Gold(III) Chloride mediated transformation of furfural to the *trans*-*N*,*N*-4,5-diaminocyclopent-2-enones in the presence of anilines

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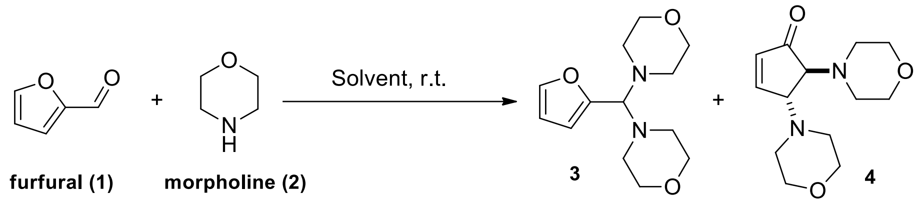
Table of Contents	**Pages**
Table S1. Ratios in terms of the price over milligram of the catalysts	2
Table S2. Solvent screening for the synthesis of **4** from the reaction between **1** and **2**	3
Table S3. Salts screening for the synthesis of cyclopentenones	4
Table S4. Catalyst screening under photoirradiation conditions (Xenon Lamp)	5
^{1}H and ^{13}C{H} NMR data of *trans*-DACPs **4**, **4a-4d**, **5a-5o**	6 - 13
Copies of ^{1}H and ^{13}C{H} NMR spectra of *trans*-DACPs **4**, **4a-4d**, **5a-5o**	14 - 33

Table S1. Ratios in terms of the price over milligram of the catalysts

Lewis Acids	**Cas Number**	**Price/mg[a]**	**Loading (%)[b]**	**Reaction Scale (mmol)[b]**	**Cost/ reaction**
$Sc(OTf)_3$	144026-79-9	0.0414	10	0.5	1.01
$Dy(OTf)_3$	139177-62-1	0.0142	10	0.5	0.43
$AuCl_3$	**13453-07-1**	**0.1092**	**1.5**	**0.5**	**0.25**
$AlCl_3$	7446-70-0	0.0234	10	0.5	0.17
$Cu(OTf)_2$	34946-82-2	0.0177	0.1	1	0.06
$ErCl_3 \cdot 6H_2O$	10025-75-9	0.0053	0.1	1	0.02

[a]All added values of pack sizes (5g) with the corresponding costs in Euro were obtained from Sigma-Aldrich. [b]Loading of the catalysts as well as the reaction scales were obtained from the corresponding articles.

Table S2. Solvent screening for the synthesis of **4** from the reaction between **1** and **2**

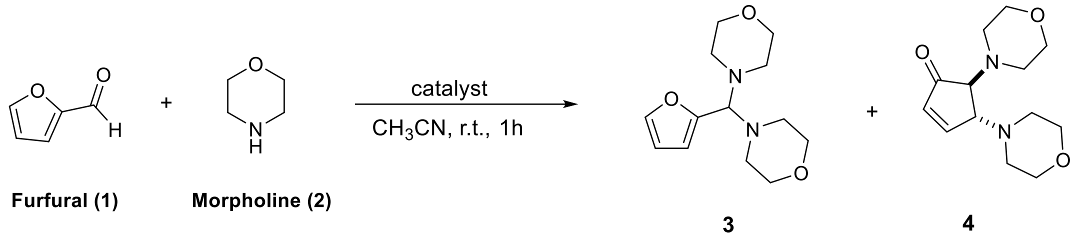


Entry	Solvent	Time (h)	1 (%)	3 (%)	4 (%)
1	MeOH	6	11	40	49
2	MeOH	18	5	10	85
3	EtOH	18	12	8	80
4	DCE	6	23	37	40
5	DCE	18	11	48	41
6	EtOAc	6	28	34	38
7	EtOAc	18	11	73	16
8	Toluene	6	17	46	37
9	Toluene	18	10	58	32
10	DMSO	6	20	65	15
11	DMSO	18	42	56	23
12	DMF	6	21	37	42
13	DMF	18	25	-	75
14	DMC	6	18	59	23
15	DMC	18	8	66	26
16	THF	6	27	40	33
17	THF	18	13	51	36
18	H_2O	1	15	65	20

[a]furfural (0.2 mmol), morpholine (0.44 mmol) and methanol (0.2 mL)

[b]furfural (0.5 mmol), morpholine (1.1 mmol) and methanol (0.2 mL)

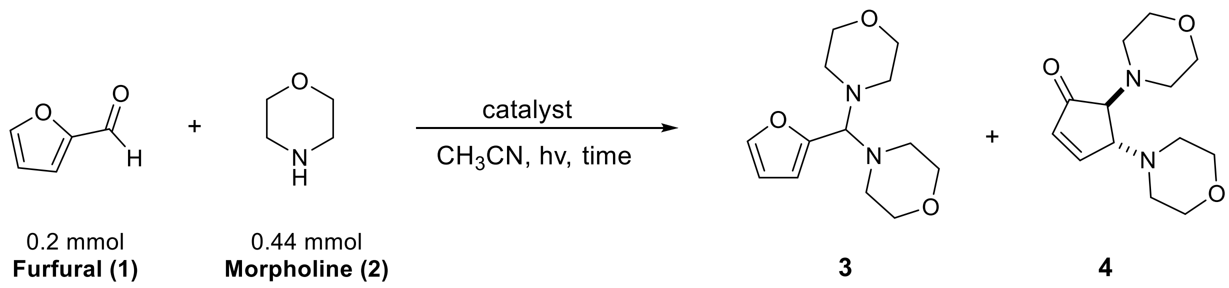
Table S3. Salts screening for the synthesis of cyclopentenones



Entry	Catalyst	Catalyst % mmol	1 (%)	3 (%)	4 (%)	Unidentified product (%)
1	HCl (6M)	6%	-	-	89	-
2	HCl (6M)	3%	-	29	40	-
4	$CuCl_2$•$2H_2O$	3%	-	-	95	-
5	CuCl	6%	15	37	22	26
6	$MgCl_2$	50%	-	-	78	22
7	$ZnCl_2$	50%	12	-	88	-
8	NH_4Cl	50%	-	-	100	-
9	NH_4Cl	10%	9	34	57	-
10	$CoCl_2$•$6H_2O$	6%	18	41	41	-
11	$Co(acac)_2$	3%	43	57	-	-
12	$Co(acac)_3$	3%	73	27	-	-
13	$Fe(acac)_3$	3%	22	50	-	28
14	$FeCl_3$	6%	12	-	88	-
15	$AgNO_3$	6%	28	50	22	-
16	AgOTf	6%	15	20	65	-

Reaction's Conditions: furfural (0.2 mmol), morpholine (0.44 mmol) in acetonitrile (0.2 ml) at room temperature. All yields were measured from the ^{1}H NMR spectra of the corresponding crude mixtures, and calculated by the addition of 1,3,5-trimethoxybenzene (0.1 mmol) as internal standard.

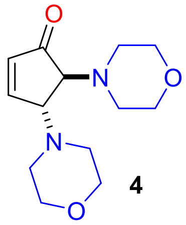
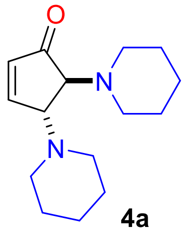
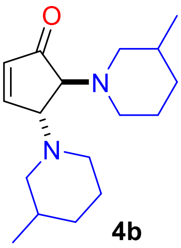
Table S4. Catalyst screening under photoirradiation conditions (Xenon Lamp)

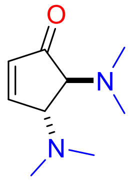
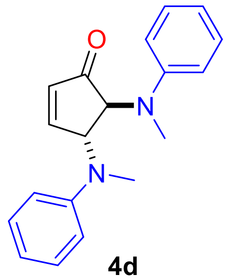
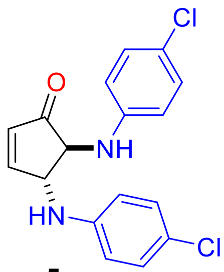


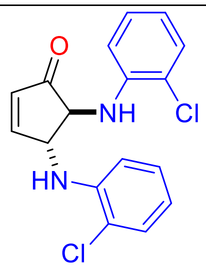
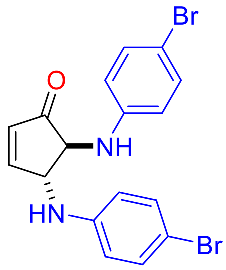
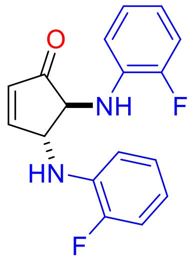
Entry[a]	Catalyst	Catalyst % mmol	Time	1 (%)	3 (%)	4 (%)
1	Au/TiO_2	2%	10 min	13	68	19
2	Au/Al_2O_3	2%	10 min	-	100	-
3	Au/ZnO	2%	10 min	13	66	21
4	$HAuCl_4$	3%	10 min	-	-	100
5	AuCl	3%	10 min	12	19	70
6[b]	Au (I)	3%	30 min	11	49	19
7[b]	Au (I)	3%	10 min	10	58	12
8[b]	Rose Bengal	1%	10 min	-	70	-
9	9,10-DCA	5%	10 min	21	69	10
10[b]	Eosin Y	2%	10 min	9	66	-

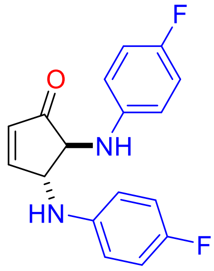
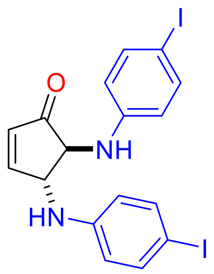
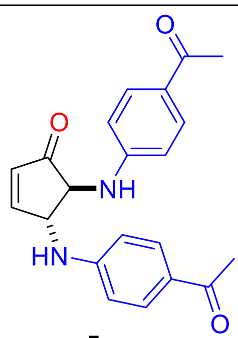
[a] Reaction conditions: 1 (0.2 mmol), 2 (0.44 mmol), CH_3CN (0.5 ml), 25 ^{o}C, Xenon lamp 300 Watt, λ>320nm. [b] Unidentified product was observed in 21%, 20%, 30% and 25% relative yield, respectively. All yields were determined from the crude ^1H NMR mixture of the reaction. and calculated by the addition of 1,3,5-trimethoxybenzene (0.1 mmol) as internal standard.

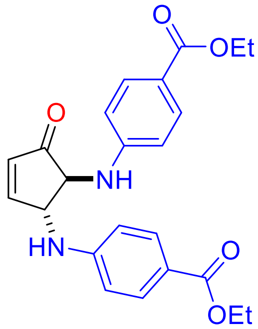
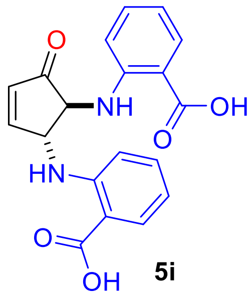
^{1}H and ^{13}C{H} NMR data of *trans*-DACPs 4, 4a-4d, 5a-5o

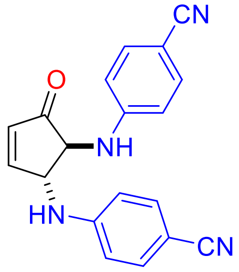
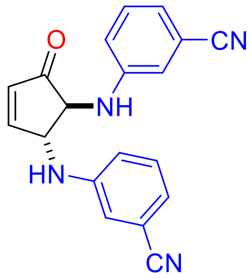
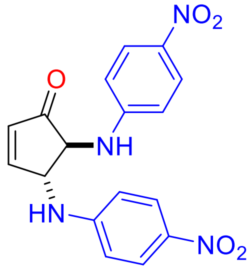
trans-4,5-dimorpholinocyclopent-2-en-1-one (***4***):[S1] 241 mg, dark red oil, 95 % yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 6.24 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 3.80 (dd, J_1 = 4.5 Hz, J_2 = 2.0 Hz, 1H), 3.72 (t, J = 5.0 Hz, 4H), 3.68 (t, J = 4.7 Hz, 4H), 3.28 (d, J = 3.0 Hz, 1H), 2.85 – 2.80 (m, 2H), 2.68 – 2.56 (m, 6H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 206.2, 160.7, 135.6, 68.2, 67.4, 67.3, 66.8, 50.3, 50.0; HRMS (ESI) $[M + H]^+$ calcd for $C_{13}H_{21}N_2O_3$: 253.1552, found: 253.1556.	 **4**
trans-4,5-di(piperidin-1-yl)cyclopent-2-en-1-one (***4a***):[S2] 154 mg, dark red oil, 62 % yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 6.13 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 3.77 (dd, J_1 = 4.5 Hz, J_2 = 2.5 Hz, 1H), 3.25 (d, J = 2.5 Hz, 1H), 2.71 (dt, J_1 = 11 Hz, J_2 = 5.0 Hz, 2H), 2.57 – 2.47 (m, 6H), 1.58 (dt, J_1 = 11.5 Hz, J_2 = 5.5 Hz, 4H), 1.52 (dt, J_1 = 11.5 Hz, J_2 = 5.5 Hz, 4H), 1.48 – 1.38 (m, 4H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 208.0, 162.1, 134.9, 68.5, 67.7, 51.2, 50.8, 26.7, 26.4, 24.5, 24.4; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{25}N_2O$: 249.1967, found : 249.1970.	 **4a**
trans-4,5-bis(3-methylpiperidin-1-yl)cyclopent-2-en-1-one (***4b***):[S1] 182 mg, dark red oil, 66 % yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (tdd, J_1 = 6.5 Hz, J_2 = 2.5 Hz, J_3 = 1.5 Hz, 1H), 6.14 – 6.12 (m, 1H), 3.80 – 3.74 (m, 1H), 3.26 – 3.24 (m, 1H), 2.85 – 2.79 (m, 1H), 2.73 – 2.58 (m, 4H), 2.41 – 2.14 (m, 3H), 1.99 – 1.78 (m, 2H), 1.70 – 1.45 (m, 6H), 0.92 – 0.80 (m, 8H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 208.1, 208.0, 207.9 (2C), 162.2, 162.1, 162.0 (2C), 134.9 (2C), 68.5, 68.4, 68.1, 68.0, 67.7, 67.4 (2C), 59.3, 59.2, 59.0 (2C), 57.4, 56.9, 56.8, 51.7, 51.6, 51.5, 50.0, 49.9, 49.4, 49.3, 33.1 (2C), 32.9, 31.9 (2C), 31.6 (2C), 31.5 (2C), 26.2 (2C), 25.9 (4C), 25.8 (2C), 19.7 (3C), 19.6 (2C); HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{29}N_2O$: 277.2280, found : 277.2284.	 **4b**

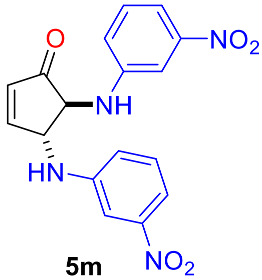
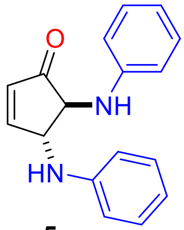
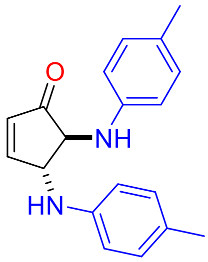
*trans-4,5-bis(dimethylamino)cyclopent-2-en-1-one (**4c**):*[S1] 103 mg, dark red oil, 61 % yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 6.19 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 3.72 (dd, J_1 = 4.5 Hz, J_2 = 2.0 Hz, 1H), 3.20 (d, J = 3.0 Hz, 1H), 2.41 (s, 6H), 2.34 (s, 6H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 207.5, 161.3, 135.3, 68.0, 67.2, 42.0, 41.9; HRMS (ESI) $[M + H]^+$ calcd for $C_9H_{17}N_2O$: 169.1340, found : 169.1341.	 **4c**
*trans-4,5-bis(methyl(phenyl)amino)cyclopent-2-en-1-one (**4d**):*[S2] 152 mg, dark red oil, 52 % yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 1H), 7.22 – 7.18 (m, 4H), 6.82 – 6.74 (m, 4H), 6.60 (d, J = 8.0 Hz, 2H), 6.48 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 5.22 – 5.20 (m, 1H), 4.36 (d, J = 3.5 Hz, 1H), 2.86 (s, 3H), 2.85 (s, 3H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 202.0, 161.4, 148.9, 148.6, 134.3, 129.1, 129.0, 118.4, 117.9, 114.1, 113.6, 69.7, 62.4, 36.7, 33.6; HRMS (ESI) $[M + H]^+$ calcd for $C_{19}H_{21}N_2O$: 293.1648, found : 293.1645.	 **4d**
*trans-4,5-bis((4-chlorophenyl)amino)cyclopent-2-en-1-one (**5a**):*[S1] 149 mg, dark red oil, 89 % yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.15 (d, J = 9.0 Hz, 2H), 7.08 (d, J = 9.0 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 6.42 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 4.51 (d, J = 7.0 Hz, 1H), 4.42 (s, 1H), 4.01 (d, J = 8.5 Hz, 1H), 3.81 (s, 1H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 203.1, 160.4, 145.7, 144.5, 132.9, 129.6, 129.3, 124.2, 123.9, 115.4, 115.2, 66.7, 62.5; HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{15}Cl_2N_2O$: 333.0556/335.0526, found : 333.0554/335.0516.	 **5a**

trans-4,5-bis((2-chlorophenyl)amino)cyclopent-2-en-1-one (***5b***)*:*[S1] 116 mg, dark red oil, 69 % yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 7.33 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.28 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.74 (t, J = 7.5 Hz, 1H), 6.69 (t, J = 8.0 Hz, 1H), 6.47 (dd, J_1 = 6.0 Hz, J_2 = 1.0 Hz, 1H), 5.09 (d, J = 4.0 Hz, 1H), 4.74 (d, J = 9.5 Hz, 1H), 4.65 (d, J = 9.0 Hz, 1H), 4.02 – 3.99 (m, 1H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 202.6, 160.0, 142.9, 142.0, 133.1, 129.7, 129.4, 128.2, 128.0, 120.2, 120.1, 119.3, 119.1, 113.0, 112.7, 66.3, 61.9; HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{15}Cl_2N_2O$: 333.0556/335.0526, found : 333.0583/335.0543.	 **5b**
trans-4,5-bis((4-bromophenyl)amino)cyclopent-2-en-1-one (***5c***)*:*[S1] 154 mg, dark red oil, 73% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 9.0 Hz, 2H), 6.56 (t, J = 9.0 Hz, 4H), 6.36 (dd, J_1 = 6.0 Hz, J_2 = 1.0 Hz, 1H), 4.47 – 4.45 (m, 2H), 4.15 (d, J = 9.5 Hz, 1H), 3.76 – 3.75 (m, 1H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 203.2, 160.5, 146.0, 144.9, 132.7, 132.3, 132.1, 115.6, 115.5, 110.8, 110.6, 66.3, 61.7; HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{15}Br_2N_2O$: 420.9546/422.9525/424.9520, found : 420.9542/422.9549/424.9533.	 **5c**
trans-4,5-bis((2-fluorophenyl)amino)cyclopent-2-en-1-one (***5d***): 108 mg, yellow oil, 72% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.05 (ddd, J_1 = 11.5 Hz, J_2 = 8.0 Hz, J_3 = 1.0 Hz, 1H), 6.99 (ddd, J_1 = 20 Hz, J_2 = 8.5 Hz, J_3 = 1.5 Hz, 1H), 6.96 (t, J = 8.0 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.80 (t, J = 8.0 Hz, 1H), 6.76 – 6.71 (m, 1H), 6.70 – 6.66 (m, 1H), 6.46 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 4.69 (s, 1H), 4.63 (dd, J_1 = 9.5 Hz, J_2 = 1.5 Hz, 1H), 4.30 (dd, J_1 = 9.5 Hz, J_2 = 3.0 Hz, 1H), 3.94 (dd, J_1 = 4.0 Hz, J_2 = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.9, 160.2, 152.0 (d, J =	 **5d**

