Bifunctional dye-based organocatalysts with enhanced activity in the conversion of CO_2 into cyclic carbonates

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Supplementary Information

Experimental section

Materials

Rhodamine B base (RhB base, 97% purity), 1-bromopropane (99%), 4-bromo-1-butene (97%) (2-bromoethyl)benzene (98%), 3-bromo-1-propanol (97%), 4-hydroxyphenethyl bromide (96%), styrene oxide (97%), potassium iodide (≥ 99%), allyl glycidyl ether (99.9 %), epichlorohydrin (≥ 99%), 1,2-epoxyhexane (97 %), anhydrous magnesium sulphate (≥ 99.5%), potassium iodide (KI, ≥ 99%), cyclohexene oxide (98%), (+)-limonene oxide (mixture of cis and trans, 97%), propylene carbonate (99.7 % purity) and deuterated solvents ($CDCl_3$ and CD_3OD, used as solvents for NMR spectroscopy) were purchased from Sigma-Aldrich. Allyl Chloride (> 98%) was obtained from TCI Chemicals. Diethyl ether (AR grade) and ethyl acetate (AR grade) were ordered from Biosolve-chemicals. Dichloromethane (AR grade) was purchased from Macron fine chemicals. 2-Bromoethanol (96 %) and propylene oxide (99.5 %) were obtained from Fisher Scientific. Acetonitrile (99.9%) and o-xylene (≥ 99%) were purchased from Honeywell. All the chemicals were used without additional purification.

Characterisation methods

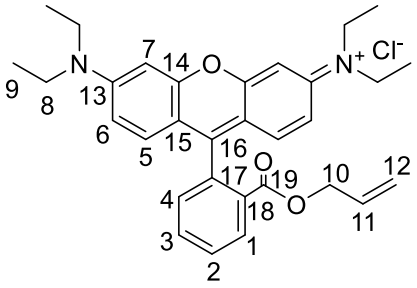
The modified dyes were characterised by Nuclear Magnetic Resonance (NMR) spectroscopy on a Varian Mercury Plus 400 MHz or Agilent MR 400 MHz apparatus. The NMR samples were prepared by dissolving 10 mg of each modified dye in 0.7 mL of $CDCl_3$ or CD_3OD. The NMR spectra were referenced using residual solvent peaks. Several NMR techniques were employed: ^{1}H NMR, ^{13}C NMR, ^{1}H-^{13}C HSQC (Heteronuclear Single Quantum Coherence), and ^{1}H-^{13}C HMBC (Heteronuclear Multiple Bond Correlation). Elemental analysis for H, C, N and S was carried out on a Vario Micro Cube elemental analyser.

Catalysts preparation

Synthesis of RhB-Allyl-Cl

RhB-Allyl-Cl was synthesised by adapting a literature procedure.[25] In a typical synthesis, RhB base (5.04 g, 11.3 mmol) was dissolved in 70 mL ethanol, and a three-fold excess of allyl chloride (2.60 g, 34.0 mmol) was added into the above solution. The reaction mixture was stirred at 70 °C for 24 h. After the reaction, the solvent was removed under reduced pressure. The obtained crude product was dissolved in 450 mL H_2O and then extracted with ethyl acetate (120 mL x 3 times) to remove the unreacted RhB base and allyl chloride (note that in this step a fraction of RhB-Allyl-Cl is also extracted to the ethyl acetate phase). Then, the RhB-Allyl-Cl was recovered from the aqueous phase by extraction with 120 mL dichloromethane. The organic phase was collected and dried with anhydrous $MgSO_4$, after which the $MgSO_4$ drying agent was removed by centrifugation at 4000 rpm for 5 min. The purified RhB-Allyl-Cl product was obtained by removing dichloromethane under reduced pressure, followed by drying at 80 °C overnight in a vacuum oven (brown powder, 2.00 g, 34% yield relative to RhB base).

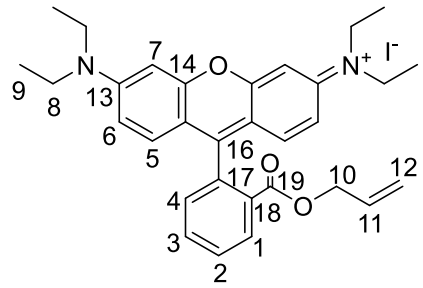
Analysis of RhB-Allyl-Cl ($C_{31}H_{35}ClN_2O_3$): ^{1}H NMR (400 MHz, chloroform-D, 25°C) δ 8.29 (dd, *J* = 7.9, 1.3 Hz, 1H, H1), 7.81 (td, *J* = 7.5, 1.4 Hz, 1H, H3), 7.73 (td, *J* = 7.7, 1.4 Hz, 1H, H2), 7.30 (dd, *J* = 7.6, 1.3 Hz, 1H, H4), 7.06 (d, *J* = 9.5 Hz, 2H, H5), 6.90 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 6.79 (d, *J* = 2.4 Hz, 2H, H7), 5.68 (ddt, *J* = 17.3, 10.3, 5.8 Hz, 1H, H11), 5.21-5.08 (m, 2H, H12), 4.49 (dt, *J* = 5.9, 1.3 Hz, 2H, H10), 3.63 (q, *J* = 7.2 Hz, 8H, H8), 1.31 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, chloroform-D, 25°C) δ 164.79, 158.85, 157.86, 155.65, 133.71, 133.27, 131.44, 131.37, 131.20, 130.53, 130.36, 130.00, 119.18 (C12), 114.38 (C6), 113.65, 96.44 (C7), 66.21 (C10), 46.28 (C8), 12.77 (C9). The full NMR spectra of RhB-Allyl-Cl can be found in the Figure S2-5. The elemental composition of the RhB-Allyl-Cl was determined by elemental analysis. Theoretical composition of RhB-Allyl-Cl: C 71.73 wt%, H 6.8 wt%, N 5.4 wt%; found: C 64.55 wt%, H 6.36 wt%, N 5.04 wt%.



Synthesis of RhB-Allyl-I

RhB-Allyl-Cl (2.01 g, 3.87 mmol) was dissolved in 50 mL Milli-Q water while stirring at 60 °C. Then, an aqueous solution of KI (1.93 g, 11.63 mmol in *ca.* 2 mL Milli-Q water) was added to the above solution upon stirring, leading to the precipitation of RhB-Allyl-I. The solution was stirred in an oil bath at 60 °C for 1 h and then placed into an ice bath, while stirring for 1 h. The precipitate was recovered by centrifugation at 4000 rpm for 5 min, washed with *ca.* 200 mL Milli-Q water and centrifuged again. The supernatant was removed and the obtained solid was dissolved in 30 mL dichloromethane and then recrystallised by slowly adding 180 mL diethyl ether to the solution. Afterwards, the recrystallised solid was dissolved in 30 mL dichloromethane and dried with anhydrous $MgSO_4$. The dry agent was removed by centrifugation at 4000 rpm for 5 min, and the solvent was removed under reduced pressure to obtain the solid product. The product was dried in a vacuum oven overnight at 80 °C (brown powder, 1.37 g, 58% yield relative to RhB-Allyl-Cl).

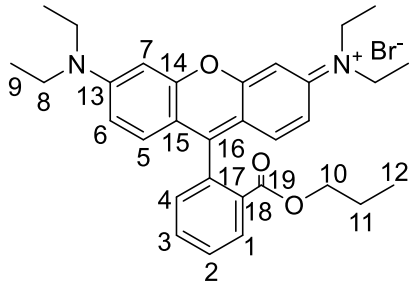
Analysis of RhB-Allyl-I ($C_{31}H_{35}IN_2O_3$): ^{1}H NMR (400 MHz, chloroform-D, 25°C) δ 8.30 (dd, *J* = 7.9, 1.3 Hz, 1H, H1), 7.83 (td, *J* = 7.5, 1.4 Hz, 1H, H3), 7.74 (td, *J* = 7.7, 1.3 Hz, 1H, H2), 7.33 (dd, *J* = 7.6, 1.3 Hz, 1H, H4), 7.06 (d, *J* = 9.5 Hz, 2H, H5), 6.89 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 6.81 (d, *J* = 2.4 Hz, 2H, H7), 5.69 (ddt, *J* = 17.3, 10.4, 5.9 Hz, 1H, H11), 5.22-5.08 (m, 2H, H12), 4.50 (dt, *J* = 5.8, 1.4 Hz, 2H, H10), 3.64 (q, *J* = 7.2 Hz, 8H, H8), 1.32 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, chloroform-D, 25°C) δ 164.83, 158.87, 157.89, 155.65, 133.71, 133.35, 131.44, 131.38, 131.22, 130.55, 130.43, 130.03, 119.22 (C12), 114.44 (C6), 113.69, 96.51 (C7), 66.23 (C10), 46.39 (C8), 12.84 (C9). The full NMR spectra of RhB-Allyl-I can be found in Figure S6-9. The elemental composition of RhB-Allyl-I was determined by elemental analysis. Theoretical composition of RhB-Allyl-I: C 60.99 wt%, H 5.78 wt%, N 4.59 wt%; found: C 59.93 wt%, H 5.81 wt%, N 4.47 wt%.



Synthesis of RhB-Pr-Br

In a typical synthesis of RhB-Pr-Br, RhB base (2.03 g, 4.59 mmol) was dissolved in 30 mL ethanol, and *ca.* three-fold excess of 1-bromopropane (1.68 g, 13.66 mmol) was added into the above solution. The reaction mixture was stirred at 70 °C for 24 h. After the reaction, the solvent was removed under reduced pressure. The obtained crude product was washed with ethyl acetate (30 mL x 9 times) to remove the unreacted RhB base and 1-bromopropane (note that in this step a fraction of RhB-Pr-Br is also extracted to the ethyl acetate phase). The solid was further purified by dissolving it in 30 mL dichloromethane, followed by extraction with H_2O (30 mL x 6 times). Then, anhydrous $MgSO_4$ was added to dry the organic solution and then removed by centrifugation at 4000 rpm for 5 min. The purified RhB-Pr-Br was obtained by removing dichloromethane under reduced pressure, followed by drying at 80 °C overnight in a vacuum oven (brown powder, 1.92 g, 74% yield relative to RhB base).

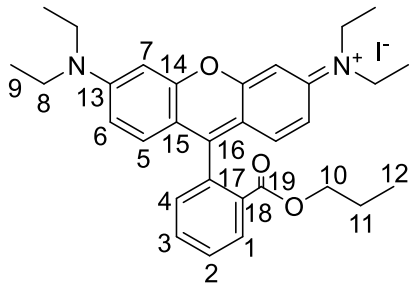
Analysis of RhB-Pr-Br ($C_{31}H_{37}BrN_2O_3$):^{1}H NMR (400 MHz, chloroform-D, 25°C) δ 8.28 (dd, *J* = 7.9, 1.4 Hz, 1H, H1), 7.80 (td, *J* = 7.5, 1.4 Hz,1H, H3), 7.72 (td, *J* = 7.7, 1.4 Hz, 1H,H2), 7.29 (dd, *J* = 7.5, 1.3 Hz, 1H, H4), 7.07 (d, *J* = 9.5 Hz, 2H, H5), 6.91 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 6.80 (d, *J* = 2.4 Hz, 2H, H7), 3.97 (t, *J* = 6.7 Hz, 2H, H10), 3.64 (q, *J* = 7.2 Hz, 8H, H8), 1.46 (h, *J* = 7.1 Hz, 2H, H11), 1.32 (t, *J* = 7.1 Hz, 12H, H9), 0.77 (t, *J* = 7.4 Hz, 3H, H12). ^{13}C NMR (400 MHz, chloroform-D, 25°C) δ 165.26, 159.04, 157.86, 155.66, 133.59, 133.13, 131.42, 131.40, 130.48, 130.32, 130.30, 114.41(C6), 113.67, 96.46 (C7), 67.34 (C10), 46.32 (C8), 21.80 (C11), 12.80 (C9), 10.37 (C12). The full NMR spectra of RhB-Pr-Br can be found in Figure S10-13. The elemental composition of the RhB-Pr-Br was determined by elemental analysis. Theoretical composition of RhB-Pr-Br: C 65.84 wt%, H 6.59 wt%, N 4.95 wt%; found: C 65.21 wt%, H 6.75 wt%, N 4.81 wt%.



Synthesis of RhB-Pr-I

RhB-Pr-I was synthesised through an ion-exchange reaction between RhB-Pr-Br (2.00 g, 3.53 mmol, dissolved in in 30 mL Milli Q water) and KI (1.78 g, 10.72 mmol dissolved in *ca.* 2 mL Milli-Q water), by following the same experimental procedure used for the synthesis of RhB-Allyl-I (RhB-Pr-I, brown powder, 1.29 g, 60% yield relative to RhB-Pr-Br).

Analysis of RhB-Pr-I ($C_{31}H_{37}IN_2O_3$): ^{1}H NMR (400 MHz, chloroform-D, 25°C) δ 8.27 (dd, *J* = 7.9, 1.4 Hz, 1H, H1), 7.80 (td, *J* = 7.5, 1.4 Hz, 1H, H3), 7.72 (td, *J* = 7.7, 1.4 Hz, 1H, H2), 7.29 (dd, *J* = 7.6, 1.3 Hz, 1H, H4), 7.05 (d, *J* = 9.5 Hz, 2H, H5), 6.88 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 6.78 (d, *J* = 2.4 Hz, 2H, H7), 3.95 (t, *J* = 6.6 Hz, 2H, H10), 3.63 (q, *J* = 7.2 Hz, 8H, H8), 1.45 (h, *J* = 7.2 Hz, 2H, H11), 1.30 (t, *J* = 7.1 Hz, 12H, H9), 0.76 (t, *J* = 7.4 Hz, 3H, H12). ^{13}C NMR (400 MHz, chloroform-D, 25°C) δ 165.22, 159.02, 157.81, 155.59, 133.49, 133.12 (C3), 131.37, 131.36, 130.46, 130.27, 130.25, 114.38 (C6), 113.61, 96.40 (C7), 67.29(C10), 46.34 (C8), 21.75 (C11), 12.79 (C9), 10.34 (C12). The full NMR spectra of RhB-Pr-I can be found in Figure S14-17. The elemental composition of

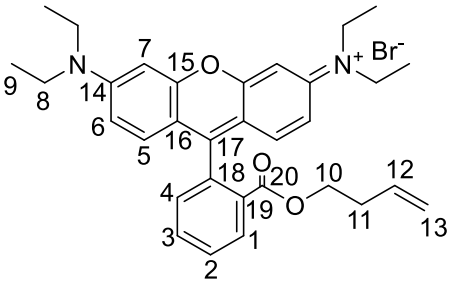


RhB-Pr-I was determined by elemental analysis. Theoretical composition of RhB-Pr-I: C 60.79 wt%, H 6.09 wt%, N 4.57 wt%; found: C 59.67 wt%, H 6.09 wt%, N 4.35 wt%.

Synthesis of RhB-Butenyl-Br

In a typical synthesis of RhB-Butene-Br, RhB base (2.00 g, 4.51 mmol) and a three-fold excess of 4-bromo-1-butene (1.83 g, 13.56 mmol) were dissolved in 30 mL ethanol. The reaction mixture was stirred at 70 °C for 24 h. Next, the solvent was removed under reduced pressure. The obtained crude solid was washed with ethyl acetate (30 mL x 6 times) to remove the unreacted RhB base and 4-bromo-1-butene (note that in this step a fraction of RhB-Butene-Br is also extracted to the ethyl acetate phase). Then, the solid was further purified by dissolving it in 30 mL dichloromethane, followed by extraction with H_2O (60 mL x 3 times). The remaining organic phase was collected, and then 180 mL diethyl ether was slowly added to it to precipitate the solid product. Afterwards, the solid product was dissolved in 30 mL dichloromethane. Anhydrous $MgSO_4$ was added to dry the solution and then removed by centrifugation at 4000 rpm for 5 min. The purified RhB-Butenyl-Br was obtained by removing dichloromethane under reduced pressure, followed by drying at 80 °C overnight in a vacuum oven (brown powder, 1.73 g, 66% yield relative to RhB base).

Analysis of RhB-Butenyl-Br ($C_{32}H_{37}BrN_2O_3$): ^{1}H NMR (400 MHz, chloroform-D, 25°C) δ 8.25 (dd, J = 7.9, 1.3 Hz, 1H, H1), 7.79 (td, J = 7.5, 1.4 Hz, 1H, H3), 7.71 (td, J = 7.7, 1.4 Hz, 1H, H2), 7.27 (d, J = 7.8 Hz, 1H, H4), 7.04 (d, J = 9.5 Hz, 2H, H5), 6.88 (dd, J = 9.5, 2.5 Hz, 2H, H6), 6.77 (d, J = 2.4 Hz, 2H, H7), 5.55 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H, H12), 5.00-4.89 (m, 2H, H13), 4.05 (t, J = 6.6 Hz, 2H, H10), 3.62 (q, J = 7.2 Hz, 8H, H8), 2.19 (qt, J = 6.6, 1.4 Hz, 2H, H11), 1.30 (t, J = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, chloroform-D, 25°C) δ 165.07, 158.88, 157.79, 155.57, 133.52, 133.44, 133.17, 131.37, 131.35, 130.47, 130.28, 130.02, 117.38 (C13), 114.35 (C6), 113.58, 96.37 (C7), 64.59 (C10), 46.28 (C8), 32.63 (C11), 12.75 (C9). The full NMR spectra of RhB-Butenyl-Br can be found in Figure S18-21. The elemental composition of RhB- Butenyl-Br was determined by elemental analysis. Theoretical composition of RhB- Butenyl-Br: C 66.55 wt%, H 6.46 wt%, N 4.85 wt%; found: C 61.9 wt%, H 6.32 wt%, N 4.62 wt%.



Synthesis of RhB-Butenyl-I

RhB-Butenyl-I was synthesised through an ion-exchange reaction between RhB-Butenyl-Br (2.09g, 3.62 mmol in 50 mL Milli-Q water) and KI (1.73 g, 10.42 mmol in *ca.* 2 mL H_2O), by following the same experimental procedure used for the synthesis of RhB-Allyl-I (RhB-Butenyl-I, brown powder, 1.72 g, 76% yield relative to RhB-Butenyl-Br).

Analysis of RhB-Butenyl-I ($C_{32}H_{37}IN_2O_3$): ^{1}H NMR (400 MHz, chloroform-D, 25°C) δ 8.27 (dd, *J* = 7.9, 1.3 Hz, 1H, H1), 7.82 (td, *J* = 7.5, 1.4 Hz, 1H, H3), 7.73 (td, *J* = 7.7, 1.4 Hz, 1H, H2), 7.31 (dd, *J* = 7.5, 1.3 Hz, 1H, H4), 7.06 (d, *J* = 9.5 Hz, 2H, H5), 6.90 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 6.81 (d, *J* = 2.4 Hz, 2H, H7), 5.58 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1H, H12), 5.02 – 4.91 (m, 2H, H13), 4.08 (t, *J* = 6.6 Hz, 2H, H10), 3.65 (q, *J* = 7.2 Hz, 8H, H8), 2.22 (qt, *J* = 6.6, 1.4 Hz, 2H, H11), 1.32 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, chloroform-D, 25°C) δ 165.15, 158.95, 157.88, 155.64, 133.61, 133.51, 133.27, 131.43, 130.52, 130.39, 130.10, 117.47 (C13), 114.44 (C6), 113.68, 96.50 (C7), 64.67 (C10), 46.38 (C8), 32.72 (C11), 12.84 (C9).

The full NMR spectra of RhB-Butenyl-I can be found in Figure S22-25. The elemental composition of RhB-Butenyl-I was determined by elemental analysis. Theoretical composition of RhB-Butenyl-I: C 61.54 wt%, H 5.97 wt%, N 4.49 wt%; found: C 60.93 wt%, H 6.08 wt%, N 4.42 wt%.

Synthesis of RhB-Ethyl-Ph-Br

RhB-Ethyl-Ph-Br was synthesised by the reaction of RhB base (2.13 g, 4.81 mmol) with (2-bromoethyl)benzene (2.52 g, 13.62 mmol) in 30 mL ethanol, by following the sample experimental procedure used for the synthesis of RhB-Butene-Br (RhB-Ethyl-Ph-Br, brown powder, 2.24 g, 74% relative to RhB base).

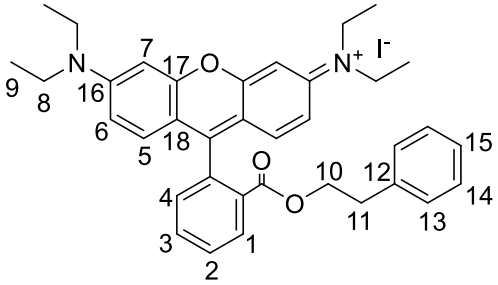
^{1}H NMR (400 MHz, methanol-D, 25°C) δ 8.26 (dd, *J* = 7.8, 1.4 Hz, 1H, H1), 7.86 (td, *J* = 7.5, 1.5 Hz, 1H, H3), 7.79 (td, *J* = 7.7, 1.4 Hz, 1H, H2), 7.42 (dd, *J* = 7.5, 1.4 Hz, 1H, H4), 7.21-7.13 (m, 3H), 7.09 (d, *J* = 9.5 Hz, 2H, H5), 7.04-6.98 (m, 4H), 6.96 (d, *J* = 2.4 Hz, 2H, H7), 4.21 (t, *J* = 6.6 Hz, 2H, H10), 3.68 (q, *J* = 7.1 Hz, 8H, H8), 2.67 (t, *J* = 6.6 Hz, 2H, H11), 1.31 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, methanol-D, 25°C) δ 166.65, 160.03, 159.23, 157.10, 138.85, 134.83, 134.09, 132.32, 132.28, 131.67, 131.64, 131.51, 129.51, 129.48, 127.53, 115.48 (C6), 114.73, 97.30 (C7), 66.90 (C10), 46.83 (C8), 35.40 (C11), 12.8 2(C9). The full NMR spectra of RhB-Ethyl-Ph-Br can be found in Figure S26-29. The elemental composition of RhB-Ethyl-Ph-Br was determined by elemental analysis. Theoretical composition of RhB-Ethyl-Ph-Br: C 68.89 wt%, H 6.26 wt%, N 4.46 wt%; found: C 66.12 wt%, H 6.35 wt%, N 4.25 wt%.

Synthesis of RhB-Ethyl-Ph-I

In a typical synthesis of RhB-Ethyl-Ph-I, RhB- Ethyl-Ph-Br (2.04 g, 3.25 mmol) was dissolved in a mixture of 30 mL Milli-Q water and 30 mL ethanol. Then, an aqueous solution of KI (1.60 g, 9.64 mmol in *ca.* 2 mL H_2O) was added to the above solution upon stirring. The reaction mixture was stirred in an oil bath at 60 °C for 1 h and then placed into an ice bath and stirred for 1 h, leading to the precipitation of RhB-Ethyl-Ph-I. Then, the ethanol was removed from the above reaction mixture under reduced pressure. The solid was recovered by centrifugation at 4000 rpm for 5 min and washed with 200 mL Milli-Q water. Next, the obtained solid was

dissolved in 30 mL dichloromethane and recrystallised by slowly adding 180 mL diethyl ether to the solution. Afterwards, the recrystallised solid was dissolved in 30 mL dichloromethane and dried with anhydrous $MgSO_4$. The dry agent was removed by centrifugation at 4000 rpm for 5 min, and the dichloromethane solvent was removed under reduced pressure to obtain the solid product. The product was dried in a vacuum oven overnight at 80 °C (brown powder, 1.59 g, 73% yield relative to RhB-Ethyl-Ph-Br).

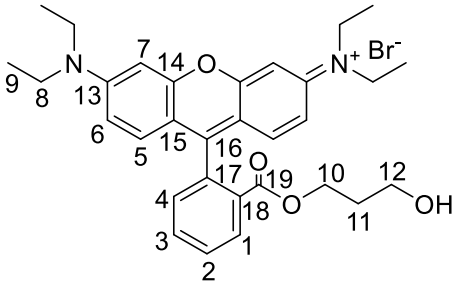
Analysis of RhB-Ethyl-Ph-I ($C_{36}H_{39}IN_2O_3$): ^{1}H NMR (400 MHz, methanol-D, 25°C) δ 8.26 (dd, *J* = 7.9, 1.4 Hz, 1H, H1), 7.86 (td, *J* = 7.5, 1.5 Hz, 1H, H3), 7.79 (td, *J* = 7.7, 1.4 Hz, 1H, H2), 7.42 (dd, *J* = 7.5, 1.3 Hz, 1H, H4), 7.22-7.14 (m, 3H), 7.09 (d, *J* = 9.5 Hz, 2H, H5), 7.04-6.99 (m, 4H), 6.96 (d, *J* = 2.4 Hz, 2H, H7), 4.21 (t, *J* = 6.6 Hz, 2H, H10), 3.68 (q, *J* = 7.1 Hz, 8H, H8), 2.67 (t, *J* = 6.6 Hz, 2H, H11), 1.31 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, methanol-D, 25°C) δ 166.67, 160.01, 159.23, 157.09, 138.85, 134.83, 134.10, 132.32, 132.28, 131.68, 131.63, 131.51, 129.51, 129.49, 127.53, 115.49 (C6), 114.73, 97.31 (C7), 66.90 (C10), 46.85 (C8), 35.40 (C11), 12.84 (C9). The full NMR spectra of RhB-Ethyl-Ph-I can be found in the supplementary information (Figure S30-33). The elemental composition of RhB-Ethyl-Ph-I was determined by elemental analysis. Theoretical composition of RhB-Ethyl-Ph-I: C 64.09 wt%, H 5.83 wt%, N 4.15 wt%; found: C 63.30 wt%, H 5.87 wt%, N 4.24 wt%.



Synthesis of RhB-PrOH-Br

RhB-PrOH-Br was synthesised by the reaction of RhB base (2.12 g, 4.79 mmol) and 1-propanol (1.93 g, 13.89 mmol) in 30 mL ethanol, by following the experimental procedure used for the synthesis of RhB-Allyl-Cl (RhB-PrOH-Br, brown powder, 1.34g, 48% yield relative to RhB Base).

Analysis of RhB-PrOH-Br ($C_{31}H_{37}BrN_2O_4$): ^{1}H NMR (400 MHz, methanol-d_4) δ 8.32 (dd, *J* = 7.8, 1.5 Hz, 1H, H1), 7.90 – 7.79 (m, 2H, H3, H2), 7.44 (dd, *J* = 7.5, 1.4 Hz, 1H, H4), 7.13 (d, *J* = 9.5 Hz, 2H, H5), 7.05 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 7.00 (d, *J* = 2.5 Hz, 2H, H7), 4.09 (t, *J* = 6.4 Hz, 2H, H10), 3.69 (q, *J* = 7.2 Hz, 8H, H8), 3.36 (t, *J* = 6.2 Hz, 2H, H12), 1.57 (p, *J* = 6.3 Hz, 2H, H11), 1.31 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, methanol-D) δ 166.71, 160.21, 159.32, 157.17, 134.87, 134.05, 132.36, 132.30, 131.76, 131.60, 131.51, 115.52 (C6), 114.79, 97.30 (C7), 63.70 (C10), 59.07 (C12), 46.84 (C8), 32.36 (C11), 12.79 (C9). The full NMR spectra of RhB-PrOH-Br can be found in Figure S34-37. The elemental composition of RhB-PrOH-Br was determined by elemental analysis. Theoretical composition of RhB-PrOH-Br C: 64.03 wt%, H 6.41 wt%, N 4.82 wt%; found: C 61.58 wt%, H 6.47 wt%, N 4.52 wt%.

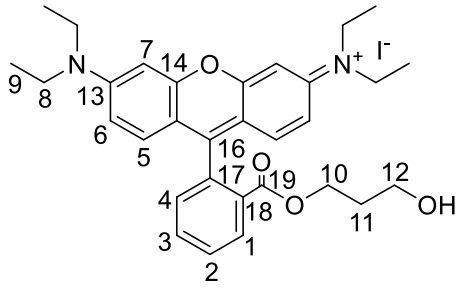


Synthesis of RhB-PrOH-I

RhB-PrOH-I was synthesised by an ion-exchange reaction between RhB-PrOH-Br (2.00 g, 3.44 mmol in 30 mL Milli-Q water,) and KI (1.71 g, 10.3 mmol in *ca.* 2 mL H_2O), by following the

same experimental procedure used for the synthesis of RhB-Allyl-I (RhB-PrOH-I, brown powder, 1.42 g, 66% yield relative to RhB Base).

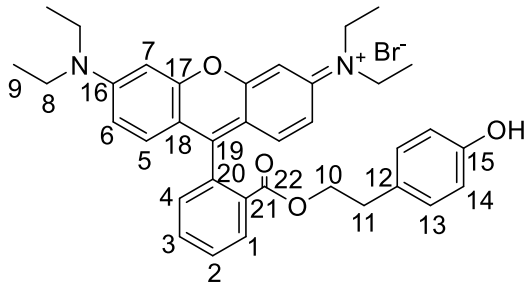
Analysis of RhB-PrOH-I ($C_{31}H_{37}IN_2O_4$): ^{1}H NMR (400 MHz, methanol-D) δ 8.32 (dd, *J* = 7.8, 1.5 Hz, 1H, H1), 7.89 – 7.79 (m, 2H, H3, H2), 7.45 (dd, *J* = 7.5, 1.4 Hz, 1H, H4), 7.13 (d, *J* = 9.5 Hz, 2H, H5), 7.05 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 7.00 (d, *J* = 2.4 Hz, 2H, H7), 4.09 (t, *J* = 6.4 Hz, 2H, H10), 3.69 (q, *J* = 7.2 Hz, 8H, H8), 3.36 (t, *J* = 6.2 Hz, 2H, H12), 1.57 (p, *J* = 6.3 Hz, 2H, H11), 1.31 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, methanol-D) δ 166.70, 160.16, 159.30, 157.14, 134.85, 134.06, 132.36, 132.29, 131.74, 131.61, 131.50, 115.55 (C6), 114.78, 97.31 (C7), 63.69 (C10), 59.06 (C12), 46.86 (C8), 32.36 (C11), 12.83 (C9). The full NMR spectra of RhB-PrOH-I can be found in Figure S38-41. The elemental composition of RhB-PrOH-I was determined by elemental analysis. Theoretical composition of RhB-PrOH-I: C 59.24 wt%, H 5.93 wt%, N 4.46 wt%; found: C 58.78 wt%, H 6.02 wt%, N 4.31 wt%.



