Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Interpretable Machining Learning Assisted Insight into Bifunctional Squaramide Catalyzed Ring-opening Polymerization of Lactide

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Materials

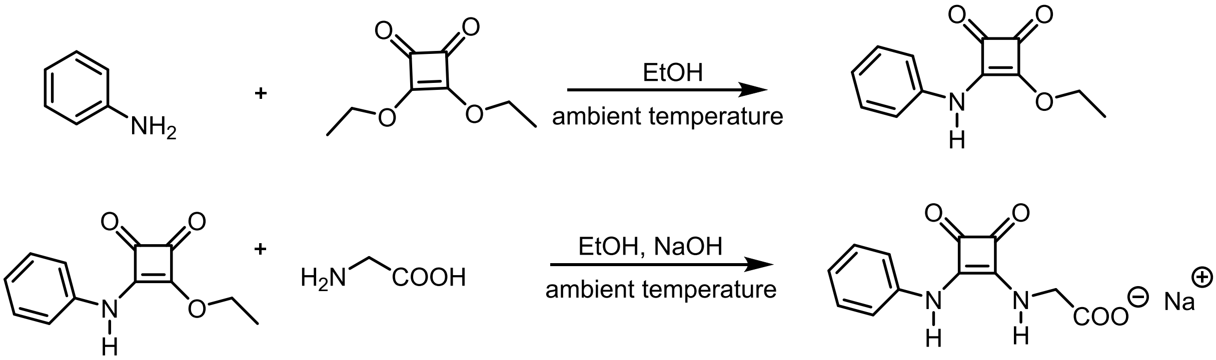
L-Lactide (L-LA; 99.5%) was purchased from Jinan Daigang Biomaterial Co. and purified by recrystallization from anhydrous toluene and dried under vacuum overnight (40 ℃). Dichloromethane (>99.5%, Sinopharm Chemical Reagent Co.) was distilled over CaH_2 in an argon environment, and further dried over 4 Å molecular sieve pellets for 48 h before use. Tetrahydrofuran (THF; HPLC, Aldrich), 3-phenylpropanol (PPA) were dried and stored over 4 Å molecular sieves under an inert atmosphere. Pentaerythritol was dried over P_2O_5 in a vacuum before use. Pentaerythritol was dried over P2O5 in a vacuum before use. Ethanol (EtOH) was purchased from Sinopharm Chemical Reagent Co. Sodium hydroxide(NaOH), Lithium hydroxide(LiOH), Potassium hydroxide(KOH) and Cesium hydroxide(CsOH) were purchased from Sinopharm Chemical Reagent Co. Aniline, Benzylamine, 3,5-bis(trifluoromethyl)aniline, 4-tert-Butylaniline, Cyclohexylamine, Butylamine and tert-Butylamine were purchased from J&K Scientific Ltd. Diethyl squarate was purchased from J&K Scientific Ltd. Glycine(Gly), L-Alanine(L-Ala) , L-Valine(L-Vla), L-Isoleucine(L-Ile), β-Alanine, 4-Aminobutyric acid, 5-Aminovaleric acid, 6-Aminocaproic acid, 7-Aminoheptanoic acid, 8-Aminooctanoic acid, 9-azanylnonanoic acid, 10-Aminodecanoic acid, 11-Aminoundecanoic acid and 12-Aminododecanoic acid were purchased from Diba Biotechnology Co. 12-Crown-4, 15-Crown-5 and 18-Crown-6 were purchased from Maclean's Biochemical Technology Co.

Instruments

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured using deuterated chloroform ($CDCl_3$) as solvent on a Bruker AVANCE Ultrashield Plus spectrometer at 298K. Positive-ion MALDI Time-Of-Flight Mass Spectrometry (MALDI-TOF-MS) was performed on a Bruker Co. Ultrafiltrate mass spectrometer equipped with a Smartbeam/Smartbeam II modified laser (Nd: YAG) at 25 kV acceleration voltage. The polymer sample was dissolved in $CHCl_3$ at a concentration of 1 mg·mL^{-1} with the addition of 50 μL of 2 mg·L^{-1} sodium iodide (NaI). 2,5-dihydroxybenzoic acid (DHB) was applied as a matrix and 1 μL of 40 mg·mL^{-1} solution was dropped to a stainless-steel target and air-dried. After the crystallization of DHB, the 1 μL of the polymer solution was dropped on the crystal and air-dried. Size Exclusion Chromatography (SEC) was performed in tetrahydrofuran (THF) at room temperature at a flow rate of 0.7 mL min^{-1} using an SSI 1500 pump equipped with a Waters column (5 μm, 300 mm × 7.8 mm), and a Wyatt Optilab rEX differential refractive index (DRI) detector with a 658 nm light source. All SEC data were analyzed using Wyatt Astra V 6.1.1 software. The molecular weight distribution (*Đ*) was determined by a calibration with standard polystyrene samples.

Experimental Procedures

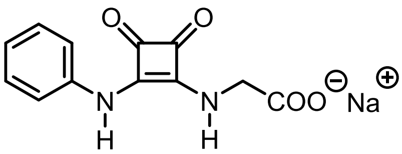
Preparation of the squaramide catalysts



Scheme S1. Synthesis of squaramide catalysts at ambient temperature

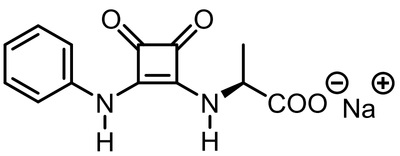
Square amide alkali metal carboxylate catalysts are synthesized by a two-step amine substitution reaction. Taking synthesis of 01 as an example. Aniline (0.93 g, 10 mmol, 1.0 equiv.) and diethyl squarate (1.7 g, 10 mmol, 1.0 equiv.) were added to a 50 mL vial and stirred using magnetic stir bar with ethanol as a solvent (20 mL) for 24 h at ambient temperature. The solvent was removed under vacuum to yield the single substituted product. Afterward, glycine (0.45 g, 5 mmol, 1.0 equiv.) and 1.0 M NaOH (5 mL) were added to a 25 mL flask at room temperature. After 8 h, 7.5 mL of ethanol was added to solubilize the single substituted product (1.1 g, 5 mmol, 1.0 equiv.). The reaction was quenched after 4 h and ethanol was removed under vacuum and dried for 24 h to yield 01 (yield = 80%. White powder.).

Catalyst 01



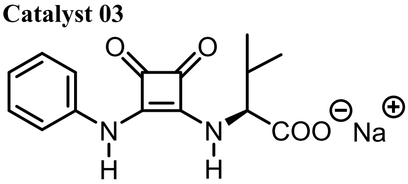
Catalyst 01 1.24 g; yield = 80%. White powder.^{1}H NMR (400 MHz, DMSO-d_6) δ 12.29 (s, 1H), 8.78 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 7.9 Hz, 2H), 6.93 (t, J = 7.3 Hz, 1H), 4.08 (d, J = 4.6 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.32, 180.31, 170.38, 168.31, 140.37, 128.75, 121.76, 118.72, 48.06, 39.52 . Chemical Formula: $C_{12}H_9N_2NaO_4$.

Catalyst 02



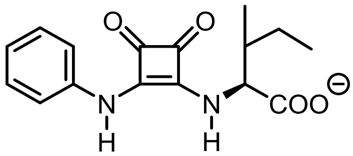
Catalyst 02 1.16 g; yield = 75%. Yellow powder.^{1}H NMR (400 MHz, DMSO-d_6) δ 12.49 (s, 1H), 9.19 (s, 1H), 7.94 (s, 2H), 7.23 (t, J = 7.6 Hz, 2H), 6.91 (t, J = 7.4 Hz, 1H), 4.40 (q, J = 7.0 Hz, 1H), 1.36 (d, J = 7.0 Hz, 3H). Chemical Formula: $C_{13}H_{11}N_2NaO_4$.

Catalyst 03



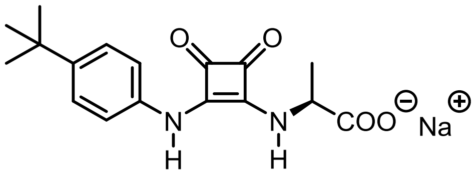
Catalyst 02 1.25 g; yield = 81%. Light yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 9.02 (s, 1H), 7.99 (d, J = 7.8 Hz, 2H), 7.31 – 7.20 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 4.38 (dd, J = 9.4, 5.4 Hz, 1H), 2.08 (dq, J = 13.7, 6.7 Hz, 1H), 0.91 (dd, J = 9.8, 6.8 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.80, 180.19, 172.65, 168.85, 163.69, 128.84, 121.73, 118.52, 32.46, 19.12, 17.78. Chemical Formula: $C_{14}H_{12}N_2NaO_4$.

Catalyst 04



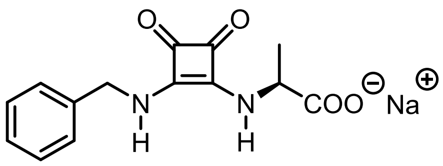
Catalyst 04 1.3 g; yield = 81%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.78 (s, 1H), 9.14 (s, 1H), 8.05 (d, 2H), 7.24 (m, 2H), 6.91 (t, 1H), 4.39 (d, 1H), 1.78 (m, 1H), 1.56 (m, 1H), 1.11 (m, 1H), 0.90 (m, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.78, 172.65, 168.70, 163.75, 128.78, 121.57, 118.61, 63.91, 39.52, 24.58, 11.74. Chemical Formula: $C_{15}H_{14}N_2NaO_4$.

Catalyst 06



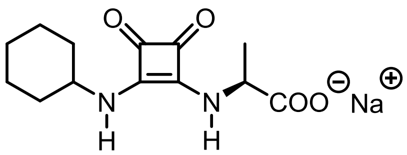
Catalyst 06 1.3 g; yield = 81%. White powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 9.09 (s, 1H), 7.86 (d, 2H), 7.28 (d, 2H), 4.40 (q, 1H), 1.38 (d, 3H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.57, 180.19, 173.82, 167.78, 164.24, 144.09, 137.76, 125.37, 118.58, 54.42, 33.87, 31.23, 22.63. Chemical Formula: $C_{17}H_{19}N_2NaO_4$.

Catalyst 07



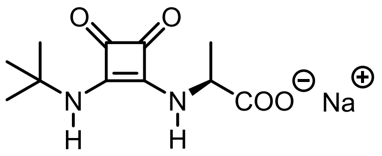
Catalyst 07 1.13 g; yield = 73%. White powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.40 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 4.66 (d, *J* = 6.6 Hz, 2H), 4.12 (p, *J* = 6.8 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 182.33, 182.08, 173.89, 167.00, 139.80, 128.40, 127.77, 126.97, 53.64, 46.43, 22.40.Chemical Formula: $C_{14}H_{13}N_2NaO_4$.

Catalyst 08



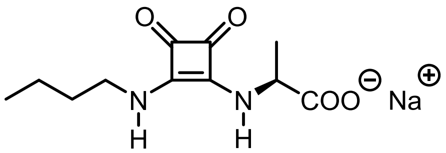
Catalyst 08 1.33 g; yield = 86%. White powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51 (s, 1H), 8.34 (s, 1H), 4.19 – 4.12 (m, 1H), 3.78 (dtd, *J* = 15.0, 7.3, 6.9, 4.0 Hz, 1H), 1.75 (d, *J* = 49.9 Hz, 6H), 1.49 (d, *J* = 35.1 Hz, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 181.93, 173.76, 167.27, 53.67, 52.15, 33.70, 24.85, 24.41, 22.42. Chemical Formula: $C_{13}H_{17}N_2NaO_4$.

Catalyst 09



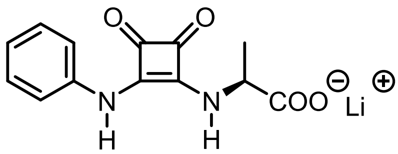
Catalyst 09 1.33 g; yield = 86%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.23 (s, 1H), 8.47 (s, 1H), 4.23 (q, 1H), 1.36 (s, 9H), 1.27 (d, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 182.08, 173.76, 167.86, 167.40, 54.03, 51.86, 30.42, 22.27. Chemical Formula: $C_{11}H_{15}N_2NaO_4$.

Catalyst 10



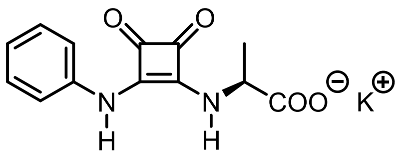
Catalyst 09 0.95 g; yield = 61%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.76 (s, 1H), 8.36 (s, 1H), 4.10 (q, 1H), 3.49 (m, 2H), 1.30 (m, 4H), 0.87 (d, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 182.27, 181.79, 173.78, 168.29, 166.72, 53.73, 42.69, 32.84, 22.53, 19.16. Chemical Formula: $C_{11}H_{15}N_2NaO_4$.

Catalyst 11



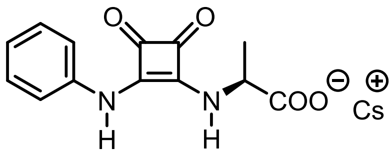
Catalyst 11 1.24 g; yield = 80%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.51 (s, 1H), 9.15 (s, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.31 – 7.20 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 4.49 – 4.40 (m, 1H), 1.37 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.85, 173.94, 167.94, 164.20, 140.47, 128.82, 121.82, 118.77, 54.54, 22.64. $C_{13}H_{11}N_2LiO_4$.

Catalyst 12



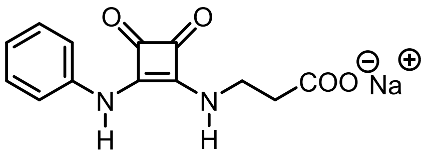
Catalyst 12 1.24 g; yield = 80%. Yellow powder.^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 9.20 (s, 1H), 8.02 (d, J = 7.4 Hz, 2H), 7.29 – 7.21 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 4.44 (s, 1H), 1.37 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.84, 180.18,173.86, 167.91, 164.20, 140.53, 128.77, 121.77, 118.80, 54.55, 22.66. Chemical Formula: $C_{13}H_{11}KN_2O_4$.

Catalyst 13



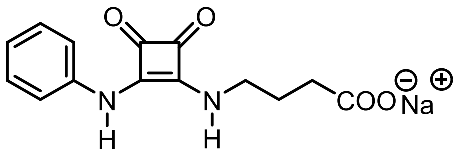
Catalyst 13 1.24 g; yield = 80%. Yellow powder.^{1}H NMR (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 9.18 (s, 1H), 8.01 (d, J = 8.7 Hz, 2H), 7.30 – 7.20 (m, 2H), 6.93 (t, J = 7.3 Hz, 1H), 4.48 – 4.39 (m, 1H), 1.37 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.83, 180.18, 173.80, 167.93, 164.19, 140.51, 128.78, 121.78, 118.78, 54.52, 22.61. Chemical Formula: $C_{13}H_{11}CsN_2O_4$.

Catalyst 14



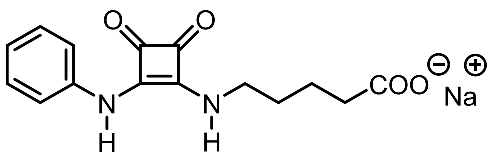
Catalyst 14 1.25 g; yield = 81%. Yellow powder.^{1}H NMR (400 MHz, DMSO-d_6) δ 12.71 (s, 1H), 9.92 (s, 1H), 7.64 (d, J = 7.8 Hz, 2H), 7.27 – 7.20 (m, 2H), 6.91 (t, J = 7.3 Hz, 1H), 3.78 (s, 2H), 2.29 – 2.23 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.35， 180.00， 174.91, 169.70, 164.36, 140.42, 128.69, 118.71, 41.53, 38.90. Chemical Formula: $C_{13}H_{11}N_2NaO_4$.

Catalyst 15



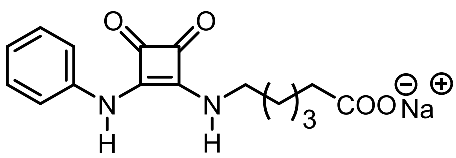
Catalyst 15 1.25 g; yield = 81%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.51 (s, 1H), 9.95 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.25 (dd, J = 8.6, 7.3 Hz, 2H), 6.93 (t, J = 7.3 Hz, 1H), 3.59 (t, J = 7.0 Hz, 2H), 2.11 (t, J = 7.3 Hz, 2H), 1.81 (p, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.10, 180.18， 176.38, 169.68, 164.38, 128.80, 121.69, 118.49, 43.71, 34.69, 28.06. Chemical Formula: $C_{14}H_{13}N_2NaO_4$.

Catalyst 16



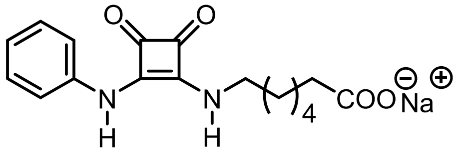
Catalyst 16 1.25 g; yield = 81%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.79 (s, 1H), 10.83 (s, 1H), 7.65 (d, J = 7.4 Hz, 2H), 7.29 – 7.18 (m, 2H), 6.94 – 6.87 (m, 1H), 3.56 (s, 2H), 2.03 (d, J = 6.8 Hz, 2H), 1.62 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.3， 179.93， 177.43, 140.52, 128.72, 118.63, 43.72, 37.74, 30.99, 23.46. Chemical Formula: $C_{15}H_{15}N_2NaO_4$.

Catalyst 17



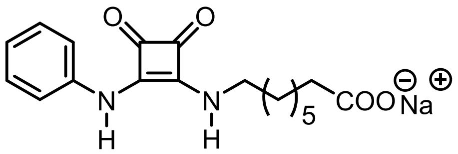
Catalyst 17 0.78 g; yield = 78%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d6) δ 12.70 (s, 1H), 10.29 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.32 – 7.20 (m, 2H), 6.92 (t, J = 7.3 Hz, 1H), 3.56 (d, J = 4.5 Hz, 2H), 2.01 (t, J = 7.3 Hz, 2H), 1.63 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, DMSO-d6) δ 184.18, 180.12, 177.70, 169.44, 128.82, 121.69, 118.50, 43.61, 37.96, 30.72, 26.19, 26.12.

Catalyst 18



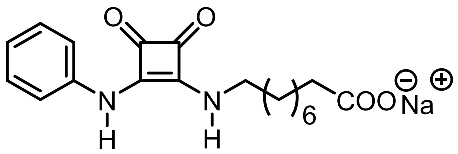
Catalyst 18 1.1 g; yield = 80%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d6) δ 12.83 (s, 1H), 10.50 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.28 – 7.21 (m, 2H), 6.91 (t, J = 7.3 Hz, 1H), 3.59 (d, J = 5.4 Hz, 2H), 2.00 (t, J = 6.9 Hz, 2H), 1.60 – 1.32 (m, 8H). ^{13}C NMR (101 MHz, DMSO-d6) δ 184.31, 180.04, 177.63, 169.82, 164.49, 128.80, 121.68, 118.56, 43.63, 38.08, 30.40, 29.02, 26.25, 26.19.

Catalyst 19



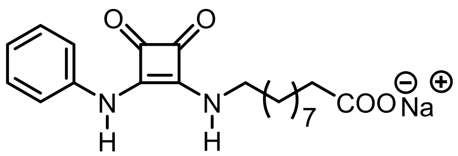
Catalyst 19 0.9 g; yield = 80%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.82 (s, 1H), 10.25 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 3.57 (d, *J* = 7.8 Hz, 2H), 1.98 (t, *J* = 7.1 Hz, 2H), 1.61 – 1.27 (m, 10H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.20, 180.11, 177.48, 169.78, 164.46, 128.81, 121.7, 118.51, 43.45, 38.05, 30.56, 29.24, 28.74, 26.23, 25.91.

Catalyst 20



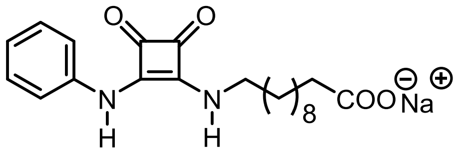
Catalyst 20 1.05 g; yield = 79%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.77 (s, 1H), 10.70 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 3.55 (q, *J* = 5.8 Hz, 2H), 1.98 (t, *J* = 7.0 Hz, 2H), 1.48 (d, *J* = 147.0 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.24, 180.16, 177.53, 128.75, 121.65, 118.63, 42.79, 39.10, 38.89, 38.09, 30.10, 28.23, 27.33, 24.62.

Catalyst 21



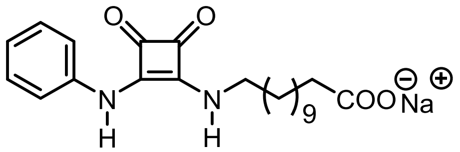
Catalyst 21 1.05 g; yield = 79%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.77 (s, 1H), 10.46 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 1.98 (t, *J* = 7.1 Hz, 2H), 1.58 – 1.26 (m, 14H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.28, 169.93, 128.77, 121.67, 118.62, 43.24, 38.83, 30.28, 29.30, 28.56, 28.01, 27.99, 25.87, 25.21.

Catalyst 22



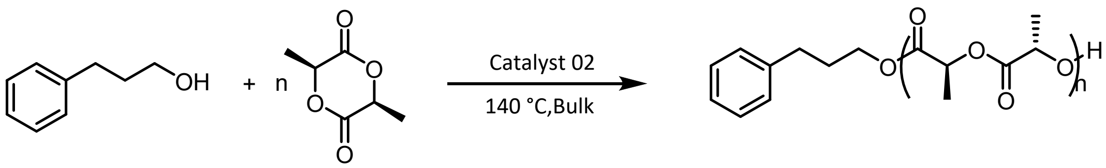
Catalyst 22 1.01 g; yield = 78%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.77 (s, 1H), 10.70 (s, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 7.8 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 3.55 (q, J = 5.8 Hz, 2H), 1.98 (t, J = 7.0 Hz, 2H), 1.27 (s, 16H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.31, 177.54, 164.58, 128.74, 121.64, 118.63, 43.02, 37.89, 30.29, 29.1, 28.56, 28.11, 28.08, 28.05, 25.96, 25.46.

Catalyst 23



Catalyst 23 1.02 g; yield = 77%. Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.86 (s, 1H), 11.10 (s, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.24 (dd, J = 8.5, 7.2 Hz, 2H), 6.92 (t, J = 7.3 Hz, 1H), 3.60 (d, J = 5.8 Hz, 2H), 2.01 – 1.98 (m, 2H), 1.57 – 1.27 (m, 18H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.42, 180.00, 177.65, 169.95, 164.51, 140.50, 128.74, 121.65, 118.71, 43.49, 37.81, 29.86, 27.82, 27.78, 27.75, 27.74, 27.70, 27.67, 27.62, 25.04.

1.2 Ring-opening polymerization of L-lactide catalyzed by squaramide-carboxylate



Scheme S2. Ring-opening polymerization of LLA using catalyst 02

In an argon-filled glovebox, L-LA (240 mg, 1.67 mmol, 25 equiv.), squaramide-carboxylate (4.7 mg, 0.017 mmol 0.25 equiv), and PPA (9 µL, 0.067 mmol 1 equiv) were charged in a 10 mL reaction vial. The reaction mixture was stirred at 140 °C. After predetermined time, the polymerization was quenched by benzoic acid. The attained polymer was dissolved in a minimum amount of CH_2Cl_2 and precipitated in cold methanol. The monomer conversion that was determined from the ^{1}H NMR spectroscopy. ^{1}H NMR($CDCl_3$) δ (ppm), 1.58 (m, 3H × n, (–CH_3)n), 1.97 (q, 2H, ArCH$_2$CH_2–), 2.67 (t, 2H, ArCH_2–), 4.15 (m, 2H, ArCH2CH2CH_2–), 4.36 (m, 1H, –CH(CH$_3$)OH), 5.10–5.23 (q, 1H × n − 1, (–CH(CH$_3$)O–)$_{n-1}$), 7.15–7.31 (m, 5H, aromatic).

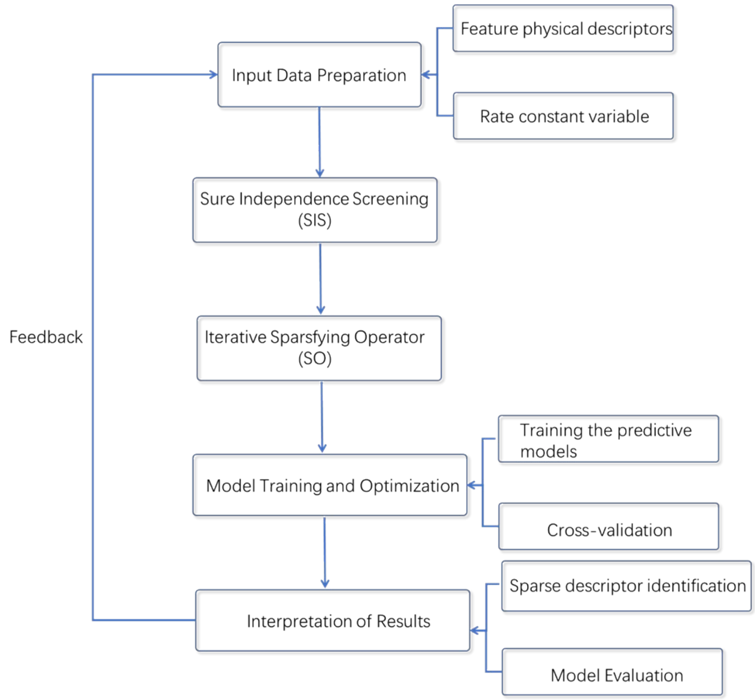


Chart S1. SISSO Algorithm Workflow Representation

Supporting Tables

Table S1. Ring-opening polymerizations of LLA catalyzed by different CS.[a]

Entry	Catalyst	Time (h)	Conv.[b] (%)	TOF[c] (h^{-1})	$M_{n,calcd}$[d] (kg mol^{-1})	$M_{n,NMR}$[e] (kg mol^{-1})	$M_{n,SEC}$ (kg mol^{-1})	$Đ$[d]
1	**01**	6	13	2.2	0.6	0.6	–	–
2	**02**	6	61	10.2	2.3	2.0	3.6	1.08
3	**03**	6	63	10.5	2.3	2.0	4.1	1.10
4	**04**	6	64	10.7	2.4	2.1	1.5	1.11
5	**05**	6	49	8.2	1.8	1.8	4.3	1.17
6	**06**	6	53	8.8	2.0	1.6	12.4	1.02
7	**07**	6	42	7.0	1.6	1.4	3.6	1.09
8	**08**	6	37	6.2	1.4	2.0	2.8	1.10
9	**09**	6	45	7.5	1.7	1.6	2.8	1.05
10	**10**	6	59	9.8	2.1	1.9	4.1	1.10

[a] $[LLA]_0/[PPA]_0/[Cat.]$ = 25/1/0.25; Temp.140°C; bulk. [b] Determined by ^1H NMR in $CDCl_3$. [b] Determined by ^1H NMR in $CDCl_3$. [c] Calculated from $([M]_0/[I]_0)$ × conv. × (M_w of LLA) + (M_w of BnOH). [d] Determined by SEC in THF using an absolute method of measurement (d*n*/d*c* = 0.05). [e] Calculated by TOF (h^{-1}) = $([M]_0$ × Conv.)/($[Cat.]_0$ × polymerization time).