239 Hz), 135.0 (dd, *J* = 126 Hz, *J* = 11 Hz), 124.9 (dd, *J* = 26 Hz, *J* = 4 Hz), 118.8 (dd, *J* = 28 Hz, *J* = 7 Hz), 118.8 (dd, *J* = 45 Hz, *J* = 19 Hz), 115.0 (dd, *J* = 28 Hz, *J* = 7 Hz), 113.8 (dd, *J* = 33 Hz, *J* = 3 Hz), 66.3, 62.0; Rf = 0.4 (Hex/EtOAc=2/1); HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{15}F_2N_2O$: 301.1152, found : 301.1149.	
*trans-4,5-bis((4-fluorophenyl)amino)cyclopent-2-en-1-one (**5e**):* 121 mg, yellow oil, 81% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 6.91 (t, *J* = 8.5 Hz, 2H), 6.84 (t, *J* = 9.0 Hz, 2H), 6.76 – 6.73 (m, 2H), 6.69 – 6.66 (m, 2H), 6.41 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 4.49 (s, 1H), 4.33 (br s, 1H), 3.91 (br s, 1H), 3.78 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 160.7, 156.8 (dd, *J* = 237 Hz, *J* = 10 Hz), 142.9 (dd, *J* = 163 Hz, *J* = 3 Hz), 132.7, 116.1 (dd, *J* = 46 Hz, *J* = 22 Hz), 115.3 (dd, *J* = 7 Hz, *J* = 3 Hz), 67.3, 63.3; Rf = 0.4 (Hex/EtOAc=2/1); HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{15}F_2N_2O$: 301.1152, found : 301.1149.	 **5e**
*trans-4,5-bis((4-iodophenyl)amino)cyclopent-2-en-1-one (**5f**):* 203 mg, red-brown oil, 79% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 6.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.52 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 6.0 Hz, 1H), 4.50 (s, 1H), 4.43 (s, 1H), 4.06 (d, *J* = 7.0 Hz, 1H), 3.80 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 160.4, 146.7, 145.5, 138.4, 138.1, 133.0, 116.4, 116.2, 80.5, 80.3, 66.4, 62.0; Rf = 0.35 (Hex/EtOAc=2/1); HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{15}I_2N_2O$: 516.9274, found : 516.9271.	 **5f**
*1,1'-((((trans)-5-oxocyclopent-3-ene-1,2-diyl)bis(azanediyl))-bis(4,1-phenylene))diethanone (**5g**):*[S1] 140 mg, dark purple semisolid, 80% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.60 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 6.68 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 6.45 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 5.04 (d, *J* = 9.0 Hz, 1H), 4.97 (d, *J* =	 **5g**

4.5 Hz, 1H), 4.70 (d, J = 8.5 Hz, 1H), 4.06 (dd, J_1 = 5.0 Hz, J_2 = 3.5 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 202.2, 196.8, 196.6, 160.1, 151.0, 150.1, 133.3, 131.1, 130.8, 128.4, 128.3, 112.9, 112.6, 65.7, 61.0, 26.3; HRMS (ESI) [M + Na]$^+$ calcd for $C_{21}H_{20}N_2O_3Na$: 371.1372, found : 371.1384.	
*diethyl 4,4'-(((trans)-5-oxocyclopent-3-ene-1,2-diyl)-bis(azanediyl))dibenzoate (**5h**):*[S1] 184 mg, purple solid, m.p. 170-171 °C, 89% yield, precipitated in the solvent system chloroform/hexane; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 9.0 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.58 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 6.66 (m, 4H), 6.44 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 4.82 (d, J = 4.5 Hz, 1H), 4.72 (d, J = 9.5 Hz, 1H), 4.66 (d, J = 8.0 Hz, 1H), 4.29 (dq, J_1 = 14.5 Hz, J_2 = 7.0 Hz, 4H), 4.00 – 3.98 (m, 1H), 1.34 (dt, J_1 = 14.0 Hz, J_2 = 7.0 Hz, 6H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 202.4, 166.7, 166.6, 160.2, 150.7, 149.7, 133.2, 131.9, 131.6, 120.9, 120.7, 112.9, 112.6, 65.9, 61.2, 60.6, 60.5, 14.5 (2C); HRMS (ESI) [M + Na]$^+$ calcd for $C_{23}H_{24}N_2O_5Na$: 431.1583, found : 431.1596.	 **5h**
*2,2'-(((trans)-5-oxocyclopent-3-ene-1,2-diyl)bis(azanediyl))dibenzoic acid (**5i**):*[S1] 138 mg, purple solid, m.p. 200-202 °C, 78% yield, precipitated in the solvent system THF/hexane; ^{1}H NMR (500 MHz, DMSO) δ 12.75 (br s, 2H), 8.33 (s, 2H), 7.82 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.79 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.73 (dd, J_1 = 6.5 Hz, J_2 = 1.5 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.61 (t, J = 7.5 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 6.48 (d, J = 6.0 Hz, 1H), 4.95 (s, 1H), 4.52 (s, 1H); ^{13}C{H} NMR (125 MHz, DMSO) δ 203.0, 170.0, 169.8, 160.7, 150.2, 149.6, 134.5, 134.2, 132.4, 131.8, 131.6, 115.5, 115.3, 112.3, 112.1, 110.9, 110.8, 64.8, 59.0; HRMS (ESI) [M + Na]$^+$ calcd for $C_{19}H_{16}N_2O_5Na$: 375.0957, found : 375.0966.	 **5i**

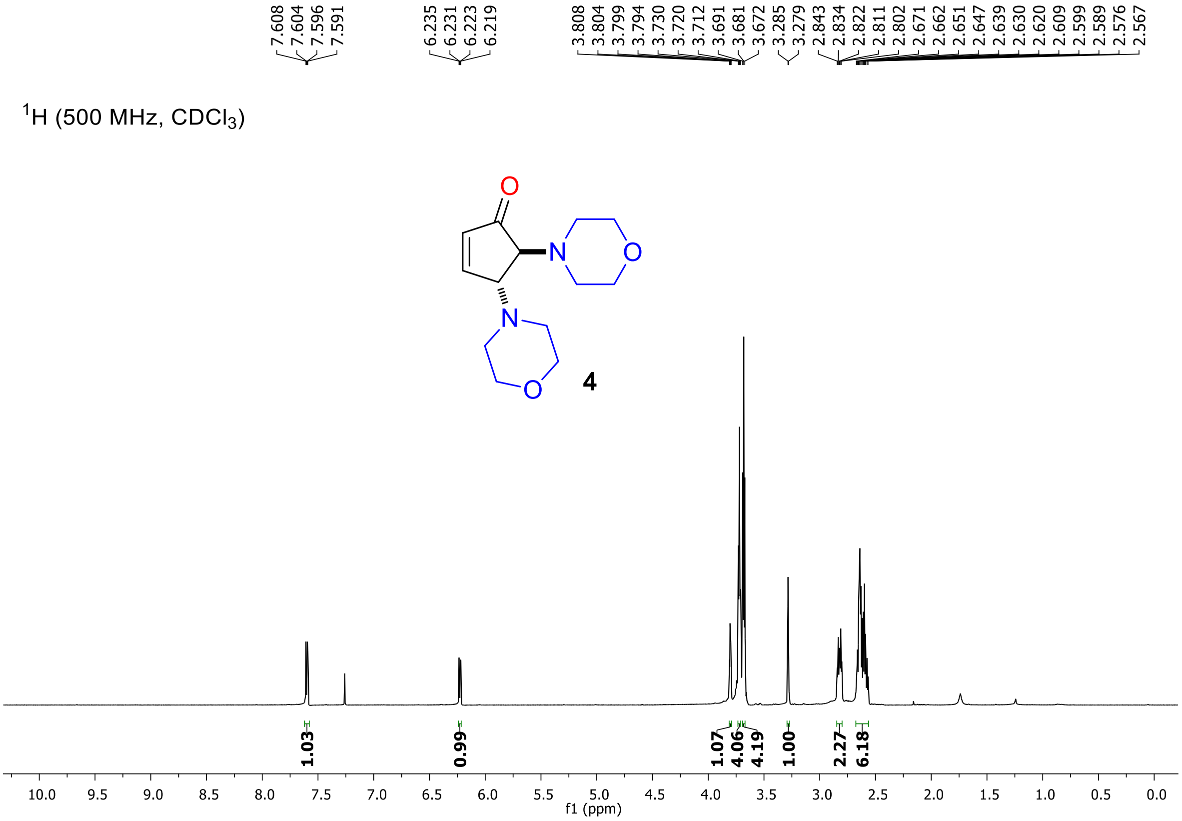
4,4'-(((trans)-5-oxocyclopent-3-ene-1,2-diyl)bis(azanediyl))dibenzonitrile (***5j***)*:* 106 mg, yellow oil, 68% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.71 (d, J = 6.0 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 6.45 (d, J = 6.0 Hz, 1H), 5.08 (br s, 2H), 4.76 (s, 1H), 4.27 (d, J = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO) δ 203.1, 160.9, 151.6, 151.0, 133.5, 133.3, 132.5, 120.4, 120.3, 112.5 (2C), 97.0, 96.7, 63.5, 58.1; Rf = 0.2 (Hex/EtOAc=2/1); HRMS (ESI) $[M + Na]^+$ calcd for $C_{19}H_{15}N_4ONa$: 337.1060, found : 337.1058.	 **5j**
3,3'-(((trans)-5-oxocyclopent-3-ene-1,2-diyl)bis(azanediyl))dibenzonitrile (***5k***): 97 mg, yellow oil, 62% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, CD_3OD) δ 7.65 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.99 – 6.87 (m, 6H), 6.41 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 4.84 (br s, 2H), 4.66 (dt, J_1 = 3.0 Hz, J_2 = 1.5 Hz, 1H), 4.08 (d, J = 3.5 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 205.5, 162.0, 149.7, 149.1, 133.7, 131.2, 131.2, 131.0, 121.8, 121.8, 121.7, 120.5, 120.2 (2C), 119.0 (2C), 118.3, 116.4, 116.4, 113.8, 113.5, 66.7, 61.4; Rf = 0.2 (Hex/EtOAc=2/1); HRMS (ESI) $[M + Na]^+$ calcd for $C_{19}H_{15}N_4ONa$: 337.1062, found : 337.1058.	 **5k**
trans-4,5-bis((4-nitrophenyl)amino)cyclopent-2-en-1-one (***5l***)*:*[S1] 121 mg, dark red oil, 68% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, CD_3CN) δ 7.98 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.63 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 6.66 (d, J = 9.0 Hz, 2H), 6.42 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 6.09 (d, J = 8.5 Hz, 1H), 5.95 (d, J = 8.0 Hz, 1H), 4.85 – 4.82 (m, 1H), 4.27 (dd, J_1 = 8.0 Hz, J_2 = 3.5 Hz, 1H); ^{13}C{H} NMR (125 MHz, CD_3CN) δ 202.6, 160.4, 154.2, 153.6, 139.2, 133.9, 127.0, 126.8 (2C), 112.8 (2C), 65.5, 60.0;	 **5l**

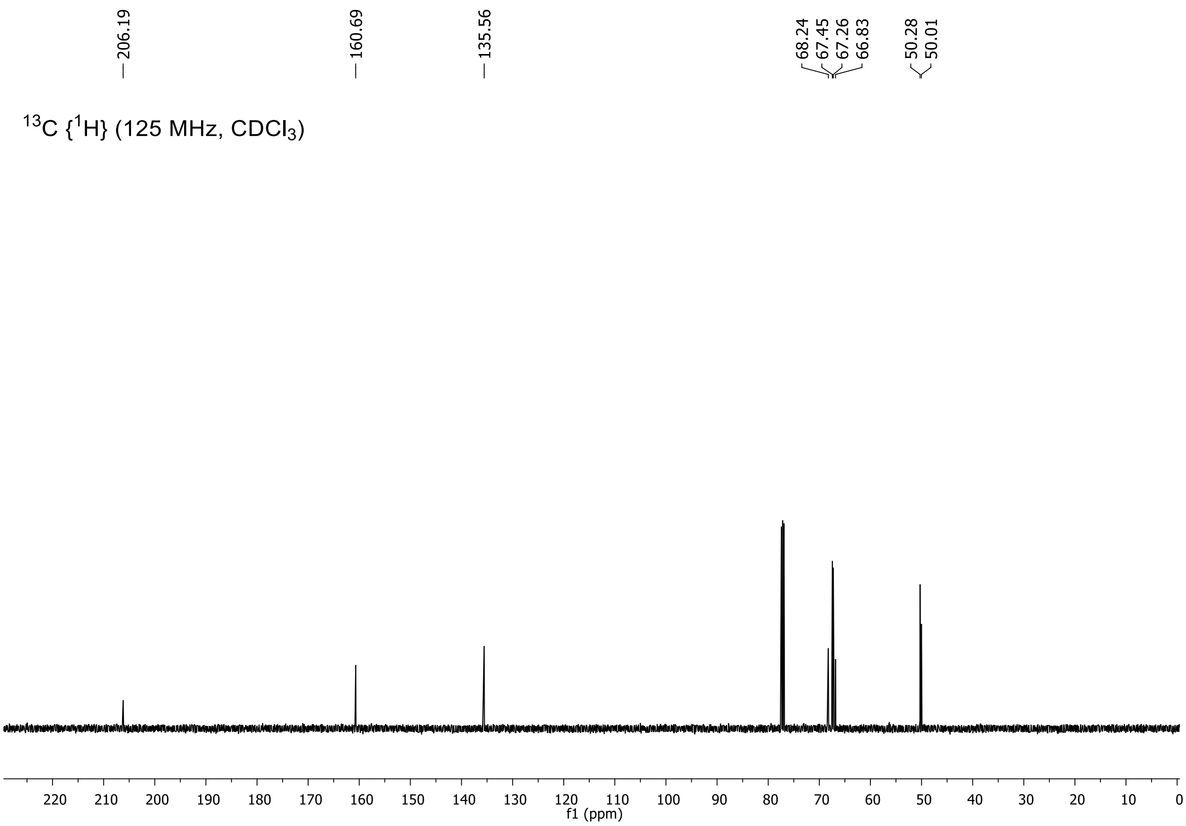
HRMS (ESI) $[M + Na]^+$ calcd for $C_{17}H_{14}N_4O_5Na$: 377.0862, found : 377.0867.	
trans-4,5-bis((3-nitrophenyl)amino)cyclopent-2-en-1-one **(5m)**:[S1] 115 mg, dark red semisolid, 65% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, CD_3OD) δ 7.70 – 7.68 (m, 1H), 7.50 (t, J = 2.5 Hz, 1H), 7.46 (t, J = 2.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.23 (dd, J = 8.5 Hz, 1H), 7.19 (d, J = 7.0 Hz, 1H), 7.05 (ddd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, J_3 = 0.5 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.44 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 1H), 4.74 (s, 1H), 4.16 (d, J = 3.0 Hz, 1H); ^{13}C{H} NMR (125 MHz, CD_3OD) δ 205.4, 161.9, 161.9, 150.6, 150.5, 150.2, 149.6, 133.9, 133.8, 130.9, 130.7, 120.4, 120.3, 112.8, 112.7, 107.8, 107.8, 67.0, 61.7; HRMS (ESI) $[M + Na]^+$ calcd for $C_{17}H_{14}N_4O_5Na$: 377.0862, found : 377.0867.	 **5m**
trans-4,5-bis(phenylamino)cyclopent-2-en-1-one **(5n)**:[S3] 71 mg, dark red oil, 54% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.23 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 8.5 Hz, 2H), 6.84 (t, J = 7.5 Hz, 1H), 6.81 – 6.77 (m, 3H), 6.73 (d, J = 7.5 Hz, 2H), 6.39 (dd, J_1 = 5.5 Hz, J_2 = 1.0 Hz, 1H), 4.60 (s, 1H), 4.46 (br s, 1H), 4.08 (br s, 1H), 3.86 (d, J = 3.0 Hz, 1H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 203.9, 161.1, 147.1, 146.0, 132.5, 129.6, 129.4, 119.1, 118.8, 114.1, 114.0, 66.3, 61.8; HRMS (ESI) $[M - H]^+$ calcd for $C_{17}H_{15}N_2O$: 263.1185, found : 263.1193 and HRMS (ESI) $[M + H]^+$ calcd for $C_{17}H_{17}N_2O$: 265.1336, found : 265.1349.	 **5n**
trans-4,5-bis(p-tolylamino)cyclopent-2-en-1-one **(5o)**:[S1] 87 mg, dark red oil, 59% yield, purified by column chromatography on a silica gel using a gradient mixture of EtOAc – Hexane (10:1 – 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 8.5 Hz, 2H), 6.38 (dd, J_1 = 5.5 Hz, J_2 = 1.0 Hz, 1H), 4.56 (s, 1H), 4.33 (br s, 1H), 3.91 (br s, 1H), 3.81 (d, J = 3.0 Hz, 1H), 2.29 (s, 3H), 2.25 (s, 3H); ^{13}C{H} NMR (125 MHz, $CDCl_3$) δ 204.2, 161.3, 144.9, 143.7, 132.4, 130.1,	 **5o**

129.9, 128.5, 128.1, 114.4, 114.3, 66.6, 62.4, 20.5 (2C); HRMS (ESI) [M - H]$^+$ calcd for $C_{19}H_{19}N_2O$: 291.1503, found : 291.1507.	

