Electronic Supplementary Material (ESI) for Green Chemistry.

Dyes as efficient and reusable organocatalysts for the synthesis of cyclic carbonates from epoxides and CO_2

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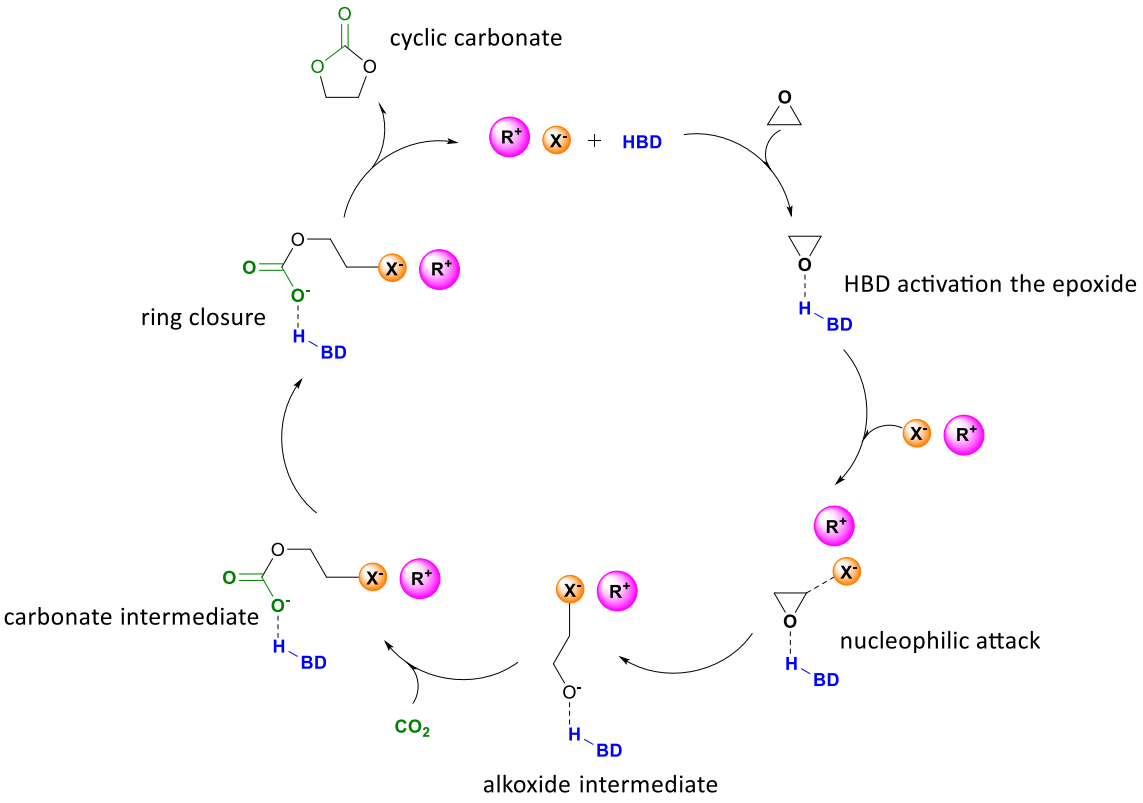
Supplementary information



Scheme S1. Proposed mechanism for the conversion of CO_2 and epoxides into cyclic carbonates catalysed by an organocatalyst, assisted by an HBD (based on refs. 8, 10, 12 in the main text).

Table S1. Visual evaluation of the solubility of the dye organocatalysts in the reaction mixture used for the conversion of styrene oxide into styrene carbonate at 80 °C.

MB			MB-Br			MB-I				
BF	80 °C	AF	BF	80 °C	AF	BF	80 °C	AF	H_2O [g]	PC [ml]
									0	0
									0	0.5
									0	1.0
									0	2.0
									0.05	1.0
									0.05	0

RhB			RhB-Br			RhB-I				
BF	80 °C	AF	BF	80 °C	AF	BF	80 °C	AF	H_2O [g]	PC [ml]
									0	0
									0.05	0

Rh6G			Rh6G-Br			Rh6G-I				
BF	80 °C	AF	BF	80 °C	AF	BF	80 °C	AF	H_2O [g]	PC [ml]
									0	0
									0	0.5
									0	1.0
									0	2.0
									0.05	1.0
									0.05	0

Solubility	Largely insoluble	Partially soluble	Soluble
Colour indication			

The solubility of the organocatalysts in the reaction mixtures was determined visually before the catalytic test, either at room temperature after sonication for ca. 10 min (BF) or at the reaction temperature (80 °C) and after the catalytic test at room temperature (AF).

Table S2. Visual evaluation of the solubility of the dye organocatalysts in the reaction mixture used for the conversion of styrene oxide into styrene carbonate at low reaction temperature (45 °C).

MB-I					Rh6G-I				
BF	45 °C	AF	H_2O [g]	PC [ml]	BF	45 °C	AF	H_2O [g]	PC [ml]
			0.05	0				0.05	0
			0.05	3.9				0.05	2.0

RhB-I					RhB-EtOH-I				
BF	45 °C	AF	H_2O [g]	PC [ml]	BF	45 °C	AF	H_2O [g]	PC [ml]
			0.05	0				0	0

Solubility	Largely insoluble	Partially soluble	Soluble
Colour indication			

The solubility of the organocatalysts in the reaction mixtures was determined visually before the catalytic test, either at room temperature after sonication for ca. 10 min (BF) or at the reaction temperature (45 °C) and after the catalytic test at room temperature (AF).

Table S3. Visual evaluation of the solubility of the dye organocatalysts in the reaction mixture used for the investigation of the conversion of different epoxides into the corresponding cyclic carbonates.

	Propylene oxide[a]					Epichlorohydrin				
	BF	35 °C	AF	H_2O [g]	PC [ml]	BF	60 °C	AF	H_2O [g]	PC [ml]
RhB-I				0.05	0				0.05	0
Rh6G-I				0.05	0				0.05	1.0
RhB-EtOH-I				0.05	0				0.05	0

	Allyl glycidyl ether					Styrene oxide				
	BF	60 °C	AF	H_2O [g]	PC [ml]	BF	60 °C	AF	H_2O [g]	PC [ml]
RhB-I				0.05	0				0.05	0
Rh6G-I				0.05	0.5				0.05	0.5
RhB-EtOH-I				0.05	0				0.05	0.5

	1,2-epoxyhexane					Cyclohexene oxide				
	BF	80 °C	AF	H_2O [g]	PC [ml]	BF	120 °C	AF	H_2O [g]	PC [ml]
RhB-I				0.05	1.0				0.05	0.5
Rh6G-I				0.05	0.7				0.05	0.5
RhB-EtOH-I[b]				0.05	0.5				0.05	0.5

	Limonene oxide[a]				
	BF	110 °C	AF	H_2O [g]	PC [ml]
RhB-I				0.05	0.5
Rh6G-I				0.05	0.5
RhB-EtOH-I				0.05	0.5

Solubility	Largely insoluble	Partially soluble	Soluble
Colour indication			

The solubility of the organocatalysts in the reaction mixtures was determined visually before the catalytic test, either at room temperature after sonication for ca. 10 min (BF) or at the reaction temperature (80 °C) and after the catalytic test at room temperature (AF). [a] In the case of propylene oxide and limonene oxide the solubility of the dyes was not tested at the reaction temperature (60 °C for propylene oxide, 120 °C for limonene oxide) but at the boiling point of this epoxide (34 °C for propylene oxide and 110 °C for limonene oxide). [b] The solubility of RhB-EtOH-I in 1,2-epoxyhexane was determined at 60 °C as this was the reaction temperature at which this organocatalyst was tested.

