Electronic Supplementary Material (ESI) for CrystEngComm.

A Highly Stable Cerium-Organic Framework: Efficient Catalyst for the Cycloaddition of CO_2 and Aziridines under Mild-Pressure

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Materials and measurements

$Ce(NO_3)_3 \cdot 6H_2O$, CH_3COONa , Acetic acid, and *N,N*-dimethylacetamide (DMA) were purchased commercially and used without purification. The ligand H_2DCTP was synthesized according to our previous work.[1] The X-ray crystallography data were acquired on an Oxford Super Nova TM diffractometer equipped with Mo Kα monochromatic radiation (λ = 0.71073) (Table S1). The crystal structure of compound **1** was solved by direct methods and refined by the full-matrix least-squares technique on F^2 with the SHELXS and SHELXL crystallographic program package. All the non-hydrogen atoms were fixed by anisotropic thermal parameters. The CCDC number is 2333439. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were conducted in a 400 MHz Bruker 400 spectrometer in $CDCl_3$. Fourier transform infrared (FT-IR) spectra were performed on the Nicolet IS10 instrument. Powder X-ray diffraction (PXRD) was carried out with an Ultima IV X-ray diffractometer with Cu-Kα radiation. Thermogravimetric analysis was obtained by an EVO2G-TG TG-DTA analyzer under the air atmosphere. X-ray photoelectron spectroscopy (XPS) analyses were recorded on Thermo Scientific ESCALab250xi.

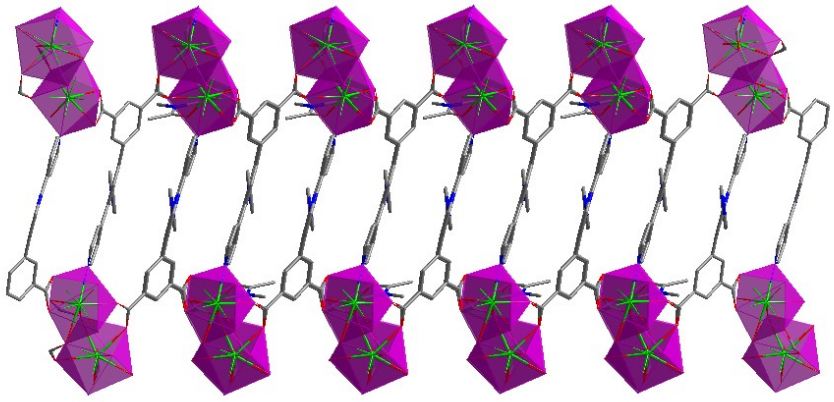


Figure S1. The pore structure diagram of **1** on the (1,1,0) crystal plane.

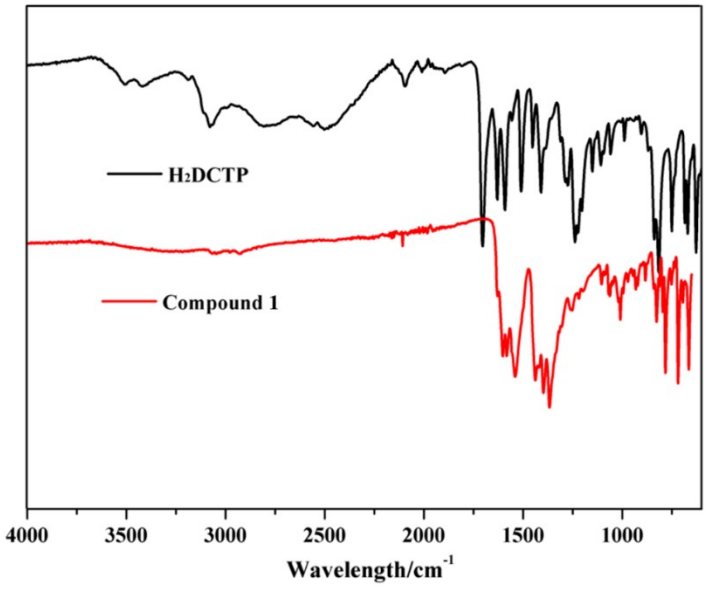


Figure S2. Infrared spectra compound **1** and H_2DCTP.

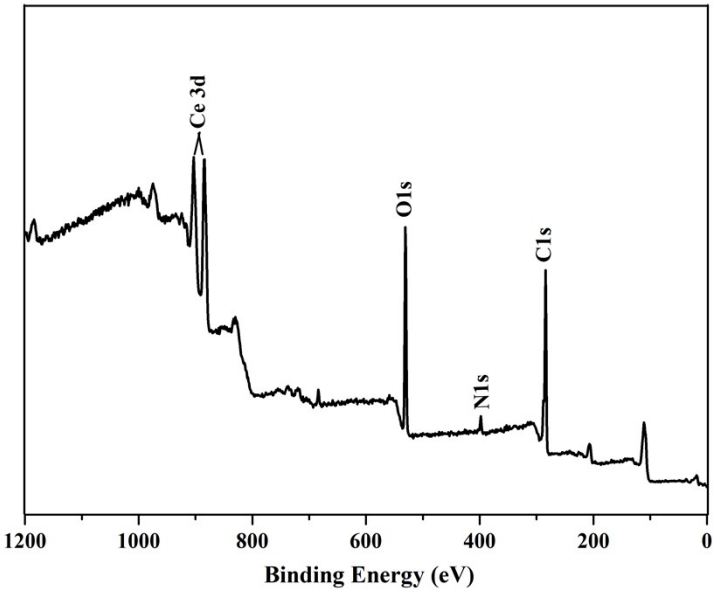


Figure S3. The full survey XPS spectrum of compound **1**.

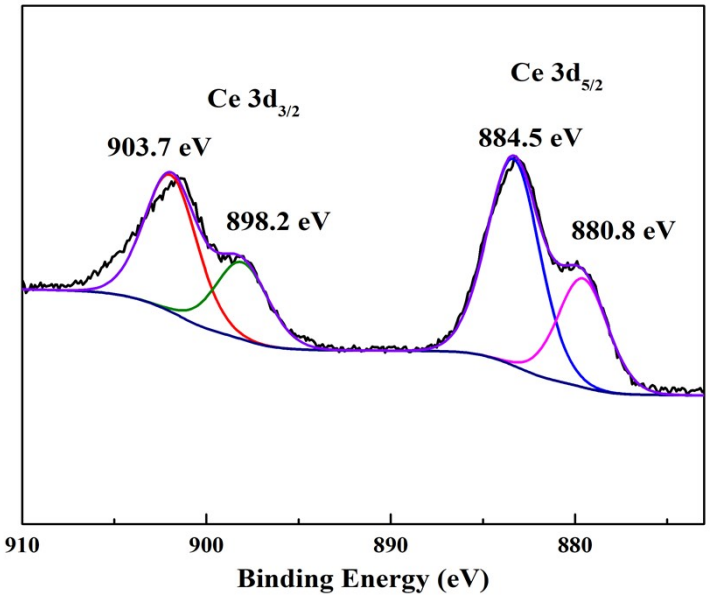


Figure S4. Ce 3d XPS spectrum in compound **1**.

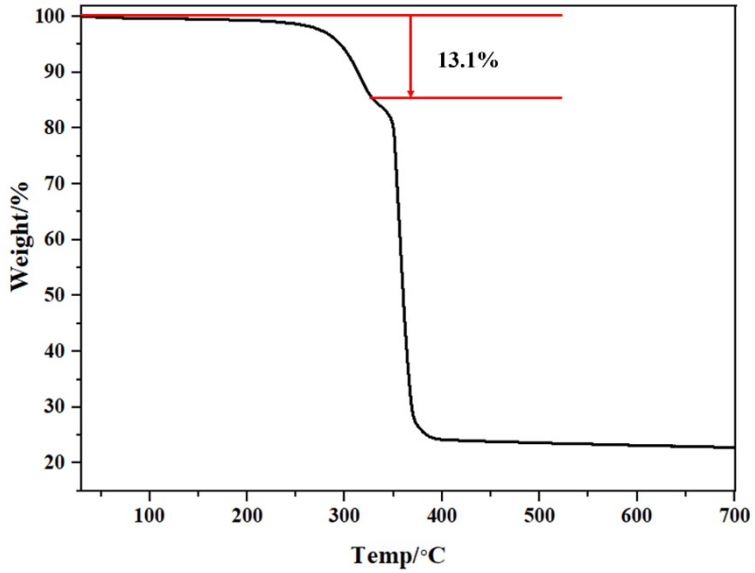


Figure S5. Thermogravimetric analysis of compound **1**.

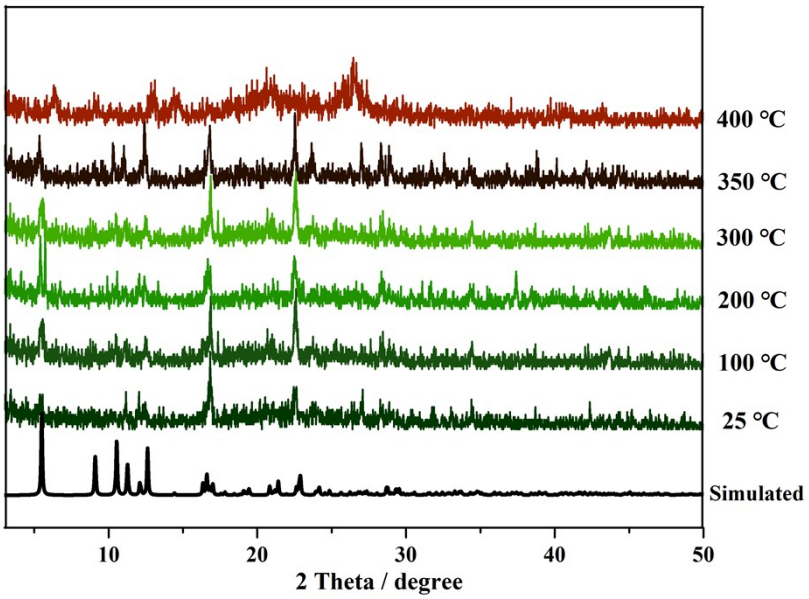


Figure S6. PXRD pattern of compound **1** heating at different temperatures.