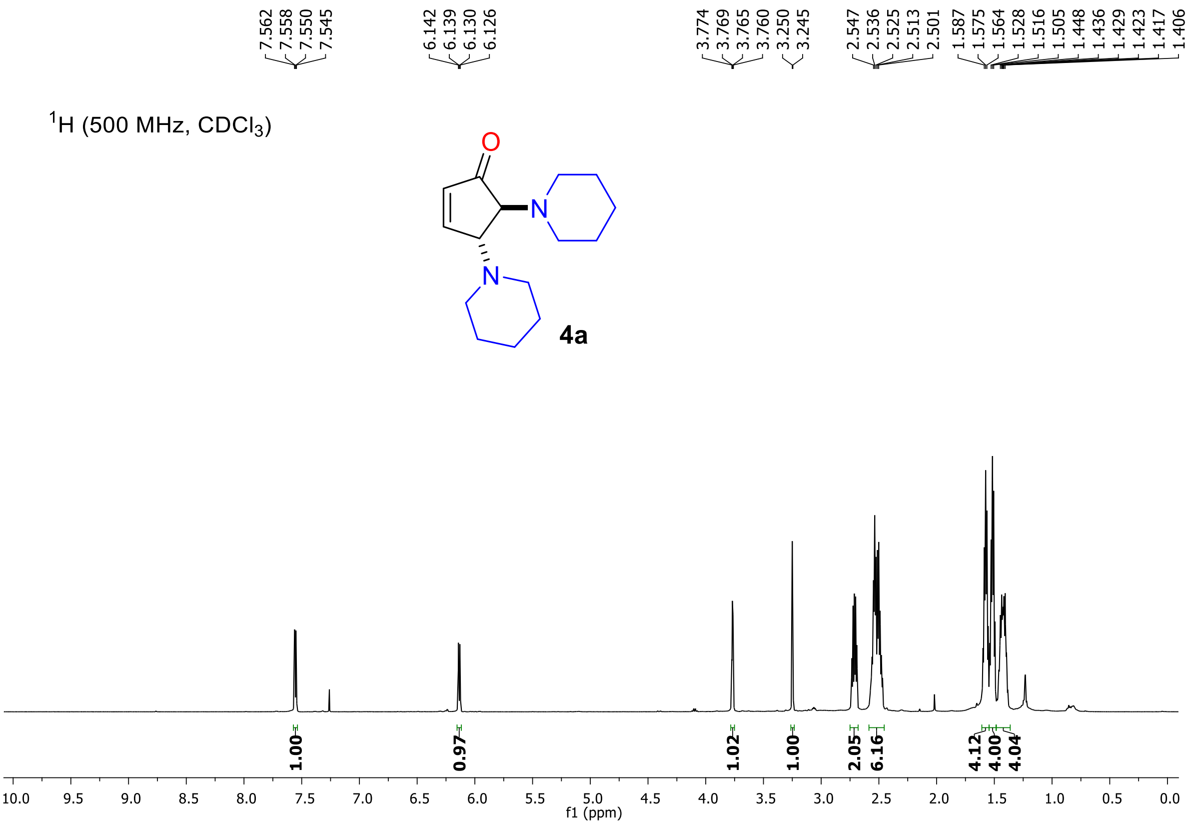
S1. Tzani, M.A.; Fountoulaki, S.; Lykakis, I.N. Polyoxometalate-Driven Ease Conversion of Valuable Furfural to *trans-N,N*-4,5-Diaminocyclopenten-2-ones. *J. Org. Chem*. **2022**, *87*, 2601–2615.
S2. Gomes, R.F.A.; Esteves, N.R.; Coelho, J.A.S.; Afonso, C.A.M. Copper(II) Triflate as a Reusable Catalyst for the Synthesis of *trans*-4,5-Diamino-cyclopent-2-enones in Water. *J. Org. Chem.* **2018**, *83*, 7509–7513.
S3. Peewasan, K.; Merkel, M.P.; Fuhr, O.; Powell, A.K.A Designed and Potentially Decadentate Ligand for use in Lanthanide(III) Catalysed Biomass Transformations: Targeting Diastereoselective *trans*-4,5-Diaminocyclopentenone Derivatives. *Dalton Trans.* **2020**, *49*, 2331–2336.

Copies of ^{1}H and ^{13}C{H} NMR spectra of *trans*-DACPs 4, 4a-4d, 5a-5o

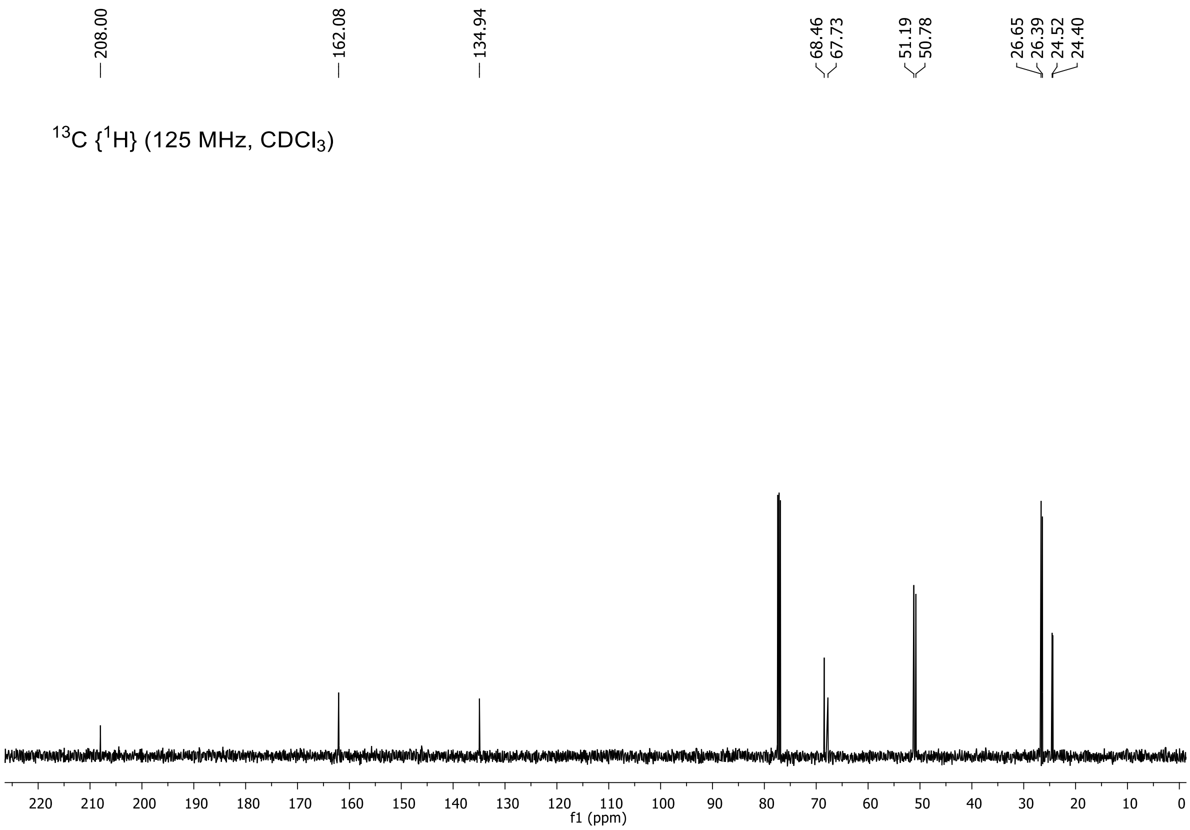


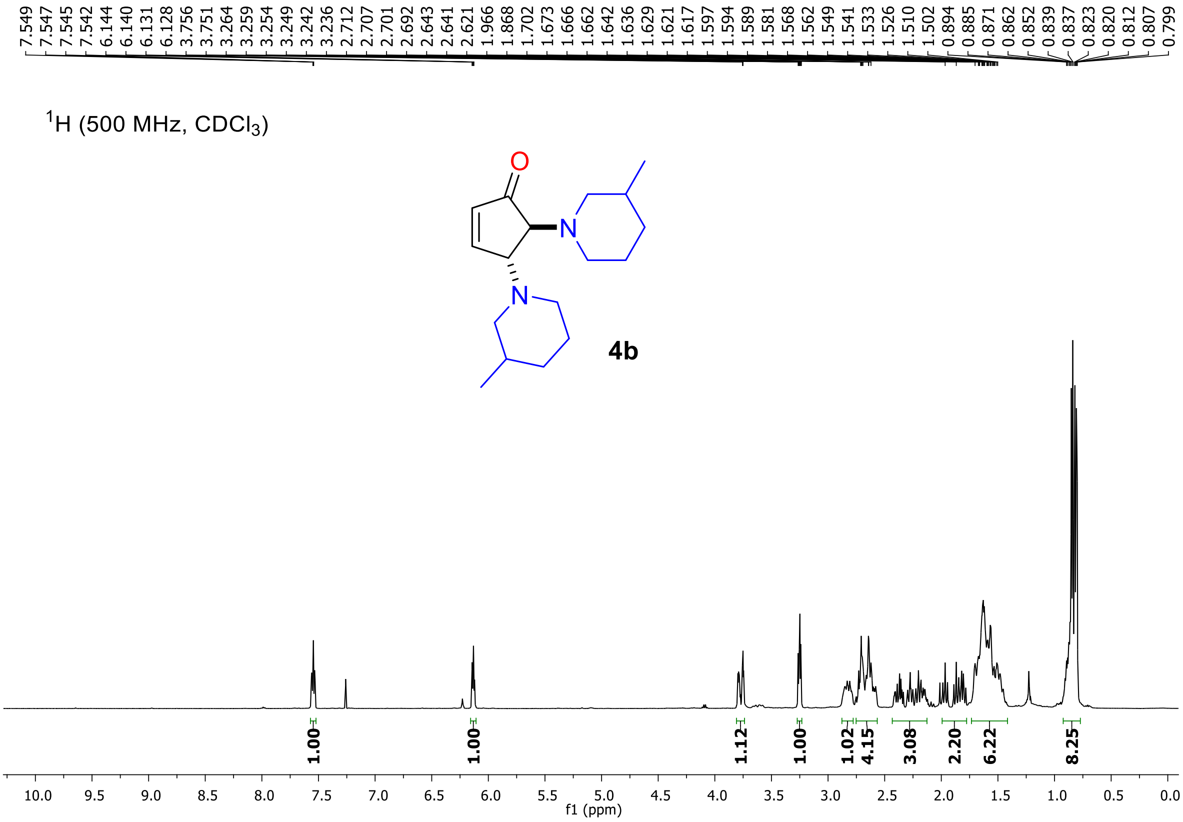


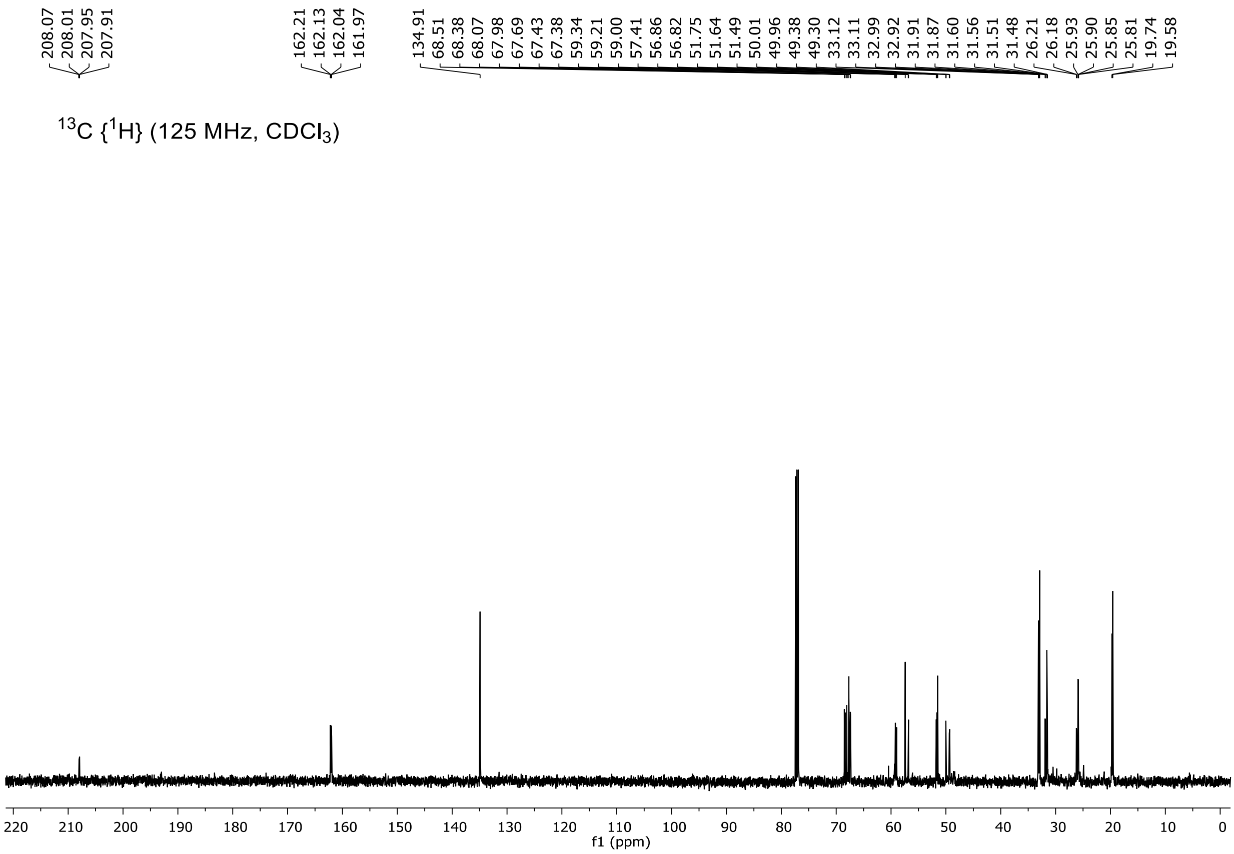
^{1}H (500 MHz, $CDCl_3$)



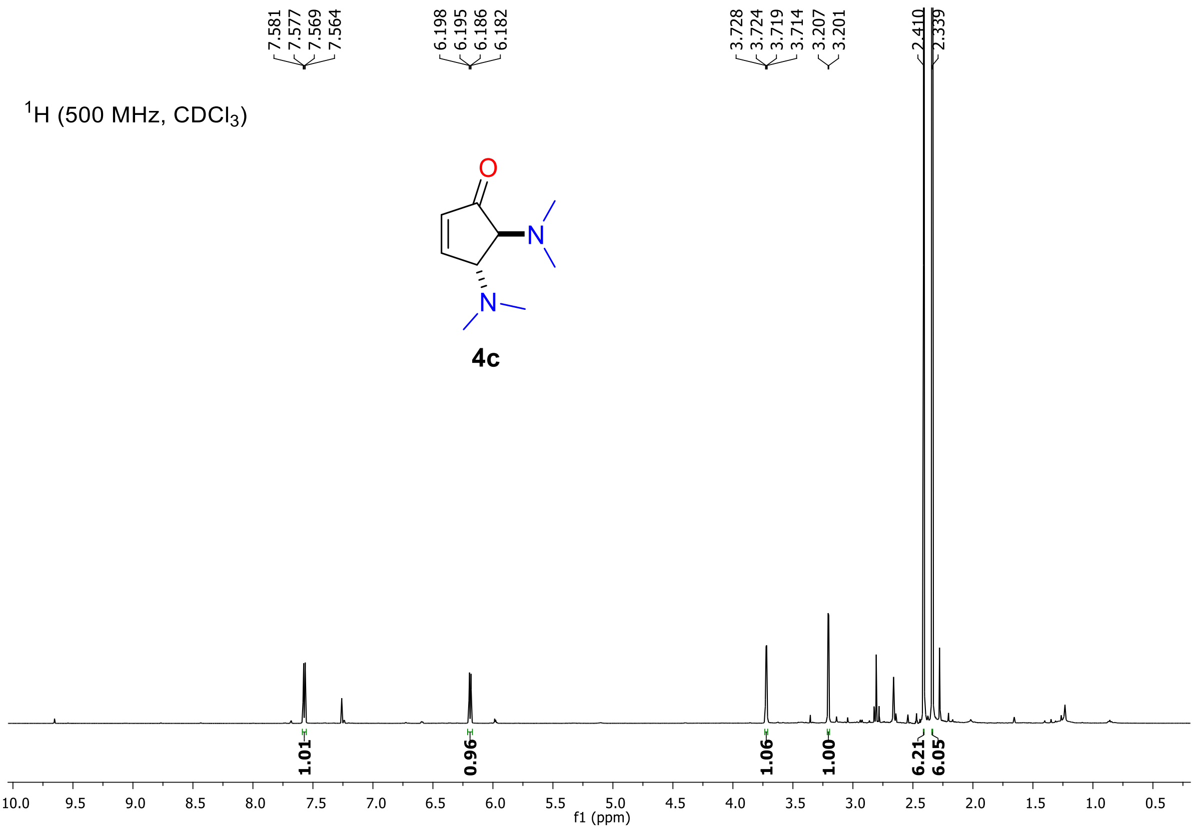
^{13}C {^{1}H} (125 MHz, $CDCl_3$)



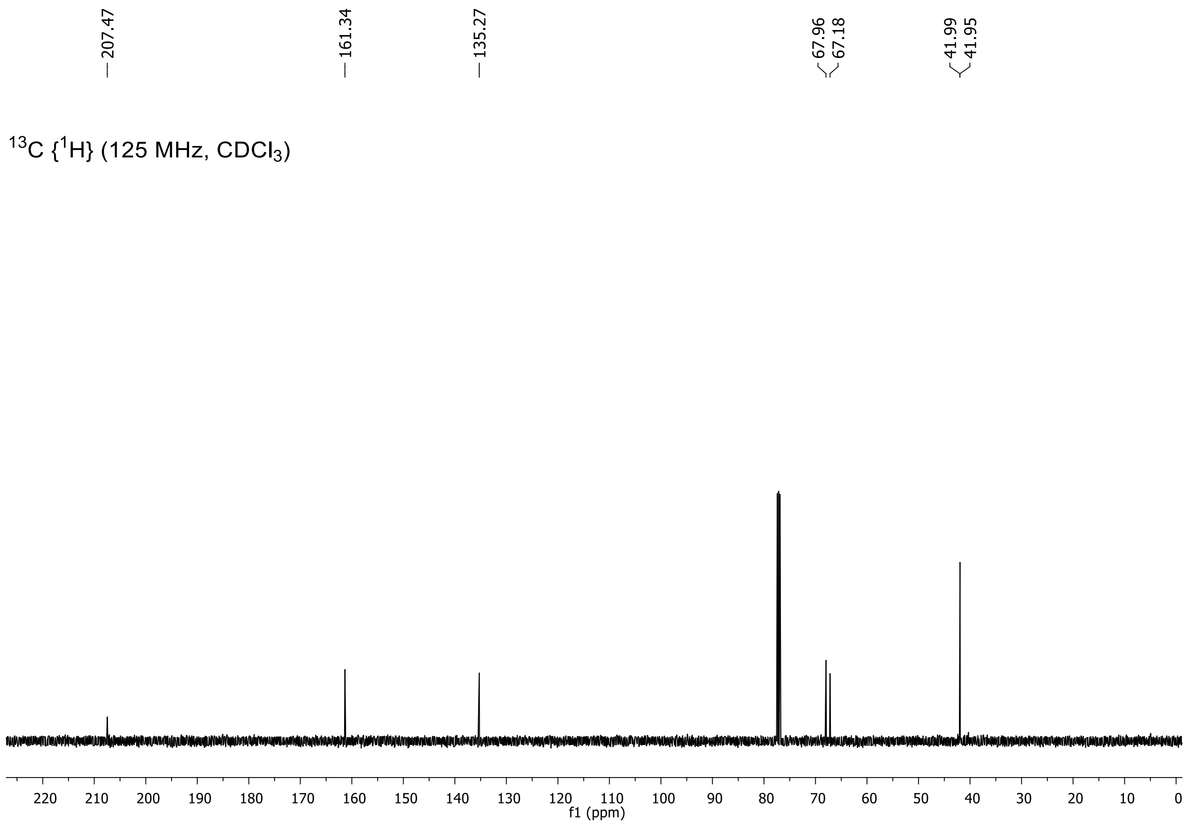

7.549 7.547 7.545 7.542 6.144 6.140 6.131 6.128 3.756 3.751 3.264 3.259 3.254 3.249 3.242 3.236 2.712 2.707 2.701 2.692 2.643 2.641 2.621 1.966 1.868 1.702 1.673 1.666 1.662 1.642 1.636 1.629 1.621 1.617 1.597 1.594 1.589 1.581 1.568 1.562 1.549 1.541 1.533 1.526 1.510 1.502 0.894 0.885 0.871 0.862 0.852 0.839 0.837 0.823 0.820 0.812 0.807 0.799
¹H (500 MHz, CDCl₃)
O
N
N
4b
1.00
1.00
1.12
1.00
1.02
4.15
3.08
2.20
6.22
8.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

