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Supporting information

Aminocyclopropenium as a novel hydrogen bonding organocatalyst for cycloaddition of carbon disulfide and epoxide to prepare cyclic dithiocarbonate

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General Information

All reactions were performed under an argon or nitrogen atmosphere unless otherwise stated. Commercially available reagents, unless otherwise noted, were utilized directly as provided. Dry solvents were distilled according to standard laboratory methods before usage. All other solvents were used without further purification. Thin-layer chromatography (TLC) analysis was carried out on 0.2 mm silica gel plates (HSGF 254) using a short-wave UV light for visualization. Flash column chromatography was performed with silica gel (200−300 mesh).

NMR spectra were recorded at room temperature on a Bruker AVANCE 400 spectrometer in deuterated solvents as noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to a residual solvent resonance as the internal standard (^{1}H δ 7.26 for $CDCl_3$, δ 2.50 for DMSO-d_6; 13C δ 77.16 for $CDCl_3$, δ 39.52 for DMSO-d_6). NMR peak multiplicities are abbreviated as follows: brs = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 6520 Q-TOF mass spectrometer using electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. Melting points were determined on a capillary melting point apparatus (Shanghai Precision & Scientific Instrument Co., LTD) in degrees Celsius (°C).

Synthesis of Catalysts

Tris(dimethylamino)cyclopropenium Chloride **(C1)** [1]

N,N-Dimethyltrimethylsilylamine (10 mL, 64 mmol, 8 equiv.) was dissolved in dichloromethane (50 mL) and cooled to 0 °C. 1,1,2,2,3-pentachlorocyclopropane (1 mL, 8 mmol, 1 equiv.) was added dropwise, and the solution was allowed to warm to ambient temperature. After stirring overnight, the solution was removed via rotary evaporation. The residue was dried under vacuum at 60 °C for 12 h and gave the product as a faint yellow solid.

Tris(diethylamino)cyclopropenium Chloride **(C2·Cl)** [2]

Diethylamine (6.6 mL, 64 mmol, 8 equiv.) was dissolved in dichloromethane (50 mL) and cooled to 0 °C. 1,1,2,2,3-pentachlorocyclopropane (1 mL, 8 mmol, 1 equiv.) was added dropwise, and the solution was allowed to warm to ambient temperature. The reaction was stirred for 24 h. Then the mixture was washed with 1 M HCl (20 mL × 3) and saturated brine (20 mL × 3). The organic layer was combined and dried with anhydrous Na_2SO_4 overnight. The filtrate was concentrated under vacuum

to give catalyst **C2**.

Tris(diethylamino)cyclopropenium Iodide **(C2·I)** [3]

The tris(diethylamino)cyclopropenium Chloride **(C2·Cl)** (0.288 g, 1 mmol, 1 equiv.) was dissolved in acetone (20 mL). Sodium iodide (0.3 g, 2 mmol, 2 equiv.) was added slowly into the solution, a white precipitate was rapidly generated. The mixture was stirred for 2 h. The result suspension was filtered and dried under vacuum. The crude product was dissolved in dichloromethane. The excess sodium iodide was removed by filtration and the filtrate was concentrated under vacuum to give catalyst **C2·I** as a brown solid.

Tris(piperidino)cyclopropenium chloride **(C3)** [2]

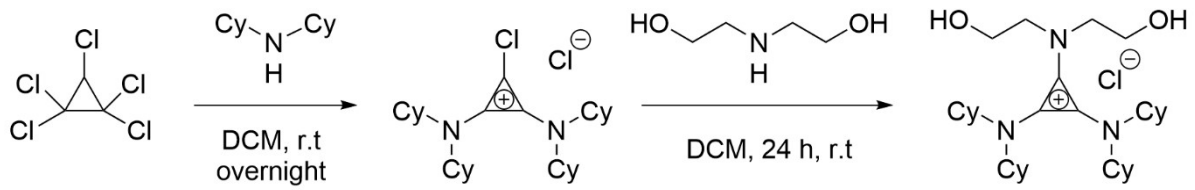
Piperidine (5.86 mL, 64 mmol, 8 equiv.) was dissolved in 50 mL of dichloromethane and cooled to 0 °C. 1,1,2,2,3-pentachlorocyclopropane (1 mL, 8 mmol, 1 equiv.) was added dropwise, and the solution was allowed to warm to ambient temperature. The reaction was stirred for 24 h. Then the mixture was washed with 1 M HCl (20 mL × 3) and saturated brine (20 mL × 3). The organic layer was combined and dried with anhydrous Na_2SO_4 overnight. The filtrate was concentrated under vacuum to give catalyst **C3**.

N-trimethylsilylaniline [4,5]

Argon airflow was employed to protect all operations progressing under the standard Schlenk techniques. Aniline (0.45 mL, 5 mmol, 2.5 equiv.) was mixed with chlorotrimethylsilane (0.25 mL, 2 mmol, 1 equiv.) in 20.0 mL of dry benzene at a reflux for 1 h. Aniline hydrochloride was removed from this system via filtration. The filtrate was dried using a rotary evaporator to obtain *N*-trimethylsilylaniline as a yellow oil.

Tris(phenylamino)cyclopropenium Chloride **(C4)** [1]

Argon airflow was employed to protect all operations progressing under the standard Schlenk techniques. Freshly obtained *N*-trimethylsilylaniline (4 equiv.) was added to 1,1,2,2,3-pentachlorocyclopropane (1 equiv.) in dry dichloromethane (50 mL) and stirred for 6 h. A cloudy white precipitate formed gradually. The obtained white solid was separated from dichloromethane. The remaining white solid was recrystallized from methanol to give target catalyst **C4**.



BACCy **C5·Cl**

1-Chloro-2,3-bis(dicyclohexylamino)cyclopropenium Chloride **(BACCy)** [2]

Dicyclohexylamine (9.54 mL, 48 mmol, 6 equiv.) was dissolved in dichloromethane (250 mL) and cooled to 0 °C. 1,1,2,2,3-pentachlorocyclopropane (1 mL, 8 mmol, 1 equiv.) was added dropwise, and the solution was allowed to warm to ambient temperature. The reaction was stirred overnight. Then the mixture was washed with concd. HCl (20 mL × 3) and saturated brine (50 mL × 3). The organic layer was combined and dried with anhydrous Na_2SO_4 overnight. The filtrate was concentrated under vacuum. The crude was triturated with hot EtOAc and collected for three times via filtration to give **BACCy** as an off-white solid.

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium Chloride **(C5·Cl)** [6]

Triethylamine (2.09 mL, 15 mmol, 3 equiv.) and diethanolamine (0.96 mL, 10 mmol, 2 equiv.) in chloroform (20 mL) were added to a solution of **BACCy** (2.34 g, 5 mmol, 1 equiv.) in chloroform (80 mL) and the reaction mixture was left to stir at room temperature overnight. The solution was then washed with brine (3 × 10 mL) and dried with anhydrous Na_2SO_4 overnight. The filtrate was concentrated under vacuum. The crude was triturated with hot EtOAc (60 mL) and collected via filtration, repeat the above steps three times to afford catalyst **C5·Cl** as off-white solid.

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium Bromide **(C5·Br)** [1]

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium chloride **(C5·Cl)** (0.536 g, 1 mmol, 1 equiv.) was stirred with 5 mL of HBr (48% w/w in water). The product was extracted with dichloromethane and washed again with HBr (48% w/w in water). It was then washed with deionized water (3 × 5 mL) until the pH was neutral and dried in vacuo to yield **C5·Br** as a dark brown solid.

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium Iodide **(C5·I)** [2]

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium chloride **(C5·Cl)** (0.536 g, 1 mmol, 1 equiv.) was dissolved in acetone (20 mL). Sodium iodide (0.3 g, 2 mmol, 2 equiv.) was added slowly into the solution, a white precipitate was rapidly generated. The mixture was stirred for 2 h. The result suspension was filtered and dried under vacuum. The crude product was dissolved in

dichloromethane. The excess sodium iodide was removed by filtration and the filtrate was concentrated under vacuum to give catalyst **C5·I** as a dark brown solid.

1-Morpholino-2,3-bis(dicyclohexylamino)cyclopropenium Chloride **(C6)** [3]

Triethylamine (2.09 mL, 15 mmol, 3 equiv.) and morpholine (0.88 mL, 10 mmol, 2 equiv.) in chloroform (20 mL) were added to a solution of **BACCy** (2.34 g, 5 mmol, 1 equiv.) in chloroform (80 mL) and the reaction mixture was left to stir at room temperature overnight. The solution was then washed with brine (3 × 10 mL) and dried with anhydrous Na_2SO_4 overnight. The filtrate was concentrated under vacuum. The crude was triturated with hot EtOAc (60 mL) and collected via filtration, repeat the above steps three times to afford catalyst **C6** as faint yellow solid.

1-Phenyl-1-ethanol-2,3-bis(dicyclohexylamino)cyclopropenium Chloride **(C7)** [3]

Triethylamine (2.09 mL, 15 mmol, 3 equiv.) and 2-(phenylamino)ethan-1-ol (1.25 mL, 10 mmol, 2 equiv.) in chloroform (20 mL) were added to a solution of **BACCy** (2.34 g, 5 mmol, 1 equiv.) in chloroform (80 mL) and the reaction mixture was left to stir at room temperature overnight. The solution was then washed with brine (3 × 10 mL) and dried with anhydrous Na_2SO_4 overnight. The filtrate was concentrated under vacuum. The crude was triturated with hot EtOAc (60 mL) and collected via filtration, repeat the above steps three times to afford catalyst **C7** as faint yellow solid.

2-Hydroxy-N-(2-hydroxyethyl)-N,N-dimethylethan-1-aminium iodide (**C8**) [7]

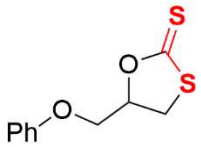
N-Methyldiethanolamine (0.57 mL, 5 mmol, 1 equiv.) was treated with iodomethane (2.49 mL, 40 mmol, 8 equiv.) in tetrahydrofuran (20 mL). The reaction was stirred at room temperature overnight. The reaction solution was rotary evaporated to remove most of the solvent and then dried overnight under vacuum to obtain catalyst **C8** as a colorless oil.

General Procedure for the Cycloaddition Reaction of Carbon Sulfide and Epoxides

All operations were performed using standard Schlenk techniques with a nitrogen atmosphere to reduce exposure to water and oxygen. A flame-dried 10 mL Schlenk tube containing a magnetic stirring bar was charged with the carbon sulfide (0.14 mL, 2.4 mmol, 1.2 equiv.), epoxide **1** (2 mmol, 1 equiv.), 1-diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium iodide (**C5·I**) (63 mg, 0.1 mmol, 0.05 equiv.) under an argon atmosphere. The reaction mixture was stirred at room temperature for 6 h. After that, the mixture was purified by silica gel flash column chromatography (PE:EA = 5:1) to give the corresponding products **2a**–**2j**.

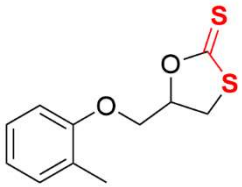
Characterization Data for Products

5-(phenoxymethyl)-1,3-oxathiolane-2-thione **(2a)**



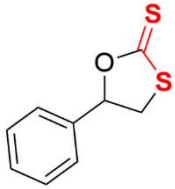
Purification by flash column chromatography furnished **2a** (82%, 95% conv. for 24h) as a yellow oil. R_f = 0.4 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 2H), 7.06 – 6.99 (m, 1H), 6.99 – 6.89 (m, 2H), 5.43 (tt, *J* = 7.7, 4.9 Hz, 1H), 4.30 (qd, *J* = 10.4, 5.0 Hz, 2H), 3.85 – 3.68 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 211.55, 157.77, 129.64, 121.94, 114.62, 87.98, 66.39, 36.29. **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{10}H_{10}O_2S_2$ 226.0117, found 226.0157. The spectral data were consistent with values reported in the literature[8].

5-((o-tolyloxy)methyl)-1,3-oxathiolane-2-thione **(2b)**



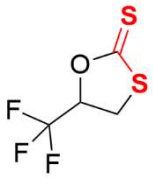
Purification by flash column chromatography furnished **2b** (88% conv.) as a colorless oil. R_f = 0.3 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 7.2 Hz, 2H), 6.93 (td, *J* = 7.4, 1.1 Hz, 1H), 6.84 – 6.78 (m, 1H), 5.48 (tdd, *J* = 7.5, 5.0, 4.1 Hz, 1H), 4.36 – 4.26 (m, 2H), 3.80 (dt, *J* = 7.5, 3.8 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 211.71, 155.92 (d, *J* = 5.4 Hz), 131.07 (d, *J* = 2.5 Hz), 127.00, 121.65, 111.07, 88.10, 66.85, 36.26, 16.22. **HRMS** (ESI-ToF) *m/z* $[M+Na]^+$ calcd for $C_{11}H_{12}O_2S_2Na$ 263.0171, found 263.0174. The spectral data were consistent with values reported in the literature[8].

5-phenyl-1,3-oxathiolane-2-thione **(2c)**



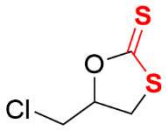
Purification by flash column chromatography furnished **2c** (92% conv.) as a yellow solid. R_f = 0.5 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H), 7.47 – 7.29 (m, 3H), 5.64 (dd, *J* = 10.4, 5.7 Hz, 1H), 4.13 – 3.99 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 134.95, 129.05, 127.32 (d, *J* = 6.2 Hz), 63.99, 49.52. **HRMS** (ESI-ToF) *m/z* $[M+NH_4]^+$ calcd for $C_9H_{12}NOS_2$ 214.0355, found 214.0346. The spectral data were consistent with values reported in the literature[8].

5-(trifluoromethyl)-1,3-oxathiolane-2-thione **(2d)**



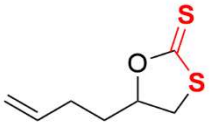
Purification by flash column chromatography furnished **2d** (94% conv.) as a faint yellow liquid. R_f = 0.2 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.34 (tq, *J* = 7.8, 5.8 Hz, 1H), 3.89 – 3.78 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 207.98, 123.56, 84.36, 33.50 (q, *J* = 1.9 Hz). **HRMS** (ESI-ToF) *m/z* $[M+H]^+$ calcd for $C_4H_4OS_2F_3$ 188.9650, found 188.9654.

5-(chloromethyl)-1,3-oxathiolane-2-thione **(2e)**



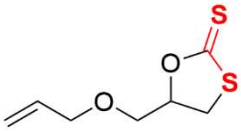
Purification by flash column chromatography furnished **2e** (86% yield) as a fiant yellow solid. R_f = 0.4 (PE : EA = 5 : 1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.38 – 5.26 (m, 1H), 3.85 (dd, *J* = 5.8, 3.1 Hz, 2H), 3.77 – 3.68 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 210.60, 88.24, 42.65, 37.05. **HRMS** (ESI-ToF) *m/z* $[M+NH_4]^+$ calcd for $C_4H_9NClOS_2$ 185.9809, found 185.9756. The spectral data were consistent with values reported in the literature[9].

5-(but-3-en-1-yl)-1,3-oxathiolane-2-thione **(2f)**



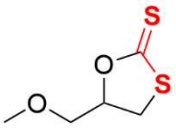
Purification by flash column chromatography furnished **2f** (85% conv.) as a fiant yellow oil. R_f = 0.3 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.92 – 5.71 (m, 1H), 5.16 – 4.97 (m, 3H), 3.59 (dd, *J* = 11.0, 6.5 Hz, 1H), 3.44 – 3.35 (m, 1H), 2.28 (dddt, *J* = 14.7, 9.4, 8.0, 4.1 Hz, 2H), 2.14 (dtd, *J* = 14.2, 7.8, 6.3 Hz, 1H), 1.90 (dddd, *J* = 14.1, 8.7, 6.7, 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 211.96, 136.22, 116.43, 90.95, 39.27, 33.33, 29.48. **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_7H_{10}OS_2$ 174.0168, found 174.0101. The spectral data were consistent with values reported in the literature[8].

5-((allyloxy)methyl)-1,3-oxathiolane-2-thione **(2g)**



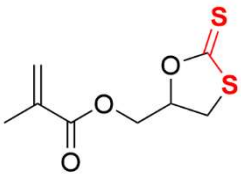
Purification by flash column chromatography furnished **2g** (92% conv.) as a fiant yellow liquid. R_f = 0.4 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.88 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.34 – 5.16 (m, 3H), 4.07 (dt, *J* = 5.9, 1.5 Hz, 2H), 3.83 – 3.72 (m, 2H), 3.69 (dd, *J* = 11.1, 8.3 Hz, 1H), 3.61 (dd, *J* = 11.1, 7.2 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 211.95, 133.82, 118.13, 89.21, 72.76, 68.57, 36.25. **HRMS** (ESI-ToF) $_{m/z}$ $[M+H]^+$ calcd for $C_7H_{11}O_2S_2$ 191.0195, found 191.0202. The spectral data were consistent with values reported in the literature[10].

5-(methoxymethyl)-1,3-oxathiolane-2-thione **(2h)**



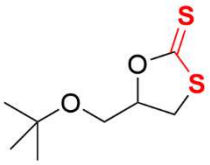
Purification by flash column chromatography furnished **2h** (75% conv.) as a fiant yellow oil. R_f = 0.3 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.21 (ddt, J = 8.5, 7.2, 4.7 Hz, 1H), 3.76 (dd, J = 10.9, 4.8 Hz, 1H), 3.71 – 3.63 (m, 2H), 3.58 (dd, J = 11.1, 7.2 Hz, 1H), 3.42 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 211.62, 88.87, 70.82, 59.37, 35.73. **HRMS** (ESI-ToF) *m/z* $[M+H]^+$ calcd for $C_5H_9O_2S_2$ 165.0038, found 165.0060.

(2-thioxo-1,3-oxathiolan-5-yl)methyl 2-oxopropanoate **(2i)**



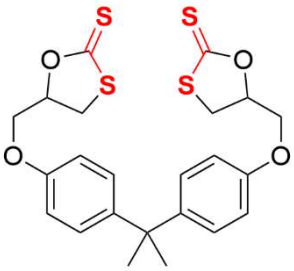
Purification by flash column chromatography furnished **2i** (90% conv.) as a fiant yellow liquid. R_f = 0.3 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.17 (q, *J* = 1.2 Hz, 1H), 5.65 (h, *J* = 1.9 Hz, 1H), 5.38 (tt, *J* = 7.7, 4.5 Hz, 1H), 4.49 (qd, *J* = 12.4, 4.5 Hz, 2H), 3.71 (dd, *J* = 11.2, 7.4 Hz, 1H), 3.57 (dd, *J* = 11.2, 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 211.12, 166.77, 135.32, 127.33, 87.60, 63.41, 36.10, 18.30. **HRMS** (ESI-ToF) *m/z* $[M+Na]^+$ calcd for $C_8H_{10}O_3S_2Na$ 240.9964, found 240.9971. The spectral data were consistent with values reported in the literature[11].

5-(tert-butoxymethyl)-1,3-oxathiolane-2-thione **(2j)**



Purification by flash column chromatography furnished **2j** (82% conv.) as a fiant yellow oil. R_f = 0.4 (PE:EA = 10:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.18 (tt, *J* = 7.4, 5.3 Hz, 1H), 3.68 (d, *J* = 5.3 Hz, 2H), 3.63 (t, *J* = 7.6 Hz, 2H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 212.41, 89.71, 74.20, 60.94, 36.57, 27.45. **HRMS** (ESI-ToF) *m/z* $[M+Na]^+$ calcd for $C_8H_{14}O_2S_2Na$ 229.0327, found 229.0386. The spectral data were consistent with values reported in the literature[11].

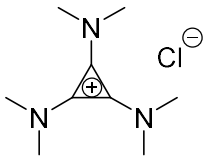
5,5'-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(1,3-oxathiolane-2-thione) **(2k)**



Purification by flash column chromatography furnished **2k** (85% conv.) as a yellow solid. R_f = 0.3 (PE:EA = 2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 – 7.11 (m, 4H), 6.86 – 6.78 (m, 4H), 5.48 – 5.37 (m, 2H), 4.35 – 4.23 (m, 4H), 3.76 (qd, *J* = 11.2, 7.5 Hz, 4H), 1.64 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 211.31, 155.66, 144.31, 127.97, 114.04, 87.78, 66.35, 41.86, 36.36, 30.99. The spectral data were consistent with values reported in the literature[12].

