

Synthesis of *N*-Substituted Oxazolidin-2-ones via Organocatalytic Aziridine-CO₂ Cycloaddition

Caterina Damiano,^{*1} Emma Gallo,¹ M. Mar Díaz-Requejo,² and Pedro J. Pérez²

Address: ¹Department of Chemistry, University of Milan, Via C. Golgi 19, 20133, Milan, Italy and ²Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21007 Huelva, Spain.

Email: Caterina Damiano - caterina.damiano@unimi.it

* Corresponding author

‡ Equal contributors

Tables of contents

1. Optimization of the reaction conditions for the synthesis of <i>N</i> -alkyl oxazolidin-2-ones	2
2. Synthesis of <i>N</i> -alkyl oxazolidin-2-ones	3
3. Optimization of the reaction condition for the synthesis of oxazolidin-2-ones 13	7
4. ¹ H and ¹³ C NMR spectra	9
5. References	23

1. Optimization of the reaction conditions for the synthesis of N-alkyl oxazolidine-2-ones

Study of the reaction dependence on the solvent

In a 10.0 mL test tube equipped with a screw cap with a silicon/PTFE septum, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1**) (4×10^{-5} mol) was dissolved in the desired solvent (0.5 mL) and then *N*-butyl phenyl aziridine (8×10^{-4} mol) was added. At this point, CO₂ was bubbled into the mixture for 15 minutes, and then a plastic balloon filled with CO₂ was attached to the top of the flask to maintain a carbon dioxide atmosphere. The reaction was stirred at 40 °C for 4 hours, then the CO₂ balloon was removed, the solvent evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S1 and summarized in figure 1A of the manuscript.

Table S1 Study of the reaction dependence on the solvent.

Entry	Solvent	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	MeCN	34	100	34	95:5
2	MeOH	8	100	8	95:5
3	EtOH	12	100	12	95:5
4	<i>i</i> PrOH	25	100	25	94:6
5	THF	26	100	26	95:5
6	2-MeTHF	6	100	6	94:6
7	cyrene	-	-	-	-
8	MEK ^[a]	-	-	-	-
9	no solvent	-	-	-	-

[a] MEK: methyl ethyl ketone.

Study of the reaction dependence on the reaction time

In a 10.0 mL test tube equipped with a screw cap with a silicon/PTFE septum, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1**) (4×10^{-5} mol) was dissolved in the MeCN (0.5 mL) and then *N*-butyl phenyl aziridine (8×10^{-4} mol) was added. At this point, CO₂ was bubbled into the mixture for 15 minutes, and then a plastic balloon filled with CO₂ was attached to the top of the flask to maintain a carbon dioxide atmosphere. The reaction was stirred at 40 °C for the desired time, then the CO₂ balloon was removed, the solvent evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S2 and summarized in figure 1B of the manuscript.

Table S2 Study of the reaction dependence on reaction time.

Entry	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	4	34	100	34	95:5
2	16	52	100	52	95:5
3	24	60	100	60	95:5
4	48	62	100	62	95:5

Study of the reaction dependence on the catalyst loading

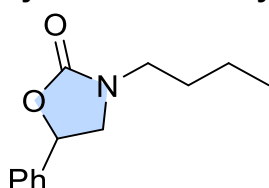
In a 10.0 mL test tube equipped with a screw cap with a silicon/PTFE septum, the desired amount of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1**) was dissolved in the MeCN (0.5 mL) and then *N*-butyl phenyl aziridine (8×10^{-4} mol) was added. At this point, CO₂ was bubbled into the mixture for 15 minutes, and then a plastic balloon filled with CO₂ was attached to the top of the flask to maintain a carbon dioxide atmosphere. The reaction was stirred at 40 °C for 24 hours, then the CO₂ balloon was removed, the solvent evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S3 and summarized in figure 1C of the manuscript.

Table S3 Study of the reaction dependence on catalyst loading.

Entry	Catalyst loading (mol%)	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	1.5	33	100	33	95:5
2	2.5	47	100	47	95:5
3	5	60	100	60	95:5
4	10	85	100	85	95:5

2. Synthesis of *N*-alkyl oxazolidin-2-ones

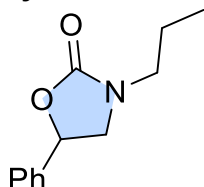
Synthesis of 3-butyl-5-phenyloxazolidin-2-one (**2**)



The general catalytic procedure was followed by using 1-butyl-2-phenyl aziridine as the reagent (0.194 mL) to obtain a yellowish oil as the product (85% yield, **A/B** = 95:5). Collected data are in accordance with those reported in literature.[1,2]

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.33 (m, 5H), 5.47 (pt, *J* = 8.0 Hz, 1H), 3.91 (pt, *J* = 8.8 Hz, 1H), 3.44 (pt, *J* = 8.0 Hz, 1H), 3.37 – 3.23 (m, 2H), 1.57 – 1.50 (m, 2H), 1.40 – 1.32 (m, 2H), 0.94 ppm (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.92, 138.94, 128.76, 127.01, 125.50, 74.32, 69.81, 59.76, 52.19, 43.94, 29.43, 19.84, 13.69 ppm. LR-MS (ESI) *m/z* calcd. for (C₁₃H₁₇NO₂): 219.13, found 220.19 [M+H]⁺.

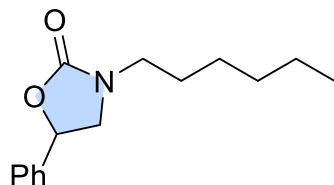
Synthesis of 3-propyl-5-phenyloxazolidin-2-one (**3**)



The general catalytic procedure was followed by using 1-propyl-2-phenyl aziridine as the reagent (0.194 mL) to obtain a yellowish oil as the product (90% yield, **A/B** = 95:5). Collected data are in accordance with those reported in literature.[3]

^1H NMR (300 MHz, CDCl_3) δ 7.40 – 7.27 (m, 5H), 5.47 (pt, J = 8.0 Hz, 1H), 3.90 (pt, J = 8.8 Hz, 1H), 3.41 (pt, J = 8.0 Hz, 1H), 3.37 – 3.19 (m, 2H), 1.60 – 1.55 (m, 2H, H_7), 0.92 ppm (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 157.97, 138.95, 128.87, 128.73, 126.98, 125.50, 74.31, 52.12, 45.79, 20.64, 11.07 ppm. LR-MS (ESI) m/z calcd. for ($\text{C}_{12}\text{H}_{15}\text{NO}_2$): 205.11, found 206.04 $[\text{M}+\text{H}]^+$.

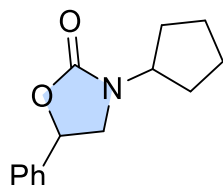
Synthesis of 3-hexyl-5-phenyloxazolidin-2-one (4)



The general catalytic procedure was followed by using 1-hexyl-2-phenyl aziridine as the reagent (0.198 mL) to obtain a yellowish oil as the product (86% yield, **A/B** = 96:4). Collected data are in accordance with those reported in literature [1,2].

^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.32 (m, 5H), 5.43 (pt, J = 8.4 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.40 – 3.37 (m, 1H), 3.30 – 3.24 (m, 2H), 1.55 – 1.49 (m, 2H), 1.32 – 1.23 (m, 6H + solvent), 0.89 – 0.80 ppm (m, 3H + solvent). ^{13}C NMR (101 MHz, CDCl_3) δ 157.78, 138.90, 129.59, 127.98, 127.92, 126.17, 124.61, 74.96, 73.43, 52.02, 50.59, 44.07, 27.19, 26.16, 14.48, 13.25. LR MS (ESI) m/z calcd. for ($\text{C}_{15}\text{H}_{21}\text{NO}_2$): 247.16, found 270.48 $[\text{M}+\text{Na}]^+$.

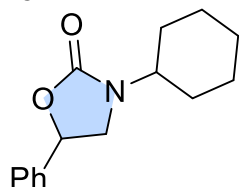
Synthesis of 3-cyclopentyl-5-phenyloxazolidin-2-one (5)



The general catalytic procedure was followed by using 1-cyclopentyl-2-phenyl aziridine as the reagent (0.193 mL) to obtain a yellowish oil as the product (87% yield, **A/B** = 90:10). Collected data are in accordance with those reported in literature. [2,3]

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.35 (m, 5H), 5.48 (pt, J = 8.0 Hz, 1H), 4.35 – 4.29 (m, 1H), 3.91 – 3.87 (m, 1H), 3.40 (pt, J = 8.2 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.73 – 1.49 ppm (m, 6H + solvent). ^{13}C NMR (101 MHz, CDCl_3) δ 156.50, 137.98, 127.88, 127.73, 124.47, 73.44, 53.66, 47.59, 28.15, 27.62, 22.90 ppm. LR MS (ESI) m/z calcd. for ($\text{C}_{14}\text{H}_{17}\text{NO}_2$): 231.29, found 232.21 $[\text{M}+\text{H}]^+$.

Synthesis of 3-hexyl-5-phenyloxazolidin-2-one (6)

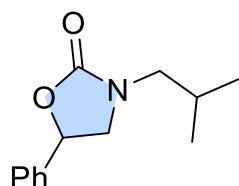


The general catalytic procedure was followed by using 1-cyclohexyl-2-phenyl aziridine as the reagent (0.219 mL) to obtain a yellowish oil as the product (63% yield, **A/B** = 92:8). Collected data are in accordance with those reported in literature [2,3].

^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.35 (m, 5H), 5.50 – 5.46 (m, 1H), 3.92 – 3.88 (m, 1H), 3.43 – 3.35 (m, 1H), 1.87 – 1.179 (m, 4H), 1.72 – 1.67 (m, 2H), 1.42 – 1.28 (m, 4H), 1.14 – 1.08 ppm

(m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.21, 138.08, 127.87, 127.71, 124.47, 73.57, 51.58, 47.33, 29.57, 29.10, 24.37, 24.32, 24.28 ppm. LR MS (ESI) m/z calcd. for ($\text{C}_{15}\text{H}_{19}\text{NO}_2$): 245.32, found 268.41 $[\text{M}+\text{Na}]^+$.

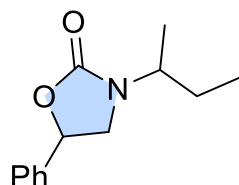
Synthesis of 3-isobutyl-5-phenyloxazolidin-2-one (7)



The general catalytic procedure was followed by using 1-isobutyl-2-phenyl aziridine as the reagent (0.195 mL) to obtain a yellowish oil as the product (88% yield, **A/B** = 95:5). Collected data are in accordance with those reported in literature.[4]

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.25 (m, 5H), 5.41 (pt, J = 8.6 Hz, 1H), 3.84 (pt, J = 8.8 Hz, 1H), 3.34 (dd, J = 8.6, 7.4 Hz, 1H), 3.06 – 2.94 (m, 2H), 1.83 – 1.78 (m, 1H), 0.87 – 0.76 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.21, 138.96, 128.85, 128.70, 125.45, 74.26, 52.75, 51.73, 26.78, 19.89, 19.85. LR MS (ESI) m/z calcd. for ($\text{C}_{13}\text{H}_{17}\text{NO}_2$): 219.13, found 242.18 $[\text{M}+\text{Na}]^+$.

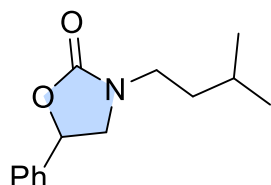
Synthesis of 3-secbutyl-5-phenyloxazolidin-2-one (8)



The general catalytic procedure was followed by using 1-secbutyl-2-phenyl aziridine as the reagent (0.195 mL) to obtain a yellowish oil as the product (55% yield, **A/B** = 93:7). Collected data are in accordance with those reported in literature.[4]

^1H NMR (300 MHz, CDCl_3) δ 7.44 – 7.35 (m, 5H), 5.51 (pt, J = 7.8 Hz, 1H), 3.98 – 3.86 (m, 2H), 3.32 (pt, J = 8.7 Hz, 1H), 1.53 – 1.45 (m, 2H), 1.21 (d, J = 6.8 Hz, 3H), 0.89 ppm (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 157.6, 139.30, 128.91, 128.71, 125.50, 74.42, 50.62, 47.41, 27.01, 18.01, 10.88 ppm. LR-MS (ESI) m/z calcd. for ($\text{C}_{13}\text{H}_{17}\text{NO}_2$) 219.13, found 242.25 $[\text{M}+\text{Na}]^+$.

