, 742, 700.

HRMS (ESI) m/z calculated for $C_{12}H_{12}NO$ ($[M\text{-}N_2\text{-}H_2O\text{+}H]^+$) 186.0919, found 186.0912.

(4*S,5*R**)-*tert*-Butyl-((-1-hydroxy-3-oxo-2-phenylcyclopentyl)methyl)carbamate (11).**



To a degassed solution of **7a** (80 mg, 0.35 mmol, 1.0 eq.) in EtOAc (0.1 M), were added 10% Pd/C (19 mg, 5 mol %) and Boc_2O (96 µL, 0.42 mmol, 1.2 eq.). The resulting mixture was stirred under H_2 balloon gaz for 16 h. Upon completion, the mixture was filtered through a plug of Celite and solvents were removed under vacuum. **11** (42 mg, 40% yield) was obtained as an orange oil after flash chromatography using petroleum ether/ethyl acetate (8:2) as the eluent. $\mathbf{R_f}$ 0.37 (50% PET/EtOAc).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 7.40 (t, *J* = 7.5 Hz, 2H), 7.36-7.31 (m, 3H), 6.47 (s, 1H), 4.25 (s, 1H), 4.23 (s, 1H), 2.94 (s, 2H), 2.72 (t, *J* = 4.1 Hz, 2H), 2.47-2.44 (m, 2H).

^{13}C-NMR (Acetone-d_6, 500 MHz) δ 206.95 (CO), 172.78 (C), 156.96 (CO), 140.21 (C), 132.76 (CH), 130.11 (2xCH), 128.81 (2xCH), 128.37 (CH), 79.17 (C), 41.42 (CH_2), 34.91 (CH_2), 28.55 ($3xCH_3$), 27.74 (CH_2).

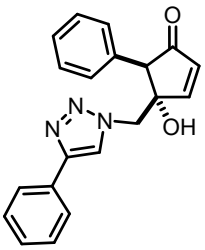
IR (ν/cm^{-1}) 3347, 2976, 1687, 1512, 1496, 1365, 1247, 1162, 1121, 1045, 761, 699.

HRMS (ESI) m/z calculated for $C_{13}H_{14}NO_3^{\bullet}$ ($[M\text{-}C_4H_9O^{\bullet}]$) 232.0974, found 232.0967.

General Procedure F for the synthesis of the 4-hydroxy-4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-5-(aryl)cyclopent-2-en-1-one compounds:

7a (1.0 eq.) was taken in a mixture of *t*-BuOH/H_2O 2:1 (0.036 M). To this, phenyl acetylene (1.1 eq.), $CuSO_4 \cdot 5H_2O$ (50 mol %) and sodium ascorbate (50 mol %) were added. The yellow solution was stirred at room temperature for 16 h. The reaction mixture was diluted with DCM and H_2O, and the aqueous layer was extracted twice with DCM. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated to dryness under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the derivatives **12** and **13**.

(4*S,5*R**)-4-Hydroxy-5-phenyl-4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)cyclopent-2-en-1-one (12).**



This compound was prepared according to the General Procedure **F** using 56 mg of **7a** (0.25 mmol), phenyl acetylene (29 µL, 0.27 mmol, 1.1 eq.), $CuSO_4 \cdot 5H_2O$ (30.5 mg, 0.12 mmol, 50 mol %) and sodium ascorbate (24.2 mg, 0.12 mmol, 50 mol %). **12** (71 mg, 88% yield) was obtained after flash chromatography using heptane/ethyl acetate (4:6) as the eluent. $\mathbf{R_f}$ 0.25 (50% PET/EtOAc).

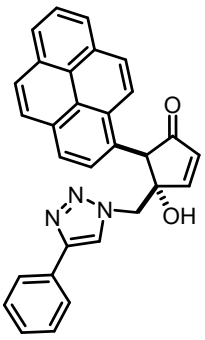
^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.61 (d, *J* = 7.4 Hz, 2H), 7.53 (s, 1H), 7.38-7.29 (m, 7H), 7.19 (d, *J* = 7.4 Hz, 2H), 6.37 (d, *J* = 5.9 Hz, 1H), 5.29 (s, 1H), 4.14 (d, *J* = 14.3 Hz, 1H), 4.01 (s, 1H), 3.95 (d, *J* = 14.4 Hz, 1H).

^{13}C-NMR ($CDCl_3$, 126 MHz) δ 205.17 (CO), 161.81 (CH), 147.42 (C), 134.74 (CH), 133.75 (C), 129.89 (2xCH), 129.79 (C), 129.20 (2xCH), 129.01 (2xCH), 128.57 (CH), 128.18 (CH), 125.67 (2xCH), 122.21 (CH), 80.99 (C), 64.16 (CH), 57.68 (CH_2).

IR (ν/cm^{-1}) 3407, 1710, 1440, 1346, 1232, 1078, 909, 802, 765, 729.

HRMS (ESI) calculated for $C_{20}H_{18}N_3O_2$ ($[M+H]^+$) 332.1399, found 332.1389.

(4*S,5*R**)-4-Hydroxy-4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-5-(pyren-1-yl)cyclopent-2-en-1-one (13).**



This compound was prepared according to the General Procedure **F** using 39 mg of **7e** (0.11 mmol), phenyl acetylene (13 µL, 0.12 mmol, 1.1 eq.), $CuSO_4 \cdot 5H_2O$ (13.7 mg, 0.055 mmol, 50 mol %) and sodium ascorbate (10.9 mg, 0.055 mmol, 50 mol %). **13** (51.0 mg, 99% yield) was obtained as a pale yellow solid after flash chromatography using petroleum ether/ethyl acetate (6:4) as the eluent. $\mathbf{R_f}$ 0.28 (50% PET/EtOAc).

^{1}H-NMR (Acetone-d_6, 500 MHz) δ 8.69 (d, J = 7.7 Hz, 1H), 8.35-8.29 (m, 4H), 8.22-8.18 (m, 2H), 8.10 (t, *J* = 7.7 Hz, 1H), 8.01 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 5.9 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 5.9 Hz, 1H), 5.88 (s, 1H), 5.15 (s, 1H), 4.34 (d, = 14.4 Hz, 1H), 3.92 (d, *J* = 14.4 Hz, 1H).

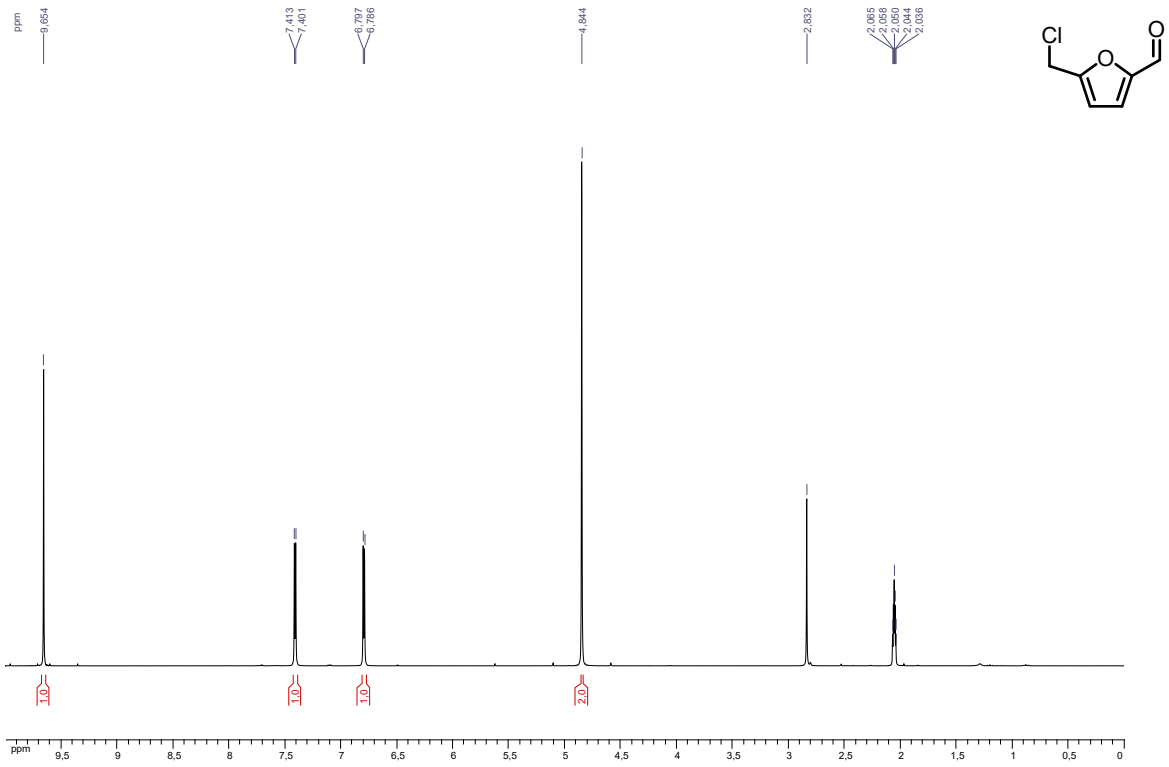
^{13}C-NMR (Acetone-d_6, 126 MHz) δ 206.02 (CO), 163.20 (CH), 147.33 (C), 134.99 (CH), 132.29 (C), 132.11 (C), 132.06 (C), 131.81 (C), 131.71 (C), 130.18 (2xC), 129.51 (2xCH), 129.09 (CH), 128.54 (2xCH), 128.48 (CH), 128.33 (CH), 127.18 (CH), 126.39 (CH), 126.11 (CH), 126.05 (2xCH), 125.80 (CH), 125.37 (C), 124.76 (CH), 123.41 (CH), 82.33 (C), 61.28 (CH), 57.97 (CH_2).

IR (ν/cm^{-1}) 3394, 1707, 1463, 1438, 1244, 1072, 849, 764, 693.

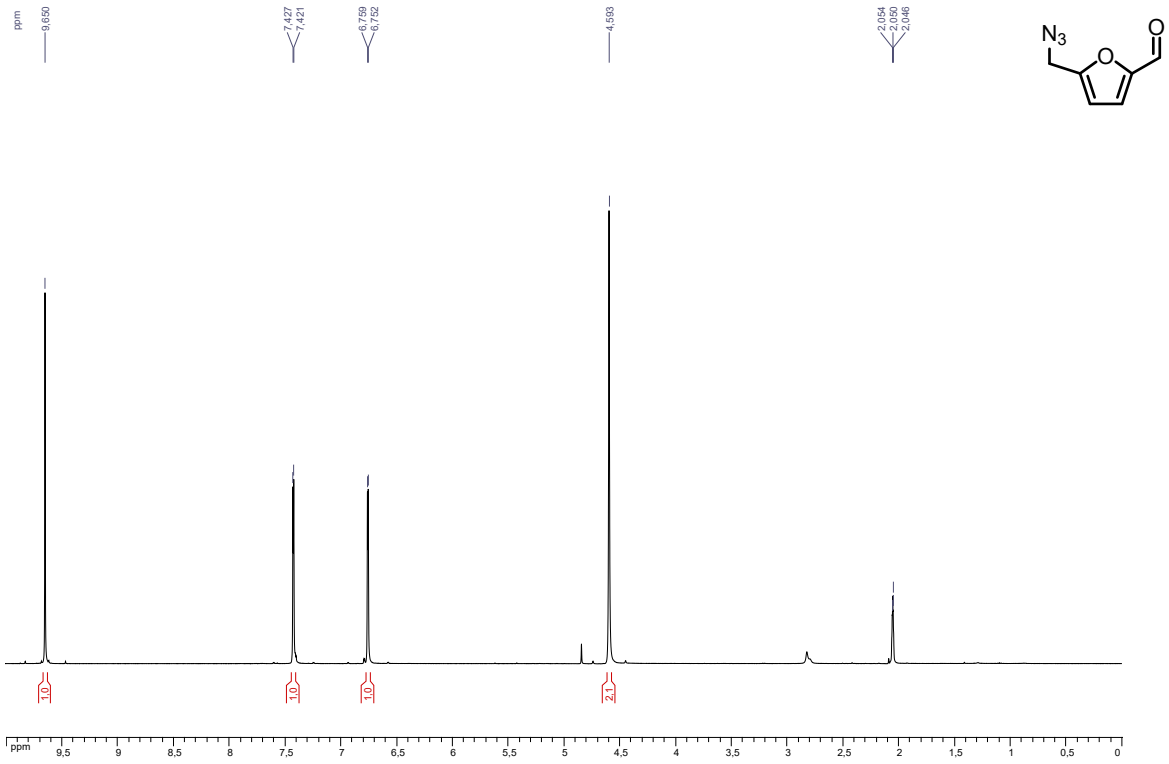
HRMS (ESI) m/z calculated for $C_{30}H_{22}N_3O_2$ ($[M+H]^+$) 456.1707, found 456.1668.

IX. NMR Spectra (^{1}H NMR, ^{13}C NMR and ^{19}F for the products concerned)

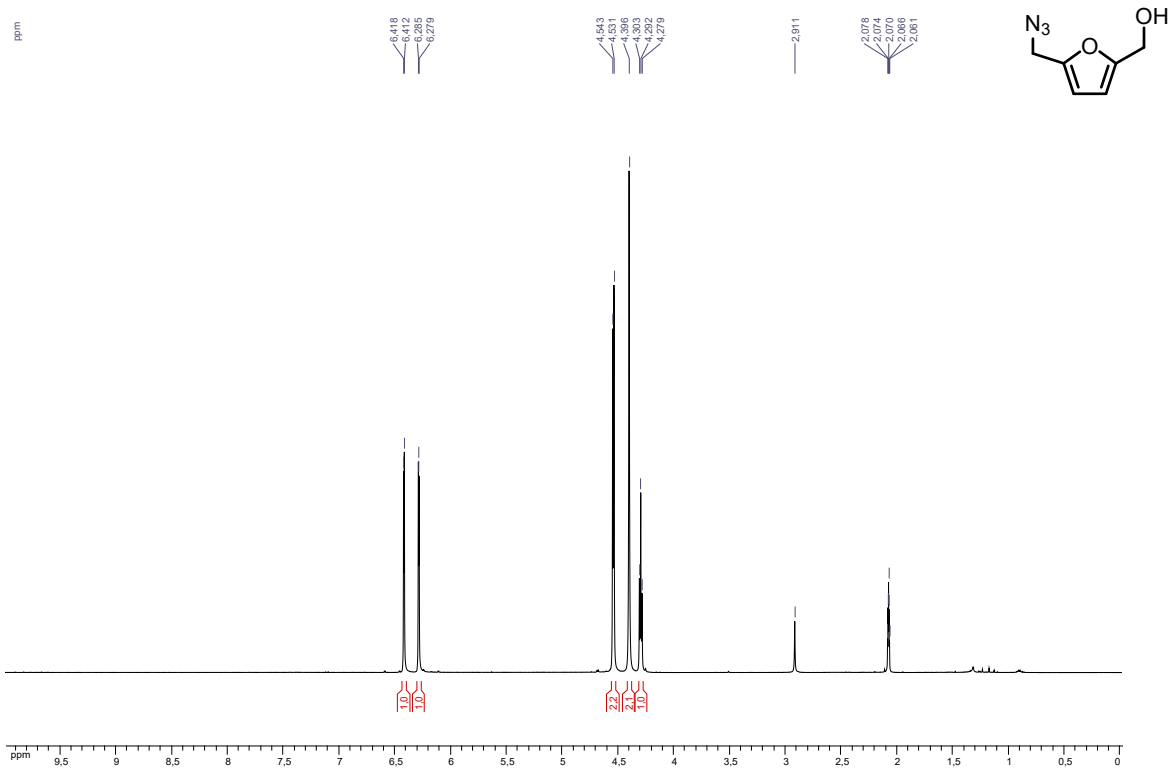
^{1}H-NMR (Acetone-d_6, 300 MHz) **(1)**



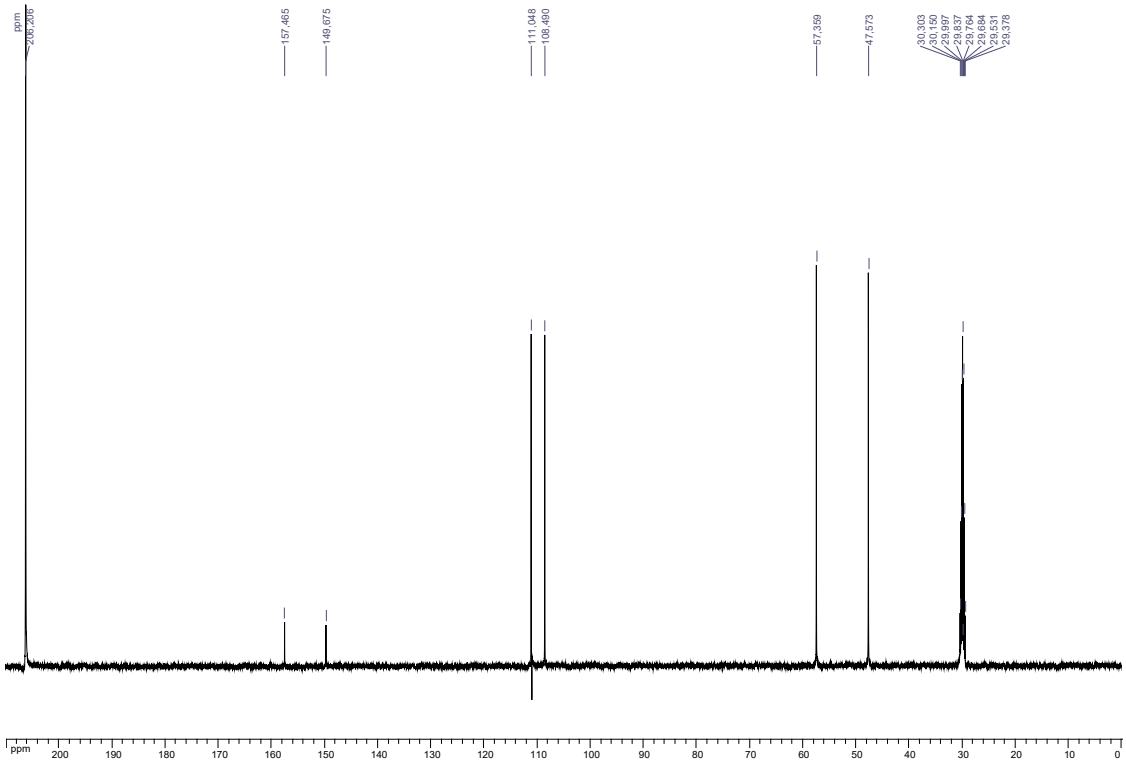
^{1}H-NMR (Acetone-d_6, 500 MHz) **(2)**



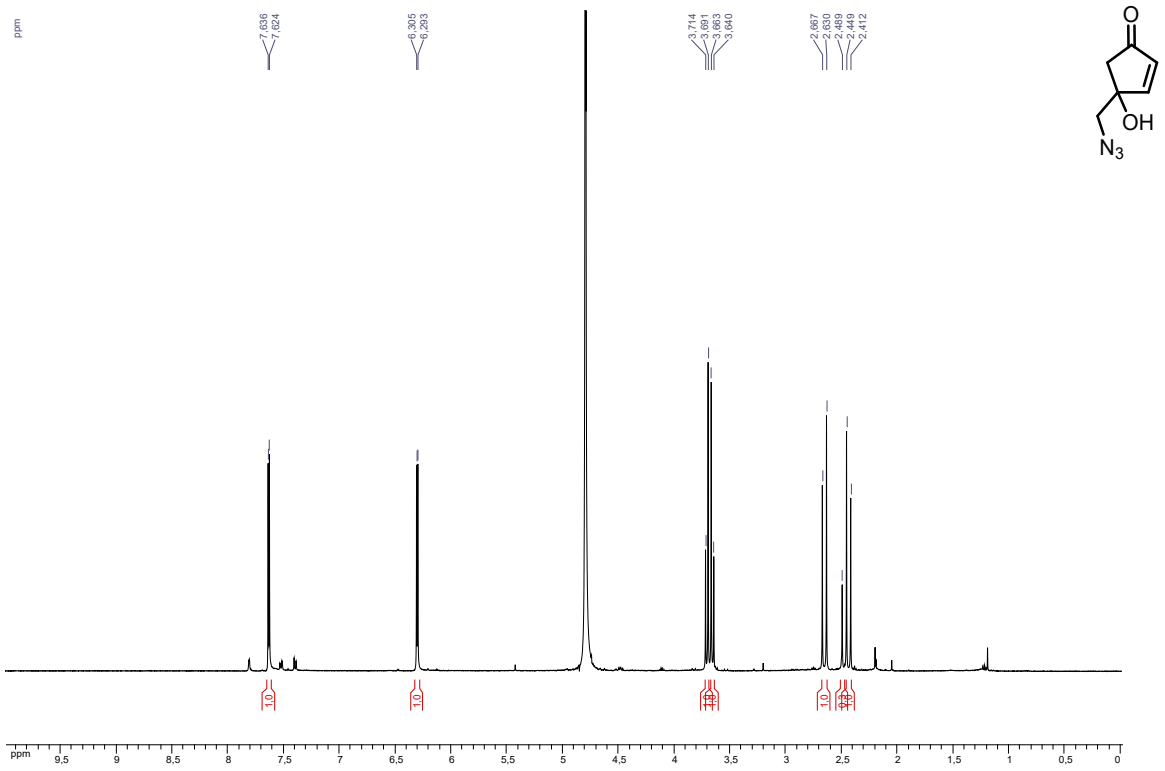
^{1}H-NMR (Acetone-d_6, 500 MHz) **(4)**



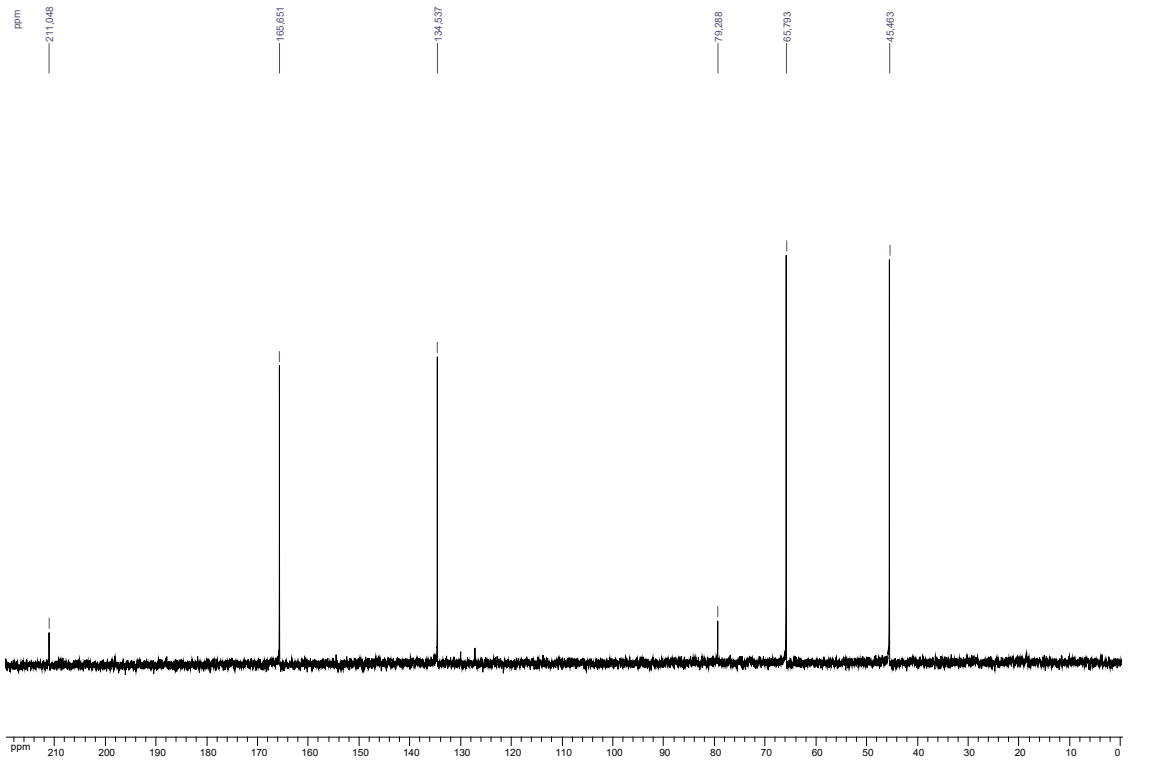
^{13}C-NMR (Acetone-d_6, 126 MHz)



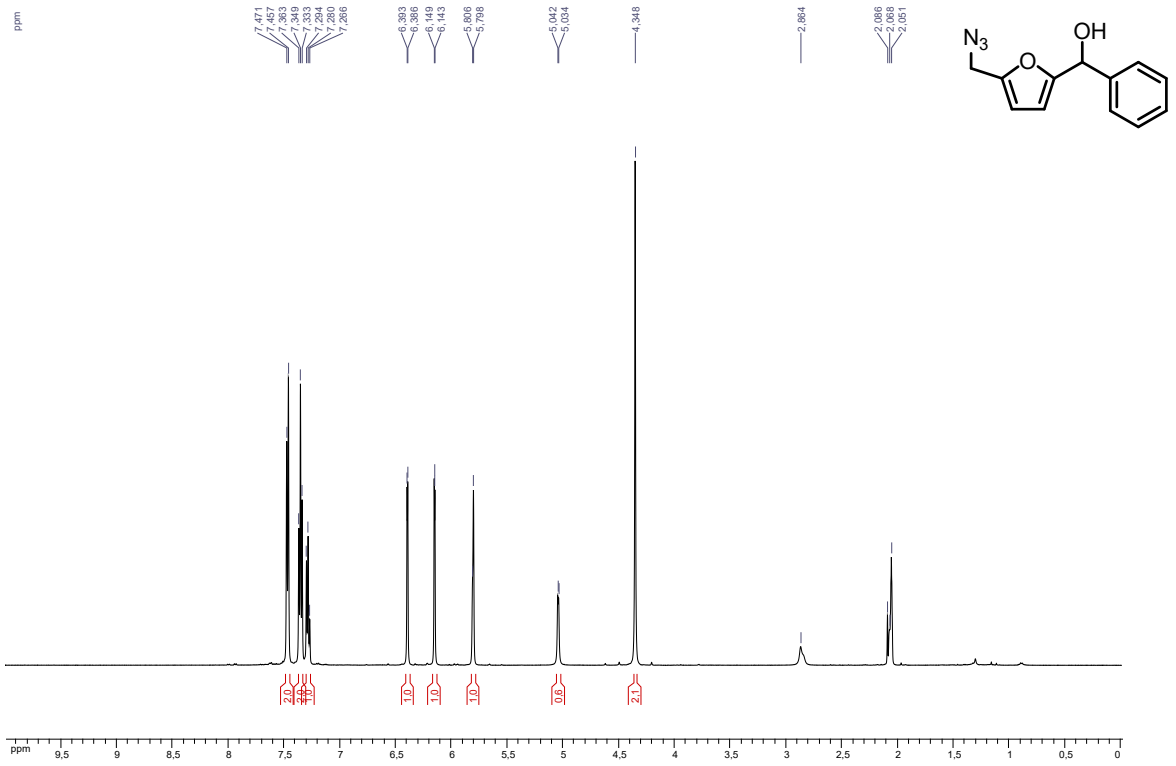
^{1}H-NMR (D_2O, 500 MHz) **(5)**



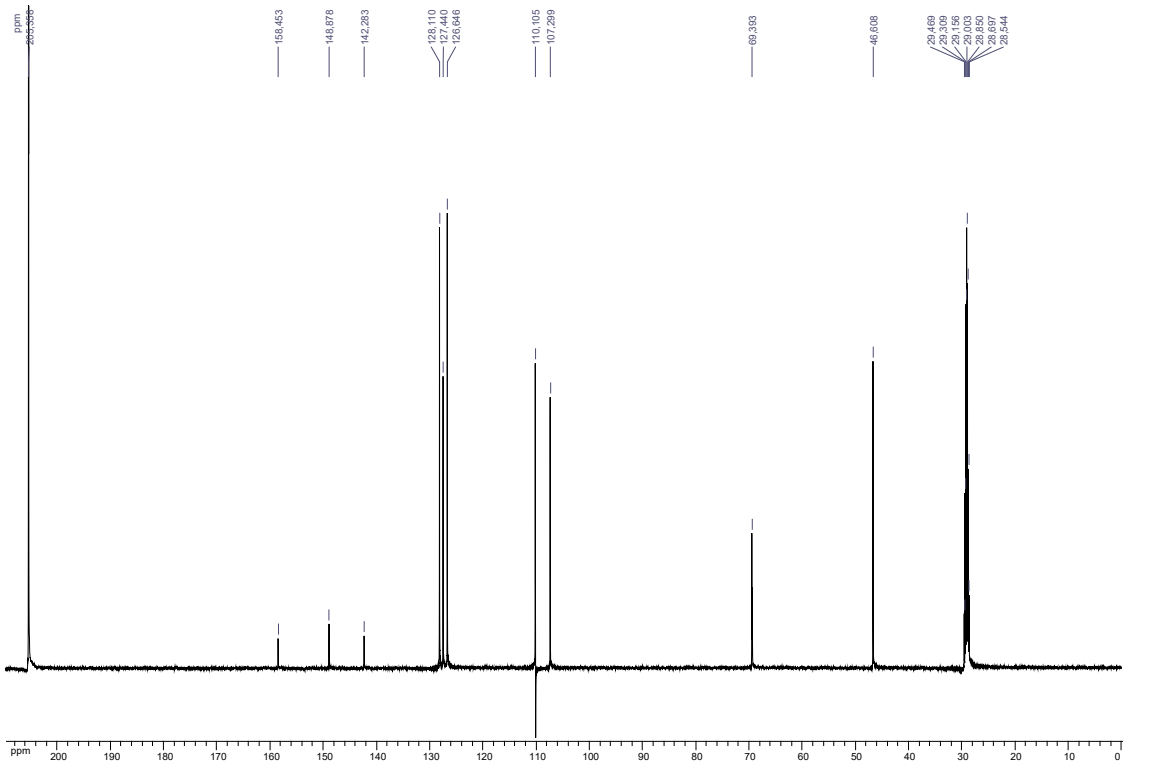
^{13}C-NMR (D_2O, 126 MHz)



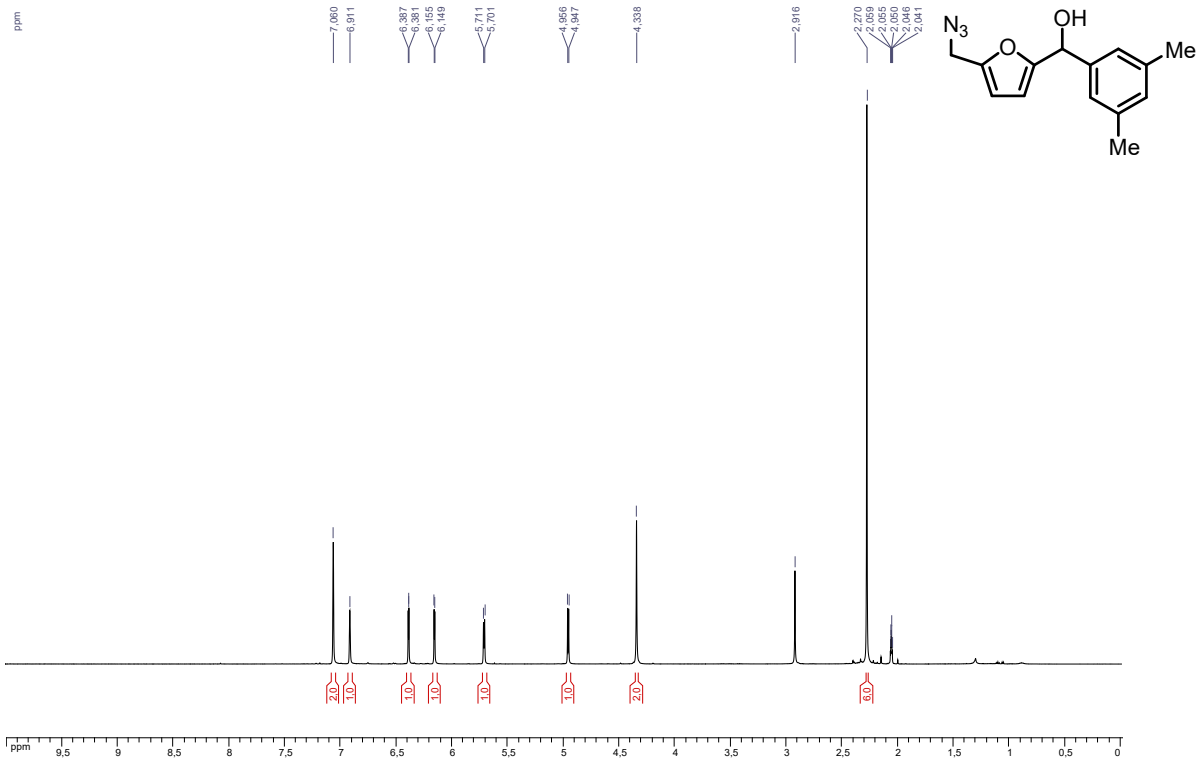
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6a)**



