Cyclopentadienone Iron Complex-Catalyzed Hydrogenation of Ketones: The Influence of the Charge-Tag on Catalytic Performance

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Supporting Information

Cyclopentadienone Iron Complex-Catalyzed Hydrogenation of Ketones: The Influence of the Charge-Tag on Catalytic Performance

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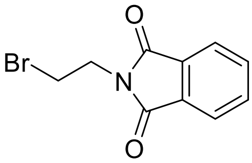
1) NMR and Mass Spectra

1.1) 2-(2-bromoethyl)isoindoline-1,3-dione



A nitrogen-flushed 50 ml round bottom flask equipped with a stir bar and a reflux condenser was charged with 1 g potassium phthalimide (5.4 mmol, 1 equiv.), 1.4 ml 1,2-dibromoethane (16.2 mmol, 3 equiv.) and 10 ml dry acetone. The mixture was stirred and refluxed overnight. The next day, the mixture was allowed to cool down to room temperature. The mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The solid residue was extracted with hexane until no more material dissolved. The volatiles were removed under reduced pressure. The product was obtained as a colorless solid (1.21 g, 88 %).

^{1}H NMR (δ, 400 MHz, $CDCl_3$): 7.92 – 7.87 (m, 2H), 7.79 – 7.74 (m, 2H), 4.13 (t, *J* = 6.7 Hz, 2H), 3.64 (t, *J* = 6.7 Hz, 2H).

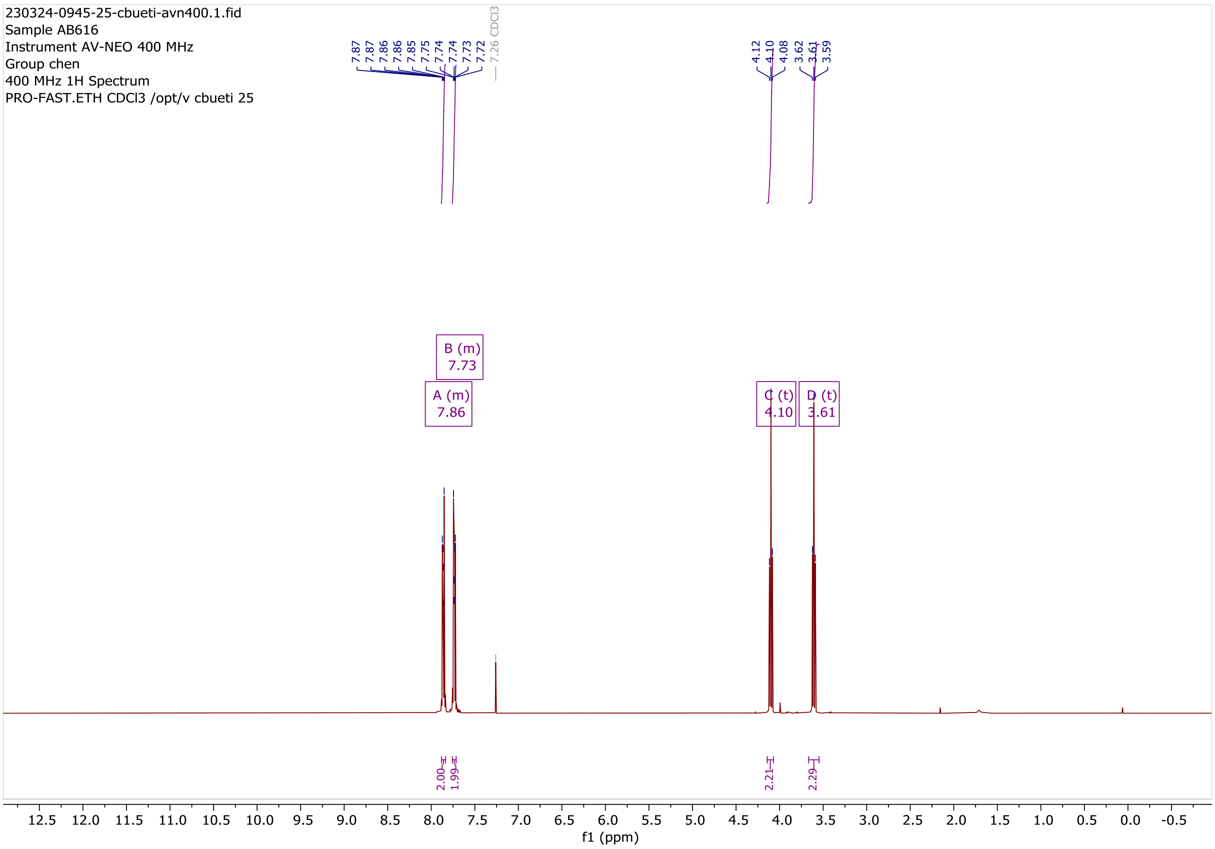
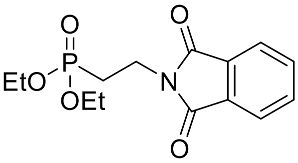


Figure S1. ^{1}H NMR spectrum recorded in $CDCl_3$.

1.2) Diethyl (2-(1,3-dioxoisoindolin-2-yl)ethyl)phosphonate



A dried and argon-flushed 50 ml 2-necked round bottom flask equipped with a stir bar and reflux condenser was charged with 1 g **1** (3.94 mmol, 1 equiv.) and 2 ml $P(OEt)_3$ (11.81 mmol, 3 equiv.). The mixture was stirred and heated to 180 °C for 3 h. The mixture was allowed to cool to room temperature. The volatiles were removed using a liquid nitrogen trap and high vacuum. The crude was purified by column chromatography (SiO_2, EtOAc). The compound was isolated as a yellow oil (1.01 g, 82 %).

TLC (SiO$_2$, EtOAc): r_f = 0.3.

^{1}H NMR (δ, 300 MHz, CDCl$_3$): 7.87 – 7-82 (m, 2H), 7.76 – 7.68 (m, 2H), 4.18 – 4.03 (m, 4H), 4.03 – 3.89 (m, 2H), 2.29 – 3.14 (m, 2H), 1.30 (t, J = 7.0 Hz, 6H).

^{31}P NMR (δ, 120 MHz, CDCl$_3$): 26.7.

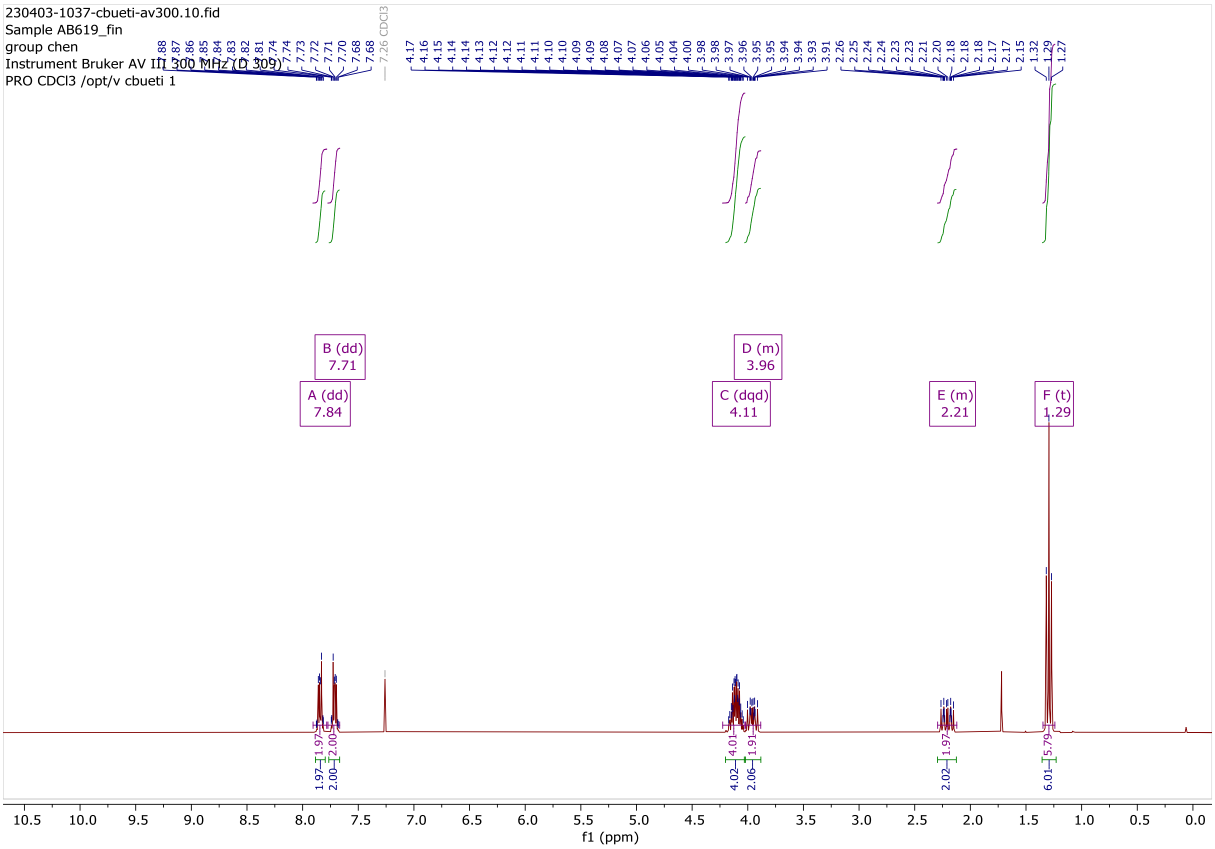


Figure S2. ^{1}H NMR spectrum recorded in CDCl$_3$.

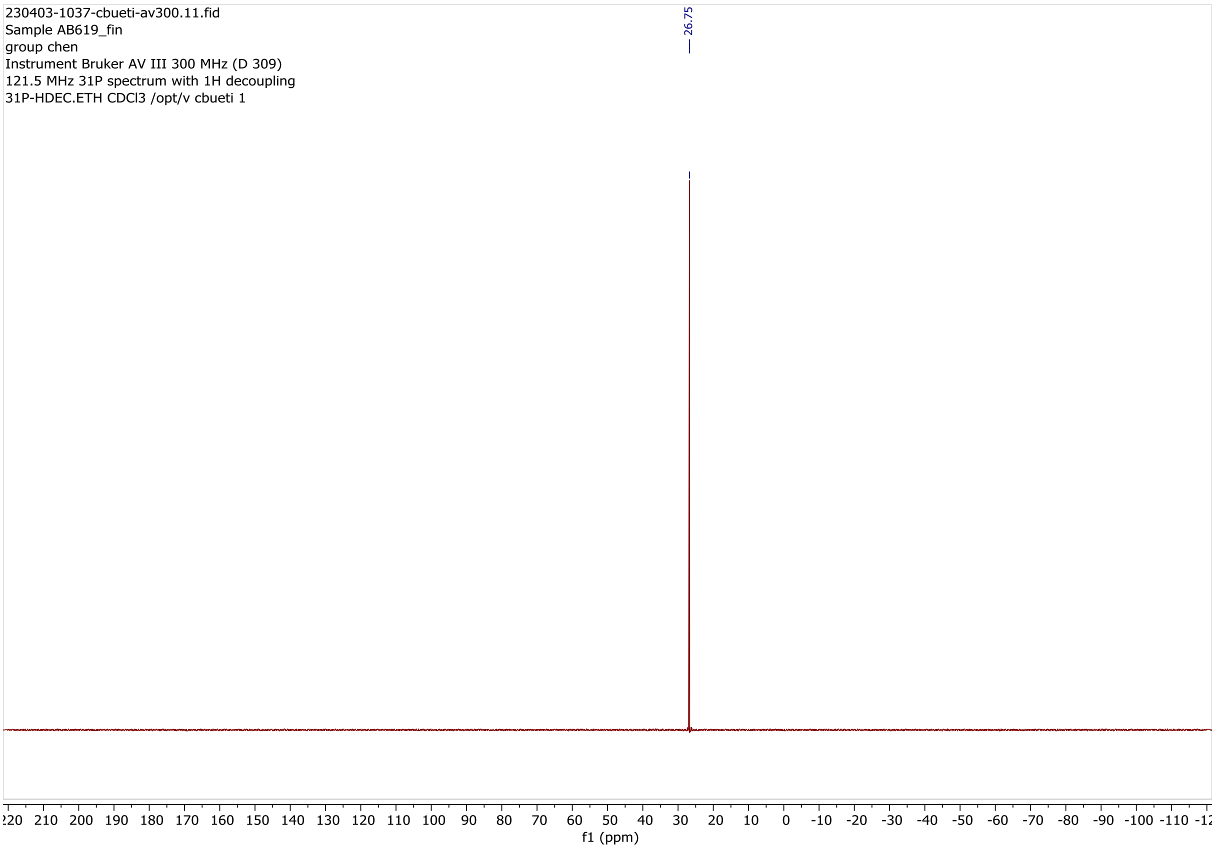
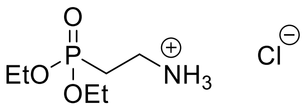


Figure S3. ^{31}P NMR spectrum recorded in CDCl$_3$.

1.3) Diethyl (2-aminoethyl)phosphonate hydrochloride



A 100 ml round bottom flask equipped with a stir bar was charged with 5 g **2** (16.06 mmol, 1 equiv.), 50 ml absolute EtOH and 1.2 ml hydrazine hydrate (24.09 mmol, 1.5 equiv.). A reflux condenser was attached and the vessel was flushed with N_2. The mixture was stirred at room temperature overnight. A white precipitate formed. The mixture was refluxed for 2 h. The mixture was allowed to cool to room temperature. The solids were removed by filtration. The solvent was removed under reduced pressure. The residue was dissolved in 50 ml THF and refluxed for 1.5 h. The mixture was allowed to cool to room temperature and then placed in a freezer overnight. The solid was removed by filtration and rinsed with cold THF. The pale yellow oil was dissolved in EtOH. Concentrated hydrochloric acid was added until the solution became turbid. The volatiles were removed under reduced pressure. The residue was suspended in acetone. The solid was filtered off. The filtrate was concentrated under reduced pressure. The residue was triturated with Et_2O. The solid was dried *in vacuo*. The product was isolated as a pale yellow solid (2.89 g, 83 %).

^{1}H NMR (δ, 400 MHz, CDCl$_3$): 8.38 (s, br, 3H), 4.20 – 4.04 (m, 4H), 3.41 – 3.23 (m, 2H), 2.50 - 2.36 (m, 2H), 1.33 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (δ, 100 MHz, CDCl$_3$): 62.9 (d, *J* = 6.4 Hz), 34.9, 23.8 (d, *J* = 141.0 Hz), 16.5 (d, *J* = 6.1 Hz).

^{31}P NMR (δ, 160 MHz, CDCl$_3$): 26.9.

LRMS (m/z): [M-Cl]$^+$ calc. for $C_6H_{17}NO_3P$: 182.09. Found: 182.25.

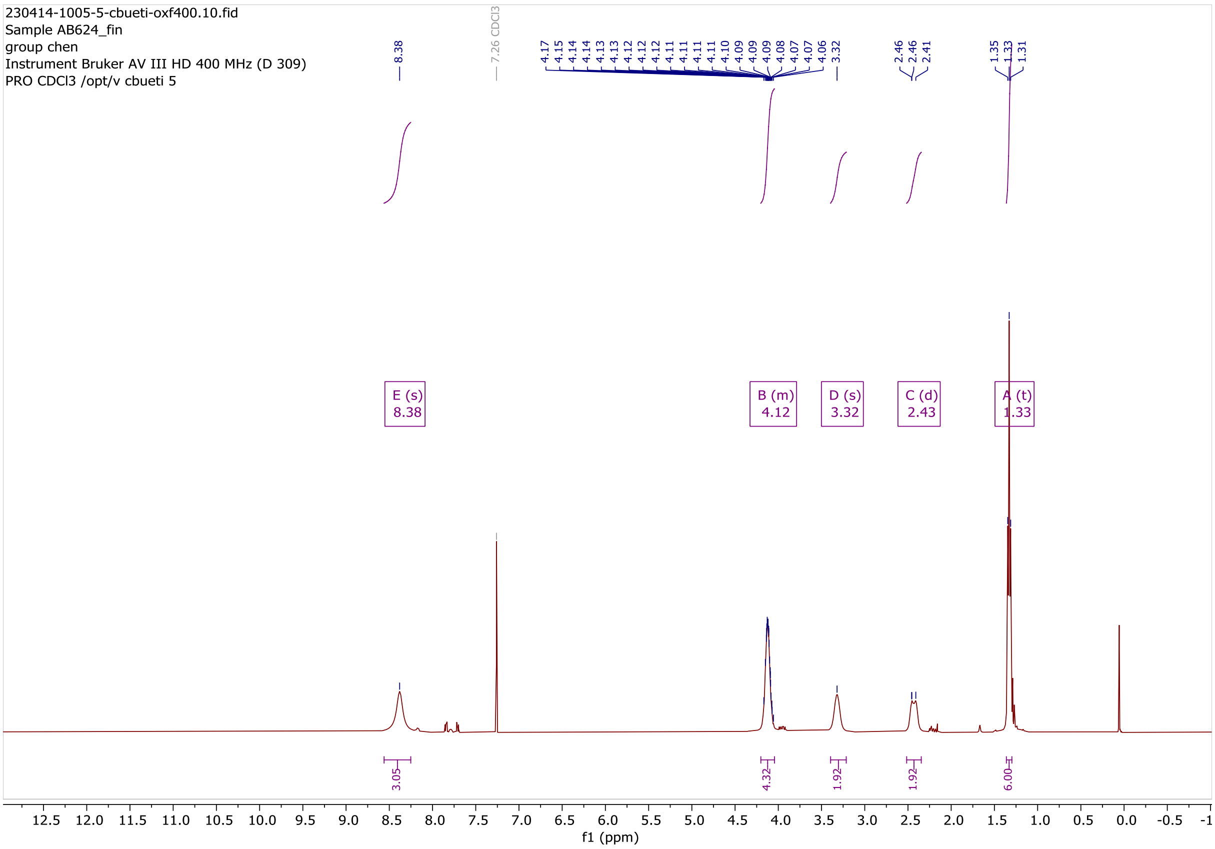


Figure S4. ^1H NMR spectrum recorded in $CDCl_3$.

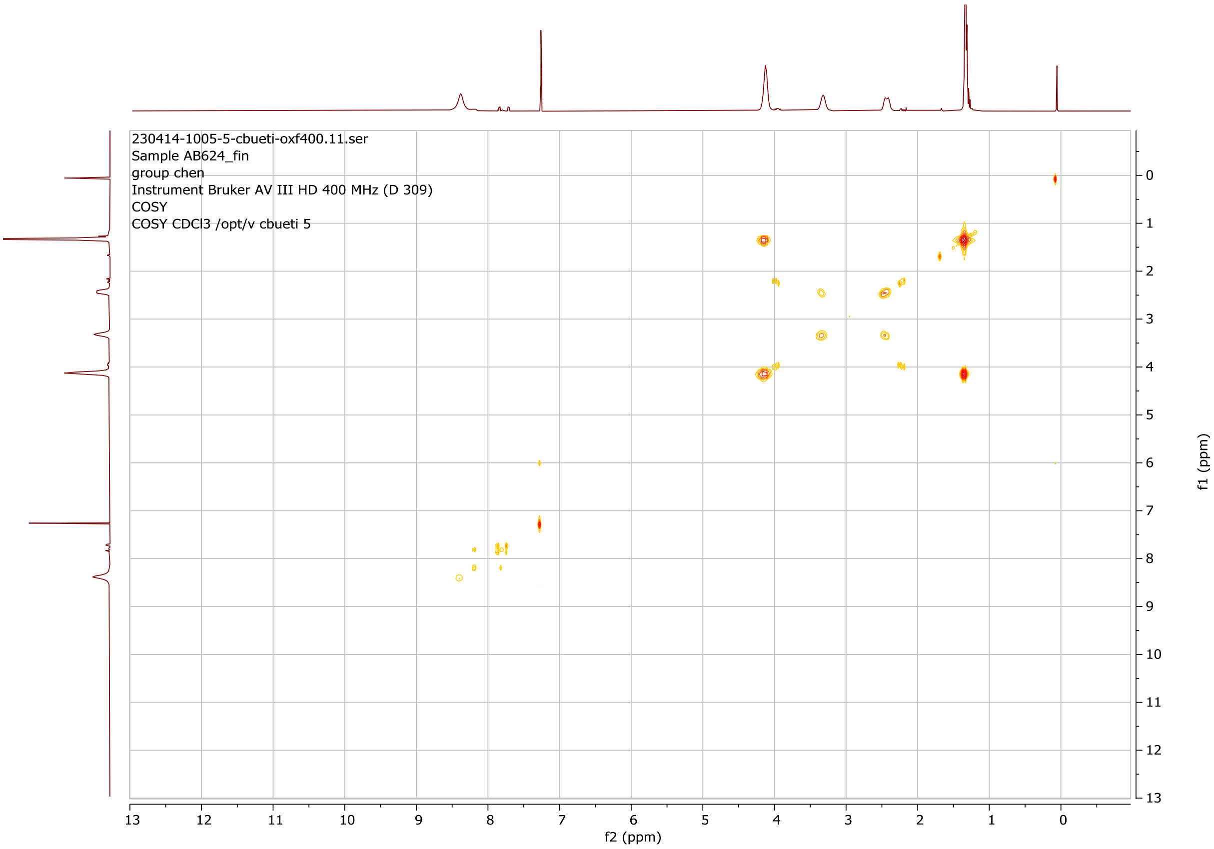


Figure S5. COSY spectrum recorded in $CDCl_3$.

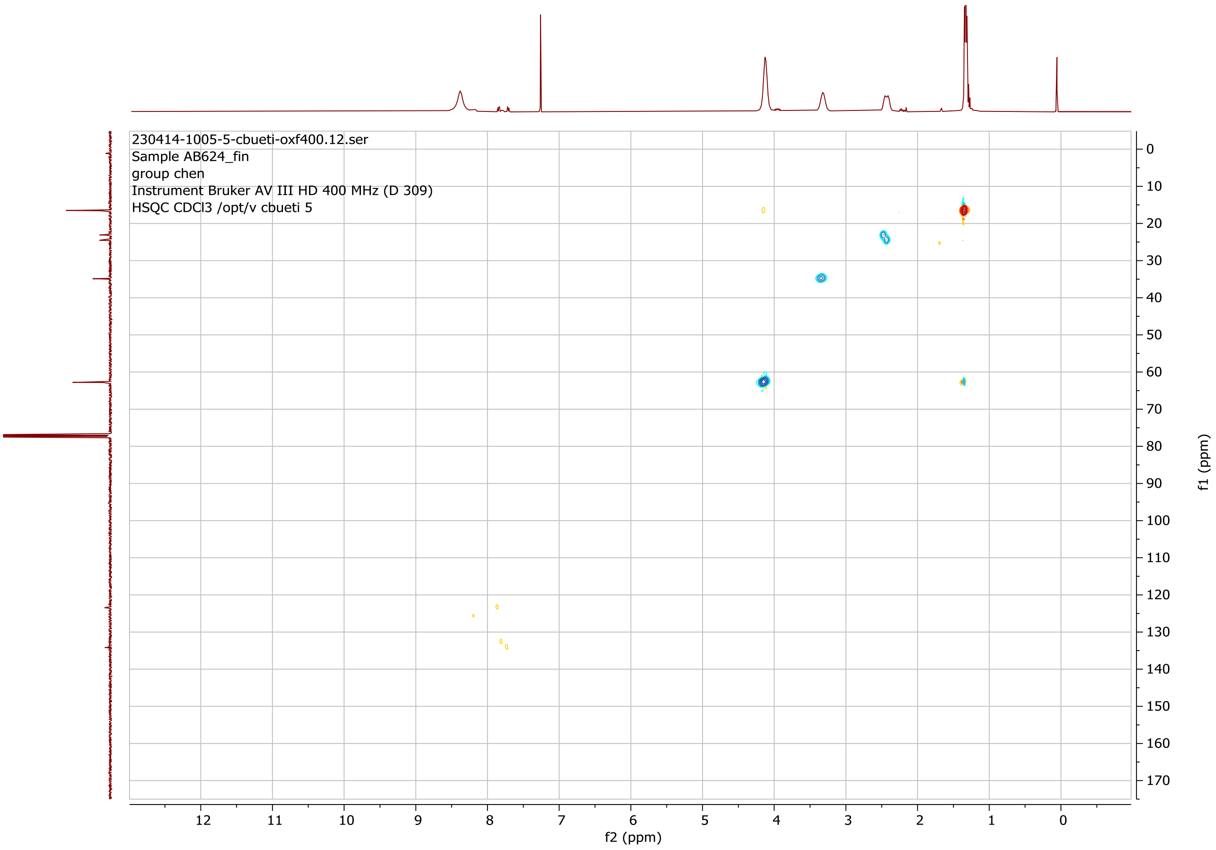


Figure S6. HSQC spectrum recorded in $CDCl_3$.

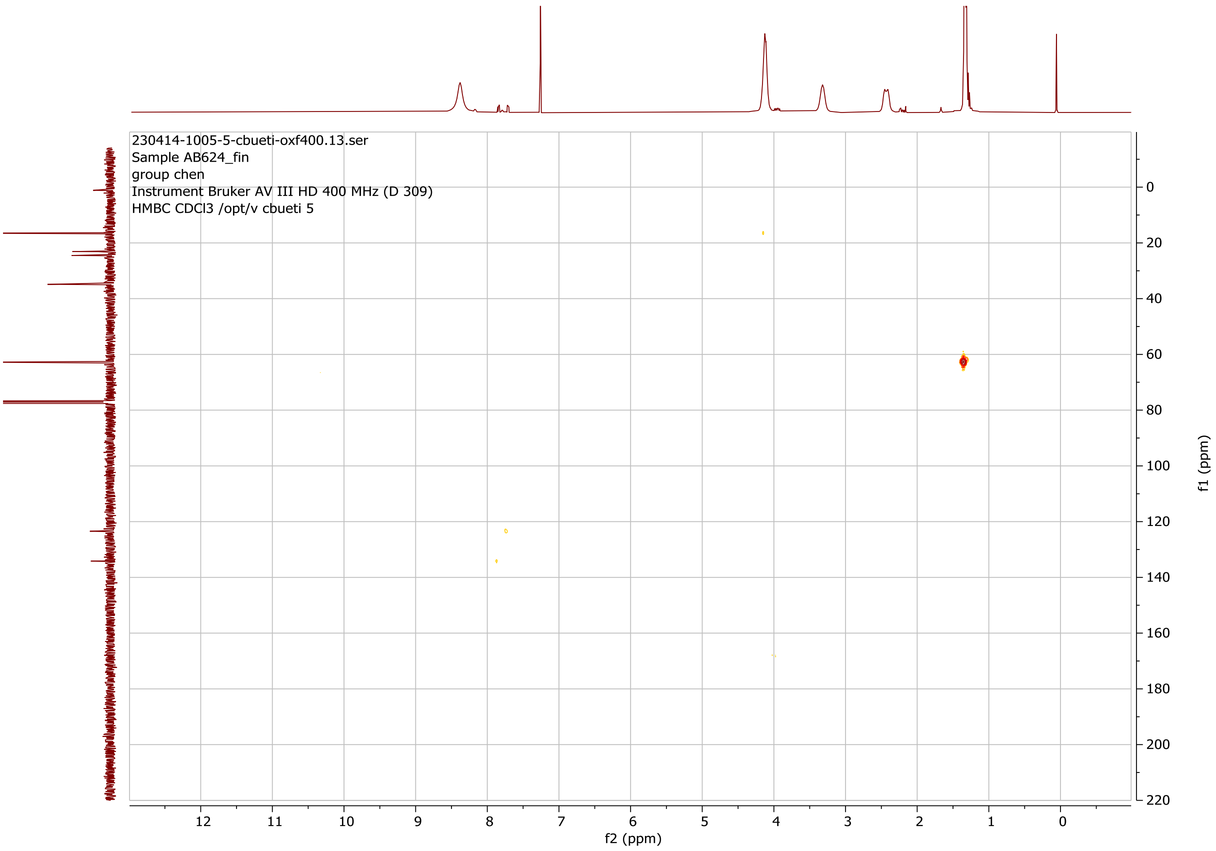


Figure S7. HMBC spectrum recorded in $CDCl_3$.

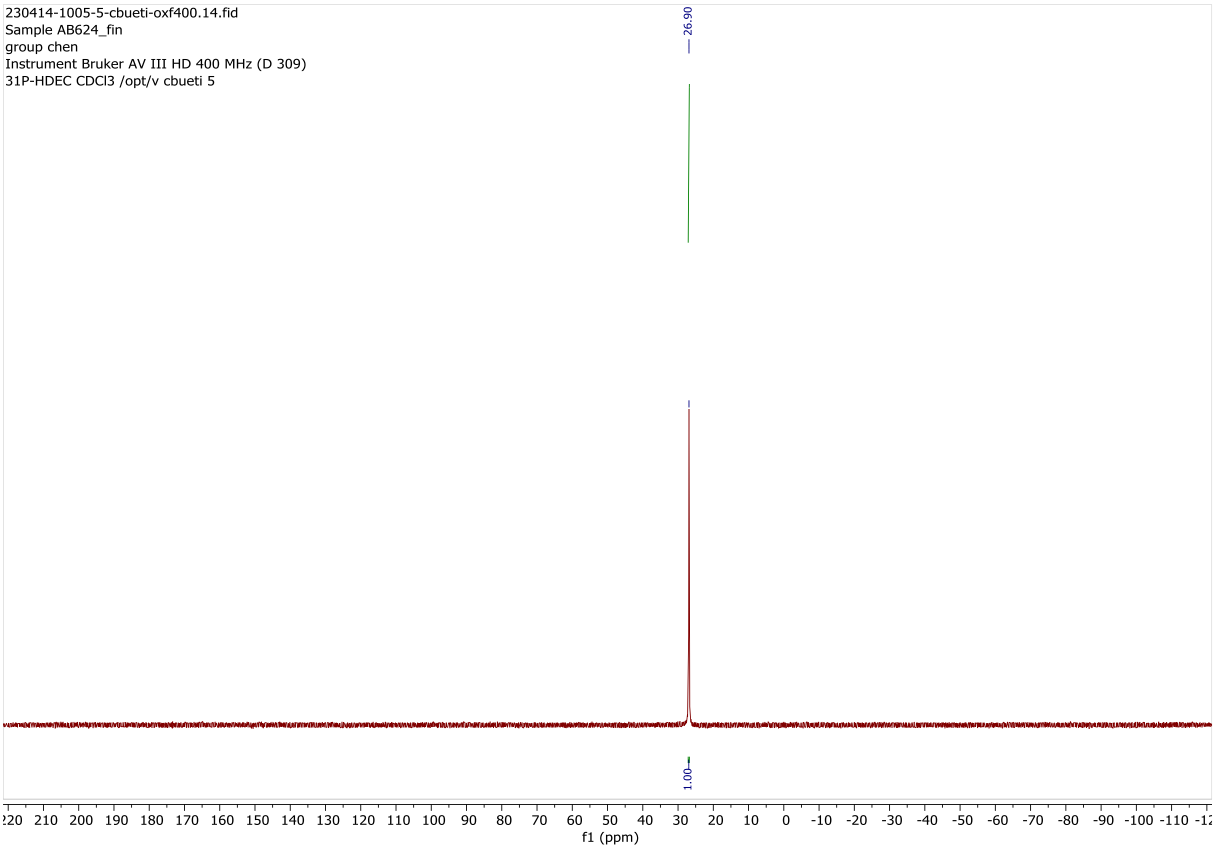


Figure S8. ^{31}P spectrum recorded in $CDCl_3$.

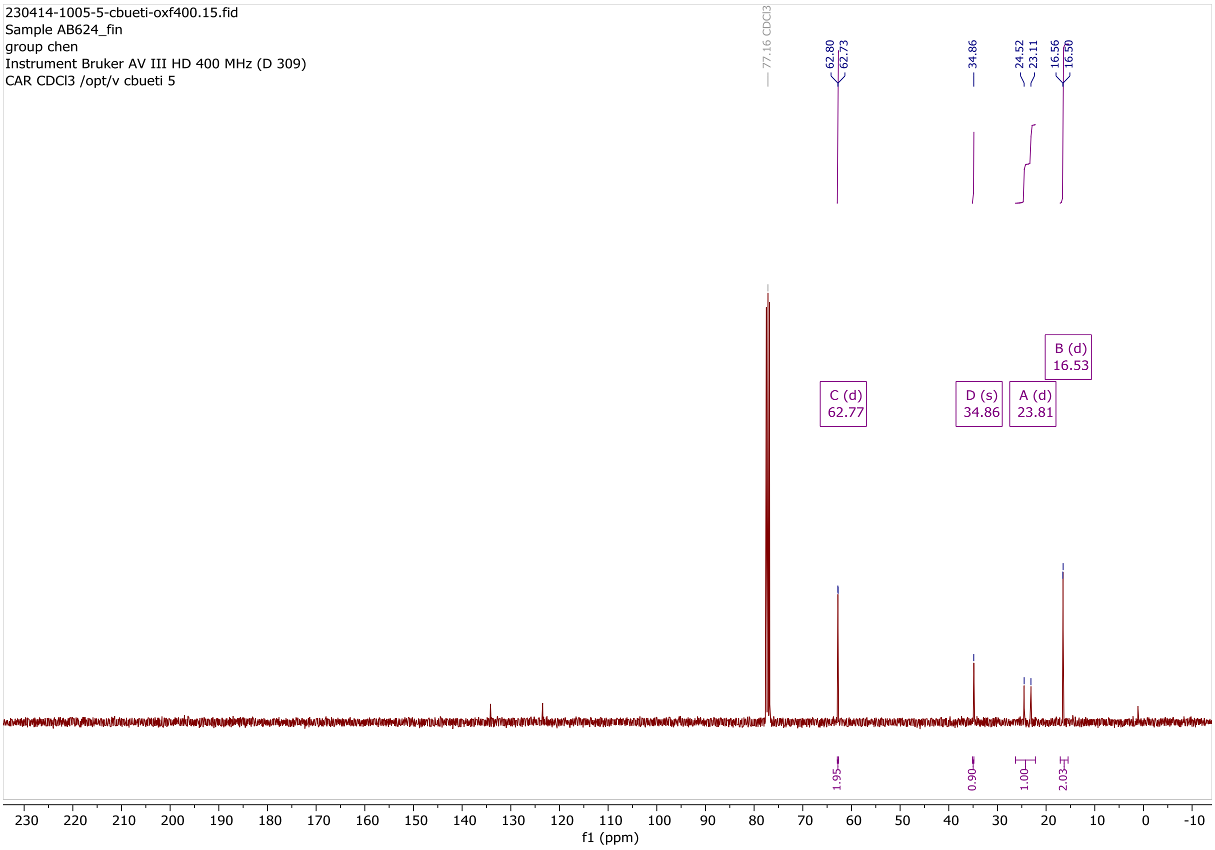


Figure S9. ^{13}C spectrum recorded in $CDCl_3$.

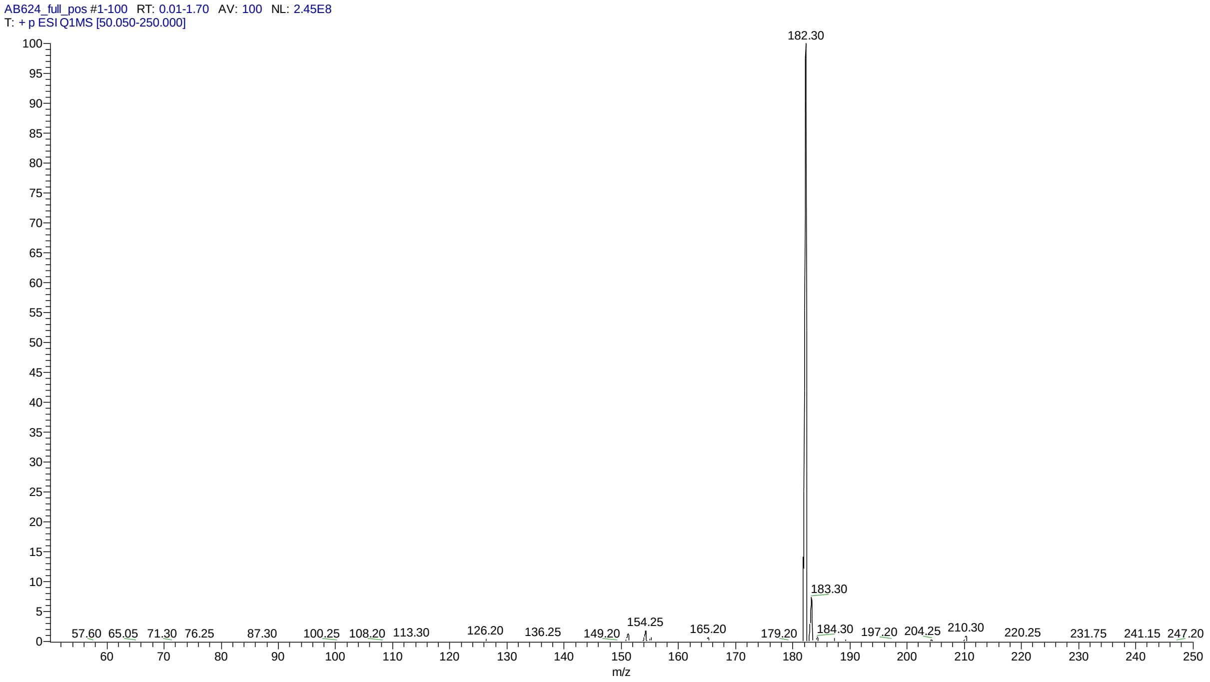
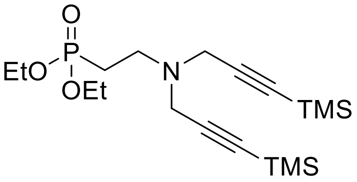


Figure S10. LRMS full spectrum. Sprayed from EtOH with a drop of formic acid.

1.4) Diethyl(2-(bis(3(trimethylsilyl)prop-2-yn-1-yl)ethyl)phosphonate



A dried and argon-flushed 50 ml Schlenk tube equipped with a stir bar was charged with 200 mg **3** (0.92 mmol, 1 equiv.) and 10 ml dry MeCN. To the pale yellow suspension, 0.26 ml (3-bromoprop-1-yn-1-yl)trimethylsilane (1.85 mmol, 2 equiv.) and 0.48 ml $^{i}Pr_2NEt$ (2.76 mmol, 3 equiv.) were added, resulting in a pale yellow, clear solution. The solution was heated to 70 °C overnight. The next day, the solution was allowed to cool to room temperature. The mixture was diluted with water and extracted three times with EtOAc. The organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting orange oil was purified by column chromatography (SiO_2, 1:1 EtOAc/hexane). The compound was isolated as a yellow oil (191 mg, 52 %).

TLC (SiO_2, 1:1 EtOAc/hexane, $KMnO_4$ stain): $r_f = 0.3$.

TLC (SiO_2, EtOAc, $KMnO_4$ stain): $r_f = 0.5$.

^{1}H NMR (δ, 400 MHz, $CDCl_3$): 4.22 – 4.01 (m, 4H), 3.42 (s, 4H), 2.91 – 2.77 (m, 2H), 2.04 – 1.91 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H), 0.16 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 100.6, 90.2, 61.7, 46.7, 43.0, 24.8 (d, *J* = 117.9 Hz), 16.5, 0.1.

^{31}P NMR (δ, 160 MHz, $CDCl_3$): 29.8.

LRMS (m/z): $[M+H]^+$ calc. for $C_{18}H_{37}NO_3PSi_2$: 402.20. Found: 402.33.

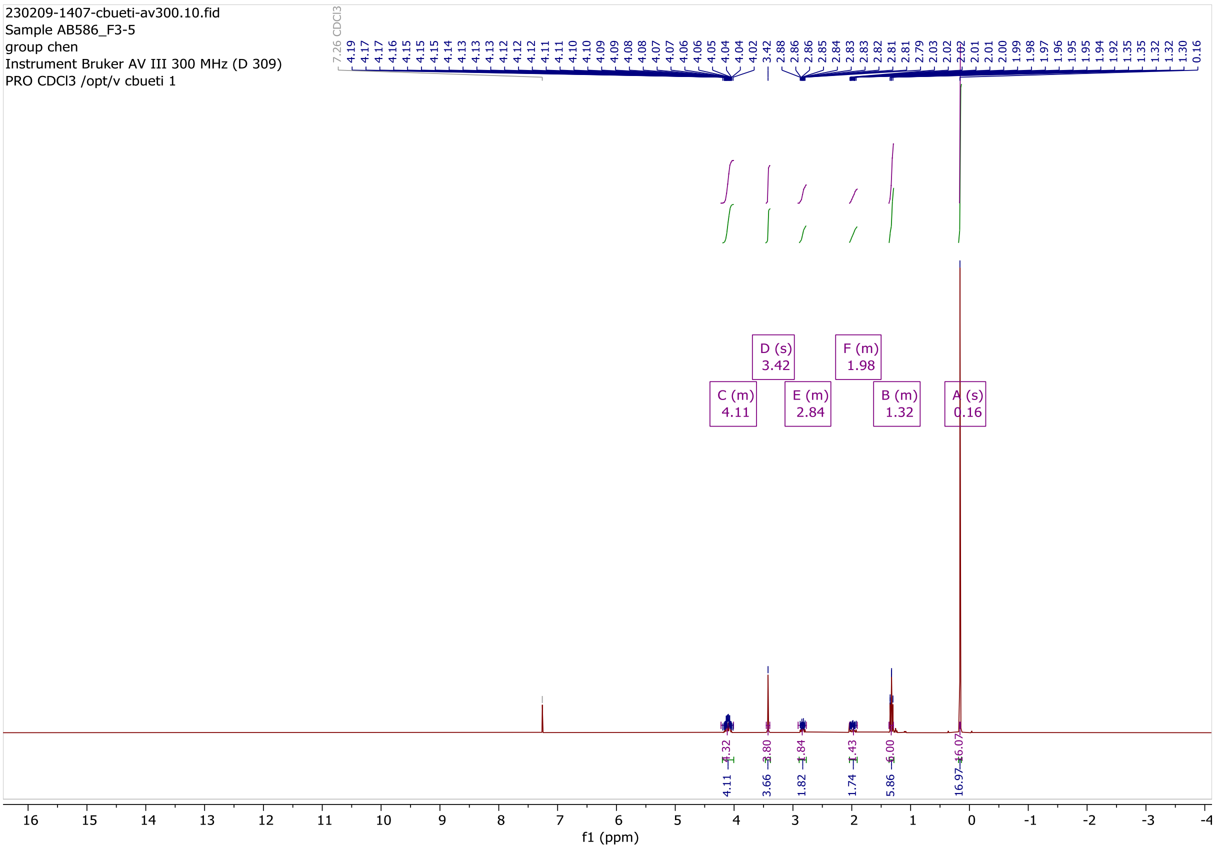


Figure S11. ^{1}H NMR spectrum recorded in $CDCl_3$.

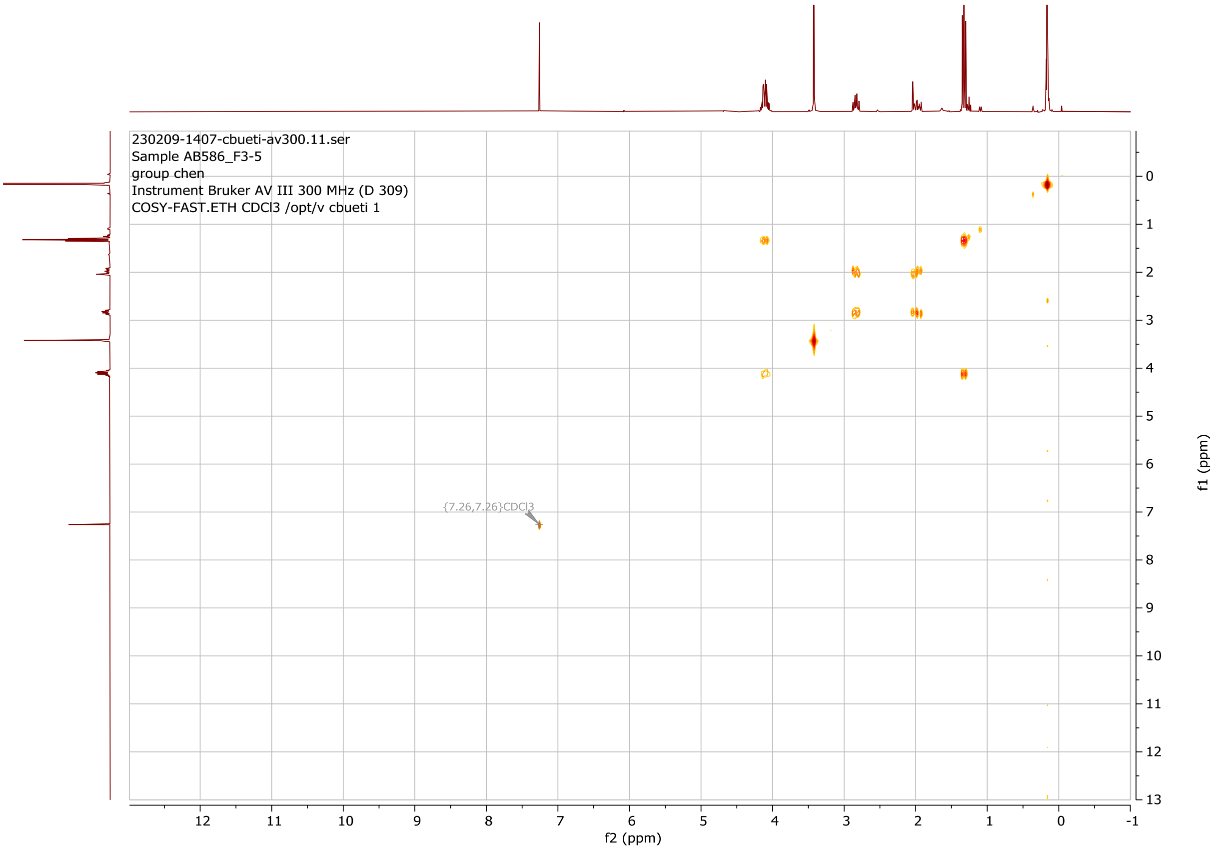


Figure S12. COSY spectrum recorded in $CDCl_3$.

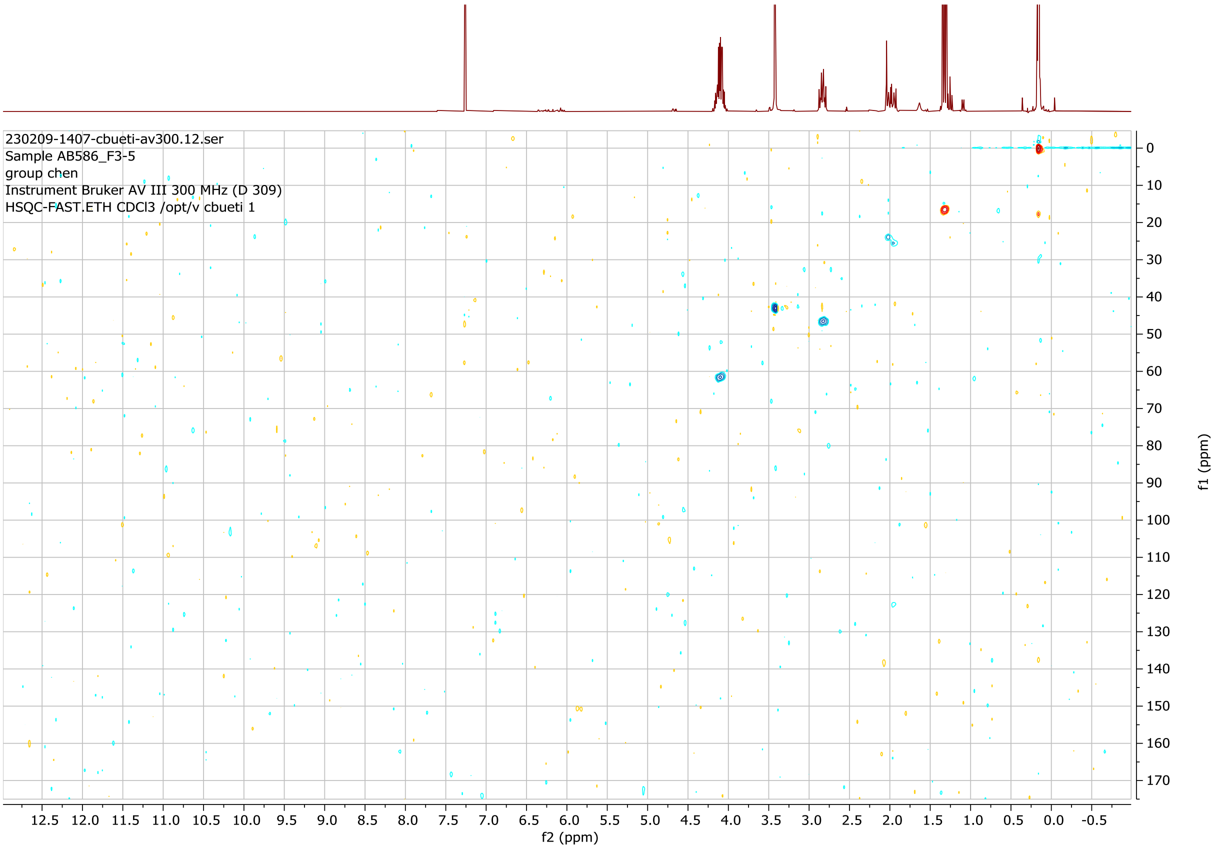


Figure S13. HSQC spectrum recorded in CDCl$_3$.

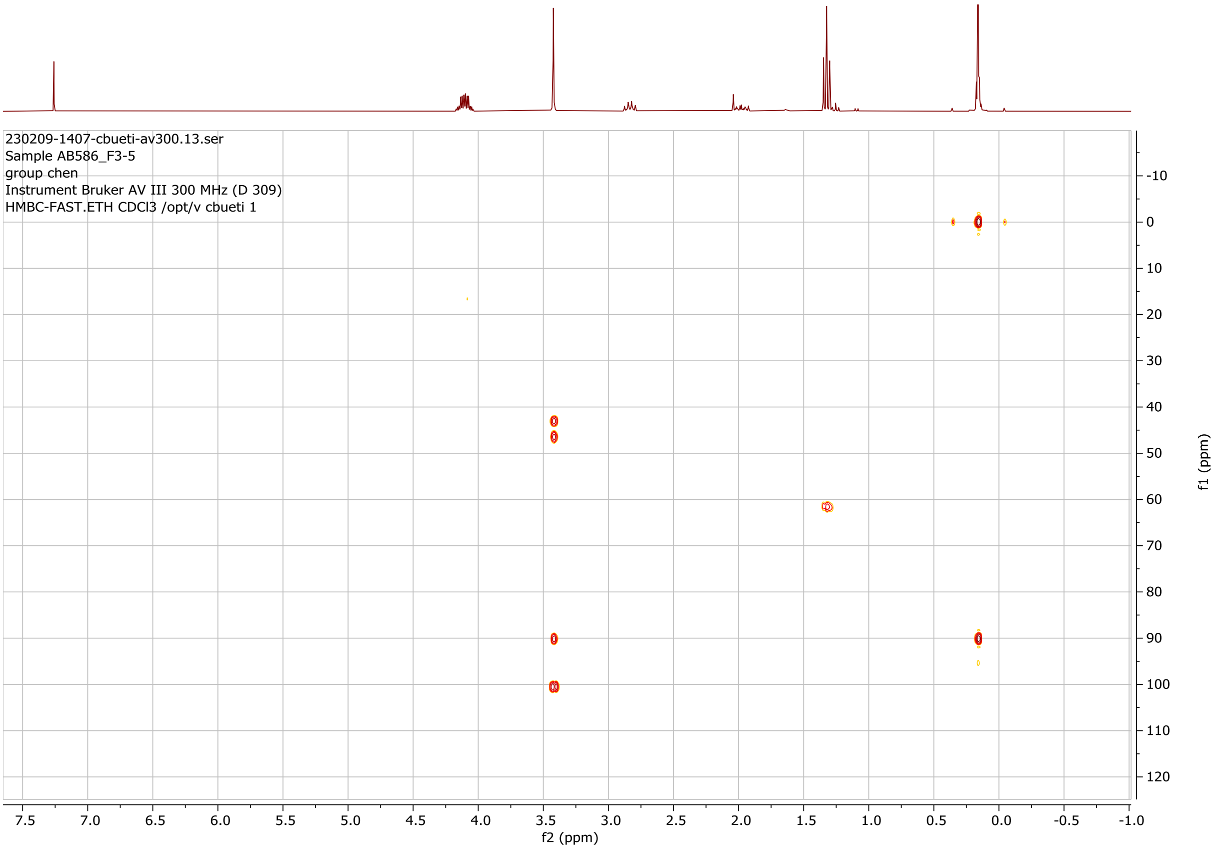


Figure S14. HMBC spectrum recorded in CDCl$_3$.

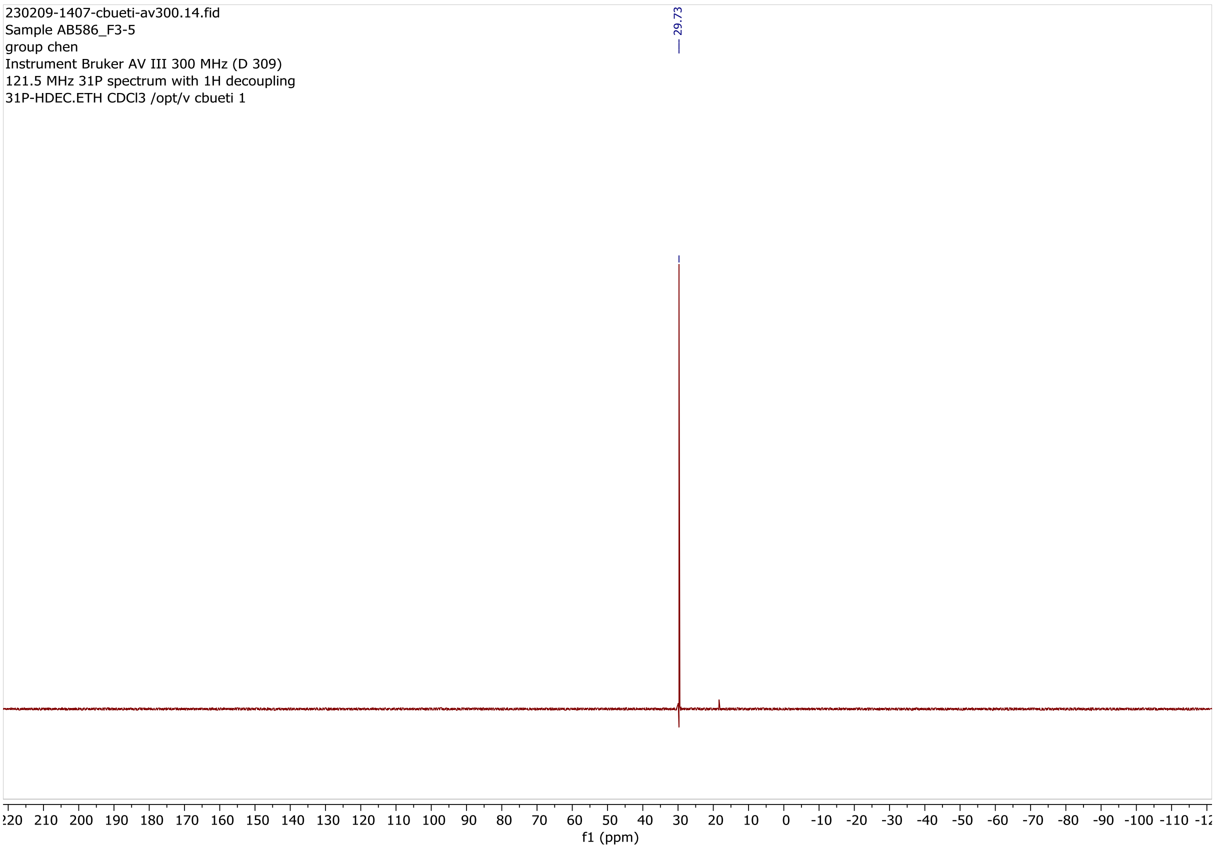


Figure S15. ^{31}P NMR spectrum recorded in $CDCl_3$.

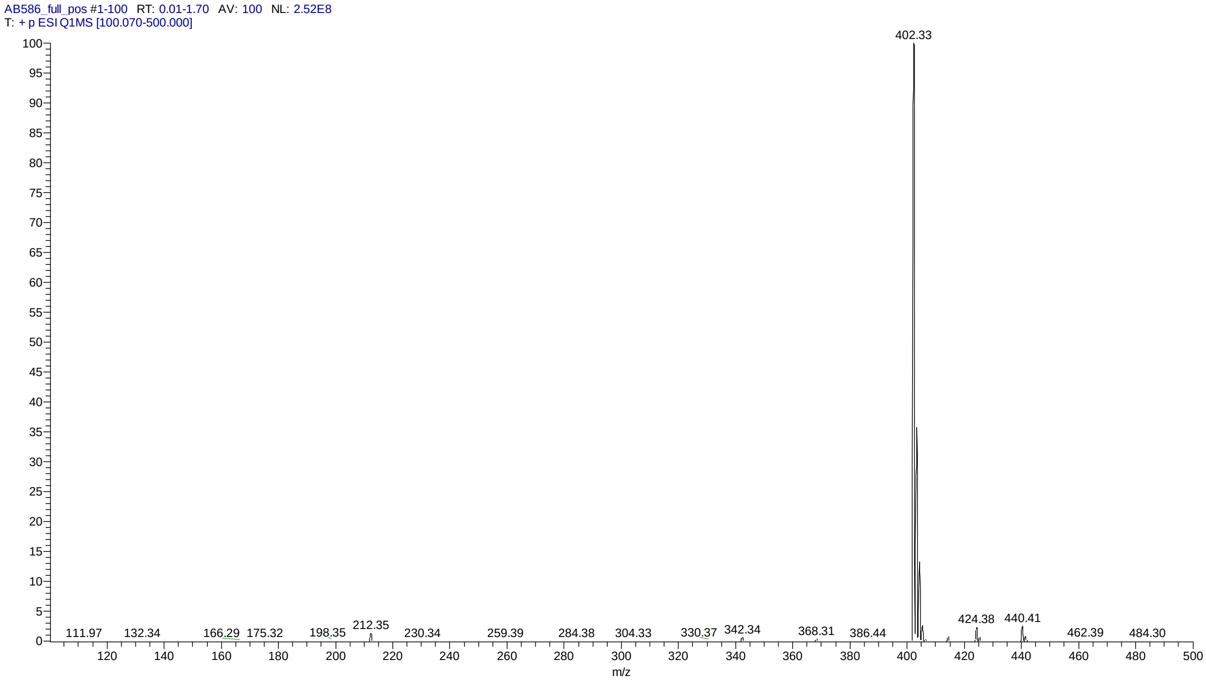
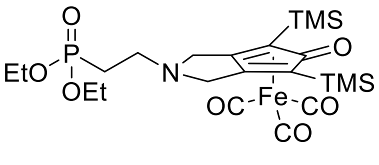


Figure S16. LRMS full spectrum. Sprayed from EtOH with a drop of formic acid.

1.5) $Fe^{TMS}(CO)_3$-P(O)(OEt)$_2$



A dried and argon-flushed 2-necked 50 ml round bottom flask equipped with a stir bar and a reflux condenser was charged with 190 mg **4** (0.48 mmol, 1 equiv.), 175 mg $Fe_2(CO)_9$ (0.48 mmol, 1 equiv.) and 5 ml dry toluene. The mixture was stirred and heated to reflux overnight. The next day, the mixture was allowed to cool to room temperature. The mixture was directly loaded onto a silica packed column and eluted with toluene until a straw orange band corresponding to $Fe(CO)_5$ had fully eluted. The $Fe(CO)_5$ dissolved in toluene was quenched with NaOCl prior to disposal. The eluent was changed to EtOAc and purification by column chromatography was continued. The relevant orange fractions were combined and concentrated under reduced pressure. The compound was dried *in vacuo* and was obtained as an orange oil (198 mg, 72 %).

TLC (SiO_2, EtOAc): r_f = 0.45.

^{1}H NMR (δ, 400 MHz, $CDCl_3$): 4.18 – 4.09 (m, 4H), 3.83 (d, *J* = 12.3 Hz, 2H), 3.36 (d, *J* = 12.3 Hz, 2H), 3.14 – 3.03 (m, 2H), 2.12 – 1.99 (m, 2H), 1.34 (td, *J* = 7.1, 0.4 Hz, 6H), 0.25 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 208.6, 182.3, 113.0, 69.4, 61.9 (d, *J* = 6.4 Hz), 53.2, 48.9, 26.0 (d, *J* = 140.1 Hz), 16.4 (d, *J* = 6.1 Hz), 0.7.

^{31}P NMR (δ, 160 MHz, $CDCl_3$): 29.3.

LRMS (m/z): [M+H]$^+$ calc. for $C_{22}H_{37}FeNO_7PSi_2$: 570.12. Found: 570.11.

ESI-MS CID (m/z): 570 [M+H]$^+$, 542 [M+H-CO]$^+$, 514 [M+H-2CO]$^+$, 486 [M+H-3CO]$^+$.

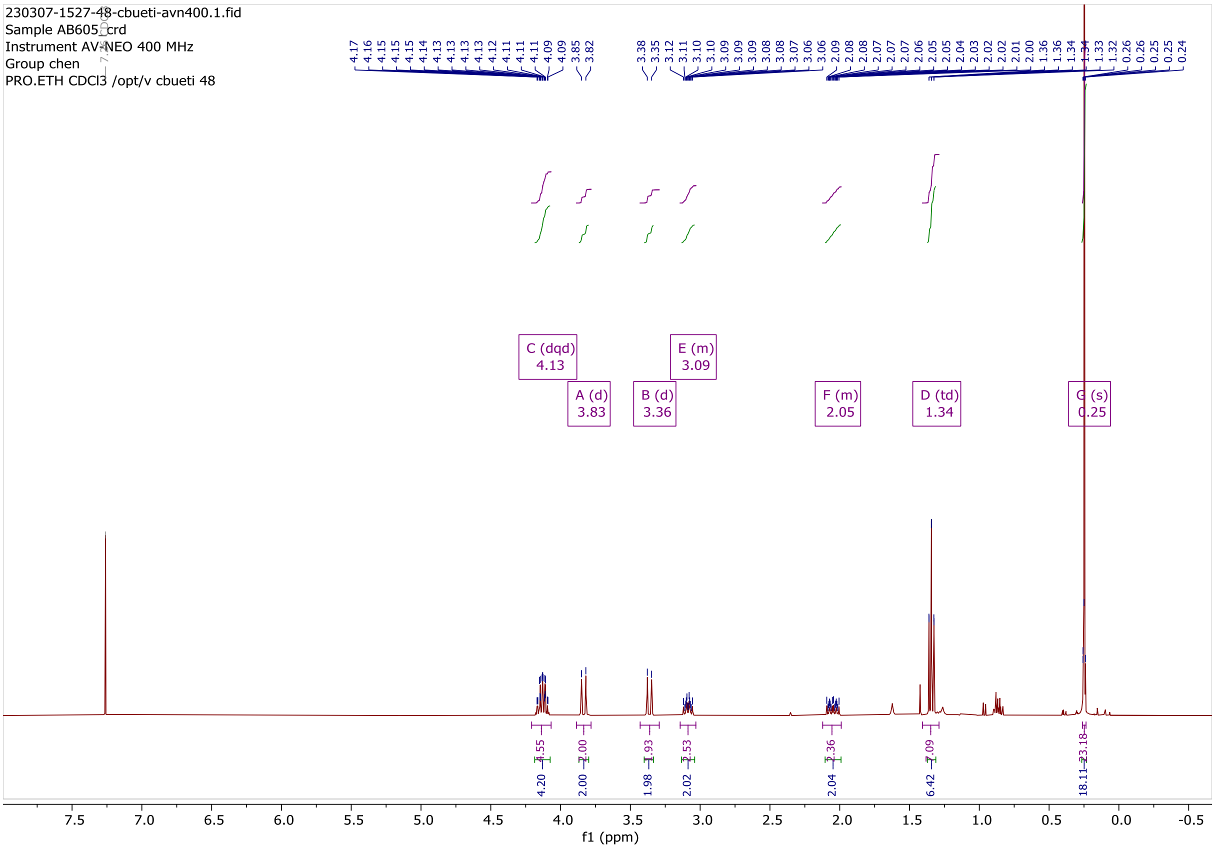


Figure S17. ^{1}H NMR spectrum recorded in $CDCl_3$.

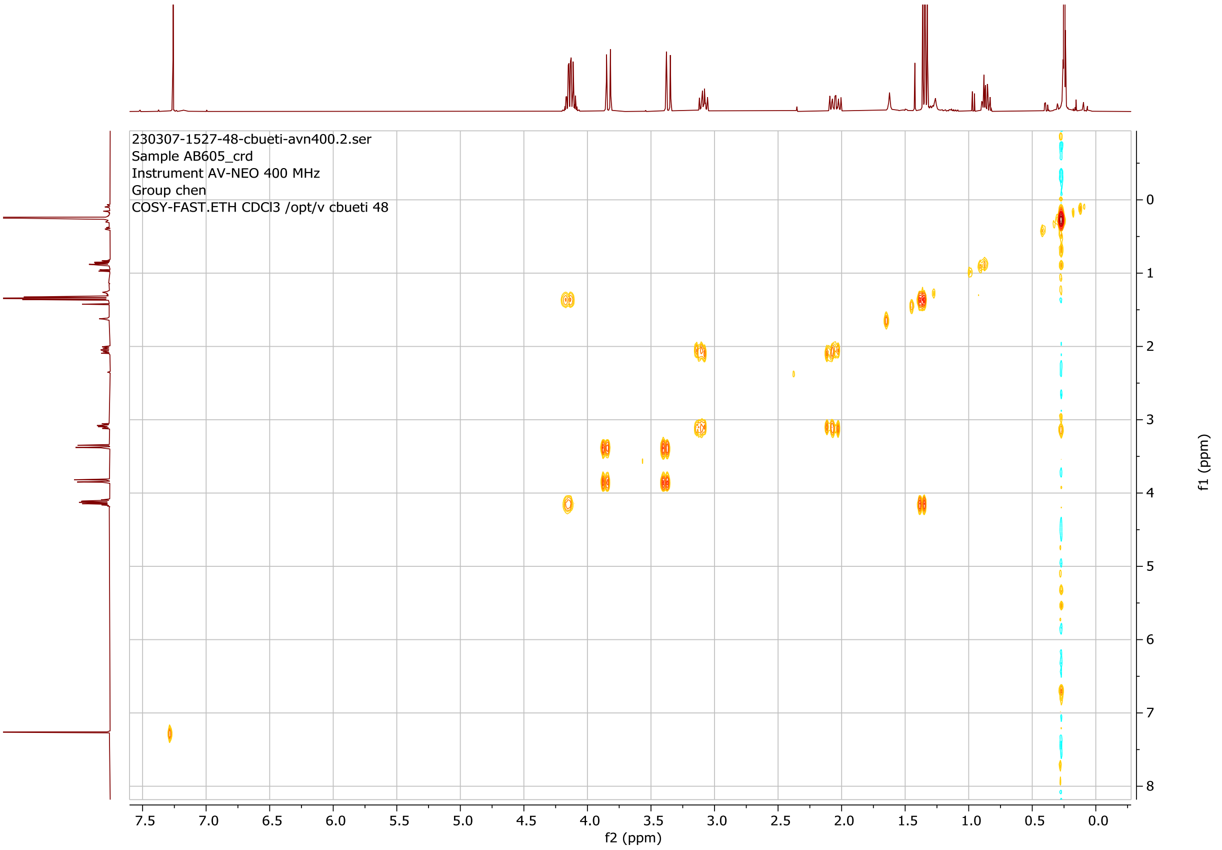


Figure S18. COSY spectrum recorded in $CDCl_3$.

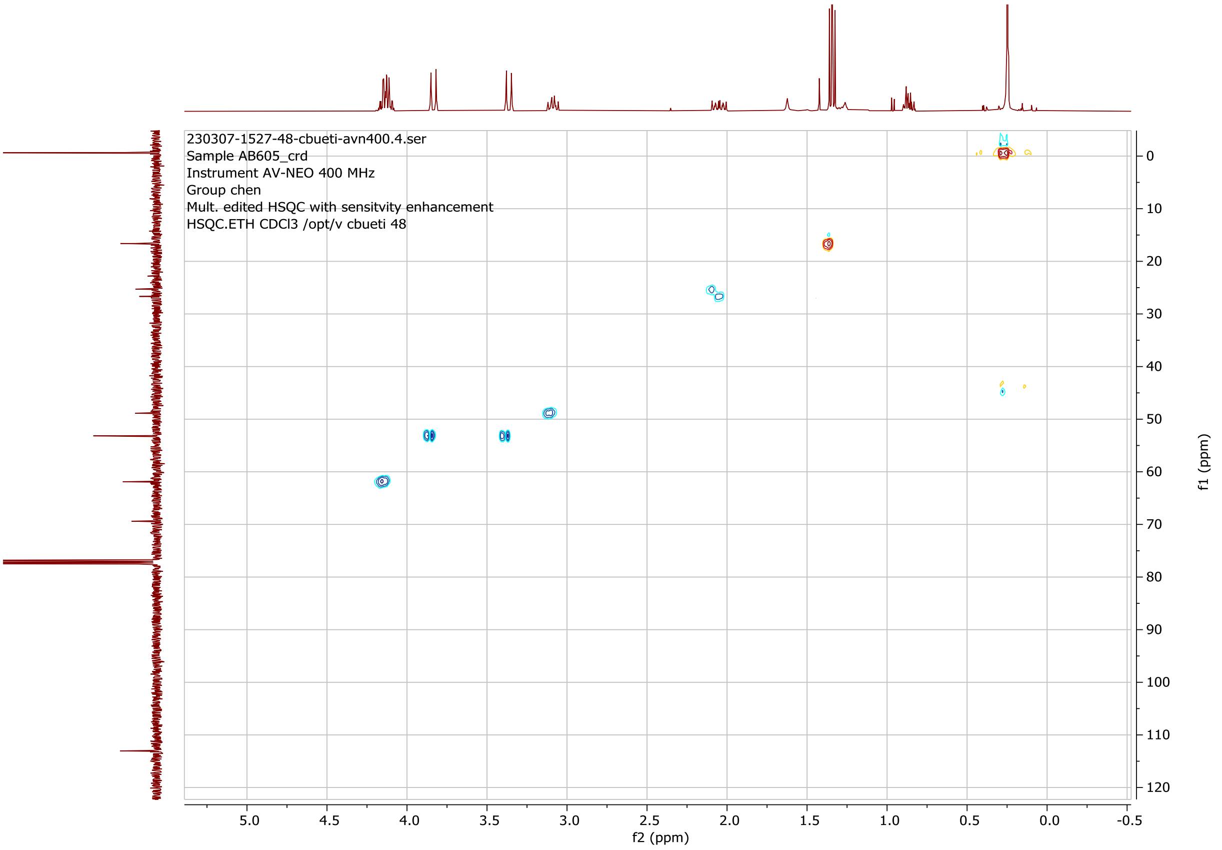


Figure S19. HSQC spectrum recorded in $CDCl_3$.

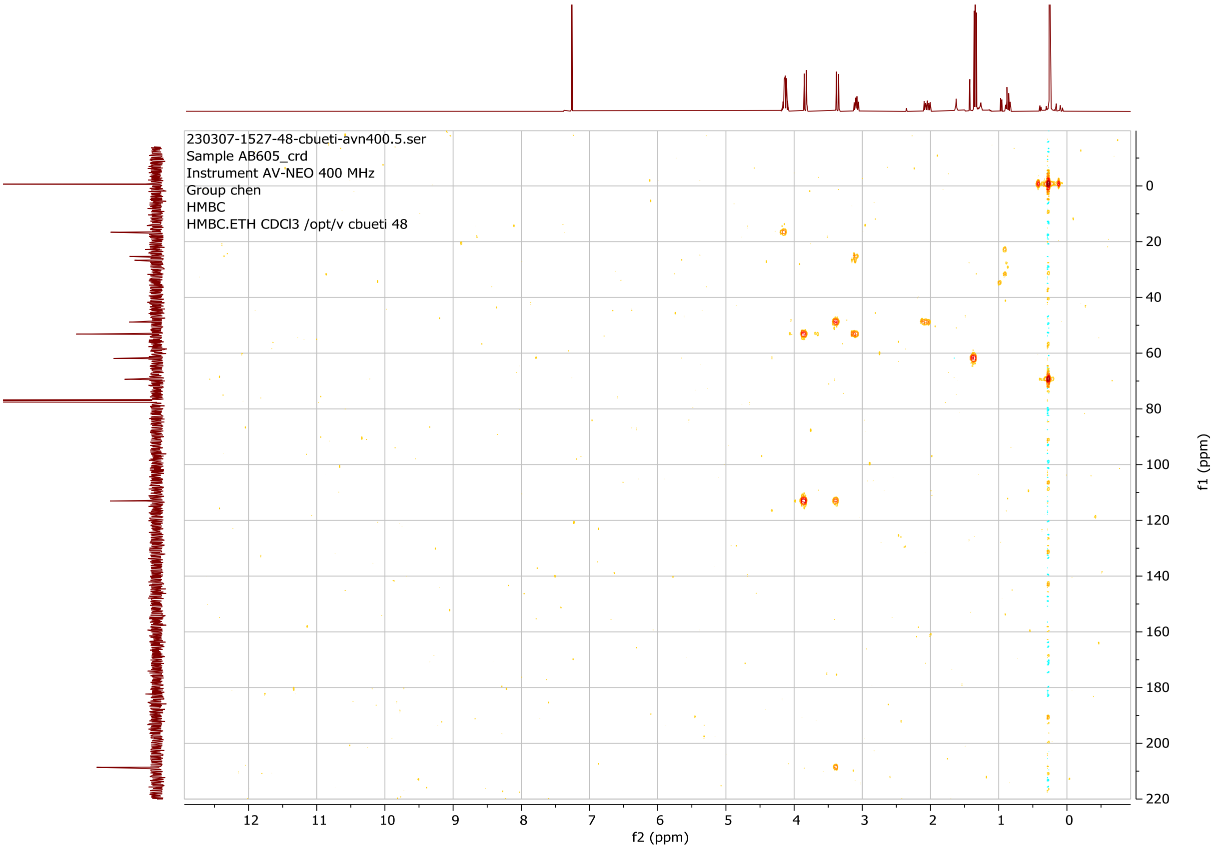


Figure S20. HMBC spectrum recorded in $CDCl_3$.