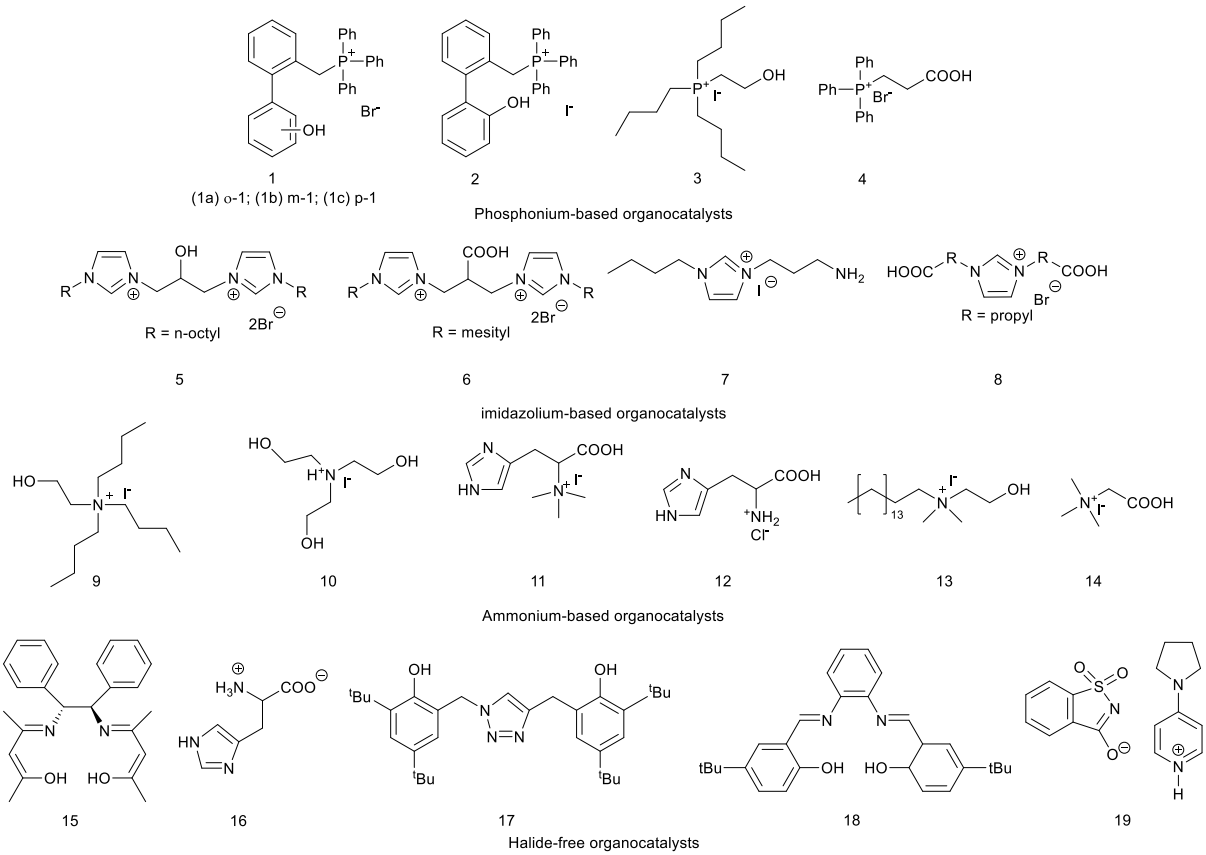


Table S4. Catalytic activity of selected organocatalysts in the CO_2 cycloaddition to styrene oxide

Entry	Catalyst	Catalyst loading [mol %]	T [°C]	P [MPa]	T [h]	Yield [%]	Selectivity [%]	TON[f]	TOF[g] [h^{-1}]	Ref.[h]
1[a]	RhB-EtOH-I	1	45	1	18	32	> 93	32	2	This
2[b]	RhB-EtOH-I	1	60	1	24	54	≥ 99	54	2	work
3	1a	1	60	0.1	24	80	-	80	3	35
4	1b	1	60	0.1	24	41	-	41	2	35
5	1c	1	60	0.1	24	65	-	65	3	35
6	2	1	60	0.1	24	91	-	91	4	35
7	3	5	45	1	18	76	-	15	1	58
8	4	0.5	130	2.5	3	≥ 99	≥ 99	198	66	65
9	5	5	70	0.4	16	90	≥ 99	18	1	66
10	6	5	70	0.4	16	93	≥ 99	19	1	67
11	7	1	120	1.5	2	85	> 99	85	43	68
12	8	1	125	2	1	95	> 99	95	95	64
13	9	5	45	1	18	89	-	18	1	34
14	10	2	110	2	6	84	99	42	7	33
15	11	0.3	120	0.1	6	95	99	317	53	69
16	12	1	130	8	48	92	-	92	2	70
17[c]	13	2	120	1.5	23	87	88	44	2	71
18	14	2	120	1.2	2	79	99	40	20	72
19	14	2.5	140	8	8	96	-	38	5	73
20	15	0.2	110	1	12	56	> 99	280	23	74
21[d]	16	0.4	120	1.2	3	64	82	160	53	75
22	17	1	120	1	24	95	-	95	4	76
23[e]	18	5	120	1	24	84	93	17	0.7	77
24	19	10	120	0.1	24	81	89	8	0.3	78

[a] 50 mg H_2O as an HBD. [b] 50 mg H_2O as an HBD, 0.5 ml propylene carbonate as a solvent. [c] 40 ml benzonitrile as a solvent. [d] 0.1 g H_2O added as a co-catalyst. [e] 2-MeTHF as a solvent. [f] Turnover number, TON = $mol_{product}/mol_{catalyst}$. [g] Turnover frequency, TOF = TON/h. [h] The reference numbers are those used in the main text of the article.

Reusability test of RhB-EtOH-I catalyst for the synthesis of propylene carbonate

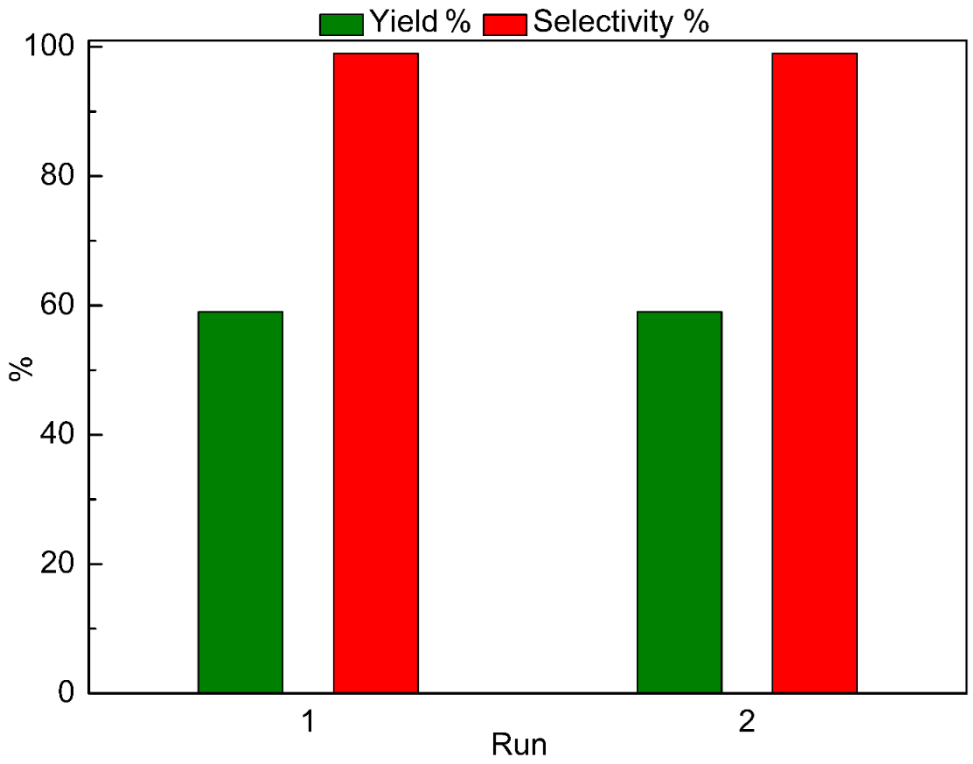


Figure S1. Reusability test of RhB-EtOH-I as catalyst for the synthesis of propylene carbonate from CO_2 and propylene oxide. Reaction conditions: 10 bar CO_2, 60 °C, 24 h.

The cumulative TON reached in these two catalytic tests is 119 (cumulative $TON = TON_{run\ 1} + TON_{run\ 2} = mol_{product,\ run\ 1}/mol_{catalyst,\ run\ 1} + mol_{product,\ run\ 2}/mol_{catalyst,\ run\ 2}$).

Nanofiltration samples

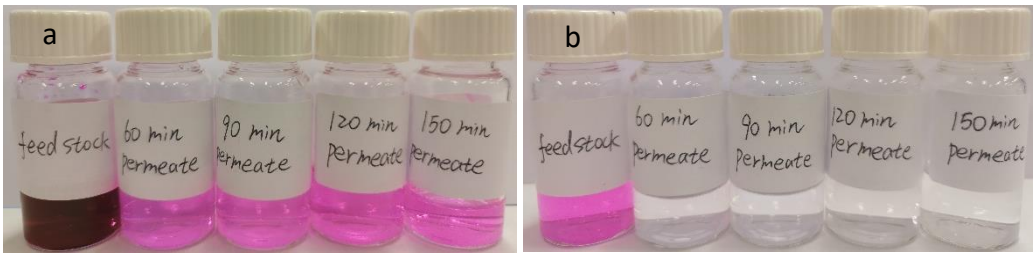


Figure S2. Samples obtained in the nanofiltration tests: feedstock (after having been recirculated for 15 min) and permeate. (a) First nanofiltration test, with the following feed composition: RhB: 0.51 g, propylene carbonate: 10.01 g, H_2O: 1 L; pressure: 1 barg, feed flow rate: 50 L h^{-1}. (b) Second nanofiltration test, with a feed composition mimicking that of the permeate of the first nanofiltration test: RhB: 0.005g, propylene carbonate: 0.14 g, H_2O: 1 L; pressure: 1 barg, feed flow rate: 50 L h^{-1}.

Photocatalytic tests with RhB-EtOH-I

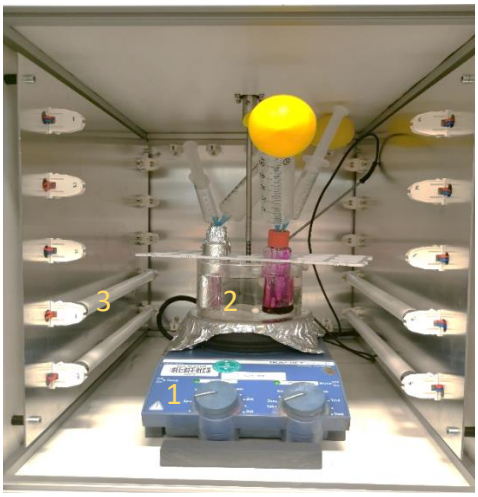


Figure S3. Photoreactor used to test the catalytic activity of RhB-EtOH-I under visible light: (1) stirring plate; (2) oil bath; (3) visible LED light (400-700 nm).