Synthesis of RhB-Ethyl-PhOH-Br

In a typical synthesis of RhB-Ethyl-PhOH-Br, 4-hydroxyphenethyl bromide (1.01 g, 5.02 mmol) and a one-and-a-half-fold excess of RhB base (3.34 g, 7.55 mmol) were dissolved in a mixture of 50 mL ethanol and 40 mL chloroform. The solution was stirred at 70 °C for 24 h. Next, the solvent was removed under reduced pressure. The crude product was washed with benzene (30 mL x 3 times) to remove the unreacted 4-hydroxyphenyl bromide. The crude product was further purified by dissolving it in 70 mL dichloromethane and washing it with Milli-Q water (60 mL x 6 times). The organic phase was collected and dichloromethane was removed under reduced pressure to obtain the solid product. Then, the obtained solid product was dissolved in 30 mL dichloromethane and then recrystallised by slowly adding 180 mL diethyl ether. Afterwards, the recrystallised solid was dissolved in 30 mL dichloromethane. Anhydrous $MgSO_4$ was added to dry the organic solution and then removed by centrifugation at 4000 rpm for 5 min. The purified RhB-Ethyl-PhOH-Br was obtained by removing the dichloromethane under reduced pressure and dried at 80 °C overnight in a vacuum oven (brown powder, 1.99 g, 62 % yield relative to 4-hydroxyphenyl bromide).

Analysis of RhB-Ethyl-PhOH-Br ($C_{36}H_{39}BrN_2O_4$): ^{1}H NMR (400 MHz, methanol-D, 25°C) δ 8.28 (dd, *J* = 7.6, 1.5 Hz, 1H, H1), 7.82 (dtd, *J* = 21.8, 7.5, 1.4 Hz, 2H, H3, H2), 7.40 (dd, *J* = 7.3, 1.4 Hz, 1H, H4), 7.07 (d, *J* = 9.5 Hz, 2H, H5), 7.00 (dd, *J* = 9.5, 2.5 Hz, 2H, H6), 6.94 (d, *J* = 2.4 Hz, 2H, H7), 6.85 – 6.77 (m, 2H, H13), 6.64-6.56 (m, 2H, H14), 4.15 (t, *J* = 6.6 Hz, 2H, H10), 3.68 (q, *J* = 7.1 Hz, 8H, H8), 2.56 (t, *J* = 6.6 Hz, 2H, H11), 1.31 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, methanol-D) δ 166.67, 160.05, 159.22, 157.09, 157.05, 134.82, 134.03, 132.32, 132.28, 131.76, 131.68, 131.49, 130.43 (C13), 129.44, 116.22 (C14), 115.46 (C6), 114.73, 97.28 (C7), 67.17 (C10), 46.84 (C8), 34.59 (C11), 12.82 (C9). The full NMR spectra of RhB-Ethyl-PhOH-Br can be found in Figure

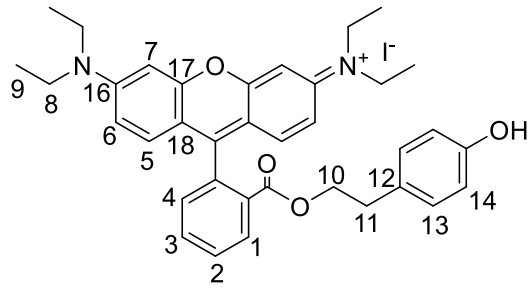


S42-45. The elemental composition of RhB-Ethyl-PhOH-Br was determined by elemental analysis. Theoretical composition of RhB-Ethyl-PhOH-Br: C 67.18 wt%, H 6.11 wt%, N 4.35 wt%; found: C 66.02 wt%, H 6.1 wt%, N 4.3 wt%.

Synthesis of RhB-Ethyl-PhOH-I

RhB-Ethyl-PhOH-I was synthesised through an ion-exchange reaction between RhB-Ethyl-PhOH-Br (2.05 g, 3.18 mmol dissolved in 30 mL Milli-Q water and 30 mL ethanol) and KI (1.55 g, 9.34 mmol dissolved in *ca.* 2 mL H_2O), by following the same experimental procedure used for the synthesis of RhB-Ethyl-Ph-I (RhB-Ethyl-PhOH-I, brown powder, 1.49 g, 68% yield relative to RhB-Ethyl-PhOH-Br).

Analysis of RhB-Ethyl-PhOH-I ($C_{36}H_{39}IN_2O_4$): ^{1}H NMR (400 MHz, methanol-D, 25 °C) δ 8.32-8.24 (m, 1H, H1), 7.82 (dtd, *J* = 22.0, 7.5, 1.4 Hz, 2H, H3,H2), 7.41 (dd, *J* = 7.4, 1.5 Hz, 1H, H4), 7.07 (d, *J* = 9.5 Hz, 2H, H5), 7.00 (dd, *J* = 9.5, 2.4 Hz, 2H, H6), 6.94 (d, *J* = 2.4 Hz, 2H, H7), 6.84-6.79 (m, 2H, H13), 6.63-6.57 (m, 2H, H14), 4.15 (t, *J* = 6.6 Hz, 2H, H10), 3.68 (q, *J* = 7.1 Hz, 8H, H8), 2.56 (t, *J* = 6.6 Hz, 2H, H11), 1.31 (t, *J* = 7.1 Hz, 12H, H9). ^{13}C NMR (400 MHz, methanol-D, 25 °C) δ 166.68, 160.04, 159.22, 157.08, 157.04, 134.82, 134.03, 132.32, 132.28, 131.76, 131.68, 131.49, 130.44, 129.44, 116.22(C14), 115.47(C6), 114.73, 97.29 (C7), 67.17 (C10), 46.85 (C8), 34.59 (C11), 12.83 (C9). The full NMR spectra of RhB-Ethyl-PhOH-I can be found in Figure S46-49. The elemental composition of RhB-PhOH-I was determined by elemental analysis. Theoretical composition of RhB-PhOH-I: C 62.61 wt%, H 5.69 wt%, N 4.06 wt%; found: C 62.04 wt%, H 5.8 wt%, N 4.09 wt%.



Catalytic tests

The catalytic activity tests of the modified dyes in the conversion of CO_2 and epoxides into cyclic carbonates were carried out in a high-throughput unit manufactured by Integrated Lab Solutions (ILS). The reactor unit consists of two reactor modules: (1) a block containing 10 individually-stirred batch reactors operated simultaneously; (2) a single batch reactor with a visualisation window. A more detailed description of this high-throughput reactor unit can be found in previous articles published by our group.[4, 8, 29] In each of the tests, the epoxide (20 mmol), the organocatalyst (1 mol % loading relative to the epoxide), Milli-Q water (50-100 mg) if employed, and *o*-xylene (1.5 mmol) as NMR internal standard were added into a glass vial (46 mL volume, 30 mm external diameter) with a magnetic stirring bar. Then, the glass vials were sealed with a screw cap equipped with a silicon/polytetrafluoroethylene septum that was pieced with two needles for gas exchange. Next, each sample was transferred into the batch reactor, and the reactor lid was closed. The reactor was first flushed with 5 bar N_2 to remove air and then with 5 bar CO_2 to remove N_2. The reactor was pressurised with CO_2 at a lower pressure than the target one, then heated to the selected reaction temperature, and further pressurised with CO_2 if it did not reach the target pressure. The reaction was performed under the chosen temperature and pressure conditions for 18 h while stirring at 950 rpm. After the reaction, the heating and stirring plate were turned off, and the reactor

was cooled to room temperature using cooling water. Then, the reactor block was depressurised to atmospheric pressure. Afterwards, the reactor block was opened, and the glass vials were removed and placed into a fume hood. The NMR samples were prepared by taking around 10 mg of the reaction solution with a pipette, and dissolving it into 0.7 mL CD_3Cl. The conversion of epoxide, the yield and selectivity of the corresponding cyclic carbonate and of possible by-products were calculated based on the ^1H NMR spectrum measured on a Varian Mercury Plus 400 MHz or Agilent MR 400 MHz spectrometer (see Figure S50-55 for representative spectra), using the following the equations:

$$Conversion_{epoxide}\ (\%) = \left(1 - \frac{mol_{epoxide,t}}{mol_{epoxide,intial}}\right) \times 100\%$$

$$Yield_{cycic\ carbonate}\ (\%) = \frac{mol_{cyclic\ carbonate,t}}{mol_{epoxide,intial}} \times 100\%$$

$$Selectivity_{cycic\ carbonate}\ (\%) = \left(\frac{Yield_{cycic\ carbonate}}{Conversion_{epoxide}}\right) \times 100\%$$

$$\frac{mol_{int.}}{mol_{compound}} = \frac{\frac{I_{int.}}{N_{int.}}}{\frac{I_{compound}}{N_{compound}}}$$

$mol_{int.} = moles\ of\ internal\ standard.$

$mol_{compound} = moles\ of\ the\ compound\ (e.g. mol_{epoxide,t}, mol_{cyclic\ carbonate,t})$.

I_{int} = *sum of integrations of the NMR spectrum peaks of the internal standard. (i.e.* $I_{O-xylene} = I_A + I_B$ *, where* I_A *and* I_B *are the integrations of the o-xylene peaks (A and B) in the NMR spectrum, see Figure S52).*

$I_{compound} = sum\ of\ the\ integrations\ of\ the\ NMR\ spectrum\ peaks\ of\ the\ compound.$
(e.g. $I_{SO.} = I_a + I_b + I_c$*, where* I_a*,* I_b *and* I_c *are the integrations of the NMR peaks a, b and c of styrene oxide, see Figure S52).*

$N_{int.}$ = *number of the protons corresponding to the integrated NMR spectrum peaks of the internal standard. (* $N_{O-xylene} = N_A + N_B$*, where* N_A *and* N_B *are the numbers of protons corresponding to the A (*$N_A = 6$*) and B (*$N_B = 4$*) peaks in the NMR spectrum of o-xylene, see Figure S52).* $N_{compound}$ = *number of protons corresponding to the integrated NMR spectrum peaks of the compound. (e.g.* $N_{SO} = N_a + N_b + N_c$*, where* N_a*,* N_b *and* N_c *are the numbers of protons corresponding to the a, b and c peaks in the NMR spectrum of SO, see Figure S52.).*

The formation of the diol by-product was confirmed by Gas Chromotography-Mass Spectrometry analysis (GC-MS), operated on an Agilent Hewlett-Packed-HP 6890 (Rxi®-5 Sil MS column, 30 m, 0.25 mm) installed with an Agilent Hewlett-Packard 5973 MSD Mass Spectrometer.

Selected catalytic activity tests were performed in duplicate or triplicate, and the average conversions and yields were reported in these cases, while the error bar correspond to the standard deviation.

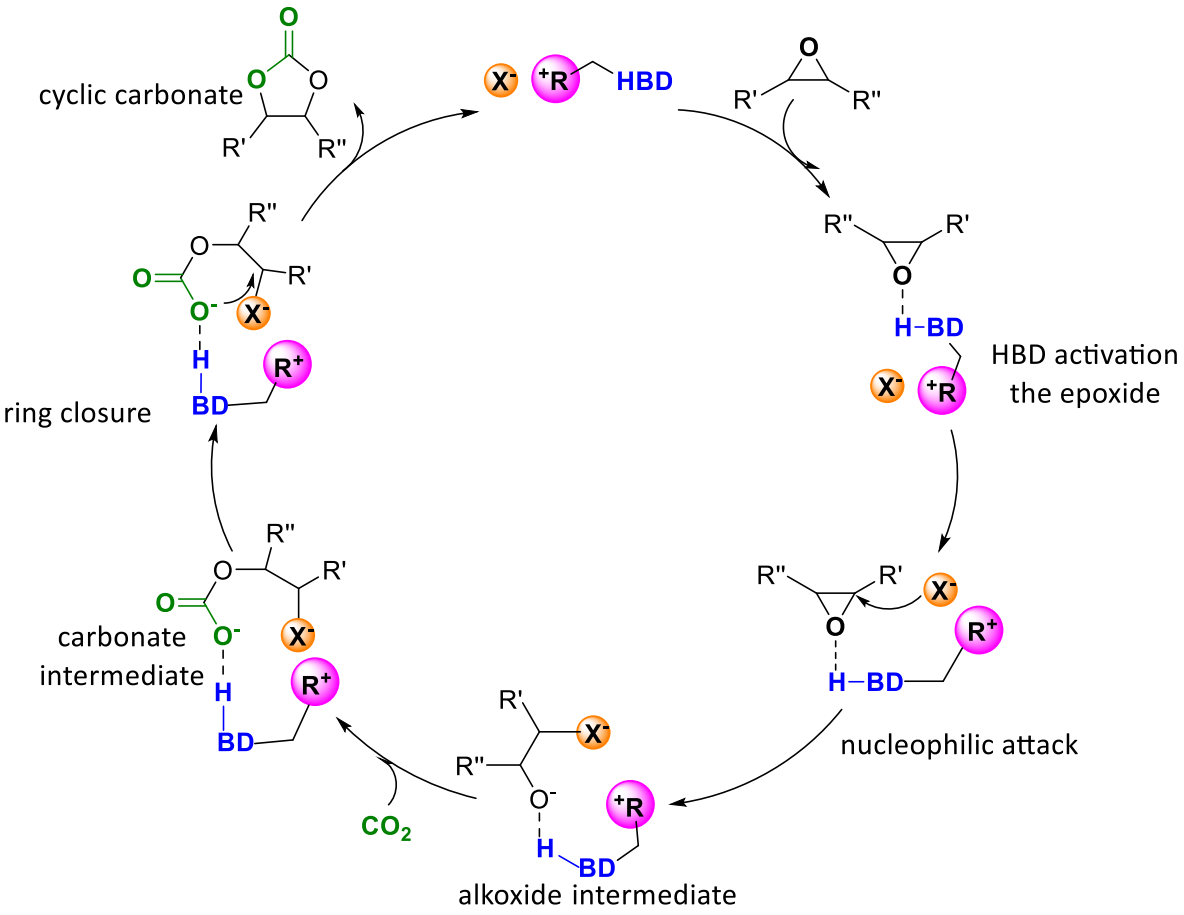
Recovery and reuse of the RhB-Ethyl-PhOH-I catalyst

The reusability test of the RhB-Ethyl-PhOH-I catalyst was conducted using propylene oxide as the substrate at 45 °C, 10 bar CO_2 for 18 h, but with all reagent quantities scaled-up by a factor of 2. Specifically, the amounts of the reagents were used as follows: propylene oxide: 2.40 g (41.4 mmol), fresh RhB-Ethyl-PhOH-I catalyst: 0.28 g (0.40 mmol), and *o*-xylene as internal standard: 0.37 g (2.98 mmol). After the test, a small aliquot of the reaction mixture was taken for ^{1}H NMR analysis to determine the selectivity and yield of propylene carbonate. Then, the reaction mixture in the glass vial (without the cap) was heated up to 80 °C for 1 h in a well-closed fume hood to remove the remaining propylene oxide. Then, the RhB-Ethyl-PhOH-I catalyst in the reaction mixture was recovered by precipitation using diethyl ether as an antisolvent.[8] The recovered RhB-Ethyl-PhOH-I catalyst was analysed on an Agilent MR 400 MHz (^{1}H NMR and ^{13}C NMR; for this analysis, 20 mg of the sample were dissolved in 0.7 mL CD_3OD). The obtained spectra are presented in Figs. S62-63.

The recovered RhB-Ethyl-PhOH-I catalyst was reused in a second catalytic run under the same reaction conditions as in the initial catalytic activity test, maintaining the same catalyst-to-substrate ratio (1 mol% catalyst loading relative to the substrate). After the test, a small aliquot of the reaction mixture was analysed for ^{1}H NMR to determine the selectivity and yield of propylene carbonate.

Purification of propylene carbonate

The propylene carbonate was purified at the end of a reaction conducted at 60 °C, 10 bar CO_2, 18 h, using propylene oxide (1.22 g, 21.0 mmol), RhB-Ehtyl-PhOH-I (0.14 g, 0.22 mmol), H_2O (55.0 mg), *o*-xylene (0.19 g, 1.76 mmol) as internal standard. At the end of the catalytic test, a small aliquot of the reaction mixture (*ca.* 10 mg) was dissolved in 0.7 mL $CDCl_3$ and analysed by ^{1}H NMR to determine the conversion of propylene oxide (98%), and the yield and selectivity of propylene carbonate (98% yield, > 99% selectivity, see Fig. S65). Then, the reaction mixture in the glass vial (without the cap) was warmed up to 80 °C for 1 h in a well-closed fume hood to remove the small amount of unreacted propylene oxide. Then, the propylene carbonate was purified by slowly adding diethyl ether (*ca.* 30 mL) into the glass vial, to precipitate the catalyst. The solution was then removed with a pipette and transferred to a beaker. An additional amount of diethyl ether (*ca.* 30 mL) was slowly added to ensure complete precipitation of the catalyst. The solution was collected by slowly pouring it into a round-bottom flask. Then, the diethyl ether was removed under reduced pressure. The purified product was dried at 110 °C in the oven overnight (1.73 g, 81% isolated yield). The purified propylene carbonate was analysed by NMR spectroscopy and GC-MS (Figures S66-68). This procedure focused on achieving high-purity propylene carbonate, but without maximising the recovery of the cyclic carbonate product (in each step, a fraction of the supernatant solution was not recovered to avoid contamination with the catalyst precipitate). A higher degree of cyclic carbonate product can be achieved by column separation.[8]



Scheme S1. Proposed mechanism for the cycloaddition of CO_2 to epoxides catalysed by bifunctional organocatalysts. The C atom of the epoxide ring at which the nucleophilic attack is more likely to occur depends on the electronic and steric effects of the R' and R" groups.[13]

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 45 °C.

RhB-Allyl-I			RhB-Pr-I			RhB-Butenyl-I				
BF	45 °C	AF	BF	45 °C	AF	BF	45 °C	AF	H_2O [g]	PC [mL]
									0	0
									0.05	0
									0.1	0

RhB-Ethyl-Ph-I			RhB-EtOH-I			RhB-PrOH-I				
BF	45 °C	AF	BF	45 °C	AF	BF	45 °C	AF	H_2O [g]	PC [mL]
									0	0
									0.05	0
									0.1	0

RhB-Ethyl-PhOH-I			RhB-I					
BF	45 °C	AF	BF	45 °C	AF		H_2O [g]	PC [mL]
							0	0
							0.05	0
							0.1	0

solubility	largely insoluble	partially soluble	soluble
colour indication			

The solubility of the organocatalysts in the reaction mixtures was determined visually before the catalytic activity test, ether at the room temperature (BF) of at the reaction temperature (45 °C) and after the catalytic activity test at room temperature (AF).

Table S2. 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				Epichlorohydrin				
	BF	AF	H_2O [g]	PC [mL]	BF	45 (°C)	AF	H_2O [g]	PC [mL]
RhB-Ethyl-Ph-I			0.05	0				0.05	0
RhB-EtOH-I			0.05	0				0.05	0
RhB-Ethyl-PhOH-I			0.05	0				0.05	0

	Styrene oxide					1,2-epoxyhexane				
	BF	45 (°C)	AF	H_2O [g]	PC [mL]	BF	45 (°C)	AF	H_2O [g]	PC [mL]
RhB-Ethyl-Ph-I				0.05	0				0.05	0.5
RhB-EtOH-I				0.05	0				0.05	0.5
RhB-Ethyl-PhOH-I				0.05	0				0.05	0.5

	Cyclohexene oxide					Limonene oxide[a]				
	BF	120 (°C)	AF	H_2O [g]	PC [mL]	BF	110 (°C)	AF	H_2O [g]	PC [mL]
RhB-Ethyl-Ph-I				0.05	0				0.05	0.5
RhB-EtOH-I				0.05	0.5				0.05	0.5
RhB-Ethyl-PhOH-I				0.05	0				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, ether at room temperature (BF) or at the reaction temperature (45 °C) and after the catalytic test at the room temperature (AF). [a]In the case of limonene oxide the solubility of the dyes was tested at its boiling point.

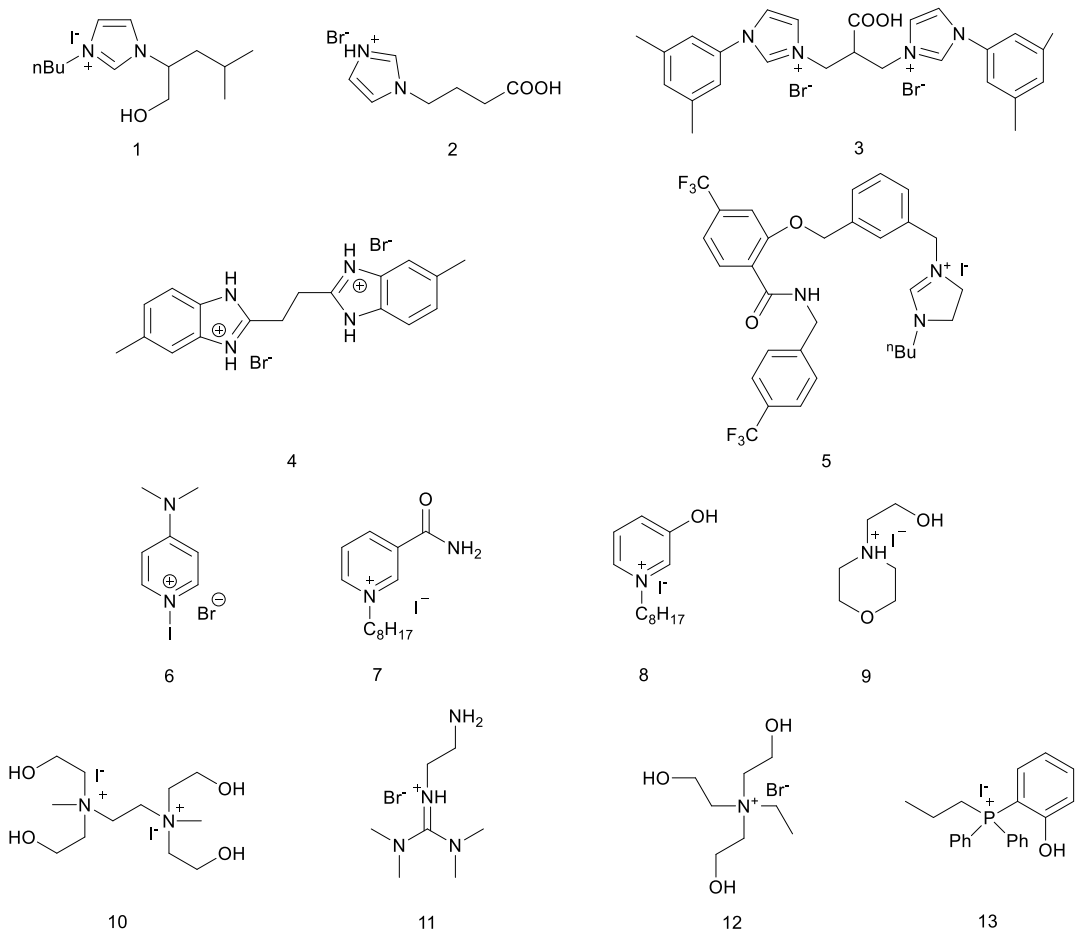


Figure S1. The structure of the selected bifunctional organocatalysts.

Table S3. Comparison of the performance of the selected bifunctional organocatalysts for the synthesis of styrene carbonate from CO_2 and styrene oxide.

Entry	Catalyst	Catalyst loading [mol %]	T [°C]	P [MPa]	T [h]	Yield [%]	Selectivity [%]	TON[b]	TOF[c] [h^{-1}]	Ref.[d]
1[a]	RhB-Ethyl-PhOH-I	1	45	1	18	49	≥ 99	49	3	This work
2	1	2	60	0.5	8	94	-	47	6	19
3	2	0.5	120	1.5	2	82	> 99	164	82	20
4	3	5	70	0.4	16	93	≥ 99	19	1	21
5	4	0.75	120	3	2	98	-	131	65	22
6	5	0.2	100	1.5	12	95	> 99	475	40	23
7	6	1	80	0.1	6	47	99	47	8	15
8	7	1	80	0.1	12	62	-	62	5	26
9	8	5	50	0.1	6	97	-	19	2	27
10	9	10	60	0.1	24	95	-	10	0.4	16
11	10	0.25	120	2	3	67	98	392	131	24
12	11	0.5	130	2	3	> 99	> 99	198	66	17
13	12	1	130	1.5	2	97	99	99	50	25
14	13	5	23	1	24	74	-	15	1	28

[a] 50 mg H_2O was added as a hydrogen bond donor (HBD). [b] Turnover number, TON = $mo_{l product}/mol_{catalyst}$. [c] Turnover frequency, TOF = TON/h. [d] The reference numbers are those used in the main text of the article.

NMR spectra of the synthesised modified dyes

NMR spectra of RhB-Allyl-Cl

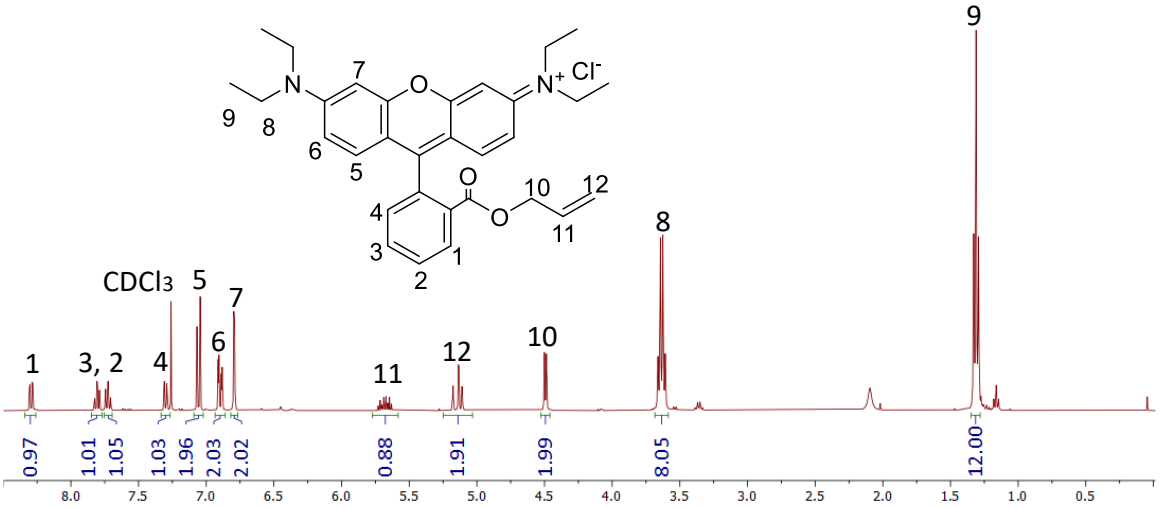


Figure S2. ^{1}H NMR spectrum of RhB-Allyl-Cl.

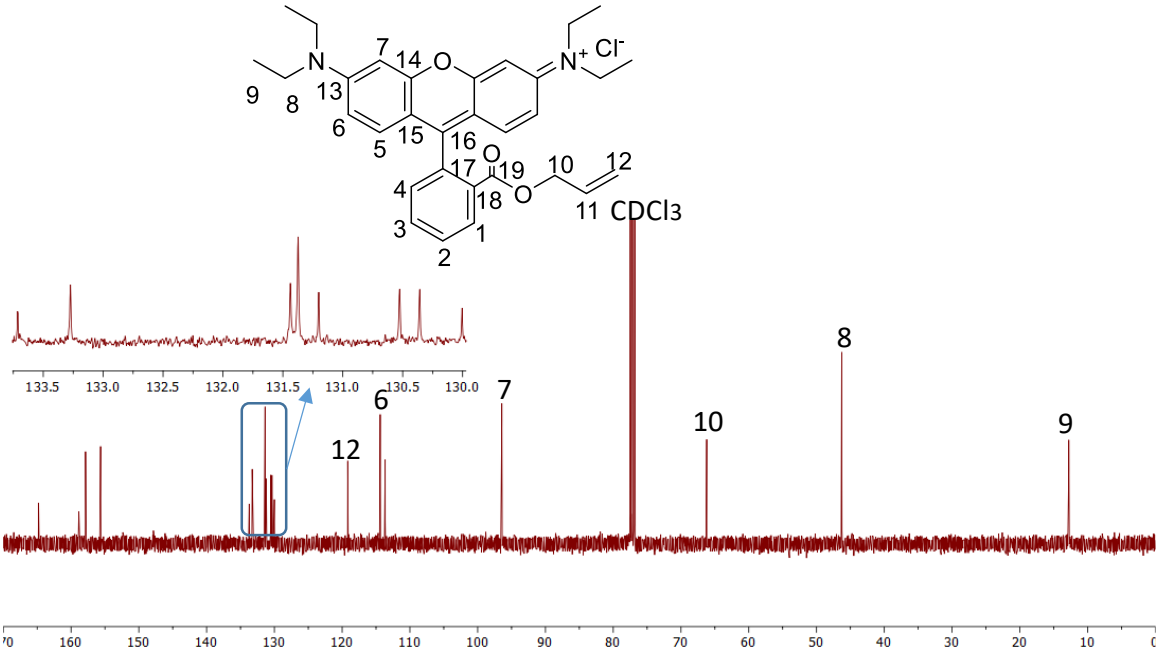


Figure S3. ^{13}C NMR spectrum of RhB-Allyl-Cl.