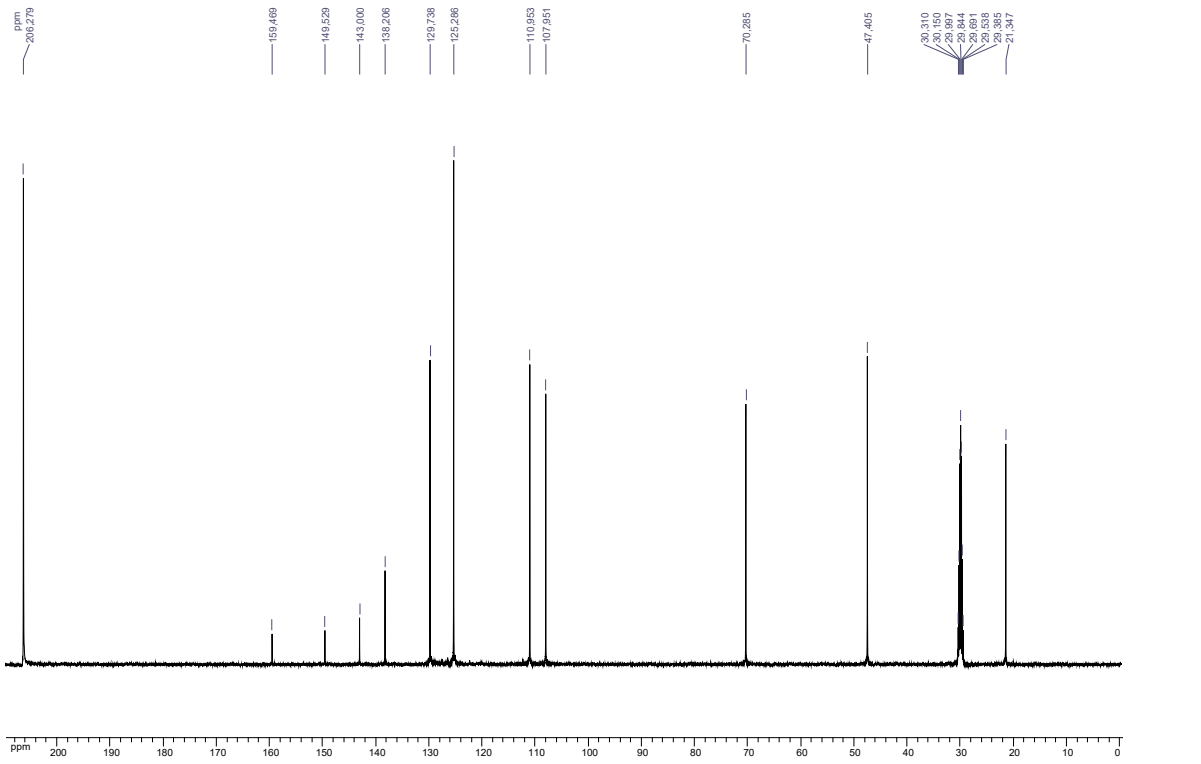
^{13}C-NMR (Acetone-d_6, 126 MHz)



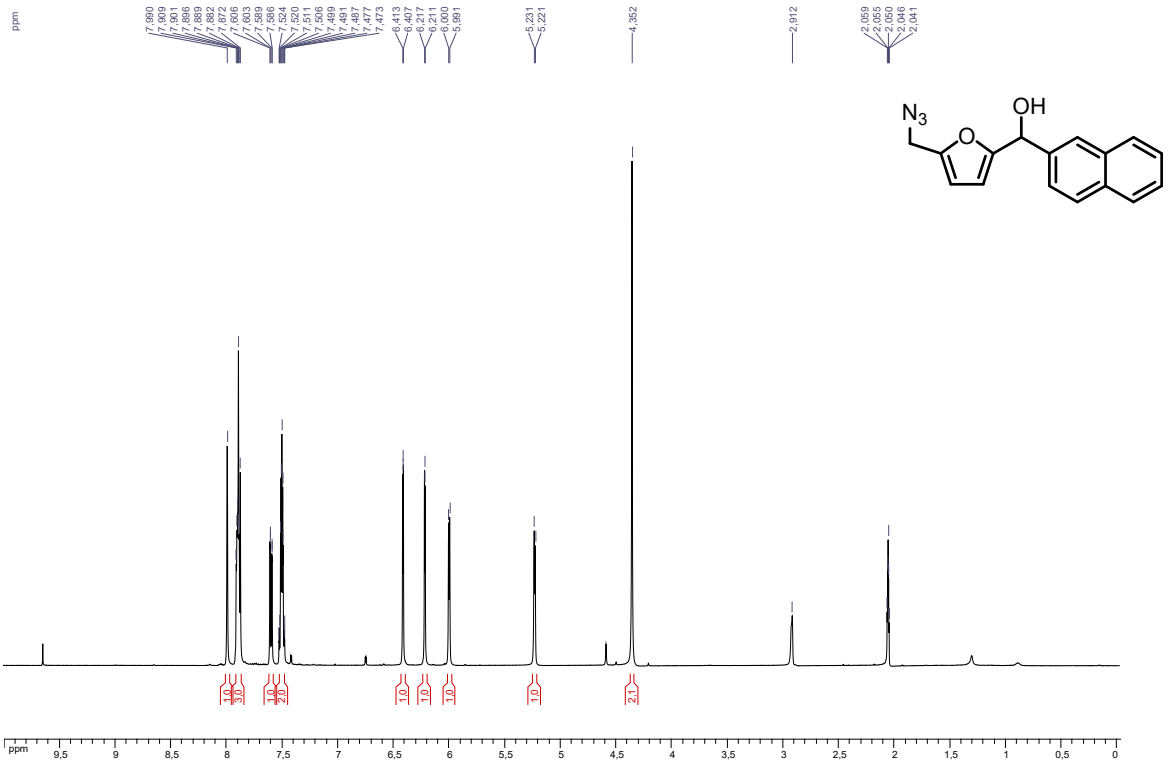
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6b)**



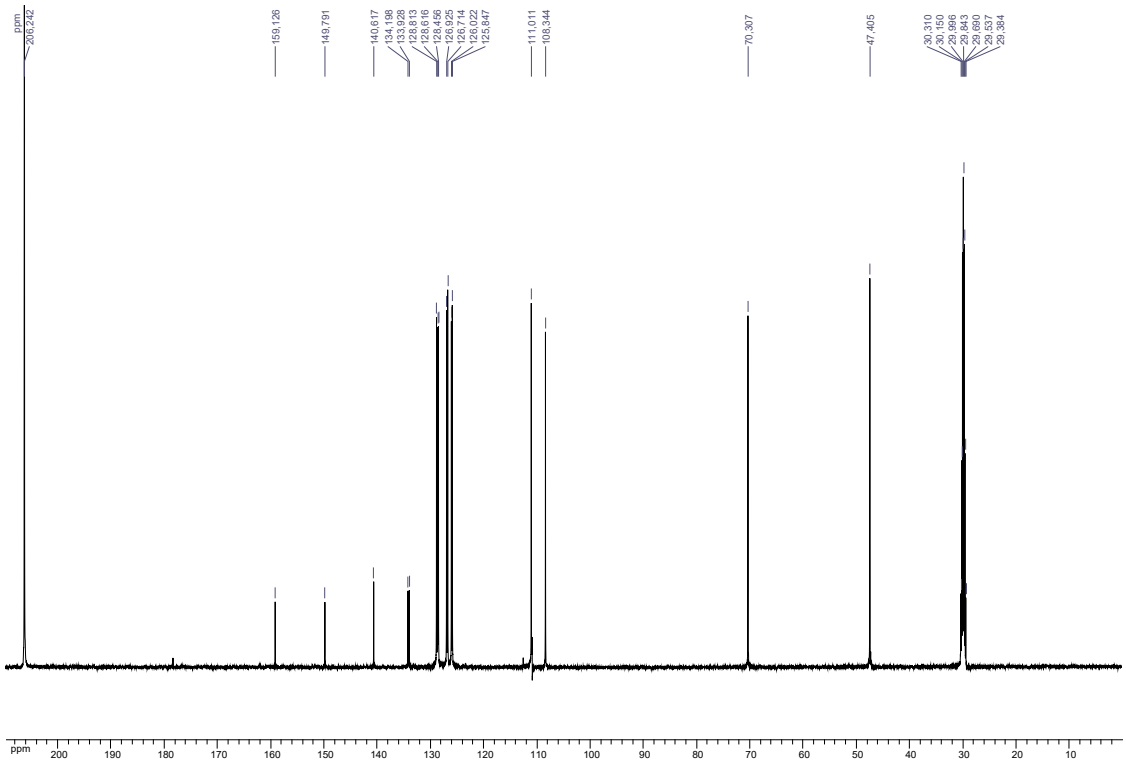
^{13}C-NMR (Acetone-d_6, 126 MHz)



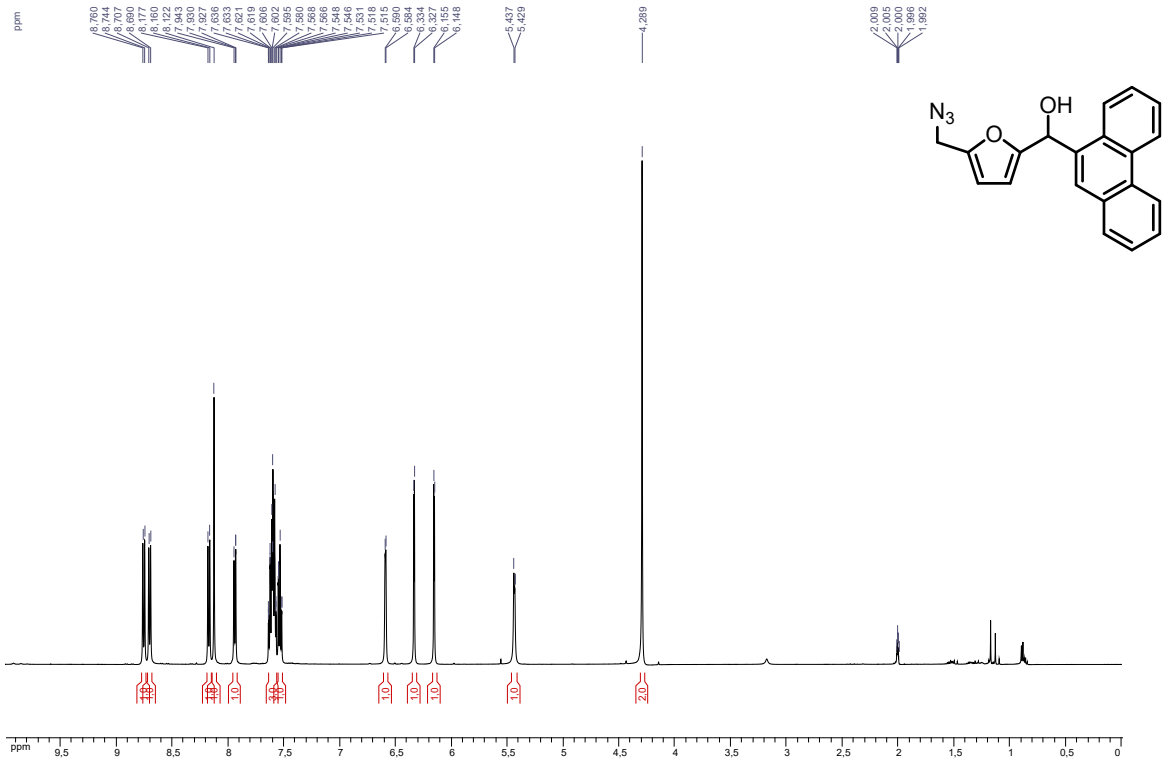
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6c)**



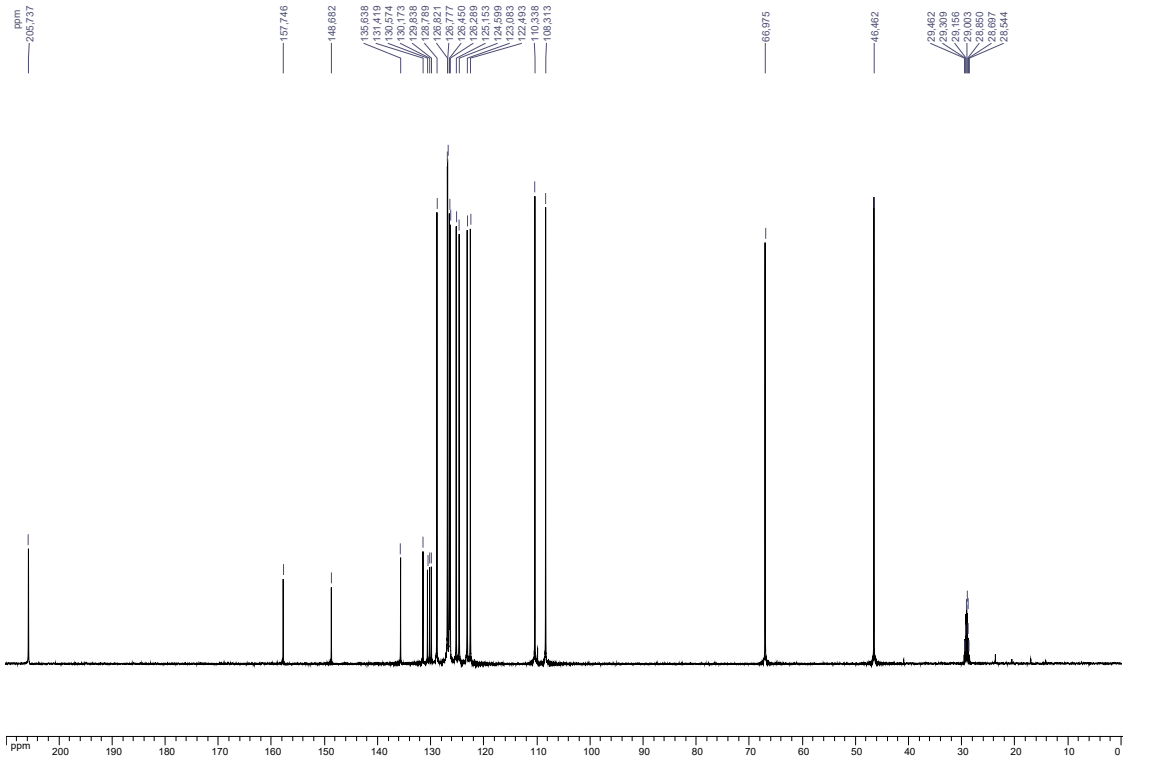
^{13}C-NMR (Acetone-d_6, 126 MHz)



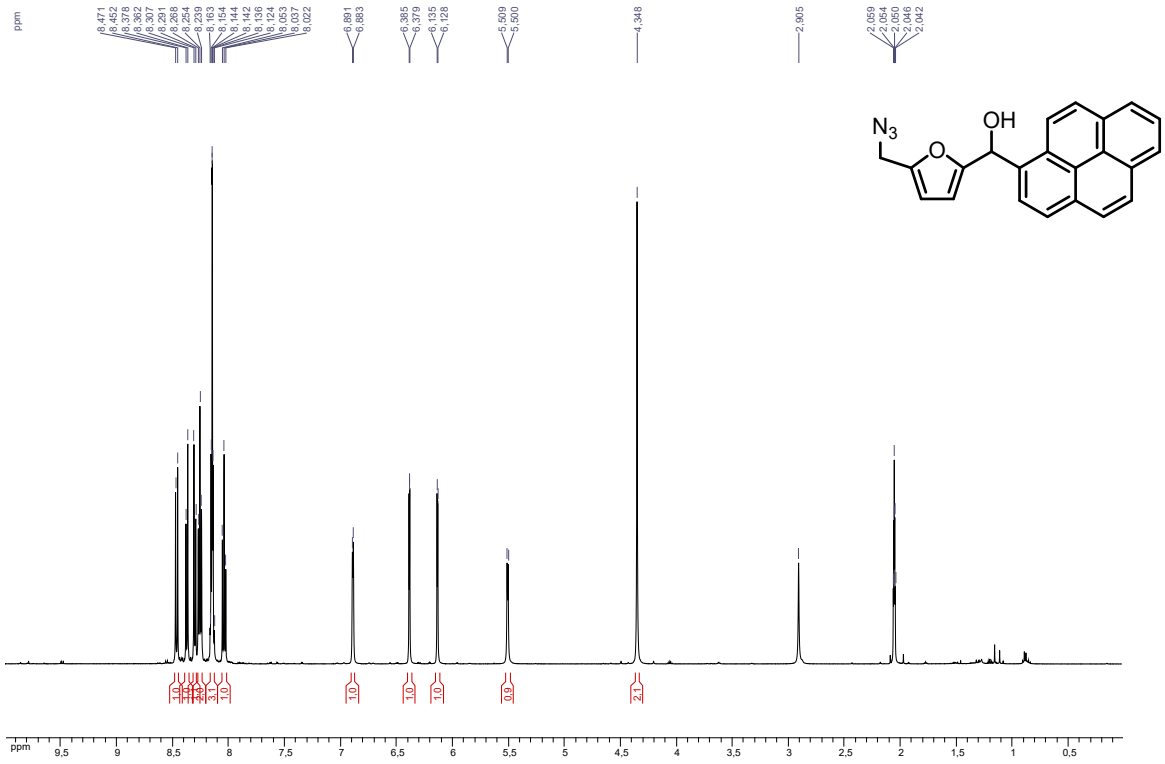
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6d)**



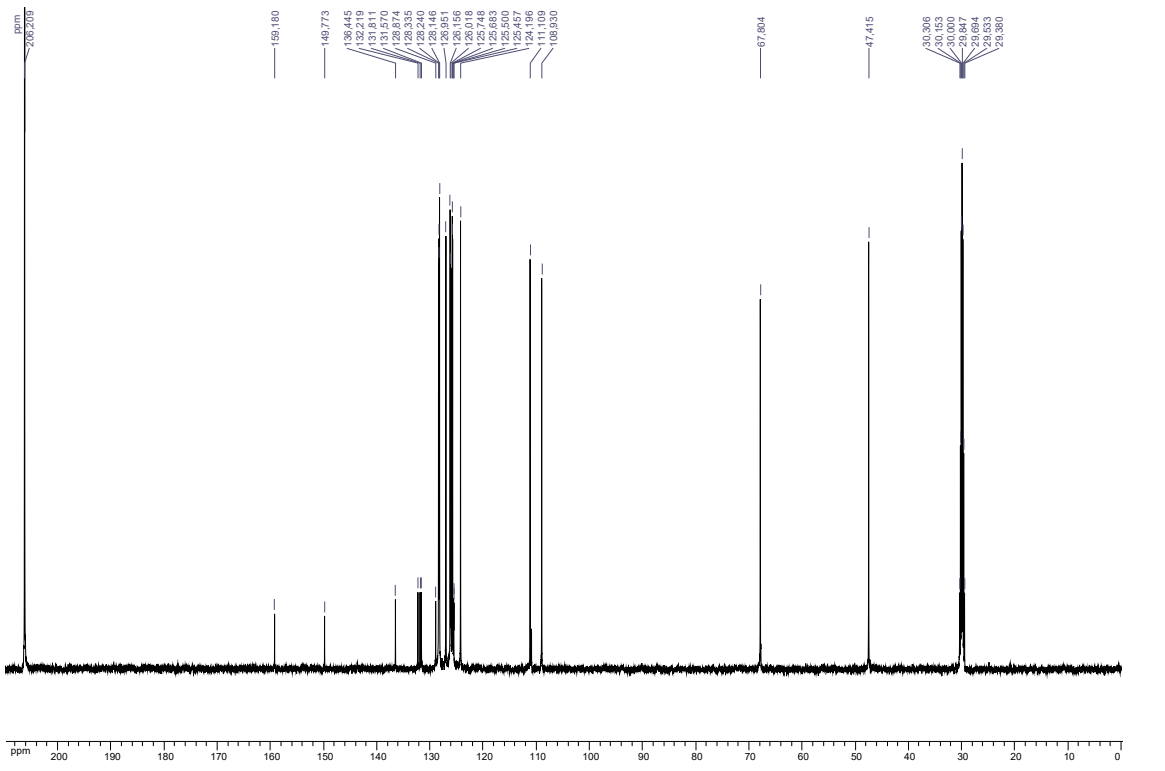
^{13}C-NMR (Acetone-d_6, 126 MHz)



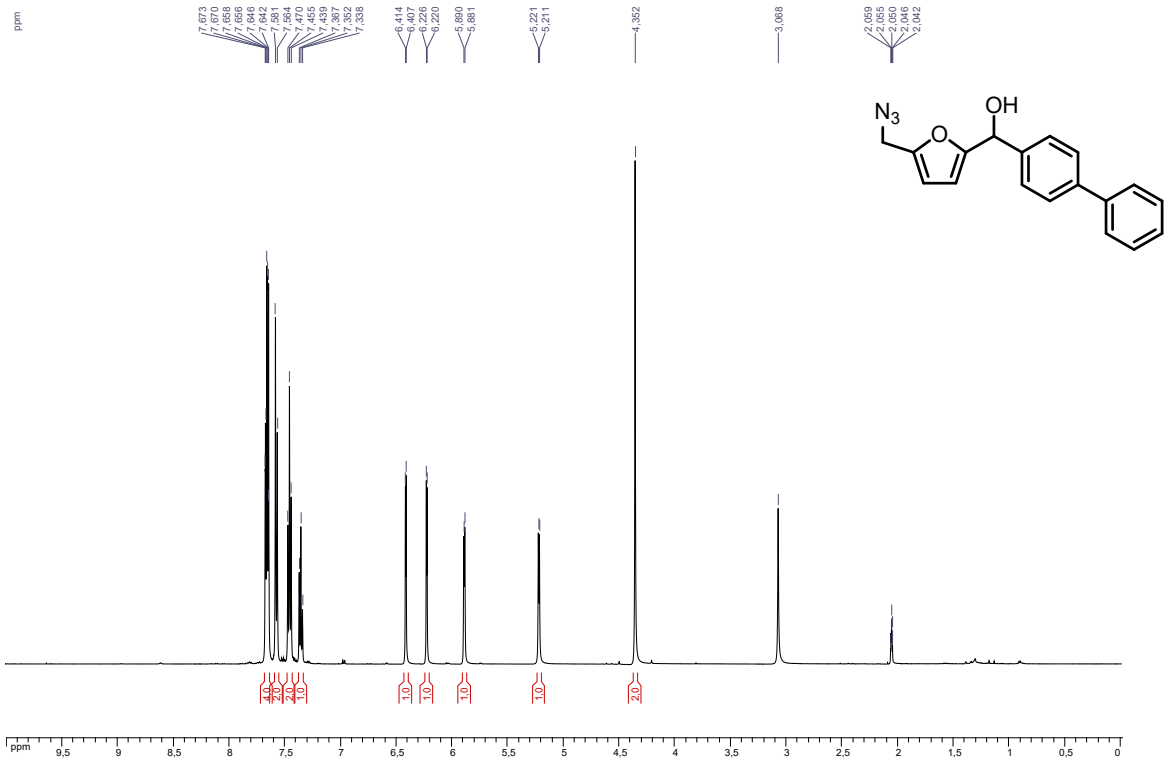
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6e)**



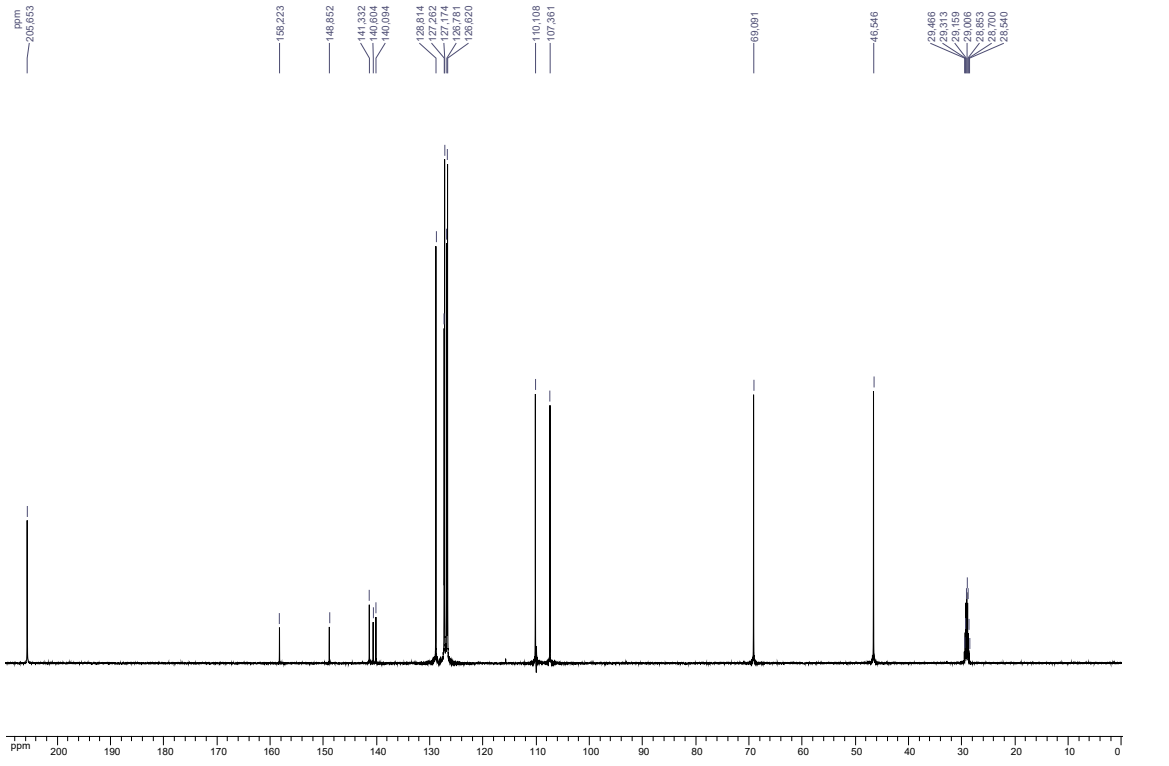
^{13}C-NMR (Acetone-d_6, 126 MHz)



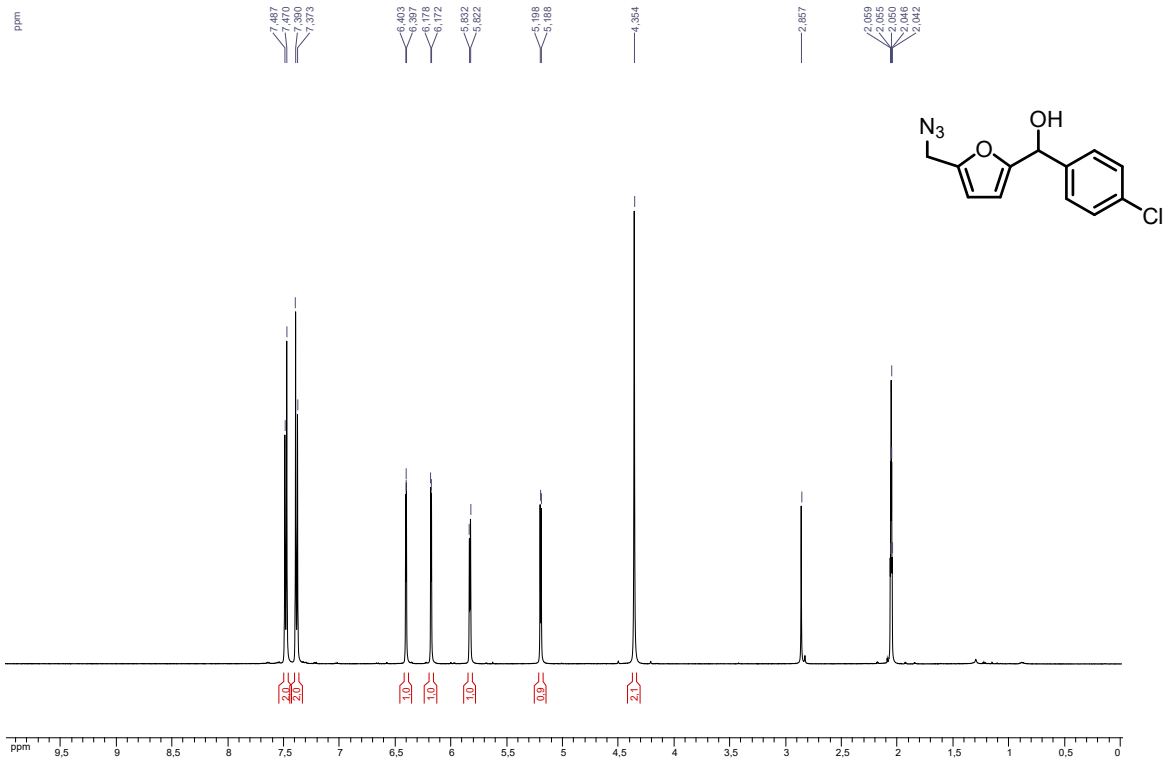
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6f)**



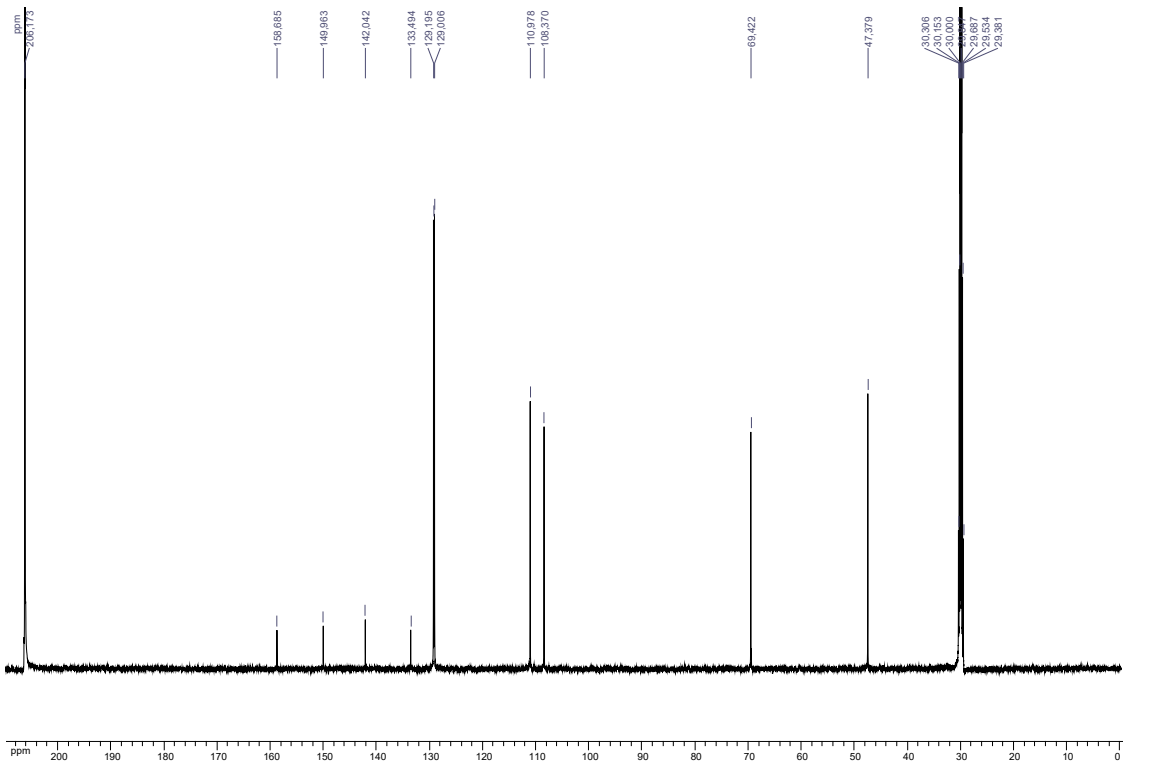
^{13}C-NMR (Acetone-d_6, 126 MHz)