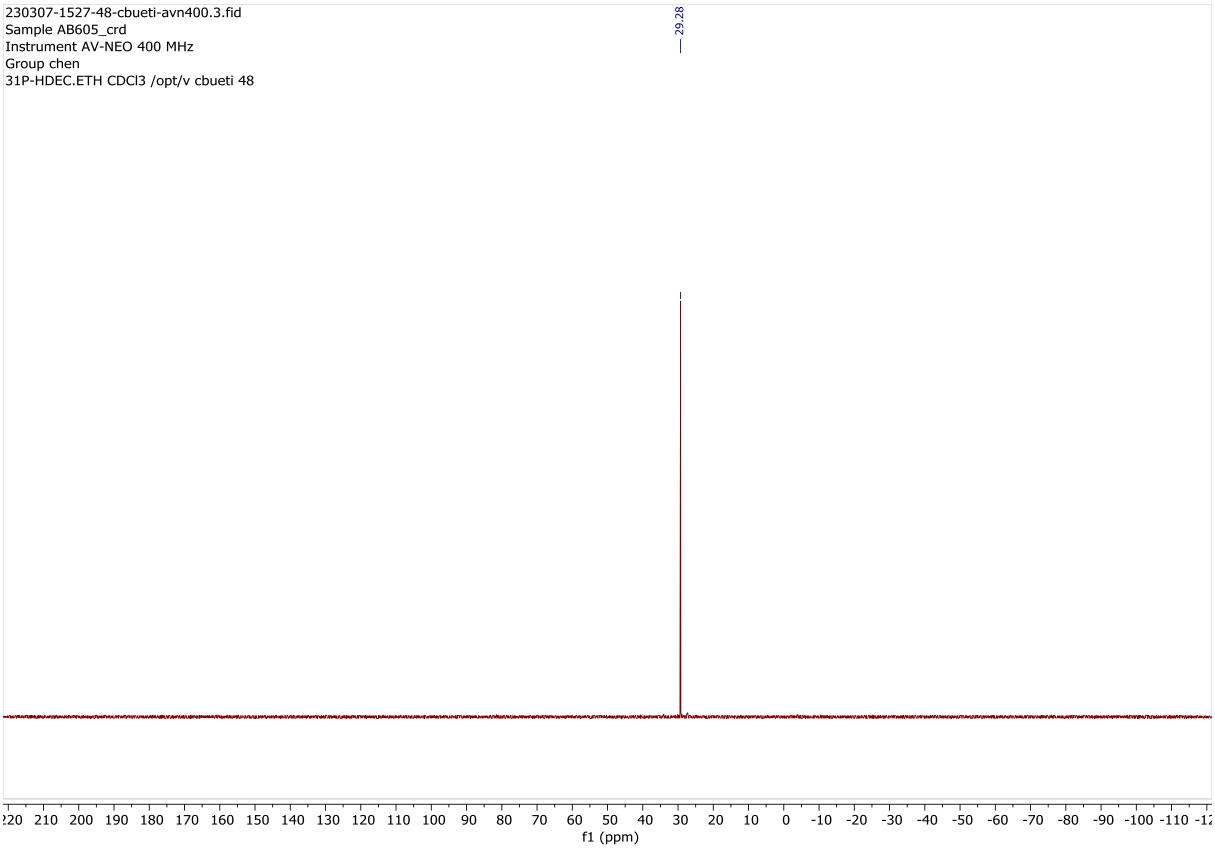


Figure S21. ^{31}P NMR spectrum recorded in $CDCl_3$.

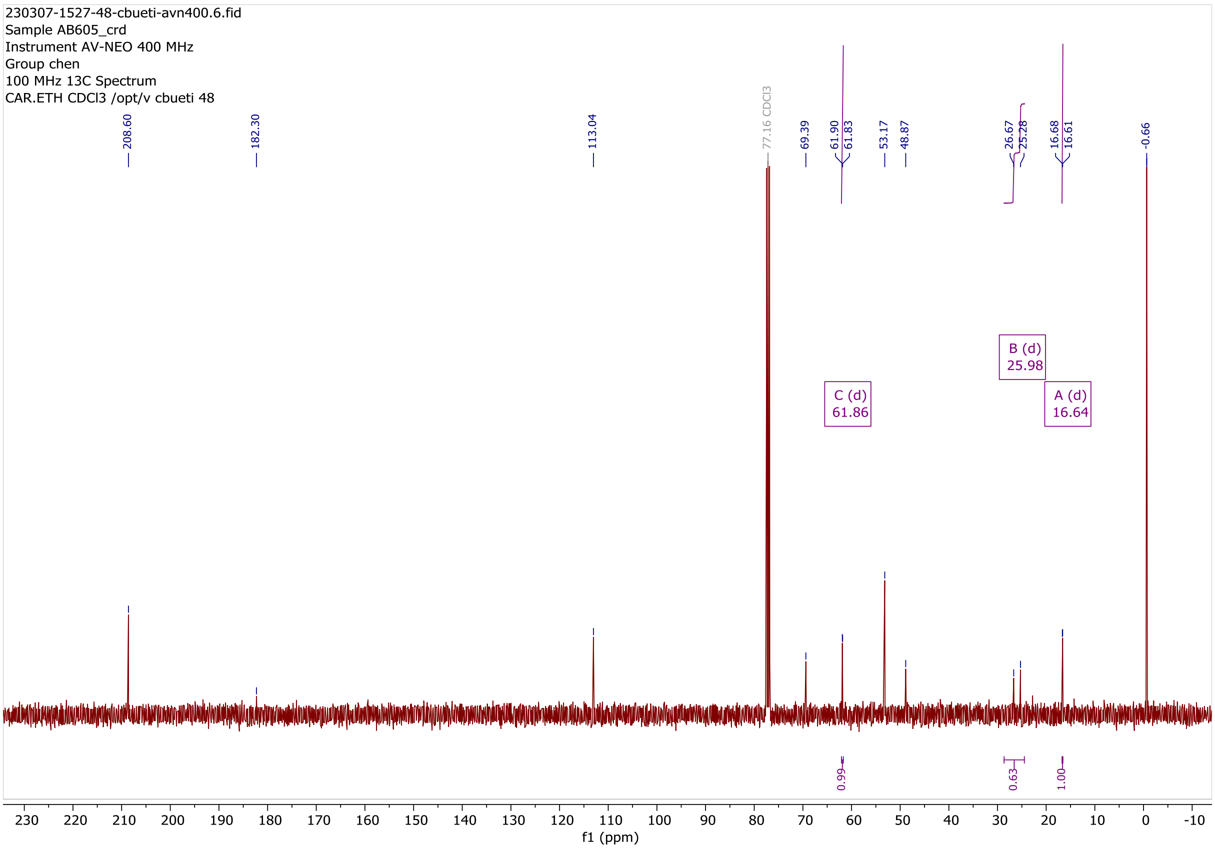


Figure S22. ^{13}C NMR spectrum recorded in CDCl$_3$.

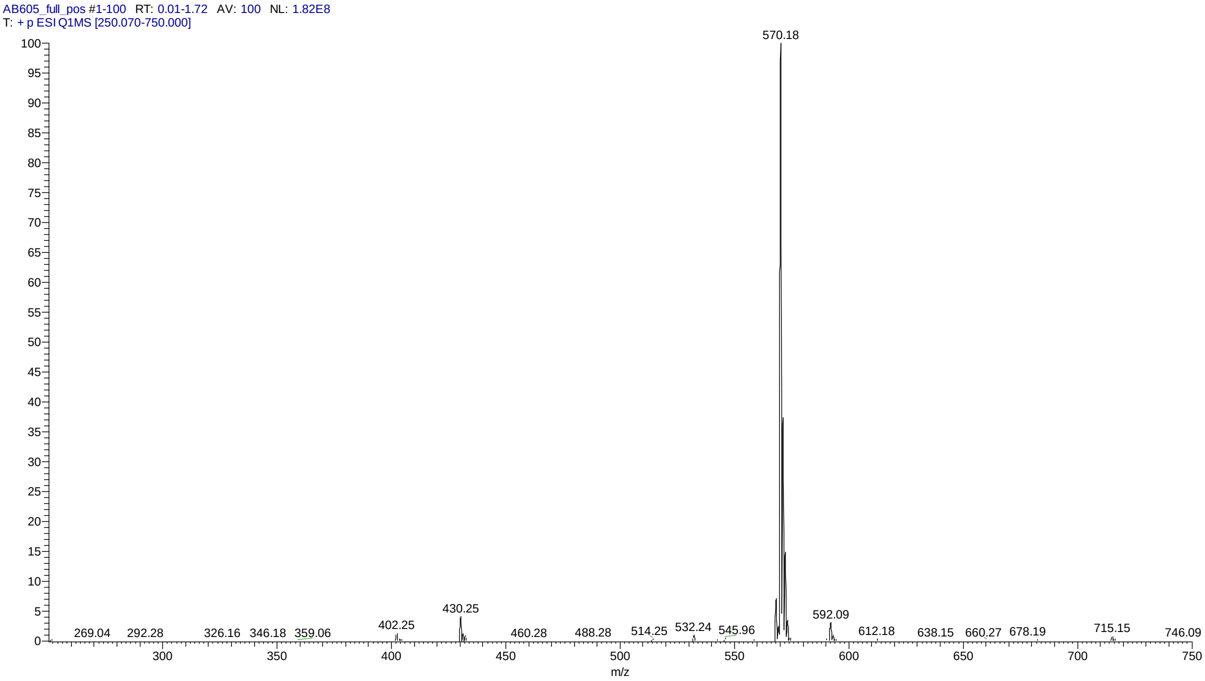


Figure S23. LRMS full spectrum. Sprayed from EtOH with a drop of formic acid.

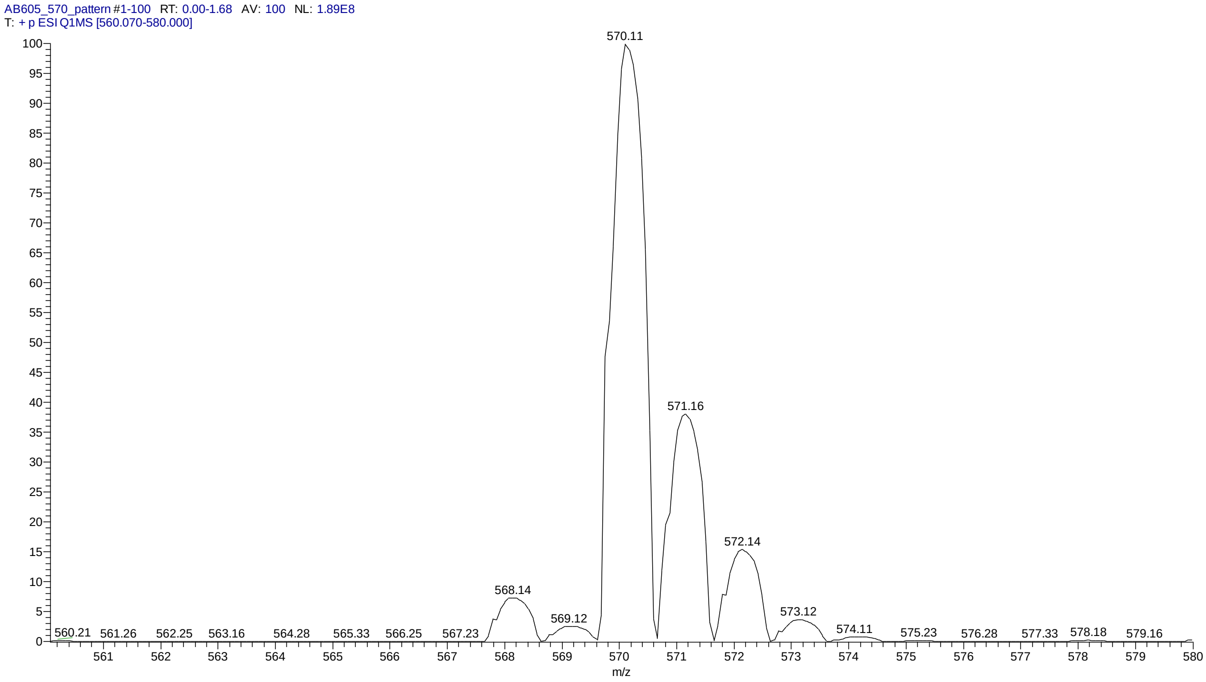


Figure S24. LRMS. Sprayed from EtOH with a drop of formic acid.

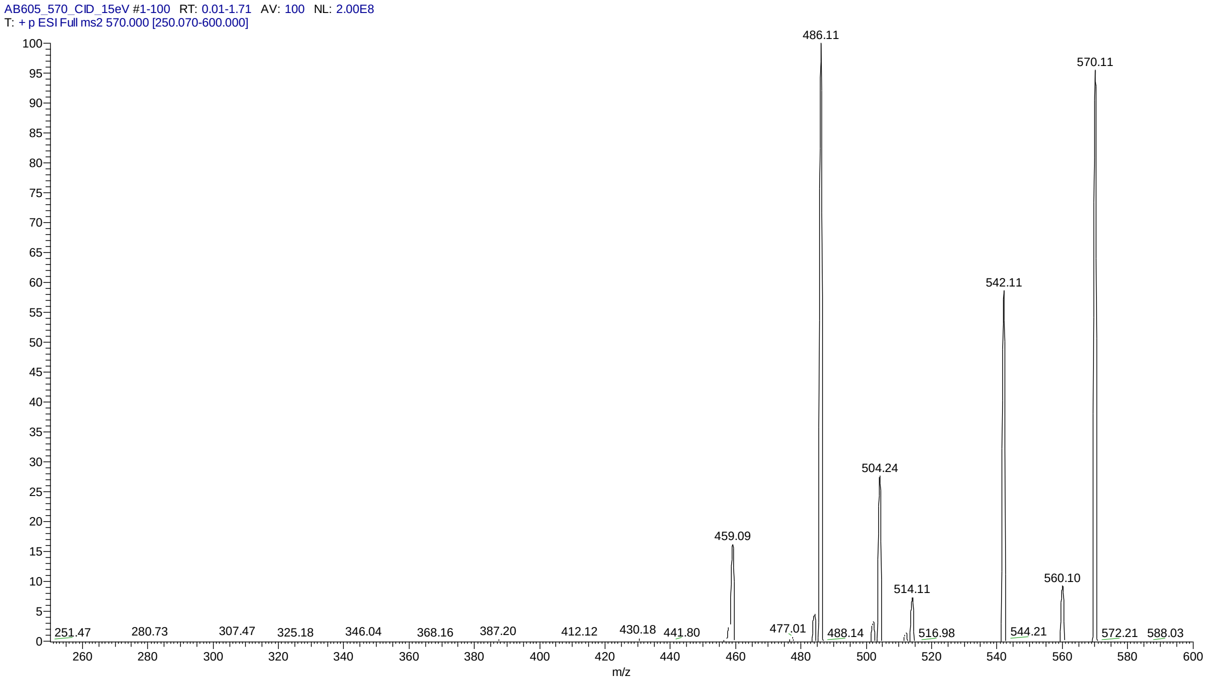
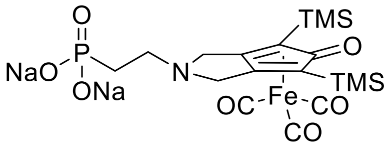


Figure S25. CID spectrum at 15 eV collision energy. Sprayed from EtOH with a drop of formic acid.

1.6) [Fe^{TMS}(CO)$_3$-PO$_3$]Na$_2$



A 100 ml round bottom flask equipped with a stir bar was charged with 590 mg **Fe^{TMS}(CO)$_3$-P(O)(OEt)$_2$** (1.03 mmol, 1 equiv.). The flask was capped with a septum and flushed with nitrogen. 20 ml dry MeCN was added. Under stirring, 1.1 ml bromotrimethylsilane (8.24 mmol, 8 equiv.) was added. The solution was stirred overnight at room temperature. The next day, the volatiles were removed under reduced pressure. The residue was dissolved in 35:5 Me$_2$CO/H$_2$O (v/v) and stirred for 1.5 h. Full hydrolysis was confirmed by LC-MS. The volatiles were removed under reduced pressure. The residue was dissolved in Me_2CO and passed through a pad of Na_2CO_3 and Celite eluting with Me_2CO. The solvent was removed under reduced pressure. After drying *in vacuo*, the product was isolated as an orange solid (515 mg, 90 %).

^1H NMR (δ, 300 MHz, D_2O): 4.17 (d, *J* = 14.3 Hz, 2H), 3.87 (d, *J* = 14.3 Hz, 2H), 3.28 – 3.16 (m, 2H), 1.99 – 1.86 (m, 2H), 0.28 (s, 18H).

^1H NMR (δ, 500 MHz, MeOH-d_4): 3.87 (d, *J* = 13.0 Hz, 2H), 3.50 (d, *J* = 13.0 Hz, 2H), 3.14 – 3.08 (m, 2H), 1.92 – 1.82 (m, 2H), 0.27 (s, 18H).

^{13}C NMR (δ, 100 MHz, D_2O): 207.2, 181.2, 111.2, 69.9, 52.5, 51.4, 26.5 (d, *J* = 127.9), -1.8.

^{13}C NMR (δ, 125 MHz, MeOH-d_4): 209.6, 183.2, 115.0, 70.1, 53.8, 51.9, 29.0, (d, *J* = 130.0 Hz), -0.8.

^{31}P NMR (δ, 120 MHz, D_2O): 19.7.

^{31}P NMR (δ, 202 MHz, MeOH-d_4): 20.9.

Anal. calc. for $C_{18}H_{26}FeNNa_2O_7PSi_2$: C, 38.79; H, 4.70; N, 2.51. Found: C, 38.05; H, 5.11; N, 2.40.

LRMS (m/z): $[M-2Na]^{2-}$ calc. for $C_{18}H_{26}FeNO_7PSi_2$: 255.52. Found: 255.51.

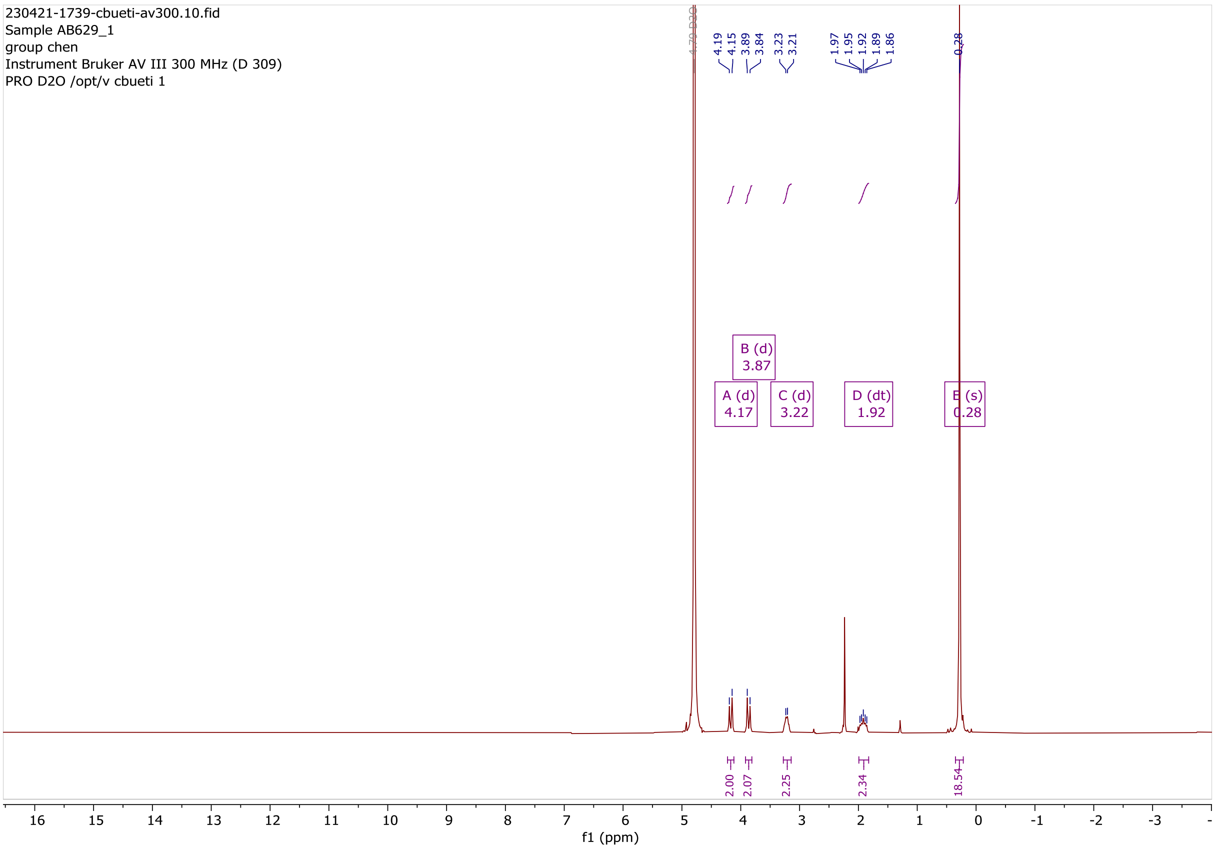


Figure S26. ^1H NMR spectrum recorded in D_2O.

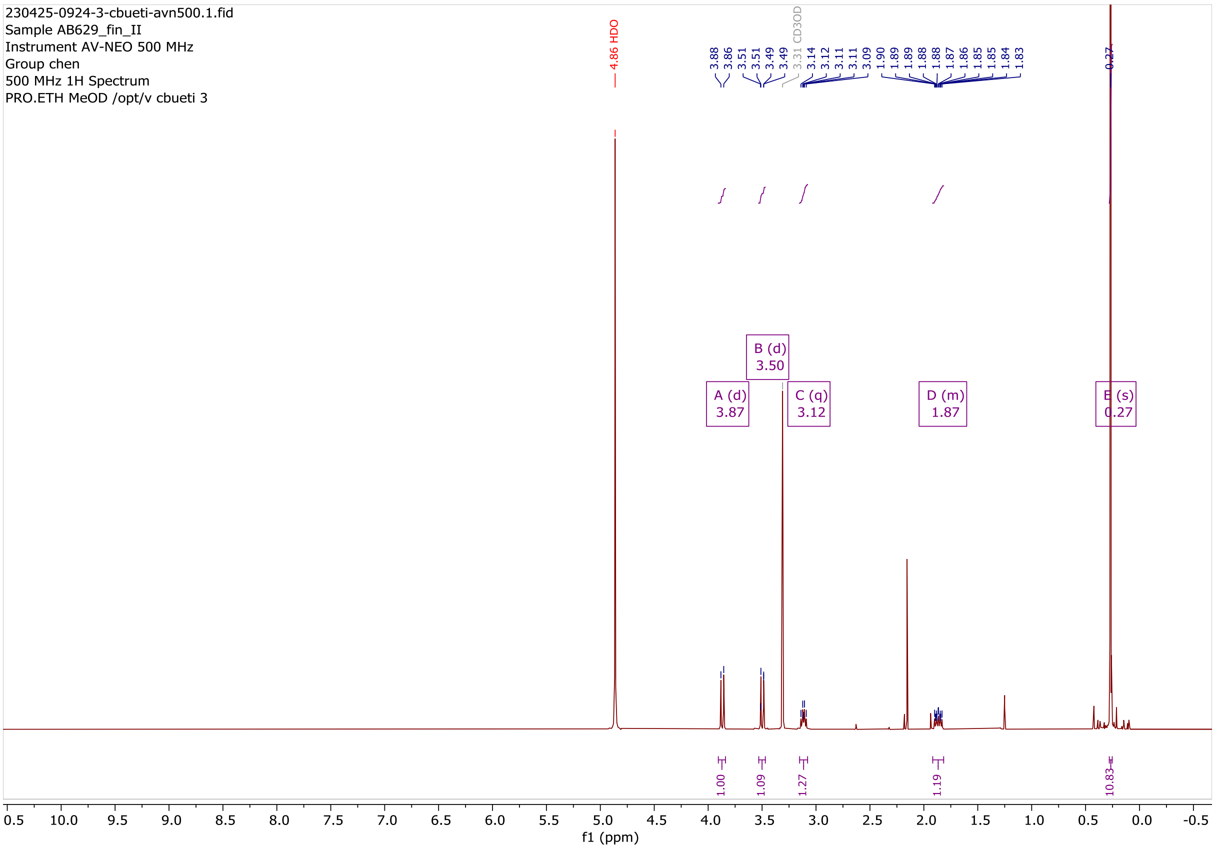


Figure S27. ^{1}H NMR spectrum recorded in MeOH-d_4.

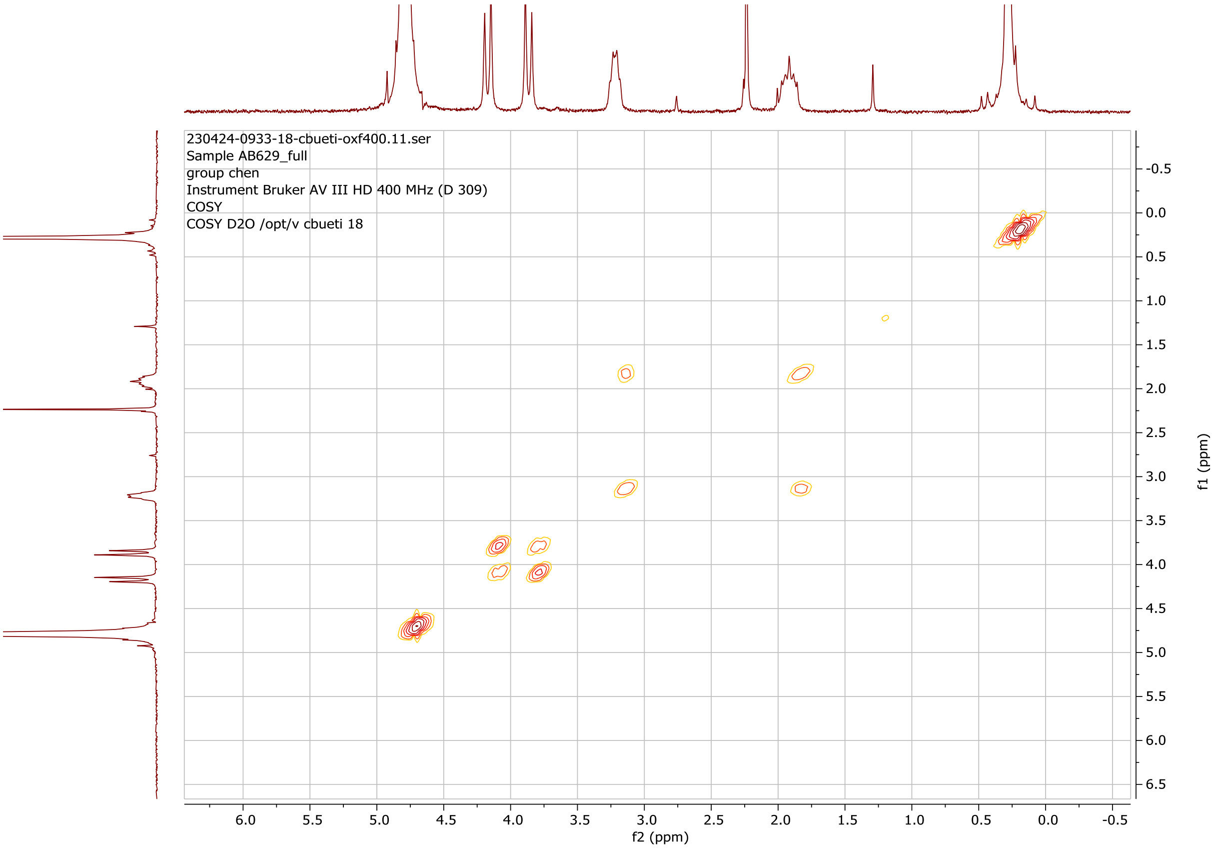


Figure S28. COSY spectrum recorded in D_2O.

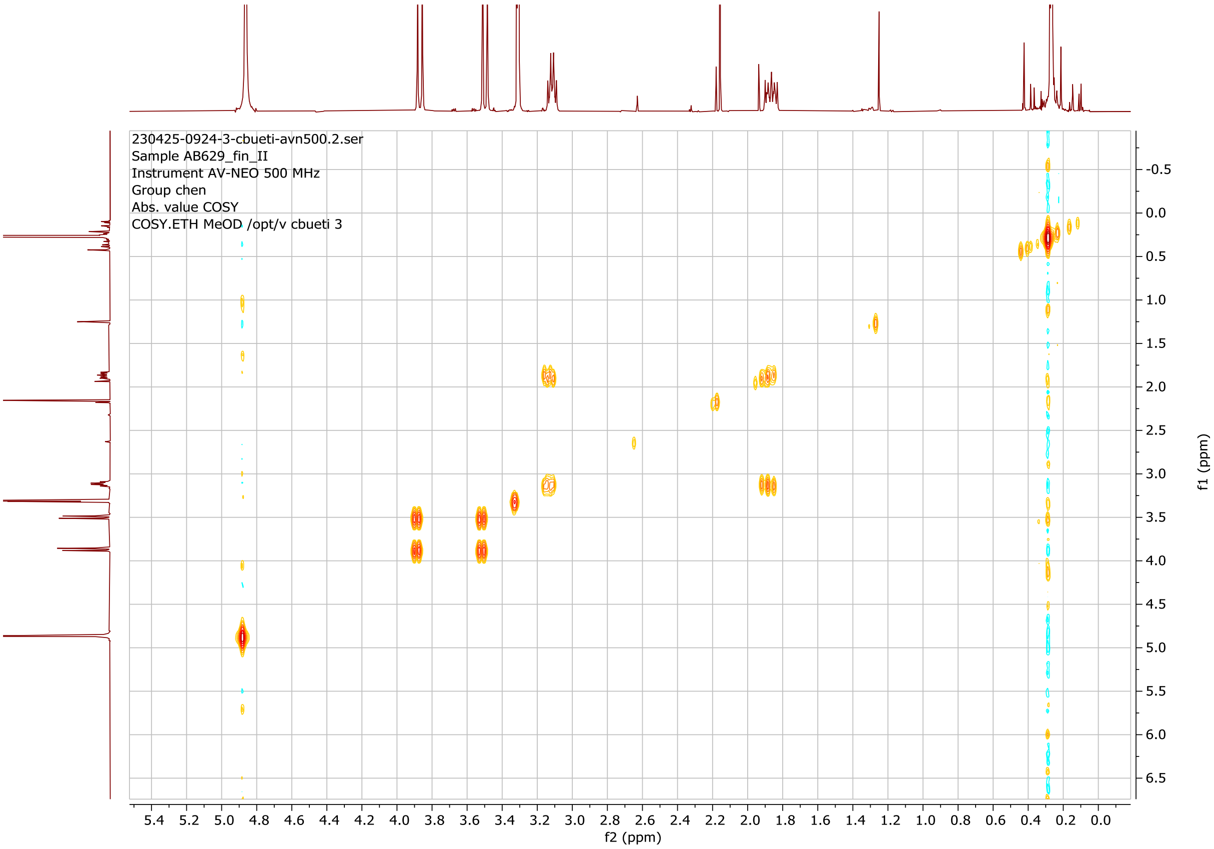


Figure S29. COSY spectrum recorded in MeOH-d_4.

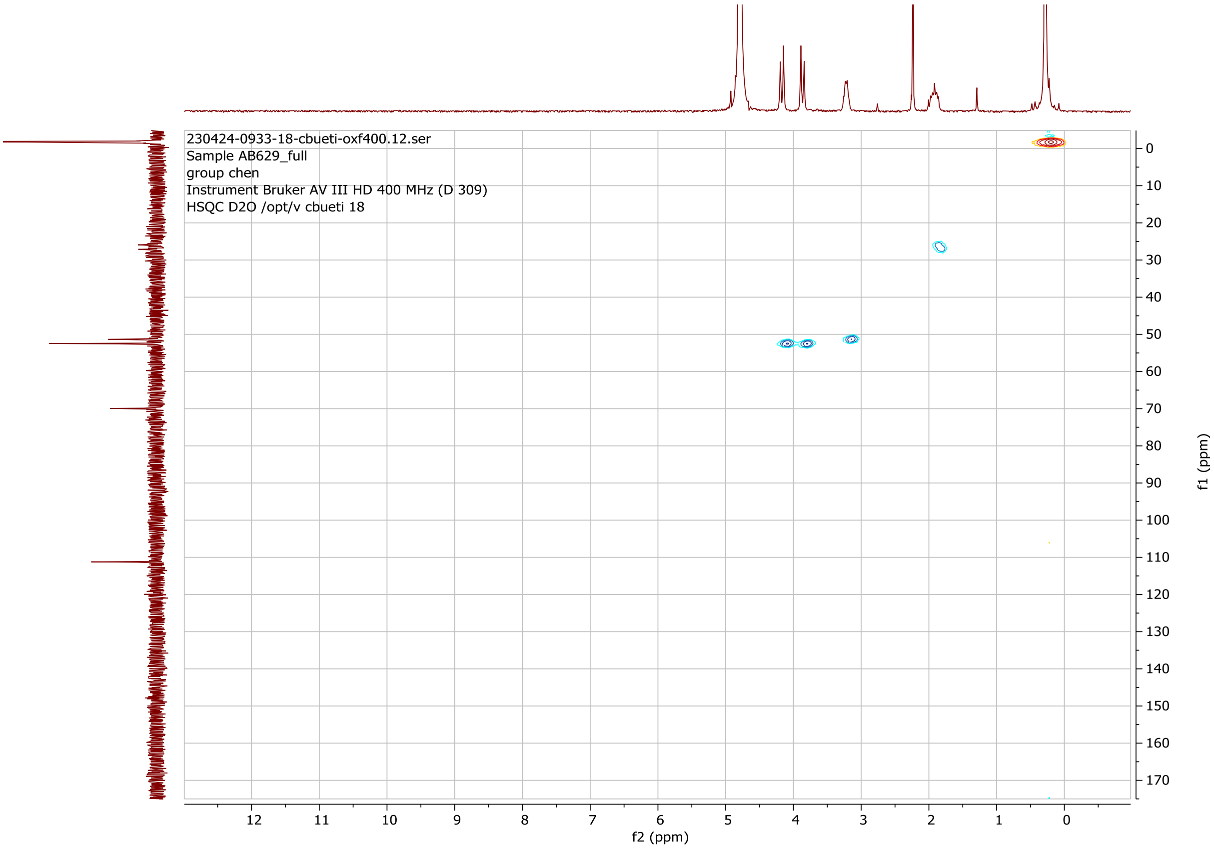


Figure S30. HSQC spectrum recorded in D_2O.

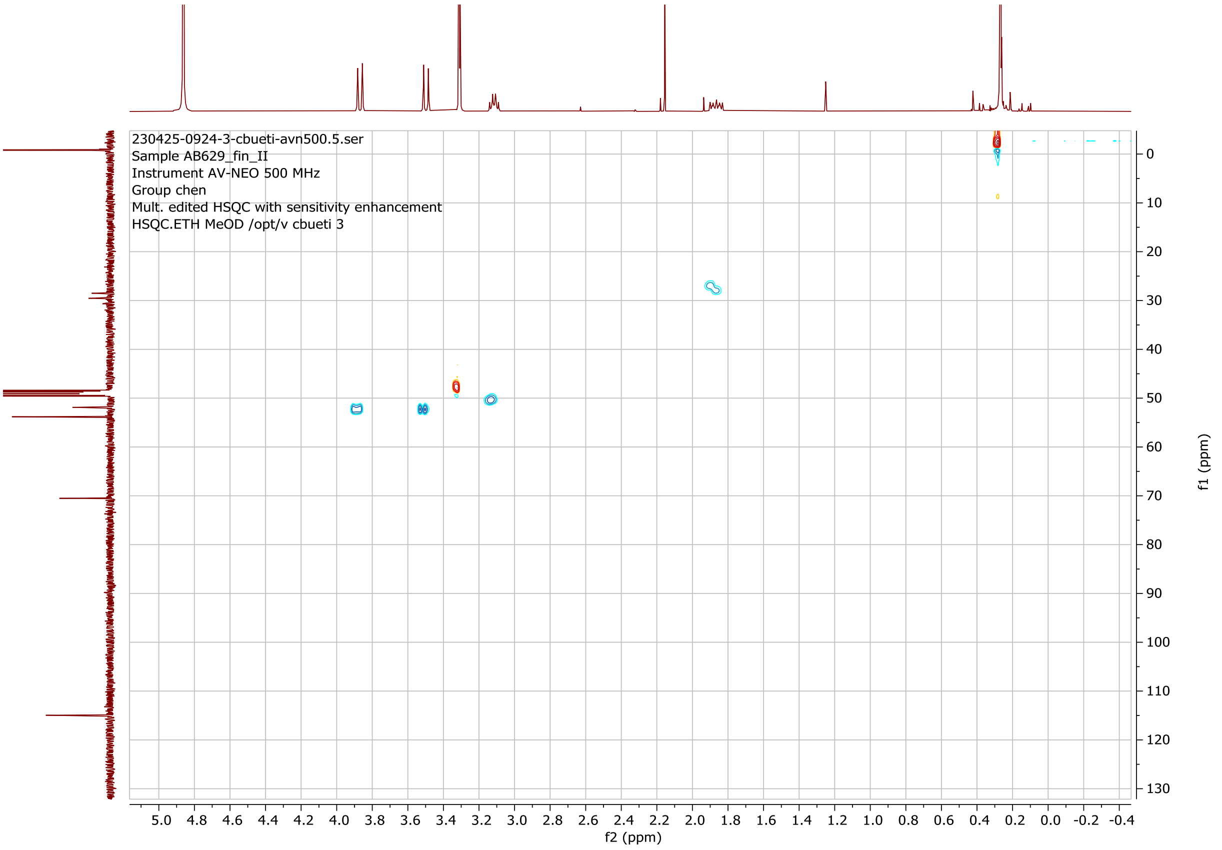


Figure S31. HSQC spectrum recorded in MeOH-d$_4$.

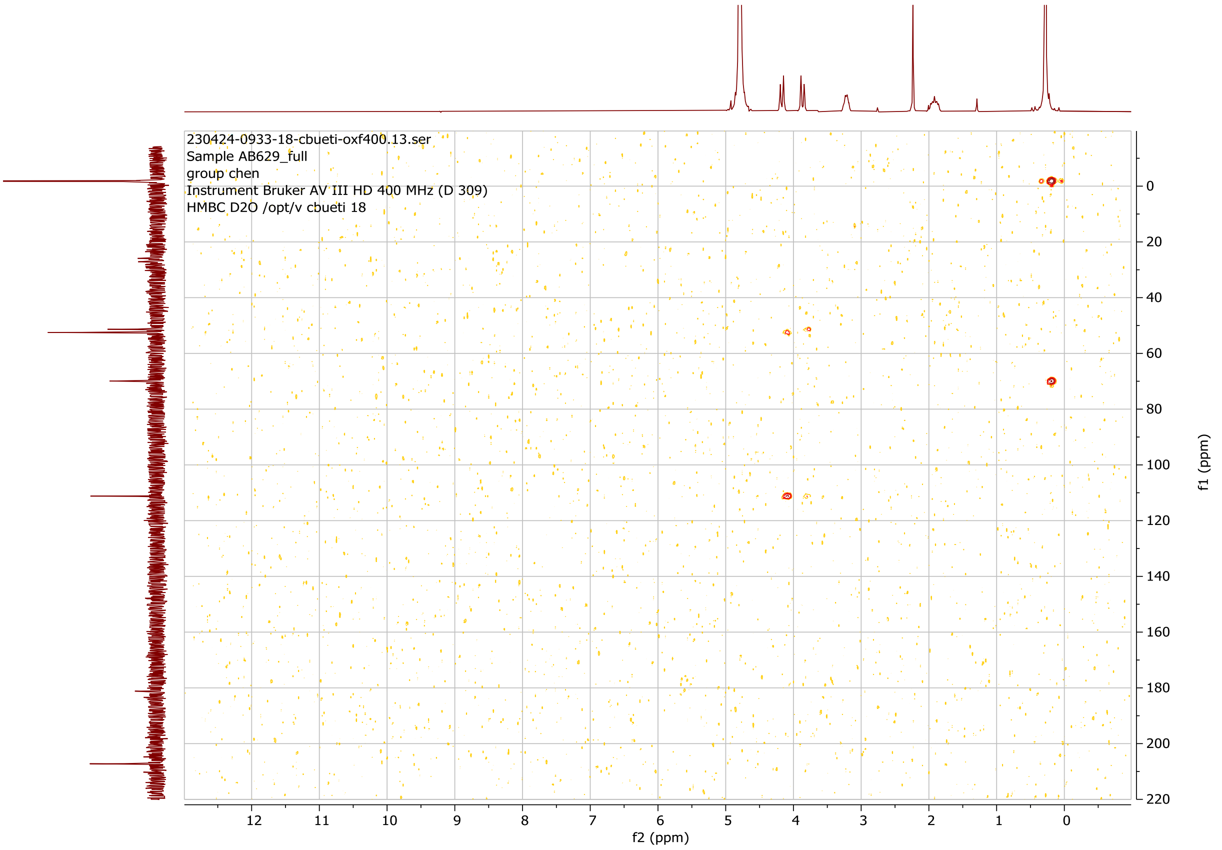


Figure S32. HMBC spectrum recorded in D$_2$O.

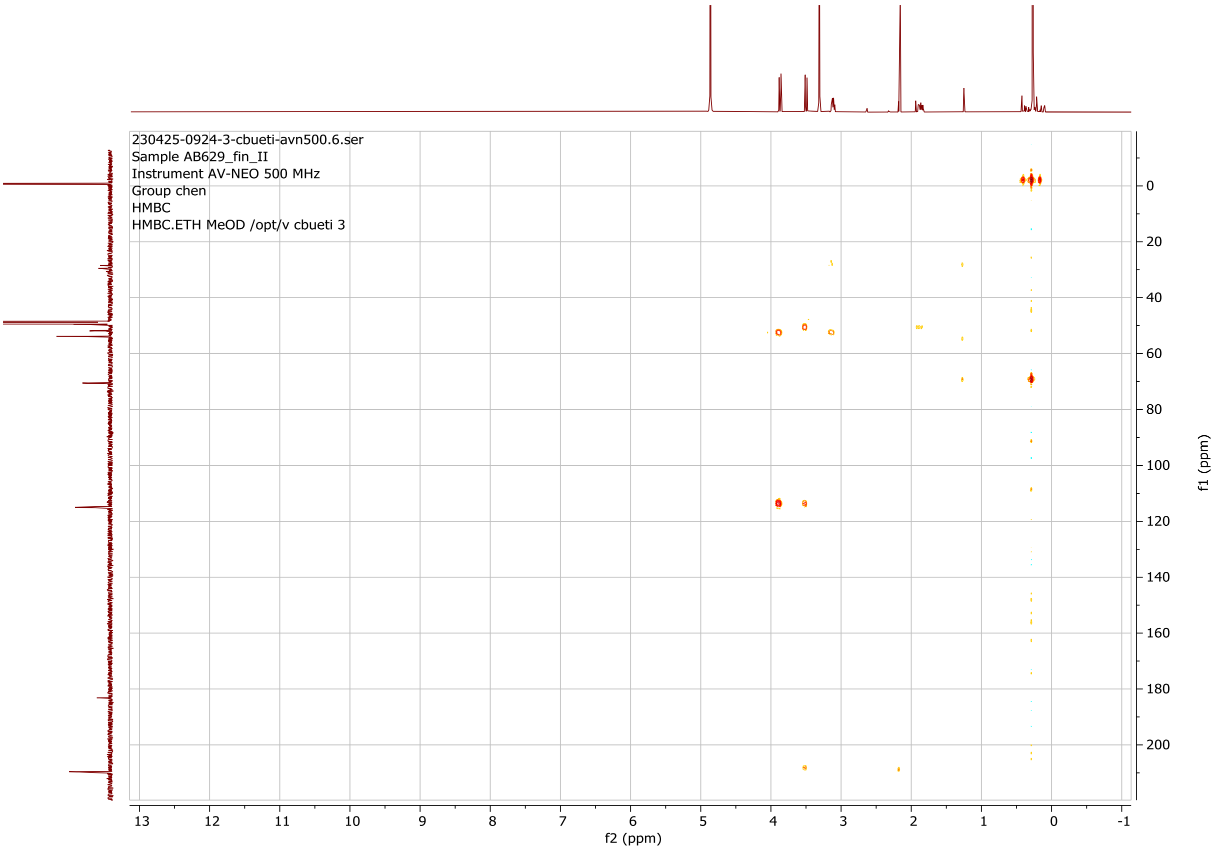


Figure S33. HMBC spectrum recorded in MeOH-d_4.

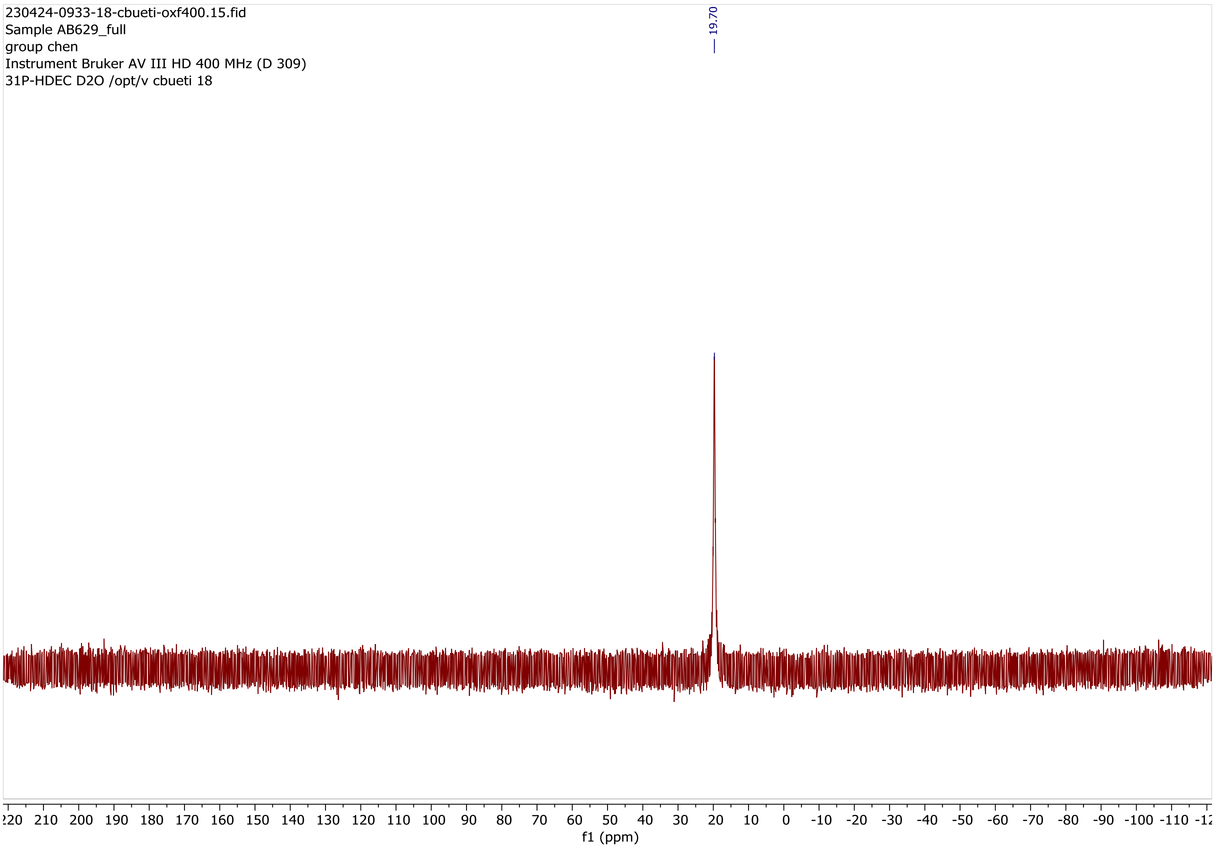


Figure S34. ^{31}P NMR spectrum recorded in D_2O.

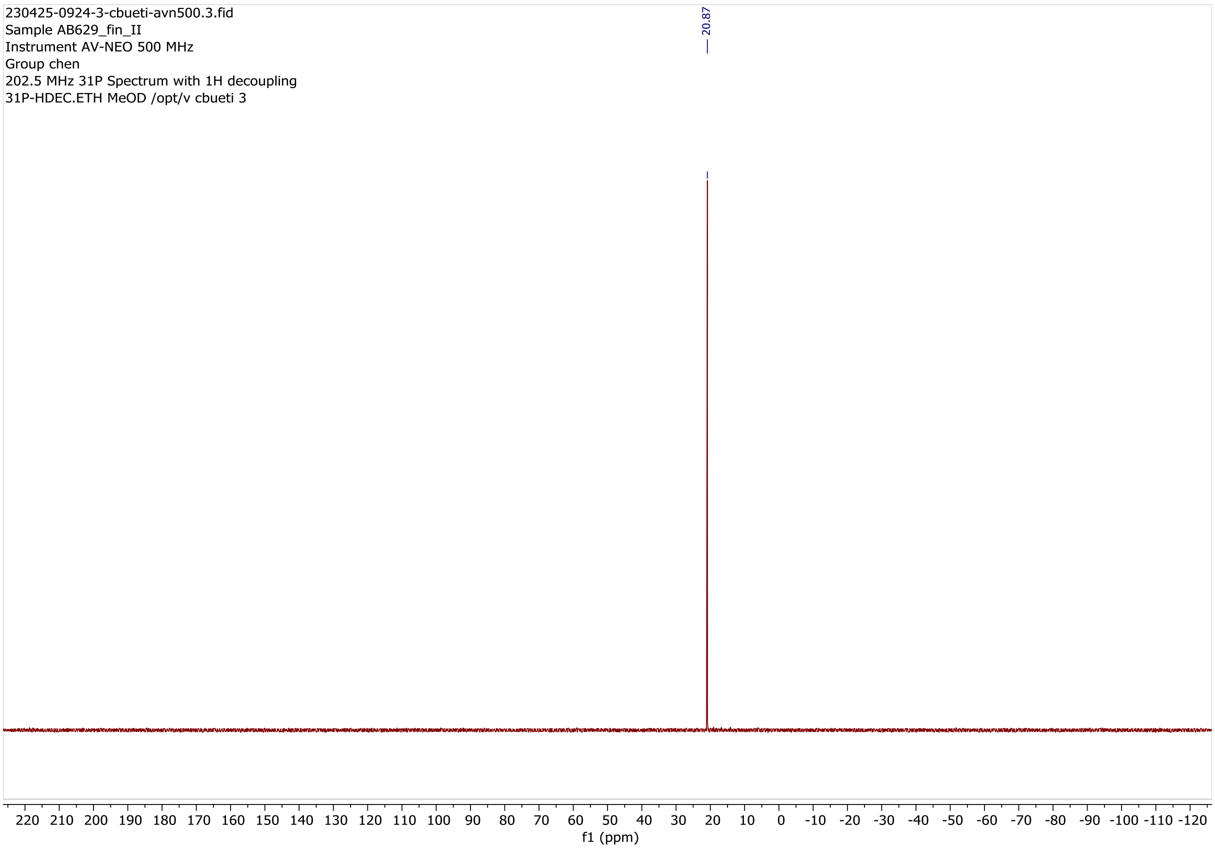


Figure S35. ^{31}P NMR spectrum recorded in MeOH-d$_4$.

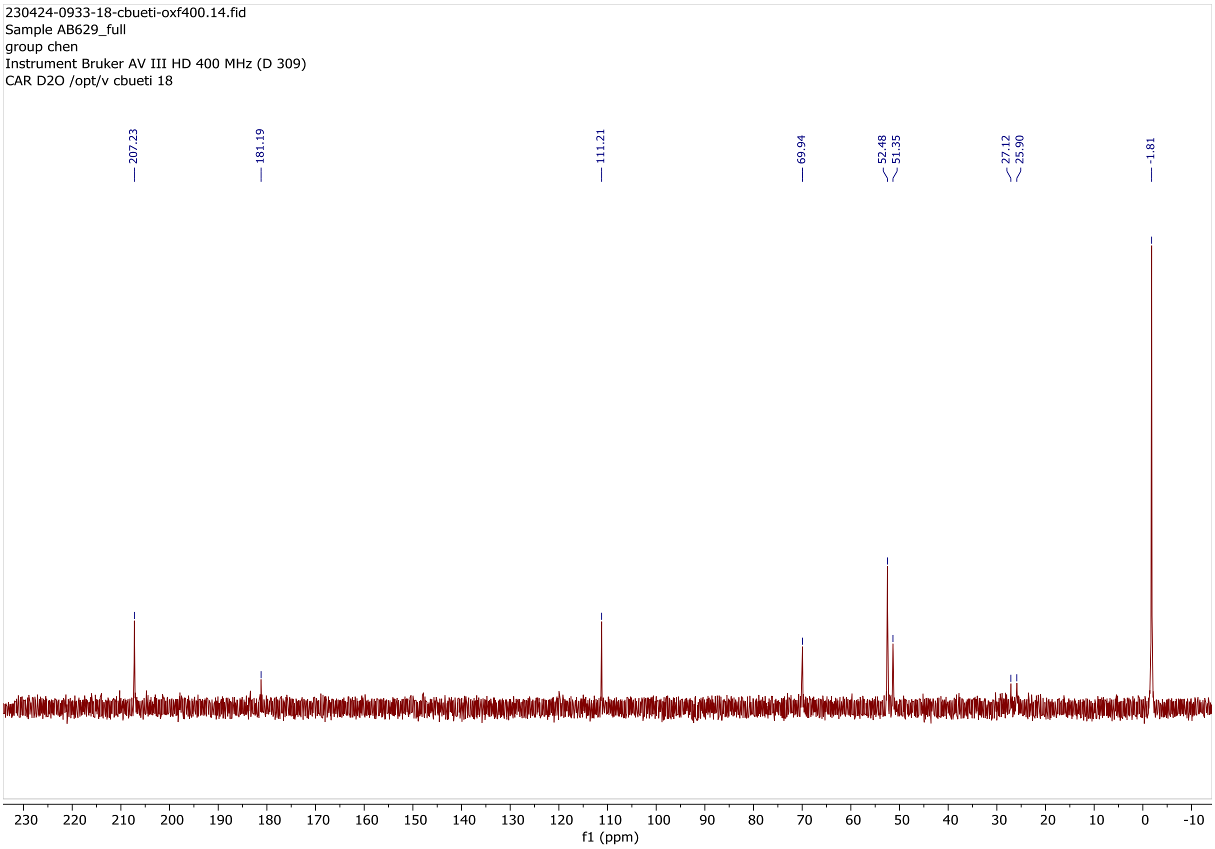


Figure S36. ^{13}C NMR spectrum recorded in D$_2$O.

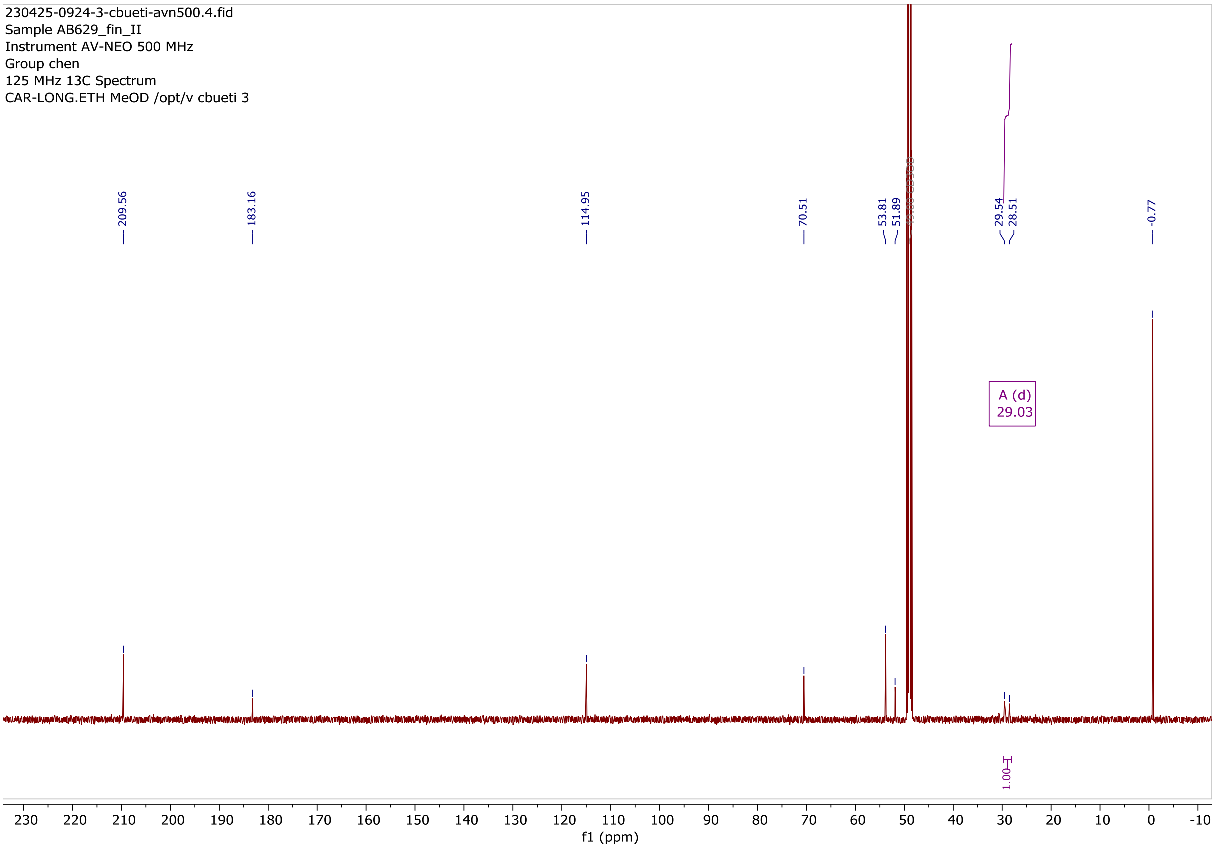


Figure S37. ^{13}C NMR spectrum recorded in MeOH-d_4.

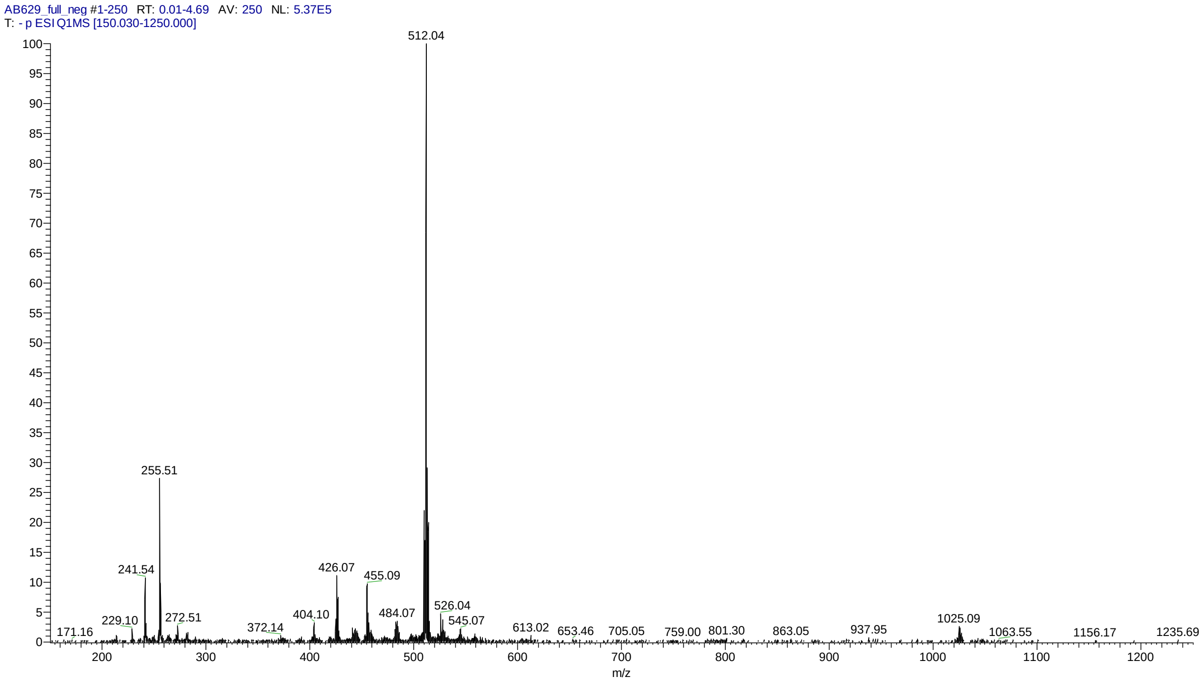
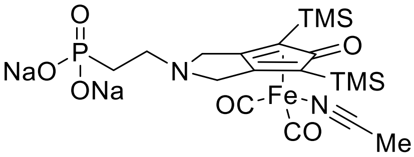


Figure S38. LRMS full spectrum. Sprayed from H_2O.

1.7) $[Fe^{TMS}(MeCN)(CO)_2\text{-}PO_3]Na_2$



A dried and argon-flushed 20 ml Schlenk tube equipped with a stir bar was charged with 50 mg **$[Fe^{TMS}(CO)_3\text{-}PO_3]Na_2$** (0.09 mmol, 1 equiv.) and 10.1 mg Me_3NO (0.13 mmol, 1.5 equiv.). While stirring, 1 ml dry MeCN was added to the solids, and the solution was protected from light. No precipitation was observed. After 4 h, the solution was layered with 6 ml dry Et_2O and left at room temperature overnight. The next day, the mixture was cannula filtered and the residue washed twice with 1.5 ml portions of dry Et_2O. The product was obtained as a yellow/orange solid after drying under reduced pressure (18 mg, 35 %).

^{1}H NMR (δ, 400 MHz, MeOH-d_4): 3.60 (d, *J* = 13.2 Hz, 2H), 3.15 (d, *J* = 13.2 Hz, 2H), 3.06 – 2.95 (m, 2H), 2.33 (s, 3H), 1.84 – 1.73 (m, 2H), 0.24 (s, 18H).

^{13}C NMR (δ, 100 MHz, MeOH-d_4): 128.4, 66.7, 52.7, 51.1, 26.7 (d, *J* = 144 Hz), 2.4, -1.9 (*shifts obtained from HSQC and HMBC spectra, remaining quaternary carbons not observed*).

^{31}P NMR (δ, 160 MHz, MeOH-d_4): 21.2.

LRMS (m/z): $[M\text{-}2Na\text{+}H]^-$ calc. for $C_{19}H_{30}FeN_2O_6PSi_2$: 525.07. Found: 525.09.

ESI-MS CID (m/z): 525 $[M\text{-}2Na\text{+}H]^-$, 484 $[M\text{-}2Na\text{+}H\text{-}MeCN]^-$, 456 $[M\text{-}2Na\text{+}H\text{-}MeCN\text{-}CO]^-$, 428 $[M\text{-}2Na\text{+}H\text{-}MeCN\text{-}2CO]^-$.

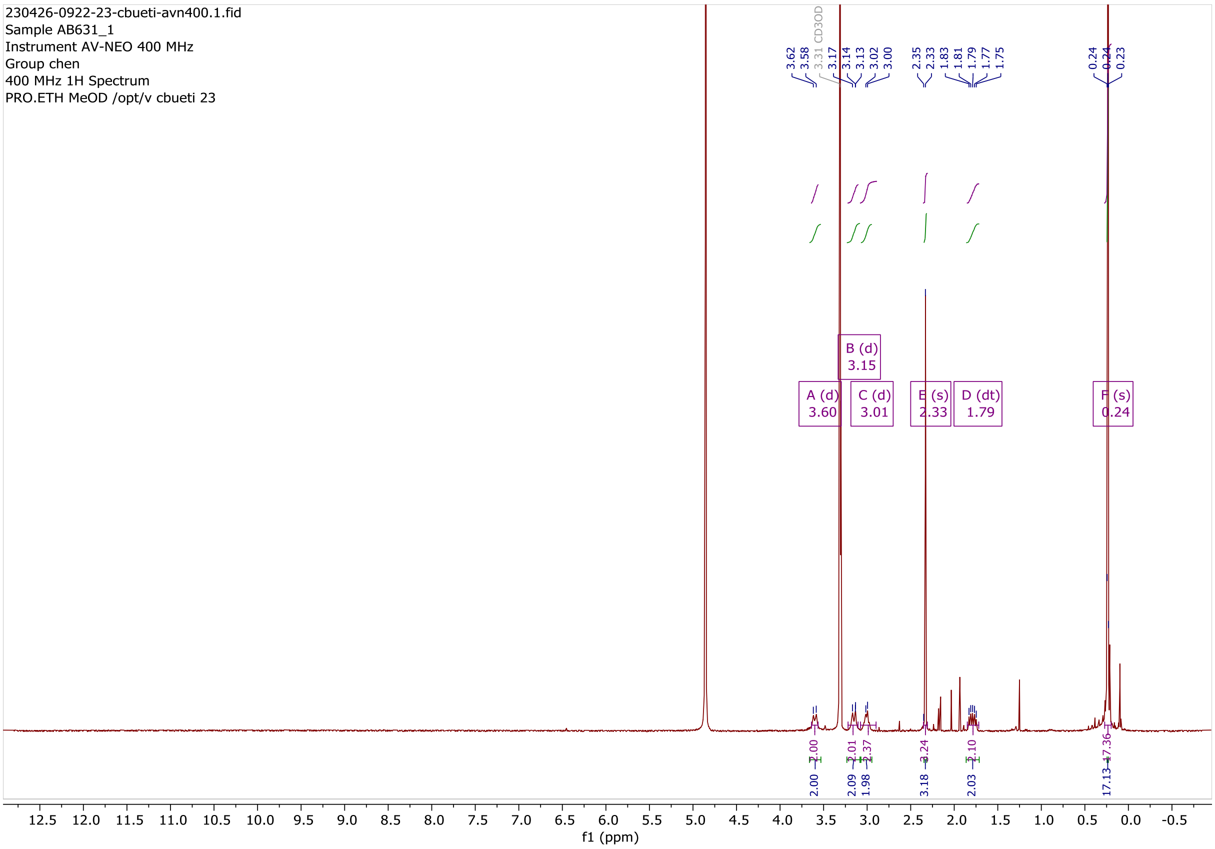


Figure S39. ^{1}H NMR spectrum recorded in MeOH-d_4.

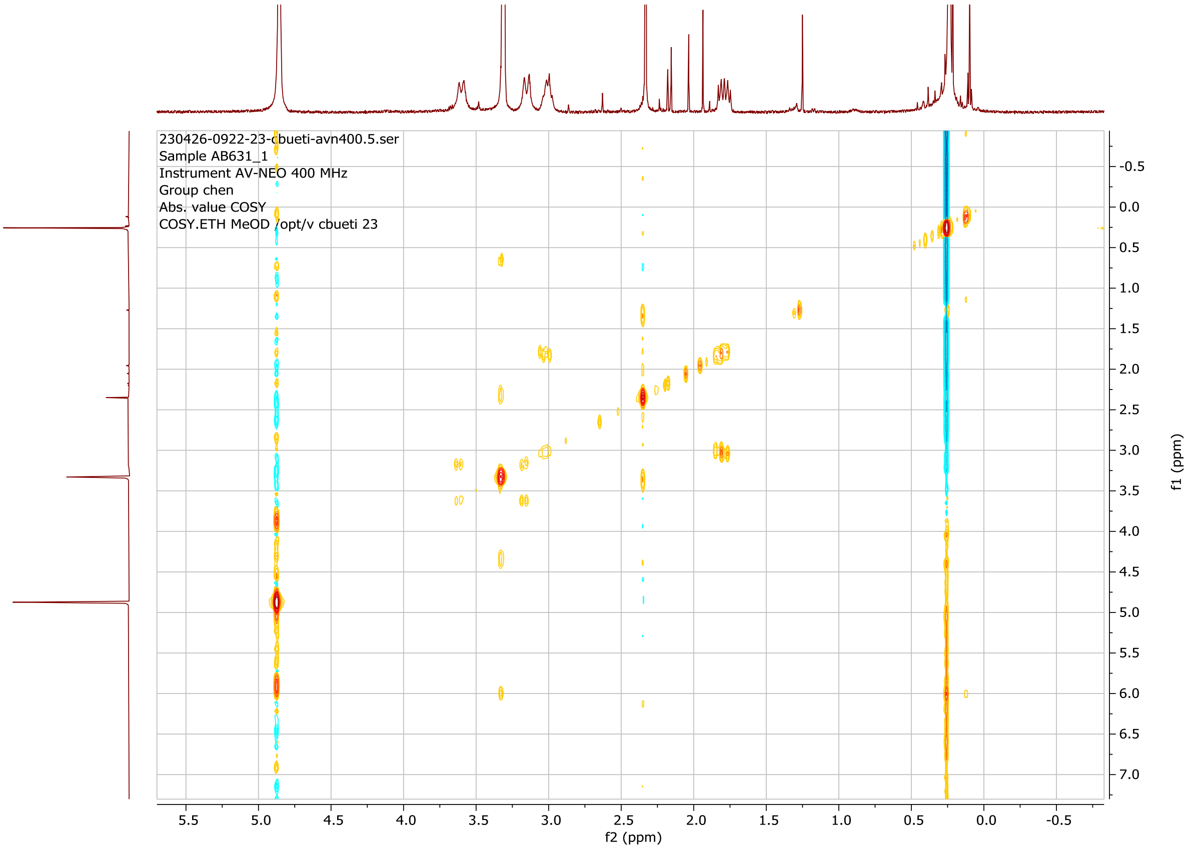


Figure S40. COSY spectrum recorded in MeOH-d$_4$.

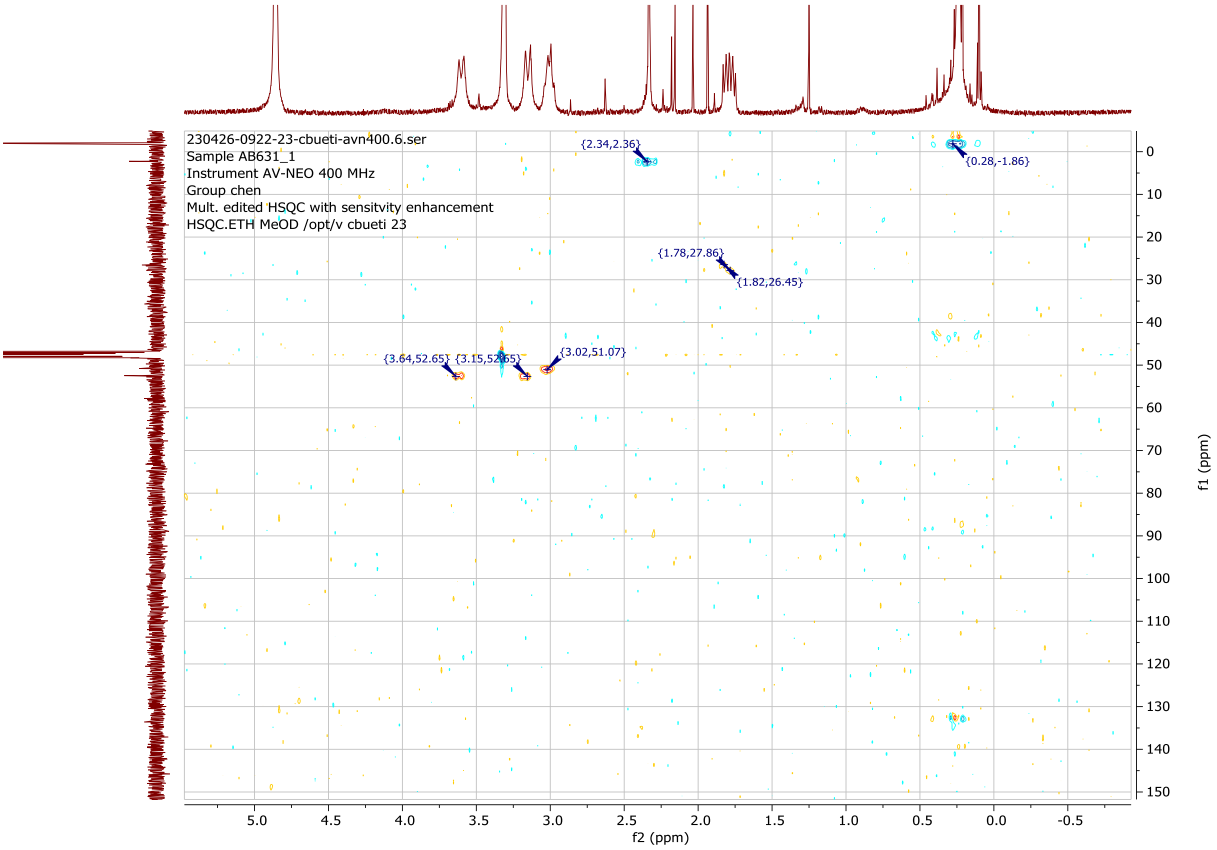


Figure S41. HSQC spectrum recorded in MeOH-d$_4$.