UV-Vis absorption spectra of RhB and RhB-EtOH-I

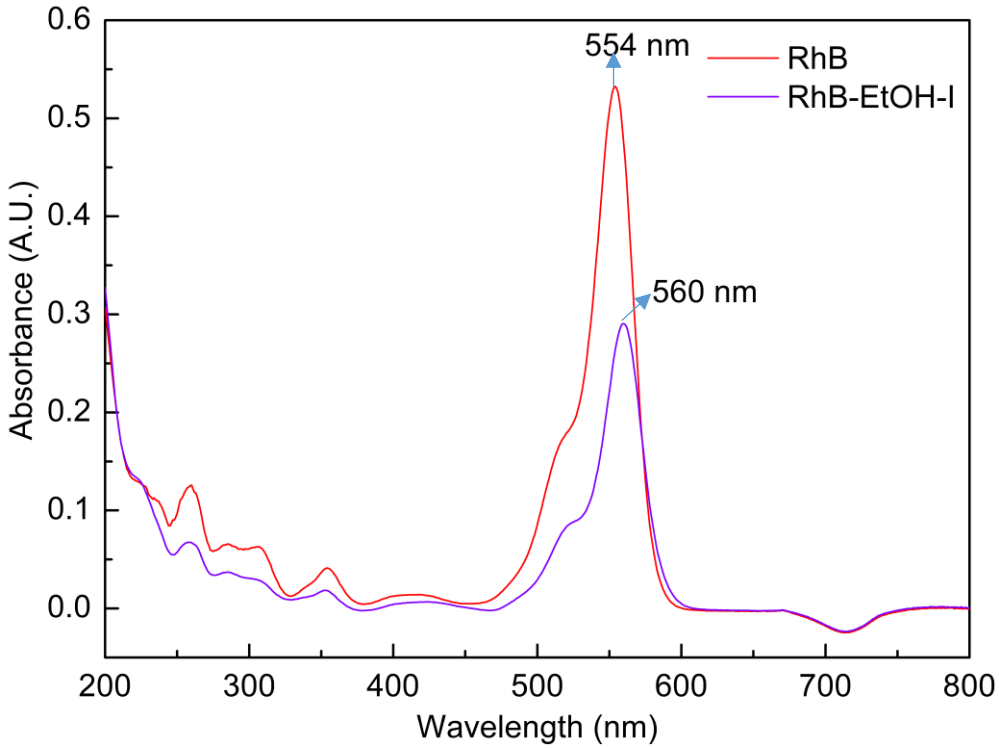


Figure S4. UV-Vis absorption spectra of RhB and RhB-EtOH-I.

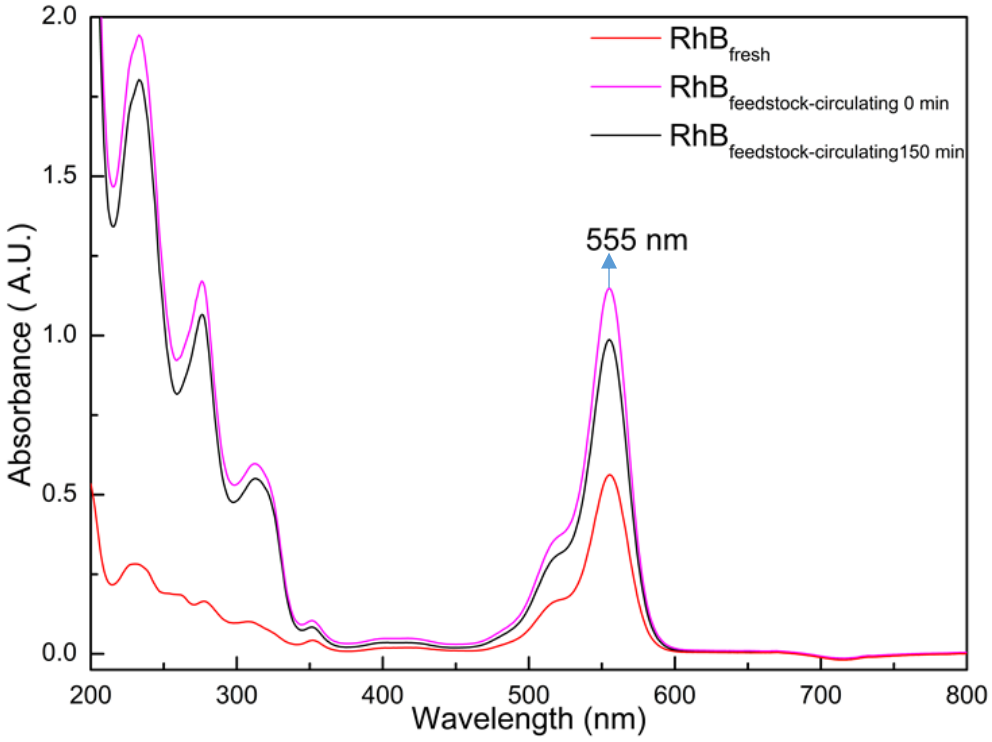


Figure S5. UV-Vis absorption spectra of RhB samples (in acetonitrile): freshly prepared solution and samples collected from the concentrated feedstock of the nanofiltration experiments [0.5 ml of a nanofiltration sample (data in Table 4) were taken and concentrated by freeze-drying. The dried sample was dissolved in 10 ml acetonitrile and measured by UV-Vis spectroscopy].

^{1}H NMR spectra of the reaction mixtures

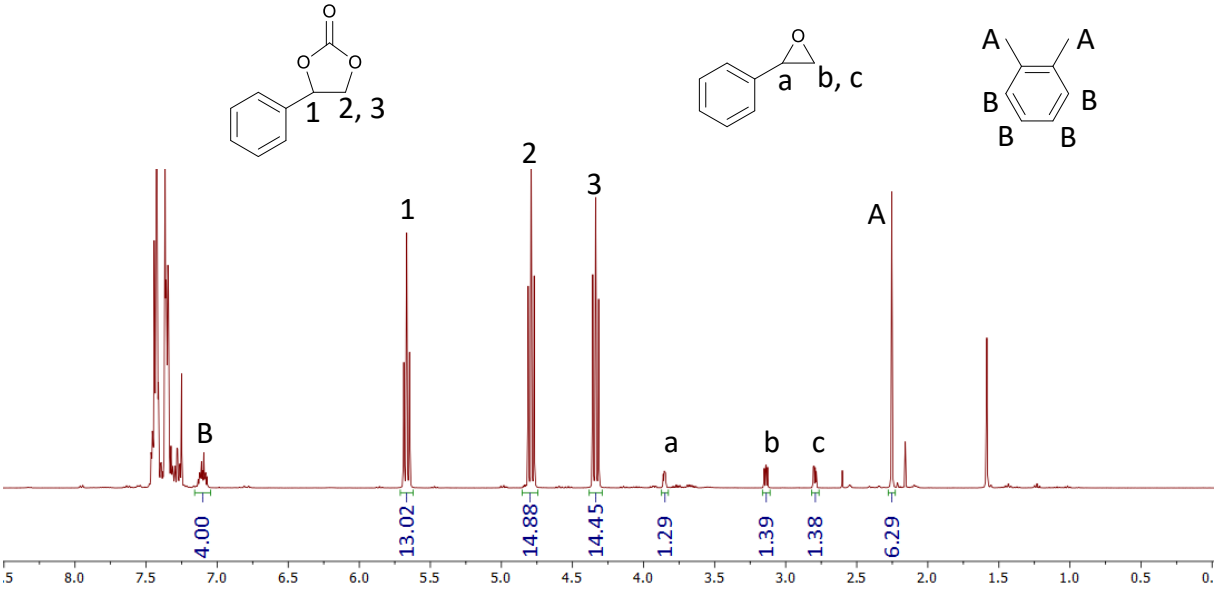


Figure S6. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to styrene oxide.

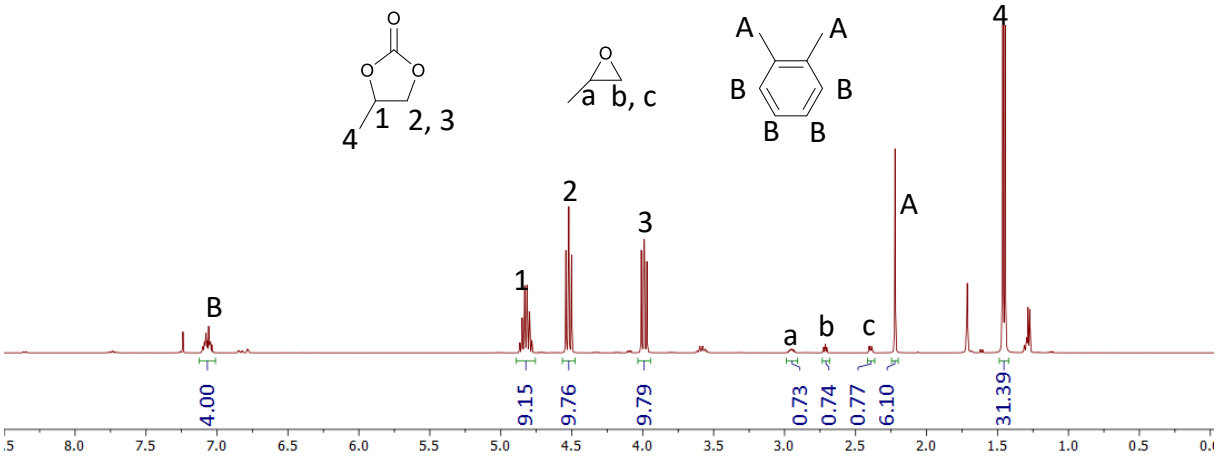


Figure S7. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to propylene oxide.