Table S2 Apparent rate constants (kobs) of the LLA polymerization.a

Entry	Crown	Cation	$[Crown]_0$ / $[Cat.]_0$	k_{obs}/× 10^{-4} min^{-1}
1	12	Li^+	0	56.9
2	12	Li^+	0.5	2.3
3	12	Li^+	1	2.6
4	12	Li^+	2	6.6
5	12	Na^+	0	96.5
6	12	Na^+	0.5	70.2
7	12	Na^+	1	70.7
8	12	Na^+	2	223.6
9	12	K^+	0	158.1
10	12	K^+	0.5	223.7
11	12	K^+	1	158.1
12	12	K^+	2	231.5
13	15	Li^+	0	56.9
14	15	Li^+	0.5	98.6
15	15	Li^+	1	4.1
16	15	Li^+	2	1.5
17	15	Na^+	0	96.5
18	15	Na^+	0.5	111.8
19	15	Na^+	1	111.8
20	15	Na^+	2	103.8
21	15	K^+	0	158.1
22	15	K^+	0.5	223.6
23	15	K^+	1	169.0
24	15	K^+	2	223.6
25	18	Li^+	0	56.9
26	18	Li^+	0.5	4.8
27	18	Li^+	1	1.1
28	18	Li^+	2	5.4
29	18	Na^+	0	96.5
30	18	Na^+	0.5	158.1
31	18	Na^+	1	174.6
32	18	Na^+	2	223.7
33	18	K^+	0	158.1
34	18	K^+	0.5	260.1
35	18	K^+	1	260.1
36	18	K^+	2	158.1

[a]Determined from the semilogarithmic plots of LLA polymerizations initiated with PPA and catalysed with different catalysts.

Reaction conditions of the polymerizations: $[LLA]_0/[PPA]_0/[\text{ Catalysis}]_0$ = 25/1/0.25, 140 °C

Table S3 Primary features derived from bench experiments and DFT simulation

Entry	Feature symbol	Description	Unit
1	c	ratio of crown ether	-
2	r_d	radius of alkali cation	Å
3	ΔE	dissociation energy of catalyst complex (electronic energy)	eV
4	ΔG	dissociation energy of catalyst complex (Gibbs free energy)	$kcal \cdot mol^{-1}$
5	ΔE_n	weight of ΔE ($\Delta E_n = \Delta E \cdot c$)	eV
6	ΔG_n	weight of ΔG ($\Delta G_n = \Delta G \cdot c$)	$kcal \cdot mol^{-1}$
7	%V_Bur[a]	percent buried volume centered on alkali cation	-
8[b]	E_N	the electronic energy of catalyst molecule	Hartree
9	E_{N-1}	the electronic energy of catalyst molecule (subtract one lectron)	Hartree
10	E_{N+1}	the electronic energy of catalyst molecule (gain one electron)	Hartree
11	$E^{N}{}_{HOMO}$	HOMO orbital energy of catalyst	Hartree
12	$E^{N-1}{}_{HOMO}$	HOMO orbital energy of catalyst	Hartree
13	V_{IP}	vertical ionization potential	Hartree
14	V_{EA}	vertical electron affinity	-
15	C_p	chemical potential	-
16	H	hardness	-
17	S	softness	$Hartree^{-1}$
18	N_i	nucleophilicity index	Hartree
19	E_i	electrophilicity index	-
20	H_{sf}	Hirshfeld charge of alkali cation	-

21	H_{adch}	atomic dipole moment-corrected Hirshfeld charges	-
22	$M_q{}^{N}$	Hirshfeld charge of alkali cation	-
23	$M_q{}^{N-1}$	Hirshfeld charge of alkali cation (subtract one electron)	-
24	$M_q{}^{N+1}$	Hirshfeld charge of alkali cation (gain one electron)	-
25	M_{f+}	condensed Fukui function (nucleophilic reaction)	-
26	M_{f-}	condensed Fukui function (electrophilic reaction)	-
27	M_{nu}	condensed local nucleophilicity	-
28	M_{s+}	relative nucleophilicity index	-
29	M_{s-}	relative electrophilicity index	-

a the optimized structures were analysed using the open-source Python package DBSTEP[1]; b data presented at entry 8-29 derived from optimized structures and further analysed by the Multiwfn software package[2].

Table S4. The correlation between k_{obs} and physical descriptors analysed by SISSO model.

Q1	$k_{obs} = b + a \cdot \left(\frac{E_N}{\Delta E_n}\right) \cdot (M_{S+} - \Delta G_n)$	R^2= 0.74 RMSE = 3.57
Q2	$k_{obs} = b + a_1\left(\left\|\left((H_{adch} \cdot c) - \left(\frac{M_{nu}}{H_{adch}}\right)\right)\right\|\right) + a_2((\frac{E_N}{\Delta E_n}) \cdot (M_{S+} - \Delta G_n))$	R^2= 0.89 RMSE = 2.34
Q3	$k_{obs} = b + a(E_N \cdot r) \cdot (M_{S+} - \Delta E)$	R^2 = 0.69 RMSE = 3.87
Q4	$k_{obs} = b + a_1\left(\frac{\sin(\Delta E_n)}{M_{S+} - \%V_{Bur}}\right) + a_2(E_N \cdot r \cdot (M_{S+} - \Delta G))$	R^2 = 0.88 RMSE = 2.45

Supporting Figures

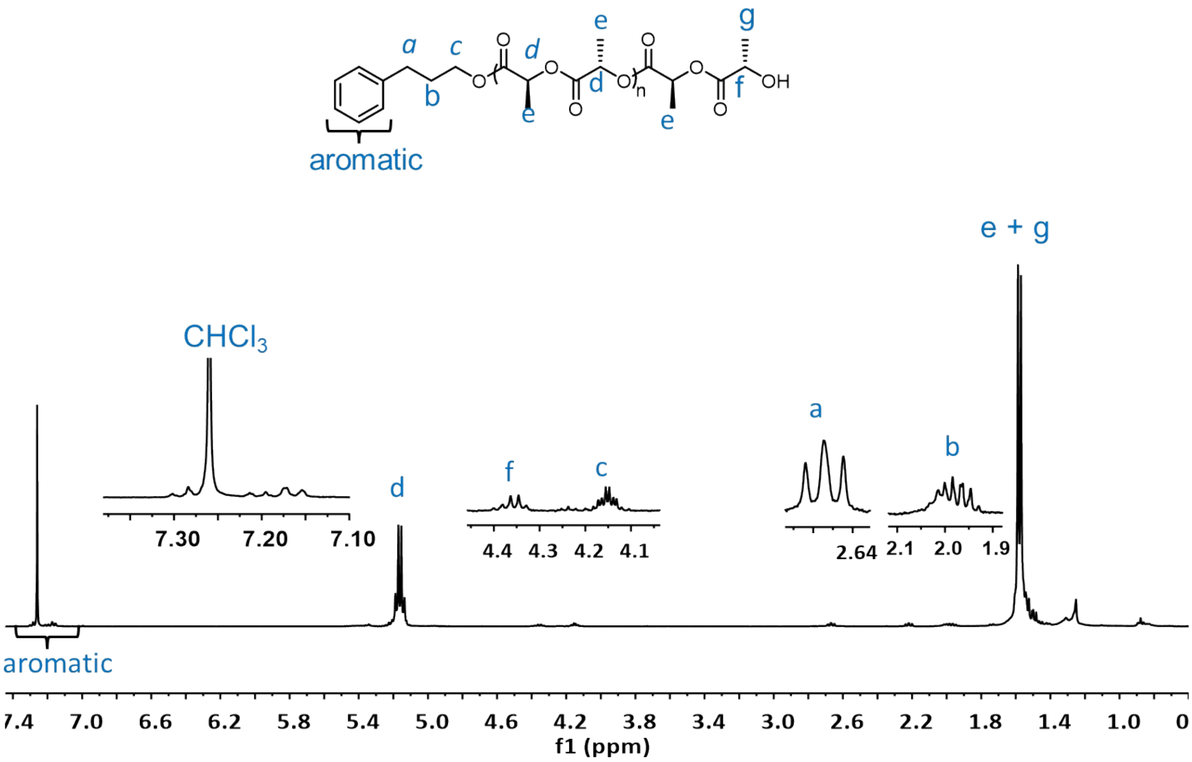


Figure S1. [1]H NMR spectrum of polylactide initiated by PPA in $CDCl_3$ (Table **1**, entry 1). Experimental conditions: 1.6 mmol LLA, $[PPA]_0/[Catalysis]_0/[LLA]_0 = 1/0.25/25$, at 140 °C, in bulk for 6 h.

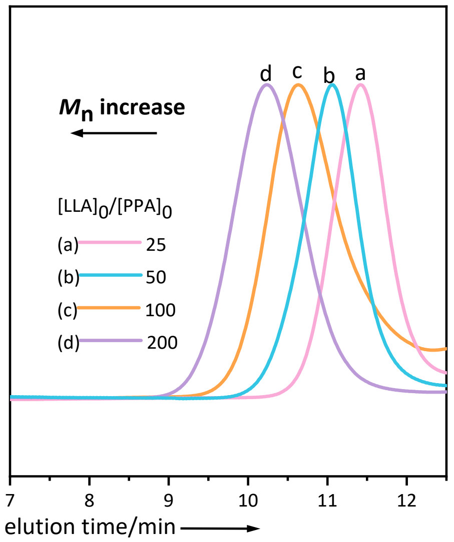
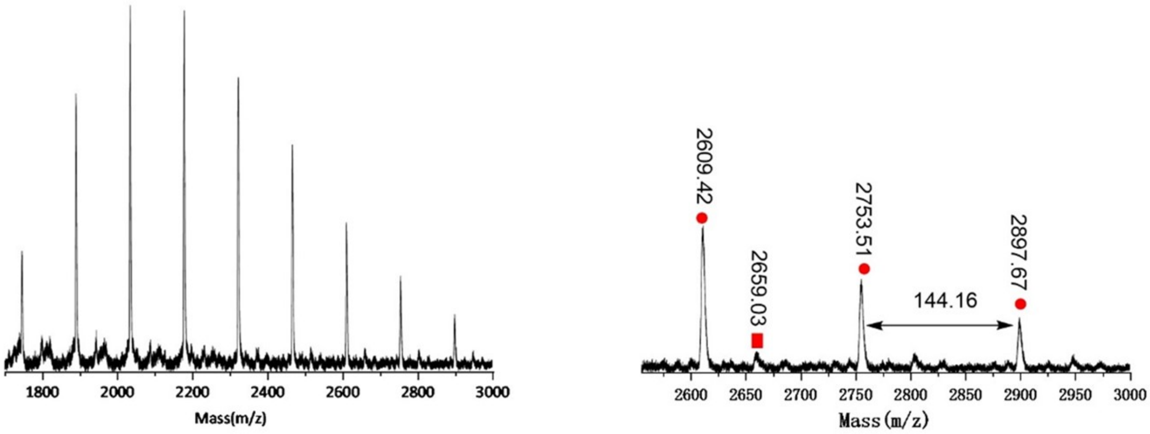
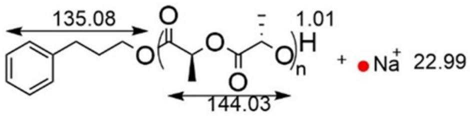


Figure S2. SEC traces of the obtained PLA samples with series ratios of $[M]_0/[I]_0$=25; 50;100; 200 (**Table 1**, entry 1-4) (eluent, THF; flow rate, 0.7 ml min^{-1}).





mass = [PPA] + [monomer unit] x n + Na^+

or

mass = [H_2O] + [monomer unit] x n + Na^+

Cationic Agent		[initiator] = PPA n 17	18	19
Na^+	Calc.	2609.29	2753.42	2897.55
	Exp.	2609.42	2753.51	2897.67

Figure S3. MALDI mass spectrum of PLLA (precipitation from ethanol), magnification between m/z = 1800 and m/z = 3000. **Table 1** entry 1. Purification was carried out by precipitation in ethanol.

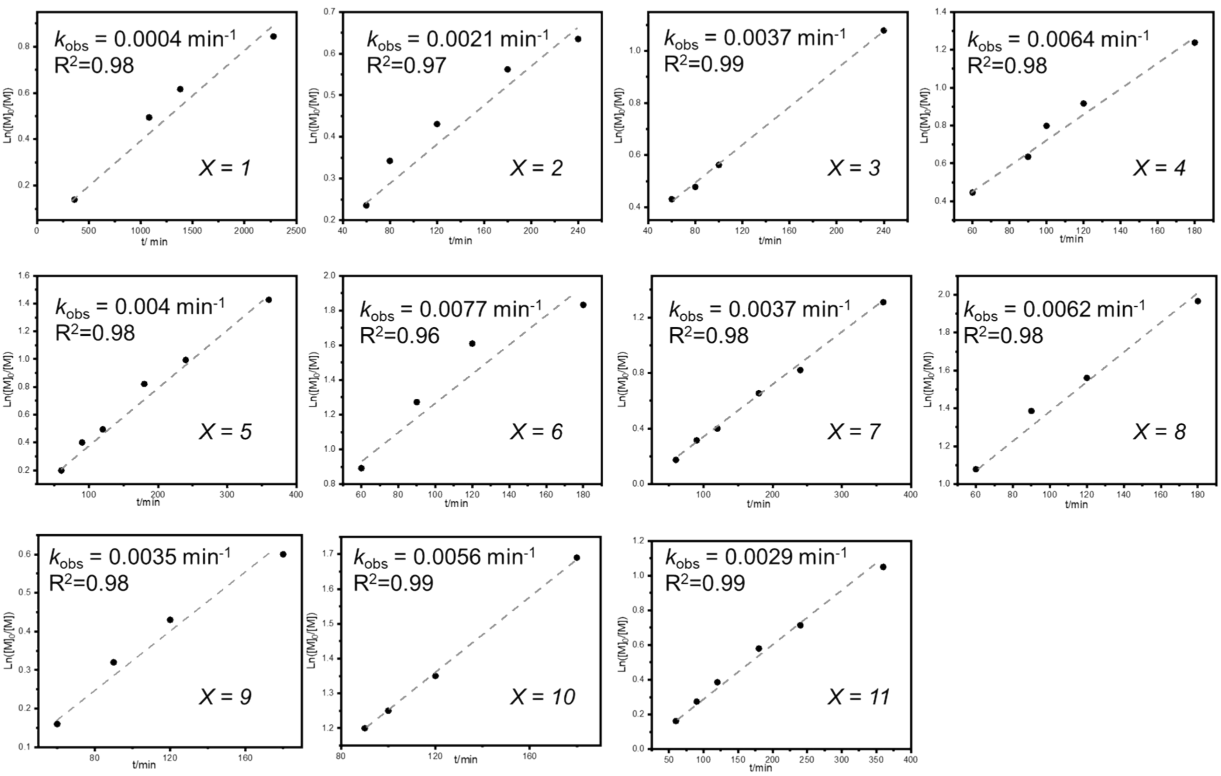


Figure S4. Semilogarithmic kinetic plot of the ROP of LLA catalyzed by squaramide-carboxylate with different lengths of CH_2 segments. Conditions: $[LLA]_0/[BnOH]_0/[Cat.] = 25/1/0.25$, T = 140°C in bulk.

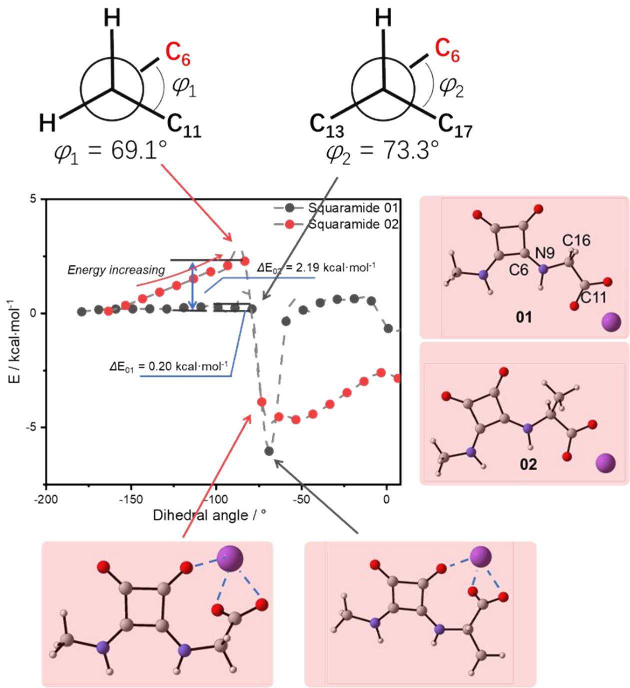


Figure S5. The relaxed scan of dihedral angle C6-N9-C16-C11. The phenyl group was replaced by methyl to reduce the cost of simulation. The gradual increase of dihedral angle leads to different the rotation energies, where the high energy required for **02** to rotate as compared to **01** (ΔE_{02} vs ΔE_{01}, 2.19 vs 0.2 kcal·mol^{-1}). This demonstrate the steric hinderance induced by methyl group enables a stable structure for the catalyzation process. Calculation level: B3LYP//6-31+G(d,p).

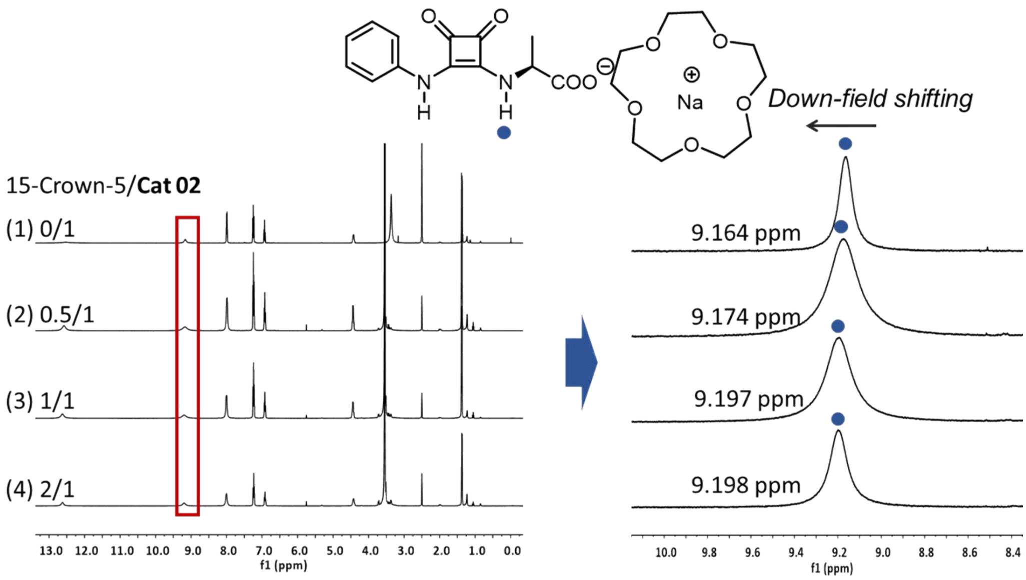


Figure S6. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of **catalyst 02** and 15-crown-5 with different ratios.

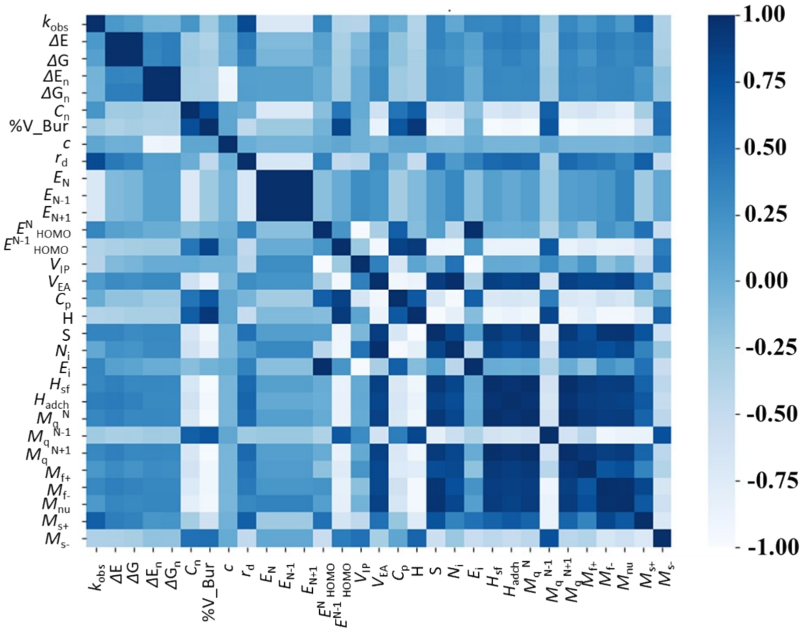


Figure S7. Heatmap representing the correlation between k_{obs} and single descriptor (electronic, thermodynamic, and bench results) for CS, deeper blue color represents stronger correlation.

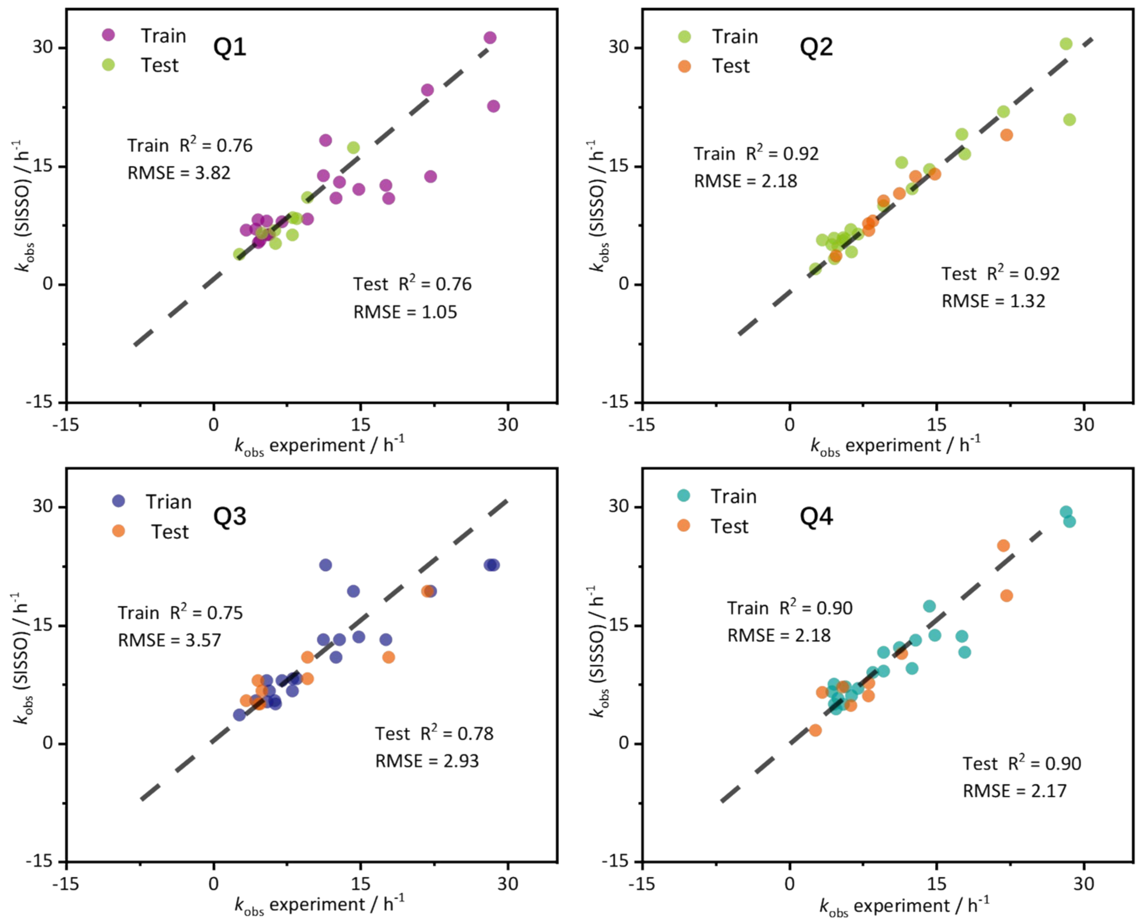


Figure S8. The visulization of the representative SISSO model with different physical descriptors. 70% of k_{obs} was randomly selected for training, while the remaining 30% was used for testing.