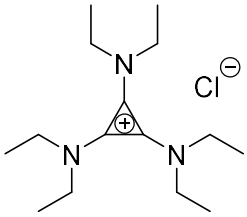
Characterization Data for Catalysts

Tris(dimethylamino)cyclopropenium chloride **(C1)**



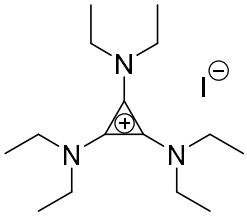
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.19 (s, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 117.81, 42.53. **HRMS** (ESI-TOF) *m/z* $[M]^+$ calcd for $C_9H_{18}N_3$ 168.1495, found 168.1434. The spectral data were consistent with values reported in the literature[1].

Tris(diethylamino)cyclopropenium chloride **(C2·Cl)**



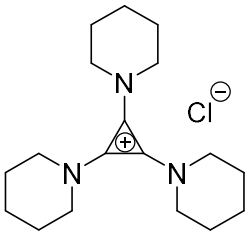
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.41 (q, *J* = 7.2 Hz, 12H), 1.25 (t, *J* = 7.2 Hz, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 115.34, 46.36, 13.50. **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{15}H_{30}N_3$ 252.2434, found 252.2432. The spectral data were consistent with values reported in the literature[1].

Tris(diethylamino)cyclopropenium iodide **(C2·Cl)**



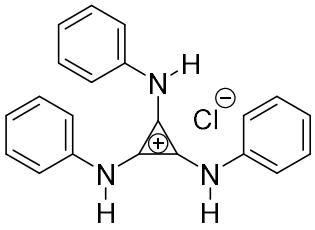
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.39 (q, *J* = 7.2 Hz, 12H), 1.25 (t, *J* = 7.2 Hz, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 115.40, 46.42, 13.57. **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{15}H_{30}N_3$ 252.2403, found 252.2434. The spectral data were consistent with values reported in the literature[1].

Tris(piperidine)cyclopropenium chloride **(C3)**



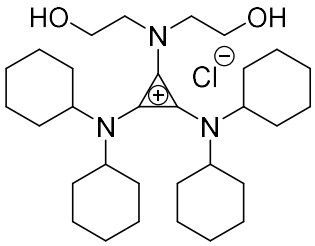
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.38 (q, *J* = 7.3 Hz, 12H), 1.24 (t, *J* = 7.2 Hz, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 116.07, 50.83, 24.30, 21.88. **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{18}H_{32}N_3$ 290.2591, found 290.2524. The spectral data were consistent with values reported in the literature[2].

Tris(phenylamino)cyclopropenium Chloride (**C4**)



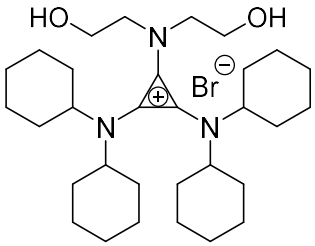
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.98 (s, 3H), 7.48 – 7.39 (m, 6H), 7.34 – 7.27 (m, 6H), 7.22 – 7.14 (m, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 139.28, 130.22, 124.48, 118.47, 113.32. **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{21}H_{18}N_3$ 312.1495, found 312.1497. The spectral data were consistent with values reported in the literature[1].

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium Chloride (**C5·Cl**)



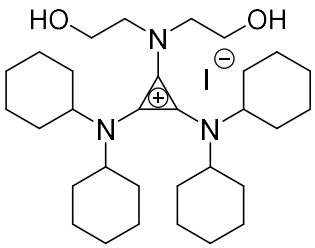
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.88 (t, J = 4.6 Hz, 4H), 3.65 (t, J = 4.8 Hz, 4H), 3.51 (tt, J = 12.4, 3.5 Hz, 4H), 1.91 – 1.81 (m, 16H), 1.71 – 1.63 (m, 4H), 1.57 (dt, J = 12.6, 6.1 Hz, 8H), 1.32 (dt, J = 16.5, 13.0 Hz, 8H), 1.12 (ddt, J = 16.6, 13.2, 6.6 Hz, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 122.15, 119.00, 60.83, 59.81, 55.41, 32.85, 28.70, 25.04. **HRMS** (ESI-ToF) *m/z* [M]+ calcd for $C_{31}H_{54}N_3O_2$ 500.4211, found 500.4212. The spectral data were consistent with values reported in the literature[6].

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium bromide (**C5·Br**)



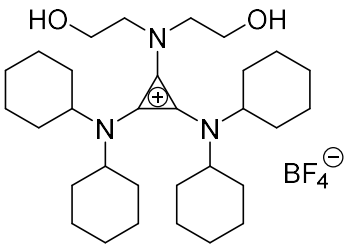
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.93 (s, 6H), 3.89 – 3.80 (m, 5H), 3.72 – 3.60 (m, 5H), 3.53 – 3.22 (m, 5H), 1.97 – 1.74 (m, 16H), 1.66 (d, *J* = 13.3 Hz, 4H), 1.53 (dtd, *J* = 37.2, 12.5, 8.9 Hz, 8H), 1.31 (qt, *J* = 13.1, 3.6 Hz, 9H), 1.24 – 1.05 (m, 4H). **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{31}H_{54}N_3O_2$ 500.4211, found 500.4212.

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium iodide (**C5·I**)



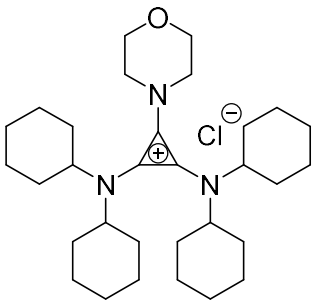
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.22 (t, *J* = 5.9 Hz, 2H), 3.87 (q, *J* = 4.2 Hz, 4H), 3.67 (t, *J* = 4.9 Hz, 4H), 3.48 (tt, *J* = 12.4, 3.7 Hz, 4H), 1.96 – 1.81 (m, 16H), 1.72 – 1.52 (m, 12H), 1.32 (qt, *J* = 13.2, 3.3 Hz, 8H), 1.13 (dddd, *J* = 16.5, 13.0, 8.2, 3.4 Hz, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 122.15, 119.00, 60.83, 59.81, 55.41, 32.85, 25.95, 25.04. **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{31}H_{54}N_3O_2$ 500.4211, found 500.4213.

1-Diethanolamino-2,3-bis(dicyclohexylamino)cyclopropenium tetrafluoroborate (**C5·BF$_4$**)



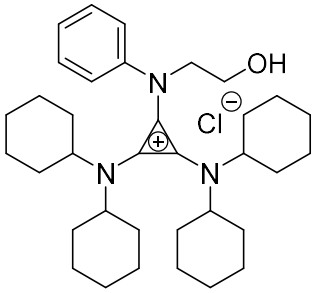
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.88 (t, *J* = 4.6 Hz, 4H), 3.65 (t, *J* = 4.8 Hz, 4H), 3.51 (tt, *J* = 12.4, 3.5 Hz, 4H), 1.94 – 1.77 (m, 16H), 1.66 (t, *J* = 10.9 Hz, 4H), 1.57 (dt, *J* = 12.7, 6.2 Hz, 8H), 1.40 – 1.26 (m, 8H), 1.11 (qt, *J* = 13.1, 3.4 Hz, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 122.06, 118.90, 60.74, 59.72, 55.31, 32.75, 25.85, 24.95. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -152.94.

1-Morpholino-2,3-bis(dicyclohexylamino)cyclopropenium chloride (**C6**)



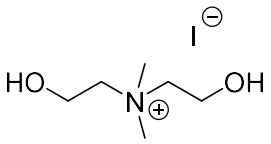
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.85 (dd, *J* = 6.0, 3.5 Hz, 4H), 3.65 (dd, *J* = 5.9, 3.5 Hz, 4H), 3.37 (tt, *J* = 12.4, 3.5 Hz, 4H), 1.95 – 1.88 (m, 16H), 1.72 (d, *J* = 12.9 Hz, 4H), 1.60 (qd, *J* = 12.1, 3.2 Hz, 8H), 1.41 – 1.21 (m, 8H), 1.11 (qt, *J* = 13.4, 3.2 Hz, 4H). **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{31}H_{52}N_3O$ 482.4105, found 482.4107.

1-Phenyl-1-ethanol-2,3-bis(dicyclohexylamino)cyclopropenium chloride (**C7**)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 4.01 (t, *J* = 5.1 Hz, 2H), 3.89 (t, *J* = 5.1 Hz, 2H), 3.77 – 3.67 (m, 1H), 3.31 (ddt, *J* = 12.4, 7.4, 3.8 Hz, 4H), 1.81 (t, *J* = 15.5 Hz, 12H), 1.60 (d, *J* = 13.1 Hz, 4H), 1.44 (qd, *J* = 12.9, 3.6 Hz, 8H), 1.27 – 1.15 (m, 8H), 0.98 (qt, *J* = 13.4, 3.6 Hz, 4H). **HRMS** (ESI-ToF) *m/z* $[M]^+$ calcd for $C_{35}H_{54}N_3O$ 532.4261, found 532.4264.

2-Hydroxy-N-(2-hydroxyethyl)-N,N-dimethylethan-1-aminium iodide (**C8**)



product was yellow oil. R_f = 0.4 (DCM:MeOH = 10:1). **^{1}H NMR** (400 MHz, Deuterium Oxide) δ 4.09 (dq, J = 5.3, 2.6 Hz, 3H), 3.66 – 3.59 (m, 3H), 3.26 (s, 6H). **^{13}C NMR** (101 MHz, Deuterium Oxide) δ 66.33 – 66.15 (m), 55.44, 52.41 – 52.22 (m). The spectral data were consistent with values reported in the literature[7].

Analysis of the ^{1}H NMR spectra of crude product

The qNMR analysis summarized from previous work[13]. The crude mixture of cyclic dithiocarbonate products was sampled of W_m mg, and then the W_i mg of internal standard dodecane was added. Using 0.5 mL $CDCl_3$ to dissolve the mixture for ^{1}H NMR measurements. The integral values (I) of epoxides, cyclic dithiocarbonates and dodecane (0.8813 ppm) in ^{1}H NMR spectra were observed as I_e, I_c, and I_i. The molecular weights of cyclic dithiocarbonates are $M_{w,c}$, and dodecane is $M_{w,i}$ (170.34 g/mol). The numbers of proton generating the selected signals for integration of cyclic dithiocarbonates N_c is 1, and the numbers of proton generating the selected signals for integration of dodecane N_i are 6. The conversion (Conv.) and the selectivity (Selec.) were calculated from equation S1 (**eq. S1**) and equation S2 (**eq. S2**), respectively.

Herein, two examples of qNMR analysis of the substrate **1a** and the most effective substrate **1d** for benchmark reaction were given below. All experimental results in this work were measured according to this method.

$$Conversion\ (\%) = \frac{I_c}{I_c + I_e} \quad (\boldsymbol{eq.S1})$$

$$Selectivity\ (\%) = \frac{N_i \times W_i \times I_c \times M_{w,c}}{N_c \times M_{w,i} \times I_i \times W_m \times Conv.} \quad (\boldsymbol{eq.S2})$$

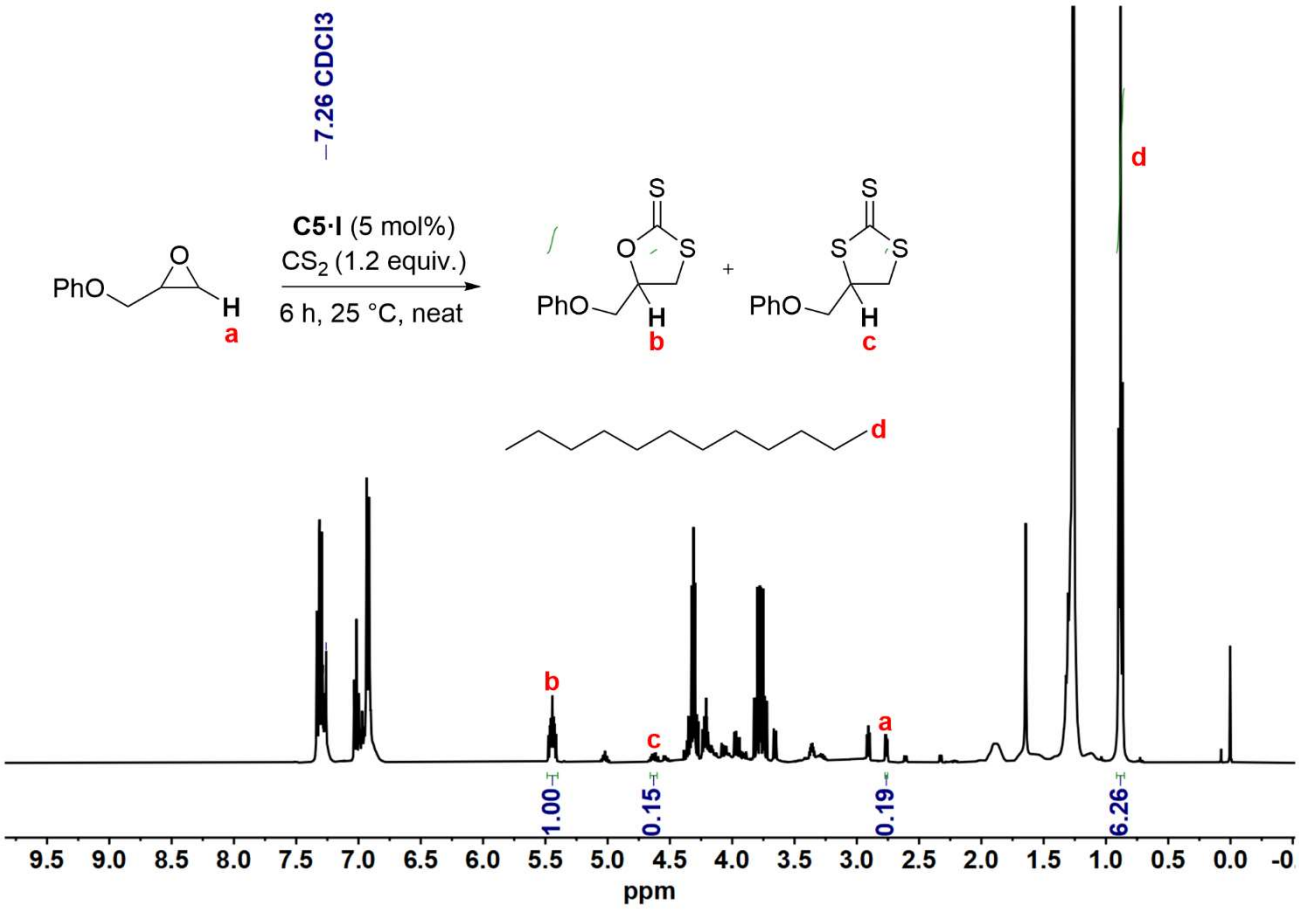


Figure S1. ^{1}**H NMR** analysis of the reaction mixture of phenyl glycidyl ether **1a**

1a (2 mmol, 1 equiv.), **C5·I** (5 mol%), CS_2 (0.14 mL, 2.4 mmol, 1.2 equiv.), 6 h, 15.1 mg crude mixture, 8.1 mg dodecane. Conversion was 84%; selectivity was 89%.

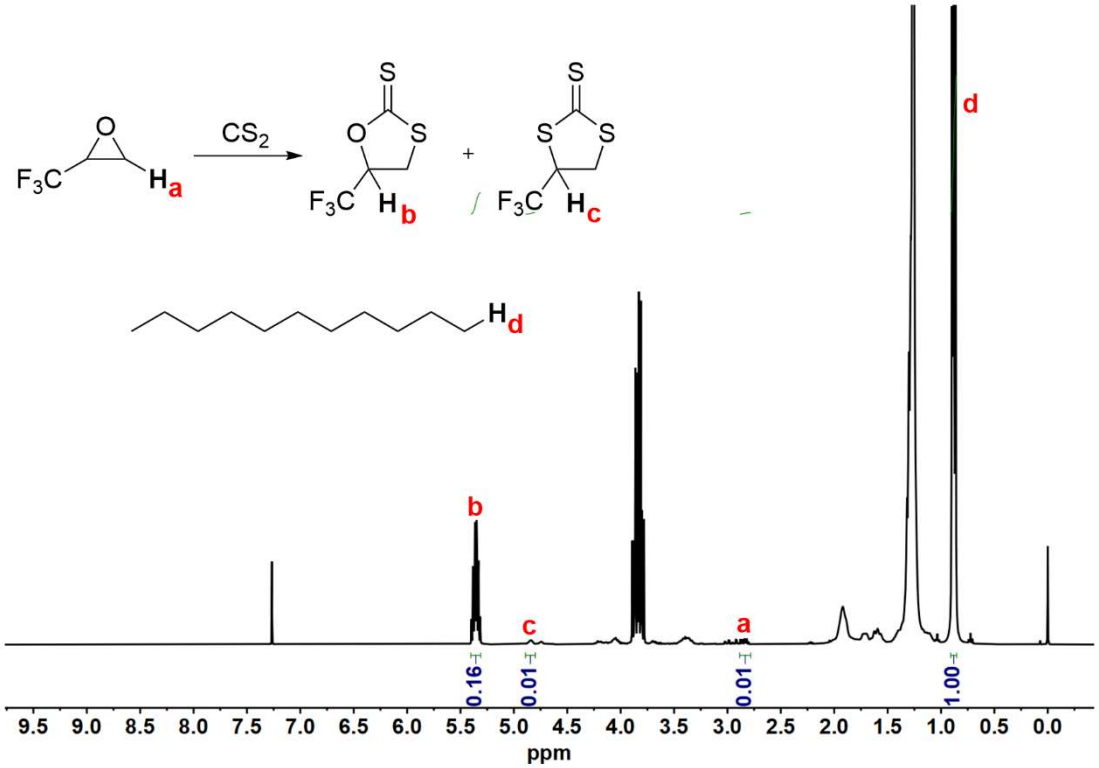
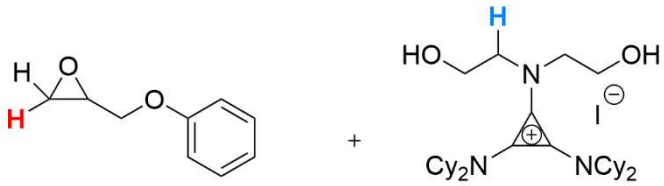


Figure S2. ^{1}**H NMR** analysis of the reaction mixture of 2-(trifluoromethyl)oxirane **1d**

1d (2 mmol, 1 equiv.), **C5·I** (5 mol%), CS_2 (0.14 mL, 2.4 mmol, 1.2 equiv.), 6 h, 27 mg crude mixture, 21.7 mg dodecane. Conversion was 94%; selectivity was 91%.