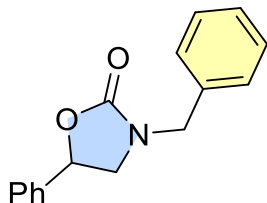
Synthesis of 3-isoamil-5-phenyloxazolidin-2-one (9)



The general catalytic procedure was followed by using 1-isoamil-2-phenylaziridine (0.166 mL) as the substrate to obtain a yellowish oil as the product (56% yield, **A/B** 90:10). Collected data are in accordance with those reported in literature.[3]

^1H NMR (300 MHz, CDCl_3) δ 7.40 – 7.37 (m, 5H), 5.50 (pt, J = 8.1 Hz, 1H), 3.92 (pt, J = 8.7 Hz, 1H), 3.44 – 3.32 (m, 3H), 1.70 – 1.56 (m, 1H), 1.50 – 1.41 (m, 2H), 0.96 – 0.94 ppm (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 129.02, 128.89, 125.63, 74.44, 52.25, 42.74, 36.23, 25.86, 22.60, 22.52 ppm. LR-MS (ESI) m/z calcd. for ($\text{C}_{14}\text{H}_{19}\text{NO}_2$): 233.14, found 234.13 $[\text{M}+\text{H}]^+$.

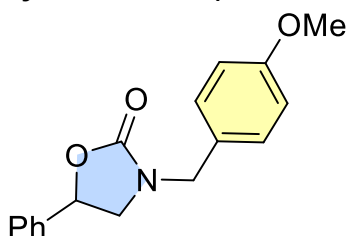
Synthesis of 3-benzyl-5-phenyloxazolidin-2-one (10)



The general catalytic procedure was followed by using 1-benzyl-2-phenyl aziridine as the reagent (0.197 mL) to obtain a yellowish oil as the product (80% yield, **A/B** = 95:5). Collected data are in accordance with those reported in literature.[2]

^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.30 (m, 10H), 5.50 – 5.46 (m, 1H), 4.56 (d, J = 15.0 Hz, 1H), 4.41 (d, J = 15.0 Hz, 1H), 3.77 (pt, J = 8.7 Hz, 1H), 3.33 – 3.29 ppm (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.99, 138.61, 135.65, 128.89, 128.80, 128.18, 128.05, 125.52, 74.54, 51.57, 48.45 ppm. LR MS (ESI) m/z calcd. for ($\text{C}_{16}\text{H}_{15}\text{NO}_2$): 253.11, found 276.27 [$\text{M}+\text{Na}$] $^+$.

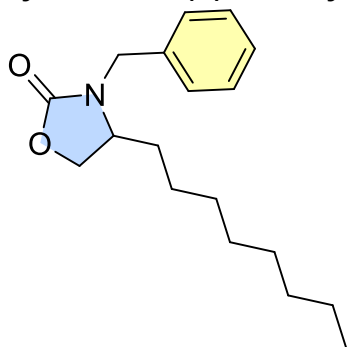
Synthesis of 3-(4-methoxybenzyl)-5-phenyloxazolidin-2-one (11)



The general catalytic procedure was followed by using 1-(4-methoxybenzyl)-2-phenyl aziridine as the reagent (0.182 mL) to obtain a yellowish oil as the product (73% yield, **A/B** = 95:5). Collected data are in accordance with those reported in literature.[1,2]

^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.30 (m, 5H), 7.22 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 5.44 (pt, J = 8.2 Hz, 1H), 4.47 (d, J = 14.7 Hz, 1H), 4.35 (d, J = 14.7 Hz, 1H), 3.80 (s, 3H), 3.74 (pt, J = 8.8 Hz, 1H), 3.28 ppm (dd, J = 8.7, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.41, 156.87, 137.64, 128.56, 127.84, 127.75, 126.65, 124.51, 73.48, 54.28, 50.40, 46.81 ppm. LR MS (ESI) m/z calcd. for ($\text{C}_{17}\text{H}_{17}\text{NO}_3$): 283.12, found 306.39 [$\text{M}+\text{Na}$] $^+$.

Synthesis of (S)-3-benzyl-4-octyloxazolidin-2-one



The general catalytic procedure was followed by using (S)-1-benzyl-2-octylaziridine as the reagent (0.120 mL) to obtain a yellowish oil as the product (54% yield, **A/B** = 19:81).

^1H NMR (400 MHz, CDCl_3) δ 7.33 (m, 5H + H_{Ar} regioisomer A), 4.81 (d, J = 15.2 Hz, 1H), 4.34 (t, J = 8.6 Hz, 1H), 4.10 (d, J = 15.2 Hz, 1H), 3.98 (dd, J = 8.6, 6.7 Hz, 1H), 3.65 – 3.57 (m, 1H), 1.78 – 1.59 (m, 2H), 1.52 – 1.40 (m, 2H), 1.31 – 1.21 (m, 10H + H regioisomer A + solvent), 0.90 (t, J = 6.9 Hz, 3H + solvent). ^{13}C NMR (101 MHz, CDCl_3) δ 158.54, 136.02, 128.82, 128.79,

128.12, 127.93, 127.89, 67.34, 54.18, 45.97, 31.79, 31.57, 29.44, 29.34, 29.12, 23.79, 22.62, 14.08. ppm. Elemental Analysis calcd. for (C₁₈H₂₇NO₂): C (74.70), H (9.40), N (4.84), found: C (75.21), H (9.63), N (4.62). LR MS (ESI) *m/z* calcd. for (C₁₈H₂₇NO₂): 289.20, found 290.28 [M+H]⁺. IR ν_{max} (CH₂Cl₂)/cm⁻¹: 1067, 1091, 1181, 1205, 1217, 1361, 1457, 1483, 1749 (C=O), 2500, 2857, 2929, 2959.

3. Optimization of the reaction conditions for the synthesis of oxazolidin-2-one 13

Study of the reaction dependence on the aziridine concentration

In a 3.5 mL glass liner equipped with a screw cap and glass wool, the desired amount of (NHC)CuCl (**12**), TBACl salt and *N*-tosyl aziridine were dissolved in DCE (0.5 mL). The vessel was transferred into a stainless-steel autoclave and 1.2 MPa CO₂ pressure was charged at room temperature. The autoclave was placed in a preheated oil bath at 85 °C, stirred for 16 hours and then quenched in an ice bath and slowly vented. The solvent was evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S4 and summarized in figure 2A of the manuscript.

Table S4 Study of the reaction dependence on the aziridine concentration.

Entry	aziridine concentration (M)	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	1	88	58	51	80:20
2	0.5	85	65	55	80:20
3	0.25	86	67	58	80:20

Study of the reaction dependence on the CO₂ pressure

In a 3.5 mL glass liner equipped with a screw cap and glass wool, (NHC)CuCl (**12**) (1.25 x 10⁻⁶ mol), TBACl salt (1.25 x 10⁻⁶ mol) and *N*-tosyl aziridine (1.25 x 10⁻⁴ mol), were dissolved in DCE (0.5 mL). The vessel was transferred into a stainless-steel autoclave and the desired CO₂ pressure was charged at room temperature. The autoclave was placed in a preheated oil bath at 85 °C, stirred for 16 hours and then quenched in an ice bath and slowly vented. The solvent was evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S5 and summarized in figure 2B of the manuscript.

Table S5 Study of the reaction dependence on the CO₂ pressure.

Entry	CO ₂ pressure (MPa)	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	1.5	86	67	58	80:20
2	2.0	89	75	67	80:20

Study of the reaction dependence on the solvent

In a 3.5 mL glass liner equipped with a screw cap and glass wool, (NHC)CuCl (**12**) (1.25 x 10⁻⁶ mol), TBACl salt (1.25 x 10⁻⁶ mol) and *N*-tosyl aziridine (1.25 x 10⁻⁴ mol), were dissolved in the desired solvent (0.5 mL). The vessel was transferred into a stainless-steel autoclave and 2.0 MPa CO₂ pressure was charged at room temperature. The autoclave was placed in a preheated oil bath at 85 °C, stirred for 16 hours and then quenched in an ice bath and slowly vented. The solvent was evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using

2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S6 and summarized in figure 2C of the manuscript.

Table S6 Study of the reaction dependence on the solvent.

Entry	Solvent	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	THF	-	-	-	-
2	MeCN	90	52	46	80:20
3	DCE	89	75	67	80:20

Study of the reaction dependence on the temperature

In a 3.5 mL glass liner equipped with a screw cap and glass wool, (NHC)CuCl (**12**) (1.25×10^{-6} mol), TBACl salt (1.25×10^{-6} mol) and *N*-tosyl aziridine (1.25×10^{-4} mol), were dissolved in DCE (0.5 mL). The vessel was transferred into a stainless-steel autoclave and 2.0 MPa CO₂ pressure was charged at room temperature. The autoclave was placed in a preheated oil bath at the desired temperature, stirred for 16 hours and then quenched in an ice bath and slowly vented. The solvent was evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S7 and summarized in figure 2D of the manuscript.

Table S7 Study of the reaction dependence on the temperature.

Entry	Temperature (°C)	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	50	36	86	31	80:20
2	65	51	99	50	80:20
3	75	85	78	66	80:20
4	85	89	75	67	80:20

Study of the reaction dependence on the time

In a 3.5 mL glass liner equipped with a screw cap and glass wool, (NHC)CuCl (**12**) (1.25×10^{-6} mol), TBACl salt (1.25×10^{-6} mol) and *N*-tosyl aziridine (1.25×10^{-4} mol), were dissolved in DCE (0.5 mL). The vessel was transferred into a stainless-steel autoclave and 2.0 MPa CO₂ pressure was charged at room temperature. The autoclave was placed in a preheated oil bath at 65°C, stirred for the desired time and then quenched in an ice bath and slowly vented. The solvent was evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S8 and summarized in figure 2E of the manuscript.

Table S8 Study of the reaction dependence on the time.