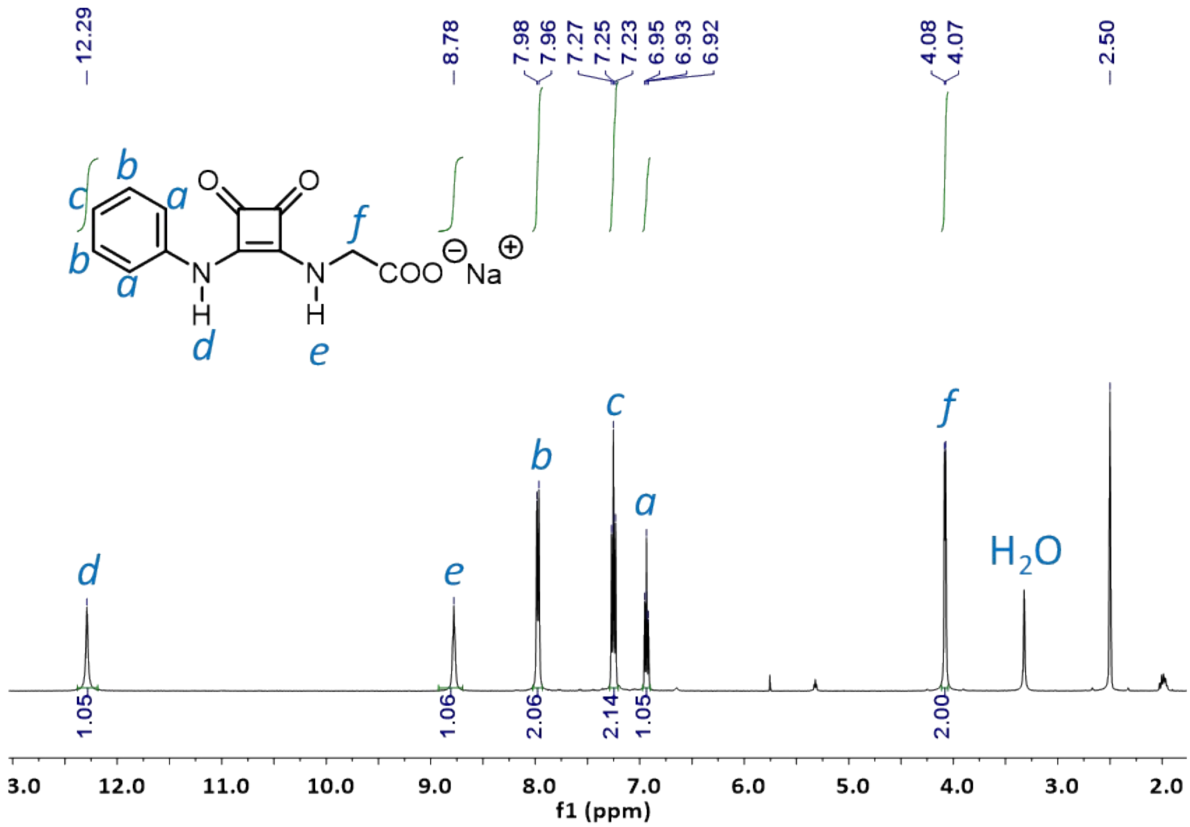


Figure S9. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 01

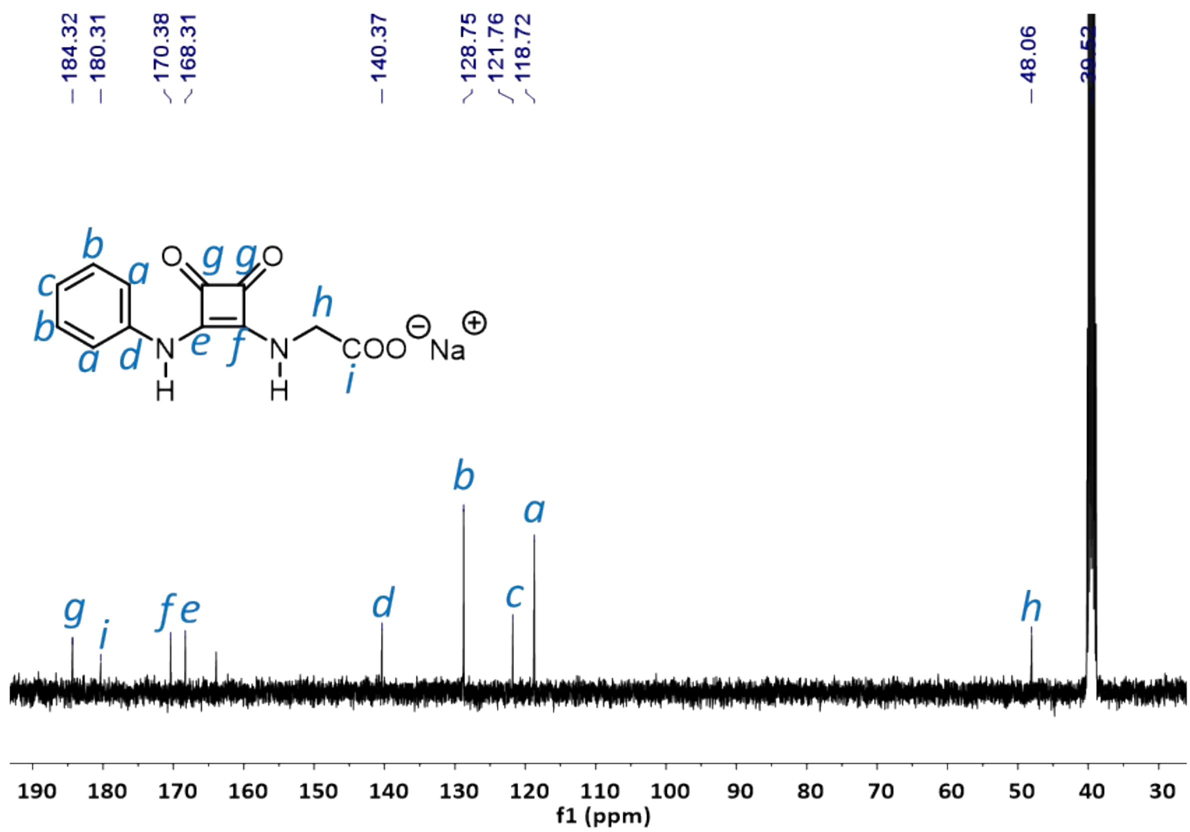


Figure S10. ^{13}C NMR spectrum (DMSO-d_6, 101 MHz) of catalyst 01

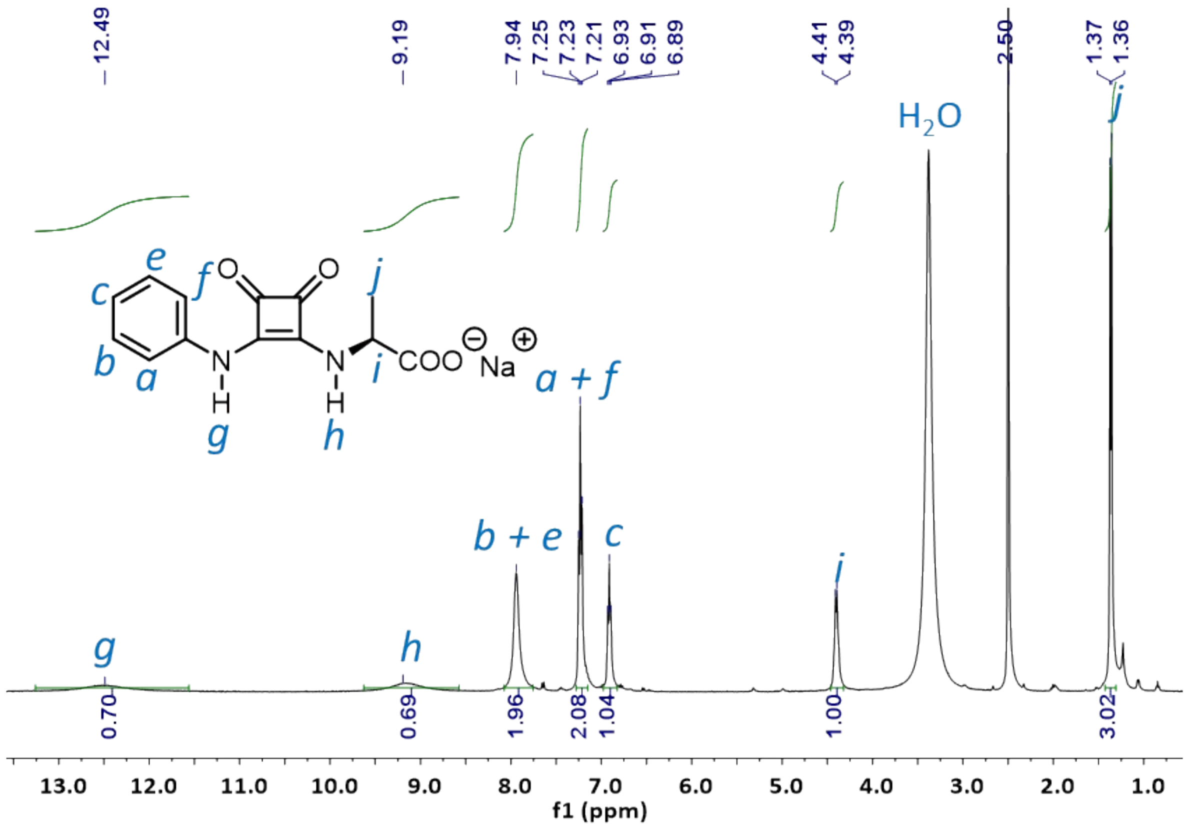


Figure S11. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 02

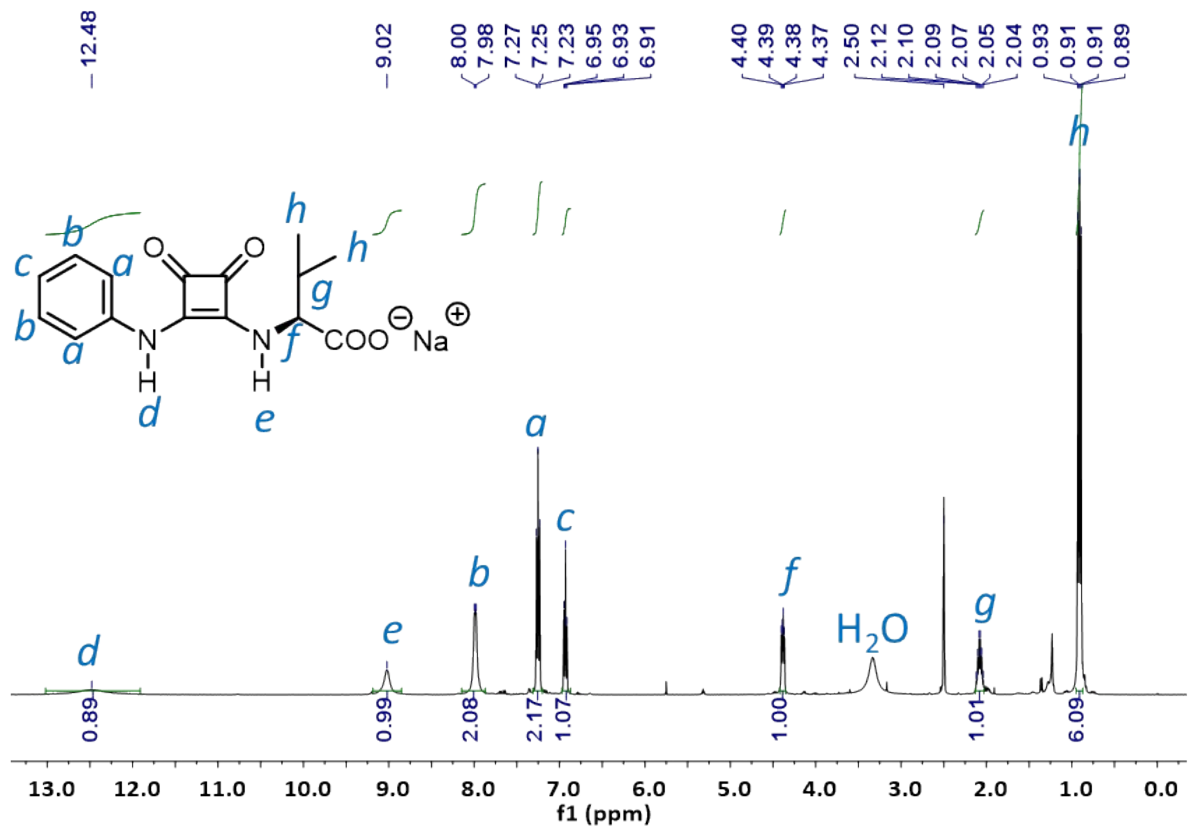


Figure S12. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 03

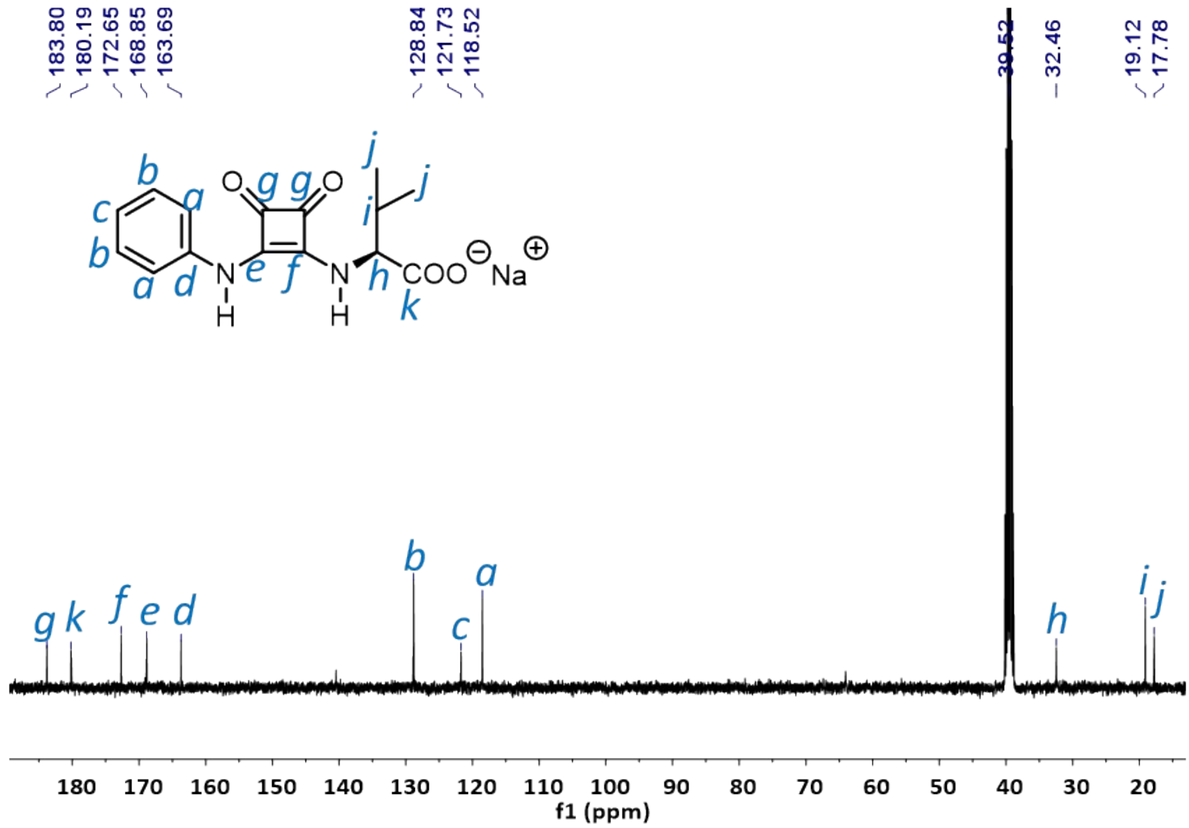


Figure S13. ^{13}C NMR spectrum (DMSO-d_6, 101 MHz) of catalyst 03

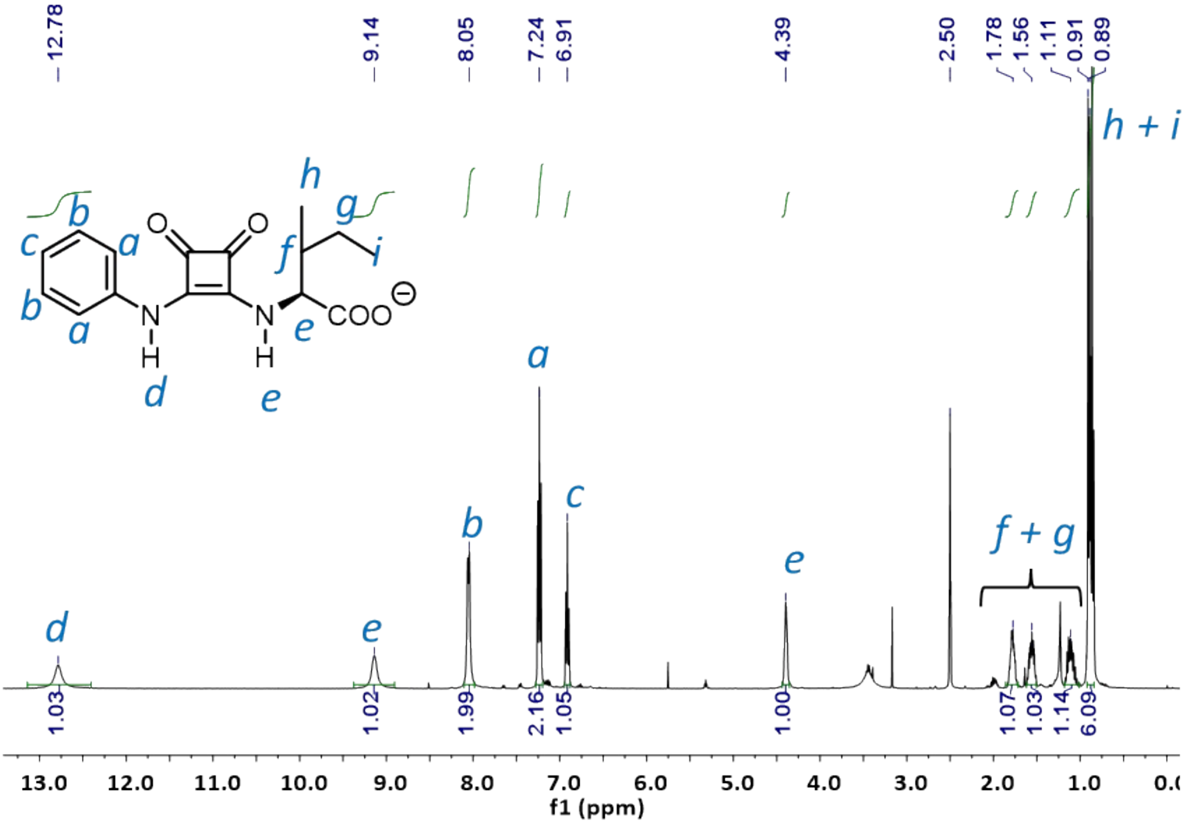


Figure S14. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 04

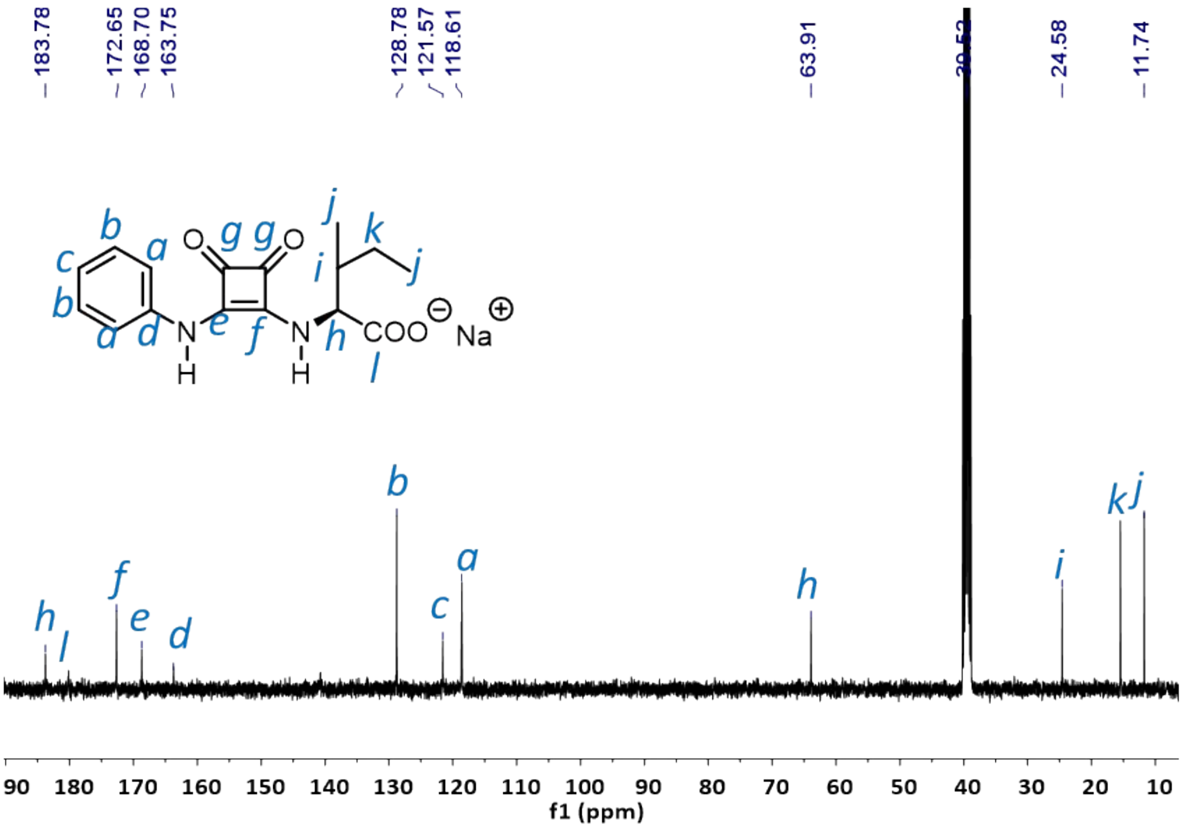


Figure S15. ^{13}C NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 04

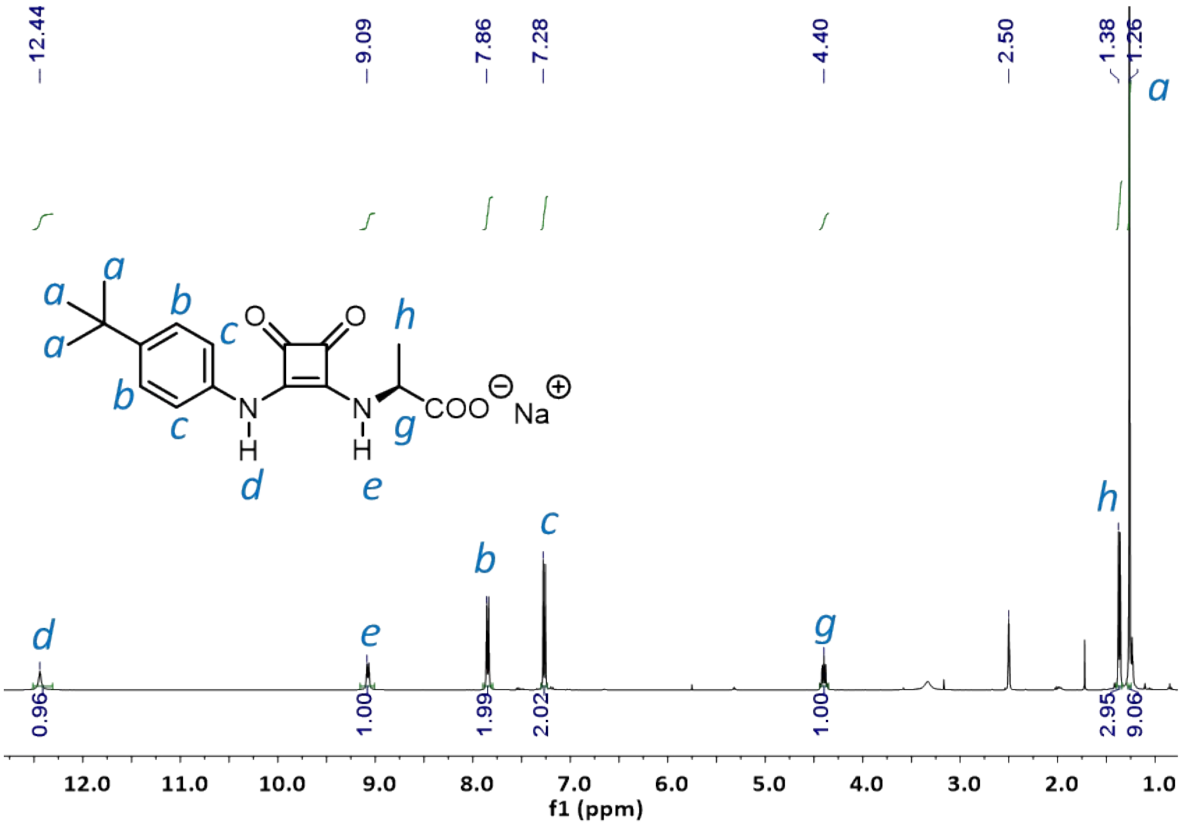


Figure S16. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 05

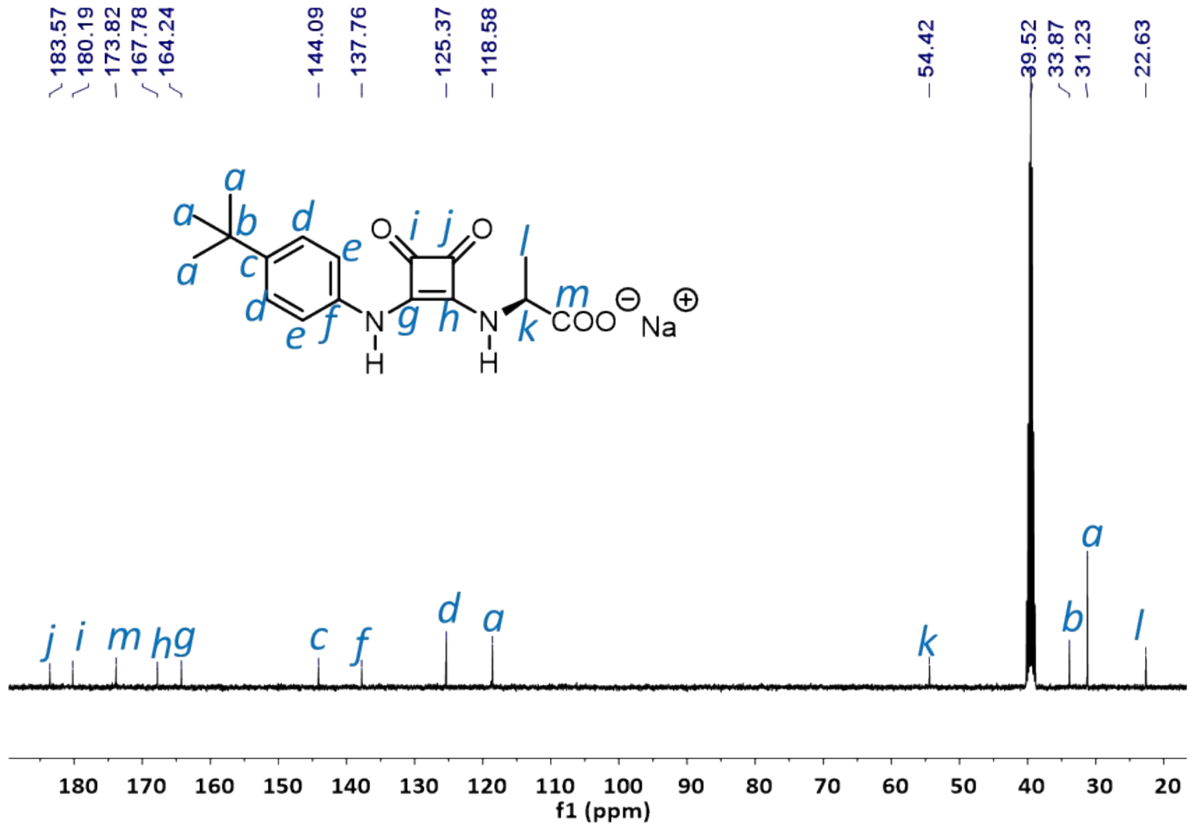


Figure S17. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 05

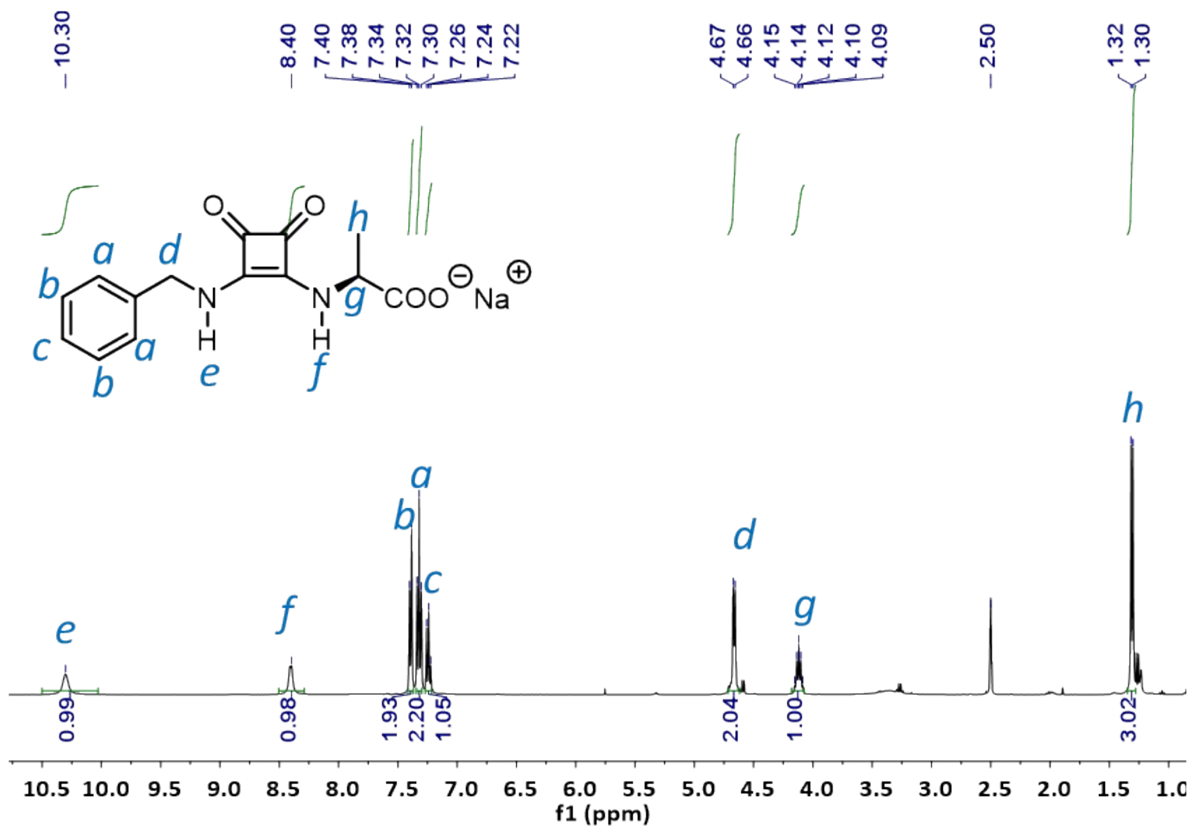


Figure S18. ^{1}H NMR spectrum (DMSO-d_6,400 MHz) of catalyst 07

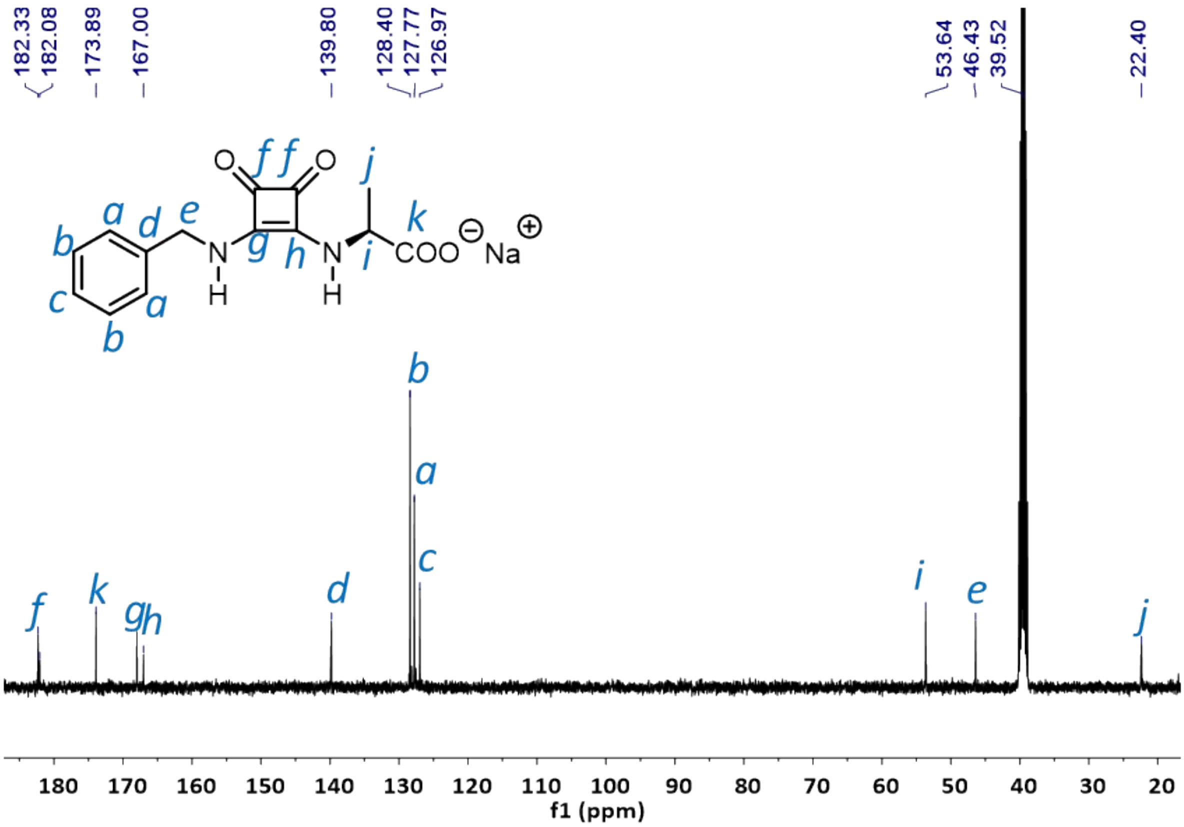


Figure S19. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 07

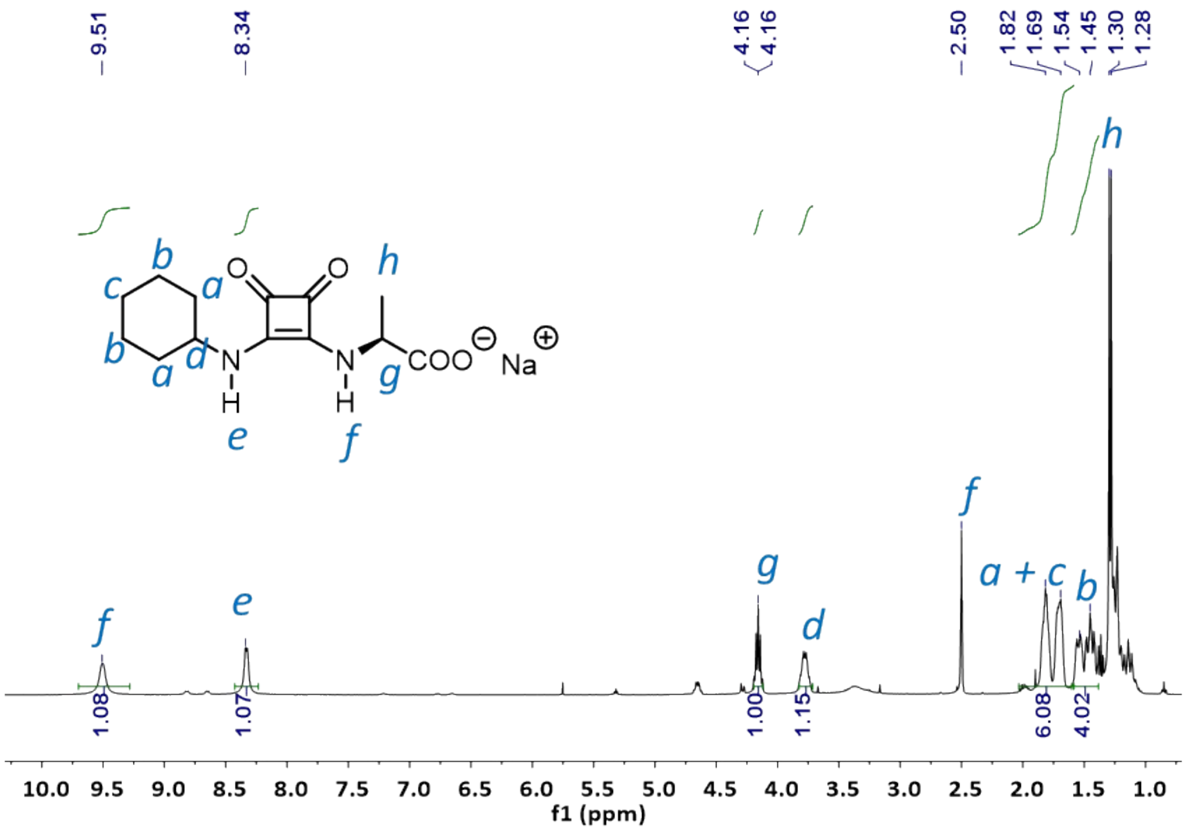


Figure S20. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 08

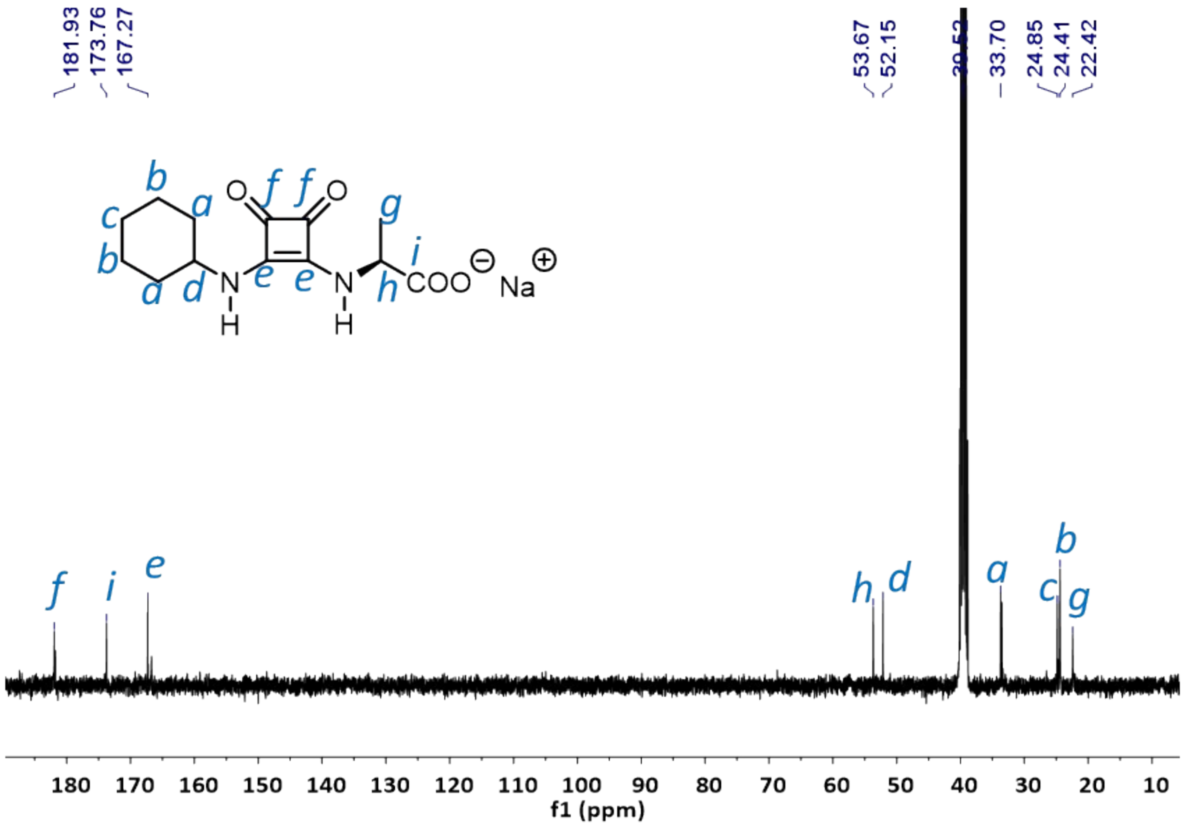


Figure S21. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 08

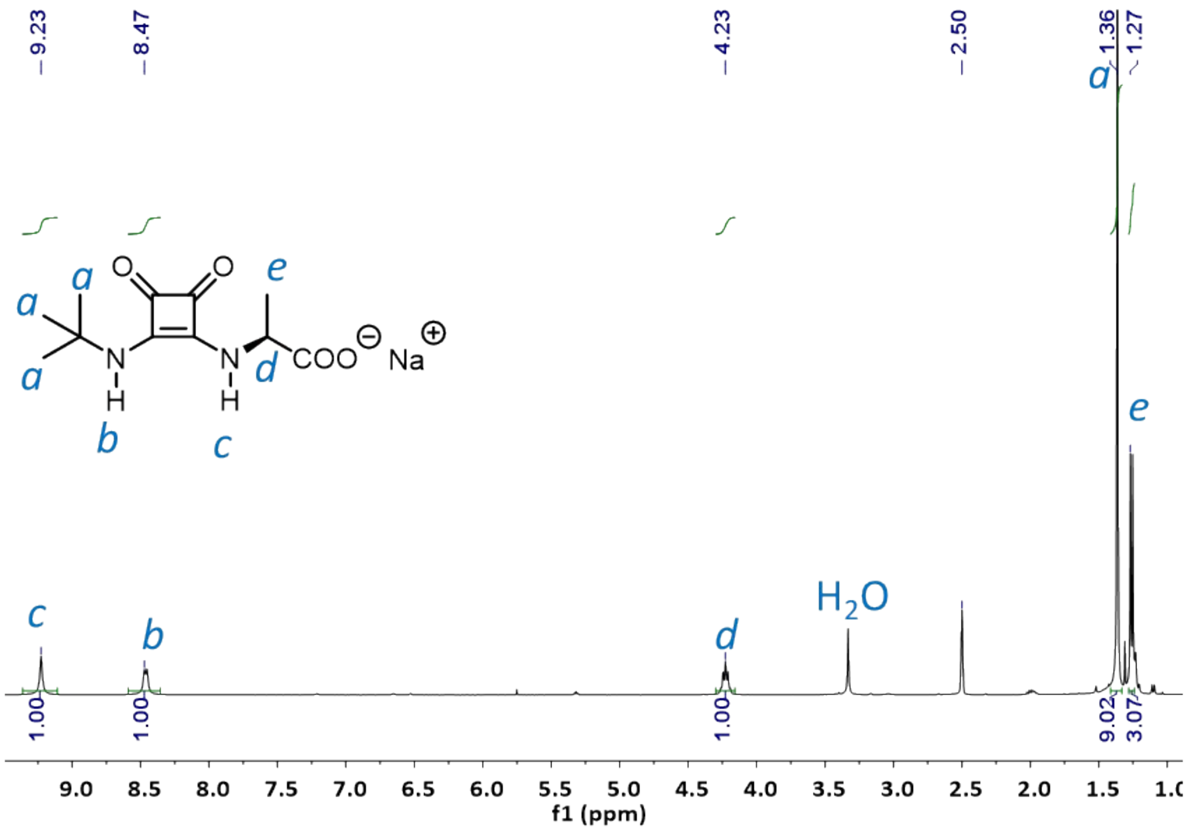


Figure S22. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 09

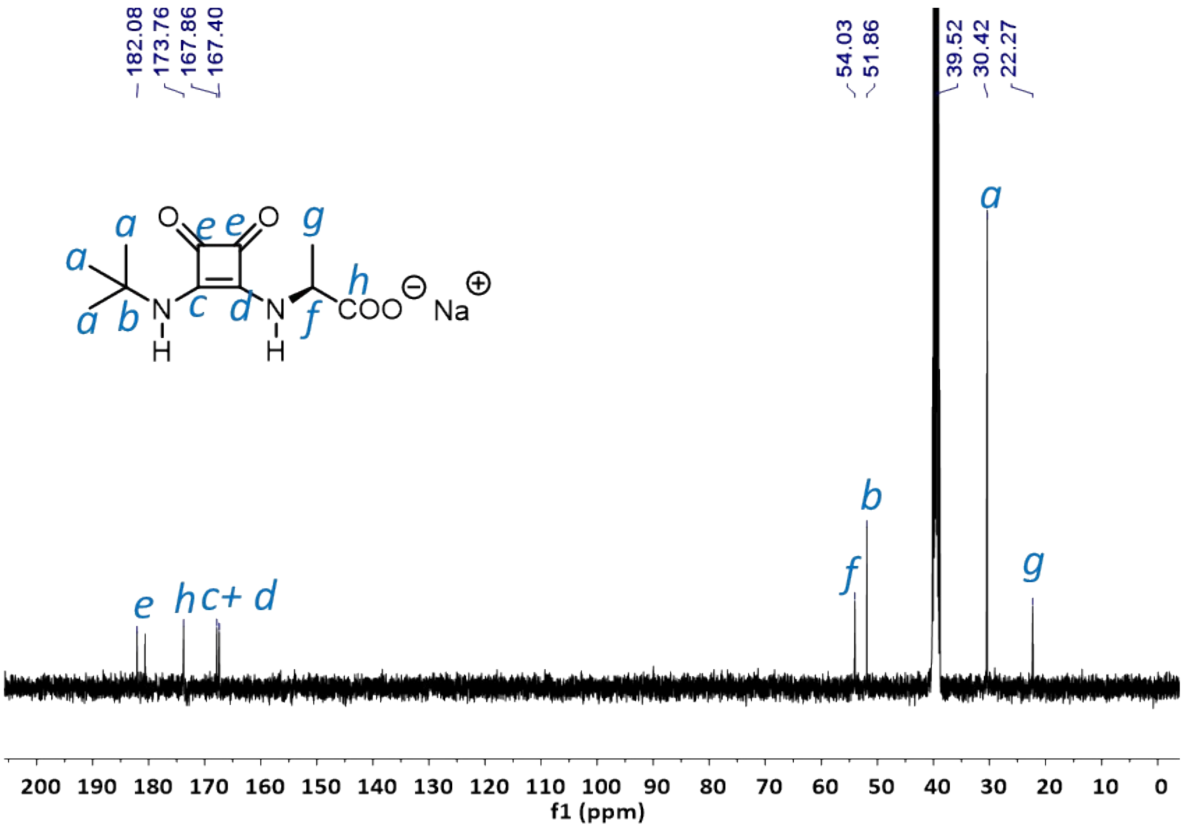


Figure S23. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 09