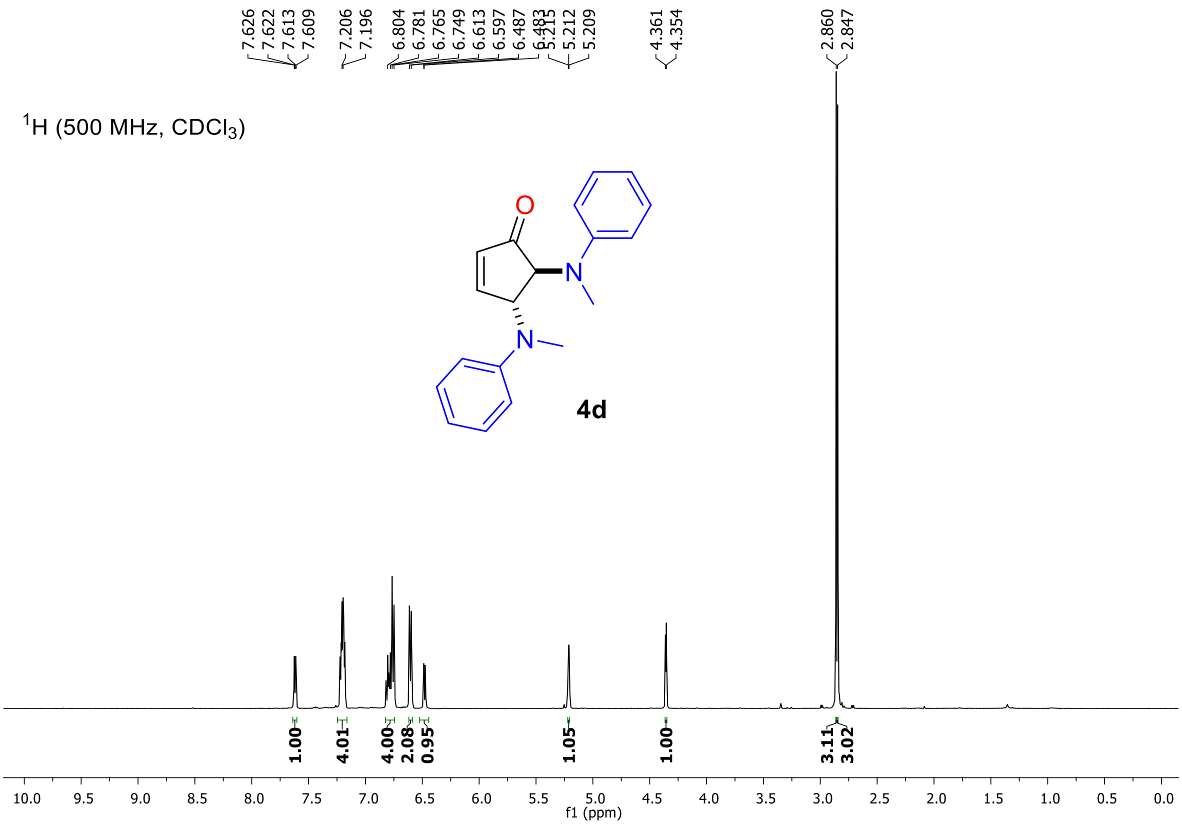

208.07 208.01 207.95 207.91
162.21 162.13 162.04 161.97
134.91 68.51 68.38 68.07 67.98 67.69 67.43 67.38 59.34 59.21 59.00 57.41 56.86 56.82 51.75 51.64 51.49 50.01 49.96 49.38 49.30 33.12 33.11 32.99 32.92 31.91 31.87 31.60 31.56 31.51 31.48 26.21 26.18 25.93 25.90 25.85 25.81 19.74 19.58
¹³C {¹H} (125 MHz, CDCl₃)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

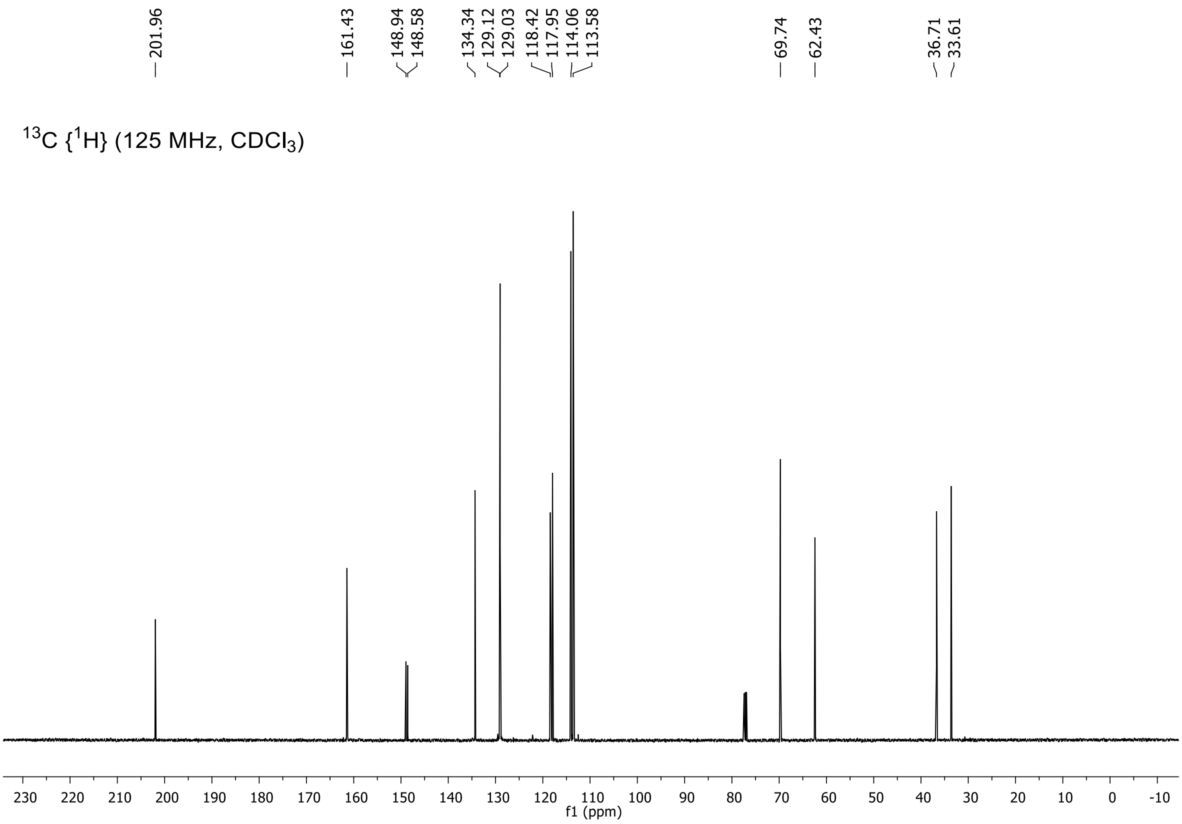
^1H (500 MHz, $CDCl_3$)

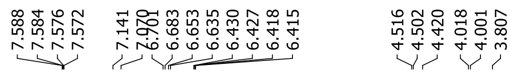


^{13}C {^1H} (125 MHz, $CDCl_3$)

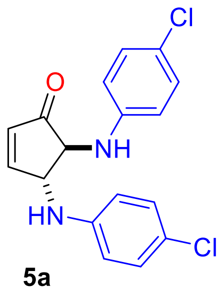



7.626
7.622
7.613
7.609
7.206
7.196
6.804
6.781
6.765
6.749
6.613
6.597
6.487
6.483
5.215
5.212
5.209
4.361
4.354
2.860
2.847
^1H (500 MHz, $CDCl_3$)
O
N
N
4d
1.00
4.01
4.00
2.08
0.95
1.05
1.00
3.11
3.02
f1 (ppm)

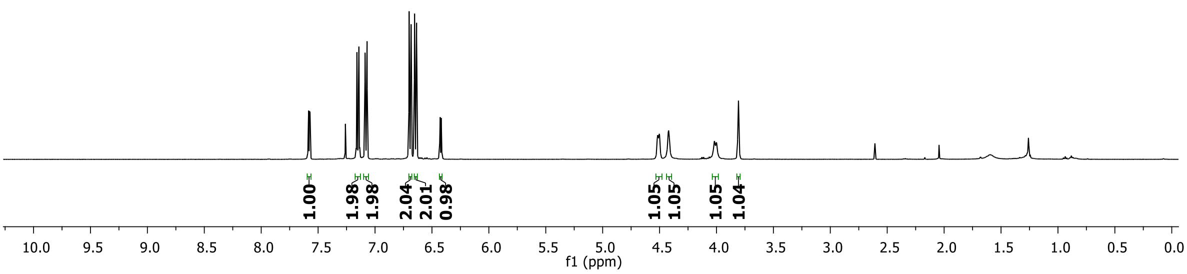

201.96
161.43
148.94
148.58
134.34
129.12
129.03
118.42
117.95
114.06
113.58
69.74
62.43
36.71
33.61
^{13}C {^1H} (125 MHz, $CDCl_3$)
f1 (ppm)

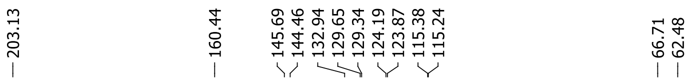


^{1}H (500 MHz, $CDCl_3$)

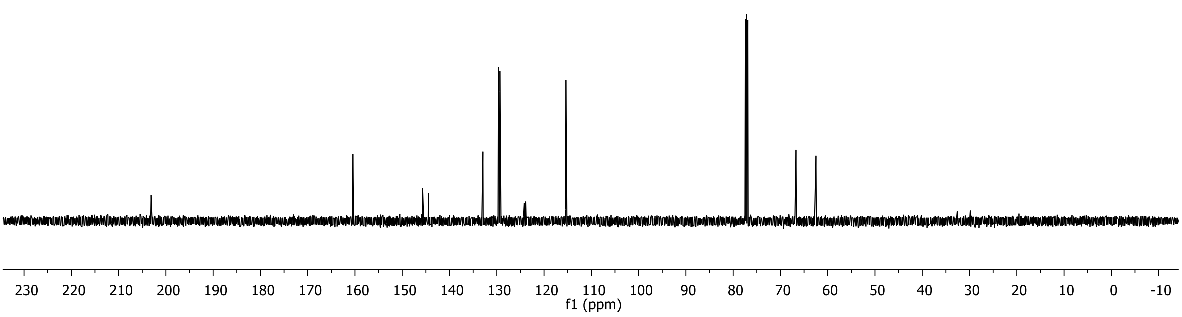


5a

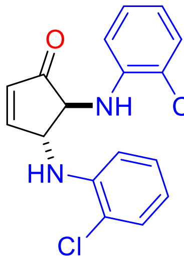




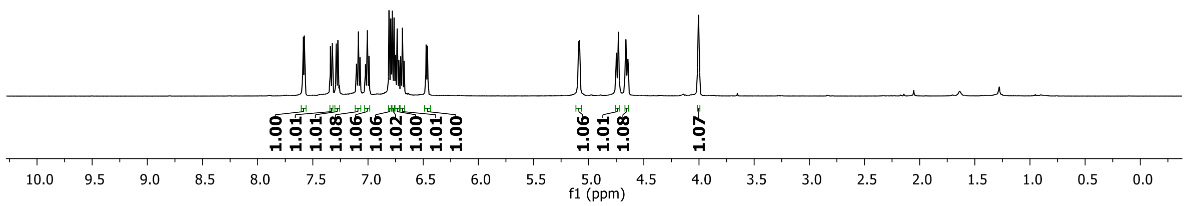
^{13}C {^{1}H} (125 MHz, $CDCl_3$)



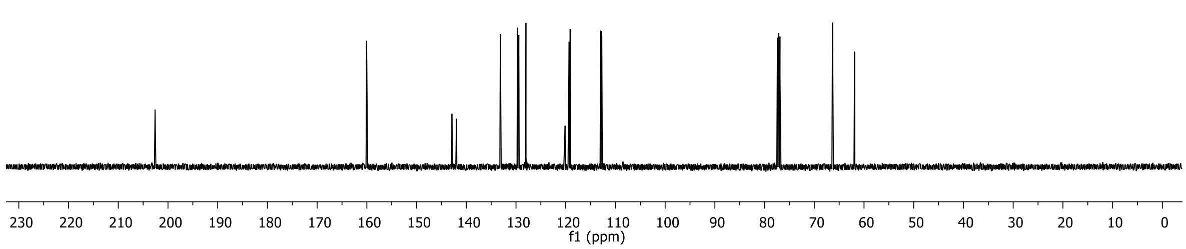
^{1}H (500 MHz, $CDCl_3$)