Entry	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	16	51	99	50	80:20
2	24	67	99	66	80:20
3	48	70	96	68	80:20
4	72	72	96	70	80:20

Study of the reaction dependence on catalyst loading

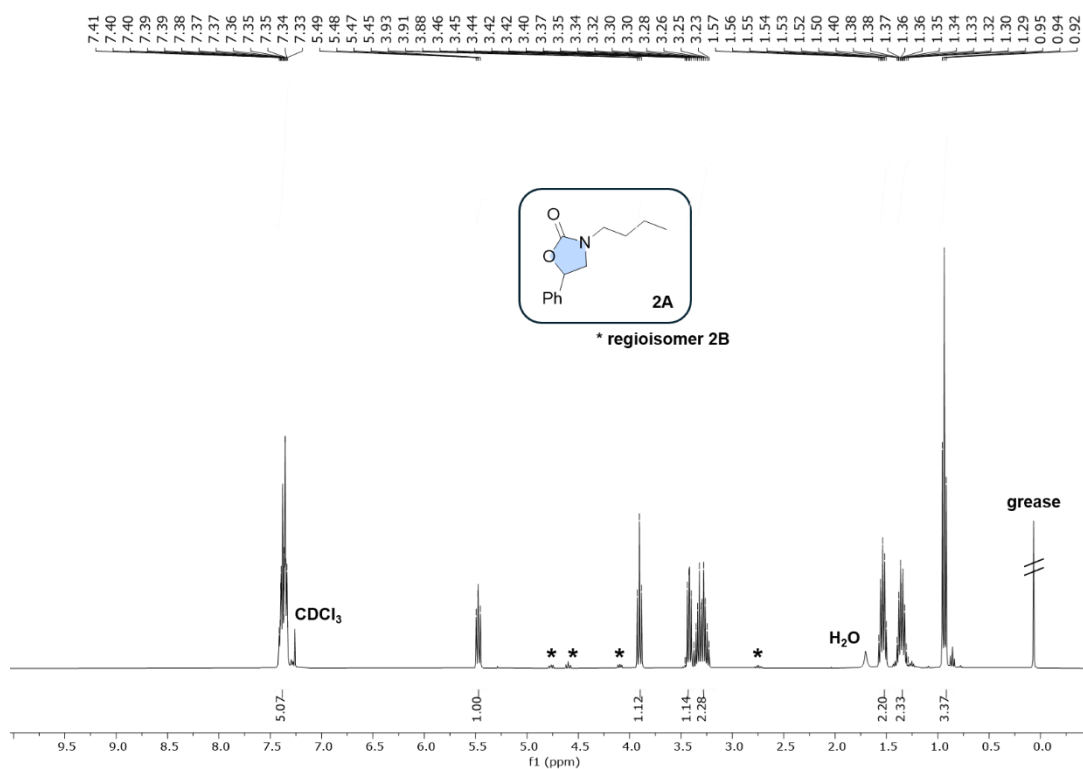
In a 3.5 mL glass liner equipped with a screw cap and glass wool, the desired amount of (NHC)CuCl (**12**) TBACl salt and *N*-tosyl aziridine (1.25×10^{-4} mol), were dissolved in DCE (0.5 mL). The vessel was transferred into a stainless-steel autoclave and 2.0 MPa CO₂ pressure was charged at room temperature. The autoclave was placed in a preheated oil bath at 65°C, stirred for 24 hours and then quenched in an ice bath and slowly vented. The solvent was evaporated to dryness and the crude analyzed by ¹H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. Obtained data are reported in Table S9 and summarized in figure 2F of the manuscript.

Table S9 Study of the reaction dependence on catalyst loading.

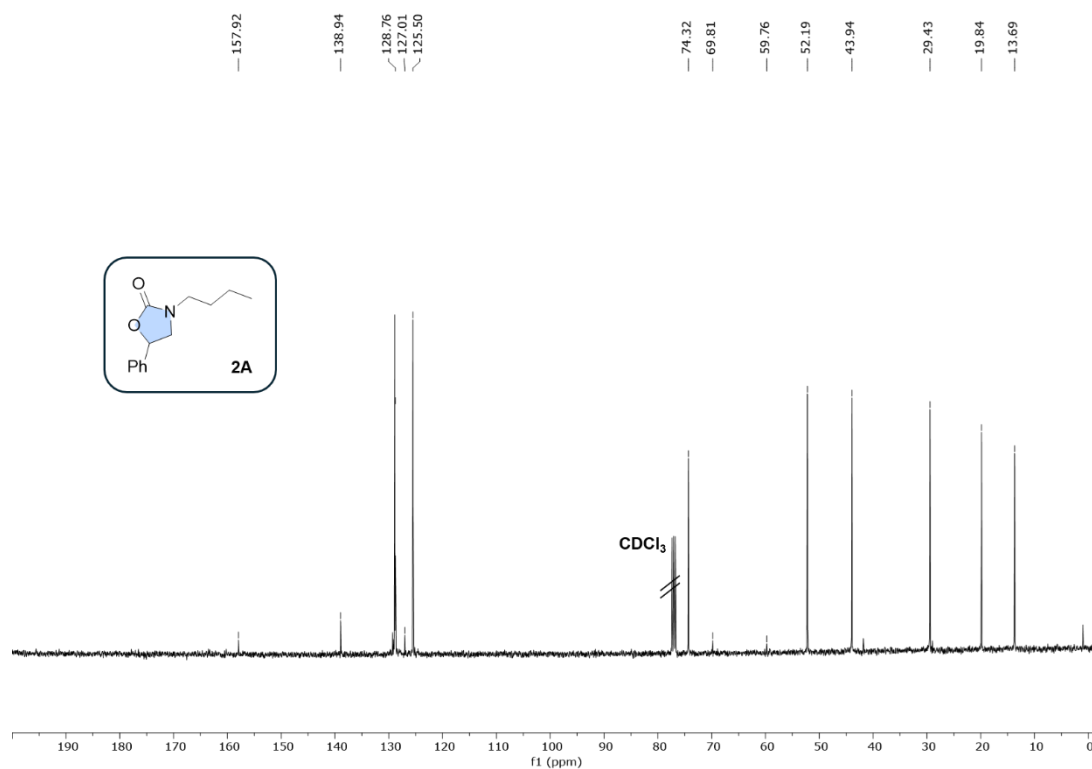
Entry	Catalyst loading (mol%)	Conversion (%)	Selectivity (%)	Yield (%)	A/B ratio
1	10	67	99	66	80:20
2	20	90	99	88	80:20

4. ¹H and ¹³C NMR spectra

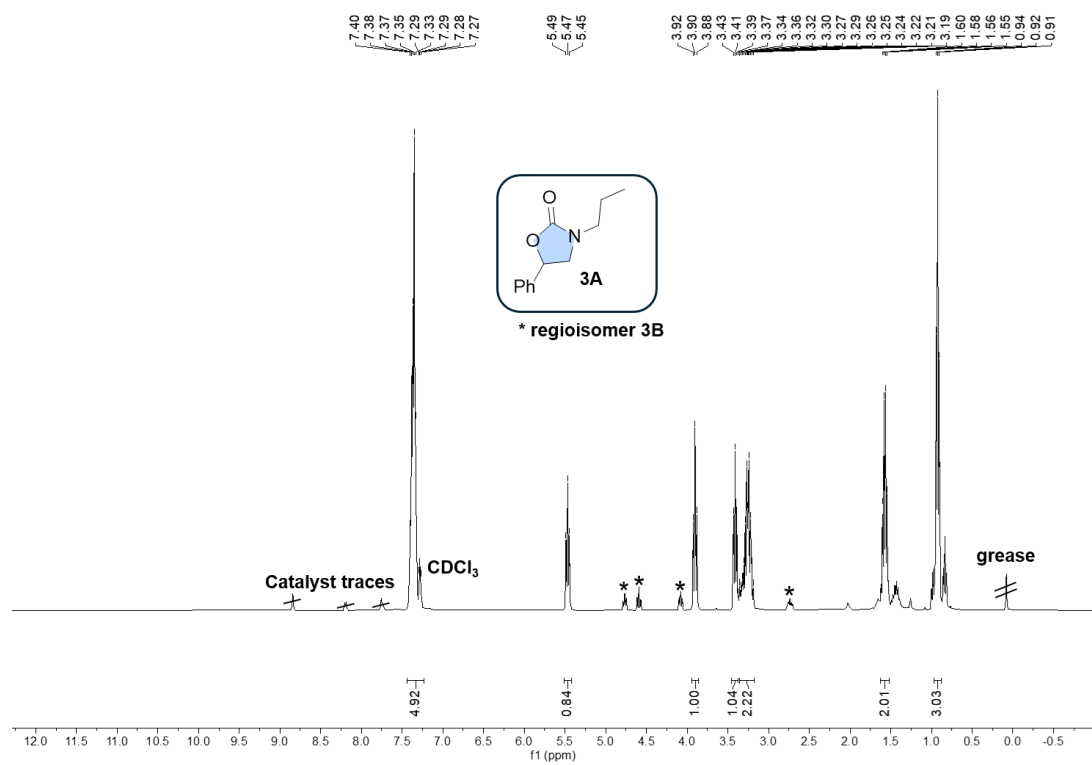
¹H NMR spectrum (400 MHz, CDCl₃, 298K) of **2**



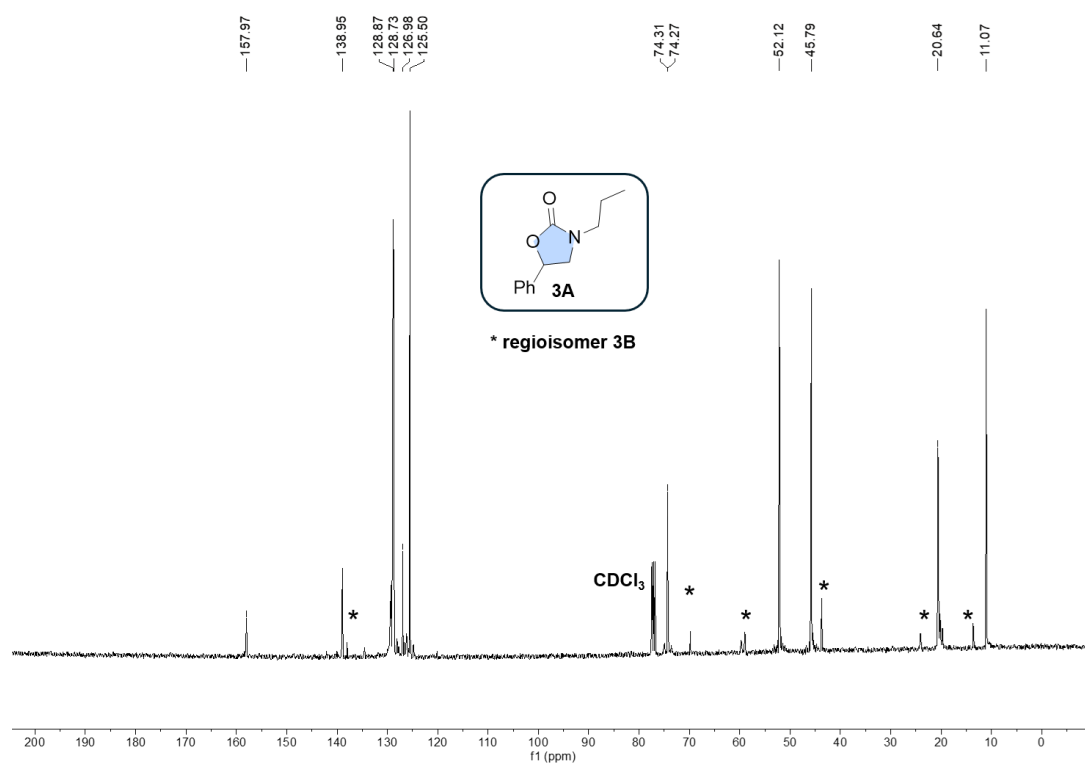
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 2



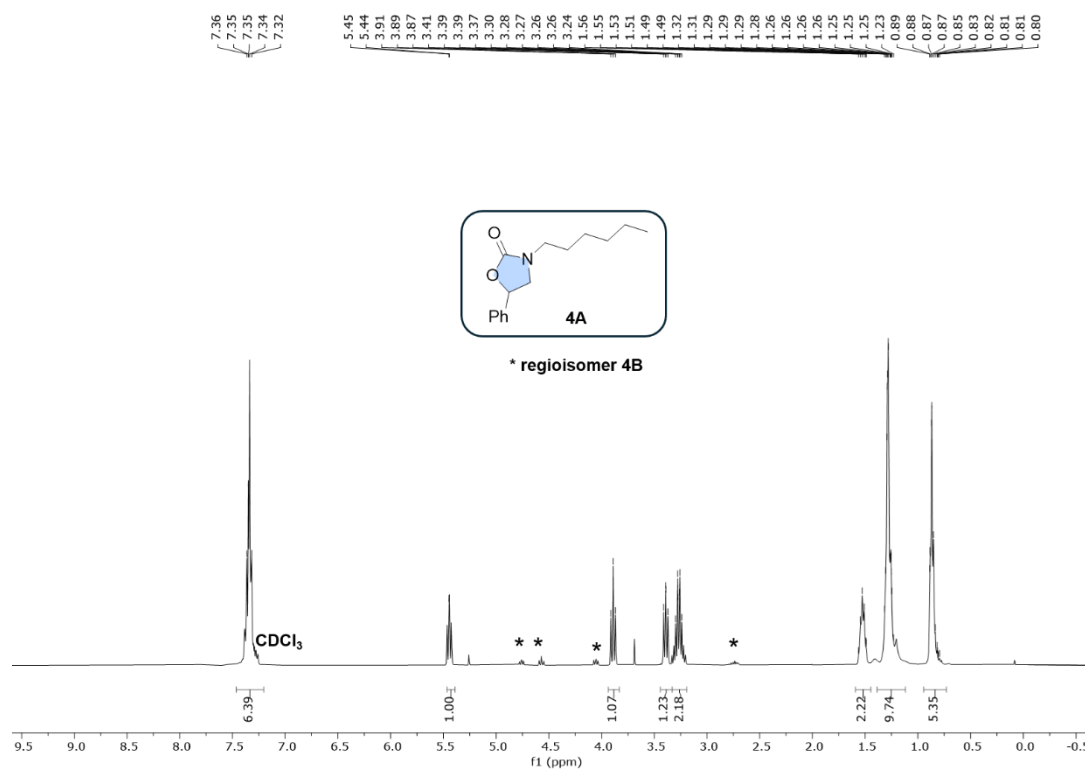
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 3