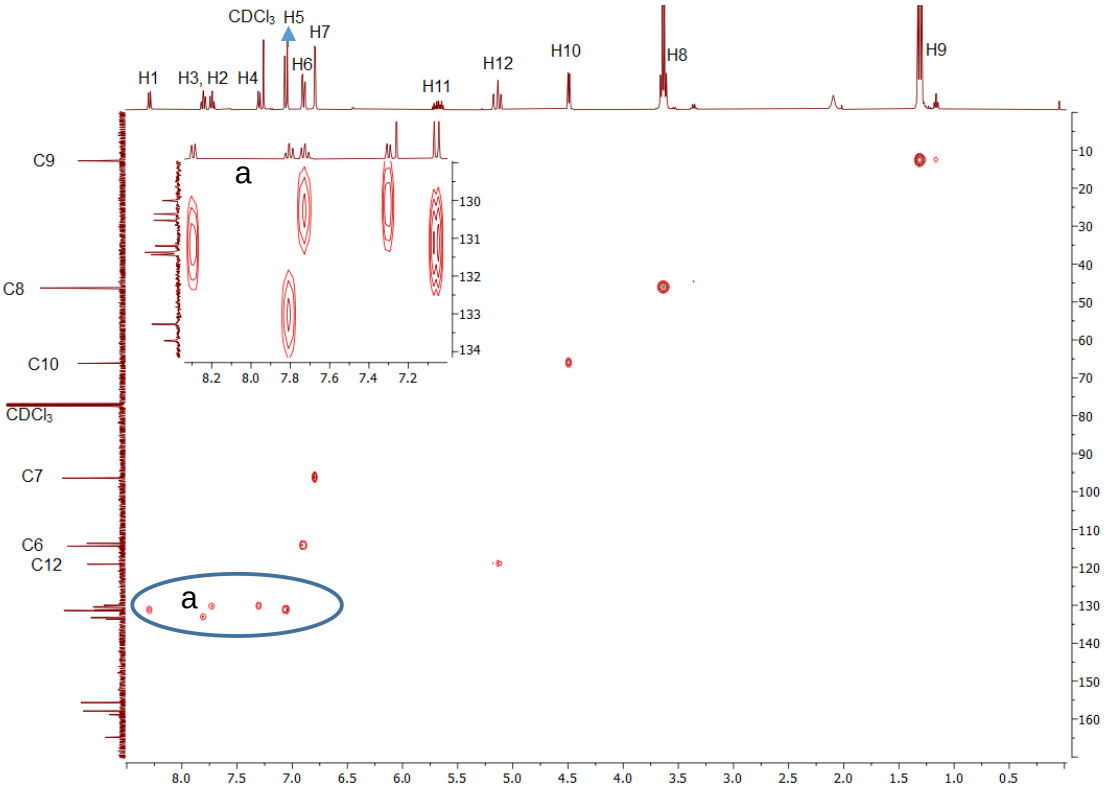


Figure S4. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Allyl-Cl.

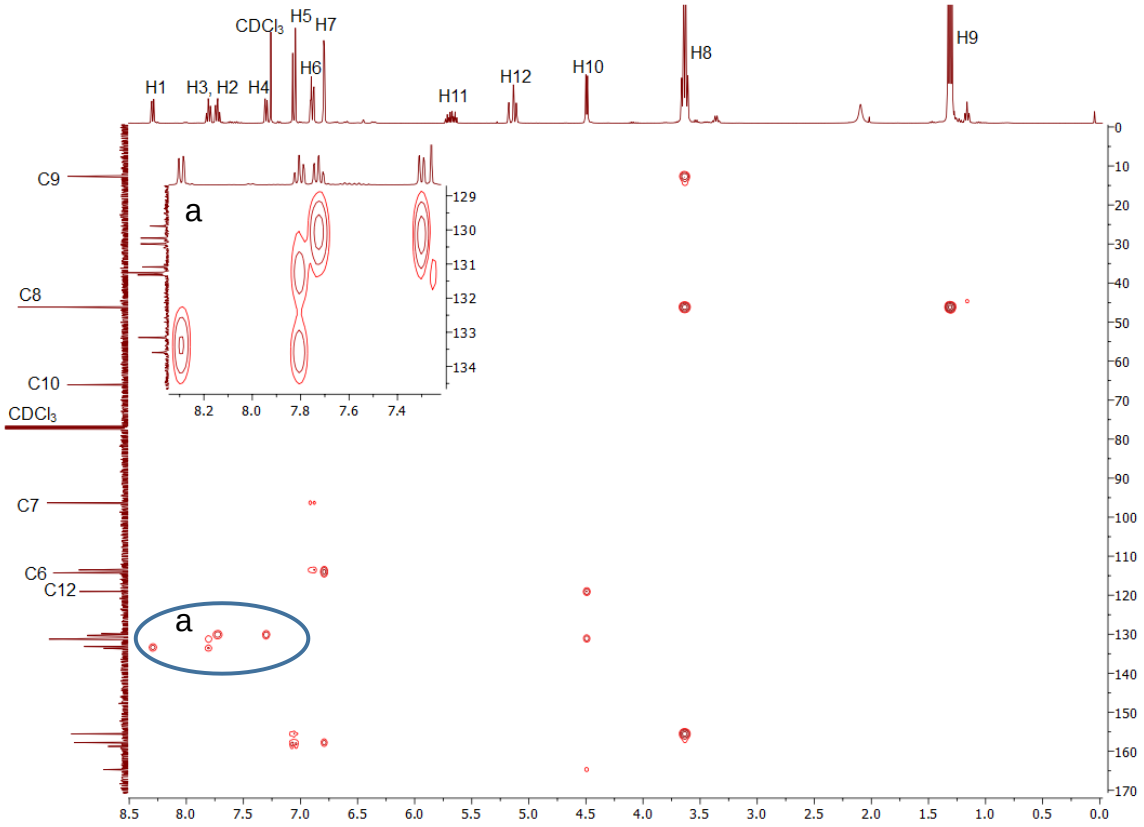


Figure S5. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Allyl-Cl.

NMR spectra of RhB-Allyl-I

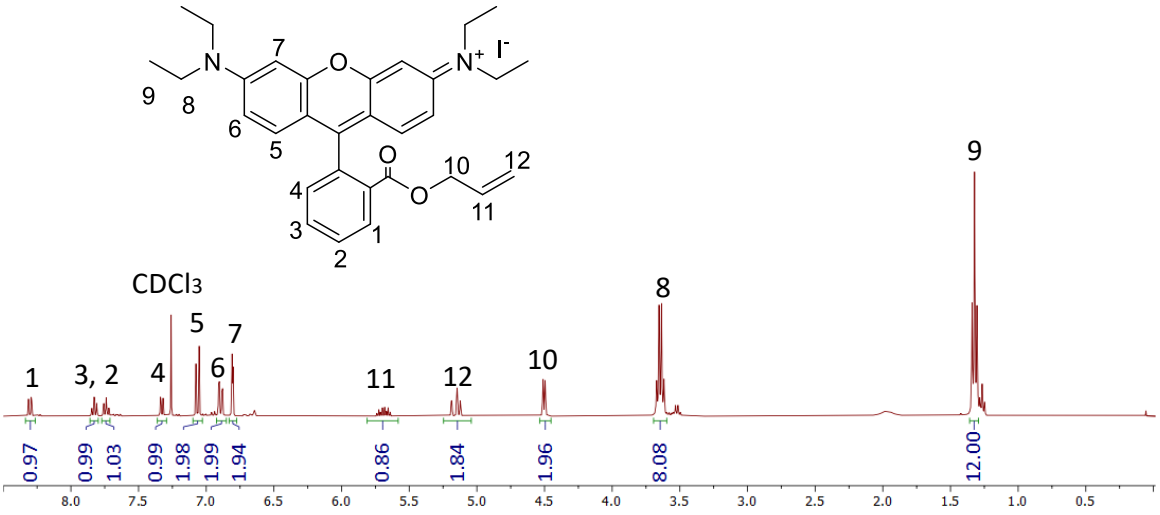


Figure S6. ^{1}H NMR spectrum of RhB-Allyl-I.

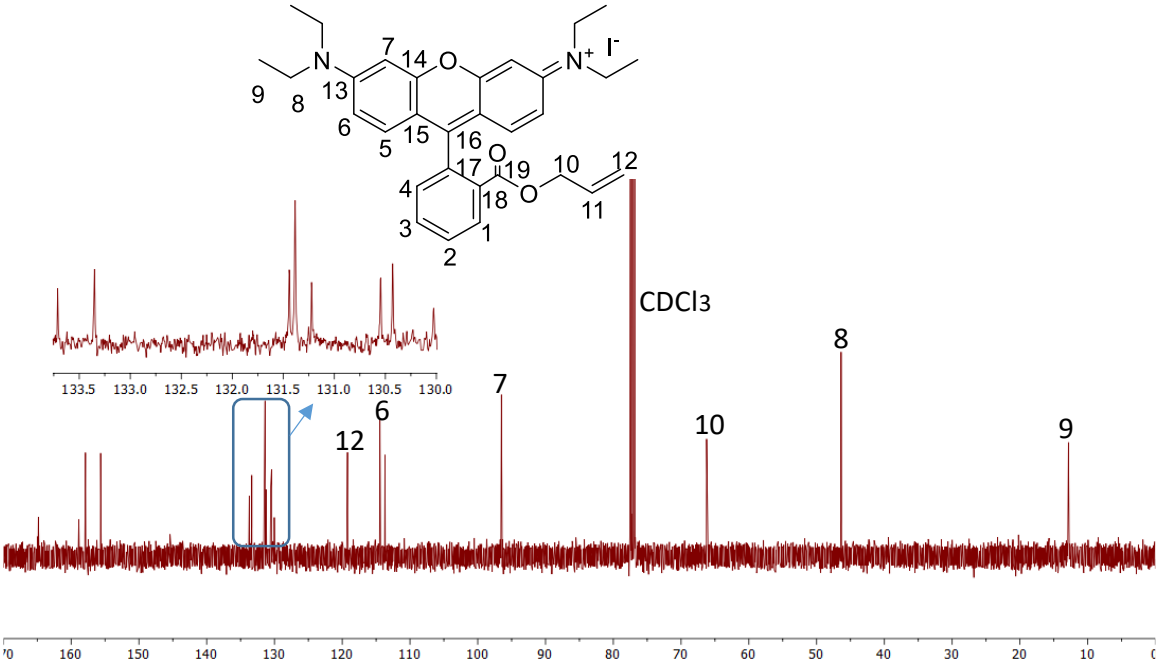


Figure S7. ^{13}C NMR spectrum of RhB-Allyl-I.

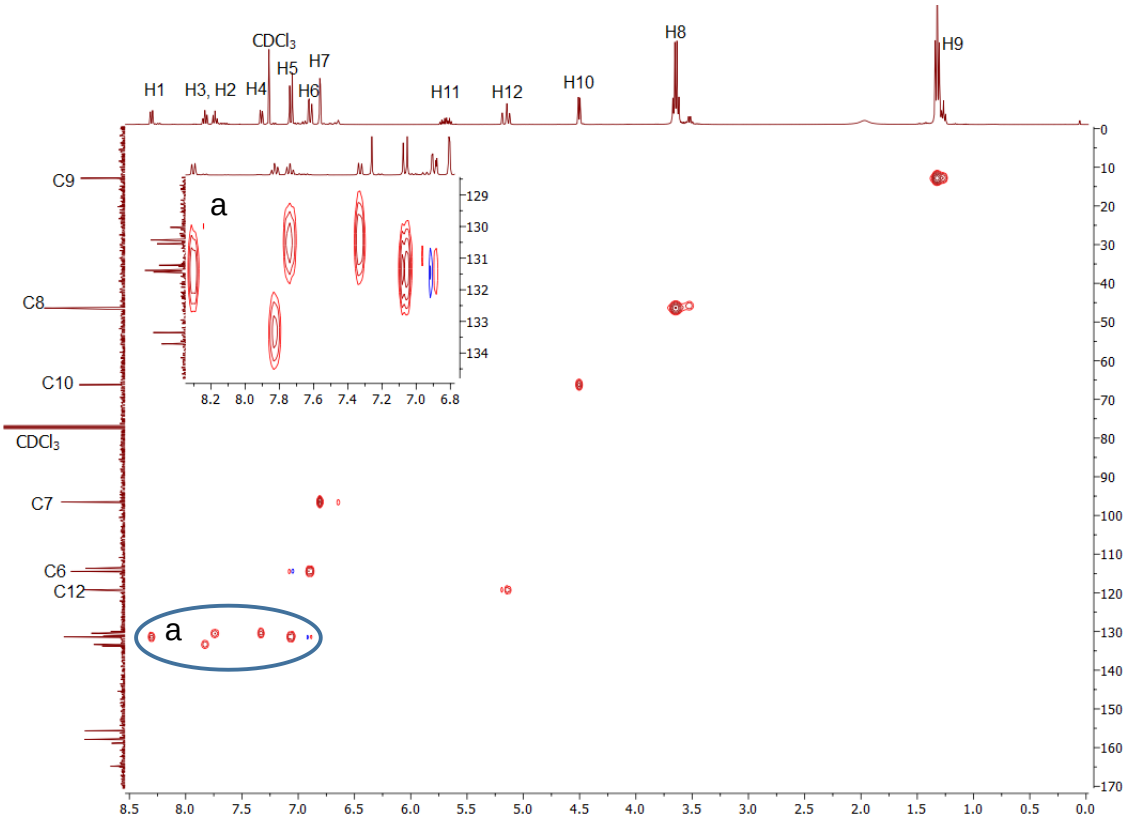


Figure S8. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Allyl-I.

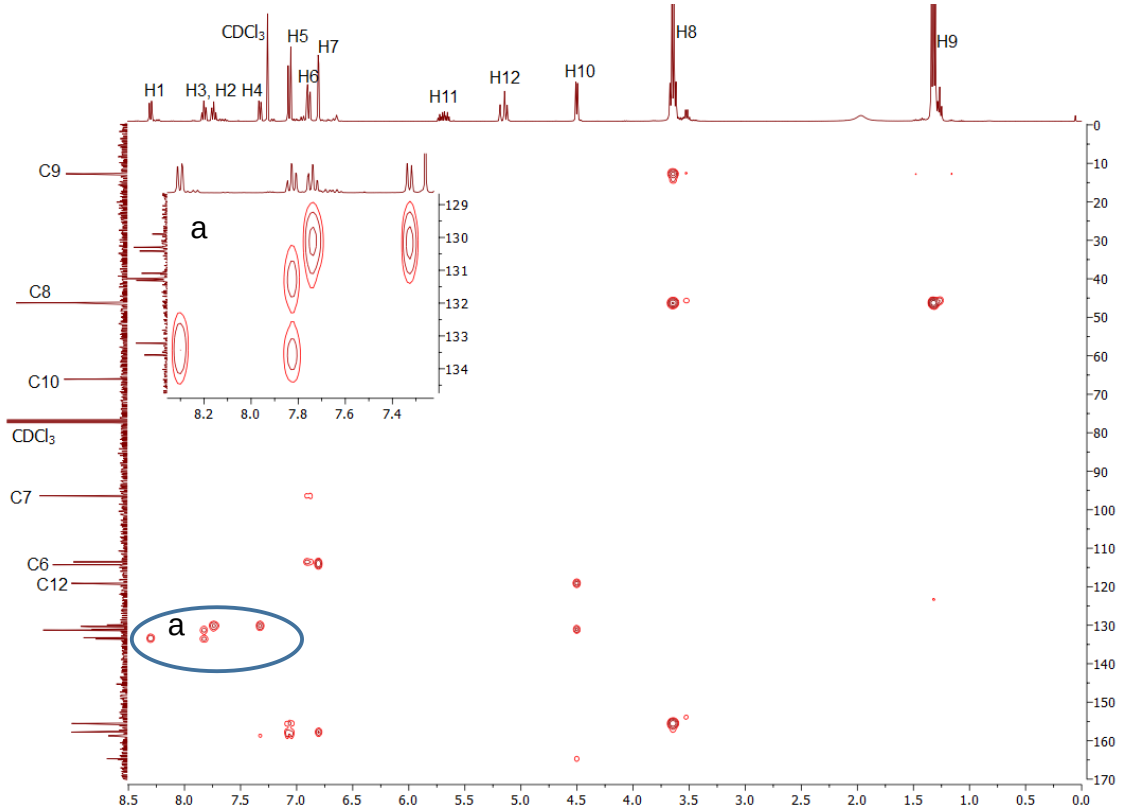


Figure S9. ^{1}H-^{13}C HMBC spectrum NMR of RhB-Allyl-I.

NMR spectra of RhB-Pr-Br

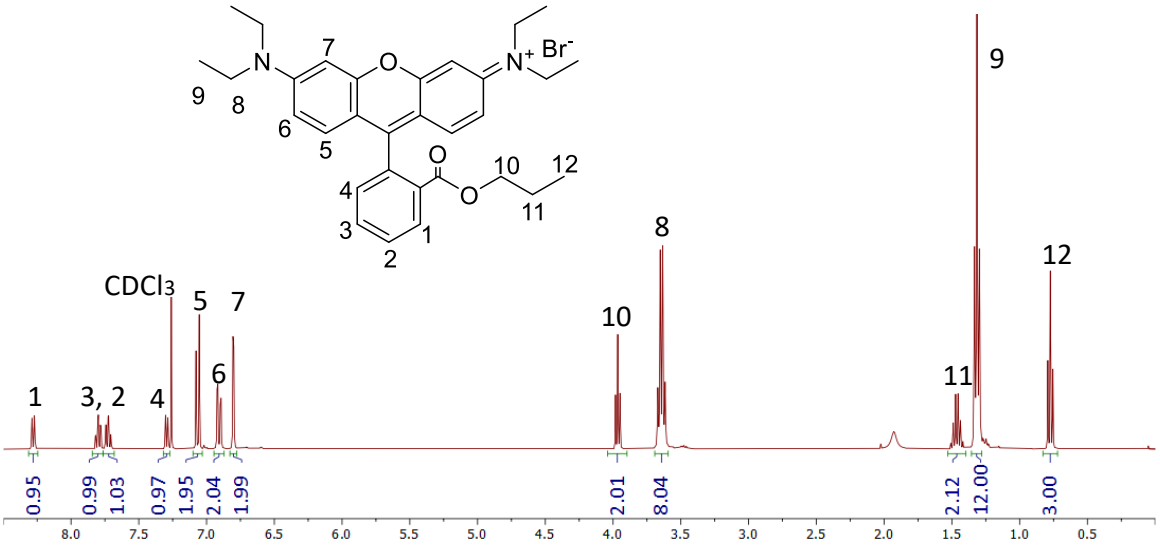


Figure S10. ^{1}H NMR spectrum of RhB-Pr-Br.

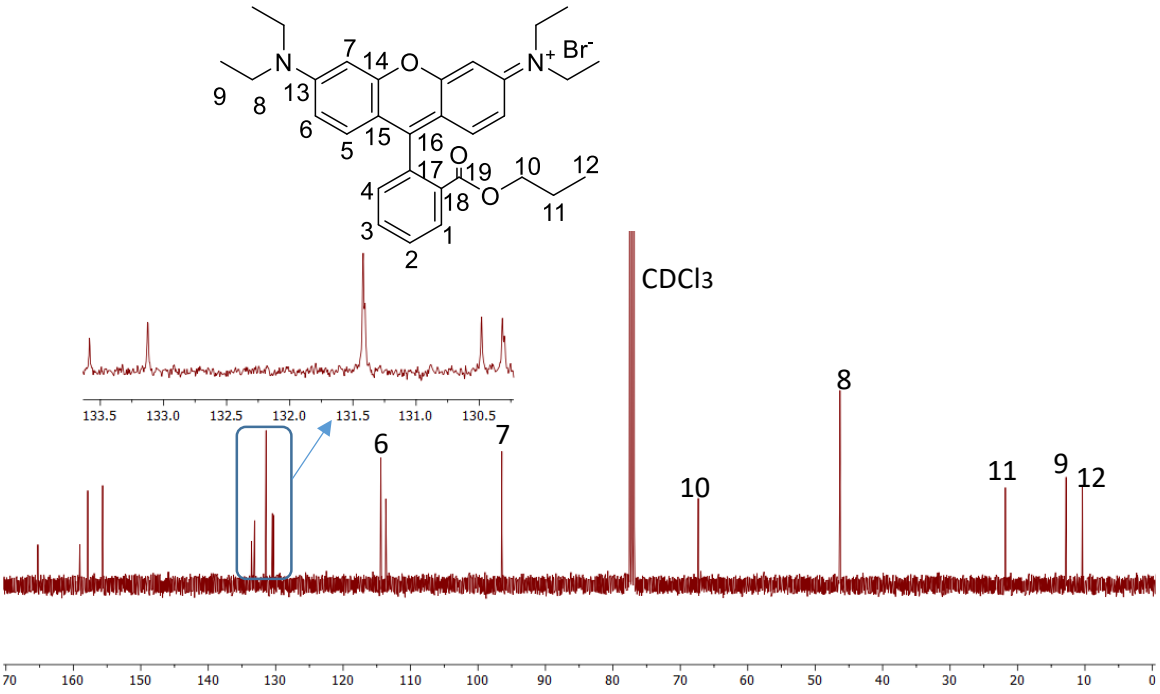


Figure S11. ^{13}C NMR spectrum of RhB-Pr-Br.

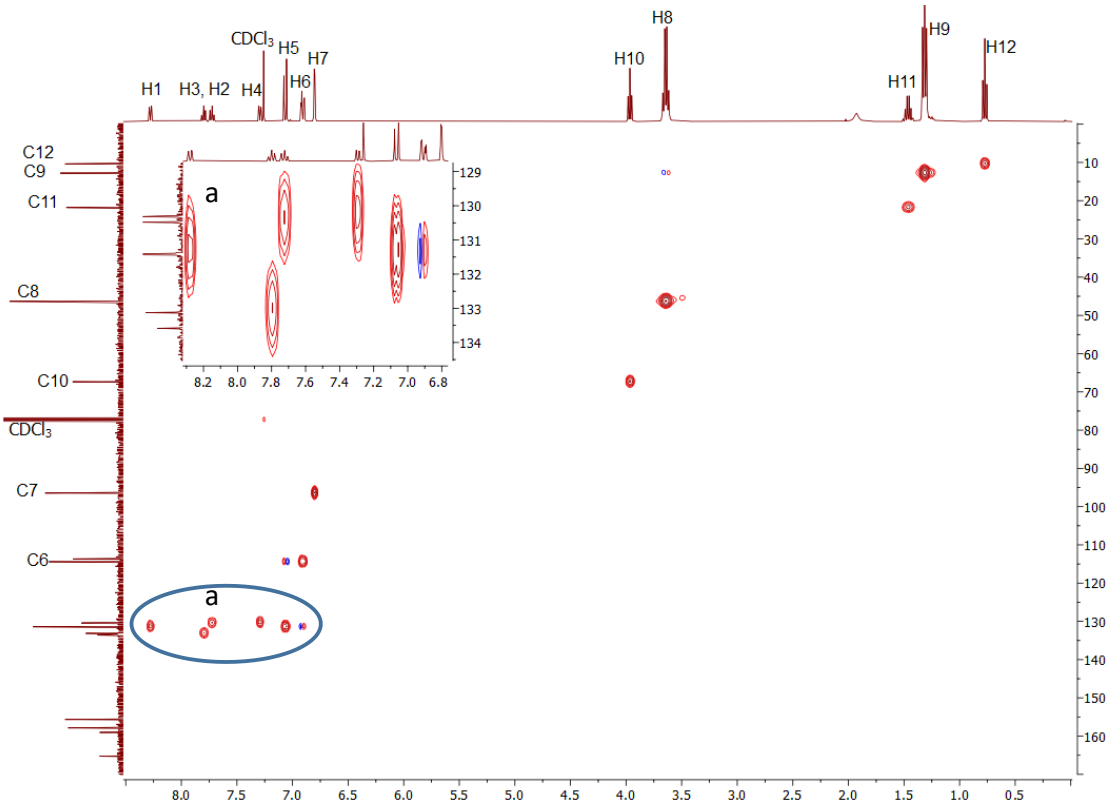


Figure S12. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Pr-Br.

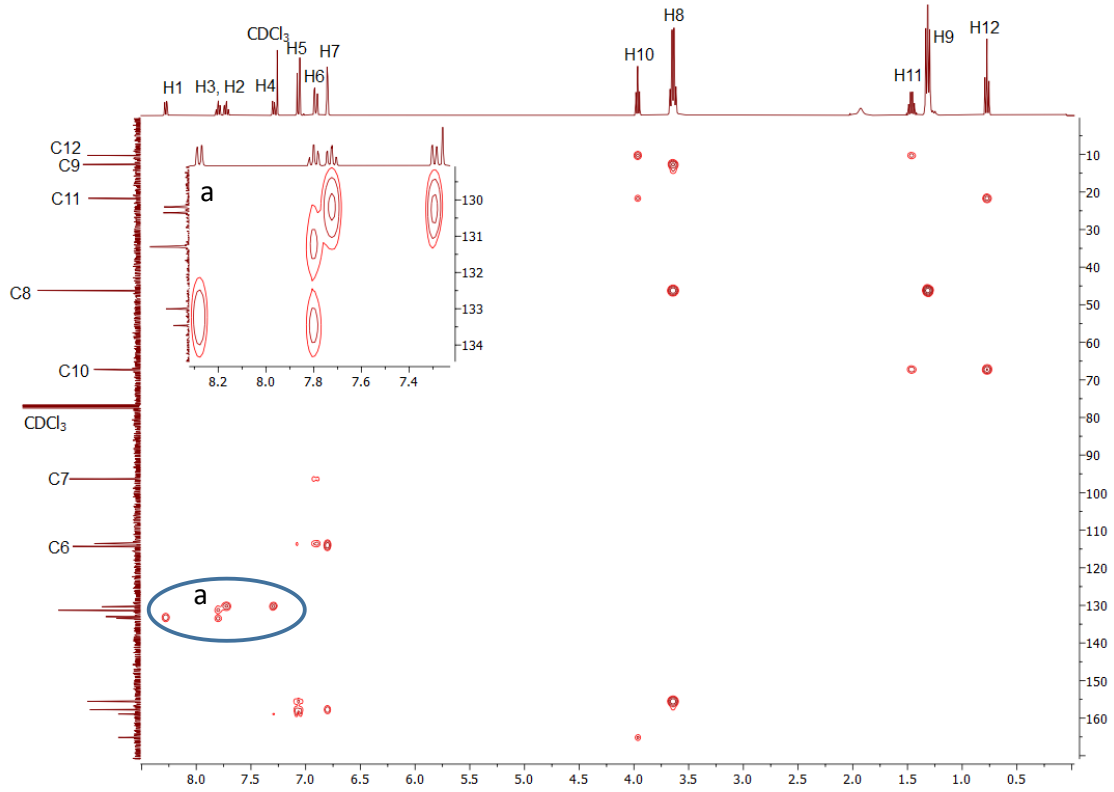


Figure S13. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Pr-Br.

NMR spectra of RhB-Pr-I

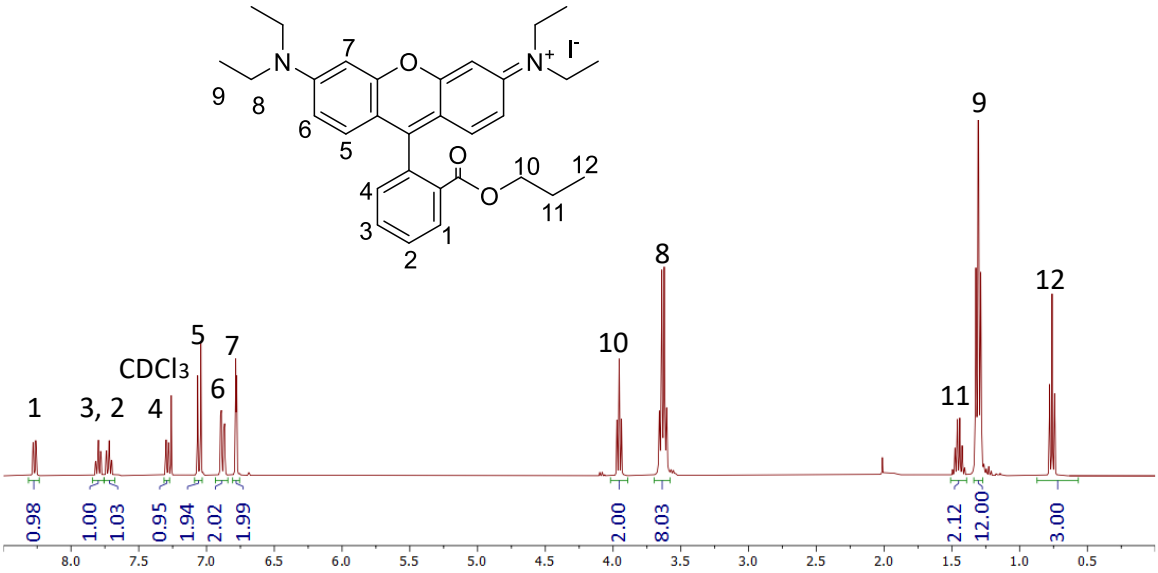


Figure S14. ^{1}H NMR spectrum of RhB-Pr-I.