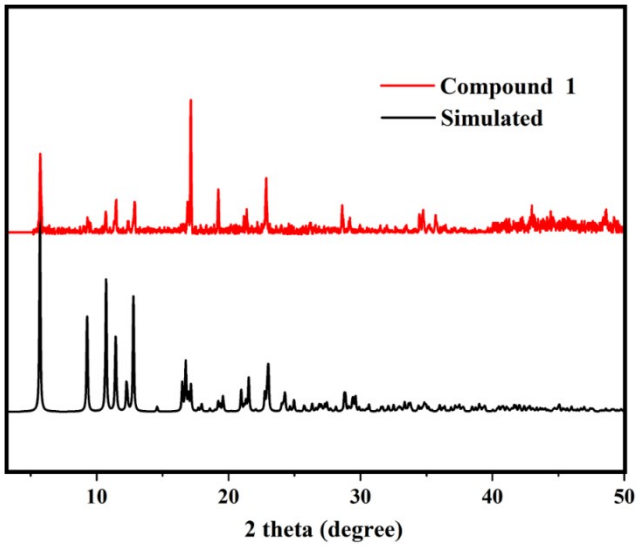


Figure S7. Powder diffraction data of compound **1**.

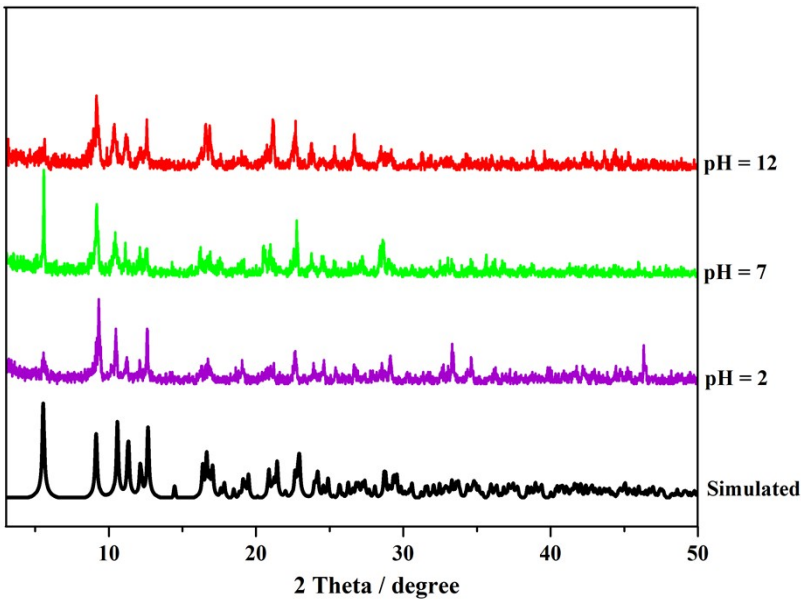


Figure S8. PXRD pattern of compound **1** after immersing in pH solution for 72 hours.

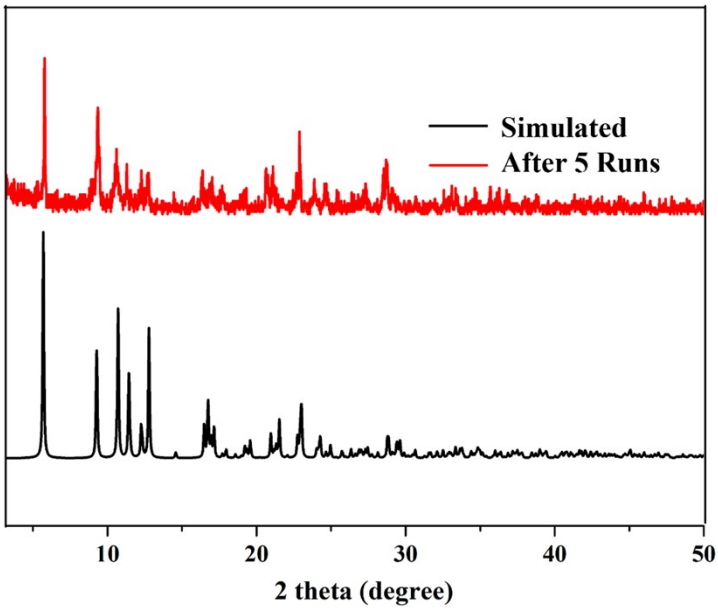


Figure S9. Powder diffraction data of **1** after five cycles.

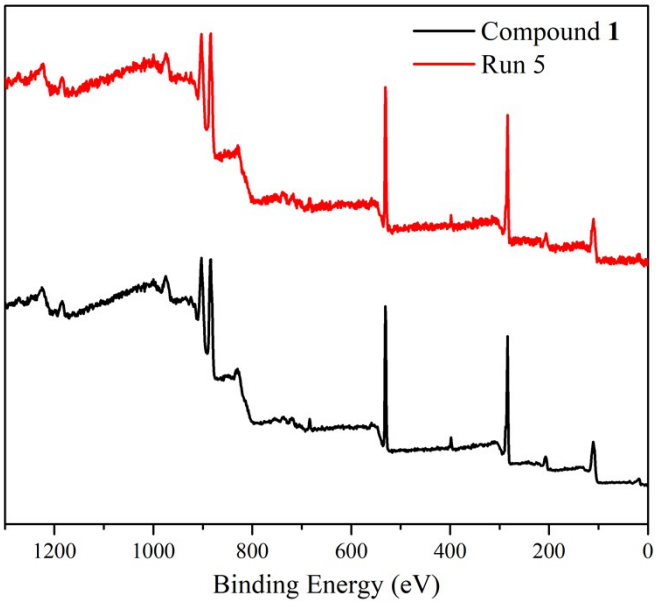


Figure S10. The full survey XPS spectrum of **1** before and after the reaction.

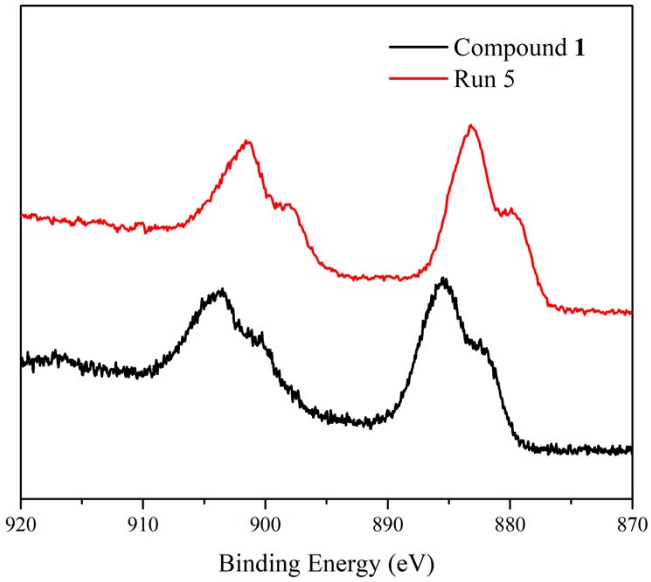


Figure S11. Ce 3d XPS spectrum of **1** before and after the reaction.

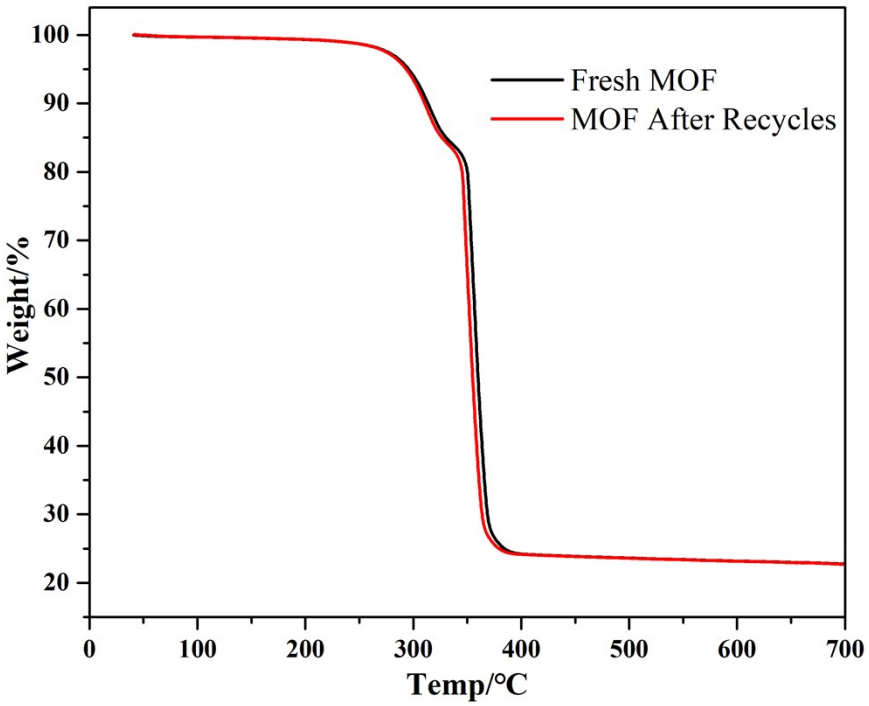


Figure S12. Thermogravimetric analysis of compound **1** before and after recycle.