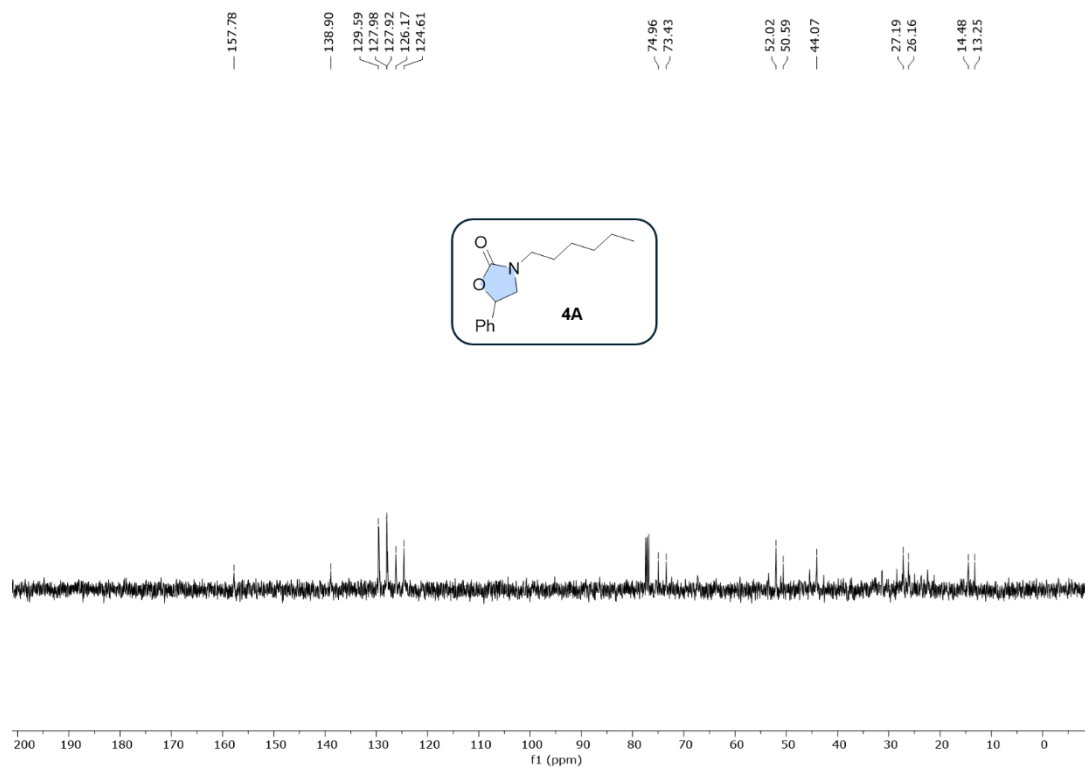
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 3



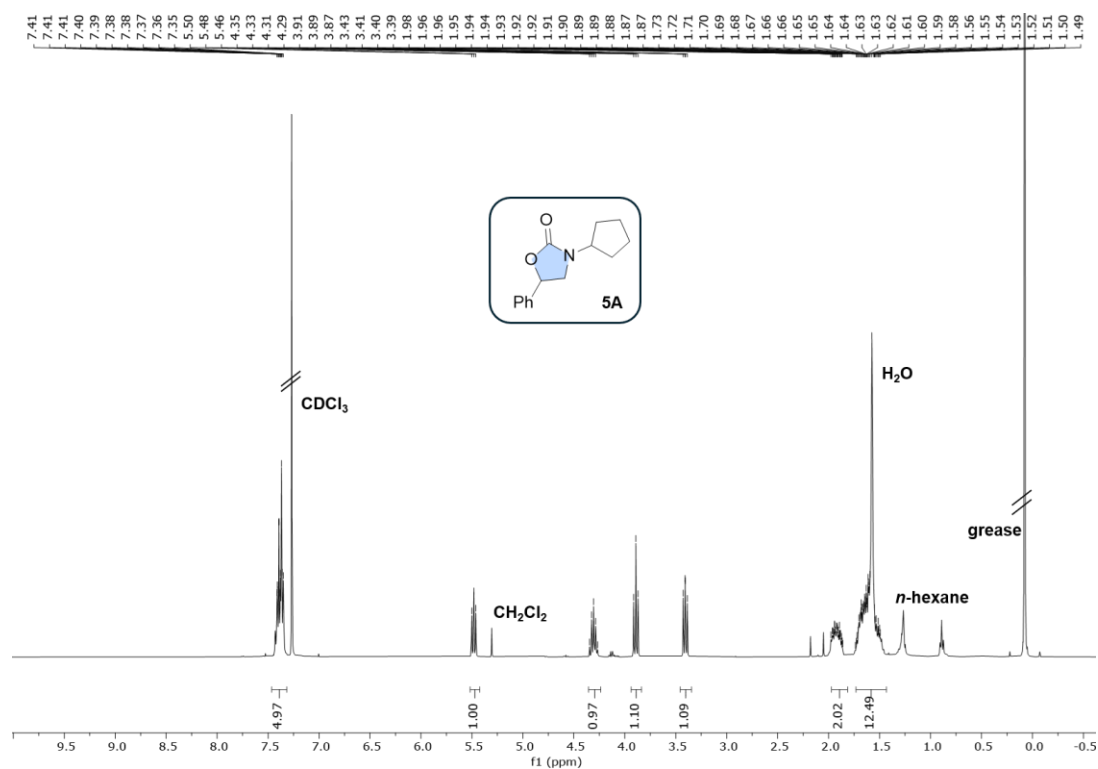
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 4



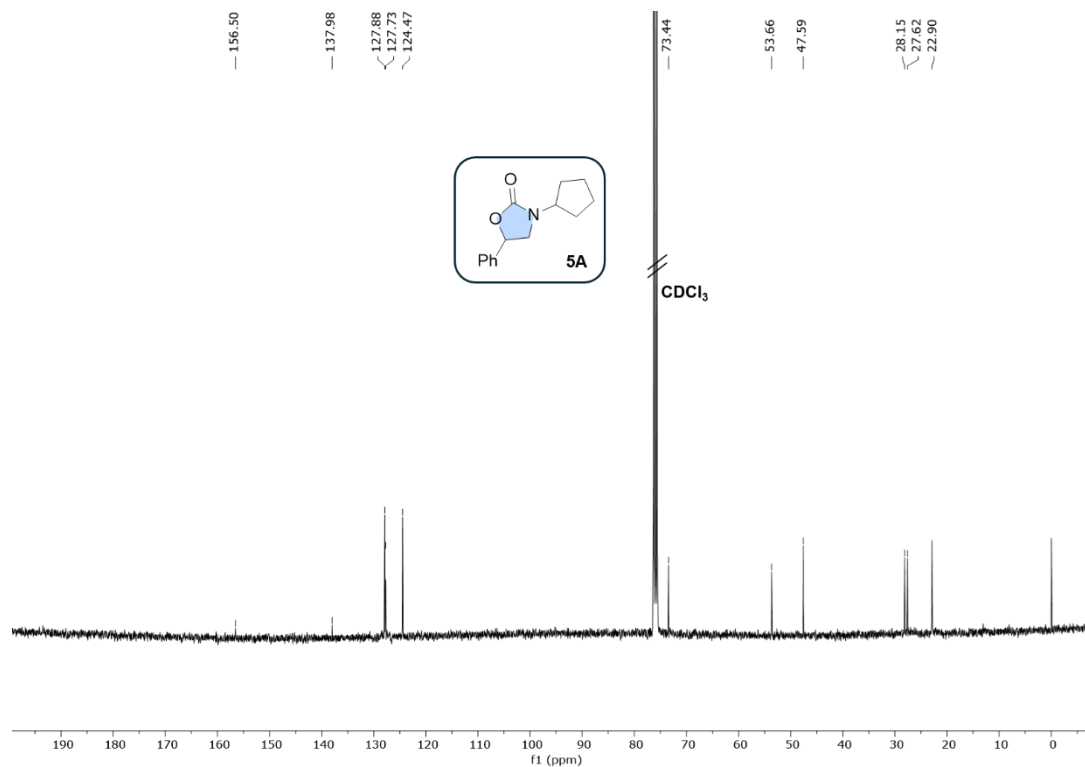
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 4



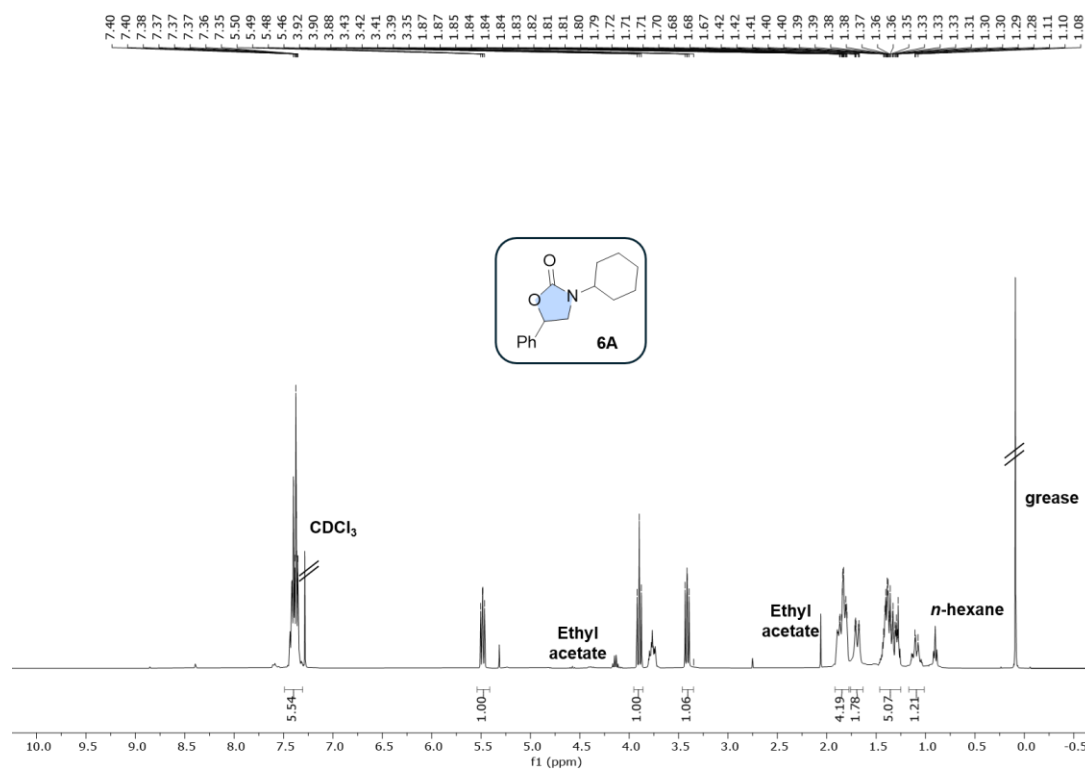
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 5