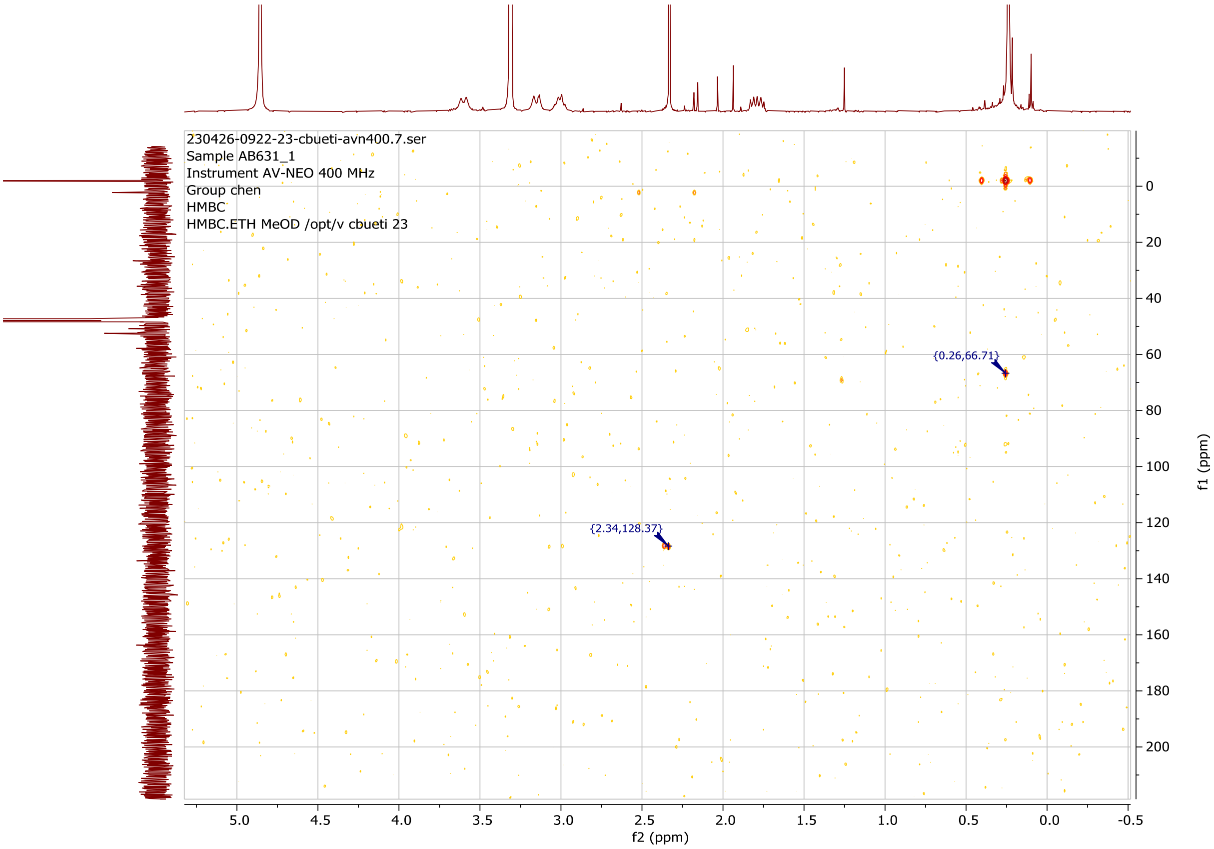


Figure S42. HMBC spectrum recorded in MeOH-d_4.

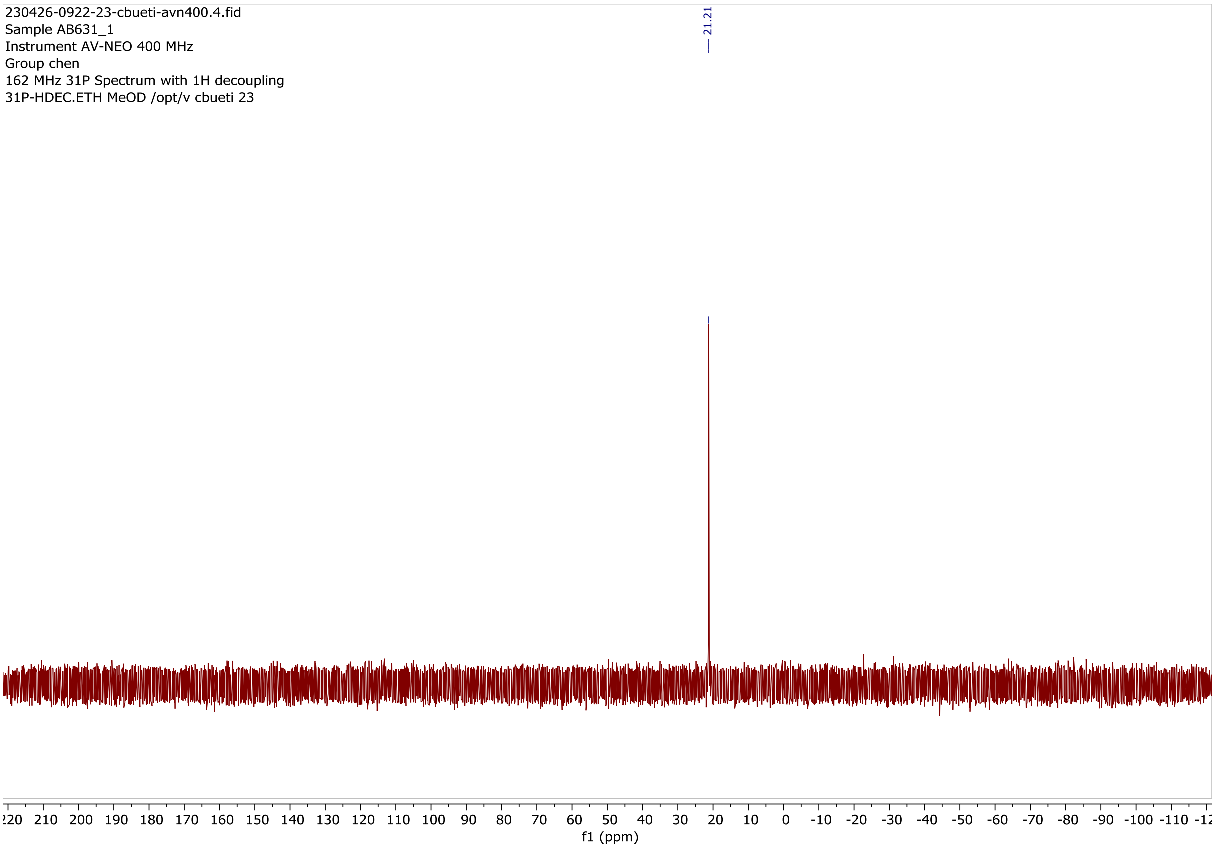


Figure S43. ^{31}P NMR spectrum recorded in MeOH-d_4.

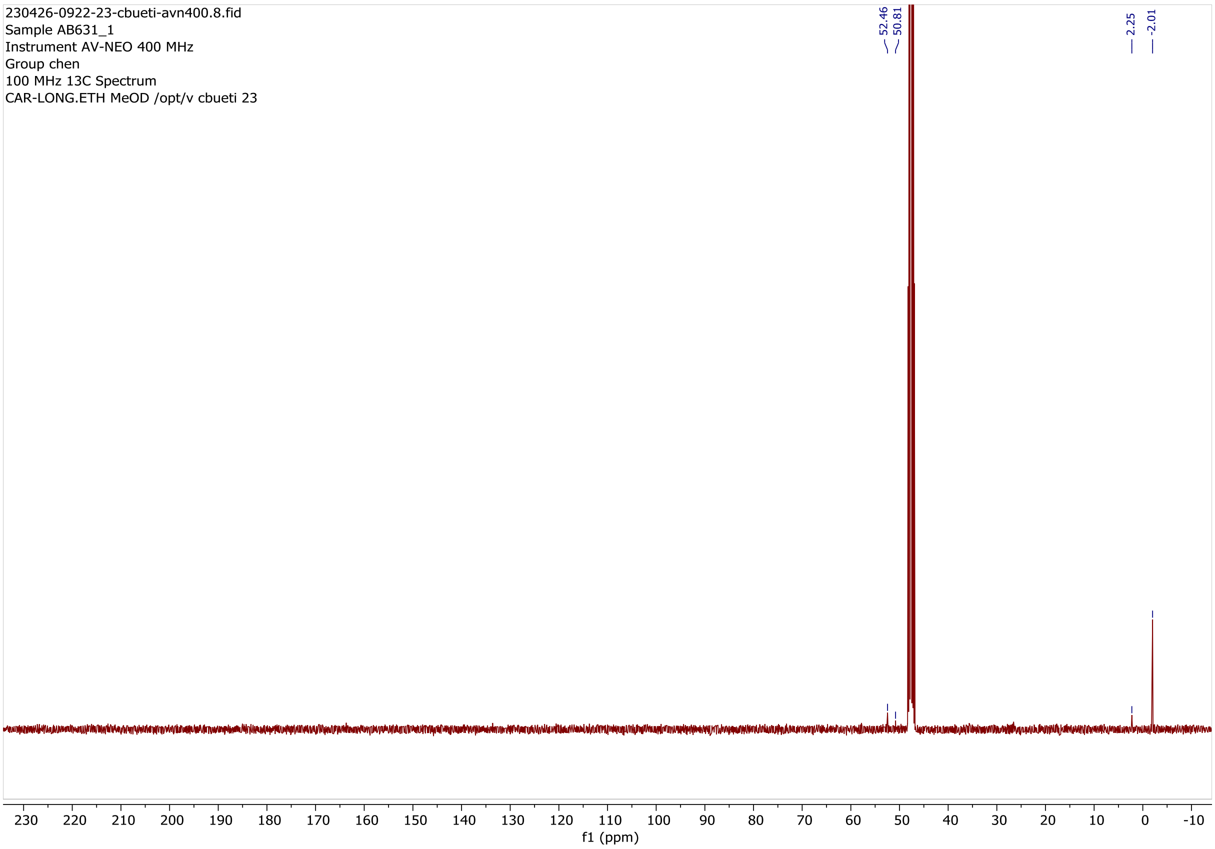


Figure S44. ^{13}C NMR spectrum recorded in MeOH-d_4.

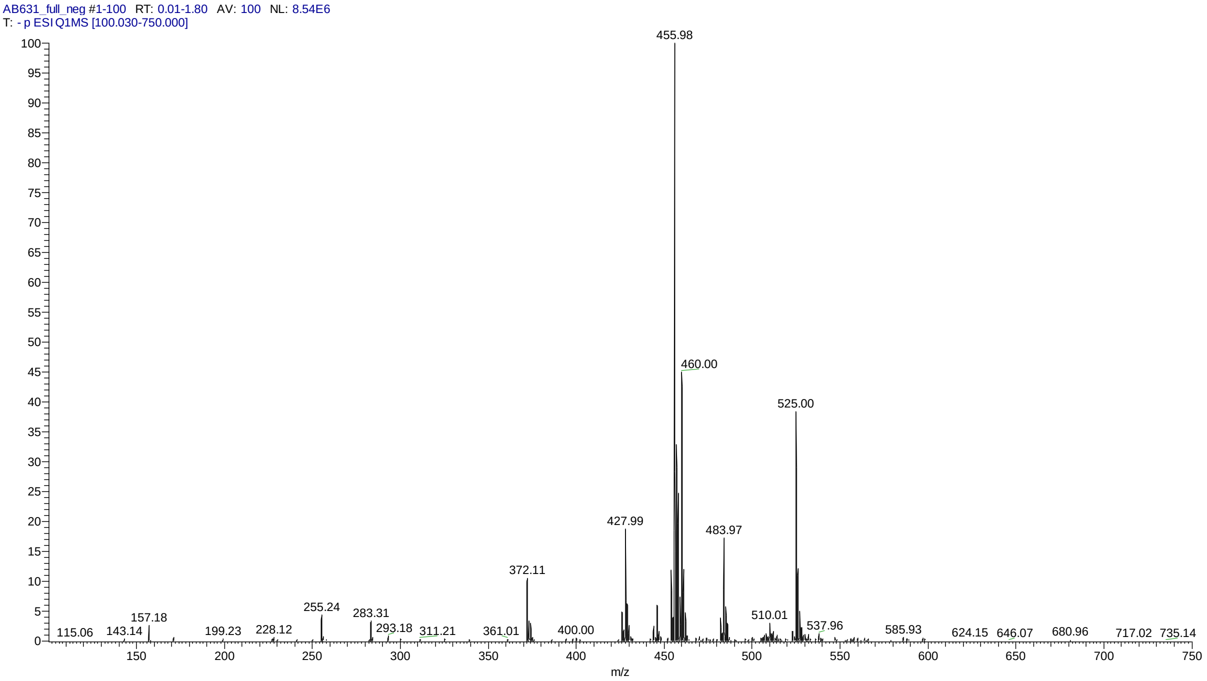


Figure S45. LRMS full spectrum. Sprayed from MeOH.

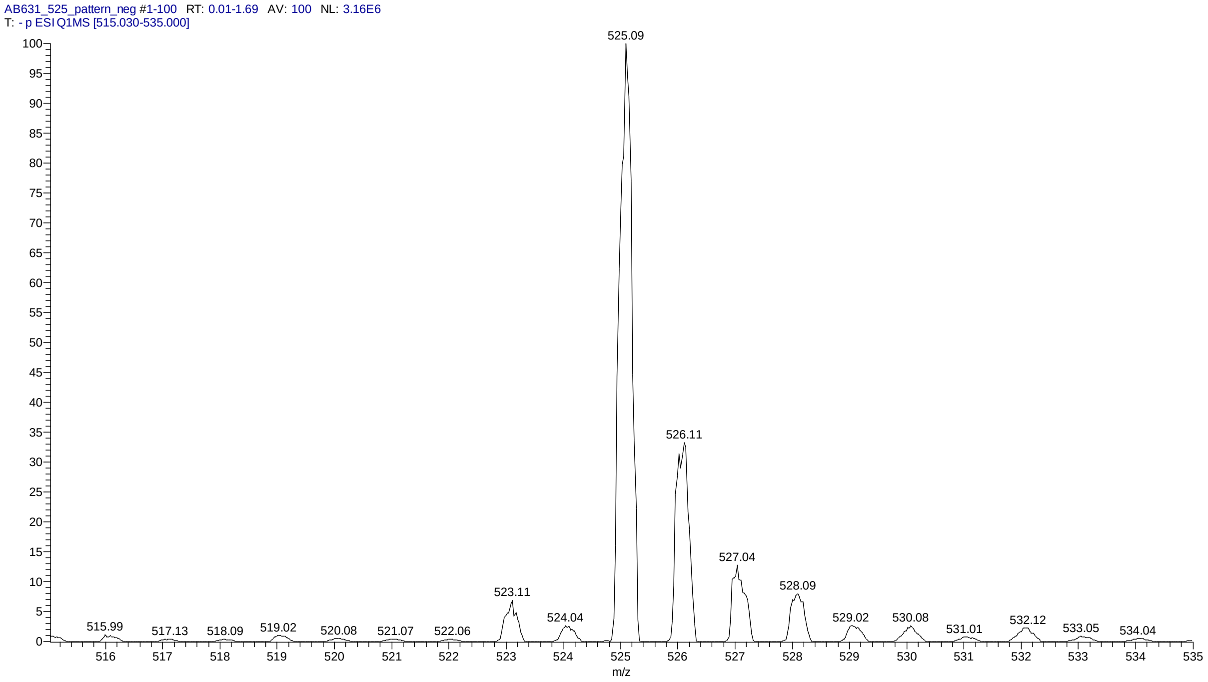


Figure S46. LRMS. Sprayed from MeOH.

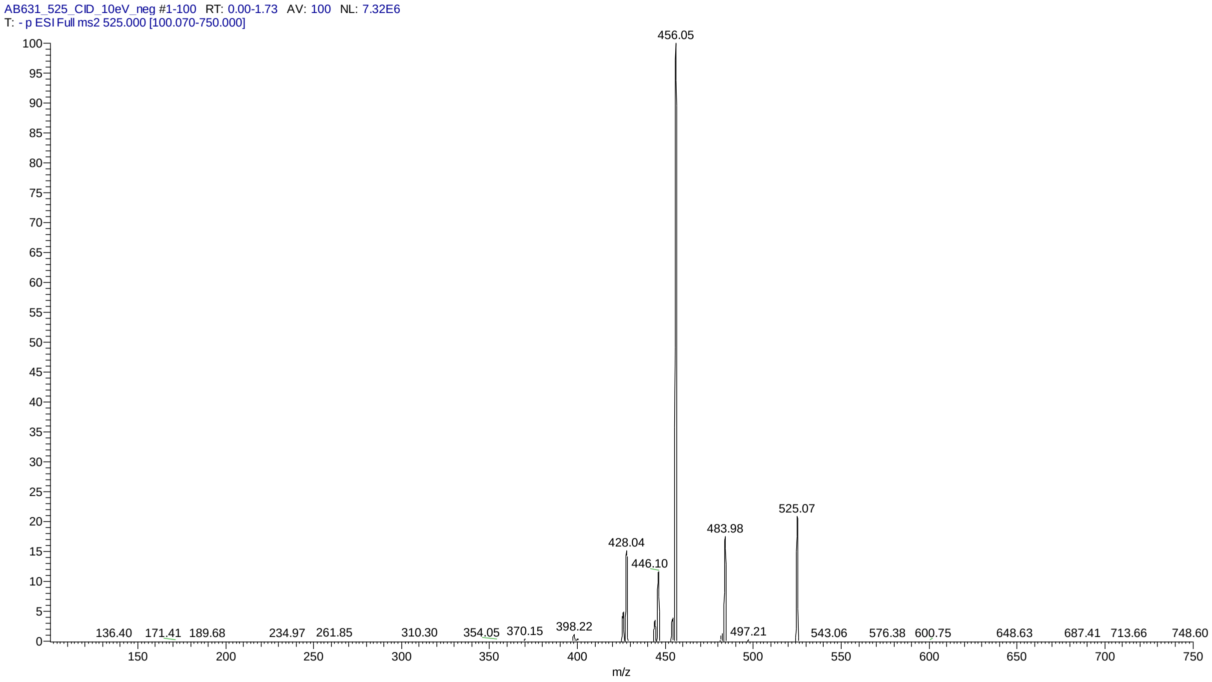
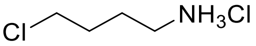


Figure S47. CID spectrum at 10 eV collision energy. Sprayed from MeOH.

1.8) 4-Chlorobutylamine hydrochloride



A dried and nitrogen-flushed 250 ml Schlenk tube equipped with a stir bar was charged with 50 ml dry toluene. 2.1 ml 4-aminobutanol (22.4 mmol, 1 equiv.) was added to the flask. To the stirred solution, 2.4 ml $SOCl_2$ (33.6 mmol, 1.5 equiv.) was added. The mixture was stirred at 80 °C for 72 h. The mixture was allowed to cool to room temperature. Addition of Et_2O lead to the precipitation of a solid. The solid was collected on a sintered glass funnel and washed with Et_2O. The solid was dried *in vacuo*. The product was obtained as a grey solid (2.95 g, 92 %). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 8.21 (s, br, 3H), 3.60 (t, *J* = 5.9 Hz, 2H), 3.09 (t, *J* = 5.9 Hz, 2H), 2.06 – 1.83 (m, 4H). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 44.2, 39.3, 29.4, 24.9.

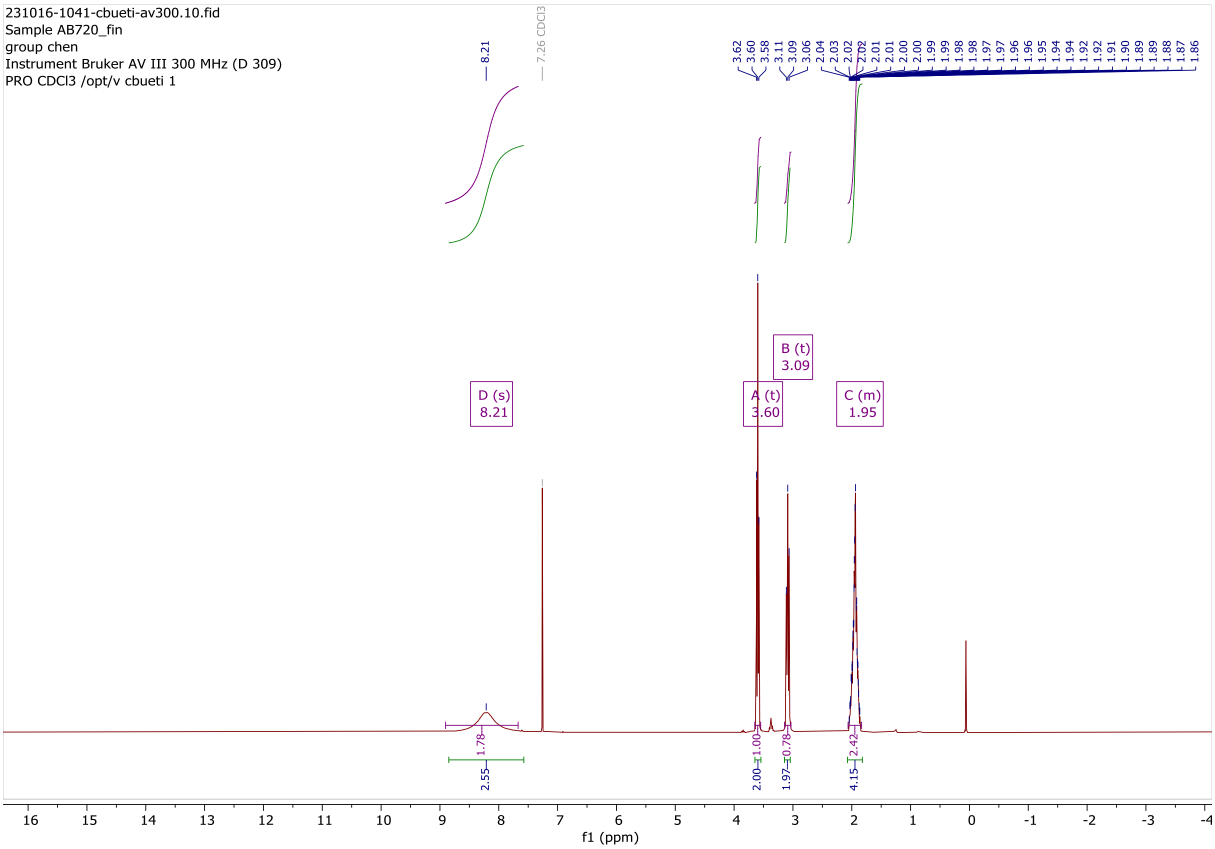


Figure S48. ^{1}H NMR spectrum recorded in CDCl$_3$.

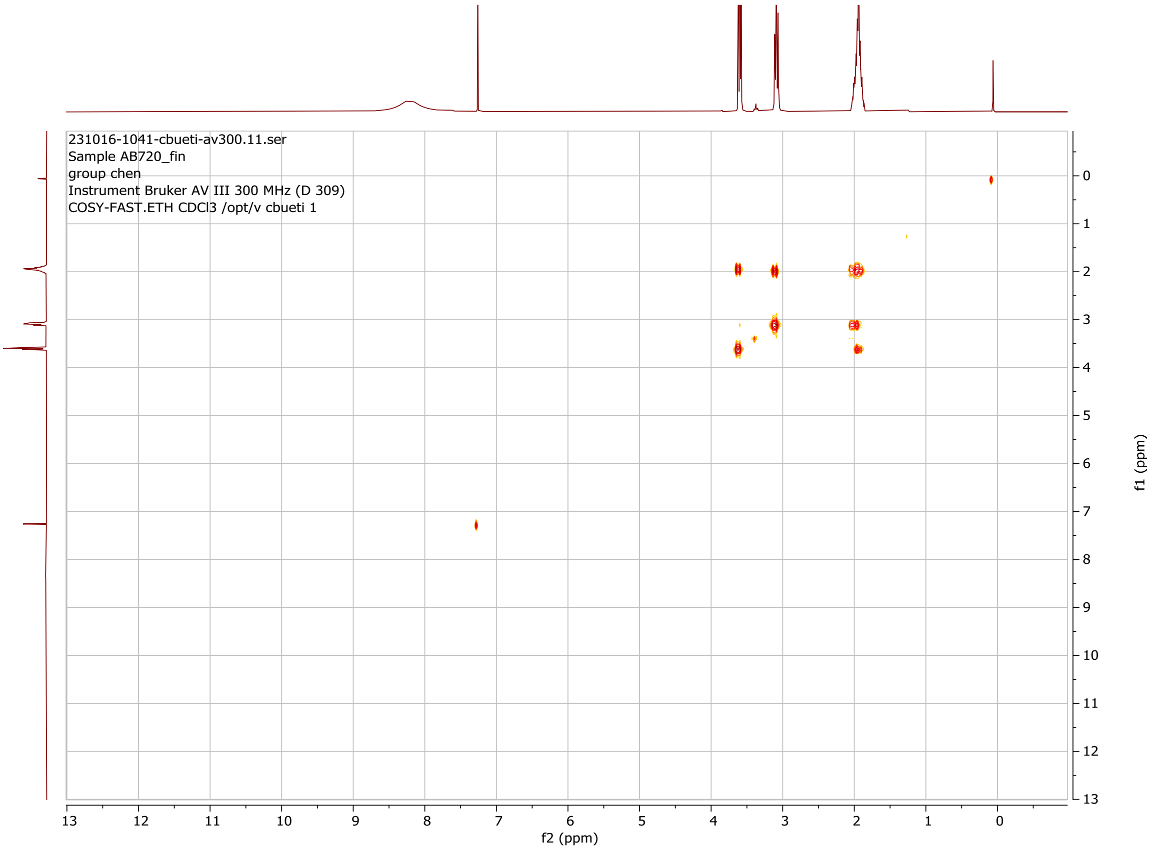


Figure S49. COSY spectrum recorded in CDCl$_3$.

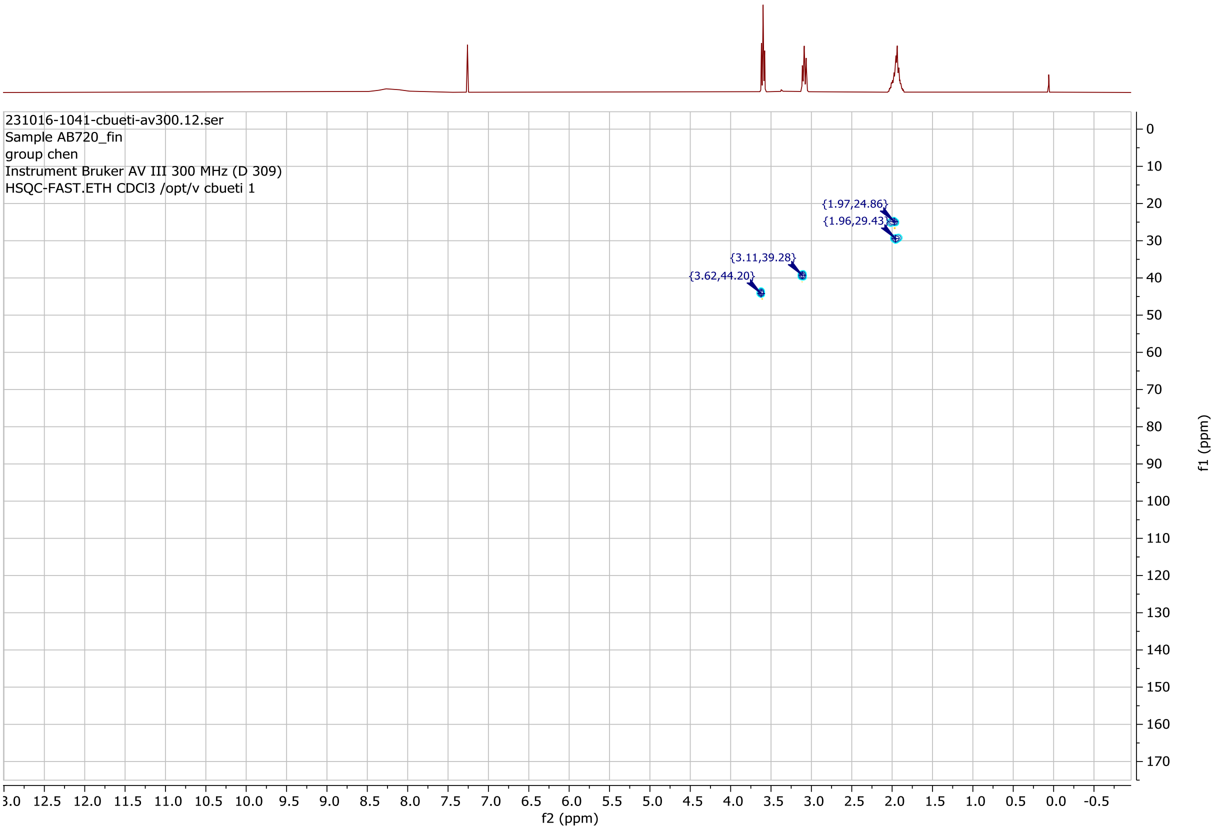
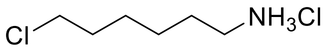


Figure S50. HSQC spectrum recorded in $CDCl_3$.

1.9) 6-Chlorohexylamine hydrochloride



6-chlorohexylamine hydrochloride: A dried and argon-flushed 50 ml Schlenk tube equipped with a stir bar was charged with 1 g 6-aminohexanol (8.54 mmol, 1 equiv.) and 20 ml dry PhMe. While stirring, 0.8 ml $SOCl_2$ (11.1 mmol, 1.3 equiv.) was added. The mixture was stirred at 80 °C for 72 h. The mixture was allowed to cool to room temperature. Addition of Et_2O lead to the precipitation of a solid. The solid was collected on a sintered glass funnel and washed with PhMe and pentane. After drying, the product was obtained as an off-white solid (1.2 g, 80 %).

^{1}H NMR (δ, 300 MHz, $CDCl_3$): 8.27 (s, 3H), 3.54 (t, *J* = 6.5 Hz, 2H), 3.07 – 2.93 (m, 2H), 1.86 – 1.72 (m, 4H), 1.56 – 1.38 (m, 4H).

^{13}C NMR (δ, 75 MHz, $CDCl_3$): 44.6, 39.6, 32.24, 32.24, 27.3 25.9.

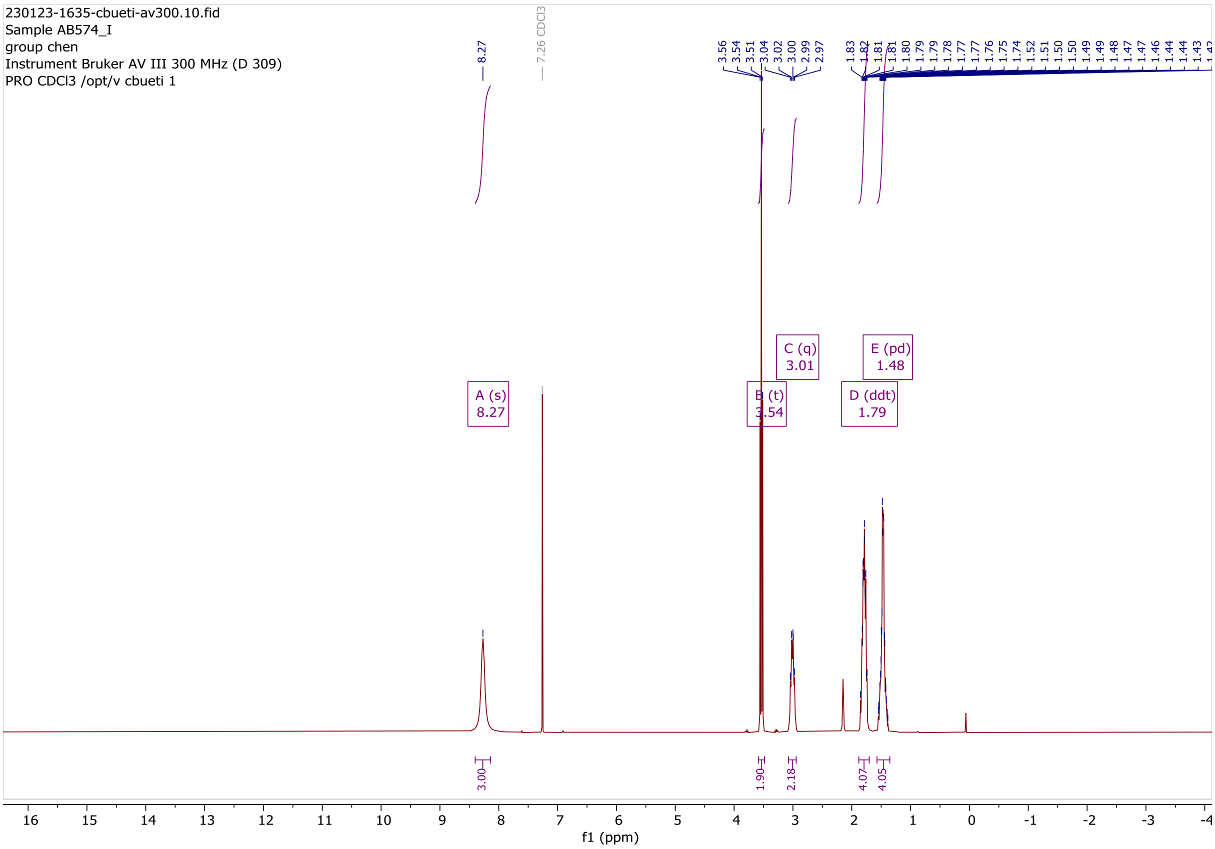


Figure S51. ^1H NMR spectrum recorded in $CDCl_3$.

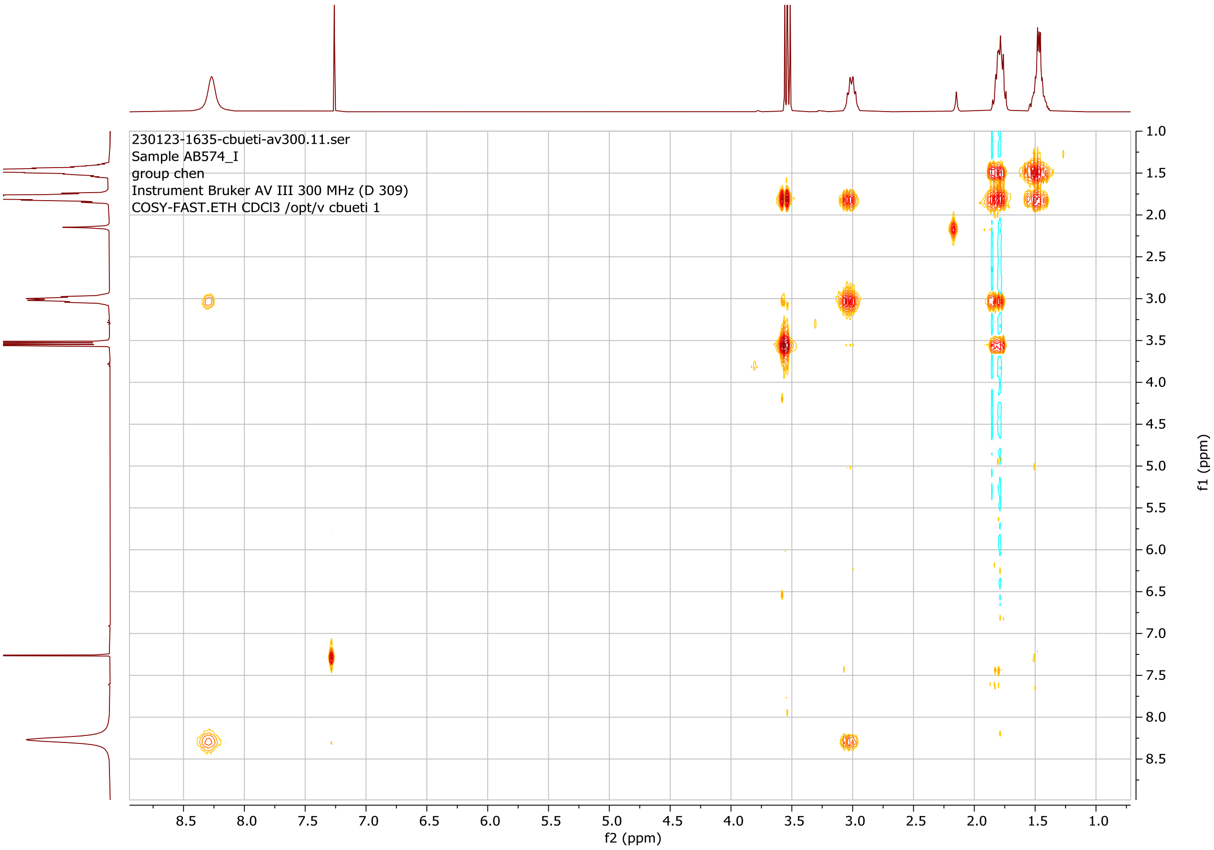


Figure S52. COSY spectrum recorded in $CDCl_3$.

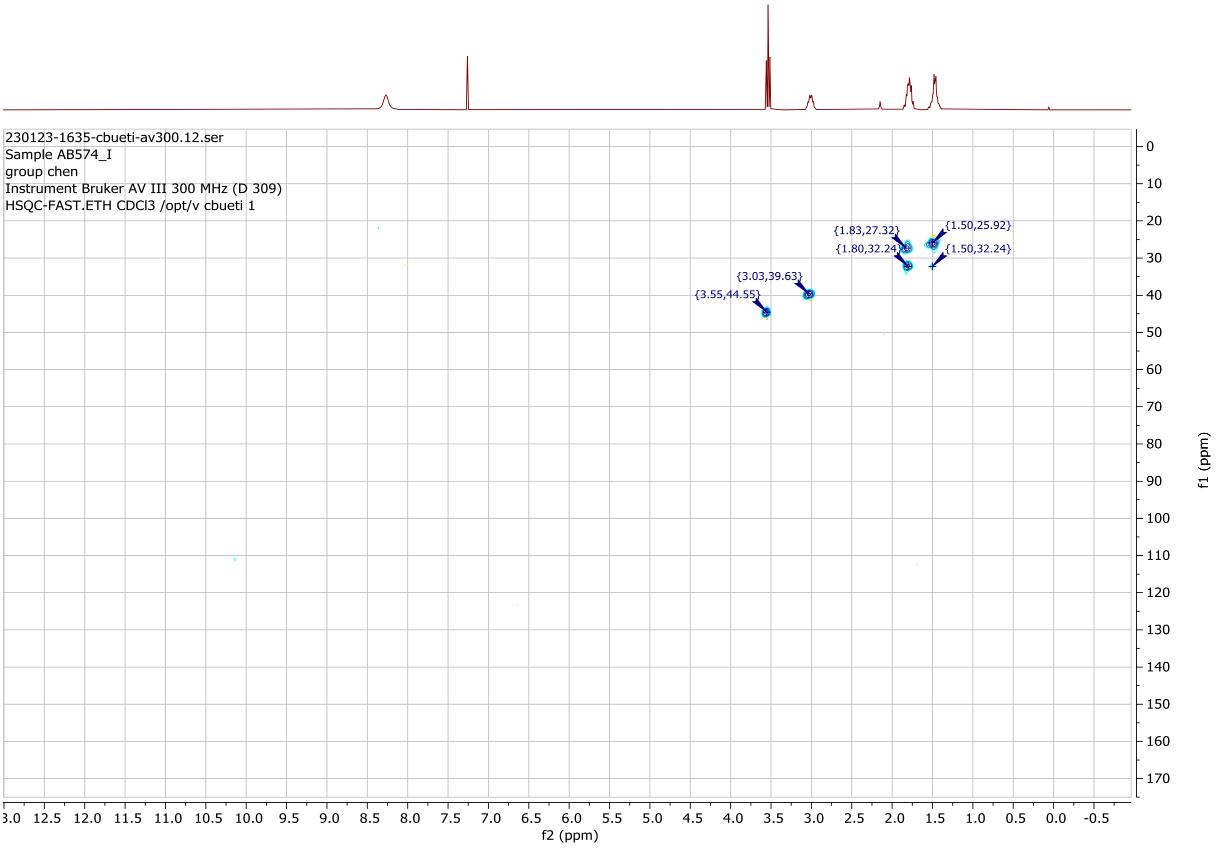
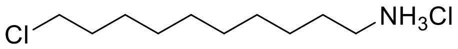


Figure S53. HSQC spectrum recorded in CDCl₃.

1.10) 10-Chlorodecylamine hydrochloride



A dried and argon flusehd 50 ml Schlenk tube equipped with a stir bar was charged with 0.5 g 10-aminodecanol (2.89 mmol, 1 equiv.). 7 ml dry toluene was added to the solid. Under stirring, 0.27 mol $SOCl_2$ (3.75 mmol, 1.3 equiv.) was added to the mixture. The reaction mixture was heated to 80 °C overnight. The next day, the orange solution was allowed to cool to room temperature. Et_2O was added, resulting in the precipitation of a colorless solid. The solid was collected on a sintered funnel and washed with Et_2O. The solid was air dried. The first crop of product was isolated as a white solid (470 mg, 72 %). The filtrate was cooled in a freezer, resulting in the precipitation of more product. The second crop was isolated as before (131 mg, 20%).

^{1}H NMR (δ, 400 MHz, $CDCl_3$): 8.30 (s, br, 3H), 3.53 (t, *J* = 6.7 Hz, 2H), 3.02 – 2.94 (m, 2H), 1.82 – 1.71 (m, 4H), 1.46 -1.35 (m, 4H), 1.35 – 1.25 (m, 8H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 45.3, 40.1, 32.8, 29.5, 29.4, 29.04, 28.96, 27.8, 27.0, 26.6.

Anal. calc. for $C_{10}H_{23}Cl_2N$ (%): C, 52.64; H, 10.16; N, 6.14. Found: C, 52.91; H, 10.13; N, 6.45.

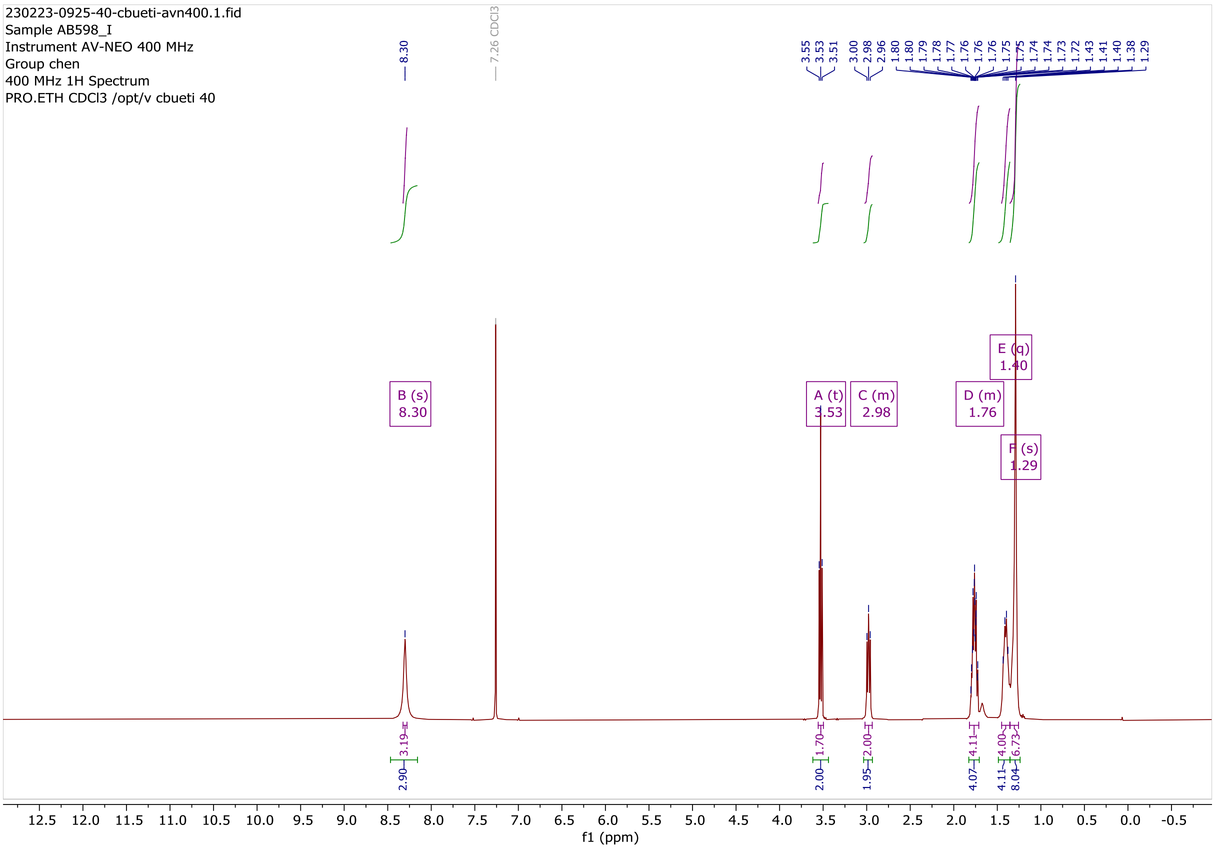


Figure S54. ^1H NMR spectrum recorded in $CDCl_3$.

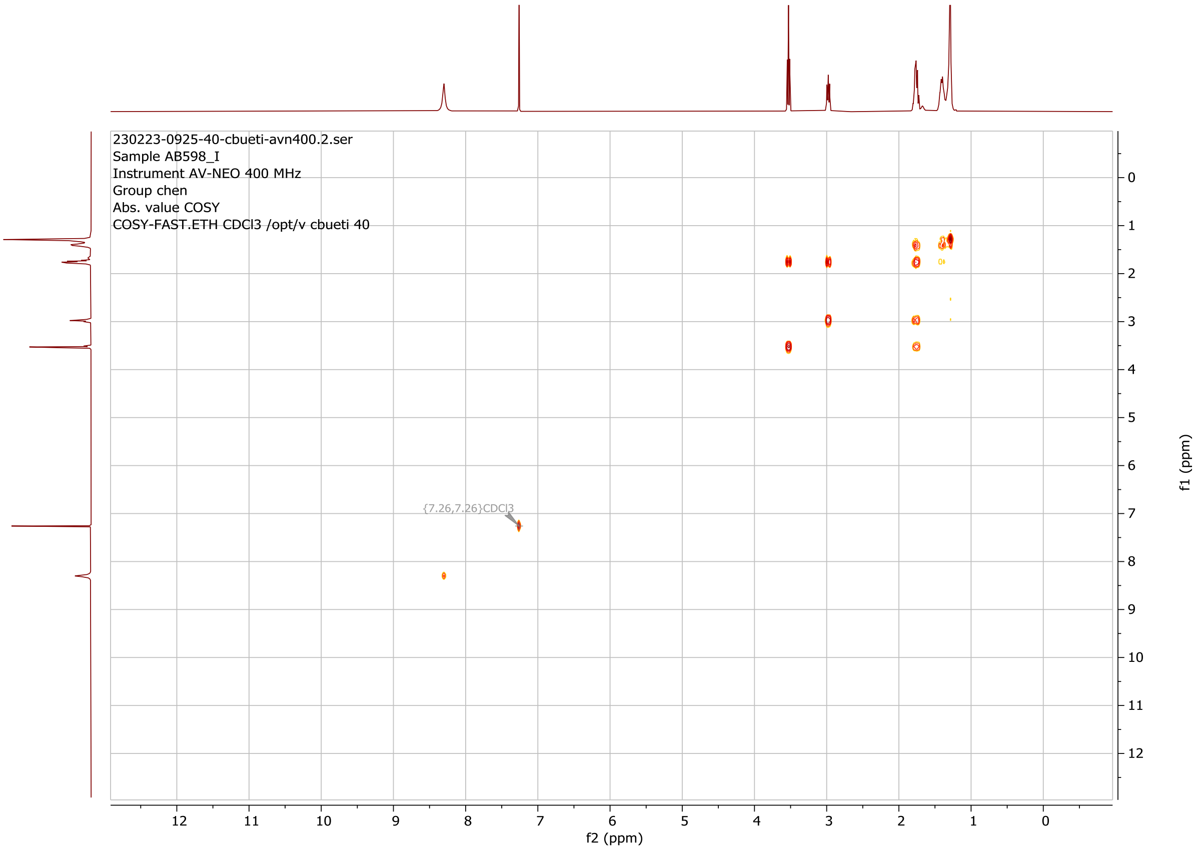


Figure S55. COSY spectrum recorded in $CDCl_3$.

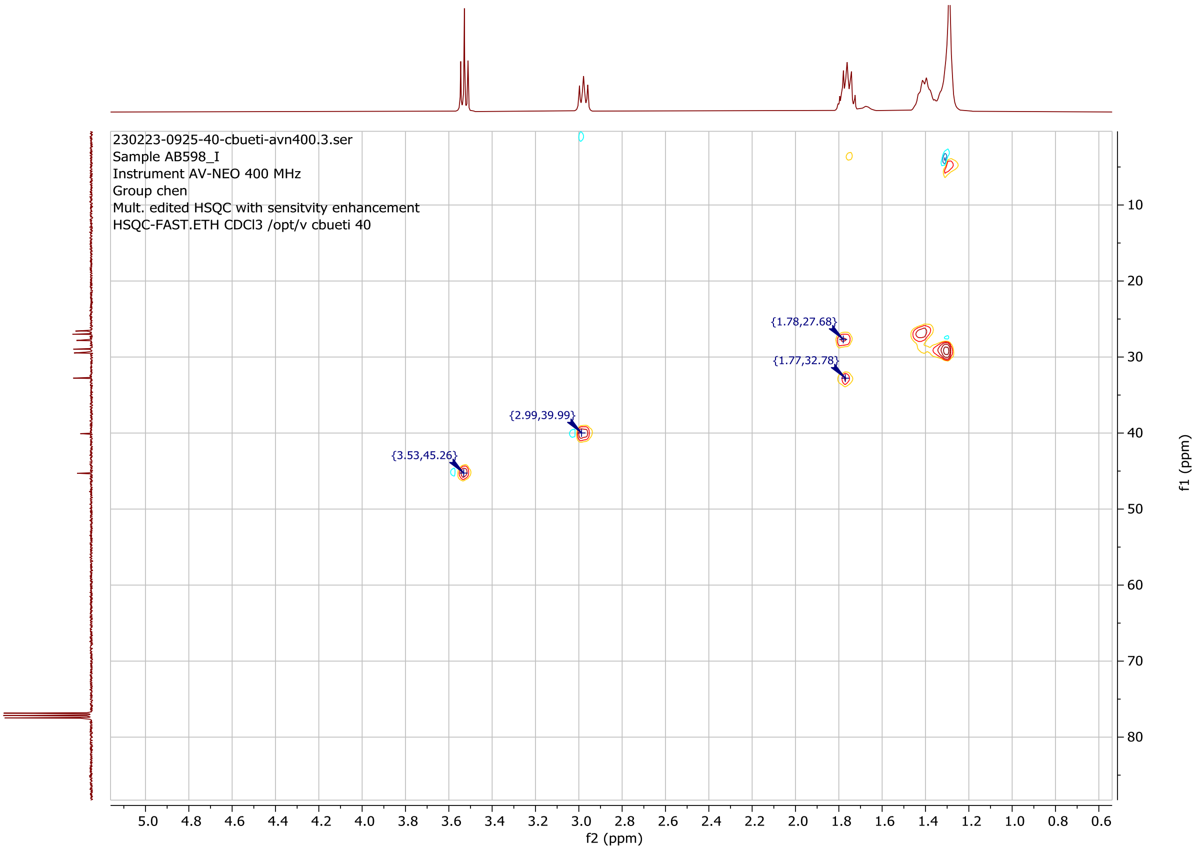


Figure S56. HSQC spectrum recorded in CDCl$_3$.

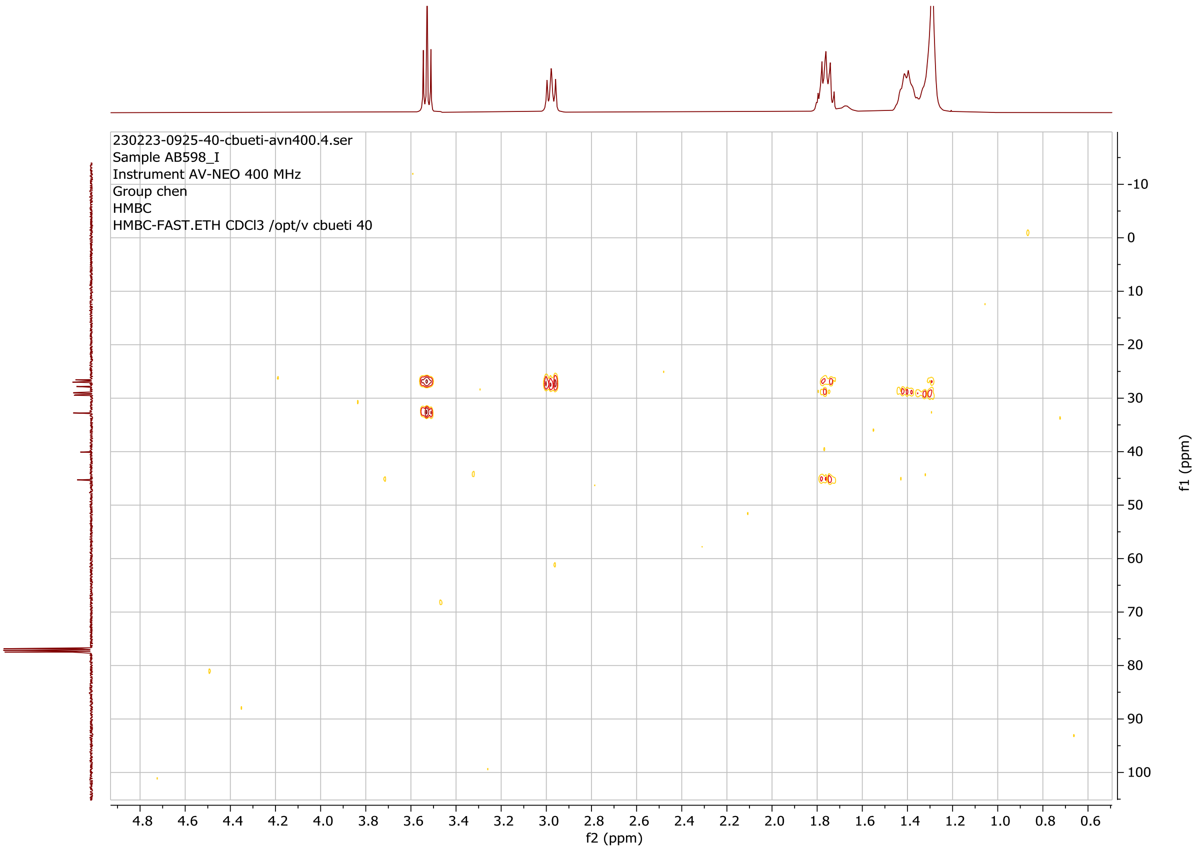


Figure S57. HMBC spectrum recorded in CDCl$_3$.

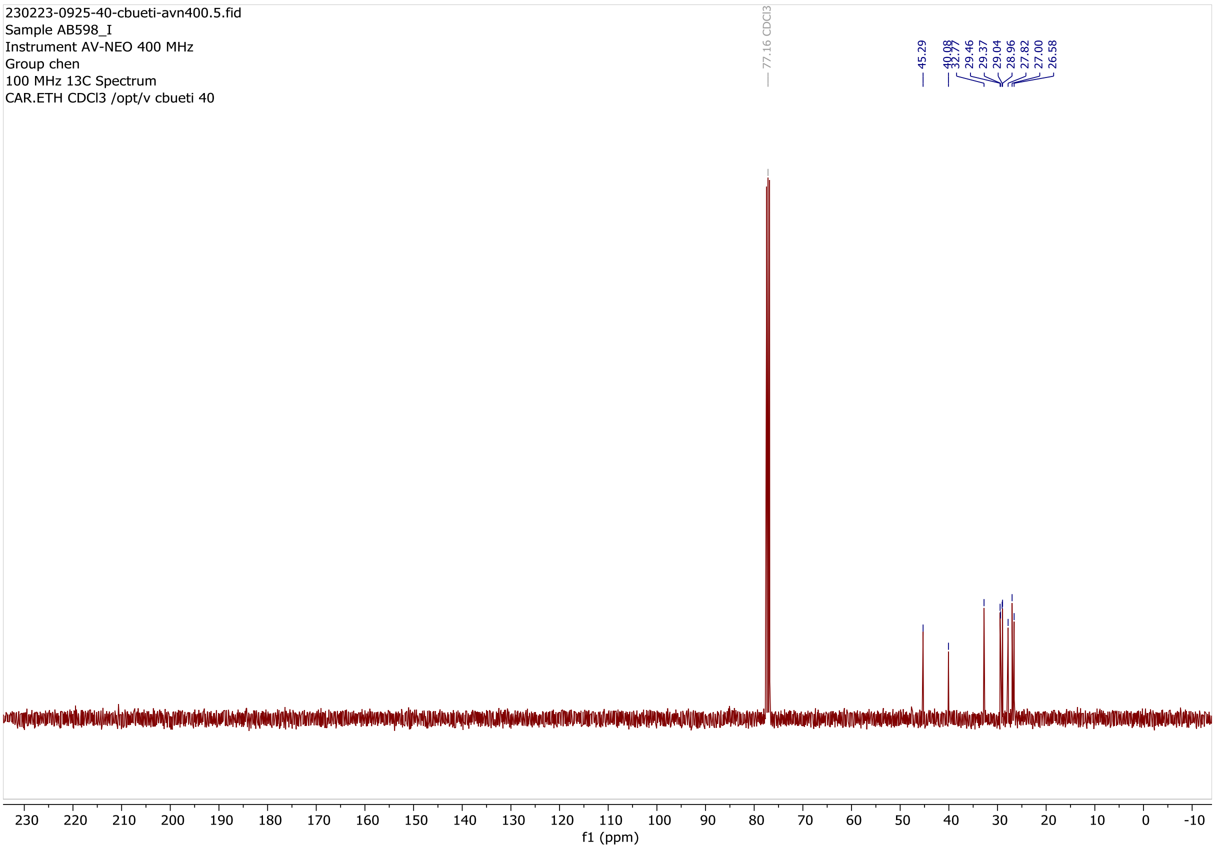
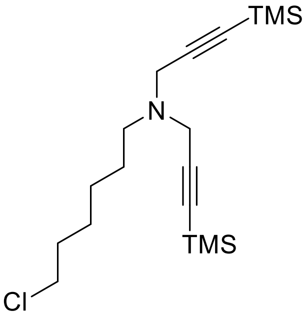


Figure S58. ^{13}C NMR spectrum recorded in $CDCl_3$.

1.11) *N*-(6-chlorohexyl)-*N*-bis(3-trimethylsilyl)prop-2-yn-1-yl)amine



A nitrogen-flushed 20 ml Schlenk tube was charged with 500 mg 6-chlorohexylamine hydrochloride (2.9 mmol, 1 equiv.), 29.7 mg CuCl (0.3 mmol, 0.1 equiv.) and 244 mg $NaHCO_3$ (2.9 mmol, 1 equiv.). 1.04 ml trimethylsilylacetylene (7.3 mmol, 2.5 equiv.) and 0.55 ml 39 % HCHO (7.3 mmol, 2.5 equiv.) were added to the solids. The reaction mixture was stirred vigorously overnight. The next day, the mixture was passed through a pad of Celite and eluted with EtOAc. A red residue remained on the pad. The orange filtrate was concentrated under reduced pressure. An orange oil with an orange precipitate remained in the flask. The mixture was passed through a pad of silica eluting with 10:1 hexane/EtOAc. The solvent was removed under reduced pressure. The product was obtained as an orange oil (790 mg, 76 %).

TLC (SiO_2, 10:1 hexane/EtOAc, $KMnO_4$ stain): r_f = 0.6.

^{1}H NMR (δ, 400 MHz, $CDCl_3$): 3.53 (t, *J* = 6.7 Hz, 2H), 3.41 (s, 4H), 2.51 (s, br, 2H), 1.83 – 1.72 (m, 2H), 1.54 – 1.41 (m, 4H), 1.40 – 1.32 (m, 2H), 0.17 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 101.4, 89.9, 52.7, 45.2, 43.6, 32.7, 27.3, 26.9, 26.8, 0.18.

HRMS (m/z): $[M+H]^+$ calc. for $C_{18}H_{34}ClNSi_2$: 356.1991. Found: 356.1988.

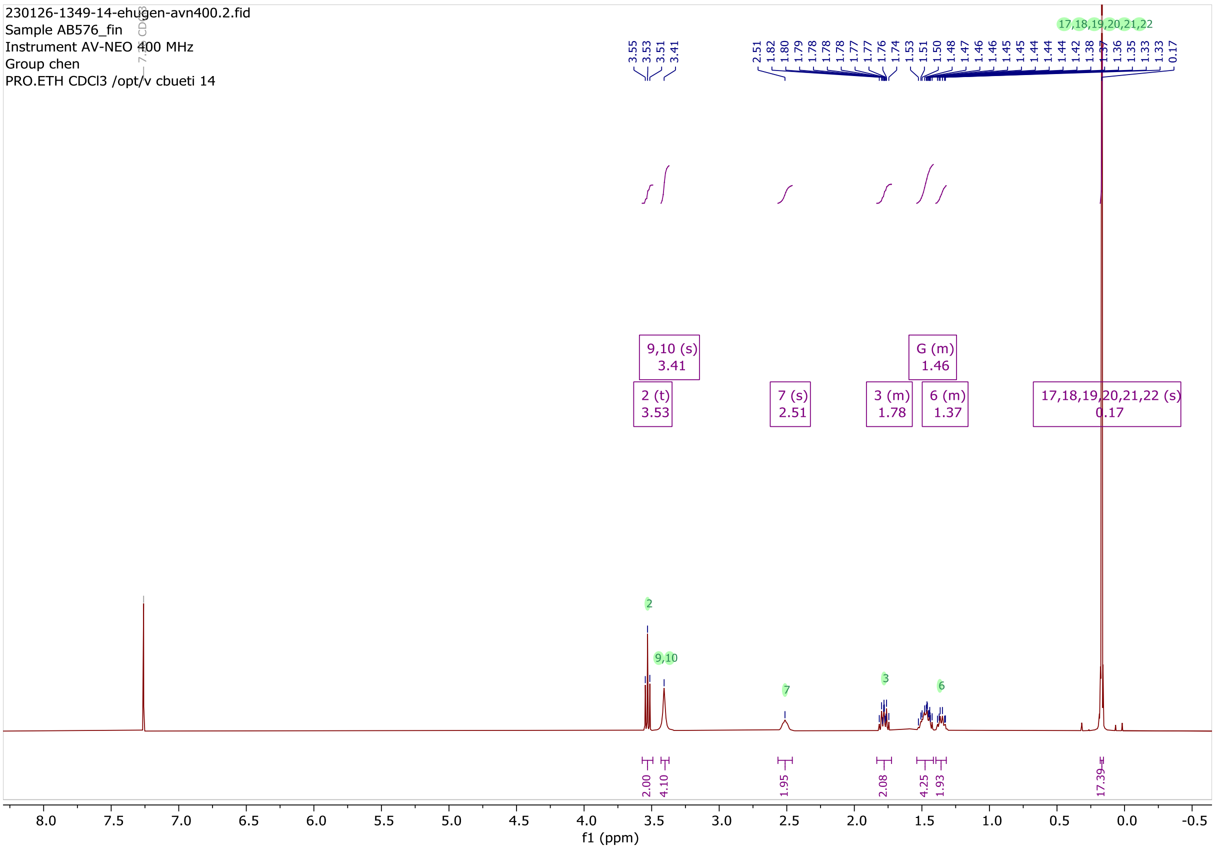


Figure S59. ^{1}H NMR spectrum recorded in $CDCl_3$.

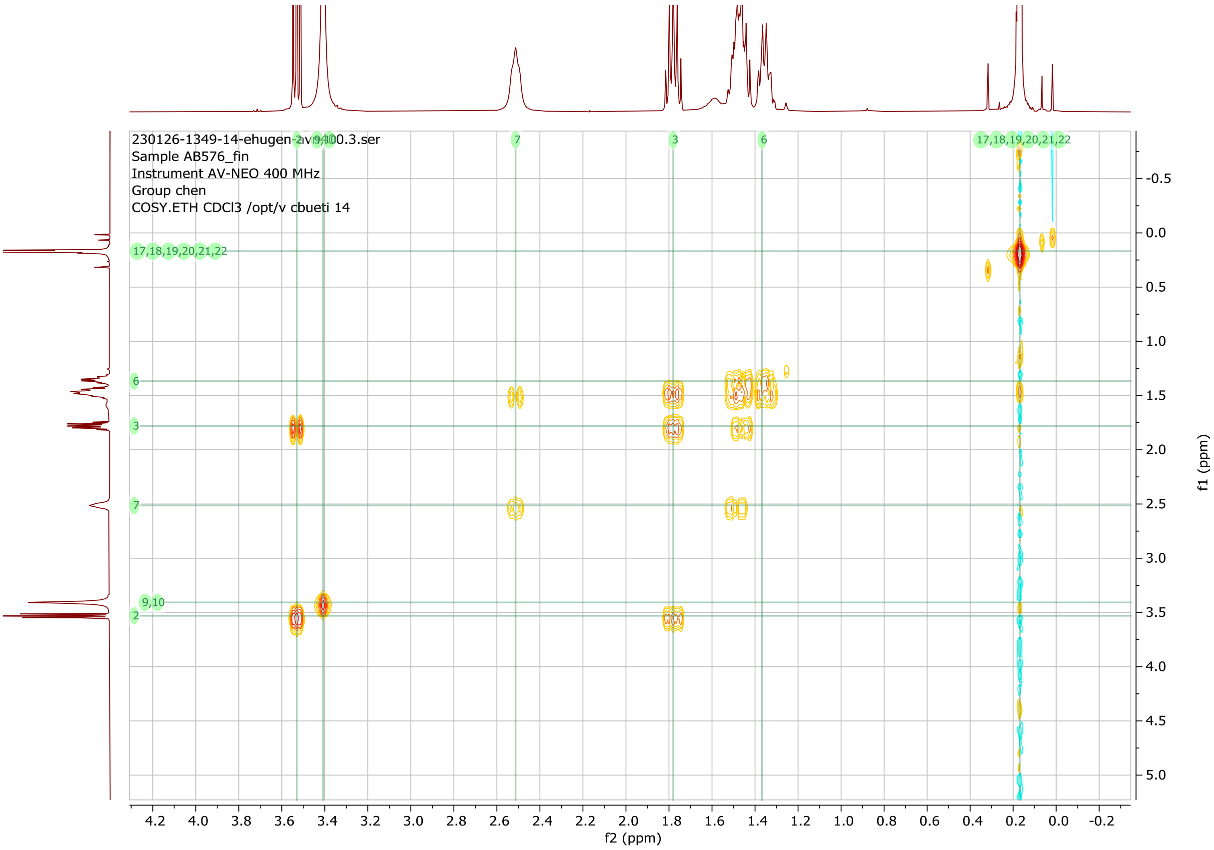


Figure S60. COSY spectrum recorded in $CDCl_3$.

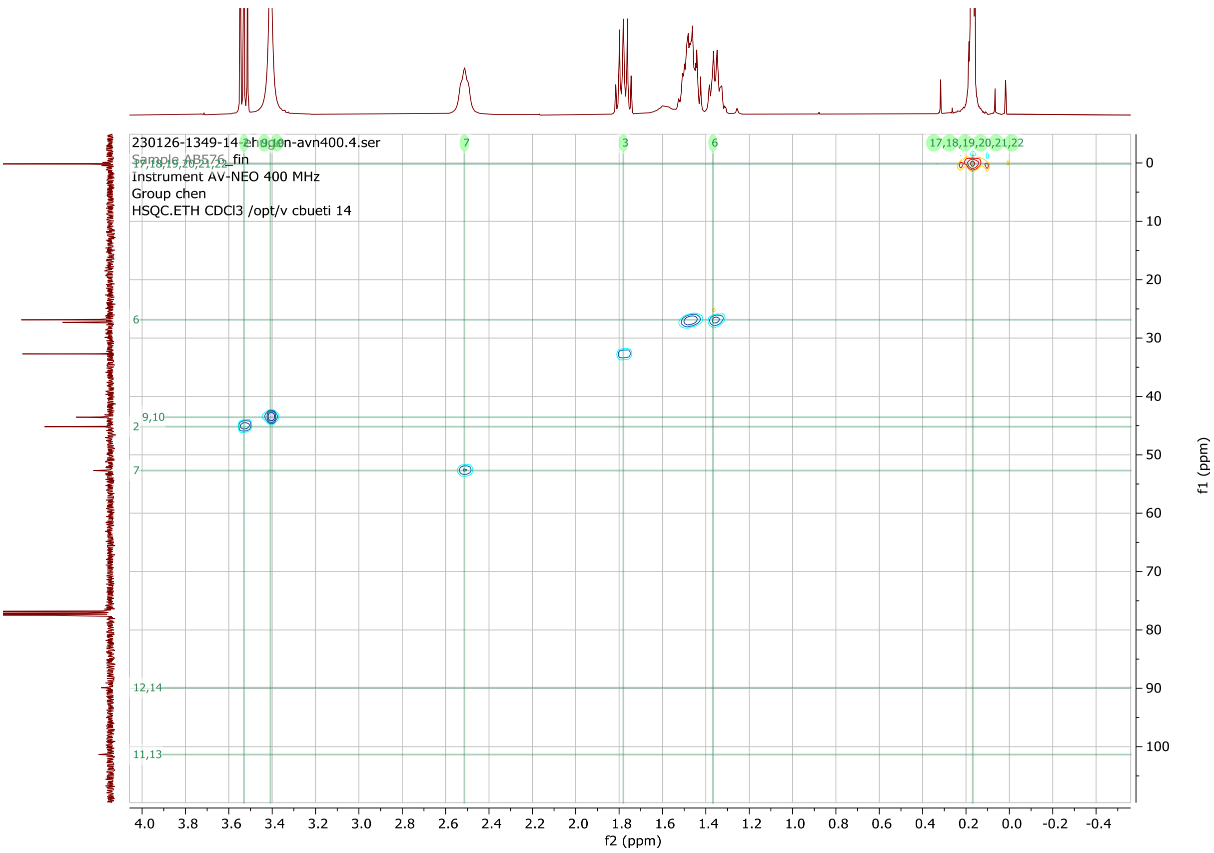


Figure S61. HSQC spectrum recorded in CDCl$_3$.

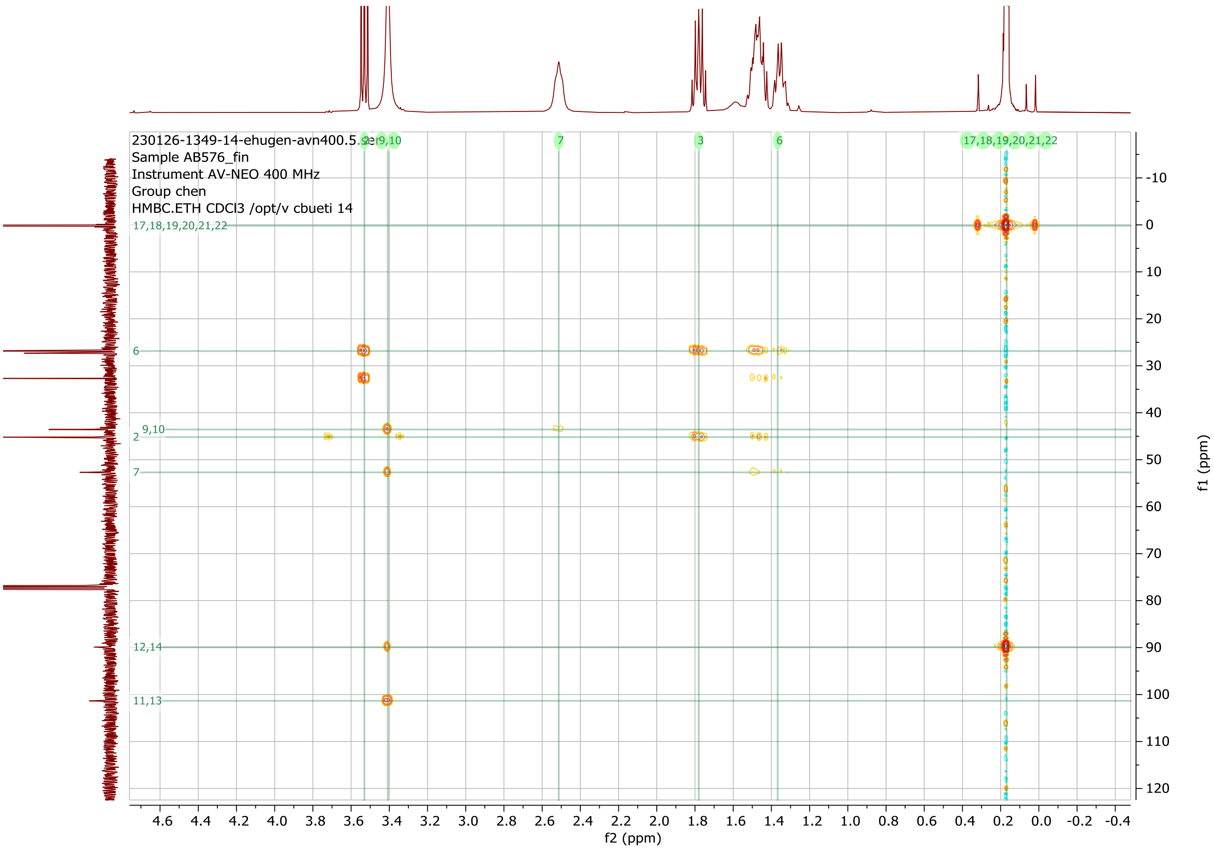


Figure S62. HMBC spectrum recorded in CDCl$_3$.

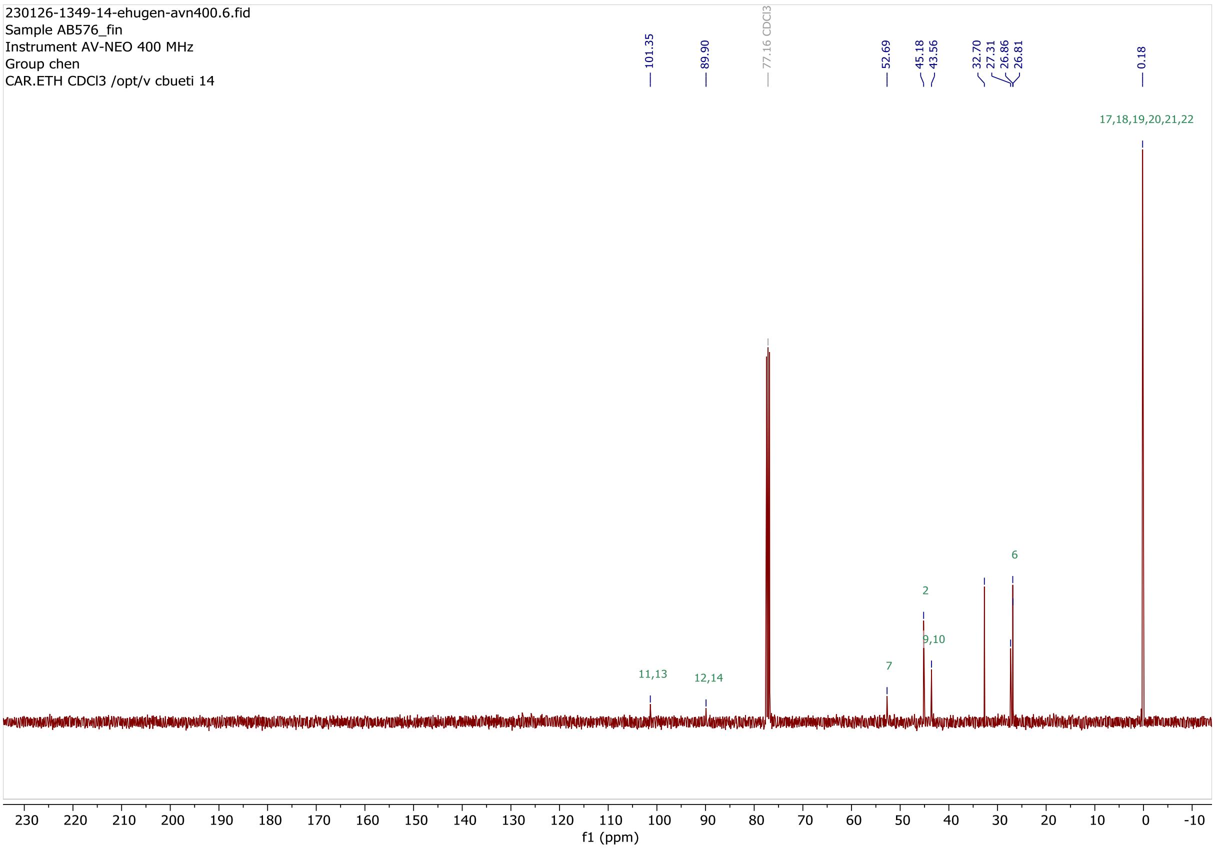


Figure S63. ^{13}C NMR spectrum recorded in CDCl$_3$.