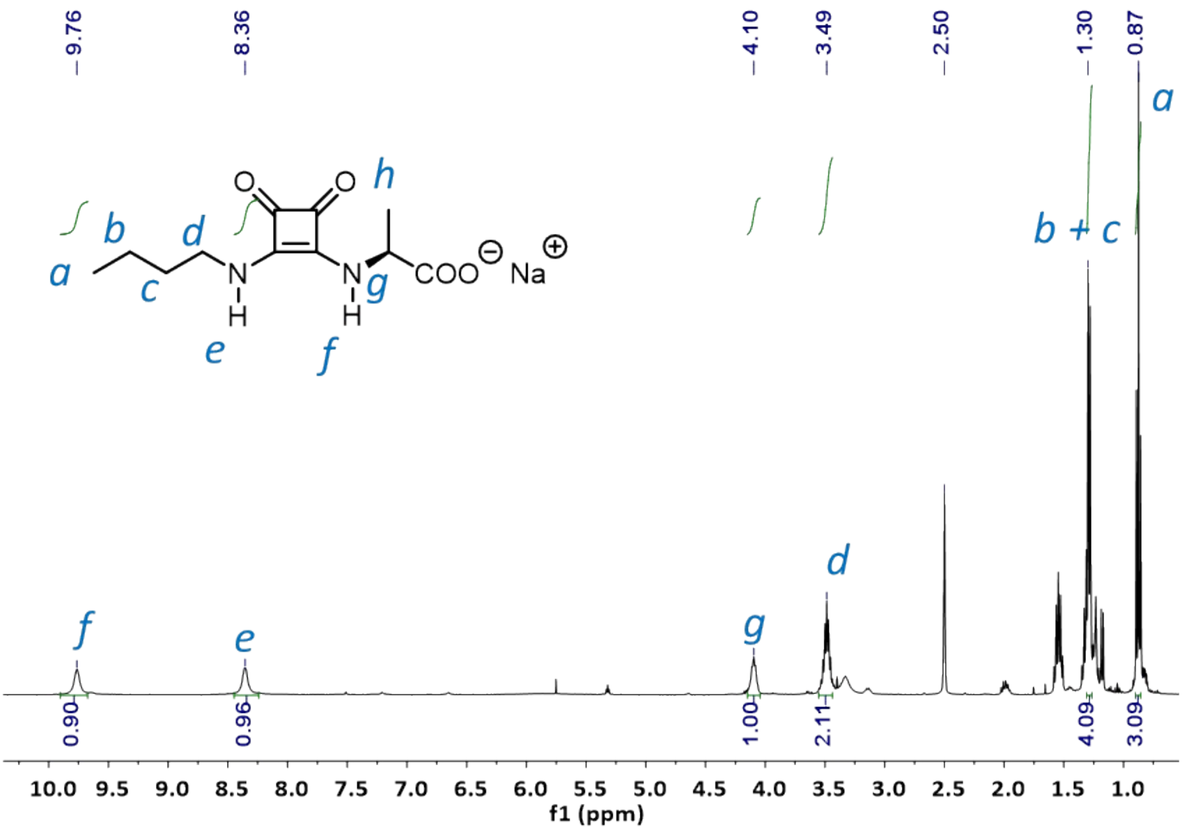


Figure S24. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 10

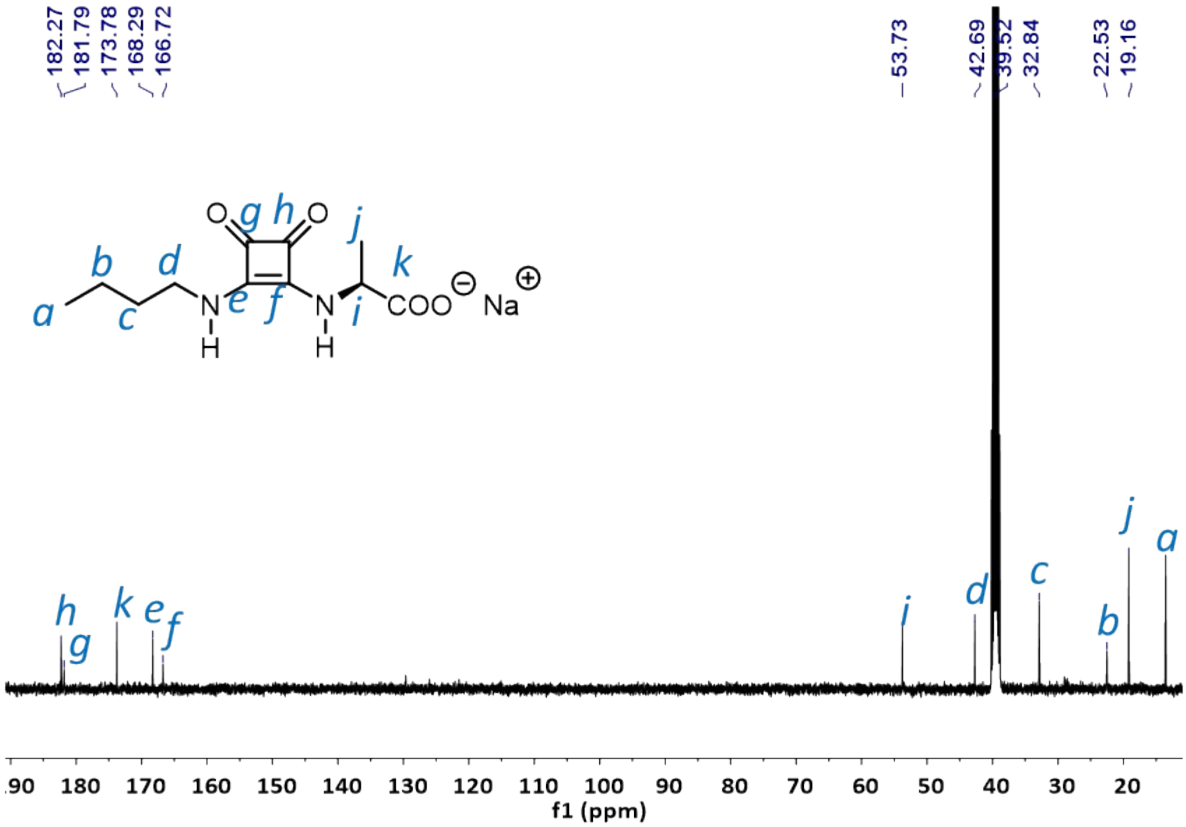


Figure S25. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 10

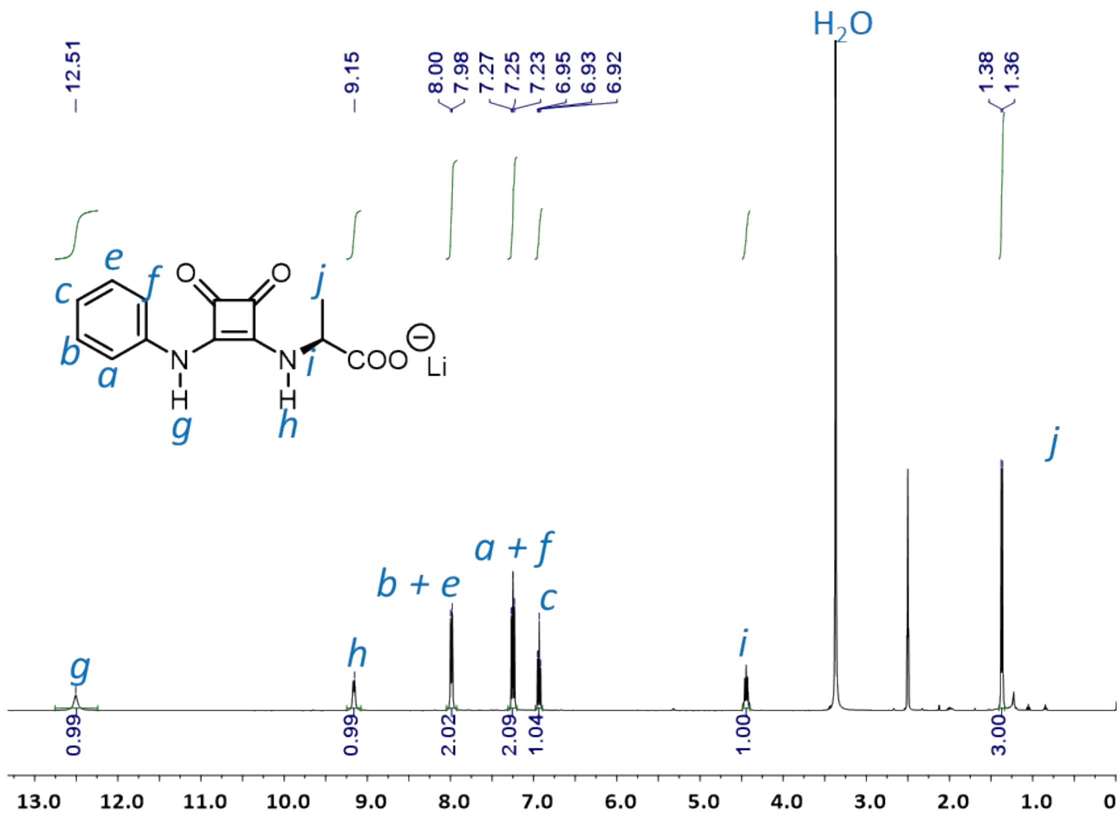


Figure S26. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 11

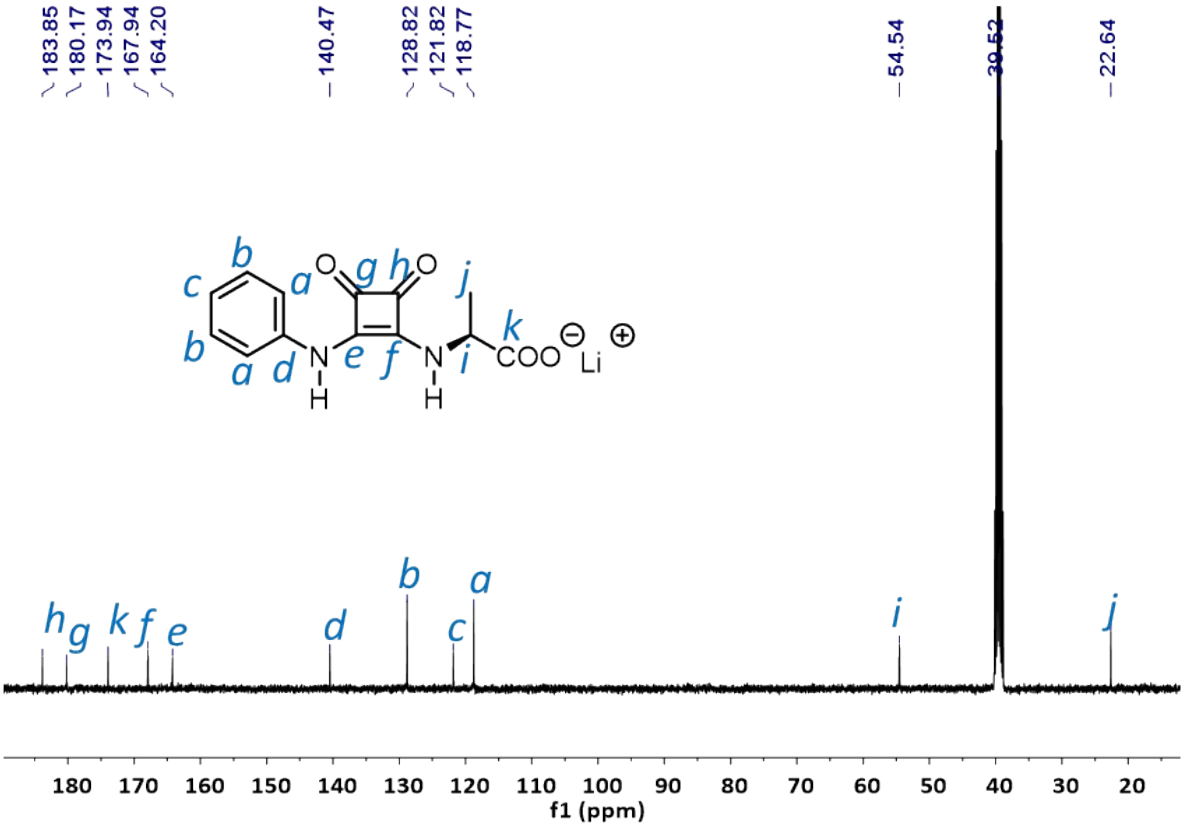


Figure S27. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 11

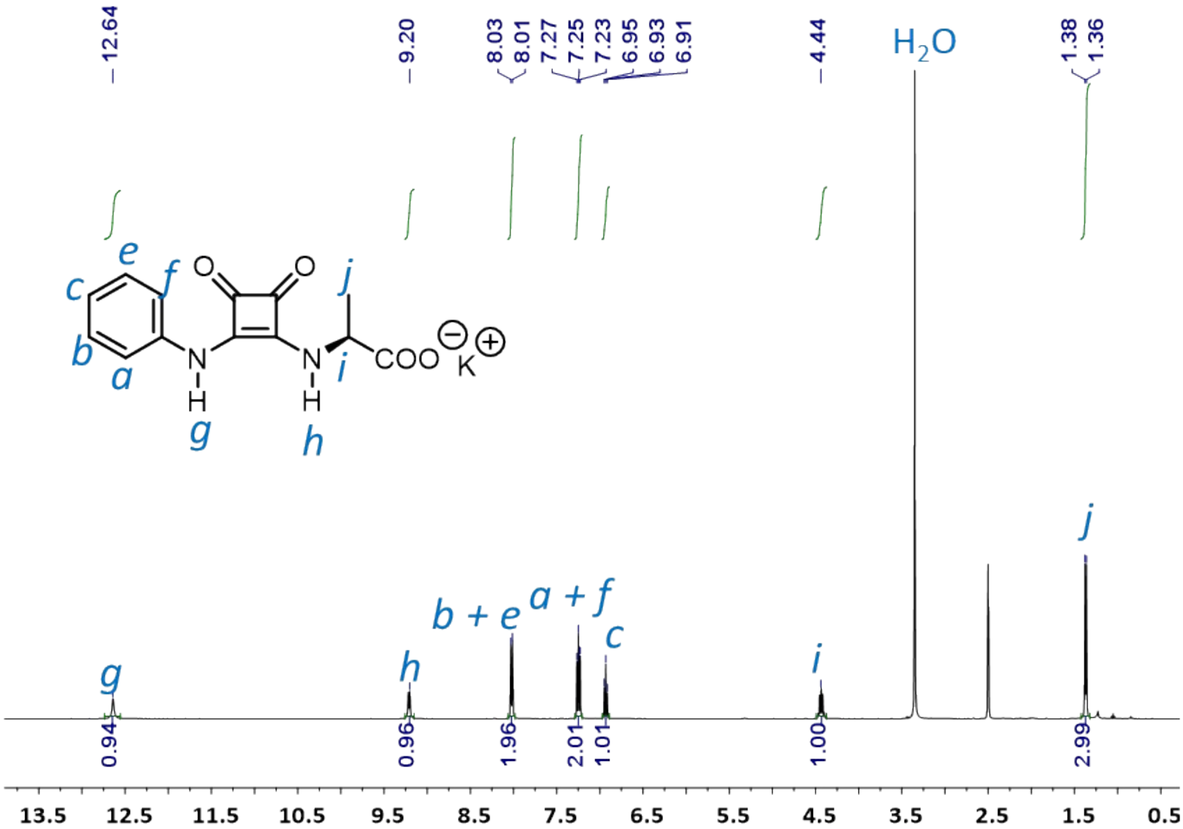


Figure S28. ^1H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 12

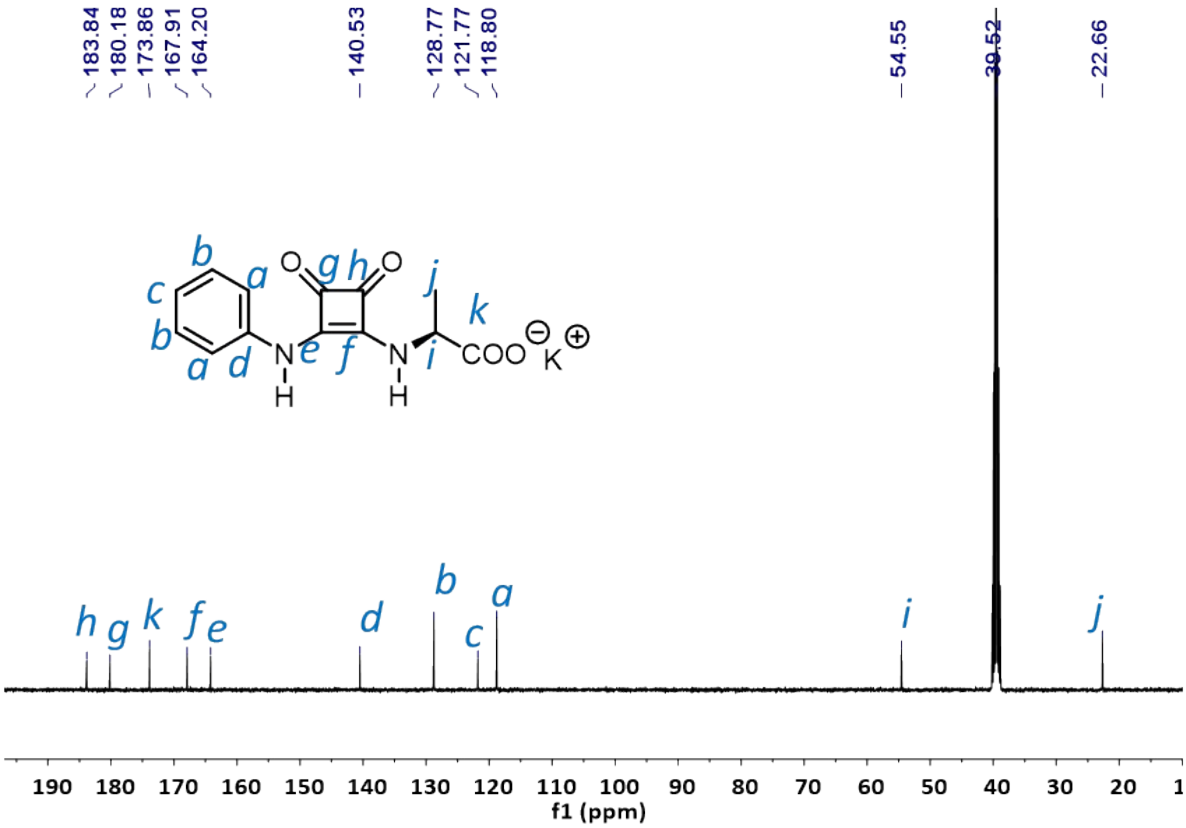


Figure S29. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 12

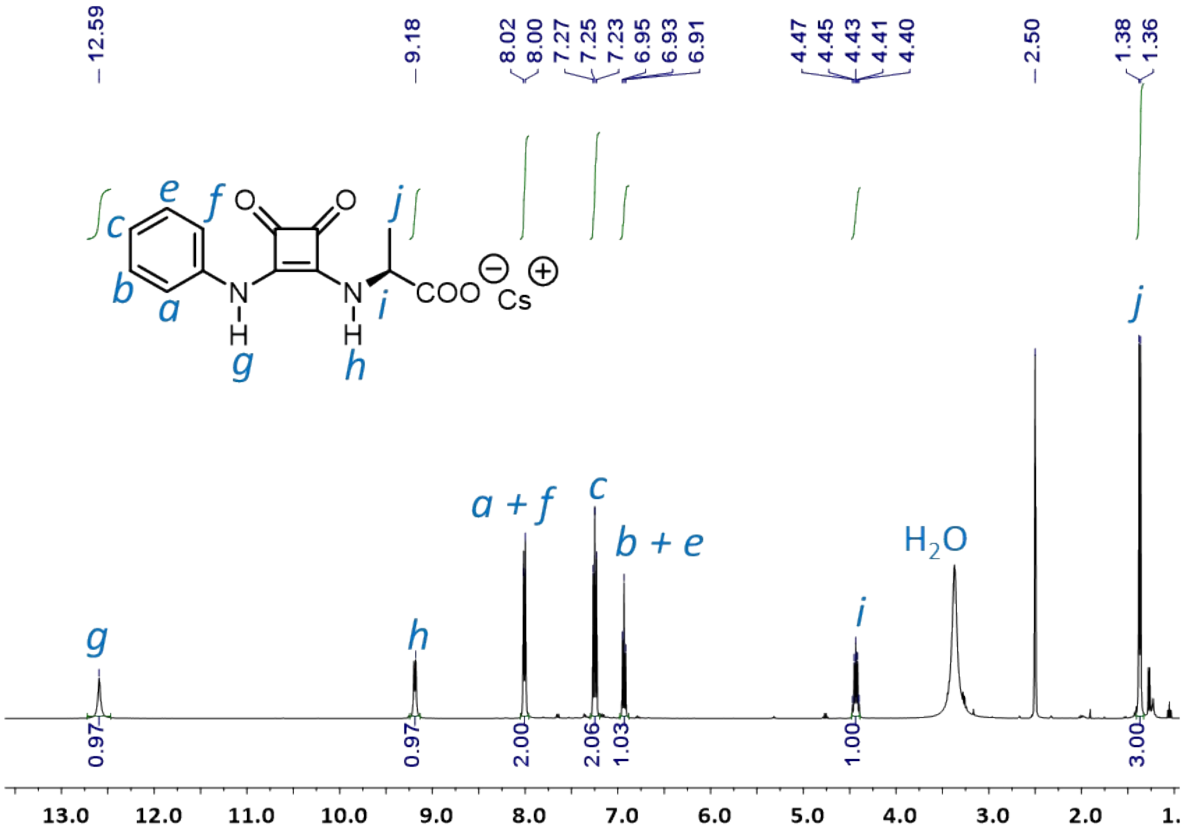


Figure S30. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 13

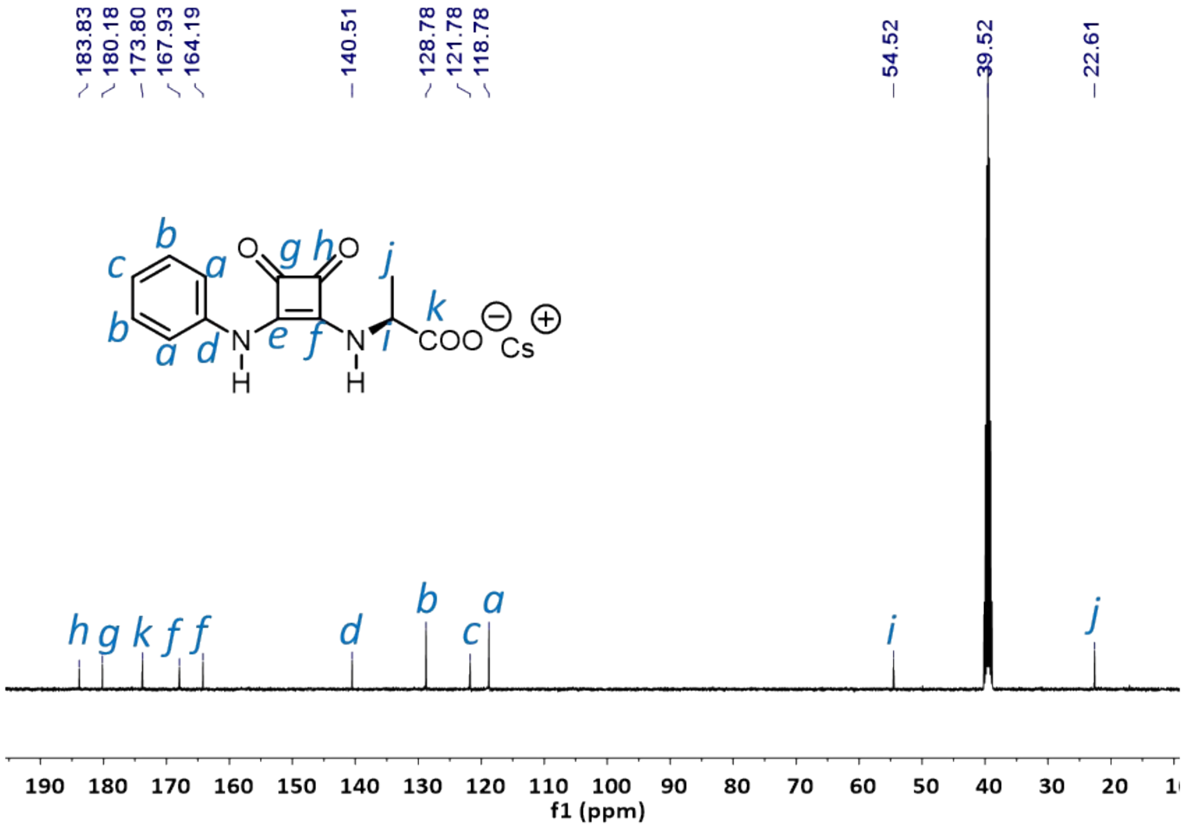


Figure S31. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 13

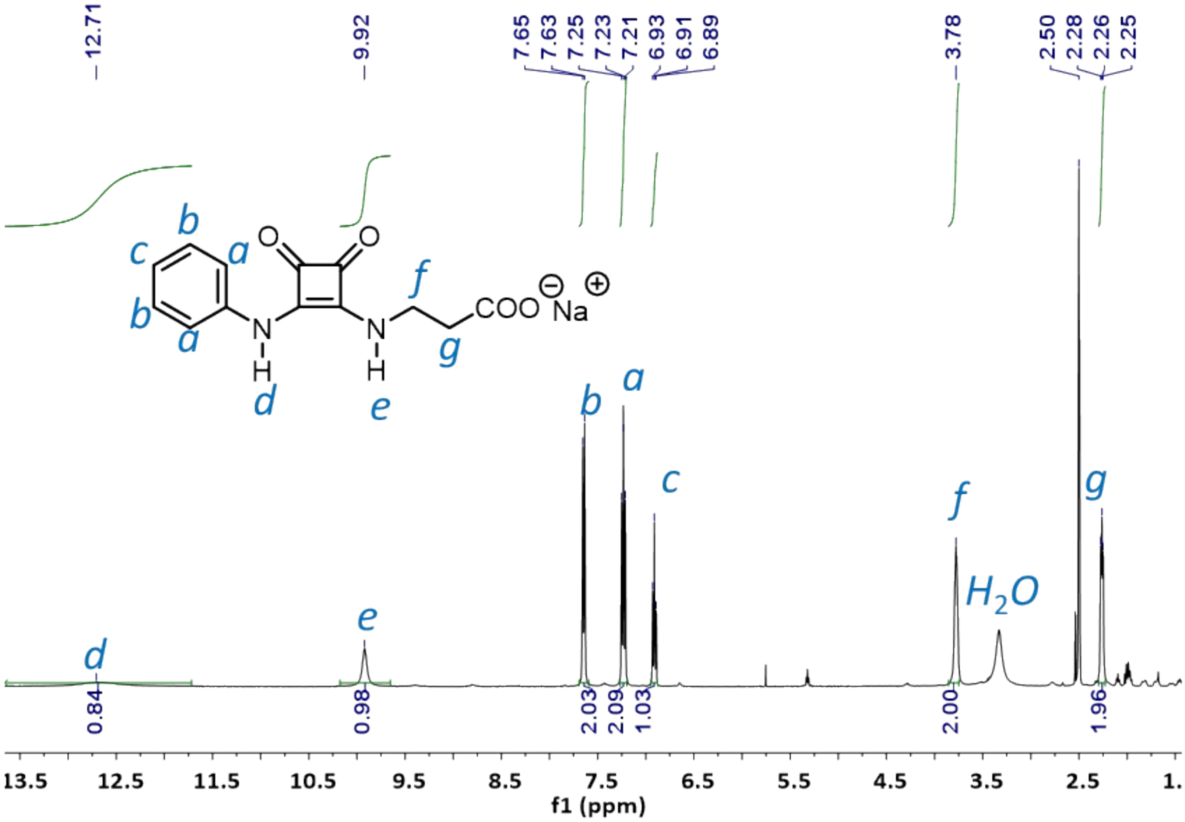


Figure S32. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 14

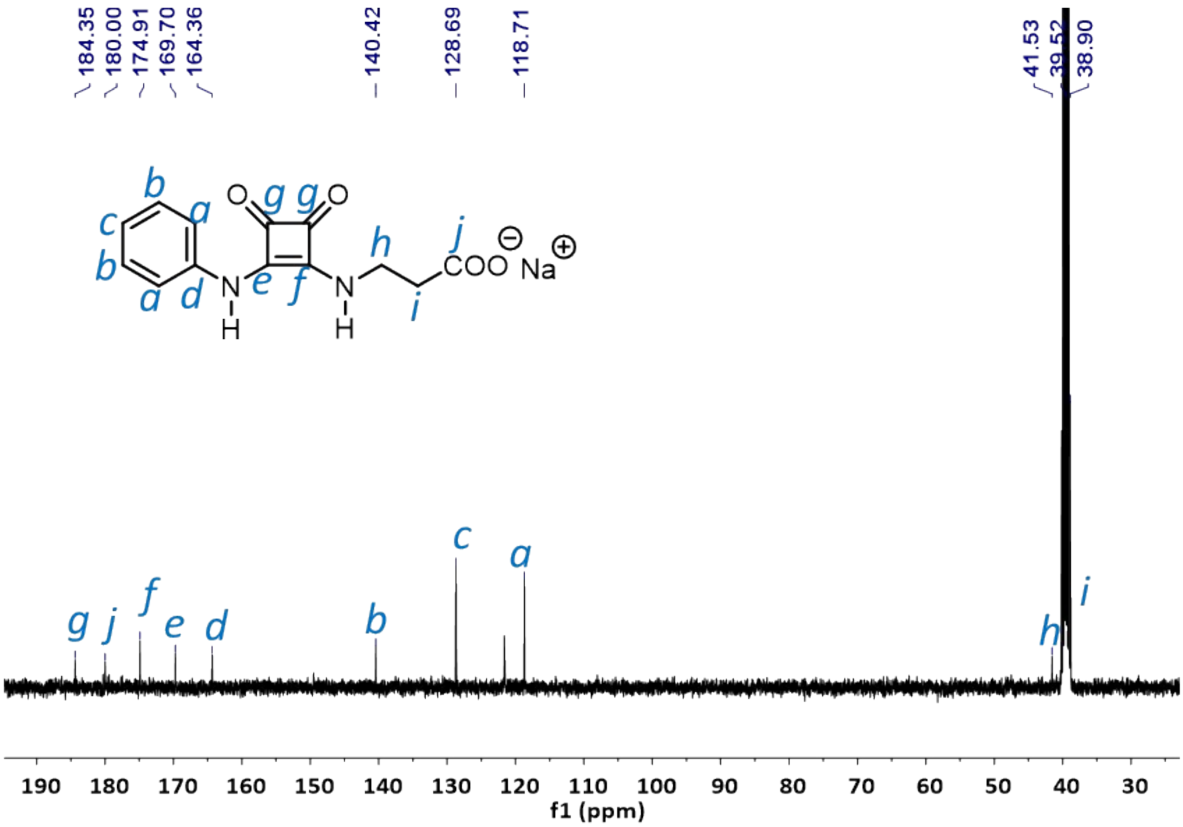


Figure S33. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 14

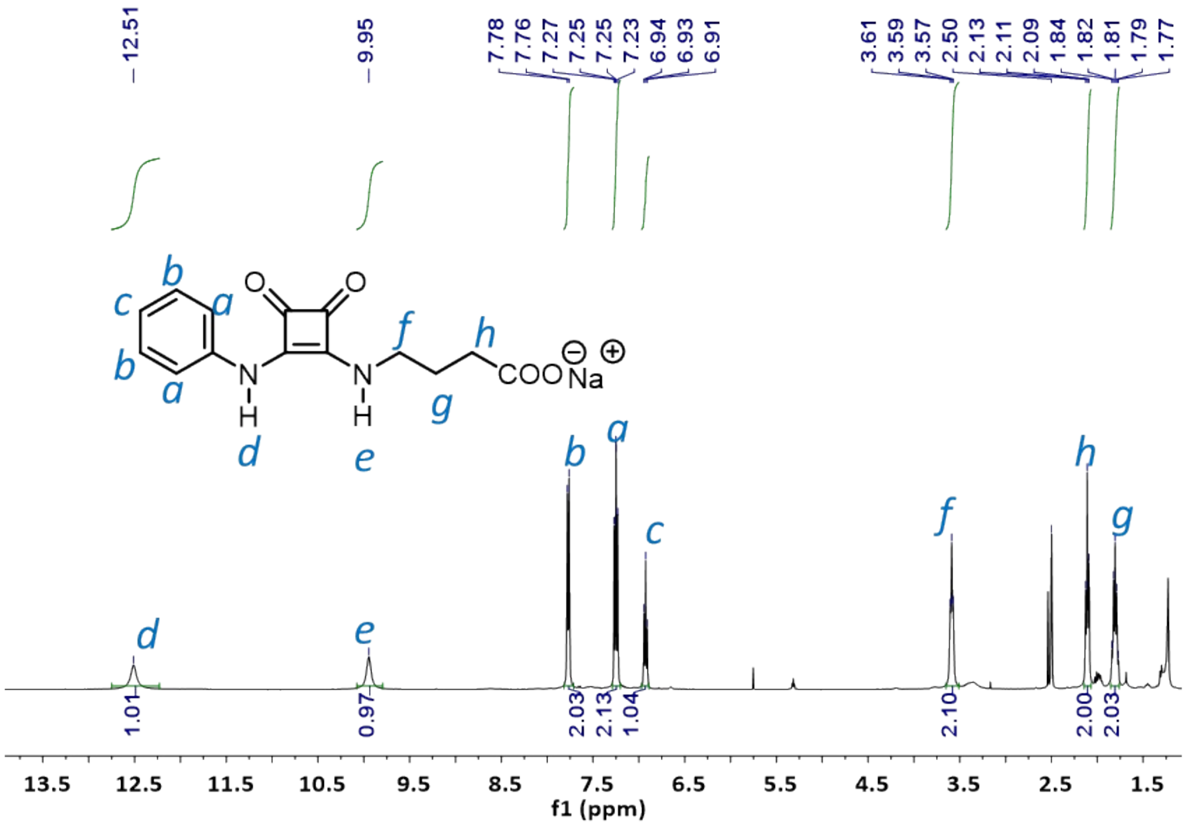


Figure S34. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 15

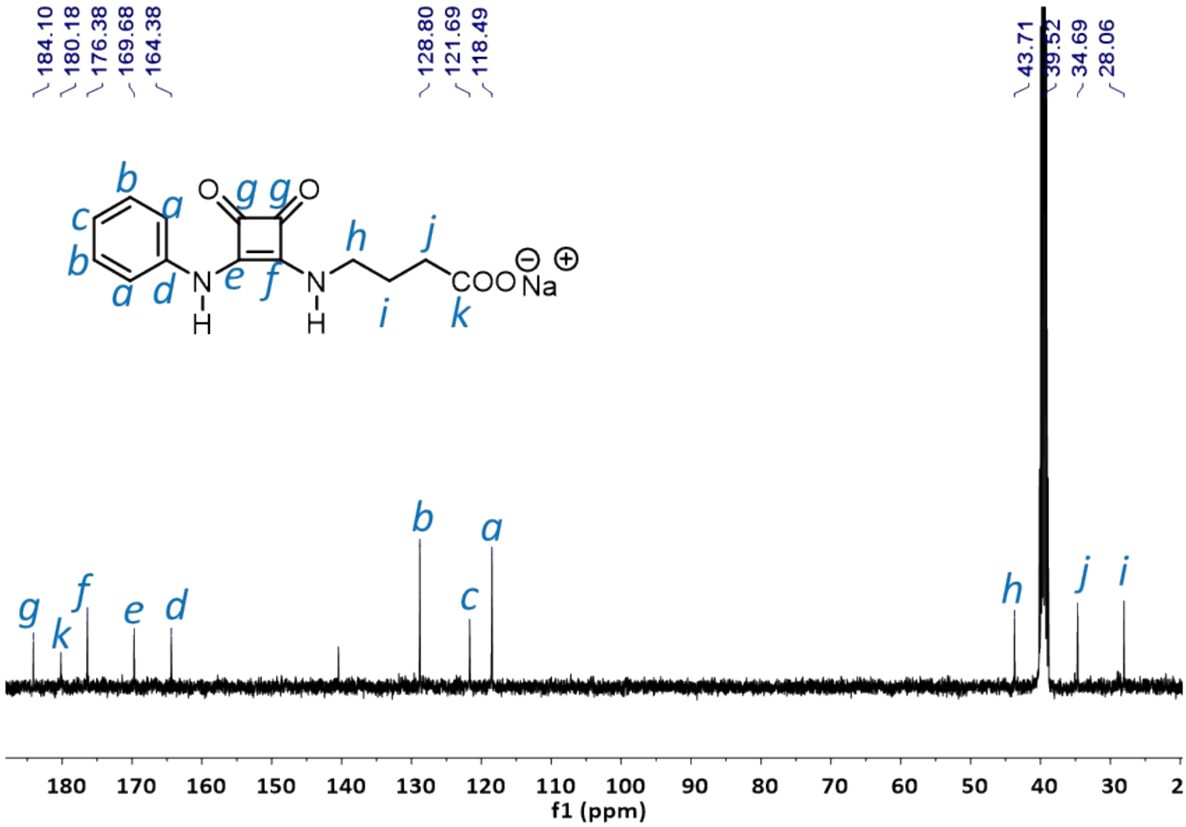


Figure S35. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 15

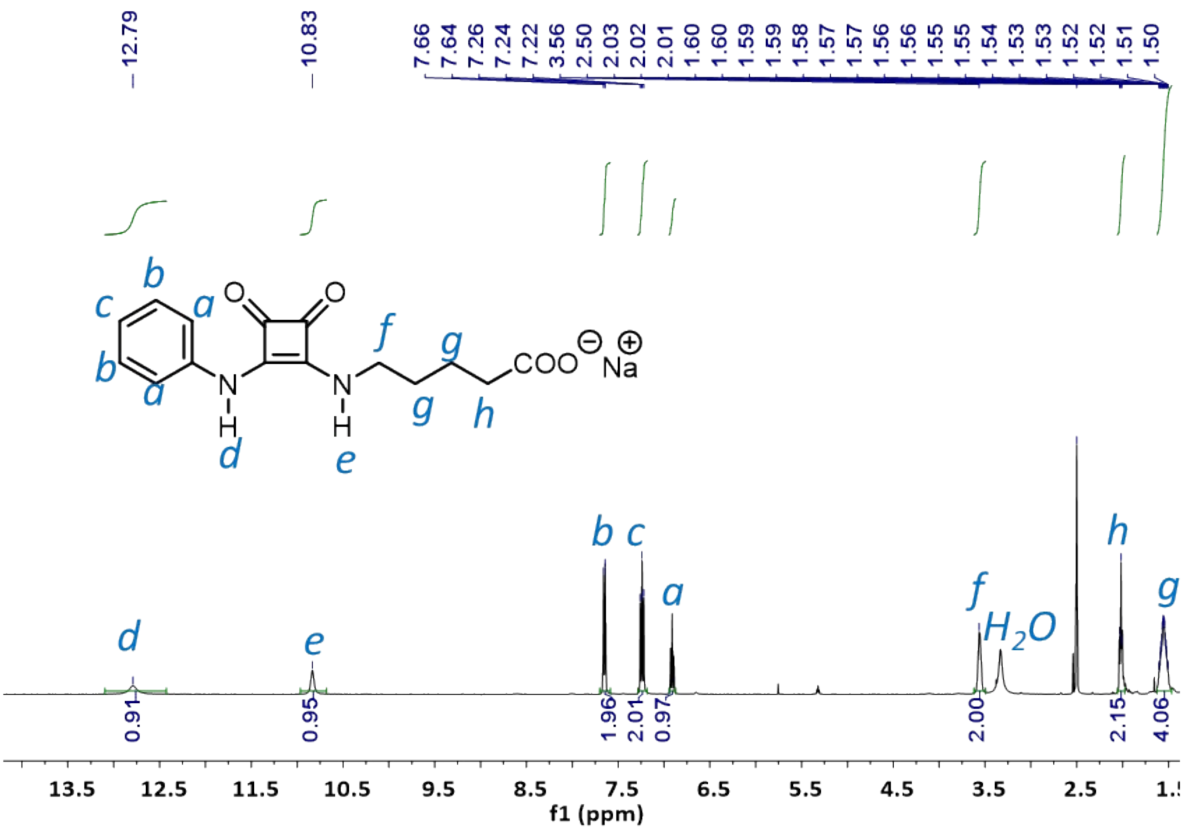


Figure S36. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 16

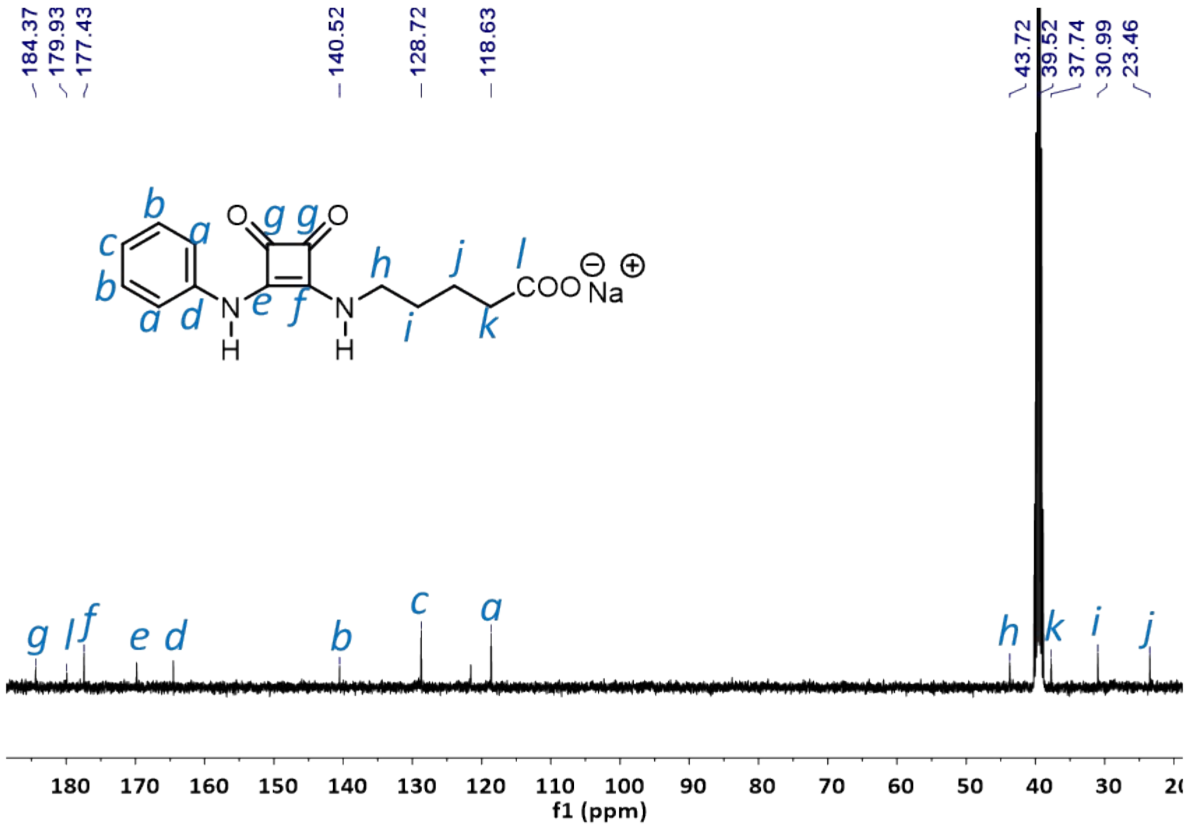


Figure S37. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 16

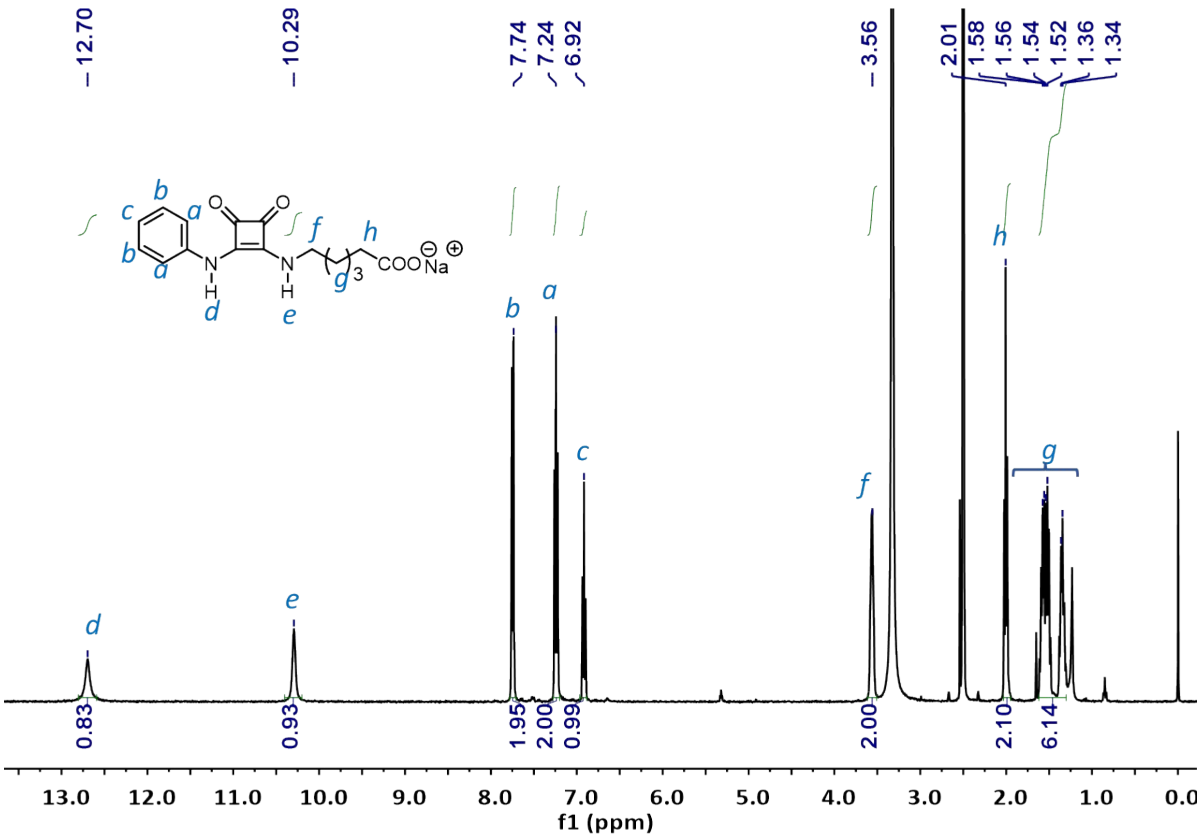


Figure S38. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 17

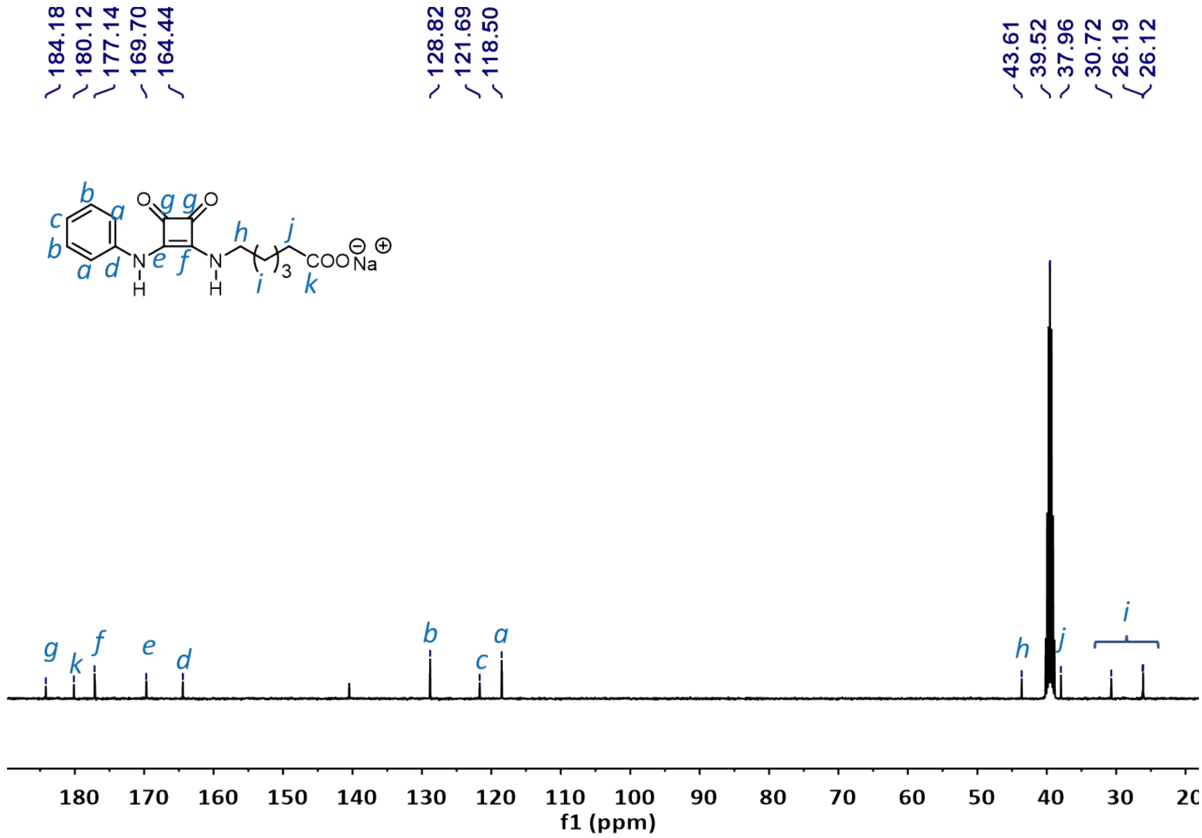