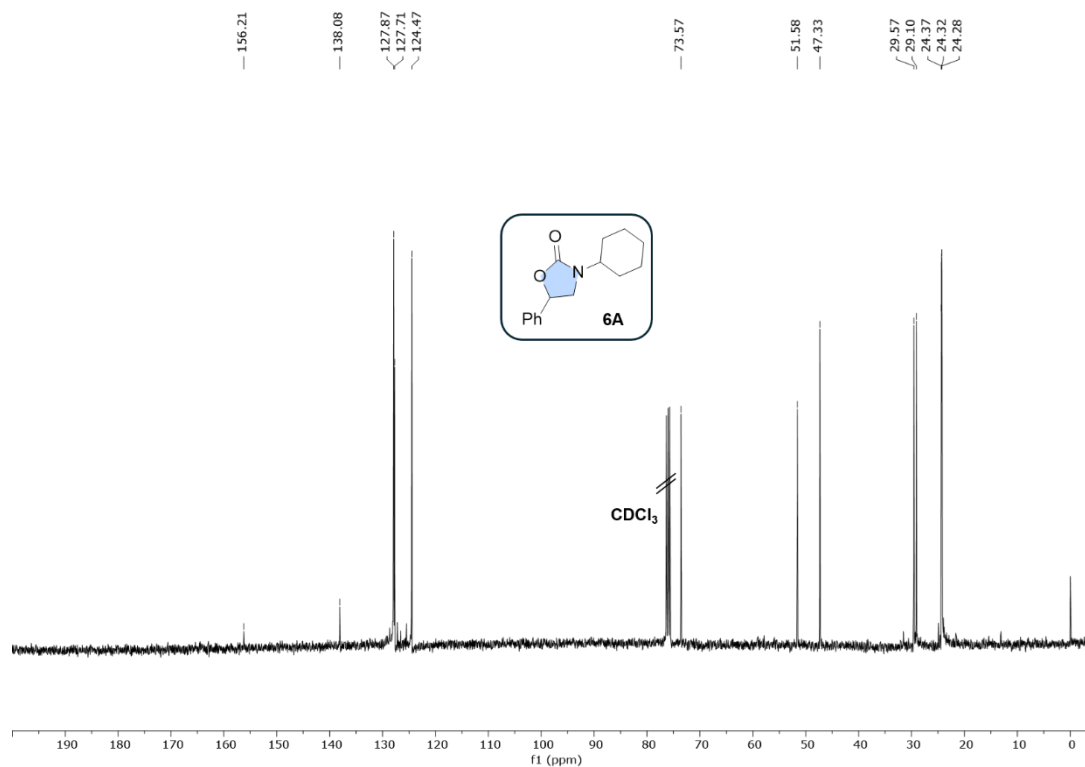
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 5



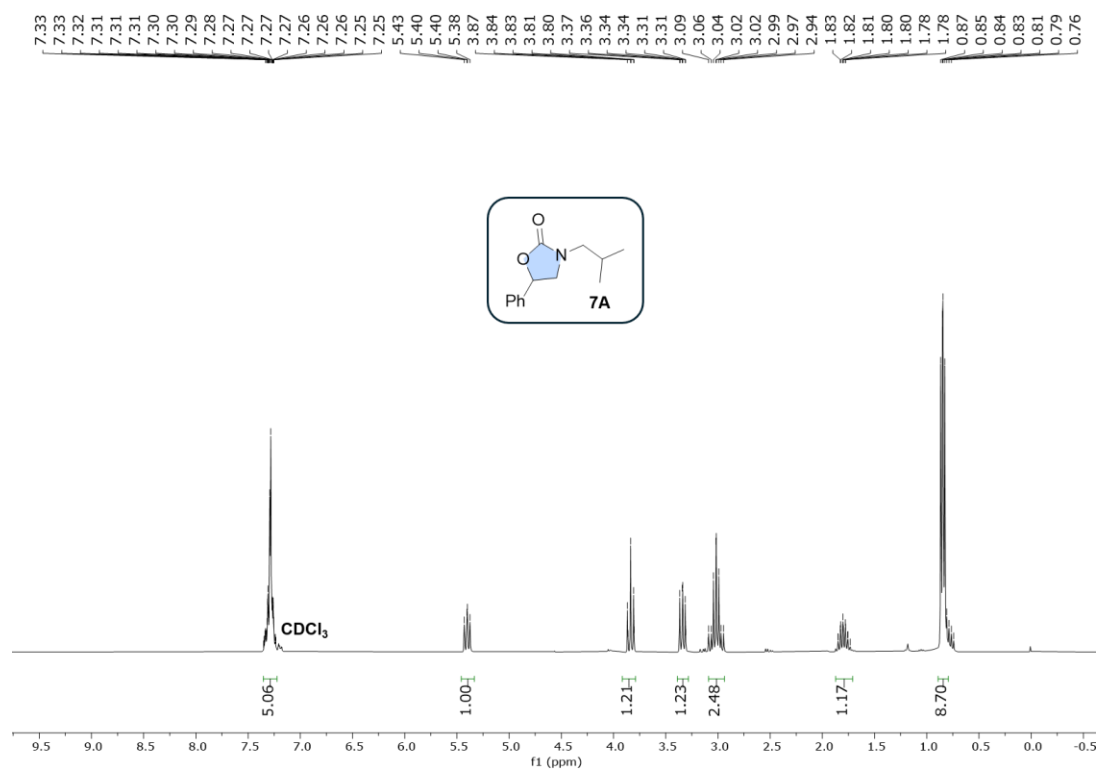
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 6



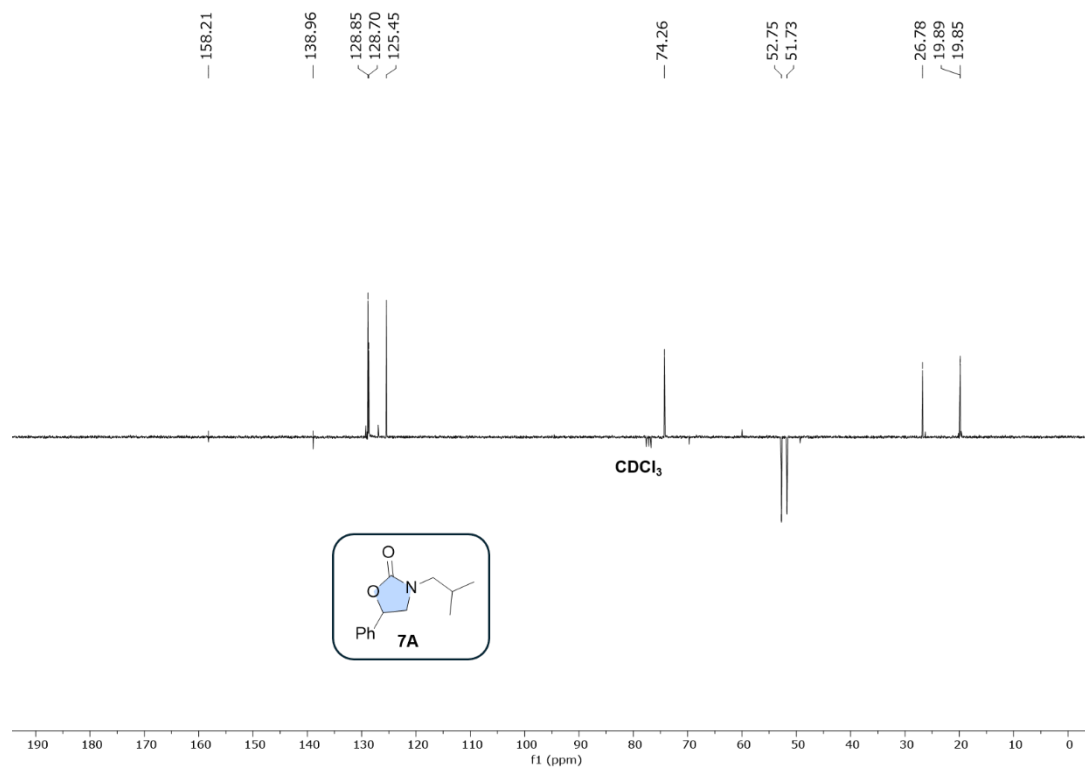
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 6



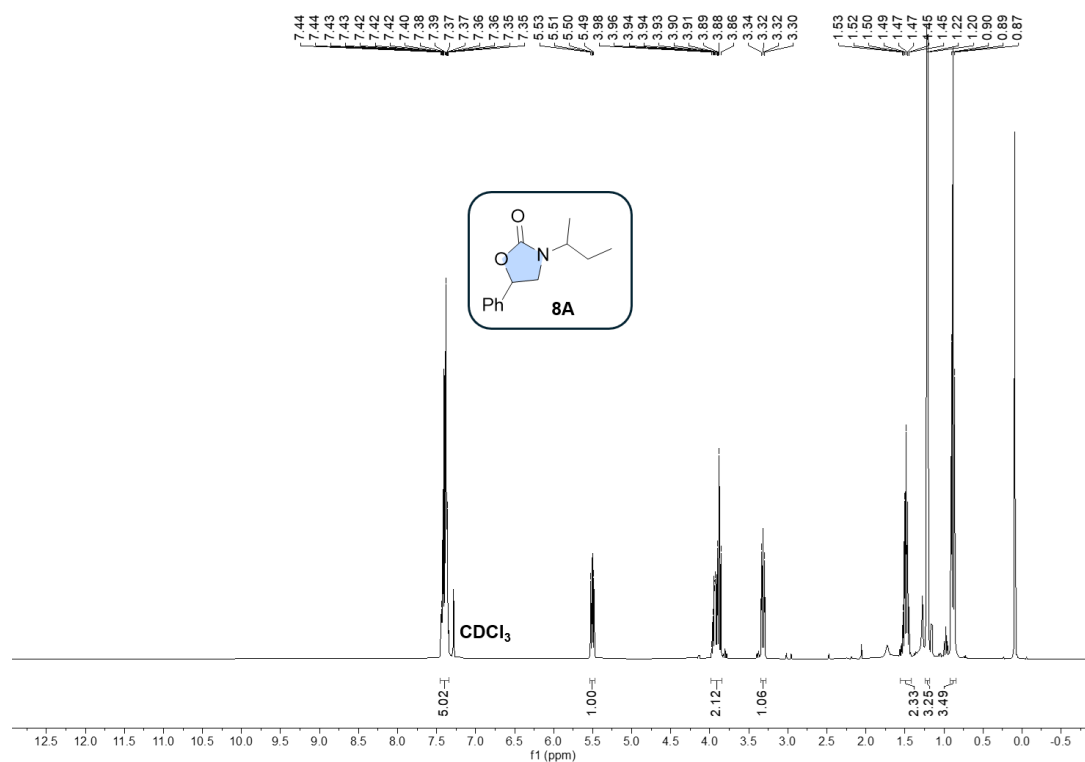
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 7