NMR titration experiments

Table S1. δ(C–**H**) of **PGE** and δ(C–**H**) of catalyst **C5·I** for Each Molar Ratio in $CDCl_3$



	PGE	C5·I			
GPE:C5·I	**PGE**	**C5·I**	$CDCl_3$	δ(C–**H**)	δ(C–**H**)
1:0	6.8μL (50 μmol)	–	600 μL	4.2363	–
1:0.2	6.8μL (50 μmol)	6.3 mg (10 μmol)	600 μL	4.2341	3.8993
1:0.4	6.8μL (50 μmol)	12.6 mg (20 μmol)	600 μL	4.2312	3.8829
1:0.6	6.8μL (50 μmol)	18.9 mg (30 μmol)	600 μL	4.2280	3.8747
1:0.8	6.8μL (50 μmol)	25.2 mg (40 μmol)	600 μL	4.2249	3.8616

1:1	6.8μL (50 μmol)	31.5 mg (50 μmol)	600 μL	4.2220	3.8529

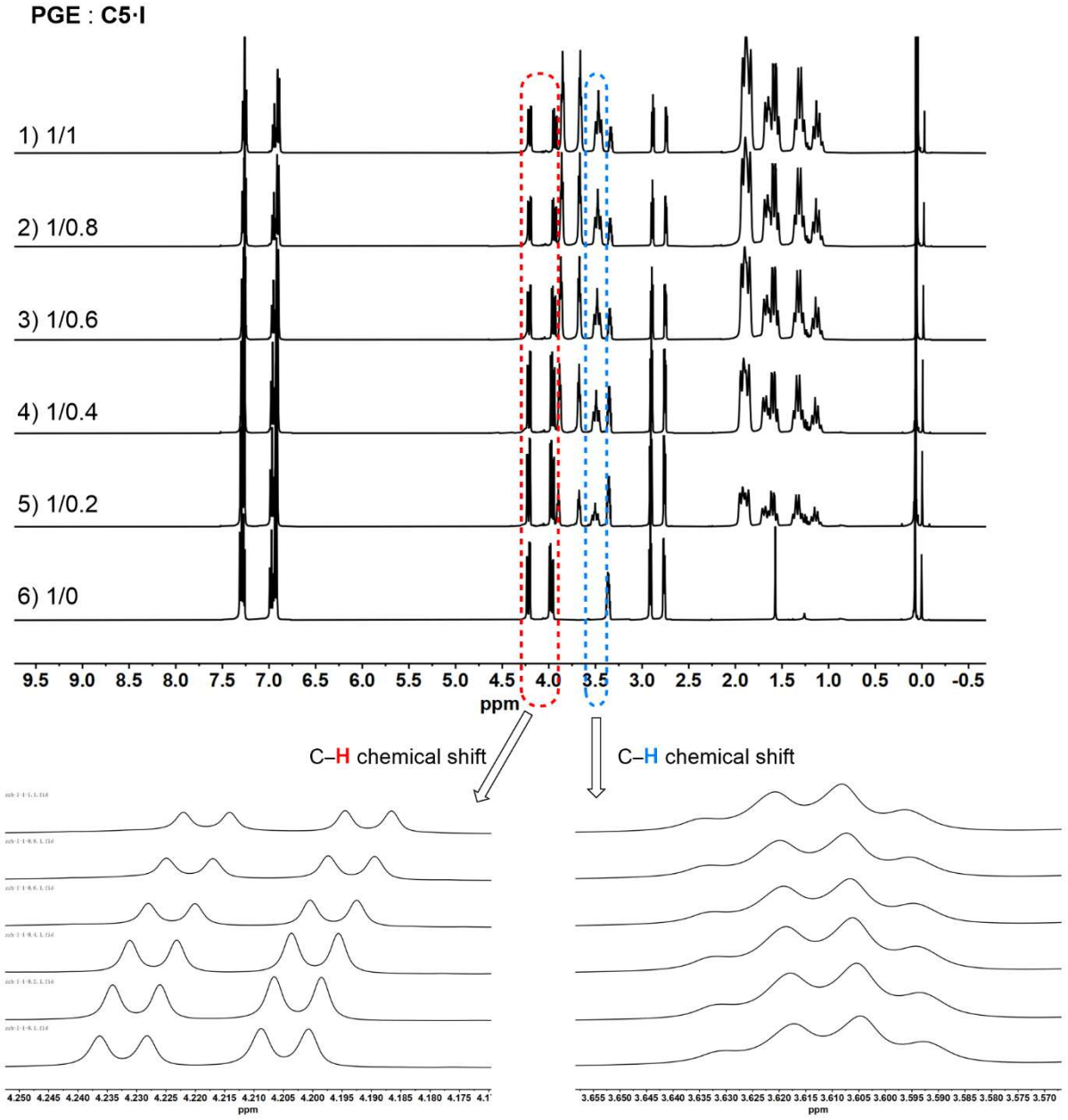
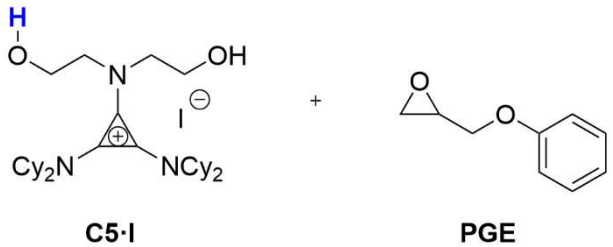


Figure S3. Full screen **^{1}H NMR** spectra of **PGE** with catalyst **C5·I** in $CDCl_3$

Table S2. δ(O–**H**) of **C5·I** for Each Molar Ratio in DMSO-d_6



C5·I + **PGE**

C5·I:PGE	C5·I	PGE	DMSO-d_6	δ(O–H)
1:0	32 mg (50 µmol)	-	600 µL	4.9688
1:0.2	32 mg (50 µmol)	1.36 µL (10 µmol)	600 µL	4.9697
1:0.4	32 mg (50 µmol)	2.72 µL (20 µmol)	600 µL	4.9703
1:0.6	32 mg (50 µmol)	4.10 µL (30 µmol)	600 µL	4.9720
1:0.8	32 mg (50 µmol)	5.44 µL (40 µmol)	600 µL	4.9727
1:1	32 mg (50 µmol)	6.80 µL (50 µmol)	600 µL	4.9734

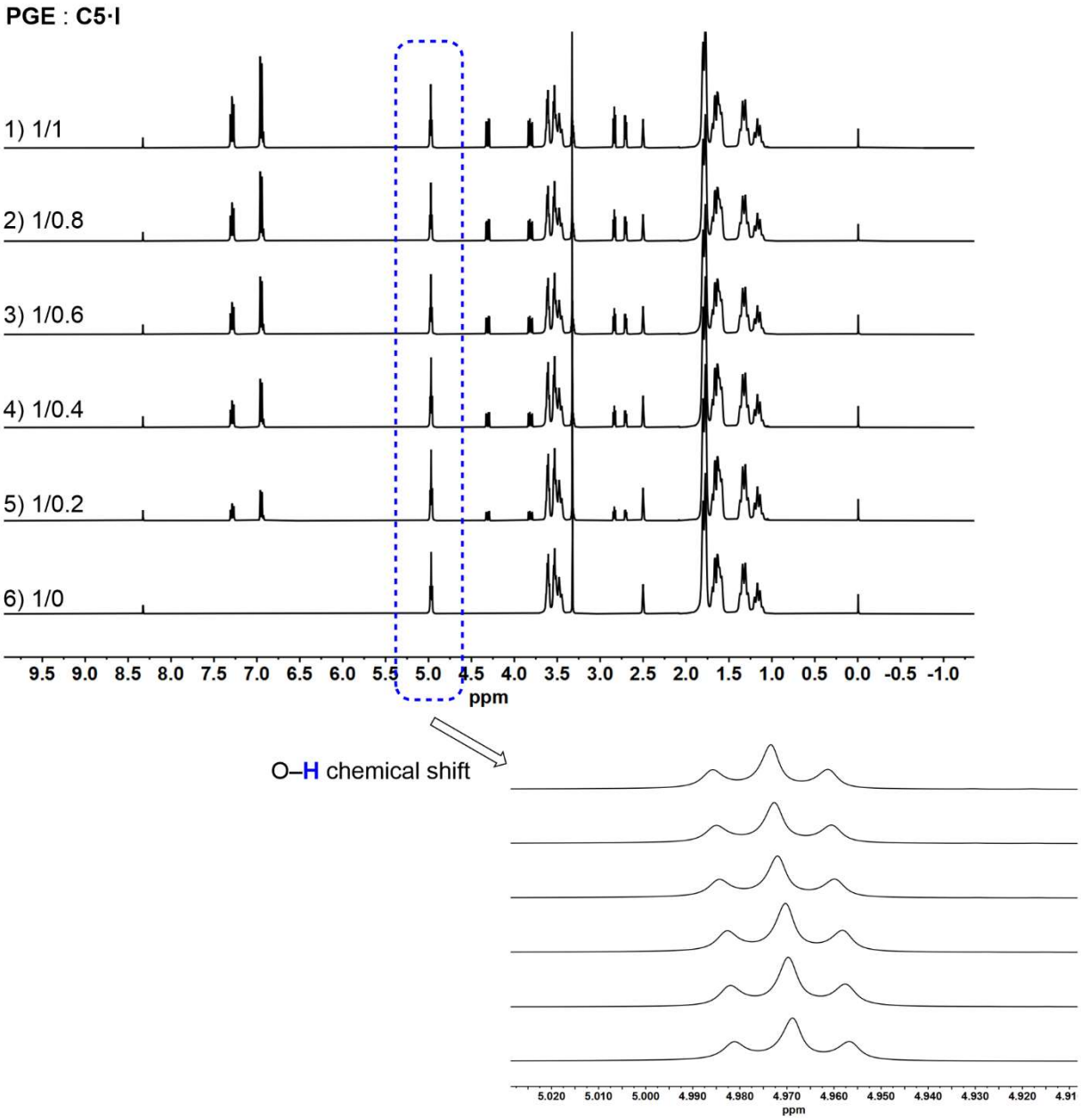


Figure S4. Full screen **^{1}H NMR** spectra of **GPE** with catalyst **C5·I** in DMSO-d_6

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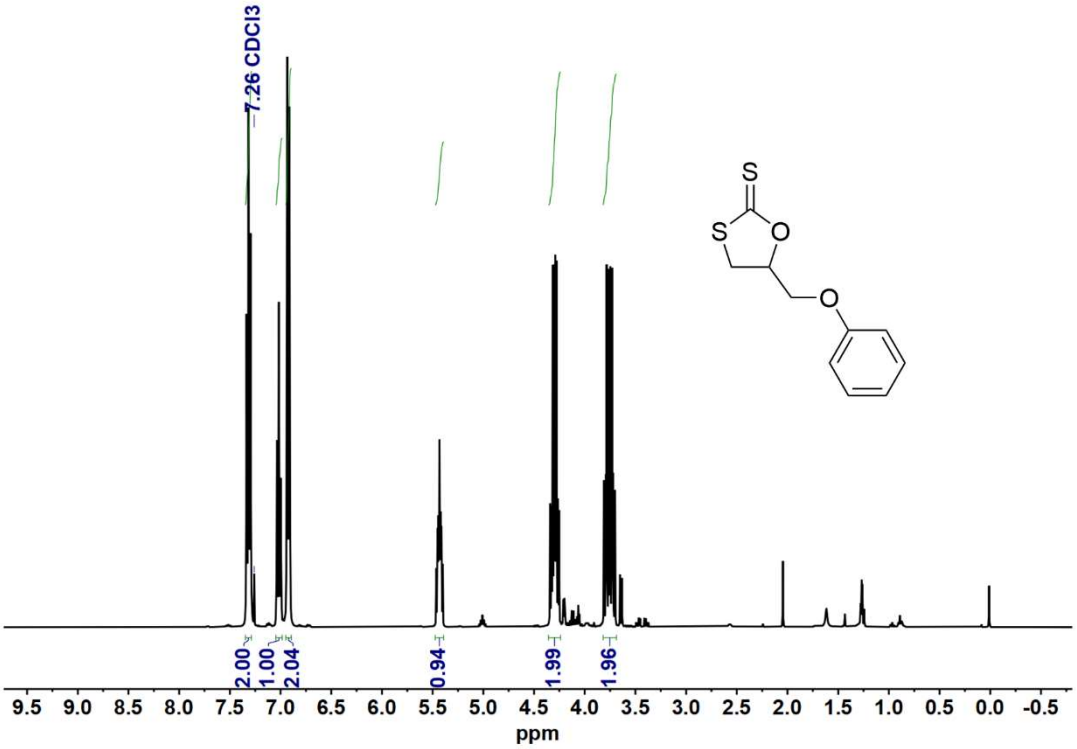
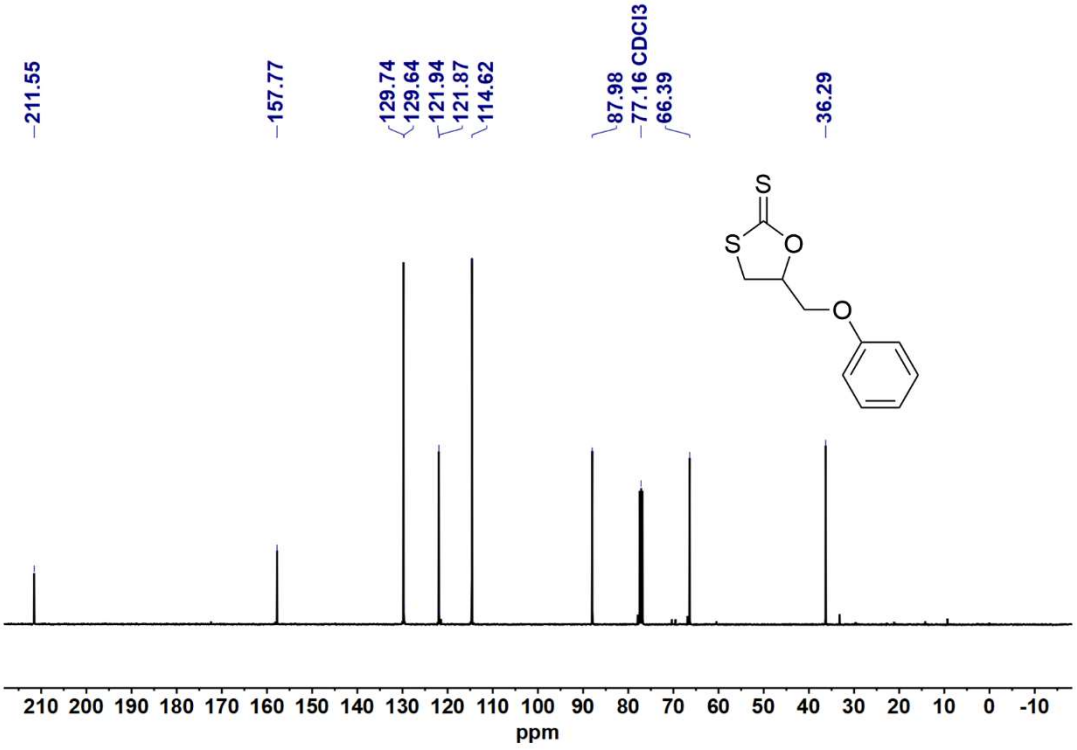
NMR Spectra of Compounds

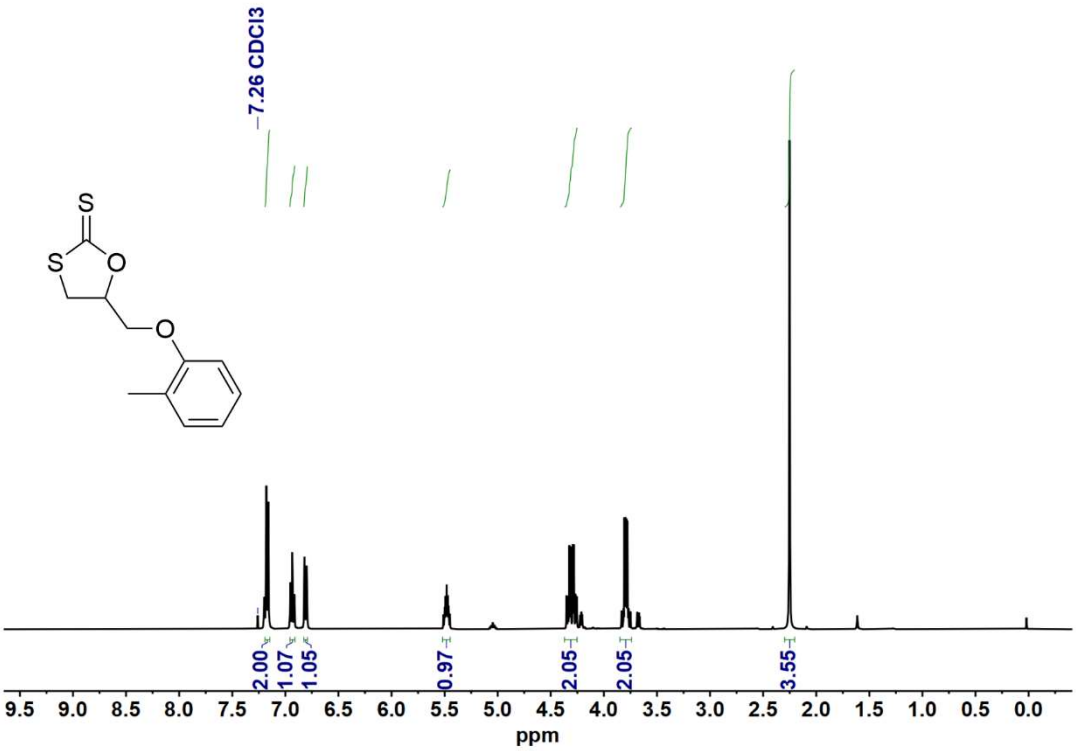
Copies of NMR spectra of cyclic dithiocarbonates



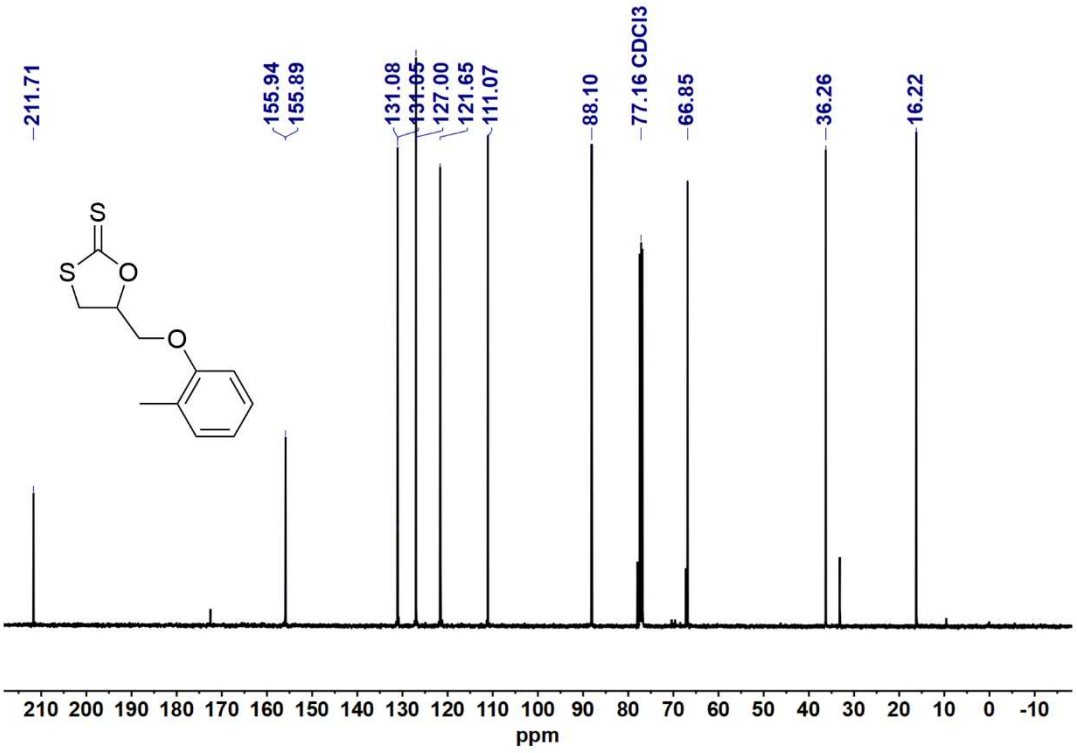
^{1}H NMR Spectrum of Compound **2a** (400 MHz, chloroform-*d*)



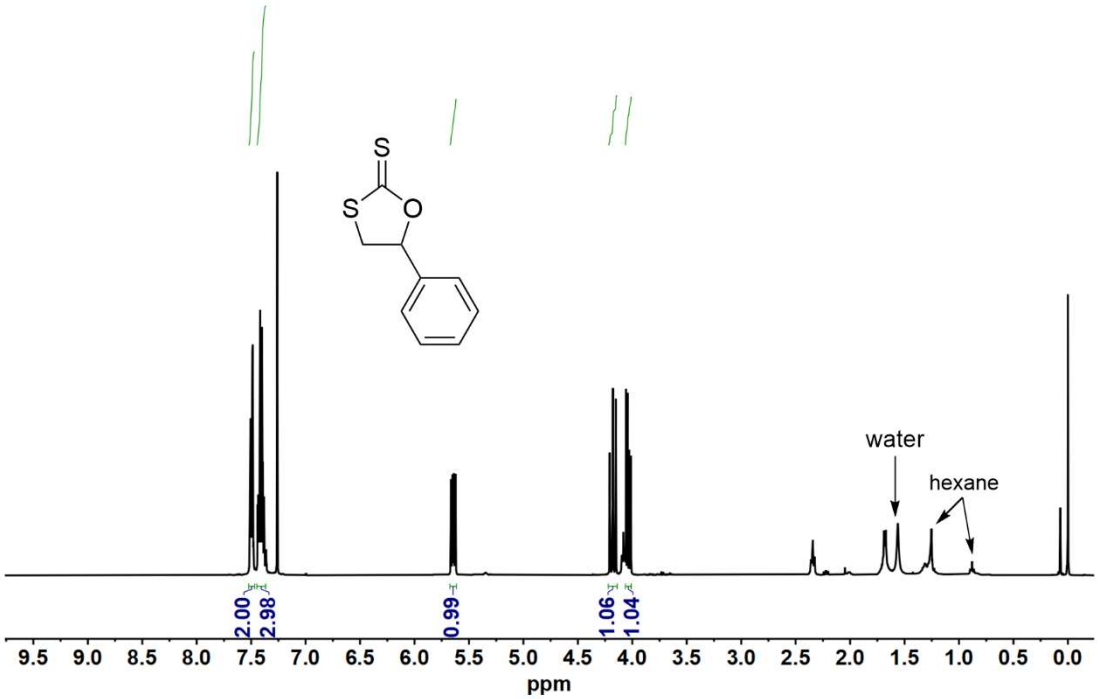
^{13}C NMR Spectrum of Compound **2a** (101 MHz, chloroform-*d*)