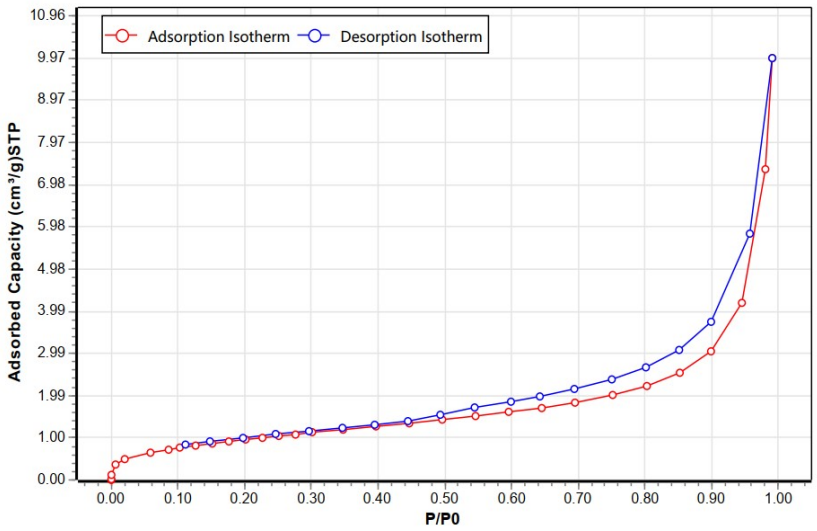


Figure S13. CO_2 adsorption-desorption of compound **1**.

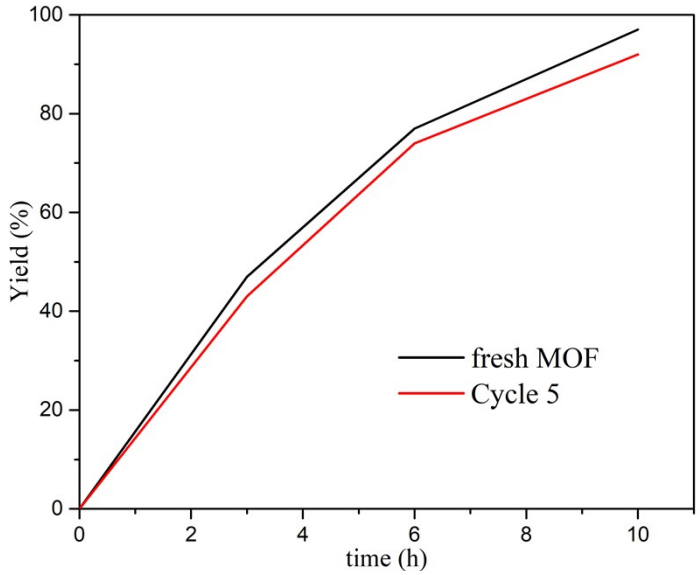


Figure S14. Kinetic curves of compound **1** for the reaction.

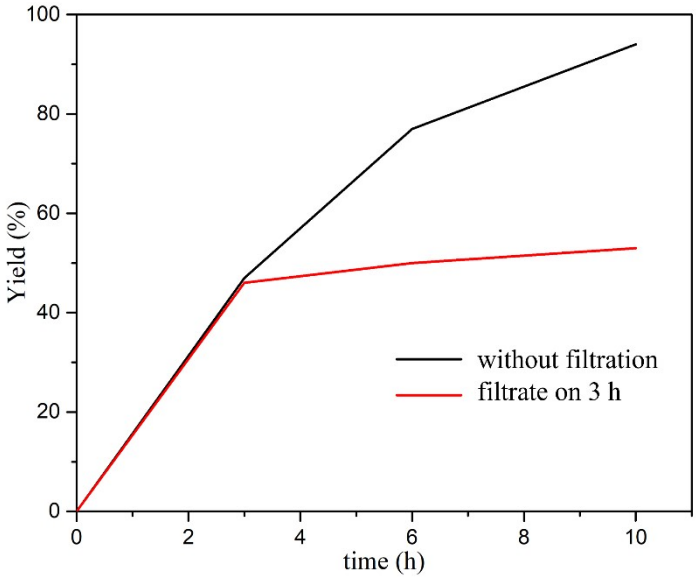


Figure S15. The hot filtration experiment of **1**.

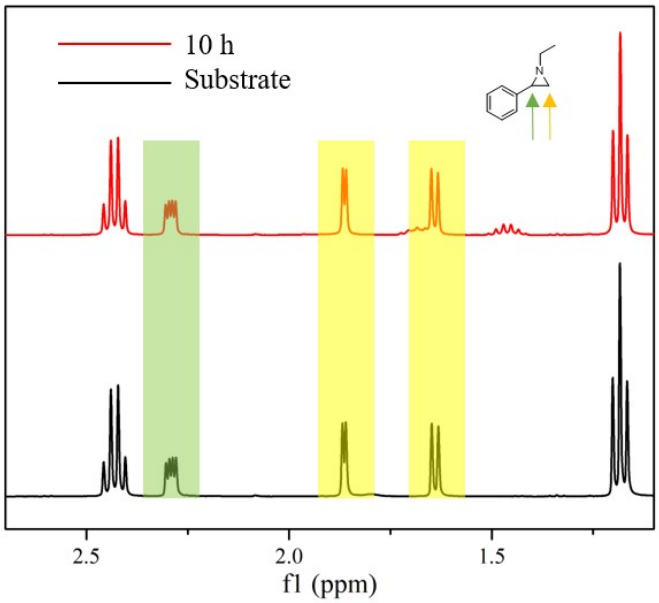


Figure S16. The activation of the aziridine substrate, $Ce(NO_3)_3$ and ligand after 10 h by ^1H NMR spectra.

Table S1. Crystal data and structure refinement details for crystal **1**.

Compound	**1**
Formula	$C_{29}H_{25}CeN_4O_7$
Mr.	681.65
Temperature (K)	293.00
Cryst. Syst.	monoclinic
Space group	*C*2/*c*
a (Å)	20.0128(4)
b (Å)	9.15790(10)
c (Å)	32.5211(8)
α (°)	90
β (°)	107.560(2)
γ (°)	90
Volume (Å^3)	5682.6(2)
Z	8
μ (mm^{-1})	1.655
F (000)	2728
2θ (°)	5.9 to 50.016
Reflections collected	6473
Independent Refl.	4110 [$R_{(int)}$ = 0.0193, $R_{(sigma)}$ = 0.0330]
Data/restraints/parameters	4110 / 0 / 374
GOF on F^2	1.032
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0251, wR_2 = 0.0568
R_1, wR_2 (all data)	R_1 = 0.0272, wR_2 = 0.0583

Table S2. Bond Lengths for **1**.

Bond	Length/Å	Bond	Length/Å
Ce1-O5	2.471(2)	N3-C16	1.324(5)
Ce1-O6	2.591(2)	N1-C23	1.326(5)
Ce1-O6[1]	2.655(2)	N1-C22	1.342(4)
Ce1-O4[2]	2.447(2)	C2-C3	1.394(4)
Ce1-O2[3]	2.516(2)	C2-C7	1.387(5)
Ce1-O7[1]	2.555(2)	C2-C1	1.496(5)
Ce1-O3[4]	2.447(2)	C8-C4	1.503(4)
Ce1-O1[3]	2.561(2)	C14-C18	1.393(5)
Ce1-N1	2.705(3)	C14-C11	1.495(5)
O5-C26	1.244(4)	C10-C9	1.393(5)
O6-Ce1[1]	2.655(2)	C3-C4	1.384(4)
O6-C29	1.280(4)	C4-C5	1.386(5)
O4-Ce1[2]	2.447(2)	C12-C13	1.386(5)
O4-C8	1.264(4)	C12-C20	1.493(4)
O2-Ce1[3]	2.516(2)	C5-C6	1.398(4)
O2-C1	1.269(4)	C7-C6	1.396(4)
O7-Ce1[1]	2.555(2)	C19-C23	1.382(5)
O7-C29	1.249(4)	C19-C20	1.394(5)
O3-Ce1[5]	2.447(2)	C18-C17	1.380(5)
O3-C8	1.256(4)	C6-C9	1.488(5)
O1-Ce1[3]	2.561(2)	N3-C17	1.343(5)
O1-C1	1.261(4)	C21-C22	1.379(5)
N4-C24	1.447(5)	C29-C28	1.506(5)
N4-C25	1.476(5)	C27-C26	1.495(5)
N4-C26	1.317(5)	C13-C9	1.392(4)
N2-C12	1.351(4)	C16-C15	1.387(5)
N2-C11	1.341(4)	C21-C20	1.373(5)

[1]1-X,+Y,1/2-Z; [2]1/2-X,1/2-Y,-Z; [3]1-X,1-Y,-Z; [4]1/2+X,1/2-Y,1/2+Z; [5]-1/2+X,1/2-Y,-1/2+Z

Table S3. Angle for **1**.