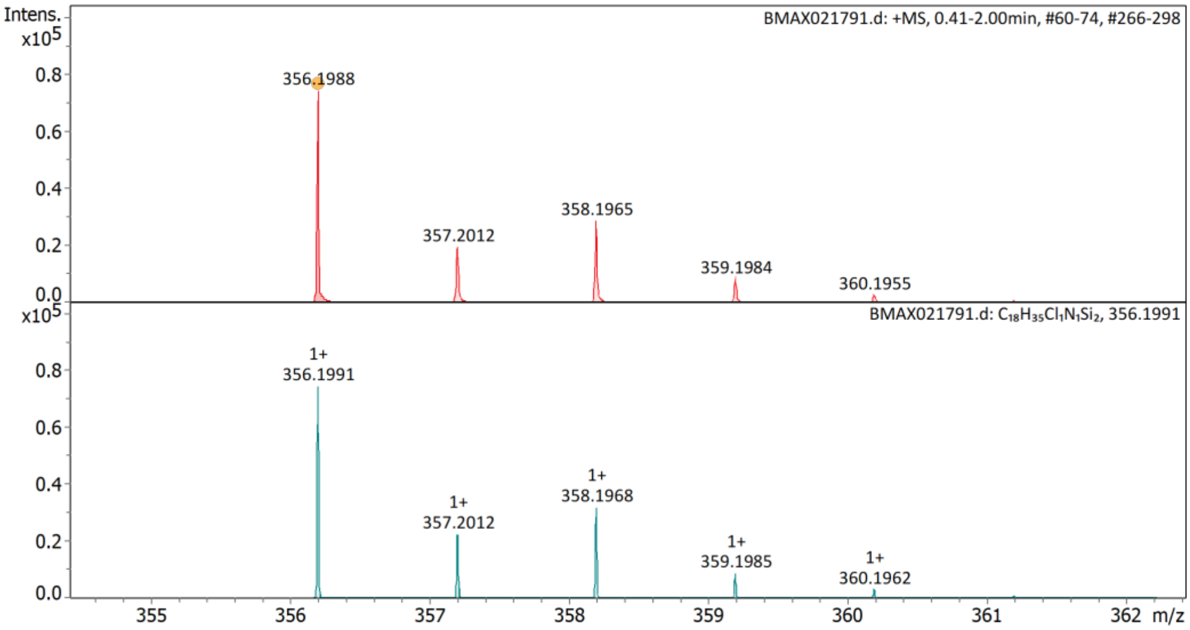
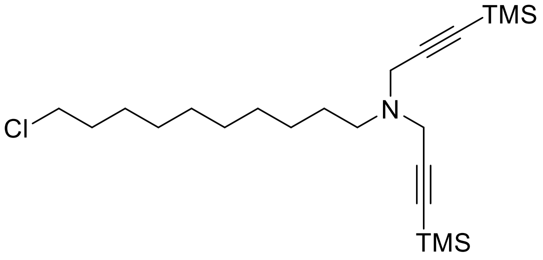


Figure S64. HRMS spectrum.

1.12) N-(10-chlorodecyl)*N*-bis(3-trimethylsilyl)prop-2-yn-1-yl)amine



A nitrogen flushed 20 ml Schlenk tube equipped with a stir bar was charged with 329 mg 10-chlorodecan-1-amine hydrochloride (1.45 mmol, 1 equiv.), 14.9 mg CuCl (0.15 mmol, 0.1 equiv), 122 mg $NaHCO_3$ (1.45 mmol, 1 equiv.), 0.52 ml trimethylsilylacetylene (3.65 mmol, 2.5 equiv.) and 0.28 ml 39 % HCHO (3.65 mmol, 2.5 equiv.). The mixture was stirred at room temperature overnight. The next day, the mixture was diluted with EtOAc and passed through a pad of Celite. The mixture was concentrated under reduced pressure. The residue was passed through a pad of silica using 1:10 EtOAc/hexane as the eluent. The solution was concentrated in vacuo. The compound was isolated as a pale yellow oil (593 mg, 99 %).

TLC (SiO_2, 1:10 EtOAc/hexane): $r_f = 0.8$.

^1H NMR (δ, 400 MHz, $CDCl_3$): 3.53 (t, *J* = 6.8 Hz, 2H) 3.40 (s, 4H), 2.54 – 2.46 (m, 2H), 1.82 – 1.70 (m, 2H), 1.52 – 1.36 (m, 4H), 1.33 – 1.24 (m, 10H), 0.16 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 101.4, 89.7, 53.0, 45.3, 43.5, 32.8, 29.61, 29.57, 29.0, 27.53, 27.48, 27.0, 0.17.

Anal. calc. for $C_{22}H_{42}ClNSi_2$ (%): C, 64.10; H, 10.27; N, 3.40. Found: C, 64.59; H, 10.65; N, 3.54.

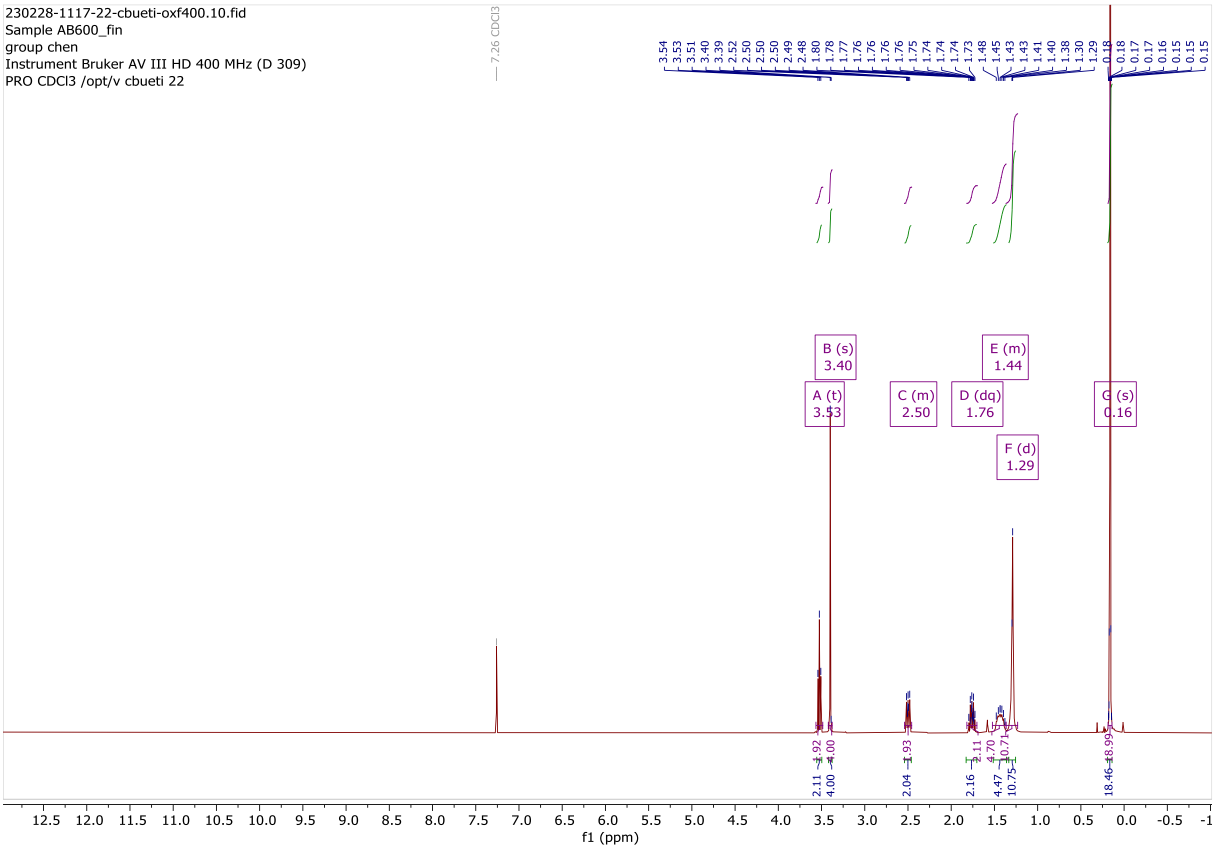


Figure S65. ^1H NMR spectrum recorded in $CDCl_3$.

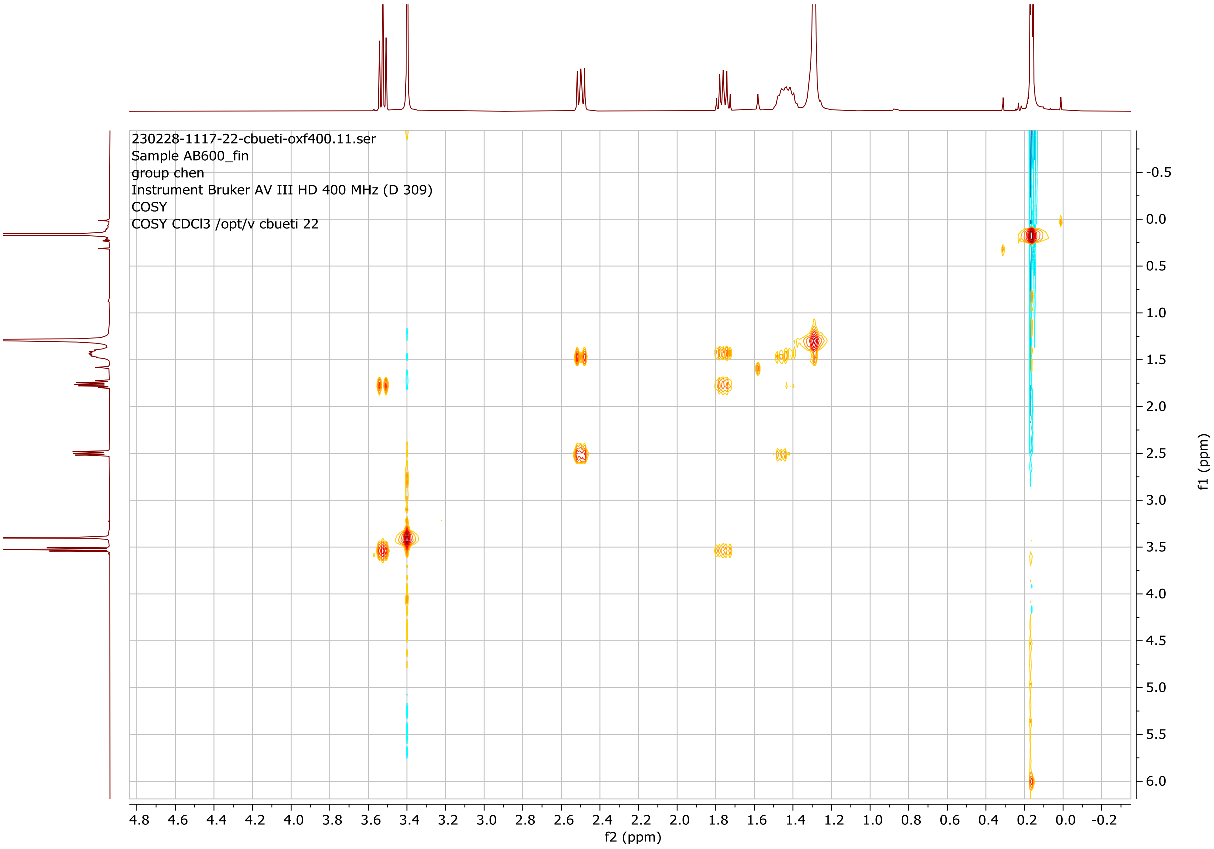


Figure S66. COSY spectrum recorded in CDCl$_3$.

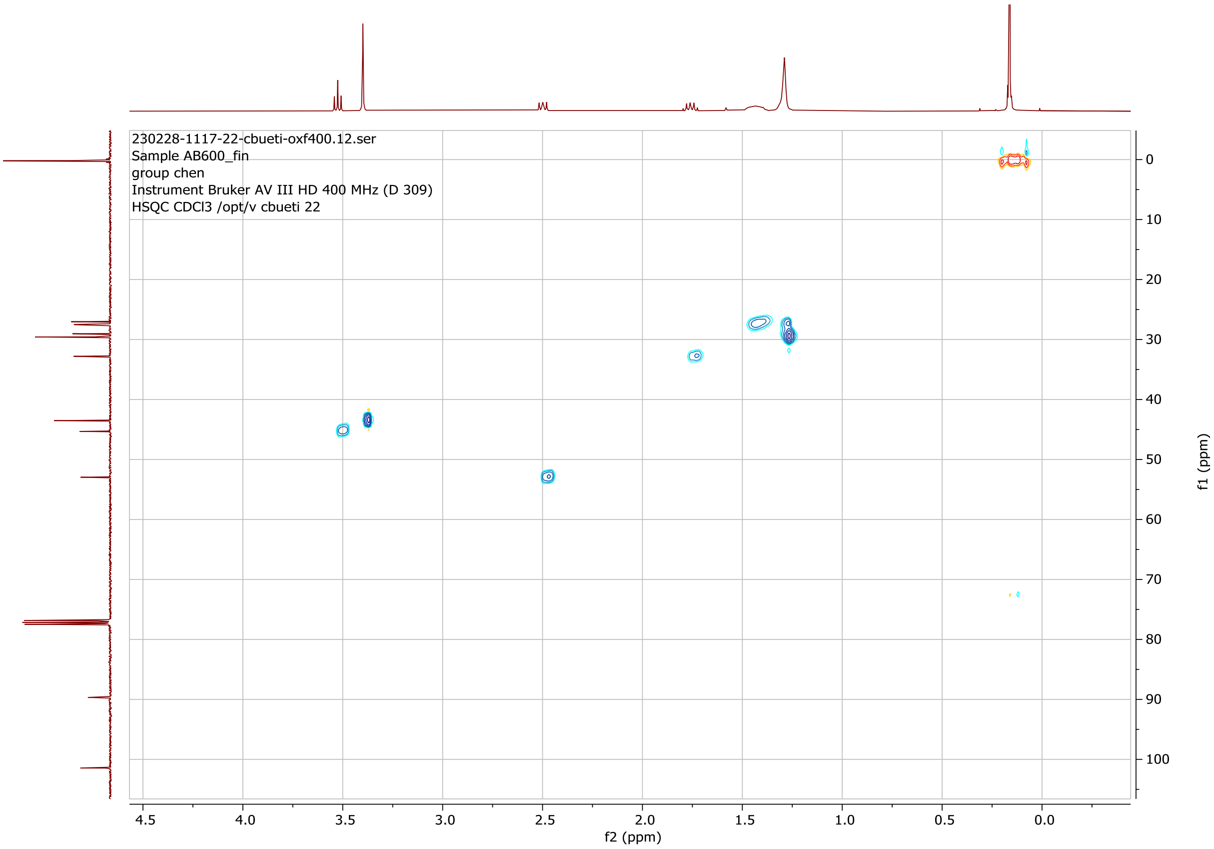


Figure S67. HSQC spectrum recorded in CDCl$_3$.

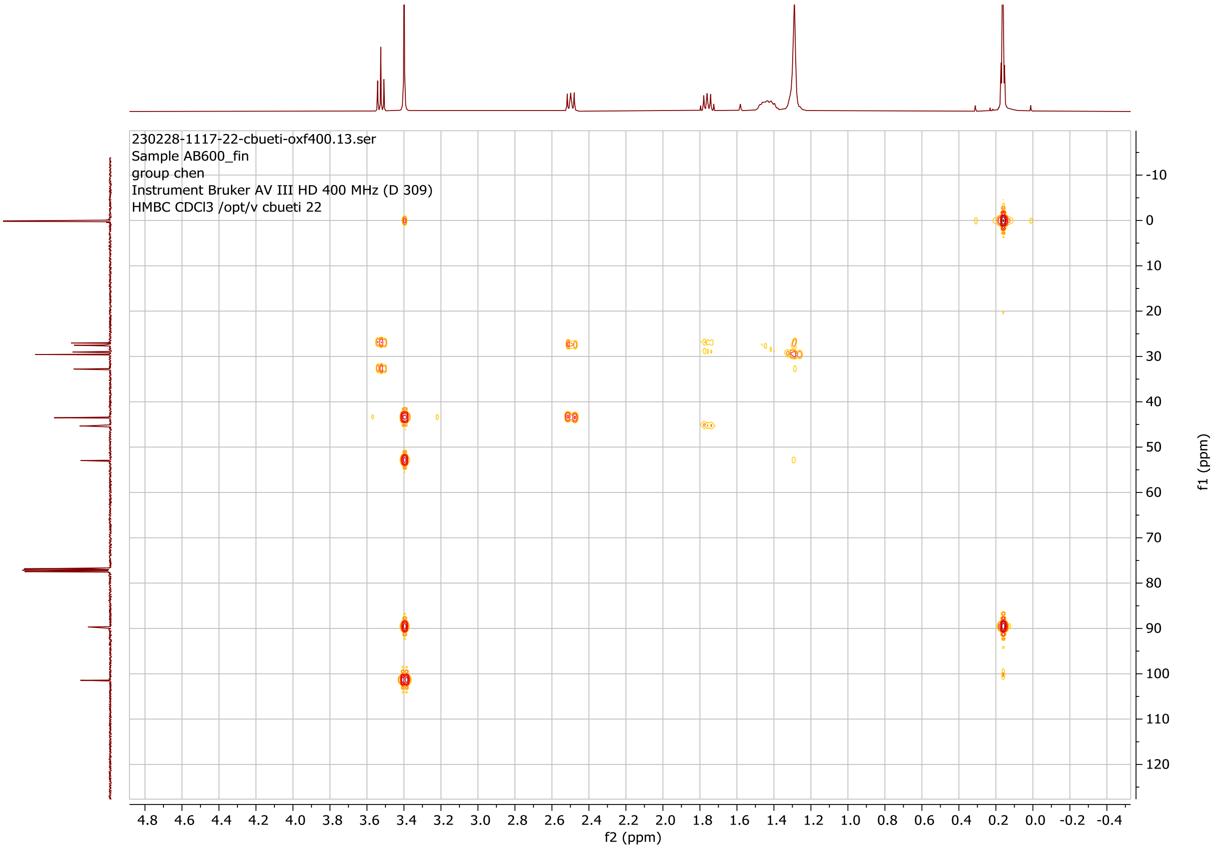


Figure S68. HMBC recorded in CDCl$_3$.

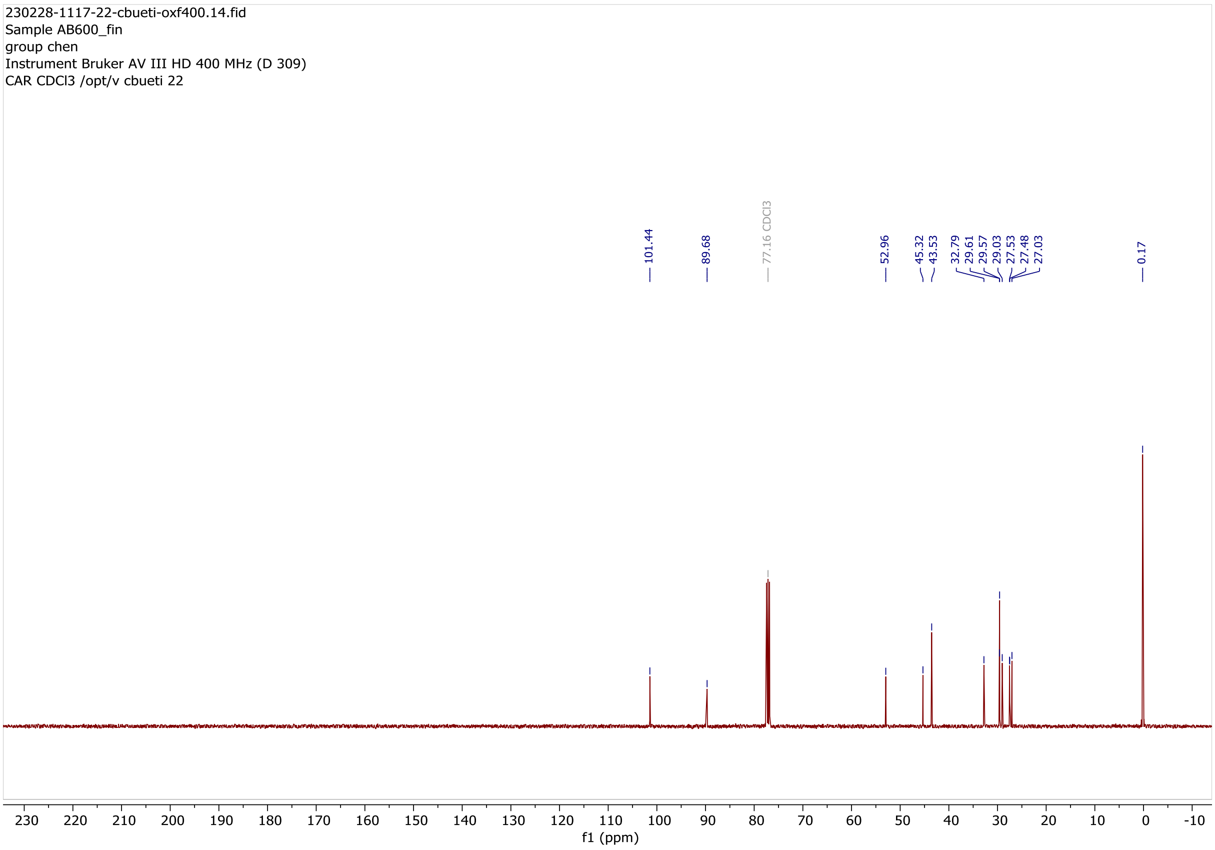
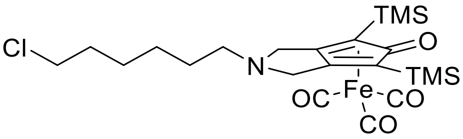


Figure S69. ^{13}C NMR spectrum recorded in CDCl$_3$.

1.13) $Fe^{TMS}(CO)_3$-$(CH_2)_6$-Cl



$Fe^{TMS}(CO)_3$-$(CH_2)_6$-Cl: A 250 ml nitrogen-flushed 2-necked round bottom flask equipped with a stir bar and a reflux condenser was charged with 790 mg *N*-(6-chlorohexyl)-*N*-bis(trimethylsilyl)prop-2-yn-1-yl)amine (2.22 mmol, 1 equiv.), 808 mg $Fe_2(CO)_9$ (2.22 mmol, 1 equiv.) and 25 ml dry toluene. The reaction mixture was stirred at reflux overnight. The next day, the mixture was allowed to cool to room temperature. The mixture was directly loaded onto a silica packed column and eluted with toluene until a straw orange band corresponding to $Fe(CO)_5$ had fully eluted. The $Fe(CO)_5$ dissolved in toluene was quenched with NaOCl prior to disposal. The eluent was changed to 10:1 hexane/EtOAc and purification by column chromatography continued. The relevant yellow fractions were combined and concentrated under reduced pressure. Drying *in vacuo* afforded the product as an orange, viscous oil (1.14 g, 98 %).

TLC (SiO_2, 10:1 hexane/EtOAc): $r_f = 0.4$.

^1H NMR (δ, 400 MHz, $CDCl_3$): 3.79 (d, *J* = 12.5 Hz, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.28 (d, *J* = 12.5 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.63 – 1.54 (m, 2H), 1.53 – 1.44 (m, 2H), 1.44 – 1.34 (m, 2H), 0.25 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 208.8, 182.5, 113.5, 69.4, 55.2, 53.4, 45.1, 32.7, 28.5, 26.8, 26.5, -0.6.

HRMS (m/z): $[M+H]^+$ calc. for $C_{22}H_{35}ClFeNO_4Si_2$: 524.1137. Found: 524.1131.

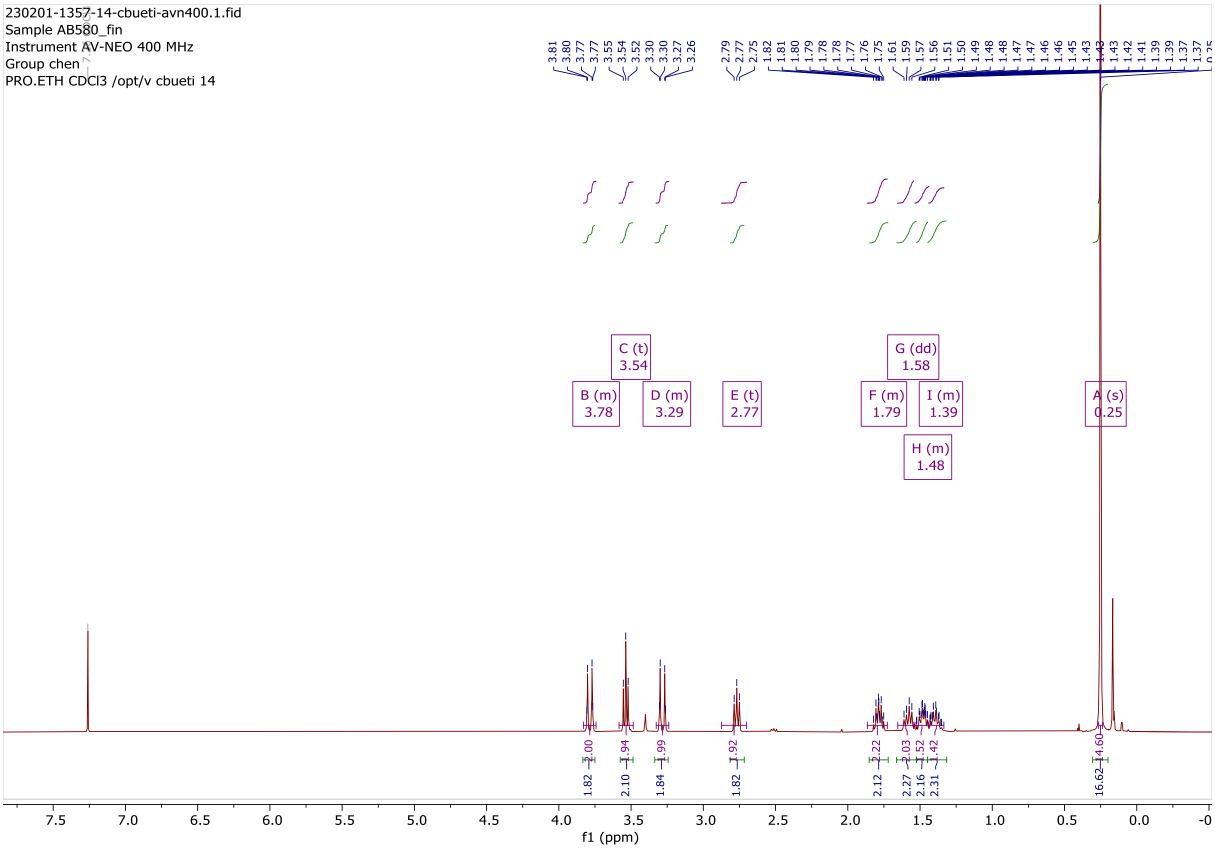


Figure S70. ^1H NMR spectrum recorded in $CDCl_3$.

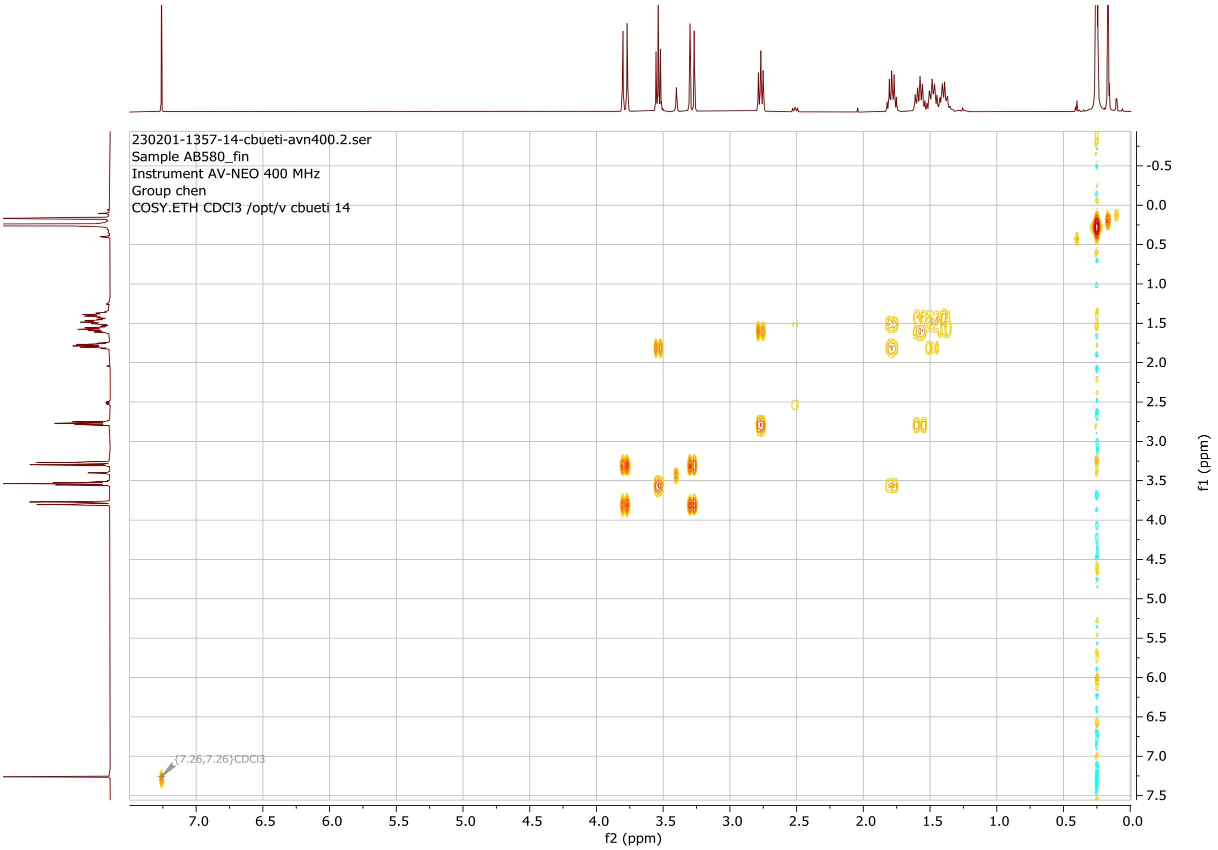


Figure S71. COSY spectrum recorded in CDCl$_3$.

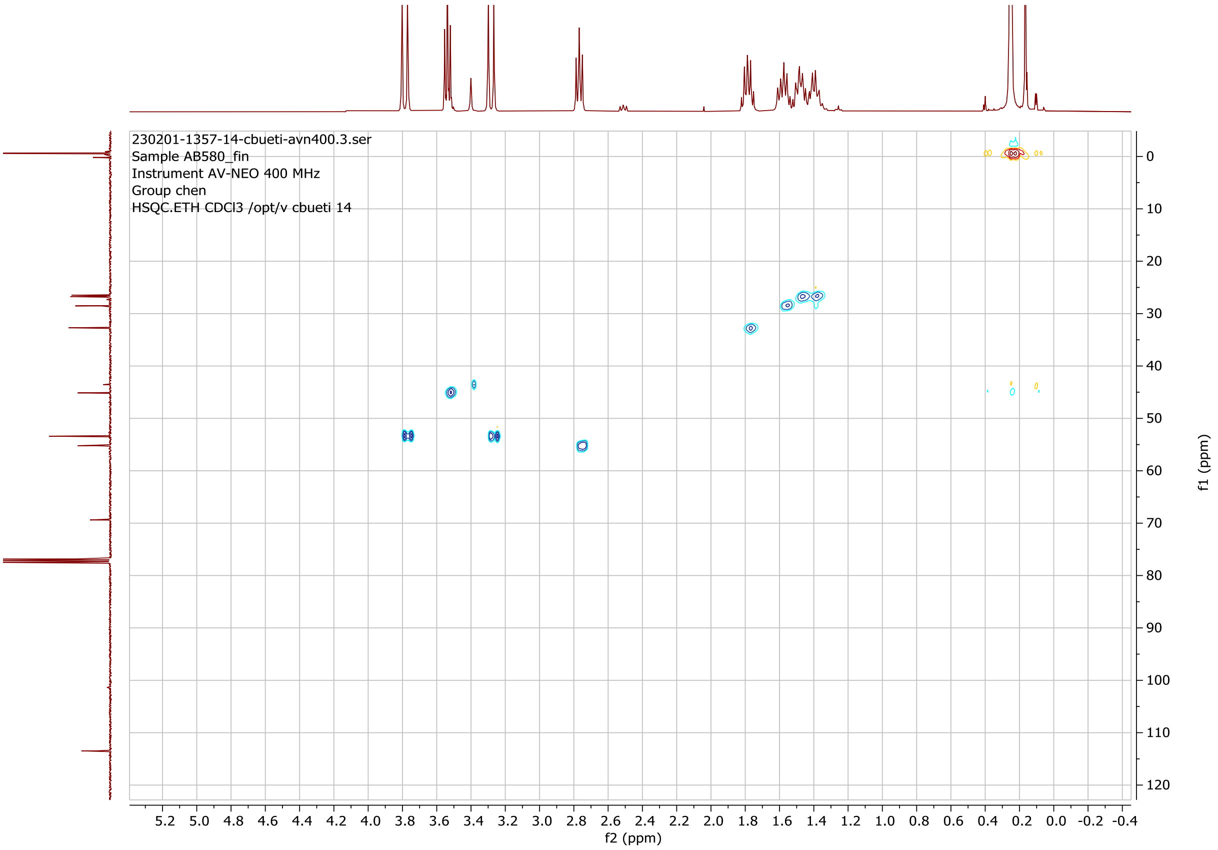


Figure S72. HSQC spectrum recorded in CDCl$_3$.

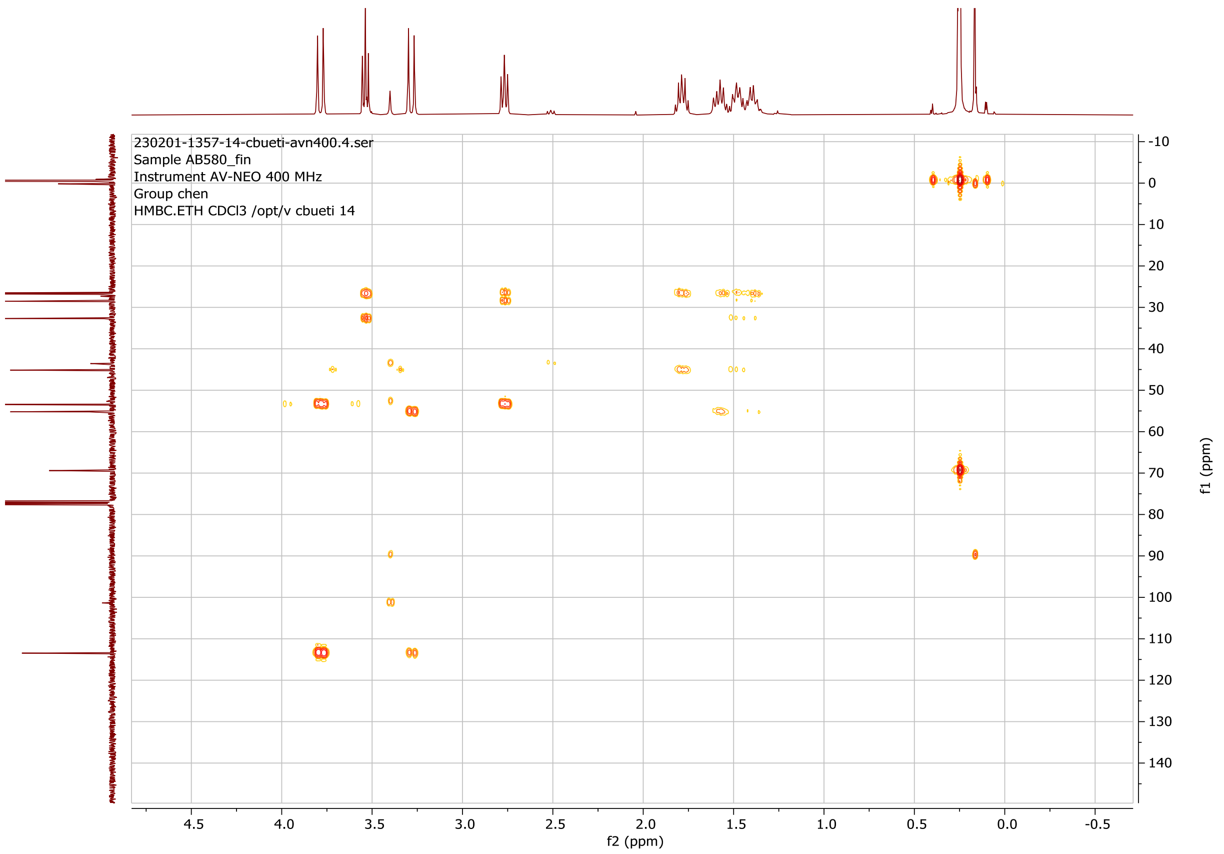


Figure S73. HMBC spectrum recorded in CDCl$_3$.

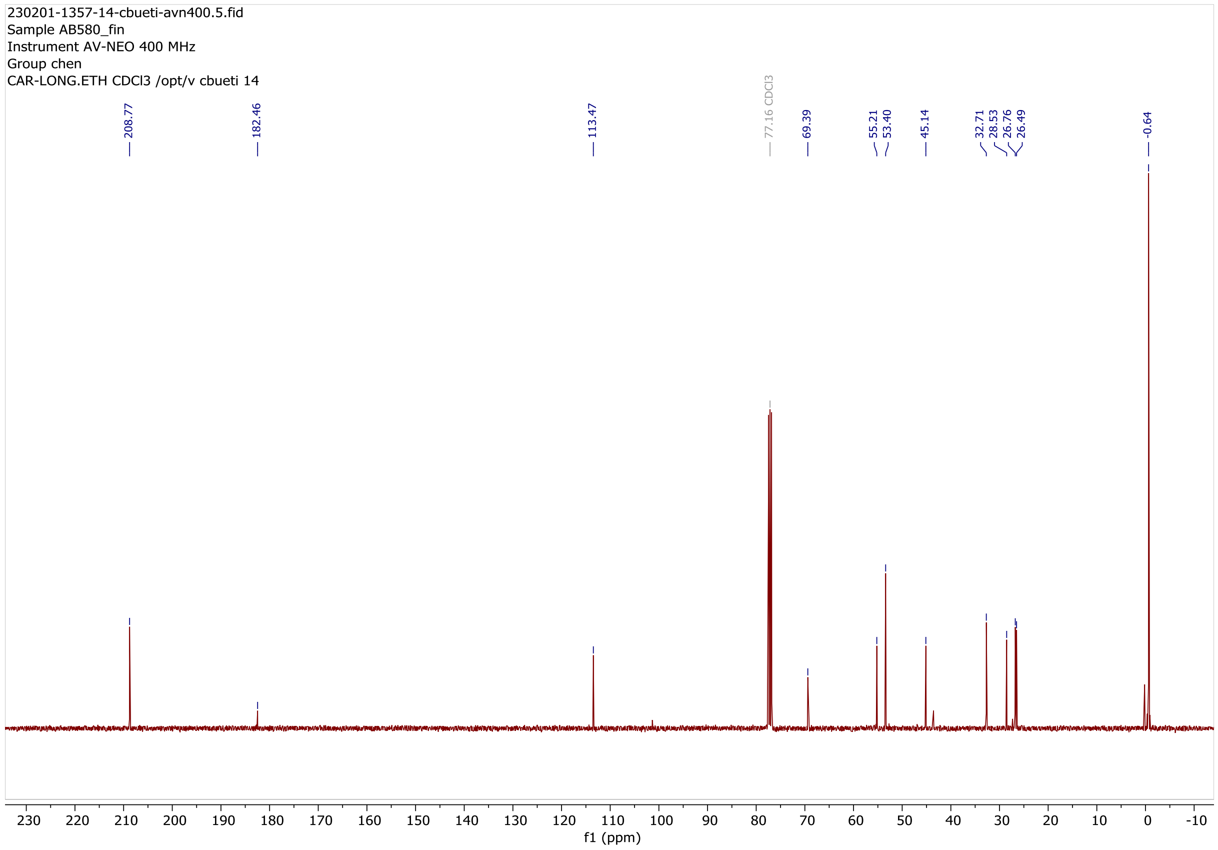


Figure S74. ^{13}C NMR spectrum recorded in CDCl$_3$.

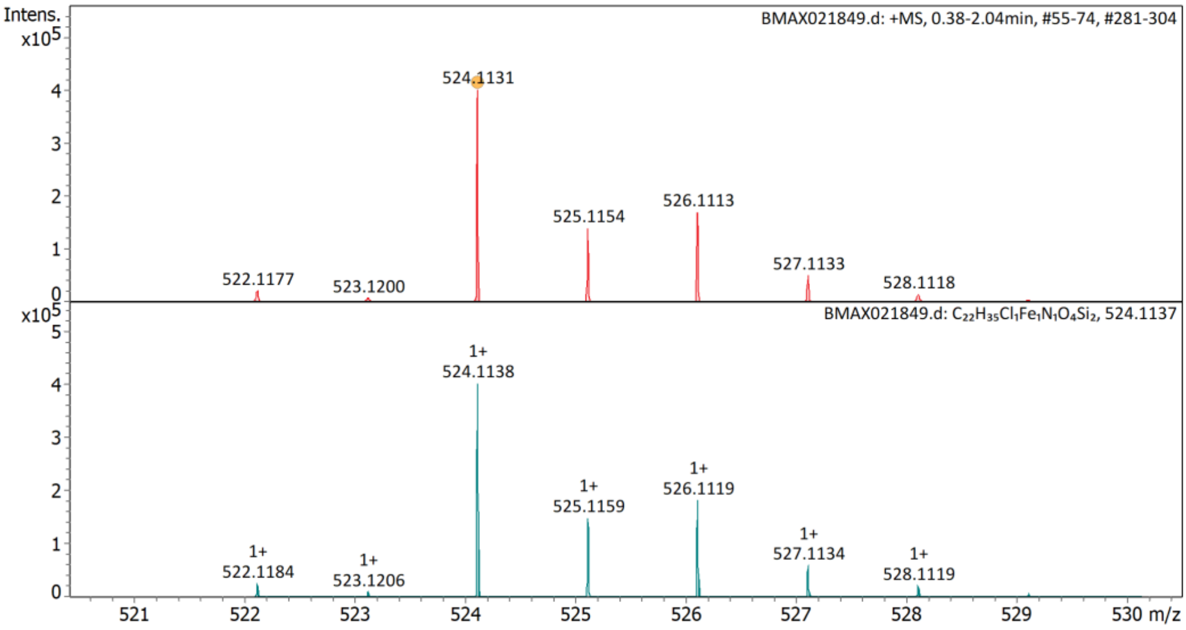
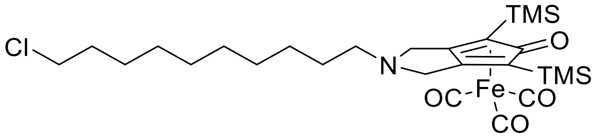


Figure S75. HRMS spectrum.

1.14) $Fe^{TMS}(CO)_3$-$(CH_2)_{10}$-Cl



A dried and argon flushed 2-necked round bottom flask equipped with a stir bar and a reflux condenser was charged with 424 mg *N*-(10-chlorodecyl)-*N*-bis(3-trimethylsilyl)prop-2-yn-1-yl)amine (1.03 mmol, equiv.), 375 mg $Fe_2(CO)_9$ (1.03 mg, 1 equiv.) and 10 ml degassed toluene. The mixture was refluxed overnight. The next day, the mixture was allowed to cool to room temperature. The mixture was directly loaded onto a silica packed column and eluted with toluene until a straw orange band corresponding to $Fe(CO)_5$ had fully eluted. The $Fe(CO)_5$ dissolved in toluene was quenched with NaOCl prior to disposal. The eluent was changed to 10:1 hexane/EtOAc and purification by column chromatography was continued. The relevant yellow fractions were combined and concentrated under reduced pressure. Drying *in vacuo* afforded the product as an orange, viscous oil (485 mg, 81%).

TLC (SiO_2, 10:1 hexane/EtOAc): $r_f = 0.4$.

^1H NMR (δ, 400 MHz, $CDCl_3$): 3.79 (d, *J* = 12.5 Hz, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 3.28 (d, *J* = 12.5 Hz, 2H), 2.80 – 1.69 (m, 2H), 1.82 – 1.71 (m, 2H), 1.59 – 1.50 (m , 2H), 1.47 – 1.38 (m, 2H), 1.37 – 1.26 (m, 10H), 0.25 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 208.8, 182.5, 113.5, 69.3, 55.5, 53.4, 45.3, 32.8, 29.6, 29.52, 29.50, 29.0, 28.7, 27.2, 27.0, -0.6.

LRMS (m/z): $[M+H]^+$ calc. for $C_{26}H_{43}ClFeNO_4Si_2$: 580.18. Found: 580.11.

ESI-MS CID (m/z): 580 $[M+H]^+$, 552 $[M+H-CO]^+$, 496 $[M+H-3CO]^+$.

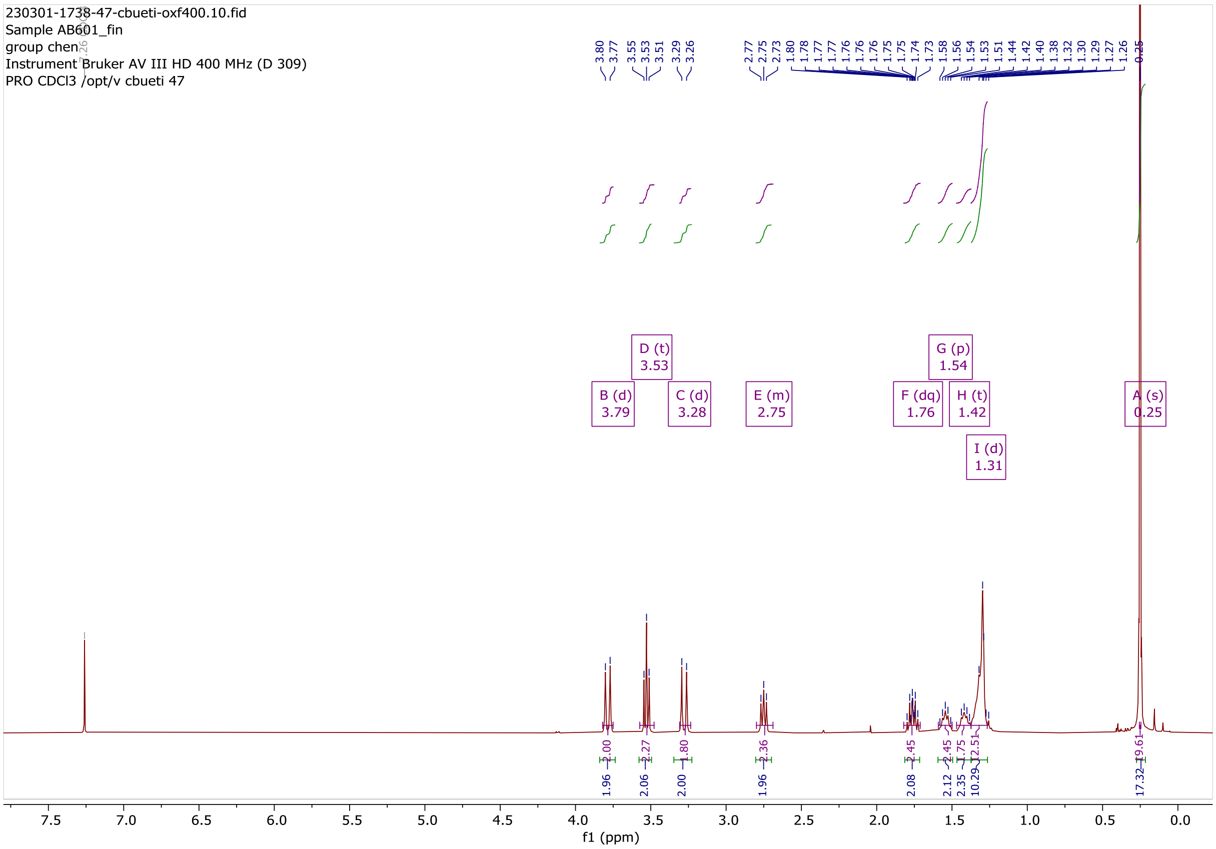


Figure S76. ^1H NMR spectrum recorded in $CDCl_3$.

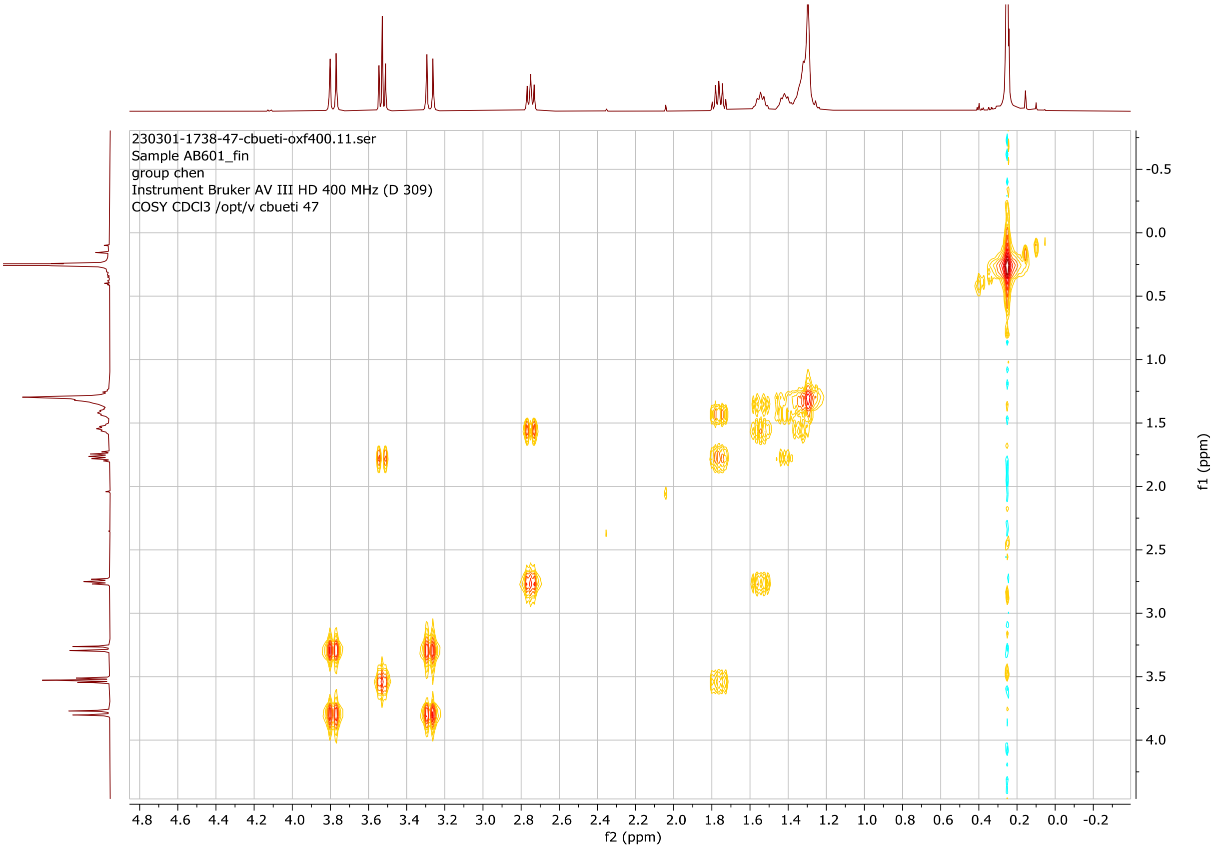


Figure S77. COSY spectrum recorded in $CDCl_3$.

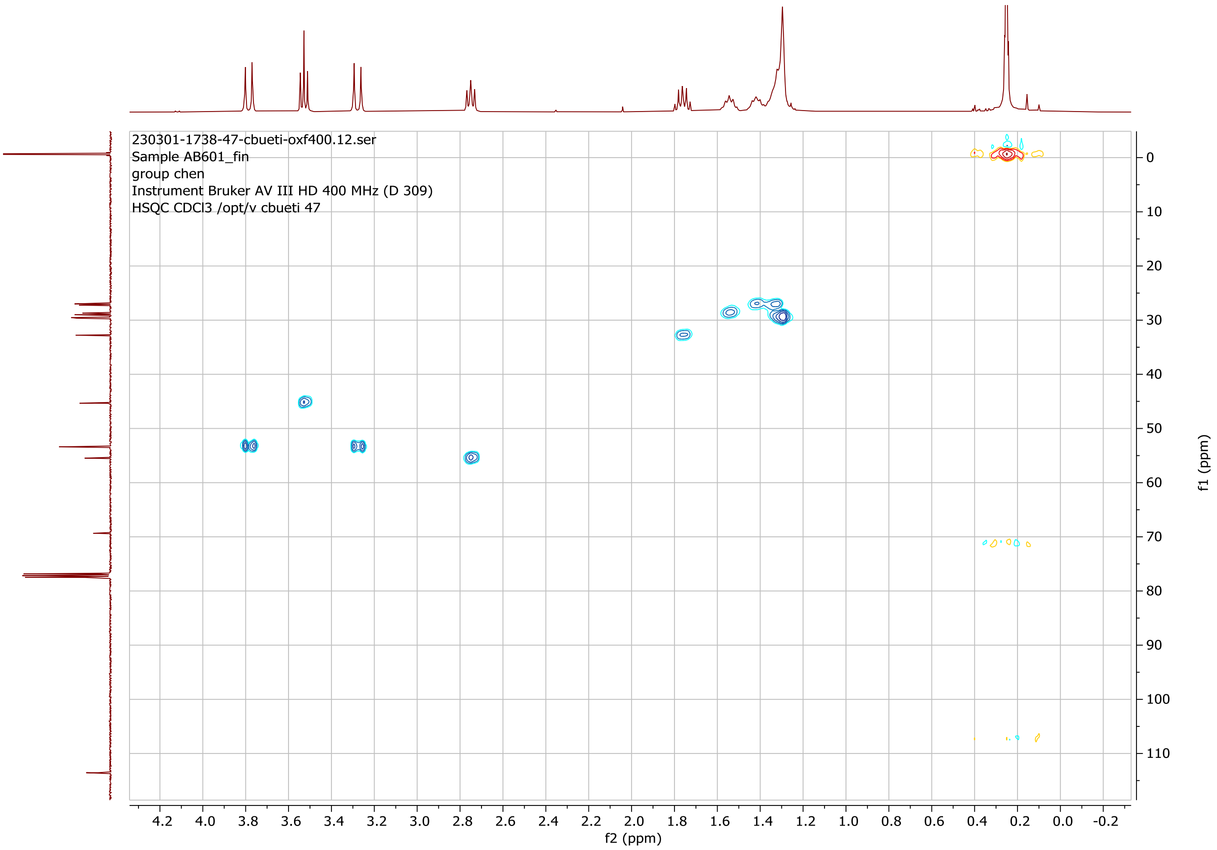


Figure S78. HSQC spectrum recorded in CDCl$_3$.

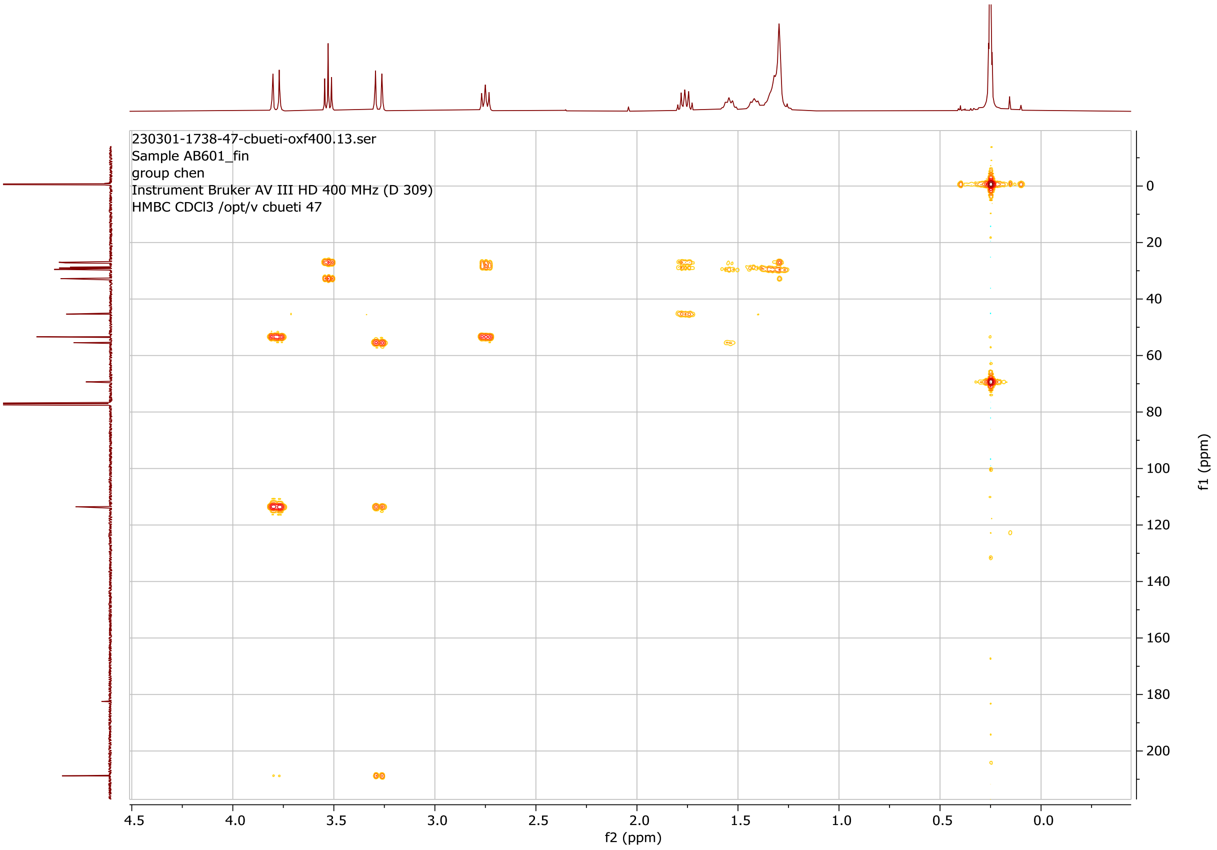


Figure S79. HMBC spectrum recorded in CDCl$_3$.

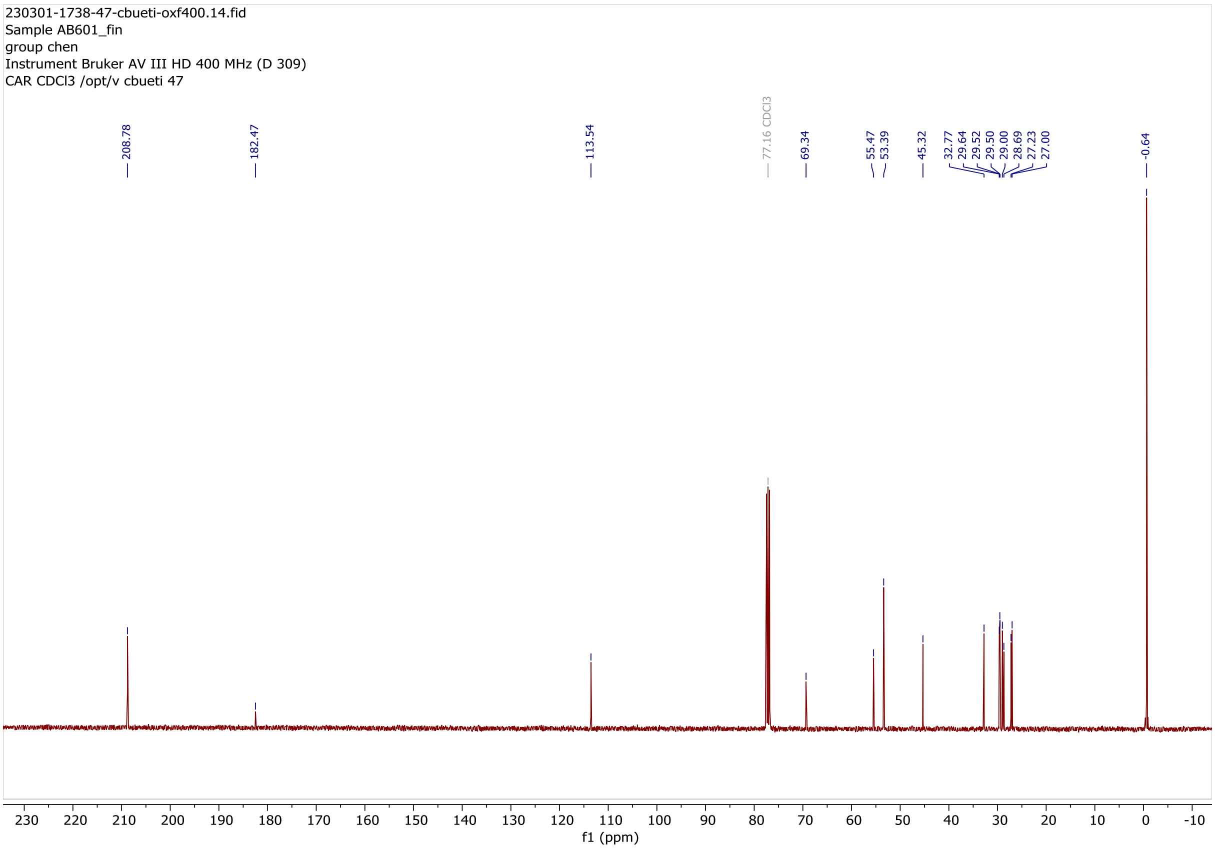


Figure S80. ^{13}C NMR spectrum recorded in $CDCl_3$.

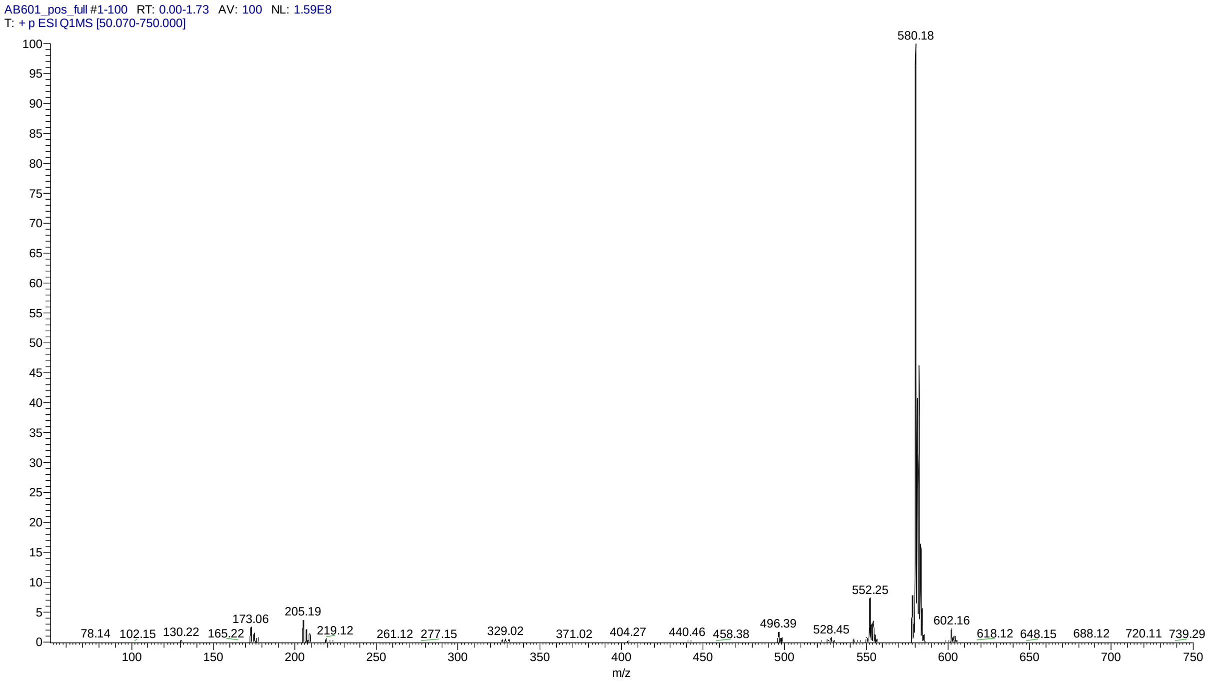


Figure S81. LRMS full spectrum. Sprayed from MeOH.

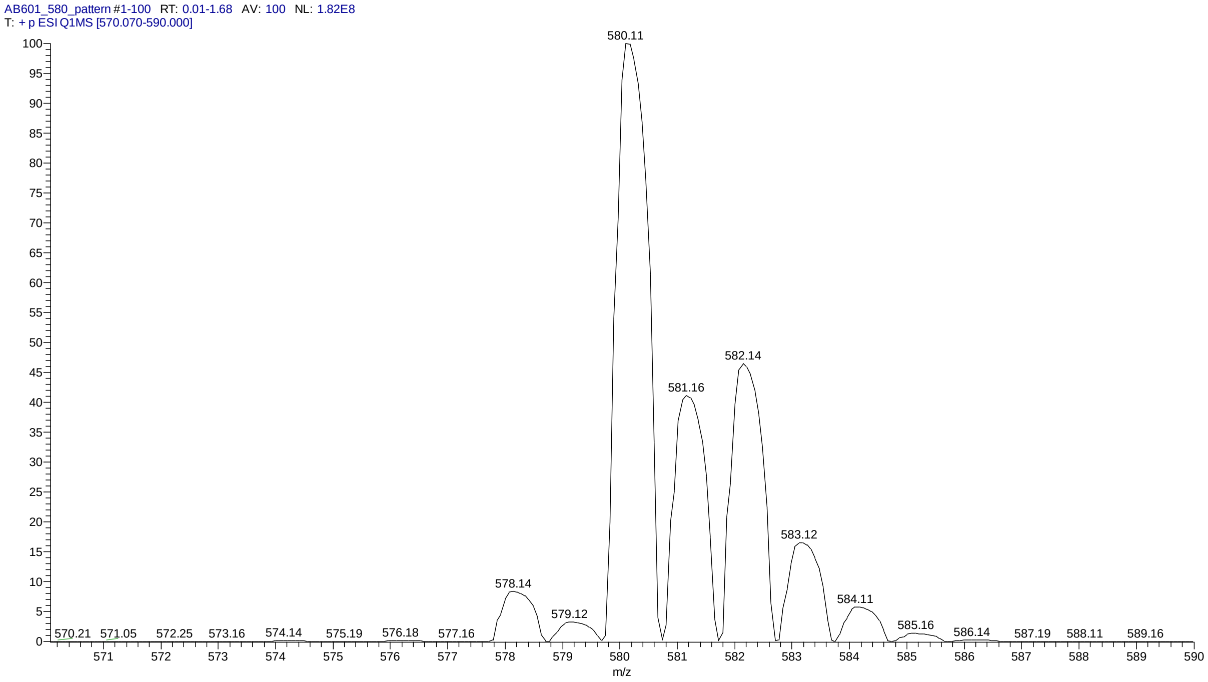


Figure S82. LRMS. Sprayed from MeOH.

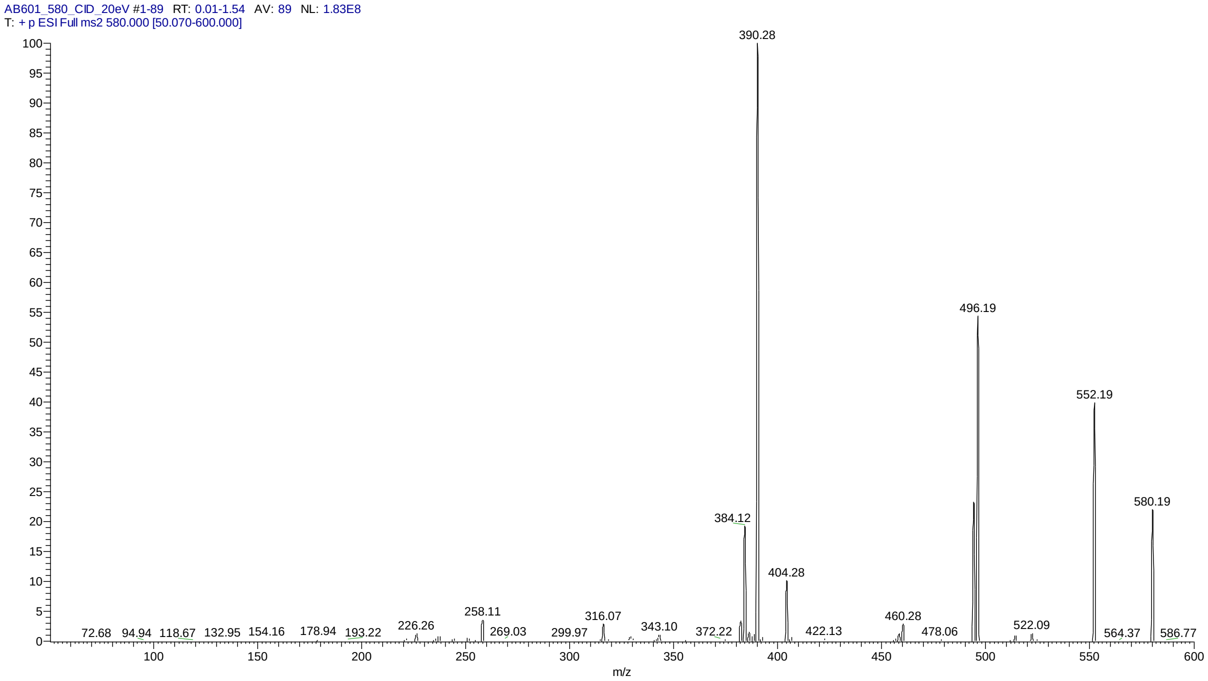
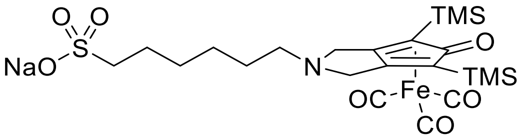


Figure S83. CID spectrum at 20 eV collision energy. Sprayed from MeOH.

1.15) [Fe^{TMS}(CO)$_3$-(CH$_2$)$_6$-SO$_3$]Na



A 100 ml round bottom flask equipped with a stir bar was charged with 1.12 g **Fe^{TMS}(CO)$_3$-(CH$_2$)$_6$-Cl** (2.11 mmol, 1 equiv.) and 2.66 g Na_2SO_3 (21.1 mmol, 10 equiv.). 20 ml 1:1 H_2O/EtOH was added to the solids. The mixture was sparged with N_2 for 30 min. The mixture was heated to 75 °C overnight. The next day, the mixture was allowed to cool to room temperature and then passed through a pad of silica eluting with EtOH. The orange solution was concentrated under reduced pressure. The crude was purified by column chromatography (SiO_2, 9:1 DCM/MeOH). The relevant yellow fractions were combined and concentrated under reduced pressure. The compound was isolated as a bright yellow powder after drying *in vacuo* (163 mg, 13 %). The starting material **$Fe^{TMS}(CO)_3$-$(CH_2)_6$-Cl** could be recovered (0.78 g, 70 %).

TLC (SiO_2, 9:1 DCM/MeOH): r_f = 0.1.

^{1}H NMR (δ, 500 MHz, MeOH-d$_4$): 3.83 (d, *J* = 13.5 Hz, 2H), 3.42 (d, *J* = 13.6 Hz, 2H), 2.90 – 2.76 (m, 4H), 1.81 (m, 2H), 1.62 (m, 2H), 1.47 (m, 4H), 0.27 (s, 18H).

^{13}C NMR (δ, 125 MHz, MeOH-d$_4$): 209.7, 183.2, 115.0, 70.6, 56.4, 54.1, 52.6, 29.6, 29.2, 27.9, 25.9, -0.7.

Anal. calc. for $C_{22}H_{34}FeNNaO_7SSi_2$ (%): C, 44.67; H, 5.79; N, 2.37. Found: C, 44.69; H, 5.92; N, 2.74.

LRMS (m/z): $[M\text{-}Na]^-$ calc. for $C_{22}H_{34}FeNO_7SSi_2$: 568.09. Found: 568.11.

ESI-MS CID (m/z): 568 $[M\text{-}Na]^-$, 512 $[M\text{-}Na\text{-}2CO]^-$, 484 $[M\text{-}Na\text{-}3CO]^-$.