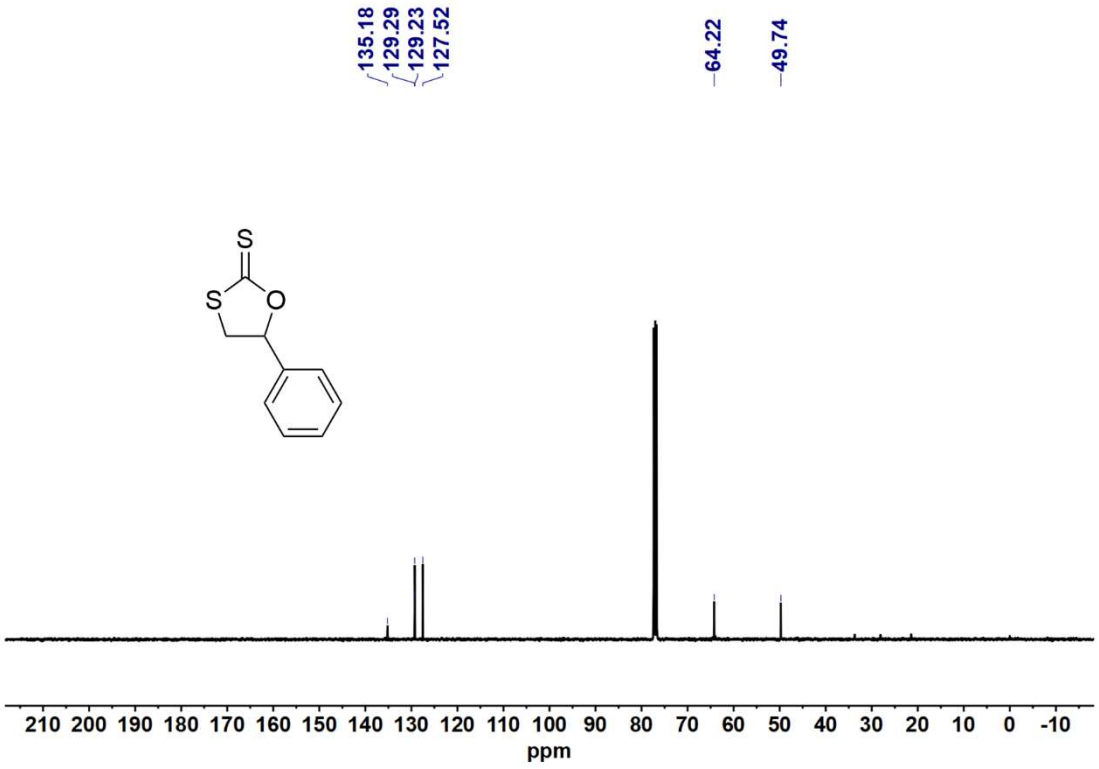
^{1}H NMR Spectrum of Compound **2b** (400 MHz, chloroform-*d*)



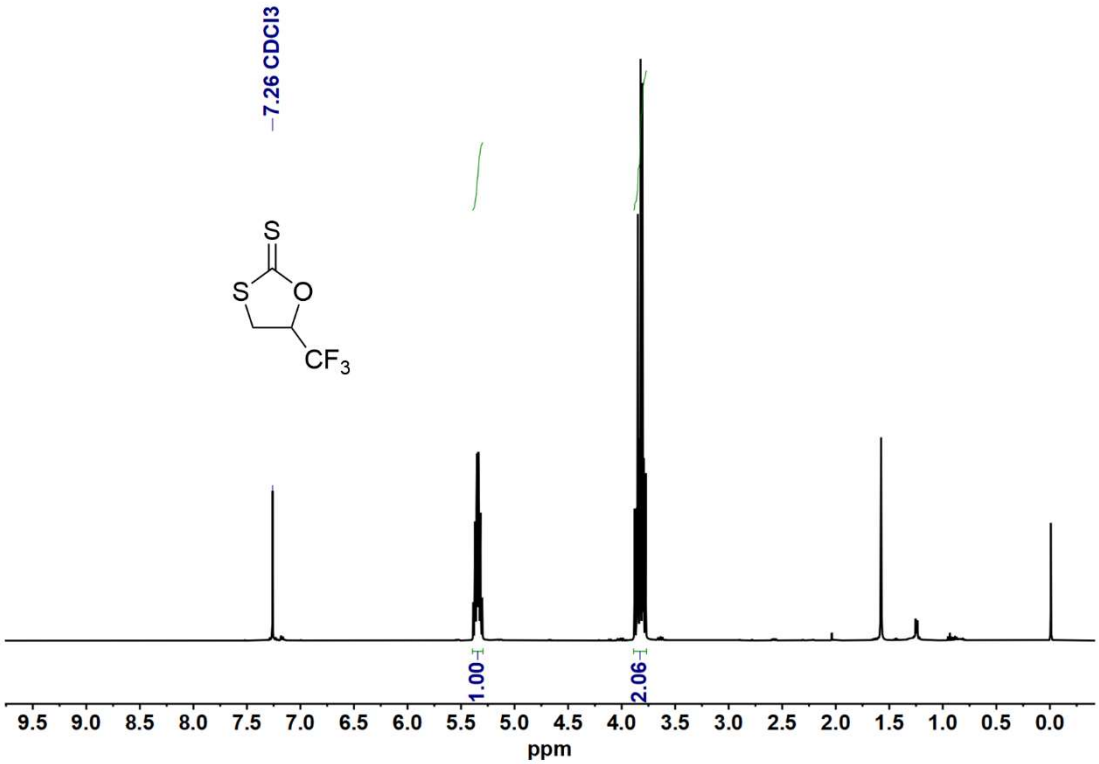
^{13}C NMR Spectrum of Compound **2b** (101 MHz, chloroform-*d*)



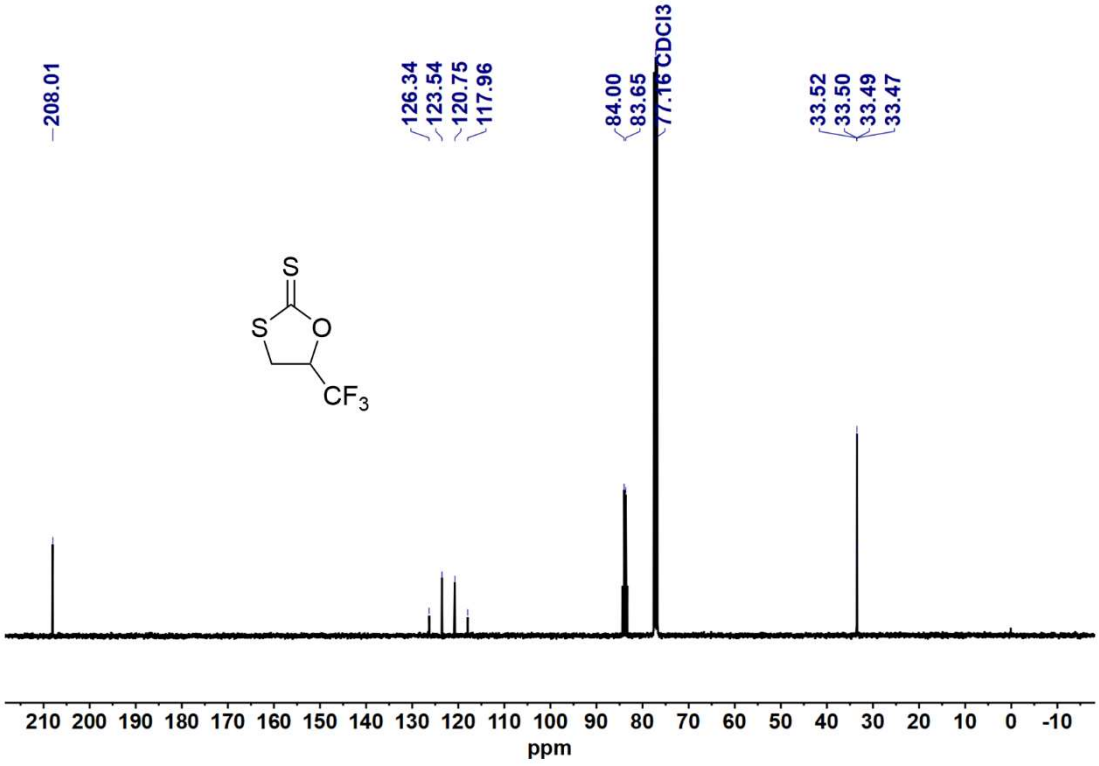
^{1}H NMR Spectrum of Compound **2c** (400 MHz, chloroform-*d*)



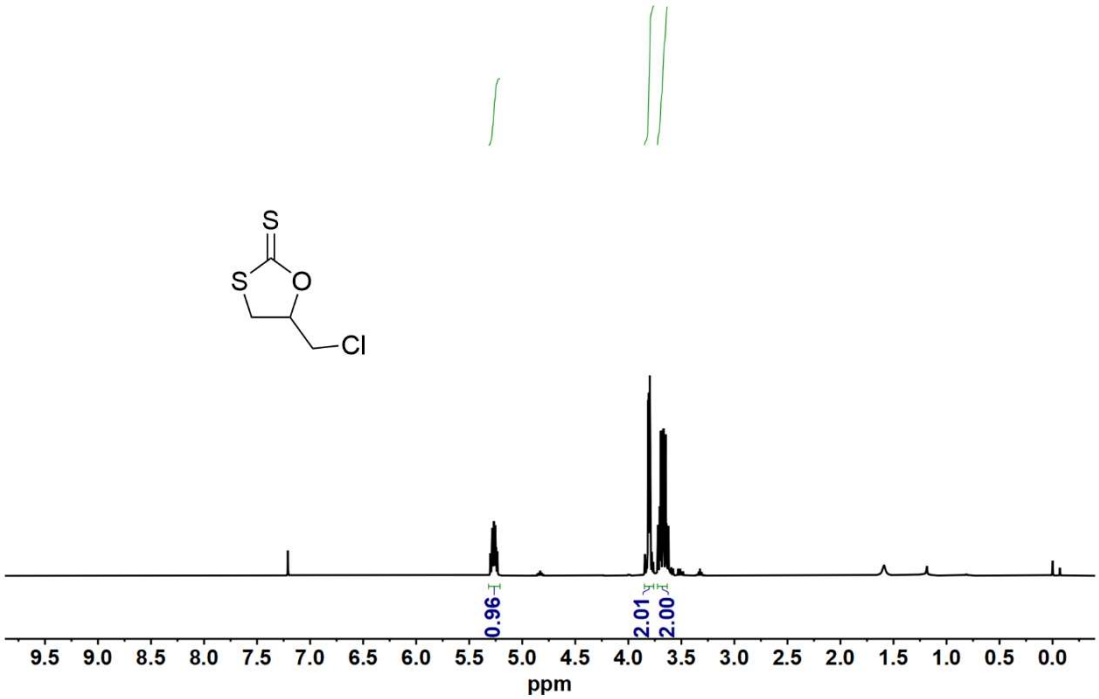
^{13}C NMR Spectrum of Compound **2c** (101 MHz, chloroform-*d*)



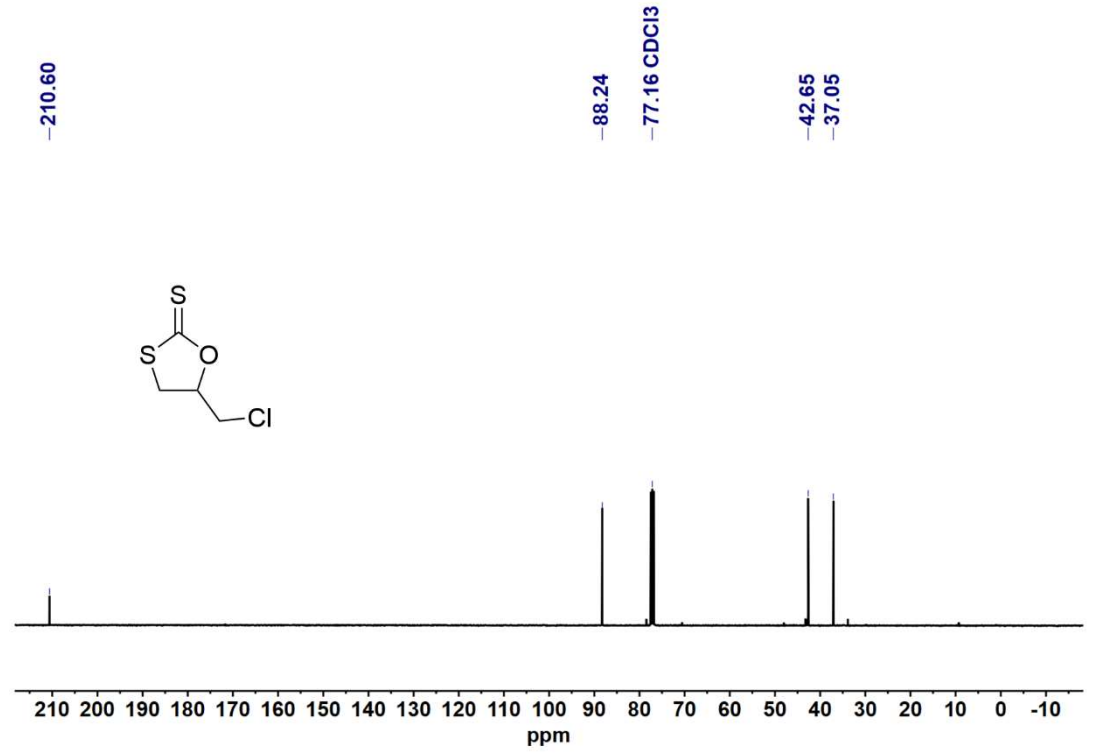
^{1}H NMR Spectrum of Compound **2d** (400 MHz, chloroform-*d*)



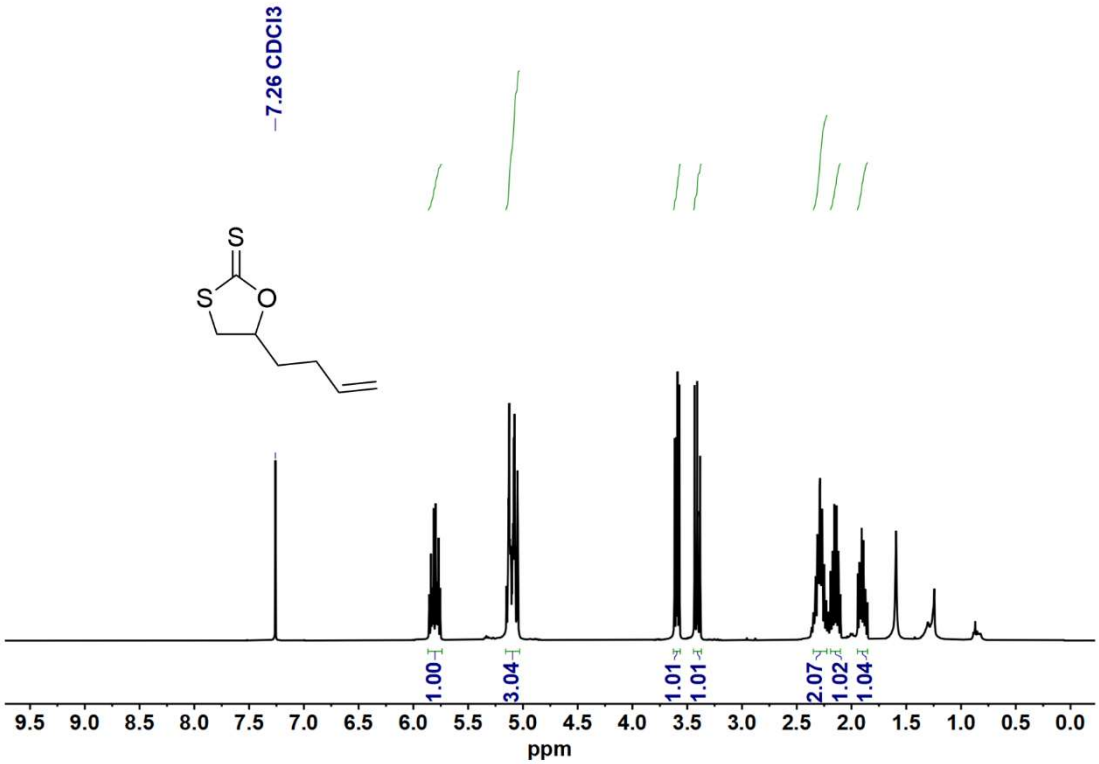
^{13}C NMR Spectrum of Compound **2d** (101 MHz, chloroform-*d*)



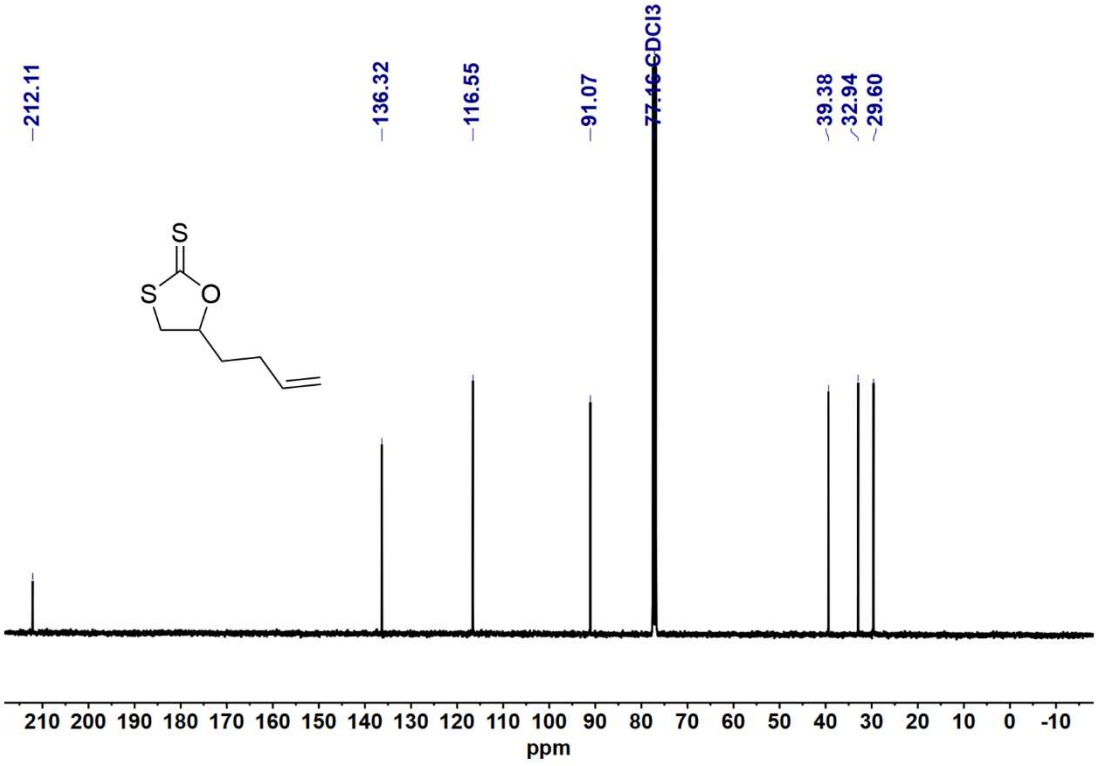
^{1}H NMR Spectrum of Compound **2e** (400 MHz, chloroform-*d*)