Atom	**Angle/°**	**Atom**	**Angle/°**	**Atom**	**Angle/°**
O5-Ce1-O6[1]	147.14(7)	C29-O6-Ce1[1]	91.8(2)	O2-C1-C2	118.0(3)
O5-Ce1-O6	139.22(7)	C8-O4-Ce1[3]	138.5(2)	O1-C1-O2	122.2(3)
O5-Ce1-O2[2]	85.90(8)	C1-O2-Ce1[2]	92.54(18)	O1-C1-C2	119.8(3)
O5-Ce1-O7[1]	143.61(8)	C29-O7-Ce1[1]	97.26(19)	O6-C29-C28	119.9(3)
O5-Ce1-O1[2]	69.02(8)	C8-O3-Ce1[5]	130.5(2)	O7-C29-O6	120.9(3)
O5-Ce1-N1	80.59(8)	C1-O1-Ce1[2]	90.7(2)	O7-C29-C28	119.2(3)
O6-Ce1-O6[1]	62.68(8)	C24-N4-C25	114.1(3)	N3-C17-C18	124.3(4)
O6-Ce1-N1	139.27(8)	C26-N4-C24	127.1(4)	C12-C13-C9	119.5(3)

O6[1]-Ce1-N1	77.95(8)	C26-N4-C25	118.8(3)	N3-C16-C15	124.8(3)
O4[3]-Ce1-O5	78.78(8)	C11-N2-C12	117.9(3)	N1-C23-C19	124.1(3)
O4[3]-Ce1-O6[1]	70.68(7)	C16-N3-C17	115.5(3)	O5-C26-N4	122.1(4)
O4[3]-Ce1-O6	103.83(7)	C23-N1-Ce1	121.1(2)	O5-C26-C27	119.6(3)
O4[3]-Ce1-O2[2]	155.60(7)	C23-N1-C22	116.2(3)	N4-C26-C27	118.3(4)
O4[3]-Ce1-O7[1]	115.19(7)	C22-N1-Ce1	122.3(2)	C20-C21-C22	120.1(3)
O4[3]-Ce1-O3[4]	76.88(7)	C3-C2-C1	119.3(3)	C19-C20-C12	122.8(3)
O4[3]-Ce1-O1[2]	135.46(7)	C7-C2-C3	119.5(3)	C21-C20-C12	120.4(3)
O4[3]-Ce1-N1	70.17(8)	C7-C2-C1	121.2(3)	C21-C20-C19	116.8(3)
O2[2]-Ce1-O6[1]	126.91(7)	O4-C8-C4	117.9(3)	N2-C11-C14	115.4(3)
O2[2]-Ce1-O6	75.83(7)	O3-C8-O4	124.9(3)	N2-C11-C10	122.5(3)
O2[2]-Ce1-O7[1]	88.32(8)	O3-C8-C4	117.2(3)	C10-C11-C14	122.1(3)
O2[2]-Ce1-O1[2]	51.74(7)	C18-C14-C11	120.6(3)	N1-C22-C21	123.5(4)
O2[2]-Ce1-N1	126.08(8)	C15-C14-C18	116.9(3)	C10-C9-C6	120.4(3)
O7[1]-Ce1-O6	72.83(7)	C15-C14-C11	122.5(3)	C13-C9-C10	117.5(3)
O7[1]-Ce1-O6[1]	49.91(7)	C11-C10-C9	119.8(3)	C13-C9-C6	122.0(3)
O7[1]-Ce1-O1[2]	79.30(8)	C4-C3-C2	120.5(3)	C14-C15-C16	119.2(4)
O7[1]-Ce1-N1	74.07(8)	C3-C4-C8	119.1(3)	C5-C6-C9	121.2(3)
O3[4]-Ce1-O5	71.83(8)	C3-C4-C5	119.3(3)	C7-C6-C5	118.4(3)
O3[4]-Ce1-O6[1]	111.38(7)	C5-C4-C8	121.6(3)	C7-C6-C9	120.4(3)
O3[4]-Ce1-O6	69.37(7)	N2-C12-C13	122.6(3)	C23-C19-C20	119.2(3)
O3[4]-Ce1-O2[2]	80.37(8)	N2-C12-C20	114.4(3)	C17-C18-C14	119.3(4)
O3[4]-Ce1-O7[1]	142.12(8)	C13-C12-C20	123.0(3)	O1[2]-Ce1-O6[1]	127.23(7)
O3[4]-Ce1-O1[2]	118.51(7)	C4-C5-C6	121.2(3)	O1[2]-Ce1-O6	120.68(7)
O3[4]-Ce1-N1	140.39(8)	C2-C7-C6	120.8(3)	O1[2]-Ce1-N1	74.79(8)

[1]1-X,+Y,1/2-Z; [2]1-X,1-Y,-Z; [3]1/2-X,1/2-Y,-Z; [4]1/2+X,1/2-Y,1/2+Z; [5]1/2+X,1/2-Y,-1/2+Z

Table S4. ICP results of fresh catalyst

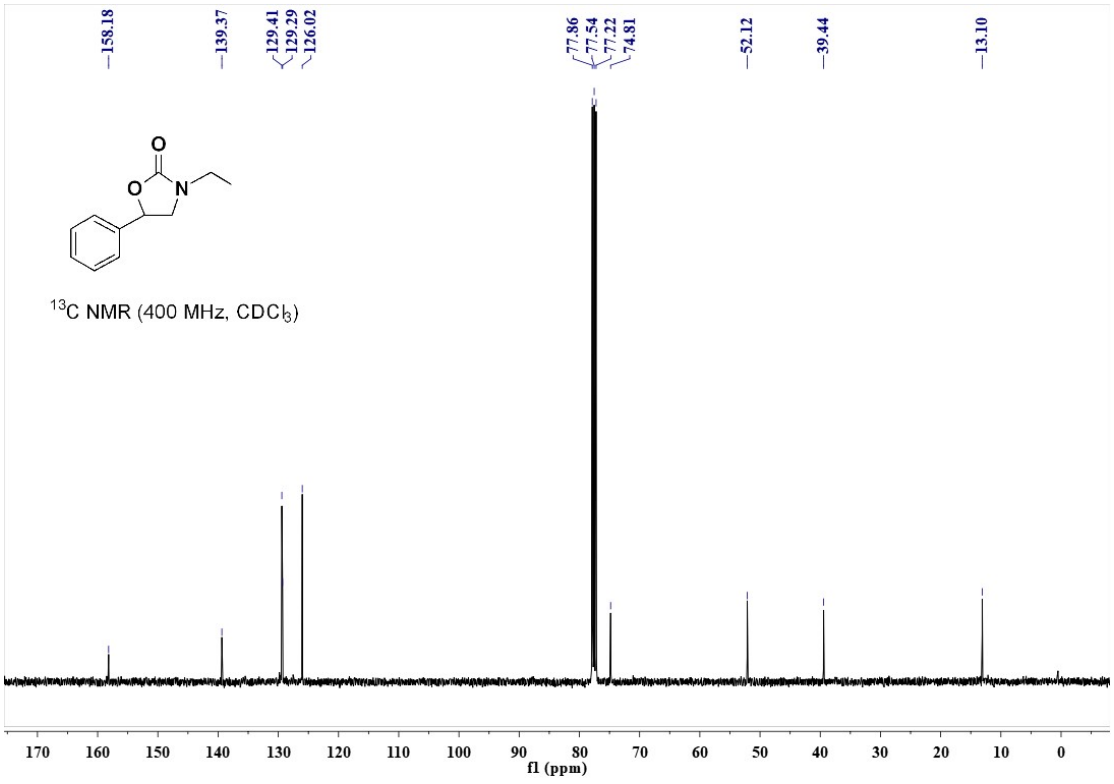
Ce-MOF	Ce^{3+} (ppm)
Filter liquor of fresh catalyst	1.32

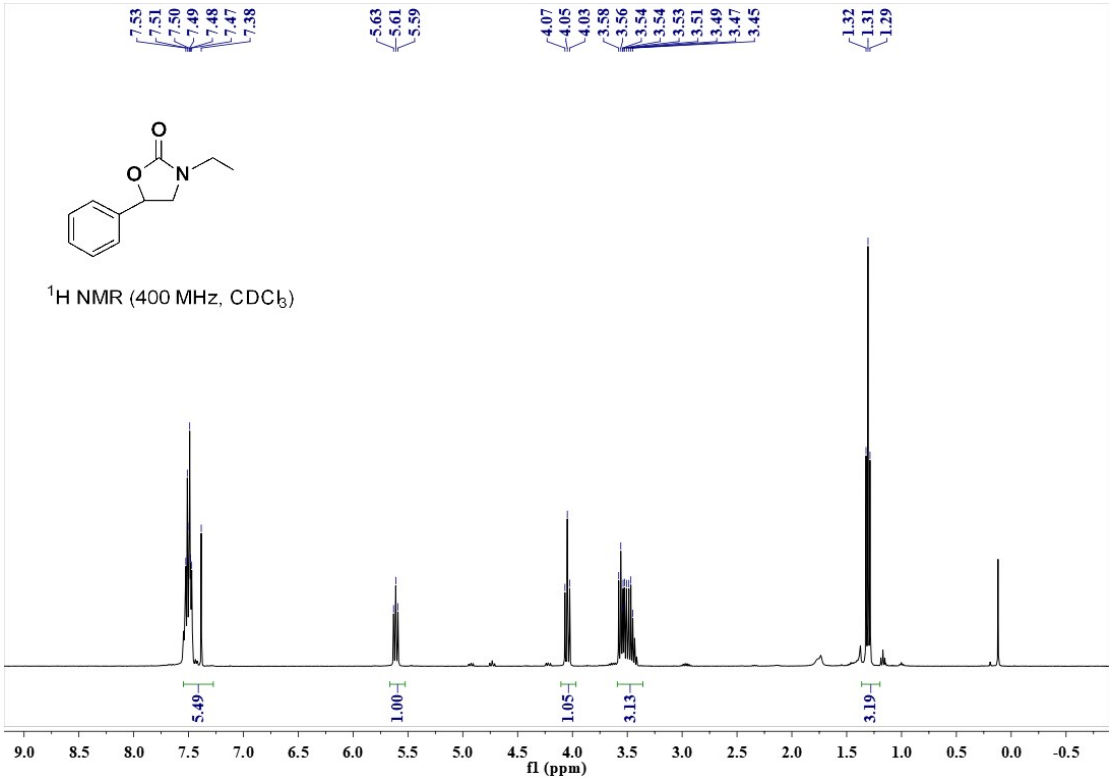
Table S5. ICP results of reaction filtrate