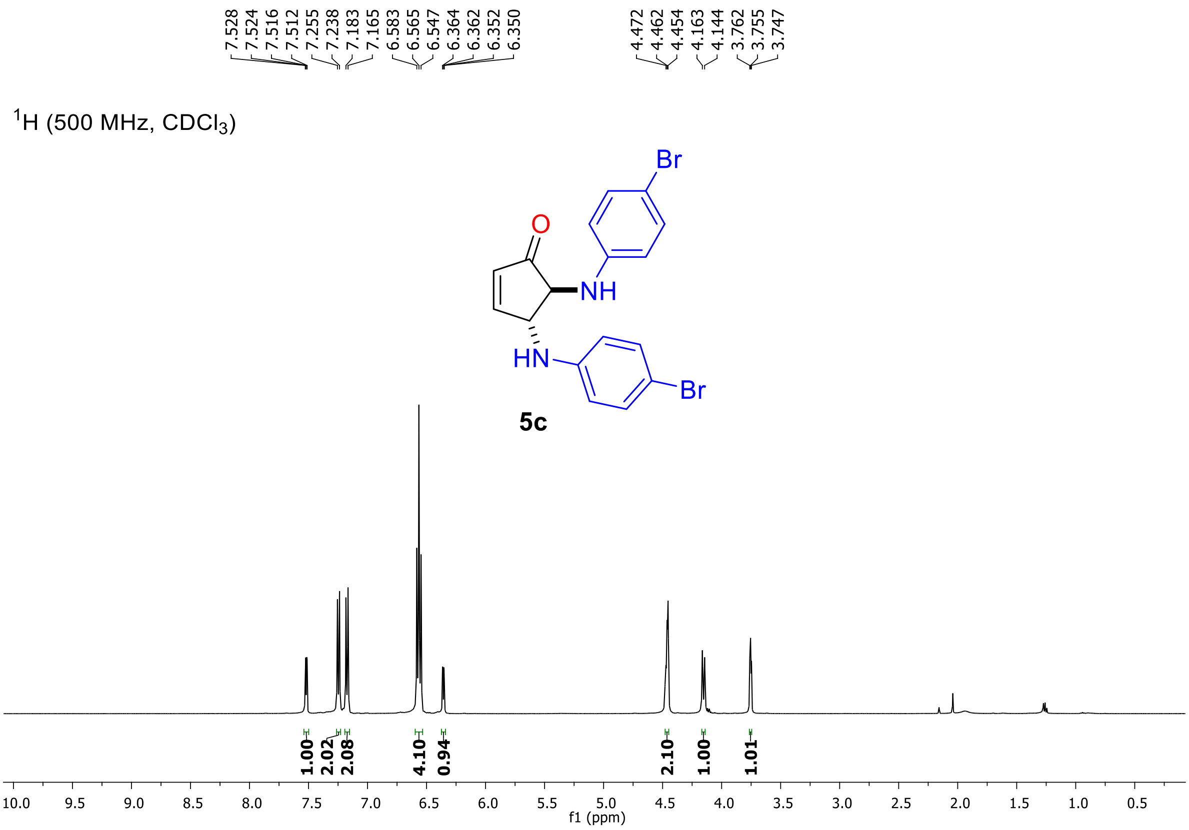


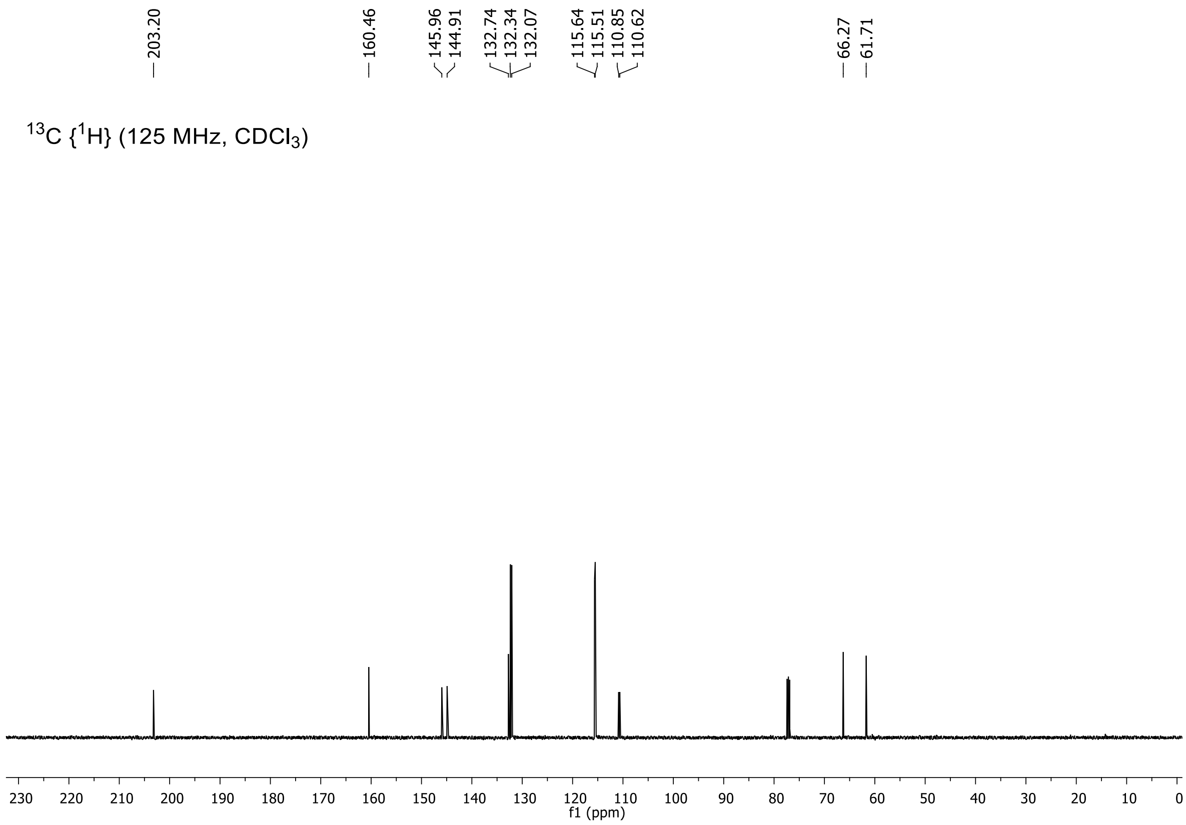
5b

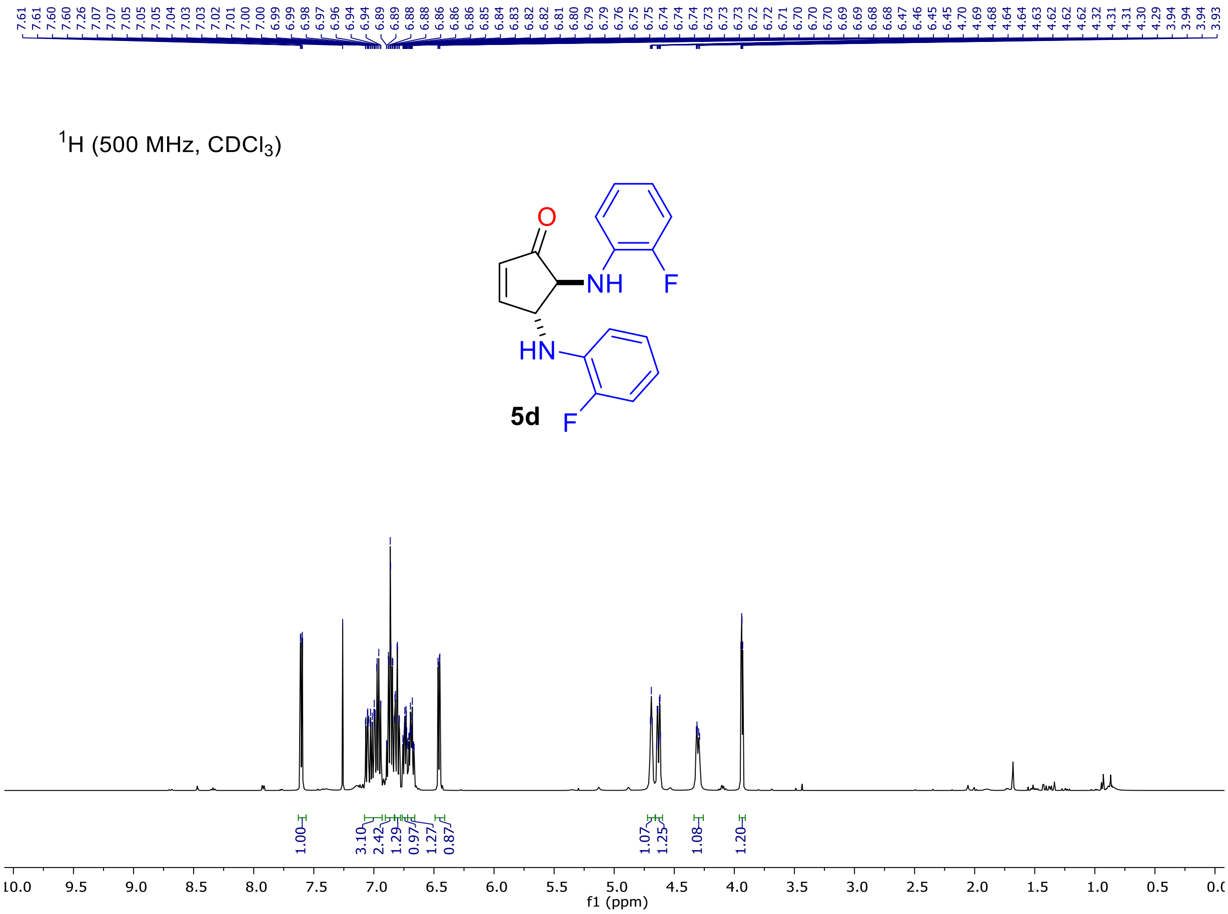


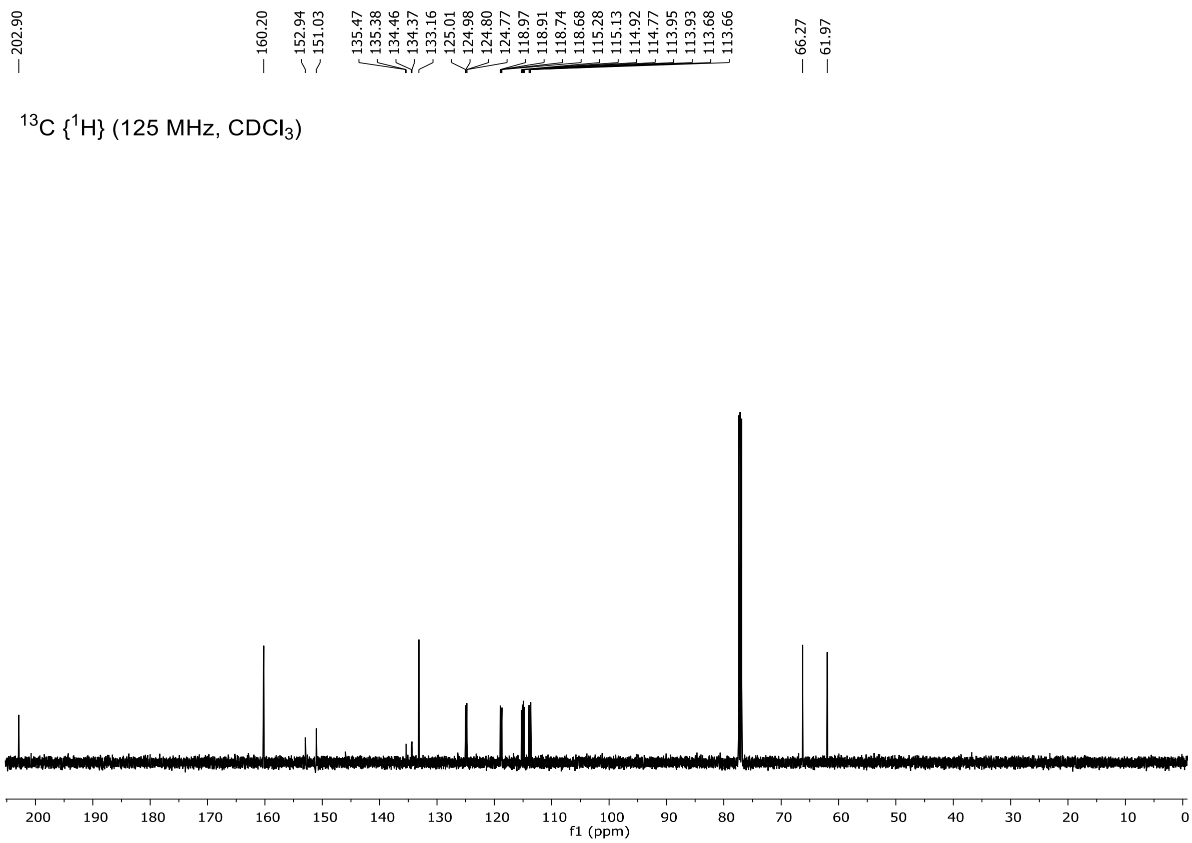
^{13}C {^{1}H} (125 MHz, $CDCl_3$)

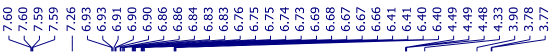



7.528
7.524
7.516
7.512
7.255
7.238
7.183
7.165
6.583
6.565
6.547
6.364
6.362
6.352
6.350
4.472
4.462
4.454
4.163
4.144
3.762
3.755
3.747
^{1}H (500 MHz, $CDCl_3$)
Br
O
NH
HN
Br
5c
1.00
2.02
2.08
4.10
0.94
2.10
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

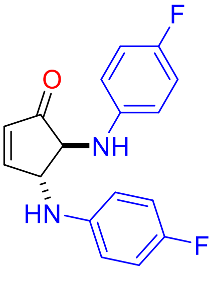

203.20
160.46
145.96
144.91
132.74
132.34
132.07
115.64
115.51
110.85
110.62
66.27
61.71
^{13}C {^{1}H} (125 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.61 7.61 7.60 7.26 7.07 7.07 7.05 7.05 7.04 7.03 7.03 7.02 7.01 7.00 7.00 6.99 6.99 6.98 6.97 6.96 6.94 6.94 6.89 6.89 6.88 6.88 6.86 6.86 6.85 6.84 6.83 6.82 6.82 6.81 6.80 6.79 6.76 6.75 6.75 6.74 6.74 6.73 6.73 6.73 6.72 6.72 6.71 6.70 6.70 6.70 6.69 6.69 6.68 6.68 6.47 6.46 6.45 6.45 4.70 4.69 4.68 4.64 4.63 4.62 4.62 4.32 4.31 4.31 4.30 4.29 3.94 3.94 3.94 3.93
1H (500 MHz, CDCl3)
O
NH
F
HN
F
5d
1.00
3.10
2.42
1.29
0.97
1.27
0.87
1.07
1.25
1.08
1.20
f1 (ppm)

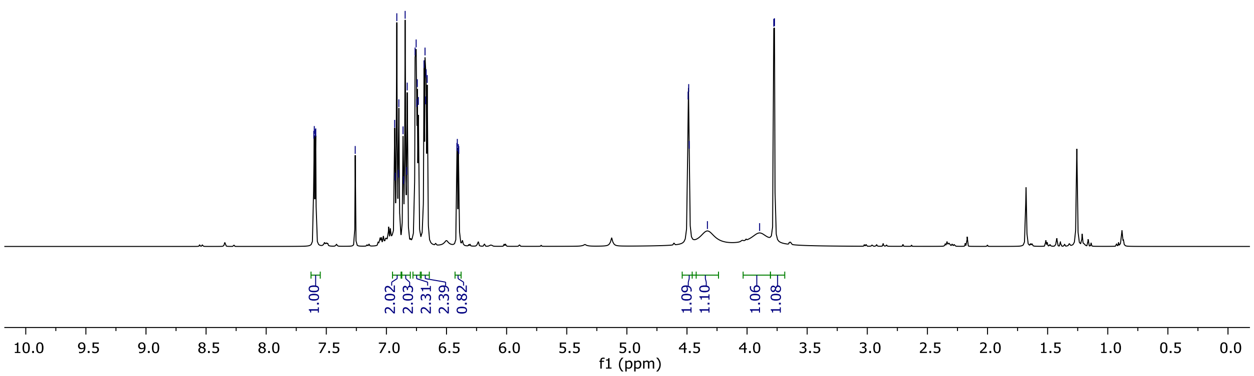

202.90
160.20
152.94
151.03
135.47
135.38
134.46
134.37
133.16
125.01
124.98
124.80
124.77
118.97
118.91
118.74
118.68
115.28
115.13
114.92
114.77
113.95
113.93
113.68
113.66
66.27
61.97
13C {1H} (125 MHz, CDCl3)
f1 (ppm)

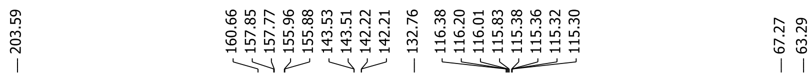


^1H (500 MHz, $CDCl_3$)

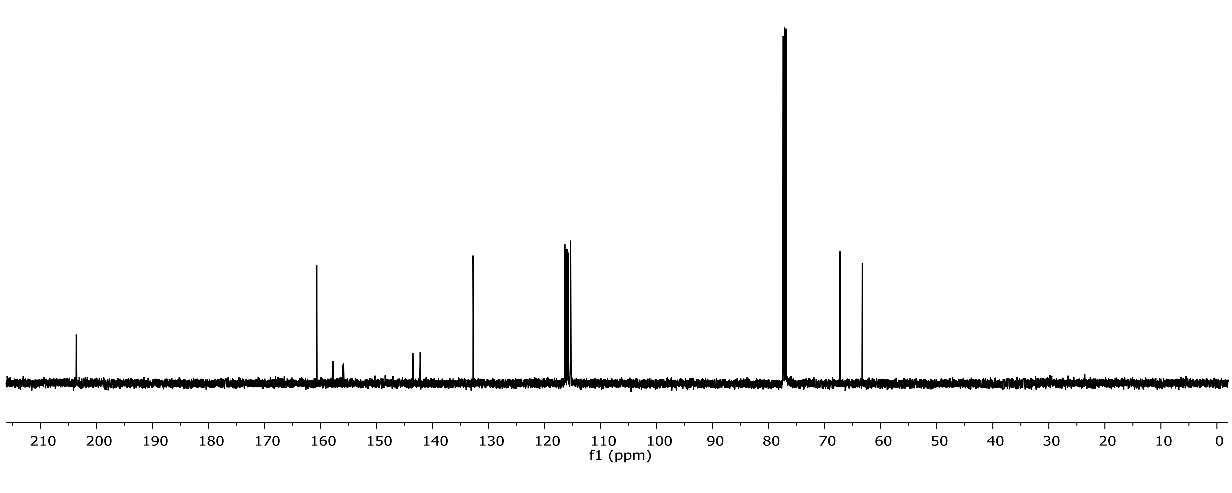


5e

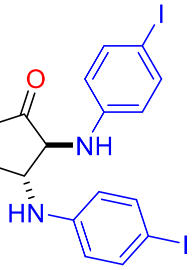




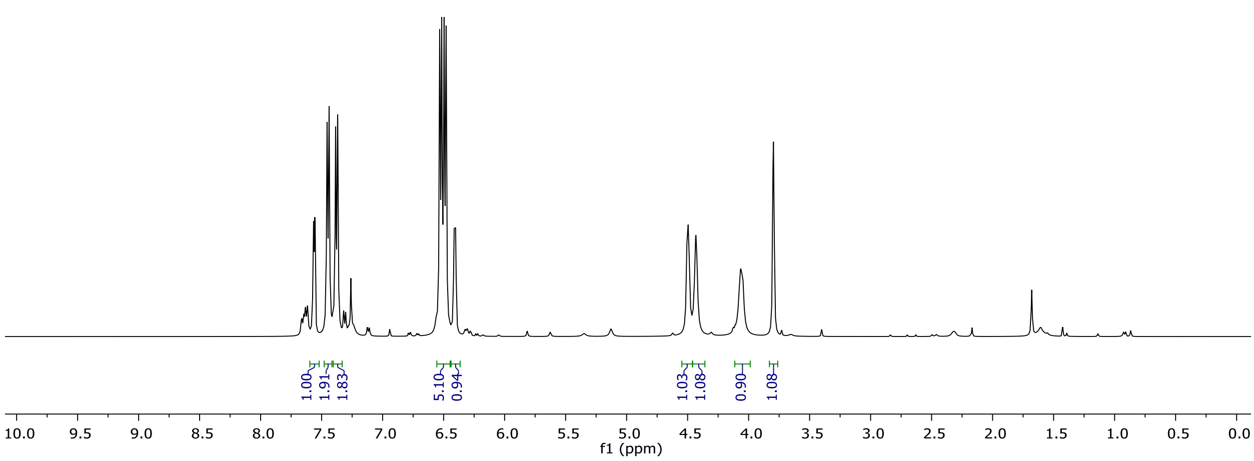
^{13}C {^1H} (125 MHz, $CDCl_3$)



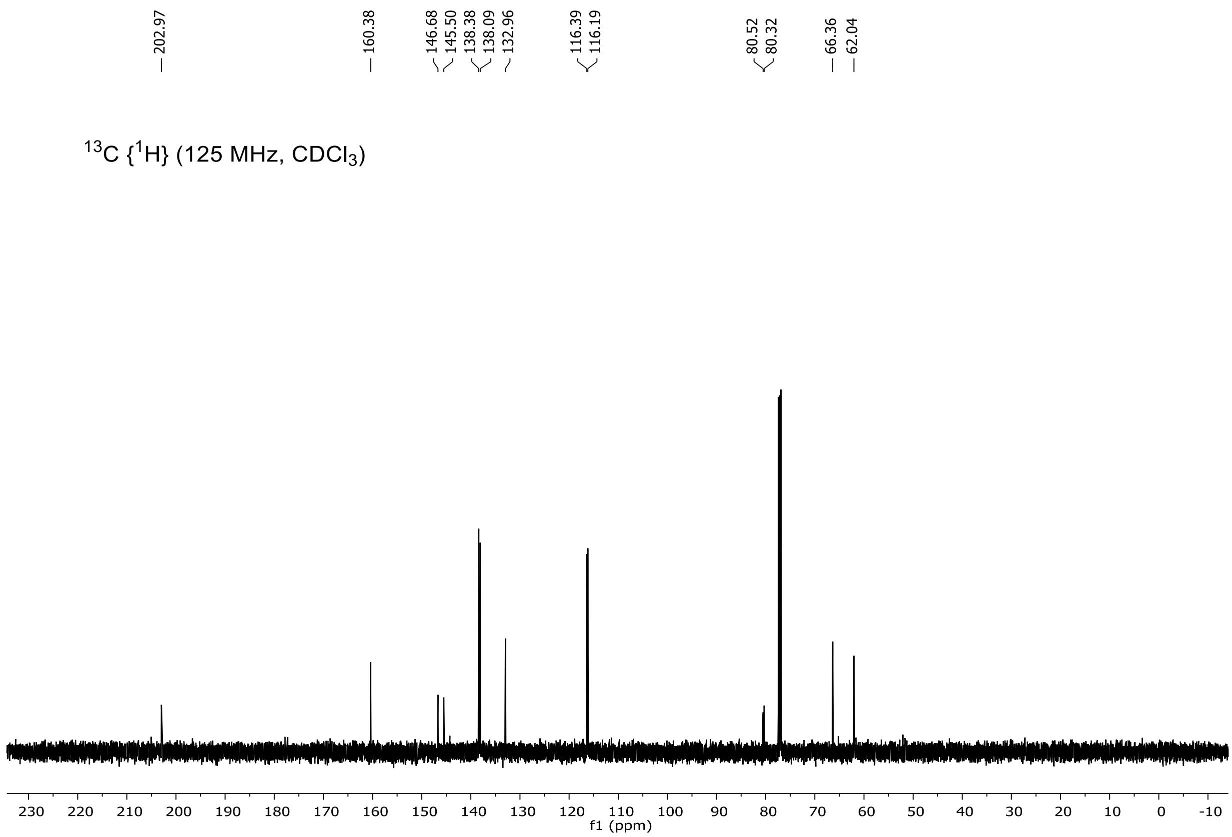
^{1}H (500 MHz, $CDCl_3$)