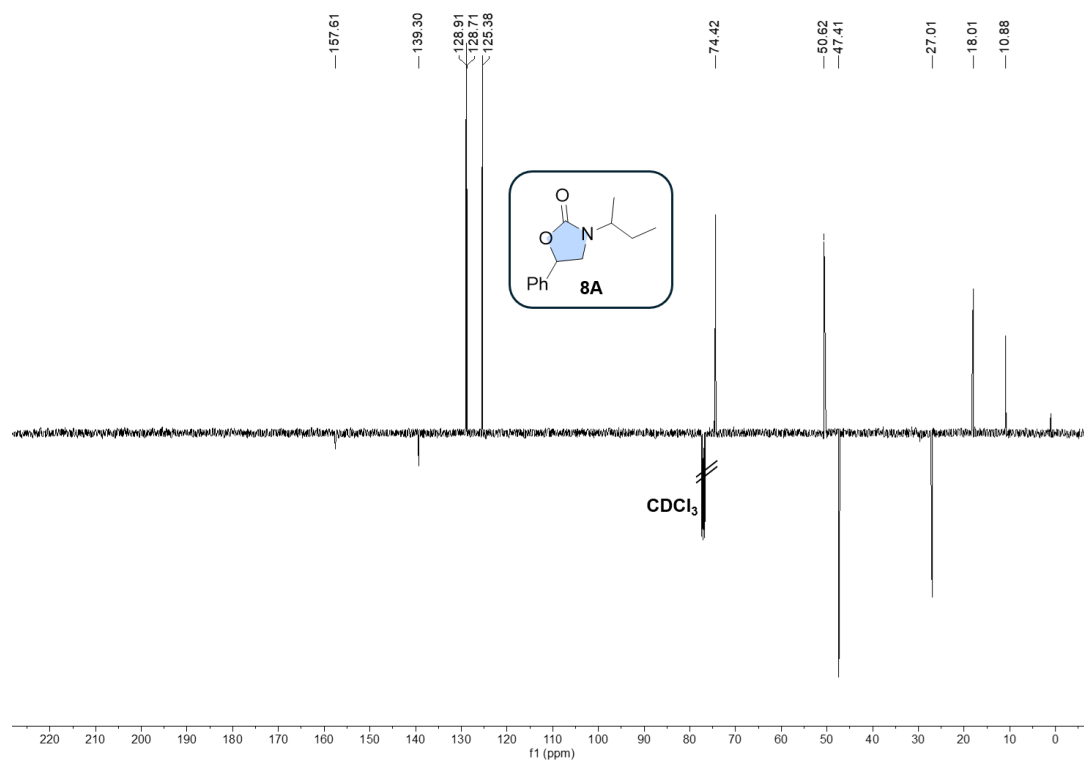
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 7



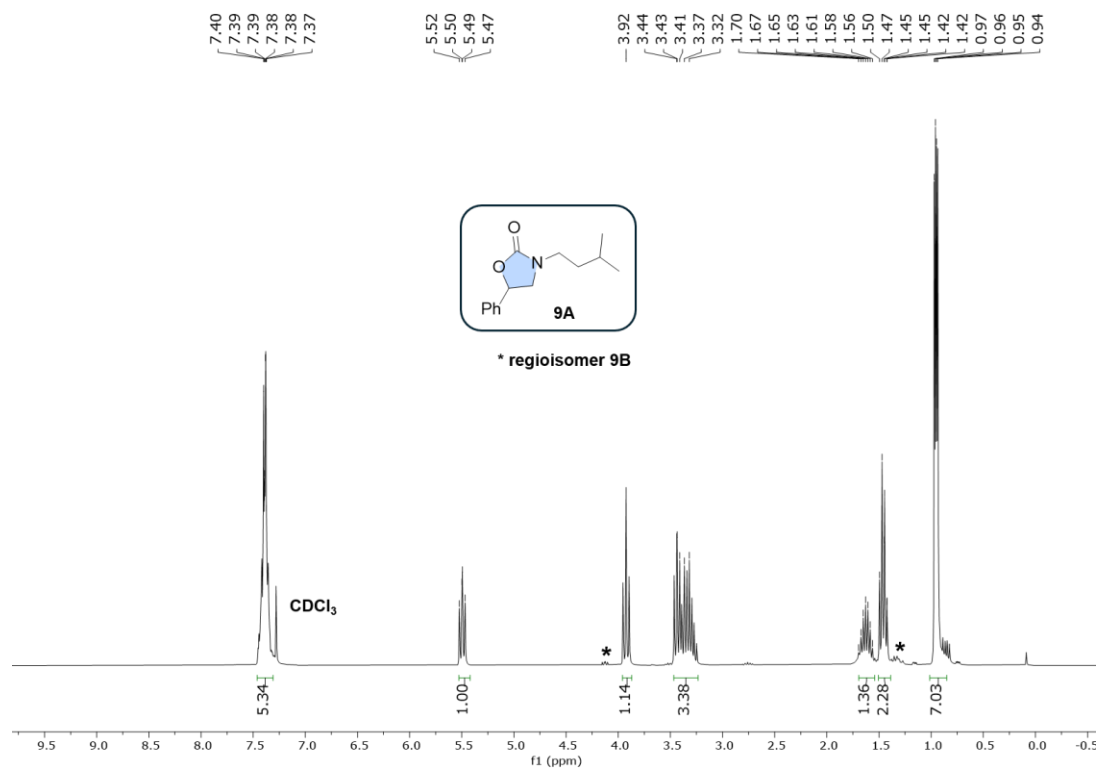
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 8



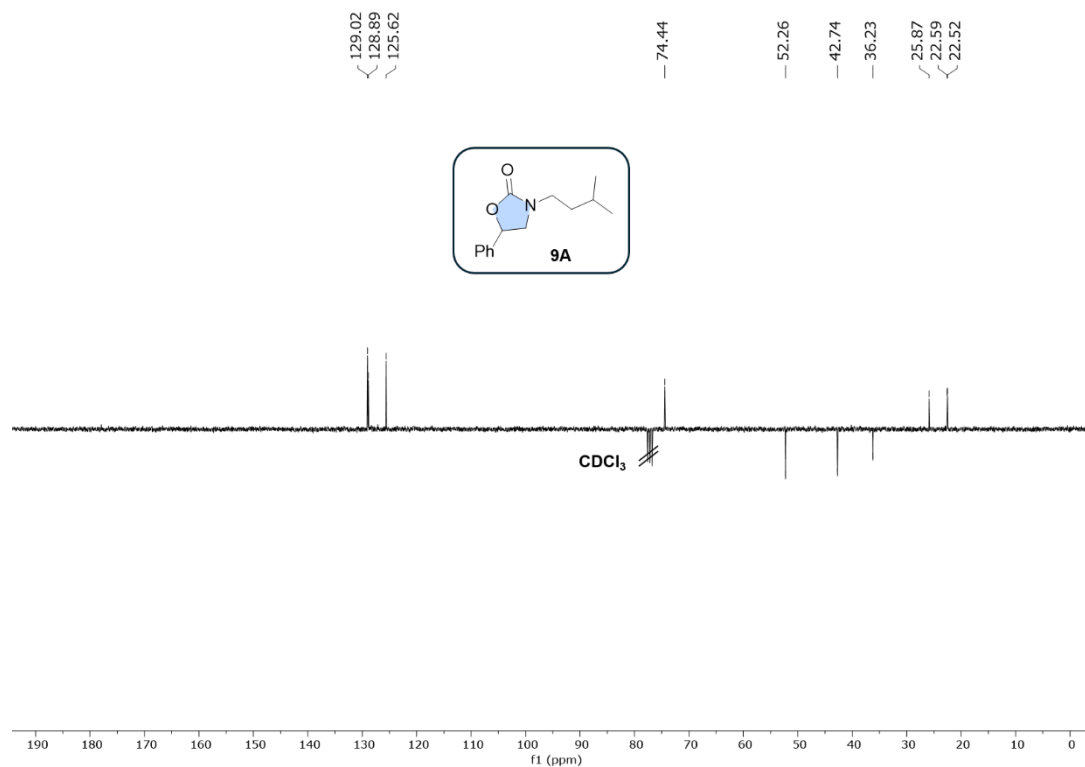
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 8



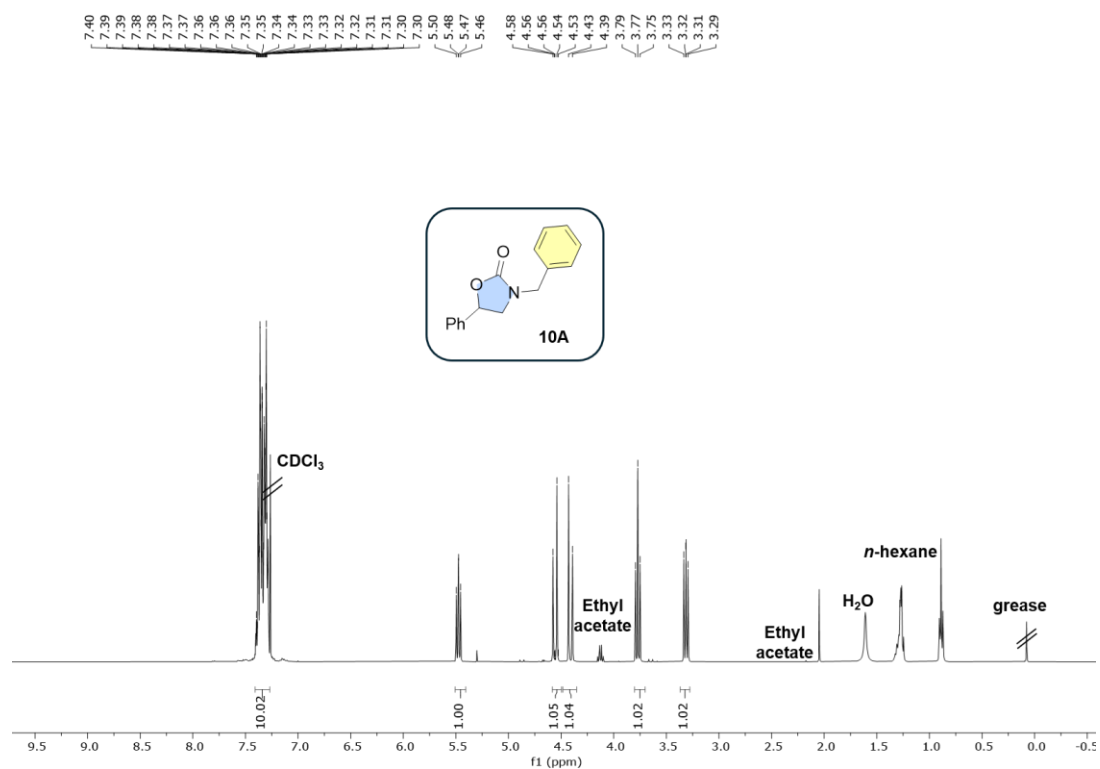
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 9



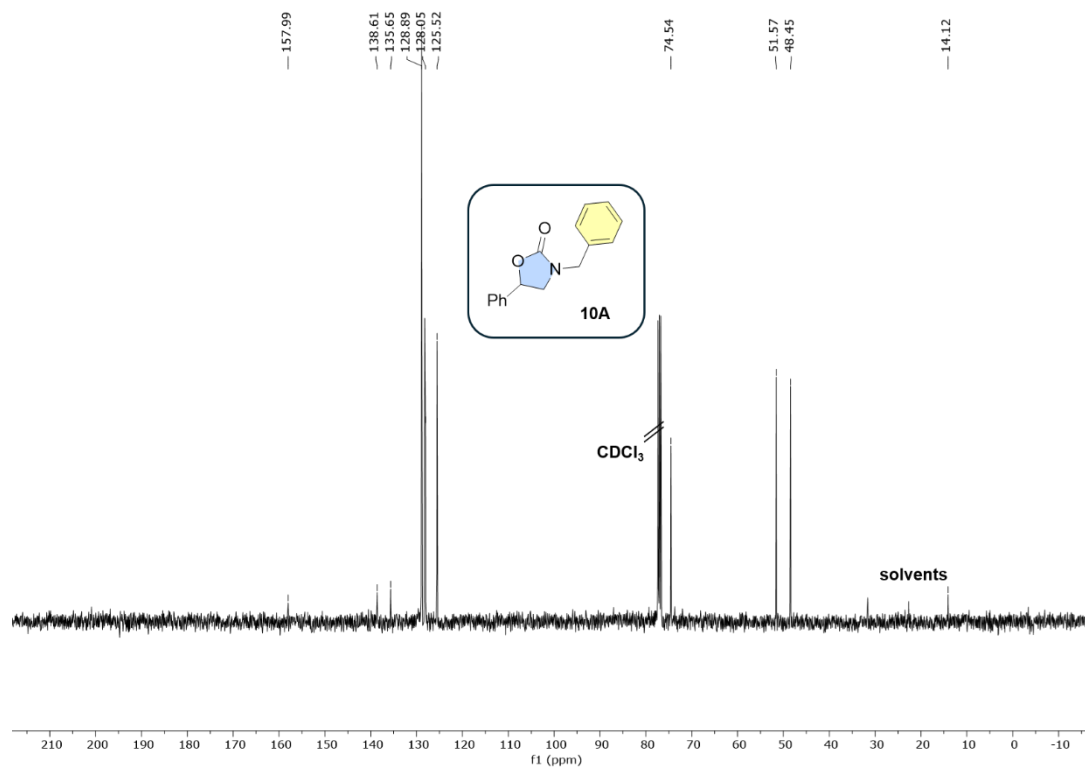
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 9