Ce-MOF	Ce^{3+} (ppm)
Filter liquor after catalytic recycling	0.3542

1-ethyl-2-phenylaziridine

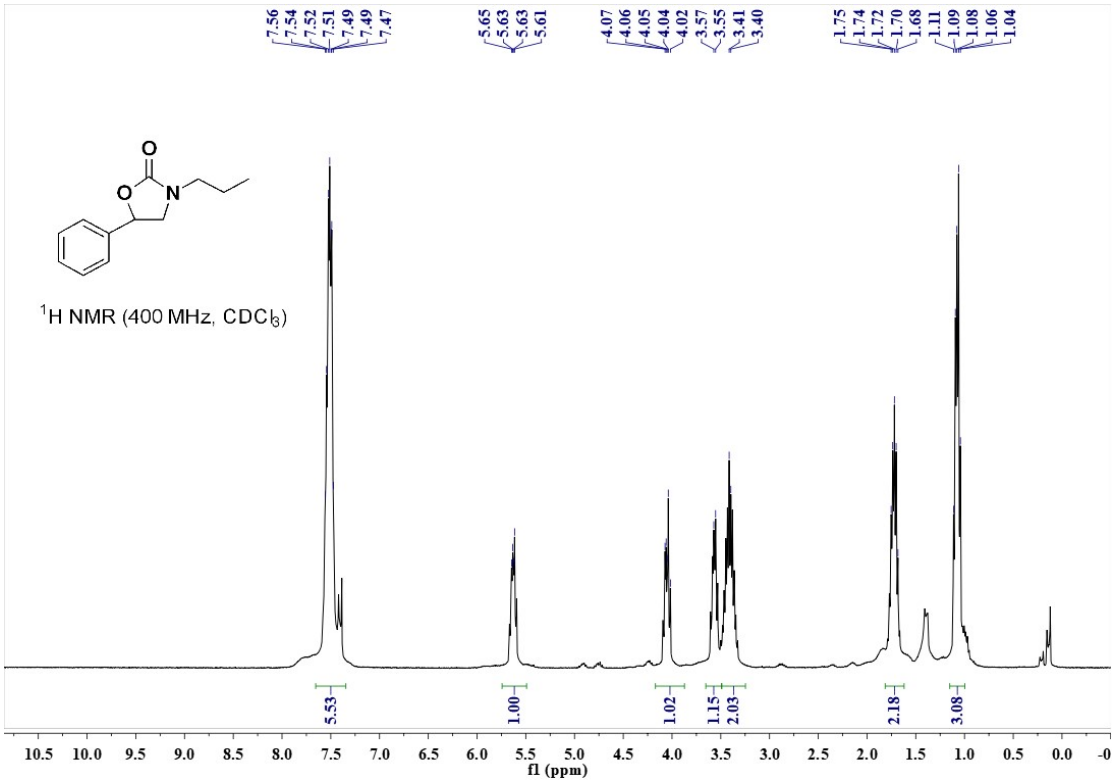
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.27 (m, 5H), 5.61 (t, *J* = 8.1 Hz, 1H), 4.05 (t, *J* = 8.7 Hz, 1H), 3.59 – 3.36 (m, 3H), 1.31 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.18 (s), 139.37 (s), 129.35 (d, *J* = 12.7 Hz), 126.02 (s), 77.86 (s), 77.54 (s), 77.22 (s), 74.81 (s), 52.12 (s), 39.44 (s), 13.10 (s).

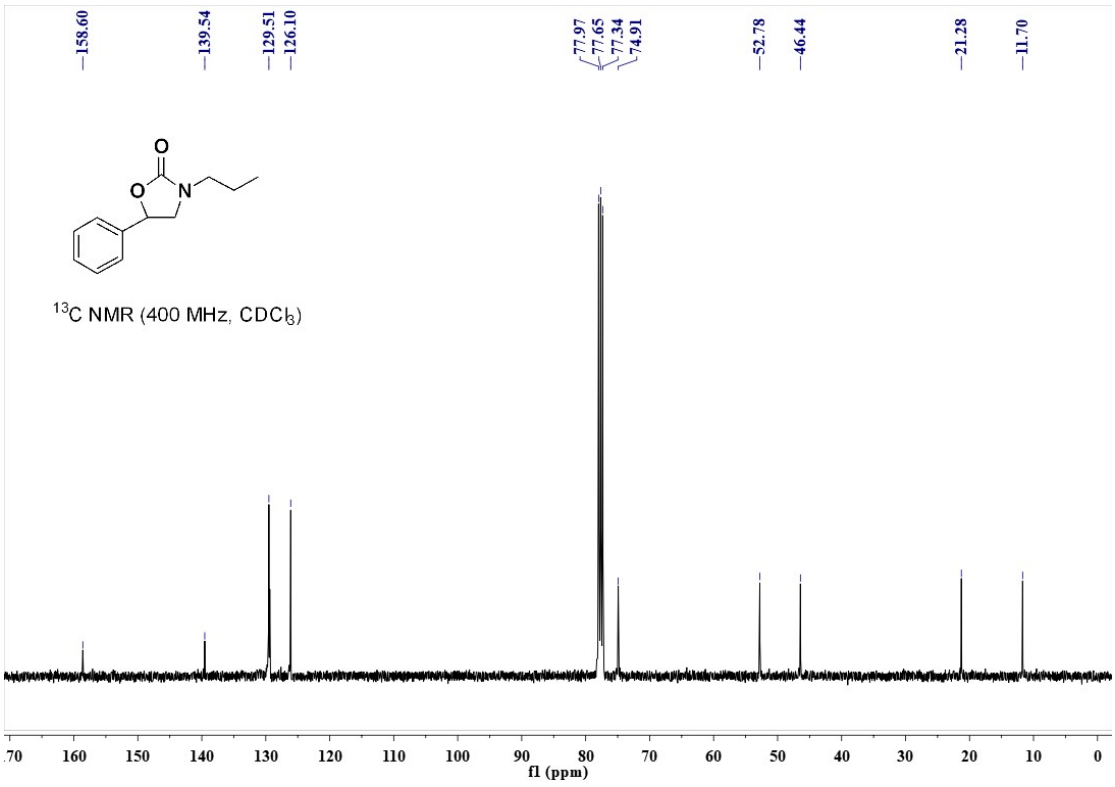




1-propyl-2-phenylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.33 (m, 5H), 5.65 – 5.61 (t, J = 8.1 Hz, 1H), 4.06 – 4.04 (t, J = 8.7 Hz, 1H), 3.57 – 3.55 (m, 1H), 3.41 – 3.40 (m, 1H), 1.75 – 1.68 (t, J = 7.6 Hz, 2H), 1.08 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.60 (s), 139.54 (s), 129.51 (s), 126.10 (s), 77.97 (s), 77.65 (s), 77.34 (s), 74.91 (s), 52.78 (s), 46.44 (s), 21.28 (s), 11.70 (s).