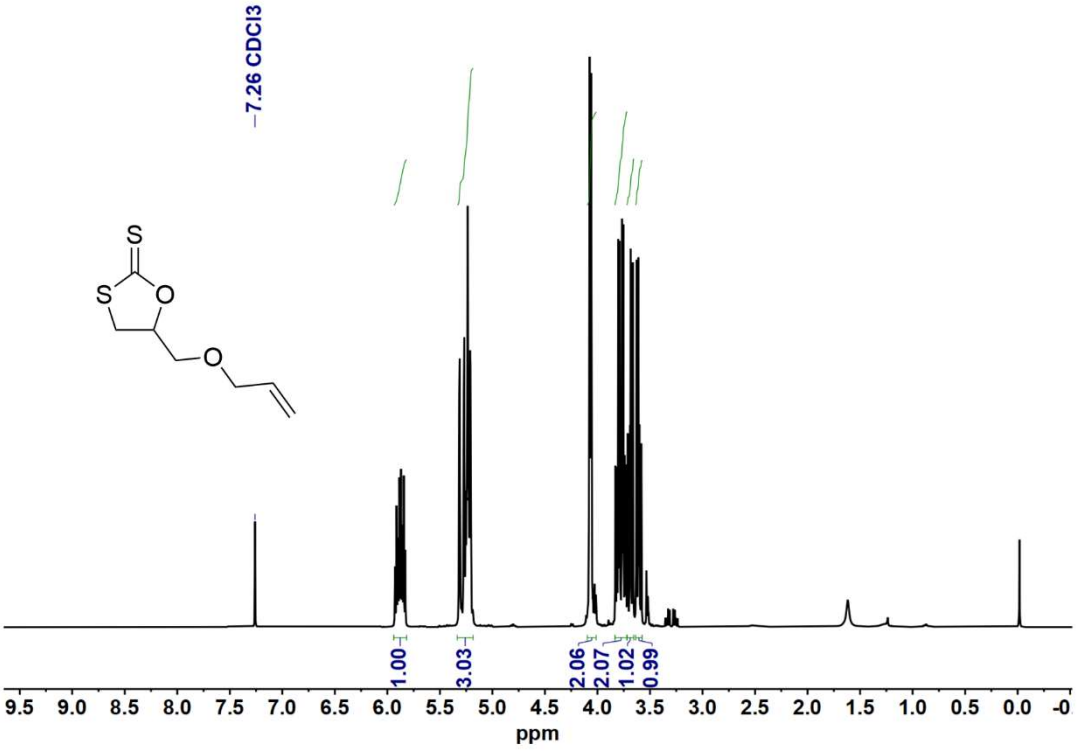
^{13}C NMR Spectrum of Compound **2e** (101 MHz, chloroform-*d*)



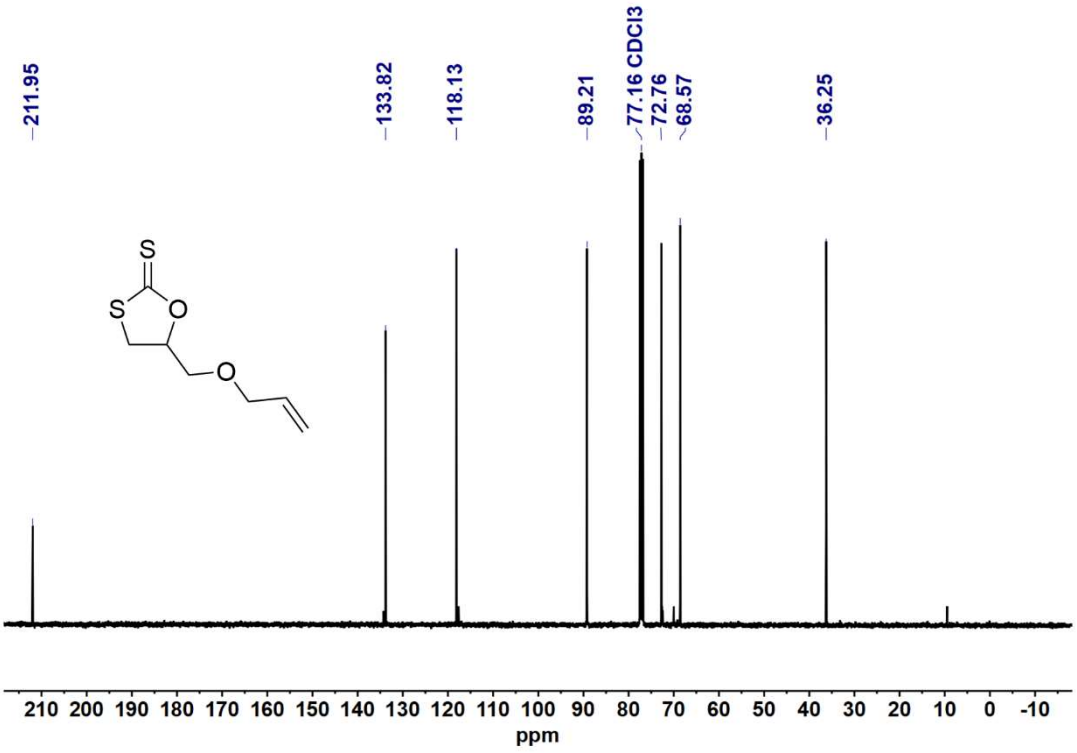
^{1}H NMR Spectrum of Compound **2f** (400 MHz, chloroform-*d*)



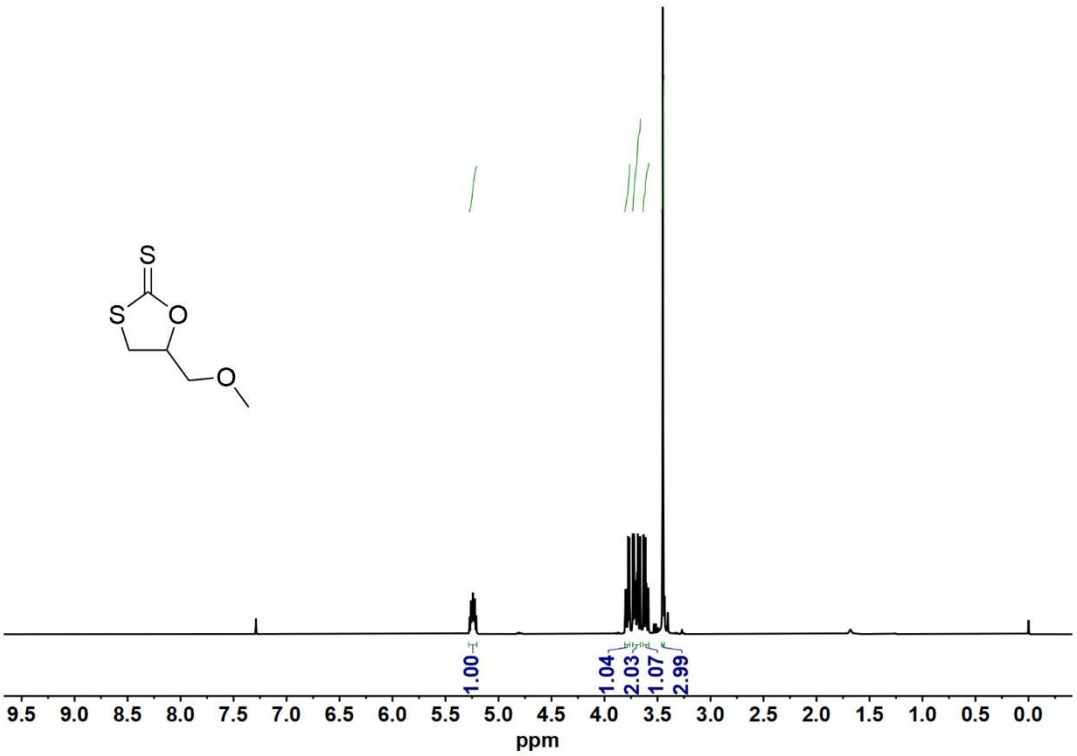
^{13}C NMR Spectrum of Compound **2f** (101 MHz, chloroform-*d*)



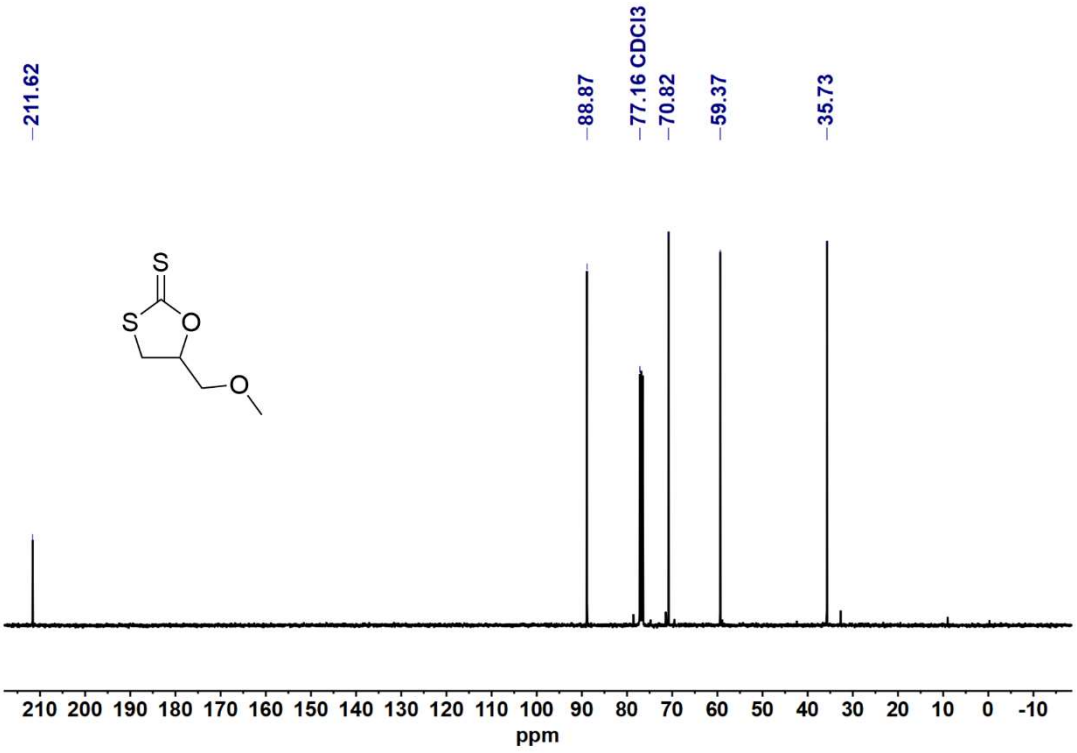
^{1}H NMR Spectrum of Compound **2g** (400 MHz, chloroform-*d*)



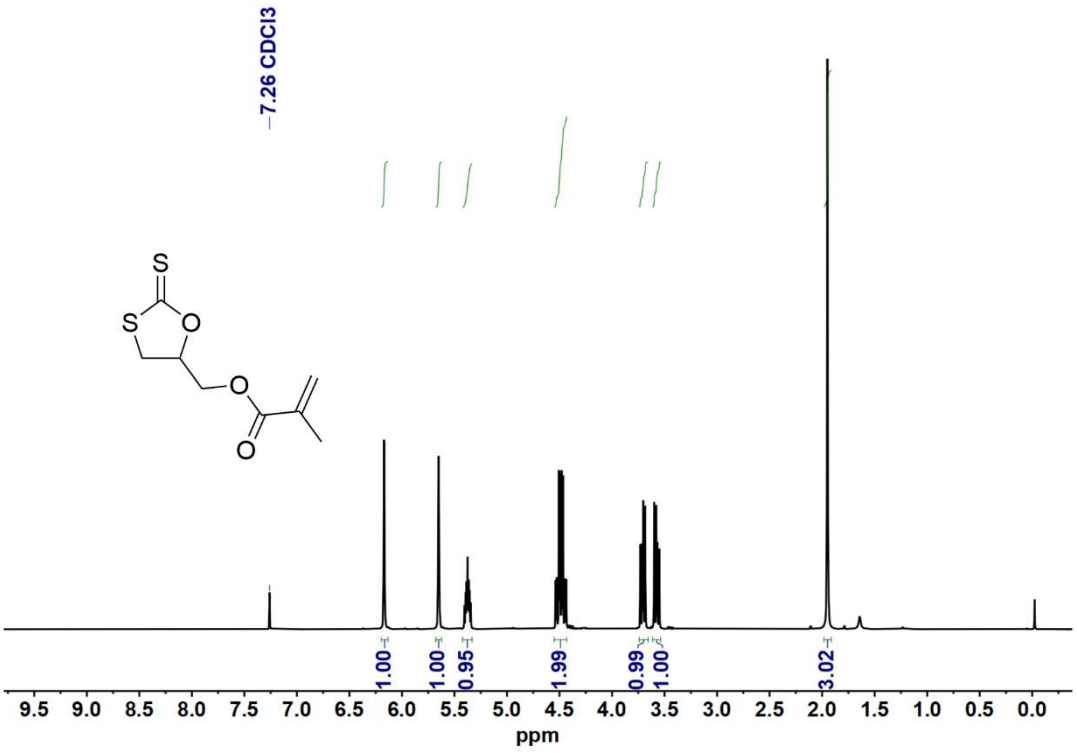
^{13}C NMR Spectrum of Compound **2g** (101 MHz, chloroform-*d*)



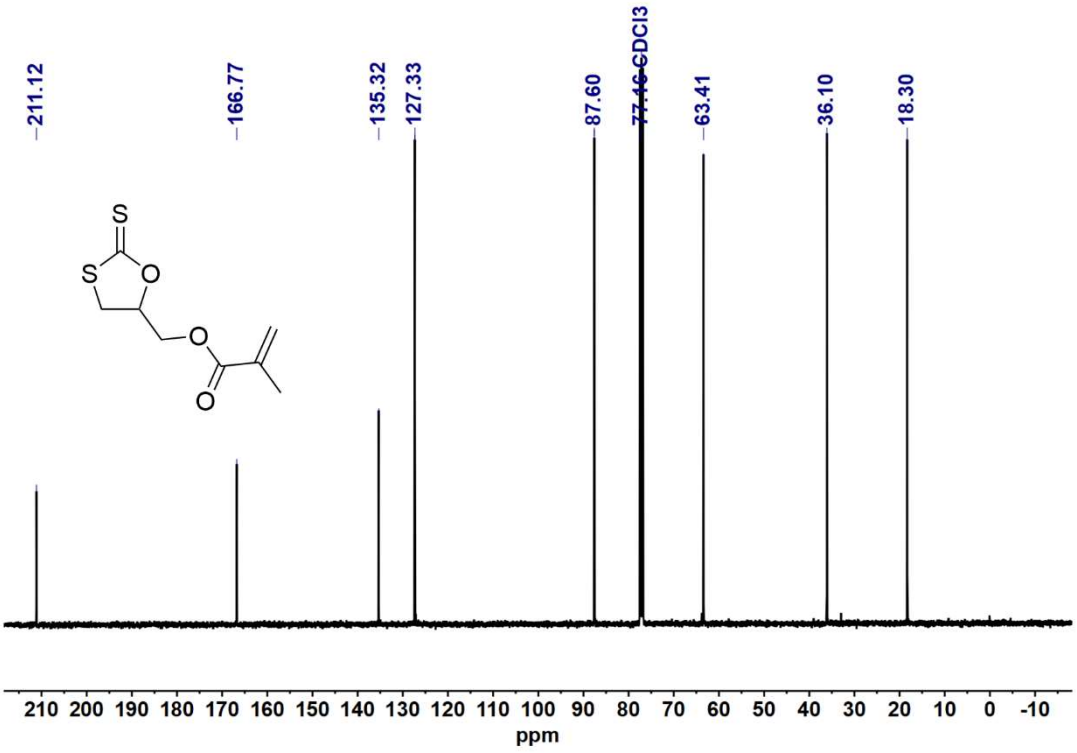
^{1}H NMR Spectrum of Compound **2h** (400 MHz, chloroform-*d*)



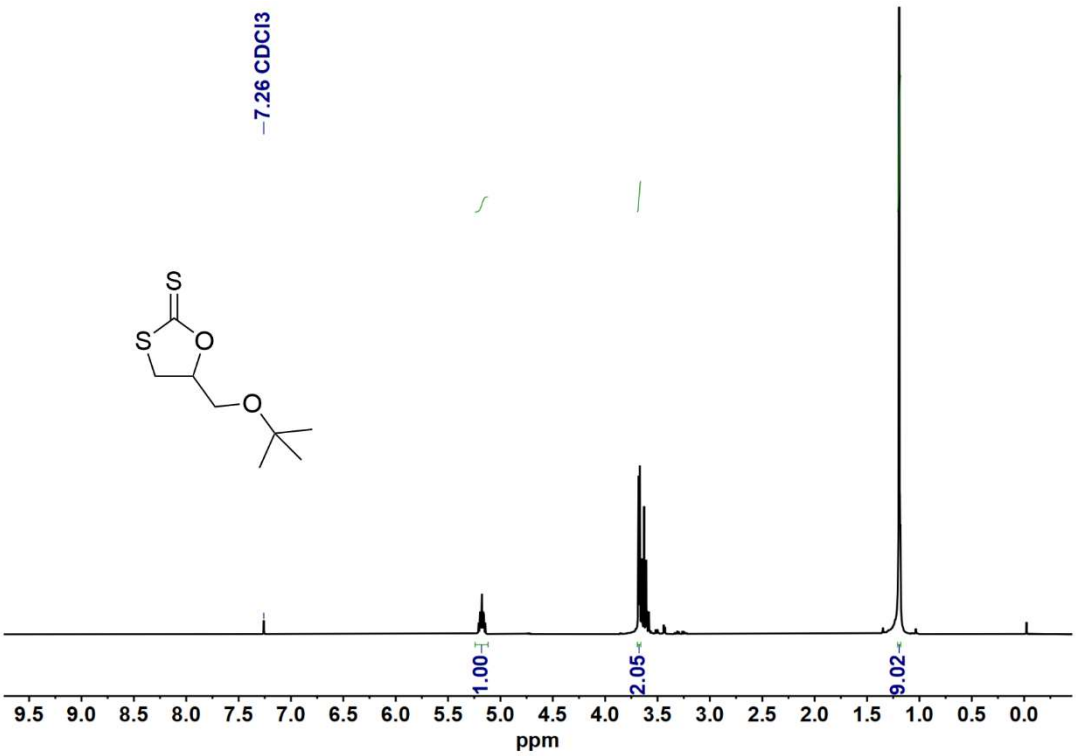
^{13}C NMR Spectrum of Compound **2h** (101 MHz, chloroform-*d*)



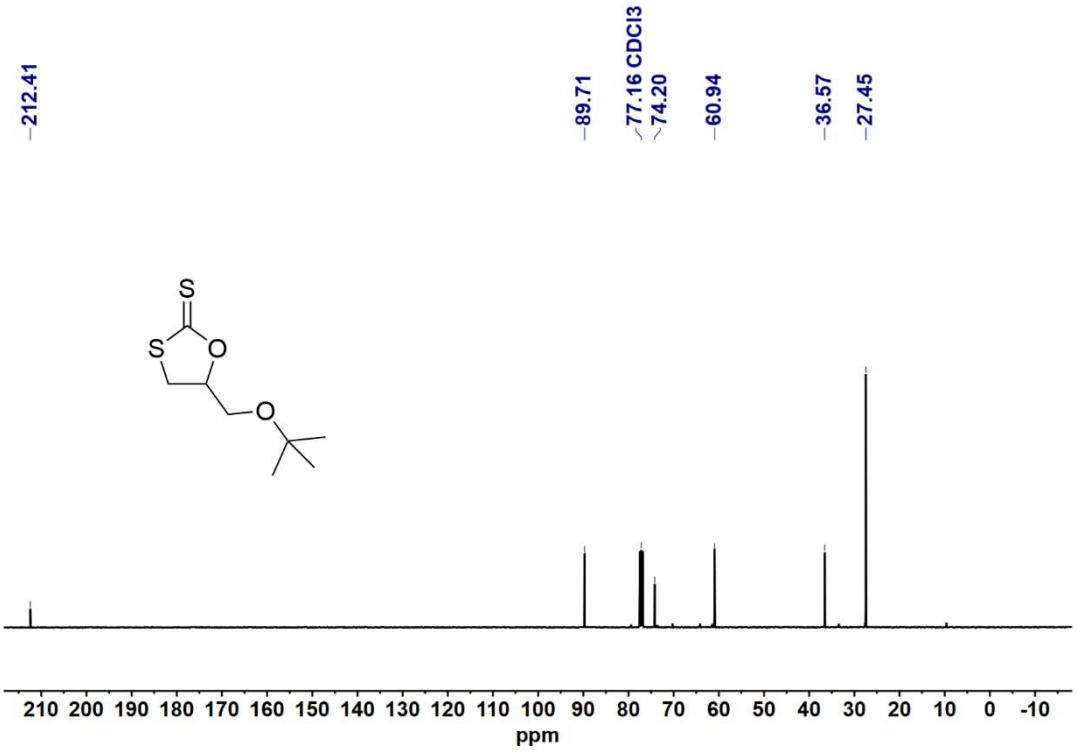
^{1}H NMR Spectrum of Compound **2i** (400 MHz, chloroform-*d*)