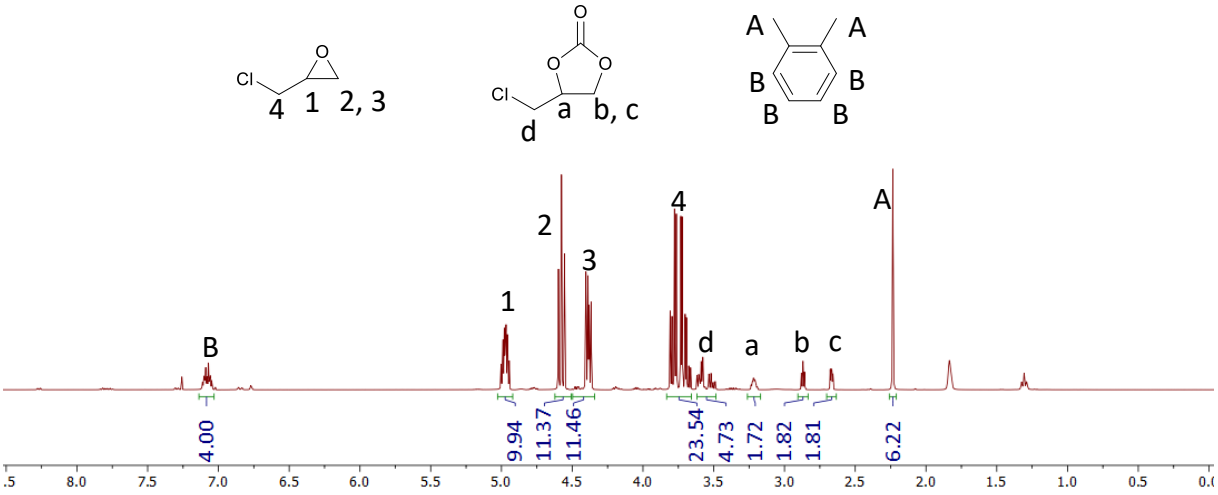


Figure S8. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to epichlorohydrin.

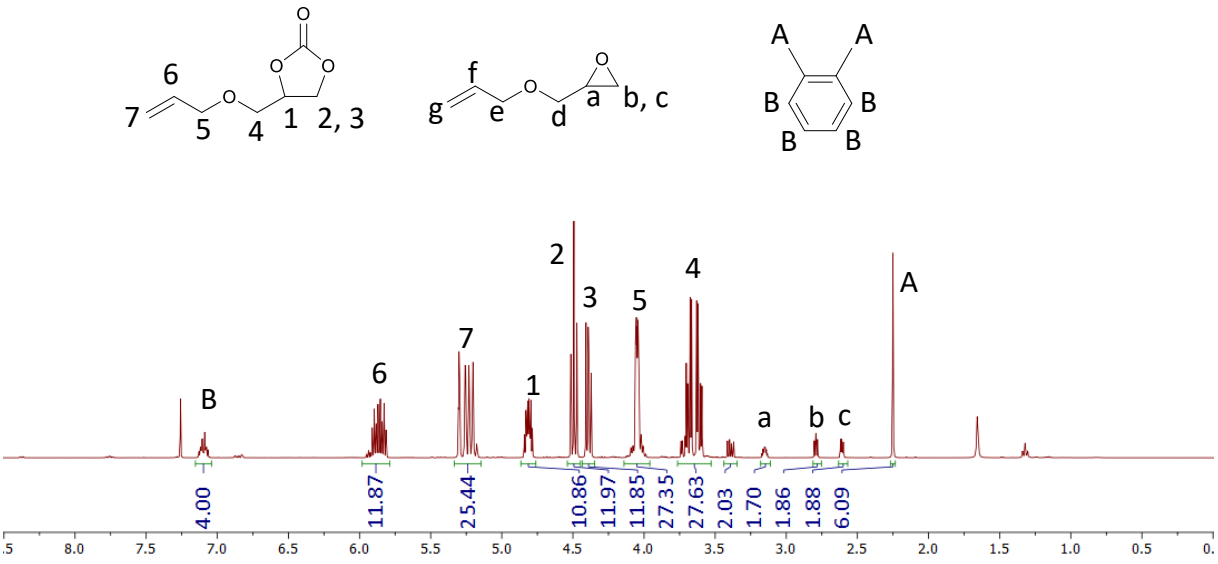


Figure S9. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to allyl glycidyl ether.

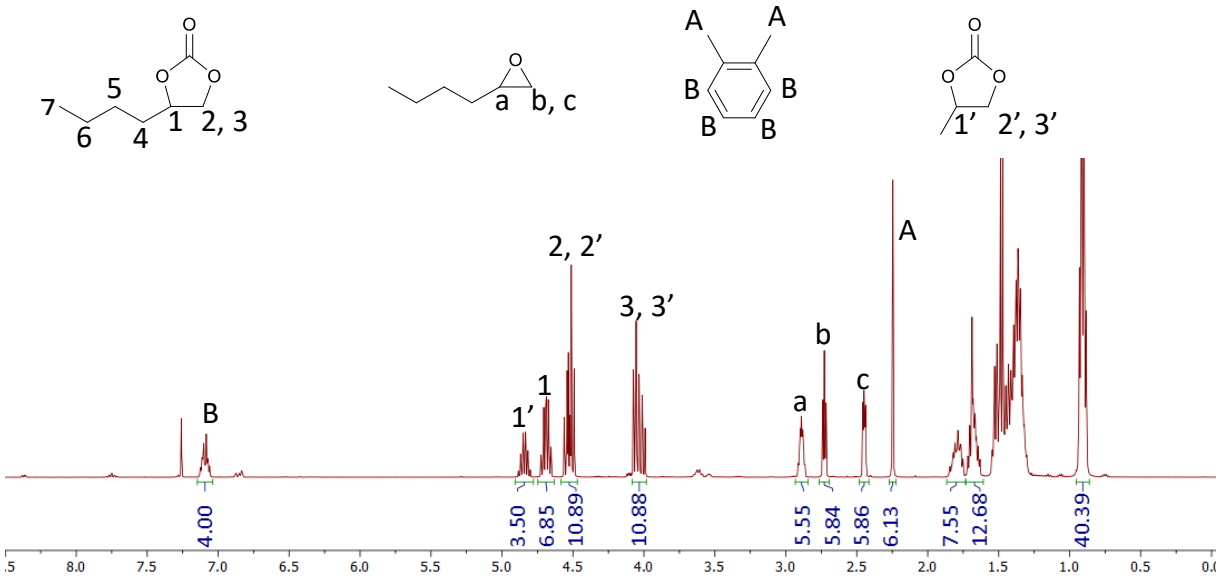


Figure S10. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to 1,2-epoxyhexane (PC as the solvent).

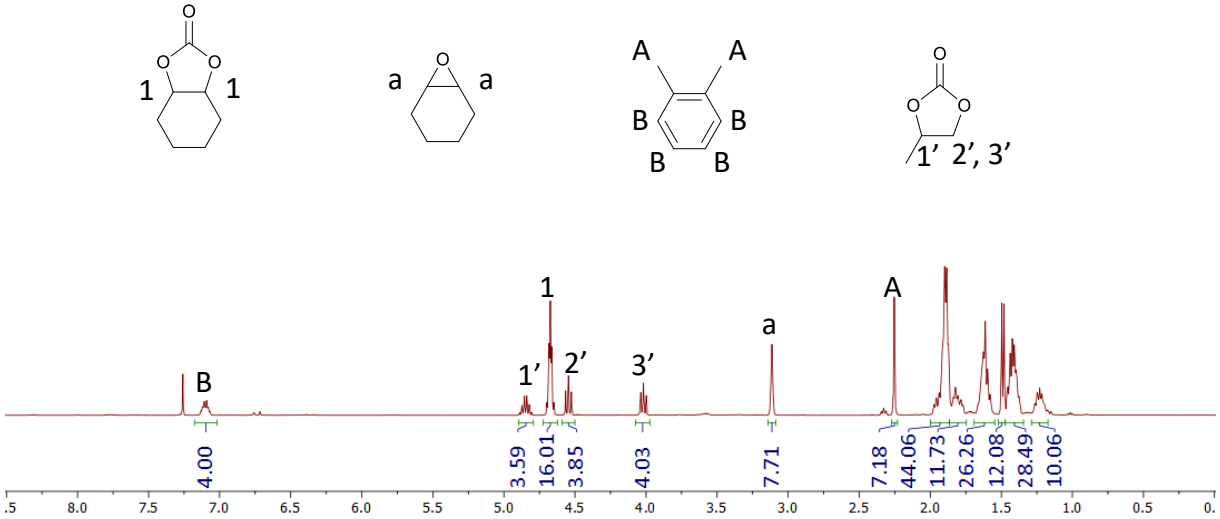


Figure S11. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to cyclohexene oxide (PC as the solvent).