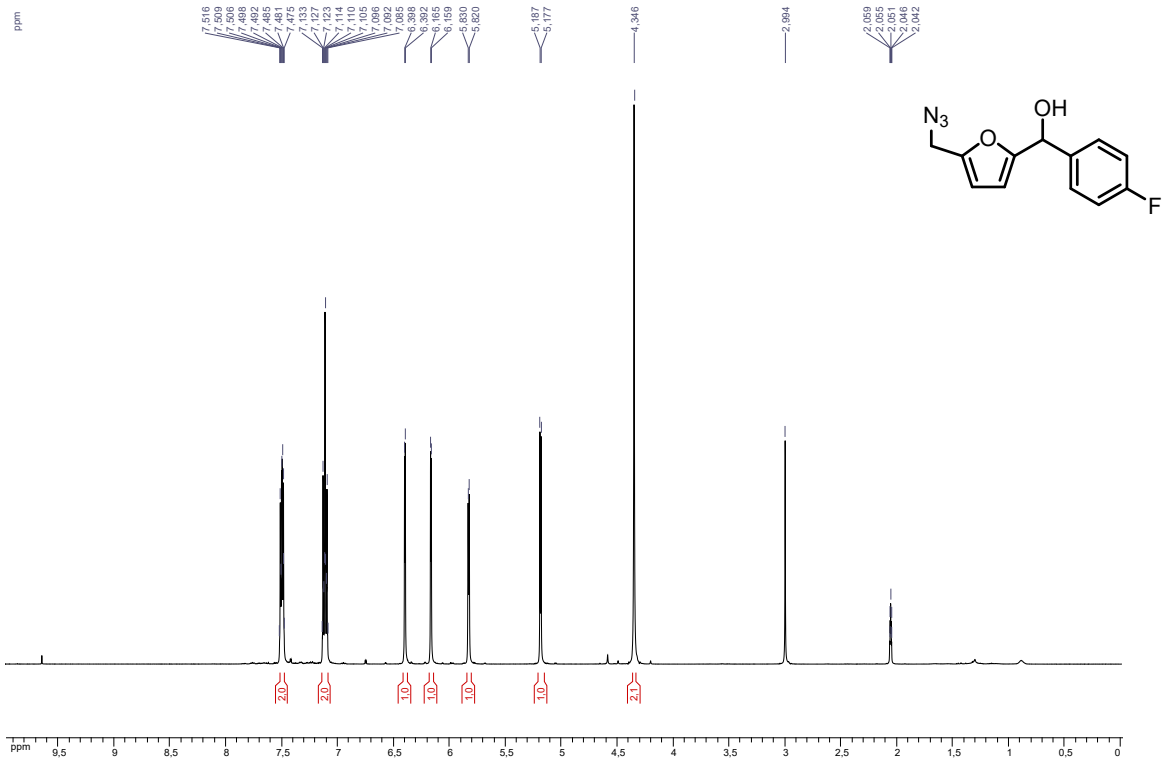
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6g)**



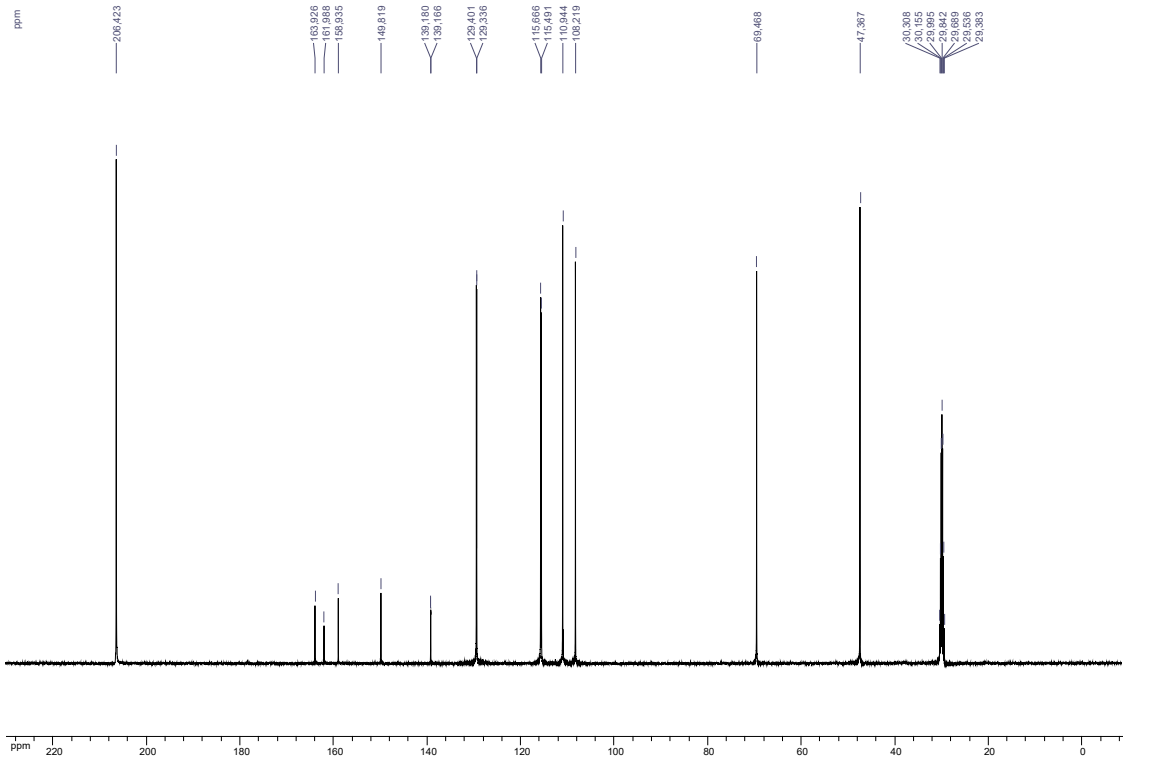
^{13}C-NMR (Acetone-d_6, 126 MHz)



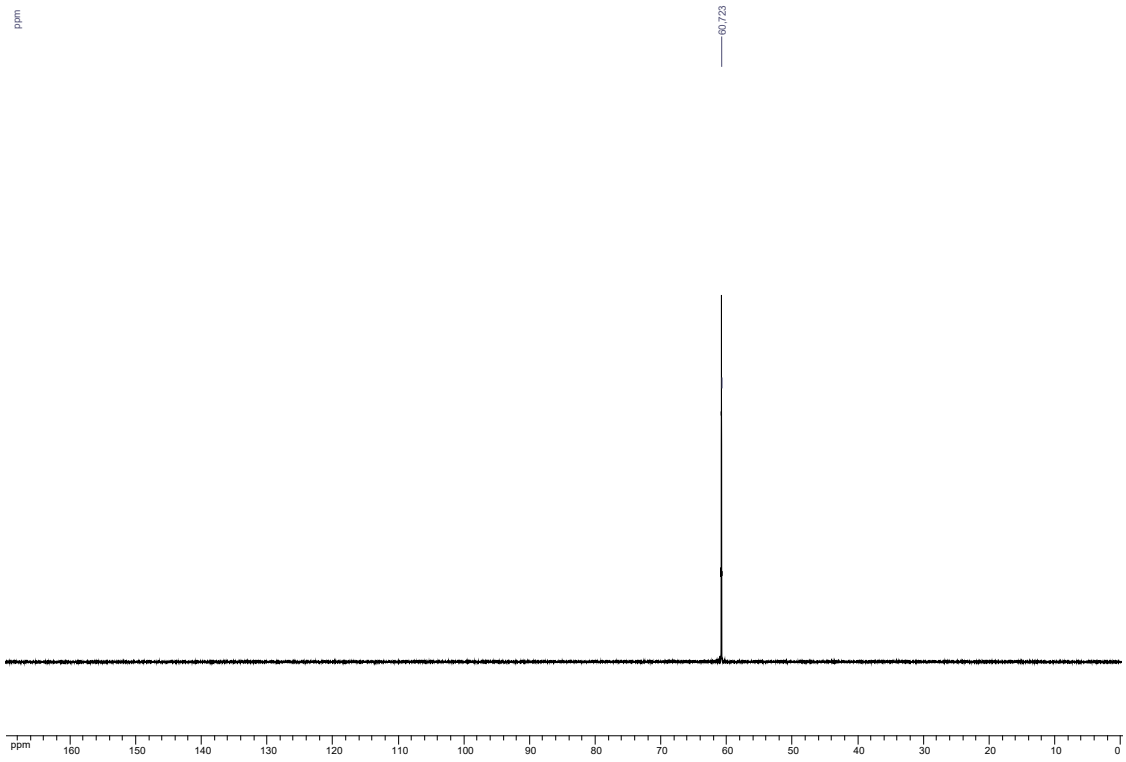
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6h)**



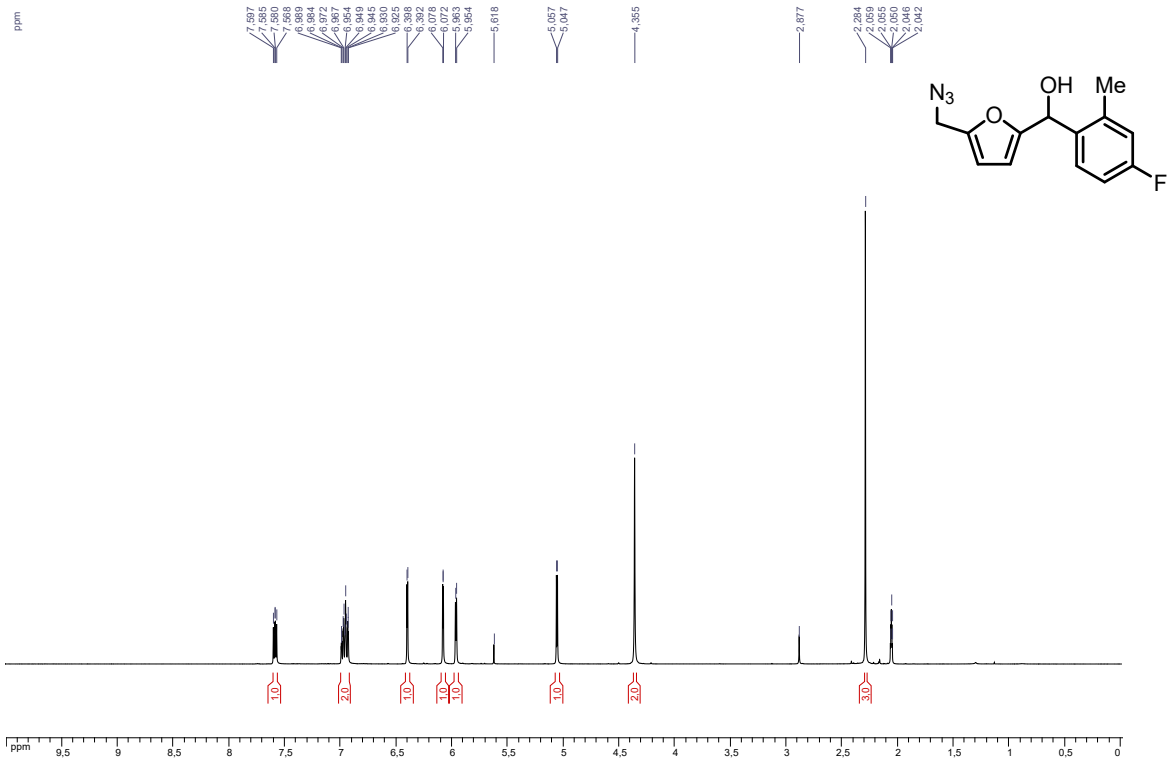
^{13}C-NMR (Acetone-d_6, 126 MHz)



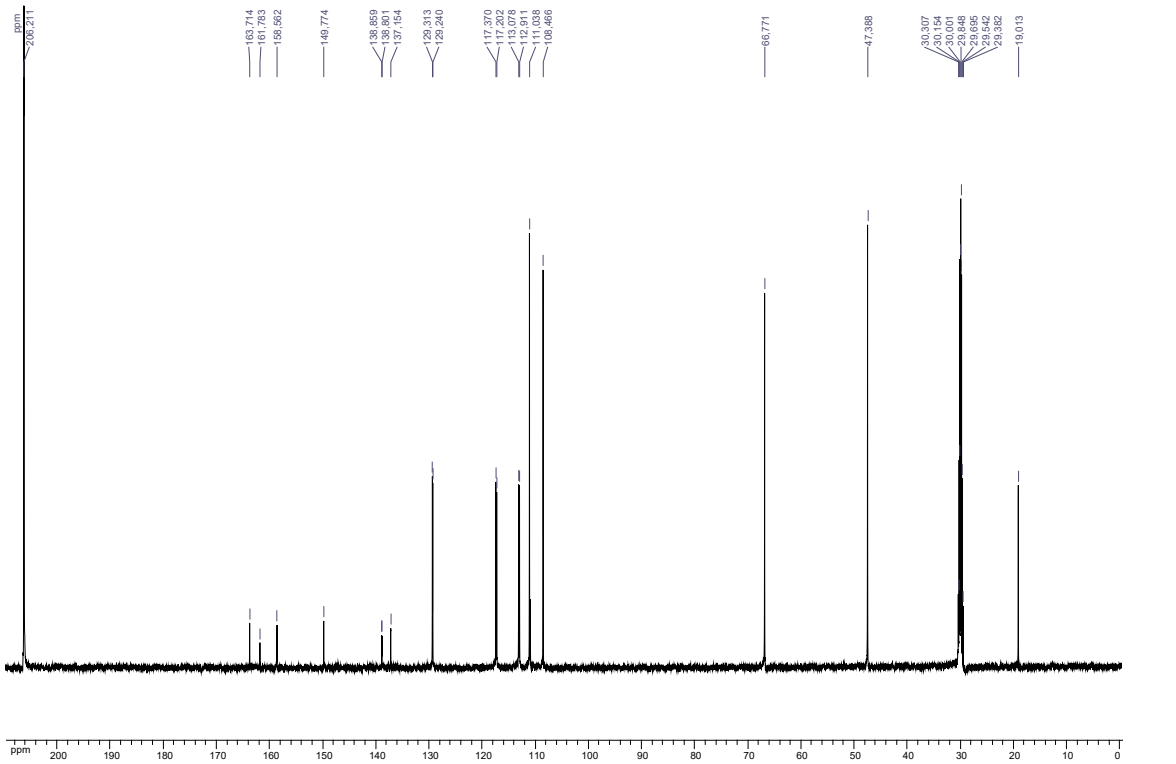
^{19}F-NMR (Acetone-d_6, 282 MHz)



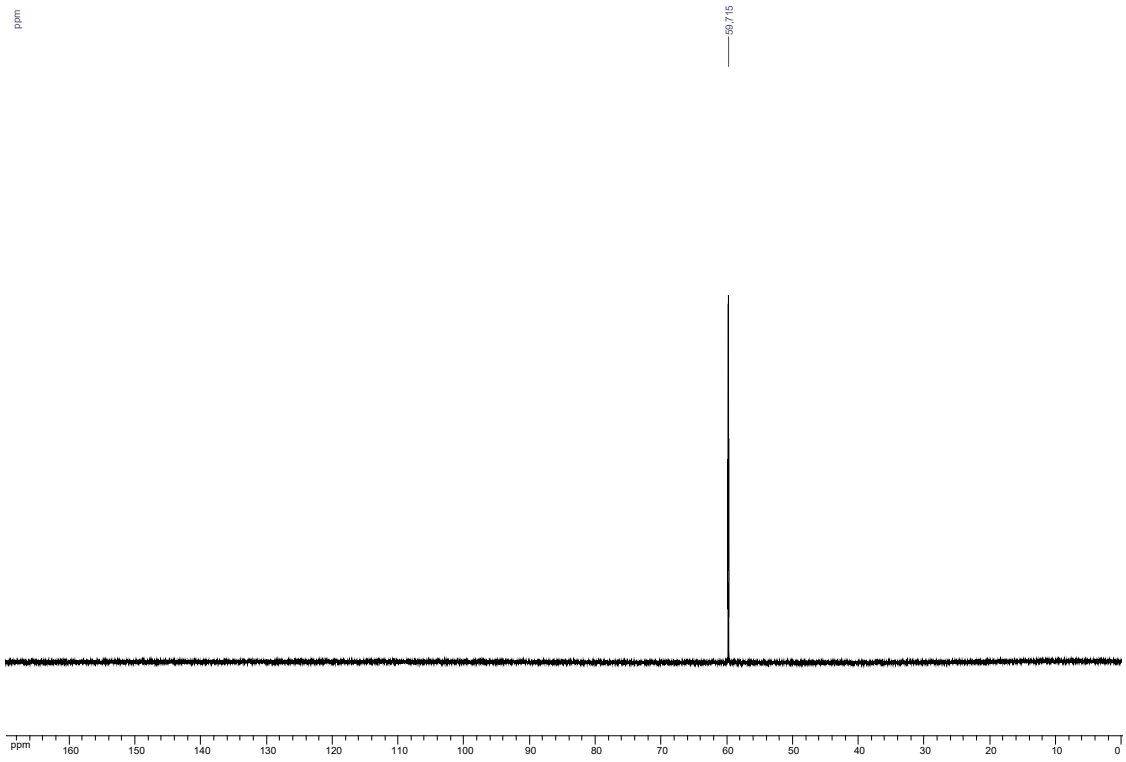
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6i)**



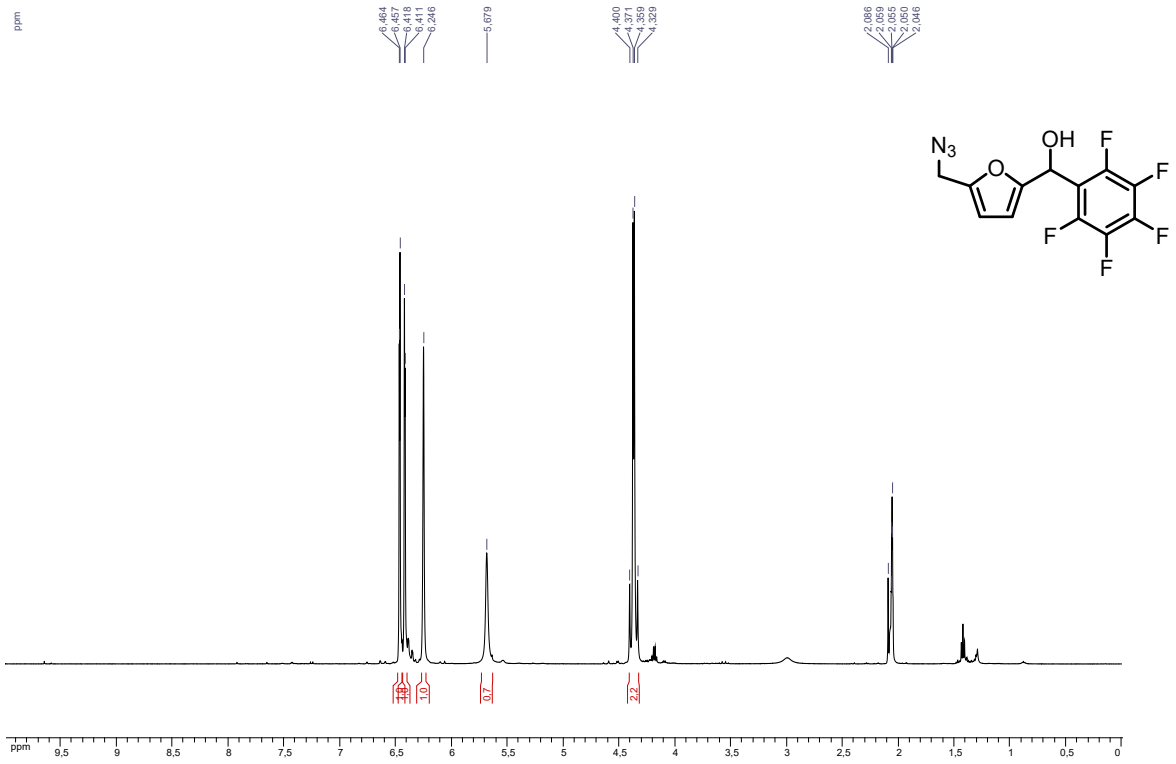
^{13}C-NMR (Acetone-d_6, 126 MHz)



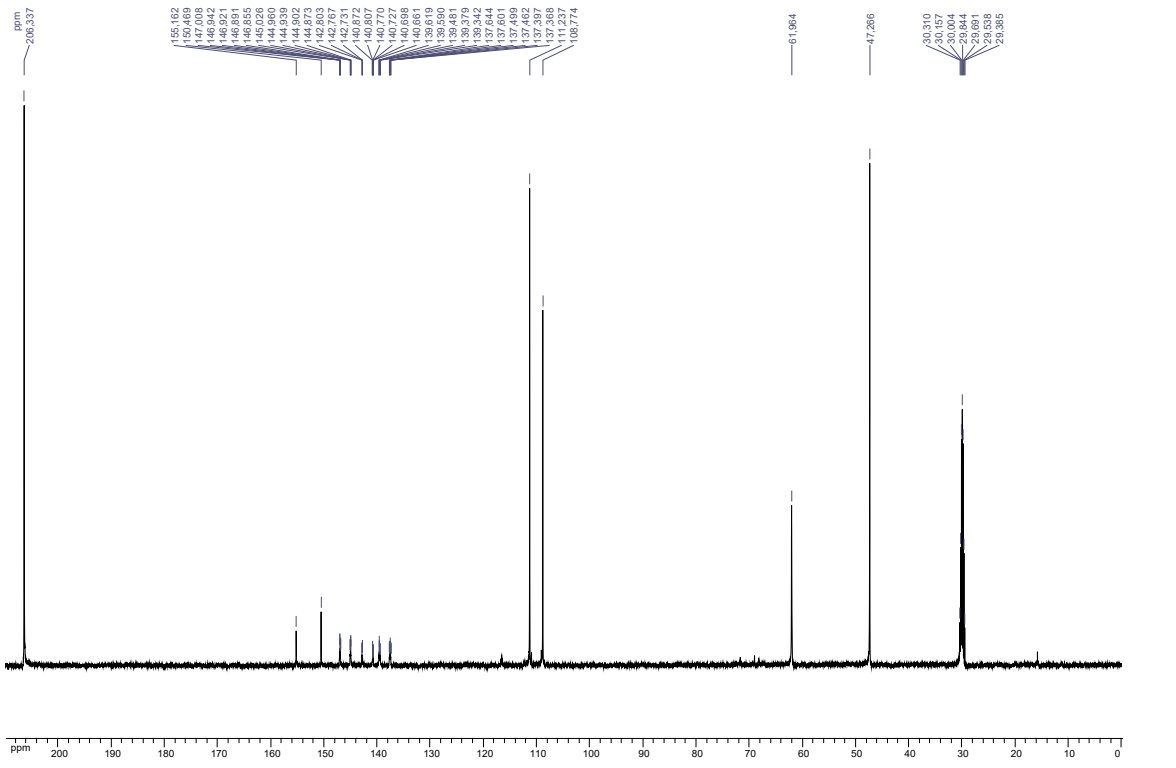
^{19}F-NMR (Acetone-d_6, 282 MHz)



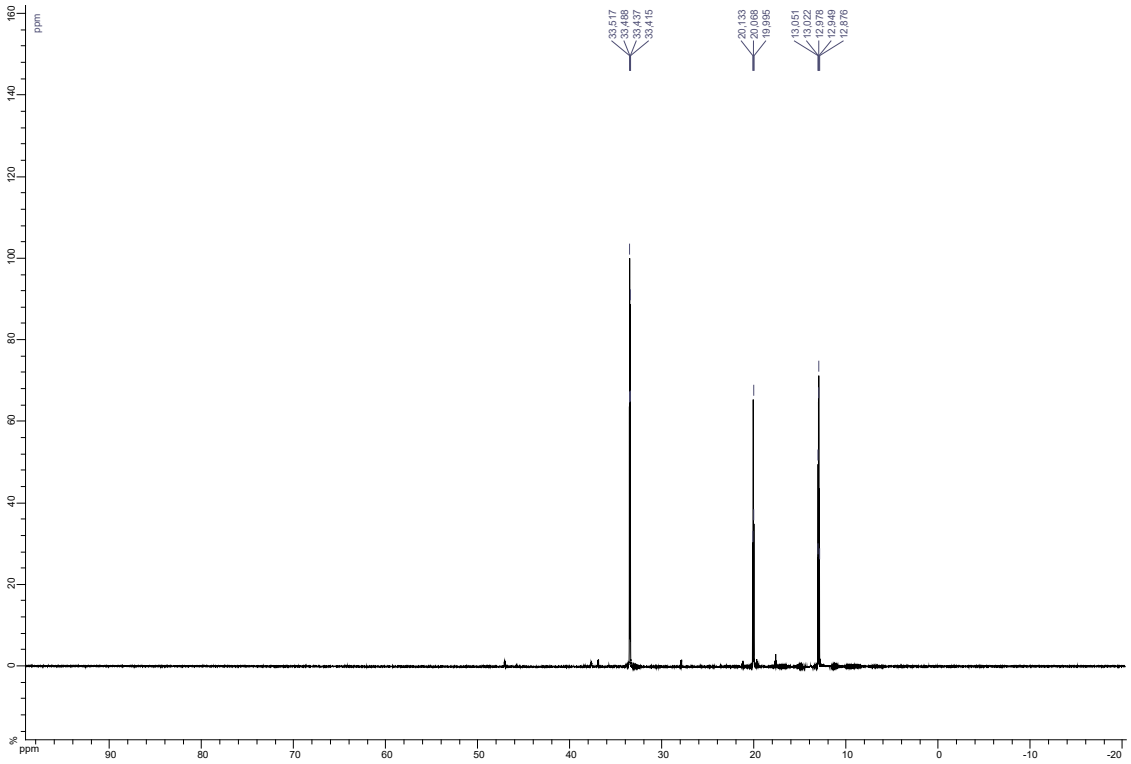
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6j)**



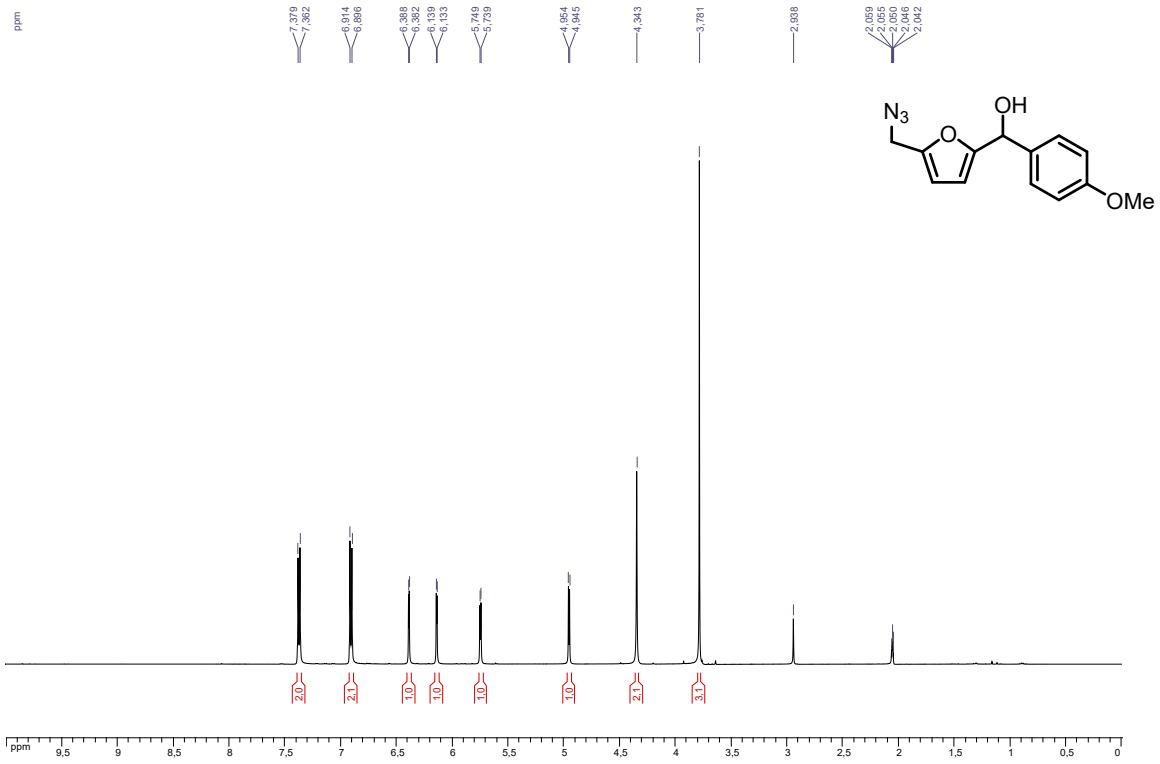
^{13}C-NMR (Acetone-d_6, 126 MHz)



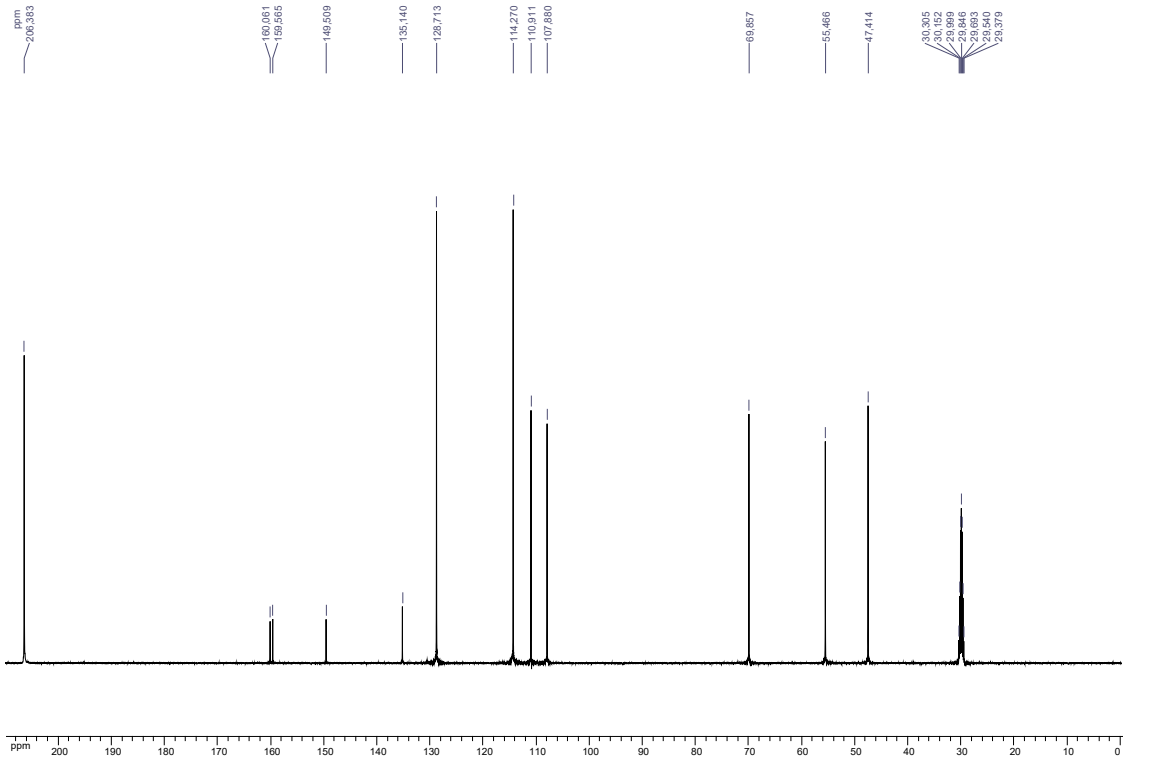
^{19}F-NMR (Acetone-d_6, 282 MHz)