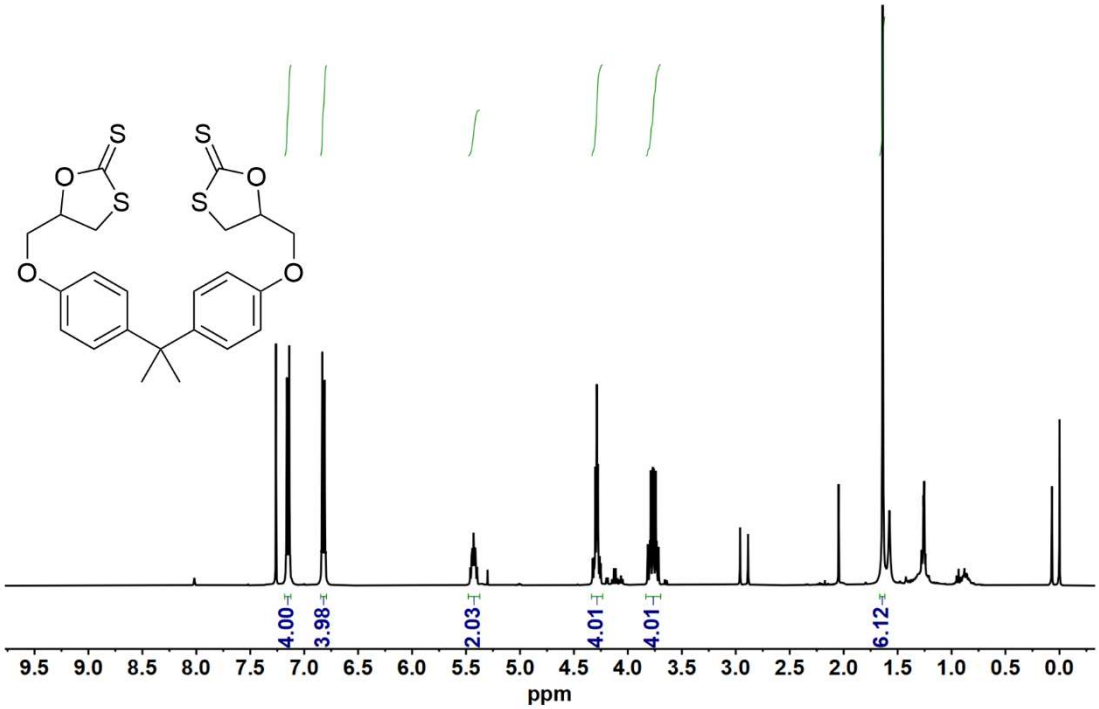
^{13}C NMR Spectrum of Compound **2i** (101 MHz, chloroform-*d*)



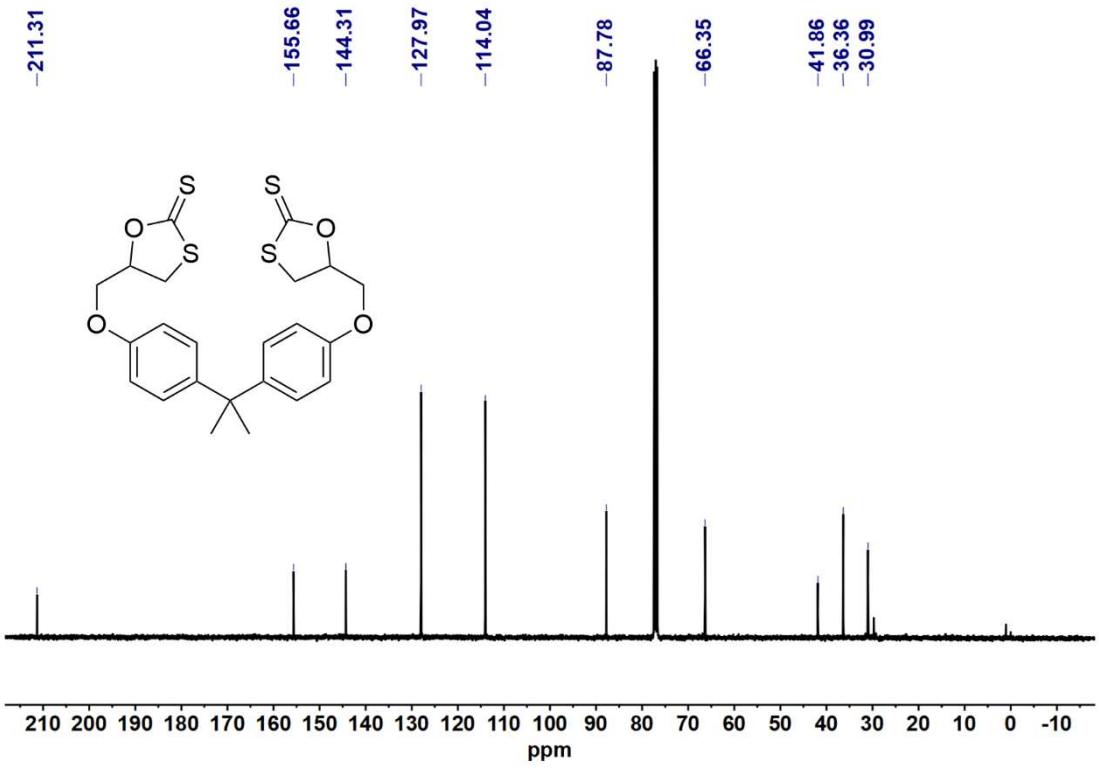
^{1}H NMR Spectrum of Compound **2j** (400 MHz, chloroform-*d*)



^{13}C NMR Spectrum of Compound **2j** (101 MHz, chloroform-*d*)

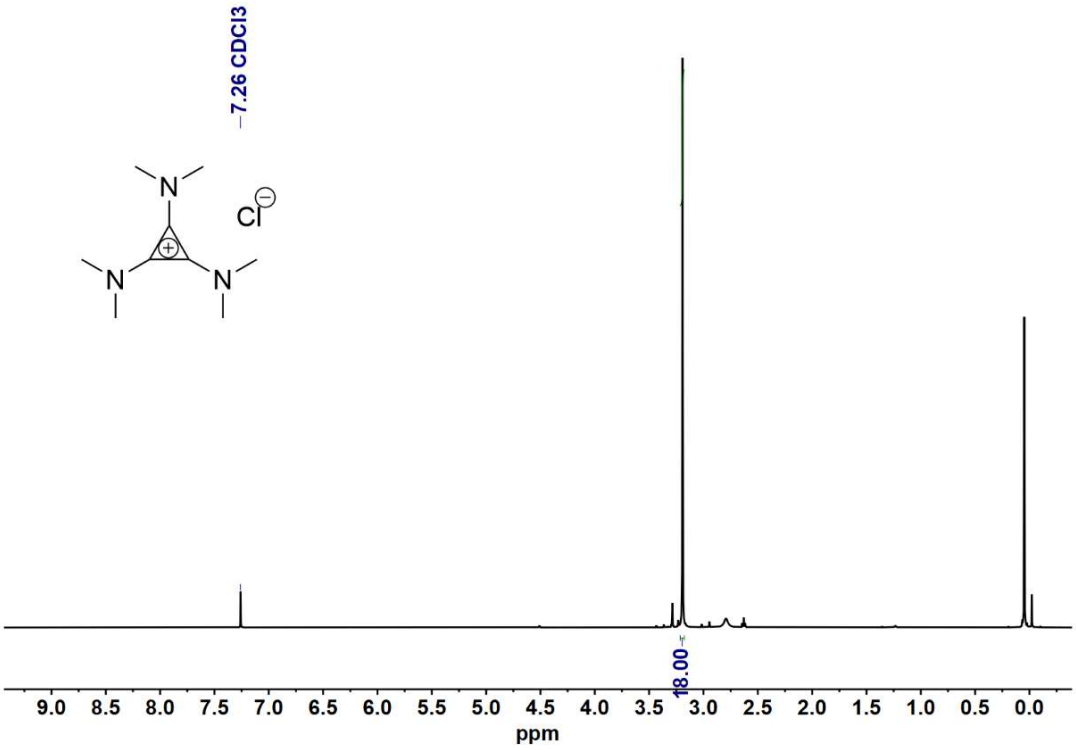


^{1}H NMR Spectrum of Compound **2k** (400 MHz, chloroform-*d*)

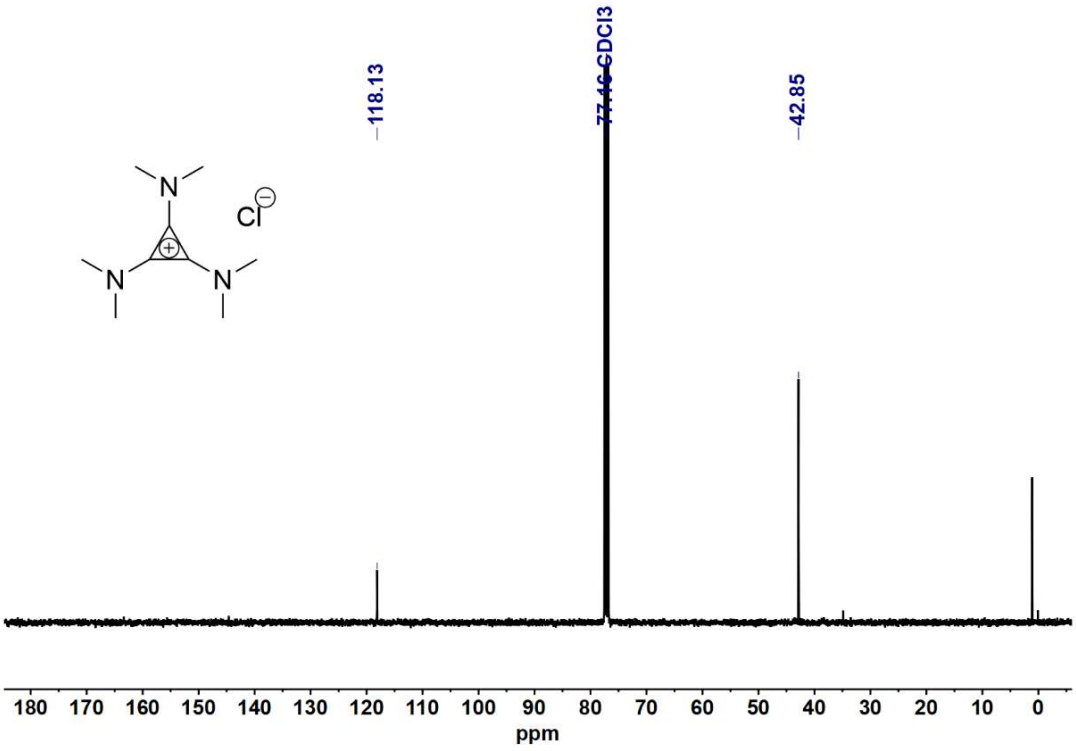


^{13}C NMR Spectrum of Compound **2k** (101 MHz, chloroform-*d*)

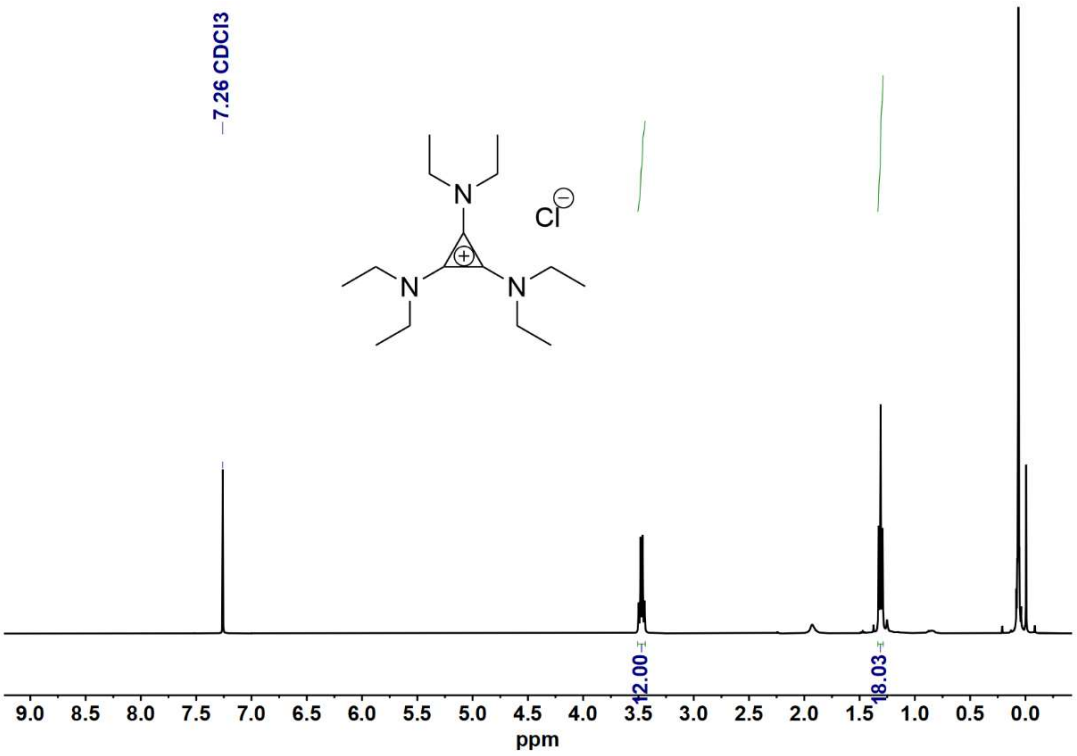
Copies of NMR spectra of catalysts



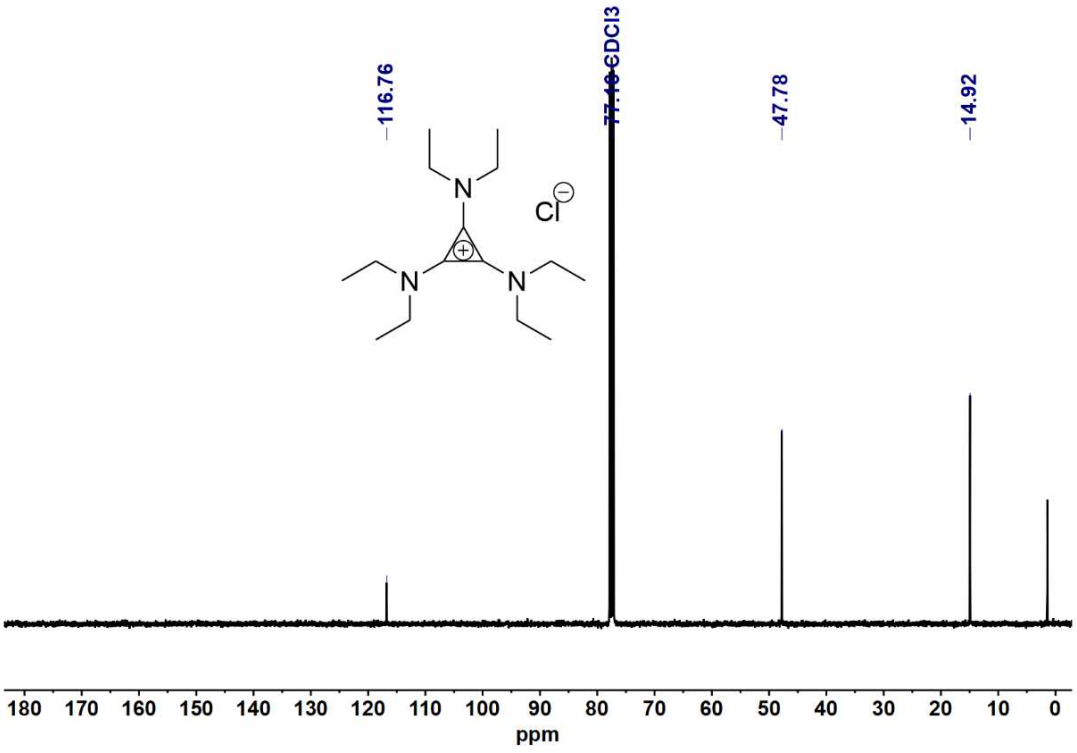
^{1}H NMR Spectrum of catalyst **C1** (400 MHz, chloroform-*d*)



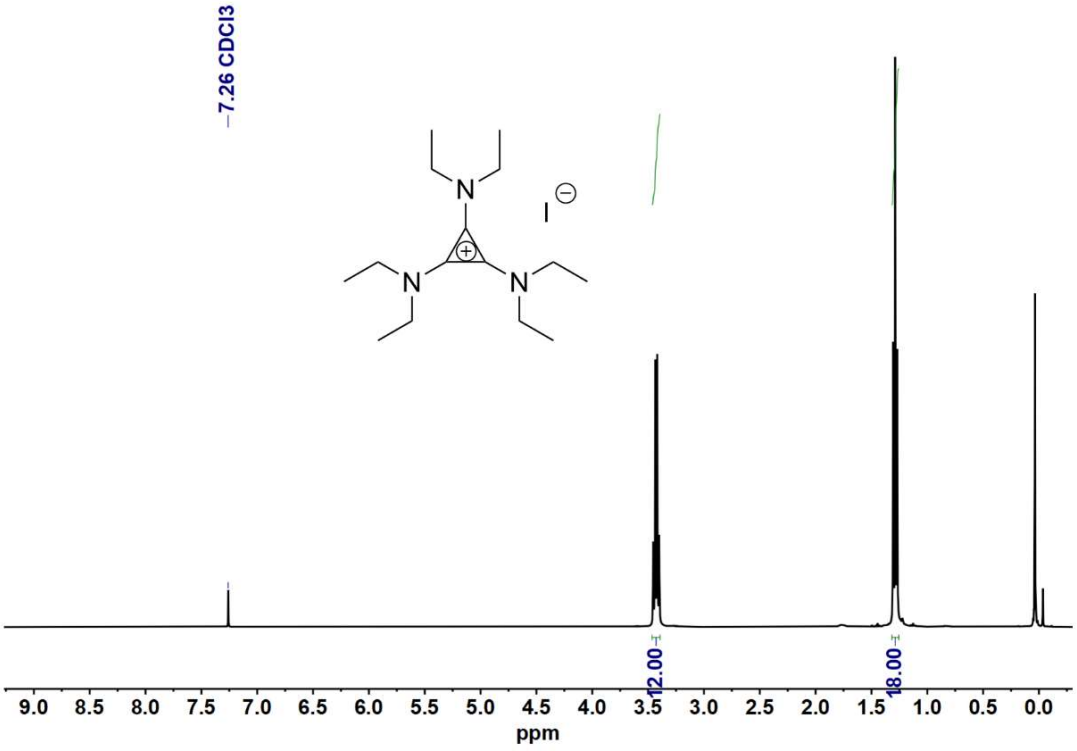
^{13}C NMR Spectrum of catalyst **C1** (101 MHz, chloroform-*d*)



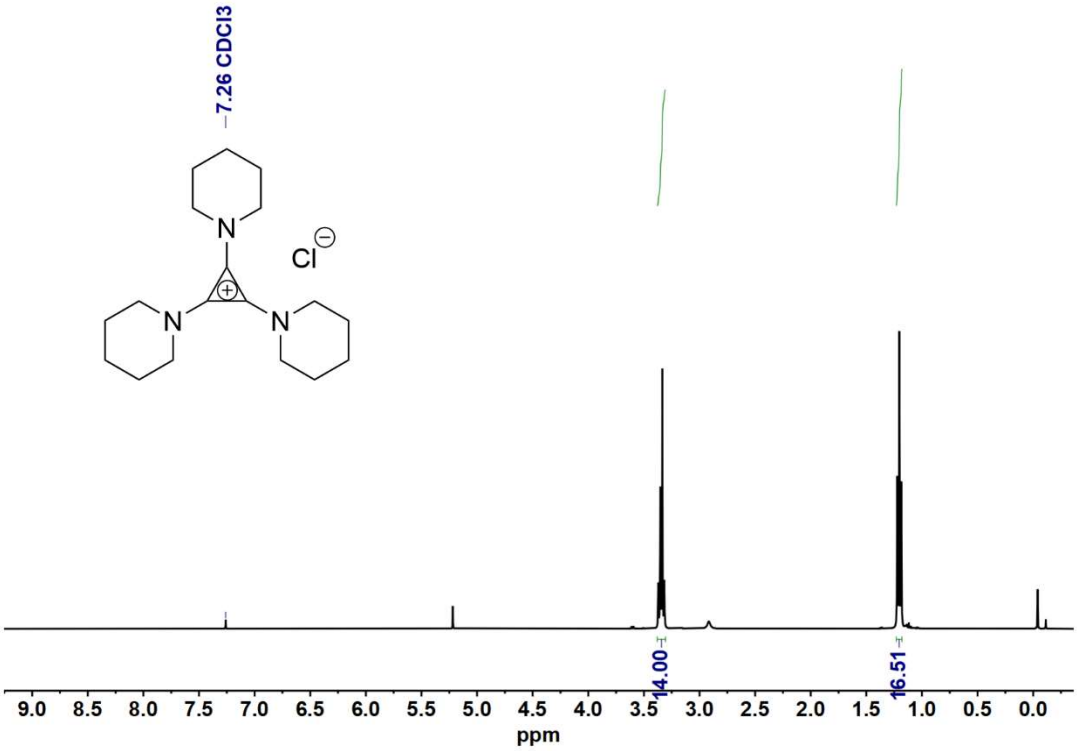
^{1}H NMR Spectrum of catalyst **C2·Cl** (400 MHz, chloroform-*d*)