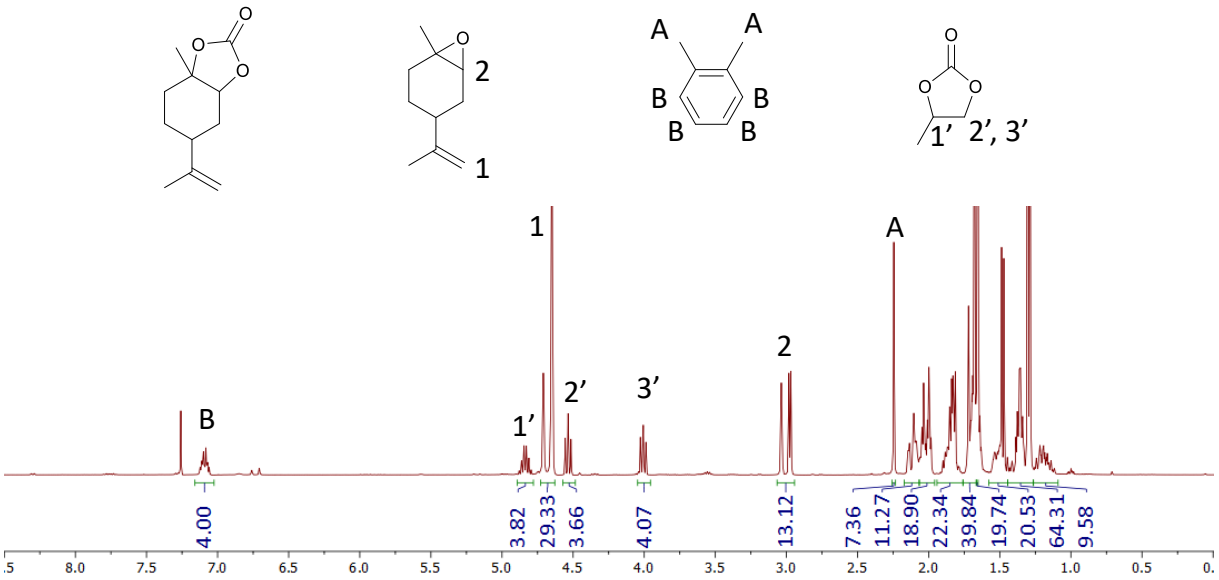


Figure S12. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to limonene oxide (PC as the solvent).

NMR spectra of RhB-EtOH-Br

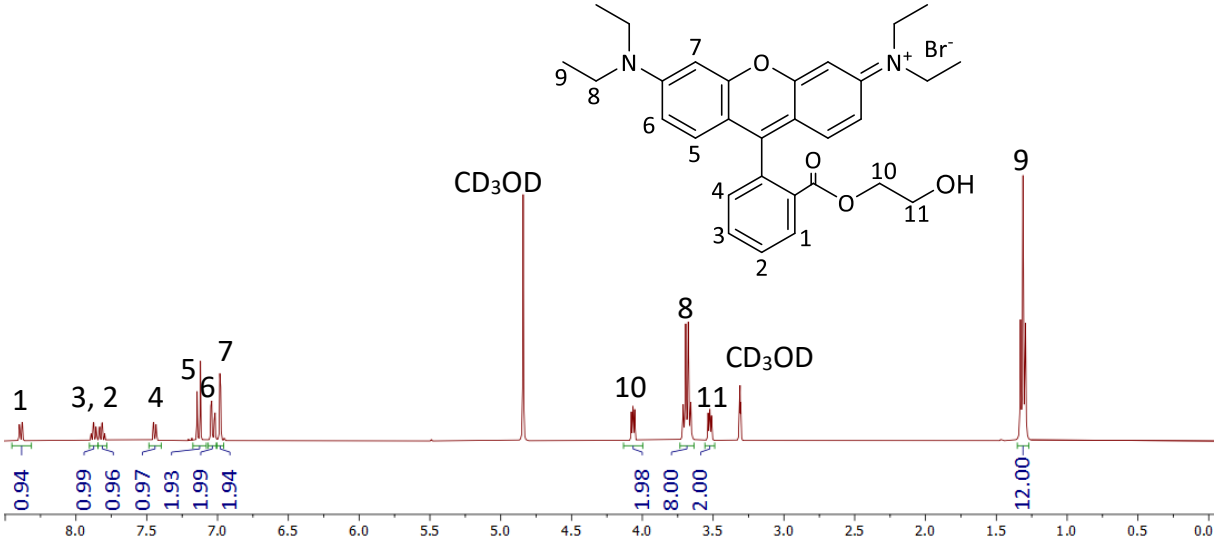


Figure S13. ^{1}H NMR spectrum of RhB-EtOH-Br.

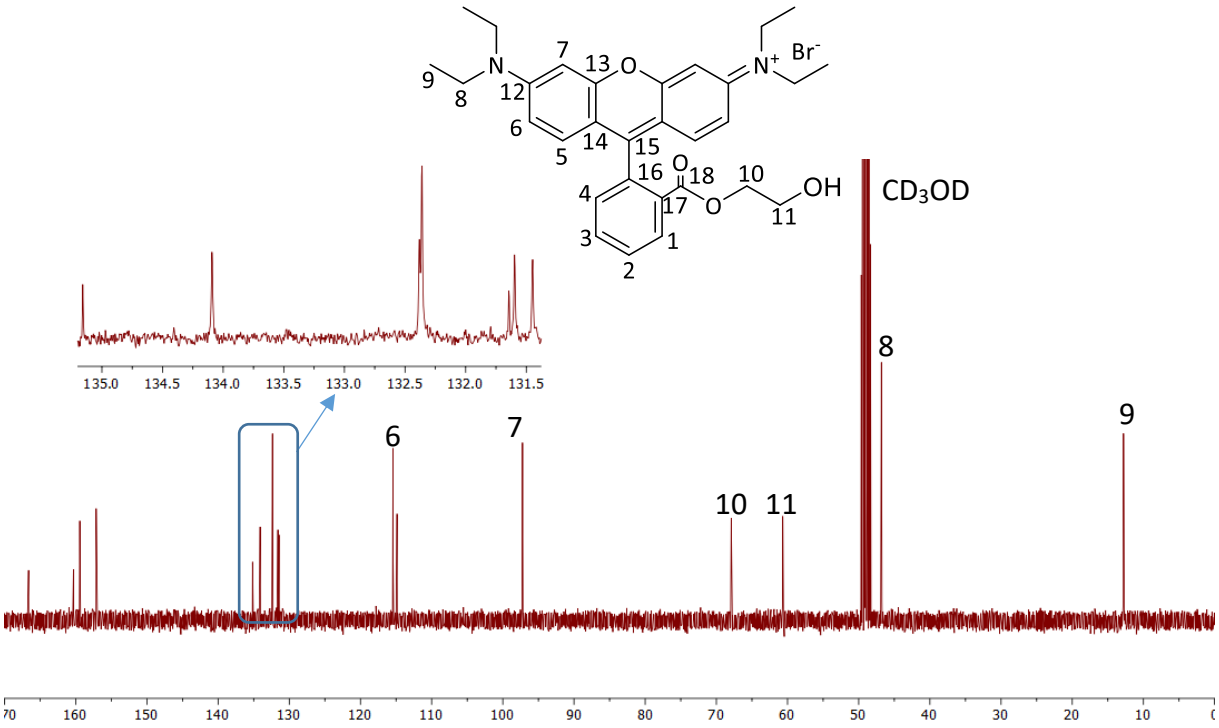


Figure S14. ^{13}C NMR spectrum of RhB-EtOH-Br.

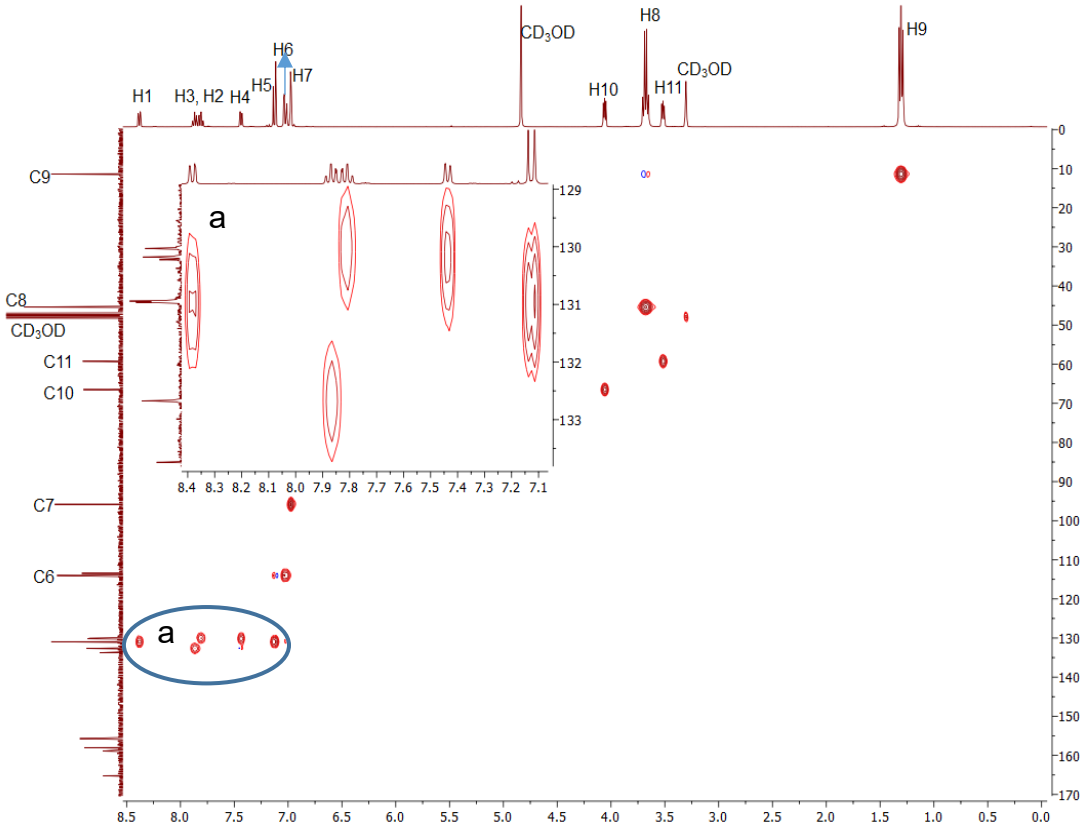


Figure S15. ^{1}H-^{13}C HSQC NMR spectrum of RhB-EtOH-Br.