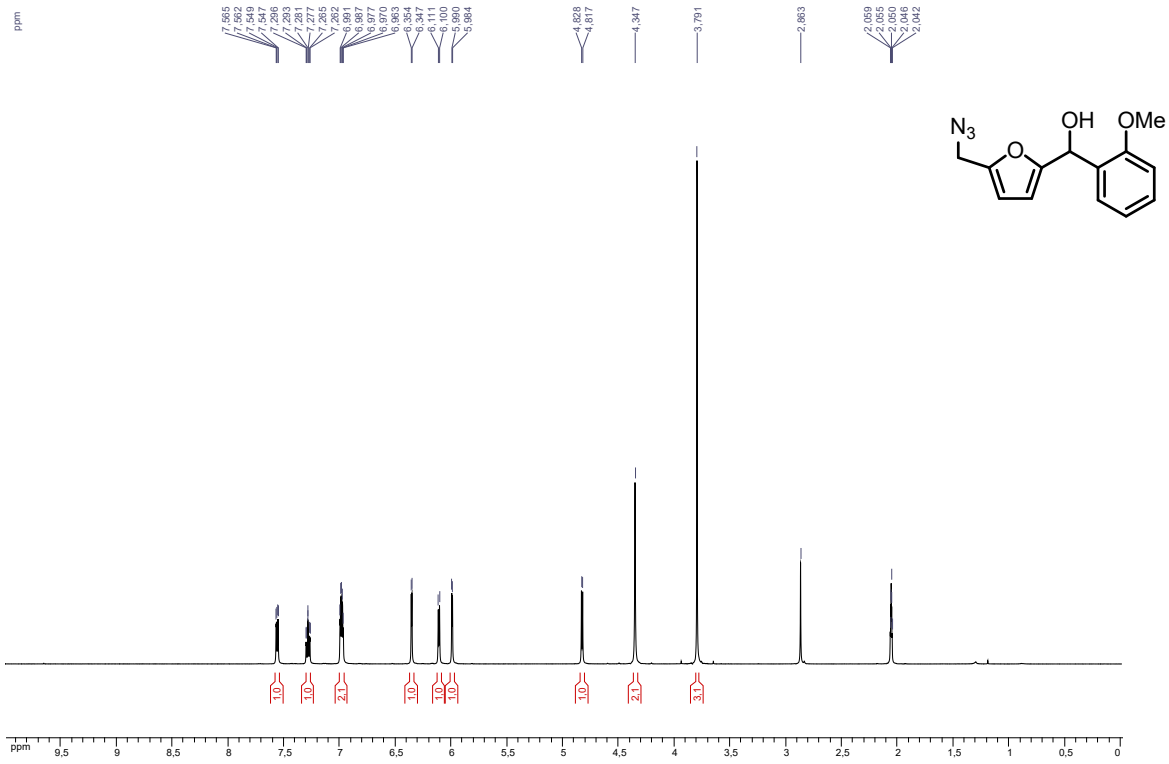
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6k)**



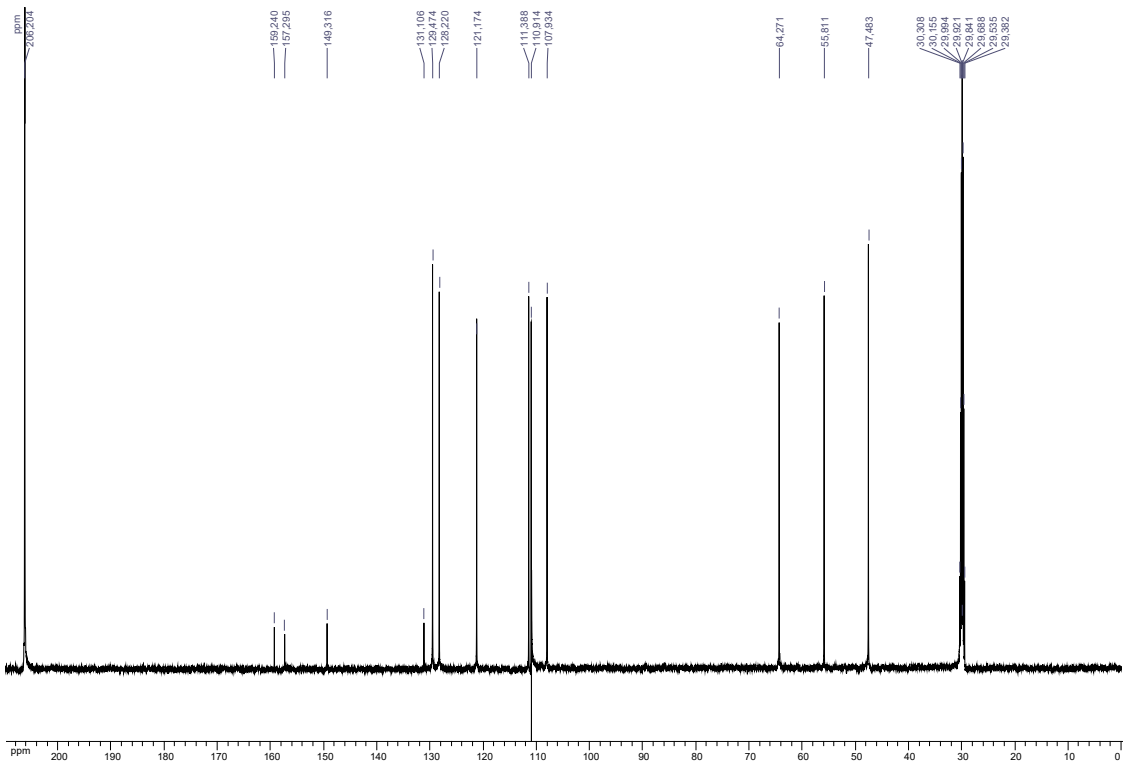
^{13}C-NMR (Acetone-d_6, 126 MHz)



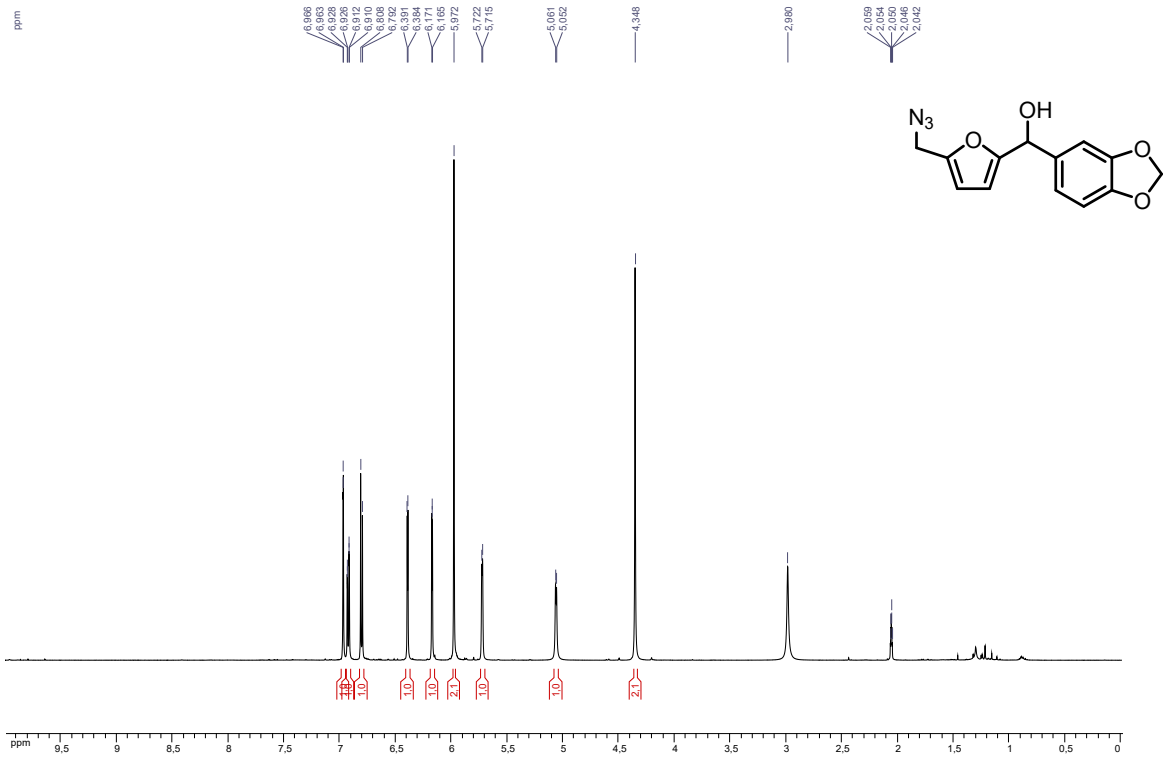
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6l)**



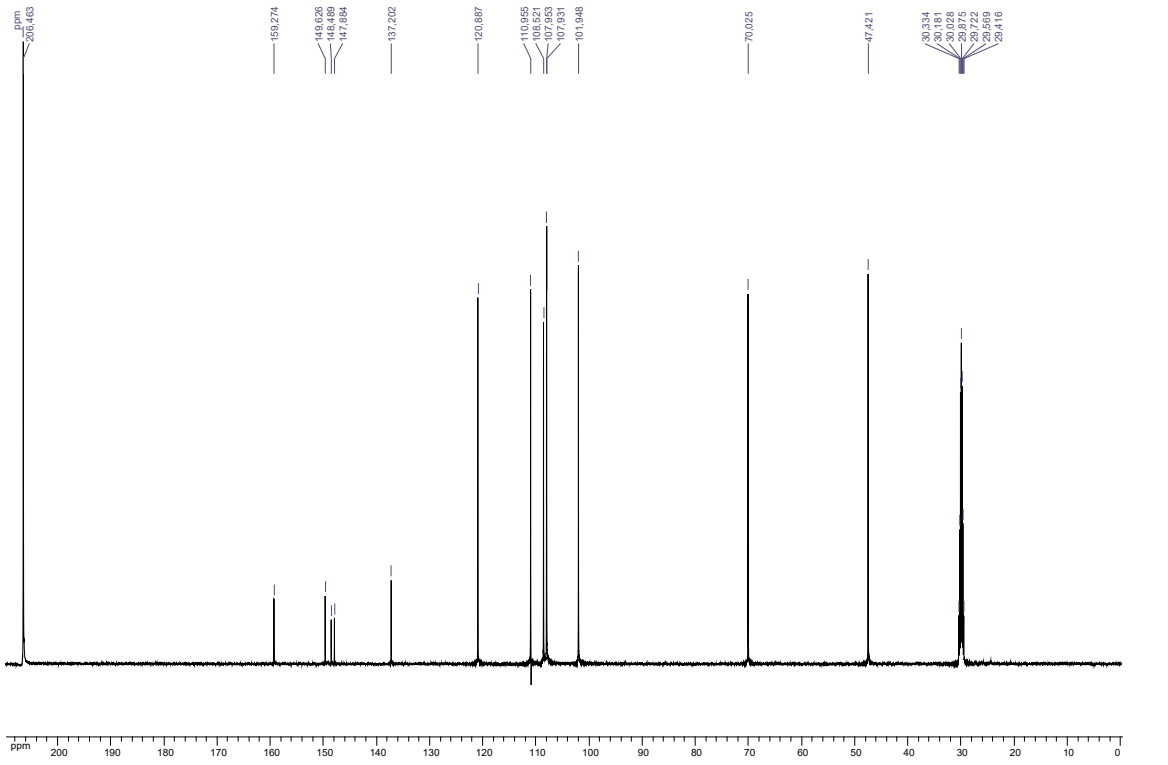
^{13}C-NMR (Acetone-d_6, 126 MHz)



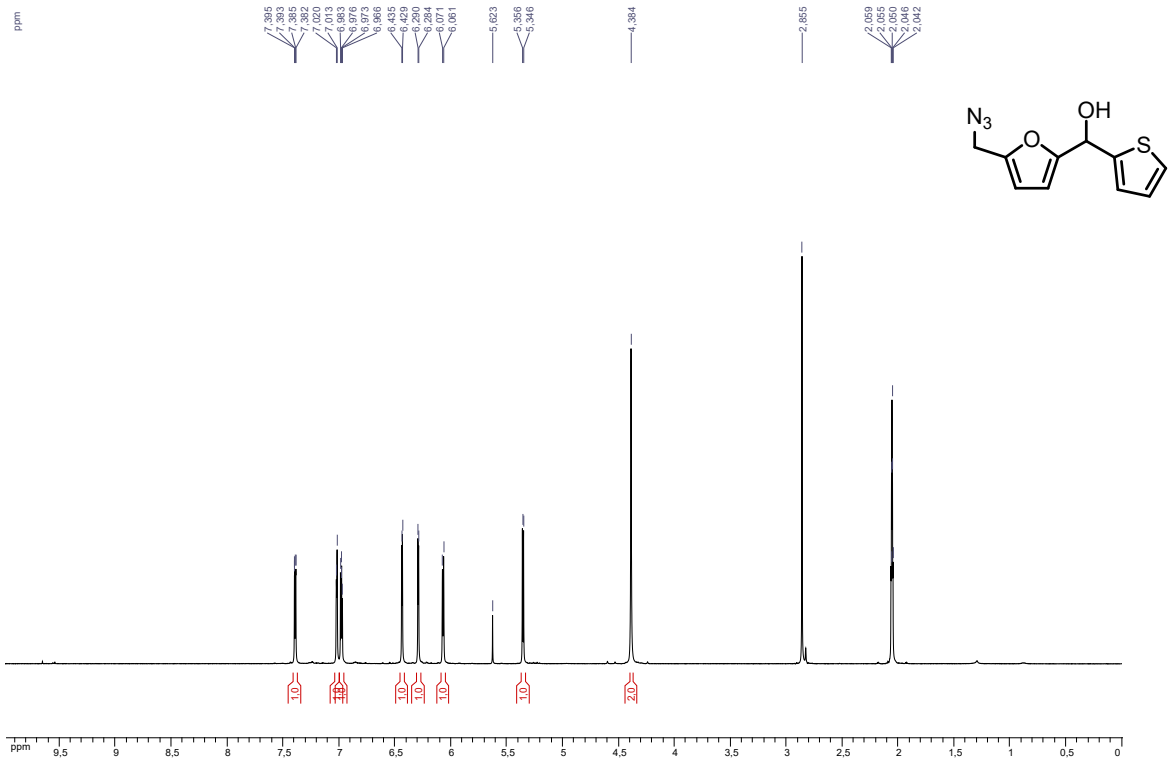
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6m)**



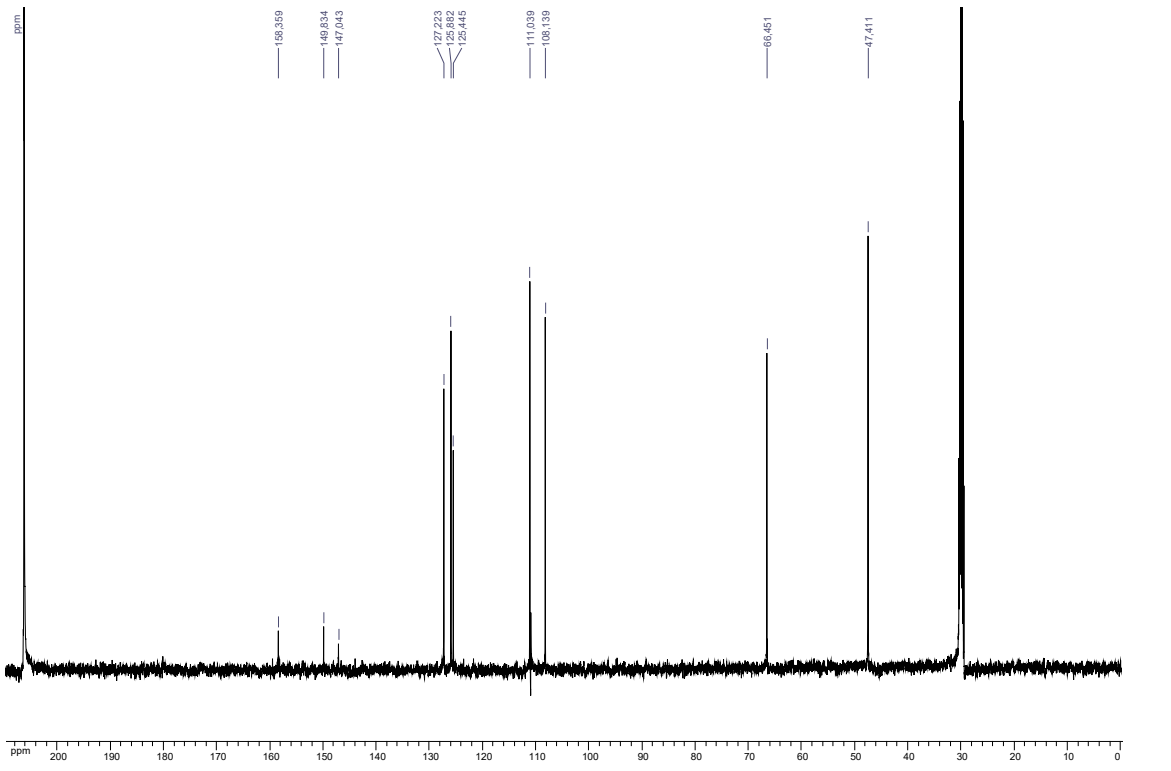
^{13}C-NMR (Acetone-d_6, 126 MHz)



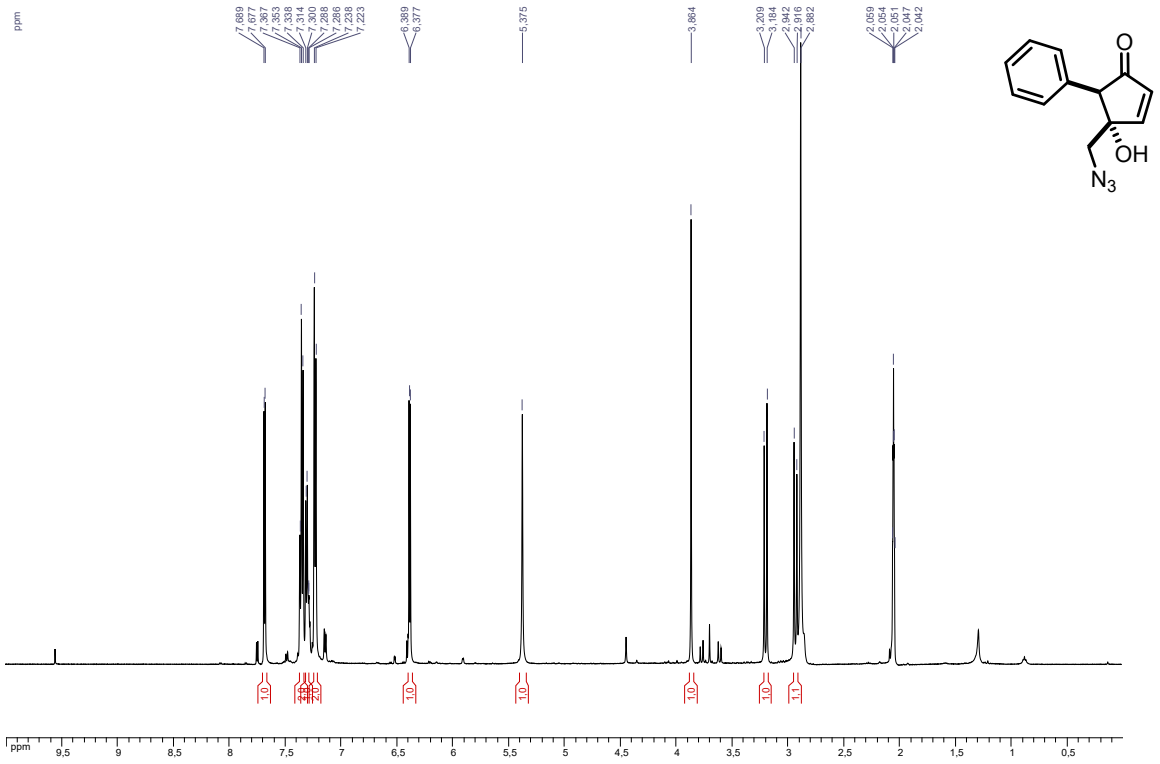
^{1}H-NMR (Acetone-d_6, 500 MHz) **(6n)**



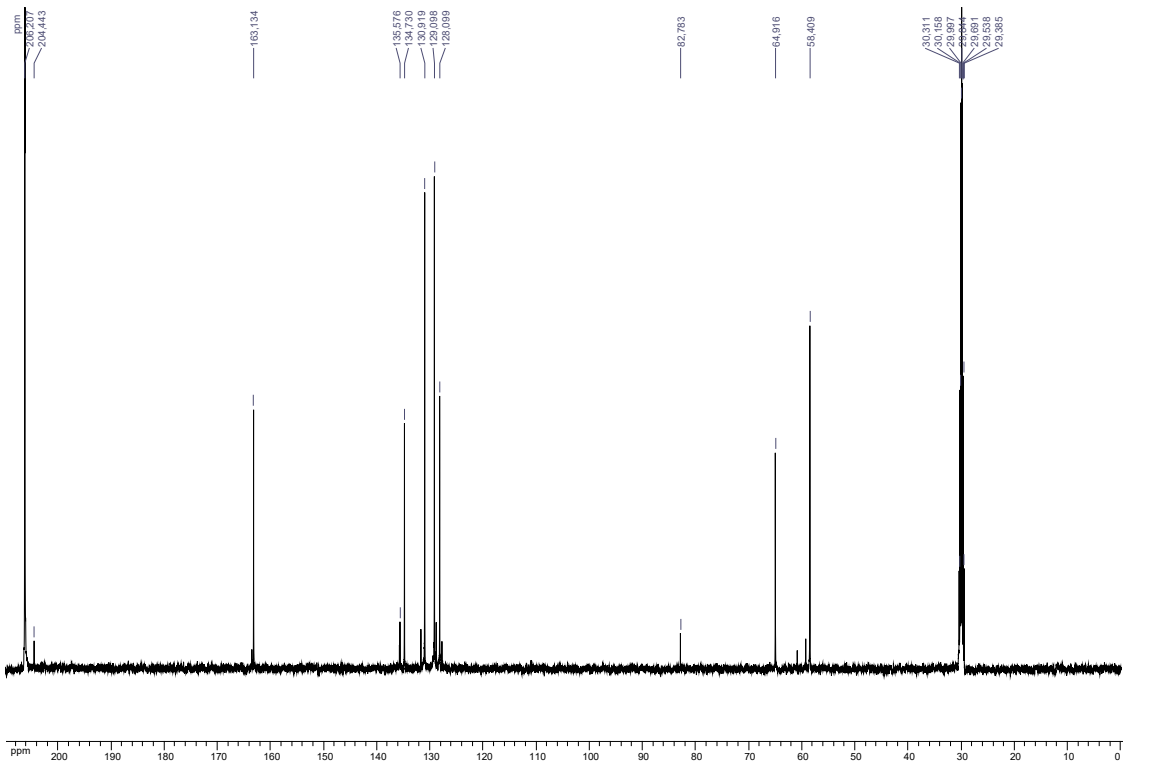
^{13}C-NMR (Acetone-d_6, 126 MHz)



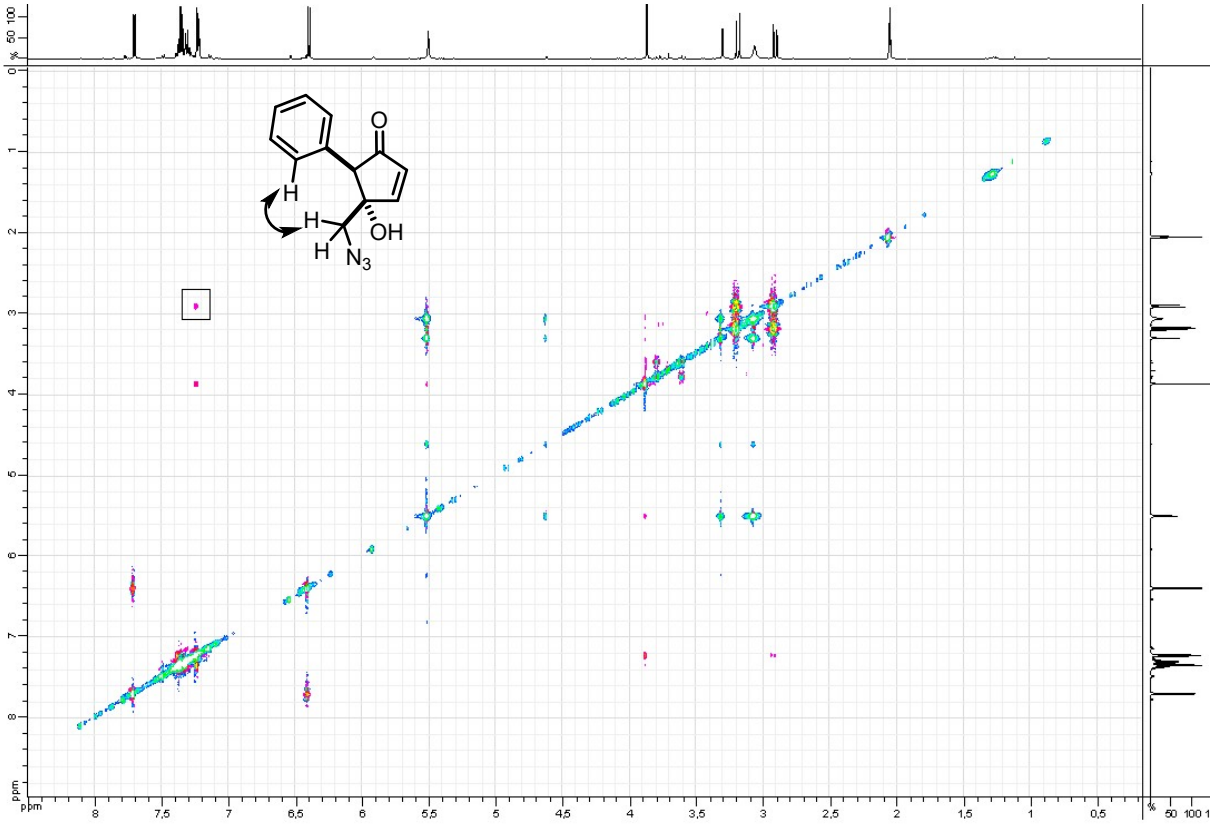
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7a)**



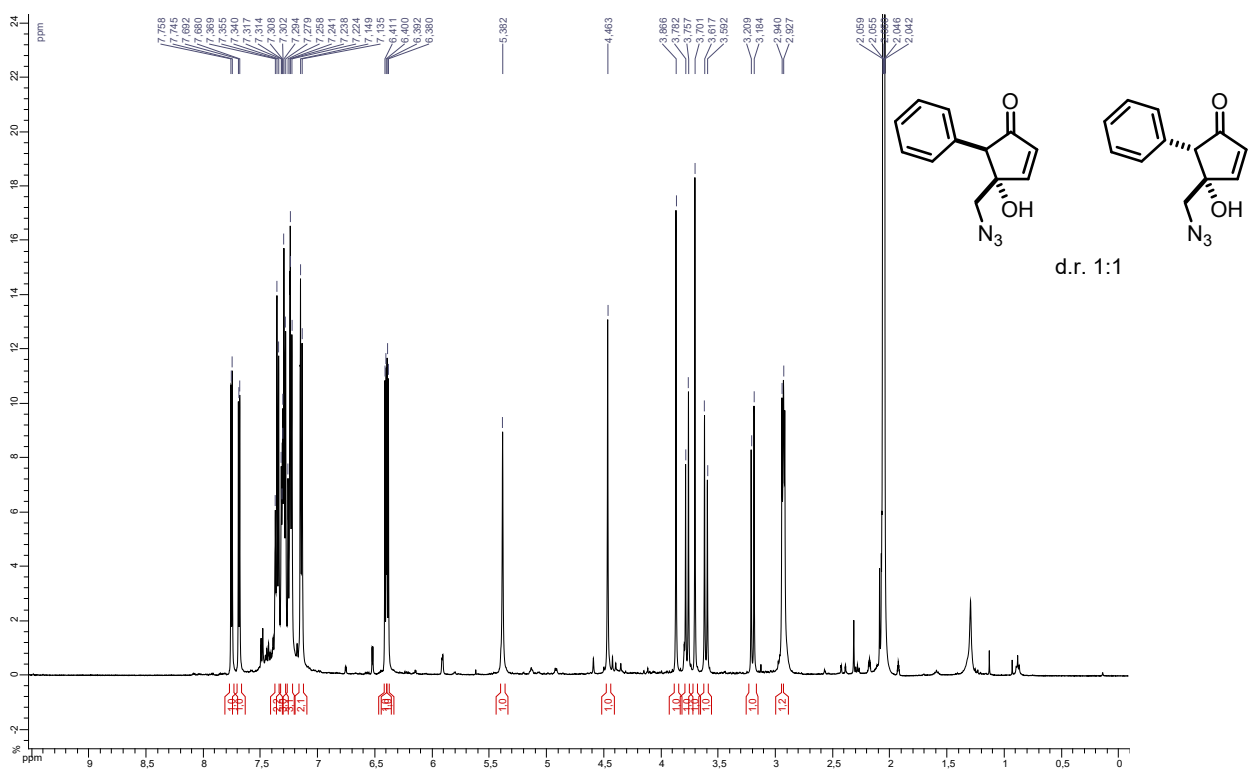
^{13}C-NMR (Acetone-d_6, 126 MHz)



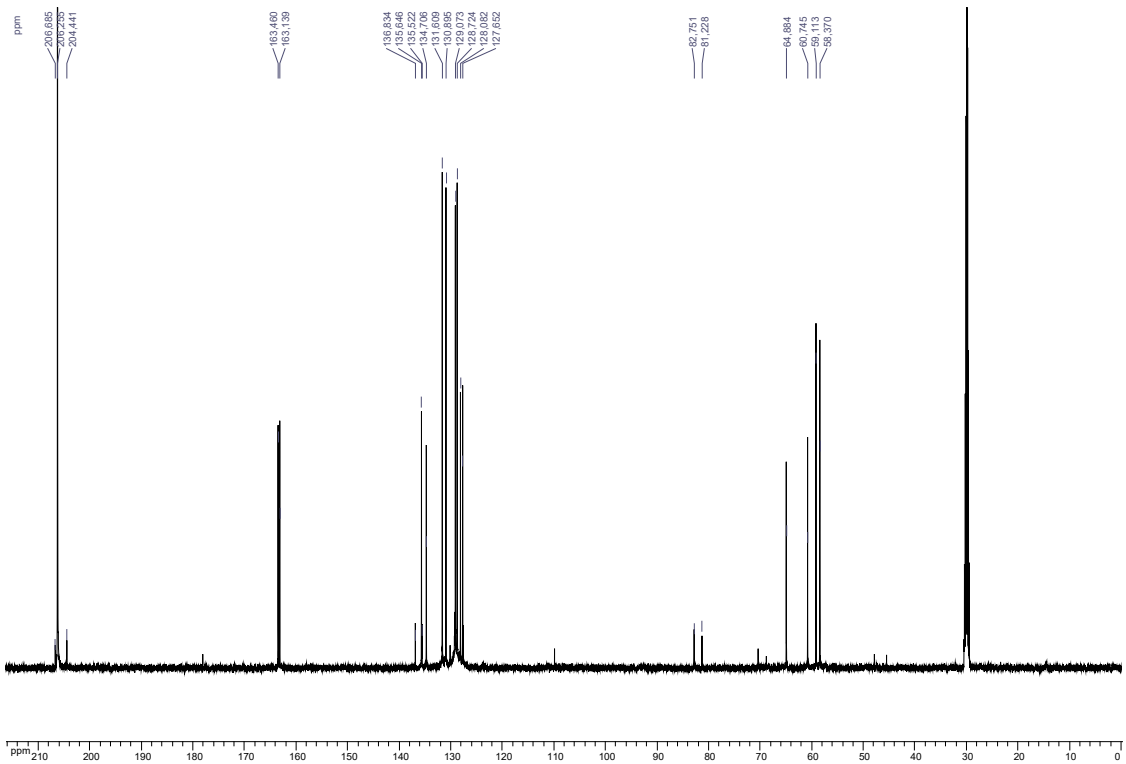
NOESY $^{1}H/^{1}H$ (Acetone-d_6, 500 MHz)