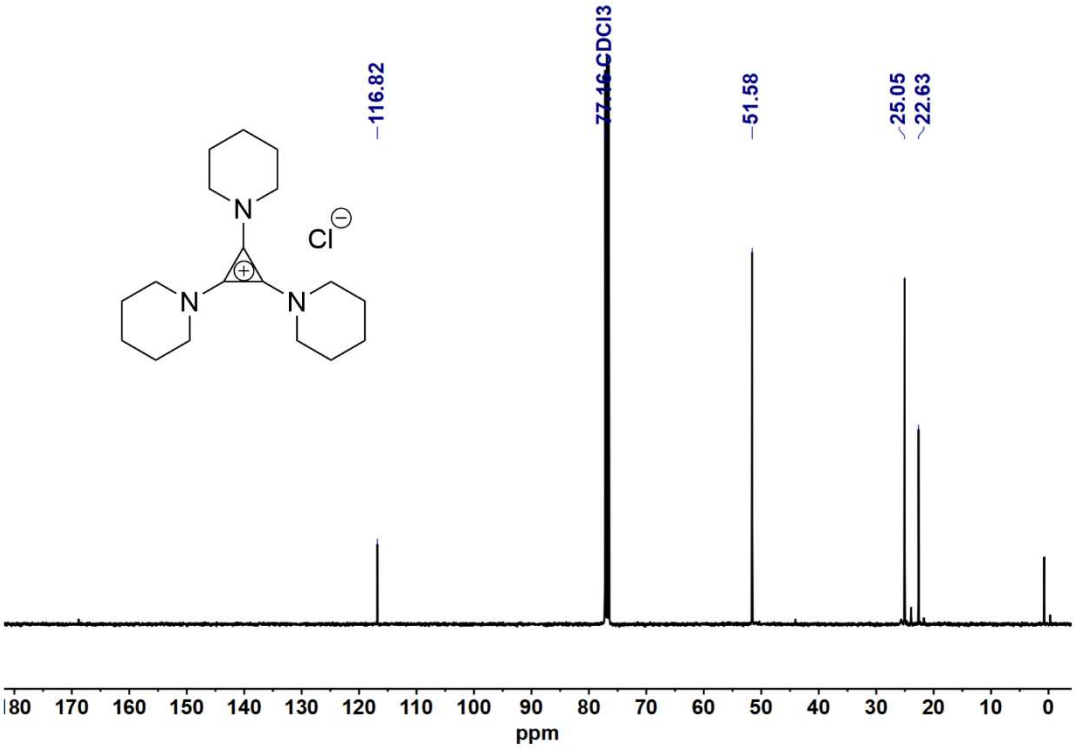
^{13}C NMR Spectrum of catalyst **C2·Cl** (101 MHz, chloroform-*d*)



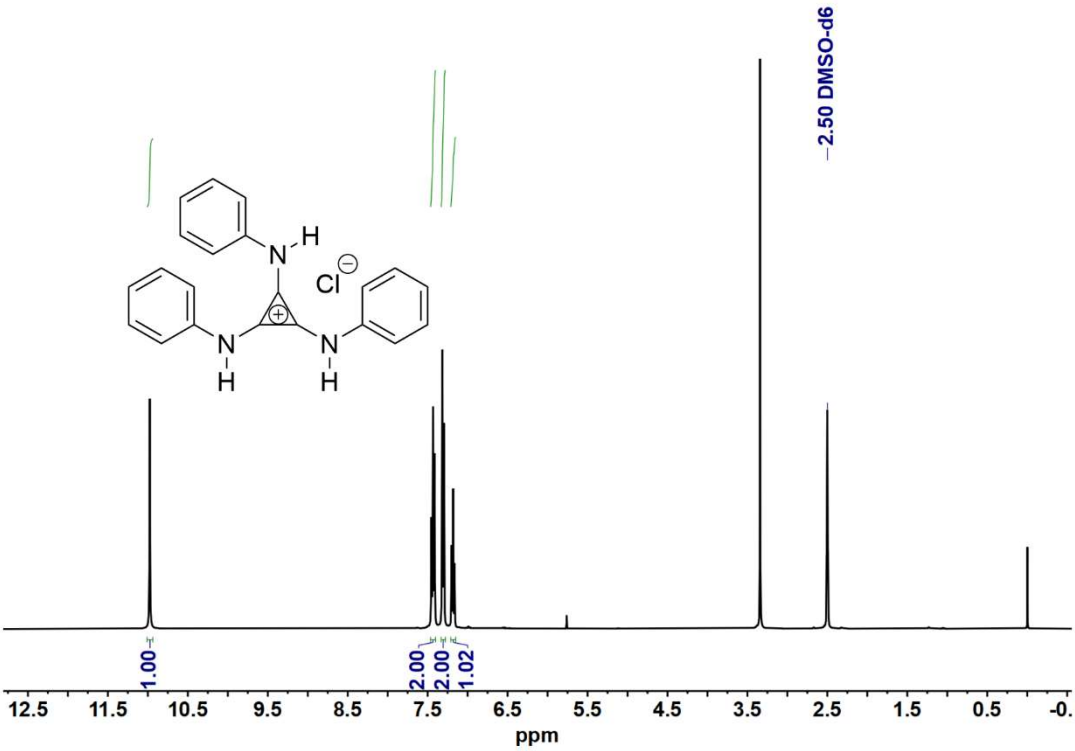
^{1}H NMR Spectrum of catalyst **C2·I** (400 MHz, chloroform-*d*)



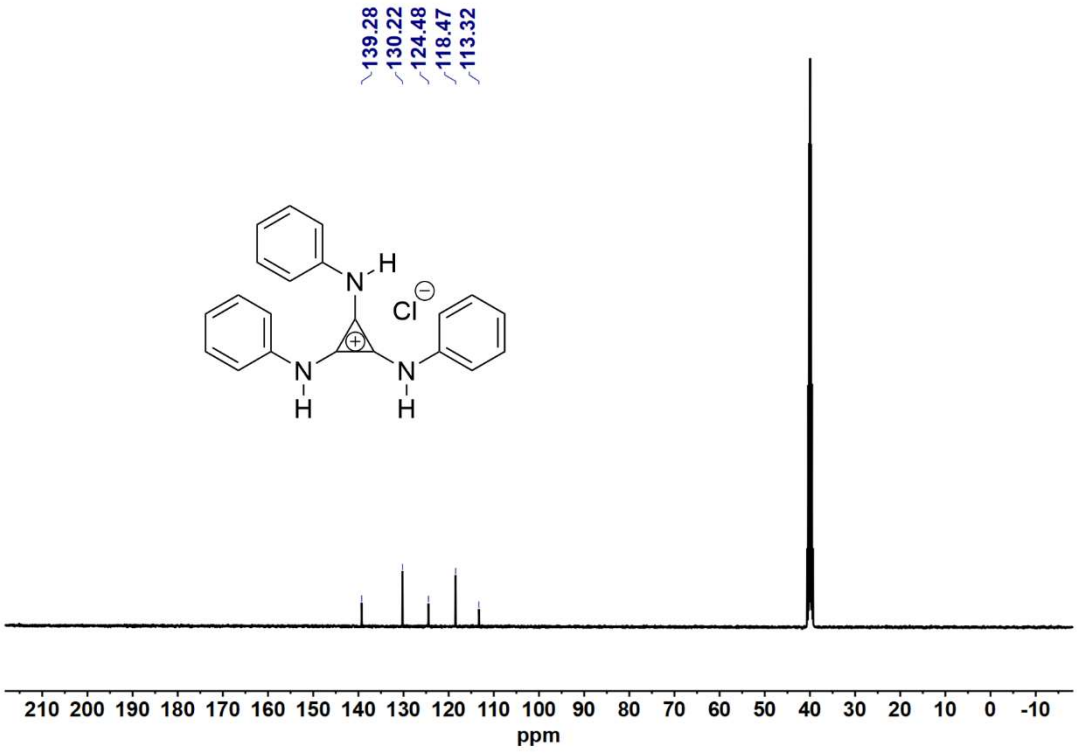
^{1}H NMR Spectrum of catalyst **C3** (400 MHz, chloroform-*d*)



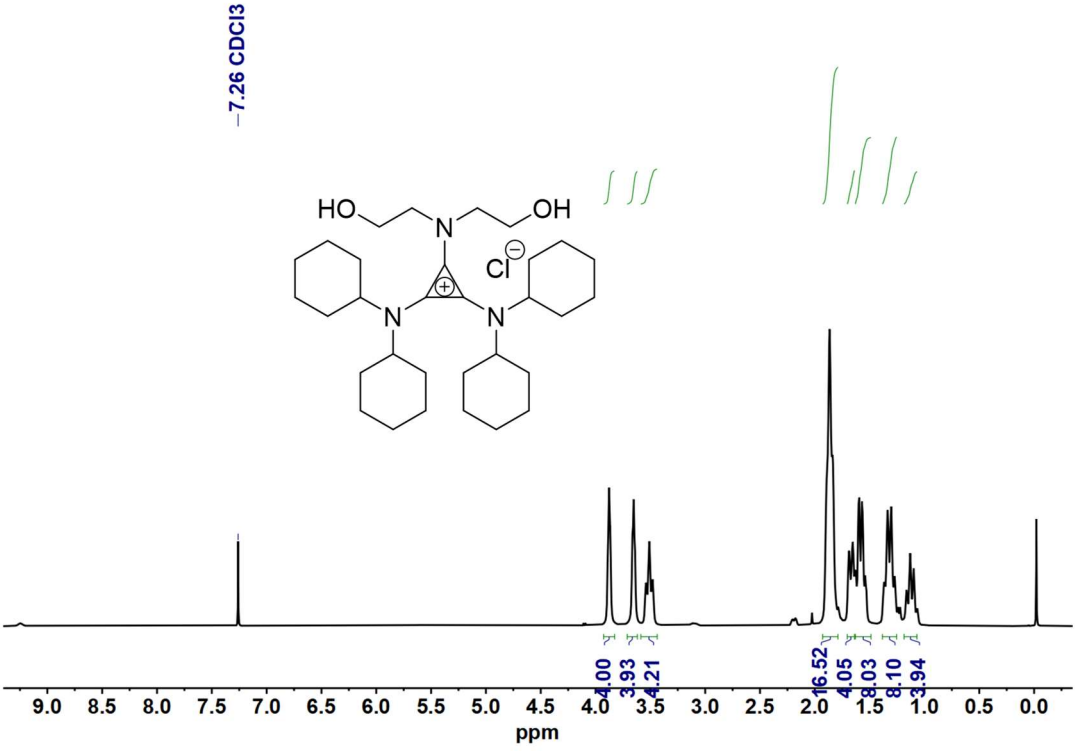
^{13}C NMR Spectrum of catalyst **C3** (101 MHz, chloroform-*d*)



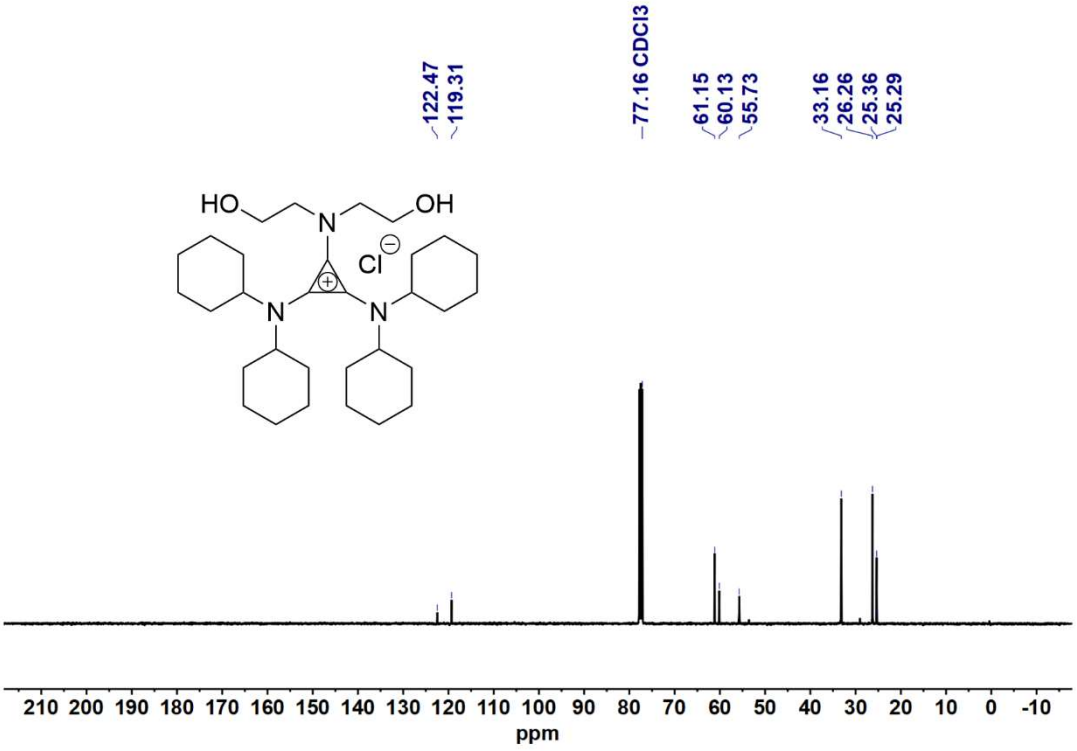
^{1}H NMR Spectrum of catalyst **C4** (400 MHz, chloroform-*d*)



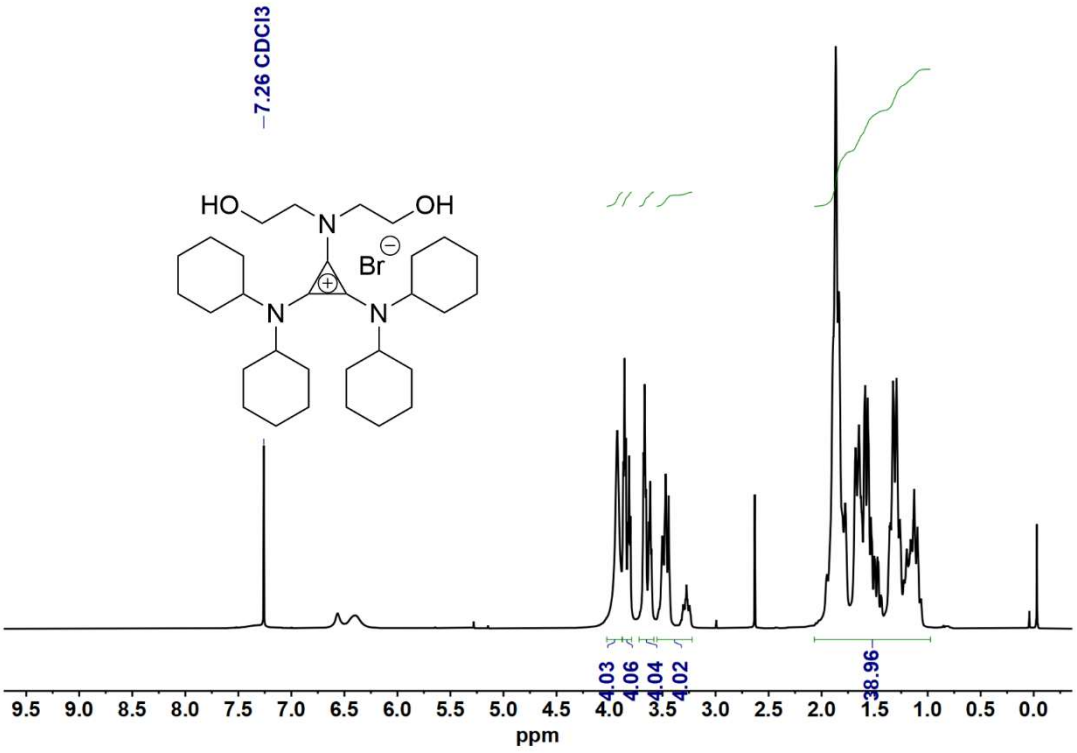
^{13}C NMR Spectrum of catalyst **C4** (101 MHz, chloroform-*d*)



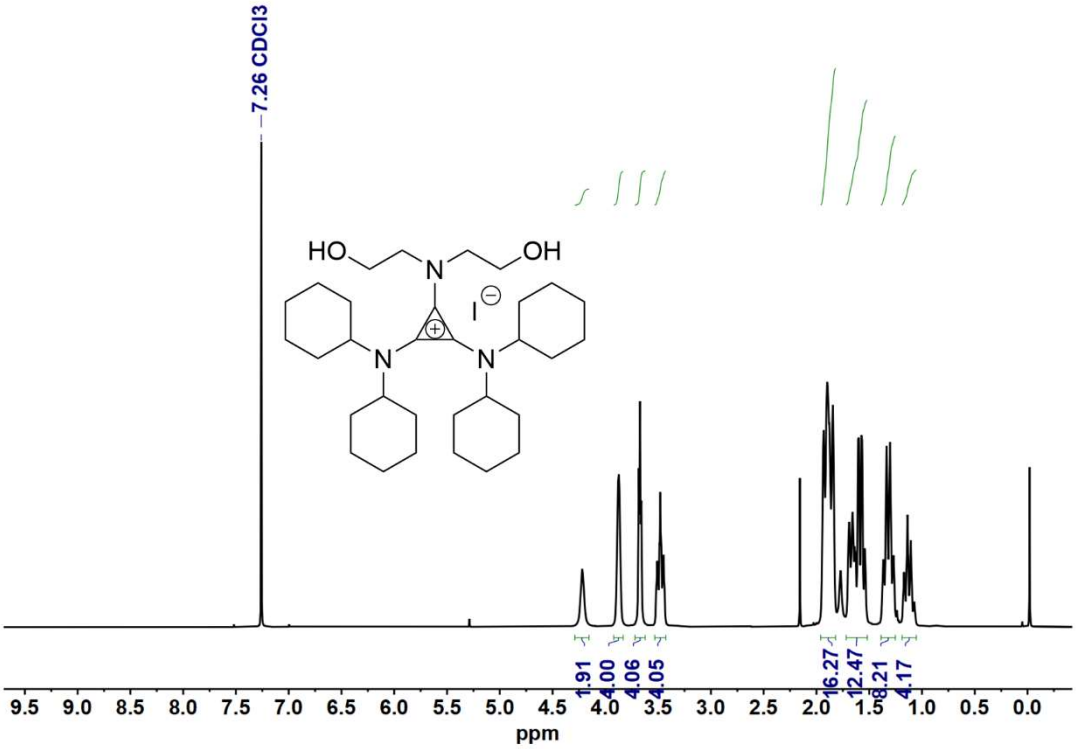
^{1}H NMR Spectrum of catalyst **C5·Cl** (400 MHz, chloroform-*d*)