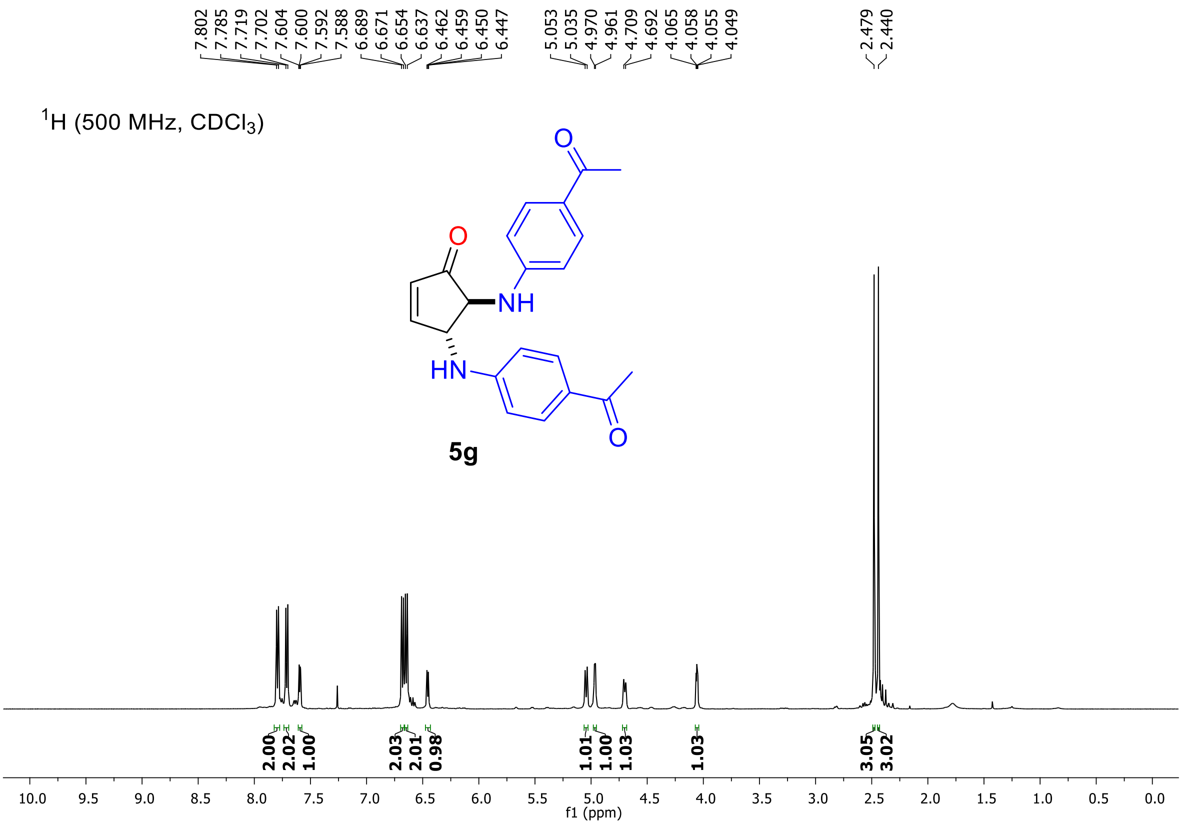


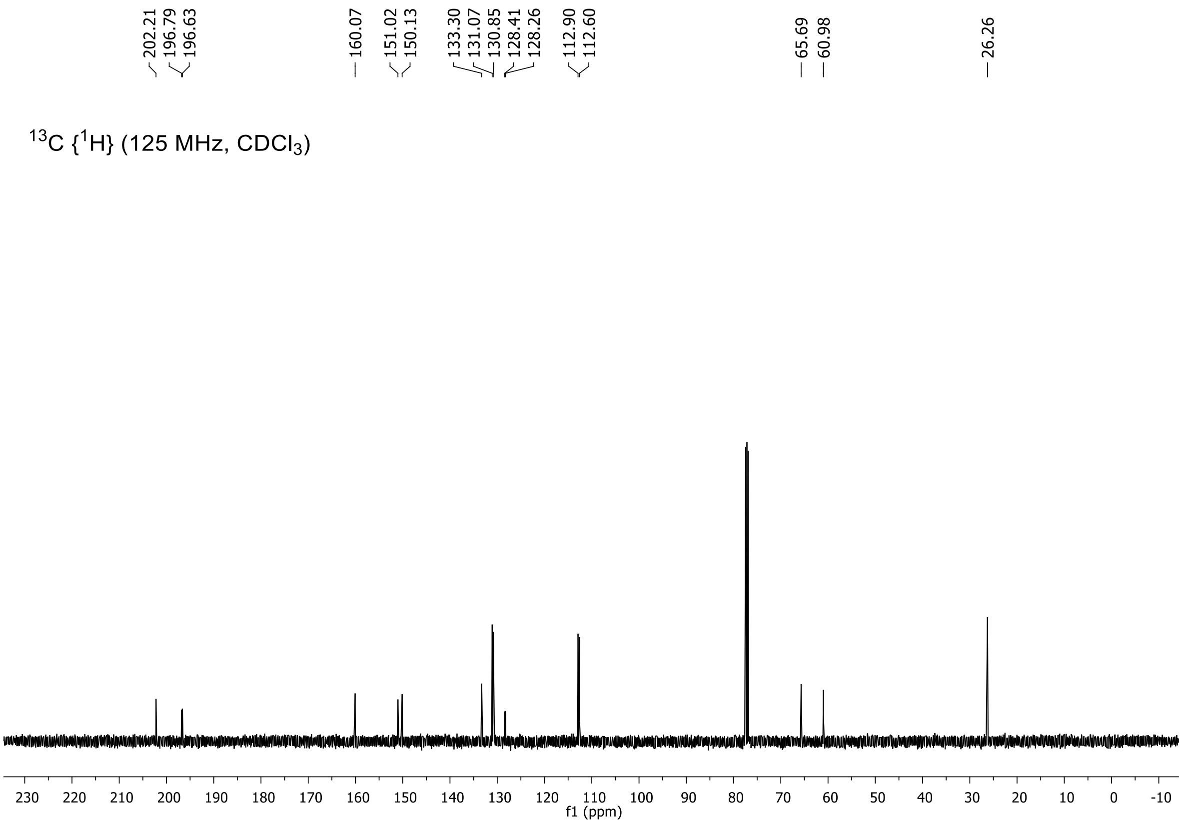
5f



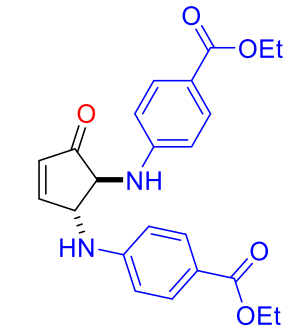
^{13}C {^{1}H} (125 MHz, $CDCl_3$)



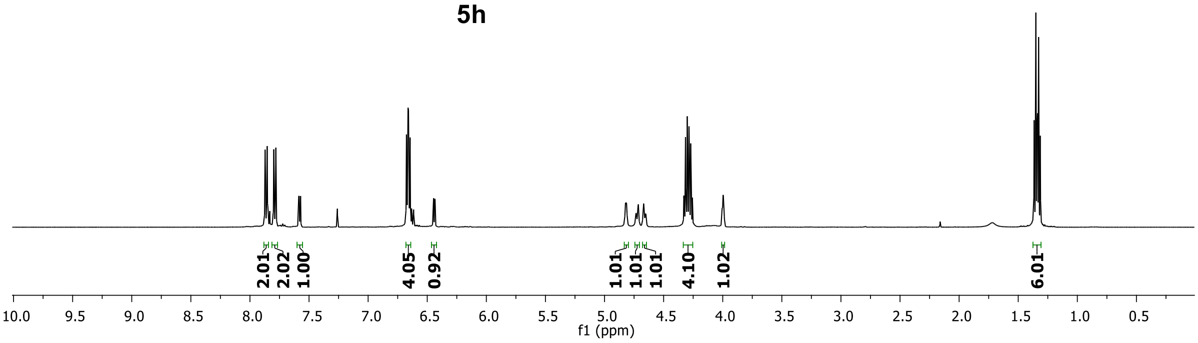

7.802
7.785
7.719
7.702
7.604
7.600
7.592
7.588
6.689
6.671
6.654
6.637
6.462
6.459
6.450
6.447
5.053
5.035
4.970
4.961
4.709
4.692
4.065
4.058
4.055
4.049
2.479
2.440
^{1}H (500 MHz, CDCl$_3$)
O
NH
HN
O
O
5g
2.00
2.02
1.00
2.03
2.01
0.98
1.01
1.00
1.03
1.03
3.05
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


202.21
196.79
196.63
160.07
151.02
150.13
133.30
131.07
130.85
128.41
128.26
112.90
112.60
65.69
60.98
26.26
^{13}C {^{1}H} (125 MHz, CDCl$_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

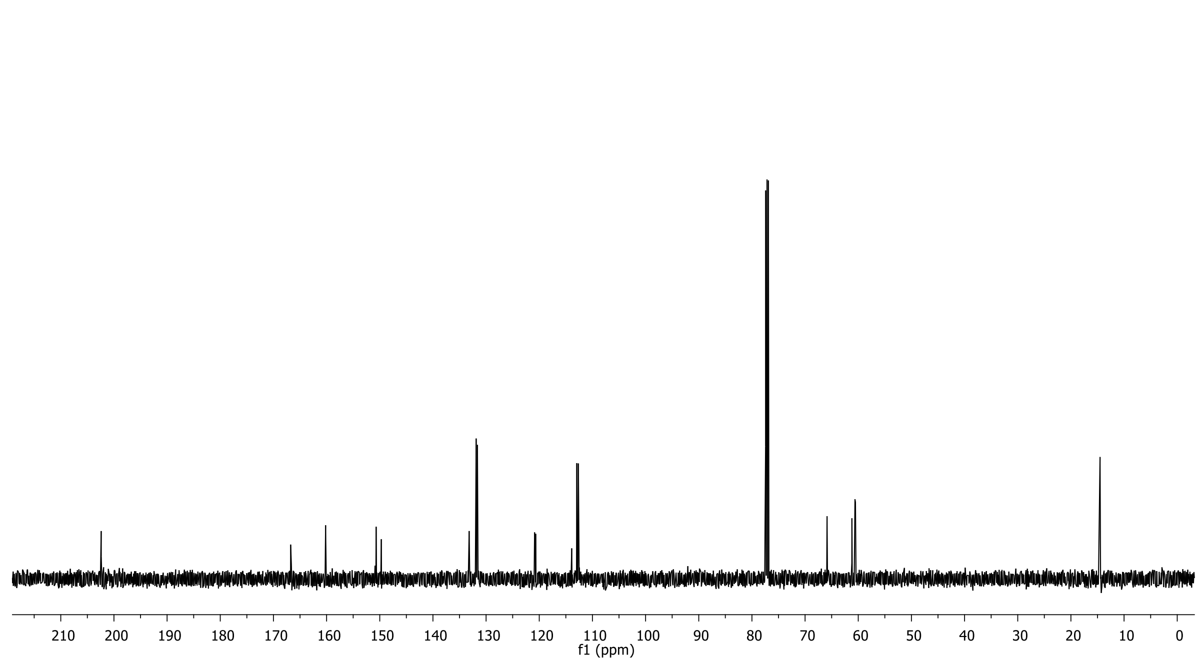
¹H (500 MHz, CDCl$_3$)