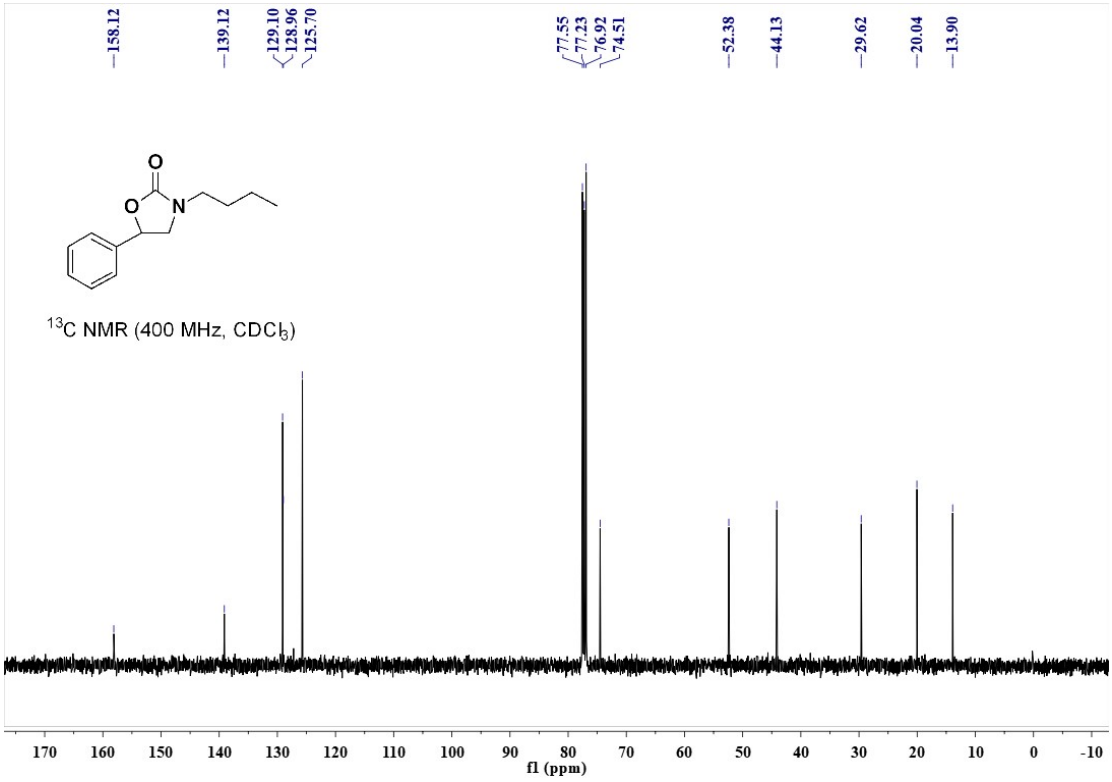


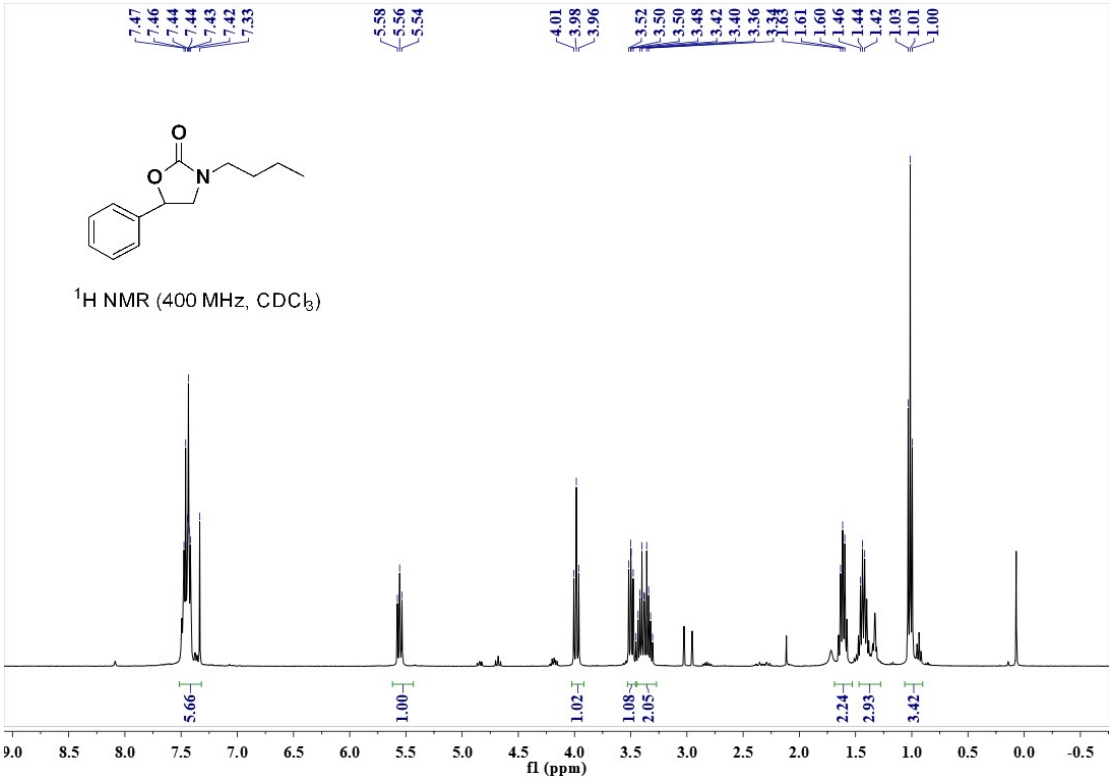


1-butyl-2-phenylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.32 (m, 5H), 5.62 – 5.43 (m, 1H), 3.98 (t, *J* =

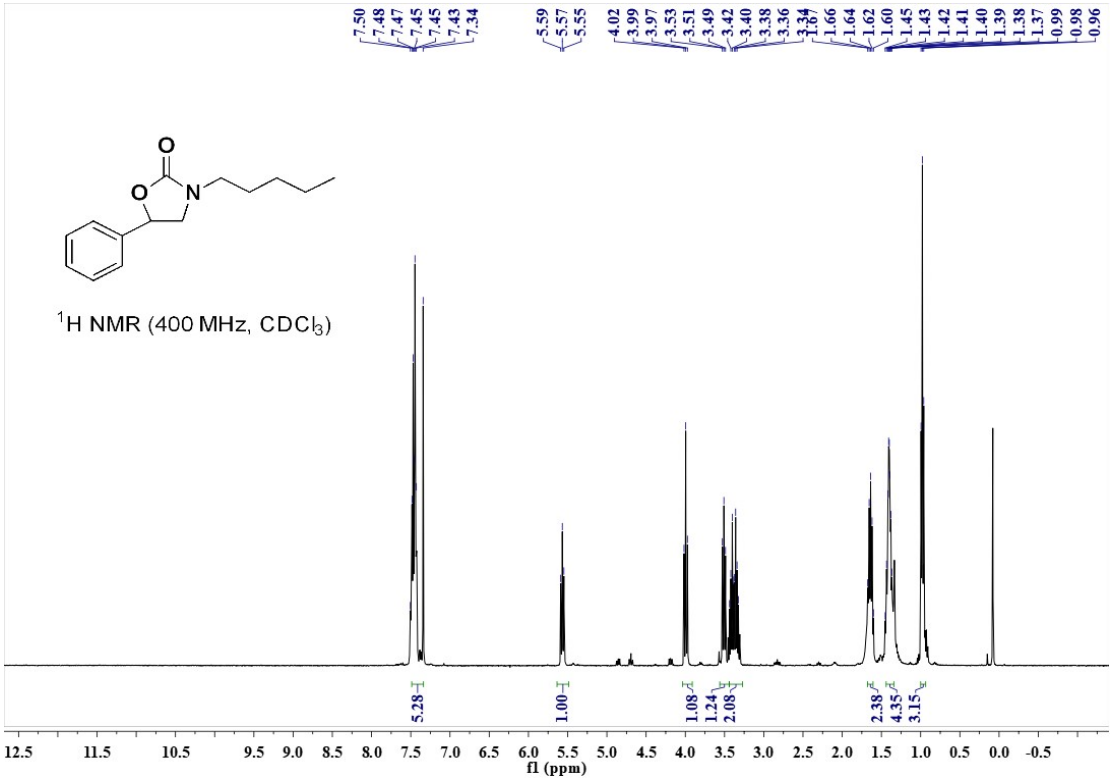
8.7 Hz, 1H), 3.50 (dd, *J* = 8.6, 7.5 Hz, 1H), 3.37 (dtd, *J* = 21.1, 13.9, 6.9 Hz, 2H), 1.69 – 1.53 (m, 2H), 1.47 – 1.28 (m, 3H), 1.01 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.12 (s), 139.12 (s), 129.03 (d, *J* = 13.7 Hz), 125.70 (s), 77.55 (s), 77.23 (s), 76.92 (s), 74.51 (s), 52.38 (s), 44.13 (s), 29.62 (s), 20.04 (s), 13.90 (s).

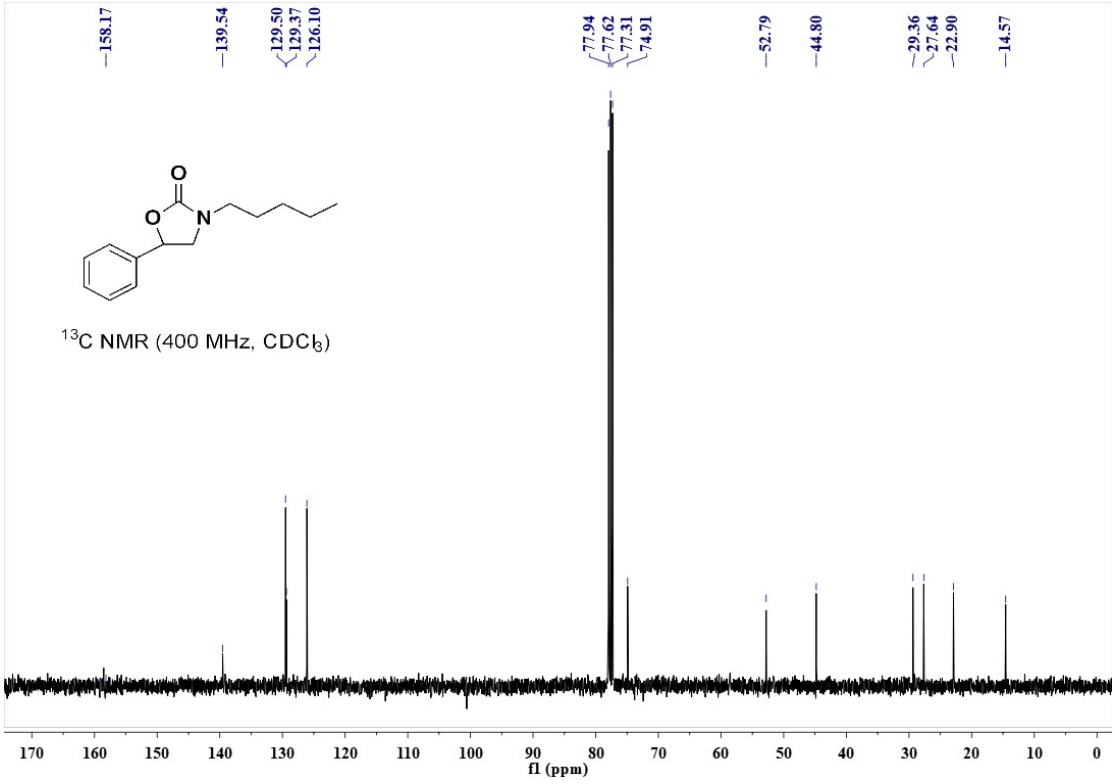




1-amyl-2-phenylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.34 (m, 5H), 5.57 (t, *J* = 8.1 Hz, 1H), 3.99 (t, *J* = 8.7 Hz, 1H), 3.56 – 3.44 (m, 1H), 3.38 (ddd, *J* = 21.2, 13.8, 6.6 Hz, 2H), 1.65 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.44 – 1.34 (m, 4H), 0.98 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.54 (s), 129.44 (d, *J* = 13.6 Hz), 126.10 (s), 77.94 (s), 77.62 (s), 77.31 (s), 74.91 (s), 52.79 (s), 44.80 (s), 29.36 (s), 27.64 (s), 22.90 (s), 14.57 (s).