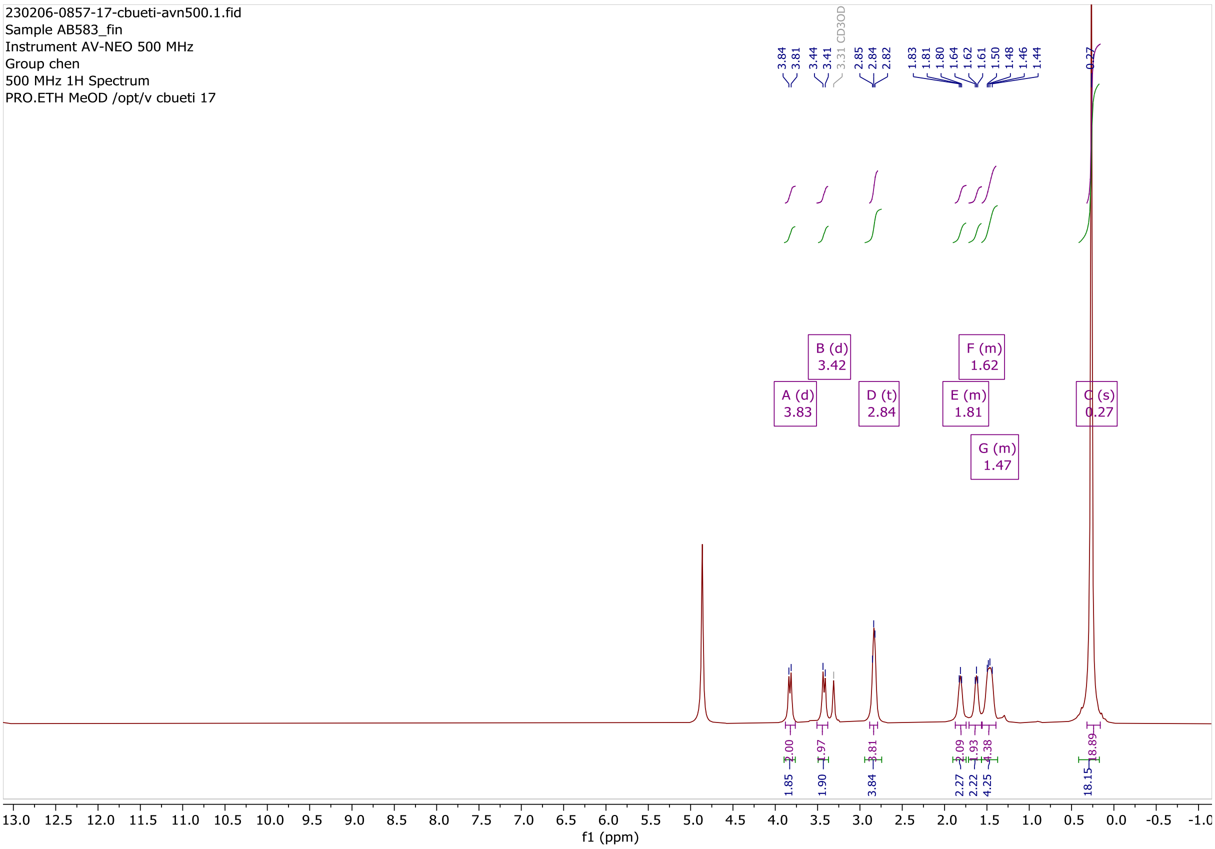


Figure S84. ^{1}H NMR spectrum recorded in MeOH-d$_4$.

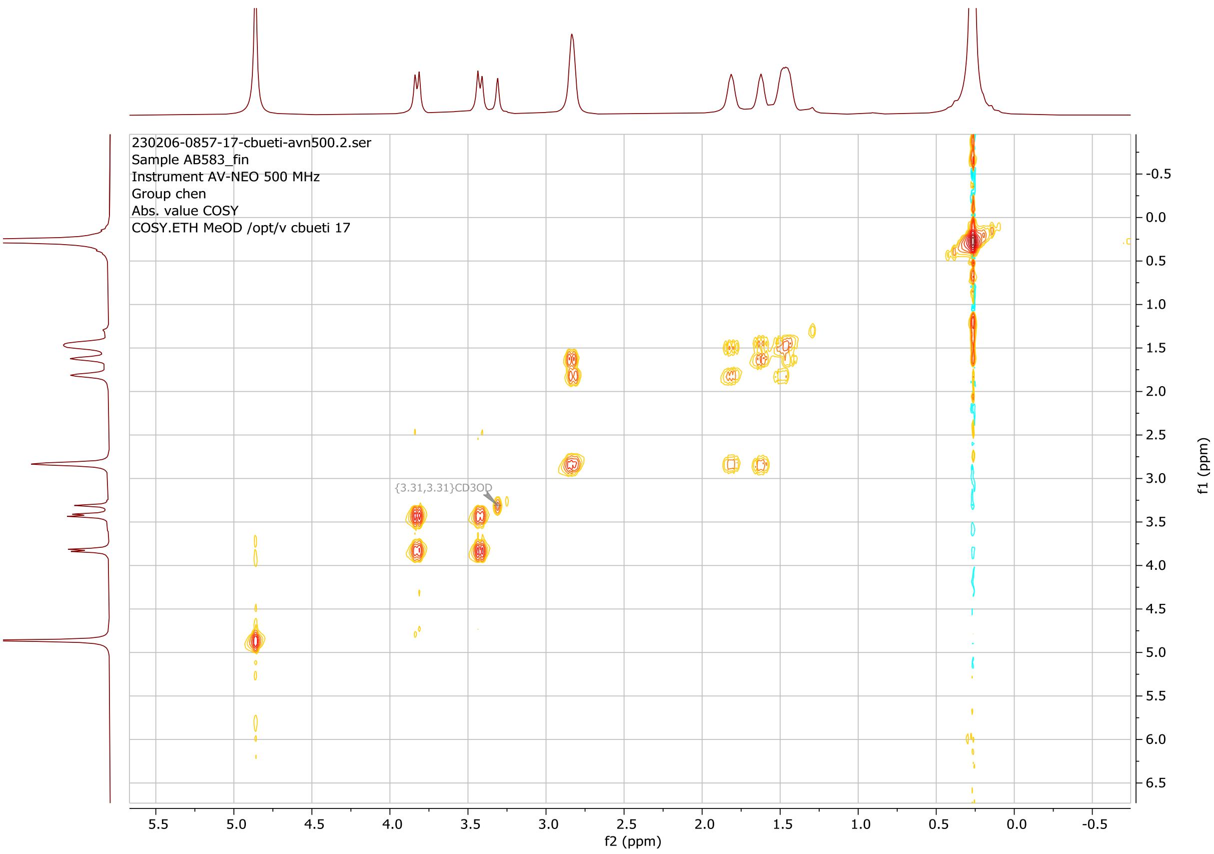


Figure S85. COSY spectrum recorded in MeOH-d_4.

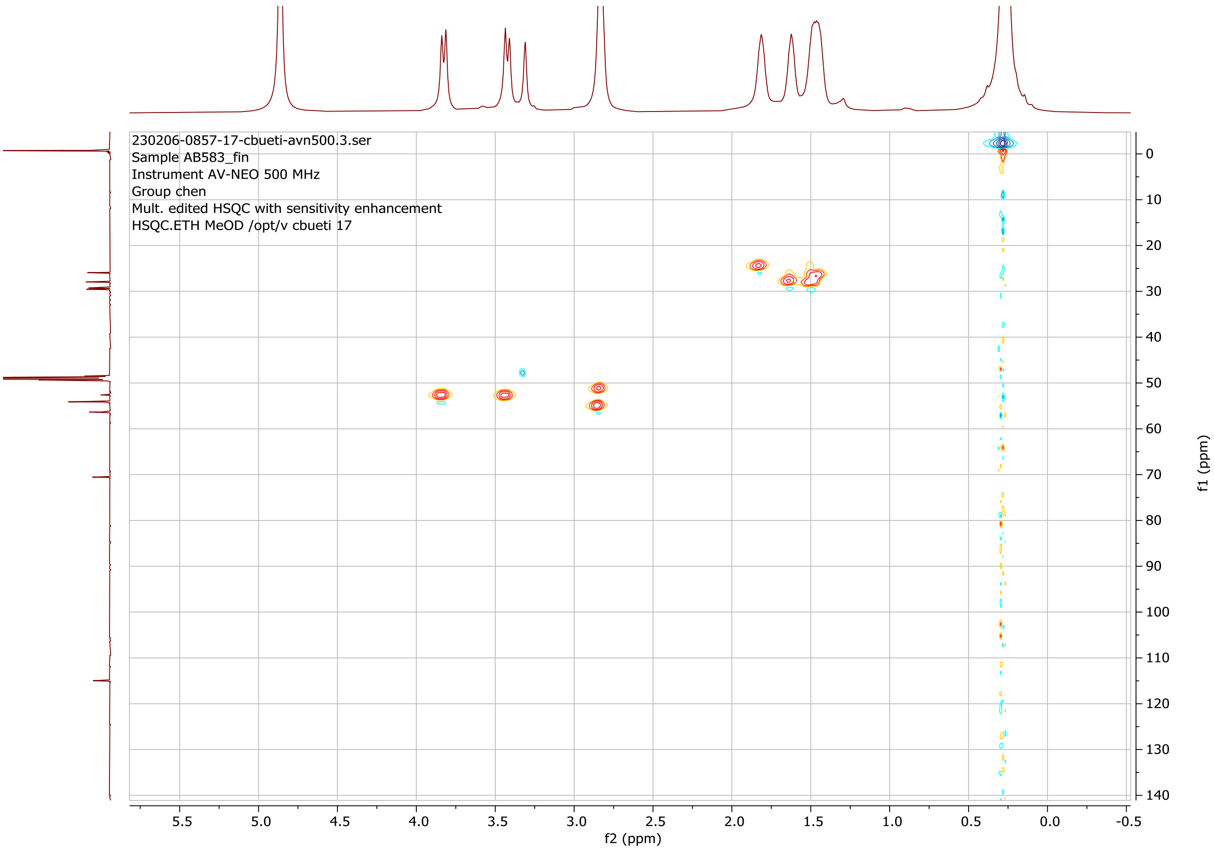


Figure S86. HSQC spectrum recorded in MeOH-d_4.

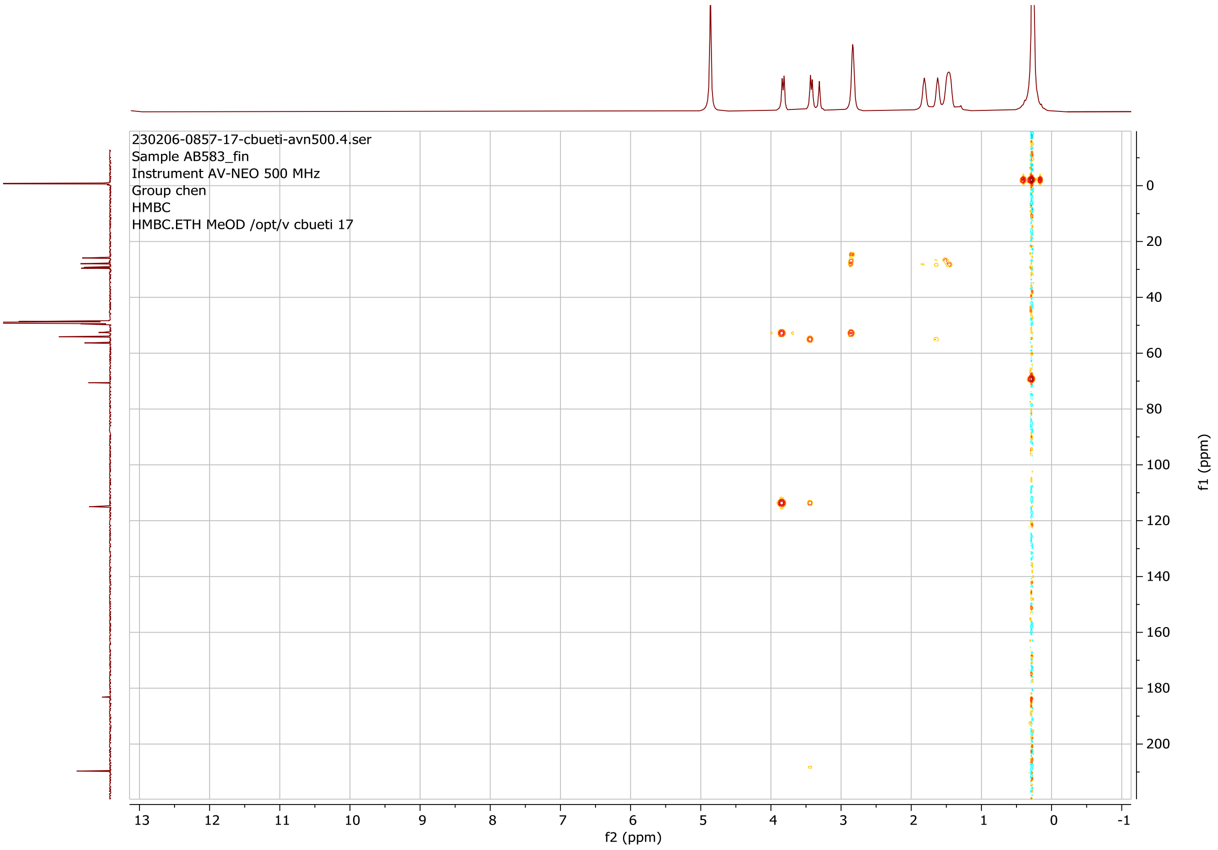


Figure S87. HMBC spectrum recorded in MeOH-d_4.

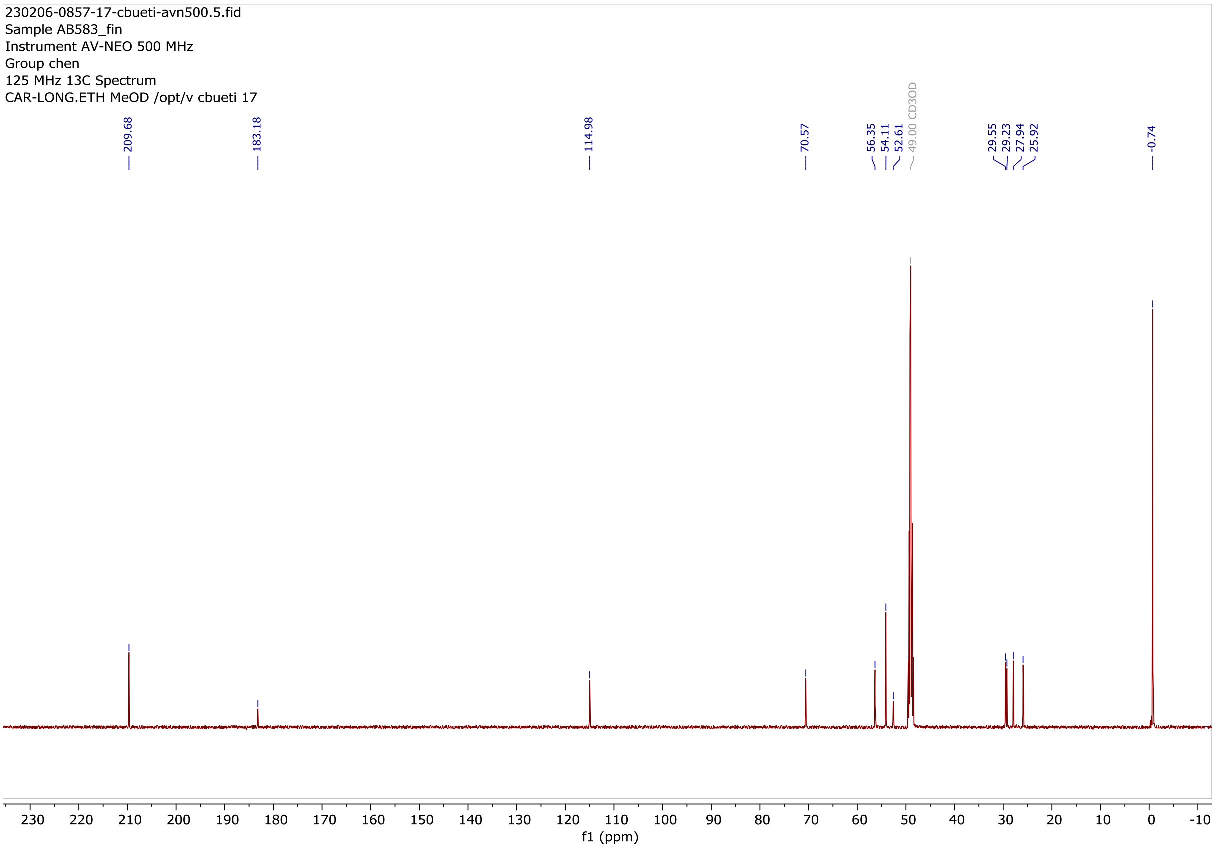


Figure S88. ^{13}C NMR spectrum recorded in MeOH-d_4.

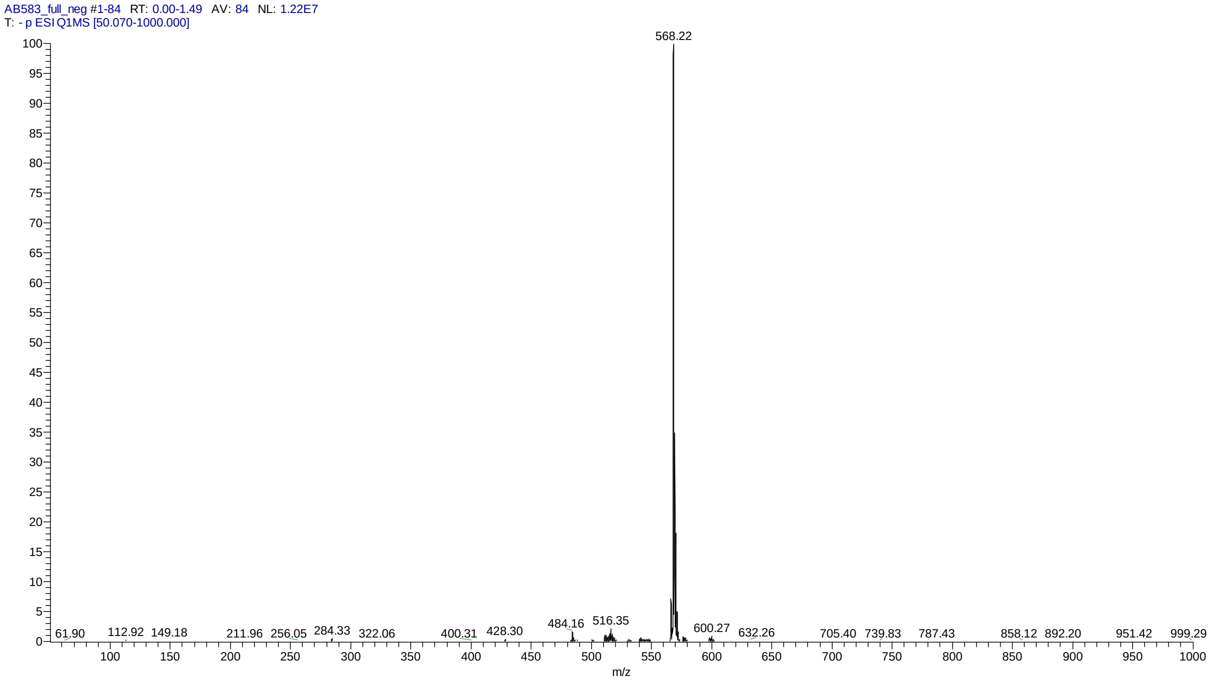


Figure S89. LRMS full spectrum. Sprayed from MeOH.

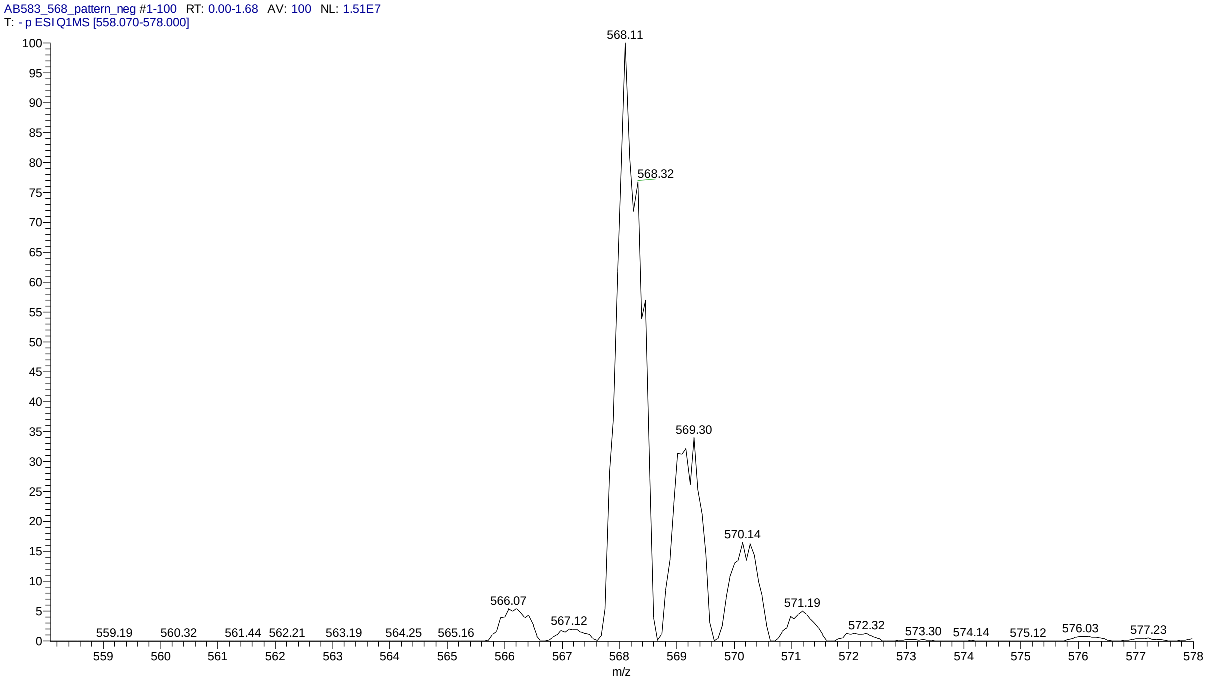


Figure S90. LRMS. Sprayed from MeOH.

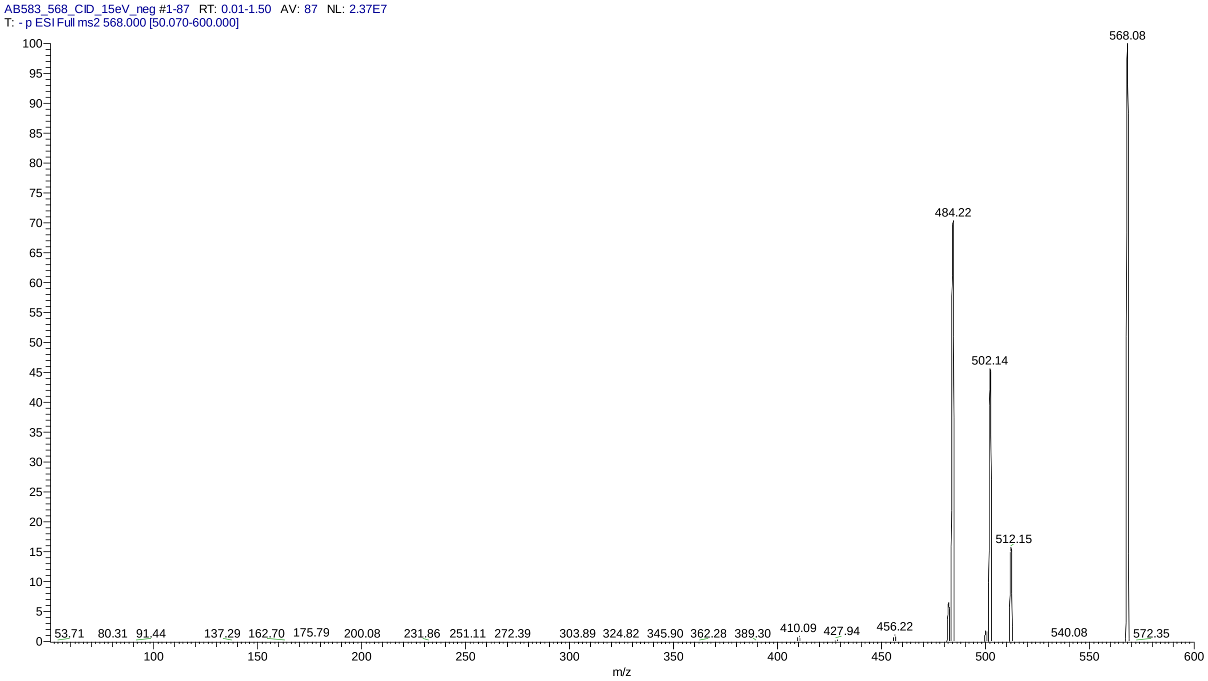
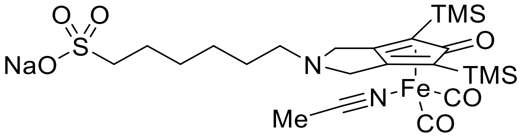


Figure S91. CID spectrum at 15 eV collision energy. Sprayed from MeOH.

1.16) $[Fe^{TMS}(MeCN)(CO)_2\text{-}(CH_2)_6\text{-}SO_3]Na$



A dried and argon-flushed 20 ml Schlenk tube equipped with a stir bar was charged with 50 mg **$[Fe^{TMS}(CO)_3\text{-}(CH_2)_6\text{-}SO_3]Na$** (0.09 mmol, 1 equiv.) and 9.5 mg Me_3NO (0.13 mmol, 1.5 equiv.). While stirring 1 ml dry MeCN was added. The solution was protected from light with aluminium foil. After 1 h, a fine solid precipitate was observed. LC-MS analysis indicated full consumption of the starting material. Et_2O was added to the mixture and the solid collected by cannula filtration. The solid was washed three times with Et_2O. After drying *in vacuo*, the product was isolated as a yellow powder (17.8 mg, 35 %).

^1H NMR (δ, 400 MHz, MeOH-d_4): 3.58 (d, *J* = 13.2 Hz, 2H), 3.15 (d, *J* = 13.2 Hz, 2H), 2.81 (t, *J* = 7.9 Hz, 2H), 2.77 – 2.71 (m 2H), 2.33 (s, 3H), 1.86 – 1.74 (m, 2H), 1.62 – 1.52 (m, 2H), 1.51 – 1.33 (m, 4H), 0.24 (s, 18H).

^{13}C NMR (δ, 100 MHz, MeOH-d_4): 128.4, 67.0, 55.5, 52.8, 51.2, 28.1, 26.5, 24.5, 2.2, -2.0 (*remaining quaternary carbons not observed*).

LRMS (m/z): $[M\text{-}Na]^-$ calc. for $C_{23}H_{37}FeN_2O_6SSi_2$: 581.13. Found: 581.05.

ESI-MS CID (m/z): 581 $[M\text{-}Na]^-$, 540 $[M\text{-}Na\text{-}MeCN]^-$, 512 $[M\text{-}Na\text{-}MeCN\text{-}CO]^-$, 484 $[M\text{-}Na\text{-}MeCN\text{-}2CO]^-$.

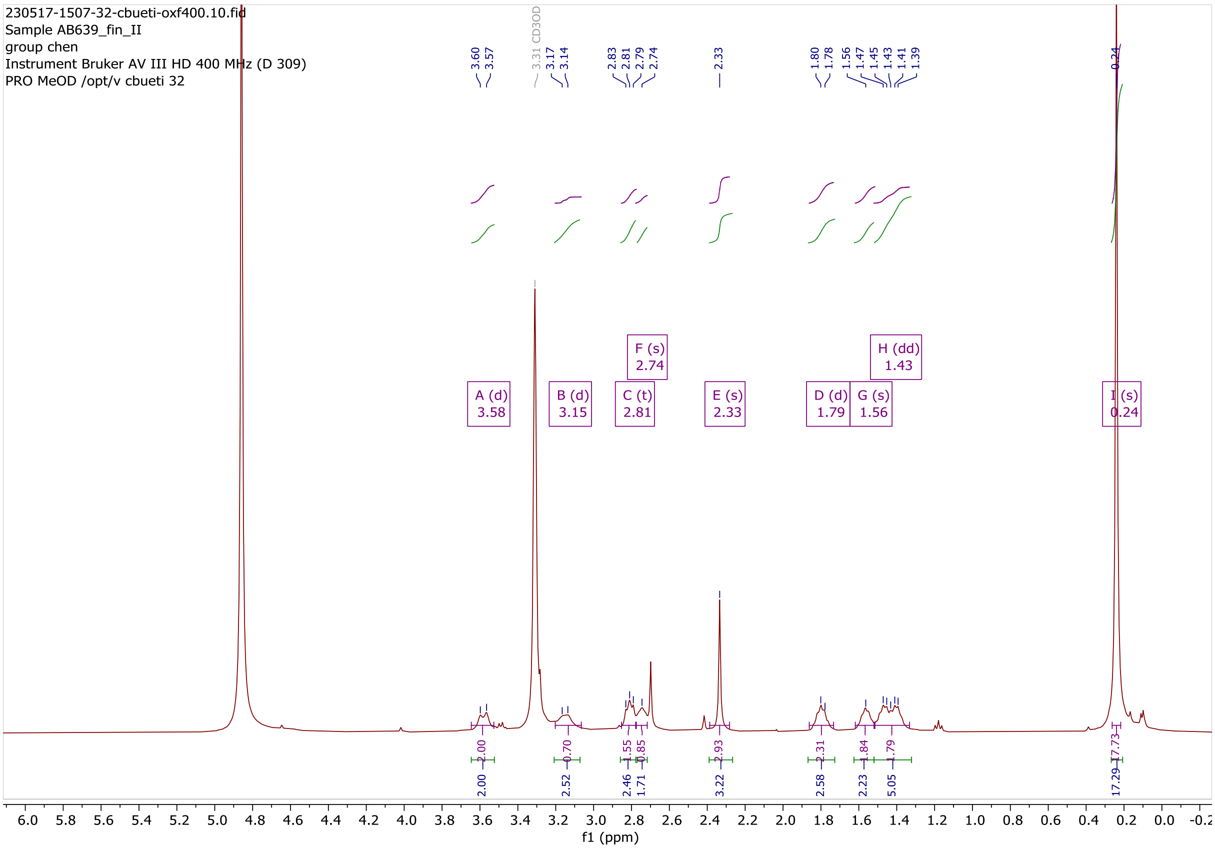


Figure S92. ^1H NMR spectrum recorded in MeOH-d$_4$.

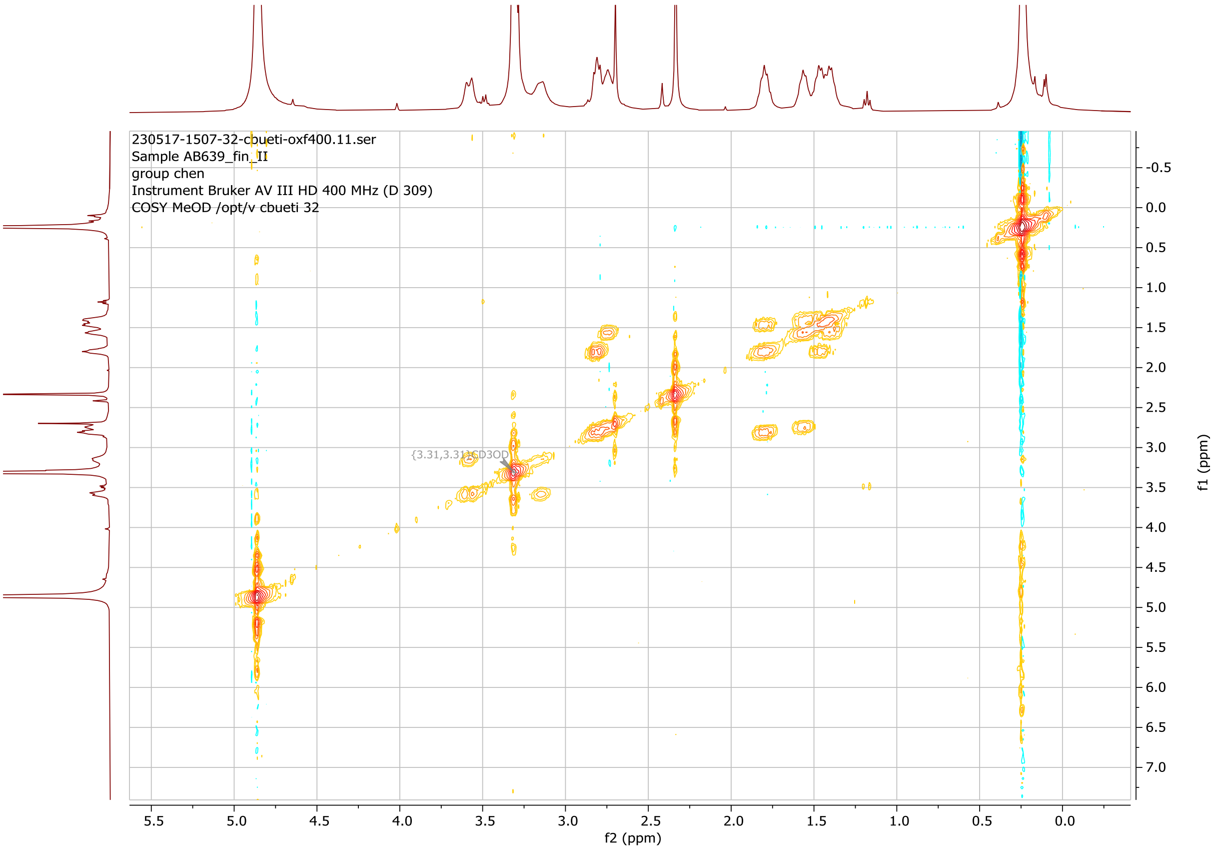


Figure S93. COSY spectrum recorded in MeOH-d$_4$.

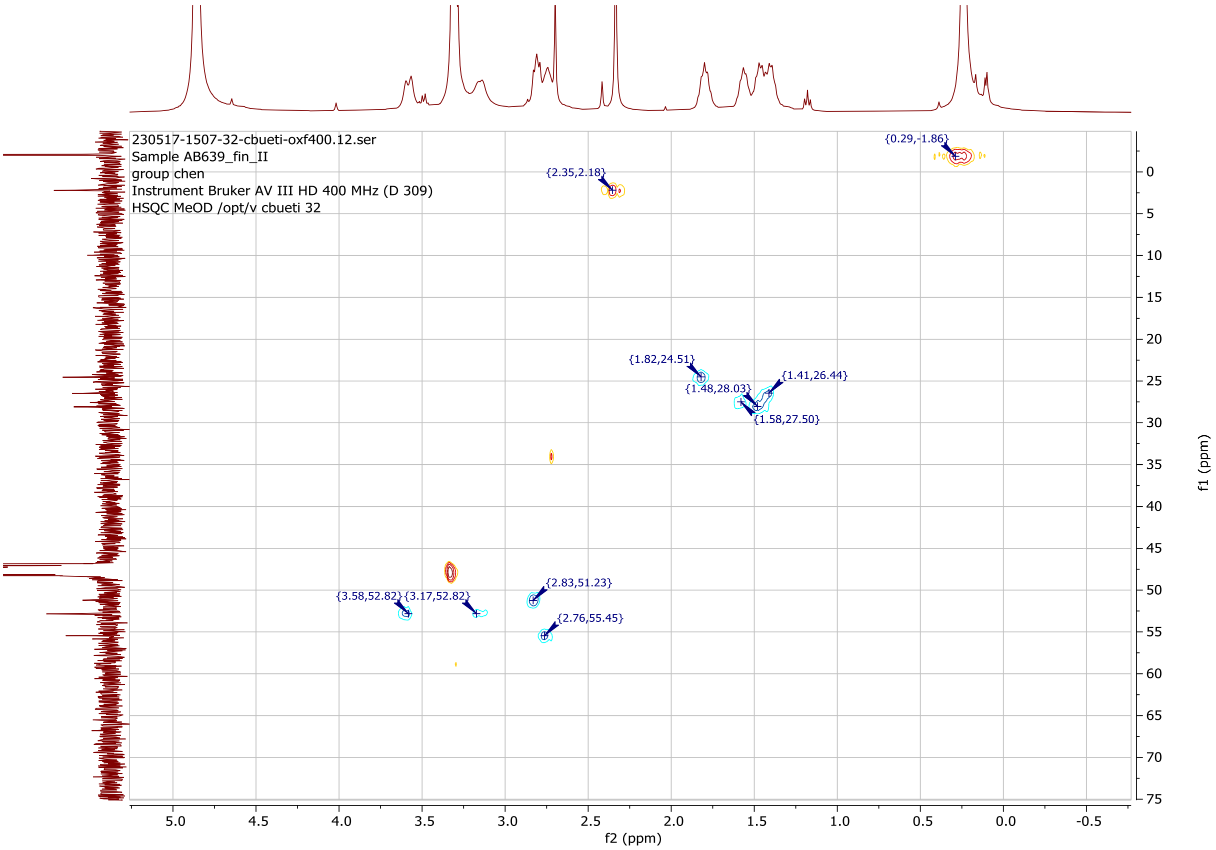


Figure S94. HSQC spectrum recorded in MeOH-d_4.

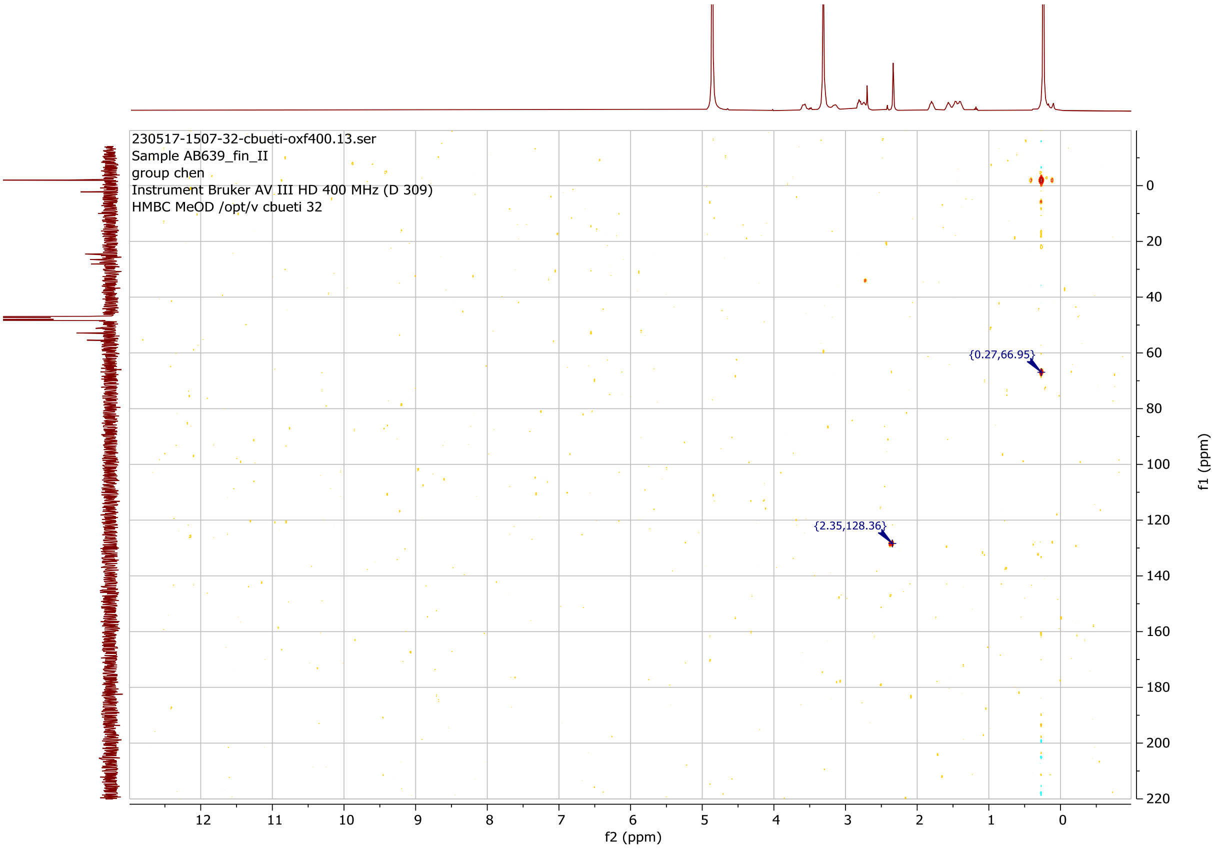


Figure S95. HMBC spectrum recorded in MeOH-d_4.

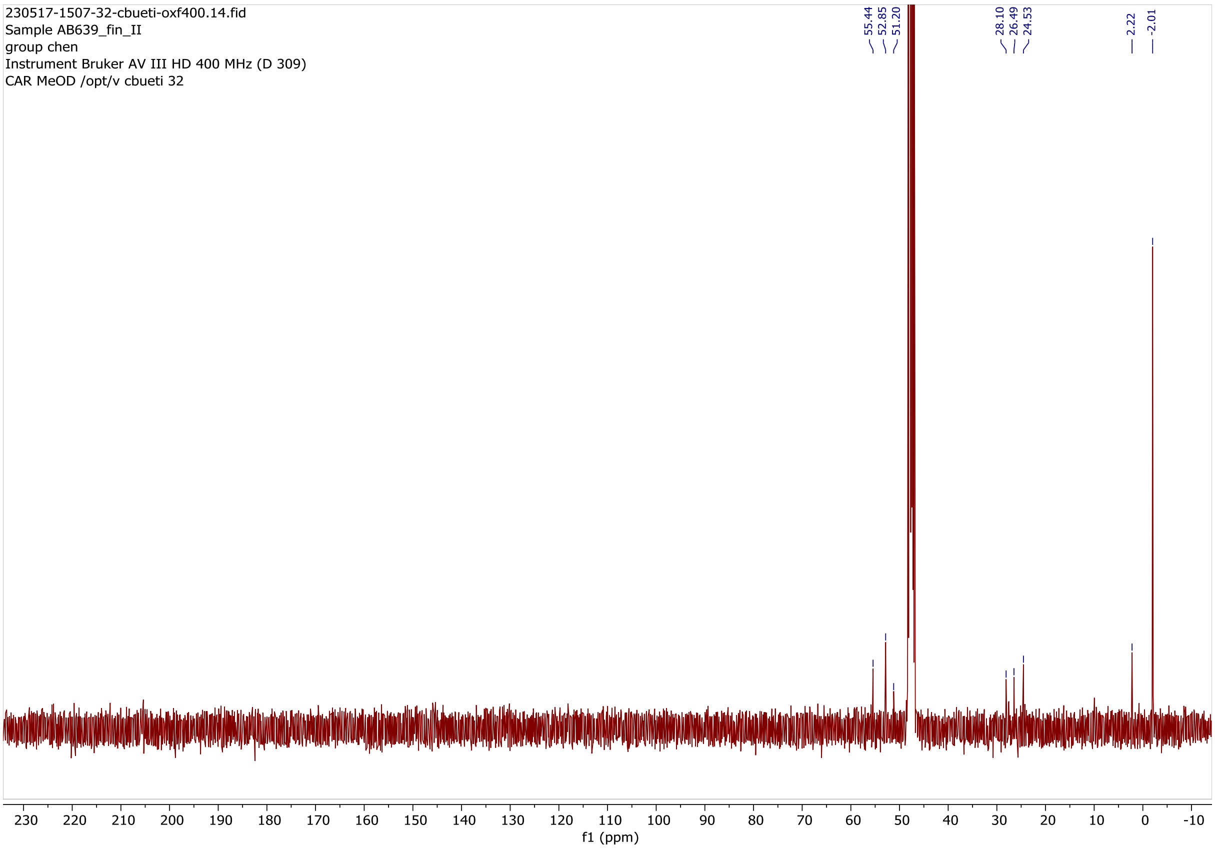


Figure S96. ^{13}C NMR spectrum recorded in MeOH-d_4.

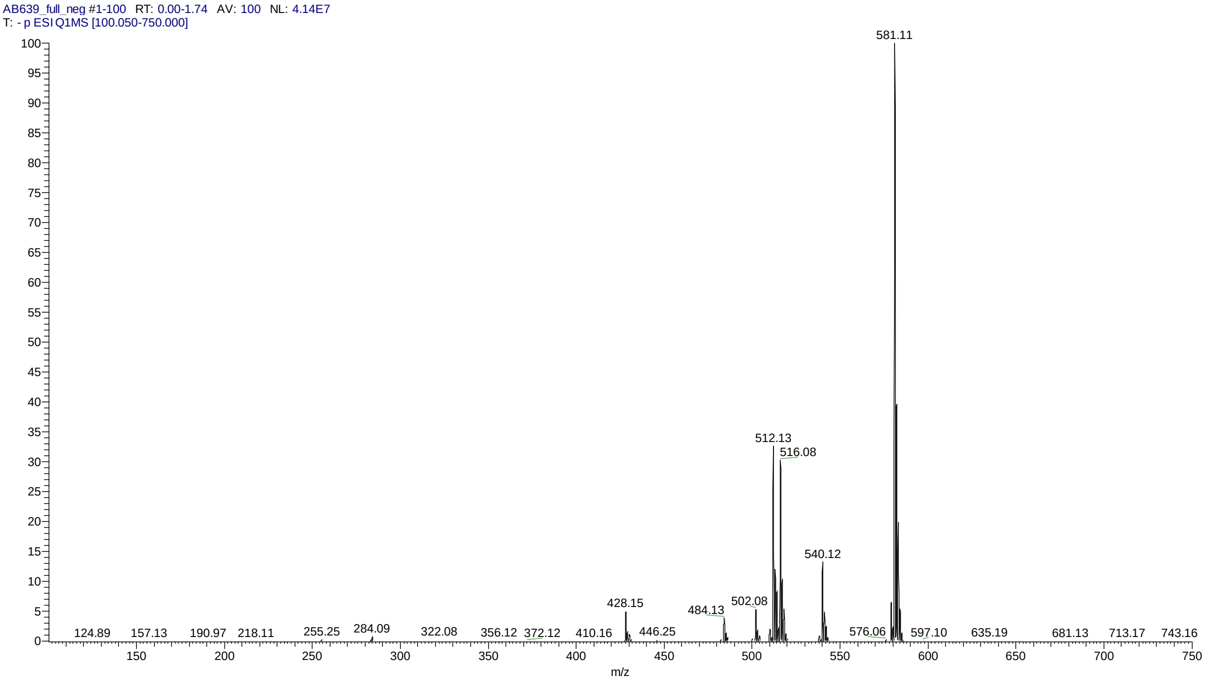


Figure S97. LRMS full spectrum. Sprayed from MeOH.

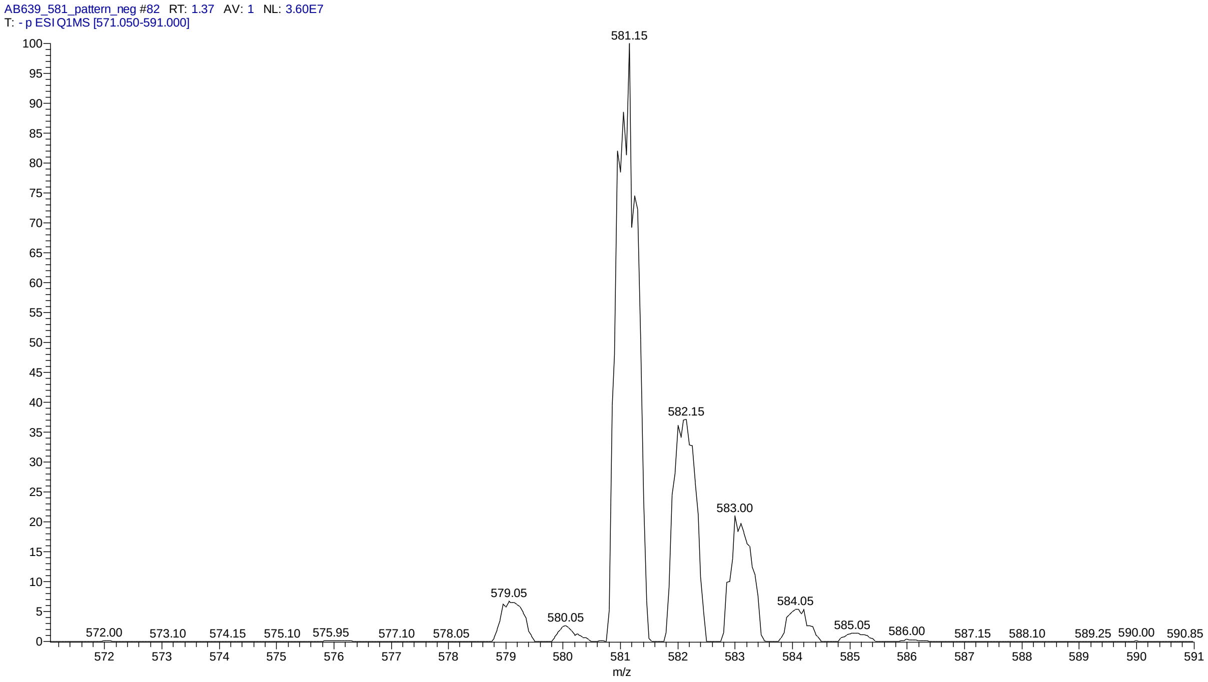


Figure S98. LRMS. Sprayed from MeOH.

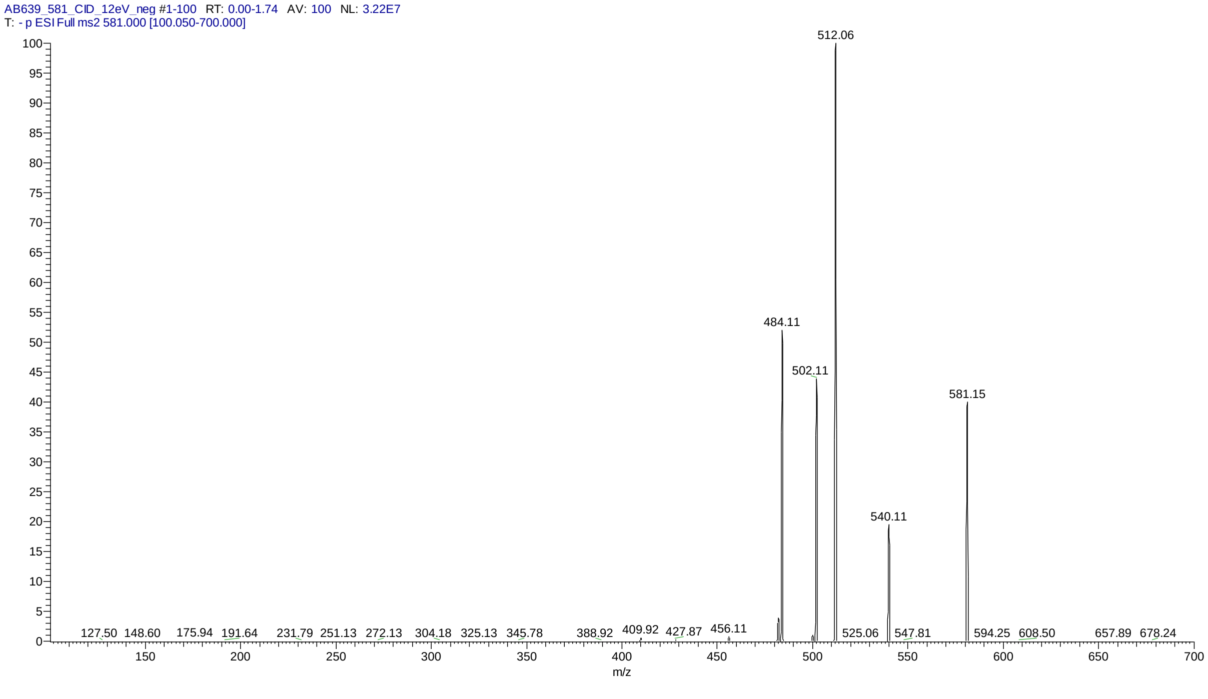
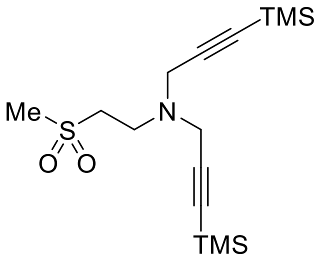


Figure S99. CID spectrum at 12 eV collision energy. Sprayed from MeOH.

1.17) *N*-(2-(methylsulfonyl)ethyl)-*N*-bis(3-trimethylsilyl)prop-2-yn-1-yl)amine



N-(2-(methylsulfonyl)ethyl)-*N*-bis(3-trimethylsilyl)prop-2-yn-1-yl)amine: A 20 ml Schlenk tube equipped with a stir bar was charged with 250 mg 2-aminoethyl methyl sulfone hydrochloride (1.57 mmol, 1 equiv.), 15.8 mg CuCl (0.16 mmol, 0.1 equiv.) and 132 mg $NaHCO_3$ (1.57 mmol, 1 equiv.). The flask was flushed with N_2. The flask was capped with a septum. 0.55 ml trimethylsilylacetylene (383 mg, 2.5 equiv.) and 0.29 ml 39% HCHO (300 mg, 2.5 equiv.) were added to the solids. The mixture was stirred vigorously overnight. Bubble formation was observed. The next day, the mixture was diluted with EtOAc and passed through a pad of Celite. The solution was concentrated under reduced pressure. The residue was passed through a pad of silica eluting with 1:1 EtOAc/hexane. The volatiles were removed under reduced pressure. The compound was isolated as a colorless oil that solidifies upon standing (410 mg, 76 %).

TLC (SiO_2, 1:1 EtOAc/hexane, $KMnO_4$ stain): r_f = 0.8.

^{1}H NMR (δ, 400 MHz, $CDCl_3$): 3.44 (s, 4H), 3.20 (t, *J* = 6.2 Hz, 2H), 3.09 (t, *J* = 6.3 Hz, 2H), 3.02 (s, 3H), 0.17 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 100.0, 90.9, 53.4, 47.2, 44.0, 42.3, -0.1.

Anal. calc. for $C_{15}H_{29}NO_2SSi_2$ (%): C, 52.43; H, 8.51; N, 4.08. Found: C, 52.31; H, 8.43; N, 4.05.

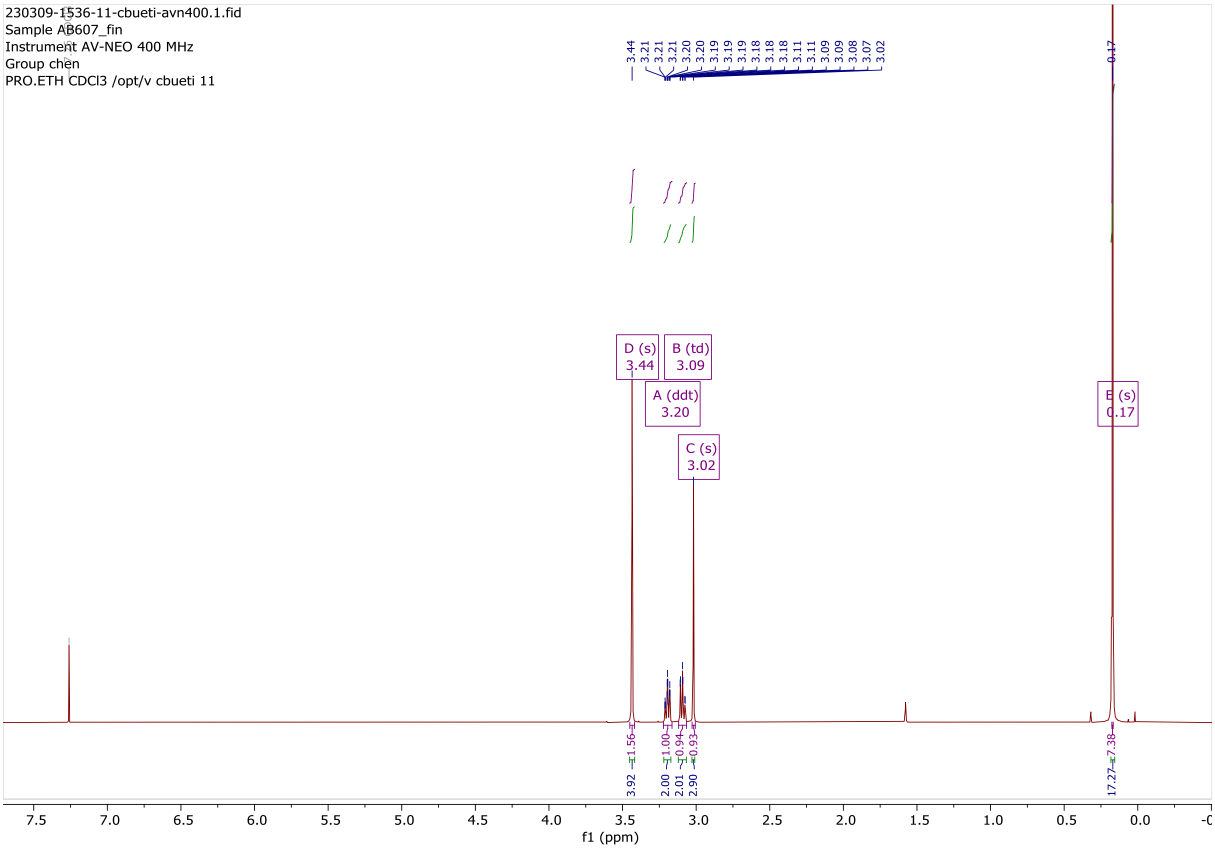


Figure S100. ^{1}H NMR spectrum recorded in $CDCl_3$.

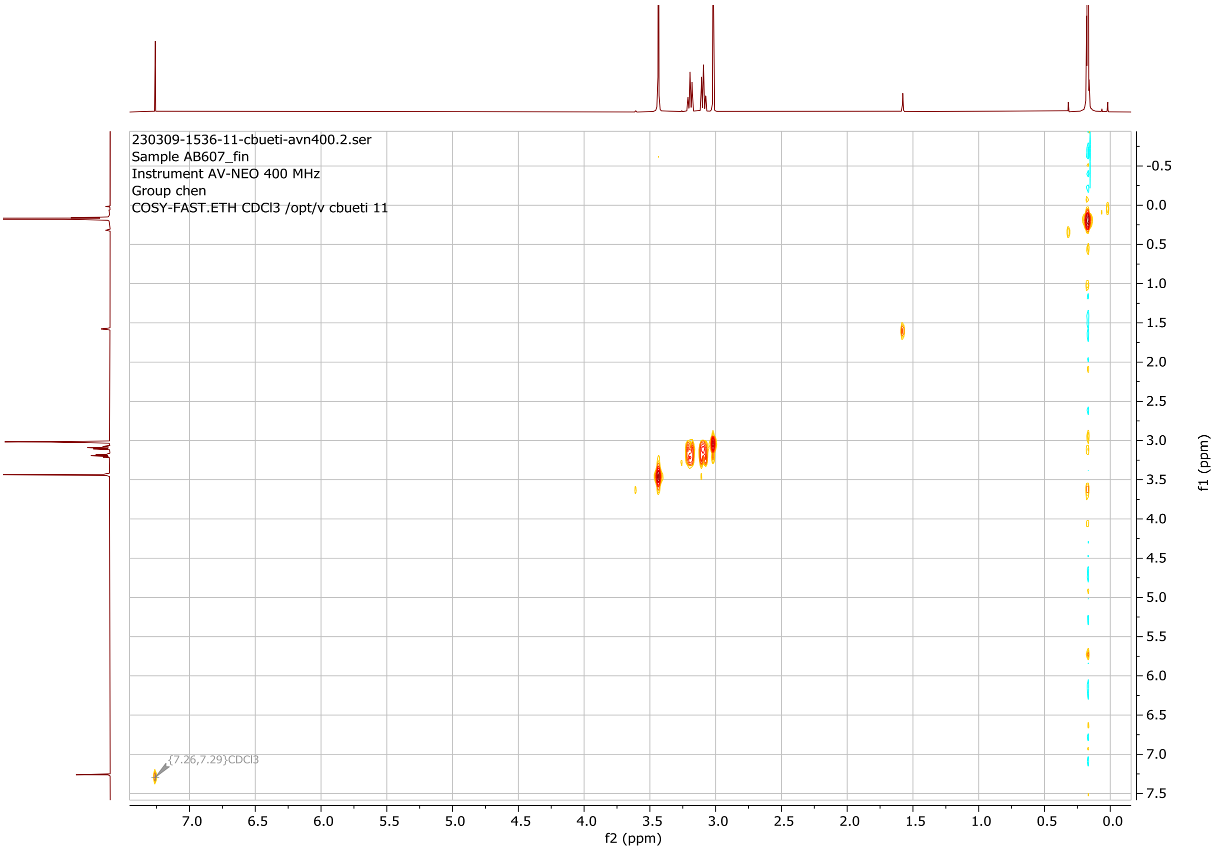


Figure S101. COSY spectrum recorded in CDCl$_3$.

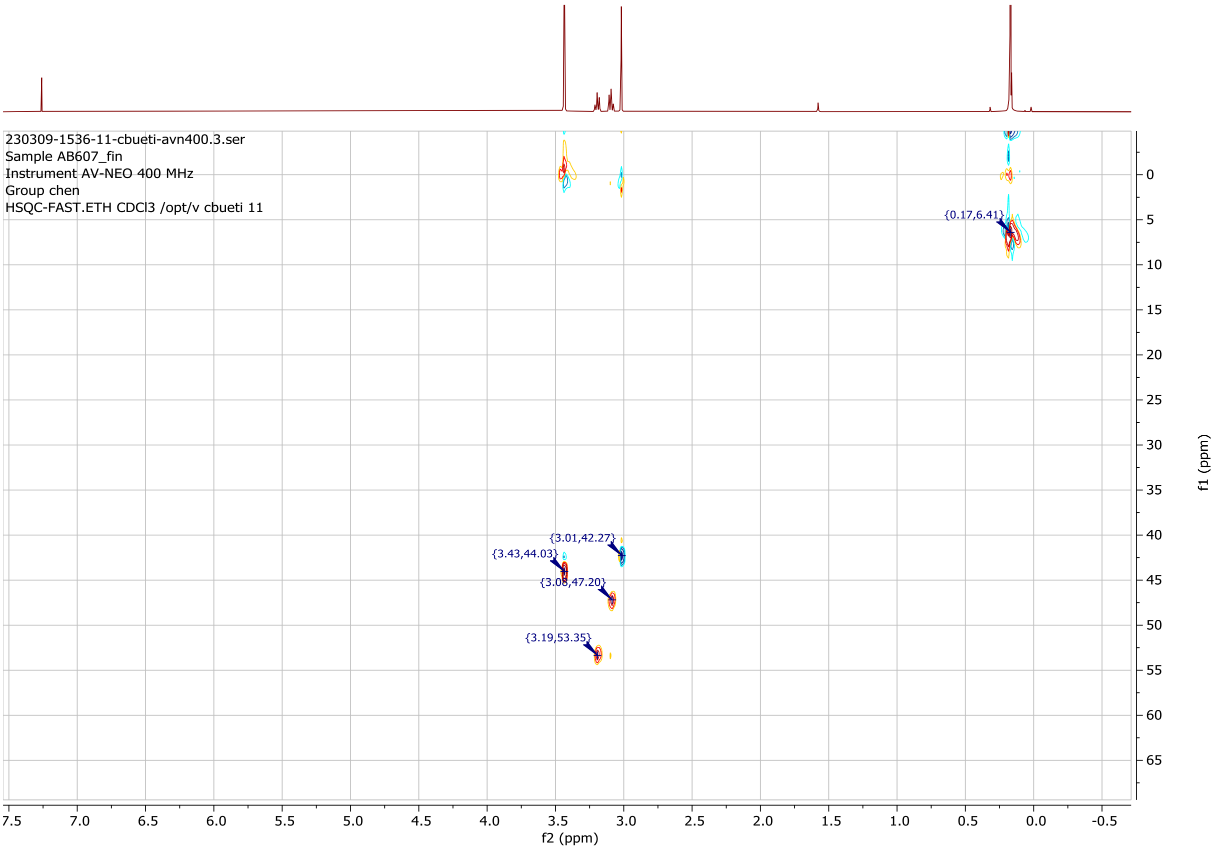


Figure S102. HSQC spectrum recorded in CDCl$_3$.

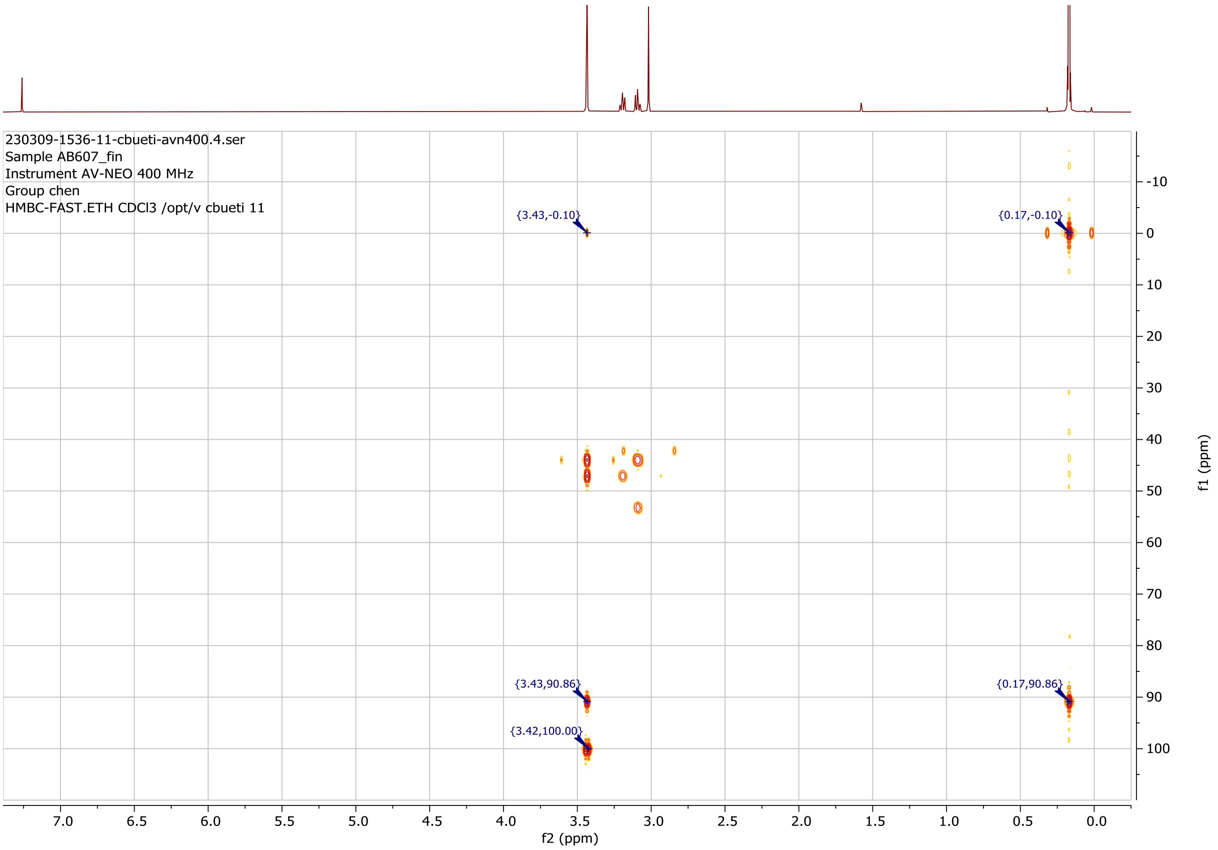
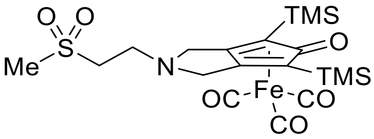


Figure S103. HMBC spectrum recorded in $CDCl_3$.

1.18) $Fe^{TMS}(CO)_3$-SO_2Me



A dried and argon-flushed 50 ml round bottom flask equipped with a stir bar and a reflux condenser was charged with 200 mg *N*-(2-(methylsulfonyl)ethyl)-*N*-bis(3-trimethylsilyl)prop-2-yn-1-yl)amine (0.58 mmol, 1 equiv.), 212 mg $Fe_2(CO)_9$ (0.58 mmol, 1 equiv.) and 10 ml dry toluene. The mixture was stirred and heated to reflux overnight. The next day, the mixture was allowed to cool to room temperature. The mixture was directly loaded onto a silica packed column and eluted with toluene until a straw orange band corresponding to $Fe(CO)_5$ had fully eluted. the $Fe(CO)_5$ dissolved in toluene was quenched with NaOCl prior to disposal. The eluent was changed to 2:1 hexane/EtOAc and purification by column chromatography was continued. The relevant yellow fractions were combined and concentrated under reduced pressure. The compound was dried *in vacuo* and was obtained as a bright orange solid (285 mg, 96 %).

TLC (SiO_2, 2:1 hexane/EtOAc): $r_f = 0.35$.

^1H NMR (δ, 400 MHz, $CDCl_3$): 3.91 (d, *J* = 12.8 Hz, 2H), 3.45 (d, *J* = 12.7 Hz, 2H), 3.38 (t, *J* = 6.1 Hz, 2H), 3.22 (t, *J* = 6.1 Hz, 2H), 3.01 (s, 3H), 0.25 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 208.5, 182.2, 112.4, 69.8, 53.7, 53.6, 49.2, 42.3, 0.7.

Anal. calc. for $C_{19}H_{29}FeNO_6SSi_2$ (%): C, 44.61; H, 5.71; N, 2.74. Found: C, 44.99; H, 5.92; N, 2.70.

LRMS (m/z): $[M+H]^+$ calc. for $C_{19}H_{30}FeNO_6SSi_2$: 512.07. Found: 512.18.

ESI-MS CID (m/z): 512 $[M+H]^+$, 484 $[M+H-CO]^+$, 456 $[M+H-2CO]^+$, 428 $[M+H-3CO]^+$.

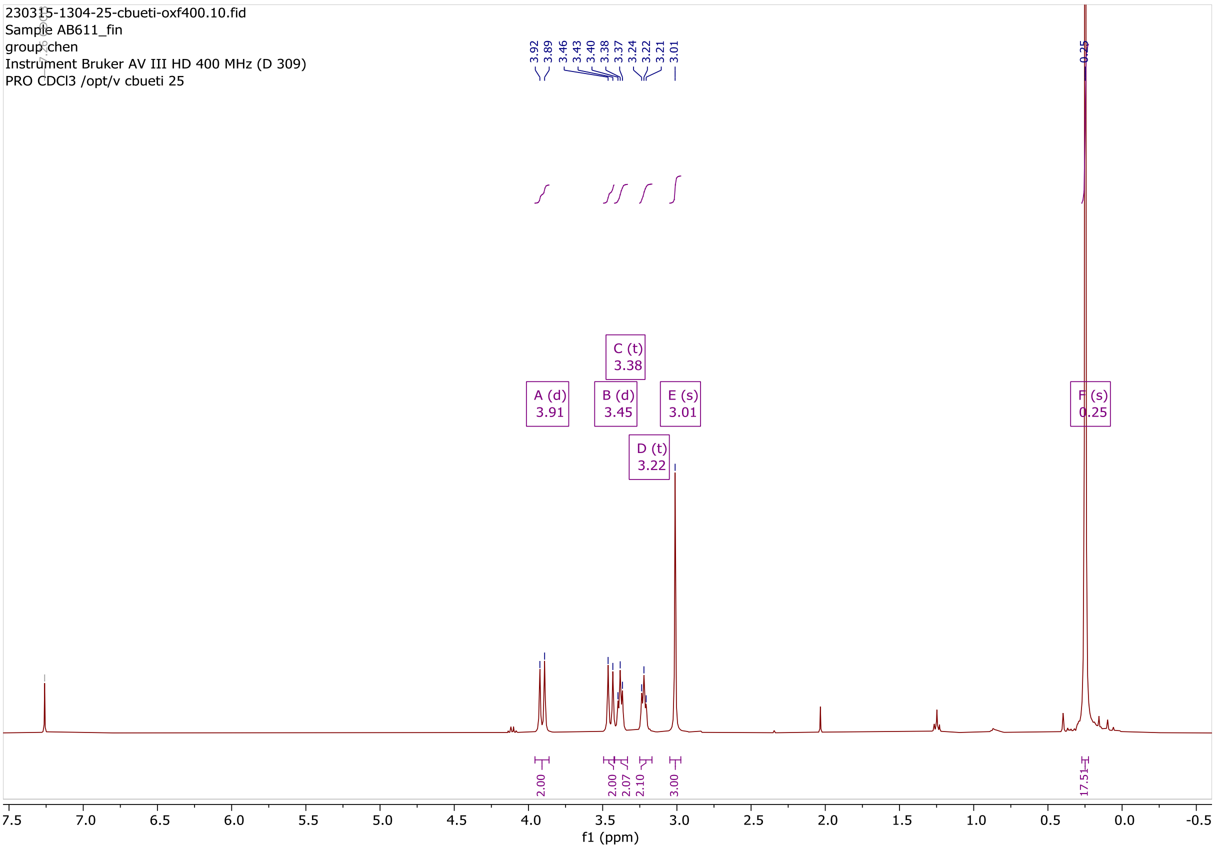


Figure S104. ^{1}H NMR spectrum recorded in $CDCl_3$.

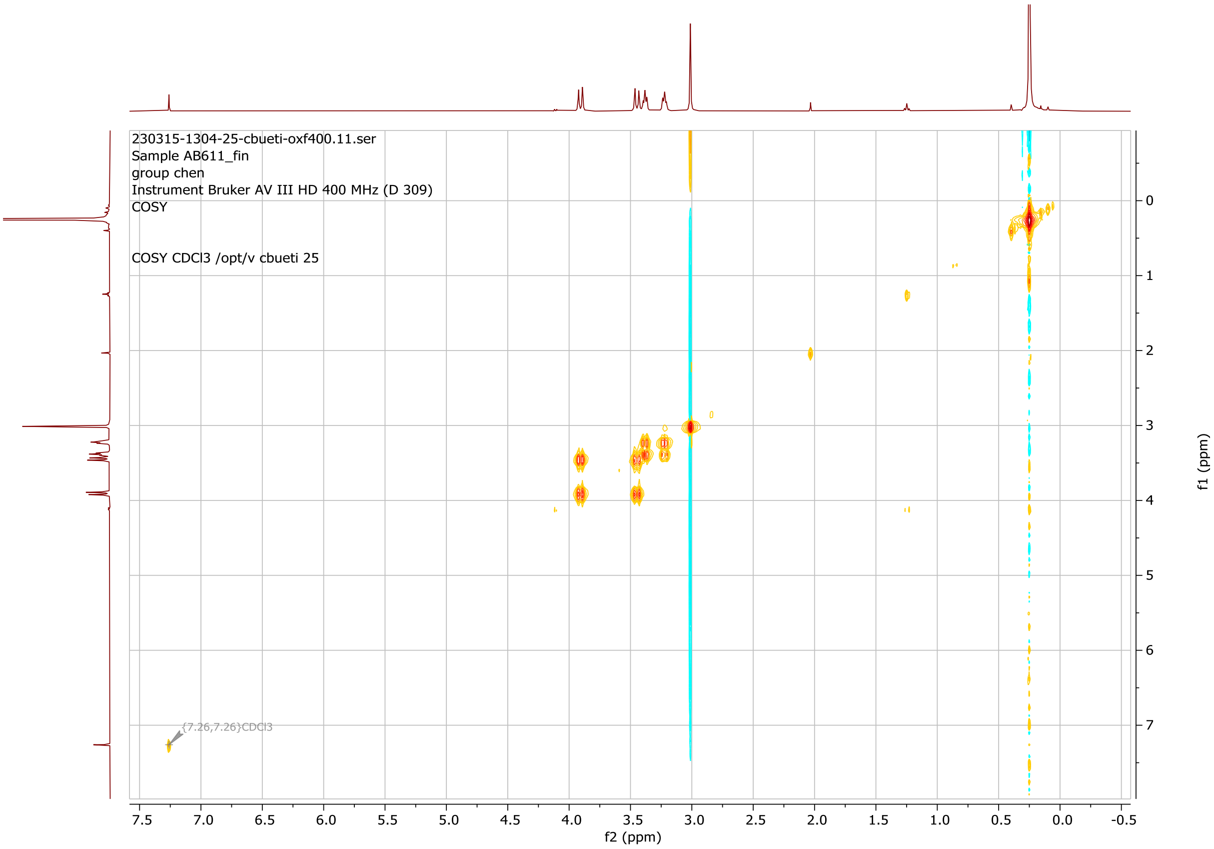


Figure S105. COSY spectrum recorded in $CDCl_3$.