Figure S39. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 17

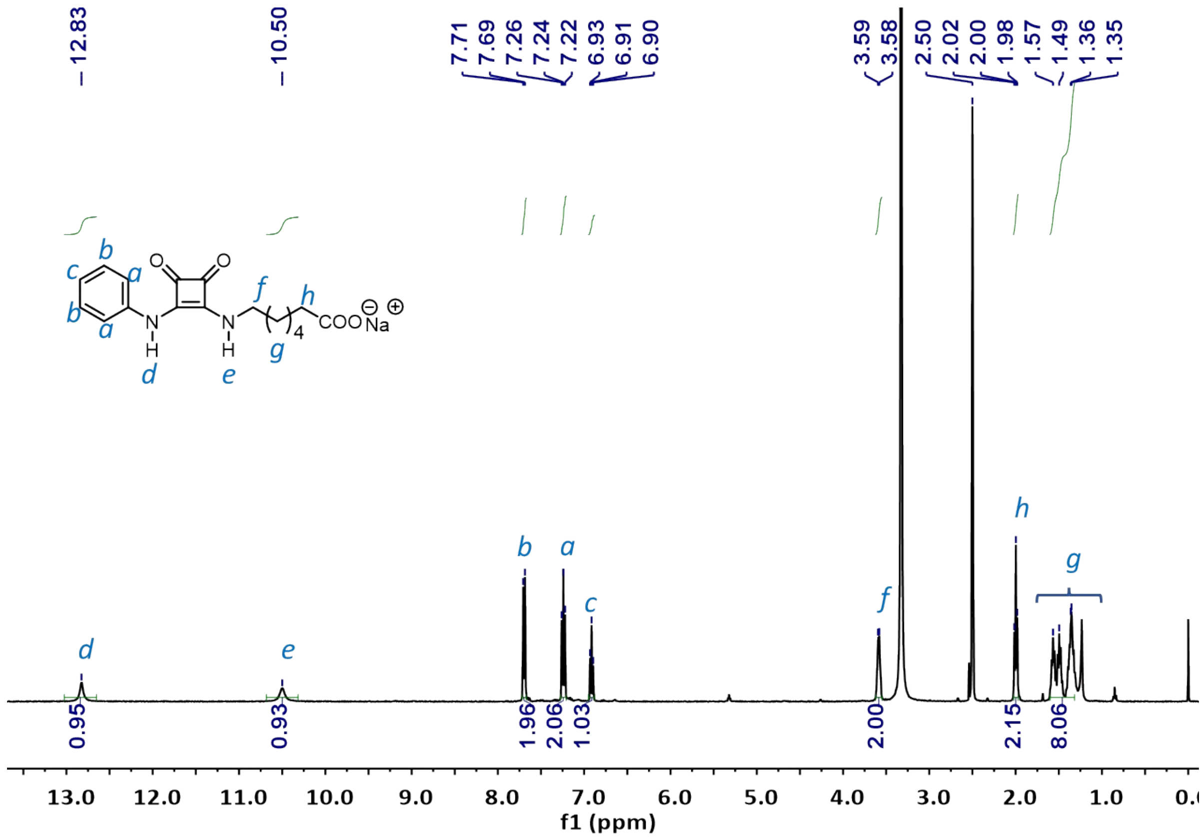


Figure S40. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 18

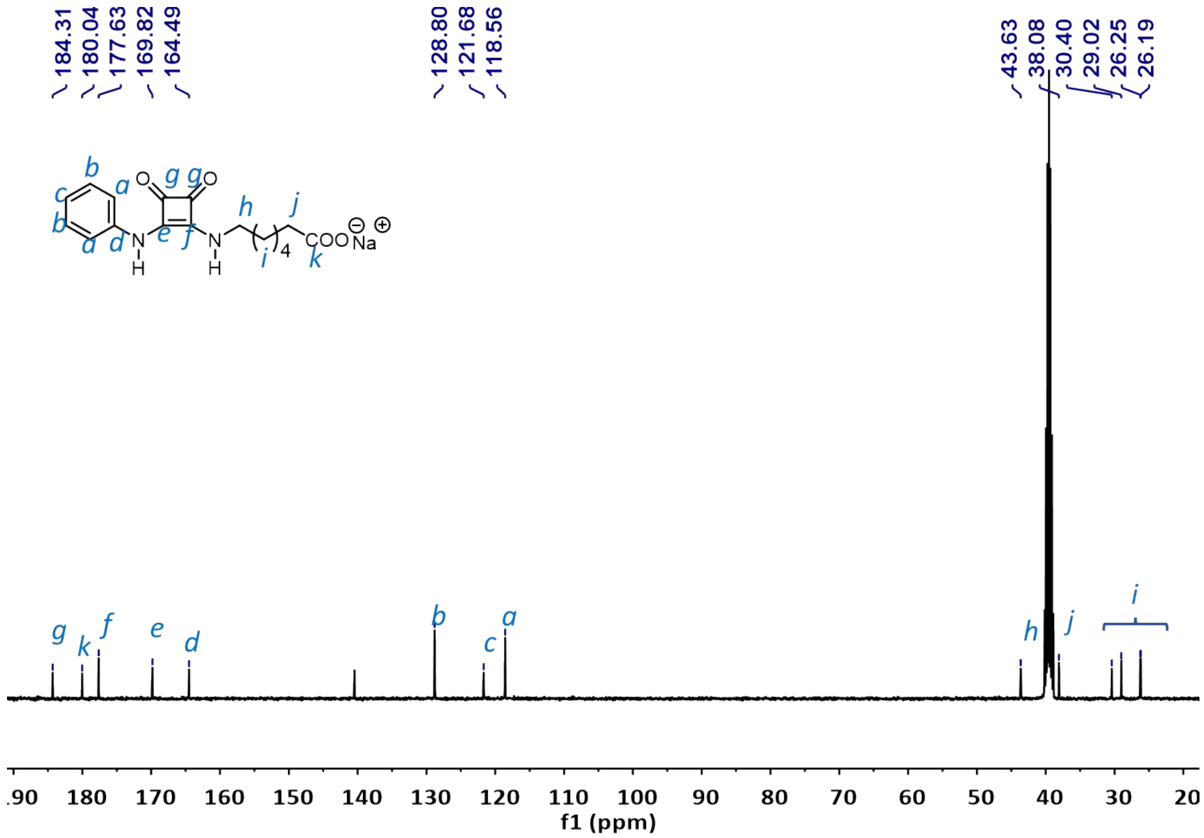


Figure S41. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 18

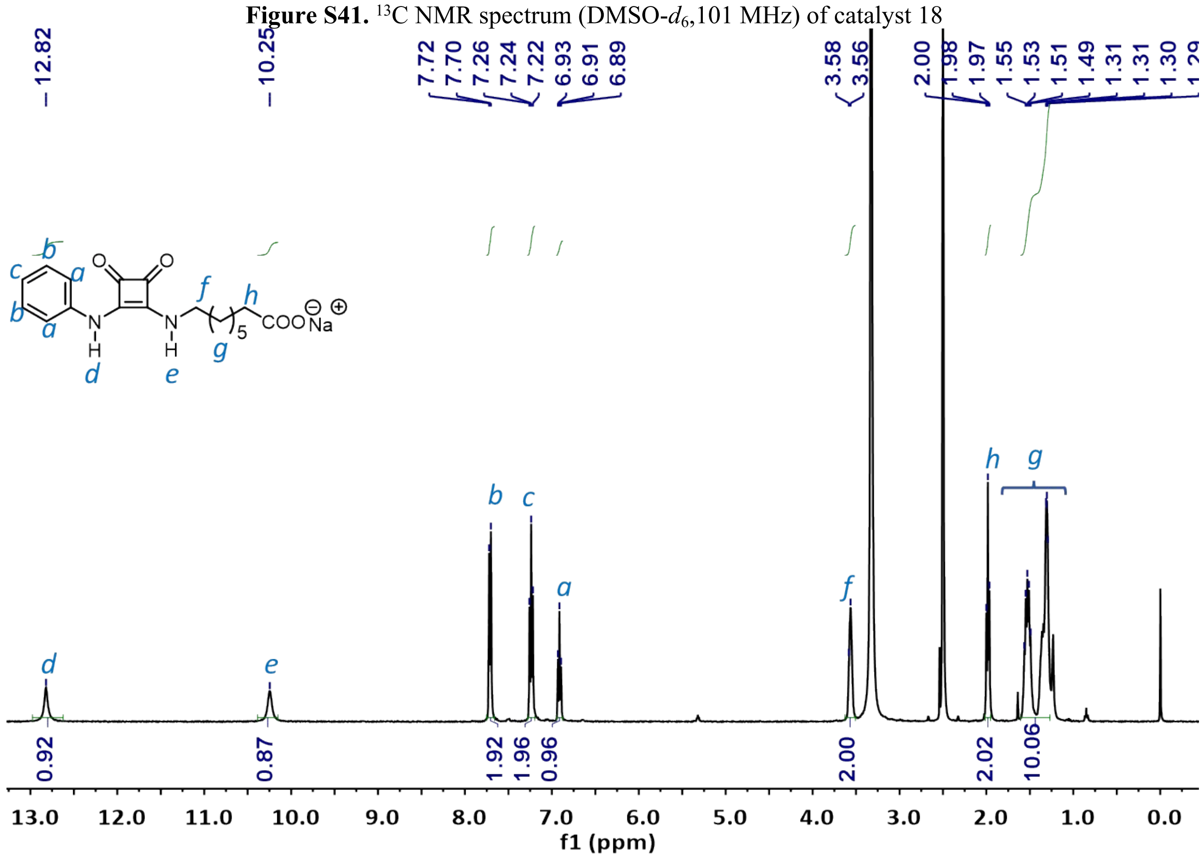


Figure S42. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 19

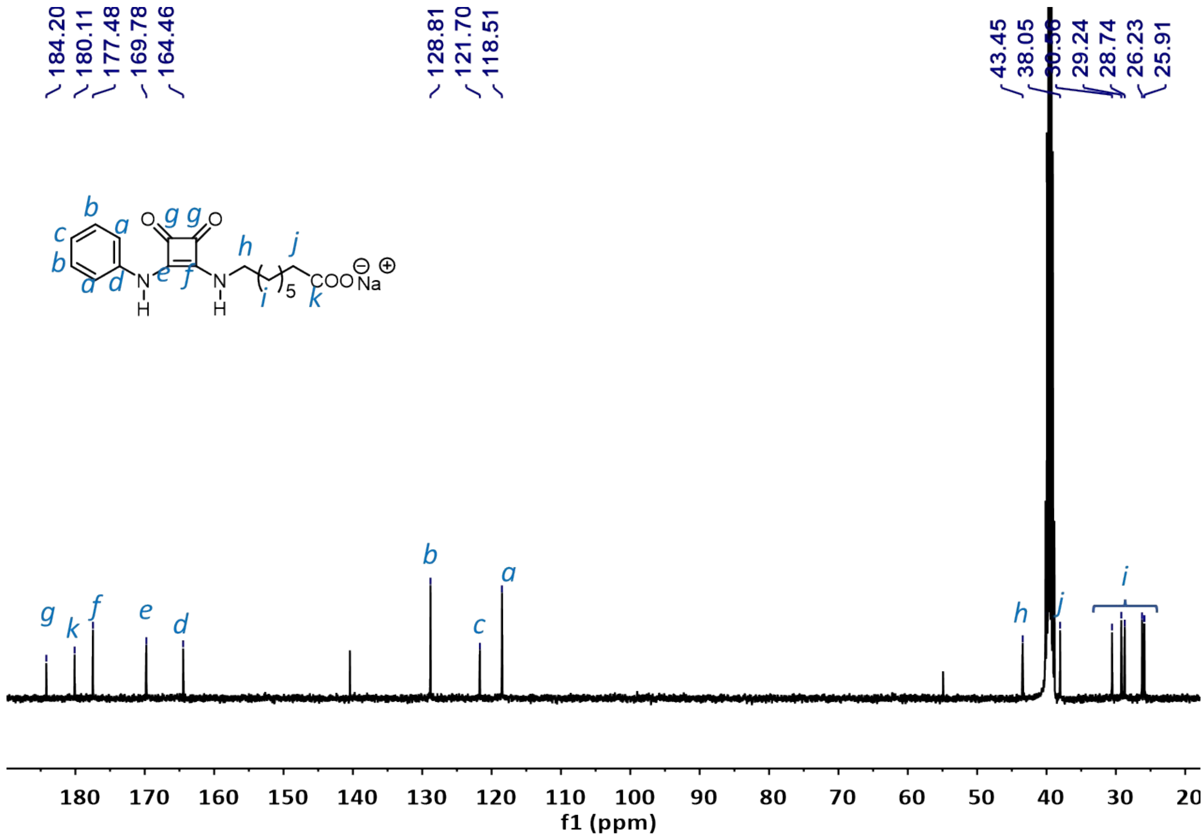


Figure S43. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 19

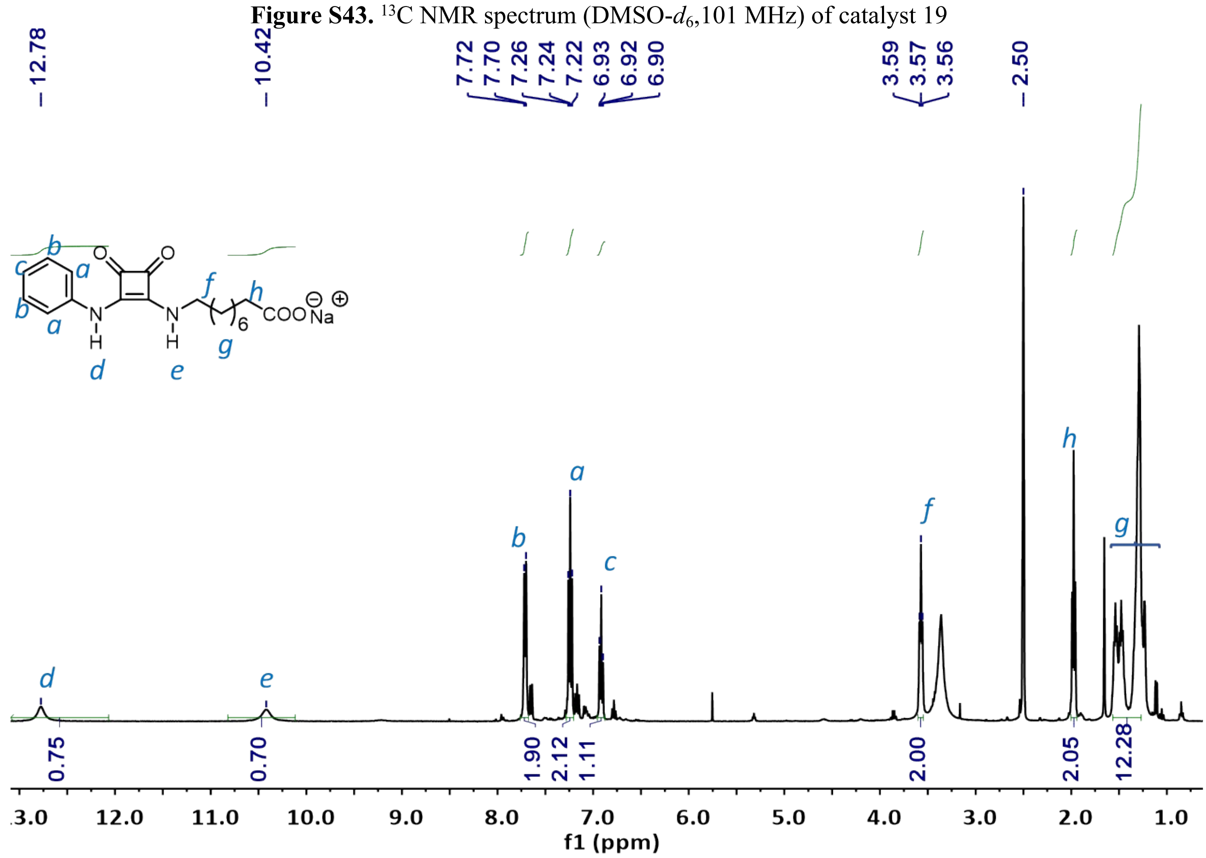


Figure S44. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 20

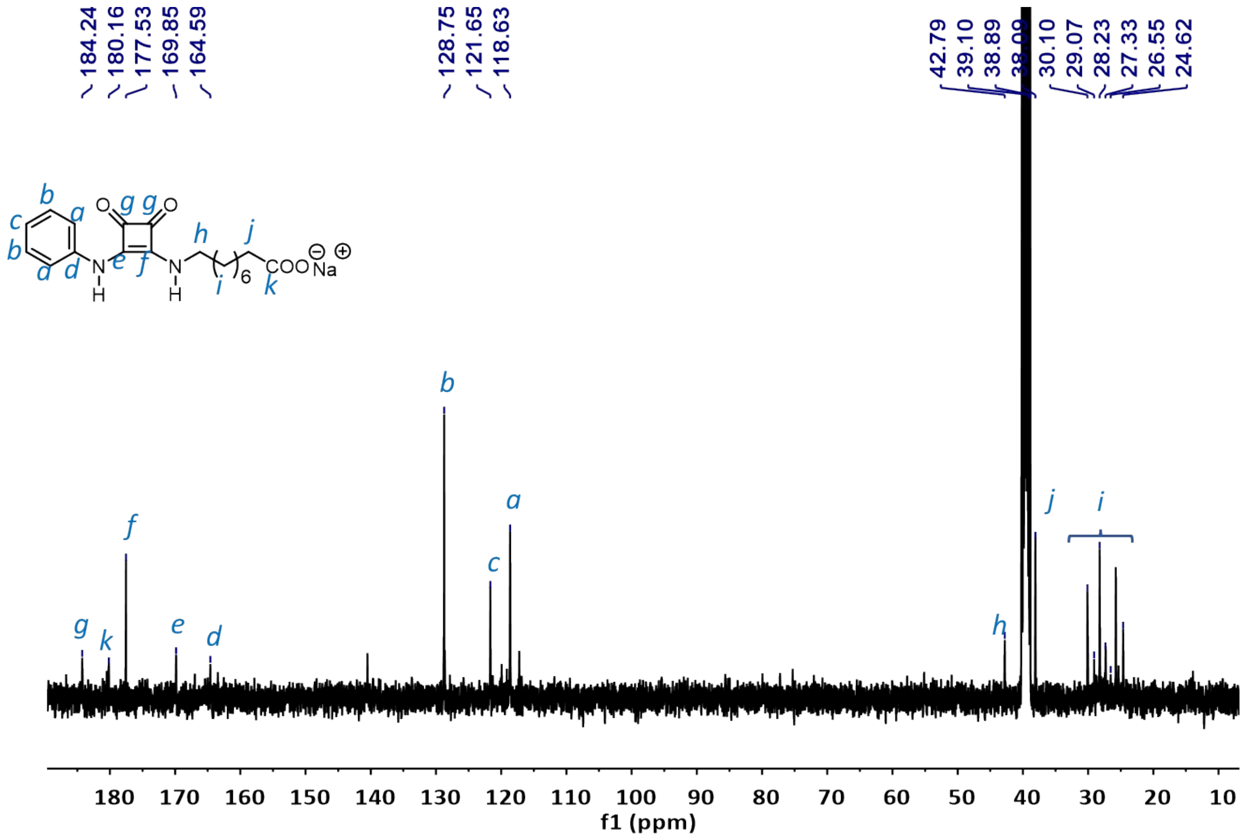


Figure S45. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 20

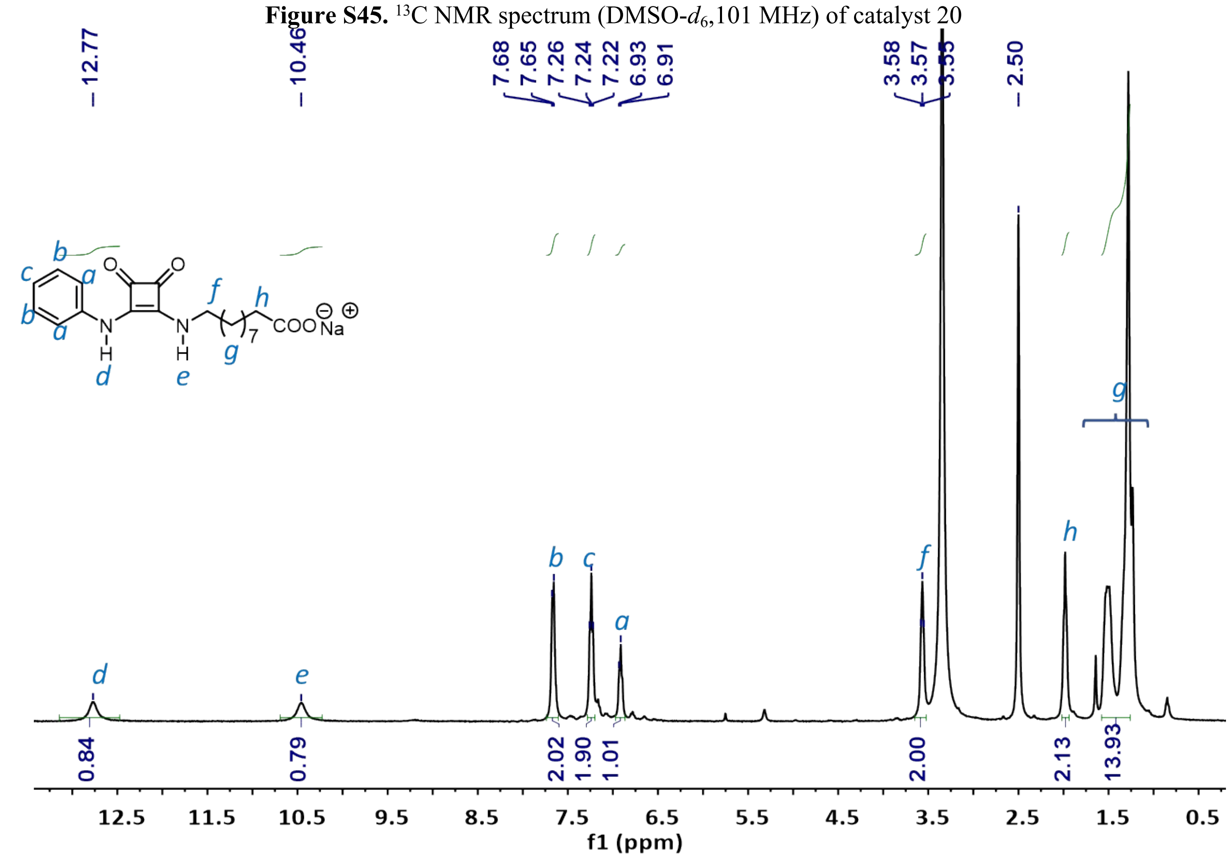


Figure S46. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 21

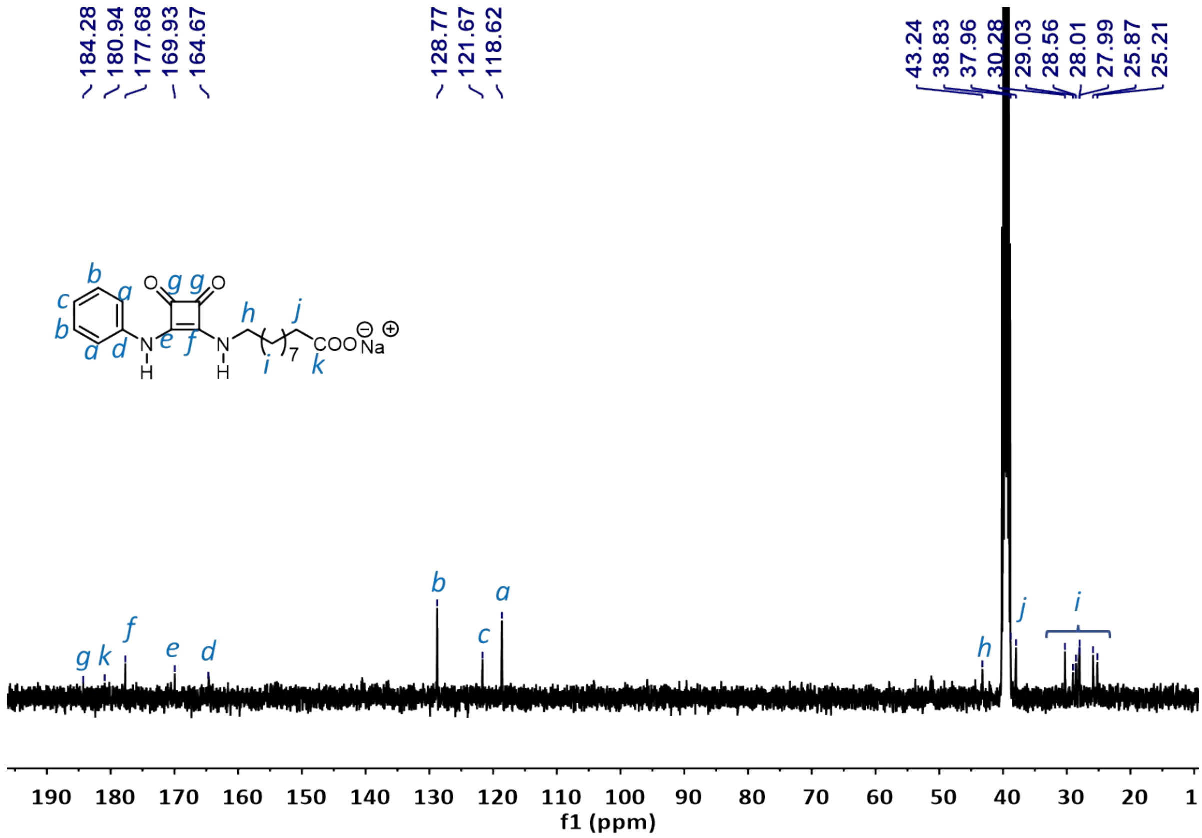


Figure S47. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 21

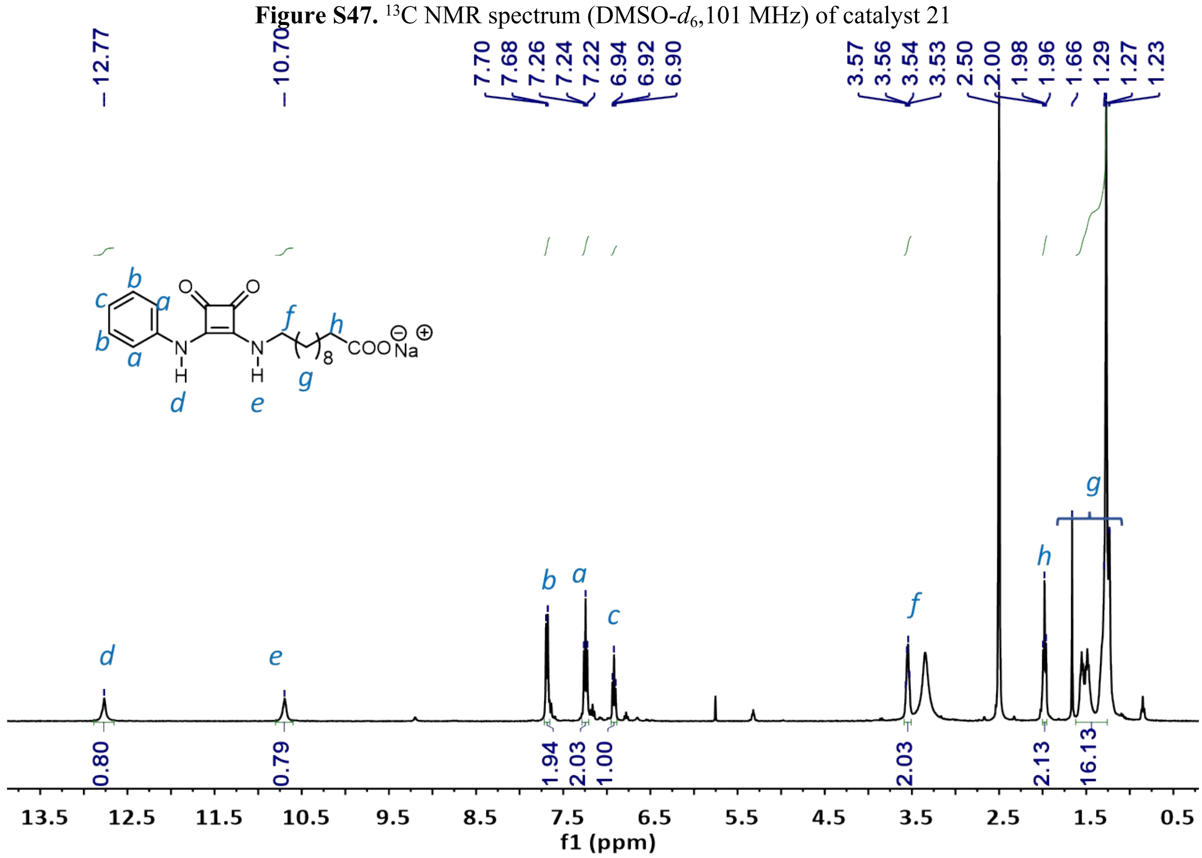


Figure S48. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 22

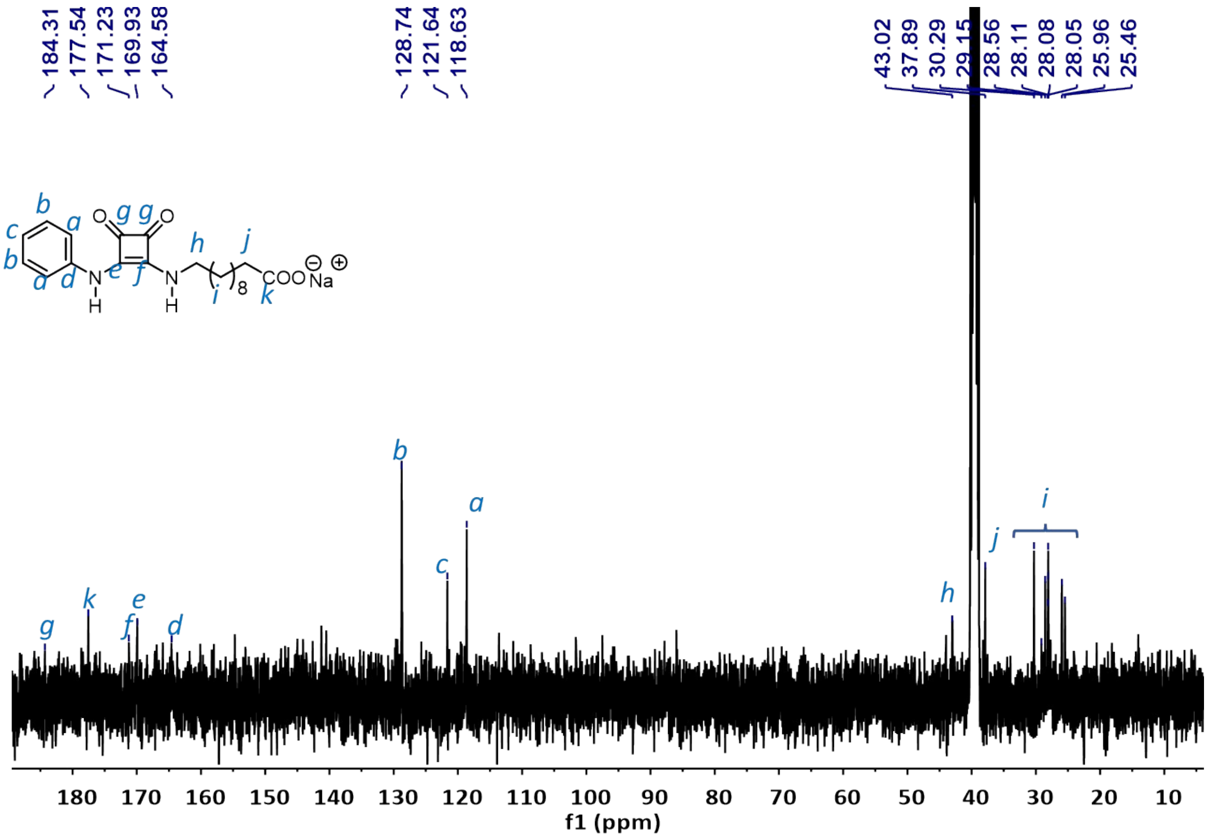


Figure S49. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 22

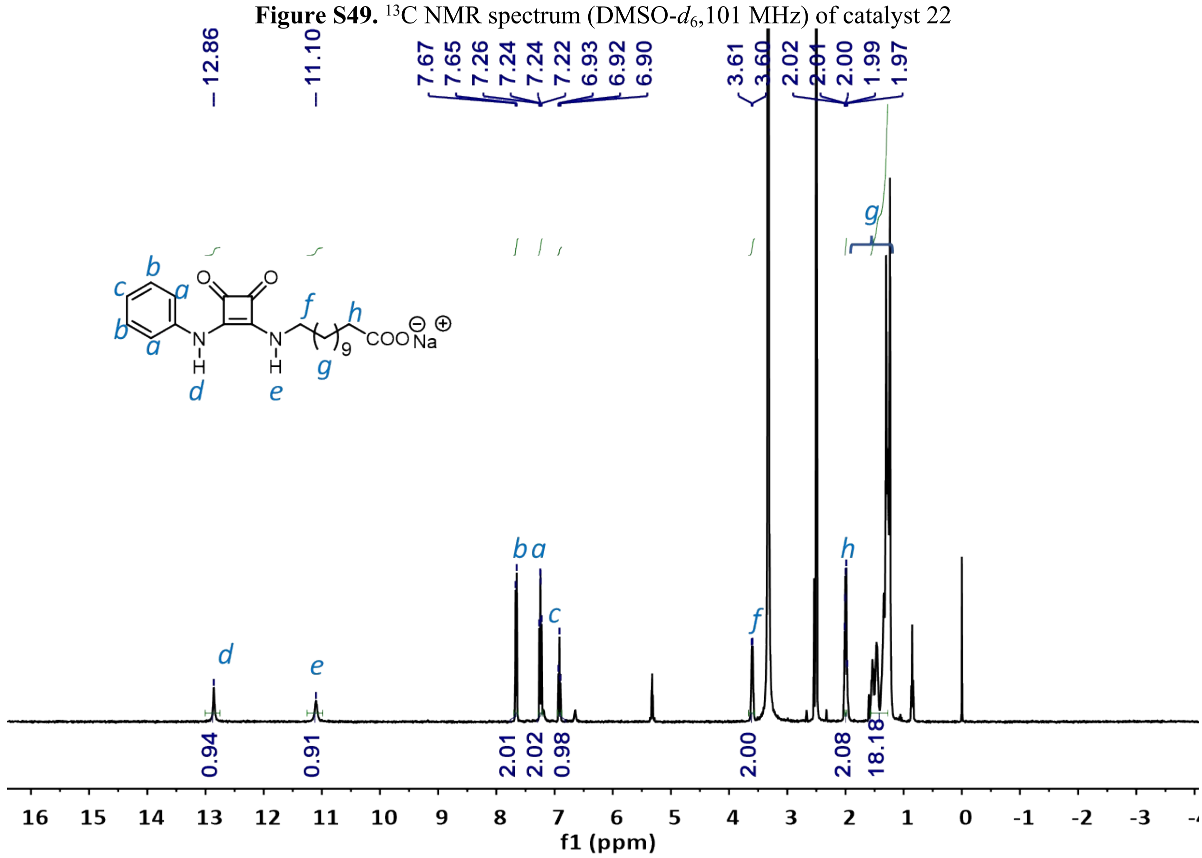


Figure S50. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of catalyst 23

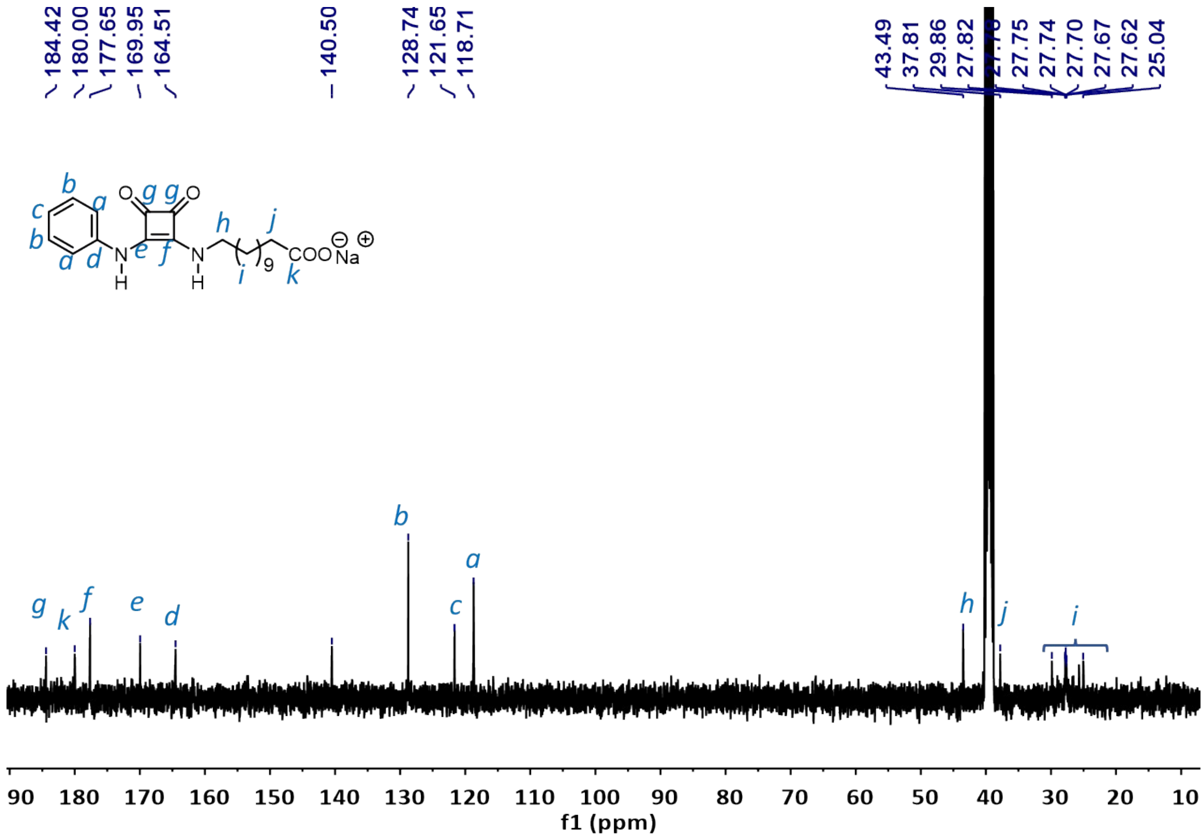
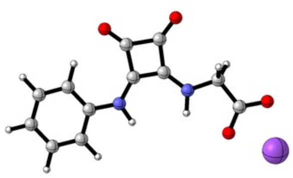


Figure S51. ^{13}C NMR spectrum (DMSO-d_6,101 MHz) of catalyst 23

Computational Methods

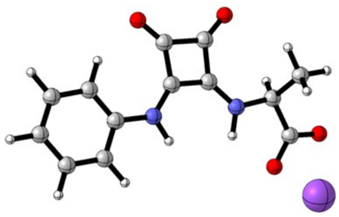