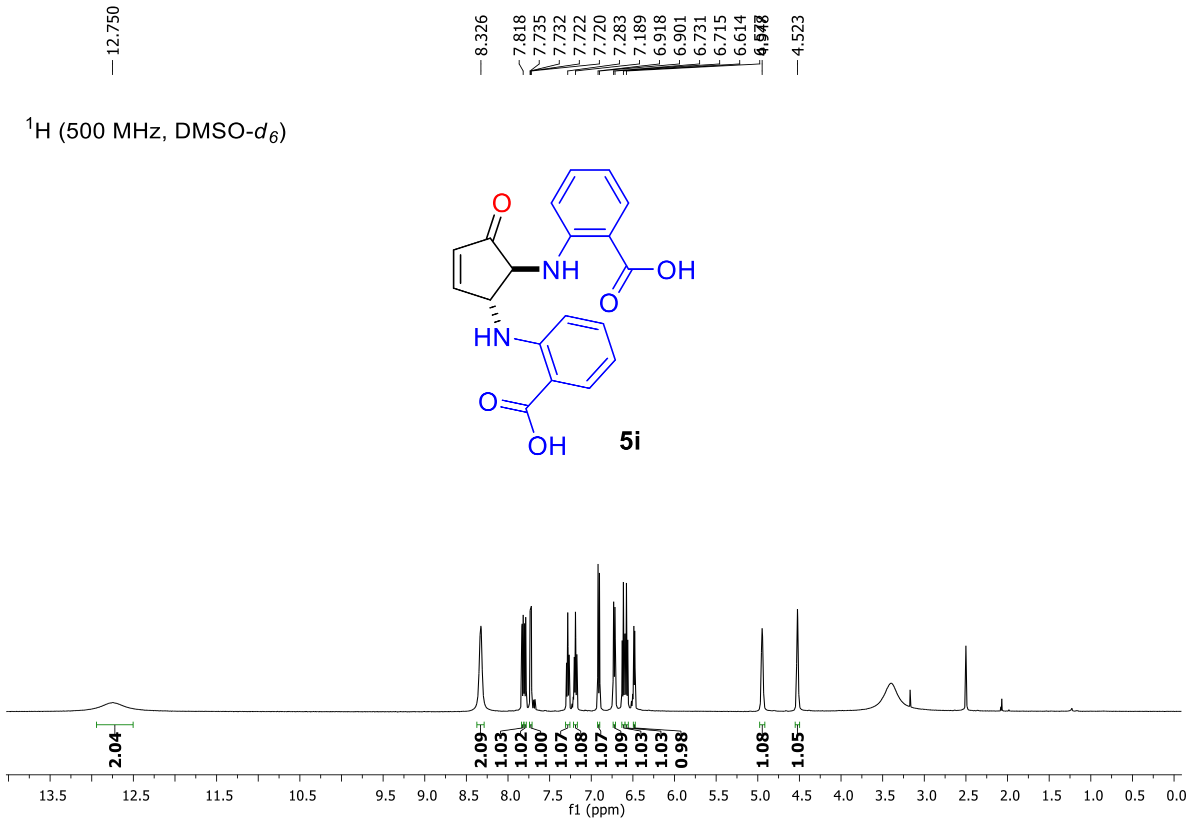


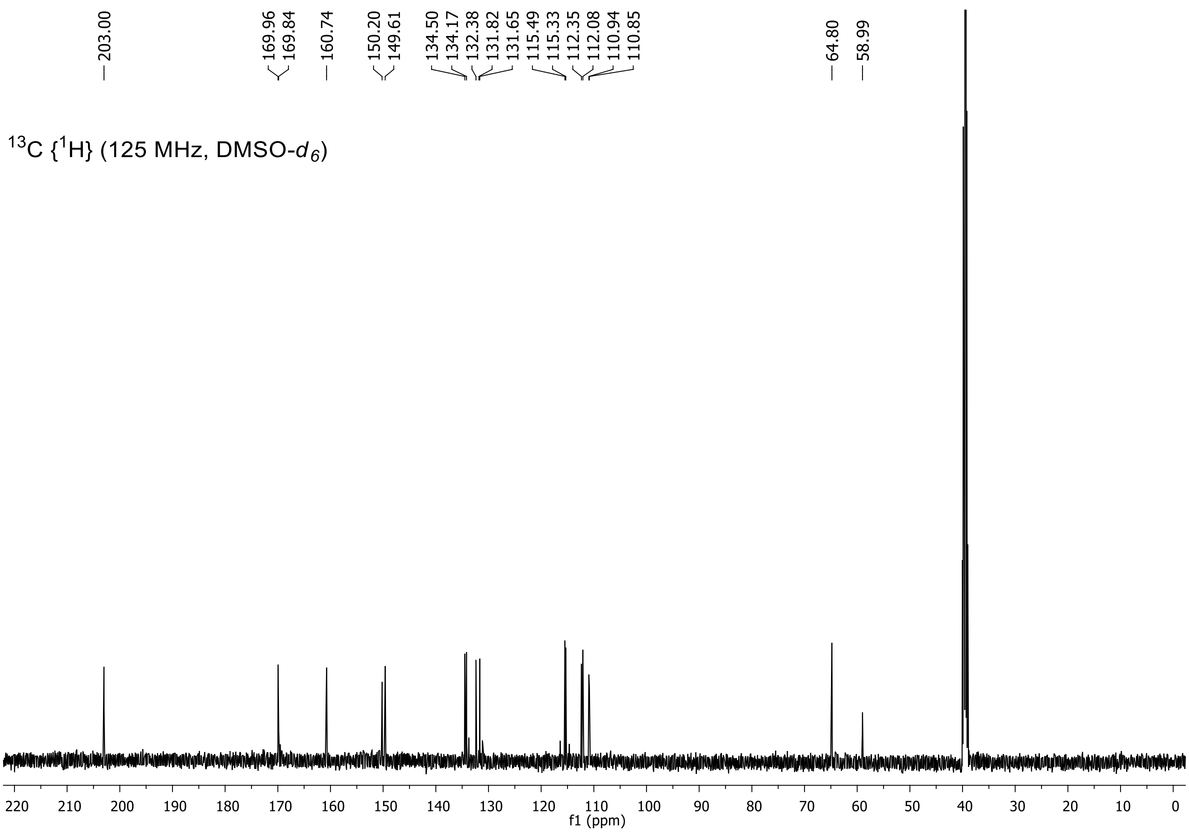
5h

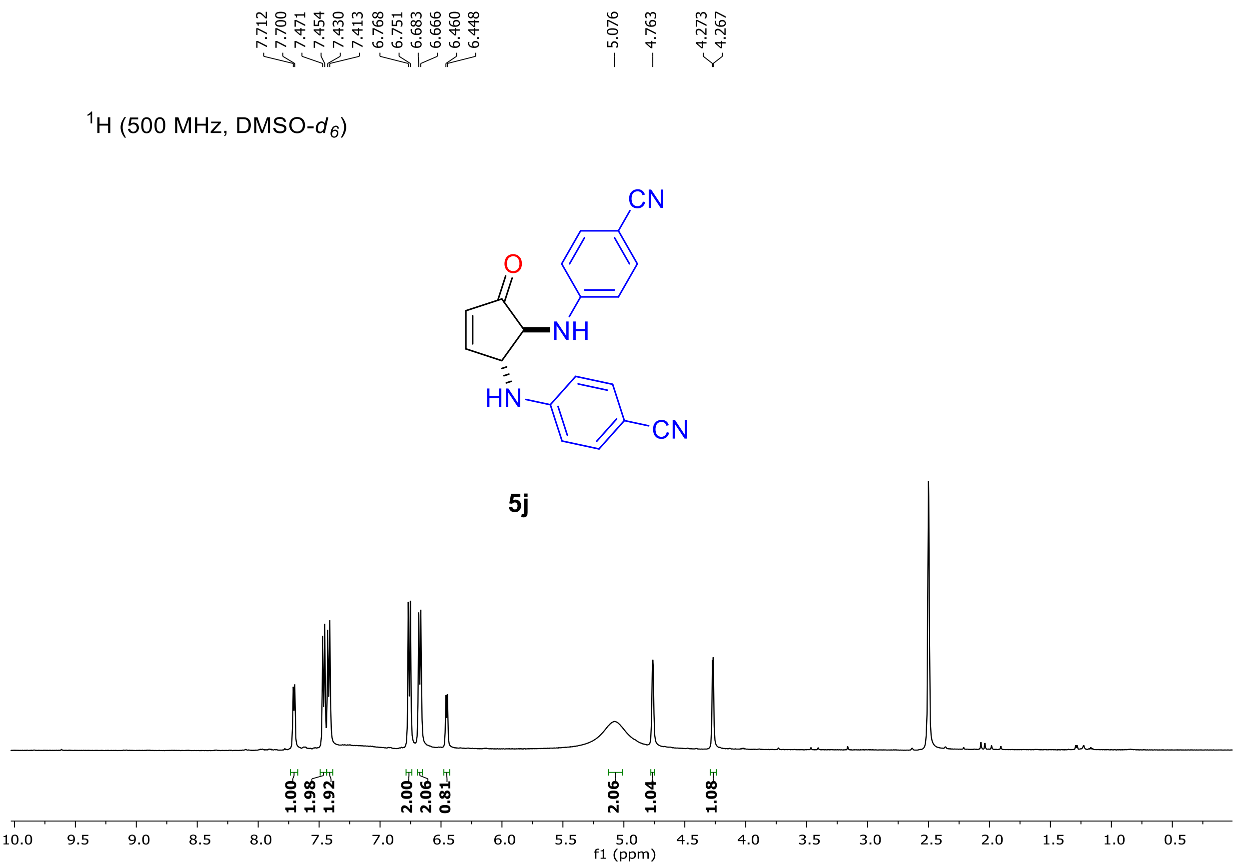


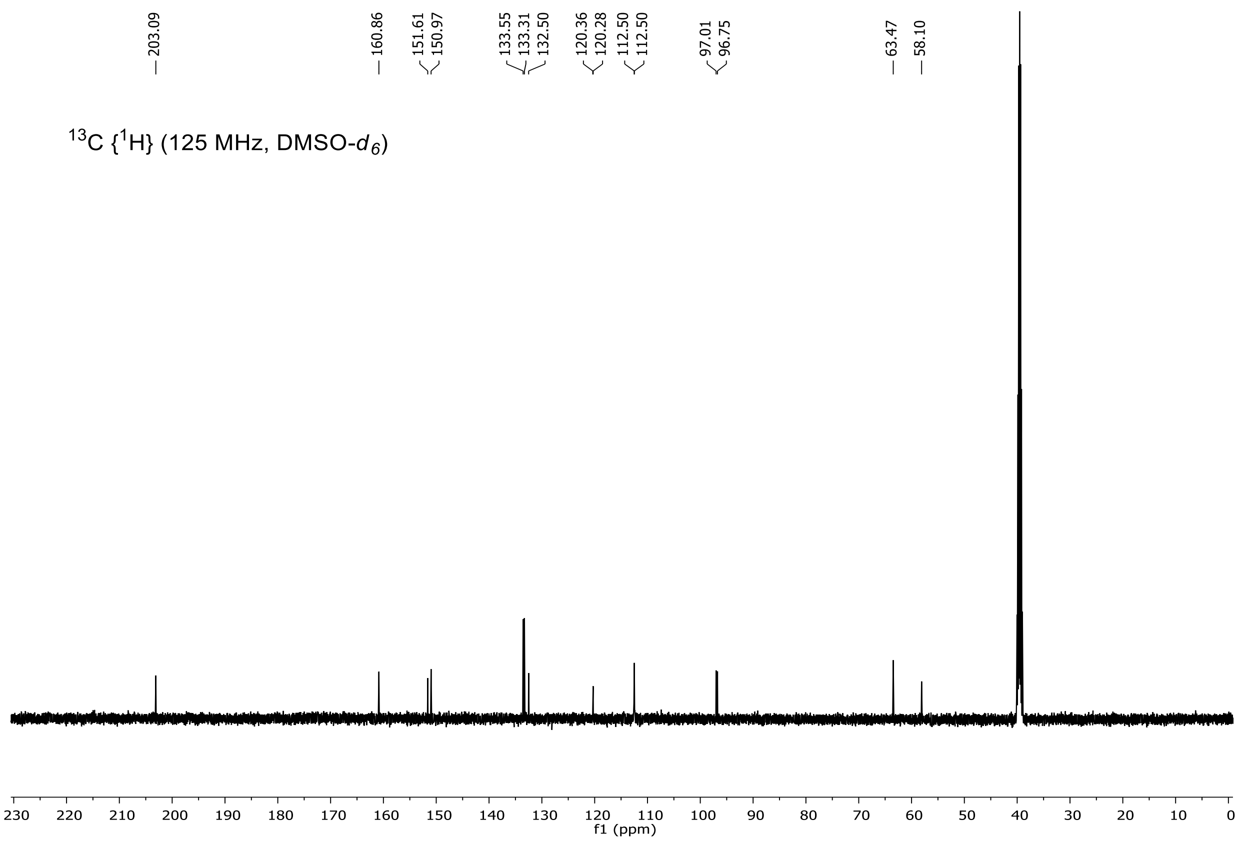
^{13}C {^{1}H} (125 MHz, CDCl$_3$)

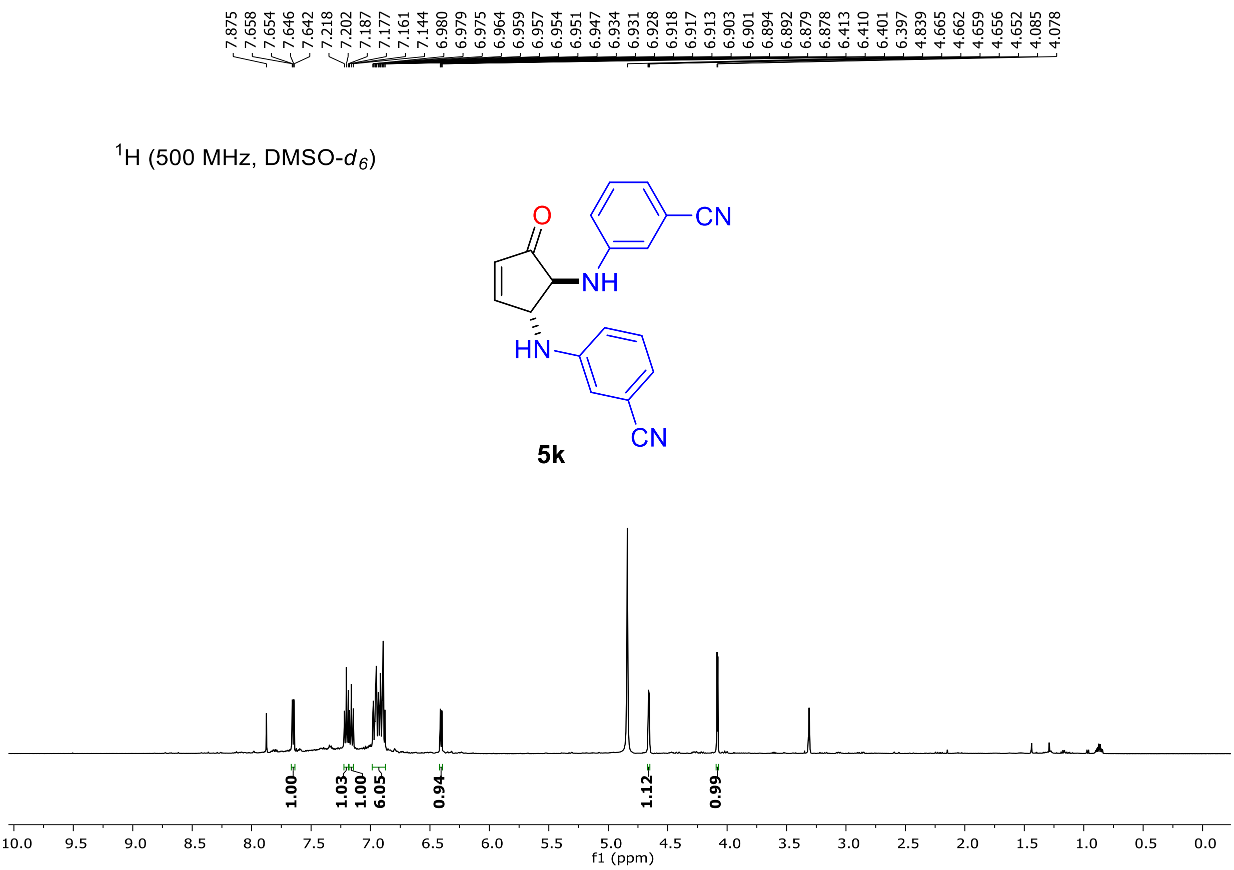


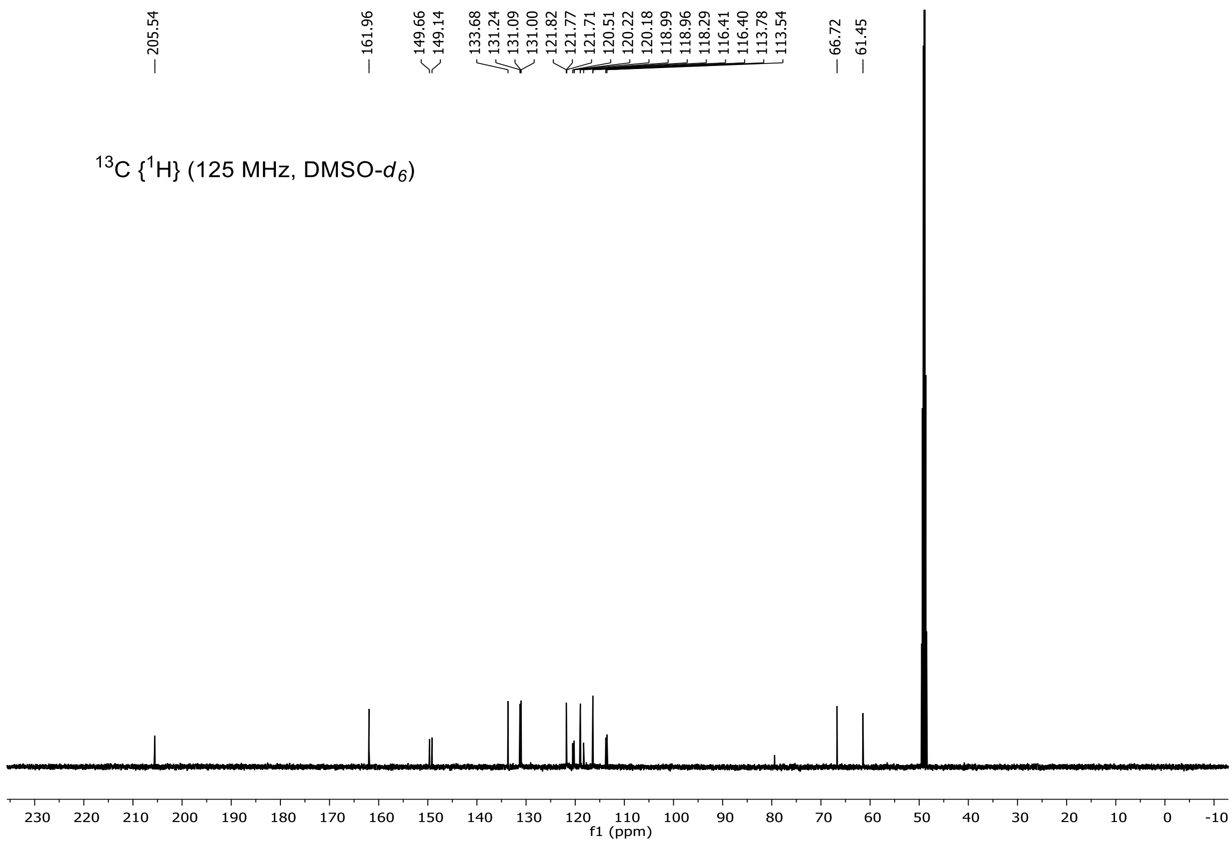

12.750
8.326
7.818
7.735
7.732
7.722
7.720
7.283
7.189
6.918
6.901
6.731
6.715
6.614
4.523
1H (500 MHz, DMSO-d6)
O
NH
OH
O
HN
O
OH
5i
2.04
2.09
1.03
1.02
1.00
1.07
1.08
1.07
1.09
1.03
1.03
0.98
1.08
1.05
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


203.00
169.96
169.84
160.74
150.20
149.61
134.50
134.17
132.38
131.82
131.65
115.49
115.33
112.35
112.08
110.94
110.85
64.80
58.99
13C {1H} (125 MHz, DMSO-d6)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

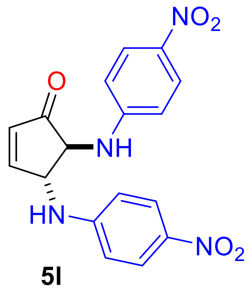

7.712
7.700
7.471
7.454
7.430
7.413
6.768
6.751
6.683
6.666
6.460
6.448
5.076
4.763
4.273
4.267
1H (500 MHz, DMSO-d6)
CN
O
NH
HN
CN
5j
1.00
1.98
1.92
2.00
2.06
0.81
2.06
1.04
1.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


203.09
160.86
151.61
150.97
133.55
133.31
132.50
120.36
120.28
112.50
112.50
97.01
96.75
63.47
58.10
13C {1H} (125 MHz, DMSO-d6)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

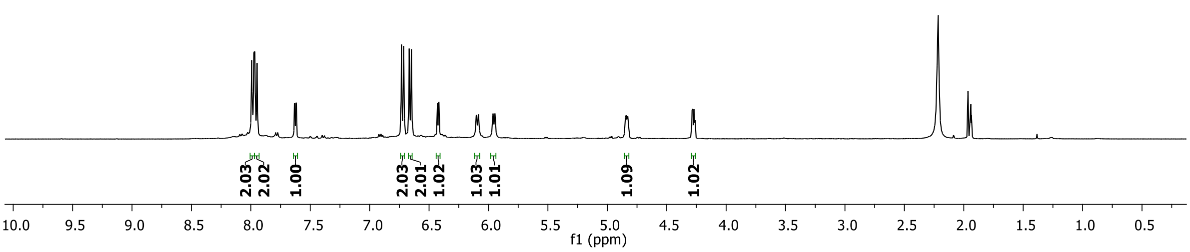

7.875
7.658
7.654
7.646
7.642
7.218
7.202
7.187
7.177
7.161
7.144
6.980
6.979
6.975
6.964
6.959
6.957
6.954
6.951
6.947
6.934
6.931
6.928
6.918
6.917
6.913
6.903
6.901
6.894
6.892
6.879
6.878
6.413
6.410
6.401
6.397
4.839
4.665
4.662
4.659
4.656
4.652
4.085
4.078
1H (500 MHz, DMSO-d6)
O
CN
NH
HN
CN
5k
1.00
1.03
1.00
6.05
0.94
1.12
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


205.54
161.96
149.66
149.14
133.68
131.24
131.09
131.00
121.82
121.77
121.71
120.51
120.22
120.18
118.99
118.96
118.29
116.41
116.40
113.78
113.54
66.72
61.45
13C {1H} (125 MHz, DMSO-d6)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

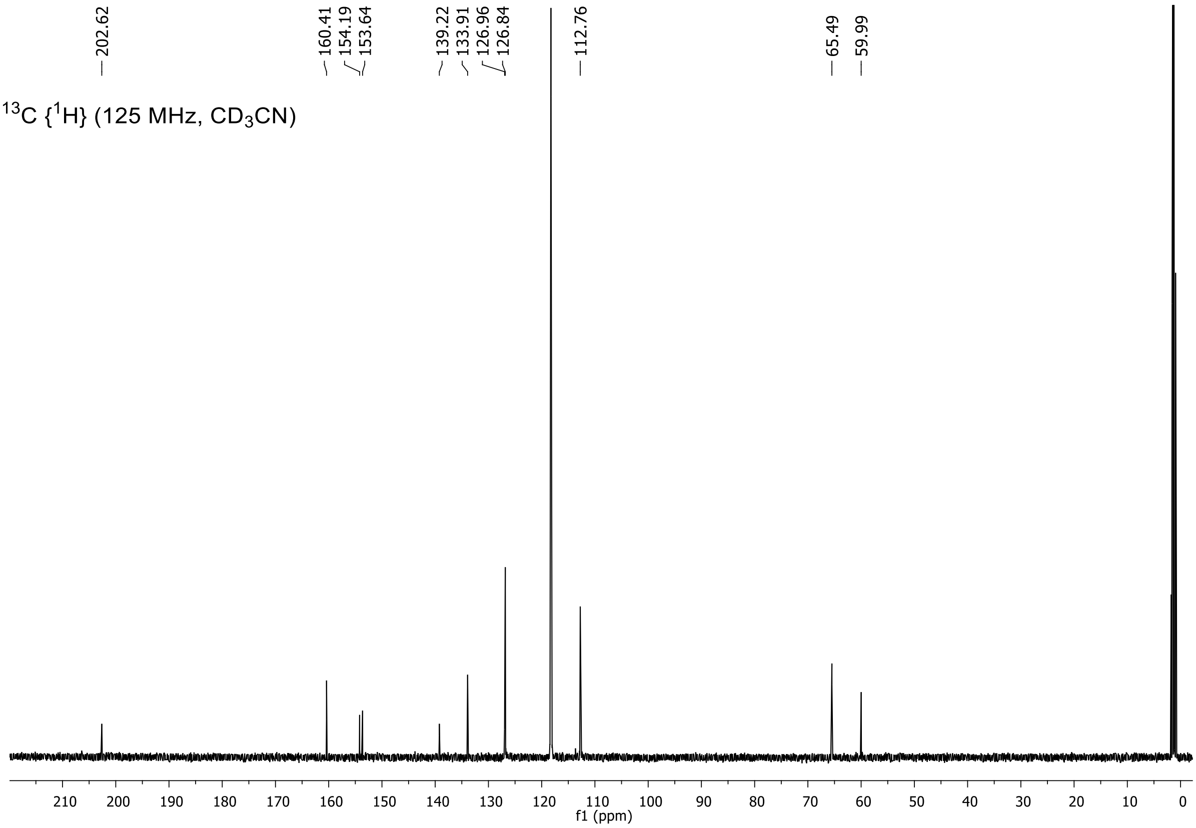
^{1}H (500 MHz, CD_3CN)