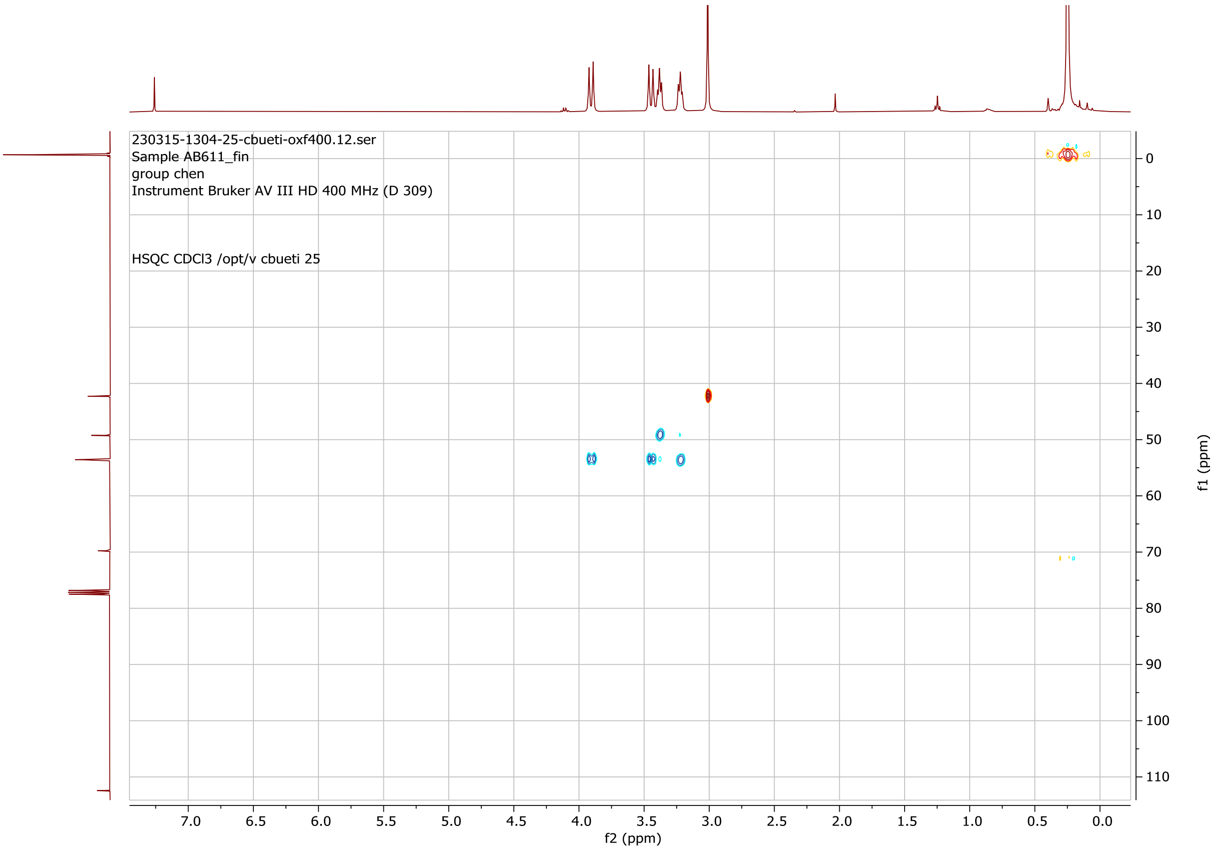


Figure S106. HSQC spectrum recorded in CDCl$_3$.

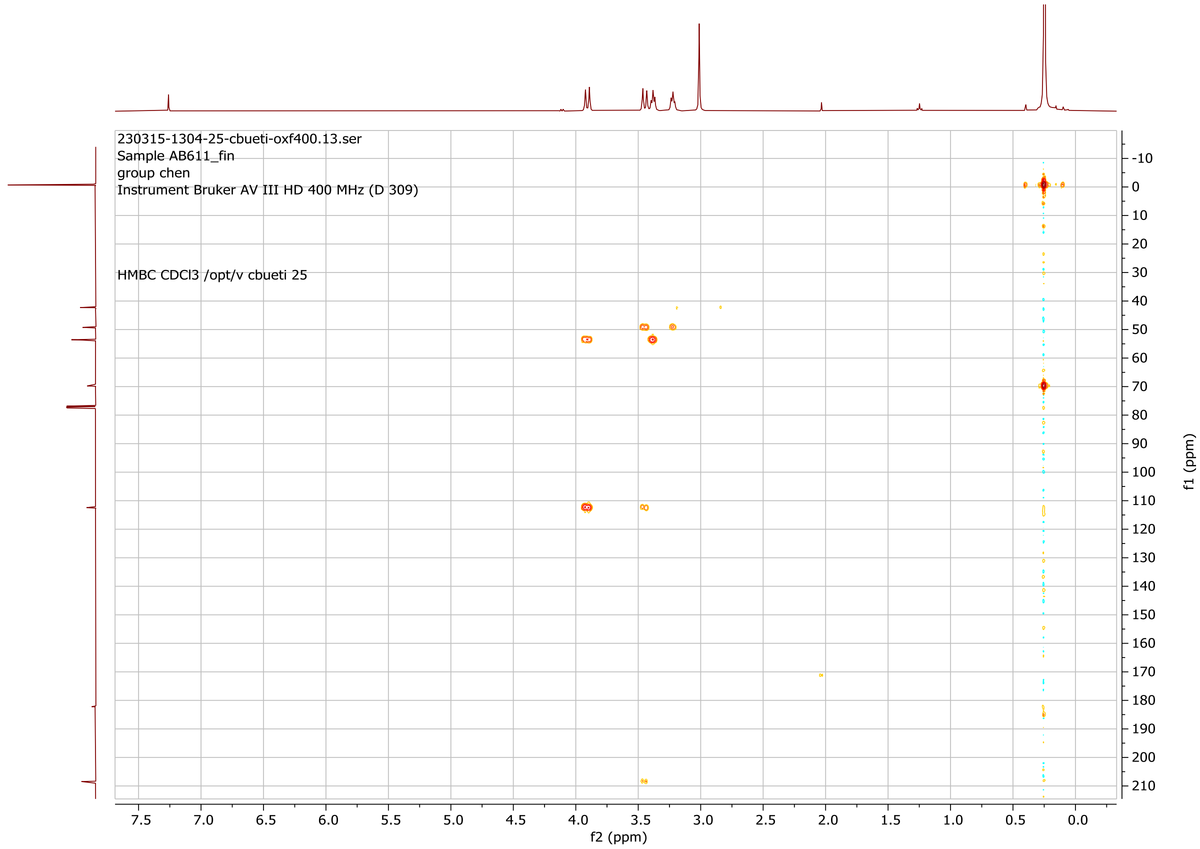


Figure S107. HMBC spectrum recorded in CDCl$_3$.

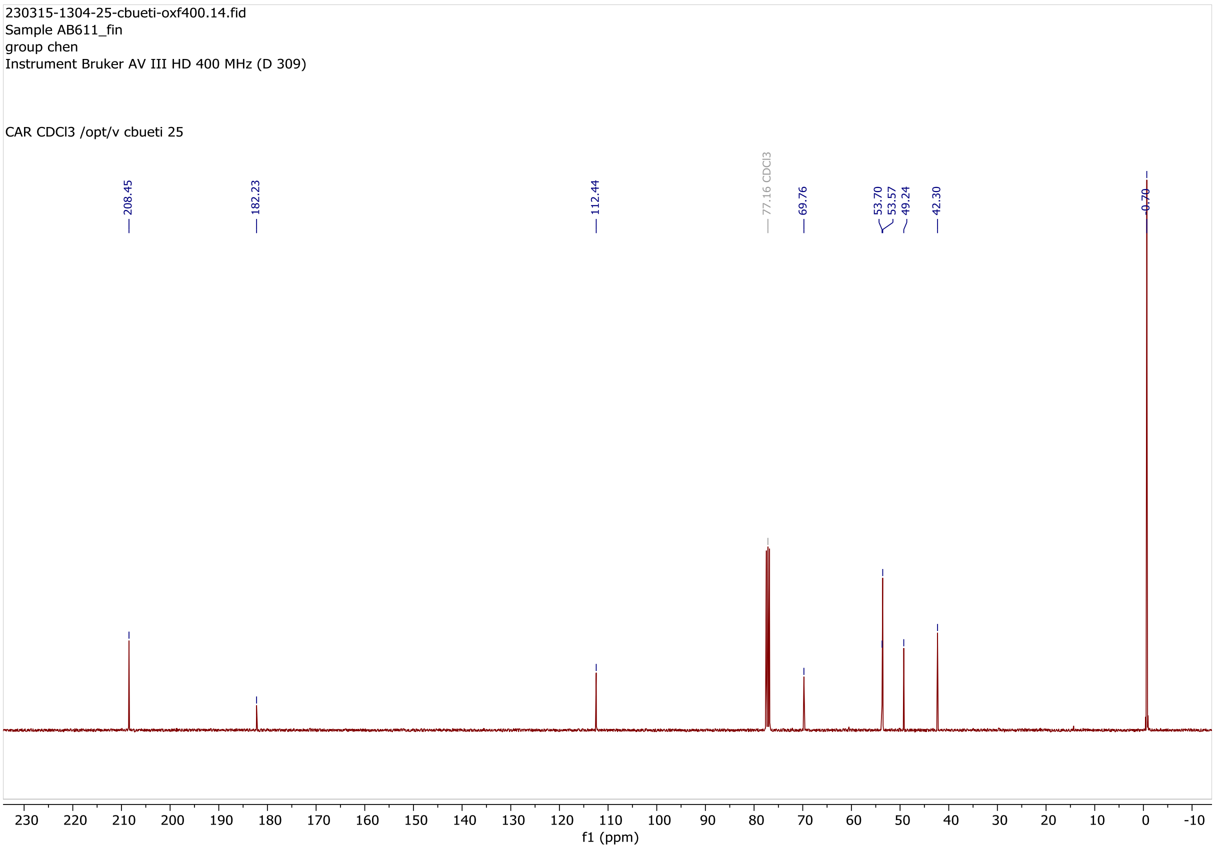


Figure S108. ^{13}C NMR spectrum recorded in CDCl$_3$.

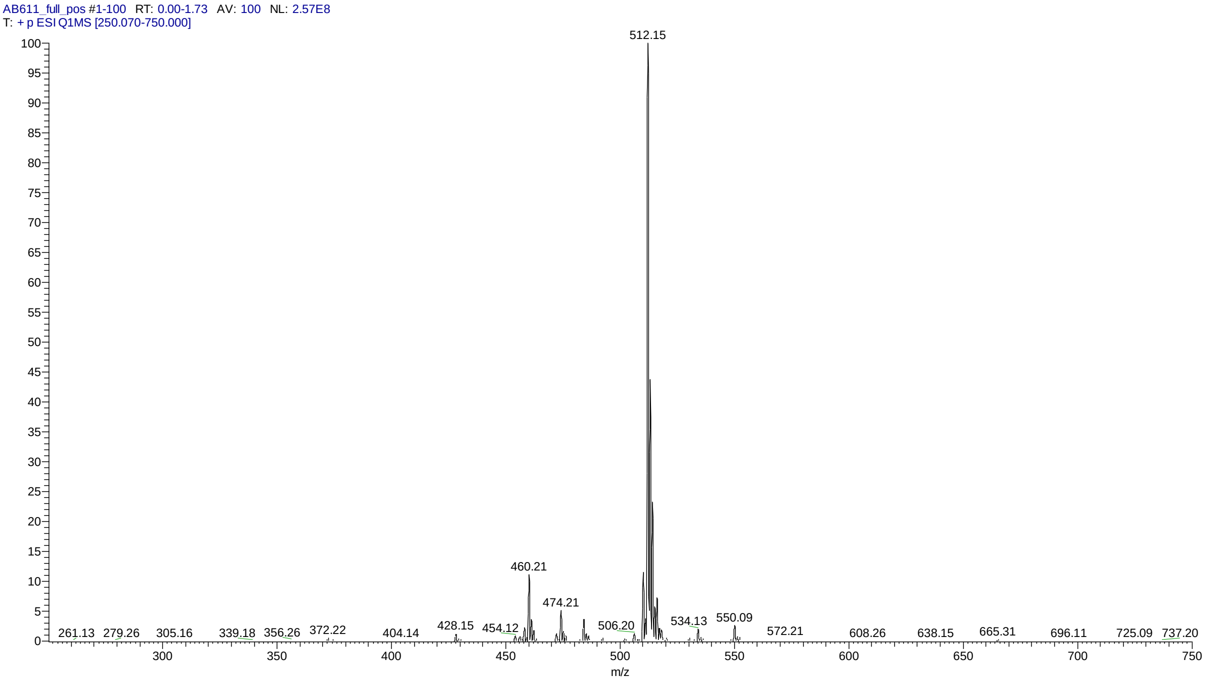


Figure S109. LRMS full spectrum. Sprayed from MeOH with a drop of formic acid.

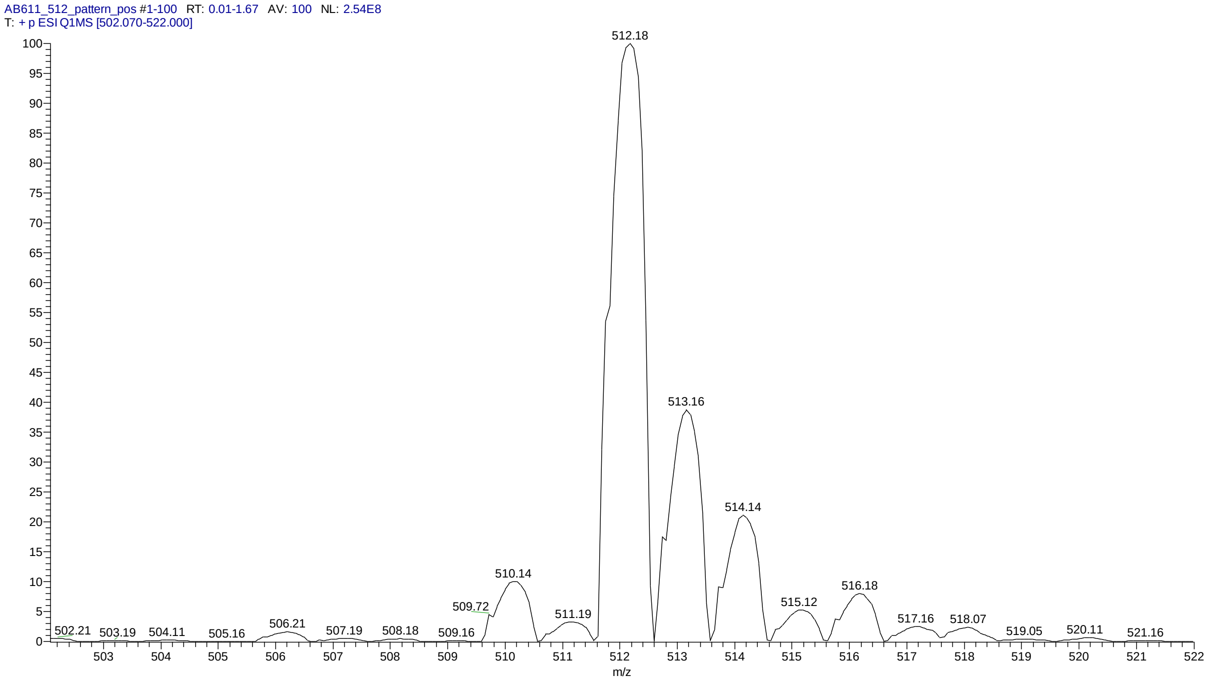


Figure S110. LRMS. Sprayed from MeOH with a drop of formic acid.

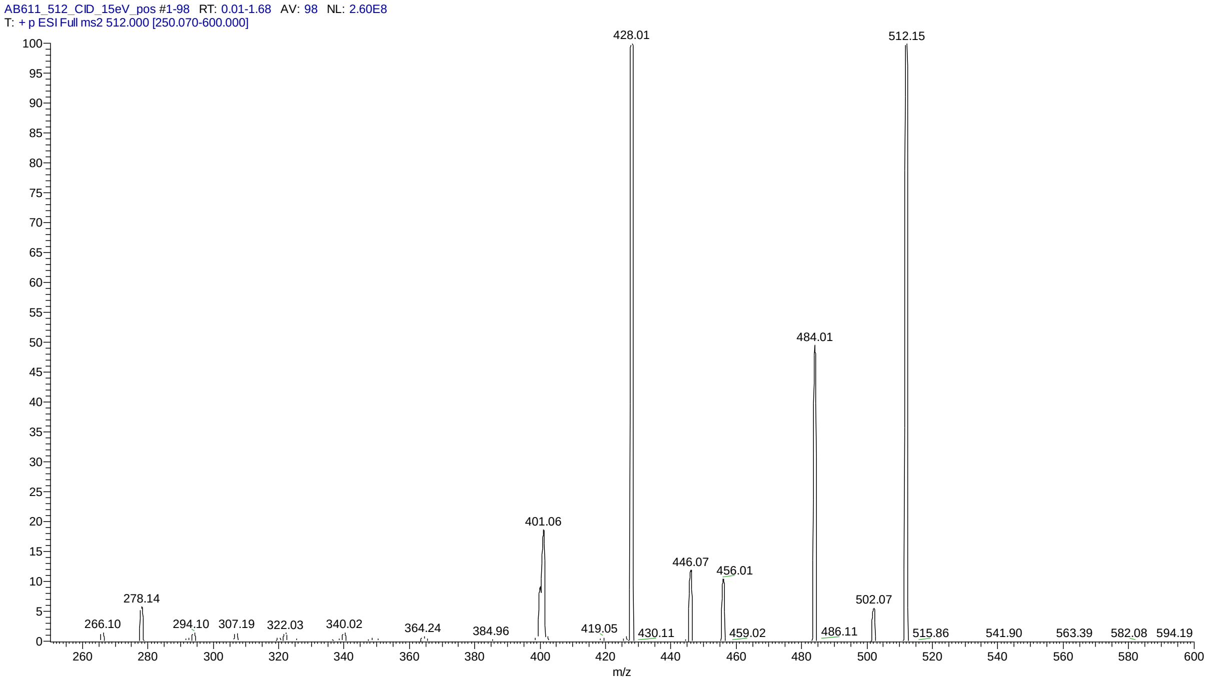
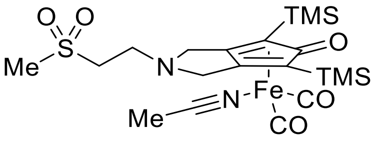


Figure S111. CID spectrum at 15 eV collision energy. Sprayed from MeOH with a drop of formic acid.

1.19) $\mathbf{Fe^{TMS}(MeCN)(CO)_2\text{-}SO_2Me}$



A dried and argon-flushed 20 ml Schlenk tube equipped with a stir bar was charged with 100 mg **$\mathbf{Fe^{TMS}(CO)_3\text{-}SO_2Me}$** (0.2 mmol, 1 equiv.) and 16.2 mg Me_3NO (0.22 mmol, 1.1 equiv.). While stirring, 1 ml dry MeCN added. The reaction mixture was protected from light. No precipitate formed. The reaction mixture was stirred at room temperature overnight. The next day, the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, 1:1 hexane/EtOAc). The product was isolated as an orange solid (97 mg, 95 %).

TLC (SiO_2, 1:1 hexane/EtOAc): $r_f = 0.25$.

^{1}H NMR (δ, 400 MHz, $CDCl_3$): 3.61 (d, *J* = 12.4 Hz, 2H), 3.24 (t, *J* = 5.3 Hz, 2H), 3.15 – 3.05 (m, 4H, *overlapping methylene and ethylene protons*), 3.02 (s, 3H), 2.26 (s, 3H), 0.21 (s, 18H).

^{13}C NMR (δ, 100 MHz, $CDCl_3$): 212.3, 181.4, 126.4, 108.3, 68.0, 53.8, 53.5, 49.8, 42.5, 4.4, -0.7.

Anal. calc. for $C_{20}H_{32}FeN_2O_5SSi_2$ (%): C, 45.79; H, 6.54; N, 4.57. Found: C, 46.18; H, 6.56; 4.55.

LRMS (m/z): $[M+H]^+$ calc. for $C_{20}H_{33}FeN_2O_5SSi_2$: 525.10. Found: 525.20.

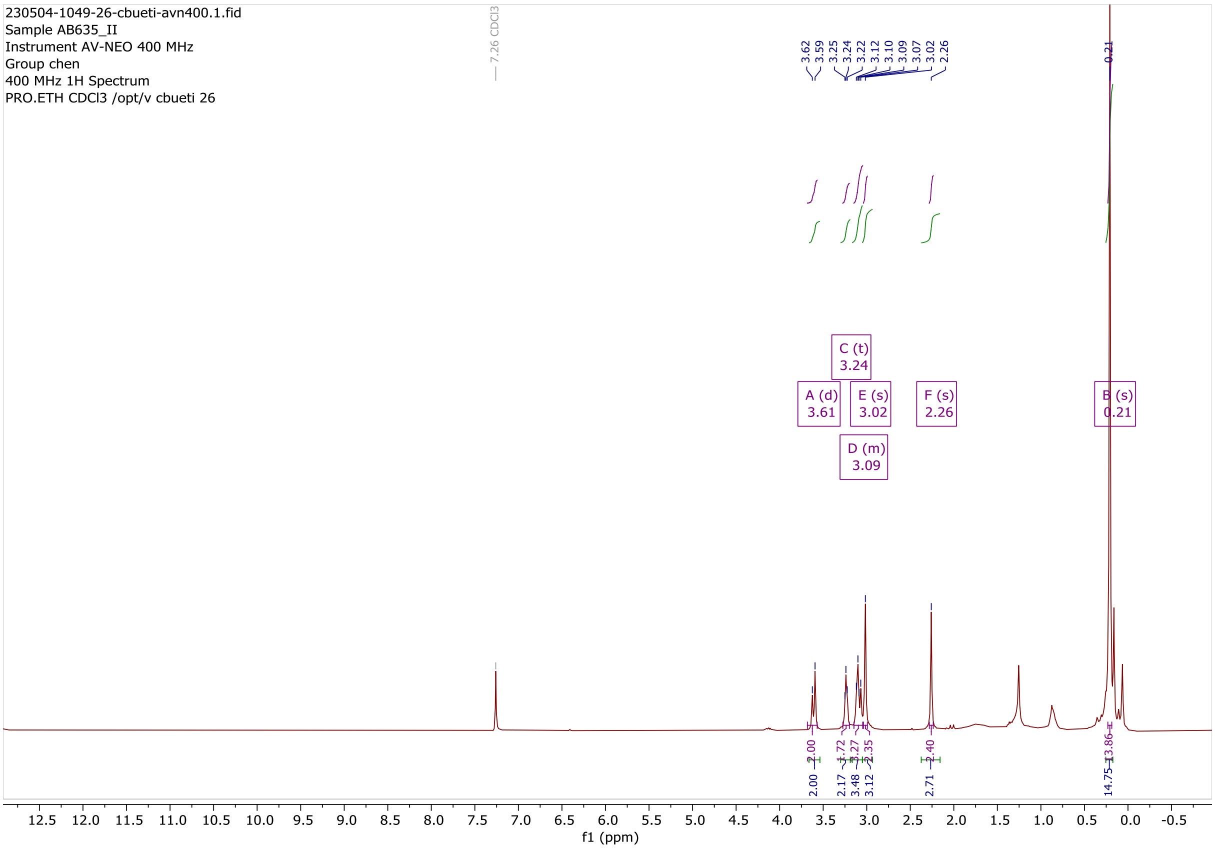


Figure S112. ^{1}H NMR spectrum recorded in $CDCl_3$.

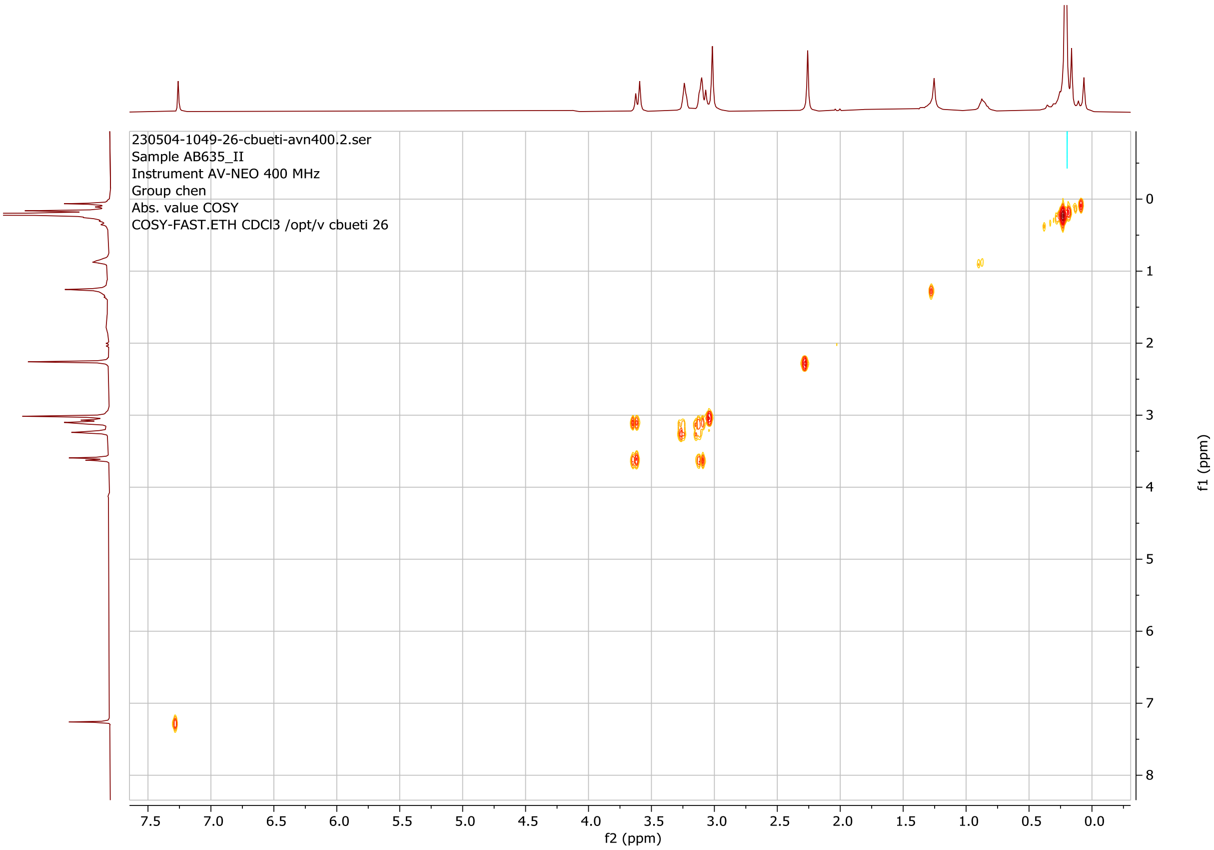


Figure S113. COSY spectrum recorded in CDCl$_3$.

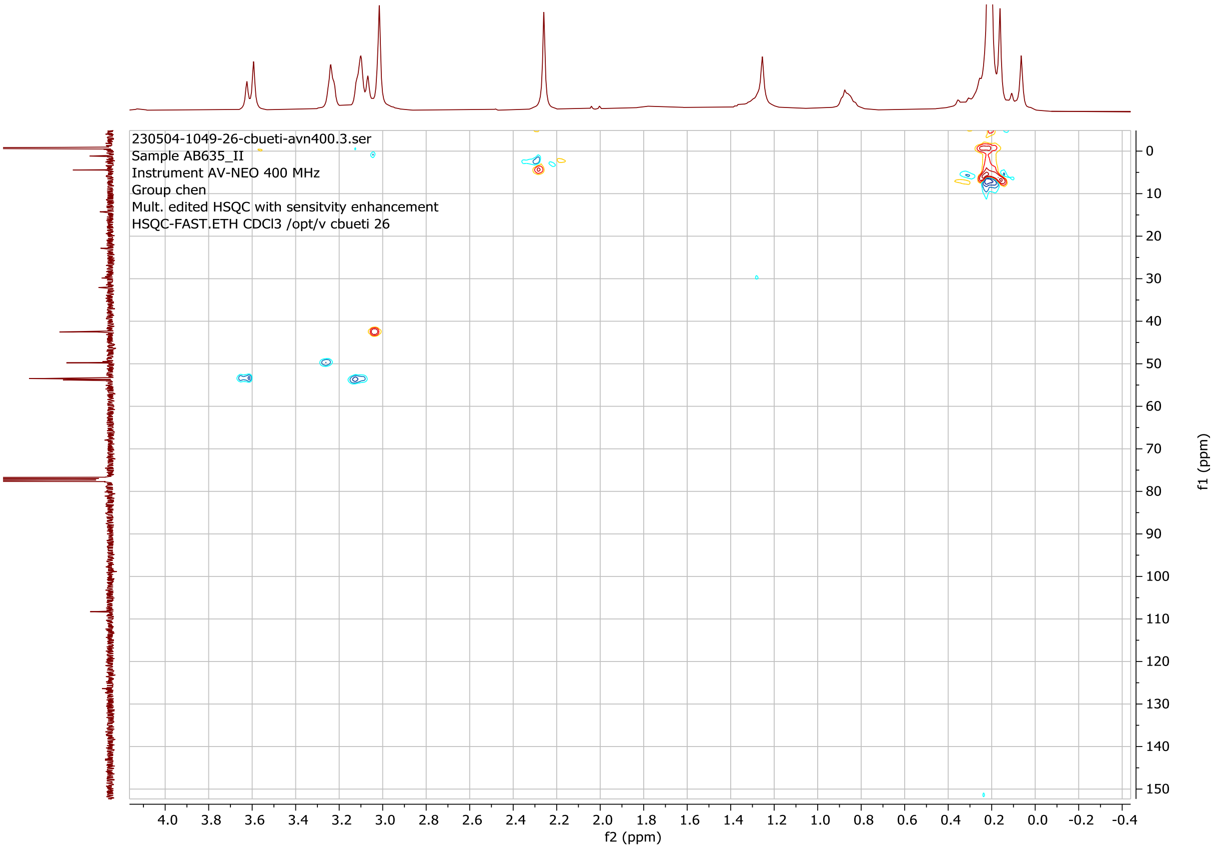


Figure S114. HSQC spectrum recorded in CDCl$_3$.

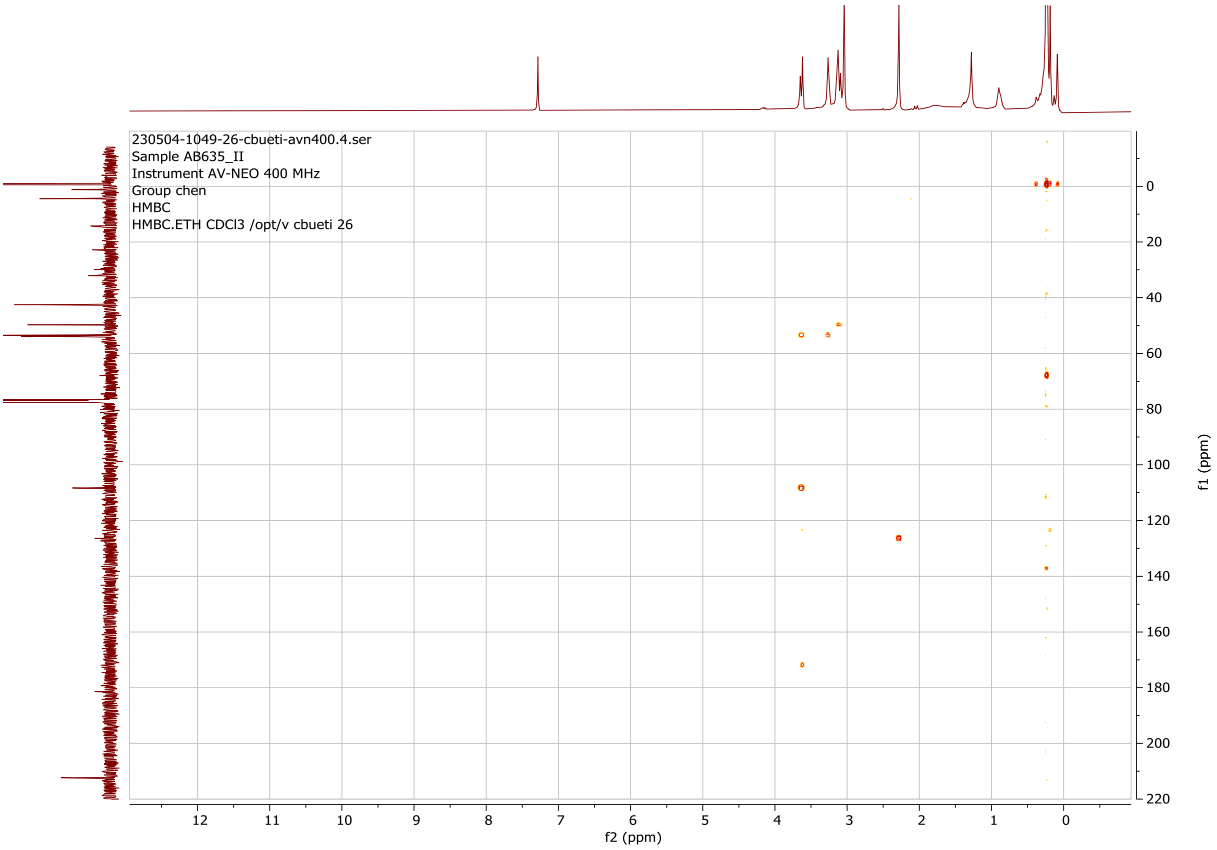


Figure S115. HMBC spectrum recorded in CDCl$_3$.

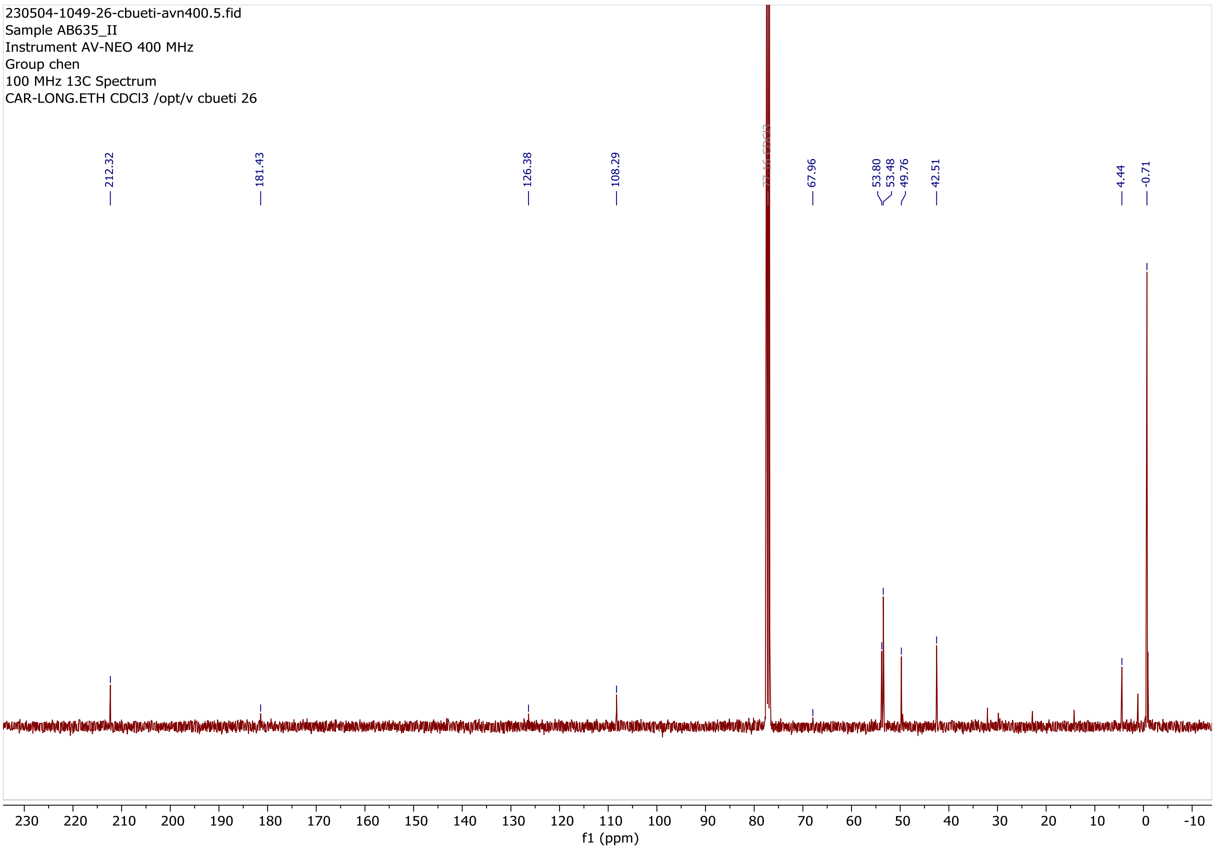


Figure S116. ^{13}C NMR spectrum recorded in CDCl$_3$.

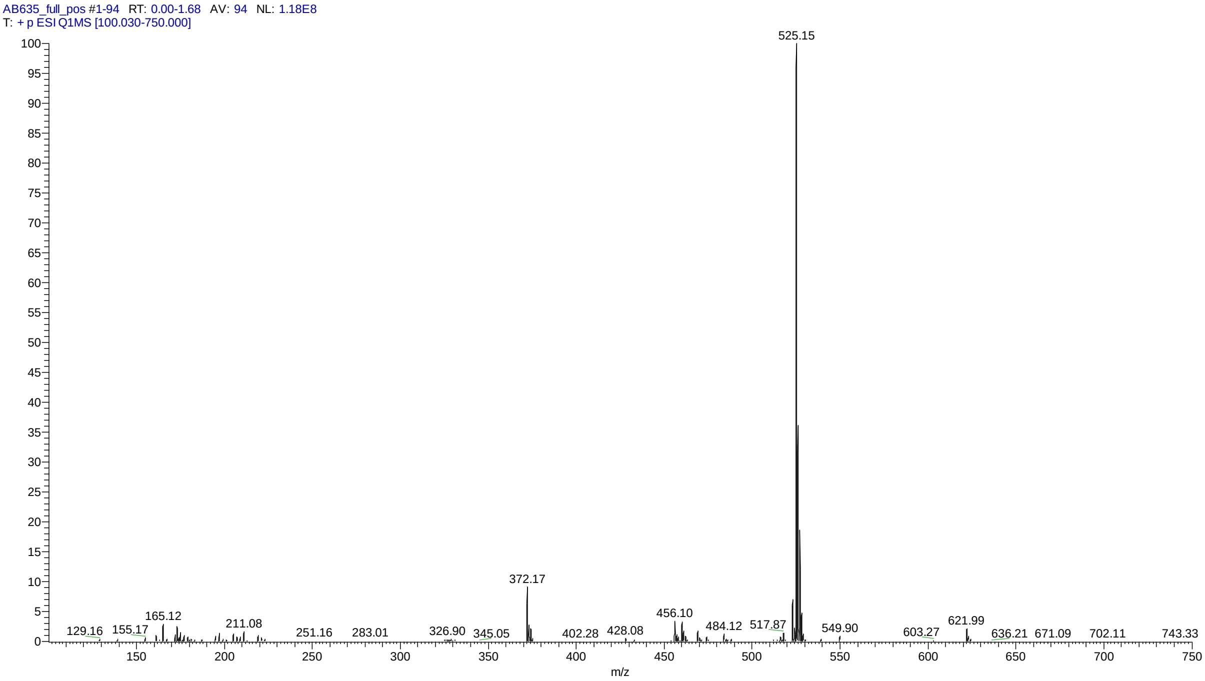


Figure S117. LRMS full spectrum. Sprayed from MeOH with a drop of formic acid.

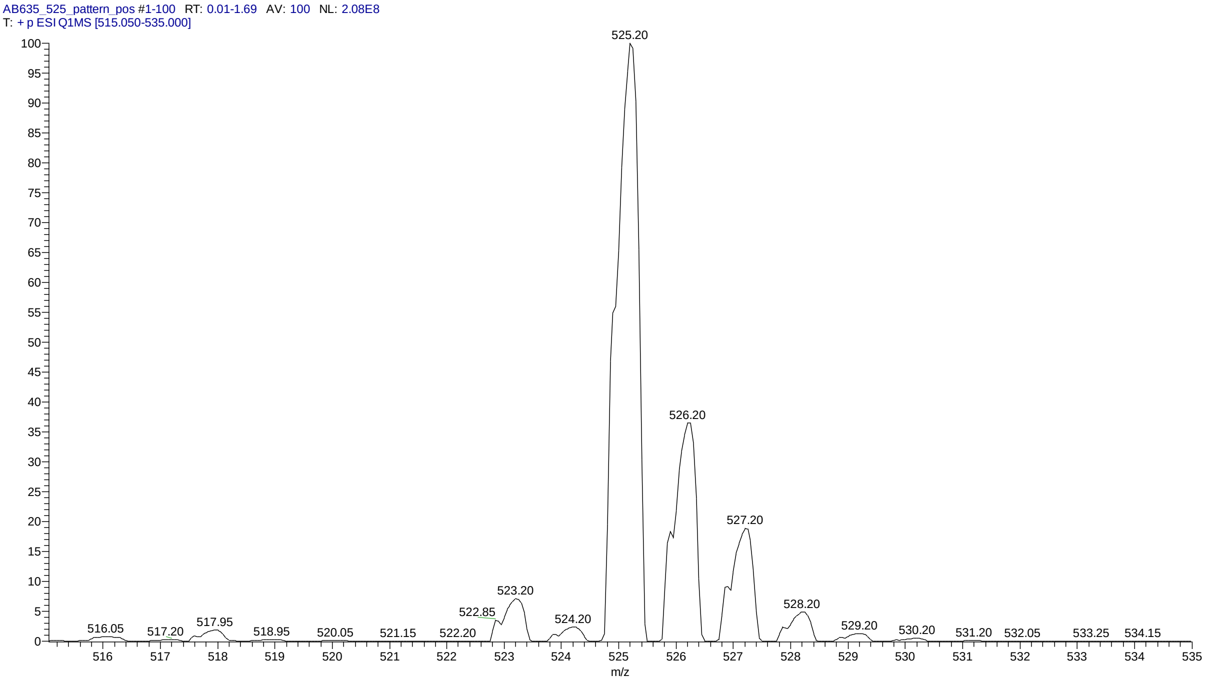
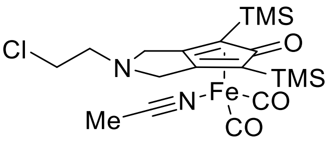


Figure S118. LRMS. Sprayed from MeOH with a drop of formic acid.

1.20) $\mathbf{Fe^{TMS}(MeCN)(CO)_2}$-Cl



A dried and argon-flushed 20 ml Schlenk tube equipped with a stir bar was charged with 100 mg **$\mathbf{Fe^{TMS}(CO)_3}$-Cl** (0.21 mmol, 1 equiv.) and 24.1 mg Me_3NO (0.32 mmol, 1.5 equiv.). While stirring, 2 ml dry MeCN was added to the solids, immediately leading to the formation of a yellow precipitate. The solution was protected from light and stirred at room temperature for 1.5 h. The mixture was cannula filtered. The residue was washed with two 1 ml portions of dry MeCN. The residue was dried at reduced pressure. The product was isolated as a yellow powder (28.2 mg, 28 %).

^{1}H NMR (δ, 300 MHz, MeOH-d$_4$): 3.74 – 3.49 (m, 4H, *overlapping methylene and ethylene protons*), 3.17 (d, *J* = 12.9 Hz, 2H), 3.03 (t, *J* = 6.7 Hz, 2H), 2.33 (s, 3H), 0.24 (s, 18H).

^{13}C NMR (δ, 100 MHz, MeOH-d$_4$): 129.5, 109.6, 68.1, 57.9, 54.1, 43.2. 3.6, -0.6 (*remaining quaternary carbons not observed*).

Anal. calc. for $C_{19}H_{29}ClFeN_2O_3Si_2$ (%): C, 47.45; H, 6.08; N, 5.83. Found: C, 47.01; H, 6.07; N, 5.75.

LRMS (m/z): [M+H]$^+$ calc. for $C_{19}H_{30}ClFeN_2O_3Si_2$: 481.08. Found: 481.00.

ESI-MS CID (m/z): 481 [M+H]$^+$, 440 [M+H-MeCN]$^+$, 412 [M+H-MeCN-CO]$^+$, 384 [M+H-MeCN-2CO]$^+$.

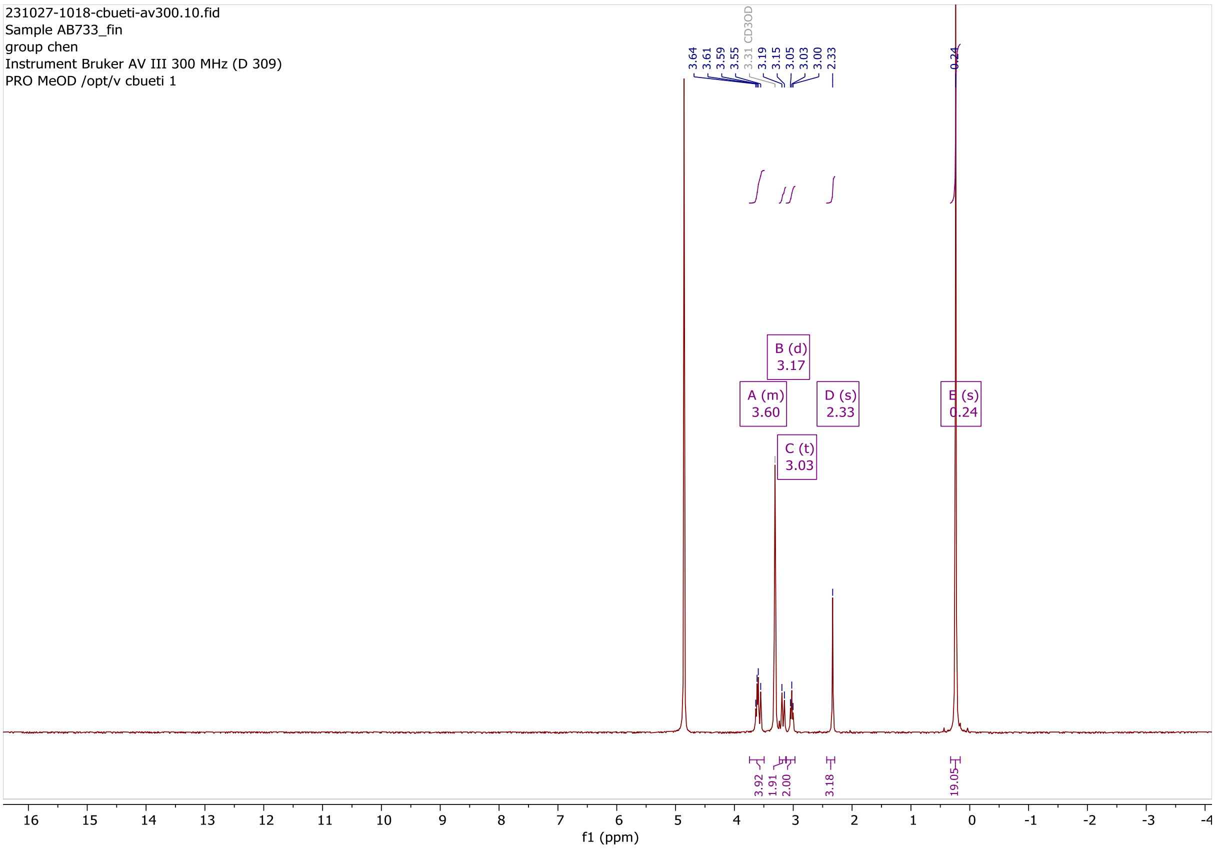


Figure S119. ^{1}H NMR spectrum recorded in MeOH-d$_4$.

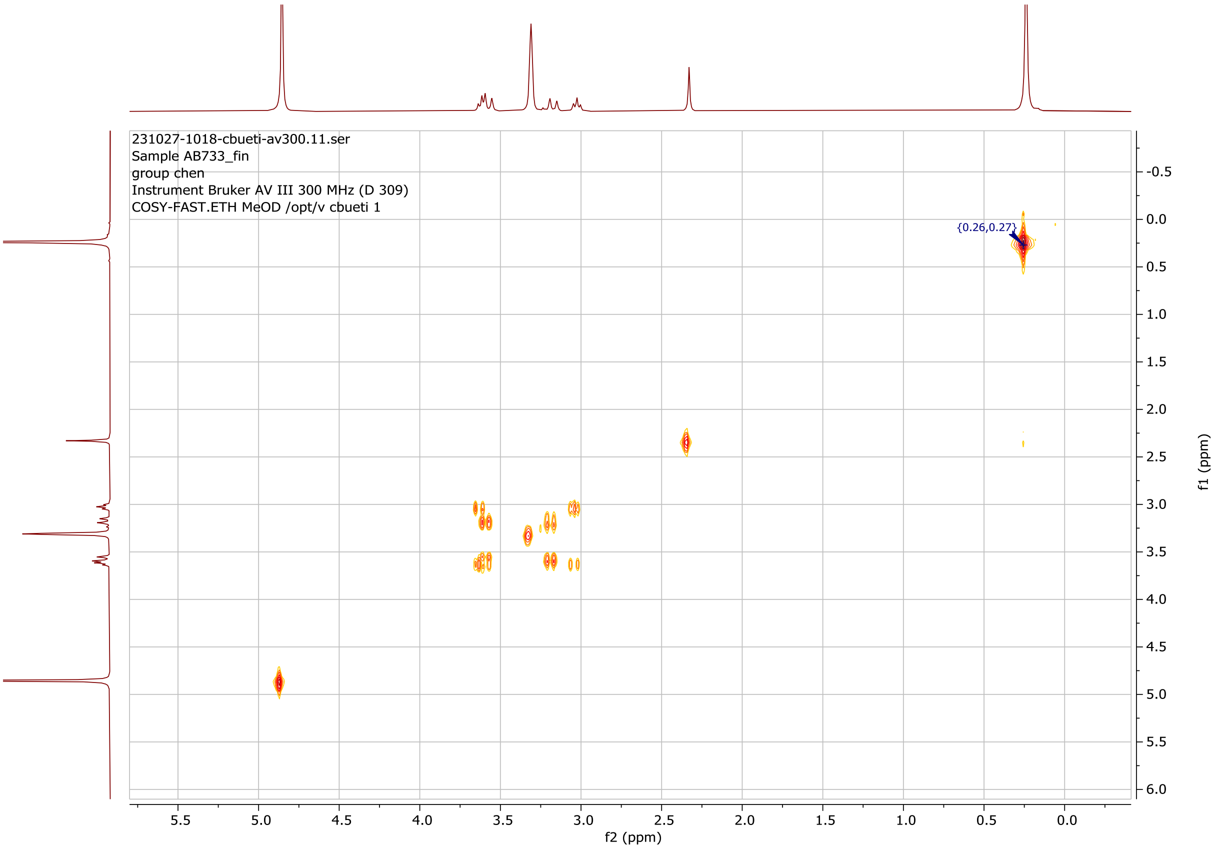


Figure S120. COSY spectrum recorded in MeOH-d_4.

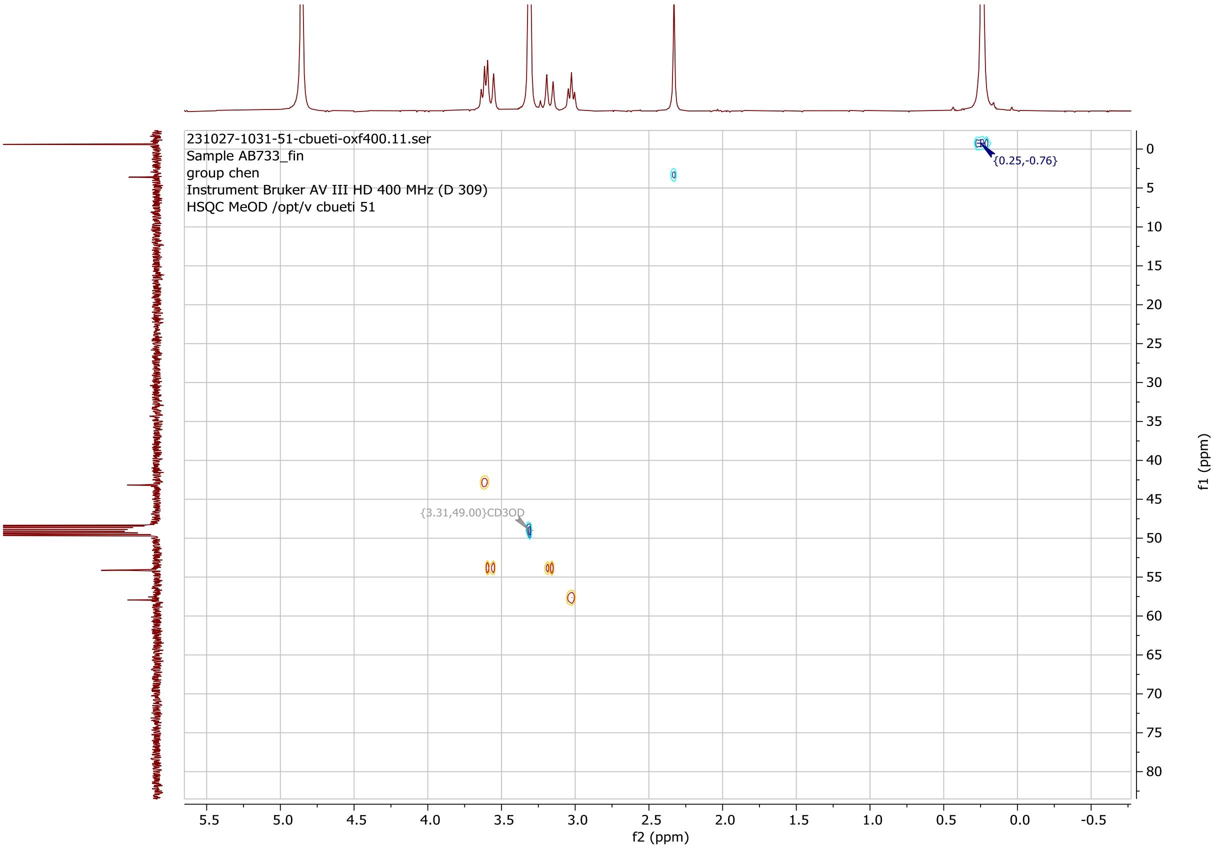


Figure S121. HSQC spectrum recorded in MeOH-d_4.

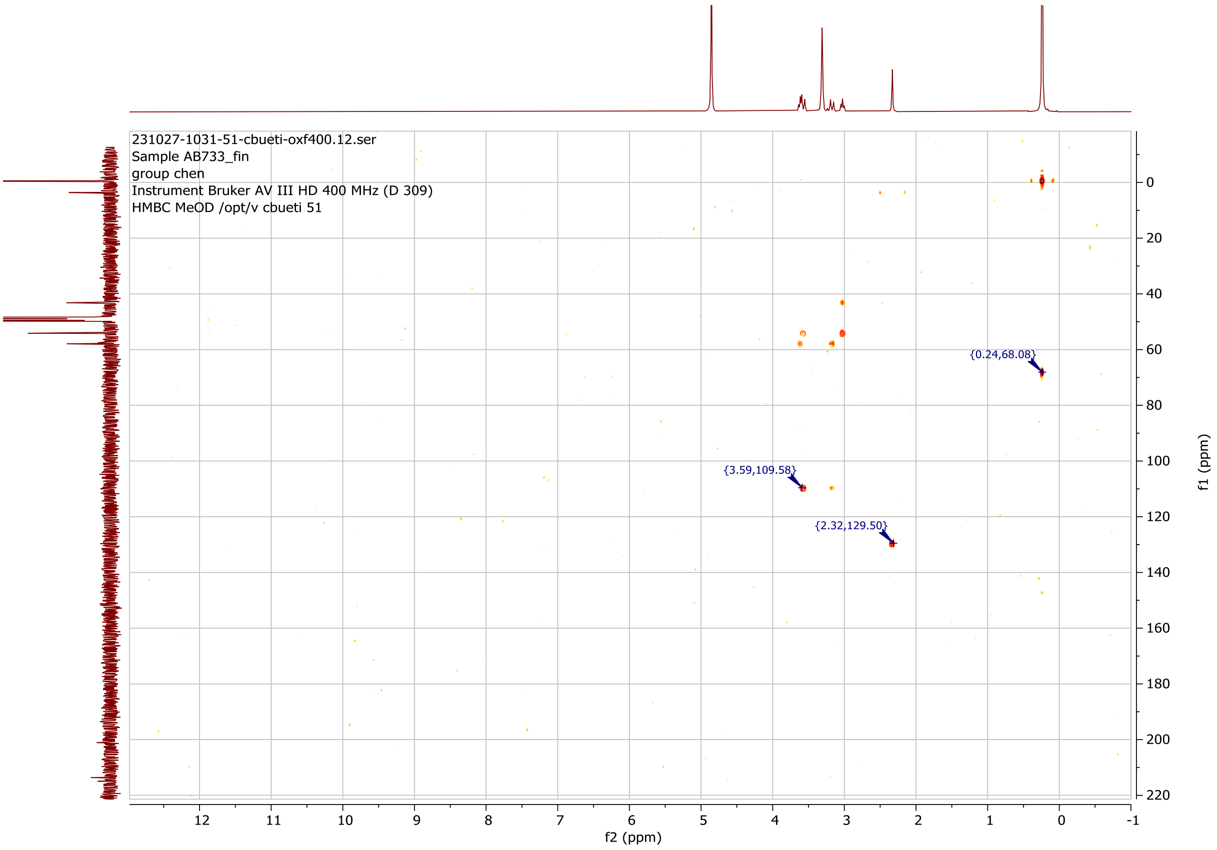


Figure S122. HMBC spectrum recorded in MeOH-d$_4$.

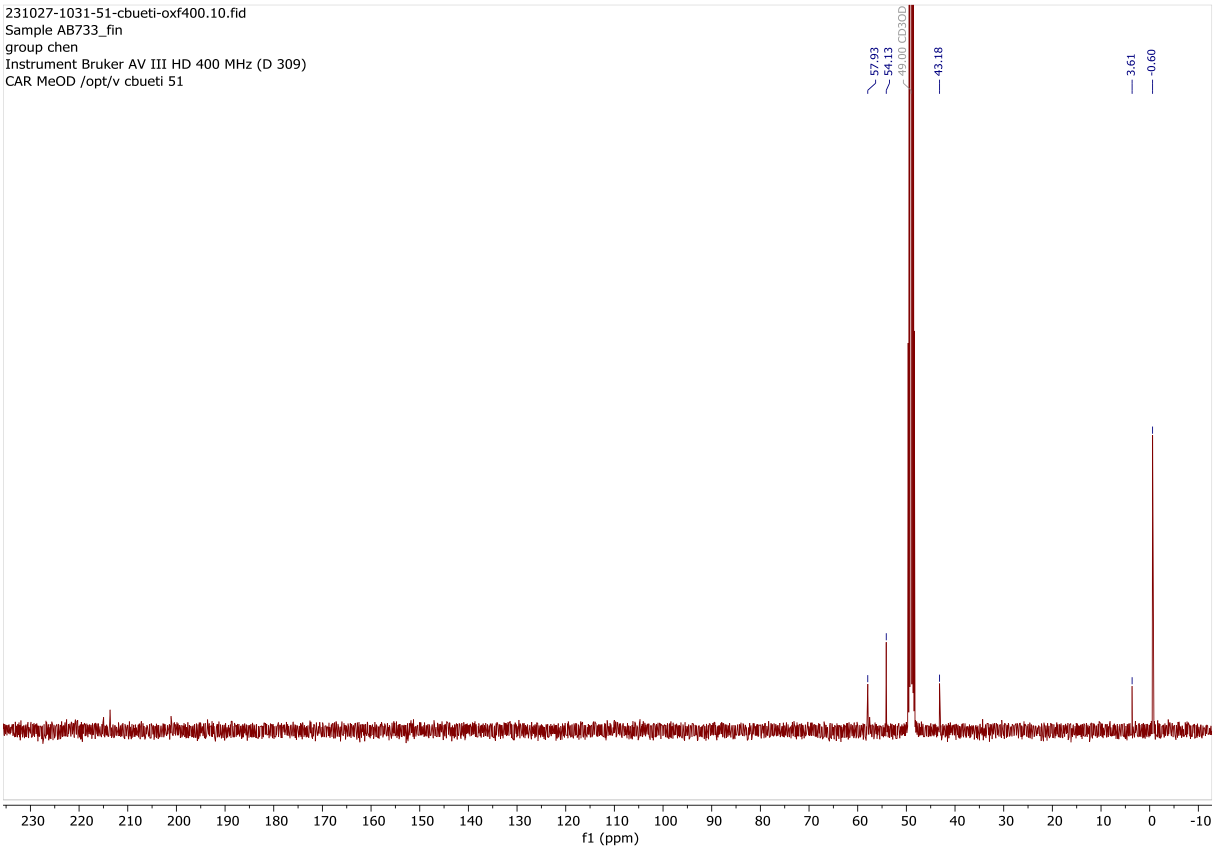


Figure S123. ^{13}C NMR spectrum recorded in MeOH-d$_4$.

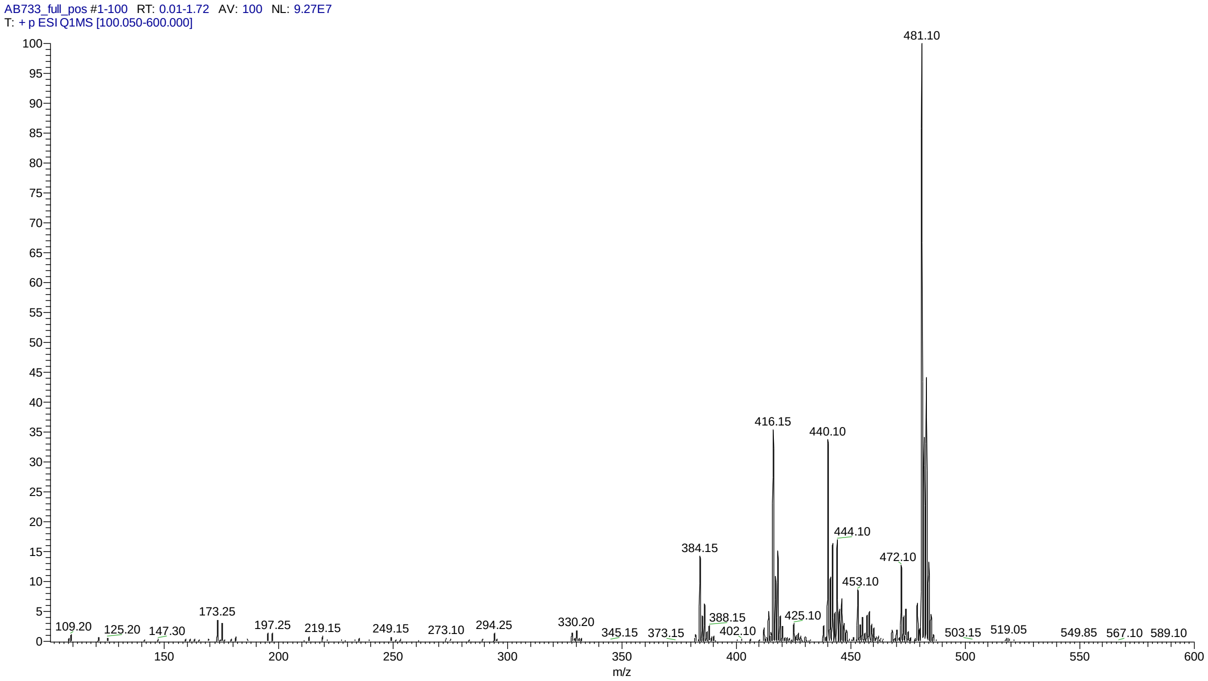


Figure S124. LRMS full spectrum. Sprayed from MeOH with a drop of formic acid.

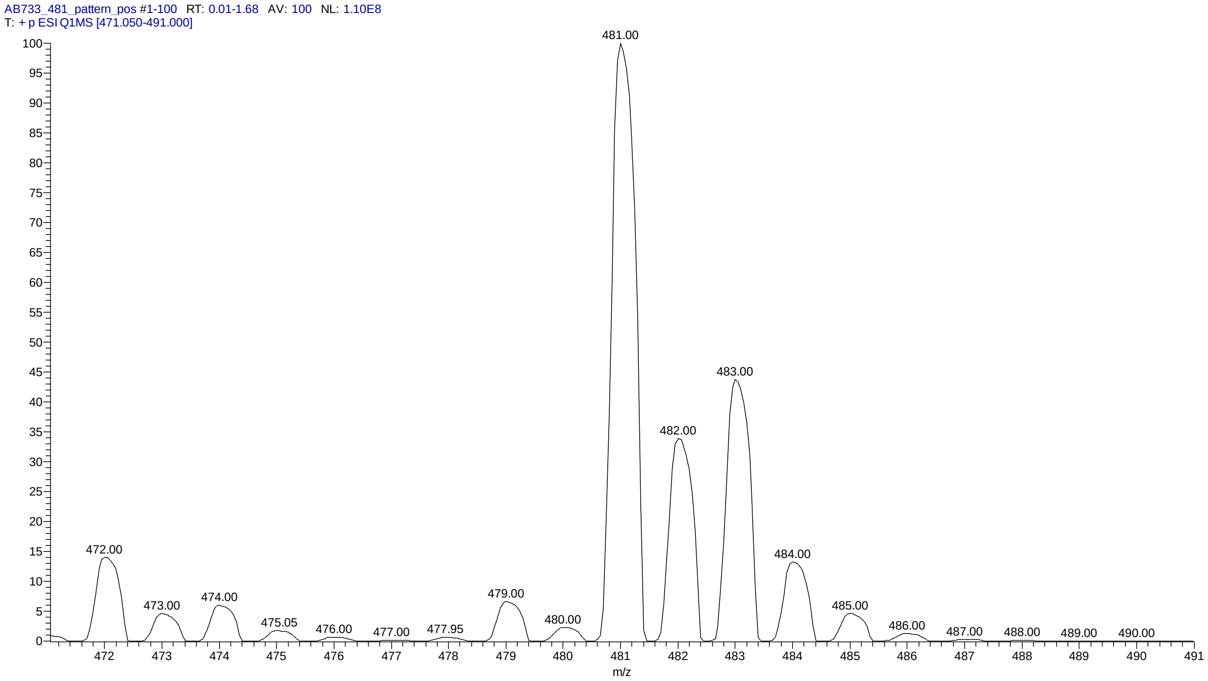


Figure S125. LRMS. Sprayed from MeOH with a drop of formic acid.

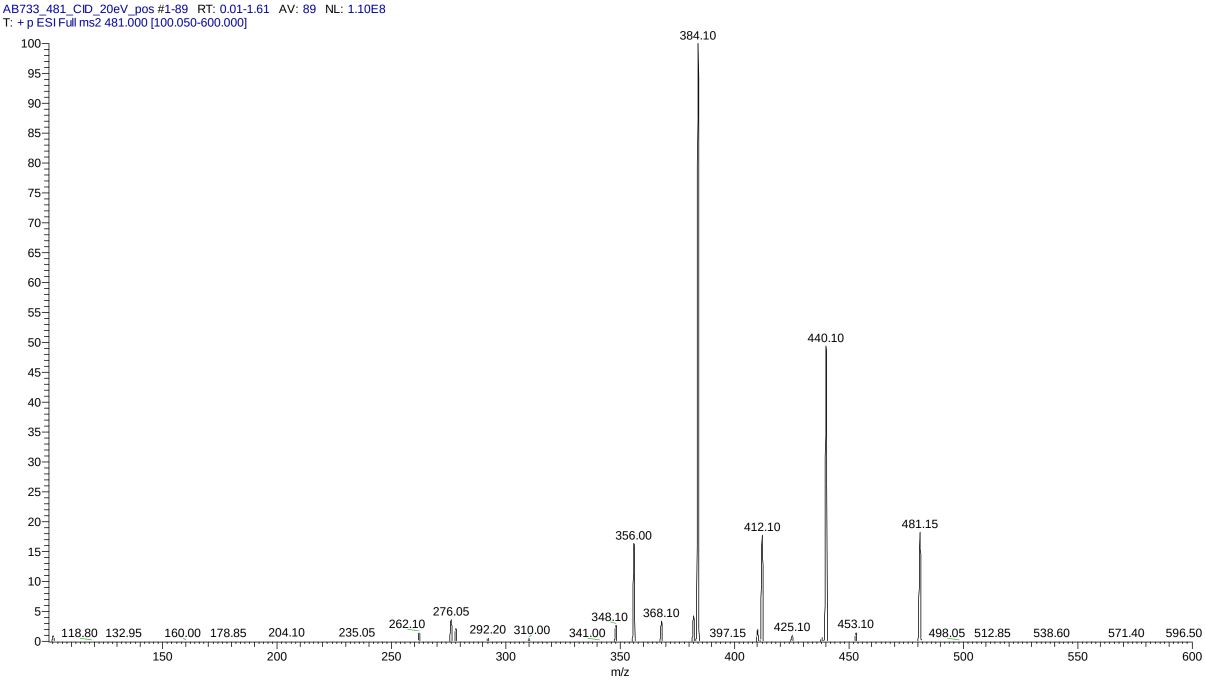
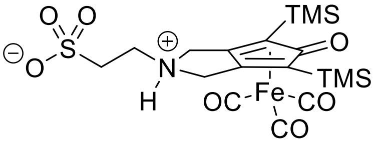


Figure S126. CID spectrum at 20 eV collision energy. Sprayed from MeOH with a drop of formic acid.

1.21) $[Fe^{TMS}(CO)_3\text{-}SO_3]H$



500 mg **[FeTMS(CO)3-SO3]Na** (0.92 mmol) was dissolved in MeOH and passed through an ion exchange column (Dowex® 50WX8 H form). The obtained orange solution was concentrated under reduced pressure. The product was isolated as a yellow/light brown solid (373 mg, 0.73 mmol, 79 %).

1H NMR (δ, 300 MHz, D_2O): 4.76 (d, *J* = 14.6 Hz, 2H), 3.47 (d, *J* = 14.6 Hz, 2H), 3.92 – 3.83 (m, 2H), 3.52 – 3.42 (m, 2H), 0.29 (s, 18H).

^{1}H NMR (δ, 400 MHz, DMSO-d_6): 4.60 (d, *J* = 14.7 Hz, 2H), 4.55 (d, *J* = 14.6 Hz, 2H), 3.77 – 3.69 (m, 2H), 3.14 – 3.03 (m, 2H), 0.20 (s, 18H).

^{1}H NMR (δ, 400 MHz, MeOH-d_4): 4.78 (d, *J* = 14.5 Hz, 2H), 4.66 (d, *J* = 14.5 Hz, 2H), 3.96 (t, *J* = 7.0 Hz, 2H), 3.39 (t, *J* = 7.1 Hz, 2H), 0.32 (s, 18H).

^{13}C NMR (δ, 100 MHz, DMSO-d_6): 207.5, 180.9, 108.0, 67.1, 53.6, 51.9, 46.4, -1.2.

Anal. calc. for $C_{18}H_{27}FeNO_7SSi_2$ (%): C, 42.10; H, 5.30; N, 2.73. Found: C, 40.64; H, 4.63, N, 3.02.

HRMS (m/z): $[M+H]^+$ calc. for $C_{18}H_{28}FeNO_7SSi_2$: 514.0469. Found: 514.0472.

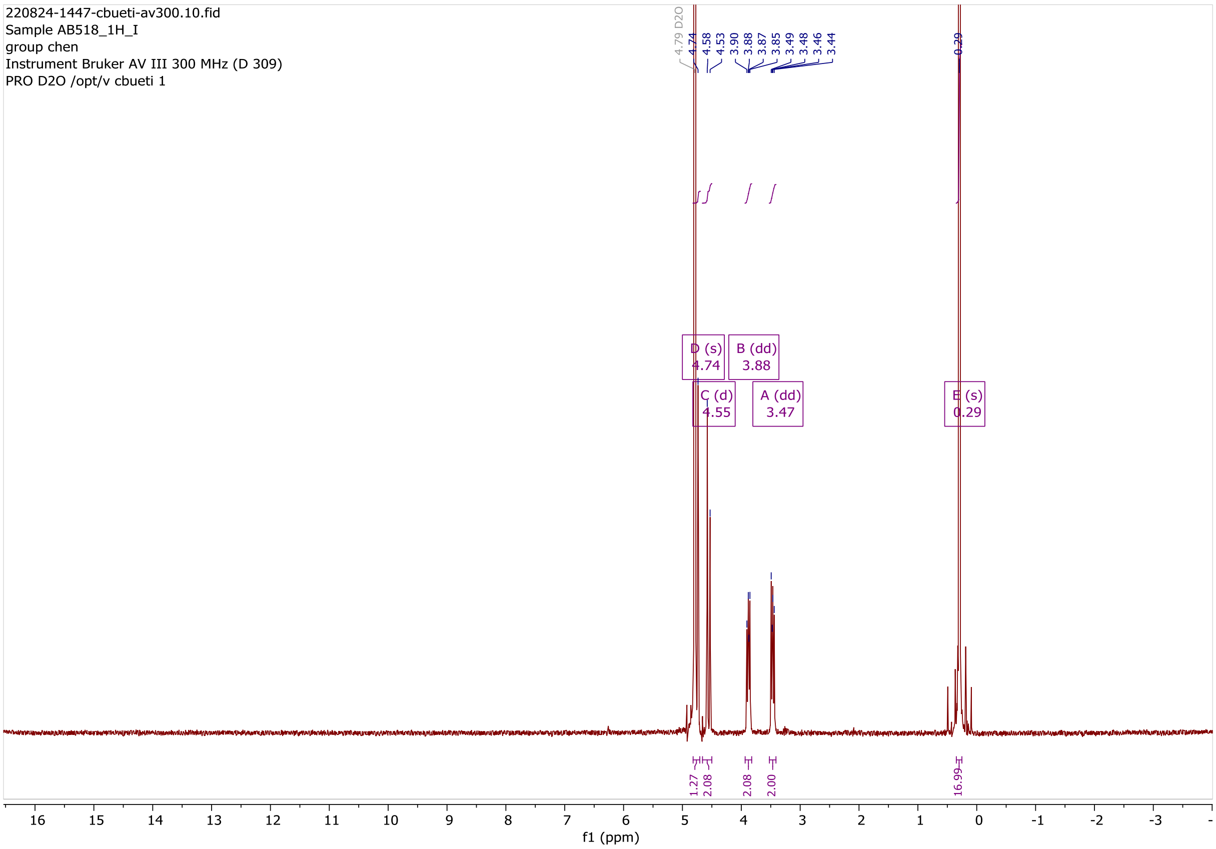


Figure S127. ${}^{1}H$ NMR spectrum recorded in D_2O.