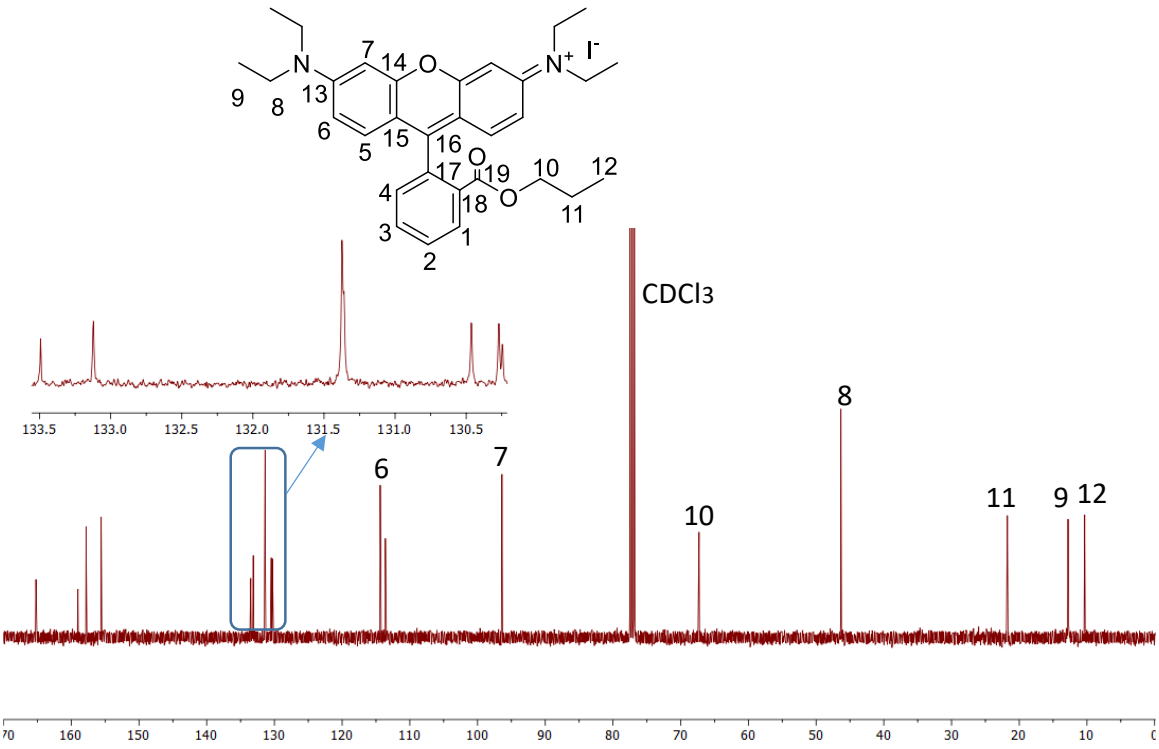


Figure S15. ^{13}C NMR spectrum of RhB-Pr-I.

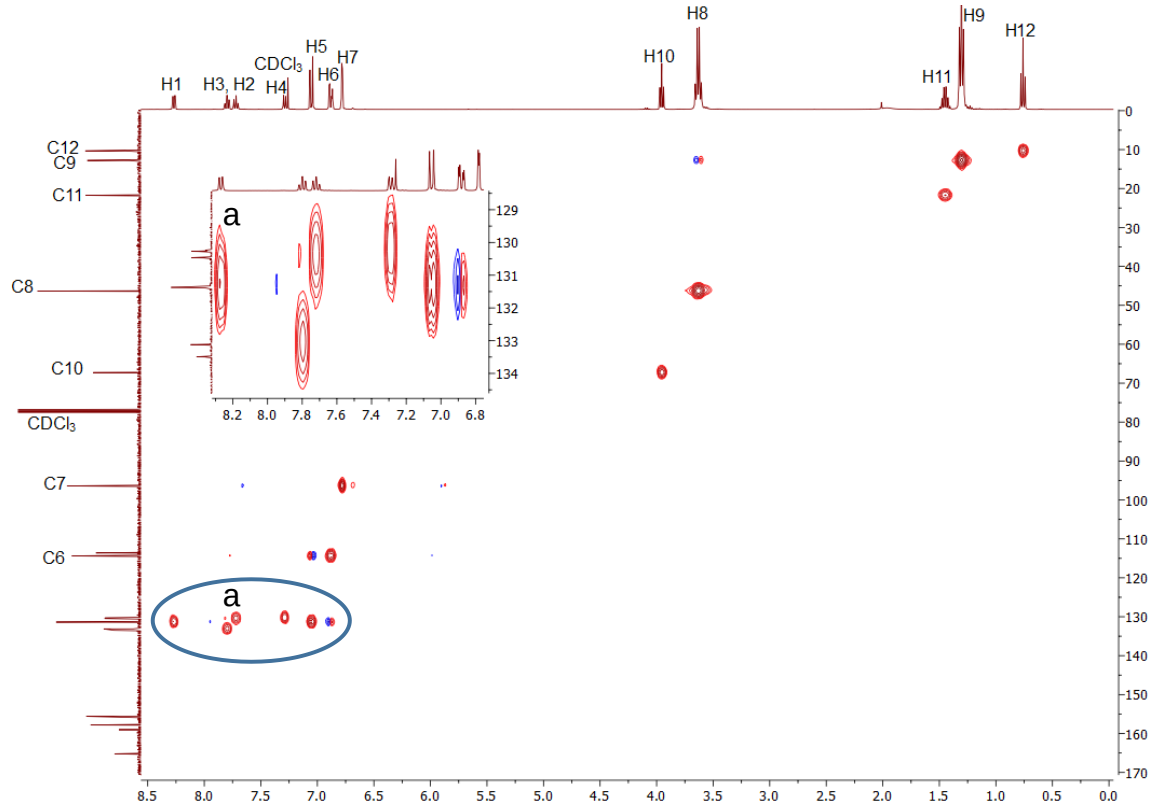


Figure S16. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Pr-I.

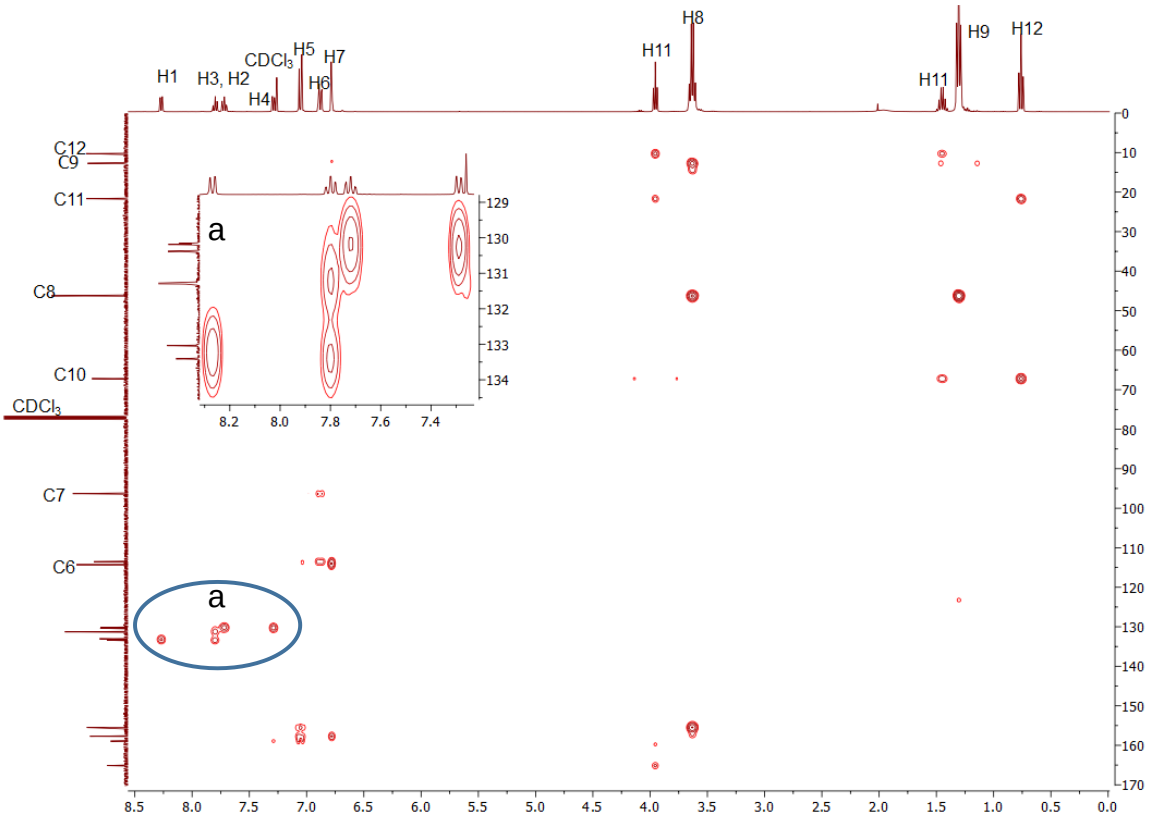


Figure S17. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Pr-I.

NMR spectra of RhB-Butenyl-Br

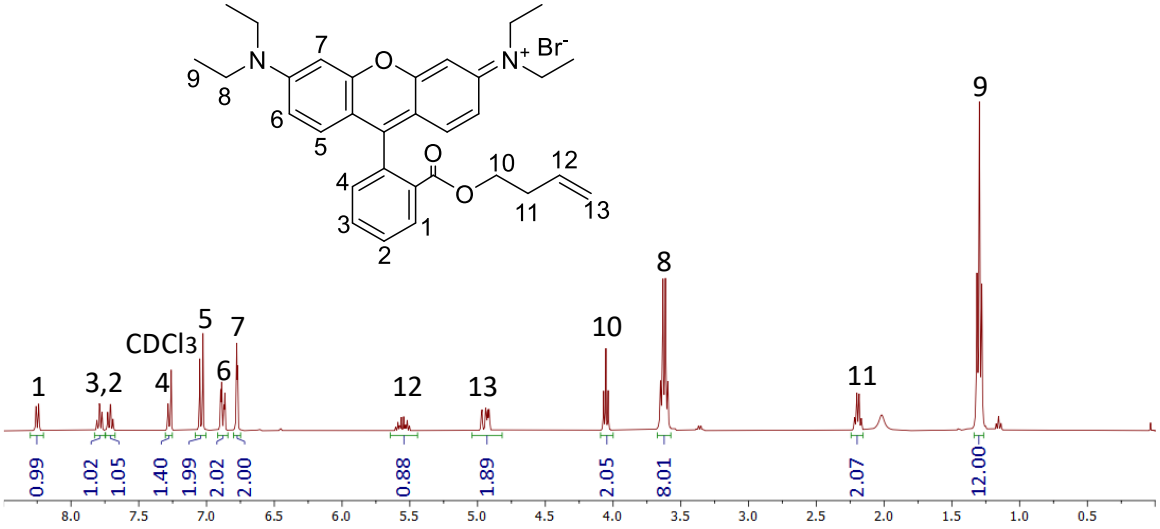


Figure S18. ^{1}H NMR spectrum of RhB-Butenyl-Br.

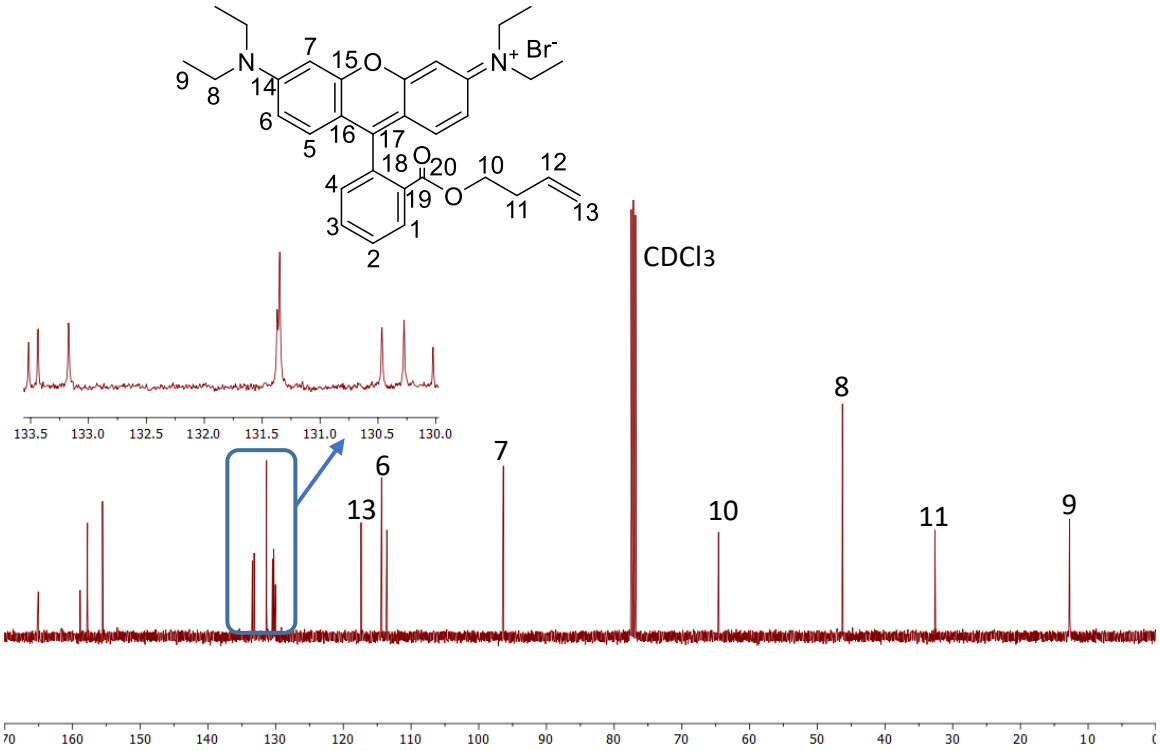


Figure S19. ^{13}C NMR spectrum of RhB-Butenyl-Br.

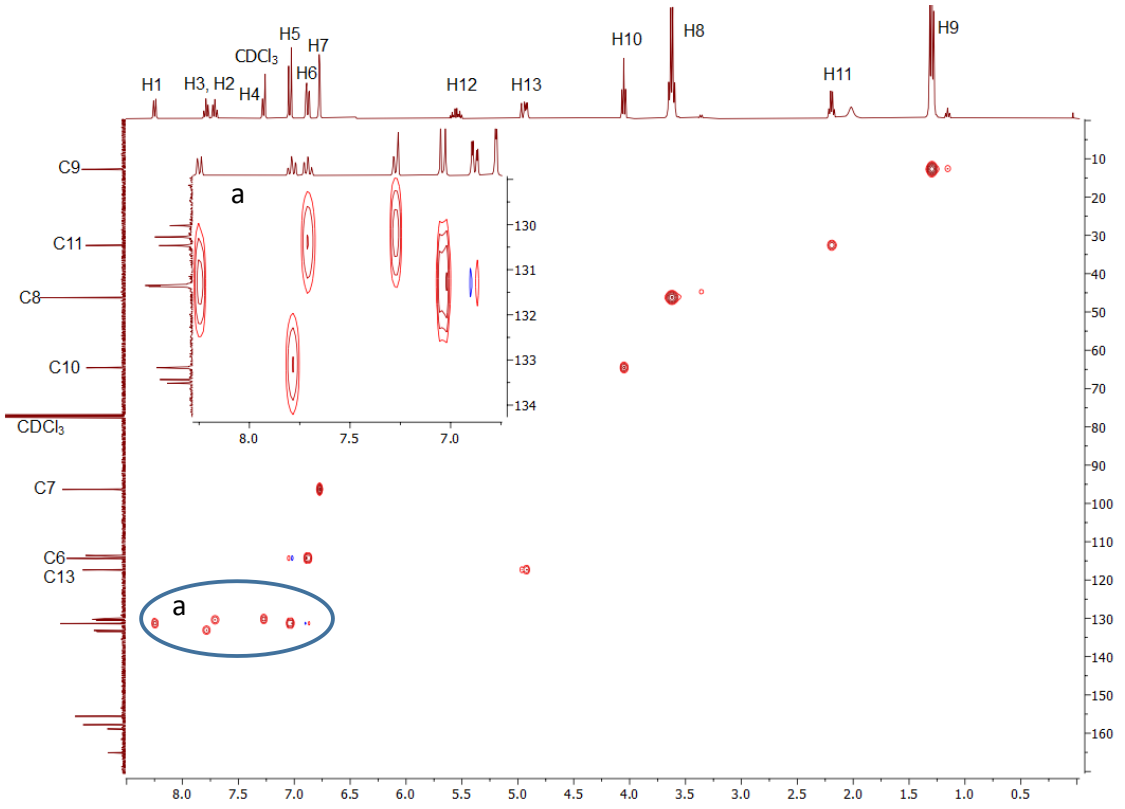


Figure S20. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Butenyl-Br

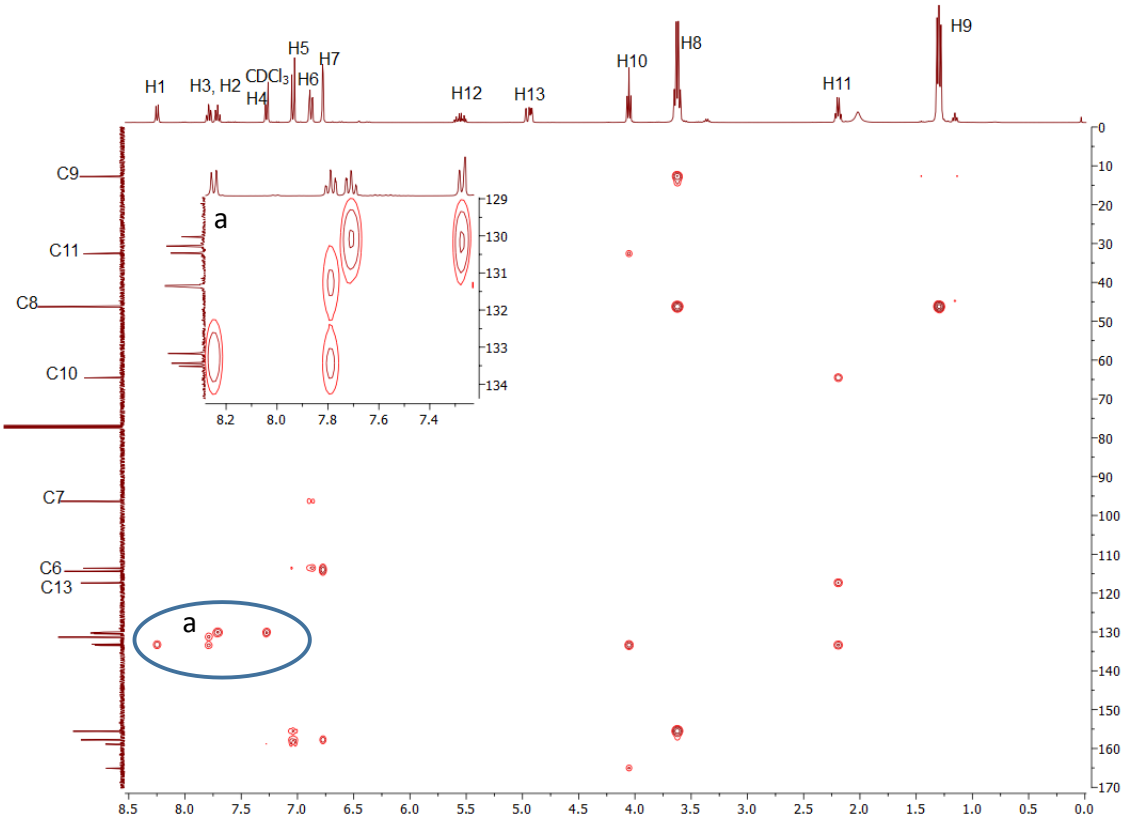


Figure S21. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Butenyl-Br

NMR spectra of RhB-Butenyl-I

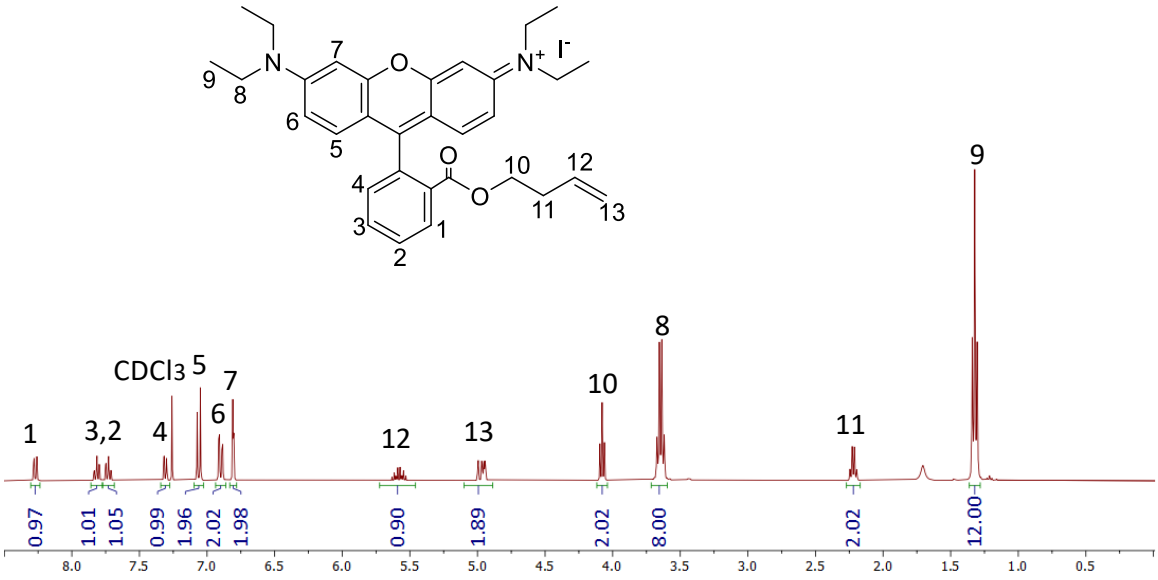


Figure S22. ^{1}H NMR spectrum of RhB-Butenyl-I.

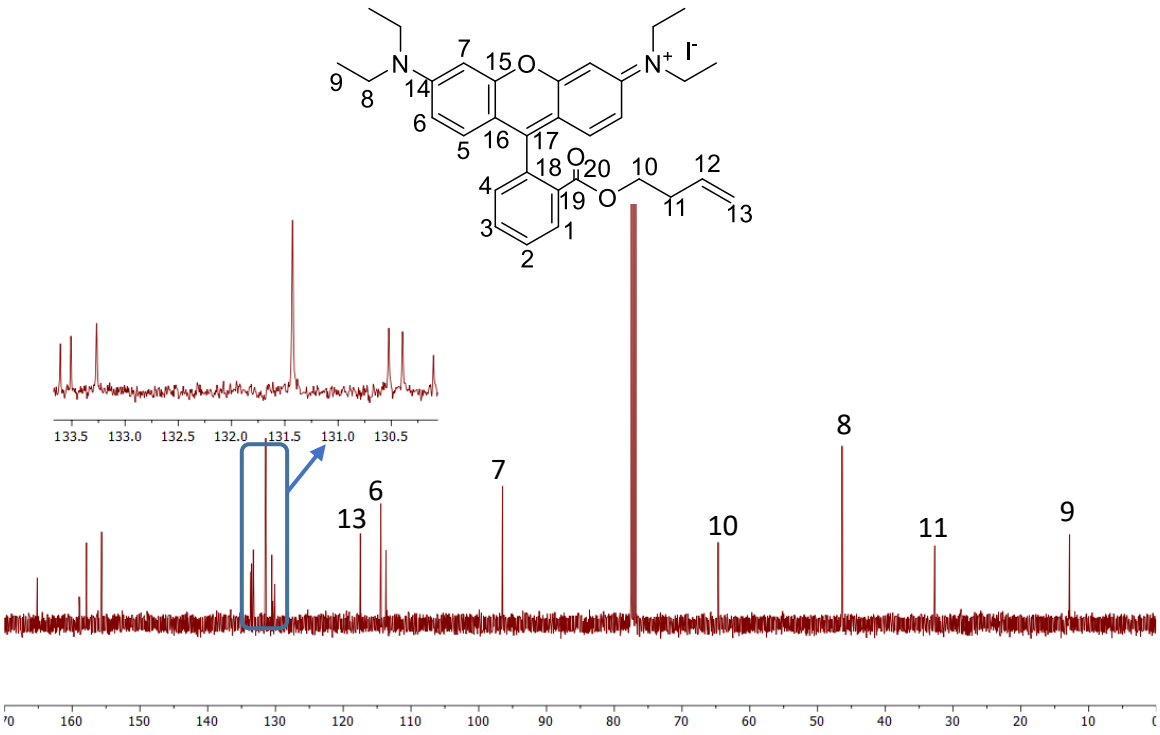


Figure S23. ^{13}C NMR spectrum of RhB-Butenyl-I.

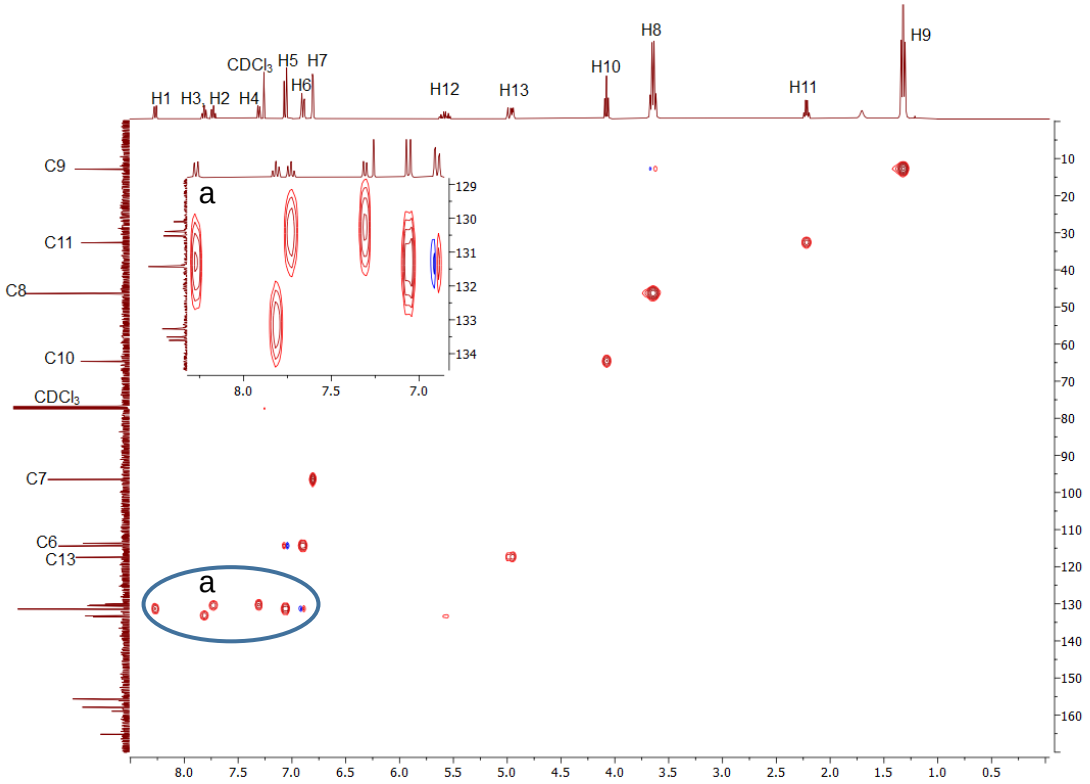


Figure S24. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Butenyl-I.