Geometry optimizations of structures, binding energy of complexes were performed using Gaussian 16 program[3], the structures were illustrated by CYLview[4]. the structures were optimized at B3LYP//Def2TZVP and single-point energy were obtained on optimized structures with B3LYP/SDD. The physical descriptors were withdrawn by the Multiwfn program[5].



01

C	-1.12488400	2.16796400	-0.00056900
C	0.38183400	2.45435400	0.00041500
O	-2.14000300	2.84018900	-0.00151500
O	1.10265000	3.43413600	0.00073700
C	-0.77711200	0.71790200	0.00018200
C	0.60215500	0.98744100	0.00065400
N	-1.41043700	-0.48617700	-0.00008600
H	-0.80538900	-1.29738300	0.00164100

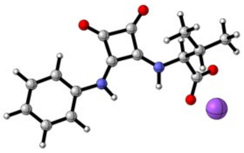
N	1.69897400	0.22444000	0.00174100
H	1.66186500	-0.79119200	0.00031500
C	4.05186800	-0.42638000	-0.00006200
O	3.58485900	-1.61383500	-0.00068400
O	5.28355600	-0.14649000	0.00010800
Na	5.69888200	-2.31410100	-0.00075300
C	3.06392600	0.73942100	0.00027500
H	3.25841300	1.36314000	0.87920800
H	3.25702100	1.36203900	-0.87980900
C	-2.78683600	-0.79983200	0.00001700
C	-3.79162800	0.17812300	-0.00040800
C	-3.13741800	-2.16040200	0.00039300
C	-5.12962200	-0.22089000	-0.00040000
H	-3.53287800	1.23205800	-0.00087600
C	-4.47828700	-2.54084900	0.00046200
H	-2.35917600	-2.92096000	0.00057300
C	-5.48596500	-1.57234100	0.00008600
H	-5.90084500	0.54398500	-0.00072900
H	-4.73233500	-3.59691000	0.00080600
H	-6.53082700	-1.86657700	0.00014100



02

C	-1.23975100	2.12698600	-0.22962900
C	0.27069400	2.38201300	-0.20033300
O	-2.23640900	2.81356800	-0.36646500
O	1.01132700	3.34360300	-0.29165600
C	-0.92877200	0.68429300	-0.02778700
C	0.45732200	0.92214900	-0.00585400
N	-1.59033400	-0.49611400	0.10949600
H	-1.00637200	-1.30680900	0.27117200
N	1.52474900	0.13065200	0.13379300
H	1.44611500	-0.88314000	0.15242300
C	2.91912900	0.58423500	0.08094400
H	3.06091300	1.22733900	-0.79498400