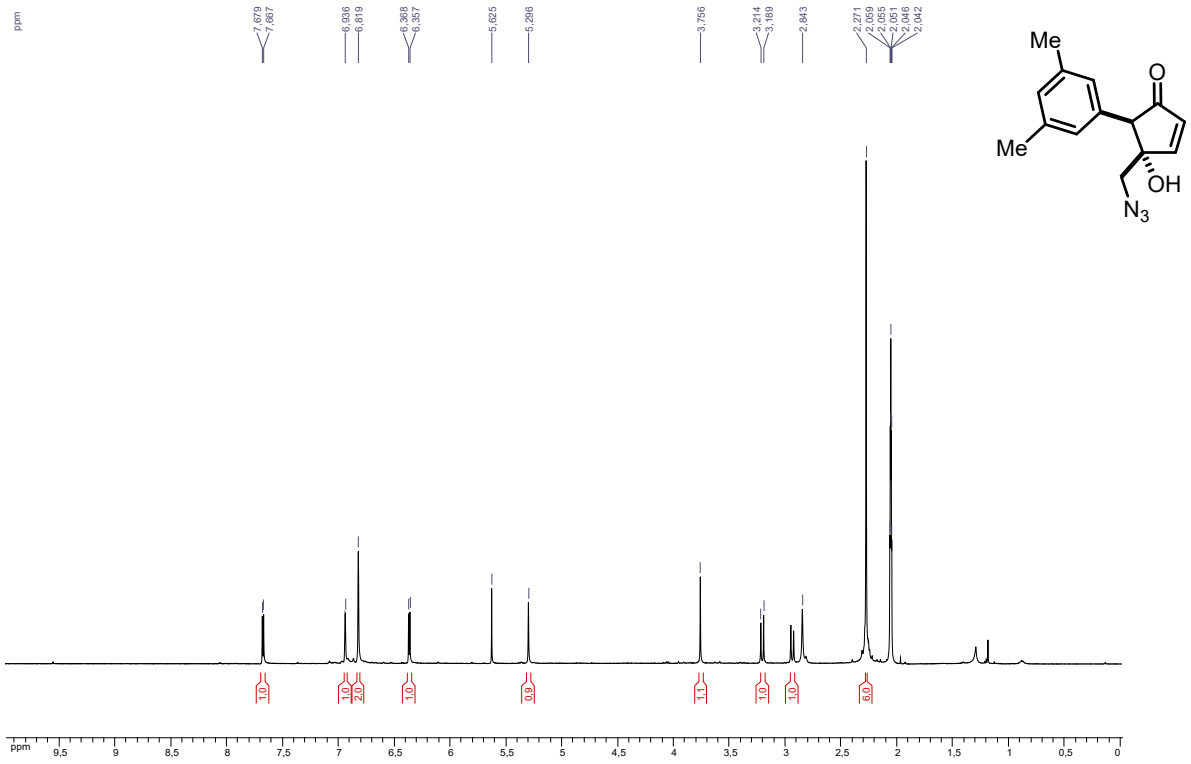
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7a+8a)**



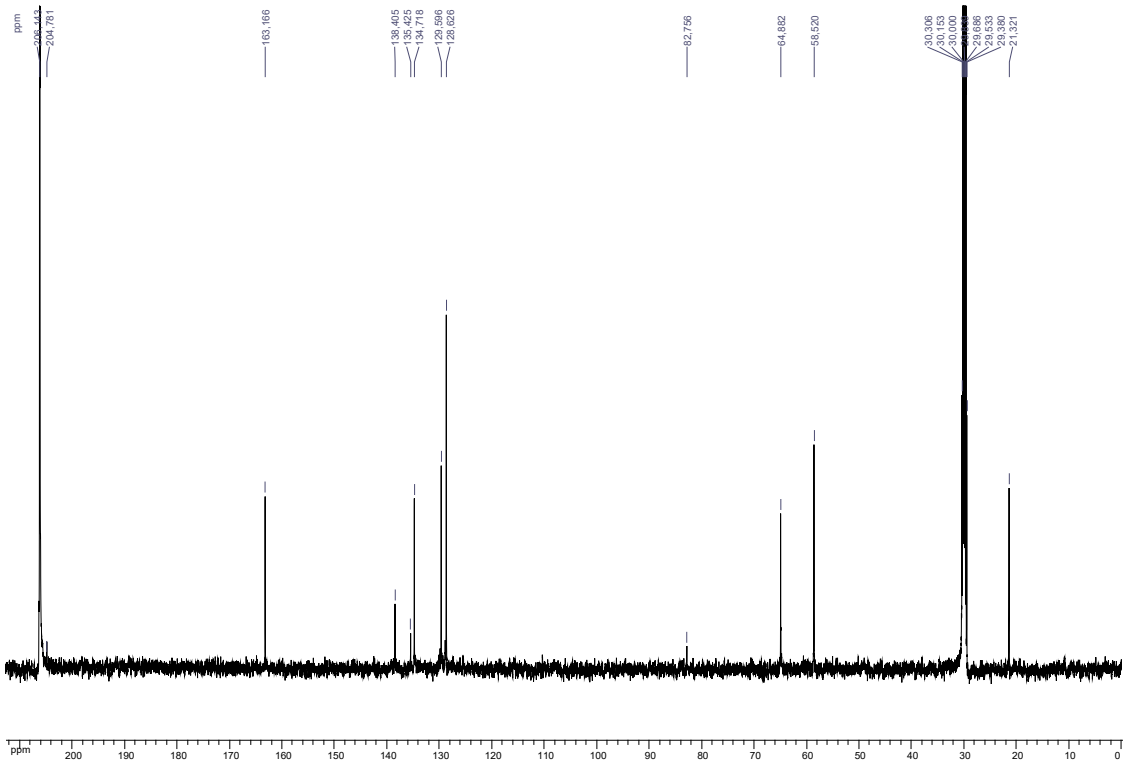
^{13}C-NMR (Acetone-d_6, 126 MHz)



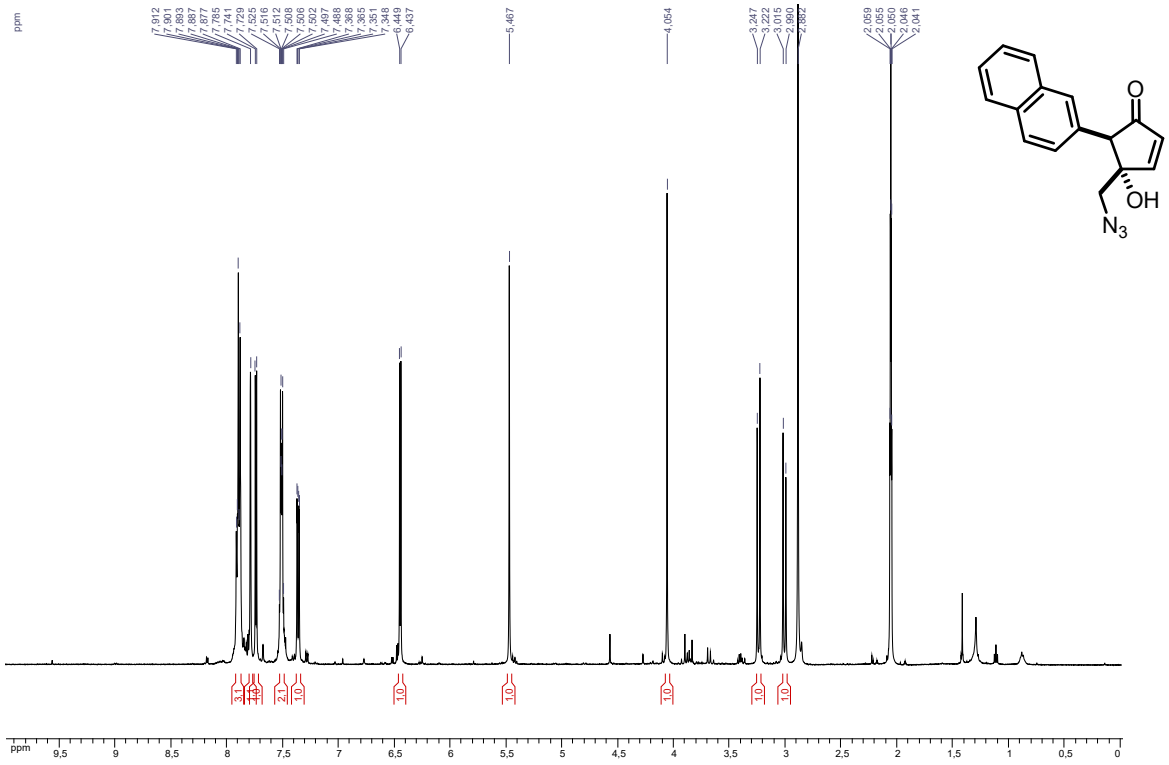
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7b)**



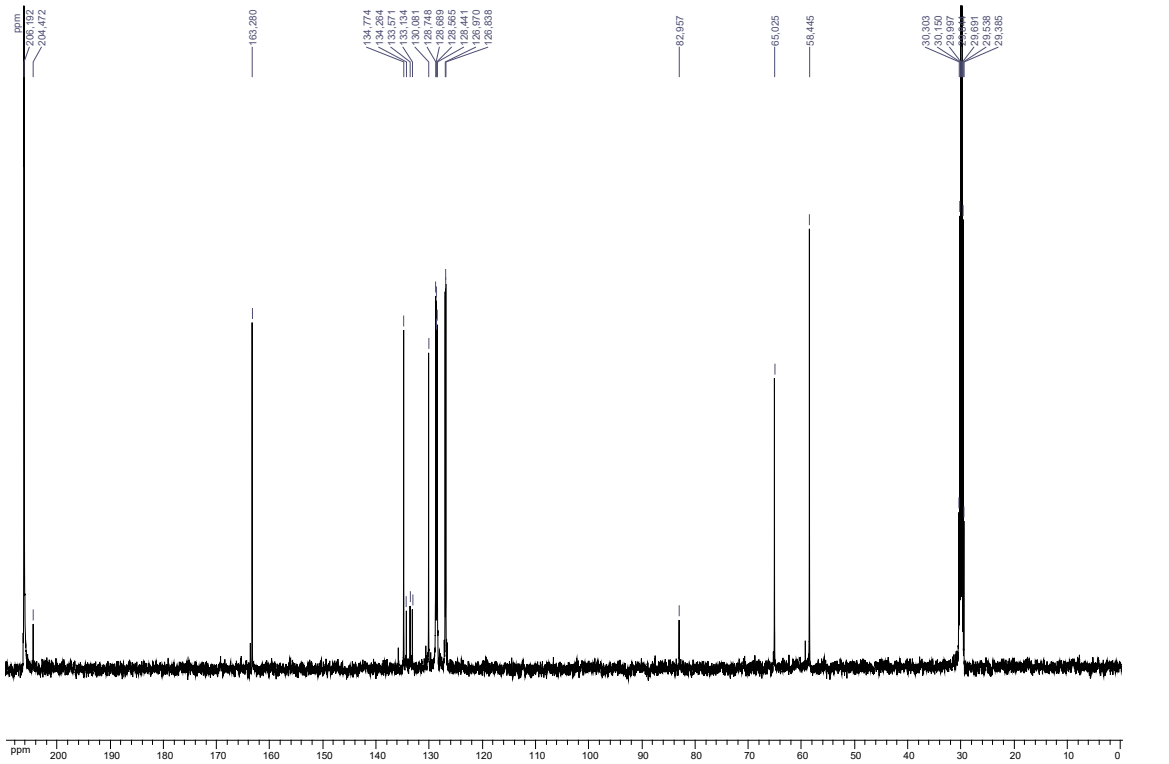
^{13}C-NMR (Acetone-d_6, 126 MHz)



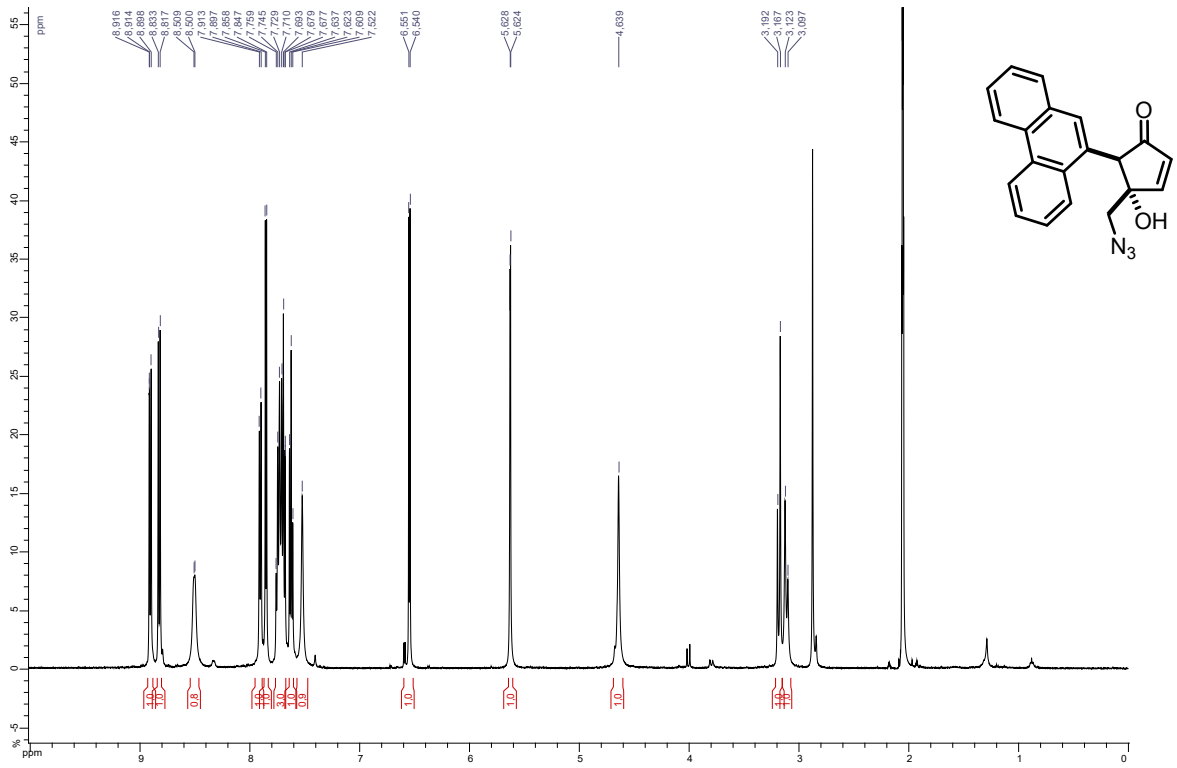
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7c)**



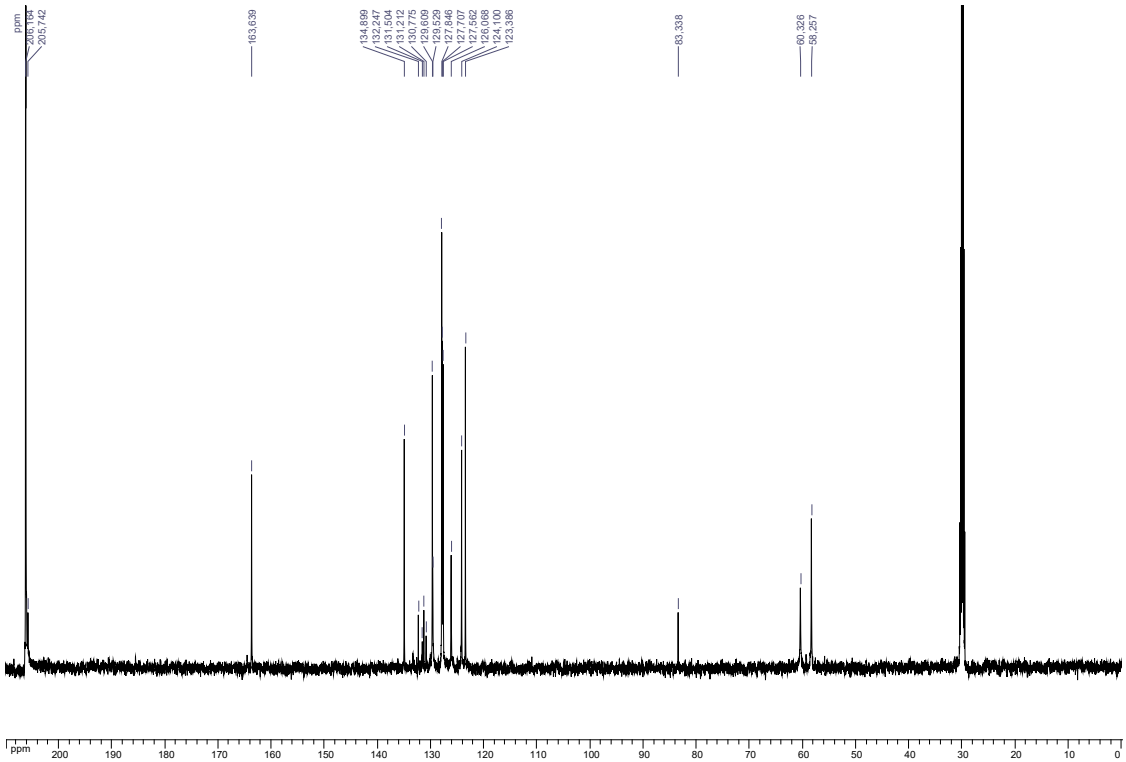
^{13}C-NMR (Acetone-d_6, 126 MHz)



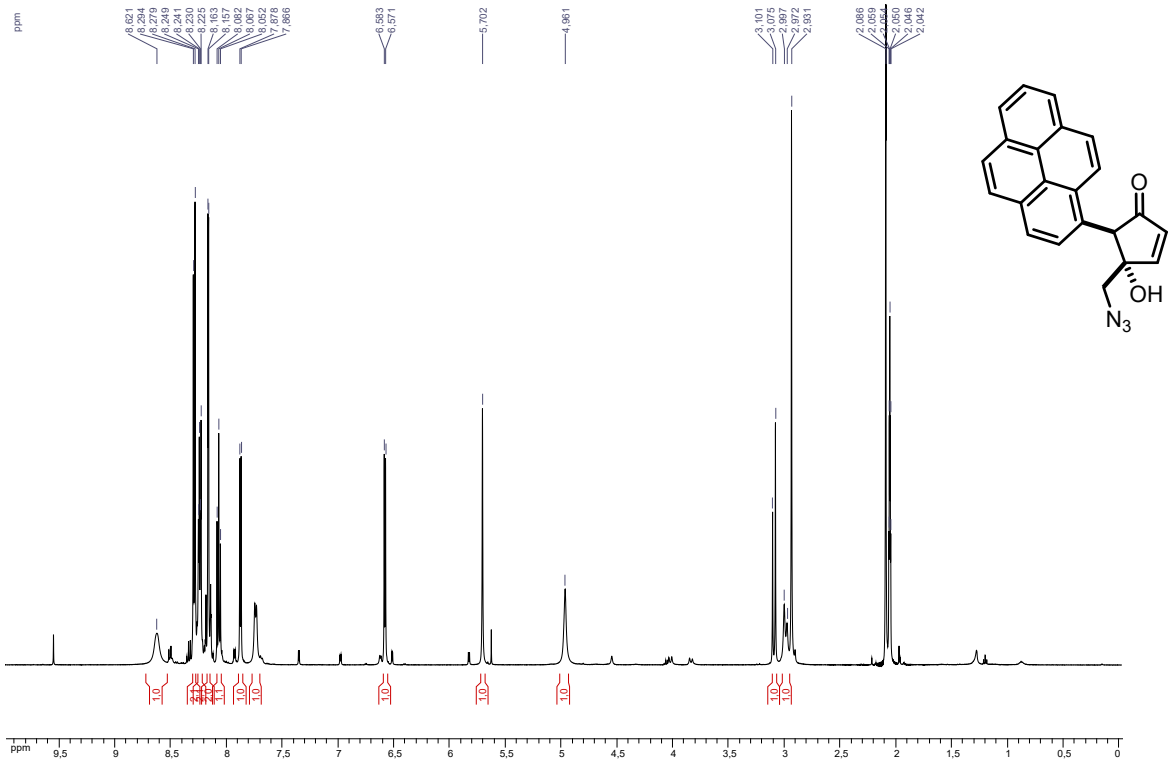
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7d)**



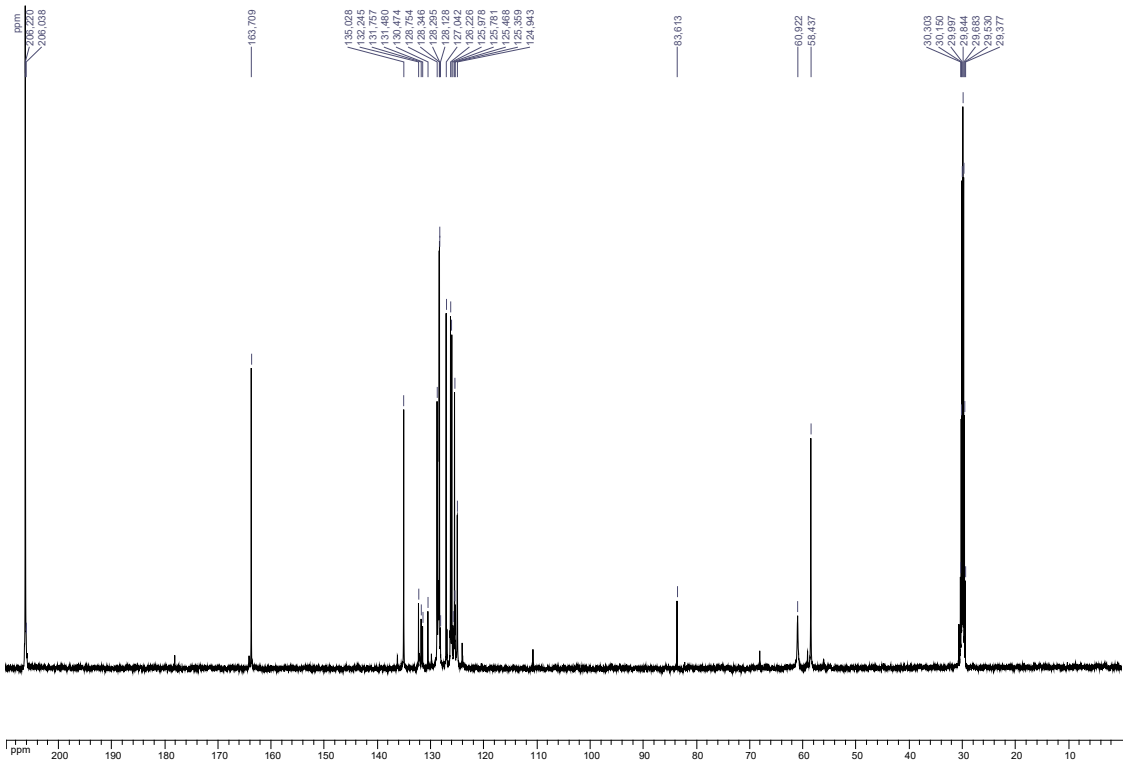
^{13}C-NMR (Acetone-d_6, 126 MHz)



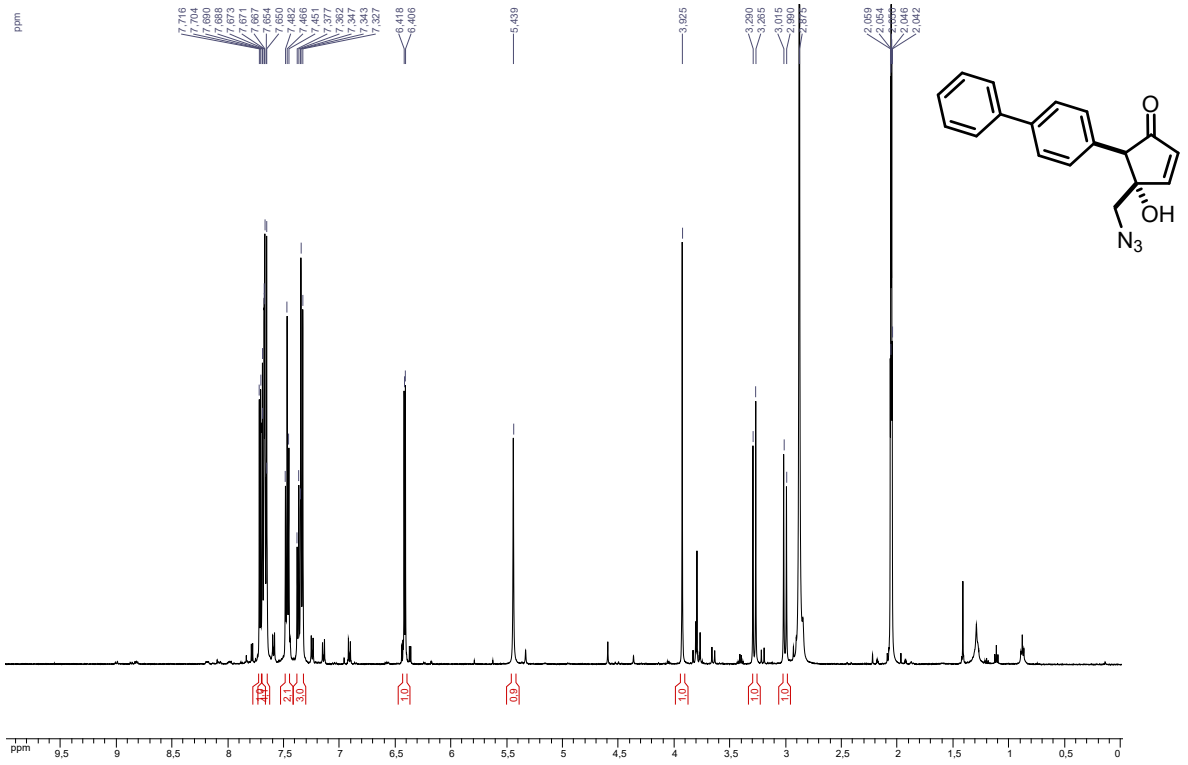
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7e)**



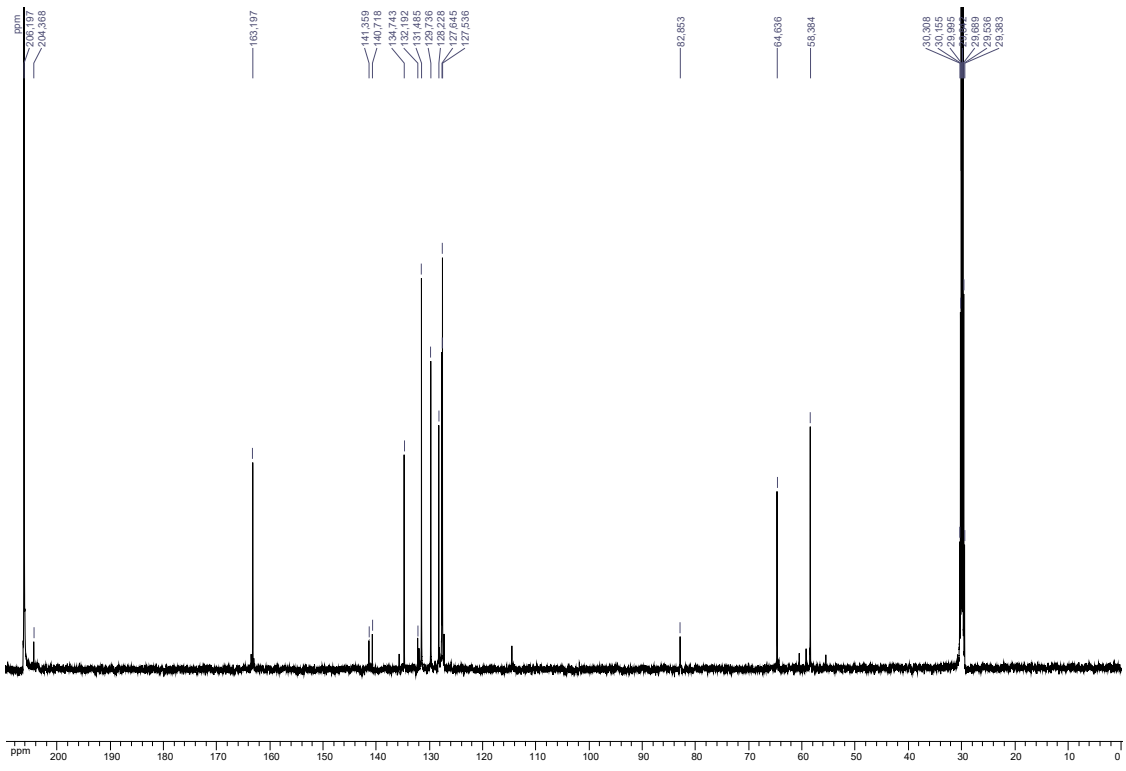
^{13}C-NMR (Acetone-d_6, 126 MHz)



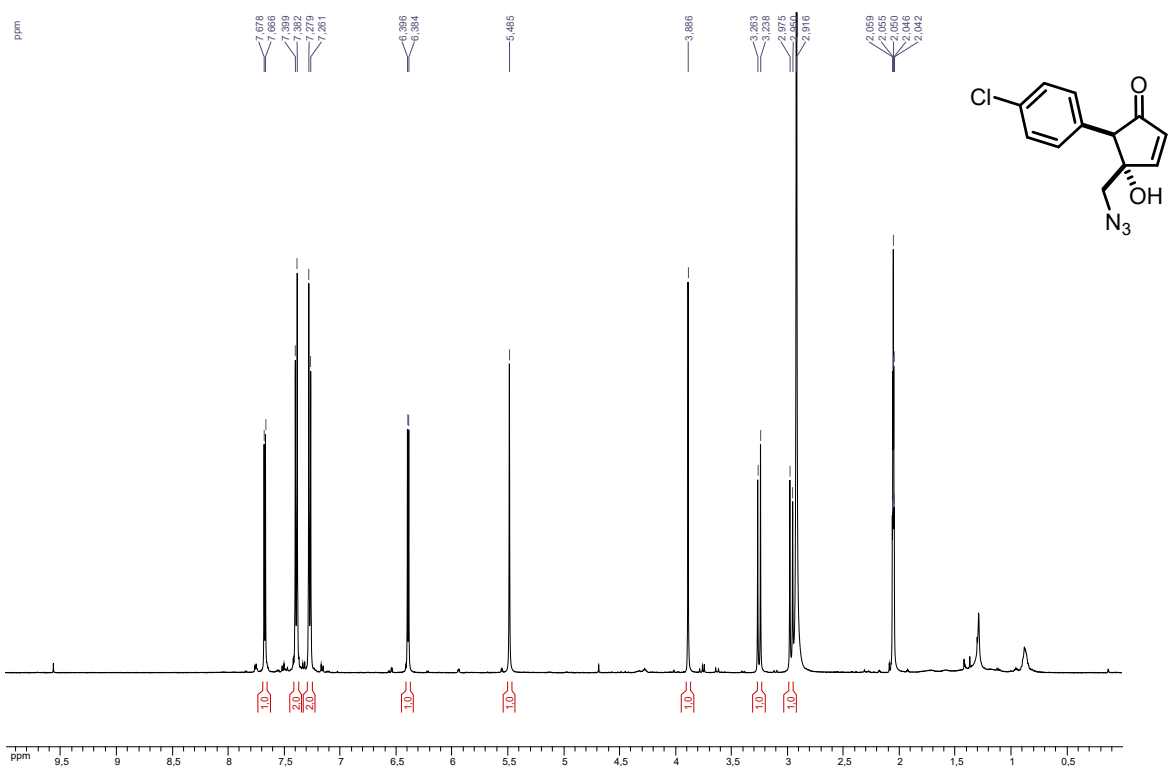
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7f)**