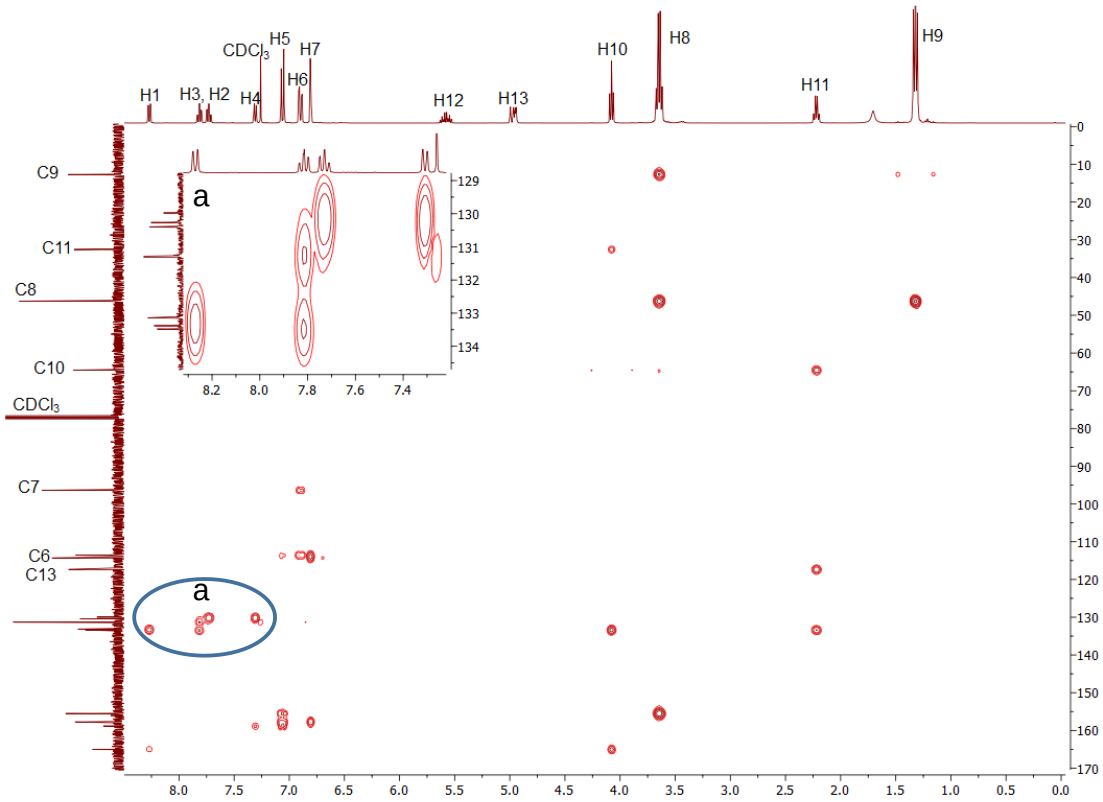


Figure S25. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Butenyl-I.

NMR spectra of RhB-Ethyl-Ph-Br

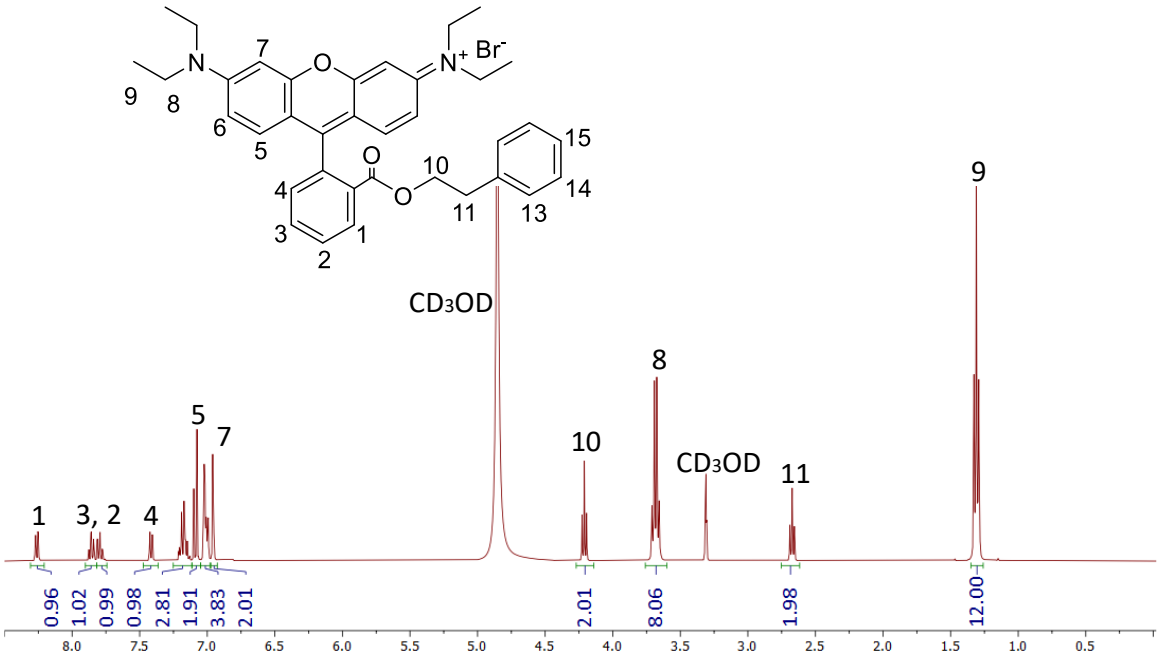


Figure S26. ^{1}H NMR spectrum of RhB-Ethyl-Ph-Br.

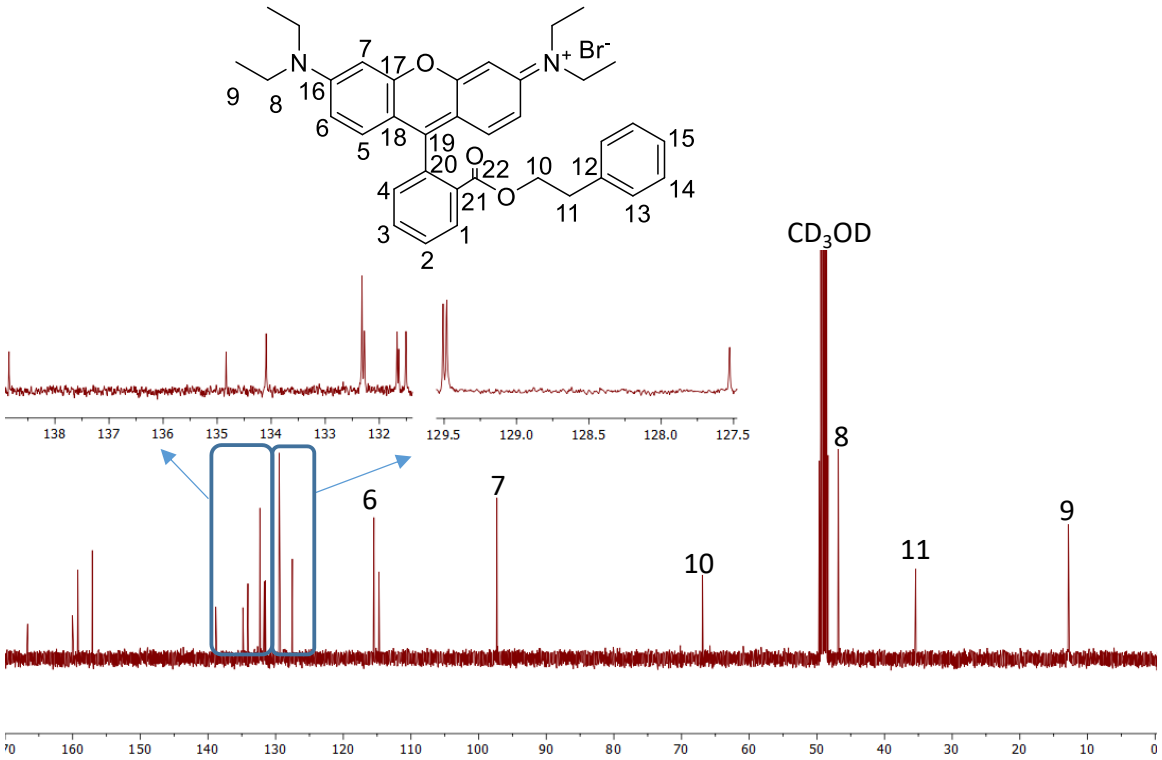


Figure S27. ^{13}C NMR spectrum of RhB-Ethyl-Ph-Br.

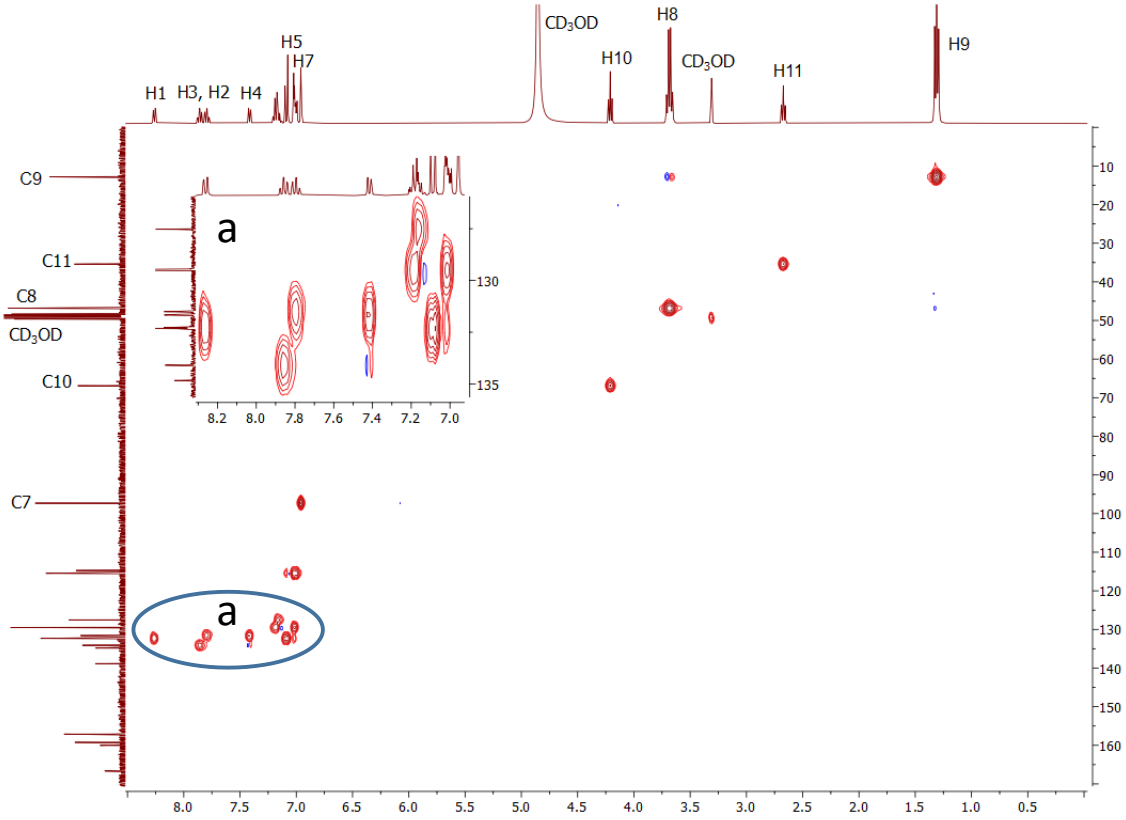


Figure S28. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Ethyl-Ph-Br.

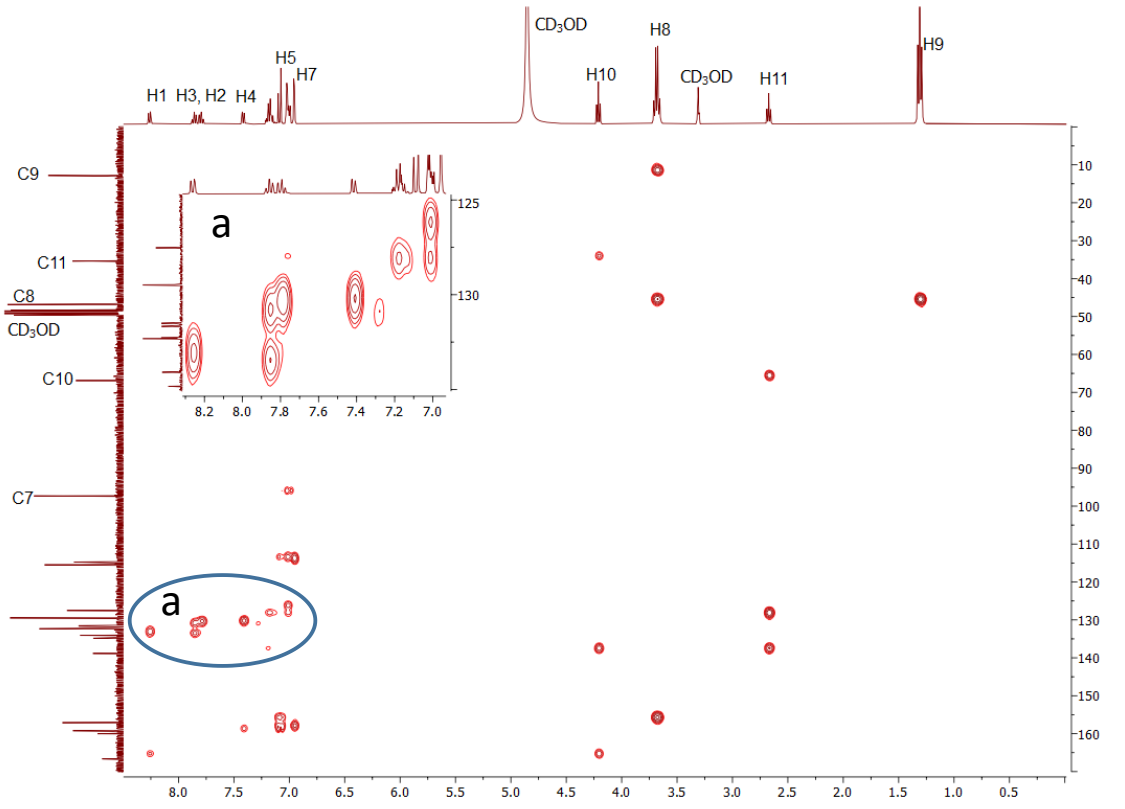


Figure S29. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Ethyl-Ph-Br.

NMR spectra of RhB-Ethyl-Ph-I

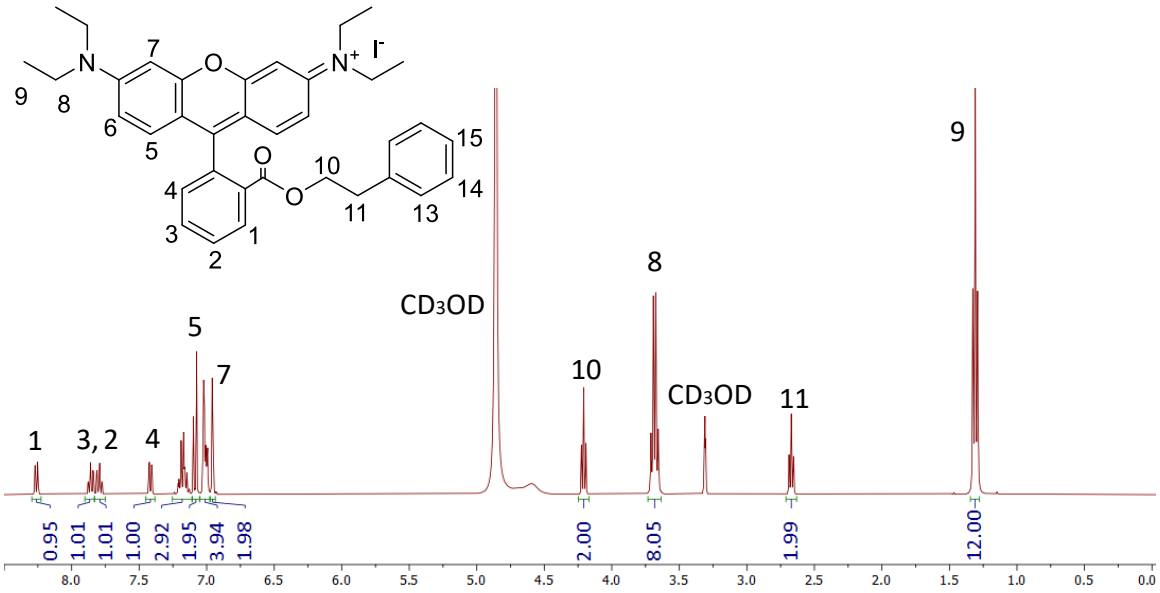


Figure S30. ^{1}H NMR spectrum of RhB-Ethyl-Ph-I.

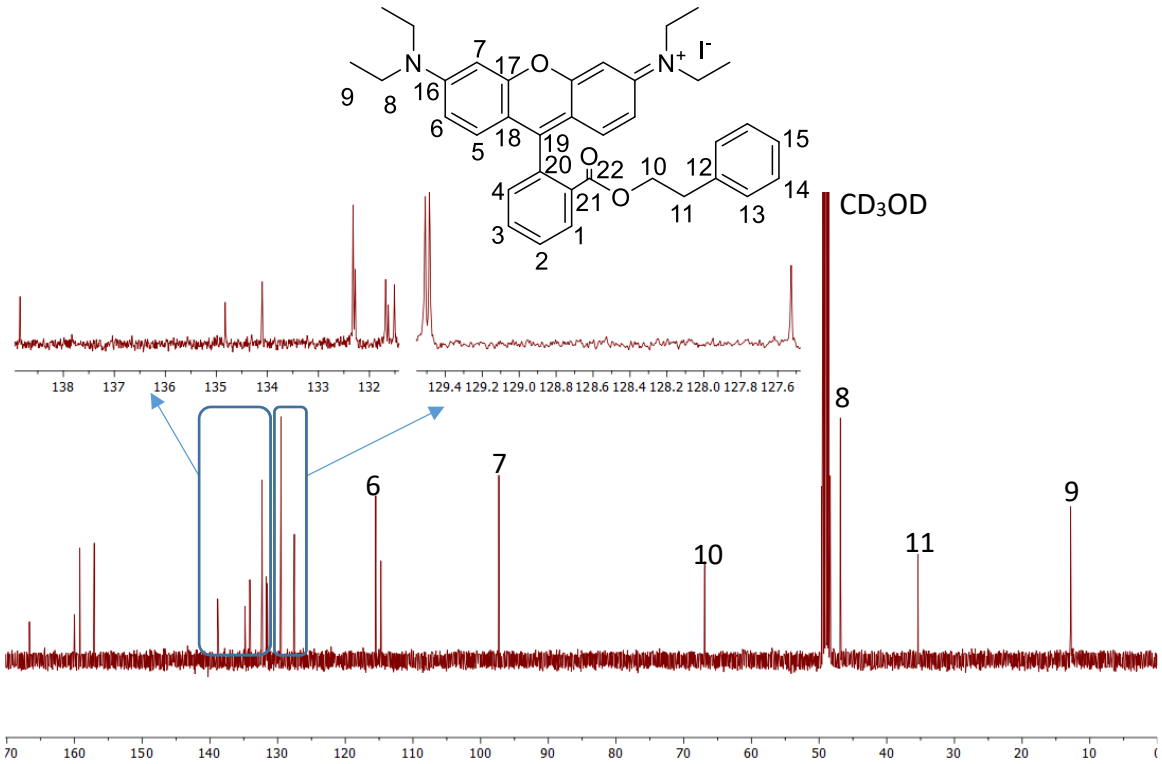


Figure S31. ^{13}C NMR spectrum of RhB-Ethyl-Ph-I.

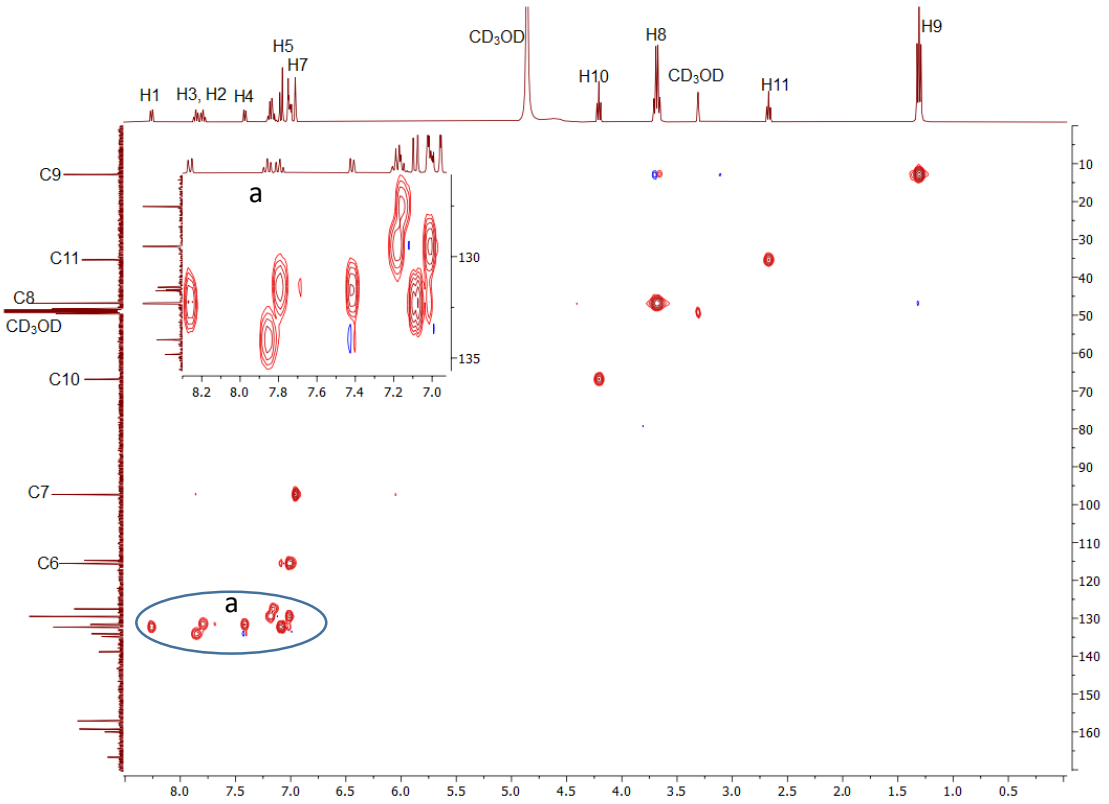


Figure S32. ^{1}H-^{13}C NMR HSQC spectrum of RhB-Ethyl-Ph-I.

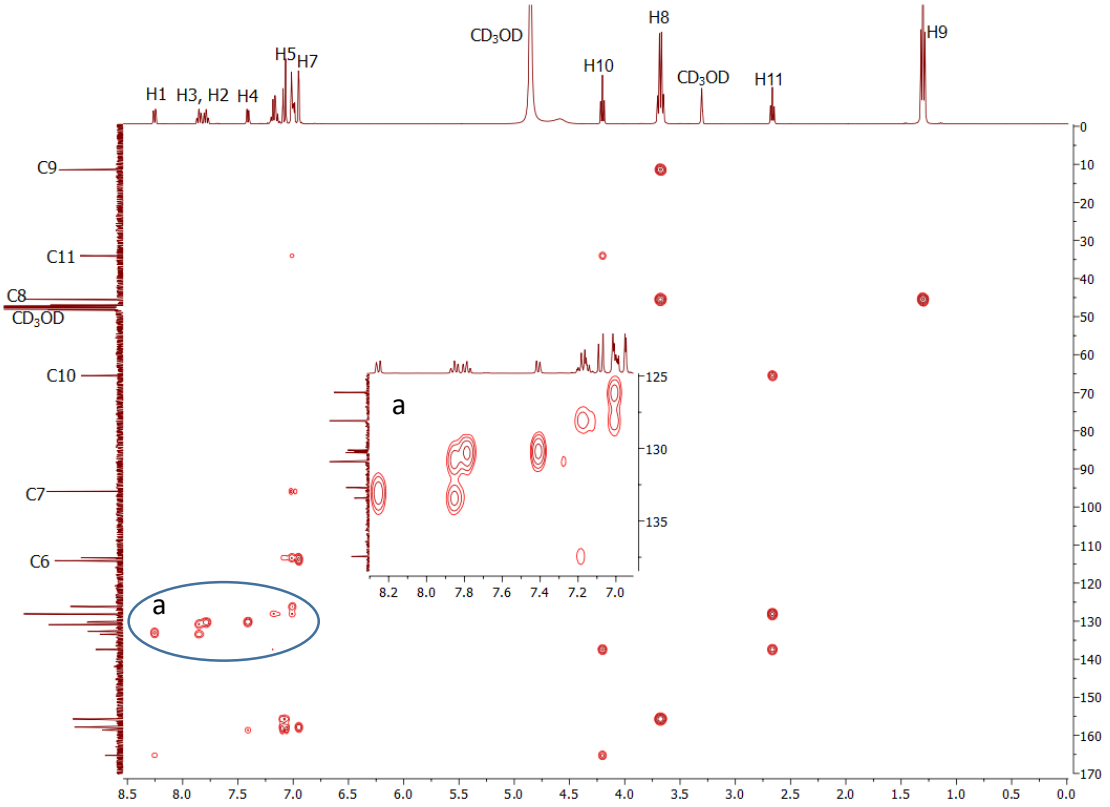


Figure S33. ^{1}H-^{13}C NMR HMBC spectrum of RhB-Ethyl-Ph-I.

NMR spectra of RhB-PrOH-Br

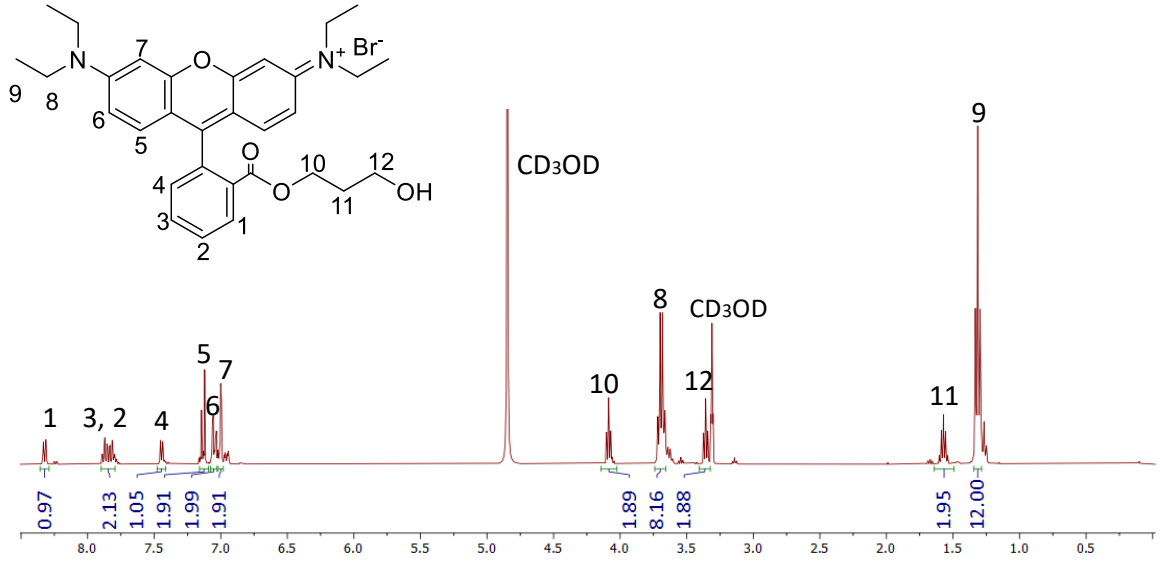


Figure S34. ^{1}H NMR spectrum of RhB-PrOH-Br.

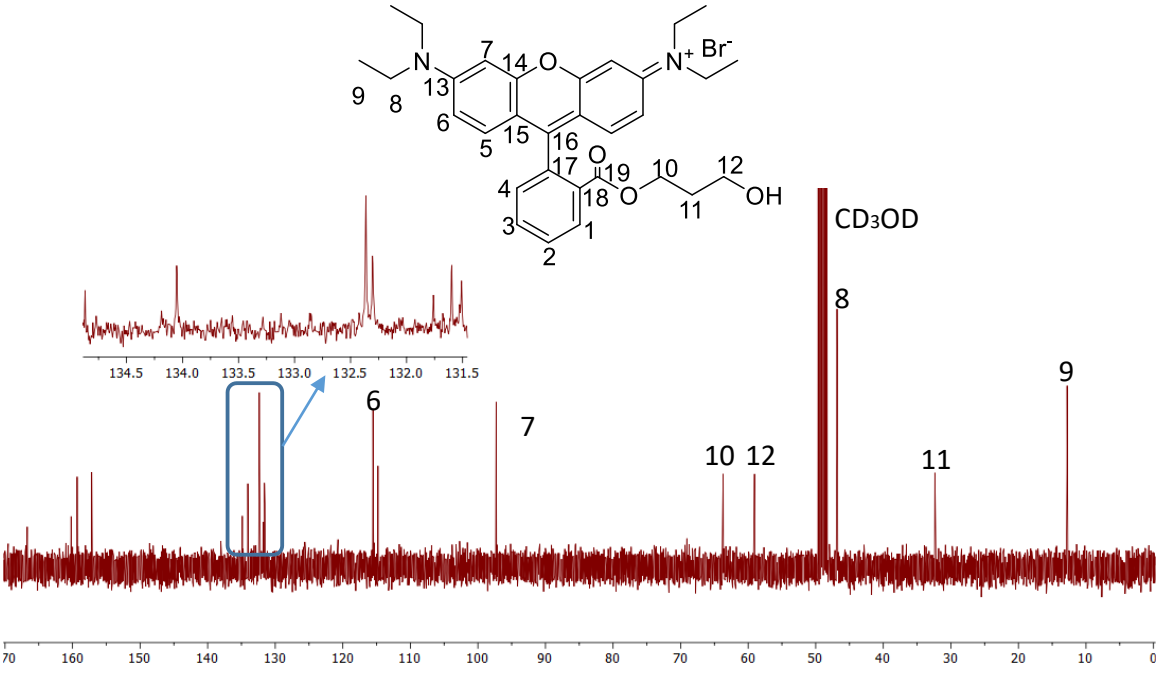


Figure S35. ^{13}C NMR spectrum of RhB-PrOH-Br.