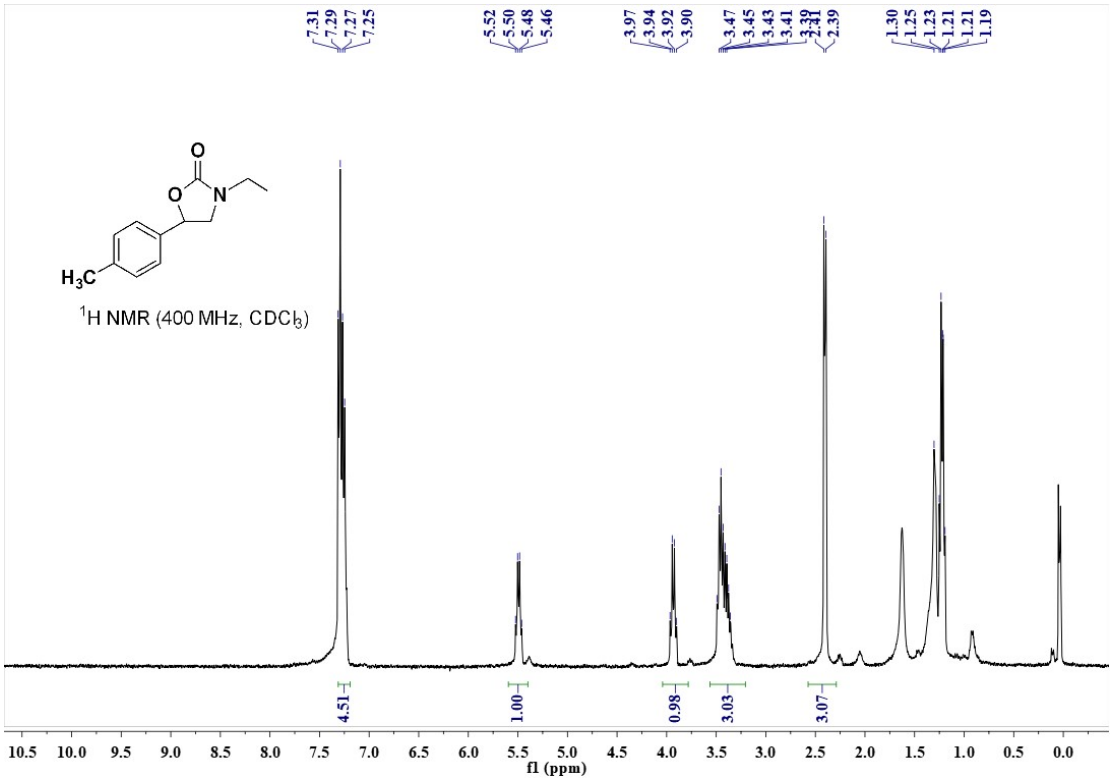


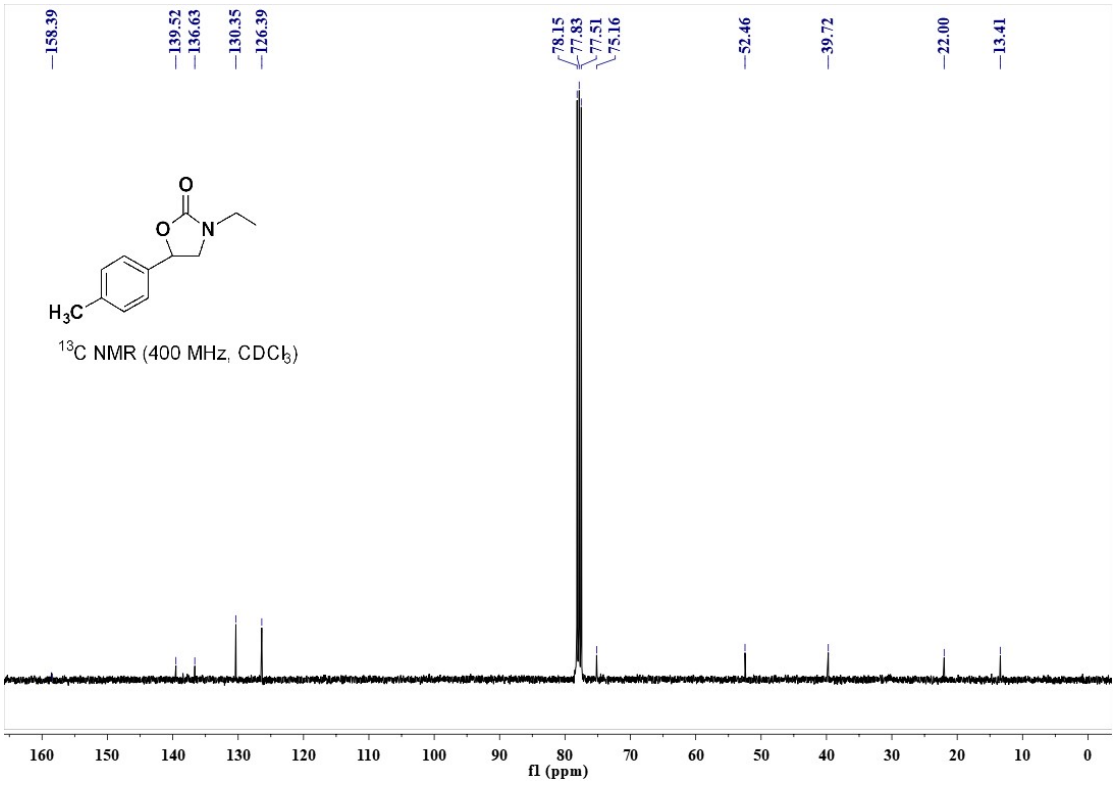


2-(4-methphenyl)-1-ethylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 5H), 5.49 (q, J = 8.3 Hz, 1H), 3.93 (q, J = 8.8 Hz, 1H), 3.56 – 3.21 (m, 3H), 2.40 (d, J = 8.6 Hz, 3H); ^{13}C NMR (101 MHz,

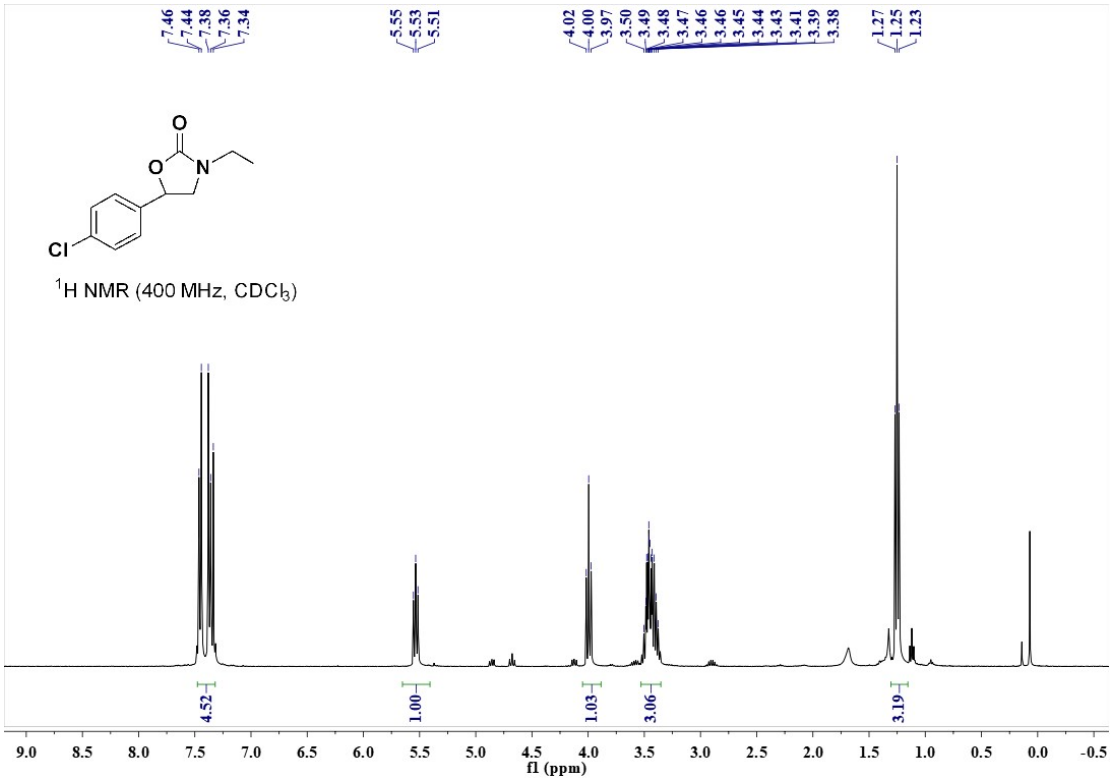
$CDCl_3$) δ 139.52 (s), 136.63 (s), 130.35 (s), 126.39 (s), 78.15 (s), 77.83 (s), 77.51 (s), 75.16 (s), 52.46 (s), 39.72 (s), 22.00 (s), 13.41 (s).