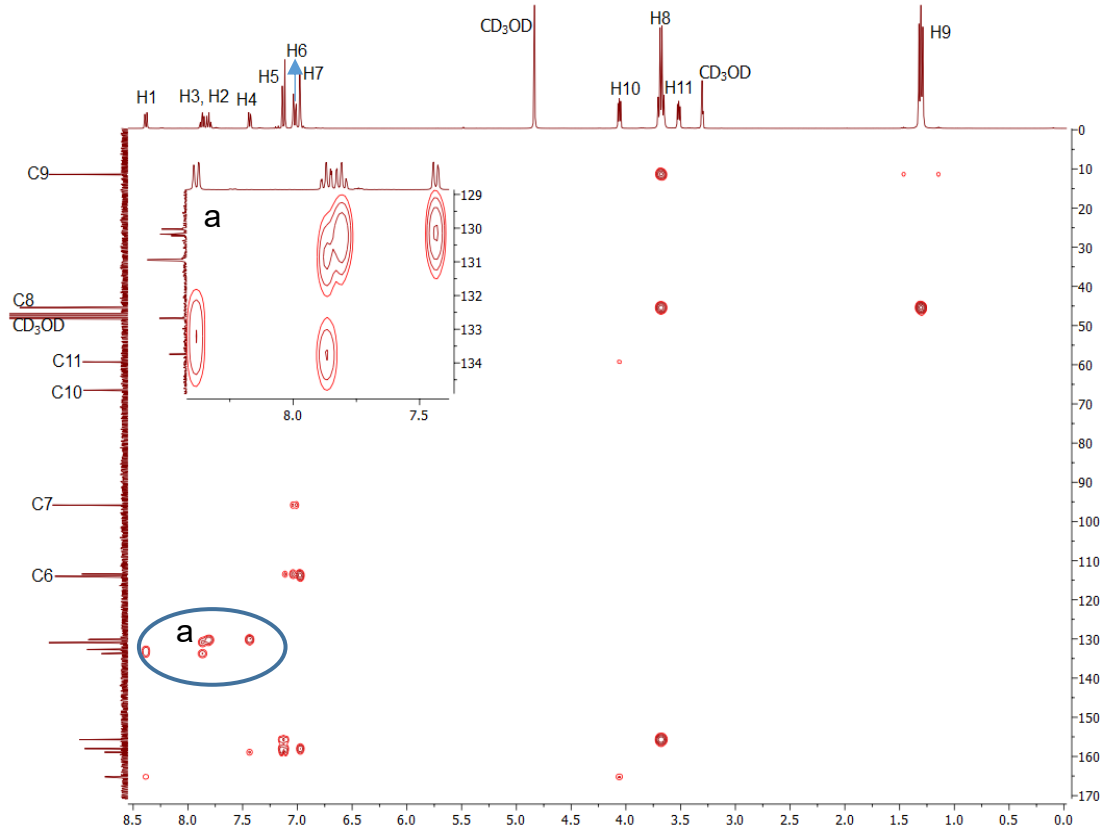


Figure S16. ^{1}H-^{13}C HMBC NMR spectrum of RhB-EtOH-Br.

NMR spectra of RhB-EtOH-I

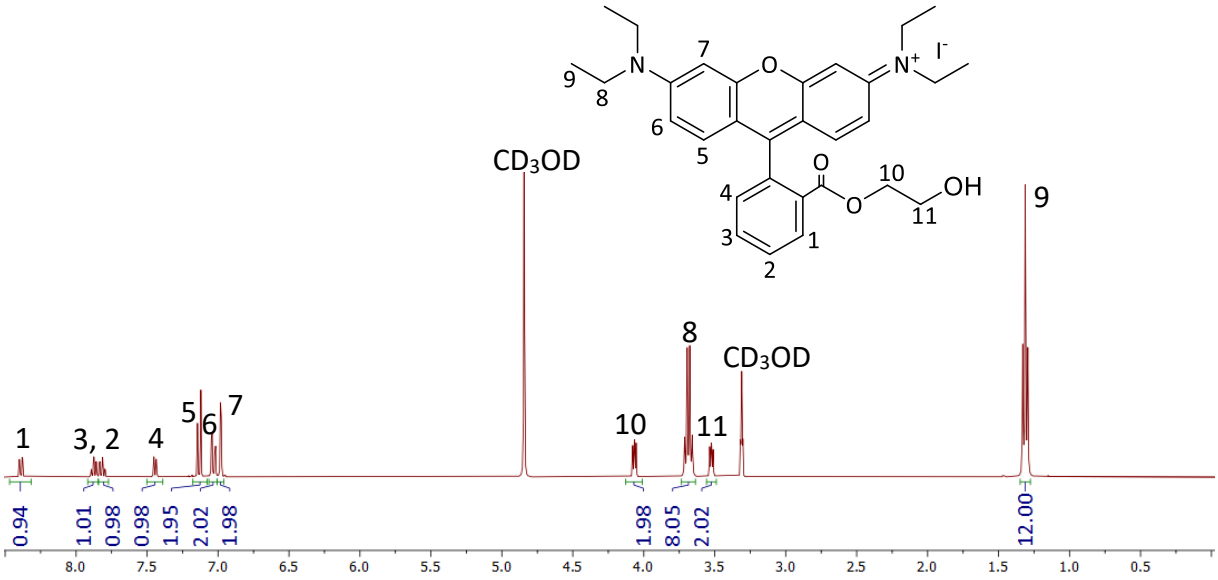


Figure S17. ^{1}H NMR spectrum of RhB-EtOH-I.

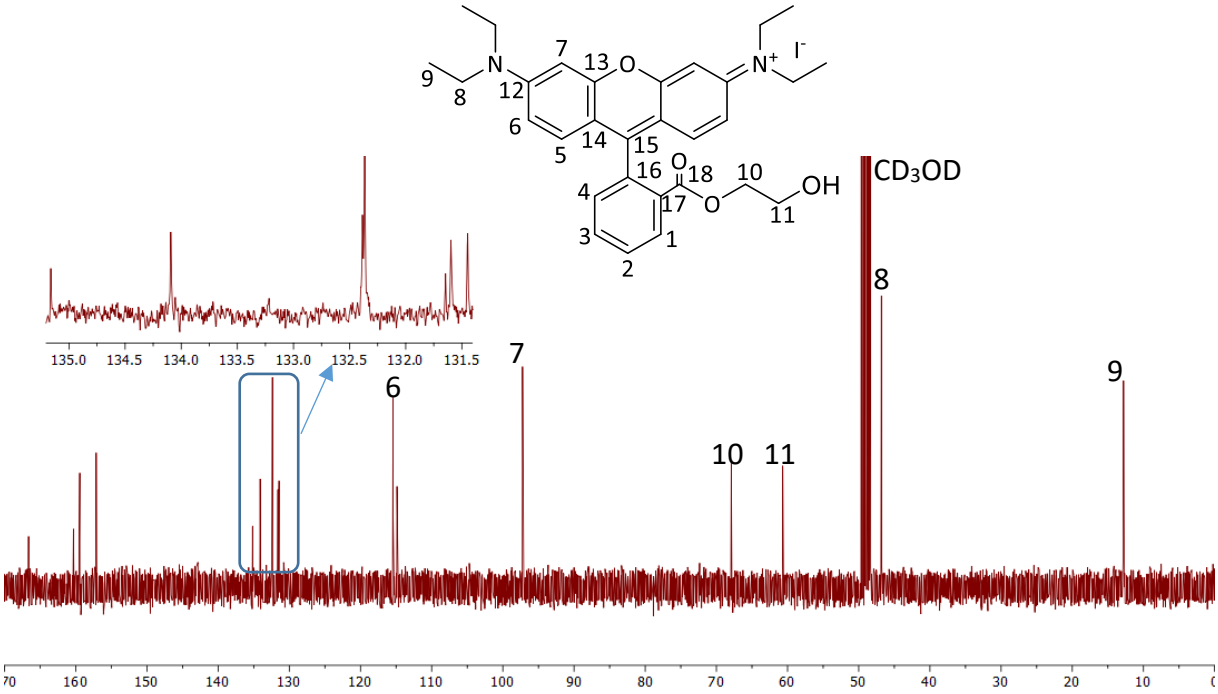


Figure S18. ^{13}C NMR spectrum of RhB-EtOH-I.