C	3.33503700	1.36905500	1.33583900
H	3.19074500	0.76219000	2.23617800
H	4.38931800	1.64579300	1.25814700
H	2.73816800	2.28052900	1.41678900
C	3.80707100	-0.65510600	-0.11467400
O	3.26078000	-1.80877500	-0.06946700

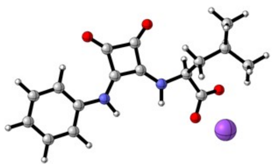
O	5.04239800	-0.46692500	-0.30234300
Na	5.28126600	-2.65490700	-0.44934300
C	-2.97185600	-0.78362900	0.07350100
C	-3.94945200	0.19954100	-0.13576000
C	-3.35655400	-2.12253400	0.25611900
C	-5.29489000	-0.17277200	-0.15913300
H	-3.66421000	1.23745700	-0.27444500
C	-4.70442500	-2.47647000	0.22957700
H	-2.59941100	-2.88684500	0.41936400
C	-5.68512100	-1.50271300	0.02103800
H	-6.04496400	0.59594500	-0.32130300
H	-4.98512000	-3.51597300	0.37264000
H	-6.73537500	-1.77631900	0.00013200



03

C	-1.39539300	1.88468000	-0.87836700
C	0.13001700	2.02617300	-0.83798600
O	-2.32097100	2.54982700	-1.30733600
O	0.95688700	2.84205200	-1.20109600
C	-1.22217700	0.58013900	-0.17931700
C	0.17750300	0.71066400	-0.15184800
N	-1.99153400	-0.42932000	0.30967700
H	-1.48992500	-1.16620700	0.78914900
N	1.16499000	-0.05349400	0.32867300
H	0.99080300	-1.02450800	0.57485400
C	2.59565000	0.22107500	0.12680900
H	2.69932700	0.99233300	-0.64063900
C	3.27680000	0.71984400	1.43869600
H	3.20452700	-0.10082200	2.16791400
C	3.23638800	-1.08220400	-0.38328100
O	2.68807000	-2.18219200	-0.03256100
O	4.27137100	-1.01176900	-1.10509400
Na	4.23098500	-3.21425400	-1.25061900
C	-3.39034300	-0.61619300	0.27655000
C	-4.26572900	0.29135800	-0.33674700
C	-3.90085300	-1.77309700	0.88886800
C	-5.63664200	0.02701500	-0.32698100
H	-3.88321400	1.19113100	-0.80783300
C	-5.27240000	-2.02139400	0.88887600
H	-3.22327000	-2.47802700	1.36639800
C	-6.15176900	-1.12200200	0.27956900