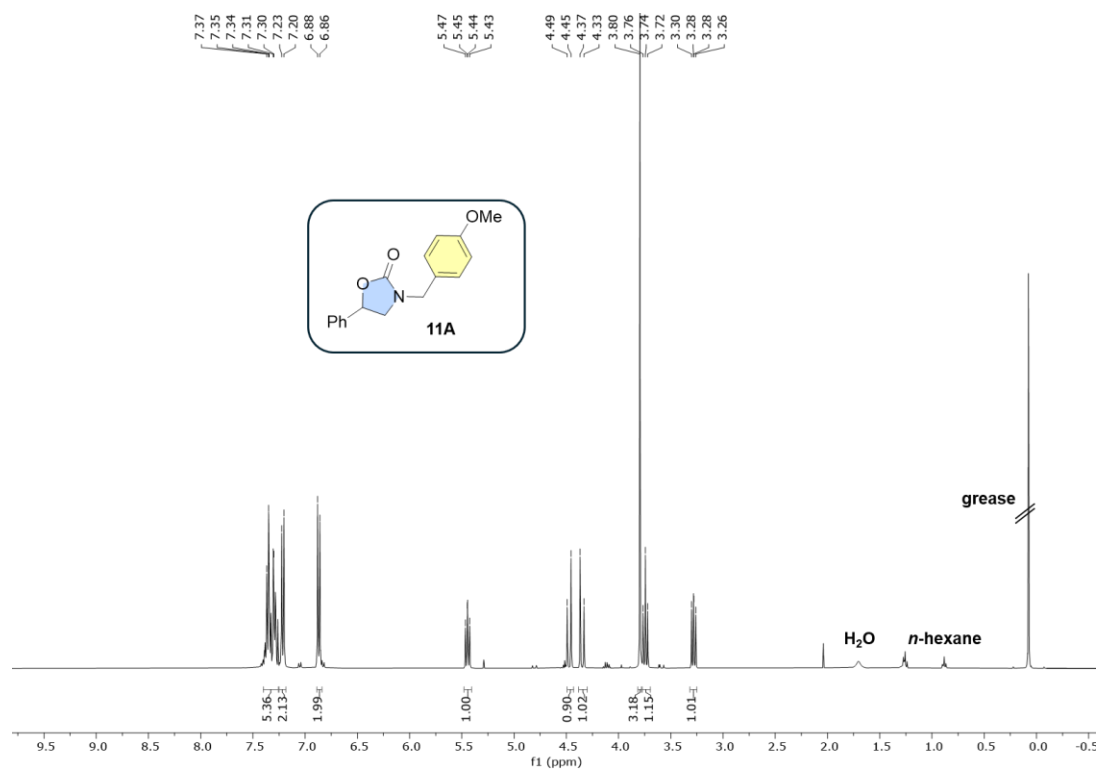
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 10



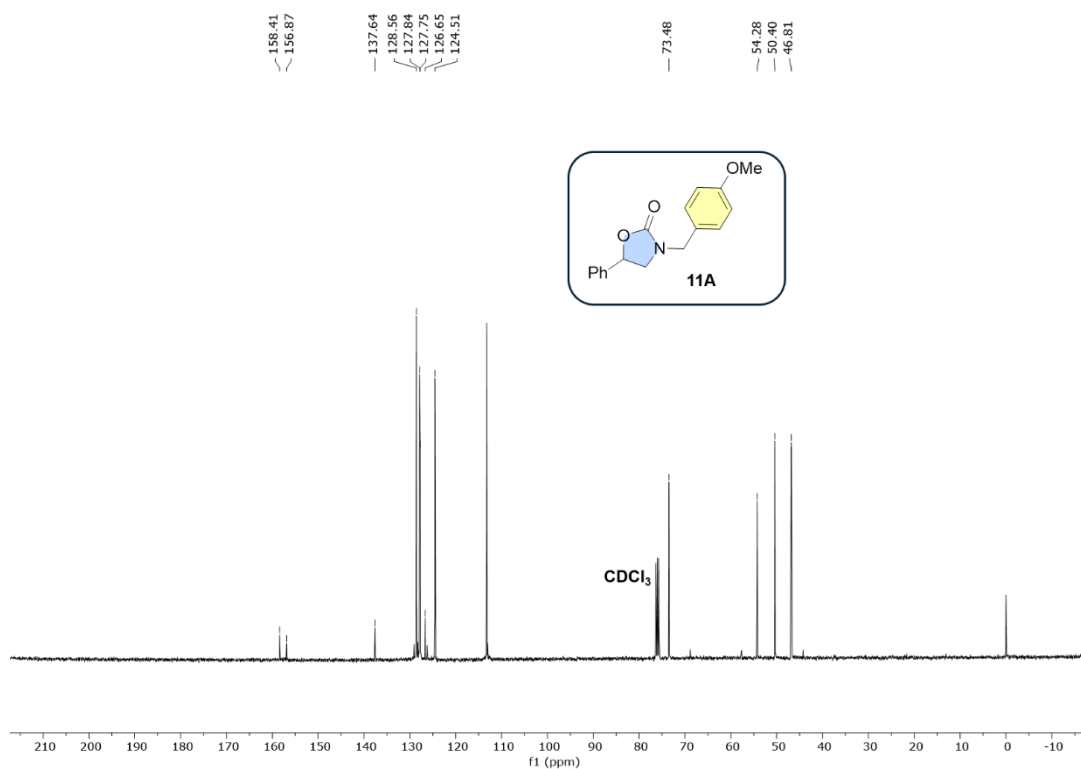
^{13}C NMR spectrum (101 MHz, CDCl_3 , 298K) of 10



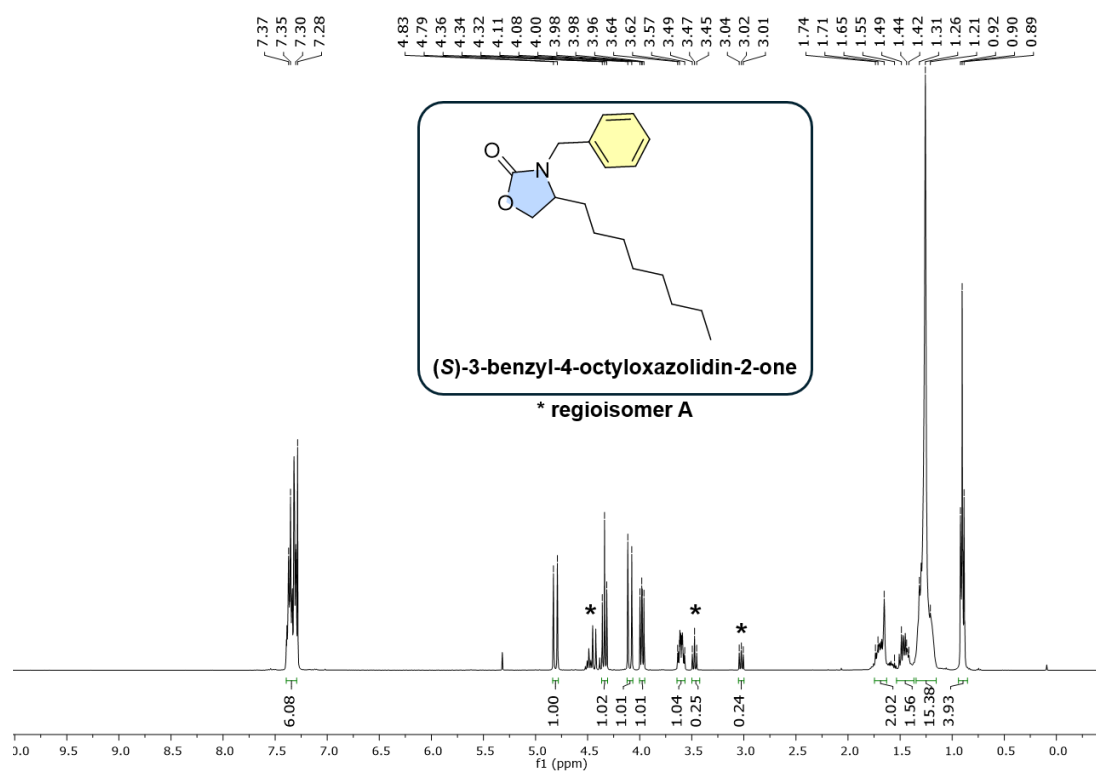
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of 11



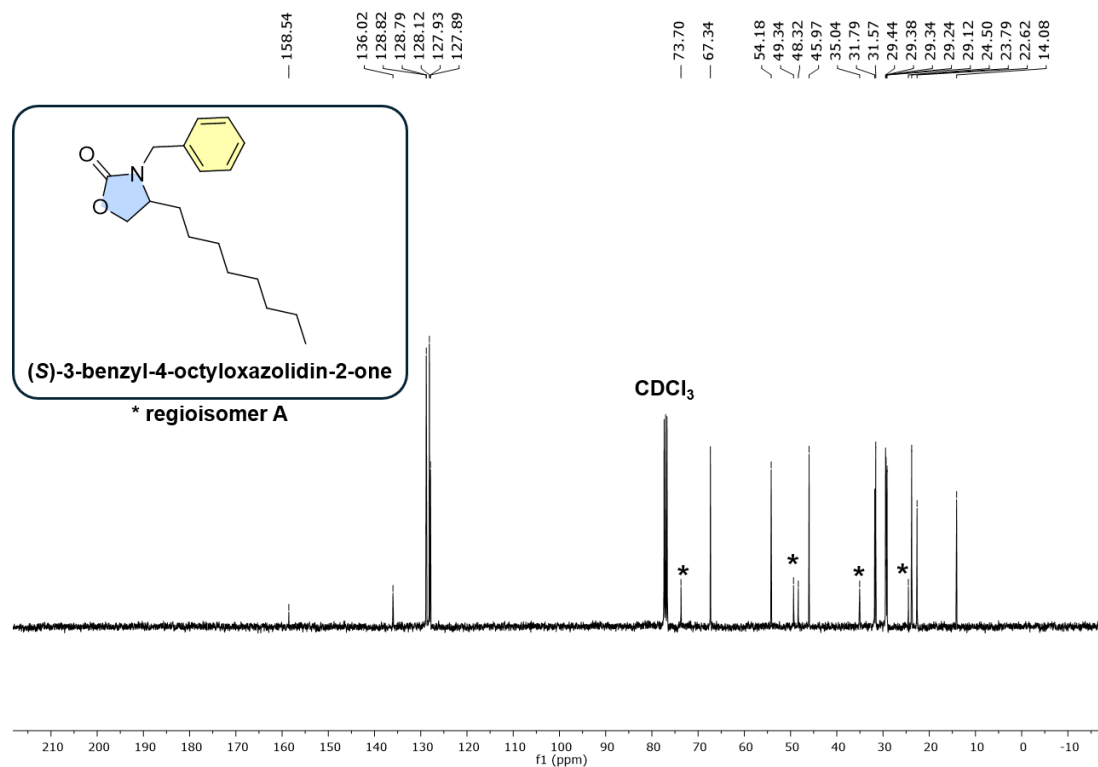
^{13}C NMR spectrum (300 MHz, CDCl_3 , 298K) of 11