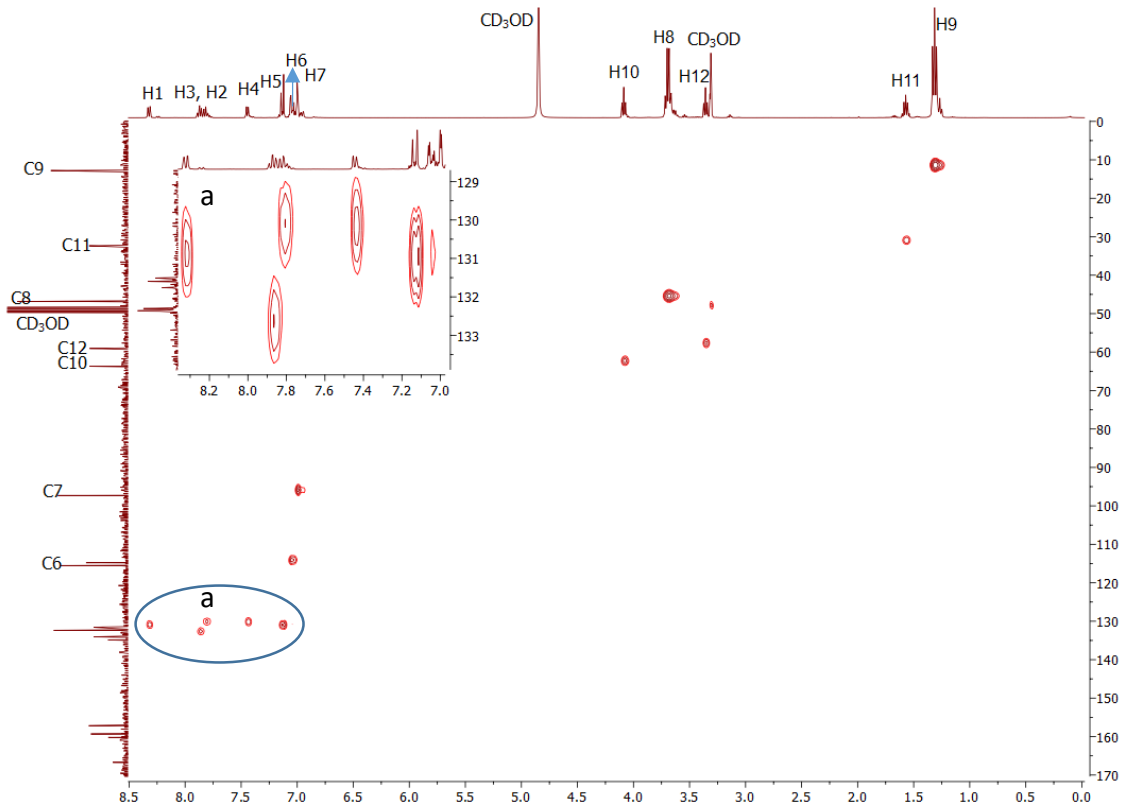


Figure S36. ^{1}H-^{13}C HSQC NMR spectrum of RhB-PrOH-Br.

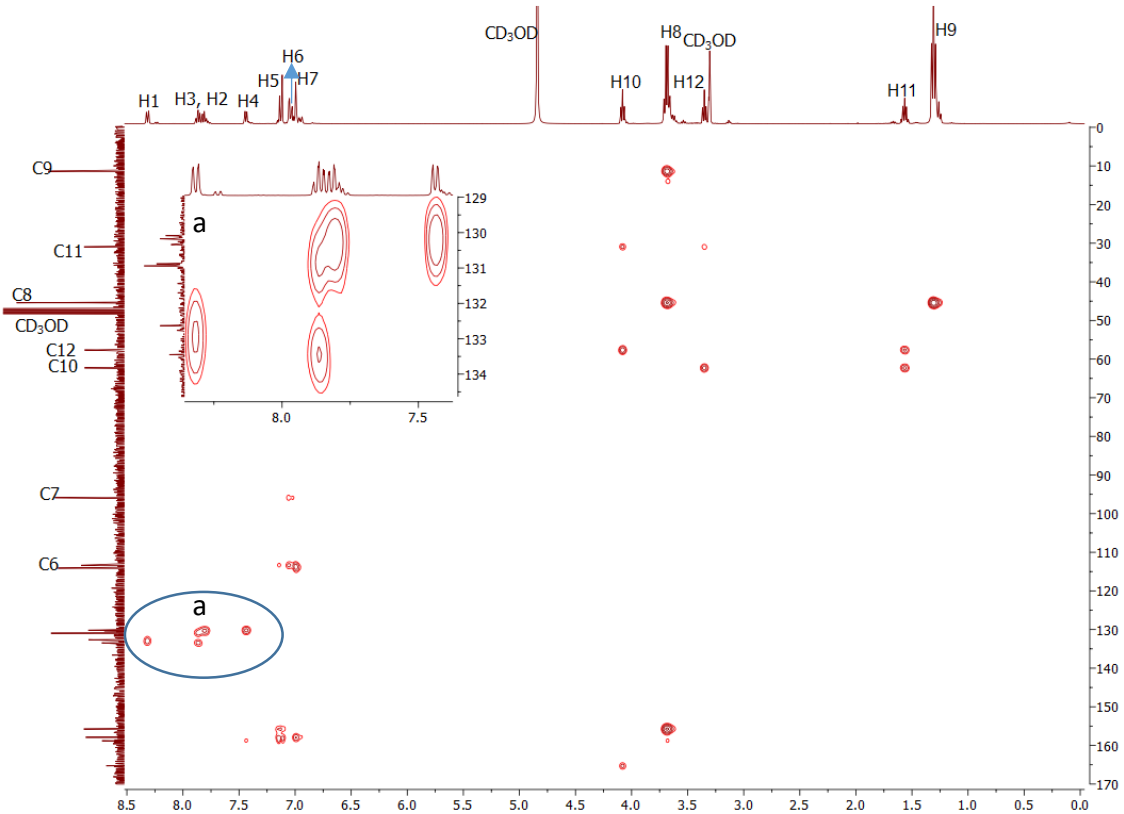


Figure S37. ^{1}H-^{13}C HMBC NMR spectrum of RhB-PrOH-Br.

NMR spectra of RhB-PrOH-I

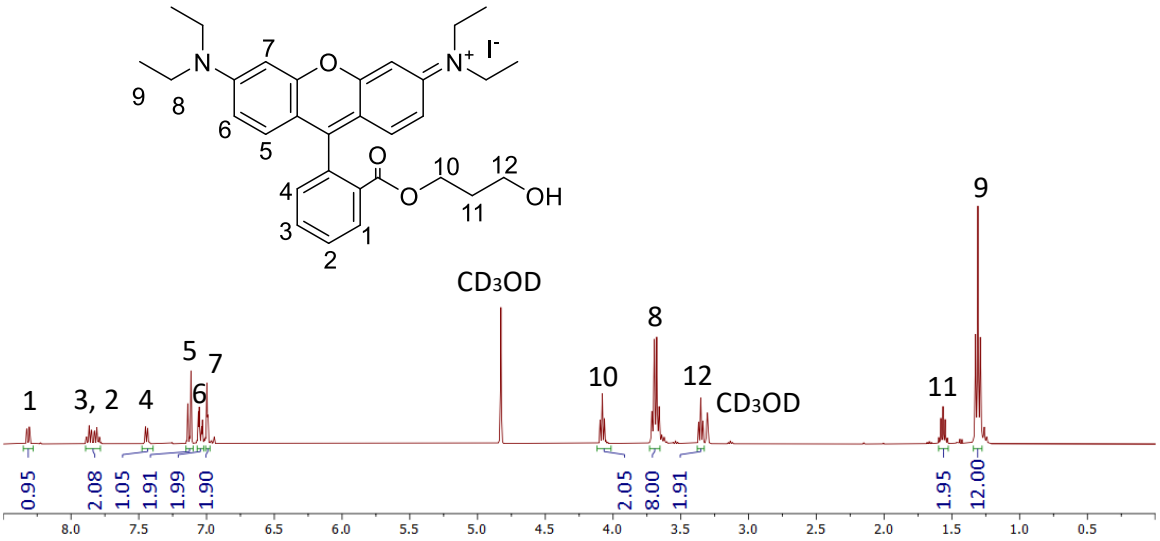


Figure S38. ^{1}H NMR spectrum of RhB-PrOH-I.

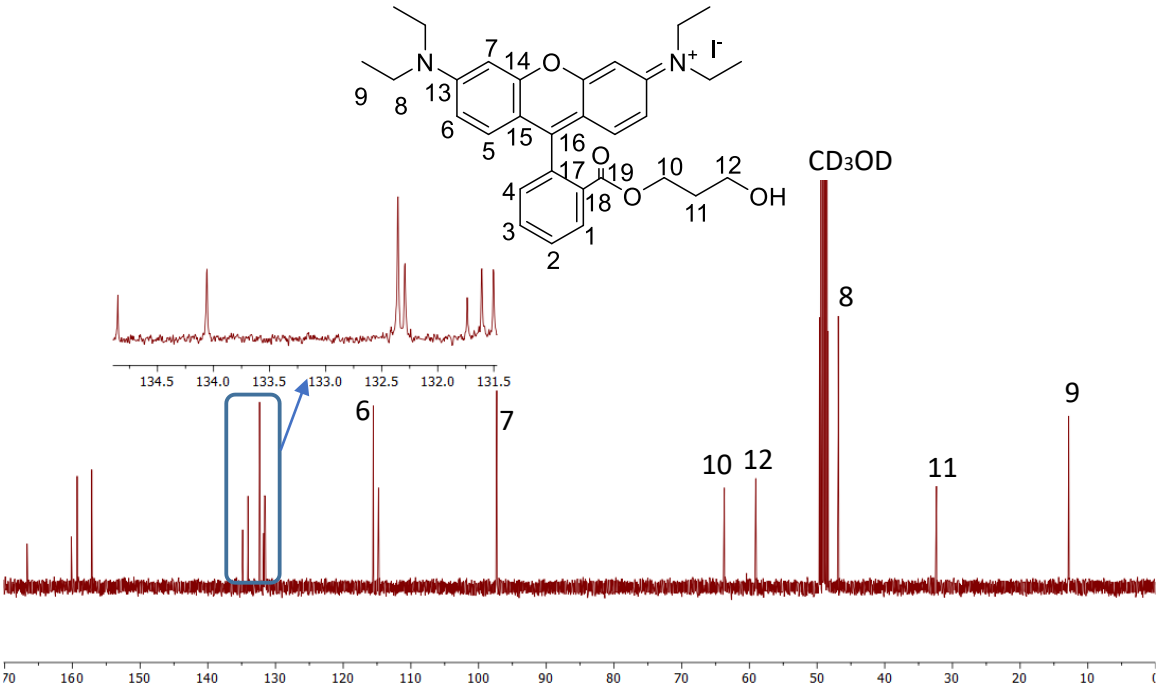


Figure S39. ^{13}C NMR spectrum of RhB-PrOH-I.

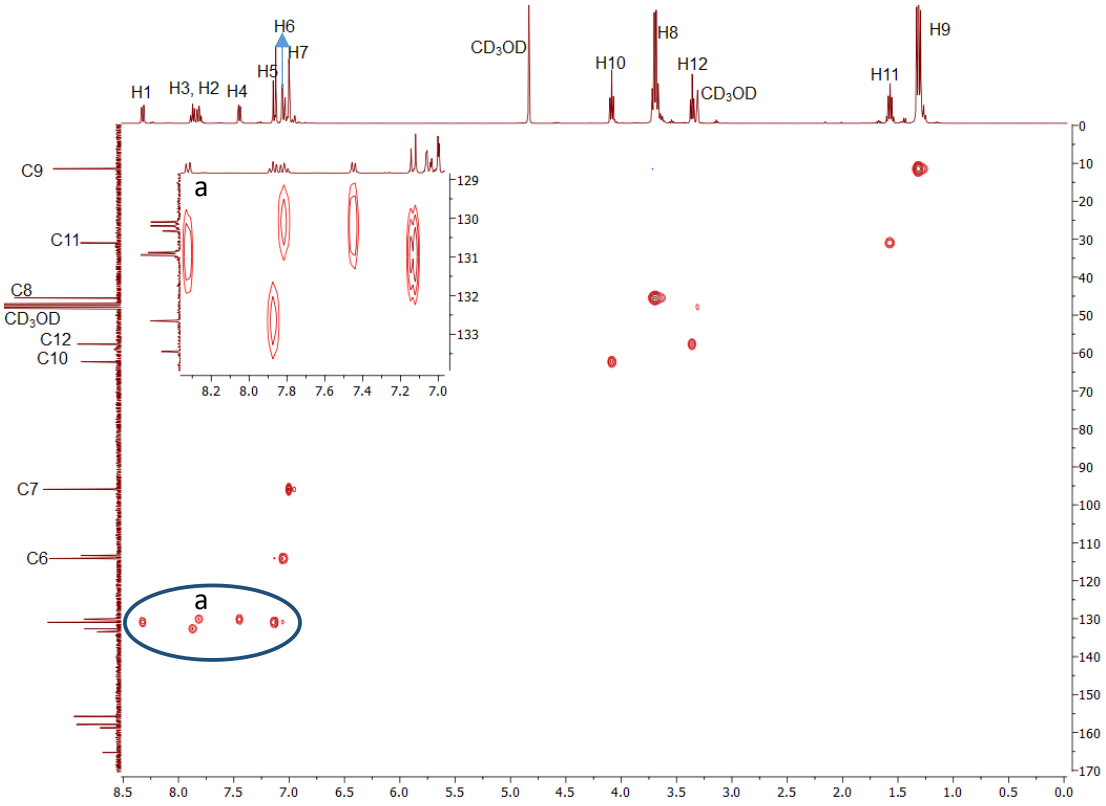


Figure S40. ^{1}H-^{13}C HSQC NMR spectrum of RhB-PrOH-I.

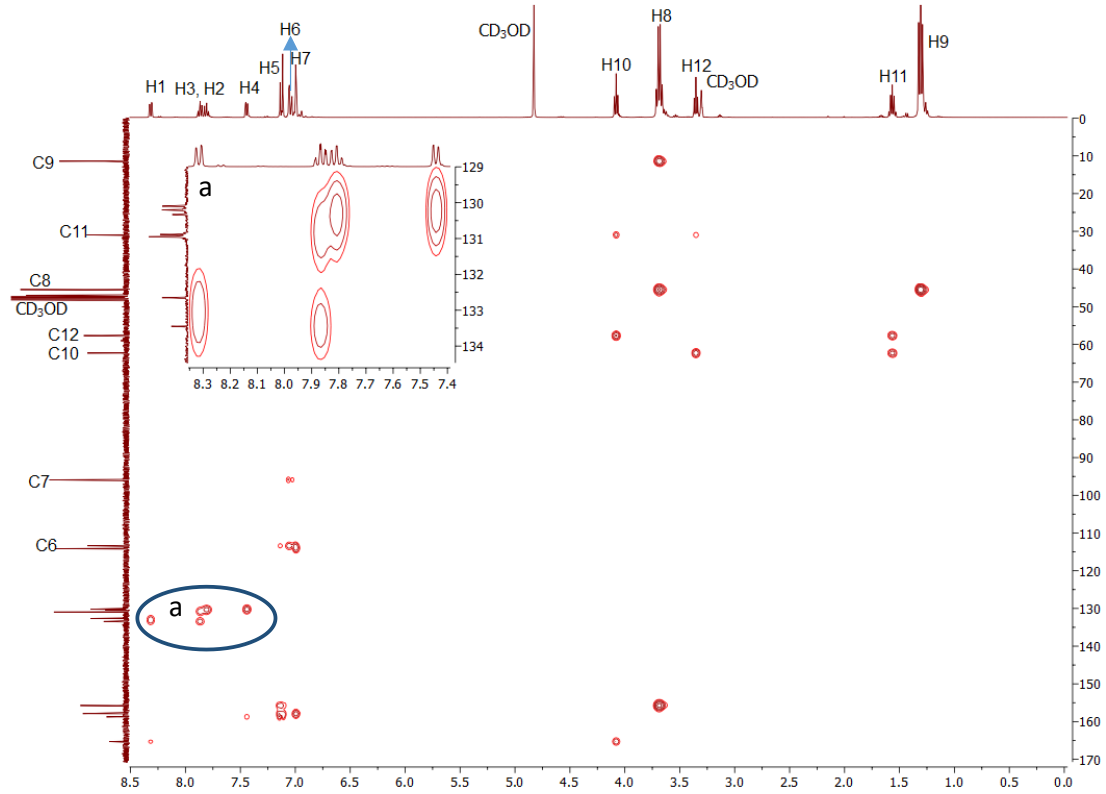


Figure S41. ^{1}H-^{13}C HMBC NMR spectrum of RhB-PrOH-I.

NMR spectra of RhB-Ethyl-PhOH-Br

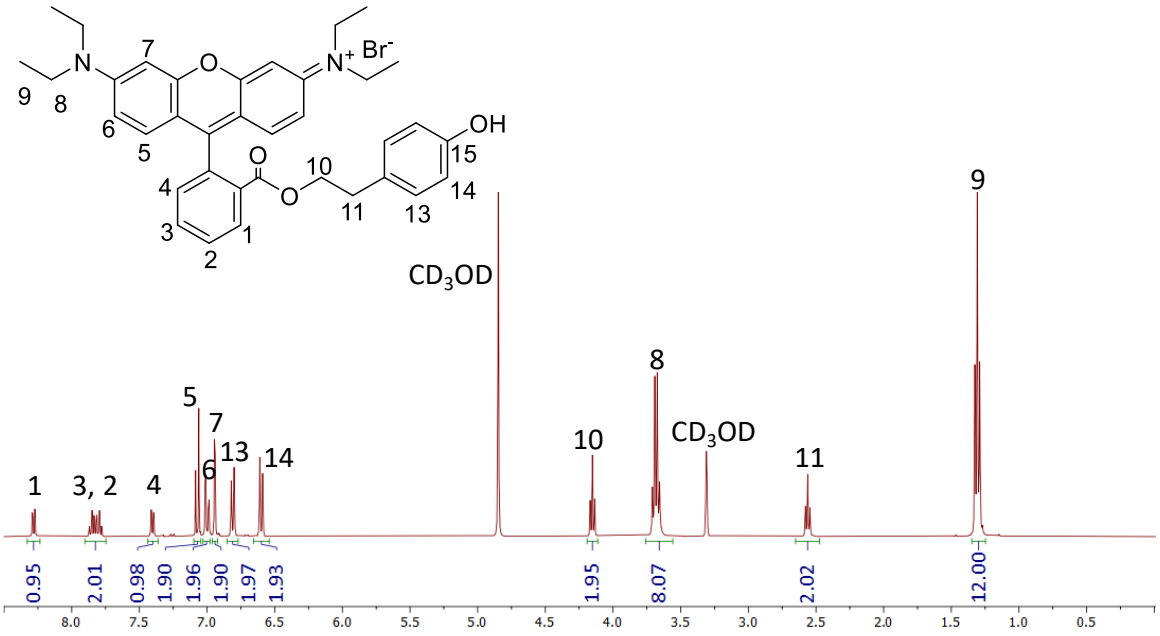


Figure S42. ^{1}H NMR spectrum of RhB-Ethyl-PhOH-Br.

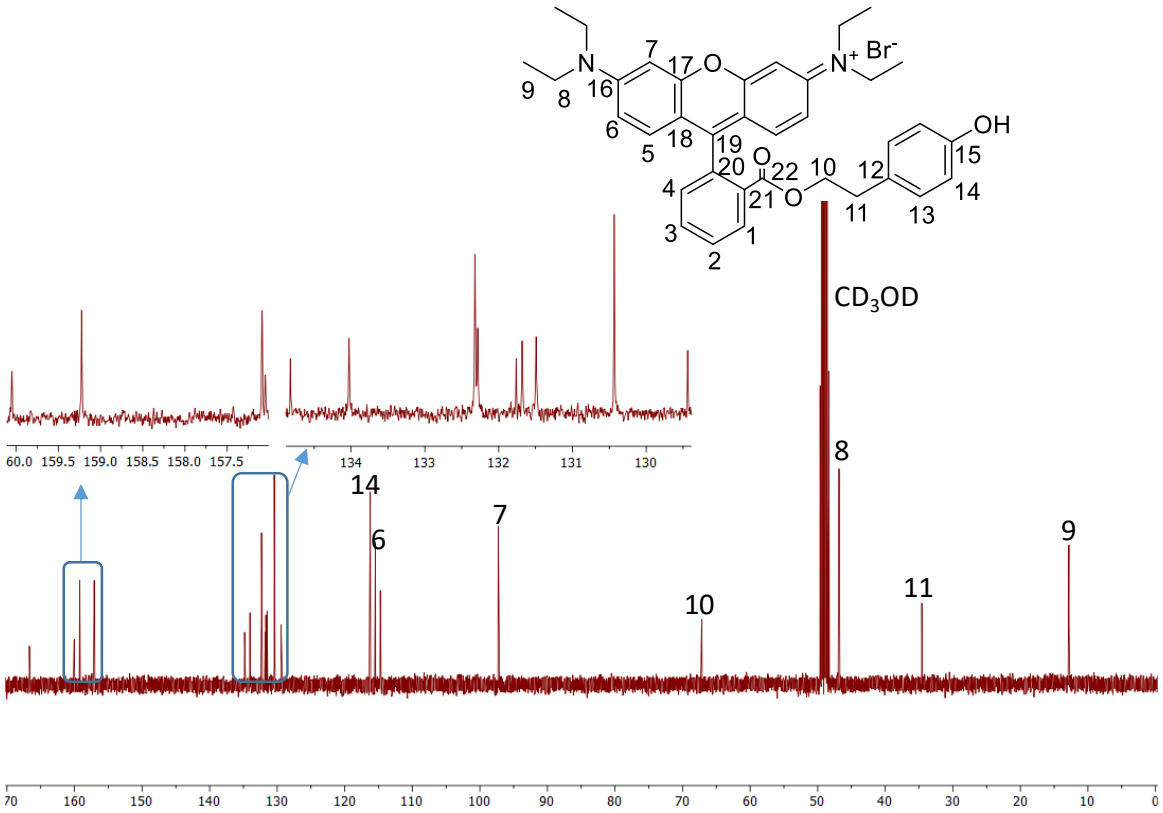


Figure S43. ^{13}C NMR spectrum of RhB-Ethyl-PhOH-Br.

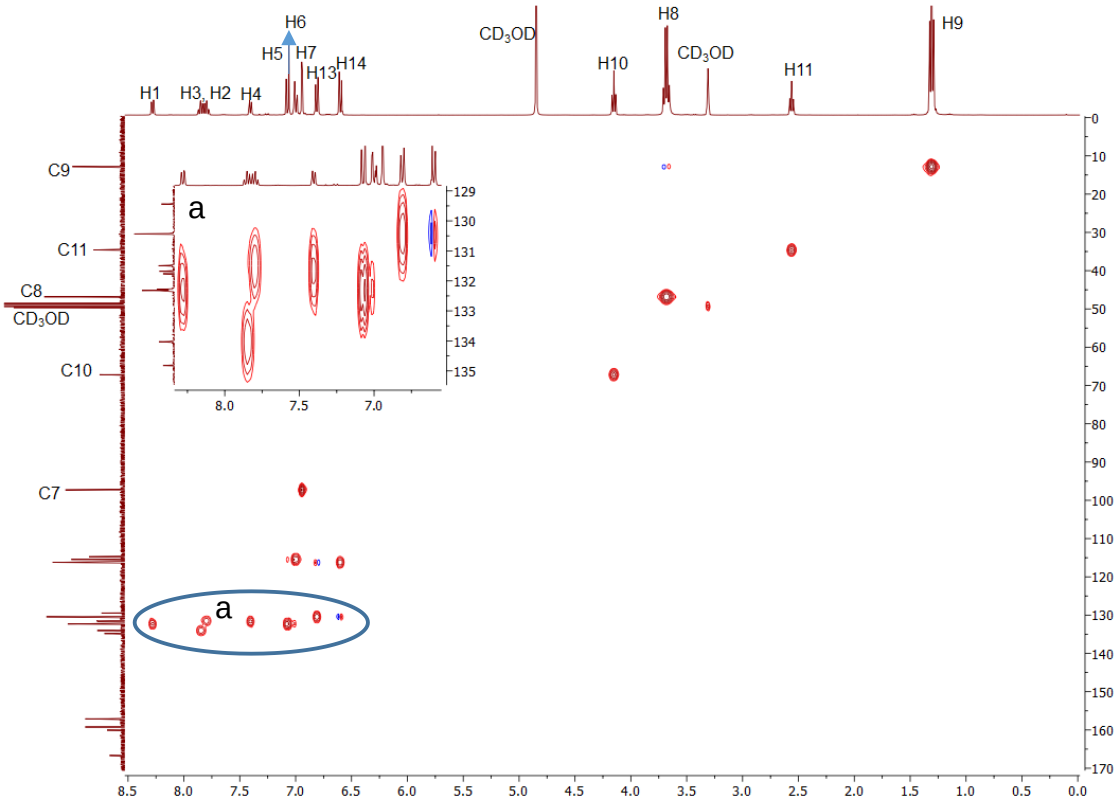


Figure S44. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Ethyl-PhOH-Br.

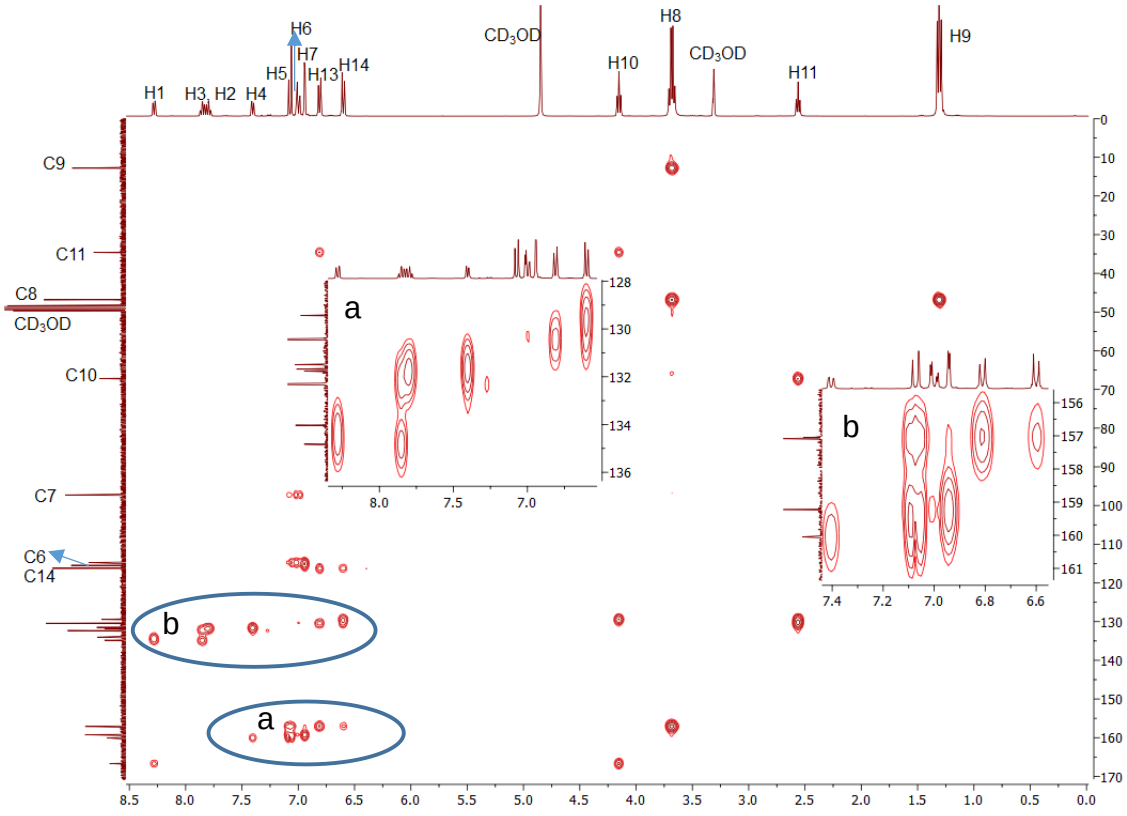


Figure S45. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Ethyl-PhOH-Br.

NMR spectra of RhB-Ethyl-PhOH-I

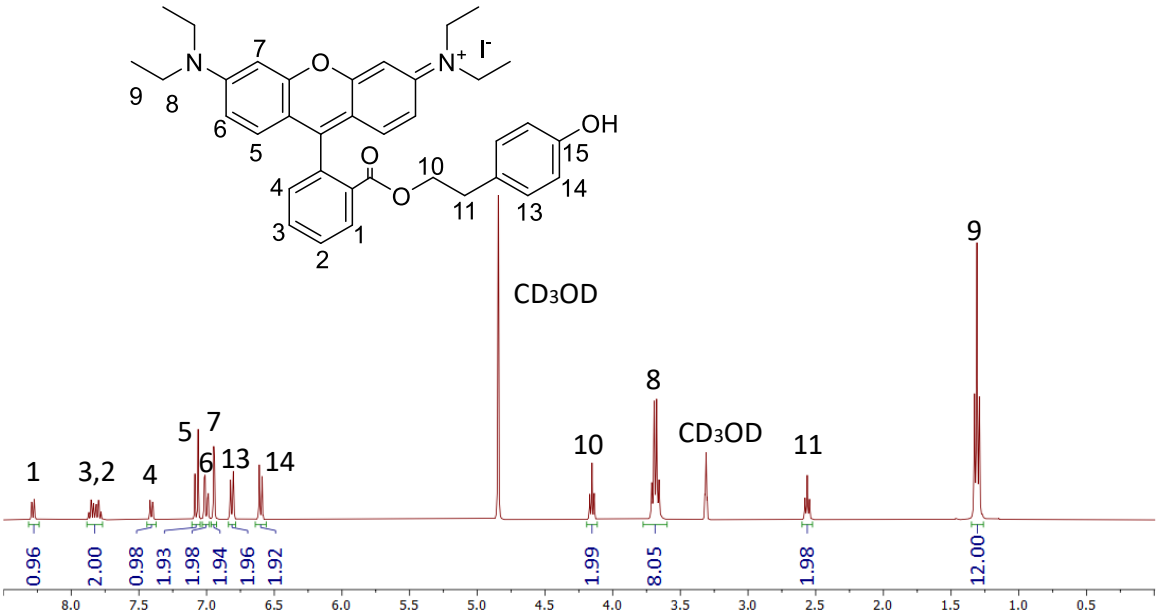


Figure S46. ^{1}H NMR spectrum of RhB-Ethyl-PhOH-I.