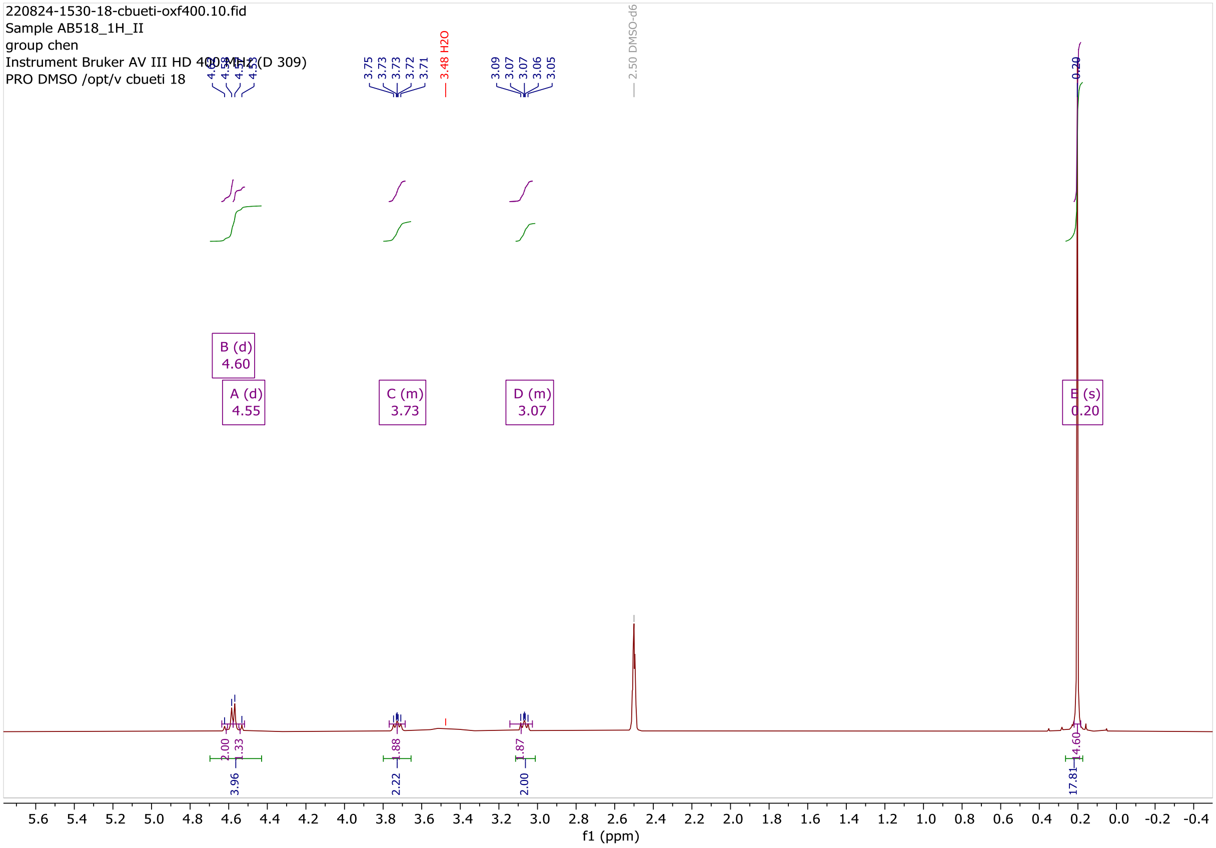


Figure S128. ${}^{1}H$ NMR spectrum recorded in DMSO-d_6.

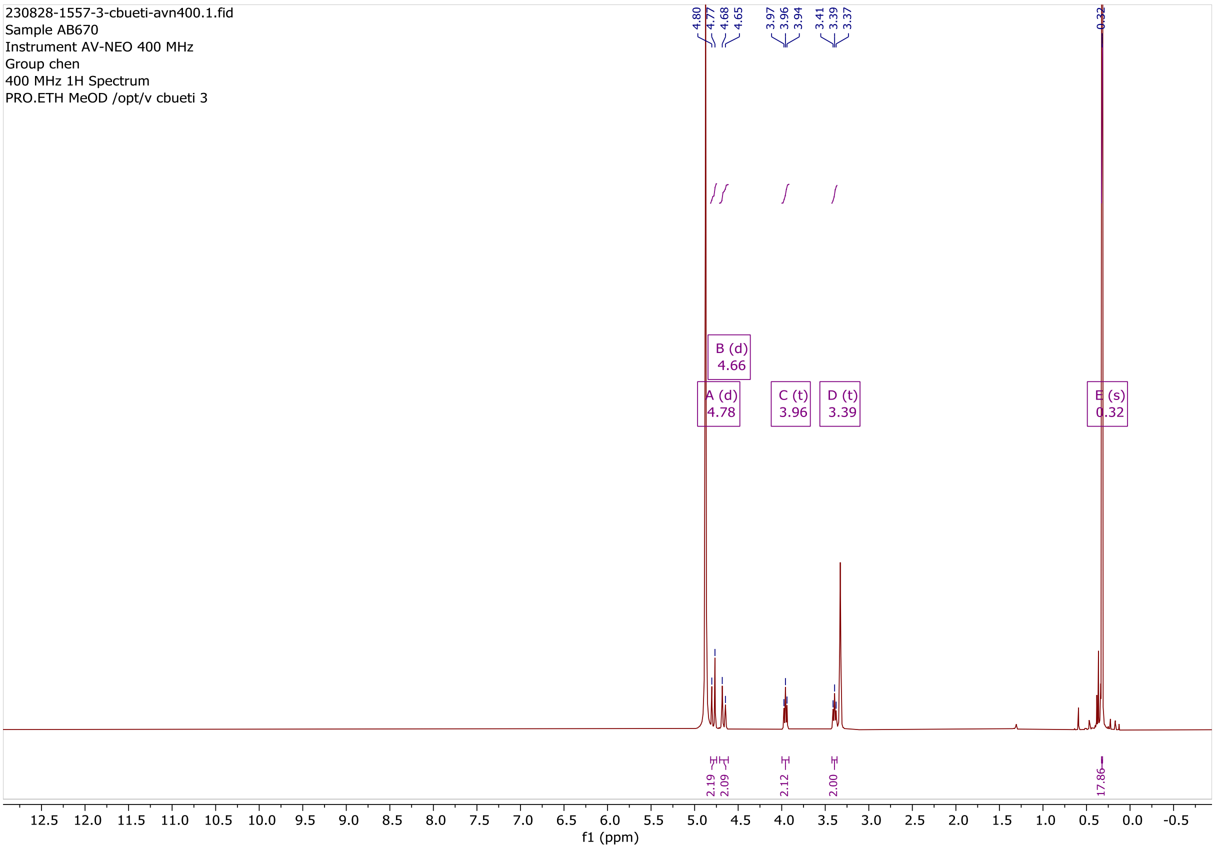


Figure S129. ^1H *NMR spectrum recorded in MeOH-d*$_4$*.*

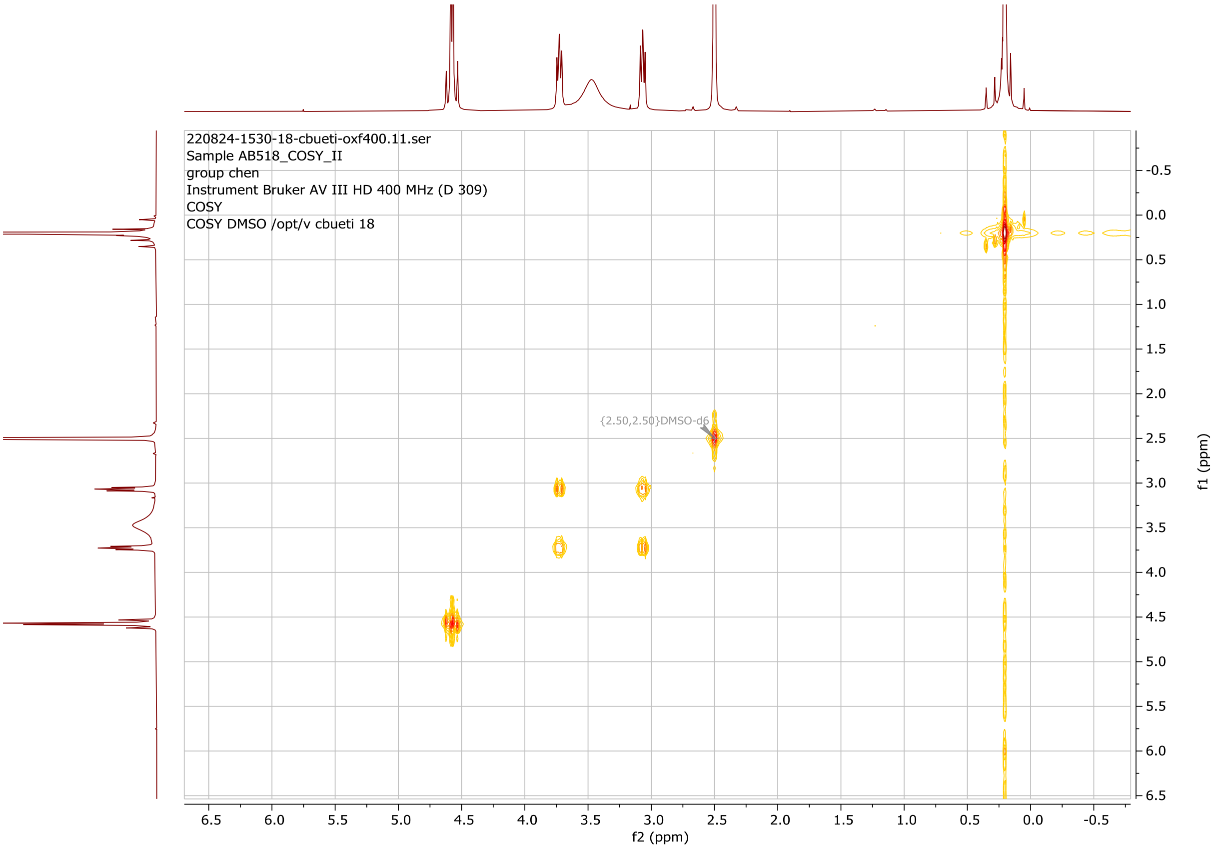


Figure S130. COSY recorded in DMSO-d$_6$*.*

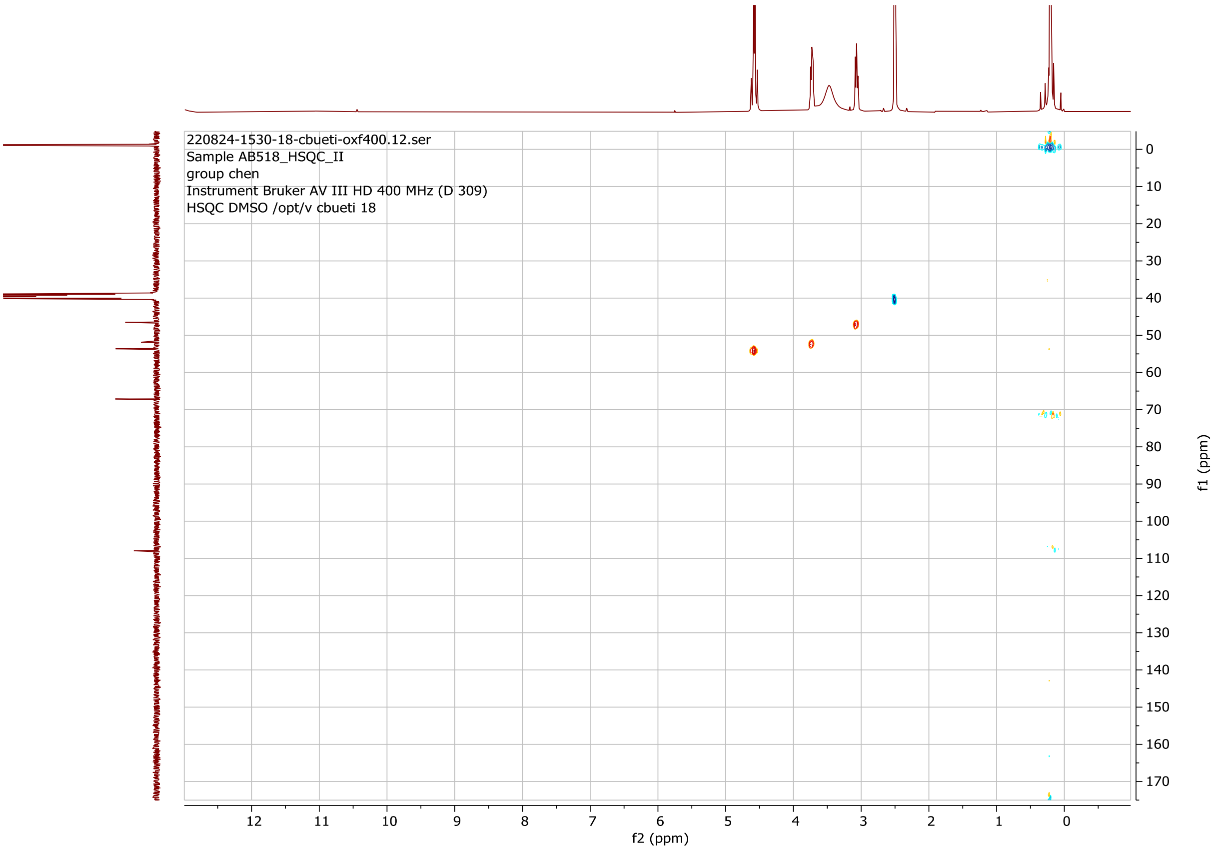


Figure S131. HSQC recorded in DMSO-d₆.

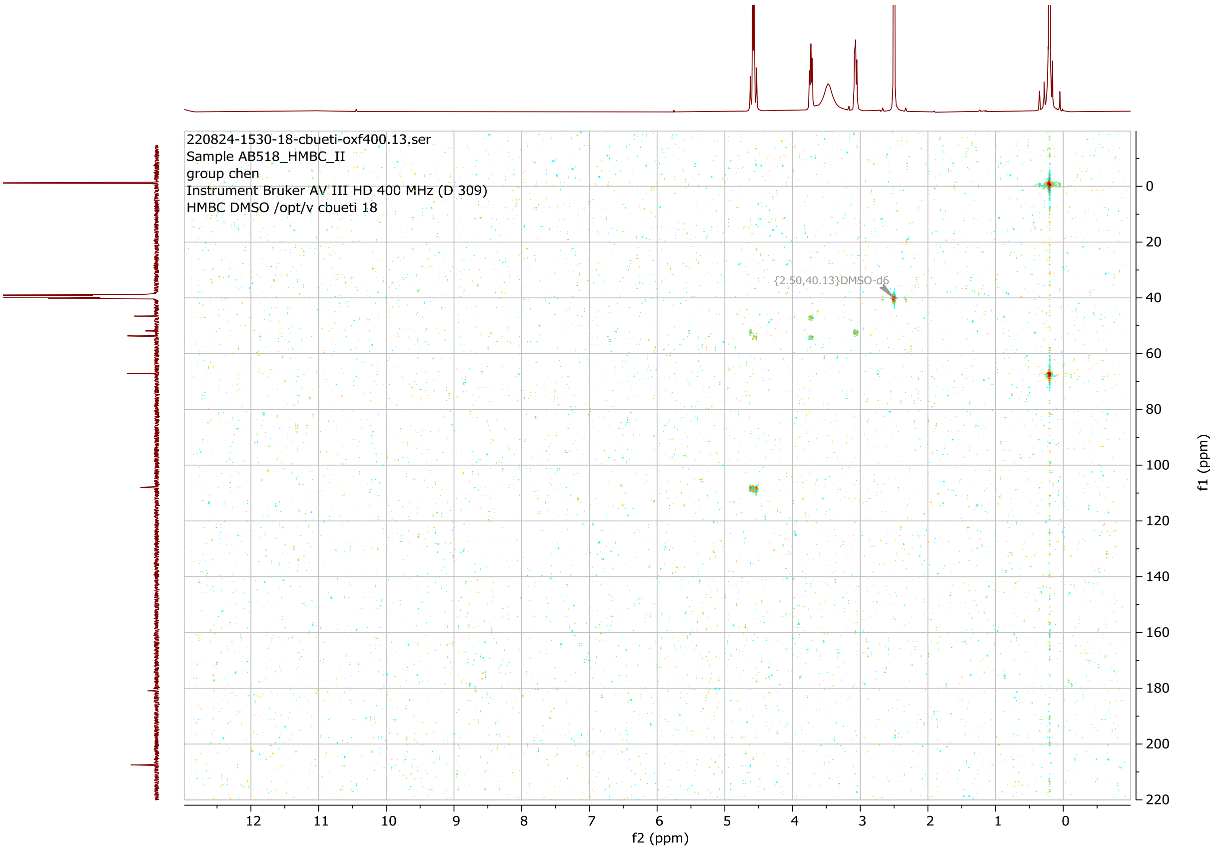


Figure S132. HMBC recorded in DMSO-d$_6$.

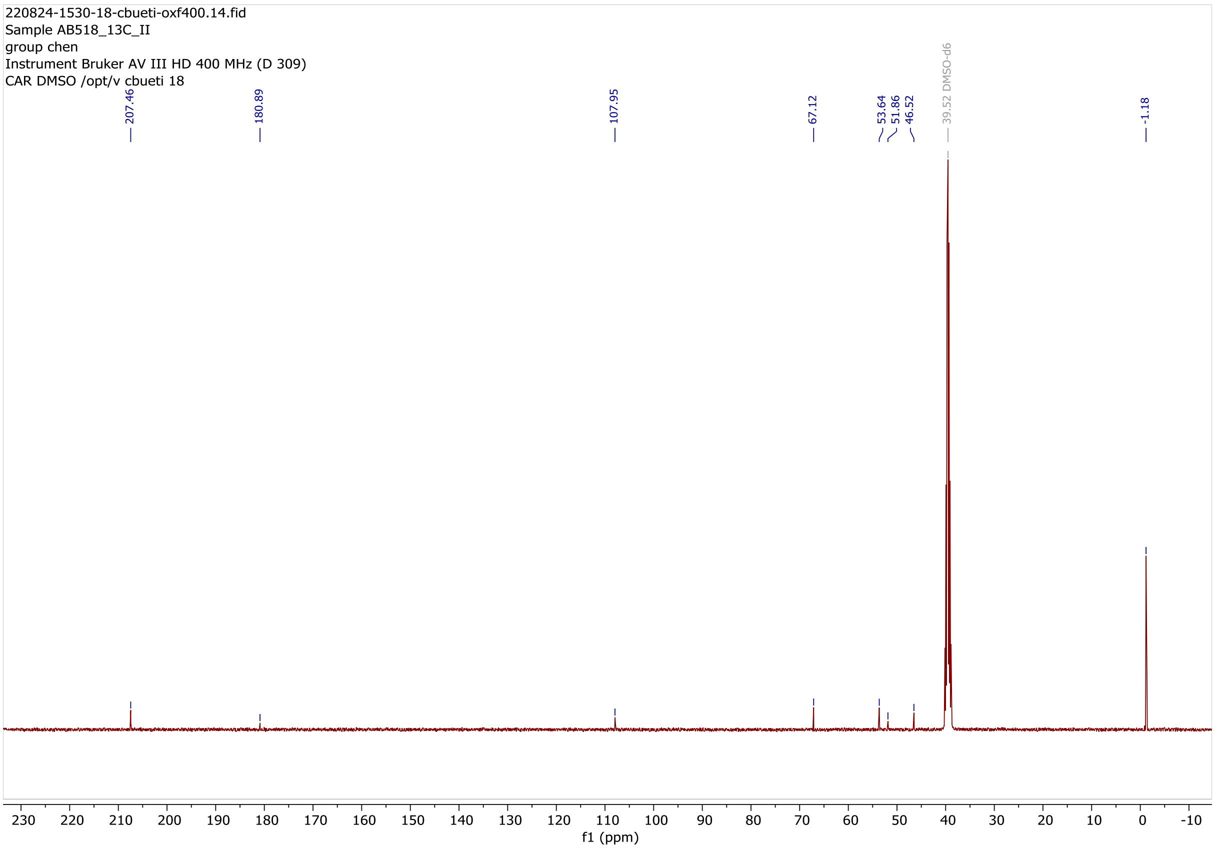


Figure S133. ^{13}C NMR spectrum recorded in DMSO-d$_6$.

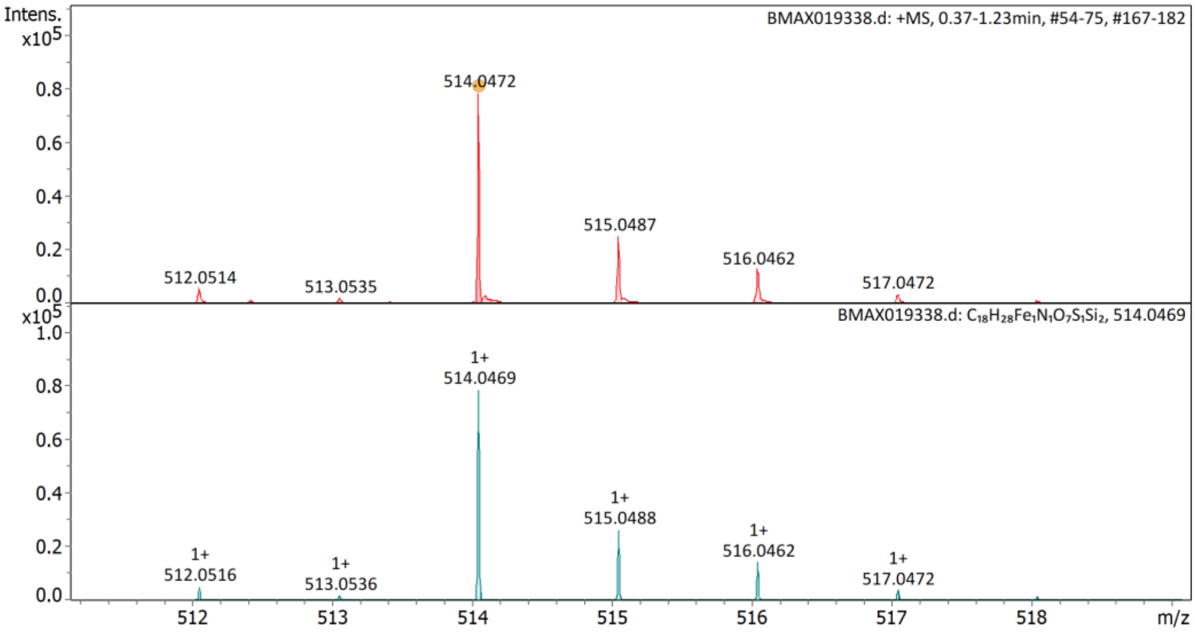


Figure S134. HRMS spectrum.

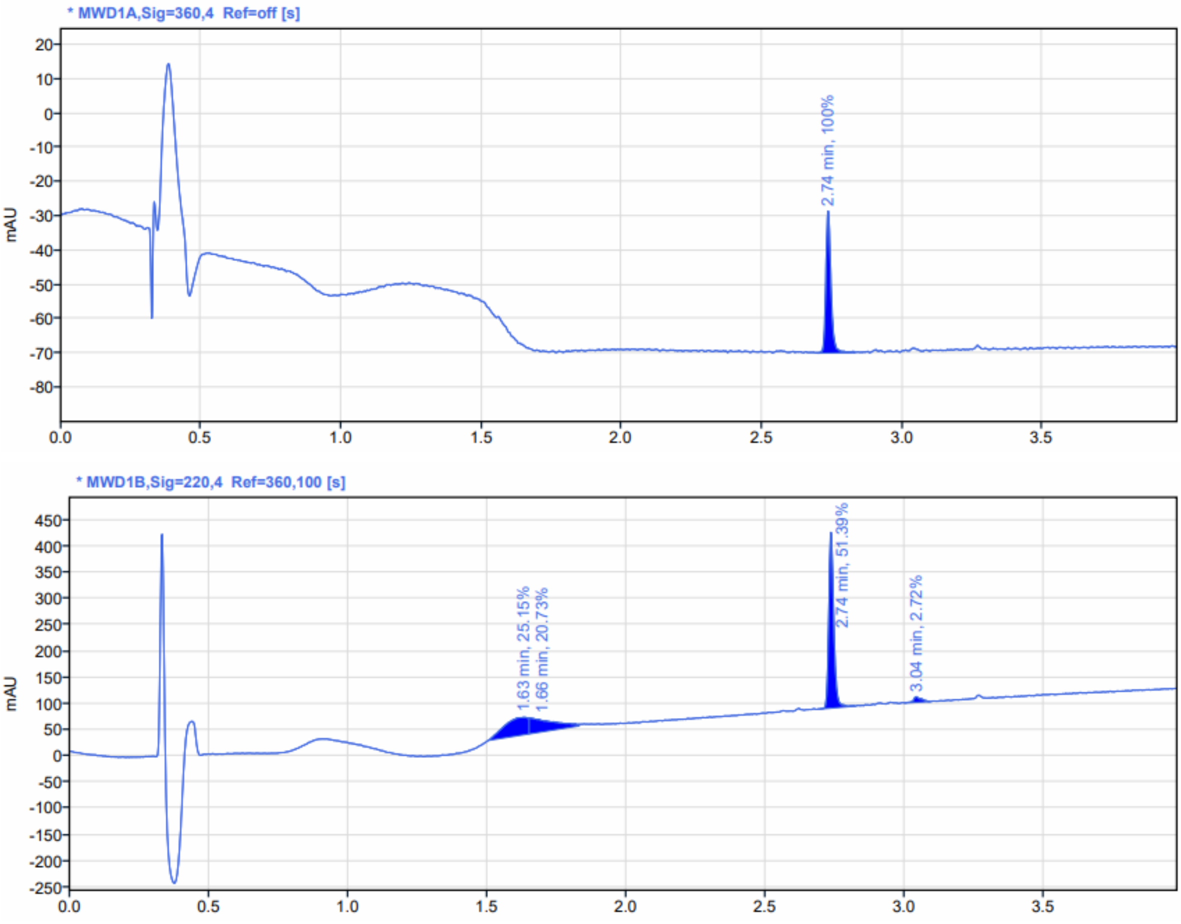
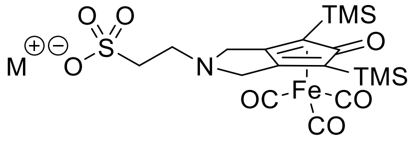


Figure S135. LC-MS UV traces. The peak at 2.74 min corresponds to the product.

1.22) **[Fe^{TMS}(CO)$_3$-SO$_3$]M** (M = Li, K, Rb, Cs)



Method A: **[Fe^{TMS}(CO)$_3$-SO$_3$]H** was dissolved in DCM (0.025 M). To the stirred solution, 3 equiv. M_2CO_3 (M = Li, K, Cs) was added. The mixture was stirred overnight. The next day, the mixture was directly loaded onto a short silica pad and eluted with 9:1 DCM/MeOH. After evaporation of the solvent and drying, the product was obtained as a yellow/orange solid (Li, 89 %; K, 15 %; Cs, 8 %).

Method B: **[Fe^{TMS}(CO)$_3$-SO$_3$]H** was dissolved in MeOH (0.019 M). To the solution, 1.05 equiv. MOH (M = Li, K, Rb, Cs) was added as a 0.1 M solution in water. The solution was concentrated under reduced pressure. The residue was purified by dissolving the residue in 9:1 DCM/MeOH and passing it through a short silica pad. After evaporation of the solvent and drying, the product was obtained as a yellow/orange solid (Li, 77 %; K, 82 %; Rb, 85 %; Cs, 72 %).

Purity and identity was confirmed by ^{1}H NMR and shows the same signals as the previously reported **[Fe^{TMS}(CO)$_3$-SO$_3$]Na** (*Organometallics* **2022**, 41, 2349).

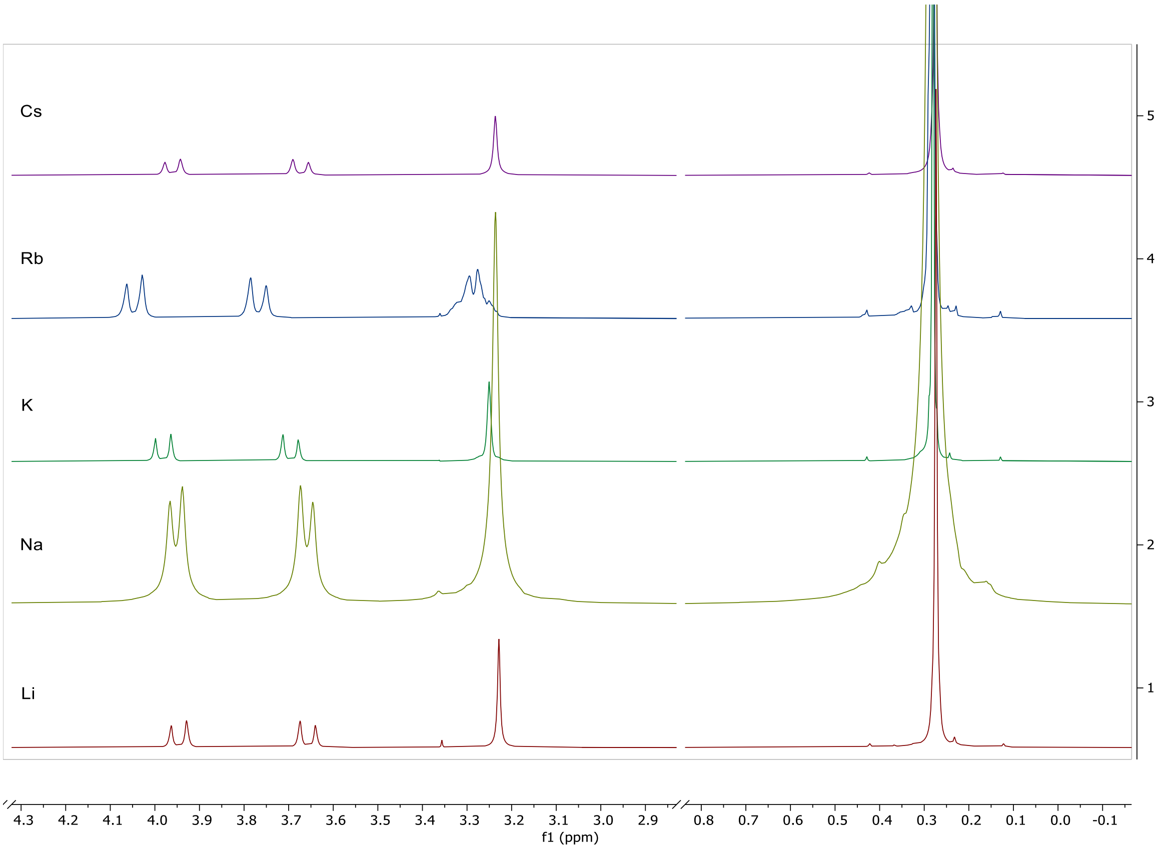
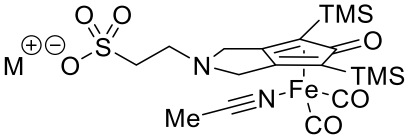


Figure S136. ^1H NMR spectra recorded in D_2O.

1.23) [Fe^{TMS}(MeCN)(CO)$_2$-SO$_3$]M (M = Li, K, Rb, Cs)



A dried and argon-flushed Schlenk tube equipped with a stir was charged with **[Fe^{TMS}(CO)$_3$-SO$_3$]M** (1 equiv.) and Me_3NO (1.5 equiv.). While stirring, dry MeCN (total concentration ca. 0.35 M). The solution was protected from light. A fine, yellow/orange precipitate was observed. After 2 h, the solution was cannula filtered. The residue was washed with MeCN. For M = Cs, diethyl ether was added to the MeCN suspension prior to cannula filtration. The washing steps were also performed with diethyl ether in this case. The residue was dried *in vacuo*. The product was obtained as a yellow/orange powder. (Li, 58 %; K, 59 %; Rb, 63 %; Cs, 77 %). Purity and identity was assessed by ^1H NMR and LC-MS and conforms to the previously reported **[Fe^{TMS}(MeCN)(CO)$_2$-SO$_3$]Na**[1].

^1H NMR (δ, 400 MHz, MeOH-d_4): 3.53 (d, *J* = 13.0 Hz, 2H), 3.16 (d, *J* = 13.0 Hz, 2H), 3.13 – 3.08 (m, 2H), 3.04 – 2.98 (m, 2H), 0.24 (s, 18H).

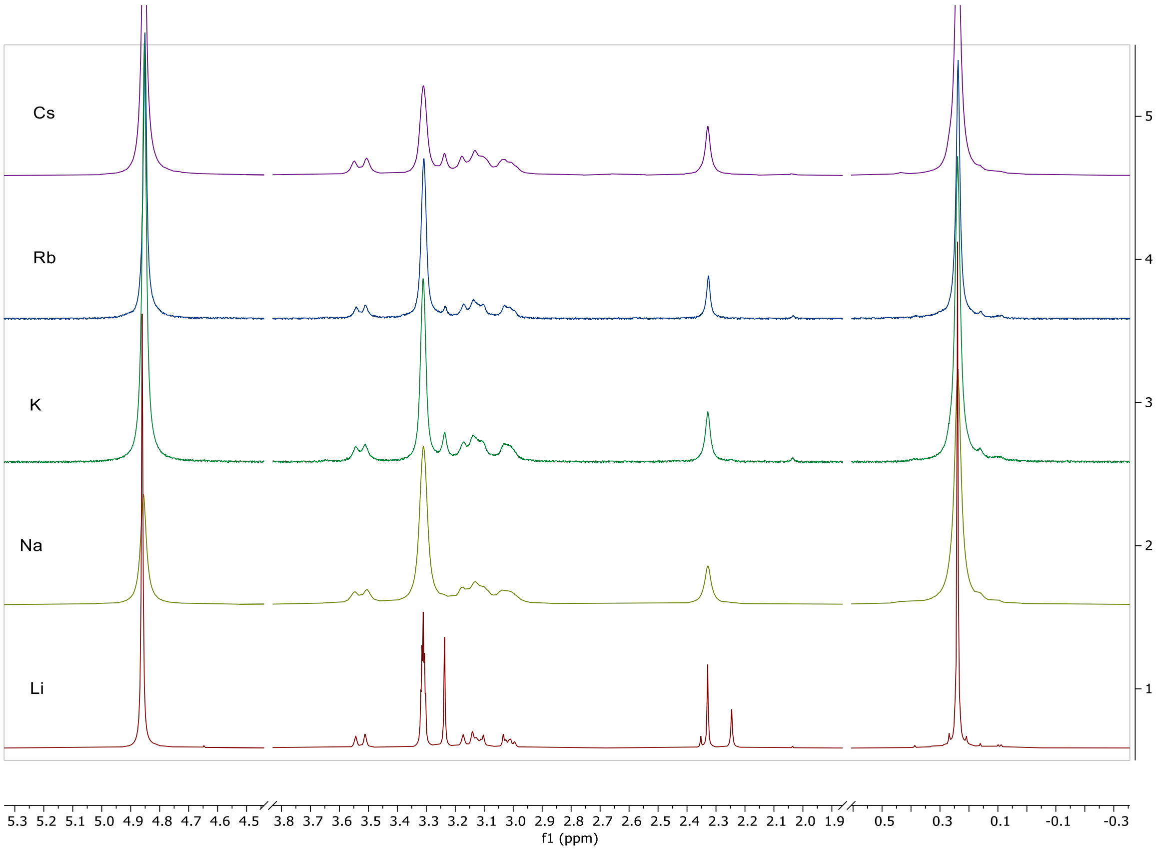


Figure S137. ^{1}H NMR spectra recorded in MeOH-d_4.

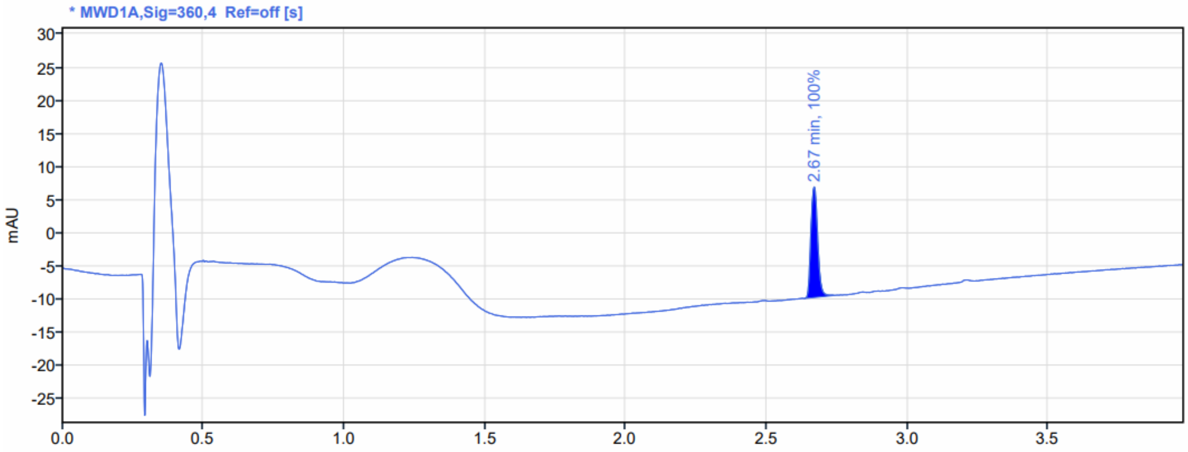
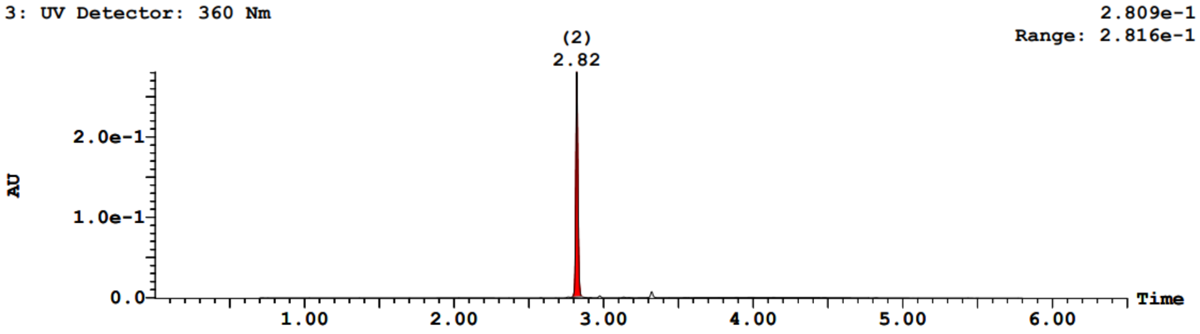


*Figure S138. LC-MS UV trace for **[Fe^{TMS}(MeCN)(CO)$_2$-SO$_3$]Li**.*



Peak Number	Time	Height	AreaAbs	Area %Total
2	2.82	280318	4746	100.00

Figure S139. LC-MS UV trace for ***[Fe^{TMS}(MeCN)(CO)$_2$-SO$_3$]Na****.*

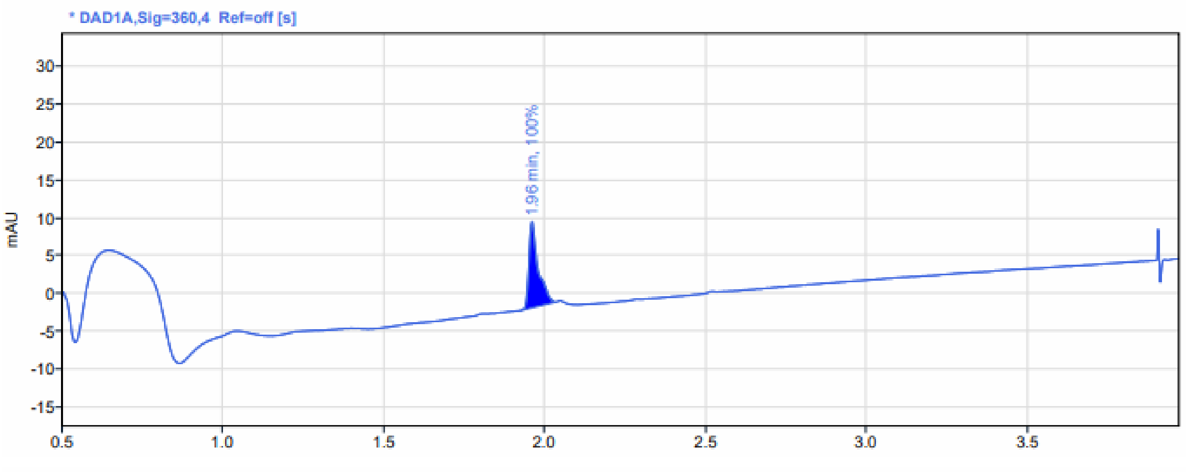


Figure S140. LC-MS UV trace for ***[Fe^{TMS}(MeCN)(CO)$_2$-SO$_3$]K****.*

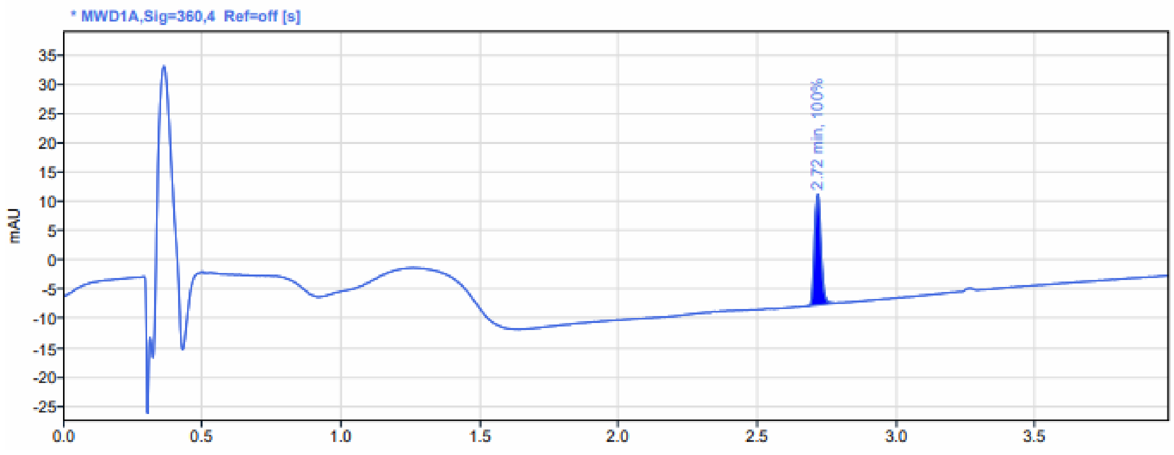


Figure S141. LC-MS UV trace for ***[Fe^{TMS}(MeCN)(CO)$_2$-SO$_3$]Rb****.*

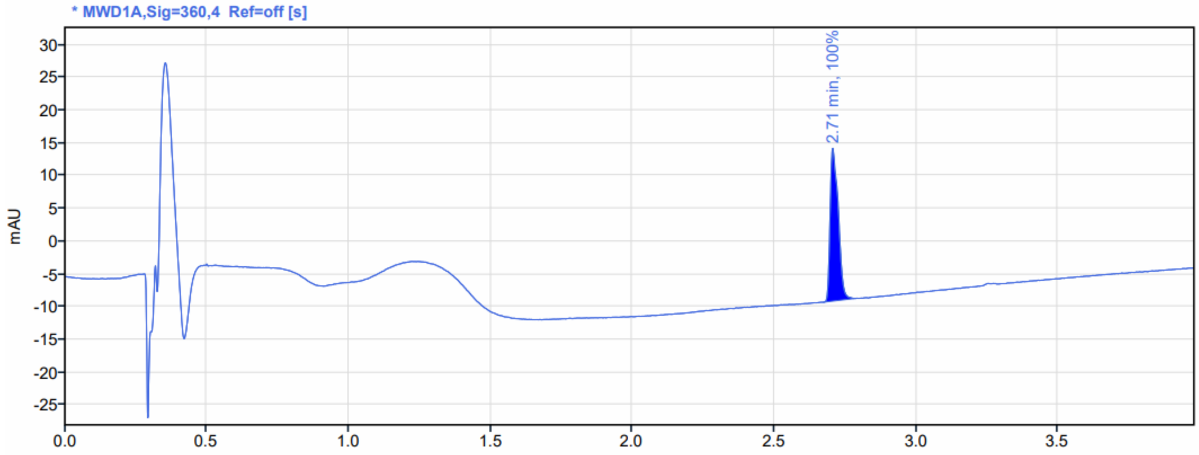
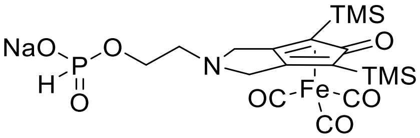


Figure S142. LC-MS UV trace for ***[Fe^{TMS}(MeCN)(CO)$_2$-SO$_3$]Cs****.*

2) Additional Syntheses

2.1) [Fe^{TMS}(CO)$_3$-OPH(O)$_2$]Na



A 50 ml round bottom flask was charged with 0.5 g **Fe^{TMS}(CO)$_3$-Cl** (0.91 mmol, 1 equiv.), 2 g disodium hydrogen phosphite pentahydrate (9.1 mmol, 10 equiv.), 5 ml H_2O and 5 ml EtOH. The flask was capped with a septum and the mixture sparged with N_2 for 30 min. The mixture was then stirred at 75 °C overnight. The mixture was allowed to cool to room temperature. The mixture was passed through a pad of silica and eluted with EtOH. The orange solution was concentrated under reduced pressure. The crude was purified by column chromatography (SiO_2, 9:1 DCM/MeOH + AcOH). The relevant fractions were collected and neutralized with aq. Na_2CO_3. The organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The remaining solid was dried *in vacuo*. The product was isolated as an orange solid (301 mg, 59 %).

TLC (SiO_2, 9:1 DCM/MeOH + AcOH): r_f = 0.1.

^{1}H NMR (δ, 500 MHz, D_2O): 6.76 (d, *J* = 635.0 Hz, 1H), 4.07 (dt, *J* = 8.0, 5.7 Hz, 2H), 3.96 (d, *J* = 13.8 Hz, 2H), 3.68 (d, *J* = 13.8 Hz, 2H), 3.10 (t, *J* = 5.7 Hz, 2H), 0.28 (s, 18H).

^{13}C NMR (δ, 125 MHz, D_2O): 207.7, 181.2, 112.9, 69.8, 61.8, 55.4, 53.0, -1.8. ^{31}P NMR (δ, 200 MHz, D_2O): 6.26 (dt, *J* = 635.0, 8.1 Hz).

^{31}P NMR (δ, 202.5 MHz, D_2O): 6.3.

Anal. calc. for $C_{18}H_{27}FeNNaO_7PSi_2$ (%): C, 40.38; H, 5.08; N, 2.62. Found: C, 40.55; H, 5.32; N, 2.56.

HRMS (m/z): $[M+H]^+$ calc. for $C_{18}H_{28}FeNNaO_7PSi_2$: 536.0375. Found: 536.0384.

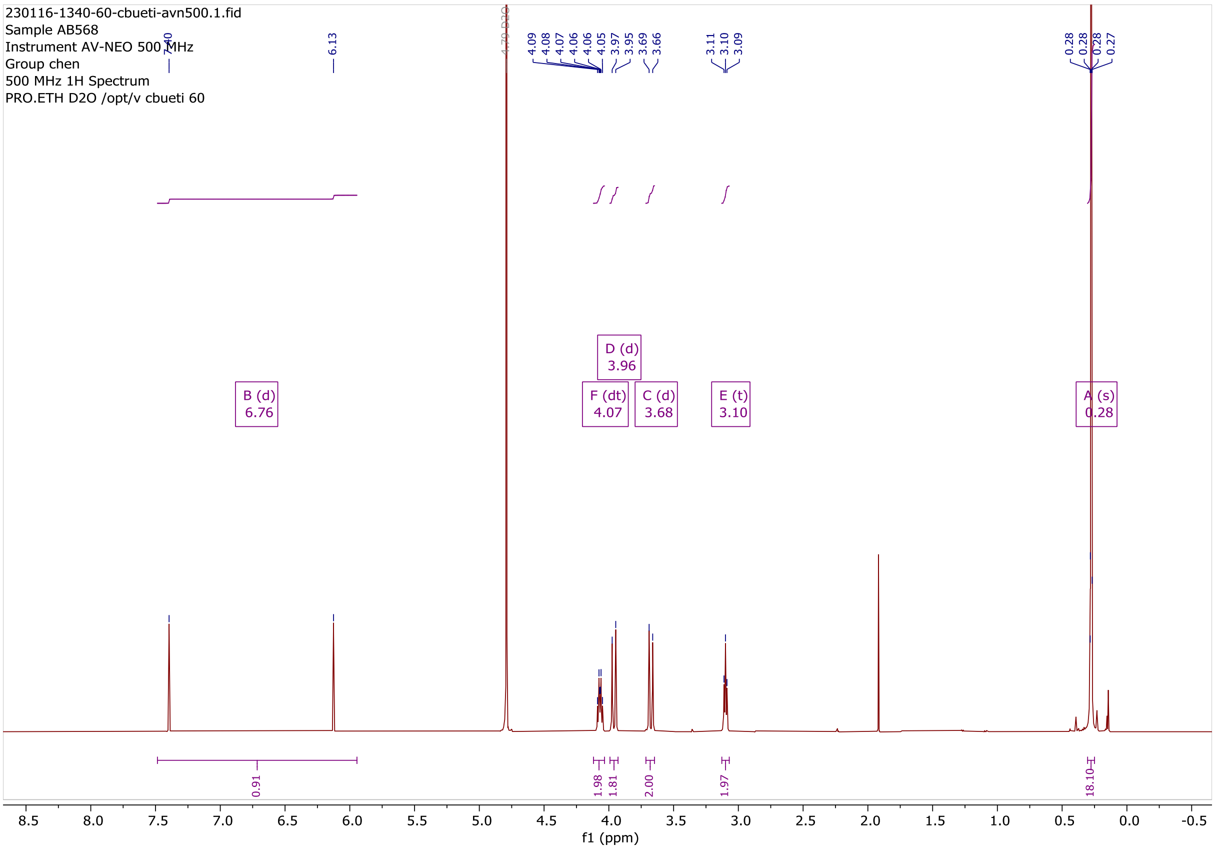


Figure S143. ^1H NMR spectrum recorded in D_2O.

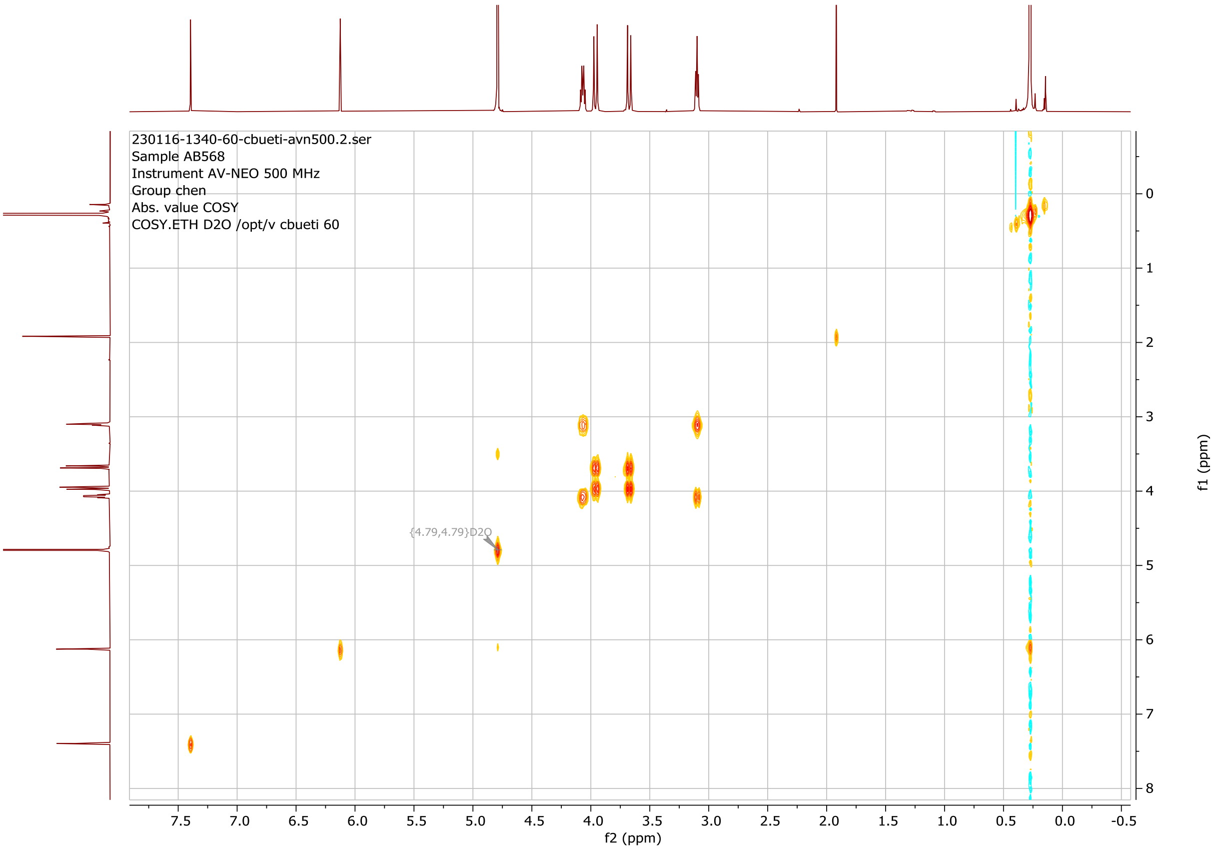


Figure S144. COSY spectrum recorded in D_2O.

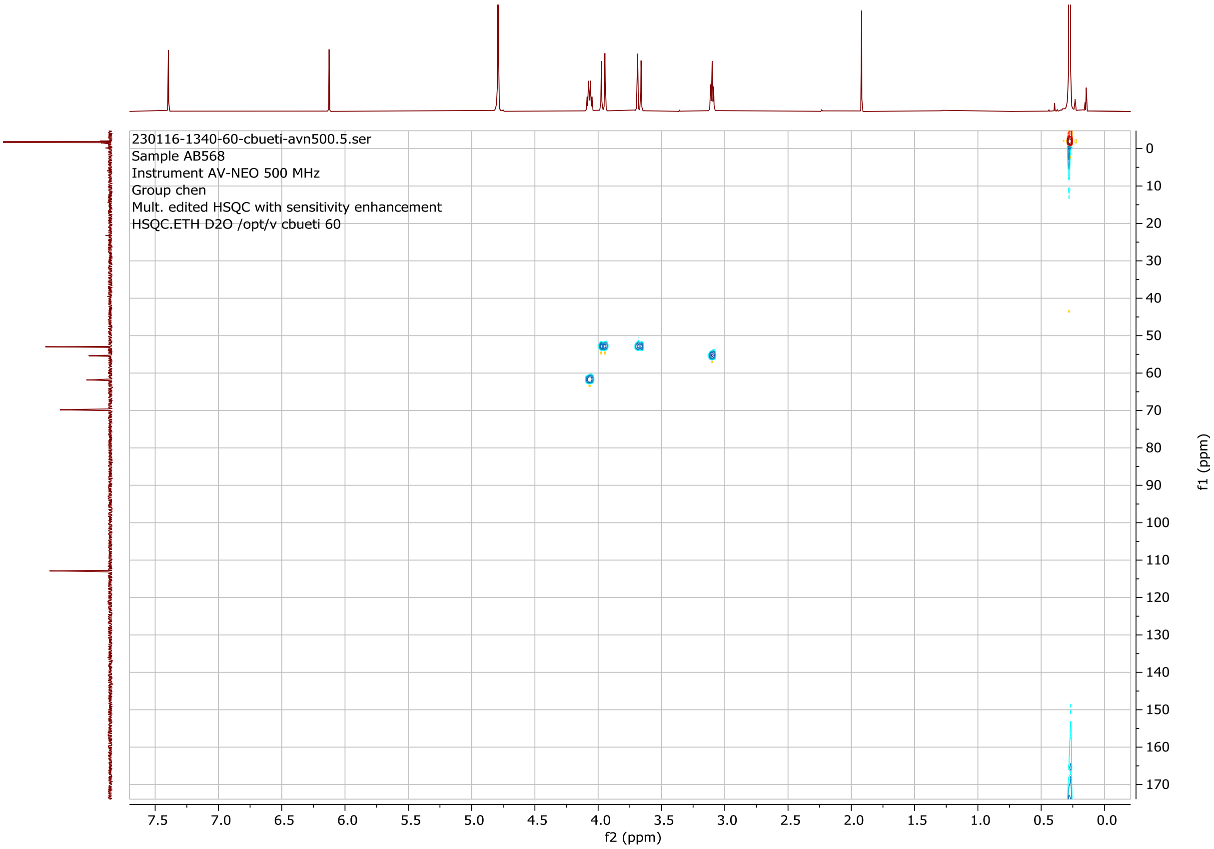


Figure S145. HSQC spectrum recorded in D_2O.

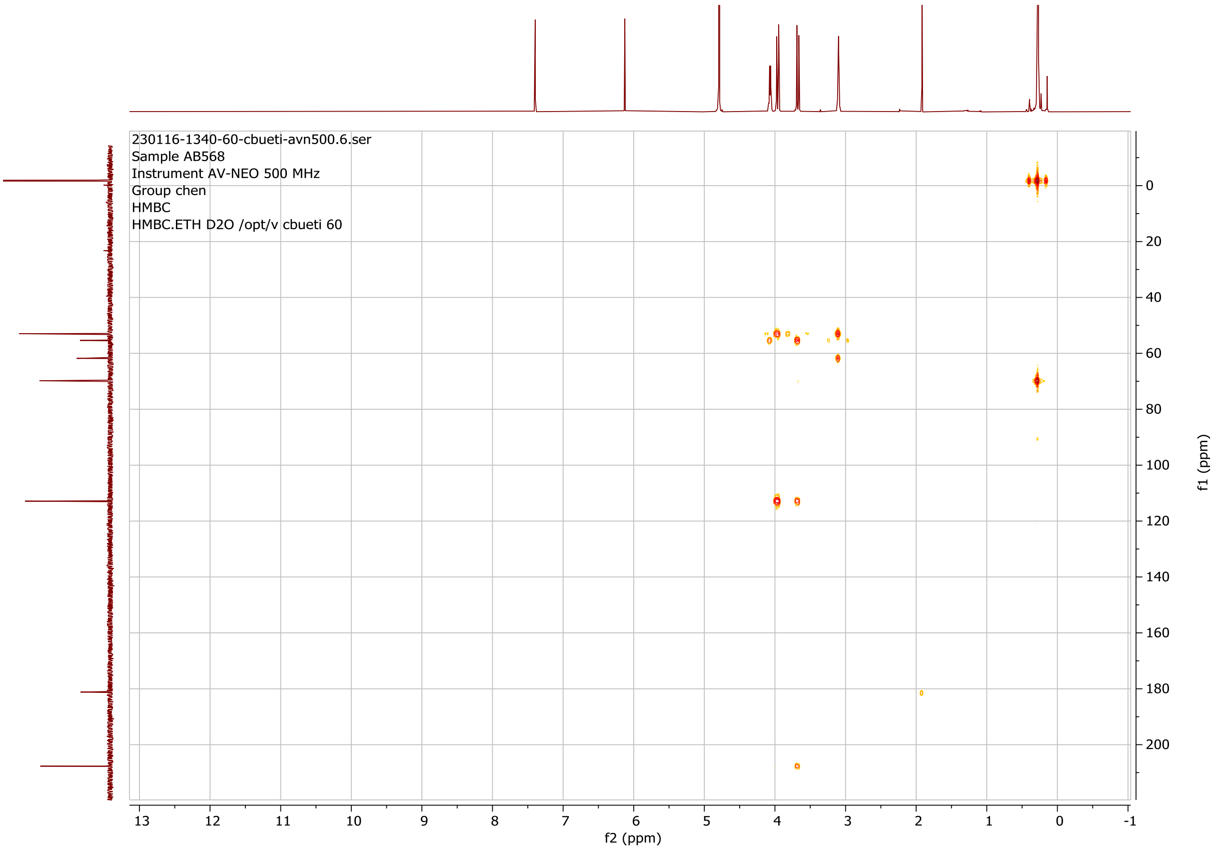


Figure S146. HMBC spectrum recorded in D_2O.

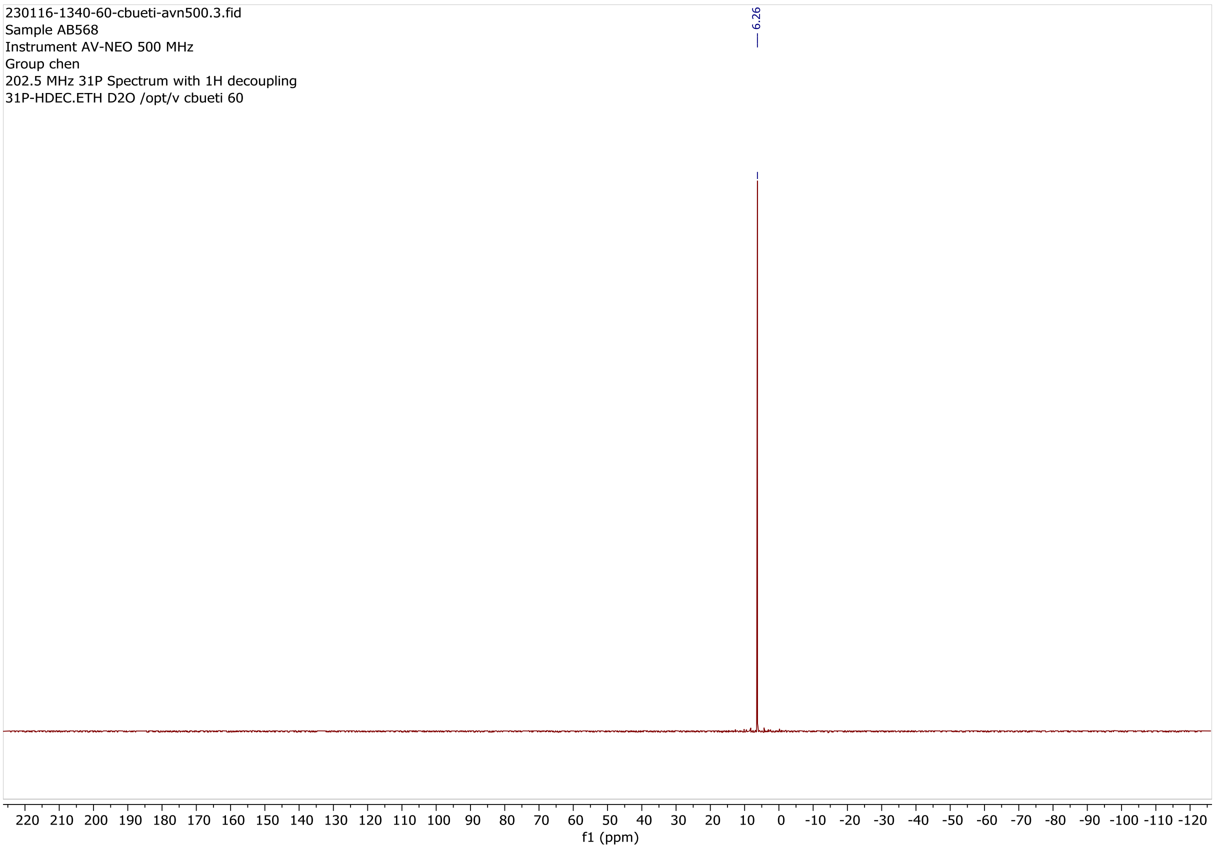


Figure S147. ^{31}P NMR spectrum recorded in D_2O with ^{1}H decoupling.

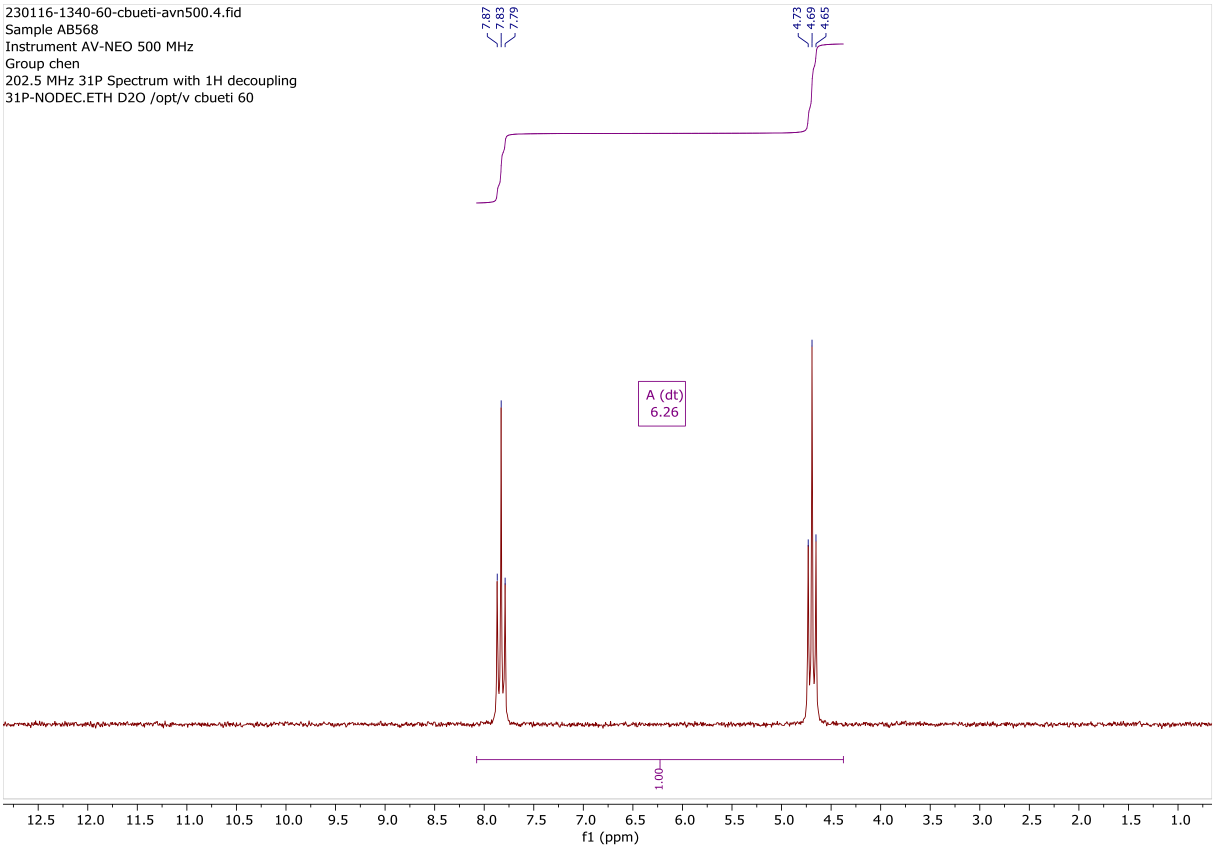


Figure S148. ^{31}P NMR spectrum recorded in D_2O without ^{1}H decoupling.

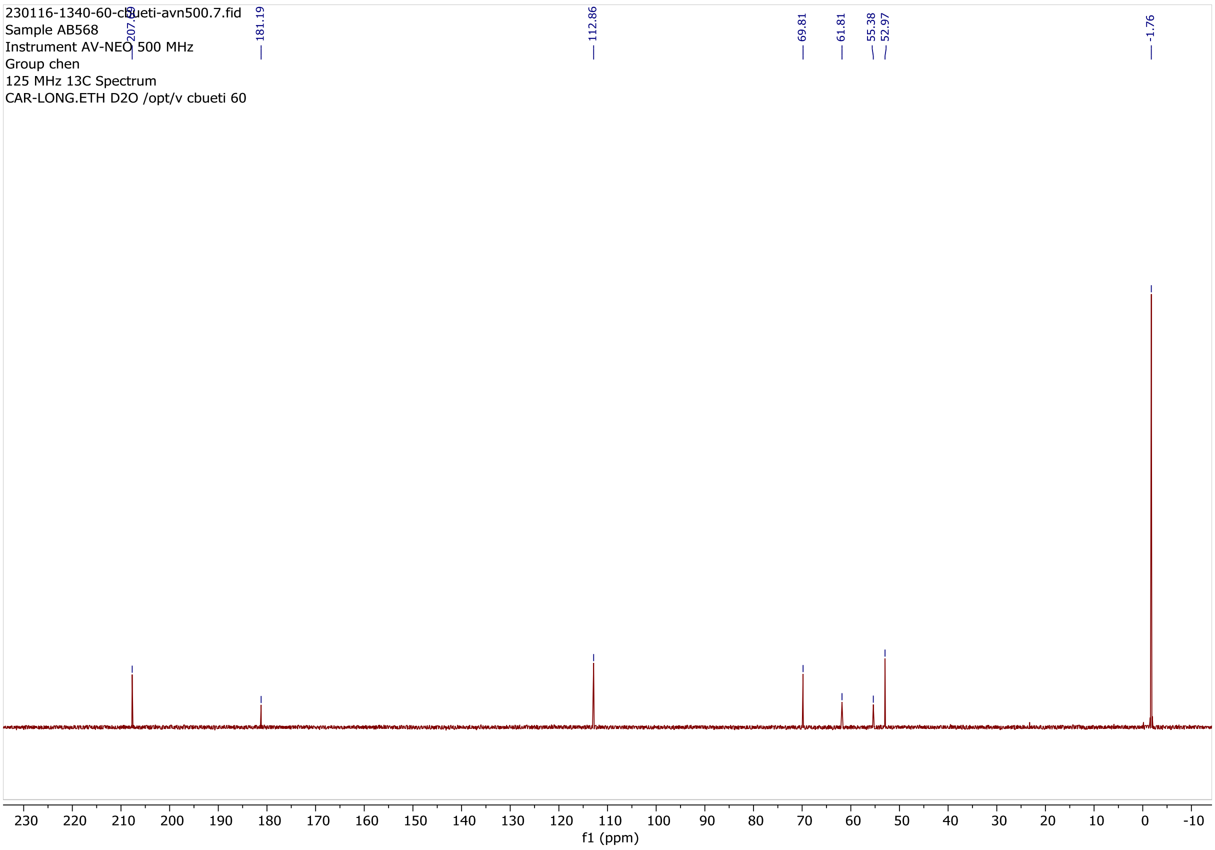


Figure S149. ^{13}C *NMR spectrum recorded in* D_2O.

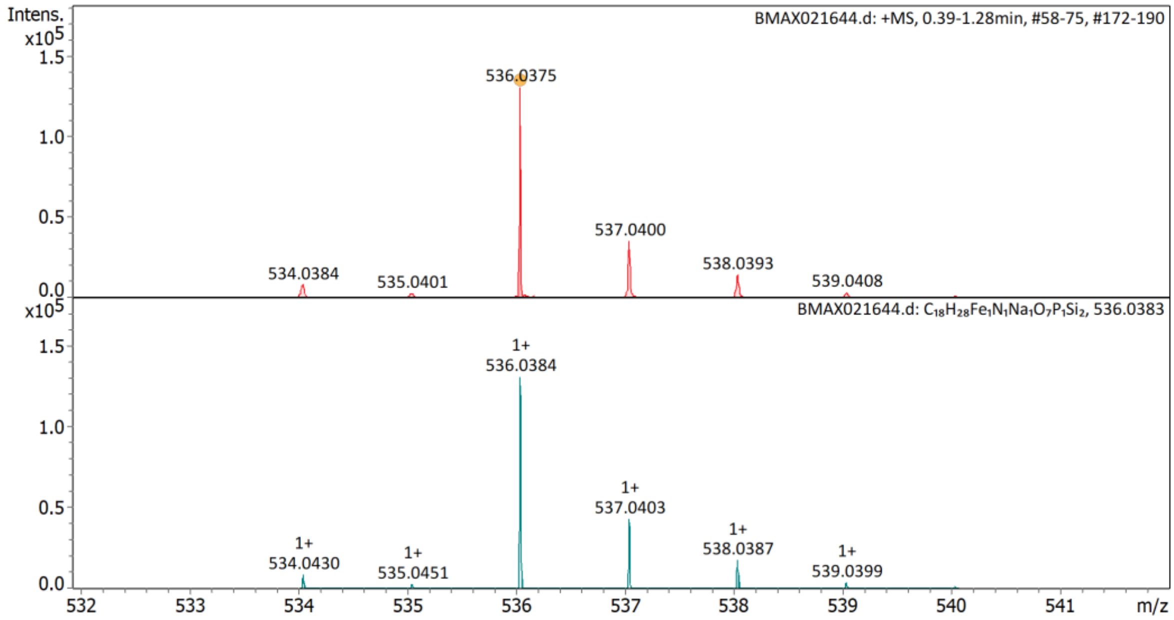


Figure S150. HRMS spectrum.