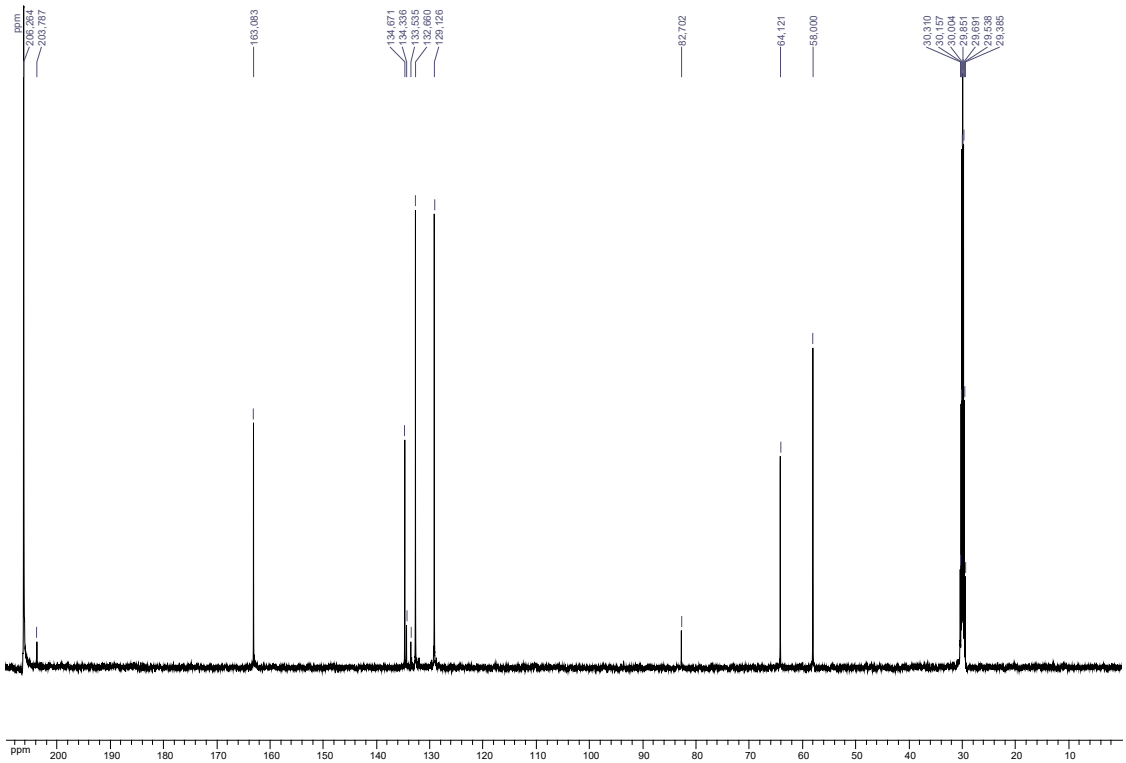
^{13}C-NMR (Acetone-d_6, 126 MHz)



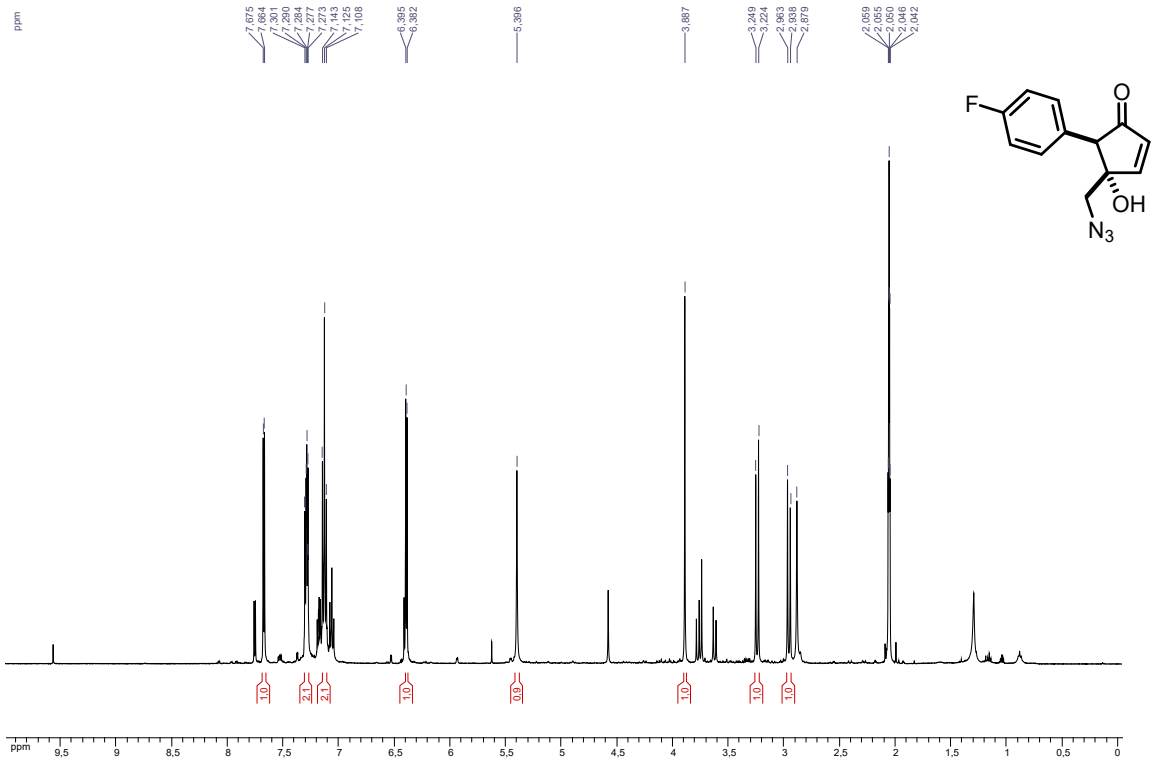
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7g)**



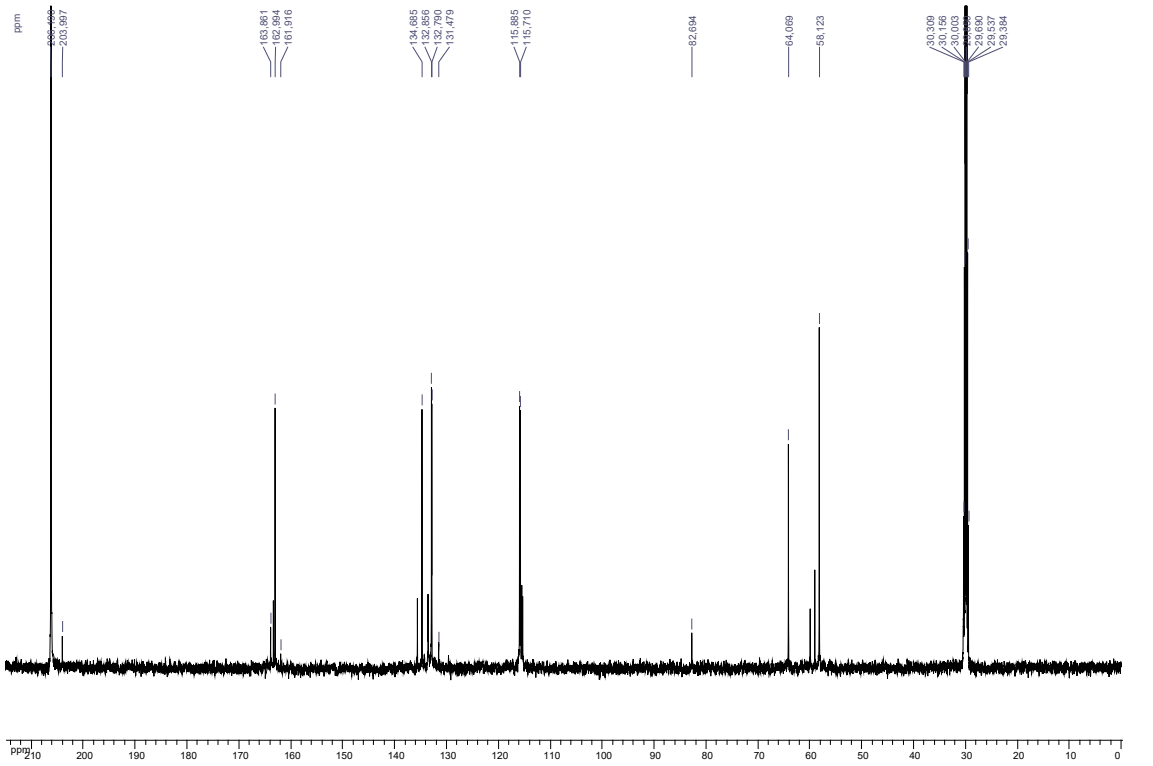
^{13}C-NMR (Acetone-d_6, 126 MHz)



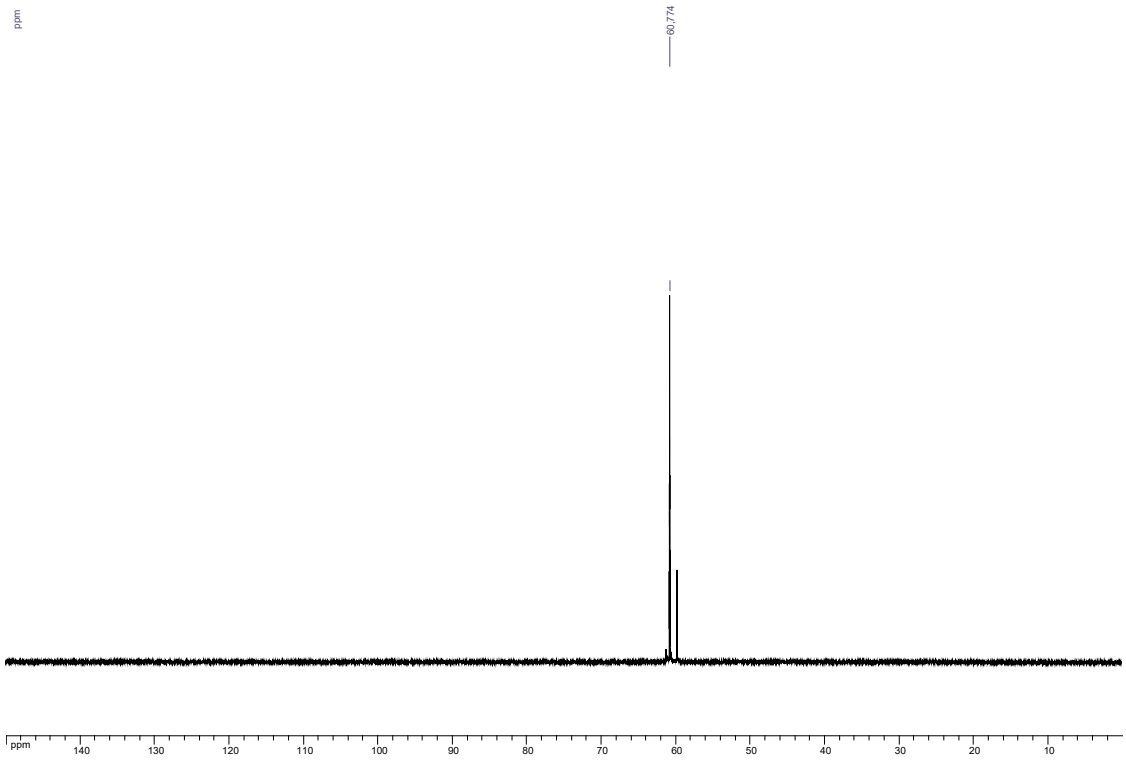
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7h)**



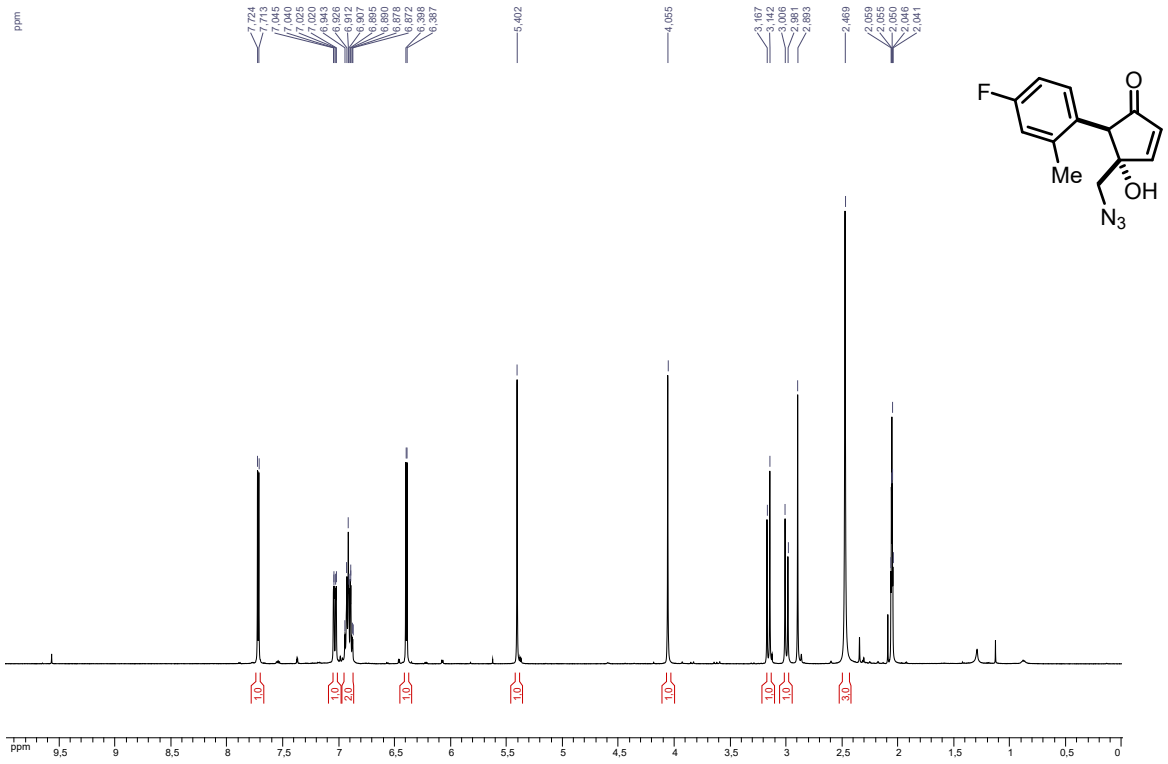
^{13}C-NMR (Acetone-d_6, 126 MHz)



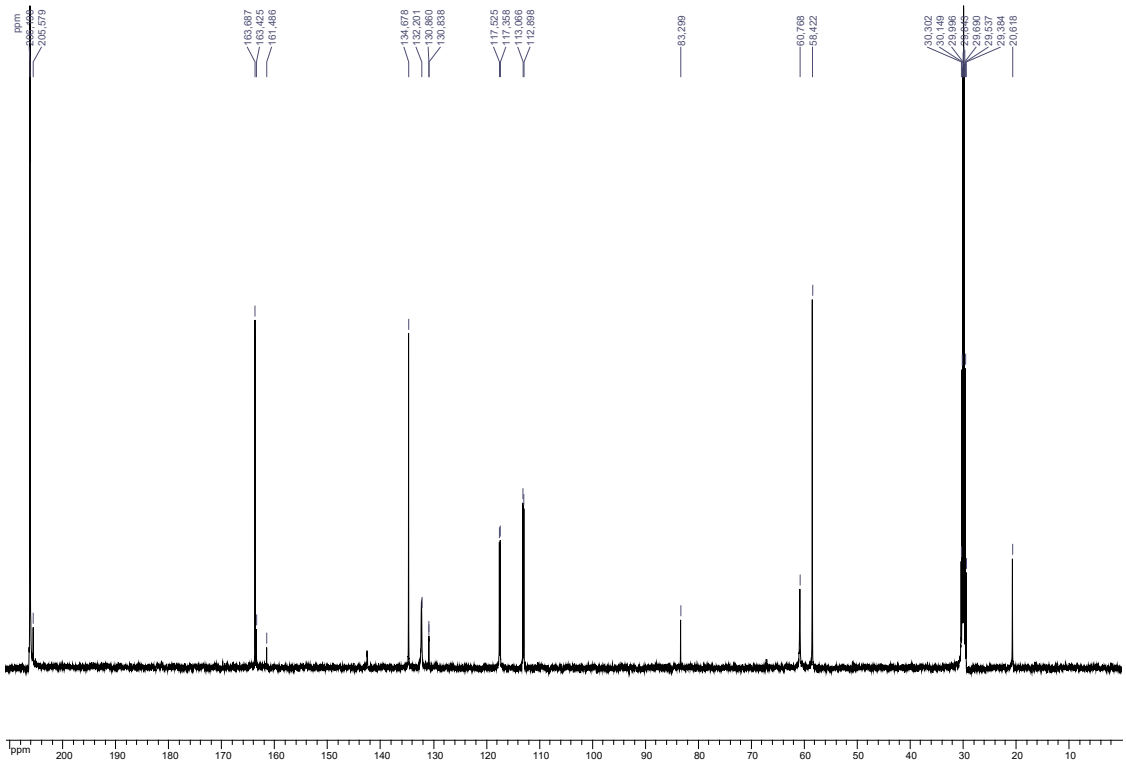
^{19}F-NMR (Acetone-d_6, 282 MHz)



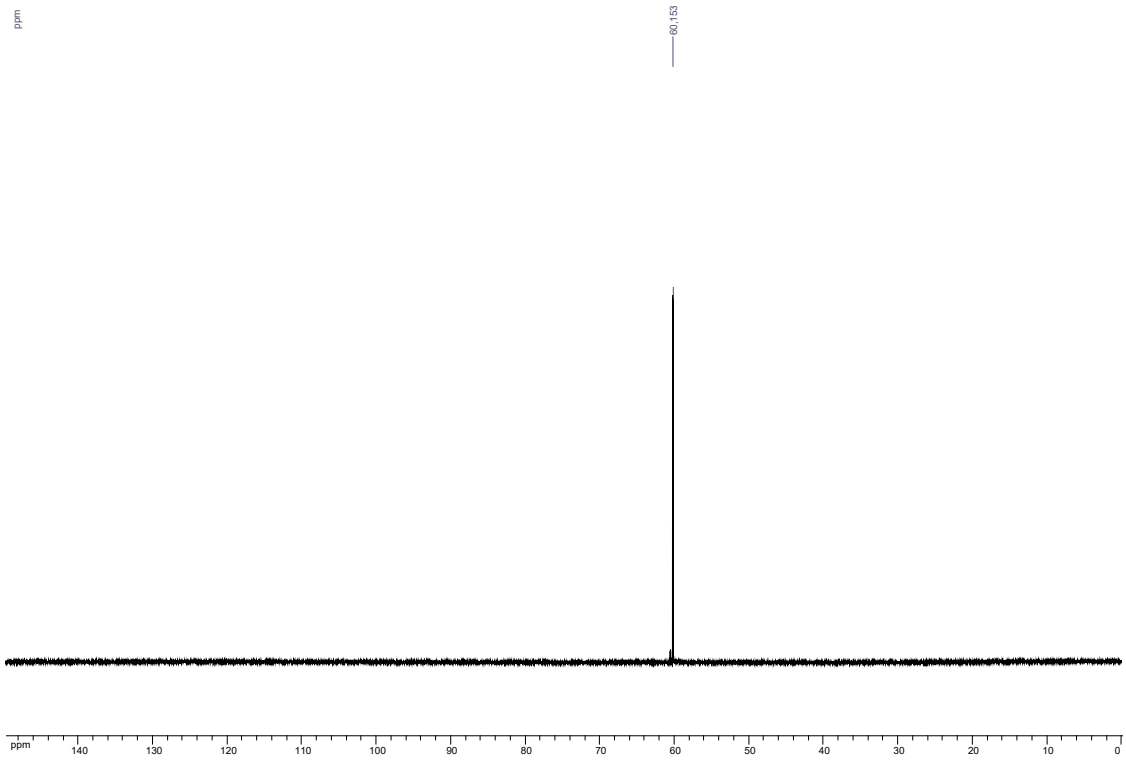
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7i)**



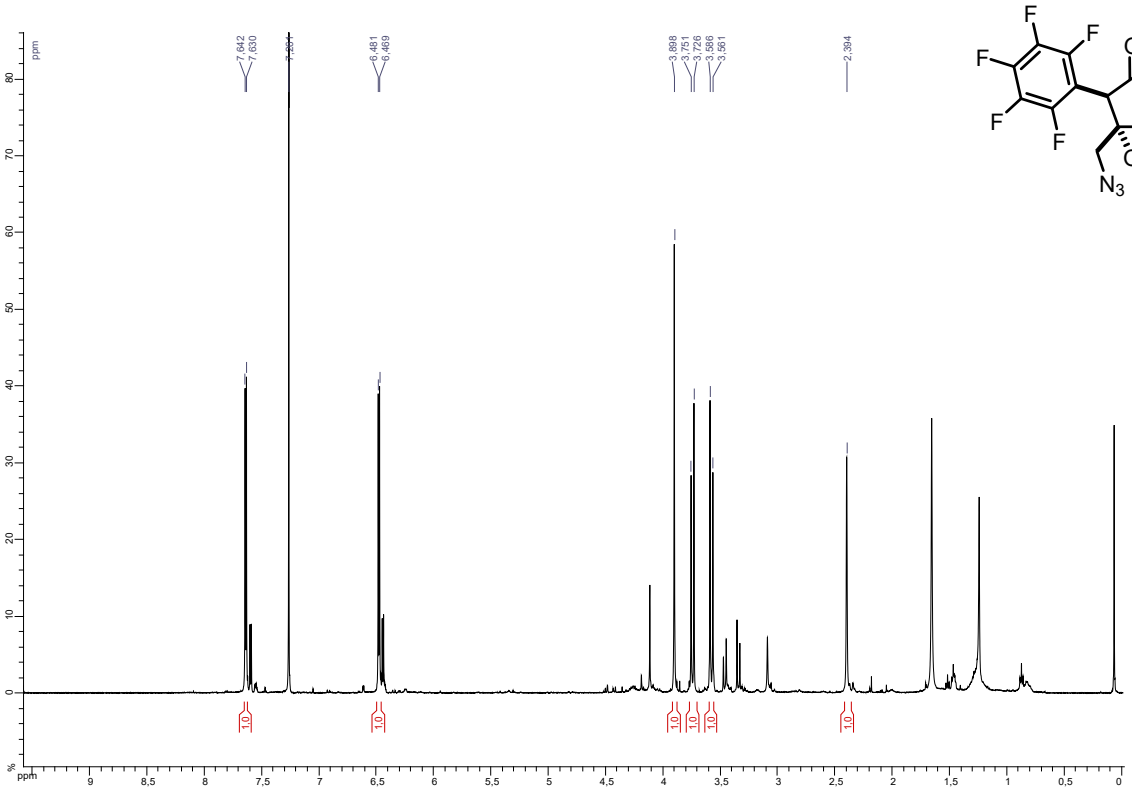
^{13}C-NMR (Acetone-d_6, 126 MHz)



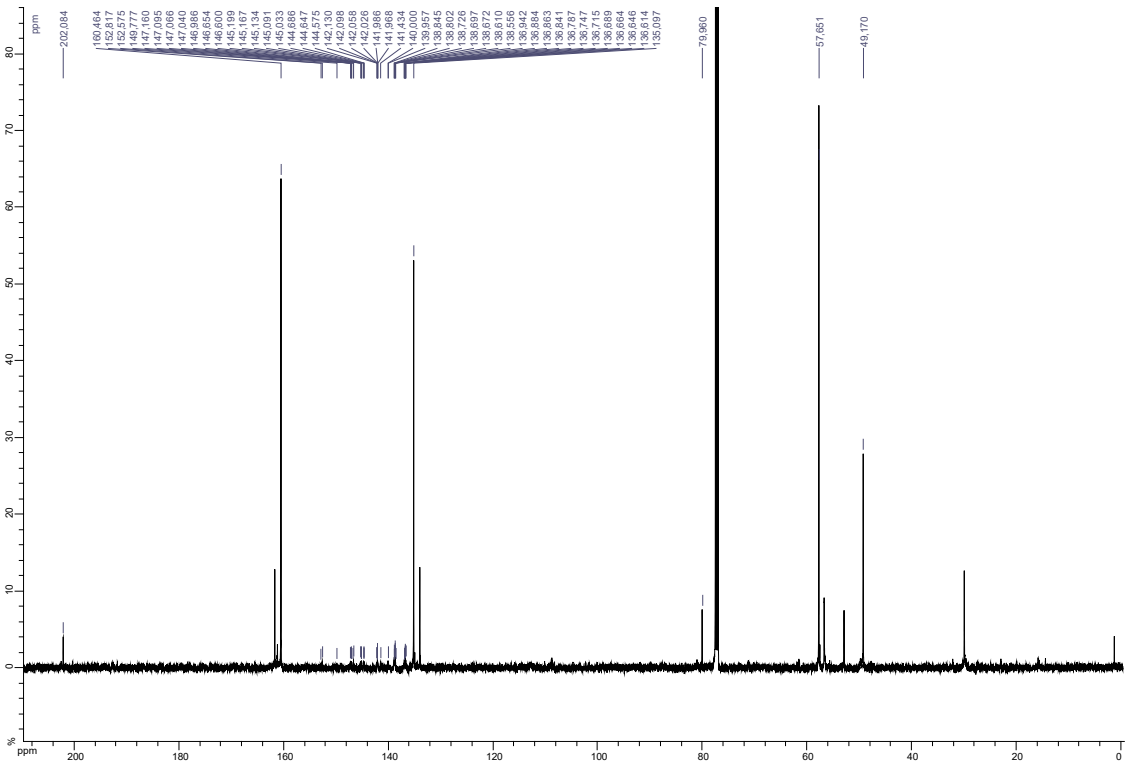
^{19}F-NMR (Acetone-d_6, 282 MHz)



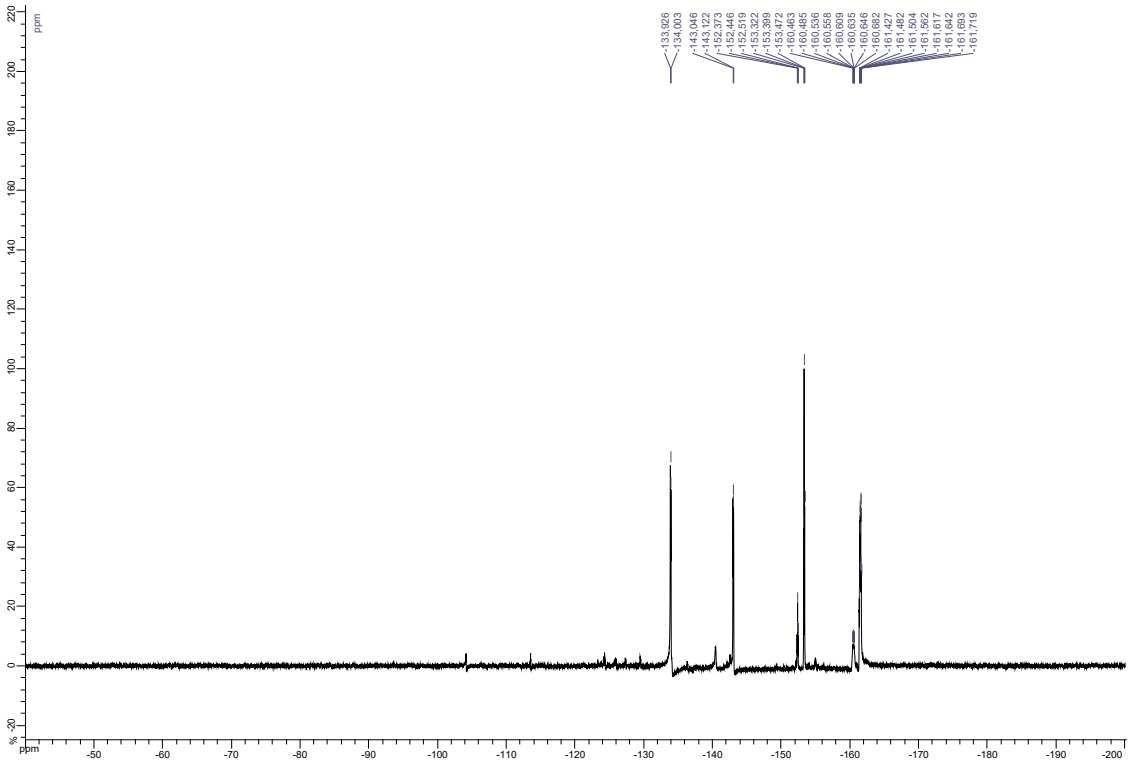
^{1}H-NMR ($CDCl_3$, 500 MHz) **(7j)**



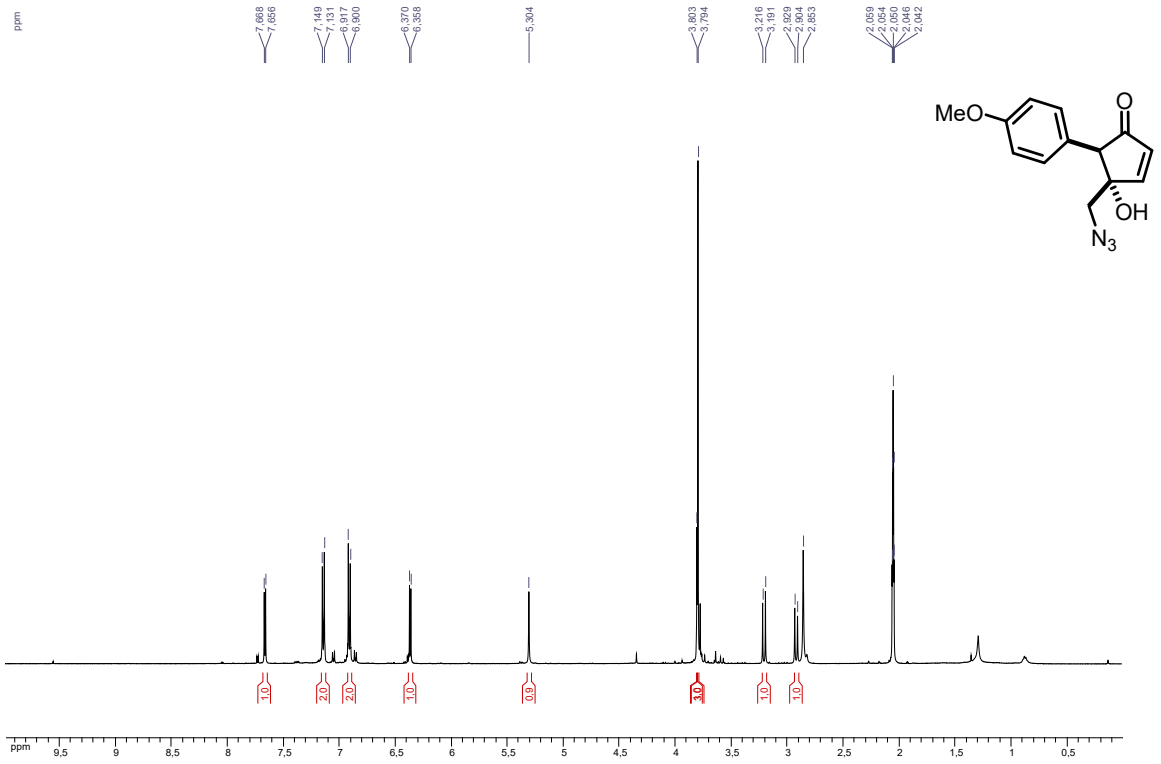
^{13}C-NMR ($CDCl_3$, 126 MHz)