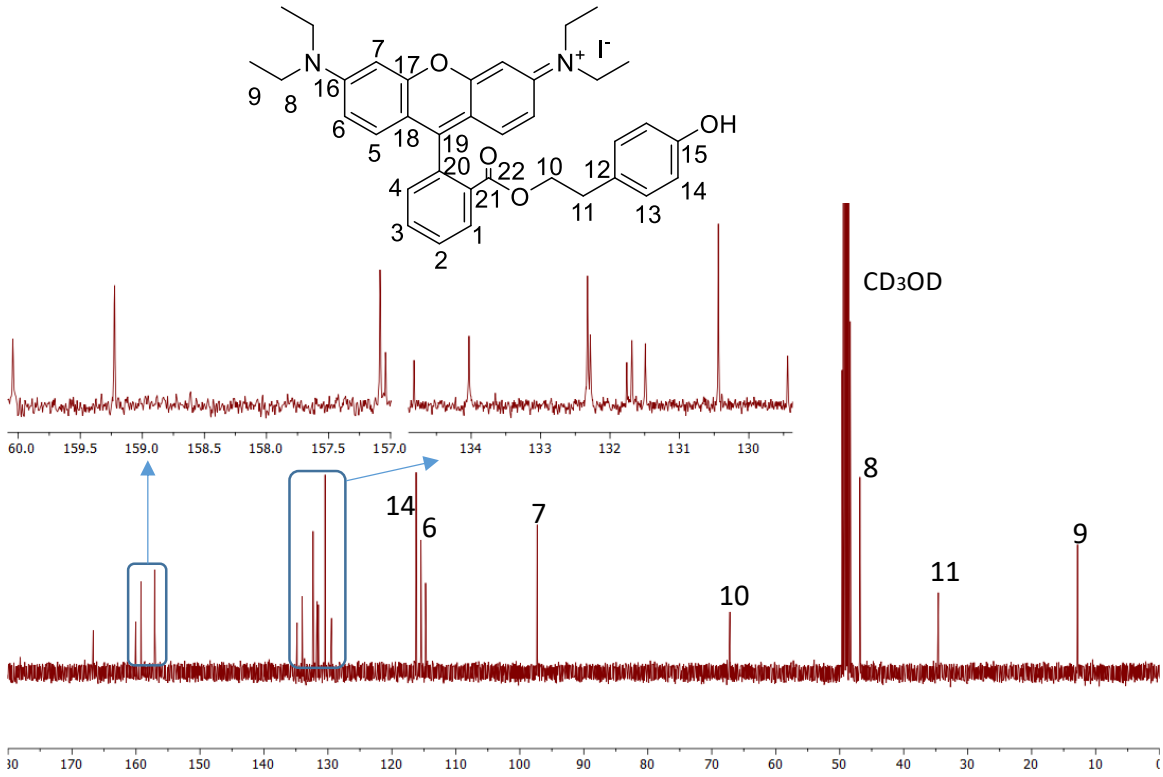


Figure S47. ^{13}C NMR spectrum of RhB-Ethyl-PhOH-I.

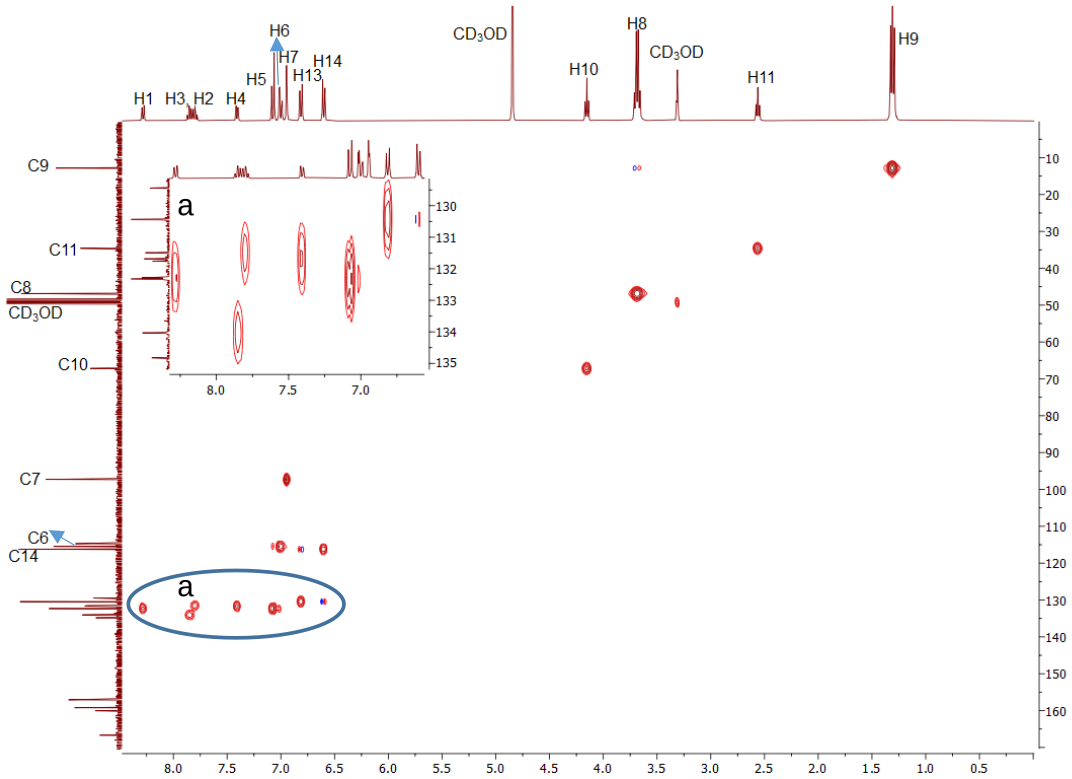


Figure S48. ^{1}H-^{13}C HSQC NMR spectrum of RhB-Ethyl-PhOH-I.

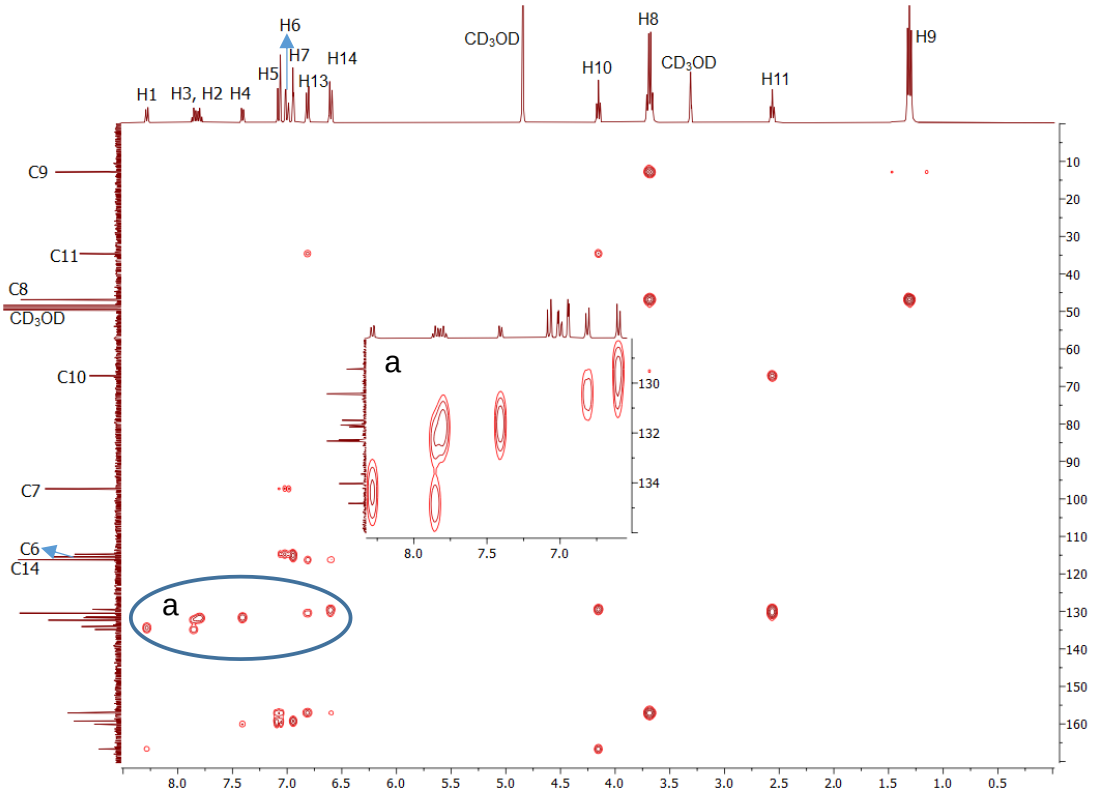


Figure S49. ^{1}H-^{13}C HMBC NMR spectrum of RhB-Ethyl-PhOH-I.

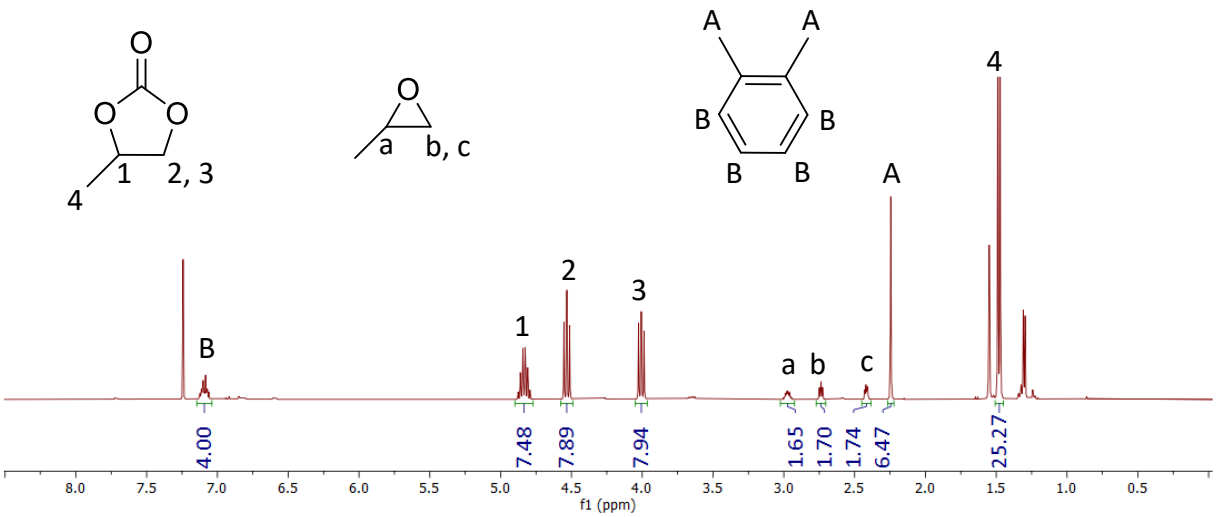


Figure S50. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to propylene oxide using RhB-Ethyl-PhOH-I as the catalyst.

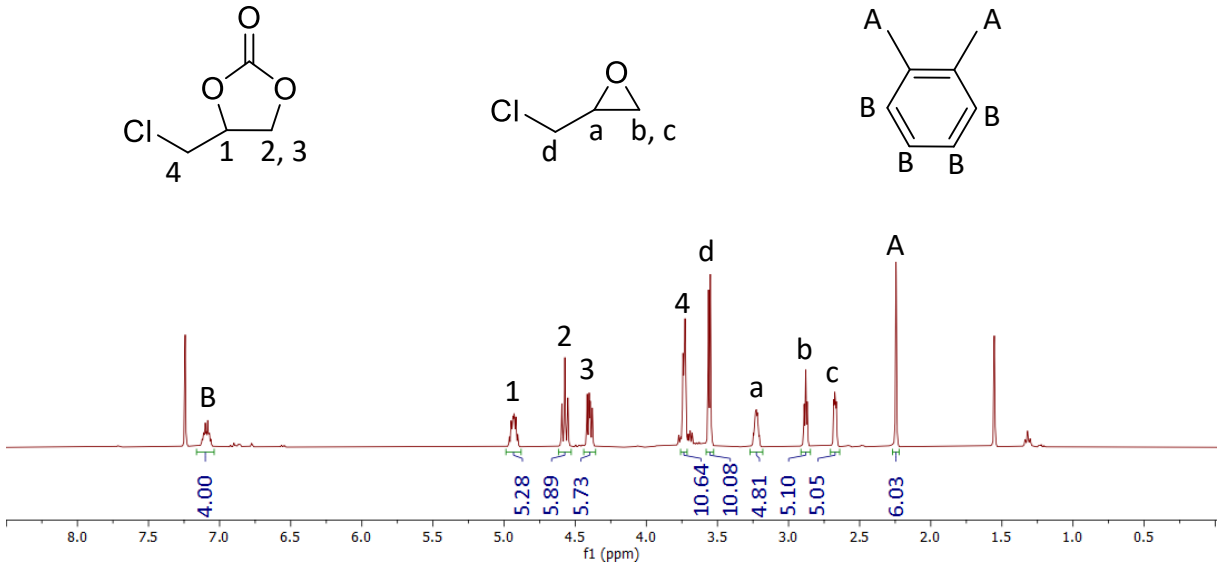


Figure S51. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to epichlorohydrin using RhB-Ethyl-PhOH-I as the catalyst.

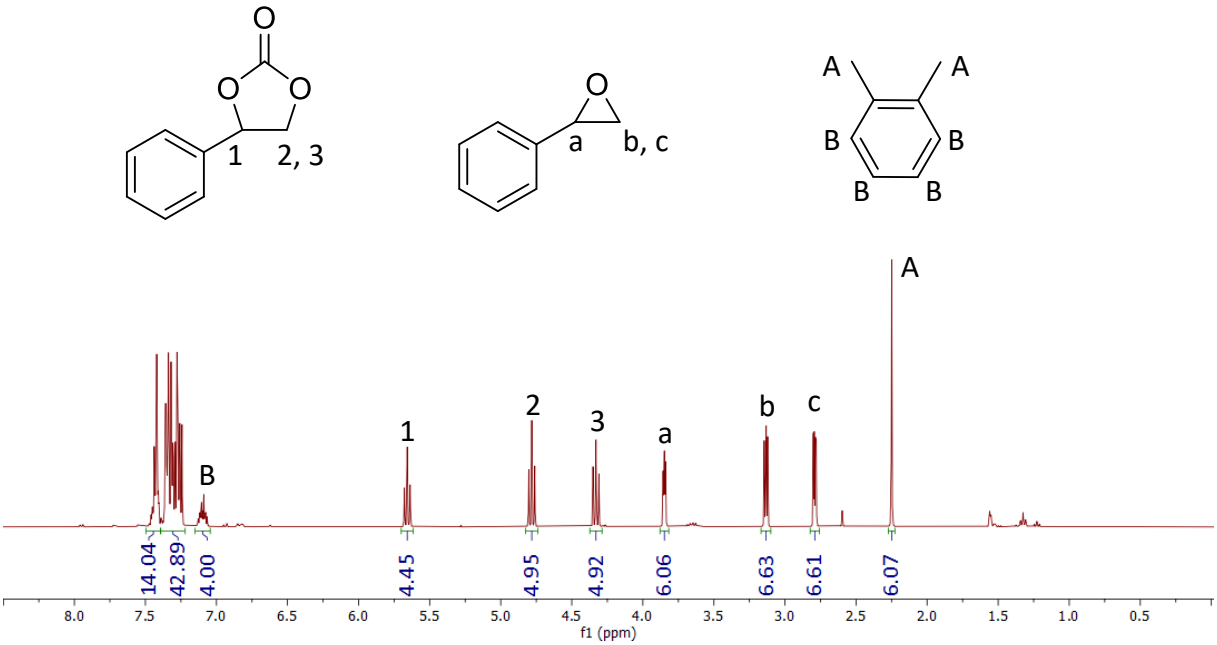


Figure S52. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to styrene oxide using RhB-Ethyl-PhOH-I as the catalyst.

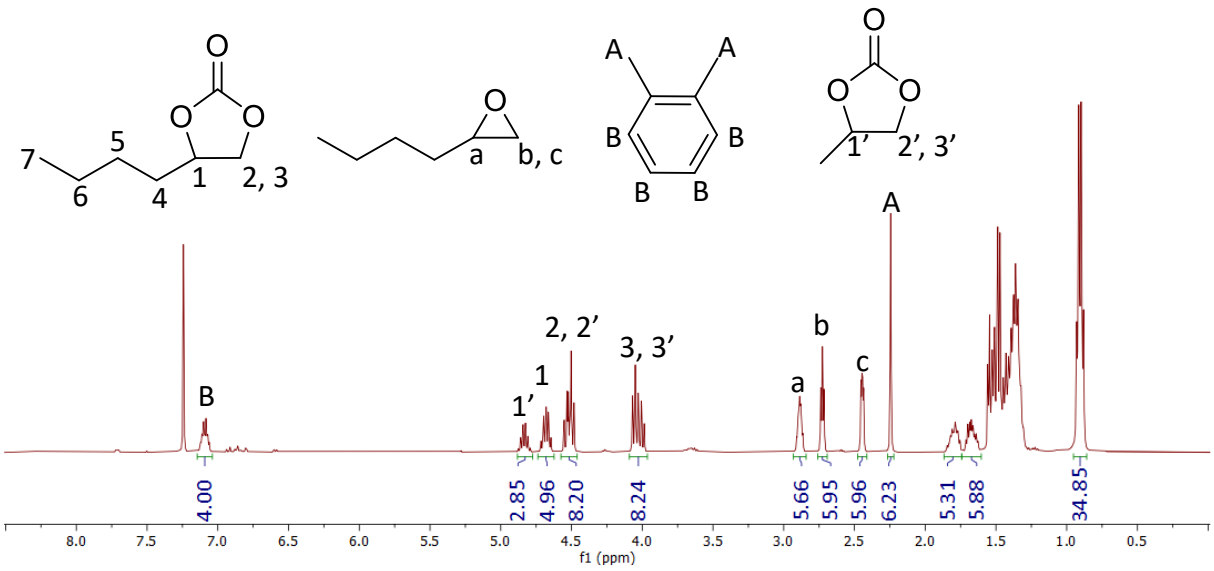


Figure S53. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to 1,2-epoxyhexane (PC as the solvent) using RhB-Ethyl-PhOH-I as the catalyst.

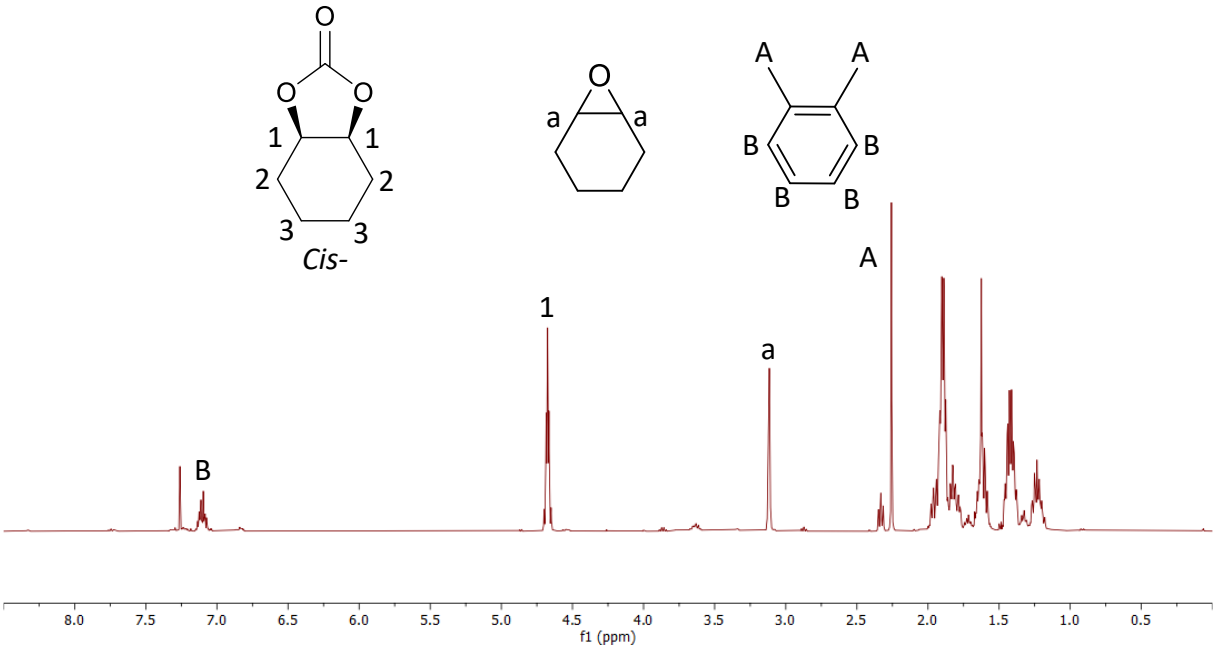


Figure S54. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to cyclohexene oxide using RhB-Ethyl-Ph-I as the catalyst.

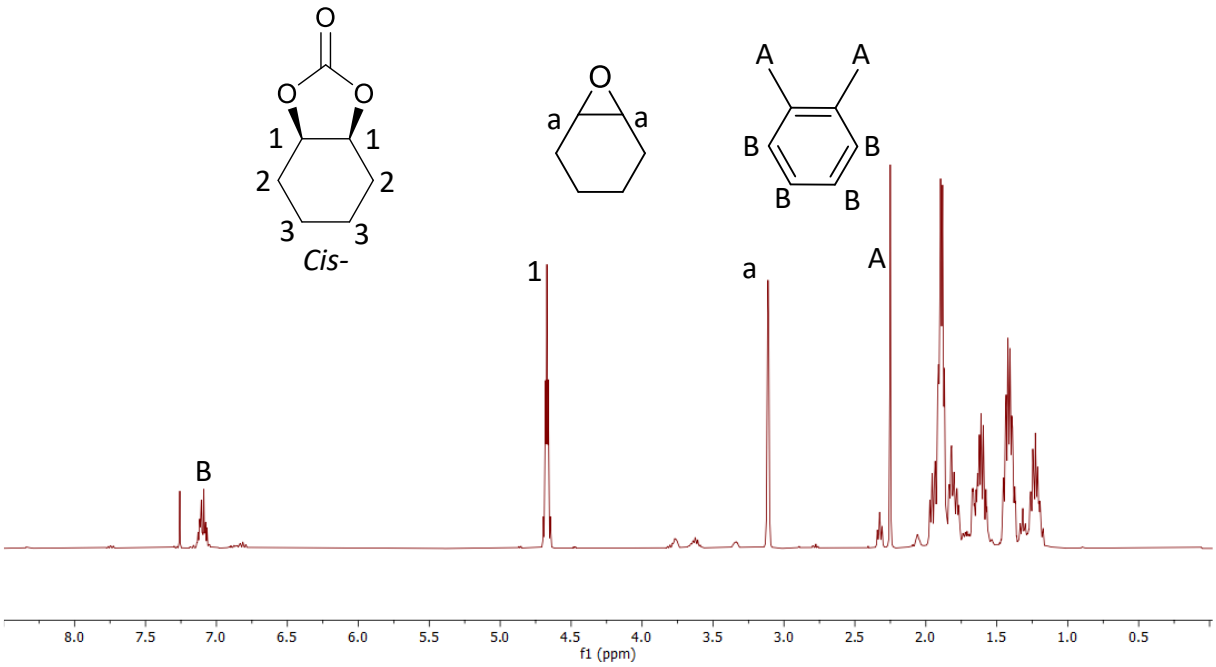


Figure S55. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to cyclohexene oxide using RhB-Ethyl-PhOH-I as the catalyst.

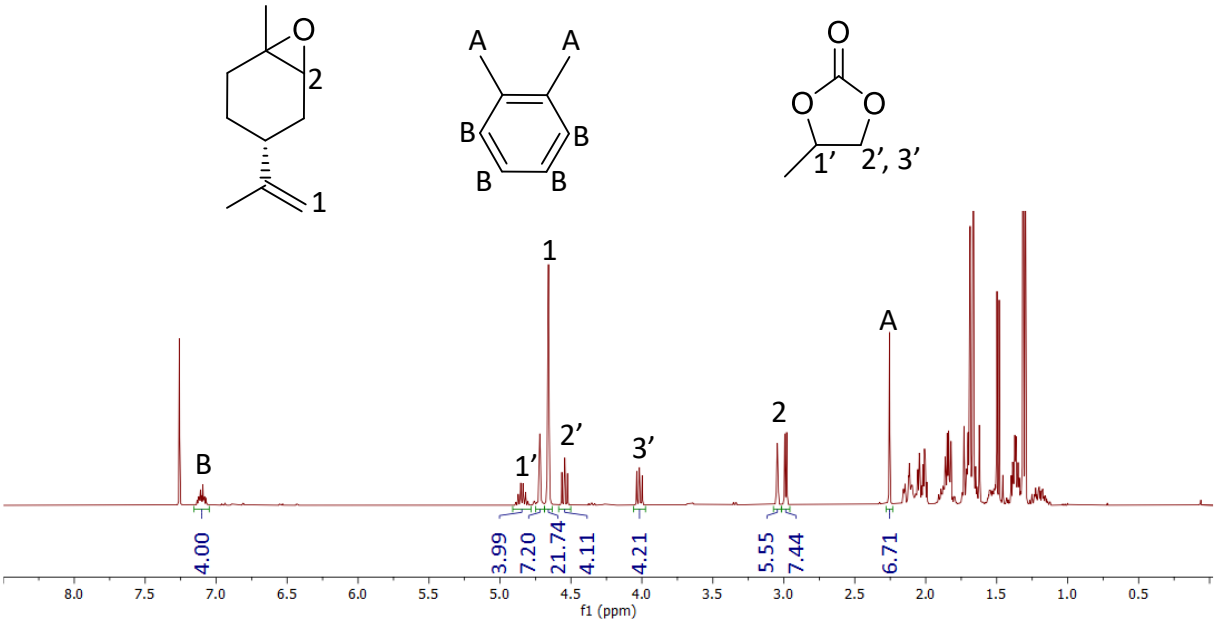


Figure S56. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to limonene oxide (PC as the solvent) using RhB-Ethyl-PhOH-I as the catalyst.

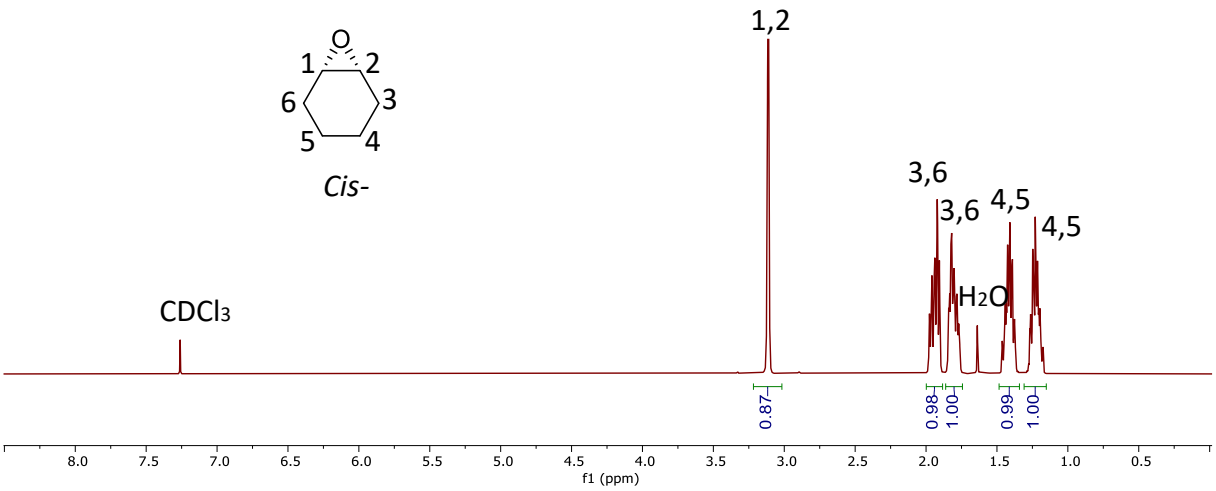


Figure S57. ^{1}H NMR spectrum of cyclohexene oxide purchased from Sigma-Aldrich.