2.2) Attempted Synthesis of $\mathbf{Fe^{TMS}(CO)_3\text{-}P(O)(OEt)_2}$ via a Michaelis-Becker Reaction

A dried and argon flushed 50 ml 3-necked round bottom flask equipped with a dropping funnel and a stir bar was charged with 280 mg KO^{t}Bu (2.5 mmol, 5 equiv.). The dropping funnel was charged with 234 mg Fe^{TMS}(CO)$_3$-Cl (0.5 mmol, 1 equiv.). The KO^{t}Bu was dissolved in 5 ml dry DMF. The **Fe^{TMS}(CO)$_3$-Cl** was dissolved in 5 ml dry DMF. The KO^{t}Bu solution was cooled with an ice bath. To the cold KO^{t}Bu solution, 0.35 ml diethylphosphite (2.5 mmol, 5.5 equiv.) was added. The **Fe^{TMS}(CO)$_3$-Cl** solution was slowly added dropwise. The solution was allowed to warm up over the weekend.

The mixture was quenched with saturated ammonium chloride solution and extracted three times with EtOAc, washed three times with water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude was subjected to column chromatography (SiO_2, EtOAc). The relevant orange fractions (r_f = 0.4) were combined and concentrated under reduced pressure. 181 mg of an orange solid was isolated. ^1H and ^{31}P NMR spectroscopy revealed a mixture of *O*- and *P*-alkylation (^{31}P NMR (δ, 400 MHz, CDCl3): 121.0 [*O*-alkylation], 29.5 [*P*-alkylation]) products in a ca. 1:1 ratio. The isomers could not be separated by column chromatography.

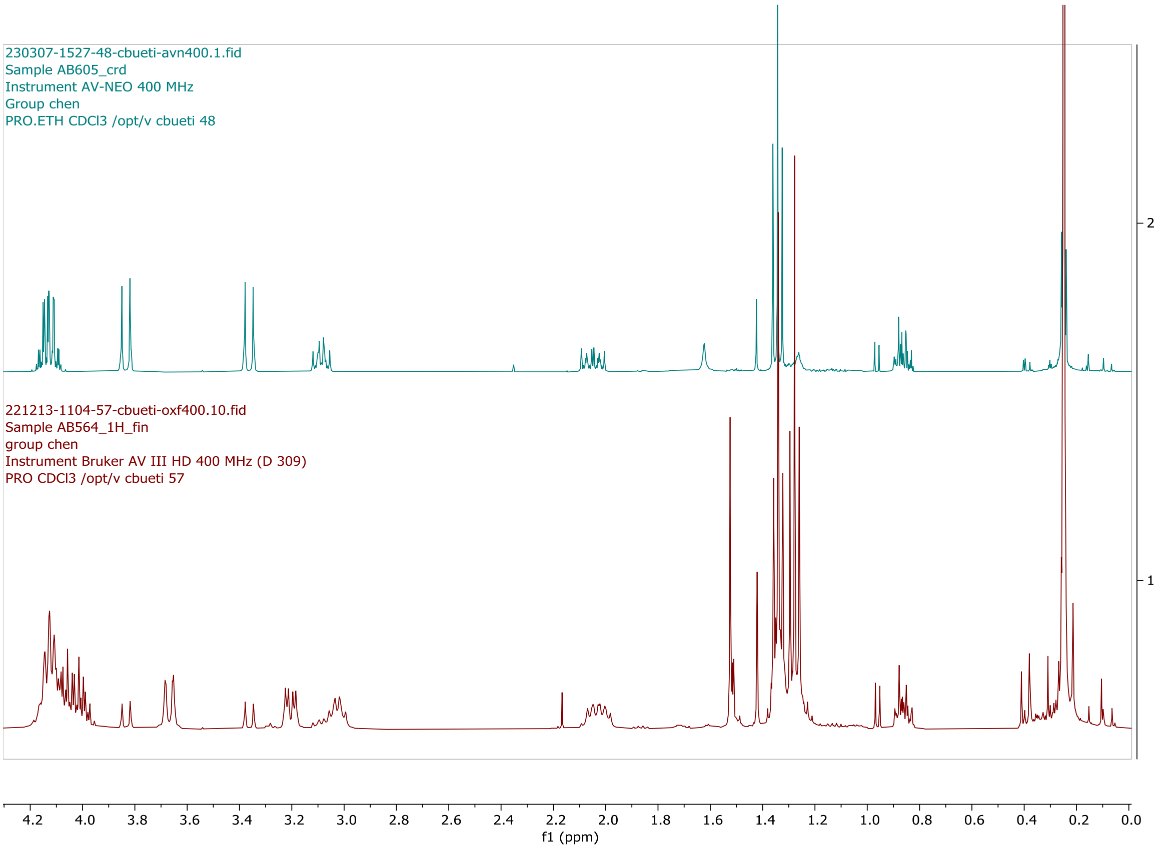


Figure S151. Stacked ^1H NMR spectra recorded in $CDCl_3$ of pure $Fe^{TMS}(CO)_3$-$P(O)(OEt)_2$ (upper spectrum) and the mixture obtained under Michaelis-Becker conditions (lower spectrum).

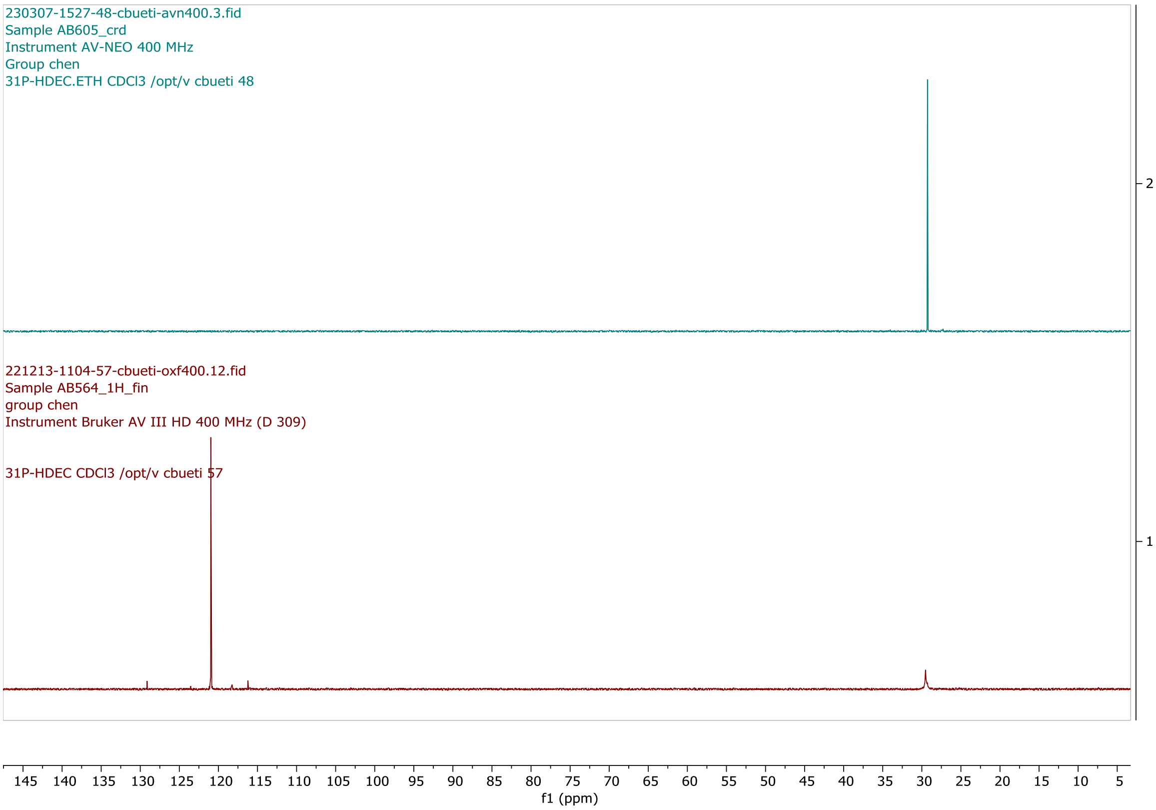


Figure S152. Stacked ^{31}P NMR spectra recorded in $CDCl_3$ of pure ***$Fe^{TMS}(CO)_3$-$P(O)(OEt)_2$*** *(upper spectrum) and the mixture obtained under Michaelis-Becker conditions (lower spectrum).*

3) [Fe^{TMS}(CO)$_3$-SO$_3$]Na activation

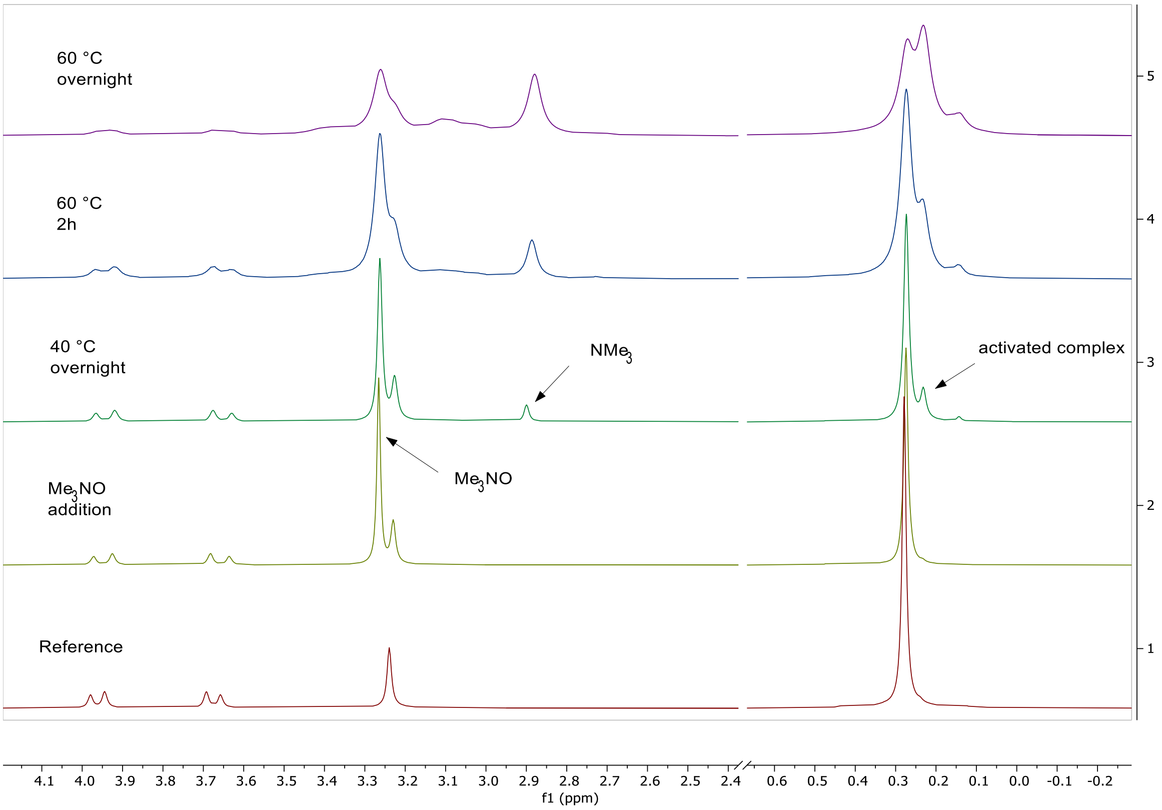


Figure S153. Activation of ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na*** *by Me$_3$NO in D$_2$O monitored by ^{1}H NMR. The signal for NMe$_3$ is located at 2.90 ppm, which corresponds to the shift of the free molecule in aqueous solution, indicating that no interaction between NMe$_3$ and the iron center takes place. No activation of the complex takes place at room temperature.*

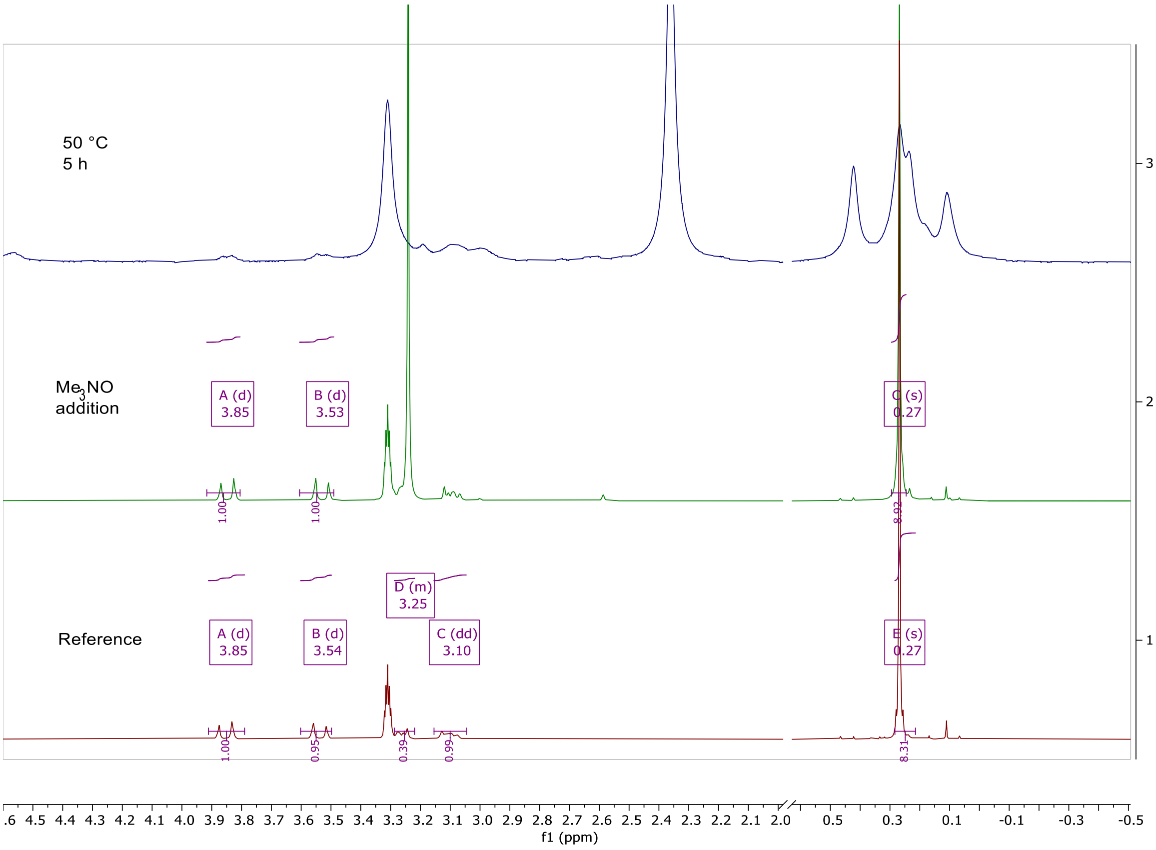


*Figure S154. Activation of **[Fe^{TMS}(CO)$_3$-SO$_3$]Na** by Me$_3$NO in MeOH-d$_4$ monitored by ^{1}H NMR. No activation of the complex takes place at room temperature.*

4) Foam Formation

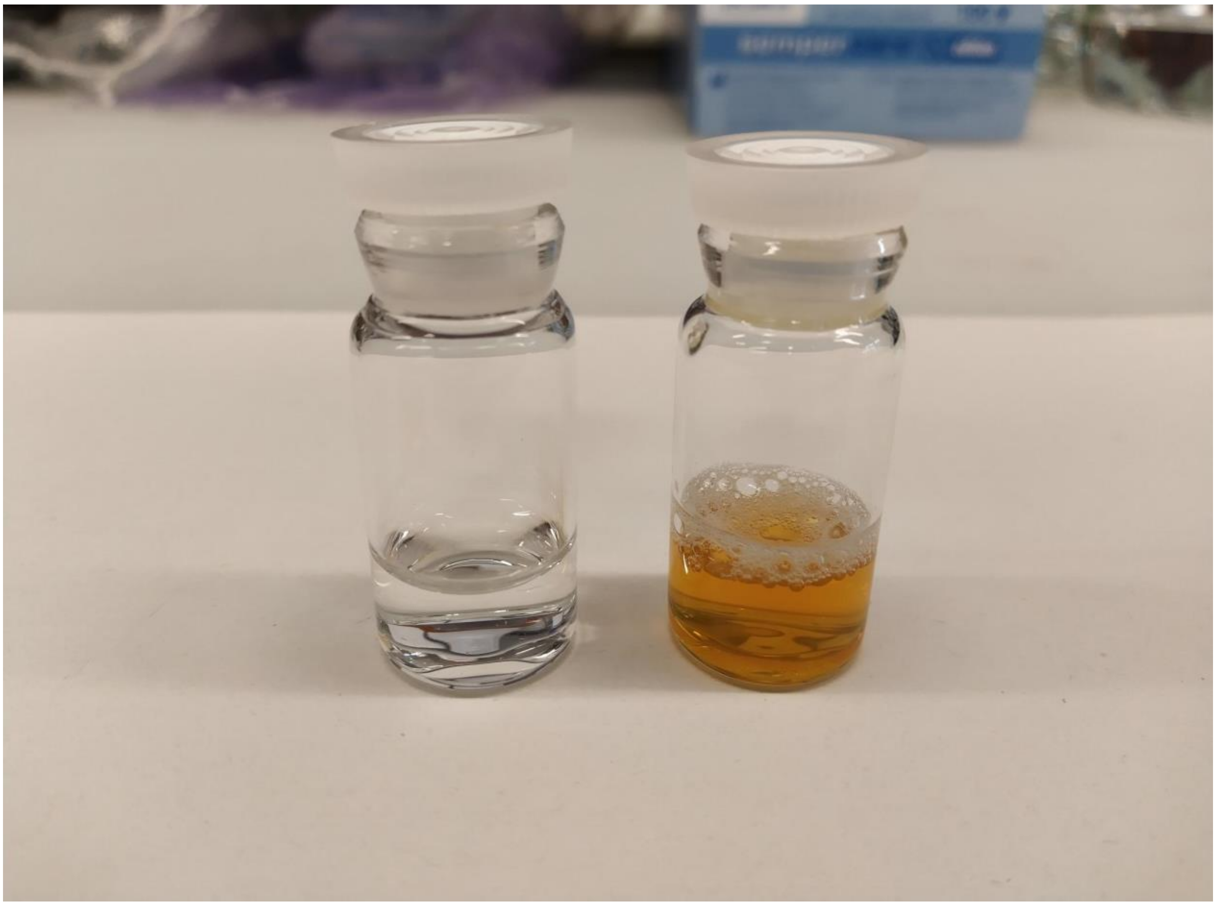


Figure S155. Photograph of distilled water (left) and ***$Fe^{TMS}(CO)_3$-SO_3Na*** *in water (right) after shaking. The orange solution containing the sulfonate charge-tagged complex displays foam formation, akin to a surfactant.*

5) In Situ Activation Kinetics

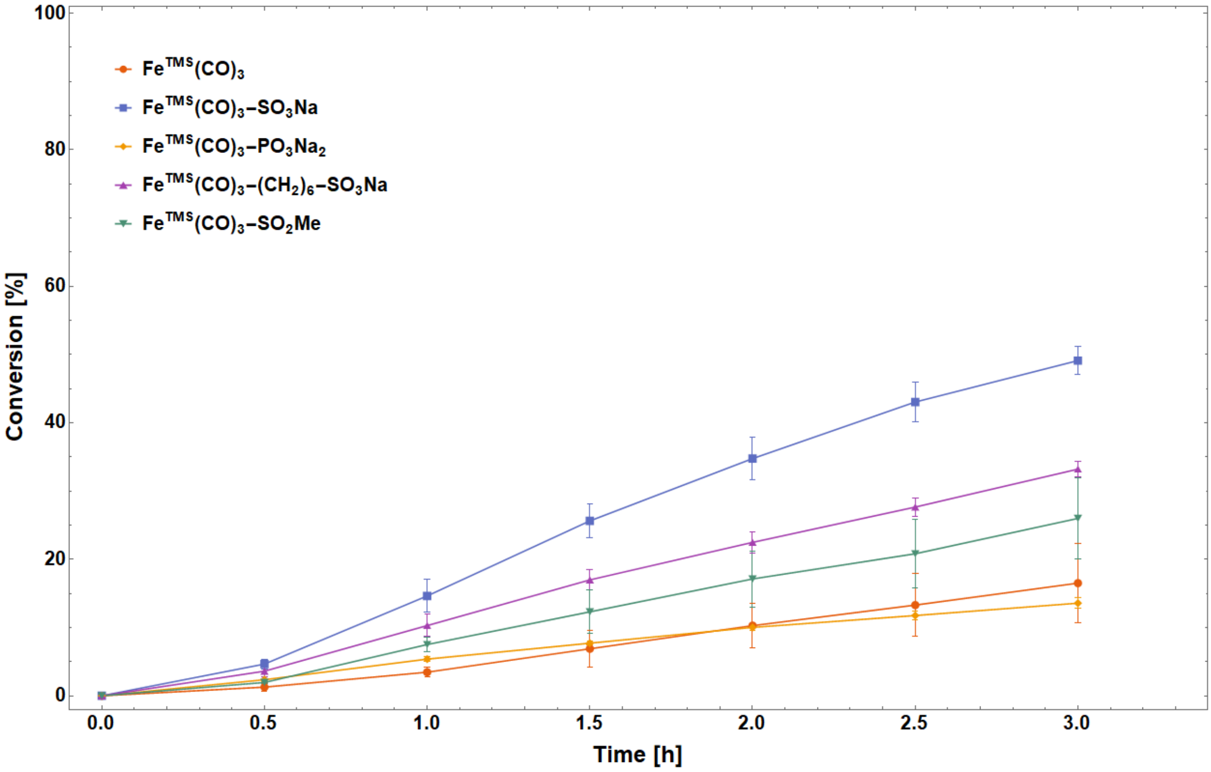


Figure S156. Kinetic profiles fro the hydrogenation of acetophenone using different charged and uncharged catalysts. Reaction conditions: 1 mol% catalyst loading, 1.5 mol% Me_3NO, 3:1 H_2O/^{i}PrOH, 90 °C 10 bar H_2, 0.5 M in acetophenone. Conversions determined by ^{1}H NMR. All traces were recorded in triplicates. Error bars denote one standard deviation.

6) Critical Micelle Concentration Determination by ^{1}H NMR

According to theory (Chachaty, C., *Progress in Nuclear Magnetic Resonance Spectroscopy* **1987**, 19, 183), under assumption of the pseudophase model and with a fast exchange rate between monomers in the bulk solution and molecules in micelles, the change in observed chemical shift $\Delta\delta$ is

$$\Delta\delta = \delta_{mic} - \frac{CMC}{c_{tot}}(\delta_{mic} - \delta_{mono})$$

where δ_{mic} is the chemical shift of the surfactant molecule in the micelle, CMC is the critical micelle concentration, c_{tot} is the total surfactant concentration and δ_{mono} and is chemical shift of the free monomer in solution. Below the CMC, the observed chemical shift corresponds to the chemical shift of the free monomer in solution δ_{mono}. Above the CMC, the chemical shift changes linearly with the inverse total concentration. Plotting $\Delta\delta$ against $\frac{1}{c_{tot}}$ therefore allows for the determination of δ_{mic} by extrapolation to $\frac{1}{c_{tot}} \rightarrow 0$ and the CMC *via* the intersection between the two linear regimes in the plots.

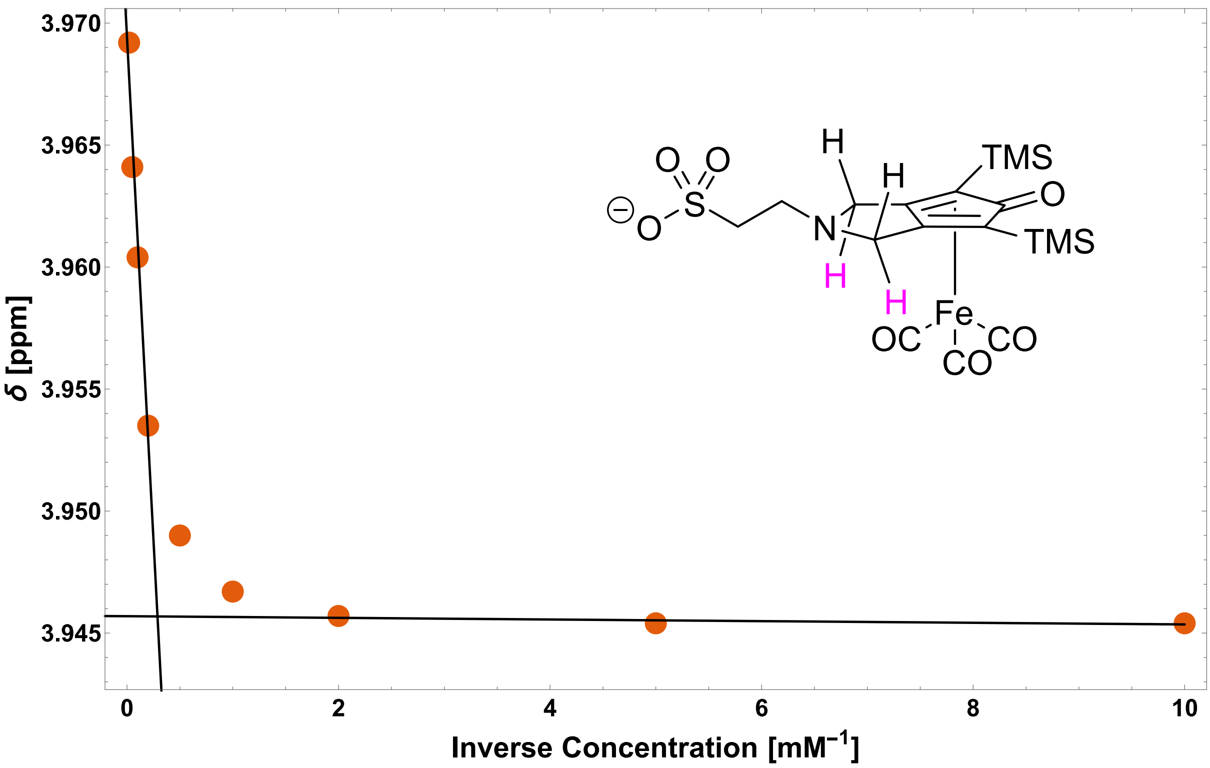


Figure S157. *^{1}H NMR shift of the endo-methylene protons in* ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na*** *depending on the inverse total concentration. The solid black lines correspond to linear regressions in the linear regimes of the plot. The intercept of the two lines gives the CMC. Chemical shifts are referenced to residual HDO at 4.79 ppm.*

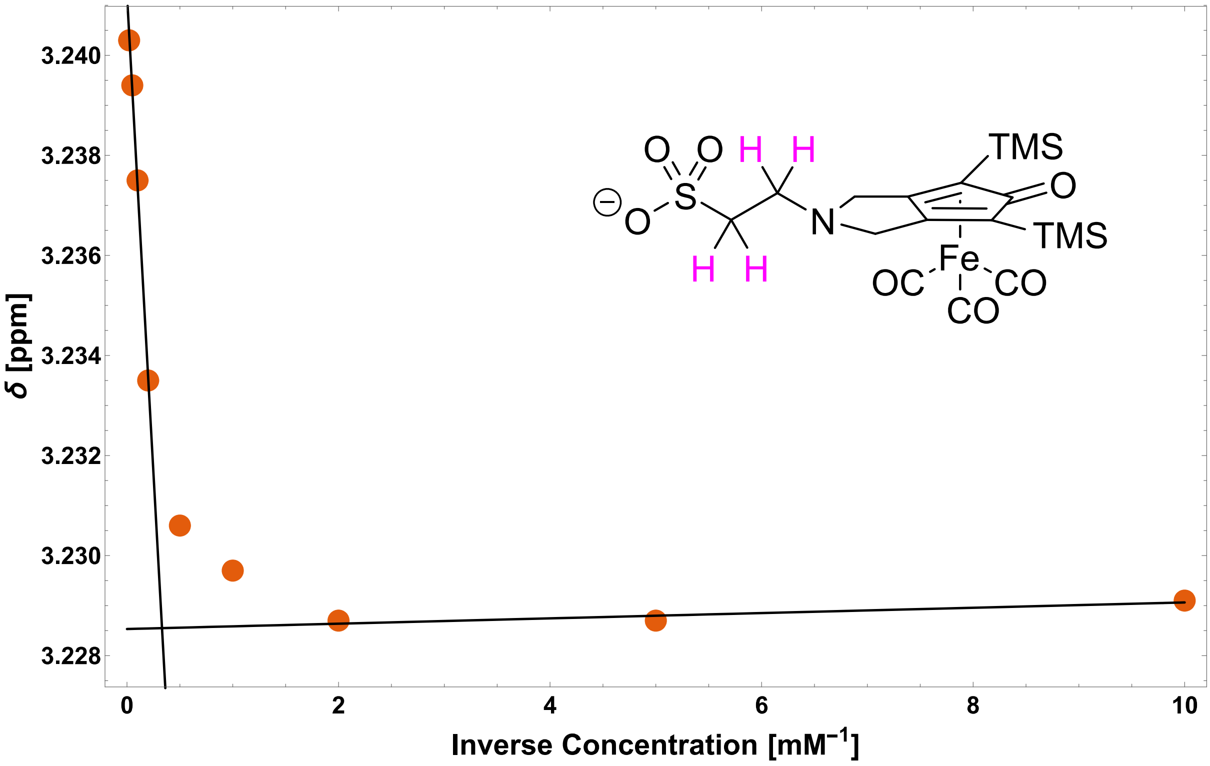


Figure S158. *^{1}H NMR shift of the ethylene protons in* ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na*** *depending on the inverse total concentration. The solid black lines correspond to linear regressions in the linear regimes of the plot. The intercept of the two lines gives the CMC. Chemical shifts are referenced to residual HDO at 4.79 ppm.*

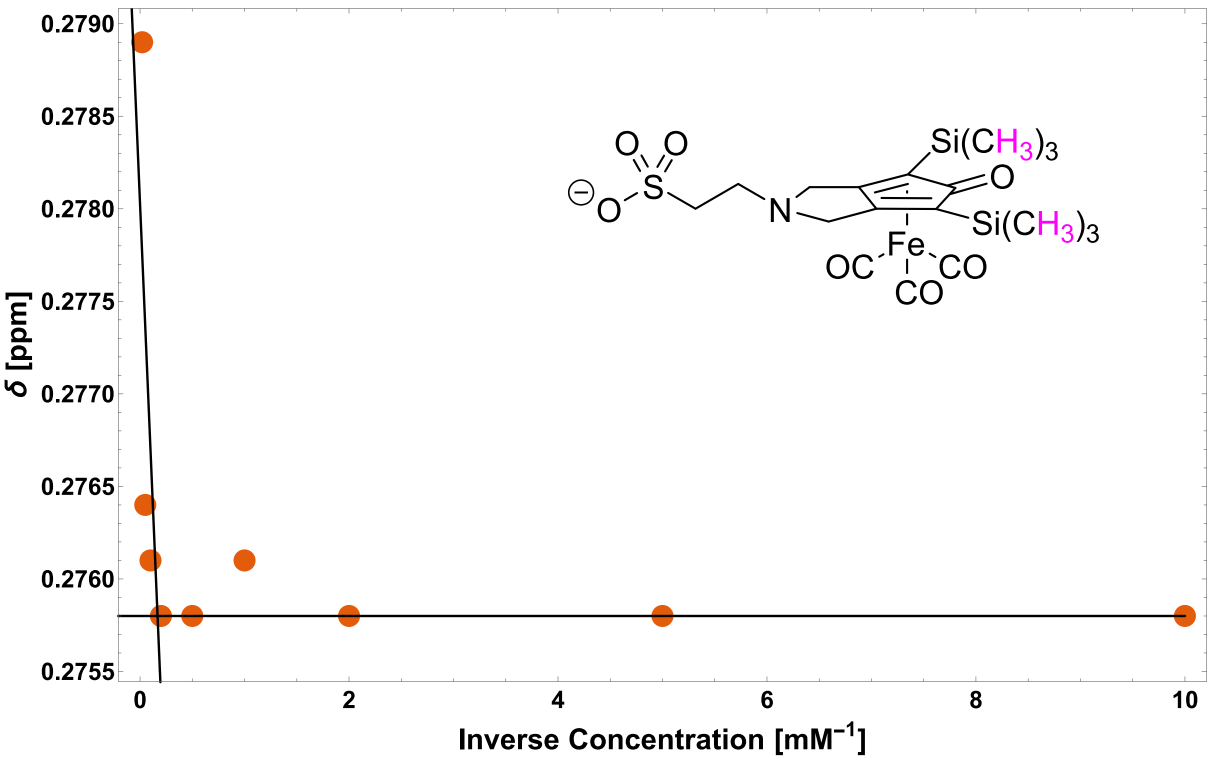


Figure S159. ^{1}H NMR shift of the TMS protons in ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na*** *depending on the inverse total concentration. The solid black lines correspond to linear regressions in the linear regimes of the plot. The intercept of the two lines gives the CMC. Chemical shifts are referenced to residual HDO at 4.79 ppm.*

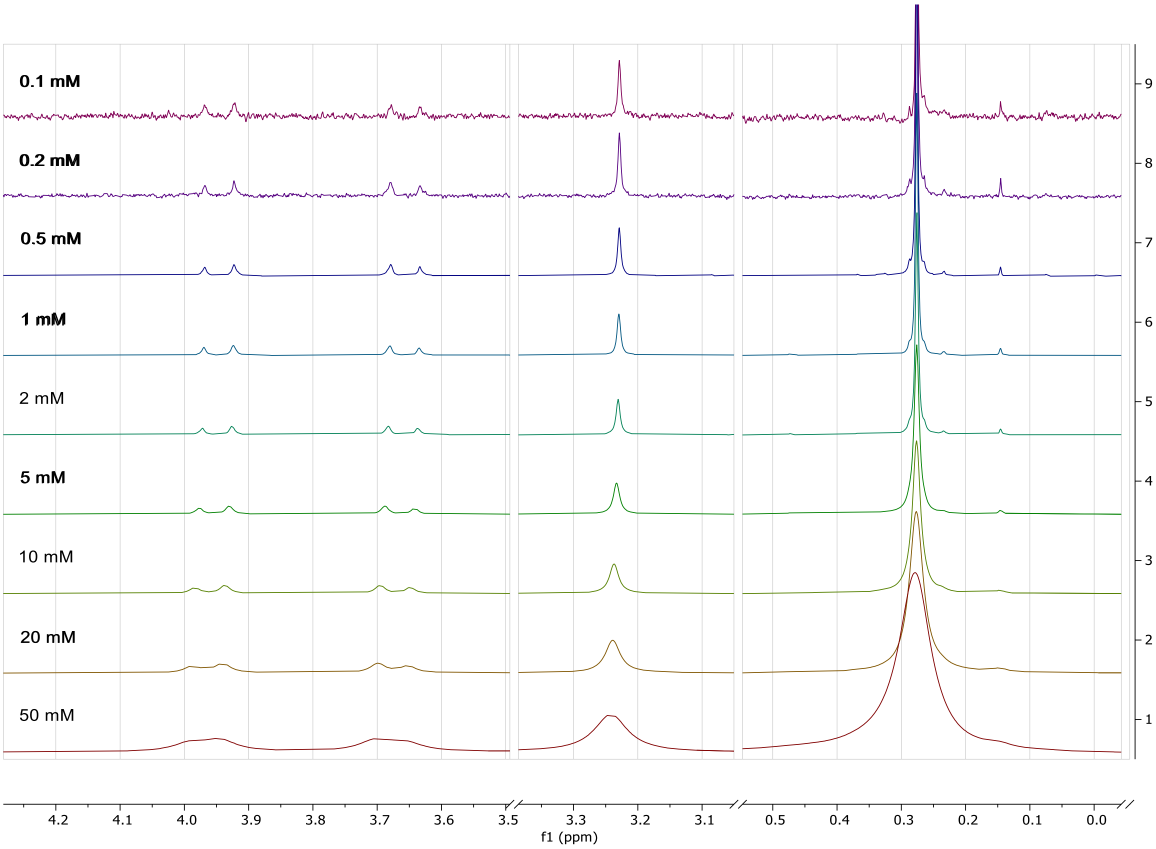


Figure S160. Stacked ^{1}H NMR spectra of ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na*** *recorded in D$_2$O at different concentrations. Spectra were obtained at room temperature on a 300 MHz spectrometer. Peaks reference to HDO at 4.79 ppm.*

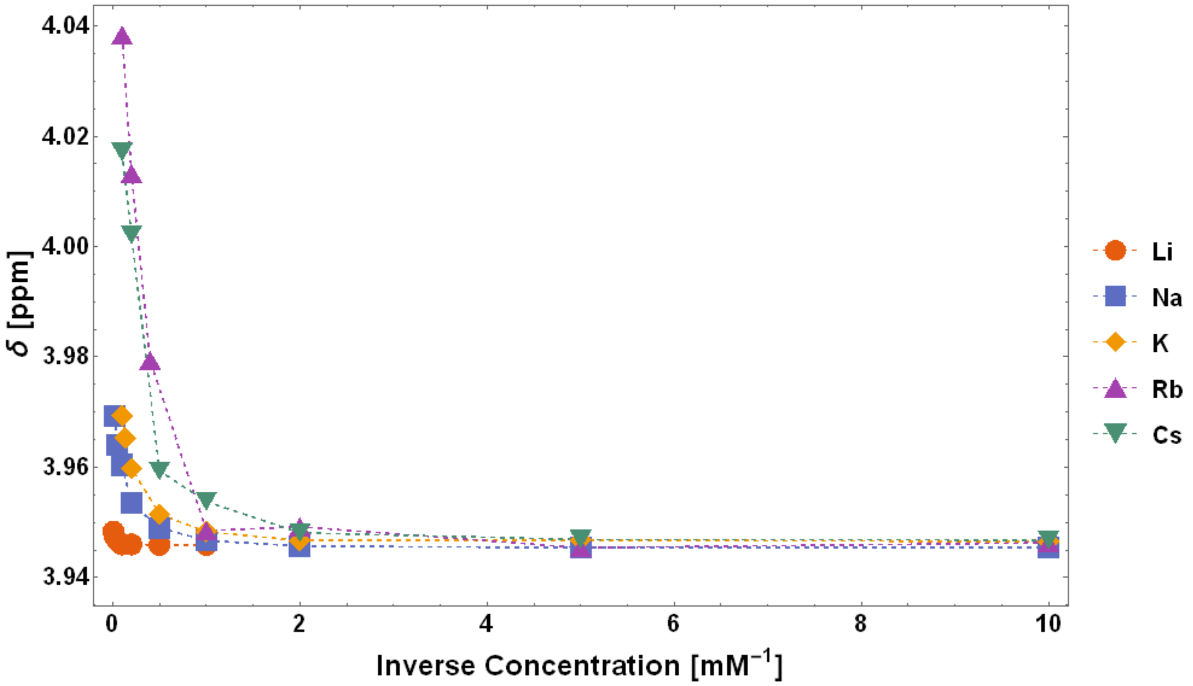


Figure S161. ^{1}H *NMR shifts vs. HDO in* D_2O *for the endo-methylene protons in* ***[Fe^{TMS}(CO)$_3$-SO$_3$]M*** *(M = Li, Na, K, Rb, Cs).*

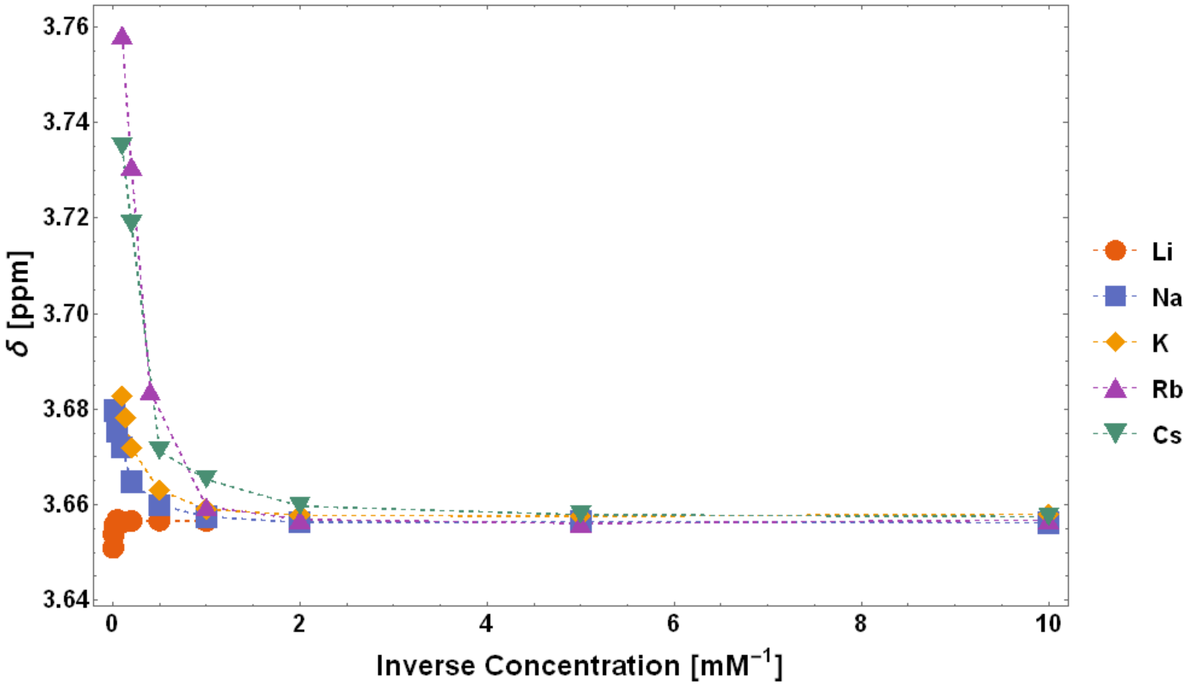


Figure S162. ^{1}H *NMR shifts vs. HDO in* D_2O *for the exo-methylene protons in* ***[Fe^{TMS}(CO)$_3$-SO$_3$]M*** *(M = Li, Na, K, Rb, Cs).*

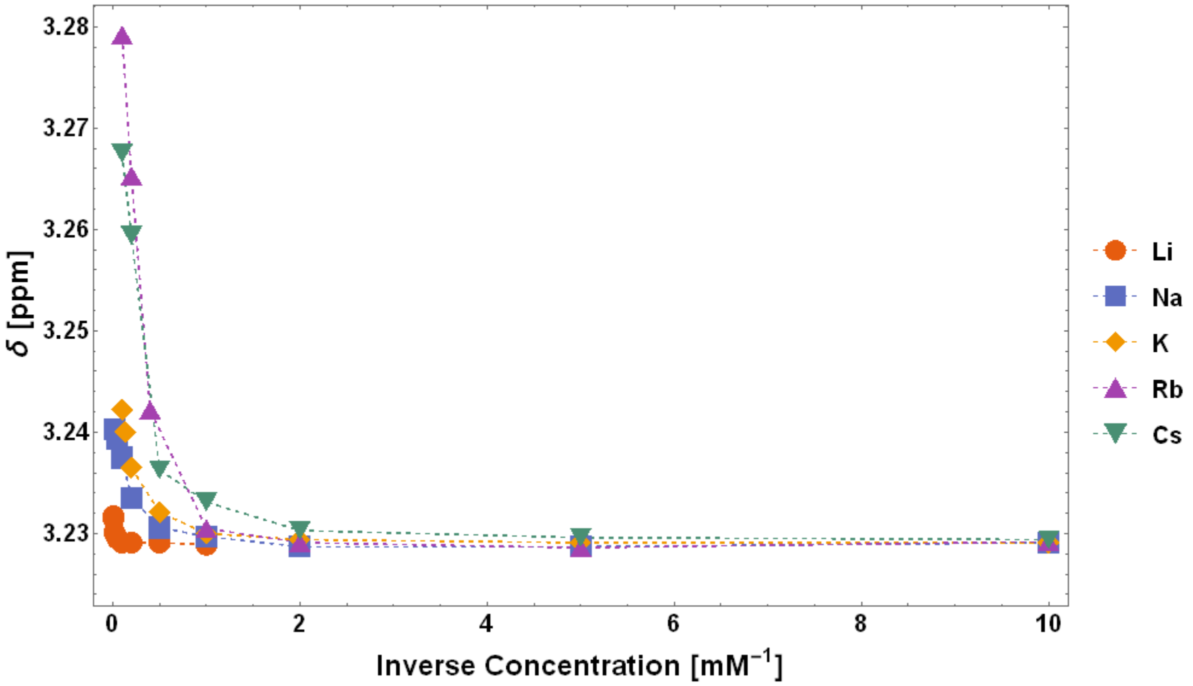


Figure S163. ^{1}H NMR shifts vs. HDO in D_2O for the ethylene protons in ***$[Fe^{TMS}(CO)_3\text{-}SO_3]M$*** *(M = Li, Na, K, Rb, Cs).*

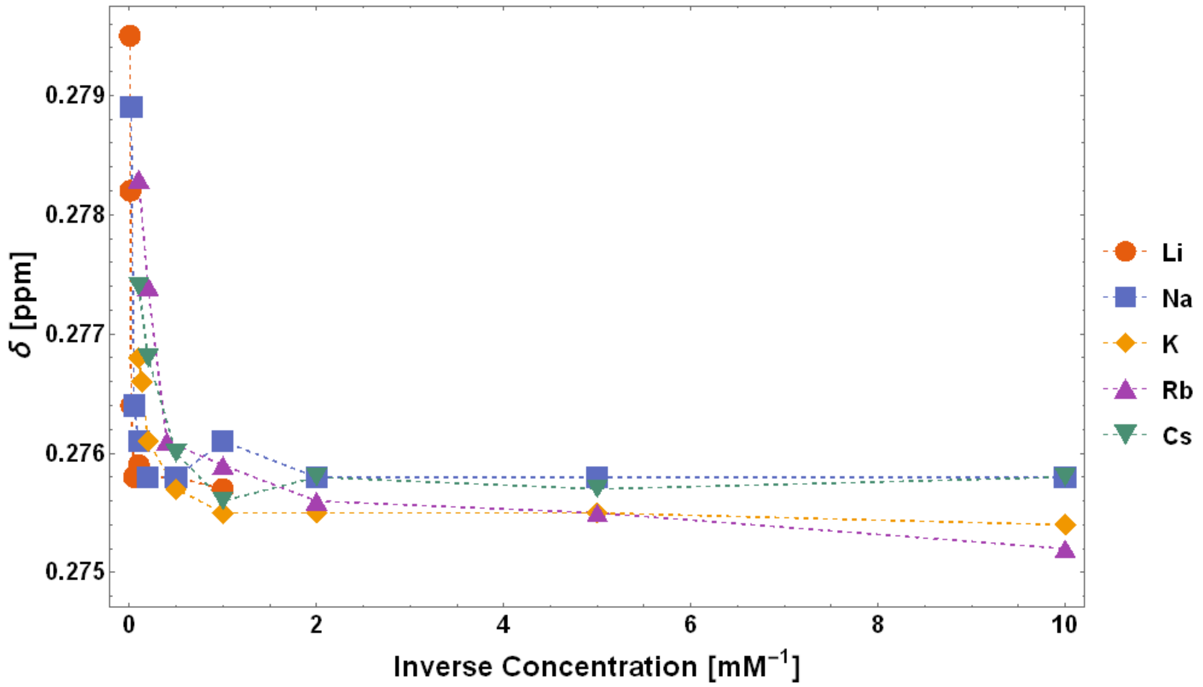


Figure S164. ^{1}H NMR shifts vs. HDO in D_2O for the TMS protons in ***$[Fe^{TMS}(CO)_3\text{-}SO_3]M$*** *(M = Li, Na, K, Rb, Cs).*

Table S1. Summary for ***$[Fe^{TMS}(CO)_3\text{-}SO_3]Li$*** *(run 1/ run 2).*

Protons	**CMC [mM]**	**δ_{mic} [ppm]**	**δ_{mono} [ppm]**	**δ_{mic} - δ_{mono} [ppm]**
Endo-Methylene	14.8 / 11.9	3.9485 / 3.9569	3.9460 / 3.9543	0.0025 / 0.0026
Exo-Methylene	22.4 / -	3.6537 / 3.6649	3.6566 / 3.6653	0.0029 / 0.0004
Ethylene	18.4 / 17.8	3.2315 / 3.2356	3.2292 / 3.2360	0.0023 / 0.0004
TMS	-	-	-	-

Table S2. Chemical shifts in ppm relative to HDO for ***[Fe^{TMS}(CO)$_3$-SO$_3$]Li****.*

c [mM]	Run 1				Run 2			
	endo-CH$_2$	*exo*-CH$_2$	Ethylene	TMS	*endo*-CH$_2$	*exo*-CH$_2$	Ethylene	TMS
100	3.9483	3.6538	3.2315	0.2782	3.9565	3.6647	3.2384	0.2822
50	3.9475	3.6558	3.2301	0.2764	3.9563	3.6672	3.2373	0.2803
20	3.9467	3.6568	3.2295	0.2758	3.9553	3.6676	3.2364	0.2796
10	3.9460	3.6563	3.2291	0.2759	3.9550	3.6676	3.2366	0.2806
5	3.9460	3.6566	3.2291	0.2758	3.9535	3.6663	3.2354	0.2797
2	3.9460	3.6567	3.2291	0.2758	3.9524	3.6653	3.2347	0.2793
1	3.9459	3.6566	3.2289	0.2757	3.9543	3.6652	3.2358	0.2809
0.5	n/a	n/a	n/a	n/a	3.9539	3.6652	3.2361	0.2812
0.2	n/a	n/a	n/a	n/a	3.9538	3.6650	3.2356	0.2811

Table S3. Summary for ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na*** *(run 1/ run 2).*

Protons	**CMC [mM]**	**δ_{mic} [ppm]**	**δ_{mono} [ppm]**	**δ_{mic} - δ_{mono} [ppm]**
Endo-Methylene	4.3 / 5.2	3.9706 / 3.9631	3.9457 / 3.9512	0.0249 / 0.0119
Exo-Methylene	3.8 / 5.9	3.6810 / 3.6728	3.6564 / 3.6622	0.0246 / 0.0106
Ethylene	3.0 / 4.4	3.2412 / 3.2417	3.2285 / 3.2337	0.0127 / 0.008
TMS	-	-	-	-

Table S4. Chemical shifts in ppm relative to HDO for ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na****.*

c [mM]	Run 1				Run 2			
	endo-CH$_2$	*exo*-CH$_2$	Ethylene	TMS	*endo*-CH$_2$	*exo*-CH$_2$	Ethylene	TMS
50	3.9692	3.6797	3.2403	0.2789	3.9625	3.6719	3.2421	0.2838
25	n/a	n/a	n/a	n/a	3.9596	3.6699	3.2394	0.2820
20	3.9641	3.6753	3.2394	0.2764	n/a	n/a	n/a	n/a
10	3.9604	3.6720	3.2375	0.2761	3.9570	3.6667	3.2369	0.2812
5	3.9535	3.6648	3.2335	0.2758	3.9531	3.6640	3.2353	0.2810
2	3.9490	3.6599	3.2306	0.2758	3.9519	3.6627	3.2347	0.2811
1	3.9467	3.6575	3.2297	0.2761	3.9527	3.6635	3.2357	0.2821
0.5	3.9457	3.6563	3.2287	0.2758	3.9514	3.6622	3.2346	0.2813
0.2	3.9454	3.6565	3.2287	0.2758	3.9508	3.6622	3.2343	0.2809
0.1	3.9454	3.6562	3.2291	0.2758	3.9516	3.6631	3.2349	0.2818

Table S5. Summary for ***[Fe^{TMS}(CO)$_3$-SO$_3$]K*** *(run 1/ run 2)..*

Protons	**CMC [mM]**	**δ_{mic} [ppm]**	**δ_{mono} [ppm]**	**δ_{mic} - δ_{mono} [ppm]**
Endo-Methylene	3.0 / 3.4	3.9787 / 3.9867	3.9468 / 3.9533	0.0319 / 0.0334
Exo-Methylene	3.0 / 3.4	3.6929 / 3.7008	3.6576 / 3.6641	0.0353 / 0.0367
Ethylene	3.1 / 3.4	3.2477 / 3.2542	3.2294 / 3.2354	0.0476 / 0.0188
TMS	-	-	-	-

Table S6. Chemical shifts in ppm relative to HDO for **$[Fe^{TMS}(CO)_3\text{-}SO_3]K$**.

c [mM]	Run 1				Run 2			
	endo-CH$_2$	*exo*-CH$_2$	Ethylene	TMS	*endo*-CH$_2$	*exo*-CH$_2$	Ethylene	TMS
10	3.9693	3.6827	3.2422	0.2768	3.9762	3.6893	3.2479	0.2819
7.5	3.9653	3.6782	3.2400	0.2766	n/a	n/a	n/a	n/a
7.14	n/a	n/a	n/a	n/a	3.9695	3.6821	3.2439	0.2806
5	3.9598	3.6719	3.2365	0.2761	3.9646	3.6767	3.2416	0.2812
2	3.9515	3.6630	3.2321	0.2757	3.9571	3.6685	3.2370	0.2802
1	3.9483	3.6591	3.2300	0.2755	3.9541	3.6651	3.2358	0.2808
0.5	3.9467	3.6578	3.2294	0.2755	3.9535	3.6645	3.2357	0.2812
0.2	3.6468	3.6576	3.2291	0.2755	3.9530	3.6637	3.2352	0.2812
0.1	3.9465	3.6580	3.2291	0.2754	3.9535	3.6645	3.2359	0.2815

Table S7. Summary for **$[Fe^{TMS}(CO)_3\text{-}SO_3]Rb$** *(run 1/ run 2)..*

Protons	**CMC [mM]**	**δ_{mic} [ppm]**	**δ_{mono} [ppm]**	**δ_{mic} - δ_{mono} [ppm]**
Endo-Methylene	1.8 / 1.6	4.0554 / 3.9840	3.9487 / 3.9541	0.1067 / 0.0299
Exo-Methylene	2.0 / 1.7	3.7820 / 3.6981	3.6566 / 3.6680	0.1254 / 0.0301
Ethylene	2.0 / 1.7	3.2908 / 3.2526	3.2288 / 3.2364	0.0620 / 0.0162
TMS	-	-	-	-

Table S8. Chemical shifts in ppm relative to HDO for **$[Fe^{TMS}(CO)_3\text{-}SO_3]Rb$**.

c [mM]	Run 1				Run 2			
	endo-CH$_2$	*exo*-CH$_2$	Ethylene	TMS	*endo*-CH$_2$	*exo*-CH$_2$	Ethylene	TMS
10	4.0384	3.7584	3.2792	0.2783	3.9795	3.6932	3.2500	0.2821
5	4.0133	3.7309	3.2653	0.2774	3.9740	3.6871	3.2468	0.2814
2.5	3.9794	3.6838	3.2422	0.2761	3.9650	3.6774	3.2416	0.2807
1	3.9485	3.6596	3.2305	0.2759	3.9571	3.6685	3.2377	0.2812
0.5	3.9492	3.6569	3.2291	0.2756	3.9549	3.6663	3.2366	0.2798
0.2	3.9454	3.6561	3.2286	0.2755	3.9537	3.6653	3.2358	0.2812
0.15	n/a	n/a	n/a	n/a	3.9540	3.6652	3.2361	0.2809
0.1	3.9463	3.6568	3.2292	0.2752	3.9535	3.6630	3.2355	0.2814

Table S9. Summary for **$[Fe^{TMS}(CO)_3\text{-}SO_3]Cs$** *(run 1/ run 2)..*

Protons	**CMC [mM]**	**δ_{mic} [ppm]**	**δ_{mono} [ppm]**	**δ_{mic} - δ_{mono} [ppm]**
Endo-Methylene	1.7 / 1.8	4.0313 / 3.9702	3.9481 / 3.9548	0.0832 / 0.0154
Exo-Methylene	1.7 / 1.7	3.7507 / 3.6824	3.6598 / 3.6650	0.0909 / 0.0174
Ethylene	1.7 / 1.7	3.2751 / 3.2450	3.2304 / 3.2359	0.0447 / 0.0091
TMS	-	-	-	-

Table S10. Chemical shifts in ppm relative to HDO for ***[Fe^{TMS}(CO)$_3$-SO$_3$]Rb****.*

c [mM]	Run 1				Run 2			
	endo-CH$_2$	*exo*-CH$_2$	Ethylene	TMS	*endo*-CH$_2$	*exo*-CH$_2$	Ethylene	TMS
10	4.0171	3.7350	3.2675	0.2774	3.9677	3.6796	3.2436	0.2817
5	4.0021	3.7187	3.2594	0.2768	3.6940	3.6761	3.2415	0.2814
2.5	n/a	n/a	n/a	n/a	3.9591	3.6705	3.2388	0.2814
2	3.9593	3.6713	3.2363	0.2760	n/a	n/a	n/a	n/a
1	3.9538	3.6653	3.2331	0.2756	3.9556	3.6670	3.2367	0.2810
0.5	3.9481	3.6597	3.2303	0.2758	3.9551	3.6660	3.2366	0.2814
0.2	3.9469	3.6579	3.2296	0.2757	3.6545	3.6654	3.2360	0.2811
0.15	n/a	n/a	n/a	n/a	3.9532	3.6651	3.2357	0.2810
0.1	3.9468	3.6575	3.2294	0.2758	3.9536	3.6656	3.2359	0.2812

7) Cation Variation Kinetics

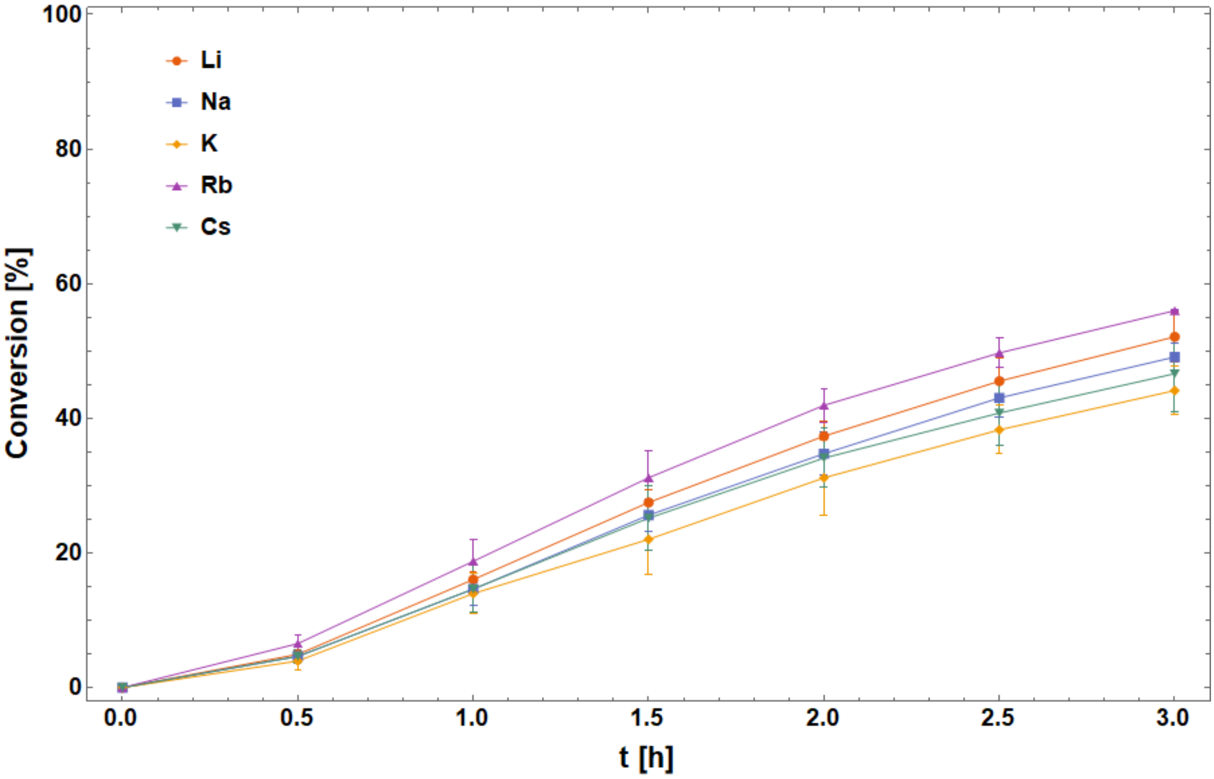


Figure S165. Kinetic profiles for the hydrogenation of acetophenone catalyzed by ***[Fe^{TMS}(CO)$_3$-SO$_3$]M*** *(M = Li, Na, K, Rb, Cs) activated by Me$_3$NO. Reaction conditions: 1 mol% catalyst loading, 1.5 mol% Me$_3$NO, 3:1 H$_2$O/^{i}PrOH, 90 °C, 10 bar H$_2$, 0.5 M in acetophenone. Conversions determined by ^{1}H NMR. For M = Na, the experiments were performed in triplicates. For the other cations, experiments were performed in duplicates. Error bars denote one standard deviation.*

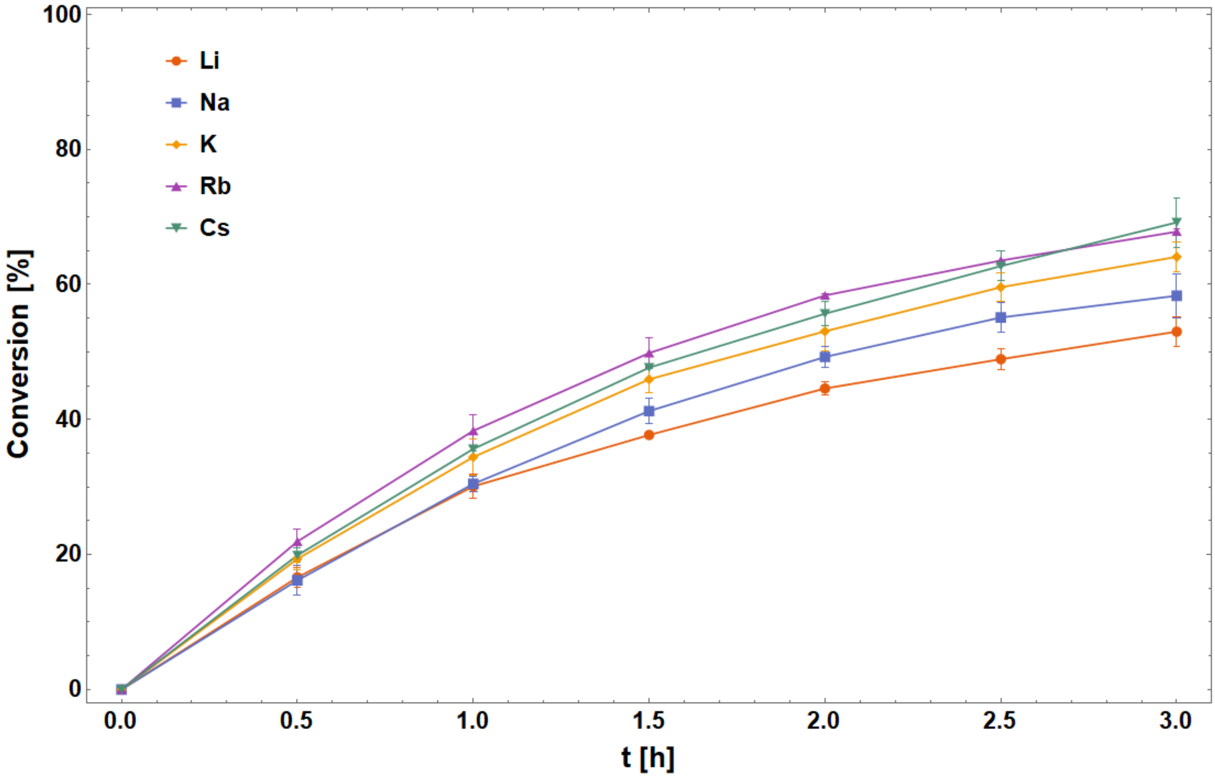


Figure S166. Kinetic profiles for the hydrogenation of acetophenone catalyzed by ***[Fe^{TMS}(MeCN)CO)$_2$-SO$_3$]M*** *(M = Li, Na, K, Rb, Cs). Reaction conditions: 1 mol% catalyst loading, 3:1 H_2O/^{i}PrOH, 90 °C, 10 bar H_2, 0.5 M in acetophenone. Conversions determined by ^{1}H NMR. For M = Na, the experiments were performed in triplicates. For the other cations, experiments were performed in duplicates. Error bars denote one standard deviation.*

8) Dynamic Light Scattering in 3:1 $H_2O/^iPrOH$

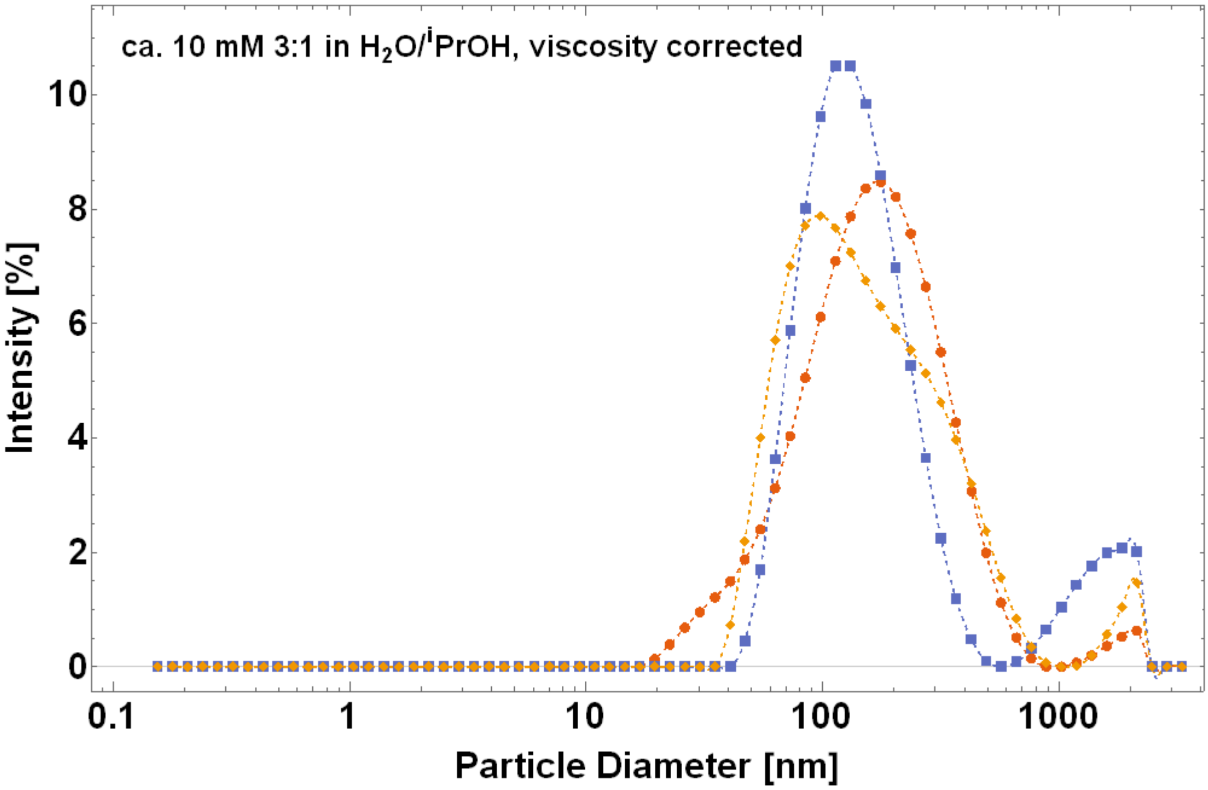


Figure S167. Particle size distribution obtained by dynamic light scattering of a ca. 10 mM solution of ***[Fe^{TMS}(CO)$_3$-SO$_3$]Na*** *in 3:1 $H^2O/^iPrOH$. The original data was collected with the viscosity settings for water. A 3:1 $H_2O/^iPrOH$ has a viscosity ca. 2.6 times higher than pure water (Park* et al.*, Journal of The Electrochemical Society* **2006**, 153(9), G811-G814*). The obtained data was adjusted accordingly. The different curves correspond to repeated measurements on the same sample. The data suggests that aggregates also form in 3:1 $H^2O/^iPrOH$, which is the solvent that is used in catalytic experiments.*

9) Transfer Hydrogenation

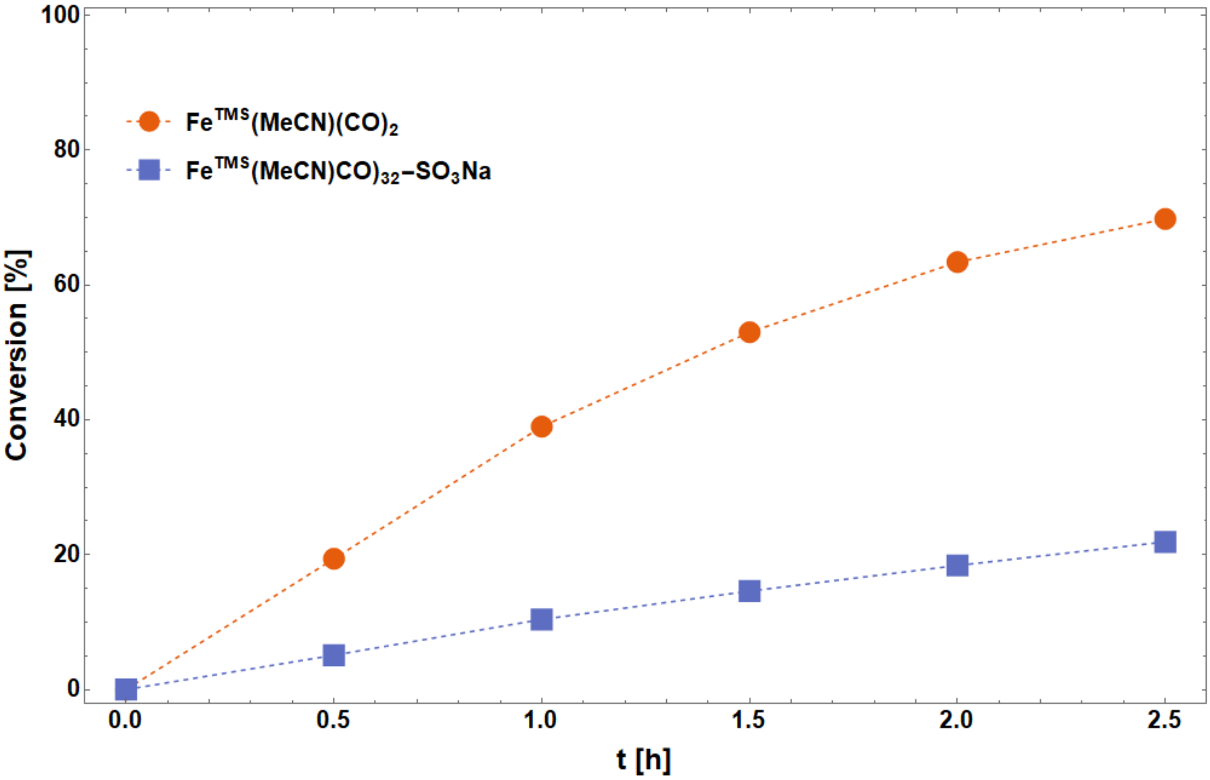


Figure S168. Kinetic profiles for the transfer hydrogenation of acetophenone in ^{i}PrOH. Reaction conditions: 2.5 mol% catalyt loading, ^{i}PrOH, 80 °C, 0.5 M in acetophenone. Conversions determined by ^{1}H NMR.

10) ^{13}C NMR to Check Electron Density in C5-Ring

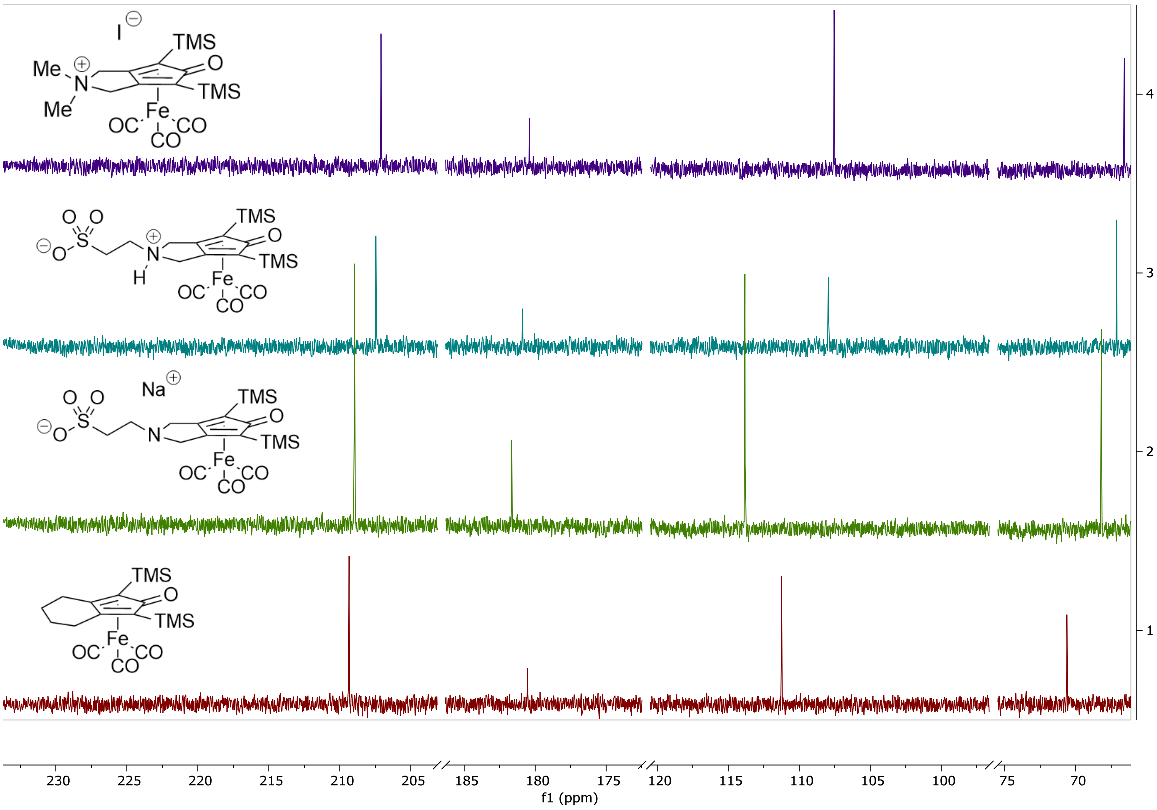


Figure S169. Partial ^{13}C NMR spectra recorded in and referenced to DMSO-d_6 of selected cyclopentadienone iron complexes. The ammonium iodide complex was prepared according to literature (Mérel et al., ChemCatChem ***2013****, 5, 2939). From left to right, the signals correspond to the carbon monoxide ligand, the ketone carbon atom, the β-carbon relative to the ketone and the α-carbon relative to the ketone respectively. No clear trend regarding electron density in the cyclopentadienone ring can be observed.*