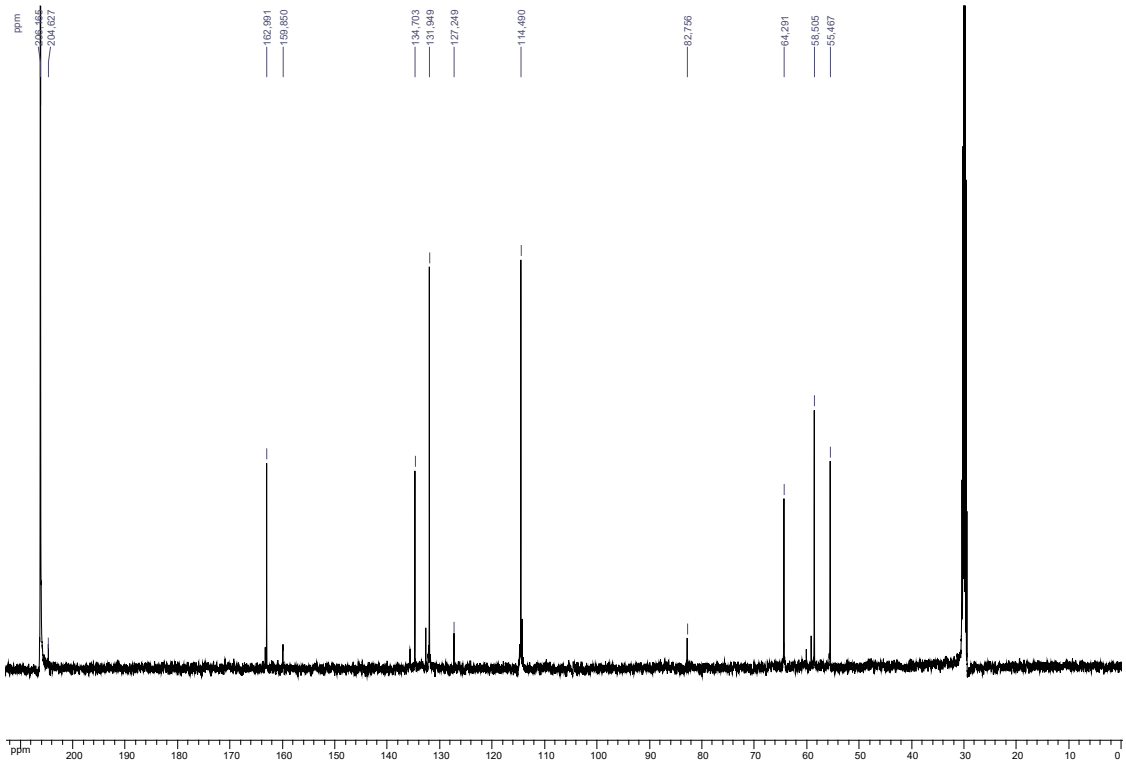
^{19}F-NMR ($CDCl_3$, 282 MHz)



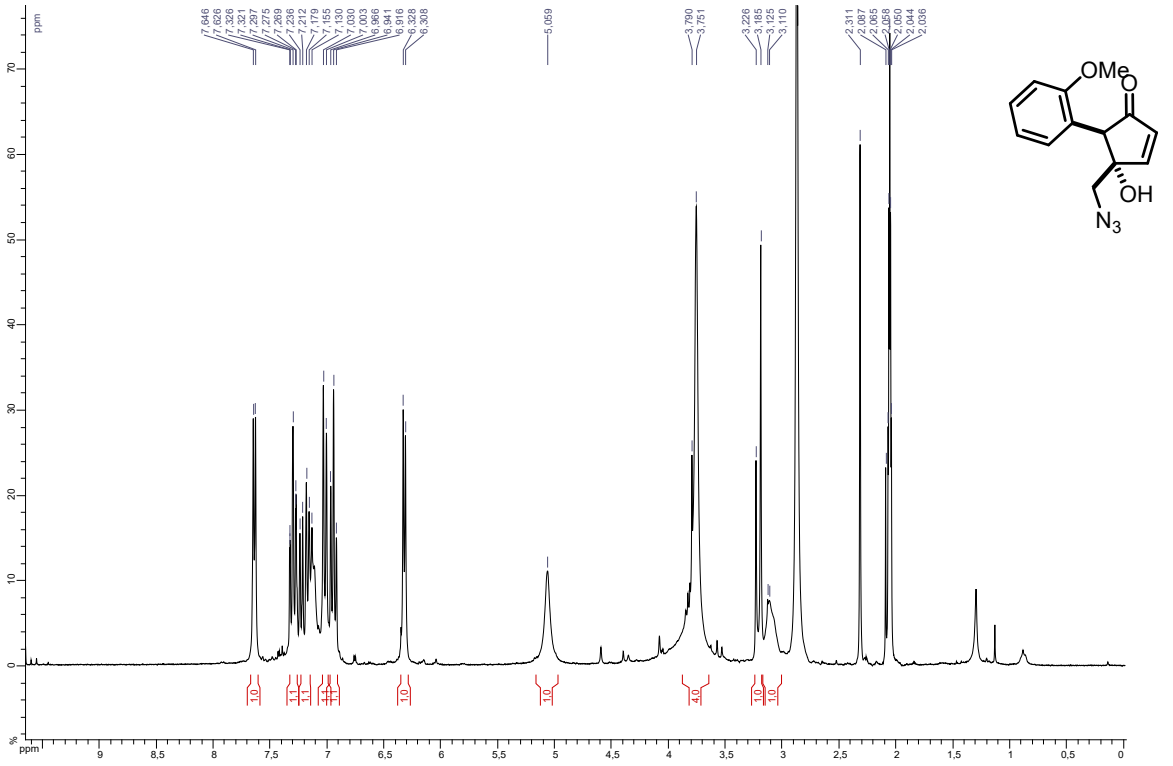
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7k)**



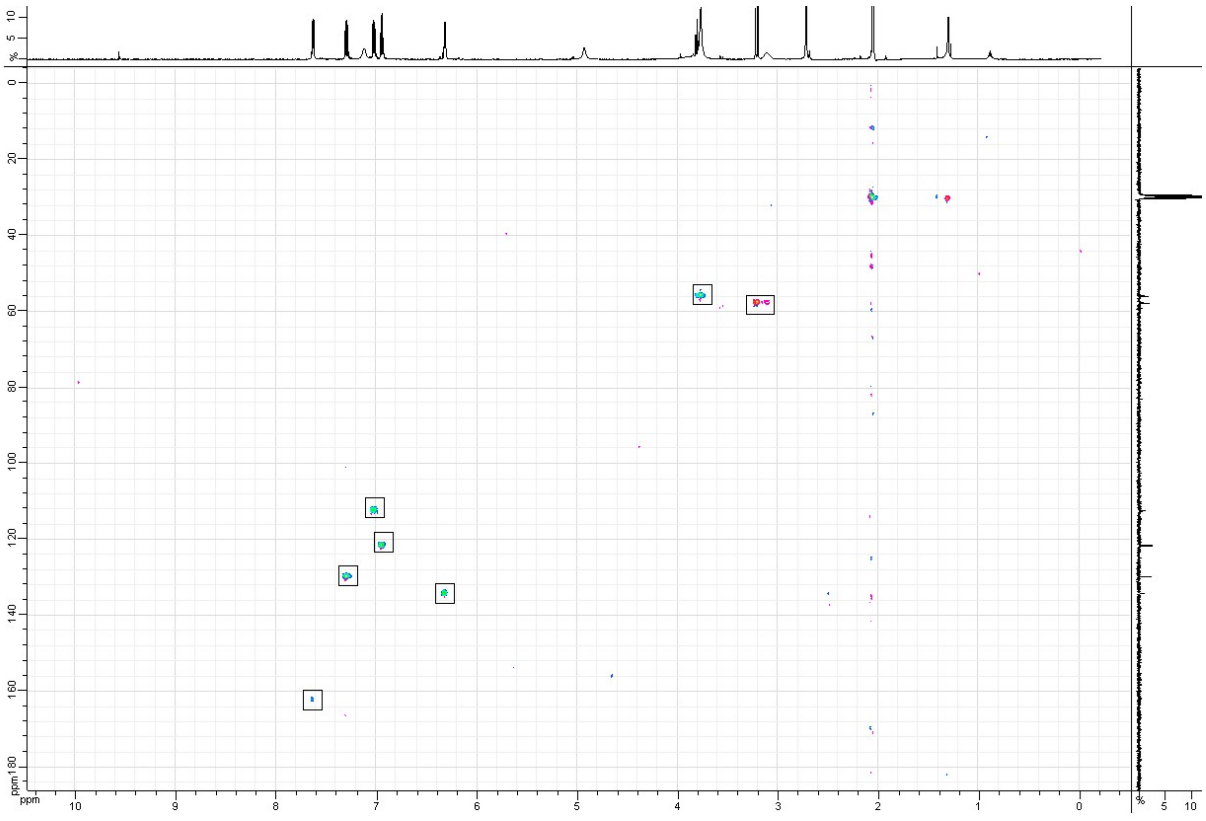
^{13}C-NMR (Acetone-d_6, 126 MHz)



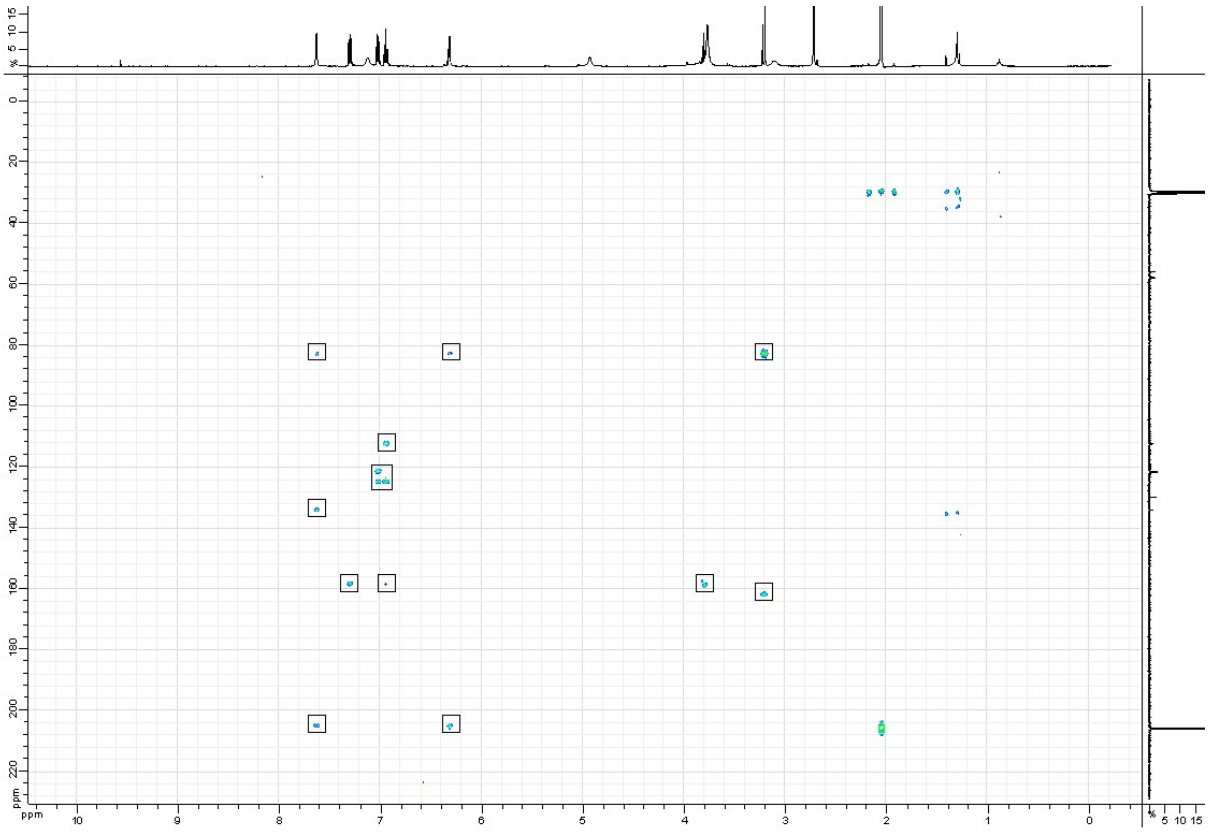
^{1}H-NMR (Acetone-d_6, 300 MHz) **(7l)**



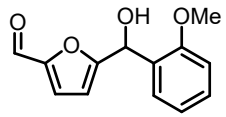
HSQC (^{1}H/^{13}C) (Acetone-d_6, 500 MHz)

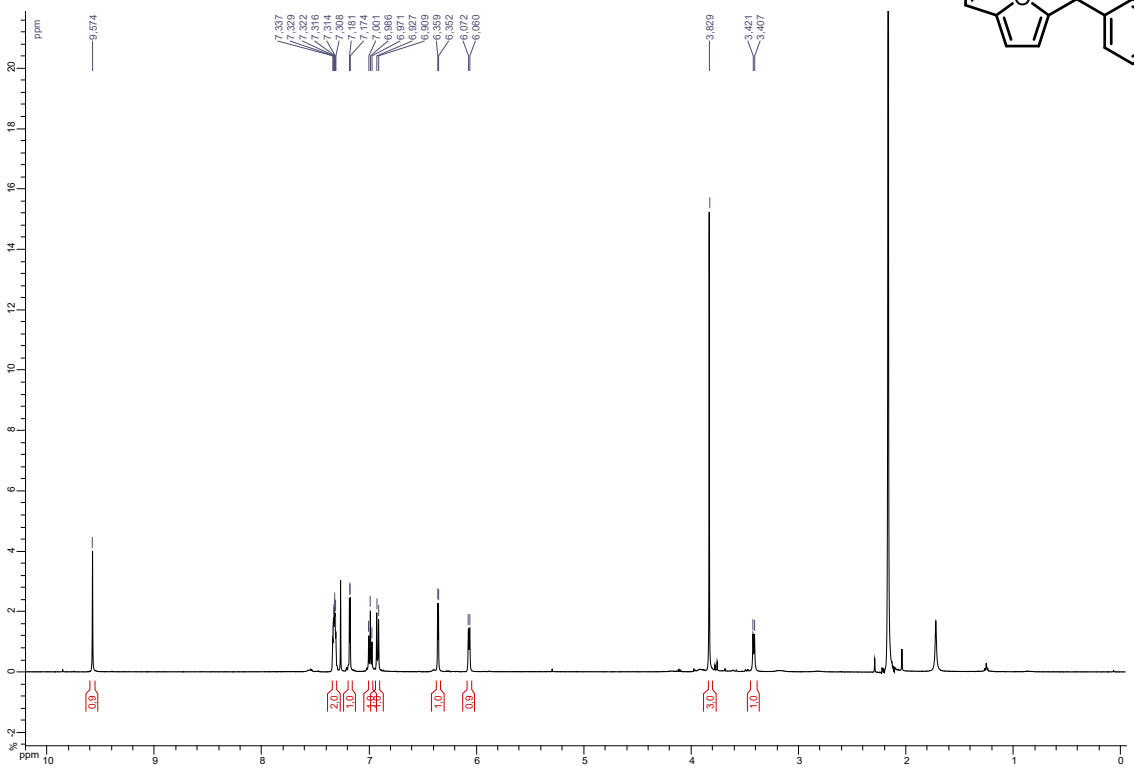


HMBC ($^{1}H/^{13}C$) (Acetone-d_6, 500 MHz)

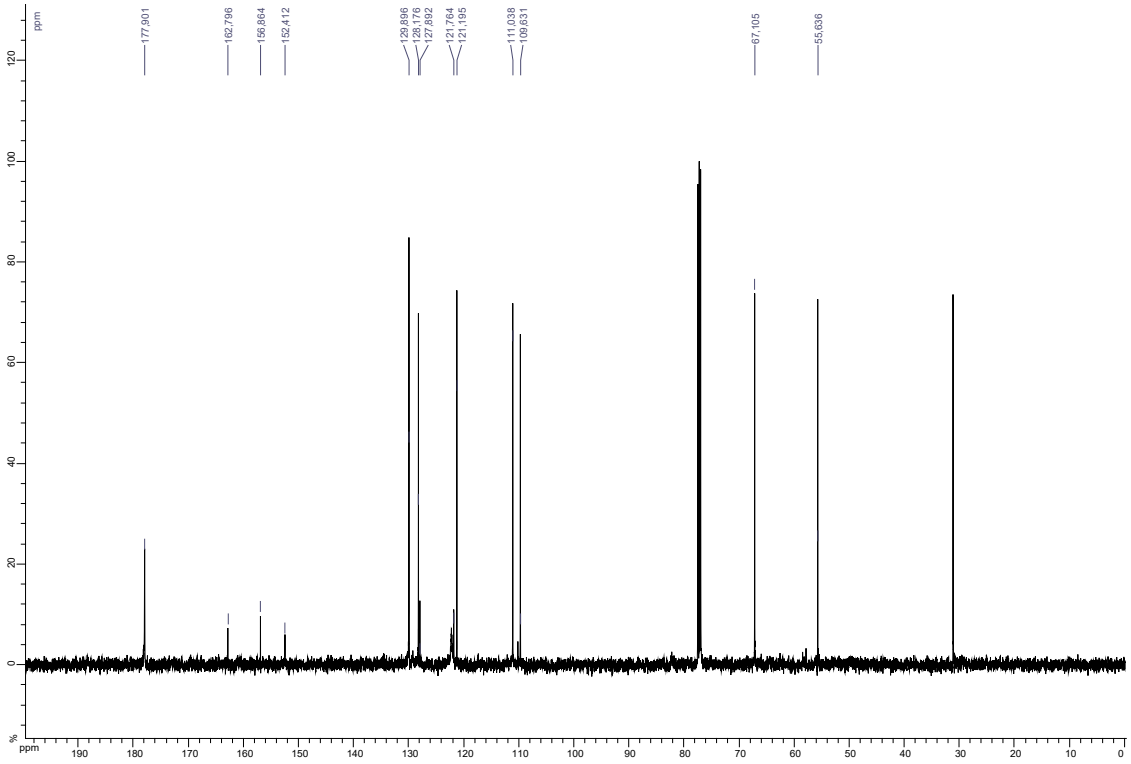


^{1}H-NMR ($CDCl_3$, 500 MHz) **(9)**

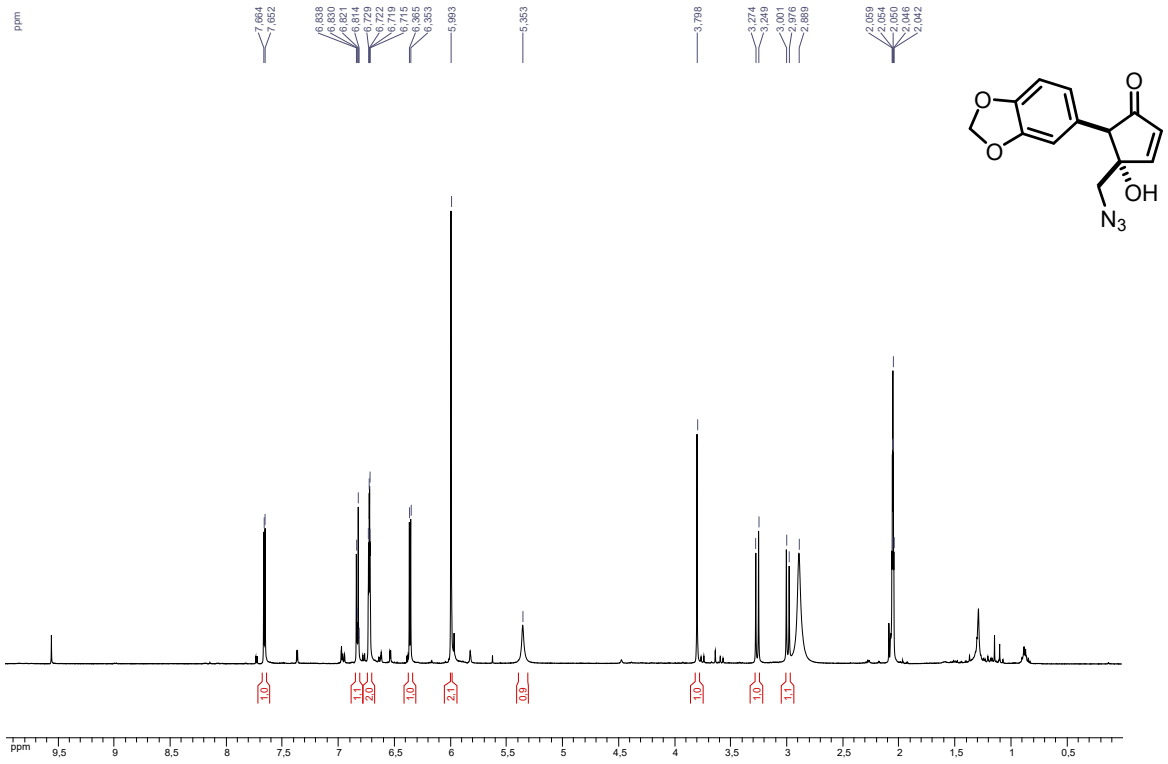




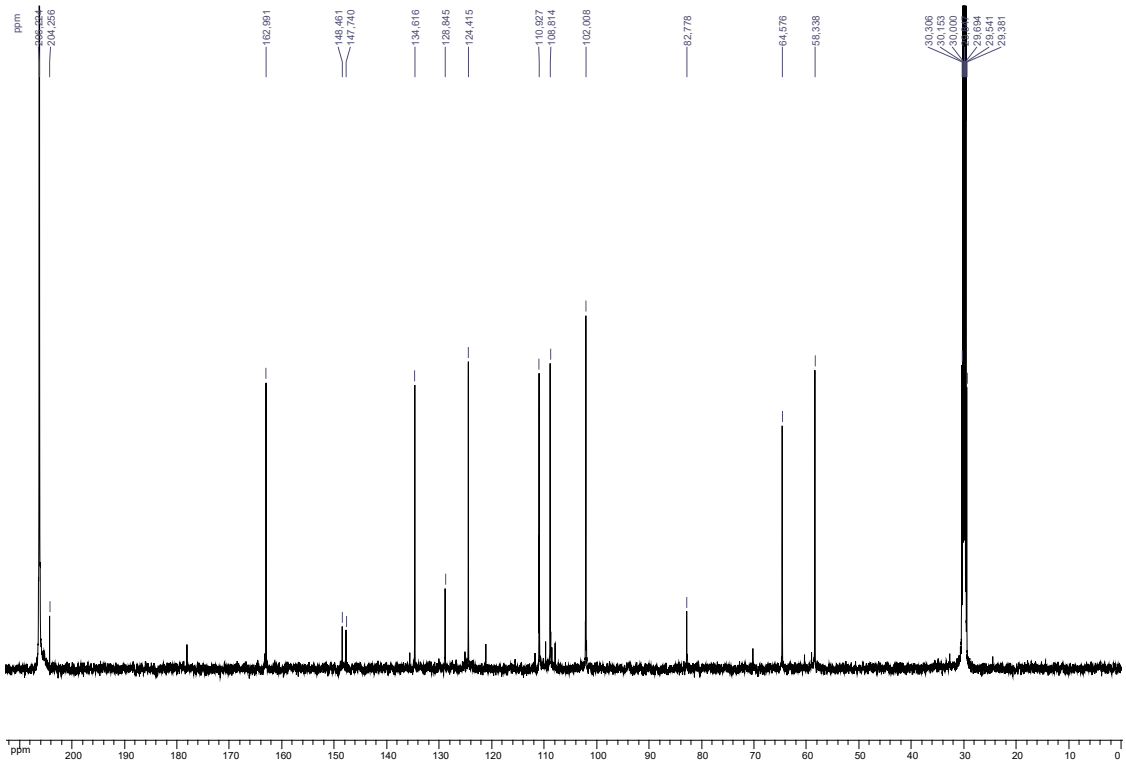
^{13}C-NMR ($CDCl_3$, 126 MHz)



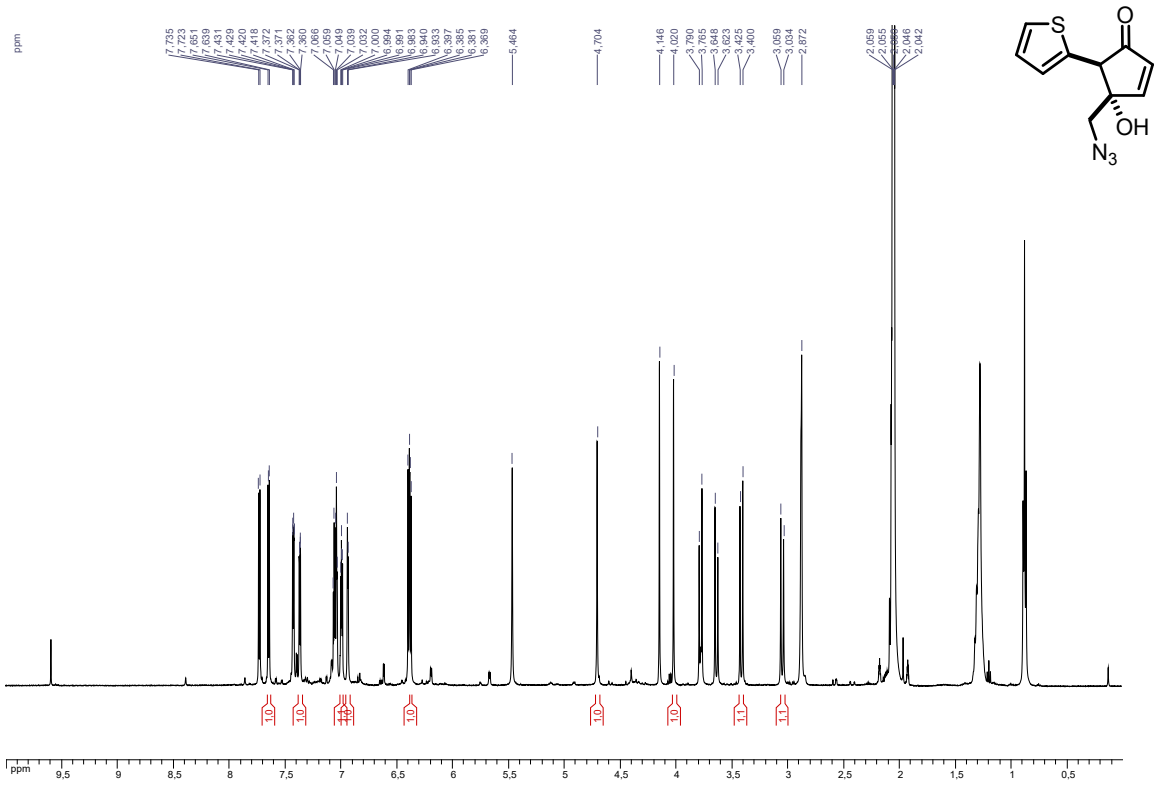
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7m)**



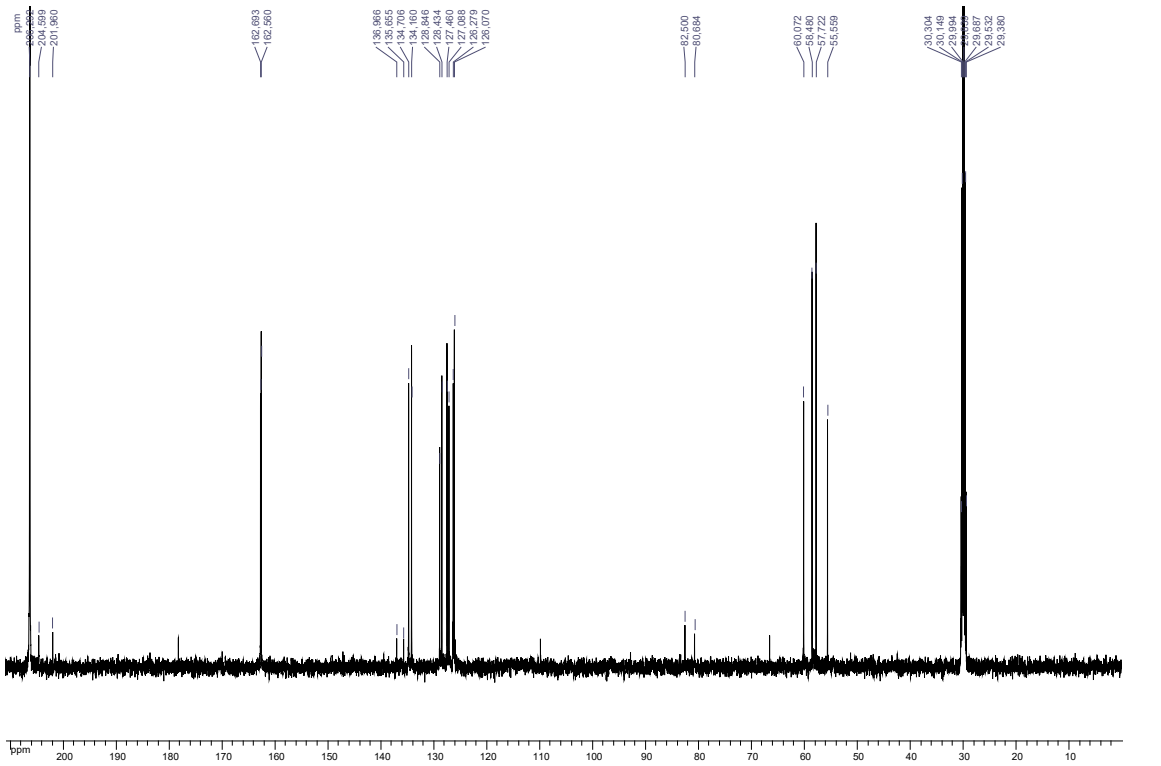
^{13}C-NMR (Acetone-d_6, 126 MHz)



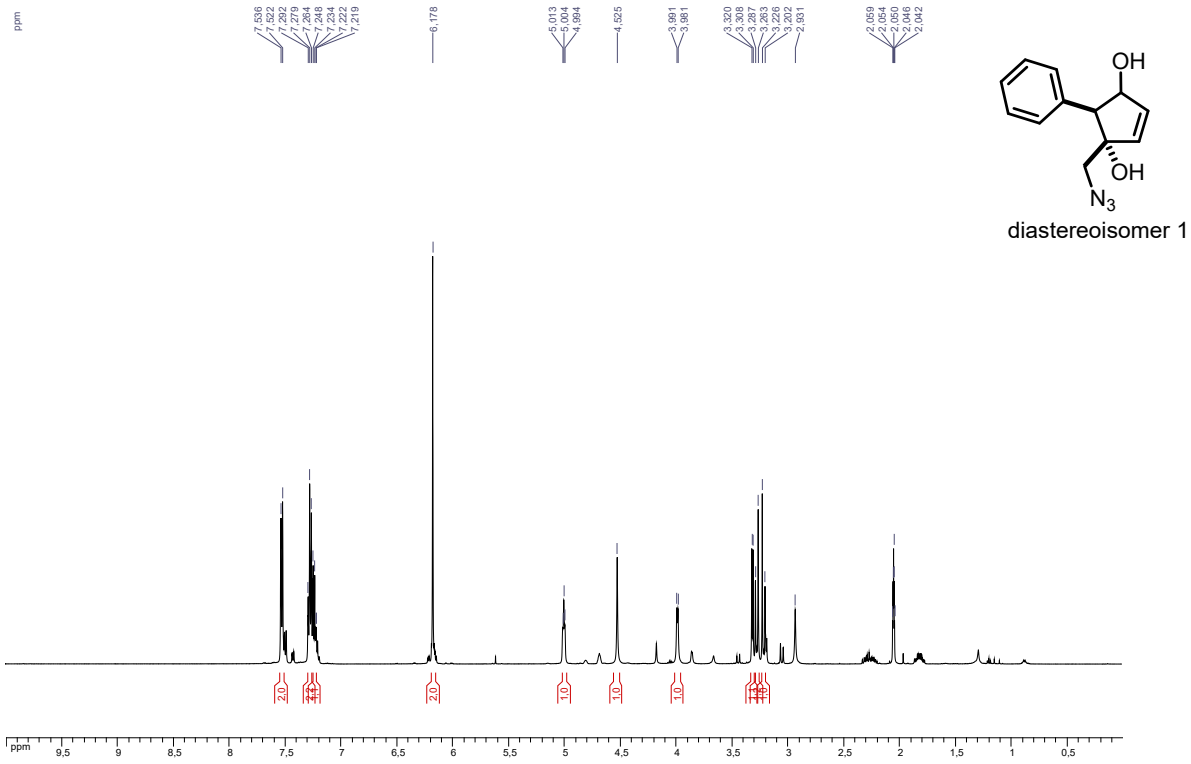
^{1}H-NMR (Acetone-d_6, 500 MHz) **(7n)**