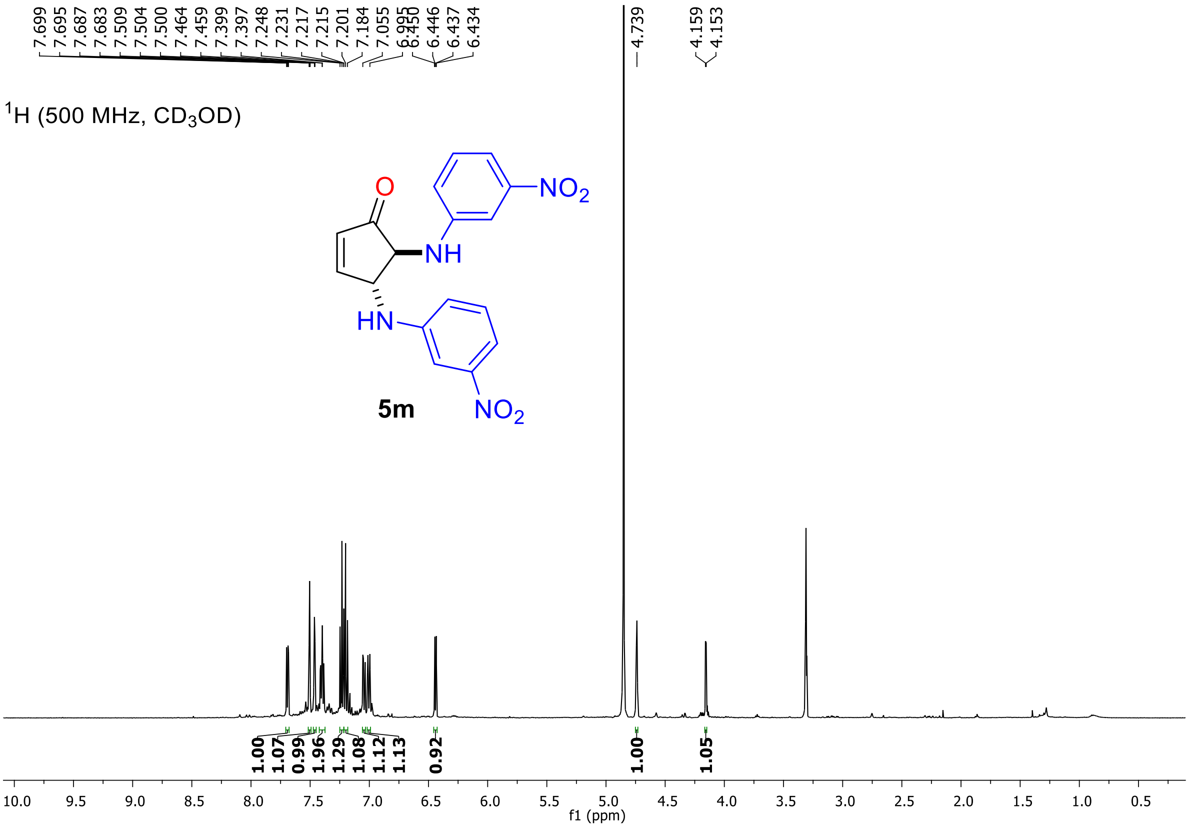


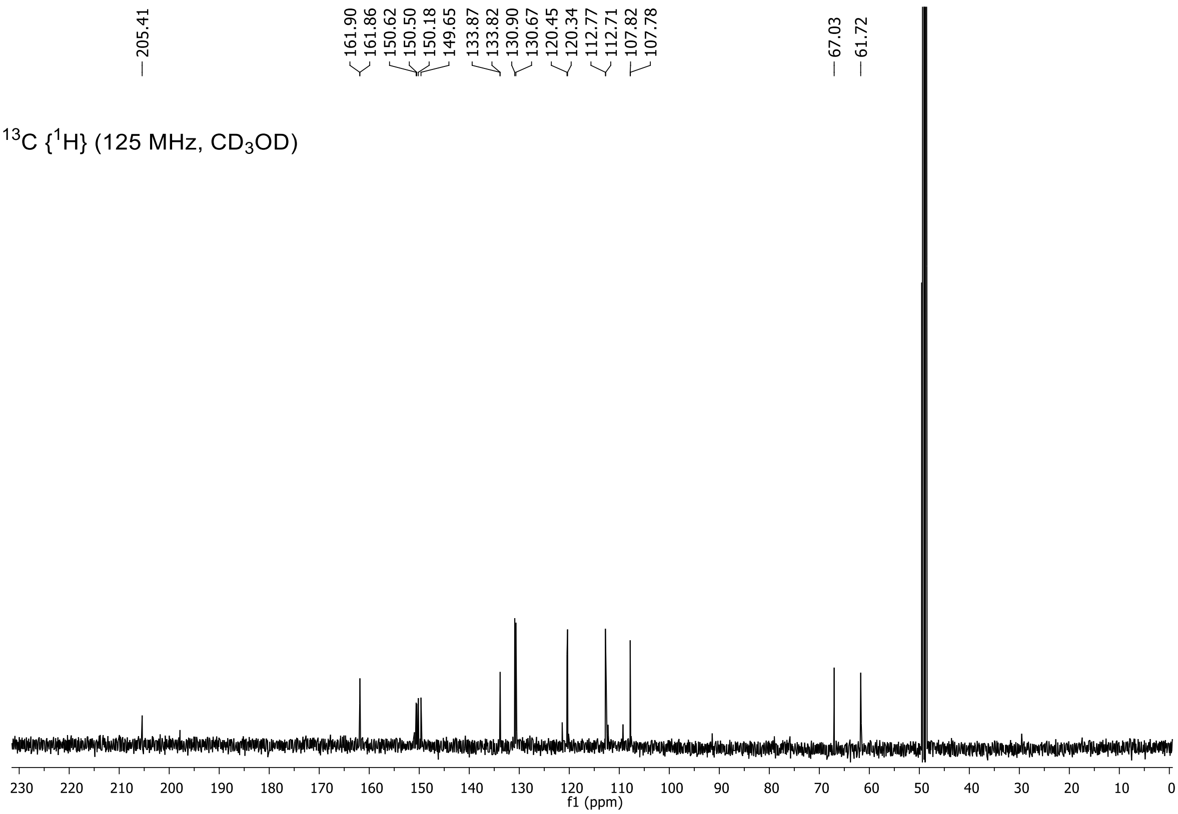
5l



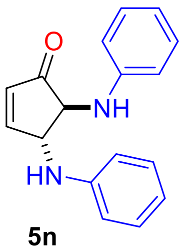
^{13}C {^{1}H} (125 MHz, CD_3CN)



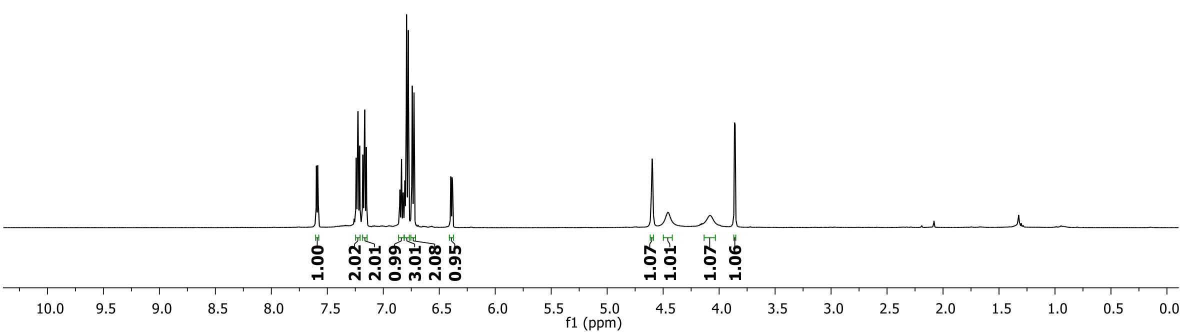

7.699
7.695
7.687
7.683
7.509
7.504
7.500
7.464
7.459
7.399
7.397
7.248
7.231
7.217
7.215
7.201
7.184
7.055
6.995
6.450
6.446
6.437
6.434
4.739
4.159
4.153
1H (500 MHz, CD3OD)
O
NH
NO2
HN
NO2
5m
1.00
1.07
0.99
1.96
1.29
1.08
1.12
1.13
0.92
1.00
1.05
f1 (ppm)


205.41
161.90
161.86
150.62
150.50
150.18
149.65
133.87
133.82
130.90
130.67
120.45
120.34
112.77
112.71
107.82
107.78
67.03
61.72
13C {1H} (125 MHz, CD3OD)
f1 (ppm)

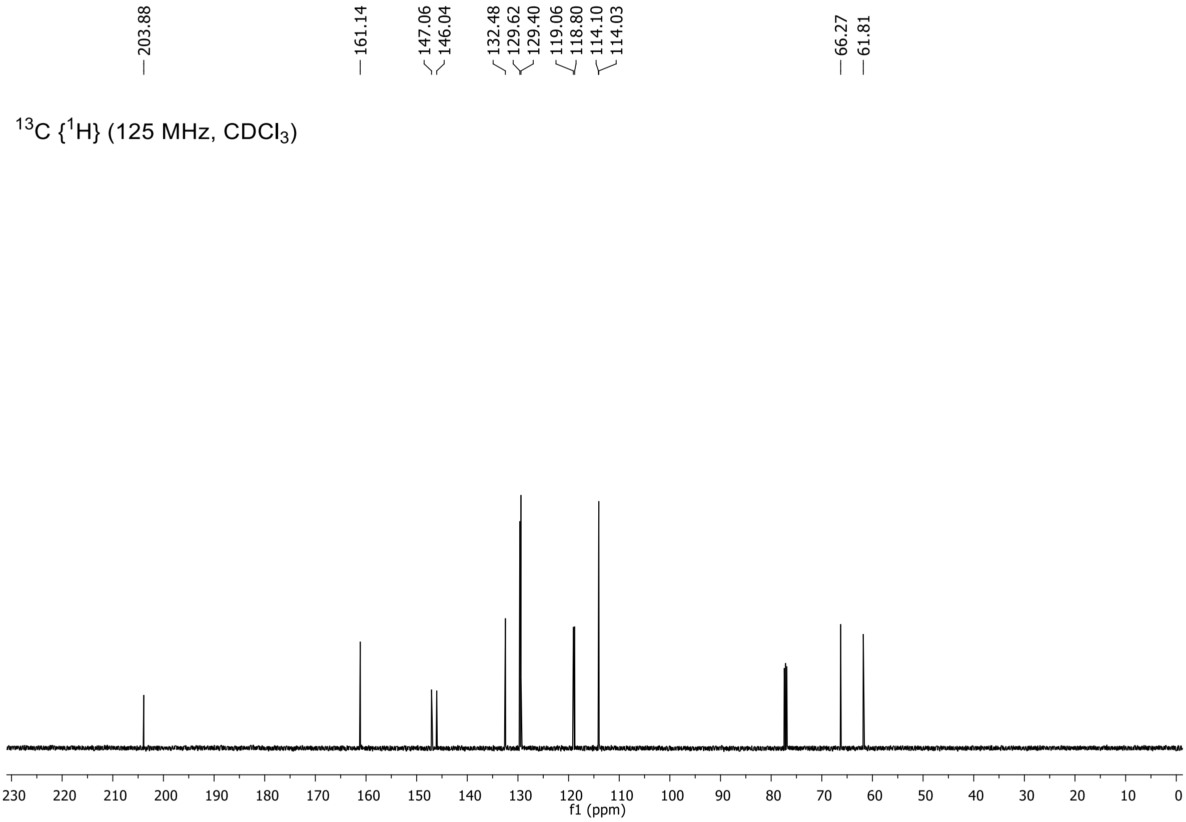
^{1}H (500 MHz, $CDCl_3$)

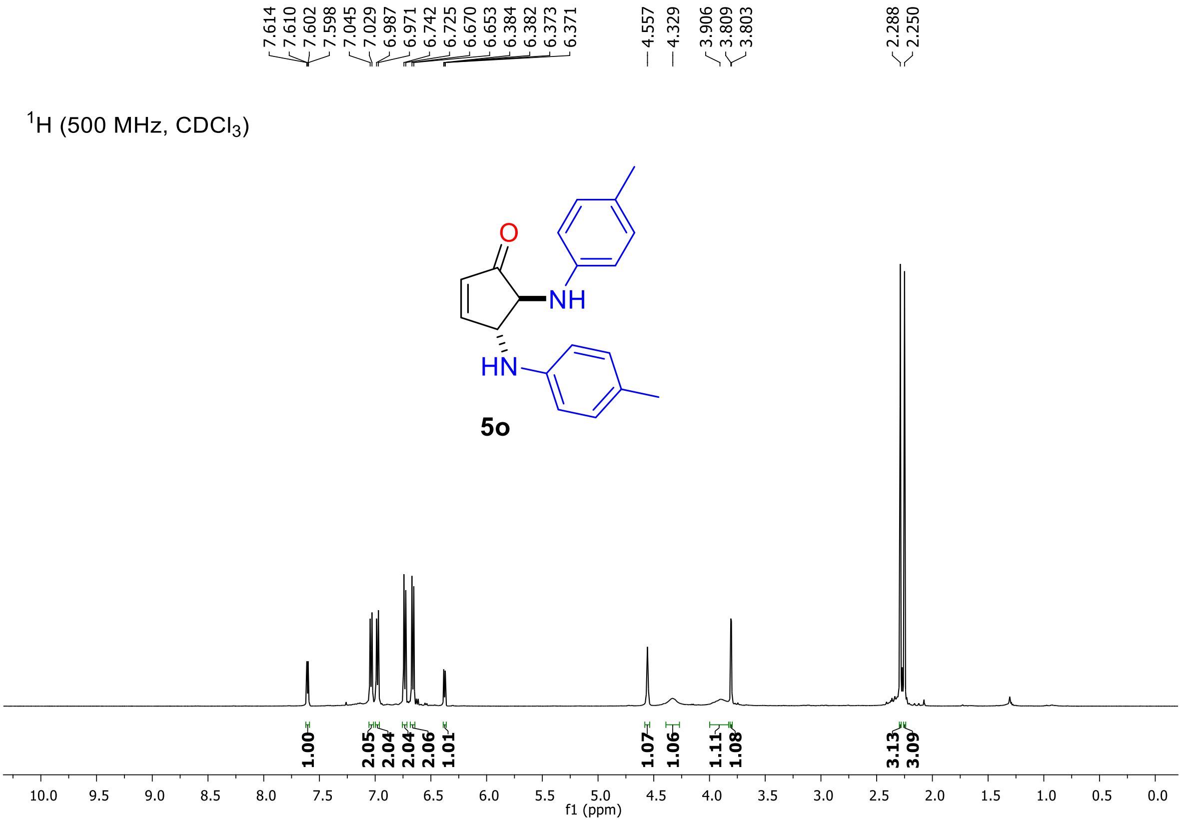


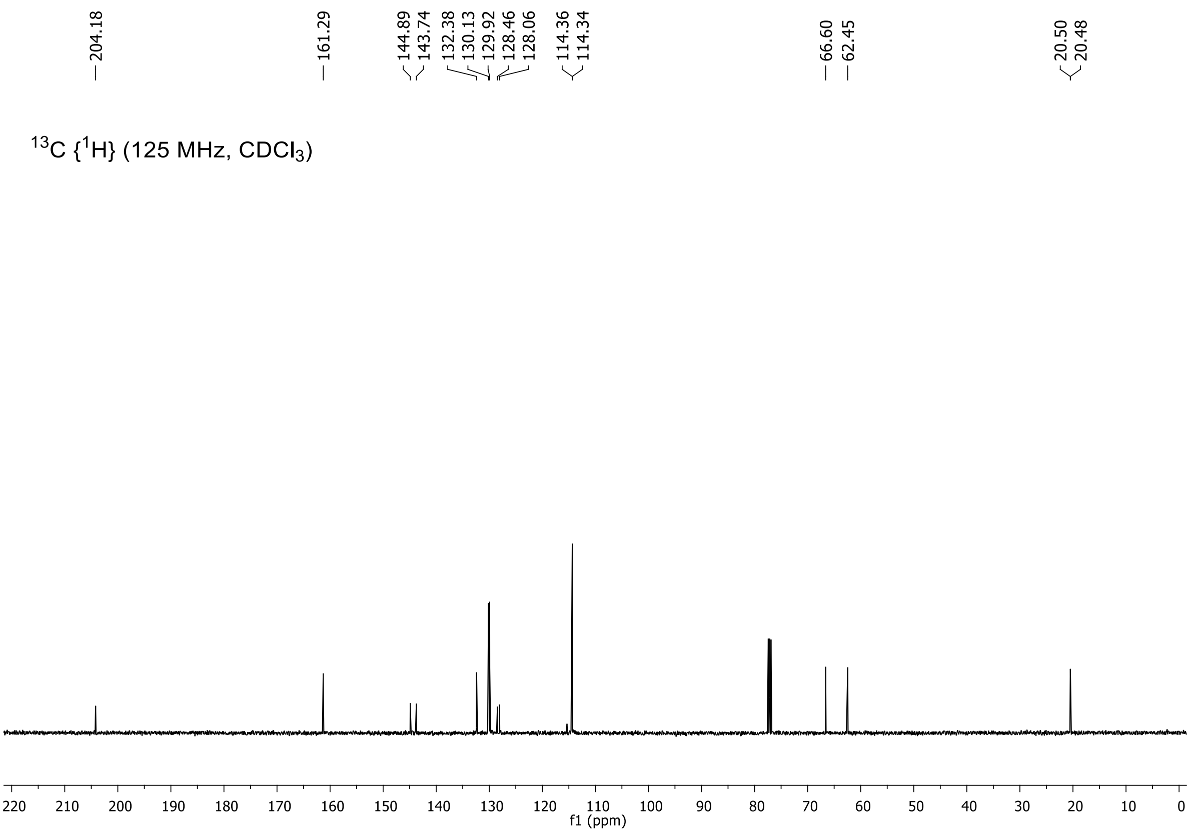
5n



^{13}C {^{1}H} (125 MHz, $CDCl_3$)




7.614
7.610
7.602
7.598
7.045
7.029
6.987
6.971
6.742
6.725
6.670
6.653
6.384
6.382
6.373
6.371
4.557
4.329
3.906
3.809
3.803
2.288
2.250
1H (500 MHz, CDCl3)
O
NH
HN
5o
1.00
2.05
2.04
2.04
2.06
1.01
1.07
1.06
1.11
1.08
3.13
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


204.18
161.29
144.89
143.74
132.38
130.13
129.92
128.46
128.06
114.36
114.34
66.60
62.45
20.50
20.48
13C {1H} (125 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)