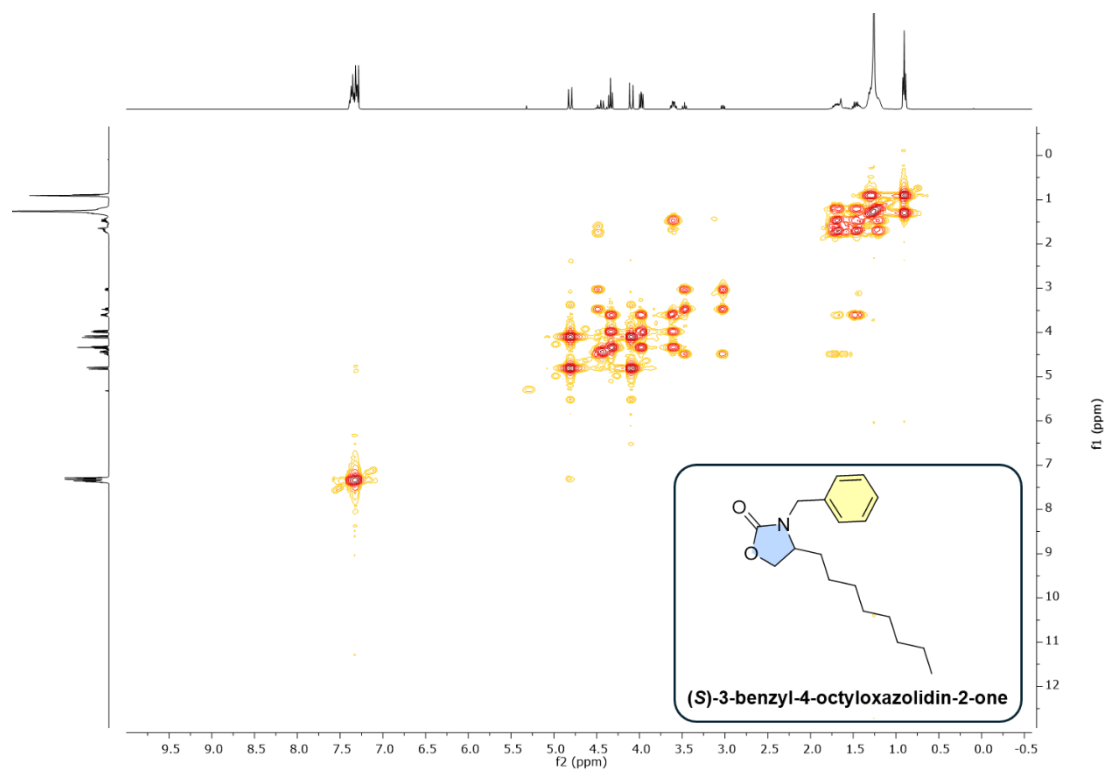
^1H NMR spectrum (400 MHz, CDCl_3 , 298K) of (S)-3-benzyl-4-octyloxazolidin-2-one



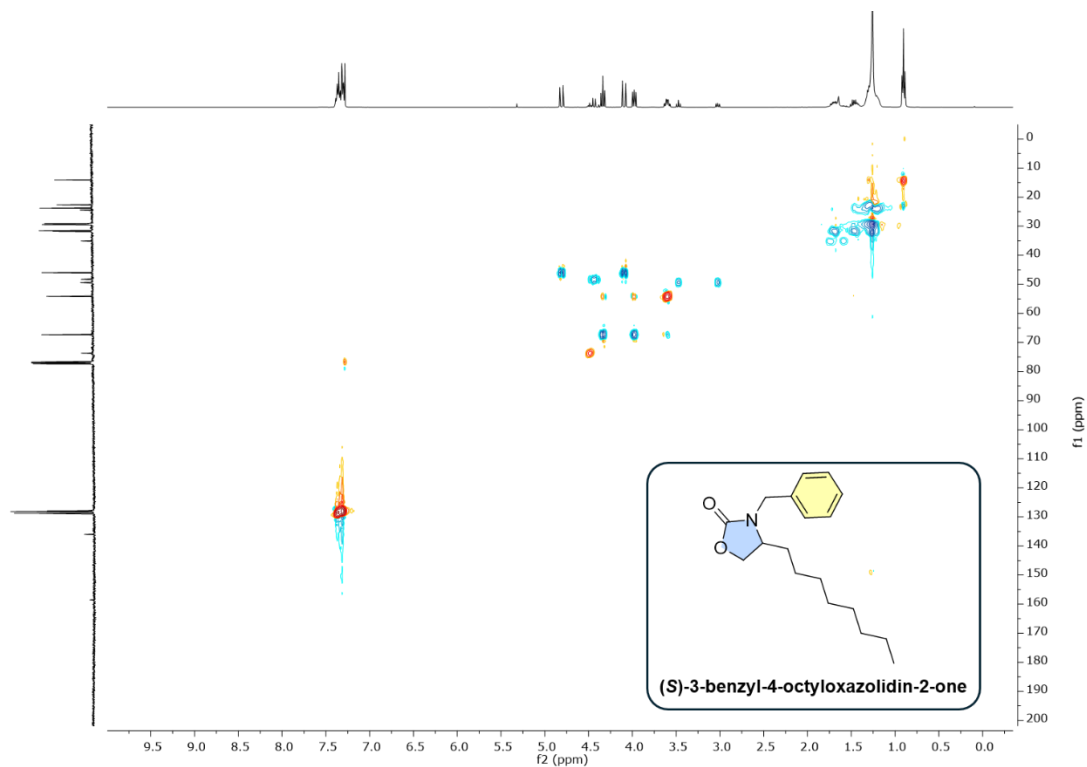
^{13}C NMR spectrum (300 MHz, CDCl_3 , 298K) of (S)-3-benzyl-4-octyloxazolidin-2-one



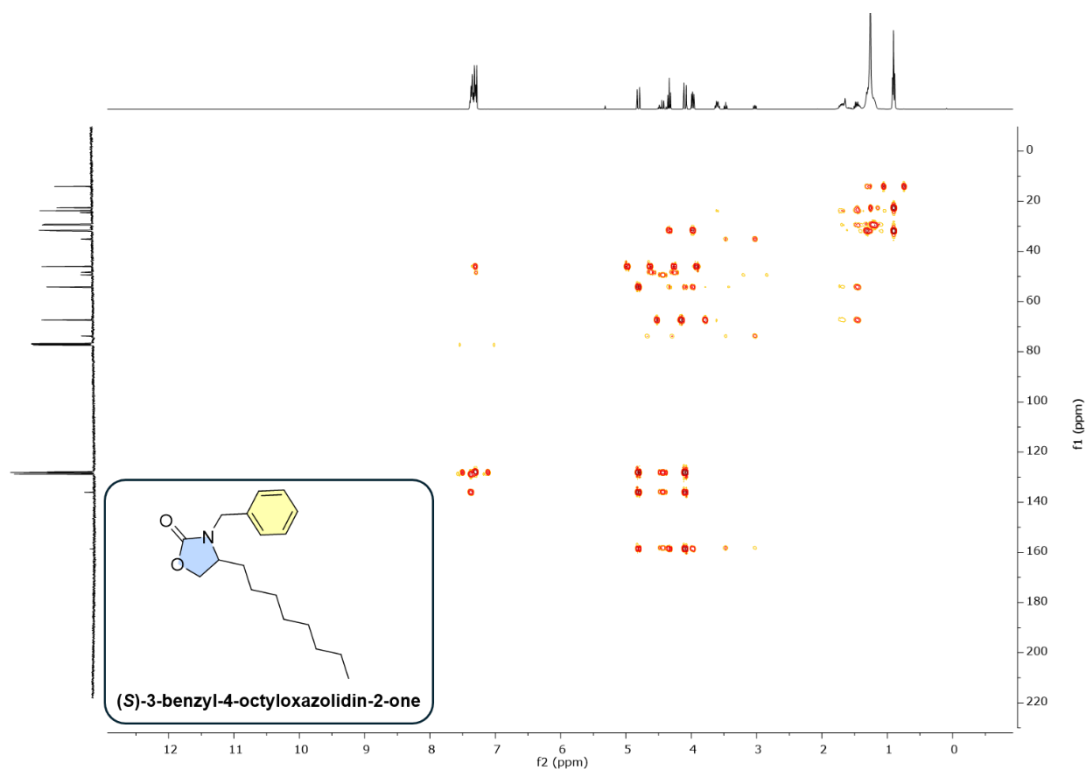
COSY spectrum of (S)-3-benzyl-4-octyloxazolidin-2-one



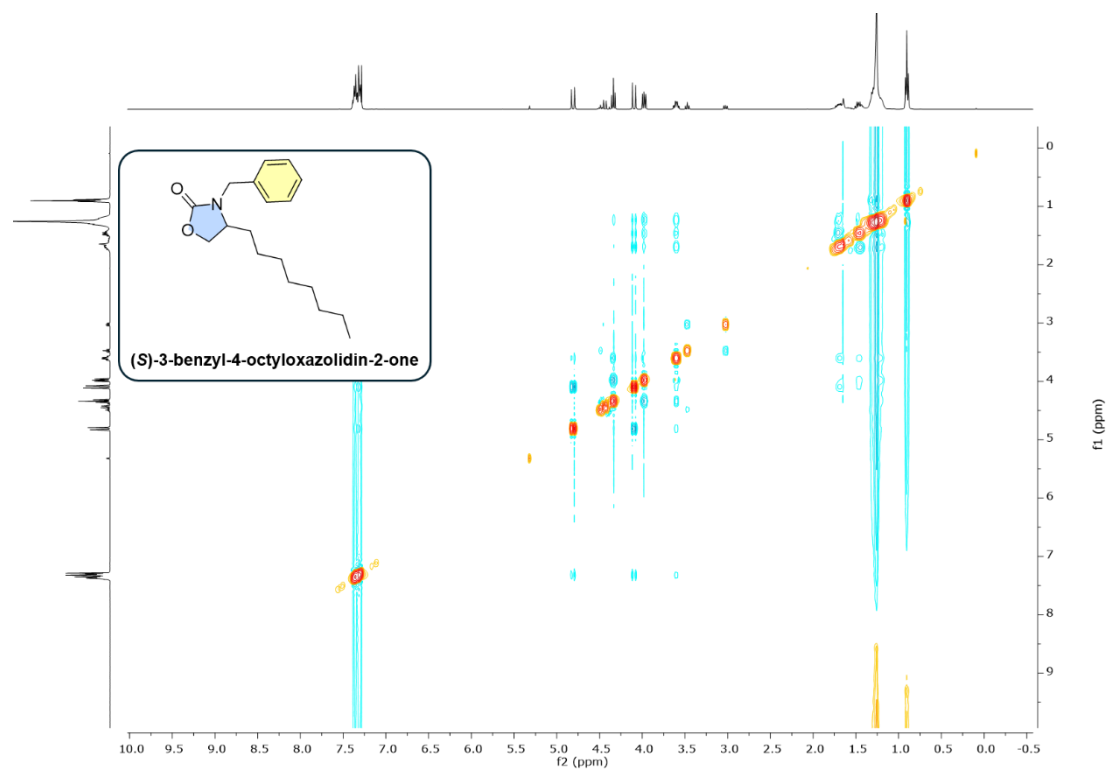
HSQC spectrum of (S)-3-benzyl-4-octyloxazolidin-2-one



HMBC spectrum of (S)-3-benzyl-4-octyloxazolidin-2-one



NOESY spectrum of (S)-3-benzyl-4-octyloxazolidin-2-one



5. References

1. Cavalleri, M.; Damiano, C.; Manca, G.; Gallo, E. *Chem. Eur. J.* **2023**, 29, e202202729.
2. Damiano, C.; Fata, A.; Cavalleri, M.; Manca, G.; Gallo, E. *Catal. Sci. Technol.* **2024**, 14, 3996.
3. Sonzini, P.; Berthet, N.; Damiano, C.; Dufaud V.; Gallo, E. *J. Catal.* **2022**, 414, 143.
4. Invernizzi, L.; Damiano C.; Gallo, E. *Chem. Eur. J.* **2025**, 31, e202500473.