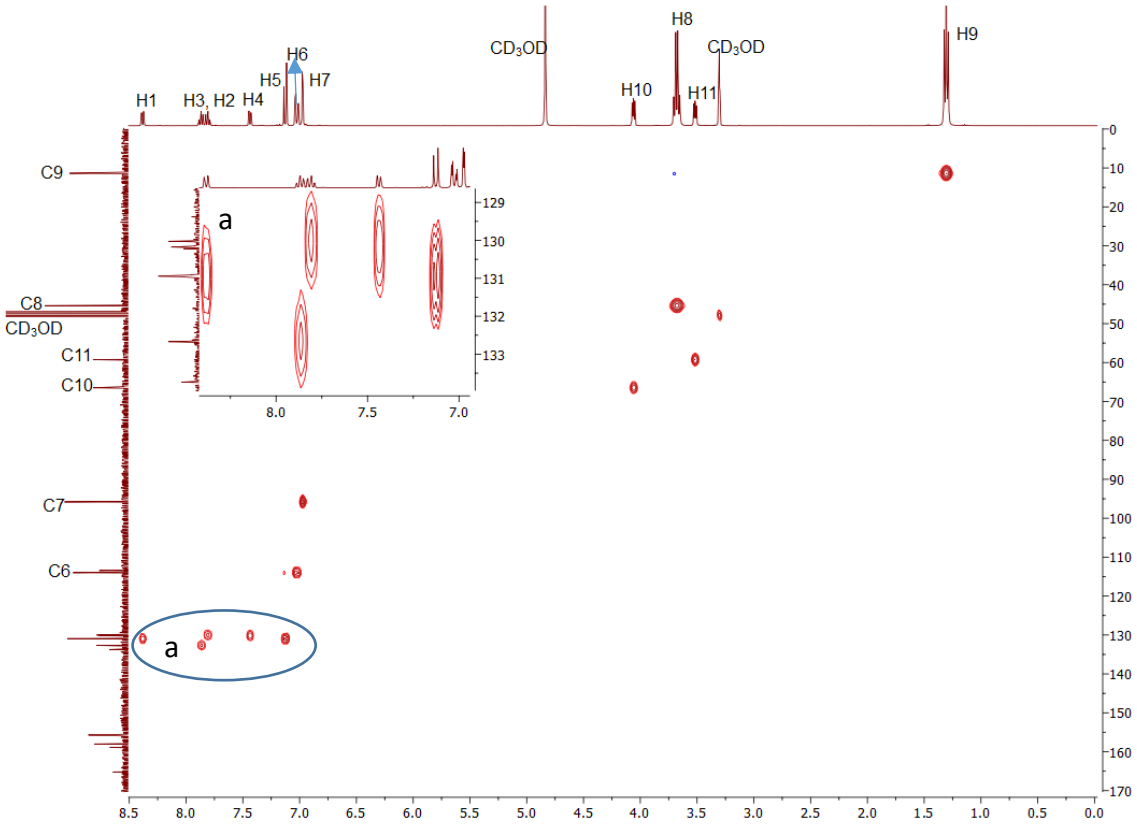


Figure S19. ^{1}H-^{13}C HSQC NMR spectrum of RhB-EtOH-I.

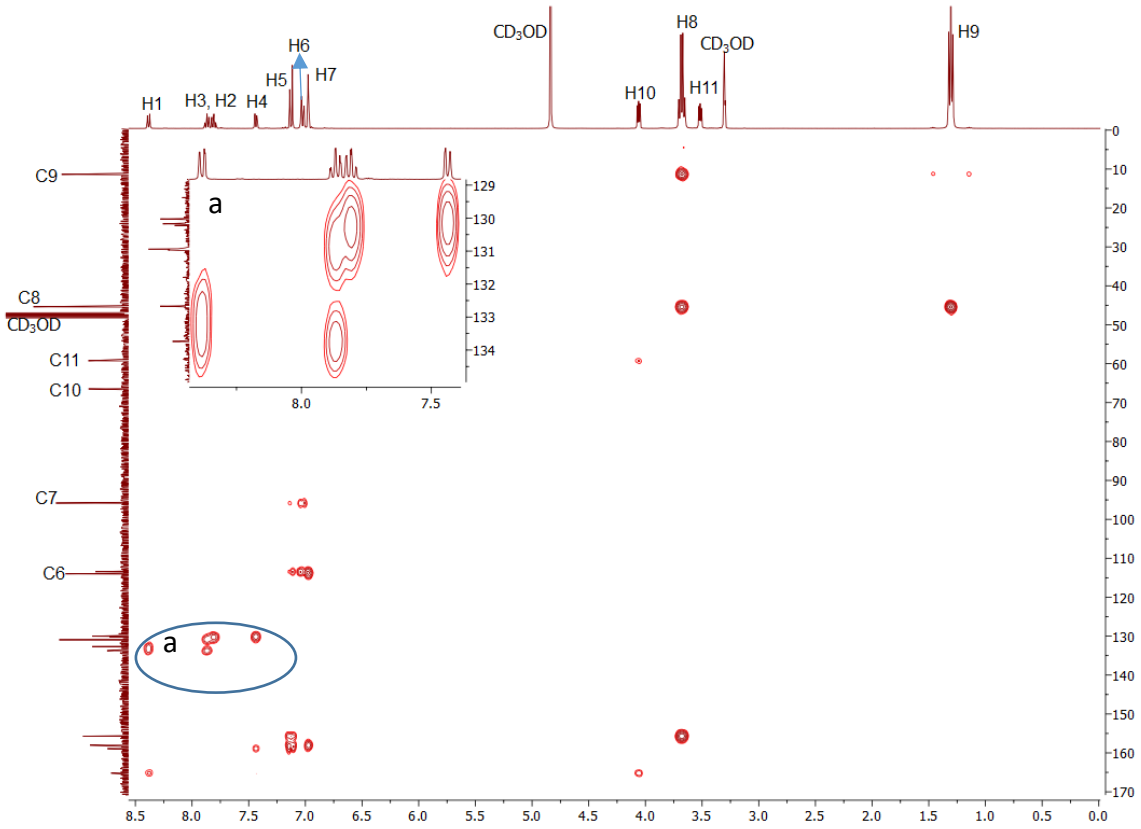


Figure S20. ^{1}H-^{13}C HMBC NMR spectrum of RhB-EtOH-I.

NMR spectra of purified styrene carbonate

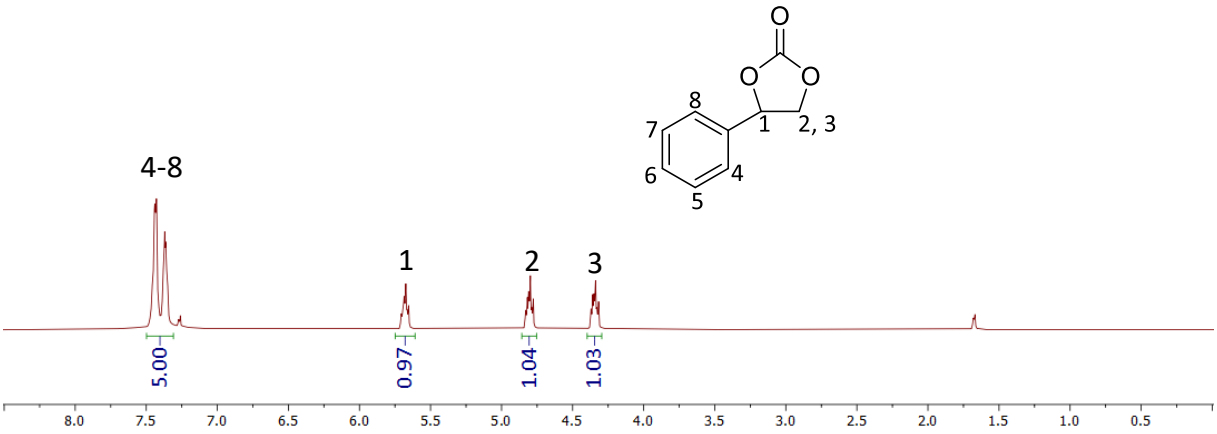


Figure S21. ^{1}H NMR spectrum of purified styrene carbonate.

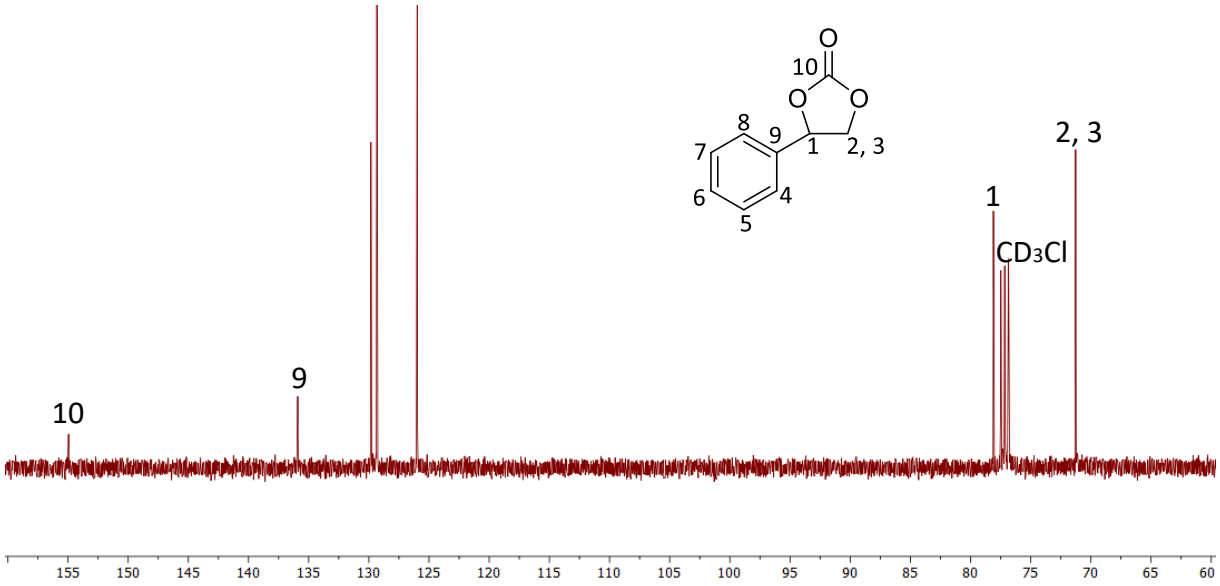


Figure S22. ^{13}C NMR spectrum of purified styrene carbonate.