^{13}C-NMR (Acetone-d_6, 126 MHz)

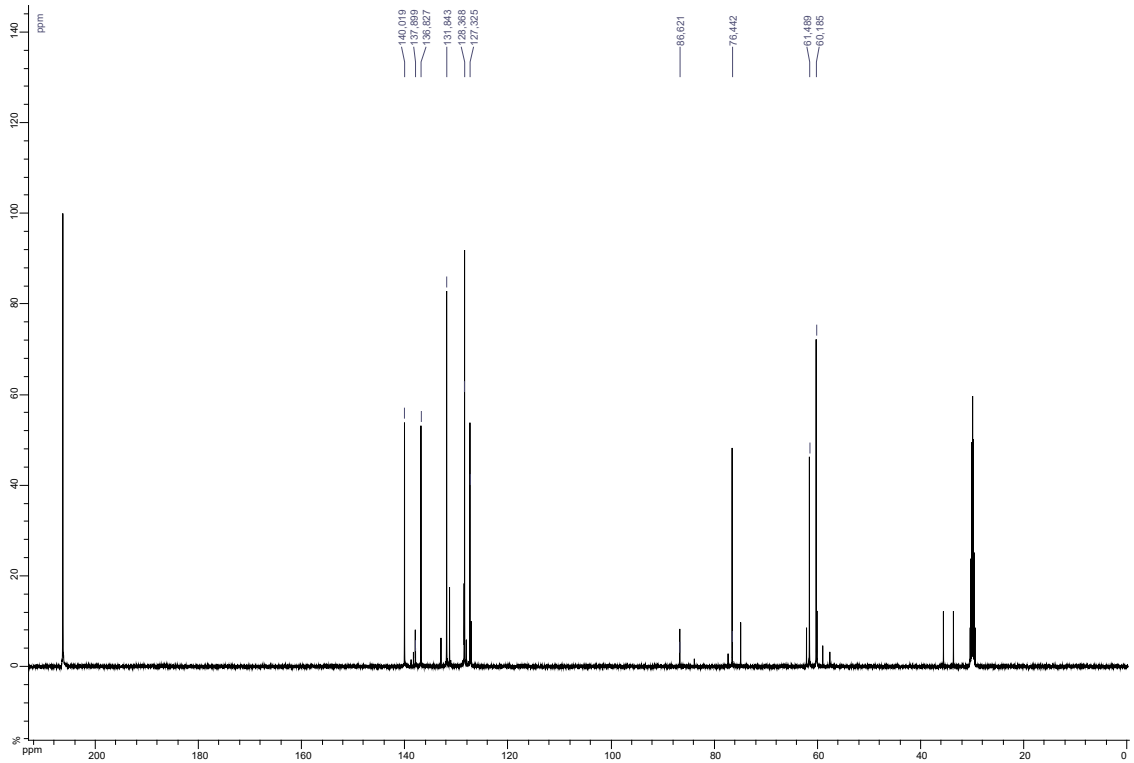


^{1}H-NMR (Acetone-d_6, 500 MHz) **(10, diastereoisomer 1)**

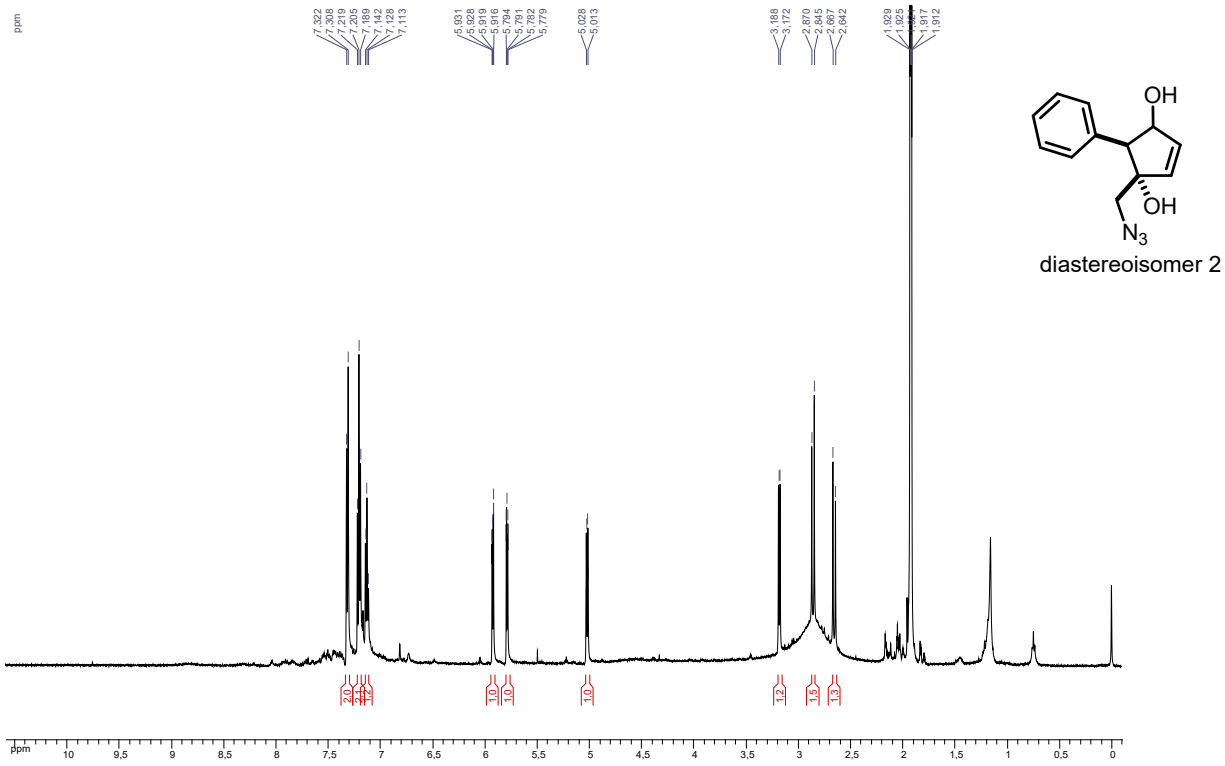


diastereoisomer 1

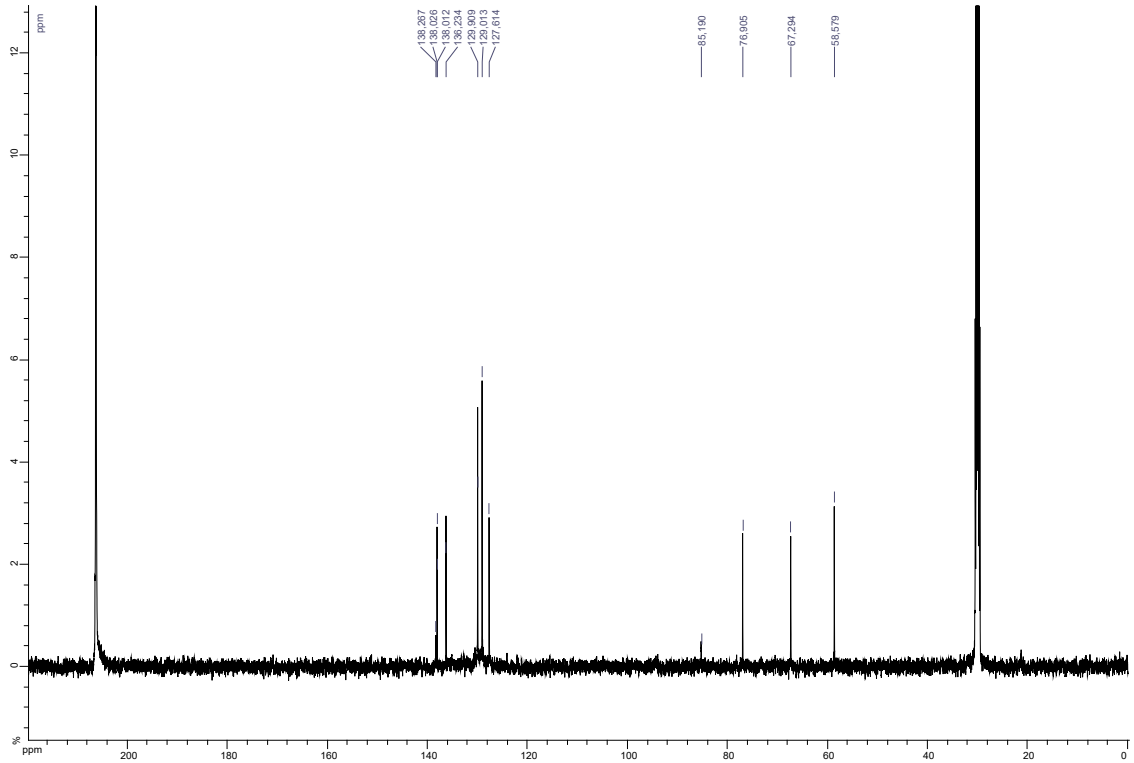
^{13}C-NMR (Acetone-d_6, 126 MHz)



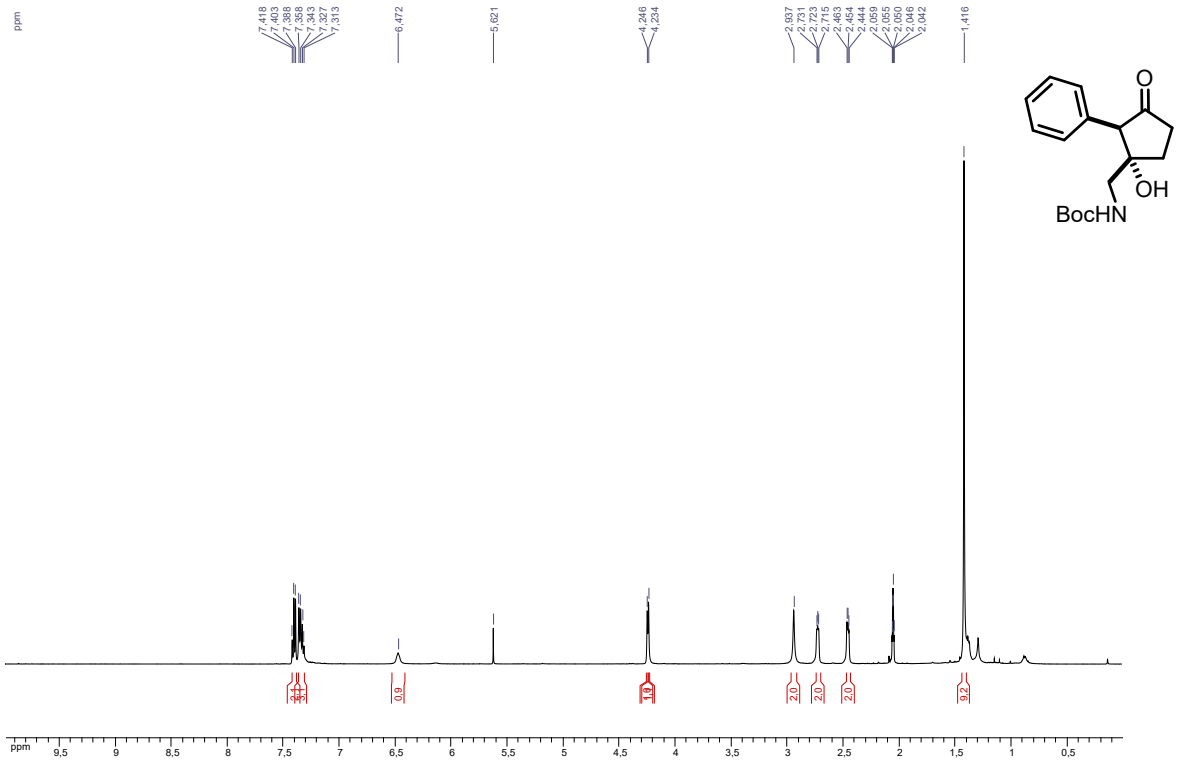
^{1}H-NMR (Acetone-d_6, 500 MHz) **(10, diastereoisomer 2)**



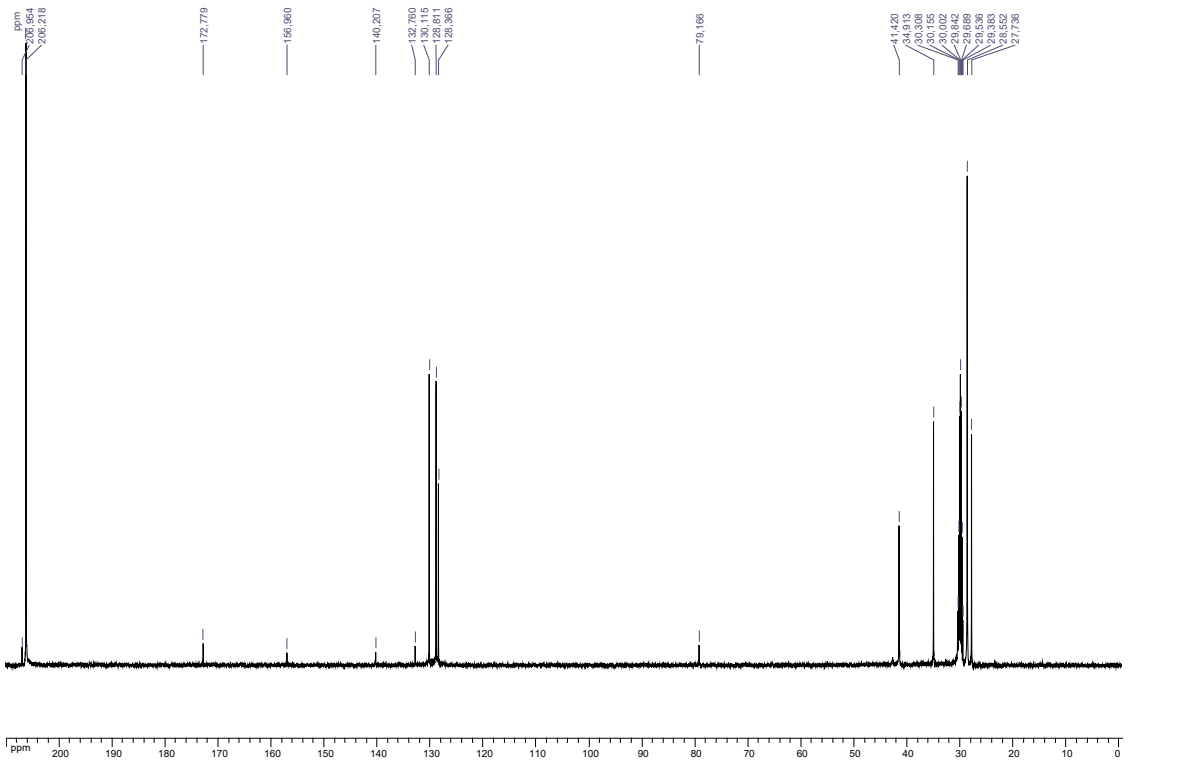
^{13}C-NMR (Acetone-d_6, 126 MHz)



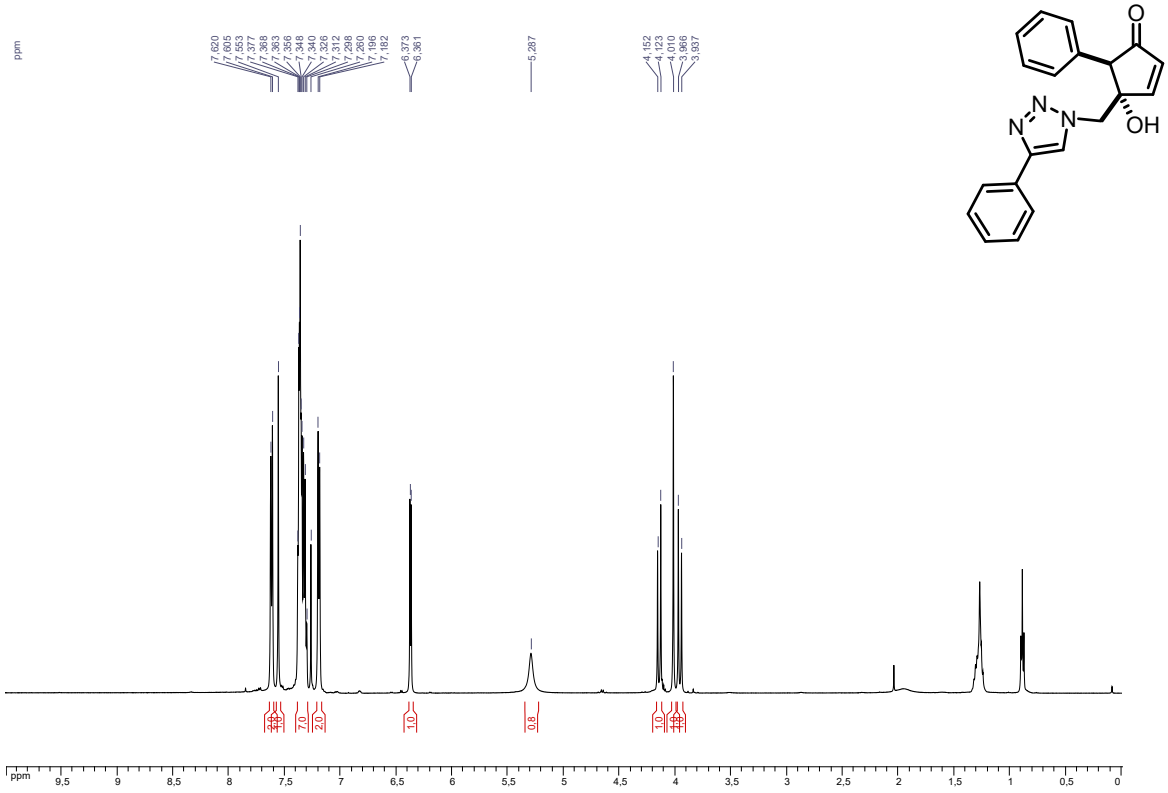
^{1}H-NMR (Acetone-d_6, 500 MHz) **(11)**



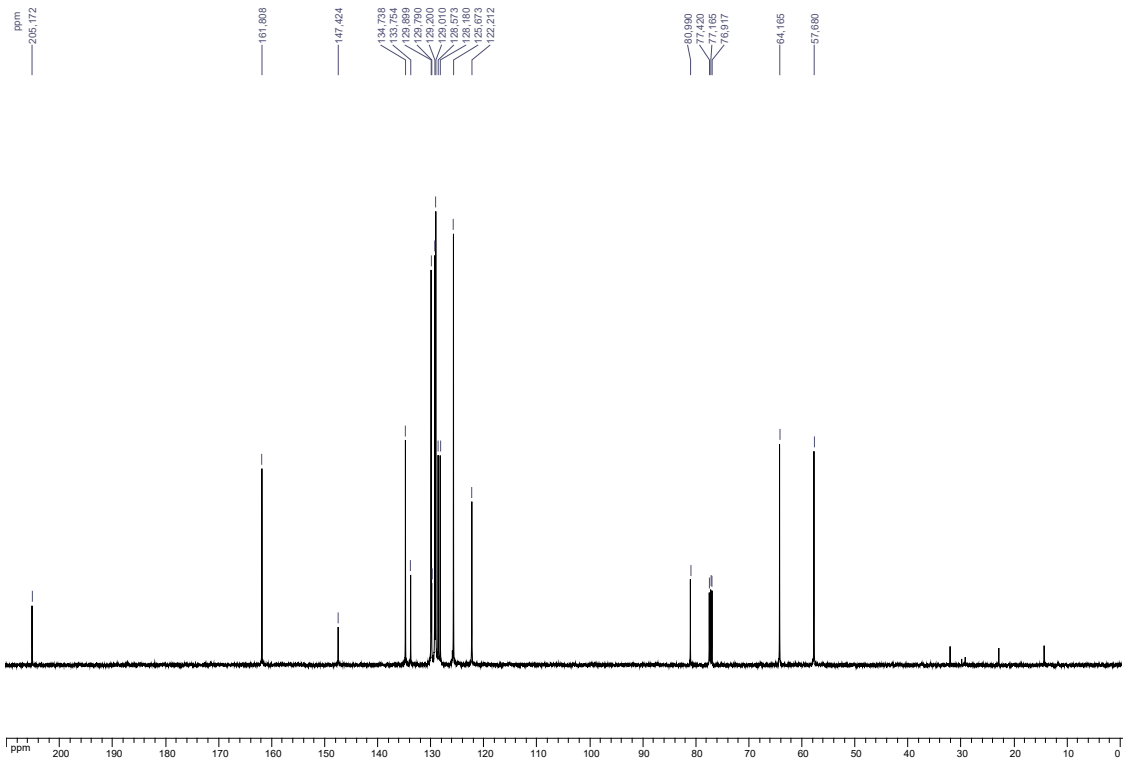
^{13}C-NMR (Acetone-d_6, 126 MHz)



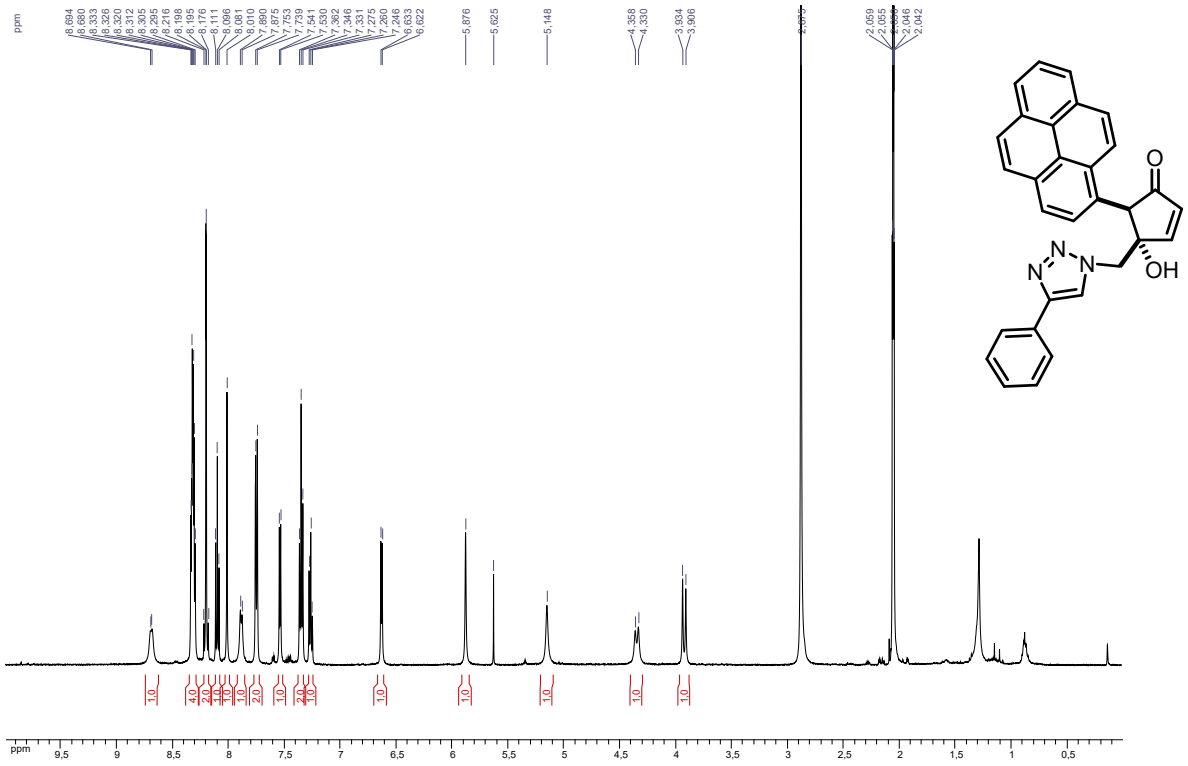
^{1}H-NMR ($CDCl_3$, 500 MHz) **(12)**



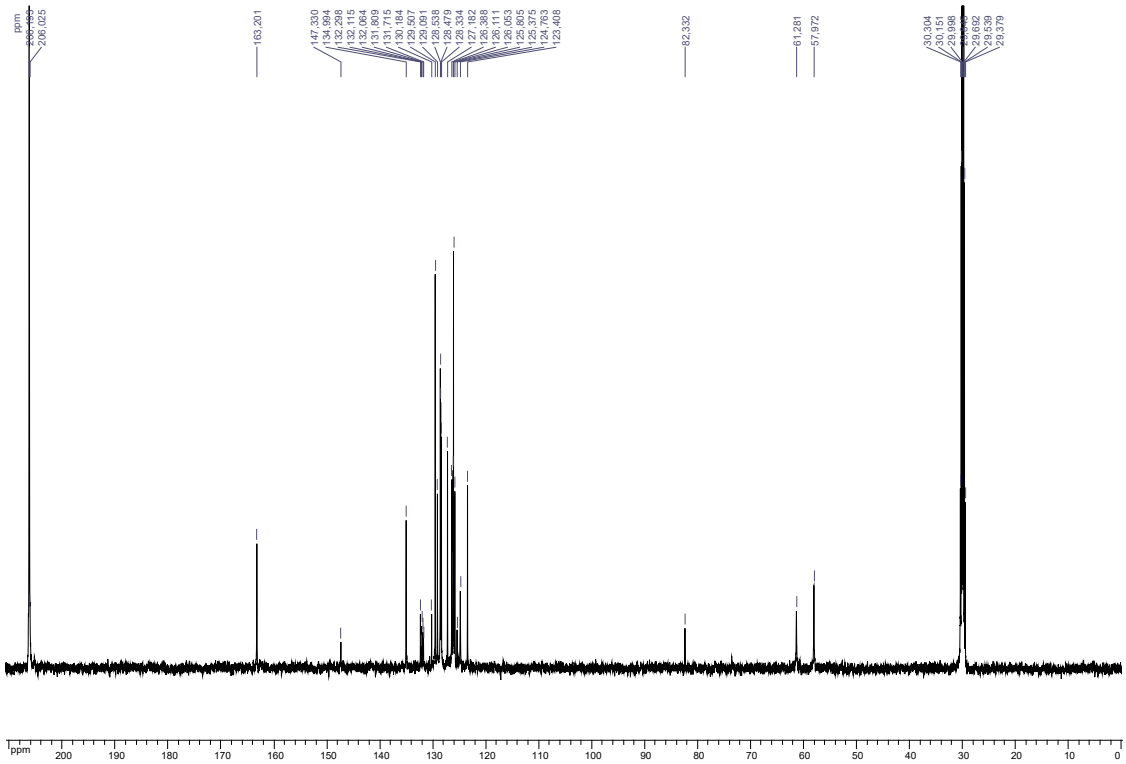
^{13}C-NMR ($CDCl_3$, 126 MHz)



^{1}H-NMR (Acetone-d_6, 500 MHz) **(13)**



^{13}C-NMR (Acetone-d_6, 126 MHz)



X. Bioassays for cytotoxicity activities of compounds 5 and 7a-n

Cancer cell lines were obtained from the American type Culture Collection (Rockville, MD) and were cultured according to the supplier's instructions.

Briefly, human HCT-116 colorectal carcinoma cells were grown in Gibco McCoy's 5A supplemented with 10% fetal calf serum and 1% glutamine.

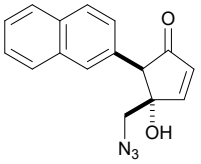
HL60 myelogenous leukemia cells were grown in RPMI 1640 supplemented with 10% fetal calf serum (FCS) and 1% glutamine.

Cell viability was determined by a luminescent assay according to the manufacturer's instructions (Promega, Madison, WI, USA).

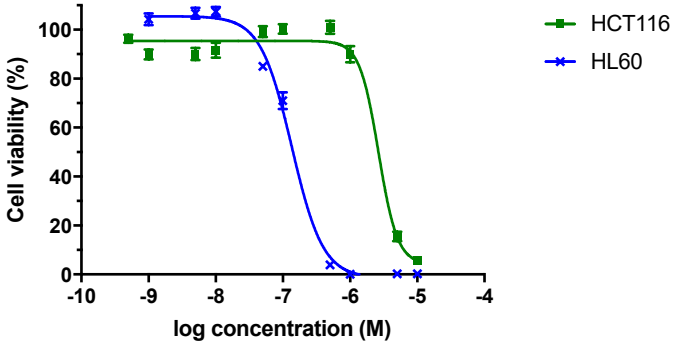
For IC_{50} determination, the cells were seeded in 96-well plates (3×10^3 cells/well) containing 90 µL of growth medium. After 24 h of culture, the cells were treated with the tested compounds at 10 different final concentrations. Each concentration was obtained from serial dilutions in culture medium starting from the stock solution. Control cells were treated with the vehicle. Experiments were performed in triplicate.

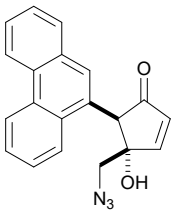
After 72 h of incubation, 100 µL of CellTiter Glo Reagent was added for 15 min before recording luminescence with a spectrophotometric plate reader PolarStar Omega (BMG LabTech). The dose-response curves were plotted with Graph Prism software and the IC_{50} values were calculated using the Graph Prism software from polynomial curves (four or five-parameter logistic equations).

Cytotoxicities (IC_{50} [nM]) of highlighted compounds **7c**, **7c** and **7h** at nanomolar concentration on HCT116 cancer cell line (in bleu color) and HL60 cancer cell line (in green color). Data are the mean ± standard error (SEM) of three independent experiments.

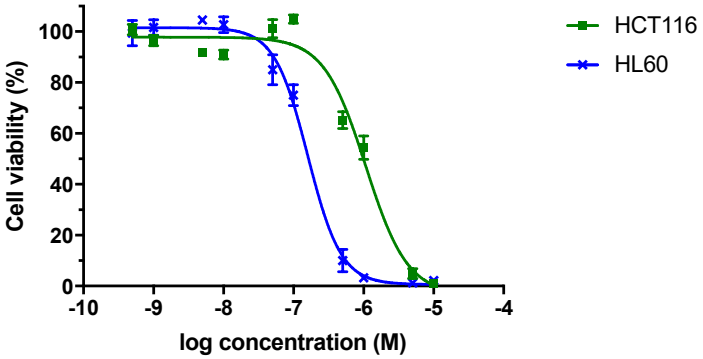


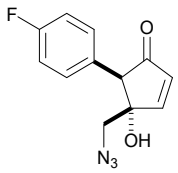
7c



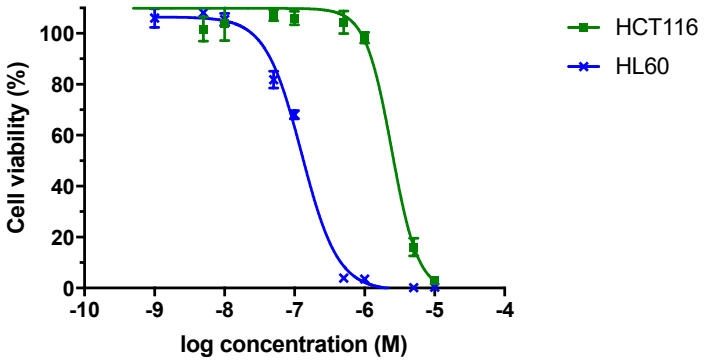


7d





7h



1. (a) C. Piutti and F. Quartieri, The Piancatelli rearrangement: new applications for an intriguing reaction, *Molecules*, 2013, **18**, 12290-12312; (b) C. Verrier, S. Moebs-Sanchez, Y. Queneau and F. Popowycz, The Piancatelli reaction and its variants: recent applications to high added-value chemicals and biomass valorization, *Org. Biomol. Chem.*, 2018, **16**, 676-687.
2. M. J. Palframan and G. Pattenden, The versatility of furfuryl alcohols and furanoxonium ions in synthesis, *Chem. Commun.*, 2014, **50**, 7223-7242.
3. R. W. Hoffmann, Conformation Design of Open-Chain Compounds, *Angew. Chem. Int. Ed.*, 2000, **39**, 2054-2070.
4. O. Nieto Faza, C. Silva López, R. Álvarez and Á. R. de Lera, Theoretical Study of the Electrocyclic Ring Closure of Hydroxypentadienyl Cations, *Chem. Eur. J.*, 2004, **10**, 4324-4333.