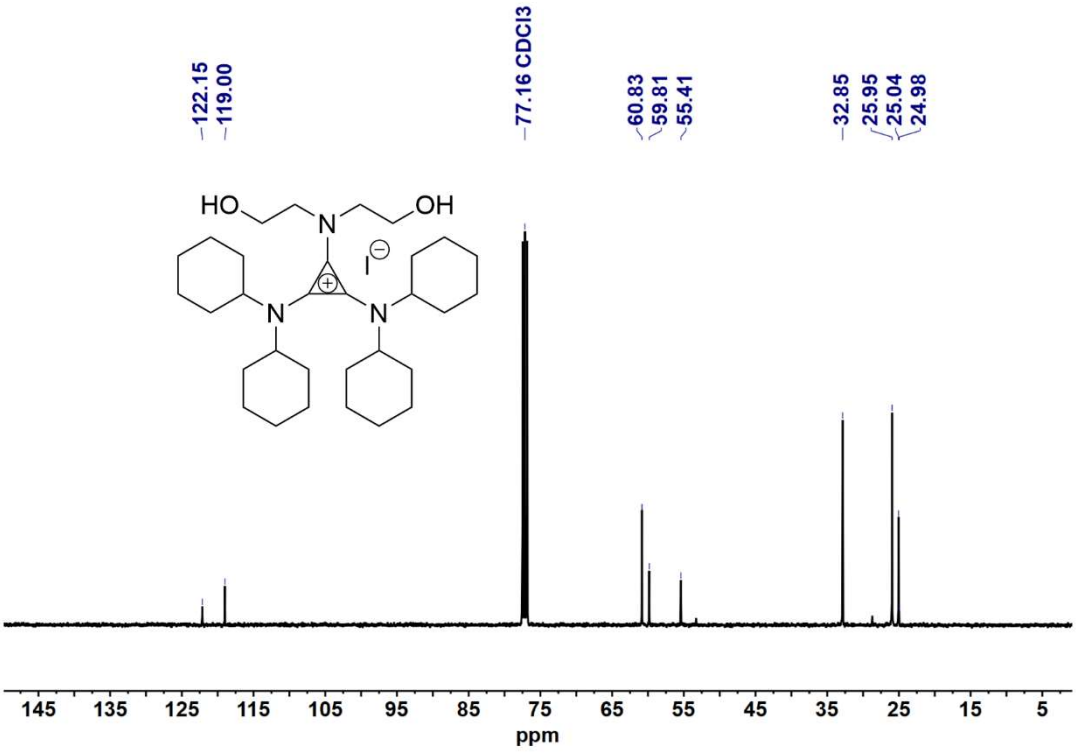
^{13}C NMR Spectrum of catalyst **C5·Cl** (101 MHz, chloroform-*d*)



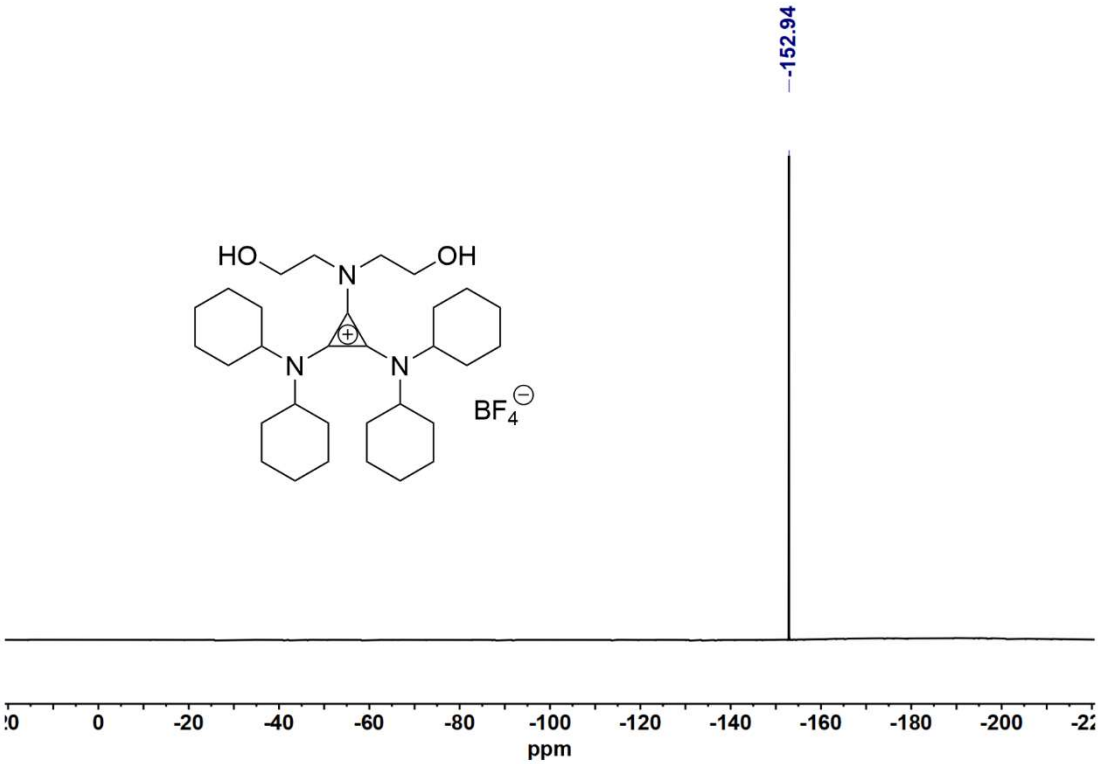
^{1}H NMR Spectrum of catalyst **C5·Br** (400 MHz, chloroform-*d*)



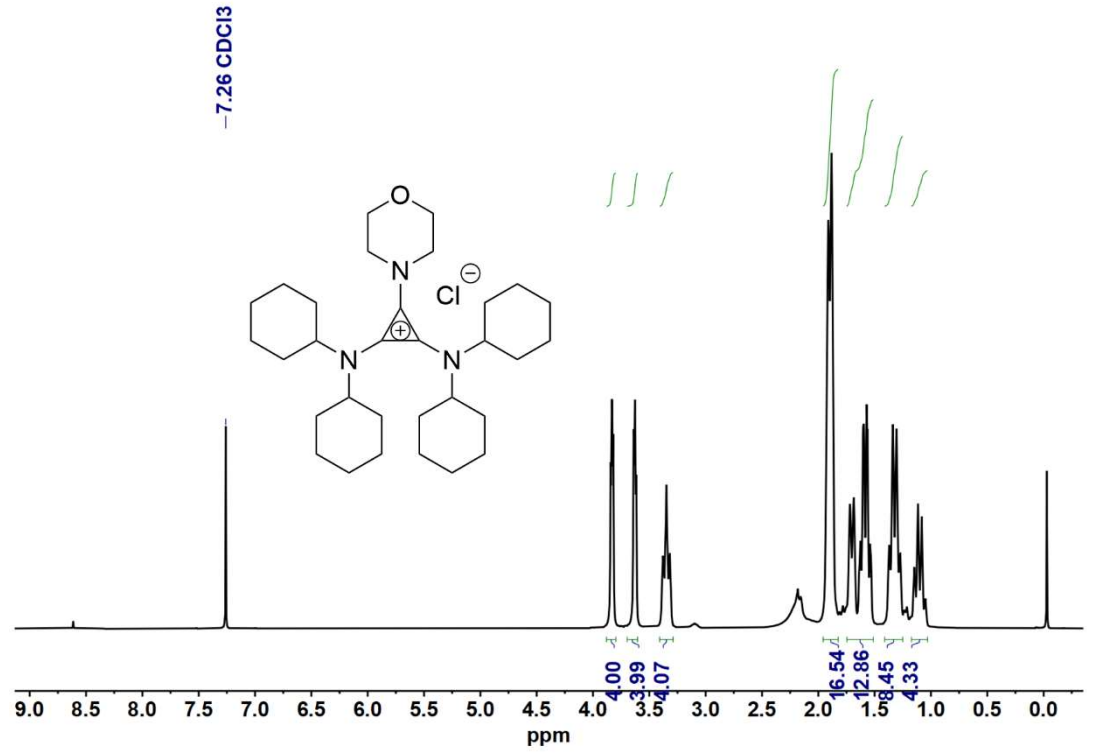
^{1}H NMR Spectrum of catalyst **C5·I** (400 MHz, chloroform-*d*)



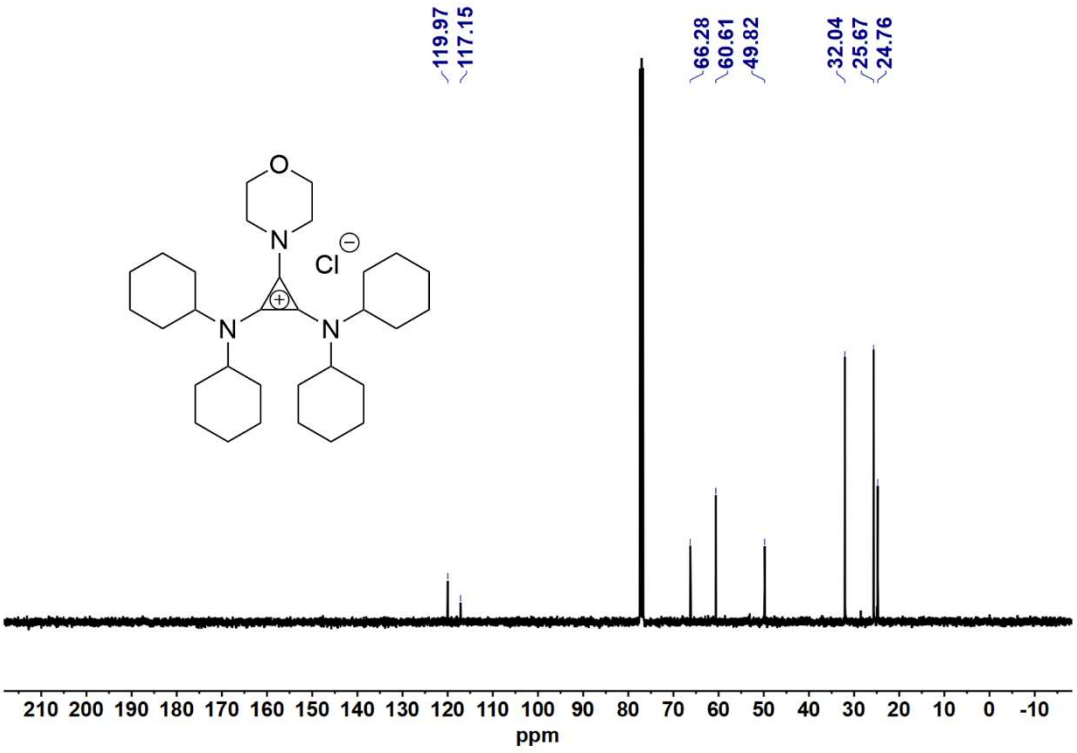
^{13}C NMR Spectrum of catalyst **C5·I** (401 MHz, chloroform-*d*)



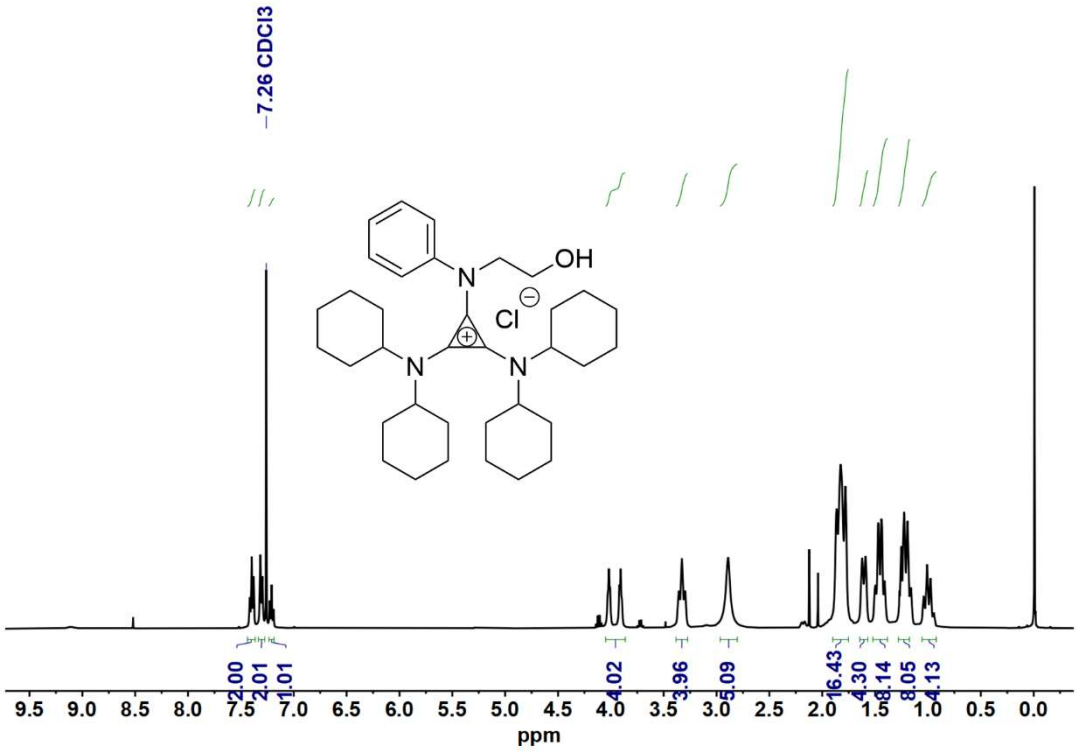
^{19}F NMR Spectrum of catalyst **C5·I** (376 MHz, chloroform-*d*)



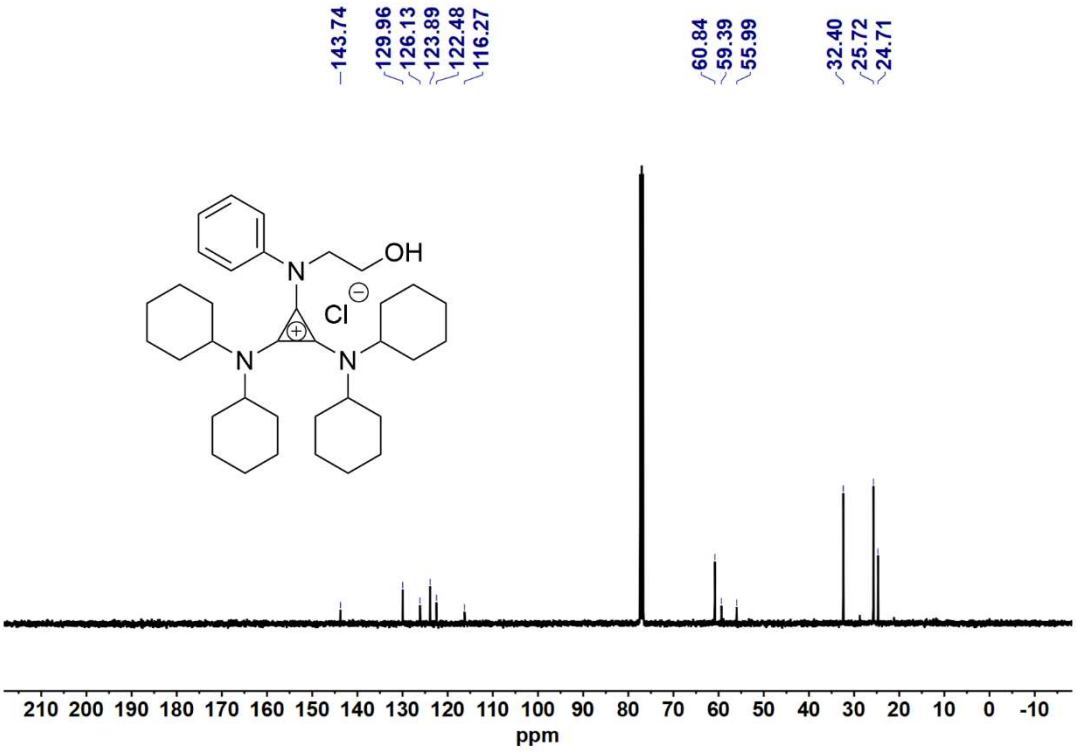
^{1}H NMR Spectrum of catalyst **C6** (400 MHz, chloroform-*d*)



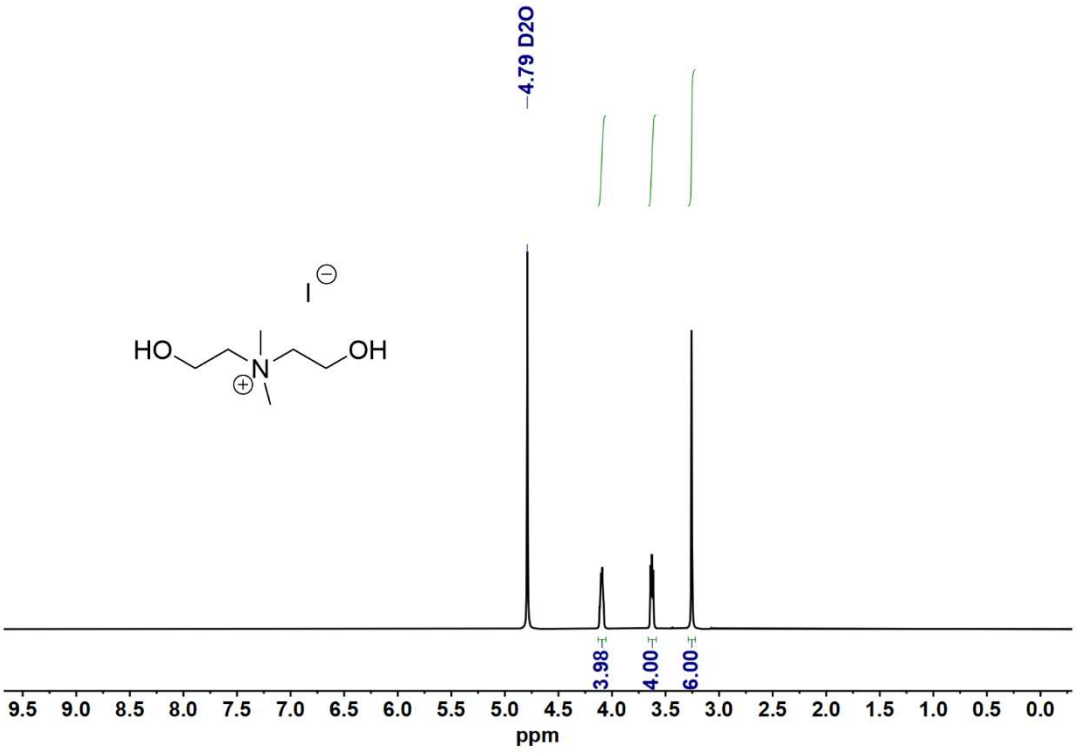
^{13}C NMR Spectrum of catalyst **C6** (101 MHz, chloroform-*d*)



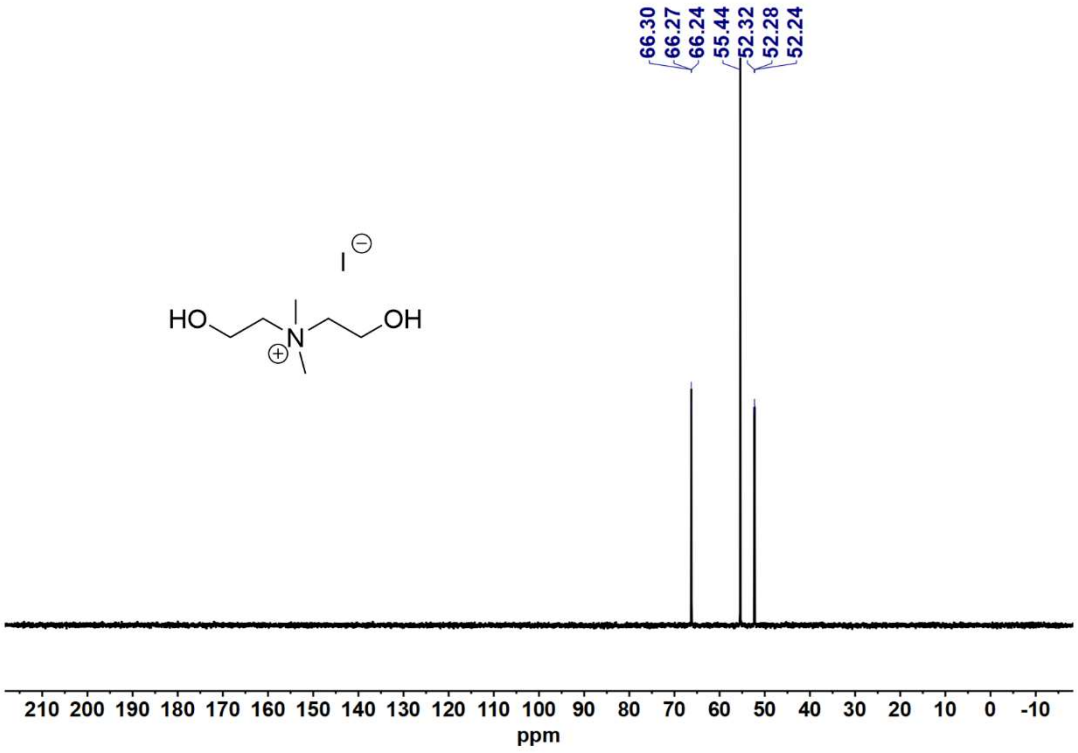
^{1}H NMR Spectrum of catalyst **C7** (400 MHz, chloroform-*d*)



^{13}C NMR Spectrum of catalyst **C7** (101 MHz, chloroform-*d*)



^{1}H NMR Spectrum of catalyst **C8** (400 MHz, chloroform-*d*)



^{13}C NMR Spectrum of catalyst **C8** (101 MHz, chloroform-*d*)