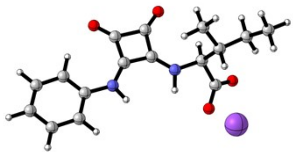
H	-6.30703600	0.73660000	-0.80330500
H	-5.65100600	-2.92002400	1.36732800
H	-7.22027200	-1.31335200	0.27895700
C	2.53768700	1.94038900	2.00914400
H	2.53796200	2.76921900	1.29225200
H	1.49847400	1.70937800	2.25920700
H	3.03183300	2.28305300	2.92472600
C	4.76132700	1.05189000	1.21822800
H	5.21243900	1.38069400	2.16078500
H	5.32907100	0.19788800	0.84187600
H	4.87200300	1.86578400	0.49212300



04

C	-1.75399900	1.93540500	-0.75325900
C	-0.22820900	1.97853500	-0.88542900
O	-2.66882100	2.71175600	-0.96282800
O	0.61314200	2.78653500	-1.23340400
C	-1.60175400	0.53497600	-0.26845700
C	-0.20126900	0.57943400	-0.39058300
N	-2.38545600	-0.49008600	0.16213600
H	-1.89174400	-1.32601700	0.44807900
N	0.77689500	-0.30206700	-0.16816800
H	0.59326200	-1.25104500	0.14492400
C	2.20897500	-0.02047800	-0.34002100
H	2.35110900	0.56931200	-1.24949200
C	2.90805300	-1.37374100	-0.53461900
O	2.34144700	-2.41159100	-0.05132900
O	4.01009700	-1.39748700	-1.15331700
Na	4.04033300	-3.58792900	-0.86851200
C	-3.78865400	-0.58449200	0.28354000
C	-4.65562800	0.46071000	-0.06574100
C	-4.31321100	-1.79093800	0.77683900
C	-6.03216300	0.28199300	0.08447400
H	-4.26152900	1.39844800	-0.44413000
C	-5.69025800	-1.95230900	0.91981400
H	-3.64199800	-2.60283700	1.04960600
C	-6.56133200	-0.91548300	0.57387300
H	-6.69573400	1.09767700	-0.18784500
H	-6.07962000	-2.89111500	1.30302200
H	-7.63405300	-1.03907100	0.68484600
C	4.22236100	1.27055400	0.76994500

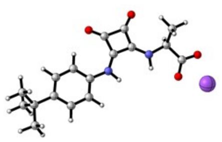
H	4.49378100	1.32952100	-0.29217000
C	2.75115600	0.79390700	0.86457600
H	2.59541200	0.21067700	1.78236100
H	2.09773600	1.67009100	0.93245600
C	4.36392200	2.67882400	1.37218600
H	5.40074600	3.02963300	1.31418400
H	3.73196000	3.40112300	0.84492600
H	4.07072500	2.68437100	2.43018100
C	5.19910200	0.29824100	1.45209400
H	4.98592400	0.22639300	2.52677700
H	5.13747800	-0.70348300	1.01865800
H	6.23334200	0.64407800	1.34109200



05

C	1.64592600	-1.79975800	-1.05749500
C	0.11668600	-1.88327000	-1.10926800
O	2.56993500	-2.46729300	-1.48628800
O	-0.71712400	-2.63695900	-1.57629400
C	1.48023400	-0.54575400	-0.26992200
C	0.07736000	-0.62221700	-0.32719900
N	2.25634200	0.39202200	0.33700600
H	1.75506700	1.11134300	0.84276700
N	-0.90766400	0.14211000	0.15692300
H	-0.71362900	1.08020600	0.49744900
C	-2.33430000	-0.06075500	-0.13693200
H	-2.42138500	-0.75702600	-0.97477700
C	-2.89728700	1.30887600	-0.55951900
O	-2.33297900	2.34866400	-0.07607100
O	-3.88776100	1.34951600	-1.34422800
Na	-3.76350500	3.55251200	-1.27242400
C	3.66061500	0.52323300	0.39567500
C	4.53616700	-0.37013600	-0.23789300
C	4.17692000	1.60801000	1.12415000
C	5.91299000	-0.16401200	-0.13191900
H	4.14878400	-1.21481300	-0.79852900
C	5.55436100	1.79884200	1.21922600
H	3.49914100	2.30162200	1.61771100
C	6.43394200	0.91313600	0.59048800
H	6.58335800	-0.86216300	-0.62488800
H	5.93736500	2.64191900	1.78696600

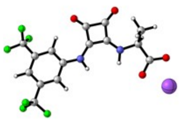
H	7.50699600	1.05976700	0.66380200
C	-3.10738900	-0.64743200	1.08942100
H	-3.11280500	0.13205800	1.86721500
C	-2.37925100	-1.88211700	1.64503600
H	-2.29896500	-2.66366900	0.88078600
H	-1.37000600	-1.63697400	1.98634600
H	-2.91991900	-2.29716400	2.50038000
C	-4.57059900	-0.97529600	0.71824300
H	-5.00038800	-0.14321200	0.15309700
H	-4.57216800	-1.83596300	0.03510500
C	-5.47058900	-1.27460100	1.92497500
H	-6.50231700	-1.44866700	1.60047500
H	-5.14982600	-2.16340600	2.47771500
H	-5.48277200	-0.43233000	2.62818400



06

C	0.48908100	2.42981700	-0.23130900
C	2.01984300	2.47619600	-0.20187300
O	-0.40491400	3.24600600	-0.36764200
O	2.88501200	3.32821800	-0.29254200
C	0.59970200	0.95775100	-0.03062800
C	2.00554700	1.00512800	-0.00839700
N	-0.21734500	-0.11970400	0.10517100
H	0.24848100	-1.00401200	0.26462300
N	2.95504600	0.07481500	0.13125400
H	2.73836200	-0.91856600	0.14867000
C	4.39803900	0.33447700	0.08092100
H	4.62766700	0.95263100	-0.79439900
C	5.11015200	-1.01363900	-0.11377600
O	4.41266900	-2.08279600	-0.07083100
O	6.36019300	-0.99460900	-0.29842500
Na	6.30050600	-3.19450700	-0.44460000
C	-1.62625100	-0.21241200	0.07469200
C	-2.46426500	0.89233100	-0.12946800
C	-2.20191800	-1.47591800	0.25631000
C	-3.84515200	0.70787000	-0.14607100
H	-2.04492500	1.88345800	-0.27005100
C	-3.58845100	-1.63555400	0.23541700
H	-1.56722200	-2.34551400	0.41637000
C	-4.45101400	-0.54881500	0.03361200
H	-4.46274800	1.58670500	-0.30609100

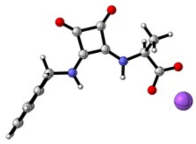
H	-3.98534600	-2.63360300	0.38122200
C	4.91459900	1.05544000	1.33683300
H	4.44706400	2.03964100	1.41669200
H	4.68710200	0.47383300	2.23669100
H	5.99691000	1.18607200	1.26136100
C	-5.98430900	-0.68320400	0.00423100
C	-6.44805400	-2.13699500	0.22118900
H	-7.54200800	-2.18153000	0.19245100
H	-6.07079400	-2.80693300	-0.55930900
H	-6.12833300	-2.52698700	1.19380700
C	-6.60247600	0.19075800	1.12304900
H	-6.34617800	1.24758400	1.00185700
H	-7.69580600	0.10885400	1.11033500
H	-6.24798000	-0.12801600	2.10928000
C	-6.51981100	-0.20743800	-1.36858600
H	-7.61249800	-0.29221100	-1.40158600
H	-6.26056300	0.83706700	-1.56619800
H	-6.10590700	-0.81399100	-2.18146300



07

C	0.86543000	2.50869700	-0.02457400
C	2.39779500	2.58899400	0.00515500
O	-0.05084700	3.30773500	-0.08790300
O	3.24269300	3.46045900	-0.01544300
C	1.01368900	1.03267200	0.04770800
C	2.41648200	1.09987700	0.07356100
N	0.21068600	-0.07224300	0.09072800
H	0.69104100	-0.95919200	0.17197600
N	3.38472300	0.18584500	0.12963400
H	3.19318300	-0.81225700	0.07125700
C	4.82467800	0.47494600	0.10418900
H	5.04288200	1.16566400	-0.71783900
C	5.55415200	-0.84451200	-0.19915400
O	4.86759600	-1.92072600	-0.24271700
O	6.80247200	-0.79495100	-0.38035000
Na	6.77264100	-2.98061400	-0.70348800
C	-1.18775400	-0.17658000	0.04698600
C	-2.03569900	0.93420100	-0.05513600
C	-1.73949600	-1.46810000	0.10522800
C	-3.41810700	0.73144300	-0.09761400
H	-1.62436600	1.93976400	-0.09974900
C	-3.11886400	-1.64218500	0.05966700

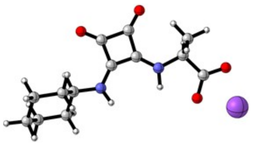
H	-1.09112500	-2.33563900	0.17993000
C	5.32826800	1.09624300	1.41665400
H	4.84781600	2.06390000	1.57900400
H	5.10987800	0.43839900	2.26461400
H	6.40851700	1.24786100	1.35367100
C	-3.97826700	-0.54399900	-0.04189800
H	-5.05122600	-0.68067900	-0.08089600
C	-3.70176800	-3.02762800	0.17291100
C	-4.30834400	1.94693200	-0.21761900
F	-4.09333800	-3.30649400	1.44530400
F	-2.81256300	-3.99134400	-0.17789400
F	-4.79409200	-3.18695600	-0.61154500
F	-4.10530500	2.81949700	0.79866600
F	-4.07709200	2.62461300	-1.36922100
F	-5.62449900	1.62263800	-0.20655800



08

C	-0.46232900	2.65060700	-0.23620200
C	1.05912100	2.55975200	-0.40189800
O	-1.34065100	3.48135000	-0.40865800
O	1.96962600	3.28976700	-0.75263500
C	-0.43142000	1.24498600	0.22350200
C	0.95981000	1.14642600	0.05453200
N	-1.39417800	0.38176100	0.60757600
H	-1.12464000	-0.53267500	0.94729000
N	1.84868700	0.16183000	0.23954800
H	1.55633200	-0.78554700	0.46178100
C	3.28106600	0.26320500	-0.05443600
H	3.42094300	0.70147100	-1.04927500
C	3.85631100	-1.16106600	-0.10098100
O	3.10042300	-2.13574500	0.22980000
O	5.06202900	-1.29476900	-0.45792800
Na	4.82275700	-3.46989800	-0.19218700
C	4.03664800	1.12887000	0.96782400
H	3.65978100	2.15375600	0.93283100
H	3.90724200	0.73098800	1.98020800
H	5.10136300	1.13738500	0.72161100
C	-2.78392200	0.79182200	0.84806600
H	-2.91840500	1.75442200	0.34620900
H	-2.94909500	0.95920300	1.92085300
C	-3.77219500	-0.23633300	0.33560000

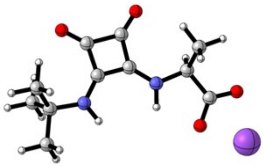
C	-3.82115300	-0.56004900	-1.02942600
C	-4.65904200	-0.87268000	1.21216700
C	-4.73832900	-1.49783700	-1.50395900
H	-3.13850600	-0.07047700	-1.71880500
C	-5.58142500	-1.81273800	0.73942400
H	-4.63328000	-0.62808000	2.27155500
C	-5.62210700	-2.12765800	-0.61972600
H	-4.76943700	-1.73377500	-2.56390000
H	-6.26407200	-2.29576100	1.43274800
H	-6.33773700	-2.85583100	-0.99046600



09

C	-0.97684700	2.09854900	-0.50183000
C	0.52695300	2.35548200	-0.34962900
O	-1.98305800	2.75216100	-0.72863700
O	1.28207100	3.31211500	-0.38104600
C	-0.69129100	0.66651600	-0.25888600
C	0.69045000	0.89241500	-0.13919000
N	-1.46826800	-0.43605200	-0.22272000
H	-1.05062800	-1.30180900	0.09883600
N	1.74240300	0.09383200	0.08776200
H	1.65142700	-0.91801400	0.08672700
C	3.13708100	0.54249700	0.12297900
H	3.33726100	1.18645600	-0.74122700
C	4.03765500	-0.69472700	-0.01653900
O	3.49382800	-1.85027200	-0.01288100
O	5.28358700	-0.50372200	-0.11995900
Na	5.53427500	-2.68813200	-0.25597800
C	3.47440500	1.32842800	1.40114400
H	2.87311100	2.23970600	1.44211500
H	3.27224700	0.72218400	2.29089100
H	4.53161300	1.60503100	1.39082900
C	-2.93832800	-0.37135800	-0.18757200
C	-3.53286600	-1.54550100	-0.97885300
C	-3.47474600	-0.34247800	1.25586100
H	-3.20817200	0.56992900	-0.67811100
C	-5.07027800	-1.52966300	-0.94381700
H	-3.16946500	-2.48997500	-0.54291100
H	-3.16790300	-1.51077200	-2.01176400
C	-5.01185300	-0.31944200	1.28476000
H	-3.11029400	-1.23525600	1.78742800

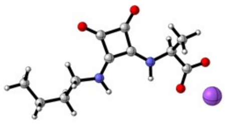
H	-3.06588700	0.53078600	1.77666500
C	-5.60756000	-1.49536400	0.49544800
H	-5.46187100	-2.40326000	-1.47864100
H	-5.43145100	-0.64454400	-1.48610600
H	-5.36462500	-0.33655600	2.32285900
H	-5.36457500	0.62671800	0.85123500
H	-6.70238200	-1.43139600	0.48770500
H	-5.35246200	-2.43862300	1.00086600



10

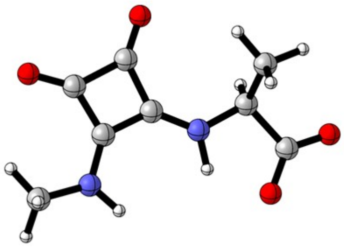
C	-1.95480400	1.65317800	-0.29377800
C	-0.50313100	2.13486400	-0.26103800
O	-3.05455800	2.16077300	-0.44759800
O	0.08878900	3.19595900	-0.36586000
C	-1.43878000	0.27979800	-0.05677700
C	-0.10331000	0.72475400	-0.03578200
N	-1.97044600	-0.95331800	0.08175400
H	-1.33543400	-1.69763300	0.33765700
N	1.06998100	0.10094200	0.13152200
H	1.13653600	-0.91270500	0.15680400
C	2.37943100	0.75692000	0.07315800
H	2.42852300	1.39856400	-0.81423700
C	3.44879500	-0.33340400	-0.09654000
O	3.08830100	-1.55732100	-0.03759700
O	4.64298500	0.04047500	-0.27856700
Na	5.21651400	-2.08396200	-0.38388200
C	2.66458400	1.62141400	1.31261900
H	1.93461100	2.43217900	1.37166500
H	2.60829300	1.01767700	2.22494300
H	3.66489100	2.05408800	1.23260500
C	-3.41645000	-1.30359100	0.09761400
C	-4.12693600	-0.57933400	1.25728200
H	-4.09093200	0.50392400	1.11718000
H	-5.17936700	-0.88069900	1.29902400
H	-3.65942200	-0.83147400	2.21537600
C	-4.05673700	-0.92549400	-1.25067700
H	-5.10890200	-1.23011300	-1.26092700
H	-4.01542800	0.15462600	-1.41120000
H	-3.54339200	-1.43063900	-2.07572400
C	-3.48032800	-2.82522400	0.30438600
H	-4.52214800	-3.15645800	0.31931500

H	-2.96970800	-3.35658200	-0.50711100
H	-3.02465100	-3.11691800	1.25856700



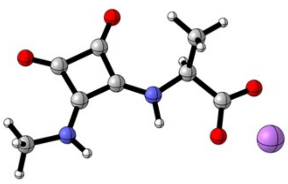
11

C	-1.52944400	1.89123500	-0.18293800
C	-0.03733700	2.23054400	-0.27419100
O	-2.59504000	2.46929500	-0.32911900
O	0.64766800	3.21074900	-0.51112300
C	-1.12775900	0.50785800	0.15751700
C	0.24124800	0.80740500	0.05572500
N	-1.82409100	-0.61654900	0.41981600
H	-1.31506200	-1.43902300	0.71807500
N	1.36103500	0.08670500	0.20683700
H	1.33334900	-0.92201900	0.32392200
C	2.71762200	0.60038800	-0.00186500
H	2.75850300	1.15561200	-0.94609600
C	3.66400800	-0.60202800	-0.14225700
O	3.19710400	-1.77403200	0.05702600
O	4.86997600	-0.36661700	-0.44156500
Na	5.23305900	-2.53854100	-0.38550700
C	3.17817300	1.53461300	1.12971500
H	2.53408400	2.41642800	1.16385600
H	3.13666200	1.01955600	2.09563700
H	4.20533800	1.85668600	0.94125300
C	-3.27937300	-0.63371200	0.60149400
H	-3.65618200	0.31518700	0.21497000
H	-3.52056800	-0.66896900	1.67478100
C	-3.92086100	-1.82786200	-0.11285000
H	-3.71936600	-1.74784900	-1.18910300
H	-3.42998800	-2.75076400	0.22973700
C	-5.43456700	-1.94951100	0.13049100
H	-5.77675500	-2.90007000	-0.29760700
H	-5.62334200	-2.01860500	1.21112600
C	-6.26456500	-0.80387600	-0.46463100
H	-7.33482200	-0.97643900	-0.30881800
H	-6.01937900	0.16264400	-0.01255500
H	-6.09527100	-0.71500100	-1.54418700



Squaramide No cation

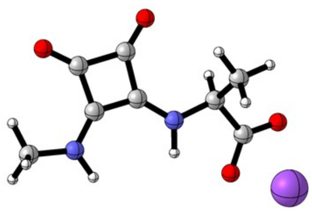
C	-2.44902000	0.81632500	-0.15463600
C	-1.10015600	1.53556500	-0.18231900
O	-3.62971900	1.12689800	-0.21188100
O	-0.70984800	2.67916500	-0.25840300
C	-1.70981300	-0.43600900	-0.03869800
C	-0.45050000	0.19168600	-0.07301800
N	-2.07382000	-1.73764700	0.02314300
H	-1.34844600	-2.40327400	0.24236800
N	0.77343400	-0.28393300	-0.01991600
H	1.00292900	-1.29157300	-0.01891000
C	2.05315300	0.41875000	-0.11560900
H	2.08416700	1.00442200	-1.03812900
C	2.32043100	1.33732000	1.07320400
H	2.27212600	0.77221200	2.00789800
H	3.32426900	1.74957000	0.97384200
H	1.59620400	2.15325400	1.11383500
C	3.14638400	-0.71564600	-0.23340100
O	2.69837600	-1.89302600	-0.16268400
O	4.31015600	-0.31976100	-0.37696800
C	-3.44025700	-2.13103200	0.32324700
H	-4.10916600	-1.34050000	-0.01140600
H	-3.68778200	-3.05578100	-0.20189200
H	-3.60465900	-2.28522100	1.39666900



Squaramide Li

C	2.56102300	-0.81416300	-0.23241700
C	1.17539200	-1.47171900	-0.22389300
O	3.71205000	-1.15431300	-0.38313100
O	0.71226400	-2.58164700	-0.34676700
C	1.87442800	0.47329100	0.01563800
C	0.60991100	-0.12058000	0.00859300
N	2.31320300	1.73395500	0.15632400
H	1.65206500	2.44490400	0.42557300

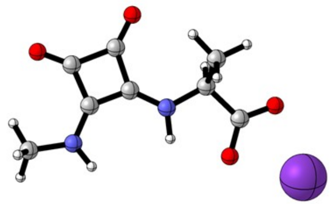
N	-0.63427500	0.34563500	0.16398100
H	-0.82442500	1.33871200	0.16867100
C	-1.83562800	-0.47487100	0.04060600
H	-1.74434700	-1.13301400	-0.82719800
C	-2.09264100	-1.34458500	1.27707900
H	-2.17460600	-0.72492200	2.17231000
H	-3.01733400	-1.90527900	1.14616200
H	-1.27143600	-2.04868100	1.40290300
C	-3.02053800	0.44868200	-0.22646400
O	-2.85693500	1.71034600	-0.18359900
O	-4.14574800	-0.06367000	-0.47486900
C	3.72826300	2.07309100	0.24073100
H	4.31030400	1.22304500	-0.10731600
H	3.94723900	2.93690900	-0.38907800
H	4.02585100	2.30161800	1.26808700
Li	-4.67670800	1.70299100	-0.59818100



Squaramide Na

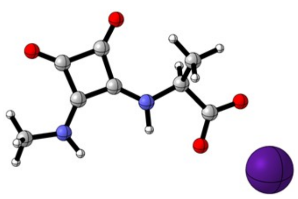
C	3.00122800	-0.62123600	-0.29584900
C	1.70166800	-1.43490000	-0.27611100
O	4.17975400	-0.82208800	-0.48789100
O	1.36762000	-2.58706900	-0.42568100
C	2.18029700	0.56755300	0.01383900
C	0.98975800	-0.16508100	0.01632500
N	2.47382800	1.86801700	0.18492400
H	1.74415400	2.48141000	0.51148100
N	-0.29084700	0.15459800	0.21484600
H	-0.59349400	1.11906200	0.26657700
C	-1.40686600	-0.78106500	0.09775800
H	-1.27631000	-1.39580300	-0.79575400
C	-1.52641000	-1.71112700	1.30976300
H	-1.64350400	-1.13170700	2.22812000
H	-2.39144900	-2.36178300	1.18773600
H	-0.63235800	-2.32844200	1.38909600
C	-2.69528300	0.02952500	-0.09801000
O	-2.63714700	1.29307500	0.00569500
O	-3.74882200	-0.61046400	-0.34285000
C	3.84334300	2.35775500	0.27674600
H	4.50941200	1.60597200	-0.14017400
H	3.95017800	3.28339600	-0.29109500

H	4.13747500	2.54498300	1.31384800
Na	-4.80933000	1.30804000	-0.42992400



Squaramide K

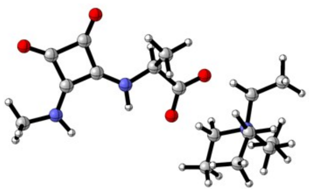
C	3.41232100	-0.45508200	-0.33841000
C	2.18969100	-1.37977800	-0.31653100
O	4.60081700	-0.54848000	-0.55562500
O	1.95640700	-2.55354000	-0.48779800
C	2.49814100	0.64871100	0.01279200
C	1.37389500	-0.18320900	0.01747000
N	2.67949800	1.96739900	0.20873800
H	1.90645500	2.50194000	0.57231800
N	0.07700600	0.02367200	0.24414500
H	-0.30806500	0.95817200	0.31903600
C	-0.96799200	-0.99057100	0.12163100
H	-0.81520900	-1.56402400	-0.79563200
C	-0.98439500	-1.96407600	1.30370900
H	-1.11882900	-1.42380600	2.24358900
H	-1.80424100	-2.67088300	1.18164300
H	-0.04663600	-2.51755500	1.34225600
C	-2.32105900	-0.26690800	-0.01731200
O	-2.33833000	0.99367600	0.11511300
O	-3.32581300	-0.98216700	-0.24715500
C	4.00383700	2.56692200	0.30798100
H	4.72425500	1.89468400	-0.15232900
H	4.02270000	3.52365500	-0.21641600
H	4.29927700	2.73038700	1.34902600
K	-4.86981700	1.02620900	-0.32410200



Squaramide Cs

C	-4.66377300	0.22610400	-0.39825000
C	-3.55046500	1.27991400	-0.37391600
O	-5.84836900	0.18201700	-0.65100400
O	-3.44179700	2.46657400	-0.57761700
C	-3.64628200	-0.75904600	0.01379300

C	-2.61930800	0.19059800	0.02143800
N	-3.68768700	-2.08388100	0.24763400
H	-2.87291200	-2.51659100	0.65326400
N	-1.31574900	0.13219800	0.28872400
H	-0.83388900	-0.75229500	0.40582100
C	-0.37918300	1.24713100	0.16329600
H	-0.56008600	1.77254000	-0.77732900
C	-0.50448500	2.25234500	1.31146800
H	-0.34630600	1.75807600	2.27282600
H	0.24182100	3.03665400	1.19063200
H	-1.49515400	2.70612900	1.30353900
C	1.04692600	0.66318700	0.09042700
O	1.18651700	-0.58299000	0.26567300
O	1.97776700	1.47320000	-0.13299200
C	-4.94169900	-2.82016800	0.33860600
H	-5.71578600	-2.25149000	-0.17150600
H	-4.83958400	-3.79463800	-0.14159600
H	-5.25147100	-2.97066200	1.37756000
Cs	4.02280200	-0.46030500	-0.14729700



Squaramide tert-butylammonium

C	5.53122500	-0.15285000	-0.56527300
C	4.45995200	-1.24683100	-0.49761000
O	6.69847600	-0.06265600	-0.88394400
O	4.38423500	-2.43361500	-0.71608500
C	4.50602900	0.78657800	-0.08035900
C	3.51236700	-0.19818600	-0.03190600
N	4.51143900	2.11003500	0.17311700
H	3.70844000	2.49938100	0.64172700
N	2.22722100	-0.18577600	0.30747200
H	1.71945000	0.67971800	0.46573300
C	1.30987100	-1.32068500	0.21803300
H	1.44284500	-1.82229000	-0.74333500
C	1.53190000	-2.34224300	1.33541000
H	1.42190800	-1.86893300	2.31407400
H	0.79596900	-3.14057100	1.24653400
H	2.53011300	-2.77351500	1.25959700
C	-0.13480800	-0.76050200	0.24777600
O	-0.27441700	0.47549600	0.44998500

O	-1.05130400	-1.59640900	0.07237100
C	5.74536300	2.88236300	0.22934800
H	6.50696300	2.36188100	-0.34690100
H	5.58653500	3.87255600	-0.20073900
H	6.10932900	2.99901400	1.25535000
C	-3.95041400	-1.11267400	-0.91146900
H	-4.23544100	-0.85419700	-1.92866900
H	-2.88924400	-1.36965600	-0.88715300
C	-3.56556000	-0.13970000	1.31388600
H	-4.34617600	-0.76844500	1.73749900
H	-2.66073100	-0.73248000	1.16645400
N	-4.04366900	0.18891700	-0.10609500
C	-5.45771700	0.71405500	-0.05723400
H	-5.42005200	1.65436100	0.48611600
H	-6.02555400	0.01352500	0.55233500
C	-3.07368000	1.16139300	-0.79768400
H	-2.07686100	0.86548400	-0.45633200
H	-3.15138200	0.94328900	-1.86108700
C	-4.78709000	-2.27415600	-0.40538600
H	-5.85585000	-2.05870200	-0.35890800
H	-4.65337000	-3.09446300	-1.11233300
H	-4.45397300	-2.63768100	0.56466800
C	-6.13695000	0.90482100	-1.40455700
H	-7.09762800	1.39275300	-1.23327800
H	-5.56377000	1.53912800	-2.07932700
H	-6.33692800	-0.04025800	-1.90719900
C	-3.29428400	2.64940900	-0.57508500
H	-4.23183600	3.02045100	-0.98955900
H	-3.23188700	2.94652900	0.46786400
H	-2.48511000	3.16031800	-1.09991900
C	-3.27453200	1.02788800	2.23801100
H	-2.37696600	1.56172600	1.93409300
H	-4.10765700	1.72254100	2.35482600
H	-3.07202500	0.60167900	3.22238300

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