NMR spectra of the fresh and recovered RhB-EtOH-I (in $CDCl_3$)

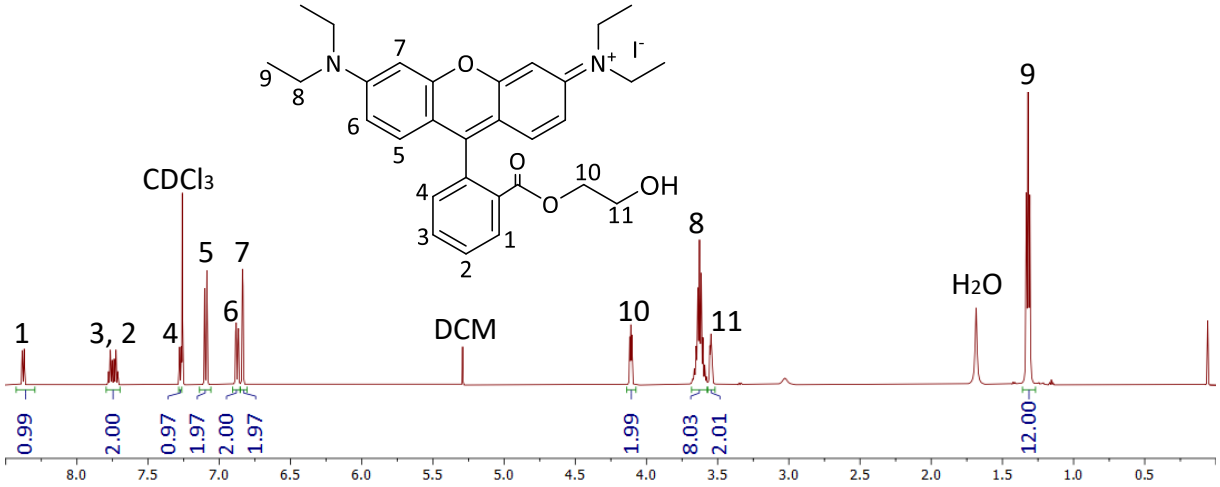


Figure S23. ^{1}H NMR spectrum (in $CDCl_3$) of the fresh RhB-EtOH-I organocatalyst.

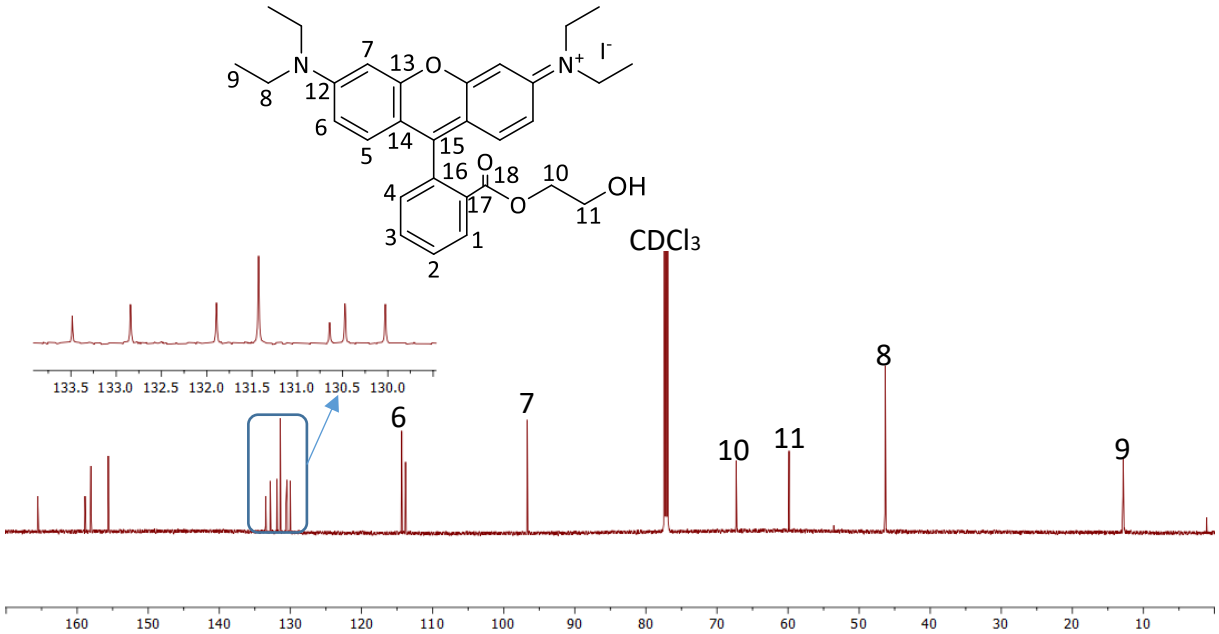


Figure S24. ^{13}C NMR spectrum (in $CDCl_3$) of the fresh RhB-EtOH-I organocatalyst.

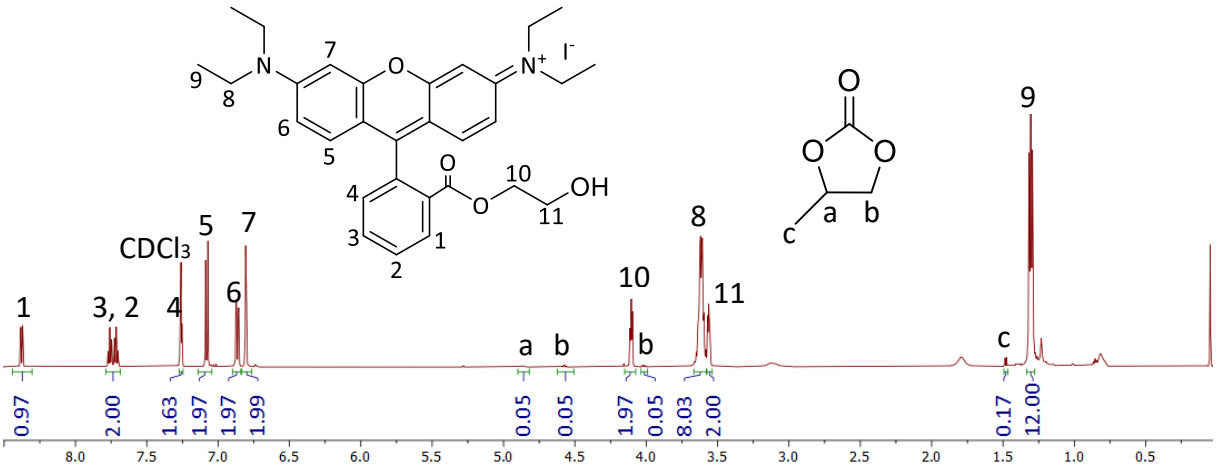


Figure S25. ^{1}H NMR spectrum (in $CDCl_3$) of the recovered RhB-EtOH-I organocatalyst.

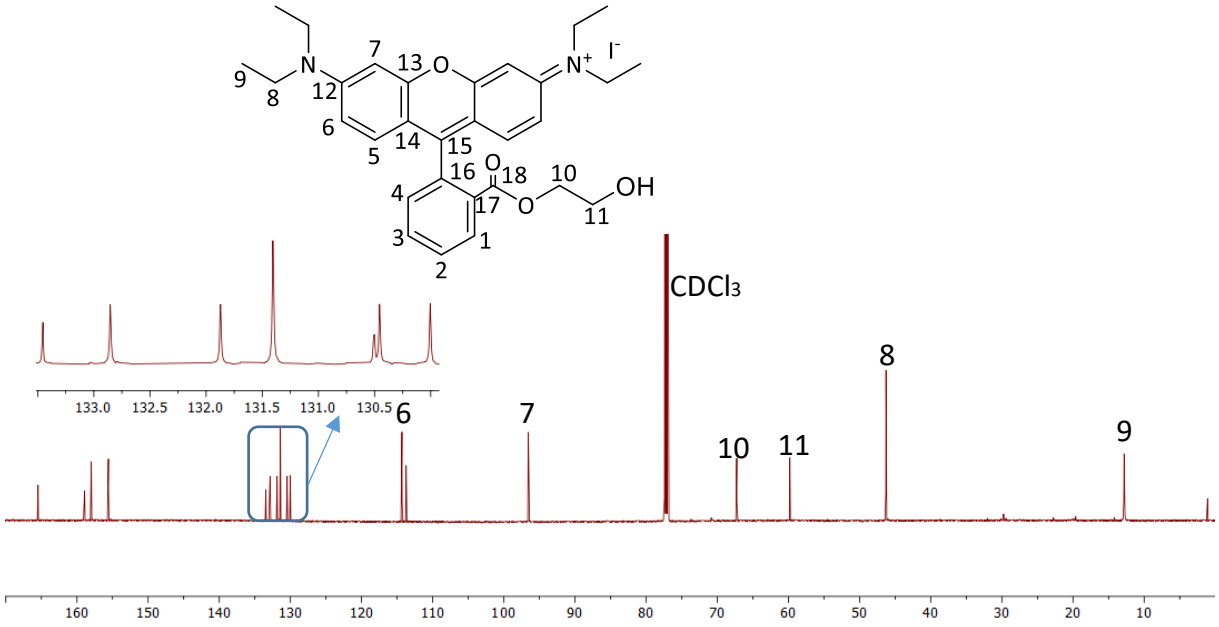


Figure S26. ^{13}C NMR spectrum (in $CDCl_3$) of the recovered RhB-EtOH-I organocatalyst.