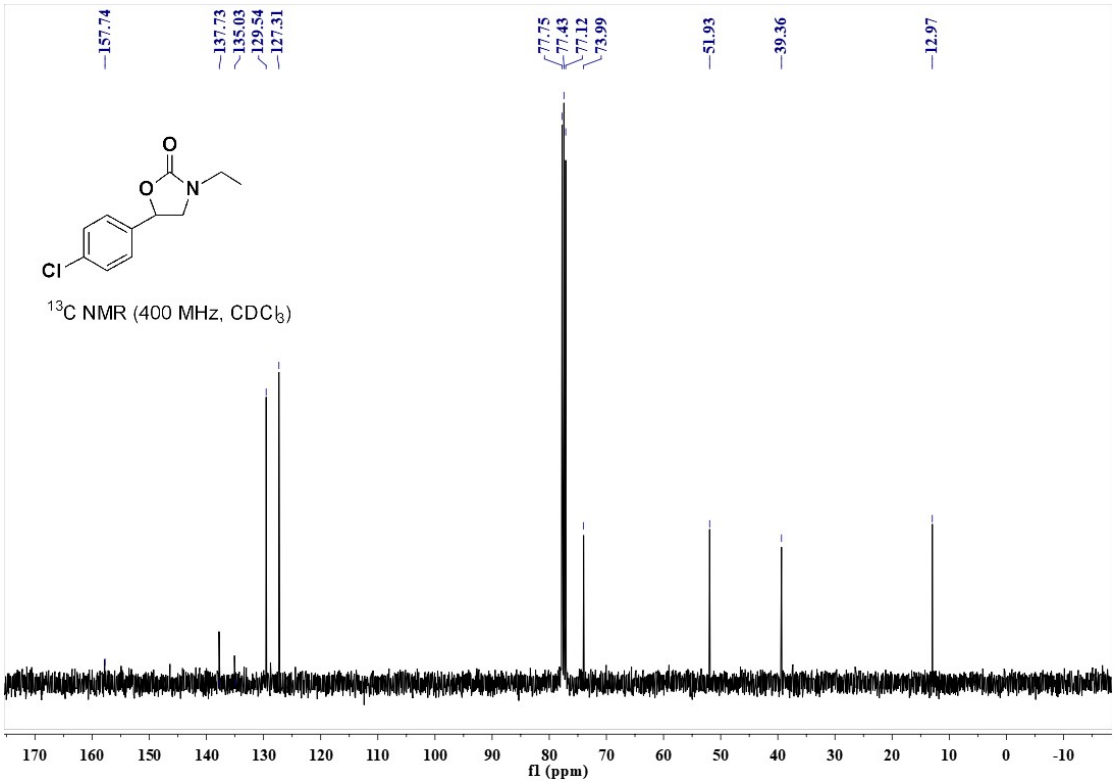




2-(4-chlorophenyl)-1-ethylaziridine

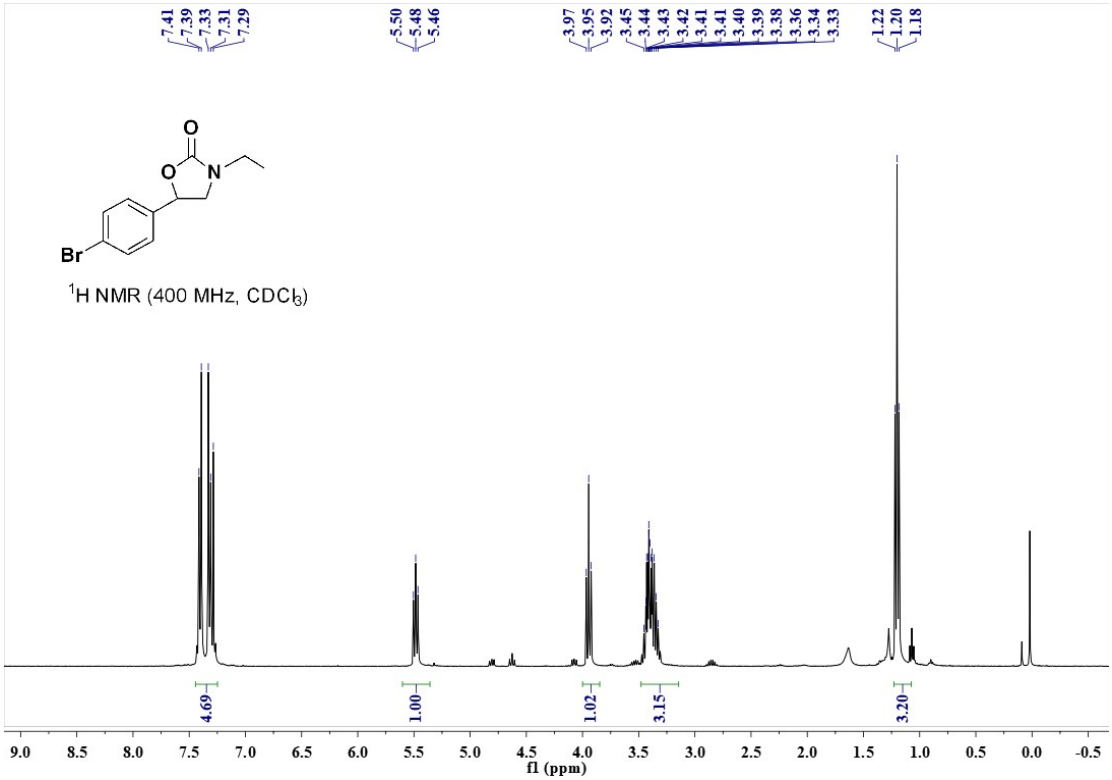
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.32 (m, 4H), 5.65 – 5.41 (m, 1H), 4.00 (t, *J* = 8.7 Hz, 1H), 3.53 – 3.35 (m, 3H), 1.25 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.74 (s), 137.83 – 137.63 (m), 135.13 – 134.93 (m), 129.54 (s), 127.31 (s), 77.75 (s), 77.43 (s), 77.12 (s), 73.99 (s), 51.93 (s), 39.36 (s), 12.97 (s).

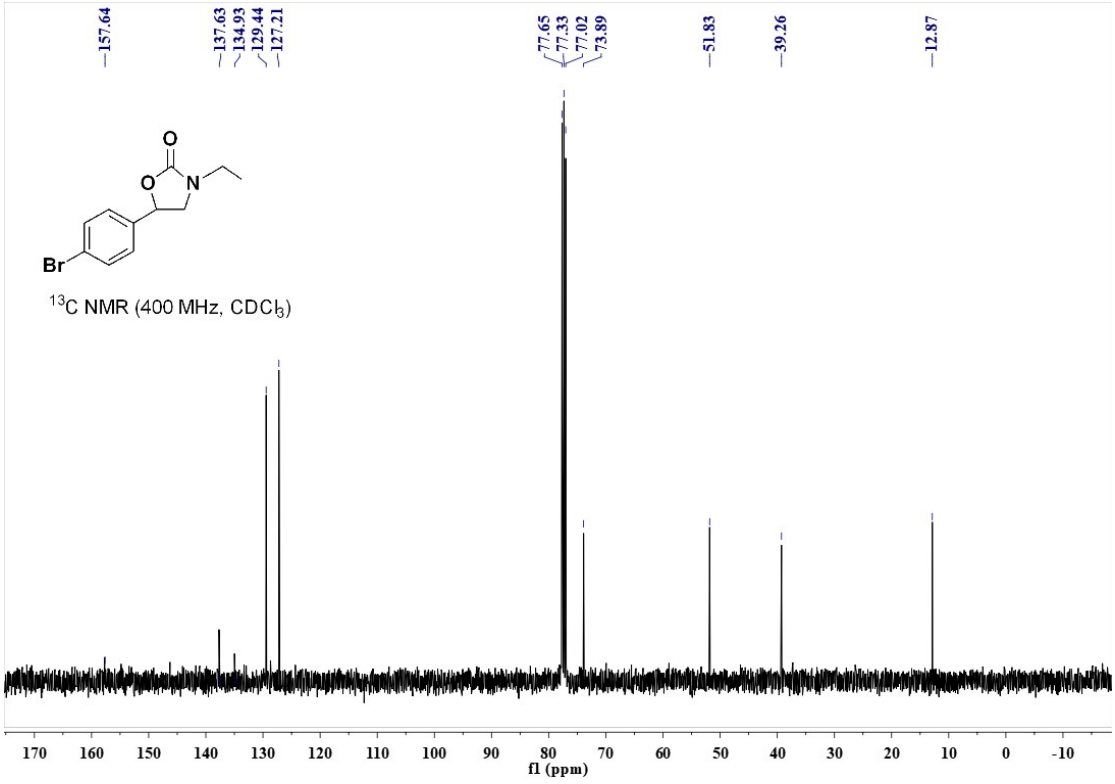




2-(4-bromophenyl)-1-ethylaziridine

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 4H), 5.60 – 5.36 (m, 1H), 3.95 (t, *J* = 8.7 Hz, 1H), 3.48 – 3.14 (m, 3H), 1.20 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.64 (s), 137.73 – 137.53 (m), 135.03 – 134.83 (m), 129.44 (s), 127.21 (s), 77.65 (s), 77.33 (s), 77.02 (s), 73.89 (s), 51.83 (s), 39.26 (s), 12.87 (s).





References

1 Z. L. Wu, C. H. Wang, B. Zhao, J. Dong, F. Lu, W. H. Wang, W. C. Wang, G. J. Wu, J. Z. Cui and P. Cheng, *Angew. Chem. Int. Ed.*, 2016, **55**, 4938–4942.