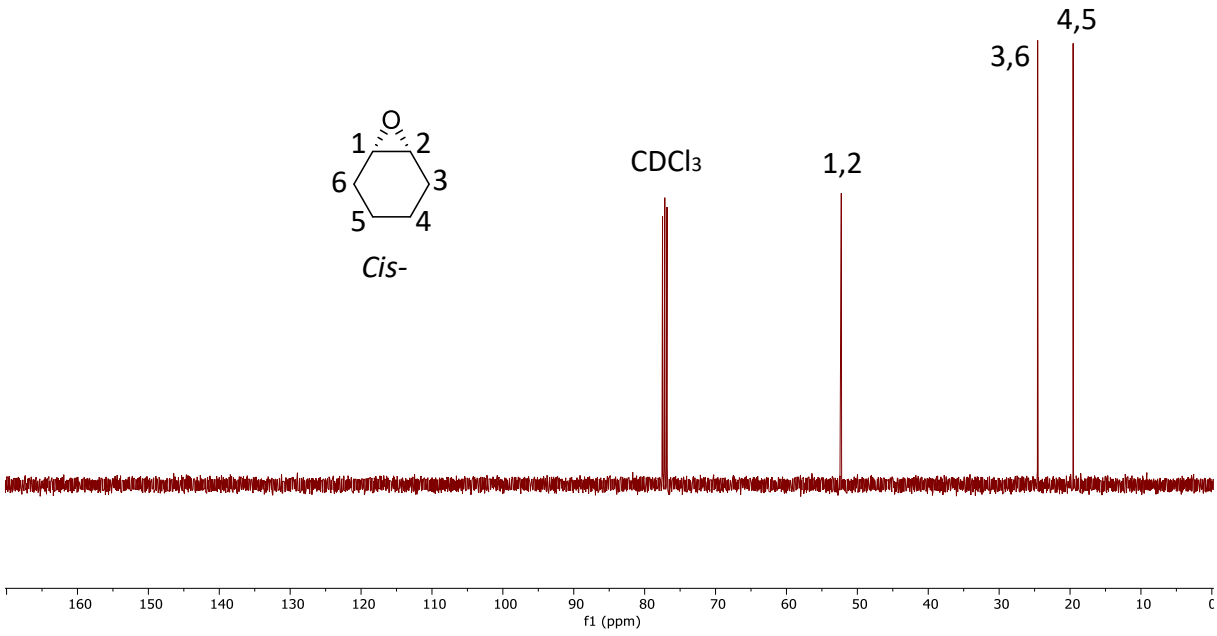


Figure S58. ^{13}C NMR spectrum of cyclohexene oxide purchased from Sigma-Aldrich.

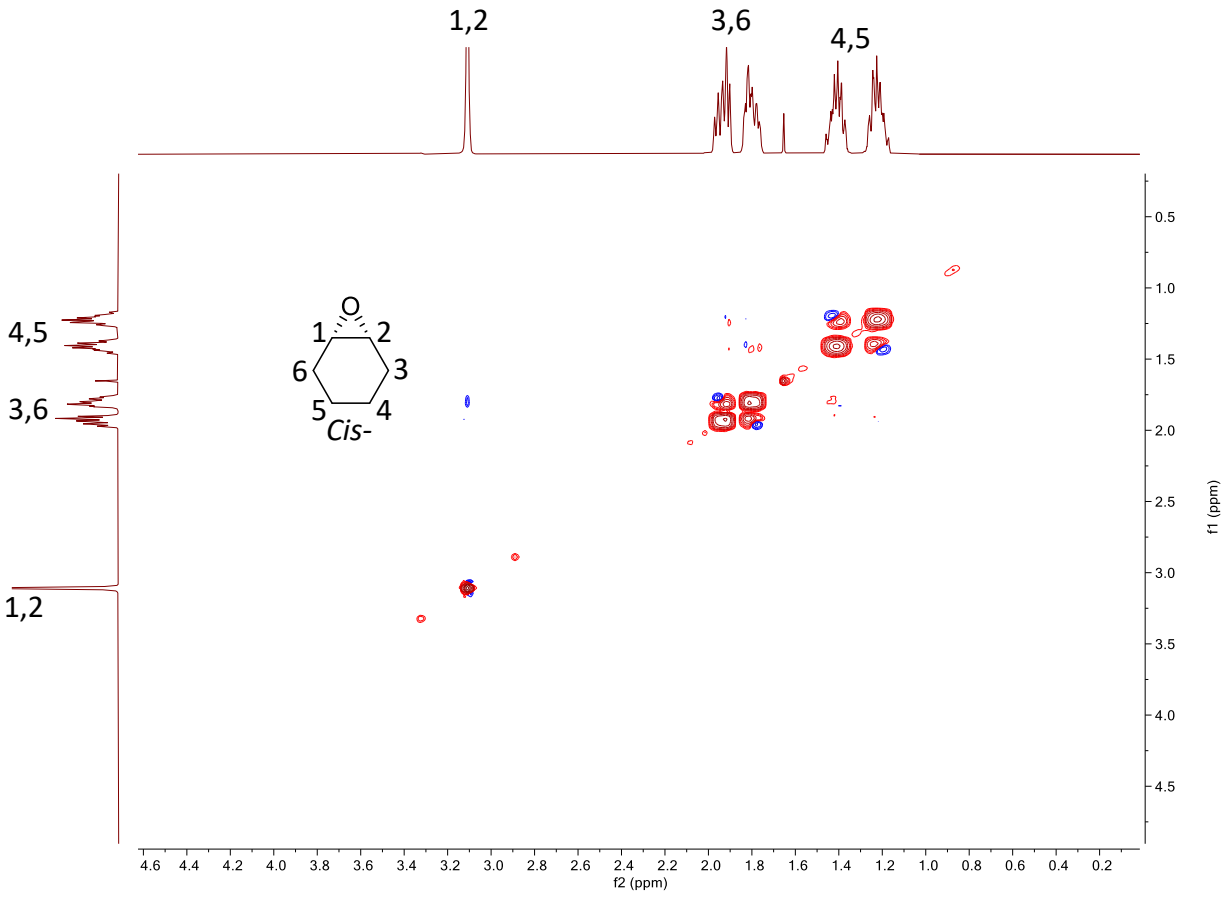


Figure S59. ^{1}H-^{1}H NOESY spectrum of cyclohexene oxide purchased from Sigma-Aldrich.

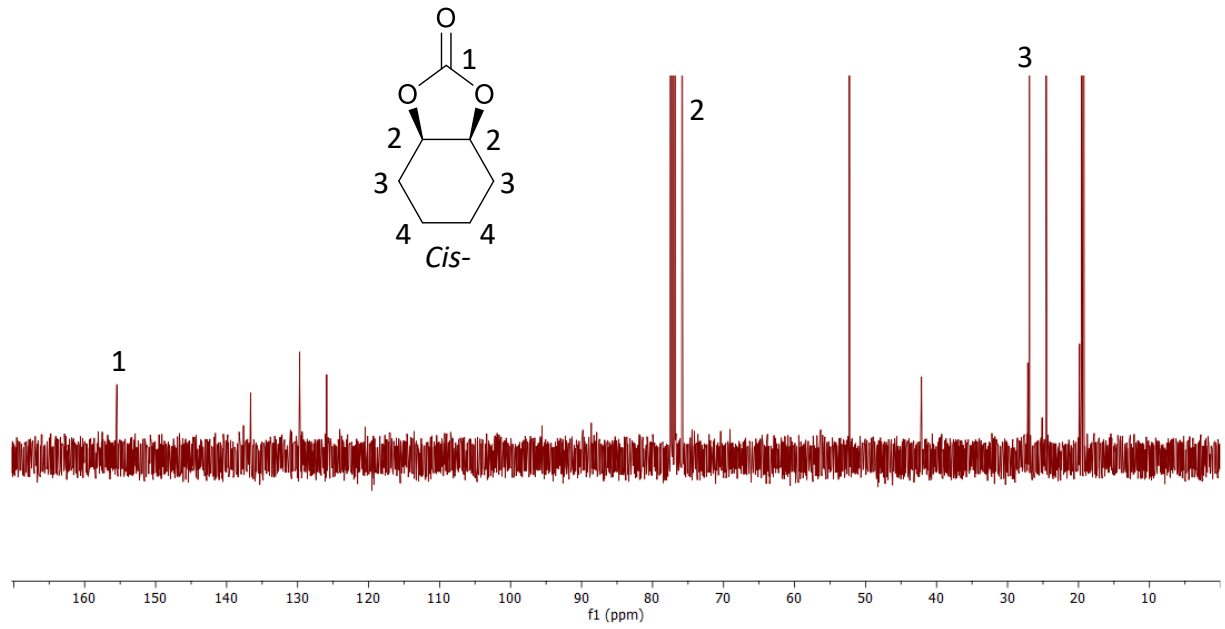


Figure S60. ^{13}C NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to cyclohexene oxide using RhB-Ethyl-Ph-I as the catalyst.

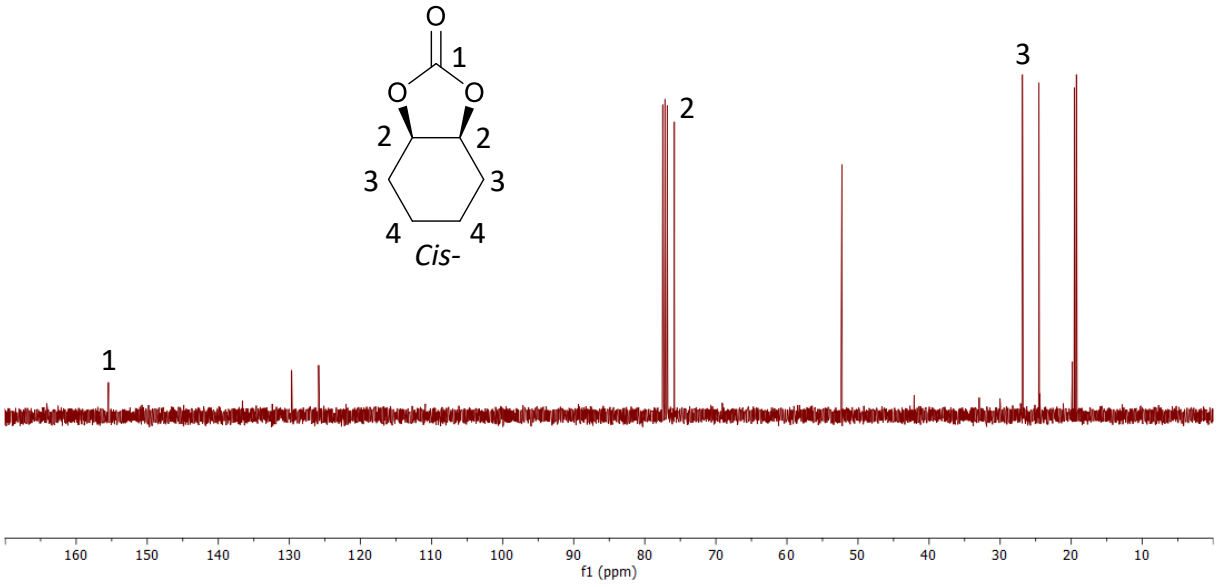


Figure S61. ^{13}C NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to cyclohexene oxide using RhB-Ethyl-PhOH-I as the catalyst.

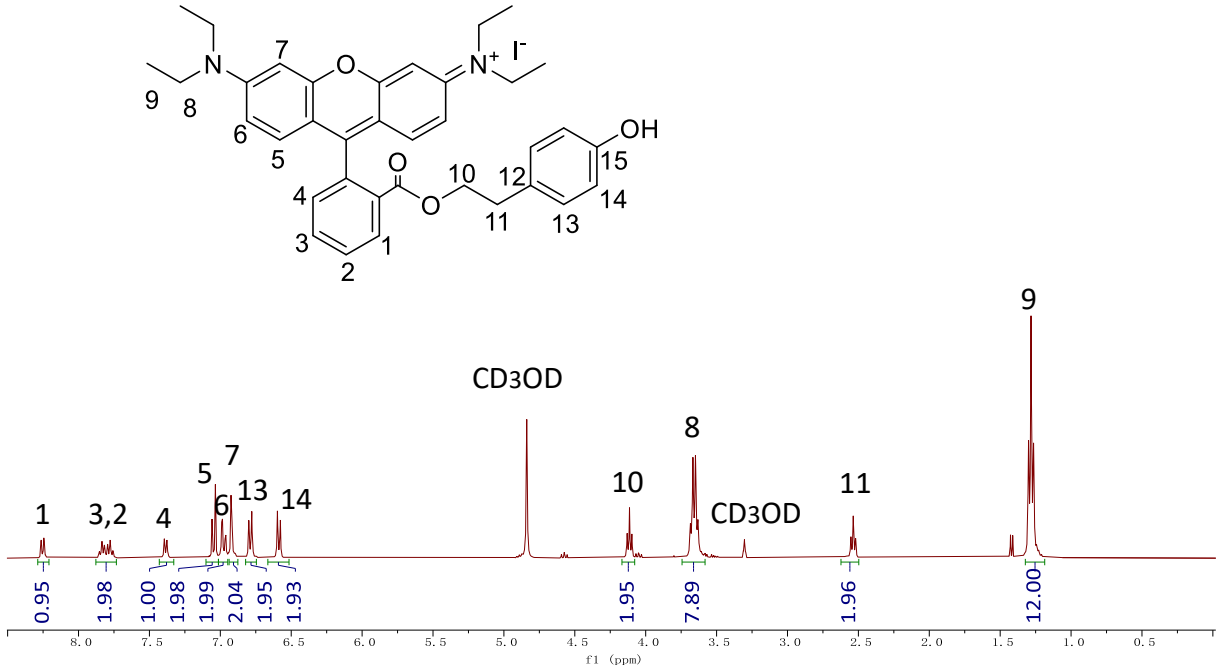


Figure S62. ^{1}H NMR spectrum of the recovered RhB-Ethyl-PhOH-I catalyst.

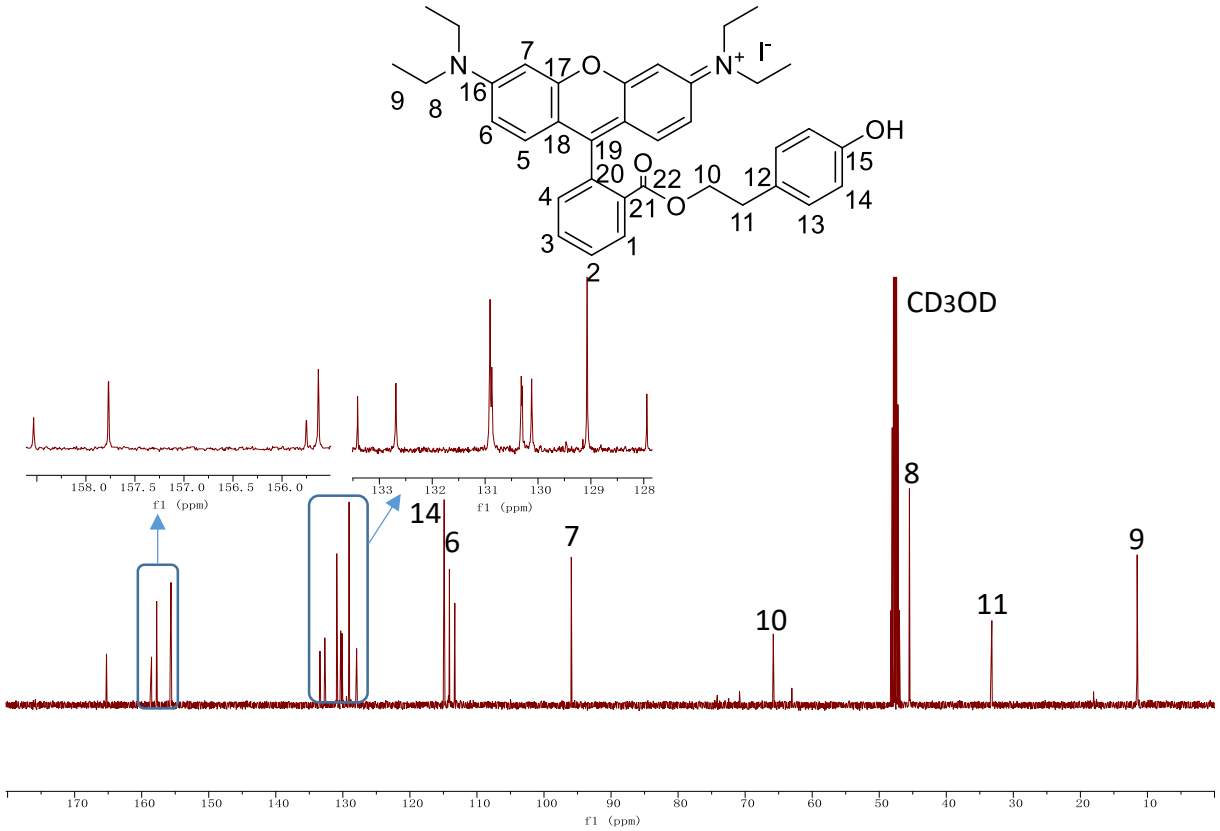


Figure S63. ^{13}C NMR spectrum of the recovered RhB-Ethyl-PhOH-I catalyst.

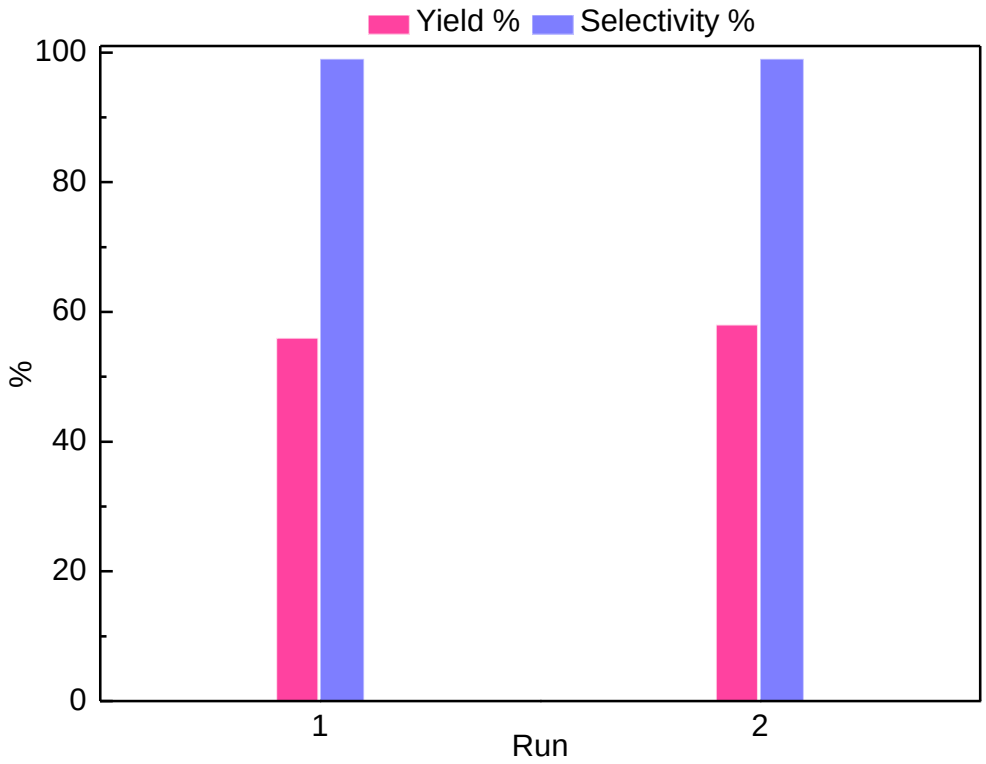


Figure S64. Reusability test of RhB-Ethyl-PhOH-I as the catalyst for the synthesis of propylene carbonate from CO_2 and propylene oxide. Reaction conditions: 45 °C, 10 bar CO_2, 18 h.

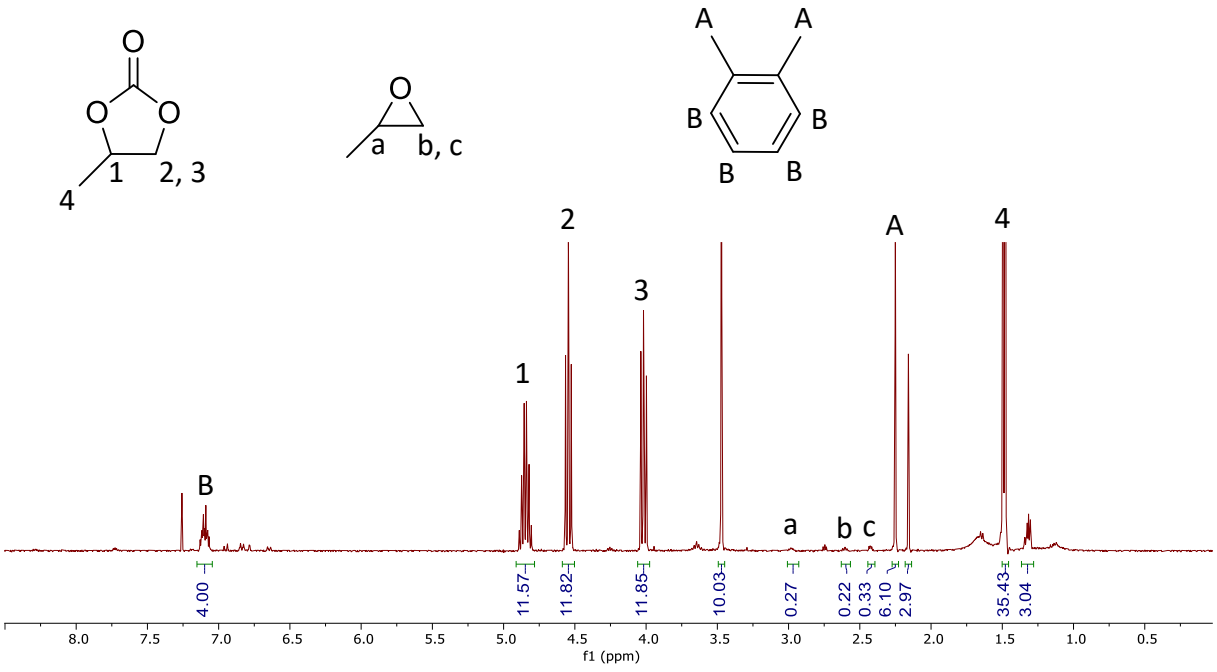


Figure S65. ^{1}H NMR spectrum of the reaction mixture for the cycloaddition of CO_2 to propylene oxide at 60 °C using RhB-Ethyl-PhOH-I as the catalyst (98% yield).

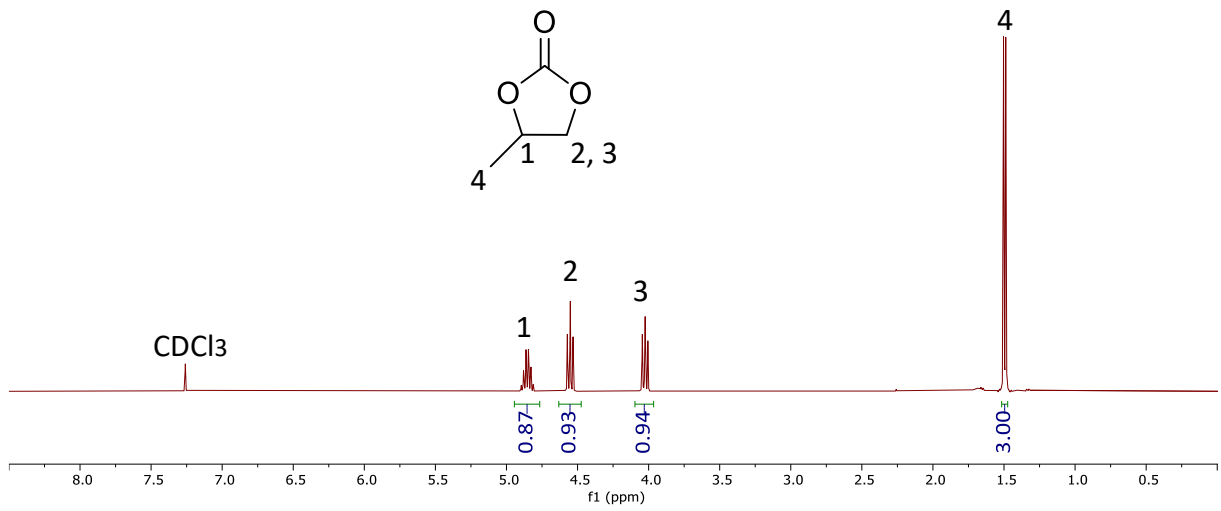


Figure S66. ^{1}H NMR spectrum of the purified propylene carbonate.

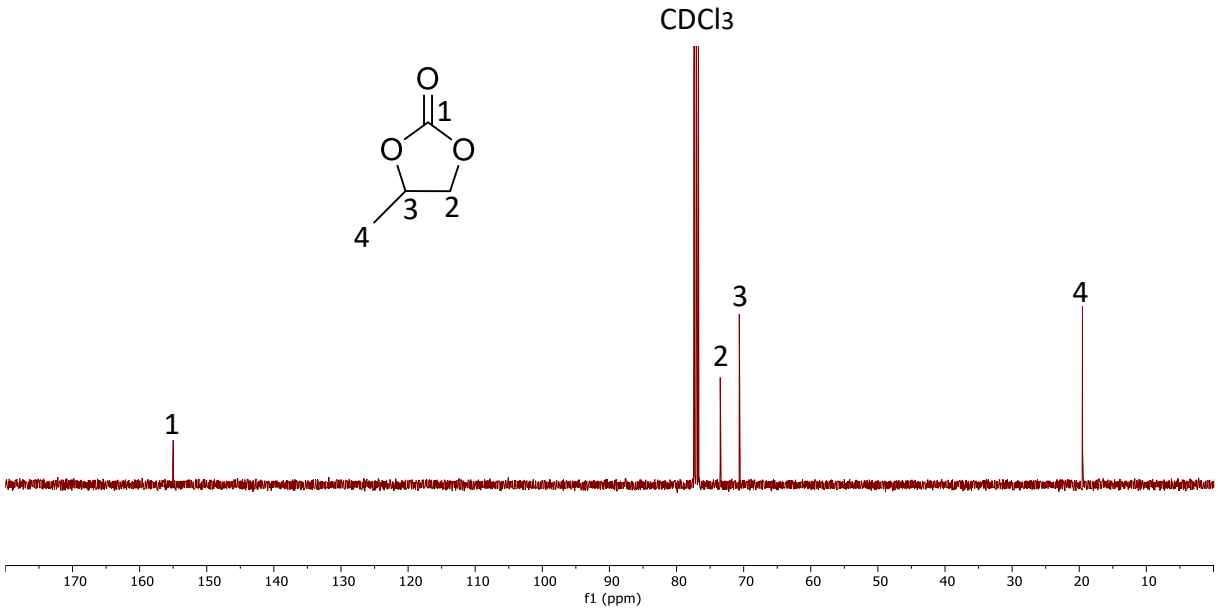


Figure S67. ^{13}C NMR spectrum of the purified propylene carbonate.

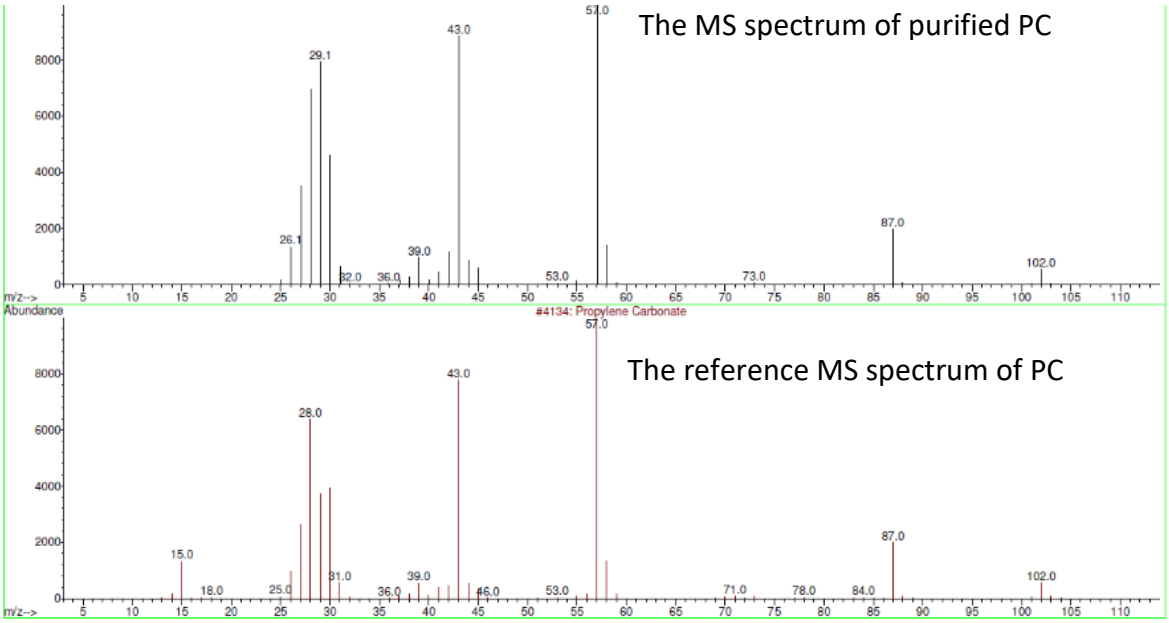


Figure S68. GC-MS spectrum of the purified propylene carbonate.